

Supporting Information

Facile Synthesis of 2-Alkyl/Aryloxy-2*H*-azirines and Their Application in the Synthesis of Pyrroles

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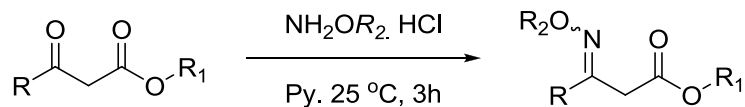
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General methods: All reactions were carried out in flame or oven dried glasswares under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate and molybdate. Photolysis was performed at 302 nm by using Rayonet Chamber Reactor RMR-600. NMR spectra were recorded at room temperature on 400 M Hz Bruker DPX 400 and 400 M Hz JEOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (0.00 ppm or 7.26 ppm for ^1H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in CDCl_3). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer.

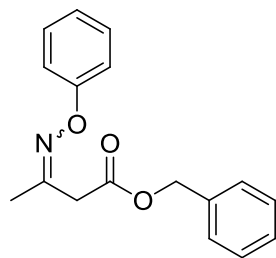
Materials: All solvents were distilled under nitrogen from the following drying agents immediately before use: acetonitrile and dichloroethane were distilled from P_2O_5 . Anhydrous benzene, pyridine and DBU were purchased from commercial suppliers and used without further purification.

General procedure for β -oximino esters:



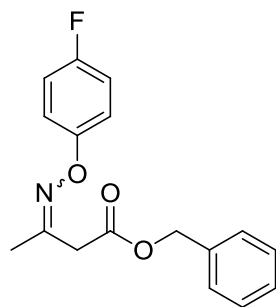
To a solution of β -ketoester (1.0 eq.) in pyridine at room temperature was added alkoxyamine hydrochloride (1.1 eq.) in one portion, and the reaction mixture was stirred at RT for 3 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with water, extracted with ethyl acetate, washed with water, brine and dried over anhydrous Na_2SO_4 . The crude material was concentrated under vacuo and purified by column chromatography using hexane: ethyl acetate (9:1).

Benzyl 3-(phenoxyimino)butanoate:



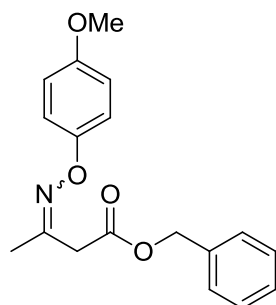
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil (*cis:trans* = 64:36). Yield: 70%. ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.25 (m, 7H), 7.17-7.12 (m, 2H), 7.10-6.98 (m, 1H), 5.18 & 5.16 (s, 2H), 3.58 & 3.41 (s, 2H), 2.13 & 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 168.2, 159.1, 158.9, 155.1, 154.0, 135.5, 135.4, 129.2, 128.6, 128.6, 128.4, 128.3, 128.2, 122.2, 122.2, 114.8, 114.7, 67.0, 66.9, 41.3, 36.0, 20.7, 15.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: 284.1287. Found: 284.1277.

Benzyl 3-((4-fluorophenoxy)imino)butanoate:



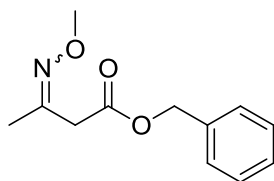
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil (*cis:trans* = 64:36). Yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.33 (m, 5H), 7.13-7.10 & 7.08-7.04 (m, 2H), 7.01-6.95 (m, 2H), 5.20 & 5.18 (s, 2H), 3.58 & 3.42 (s, 2H), 2.13 & 2.12 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 168.0, 159.4, 159.3, 157.0, 156.9, 155.2, 154.9, 154.9, 154.1, 135.4, 135.3, 128.6, 128.5, 128.4, 128.3, 128.2, 116.1, 116.0, 116.0, 115.9, 115.6, 115.4, 67.0, 66.9, 41.2, 35.9, 20.7, 15.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{FNO}_3$: 302.1192. Found: 302.1195.

Benzyl 3-((4-methoxyphenoxy)imino)butanoate:



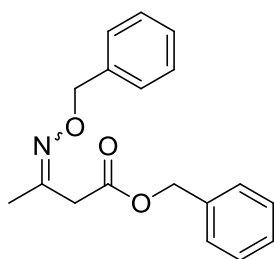
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil (*cis:trans* = 74:26). Yield: 57%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 5H), 7.09-7.07 & 7.04-7.02 (m, 2H), 6.84-6.80 (m, 2H), 5.18 & 5.16 (s, 2H), 3.77 (s, 3H), 3.57 & 3.39 (s, 2H), 2.11 & 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 168.3, 155.1, 155.0, 154.5, 153.3, 153.3, 153.1, 135.4, 128.6, 128.6, 128.4, 128.3, 128.2, 116.3, 116.2, 114.3, 114.3, 66.9, 66.9, 55.7, 41.3, 35.9, 20.7, 15.2 ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: 314.1392. Found: 314.1397.

Benzyl 3-(methoxyimino)butanoate:



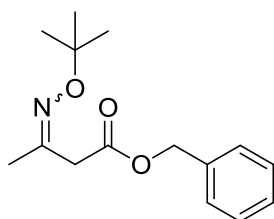
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 58:42). Yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.31 (m, 5H), 5.16 & 5.15 (s, 2H), 3.86 & 3.80 (s, 3H), 3.37 & 3.26 (s, 2H), 1.96 & 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 168.7, 151.2, 150.1, 135.7, 135.5, 128.6, 128.5, 128.4, 128.3, 128.2, 66.8, 66.7, 61.5, 61.4, 41.3, 35.3, 20.6, 14.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: 222.1130. Found: 222.1124.

Benzyl 3-((benzyloxy)imino)butanoate:



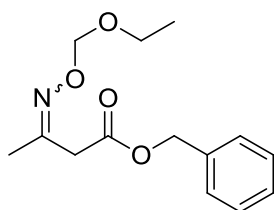
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 50:50). Yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.30 (m, 10H), 5.16 & 5.11 (s, 2H), 5.11 & 5.07 (s, 2H), 3.43 & 3.28 (s, 2H), 1.98 & 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 168.6, 151.7, 150.7, 137.9, 137.8, 135.6, 135.5, 128.6, 128.5, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 75.7, 75.5, 66.8, 66.7, 41.4, 35.6, 20.7, 14.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_3$: 298.1443. Found: 298.1442.

Benzyl 3-(*tert*-butoxyimino)butanoate:



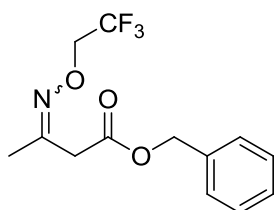
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 69:31). Yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.31 (m, 5H), 5.16 & 5.14 (s, 2H), 3.34 & 3.27 (s, 2H), 1.96 & 1.89 (s, 3H), 1.26 & 1.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 169.2, 149.3, 148.3, 135.8, 135.7, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 78.0, 78.0, 66.6, 66.5, 41.7, 35.5, 27.5, 27.5, 20.9, 14.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3$: 264.1600. Found: 264.1603.

Benzyl 3-((ethoxymethoxy)imino)butanoate:



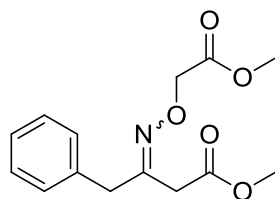
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 55:45). Yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.31 (m, 5H), 5.15 & 5.15 (s, 2H), 5.14 & 5.08 (s, 2H), 3.65 & 3.59 (q, $J = 7.1$ Hz, $J = 6.9$ Hz, 2H), 3.42 & 3.31 (s, 2H), 1.99 & 1.96 (s, 3H), 1.22-1.16 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 168.4, 153.0, 151.7, 135.6, 135.5, 128.5, 128.3, 128.3, 128.2, 128.2, 97.0, 96.8, 66.8, 66.7, 64.4, 64.2, 41.3, 35.6, 20.7, 15.1, 15.1, 14.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4$: 266.1392. Found: 266.1396.

Benzyl 3-((2,2,2-trifluoroethoxy)imino)butanoate:



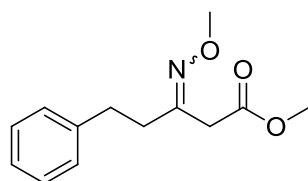
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 54:46). Yield: 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.32 (m, 5H), 5.16 & 5.15 (s, 2H), 4.44-4.33 (m, 2H), 3.42 & 3.27 (s, 2H), 1.97 & 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 168.0, 154.2, 153.1, 135.5, 135.4, 128.6, 128.6, 128.4, 128.4, 128.3, 128.2, 123.6 (m), 69.0 (m), 67.0, 66.9, 41.0, 35.4, 20.5, 14.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_3$: 290.1004. Found: 290.1006.

