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Supporting Information

Thermal [2+2]-Cycloaddition of CF₃-Substituted Allenynes: Access to Novel Cyclobutene-Containing α-Amino Acids

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1. General remarks

All solvents were freshly distilled from appropriate drying agents before use. All other reagents were re-crystallized or distilled as necessary. Reactions were performed under an argon atmosphere. Analytical TLC was performed with Merck silica gel 60 F254 plates. Visualization was accomplished by UV light or spraying by Ce(SO$_4$)$_2$, solution in 5% H$_2$SO$_4$. Column chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM) and ethyl acetate/ hexanes as eluent. NMR spectra were recorded at room temperature on a Bruker AV-200, AV-300, AV-600 spectrometers operating at 200 MHz, 300 MHz, 600 MHz, respectively (TMS reference) for $^1$H; 50, 75 and 151 MHz for $^{13}$C; 282 MHz for $^{19}$F (CF$_3$COOH reference).

N-Methyl-N-prop-2-yn-1-ylbut-3-yn-1-amine. 4-Bromo-1-butyn (4.55g, 34.2 mmol) was added to refluxed mixture of N-methyl-N-propargylamine (2.36 g, 34.2 mmol), cesium carbonate (16.7 g, 51.2 mmol) and potassium iodide (1g, 6 mmol) in dry acetonitryle (45ml). Then reaction mixture was refluxed under vigorous stirring overnight. Inorganic precipitate was filtered off, solvent was removed by distillation at atmospheric pressure, and residue was distilled in vacuum (30 mmHg) to give product 2.5 g (60%) as yellowish liquid. Bp. 70-73°C (30 mmHg); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.45 (d, $J$ = 2.3 Hz, 2H, NCH$_2$), 2.70 (t, $J$ = 7.2 Hz, 2H, NCH$_2$), 2.45–2.38 (m, 5H, CH$_2$+NCH$_3$), 2.28 (t, $J$ = 2.4 Hz, 1H, CH), 2.04 (t, $J$ = 2.6 Hz, 1H, CH). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 82.26, 77.89, 73.25, 68.94, 53.82, 45.16, 41.33, 17.32. Anal. calcd for C$_8$H$_{11}$N (%): C, 79.29; H, 9.15; N, 11.56. Found: C, 79.33; H, 9.01; N, 11.78.

Methyl 2-[but-3-yn-1-yl(methyl)amino]-2-(trifluoromethyl)penta-3,4-dienoate 3. A mixture of N-homopropargyl-N-propargyl-N-methylamine (1.0 g, 8.3 mmol), copper trifluoroacetylacetonate (0.3 g, 10 mol %) and diazocompound 1 (1.4 g, 8.3 mmol) in anhydrous
toluene (20 mL) was stirred under heating (100°C) for 2-3 h. After the reaction completion (TLC) the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (EtOAc-hexanes: 1 - 15). Yield: 60% (colorless oil); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.38 (t, $J = 6.8$ Hz, 1H, CH$_{\text{allene}}$), 5.04 (d, $J = 6.8$ Hz, 2H, CH$_{2\text{allene}}$), 3.84 (s, 3H, COOMe), 2.97 (t, $J = 7.4$ Hz, 2H, CH$_2$), 2.56 (s, 3H, NMe), 2.40 (td, $J = 7.4$, 2.6 Hz, 2H, CH$_2$), 2.01 (t, $J = 2.6$ Hz, 1H, CH). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 208.90, 167.41, 124.53 (q, $J = 290.7$ Hz), 87.72, 82.10, 78.95, 74.32 (q, $J = 24.7$ Hz), 69.11, 52.34, 52.22, 37.25, 18.90. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: 9.57 (s, 3F, CF$_3$). Anal. calcd for C$_{12}$H$_{14}$F$_3$NO$_2$ (%): C, 55.17; H, 5.40; N, 5.36. Found: C, 55.30; H, 5.24; N, 5.54.

2. General procedure for Sonogashira coupling

Solution of corresponding aryl iodide (1.04 mmol) and 1,5- or 1,6 allenyne (0.81 mmol) in dry DMF (3 ml) was placed in flame dried Schlenk tube, then triethylamine (0.5 ml) was added, and reaction mixture was cooled to -78°C and air atmosphere was replaced by argon. Then PdCl$_2$(PPh$_3$)$_2$ (0.04 mmol) and CuI (0.04 mmol) were added sequentially in an argon flow, and the reaction mixture was allowed to stay overnight at rt under vigorous stirring. The mixture was diluted with EtOAc and washed with water twice. The organic layer was separated, washed with 1 N HCl, dried over MgSO$_4$, and evaporated in vacuum to give crude product, which was chromatographed on silica gel eluting with hexanes- EtOAc mixture to give pure product.

