Received: 4 November 2016 | Revised: 2 January 2017 | Accepted: 17 January 2017

DOI 10.1002/aoc.3759

FULL PAPER

WILEY Applied Organometallic Chemistry

Modified cyclopentadienyl molybdenum compounds with enhanced cytotoxic activity towards MOLT-4 leukaemia cells

Iva Honzíčková[1] | Jaromír Vinklárek[1] | Zdeňka Růžičková[1] | Martina Řezáčová[2] | Jan Honzíček[3]

[1] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

[2] Department of Medical Biochemistry, Faculty of Medicine in Hradec Králové, Charles University in Prague, Šimkova 870, 500 01 Hradec Králové, Czech Republic

[3] Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

Correspondence
Jan Honzíček, Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic.
Email: jan.honzicek@upce.cz

A series of new cyclopentadienyl molybdenum compounds bearing substituted phenanthroline ligands $[(\eta^5\text{-}C_5H_4CH_2C_6H_4X\text{-}4)Mo(CO)_2(^{N,N}L)][BF_4]$ (X = F, Cl, Br; $^{N,N}L$ = phen, 5-NH_2-phen, 4,7-Ph_2-phen) was prepared and characterized using infrared and NMR spectroscopies. Crystal structures of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4F\text{-}4)Mo(CO)_2(NCMe)_2][BF_4]$, $[(\eta^5\text{-}C_5H_4CH_2C_6H_4X\text{-}4)Mo(CO)_2(phen)][BF_4]$ (X = F, Cl, Br) and $[(\eta^5\text{-}C_5H_4CH_2C_6H_4Cl\text{-}4)Mo(CO)_2(4,7\text{-}Ph_2\text{-}phen)][BF_4]\cdot(4,7\text{-}Ph_2\text{-}phen)\cdot HBF_4$ were determined using X-ray diffraction analysis. Biological studies revealed a strong cytotoxic effect of the chelating ligands. Although the cytostatic effect of the halogen in the side chain of the cyclopentadienyl ring is negligible, it could be used for future post-modification of these types of cytotoxic active molybdenum-based compounds.

KEYWORDS
cyclopentadienyl, cytotoxicity, fulvene, leukaemia therapy, molybdenum, X-ray diffraction analysis

1 | INTRODUCTION

Despite our constantly deepening knowledge about pathobiochemical mechanisms of various haematological malignancies, many leukaemias remain incurable and have very poor survival prognoses. Although targeted therapy, such as tyrosin kinase inhibitors or specific monoclonal antibodies, has been a great revolution for the therapy of some types of leukaemias, others rely fully on classical chemotherapy.[1] For example, the core of the treatment regimen of acute myeloid leukaemia has remained nearly unchanged for 40 years, and the prognosis remains poor, mainly in elderly patients. Therefore, research continues on novel cytostatics that would provide fewer undesirable side effects while maintaining potent anti-tumour activity.[2]

In 2005, the molybdenum(II) compounds $[(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Br]$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_2L_2][BF_4]$ and $[(\eta^5\text{-}C_9H_7)Mo(CO)_2L_2][BF_4]$ (L_2 = N,N-, S,S- and P,P-chelating ligands) were established as a new class of cytotoxic active compounds against several tumour cell lines.[3] The most potent cytotoxic effect was observed for indenyl complexes bearing 1,4-bis(4-tolyl)-1,4-diazabuta-1,3-diene, 4,7-diphenyl-1,10-phenanthroline, 1,2-bis(diphenylphosphino) ethane and 1,4,7-trithiacyclononane. Their half maximal inhibitory concentration (IC_{50}) towards Ehrlich-ascites cell line ranges from 6 to 10 μmol l^{-1}.[3] Subsequent studies have extended the series of cytotoxic active compounds and brought an early insight into the mechanism of their action.[4–12]

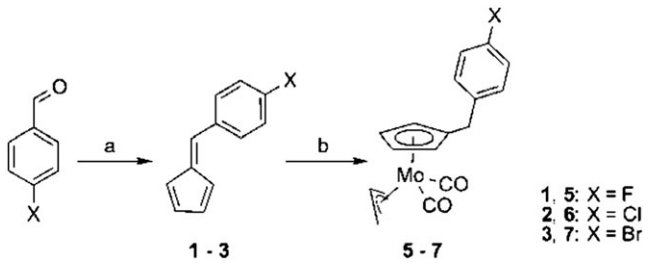
The aim of the work presented here was to enhance the cytotoxicity of cyclopentadienyl molybdenum compounds through modification of the active species. Two approaches were chosen to achieve this goal. These were the attachment of new halogenobenzyl substituents on the cyclopentadienyl ring and coordination of substituted phenanthroline ligands.

The substitution effects were evaluated for human MOLT-4 leukaemia cells. This cell line is derived from human T-lymphoblastic leukaemia and shows specific surface signs: $CD1^+$ (49%), $CD4^+$ (55%), $CD5^+$ (72%) and $CD7^+$ (77%). MOLT-4 contains wild type of protein p53, which is crucial in the cell response to cytostatic therapy and radiotherapy of p53wt tumours. The intact p53 pathway predicts the cell line to be an excellent model for study of molecular mechanism responding mainly to DNA damage.[13,14]

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of Allyl molybdenum precursors

Allyl molybdenum compounds $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_4CH_2C_6H_4X\text{-}4)Mo(CO)_2]$ (**5**: X = F; **6**: X = Cl; **7**: X = Br) were prepared by reaction of appropriate substituted lithium cyclopentadienide $Li(C_5H_4CH_2C_6H_4X\text{-}4)$ (**1-Li**: X = F; **2-Li**: X = Cl; **3-Li**: X = Br) with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**4**) according to the protocol developed for the unsubstituted analogue.[15] The halogenobenzyl substituents were attached to the cyclopentadienyl framework using a well-established fulvene protocol.[16,17] The substituted benzaldehydes react with cyclopentadiene under basic conditions to give fulvenes **1–3** (Scheme 1). These intermediates were isolated and treated with SuperHydride to give reactive cyclopentadienides **1-Li–3-Li**.



