Electronic Supplementary Material (ESI) for ChemComm.

Amino acid bioconjugation via iClick reaction of an oxanorbornadiene-masked alkyne with a $Mn^{I}(bpy)(CO)_3$-coordinated azide

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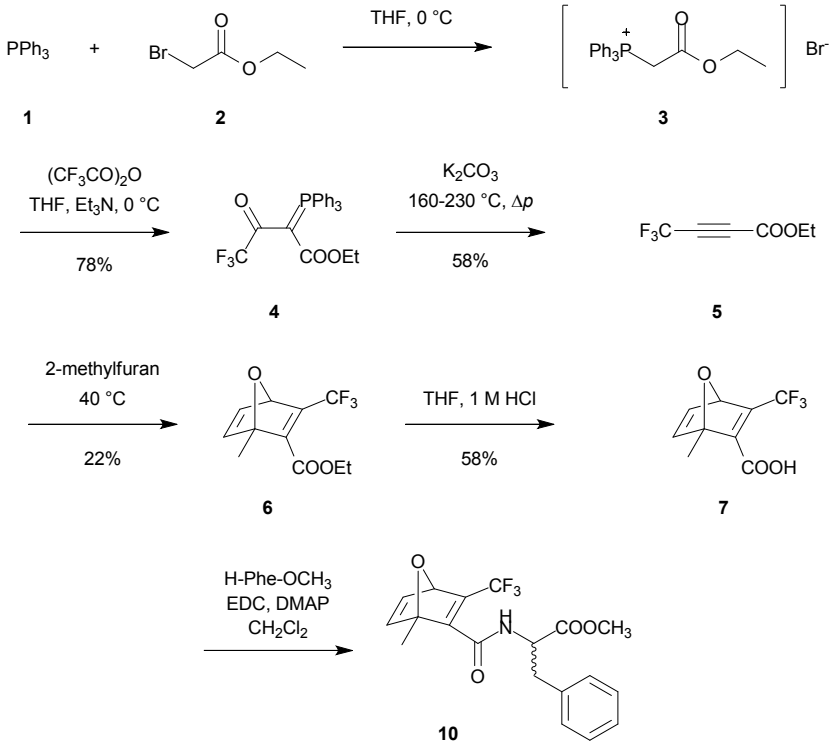
Supporting Information



Scheme S1 Synthesis of oxanorbornadiene(OND)-masked alkynes **6** and **10** for use in "iClick" reactions with metal-coordinated azides.

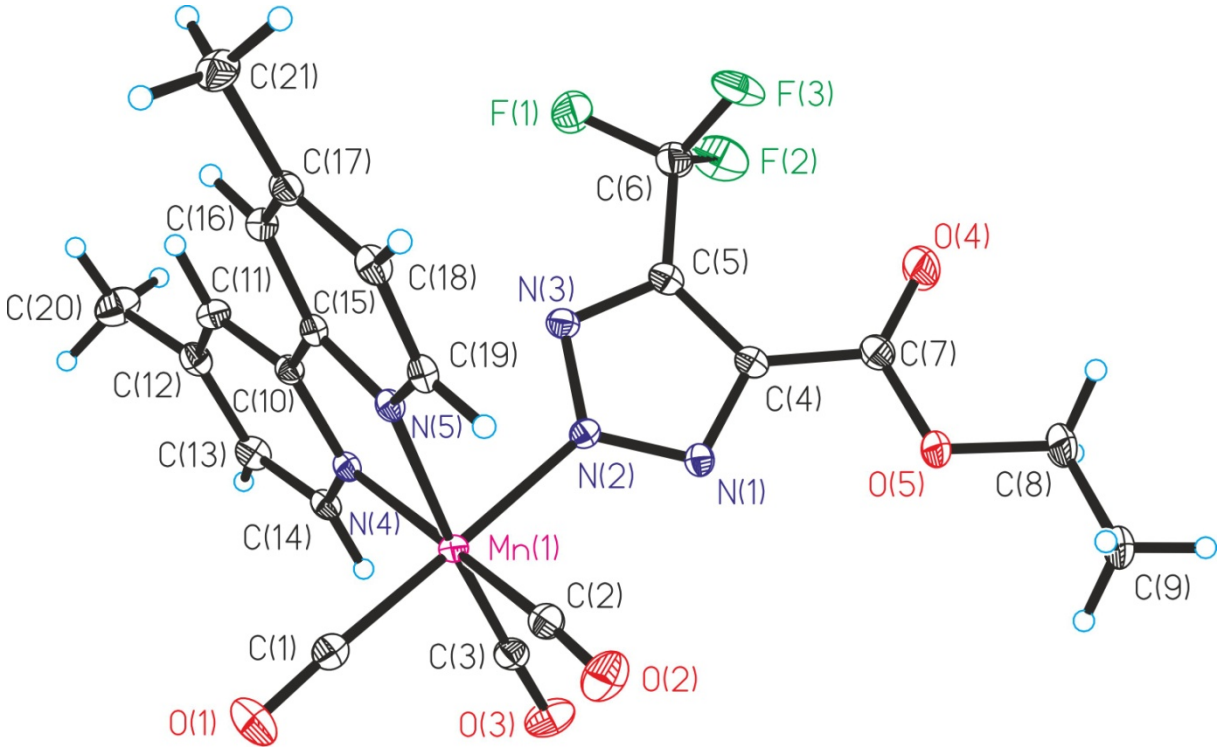


Fig. S1 Molecular structure of **15** with atomic displacement ellipsoids drawn at the 50% probability level.