Methyl 2-[methyl(3-phenylprop-2-yn-1-yl)amino]-2-(trifluoromethyl)penta-3,4-dienoate 4a.

Yield: 82% (colorless oil); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 7.51 – 7.39 (m, 2H, H$_{\text{arom.}}$), 7.38 – 7.25 (m, 3H, H$_{\text{arom.}}$), 5.46 (t, $J = 6.8$ Hz, 1H, CH$_{\text{allene}}$), 5.06 (d, $J = 6.8$ Hz, 2H, CH$_{2\text{allene}}$), 3.87 (s, 2H, CH$_2$), 3.84 (s, 3H, COOMe), 2.73 (s, 3H, NMe) $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 209.64, 167.48, 132.07, 128.64, 128.53, 125.04 (q, $J = 290.3$ Hz), 123.54, 87.84 (q, $J = 1.5$ Hz), 86.10, 84.56, 79.63, 73.98 (q, $J = 25.2$ Hz), 53.04, 43.36 (q, $J = 2.0$ Hz), 37.85 (q, $J = 1.7$ Hz). $^{19}$F NMR (188 MHz, CDCl$_3$) $\delta$: -67.80 (s, 3F, CF$_3$). Anal. calcd for C$_{17}$H$_{16}$F$_3$NO$_2$ (%):C, 63.15; H, 4.99; N, 4.33. Found: C, 63.39; H, 5.14; N, 4.81.
Methyl 2-{methyl[3-(4-methylphenyl)prop-2-yn-1-yl]amino}-2-(trifluoromethyl)penta-3,4-dienoate 4b. Yield: 74% (colorless oil); $^1$H NMR (200 MHz, C$_6$D$_6$) $\delta$ 7.36 (d, $J$ = 8.1 Hz, 2H, H$_{arom}$), 6.81 (d, $J$ = 8.1 Hz, 2H, H$_{arom}$), 5.36 (t, $J$ = 6.8 Hz, 1H, CH$_{allene}$), 4.58 (d, $J$ = 6.9 Hz, 2H, CH$_{2allene}$), 3.85 (s, 2H, CH$_2$), 3.28 (s, 3H, COOMe), 2.68 (s, 3H, NMe), 1.98 (s, 3H, CH$_3$). $^{13}$C NMR (50 MHz, C$_6$D$_6$) $\delta$ 209.54, 166.93, 138.31, 132.01, 129.42, 125.49 (q, $J$ = 290.2 Hz), 120.88, 97.84, 88.18, 84.74, 79.03, 72.47 (q, $J$ = 25.3 Hz), 52.04, 43.38, 37.65, 21.28. $^{19}$F NMR (188 MHz, C$_6$D$_6$) $\delta$: -67.81 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_2$ (%): C, 64.09; H, 5.38; N, 4.15; Found: C, 64.73; H, 5.59; N, 3.88.

Methyl 2-{methyl[3-(2-methylphenyl)prop-2-yn-1-yl]amino}-2-(trifluoromethyl)penta-3,4-dienoate 4c. Yield: 81% (colorless oil); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J$ = 7.3 Hz, 1H, H$_{arom}$), 7.33 – 7.03 (m, 3H, H$_{arom}$), 5.48 (t, $J$ = 6.8 Hz, 1H, CH$_{allene}$), 5.06 (d, $J$ = 6.8 Hz, 2H, CH$_{2allene}$), 3.92 (s, $J$ = 8.4 Hz, 2H, CH$_2$), 3.83 (s, 3H, COOCH$_3$), 2.75 (s, 3H, NCH$_3$), 2.46 (s, 3H, CH$_3$). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 208.19, 166.10, 139.13, 130.96, 128.32, 127.07, 124.42, 123.59 (q, $J$ = 290.5 Hz), 121.88, 88.52, 86.43 (q, $J$ = 1.4 Hz), 82.01, 78.18, 72.55 (q, $J$ = 25.2 Hz), 51.60, 42.00 (q, $J$ = 2.1 Hz), 36.38 (q, $J$ = 2.0 Hz), 19.63. $^{19}$F NMR (188 MHz, CDCl$_3$) $\delta$: -67.95 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_2$ (%): C, 64.09; H, 5.38; N, 4.15; Found: C, 63.79; H, 5.57; N, 4.33.