SCHEME 1 Synthesis of compounds **1–3** and molybdenum compounds **5–7**. Reaction conditions: (a) C_5H_6, pyrrolidine/MeOH; (b) $Li[Et_3BH]/Et_2O$, $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**4**)/tetrahydrofuran

The allyl molybdenum compounds **5–7** were characterized using infrared and NMR spectroscopies. The infrared spectra show two CO stretching bands in the range typical of terminal carbonyl ligands bound to molybdenum(II) (Table 1). ^{1}H NMR spectra show a broadened signal at 5.13 ppm (4H) that is assigned to protons of the monosubstituted cyclopentadienyl ligand. The allyl ligands give two doublets at *ca* 2.71 and *ca* 0.94 ppm and one multiplet at *ca* 3.91 ppm that is typical for the η^3-coordination mode. The protons of the methylene bridge between the cyclopentadienyl and benzene ring appear as one singlet at *ca* 3.55 ppm. The 1,4-disubstituted benzene ring gives two doublets in the range 7.0–7.4 ppm with interaction constant $^3J(^1H,^1H) \sim 8.4$ Hz. In the spectrum of **5**, the signals of the benzene protons are split by ^{19}F ($^3J = 8.7$ Hz, $^4J = 5.4$ Hz). The $^{19}F\{^1H\}$ NMR spectrum of **5** shows a single resonance at 116.4 ppm.

2.2 | Synthesis of Phenanthroline complexes

The allyl compounds **5–7** react with tetrafluoroboric acid in the presence of acetonitrile to give stable cationic complexes $[(\eta^5\text{-}C_5H_4CH_2C_6H_4X\text{-}4)Mo(CO)_2(NCMe)_2][BF_4]$ (**8**: X = F; **9**: X = Cl; **10**: X = Br). The infrared spectra of compounds **8–10** show the CO stretching bands at considerably higher wavenumbers than those of the allyl precursors **5–7** (Table 1). This shift is due to much lower electron density on the central metal in cationic compounds **8–10**. The

TABLE 1 Summary of infrared data for molybdenum compounds[a]

	ν_a(C≡O)	ν_s(C≡O)		ν_a(C≡O)	ν_s(C≡O)
5	1932	1844	**13**	1968	1896
6	1941	1854	**14**	1966	1885
7	1936	1846	**15**	1966	1885
8	1971	1903	**16**	1966	1886
9	1976	1895	**17**	1967	1888
10	1975	1893	**18**	1967	1889
11	1966	1885	**19**	1966	1885
12	1970	1898			

[a]Wavenumbers are given in cm^{-1}.

cationic character of **8**–**10** is further supported by a broad B—F stretching band at *ca* 1040 cm^{-1}. ^1H NMR spectra show two apparent triplets of cyclopentadienyl protons at 5.7 and 5.5 ppm ($^3J = {}^4J = 2.2$ Hz). A signal at *ca* 2.5 ppm is assigned to protons of coordinated acetonitrile. The

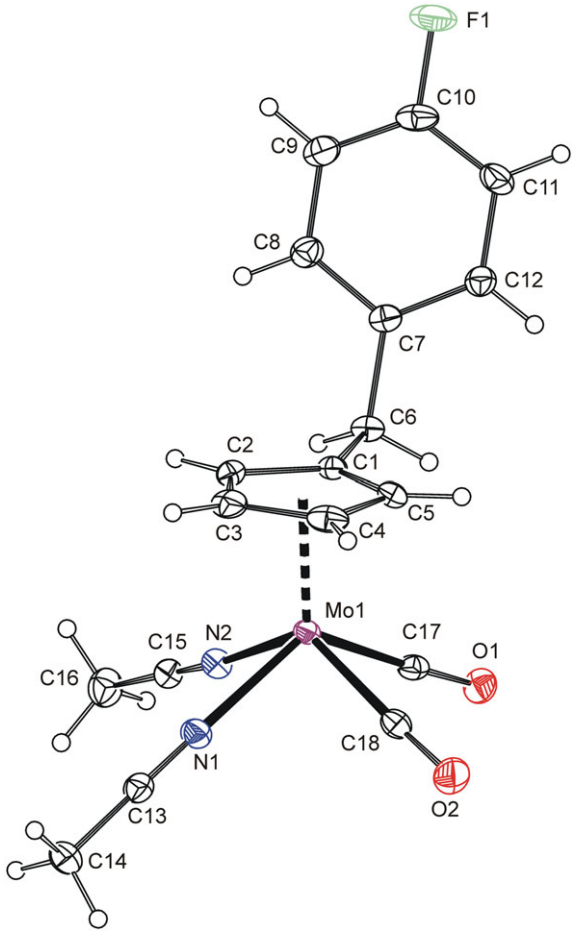
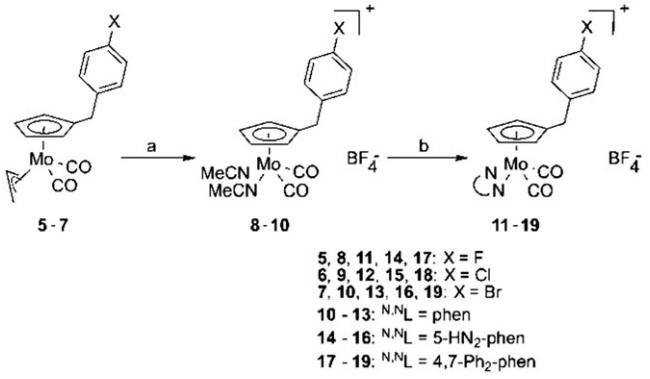


FIGURE 1 ORTEP drawing of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4F\text{-}4)Mo(CO)_2(NCMe)_2]^+$ present in crystal structure of **8**. Thermal ellipsoids are drawn at the 30% probability level



SCHEME 2 Synthesis of cationic molybdenum compounds. Reaction conditions: (a) $HBF_4{\cdot}Et_2O/CH_2Cl_2$, MeCN; (b) $^{N,N}L/CH_2Cl_2$

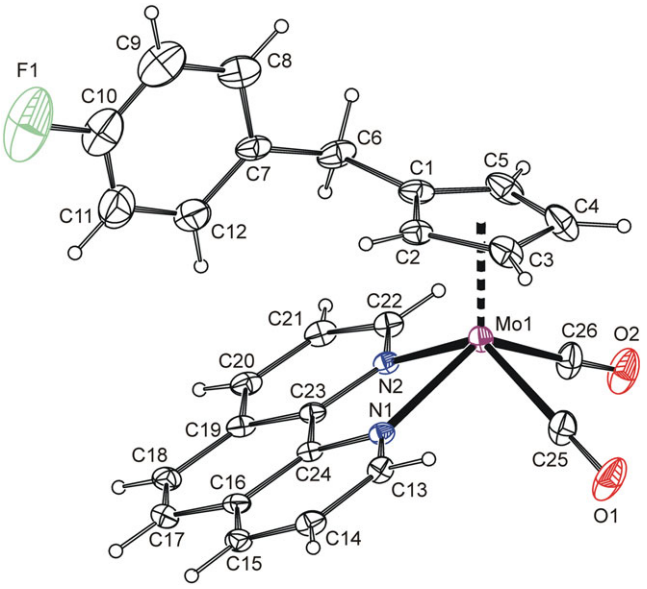


FIGURE 2 ORTEP drawing of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4F\text{-}4)Mo(CO)_2(phen)]^+$ present in crystal structure of **11**. The labelling for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 20% probability level. The alternate position of disordered substituent of the cyclopentadienyl ring is omitted for clarity

