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Azide Radical Initiated Ring Opening of Cyclopropenes Leading to Alkenyl Nitriles and Polycyclic Aromatic Compounds

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Abstract: We report herein a radical-mediated amination of cyclopropenes. The transformation proceeds through a cleavage of the three-membered ring after the addition of an azide radical on the strained double bond and leads to tetrasubstituted alkenyl nitrile derivatives upon loss of N₂. With 1,2-diaryl substituted cyclopropenes, this methodology could be extended to a one pot synthesis of highly functionalized polycyclic aromatic compounds (PACs). This transformation allows the synthesis of nitrile-substituted alkenes and aromatic compounds from rapidly accessed cyclopropenes using only commercially available reagents.

Alkenyl nitriles and polycyclic aromatic compounds (PACs) are important scaffolds in organic chemistry, material sciences and medicine.^[1] Alkenyl nitriles are key structural motifs in pharmaceuticals such as Entacapone used in the treatment of Parkinson's disease,^[2] or the reverse transcriptase inhibitor Rilpivirine.^[3] In addition, they are valuable synthetic intermediates that have been used as electrophilic partners in conjugate additions.^[4] PACs are also present in biologically active compounds,^[5] and have found many applications as organic materials for semiconductors^[6] and light-emitting diodes.^[7] For these reasons, developing new methods for the synthesis of PACs has been the focus of intensive research.^[8] Nevertheless, there is still a strong demand for modular methods to access selectively polysubstituted PACs.

Cyclopropenes have emerged in the past decades as important three-carbon building blocks, due to efficient methods for their synthesis combined with a versatile reactivity.^[9] Reaction at the double bond with organometallic intermediates or transition metal catalysts gives access to either functionalized cyclopropanes^[10] or substituted alkenes after ring-opening via vinyl carbene intermediates^[11] (Scheme 1, a). The formation of a reactive cyclopropyl radical intermediate upon the addition of a radical onto the alkene has been less explored. Nakamura and co-workers reported in 1994 the hydrostannylation of cyclopropenes.^[12] Several reports have later described the addition of carbon-centered radicals, with a functionalization of the resulting cyclopropyl radical through C-S bond formation,^[13] H-abstraction,^[14] or a second C-C bond forming event.^[15] We recently developed a photoredox-mediated (3+2) annulation with cyclopropylanilines to access bicyclo[3.1.0]hexanes.^[16] In contrast, examples of a radical functionalization of cyclopropenes leading to a cleavage of the three-membered ring are scarce (Scheme 1, b). Miyata and co-workers reported a ring opening rearrangement after the addition of a trichloromethyl radical to

alkyl-substituted cyclopropenes, followed by trapping of the radical by dimethyl zinc (Scheme 1, b) 1.).^[14a] Landais and co-workers developed a radical-mediated dicarbofunctionalization of cyclopropenes, followed by a base-mediated fragmentation of the *in situ* formed cyclopropane (Scheme 1, b) 2.).^[17]

Scheme 1. Synthetic strategies towards functionalized cyclopropanes and substituted alkenes from cyclopropenes (a). Previous reports leading to a cleavage of the three-membered ring after a radical functionalization of cyclopropenes (b). This work: radical amination of cyclopropenes with an azide radical for the synthesis of alkenyl nitriles and substituted PACs (c).

Although examples of amination reactions of cyclopropenes have been reported in the presence of transition metals or lanthanides combined with electrophilic,^[18] or nucleophilic sources of nitrogen,^[19] the addition of *N*-centered radicals has not been reported to date. We report herein a ring-opening reaction initiated by the addition of an azide radical (Scheme 1, c). This transformation led to the formation of alkenyl nitriles after the rearrangement of a putative azido-cyclopropyl radical (I). With 1,2-diaryl substituted cyclopropenes we developed a one-pot radical amination / oxidative photocyclization to access highly substituted PACs. While azide radicals have already been used for the synthesis of alkenyl nitriles through C-H or C-C bond cleavage of alkenes and alkynes, these processes were limited to

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the synthesis of trisubstituted olefins and cyclopropenes were not reported as substrates.^[20]

Our investigations started with cyclopropene **1** employing ABZ (**3**) as safe azidation reagent under mild photoredox-catalyzed conditions known to generate azide radicals (Table 1).^[21] Under green LED irradiation with Cu(dap)₂Cl as photocatalyst, alkenyl nitrile **2** was formed in 82% yield (entry 1). When reducing the equivalents of ABZ from 2.0 to 1.4, **2** was obtained in 78% yield (entry 2). In the presence of inexpensive CuCl₂ and ABZ (**3**) without irradiation, **2** was formed in 62% yield (entry 3). Employing 2 equivalents of PIDA and TMS-N₃ as commercial reagents,^[22] **2** was obtained in 56% yield after 30 minutes of reaction (entry 4). Adding 10 mol% of CuCl₂ led to a high yield of 94% (entry 5).^[23] While going from 2.0 to 1.5 equivalent led to a decrease in yield to 85% (entry 6), we found 1.8 equivalent to be optimal combined with a reduced loading of CuCl₂ to 5 mol% (entry 7). Under these conditions, **2** could be isolated in 88% yield.

Table 1. Discovery and optimization of the radical amination.^[a]

Entry	Azide Source (equiv.)	Cat. (mol%)	Oxidant (equiv.)	Time	Yield ^[b]
1 ^[c]	ABZ (2)	Cu(dap) ₂ Cl (1)	-	O/N	82%
2 ^[c]	ABZ (1.4)	Cu(dap) ₂ Cl (1)	-	O/N	78%
3	ABZ (1.4)	CuCl ₂ (10)	-	O/N	62%
4	TMS-N ₃ (2)	-	PIDA (2)	30 min	56%
5	TMS-N ₃ (2)	CuCl ₂ (10)	PIDA (2)	30 min	94%
6	TMS-N ₃ (1.5)	CuCl ₂ (10)	PIDA (1.5)	30 min	85%
7	TMS-N ₃ (1.8)	CuCl ₂ (5)	PIDA (1.8)	30 min	90% (88% ^[d])

[a] Reaction conditions: 0.1 mmol scale, O/N: overnight, dap = 2,9 - bis(para-anisyl) - 1,10 - phenanthroline. [b] Yields determined by ¹H NMR using CH₂Br₂ as internal standard. [c] Reaction performed under Green LED irradiation. [d] Isolated yield on 0.1 mmol scale.

With optimized conditions in hands, we carried some preliminary scope investigations (Scheme 2). On a 0.3 mmol scale, cyclopropene **1** delivered alkenyl nitrile **2** in 91% yield. Dibenzyl- and ditrifluoroethyl-ester substituted cyclopropenes gave products **4** and **5** in 74% and 72% yield, respectively. Both electron-donating and -withdrawing groups in *para*-position on the aromatic substituent of the cyclopropene were compatible with the reaction (products **6** and **7**).^[24] *Meta*-substitution was also tolerated (product **8**, 81% yield). The reaction proceeded as well with a 2-naphthyl substituent, delivering **9** in 94% yield. For **9**, an X-Ray structure could be obtained.^[25] An *ortho*-CF₃ substituted cyclopropene led to the formation of **10** in 77% yield. As shown with examples **11**, **12** and **13** for which only traces of the alkenyl nitriles were observed, having an aryl-substituent on the unsaturated bond was essential. With aryl groups both in position 1 and 2 of the cyclopropene ring, the reaction proceeded in high

yield, with **14** isolated in 84% yield on a 1.6 mmol scale, albeit with almost no stereoselectivity.

Scheme 2. Preliminary scope investigations of the radical amination. Reaction conditions: 0.3 mmol scale. [a] Yield on 1.6 mmol scale.

Alkenyl nitrile **2** could be obtained in 92% yield on gram scale (Scheme 3). Taking advantage of the electrophilic nature of **2**, it was successfully engaged in several transformations. A Corey–Chaykovsky cyclopropanation led to **15** in 54% yield.^[26] Alkene **2** underwent a (3+2) annulation with allenolate **16**, delivering cyclopentene **17** in 89% yield.^[27] **2** could also be engaged in a Diels–Alder cycloaddition with Danishefsky's diene **18**,^[28] leading to cyclohexenone **19** after acidic deprotection in 64% yield. We then investigated the possibility to engage cyano-stilbene derivatives such as **14** into an oxidative photocyclization.^[29] Under irradiation, *E* to *Z* isomerization would occur, allowing converting both isomers to the product. While straightforward methods now exist for the synthesis of simple disubstituted stilbenes,^[30] accessing tetrasubstituted stilbenes with four different substituents as obtained in our work still constitutes an important challenge.^[31] In the presence of 1.1 equivalent of DDQ in acetonitrile (0.05 M) under UV irradiation (365 nm) for 20 hours, cyano-phenanthrene **20** could be isolated in 74% yield.

A one-pot process from 1,2-diaryl substituted cyclopropenes allowed to directly access the corresponding PACs (Scheme 4, see SI for details). On a 0.3 mmol scale, **20** could be isolated in 80% yield. A *tert*-butyl ester, a ketone and a trifluoromethyl group in position 1 of the cyclopropene led to phenanthrenes **21**, **22** and **23** in 51–75% yields. Both electron-donating and -withdrawing substituents in *para* position of both aromatic groups were well tolerated, delivering products **24–27**. Substitutions in *ortho* and *meta* positions were also tolerated (**28–31**). A 1-thienyl substituted cyclopropene gave heteroaromatic product **32** in 61% yield.

Scheme 3. Gram-scale synthesis of **2** and further functionalizations of alkenyl nitriles **2** and **14**. [a] Isolated as a 4.2:1 mixture of regioisomers, major regioisomer drawn.

We then investigated the synthesis of extended PACs. Cyclopropenes substituted with 2-naphthyl groups gave functionalized [4]helicenes **33–35** in good yields. Chrysene and benzo[*g*]chrysene derivatives could also be accessed (products **36** and **37**). Substituted picene **38** was obtained in a slightly lower yield of 54%. For all the substrates, full conversion of the starting material towards the corresponding alkenyl nitriles was observed. Hence when lower yields were obtained, the oxidative photocyclization was the limiting step.

Based on experimental observations and literature precedence in the use of azides to generate nitrile-containing compounds,^[32] a speculative mechanism can be proposed (Scheme 5A). The reaction of PIDA with TMS-N₃ would lead to the formation of unstable hypervalent iodine compounds **I** and **II**, which will dissociate into a iodanyl and an azide radical **III** and **IV**.^[22, 33] **IV** would most likely add onto the C-C double bond of the cyclopropene to generate azido-cyclopropyl radical **V**.^[34] Two different paths can then be proposed. In path A, cyclopropyl radical **V** would be oxidized to cyclopropyl cation **VI**, probably by an hypervalent iodine intermediate. From the latter a ring-opening rearrangement initiated by the azide group would occur, leading to the formation of **VII**. From **VII**, a base-mediated (azide or acetate)^[35] fragmentation would then lead to the alkenyl nitrile upon loss of nitrogen.^[36] Another possibility from intermediate **V** would be a direct rearrangement triggered by the azide group with loss of nitrogen to give iminyl radical **VIII** (path b).^[37] The rearrangement of cyclopropyl to allyl radicals is a relatively easy process, with an energy barrier of only 22 kcal/mol for the cyclopropyl radical.^[38] In this case, coupling it with nitrogen release may even lower further the activation energy, although this remains highly speculative. From this intermediate, oxidation,

most probably by hypervalent iodine reagent intermediates **I** or **II**, would give the nitrile product.^[39]

The role of the copper catalyst is still unclear. When the reaction was performed with cyclopropene **39** in absence of CuCl₂ (Scheme 5B), alkenyl nitrile **14** could be still isolated in 30% yield, but quinoline **40** was also obtained in 34%. Quinoline **40** may be formed by addition of the iminyl radical in intermediate **VIII** onto the benzene ring, followed by oxidation and rearomatization. Its formation therefore further support path **b** of the proposed mechanism. One role for copper may be to recombine with the imine radical, preventing cyclization and facilitating formation of the nitrile via deprotonation, eventually after oxidation by the hypervalent iodine reagent.^[40]

Scheme 4. Scope of the one-pot radical amination / oxidative photocyclization. Reaction conditions: 0.3 mmol scale.

In conclusion, we have developed a radical amination/ring-opening of cyclopropenes using azides as nitrogen source. This transformation constitutes the first example of addition of an *N*-centered radical onto cyclopropenes and is one of the few reports of a ring-opening event after a radical functionalization of the unsaturated bond. The obtained tetrasubstituted alkenyl nitriles could be further engaged in several transformations. In the case of 1,2-diaryl-substituted cyclopropenes, a one-pot process could be developed to access highly functionalized PACs. This methodology therefore provides a new way to use cyclopropenes as starting materials for the synthesis of valuable nitrile-containing scaffolds using commercially available reagents.

Scheme 5. Speculative mechanism and control experiment in absence of copper catalyst with cyclopropene **39**.

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Keywords: cyclopropenes • amination • radicals • nitriles • polycyclic aromatic compounds

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A radical amination of cyclopropenes has been developed. The transformation proceeds through a cleavage of the three-membered ring and provides access to alkenyl nitriles, without the need of an external cyanide source. With 1,2-diaryl substituted cyclopropenes, a one-pot process could be developed to access a wide range of highly functionalized polycyclic aromatic compounds.

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1. General Methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere (H₂O content < 10 ppm, Karl-Fischer titration). The solvents were degassed by Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem, Fluorochem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ¹H-NMR spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in chloroform-*d*, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation). ¹⁹F-NMR spectra were recorded on a Bruker DPX-400 376 MHz spectrometer in CDCl₃ or SO(CD₃)₂. ¹³C-NMR spectra were recorded with ¹H-decoupling on a Bruker DPX-400 100 MHz spectrometer in chloroform-*d*, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API.

For reactions under the irradiation of UV light (365 nm), reactions were performed in borosilicate glass tubes which were placed around 7 cm far away from lamps (CAMAG UV Lamp 4, long-wave UV light 365 nm) in a Rayonet RPR-100 photochemical reactor. For reactions under the irradiation of green light, reactions were performed in 12*75 mm borosilicate glass tubes which were held using a rack for test tubes placed at the center of a crystallization flask. On this flask were attached the green LEDs (LED ribbon cable with open ends, Barthelme Y51515213 182007 12 V 502 cm green 1 pc(s), purchased directly on www.conrad.ch/fr). The distance between the LEDs and the test tubes was approximately 3–4 cm. Long irradiation for more than 2 h resulted in the temperature increasing up to 34 °C.

2. Preparation of Starting Materials

2.1 Synthesis of Diazo Compounds

General procedure A: Synthesis of α -aryldiazo compounds.

Following a slightly modified procedure,¹ DBU (1.6 equiv.) and the indicated α -aryl-acetate or -ketone (1.0 equiv.) were added to a solution of p ABSA (1.5 equiv.) in CH_3CN (0.5 M) at room temperature and the resulting mixture was stirred for 18 hours. The reaction mixture was then diluted with distilled water and extracted with diethyl ether. The combined organic layers were washed with a 10% $NaHCO_3$ solution and brine, then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography with the indicated solvents.

Dimethyl 2-diazomalonate (**42**)

Following a modified procedure,² triethylamine (13.4 mL, 96.0 mmol, 2.4 equiv.) and dimethyl malonate (**41**) (4.60 mL, 40.0 mmol, 1.0 equiv.) were added to a solution of p ABSA (14.4 g, 60.0 mmol, 1.5 equiv.) in CH_3CN (160 mL) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH_2Cl_2 (100 mL), the remaining solids were filtered off and the solvent was evaporated. The crude residue was purified by column chromatography (SiO_2 , Pentane:EtOAc 95:5 to 90:10) to afford compound **42** (6.26 g, 39.6 mmol, 99 % yield) as a yellow oil. 1H NMR (400 MHz, Chloroform- d) δ 3.84 (s, 6H, CH_3); ^{13}C NMR (101 MHz, Chloroform- d) δ 161.2, 52.4. One carbon was not resolved. The characterization data is corresponding to the reported values.²

Dibenzyl 2-diazomalonate (**44**)

¹ W.-Y. Yu, Y.-T. Tsoi, Z. Zhou, A. S. C. Chan, *Org. Lett.* **2009**, *11*, 469–472.

² F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.* **2011**, *50*, 12075–12079.