Methyl 3-((2-methoxy-2-oxoethoxy)imino)-4-phenylbutanoate:



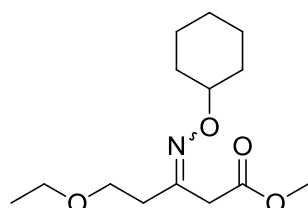
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 86:14). Yield: 61%. ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.29 (m, 2H), 7.26-7.21 (m, 3H), 4.70 & 4.67 (s, 2H), 3.90 & 3.63 (s, 2H), 3.79 & 3.77 (s, 3H), 3.63 & 3.62 (s, 3H), 3.30 & 3.11 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 169.7, 168.8, 155.0, 154.5, 135.6, 135.5, 129.4, 129.2, 128.7, 127.0, 126.8, 70.5, 70.4, 52.1, 51.8, 40.5, 38.4, 34.2, 33.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_5$: 280.1185. Found: 280.1187.

Methyl 3-(methoxyimino)-5-phenylpentanoate:



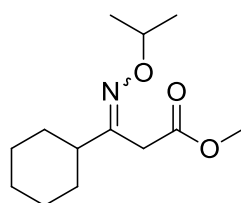
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 66:34). Yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.27 (m, 2H), 7.22-7.18 (m, 3H), 3.87 & 3.85 (s, 3H), 3.70 & 3.69 (s, 3H), 3.32 & 3.11 (s, 2H), 2.89-2.79 (m, 2H), 2.70-2.66 & 2.60-2.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 169.3, 154.2, 152.6, 141.0, 141.0, 128.4, 128.4, 128.3, 126.2, 126.1, 61.6, 61.5, 52.1, 39.8, 36.5, 34.2, 32.4, 31.4, 30.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$: 236.1287. Found: 236.1279.

Methyl 3-((cyclohexyloxy)imino)-5-ethoxypentanoate:



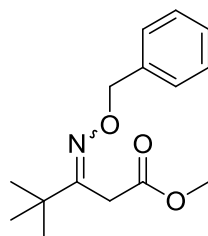
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 62:38). Yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 4.06-4.02 (m, 1H), 3.69 & 3.67 (s, 3H), 3.63-3.56 (m, 2H), 3.49-3.42 (m, 2H), 3.36 & 3.29 (s, 2H), 2.69 & 2.55 (t, $J = 6.6$ Hz, $J = 6.8$ Hz, 2H), 1.89-1.82 (m, 2H), 1.69-1.67 (m, 2H), 1.51-1.48 (m, 1H), 1.41-1.23 (m, 5H), 1.17 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 169.7, 152.0, 150.9, 80.4, 80.2, 67.8, 66.6, 66.2, 66.1, 51.9, 51.8, 40.2, 35.1, 34.6, 31.6, 31.5, 29.1, 25.7, 25.7, 23.7, 23.5, 15.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_4$: 272.1862. Found: 272.1860.

Methyl 3-cyclohexyl-3-(isopropoxyimino)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 91:9). Yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 4.29-4.23 (m, 1H), 3.67 & 3.64 (s, 3H), 3.17 & 3.14 (s, 2H), 3.00-2.96 & 2.24-2.18 (m, 1H), 1.80-1.75 (m, 4H), 1.67-1.64 (m, 1H), 1.31-1.23 (m, 4H), 1.21-1.18 (m, 1H), 1.17-1.11 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 170.0, 157.2, 156.4, 75.0, 74.9, 51.9, 51.8, 51.7, 43.8, 40.2, 37.6, 37.3, 33.0, 30.0, 29.8, 28.6, 26.0, 26.0, 25.9, 25.7, 21.6, 21.5, 21.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_3$: 242.1756. Found: 242.1749.

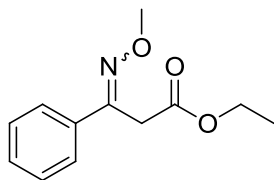
Methyl 3-((benzyloxy)imino)-4,4-dimethylpentanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 0:100). Yield: 65%. ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.29 (m, 4H), 7.28-7.25 (m, 1H), 5.07 (s, 2H), 3.55 (s, 3H), 3.24 (s, 2H), 1.14 (s, 9H);

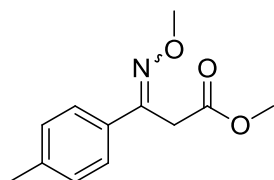
^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 159.9, 137.9, 128.1, 127.9, 127.5, 75.6, 51.8, 36.9, 31.7, 27.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3$: 264.1600. Found: 264.1608.

Ethyl 3-(methoxyimino)-3-phenylpropanoate:



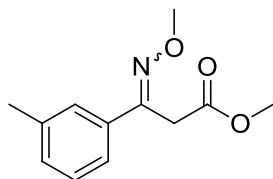
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 7:93). Yield: 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.61 & 7.48-7.46 (m, 2H), 7.41-7.35 (m, 3H), 4.18-4.07 (m, 2H), 4.01 & 3.89 (s, 3H), 3.75 & 3.57 (s, 2H), 1.21 & 1.16 (t, $J = 7.0$ Hz, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 168.8, 151.3, 150.9, 135.3, 129.3, 129.1, 128.5, 128.1, 128.0, 126.2, 62.2, 62.1, 61.1, 41.2, 33.2, 14.0, 14.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: 222.1130. Found: 222.1135.

Methyl 3-(methoxyimino)-3-(p-tolyl)propanoate :



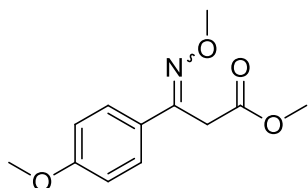
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 8:92). Yield: 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.53 & 7.40 (d, $J = 8.0$ Hz, $J = 8.4$ Hz, 2H), 7.21-7.17 (m, 2H), 4.00 & 3.89 (s, 3H), 3.76 & 3.58 (s, 2H), 3.68 & 3.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 151.0, 139.4, 132.4, 129.2, 128.9, 128.0, 126.0, 62.2, 62.1, 52.2, 52.1, 40.9, 32.8, 21.4, 21.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: 222.1130. Found: 222.1134.

Methyl 3-(methoxyimino)-3-(m-tolyl)propanoate:



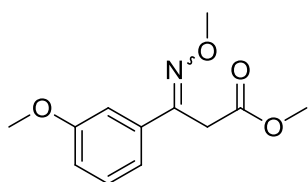
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 8:92). Yield: 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.17 (d, J = 7.6 Hz, 1H), 3.99 & 3.87 (s, 3H), 3.74 & 3.56 (s, 2H), 3.67 & 3.63 (s, 3H), 2.36 & 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 169.2, 151.2, 150.8, 138.1, 137.7, 135.1, 132.7, 130.1, 129.9, 128.3, 128.0, 126.6, 125.0, 123.2, 62.1, 62.0, 52.1, 52.0, 40.9, 32.8, 21.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: 222.1130. Found: 222.1131.

Methyl 3-(methoxyimino)-3-(4-methoxyphenyl)propanoate:



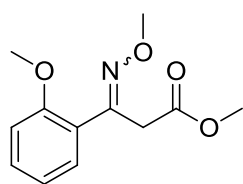
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 7:93). Yield: 85%. ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.57 & 7.54-7.51 (m, 2H), 6.91-6.87 (m, 2H), 3.98 & 3.90 (s, 3H), 3.81 (s, 3H), 3.75 & 3.58 (s, 2H), 3.68 & 3.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 160.6, 150.6, 129.9, 127.7, 127.5, 113.9, 113.5, 62.1, 55.3, 55.2, 52.2, 52.1, 40.8, 32.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_4$: 238.1079. Found: 238.1077.

Methyl 3-(methoxyimino)-3-(3-methoxyphenyl)propanoate:



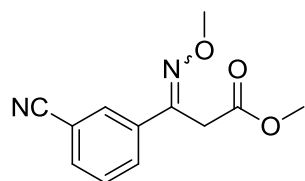
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 8:92). Yield: 84%. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.27 (m, 1H), 7.23-7.22 (m, 1H), 7.19-7.17 & 7.05-7.00 (m, 1H), 6.94-6.88 (m, 1H), 4.01 & 3.89 (s, 3H), 3.83 & 3.81 (s, 3H), 3.76 & 3.57 (s, 2H), 3.69 & 3.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 169.2, 159.7, 159.3, 150.9, 150.5, 136.6, 134.1, 129.5, 129.3, 120.2, 118.7, 115.4, 114.7, 113.9, 111.4, 62.3, 62.2, 55.3, 55.2, 52.2, 52.1, 41.0, 32.9; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₂H₁₅NO₄: 238.1079. Found: 238.1088.

Methyl 3-(methoxyimino)-3-(2-methoxyphenyl)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 8:92). Yield: 96%. ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.44 (m, 1H), 7.37-7.32 (m, 1H), 6.99-6.95 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.98 & 3.86 (s, 3H), 3.82 & 3.81 (s, 3H), 3.76 & 3.59 (s, 2H), 3.65 & 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 157.3, 152.4, 130.6, 130.2, 130.1, 125.0, 120.8, 120.3, 111.0, 110.8, 62.0, 55.5, 55.3, 51.9, 40.3, 35.1; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₂H₁₅NO₄: 238.1079. Found: 238.1079.