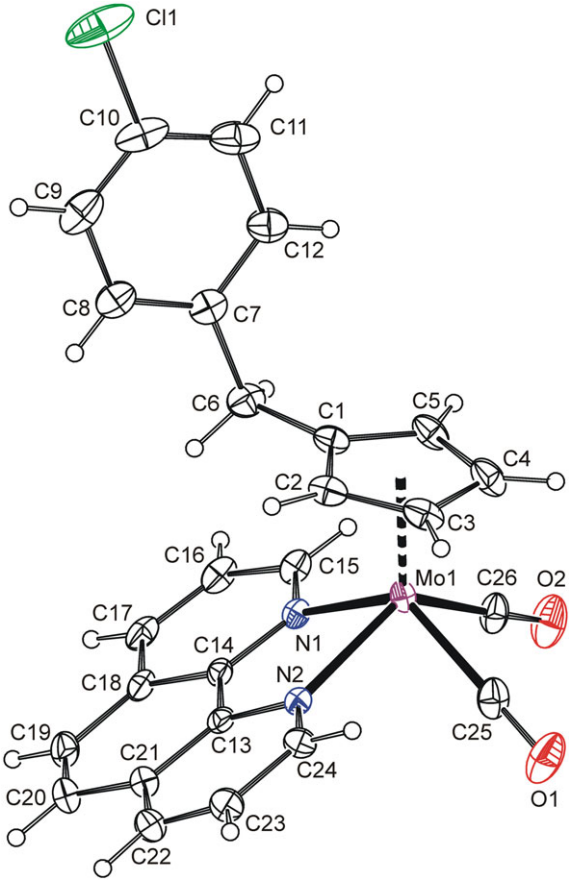


FIGURE 3 ORTEP drawing of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4Cl\text{-}4)Mo(CO)_2(phen)]^+$ present in crystal structure of **12**. Thermal ellipsoids are drawn at the 30% probability level

cyclopentadienyl ring substituents exhibit very similar ^{1}H NMR and $^{19}F\{^{1}H\}$ NMR spectral features as described above for allyl complexes **5**–**7**.

The structure of **8** was determined using single-crystal X-ray diffraction analysis. The cation has a square-pyramidal structure with the η^5-cyclopentadienyl ligand in the apical position (Figure 1). The equatorial plane is occupied with two *cis*-coordinated terminal carbonyl ligands and two nitrogen donor atoms of coordinated acetonitrile molecules.

The acetonitrile complexes **8**–**10** are the key intermediates for the synthesis of stable derivatives bearing chelating ligands. The compounds with substituted 1,10-phenanthroline ligands $[(\eta^5\text{-}C_5H_4CH_2C_6H_4X\text{-}4)Mo(CO)_2(^{N,N}L)][BF_4]$ (**11**–**19**) are available via ligand-exchange reaction (Scheme 2). The reaction products were characterized using infrared and NMR spectroscopies. The exchange of the acetonitrile ligands with N,N-chelating ligands has only a minor effect on the carbonyl stretching frequencies. Molecular structures of **11**, **12**, **13** and **18**·Ph_2phen·HBF_4 in the solid state were determined using single-crystal X-ray diffraction analysis. Molecular structures of the complex cations are depicted in Figures 2–5. Selected geometric parameters describing the coordination sphere of molybdenum are summarized in Table 2. Due to the geometric constraint imposed by five-membered chelate ring, compounds **11**, **12**, **13** and **18** exhibit more acute N–Mo–N angle (73.69(11)–74.11(9)°) than the bisacetonitrile complex **8** (77.34(19)°). This phenanthroline-imposed feature is the only significant structural difference in the coordination geometries at the molybdenum centres of **11**, **12**, **13** and **18** relative that in **8**.

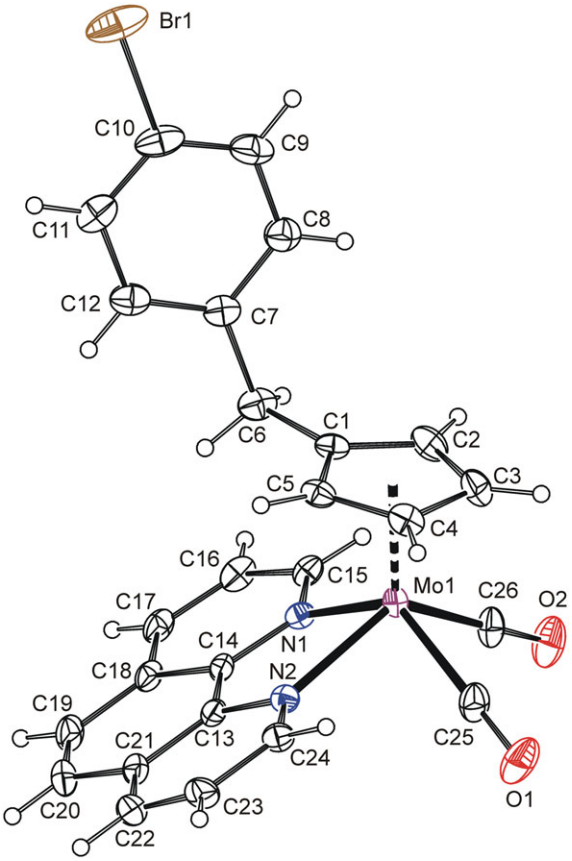


FIGURE 4 ORTEP drawing of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4Br\text{-}4)Mo(CO)_2(phen)]^+$ present in crystal structure of **13**. Thermal ellipsoids are drawn at the 30% probability level

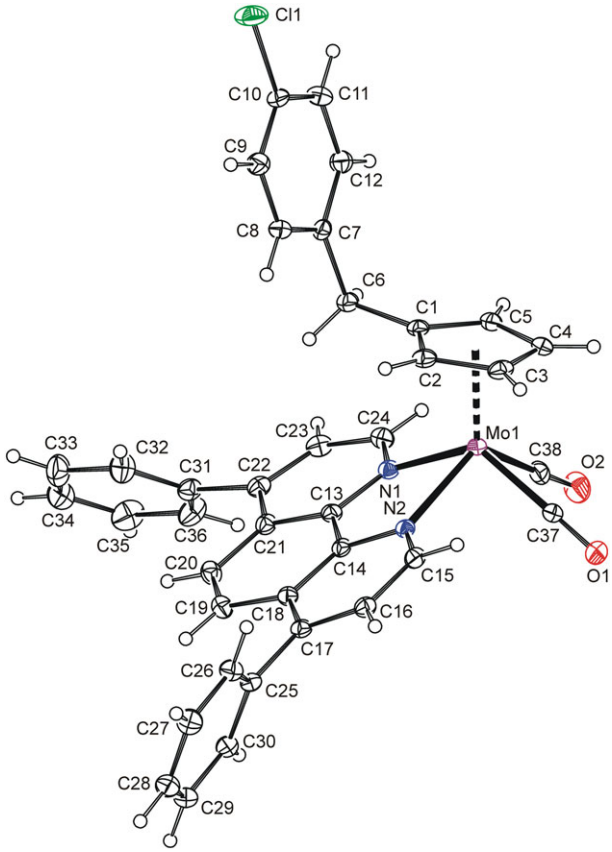


FIGURE 5 ORTEP drawing of $[(\eta^5\text{-}C_5H_4CH_2C_6H_4Cl\text{-}4)Mo(CO)_2(4,7\text{-}Ph_2\text{-}phen)]^+$ present in crystal structure of **18**·phen·HBF_4. Thermal ellipsoids are drawn at the 30% probability level