Experimental

General remarks

Reactions were carried out in oven-dried Schlenk glassware under an atmosphere of pure dinitrogen and reaction vessels were protected from light by wrapping them with aluminium foil if necessary, in particular for the carbonyl complexes. All chemicals were purchased from commercial sources and used as received. Manganese pentacarbonyl bromide was supplied by Strem. IR spectra were measured on pure solid samples using a Nicolet 380 FT-IR spectrometer fitted with a smart iTR accessory. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker Avance 200, DPX 200, DRX 300, Avance 400, and Avance 500 spectrometers (^{1}H, 199.93 and 500.13 MHz; ^{13}C, 50.27, 75.48 and 125.76 MHz; ^{19}F, 188.09, 376.50, and 470.59 MHz; ^{31}P, 80.93 MHz). The elemental composition of the compounds was determined with a Vario MICRO cube CHN analyzer.

HPLC analysis and purification

The analytical and preparative HPLC chromatography was performed on a Dionex Ultimate 3000 system equipped with a diode array detector and a ReproSil 100 column (C18, 5 μm, 4.6 mm or 10 mm diameter, 250 mm length) using a linear gradient gradient of 20–90% acetonitrile/water over 40 min at a flow rate of 0.6 mL min^{-1} for analytical and 3.0 mL min^{-1} for preparative chromatography.

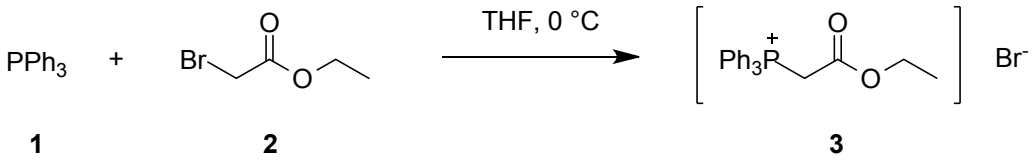
X-ray crystallographic data collection and refinement of structures 15 and 16

Clear light yellow single crystals of **15** were obtained by evaporation of a dichloromethane/*n*-hexane solution, those of **16** by diffusion of *n*-hexane into a solution of the compound in dichloromethane. A suitable single crystal was selected, soaked in perfluoro polyether oil, and mounted on a MiTeGen sample holder. Data were collected on a Nonius Kappa three circle diffractometer utilizing graphite monochromated Mo Kα radiation (λ = 0.71073 Å) from a rotating anode tube run at 50 kV and 30 mA, equipped with an APEXII area detector. The instrument was equipped with an open-flow N_2 Cryoflex II (Bruker) device and measurements were performed at 100 and 296 K, respectively. Using Olex2,[1] the structure was solved with the olex2.solve structure solution program,[2] using the Charge Flipping solution method. The model was refined with the olex2.refine refinement package using Gauss-Newton minimisation.[3]

Density functional theory calculations

DFT calculations were carried out on the Linux cluster of the Leibniz-Rechenzentrum (LRZ) in Munich with ORCA version 2.8,[4] using the BP86 functional with the resolution-of-the-identity (RI) approximation, a def2-TZVP/def2-TZVP/J basis set,[5] the `tightscf` and `grid4` options, and the COSMO solvation model with dimethylsulfoxide as the solvent for geometry optimization and subsequent calculation of vibrational frequencies to characterize the structure obtained as a minimum by inspection for absence of imaginary modes. Then, a relaxed surface scan was carried out in 15° steps for the full 360° rotation of the triazolate mean plane relative to the central C2-C2' axis of the 2,2'-bipyridine ligand while allowing all other variables to relax. The perpendicular orientation of the triazolate ring relative to the bpy C2-C2' axis with the CF_3 group pointing towards the bpy ligand is set to 90°. Clockwise rotation then gives negative angles and counter-clockwise rotation positive ones. The maxima on the resulting potential energy curve where then further characterized as transition states using the `optTS` keyword in separate runs.

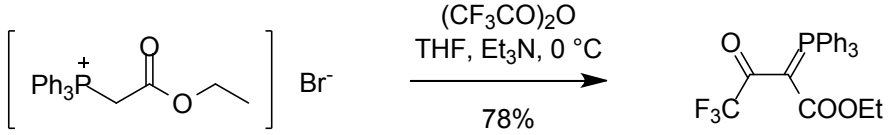
Synthesis of (carboxymethyl)triphenylphosphonium bromide (3)[6]



1 **2** **3**

Under a dinitrogen atmosphere, triphenylphosphane **1** (131.2 g, 0.50 mol) was dissolved in anhydrous degassed tetrahydrofuran (450 mL) in a 1 L flask and cooled in an ice bath. Then, bromoacetic acid ethyl ester **2** (56 mL, 84.3 g, 0.51 mol) was slowly added over 25 min at 0 °C. The reaction mixture turned turbid and was allowed to warm to room temperature with continued stirring overnight. The white solid which had precipiated was directly used in the next step without isolation.

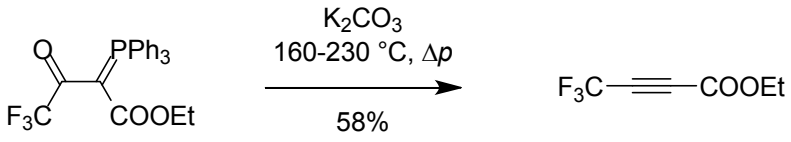
Synthesis of 4,4,4-trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanoic acid ethyl ester (4)[6, 7]