Following a modified procedure,³ triethylamine (1.0 mL, 7.2 mmol, 2.4 equiv.) and dibenzyl malonate (**43**) (0.75 mL, 4.0 mmol, 1.0 equiv.) were added to a solution of *p*ABSA (1.08 g, 4.50 mmol, 1.5 equiv.) in CH₃CN (16.0 mL) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH₂Cl₂ (15 mL), the remaining solids were filtered off and the solvent was evaporated. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 95:5) to afford compound **44** (889 mg, 2.86 mmol, 95% yield) as a yellow oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39- 7.34 (m, 10H, ArH), 5.28 (s, 4H, CH₂); ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.9, 135.3, 128.8, 128.6, 128.5, 67.3. One carbon was not resolved. The characterization data correspond to the reported values.³

Bis(2,2,2-trifluoroethyl) malonate (**47**)

Following a reported procedure,² H₂SO₄ (1.00 mL, 18.8 mmol, 0.25 equiv.) was added to a solution of trifluoroethanol (**46**) (29.9 mL, 415 mmol, 5.4 equiv.) and malonic acid **45** (8.00 g, 77.0 mmol, 1.0 equiv.) in toluene (40.0 mL) and the resulting mixture was heated to reflux for 8 hours. After cooling to room temperature, toluene (80.0 mL) was added and the mixture was washed with aq. NaOH (200 mL, 1 M), water (200 mL) and brine (200 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure to afford the title compound **47** (6.80 g, 25.4 mmol, 33% yield) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.55 (q, *J* = 8.2 Hz, 4H, OCH₂), 3.61 (s, 2H, CH₂); ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.4, 122.8 (q, *J* = 277.3 Hz), 61.4 (q, *J* = 37.0 Hz), 40.3. The characterization data correspond to the reported values.²

Bis(2,2,2-trifluoroethyl) 2-diazomalonate (**48**)

Following a modified procedure,² triethylamine (6.00 mL, 43.3 mmol, 2.4 equiv.) and bis(trifluoroethyl)malonate (**47**) (4.84 g, 18.0 mmol, 1.0 equiv.) were added to a solution of *p*ABSA (6.50 g, 27.1 mmol, 1.5 equiv.) in CH₃CN (72.0 mL) at room temperature and the resulting mixture was stirred for 18 hours. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH₂Cl₂ (50 mL), the solids were filtered off and the solvent was evaporated. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 95:5 to 90:10) to afford compound **48** (5.26 g, 17.9 mmol, 99 % yield) as a yellow oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.62 (q, 4 H, *J* = 8.2 Hz, CH₂); ¹³C NMR (101 MHz, Chloroform-*d*) δ

³ F. de Nanteuil, J. Loup, J. Waser, *Org. Lett.* **2013**, *15*, 3738-3741.

158.7, 122.6 (q, $J = 277.3$ Hz), 60.9 (q, $J = 37.0$ Hz). One carbon was not resolved. The characterization data correspond to the reported values.²

Methyl 2-diazo-2-phenylacetate (**49**)

Following the general procedure A, starting from methyl 2-phenylacetate (3.00 mL, 21.3 mmol, 1.0 equiv.), the title compound **49** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 95:5) as a red oil (2.72 g, 15.4 mmol, 73 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.53 – 7.45 (m, 2H, ArH), 7.43 – 7.33 (m, 2H, ArH), 7.23 – 7.14 (m, 1H, ArH), 3.87 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 168.1, 131.5, 128.3, 127.7, 126.4, 54.3. One carbon was not resolved. The characterization data correspond to the reported values.⁴

Tert-butyl 2-diazo-2-phenylacetate (**52**)

Following a reported procedure,⁵ 2-phenylacetic acid (**50**) (1.09 g, 8.00 mmol, 1.0 equiv), Boc₂O (3.90 mL, 16.8 mmol, 2.1 equiv.) and DMAP (293 mg, 2.40 mmol, 0.3 equiv.) were dissolved in ^tBuOH (20 mL). The mixture was stirred at 30 °C overnight. After cooling to room temperature, the solvent was evaporated and the crude residue was purified by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 98:2) to afford compound **51** (673 mg, 3.50 mmol, 44 % yield) as a colorless oil. **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.37–7.04 (m, 5H, ArH), 3.45 (s, 2H, CH₂), 1.36 (s, 9H, ^tBu); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 135.1, 129.4, 128.8, 127.3, 81.1, 42.8, 28.3. The characterization data correspond to the reported values.⁶

Following the general procedure A, starting from *tert*-butyl 2-phenylacetate (**51**) (673 mg, 3.50 mmol, 1.0 equiv.), the title compound **52** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (560 mg, 2.57 mmol, 73 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.37 (m, 2H, ArH), 7.37 – 7.32 (m, 2H, ArH), 7.21 – 7.13 (m, 1H), 1.55 (s, 9H, ^tBu); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 164.6, 128.9, 126.4, 125.8, 124.2, 82.2, 28.5. One carbon was not resolved. The characterization data correspond to the reported values.⁷

⁴ H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.* **2000**, *122*, 3063–3070.

⁵ M. Gao, Y. Zhao, C. Zhong, S. Liu, P. Liu, Q. Yin, L. Hu, *Org. Lett.* **2019**, *21*, 5679–5684.

⁶ T. Hama, J. F. Hartwig, *Org. Lett.* **2008**, *10*, 1549–1552.

⁷ M. Buchsteiner, L. Martinez-Rodriguez, P. Jerabek, I. Pozo, M. Patzer, N. Nöthling, C. W. Lehmann, A. Fürstner, *Chem. Eur. J.* **2020**, *26*, 2509–2515.

1-Diazo-1-phenylbutan-2-one (**53**)

Following the general procedure A, starting from 1-phenylbutan-2-one (0.75 mL, 5.0 mmol, 1.0 equiv.), the title compound **53** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a yellow solid (468 mg, 2.69 mmol, 54 % yield). ¹H NMR (400 MHz, Chloroform-*d*) 7.52 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.41 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.28 (t, *J* = 7.6 Hz, 1H, Ar*H*), 2.63 (q, *J* = 7.6 Hz, 2H, CH₂CH₃), 1.21 (t, *J* = 7.6 Hz, 3H, CH₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 193.7, 129.1, 127.0, 126.0, 124.1, 32.6, 8.7. One carbon was not resolved. The characterization data correspond to the reported values.⁸

(1-Diazo-2,2,2-trifluoroethyl)benzene (**56**)

Following a reported procedure,⁹ TsNHNH₂ (2.24 g, 12.0 mmol, 1.0 equiv) was stirred in MeOH (8 mL) at reflux until complete dissolution. Then the reaction vessel was cooled to room temperature and 2,2,2-trifluoro-1-phenylethanone (**54**) (1.69 mL, 12.0 mmol, 1.0 equiv.) was added in one portion. The resulting reaction mixture was then stirred at 65 °C for 12 hours, after which it was cooled to 0 °C, leading to the precipitation of the desired product. The latter was collected by vacuum filtration and washed with pentane, leading to **55** (1.85 g, 5.40 mmol, 45 % yield) as a white solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H, NH) 7.86 – 7.81 (m, 2H, Ar*H*), 7.59 – 7.48 (m, 3H, Ar*H*), 7.37 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.25 (d, *J* = 8.0 Hz, 2H, Ar*H*), 2.47 (s, 3H, CH₃). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.2, 141.5 (q, *J* = 35.7 Hz), 134.7, 131.6, 130.3, 129.9, 128.6, 128.2, 125.3, 120.2 (q, *J* = 273 Hz), 21.9. The characterization data correspond to the reported values.⁹

Following a reported procedure,⁹ 4-methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (**55**) (1.85 g, 5.40 mmol, 1.0 equiv.) was added to a solution of KOH (606 mg, 10.8 mmol, 2.0 equiv.) in MeOH (13.5 mL) and the resulting suspension was heated to reflux for two hours. The reaction was then cooled to room temperature and diluted with distilled water (25 mL). It was then extracted with DCM (3 x 20 mL) and washed with a saturated aqueous solution of NaHCO₃ (20 mL) and brine (20 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane) leading to the title compound

⁸ H. Tomioka, H. Okuno, S. Hondo, Y. Izawa, *J. Am. Chem. Soc.* **1980**, *102*, 7123–7125.

⁹ E. Emer, J. Twilton, M. Tredwell, S. Calderwood, T. L. Collier, B. Liégault, M. Taillefer, V. Gouverneur, *Org. Lett.* **2014**, *16*, 6004–6007.

56 (352 mg, 1.89 mmol, 35 % yield) as a volatile red liquid. **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.38 (m, 2H, ArH), 7.25 – 7.19 (m, 1H, ArH), 7.17 – 7.08 (m, 2H, ArH); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 129.4, 126.4 (q, J = 270 Hz), 125.9, 123.2, 122.7. One carbon was not resolved. The characterization data correspond to the reported values.⁹

Ethyl 2-(4-bromophenyl)-2-diazoacetate (**57**)

Following the general procedure A, starting from ethyl 2-(4-bromophenyl)acetate (1.30 g, 5.35 mmol, 1.0 equiv.), the title compound **57** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as an orange solid (1.33 g, 4.94 mmol, 92 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.45 (m, 2H, ArH), 7.40 – 7.32 (m, 2H, ArH), 4.33 (q, J = 7.1 Hz, 2H, CO₂CH₂CH₃), 1.34 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.3, 132.1, 125.4, 125.2, 119.5, 61.3, 14.7. One carbon was not resolved. The characterization data correspond to the reported values.¹⁰

Methyl 2-diazo-2-(4-methoxyphenyl)acetate (**58**)

Following the general procedure A, starting from methyl 2-(4-methoxyphenyl)acetate (1.20 g, 6.66 mmol, 1.0 equiv.), the title compound **58** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as an orange solid (838 mg, 4.06 mmol, 61 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.34 (m, 2H, ArH), 6.99 – 6.87 (m, 2H, ArH), 3.85 (s, 3H, CO₂CH₃), 3.81 (s, 3H, OCH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.2, 158.2, 126.1, 116.7, 114.5, 55.5, 51.7. One carbon was not resolved. The characterization data correspond to the reported values.⁴

Methyl 2-diazo-2-(*p*-tolyl)acetate (**59**)

Following the general procedure A, starting from methyl 2-(*p*-tolyl)acetate (800 mg, 4.87 mmol, 1.0 equiv.), the title compound **59** was obtained after purification by column chromatography on

¹⁰ N. D. Hahn, M. Nieger, K. H. Dötz, *J. Organomet. Chem.* **2004**, *16*, 2662–2673.

Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a red liquid (840 mg, 4.42 mmol, 91 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.32 (m, 2H, *ArH*), 7.23 – 7.17 (m, 2H, *ArH*), 3.86 (s, 3H, CO₂CH₃), 2.35 (s, 3H, CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.9, 135.8, 129.7, 124.2, 122.1, 52.0, 21.1. One carbon was not resolved. The characterization data correspond to the reported values.⁴

Methyl 2-diazo-2-(2-fluorophenyl)acetate (**60**)

Following the general procedure A, starting from methyl 2-(2-fluorophenyl)acetate (800 mg, 4.76 mmol, 1.0 equiv.), the title compound **60** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (900 mg, 4.64 mmol, 97 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (td, *J* = 7.8, 2.0 Hz, 1H, *ArH*), 7.29 – 7.15 (m, 2H, *ArH*), 7.08 (ddd, *J* = 11.2, 8.0, 1.7 Hz, 1H, *ArH*), 3.86 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.9, 158.7 (d, *J* = 248.9 Hz), 129.8, 128.9 (d, *J* = 8.4 Hz), 124.6 (d, *J* = 3.5 Hz), 116.1 (d, *J* = 21.3 Hz), 113.9 (d, *J* = 11.9 Hz), 52.4. One carbon was not resolved. The characterization data correspond to the reported values.¹¹

Methyl 2-(2-chloro-4-fluorophenyl)-2-diazoacetate (**61**)

Following the general procedure A, starting from methyl 2-(2-chloro-4-fluorophenyl)acetate (900 mg, 4.44 mmol, 1.0 equiv.), the title compound **61** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (941 mg, 4.12 mmol, 93 % yield). **R_f** 0.55 (Pentane:EtOAc 95:5); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.52 (dd, *J* = 8.8, 6.0 Hz, 1H, *ArH*), 7.19 (dd, *J* = 8.4, 2.7 Hz, 1H, *ArH*), 7.06 (ddd, *J* = 8.8, 7.8, 2.7 Hz, 1H, *ArH*), 3.84 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.0, 162.5 (d, *J* = 252.4 Hz), 135.1 (d, *J* = 10.6 Hz), 133.8 (d, *J* = 9.1 Hz), 120.2 (d, *J* = 3.7 Hz), 117.5 (d, *J* = 25.1 Hz), 115.0 (d, *J* = 21.6 Hz), 61.1, 52.5; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -110.6; **IR** $\tilde{\nu}_{\text{max}}$ 3082 (w), 3001 (w), 2956 (w), 2100 (s), 1703 (s), 1598 (m), 1495 (s), 1442 (m), 1394 (m), 1347 (m), 1290 (s), 1258 (s), 1201 (s), 1161 (m), 1066 (m), 1023 (m), 920 (m), 891 (m), 865 (m), 822 (m), 743 (m), 694 (w), 607 (m); **HRMS (ESI)** calcd for C₉H₇ClF₁N₂O₂⁺ [M+H]⁺ 229.0175; found 229.0170.

¹¹ T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, 128, 4594–4595.

Methyl 2-diazo-2-(thiophen-3-yl)acetate (**62**)

Following the general procedure A, starting from methyl 2-(thiophen-3-yl)acetate (830 mg, 5.31 mmol, 1.0 equiv.), the title compound **62** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a red liquid (758 mg, 4.16 mmol, 78 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.35 (m, 2H, HetArH), 7.04 (dd, J = 5.0, 1.4 Hz, 1H, HetArH), 3.87 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.9, 126.4, 123.8, 123.4, 117.6, 52.1. One carbon was not resolved. The characterization data correspond to the reported values.¹²

Ethyl 2-diazo-2-(naphthalen-2-yl)acetate (**63**)

Following the general procedure A, starting from ethyl 2-(naphthalen-2-yl)acetate (952 mg, 4.45 mmol, 1.0 equiv.), the title compound **63** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as an orange solid (897 mg, 3.73 mmol, 84 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.02 (d, J = 1.9 Hz, 1H, ArH), 7.85 (d, J = 8.7 Hz, 1H, ArH), 7.80 (d, J = 8.8 Hz, 2H, ArH), 7.55 (dd, J = 8.7, 2.0 Hz, 1H, ArH), 7.51 – 7.40 (m, 2H, ArH), 4.38 (q, J = 7.1 Hz, 2H, CH₂CH₃), 1.38 (t, J = 7.1 Hz, 3H, CH₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.5, 133.8, 131.6, 128.8, 127.8, 127.8, 126.7, 125.9, 123.0, 122.7, 122.1, 61.2, 14.7. One carbon was not resolved. The characterization data correspond to the reported values.¹³

Methyl 2-diazo-2-(naphthalen-1-yl)acetate (**64**)

Following the general procedure A, starting from methyl 2-(naphthalen-1-yl)acetate (2.00 g, 9.99 mmol, 1.0 equiv.), the title compound **64** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a red liquid (2.05 g, 9.04 mmol, 90 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.94 – 7.85 (m, 3H, ArH),

¹² H. M. L. Davies, R. J. Townsend, *J. Org. Chem.* **2001**, 66, 6595–6603.

¹³ G. Chen, J. Song, Y. Yu, X. Luo, C. Li, X. Huang, *Chem. Sci.* **2016**, 7, 1786–1790.

7.66 – 7.51 (m, 4H, ArH), 3.86 (s, 3H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.8, 134.2, 131.5, 129.7, 129.6, 128.7, 126.4, 126.2, 125.3, 124.4, 122.2, 52.1. One carbon was not resolved. The characterization data correspond to the reported values.¹²

2.2 Synthesis of Cyclopropenes

General procedure B: Synthesis of cyclopropenes from diazo compounds.

Following a modified procedure,¹⁴ the diazo compound was dissolved in DCM (0.5 M) and the resulting solution was added via syringe pump to a suspension of Rh₂(OAc)₄ (0.01 equiv.) and the indicated acetylene (3.0 equiv.) in DCM (0.8 M) at room temperature over 10 hours. After the addition was complete, the reaction mixture was allowed to stir for another 10 hours. The reaction mixture was then filtered through a small pad of silica eluting with CH₂Cl₂ and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography with the indicated solvents.

Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**1**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (5.10 g, 32.0 mmol, 1.0 equiv.) and phenylacetylene (10.54 mL, 96.00 mmol, 3.0 equiv.), the title compound **1** was obtained after purification by column chromatography (SiO₂, Pentane:Et₂O 80:20) as a pale yellow solid (5.08 g, 21.9 mmol, 68 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H, ArH), 7.48 – 7.41 (m, 3H, ArH), 6.89 (s, 1H, C=CH), 3.74 (s, 6H, CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) 171.3, 130.8, 130.4, 128.8, 123.5, 112.2, 95.1, 52.3, 32.8. The characterization data correspond to the reported values.¹⁵

Dibenzyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**65**)

¹⁴ S. Chuprakov, M. Rubin, V. Gevorgyan, *J. Am. Chem. Soc.* **2005**, *127*, 3714–3715.

¹⁵ L.-A. Liao, F. Zhang, N. Yan, J. A. Golen, J. M. Fox, *Tetrahedron* **2004**, *60*, 1803–1816.

