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可见光诱导活化烯烃的芳基氟烷基化反应

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摘要 含氟化合物在生物医药和材料领域有着广泛的应用，含氟化合物的合成方法学研究有着重要意义. 以 *fac*-Ir(ppy)$_3$ 为光催化剂，可见光诱导下 *N*-芳基-*N*-(芳基磺酰基)-2-甲基丙烯酰胺经氟烷基自由基加成、芳基迁移、脱砜基历程得到含氟烷基取代 *α*-季碳中心结构的酰胺类化合物，反应条件温和，官能团兼容性良好.
关键词 光催化；氟烷基化；芳基迁移；脱砜基；*α*-季碳中心；酰胺

Visible Light Induced Arylfluoroalkylation of Activated Alkenes

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Abstract Fluorine-containing compounds have a wide range of applications in the fields of biomedicine and materials, and the development of synthetic methodology for fluorine-containing compounds is very important. Using *fac*-Ir(ppy)$_3$ as catalyst, a wide variety of amides containing fluoroalkyl substituted *α*-quaternary carbon center were prepared with *N*-aryl-*N*-(arylsulfonyl)-2-methyl acrylamides as starting materials by visible light induced cascade fluoroalkyl radical addition, aryl migration and desulfonylation. The reaction conditions are mild, and possess good functional group compatibility.
Keywords photocatalysis; fluoroalkylation; aryl migration; desulfonylation; *α*-quaternary carbon center; amide

含三氟甲基化合物在现代医药、农药和材料中有着非常广泛的应用[1]. 向药物或生物活性分子中选择性引入三氟甲基后，亲脂性、代谢稳定性、与靶标蛋白结合能力、细胞膜穿透性和生物可利用度通常比母体分子都有明显的提升[2]. 例如除草剂氟磺隆(CGA-152005)[3]、新烟碱类杀虫剂氟吡呋喃酮(Flupyradifurone)[4]为典型的具有药物活性的含氟分子(Figure 1). 近年来，向有机分子中选择性高效引入三氟甲基的新策略不断涌现，适用不同反应体系的三氟甲基化试剂被不断开发出来[5]. 其中，CF_3CH_2I 作为廉价易得的含三氟甲基的试剂也被广泛用于各种含三氟甲基化合物的构建中[6].

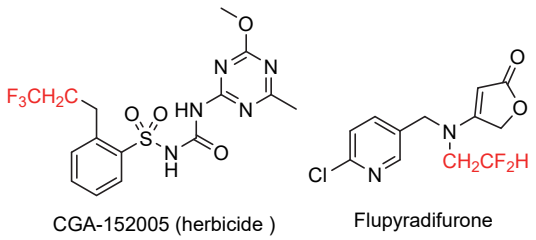

图 1 典型的含氟生物活性分子
Figure 1 Typical fluorine-containing bioactive molecules

N-(芳基磺酰)丙烯酰胺作为多功能的合成砌块，常被用于合成含季碳中心结构的酰胺[7]. 2013 年，Nevado 课题组[8]首次报道了以 Togni II 试剂为三氟甲基源，通过三氟甲基化、芳基迁移、脱磺酰化和 N—H 键或 C(sp^2)—N 键形成的串联反应，其中 *N*-(芳基磺酰)丙烯酰胺为 *N*-烷基取代时得到吲哚酮，为 *N*-芳基取代时得到含季碳中心的 *α*-芳基-*β*-三氟甲基酰胺(Scheme 1). 随后，应用不同自由基前体都能成功引发 *N*-(芳基磺酰)丙

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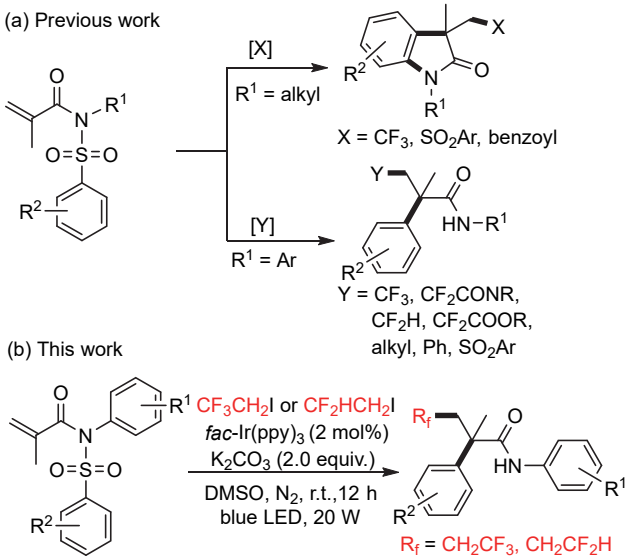
烯酰胺的类似串联反应. 当 R^1 为烷基时, 以苯甲醛[9]为苯甲酰基自由基、以芳基磺酰肼[10]为苯磺酰基自由基、以偶氮二异丁腈[11]为烷基自由基前体, 可以得到各种基团取代的吲哚酮化合物; 当 R^1 为芳基时, 以不饱和的羧酸[12]、环烷烃[13]、肟酯[14]、醛[15]、过氧化物[16]、苯胺[17]、芳基磺酰肼[18]等不含氟的自由基源以及 CF_3SO_2Cl[19]、HCF_2SO_2Na[20]、$BrCF_2COOEt$[21]、$TMSCF_2CONR_2$[22]等含氟烷基自由基源, 得到结构多样的含季碳中心酰胺类化合物(Scheme 1a). 基于我们课题组对三氟乙基化反应的研究兴趣[23], 本文探究了 *N*-芳基-*N*-(芳基磺酰)-2-甲基丙烯酰胺与三氟碘乙烷和二氟碘乙烷的自由基加成、芳基迁移、脱砜基串联反应, 构建了一系列含有三氟甲基或二氟甲基的含季碳中心的酰胺类化合物(Scheme 1b).



图式 1 以 *N*-(芳基磺酰)-2-甲基丙烯酰胺为底物构建含季碳中心酰胺

Scheme 1 Construction of amides containing quaternary carbon center with *N*-(arylsulfonyl)-2-methylacrylamides as substrates

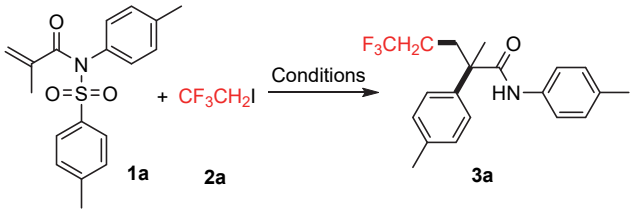
1 结果与讨论

1.1 反应条件的优化

以 *N*-对甲苯基-*N*-(对甲苯磺酰)-2-甲基丙烯酰胺(**1a**) (1.0 equiv.)为模板底物, CF_3CH_2I (**2a**) (3.0 equiv.)为三氟乙基自由基源, Et_3N (2.0 equiv.)为碱, *fac*-Ir(ppy)$_3$ (2 mol%)为光催化剂, 二甲基亚砜(DMSO)为溶剂, 室温氮气氛围中反应 12 h, 以 42%的产率检测到了目标产物**3a** (Table 1, Entry 1). 筛选 *N*,*N*,*N*′,*N*′-四甲基乙二胺(TMEDA)、1,8-二偶氮杂双螺环[5.4.0]十一-7-烯(DBU)、碳酸铯(Cs_2CO_3)、碳酸氢钠($NaHCO_3$)和碳酸钾(K_2CO_3)等一系列不同的有机碱和无机碱, 结果表明当以 K_2CO_3 为碱时, **3a** 的产率可提高至 83% (Table 1, Entries 2～6). 光催化剂的种类筛选实验表明: 当采用三联吡啶氯化钌[$Ru(bpy)_3Cl_2$]、曙红(Eosin Y)、(4,4′-二叔丁基-2,2′-联吡啶)双[(2-吡啶基)苯基]铱(III)六氟磷酸盐[$Ir(ppy)_2(dtbbpy)PF_6$]或三(2,2′-联吡啶)钌二(六氟磷酸)盐[$Ru(bpy)_3(PF_6)_2$]时, 催化效果都明显低于 *fac*-Ir(ppy)$_3$ (Table 1, Entries 7～10). 随后考察了乙腈(MeCN)、四氢呋喃(THF)、二氯乙烷(DCE)、丙酮和 *N*,*N*-二甲基甲酰胺(DMF)等常用溶剂, 结果表明反应不能进行或产物产率较低(Table 1, Entries 11～15). 最后, 将反应时间由 12 h 缩短为 10 h, 产率降低; 延长至 14 h 时, 产物产率没有明显变化(Table 1, Entries 16～17). 综上所述, 确定了该反应的最优条件为: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), *fac*-Ir(ppy)$_3$ (2 mol%), K_2CO_3 (1.0 mmol, 2.0 equiv.), DMSO (3.5 mL), r.t., N_2, 12 h.