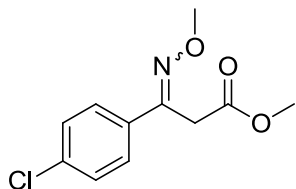
Methyl 3-(3-cyanophenyl)-3-(methoxyimino)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as white solid (*cis:trans* = 11:89). mp: 69-71 °C. Yield: 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.97-7.96 (m, 1H), 7.88-7.81 (m, 1H), 7.69-7.64 (m, 1H), 7.53-7.47 (m, 1H), 4.04 & 3.90 (s, 3H), 3.76 & 3.59 (s, 2H), 3.71 & 3.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

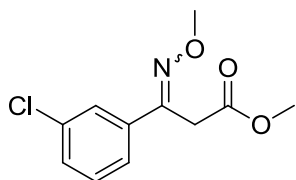
169.6, 168.7, 149.0, 148.4, 136.5, 134.0, 132.5, 132.3, 132.0, 130.2, 129.8, 129.4, 129.1, 118.4, 112.9, 62.7, 62.4, 52.4, 52.3, 40.3, 32.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{12}N_2O_3$: 233.0926. Found: 233.0927.

Methyl 3-(4-chlorophenyl)-3-(methoxyimino)propanoate:



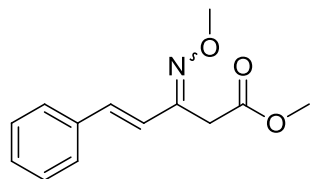
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 9:91). Yield: 92%. 1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 & 7.45-7.43 (m, 2H), 7.37-7.32 (m, 2H), 4.01 & 3.89 (s, 3H), 3.74 & 3.57 (s, 2H), 3.69 & 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.1, 149.9, 149.5, 135.4, 135.1, 133.6, 131.0, 129.6, 128.7, 128.5, 127.4, 62.4, 62.2, 52.3, 52.2, 40.7, 32.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{12}ClNO_3$: 242.0584. Found: 242.0575.

Methyl 3-(3-chlorophenyl)-3-(methoxyimino)propanoate:



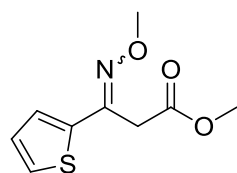
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 10:90). Yield: 78%. 1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.66 (m, 1H), 7.50-7.48 (m, 1H), 7.36-7.28 (m, 2H), 4.02 & 3.89 (s, 3H), 3.74 & 3.56 (s, 2H), 3.69 & 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.8, 149.2, 136.9, 134.6, 129.7, 129.5, 129.3, 129.3, 128.2, 126.2, 126.1, 124.2, 62.5, 62.3, 52.3, 52.2, 40.6, 32.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{12}ClNO_3$: 242.0584. Found: 242.0579.

(4E)-methyl 3-(methoxyimino)-5-phenylpent-4-enoate:



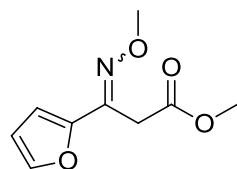
The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 21:79). Yield: 97%. ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.41 (m, 2H), 7.36-7.27 (m, 3H), 6.91-6.80 (m, 2H), 3.98 & 3.97 (s, 3H), 3.72 & 3.71 (s, 3H), 3.65 & 3.52 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 169.1, 151.8, 149.6, 136.3, 136.1, 136.0, 133.5, 129.2, 128.7, 128.6, 127.5, 126.9, 124.5, 116.3, 62.3, 62.1, 52.3, 37.3, 30.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: 234.1130. Found: 234.1132.

Methyl 3-(methoxyimino)-3-(thiophen-2-yl)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 36:64). Yield: 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.52 & 7.30-7.28 (m, 1H), 7.41-7.40 & 7.21-7.20 (m, 1H), 7.08-7.06 & 7.02-7.00 (m, 1H), 4.09 & 3.98 (s, 3H), 3.76 & 3.70 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 168.8, 146.9, 143.7, 138.9, 131.6, 130.8, 129.3, 127.3, 127.1, 126.5, 125.7, 62.4, 62.3, 52.4, 52.3, 39.7, 33.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{11}\text{NO}_3\text{S}$: 214.0538. Found: 214.0541.

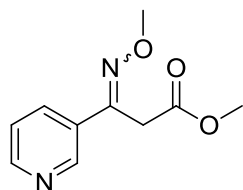
Methyl 3-(furan-2-yl)-3-(methoxyimino)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 18:82). Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ

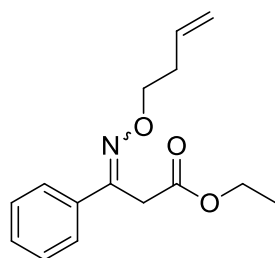
7.47-7.41 (m, 1H), 7.32-7.31 & 6.67-6.66 (m, 1H), 6.50-6.44 (m, 1H), 4.03 & 4.00 (s, 3H), 3.69 (s, 3H), 3.67 & 3.63 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 168.7, 149.0, 145.2, 143.9, 143.4, 142.6, 140.6, 117.9, 112.1, 111.5, 110.3, 62.6, 62.6, 52.3, 52.2, 37.3, 31.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{11}\text{NO}_4$: 198.0766. Found: 198.0771.

Methyl 3-(methoxyimino)-3-(pyridin-3-yl)propanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 18:82). Yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 8.86-8.85 & 8.72-8.71 (m, 1H), 8.60-8.57 (m, 1H), 7.97-7.94 & 7.84-7.82 (m, 1H), 7.34-7.28 (m, 1H), 4.03 & 3.90 (s, 3H), 3.77 & 3.61 (s, 2H), 3.69 & 3.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 168.8, 150.2, 150.0, 148.9, 148.7, 147.9, 147.4, 135.8, 133.4, 131.0, 128.8, 123.3, 123.0, 62.6, 62.3, 52.4, 52.3, 40.4, 32.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$: 209.0926. Found: 209.0923.

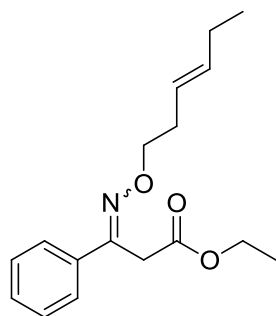
Ethyl 3-((but-3-en-1-yloxy)imino)-3-phenylpropanoate:



The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 9:91). Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.62 & 7.52-7.49 (m, 2H), 7.39-7.36 (m, 3H), 5.91-5.80 (m, 1H), 5.15-5.04 (m, 2H), 4.28-4.21 (m, 2H), 4.17-4.08 (m, 2H), 3.75 & 3.58 (s, 2H), 2.51-2.42 (m, 2H), 1.22 & 1.16 (t, $J = 7.2$ Hz, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 168.8, 151.2, 150.5, 135.5, 134.7, 134.7, 133.7, 129.2, 129.0, 128.7, 128.4, 126.1, 126.0, 116.6, 116.5, 73.6, 73.5, 61.4,

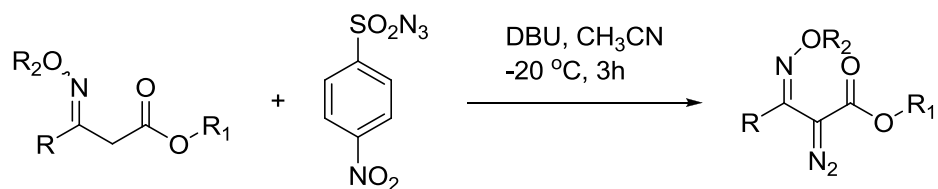
61.0, 45.9, 41.1, 33.7, 33.3, 14.0, 13.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{19}NO_3$: 262.1443. Found: 262.1443.

Ethyl 3-(((E)-hex-3-en-1-yloxy)imino)-3-phenylpropanoate:

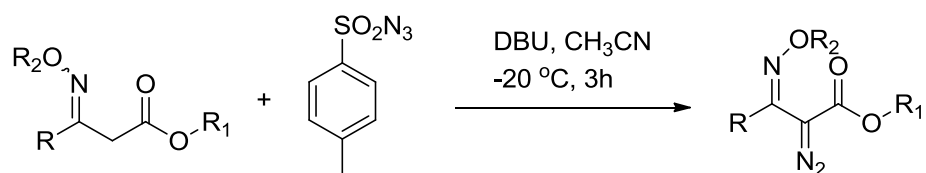


The title compound was prepared according to the general procedure. The product was obtained as colorless oil (*cis:trans* = 7:93). Yield: 86%. 1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 & 7.52-7.50 (m, 2H), 7.39-7.35 (m, 3H), 5.60-5.53 (m, 1H), 5.47-5.39 (m, 1H), 4.22 (t, $J = 7.0$ Hz, 2H), 4.17-4.08 (m, 2H), 3.75 & 3.58 (s, 2H), 2.43-2.35 (m, 2H), 2.06-1.97 (m, 2H), 1.22 & 1.16 (t, $J = 7.0$ Hz, $J = 7.2$ Hz, 3H), 1.00-0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 151.1, 135.5, 134.4, 129.2, 129.0, 128.4, 128.2, 128.0, 126.1, 124.7, 124.7, 74.3, 74.0, 61.0, 41.1, 33.3, 32.5, 32.4, 25.6, 14.0, 13.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{23}NO_3$: 290.1756. Found: 290.1758.