Following the general procedure B, starting from dibenzyl 2-diazomalonate (**44**) (889 mg, 2.86 mmol, 1.0 equiv.) and phenylacetylene (0.95 mL, 8.5 mmol, 3.0 equiv.), the title compound **65** was obtained after purification by column chromatography (SiO₂, Pentane:Et₂O 80:20 to 70:30) as a pale yellow solid (738 mg, 1.92 mmol, 67 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H, ArH), 7.44 – 7.40 (m, 3H, ArH), 7.31 – 7.26 (m, 10H, ArH), 6.91 (s, 1H, C=CH), 5.18 (s, 4H, CH₂); ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.7, 135.9, 130.7, 130.5, 129.0, 128.6, 128.2, 128.0, 124.1, 112.5, 95.3, 67.0, 33.5. The characterization data correspond to the reported values.¹⁶

Bis(2,2,2-trifluoroethyl) 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**66**)

Following the general procedure B, starting from bis(2,2,2-trifluoroethyl) 2-diazomalonate (**48**) (935 mg, 3.18 mmol, 1.0 equiv.) and phenylacetylene (1.05 mL, 9.54 mmol, 3.0 equiv.), the title compound **66** was obtained after purification by column chromatography (SiO₂, Pentane:Et₂O 90:10 to 80:20) as a pale yellow oil (542 mg, 1.47 mmol, 46 % yield). *R*_f 0.55 (Pentane:Et₂O 80:20). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 2H, ArH), 7.51 – 7.44 (m, 3H, ArH), 6.92 (s, 1H, C=CH), 4.53 (qd, *J* = 8.3, 6.3 Hz, 4H, CH₂); ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.6, 131.4, 130.5, 129.2, 123.0, 122.8 (q, *J* = 277.3 Hz), 111.7, 93.9, 61.1 (q, *J* = 37.0 Hz), 32.5. The characterization data correspond to the reported values.¹⁷

Dimethyl 2-(4-bromophenyl)cycloprop-2-ene-1,1-dicarboxylate (**67**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (395 mg, 2.50 mmol, 1.0 equiv.) and 1-bromo-4-ethynylbenzene (1.36 g, 7.50 mmol, 3.0 equiv.), the title compound **67** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 95:5 to 85:15) as a pale yellow oil (554 mg, 1.78 mmol, 71 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 2H, ArH), 7.51 – 7.46 (m, 2H, ArH), 6.94 (s, 1H, C=CH), 3.73 (s, 6H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.0, 132.4, 131.9, 125.4, 123.1, 111.7, 96.4, 52.7, 33.0. The characterization data correspond to the reported values.¹⁸

¹⁶ Y. Wang, E. A. F. Fordyce, F. Y. Chen, H. W. Lam, *Angew. Chem. Int. Ed.* **2008**, 47, 7350–7353.

¹⁷ B. Muriel, A. Gagnebin, J. Waser, *Chem. Sci.* **2019**, 10, 10716–10722.

¹⁸ E. A. F. Fordyce, T. Luebbers, H. W. Lam, *Org. Lett.* **2008**, 10, 3993–3996.

Dimethyl 2-(4-(*tert*-butyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate (**68**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (395 mg, 2.50 mmol, 1.0 equiv.) and 1-(*tert*-butyl)-4-ethynylbenzene (1.35 mL, 7.50 mmol, 3.0 equiv.), the title compound **68** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 95:5 to 90:10) as an orange solid (517 mg, 1.79 mmol, 72 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H, ArH), 7.49 – 7.44 (m, 2H, ArH), 6.82 (s, 1H, C=CH), 3.73 (s, 6H, OCH₃), 1.33 (s, 9H, *t*Bu); ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.4, 154.3, 130.3, 126.1, 121.2, 112.1, 94.3, 52.5, 35.2, 32.8, 31.3. The characterization data correspond to the reported values.¹⁹

Dimethyl 2-(4-methoxyphenyl)cycloprop-2-ene-1,1-dicarboxylate (**69**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (316 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynyl-4-methoxybenzene (0.8 mL, 6 mmol, 3.0 equiv.), the title compound **69** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 95:5 to 85:15) as a white solid (157 mg, 0.599 mmol, 30% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.43 (m, 2H, ArH), 6.95 – 6.87 (m, 2H, ArH), 6.70 (s, 1H, C=CH), 4.19 (s, 3H, OCH₃), 3.83 (s, 3H, CO₂CH₃), 3.82 (s, 3H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.6, 161.5, 159.1, 143.8, 124.5, 122.9, 114.4, 104.6, 93.1, 58.3, 55.5, 51.5. The characterization data correspond to the reported values.²⁰

Dimethyl 2-(3-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (**70**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (316 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynyl-3-fluorobenzene (0.69 mL, 6.0 mmol, 3.0 equiv.), the title compound **70** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc

¹⁹ Y. Liu, Q. Yu, S. Ma, *Eur. J. Org. Chem.* **2013**, 3033–3040.

²⁰ Q. Ye, H. Ye, D. Cheng, X. Li, X. Xu, *Tetrahedron Lett.* **2018**, 59, 2546–2549.

90:10) as a pale yellow oil (282 mg, 1.13 mmol, 56 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.40 (m, 2H, Ar*H*), 7.33 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar*H*), 7.18 – 7.11 (m, 1H, Ar*H*), 6.96 (s, 1H, C=CH), 3.75 (s, 6H, OCH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 171.0, 162.9 (d, *J* = 248.0 Hz), 130.7 (d, *J* = 8.4 Hz), 126.3 (d, *J* = 3.1 Hz), 126.1 (d, *J* = 8.3 Hz), 117.9 (d, *J* = 21.2 Hz), 117.1 (d, *J* = 22.7 Hz), 111.7 (d, *J* = 3.4 Hz), 97.0, 52.7, 33.2. The characterization data correspond to the reported values.¹⁷

Dimethyl 2-(naphthalen-1-yl)cycloprop-2-ene-1,1-dicarboxylate (**71**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (316 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynynaphthalene (0.85 mL, 6.0 mmol, 3.0 equiv.), the title compound **71** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 90:10) as a pale yellow solid (288 mg, 1.02 mmol, 51 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.39-8.34 (m, 1H, Ar*H*), 7.98-7.91 (m, 2H, Ar*H*), 7.79-7.76 (m, 1H, Ar*H*), 7.70-7.54 (m, 3H, Ar*H*), 7.22 (s, 1H, C=CH), 3.75 (s, 6H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 133.6, 132.3, 131.6, 131.0, 128.8, 127.7, 126.8, 125.6, 124.5, 120.5, 110.8, 97.5, 52.6, 31.5. The characterization data correspond to the reported values.¹⁸

Dimethyl 2-(2-(trifluoromethyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate (**72**)

Following the general procedure B, starting from dimethyl 2-diazomalonate (**42**) (316 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynyl-2-(trifluoromethyl)benzene (0.84 mL, 6.0 mmol, 3.0 equiv.), the title compound **72** was obtained after purification by column chromatography (SiO₂, Pentane:EtOAc 90:10) as a white solid (307 mg, 1.02 mmol, 51 % yield). **R_f** 0.35 (Pentane:EtOAc 80:20); **m.p** = 119-120 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.78 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.72 – 7.61 (m, 2H, Ar*H*), 7.54 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.10 (s, 1H, C=CH), 3.74 (s, 6H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 170.7, 132.8, 132.3, 130.5, 129.9 (q, *J* = 32.3 Hz), 126.6 (q, *J* = 5.1 Hz), 123.6 (q, *J* = 273.4 Hz), 121.9, 109.2, 101.2 (q, *J* = 4.1 Hz), 52.5, 33.2; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -62.7; **IR** $\tilde{\nu}_{\text{max}}$ 3421 (w), 3147 (w), 3040 (w), 2957 (w), 2847 (w), 1752 (s), 1442 (m), 1282 (s), 1174 (s), 1114 (s), 1066 (s), 981 (w), 909 (w), 778 (m), 743 (m), 701 (m), 642 (w); **HRMS (ESI)** calcd for C₁₄H₁₁F₃NaO₄⁺ [**M**+Na]⁺ 323.0502; found 323.0510.

Dimethyl 2-butylcycloprop-2-ene-1,1-dicarboxylate (**74**)

A solution of dimethyl 2-diazomalonate (**42**) (395 mg, 2.50 mmol, 1.0 equiv.) in DCM (1.75 mL) was added using a syringe pump over 15 hours to a stirred mixture of hex-1-yne (**73**) (1.15 mL, 10.0 mmol, 4.0 equiv.) and $\text{Rh}_2(\text{OAc})_4$ (11 mg, 0.025 mmol, 0.01 equiv.) in DCM (2.0 mL). After the addition was complete, the mixture was stirred for additional 3 hours. The suspension was then filtered through a small pad of silica gel eluting with DCM, and the filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO_2 , Pentane:EtOAc 90:10) affording the title compound **74** (240 mg, 1.13 mmol, 45 % yield) as a pale yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.35 (t, J = 1.4 Hz, 1H, C=CH), 3.71 (s, 6H, OCH_3), 2.55 (td, J = 7.4, 1.4 Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.60 – 1.53 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.44 – 1.32 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91 (t, J = 7.3 Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (101 MHz, Chloroform-*d*) 172.5, 114.8, 93.8, 52.8, 32.4, 29.1, 24.5, 22.5, 14.2. The characterization data correspond to the reported values.¹⁵

Dimethyl 2-(trimethylsilyl)cycloprop-2-ene-1,1-dicarboxylate (**76**)

Following a modified procedure,²¹ a solution of dimethyl 2-diazomalonate (**42**) (0.79 g, 5.0 mmol, 1.0 equiv.) in ethynyltrimethylsilane (**75**) (2 mL) was added using a syringe pump over 18 hours to a refluxing stirred suspension of $\text{Rh}_2(\text{OAc})_4$ (22 mg, 0.050 mmol, 0.01 equiv.) in ethynyltrimethylsilane (**75**) (10 mL). After the addition was complete, the reaction mixture was stirred at reflux for an additional 4 hours. The suspension was then filtered through a small pad of silica gel eluting with DCM, and the filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO_2 , Pentane:EtOAc 90:10) affording the title compound **76** (824 mg, 3.61 mmol, 72 % yield) as a colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.05 (s, 1H, C=CH), 3.70 (s, 6H, OCH_3), 0.25 (s, 9H, TMS); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 113.5, 110.8, 52.8, 30.8, -1.7. The characterization data correspond to the reported values.²¹

Dimethyl cycloprop-2-ene-1,1-dicarboxylate (**77**)

²¹ S. Chuprakov, D. A. Malyshev, A. Trofimov, V. Gevorgyan, *J. Am. Chem. Soc.* **2007**, *129*, 14868-14869.

Following a reported procedure,²² to a stirred solution of dimethyl 2-(trimethylsilyl)cycloprop-2-ene-1,1-dicarboxylate (**76**) (355 mg, 1.55 mmol, 1 equiv.) in THF (3 mL) was added dropwise a 10% aq. K₂CO₃ solution (2 mL). The reaction mixture was stirred for 30 min at 0 °C and 30 min at room temperature. Then brine (5 mL) was added and the layers were separated. The organic layer was further washed with brine (2 x 5 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 85:15) affording compound **77** (150 mg, 0.961 mmol, 62 % yield) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.90 (s, 2H, HC=CH), 3.73 (s, 6H, OCH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.9, 102.5, 52.7, 30.3. The characterization data correspond to the reported values.²²

Methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**39**)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (700 mg, 3.97 mmol, 1.0 equiv.) and phenylacetylene (1.31 mL, 11.9 mmol, 3.0 equiv.), the title compound **39** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a pale yellow oil (667 mg, 2.66 mmol, 67 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H, ArH), 7.45 – 7.37 (m, 5H, ArH), 7.33 – 7.26 (m, 2H, ArH), 7.23 – 7.18 (m, 2H, ArH & C=CH), 3.72 (s, 3H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 141.0, 130.1, 130.1, 129.0, 128.3, 128.2, 126.7, 125.6, 117.5, 100.5, 52.4, 33.7. The characterization data correspond to the reported values.¹⁵

Tert-butyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**78**)

Following the general procedure B, starting from *tert*-butyl 2-diazo-2-phenylacetate (**52**) (560 mg, 2.57 mmol, 1.0 equiv.) and phenylacetylene (0.85 mL, 7.7 mmol, 3.0 equiv.), the title compound **78** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 85:15) as an orange oil (310 mg, 1.06 mmol, 41 % yield). *R*_f 0.36 (Pentane:EtOAc 80:20); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H, ArH), 7.45 – 7.36 (m, 5H, ArH), 7.29 – 7.25 (m, 2H, ArH), 7.21 – 7.17 (m, 2H, ArH & C=CH), 1.44 (s, 9H, ^tBu); ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.9, 141.7, 129.9, 129.9, 128.9, 128.3, 128.0, 126.3, 126.0, 117.6, 100.9, 80.8, 34.8, 28.2; IR $\tilde{\nu}_{\text{max}}$ 3134 (w), 3059 (w), 3026 (w), 2932 (w), 1953

²² K. Krämer, P. Leong, M. Lautens, *Org. Lett.* **2011**, *13*, 819-821.

(w), 1711 (s), 1600 (w), 1491 (m), 1449 (m), 1390 (w), 1367 (m), 1247 (m), 1156 (s), 1074 (w), 1031 (w), 984 (m), 915 (w), 848 (m), 764 (m), 697 (s); **HRMS (ESI)** calcd for $C_{20}H_{20}NaO_2^+$ $[M+Na]^+$ 315.1356; found 315.1355.

1-(1,2-Diphenylcycloprop-2-en-1-yl)propan-1-one (**79**)

Following the general procedure B, starting from 1-diazo-1-phenylbutan-2-one (**53**) (468 mg, 2.69 mmol, 1.0 equiv.) and phenylacetylene (0.89 mL, 8.1 mmol, 3.0 equiv.), the title compound **79** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (280 mg, 1.13 mmol, 39 % yield, 92% purity). R_f 0.38 (Pentane:EtOAc 90:10); 1H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H, ArH), 7.41 – 7.34 (m, 3H, ArH), 7.31 – 7.27 (m, 2H, ArH), 7.26 – 7.20 (m, 3H, ArH & C=CH), 7.18 – 7.12 (m, 1H, ArH), 2.39 (dq, J = 17.7, 7.3 Hz, 1H, CH₂), 2.24 (dq, J = 17.7, 7.2 Hz, 1H, CH₂), 0.96 (t, J = 7.3 Hz, 3H, CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.1, 141.2, 130.3, 130.0, 129.2, 128.7, 128.3, 126.7, 125.7, 119.4, 101.9, 42.1, 32.4, 8.4; **IR** $\tilde{\nu}_{max}$ 3126 (w), 3059 (w), 3028 (w), 2976 (w), 2936 (w), 1755 (w), 1687 (m), 1600 (w), 1553 (w), 1492 (m), 1449 (m), 1409 (w), 1343 (w), 1210 (w), 1148 (m), 1070 (m), 1027 (w), 989 (w), 913 (m), 851 (w), 814 (w), 762 (s), 732 (m), 698 (s); **HRMS (ESI)** calcd for $C_{18}H_{17}O^+$ $[M+H]^+$ 249.1274; found 249.1279.

(1-(Trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (**80**)

Following the general procedure B, starting from (1-diazo-2,2,2-trifluoroethyl)benzene (**56**) (1.0 g, 5.4 mmol, 1.0 equiv.) and phenylacetylene (1.77 mL, 16.1 mmol, 3.0 equiv.), the title compound **80** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane) as a yellow oil (867 mg, 3.33 mmol, 62 % yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H, ArH), 7.50 – 7.39 (m, 5H, ArH), 7.35 – 7.29 (m, 2H, ArH), 7.29 – 7.24 (m, 1H, ArH), 7.17 (q, J = 1.6 Hz, 1H, C=CH); ^{13}C NMR (101 MHz, Chloroform-*d*) 138.3, 130.5, 130.0, 128.9, 128.4, 126.7 (q, J = 278.4 Hz), 127.9 (q, J = 1.7 Hz), 125.3, 117.4 (q, J = 2.4 Hz), 98.9 (q, J = 3.3 Hz), 32.1 (q, J = 35.6 Hz). The characterization data correspond to the reported values.²³

²³ M. Uehara, H. Suematsu, Y. Yasutomi, T. Katsuki, *J. Am. Chem. Soc.* **2011**, *133*, 170–171.

Ethyl 1-(4-bromophenyl)-2-phenylcycloprop-2-ene-1-carboxylate (**81**)

Following the general procedure B, starting from ethyl 2-(4-bromophenyl)-2-diazoacetate (**57**) (1.32 g, 4.91 mmol, 1.0 equiv.) and phenylacetylene (1.62 mL, 14.7 mmol, 3.0 equiv.), the title compound **81** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a pale yellow oil (869 mg, 2.53 mmol, 52 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H, ArH), 7.45 – 7.35 (m, 5H, ArH), 7.27 – 7.22 (m, 2H, ArH), 7.16 (s, 1H, C=CH), 4.18 (q, *J* = 7.1 Hz, 2H, CH₂CH₃), 1.20 (t, *J* = 7.1 Hz, 3H, CH₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.2, 140.1, 131.3, 130.3, 130.2, 130.0, 129.0, 125.3, 120.5, 117.1, 99.8, 61.3, 33.4, 14.4. The characterization data correspond to the reported values.²⁴

Methyl 1-(4-methoxyphenyl)-2-phenylcycloprop-2-ene-1-carboxylate (**82**)

Following the general procedure B, starting from methyl 2-diazo-2-(4-methoxyphenyl)acetate (**58**) (412 mg, 2.00 mmol, 1.0 equiv.) and phenylacetylene (0.66 mL, 6.0 mmol, 3.0 equiv.), the title compound **82** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a yellow oil (252 mg, 0.899 mmol, 45 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 2H, ArH), 7.46 – 7.36 (m, 3H, ArH), 7.34 – 7.28 (m, 2H, ArH), 7.21 (s, 1H, C=CH), 6.89 – 6.79 (m, 2H, ArH), 3.78 (s, 3H, OCH₃), 3.71 (s, 3H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.5, 158.4, 133.2, 130.1, 130.0, 129.4, 129.0, 125.6, 117.8, 113.7, 100.7, 55.4, 52.4, 33.0. The characterization data correspond to the reported values.²⁵

Methyl 2-(4-(tert-butyl)phenyl)-1-(p-tolyl)cycloprop-2-enecarboxylate (**83**)

²⁴ R. Hommelsheim, Y. Guo, Z. Yang, C. Empel, R. M. Koenigs, *Angew. Chemie Int. Ed.* **2019**, 58, 1203–1207.