The crystal structures of **12** and **13** are stabilized by π–π interactions. A sandwich π–π stacking, involving the phenanthroline ligand and the halogeno-substituted benzene ring, connects neighbouring molecules into zigzag chains. The perpendicular distances between centroid of the benzene ring (C7–C12) and central ring of phenanthroline (C13–C21) are 3.4815(16) and 3.452(2) Å for compounds **12** and **13**, respectively. Such zigzag chains are crosslinked into layers through T-shaped interactions between halide of the C_6H_5X moiety and a face of the phenanthroline ligand. The perpendicular distances between halide and side ring of phenanthroline (N2–C24) are 3.466 and 3.446 Å for compounds **12** and **13**, respectively.

In the crystal structure of **18**·phen·HBF_4, a weak N—H···F—BF_3 hydrogen bond (N···F = 2.774(4) Å) connects

TABLE 2 Selected bond lengths and bond angles of molybdenum compounds[a]

	8	11	12	13	18·Ph_2phen·HBF_4
Mo–Cg(C_5)[b]	1.984(2)	1.995(3)	1.9823(16)	1.984(3)	1.9817(15)
Mo–C(CO)	1.966(5) 1.967(5)	1.967(6) 1.981(7)	1.969(3) 1.984(4)	1.982(5) 1.983(6)	1.964(4) 1.968(4)
Mo–N	2.174(5) 2.160(5)	2.187(5) 2.194(4)	2.175(2) 2.194(2)	2.195(5) 2.190(4)	2.178(3) 1.179(3)
(OC)C–Mo–C(CO)	73.3(2)	76.1(3)	75.25(15)	75.7(3)	75.90(15)
N–Mo–N	77.34(19)	73.72(18)	74.11(9)	74.0(2)	73.69(11)

[a]Distances are given in Å; angles and dihedral angles are given in °.

[b]Cg(C_5) is centre of gravity of the cyclopentadienyl ring.

the protonated phenanthroline with one tetrafluoroborate. The phenanthroline molecule is further connected with a C_6H_5Cl moiety of the molybdenum complex via sandwich π–π stacking (Cg(C7–C12)–Pl(39–47) = 3.4011(16) Å).

2.3 | Cytotoxicity study

The cytotoxic activity of phenanthroline molybdenum compounds **11**–**19** was evaluated on human T-lymphocytic MOLT-4 leukaemia cells using procedures described previously.[18] All new phenanthroline molybdenum complexes display high cytotoxic activity against MOLT-4 leukaemia cells as evidenced by IC_{50} values obtained using standard WST-1 viability assays (Table 3).

The activity strongly depends on the substitution pattern of the phenanthroline framework. Very high activity is observed mainly for complexes with coordinated 5-NH_2-phen (**14**–**16**: IC_{50} = 1.9–3.7 μmol l^{-1}) and 4,7-Ph_2-phen (**17**–**19**: IC_{50} = 0.9–1.9 μmol l^{-1}). Complexes bearing unsubstituted 1,10-phenanthroline show lower activity (**11**–**13**: IC_{50} = 14.1–16.2 μmol l^{-1}) but even here the IC_{50} values are comparable with that of cisplatin (DDP; IC_{50} = 15.8 ± 1.9 μmol l^{-1}). The substitution in the cyclopentadienyl ligand has only a minor effect on cytotoxicity. Hence, complexes bearing unsubstituted 1,10-phenathroline have IC_{50} values near to that of the analogue with unsubstituted cyclopentadienyl ring [(η^5-C_5H_5)Mo(CO)$_2$(phen)][BF_4] (**20**; IC_{50} = 19.9 ± 0.7 μmol l^{-1}).[7]

TABLE 3 Cytotoxicity data for complexes bearing N,N-chelating ligands[a]

	IC_{50}		IC_{50}		IC_{50}
11	16.2 ± 0.5	**14**	1.9 ± 0.4	**17**	1.4 ± 0.1
12	14.5 ± 0.9	**15**	3.7 ± 0.5	**18**	0.9 ± 0.1
13	14.1 ± 1.1	**16**	2.8 ± 0.2	**19**	1.9 ± 0.2
20	19.9 ± 0.7	DDP	15.8 ± 1.9[b]		

[a]IC_{50} values towards MOLT-4 cell line are given in μmol l^{-1}.

[b]Data published elsewhere.[30]

The highest cytotoxicity is observed for compounds bearing 4,7-diphenyl-1,10-phenanthroline and cyclopentadienyl ligand modified by 4-fluorobenzyl (**17**) and 4-chlorobenzyl (**18**). These species have about one order of magnitude higher activity than that reported for DDP.

3 | CONCLUSIONS

This study demonstrates that introduction of substituents to the phenanthroline and cyclopentadienyl ligands of [(η^5-C_5H_5)Mo(CO)$_2$(phen)][BF_4] results in complexes with varied cytotoxicity. The activity towards MOLT-4 leukaemia cells exhibited by complexes bearing 4,7-Ph_2-phen (**17**–**19**) is roughly ten times greater than that of DDP. Complexes with 5-NH_2-phen (**14**–**16**) are less active than **17**–**19** but still an improvement over DDP. Complexes **11**–**13** with unsubstituted phenanthroline show activities very similar to that of DDP. The presence of pendant $CH_2C_6H_4X$ (X = F, Cl, Br) cyclopentadienyl substituents in **11**–**19** results in small differences in activity for complexes with a given N,N-ligand. While the modulation of X within complexes **11**–**13**, **14**–**16** and **17**–**19** offers little advantage in terms of cytotoxicity enhancement, these functional groups provide a convenient entry point for pendant group elaboration to further explore the cytotoxicity of complexes with the [(η^5-C_5H_5)Mo(CO)$_2$(phen)]$^+$ core. The successful attachment of $CH_2C_6H_4X$ group is also important from the synthetic point of view. It could be utilized for post-modification of molybdenum species using C─C cross-coupling reactions.[19,20]

4 | EXPERIMENTAL

4.1 | Methods and materials

All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods.[21] Starting materials were available commercially or prepared according to literature

procedures: $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**4**).[15] The infrared spectra were recorded in the 400–4000 cm^{-1} region (resolution of 1 cm^{-1}) with a Nicolet iS50 FT-IR spectrometer using a Diamond Smart Orbit ATR. ^1H NMR and $^{19}F\{^1H\}$ NMR spectra were measured with a Bruker Avance 400 spectrometer at room temperature. The chemical shifts are given in ppm relative to tetramethylsilane. Elemental analysis (C, H, N) was performed using a Flash 2000 CHNS elemental analyser (Thermo Scientific).

