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Supporting Information

Cyanomethyl Anion Transfer Reagents for Diastereoselective Corey Chaykovsky Cyclopropanation Reactions

Renè Hommelsheim,^[a] Katharina J. Hock,^[a] Christian Schumacher,^[a] Mohanad Hussein,^[b] Thanh Vinh Nguyen,^{*[b]} René M. Koenigs^{*[a]}

 [a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
[b] School of Chemistry, University of New South Wales, Sydney, Australia

rene.koenigs@rwth-aachen.de

t.v.nguyen@unsw.edu.au

General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, ABCR and Fischer Scientific. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica-gel aluminum plates with F-254 indicator, visualized by irradiation under UV light. Column chromatography was performed using silica-gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

¹H NMR, ¹⁹F NMR and ¹³C NMR were recorded on a Varian AV600 or AV400 spectrometer in CDCl₃. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), p (pentelet) m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization. EI MS data were recorded on a Finnigan SSQ 7000 using EI Ionization at 70 eV. IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm⁻¹). Elemental analysis was performed on an Elementar VarioEL instrument.

Experimental Procedure

Initial investigations on the cyanomethyl anion transfer reaction.

In a test tube with septum nitro-styrene (0.2 mmol), the respective base (1.5 eq.), halo acetonitrile (2.0 eq.) and the respective additive (2.0 eq.) were suspended in 2 ml DCM under argon atmosphere and stirred over night at room temperature. After evaporation of the solvent under reduced pressure the crude product was purified by column chromatography on silica gel (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) to afford the desired product.

Synthesis of Cyanomethyl dimethyl sulfonium bromide (8)

Dimethyl sulfide (2.59 g, 41.7 mmol, 1.0 eq.) and bromo acetonitrile (5.00 g, 41.7 mmol, 1.0 eq.) were stirred under argon atmosphere at room temperature until the reaction mixture completely solidified. The resulting solid was suspended in DCM and evaporated at 50 °C to obtain a colorless solid (5.55 g, 73%), which was stored *in vacuo* until next use.

Synthesis of vinyl ketones

All vinyl ketones were prepared according to the literature procedure.^[1] Diisopropylammonium trifluoroacetate (1.94 g, 9.00 mmol, 1.0 eq.), Paraformaldehyde (1.08 g, 36.0 mmol (based on the monomer), 4.0 eq.) and the corresponding carbonyl compound (9.00 mmol, 1.0 eq.) were suspended in THF (5 mL). Trifluoroacetic acid (0.103 g, 0.900 mmol, 0.1 eq.) was added and the reaction mixture was refluxed overnight under air cooling. Thereafter, the solvent was removed under reduced pressure and the residue taken up in Et₂O (30 mL). The organic phase was washed with 1 M HCl (30 mL), 2 M NaOH (20 mL) and brine (30 mL). Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (*n*-pentane : diethyl ether).

Standard procedure for the cyclopropanation of nitro-styrenes

In a test tube with septum nitro-styrene (0.2 mmol), Na₂CO₃ (1.5 eq.) and cyanomethyl dimethyl sulfonium bromide (8) (2.0 eq.) were suspended in 2 ml DCM under argon atmosphere and stirred over night at room temperature. After evaporation of the solvent under reduced pressure the crude product was purified by column chromatography on silica gel (*n*-pentane : diethyl ether $20:1 \rightarrow 9:1 \rightarrow 4:1$) to afford the desired product.

Procedure for the gram-scale cyclopropanation of nitro styrene (7a)

To nitro styrene (6.7 mmol, 1.00 g), Na₂CO₂ (10.1 mmol, 1.07 g, 1.5 eq.) and cyanomethyl dimethyl sulfonium bromide (8) (13.4 mmol, 2.44 g, 2.0 eq.) were added 67 ml DCM under inert atmosphere. The suspension was stirred over night at room temperature. Silica was added, and volatiles were removed *in vacuo*. After column chromatography on silica gel (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) the cyclopropane 7a was obtained as a single diastereomer in 82% yield (1.04 g) as a white solid.

Standard procedure for the cyclopropanation of α , β unsaturated ketones

To the α,β -unsaturated ketone (0.2 mmol), Na₂CO₃ (1.5 eq.) and cyanomethyl dimethyl sulfonium bromide (8) (2.0 eq.) were added 2 ml DCM under argon atmosphere. The resulting suspension was stirred for 6 h at room temperature. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (*n*-pentane: diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) to afford the desired product.

Synthesis of methyl 2-phenylacrylate (12)

Methyl phenylacetate (42 mmol, 6.2 g), paraformaldehyde (84 mmol, 2.0 eq.), potassium carbonate (84 mmol, 2.0 eq.) and tetrabutylammonium iodide (4.2 mmol, 0.1 eq.) were dissolved in DMF (25 mL) and stirred at 85 °C for 2 hours. Then ethyl acetate (100 mL) was added and the organic layer was extracted three times with brine (25 mL), dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-pentane: diethyl ether 40:1 \rightarrow 9:1) to afford the methyl 2-phenylacrylate.

Procedure for the cyclopropanation of methyl 2-phenylacrylate

To methyl 2-phenylacrylate (12, 0.2 mmol), Cs_2CO_3 (0.35 mmol, 1.75 eq.) and cyanomethyl dimethyl sulfonium bromide (8) (0.4 mmol, 2.0 eq.) were added 2 ml 1,4-dioxane under argon atmosphere. The resulting suspension was stirred over night at room temperature. Silica was added, and the solvent was removed under reduced pressure. After purification using column chromatography on silica gel (*n*-pentane: diethyl ether $20:1 \rightarrow 9:1 \rightarrow 4:1$) the cyclopropane 11 was isolated as mixture of diastereoisomers as a yellowish oil in 92% yield (37 mg, d.r. 6:1).

Procedure for the gram-scale cyclopropanation of methyl 2-phenylacrylate

To methyl 2-phenylacrylate (12, 1.00 g, 6.17 mmol), Cs_2CO_3 (10.8 mmol, 3.52 g, 1.75 eq.) and cyanomethyl dimethyl sulfonium bromide (8) (12.3 mmol, 2.25 g, 2.0 eq.) were added 64 ml 1,4-dioxane under argon atmosphere. The resulting suspension was stirred over night at room temperature. Silica was added, and the solvent was removed under reduced pressure. After purification using column chromatography on silica gel (*n*-pentane: diethyl ether $20:1 \rightarrow 9:1 \rightarrow 4:1$) the cyclopropane was isolated as mixture of diastereoisomers as a yellow oil in 89% yield (1.11 g, d.r. 6:1).