²⁵ H. M. L. Davies, G. H. Lee, *Org. Lett.* **2004**, 6, 1233–1236.

Following the general procedure B, starting from methyl 2-diazo-2-(*p*-tolyl)acetate (**59**) (380 mg, 2.00 mmol, 1.0 equiv.) and 1-(*tert*-butyl)-4-ethynylbenzene (1.1 mL, 6.0 mmol, 3.0 equiv.), the title compound **83** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (282 mg, 0.880 mmol, 44 % yield). R_f 0.48 (Pentane:EtOAc 90:10); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H, ArH), 7.47 – 7.43 (m, 2H, ArH), 7.31 – 7.26 (m, 2H, ArH), 7.14 (s, 1H, C=CH), 7.12 – 7.07 (m, 2H, ArH), 3.71 (s, 3H, CO₂CH₃), 2.31 (s, 3H, CH₃), 1.33 (s, 9H, ^{*t*}Bu); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 175.5, 153.5, 138.2, 136.2, 129.8, 128.9, 128.3, 126.0, 122.8, 117.4, 99.4, 52.3, 35.1, 33.3, 31.3, 21.2; IR $\tilde{\nu}_{\text{max}}$ 3666 (w), 3134 (w), 2961 (s), 2912 (m), 1910 (w), 1720 (s), 1608 (w), 1508 (m), 1457 (m), 1442 (m), 1402 (m), 1371 (m), 1277 (s), 1212 (s), 1109 (m), 1027 (s), 904 (m), 833 (s), 766 (m), 732 (m), 689 (m); HRMS (ESI) calcd for C₂₂H₂₅O₂⁺ [M+H]⁺ 321.1849; found 321.1843.

Methyl 1-(*p*-tolyl)-2-(4-(trifluoromethoxy)phenyl)cycloprop-2-enecarboxylate (**84**)

Following the general procedure B, starting from methyl 2-diazo-2-(*p*-tolyl)acetate (**59**) (380 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynyl-4-(trifluoromethoxy)benzene (0.92 mL, 6.0 mmol, 3.0 equiv.), the title compound **84** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (312 mg, 0.896 mmol, 40 % yield, 94% purity). R_f 0.45 (Pentane:EtOAc 90:10); $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.85 – 7.77 (m, 2H, ArH), 7.46 – 7.41 (m, 5H, ArH & C=CH), 7.31 – 7.25 (m, 2H, ArH), 3.89 (s, 3H, CO₂CH₃), 2.49 (s, 3H, CH₃); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 175.0, 150.5 – 150.0 (m), 137.6, 136.5, 131.5, 129.1, 128.1, 124.4, 121.5, 120.4 (q, J = 278.2 Hz), 116.8, 101.5, 52.0, 33.6, 21.2; $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -57.7; IR $\tilde{\nu}_{\text{max}}$ 3133 (w), 2995 (w), 2952 (w), 1721 (m), 1597 (w), 1506 (m), 1441 (w), 1255 (s), 1212 (s), 1169 (s), 1113 (m), 1024 (m), 906 (m), 848 (m), 819 (m), 766 (w), 731 (m), 692 (w); HRMS (ESI) calcd for C₁₉H₁₆F₃O₃⁺ [M+H]⁺ 349.1046; found 349.1052.

Methyl 2-(2-chlorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (**85**)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (352 mg, 2.00 mmol, 1.0 equiv.) and 1-chloro-2-ethynylbenzene (0.73 mL, 6.0 mmol, 3.0 equiv.), the title compound **85** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (329 mg, 1.16 mmol, 58 % yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 1H, ArH), 7.51 – 7.47 (m, 1H, ArH), 7.45 (s, 1H, C=CH), 7.41 – 7.36 (m, 2H, ArH), 7.35 – 7.27 (m, 4H, ArH), 7.25 – 7.19 (m, 1H, ArH), 3.73 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 174.8, 140.6, 136.4, 131.7, 131.0, 130.2, 128.3, 128.3, 127.1, 126.8, 124.4, 115.1, 105.1, 52.4, 33.4. The characterization data correspond to the reported values.²⁶

Methyl 1-(2-fluorophenyl)-2-phenylcycloprop-2-ene-1-carboxylate (**86**)

Following the general procedure B, starting from methyl 2-diazo-2-(2-fluorophenyl)acetate (**60**) (900 mg, 4.64 mmol, 1.0 equiv.) and phenylacetylene (1.53 mL, 13.9 mmol, 3.0 equiv.), the title compound **86** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a pale yellow oil (734 mg, 2.74 mmol, 59 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.73 – 7.66 (m, 2H, ArH), 7.48 – 7.38 (m, 3H, ArH), 7.27 (s, 1H, C=CH), 7.25 – 7.16 (m, 2H, ArH), 7.09 – 7.05 (m, 1H, ArH), 7.05 – 7.01 (m, 1H, ArH), 3.71 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 174.9, 161.7 (d, *J* = 244.6 Hz), 130.2, 130.1, 130.0 (d, *J* = 4.5 Hz), 129.2, 128.9 (d, *J* = 8.7 Hz), 125.4, 124.2 (d, *J* = 3.4 Hz), 119.2, 115.5 (d, *J* = 22.1 Hz), 99.7, 52.3, 29.8. The characterization data correspond to the reported values.²⁴

Methyl 1-(2-chloro-4-fluorophenyl)-2-(p-tolyl)cycloprop-2-enecarboxylate (**87**)

Following the general procedure B, starting from methyl 2-(2-chloro-4-fluorophenyl)-2-diazoacetate (**61**) (941 mg, 4.12 mmol, 1.0 equiv.) and 1-ethynyl-4-methylbenzene (1.60 mL, 12.4 mmol, 3.0 equiv.), the title compound **87** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as an orange oil (439 mg, 1.39 mmol, 32 % yield, 95% purity). *R_f* 0.32 (Pentane:EtOAc 90:10); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.52 (d, *J* = 8.1 Hz, 2H, ArH), 7.21 – 7.17 (m, 3H, ArH), 7.16 (s, 1H, C=CH) 7.02 (dd, *J* = 8.5, 2.6 Hz, 1H, ArH), 6.77 (ddd, *J* = 8.5, 8.0, 2.6 Hz, 1H, ArH), 3.63 (s, 3H, CO₂CH₃), 2.32 (s, 3H, CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 174.6, 161.6 (d, *J* = 248.9 Hz), 140.7, 136.2 (d, *J* = 3.7 Hz), 135.7 (d, *J* = 10.4 Hz), 130.9 (d, *J* = 8.8 Hz), 129.9, 129.7, 122.6, 118.1, 116.9 (d, *J* = 24.8 Hz), 114.0 (d, *J* = 21.0 Hz), 100.6, 52.5, 32.7, 21.6; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -113.4 (td, *J* = 8.2, 5.9 Hz); **IR $\tilde{\nu}_{\text{max}}$** 3139 (w), 3028 (w), 2951 (w), 1723 (s), 1597 (m), 1490 (m), 1442 (m), 1386 (w), 1224 (s), 1115 (w), 1049 (m), 1012 (m), 912 (m), 862

²⁶ L. Chen, D. Leslie, M. G. Coleman, J. Mack, *Chem. Sci.* **2018**, 9, 4650–4661.

(m), 821 (m), 776 (m), 730 (s), 687 (m), 654 (w), 604 (w) ; **HRMS (ESI)** calcd for $C_{18}H_{15}ClFO_2^+$ $[M+H]^+$ 317.0739; found 317.0745.

Methyl 2-(3,5-bis(trifluoromethyl)phenyl)-1-phenylcycloprop-2-ene-1-carboxylate (88)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (352 mg, 2.00 mmol, 1.0 equiv.) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (1.1 mL, 6.0 mmol, 3.0 equiv.), the title compound **88** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 97:3) as a yellow oil (333 mg, 0.862 mmol, 43 % yield). R_f 0.30 (Pentane:EtOAc 95:5); 1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 2H, ArH), 7.86 (s, 1H, ArH), 7.50 (s, 1H, C=CH), 7.34 – 7.31 (m, 2H, ArH), 7.31 – 7.28 (m, 2H, ArH), 7.26 – 7.23 (m, 1H, ArH), 3.73 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.2, 139.7, 132.7 (q, J = 33.8 Hz), 129.7 – 129.4 (m), 128.6, 128.1, 128.0, 127.3, 123.5 (p, J = 3.8 Hz), 123.0 (q, J = 272.9 Hz), 116.4, 105.2, 52.7, 34.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1; IR $\tilde{\nu}_{max}$ 3136 (w), 3031 (w), 2956 (w), 2851 (w), 1725 (m), 1610 (w), 1495 (w), 1443 (w), 1373 (m), 1278 (s), 1176 (s), 1131 (s), 1013 (m), 904 (m), 841 (m), 704 (m), 692 (m); **HRMS (ESI)** calcd for $C_{19}H_{12}F_6O_2^+$ $[M]^+$ 386.0736; found 386.0743.

Methyl 2-phenyl-1-(thiophen-3-yl)cycloprop-2-enecarboxylate (89)

Following the general procedure B, starting from methyl 2-diazo-2-(thiophen-3-yl)acetate (**62**) (758 mg, 4.16 mmol, 1.0 equiv.) and phenylacetylene (1.37 mL, 12.5 mmol, 3.0 equiv.), the title compound **89** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 96:4) as a brown oil (490 mg, 1.91 mmol, 46 % yield). 1H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H, ArH), 7.46 – 7.39 (m, 3H, ArH), 7.35 (dd, J = 3.0, 1.3 Hz, 1H, HetArH), 7.19 (dd, J = 5.0, 3.0 Hz, 1H, HetArH), 7.11 (s, 1H, C=CH), 7.05 (dd, J = 5.0, 1.4 Hz, 1H, HetArH), 3.72 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 142.1, 130.0, 129.9, 128.7, 127.7, 125.0, 124.5, 121.6, 115.6, 99.9, 52.2, 33.0. The characterization data correspond to the reported values.²⁵

Methyl 2-(naphthalen-2-yl)-1-phenylcycloprop-2-ene-1-carboxylate (**90**)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (352 mg, 2.00 mmol, 1.0 equiv.) and 2-ethynylnaphthalene (913 mg, 6.00 mmol, 3.0 equiv.), the title compound **90** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a white solid (389 mg, 1.29 mmol, 65 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.09 – 8.06 (m, 1H, ArH), 7.91 – 7.82 (m, 3H, ArH), 7.72 (dd, J = 8.4, 1.6 Hz, 1H, ArH), 7.56 – 7.49 (m, 2H, ArH), 7.48 – 7.42 (m, 2H, ArH), 7.33 – 7.27 (m, 3H, ArH & C=CH), 7.25 – 7.20 (m, 1H, ArH), 3.74 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 175.2, 141.0, 134.0, 133.3, 130.1, 128.9, 128.6, 128.4, 128.3, 128.0, 127.5, 126.9, 126.7, 126.7, 122.9, 117.2, 101.3, 52.4, 33.9. The characterization data correspond to the reported values.²⁵

Methyl 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)cycloprop-2-enecarboxylate (**91**)

Following the general procedure B, starting from methyl 2-diazo-2-(4-methoxyphenyl)acetate (**58**) (412 mg, 2.00 mmol, 1.0 equiv.) and 2-ethynylnaphthalene (913 mg, 6.00 mmol, 3.0 equiv.), the title compound **91** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a yellow oil (220 mg, 0.666 mmol, 29 % yield, 88% purity). **R_f** 0.32 (Pentane:EtOAc 90:10); **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.10 – 8.05 (m, 1H, ArH), 7.91 – 7.82 (m, 3H, ArH), 7.72 (dd, J = 8.5, 1.6 Hz, 1H, ArH), 7.55 – 7.50 (m, 2H, ArH), 7.42 – 7.35 (m, 2H, ArH), 7.31 (s, 1H, C=CH), 6.88 – 6.82 (m, 2H, ArH), 3.78 (s, 3H, CO₂CH₃), 3.74 (s, 3H, OCH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 175.4, 158.3, 133.9, 133.2, 133.1, 129.9, 129.4, 128.8, 128.5, 127.9, 127.4, 126.8, 126.6, 122.9, 117.5, 113.6, 101.5, 55.3, 52.3, 33.1; **IR $\tilde{\nu}_{\text{max}}$** 3134 (m), 3051 (m), 3003 (m), 2952 (m), 2843 (m), 2359 (m), 2333 (m), 1718 (s), 1604 (s), 1511 (s), 1460 (s), 1341 (m), 1242 (s), 1218 (s), 1173 (s), 1103 (m), 1029 (s), 904 (s), 859 (s), 822 (s), 738 (s), 653 (s); **HRMS (ESI)** calcd for C₂₂H₁₈NaO₃⁺ [M+Na]⁺ 353.1148; found 353.1150.

Ethyl 2-(4-bromophenyl)-1-(naphthalen-2-yl)cycloprop-2-enecarboxylate (**92**)

Following the general procedure B, starting from ethyl 2-diazo-2-(naphthalen-2-yl)acetate (**63**) (481 mg, 2.00 mmol, 1.0 equiv.) and 1-bromo-4-ethynylbenzene (1.09 g, 6.00 mmol, 3.0 equiv.), the title compound **92** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a fluffy white solid (543 mg, 1.38 mmol, 69 % yield). **R_f** 0.28 (Pentane:EtOAc 90:10); **m.p** = 129-130 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.81 – 7.73 (m, 4H, *ArH*), 7.59 – 7.55 (m, 2H, *ArH*), 7.54 – 7.48 (m, 3H, *ArH*), 7.45 – 7.38 (m, 2H, *ArH*), 7.33 (s, 1H, C=CH), 4.23 (q, *J* = 7.1 Hz, 2H, CO₂CH₂CH₃), 1.23 (t, *J* = 7.1 Hz, 3H, CO₂CH₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 174.2, 138.3, 133.3, 132.3, 132.2, 131.3, 127.8, 127.6, 127.6, 126.6, 126.5, 126.0, 125.6, 124.5, 124.4, 116.8, 101.3, 61.1, 34.0, 14.3; **IR** $\tilde{\nu}_{\text{max}}$ 3135 (w), 3056 (w), 2983 (m), 1715 (s), 1593 (m), 1477 (m), 1392 (m), 1360 (m), 1242 (s), 1213 (s), 1176 (s), 1104 (m), 1075 (m), 1033 (s), 909 (m), 825 (s), 745 (s), 681 (m); **HRMS (ESI)** calcd for C₂₂H₁₇⁷⁹BrNaO₂⁺ [*M*+Na]⁺ 415.0304; found 415.0315.

Methyl 2-(phenanthren-9-yl)-1-phenylcycloprop-2-enecarboxylate (**93**)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (352 mg, 2.00 mmol, 1.0 equiv.) and 9-ethynylphenanthrene (1.21 g, 6.00 mmol, 3.0 equiv.), the title compound **93** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow powder (342 mg, 0.976 mmol, 49 % yield). **R_f** 0.35 (Pentane:EtOAc 90:10); **m.p** = 150-151 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.78 – 8.71 (m, 1H, *ArH*), 8.68 (d, *J* = 8.3 Hz, 1H, *ArH*), 8.57 – 8.48 (m, 1H, *ArH*), 8.01 (s, 1H, *ArH*), 7.91 (dd, *J* = 7.9, 1.4 Hz, 1H, *ArH*), 7.76 – 7.68 (m, 3H, *ArH*), 7.64 – 7.59 (m, 2H, *ArH* & C=CH), 7.55 – 7.50 (m, 2H, *ArH*), 7.35 – 7.28 (m, 2H, *ArH*), 7.25 – 7.20 (m, 1H, *ArH*), 3.76 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 175.1, 140.8, 132.0, 131.3, 131.2, 130.8, 130.6, 129.7, 128.5, 128.4, 128.3, 127.5, 127.4, 127.3, 126.7, 125.4, 123.2, 122.8, 120.5, 115.1, 103.9, 52.4, 32.1; **IR** $\tilde{\nu}_{\text{max}}$ 3130 (w), 3060 (w), 3027 (w), 2951 (w), 2253 (w), 1717 (s), 1601 (w), 1495 (m), 1442 (m), 1283 (m), 1217 (s), 1114 (m), 1027 (m), 907 (s), 857 (m), 733 (s), 613 (m); **HRMS (ESI)** calcd for C₂₅H₁₉O₂⁺ [*M*+H]⁺ 351.1380; found 351.1385.