4.2 | Synthesis of ligand precursors

4.2.1 | Synthesis of 6-(4′-fluorophenyl)fulvene (1)

Pyrrolidine (6 ml, 73 mmol) was added dropwise to a mixture of freshly cracked cyclopentadiene (10 ml, 119 mmol) and 4-fluorobenzaldehyde (6.45 g, 52 mmol) in methanol (150 ml). After addition, the solution was stirred at room temperature for 2 h. The reaction was quenched by a solution of acetic acid (4 ml, 70 mmol) in distilled water (50 ml). The mixture was extracted using pentane (3 × 50 ml), and the organic phases were collected and dried with anhydrous magnesium sulfate. Volatiles were vacuum-evaporated and the crude product was purified by column chromatography on silica using a hexane–diethyl ether (1:1) mixture as the eluent. Yield: 5.10 g (30 mmol, 57%). Orange solid. Analytical and spectroscopic data are in agreement with those reported elsewhere.[22]

4.2.2 | Synthesis of 6-(4′-chlorophenyl)fulvene (2)

The steps of synthesis followed the procedure for compound **1**. Reagents: freshly cracked cyclopentadiene (10 ml, 119 mmol), 4-chlorobenzaldehyde (7.31 g, 50 mmol), pyrrolidine (6 ml, 73 mmol), acetic acid (4 ml, 70 mmol). The crude product was purified by column chromatography on silica using a hexane–diethyl ether (1:1) mixture as the eluent ($R_{f,TLC} = 0.75$). Yield: 7.92 g (42 mmol, 60%). Red oil. Analytical and spectroscopic data are in agreement with those reported elsewhere.[23,24]

4.2.3 | Synthesis of 6-(4′-bromophenyl)fulvene (3)

The steps of synthesis followed the procedure for compound **1**. Reagents: freshly cracked cyclopentadiene (10 ml, 119 mmol), 4-bromobenzaldehyde (9.21 g, 50 mmol), pyrrolidine (6 ml, 73 mmol), acetic acid (4 ml, 70 mmol). The crude product was purified by column chromatography on silica using a hexane–diethyl ether (1:1) mixture as the eluent ($R_{f,TLC} = 0.75$). Yield: 5.36 g (23 mmol, 46%), Red oil. Analytical and spectroscopic data are in agreement those reported elsewhere.[23]

4.3 | Synthesis of molybdenum compounds

4.3.1 | Synthesis of $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_4CH_2C_6H_4F\text{-}4)Mo(CO)_2]$ (5)

A solution of **1** (0.28 g, 1.61 mmol) was dissolved in diethyl ether (10 ml) and treated with a solution of SuperHydride (1 M in tetrahydrofuran (THF), 1.65 ml, 1.65 mmol). The reaction mixture was stirred overnight. The white precipitate was decanted, washed with diethyl ether (3 × 5 ml) and vacuum dried. The white solid was dissolved in THF (10 ml) and added to the solution of **4** (0.50 g, 1.61 mmol) in THF (10 ml) precooled at −80 °C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The crude product was extracted with hot hexane (3 × 10 ml). The volatiles were vacuum evaporated. The product was recrystallized from a hexane–diethyl ether (2:1) mixture at −80 °C. Yield: 440 mg (75%, 1.21 mmol). Yellow viscous oil. Anal. Calcd for $C_{17}H_{15}FMoO_2$ (%): C, 55.75; H, 4.13. Found (%): C, 55.68; H, 4.21. ^1H NMR ($CDCl_3$; 400 MHz; δ, ppm): 7.12 (dd, $^3J(^1H,^1H)$ = 8.1 Hz, $^4J(^1H,^{19}F)$ = 5.4 Hz, 2H, C_6H_4), 6.97 (dd, $^3J(^1H,^1H)$ = 8.1 Hz, $^3J(^1H,^{19}F)$ = 8.7 Hz, 2H, C_6H_4), 5.13 (s, 4H, C_5H_4), 3.91 (tt, $^3J(^1H,^1H)$ = 10.7 Hz, $^3J(^1H,^1H)$ = 7.0 Hz, 1H, *meso*-C_3H_5), 3.56 (s, 2H, $C_5H_4CH_2C_6H_4F$), 2.71 (d, $^3J(^1H,^1H)$ = 7.0 Hz, 2H, *syn*-C_3H_5), 0.94 (d, $^3J(^1H,^1H)$ = 10.7 Hz, 2H, *anti*-C_3H_5). $^{19}F\{^1H\}$ NMR ($CDCl_3$; 376 MHz; δ, ppm): −116.4 (C_6H_4F). FT-IR (ATR; cm^{-1}): 1932 vs (ν_a(CO)), 1844 vs (ν_s(CO)).

4.3.2 | Synthesis of $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_4CH_2C_6H_4Cl\text{-}4)Mo(CO)_2]$ (6)

The steps of synthesis followed the procedure for compound **5**. Reagents: **4** (0.50 g, 1.61 mmol), **2** (0.30 g, 1.61 mmol), Super-Hydride (1 M in THF, 1.65 ml, 1.65 mmol). Yield: 460 mg (59%, 0.95 mmol). Yellow powder. M.p. 50–60 °C. Anal. Calcd for $C_{17}H_{15}ClMoO_2$ (%): C, 53.35; H, 3.95. Found (%): C, 53.26; H, 4.03. ^1H NMR ($CDCl_3$; 400 MHz; δ, ppm): 7.25 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 2H, C_6H_4), 7.10 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 2H, C_6H_4), 5.13 (s, 4H, C_5H_4), 3.91 (tt, $^3J(^1H,^1H)$ = 10.7 Hz, $^3J(^1H,^1H)$ = 7.0 Hz, 1H, *meso*-C_3H_5), 3.56 (s, 2H, $C_5H_4CH_2C_6H_4Cl$), 2.71 (d, $^3J(^1H,^1H)$ = 7.0 Hz, 2H, *syn*-C_3H_5), 0.94 (d, $^3J(^1H,^1H)$ = 10.8 Hz, 2H, *anti*-C_3H_5). FT-IR (ATR; cm^{-1}): 1941 vs (ν_a(CO)), 1854 vs (ν_s(CO)).

