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Mg-Prompted Polyfluoroarene C−H Functionalization: Formal Synthesis of Transfluthrin, Fenfluthrin, and Tefluthrin

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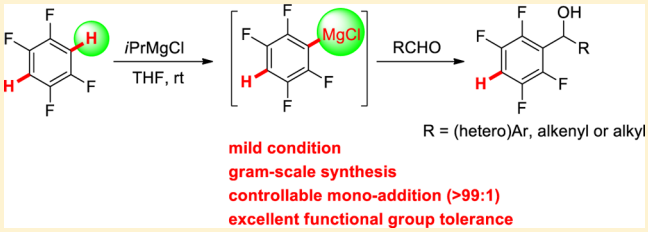
Supporting Information

ABSTRACT: Directing group and transition metal free C−H bond functionalization of a simple molecule is an ideal but challenging chemical transformation. Herein, we report a general Mg-prompted approach to synthesize versatile polyfluoroaryl carbinols at ambient temperature via polyfluoroarene C−H bond addition to aldehydes, which featured excellent monoaddition selectivity and broad functional group compatibility. The usefulness of this practical and efficient method was demonstrated in gram-scale formal synthesis of pyrethroid insecticides transfluthrin, tefluthrin, and fenfluthrin.



INTRODUCTION

Polyfluoroarenes and derivatives serve as core structures in many pharmaceuticals, agrochemicals, and materials. For example, the oral diabetes medicine blockbuster Januvia and the widely used pyrethroid insecticides, such as transfluthrin, fenfluthrin, tefluthrin, and metofluthrin (SumiOne),[1] all contain polyfluoroaryl units (Figure 1). Especially for the latter, the

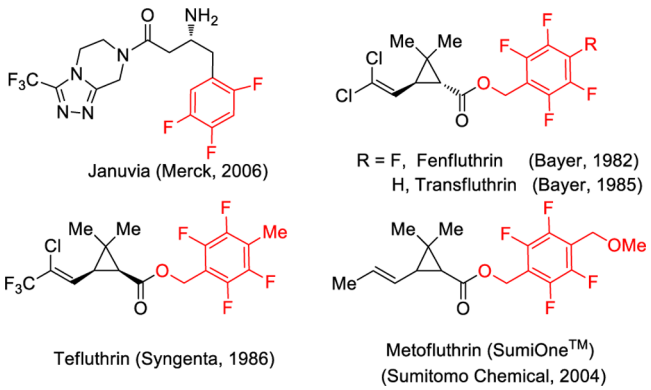
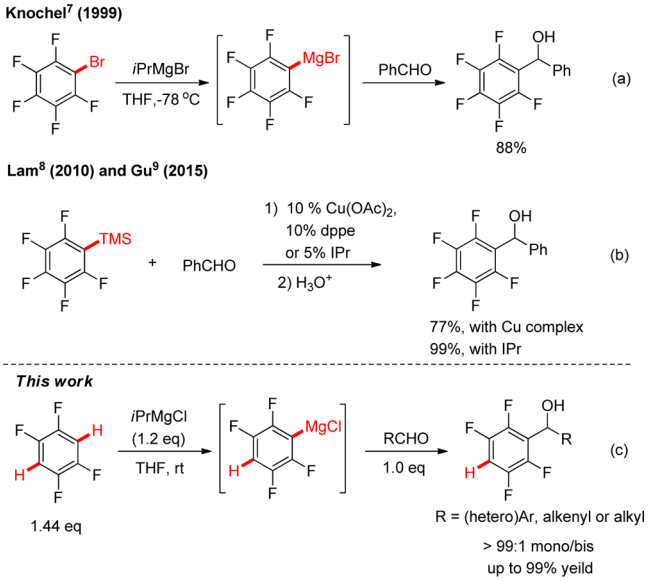


Figure 1. Januvia and pyrethroid insecticides all containing polyfluoroaryl units.

introduction of polyfluorobenzyl alcohols into the traditional pyrethroids has become an effective way to develop a new generation of pyrethroid insecticides over the past two decades, which leads to the dramatic improvement of the biological activity and vector controllability.[2] Hence, identifying an efficient process to access various fluorinated aryl carbinols is of great interest for discovering desirable insecticides.

The existing approach to synthesizing these vital benzyl alcohols mainly applied the manipulation of polyfluoroaryl acids and derivatives, such as reduction of polyfluoroaryl acid,[3] ester,[4] acyl chloride,[5] and nitrile.[6] To obtain all kinds of fluorinated aryl carbinols, an alternative strategy involved in polyfluoroaryl carbanion addition to aldehyde was gradually established. Knochel[7] first used fluorinated aryl bromide as the precursor of carbanion to perform multifluorophenylation of aldehydes via Br/Mg exchange at low temperatures with limited aldehydes (Scheme 1a). Very recently, Lam[8] and Gu[9] independently developed a new way to access the polyfluor-

Scheme 1. Approaches To Access Polyfluoroaryl Carbinols via Addition to Aldehydes



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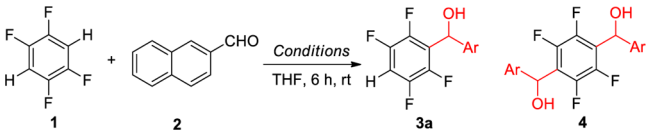
oaryl carbinols using polyfluorophenyltrimethylsilane as a nucleophile under copper-bisphosphine or NHC catalysis (Scheme 1b). While, in terms of atom economy and step efficiency, the most straightforward way to prepare polyfluoroaryl carbinols is direct C−H metalation of fluorinated arenes and addition to aldehydes. Because of the acidic property of the polyfluoroarene C−H bond,[10] great progress has been made to directly functionalize these molecules to prepare useful fluorinated compounds in this decade, including (hetero)arylation,[11] vinylation,[12] allylation,[13] benzylation,[14] and alkynylation.[15] The challenging issues using this desirable way to prepare polyfluoroaryl carbinols probably arose from the difficulty in the selective C−H metalation of polyfluoroarene lacking a directing group when possessing more than one acidic C−H bonds,[11a−c] poor functional group tolerance when a strong base such as *n*BuLi was used even under cold conditions,[16] and lower nucleophilicity of polyfluorinated arene−transition metal complexes toward aldehydes.[17] Until recently, Daugulis[18] disclosed such a protocol for the synthesis of polyfluoroaryl carbinols in the presence of base *t*BuOLi, but the substrates were only limited to substituted tetrafluorobenzenes. Hence, with respect to the growing concern about the contamination of heavy metal in pharmaceutical and agrochemical industry, a general and transition metal free, environmentally benign, and practical approach to access various polyfluoroaryl carbinols is strongly desired.[19] We envisioned that commercially available Grignard reagent may serve as suitable base to metalate the C−H bond,[20] leading to the formation of useful magnesated polyfluoroarenes to mimic the Grignard reaction for further transformation. As shown in Scheme 1, we describe a convenient Mg-prompted polyfluoroarene C−H bond addition to aldehydes approach to prepare versatile fluorinated adducts, which features controllable C−H bond addition to aldehyde (>99/1 mono/bis selectivity), excellent functional group tolerance, and practical and mild reaction conditions (Scheme 1*c*). The utility of the methodology was demonstrated by the formal synthesis of transfluthrin, tefluthrin, and fenfluthrin.

RESULTS AND DISCUSSION

We commenced this study with 1,2,4,5-tetrafluorobenzene **1**, possessing two acidic C−H bonds, and 2-naphthaldehyde **2** as model substrates. As described in Table 1, the commercially available Grignard reagent PhMgBr was first tested to examine the efficiency and selectivity of the C−H metalation of fluorobenzene **1**. Surprisingly, the reagent PhMgBr failed to metalate the C−H bond of tetrafluorobenzene and mainly afforded undesired alcohol by direct self-addition to aldehyde **2**. Interestingly, when switched into more basic alkyl Grignard reagent *i*PrMgCl, the desired monoaddition product **3** was obtained with excellent selectively (99/1) in 97% yield at room temperature. *i*PrMgBr and EtMgBr gave similar results. However, less bulky MeMgI gave complicated results. *t*BuOLi, reported by Daugulis[18] in the lithiation of substituted tetrafluorobenzene, afforded only 34% yields under this condition, along with some corresponding reduction products. The high mono/bis adduct ratio may result from the mild reaction conditions because the selectivity decreased when the reaction temperature increased. Finally, the ratio of tetrafluorobenzene to *i*PrMgCl and aldehyde was further studied. The optimal condition was as follows: 1.44/1.2/1.0 polyfluorobenzene/*i*PrMgCl/aldehyde ratio with a concentration of 0.4 M in THF.

