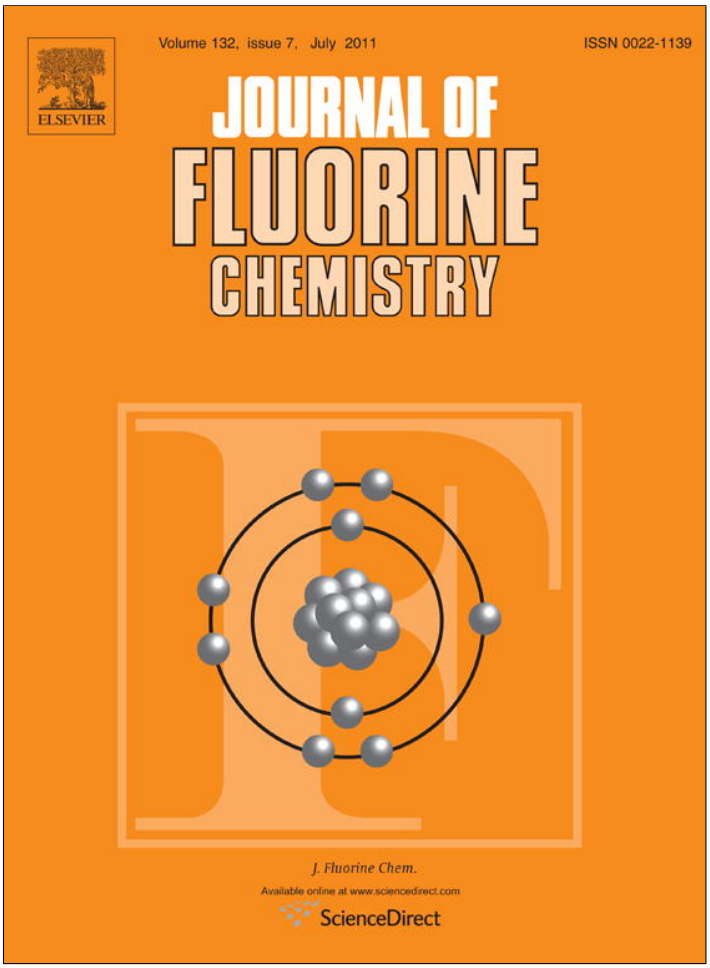

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Polyfluoroalkylated tripyrazolylmethane ligands: Synthesis and complexes

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ABSTRACT

Tripyrazolylmethanes represent a novel class of uncharged ligands analogous to charged tripyrazolylborates (scorpionates), which are isoelectronic and isolobal with cyclopentadienides. We report here a straightforward synthesis of the first polyfluoroalkylated tripyrazolylmethane ligands bearing C_4F_9–$C_{12}F_{25}$ ponytails, based on allylation/perfluoroalkylation/reduction sequence of transformations of 2,2,2-tripyrazol-1-ylethanol. Model complexation reactions of these ligands gave sandwich complexes of copper(II), nickel(II), cobalt(II) and iron(II), the structure of which was confirmed by detailed MS analysis, as well as by NMR spectroscopy for the fourth diamagnetic complex. Fluorophilicity of the ligands and their complexes peaks for $C_{10}F_{21}$ ponytail but lies below zero.

1. Introduction

Both heavy and light fluorous chemistry, albeit still a newcomer in the field of organic and organometallic chemistry, had already established a distinguished place in science [1]. Among numerous applications, robust fluorous ligands allowing recycle of often highly valued and expensive homogeneous catalysts still remain a formidable challenge for organofluorine chemists. Due to simple preparation and substantial variability, polyfluorinated phosphane-based ligands still represent a major class of fluorous ligands despite their low oxidation stability limiting their recycle [2].

Surprisingly little attention has been paid to the synthesis of fluorous cyclopentadienes and cyclopentadienide sandwich complexes derived from them, especially having in mind broad impact and wide industrial use of their non-fluorinated counterparts. Nevertheless, several classes of light fluorous cyclopentadienes and cyclopentadienides are known differing mainly in the character of the polyfluorinated ponytail and the length of the non-fluorinated spacer separating it from the core. Thus, ligands and complexes with the fluoroalkyl chains with no spacer [3], methylene [4], ethylene [5], or trimethylene [6] spacer, as well as with fluorosilyl chains [7] have been synthesized.

On the other hand, a number of heavy fluorous cyclopentadienes and cyclopentadienides known, which generally require multiple polyfluorinated chains attached, is highly limited [8], the main problem in their synthesis being the regioselectivity issue [8b,8c]. Moreover, multiple polyfluoroalkylation severely limits their complexation ability, probably due to excessive steric hindrance of polyfluorinated ponytails [8f]. This prompted our search for cyclopentadienide analogues allowing both selective multiple regioselective polyfluoroalkylation and facile complexation of multiply polyfluoroalkylated ligands.

Tripyrazolylborates (also nicknamed scorpionates due to their ability of optional two- or threefold coordination in analogy to a scorpion biting its prey with two claws and optionally with a tail) represent a comparably novel class of wide scope ligands with a three-dimensional character [9] (in contrast to the two-dimensional cyclopentadienides), isoelectronic and isolobal with the cyclopentadienides. Scorpionates can be modified with a high level of regioselectivity [10], however, their anionic borate core does not allow purification by column chromatography. In contrast to that, analogous tripyrazolylmethane ligands retain high proneness to regioselective functionalization while being much more easily purifyable [11] and thus logically attracted our attention as the first candidate for the cyclopentadiene substitute. In this paper we

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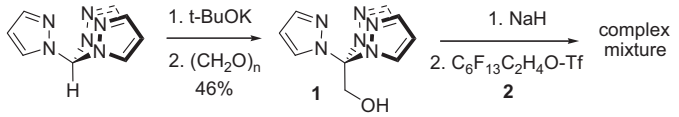


Scheme 1.

wish to report our approach to the polyfluoroalkylated tripyrazolylmethanes based on the modification of the methine carbon of the tripyrazolylmethane core.

2. Results and discussion

2.1. Synthesis of the ligands

In contrast to the two-dimensional cyclopentadienide anions containing five identical carbons, tripyrazolylmethanes offer in principle four different positions for selective modifications, viz. C3, C4 and C5 carbons of the pyrazole rings, and the methine carbon connecting the three heteroaromatic rings. The simplest way how to modify the methine carbon consists of lithiation followed by attack on an electrophile [12]. Due to the inferior reactivity of polyfluoroalkylated electrophiles [8a] and potential problems with complexations caused by steric hindrance of the methine-substituted tripyrazolylmethanes [13], we decided to modify the parent skeleton first with a hydroxymethyl group according to the original Reger's paper [14] and obtained the key intermediate, 2,2,2-tripyrazol-1-ylethanol (**1**), in an acceptable yield.