Reaction Optimization

Table 1. Optimization of reaction conditions for the reaction with unsaturated ketones

	→ + Br CN S ⊕	1.5 eq. base 2 mL solvent 6 h, rt	
entry	Solvent	Base	%yield (10a)
1	DCM	K ₂ CO ₃	47%
2	DCM	Na ₂ CO ₃	90%
3	DCM	Cs ₂ CO ₃	71%
4	DCM	CsF	70%
5	EtOAc	Na ₂ CO ₃	55%
6	THF	Na ₂ CO ₃	58%
7	CHCl ₃	Na ₂ CO ₃	72%
9	1,4-dioxane	Na ₂ CO ₃	65%
10	MeCN	Na ₂ CO ₃	82%

Reaction conditions: unsaturated ketone (0.2 mmol), 2 eq. cyanomethyl dimethyl sulfonium bromide (8) and 1.5 eq. of base were stirred in 2 mL of the indicated solvent for 6 h at rt. Yields refer to isolated products.

Table 2. Optimization of reaction conditions for the reaction with 2-phenyl acrylic acid ester.

12		CN 1.75 eq. base MeC 2 mL solvent 12 h, rt		
entry	Solvent	Base	%yield (11)	d.r.
1	DCM	Na ₂ CO ₃ ^{<i>a</i>}	No rct.	-
2	PhMe	DBU	98	3:1
3	PhMe	CsF	75	4:1
4	PhMe	K ₂ CO ₃	56	4:1
5	PhMe	Cs ₂ CO ₃	87	4:1
6	EtOAc	Cs ₂ CO ₃	94	4:1
7	THF	Cs ₂ CO ₃	86	4:1
8	1,4-dioxane	Cs ₂ CO ₃	93	6:1

Reaction conditions: **12** (0.2 mmol), 2.0 eq. **8** and 1.75 eq. of the respective base were stirred in 2 ml of the indicated solvent for 12 h at rt. Yields refer to isolated products. Diastereomeric ratio was determined via ¹H NMR. ^{*a*}1.5 eq. Na₂CO₃.

NOESY Experiments

Determination of relative stereochemistry of 7a

NOESY spectrum of **7a** (NMR spectral region of the cyclopropane ring protons) NOE crosspeak observed between CH-Ph and CH-CN



Determination of relative stereochemistry of 7r

NOESY spectrum of **7r** NOE crosspeak observed between CH-Ph and CH-CN NOE crosspeaks observed between Ph and Me



Determination of relative stereochemistry of 9

NOESY spectrum of **9** (NMR spectral region of the cyclopropane ring protons) NOE crosspeak observed between CH-CN and CH-Ph



Determination of relative stereochemistry of 10a

NOESY spectrum of **10a** (NMR spectral region of the cyclopropane ring protons) NOE crosspeak observed between CH_2 and both adjacent cyclopropane CH protons No NOE crosspeak observed between CH-COPh and CH-CN



Determination of relative stereochemistry of 10k

NOESY spectrum of **10k** (NMR spectral region of the cyclopropane ring protons) NOE crosspeak observed between Methyl CH₂ and cyclopropane CH protons NOE crosspeak observed between CH-CN and CH-Me No NOE crosspeak observed between CH-CN and CH-COPh



Determination of relative stereochemistry of 10l

NOESY spectrum of **101** (NMR spectral region of the cyclopropane ring protons) NOE crosspeak observed between CH-CN and CH-Me No NOE crosspeak observed between CH-CN and CH-COPh



Physical Data

Cyanomethyl dimethyl sulfonium bromide (8)



m.p.: 108.5 °C – 111.2 °C; ¹H NMR (400 MHz, CD₃OD): $\delta = 4.82$ (s, 2H), 3.14 (s, 6H) ppm; ¹³C NMR (101 MHz, CD₃OD): $\delta = 110.9$, 30.1, 25.9 ppm; HRMS (ESI): mass found: 102.03734, calculated mass for C₄H₈NS⁺: 102.03720; IR (KBr): 3419, 3000, 2949, 2916, 2878, 2759, 2343, 2252, 2120, 1804, 1691, 1423, 1393, 1327, 1214, 1161, 1039, 1001, 928, 848, 747, 717 cm⁻¹. The analytical data is consistent with the literature.^[2]

(1R,2R,3R)-2-nitro-3-phenylcyclopropane-1-carbonitrile (7a)



Compound **7a** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 93% yield (35 mg): m.p.: 87.9 °C - 90.3 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.47 - 7.38 (m, 3H), 7.34 - 7.29 (m, 2H), 4.98 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.56 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.09 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 129.9, 129.47, 129.45, 128.1, 114.0, 62.4, 32.7, 16.7 ppm; MS (EI): m/z = 142.0 (100%), 115.1 (79%), 77.1 (3%); IR (KBr): 3037, 2920, 2855, 2655, 2249, 2026, 1900, 1821, 1740, 1631, 1554, 1498, 1447, 1394, 1364, 1253, 1063, 1025, 929, 903, 778, 733, 695 cm⁻¹; Elemental analysis calculated (%) for C₁₀H₈N₂O₂: C, 63.83; H, 4.29; N, 14.89. Found: C, 64.01; H, 4.39; N, 14.65.

(1R,2R,3R)-2-(4-fluorophenyl)-3-nitrocyclopropane-1-carbonitrilecarbonitrile (7b)



Compound **7b** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 78% yield (32 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.34 – 7.28 (m, 2H), 7.16 – 7.11 (m, 2H), 4.94 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.55 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.08 (dd, *J* = 10.4, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 163.2 (d, *J* = 249.8 Hz), 130.1 (d, *J* = 8.9 Hz), 125.7 (d, *J* = 3.8 Hz), 116.7 (d, *J* = 22.2 Hz), 113.9, 62.4, 32.0, 16.7 ppm; ¹⁹F NMR (564 MHz, CDCl₃): δ = -111.20 (ddd, *J* = 13.3, 8.6, 5.0 Hz) ppm; HRMS (ESI): mass found: 206.04962, calculated mass for C₁₀H₇FN₂O₂⁺: 206.04861; IR (KBr): 3042, 2924, 2256, 2089, 1911, 1740, 1552, 1369, 1218, 1063, 930, 823, 724 cm⁻¹.