Table 1. Optimization of Magnesium-Mediated Polyfluoroarene C−H Bond Metalation/Addition to Aldehyde[a]



entry[a]	RMX	1/RMX/2 ratio	yield of 3[b] (%)	3/4[c] ratio
1	PhMgBr	2.25/1.5/1	nd[d]	nd
2	*i*PrMgCl	2.25/1.5/1	97	99/1
3	*i*PrMgBr	2.25/1.5/1	92	99/1
4	EtMgCl	2.25/1.5/1	93	98/2
5	CH_3MgI	2.25/1.5/1	nd	nd
6	K_3PO_4	2.25/1.5/1	nd	nd
7	LiO*t*Bu	2.25/1.5/1	34	98/2
8	NaO*t*Bu	2.25/1.5/1	63	98/2
9	KO*t*Bu	2.25/1.5/1	<10	nd
10	*i*PrMgCl	1.8/1.5/1	97	99/1
11	*i*PrMgCl	1.5/1.5/1	83	97/3
12	*i*PrMgCl	1.44/1.2/1	97	99/1

[a]Reactions performed using 0.5 mmol of aldehyde, after tetrafluorobenzene **1** was stirred with Grignard reagent for 12 h at room temperature. [b]Isolated yield. [c]The ratio was judged by HPLC analysis. [d]Mainly gave the self-addition product.

With the optimized condition in hand, we investgated the aldehyde scope and functional group tolerance with a variety of aldehydes. As shown in Scheme 2, the addition reaction proceeded smoothly and selectively with *ortho*-, *meta*-, and *para*-substituted aryl aldehydes with excellent yields. The electron-donating methoxyl group did not obviously reduce the reactivity. It is noteworthy that the chloro- and bromo-containing aryl aldehydes coupled efficiently while carbon−halogen bonds were kept intact, which provides a chance for further manipulation of the products. Importantly, aldehydes containing cyano, nitro, and ester groups that are well-known to be sensitive to Grignard reagent also afforded the desired alcohols in high yields using lithium chloride as an additive.[21] In the absence of $ZnCl_2$,[22] the success of addition to the aldehydes possessing ester and nitro groups may lie in the lower nucleophilicity of polyfluoroarylmagnesium species compared with common arylmetal ones. Notably, the addition to aliphatic aldehydes, including bulky pivalaldehyde, and enal also proceeded efficiently without the formation of detectable aldol or 1,4-addition byproducts. Finally, the coupling reaction between heteroaromatic aldehydes and tetrafluorobenzene was studied. Aldehydes possessing thiophene, pyridine, quinoline, and indole heterocycle core structures all were coupled efficiently as well as aromatic aldehydes.

We next examined the scope with respect to polyfluoroarenes in Scheme 3. Substituted tetrafluorobenzenes were first investigated to understand the influence of the electronic effect on H/Mg exchange. An electron-donating group, such as methoxyl and *tert*-butyldimethylsilyl, gave a yield slightly lower than those containing electron−neutron or withdrawing groups, such as benzyl, methyl, methoxymethyl, allyl, and trifluoromethyl substituents. The success of the coupling reaction with broad electronic group substitution further revealed the generality of this approach for preparing fluorinated aryl carbinols. The polyfluorobenzyl alcohols produced here may be employed as interesting precursors for

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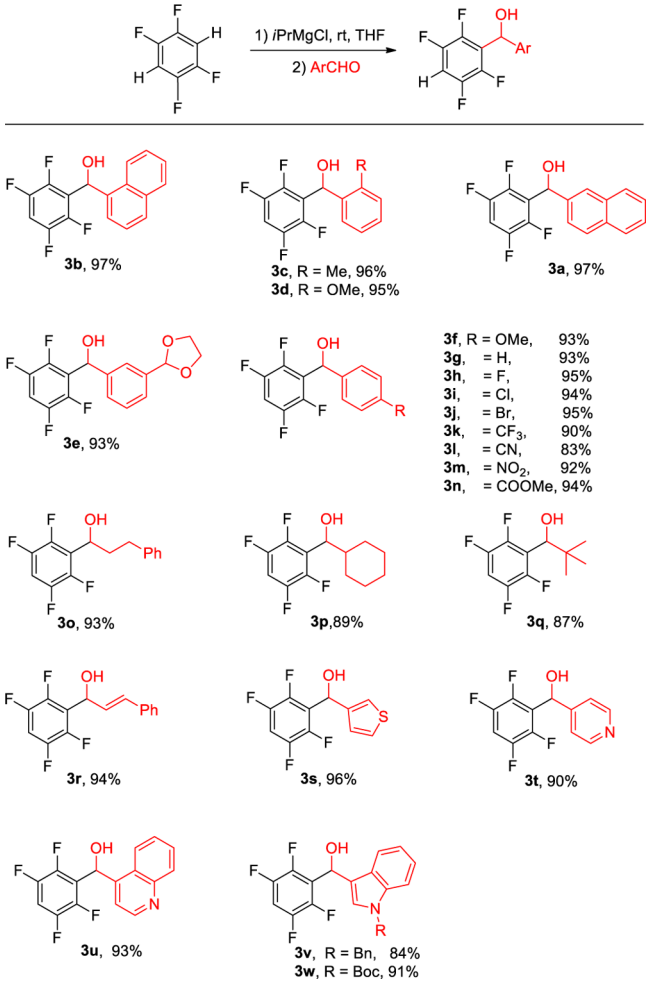
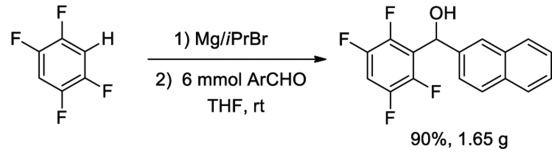
Scheme 2. Coupling with Various Aldehydes (Boc = *tert*-butoxycarbonyl; Bn = benzyl)



developing new pyrethroid insecticides.[23] Under the standard condition, pentafluorobenzene also coupled efficiently with different aldehydes in high yields, including (hetero) aromatic and aliphatic aldehydes. Both 1,2,3,5-tetrafluorobenzene and 1,2,4-trifluorobenzenze can react with the aldehyde smoothly. 1,2,3,4-Tetrafluorobenzene, whose acidic C−H bond was not flanked by two C−F bonds,[24] was not as efficient as the other two tetrafluorobenzenes, which afforded the addition product in moderate yield. 1,3,5-Trifluorobenzene containing less acidic C−H bonds coupled with aldehyde in acceptable yields. Finally, polyfluoropyridines were tested in the addition reaction. Both tetra- and trifluoro-substituted pyridines reacted with aldehyde in excellent yields.

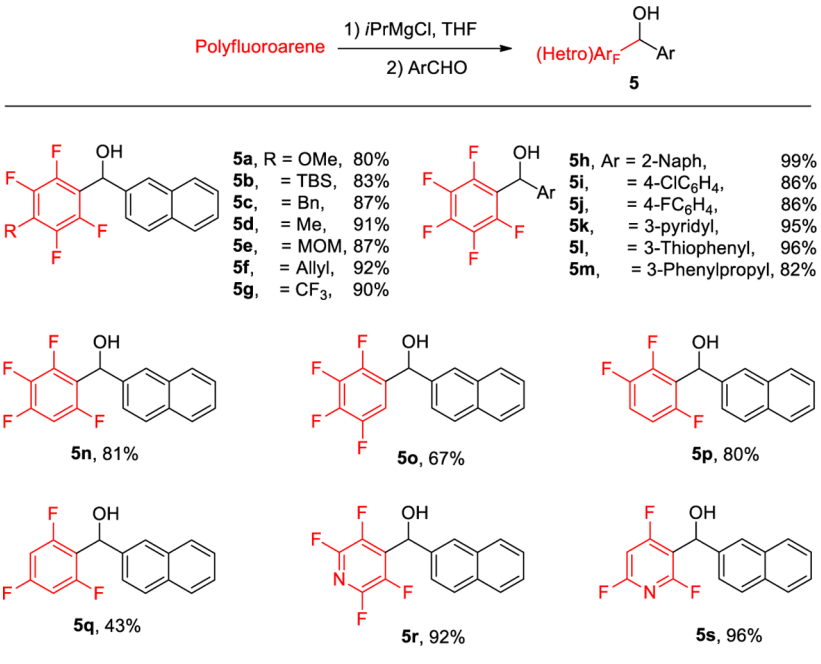
We have also performed the one-pot gram-scale synthesis of polyfluoroaryl carbinol to demonstrate the practical utility and efficiency of our method. For example, the lab-made *i*PrMgBr from *i*PrBr and magnesium turnings was used for directly deprotonating 1,2,4,5-tetrafluorobenzene, which afforded a similar yield with a commercially available Grignard reagent (Scheme 4). It suggests that our approach may be highly useful for large-scale synthesis of interesting fluorinated aryl carbinols.

