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Unusual methylation reaction of *gem*-bromofluorospiropentanes with methyllithium

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ABSTRACT

A series of novel *gem*-bromofluorospiropentanes were synthesized and investigated in the reaction with methyllithium. Either substitution of the fluorine atom for a methyl group or rearrangement into methylated cyclobutene derivatives occurred under these conditions.

1. Introduction

Previously we have reported an unusual skeletal rearrangement of *gem*-dibromospiropentanes under treatment with methyllithium at low temperatures (Scheme 1).[1] In general, the reaction of dibromides **I** with methyllithium gives corresponding allenes **III** as major products (Scheme 1, route A). This transformation, so-called Doering–Scattebol–Moore reaction, is well documented.[2] We have found that lowering the reaction temperature to −55 °C favors the formation of rearranged products **IV**–**VII** and disfavors the formation of allenes **III**.[1] We have demonstrated the general character of this process and found that the formation of 'monomeric' (**IV**, **V**; Scheme 1, route B) or 'dimeric' (**VI**, **VII**; Scheme 1, route C) products was possible depending on the substituents in the dibromocyclopropane fragment.[3] In several cases we have also observed the products of type **VIII** arised from the insertion of some intermediate into C–H bond of diethyl ether used as a solvent.[4]

The general mechanistic scheme was supposed to include the nucleophilic attack of neighboring three-membered C–C bond at intermediate Li–carbenoid **II** with Br as a leaving group.[3c] Studying the reaction mechanism, we were interested in the influence of the halogen atom nature on the direction of the dihalogenospiropentane reactions with MeLi. Since no data concerning this problem was available,[5] in this paper we have synthesized a series of model *gem*-bromofluorospiropentanes **11**–**20** and investigated their reaction with methyllithium.

2. Results and discussion

Bromofluorospiropentanes **11**–**20** were synthesized in good yields by the cycloaddition of bromofluorocarbene[6] to corresponding methylenecyclopropanes **1**–**10** (Table 1). The compounds **14**–**16** and **19** are obtained as mixtures of two diastereomeres (of four possible ones for **14** and **15**). Indeed, in NMR spectra of compounds **14** and **15** we can see only two sets of signals, corresponding just two diastereomeres (A and B). Thus, addition of bromofluorocarbene to alkenes **4**, **5** is in a sense a diastereoselective process. Consideration of spin–spin coupling constants J_{HH}, J_{HF} and J_{CF} allowed us to determine relative configurations for the diastereomeres **14** (A) and **14** (B) (Scheme 2). (The detailed description of NMR parameters for **14** (A) and **14** (B) including results of iterative analysis of ^{1}H spectrum is given in Experimental).

The stereospecificity of long-range coupling constant J_{HH} for the spiropentane has previously been pointed out.[7] The sign and value of $^4J_{HH}$ depend on the path of spin–spin interaction. We have found that value of $^4J_{HF}$ also has a strong geometric dependence. Thus for isomer **14** (A) $^4J_{H5aF}$ is equal ca. 9 Hz whereas other $^4J_{HF}$ for both isomers **14** (A) and **14** (B) have value <1 Hz.

In the NMR spectra of bromofluorospiropentanes **16** and **19** we can observe two sets of signals that corresponds two possible diastereomeres. Basing on characteristic coupling constants $^4J_{HF}$

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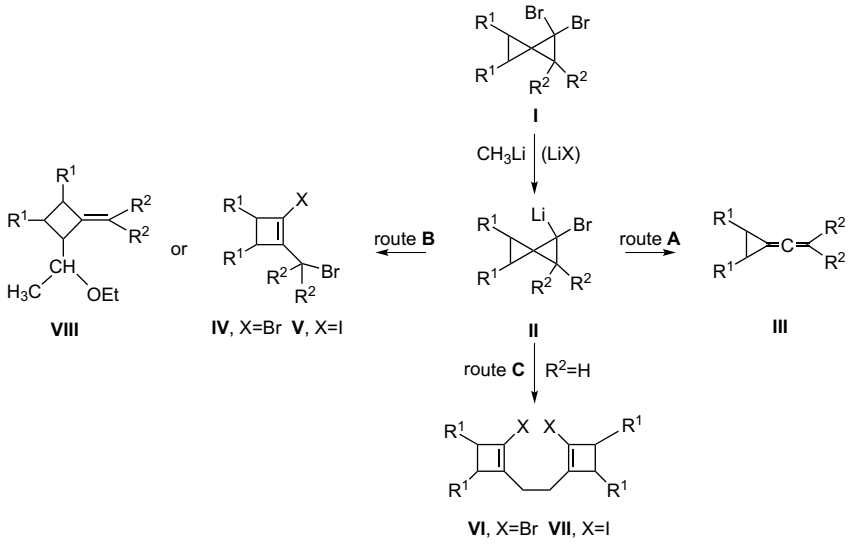
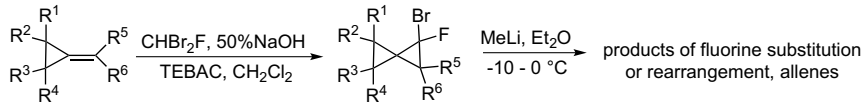


Scheme 1.

Table 1
Synthesis of *gem*-bromofluorospiropentanes and their reaction with methyllithium



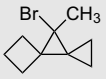
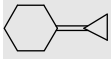
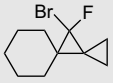
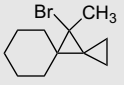
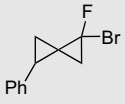
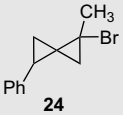
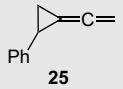
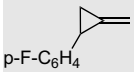
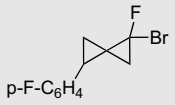
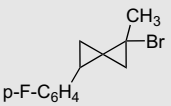
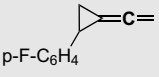
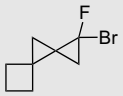
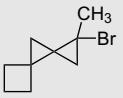
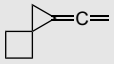
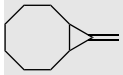
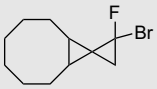
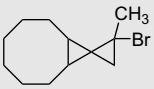
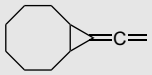
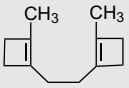
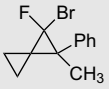
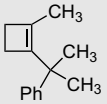
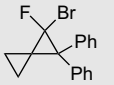
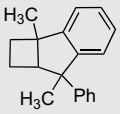
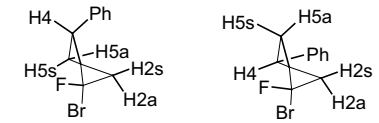
Alkenes	*gem*-Bromofluorospiropentanes	Yield (%)	Products	Yield (%)
 **1**	 **11**	59	 **21**	90
 **2**	 **12**	53	 **22**	25
 **3**	 **13**	92	 **23**	45
 **4**	 **14**	52	 **24**	27
			 **25**	27
 **5**	 **15**	35	 **26**	20
			 **27**	41

Table 1 (*continued*)

Alkenes	*gem*-Bromofluorospiropentanes	Yield (%)	Products	Yield (%)
 **6**	 **16**	65	 **28**	28
			 **29**	14
 **7**	 **17**	39	 **30**	28
			 **31**	55
 **8**	 **18**	64	 **32**	40
 **9**	 **19**	39	 **33**	45
 **10**	 **20**	35	 **34**	51



Scheme 2.

and $^{3}J_{CF}$ we have also determined relative configurations of stereoisomeres for compounds **16** and **19** (see Experimental).

It is obvious that in the majority of cases (compounds **14**–**16**) we observe preferential formation of less sterically hindered isomers, where the bromine atom is maximally distant from the most bulky substituents.

Dihalogenides **11**–**20** were treated with commercial MeLi free from LiBr or LiI to avoid the formation of a mixture of Br- and I-substituted molecules.[3,4] The reactions of **11** and **18** with 1 equiv of MeLi were at first performed at −55 °C, because this temperature favored the formation of the rearranged products of types **IV** and **VI**.[3c] However, only the starting bromofluorospiranes **11** and **18** were observed at this temperature in the reaction mixture. Optimizing the conditions for compounds **11** and **18**, we found out that the reactions between compounds **11**–**20** and 2 equiv of MeLi were complete at −10 to 0 °C. It seems to be the result of a greater stability of bromofluorospiranes toward alkyllithium reagents relative to analogous dibromospiranes and thus they need more harsh reaction conditions. The results of the reactions for compounds **11**–**20** under the selected conditions are summarized in Table 1. The structures of the products obtained (**21**–**34**, Table 1) were proved unambiguously by NMR and mass spectra.

