Supporting Information

for

Tetrabutylammonium iodide-catalyzed oxidative α-azidation of β-ketocarbonyl compounds using sodium azide

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Full experimental and analytical details and copies of NMR spectra
# Table of Contents

1. General information ............................................................................................................. S2
2. Handling of azido compounds ............................................................................................ S3
3. Synthesis of substrates ....................................................................................................... S4
4. Oxidative α-azidation reactions ......................................................................................... S5
   General procedure ............................................................................................................... S5
   Characterization of the α-azidation products...................................................................... S5
5. Oxidative α-nitration reactions .......................................................................................... S16
   General procedure ............................................................................................................... S16
   Characterization of the α-nitration products...................................................................... S16
6. NMR spectra ....................................................................................................................... S18
7. Infrared spectra .................................................................................................................. S43
8. High-resolution mass spectra ............................................................................................ S55
9. References ........................................................................................................................ S67
1. General Information

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 300 MHz spectrometer with a broad band observe probe and a sample changer for 16 samples, on a Bruker Avance DRX 500 MHz spectrometer, and on a Bruker Avance III 700 MHz spectrometer with an Ascend magnet and TCI cryoprobe, which are all property of the Austro Czech NMR Research Center “RERI uasb”. All NMR spectra were referenced on the solvent residual peak (CDCl₃: δ = 7.26 ppm for ¹H NMR, δ = 77.16 ppm for ¹³C NMR, ¹⁹F NMR is unreferenced). ¹H NMR and ¹⁹F NMR spectra are reported as follows: chemical shift (δ/ppm) (multiplicity, coupling constants, number of protons). Peak multiplicities are denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublet, etc. Infrared (IR) spectra were recorded on a Bruker Alpha II FTIR spectrometer with diamond ATR-module using OPUS software package and are reported in 𝜈/ cm⁻¹. High-resolution mass spectra (HRMS) were recorded on an Agilent QTOF 6520 with an ESI source, owned and operated by the Institute of Analytical and General Chemistry, JKU. Melting points (MP) are recorded using a Büchi M-560 apparatus and are reported uncorrected in ϑm/°C. Thin layer chromatography (TLC) was performed on Macherey-Nagel pre-coated TLC plates (silica gel, 60 F₂₅₄, 0.20 mm, ALUGRAM® Xtra SIL). TLC plates were visualized by irradiation with UV light at λmax = 254 nm or using permanent staining with permanganate. Preparative column chromatography was carried out using Davisil LC 60A 70–200 MICRON silica gel. The term in vacuo refers to removal of solvents by rotary evaporation (40 °C, 950–20 mbar) followed by drying at high vacuum. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated.

**Anhydrous dibenzoyl peroxide (DBPO)** was prepared from the commercially available 70–75% hydrate:¹ To a solution of wet dibenzoyl peroxide (10 g, 75%, remainder water, Sigma-Aldrich) in 100 mL of CH₂Cl₂ was added anhydrous Na₂SO₄ (10 g) at 0 °C. The suspension was stirred for 30 min and then filtered through a sintered glass funnel. The solvent was removed in vacuo (water bath temperature <40 °C) and dried under high vacuum to obtain a free-flowing white solid which was stored at 4 °C under argon.

**Deactivated silica gel** was prepared from the commercially available Davisil LC 60A 70–200 MICRON silica gel: To a suspension of silica gel (300 g) in 400 mL of Et₂O, triethylamine (10.0 mL) was added. Then, the solvent was removed in vacuo and dried under high vacuum to obtain a free-flowing white solid which was stored on the bench.
2. Handling of azido compounds

Sodium azide (NaN₃, CAS: 26628-22-8) is acutely toxic (LD₅₀, mouse = 27 mg kg⁻¹) and should be handled only under adequate safety precautions. Sodium azide reacts with acids to form hydrazoic acid (HN₃) which is both toxic (LD₅₀, mouse = 22 mg kg⁻¹) and a spontaneously explosive gas. Excess NaN₃ adhered on any surface (flasks, paper, etc.) should be destroyed in a fume hood by soaking with acidified sodium nitrite or by oxidation with cerium(IV) ammonium nitrate. Organic azides are potentially explosive chemicals (PECs) that decompose with introduction of external energy (heat, light, shock and pressure). Azides with a (C + O) / N ratio of <1 are potentially explosive and should never be isolated. Azides with a (C + O) / N ratio between 1 and 3 can be isolated but should be stored as solutions (≤1 M) below room temperature with less than 5 grams of material. Azides with a (C + O) / N ratio of ≥3 are normally stable and can be isolated and stored in pure form. Any azide synthesized should be stored below room temperature and in the dark.
3. Synthesis of Substrates

<table>
<thead>
<tr>
<th>Indanone based ketoesters:</th>
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<th>Indanone based diketones:</th>
<th>Lactone based ketoesters:</th>
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<tbody>
<tr>
<td>X = OMe, R = H: 1a</td>
<td>X = Me, R = Ph: 1p</td>
<td>X = OMe, R = H: 11a</td>
<td>X = OMe: 11a</td>
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<tr>
<td>X = Oally, R = H: 1c</td>
<td>X = Ph, R = H: 1q</td>
<td>X = Oally: 11b</td>
<td>X = Oally: 11c</td>
</tr>
<tr>
<td>X = OBN, R = H: 1d</td>
<td>X = OIBu, R = 5-OMe: 1f</td>
<td>X = Oally, R = H: 1r</td>
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<tr>
<td>X = OAd, R = H: 1e</td>
<td>X = OIBu, R = 5-Br: 1k</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = OCum, R = H: 1f</td>
<td>X = OIBu, R = 6-OMe: 1m</td>
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All substrates are known compounds and prepared by following the literature procedures:

The indanone based tert-butyl β-ketoesters 1a<sup>1,4</sup>, 1g–n<sup>1,4</sup> were prepared starting from 1-indanone, CAS 83-33-0 or the respective commercially available 1-indanone derivatives using Boc-pyrole, CAS 5176-27-2 as transfer-reagent. The other indanone based β-ketoesters 1b<sup>7</sup>, 1c<sup>6</sup>, were prepared starting from 1-indanone and their respective commercially available dialkyl carbonates. The indanone based β-ketoesters 1d–f<sup>7</sup> as well as the β-ketoamide 1r<sup>3</sup> were prepared starting from methyl 1-indanone-2-carboxylate (1b). The indanone based 1,3-diketones 1p–q<sup>1,4</sup> were prepared according to a very similar procedure, but using imidazole based transfer reagents. These 1-acylimidazoles<sup>4,9</sup> which are prepared from imidazole, CAS 288-32-4 and the respective commercially available acyl chlorides for diketones or chloroformates for β-ketoesters. Since these 1-acylimidazole reagents are more reactive then Boc-pyrole, the reaction can be carried out at room temperature and is also a powerful alternative to prepare the β-ketoesters 1a–c. The lactone based β-ketoesters 11a–e<sup>10,11,12</sup> were prepared from γ-butyrolactone, CAS 96-48-0 and the respective commercially available dialkyl carbonates or acyl chlorides, whereas also in this case the use of the previously described 1-acylimidazole transfer reagents turned out to be beneficial in terms of yield and selectivity.
4. Oxidative α-azidation reactions

General procedure

\[
\text{O} \quad \text{EWG} \xrightarrow{\text{TBAI (20 mol%)}} \quad \text{O} \quad \text{N}_{3} \quad \text{EWG}
\]

Sodium azide (7.8 mg, 120 µmol, 1.2 equiv) and TBAI (7.4 mg, 20 µmol, 20 mol %) were suspended in a stirred solution (900–1000 rpm) of the respective substrate (100 µmol, 1.00 equiv) in 1.0 mL of DCE at rt. Then, a solution of anhydrous benzoyl peroxide (29.1 mg, 120 µmol, 1.2 equiv) in 1.0 mL of DCE was added to the suspension and stirred for 20 h.