4.3.3 | Synthesis of [(η^3-C_3H_5)(η^5-$C_5H_4CH_2C_6H_4Br$-4)$Mo(CO)_2$] (7)

The steps of synthesis followed the procedure for compound **5**. Reagents: **4** (0.50 g, 1.61 mmol), **3** (0.38 g, 1.61 mmol), Super-Hydride (1 M in THF, 1.65 ml, 1.65 mmol). Yield: 450 mg (65%, 1.05 mmol). Yellow powder. M.p. 70–80 °C. Anal. Calcd for $C_{17}H_{15}BrMoO_2$ (%): C, 47.80; H, 3.54. Found (%): C, 48.02; H, 3.49. ^{1}H NMR ($CDCl_3$; 400 MHz; δ, ppm): 7.40 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 7.04 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 5.13 (s, 4H, C_5H_4), 3.91 (tt, $^3J(^1H,^1H)$ = 10.8 Hz, $^3J(^1H,^1H)$ = 7.0 Hz, 1H, *meso*-C_3H_5), 3.54 (s, 2H, $C_5H_4CH_2C_6H_4Br$), 2.72 (d, $^3J(^1H,^1H)$ = 7.0 Hz, 2H, *syn*-C_3H_5), 0.94 (d, $^3J(^1H,^1H)$ = 10.8 Hz, 2H, *anti*-C_3H_5). FT-IR (ATR; cm^{-1}): 1936 vs (ν_a(CO)), 1846 vs (ν_s(CO)).

4.3.4 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4F$-4)$Mo(CO)_2(NCMe)_2$][BF_4] (8)

Compound **5** (366 mg, 1.00 mmol) was dissolved in 10 ml of a CH_2Cl_2–MeCN mixture (10:1), cooled at 0 °C and treated with $HBF_4{\cdot}Et_2O$ (136 µl, 1.00 mmol). The solution immediately changed colour from yellow to dark red. The reaction mixture was slowly warmed to room temperature and stirred for an additional 2 h. The volatiles were vacuum evaporated. The crude product was washed with Et_2O (5 ml), recrystallized from a MeCN–Et_2O mixture and vacuum dried. Yield: 456 mg (92%, 0.92 mmol). Dark orange powder. M.p. 120–130 °C (dec.). Anal. Calcd for $C_{18}H_{16}BF_5MoN_2O_2$ (%): C, 43.76; H, 3.26; N, 5.67. Found (%): C, 43.81; H, 3.18; N, 5.72. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 7.32 (dd, $^3J(^1H,^1H)$ = 8.9 Hz, $^4J(^1H,^{19}F)$ = 5.4 Hz, 2H, C_6H_4), 7.10 (dd, $^3J(^1H,^1H)$ = 8.9 Hz, $^3J(^1H,^{19}F)$ = 8.9 Hz, 2H, C_6H_4), 5.75 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 5.53 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 3.58 (s, 2H, $C_5H_4CH_2C_6H_4F$), 2.46 (s, 6H, CH_3CN). $^{19}F\{^1H\}$ NMR (CD_3CN; 376 MHz; δ, ppm): −117.7 (C_6H_4F), −151.6 (BF_4). FT-IR (ATR; cm^{-1}): 1971 vs (ν_a(CO)), 1903 vs (ν_s(CO)), 1040 vs-br (ν(BF)). Single crystals of **8** suitable for X-ray diffraction analysis were prepared by overlayering of the MeCN solution with Et_2O.

4.3.5 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Cl$-4)$Mo(CO)_2(NCMe)_2$][BF_4] (9)

The steps of synthesis followed the procedure for compound **8**. Reagents: **6** (383 mg, 1.00 mmol), $HBF_4{\cdot}Et_2O$ (136 µl, 1.00 mmol). Yield: 439 mg (86%, 0.86 mmol). Dark orange powder. M.p. 120–130 °C (dec.). Anal. Calcd for $C_{18}H_{16}BClF_4MoN_2O_2$ (%): C, 42.35; H, 3.16; N, 5.49. Found (%): C, 42.32; H, 3.21; N, 5.57. ^{1}H NMR ($CDCl_3$; 400 MHz; δ, ppm): 7.28 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 7.20 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.63 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2H, C_5H_4), 5.49 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 3.57 (s, 2H, $C_5H_4CH_2C_6H_4Cl$), 2.52 (s, 6H, CH_3CN). FT-IR (ATR; cm^{-1}): 1976 vs (ν_a(CO)), 1895 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.6 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Br$-4)$Mo(CO)_2(NCMe)_2$][BF_4] (10)

The steps of synthesis followed the procedure for compound **8**. Reagents: **7** (428 mg, 1.00 mmol), $HBF_4{\cdot}Et_2O$ (136 µl, 1.00 mmol). Yield: 502 mg (90%, 0.90 mmol). Dark orange powder. M.p. 120–130 °C (dec.). Anal. Calcd for $C_{18}H_{16}BBrF_4MoN_2O_2$ (%): C, 38.95; H, 2.91; N, 5.05. Found (%): C, 39.02; H, 2.83; N, 5.12. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 7.55 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 7.28 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.79 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2H, C_5H_4), 5.57 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2H, C_5H_4), 3.60 (s, 2H, $C_5H_4CH_2C_6H_4Br$), 2.49 (s, 6H, CH_3CN). FT-IR (ATR; cm^{-1}): 1975 vs (ν_a(CO)), 1893 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.7 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4F$-4)$Mo(CO)_2$(phen)][BF_4] (11)

Compound **8** (99 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (10 ml) and treated with 1,10-phenanthroline (36 mg, 0.20 mmol). The solution was stirred at room temperature overnight. The volatiles were vacuum evaporated. The crude product was washed with ether and recrystallized from a CH_2Cl_2–Et_2O mixture and vacuum dried. Yield: 112 mg (95%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{18}BF_5MoN_2O_2$ (%): C, 52.73; H, 3.06; N, 4.73. Found (%): C, 52.82; H, 2.98; N, 4.79. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.42 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 2H, $C_{12}H_8N_2$), 8.78 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 2H, $C_{12}H_8N_2$), 8.22 (s, 2H, $C_{12}H_8N_2$), 7.97 (dd, $^3J(^1H,^1H)$ = 8.2 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 2H, $C_{12}H_8N_2$), 6.88 (dd, $^3J(^1H,^1H)$ = 8.9 Hz, $^4J(^1H,^{19}F)$ = 5.4 Hz, 2H, C_6H_4), 6.86 (dd, $^3J(^1H,^1H)$ = 8.9 Hz, $^3J(^1H,^{19}F)$ = 8.9 Hz, 2H, C_6H_4), 5.78 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.70 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 2.97 (s, 2H, $C_5H_4CH_2C_6H_4F$). $^{19}F\{^1H\}$ NMR (CD_3CN 376 MHz; δ, ppm): −117.8 (C_6H_4F), −151.6 (BF_4). FT-IR (ATR; cm^{-1}): 1966 vs (ν_a(CO)), 1885 vs (ν_s(CO)), 1040 vs-br (ν(BF)). Single crystals of **11** suitable for X-ray diffraction analysis were prepared by overlayering of the CH_2Cl_2 solution with hexane.