We have observed the following general features: (1) in the case of compounds **11**–**13**, containing internal dihalogenocyclopropane moiety, the only isolated products of the reaction were the corresponding methylbromides **21**–**23**. (2) In the case of terminal bromofluorides **14**–**17** together with the formation of methylation products **24**, **26**, **28**, **30**, allenes were formed by a competing reaction path (Scheme 1, route A), i.e., the classical variant of dihalogenocyclopropanes reaction with alkyllithium was partially realized. (3) Bromofluorospiranes **18**–**20** reacted with methyllithium to form the products of the above mentioned rearrangement,[1,3] namely the corresponding cyclobutenes **32**–**34**. However, in a sharp contrast with the reaction of analogous dibromides with methyllithium,[1,3] the resulting structures did not contain halogen atom(s). In fact, structures **32** and **33** observed here correspond to the previously obtained rearranged structures of types **IV**–**VII**,[1,3] but with a formal substitution of bromine atom for methyl group(s). Thus, fluorine containing dihalogenospiropentanes seem to possess a characteristic feature to give

methylation products. Moreover, the monomeric intermediate(s) in the reaction of diphenylsubstituted bromofluorospiropentane **20** similarly undergo double methylation followed by cyclization leading to the tricyclic molecule **34**. The observed general substitution of fluorine atom for methyl group in cyclopropane moiety is quite an unexpectable result.[5]

The majority of literature data for the reaction of *gem*-bromofluorocyclopropanes with alkyllithium reagents claims the formation of allenes as main products.[8] At low temperature (about −100 °C) *gem*-bromofluorocyclopropanes are known to give fluorolithium carbenoids with alkyllithium reagents, which can be carboxylated.[6a,9] However, when the reaction temperature was increased, a complex mixture containing bromo- and fluorosubstituted cyclopropanes was detected.[6a] Thus, based upon literature data, one cannot unambiguously state, which halogen–carbon bond (C–F or C–Br) participates at the first step of the reaction at −10 °C.

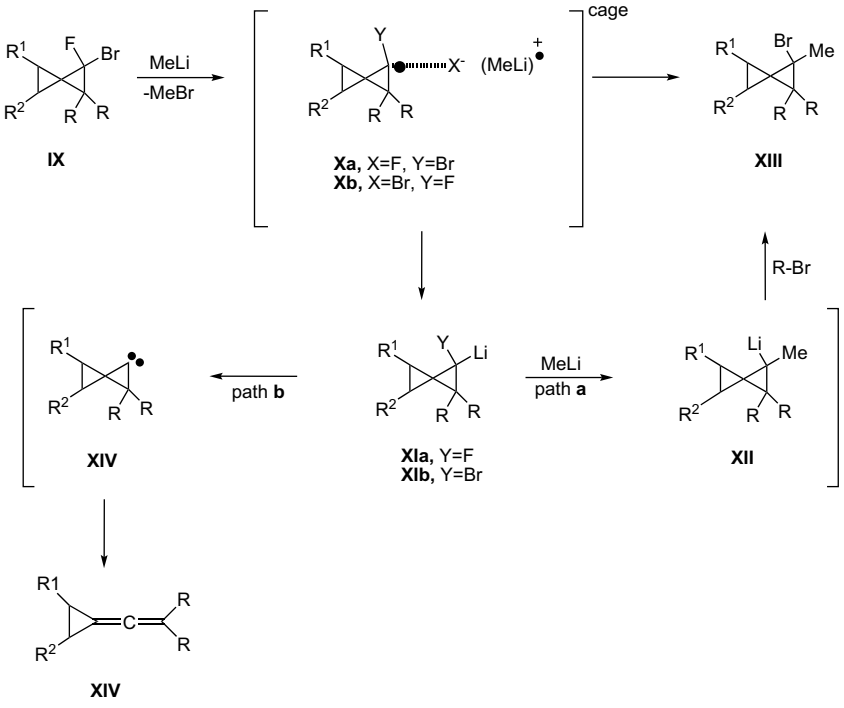
Only one example of an unusual reactivity of *gem*-bromofluorosubstituted polyspirocyclopropanes is known.[10] The treatment of highly spirocyclopropanated fluorobromo-[15]-triangulane with butyllithium at −10 to −5 °C led to a remarkable skeletal rearrangement accompanied by two consecutive cyclopropylcarbene to cyclobutene enlargements and incorporation of two *n*-butyl groups resulting in a bicyclo[2.2.0]hexane derivative as the main product.[10]

Contrary to the results given above our strained *gem*-bromofluorosubstituted polyspirocyclopropanes **11**–**20** react with alkyllithium reagents in an unusual manner. The reaction of these substrates with methyllithium proceeded with the formal substitution of a fluorine atom, in some cases followed by either transformation into allenes or by the rearrangement of carbocationic type. This is a good example of the unusual reactivity of polyspirocyclopropanes.

There is a principle question: which has to be solved for studied *gem*-bromofluorocyclopropanes, which halogen atom undergoes substitution by Li at the first step of the reaction. Indeed, any mechanism proposed to explain the dependence of the product on the halogen has to involve the halogen leaving at some stages of product formation. Consider first the fact of a smooth substitution of fluorine for Me group (e.g., **11**→**21**; Table 1). Known is the example of analogous substitution of bromine atom for Ph group in 13,13-dibromodispiro[5.0.5.1]tridecane under the treatment with an excess of PhLi and this phenylation was considered to be a surprising result.[11] The formation of bromophenylsubstituted cyclopropane moiety was explained by involving single electron transfer (SET) mechanism[12] and by the assumption of a fast coupling in a caged radical pair.[11] Application of this concept to our results means that (i) the first step of the reaction Li–F exchange proceeds faster than does Li–Br one and it leads to a caged radical ion pair **Xa** (Scheme 3; intermediates **X** were suggested by applying Scheme IV in Ref. 12c, using monomeric MeLi); (ii) coupling in a caged radical pair (Me• and •C–Br) is extremely fast. This concept explains the formation of monomethylated bromides **21**–**24**, **26**, **28**, **30**, but the general assumption of a fast Li–F exchange seems questionable.[6a,9,13]

Moreover, the SET mechanism cannot explain the formation of rearranged product(s), which arises from some ionic pathway(s) and one needs to assume the carbenoid intermediates of type **XI** for this process. Then, taking into account literature data[6a,9] (via carboxylation of intermediate fluorolithium carbenoid) the formation of intermediate fluorolithium cyclopropane carbenoid **XIa** (Scheme 3) is also quite possible.

It seems that initially formed fluorolithium cyclopropane carbenoid **XIa** can react with the second molecule of methyllithium via nucleophilic substitution of the fluorine with a methyl group to give methyllithium intermediate **XII** (path a, Scheme 3). It may appear that intermediate **XII** is formed according to metal assisted ionization (MAI)[14] of the C–F bond in the carbenoid **XIa** as it is known for cyclopropyl halogenolithium carbenoids.[14c,15] Then the reaction of **XIa** with alkyl bromide (starting dihalospiropentane **IX**) leads to the methylated bromide **XIII**, which is the main pathway for many cases (compounds **21**–**24**, **26**, **28**, **30**). Some bromofluorides (**14**–**17**) react with methyllithium along two ways (a and b, Scheme 3) forming methylated products (**24**, **26**, **28**, **30**) as discussed above and allenes (**25**, **27**, **29**, **31**) via corresponding carbenes **XIV**. This



Scheme 3.

fact gives evidence that fluorocarbenoid precursors **XIa** undergo both α-elimination and methylation to give the products of pathways a and b (Scheme 3).

The most interesting fact is that carbenoids generated from bromofluorides **18**–**20** formed only rearranged products **32**–**34**. This can be explained as a result of intramolecular nucleophilic attack at the carbenoid carbon by a neighbor C–C bond with cyclopropane ring opening followed by the isomerization of bicyclo[2.1.0]pentane derivative **XVI** into four-membered cyclic intermediate **XVII** (Scheme 4). Apparently intermediates **XVI** and **XVII** may be represented as carbon cation—fluorine anion tight ion pairs and methyl group is incorporated in the structure **XVII** via its reaction with methyllithium likewise nucleophilic substitution of fluorine by methyl group proceeds in carbenoid **XIa** (Scheme 4).

This process leads to intermediate **XVIII**, which is lithium allylic derivative and may be prone to [1,3]-sigmatropic migration of C–Li bond to give the lithium derivative **XIX**. The sigmatropic tautomerism of allyl lithium derivatives (or even acceptance of pure ionic structure) is well documented in literature.[16] Cyclobutene intermediate **XIX** can react with either parent dihalospiropentane **IX** or with methyl bromide giving rearranged products **33** or **XX**, respectively. If there are no substituents in α-position of the starting dihalogenide **IX** the molecule of bromide **XX** reacts with lithium intermediate **XIX**, yielding 'dimeric' rearranged product **32**.