The reaction solution was then diluted with 8 mL dichloromethane and extracted with 5 mL of sat. aq NaHCO₃. The aqueous phase was then extracted twice with 10 mL of DCM. The organic layer and the extracts were then filtered consecutively through a pad of anhydrous sodium sulfate and deactivated silica gel. The solvents were removed in vacuo. In most cases the products were already obtained in high purity (>95 %) after this work up. If necessary, further purification can be achieved by silica gel column chromatography.

Characterization of the α-azidation products

\[
\text{tBu} \quad \text{OtBu} \quad \text{N}_{3}
\]

**tert-Butyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2a):**

Obtained in 94% yield (25.7 mg, 94.0 µmol). *cf.:* 1.0 mmol scale, 94% yield (256.9 mg, 940.0 µmol). This compound was purified by column chromatography on silica gel (eluent: heptanes/EtOAc = 19:1). Yellowish-white solid; ¹H-NMR (300 MHz, CDCl₃, 298 K, δ / ppm): 7.82 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.48 - 7.39 (m, 2H), 3.64 (d, J = 17.2 Hz, 1H), 2.99 (d, J = 17.2 Hz, 1H), 1.45 (s, 9H); ¹³C-NMR (75 MHz, CDCl₃, 298 K, δ / ppm): 198.1, 167.4, 152.3, 136.4, 133.3, 128.4, 126.5, 125.6, 84.6, 70.6, 38.6, 28.0; IR (neat, FT-ATR, 298 K, ν / cm⁻¹): 2984, 2928, 2853, 2110, 1747, 1736, 1718, 1604, 1589, 1548, 1466, 1431, 1397, 1372, 1353, 1326, 1271, 1259, 1215, 1145, 1091, 1054, 1027, 961, 913, 871, 844, 834, 818, 804, 756, 729, 711, 688, 661, 623, 598, 561, 533, 459, 416; HRMS (ESI⁺-QqTOF, m/z): calculated for C₁₄H₁₅N₃O₃ [M+H⁺]: 274.1186, found: 274.1186; calculated for C₁₄H₁₅N₃O₃Na [M+Na⁺]: 291.1452, found: 291.1452 (major); calculated for C₁₄H₁₅N₃O₃K [M+K⁺]: 312.0745, found: 312.0745, TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.64; MP (uncorrected, δm / °C): 65.0 - 67.5.
Methyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2b): Obtained in 96% yield (22.2 mg, 96.0 µmol); white solid; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.83 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.55 - 7.41 (m, 2H), 3.81 (s, 3H), 3.68 (d, J = 7.7 Hz, 1H), 3.04 (d, J = 17.3 Hz, 1H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 197.5, 169.1, 152.2, 136.6, 133.1, 128.6, 126.6, 125.8, 70.3, 53.7, 38.6; IR (neat, FT-ATR, 298 K, v / cm$^{-1}$): 3475, 3409, 3187, 3082, 3040, 3010, 2956, 2922, 2851, 2449, 2428, 2326, 2278, 2178, 2135, 2099, 2081, 1744, 1710, 1601, 1587, 1479, 1467, 1440, 1427, 1344, 1326, 1305, 1278, 1218, 1186, 1161, 1122, 1098, 1050, 998, 965, 951, 903, 826, 806, 777, 739, 696, 626, 599, 550, 469, 437, 406; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{11}$H$_{10}$N$_3$O$_3$ [M+H]$^+$: 232.0717, found: 232.0717; calculated for C$_{11}$H$_{10}$N$_3$O$_3$ [M+Na]$^+$: 249.0982, found: 249.0982 (major), calculated for C$_{11}$H$_{10}$N$_3$O$_3$ [M+K]$^+$: 254.0536, found: 254.0539; calculated for C$_{11}$H$_{10}$N$_3$O$_3$K [M+K]$^+$: 270.0275, found: 270.0275; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.50; MP (uncorrected, δ$_m$ / °C): 54.7 - 56.5.

Allyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2c): Obtained in 98% yield (25.2 mg, 98.0 µmol); yellow solid; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.84 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 5.85 (ddt, J = 17.2, 10.5, 5.6 Hz, 1H), 5.29 - 5.19 (m, 2H), 4.70 (tt, J = 5.8, 1.4 Hz, 2H), 3.69 (d, J = 17.3 Hz, 1H), 3.05 (d, J = 17.3 Hz, 1H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 197.4, 168.3, 152.2, 136.6, 133.2, 130.9, 128.6, 126.6, 125.8, 119.3, 70.4, 67.2, 38.7; IR (neat, FT-ATR, 298 K, v / cm$^{-1}$): 3077, 2954, 2923, 2852, 2109, 1744, 1713, 1649, 1605, 1588, 1464, 1426, 1377, 1362, 1328, 1265, 1227, 1213, 1179, 1124, 1089, 1046, 994, 938, 908, 865, 826, 806, 749, 697, 617, 599, 550, 468, 423; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{15}$H$_{14}$N$_3$O$_3$ [M+H]$^+$: 258.0873, found: 258.0874; calculated for C$_{15}$H$_{14}$N$_3$O$_3$ [M+Na]$^+$: 275.1139, found: 275.1139 (major), calculated for C$_{15}$H$_{14}$N$_3$O$_3$K [M+K]$^+$: 296.0432, found: 296.0432; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.55; MP (uncorrected, δ$_m$ / °C): 80.1 - 84.7.
Benzyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2d): Obtained in 87% yield (26.7 mg, 87.0 μmol); yellow oil; 1H-NMR (500 MHz, CDCl3, 298 K, δ / ppm): 7.84 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.49 - 7.43 (m, 2H), 7.36 - 7.31 (m, 3H), 7.28 - 7.24 (m, 2H), 5.30 (d, J = 12.3 Hz, 1H), 5.20 (d, J = 12.3 Hz, 1H), 3.66 (d, J = 17.3 Hz, 1H), 3.04 (d, J = 17.3 Hz, 1H); 13C-NMR (126 MHz, CDCl3, 298 K, δ / ppm): 197.4, 168.5, 152.1, 136.6, 134.8, 133.2, 128.8, 128.6, 128.2, 126.6, 125.8, 70.4, 68.4, 38.6; IR (neat, FT-ATR, 298 K, v / cm⁻¹): 3474, 3407, 3343, 3194, 3096, 3066, 3032, 2981, 2930, 2848, 2681, 2638, 2607, 2485, 2442, 2359, 2317, 2110, 1954, 1920, 1742, 1710, 1607, 1583, 1491, 1465, 1437, 1392, 1370, 1339, 1292, 1260, 1243, 1212, 1168, 1151, 1132, 1099, 1050, 1026, 961, 924, 904, 892, 866, 839, 798, 749, 730, 700, 653, 617, 601, 561, 548, 497, 468, 441, 416; HRMS (ESI-QqTOF, m/z): calculated for C_{17}H_{14}N_{3}O_{3} [M+H]^+: 308.1030, found: 308.1032; calculated for C_{17}H_{12}N_{3}O_{3} [M+NH_{4}]^+: 325.1295, found: 325.1295 (major); calculated for C_{17}H_{12}N_{3}O_{3}Na [M+Na]^+: 330.0849, found: 330.0849; calculated for C_{17}H_{12}N_{3}O_{3}K [M+K]^+: 346.0588, found: 346.0588; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.55; MP (uncorrected, θ_m / °C): < r.t.