Scheme 4. One-Pot Gram-Scale Synthesis Using Lab-Made *i*PrMgBr



As shown in Scheme 5, using this protocol, we attempted to prepare some important polyfluorobenzyl alcohols, such as pentafluorobenzyl alcohol **6**, 2,3,5,6-tetrafluorobenzyl alcohol **7**, and 4-methyl-2,3,5,6-tetrafluorobenzyl alcohol **8** in gram scale, which are the key intermediates of widely used pyrethroid

Scheme 3. Different Polyfluoroarenes Coupling with Aldehydes (TBS = *tert*-butyldimethyl, MOM = methoxymethyl, Bn = benzyl)



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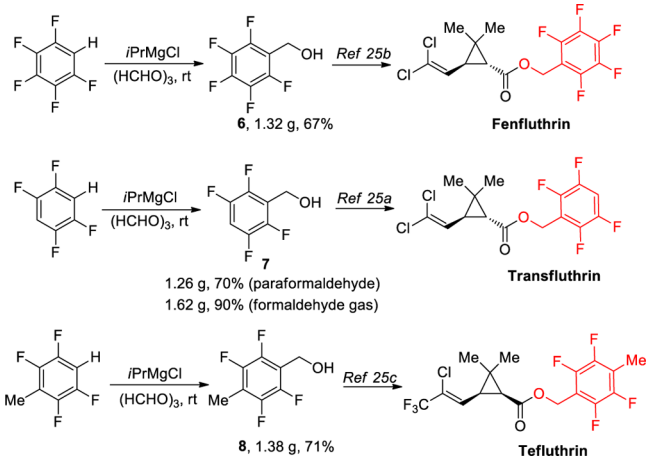
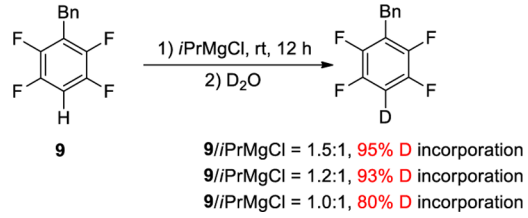
Scheme 5. Formal Synthesis of Pyrethroid Insecticides Fenfluthrin, Transfluthrin, and Tefluthrin



insecticides fenfluthrin, transfluthrin, and tefluthrin, respectively. With excess paraformaldehyde, the three alcohols were obtained in ~70% yield. Notably, the yield of the alcohols can be improved to 90% when formaldehyde gas formed by depolymerization was bubbled into the solution of Grignard reagent. Therefore, compared to procedures reported via multistep synthesis under harsh conditions, our method was highly efficient and practical for the formal synthesis of the corresponding insecticides under esterification conditions.[25]

We finally performed the H/D exchange experiment to understand Mg-mediated metalation of polyfluorobenzene C–H bond (Scheme 6). Indeed, at both 1.5:1 and 1.2:1 ratios of

Scheme 6. Deuteration under Reaction Conditions



benzyltetrafluorobenzene **9** to Grignard reagent *i*PrMgCl, the incorporation of deuteration was realized in 95 and 93% yields, respectively, while 80% deuteration was obtained when a 1:1 ratio was used. The data were consistent with the aforementioned isolated yield. It suggested that *i*PrMgCl can efficiently prompt H/Mg exchange at room temperature to produce useful magnesated polyfluoroarenes, and the resulting polyfluoroarylmagnesium species should be stable enough because no significant amount of benzyne-derived products[24] was detected after being quenched with aldehydes or deuterium oxide.

CONCLUSION

We have developed an efficient, general, and practical approach for synthesizing versatile polyfluoroaryl carbinols with excellent functional group compatibility at room temperature, which featured efficient H/Mg exchange with a series of polyfluoroarenes in the presence of *i*PrMgCl. It proved to be highly useful for the synthesis of widely used pyrethroid insecticides fenfluthrin, transfluthrin, and tefluthrin. The mild metalation conditions allow the resulting labile polyfluoroaryl-magnesium species to have a sufficient lifetime for further transformation, which will be highly useful in preparing other important polyfluoroaryl-containing molecules.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR spectra were acquired at 400 or 600 MHz, and chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents [$CDCl_3$, δ 7.26; $(CD_3)_2OS$, δ 2.50]. Multiplicities were given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The number of protons (*n*) for a given resonance was indicated by *n*H. Coupling constants are reported as *J* values in hertz. ^{13}C NMR spectra were obtained at 100 on 400 MHz or 150 on 600 MHz instruments, and chemical shifts were recorded relative to the solvent resonance [$CDCl_3$, δ 77.16; $(CD_3)_2OS$, δ 39.52]. The proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra.

Dry THF was freshly distilled from sodium/benzophenone under nitrogen before use. All anhydrous solvents were stored over activated 4 Å molecular sieve beans in Schlenk tubes in the glovebox. Unless noted otherwise, commercially available chemicals were used without further purification. Glassware was dried at 120 °C for at least 3 h before being used. Flash chromatography was preformed using Merck 40-63D 60 Å silica gel. HRMS was conducted in ESI mode, and the mass analyzer of the HRMS was an ion trap. GC–MS analysis was conducted with GC column HP-5-MS.

General Procedure for Addition of Mg-Mediated C–H Bonds to Aldehydes. In the nitrogen-filled glovebox, a flame-dried 10 mL Schlenk tube was successively charged with 1,2,4,5-tetrafluorobenzene (81 μL, 0.72 mmol), dry THF (1 mL), and an *i*PrMgCl solution (2 M, 0.3 mL, 0.6 mmol). After the resulting solution was stirred for 12 h at room temperature, aldehyde (0.5 mmol) was added in one portion at room temperature. Until all the material was consumed (monitored by TLC), the reaction was quenched with methanol dropwise (2 mL) at room temperature. The mixture solution was stirred for 30 min and filtered through a pad of silica gel. The filter cake was washed with diethyl ether until no more product was washed out (monitored by TLC). The filtrate was concentrated under vacuum, and the resulting residue was purified by chromatography using the ethyl acetate (EA)/petroleum ether (PE) solvent as the eluent.

*2,3,5,6-Tetrafluorophenyl-(2-naphthyl) Carbinol (**3a**).* White solid (148 mg, 97% yield): mp 116–117 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.86–7.83 (m, 3H), 7.52–7.49 (m, 3H), 7.06–6.98 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H), 3.04 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5–147.3 (m), 145.7–145.5 (m), 145.0–144.8 (m), 143.2–143.1 (m), 138.1, 133.2, 133.1, 128.7, 128.2, 127.8, 126.6, 126.5, 124.3, 123.5, 122.6 (t, J_F = 14.4 Hz), 105.6 (t, J_F = 22.5 Hz), 68.2; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.4 (dd, J_F = 22.6, 13.4 Hz, 2F), −143.5 (dd, J_F = 22.1, 13.4 Hz, 2F); HRMS (ESI) calcd for $C_{17}H_{10}F_4NaO$ $(M + Na)^+$ 329.0565, found 329.0546.

*2,3,5,6-Tetrafluorophenyl-(1-naphthyl) Carbinol (**3b**).* White solid (148.5 mg, 97% yield): mp 107–108 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 1H), 7.92–7.85 (m, 2H), 7.63–7.46 (m, 4H), 7.07–6.98 (m, 1H), 6.9 (s, 1H), 3.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5–147.3 (m), 146.0–145.8 (m), 145.1–144.8 (m), 143.5–143.4 (m), 135.2, 133.9, 130.6, 129.4, 129.0, 126.8, 126.0, 125.2, 124.1, 123.1, 121.8 (t, J_F = 13.9 Hz), 105.8 (t, J_F = 22.5 Hz), 65.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.4 (dd, J_F = 21.6, 13.2 Hz, 2F), −142.6 (dd, J_F = 21.6, 12.6 Hz, 2F); HRMS (ESI) calcd for $C_{17}H_{10}F_4NaO$ $(M + Na)^+$ 329.0565, found 329.0545.

*2,3,5,6-Tetrafluorophenyl-(o-tolyl) Carbinol (**3c**).* White solid (130 mg, 96% yield): mp 81–82 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.24–7.21 (m, 2H), 7.17–7.15 (m, 1H), 7.05–6.97 (m, 1H), 6.32 (s, 1H), 2.7 (br, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6–147.3 (m), 146.0–145.7 (m), 145.1–144.8 (m), 143.5–143.3 (m), 138.2, 135.8, 130.9, 128.5, 126.3, 126.0, 121.8 (t, J_F = 14.1 Hz), 105.7 (t, J_F = 22.6 Hz), 65.9, 19.1; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.2 (dd, J_F = 17.0, 11.3 Hz, 2F),

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−146.6 (dd, J_F = 22.6, 11.3 Hz, 2F); HRMS (ESI) calcd for $C_{14}H_{10}F_4NaO$ $(M + Na)^+$ 293.0565, found 293.0549.