Consider now the formation of tricyclic compound **34**. The most probable intermediate for its formation is the corresponding methylenecyclobutane derivative **XVII** (R^1=R^2=Ph). Thus, one may accept the electrophilic substitution at the *ortho*-position of one phenyl group and subsequent reaction with methyllithium and methyl bromide (Scheme 4).

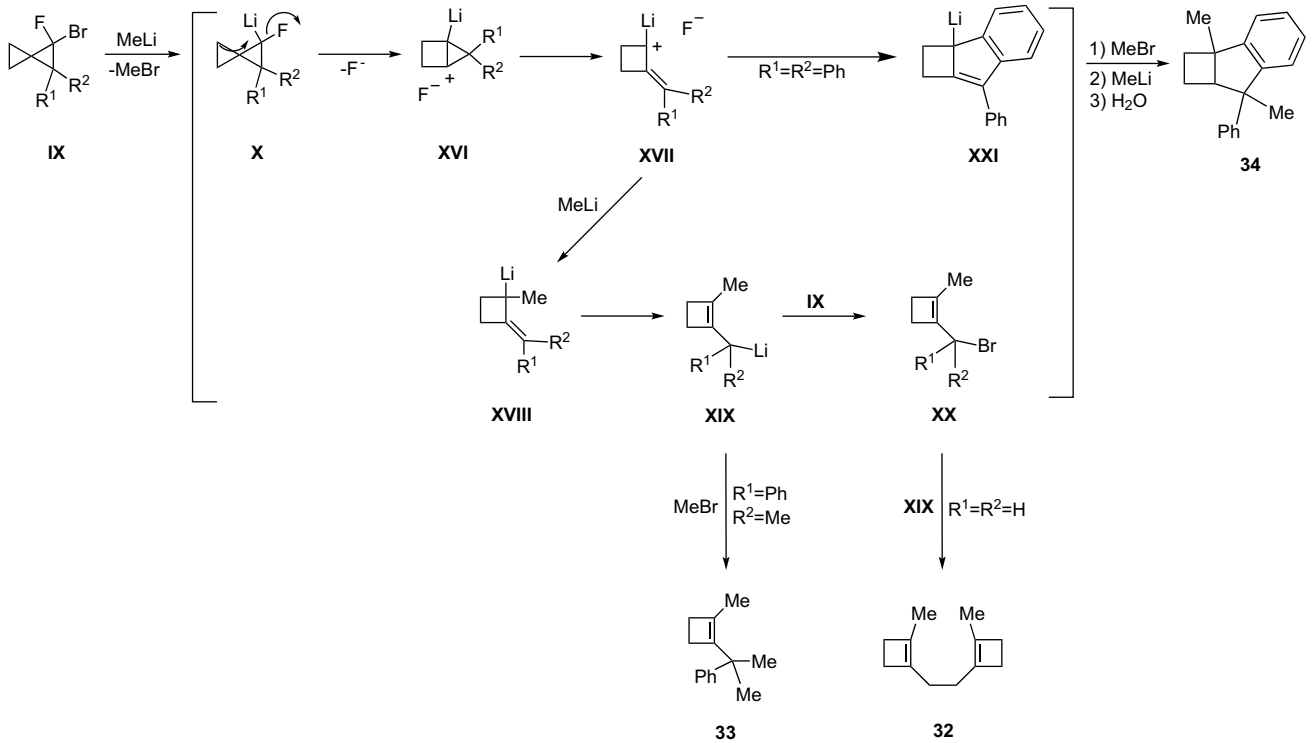
Thus, our experimental results demonstrate that in contrast with *gem*-dibromospiropentanes the reactions of bromofluorospiropentanes **11**–**20** with methyllithium at relatively high temperatures (−10 to 0 °C) proceed as the unexpected methylation and may proceed via at least three pathways depending on the substituents at the carbenoid center: (a) nucleophilic substitution of fluorine with methyl group, which occurred in majority reactions, (b) α-elimination forming the allenes, (c) intramolecular nucleophilic substitution of fluorine with C–C bond combined with methylation which yielded the rearranged products **32**–**34**.

The unusual reactivity of spiropentane bromofluorides **IX** in the reactions with methyllithium can be explained by their ambiphilic nature because fluorolithium carbenoids can act as both electrophilic and nucleophilic agents. Nevertheless, the detailed mechanism of this process is still a subject of further investigation.

3. Experimental

3.1. General

NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively) at room temperature; chemical shifts δ were measured with reference to the solvent (^{1}H: $CDCl_3$, δ=7.24 ppm; ^{13}C: $CDCl_3$, δ=77.13 ppm). Mass spectra were taken on a Finnigan MAT 95 XL spectrometer (70 eV) using electron impact ionization (EI) and GC–MS coupling. MALDI-TOF spectra were recorded in positive mode using Bruker Ultraflex mass spectrometer with dithranol as a matrix. Accurate mass measurements (HRMS) were carried out using a Bruker micro TOF-Q™ ESI-TOF mass spectrometer. Microanalyses were performed on a Carlo Erba 1106 instrument. Infrared spectra were recorded on a Thermo Nicolet FTIR-200 spectrometer. Analytical thin layer chromatography (TLC) was carried out with Silufol silica gel plates (supported on aluminum); the detection was done by UV lamp (254 and 365 nm) and chemical staining (iodine vapor). Column chromatography was performed using silica gel 60 (230–400 mesh, Merck). GLC analyses and separation were performed using silicone E-301 (15% on Inerton AW). Petroleum ether used refers to the fraction boiling at 40–60 °C. All reagents except commercial products of satisfactory quality were purified by literature procedures prior to use. Starting compounds: bicyclopropylidene (**1**),[17] cyclopropylidenecyclobutane (**2**),[18] cyclopropylidenecyclohexane (**3**),[18] (2-methylenecyclopropyl)benzene (**4**),[19,20] 1-fluoro-4-(2-methylenecyclopropyl)benzene (**5**),[20] 1-methylenespiro[2.3]hexane



Scheme 4.

(**6**),[20,21] 9-methylenebicyclo[6.1.0]nonane (**7**),[20] methylenecyclopropane (**8**),[22] (1-cyclopropylideneethyl)benzene (**9**),[23] 1,1′-(cyclopropylidenemethylene)dibenzene (**10**),[23] were synthesized by known procedures.

3.2. General procedure 1: addition of bromofluorocarbene to alkenes 1–10

A 50% aqueous solution (10 mL) of NaOH was added to 16.0 mmol of the corresponding alkene, 9.22 g (48.0 mmol) of $CHBr_2F$ and 0.73 g (2.6 mmol) of TEBAC in 10 mL of dichloromethane at 0 °C in 0.5 h. Then a drop of ethanol was added. The reaction mixture was warmed up to room temperature and stirred for 48 h. Then it was treated with 25 mL of cold water. The organic phase was separated and the water phase extracted with dichloromethane (3×50 mL). The combined organic fractions were washed with 100 mL of water and dried over $MgSO_4$. The solvent was evaporated, the residue was distilled or purified by column chromatography.

3.3. 7-Bromo-7-fluorodispyro[2.0.2.1]heptane 11

Yield 1.80 g (59%), colorless liquid, bp 55–60 °C/60 torr. IR (film): ν 3078, 2993, 1458, 1435, 1317, 1200, 1090, 1005, 964, 910, 866, 609, 510 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.93–1.00 (m, 2H), 1.04–1.15 (m, 4H), 1.34–1.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 7.7 ($^1J_{CH}$ 164, 2×CH_2), 9.1 ($^1J_{CH}$ 163, 2×CH_2), 25.9 ($^2J_{CF}$ 11, 2×C-spiro), 90.8 ($^1J_{CF}$ 312, CFBr). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −133.34 (t, 1F, $^4J_{HF}$ 8.5). Anal. Calcd for C_7H_8BrF: C, 44.01; H, 4.22%. Found: C, 43.98; H, 4.03%.