[Diagram]

Adamantyl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2e): Obtained in 77% yield (27.1 mg, 77.0 μmol); colourless oil; 1H-NMR (500 MHz, CDCl3, 298 K, δ / ppm): 7.81 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.55 - 7.38 (m, 2H), 3.64 (d, J = 17.1 Hz, 1H), 2.98 (d, J = 17.1 Hz, 1H), 2.15 (s, 3H), 2.07 (d, J = 3.0 Hz, 6H), 1.63 (t, J = 2.8 Hz, 6H); 13C-NMR (126 MHz, CDCl3, 298 K, δ / ppm): 198.2, 167.1, 152.4, 136.3, 133.4, 128.4, 126.4, 125.6, 84.7, 70.6, 41.2, 38.7, 36.1, 31.0; IR (neat, FT-ATR, 298 K, v / cm⁻¹): 2911, 2853, 2110, 1742, 1714, 1607, 1589, 1457, 1426, 1355, 1264, 1230, 1213, 1182, 1155, 1103, 1090, 1046, 963, 912, 862, 835, 806, 749, 722, 698, 636, 549, 469, 419; HRMS (ESI-QqTOF, m/z): calculated for C_{20}H_{22}N_{3}O_{3} [M+H]^+: 352.1656, found: 352.1653; calculated for C_{20}H_{22}N_{3}O_{3} [M+NH_{4}]^+: 369.1921, found: 369.1922 (major); calculated for C_{20}H_{22}N_{3}O_{3}Na [M+Na]^+: 374.1475, found: 374.1478; calculated for C_{20}H_{22}N_{3}O_{3}K [M+K]^+: 390.1214, found: 390.1213; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.65; MP (uncorrected, θ_m / °C): < r.t.
2-Phenylpropan-2-yl 2-azido-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2f): Obtained in 61% yield (20.5 mg, 61.0 µmol); yellow oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.85 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.52 - 7.43 (m, 1H), 7.33 - 7.27 (m, 1H), 7.27 - 7.20 (m, 2H), 3.67 (d, J = 17.2 Hz, 1H), 3.03 (d, J = 17.2 Hz, 1H), 1.81 (s, 3H), 1.77 (s, 3H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 197.9, 166.7, 152.2, 144.5, 136.4, 133.4, 128.5, 128.5, 127.6, 126.5, 125.6, 124.3, 85.5, 70.6, 38.6, 28.7, 28.1; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 2983, 2933, 2116, 1746, 1722, 1619, 1291, 1268, 1186, 1164, 1147, 1048, 1035, 992, 868, 833, 813, 774, 746, 717, 686, 580, 551, 500, 469, 463; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{19}$H$_{14}$N$_3$O$_3$[M+NH$_4$]$^+$: 353.1608, found: 353.1608 (major); calculated for C$_{19}$H$_{14}$N$_3$O$_3$Na [M+Na]$^+$: 358.1162, found: 358.1163; calculated for C$_{19}$H$_{14}$N$_3$O$_3$K [M+K]$^+$: 374.0901, found: 374.0901; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$/1): 0.57; MP (uncorrected, θ$_m$ / °C): < r.t.

tert-Butyl 2-azido-4-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2g): Obtained in 89% yield (25.9 mg, 89.0 µmol); yellow oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.63 (d, J = 7.5 Hz, 1H), 7.45 (td, J = 7.8, 4.5 Hz, 1H), 7.35 (t, J = 8.3 Hz, 1H), 3.64 (d, J = 17.5 Hz, 1H), 2.98 (d, J = 17.5 Hz, 1H), 1.46 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 197.1 (d, J = 2.8 Hz), 167.0, 159.7 (d, J = 251.6 Hz), 138.2 (d, J = 19.5 Hz), 136.0 (d, J = 5.0 Hz), 130.4 (d, J = 6.4 Hz), 122.5 (d, J = 20.0 Hz), 121.3 (d, J = 4.0 Hz), 85.0, 70.3, 34.6, 28.0; $^{19}$F-NMR (471 MHz, CDCl$_3$, 298 K, δ / ppm): -118.29 (dd, J = 8.6, 4.5 Hz, 1F); IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 2981, 2933, 2116, 1746, 1722, 1619, 1594, 1482, 1458, 1426, 1395, 1371, 1339, 1264, 1244, 1186, 1147, 1048, 1035, 992, 868, 833, 813, 774, 746, 717, 686, 580, 551, 500, 469, 463; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{14}$H$_{14}$F$_2$N$_3$O$_3$ [M+NH$_4$]$^+$: 309.1357, found: 309.1357 (major); calculated for C$_{14}$H$_{14}$F$_2$N$_3$O$_3$Na [M+Na]$^+$: 314.0911, found: 314.0911; calculated for C$_{14}$H$_{14}$F$_2$N$_3$O$_3$K [M+K]$^+$: 330.0651, found: 330.0651; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$/1): 0.67; MP (uncorrected, θ$_m$ / °C): < r.t.
**tert-Butyl 2-azido-4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2h):** Obtained in 91% yield (26.1 mg, 91.0 µmol); yellowish oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.65 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 3.52 (d, J = 17.2 Hz, 1H), 2.86 (d, J = 17.2 Hz, 1H), 2.33 (s, 3H), 1.47 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 198.3, 167.6, 151.3, 136.9, 135.8, 133.1, 128.6, 123.0, 84.6, 70.5, 37.6, 28.0, 17.9; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3079, 2980, 2932, 2870, 2444, 2361, 2297, 2112, 1742, 1715, 1606, 1592, 1479, 1458, 1421, 1395, 1370, 1336, 1264, 1250, 1201, 1148, 1050, 1027, 953, 895, 859, 839, 830, 813, 769, 746, 721, 691, 661, 626, 574, 550, 509, 461; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{15}$H$_{18}$N$_2$O$_3$ [M+H]$^+$: 288.1343, found: 288.1343; calculated for C$_{15}$H$_{18}$N$_2$O$_3$ [M+Na]$^+$: 310.1608, found: 305.1608 (major); calculated for C$_{15}$H$_{18}$N$_2$O$_3$Na [M+Na]$^+$: 310.1162, found: 310.1162; calculated for C$_{15}$H$_{18}$N$_2$O$_3$K [M+K]$^+$: 326.0901, found: 326.0901; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.67; MP (uncorrected, θ$_m$ / ℃): 65.0 - 67.5.

