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Electrolytic Partial Fluorination of Organic Compounds. 79. Anodic Fluorination of Spiropyrazoline-5,3′-chroman-4-ones and Thiochromanone Analogues. A Route to Aroyl Fluoride Derivatives

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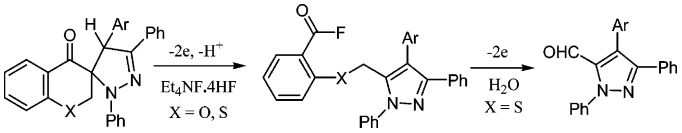
Received April 14, 2005



Anodic fluorination of spiropyrazole-5,3′-chroman-4-ones and their thiochromanone analogues in dimethoxyethane containing $Et_4NF{\cdot}4HF$ resulted in ring opening of spiroheterocycles, which led to the formation of (5-pyrazolyl)methyl *o*-carbomethoxyphenyl ethers and their thioether analogues via benzoyl fluoride derivatives.

Fluorinated heterocycles are well known to be highly biologically active candidates.[1−3] Therefore, we developed the selective anodic fluorination of various heterocyclic systems;[4−8] however, there has been no report dealing with anodic fluorination of spiroheterocycles thus far. Chromanone,[9,10] thiochromanone,[11] and pyrazole[12,13] derivatives are biologically active heterocycles and have been utilized in diverse agricultural and pharmaceutical applications. Recently, we carried out anodic fluorination of chromanones **2a**,**b** and thiochromanones **3a**,**b**, and it was found that the fluorination took place at α to the ring oxygen and sulfur atoms, respectively.[14−16] These facts prompted us to investigate anodic fluorination of spiroheterocycles such as 1,3,4-triarylspiropyrazole-5,3′-chroman-4-ones **4a**,**b** and their thio-analogues **5a**,**b**, which have two different heterocyclic rings to be fluorinated.

Preparation of the Spiroheterocycles 4a,b and 5a,b. 1,3,4-Triarylspiropyrazole-5,3′-chroman-4-one derivatives **4a**,**b** were prepared from the reaction of (*E*)-3-benzylidenechroman-4-ones **2a**,**b** with the hydrazonoyl chloride **1** in dry benzene and triethylamine at room temperature as reported in the literature.[17] 1,3,4-Triarylspiropyrazole-5,3′-thiochroman-4-one derivatives **5a**,**b** were similarly prepared from (*E*)-3-benzylidenethiochroman-4-ones **2a**,**b** with hydrazonoyl chloride **3** under reflux conditions (Scheme 1).

Oxidation Potentials of the Spiroheterocycles 4a,b and 5a,b. The oxidation peak potentials (E_p^{ox}) of compounds **4a**,**b** and **5a**,**b** were measured by cyclic voltammetry in an anhydrous acetonitrile solution containing 0.1 M $Bu_4N{\cdot}BF_4$ using platinum electrodes and

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10.1021/jo0507587 CCC: $30.25
Published on Web 08/18/2005

SCHEME 1

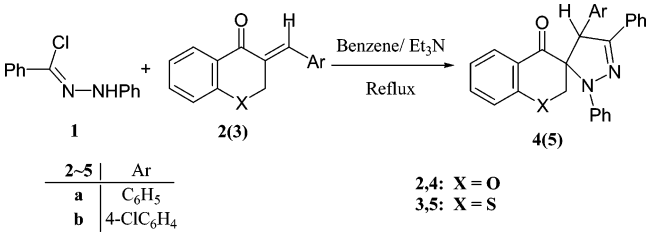
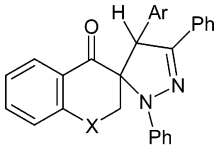


TABLE 1. Oxidation Peak Potentials E_p^{ox} of the Starting Substrates[a]

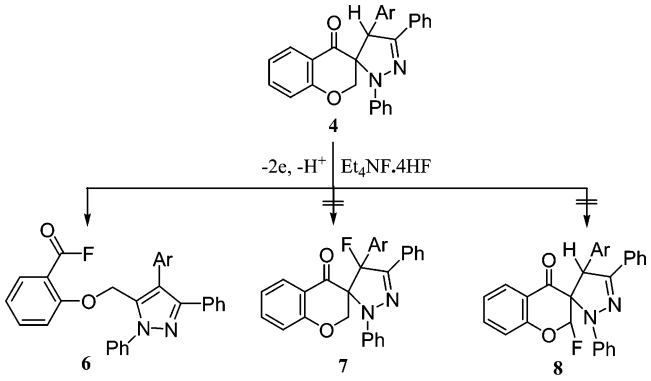


4,5

substrate	X	Ar	E_p^{ox}/V vs SSCE E_{p1}^{ox}	E_{p2}^{ox}
4a	O	C_6H_5	1.11	2.17
4b	O	4-ClC_6H_4	1.12	2.25
5a	S	C_6H_5	1.06	1.83
5b	S	4-ClC_6H_4	1.09	1.87

[a] Pt electrodes; 0.1 M Bu_4NBF_4/MeCN. Sweep rate 100 mV s^{-1}.