(1R,2R,3R)-2-(4-chlorophenyl)-3-nitrocyclopropane-1-carbonitrilecarbonitrilecarbonitrile (7c)



Compound 7c was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 78% yield (35 mg): m.p.: 95.7 °C – 97.5 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.42 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.95 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.54 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.10 (dd, *J* = 10.4, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 135.7, 129.7, 129.5, 128.4, 113.8, 62.2, 32.0, 16.7 ppm; HRMS (ESI): mass found: 222.01964, calculated mass for C₁₀H₇ClN₂O₂⁺: 222.01906; IR (KBr): 3084, 3038, 2923, 2854, 2673, 2324, 2246, 2069, 2004, 1782, 1681, 1598, 1552, 1494, 1356, 1256, 1166, 1091, 1060, 1013, 957, 936, 908, 826, 761, 734, 700, 661 cm⁻¹.

(1R,2R,3R)-2-nitro-3-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (7d)



Compound 7d was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 71% yield (36 mg): m.p.: 108.6 °C – 110.1 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.71 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 5.01 (dd, *J* = 4.7, 3.7 Hz, 1H), 3.62 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.16 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 133.8, 131.8 (q, *J* = 33.5 Hz), 128.7, 126.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.4 Hz), 113.6, 62.1, 32.0, 16.7 ppm; ¹⁹F NMR (564 MHz, CDCl₃): δ = -62.93 ppm; MS (EI): m/z = 210.2 (100%), 190.2 (67%), 183.1 (54%), 141.1 (28%); IR (KBr): 3055, 2926, 2256, 2090, 1933, 1741, 1555, 1326, 1113, 837, 728 cm⁻¹; Elemental analysis calculated (%) for C₁₁H₇F₃N₂O₂: C, 51.57; H, 2.75; N, 10.94. Found: C, 52.00; H, 2.56; N, 10.90.

(1R,2R,3R)-2-(4-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7e)



Compound 7e was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 80% yield (35 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.92 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.82 (s, 3H), 3.51 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.05 (dd, *J* = 10.3, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 160.4, 129.4, 121.7, 114.8, 114.3, 62.6, 55.5, 32.4, 16.8 ppm; HRMS (ESI): mass found: 218.06879, calculated mass for C₁₁H₁₀N₂O₃⁺: 218.06859; IR (KBr): 3768, 3463, 2995, 2614, 2154, 2023, 1740, 1554, 1369, 1217, 1021, 910, 726 cm⁻¹.

(1R,2R,3R)-2-nitro-3-(p-tolyl)cyclopropane-1-carbonitrile (7f)



Compound **7f** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 82% yield (33 mg): m.p.: 81.9 °C - 83.5 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.99 - 4.90 (m, 1H), 3.52 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.06 (dd, *J* = 10.4, 3.7 Hz, 1H),

2.37 (s, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 139.5, 130.1, 127.9, 126.8, 114.2, 62.4, 32.6, 21.3, 16.8 ppm; HRMS (ESI): mass found: 202.07375, calculated mass for C₁₁H₁₀N₂O₂⁺: 202.07368; IR (KBr): 3059, 2923, 2647, 2249, 2081, 1915, 1736, 1662, 1556, 1363, 1253, 1208, 1120, 1054, 947, 817, 724 cm⁻¹.

(1R,2R,3R)-2-(3-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7g)



Compound 7g was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless oil in 89% yield (39 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.34 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.83 (t, *J* = 2.2 Hz, 1H), 4.97 (dd, *J* = 4.7, 3.7 Hz, 1H), 3.83 (s, 3H), 3.53 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.08 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 160.2, 131.3, 130.6, 120.1, 114.8, 114.06, 114.01, 62.4, 55.5, 32.7, 16.7 ppm; HRMS (ESI): mass found: 218.06844, calculated mass for C₁₁H₁₀N₂O₃⁺: 218.06859; IR (KBr): 3084, 3042, 2947, 2839, 2653, 2251, 2087, 1929, 1738, 1554, 1493, 1457, 1359, 1260, 1154, 1041, 956, 870, 786, 703 cm⁻¹.

(1R,2R,3R)-2-(2-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7h)



Compound **7h** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless solid in 82% yield (36 mg): m.p.: 91.9 °C – 93.6 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.41 – 7.34 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.98 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.89 (s, 3H), 3.54 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.07 (dd, *J* = 10.4, 3.6 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 158.4, 130.8, 128.9, 121.0, 118.3, 114.7, 111.1, 62.3, 55.7, 29.2, 16.1 ppm; HRMS (ESI): mass found: 218.06873, calculated mass for C₁₁H₁₀N₂O₃⁺: 218.06859; IR (KBr): 3080, 3037, 2929, 2842, 2599, 2244, 2090, 1933, 1727, 1547, 1488, 1361, 1242, 1163, 1111, 1025, 967, 898, 748 cm⁻¹.

(1R,2R,3R)-2-nitro-3-(2-nitrophenyl)cyclopropane-1-carbonitrile (7i)



Compound 7i was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 9:1 \rightarrow 4:1 \rightarrow 2:1 \rightarrow 1:2) as a yellowish solid in 67% yield (31 mg): m.p.: 143.9 °C – 146.3 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.28 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.76 (td, *J* = 7.6, 1.3 Hz, 1H), 7.66 (td, *J* = 7.7, 7.2, 1.0 Hz, 1H), 7.57 (dt, *J* = 7.7, 1.1 Hz, 1H), 4.94 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.06 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.26 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 149.1, 134.6, 130.9, 126.4, 125.7, 113.8, 62.6, 31.4, 16.3 ppm; HRMS (ESI): mass found: 256.03293, calculated mass for C₁₀H₇N₃NaO₄ ⁺: 256.03288; IR (KBr): 3092, 3054,

2921, 2858, 2656, 2249, 2104, 1990, 1831, 1733, 1562, 1516, 1349, 1155, 1074, 965, 929, 848, 784, 738, 702 cm⁻¹; Elemental analysis calculated (%) for $C_{10}H_7N_3O_4$: C, 51.51; H, 3.03; N, 18.02. Found: C, 51.70; H, 3.11; N, 17.40.