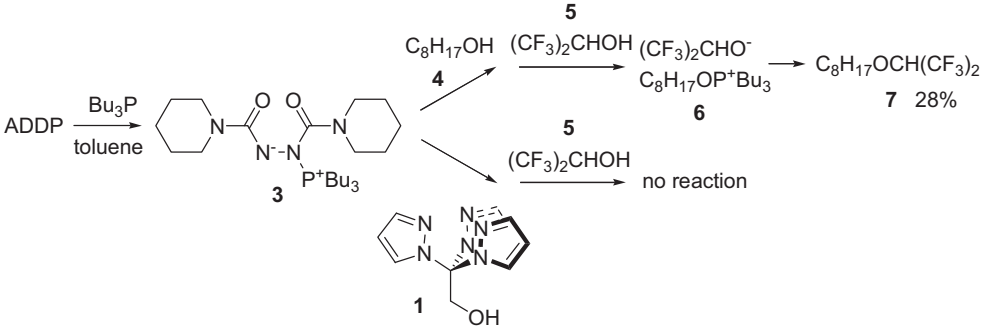
To obtain the ligands with as high fluorophilicity as possible we attempted to keep the non-fluorinated spacer between the perfluoroalkyl chain and the tripyrazolylmethane core as short as possible and hence our first approach employed the reaction of 2,2,2-tripyrazol-1-ylethoxide with polyfluoroalkylated triflate **2** (Scheme 1). However, at low temperatures no reaction occurred while under more forcing conditions a complex mixture was formed probably as a result of thiophilic attack of hard nucleophile on a sulfonyl group of the triflate [15].

We therefore turned our attention to Mitsunobu reaction as polyfluoroalkanols with short spacer between the hydroxy group and the perfluorinated group are sufficiently acidic to undergo ether formation providing more efficient protocol using ADDP 1,1′-(azodicarbonyl)dipiperidine in combination with tributylphosphane is employed [16]. Indeed, model reaction of octan-1-ol (**4**) with 1,1,1,3,3,3-hexafluoropropan-2-ol (**5**, HFIP) gave the target product **7**, where a low yield of 28% was caused mainly by a small scale distillation. In contrast to that, only starting tripyrazolylethanol **1** was identified in the crude reaction mixture in an analogous reaction. Detailed ^{31}P NMR analysis of both reactions revealed primary formation of betain **3** formed from ADDP and Bu_3P resonating at +57.6 ppm. In the case of the former model reaction a signal at +97.8 ppm of intermediary alkoxyphosphonium **6** salt was observed after addition of fluoroalcohol **5**, while no such intermediate was detected in the latter reaction probably as a result of excessive steric hindrance around the reaction centre of the alcohol **1** (Scheme 2).

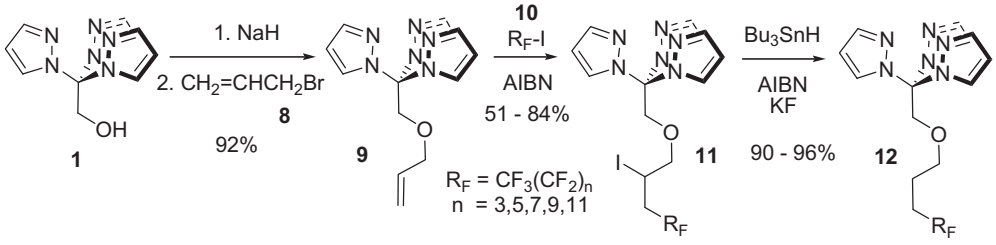
We finally turned our attention to the "conservative" strategy consisting of allylation, radical addition of perfluoroalkyl iodide and removal of the iodine atom. In contrast to the reaction with polyfluoroalkyl triflate **2,** substitution with allyl bromide (**8**) in analogy to Ref. [12] afforded excellent yield of the corresponding allyl ether **9**. Subsequent radical addition was performed with a series of perfluoroalkyl iodides **10** with the aim to observe how the length of the perfluorinated chain influences fluorophilicity pattern. Among various approaches, initiation with AIBN in the solvent-free system [17] used previously successfully by us [18] gave the best yields of the respective adducts **11** (Scheme 3, Table 1). Final removal of iodine atom with tributylstannane under radical condition following the conditions of Ref. [19] led to very good yields of the target ligands **12** after anhydrous work-up consisting of treatment with potassium fluoride [20] followed by filtration through a short silica plug (Scheme 3, Table 1).

2.2. Model complexations of ligand 12b

For comparison of complexing properties of the obtained polyfluoroalkylated ligands **12** with the parent tripyrazolylmethane ligand, we synthesized model complexes **13**–**16** using Cu(II), Ni(II) and Co(II) nitrates, as well as Fe(II) tetrafluoroborate



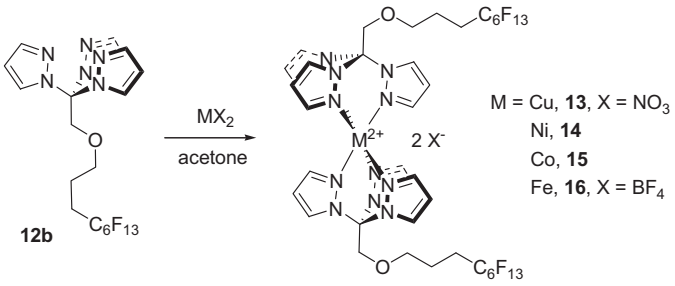
Scheme 2.



Scheme 3.

Table 1
Yields of perfluoroalkylation/reduction of allyl ether **9**.

R_F	Compound	Yield (%)	Compound	Yield (%)
C_4F_9	**11a**	51	**12a**	94
C_6F_{13}	**11b**	72	**12b**	96
C_8F_{17}	**11c**	84	**12c**	95
$C_{11}F_{21}$	**11d**	58	**12d**	94
$C_{12}F_{25}$	**11e**	60	**12e**	90



Scheme 4.

by stirring the ligand **12b** and the respective metal salt in a 2:1 ratio. In contrast to the original procedure for non-fluorinated tripyrazolylmethane in which the complexation has been accomplished in water [21], we had to employ acetone as the solvent due to hydrophobic properties of ligands **12**. Complexes **13**–**16** were isolated in a quantitative yield by simple evaporation of the solvent and optional reprecipitation of their acetone solution with hexane (Scheme 4). Due to paramagnetic properties of complexes **13**–**15**, they were identified only by IR, MS and HRMS spectroscopy. Detailed analysis of isotopic patterns in zoom peaks of the MS spectra confirmed the presence of the respective cations by comparison with the simulated spectra. On the other hand, Fe complex **16** is diamagnetic and hence ^{1}H, ^{13}C and ^{19}F NMR spectra could be recorded with the complete characterization of the sandwich.