表 1 *N*-芳基-*N*-(芳基磺酰)-2-甲基丙烯酰胺三氟乙基化的优化[a]

Table1 Optimization of trifluoroethylation of *N*-aryl-*N*-(arylsulfonyl)-2-methyl acrylamide



Entry	Catalyst	Base	Solvent	Time/h	Yield[b]/%
1	*fac*-Ir(ppy)$_3$	Et_3N	DMSO	12	42
2	*fac*-Ir(ppy)$_3$	TMEDA	DMSO	12	49
3	*fac*-Ir(ppy)$_3$	DBU	DMSO	12	44
4	*fac*-Ir(ppy)$_3$	Cs_2CO_3	DMSO	12	75
5	*fac*-Ir(ppy)$_3$	$NaHCO_3$	DMSO	12	42
6	*fac*-Ir(ppy)$_3$	K_2CO_3	DMSO	12	83
7	$Ru(bpy)_3Cl_2$	K_2CO_3	DMSO	12	42
8	Eosin Y	K_2CO_3	DMSO	12	49
9	$Ir(ppy)_2(dtbbpy)PF_6$	K_2CO_3	DMSO	12	32
10	$Ru(bpy)_3(PF_6)_2$	K_2CO_3	DMSO	12	39
11	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	12	NR
12	*fac*-Ir(ppy)$_3$	K_2CO_3	THF	12	NR
13	*fac*-Ir(ppy)$_3$	K_2CO_3	DCE	12	15
14	*fac*-Ir(ppy)$_3$	K_2CO_3	Acetone	12	35
15	*fac*-Ir(ppy)$_3$	K_2CO_3	DMF	12	20
16	*fac*-Ir(ppy)$_3$	K_2CO_3	DMSO	10	56
17	*fac*-Ir(ppy)$_3$	K_2CO_3	DMSO	14	81

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst (2 mol%), base (1.0 mmol) in solvent (3.5 mL) were irradiated with a 20 W blue LED at room temperature under N_2; [b] Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

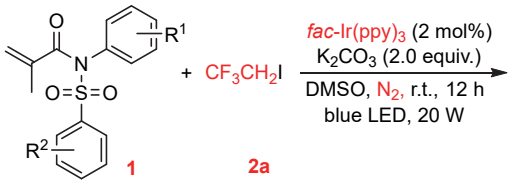
1.2 底物范围拓展

在上述最优反应条件下, 考察了不同官能团取代的 *N*-芳基-*N*-(芳基磺酰)-2-甲基丙烯酰胺(**1**)与 CF_3CH_2I 的

三氟乙基化、芳基迁移、脱砜基串联反应(Table 2). 结果表明: *N*-芳基上的取代基(R^1)对反应影响较小, 无论是吸电子基(X)还是供电子基(CH_3, OCH_3 和 ^{t}Bu)取代在邻位或对位时, 反应均能以中等至良好的产率得到目标产物(**3a**～**3n**). 串联反应中涉及了芳基迁移, 因此, 芳基磺酰基中芳环上取代基对反应的影响较为明显. 当给电子基取代时(**3o**～**3q**, **3t**), 产物产率中等; 当取代基为氯原子和三氟甲基等吸电子基时(**3r**, **3s**, **3u**), 产物产率偏低. 当芳基磺酰基中的芳基为萘环和噻吩环时(**3w**, **3x**), 反应也能顺利进行, 但产率偏低. 产物 **3m** 的结构经 X-ray 单晶分析进一步确证[24].

表 2 反应底物拓展 [a,b]

Table 2 Exploration of reaction substrates



3a (R^1 = 4-CH_3), 63%
3b (R^1 = 4-OCH_3), 68%
3c (R^1 = 4-F), 59%
3d (R^1 = 4-Cl), 60%
3e (R^1 = 4-Br), 61%
3f (R^1 = 4-I), 51%
3g (R^1 = 4-^{t}Bu), 49%
3h (R^1 = 2-CH_3), 66%
3i (R^1 = 2-OCH_3), 70%
3j (R^1 = 2-F), 51%
3k (R^1 = 2-Cl), 53%
3l (R^1 = 2-Br), 53%
3m (R^1= 2-I), 51%
3n (R^1 = 3-CH_3), 45%

3o (R^2 = 4-CH_3), 53%
3p (R^2 = 4-H), 52%
3q (R^2 = 4-OCH_3), 45%
3r (R^2 = 4-Cl), 37%
3s (R^2 = 4-CF_3), 25%
3t (R^2 = 2-CH_3), 43%
3u (R^2 = 3-Cl), 38%

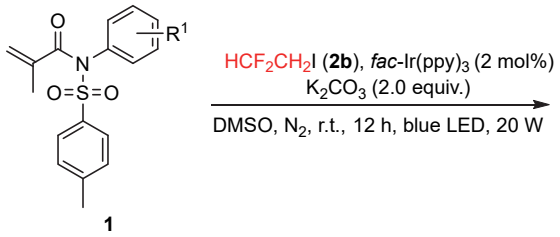
3v 43%

3w 40%

3x 38%

[a] Reaction conditions: **1** (0.5 mmol), **2a** (1.5 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), K_2CO_3 (1.0 mmol), DMSO (3.5 mL) were irradiated with a 20 W blue LED at room temperature for 12 h under N_2; [b] Isolated yields.

通常三氟碘乙烷和二氟碘乙烷具有类似的反应活性[25]. 在上述最优反应条件下(Scheme 2), *N*-芳基-*N*-(对甲苯基磺酰)-2-甲基丙烯酰胺也可以和二氟碘乙烷(**2b**)顺利反应. 当底物 **1** 中的 *N*-芳基上的取代基(R^1)为给电子基(CH_3 和 OCH_3)取代时(**4a**～**4b**), 产率良好, 达到60%以上; 当邻位和对位为卤素(**4c**～**4f**, **4h**～**4k**)、甲基取代在间位(**4g**)和三甲基取代(**4l**)时产率下降至中等(40%～53%).



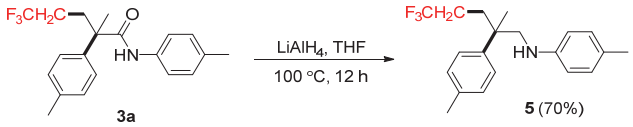
4a (R^1 = 4-CH_3), 60%
4b (R^1 = 4-OCH_3), 63%
4c (R^1 = 4-F), 46%
4d (R^1 = 4-Cl), 51%
4e (R^1 = 4-Br), 53%
4f (R^1 = 4-I), 44%
4g (R^1 = 3-CH_3), 43%
4h (R^1 = 2-F), 40%
4i (R^1 = 2-Cl), 49%
4j (R^1 = 2-Br), 51%
4k (R^1 = 2-I), 40%
4l (R^1 = 2,4,6-$(CH_3)_3$), 41%

图式 2 *N*-(对甲苯基磺酰)-2-甲基丙烯酰胺的二氟乙基化

Scheme 2 Difluoroethylation of *N*-aryl-*N*-(*p*-methylphenyl sulfonyl)-2-methylacrylamides

1 (0.5 mmol), **2b** (1.5 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), K_2CO_3 (1.0 mmol), DMSO (3.5 mL) were irradiated with a 20 W blue LED at room temperature for time under N_2. Isolated yields

为了探索反应体系的应用价值, 在相同反应条件下, 反应规模放大到 5 mmol, 仍可以 58%的产率分离得到目标产物 **3a** (1.01 g); 参考文献方法[26], 在四氢铝锂作用下实现了将酰胺(**3a**)还原到仲胺(**5**)的转化, 产率为70% (Scheme 3).