Methyl 2-[[3-(4-methoxyphenyl)prop-2-yn-1-yl](methyl)amino]-2-(trifluoromethyl)penta-3,4-dienoate 4d. Yield: 77% (yellowish oil); $^1$H NMR (200 MHz, C$_6$D$_6$) $\delta$ 7.37 (d, $J$ = 8.6 Hz, 2H, H$_{arom}$), 7.22 – 7.08 (m, 3H, H$_{arom}$), 5.43 (t, $J$ = 8.6 Hz, 1H, CH$_{allene}$), 4.39 (d, $J$ = 8.6 Hz, 2H, CH$_{2allene}$), 3.82 (s, 3H, COOMe), 2.67 (s, 3H, NMe), 1.97 (s, 3H, CH$_3$). $^{13}$C NMR (50 MHz, C$_6$D$_6$) $\delta$ 209.34, 166.92, 138.98, 132.03, 129.43, 125.54 (q, $J$ = 290.3 Hz), 120.89, 97.85, 88.23, 84.75, 79.05, 72.48 (q, $J$ = 25.3 Hz), 52.03, 43.39, 37.66, 21.29. $^{19}$F NMR (188 MHz, C$_6$D$_6$) $\delta$: -67.82 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_2$ (%): C, 64.09; H, 5.38; N, 4.15; Found: C, 63.79; H, 5.57; N, 4.33.
2H, H$_{\text{arom.}}$), 6.59 (d, $J = 8.6$ Hz, 2H, H$_{\text{arom.}}$), 5.38 (t, $J = 6.8$ Hz, 1H, CH$_2$allene), 4.59 (d, $J = 6.8$ Hz, 2H, CH$_2$allene), 3.88 (s, 2H, CH$_2$), 3.29 (s, 3H, COOMe), 3.19 (s, 3H, OCH$_3$), 2.70 (s, 3H, NCH$_3$).

$^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 209.08, 166.53, 159.61, 133.10, 125.08 (q, $J = 289.8$ Hz), 115.47, 113.91, 87.78, 84.62, 84.14, 78.60, 73.70 (q, $J = 25.1$ Hz), 54.34 (q, $J = 2.8$ Hz), 51.61 (q, $J = 4.4$ Hz), 43.03, 37.26. $^{19}$F NMR (188 MHz, C$_6$D$_6$) $\delta$: -67.87 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_3$ (%): C, 61.19; H, 5.13; N, 3.96. Found: C, 61.46; H, 5.31; N, 3.58.

Methyl 2-[[3-(2-methoxyphenyl)prop-2-yn-1-yl](methyl)amino]-2-(trifluoromethyl)penta-3,4-dienoate 4e. Yield: 73% (yellowish oil); $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 7.56 (dd, $J = 7.5$, 1.6 Hz, 1H, H$_{\text{arom.}}$), 7.10 (td, $J = 7.9$, 1.6 Hz, 1H, H$_{\text{arom.}}$), 6.79 (t, $J = 7.5$ Hz, 1H, H$_{\text{arom.}}$), 6.54 (d, $J = 8.3$ Hz, 1H, H$_{\text{arom.}}$), 5.50 (t, $J = 6.8$ Hz, 1H, CH$_2$allene), 4.68 (d, $J = 6.8$ Hz, 2H, CH$_2$allene), 4.01 (s, 2H, CH$_2$), 3.40 (s, 3H, COOCH$_3$), 3.38 (s, 3H, OCH$_3$), 2.84 (s, 3H, NCH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 209.07, 166.51, 160.42, 133.52, 129.22, 125.06 (q, $J = 289.8$ Hz), 120.16, 112.87, 110.51, 90.14, 87.68, 80.81, 78.50, 73.75 (q, $J = 25.0$ Hz), 54.72 (q, $J = 3.7$ Hz), 51.54 (q, $J = 3.6$ Hz), 43.23, 37.22. $^{19}$F NMR (282 MHz, C$_6$D$_6$) $\delta$: 10.23 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_3$ (%): C, 61.19; H, 5.13; N, 3.96. Found: C, 61.05; H, 5.35; N, 4.15.

Methyl 2-[(methyl)[3-(4-nitrophenyl)prop-2-yn-1-yl]amino]-2-(trifluoromethyl)penta-3,4-dienoate 4f. Yield: 80% (yellowish oil); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 8.14 (d, $J = 8.9$ Hz, 2H, H$_{\text{arom.}}$), 7.54 (d, $J = 8.9$ Hz, 2H, H$_{\text{arom.}}$), 5.40 (t, $J = 6.8$ Hz, 1H, CH$_2$allene), 5.04 (d, $J = 6.8$ Hz, 2H, CH$_2$allene), 3.87 (s, 2H, CH$_2$), 3.81 (s, 3H, COOCH$_3$), 2.69 (s, 3H, NCH$_3$). $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 209.65, 167.31, 147.34, 132.78, 130.43, 124.95 (q, $J = 290.5$ Hz), 123.86, 92.03, 87.73 (q, $J = 1.4$ Hz), 82.75, 79.78, 73.97 (q, $J = 25.4$ Hz), 53.11, 43.37 (d, $J = 2.0$ Hz), 37.97 (d, $J =
2.0 Hz). $^{19}$F NMR (188 MHz, CDCl$_3$) $\delta$: -67.92 (s, 3F, CF$_3$). Anal. Calcd for C$_{17}$H$_{15}$F$_3$N$_2$O$_4$ (%): C, 55.44; H, 4.11; N, 7.61. Found: C, 55.69; H, 4.41; N, 7.78.