3.4. 8-Bromo-8-fluorodispiro[2.0.3.1]octane 12

Yield 1.74 g (53%), colorless liquid, bp 114 °C/60 torr. IR (film): ν 3080, 2998, 1445, 1315, 1020, 930, 824, 725, 606, 522 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.90–0.95 (m, 1H, CH_2, *c*-Pr), 0.95–1.04 (m, 1H, CH_2, *c*-Pr), 1.11–1.16 (m, 1H, CH_2, *c*-Pr), 1.17–1.24 (m, 1H, CH_2, *c*-Pr), 1.86–2.03 (m, 3H, CH_2, *c*-Bu), 2.05–2.13 (m, 1H, CH_2, *c*-Bu), 2.23–2.32 (m, 1H, CH_2, *c*-Bu), 2.33–2.42 (m, H, CH_2, *c*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 7.4 (CH_2), 9.0 (CH_2), 15.42 (CH_2), 23.0 (CH_2), 26.8 (CH_2), 29.2 ($^2J_{CF}$ 10, C-spiro), 35.2 ($^2J_{CF}$ 12, C-spiro), 92.8 ($^1J_{CF}$ 311, CBrF). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −136.10 (br d, 1F, $^4J_{HF}$ 8.6). Anal. Calcd for $C_8H_{10}BrF$: C, 46.86; H, 4.92%. Found: C, 46.76; H, 5.07%.

3.5. 10-Bromo-10-fluorodispyro[2.0.5.1]decane 13

Yield 3.28 g (86%), colorless oil, bp 115 °C/8 torr. IR (film): ν 3076, 3002, 2850, 1452, 1380, 1250, 1010, 720, 609, 569 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.83–0.88 (m, 1H, CH_2, *c*-Pr), 0.94–1.02 (m, 1H, CH_2, *c*-Pr), 1.08–1.18 (m, 2H, CH_2, *c*-Pr), 1.35–1.75 (m, 10H, 5×CH_2, *c*-Hex). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 5.7 ($^1J_{CH}$ 164, CH_2, *c*-Pr), 7.5 ($^1J_{CH}$ 163, CH_2, *c*-Pr), 24.8 ($^1J_{CH}$ 127, CH_2, *c*-Hex), 25.2 ($^1J_{CH}$ 127, CH_2, *c*-Hex), 25.9 ($^1J_{CH}$ 130, CH_2, *c*-Hex), 28.4 ($^1J_{CH}$ 131, $^2J_{CF}$ 4, CH_2, *c*-Hex), 30.0 ($^2J_{CF}$ 10, C-spiro), 32.7 ($^2J_{CF}$ 9, C-spiro), 33.1 ($^1J_{CH}$ 127, CH_2, *c*-Hex), 97.7 ($^1J_{CF}$ 310, CFBr). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −140.51 (br d, 1F, $^4J_{HF}$ 8.9). Anal. Calcd for $C_{10}H_{14}BrF$: C, 51.52; H, 6.05%. Found: C, 51.60; H, 6.15%.

3.6. 1-Bromo-1-fluoro-4-phenylspiro[2.2]pentane 14

Yield 2.01 g (52%), colorless liquid, bp 120 °C/8 torr. Two isomers, (1*S*,3*R*,4*R*)*-A:(1*S*,3*S*,4*S*)*-B=1:0.9. IR (film): ν 3080, 3020, 3000, 2835, 1600, 1580, 1450, 1350, 1200, 1010, 720, 610, 504 cm^{-1}. ^1H NMR (600 MHz, C_6D_6), alicyclic protons (ABCDE part of ABCDEX system, **X**=^{19}F), major isomer (A), δ: 1.038 (1H, $^2J_{AB}$ −5.13, $^3J_{AC}$ 5.54, $^4J_{AE}$ −0.74, $^4J_{HF}$ 8.95, CH_2, A=H5a), 1.437 (1H, $^2J_{DE}$ −7.36, $^4J_{BD}$ −0.68, $^4J_{CD}$ 0.86, $^3J_{HF}$ 3.25, CH_2, D=H2a), 1.447 (1H, $^2J_{AB}$ −5.13, $^3J_{BC}$ 8.70, $^4J_{BD}$ −0.68, $^4J_{BE}$ 0.98, CH_2, B=H5s), 1.555 (1H, $^2J_{DE}$ −7.36, $^4J_{AE}$ −0.74, $^4J_{BE}$ 0.98, $^4J_{CE}$ −0.71, $^3J_{HF}$ 12.32, CH_2, E=H2s), 2.482 (1H, $^3J_{AC}$ 5.54, $^3J_{BC}$ 8.70, $^4J_{CD}$ 0.86, $^4J_{CE}$ −0.71, $^4J_{HF}$ 0.55, CH, C=H4), minor isomer (B), δ: 1.237 (1H, $^2J_{AB}$ −5.10, $^3J_{AC}$ 5.80, $^4J_{AD}$ −0.78, $^4J_{AE}$ −0.10, $^4J_{HF}$ 0.77, CH_2, A=H5a), 1.317 (1H, $^2J_{DE}$ −7.33, $^4J_{AD}$ −0.78, $^4J_{BD}$ 0.94, $^4J_{CD}$ −0.71, $^3J_{HF}$ 3.60, CH_2, D=H2a), 1.633 (1H, $^2J_{DE}$ −7.33, $^4J_{AE}$ −0.10, $^4J_{BE}$ −0.65, $^4J_{CE}$ 1.01, $^3J_{HF}$ 12.05, CH_2, E=H2s),1.644 (1H, $^2J_{AB}$ −5.10, $^3J_{BC}$ 8.68, $^4J_{BD}$ 0.94, $^4J_{BE}$ −0.65, $^4J_{HF}$ 0.94, CH_2, B=H5s), 2.331 (1H, $^3J_{AC}$ 5.80, $^3J_{BC}$ 8.68, $^4J_{CD}$ −0.71, $^4J_{CE}$ 1.01, $^4J_{HF}$ 0.90, CH, C=H4), aromatic protons δ: 6.90–6.93 (m, 2H, Ph, A), 6.93–6.96 (m, 2H, Ph, B), 7.10–7.13 (m, 2H, Ph, A+B), 7.16–7.20 (m, 4H, Ph, A+B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 17.0 ($^3J_{CF}$ 3.6, CH_2, B), 18.7 (CH_2, A), 21.8 ($^2J_{CF}$ 11.7, CH_2, A), 22.0 ($^2J_{CF}$ 11.7, CH_2, B), 24.0 ($^3J_{CF}$ 2.7, CH, A), 25.6 ($^3J_{CF}$ 0.5, CH, B), 29.8 ($^2J_{CF}$ 9.7, C-spiro, A), 30.1 ($^2J_{CF}$ 10.6, C-spiro, B), 84.4 ($^1J_{CF}$ 306.3, CBrF, A+B), 84.4 ($^1J_{CF}$ 305.0, CBrF, A+B), 126.4 (2CH, Ph, A+2CH, Ph, B), 126.5 (CH, Ph, A+CH, Ph, B), 128.5 (2CH, Ph, A+2CH, Ph, B), 139.0 (C, Ph, A), 139.6 (C, Ph, B). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −134.56 (X part of ABCDEX system, 1F, $^3J_{HF}$ 3.25, $^3J_{HF}$ 12.32, $^4J_{HF}$ 0.55, $^4J_{HF}$ 8.95, A), −133.44 (X part of ABCDEX system, 1F, $^3J_{HF}$ 3.60, $^3J_{HF}$ 12.05, $^4J_{HF}$ 0.77, $^4J_{HF}$ 0.94, $^4J_{HF}$ 0.90, B). Anal. Calcd for $C_{11}H_{10}BrF$: C, 54.80; H, 4.18%. Found: C, 54.60; H, 4.02%.