4.3.8 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Cl$-4)Mo(CO)$_2$(phen)][BF_4] (12)

The steps of synthesis followed the procedure for compound **11**. Reagents: **9** (102 mg, 0.20 mmol), 1,10-phenanthroline (36 mg, 0.20 mmol). Yield: 98 mg (81%, 0.16 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{18}BClF_4MoN_2O_2$ (%): C, 51.31; H, 2.98; N, 4.60. Found (%): C, 51.39; H, 3.06; N, 4.51. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.41 (d, $^3J(^1H,^1H)$ = 5.5 Hz, 2H, $C_{12}H_8N_2$), 8.78 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, $C_{12}H_8N_2$), 8.22 (s, 2H, $C_{12}H_8N_2$), 7.97 (dd, $^3J(^1H,^1H)$ = 8.3 Hz, $^3J(^1H,^1H)$ = 5.5 Hz, 2H, $C_{12}H_8N_2$), 7.11 (d, $^3J(^1H,^1H)$ = 8.6 Hz, 2H, C_6H_4), 6.85 (d, $^3J(^1H,^1H)$ = 8.6 Hz, 2H, C_6H_4), 5.80 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.70 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 2.99 (s, 2H, $C_5H_4CH_2C_6H_4Cl$). FT-IR (ATR; cm^{-1}): 1970 vs (ν_a(CO)), 1898 vs (ν_s(CO)), 1040 vs-br (ν(BF)). Single crystals of **12** suitable for X-ray diffraction analysis were prepared by overlayering of the CH_2Cl_2 solution with hexane.

4.3.9 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Br$-4)Mo(CO)$_2$(phen)][BF_4] (13)

The steps of synthesis followed the procedure for compound **11**. Reagents: **10** (111 mg, 0.20 mmol), 1,10-phenanthroline (36 mg, 0.20 mmol). Yield: 121 mg (92%, 0.18 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{18}BBrF_4MoN_2O_2$ (%): C, 47.82; H, 2.78; N, 4.29. Found (%): C, 47.78; H, 2.75; N, 4.38. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.41 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 2H, $C_{12}H_8N_2$), 8.77 (d, $^3J(^1H,^1H)$ = 8.2 Hz, 2H, $C_{12}H_8N_2$), 8.21 (s, 2H, $C_{12}H_8N_2$), 7.97 (dd, $^3J(^1H,^1H)$ = 8.2 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 2H, $C_{12}H_8N_2$), 7.24 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 6.77 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.80 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 5.69 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 2.97 (s, 2H, $C_5H_4CH_2C_6H_4Br$). FT-IR (ATR; cm^{-1}): 1968 vs (ν_a(CO)), 1896 vs (ν_s(CO)), 1040 vs-br (ν(BF)). Single crystals of **13** suitable for X-ray diffraction analysis were prepared by overlayering of the CH_2Cl_2 solution with hexane.

4.3.10 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4F$-4)Mo(CO)$_2$(5-NH_2-phen)][BF_4] (14)

The steps of synthesis followed the procedure for compound **11**. Reagents: **8** (99 mg, 0.20 mmol), 1,10-phenanthrolin-5-amine (39 mg, 0.20 mmol). Yield: 116 mg (96%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{19}BF_5MoN_3O_2$ (%): C, 51.43; H, 3.15; N, 6.92. Found (%): C, 51.36; H, 3.21; N, 6.84. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.38 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 9.03 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 8.77 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 1H, $C_{12}H_7N_2$), 8.37 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 1H, $C_{12}H_7N_2$), 7.92 (dd, $^3J(^1H,^1H)$ = 8.4 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 7.73 (dd, $^3J(^1H,^1H)$ = 8.3 Hz, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, $C_{12}H_7N_2$), 7.15 (s, 1H, $C_{12}H_7N_2$), 6.88 (s-br, 2H, C_6H_4), 6.86 (s-br, 2H, C_6H_4), 5.73 (m, 2H, C_5H_4), 5.67 (m, 1H, C_5H_4), 5.65 (m, 1H, C_5H_4), 5.60 (s, 2H, NH_2), 2.94 (s, 2H, $C_5H_4CH_2C_6H_4F$). ^{19}F{^{1}H} NMR (CD_3CN; 376 MHz; δ, ppm): −117.8 (C_6H_4F), −151.7 (BF_4). FT-IR (ATR; cm^{-1}): 3382 m (ν(NH)), 1966 vs (ν_a(CO)), 1885 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.11 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Cl$-4)Mo(CO)$_2$(5-NH_2-phen)][BF_4] (15)

The steps of synthesis followed the procedure for compound **11**. Reagents: **9** (102 mg, 0.20 mmol), 1,10-phenanthrolin-5-amine (39 mg, 0.20 mmol). Yield: 117 mg (94%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{19}BClF_4MoN_3O_2$ (%): C, 50.07; H, 3.07; N, 6.74. Found (%): C, 50.15; H, 2.98; N, 6.67. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.38 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 9.02 (d, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, $C_{12}H_7N_2$), 8.77 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 1H, $C_{12}H_7N_2$), 8.37 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 1H, $C_{12}H_7N_2$), 7.92 (dd, $^3J(^1H,^1H)$ = 8.4 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 7.73 (dd, $^3J(^1H,^1H)$ = 8.3 Hz, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, $C_{12}H_7N_2$), 7.15 (s, 1H, $C_{12}H_7N_2$), 7.12 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 6.84 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 5.75 (m, 2H, C_5H_4), 5.68 (m, 1H, C_5H_4), 5.65 (m, 1H, C_5H_4), 5.57 (s, 2H, NH_2), 2.96 (s, 2H, $C_5H_4CH_2C_6H_4Cl$). FT-IR (ATR; cm^{-1}): 3384 m (ν(NH)), 1966 vs (ν_a(CO)), 1885 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.12 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Br$-4)Mo(CO)$_2$(5-NH_2-phen)][BF_4] (16)