Methyl 2-{methyl[3-(2-nitrophenyl)prop-2-yn-1-yl]amino}-2-(trifluoromethyl)penta-3,4-dienoate 4g. Yield: 82% (yellowish oil); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.99 (d, $J = 8.0$ Hz, 1H, H$_{arom}$.), 7.71 – 7.30 (m, 3H, H$_{arom}$.), 5.41 (t, $J = 6.8$ Hz, 1H, CH$_{allene}$), 5.02 (d, $J = 6.8$ Hz, 2H, CH$_2$allene), 3.90 (s, 2H, CH$_2$), 3.79 (s, 3H, COOCH$_3$), 2.71 (s, 3H, NCH$_3$). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 209.24, 166.54, 150.15, 134.38, 132.01, 128.12, 127.07 (q, $J = 298.4$ Hz), 124.14, 118.22, 94.64, 87.62, 79.29, 78.83, 73.79 (q, $J = 25.3$ Hz), 51.79, 43.20 (q, $J = 1.6$ Hz), 37.44 (q, $J = 1.7$ Hz). $^{19}$F NMR (188 MHz, CDCl$_3$) $\delta$: -68.06 (s, 3F, CF$_3$). Anal. Calcd for C$_{17}$H$_{15}$F$_3$N$_2$O$_4$ (%): C, 55.44; H, 4.11; N, 7.61. Found: C, 55.71; H, 4.32; N, 7.78.

Methyl 2-[methyl(4-phenylbut-3-yn-1-yl)amino]-2-(trifluoromethyl)penta-3,4-dienoate 5a. Yield: 84% (yellowish oil); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.55 – 7.41 (m, 2H, CH$_{arom}$.), 7.40 – 7.24 (m, 3H, CH$_{arom}$.), 5.45 (t, $J = 6.8$ Hz, 1H, CH$_{allene}$), 5.07 (d, $J = 6.8$ Hz, 2H, CH$_2$allene), 3.87 (s, 3H, COOMe), 3.08 (t, $J = 7.4$ Hz, 2H, CH$_2$), 2.77 – 2.52 (m, 5H, CH$_2$+NMe). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 208.94, 167.54, 131.39, 128.09, 127.58, 124.63 (q, $J = 290.7$ Hz), 123.54, 87.85, 87.79, 81.40, 79.01, 74.45 (d, $J = 24.7$ Hz), 52.47, 52.38, 37.39, 19.95. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: 9.69 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{18}$F$_3$NO$_2$ (%): C, 64.09; H, 5.38; N, 4.15. Found: C, 64.25; H, 5.01; N, 4.38.
Methyl 2-{methyl[4-(4-nitrophenyl)but-3-yn-1-yl]amino}-2-(trifluoromethyl)penta-3,4-dienoate 5b. Yield: 65% (yellowish oil); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.8$ Hz, 2H, CH$_{arom.}$), 6.87 (d, $J = 8.8$ Hz, 2H, CH$_{arom.}$), 5.44 (t, $J = 6.8$ Hz, 1H, CH$_{arom.}$), 5.06 (d, $J = 6.8$ Hz, 2H, CH$_{arom.}$), 3.86 (s, 3H, COOMe), 3.85 (s, 3H, OMe), 3.05 (t, $J = 7.4$ Hz, 2H, CH$_2$), 2.71 – 2.50 (m, 5H, CH$_2$+NMe). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 209.09, 167.70, 159.16, 138.19, 132.89, 124.78 (q, $J = 290.7$ Hz), 113.85, 88.00, 86.28, 81.28, 79.13, 74.59 (q, $J = 24.7$ Hz), 55.22, 52.74, 52.53, 37.53, 20.09. $^{19}$F NMR (282 MHz, CDCl$_3$) δ: 9.68 (s, 3F, CF$_3$). Anal. Calcd for C$_{19}$H$_{20}$F$_3$NO$_3$ (%): C, 62.12; H, 5.49; N, 3.81. Found: C, 61.93; H, 5.61; N, 3.41.