Methyl 2-(naphthalen-1-yl)-1-phenylcycloprop-2-enecarboxylate (**94**)

Following the general procedure B, starting from methyl 2-diazo-2-phenylacetate (**49**) (640 mg, 3.63 mmol, 1.0 equiv.) and 1-ethynylnaphthalene (1.55 mL, 10.9 mmol, 3.0 equiv.), the title compound **94** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 95:5) as a yellow oil (556 mg, 1.85 mmol, 51 % yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.45 (d, J = 8.1 Hz, 1H, ArH), 7.92 (dd, J = 7.8, 3.0 Hz, 2H, ArH), 7.75 (dd, J = 7.1, 1.2 Hz, 1H, ArH), 7.71 – 7.63 (m, 1H, ArH), 7.62 – 7.48 (m, 5H, ArH), 7.34 – 7.28 (m, 2H, ArH), 7.28 – 7.21 (m, 1H, ArH), 3.76 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 175.1, 140.9, 133.7, 132.4, 130.9, 130.0, 128.8, 128.7, 128.4, 128.2, 127.5, 126.7, 126.6, 124.4, 121.8, 115.4, 102.9, 52.4, 32.1. The characterization data correspond to the reported values.²⁷

Methyl 1,2-di(naphthalen-1-yl)cycloprop-2-enecarboxylate (**95**)

Following the general procedure B, starting from methyl 2-diazo-2-(naphthalen-1-yl)acetate (**64**) (588 mg, 2.60 mmol, 1.0 equiv.) and 1-ethynylnaphthalene (1.1 mL, 7.8 mmol, 3.0 equiv.), the title compound **95** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as an orange powder (143 mg, 0.408 mmol, 14 % yield, 90% purity). **R_f** 0.29 (Pentane:EtOAc 90:10); **m.p** = 172-173 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.42 – 8.35 (m, 1H, ArH), 8.22 (dt, J = 8.4, 1.0 Hz, 1H, ArH), 8.01 – 7.87 (m, 4H, ArH), 7.84 (s, 1H, C=CH), 7.76 (dt, J = 8.2, 1.2 Hz, 1H, ArH), 7.62 – 7.55 (m, 5H, ArH), 7.54 – 7.50 (m, 1H, ArH), 7.31 (dd, J = 8.2, 7.1 Hz, 1H, ArH), 3.70 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 176.1, 139.0, 134.0, 133.8, 132.6, 132.5, 131.0, 129.6, 129.0, 128.8, 128.0, 127.5, 126.8, 126.3, 125.9, 125.8, 125.8, 125.6, 124.8, 124.6, 122.7, 116.4, 106.6, 52.7, 31.0; **IR** $\tilde{\nu}_{\text{max}}$ 3132 (w), 3054 (m), 2949 (w), 1939 (w), 1714 (s), 1589 (m), 1504 (m), 1439 (m), 1397 (m), 1288 (m), 1226 (s), 1174 (m), 1084 (m), 1053 (m), 1011 (m), 994 (m), 910 (s), 778 (s), 731 (s), 647 (m); **HRMS (ESI)** calcd for C₂₅H₁₉O₂⁺ [M+H]⁺ 351.1380; found 351.1380.

²⁷ C. Li, Y. Zeng, J. Wang, *Tetrahedron Lett.* **2009**, 50, 2956–2959.

3. Synthesis of the ABZ Reagent 3

2-Iodo-*N*-tosylbenzamide (**97**)

Following a reported procedure,²⁸ SOCl_2 (3.53 mL, 48.4 mmol, 1.2 equiv) followed by DMF (0.20 mL, 2.6 mmol, 0.06 equiv) were added dropwise to a solution of 2-iodobenzoic acid (**96**) (10.0 g, 40.3 mmol, 1.0 equiv.) in DCM (200 mL, 0.2 M), and the resulting mixture was stirred for 3 h at room temperature. Thereafter, the solvent was evaporated, the residue was dissolved in toluene (32 mL), and then the mixture was added to a solution of 4-toluenesulfonamide (6.90 g, 40.3 mmol, 1.0 equiv.), triethylamine (14.0 mL, 101 mmol, 2.5 equiv), and DMAP (250 mg, 2.02 mmol, 0.05 equiv.) in EtOAc (80 mL). The mixture was heated for 1 h to 60 °C, then cooled to room temperature, and quenched with 1 M HCl (50 mL). The mixture was extracted with EtOAc (3 × 50 mL), and the combined organic extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO_2 , DCM) affording **97** (15.8 g, 39.5 mmol, 98 % yield) as a colorless oil. **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.78 (s, 1H, NH), 8.01 (d, J = 8.4 Hz, 2H, ArH), 7.80 (dd, J = 8.0, 1.0 Hz, 1H, ArH), 7.43 – 7.31 (m, 4H, ArH), 7.10 (ddd, J = 8.0, 7.2, 2.0 Hz, 1H, ArH), 2.44 (s, 3H, CH_3); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.6, 145.3, 140.2, 138.4, 134.9, 132.4, 129.5, 128.8, 128.7, 128.3, 91.6, 21.7. The characterization data is corresponding to the reported values.²⁸

3-Oxo-2-tosyl-2,3-dihydro-1H-1 λ^3 -benzo[*d*][1,2]iodazol-1-yl acetate (**98**)

Caution: For safety reasons, the reaction was carried out behind an antiblast shield. Following a reported procedure,²⁸ $m\text{CPBA}$ (77% pure; 8.85 g, 39.6 mmol, 1.0 equiv.) was added to a solution of **97** (15.8 g, 39.5 mmol, 1.0 equiv.) and Ac_2O (160 mL, 1.68 mol, 42.4 equiv.) in AcOH (158 mL, 0.10 M), and the resulting mixture was heated for 48 h to 80 °C. Thereafter, the mixture was cooled to room temperature, and diethyl ether (150 mL) was added. Compound **98** (7.13 g, 15.5 mmol, 39% yield) crystallized at 0 °C from the solution and was collected by filtration. **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.95 (m, 2H, ArH), 7.95 – 7.89 (m, 2H, ArH), 7.86 (dd, J = 8.8, 0.9 Hz, 1H, ArH), 7.80 – 7.71 (m, 1H, ArH), 7.44 (d, J = 8.1 Hz, 2H, ArH), 2.38 (s, 3H, CH_3), 2.26 (s, 3H, OCOCH_3); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 174.1, 162.4, 144.5, 136.8, 136.0, 132.3, 131.4, 131.2, 129.7, 128.8, 127.9, 118.0, 21.1, 20.2. The characterization data is corresponding to the reported values.²⁸

²⁸ S. Alazet, J. Preindl, R. Simonet-Davin, S. Nicolai, A. Nanchen, T. Meyer, J. Waser, *J. Org. Chem.* **2018**, 83, 12334–12356.

1-azido-2-tosyl-1,2-dihydro-3H-1 λ ³-benzo[*d*][1,2]iodazol-3-one (ABZ, **3)**

Caution: For safety reasons, the reaction was carried out behind an antiblast shield. Following a reported procedure,²⁸ TMSOTf (14 μ L, 0.080 mmol, 0.005 equiv) was added dropwise to a suspension of **98** (7.13 g, 15.5 mmol, 1.0 equiv.) and TMSN₃ (3.0 mL, 23 mmol, 1.5 equiv.) in DCM (31 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C, and thereafter, the formed solid was filtered, washed with DCM and then pentane, and dried in vacuo to afford ABZ (**3**) (5.38 g, 12.2 mmol, 78%) as a pale yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.17 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 8.03–7.93 (m, 2H, Ar*H*), 7.93–7.87 (m, 2H, Ar*H*), 7.75 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 7.46 – 7.37 (m, 2H, Ar*H*), 2.38 (s, 3H, CH₃); ¹³C NMR (400 MHz, DMSO-*d*₆) δ 162.6, 144.0, 136.7, 136.3, 132.5, 131.2, 131.2, 129.5, 128.5, 127.8, 118.2, 21.1. The characterization data is corresponding to the reported values.²⁸

4. Radical Amination of Cyclopropenes for the Synthesis of Alkenyl Nitriles

General procedure C

A 5 mL test tube was charged with CuCl_2 (2 mg, 0.05 mmol, 0.05 equiv.), the cyclopropene (0.30 mmol, 1.0 equiv.) and PIDA (174 mg, 0.540 mmol, 1.8 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then CH_3CN (3 mL, 0.1 M) and TMS-N_3 (72 μL , 0.54 mmol, 1.8 equiv.) were added via syringe and the resulting mixture was stirred at room temperature for 30 minutes. The reaction mixture was then filtered through a small pad of silica gel eluting with Et_2O , and the filtrate was concentrated under reduced pressure. The obtained crude residue was then subjected to column chromatography using the indicated solvents.

Dimethyl 2-(cyano(phenyl)methylene)malonate (**2**)

Following the general procedure C, starting from dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**1**) (70 mg, 0.30 mmol, 1.0 equiv.), the title compound **2** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 80:20) as a grey solid (67 mg, 0.27 mmol, 91 % yield). R_f 0.33 (Pentane:EtOAc 80:20); $m.p$ = 74–75 $^{\circ}\text{C}$; $^1\text{H NMR}$ (400 MHz, CHCl_3) δ 7.55 – 7.38 (m, 5H, ArH), 3.94 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3); $^{13}\text{C NMR}$ (101 MHz, CHCl_3) δ 164.2, 161.7, 137.0, 132.0, 131.6, 129.3, 128.3, 125.8, 115.6, 53.7, 53.3; IR $\tilde{\nu}_{\text{max}}$ 2956 (w), 1737 (s), 1608 (w), 1436 (m), 1309 (m), 1256 (s), 1229 (s), 1187 (m), 1098 (m), 1021 (m), 982 (w), 929 (w), 862 (w), 768 (s), 697 (m); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 246.0761; found 246.0764.

Dibenzyl 2-(cyano(phenyl)methylene)malonate (**4**)

Following the general procedure C, starting from dibenzyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**65**) (115 mg, 0.300 mmol, 1.0 equiv.), the title compound **4** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a colorless oil (88 mg, 0.22 mmol, 74 % yield). R_f 0.52 (Pentane:EtOAc

80:20); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.40 (m, 3H, ArH), 7.37 (m, 5H, ArH), 7.33 – 7.29 (m, 3H, ArH), 7.27 – 7.24 (m, 2H, ArH), 7.10 – 7.05 (m, 2H, ArH), 5.35 (s, 2H, CH₂), 5.10 (s, 2H, CH₂); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 163.4, 161.0, 137.2, 134.6, 134.1, 131.9, 131.5, 129.2, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.4, 126.0, 115.6, 68.5, 68.4; **IR $\tilde{\nu}_{\text{max}}$** 3655 (w), 3453 (w), 3064 (m), 3035 (m), 2951 (w), 2113 (w), 1959 (w), 1733 (s), 1605 (w), 1496 (w), 1451 (m), 1377 (w), 1303 (m), 1214 (s), 1095 (m), 1014 (m), 975 (w), 955 (m), 907 (w), 738 (s), 694 (s), 638 (w); **HRMS (ESI)** calcd for C₂₅H₁₉NNaO₄⁺ [M+Na]⁺ 420.1206; found 420.1206.

Bis(2,2,2-trifluoroethyl) 2-(cyano(phenyl)methylene)malonate (**5**)

Following the general procedure C, starting from bis(2,2,2-trifluoroethyl) 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**66**) (110 mg, 0.300 mmol, 1.0 equiv.), the title compound **5** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a colorless oil (82 mg, 0.22 mmol, 72 % yield). **R_f** 0.25 (Pentane:EtOAc 90:10); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.59 – 7.43 (m, 5H, ArH), 4.70 (q, *J* = 8.1, 2H, CH₂CF₃), 4.49 (q, *J* = 8.2, 2H, CH₂CF₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 161.6, 159.2, 133.5, 132.5, 131.3, 129.7, 129.6, 128.4, 122.4 (q, *J* = 277.3 Hz), 122.2 (q, *J* = 277.6 Hz), 114.8, 62.0 (q, *J* = 37.8 Hz), 61.7 (q, *J* = 37.6 Hz); **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ = -73.5, -73.6; **IR $\tilde{\nu}_{\text{max}}$** 2981 (w), 1757 (m), 1608 (w), 1576 (w), 1446 (w), 1413 (m), 1287 (s), 1210 (s), 1166 (s), 1100 (m), 1050 (m), 1018 (w), 980 (m), 846 (w), 766 (m), 697 (m), 656 (m); **HRMS (APPI)** calcd for C₁₅H₁₀F₆NO₄⁺ [M+H]⁺ 382.0509; found 382.0521.

Dimethyl 2-((4-bromophenyl)(cyano)methylene)malonate (**6**)

Following the general procedure C, starting from dimethyl 2-(4-bromophenyl)cycloprop-2-ene-1,1-dicarboxylate (**67**) (93 mg, 0.30 mmol, 1.0 equiv.), the title compound **6** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 85:15) as a white solid (86 mg, 0.27 mmol, 88 % yield). **R_f** 0.30 (Pentane:EtOAc 80:20); **m.p.** = 66–67 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.55 (m, 2H, ArH), 7.41 – 7.33 (m, 2H, ArH), 3.94 (s, 3H, CO₂CH₃), 3.72 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 163.9, 161.5, 137.4, 132.6, 130.8, 129.8, 126.5, 124.6, 115.3, 53.8, 53.5; **IR $\tilde{\nu}_{\text{max}}$** 3664 (w), 2960 (m), 2902 (w), 1736 (s), 1593 (m), 1485 (m), 1441 (m), 1399 (m), 1308 (s), 1232 (s), 1083 (s), 1020 (m), 981 (m), 928 (w), 832 (m), 774 (m), 722 (m), 654 (w); **HRMS (ESI)** calcd for C₁₃H₁₁BrNO₄⁺ [M+H]⁺ 323.9866; found 323.9874.

Dimethyl 2-((4-(tert-butyl)phenyl)(cyano)methylene)malonate (**7**)

Following the general procedure C, starting from dimethyl 2-(4-(tert-butyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate (**68**) (87 mg, 0.30 mmol, 1.0 equiv.), the title compound **7** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a colorless oil (86 mg, 0.29 mmol, 95 % yield). R_f 0.48 (Pentane:EtOAc 80:20); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, J = 1.0 Hz, 4H, Ar*H*), 3.92 (s, 3H, CO₂CH₃), 3.73 (s, 3H, CO₂CH₃), 1.32 (s, 9H, *t*Bu); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 161.8, 155.4, 135.8, 129.0, 128.3, 126.3, 125.8, 115.7, 53.6, 53.3, 35.1, 31.1; IR $\tilde{\nu}_{\text{max}}$ 3670 (w), 3461 (w), 2960 (m), 2872 (w), 2224 (w), 2120 (w), 1737 (s), 1601 (m), 1510 (w), 1308 (m), 1257 (s), 1092 (s), 1026 (m), 984 (w), 930 (w), 840 (m), 737 (s), 663 (w); HRMS (ESI) calcd for C₁₇H₁₉NNaO₄⁺ [M+Na]⁺ 324.1206; found 324.1208.

Dimethyl 2-(cyano(3-fluorophenyl)methylene)malonate (**8**)

Following the general procedure C, starting from dimethyl 2-(3-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (**70**) (75 mg, 0.30 mmol, 1.0 equiv.), the title compound **8** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 85:15) as a white solid (67 mg, 0.26 mmol, 81 % yield, 96% purity).²⁹ R_f 0.38 (Pentane:EtOAc 80:20); m.p = 62-63 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 1H, Ar*H*), 7.32 – 7.27 (m, 1H, Ar*H*), 7.24 – 7.15 (m, 2H, Ar*H*), 3.94 (s, 3H, CO₂CH₃), 3.72 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.7, 162.7 (d, J = 249.5 Hz), 161.4, 138.0, 133.7 (d, J = 8.1 Hz), 131.1 (d, J = 8.4 Hz), 124.2, 124.2 (d, J = 3.6 Hz), 118.7 (d, J = 21.2 Hz), 115.5 (d, J = 23.9 Hz), 115.2, 53.8, 53.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.3; IR $\tilde{\nu}_{\text{max}}$ 3077 (w), 3012 (w), 2959 (w), 2849 (w), 1738 (s), 1587 (m), 1484 (w), 1440 (m), 1317 (m), 1242 (s), 1191 (m), 1099 (m), 1031 (m), 928 (m), 840 (w), 792 (m), 697 (m), 652 (w); HRMS (ESI) calcd for C₁₃H₁₀FNNaO₄⁺ [M+Na]⁺ 286.0486; found 286.0492.

²⁹ For characterization purposes, a small sample of the product was re-purified.

Dimethyl 2-(cyano(naphthalen-1-yl)methylene)malonate (**9**)

Following the general procedure C, starting from dimethyl 2-(naphthalen-1-yl)cycloprop-2-ene-1,1-dicarboxylate (**71**) (85 mg, 0.30 mmol, 1.0 equiv.), the title compound **9** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 85:15) as a yellow solid (83 mg, 0.28 mmol, 94 % yield). R_f 0.35 (Pentane:EtOAc 80:20); $m.p$ = 138-139 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.87 (m, 3H, ArH), 7.64 – 7.55 (m, 2H, ArH), 7.50 – 7.40 (m, 2H, ArH), 4.00 (s, 3H, CO₂CH₃), 3.43 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.2, 161.6, 140.5, 133.6, 131.5, 130.1, 129.0, 128.9, 127.8, 127.2, 127.1, 125.1, 125.0, 124.4, 115.1, 53.7, 53.1; IR $\tilde{\nu}_{max}$ 3135 (w), 3025 (w), 2951 (w), 1718 (s), 1601 (w), 1492 (m), 1445 (m), 1434 (m), 1288 (m), 1212 (s), 1112 (w), 1073 (w), 1020 (m), 763 (m), 699 (s); HRMS (ESI) calcd for C₁₇H₁₄NO₄⁺ [M+H]⁺ 296.0917; found 296.0911.