*2,3,5,6-Tetrafluorophenyl-(o-anisyl) Carbinol (**3d**).* White solid (136 mg, 95% yield): mp 79−80 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.5 Hz, 1H), 7.33−7.29 (s, 1H), 7.02−6.96 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H), 6.41 (s, 1H), 3.82 (s, 1H), 3.29 (d, J = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 147.4−147.1 (m), 146.0−145.8 (m), 144.9−144.7 (m), 143.5−143.4 (m), 129.5, 128.6, 127.0, 122.2 (t, J_F = 14.0 Hz), 120.8, 110.6, 105.1 (t, J_F = 22.5 Hz), 65.1, 55.5; ^{19}F NMR (566 MHz, $CDCl_3$) δ −139.6 (dd, J_F = 22.6, 15.1 Hz, 2F), −143.0 (dd, J_F = 22.6, 15.1 Hz, 2F); HRMS (ESI) calcd for $C_{14}H_{10}F_4NaO_2$ $(M + Na)^+$ 309.0515, found 309.0524.

*2,3,5,6-Tetrafluorophenyl-[3-(1,3-dioxolanyl)-phenyl] Carbinol (**3e**).* White solid (153 mg, 93% yield): mp 61−62 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.42−7.36 (m, 3H), 7.05−6.96 (m, 1H), 6.19 (d, J = 7.4 Hz, 1H), 5.78 (s, 1H), 4.13−4.1 (m, 2H), 4.07−4.0 (m, 2H), 3.12 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5−147.2 (m), 145.6−145.5 (m), 145.0−144.7 (m), 143.2−143.0 (m), 141.2, 138.4, 128.9, 126.4, 126.3, 123.8, 122.7 (t, J_F = 14.5 Hz), 105.6 (t, J_F = 22.5 Hz), 103.6, 67.7, 65.4 (d, J_F = 1.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.4 (dd, J_F = 22.6, 11.3 Hz, 2F), −142.6 (dd, J_F = 22.6, 15.1 Hz, 2F); HRMS (ESI) calcd for $C_{16}H_{12}F_4NaO_3$ $(M + Na)^+$ 351.0620, found 351.0628.

*2,3,5,6-Tetrafluorophenyl-(p-anisyl) Carbinol (**3f**).* Colorless oil (133 mg, 93% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.5 Hz, 2H), 7.05−6.96 (m, 1H), 6.88 (d, J = 8.5 Hz, 2H), 6.2 (d, J = 4.2 Hz, 1H), 3.8 (s, 3H), 2.94 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.5−147.3 (m), 145.6−145.4 (m), 145.0−144.8 (m), 143.2−142.9 (m), 133.0, 127.1, 123.0 (t, J_F = 14.5 Hz), 114.2, 105.4 (t, J_F = 22.5 Hz), 68.8, 55.4; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.5 (dd, J_F = 22.6, 11.3 Hz, 2F), −144.0 (dd, J_F = 22.6, 16.9 Hz, 2F); HRMS (ESI) calcd for $C_{14}H_{10}F_4NaO_2$ $(M + Na)^+$ 309.0515, found 309.0523.

*2,3,5,6-Tetrafluorophenyl-(phenyl) Carbinol (**3g**).*[8b] White solid (119 mg, 93% yield): mp 38−39 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.30 (m, 5H), 7.07−6.98 (m, 1H), 6.27 (d, J = 7.7 Hz, 1H), 2.86 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6−147.3 (m), 145.7−145.5 (m), 145.1−144.8 (m), 143.2−143.0 (m), 140.9, 128.9, 128.3, 125.6, 122.8 (t, J_F = 14.5 Hz), 105.6 (t, J_F = 22.5 Hz), 68.1; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.6 (dd, J_F = 22.1, 12.4 Hz, 2F), −143.7 (dd, J_F = 21.8, 13.1 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_8F_4NaO$ $(M + Na)^+$ 279.0409, found 279.0392.

*2,3,5,6-Tetrafluorophenyl-(4-fluorophenyl) Carbinol (**3h**).* White solid (130 mg, 95% yield): mp 60−61 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.36 (m, 2H), 7.07−7.02 (m, 3H), 6.23 (d, J = 7.2 Hz, 1H), 2.94 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.4, 147.4−147.3 (m), 145.5−145.4 (m), 145.1−144.8 (m), 143.1−142.9 (m), 136.6 (d, J_F = 2.6 Hz), 127.5 (d, J_F = 8.3 Hz), 122.6 (t, J_F = 14.3 Hz), 115.8, 115.6, 105.8 (t, J_F = 16.1 Hz), 67.5; ^{19}F NMR (566 MHz, $CDCl_3$) δ −113.8 to −114.0 (m, F), −138.3 (d, J_F = 11.3 Hz, 2F), −143.8 (d, J_F = 16.9 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_7F_5NaO$ $(M + Na)^+$ 297.0315, found 297.0326.

*2,3,5,6-Tetrafluorophenyl-(4-chlorophenyl) Carbinol (**3i**).* White solid (137 mg, 94% yield): mp 67−68 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.30 (m, 4H), 7.08−7.0 (m, 1H), 6.23 (s, 1H), 2.83 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6−147.3 (m), 145.7−145.4 (m), 145.1−144.8 (m), 143.2−143.0 (m), 139.3, 134.1, 129.0, 127.0, 122.4 (t, J_F = 14.4 Hz), 105.9 (t, J_F = 22.4 Hz), 67.4; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.1 (dd, J_F = 21.2, 12.9 Hz, 2F), −143.6 (dd, J_F = 21.5, 13.2 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_7ClF_4NaO$ $(M + Na)^+$ 313.0019, found 313.0022.

*2,3,5,6-Tetrafluorophenyl-(4-bromophenyl) Carbinol (**3j**).* White solid (160 mg, 95% yield): mp 80−81 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.21 (s, 1H), 7.21−7.18 (m, 2H), 6.98−6.93 (m, 1H), 6.13 (d, J = 4.2 Hz, 1H), 2.72 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6−147.3 (m), 145.6−145.5 (m), 145.1−144.9 (m), 143.2−143.0 (m), 139.9, 132.0, 127.4, 122.1, 122.3 (t, J_F = 5.8 Hz), 106.0 (t, J_F = 22.3 Hz), 67.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.1 (dd, J_F = 21.9, 13.0 Hz, 2F), −143.6 (dd, J_F = 21.5, 12.9 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_7BrF_4NaO$ $(M + Na)^+$ 356.9514, found 356.9525.

*2,3,5,6-Tetrafluorophenyl-(4-trifluoromethylphenyl) Carbinol (**3k**).* White solid (146 mg, 90% yield): mp 65−66 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.52 (m, 4H), 7.09−7.01 (m, 1H), 6.32 (s, 1H), 2.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6−147.4 (m), 145.7−145.5 (m), 145.2−144.9 (m), 144.7, 143.2−143.1 (m), 130.7, 130.3, 125.5, 122.8, 125.9−125.8 (m), 122.1 (t, J_F = 14.6 Hz), 106.2 (t, J_F = 22.4 Hz), 67.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.7 (s, 3F), −137.9 (dd, J_F = 21.5, 13.1 Hz, 2F), −143.6 (dd, J_F = 21.8, 13.0 Hz, 2F); HRMS (ESI) calcd for $C_{14}H_7F_7NaO$ $(M + Na)^+$ 347.0283, found 347.0275.

*2,3,5,6-Tetrafluorophenyl-(4-nitrilephenyl) Carbinol (**3l**).* LiCl (0.5 M in THF, 1.8 mL, 0.9 mmol) was stirred with *in situ*-formed Grignard reagent for 30 min. Then, the corresponding aldehyde was added to the mixture at 0 °C, and the resulting mixture was stirred at this temperature for 5 h. White solid (117 mg, 83% yield): mp 133−134 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.1−7.01 (m, 1H), 6.31 (d, J = 5.7 Hz, 1H), 3.3 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4−147.3 (m), 146.2, 145.6−145.5 (m), 145.0−144.8 (m), 143.2−143.0 (m), 132.5, 126.4, 121.9 (t, J_F = 14.6 Hz), 118.6, 111.7, 106.3 (t, J_F = 22.4 Hz), 66.6; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.5 (dd, J_F = 22.6, 11.3 Hz, 2F), −143.9 (dd, J_F = 22.6, 16.9 Hz, 2F); HRMS (ESI) calcd for $C_{14}H_7F_4NNaO$ $(M + Na)^+$ 304.0361, found 304.0343.

*2,3,5,6-Tetrafluorophenyl-(4-nitrophenyl) Carbinol (**3m**).* LiCl (0.5 M in THF, 1.8 mL, 0.9 mmol) was stirred with *in situ*-formed Grignard reagent for 30 min. Then, the corresponding aldehyde was added to the mixture at −78 °C, and the resulting mixture was stirred at this temperature for 5 h. White solid (139 mg, 92% yield): mp 125−126 °C; EA/PE (1:6) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8 Hz, 2H), 7.13−7.04 (m, 1H), 6.37 (d, J = 6.8 Hz, 1H), 2.89 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 147.7, 147.6−147.5 (m), 145.7−145.5 (m), 145.0−144.9 (m), 143.3−143.1 (m), 126.5, 124.0, 121.7 (t, J_F = 14.5 Hz), 106.6 (t, J_F = 22.4 Hz), 66.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −137.6 (dd, J_F = 22.2, 13.2 Hz, 2F), −143.3 (dd, J_F = 20.9, 12.7 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_7F_4NNaO_3$ $(M + Na)^+$ 324.0260, found 324.0242.