3 **4**

The white phosphonium salt product **3** obtained in the previous step was dissolved again by addition of more anhydrous degassed tetrahydrofuran (450 mL). Then, the reaction mixture was cooled to 0 °C and triethylamine (150 mL, 108.9 g, 1.08 mol) was added dropwise over 20 min while keeping the temperature at 0 °C. Stirring was continued for another 30 min and then, trifluoroacetic acid anhydride (78 mL, 117.1 g, 0.56 mol) was added over 2 h while keeping the temperature at 0 °C. Then, the reaction mixture was allowed to warm up to room temperature overnight. The white solid which had precipitated was collected by filtration, washed with ice-cold tetrahydrofuran (3 × 150 mL) and discarded. The filtrate was concentrated under vacuum to obtain an orange oil which became solid upon cooling. This crude product was dissolved in hot methanol (900 mL) and then water (500 mL) added to precipitate the product. The flask was stored in a refrigerator at 4 °C overnight and the resulting solid collected by filtration, washed with ice-cold water (3 × 100 mL), and the pale yellow product dried under vacuum overnight. Yield: 78% (172.6 g, 0.39 mol). Elemental analysis (%): calc. for $C_{24}H_{20}F_3O_3P$: C 64.87, H 4.54, found: C 65.40, H 4.55; IR (ATR, cm^{-1}): 3072 (w), 2964 (w), 1695 (s), 1586 (s), 1439 (m), 1391 (m), 1256 (s), 1152 (s), 1073 (s), 1012 (m), 753 (m); ^{1}H NMR (199.93 MHz, $CDCl_3$): δ 7.45–7.72 (m, 15H, C_6H_5), 3.83 (q, 2H, CH_2CH_3, $^3J_{H\text{-}H}$ = 7.2 Hz), 0.89 (t, 3H, CH_2CH_3, $^3J_{H\text{-}H}$ = 7.1 Hz) ppm; ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 175.0 (dd, $COCF_3$, $^2J_{C\text{-}F}$ = 34.2 Hz, $^2J_{C\text{-}P}$ = 6.2 Hz), 165.8 (d, C=O $^2J_{C\text{-}P}$ = 13.0 Hz), 133.3 (d, C-3, $^3J_{C\text{-}P}$ = 10.1 Hz), 132.5 (d, C-4, $^4J_{C\text{-}P}$ = 3.0 Hz), 128.9 (d, C-2, $^2J_{C\text{-}P}$ = 12.8 Hz), 124.1 (d, C-1, $^1J_{C\text{-}P}$ = 93.8 Hz), 118.0 (dd, CF_3, $^1J_{C\text{-}F}$ = 289.3 Hz, $^3J_{C\text{-}P}$ = 14.8 Hz), 70.1 (d, C=P, $^1J_{C\text{-}P}$ = 106.7 Hz) 60.0 (s, CH_2CH_3), 13.6 (s, CH_2CH_3); ^{19}F NMR (188.09 MHz, $CDCl_3$): δ -71.4 ($^3J_{P\text{-}F}$ = 1.7 Hz) ppm; ^{31}P NMR (80.93 MHz, $CDCl_3$): δ 19.5 ppm.

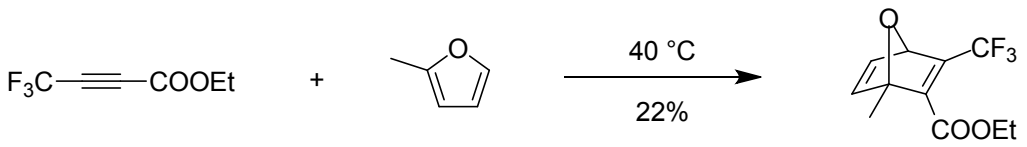
Synthesis of 4,4,4-trifluoro-2-butynoic acid ethyl ester (5)[6]



4 **5**

Solid 4,4,4-trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanoic acid ethyl ester **4** (50.0 g, 113 mmol) was placed in a 250 mL three-neck flask and mixed with potassium carbonate (10.0 g, 72 mmol). After addition of a magnetic stirring bar, the flask was fitted *via* a wide-bore glass tube to a Schlenk flask which was cooled by immersion in liquid dinitrogen in a Dewar vessel. This setup was connected to the vacuum line *via* an efficient cold trap also immersed in liquid dinitrogen. The pressure was carefully reduced to $1.5 \cdot 10^{-2}$ mbar and the solid mixture then heated with an oil bath to 50 °C over 10 min. Then, the temperature was rised to 160 °C over 2 h. At a bath temperature of 150 °C, the mixture started to melt. This temperature was kept until melting of the mixture was complete. Heating was then continued for 2.5 h at 230 °C and the product collected in the cooled Schlenk flask. It is mandatory to ensure that there is always sufficient liquid dinitrogen present in the Dewar and cold trap. The collected yellow liquid was cooled to room temperature. If some material already solidifies in the glass tube, it can be removed by melting with a heatgun. The crude material was purified by fractional destillation and the product collected as a colorless oil with a boiling point of 89–94 °C at atmospheric pressure. Yield: 58% (10.99 g, 66 mmol). Elemental analysis (%): calc. for $C_6H_5F_3O_2$: C 43.39, H 3.03, found: C 43.55, H 3.09; IR (ATR, cm^{-1}): 1728 (s), 1266 (s), 1154 (s), 1020 (m); ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 4.32 (q, 2H, CH_2, $^3J_{H\text{-}H}$ = 7.2 Hz), 1.34 (t, 3H, CH_3, $^3J_{H\text{-}H}$ = 7.2 Hz) ppm; ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 151.1 (d, *C*OO, $^4J_{C\text{-}F}$ = 1.5 Hz), 113.8 (q, *C*F_3, $^1J_{C\text{-}F}$ = 260.1 Hz,), 77.1 (m, *C*CO), 70.3 (q, *C*CF_3, $^2J_{C\text{-}F}$ = 54.7 Hz), 63.9 (s, *C*H_2), 14.2 (s, *C*H_3) ppm; ^{19}F NMR (188.12 MHz, $CDCl_3$): δ -52.3 ppm.