2.3. Fluorophilicity measurements

Fluorophilicities f_i were calculated as natural logarithms of fluorous partition coefficients P_i(FBS) between perfluoro(methylcyclohexane) and toluene obtained from gravimetric measurements according to our previous approach [22]. Due to a low content of fluorine all ligands **12** have fluorous partition coefficients lower than 1 and their fluorophilicity hence lies below zero. The highest value was achieved for ligand **12d**, i.e. $R_F = C_{10}F_{21}$, which is in agreement with previous experimental observations: for very long perfluorinated chains fluorophilicity sinks due to decreasing solubility in perfluorinated solvents [3a]. Surprisingly, charged complexes **13**–**16** have little higher P_i(FBS) and f_i values, again with very low solubility both in toluene and in perfluoromethylcyclohexane. The results of all fluorophilicity and solubility measurements are listed in Table 2.

Table 2
Fluorous partition coefficient and fluorophilicity values of ligands **12** and complexes **13**–**16** and solubilities of complexes **13**–**16**.

Compound	P_i(FBS)	f_i	Compound	P_i(FBS)	f_i	Solubility (mg/ml)	
						PFMC	Toluene
12a	0.04	−3.22	**13**	0.40	−0.92	1.4	3.6
12b	0.05	−3.00	**14**	0.25	−1.39	1.3	5.3
12c	0.07	−2.66	**15**	0.72	−0.33	1.0	1.4
12d	0.34	−1.08	**16**	0.23	−1.47	0.6	2.6
12e	0.24	−1.43					

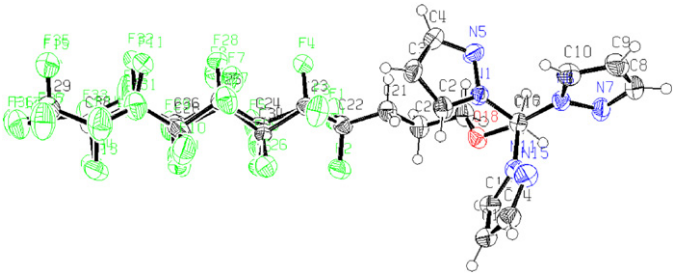


Fig. 1. ORTEP [24] plot (50% probability) of ligand **12c**.

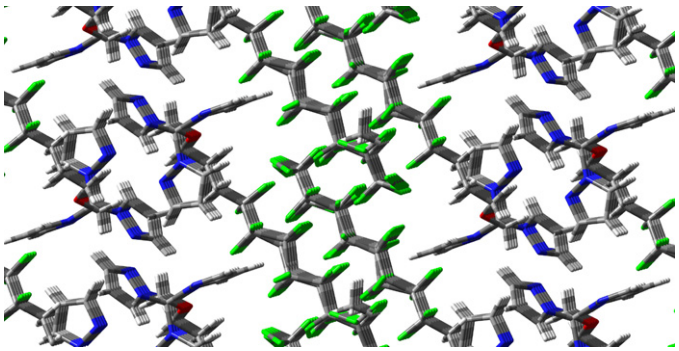


Fig. 2. Crystal packing of ligand **12c**.

2.4. Crystal structure of ligand 12c

White crystals of sufficient quality for X-ray diffraction spectroscopy were obtained after several recrystallizations from chloroform. The crystal is highly disordered in the perfluoroalkyl part where two distinguished conformations could be recognized, probably due to loose packing of perfluorinated chains assembled into fluorous layers (Figs. 1 and 2) [23].

3. Conclusions

2,2,2-Tripyrazol-1-ylethanol was employed as the key intermediate for the synthesis of the first example of tripyrazolylmethane ligands containing long polyfluoroalkylated chains. Although strategies employing either nucleophilic substitution of polyfluoroalkyl triflate with tripyrazolylmethane-based alkoxide or Mitsunobu protocol with polyfluorinated alcohols were unsuccessful, allylation of the key intermediate followed by radical perfluoroalkylation/reduction sequence afforded a series of tripyrazolylmethane ligands bearing polyfluoroalkoxyalkyl ponytail on the central methine carbon. Model complexations with Cu(II), Ni(II) and Co(II) nitrates yielded coloured paramagnetic sandwich complexes, the structure of which was confirmed by IR, MS and HRMS spectroscopy. In contrast to that, complexation with Fe(II) tetrafluoroborate led to diamagnetic complex which was identified by NMR spectroscopy. The ligands and their complexes displayed limited solubility in perfluorinated solvents and due to low fluorine content are not fluorophilic.

4. Experimental

4.1. General description of methods and materials

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz and ^{13}C NMR spectra at 75.43 MHz using residual deuterated solvent signals as the internal standards, ^{19}F NMR spectra at 282.22 MHz using CCl_3F as the internal standard.

Chemical shifts are given in ppm, coupling constants in Hz. IR spectra were taken with a FTIR Nicolet 6700 instrument in $CHCl_3$ or KBr pellets. Mass spectra (ESI, APCI) were measured with a LCQ Fleet (Finnigan) instrument, HRMS spectra (ESI, APCI, FAB) with a LTQ Orbitrap XL (Thermo Fisher Scientific) or ZAB-EQ (VG Analytical) instruments.

All reactions were performed in dry inert atmosphere (Ar) in an oven-dried flasks. 2,2,2-(Tripyrazol-1-yl)ethan-1-ol (**1**, $TpmCH_2OH$) was prepared according to Ref. [14], (perfluorohexyl)methyl triflate (**2**) according to Ref. [8a]. Perfluoroalkyl iodides **11a**–**11e** were kindly gifted by Atochem. Perfluoro(methylcyclohexane) was purchased from Apollo Scientific, other reagents from Sigma–Aldrich. Dry DMF was obtained from Acros, toluene was dried over Na and distilled.

4.2. Attempted preparation of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl 2,2,2-tripyrazol-1-ylethyl ether based on polyfluoroalkylated triflate

A flask was charged with sodium hydride (73.7 mg, 1.02 mmol), tripyrazolylethanol **1** (250 mg, 1.02 mmol) and THF (20 mL), followed by addition of solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl triflate (**2**, 508 mg, 1.02 mmol) in THF (11 mL). The mixture was then refluxed for 5 h. Quenching the reaction with water, extraction with diethyl ether (3× 15 mL), drying the organic solution with sodium sulfate and evaporation of solvents on rotary vacuum evaporator gave unseparable mixture of products.