*2,3,5,6-Tetrafluorophenyl-(4-methoxycarbonylphenyl) Carbinol (**3n**).* LiCl (0.5 M in THF, 1.8 mL, 0.9 mmol) was stirred with *in situ*-formed Grignard reagent for 30 min. Then, the corresponding aldehyde was added to the mixture at 0 °C, and the resulting mixture was stirred at this temperature for 5 h. Colorless oil (147 mg, 94% yield): EA/PE (1:8) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.05−6.98 (m, 1H), 6.29 (d, J = 6 Hz, 1H), 2.88 (s, 3H), 3.55 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 147.5−147.2 (m), 146.0, 145.7−145.5 (m), 145.0−144.7 (m), 143.2−143.1 (m), 129.9, 129.6, 125.6, 122.4 (t, J_F = 14.6 Hz), 105.9 (t, J_F = 22.5 Hz), 67.1, 52.3; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.6 (dd, J_F = 22.6, 11.3 Hz, 2F), −144.1 (dd, J_F = 21.5, 11.4 Hz, 2F); HRMS (ESI) calcd for $C_{15}H_{10}F_4NaO_3$ $(M + Na)^+$ 337.0464, found 337.0470.

*2,3,5,6-Tetrafluorophenyl-(2-phenylethyl) Carbinol (**3o**).* White solid (132 mg, 93% yield): mp 73−74 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.25 (m, 2H), 7.21−7.17 (m, 3H), 7.02−6.93 (m, 1H), 5.12−5.06 (m, 1H), 2.87−2.80 (m, 1H), 2.69−2.62 (m, 1H), 2.4−2.32 (m, 1H), 2.28 (d, J = 8.2 Hz, 1H), 2.2−2.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3−147.2 (m), 145.7−145.6 (m), 145.0−144.7 (m), 143.2−143.1 (m), 140.8, 128.7, 128.5, 126.3, 122.9 (t, J_F = 14.7 Hz), 105.3 (t, J_F = 22.3 Hz), 66.4, 38.4, 32.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.8 to −138.9 (m, 2F), −144.4 to −144.5 (m, 2F); HRMS (ESI) calcd for $C_{15}H_{12}F_4NaO$ $(M + Na)^+$ 307.0722, found 307.0723.

*2,3,5,6-Tetrafluorophenyl-(cyclohexyl) Carbinol (**3p**).* White solid (117 mg, 89% yield): mp 74−75 °C; EA/PE (1:15) as the eluent; ^{1}H

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NMR (400 MHz, $CDCl_3$) δ 7.03−6.94 (m, 1H), 4.72 (t, J = 8.9 Hz, 1H), 2.29 (d, J = 8.7 Hz, 1H), 2.18 (d, J = 13.0 Hz, 1H), 1.88−1.80 (m, 2H), 1.71−1.64 (m, 2H), 1.31−1.24 (m, 2H), 1.22−1.14 (m, 2H), 1.12−1.05 (m, 1H), 1.00−0.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6−148.5 (m), 146.7−146.9 (m), 146.2−145.9 (m), 144.6−144.5 (m), 123.9 (t, J = 15.0 Hz), 106.3 (t, J = 22.6 Hz), 73.2, 44.9, 31.1, 30.4, 27.6, 27.1, 27.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −139.2 (dd, J_F = 22.6, 15.1 Hz, 2F), −143.6 (dd, J_F = 22.6, 15.1 Hz, 2F); HRMS (ESI) calcd for $C_{13}H_{14}F_4NaO$ $(M + Na)^+$ 285.0878, found 285.0872.

*2,3,5,6-Tetrafluorophenyl-(tert-butyl) Carbinol (**3q**).* White solid (103 mg, 87% yield): mp 60−61 °C; EA/PE (1:15) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−6.96 (m, 1H), 4.81 (d, J = 10.0 Hz, 1H), 2.52−2.48 (m, 1H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5−147.4 (m), 145.7−145.5 (m), 144.9−144.7 (m), 143.3−143.2 (m), 121.4 (t, J = 14.5 Hz), 105.1 (t, J = 22.4 Hz), 76.2, 37.4, 25.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −140.0 (dd, J_F = 18.9, 7.5 Hz, 2F), −140.9 (dd, J_F = 18.9, 11.3 Hz, 2F); HRMS (ESI) calcd for $C_{11}H_{12}F_4NaO$ $(M + Na)^+$ 259.0722, found 259.0718.

*2,3,5,6-Tetrafluorophenyl-[(E)-2-phenylvinyl] Carbinol (**3r**).* Colorless oil (132 mg, 94% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 1.3 Hz, 2H), 7.35−7.26 (m, 3H), 7.07−6.98 (m, 1H), 6.69 (d, J = 15.9 Hz, 1H), 6.54 (dd, J = 15.8, 6.8 Hz, 1H), 5.77 (t, J = 7 Hz, 1H), 2.44 (d, J = 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5−147.4 (m), 145.7−146.6 (m), 145.3−145.0 (m), 143.1−142.8 (m), 135.9, 132.9, 128.8, 128.0, 127.7, 126.9, 121.9 (t, J_F = 14.7 Hz), 105.6 (t, J_F = 22.3 Hz), 67.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.6 (dd, J_F = 21.6, 13.2 Hz, 2F), −144.1 (dd, J_F = 21.5, 13.1 Hz, 2F); HRMS (ESI) calcd for $C_{15}H_{10}F_4NaO$ $(M + Na)^+$ 305.0565, found 305.0576.

*2,3,5,6-Tetrafluorophenyl-(3-thiophenyl) Carbinol (**3s**).* White solid (125 mg, 96% yield): mp 39−40 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.32 (m, 1H), 7.23 (s, 1H), 7.08−7.06 (m, 1H), 7.04−6.99 (m, 1H), 6.26 (s, 1H), 2.83 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5−147.2 (m), 145.6−145.4 (m), 145.0−144.8 (m), 143.2−142.9 (m), 142.1, 126.9, 125.8, 122.4 (t, J_F = 14.2 Hz), 121.9, 105.6 (t, J_F = 22.5 Hz), 65.0; ^{19}F NMR (566 MHz, $CDCl_3$) δ −138.5 (dd, J_F = 21.6, 12.6 Hz, 2F), −149.9 (dd, J_F = 22.0, 13.6 Hz, 2F); HRMS (ESI) calcd for $C_{11}H_6F_4NaOS$ $(M + Na)^+$ 284.9973, found 284.9966.

*2,3,5,6-Tetrafluorophenyl-(4-pyridyl) Carbinol (**3t**).* White solid (116 mg, 90% yield): mp 45−46 °C; EA/PE (1:5) as the eluent; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.53 (d, J = 5.8 Hz, 2H), 7.86−7.77 (m, 1H), 7.38 (d, J = 5.3 Hz, 2H), 6.78 (d, J = 4 Hz, 1H), 6.15 (d, J = 4 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 150.9, 149.6, 146.9−146.7 (m), 145.4−145.2 (m), 144.5−144.2 (m), 142.9−142.7 (m), 122.7 (t, J_F = 15.3 Hz), 120.6, 106.6 (t, J_F = 23.3 Hz), 64.0; ^{19}F NMR (566 MHz, d_6-DMSO) δ −139.2 to −139.3 (m, 2F), −143.1 to −143.2 (m, 2F); HRMS (ESI) calcd for $C_{12}H_7F_4NNaO$ $(M + Na)^+$ 280.0361, found 280.0379.

*2,3,5,6-Tetrafluorophenyl-(4-quinolinyl) Carbinol (**3u**).* White solid (116 mg, 93% yield): mp 45−46 °C; EA/PE (1:5) as the eluent; ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.0 (d, J = 3.6 Hz), 8.1 (d, J = 8.3 Hz), 7.9 (s, 1H), 7.9−7.8 (m, 1H). 7.8 (d, J = 8.4 Hz), 7.7 (t, J = 7.2 Hz), 7.6 (t, J = 7.4 Hz), 6.9 (s, 1H), 6.8 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 150.3, 147.7, 146.1, 144.8−144.7 (m), 143.9−143.7 (m), 139.0, 129.0, 127.0, 124.6, 122.3, 122.1−122 (m), 118.8, 106.7 (t, J_F = 22.9 Hz), 62.0; ^{19}F NMR (377 MHz, d_6-DMSO) δ −138.9 (dd, J_F = 22.6, 11.3 Hz, 2F), −142.6 (dd, J_F = 22.6, 11.3 Hz, 2F); HRMS (ESI) calcd for $C_{16}H_{10}F_4NO$ $(M + H)^+$ 308.0699, found 308.0679.