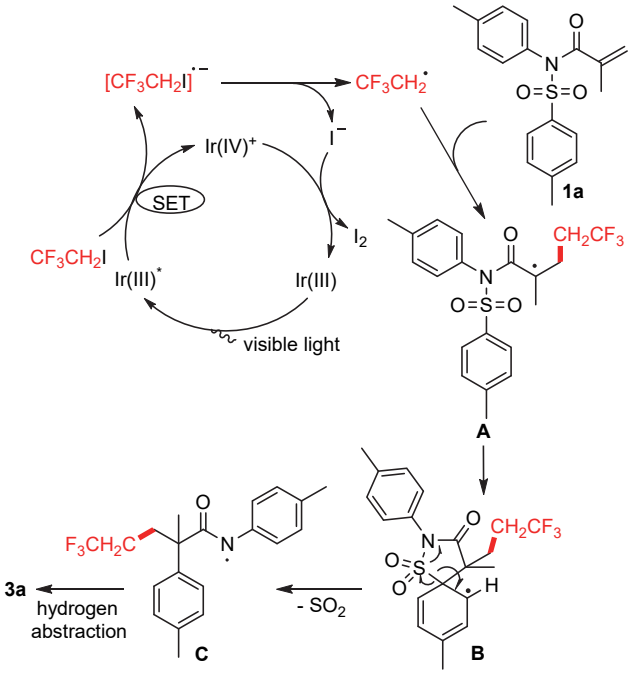
图式 3 转化实验

Scheme 3 Transformation experiment

1.3 机理探究

为了探索反应的机理, 进行了控制实验, 向反应体系中加入自由基捕获剂 2,2,6,6-四甲基-1-哌啶氧化物(TEMPO), 目标产物**3a**没有生成, 反应被完全抑制并检测到 TEMPO 与三氟乙基结合的产物(见辅助材料), 表明反应可能经自由基历程完成. 根据上述实验事实, 结合相关文献报道[27], 提出可能的机理(Scheme 4). 首先,

在光照的情况下，*fac*-Ir(III)(ppy)$_3$ 变成激发态[*fac*-Ir*(III)(ppy)$_3$]，将 CF_3CH_2I 还原成三氟乙基自由基和碘负离子，同时自身被氧化为[*fac*-Ir(IV)(ppy)$_3$]$^+$配合物，随后三氟乙基自由基进攻 *N*-芳基-*N*-(芳基磺酰)-2-甲基丙烯酰胺的双键，生成自由基中间体 **A**；随后进行分子内的环化反应生成自由基中间体 **B**；再通过脱二氧化硫反应生成自由基中间体 **C**；自由基中间体 **C** 从反应介质中攫取氢，得到三氟乙基化的芳基迁移产物 **3a**.



图式 4 可能的反应机理

Scheme 4 Proposed reaction mechanism

2 结论

以三氟碘乙烷和二氟碘乙烷为氟烷基自由基源，在光催化剂*fac*-Ir(ppy)$_3$的催化下实现了对 *N*-芳基-*N*-(芳基磺酰)-2-甲基丙烯酰胺的三氟乙基化、二氟乙基化反应. 此反应经历了氟烷基自由基对双键的加成、芳基迁移、脱砜基历程，反应条件简单温和，底物的普适性良好，官能团耐受性好，产率优良，为合成同时含有三氟乙基/二氟乙基和季碳中心酰胺结构的化合物提供了一种新的途径.

3 实验部分

3.1 仪器与试剂

熔点由 AGILENT1100 型显微熔点仪测定；核磁共振在 Bruker AM 400/600 MHz 型核磁共振仪上测定，$CDCl_3$ 作为溶剂；红外光谱用傅里叶变换红外光谱仪(Nicolet iS10)测定；高分辨质谱数据使用 Waters G2-Xs QTOF 型质谱仪测定. 底物 **1a**～**1x** 根据文献方法[19-20]制备，其他试剂为国产市售分析纯.

3.2 实验方法

3.2.1 **3** 或 **4** 的合成

室温下，在装有磁力搅拌子的 10 mL 封管中，加入 **1** (0.5 mmol, 1.0 equiv.)、无水碳酸钾(1.0 mmol, 2.0 equiv.)、*fac*-Ir(ppy)$_3$ (0.01 mmol, 2 mol%)，抽换氮气三次，在抽换氮气的同时，向封管中加入 **2a** 或 **2b** (1.5 mmol, 3.0 equiv.)和 DMSO (3.5 mL)，随后立即置于已经调好的 20 W 的蓝光下，室温反应 12 h. 反应结束后，用水(10 mL)淬灭，乙醚(6 mL×3)萃取，有机相用饱和食盐水(10 mL)洗涤，无水硫酸钠干燥，过滤、浓缩后，快速柱层析纯化[硅胶，*V*(石油醚)：*V*(乙酸乙酯)＝15：1～30：1].

5,5,5-三氟-2-甲基-*N*,2-二(对甲基苯基)戊酰胺(**3a**): 110.1 mg，白色固体，产率 63%. m.p. 147.3～147.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, J=8.5 Hz, 2H), 7.15 (t, J=2.8 Hz, 2H), 7.12 (d, J=2.5 Hz, 2H), 6.98 (d, J=8.2 Hz, 2H), 6.69 (s, 1H), 2.28 (s, 3H), δ: 2.22 (d, J=5.2 Hz, 1H), 2.19 (s, 3H), 2.17～2.13 (m, 1H), 2.05～1.87 (m, 1H), 1.86～1.70 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.34 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.3, 137.7, 136.7, 134.1, 133.0, 128.9, 128.3, 126.3 (q, J=277.2 Hz), 125.7, 118.9, 48.9, 30.3 (q, J=2.9 Hz), 28.6 (q, J=28.7 Hz), 22.4, 19.9, 19.8; IR (film) ν: 3271, 2976, 2366, 1646, 1512, 1441, 1393, 1322, 1262, 1128, 1066, 965, 825, 524, 483 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}NOF_3$ $[M+H]^+$ 350.1732, found 350.1732.

5,5,5-三氟-*N*-(4-甲氧基苯基)-2-甲基-2-(对甲基苯基)戊酰胺(**3b**): 124.2 mg，白色固体，产率 68%. m.p. 140.8～141.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～6.99 (m, 6H), 6.70 (d, J=8.8 Hz, 3H), 3.66 (s, 3H), 2.28 (s, 3H), 2.19 (dt, J=11.3, 5.4 Hz, 2H), 1.98～1.94 (m, 1H), 1.81～1.75 (m, 1H), 1.55 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.32 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.3, 155.5, 137.8, 136.6, 129.7, 128.9, 126.3 (q, J=277.29 Hz), 125.7, 120.8 (d, J=3.2 Hz), 113.0, 54.4, 48.8, 30.3 (d, J=2.7 Hz), 28.6 (q, J=28.7 Hz), 22.4 (q, J=2.1 Hz), 19.9; IR (film) ν: 3265, 2973, 1655, 1601, 1512, 1241, 1134, 1024, 962, 831, 765, 614, 575, 551 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}NO_2F_3$ $[M+H]^+$ 366.1681, found 366.1681.

5,5,5-三氟-*N*-(4-氟苯基)-2-甲基-2-(对甲苯基)戊酰胺(**3c**): 104.2 mg，白色固体，产率 59%. m.p. 147.1～

148.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.11 (m, 6H), 6.88～6.80 (m, 2H), 6.77 (s, 1H), 2.28 (s, 3H), 2.26～2.11 (m, 2H), 2.04～1.92 (m, 1H), 1.85～1.66 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.35 (t, J=10.6 Hz), −117.81～−117.89 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 158.4 (d, J=243.7 Hz), 137.5, 136.8, 132.6 (d, J=2.9 Hz), 129.0, 126.3 (q, J=277.2 Hz), 125.7, 120.8 (d, J=7.8 Hz), 114.5 (d, J=22.5 Hz), 48.9, 30.3(q, J=2.9 Hz), 28.6 (q, J=28.8 Hz), 22.2, 19.9; IR (film) ν: 3265, 2979, 2908, 2363, 1658, 1509, 1411, 1310, 1212, 1131, 1099, 1051, 843, 614, 521 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_4$ $[M+H]^+$ 354.1481, found 354.1481.