General procedure for α -diazo oxime ethers (1a-z):

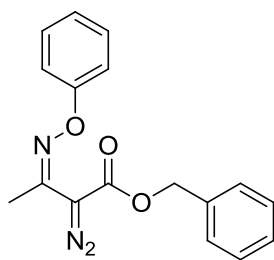


or



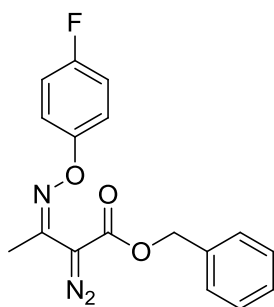
To a solution of β -oximino ester (1.0 eq.) and 4-nitrobenzenesulfonyl azide or TsN₃ (1.1 eq.) in CH₃CN at -20 °C was added DBU (1.1 eq.) dropwise. The resulting orange color solution was stirred for 2 h at -20 °C and slowly brought to RT. Upon completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure, and the crude material was purified by column chromatography using hexane:ethyl acetate (9:1).

(Z)-benzyl 2-diazo-3-(phenoxyimino)butanoate (1a):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.35 (m, 5H), 7.32-7.28 (m, 2H), 7.13-7.11 (m, 2H), 7.03-7.00 (m, 1H), 5.26 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 158.4, 145.6, 135.4, 129.3, 128.7, 128.5, 128.2, 122.4, 114.2, 66.9, 19.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₇H₁₅N₃O₃: 310.1192. Found: 310.1195.

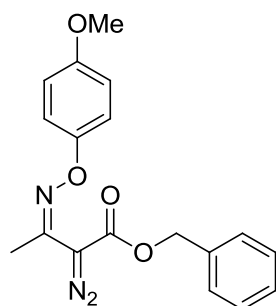
(Z)-benzyl 2-diazo-3-((4-fluorophenoxy)imino)butanoate (1b):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 52%. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.36 (m, 5H), 7.09-7.06 (m, 2H), 7.01-6.97 (m, 2H), 5.27 (s, 2H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 159.5, 157.1, 154.5, 154.5, 145.7, 135.3, 128.7, 128.5, 128.2, 115.8, 115.6,

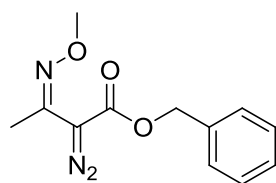
115.5, 67.0, 19.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{14}FN_3O_3$: 328.1097. Found: 328.1105.

(Z)-benzyl 2-diazo-3-((4-methoxyphenoxy)imino)butanoate (1c):



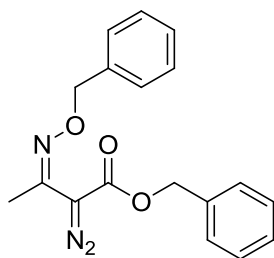
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 61-63 °C. Yield: 20%. 1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 5H), 7.07-7.02 (m, 2H), 6.86-6.82 (m, 2H), 5.26 (s, 2H), 3.77 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.2, 152.6, 144.9, 135.4, 128.7, 128.5, 128.2, 115.7, 114.4, 66.9, 55.7, 19.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{17}N_3O_4$: 340.1297. Found: 340.1302.

(Z)-benzyl 2-diazo-3-(methoxyimino)butanoate (1d):



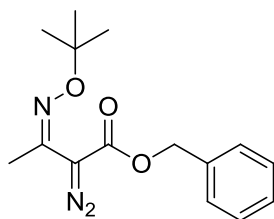
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 64%. 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5H), 5.23 (s, 2H), 3.83 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 141.4, 135.6, 128.6, 128.4, 128.1, 66.7, 61.7, 19.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_3O_3$: 248.1035. Found: 248.1038.

(Z)-benzyl 3-((benzyloxy)imino)-2-diazobutanoate (1e):



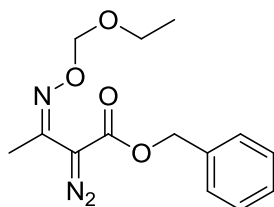
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 55%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.30 (m, 10H), 5.22 (s, 2H), 5.07 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 141.8, 137.0, 135.5, 128.6, 128.4, 128.1, 128.0, 76.4, 66.7, 19.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$: 324.1348. Found: 324.1355.

(Z)-benzyl 3-(tert-butoxyimino)-2-diazobutanoate (1f):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 52%. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.32 (m, 5H), 5.23 (s, 2H), 2.16 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 139.1, 135.7, 128.6, 128.3, 128.1, 79.4, 66.5, 27.3, 19.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3$: 290.1505. Found: 290.1513.

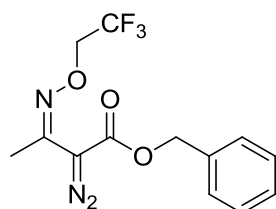
(Z)-benzyl 2-diazo-3-((ethoxymethoxy)imino)butanoate (1g):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 50%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.34 (m, 5H), 5.23 (s, 2H), 5.10 (s, 2H), 3.63 (q, $J = 7.1$ Hz, 2H), 2.19 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C

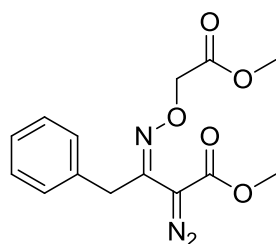
NMR (100 MHz, CDCl₃) δ 163.6, 143.0, 135.5, 128.6, 128.4, 128.1, 97.2, 66.8, 64.9, 19.4, 15.1; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₄H₁₇N₃O₄: 292.1297. Found: 292.1304.

(Z)-benzyl 2-diazo-3-((2,2,2-trifluoroethoxy)imino)butanoate (1h):



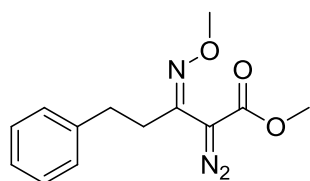
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.34 (m, 5H), 5.23 (s, 2H), 4.38 (q, J = 8.5 Hz, 2H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 144.7, 135.4, 128.7, 128.5, 128.2, 123.4 (q, J = 278.0 Hz), 70.9 (q, J = 33.9 Hz), 66.9, 19.1; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₃H₁₂F₃N₃O₃: 316.0909. Found: 316.0910.

(Z)-methyl 2-diazo-3-((2-methoxy-2-oxoethoxy)imino)-4-phenylbutanoate (1i):



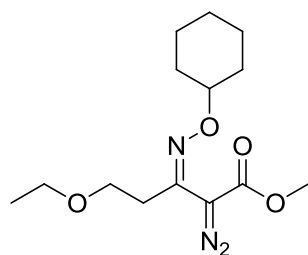
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 47%. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.21 (m, 5H), 4.69 (s, 2H), 3.93 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 163.6, 146.4, 137.0, 128.8, 128.4, 126.7, 70.7, 52.0, 51.9, 37.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₄H₁₅N₃O₅: 306.1090. Found: 306.1078.

(Z)-methyl 2-diazo-3-(methoxyimino)-5-phenylpentanoate (1j):



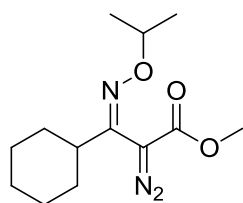
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.26 (m, 2H), 7.23-7.17 (m, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.90-2.87 (m, 2H), 2.86-2.81 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 144.2, 141.0, 128.5, 128.3, 126.0, 61.8, 52.1, 34.3, 33.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_3$: 262.1192. Found: 262.1187.

(Z)-methyl 3-((cyclohexyloxy)imino)-2-diazo-5-ethoxypentanoate (1k):



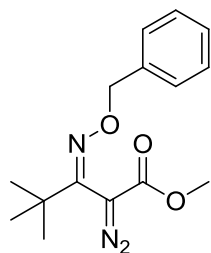
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 43%. ^1H NMR (400 MHz, CDCl_3) δ 4.09-4.04 (m, 1H), 3.79 (s, 3H), 3.60 (t, $J = 6.7$ Hz, 2H), 3.49 (q, $J = 7.0$ Hz, 2H), 2.86 (t, $J = 6.7$ Hz, 2H), 1.90-1.86 (m, 2H), 1.68-1.67 (m, 2H), 1.51-1.26 (m, 6H), 1.17 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 141.1, 81.2, 68.1, 65.9, 52.0, 32.4, 31.3, 25.6, 23.5, 15.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_4$: 298.1767. Found: 298.1762.