4.3. Model Mitsunobu preparation of 1,1,1,3,3,3-hexafluoropropan-2-yl octyl ether (7)

A flask was charged with octan-1-ol (**4**, 110 mg, 0.767 mmol), ADDP (1,1′-(azodicarbonyl)dipiperidine, 388 mg, 1.54 mmol), tributylphosphane (311 mg, 1.54 mmol) and toluene (11 mL). After 11 min, 1,1,1,3,3,3-hexafluoropropan-2-ol (**5**, 258 mg, 1.54 mmol) was added and the mixture was stirred overnight. White precipitate was filtered off and solvent was evaporated on rotary vacuum evaporator. Vacuum distillation (2.5 Pa) gave 60 mg (28%) of the target product **7**. ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 0.89 (t, $^3J_{H-H}$ = 6.0 Hz, 3H, C**H**$_3$), 1.20–1.45 (m, 12H, CC**H**$_2$C), 3.82 (t, $^3J_{H-H}$ = 6.5 Hz, 2H, CH_2C**H**$_2$O), 4.00 (septet, $^3J_{H-F}$ = 6.2 Hz, 1H, C**H**$(CF_3)_2$) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −74.7 (d, $^3J_{H-F}$ = 6 Hz, 6F, CH(C**F**$_3)_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 14.0 (**C**H_3), 22.6 (**C**H_2), 25.5 (**C**H_2), 29.2–29.4 (3C, **C**H_2), 31.8 (**C**H_2CH_2O), 75.7 (**C**H_2O), 76.4 (m, **C**$H(CF_3)_2$, 121.6 (q, $^1J_{C-F}$ = 284 Hz) ppm. IR (ν/cm^{-1}): 2959 m, 2933 m, 2860 w, 1373 m, 1289 s, 1267 m, 1209 s, 1141 m, 1115 m. EA calcd. for $C_{11}H_{18}F_6O$ 48.96% C, 6.73% H, found 47.14% C, 6.47% H.

4.4. Attempted Mitsunobu preparation of hexafluoropropan-2-yl 2,2,2-tripyrazol-1-ylethyl ether

A flask was charged with tripyrazolylethanol **1** (110 mg, 0.409 mmol), ADDP (206 mg, 0.819 mmol, toluene (11 mL) and tributylphosphane (166 mg, 0.819 mmol). After 11 min 1,1,1,3,3,3-hexafluoropropan-2-ol (**5**, 138 mg, 0.819 mmol) was added and the mixture was stirred overnight. White precipitate formed was filtered off and the solvent was removed on the rotary vacuum evaporator. By ^{1}H NMR analysis only starting tripyrazolylethanol **1** was detected in the reaction mixture.

4.5. Allyl 2,2,2-tripyrazol-1-ylethyl ether (9)

A flask was charged with NaH (60 mg, 2.5 mmol), 2,2,2-(tripyrazol-1-yl)ethan-1-ol (**1**, 500 mg, 2.05 mmol) and DMF (50 mL). Allyl bromide (**8**) was added and the mixture was stirred at r.t. for 24 h. After addition of diethyl ether (20 mL), the mixture was extracted with water (3× 110 mL). The organic phase was dried with anh. Na_2SO_4 and solvents were removed on a rotary vacuum evaporator (50 °C/2 h/2 kPa). Column chromatography (eluent: dichloromethane/ethyl acetate 3:1) of the residue gave ether **9** (0.53 g, 92%, light yellow viscous oil). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 3.97 (dt, $^3J_{H-H}$ = 9.0 Hz, $^4J_{H-H}$ = 1.5 Hz, 2H, =CHC**H**$_2$), 5.09 (s, 2H, OC**H**$_2$C); 5.17 (ddt, $^2J_{H-H}$ = 1.5 Hz, $^3J_{H-H}$ = 9.5 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, *cis*-C**H**$_2$=), 5.21 (ddt, $^2J_{H-H}$ = 1.5 Hz, $^3J_{H-H}$ = 16.6 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, *trans*-C**H**$_2$=), 5.78 (ddt, $^3J_{H-H}$ = 9.0 Hz, $^3J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 16.6 Hz, 1H, =C**H**CH_2), 6.33 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.42 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 72.9 (O**C**H_2C), 73.1 (O**C**H_2CH=), 89.8 (CH_2**C**), 116.4 (C**C**H=C), 117.9 (=**C**H_2), 130.8 (**C**H=CH_2), 133.5 (=**C**HN), 141.3 (**C**H=N) ppm. IR (ν/cm^{-1}): 3130 w, 3116 w, 1515 m, 1423 m, 1387 s, 1322 s, 1200 s, 1163 s. MS (APCI), m/z (%): 285 $[M+H]^+$ (60), 213 $[Pz_3C]^+$ (110), 146 $[Pz_2C]^+$ (90). HRMS (ESI): $[M+Na]^+$ calcd. for $C_{14}H_{16}N_6NaO$ 307.1278, found 307.1273.

4.6. 2-Iodo-3-(perfluoroalkyl)propyl 2,2,2-tripyrazol-1-ylethyl ether (11). General procedure

A flask was charged with allyl ether **9**, AIBN and perfluoroalkyl iodide **11**. A neat mixture was stirred for 3 h at 110 °C. After cooling the mixture to r.t., product **11** was isolated by column chromatography.

4.7. 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl 2,2,2-tripyrazol-1-ylethyl ether (11a)

According to the general procedure, allyl ether **9** (250 mg, 0.88 mmol), perfluorobutyl iodide (**10a**, 465 mg, 1.32 mmol) and AIBN (5 mg, 0.026 mmol) yielded polyhalogenated ether **11a** (280 mg, 50.5%, m.p. 48.6–49.2 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 2.59 (m, 2H, C**H**$_2CF_2$), 3.73 (m, 2H, CHIC**H**$_2$), 4.23 (m, 1H, C**H**I), 5.19 (s, 2H, C**H**$_2$C), 6.35 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.40 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.4 (t, $^4J_{F-F}$ = 9 Hz, 3F, C**F**$_3$), −113.4 (m, 2F, CH_2C**F**$_2$), −124.8 (m, 2F, C**F**$_2$), 126.3 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 13.2 (**C**HI), 37.2 (t, $^2J_{C-F}$ = 21 Hz, **C**H_2CF_2), 74.0 (O**C**H_2C), 76.7 (O**C**H_2CHI), 89.5 (CH_2**C**), 116.7 (CH**C**H=CH), 112–120 (m, 4C, **C**F_2 and **C**F_3), 130.8 (=**C**HN), 141.5 (**C**H=N) ppm. IR (ν/cm^{-1}): 3123 w, 2940 w, 1516 m, 1426 m, 1228 s, 1132 s, 1117 s, 1188 s. MS (APCI), m/z (%): 630 $[M]^+$ (5), 594 [M-pz+MeOH]$^+$ (40), 563 $[M-pz]^+$ (30), 527 $[MH-I+Na]^+$ (90), 491 $[MH-I-pz+MeOH+Na]^+$ (110). HRMS (ESI): calcd. for $C_{18}H_{17}F_9IN_6O$ ($[MH]^+$) 631.0359, found 631.0358.