N-(4-氯苯基)-5,5,5-三氟-2-甲基-2-(对甲基苯)戊酰胺(**3d**): 110.9 mg, 白色固体, 产率 60%. m.p. 166.5～167.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25～7.05 (m, 8H), 6.76 (s, 1H), 2.29 (s, 3H), 2.25～2.13 (m, 2H), 1.98～1.91 (m, 1H), 1.81～1.75 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.35 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 137.3, 136.9, 135.2, 129.1, 128.3, 127.9, 126.2 (q, J=277.2 Hz), 125.7, 120.1, 49.04, 30.3 (q, J=3.0 Hz), 28.5 (q, J=28.7 Hz), 22.2, 19.9; IR (film) ν: 3271, 3184, 2982, 2905, 2360, 1655, 1596, 1491, 1307, 1134, 1090, 1045, 1018, 837, 765, 661, 566, 507 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3Cl$ $[M+H]^+$ 370.1186, found 370.1186.

N-(4-溴苯基)-5,5,5-三氟-2-甲基-2-(对甲基苯)戊酰胺(**3e**): 126.4 mg, 白色固体, 产率 61%. m.p. 166.5～167.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J=8.6 Hz, 2H), 7.15 (d, J=9.2 Hz, 6H), 6.75 (s, 1H), 2.30 (s, 3H), 2.24～2.13 (m, 2H), 2.03～1.87 (m, 1H), 1.85～1.67 (m, 1H), 1.57 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.34 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 137.2, 136.9, 135.7, 130.8, 129.1, 126.2 (q, J=277.2 Hz), 125.7, 120.4, 115.9, 49.1, 30.2 (q, J=3.0 Hz), 28.5 (q, J=28.8 Hz), 22.3, 19.9; IR (film) ν: 3271, 2973, 2366, 1646, 1515, 1408, 1274, 1241, 1117, 1051, 911, 852, 646, 527 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3Br$ $[M+H]^+$ 414.0680, found 414.0675.

5,5,5-三氟-*N*-(4-碘苯基)-2-甲基-2-(对甲苯基)戊酰胺(**3f**): 117.6 mg, 白色固体, 产率 51%. m.p. 157.3～165.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.44 (m, 2H), 7.16 (s, 4H), 7.07～7.01 (m, 2H), 6.72 (s, 1H), 2.30 (s, 3H), 2.23～2.14 (m, 2H), 2.03～1.88 (m, 1H), 1.86～1.69 (m, 1H), 1.57 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.35 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 137.2, 136.9, 136.8, 136.4, 129.1, 126.2 (q, J=277.2 Hz), 125.7, 120.6, 86.5, 49.1, 30.2 (q, J=2.9 Hz), 28.5 (q, J=28.8 Hz), 22.3, 19.9; IR (film) ν: 3250, 2964, 2360, 1661, 1590, 1509, 1480, 1396, 1304, 1253, 1158, 1128, 1090, 1051, 1003, 819, 760, 629, 569, 510 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3I$ $[M+H]^+$ 462.0542, found 462.0545.

N-(4-叔丁基苯基)-5,5,5-三氟-2-甲基-2-(对甲基苯)戊酰胺(**3g**): 95.9 mg, 白色固体, 产率 49%. m.p. 171.5～174.9.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30～7.03 (m, 8H), 6.71 (s, 1H), 2.28 (s, 3H), 2.26～2.12 (m, 2H), 2.07～1.90 (m, 1H), 1.89～1.71 (m, 1H), 1.56 (s, 3H), 1.19 (s, 9H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.33 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 146.4, 137.8, 136.7, 134.0, 128.9, 126.3 (q, J=277.2 Hz), 125.7, 124.7, 118.6, 48.9, 33.3, 30.3, 28.6 (q, J=28.6 Hz), 22.4, 19.9; IR (film) ν: 3291, 2958, 2357, 1655, 1599, 1319, 1259, 1155, 1122, 1072, 965, 834, 736, 673, 560, 536 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{29}NOF_3$ $[M+H]^+$ 392.2201, found 392.2205.

5,5,5-三氟-2-甲基-*N*-(邻甲苯基)-2-(对甲苯基)戊酰胺(**3h**): 115.3 mg, 白色固体, 产率 66%. m.p. 70.2～70.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (dd, J=8.1, 1.2 Hz, 1H), 7.23 (d, J=8.1 Hz, 4H), 7.13 (td, J=7.7, 1.7 Hz, 1H), 7.04 (dd, J=7.6, 1.7 Hz, 1H), 6.98 (td, J=7.5, 1.3 Hz, 1H), 6.78 (s, 1H), 2.36 (s, 3H), 2.33～2.24 (m, 2H), 2.17～1.98 (m, 1H), 1.98～1.82 (m, 1H), 1.81 (s, 3H), 1.65 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.26 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.6, 138.8, 137.8, 135.7, 130.4, 130.0, 128.8, 127.5 (q, J=277.2 Hz), 126.8, 126.7, 125.0, 122.5, 50.0, 31.0 (q, J=2.9 Hz), 29.6 (q, J=28.7 Hz), 23.2, 20.9, 17.1; IR (film) ν: 3271, 2982, 2372, 1658, 1590, 1518, 1453, 1331, 1256, 1128, 1060, 825, 745, 673, 575, 545 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}NOF_3$ $[M+H]^+$ 350.1732, found 350.1731.

5,5,5-三氟-*N*-(2-甲氧苯基)-2-甲基-2-(对甲苯基)戊酰胺(**3i**): 127.89 mg, 白色固体, 产率 70%. m.p. 87.3～99.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (dd, J=7.8, 1.8 Hz, 1H), 7.63 (s, 1H), 7.28 (d, J=8.3 Hz, 2H), 7.25～7.19 (m, 2H), 7.00～6.87 (m, 2H), 6.74 (dd, J=8.0, 1.6 Hz, 1H), 3.60 (s, 3H), 2.35 (s, 3H), 2.34～2.25 (m, 2H), 2.18～2.00 (m, 1H), 1.98～1.82 (m, 1H), 1.66 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.30 (t, J=10.7 Hz); ^{13}C

NMR (101 MHz, $CDCl_3$) δ: 174.2, 148.2, 138.8, 137.5, 129.8, 127.6, 127.5 (q, J=277.2 Hz), 126.7, 123.8, 121.0, 119.63, 110.1, 55.7, 50.3, 31.3 (q, J=2.9 Hz), 29.7 (q, J=28.7 Hz), 23.3, 20.9; IR (film) ν: 3393, 2958, 1688, 1604, 1521, 1488, 1465, 1390, 1319, 1253, 1122, 1051, 956, 825, 748, 623, 545 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}NO_2F_3$ $[M+H]^+$ 366.1681, found 366.1682.

5,5,5-三氟-2-甲基-*N*-(2-氟苯基)-2-(对甲苯基)戊酰胺(**3j**): 90.1 mg, 白色固体, 产率 51%. m.p. 98.1～98.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.15 (td, J=8.0, 1.6 Hz, 1H), 7.21 (d, J=8.4 Hz, 2H), 7.19 (s, 1H), 7.16 (s, 1H), 7.08～7.00 (m, 2H), 6.98～6.88 (m, 2H), 2.30 (s, 3H), 2.27～2.20 (m, 2H), 2.07～1.92 (m, 1H), 1.89～1.72 (m, 1H), 1.61 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.40 (t, J=10.5 Hz), −131.39～−131.50 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 151.6 (d, J=243.4 Hz), 136.9 (d, J=31.6 Hz), 129.0, 125.6, 126.3 (q, J=277.2 Hz), 125.1 (d, J=10.1 Hz), 123.5, 123.5 (d, J=1.4 Hz), 123.4, 120.8, 113.7 (d, J=19.2 Hz), 49.2, 30.2 (q, J=2.9 Hz), 28.5 (q, J=28.8 Hz), 22.2, 19.9; IR (film) ν: 3280, 2988, 2363, 1667, 1619, 1539, 1453, 1304, 1265, 1152, 1128, 1090, 1045, 965, 825, 762, 563 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_4$ $[M+H]^+$ 354.1481, found 354.1483.