(Z)-methyl 3-cyclohexyl-2-diazo-3-(isopropoxyimino)propanoate (1l):



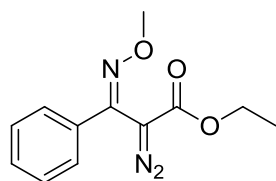
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 61%. ^1H NMR (400 MHz, CDCl_3) δ 4.34-4.25 (m, 1H), 3.77 (s, 3H), 2.82-2.76 (m, 1H), 1.91-1.88 (m, 2H), 1.77-1.74 (m, 2H), 1.68-1.65 (m, 1H), 1.40-1.24 (m, 5H), 1.21 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 146.8, 75.8, 51.9, 40.2, 31.5, 26.4, 26.2, 21.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}_3$: 268.1661. Found: 268.1655.

(Z)-methyl 3-((benzyloxy)imino)-2-diazo-4,4-dimethylpentanoate (1m):



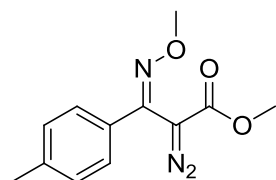
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 42%. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.29 (m, 5H), 5.14 (s, 2H), 3.72 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 150.0, 137.5, 128.2, 128.1, 127.8, 76.3, 52.1, 39.1, 28.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_3$: 290.1505. Found: 290.1510.

(Z)-ethyl 2-diazo-3-(methoxyimino)-3-phenylpropanoate (1n):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 58-60 °C. Yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.52 (m, 2H), 7.39-7.34 (m, 3H), 4.11 (q, $J = 7.1$ Hz, 2H), 4.05 (s, 3H), 1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 144.2, 133.7, 129.6, 128.2, 127.7, 62.6, 61.2, 14.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3$: 248.1035. Found: 248.1035.

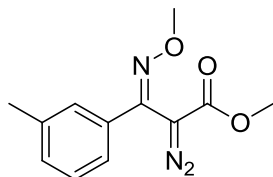
(Z)-methyl 2-diazo-3-(methoxyimino)-3-(p-tolyl)propanoate (1o):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H),

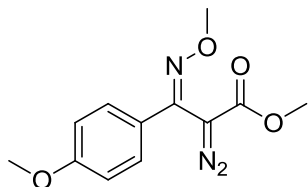
7.17 (d, $J = 8.0$ Hz, 2H), 4.03 (s, 3H), 3.68 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 143.9, 139.8, 130.6, 129.1, 127.5, 62.6, 52.1, 21.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3$: 248.1035. Found: 248.1044.

(Z)-methyl 2-diazo-3-(methoxyimino)-3-(m-tolyl)propanoate (1p):



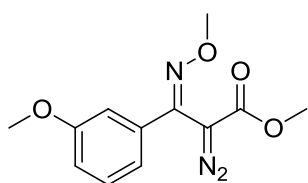
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 87%. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (s, 1H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 2H), 4.05 (s, 3H), 3.68 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 144.1, 138.0, 133.4, 130.5, 128.1, 128.0, 124.9, 62.6, 52.1, 21.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3$: 248.1035. Found: 248.1035.

(Z)-methyl 2-diazo-3-(methoxyimino)-3-(4-methoxyphenyl)propanoate (1q):



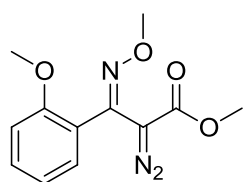
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 75-77 °C. Yield: 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 9.2$ Hz, 2H), 4.02 (s, 3H), 3.81 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 160.9, 143.5, 129.0, 125.8, 113.8, 62.5, 55.3, 52.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$: 264.0984. Found: 264.0986.

(Z)-methyl 2-diazo-3-(methoxyimino)-3-(3-methoxyphenyl)propanoate (1r):



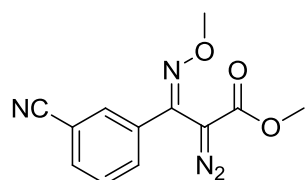
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 96%. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.26 (m, 1H), 7.12-7.10 (m, 2H), 6.96-6.93 (m, 1H), 4.05 (s, 3H), 3.83 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 159.5, 143.8, 134.9, 129.3, 120.2, 115.6, 112.8, 62.7, 55.3, 52.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$: 264.0984. Found: 264.0984.

(Z)-methyl 2-diazo-3-(methoxyimino)-3-(2-methoxyphenyl)propanoate (1s):



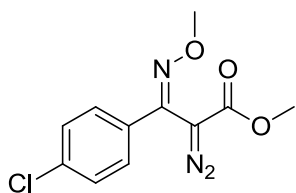
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 16%. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 2H), 7.00-6.96 (m, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 4.00 (s, 3H), 3.79 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 157.7, 142.8, 130.9, 130.5, 122.8, 120.7, 110.5, 62.4, 55.6, 51.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$: 264.0984. Found: 264.0980.

(Z)-methyl 3-(3-cyanophenyl)-2-diazo-3-(methoxyimino)propanoate (1t):



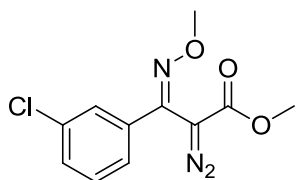
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 128-130 °C. Yield: 91%. ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.83 (m, 1H), 7.76-7.73 (m, 1H), 7.68-7.66 (m, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 4.07 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 142.3, 135.0, 132.8, 131.9, 131.3, 129.1, 118.4, 112.6, 63.1, 52.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_3$: 259.0831. Found: 259.0835.

(Z)-methyl 3-(4-chlorophenyl)-2-diazo-3-(methoxyimino)propanoate (1u):



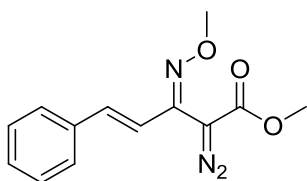
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 61-63 °C. Yield: 97%. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.8$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 4.04 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 143.0, 135.7, 132.0, 128.9, 128.6, 62.8, 52.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{O}_3$: 268.0489. Found: 268.0490.

(Z)-methyl 3-(3-chlorophenyl)-2-diazo-3-(methoxyimino)propanoate (1v):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 59-61 °C. Yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.55 (m, 1H), 7.41-7.35 (m, 2H), 7.32-7.28 (m, 1H), 4.06 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 135.4, 134.3, 129.7, 129.4, 127.6, 125.9, 62.9, 52.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{O}_3$: 268.0489. Found: 268.0482.

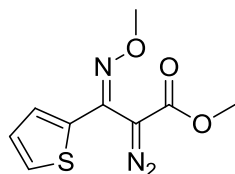
(3Z,4E)-methyl 2-diazo-3-(methoxyimino)-5-phenylpent-4-enoate (1w):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 77%. ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.45 (m, 2H), 7.36-7.27 (m, 3H), 6.99 (d, $J = 16.4$ Hz, 1H), 6.81 (d, $J = 16.0$ Hz, 1H), 4.01 (s, 3H), 3.80 (s,

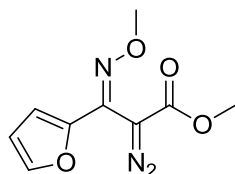
3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 142.7, 136.1, 135.0, 128.7, 128.6, 127.1, 121.7, 62.7, 52.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3$: 260.1035. Found: 260.1028.

(E)-methyl 2-diazo-3-(methoxyimino)-3-(thiophen-2-yl)propanoate (1x):



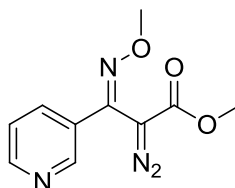
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 58-60 °C. Yield: 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.32 (m, 1H), 7.21-7.20 (m, 1H), 7.04-7.02 (m, 1H), 4.04 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 138.6, 136.3, 128.4, 127.5, 127.2, 62.9, 52.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{O}_3\text{S}$: 240.0443. Found: 240.0437.

(E)-methyl 2-diazo-3-(furan-2-yl)-3-(methoxyimino)propanoate (1y):



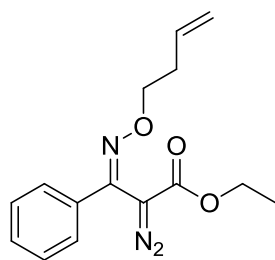
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 84%. ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.47 (m, 1H), 6.66-6.65 (m, 1H), 6.46-6.45 (m, 1H), 4.05 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 146.8, 143.9, 135.4, 111.7, 111.6, 63.0, 52.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{O}_4$: 224.0671. Found: 224.0671.