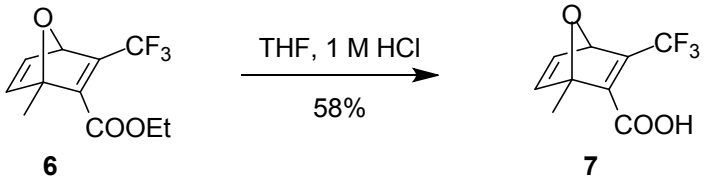
Synthesis of 1-methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-carboxylic acid ethyl ester (6)[8]



5 **6**

Under dinitrogen, 2-methylfuran (5.91 g, 72 mmol) and 4,4,4-trifluoro-2-butynoic acid ethyl ester **5** (10.0 g, 60 mmol) were stirred without any solvent at 40 °C for 7 d. The resulting crude product was purified by two runs of column chromatography on silica, first using *n*-hexane/ethyl acetate (5:1, v/v) and then *n*-hexane/ethyl acetate (8:1, v/v) as the eluent. The product was obtained as a colorless oil. Yield: 22% (3.30 g, 13 mmol). Elemental analysis (%): calc. for $C_{11}H_{11}F_3O_3$: C 53.23, H 4.47, found: C 52.76, H 4.51; IR (ATR, cm^{-1}): 2988 (w), 1726 (m), 1667 (w), 1461 (w), 1382 (w), 1273 (s), 1237 (s), 1201 (s), 1126 (s), 1087 (m), 1020 (w), 854 (w); ^{1}H NMR (199.93 MHz, $CDCl_3$): δ 7.15 (dd, 1H, H-5, $^3J_{H\text{-}H}$ = 5.2 Hz, $^3J_{H\text{-}H}$ = 1.8 Hz), 7.04 (d, 1H, H-6, $^3J_{H\text{-}H}$ = 5.2 Hz), 5.52 (d, 1H, H-4, $^3J_{H\text{-}H}$ = 1.8 Hz), 4.16–4.42 (m, 2H, CH_2CH$_3$), 1.81 (s, 3H, CCH_3), 1.31 (t, 3H, CH$_2$CH_3, $^3J_{H\text{-}H}$ = 7.1 Hz) ppm; ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 163.5 (q, *C*OO, $^4J_{C\text{-}F}$ = 1.4 Hz), 153.4 (q, C-2, $^3J_{C\text{-}F}$ = 5.0 Hz), 150.7 (q, C-3, $^2J_{C\text{-}F}$ = 37.0 Hz), 147.0 (s, C-6), 144.2 (s, C-5), 123.1 (q, *C*F$_3$, $^1J_{C\text{-}F}$ = 269.2 Hz), 94.5 (s, C-1), 82.7 (q, C-4, $^3J_{C\text{-}F}$ = 2.5 Hz), 62.1 (s, *C*H$_2$), 15.5 (s, *C*H$_3$), 14.3 (s, *C*H$_3$); ^{19}F NMR (188.12 MHz, $CDCl_3$): δ -62.9 ppm.

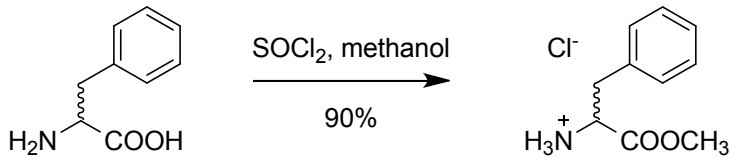
Synthesis of 1-methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-carboxylic acid (7)



6 **7**

1-Methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-carboxylic acid ethyl ester **6** (2.01 g, 8.1 mmol) was dissolved in tetrahydrofuran (50 mL) and cooled in an ice bath. Then, sodium hydroxide (0.80 g, 20 mmol) in water (20 mL) was added dropwise over 15 min and the mixture stirred at room temperature overnight. The volume of the solution was reduced to half and then water (50 mL) added. The mixture was extracted with ethyl acetate (2 × 50 mL) and the combined organic phases discarded. The aqueous phase was adjused to pH = 2 with 1 M hydrochloric acid and extracted with ethyl acetate (3 × 100 mL). These combined organic phases were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The resulting brown oil was dissolved in *n*-hexane (150 mL), some insoluble brown material removed by filtration, and the solvent removed under reduced pressure to obtain a yellow solid. Yield: 58% (1.04 g, 4.7 mmol). Elemental analysis (%): calc. for $C_9H_7F_3O_3$: C 49.10, H 3.20, found: C 49.65, H 3.41; IR (ATR, cm^{-1}): 2834 (w), 1696 (s), 1650 (m), 1427 (m), 1314 (s), 1277 (s), 1125 (s), 919 (m), 853 (m); ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 7.09–7.11 (m, 1H, H-5), 6.98 (d, 1H, H-6, ^3J = 5.2 Hz), 5.50 (d, 1H, H-4, $^3J_{H\text{-}H}$ = 2.0 Hz), 1.80 (s, 3H, CCH_3) ppm; ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 167.9 (*C*OOH), 153.6 (q, C-3, $^2J_{C\text{-}F}$ = 37.5 Hz), 152.1 (q, C-2, $^3J_{C\text{-}F}$ = 4.9 Hz), 146.8 (s, C-6), 143.9 (s, C-5), 121.5 (q, *C*F_3, $^1J_{C\text{-}F}$ = 269.7 Hz), 94.4 (s, C-1), 82.6 (q, C-4, $^3J_{C\text{-}F}$ = 2.6 Hz), 15.4 (s, C*C*H_3) ppm; ^{19}F NMR (470.59 MHz, $CDCl_3$): δ -62.9 ppm.