N-(2-氯苯基)-5,5,5-三氟-2-甲基-2-(对甲苯基)戊酰胺(**3k**): 97.9 mg, 白色固体, 产率 53%. m.p. 56.4～57.3 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.18 (dd, J=8.8, 1.4 Hz, 1H), 7.38 (s, 1H), 7.23～7.14 (m, 2H), 7.15～7.03 (m, 4H), 6.82 (td, J=7.7, 1.6 Hz, 1H), 2.30～2.24 (m, 1H), 2.23 (s, 3H), 2.21～2.15 (m, 1H), 2.07～1.85 (m, 1H), 1.86～1.66 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.28 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 136.9, 136.8, 133.5, 129.0, 127.9, 126.5, 126.3 (q, J=277.2 Hz), 125.7, 123.6, 122.1, 120.4, 49.3, 29.9 (q, J=2.9 Hz), 28.5 (q, J=28.8 Hz), 22.1, 19.7; IR (film) ν: 3303, 2970, 2363, 1667, 1593, 1512, 1441, 1384, 1298, 1256, 1125, 1045, 825, 748, 697, 614, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3Cl$ $[M+H]^+$ 370.1186, found 370.1187.

N-(2-溴苯基)-5,5,5-三氟-2-甲基-2-(对甲苯基)戊酰胺(**3l**): 109.8 mg, 无色液体, 产率 53%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.21 (dd, J=8.2, 1.5 Hz, 1H), 7.42～7.31 (m, 2H), 7.27～7.14 (m, 5H), 6.84 (td, J=7.7, 1.6 Hz, 1H), 2.41～2.14 (m, 5H), 2.13～1.90 (m, 1H), 1.86～1.74 (m, 1H), 1.62 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.36 (td, J=10.6, 2.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 136.9, 136.8, 134.6, 131.1, 129.1, 127.3, 126.2 (q, J=277.2 Hz), 125.8, 124.1, 120.5, 112.5, 49.3, 29.9 (d, J=3.0 Hz), 28.5 (q, J=28.9 Hz), 22.2, 19.9; IR (film) ν: 3309, 2985, 2363, 1691, 1601, 1509, 1435, 1399, 1262, 1131, 1060, 1027, 965, 819, 757, 560 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3Br$ $[M+H]^+$ 414.0680, found 414.0679.

5,5,5-三氟-2-甲基-*N*-(2-碘苯基)-2-(对甲苯基)戊酰胺(**3m**): 117.6 mg, 白色固体, 产率 51%. m.p. 74.6～77.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.21 (dd, J=8.2, 1.5 Hz, 1H), 7.40 (s, 1H), 7.34 (dd, J=8.0, 1.5 Hz, 1H), 7.26～7.15 (m, 5H), 6.84 (td, J=7.7, 1.6 Hz, 1H), 2.36～2.28 (m, 1H), 2.28 (s, 3H), 2.27～2.19 (m, 1H). 2.09～1.92 (m, 1H), 1.89～1.71 (m, 1H), 1.62 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.31 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.7, 137.7, 137.1, 137.0, 136.8, 129.1, 128.1, 126.3 (q, J=277.3 Hz), 125.9, 124.8, 120.5, 88.5, 49.2, 29.9 (q, J=3.0 Hz), 28.5 (q, J=28.8 Hz), 22.2, 19.9; IR (film) ν: 3348, 2979, 2363, 1694, 1587, 1512, 1429, 1393, 1298, 1134, 1048, 1012, 828, 751, 626, 554 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NOF_3I$ $[M+H]^+$ 462.0542, found 462.0542.

5,5,5-三氟-2-甲基-*N*-(间甲苯基)-2-(对甲苯基)戊酰胺(**3n**): 78.6 mg, 白色固体, 产率 45%. m.p. 128.4～128.9 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29～7.19 (m, 5H), 7.18～7.08 (m, 2H), 6.91～6.86 (m, 1H), 6.77 (s, 1H), 2.37 (s, 3H), 2.32～2.28 (m, 1H), 2.29 (s, 3H), 2.26～2.21 (m, 1H)., 2.15～1.97 (m, 1H), 1.98～1.79 (m, 1H), 1.65 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.37 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.4, 138.9, 138.7, 137.8, 137.6, 130.0, 128.8, 127.3 (q, J=277.2 Hz), 126.7, 125.2, 120.4, 116.9, 50.1, 31.4 (q, J=2.8 Hz), 29.7 (q, J=28.7 Hz), 23.5, 21.4, 20.9; IR (film) ν: 3268, 2976, 1655, 1596, 1539, 1429, 1384, 1295, 1253, 1131, 1051, 956, 765, 765, 694, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}NOF_3$ $[M+H]^+$ 350.1732, found 350.1732.

5,5,5-三氟-2-甲基-*N*-苯基-2-(对甲苯基)戊酰胺(**3o**): 88.9 mg, 白色固体, 产率 53%. m.p. 145.4～147.5 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J=7.9 Hz, 2H), 7.21～7.13 (m, 6H), 6.99 (t, J=7.3 Hz, 1H), 6.74 (s, 1H), 2.29 (s, 3H), 2.26～2.12 (m, 2H), 2.07～1.86 (m, 1H), 1.85～1.71 (m, 1H), 1.57 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.33 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.4, 137.5, 136.8, 136.6, 128.9, 127.9, 126.3

(q, J=277.2 Hz) 125.7, 123.4, 118.8, 49.0, 30.3 (q, J=3.0 Hz), 28.6 (q, J=28.8 Hz), 22.4, 19.9; IR (film) ν: 3280, 2946, 1658, 1601, 1518, 1447, 1399, 1316, 1256, 1140, 1051, 905, 825, 762, 703, 626, 554, 513 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_3$ $[M+H]^+$ 336.1575, found 336.1576.

5,5,5-三氟-2-甲基-*N*,2-二苯基戊酰胺(**3p**): 83.5 mg, 白色固体, 产率 52%. m.p. 134.6～135.3 ℃; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.47 (t, J=7.6 Hz, 2H), 7.44～7.35 (m, 5H), 7.34～7.26 (m, 2H), 7.14～7.08 (m, 1H), 6.81 (s, 1H), 2.41～2.28 (m, 2H), 2.15～2.04 (m, 1H), 1.97～1.87 (m, 1H), 1.72 (s, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ: −66.37 (t, J=10.7 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 174.2, 141.8, 137.6, 129.4, 128.9, 128.0, 127.3 (q, J=276.3 Hz), 126.8, 124.5, 119.9, 50.4, 31.4 (q, J=2.9 Hz), 29.6 (q, J=28.8 Hz), 23.4; IR (film) ν: 3256, 2982, 2351, 1658, 1593, 1530, 1444, 1387, 1322, 1250, 1125, 1057, 968, 822, 754, 697, 599, 557, 516 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{19}NOF_3$ $[M+H]^+$ 322.1419, found 322.1417.

5,5,5-三氟-2-(4-甲氧苯基)-2-甲基-*N*-苯基戊酰胺(**3q**): 79.0 mg, 白色固体, 产率 45%. m.p. 125.7～126.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.18 (m, 6H), 7.06 (t, J=7.1 Hz, 1H), 6.98～6.92 (m, 2H), 6.87 (s, 1H), 3.83 (s, 3H), 2.40～2.16 (m, 2H), 2.34～2.21 (m, 1H), 1.92～1.75 (m, 1H), 1.64 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.30 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.6, 159.1, 137.7, 133.4, 128.9, 128.1, 127.3 (q, J=276.7 Hz), 124.4, 119.9, 114.7, 55.3, 49.7, 31.4 (q, J=2.9 Hz), 29.6 (q, J=28.7 Hz), 23.5; IR (film) ν: 3268, 2970, 1661, 1601, 1518, 1444, 1393, 1253, 1188, 1131, 1053, 965, 834, 751, 700, 614, 557, 516 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NO_2F_3$ $[M+H]^+$ 352.1524, found 352.1525.

2-(4-氯苯基)-5,5,5-三氟-2-甲基-*N*-苯基戊酰胺(**3r**): 65.8 mg, 白色固体, 产率 37%. m.p. 140.5～141.3 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=8.5 Hz, 2H), 7.28～7.24 (m, 3H), 7.23～7.17 (m, 3H), 7.01 (t, J=7.3 Hz, 1H), 6.71 (s, 1H), 2.29～2.10 (m, 2H), 2.07～1.90 (m, 1H), 1.89～1.72 (m, 1H), 1.58 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.36 (t, J=10.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4, 139.4, 136.3, 132.9, 128.5, 127.9, 127.1, 126.1 (q, J=277.3 Hz), 123.7, 118.9, 48.9, 30.5 (q, J=3.0 Hz), 28.6 (q, J=28.9 Hz), 22.3; IR (film) ν: 3274, 2940, 1655, 1599, 1536, 1491, 1393, 1259, 1018, 923, 837, 757, 694, 605, 554 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{18}NOF_3Cl$ $[M+H]^+$ 356.1029, found 356.1027.