Methyl 2-{methyl[4-(4-nitrophenyl)but-3-yn-1-yl]amino}-2-(trifluoromethyl)penta-3,4-dienoate 5c. Yield: 80% (yellowish oil); $^1$H NMR (300 MHz, CDCl$_3$) δ 8.21 (d, $J = 8.9$ Hz, 2H, H$_{arom.}$), 7.57 (d, $J = 8.9$ Hz, 2H, H$_{arom.}$), 5.42 (t, $J = 6.8$ Hz, 1H, CH$_{allene}$), 5.07 (d, $J = 6.8$ Hz, 2H, CH$_{allene}$), 3.87 (s, 3H, COOMe), 3.09 (t, $J = 7.2$ Hz, 2H, CH$_2$), 2.68 (t, $J = 7.2$ Hz, 2H, CH$_2$), 2.63 (s, 3H, NMe). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 208.96, 167.42, 146.56, 132.12, 130.63, 124.56 (q, $J = 290.4$ Hz), 123.38, 94.02, 87.76, 80.05, 79.13, 74.44 (q, $J = 24.8$ Hz), 52.44, 52.06, 37.39, 20.06. $^{19}$F NMR (282 MHz, CDCl$_3$) δ: 9.61 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{17}$F$_3$N$_2$O$_4$ (%): C, 56.55; H, 4.48; N, 7.33. Found: C, 56.88; H, 4.70; N, 7.06.
3. General procedure for [2+2]-cycloaddition of 1,5-allenynes

Solution of the corresponding 1,6-allenyne (200 mg) in dry toluene (4 ml) was placed in flame dried Schlenk tube and heated up to 110°C for 2 hours in an argon atmosphere. Then reaction mixture was cooled down to rt and TLC showed complete disappearance of starting material. Solvent was removed under reduced pressure, and the residual oil was chromatographed with mixture of hexanes-EtOAc furnishing bicyclic products.

Methyl 3-methyl-8-phenyl-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6a. Yield: 80% (yellowish oil); \(^1^H\) NMR (200 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.21 – 6.92 (m, 5H, H\(_{\text{arom.}}\)), 5.33 (s, 1H, CH), 3.58 (s, 2H, CH\(_2\)), 3.35 (s, 3H, COOCH\(_3\)), 3.00 (t, \(J = 3.0\) Hz, 2H), 2.52 (q, \(J = 1.7\) Hz, 3H, NCH\(_3\)). \(^{13}\)C NMR (50 MHz, C\(_6\)D\(_6\)) \(\delta\) 167.27, 139.40, 137.95, 135.06, 127.39, 127.09, 126.92, 125.58, 125.11 (q, \(J = 292.2\) Hz), 101.23 (q, \(J = 2.2\) Hz), 68.61 (q, \(J = 25.2\) Hz), 50.86, 47.08, 39.18 (q, \(J = 1.6\) Hz), 34.38. \(^{19}\)F NMR (188 MHz, C\(_6\)D\(_6\)) \(\delta\): -67.22 (s, 3F, CF\(_3\)). Anal. Calcd for C\(_{17}\)H\(_{16}\)F\(_3\)NO\(_2\) (%): C, 63.15; H, 4.99; N, 4.33. Found: C, 63.31; H, 4.73; N, 4.55.

Methyl 3-methyl-8-(4-methylphenyl)-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6b. Yield: 80% (white solid) mp = 101-103 °C; \(^1^H\) NMR (200 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.05 (s, 4H, H\(_{\text{arom.}}\)), 5.43 (s, 1H, CH), 3.69 (s, 2H, CH\(_2\)), 3.40 (s, 3H, COOCH\(_3\)), 3.11 (t, \(J = 2.8\) Hz, 2H, CH\(_2\)), 2.61 (q, \(J = 1.4\) Hz, 3H, NCH\(_3\)), 2.19 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (50 MHz, C\(_6\)D\(_6\)) \(\delta\) 168.78, 140.97, 139.42, 138.34, 135.60, 131.91, 129.60, 128.41, 127.09, 126.60 (q, \(J = 292.5\) Hz), 102.23 (q, \(J = 2.4\) Hz), 52.22, 48.58, 40.65 (q, \(J = 2.3\) Hz), 35.88, 21.44. \(^{19}\)F NMR (188 MHz, C\(_6\)D\(_6\)) \(\delta\): -67.12 (s, 3F, CF\(_3\)). Anal. Calcd for C\(_{18}\)H\(_{18}\)F\(_3\)NO\(_2\) (%): C, 64.09; H, 5.38; N, 4.15. Found: C, 64.34; H, 5.53; N, 4.44.
Methyl 3-methyl-8-(2-methylphenyl)-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6c. Yield: 90% (yellowish oil); \(^1\)H NMR (200 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.06 – 6.87 (m, 4H, H\(_{\text{arom.}}\)), 5.35 (s, 1H, CH), 3.65 (s, 2H, CH\(_2\)), 3.34 (s, 3H, COOCH\(_3\)), 3.12 (t, \(J = 3.0\) Hz, 2H, CH\(_2\)), 2.51 (q, \(J = 1.7\) Hz, 3H, NCH\(_3\)), 2.06 (s, 3H, CH\(_3\)). \(^1\)C NMR (50 MHz, C\(_6\)D\(_6\)) \(\delta\) 167.27, 140.02, 138.69, 135.50, 134.42, 132.15, 129.79, 127.45, 127.23, 125.15 (q, \(J = 292.2\) Hz), 124.80, 100.89, 68.49 (q, \(J = 25.1\) Hz), 50.80, 48.49, 39.15, 37.12, 19.56. \(^1\)F NMR (188 MHz, C\(_6\)D\(_6\)) \(\delta\): -67.12 (s, 3F, CF\(_3\)).