*2,3,5,6-Tetrafluorophenyl-(N-benzyl-3-indolyl) Carbinol (**3v**).* White solid (162 mg, 84% yield): mp 101−102 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 1H), 7.27−7.14 (m, 5H), 7.06 (d, J = 6.8 Hz, 2H), 7.0 (s, 2H), 6.6 (s, 1H), 5.24 (s, 2H), 2.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5−147.4 (m), 145.9−145.8 (m), 145.1−144.8 (m), 143.5−143.4 (m), 137.2, 137.1, 129.0, 127.9, 126.8, 126.4, 126.3, 122.9 (t, J_F = 14.2 Hz), 122.7, 120.3, 119.5, 115.6, 110.3, 105.3 (t, J_F = 22.6 Hz), 62.7, 50.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.7 (dd, J_F = 22.6, 15.1 Hz, 2F), −143.8 (dd, J_F = 22.6, 11.3 Hz, 2F); HRMS (ESI) calcd for $C_{22}H_{15}F_4NNaO$ $(M + Na)^+$ 408.0987, found 408.0967.

*2,3,5,6-Tetrafluorophenyl-(N-Boc-3-indolyl) Carbinol (**3w**).* White solid (178 mg, 91% yield): mp 108−109 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.1 (d, J = 8 Hz, 1H), 7.6 (d, J = 7.8 Hz, 1H), 7.5 (s, 1H), 7.35−7.31 (m, 1H), 7.26−7.22 (m, 1H), 7.08−7.01 (m, 1H), 6.5 (s, 1H), 2.89 (s, 9H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 147.5−147.4 (m), 145.9−145.7 (m), 144.9−144.8 (m), 143.4−143.3 (m), 135.8, 128.3, 125.1, 123.4, 123.1, 121.7 (t, J_F = 14.1 Hz), 120.7, 119.4, 115.6, 105.8 (t, J_F = 22.3 Hz), 84.5, 62.3, 28.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.3 (dd, J_F = 21.7, 13.2 Hz, 2F), −143.6 (dd, J_F = 21.8, 13 Hz, 2F); HRMS (ESI) calcd for $C_{20}H_{17}F_4NNaO_3$ $(M + Na)^+$ 418.1042, found 418.1025.

*2,3,5,6-Tetrafluoro-4-methoxyphenyl-(2-naphthyl) Carbinol (**5a**).* White solid (135 mg, 80% yield): mp 69−70 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85−7.83 (m, 3H), 7.51−7.48 (m, 3H), 6.37 (d, J = 6.4 Hz, 1H), 4.07 (s, 3H), 2.93 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4−146.1 (m), 143.9−143.7 (m), 142.4−142.2 (m), 139.9−139.8 (m), 138.6, 138.3−138.1 (m), 133.3, 133.1, 128.7, 128.3, 127.8, 126.6, 126.4, 124.2, 123.6, 115.1 (t, J_F = 15.2 Hz), 67.8, 62.2 (t, J_F = 3.7 Hz); ^{19}F NMR (566 MHz, $CDCl_3$) δ −144.7 to −144.8 (m, 2F), −157.5 (dd, J_F = 20.9, 7.4 Hz, 2F); HRMS (ESI) calcd for $C_{18}H_{12}F_4NaO$ $(M + Na)^+$ 343.0722, found 343.0731.

*2,3,5,6-Tetrafluoro-4-tert-butyldimethylsilylphenyl-(2-naphthyl) Carbinol (**5b**).* White solid (174 mg, 83% yield): mp 91−92 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.87−7.83 (m, 3H), 7.55−7.49 (m, 3H), 6.43 (s, 1H), 3.01 (s, 1H), 0.95 (s, 9H), 0.4 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6−150.5 (m), 148.3−148.1 (m), 145.5−145.3 (m), 143.0−142.8 (m), 138.4, 133.3, 133.2, 128.8, 128.3, 127.8, 126.6, 126.5, 124.4, 123.7, 123.3 (t, J_F = 14.7 Hz), 114.8 (t, J_F = 32.8 Hz), 68.4, 26.3, 17.8, −3.9 (t, J_F = 4.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −124.7 (dd, J_F = 24.2, 14.8 Hz, 2F), −143.7 (dd, J_F = 23.5, 14.1 Hz, 2F); HRMS (ESI) calcd for $C_{23}H_{24}F_4NaOSi$ $(M + Na)^+$ 443.1430, found 443.1439.

*2,3,5,6-Tetrafluoro-4-benzylphenyl-(2-naphthyl) Carbinol (**5c**).* White solid (171 mg, 87% yield): mp 78−79 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.72−7.7 (m, 3H), 7.38−7.36 (m, 3H), 7.2−7.1 (m, 5H), 6.28 (d, J = 6.9 Hz, 1H), 3.93 (s, 2H), 2.74 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3−146.1 (m), 145.9−145.8 (m), 143.8−143.7 (m), 143.5−143.1 (m), 138.4, 137.7, 133.3, 133.1, 128.9, 128.7, 128.6, 128.3, 127.8, 127.0, 126.6, 126.5, 124.3, 123.7, 120.0 (t, J_F = 14.6 Hz), 119.5 (t, J_F = 18.4 Hz), 68.1, 28.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −143.31 (dd, J_F = 22.3, 12.7 Hz, 2F), −144.0 (dd, J_F = 21.9, 12.4 Hz, 2F); HRMS (ESI) calcd for $C_{24}H_{16}F_4NaO$ $(M + Na)^+$ 419.1035, found 419.1009.

*2,3,5,6-Tetrafluoro-4-methylphenyl-(2-naphthyl) Carbinol (**5d**).* White solid (126 mg, 91% yield): mp 112−113 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.82 (m, 4H), 7.51−7.49 (m, 3H), 6.4 (d, J = 8 Hz, 2H), 3.09 (d, J = 7.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1−146.0 (m), 145.1−145.0 (m), 144.5−144.4 (m), 143.5−143.4 (m), 138.6, 133.3, 133.1, 128.7, 128.3, 127.8, 126.5, 126.4, 124.3, 123.7, 119.1 (t, J_F = 15 Hz), 116.0 (t, J_F = 18.9 Hz), 68.0, 7.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −143.3 (dd, J_F = 21.7, 12.5 Hz, 2F), −145.2 (dd, J_F = 21.9, 12.6 Hz, 2F); HRMS (ESI) calcd for $C_{18}H_{12}F_4NaO$ $(M + Na)^+$ 343.0722, found 343.0731.

*2,3,5,6-Tetrafluoro-4-methoxymethylphenyl-(2-naphthyl) Carbinol (**5e**).* Colorless oil (152 mg, 87% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 4H), 7.51−7.49 (m, 3H), 6.41 (d, J = 6.8 Hz, 1H), 4.56 (s, 2H), 3.39 (s, 3H), 3.17 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9−146.7 (m), 145.5−145.4 (m), 144.3−144.0 (m), 143.1−142.9 (m), 138.2, 133.2, 133.1, 128.7, 128.2, 127.8, 126.6, 126.4, 124.3, 123.6, 122.3 (t, J_F = 14.5 Hz), 115.7 (t, J_F = 17.6 Hz), 68.0, 61.5, 58.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −143.2 (dd, J_F = 22.9, 13.8 Hz, 2F), −143.6 (dd, J_F = 21.6, 12.6 Hz, 2F); HRMS (ESI) calcd for $C_{19}H_{14}F_4NaO_2$ $(M + Na)^+$ 373.0828, found 373.0831.

*2,3,5,6-Tetrafluoro-4-allylphenyl-(2-naphthyl) Carbinol (**5f**).* Yellow oil (160 mg, 92% yield): EA/PE (1:10) as the eluent; ^{1}H NMR

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(400 MHz, $CDCl_3$) δ 7.91−7.83 (m, 4H), 7.53−7.5 (m, 3H), 6.42 (d, J = 6.6 Hz, 1H), 5.95−5.88 (m, 1H), 5.14 (d, J = 11.2 Hz, 1H), 3.47 (d, J = 6.4 Hz, 2H), 3.27 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4−146.1 (m), 145.8−145.4 (m), 143.9−143.6 (m), 143.2−143.0 (m), 138.5, 133.3, 133.1, 133.0, 128.6, 128.2, 127.8, 126.5, 126.4, 124.3, 123.6, 119.8 (t, J_F = 14.5 Hz), 118.1 (t, J_F = 17.9 Hz), 117.2, 68.1, 26.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −144.0 to −144.2 (m, 2F), −144.2 to −144.3 (m, 2F); HRMS (ESI) calcd for $C_{20}H_{14}F_4NaO$ $(M + Na)^+$ 369.0878, found 369.0888.