(1R,2R,3R)-2-(2-fluorophenyl)-3-nitrocyclopropane-1-carbonitrile (7j)



Compound **7j** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish solid in 76% yield (31 mg): m.p.: 118.0 °C – 120.0 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.42 (tdd, *J* = 7.5, 5.2, 1.7 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.15 (m, 1H), 5.04 – 4.99 (m, 1H), 3.61 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.13 (dd, *J* = 10.4, 3.7, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 161.7 (d, *J* = 249.6 Hz), 131.4 (d, *J* = 8.3 Hz), 129.0 (d, *J* = 2.2 Hz), 125.0 (d, *J* = 3.7 Hz), 117.5 (d, *J* = 13.6 Hz), 116.5 (d, *J* = 21.3 Hz), 114.0, 61.7, 27.2 (d, *J* = 3.9 Hz), 16.0 ppm; ¹⁹F NMR (564 MHz, CDCl₃): δ = -115.43 (ddd, *J* = 10.2, 7.1, 5.3 Hz) ppm; HRMS (ESI): mass found: 206.04864, calculated mass for C₁₀H₇FN₂O₂⁺: 206.04861; IR (KBr): 3100, 3059, 2924, 2855, 2252, 2069, 2004, 1930, 1800, 1708, 1621, 1562, 1493, 1452, 1362, 1240, 1196, 1169, 1107, 1059, 1022, 975, 946, 912, 856, 815, 760, 729, 685 cm⁻¹.

(1R,2R,3R)-2-nitro-3-(o-tolyl)cyclopropane-1-carbonitrile (7k)



Compound 7k was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless oil in 79% yield (32 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 4.97 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.52 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.07 (dd, *J* = 10.5, 3.7 Hz, 1H), 2.38 (s, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 139.3, 130.2, 129.8, 129.3, 128.8, 125.1, 114.1, 62.3, 32.8, 21.5, 16.7 ppm; HRMS (ESI): mass found: 225.06334, calculated mass for C₁₁H₁₀N₂NaO₂⁺: 225.06345; IR (KBr): 3042, 2921, 2251, 2089, 1949, 1738, 1608, 1553, 1359, 1255, 1181, 1054, 926, 790, 708 cm⁻¹.

(1R,2R,3R)-2-(3,4-dichlorophenyl)-3-nitrocyclopropane-1-carbonitrile (7l)



Compound **71** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 65% yield (33 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.95 (dd, *J* = 4.6, 3.7 Hz, 1H), 3.52 (dd, *J* = 10.5, 4.6 Hz, 1H), 3.11 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 134.2, 133.9, 131.5, 130.4, 129.9, 127.2, 113.5, 61.9, 31.3, 16.6 ppm; HRMS (ESI): mass found: 255.98059, calculated mass for C₁₀H₆Cl₂N₂O₂⁺:

255.98008; IR (KBr): 3421, 3083, 3040, 2922, 2857, 2663, 2248, 2101, 2004, 1907, 1726, 1652, 1556, 1476, 1359, 1135, 1031, 947, 910, 807, 727 cm⁻¹.

(1R,2R,3R)-2-(naphthalen-2-yl)-3-nitrocyclopropane-1-carbonitrile (7m)



Compound **7m** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish solid in 65% yield (31 mg): m.p.: 169.1 °C – 171.4 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.92 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.81 – 7.78 (m, 1H), 7.59 – 7.51 (m, 2H), 7.38 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.12 (dd, *J* = 4.7, 3.6 Hz, 1H), 3.73 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.16 (dd, *J* = 10.4, 3.6 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 133.5, 133.2, 129.6, 128.1, 128.0, 127.8, 127.3, 127.2, 127.1, 125.0, 114.1, 62.4, 33.0, 16.8 ppm; HRMS (ESI): mass found: 238.07330, calculated mass for C₁₄H₁₀N₂O₂⁺: 238.07368; IR (KBr): 3460, 3041, 2928, 2649, 2322, 2252, 2103, 1991, 1935, 1738, 1555, 1362, 1216, 1047, 958, 912, 817, 744 cm⁻¹.

(1R,2R,3R)-2-nitro-3-(pyridin-3-yl)cyclopropane-1-carbonitrile (7n)



Compound **7n** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 9:1 \rightarrow 4:1 \rightarrow 2:1 \rightarrow 1:1) as a colorless oil in 61% yield (23 mg): ¹H NMR (600 MHz, CDCl₃): δ = 8.70 – 8.63 (m, 2H), 7.61 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.02 (dd, *J* = 4.7, 3.7 Hz, 1H), 3.58 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.16 (dd, *J* = 10.5, 3.7 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 150.6, 149.8, 134.8, 126.0, 123.8, 113.4, 61.6, 29.9, 16.3 ppm; HRMS (ESI): mass found: 190.06104, calculated mass for C₉H₈N₃O₂⁺: 190.06110; IR (KBr): 3645, 3043, 2251, 2093, 1901, 1555, 1484, 1359, 1260, 1193, 1124, 1025, 918, 811, 709 cm⁻¹.

(1R,2S,3S)-2-(furan-2-yl)-3-nitrocyclopropane-1-carbonitrile (70)



Compound **70** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 65% yield (23 mg): m.p.: 50.0 °C - 53.4 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.50 - 7.39 (m, 1H), 6.50 (d, *J* = 3.3 Hz, 1H), 6.42 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.03 (t, *J* = 4.2 Hz, 1H), 3.54 (dd, *J* = 10.1, 4.5 Hz, 1H), 3.06 (dd, *J* = 10.1, 4.0 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 143.9, 143.7, 113.9, 111.3, 110.5, 61.4, 26.3, 15.6 ppm; MS (EI): m/z = 132.1 (56%), 104.1 (39%), 77.1 (89%), 51.2 (100%); IR (KBr): 3778, 3456, 3154, 3090, 3049, 2921, 2648, 2451, 2254, 2075, 1929, 1737, 1630, 1555, 1360, 1246, 1147, 1056, 1014, 951, 902, 820, 744 cm⁻¹; Elemental analysis calculated (%) for C₈H₆N₂O₃: C, 53.94; H, 3.39; N, 15.73. Found: C, 54.00; H, 3.23; N, 16.30.