Anal. Calcd for C\(_{18}\)H\(_{18}\)F\(_3\)NO\(_2\) (%): C, 64.09; H, 5.38; N, 4.15; Found: C, 64.21; H, 5.47; N, 4.35.

Methyl 8-(4-methoxyphenyl)-3-methyl-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6d. Yield: 86% (colorless oil); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 6.97 (d, \(J = 8.6\) Hz, 2H, H\(_{\text{arom.}}\)), 6.74 (d, \(J = 8.6\) Hz, 2H, H\(_{\text{arom.}}\)), 5.35 (s, 1H, CH), 3.62 (s, 2H, CH\(_2\)), 3.33 (s, 3H, COOCH\(_3\)), 3.29 (s, 3H, OCH\(_3\)), 3.04 (t, \(J = 2.9\) Hz, 2H, CH\(_2\)), 2.56 (q, \(J = 1.1\) Hz, 3H, NCH\(_3\)). \(^1\)C NMR (151 MHz, C\(_6\)D\(_6\)) \(\delta\) 168.57, 159.95, 140.71, 138.87, 133.87, 128.29, 127.19, 126.38 (q, \(J = 292.1\) Hz), 114.20, 101.18 (q, \(J = 2.2\) Hz), 69.84 (q, \(J = 25.2\) Hz), 54.60, 51.94, 48.30, 40.41, 35.67. \(^1\)F NMR (188 MHz, C\(_6\)D\(_6\)) \(\delta\): -67.19 (s, 3F, CF\(_3\)). Calcd for C\(_{18}\)H\(_{18}\)F\(_3\)NO\(_3\) (%): C, 61.19; H, 5.13; N, 3.96. Found: C, 61.41; H, 5.27; N, 4.20.

Methyl 8-(2-methoxyphenyl)-3-methyl-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6e. Yield: 74% (yellowish oil); \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.17 – 7.10 (m, 1H), 7.02 (dd, \(J = 7.5\), 1.7 Hz, 1H, H\(_{\text{arom.}}\)), 6.87 (td, \(J = 7.4\), 0.9 Hz, 1H, H\(_{\text{arom.}}\)), 6.51 (d, \(J = 1.5\) Hz, 1H, H\(_{\text{arom.}}\)), 6.48 (d, \(J = 1.5\) Hz, 1H, H\(_{\text{arom.}}\)), 6.34 (d, \(J = 1.5\) Hz, 1H, H\(_{\text{arom.}}\)), 6.21 (d, \(J = 1.5\) Hz, 1H, H\(_{\text{arom.}}\)).
8.2 Hz, 1H, H_{arom.}), 5.54 (s, 1H), 4.04 (s, 2H, CH₂), 3.45 (s, 3H, COOCH₃), 3.24 (s, 3H, OCH₃), 3.22 (t, J = 3.0 Hz, 2H, CH₂), 2.75 (q, J = 1.7 Hz, 3H, NCH₃). ¹³C NMR (151 MHz, C₆D₆) δ 168.67, 156.89, 141.69, 137.65, 129.73, 128.48, 126.46 (q, J = 292.3 Hz), 123.37, 120.51, 110.13, 101.98 (q, J = 1.8 Hz), 69.85 (q, J = 25.2 Hz), 54.26, 51.91, 50.25, 40.47, 36.16. ¹⁹F NMR (282 MHz, C₆D₆) δ: 11.65 (s, 3F, CF₃). Calcd for C₁₈H₁₈F₃NO₃ (%): C, 61.19; H, 5.13; N, 3.96. Found: C, 61.32; H, 4.89; N, 3.77.

Methyl 3-methyl-8-(4-nitrophenyl)-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6f. Yield: 87% (red solid) mp = 129-131°C; ¹H NMR (200 MHz, CDCl₃) δ 7.88 (d, J = 8.8 Hz, 2H, H_{arom.}), 6.58 (d, J = 8.8 Hz, 2H, H_{arom.}), 5.40 (s, 1H, CH), 3.45 (s, 2H, CH₂), 3.33 (s, 3H, COOCH₃), 2.81 (t, J = 3.0 Hz, 2H, CH₂), 2.52 (q, J = 1.6 Hz, 3H, NCH₃). ¹³C NMR (50 MHz, C₆D₆) δ 166.77, 145.60, 139.45, 138.64, 138.07, 135.42, 125.50, 124.89 (q, J = 292.2 Hz), 122.55, 104.16, 68.54 (q, J = 24.8 Hz), 50.97, 46.93, 39.13, 34.34. ¹⁹F NMR (188 MHz, C₆D₆) δ: -67.16 (s, 3F, CF₃). Anal. Calcd for C₁₇H₁₅F₃N₂O₄ (%): C, 55.44; H, 4.11; N, 7.61. Found: C, 55.68; H, 4.33; N, 7.81.