3.7. 1-Bromo-1-fluoro-4-(4-fluorophenyl)spiro[2.2]-pentane 15

Yield 1.82 g (44%), colorless liquid, R_f 0.4 (petroleum ether). Two isomers, A:B 1:0.9. IR (film): ν 3060, 3010, 2940, 2860, 1600, 1508, 1260, 1190, 1090, 840, 595 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.33 (ddd, 1H, $^2J_{HH}$ 5.2, $^3J_{HH}$ 5.4, $^3J_{HF}$ 8.7, CH_2, A), 1.52–1.57 (m, 2H, CH_2, B), 1.70 (dd, 1H, $^2J_{HH}$ 5.2, $^3J_{HH}$ 8.5, CH_2, A), 1.73–1.83 (m, 2H, CH_2, A), 1.94–2.01 (m, 2H, CH_2, B), 2.50 (dd, 1H, $^3J_{HH}$ 5.6, $^3J_{HH}$ 8.5, CH, B), 2.75 (dd, 1H, $^3J_{HH}$ 5.4, $^3J_{HH}$ 8.5, CH, A), 6.97–7.10 (m, 4H, CH, Ph, A+4H, CH, Ph, B). ^{13}C NMR (101 MHz, $CDCl_3$) (A+B) δ: 16.9 ($^3J_{CF}$ 4, $^1J_{CH}$ 165, CH_2), 18.5 ($^1J_{CH}$ 165, CH_2), 21.7 ($^2J_{CF}$ 12, $^1J_{CH}$ 163, CH_2), 21.8 ($^2J_{CF}$ 12, $^1J_{CH}$ 165, CH_2), 23.3 ($^1J_{CH}$ 162, CH, B), 24.9 ($^1J_{CH}$ 163, CH), 29.9 ($^2J_{CF}$ 10, $C_{\text{-spiro}}$), 39.9 ($^2J_{CF}$ 10, $C_{\text{-spiro}}$), 84.1 ($^1J_{CF}$ 305, 2CBrF), 115.3 ($^1J_{CH}$ 163, 2CH, Ph), 115.5 ($^1J_{CH}$ 163, 2CH, Ph), 127.9 ($^2J_{CF}$ 7, $^1J_{CH}$ 160, 4CH, Ph), 134.5 (C, Ph, A), 135.3 (C, Ph, B), 161.7 ($^1J_{CF}$ 244, 2CF, Ph). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −134.74 (ddd, 1F, $^3J_{HF}$ 3.4, $^3J_{HF}$ 12.2, $^4J_{HF}$ 8.7, A), −133.77 (br dd, 1F, $^3J_{HF}$ 3.4, $^3J_{HF}$ 12.3, B), −117.20 to −117.31 (m, 1F, Ph, A+1F, Ph, B). Anal. Calcd for $C_{11}H_9BrF_2$: C, 50.99; H, 3.50%. Found: C, 51.09; H, 3.60%.

3.8. 1-Bromo-1-fluorodispiro[2.0.3.1]octane 16

Yield 2.13 g (65%), colorless liquid, bp 110 °C/110 torr. Two isomers, (1*S*,3*R*)*-A:(1*S*,3*S*)*-B=5:1. IR (film): ν 3050, 2925, 2850, 1480, 1024, 910, 720, 610, 515 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.03 (dd, 1H, $^2J_{HH}$ 5.4, $^4J_{HF}$ 8.3, C(8)H_2, *c*-Pr, A), 1.09 (d, 1H, $^2J_{HH}$ 5.2, C(8)H_2, *c*-Pr, B), 1.13 (d, 1H, $^2J_{HH}$ 5.4, C(8)H_2, *c*-Pr, A), 1.28 (d, 1H, $^2J_{HH}$ 5.2, C(8)H_2, *c*-Pr, B), 1.51 (dd, 1H, $^2J_{HH}$ 6.9, $^3J_{HF}$ 2.9, C(2)H_2, *c*-Pr, A), 1.65 (dd, 1H, $^2J_{HH}$ 6.8, $^3J_{HF}$ 2.8, C(2)H_2, *c*-Pr, B), 1.73 (dd, 1H, $^2J_{HH}$ 6.8, $^3J_{HF}$ 11.6, C(2)H_2, *c*-Pr, B), 1.86 (dd, 1H, $^2J_{HH}$ 6.9, $^3J_{HF}$ 12.9, C(2)H_2, *c*-Pr, A), 1.92–2.31 (m, 5H, CH_2, *c*-Bu, A+5H, CH_2, *c*-Bu, B), 2.34–2.43 (m, 1H, CH_2, *c*-Bu, A), 2.64–2.72 (m, 1H, CH_2, *c*-Bu, B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 16.8 (CH_2, *c*-Bu, B), 17.0 (CH_2, *c*-Bu, A), 18.0 ($^3J_{CF}$ 3.0, CH_2, *c*-Pr, B), 21.3 (CH_2, *c*-Pr, A), 21.8 ($^2J_{CF}$ 11.7, CH_2, *c*-Pr, A), 22.4 ($^2J_{CF}$ 11.0, CH_2, *c*-Pr, B), 25.7 (CH_2, *c*-Bu, B), 27.7 (CH_2, *c*-Bu, A), 27.9 (C-spiro, B), 28.1 ($^3J_{CF}$ 4.3, C-spiro, A), 29.1 (CH_2, *c*-Bu, A+CH_2, *c*-Bu, B), 30.0 ($^2J_{CF}$ 10.2, C-spiro, A), 30.5 ($^2J_{CF}$ 11.0, C-spiro, B), 85.4 ($^1J_{CF}$ 307, CBrF, B), 86.5 ($^1J_{CF}$ 305, CBrF, A). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −139.75 (ddd, 1F, $^3J_{HF}$ 2.9, $^3J_{HF}$ 12.9, $^4J_{HF}$ 8.3, A), −130.08 (dd, 1F, $^3J_{HF}$ 2.8, $^3J_{HF}$ 11.6, B). Anal. Calcd for $C_8H_{10}BrF$: C, 46.86; H, 4.92%. Found: C, 49.93; H, 4.73%.

3.9. 2′-Bromo-2′-fluorospiro[bicyclo[6.1.0]nonane-9,1′-cyclopropane] 17

Yield 1.54 g (39%), colorless liquid, R_f 0.5 (petroleum ether). IR (film): ν 3045, 2995, 2923, 2854, 1467, 1163, 1061, 1024, 858, 815, 760, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02–1.21 (m, 2H), 1.24–1.32 (m, 2H), 1.39–1.88 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 19.1 ($^2J_{CF}$ 12, CH_2, *c*-Pr), 22.9 ($^3J_{CF}$ 2, CH, *c*-Pr), 23.7 (CH_2, *c*-Oct), 24.3 (CH, *c*-Pr), 24.7 (CH_2, *c*-Oct), 26.5 ($2CH_2$, *c*-Oct), 28.6 (CH_2, *c*-Oct), 28.7 (CH_2, *c*-Oct), 30.3 ($^2J_{CF}$ 10, C-spiro), 85.3 ($^1J_{CF}$ 305, CBrF). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −129.98 (dd, 1F, $^3J_{HF}$ 2.5, $^3J_{HF}$ 11.7, B). Anal. calcd for $C_{11}H_{16}BrF$: C, 53.46; H, 6.53%. Found: C, 53.18; H, 6.60%.

3.10. 1-Bromo-1-fluorospyropentane 18

Yield 1.69 g (64%), colorless liquid, bp 110–111 °C. IR (film): ν 3082, 3005, 1435, 1394, 1194, 1109, 1072, 1018, 930, 822, 594 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04–1.12 (m, 2H), 1.22–1.30 (m, 1H), 1.30–1.38 (m, 1H), 1.68 (dd, 1H, $^2J_{HH}$ 7.1, $^3J_{HF}$ 3.2), 1.91 (dd, 1H, $^2J_{HH}$ 7.1, $^3J_{HF}$ 12.4). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 8.0 ($^1J_{CH}$ 164, $^3J_{CF}$ 3, CH_2), 9.7 ($^1J_{CH}$ 165, CH_2), 22.1 ($^2J_{CF}$ 10, C-spiro), 23.0 ($^1J_{CH}$ 165, $^2J_{CF}$ 12, CH_2), 85.3 ($^1J_{CF}$ 305, CFBr). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −134.46 to −134.53 (m, 1F). Anal. Calcd for C_5H_6BrF: C, 36.40; H, 3.67%. Found: C, 36.67; H, 3.98%.

3.11. 1-Bromo-1-fluoro-2-methyl-2-phenylspiro[2.2]-pentane 19

Yield 1.59 g (39%), colorless liquid, R_f 0.4 (petroleum ether). Two isomers, (1*R*,2*R*)*-A:(1*R*,2*R*)*-B=1:0.95. IR (film): ν 3070, 3030, 3000, 2930, 2880, 1600, 1500, 1450, 1380, 1190, 1100, 1005, 980, 875, 780, 710, 640 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10 (ddd, 1H, CH_2), 1.13–1.32 (m, 4H, CH_2), 1.42–1.48 (m, 1H, CH_2), 1.50–1.58 (m, 2H, CH_2), 1.63 (d, 3H, $^4J_{HF}$ 2.0, CH_3), 1.64 (d, 3H, $^4J_{HF}$ 2.5, CH_3), 7.28–7.41 (m, 5H, Ph, A+5H, Ph, B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 6.2 ($^3J_{CF}$ 4.0, CH_2, B), 8.9 (CH_2, A), 9.0 ($^3J_{CF}$ 3.8, CH_2, A), 10.8 (CH_2, B), 20.4 ($^3J_{CF}$ 5.1, CH_3, B), 24.9 ($^3J_{CF}$ 3.9, CH_3, A), 30.9 ($^2J_{CF}$ 8.4, C-spiro, A), 31.0 ($^2J_{CF}$ 9.8, C-spiro, B), 34.5 ($^2J_{CF}$ 9.8, C, A), 35.3 ($^2J_{CF}$ 11.0, C, B), 94.0 ($^1J_{CF}$ 314, CBrF), 94.9 ($^1J_{CF}$ 308, CBrF), 127.0 (2CH, Ph), 128.3 (2CH, Ph), 128.3 (2CH, Ph), 128.4 (2CH, Ph), 128.4 (2CH, Ph), 138.9 (C, Ph), 141.9 (C, Ph). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −136.60 (br d, 1F, $^4J_{HF}$ 8.6, B), −130.67 (br d, 1F, $^4J_{HF}$ 8.1, A). Anal. Calcd for $C_{12}H_{12}BrF$: C, 56.49; H, 4.74%. Found: C, 56.70; H, 4.74%.