Dimethyl 2-(cyano(2-(trifluoromethyl)phenyl)methylene)malonate (**10**)

Following the general procedure C, starting from dimethyl 2-(2-(trifluoromethyl)phenyl)-cycloprop-2-ene-1,1-dicarboxylate (**72**) (90 mg, 0.30 mmol, 1.0 equiv.), the title compound **10** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 80:20) as a colorless oil (72 mg, 0.23 mmol, 77 % yield). R_f 0.30 (Pentane:EtOAc 80:20); 1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 1H, ArH), 7.66 – 7.57 (m, 2H, ArH), 7.39 – 7.32 (m, 1H, ArH), 3.98 (s, 3H, CO₂CH₃), 3.56 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.0, 161.6, 140.6, 132.4, 130.8, 130.1, 129.4 (q, J = 2.6 Hz), 128.6 (q, J = 31.6 Hz), 127.3 (q, J = 4.7 Hz), 123.5, 123.4 (q, J = 274.0 Hz), 114.2, 53.9, 53.2; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -59.0; IR $\tilde{\nu}_{max}$ 3012 (w), 2960 (w), 2850 (w), 1740 (s), 1623 (w), 1442 (m), 1313 (s), 1261 (s), 1176 (s), 1121 (s), 1060 (m), 1029 (m), 978 (m), 928 (w), 766 (s), 707 (w), 659 (m); HRMS (ESI) calcd for C₁₄H₁₁F₃NO₄⁺ [M+H]⁺ 314.0635; found 314.0640.

Methyl 3-cyano-2,3-diphenylacrylate (**14**)

Following the general procedure C, starting from methyl 1,2-diphenylcycloprop-2-enecarboxylate (**39**) (400 mg, 1.60 mmol, 1.0 equiv.), the title compound **14** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 40 g, Pentane:EtOAc 90:10) as a white solid (370 mg, 1.41 mmol, 84 % yield, 95% purity) and as an inseparable 1:1.18 mixture of unassigned Z/E isomers.²⁹ **R_f** 0.32 (Pentane:EtOAc 90:10); **m.p** = 85-86 °C; **¹H NMR (400 MHz, Chloroform-*d*) δ (Major isomer)** 7.64 – 7.62 (m, 1H, *ArH*), 7.49 – 7.46 (m, 2H, *ArH*), 7.45 – 7.44 (m, 1H, *ArH*), 7.26 – 7.23 (m, 3H, *ArH*), 7.22 – 7.21 (m, 2H, *ArH*), 7.15 – 7.13 (m, 1H, *ArH*), 3.93 (s, 3H, CO₂CH₃); **¹H NMR (400 MHz, Chloroform-*d*) δ (Minor isomer)** 7.65 – 7.63 (m, 1H, *ArH*), 7.53 – 7.49 (m, 2H, *ArH*), 7.43 – 7.42 (m, 1H, *ArH*), 7.33 – 7.26 (m, 3H, *ArH*), 7.24 – 7.22 (m, 2H, *ArH*), 7.13 – 7.11 (m, 1H, *ArH*), 3.65 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*) δ (Major isomer)** 166.7, 146.7, 133.3, 132.6, 130.1, 129.7, 129.6, 129.1, 128.7, 128.1, 118.7, 117.7, 53.4; **¹³C NMR (101 MHz, Chloroform-*d*) δ (Minor isomer)** 167.5, 148.3, 133.7, 133.5, 130.7, 129.7, 129.6, 129.1, 128.7, 128.4, 117.7, 116.0, 53.0; **IR $\tilde{\nu}_{\text{max}}$** 3060 (w), 2953 (w), 2217 (w), 2111 (w), 1729 (s), 1592 (w), 1494 (w), 1445 (m), 1326 (m), 1306 (m), 1255 (s), 1211 (s), 1084 (w), 1065 (w), 1013 (m), 986 (w), 924 (w), 852 (w), 762 (m), 738 (s), 698 (s), 648 (w); **HRMS (ESI)** calcd for C₁₇H₁₄NO₂⁺ [M+H]⁺ 264.1019; found 264.1019.

5. Gram-scale Synthesis of **2** and Product Modifications of **2** and **14**

Procedure for the gram scale radical amination of cyclopropene **1**

A 100 mL round bottom flask was charged with CuCl_2 (29 mg, 0.22 mmol, 0.05 equiv.), dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (**1**) (1.00 g, 4.31 mmol, 1.0 equiv.) and PIDA (2.49 g, 7.75 mmol, 1.8 equiv.). The flask was sealed, evacuated and back-filled with nitrogen (3 times). Then CH_3CN (43 mL, 0.1 M) and TMS-N_3 (1.02 mL, 7.75 mmol, 1.8 equiv.) were added via syringe and the resulting mixture was stirred at room temperature for 30 minutes. The reaction mixture was then filtered through a small pad of silica gel eluting with Et_2O , and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO_2 , Pentane: EtOAc 80:20) affording **2** (971 mg, 3.96 mmol, 92 % yield) as a grey solid. Characterization as described in section 4.

Dimethyl 2-cyano-2-phenylcyclopropane-1,1-dicarboxylate (**15**)

NaH (9.6 mg, 0.24 mmol, 1.2 equiv.) and SOMe_3I (62 mg, 0.28 mmol, 1.4 equiv.) were placed in a 5 mL microwave vial. DMSO (1.0 mL) was then added and the reaction mixture was stirred until gas evolution has ceased and the mixture was homogeneous. At this point a solution of dimethyl 2-(cyano(phenyl)methylene)malonate (**2**) (49 mg, 0.20 mmol, 1.0 equiv.) in DMSO (1.0 mL) was added via syringe and the resulting mixture was left stirring for 3 hours at room temperature. It was then quenched with water (2 mL), and extracted with Et_2O (2 x 10 mL). The aqueous layer was further washed with Et_2O (2 x 10 mL) and the combined organic layers were washed with water (5 x 10 mL) and brine (10 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO_2 , Pentane: EtOAc 75:25) affording **15** (28 mg, 0.11 mmol, 54 % yield) as a colorless oil. R_f 0.32 (Pentane: EtOAc 75:25); ^1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.33 (m, 5H, ArH), 3.91 (s, 3H, CO_2CH_3), 3.35 (s, 3H, CO_2CH_3), 2.60 (d, J = 6.2 Hz, 1H, CH_2), 2.37 (d, J = 6.2 Hz, 1H, CH_2). ^{13}C NMR (101 MHz, Chloroform-d) δ 166.2, 164.5, 130.6, 129.6, 129.0, 128.9, 118.3, 53.8, 53.1, 42.2, 28.2, 22.7; IR $\tilde{\nu}_{\text{max}}$ 2956 (w), 2241 (w), 1739 (s), 1495 (w), 1438 (m), 1341 (s), 1262 (s), 1233 (s), 1196 (w), 1078 (w), 983 (w), 906 (w), 735 (m), 699 (m); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$ 260.0917; found 260.0929.

3-Ethyl 1,1-dimethyl 2-cyano-2-phenylcyclopent-3-ene-1,1,3-tricarboxylate (**17**)

A 5 mL test tube was charged with PPh₃ (11 mg, 0.040 mmol, 0.2 equiv.) and dimethyl 2-(cyano(phenyl)methylene)malonate (**2**) (49 mg, 0.20 mmol, 1.0 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then DCM (2.0 mL) and ethyl buta-2,3-dienoate (**16**) (46 μ L, 0.40 mmol, 2.0 equiv.) were added via syringe, and the resulting reaction mixture was left stirring overnight at room temperature. The mixture was then filtered through a small plug of celite eluting with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 90:10 to 70:30) affording **17** (64 mg, 0.18 mmol, 89 % yield) as a colorless oil. **R_f** 0.38 (Pentane:EtOAc 70:30); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.44 – 7.38 (m, 2H, ArH), 7.37 – 7.30 (m, 3H, ArH), 7.19 (t, *J* = 2.6 Hz, 1H, C=CH), 4.11 (q, *J* = 7.2 Hz, 2H, CH₂CH₃), 3.84 (s, 3H, CO₂CH₃), 3.51 (dd, *J* = 19.3, 2.5 Hz, 1H, CH₂), 3.27 (s, 3H, CO₂CH₃), 3.03 (dd, *J* = 19.4, 2.9 Hz, 1H, CH₂), 1.11 (t, *J* = 7.1 Hz, 3H, CH₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 169.1, 167.3, 161.5, 144.2, 135.8, 133.5, 129.1, 128.7, 127.0, 118.7, 69.8, 61.3, 58.2, 53.6, 52.8, 39.4, 13.9; **IR $\tilde{\nu}_{\text{max}}$** 2985 (w), 2956 (w), 2253 (w), 1739 (s), 1719 (s), 1642 (w), 1495 (w), 1448 (m), 1436 (m), 1371 (m), 1331 (m), 1267 (s), 1247 (s), 1196 (m), 1159 (m), 1137 (m), 1110 (m), 1092 (m), 1028 (m), 957 (w), 914 (m), 863 (w), 841 (w), 775 (m), 733 (s), 700 (m), 647 (w); **HRMS (ESI)** calcd for C₁₉H₁₉NNaO₆⁺ [*M*+Na]⁺ 380.1105; found 380.1109.

Dimethyl 1-cyano-4-oxo-3,4-dihydro-[1,1'-biphenyl]-2,2(1H)-dicarboxylate (**19**) and dimethyl 1-cyano-5-oxo-5,6-dihydro-[1,1'-biphenyl]-2,2(1H)-dicarboxylate (**99**)

To a solution of dimethyl 2-(cyano(phenyl)methylene)malonate (**2**) (49 mg, 0.20 mmol, 1.0 equiv.) in toluene (2 mL) was added (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (**18**) (81 μ L, 0.40 mmol, 2.0 equiv.) and the resulting reaction mixture was stirred at 120 °C for 36 hours. The reaction mixture was then concentrated under reduced pressure. To the residue was added DCM (2 mL) and one drop of TFA. The reaction mixture was stirred at room temperature for 2 hours and poured into a saturated NaHCO₃ solution (5 mL). The aqueous layer was then extracted with DCM (3 x 10 mL) and the combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 75:25) affording **19** and **99** as an inseparable 4.2:1 mixture of putative regioisomers (determined by integration of the olefinic proton peaks in beta position of

the ketone in ^1H NMR) and as a colorless oil (40 mg, 0.13 mmol, 64 % yield).³⁰ R_f 0.35 (Pentane:EtOAc 70:30); ^1H NMR (400 MHz, Chloroform- d) δ (Major, **19**) 7.51 – 7.46 (m, 2H, ArH), 7.45 – 7.41 (m, 3H, ArH), 6.90 (d, J = 10.1 Hz, 1H, HC=CHCO), 6.41 (d, J = 10.0 Hz, 1H, HC=CHCO), 3.80 (s, 3H, CO₂CH₃), 3.66 (s, 3H, CO₂CH₃), 3.04 (d, J = 17.8 Hz, 1H, CH₂), 2.93 (d, J = 17.8 Hz, 1H, CH₂); ^1H NMR (400 MHz, Chloroform- d) δ (Minor, **98**) 7.42 – 7.39 (m, 2H, ArH), 7.36 – 7.31 (m, 3H, ArH), 7.20 (d, J = 10.4 Hz, 1H, HC=CHCO), 6.36 (d, J = 10.4 Hz, 1H, HC=CHCO), 3.86 (s, 3H, CO₂CH₃), 3.83 (hidden d, 1H, CH₂), 3.64 (s, 3H, CO₂CH₃), 3.50 (d, J = 23.2 Hz, 1H, CH₂); ^{13}C NMR (101 MHz, Chloroform- d) δ (Major, **19**) 193.1, 168.0, 166.5, 143.8, 130.1, 129.3, 129.0, 128.4, 127.5, 119.2, 54.0, 53.4, 48.1, 45.5, 39.8; ^{13}C NMR (101 MHz, Chloroform- d) δ (Minor, **98**) 192.6, 168.0, 166.3, 142.0, 135.1, 130.9, 129.4, 129.0, 128.6, 120.4, 62.7, 54.3, 53.7, 47.9, 45.5; IR $\tilde{\nu}_{\text{max}}$ 3060 (w), 3009 (w), 2957 (w), 2844 (w), 1743 (s), 1694 (s), 1493 (w), 1449 (m), 1436 (m), 1382 (w), 1277 (s), 1239 (s), 1200 (m), 1175 (m), 1137 (w), 1105 (w), 1070 (w), 1053 (w), 1023 (w), 955 (w), 933 (m), 854 (w), 759 (m), 738 (m), 702 (m); HRMS (ESI) calcd for C₁₇H₁₅NNaO₅⁺ [M+Na]⁺ 336.0842; found 336.0840.

Methyl 10-cyanophenanthrene-9-carboxylate (**20**)

A 10 mL test tube was charged with methyl 3-cyano-2,3-diphenylacrylate (**14**) (1:1.18 unassigned mixture of Z/E isomers, 79 mg, 0.30 mmol, 1.0 equiv.) and DDQ (75 mg, 0.33 mmol, 1.1 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then CH₃CN (6.0 mL) was added to the reaction mixture before being placed under UV irradiation (365 nm) in a Rayonet reactor for 20 hours. The reaction mixture was then diluted with EtOAc and concentrated under reduced pressure. The obtained residue was filtered through a small pad of silica gel eluting with a 1:1 mixture of pentane:DCM and the filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 90:10) affording **20** (58 mg, 0.22 mmol, 74 % yield) as a white solid. R_f 0.28 (Pentane:EtOAc 90:10); $m.p$ = 118–119 °C; ^1H NMR (400 MHz, Chloroform- d) δ 8.76 – 8.65 (m, 2H, ArH), 8.42 – 8.34 (m, 1H, ArH), 8.10 (ddd, J = 8.3, 1.4, 0.6 Hz, 1H, ArH), 7.86 – 7.75 (m, 3H, ArH), 7.71 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H, ArH), 4.19 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform- d) δ 167.0, 137.8, 131.8, 130.5, 130.2, 129.5, 128.7, 128.3, 127.9, 127.2, 127.1, 126.8, 123.2, 123.2, 116.1, 109.1, 53.6; IR $\tilde{\nu}_{\text{max}}$ 3067 (w), 2954 (w), 2225 (m), 1731 (s), 1611 (w), 1526 (w), 1494 (w), 1448 (s), 1381 (m), 1331 (w), 1318 (w), 1298 (w), 1253 (s), 1215 (s), 1153 (m), 1063 (m), 986 (m), 799 (w), 760 (s), 740 (m), 722 (s), 677 (w), 652 (w), 616 (w); HRMS (ESI) calcd for C₁₇H₁₂NO₂⁺ [M+H]⁺ 262.0863; found 262.0868.

³⁰ Complete characterization of compound **99** could not be achieved with 2D NMR experiments, the structure proposed here is the one that seemed most likely of the other possible regioisomer, based on ^1H and ^{13}C NMR analysis.

6. Optimization of the One-pot Synthesis of PACs from Cyclopropenes

General method for the optimization:

A 5 mL test tube was charged with CuCl₂ (0.7 mg, 0.05 mmol, 0.05 equiv.), methyl 1,2-diphenylcycloprop-2-enecarboxylate (**39**) (25 mg, 0.10 mmol, 1.0 equiv.) and PIDA (58 mg, 0.18 mmol, 1.8 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then CH₃CN (1 mL, 0.1 M) and TMS-N₃ (24 μ L, 0.18 mmol, 1.8 equiv.) were added via syringe and the resulting mixture was stirred at room temperature for 30 minutes. Then a solution of DDQ in CH₃CN was added to the reaction mixture before being placed under UV irradiation (365 nm) in a Rayonet reactor for 20 hours. The reaction mixture was then diluted with EtOAc and concentrated under reduced pressure. The obtained residue was filtered through a small pad of silica gel eluting with a 1:1 mixture of pentane:DCM and the filtrate was evaporated under reduced pressure. When product **20** was isolated, the obtained crude residue was subjected to purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10).

Table S1: Optimization of the one-pot synthesis of PACs from cyclopropene **39**

Entry	X equiv.	Y mL	Yield of 20 ^a	Yield of 100 ^a	Yield of 14 ^a
1	-	-	42%	39%	-
2 ^b	-	-	61%	15%	-
3	1.1 equiv.	1 mL	69%	-	22%
4	1.5 equiv.	1 mL	67%	-	20%
5	0.5 equiv.	1 mL	60%	15%	7%
6 ^c	1.1 equiv.	1 mL	37%	32%	-
7 ^d	1.1 equiv.	1 mL	72%	-	16%
8 ^d	1.1 equiv.	2 mL	82% (80% ^e)	-	10%

(a) Yields estimated by ¹H NMR of the crude reaction mixture using dibromomethane as internal standard.

(b) 3.0 equivalents of PIDA were used. (c) After the first step, the reaction vessel was placed for 20 h under UV irradiation, then the diluted DDQ solution was added and the reaction was stopped after 6 h. (d) commercial DDQ recrystallized from distilled CHCl₃ was used. (e) Isolated yield on 0.3 mmol.