**tert-Butyl 2-azido-5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2i):** Obtained in 93% yield (27.1 mg, 93.0 µmol); yellowish solid; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.82 (dd, J = 8.3, 5.2 Hz, 1H), 7.19 - 7.04 (m, 2H), 3.62 (d, J = 17.4 Hz, 1H), 2.96 (d, J = 17.4 Hz, 1H), 1.45 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 196.2, 168.1 (d, J = 259.3 Hz), 167.1, 155.4 (d, J = 10.5 Hz), 129.7 (d, J = 1.8 Hz), 128.0 (d, J = 10.7 Hz), 116.9 (d, J = 23.8 Hz), 113.3 (d, J = 22.8 Hz), 84.8, 70.7, 38.5 (d, J = 2.2 Hz), 28.0; $^1$F-NMR (471 MHz, CDCl$_3$, 298 K, δ / ppm): -99.4 (dt, J = 8.5, 5.1 Hz, 1F); IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3432, 3102, 3073, 2988, 2925, 2853, 2675, 2426, 2289, 2242, 2107, 1920, 1796, 1734, 1720, 1614, 1593, 1483, 1455, 1432, 1398, 1371, 1335, 1298, 1253, 1192, 1148, 1086, 1046, 942, 906, 900, 867, 830, 802, 787, 759, 738, 691, 655, 629, 620, 551, 503, 476, 438; HRMS (ESI$^+$-QqTOF, m/z): calculated for C$_{15}$H$_{18}$FN$_2$O$_3$ [M+H]$^+$: 309.1357, found: 309.1357; calculated for C$_{15}$H$_{18}$FN$_2$O$_3$ [M+Na]$^+$: 309.1357, found: 309.1357 (major); calculated for C$_{15}$H$_{18}$FN$_2$O$_3$Na [M+Na]$^+$: 314.0911, found: 314.0911; calculated for C$_{15}$H$_{18}$FN$_2$O$_3$K [M+K]$^+$: 330.0651, found: 330.0651; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.67; MP (uncorrected, θ$_m$ / ℃): 62.0 - 65.0
**tert-Butyl 2-azido-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2j):** Obtained in 78% yield (24.0 mg, 78.0 μmol); yellow solid; \(^1\)H-NMR (500 MHz, CDCl\(_3\), 298 K, δ / ppm): 7.74 (d, J = 8.2 Hz, 1H), 7.46 (s, 1H), 7.42 (d, J = 8.2 Hz, 1H), 3.61 (d, J = 17.4 Hz, 1H), 2.96 (d, J = 17.4 Hz, 1H), 1.46 (s, 9H); \(^{13}\)C-NMR (126 MHz, CDCl\(_3\), 298 K, δ / ppm): 196.8, 167.1, 153.7, 143.1, 131.8, 129.3, 126.7, 126.6, 84.9, 70.6, 38.3, 28.0; IR (neat, FT-ATR, 298 K, v / cm\(^{-1}\)): 3093, 3065, 2989, 2928, 2854, 2359, 2326, 2293, 2164, 2116, 1918, 1742, 1716, 1599, 1578, 1456, 1423, 1396, 1370, 1323, 1297, 1279, 1261, 1245, 1210, 1146, 1069, 1048, 914, 868, 834, 797, 787, 755, 735, 722, 688, 612, 550, 524, 480, 451, 435; HRMS (ESI+-QqTOF, m/z): calculated for C\(_{14}\)H\(_{16}\)ClN\(_3\)O\(_3\) [M+H]^+: 308.0796, found: 308.0799; calculated for C\(_{14}\)H\(_{16}\)ClN\(_3\)O\(_3\) [M+NH\(_4\)]^+: 325.1062, found: 325.1061 (major); calculated for C\(_{14}\)H\(_{16}\)ClN\(_3\)O\(_3\)Na [M+Na]^+: 330.0616, found: 330.0616; calculated for C\(_{14}\)H\(_{16}\)ClN\(_3\)O\(_3\)K [M+K]^+: 346.0355, found: 346.0355; calculated for C\(_{14}\)H\(_{16}\)ClN\(_3\)O\(_3\)K [M+K]^+: 348.0331, found: 348.0331; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.67; MP (uncorrected, °C): 76.0 - 78.9.

**tert-Butyl 2-azido-5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2k):**\(^{13,15}\) Obtained in 96% yield (33.8 mg, 96.0 μmol); white solid; \(^1\)H-NMR (500 MHz, CDCl\(_3\), 298 K, δ / ppm): 7.67 (d, J = 8.2 Hz, 1H), 7.64 (s, 1H), 7.58 (d, J = 8.2 Hz, 1H), 3.61 (d, J = 17.4 Hz, 1H), 2.96 (d, J = 17.4 Hz, 1H), 1.46 (s, 9H); \(^{13}\)C-NMR (126 MHz, CDCl\(_3\), 298 K, δ / ppm): 197.0, 167.0, 153.8, 132.2, 132.1, 132.0, 129.8, 126.7, 84.9, 70.5, 38.2, 28.0; IR (neat, FT-ATR, 298 K, v / cm\(^{-1}\)): 3089, 3002, 2981, 2926, 2852, 2493, 2308, 2162, 2111, 1816, 1736, 1718, 1592, 1468, 1455, 1418, 1396, 1371, 1322, 1299, 1280, 1244, 1212, 1196, 1177, 1143, 1131, 1101, 1058, 1046, 1036, 913, 868, 847, 834, 792, 749, 730, 713, 687, 615, 596, 550, 517, 477, 460, 439, 424, 406; HRMS (ESI+-QqTOF, m/z): calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\) [M+H]^+: 352.0291, found: 352.0291; calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\) [M+H]^+: 354.0272, found: 354.0272; calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\) [M+NH\(_4\)]^+: 369.0557, found: 369.0557; calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\) [M+NH\(_4\)]^+: 371.0538, found: 369.0538 (major); calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\)K [M+K]^+: 389.9850, found: 389.9850; calculated for C\(_{14}\)H\(_{16}\)BrN\(_3\)O\(_3\)K [M+K]^+: 391.9831, found: 391.9831; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.68; MP (uncorrected, °C): 91.3 - 93.6.
**tert-Butyl 2-azido-5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2i)**: Obtained in 90% yield (27.3 mg, 90.0 µmol); yellow oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.73 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 8.9 Hz, 1H), 6.86 (s, 1H), 3.89 (s, 3H), 3.57 (d, J = 17.2 Hz, 1H), 2.91 (d, J = 17.1 Hz, 1H), 1.45 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 195.9, 167.7, 166.6, 155.5, 127.3, 126.3, 116.5, 109.6, 84.4, 70.9, 55.9, 38.6, 28.0; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3476, 3406, 3191, 3096, 3066, 3031, 2981, 2931, 2845, 2680, 2633, 2606, 2485, 2441, 2361, 2316, 2185, 2111, 2059, 1920, 1742, 1710, 1607, 1582, 1491, 1465, 1437, 1392, 1370, 1339, 1293, 1259, 1244, 1208, 1144, 1132, 1098, 1052, 925, 904, 891, 866, 839, 797, 756, 729, 703, 653, 617, 601, 561, 547, 478, 462, 441; HRMS (ESI-QqTOF, m/z): calculated for C$_{18}$H$_{19}$N$_3$O$_4$ [M+H]$^+$: 304.1292, found: 304.1292; calculated for C$_{18}$H$_{20}$N$_4$O$_4$ [M+NH$_4$]$^+$: 321.1557, found: 321.1557 (major); calculated for C$_{18}$H$_{21}$N$_3$O$_4$Na [M+Na]$^+$: 326.1111, found: 326.1111; calculated for C$_{18}$H$_{19}$N$_3$O$_4$K [M+K]$^+$: 342.0851, found: 342.0852; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.50; MP (uncorrected, δ$_m$ / °C): < r.t.