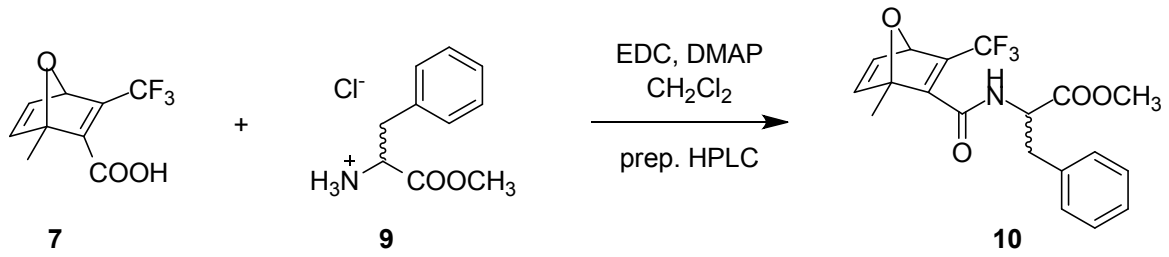
Synthesis of DL-phenylalanine methylester hydrochloride (9)



8 **9**

Under cooling with ice, thionylchloride (10 mL, 16.4 g, 138 mmol) was added dropwise to anhydrous methanol (60 mL). Then, a suspension of DL-phenylalanine **8** (5.0 g, 30 mmol) in methanol (30 mL) was added under cooling with ice and the resulting mixture heated to reflux for 14 h. After cooling to room temperature, the solvent was removed under vacuum and the remaining white residue redissolved in a minimum amount of methanol. This solution was added dropwise into diethylether (250 mL). A white precipitate formed which was filtered off, washed with diethylether (3 × 25 mL), and dried under vacuum to give the product as a white solid. Yield: 90% (5.8 g, 27 mmol). Elemental analysis (%): calc. for $C_{10}H_{14}ClNO_2$: C 55.69, H 6.54, N 6.49, found: C 55.39, H 6.57, N 6.48; IR (ATR, cm^{-1}): 2914 (s), 2840 (s), 2620 (m), 1744 (s), 1238 (s), 741 (s), 701 (s); ^{1}H NMR (200.13 MHz, DMSO-d_6): δ 8.78 (s, 2H, NH_2), 7.23–7.35 (m, 5H, C_6H_5), 4.22 (dd, 1H, H-α, ^3J = 7.6 Hz, ^3J = 5.6 Hz), 3.65 (s, 3H, CH_3), 3.22 (dd, 1H, H-β, ^3J = 14.0 Hz, ^3J = 5.7 Hz), 3.10 (dd, 1H, H-β, ^3J = 13.8 Hz, ^3J = 7.4 Hz) ppm; ^{13}C NMR (50.62 MHz, DMSO-d_6): δ 169.3 (C=O), 134.7 (C_6H_5), 129.3 (C_6H_5), 128.5 (C_6H_5), 127.2 (C_6H_5), 53.2 (OCH_3), 52.5 (C-α), 35.8 (C-β) ppm.

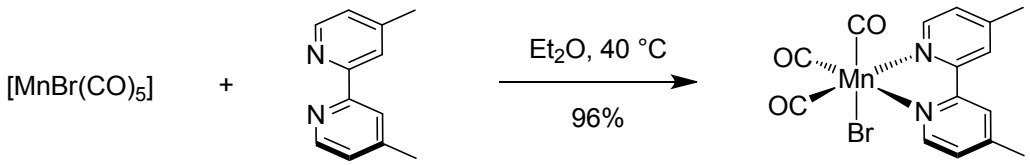
Synthesis of *N*-((1-methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-yl)-carbonyl)-L-phenylalanine methyl ester (10)



7 **9** **10**

1-Methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-carboxylic acid **7** (510 mg, 2.3 mmol) and DL-Phenylalanine methylester hydrochloride **9** (500 mg, 2.3 mmol) were dissolved in dichloromethane (20 mL). Then, 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 567 mg, 4.6 mmol) was added to the solution. After cooling in an ice bath, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCl, 396 mg, 2.1 mmol) was added and the reaction mixture stirred at 0 °C for 30 min. It was then allowed to warm to room temperature overnight. The reaction was quenched by addition of 2 M hydrochloric acid (~2 mL) until the pH has dropped to 1–2, and then the mixture is extracted with dichloromethane (2 × 15 mL). The combined organic layers were dried over magnesium sulfate and concentrated under vaccum. The resulting orange oil was redissolved in dichloromethane (10 mL) and extracted with 0.1 M aqueous sodium hydrogen carbonate (3 × 10 mL). The organic phase was separated, dried over magnesium sulfate, and the solvent removed under vacuum. A part of the oily orange crude product was dissolved in a mixture of acetonitrile and water and purified in several batches by preparative HPLC as described above. The product was obtained as a white solid after lyophilization of the combined batches on a scale of about 50 mg. Due to the small amount of sample purified this way, no elemental analysis was carried out. IR (ATR, cm^{-1}): 3275 (m), 1741 (m), 1631 (s), 1549 (m), 1273 (w), 1168 (m), 1111 (s); ^{1}H NMR (199.93 MHz, CD_3OD): δ isomer A: 7.20–7.30 (m, 5H, C_6H_5), 7.12–7.19 (m, 1H, H-5), 6.99 (d, 1H, H-6, ^3J = 5.2 Hz), 5.50 (t, 1H, H-4, ^3J = 1.8 Hz), 4.90–4.98 (m, 1H, H-α), 3.72 (s, 3H, COOCH_3), 3.18–3.28 (m, 2H, H-β), 1.56 (s, 3H, CCH_3) ppm; isomer A*: 7.20–7.30 (m, 5H, C_6H_5), 7.12–7.19 (m, 1H, H-5), 6.95 (d, 1H, H-6, ^3J = 5.2 Hz), 5.50 (t, 1H, H-4, ^3J = 1.8 Hz), 4.68–4.79 (m, 1H, H-α), 3.71 (s, 3H, COOCH_3), 2.87–3.02 (m, 2H, H-β), 1.26 (s, 3H, CCH_3) ppm; ^{19}F NMR (188.12 MHz, CD_3OD): δ isomer A: -65.67, isomer A:* -65.87 ppm; no ^{13}C NMR spectra were recorded due to the low amount of sample available; HPLC: t_r = 22.4 min.