Methyl 3-methyl-8-(2-nitrophenyl)-4-(trifluoromethyl)-3-azabicyclo[4.2.0]octa-1(8),5-diene-4-carboxylate 6g. Yield: 93% (reddish oil); ¹H NMR (200 MHz, C₆D₆) δ 7.08 (d, J = 8.0 Hz, 1H, H_{arom.}), 6.78 (t, J = 8.1 Hz, 1H, H_{arom.}), 6.69 – 6.50 (m, 2H, H_{arom.}), 5.33 (s, 1H, CH), 3.56 (s, 2H, CH₂), 3.27 (s, 3H, COOCH₃), 3.00 (t, J = 2.7 Hz, 2H, CH₂), 2.44 (q, J = 1.5 Hz, 3H, NCH₃). ¹³C NMR (50 MHz, C₆D₆) δ 166.79, 147.03, 140.86, 138.87, 131.83, 129.87, 128.21, 126.92, 126.75, 124.86 (q, J = 291.9 Hz), 122.28, 103.87, 68.44 (q, J = 25.0 Hz), 50.82, 47.76, 39.02, 35.73. ¹⁹F NMR (188 MHz, C₆D₆) δ: -67.23 (s, 3F, CF₃). Anal. Calcd for C₁₇H₁₅F₃N₂O₄ (%): C, 55.44; H, 4.11; N, 7.61. Found: C, 55.31; H, 4.35; N, 7.81.
4. General procedure for [2+2]-cycloaddition of 1,6-allenynes.

Solution of corresponding 1,6-allenyne (100 mg) in dry xylenes (3 ml) was placed in flame-dried Schlenk tube and heated up to 185°C for 36 hours in an argon atmosphere. Then reaction mixture was cooled down to rt and TLC showed complete disappearance of starting material. The resulting mixture was directly subjected on column with silica gel and chromatographed eluenting with hexanes-EtOAc mixture to give target [2+2]-adducts.

**Methyl 4-methyl-8-phenyl-3-(trifluoromethyl)-4-azabicyclo[5.2.0]nona-1,7-diene-3-carboxylate 7a.** Yield: 87% (colorless oil); \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)) \(\delta 7.36 – 7.13 \text{ (m, 5H, C}_6\text{H}_5\)), 5.51 (s, 1H, CH), 3.46 (s, 3H, COOMe), 3.43 – 3.24 (m, 1H, CH\(_2\)), 2.98 (s, 2H, CH\(_2\)), 2.93 – 2.77 (m, 1H, CH\(_2\)), 2.63 (s, 3H, NMe), 2.48 – 2.21 (m, 2H, CH\(_2\)). \(^{13}\)C NMR (75 MHz, C\(_6\)D\(_6\)) \(\delta 168.19, 143.51, 143.15, 141.10, 134.54, 128.36, 126.43, 125.56 \text{ (d, } J = 291.4 \text{ Hz)}, 127.49, 107.80, 77.10 \text{ (q, } J = 24.6 \text{ Hz)}, 52.11 \text{ (q, } J = 7.3 \text{ Hz)}, 50.69, 38.66, 33.85, 28.91. \(^{19}\)F NMR (282 MHz, C\(_6\)D\(_6\)) \(\delta: 10.38 \text{ (s, 3F, CF}_3\)). Anal. Calcd for C\(_{18}\)H\(_{18}\)F\(_3\)NO\(_2\) (%): C, 64.09; H, 5.38; N, 4.15. Found: C, 63.81; H, 5.53; N, 4.31.