(1R,2S,3S)-2-nitro-3-(thiophen-2-yl)cyclopropane-1-carbonitrile (7p)



Compound **7p** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish solid in 88% yield (34 mg): m.p.: 83.3 °C - 83.7 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.35 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.11 (dt, *J* = 3.6, 1.1 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.94 (dd, *J* = 4.5, 3.8 Hz, 1H), 3.68 (ddd, *J* = 10.1, 4.5, 1.0 Hz, 1H), 3.11 (dd, *J* = 10.1, 3.8 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 131.9, 127.8, 127.5, 127.1, 113.9, 63.3, 28.1, 17.6 ppm; MS (EI): m/z = 148.1 (100%), 121.1 (40%), 104.1 (37%); IR (KBr): 3020, 2931, 2255, 1740, 1548, 1366, 1236, 1058, 828, 709 cm⁻¹; Elemental analysis calculated (%) for C₈H₆N₂O₂S: C, 49.48; H, 3.11; N, 14.42. Found: C, 49.69; H, 3.19; N, 14.46.

(1R,2S,3R)-2-cyclohexyl-3-nitrocyclopropane-1-carbonitrile (7q)



Compound **7q** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless oil in 67% yield (26 mg): ¹H NMR (600 MHz, CDCl₃): δ = 4.41 (dd, *J* = 4.3, 3.3 Hz, 1H), 2.73 (dd, *J* = 10.1, 3.3 Hz, 1H), 2.14 (td, *J* = 10.1, 4.3 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.89 – 1.82 (m, 1H), 1.81 – 1.75 (m, 2H), 1.74 – 1.66 (m, 1H), 1.35 – 1.11 (m, 6H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 115.0, 61.9, 37.6, 35.2, 32.1, 31.5, 25.9, 25.6, 25.5, 14.4 ppm; HRMS (ESI): mass found: 217.09447, calculated mass for C₁₀H₁₄N₂NaO₂⁺: 217.09475; IR (KBr): 3084, 2927, 2855, 2248, 2073, 1991, 1738, 1551, 1448, 1362, 1265, 1193, 1057, 964, 913, 850, 819, 787, 731 cm⁻¹; Elemental analysis calculated (%) for C₁₀H₁₄N₂O₂: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.80; H, 6.93; N, 15.12.

(1S,2S,3S)-2-methyl-2-nitro-3-phenylcyclopropane-1-carbonitrile (7r)



Compound **7r** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless oil in 30% yield (12 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.46 – 7.38 (m, 3H), 7.38 – 7.34 (m, 2H), 3.69 (d, *J* = 10.6 Hz, 1H), 3.24 (d, *J* = 10.6 Hz, 1H), 1.78 (s, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 129.6, 129.4, 129.3, 129.1, 114.6, 67.4, 35.9, 19.5, 13.8 ppm; HRMS (ESI): mass found: 202.07378, calculated mass for C₁₁H₁₀N₂O₂⁺: 202.07368; IR (KBr): 3750, 3327, 3052, 2924, 2859, 2646, 2244, 2079, 1962, 1904, 1737, 1644, 1546, 1447, 1345, 1218, 1087, 962, 883, 744, 692 cm⁻¹.

(2R,3R)-3-phenylcyclopropane-1,1,2-tricarbonitrile (9)



Compound **9** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 31% yield (12 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.52 – 7.47 (m, 3H), 7.32 – 7.28 (m, 2H), 3.69 (d, *J* = 8.0 Hz, 1H), 3.06 (d, *J* = 8.0 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 130.9, 129.8, 128.2, 127.3, 112.9, 111.2, 109.9, 39.3, 20.1, 14.2 ppm; HRMS (ESI): mass found: 193.06295, calculated mass for C₁₂H₇N₃⁺: 193.06345; IR (KBr): 3658, 3036, 2255, 2066, 1977, 1893, 1739, 1598, 1499, 1453, 1401, 1288, 1211, 1083, 1004, 910, 851, 737, 696 cm⁻¹. The analytical data is consistent with the literature.^[3]

(1R,2R)-2-benzoylcyclopropane-1-carbonitrile (10a)



Compound **10a** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless oil in 90% yield (31 mg): ¹H NMR (600 MHz, CDCl₃): $\delta = 8.05 - 7.99$ (m, 2H), 7.68 - 7.62 (m, 1H), 7.58 - 7.50 (m, 2H), 3.28 (ddd, J = 8.7, 5.9, 4.3 Hz, 1H), 2.17 (ddd, J = 9.1, 6.1, 4.2 Hz, 1H), 1.69 (ddd, J = 9.1, 5.9, 4.4 Hz, 1H), 1.64 (ddd, J = 8.6, 6.1, 4.4 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): $\delta = 195.2, 136.3, 134.2, 129.1, 128.5, 120.0, 24.2, 17.0, 7.5 ppm; HRMS (ESI): mass found: 194.05780, calculated mass for C₁₁H₉NNaO⁺: 194.05764; IR (KBr): 3055, 2925, 2854, 2664, 2329, 2244, 2090, 1996, 1954, 1917, 1819, 1673, 1595, 1494, 1448, 1395, 1303, 1224, 1180, 1066, 1012, 912, 853, 813, 771, 697 cm⁻¹. The analytical data is consistent with the literature.^[4]$

(1R,2R)-2-(4-chlorobenzoyl)cyclopropane-1-carbonitrile (10b)



Compound **10b** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 85% yield (35 mg): m.p.: 75.5 °C – 77.2 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 3.22 (ddd, *J* = 9.0, 5.8, 4.3 Hz, 1H), 2.17 (ddd, *J* = 9.4, 6.2, 4.3 Hz, 1H), 1.69 (ddd, *J* = 9.4, 5.8, 4.6 Hz, 1H), 1.65 (ddd, *J* = 8.9, 6.1, 4.5 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 194.0, 140.9, 134.6, 129.9, 129.5, 119.8, 24.1, 17.2, 7.7 ppm; HRMS (ESI): mass found: 228.01866, calculated mass for C₁₁H₈CINNaO⁺: 228.01866; IR (KBr): 3319, 3095, 2926, 2854, 2575, 2241, 2105, 1977, 1930, 1740, 1660, 1582, 1403, 1305, 1221, 1084, 1012, 910, 843, 799, 730, 673 cm⁻¹.