5,5,5-三氟-2-甲基-*N*-苯基-2-(4-(三氟甲基苯)苯基)戊酰胺(**3s**): 48.7 mg, 白色固体, 产率 25%. m.p. 157.8.4～159.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J=8.2 Hz, 2H), 7.53 (d, J=8.2 Hz, 2H), 7.41～7.34 (m, 2H), 7.30 (dd, J=8.6, 7.2 Hz, 2H), 7.11 (td, J=7.2, 1.3 Hz, 1H), 6.73 (s, 1H), 2.44～2.21 (m, 2H), 2.21～2.04 (m, 1H), 2.01～1.89 (m, 1H), 1.72 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.73, −66.45 (t, J=10.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.8, 146.3, 137.2, 129.1, 127.1, 127.0 (q, J=277.75 Hz), 126.5 (q, J=275.7 Hz), 126.3 (q, J=3.7 Hz), 124.9, 120.1, 50.4, 31.7 (d, J=3.0 Hz), 29.7 (q, J=29.0 Hz), 23.4; IR (film) ν: 3277, 2920, 1655, 1601, 1539, 1441, 1393, 1340, 1310, 1256, 1126, 1099, 1069, 840, 751, 703, 620, 542, 510 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{18}NOF_6$ $[M+H]^+$ 390.1293, found 390.1290.

5,5,5-三氟-2-甲基-*N*-苯基-2-(邻甲基苯)戊酰胺(**3t**): 72.1 mg, 白色固体, 产率43%. m.p. 108.6～110.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.29 (m, 1H), 7.28～7.10 (m, 7H), 7.00 (dt, J=7.4, 3.6 Hz, 1H), 6.77 (d, J=4.6 Hz, 1H), 2.40～2.25 (m, 2H), 2.23 (d, J=2.0 Hz, 3H), 2.07～1.88 (m, 1H), 1.60 (d, J=2.0 Hz, 3H), 1.55～1.46 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.34 (t, J=10.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.2, 139.1, 137.7, 137.4, 132.9, 129.2, 128.3, 127.3 (q, J=277.8 Hz), 127.1, 126.7, 124.5, 119.9 (d, J=1.4 Hz), 50.1, 29.6 (q, J=28.8 Hz), 28.9 (q, J=3.1 Hz), 24.6, 20.5; IR (film) ν: 3256, 3128, 3062, 2961, 1661, 1607, 1542, 1500, 1450, 1387, 1313, 1253, 1137, 1030, 757, 697, 599, 563, 474 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_3$ $[M+H]^+$ 336.1575, found 336.1574.

2-(3-氯苯基)-5,5,5-三氟-2-甲基-*N*-苯基戊酰胺(**3u**): 67.6 mg, 白色固体, 产率38%. m.p. 118.4～119.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.31 (m, 5H), 7.32～7.23 (m, 3H), 7.09 (td, J=7.3, 1.5 Hz, 1H), 6.81 (d, J=5.1 Hz, 1H), 2.38～2.17 (m, 2H), 2.13～2.03 (m, 1H), 1.99～1.82 (m, 1H), 1.66 (d, J=1.6 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.36 (td, J=10.6, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.2, 144.2, 137.4, 135.3, 130.6, 129.0, 128.2, 127.1 (q, J=277.8 Hz), 126.8, 125.1, 124.8, 120.1 (d, J=2.0 Hz), 50.3, 31.5 (q, J=2.9 Hz), 29.6 (q, J=28.8 Hz), 23.2; IR (film) ν: 3303, 2976, 1661, 1599, 1548, 1497, 1453, 1390, 1319, 1256, 1131, 1105, 1054,

959, 917, 837, 760, 709, 694, 611, 462 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{18}NOF_3Cl$ $[M+H]^+$ 356.1029, found 356.1028.

5,5,5-三氟-*N*-1,3,5-三甲基苯-2-甲基-2-(对甲苯基)戊酰胺(**3v**): 81.2 mg, 白色固体, 产率 43%. m.p. 136.7～137.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, J=8.3 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 6.70 (s, 2H), 6.32～6.22 (m, 1H), 2.27 (s, 3H), 2.23 (dd, J=6.3, 4.8 Hz, 1H), 2.17 (dd, J=13.7, 4.3 Hz, 1H), 2.12 (s, 3H), 2.07～1.91 (m, 1H), 1.89 (s, 6H), 1.82～1.63 (m, 1H), 1.59 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.24 (t, J=10.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.5, 137.9, 136.6, 135.7, 133.9 (d, J=1.4 Hz), 130.0 (d, J=1.8 Hz), 128.8, 127.8, 126.4 (q, J=277.3 Hz), 125.8, 48.3, 29.9 (q, J=2.9 Hz), 28.5 (q, J=28.7 Hz), 21.9 (d, J=2.0 Hz), 19.9, 19.8, 17.2; IR (film) v: 3277, 2970, 2363, 1652, 1509, 1447, 1247, 1128, 1057, 914, 848, 739, 602, 533 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{27}NOF_3$ $[M+H]^+$ 378.2045, found 378.2043.

5,5,5-三氟-2-甲基-2-(1-萘基)-*N*-苯基戊酰胺(**3w**): 74.3 mg, 白色固体, 产率 40%. m.p. 125.6～126.9 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.80 (tt, J=8.6, 2.2 Hz, 4H), 7.54～7.41 (m, 2H), 7.35 (dt, J=8.7, 2.2 Hz, 1H), 7.23 (dd, J=8.0, 2.2 Hz, 2H), 7.17 (dt, J=8.8, 4.4 Hz, 2H), 7.03～6.92 (m, 1H), 6.74 (s, 1H), 2.39～2.28 (m, 2H), 2.12～1.96 (m, 1H), 1.85～1.72 (m, 1H), 1.70 (d, J=2.3 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.32 (t, J=10.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.1, 139.1, 137.6, 133.3, 132.7, 129.4, 128.9, 128.1, 127.7, 127.3 (q, J=277.3 Hz), 126.9, 126.8, 125.5, 124.9, 124.5, 119. 9, 50.6, 31.1 (q, J=3.0 Hz), 29.7 (q, J=28.8 Hz), 23.3; IR (film) v: 3241, 2967, 1661, 1601, 1542, 1491, 1444, 1393, 1259, 1131, 1039, 968, 745, 700, 599, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{21}NOF_3$ $[M+H]^+$ 372.1575, found 372.1572.

5,5,5-三氟-2-甲基-*N*-苯基-2-(2-噻吩基)戊酰胺(**3x**): 62.2 mg, 白色固体, 产率 38%. m.p. 96.7～98.2 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29～7.22 (m, 3H), 7.20～7.11 (m, 3H), 7.04～6.93 (m, 3H), 2.31～2.17 (m, 2H), 2.12～1.98 (m, 1H), 1.99～1.87 (m, 1H), 1.63 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −66.21 (td, J=10.5, 3.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.8, 146.5, 137.4, 128.9, 127.6, 127.2 (q, J=277.3 Hz), 126.1, 125.9, 124.7, 120.1 (d, J=1.6 Hz), 48.8, 32.3 (q, J=3.1 Hz), 29.7 (q, J=28.8 Hz), 24.7; IR (film) v: 3297, 2985, 1670, 1596, 1545, 1438, 1390, 1319, 1259, 1206, 1120, 1072, 971, 762, 694, 504, 493 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{17}NOF_3S$ $[M+H]^+$ 328.0983, found 328.0984.

5,5-二氟-2-甲基-*N*,2-二(对甲苯基)戊酰胺(**4a**): 99.42 mg, 白色固体, 产率 60%. m.p. 121.9～122.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19～7.16 (m, 2H), 7.13 (tt, J=4.9, 2.4 Hz, 4H), 7.01～6.90 (m, 2H), 6.72 (s, 1H), 5.66 (tt, J=56.9, 4.4 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H), 2.19～2.01 (m, 2H), 1.80～1.60 (m, 1H), 1.58～1.44 (m, 1H), 1.54 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −115.74 (ddt, J=56.9, 17.4, 2.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 138.2, 136.4, 134.2, 132.9, 128.8, 128.3, 125.7, 118.9, 116.3 (t, J=239.3 Hz), 49.2, 30.3 (t, J=5.3 Hz), 28.6 (t, J=21.1 Hz), 22.5, 19.9, 19.8; IR (film) v: 3312, 2976, 2922, 1661, 1601, 1512, 1408, 1316, 1235, 1054, 1012, 905, 819, 736, 703, 521, 477 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{24}NOF_2$ $[M+H]^+$ 332.1826, found 332.1827.