3.12. 1-Bromo-1-fluoro-2,2-diphenylspiro[2.2]pentane 20

Yield 1.77 g (35%), colorless solid, mp 106–108 °C, R_f 0.2 (petroleum ether). IR (film): ν 3068, 3040, 2970, 2940, 2860, 1600, 1500, 1470, 1390, 1180, 1060, 715, 650, 605 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (ddd, 1H, $^2J_{HH}$ 5.1, $^3J_{HH}$ 6.7, $^3J_{HH}$ 9.5, CH_2), 1.45 (ddd, 1H, $^2J_{HH}$ 5.0, $^3J_{HH}$ 6.4, $^3J_{HH}$ 9.5, CH_2), 1.52 (dddd, 1H, $^2J_{HH}$ 5.0, $^3J_{HH}$ 6.7, $^3J_{HH}$ 9.1, $^4J_{HF}$ 0.9, CH_2), 1.72 (dddd, 1H, $^2J_{HH}$ 5.1, $^3J_{HH}$ 6.4, $^3J_{HH}$ 9.1, $^4J_{HF}$ 9.0, CH_2), 7.24–7.38 (m, 10H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 8.3 ($^3J_{CF}$ 4, CH_2), 11.3 (CH_2), 32.0 ($^2J_{CF}$ 9, C-spiro), 43.0 ($^2J_{CF}$ 10, C), 93.3 ($^1J_{CF}$ 312, CBrF), 127.2 (CH, Ph), 127.2 (CH, Ph), 128.2 (2CH, Ph), 128.5 (2CH, Ph), 129.3 (2CH, Ph), 129.5 (2CH, Ph), 139.0 (C, Ph), 141.0 ($^3J_{CF}$ 4, C, Ph). MS (EI, 70 eV) *m*/*z*: 318 (M^+, 12), 316 (M^+, 12), 237 ([M−Br]$^+$, 100), 222 (29), 203 (35), 159 (32), 115 (19), 109 (21), 91 (43). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −128.15 (br d, 1F, $^4J_{HF}$ 9.0). Anal. Calcd for $C_{17}H_{14}BrF$: C, 64.37; H, 4.95%. Found: C, 65.37; H, 4.75%.

3.13. General procedure 2: reaction of *gem*-bromofluorospiropentanes 11–20 with methyllithium

A solution (5.4 mL) of 1.5 N (8.0 mmol) methyllithium in ether was added dropwise to solution of 4.0 mmol bromofluorospiropentane in 10 mL of absolute ether at −55 °C in argon. The reaction mixture was warmed up to −10 °C and stirred for 72 h. Then it was warmed up to 0 °C and quenched with equal amount of cold water. The organic phase was separated, the water phase extracted with ether (3×3 mL). The combined organic fractions were washed with 5 mL of water and dried over $MgSO_4$. The solvent was evaporated, the products were isolated by preparative column chromatography or GLC (column 3000×5 mm, silicone E-301, 15% on Inerton AW).

3.14. 7-Bromo-7-methylbicyclo[2.0.2.1]heptane 21[24]

Yield 0.67 g (90%), colorless liquid, R_f 0.5 (petroleum ether). IR (film): ν 3070, 2990, 2870, 1470, 1380, 1200, 964, 912, 865, 605 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.73–0.77 (m, 2H), 0.82–0.85 (m, 2H), 0.93–1.04 (m, 4H), 1.70 (s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 7.0 ($^1J_{CH}$ 165, 2×CH_2), 8.5 ($^1J_{CH}$ 159, 2×CH_2), 25.9 ($^1J_{CH}$ 129, CH_3), 26.9 (2×C-spiro), 44.0 (CBr). MS (FAB): 187, 185 (2, M−1), 91 (100, M−Br−Me). MS (EI, 70 eV) *m*/*z*: 187 ([M−1]$^+$, 2), 185 ([M−1]$^+$, 2), 173 (4), 171 (4), 107 ([M−Br]$^+$, 33), 91 (100), 79 (93), 65 (26), 51 (21), 41 (22), 39 (28).

3.15. 8-Bromo-8-methyldispiro[2.0.3.1]octane 22

Yield 0.20 g (25%), colorless liquid, R_f 0.2 (petroleum ether). IR (film): ν 3075, 2996, 2870, 1465, 1378, 915, 820, 718, 609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81–0.84 (m, 1H, CH_2, *c*-Pr), 0.89–0.92 (m, 1H, CH_2, *c*-Pr), 0.93–0.98 (m, 2H, CH_2, *c*-Pr), 1.65 (s, 3H, CH_3), 1.92–2.01 (m, 4H, $2CH_2$, *c*-Bu), 2.23–2.28 (m, 1H, CH_2, *c*-Bu), 2.38–2.44 (m, 1H, CH_2, *c*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 7.1 (CH_2), 8.7 (CH_2), 14.9 (CH_2), 23.9 (CH_2), 24.3 (CH_3), 26.2 (C-spiro), 28.1 (CH_2), 30.2 (C-spiro), 46.7 (CBr). MS MALDI-TOF calcd for $C_9H_{13}{}^{79}Br$ (M^+): 200.02, found: 200.60; MS (EI, 70 eV) *m*/*z*: 174 ([M−C_2H_4]$^+$, 58), 172 ([M−C_2H_4]$^+$, 62), 159 (3), 157 (3), 121 (8), 105 (12), 93 (100), 91 (66), 79 (37), 77 (75), 65 (37), 55 (12), 53 (23), 41 (19), 39 (35). Anal. Calcd for $C_9H_{13}Br$: C, 53.75; H, 6.52%. Found: C, 53.37; H, 6.75%.

3.16. 10-Bromo-10-methyldispyro[2.0.5.1]decane 23[25]

Yield 0.41 g (45%), colorless liquid, R_f 0.4 (petroleum ether). IR (film): ν 3070, 3000, 2856, 1462, 1380, 725, 612 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.73–0.79 (m, 1H, CH_2, *c*-Pr), 0.86–0.90 (m, 2H, CH_2, *c*-Pr), 0.94–0.99 (m, 1H, CH_2, *c*-Pr), 1.30–1.78 (m, 10H, CH_2, *c*-Hex), 1.81 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 5.6 (CH_2, *c*-Pr), 7.3 (CH_2, *c*-Pr), 24.3 (CH_3), 25.4 (CH_2, *c*-Hex), 25.6 (CH_2, *c*-Hex), 26.0 (CH_2, *c*-Hex), 29.5 (C-spiro), 30.1 (CH_2, *c*-Hex), 30.9 (C-spiro), 35.0 (CH_2, *c*-Hex), 50.9 (CBr). MS (EI, 70 eV) *m*/*z*: 230 (M^+, 36), 228 (M^+, 37), 149 ([M−Br]$^+$, 80), 119 (8), 107 (18), 91 (28), 81 (73), 67 (100), 55 (8), 41 (12).