4.8. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-iodononyl 2,2,2-tripyrazol-1-ylethyl ether (11b)

According to the general procedure, allyl ether **9** (250 mg, 0.88 mmol), perfluorohexyl iodide (**10b**, 588 mg, 1.32 mmol) and AIBN (5 mg, 0.026 mmol) yielded polyhalogenated ether **11b** (398 mg, 72.1%, m.p. 75.1–76.0 °C, white crystals). ^{1}H NMR (299.97 MHz, acetone-d_6): δ 2.74 (m, 2H, C**H**$_2CF_2$), 3.89 (m, 2H, CHIC**H**$_2$), 4.42 (m, 1H, C**H**I), 5.21 (s, 2H, C**H**$_2$C), 6.37 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.50 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.62 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, acetone-d_6): δ −80.6 (t, $^4J_{F-F}$ = 11 Hz, 3F, C**F**$_3$), −113.2 (m, 2F, CH_2C**F**$_2$), −121.3 (m, 2F, C**F**$_2$), −122.3 (m, 2F, C**F**$_2$), −123.1 (m, 2F, C**F**$_2$), −125.7 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, acetone-d_6): δ 15.0 (**C**HI), 38.3 (t, $^2J_{C-}$

$_F$ = 21 Hz, **C**H_2CF_2), 75.1 (O**C**H_2C), 78.2 (O**C**H_2CHI), 90.6 (CH_2**C**), 117.7 (CH**C**H=CH), 111–128 (m, 6C, **C**F_2 and **C**F_3), 132.5 (=**C**HN), 142.4 (**C**H=N) ppm. IR (ν/cm^{-1}): 3123 w, 2941 w, 1516 m, 1425 m, 1235 s, 1140 s, 1188 s. MS (APCI), *m*/*z* (%): 730 $[M]^+$ (20), 695 [M-pz+MeOH]$^+$ (110), 664 [M-pz]$^+$ (80), 627 [MH−I+Na]$^+$ (60), 591 [MH−I-pz+MeOH+Na]$^+$ (20). HRMS (ESI): calcd. for $C_{20}H_{16}F_{13}IN_6$-NaO ([M+Na]$^+$) 753.0115, found 753.0098.

4.9. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-2-iodoundecyl 2,2,2-tripyrazol-1-ylethyl ether (11c)

According to the general procedure, allyl ether **9** (250 mg, 0.88 mmol), perfluorooctyl iodide (**10c**, 720 mg, 1.32 mmol) and AIBN (5 mg, 0.026 mmol) yielded polyhalogenated ether **11c** (686 mg, 83.8%, m.p. 93.3–93.9 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 2.59 (m, 2H, C**H**$_2CF_2$), 3.76 (m, 2H, CHIC**H**$_2$), 4.23 (m, 1H, C**H**I), 5.19 (s, 2H, C**H**$_2$C), 6.34 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.40 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.1 (t, $^4J_{F-F}$ = 11 Hz, 3F, C**F**$_3$), −114.3 (m, 2F, CH_2C**F**$_2$), −122.0 (m, 2F, C**F**$_2$), 122.4 (m, 4F, C**F**$_2$), −123.1 (m, 2F, C**F**$_2$), −124.0 (m, 2F, C**F**$_2$), −126.5 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 13.3 (**C**HI), 37.4 (t, $^2J_{C-F}$ = 17 Hz, **C**H_2CF_2), 74.0 (O**C**H_2C), 76.7 (O**C**H_2CHI), 89.5 (CH_2**C**), 116.7 (CH**C**H=CH), 118–124 (m, 8C, **C**F_2 and **C**F_3), 130.8 (=**C**HN), 141.5 (**C**H=N) ppm. IR (ν/cm^{-1}): 3124 w, 2923 w, 1516 m, 1426 m, 1244 s, 1202 s, 1146 s, 1117 s, 1141 s. MS (APCI), *m*/*z* (%): 830 $[M]^+$ (5), 794 [M-pz+MeOH]$^+$ (90), 763 [M-pz]$^+$ (50), 727 [MH−I+Na]$^+$ (110), 691 [MH−I-pz+MeOH+Na]$^+$ (80). HRMS (ESI): calcd. for $C_{22}H_{17}F_{17}IN_6O$ ([MH]$^+$) 831.0232, found 831.0240.

4.10. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heneicosafluoro-2-iodotridecyl 2,2,2-tripyrazol-1-ylethyl ether (11d)

According to the general procedure, allyl ether **9** (250 mg, 0.88 mmol), perfluorodecyl iodide (**10d**, 853 mg, 1.32 mmol) and AIBN (5 mg, 0.026 mmol) yielded polyhalogenated ether **11d** (475 mg, 58.1%, m.p. 114.1–114.8 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 2.58 (m, 2H, C**H**$_2CF_2$), 3.76 (m, 2H, CHIC**H**$_2$), 4.23 (m, 1H, C**H**I), 5.20 (s, 2H, C**H**$_2$C), 6.34 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.40 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.3 (t, $^4J_{F-F}$ = 9 Hz, 3F, C**F**$_3$), −114.3 (m, 2F, CH_2C**F**$_2$), −122.3 (m, 11F, C**F**$_2$), −123.3 (m, 2F, C**F**$_2$), −124.0 (m, 2F, C**F**$_2$), −126.7 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 15.6 (**C**HI), 37.5 (t, $^2J_{C-F}$ = 18 Hz, **C**H_2CF_2), 74.0 (O**C**H_2C), 76.7 (O**C**H_2CHI), 89.3 (CH_2**C**), 116.6 (CH**C**H=CH), 117–126 (m, 10C, **C**F_2 and **C**F_3), 130.9 (=**C**HN), 141.4 (**C**H=N) ppm. IR (ν/cm^{-1}): 3123 w, 2941 w, 1424 m, 1245 m, 1209 s, 1150 s, 1141 m. MS (APCI), *m*/*z* (%): 930 $[M]^+$ (20), 894 [M-pz+MeOH]$^+$ (40), 827 [MH−I+Na]$^+$ (30), 791 [MH−I-pz+MeOH+Na]$^+$. HRMS (ESI): calcd. for $C_{24}H_{16}F_{21}IN_6NaO$ ([M+Na]$^+$) 952.9987, found 952.9982.