**tert-Butyl 2-azido-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2m)**: Obtained in 96% yield (23.7 mg, 78.0 µmol); yellow oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.33 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 8.4, 2.6 Hz, 1H), 7.21 (d, J = 2.6 Hz, 1H), 3.84 (s, 3H), 3.54 (d, J = 16.9 Hz, 1H), 2.90 (d, J = 16.8 Hz, 1H), 1.44 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 198.0, 167.4, 160.0, 145.3, 134.5, 127.1, 125.8, 106.4, 84.5, 71.3, 55.8, 38.0, 27.9; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3403, 3299, 3067, 2993, 2972, 2852, 2727, 2680, 2622, 2576, 2445, 2422, 2359, 2272, 2110, 2022, 1912, 1735, 1711, 1613, 1585, 1547, 1492, 1460, 1432, 1395, 1370, 1341, 1304, 1277, 1234, 1211, 1190, 1157, 1128, 1092, 1056, 1033, 1022, 959, 895, 876, 841, 824, 801, 787, 772, 739, 690, 634, 589, 555, 539, 524, 480, 463, 450, 435, 423; HRMS (ESI-QqTOF, m/z): calculated for C$_{18}$H$_{19}$N$_3$O$_4$ [M+H]$^+$: 304.1292, found: 304.1291; calculated for C$_{18}$H$_{20}$N$_4$O$_4$ [M+NH$_4$]$^+$: 321.1557, found: 321.1557 (major); calculated for C$_{18}$H$_{21}$N$_3$O$_4$Na [M+Na]$^+$: 326.1111, found: 326.1111; calculated for C$_{18}$H$_{19}$N$_3$O$_4$K [M+K]$^+$: 342.0851, found: 342.0851; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.60; MP (uncorrected, δ$_m$ / °C): < r.t.
**tert-Butyl 2-azido-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (2n):** Obtained in 78% yield (27.6 mg, 96.0 μmol); yellow oil; $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm): 7.59 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 3.57 (d, J = 17.1 Hz, 1H), 2.93 (d, J = 17.1 Hz, 1H), 2.41 (s, 3H), 1.44 (s, 9H); $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm): 198.1, 167.5, 149.8, 138.5, 137.6, 133.4, 126.1, 125.4, 84.5, 70.9, 38.3, 27.9, 21.2; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 2980, 2932, 2870, 2358, 2325, 2286, 2110, 1742, 1715, 1617, 1584, 1494, 1457, 1424, 1395, 1276, 1241, 1202, 1147, 1102, 1047, 1102, 1046, 1036, 950, 905, 889, 839, 825, 798, 789, 748, 731, 695, 626, 584, 551, 503, 476, 453, 439, 417; HRMS (ESI-QqTOF, m/z): calculated for C$_{15}$H$_8$N$_3$O$_3$ [M+H]+: 288.1343, found: 288.1343; calculated for C$_{15}$H$_8$N$_3$O$_3$ [M+NH$_4$]+: 305.1608, found: 305.1608 (major); calculated for C$_{15}$H$_8$N$_3$O$_3$Na [M+Na]+: 310.1162, found: 310.1163; calculated for C$_{15}$H$_8$N$_3$O$_3$K [M+K]+: 326.0901, found: 326.0907; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.67; MP (uncorrected, δ$_m$ / °C): < r.t.

![Image of 2-Acetyl-2-azido-2,3-dihydro-1H-inden-1-one (5a)]

**2-Acetyl-2-azido-2,3-dihydro-1H-inden-1-one (5a):** Obtained in 61% yield (13.1 mg, 61.0 μmol); yellow oil; $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, δ / ppm): 7.82 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 3.71 (d, J = 17.4 Hz, 1H), 3.08 (d, J = 17.4 Hz, 1H), 2.29 (s, 3H); $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, δ / ppm): 200.8, 197.8, 152.2, 136.8, 133.5, 128.8, 126.7, 125.7, 77.8, 37.1, 26.1; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3412, 3077, 2954, 2926, 2854, 2362, 2342, 2324, 2100, 1726, 1708, 1606, 1588, 1465, 1424, 1356, 1334, 1301, 1256, 1211, 1188, 1154, 1090, 1053, 1025, 982, 959, 901, 877, 813, 778, 739, 704, 671, 644, 583, 564, 549, 524, 502, 468, 426; HRMS (ESI-QqTOF, m/z): calculated for C$_{11}$H$_6$N$_3$O$_2$ [M+H]+: 216.0768, found: 216.0770; calculated for C$_{11}$H$_6$N$_3$O$_2$ [M+NH$_4$]+: 233.1033, found: 233.1033 (major); calculated for C$_{11}$H$_6$N$_3$O$_2$ [M+HCOO]: 260.0677, found: 260.0684; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, R$_f$ / 1): 0.43; MP (uncorrected, δ$_m$ / °C): < r.t.
2-Azido-2-benzoyl-2,3-dihydro-1H-inden-1-one (5b): Obtained in 83% yield (23.0 mg, 83.0 µmol); yellow oil; \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, \(\delta / ppm\)): 7.92 (d, \(J = 7.7\) Hz, 1H), 7.85 (d, \(J = 8.2\) Hz, 2H), 7.72 (d, \(J = 7.4\) Hz, 1H), 7.57 (t, \(J = 7.4\) Hz, 1H), 7.52 (t, \(J = 7.6\) Hz, 1H), 7.49 (d, \(J = 7.6\) Hz, 1H), 7.41 (t, \(J = 7.8\) Hz, 2H), 3.77 (d, \(J = 17.5\) Hz, 1H), 3.25 (d, \(J = 17.5\) Hz, 1H); \(^{13}\)C-NMR (176 MHz, CDCl\(_3\), 298 K, \(\delta / ppm\)): 197.9, 194.5, 151.2, 136.6, 134.0, 133.9, 133.5, 129.2, 128.9, 128.9, 126.9, 126.0, 76.3, 39.2; IR (neat, FT-ATR, 298 K, \(\tilde{\nu} / \text{cm}^{-1}\)): 3068, 2925, 2853, 2449, 2280, 2099, 1786, 1763, 1716, 1681, 1598, 1465, 1448, 1429, 1303, 1257, 1234, 1213, 1155, 1089, 1032, 994, 961, 946, 899, 871, 846, 799, 777, 741, 701, 688, 671, 610, 550, 468, 443, 419; HRMS (ESI-QqTOF, \(m/z\)): calculated for C\(_{16}\)H\(_{12}\)N\(_2\)O\(_2\) [M+H]: 278.0924, found: 278.0924; calculated for C\(_{16}\)H\(_{15}\)N\(_2\)O\(_2\) [M+NH\(_4\)]: 295.1190, found: 295.1190 (major); calculated for C\(_{16}\)H\(_{11}\)N\(_2\)O\(_2\)Na [M+Na]: 300.0743, found: 300.0743; calculated for C\(_{16}\)H\(_{11}\)N\(_2\)O\(_2\)K [M+K]: 316.0483, found: 316.0483; calculated for C\(_{16}\)H\(_{11}\)N\(_3\)O\(_3\) [M+HCOO]: 322.0833, found: 322.0833; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, \(R_t / 1\)): 0.48; MP (uncorrected, \(\vartheta_m / ^\circ\text{C}\)): < r.t.

2-Azido-2-(morpholin-4-ylcarbonyl)-2,3-dihydro-1H-inden-1-one (6): Obtained in 78% yield (22.3 mg, 78.0 µmol); yellow solid; \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, \(\delta / ppm\)): 7.84 (d, \(J = 7.4\) Hz, 1H), 7.67 (t, \(J = 7.5\) Hz, 1H), 7.48 - 7.43 (m, 2H), 3.81 - 3.54 (m, 9H), 3.17 (d, \(J = 16.9\) Hz, 1H); \(^{13}\)C-NMR (176 MHz, CDCl\(_3\), 298 K, \(\delta / ppm\)): 197.5, 165.8, 150.3, 136.5, 133.6, 129.2, 128.8, 126.6, 125.7, 72.4, 66.9, 38.6; IR (neat, FT-ATR, 298 K, \(\tilde{\nu} / \text{cm}^{-1}\)): 2964, 2922, 2856, 2360, 2249, 2099, 1718, 1638, 1607, 1558, 1457, 1425, 1361, 1330, 1301, 1270, 1255, 1233, 1213, 1184, 1155, 1113, 1090, 1065, 1010, 942, 914, 873, 852, 836, 808, 795, 759, 732, 703, 674, 646, 626, 582, 550, 534, 478, 454, 418; HRMS (ESI\(^+\)-QqTOF, \(m/z\)): calculated for C\(_{16}\)H\(_{15}\)N\(_2\)O\(_3\) [M+H]: 287.1139, found: 287.1139 (major); calculated for C\(_{16}\)H\(_{15}\)N\(_2\)O\(_3\)Na [M+Na]: 309.0958, found: 309.0958; calculated for C\(_{16}\)H\(_{15}\)N\(_3\)O\(_3\)K [M+K]: 325.0697, found: 325.0694; TLC (silica gel K60, 200 µm, F254, heptanes/IPA = 7:3, 298 K, \(R_t / 1\)): 0.36; MP (uncorrected, \(\vartheta_m / ^\circ\text{C}\)): 125.0 - 127.0.
Methyl 3-azido-2-oxotetrahydrofuran-3-carboxylate (7a): Obtained in 55% yield (10.2 mg, 55.0 µmol); yellowish oil; $^1$H-NMR (700 MHz, CDCl₃, 298 K, δ / ppm): 4.45 (2 × ddd, J = 8.9, 7.7, 6.1 Hz, 2H), 3.91 (s, 3H), 2.77 (ddd, J = 13.3, 7.6, 5.5 Hz, 1H), 2.29 (ddd, J = 13.6, 7.9, 6.6 Hz, 1H); $^{13}$C-NMR (176 MHz, CDCl₃, 298 K, δ / ppm): 170.7, 167.4, 66.6, 66.5, 54.2, 33.6; IR (neat, FT-ATR, 298 K, $\bar{\nu}$/cm⁻¹): 2960, 2925, 2852, 2360, 2114, 1775, 1748, 1669, 1600, 1559, 1483, 1451, 1380, 1245, 1216, 1171, 1118, 1019, 996, 955, 918, 841, 803, 791, 745, 705, 687, 634, 615, 601, 552, 469, 455, 434; HRMS (ESI-QqTOF, m/z): calculated for C₆H₈N₃O₄ [M+H]⁺: 186.0509, found: 186.0508; calculated for C₆H₈N₃O₄ [M+NH₄]⁺: 203.0775, found: 203.0776 (major); TLC (silica gel K60, 200 µm, F254, heptanes/IPA = 7:3, 298 K, Rt / 1): 0.34; MP (uncorrected, $\delta$ m / °C): < r.t.