*2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl-(2-naphthyl) Carbinol (**5g**).* H/Mg exchange was performed at 0 °C for 3 h. 2-Naphthaldehyde (78 mg, 0.5 mmol) was added as a solid under N_2. The resulting mixture was warmed to room temperature slowly and stirred for ∼7 h. Colorless oil (168 mg, 90% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.84 (m, 4H), 7.55−7.48 (m, 3H), 6.45 (d, J = 6.8 Hz, 1H), 2.95 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0−145.9 (m), 145.7−145.6 (m), 143.6−143.3 (m), 143.1−143.0 (m), 137.2, 133.3, 133.2, 129.1, 128.3, 127.9, 126.9, 126.8, 126.3 (t, J_F = 14.1 Hz), 124.6, 123.3, 109.9−109.3 (m), 68.3; ^{19}F NMR (566 MHz, $CDCl_3$) δ −56.4 (s, 3F), −139.9 to −140.0 (m, 2F), −140.8 to −141.8 (m, 2F); HRMS (ESI) calcd for $C_{18}H_9F_7NaO$ $(M + Na)^+$ 397.0439, found 397.0442.

*Pentafluorophenyl-(2-naphthyl) Carbinol (**5h**).*[9] White solid (160 mg, 99% yield): mp 99−100 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.83 (m, 4H), 7.54−7.46 (m, 3H), 6.39 (s, 1H), 2.9 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2−146.1 (m), 143.7−143.5 (m), 142.9−142.3 (m), 140.0−139.8 (m), 139.3−139.0 (m), 138.0, 136.7−136.6 (m), 133.2, 133.1, 128.9, 128.3, 127.8, 126.7, 126.6, 124.3, 123.4, 117.0 (t, J_F = 13.1 Hz), 67.9; ^{19}F NMR (566 MHz, $CDCl_3$) δ −142.8 (dd, J_F = 22.3, 7.9 Hz, 2F), −154.3 (t, J_F = 20.9 Hz, 1F), −161.3 (ddd, J_F = 42.6, 21.8, 7.6 Hz, 2F); HRMS (ESI) calcd for $C_{17}H_9F_5NaO$ $(M + Na)^+$ 347.0471, found 347.0451.

*Pentafluorophenyl-(4-chlorophenyl) Carbinol (**5i**).*[9] White solid (133 mg, 85% yield): mp 61−62 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.30 (m, 4H), 6.2 (d, J = 6 Hz, 1H), 2.87 (d, J = 6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0−145.9 (m), 143.6−143.4 (m), 142.6−142.3 (m), 140.0−139.7 (m), 139.1, 139.0−138.9 (m), 136.8−136.7 (m), 134.3, 129.0, 126.9, 116.7 (t, J_F = 11.0 Hz), 67.0; ^{19}F NMR (566 MHz, $CDCl_3$) δ −142.9 (dd, J_F = 21.8, 7.6 Hz, 2F), −153.9 (t, J_F = 20.9 Hz, 1F), −161.1 (ddd, J_F = 42.5, 21.7, 7.5 Hz, 2F); GCMS (EI) calcd for $C_{13}H_6ClF_5O$ (M) 308, found 308.

*Pentafluorophenyl-(4-fluorophenyl) Carbinol (**5j**).*[9] Colorless oil (126 mg, 86% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.36 (m, 2H), 7.08−7.04 (m, 2H), 6.23 (d, J = 5.6 Hz, 1H), 2.65 (d, J = 6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.4, 146.1−145.9 (m), 143.6−143.4 (m), 142.3−142.2 (m), 139.9−139.8 (m), 139.1−139.0 (m), 136.7−136.6 (m), 136.5, 127.4, 127.3, 116.9 (t, J_F = 17.4 Hz), 115.9, 115.7, 67.1; ^{19}F NMR (566 MHz, $CDCl_3$) δ −113.8 (s, 1F), −143.1 (dd, J_F = 22.0, 7.2 Hz, 2F) −154.2 (t, J_F = 20.7 Hz, 1F), −161.2 (ddd, J_F = 42.8, 21.2, 7.9 Hz, 2F); GC−MS (EI) calcd for $C_{13}H_6F_6O$ (M) 292, found 292.

*Pentafluorophenyl-(3-pyridyl) Carbinol (**5k**).* White solid (122 mg, 95% yield): mp 103−104 °C; EA/PE (1:5) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.35 (d, J = 4 Hz, 1H), 7.84 (d, J = 4.9 Hz, 1H), 6.46 (s, 1H), 6.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 146.7, 146.2−146.0 (m), 143.7−143.5 (m), 142.6−142.3 (m), 140.0−139.8 (m), 139.2−138.9 (m), 137.7, 136.7−136.4 (m), 134.3, 123.9, 116.9 (t, J_F = 13.1 Hz), 64.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −142.8 (dd, J_F = 22.2, 7.2 Hz, 2F), −153.9 (t, J_F = 20.7 Hz, F), −161.3 (ddd, J_F = 42.7, 21.8, 7.6 Hz, 2F); HRMS (ESI) calcd for $C_{12}H_7F_5NO$ $(M + H)^+$ 276.0448, found 276.0462.

*Pentafluorophenyl-(3-thiophenyl) Carbinol (**5l**).* White solid (135 mg, 96% yield): mp 74−75 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.32 (m, 1H), 7.22 (s, 1H), 7.05 (d, J = 4.9 Hz, 1H), 6.23 (s, 1H), 2.99 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5−146.0 (m), 143.5−143.0 (m), 142.3−142.2 (m), 141.9, 139.7−139.5 (m), 139.1−139.0 (m), 136.6−136.5 (m), 127.1, 125.6, 121.9, 116.7 (t, J_F = 14.2 Hz), 64.7; ^{19}F NMR (566 MHz, $CDCl_3$) δ −143.4 (dd, J_F = 22.4, 7.6 Hz, 2F), −154.5 (t, J_F = 20.8 Hz, 1F), −161.4 (ddd, J_F = 42.9, 21.8, 7.9 Hz, 2F); HRMS (ESI) calcd for $C_{11}H_5F_5NaOS$ $(M + Na)^+$ 302.9879, found 302.9850.

*Pentafluorophenyl-(3-phenylpropyl) Carbinol (**5m**).*[9] White solid (124 mg, 82% yield): mp 79−80 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.23−7.18 (m, 3H), 5.1−5.04 (m, 1H), 2.87−2.80 (m, 1H), 2.69−2.62 (m, 1H), 2.42−2.34 (m, 1H), 2.32−2.29 (m, 1H), 2.21−2.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2−146.0 (m), 143.7−143.5 (m), 142.1−141.8 (m), 140.5, 139.6−139.3 (m), 139.1−138.8 (m), 136.6−136.3 (m), 128.7, 128.4, 126.4, 117.1 (t, J_F = 15.2 Hz), 66.0, 38.3, 32.2; ^{19}F NMR (566 MHz, $CDCl_3$) δ −143.7 (dd, J_F = 22.3, 7.2 Hz, 2F), −155.1 (t, J_F = 20.7 Hz, 1F), −161.7 (ddd, J_F = 42.8, 21.9, 7.8 Hz, 2F); HRMS (ESI) calcd for $C_{15}H_{11}F_5NaO$ $(M + Na)^+$ 325.0628, found 325.0613.

*2,3,4,6-Tetrafluorophenyl-(2-naphthyl) Carbinol (**5n**).* Yellow oil (124 mg, 81% yield): EA/PE(1:10) as the eluent; ^{1}H NMR (400 MHz, d_6-MeOH) δ 7.92 (s, 1H), 7.80−7.76 (m, 3H), 7.46−7.40 (m, 3H), 7.02−6.96 (m, 1H), 6.34 (s, 1H), 4.87 (s, 1H); ^{13}C NMR (100 MHz, d_6-MeOH) δ 157.8−157.7 (m), 155.3−155.2 (m), 152.9−152.7 (m), 152.2−152.1 (m), 150.4−150.2 (m), 149.7−149.6 (m), 140.6, 139.9−139.6 (m), 137.3−137.2 (m), 134.6, 134.2, 129.1, 128.9, 128.6, 127.2, 126.9, 125.1, 124.7, 119.4−119.2 (m), 102.5−101.9 (m), 67.3; ^{19}F NMR (566 MHz, d_6-MeOH) δ −118.4 (d, J_F = 11.3 Hz, 1F), −135.6 to −135.7 (m, 1F), −137.05 (dm, J_F = 18.9, 3.8 Hz, 1F), −168.0 (ddd, J_F = 41.5, 18.9, 11.3 Hz, 1F); HRMS (ESI) calcd for $C_{17}H_{10}F_4NaO$ $(M + Na)^+$ 329.0565, found 329.0545.

*2,3,4,5-Tetrafluorophenyl-(2-naphthyl) Carbinol (**5o**).* Colorless oil (153 mg, 67% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 4H), 7.55−7.53 (m, 2H), 7.44−7.42 (m, 1H), 7.29−7.26 (m, 1H), 6.23 (s, 1H), 2.69 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1−148.0 (m), 146.5−146.4 (m), 145.4−145.3 (m), 143.8−143.7 (m), 141.5−141.4 (m), 140.7−140.6 (m), 139.8−139.6 (m), 139.0−138.8 (m), 138.7, 133.2, 128.9, 128.1, 127.8, 127.4 (t, J_F = 6.9 Hz), 126.6, 126.5, 125.3, 123.8, 108.6 (t, J_F = 17.1 Hz), 69.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −138.4 to −138.5 (m, 1F), −143.7 to −143.8 (m, 1F), −155.5 to −156.7 (m, 1F), −156.6 to −156.7 (m, 1F); HRMS (ESI) calcd for $C_{17}H_{10}F_4NaO$ $(M + Na)^+$ 329.0565, found 329.0546.