(Z)-methyl 2-diazo-3-(methoxyimino)-3-(pyridin-3-yl)propanoate (1z):



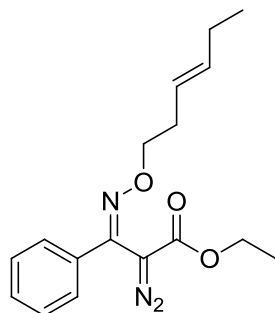
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 93%. ^1H NMR (400 MHz, CDCl_3) δ 8.73-8.72 (m, 1H), 8.60-8.59 (m, 1H), 7.82-7.79 (m, 1H), 7.29-7.27 (m, 1H), 4.05 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 150.3, 148.7, 141.5, 134.9, 129.5, 122.9, 62.9, 52.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_3$: 235.0831. Found: 235.0835.

(Z)-ethyl 3-((but-3-en-1-yloxy)imino)-2-diazo-3-phenylpropanoate (5a):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.52 (m, 2H), 7.41-7.34 (m, 3H), 5.90-5.80 (m, 1H), 5.17-5.07 (m, 2H), 4.30 (t, $J = 6.6$ Hz, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 2.54-2.48 (m, 2H), 1.08 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 144.1, 134.4, 133.9, 129.5, 128.2, 127.7, 116.9, 74.2, 61.2, 33.6, 14.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3$: 288.1348. Found: 288.1356.

(Z)-ethyl 2-diazo-3-(((E)-hex-3-en-1-yloxy)imino)-3-phenylpropanoate (5b):

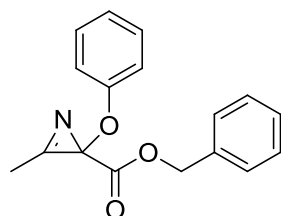


The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 82%. ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.52 (m, 2H), 7.39-7.35 (m, 3H), 5.61-5.55 (m, 1H), 5.46-5.38 (m, 1H), 4.26 (t, $J = 6.6$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 2.46-2.41 (m, 2H), 2.05-2.00 (m, 2H), 1.08 (t, $J = 7.0$ Hz, 3H), 0.98 (t, $J = 7.4$

Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 143.9, 134.7, 134.0, 129.4, 128.2, 127.6, 124.5, 74.8, 61.2, 32.4, 25.6, 14.0, 13.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_3$: 316.1661. Found: 316.1658.

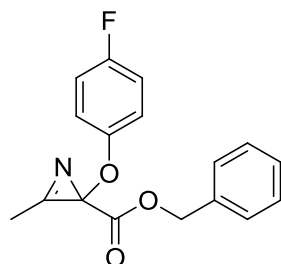
General procedure for 2*H*-azirines: A solution of α -diazo oxime ethers in benzene was irradiated at 302 nm in Rayonet photoreactor for 2-5 h. After the completion of the reaction, the solvent was evaporated under reduced pressure, and the crude material was purified by flash column chromatography (silica gel, hexane: ethyl acetate = 9:1) to give 2*H*-azirines.

Benzyl 3-methyl-2-phenoxy-2*H*-azirine-2-carboxylate (2a):



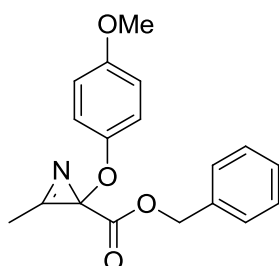
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 62-64 °C. Yield 84%. ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.24 (m, 5H), 7.15-7.09 (m, 4H), 7.05-7.01 (m, 1H), 5.20 (d, $J = 12.4$ Hz, 1H), 5.12 (d, $J = 12.4$ Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 164.8, 155.3, 135.0, 129.5, 128.4, 128.2, 127.9, 122.6, 67.6, 64.5, 11.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$: 282.1130. Found: 282.1128.

Benzyl 2-(4-fluorophenoxy)-3-methyl-2*H*-azirine-2-carboxylate (2b):



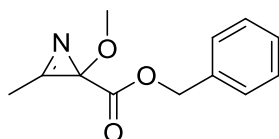
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.30 (m, 3H), 7.19-7.16 (m, 2H), 7.08-7.05 (m, 2H), 6.98-6.93 (m, 2H), 5.22 (d, $J = 12.4$ Hz, 1H), 5.12 (d, $J = 12.4$ Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 164.7, 159.6, 157.2, 151.3, 151.3, 135.0, 128.5, 128.4, 128.0, 117.9, 117.8, 116.1, 115.9, 67.8, 65.1, 11.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{14}\text{FNO}_3$: 300.1036. Found: 300.1039.

Benzyl 2-(4-methoxyphenoxy)-3-methyl-2H-azirine-2-carboxylate (2c):



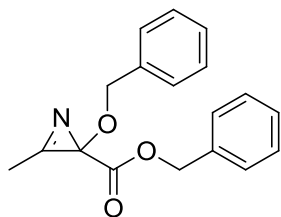
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 71%. ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.28 (m, 3H), 7.21-7.18 (m, 2H), 7.05-7.01 (m, 2H), 6.82-6.77 (m, 2H), 5.22 (d, $J = 12.8$ Hz, 1H), 5.13 (d, $J = 12.4$ Hz, 1H), 3.77 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 164.8, 155.3, 149.0, 135.1, 128.5, 128.3, 128.0, 118.0, 114.6, 67.6, 65.4, 55.6, 11.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$: 312.1236. Found: 312.1229.

Benzyl 2-methoxy-3-methyl-2H-azirine-2-carboxylate (2d):



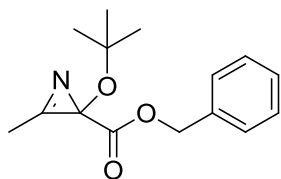
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 92%. ^1H NMR (400 MHz, CDCl_3) 7.38-7.31 (m, 5H), 5.23 (d, $J = 12.4$ Hz, 1H), 5.14 (d, $J = 12.0$ Hz, 1H), 3.45 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 166.3, 135.3, 128.6, 128.4, 128.1, 67.4, 66.4, 54.0, 12.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$: 220.0974. Found: 220.0978.

Benzyl 2-(benzyloxy)-3-methyl-2H-azirine-2-carboxylate (2e):



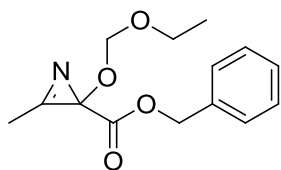
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 88%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.28 (m, 10H), 5.25 (d, $J = 12.4$ Hz, 1H), 5.18 (d, $J = 12.4$ Hz, 1H), 4.89 (d, $J = 11.2$ Hz, 1H), 4.63 (d, $J = 11.2$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 166.5, 136.9, 135.3, 128.6, 128.4, 128.4, 128.3, 128.2, 128.0, 69.1, 67.5, 65.7, 11.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_3$: 296.1287. Found: 296.1280.

Benzyl 2-(tert-butoxy)-3-methyl-2H-azirine-2-carboxylate (2f):



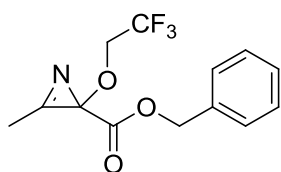
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.31 (m, 5H), 5.20 (d, $J = 12.4$ Hz, 1H), 5.13 (d, $J = 12.4$ Hz, 1H), 2.52 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 167.5, 135.5, 128.5, 128.3, 128.1, 78.4, 67.3, 62.4, 28.9, 12.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: 262.1443. Found: 262.1442.

Benzyl 2-(ethoxymethoxy)-3-methyl-2H-azirine-2-carboxylate (2g):



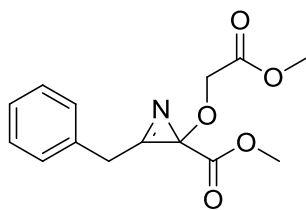
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.31 (m, 5H), 5.22-5.15 (m, 2H), 4.84 (d, $J = 6.8$ Hz, 1H), 4.69 (d, $J = 6.8$ Hz, 1H), 3.60-3.53 (m, 2H), 2.56 (s, 3H), 1.14 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 167.0, 135.3, 128.5, 128.3, 128.1, 92.3, 67.5, 64.2, 64.0, 14.9, 12.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$: 264.1236. Found: 264.1246.

Benzyl 3-methyl-2-(2,2,2-trifluoroethoxy)-2H-azirine-2-carboxylate (2h):



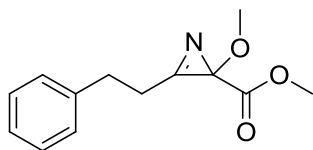
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 94%. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.30 (m, 5H), 5.22 (d, $J = 12.4$ Hz, 1H), 5.16 (d, $J = 12.4$ Hz, 1H), 4.35-4.26 (m, 1H), 4.05-3.95 (m, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 165.9, 134.9, 128.7, 128.6, 128.1, 123.1 (q, $J = 275.9$ Hz), 67.7, 66.1, 64.3 (q, $J = 18.4$ Hz), 11.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}_3$: 288.0848. Found: 288.0837.