The steps of synthesis followed the procedure for compound **11**. Reagents: **10** (111 mg, 0.20 mmol), 1,10-phenanthrolin-5-amine (39 mg, 0.20 mmol). Yield: 125 mg (94%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{26}H_{19}BBrF_4MoN_3O_2$ (%): C, 46.74; H, 2.87; N, 6.29. Found (%): C, 46.62; H, 2.80; N, 6.36. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.37 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 9.02 (d, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 8.77 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 1H, $C_{12}H_7N_2$), 8.36 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 1H, $C_{12}H_7N_2$), 7.92 (dd, $^3J(^1H,^1H)$ = 8.4 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 7.72 (dd, $^3J(^1H,^1H)$ = 8.3 Hz, $^3J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{12}H_7N_2$), 7.25 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 7.15 (s, 1H, $C_{12}H_7N_2$), 6.77 (d, $^3J(^1H.^1H)$ = 8.5 Hz, 2H, C_6H_4), 5.75 (m, 2H, C_5H_4), 5.67 (m, 1H, C_5H_4), 5.65 (m, 1H,

C_5H_4), 5.61 (s, 2H, NH_2), 2.94 (s, 2H, $C_5H_4CH_2C_6H_4Br$). FT-IR (ATR; cm^{-1}): 3385 Mm (ν(NH)), 1966 vs (ν_a(CO)), 1886 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.13 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4F$-4)Mo(CO)$_2$(4,7-Ph$_2$-phen)][BF_4] (17)

The steps of synthesis followed the procedure for compound **11**. Reagents: **8** (99 mg, 0.20 mmol), 4,7-diphenyl-1,10-phenanthroline (67 mg, 0.20 mmol). Yield: 145 mg (97%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{38}H_{26}BF_5MoN_2O_2$ (%): C, 61.31; H, 3.52; N, 3.76. Found (%): C, 61.24; H, 3.58; N, 3.68. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.46 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 8.15 (s, 2H, $C_{12}H_6N_2$), 7.93 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 7.67 (s, 10H, C_6H_5), 7.07 (d, 2H, $^3J(^1H,^1H)$ = 8.5 Hz, C_6H_4), 6.85 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 5.88 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 5.76 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 3.09 (s, 2H, $C_5H_4CH_2C_6H_4F$). $^{19}F\{^1H\}$ NMR (CD_3CN; 376 MHz; δ, ppm): −117.8 (C_6H_4F), −151.6 (BF_4). FT-IR (ATR; cm^{-1}): 1967 vs (ν_a(CO)), 1888 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.3.14 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Cl$-4)Mo(CO)$_2$(4,7-Ph$_2$-phen)][BF_4] (18)

The steps of synthesis followed the procedure for compound **11**. Reagents: **9** (102 mg, 0.20 mmol), 4,7-diphenyl-1,10-phenanthroline (67 mg, 0.20 mmol). Yield: 142 mg (93%, 0.19 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{38}H_{26}BClF_4MoN_2O_2$ (%): C, 59.99; H, 3.44; N, 3.68. Found (%): C, 59.91; H, 3.49; N, 3.72. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.46 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 8.15 (s, 2H, $C_{12}H_6N_2$), 7.93 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 7.67 (s, 10H, C_6H_5), 7.07 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 6.85 (d, $^3J(^1H,^1H)$ = 8.5 Hz, 2H, C_6H_4), 5.88 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 5.76 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 3.09 (s, 2H, $C_5H_4CH_2C_6H_4Cl$). FT-IR (ATR; cm^{-1}): 1967 vs (ν_a(CO)), 1889 vs (ν_s(CO)), 1040 vs-br (ν(BF)). Single crystals of **18**·Ph$_2$phen·HBF_4 suitable for X-ray diffraction analysis were prepared by overlayering of the CH_2Cl_2 solution of the crude product with hexane.

4.3.15 | Synthesis of [(η^5-$C_5H_4CH_2C_6H_4Br$-4)Mo(CO)$_2$(4,7-Ph$_2$-phen)][BF_4] (19)

The steps of synthesis followed the procedure for compound **11**. Reagents: **10** (111 mg, 0.20 mmol), 4,7-diphenyl-1,10-phenanthroline (67 mg, 0.20 mmol). Yield: 158 mg (98%, 0.20 mmol). Red powder. M.p. 150–160 °C (dec.). Anal. Calcd for $C_{38}H_{26}BBrF_4MoN_2O_2$ (%): C, 56.68; H, 3.25; N, 3.48. Found (%): C, 56.62; H, 3.31; N, 3.52. ^{1}H NMR (CD_3CN; 400 MHz; δ, ppm): 9.45 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 8.15 (s, 2H, $C_{12}H_6N_2$), 7.93 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_6N_2$), 7.67 (s, 10H, C_6H_5), 7.20 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 6.77 (d, $^3J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.88 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.76 (dd, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 3.08 (s, 2H, $C_5H_4CH_2C_6H_4Br$). FT-IR (ATR; cm^{-1}): 1966 vs (ν_a(CO)), 1885 vs (ν_s(CO)), 1040 vs-br (ν(BF)).

4.4 | X-ray crystallography

The X-ray data for crystals of compounds **8**, **11**, **12**, **13** and **18**·phen·HBF_4 were obtained at 150 K using an Oxford Cryostream low-temperature device with a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reductions were performed with DENZO-SMN.[25] The absorption was corrected by integration methods.[26] Structures were solved by direct methods (Sir92)[27] and refined by full-matrix least squares based on F^2 (SHELXL97).[28] Hydrogen atoms were mostly localized on a difference Fourier map. However, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors U_{iso}(H) = 1.2(U_{eq}(pivot atom)) or 1.5U_{eq} for the methyl moiety with C—H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings or the allyl moiety, respectively. The tetrafluoroborate structure within **8** contains positionally disordered fluorine atoms. Three of the fluorine atoms were split into two positions with occupancy of 1:1. This disorder has been treated by Shelxl software instructions.[29] SAME Shelxl software instruction was used in the case of **11**, which contains a disordered benzyl group. It was split into two positions with occupancy of about 5:1. The hydrogen atom of the protonated ligand in **18** was localized on the Fourier difference electron density map close to one of the nitrogen atoms. The N—H distance was fixed to be 0.92 Å in the appropriate direction for the N—H···F—BF_3 hydrogen bond. CCDC 1511587 (for **8**), 1511588 (for **11**), 1511589 (for **13**), 1511590 (for **12**) and 1511591 (for **18**·phen·HBF_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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How to cite this article: Honzíčková I, Vinklárek J, Růžičková Z, Řezáčová M, Honzíček J. Modified cyclopentadienyl molybdenum compounds with enhanced cytotoxic activity towards MOLT-4 leukaemia cells. *Appl Organometal Chem*. 2017; e3759. https://doi.org/10.1002/aoc.3759