(1R,2R)-2-(4-methoxybenzoyl)cyclopropane-1-carbonitrile (10c)



Compound **10c** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless oil in 85% yield (34 mg): ¹H NMR (600 MHz, CDCl₃): δ = 8.01 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.22 (ddd, *J* = 8.7, 5.9, 4.3 Hz, 1H), 2.13 (ddd, *J* = 9.1, 6.1, 4.3 Hz, 1H), 1.66 (ddd, *J* = 8.7, 5.9, 4.4 Hz, 1H), 1.59 (ddd, *J* = 9.1, 6.1, 4.4 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 193.3, 164.5, 130.9, 129.4, 120.2, 114.3, 55.8, 23.9, 16.7, 7.2 ppm; HRMS (ESI): mass found: 224.06754, calculated mass for C₁₂H₁₁NNaO₂⁺: 224.06820; IR (KBr): 3630, 3045, 2943, 2840, 2637, 2329, 2242, 2085, 1998, 1918, 1741, 1662, 1593, 1511, 1398, 1310, 1232, 1175, 1018, 914, 840, 740, 684 cm⁻¹.

(1R,2R)-2-(3-methoxybenzoyl)cyclopropane-1-carbonitrile (10d)



Compound **10e** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless oil in 85% yield (34 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.66 – 7.60 (m, 1H), 7.52 – 7.48 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.16 (m, 1H), 3.87 (s, 3H), 3.25 (ddd, *J* = 8.8, 5.8, 4.3 Hz, 1H), 2.16 (ddd, *J* = 9.4, 6.1, 4.3 Hz, 1H), 1.68 (ddd, *J* = 9.4, 5.7, 4.6 Hz, 1H), 1.63 (ddd, *J* = 8.7, 6.1, 4.5 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 195.0, 160.2, 137.7, 130.1, 121.2, 120.7, 119.9, 112.6, 55.7, 24.3, 17.1, 7.5 ppm; HRMS (ESI): mass found: 224.06784, calculated mass for C₁₂H₁₁NNaO₂⁺: 224.06820; IR (KBr): 3333, 3052, 2949, 2840, 2244, 2104, 1947, 1673, 1588, 1446, 1396, 1304, 1259, 1201, 1026, 915, 876, 787, 725, 682 cm⁻¹.

(1R,2R)-2-(2-methylbenzoyl)cyclopropane-1-carbonitrile (10e)



Compound **10d** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 76% yield (28 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.80 (d, *J* = 7.7 Hz, 1H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 3.09 (ddd, *J* = 8.8, 5.9, 4.3 Hz, 1H), 2.50 (s, 3H), 2.15 (ddd, *J* = 9.2, 6.1, 4.3 Hz, 1H), 1.68 (ddd, *J* = 9.3, 5.9, 4.4 Hz, 1H), 1.62 (ddd, *J* = 8.7, 6.2, 4.4 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 198.2, 138.5, 136.9, 132.3, 132.1, 129.1, 126.0, 119.8, 26.9, 21.2, 17.0, 7.5 ppm; HRMS (ESI): mass found: 208.07321, calculated mass for C₁₂H₁₁NNaO⁺: 208.07329; IR (KBr): 3099, 3046, 2927, 2853, 2240, 2069, 2004, 1942, 1864, 1823, 1778, 1672, 1600, 1570, 1487, 1454, 1393, 1306, 1216, 1132, 1052, 1011, 953, 915, 807, 771, 730, 693 cm⁻¹.

(1R,2R)-2-(2,4-dimethylbenzoyl)cyclopropane-1-carbonitrile (10f)



Compound **10f** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 87% yield (35 mg): m.p.: 80.2 °C - 81.2 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.74 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 3.09 (ddd, *J* = 8.6, 5.9, 4.3 Hz, 1H), 2.48 (s, 3H), 2.39 (s, 3H), 2.12 (ddd, *J* = 8.9, 6.1, 4.3 Hz, 1H), 1.66 (ddd, *J* = 9.4, 5.9, 4.3 Hz, 1H), 1.59 (ddd, *J* = 8.6, 6.1, 4.3 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 197.5, 143.4, 139.1, 134.1, 133.2, 129.8, 126.8, 120.1, 26.7, 21.6,

21.5, 17.0, 7.4 ppm; HRMS (ESI): mass found: 200.10693, calculated mass for $C_{13}H_{14}NO^+$: 200.10699; IR (KBr): 3318, 3114, 3038, 2983, 2927, 2856, 2239, 2180, 2005, 1970, 1928, 1766, 1663, 1609, 1562, 1497, 1445, 1386, 1307, 1218, 1144, 1080, 1015, 967, 945, 913, 885, 832, 802, 737, 690 cm⁻¹.

(1R,2R)-2-(2-naphthoyl)cyclopropane-1-carbonitrile (10g)



Compound **10g** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellow solid in 91% yield (41 mg): m.p.: 101 °C – 102 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.58 (s, 1H), 8.07 – 8.00 (m, 2H), 7.97 – 7.93 (m, 1H), 7.93 – 7.89 (m, 1H) 7.69 – 7.63 (m, 1H), 7.64 – 7.58 (m, 1H), 3.45 (ddd, *J* = 8.8, 5.9, 4.3 Hz, 1H), 2.23 (ddd, *J* = 9.1, 6.2, 4.3 Hz, 1H), 1.75 (ddd, *J* = 9.2, 5.9, 4.4 Hz, 1H), 1.69 (ddd, *J* = 8.7, 6.1, 4.4 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 195.0, 136.1, 133.7, 132.6, 130.7, 129.9, 129.3, 129.1, 128.0, 127.4, 123.7, 120.1, 24.3, 17.1, 7.6 ppm; HRMS (ESI): mass found: 221.08296, calculated mass for C₁₅H₁₁NO⁺: 221.08352; IR (KBr): 3316, 3046, 2645, 2317, 2244, 2177, 2070, 1964, 1741, 1663, 1461, 1388, 1302, 1204, 1119, 1067, 1012, 959, 912, 876, 826, 753 cm⁻¹.

(1R,2R)-2-(benzo[d][1,3]dioxole-5-carbonyl)cyclopropane-1-carbonitrile (10h)



Compound **10h** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a colorless oil in 85% yield (36 mg): ¹H NMR (600 MHz, CDCl₃): δ = 7.66 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.09 (s, 2H), 3.17 (ddd, *J* = 8.6, 5.9, 4.3 Hz, 1H), 2.13 (ddd, *J* = 9.1, 6.1, 4.3 Hz, 1H), 1.65 (ddd, *J* = 9.2, 5.9, 4.4 Hz, 1H), 1.59 (ddd, *J* = 8.6, 6.1, 4.4 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 193.0, 152.9, 148.7, 131.2, 125.2, 120.1, 108.3, 108.0, 102.3, 24.0, 16.8, 7.3 ppm; HRMS (ESI): mass found: 216.06549, calculated mass for C₁₂H₁₀NO₃⁺: 216.06552; IR (KBr): 3055, 2908, 2244, 2068, 1856, 1662, 1607, 1495, 1443, 1399, 1355, 1304, 1247, 1105, 1029, 921, 806, 727 cm⁻¹.