Methyl 3-benzyl-2-(2-methoxy-2-oxoethoxy)-2H-azirine-2-carboxylate (2i):



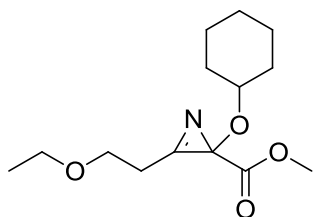
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 46-47 °C. Yield 84%. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.31 (m, 5H), 4.43 (d, $J = 16.0$ Hz, 1H), 4.28-4.16 (m, 3H), 3.74 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 169.2, 168.9, 131.5, 129.0, 128.9, 127.8, 66.7, 64.1, 52.8, 52.0, 32.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_5$: 278.1028. Found: 278.1026.

Methyl 2-methoxy-3-phenethyl-2*H*-azirine-2-carboxylate (2j):



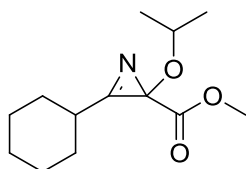
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 91%. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.30 (m, 2H), 7.26-7.22 (m, 3H), 3.71 (s, 3H), 3.40 (s, 3H), 3.19-3.15 (m, 2H), 3.13-3.08 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 169.0, 139.2, 128.7, 128.3, 126.8, 66.8, 53.9, 52.8, 30.3, 28.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: 234.1130. Found: 234.1133.

Methyl 2-(cyclohexyloxy)-3-(2-ethoxyethyl)-2*H*-azirine-2-carboxylate (2k):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 93%. ^1H NMR (400 MHz, CDCl_3) δ 3.84-3.74 (m, 2H), 3.73 (s, 3H), 3.71-3.66 (m, 1H), 3.54-3.49 (m, 2H), 3.17-3.03 (m, 2H), 1.95-1.85 (m, 2H), 1.75-1.66 (m, 2H), 1.52-1.22 (m, 6H), 1.18 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 168.3, 66.6, 64.9, 64.8, 52.7, 33.0, 32.7, 27.8, 25.4, 24.1, 24.1, 15.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_4$: 270.1705. Found: 270.1708.

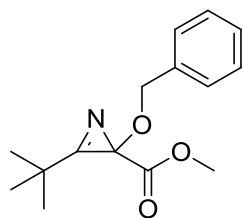
Methyl 3-cyclohexyl-2-isopropoxy-2*H*-azirine-2-carboxylate (2l):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 93%. ^1H NMR (400 MHz, CDCl_3) δ 4.06-4.00 (m, 1H), 3.73

(s, 3H), 2.95-2.90 (m, 1H), 2.03-1.93 (m, 2H), 1.79-1.73 (m, 2H), 1.67-1.59 (m, 2H), 1.57-1.52 (m, 1H), 1.45-1.34 (m, 3H), 1.24 (d, $J = 6.0$ Hz, 3H), 1.17 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 171.1, 71.2, 65.4, 52.6, 35.7, 28.1, 28.0, 25.6, 24.8, 24.7, 23.1, 22.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: 240.1600. Found: 240.1598.

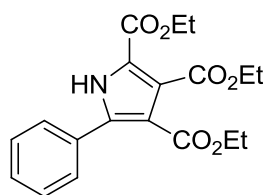
Methyl 2-(benzyloxy)-3-(tert-butyl)-2H-azirine-2-carboxylate (2m):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 52-54 °C. Yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.28 (m, 5H), 4.87 (d, $J = 11.2$ Hz, 1H), 4.65 (d, $J = 10.8$ Hz, 1H), 3.76 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 170.4, 137.1, 128.3, 128.0, 127.8, 68.8, 67.5, 52.7, 33.5, 26.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: 262.1443. Found: 262.1446.

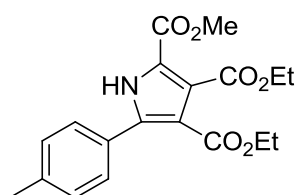
General procedure for pyrroles via intermolecular reaction: A solution of α -diazo oxime ethers (1.0 eq.) and diethyl fumarate (5.0 eq.) in benzene was irradiated at 302 nm in Rayonet photoreactor at RT for 12-18 h. After concentration, the crude material was dissolved in THF and treated with aqueous 1 N HCl at RT overnight. After the completion of the reaction, the mixture was diluted with CH_2Cl_2 , dried over anhydrous MgSO_4 and concentrated under reduced pressure. The crude compound was purified by column chromatography using hexane: ethyl acetate (3:2) to give pyrroles.

Triethyl 5-phenyl-1H-pyrrole-2,3,4-tricarboxylate (4n):



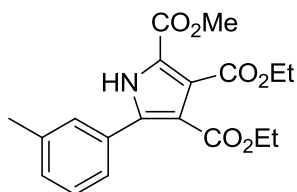
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 117-119 °C. Yield: 72%. ^1H NMR (400 MHz, CDCl_3) δ 9.77 (br, 1H), 7.57-7.54 (m, 2H), 7.43-7.41 (m, 3H), 4.40 (q, $J = 7.1$ Hz, 2H), 4.22-4.15 (m, 4H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 162.7, 159.9, 140.0, 130.2, 129.4, 129.4, 128.1, 124.9, 119.6, 112.2, 61.6, 61.4, 60.4, 14.1, 14.1, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: 360.1447. Found: 360.1460.

3,4-diethyl 2-methyl 5-(p-tolyl)-1H-pyrrole-2,3,4-tricarboxylate (4o):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 108-110 °C. Yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 9.66 (br, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 4.41 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 2.38 (s, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.21 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 162.7, 160.3, 140.3, 139.6, 129.2, 128.8, 127.1, 125.1, 119.1, 112.1, 61.6, 60.4, 52.1, 21.3, 14.1, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: 360.1447. Found: 360.1447.

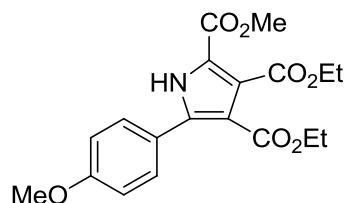
3,4-diethyl 2-methyl 5-(m-tolyl)-1H-pyrrole-2,3,4-tricarboxylate (4p):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 79-81 °C. Yield: 45%. ^1H NMR (400 MHz, CDCl_3) δ 9.44 (br, 1H), 7.37-7.33 (m, 2H), 7.31-7.29 (m, 1H), 7.25-7.23 (m, 1H), 4.43 (q, $J = 7.2$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 2.39 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz,

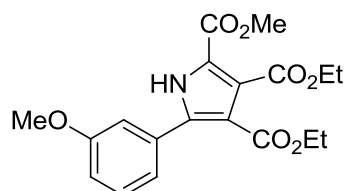
3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 162.7, 160.2, 140.1, 137.9, 130.3, 130.0, 129.8, 128.1, 126.5, 125.1, 119.2, 112.3, 61.7, 60.4, 52.2, 21.4, 14.2, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: 360.1447. Found: 360.1451.

3,4-diethyl 2-methyl 5-(4-methoxyphenyl)-1H-pyrrole-2,3,4-tricarboxylate (4q):



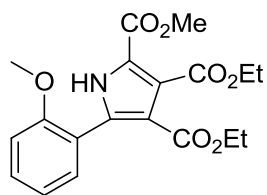
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 113-115 °C. Yield: 55%. ^1H NMR (400 MHz, CDCl_3) δ 9.35 (br, 1H), 7.51 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.42 (q, $J = 7.2$ Hz, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 3.84 (s, 3H), 1.41 (t, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 162.7, 160.6, 160.2, 140.1, 130.7, 125.1, 122.3, 119.0, 113.7, 111.8, 61.6, 60.4, 55.4, 52.2, 14.2, 14.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_7$: 376.1396. Found: 376.1385.

3,4-diethyl 2-methyl 5-(3-methoxyphenyl)-1H-pyrrole-2,3,4-tricarboxylate (4r):



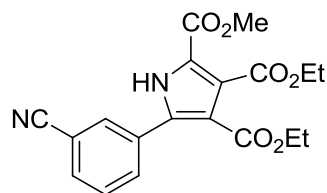
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 93-95 °C. Yield: 63%. ^1H NMR (400 MHz, CDCl_3) δ 9.62 (br, 1H), 7.33 (t, $J = 8.2$ Hz, 1H), 7.13-7.11 (m, 2H), 6.98-6.95 (m, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 162.6, 160.2, 159.2, 139.7, 131.2, 129.3, 125.1, 121.6, 119.3, 115.1, 115.0, 112.4, 61.7, 60.5, 55.3, 52.2, 14.1, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_7$: 376.1396. Found: 376.1390.