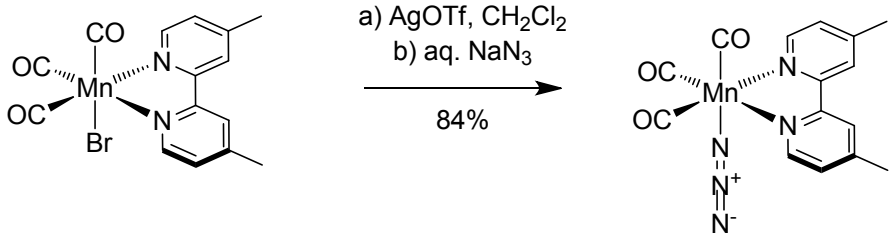
Synthesis of (*OC*-6-33)-bromotricarbonyl(4,4'-dimethyl-2,2'-bipyridine)manganese(I) [MnBr(bpy^{CH3,CH3})(CO)$_3$] (13)[9]



11 **12** **13**

Manganese pentacarbonyl bromide **11** (500 mg, 1.82 mmol) and 4,4'-dimethyl-2,2'-bipyridine (370 mg, 2.01 mmol) were dissolved in diethyl ether (40 mL) and heated to reflux for 3 h under exclusion of light. The precipitate formed was filtered off, washed with diethyl ether (3 × 10 mL), and dried under vacuum to obtain a yellow powder. Yield: 96% (705 mg, 1.75 mmol). Elemental analysis (%): calc. for $C_{15}H_{12}Br_1Mn_1N_2O_3$: C 44.69, H 3.00, N 6.95, found: C 44.97, H 3.03, N 6.97; IR (ATR, cm^{-1}): 2021 (s), 1939 (s), 1926 (s), 1892 (s), 1620 (m), 827 (m); ^{1}H NMR (200.13 MHz, DMSO-d$_6$): δ 8.98 (d, 2H, H-6/6', ^3J = 5.4 Hz), 8.48 (s, 2H, H-3/3'), 7.54 (d, 2H, H-5/5', ^3J = 5.2 Hz), 2.52 (s, 6H, CH_3) ppm; ^{13}C NMR (50.32 MHz, DMSO-d$_6$): δ 154.8 (C-2), 152.7 (C-6), 151.0 (C-3), 127.5 (C-5), 123.8 (C-4), 20.6 (*C*H$_3$) ppm. As commonly encountered with similar manganese carbonyl complexes, the ^{13}C NMR signals of the coordinated carbonyl ligands could not be observed.

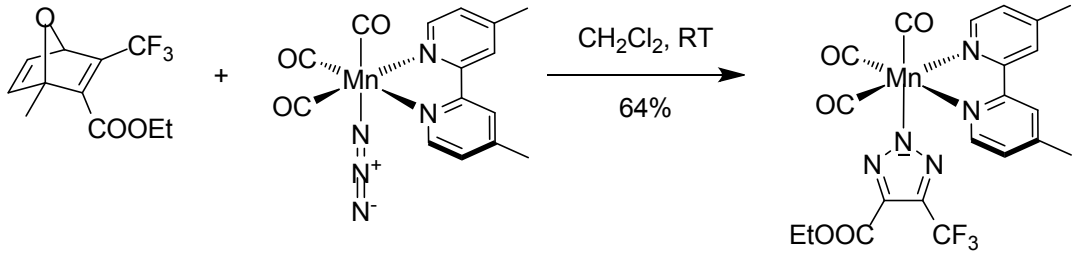
Synthesis of (*OC*-6-33)-azidotricarbonyl(4,4'-dimethyl-2,2'-bipyridine)manganese(I) [$Mn(N_3)(bpy^{CH3,CH3})(CO)_3$] (14)



13 **14**

[$MnBr(bpy^{CH3,CH3})(CO)_3$] **13** (300 mg, 0.74 mmol) was dissolved in anhydrous degassed dichloromethane (60 mL). Then, silver trifluoromethanesulfonate (228 mg, 0.89 mmol) was added and the mixture stirred under exclusion of light at room temperature for 3 h. The white solid which had precipitated was filtered off and an aqueous solution of sodium azide (138 mg, 2.12 mmol) added. Stirring was continued under exclusion of light overnight. Then, the two phases were separated and the organic phase washed with water (3 × 15 mL). The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure to obtain the product as a yellow solid which was dried under vacuum. Yield: 84% (228 mg, 0.62 mmol). Elemental analysis (%): calc. for $C_{15}H_{12}Mn_1N_5O_3$: C 49.33, H 3.31, N 19.18, found: C 49.30, H 3.28, N 18.62; IR (ATR, cm^{-1}): 2049 (m), 2006 (s), 1927 (s), 1886 (s), 1620 (s); ^{1}H NMR (200.13 MHz, DMSO-d_6): δ 8.92 (d, 2H, H-6/6', ^3J = 6.0 Hz), 8.53 (s, 2H, H-3/3'), 7.57 (d, 2H, H-5/5', ^3J = 6.0 Hz), 2.53 (s, 6H, CH_3) ppm; ^{13}C NMR (50.32 MHz, DMSO-d_6): δ 154.6 (C-2), 152.3 (C-6), 151.3 (C-3), 127.7 (C-5), 123.8 (C-4), 20.6 (*C*H_3) ppm. As commonly encountered with similar manganese carbonyl complexes, the ^{13}C NMR signals of the coordinated carbonyl ligands could not be observed.