(1R,2R)-2-(thiophene-2-carbonyl)cyclopropane-1-carbonitrile (10i)



Compound **10i** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1 \rightarrow 2:1) as a yellowish solid in 87% yield (31 mg): m.p.: 65.0 °C - 67.0 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.90 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.76 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.25 - 7.20 (m, 1H), 3.13 (ddd, *J* = 8.6, 5.8, 4.2 Hz, 1H), 2.16 (ddd, *J* = 9.1, 6.2, 4.2 Hz, 1H), 1.71 (ddd, *J* = 8.9, 5.8, 4.5 Hz, 1H), 1.62 (ddd, *J* = 8.6, 6.2, 4.5 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 187.4, 143.4, 135.5, 133.3, 128.8, 119.8, 25.1, 16.7, 7.3 ppm; HRMS (ESI): mass found: 178.03215, calculated mass for C₉H₈NOS⁺: 178.03211; IR (KBr): 3263, 3087, 3047, 2928, 2768, 2650, 2489, 2324, 2238, 2175, 1967, 1871, 1798, 1633, 1523, 1420, 1357, 1312, 1253, 1229, 1190, 1125, 1094, 1068, 988, 915, 859, 796, 738, 710 cm⁻¹.

(1R,2R)-2-(cyclohexanecarbonyl)cyclopropane-1-carbonitrile (10j)



Compound **10j** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless oil in 71% yield (25 mg): ¹H NMR (600 MHz, CDCl₃): $\delta = 2.62 - 2.52$ (m, 2H), 1.99 - 1.91 (m, 2H), 1.90 (ddd, J = 8.6, 6.5, 4.3 Hz, 1H), 1.84 - 1.77 (m, 2H), 1.73 - 1.65 (m, 1H), 1.44 (ddt, J = 8.7, 6.3, 3.3 Hz, 2H), 1.40 - 1.28 (m, 4H), 1.28 - 1.13 (m, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): $\delta = 208.6, 119.9, 51.7, 28.2, 28.1, 25.9, 25.8, 25.59, 25.57, 16.4, 6.8 ppm; HRMS (ESI): mass found: 200.10420, calculated mass for C₁₁H₁₅NNaO⁺: 200.10459; IR (KBr): 3370, 3041, 2924, 2854, 2665, 2241, 2109, 2027, 1829, 1689, 1447, 1402, 1312, 1234, 1192, 1148, 1101, 1058, 1011, 911, 803, 716 cm⁻¹.$

(1R,2R,3S)-2-benzoyl-3-methylcyclopropane-1-carbonitrile (10k)



Compound **10k** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 28% yield (10 mg): m.p.: 38.7 °C – 41.7 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.99 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 2.92 (t, *J* = 4.9 Hz, 1H), 2.35 (dd, *J* = 8.7, 4.5 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.48 (d, *J* = 6.2 Hz, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 195.1, 136.5, 134.1, 129.1, 128.4, 118.4, 32.3, 24.3, 14.5, 14.3 ppm; MS (EI) m/z (%) = 146.1 (60%), 131.0 (92%), 102.9 (100%); IR (KBr): 3872, 3665, 3352, 3192, 3052, 2925, 2509, 2245, 2099, 1982, 1908, 1818, 1736, 1675, 1595, 1494, 1443, 1354, 1319, 1259, 1175, 1074, 976, 902, 839, 748, 688 cm⁻¹. The analytical data is consistent with the literature.^[5]

(1R,2R,3S)-2-benzoyl-3-phenylcyclopropane-1-carbonitrile (10l)



Compound **101** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a colorless solid in 25% yield (12 mg): m.p.: 105 °C – 108 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.10 – 8.01 (m, 2H), 7.69 – 7.63 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 3.63 (t, *J* = 5.4 Hz, 1H), 3.07 (dd, *J* = 9.0, 5.9 Hz, 1H), 2.73 (dd, *J* = 9.0, 4.9 Hz, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 194.3, 136.1, 134.2, 133.4, 129.0, 128.9, 128.4, 128.3, 127.9, 117.4, 33.1, 30.7, 15.4 ppm; MS (EI) m/z = 116.1 (2%), 105.0 (100%); IR (KBr): 3319, 3045, 2923, 2856, 2655, 2447, 2331, 2243, 1897, 1819, 1737, 1663, 1590, 1502, 1414, 1356, 1293, 1222, 1084, 1013, 921, 858, 743, 689 cm⁻¹. The analytical data is consistent with the literature.^[6]

benzyl (1R,2R)-2-cyanocyclopropane-1-carboxylate (10m)



Compound **10m** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a yellowish oil in 42% yield (17 mg): ¹H NMR (400 MHz, CDCl₃): δ = 7.46 – 7.32 (m, 5H), 5.16 (s, 2H), 2.31 (ddd, *J* = 8.8, 6.0, 4.3 Hz, 1H), 1.97 (ddd, *J* = 9.2, 6.3, 4.3 Hz, 1H), 1.55 (ddd, *J* = 9.2, 6.0, 4.9 Hz, 1H), 1.50 (ddd, *J* = 8.9, 6.3, 4.9 Hz, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃): δ = 170.2, 135.1, 128.9, 128.8, 128.6, 119.3, 67.7, 21.2, 14.9, 6.0 ppm; MS (EI): m/z = 202.1 (1%), 107.6 (14%), 93.8 (26%), 90.7 (81%), 76.8 (58%), 65.5 (100%), 51.5 (48%); IR (KBr): 3660, 3447, 3038, 2957, 2245, 1961, 1734, 1587, 1543, 1498, 1452, 1408, 1308, 1269, 1179, 1056, 1005, 911, 868, 810, 746, 699, 584, 533, 495 cm⁻¹. The analytical data is consistent with the literature.^[7]

Methyl (1R,2R)-2-cyano-1-phenylcyclopropane-1-carboxylate (11)