Allyl 3-azido-2-oxotetrahydrofuran-3-carboxylate (7b): Obtained in 74% yield (15.6 mg, 74.0 µmol); yellowish oil; $^1$H-NMR (700 MHz, CDCl₃, 298 K, δ / ppm): 5.93 (ddt, J = 16.6, 10.3, 5.8 Hz, 1H), 5.39 (dd, J = 17.1, 1.4 Hz, 1H), 5.33 (dd, J = 10.4, 1.3 Hz, 1H), 4.85 - 4.74 (m, 2H), 4.53 - 4.40 (m, 2H), 2.78 (ddd, J = 13.3, 7.6, 5.4 Hz, 1H), 2.30 (ddd, J = 13.5, 8.0, 6.6 Hz, 1H); $^{13}$C-NMR (176 MHz, CDCl₃, 298 K, δ / ppm): 170.7, 166.6, 130.5, 120.3, 67.9, 66.6, 66.5, 33.6; IR (neat, FT-ATR, 298 K, $\bar{\nu}$/cm⁻¹): 3090, 2990, 2956, 2928, 2862, 2115, 1775, 1747, 1650, 1483, 1447, 1424, 1379, 1316, 1270, 1241, 1211, 1171, 1117, 1020, 975, 937, 843, 790, 740, 714, 688, 661, 640, 597, 551, 535; HRMS (ESI-QqTOF, m/z): calculated for C₈H₁₃N₃O₄ [M+H]⁺: 212.0666, found: 212.0666; calculated for C₈H₁₃N₃O₄ [M+NH₄]⁺: 229.0931, found: 229.0931 (major); calculated for C₈H₁₃N₃O₄Na [M+Na]⁺: 234.0485, found: 234.0488; calculated for C₈H₁₃N₃O₄K [M+K]⁺: 250.0225, found: 250.0223; TLC (silica gel K60, 200 µm, F254, heptanes/IPA = 7:3, 298 K, Rt / 1): 0.57; MP (uncorrected, $\delta$ m / °C): < r.t.
3-Azido-3-benzoxydihydrofuran-2(3H)-one (7c): Obtained in 69% yield (16.0 mg, 69.0 µmol); yellowish oil;  
$^1$H-NMR (700 MHz, CDCl$_3$, 298 K, δ / ppm): 5.93 (ddt, J = 16.6, 10.3, 5.8 Hz, 1H), 5.39 (dd, J = 17.1, 1.4 Hz, 1H), 5.33 (dd, J = 10.4, 1.3 Hz, 1H), 4.85 - 4.74 (m, 2H), 4.53 - 4.40 (m, 2H), 2.78 (ddd, J = 13.3, 7.6, 5.4 Hz, 1H), 2.30 (ddd, J = 13.5, 8.0, 6.6 Hz, 1H); $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, δ / ppm): 170.7, 166.6, 130.5, 120.3, 67.9, 66.6, 66.5, 33.6; IR (neat, FT-ATR, 298 K, ν / cm$^{-1}$): 3067, 2983, 2923, 2858, 2355, 2107, 1771, 1673, 1596, 1579, 1482, 1449, 1377, 1308, 1272, 1243, 1214, 1176, 1102, 1021, 1001, 953, 886, 844, 796, 760, 718, 686, 650, 616, 579, 540, 499, 418; HRMS (ESI$^-$-QqTOF, m/z): calculated for C$_{11}$H$_{10}$N$_3$O$_3$ [M+H]$^+$: 232.0717, found: 232.0717; calculated for C$_{11}$H$_{13}$N$_4$O$_3$ [M+NH$_4$]$^+$: 249.0982, found: 287.0982 (major); calculated for C$_{11}$H$_{9}$N$_3$O$_3$Na [M+Na]$^+$: 254.0536, found: 254.0536; calculated for C$_{11}$H$_{9}$N$_3$O$_3$K [M+K]$^+$: 270.0275, found: 270.0276; TLC (silica gel K60, 200 µm, F254, heptanes/IPA = 7:3, 298 K, R$_f$ / 1): 0.51; MP (uncorrected, θ$_m$ / °C): < r.t.
5. Oxidative α-nitration reactions

General procedure

Sodium azide (7.9 mg, 120 µmol, 1.2 equiv) and TBAI (7.5 mg, 20 µmol, 20 mol %) were suspended in a stirred solution (900–1000 rpm) of the respective substrate (100 µmol, 1.00 equiv) in 1.0 mL of DCE at rt. Then, a solution of anhydrous benzoyl peroxide (29.1 mg, 120 µmol, 1.2 equiv) in 1.0 mL of DCE was added to the suspension and stirred for 20 h.

The reaction solution was then diluted with 8 mL dichloromethane and extracted with 5 mL of sat. aq NaHCO₃. The aqueous phase was then extracted twice with 10 mL of DCM. The organic layer and the extracts were then filtered consecutively through a pad of anhydrous sodium sulfate and deactivated silica gel. The solvents were removed in vacuo. In most cases the products were already obtained in high purity (>95 %) after this work up. If necessary, further purification can be achieved by silica gel column chromatography.