3,4-diethyl 2-methyl 5-(2-methoxyphenyl)-1H-pyrrole-2,3,4-tricarboxylate (4s):



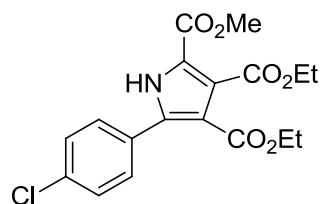
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 42%. ^1H NMR (400 MHz, CDCl_3) δ 9.62 (br, 1H), 7.52-7.49 (m, 1H), 7.41-7.37 (m, 1H), 7.03-6.96 (m, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.2$ Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 162.9, 160.2, 156.8, 136.0, 132.2, 130.9, 124.4, 120.3, 119.0, 118.4, 113.4, 111.0, 61.6, 60.3, 55.6, 52.1, 14.2, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_7$: 376.1396. Found: 376.1392.

3,4-diethyl 2-methyl 5-(3-cyanophenyl)-1H-pyrrole-2,3,4-tricarboxylate (4t):



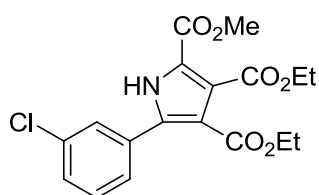
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 111-113 °C. Yield: 50%. ^1H NMR (400 MHz, CDCl_3) δ 10.00 (br, 1H), 7.90-7.89 (m, 1H), 7.83-7.81 (m, 1H), 7.73-7.70 (m, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 4.42 (q, $J = 7.2$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.80 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.0, 162.3, 160.2, 137.1, 133.9, 133.1, 132.7, 131.4, 129.1, 125.2, 120.2, 118.0, 113.1, 112.5, 61.8, 60.8, 52.4, 14.1, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_6$: 371.1243. Found: 371.1240.

3,4-diethyl 2-methyl 5-(4-chlorophenyl)-1H-pyrrole-2,3,4-tricarboxylate (4u):



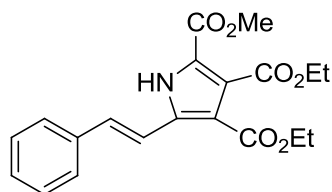
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 104-106 °C. Yield: 51%. ¹H NMR (400 MHz, CDCl₃) δ 9.69 (br, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 162.5, 160.2, 138.7, 135.7, 130.7, 128.5, 125.1, 119.6, 112.6, 61.7, 60.6, 52.3, 14.1, 13.9; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₈H₁₈ClNO₆: 380.0901. Found: 380.0905.

3,4-diethyl 2-methyl 5-(3-chlorophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4v):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 97-99 °C. Yield: 64%. ¹H NMR (400 MHz, CDCl₃) δ 9.67 (br, 1H), 7.57-7.56 (m, 1H), 7.46-7.34 (m, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 162.4, 160.1, 138.0, 134.1, 131.8, 129.5, 129.5, 129.5, 127.6, 125.2, 119.8, 112.9, 61.7, 60.6, 52.3, 14.1, 13.9; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₈H₁₈ClNO₆: 380.0901. Found: 380.0907.

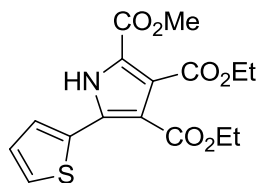
(E)-3,4-diethyl 2-methyl 5-styryl-1*H*-pyrrole-2,3,4-tricarboxylate (4w):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 51%. ¹H NMR (400 MHz, CDCl₃) δ 9.63 (br, 1H), 7.77 (d, *J* = 16.8 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.06 (d, *J* = 16.8 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.39 (t, *J* = 7.0

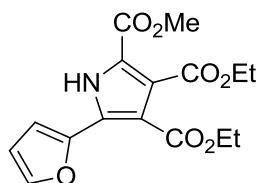
Hz, 3H), 1.35 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 163.0, 160.2, 137.5, 135.8, 132.1, 128.9, 128.8, 127.0, 124.9, 119.5, 116.1, 112.8, 61.7, 60.5, 52.3, 14.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_6$: 372.1447. Found: 372.1450.

3,4-diethyl 2-methyl 5-(thiophen-2-yl)-1H-pyrrole-2,3,4-tricarboxylate (4x):



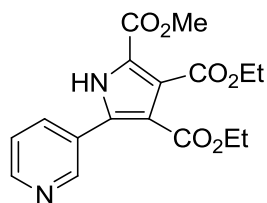
The title compound was prepared according to the general procedure. The product was obtained as light brown solid. mp: 105-107 °C. Yield: 50%. ^1H NMR (400 MHz, CDCl_3) δ 9.41 (br, 1H), 7.58-7.57 (m, 1H), 7.46-7.44 (m, 1H), 7.12-7.09 (m, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.86 (s, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 162.5, 159.9, 133.0, 130.4, 129.5, 128.1, 127.4, 125.2, 119.4, 112.4, 61.7, 60.7, 52.3, 14.1, 14.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_6\text{S}$: 352.0855. Found: 352.0861.

3,4-diethyl 2-methyl 5-(furan-2-yl)-1H-pyrrole-2,3,4-tricarboxylate (4y):



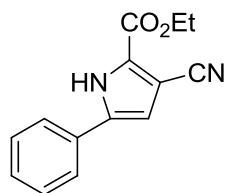
The title compound was prepared according to the general procedure. The product was obtained as pale yellow solid. mp: 115-117 °C. Yield: 37%. ^1H NMR (400 MHz, CDCl_3) δ 9.60 (br, 1H), 7.61-7.61 (m, 1H), 7.50-7.49 (m, 1H), 6.54-6.53 (m, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 4.30 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.34 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 162.4, 159.8, 144.0, 143.0, 129.8, 125.3, 119.0, 113.9, 112.5, 110.4, 61.6, 60.7, 52.2, 14.1, 14.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_7$: 336.1083. Found: 336.1085.

3,4-diethyl 2-methyl 5-(pyridin-3-yl)-1H-pyrrole-2,3,4-tricarboxylate (4z):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 148-150 °C. Yield: 40%. ^1H NMR (400 MHz, CDCl_3) δ 10.77 (br, 1H), 8.66 (br, 2H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.39 (br, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.20 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.3, 162.4, 160.2, 150.1, 149.4, 137.7, 136.4, 126.7, 125.2, 122.9, 120.4, 113.1, 61.8, 60.7, 52.4, 14.2, 13.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_6$: 347.1243. Found: 347.1239.

Ethyl 3-cyano-5-phenyl-1H-pyrrole-2-carboxylate (4aa):

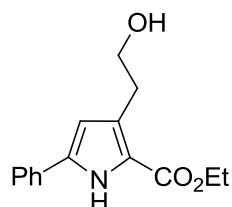


The title compound was prepared according to the general procedure. The product was obtained as colorless solid. mp: 181-183 °C. Yield: 30%. ^1H NMR (400 MHz, CDCl_3) δ 10.0 (br, 1H), 7.59-7.57 (m, 2H), 7.47-7.43 (m, 2H), 7.41-7.37 (m, 1H), 6.81 (d, $J = 2.4$ Hz, 1H), 4.43 (q, $J = 7.2$ Hz, 2H), 1.43 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 136.8, 129.5, 129.3, 129.0, 127.2, 125.2, 114.7, 111.8, 99.5, 62.0, 14.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: 241.0977. Found: 241.0972. For NOESY data, see p. 123 and 124.

General procedure for pyrroles via intramolecular reaction: A solution of α -diazo oxime ethers in ACN was irradiated at 302 nm under Rayonet photoreactor at RT for 16 h. Then the mixtures were treated with aqueous 1N HCl at RT overnight. After the completion of the reaction, it was diluted with CH_2Cl_2 , dried over anhydrous MgSO_4 and evaporated under

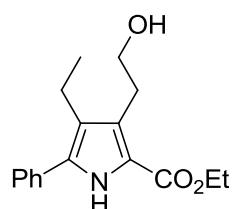
reduced pressure. The crude compound was purified by column chromatography using hexane: ethyl acetate (3:2) to give pyrroles.

Ethyl 3-(2-hydroxyethyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (6a):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 103-105 °C. Yield: 48%. ¹H NMR (400 MHz, CDCl₃) δ 9.31 (br, 1H), 7.55-7.53 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.28 (m, 1H), 6.46 (d, *J* = 2.8 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.90 (t, *J* = 6.2 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 135.6, 131.1, 130.4, 129.0, 127.8, 124.7, 120.0, 109.7, 63.4, 60.4, 30.6, 14.5; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₅H₁₇NO₃: 260.1287. Found: 260.1292.

Ethyl 4-ethyl-3-(2-hydroxyethyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (6b):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 81-83 °C. Yield: 43%. ¹H NMR (400 MHz, CDCl₃) δ 8.84 (br, 1H), 7.47-7.42 (m, 4H), 7.38-7.34 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.09 (t, *J* = 6.6 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.30 (br, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 133.0, 132.4, 128.9, 128.6, 127.8, 127.4, 124.8, 119.1, 63.8, 60.2, 28.4, 17.3, 16.2, 14.5; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₂₁NO₃: 288.1600. Found: 288.1601.