Compound **11** was prepared according to general procedure and was obtained after column chromatography (*n*-pentane : diethyl ether 20:1 \rightarrow 9:1 \rightarrow 4:1) as a mixture of diastereoisomers as a yellowish oil in 93% yield (37 mg, d.r. 6:1): ¹H NMR (600 MHz, CDCl₃): δ = 7.44 – 7.32 (m, 5H), 3.75 and 3.67 (s, 3H), 2.55 (dd, *J* = 9.4, 6.4 Hz, 0.85 H) AND 2.28 (dd, *J* = 6.7, 5.0 Hz, 0.15 H), 2.09 (dd, *J* = 9.3, 6.7 Hz, 0.15 H) AND 2.04 (dd, *J* = 9.4, 4.8 Hz, 0.85 H), 1.86 (dd, *J* = 6.1, 5.1 Hz, 0.85 H) AND 1.73 (dd, *J* = 9.3, 5.0 Hz, 0.15 H) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 171.5, 169.7, 136.1, 133.2, 130.8, 130.0, 128.9, 128.8, 128.7, 128.6, 117.8, 53.50, 53.48, 36.6, 35.4, 21.1, 20.4, 13.5, 13.2 ppm; MS (EI): m/z = 201.1 (6%), 174.0 (4%), 141.0 (18%), 115.0 (100%); IR (KBr): 3446, 3036, 2955, 2849, 2668, 2328, 2244, 2086, 1992, 1955, 1811, 1726, 1603, 1546, 1497, 1437, 1353, 1262, 1195, 1166, 1081, 1028, 975, 940, 872, 815, 782, 737, 699, 663 cm⁻¹. The analytical data is consistent with the literature.^[8]

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NMR Spectra of Compounds

(Cyanomethyl)dimethylsulfonium bromide (8)

¹H-NMR (400 MHz, CD₃OD)





(*1R,2R,3R*)-2-nitro-3-phenylcyclopropane-1-carbonitrile (7a) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(4-fluorophenyl)-3-nitrocyclopropane-1-carbonitrilecarbonitrile (7b) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(4-chlorophenyl)-3-nitrocyclopropane-1-carbonitrilecarbonitrilecarbonitrile (7c) ¹H NMR (600 MHz, CDCl₃)







(*1R,2R,3R*)-2-nitro-3-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (7d) ¹H NMR (600 MHz, CDCl₃)





(*1R,2R,3R*)-2-(4-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7e) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-nitro-3-(p-tolyl)cyclopropane-1-carbonitrile (7f) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(3-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7g) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(2-methoxyphenyl)-3-nitrocyclopropane-1-carbonitrile (7h) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-nitro-3-(2-nitrophenyl)cyclopropane-1-carbonitrile (7i) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(2-fluorophenyl)-3-nitrocyclopropane-1-carbonitrile (7j) ¹H NMR (600 MHz, CDCl₃)





(*1R,2R,3R*)-2-nitro-3-(o-tolyl)cyclopropane-1-carbonitrile (7k) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(3,4-dichlorophenyl)-3-nitrocyclopropane-1-carbonitrile (7l) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-(naphthalen-2-yl)-3-nitrocyclopropane-1-carbonitrile (7m) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3R*)-2-nitro-3-(pyridin-3-yl)cyclopropane-1-carbonitrile (7n) ¹H NMR (600 MHz, CDCl₃)



(*1R,2S,3S*)-2-(furan-2-yl)-3-nitrocyclopropane-1-carbonitrile (7o) ¹H NMR (600 MHz, CDCl₃)



(*1R,2S,3S*)-2-nitro-3-(thiophen-2-yl)cyclopropane-1-carbonitrile (7p) ¹H NMR (600 MHz, CDCl₃)



(*1R,2S,3R*)-2-cyclohexyl-3-nitrocyclopropane-1-carbonitrile (7q) ¹H NMR (600 MHz, CDCl₃)



(*1S*,*2S*,*3S*)-2-methyl-2-nitro-3-phenylcyclopropane-1-carbonitrile (7r) ¹H NMR (600 MHz, CDCl₃)



(2R,3R)-3-phenylcyclopropane-1,1,2-tricarbonitrile (9) ¹H NMR (600 MHz, CDCl₃)

-220 -210 . -200 . -190 N N 0 . -180 -170 -160 -150 -140 . -130 . -120 . -110 -100 -90 . -80 -70 -60 . -50 . -40 . -30 . -20 . -10 . -0 --10 1.00-1 1.044 1.94-1 0.97 0.94-I -20 4.5 f1 (ppm) 8.0 .0 8.5 7.5 7.0 6.5 6.0 5.5 5.0 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ¹³C NMR (151 MHz, CDCl₃) −136.3 −134.2 ₹129.4 120.0 --7.5 -500 -450 N 0 -400 -350 -300 -250 -200 -150 -100 -50 -0 -50)0 190 180 170 160 150 140 130 120 110 100 f1 (ppm) 90 80 70 60 50 40 30 20 10 0

(*1R,2R*)-2-benzoylcyclopropane-1-carbonitrile (10a) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(4-chlorobenzoyl)cyclopropane-1-carbonitrile (10b) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(4-methoxybenzoyl)cyclopropane-1-carbonitrile (10c) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(3-methoxybenzoyl)cyclopropane-1-carbonitrile (10d) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(2-methylbenzoyl)cyclopropane-1-carbonitrile (10e) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(2,4-dimethylbenzoyl)cyclopropane-1-carbonitrile (10f) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(2-naphthoyl)cyclopropane-1-carbonitrile (10g) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(benzo[d][1,3]dioxole-5-carbonyl)cyclopropane-1-carbonitrile (10h) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(thiophene-2-carbonyl)cyclopropane-1-carbonitrile (10i) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R*)-2-(cyclohexanecarbonyl)cyclopropane-1-carbonitrile (10j) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3S*)-2-benzoyl-3-methylcyclopropane-1-carbonitrile (10k) ¹H NMR (600 MHz, CDCl₃)



(*1R,2R,3S*)-2-benzoyl-3-phenylcyclopropane-1-carbonitrile (10l) ¹H NMR (600 MHz, CDCl₃)



Benzyl (1*R***,2***R***)-2-cyanocyclopropane-1-carboxylate (10m)** ¹H NMR (400 MHz, CDCl₃)



Methyl (*1R,2R***)-2-cyano-1-phenylcyclopropane-1-carboxylate (11)** ¹H NMR (600 MHz, CDCl₃)