Characterization of the α-nitration products

**tert-Butyl 2-nitro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (10a):** Obtained in 84% yield (23.3 mg, 94.0 µmol); white solid; ¹H-NMR (700 MHz, CDCl₃, 298 K, δ / ppm): 7.86 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 4.11 (d, J = 17.9 Hz, 1H), 3.99 (d, J = 17.9 Hz, 1H), 1.49 (s, 9H); ¹³C-NMR (126 MHz, CDCl₃, 298 K, δ / ppm): 188.4, 162.0, 150.1, 137.0, 132.9, 129.1, 126.5, 126.2, 96.7, 86.1, 37.5, 27.8; IR (neat, FT-ATR, 298 K, ν / cm⁻¹): 2984, 2930, 2878, 2854, 1748, 1719, 1656, 1604, 1589, 1548, 1465, 1431, 1396, 1371, 1353, 1325, 1272, 1260, 1215, 1145, 1091, 1056, 1026, 961, 912, 871, 844, 834, 818, 803, 755, 730, 711, 688, 661, 625, 598, 561, 533, 459, 414; HRMS (ESI⁺-QqTOF, m/z): calculated for C₁₄H₁₉N₂O₅ [M+H]⁺: 278.1023, found: 278.1024; calculated for C₁₄H₁₉N₂O₅ [M+NH₄]⁺: 295.1288, found: 295.1288 (major); calculated for C₁₄H₁₉N₂O₅ Na [M+Na]⁺: 300.0842, found: 300.0842; calculated for C₁₄H₁₉N₂O₅K [M+K]⁺: 316.0582, found: 316.0582; TLC (silica gel K60, 200 µm, F254, heptanes/EtOAc = 7:3, 298 K, Rf / 1): 0.47; MP (uncorrected, ϑm / °C): 75.9 – 78.4.
Methyl 2-nitro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (10b): Obtained in 86% yield (19.9 mg, 96.0 μmol); colourless oil; \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, δ / ppm): 7.87 (d, \(J = 7.8\) Hz, 1H), 7.73 (t, \(J = 7.5\) Hz, 1H), 7.54 (d, \(J = 7.8\) Hz, 1H), 7.50 (t, \(J = 7.6\) Hz, 1H), 4.15 (d, \(J = 18.0\) Hz, 1H), 4.05 (d, \(J = 18.0\) Hz, 1H), 3.89 (s, 3H); \(^{13}\)C-NMR (126 MHz, CDCl\(_3\), 298 K, δ / ppm): 188.0, 163.8, 150.0, 137.3, 132.7, 129.3, 126.5, 126.4, 96.1, 54.5, 37.5; IR (neat, FT-ATR, 298 K, \(\tilde{\nu} / \text{cm}^{-1}\)): 2959, 1755, 1729, 1605, 1552, 1434, 1264, 1215, 1202, 1181, 1091, 1023, 949, 903, 894, 798, 761, 689, 663, 632, 467; HRMS (ESI\(^{−}\)-QqTOF, \(m/z\)): calculated for C\(_{10}\)H\(_9\)NO\(_3\) [M+H]\(^{+}\): 236.0553, found: 236.0553; calculated for C\(_{10}\)H\(_9\)NO\(_3\)Na [M+Na]\(^{+}\): 253.0820, found: 253.0820 (major); calculated for C\(_{10}\)H\(_9\)NO\(_3\)K [M+K]\(^{+}\): 274.0112, found: 274.0112; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, \(R_{f}/1\)): 0.29; MP (uncorrected, \(\theta_m / ^{\circ}\mathrm{C}\)): < r.t.

Allyl 2-nitro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (10c): Obtained in 75% yield (19.3 mg, 75.0 μmol); yellowish oil; \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, δ / ppm): 7.88 (d, \(J = 7.7\) Hz, 1H), 7.73 (t, \(J = 7.5\) Hz, 1H), 7.54 (d, \(J = 7.7\) Hz, 1H), 7.50 (t, \(J = 7.5\) Hz, 1H), 5.89 (ddt, \(J = 16.5, 11.0, 5.7\) Hz, 1H), 5.38 - 5.27 (m, 2H), 4.81 - 4.74 (m, 2H), 4.16 (d, \(J = 18.0\) Hz, 1H), 4.05 (d, \(J = 18.0\) Hz, 1H); \(^{13}\)C-NMR (126 MHz, CDCl\(_3\), 298 K, δ / ppm): 188.0, 163.0, 150.0, 137.2, 132.7, 130.3, 129.3, 126.5, 126.5, 120.1, 96.1, 68.2, 37.5; IR (neat, FT-ATR, 298 K, \(\tilde{\nu} / \text{cm}^{-1}\)): 3063, 2940, 2453, 2324, 1920, 1782, 1757, 1731, 1656, 1599, 1557, 1466, 1450, 1423, 1350, 1296, 1275, 1255, 1217, 1178, 1134, 1093, 1070, 1034, 1019, 995, 941, 926, 902, 840, 809, 794, 755, 692, 616, 601, 555, 500, 467, 437, 416; HRMS (ESI\(^{−}\)-QqTOF, \(m/z\)): calculated for C\(_{11}\)H\(_{10}\)NO\(_3\) [M+H]\(^{+}\): 262.0710, found: 262.0710; calculated for C\(_{11}\)H\(_{10}\)NO\(_3\)Na [M+Na]\(^{+}\): 279.0975, found: 279.0975 (major); calculated for C\(_{11}\)H\(_{10}\)NO\(_3\)K [M+K]\(^{+}\): 300.0269, found: 300.0272; TLC (silica gel K60, 200 μm, F254, heptanes/EtOAc = 7:3, 298 K, \(R_{f}/1\)): 0.62; MP (uncorrected, \(\theta_m / ^{\circ}\mathrm{C}\)): < r.t.
6. NMR spectra

2a, $^1$H-NMR (300 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

![1H-NMR spectrum of 2a](image)

2a, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

![13C-NMR spectrum of 2a](image)
2b, $^1$H-NMR (500 MHz, CDCl₃, 298 K, $\delta$ / ppm):

2b, $^{13}$C-NMR (126 MHz, CDCl₃, 298 K, $\delta$ / ppm):
2c, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![H-NMR spectrum]

2c, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![C-NMR spectrum]
2d, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

2d, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
2e, \(^1\)H-NMR (500 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):

![H-NMR spectrum](image)

2e, \(^{13}\)C-NMR (126 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):
2f, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

2f, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
$2g$, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

$2g$, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
$2g$, $^{19}F$-NMR (471 MHz, CDCl$_3$, 298 K, δ / ppm):
2h, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![NMR spectrum](image)

2h, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![NMR spectrum](image)
$2i$, $^1H$-NMR (500 MHz, CDCl$_3$, 298 K, $\delta / \text{ppm}$):

![$^1H$-NMR spectrum](image)

$2i$, $^{13}C$-NMR (126 MHz, CDCl$_3$, 298 K, $\delta / \text{ppm}$):

![$^{13}C$-NMR spectrum](image)
2i, $^{19}$F-NMR (471 MHz, CDCl$_3$, 298 K, $\delta$/ppm):
2j, ^1H-NMR (500 MHz, CDCl₃, 298 K, δ / ppm):

2j, ^13C-NMR (126 MHz, CDCl₃, 298 K, δ / ppm):
2k, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

2k, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
21, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, δ / ppm):

![H-NMR spectrum](image)

21, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, δ / ppm):

![C-NMR spectrum](image)
2m, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

![NMR spectrum of 2m]

2m, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

![NMR spectrum of 2m]
2n, $^1$H-NMR (500 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![NMR Spectrum of 2n](image1)

2n, $^{13}$C-NMR (126 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

![NMR Spectrum of 2n](image2)
5a, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$/ppm):

5a, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$/ppm):
5b, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

5b, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
6, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

6, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
7a, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

7a, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
7b, \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):

![NMR spectrum of 7b, \(^1\)H-NMR](image)

7b, \(^{13}\)C-NMR (176 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):

![NMR spectrum of 7b, \(^{13}\)C-NMR](image)
7c, \(^1\)H-NMR (700 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):

![\(^1\)H-NMR Spectrum](image)

7c, \(^{13}\)C-NMR (176 MHz, CDCl\(_3\), 298 K, \(\delta / \text{ppm}\)):

![\(^{13}\)C-NMR Spectrum](image)
10a, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, δ / ppm):

10a, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, δ / ppm):
10b, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

10b, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
10c, $^1$H-NMR (700 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):

10c, $^{13}$C-NMR (176 MHz, CDCl$_3$, 298 K, $\delta$ / ppm):
7. Infrared spectra

2a, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

2b, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):
2c, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![Graph of IR spectrum for 2c, showing various wavenumbers and bands.]