*2,3,6-Trifluorophenyl-(2-naphthyl) Carbinol (**5p**).* Colorless oil (115 mg, 64% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.85−7.83 (m, 3H), 7.53−7.49 (m, 3H), 7.13−7.05 (m, 1H), 6.87−6.82 (m, 1H), 6.42 (d, J = 7.7 Hz, 1H), 3.15 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8−154.7 (m), 153.5−153.0 (m), 150.0−149.7 (m), 147.7−147.2 (m), 146.3−146.1 (m), 138.8, 133.3, 133.0, 128.6, 128.3, 127.8, 126.5, 126.3, 124.3, 123.8, 121.5−121.2 (m), 116.7−116.4 (m), 111.6−111.5 (m), 111.3−111.2 (m), 68.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −119.3 (d, J_F = 15.0 Hz, 1F), −137.5 (d, J_F = 20.7 Hz, 1F), −144.5 (dd, J_F = 21.1, 15.3 Hz, 1F); HRMS (ESI) calcd for $C_{17}H_{11}F_3NaO$ $(M + Na)^+$ 311.0660, found 311.0664.

*2,4,6-Trifluorophenyl-(2-naphthyl) Carbinol (**5q**).* Colorless oil (62 mg, 43% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9−7.83 (m, 4H), 7.52−7.51 (m, 3H), 6.72−6.68 (m, 2H), 6.39 (s, 1H), 3.29 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3−163.0 (m), 162.1−161.9 (m), 161.6−161.4 (m), 160.4−160.2 (m), 139.2, 133.3, 132.9, 128.4, 128.2, 127.7, 126.4, 126.2, 124.1, 123.8, 116.0−115.8 (m), 101.0−100.7 (m), 67.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −107.8 (t, J_F = 6.2 Hz, F), −110.8 (d, J_F = 5.8 Hz, 2F); HRMS (ESI) calcd for $C_{17}H_{11}F_3NaO$ $(M + Na)^+$ 311.0660, found 311.0665.

*2,3,5,6-Tetrafluoropyridyl-(2-naphthyl) Carbinol (**5r**).* H/Mg exchange was performed at −20 °C for 30 min. 2-Naphthaldehyde (78 mg, 0.5 mmol) was added as a solid under N_2. The resulting mixture was warmed to room temperature slowly and stirred for ∼6 h. Colorless oil (125 mg, 92% yield): EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.88−7.83 (m, 3H), 7.55−7.5 (m, 3H), 6.42 (d, J = 6.9 Hz, 1H), 3.0 (d, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0−144.7 (m), 142.6−142.3 (m), 141.1−140.8 (m), 138.5−138.2 (m), 136.5, 135.3 (t, J_F = 13.1 Hz), 133.3, 133.1, 129.2, 128.2, 127.8, 126.8 (2C), 124.7, 123.1, 68.6; ^{19}F NMR (566 MHz, $CDCl_3$) δ −89.9 (ddd, J_F = 52.9, 29.0, 13.8 Hz, 2F),

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−143.8 (ddd, J_F = 53.1, 28.9, 13.7 Hz, 2F); HRMS (ESI) calcd for $C_{16}H_9F_4NNaO$ $(M + Na)^+$ 330.0518, found 330.0503.

*2,4,6-Trifluoropyridyl-(2-naphthyl) Carbinol (**5s**).* White solid (139 mg, 96% yield): mp 88−89 °C; EA/PE (1:10) as the eluent; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.84−7.80 (m, 3H), 7.53−7.45 (m, 3H), 6.53−6.5 (m, 1H), 6.3 (d, J = 6.4 Hz, 1H), 3.53 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1−172.0 (m), 169.6−169.4 (m), 162.6−162.2 (m), 161.6−160.8 (m), 160.1−159.8 (m), 158.7−158.4 (m), 138.1, 133.1, 133.0, 128.7, 128.2, 127.7, 126.6, 126.4, 124.2, 123.4, 111.8−111.1 (m), 96.4−95.7 (m), 66.8; ^{19}F NMR (566 MHz, $CDCl_3$) δ −64.9 to −65.0 (m, F), −66.9 to −67.0 (m, F), −94.0 to −94.1 (m, F); HRMS (ESI) calcd for $C_{16}H_{10}F_3NNaO$ $(M + Na)^+$ 312.0612, found 312.0595.

Gram-Scale Synthesis Using *in Situ*-Generated *i*PrMgBr. Under argon, to a 100 mL flame-dried three-necked RBF were added magnesium turnings (173 mg, 7.2 mmol) and freshly distilled THF (3 mL). Then, a portion of isopropyl bromide (0.3 mL, 3.2 mmol) was added to the resulting mixture to initiate the reaction. After the reaction was started, the remaining isopropyl bromide (0.52 mL, 5.0 mmol) in THF (9 mL) was added dropwise. When magnesium turnings had been completely consumed, and the resulting solution was cooled to room temperature, 1,2,4,5-tetrafluorobenzene (0.9 mL, 8.6 mmol) was added dropwise. After the resulting solution was stirred for 12 h at room temperature, 2-naphthaldehyde (936 mg, 6 mmol) was added as a solid under argon. Once all the material had been consumed (monitored by TLC), the reaction was quenched with methanol (4 mL) at room temperature. The mixture was stirred for 30 min, filtered through a pad of silica gel, and washed with diethyl ether until no more product was washed out (monitored by TLC). The filtrate was concentrated under vacuum, and the resulting residue was purified by chromatography using EA/PE (1:10) as the eluent, which afforded the desired compound (1.65 g, 90% yield) as a white solid.

Formal Synthesis of Transfluthrin, Fenfluthrin, and Tefluthrin. *Pentafluorobenzyl Alcohol (**6**).*[3] The synthesis was performed according to the general procedure in freshly distilled THF (20 mL) with paraformaldehyde (2.7 g, 30 mmol, 3 equiv). The reaction was finished after ∼6 h at room temperature. The title compound was obtained as a colorless oil (1.32 g, 67% yield) by flash chromatography using EA/PE (1:10) as the eluent: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (d, J = 8.8 Hz), 2.08 (s, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ −144.4 (dd, J_F = 22.6, 11.3 Hz, 2F), −154.1 (t, J_F = 22.6 Hz, 1F), −161.8 (ddd, J_F = 45.2, 22.6, 11.3 Hz, 2F); GC−MS (EI) calcd for $C_7H_3F_5O$ (M) 198, found 198.

*2,3,5,6-Tetrafluorobenzyl Alcohol (**7**).*[3] White solid (1.26 g, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07−6.98 (m, 1H), 4.77 (d, J = 4.4 Hz, 2H), 2.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3−147.0 (m), 146.3−146.1 (m), 144.8−144.5 (m), 143.9−143.6 (m), 119.4 (t, J_F = 17.3 Hz), 106.0 (t, J_F = 22.5 Hz), 52.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −139.9 (dd, J_F = 22.6, 15.1 Hz, 2F), −145.7 (dd, J_F = 22.6, 15.1 Hz, 2F); GC−MS (EI) calcd for $C_7H_4F_4O$ (M) 180, found 180.

*2,3,5,6-Tetrafluoro-4-methylbenzyl Alcohol (**8**).*[3] White solid (1.38 g, 71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (s, 2H), 2.31 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7−145.4 (m, 2C), 144.1−143.8 (m, 2C), 116.2 (t, J_F = 19.1 Hz), 115.7 (t, J_F = 17.7 Hz), 52.8, 7.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −143.9 (dd, J_F = 21.5, 13.2 Hz, 2F), −146.8 (dd, J_F = 21.8, 13.3 Hz, 2F); HRMS (ESI) calcd for $C_8H_6F_4NaO$ $(M + Na)^+$ 217.0252, found 217.0249.

Deuteration Experiment. In the glovebox, a 10 mL flame-dried Schenk tube was successively charged with 1-benzyl-2,3,5,6-tetrafluorobenzene (50 mg, 0.21 mmol), dry THF (0.5 mL), and an *i*PrMgCl solution (2 M, 70 μL, 0.14 mmol). After the resulting solution had been stirred at room temperature for 12 h, the reaction was quenched with deuterium oxide (0.2 mL) and the mixture diluted with a saturated aqueous solution of NH_4Cl. The mixture was extracted with EA (3 × 8 mL), and the combined organic layer was dried with $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was analyzed by ^{1}H NMR (see the Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02022.

Detailed experimental procedures and characterization data for new compounds, including ^{1}H, ^{13}C, and ^{19}F NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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