4.11. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-Pentacosafluoro-2-iodopentadecyl 2,2,2-tripyrazol-1-ylethyl ether (11e)

According to the general procedure, allyl ether **9** (250 mg, 0.88 mmol), perfluorododecyl iodide (**10e**, 953 mg, 1.32 mmol) and AIBN (5 mg, 0.026 mmol) yielded polyhalogenated ether **11e** (544 mg, 60.1%, m.p. 130.5–131.0 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 2.56 (m, 2H, C**H**$_2CF_2$), 3.76 (m, 2H, CHIC**H**$_2$), 4.23 (m, 1H, C**H**I), 5.19 (s, 2H, C**H**$_2$C), 6.35 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.40 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.2 (t, $^4J_{F-F}$ = 11 Hz, 3F, C**F**$_3$), −114.3 (m, 2F, CH_2C**F**$_2$), −122.2 (m, 12F, C**F**$_2$), −123.2 (m, 2F, C**F**$_2$), −124.0 (m, 2F, C**F**$_2$), −126.6 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 14.6 (**C**HI), 38.7 (t, $^2J_{C-F}$ = 19 Hz, **C**H_2CF_2), 74.0 (O**C**H_2C), 76.7 (O**C**H_2CHI), 89.6 (CH_2**C**), 116.7 (CH**C**H=CH), 118–126 (m, 12C, **C**F_2 and **C**F_3), 130.8 (=**C**HN), 141.6 (**C**H=N) ppm. IR (ν/cm^{-1}): 3120 w, 2942 w, 1516 m, 1425 m, 1241 m, 1147 s, 1111 m, 1141 m. MS (APCI), *m*/*z* (%): 1130 $[M]^+$ (11), 994 [M-pz+MeOH]$^+$ (40), 927 [MH−I+Na]$^+$ (60), 891 [MH−I-pz+MeOH+Na]$^+$ (110). HRMS (ESI): calcd. for $C_{26}H_{17}F_{25}IN_6O$ ([MH]$^+$) 1131.0114, found 1131,0115.

4.12. 3-(Perfluoroalkyl)propyl 2,2,2-tripyrazol-1-ylethyl ether (12). General procedure

A flask was charged with polyhalogenated ether **11**, AIBN and toluene, followed by Bu_3SnH. The mixture was heated to 75 °C for 1 h. After cooling to r.t., KF was added and the precipitate formed was separated by filtration. Toluene was removed on a rotary vacuum evaporator (60 °C/2 h/2 kPa). Column chromatography (eluent: dichloromethane/ethyl acetate 6:1) of the residue gave the target ligand **12**.

4.13. 4,4,5,5,6,6,7,7,7-Nonafluoroheptyl 2,2,2-tripyrazol-1-ylethyl ether (12a)

According to the general procedure, polyhalogenated ether **11a** (100 mg, 0.158 mmol), Bu_3SnH (92 mg, 0.32 mmol) and AIBN (2 mg, 0.016 mmol) in toluene (3 mL) yielded after treatment with KF (18 mg, 0.32 mmol) polyfluorinated ether **12a** (75 mg, 94%, m.p. 76.7–77.4 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 1.80 (m, 4H, CF_2C**H**$_2$ and CF_2CH_2C**H**$_2$), 3.57 (t, $^3J_{H-H}$ = 5.6 Hz, 2H, CH_2C**H**$_2$O), 5.09 (s, 2H, C**H**$_2$C), 6.33 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.37 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.64 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.6 (t, $^4J_{F-F}$ = 9 Hz, 3F, C**F**$_3$), −115.3 (m, 2F, CH_2C**F**$_2$), −125.0 (m, 2F, C**F**$_2$), 126.6 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 20.5 (CH_2C**H**$_2CH_2$), 27.4 (t, $^2J_{C-F}$ = 23 Hz, CF_2C**H**$_2$), 70.7 (O**C**H_2C), 74.0 (O**C**H_2CH_2), 89.7 (CH_2**C**), 116.5 (CH**C**H=CH), 113–122 (m, 4C, **C**F_2 and **C**F_3), 130.7 (=**C**HN), 141.3 (**C**H=N) ppm. IR (ν/cm^{-1}): 3138 w, 2945 w, 1518 m, 1426 m, 1230 s, 1129 s, 1163 m. MS (APCI), *m*/*z* (%): 505 $[M]^+$ (5), 469 [M-pz+MeOH]$^+$ (110), 438 [M-pz]$^+$ (50). HRMS (ESI): calcd. for $C_{18}H_{17}F_9N_6NaO$ ([M+Na]$^+$) 527.1212, found 527.1208.

4.14. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl 2,2,2-tripyrazol-1-ylethyl ether (12b)

According to the general procedure, polyhalogenated ether **11b** (100 mg, 0.137 mmol), Bu_3SnH (80 mg, 0.27 mmol) and AIBN (2 mg, 0.016 mmol) in toluene (3 mL) yielded after treatment with KF (16 mg, 0.27 mmol) polyfluorinated ether **12b** (79 mg, 96%, m.p. 80.9–81.7 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 1.80 (m, 4H, CF_2C**H**$_2$ and CF_2CH_2C**H**$_2$), 3.58 (t, $^3J_{H-H}$ = 5.6 Hz, 2H, CH_2C**H**$_2$O), 5.09 (s, 2H, C**H**$_2$C), 6.33 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHC**H**=CH), 7.37 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =C**H**N), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, C**H**=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.3 (t, $^4J_{F-F}$ = 11 Hz, 3F, C**F**$_3$), −115.1 (m, 2F, C**F**$_2$), −122.5 (m, 2F, C**F**$_2$), −123.5 (m, 2F, C**F**$_2$), −124.1 (m, 2F, C**F**$_2$), −126.7 (m, 2F, CF_3C**F**$_2$) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 20.5 (CH_2C**H**$_2CH_2$), 27.5 (t, $^2J_{C-F}$ = 23 Hz, CF_2C**H**$_2$), 70.7 (O**C**H_2C), 74.0 (O**C**H_2CH_2), 89.7 (CH_2**C**), 116.5 (CH**C**H=CH), 111–125 (m, 6C, **C**F_2 and **C**F_3), 130.7 (=**C**HN), 141.4 (**C**H=N) ppm. IR (ν/cm^{-1}): 3145 w, 2942 w, 1518 m, 1425 m, 1225 s, 1141 s, 1161 m. MS (APCI), *m*/*z* (%): 604 $[M]^+$ (11), 568 [M-pz+MeOH]$^+$ (110), 537 [M-pz]$^+$ (80). HRMS

(ESI): calcd. for $C_{20}H_{18}F_{13}N_6O$ ([MH]$^+$) 605.1329, found 605.1328.