7. One-pot Synthesis of PACs from Cyclopropenes

General procedure D

A 10 mL test tube was charged with CuCl_2 (2 mg, 0.05 mmol, 0.05 equiv.), the cyclopropene (0.30 mmol, 1.0 equiv.) and PIDA (174 mg, 0.540 mmol, 1.8 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then CH_3CN (3 mL, 0.1 M) and TMS- N_3 (72 μL , 0.54 mmol, 1.8 equiv.) were added via syringe and the resulting mixture was stirred at room temperature for 30 minutes. Then a solution of DDQ (commercial batch recrystallized from distilled CHCl_3 , 75 mg, 0.33 mmol, 1.1 equiv.) in CH_3CN (6 mL) was added to the reaction mixture before being placed under UV irradiation (365 nm) in a Rayonet reactor for 20 hours. The reaction mixture was then diluted with EtOAc and concentrated under reduced pressure. The obtained residue was filtered through a small pad of silica gel eluting with a 1:1 mixture of pentane:DCM and the filtrate was evaporated under reduced pressure. The obtained crude residue was then subjected to column chromatography using the indicated solvents.

Methyl 10-cyanophenanthrene-9-carboxylate (**20**)

Following the general procedure D, starting from methyl 1,2-diphenylcycloprop-2-enecarboxylate (**39**) (75 mg, 0.30 mmol, 1.0 equiv.), the title compound **20** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a white solid (63 mg, 0.24 mmol, 80 % yield). Characterization as described in section 5.

Tert-butyl 10-cyanophenanthrene-9-carboxylate (**21**)

Following the general procedure D, starting from *tert*-butyl 1,2-diphenylcycloprop-2-enecarboxylate (**78**) (88 mg, 0.30 mmol, 1.0 equiv.), the title compound **21** was obtained after

purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (68 mg, 0.22 mmol, 75 % yield). **R_f** 0.32 (Pentane:EtOAc 95:5); **m.p** = 125-126 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.75 – 8.67 (m, 2H, Ar*H*), 8.41 – 8.34 (m, 1H, Ar*H*), 8.13 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar*H*), 7.85 – 7.75 (m, 3H, Ar*H*), 7.75 – 7.69 (m, 1H, Ar*H*), 1.78 (s, 9H, CO₂C(CH₃)₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.7, 139.2, 131.9, 130.3, 130.1, 129.2, 128.6, 128.2, 128.1, 127.1, 126.9, 126.9, 123.2, 123.1, 116.2, 108.1, 85.0, 28.2; **IR** $\tilde{\nu}_{\text{max}}$ 3073 (w), 2980 (m), 2933 (m), 2113 (w), 1720 (s), 1610 (w), 1526 (w), 1453 (m), 1378 (s), 1295 (w), 1254 (s), 1215 (m), 1152 (s), 1058 (m), 959 (w), 910 (w), 841 (m), 756 (s), 729 (s), 625 (w); **HRMS (APCI)** calcd for C₂₀H₁₇NNaO₂⁺ [M+Na]⁺ 326.1151; found 326.1152.

10-propionylphenanthrene-9-carbonitrile (**22**)

Following the general procedure D, starting from 1-(1,2-diphenylcycloprop-2-en-1-yl)propan-1-one (**79**) (75 mg, 0.30 mmol, 1.0 equiv.), the title compound **22** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a colorless oil (40 mg, 0.15 mmol, 51 % yield). **R_f** 0.27 (Pentane:EtOAc 95:5); **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.82 – 8.71 (m, 2H, Ar*H*), 8.41 – 8.34 (m, 1H, Ar*H*), 7.90 – 7.79 (m, 3H, Ar*H*), 7.78 – 7.67 (m, 2H, Ar*H*), 3.18 (q, *J* = 7.2 Hz, 2H, CH₂), 1.41 (t, *J* = 7.2 Hz, 3H, CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 206.5, 147.6, 132.1, 130.3, 130.0, 129.1, 128.8, 128.3, 128.0, 126.7, 126.6, 126.5, 123.6, 123.2, 116.3, 105.3, 38.4, 7.9; **IR** $\tilde{\nu}_{\text{max}}$ 3389 (w), 3065 (w), 2977 (m), 2928 (m), 2224 (m), 2103 (w), 1706 (s), 1606 (w), 1450 (m), 1377 (m), 1340 (m), 1246 (m), 1168 (m), 1128 (m), 1047 (m), 905 (m), 852 (m), 758 (s), 731 (s); **HRMS (ESI)** calcd for C₁₈H₁₄NO⁺ [M+H]⁺ 260.1070; found 260.1077.

10-(Trifluoromethyl)phenanthrene-9-carbonitrile (**23**)

Following the general procedure D, starting from (1-(trifluoromethyl)cycloprop-2-ene-1,2-diyl)dibenzene (**80**) (78 mg, 0.30 mmol, 1.0 equiv.), the title compound **23** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (53 mg, 0.20 mmol, 65 % yield). **R_f** 0.29 (Pentane:EtOAc 95:5); **m.p** = 208-209 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.78 (ddd, *J* = 13.7, 8.3, 1.3 Hz, 2H, Ar*H*), 8.59 (dd, *J* = 8.1, 1.5 Hz, 1H, Ar*H*), 8.35 (dt, *J* = 6.3, 2.1 Hz, 1H, Ar*H*), 7.94 – 7.82 (m, 3H, Ar*H*), 7.78 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H, Ar*H*); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 132.2,

131.2, 131.1 (t, $J = 29.9$ Hz), 130.5, 130.3, 129.1, 128.5, 127.9, 127.8, 126.8 (q, $J = 4.1$ Hz), 125.9, 123.4, 123.3 (q, $J = 276.8$ Hz), 123.1, 114.9, 109.6 (q, $J = 3.3$ Hz); **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -54.8 (d, $J = 2.2$ Hz); **IR** $\tilde{\nu}_{\text{max}}$ 2928 (m), 2853 (m), 2360 (w), 2229 (w), 2113 (m), 1740 (m), 1528 (m), 1453 (m), 1373 (m), 1314 (m), 1249 (m), 1164 (s), 1123 (s), 1024 (m), 766 (m), 714 (m); **HRMS (APPI)** calcd for $\text{C}_{16}\text{H}_8\text{F}_3\text{N}^+$ $[\text{M}]^+$ 271.0603; found 271.0610.

Ethyl 6-bromo-10-cyanophenanthrene-9-carboxylate (**24**)

Following the general procedure D, starting from ethyl 1-(4-bromophenyl)-2-phenylcycloprop-2-enecarboxylate (**81**) (103 mg, 0.300 mmol, 1.0 equiv.), the title compound **24** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:DCM 60:40) as a white solid (75 mg, 0.21 mmol, 71 % yield). **R_f** 0.42 (Pentane:DCM 50:50); **m.p** = 159–160 °C; **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.69 (d, $J = 2.0$ Hz, 1H, ArH), 8.54 – 8.45 (m, 1H, ArH), 8.35 – 8.26 (m, 1H, ArH), 7.95 (d, $J = 8.9$ Hz, 1H, ArH), 7.83 – 7.68 (m, 3H, ArH), 4.66 (q, $J = 7.2$ Hz, 2H, CH_2CH_3), 1.56 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.9, 137.1, 132.9, 131.4, 129.7, 129.3, 129.1, 128.6, 128.2, 127.1, 126.0, 125.3, 125.2, 123.1, 115.7, 109.4, 63.2, 14.2; **IR** $\tilde{\nu}_{\text{max}}$ 3668 (w), 2981 (m), 2361 (w), 2227 (w), 1727 (s), 1593 (m), 1485 (m), 1449 (m), 1389 (m), 1319 (m), 1242 (s), 1209 (s), 1158 (m), 1065 (s), 1013 (s), 957 (w), 905 (w), 865 (m), 818 (m), 758 (s); **HRMS (ESI)** calcd for $\text{C}_{18}\text{H}_{12}^{79}\text{BrNNaO}_2^+$ $[\text{M}+\text{Na}]^+$ 375.9944; found 375.9954.

Methyl 10-cyano-6-methoxyphenanthrene-9-carboxylate (**25**)

Following the general procedure D, starting from methyl 1-(4-methoxyphenyl)-2-phenylcycloprop-2-enecarboxylate (**82**) (84 mg, 0.30 mmol, 1.0 equiv.), the title compound **25** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (61 mg, 0.21 mmol, 70 % yield). **R_f** 0.34 (Pentane:EtOAc 90:10); **m.p** = 163–164 °C; **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.67 – 8.59 (m, 1H, ArH), 8.41 – 8.33 (m, 1H, ArH), 8.10 – 8.00 (m, 2H, ArH), 7.83 – 7.74 (m, 2H, ArH), 7.33 (dd, $J = 9.2, 2.5$ Hz, 1H, ArH), 4.17 (s, 3H, CO_2CH_3), 4.06 (s, 3H, OCH_3); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.1, 161.1, 137.6, 134.0, 129.9, 129.0, 128.9, 128.6, 127.1, 123.2, 121.4, 118.5, 116.5, 106.4, 104.5, 55.8, 53.5; **IR** $\tilde{\nu}_{\text{max}}$ 3010 (w), 2952 (w), 2846 (w), 2358 (m), 2224 (m), 2052 (w), 1729 (s), 1616 (s), 1515 (m), 1446 (m), 1386 (m), 1325 (m), 1241 (s), 1155 (m), 1065 (m), 1025 (m), 988

(m), 912 (m), 835 (m), 767 (m), 736 (m), 669 (m), 627 (m); **HRMS (ESI)** calcd for $C_{18}H_{14}NO_3^+$ $[M+H]^+$ 292.0968; found 292.0968.

Methyl 3-(tert-butyl)-10-cyano-6-methylphenanthrene-9-carboxylate (**26**)

Following the general procedure D, starting from methyl 2-(4-(*tert*-butyl)phenyl)-1-(*p*-tolyl)cycloprop-2-enecarboxylate (**83**) (96 mg, 0.30 mmol, 1.0 equiv.), the title compound **26** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:DCM 60:40) as a white solid (80 mg, 0.24 mmol, 80 % yield). **R_f** 0.47 (Pentane:DCM 50:50); **m.p** = 184-185 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.67 (d, J = 1.9 Hz, 1H, ArH), 8.52 (s, 1H, ArH), 8.32 (d, J = 8.6 Hz, 1H, ArH), 8.02 (d, J = 8.4 Hz, 1H, ArH), 7.85 (dd, J = 8.7, 1.9 Hz, 1H, ArH), 7.52 (dd, J = 8.5, 1.6 Hz, 1H, ArH), 4.16 (s, 3H, CO₂CH₃), 2.68 (s, 3H, CH₃), 1.52 (s, 9H, *t*Bu); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.2, 152.6, 140.5, 136.8, 132.1, 130.0, 129.9, 127.1, 127.1, 126.8, 126.2, 125.0, 122.8, 118.7, 116.5, 107.9, 53.4, 35.7, 31.5, 22.5; **IR $\tilde{\nu}_{\max}$** 2961 (w), 2872 (w), 2255 (w), 2226 (w), 1731 (m), 1616 (w), 1509 (w), 1444 (w), 1378 (w), 1314 (w), 1258 (m), 1221 (m), 1168 (m), 1073 (w), 988 (w), 909 (s), 732 (s), 650 (w); **HRMS (ESI)** calcd for $C_{22}H_{22}NO_2^+$ $[M+H]^+$ 332.1645; found 332.1650.

Methyl 10-cyano-6-methyl-3-(trifluoromethoxy)phenanthrene-9-carboxylate (**27**)

Following the general procedure D, starting from methyl 1-(*p*-tolyl)-2-(4-(trifluoromethoxy)phenyl)cycloprop-2-enecarboxylate (**84**) (104 mg, 0.300 mmol, 1.0 equiv.), the title compound **27** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (82 mg, 0.23 mmol, 76 % yield). **R_f** 0.42 (Pentane:EtOAc 90:10); **m.p** = 197-198 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.44 – 8.39 (m, 1H, ArH), 8.36 (d, J = 9.0 Hz, 1H, ArH), 8.30 (s, 1H, ArH), 7.97 (d, J = 8.5 Hz, 1H, ArH), 7.60 (ddd, J = 8.9, 2.4, 1.1 Hz, 1H, ArH), 7.53 (dd, J = 8.5, 1.7 Hz, 1H, ArH), 4.18 (s, 3H, CO₂CH₃), 2.65 (s, 3H, CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.6, 149.6 (d, J = 2.3 Hz), 141.3, 138.0, 131.4, 131.1, 130.8, 129.2, 127.2, 126.4, 125.0, 123.0, 121.7, 120.7 (q, J = 258.6 Hz), 115.9, 114.7, 107.4, 53.6, 22.4; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -57.5; **IR $\tilde{\nu}_{\max}$** 3087 (w), 2921 (w), 2227 (w), 1742 (m), 1618 (w), 1513 (w), 1442 (w), 1378 (w), 1249 (s), 1206 (s), 1161 (s), 1069 (w), 976 (w), 908 (m), 867 (m), 809 (w), 734 (s), 648 (w); **HRMS (ESI)** calcd for $C_{19}H_{12}F_3NNaO_3^+$ $[M+Na]^+$ 382.0661; found 382.0654.

Methyl 1-chloro-10-cyanophenanthrene-9-carboxylate (**28**)

Following the general procedure D, starting from methyl 2-(2-chlorophenyl)-1-phenylcycloprop-2-enecarboxylate (**85**) (85 mg, 0.30 mmol, 1.0 equiv.), the title compound **28** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5 to 90:10) as a grey solid (57 mg, 0.19 mmol, 61 % yield, 95% purity).²⁹ **R_f** 0.37 (Pentane:EtOAc 80:20); **m.p** = 171-172 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.72 – 8.64 (m, 2H, ArH), 7.89 – 7.82 (m, 2H, ArH), 7.81 – 7.65 (m, 3H, ArH), 4.19 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.5, 144.3, 132.7, 132.4, 131.6, 131.1, 131.0, 129.0, 128.9, 127.0, 126.5, 124.9, 123.7, 122.4, 117.4, 104.9, 54.0; **IR $\tilde{\nu}_{\text{max}}$** 3072 (w), 2951 (m), 2925 (m), 2221 (w), 2109 (w), 1736 (s), 1603 (w), 1521 (m), 1442 (s), 1375 (m), 1248 (s), 1213 (s), 1165 (m), 1127 (m), 1051 (m), 985 (m), 918 (m), 799 (m), 756 (s), 690 (m), 642 (m); **HRMS (ESI)** calcd for C₁₇H₁₁ClNO₂⁺ [M+H]⁺ 296.0473; found 296.0476.

Methyl 10-cyano-8-fluorophenanthrene-9-carboxylate (**29**)

Following the general procedure D, starting from methyl 1-(2-fluorophenyl)-2-phenylcycloprop-2-enecarboxylate (**86**) (80 mg, 0.30 mmol, 1.0 equiv.), the title compound **29** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a white solid (62 mg, 0.22 mmol, 70 % yield, 95% purity).²⁹ **R_f** 0.27 (Pentane:EtOAc 90:10); **m.p** = 171-172 °C ; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.59 – 8.51 (m, 1H, ArH), 8.40 (d, *J* = 8.4 Hz, 1H, ArH), 8.26 – 8.19 (m, 1H, ArH), 7.79 – 7.68 (m, 3H, ArH), 7.31 (ddd, *J* = 11.4, 7.9, 1.0 Hz, 1H, ArH), 4.14 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.6, 158.5 (d, *J* = 255.2 Hz), 134.3, 133.4 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 9.5 Hz), 129.7, 129.3, 129.2 (d, *J* = 2.6 Hz), 127.8, 126.7, 123.5, 119.2 (d, *J* = 3.8 Hz), 116.5 (d, *J* = 12.5 Hz), 115.5, 113.4 (d, *J* = 21.5 Hz), 109.0, 53.8; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -110.8 (dd, *J* = 11.3, 5.7 Hz); **IR $\tilde{\nu}_{\text{max}}$** 3068 (w), 2952 (w), 2854 (w), 2226 (w), 1739 (s), 1620 (w), 1579 (w), 1522 (w), 1453 (s), 1371 (m), 1325 (w), 1249 (s), 1207 (s), 1158 (m), 1067 (m), 987 (m), 917 (m), 751 (s); **HRMS (ESI)** calcd for C₁₇H₁₁FNO₂⁺ [M+H]⁺ 280.0768; found 280.0774.

Methyl 8-chloro-10-cyano-6-fluoro-3-methylphenanthrene-9-carboxylate (**30**)

Following the general procedure D, starting from methyl 1-(2-chloro-4-fluorophenyl)-2-(p-tolyl)cycloprop-2-enecarboxylate (**87**) (95 mg, 0.30 mmol, 1.0 equiv.), the title compound **30** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:DCM 60:40) as a white solid (57 mg, 0.17 mmol, 55 % yield, 95% purity).²⁹ **R_f** 0.42 (Pentane:DCM 50:50); **m.p** = 185–186 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.25 – 8.18 (m, 2H, *ArH*), 8.13 (d, *J* = 8.3 Hz, 1H, *ArH*), 7.62 – 7.55 (m, 1H, *ArH*), 7.46 (dd, *J* = 7.8, 2.5 Hz, 1H, *ArH*), 4.05 (s, 3H, CO₂CH₃), 2.59 (s, 3H, CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.9, 162.0 (d, *J* = 254.2 Hz), 140.5, 135.5 (d, *J* = 1.8 Hz), 135.3 (d, *J* = 9.2 Hz), 133.7 (d, *J* = 11.2 Hz), 131.9, 129.5 (d, *J* = 4.4 Hz), 126.8, 126.0, 123.4, 121.6 (d, *J* = 2.3 Hz), 119.7 (d, *J* = 26.9 Hz), 115.7, 110.5 (d, *J* = 2.9 Hz), 108.1 (d, *J* = 22.4 Hz), 53.9, 22.4; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -106.9 (dd, *J* = 9.9, 7.8 Hz); **IR** $\tilde{\nu}_{\text{max}}$ 2955 (m), 2928 (m), 2359 (m), 2226 (m), 2054 (m), 1734 (s), 1612 (s), 1577 (m), 1508 (m), 1437 (m), 1374 (m), 1314 (m), 1236 (s), 1195 (s), 1177 (s), 1130 (m), 1070 (m), 986 (m), 908 (m), 863 (s), 820 (m), 775 (m), 739 (m), 634 (m); **HRMS (ESI)** calcd for C₁₈H₁₂ClFNO₂⁺ [M+H]⁺ 328.0535; found 328.0536.