5,5-二氟-*N*-(4-甲氧基苯基)-2-甲基-2-(对甲苯基)戊酰胺(**4b**): 109.4 mg, 白色固体, 产率 63%. m.p. 116.3～123.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.21～7.17 (m, 3H), 7.16～7.11 (m, 3H), 6.72 (d, J=8.7 Hz, 2H), 6.68 (s, 1H), 5.69 (tt, J=56.9, 4.4 Hz, 1H), 3.68 (s, 3H), 2.29 (s, 3H), 2.18～2.02 (m, 2H), 1.73～1.47 (m, J=27.3, 13.9, 8.9 Hz, 1H), 1.59～1.47 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −115.8 (ddt, J=56.1, 17.7, 56.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 155.4, 138.3, 136.4, 129.8, 128.8, 125.7, 120.7, 116.3 (t, J=239.2 Hz), 113.4, 54.4, 49.1, 30.3 (t, J=5.4 Hz), 28.7 (t, J=21.1 Hz), 22.5, 19.9; IR (film) v: 3277, 2967, 2357, 1655, 1599, 1506, 1408, 1301, 1236, 1030, 947, 819, 765, 688, 554, 513 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{24}NO_2F_2$ $[M+H]^+$ 348.1775, found 348.1776.

5,5-二氟-*N*-(4-氟苯基)-2-甲基-2-(对甲苯基)戊酰胺(**4c**): 77.1 mg, 白色固体, 产率 46%. m.p. 141.4～141.9 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.16 (m, 4H), 7.14 (d, J=8.3 Hz, 2H), 6.85 (t, J=8.6 Hz, 2H), 6.80～6.73 (m, 1H), 5.67 (tt, J=56.8, 4.3 Hz, 1H), 2.28 (s, 3H), 2.17～2.03 (m, 2H), 1.81～1.62 (m, 1H), 1.64～1.50 (m, 1H), 1.55 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: −115.82 (ddt, J=56.8, 17.4, 3.4 Hz), −117.99 (tt, J=8.7, 4.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.8, 158.3 (d, J=243.6 Hz), 137.9, 136.6, 132.7 (d, J=2.8 Hz), 128.9, 125.7, 120.7 (dd, J=7.9, 1.6 Hz), 116.2 (t, J=240.16 Hz), 114.6, 114.4, 49.2, 30.2 (t, J=5.4 Hz), 28.6 (t,

J=21.1 Hz), 22.4, 19.9; IR (film) *v*: 3277, 2961, 1658, 1613, 1509, 1468, 1402, 1310, 1215, 1125, 1054, 950, 837, 771, 685, 521, 471 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_3$ $[M+H]^+$ 336.1575, found 336.1578.

N-(4-氯苯基)-5,5-二氟-2-甲基-2-(对甲苯基)戊酰胺(**4d**): 89.7 mg, 白色固体, 产率 51%. m.p. 149.6～150.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.44～7.04 (m, 8H), 6.83 (s, 1H), 5.76 (tt, *J*=56.8, 4.3 Hz, 1H), 2.37 (s, 3H), 2.27～2.10 (m, 2H), 1.91～1.68 (m, 1H), 1.69～1.59 (m, 1H), 1.63 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.86 (dt, *J*=56.8, 17.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 173.8, 137.8, 136.7, 135.3, 128.9, 128.2, 127.8, 125.7, 120.0, 116.2 (t, *J*=239.3 Hz), 49.3, 30.2 (t, *J*=5.4 Hz), 28.6 (t, *J*=21.2 Hz), 22.4, 19.9; IR (film) *v*: 3277, 2978, 1695, 1596, 1512, 1432, 1411, 1381, 1304, 1131, 1055, 951, 825, 753, 681, 552, 501 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2Cl$ $[M+H]^+$ 352.1280, found 352.1277.

N-(4-溴苯基)-5,5-二氟-2-甲基-2-(对甲苯基)戊酰胺(**4e**): 105.1 mg, 白色固体, 产率 53%. m.p. 149.7～151.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.34～7.24 (m, 2H), 7.22～7.10 (m, 6H), 6.74 (s, 1H), 5.68 (tt, *J*=56.8, 4.3 Hz, 1H), 2.29 (s, 3H), 2.09 (td, *J*=13.6, 12.3, 7.0 Hz, 2H), 1.83～1.61 (m, 1H), 1.61～1.51 (m, 1H), 1.56 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.87 (dt, *J*=56.8, 17.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 173.8, 137.8, 136.7, 135.8, 130.8, 128.9, 125.7, 120.2, 116.2 (t, *J*=240.2 Hz), 115.8, 49.4, 30.2 (t, *J*=5.3 Hz), 28.6 (t, *J*=21.2 Hz), 22.4, 19.9; IR (film) *v*: 3277, 2970, 2925, 2360, 1643, 1512, 1405, 1277, 1241, 1128, 1057, 914, 825, 643, 602, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2Br$ $[M+H]^+$ 396.0775, found 396.0775.

5,5-二氟-*N*-(4-碘苯基)-2-甲基-2-(对甲苯基)戊酰胺(**4f**): 97.5 mg, 白色固体, 产率 44%. m.p. 135.4～136.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.44 (dd, *J*=8.7, 1.7 Hz, 2H), 7.22～7.08 (m, 4H), 7.06～6.99 (m, 2H), 6.77 (d, *J*=7.7 Hz, 1H), 6.25～5.40 (m, 1H), 2.28 (s, 3H), 2.16～2.00 (m, 2H), 1.81～1.58 (m, 1H), 1.59～1.49 (m, 1H), 1.54 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.79 (dt, *J*=56.9, 17.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 173.8, 137.8, 136.7, 136.6, 136.5, 128.9, 125.7, 120.6 (d, *J*=2.4 Hz), 116.2 (t, *J*=239.4 Hz), 86.4, 49.4, 30.2 (t, *J*=5.3 Hz), 28.6 (t, *J*=21.1 Hz), 22.3, 19.9; IR (film) *v*: 3274, 2967, 1661, 1590, 1521, 1482, 1396, 1244, 1125, 1057, 1012, 947, 816, 709, 556, 516 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2I$ $[M+H]^+$ 444.0636, found 444.0633.

5,5-二氟-2-甲基-*N*-(间甲苯基)-2-(对甲苯基)戊酰胺(**4g**): 71.3 mg, 白色固体, 产率 43%. m.p. 89.0～90.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.31～7.24 (m, 2H), 7.24～7.19 (m, 3H), 7.17～7.08 (m, 2H), 6.88 (d, *J*=7.2 Hz, 1H), 6.78 (s, 1H), 6.18～5.41 (m, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.27～2.11 (m, 2H), 1.91～1.82 (m, 1H), 1.69 (dd, *J*=16.9, 4.3 Hz, 1H), 1.64 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.63 (dt, *J*=56.7, 17.2, 2.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 174.7, 139.2, 138.9, 137.7, 137.5, 129.9, 128.7, 126.8, 125.1, 120.4, 119.6, 117.3 (t, *J*=239.3 Hz), 116.8, 114.9, 50.4, 31.3, 29.7 (t, *J*=21.1 Hz), 23.6, 21.4, 21.0; IR (film) *v*: 3274, 2973, 1658, 1610, 1533, 1488, 1402, 1307, 1247, 1131, 1042, 941, 876, 777, 697, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{24}NOF_2$ $[M+H]^+$ 332.1826, found 332.1823.