4.15. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl 2,2,2-tripyrazol-1-ylethyl ether (12c)

According to the general procedure, polyhalogenated ether **11c** (100 mg, 0.121 mmol), Bu_3SnH (71 mg, 0.24 mmol) and AIBN (2 mg, 0.016 mmol) in toluene (3 mL) yielded after treatment with KF (14 mg, 0.24 mmol) polyfluorinated ether **12c** (81 mg, 95%, m.p. 90.4–91.0 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 1.81 (m, 4H, CF_2CH_2 and $CF_2CH_2CH_2$), 3.57 (t, $^3J_{H-H}$ = 5.0 Hz, 2H, CH_2CH_2O), 5.11 (s, 2H, CH_2C), 6.33 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHCH=CH), 7.38 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =CHN), 7.66 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, CH=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.3 (t, $^4J_{F-F}$ = 11 Hz, 3F, CF_3), −115.1 (bs, 2F, CH_2CF_2), −122.5 (bs, 6F, CF_2), 123.3 (bs, 2F, CF_2), −124.1 (bs, 2F, CF_2), −126.7 (bs, 2F, CF_3CF_2) ppm. ^{13}C NMR ($CDCl_3$): δ 20.4 ($CH_2CH_2CH_2$), 27.5 (t, $^2J_{C-F}$ = 23 Hz, CF_2CH_2), 70.7 (OCH_2C), 74.0 (OCH_2CH_2), 89.7 (CH_2C), 116.5 (CHCH=CH), 118–125 (m, 8C, CF_2 and CF_3), 130.7 (=CHN), 141.4 (=CHN) ppm. IR (ν/cm^{-1}): 3159 w, 3144 w, 2960 w, 2888 w, 1518 m, 1426 m, 1386 m, 1330 s, 1287 s, 1251 s, 1209 s, 1155 s, 1111 s, 1161 s, 1119 m, 917 m, 865 m, 786 s, 769 s, 758 s, 658 m. MS (APCI): 704 [M]$^+$ (50), 637 [M-pz]$^+$ (60), 601 (110), 565 (50). NaHRMS (ESI): calcd. for $C_{22}H_{17}F_{17}N_6NaO$ ([M+Na]$^+$) 727.1185, found 727.1179.

4.16. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heneicosafluorotridecyl 2,2,2-tripyrazol-1-ylethyl ether (12d)

According to the general procedure, polyhalogenated ether **11d** (100 mg, 0.117 mmol), Bu_3SnH (69 mg, 0.21 mmol) and AIBN (2 mg, 0.016 mmol) in toluene (3 mL) yielded after treatment with KF (12 mg, 0.21 mmol) polyfluorinated ether **12d** (81 mg, 94%, m.p. 115.6–116.4 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 1.77 (m, 4H, CF_2CH_2 and $CF_2CH_2CH_2$), 3.57 (t, $^3J_{H-H}$ = 5.4 Hz, 2H, CH_2CH_2O), 5.09 (s, 2H, CH_2C), 6.33 (dd, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHCH=CH), 7.37 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =CHN), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, CH=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.2 (t, $^4J_{F-F}$ = 9 Hz, 3F, CF_3), −115.0 (m, 2F, CF_2), −122,2 (m, 11F, CF_2), −123.1 (m, 2F, CF_2), −124.0 (m, 2F, CF_2), 126.5 (m, 2F, CF_2) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 20,5 ($CH_2CH_2CH_2$), 27.5 (t, $^2J_{C-F}$ = 23 Hz, CF_2CH_2), 70.7 (OCH_2C), 74.0 (OCH_2CH_2), 89.7 (CH_2C), 116.5 (CHCH=CH), 118–125 (m, 10C, CF_2 and CF_3), 130.7 (=CHN), 141.4 (CH=N) ppm. IR (ν/cm^{-1}): 3143 w, 2942 w, 2886 w, 1517 m, 1425 m, 1390 m, 1325 m, 1248 m, 1206 s, 1155 s, 1159 m, 1141 m, 1118 m, 948 m, 913 m, 864 m, 754 m. MS (APCI), m/z (%): 804 [M]$^+$ (50), 768 [Mpz+MeOH]$^+$ (90), 737 [M-pz]$^+$ (110). HRMS (ESI): calcd. for $C_{24}H_{18}F_{21}N_6ONa$ ([M+Na]$^+$) 827.1121, found 827.1115.

4.17. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-Pentacosafluoropentadecyl 2,2,2-tripyrazol-1-ylethyl ether (12e)

According to the general procedure, polyhalogenated ether **11e** (100 mg, 0.097 mmol), Bu_3SnH (58 mg, 0.19 mmol) and AIBN (2 mg, 0.016 mmol) in toluene (3 mL) yielded after treatment with KF (12 mg, 0.21 mmol) polyfluorinated ether **12e** (79 mg, 90%, m.p. 121.9–122.5 °C, white crystals). ^{1}H NMR (299.97 MHz, $CDCl_3$): δ 1.81 (m, 4H, CF_2CH_2 and $CF_2CH_2CH_2$), 3.58 (t, $^3J_{H-H}$ = 5.5 Hz, 2H, CH_2CH_2O), 5.11 (s, 2H, CH_2C), 6.33 (dd, 3H, $^3J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 1.8 Hz, 3H, CHCH=CH), 7.37 (dd, $^3J_{H-H}$ = 2.6 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, =CHN), 7.65 (dd, $^3J_{H-H}$ = 1.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 3H, CH=N) ppm. ^{19}F NMR (282.23 MHz, $CDCl_3$): δ −81.2 (t, $^4J_{F-F}$ = 9 Hz, 3F, CF_3), −113.3 (m, 2F, CF_2), −122.2 (m, 12F, CF_2), −123.2 (m, 2F, CF_2), 124.1 (m, 2F, CF_2), −126.6 (m, 2F, CF_2) ppm. ^{13}C NMR (75.44 MHz, $CDCl_3$): δ 20.5 ($CH_2CH_2CH_2$), 27.5 (t, $^2J_{C-F}$ = 23 Hz, CF_2CH_2), 70.7 (OCH_2C), 74.0 (OCH_2CH_2), 89.7 (CH_2C), 116.5 (CHCH=CH), 118–126 (m, 4C, CF_2 a CF_3), 130.7 (=CHN), 141.4 (CH=N) ppm. IR (ν/cm^{-1}): 3158 w, 2943 w, 2888 w, 1517 m, 1425 m, 1389 m, 1320 m, 1284 m, 1199 s, 1153 s, 1196 m, 1162 m, 1117 m, 948 m, 914 m, 863 m, 753 m. MS (APCI), m/z (%): 904 [M]$^+$ (50), 837 [M-pz]$^+$ (110). HRMS (ESI): calcd. for $C_{24}H_{18}F_{21}N_6ONa$ ([M+Na]$^+$) 927.0957, found 927.0955.