Methyl 10-cyano-2,4-bis(trifluoromethyl)phenanthrene-9-carboxylate (**31**)

Following the general procedure D, starting from methyl 2-(3,5-bis(trifluoromethyl)phenyl)-1-phenylcycloprop-2-enecarboxylate (**88**) (116 mg, 0.300 mmol, 1.0 equiv.), the title compound **31** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 90:10) as a white solid (81 mg, 0.20 mmol, 68 % yield). **R_f** 0.35 (Pentane:EtOAc 90:10); **m.p** = 177–178 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.87 (s, 1H, *ArH*), 8.84 – 8.77 (m, 1H, *ArH*), 8.44 (s, 1H, *ArH*), 8.17 – 8.09 (m, 1H, *ArH*), 7.92 – 7.84 (m, 2H, *ArH*), 4.21 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.0, 140.8, 131.5, 130.4, 130.3, 130.0, 129.9 – 129.7 (m), 129.6 – 129.2 (m), 128.8, 128.7, 128.6 – 128.2 (m), 128.0, 127.0, 126.8 – 126.3 (m), 123.1 (q, *J* = 272.7 Hz), 123.0 (q, *J* = 273.4 Hz), 115.1, 108.7, 54.0; **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ -54.6, -62.6; **IR** $\tilde{\nu}_{\text{max}}$ 2959 (w), 1739 (m), 1632 (w), 1586 (w), 1532 (m), 1443 (m), 1347 (m), 1272 (s), 1171 (s), 1131 (s), 1005 (m), 911 (s), 861 (m), 777 (m), 732 (s), 689 (m), 672 (m); **HRMS (ESI)** calcd for C₁₉H₉F₆NNaO₂⁺ [M+Na]⁺ 420.0430; found 420.0439.

Methyl 5-cyanonaphtho[1,2-*b*]thiophene-4-carboxylate (**32**)

Following the general procedure D, starting from methyl 2-phenyl-1-(thiophen-3-yl)cycloprop-2-enecarboxylate (**89**) (77 mg, 0.30 mmol, 1.0 equiv.), the title compound **32** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (49 mg, 0.18 mmol, 61 % yield). R_f 0.20 (Pentane:EtOAc 95:5); $m.p$ = 166-167 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 8.49 – 8.43 (m, 1H, ArH), 8.22 – 8.15 (m, 1H, ArH), 7.96 (d, J = 5.5 Hz, 1H, HetArH), 7.78 – 7.70 (m, 2H, ArH), 7.66 (d, J = 5.6 Hz, 1H, HetArH), 4.15 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 143.2, 134.0, 130.6, 129.9, 129.7, 128.6, 128.5, 127.7, 127.4, 125.8, 124.2, 116.5, 109.0, 53.3; IR $\tilde{\nu}_{max}$ 3097 (w), 2952 (w), 2849 (w), 2224 (w), 1724 (s), 1619 (w), 1552 (w), 1440 (m), 1308 (m), 1269 (m), 1223 (s), 1157 (m), 1096 (m), 975 (m), 896 (w), 804 (m), 762 (s), 662 (m); HRMS (ESI) calcd for C₁₅H₁₀NO₂S⁺ [M+H]⁺ 268.0427; found 268.0427.

Methyl 6-cyanobenzo[c]phenanthrene-5-carboxylate (**33**)

Following the general procedure D, starting from methyl 2-(naphthalen-2-yl)-1-phenylcycloprop-2-enecarboxylate (**90**) (90 mg, 0.30 mmol, 1.0 equiv.), the title compound **33** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a yellow solid (71 mg, 0.23 mmol, 76 % yield). R_f 0.22 (Pentane:EtOAc 95:5); $m.p$ = 134-135 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 9.04 (d, J = 8.6 Hz, 1H, ArH), 8.98 – 8.91 (m, 1H, ArH), 8.29 (d, J = 8.8 Hz, 1H, ArH), 8.24 (dd, J = 8.3, 1.4 Hz, 1H, ArH), 8.09 – 8.02 (m, 2H, ArH), 7.82 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H, ArH), 7.77 – 7.69 (m, 3H, ArH), 4.21 (s, 3H, CO₂CH₃); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 136.7, 134.2, 131.7, 129.9, 129.4, 129.3, 129.3, 128.9, 128.7, 128.4, 128.3, 127.8, 127.8, 127.5, 127.3, 126.7, 123.3, 116.4, 108.8, 53.6; IR $\tilde{\nu}_{max}$ 3058 (w), 2953 (w), 2849 (w), 2225 (m), 2111 (w), 1728 (s), 1610 (w), 1573 (w), 1496 (m), 1430 (m), 1393 (m), 1261 (s), 1223 (s), 1151 (m), 1005 (m), 958 (m), 905 (m), 824 (s), 743 (s), 662 (m); HRMS (ESI) calcd for C₂₁H₁₄NO₂⁺ [M+H]⁺ 312.1019; found 312.1012.

Methyl 6-cyano-2-methoxybenzo[c]phenanthrene-5-carboxylate (**34**)

Following the general procedure D, starting from methyl 1-(4-methoxyphenyl)-2-(naphthalen-2-yl)cycloprop-2-enecarboxylate (**91**) (99 mg, 0.30 mmol, 1.0 equiv.), the title compound **34** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a white solid (76 mg, 0.22 mmol, 74 % yield). **R_f** 0.33 (Pentane:EtOAc 90:10); **m.p** = 166-167 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.12 – 9.03 (m, 1H, *ArH*), 8.51 (d, *J* = 2.5 Hz, 1H, *ArH*), 8.29 (d, *J* = 8.8 Hz, 1H, *ArH*), 8.19 (d, *J* = 9.2 Hz, 1H, *ArH*), 8.11 – 8.02 (m, 2H, *ArH*), 7.75 – 7.67 (m, 2H, *ArH*), 7.38 (dd, *J* = 9.2, 2.5 Hz, 1H, *ArH*), 4.19 (s, 3H, CO₂CH₃), 4.03 (s, 3H, OCH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.1, 160.7, 136.5, 134.1, 133.8, 130.0, 129.7, 129.1, 128.5, 128.4, 128.3, 127.6, 127.5, 127.1, 123.6, 123.4, 118.4, 116.8, 109.8, 106.2, 55.8, 53.5; **IR** $\tilde{\nu}_{\text{max}}$ 3052 (w), 3015 (w), 2952 (m), 2843 (w), 2359 (m), 2224 (m), 2051 (m), 1730 (s), 1614 (m), 1512 (m), 1439 (m), 1407 (m), 1334 (m), 1232 (s), 1150 (m), 1111 (m), 1038 (m), 911 (m), 821 (s), 735 (s), 660 (m); **HRMS (ESI)** calcd for C₂₂H₁₆NO₃⁺ [M+H]⁺ 342.1125; found 342.1132.

Ethyl 2-bromo-5-cyanobenzo[*c*]phenanthrene-6-carboxylate (**35**)

Following the general procedure D, starting from ethyl 2-(4-bromophenyl)-1-(naphthalen-2-yl)cycloprop-2-enecarboxylate (**92**) (118 mg, 0.300 mmol, 1.0 equiv.), after UV irradiation the crude mixture was directly filtered in order to recover the formed precipitate. The filter cake was washed with cold acetonitrile and pentane, and dried under reduced pressure to afford **35** (85 mg, 0.21 mmol, 70% yield) as a grey powder, without further purification. **R_f** 0.25 (Pentane:EtOAc 90:10); **m.p** = 202-203 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.21 (d, *J* = 1.9 Hz, 1H, *ArH*), 8.96 – 8.88 (m, 1H, *ArH*), 8.38 (d, *J* = 8.8 Hz, 1H, *ArH*), 8.09 – 8.04 (m, 1H, *ArH*), 8.04 – 7.97 (m, 2H, *ArH*), 7.91 (dd, *J* = 8.8, 1.9 Hz, 1H, *ArH*), 7.82 – 7.73 (m, 2H, *ArH*), 4.68 (q, *J* = 7.2 Hz, 2H, CH₂CH₃), 1.56 (t, *J* = 7.2 Hz, 3H, CH₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.5, 137.4, 134.5, 131.6, 131.4, 131.1, 129.9, 129.9, 129.2, 128.9, 128.5, 128.5, 128.3, 128.1, 127.8, 126.6, 123.6, 122.9, 115.8, 108.1, 63.3, 14.2; **IR** $\tilde{\nu}_{\text{max}}$ 2990 (m), 1731 (s), 1599 (m), 1491 (m), 1457 (m), 1397 (s), 1359 (m), 1298 (m), 1266 (s), 1220 (s), 1154 (s), 1076 (s), 1012 (m), 913 (s), 852 (m), 737 (s), 660 (m); **HRMS (APPI)** calcd for C₂₂H₁₅⁷⁹BrNO₂⁺ [M+H]⁺ 404.0281; found 404.0295.

Methyl 5-cyanobenzo[*g*]chrysene-6-carboxylate (**36**)

Following the general procedure D, starting from methyl 2-(phenanthren-9-yl)-1-phenylcycloprop-2-enecarboxylate (**93**) (105 mg, 0.300 mmol, 1.0 equiv.), the title compound **36** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:DCM 60:40) as a yellow solid (78 mg, 0.22 mmol, 72 % yield). **R_f** 0.35 (Pentane:DCM 50:50); **m.p** = 163-164 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.21 – 9.14 (m, 1H, *ArH*), 8.70 – 8.64 (m, 1H, *ArH*), 8.63 – 8.56 (m, 2H, *ArH*), 8.52 (d, *J* = 8.3 Hz, 1H, *ArH*), 8.08 – 8.01 (m, 1H, *ArH*), 7.74 – 7.65 (m, 5H, *ArH*), 7.57 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H, *ArH*), 4.23 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.5, 139.1, 131.6, 131.1, 130.9, 130.5, 129.7, 129.3, 129.0, 128.6, 128.5, 128.2, 128.1, 127.9, 127.6, 127.6, 127.0, 126.4, 125.9, 125.8, 123.9, 123.5, 118.9, 104.3, 53.7; **IR** $\tilde{\nu}_{\text{max}}$ 3064 (w), 2952 (w), 2351 (w), 2221 (w), 1730 (s), 1610 (w), 1496 (m), 1442 (m), 1376 (m), 1245 (s), 1214 (s), 1154 (m), 1035 (m), 974 (m), 909 (w), 761 (s), 733 (s), 626 (m); **HRMS (ESI)** calcd for C₂₅H₁₆NO₂⁺ [M+H]⁺ 362.1176; found 362.1186.

Methyl 5-cyanochrysene-6-carboxylate (**37**)

Following the general procedure D, starting from methyl 2-(naphthalen-1-yl)-1-phenylcycloprop-2-enecarboxylate (**94**) (90 mg, 0.30 mmol, 1.0 equiv.), the title compound **37** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:DCM 60:40) as a white solid (64 mg, 0.21 mmol, 66 % yield, 96% purity).²⁹ **R_f** 0.38 (Pentane:DCM 50:50); **m.p** = 135-136 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.72 (d, *J* = 8.6 Hz, 1H, *ArH*), 8.72 (d, *J* = 8.5 Hz, 1H, *ArH*), 8.59 (d, *J* = 9.1 Hz, 1H, *ArH*), 8.05 (d, *J* = 9.1 Hz, 1H, *ArH*), 8.00 – 7.91 (m, 2H, *ArH*), 7.82 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, *ArH*), 7.78 – 7.62 (m, 3H, *ArH*), 4.23 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 167.9, 141.7, 133.0, 132.0, 130.7, 130.3, 130.0, 129.4, 128.9, 128.3, 127.8, 127.6, 126.8, 126.6, 125.1, 124.5, 123.9, 120.5, 119.6, 104.5, 53.9; **IR** $\tilde{\nu}_{\text{max}}$ 3060 (w), 2953 (w), 2217 (m), 1732 (s), 1605 (w), 1568 (w), 1518 (m), 1475 (w), 1436 (m), 1364 (m), 1230 (s), 1150 (m), 1038 (m), 965 (m), 910 (m), 859 (m), 823 (m), 754 (s), 735 (s), 654 (m); **HRMS (ESI)** calcd for C₂₁H₁₄NO₂⁺ [M+H]⁺ 312.1019; found 312.1018.

Methyl 14-cyanopicene-13-carboxylate (**38**)

Following the general procedure D, starting from methyl 1,2-di(naphthalen-1-yl)cycloprop-2-enecarboxylate (**95**) (105 mg, 0.300 mmol, 1.0 equiv.), the title compound **38** was obtained after purification by column chromatography on Biotage (Büchi flashpure cartridge 25 g, Pentane:EtOAc 95:5) as a light brown solid (61 mg, 0.17 mmol, 54% yield, 95% purity).²⁹ **R_f** 0.42 (Pentane:EtOAc 95:5); **m.p** = 158-159 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.64 (dt, J = 8.6, 0.9 Hz, 1H, Ar*H*), 8.63 (dd, J = 9.2, 4.5 Hz, 2H, Ar*H*), 8.47 – 8.38 (m, 1H, Ar*H*), 8.12 – 8.03 (m, 2H, Ar*H*), 8.01 – 7.95 (m, 2H, Ar*H*), 7.79 (ddd, J = 8.6, 7.0, 1.6 Hz, 1H, Ar*H*), 7.75 – 7.66 (m, 3H, Ar*H*), 4.20 (s, 3H, CO₂CH₃); **¹³C NMR (101 MHz, Chloroform-*d*)** δ 170.4, 138.9, 133.0, 132.8, 132.3, 131.9, 130.8, 130.1, 129.1, 129.1, 128.9, 128.8, 128.3, 127.9, 127.7, 127.6, 126.5, 125.9, 125.4, 124.8, 121.0, 120.7, 119.8, 105.6, 54.1; **IR $\tilde{\nu}_{\text{max}}$** 3052 (w), 2950 (m), 2860 (w), 2218 (m), 2106 (m), 1731 (s), 1607 (m), 1515 (m), 1439 (m), 1371 (m), 1337 (m), 1265 (s), 1227 (s), 1193 (m), 1164 (m), 1037 (m), 967 (m), 912 (s), 806 (s), 738 (s), 660 (m); **HRMS (ESI)** calcd for C₂₅H₁₆NO₂⁺ [M+H]⁺ 362.1176; found 362.1178.

8. Crystal Structure of **9**

A single crystal was obtained by recrystallisation of **9** from a 1:1 DCM/Pentane mixture at room temperature. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (**2027422**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

9. Control Experiment and Characterization of **40**

A 5 mL test tube was charged with cyclopropene **39** (50 mg, 0.20 mmol, 1.0 equiv.) and PIDA (129 mg, 0.400 mmol, 2.0 equiv.). The tube was sealed, evacuated and back-filled with nitrogen (3 times). Then CH₃CN (2 mL, 0.1 M) and TMS-N₃ (53 μL, 0.40 mmol, 2.0 equiv.) were added via syringe and the resulting mixture was stirred at room temperature overnight. The reaction mixture was then filtered through a small pad of silica gel eluting with Et₂O, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, Pentane:EtOAc 90:10) affording compounds **14** (16 mg, 0.060 mmol, 30 % yield) as a pale yellow oil and compound **40** (18 mg, 0.068 mmol, 34% yield) as a yellow oil. For **14** the characterization data is the same as the one reported in section 4. For compound **40**: *R_f* 0.42 (Pentane:EtOAc 90:10); ¹H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H, HetAr*H*), 8.19 (d, *J* = 8.3 Hz, 1H, HetAr*H*), 7.92 (d, *J* = 8.5 Hz, 1H, HetAr*H*), 7.78 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, HetAr*H*), 7.65 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H, HetAr*H*), 7.53 – 7.45 (m, 5H, Ar*H*), 3.78 (s, 3H, CO₂CH₃); ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.1, 151.5, 147.3, 137.2, 137.1, 131.8, 130.0, 129.9, 129.0, 128.8, 128.5, 128.2, 125.1, 123.9, 52.7; IR $\tilde{\nu}_{\text{max}}$ 3060 (m), 2924 (m), 2855 (m), 1731 (s), 1611 (m), 1575 (m), 1500 (m), 1442 (m), 1375 (m), 1321 (m), 1255 (s), 1223 (s), 1133 (m), 1096 (m), 1029 (m), 951 (m), 765 (s), 705 (s); HRMS (ESI) calcd for C₁₇H₁₄NO₂⁺ [M+H]⁺ 264.1019; found 264.1020.

10. Spectra of New Compounds

61

^{19}F NMR
376 MHz CDCl_3

^{19}F NMR
376 MHz CDCl_3

29
 ^{19}F NMR
 376 MHz CDCl_3

¹⁹F NMR
 376 MHz CDCl₃