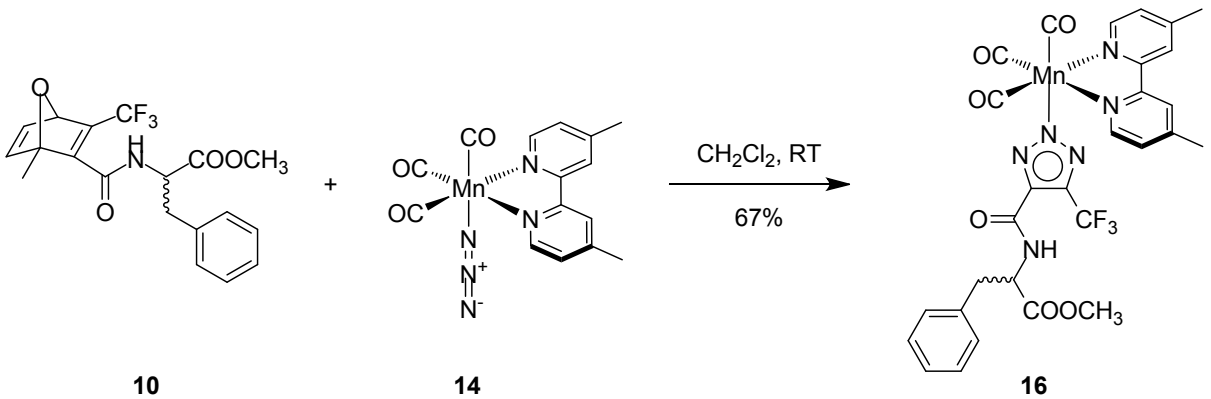
Synthesis of (*OC*-6-33)-(4-carbethoxy-5-trifluoromethyl-2*H*-1,2,3-triazolato-N^2) tricarbonyl(4,4'-dimethyl-2,2'-bipyridine)manganese(I) [Mn(triazolate^{COOEt,CF3})(bpy^{CH3,CH3})(CO)$_3$] (15)



6 **14** **15**

1-Methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-carboxylic acid ethyl **6** ester (63.7 mg, 0.27 mmol) and [Mn(N$_3$)(bpy^{CH3,CH3})(CO)$_3$] **14** (50.0 mg, 0.14 mmol) were dissolved in degassed anhydrous dichloromethane (20 mL) and the mixture stirred for 5 d at room temperature under exclusion of light. Then, the solvent was removed under pressure and the resulting yellow solid washed with *n*-hexane (3 × 5 mL) and dried in vacuum. Diffusion of *n*-hexane into a solution of the crude product in dichloromethane gave yellow single crystals which were suitable for X-ray structure analysis. Yield: 64% (47.0 mg, 0.09 mmol). Elemental analysis (%): calc. for $C_{21}H_{17}F_3Mn_1N_5O_5$: C 47.47, H 3.22, N 13.18, found: C 46.70, H 3.35, N 12.04; IR (ATR, cm^{-1}): 2026 (s), 1929 (s), 1912 (s), 1727 (m), 1622 (w), 1546 (w), 1433 (w), 1307 (m), 1154 (m), 1130 (m), 1048 (m), 824 (w); ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 9.06 (d, 2H, H-6/6', ^3J = 5.6 Hz), 7.82 (s, 2H, H-3/3'), 7.31 (d, 2H, H-5/5', ^3J = 5.7 Hz), 4.23 (q, 2H, CH_2CH$_3$, ^3J = 7.2 Hz), 2.53 (s, 6H, CH_3), 1.26 (t, 3H, CH$_2$CH_3, ^3J = 7.1 Hz) ppm; ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 161.2 (C=O), 155.8 (C-2), 153.6 (C-6), 150.7 (C-4), 127.3 (C-5), 122.5 (C-3), 60.6 (*C*H$_2$), 21.6 (*C*H$_3$), 14.2 (*C*H$_3$); ^{19}F NMR (376.50 MHz, $CDCl_3$): δ -59.9 ppm. As commonly encountered with similar manganese carbonyl complexes, the ^{13}C NMR signals of the coordinated carbonyl ligands could not be observed. Furthermore, no peaks could be detected for the CF$_3$ and triazolate C-4 and C-5 carbon atoms.

Synthesis of (*OC*-6-33)-tricarbonyl(4,4'-dimethyl-2,2'-bipyridine)(*N*-((5-trifluoro-2*H*-1,2,3-triazolato-4-yl)carbonyl)-L-phenylalanine methyl ester-N^2) manganese(I) [Mn(triazolate$^{CO\text{-}Phe\text{-}OCH3,CF3}$)(bpy^{CH3,CH3})(CO)$_3$] (16)