4.18. Preparation of complexes of tripyrazolylmethane 12b. General procedure

A flask was charged with tripyrazolylmethane **12b**, metal nitrate and acetone. The mixture was stirred at r.t. overnight and the solvent was removed on the rotary vacuum evaporator (40 °C, 0.5 h, 11 kPa).

4.19. Bis{η^3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) (2,2,2-tripyrazol-1-ylethyl-κ^3N,N′,N″) ether}copper(II) nitrate (13)

According to the general procedure, polyhalogenated ether **12b** (100 mg, 0.165 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (17 mg, 0.069 mmol) in acetone (11 mL) gave quantitative yield of polyfluorinated complex **13** (115 mg, 99.6%, blue crystals). IR (ν/cm^{-1}): 3135 w, 2952 w, 2890 w, 1519 m, 1484 m, 1413 m, 1390 m, 1337 s, 1237 s, 1204 s, 1145 s, 1111 m, 1127 m, 856 w, 761 m. MS (ESI), m/z (%): 1332 [MNO_3^-]$^+$ (110), 729 [M-tpm^F−NO_3^-]$^+$ (110), 636 [M−2NO_3^-]$^{2+}$ (40).

4.20. Bis{η^3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) (2,2,2-tripyrazol-1-ylethyl-κ^3N,N′,N″) ether}nickel(II) nitrate (14)

According to the General procedure, polyhalogenated ether **12b** (100 mg, 0.165 mmol) and $Ni(NO_3)_2{\cdot}3H_2O$ (20 mg, 0.069 mmol) in acetone (11 mL) gave quantitative yield of polyfluorinated complex **14** (115 mg, 99.9%, light violet crystals). IR (ν/cm^{-1}): 3132 w, 2950 w, 2895 w, 1519 m, 1413 m, 1360 m, 1319 s, 1224 s, 1188 s, 1140 s, 1116 m, 1178 m, 1124 m, 975 m, 851 m, 756 m. MS (ESI), m/z (%): 1328 [M−NO_3^-]$^+$ (40), 725 [M-tpm^F−NO_3^-]$^+$ (110), 633 [M−2NO_3^-]$^{2+}$ (11). HRMS (ESI): calcd. for $C_{40}H_{34}F_{26}N_{12}NiO_2/2$ ([M−2NO_3^-]$^{2+}$) 633.0933, found 633.0930.

4.21. Bis{η^3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) (2,2,2-tripyrazol-1-ylethyl- κ^3N,N′,N″) ether}cobalt(II) nitrate (15)

According to the general procedure, polyhalogenated ether **12b** (100 mg, 0.165 mmol) and $Co(NO_3)_2{\cdot}6H_2O$ (20 mg, 0.069 mmol) in acetone (11 mL) gave quantitative yield of polyfluorinated complex **15** (115 mg, 99.8%, yellow crystals). IR (ν/cm^{-1}): 3136 w, 2950 w, 2893 w, 1519 m, 1413 m, 1387 m, 1343 s, 1250 s, 1211 s, 1147 m, 1111 m, 1129 m, 853 m, 757 m. MS (ESI), m/z (%): 1329 [M−NO_3^-]$^+$ (110), 725 [M-tpm^F−NO_3^-]$^+$ (50), 634 [M−2NO_3^-]$^{2+}$ (40).

4.22. Bis{η^3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl) (2,2,2-tripyrazol-1-ylethyl- κ^3N,N′,N″) ether}iron(II) tetrafluoroborate (16)

According to the general procedure, polyhalogenated ether **12b** (100 mg, 0.165 mmol) and $Fe(BF_4)_2{\cdot}6H_2O$ (28 mg, 0.083 mmol) in methanol (5 mL) gave quantitative yield of polyfluorinated complex **16** (111 mg, 99.6%, dark pink crystals). ^{1}H NMR (299.97 MHz, CD_3CN): δ 2.34 (m, 8H, CF_2CH_2 and $CF_2CH_2CH_2$), 4.22 (bs, 4H, CH_2CH_2O), 5.62 (bs, 4H, CH_2C), 6.58 (bs, 6H, CHCH=CH), 7.30 (bs, 6H, =CHN), 8.51 (bs, 6H, CH=N) ppm.^{19}F NMR (282.23 MHz, CD_3CN): δ −80.6 (m, 6F, CF_3), −113.6 (m, 4F,

CF_2CH_2), −121.3 (m, 4F, CF_2), −122.3 (m, 4F, CF_2), −122.9 (m, 4F, CF_2), −125.7 (m, 4F, CF_2), −149.8 (m, 4F, BF_4) ppm. ^{13}C NMR (75.44 MHz, CD_3CN): δ 21.8 ($CH_2CH_2CH_2$), 28.7 (t, $^2J_{C-F}$ = 23 Hz, CF_2CH_2), 68.3 (OCH_2C), 71.9 (OCH_2CH_2), 84.6 (CH_2C), 110.6 (CHCH=CH), 111–125 (m, 6C, CF_2 and CF_3), 138.1 (=CHN), 151.1 (CH=N) ppm. MS (ESI), m/z (%): 632 $[M-2BF_4^-]^{2+}$ (100). HRMS (ESI): calcd. for $C_{40}H_{34}F_{26}N_{12}O_2Fe/2$ ($[M-2BF_4^-]^{2+}$) 632.09255, found 632.09266.

4.23. Example of partition coefficient and fluorophilicity measurement: ligand 12d

The vial was charged with polyfluoroalkylated tripyrazolylmethane **12d**, toluene (1 mL) and perfluoro(methylcyclohexane) (1 mL). The mixture was stirred for 2 h while termostatted to 25 °C (298 K) and left to stand for 2 h. 0.5 mL of each layer was removed and evaporated on rotary vacuum evaporator (25 °C, 1 h, 11 kPa). Both residues were carefully weighted yielding 0.86 mg of compound **12d** in the fluorous and 2.55 mg of compound **12d** in the toluene layer, which corresponds to P_i(FBS) = 0.34 and fluorophilicity value f_i = −1.1.

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