3.17. 1-Bromo-1-methyl-4-phenylspiro[2.2]pentane 24

Yield 0.26 g (27%), two isomers, A:B 1:0.6, colorless oil, R_f 0.2 (petroleum ether). IR (film): ν 3078, 3020, 3000, 2850, 1600, 1458, 1376, 1230, 720, 610 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (d, 1H, $^2J_{HH}$ 5.8, CH_2, B), 1.32 (d, 1H, $^2J_{HH}$ 5.8, CH_2, A), 1.33 (dd, 1H, $^2J_{HH}$ 4.7, $^3J_{HH}$ 5.5, CH_2, A), 1.37 (dd, 1H, $^2J_{HH}$ 4.9, $^3J_{HH}$ 5.0, CH_2, B), 1.46 (d, 1H, $^2J_{HH}$ 5.8, CH_2, A), 1.65 (d, 1H, $^2J_{HH}$ 5.8, CH_2, B), 1.68 (dd, 1H, $^2J_{HH}$ 4.9, $^3J_{HH}$ 8.4, CH_2, B), 1.76 (dd, 1H, $^2J_{HH}$ 4.7, $^3J_{HH}$ 8.4, CH_2, A), 1.81 (s, 3H, CH_3, B), 1.86 (s, 3H, CH_3, A), 2.45 (dd, $^3J_{HH}$ 5.5, $^3J_{HH}$ 8.4, CH, A), 2.53 (dd, $^3J_{HH}$ 5.0, $^3J_{HH}$ 8.4, CH, B), 7.08–7.12 (m, 2H, Ph, B), 7.16–7.19 (m, 2H, Ph, A), 7.20–7.25 (m, 2H, Ph, A+B), 7.28–7.35 (m, 4H, Ph, A+B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 17.3 ($^1J_{CH}$ 163, CH_2, A), 19.3 ($^1J_{CH}$ 163, CH_2, B), 22.0 ($^1J_{CH}$ 161, CH_2, B), 22.1 ($^1J_{CH}$ 161, CH_2, A), 23.8 ($^1J_{CH}$ 166, CH, B), 25.5 ($^1J_{CH}$ 166, CH, A), 27.6 ($^1J_{CH}$ 130, CH_3, A), 27.7 ($^1J_{CH}$ 129, CH_3, B), 31.6 (C-spiro, B), 31.8 (C-spiro, A), 36.9 (CBr, B), 37.5 (CBr, A), 125.9 (2CH, Ph), 126.0 (2CH, Ph), 126.5 (2CH, Ph), 128.3 (2CH, Ph),

128.4 (2CH, Ph), 141.1 (C, Ph, A), 141.2 (C, Ph, B). Anal. Calcd for $C_{12}H_{13}Br$: C, 60.78; H, 5.53%. Found: C, 60.68; H, 5.29%.

3.18. (2-Vinylidenecyclopropyl)benzene 25[26]

Yield 0.15 g (27%), colorless liquid, R_f 0.4 (petroleum ether). IR (film): ν 3080, 3020, 3005, 2835, 1970, 1585, 1450, 1350, 1062, 865 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.69–1.80 (m, 1H, CH_2), 2.11–2.17 (m, 1H, CH_2), 3.00–3.07 (m, 1H, CH), 4.95–5.01 (m, 2H, CH_2=), 7.18–7.43 (m, 5H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 18.1 (CH_2), 25.1 (CH), 77.8 (CH_2=), 81.0 (C=), 126.4 (CH, Ph), 126.6 (2CH, Ph), 128.2 (2CH, Ph), 140.5 (C, Ph), 194.3 (=C=). MS MALDI-TOF calcd for $C_{11}H_{10}$ (M^+): 142.08, found: 141.98.

3.19. 1-Bromo-1-methyl-4-(4-fluorophenyl)spiro[2.2]-pentane 26

Yield 0.42 g (43%), two isomers, A:B 1:0.65, colorless oil, R_f 0.2 (petroleum ether). IR (film): ν 3060, 3010, 2955, 2868, 1600, 1508, 1260, 1180, 840, 593 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.13 (d, 1H, $^2J_{HH}$ 6.0, CH_2, B), 1.26–1.32 (m, 2H, CH_2, A+1H, CH_2, B), 1.41 (d, 1H, $^2J_{HH}$ 6.1, CH_2, A), 1.61 (d, 1H, $^2J_{HH}$ 6.0, CH_2, B), 1.63–1.70 (m, 1H, CH_2, B), 1.73 (dd, $^2J_{HH}$ 5.0, $^3J_{HH}$ 8.5, 1H, CH_2, A), 1.79 (s, 3H, CH_3, B), 1.84 (s, 3H, CH_3, A), 2.41 (dd, $^3J_{HH}$ 5.3, $^3J_{HH}$ 8.5, 1H, CH, A), 2.76 (dd, $^3J_{HH}$ 5.6, $^3J_{HH}$ 8.6, 1H, CH, B), 6.95–7.21 (m, 4H, 4CH, Ph, A+4H, 4CH, Ph, B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 17.0 ($^1J_{CH}$ 162, CH_2, A), 19.1 ($^1J_{CH}$ 163, CH_2, B), 21.9 ($^1J_{CH}$ 164, CH_2, B), 22.0 ($^1J_{CH}$ 164, CH_2, A), 24.3 ($^1J_{CH}$ 162, CH, B), 24.8 ($^1J_{CH}$ 160, CH, A), 27.5 ($^1J_{CH}$ 129, CH_3, A), 27.7 ($^1J_{CH}$ 129, CH_3, B), 31.4 (C-spiro, A), 31.6 (C-spiro, B), 36.6 (CBr, B), 37.7 (CBr, A), 115.1 ($^2J_{CF}$ 13, 2CH, Ph, A), 115.2 ($^2J_{CF}$ 13, 2CH, Ph, B), 127.3 ($^3J_{CF}$ 7, 2CH, Ph), 127.9 ($^3J_{CF}$ 7, 2CH, Ph), 136.7 (C, Ph, A+C, Ph, B), 161.6 ($^1J_{CF}$ 243, CF, Ph, A+CF, Ph, B). MS (EI, 70 eV) m/z: 175 ([M−Br]$^+$, 100), 160 (19), 147 (28), 134 (80), 122 (46), 109 (13), 96 (6). HRMS (ESI) calcd for $C_9H_{13}Br$ (M−Br)$^+$: 175.0923, found: 175.0918.

3.20. 1-Fluoro-4-(2-vinylidenecyclopropyl)benzene 27

Yield 0.18 g (28%), colorless liquid, R_f 0.4 (petroleum ether). IR (film): ν 3065, 3020, 3000, 2840, 1956, 1578, 1457, 1360, 1080, 1045, 785 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.64–1.69 (m, 1H, CH_2), 2.09–2.15 (m, 1H, CH_2), 2.98–3.03 (m, 1H, CH), 4.95–5.00 (m, 2H, CH_2=), 7.95–7.13 (m, 4H, 4CH, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 18.0 (CH_2), 24.3 (CH), 77.9 (CH_2=), 81.3 (C=), 115.3 ($^2J_{CF}$ 13, 2CH, Ph), 127.9 ($^3J_{CF}$ 7, 2CH, Ph), 161.8 ($^1J_{CF}$ 244, CF, Ph), 194.4 (=C=). MS (EI, 70 eV) m/z: 160 (M^+, 35), 159 (100), 133 (37), 120 (6), 109 (9). HRMS (ESI) calcd for $C_{11}H_9F$ (M−H)$^-$: 159.0610, found: 159.0614.

3.21. 1-Bromo-1-methyldispiro[2.0.3.1]octane 28

Yield 0.23 g (28%), two isomers, A:B 1:0.8, colorless liquid, R_f 0.2 (petroleum ether). IR (film): ν 3078, 3000, 2962, 2870, 1452, 1375, 1335, 1280, 962, 810, 725, 567 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.75 (d, $^2J_{HH}$ 4.5, 1H, CH_2, *c*-Pr, B), 0.98 (d, $^2J_{HH}$ 4.5, 1H, CH_2, *c*-Pr, B), 0.99 (br s, 2H, CH_2, *c*-Pr, B), 1.03 (d, $^2J_{HH}$ 5.3, 1H, CH_2, *c*-Pr, A), 1.14 (d, $^2J_{HH}$ 5.3, 1H, CH_2, *c*-Pr, A), 1.32 (d, $^2J_{HH}$ 5.6, 1H, CH_2, *c*-Pr, A), 1.50 (d, $^2J_{HH}$ 5.6, 1H, CH_2, *c*-Pr, A), 1.79 (s, 3H, CH_3, B), 1.90 (s, 3H, CH_3, A), 1.94–2.22 (m, 5H, CH_2, *c*-Bu, A+5H, CH_2, *c*-Bu, B), 2.23–2.29 (m, H, CH_2, *c*-Bu, A), 2.70–2.76 (m, H, CH_2, *c*-Bu, B). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 16.9 ($^1J_{CH}$ 142, CH_2, *c*-Bu, B), 17.1 ($^1J_{CH}$ 142, CH_2, *c*-Bu, A), 18.0 ($^1J_{CH}$ 161, CH_2, *c*-Pr, B), 21.0 ($^1J_{CH}$ 161, CH_2, *c*-Pr, A), 22.0 ($^1J_{CH}$ 161, CH_2, *c*-Pr, A), 22.7 ($^1J_{CH}$ 161, CH_2, *c*-Pr, B), 26.2 ($^1J_{CH}$ 137, CH_2, *c*-Bu, B), 27.5 ($^1J_{CH}$ 129, CH_3), 27.7 ($^1J_{CH}$ 137, CH_2, *c*-Bu, A), 28.5 ($^1J_{CH}$ 128, CH_3), 28.6 (C-spiro, B), 29.1 (C-spiro, A), 29.3 ($^1J_{CH}$ 140, CH_2, *c*-Bu, B), 29.5 ($^1J_{CH}$ 140, CH_2, *c*-Bu, A), 30.2 (C-spiro, B), 30.7 (C-spiro, A), 39.3 (CBr, B), 39.4 (CBr, A). MS (EI, 70 eV) m/z: 174 ([M−C_2H_4]$^+$, 3), 172 ([M−C_2H_4]$^+$, 3), 121 (9), 105 (28), 93 (69), 91 (42), 79 (100), 77 (42), 65 (15), 53 (20), 41 (22), 39 (28). Anal. Calcd for $C_9H_{13}Br$: C, 53.75; H, 6.52%. Found: C, 53.45; H, 6.82%.