2d, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![Graph of IR spectrum for 2d, showing various wavenumbers and bands.]

S44
2e, IR (neat, FT-ATR, 298 K, $\bar{\nu}$ / cm$^{-1}$): 

![IR spectrum of 2e](image)

2f, IR (neat, FT-ATR, 298 K, $\bar{\nu}$ / cm$^{-1}$): 

![IR spectrum of 2f](image)
2g, IR (neat, FT-ATR, 298 K, $\bar{\nu}$ / cm$^{-1}$):

![IR Spectrum of 2g](image1)

2h, IR (neat, FT-ATR, 298 K, $\bar{\nu}$ / cm$^{-1}$):

![IR Spectrum of 2h](image2)
**2i, IR** (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR Spectrum of Compound 2i]

**2j, IR** (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR Spectrum of Compound 2j]
2k, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR spectrum of 2k](image)

2l, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR spectrum of 2l](image)
2m, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR Spectrum of 2m](image)

2n, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR Spectrum of 2n](image)
5a, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR spectrum of 5a](image)

5b, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

![IR spectrum of 5b](image)
6, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):

7a, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$ / cm$^{-1}$):
7b, IR (neat, FT-ATR, 298 K, $\tilde{v}$ / cm⁻¹):

![Graph showing IR spectra for 7b](image)

7c, IR (neat, FT-ATR, 298 K, $\tilde{v}$ / cm⁻¹):

![Graph showing IR spectra for 7c](image)
10a, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$/ cm$^{-1}$):

10b, IR (neat, FT-ATR, 298 K, $\tilde{\nu}$/ cm$^{-1}$):
10c, IR (neat, FT-ATR, 298 K, $\bar{\nu}$ / cm$^{-1}$):
8. High-resolution mass spectra
(major only)

2a, HRMS (ESI⁺-QqTOF, m/z):
calculated for C₁₄H₁₉N₄O₃ [M+NH₄]⁺: 291.1452, found: 291.1452 (0.00 ppm)

2b, HRMS (ESI⁺-QqTOF, m/z):
calculated for C₁₁H₁₃N₄O₃ [M+NH₄]⁺: 249.0982, found: 249.0982 (0.00 ppm)
2c, HRMS (ESI'-QqTOF, m/z):
calculated for C_{13}H_{15}N_{4}O_{3}Na [M+NH_{4}]^{+}: 275.1139, found: 275.1139 (0.00 ppm)

2d, HRMS (ESI'-QqTOF, m/z):
calculated for C_{17}H_{17}N_{4}O_{3} [M+NH_{4}]^{+}: 325.1295, found: 325.1295 (0.00 ppm)
2e, IR HRMS (ESI^+–QqTOF, m/z):
calculated for C_{20}H_{26}N_{4}O_{3} [M+NH_{4}]^+: 369.1921, found: 369.1922 (0.27 ppm)

2f, HRMS (ESI^+–QqTOF, m/z):
calculated for C_{19}H_{21}N_{4}O_{3} [M+NH_{4}]^+: 353.1608, found: 353.1608 (0.00 ppm)
2g, HRMS (ESI'-QqTOF, m/z):
calculated for C₁₄H₁₈F₃N₄O₃ [M+NH₄]⁺: 309.1357, found: 309.1357 (0.00 ppm)

2h, HRMS (ESI'-QqTOF, m/z):
calculated for C₁₅H₂₁N₄O₃ [M+NH₄]⁺: 305.1608, found: 305.1608 (0.00 ppm)
2i, HRMS (ESI⁺-QqTOF, m/z):

Calculated for C\textsubscript{14}H\textsubscript{18}F\textsubscript{2}N\textsubscript{4}O\textsubscript{3} [M+NH\textsubscript{4}]⁺: 309.1357, found: 309.1357 (0.00 ppm)

2j, HRMS (ESI⁺-QqTOF, m/z):

Calculated for C\textsubscript{14}H\textsubscript{18}Cl\textsubscript{35}N\textsubscript{4}O\textsubscript{3} [M+NH\textsubscript{4}]⁺: 325.1062, found: 325.1061 (-0.31 ppm)
2k, HRMS (ESI\(^+-\)/QqTOF, \(m/z\)):

calculated for C\(_{14}\)H\(_{18}\)\(^{81}\)BrN\(_{4}\)O\(_{3}\) [M+NH\(_{4}\)]\(^+\): 371.0538, found: 369.0538 (0.00 ppm)

2l, HRMS (ESI\(^+-\)/QqTOF, \(m/z\)):

calculated for C\(_{15}\)H\(_{21}\)N\(_{4}\)O\(_{4}\) [M+NH\(_{4}\)]\(^+\): 321.1557, found: 321.1557 (0.00 ppm)
2m, HRMS (ESI⁺-QqTOF, m/z):
calculated for C₁₅H₂₁N₄O₄ [M+NH₄]⁺: 321.1557, found: 321.1557 (0.00 ppm)

2n, HRMS (ESI⁺-QqTOF, m/z):
calculated for C₁₅H₂₁N₄O₃ [M+NH₄]⁺: 305.1608, found: 305.1608 (0.00 ppm)
5a, HRMS (ESI+-QqTOF, m/z):
calculated for C_{11}H_{13}N_{4}O_{2} [M+NH\textsubscript{4}]\textsuperscript{+}: 233.1033, found: 233.1033 (0.00 ppm)

5b, HRMS (ESI+-QqTOF, m/z):
calculated for C_{16}H_{15}N_{4}O_{2} [M+NH\textsubscript{4}]\textsuperscript{+}: 295.1190, found: 295.1190 (0.00 ppm)
6, HRMS (ESI\(^+\)-QqTOF, m/z):
calculated for C\(_{14}\)H\(_{15}\)N\(_4\)O\(_3\) [M+H]\(^+\): 287.1139, found: 287.1139 (0.00 ppm)

7a, HRMS (ESI\(^+\)-QqTOF, m/z):
calculated for C\(_{6}\)H\(_8\)N\(_3\)O\(_4\) [M+NH\(_4\)]\(^+\): 203.0775, found: 203.0776 (0.49 ppm)
7b, HRMS (ESI\textsuperscript{-}-QqTOF, \textit{m/z}): 

calculated for C\textsubscript{8}H\textsubscript{13}N\textsubscript{4}O\textsubscript{4} [M+NH\textsubscript{4}]\textsuperscript{+}: 229.0931, found: 229.0931 (0.00 ppm)

7c, HRMS (ESI\textsuperscript{-}-QqTOF, \textit{m/z}): 

calculated for C\textsubscript{11}H\textsubscript{13}N\textsubscript{4}O\textsubscript{3} [M+NH\textsubscript{4}]\textsuperscript{+}: 249.0982, found: 287.0982 (0.00 ppm)
10a, HRMS (ESI\textsuperscript{+}-QqTOF, m/z):
calculated for C\textsubscript{14}H\textsubscript{19}N\textsubscript{2}O\textsubscript{5} [M+NH\textsubscript{4}]\textsuperscript{+}: 295.1288, found: 295.1288 (0.00 ppm)

![Graph 1](image1)

10b, HRMS (ESI\textsuperscript{+}-QqTOF, m/z):
calculated for C\textsubscript{11}H\textsubscript{13}N\textsubscript{2}O\textsubscript{5} [M+NH\textsubscript{4}]\textsuperscript{+}: 253.0820, found: 253.0820 (0.00 ppm)

![Graph 2](image2)
10c, HRMS (ESI\textsuperscript+-QqTOF, m/z):
calculated for C\textsubscript{13}H\textsubscript{15}N\textsubscript{2}O\textsubscript{5} [M+NH\textsubscript{4}\textsuperscript{+}]: 279.0975, found: 279.0975 (0.00 ppm)
9. References