N-(1-Methyl-3-trifluoromethyl-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-yl)carbonyl)-L-phenyl-alanine methyl ester **10** (35.0 mg, 0.09 mmol) and [Mn(N$_3$)(bpy^{CH3,CH3})(CO)$_3$] **14** (22.4 mg, 0.06 mmol) were dissolved in dichloromethane (5 mL) and stirred at room temperature under exclusion of light for 7 d. Then, the solvent was removed under vacuum and the crude product purified by column chromatography on silica using ethyl acetate/petroleum ether (1:1, v/v) as the eluent. Single crystals suitable for X-ray structure analysis were grown by diffusion of *n*-hexane into a solution of the compound in dichloromethane. Yield: 67% (28.4 mg, 0.04 mmol). Elemental analysis (%): calc. for $C_{29}H_{24}F_3Mn_1N_6O_6$: C 52.42, H 3.64, N 12.65, found: C 53.94, H 4.18, N 11.61; IR (ATR, cm^{-1}): 2025 (s), 1933 (s), 1909 (s), 1740 (m), 1680 (m), 1485 (m), 1159 (m), 1129 (m), 1060 (m); ^{1}H NMR (199.93 MHz, $CDCl_3$): δ 8.95 (t, 2H, H-3/3', ^3J = 5.3 Hz), 7.79 (d, 2H, H-6/6', ^3J = 8.1 Hz), 7.00–7.35 (m, 5H, C_6H_5), 6.88 (d, 2H, H-5/5', ^3J = 7.4 Hz), 4.88 (m, 1H, H-α), 3.68 (s, 3H, COOCH_3), 3.10 (d, 2H, H-β, ^3J = 4.9 Hz), 2.45 (d, 6H, CH_3, ^4J = 7.8 Hz) ppm; ^{13}C NMR (50.27 MHz, $CDCl_3$): δ 155.9 (C-2/2'), 153.3 (C-6/6'), 153.2 (C-3/3'), 136.4 (C-1), 129.7 (C-3/5), 128.5 (C-2/6), 127.2 (C-4), 127.0 (C-5/5'), 122.6 (C-4/4'), 52.6 (C-α), 52.1 (COO*C*H3), 38.3 (C-β), 21.50 (*C*H$_3$) ppm; ^{19}F NMR (188.12 MHz, $CDCl_3$): δ -59.6 ppm. As commonly encountered with similar manganese carbonyl complexes, the ^{13}C NMR signals of the coordinated carbonyl ligands could not be observed. Furthermore, no peaks could be detected for the CF_3 and triazolate C-4 and C-5 carbon atoms due to low concentration because of the small amout of sample.

Table S1 Crystallographic data for complexes **15** and **16**

Compound	**15**	**16**
Empirical formula	$C_{21}H_{17}F_3Mn_1N_5O_5$	$C_{29}H_{24}F_3Mn_1N_6O_6$
Formula weight	531.33	664.48
Dimensions (mm)	0.49 × 0.15 × 0.11	0.65 × 0.41 × 0.38
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1$
a (Å)	16.0897(7)	9.2447(8)
b (Å)	14.5131(6)	15.2085(12)
c (Å)	19.1832(8)	10.6362(9)
α (°)	90	90
β (°)	90	98.280(3)
γ (°)	90	90
V (Å^3)	4479.5(3)	1479.8(2)
Z	8	2
ρ_{calc} (g cm^{-3})	1.576	1.491
T (K)	100	296
μ (mm^{-1})	0.658	0.518
λ (Å) (Mo K_α)	0.71073	0.71073
$2\Theta_{max}$ (°)	27.12	26.00
Reflections measured	59029	18131
Unique refl. / [$I > 2\sigma(I)$]	4957 / 3800	5767 / 5342
Data completeness	0.999	0.993
Variables	318	408
R ($I > 2\sigma(I)$)	0.0306	0.0329
wR ($I > 2\sigma(I)$)	0.0783	0.0750
Largest difference map peak/hole in e Å^{-3}	0.408 / -0.417	0.342 / -0.269
Goodness of fit (GOF)	1.043	1.037

Table S2 Selected bond lengths [Å] and angles (°) for complexes **15** and **16**

	15		**16**
Mn1-C1	1.8173(19)	Mn1-C1	1.811(2)
Mn1-C2	1.8046(19)	Mn1-C2	1.792(3)
Mn1-C3	1.807(2)	Mn1-C3	1.802(3)
Mn1-N2	2.0448(15)	Mn1-N2	2.0368(18)
Mn1-N4	2.0418(15)	Mn1-N4	2.0362(19)
Mn1-N5	2.0422(15)	Mn1-N5	2.032(2)
C1-O1	1.146(2)	C1-O1	1.136(3)
C2-O2	1.147(2)	C2-O2	1.142(3)
C3-O3	1.147(2)	C3-O3	1.142(3)
N1-N2	1.338(2)	N1-N2	1.320(2)
N2-N3	1.340(2)	N2-N3	1.332(3)
N3-C5	1.338(2)	N3-C5	1.336(3)
C4-C5	1.395(3)	C4-C5	1.375(3)
C7-O4	1.202(2)	C7-O4	1.219(3)
C1-Mn1-N2	178.79(7)	C1-Mn1-N2	177.73(10)
C2-Mn1-N4	175.07(7)	C2-Mn1-N4	175.01(10)
C3-Mn1-N5	172.79(7)	C3-Mn1-N5	174.95(10)
C1-Mn1-N5	94.91(7)	C1-Mn1-N5	92.17(9)
C1-Mn1-C3	90.77(8)	C1-Mn1-C3	90.46(11)
N2-Mn1-C3	90.08(7)	N2-Mn1-C3	91.78(9)
N2-Mn1-N5	84.18(6)	N2-Mn1-N5	85.57(7)
C2-Mn1-C3	87.70(8)	C2-Mn1-C3	88.25(12)
C2-Mn1-N5	96.93(7)	C2-Mn1-N5	96.19(10)
N4-Mn1-C3	96.87(2)	N4-Mn1-C3	96.45(10)
N4-Mn1-N5	78.70(6)	N4-Mn1-N5	79.05(8)
C1-Mn1-N4	90.06(7)	C1-Mn1-N4	94.44(9)
C1-Mn1-C2	88.02(8)	C1-Mn1-C2	87.18(11)
N2-Mn1-N4	88.98(6)	N2-Mn1-N4	84.93(7)
N2-Mn1-C2	92.88(7)	N2-Mn1-C2	93.27(9)

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