5,5-二氟-*N*-(2-氟苯基)-2-甲基-2-(对甲苯基)戊酰胺(**4h**): 67.1 mg, 白色固体, 产率 40%. m.p. 79.1～80.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.11 (t, *J*=8.0 Hz, 1H), 7.22～7.08 (m, 4H), 7.08～7.03 (m, 1H), 7.02～6.95 (m, 1H), 6.92～6.82 (m, 2H), 5.66 (tt, *J*=56.8, 4.4 Hz, 1H), 2.25 (s, 3H), 2.11 (dt, *J*=11.3, 5.4 Hz, 2H), 1.82～1.61 (m, 1H), 1.55 (s, 3H), 1.62～1,50 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.77 (ddt, *J*=56.6, 17.3, 3.8 Hz), −131.18～−131.25 (m); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 174.8, 152.7 (d, *J*=243.4 Hz), 138.8, 137.6, 129.9, 126.7, 126.3 (d, *J*=10.1 Hz), 124.5, 124.4 (d, *J*=3.6 Hz), 121.9, 117.3 (t, *J*=239.3 Hz), 114.8 (d, *J*=19.2 Hz), 50.6, 31.2 (t, *J*=5.4 Hz), 29.7 (t, *J*=21.1 Hz), 23.4, 20.9; IR (film) *v*: 3223, 3036, 2970, 1664, 1503, 1456, 1417, 1384, 1304, 1265, 1221, 1120, 1051, 917, 816, 757, 676, 551, 465 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_3$ $[M+H]^+$ 336.1575, found 336.1575.

N-(2-氯苯基)-5,5-二氟-2-甲基-2-(对甲苯基)戊酰胺(**4i**): 86.2 mg, 无色液体, 产率 49%. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.20 (dd, *J*=8.4, 1.6 Hz, 1H), 7.39 (s, 1H), 7.24～7.16 (m, 2H), 7.14～7.04 (m, 4H), 6.82 (td, *J*=7.7, 1.6 Hz, 1H), 5.65 (tt, *J*=56.8, 4.3 Hz, 1H), 2.23 (s, 3H), 2.20～2.05 (m, 2H), 1.81～1.62 (m, 1H), 1.55 (s, 3H), 1.60～1.52 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −115.68 (ddt, *J*=56.8, 17.4, 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 174.9, 138.6, 137.6, 134.6, 129.9, 128.9, 127.6, 126.8, 124.6, 123.1, 121.4, 117.3 (t, *J*=239.3 Hz), 50.7, 31.0 (t, *J*=5.3 Hz), 29.6 (t, *J*=21.2 Hz), 23.3, 20.9;

IR (film) *v*: 3303, 2970, 2920, 2360, 1667, 1593, 1512, 1441, 1384, 1298, 1256, 1125, 1045, 989, 825, 748, 697, 614, 557 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2Cl$ $[M+H]^+$ 352.1280, found 352.1282.

N-(2-溴苯基)-5,5-二氟-2-甲基-2-(对甲苯基)戊酰胺(**4j**): 101.1 mg, 白色固体, 产率 51%. m.p. 81.5～82.3 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.32～8.00 (m, 1H), 7.39 (s, 1H), 7.26 (dd, *J*=8.1, 1.4 Hz, 1H), 7.22～7.06 (m, 5H), 6.75 (td, *J*=7.7, 1.5 Hz, 1H), 5.65 (tt, *J*=56.8, 4.4 Hz, 1H), 2.22 (s, 3H), 2.17～2.09 (m, 2H), 1.76～1.68 (m, 1H), 1.55 (s, 3H), 1.58～1.50 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: －115.63 (ddt, *J*=56.9, 17.3, 7.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 138.6, 137.6, 135.8, 132.2, 130.0, 128.3, 126.9, 125.1, 121.6, 117.3 (t, *J*=239.3 Hz), 113.6, 50.7, 30.9 (t, *J*=5.3 Hz), 29.6 (t, *J*=21.2 Hz), 23.3, 21.0; IR (film) *v*: 3309, 2985, 2922, 2363, 1691, 1601, 1509, 1435, 1399, 1319, 1262, 1131, 1060, 1021, 965, 819, 757, 560 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2Br$ $[M+H]^+$ 396.0775, found 396.0772.

5,5-二氟-*N*-(2-碘苯基)-2-甲基-2-(对甲苯基)戊酰胺(**4k**): 88.7 mg, 白色固体, 产率40%. m.p. 62.2～62.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, *J*=8.2, 1.5 Hz, 1H), 7.52 (dd, *J*=8.0, 1.5 Hz, 1H), 7.30～7.02 (m, 6H), 6.63 (td, *J*=7.7, 1.6 Hz, 1H), 5.67 (tt, *J*=56.7, 4.3 Hz, 1H), 2.24 (s, 3H), 2.22～2.06 (m, 2H), 1.78～1.68 (m, 1H), 1.57 (s, 3H), 1.60～1.54 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: －115.41～－115.68 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.9, 137.7, 137.6, 137.2, 136.5, 128.9, 128.0, 125.9, 124.7, 120.4, 116.2 (t, *J*=239.3 Hz), 88.5, 49.5, 29.9 (t, *J*=5.3 Hz), 28.5 (t, *J*=21.1 Hz), 22.2, 19.9; IR (film) *v*: 3351, 2967, 1691, 1581, 1512, 1295, 1131, 1054, 1012, 947, 908, 819, 762, 554 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NOF_2I$ $[M+H]^+$ 444.0636, found 444.0632.

5,5-二氟-*N*-1,3,5-三甲基苯-2-甲基-2-(对甲苯基)戊酰胺(**4l**): 73.7 mg, 白色固体, 产率 41%. m.p. 119.2～121.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J*=8.0 Hz, 2H), 7.20 (d, *J*=8.0 Hz, 2H), 6.78 (s, 2H), 6.43 (s, 1H), 5.70 (tt, *J*=56.9, 4.4 Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H), 2.19～2.09 (m, 2H), 1.96 (s, 6H), 1.88～1.68 (m, 1H), 1.64 (s, 3H), 1.60～1.44 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: －115.44 (ddt, *J*=56.6, 21.7, 17.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 139.5, 137.4, 136.6, 135.0, 131.3, 129.7, 128.9, 126.9, 117.5 (t, *J*=239.2 Hz), 49.7, 31.1 (t, *J*=5.4 Hz), 29.7 (t, *J*=21.1 Hz), 22.9, 20.9, 20.9, 18.3; IR (film) *v*: 3277, 2973, 2369, 1646, 1509, 1405, 1271, 1233, 1122, 1054, 914, 816, 635, 521 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{28}NOF_2$ $[M+H]^+$ 360.2139, found 360.2137.

3.2.2 转化实验

在装有磁力搅拌子的 10 mL 封管中加入 **3a** (0.2 mmol, 1.0 equiv.), $LiAlH_4$ (0.4 mmol, 2.0 equiv.), THF (1.5 mL), 置于 100 ℃下, 反应 12 h. 待反应结束后, 用饱和食盐水(5 mL)淬灭, 乙酸乙酯萃取(4 mL×3), 合并有机相, 有机相用饱和食盐水(5 mL)洗涤, 无水硫酸钠干燥, 过滤、浓缩后, 快速柱层析纯化得到 **5** [硅胶, *V*(石油醚)∶*V*(乙酸乙酯)=20∶1].

4-甲基-*N*-(5,5,5-三氟-2-甲基-2-(对甲苯基)戊基)苯胺(**5**): 47.0 mg, 棕色液体, 产率 70%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32～7.07 (m, 4H), 6.94 (d, *J*=8.2 Hz, 2H), 6.57～6.32 (m, 2H), 3.37～3.08 (m, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 2.10 (td, *J*=12.2, 2.9 Hz, 1H), 2.04～1.90 (m, 1H), 1.90～1.74 (m, 2H), 1.41 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ: －66.40 (t, *J*=10.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.2, 140.2, 136.4, 129.7, 129.6, 127.4 (q, *J*=276.7 Hz), 126.3, 113.2, 55.7, 41.1, 32.5 (d, *J*=2.7 Hz), 29.2 (d, *J*=28.6 Hz), 22.7, 20.9, 20.4; IR (film) *v*: 3320, 2970, 2925, 2869, 2360,1625, 1527, 1381, 1313, 1259, 1131, 1075, 980, 813, 727, 602, 507 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{25}NF_3$ $[M+H]^+$ 336.1939, found 336.1936.

辅助材料(Supporting Information) 化合物 **1u**～**1v** 的合成方法及表征数据, 以及产物 **3a**～**3x**、**4a**～**4l**、**5** 的 ^1H NMR、^{19}F NMR、^{13}C NMR 图, 控制实验的 GC-MS 图, **3m** 的单晶数据, 这些材料可以免费从本刊网站(http://sioc-journal.cn/)上下载.

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