**Methyl 8-(4-methoxyphenyl)-4-methyl-3-(trifluoromethyl)-4-azabicyclo[5.2.0]nona-1,7-diene-3-carboxylate 7b.** Yield: 88% (colorless oil); \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)) \(\delta 7.23 \text{ (d, } J = 8.7 \text{ Hz, 2H}), 6.90 \text{ (d, } J = 8.7 \text{ Hz, 2H}), 5.51 \text{ (s,1H, CH), 3.46 (s, 3H, COOMe), 3.41 (s, 3H, OMe), 3.41 – 3.32 (m, 1H, CH\(_2\)), 3.00-2.96 (m, 2H, CH\(_2\)), 2.96-2.82 (m, 1H, CH\(_2\)), 2.66 (s, 3H, NMe), 2.53 – 2.27 (m, 2H, CH\(_2\)). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 168.46, 159.92, 143.47, 143.44, 138.73, 128.08, 127.80, 125.78 \text{ (q, } J = 291.6 \text{ Hz)}, 114.12, 106.66, 77.28 \text{ (q, } J = 24.6 \text{ Hz), 54.54, 52.20, 50.94, 38.82, 34.11, 28.96. \(^{19}\)F NMR (282 MHz, C\(_6\)D\(_6\)) \(\delta: 10.38 \text{ (s, 3F, CF}_3\)). Anal. Calcd for C\(_{19}\)H\(_{20}\)F\(_3\)NO\(_3\) (%): C, 62.12; H, 5.49; N, 3.81. Found: C, 61.88; H, 5.38; N, 4.03.
Methyl 4-methyl-8-(4-nitrophenyl)-3-(trifluoromethyl)-4-azabicyclo[5.2.0]nona-1,7-diene-3-carboxylate 7c. Yield: 91% (yellow solid) mp = 160-162°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J$ = 8.9 Hz, 2H, H$_{arom}$), 7.51 (d, $J$ = 8.9 Hz, 2H, H$_{arom}$), 5.42 (s, 1H, CH), 3.90 (s, 3H, COOMe), 3.49 (dt, $J$ = 14.8, 5.7 Hz, 1H, CH$_2$), 3.3-3.23 (m, 2H, CH$_2$), 3.11 (dt, $J$ = 14.8, 5.7 Hz, 1H), 2.91–2.81 (m, 2H, CH$_2$), 2.65 (s, 3H, NMe). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.28, 146.53, 145.39, 142.25, 141.42, 140.19, 126.59, 124.31 (q, $J$ = 290.4 Hz), 123.90, 110.46, 76.87 (q, $J$ = 25.4 Hz), 53.32, 50.07, 37.76, 34.02, 28.56. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: 9.85 (s, 3F, CF$_3$). Anal. Calcd for C$_{18}$H$_{17}$F$_3$N$_2$O$_4$ (%): C, 56.55; H, 4.48; N, 7.33. Found: C, 56.71; H, 4.29; N, 7.17.
5. $^1$H and $^{13}$C NMR spectra of synthesized compounds.
$^1$H NMR spectra of N-Methyl-N-prop-2-yn-1-ylbut-3-yn-1-amine
$^{13}$C NMR spectra of N-Methyl-N-prop-2-yn-1-ylbut-3-yn-1-amine
$^1$H NMR spectra of compound 3
$^{13}$C NMR spectra of compound 3
$^1$H NMR spectra of compound 4a
$^{13}$C NMR spectra of compound 4a
$^1$H NMR spectra of compound 4b
$^{13}$C NMR spectra of compound 4b
$^1$H NMR spectra of compound 4c
$^{13}$C NMR spectra of compound 4c
$^{1}$H NMR spectra of compound 4d
$^{13}$C NMR spectra of compound 4d
$^1$H NMR spectra of compound 4e

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\begin{array}{c}
\text{Me} - \text{N} - \text{C} = \text{C} - \text{MeO} \\
\text{MeO}_2\text{C} - \text{C} = \text{C} - \text{MeO}
\end{array}
\]
$13^C$ NMR spectra of compound 4e
$^{1}$H NMR spectra of compound 4f
$^{13}$C NMR spectra of compound 4f
$^1$H NMR spectra of compound 4g
$^{13}$C NMR spectra of compound 4g
$^{1}$H NMR spectra of compound 5a
$^{13}C$ NMR spectra of compound 5a
$^1$H NMR spectra of compound 5b
$^{13}$C NMR spectra of compound 5b
$^1$H NMR spectra of compound 5c
$^{13}$C NMR spectra of compound 5c
$^1$H NMR spectra of compound 6a
$^{13}$C NMR spectra of compound 6a
$^{1}$H NMR spectra of compound 6b
$^{13}$C NMR spectra of compound 6b
$^{1}$H NMR spectra of compound 6c
$^{13}$C NMR spectra of compound 6c
$^1$H NMR spectra of compound 6d
$^{13}$C NMR spectra of compound 6d
$^1$H NMR spectra of compound 6e
$^{13}$C NMR spectra of compound 6e
\( ^1H\) NMR spectra of compound 6f
$^{13}$C NMR spectra of compound 6f
$^{1}$H NMR spectra of compound 6g
$^{13}$C NMR spectra of compound 6g
$^1$H NMR spectra of compound 7a
$^{13}$C NMR spectra of compound 7a
$^{1}$H NMR spectra of compound 7b
$^{13}$C NMR spectra of compound 7b
1H NMR spectra of compound 7c
$^{13}$C NMR spectra of compound 7c