3.22. 1-Ethenylidenespiro[2.3]hexane 29

Yield 0.06 g (14%), colorless liquid, R_f 0.3 (petroleum ether). IR (film): ν 3068, 2995, 2897, 1958, 1470, 1440, 1062, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.57–1.62 (m, 2H, CH_2, *c*-Pr), 2.00–2.15 (m, 2H, CH_2, *c*-Bu), 2.16–2.26 (m, 2H, CH_2, *c*-Bu), 2.37–2.47 (m, 2H, CH_2, *c*-Bu), 4.81 (m, 2H, CH_2=). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 16.8 ($^1J_{CH}$ 137, CH_2, *c*-Bu), 21.5 ($^1J_{CH}$ 163, CH_2, *c*-Pr), 27.9 (C-spiro), 30.7 ($^1J_{CH}$ 137, $2CH_2$, *c*-Bu), 76.2 ($^1J_{CH}$ 168, CH_2=), 83.4 (C=), 193.5 (=C=). MS (EI, 70 eV) m/z: 106 (M^+, 3), 105 (31), 91 (100), 78 (94), 65 (25), 52 (36), 39 (28). Anal. Calcd for $C_8H_{10}Br$: C, 90.51; H, 9.49%. Found: C, 90.19; H, 9.35%.

3.23. 2′-Bromo-2′-methylspiro[bicyclo[6.1.0]nonane-9,1′-cyclopropane] 30

Yield 0.27 g (28%), colorless liquid, R_f 0.5 (petroleum ether). IR (film): ν 3060, 2995, 2960, 2856, 1446, 1361, 1162, 1060, 858, 761, 521 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.94 (d, 1H, $^2J_{HH}$ 5.4, CH_2, *c*-Pr), 1.03–1.19 (m, 2H), 1.25–1.31 (m, 1H), 1.25 (d, 1H, $^2J_{HH}$ 5.4, CH_2, *c*-Pr), 1.37–1.79 (m, 10H), 1.72 (s, 3H, CH_3), 1.81–1.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 19.2 ($^1J_{CH}$ 162, CH_2, *c*-Pr), 22.4 ($^1J_{CH}$ 160, CH, *c*-Pr), 24.0 ($^1J_{CH}$ 160, CH, *c*-Pr), 25.0 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 25.1 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 26.6 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 26.7 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 27.8 ($^1J_{CH}$ 128, CH_3), 29.0 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 29.1 ($^1J_{CH}$ 125, CH_2, *c*-Oct), 31.5 (C-spiro), 38.3 (CBr). Anal. Calcd for $C_{12}H_{19}Br$: C, 59.27; H, 7.88%. Found: C, 59.42; H, 7.79%.

3.24. 9-Vinylidenebicyclo[6.1.0]nonane 31

Yield 0.33 g (55%), colorless liquid, R_f 0.6 (petroleum ether). IR (film): ν 2935, 2870, 1970, 1470, 1440, 1340, 1170, 1062, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.22–1.33 (m, 2H), 1.35–1.49 (m, 4H), 1.55–1.67 (m, 4H), 1.77–1.87 (m, 2H), 2.02–2.10 (m, 2H), 4.74 (t, 2H, $^5J_{HH}$ 3.8, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.8 (2CH), 26.0 ($2CH_2$), 26.3 ($2CH_2$), 29.1 ($2CH_2$), 75.6 ($=CH_2$), 83.7 (C=), 193.3 (=C=). MS (EI, 70 eV) m/z: 148 (M^+, 2), 147 (3), 133 (29), 119 (34), 105 (63), 91 (100), 79 (77), 67 (29), 55 (23), 41 (34), 39 (30). HRMS (ESI) calcd for $C_{11}H_{16}$ ($M)^-$: 148.1252, found: 148.1259.

3.25. 1,1′-Ethane-1,2-diylbis(2-methylcyclobutene) 32

Yield 0.26 g (40%), colorless oil, R_f 0.6 (petroleum ether). IR (film): ν 2980, 2950, 2860, 1660, 1465, 1378, 1270, 1215, 1090, 1070, 945, 880, 720, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.61 (br s, 6H, CH_3), 2.09 (br s, 4H), 2.22–2.29 (br m, 8H, *c*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 13.8 ($^1J_{CH}$ 125, 2×CH_3), 26.2 ($^1J_{CH}$ 127, 2×CH_2), 27.7 ($^1J_{CH}$ 137, 2×CH_2, *c*-Bu), 29.5 ($^1J_{CH}$ 136, 2×CH_2, *c*-Bu), 136.1 (C=), 140.5 (C=). MS (EI, 70 eV) m/z: 162 (M^+, 12), 147 (25), 133 (9), 119 (12), 105 (10), 91 (10), 81 (100), 79 (46), 67 (7), 53 (23), 41 (19), 39 (18). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18%. Found: C, 88.62; H, 11.10%.

3.26. (2-(2-Methylcyclobut-1-enyl)propan-2-yl)benzene 33

Yield 0.33 g (45%), colorless solid, R_f 0.3 (petroleum ether). IR (film): ν 3030, 3000, 2970, 2875, 1665, 1600, 1475, 1430, 1372, 1250, 1170, 1145, 772, 730, 715, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.48 (br s, 6H, $2CH_3$), 1.57 (br s, 3H, CH_3), 2.20–2.28 (br m, 4H, $2CH_2$), 7.18–7.24 (m, 1H, CH, Ph), 7.32–7.43 (m, 4H, 4CH, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 15.4 ($^1J_{CH}$ 126, CH_3), 25.8 ($^1J_{CH}$ 137, CH_2), 28.1 ($^1J_{CH}$ 127, $2CH_3$), 28.9 ($^1J_{CH}$ 137, CH_2), 29.8 (C), 125.6 (CH, Ph), 126.3 (2CH, Ph), 128.0 (2CH, Ph), 135.1 (C, Ph), 146.6 (C=), 148.7 (C=). MS (EI, 70 eV) m/z: 186 (M^+, 12), 171 (100), 156 (12), 143 (48), 129 (21),

115 (11), 91 (23), 77 (9), 41 (10), 39 (5). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%. Found: C, 90.32; H, 9.71%.

3.27. 2a,7-Dimethyl-7-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]indene 34

Yield 0.50 g (51%), colorless oil, R_f 0.2 (petroleum ether). IR (film): ν 3020, 2985, 2950, 2925, 2870, 1600, 1525, 1500, 1470, 1430, 1380, 1125, 1080, 940, 772, 750, 730, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.94–1.02 (m, 1H, CH_2), 1.43 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.61–1.72 (m, 1H, CH_2), 1.91–2.01 (m, 1H, CH_2), 2.36–2.47 (m, 1H, CH_2), 3.30–3.35 (m, 1H, CH), 7.18–7.24 (m, 1H, Ph), 7.25–7.38 (m, 6H, Ph), 7.42–7.48 (m, 2H, Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 18.6 ($^1J_{CH}$ 125, CH_3), 23.0 ($^1J_{CH}$ 138, CH_2), 26.2 ($^1J_{CH}$ 128, CH_3), 28.9 ($^1J_{CH}$ 138, CH_2), 48.4 ($^1J_{CH}$ 138, CH), 52.3 (C), 57.9 (C), 125.5 (CH, Ph), 125.8 (CH, Ph), 125.9 (CH, Ph), 126.5 (CH, Ph), 127.0 (CH, Ph), 127.6 (2CH, Ph), 127.7 (2CH, Ph), 143.3 (C, Ph), 146.7 (C, Ph), 151.5 (C, Ph). MS (EI, 70 eV) *m*/*z*: 248 (M^+, 26), 233 (15), 220 (54), 205 (100), 192 (20), 178 (15), 143 (26), 128 (13), 115 (9), 91 (14), 77 (4). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12%. Found: C, 91.63; H, 8.34%.

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