TABLE 2. Anodic Fluorination of Spiropyrazoline-5,3′-chroman-4-one Derivatives 4a,b



a: Ar = C_6H_5; **b**: Ar = 4-ClC_6H_4

run	substrate **4** Ar	cell/solvent	charge passed[a] F/mole	yield %[b] **6**
1	C_6H_5	undivided/DME	10	87 (85)
2	C_6H_5	divided/DME	10	88 (83)
3	C_6H_5	undivided/MeCN	6	60
4	4-ClC_6H_4	undivided/DME9	9	92 (89)
5	4-ClC_6H_4	undivided/MeCN	6	58

[a] Constant current (6 mA cm^{-2}) was applied; anode and cathode were Pt sheets (2 × 2 cm). [b] Determined on the basis of ^{19}F NMR, and the isolated yields are in parentheses.

a saturated calomel electrode (SCE) as a reference electrode. All the compounds **4a**,**b** and **5a**,**b** showed two irreversible waves in their cyclic voltammograms as shown in Table 1. The oxidation peak values (E_p^{ox}) of the spirochromanones are higher than those of their thio-analogues.

Anodic Fluorination of Spiropyrazoline-5,3′-chroman-4-ones 4a,b and Their Thio-Derivatives 5a,b. Electrolytic fluorination of 1,3,4-triphenylspiropyrazoline-5,3′-chroman-4-one (**4a**) was carried out with platinum electrodes in a 0.3 M $Et_4NF{\cdot}4HF$ in dimethoxyethane using a divided cell under a nitrogen atmosphere at room temperature. A constant current was applied until the starting substrate **4a** was completely consumed. The anodic fluorination was found to be straightforward and afforded only one isolable product as examined by TLC. It was expected that a fluorine atom would be introduced to the position α to the oxygen atom of chromanone moiety similarly to our reported results.[14,15] However, the ^{19}F NMR spectrum of the electrolysis product showed the absence of any doublet signal, and only a singlet appeared at δ −128.84 ppm, which implies that a proton at the 4-position of the pyrazole ring might be replaced by a fluorine atom to give the 4-fluorospiropyrazole derivative **7a** (Table 2). The ^1H NMR spectrum revealed also the presence of the methylene protons α to the oxygen atom and the absence of the methine proton of the pyrazole moiety, which rules out the possibility of the formation of structure **8a**. The ^{13}C NMR spectrum showed, however, only one sp^3 carbon at δ 60.31. All these spectral data strongly support the structure **6a** and rule out the other structures **7a** and **8a**. In addition, anodic fluorination of the spiropyrazoline-5,3′-chroman-4-one derivative **4b** was similarly attempted using $Et_4NF{\cdot}4HF$ in dimethoxyethane to give the benzoyl fluoride derivative **6b** in excellent yield. In addition to spectral data (MS, ^1H, ^{19}F, and ^{13}C NMR), the structure **6b** was further unequivocally confirmed by carrying out its single-crystal X-ray analysis.

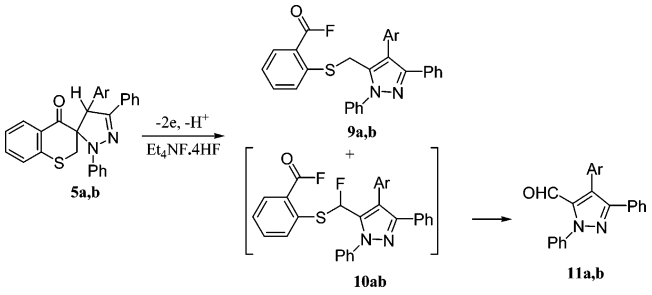
Acetonitrile was found to be not so effective for the anodic fluorination of these heterocyclic systems (runs 3 and 5, Table 2). The use of a divided cell did not affect on the product yield (run 2, Table 2).

Next, anodic fluorination of the 1,3,4-triphenylspiropyrazoline-5,3′-thiochroman-4-one (**5a**) was first undertaken under a constant current (6 mA cm^{-2}) using a divided cell as shown in Table 3 (run 1).

The fluorination reaction resulted in the formation of the benzoyl fluoride derivative **9a**, similar to **6a**, in a moderate yield (46%) in addition to the difluorinated product **10a** in 7% yield. The benzoyl fluoride derivative **9a** was obtained solely in a high yield (Table 3, run 2) when compound **5a** was anodically fluorinated under constant applied potential of 1.06 V versus SCE, which is the first oxidation potential of **5a**. Constant potential electrolysis of compound **5a** at its second oxidation peak potential (E_p^{ox} = 1.83 V versus SCE) resulted in the reversed product selectivity and led to the formation of the difluorinated derivative **10a** as the major product in addition to a small amount (8%) of the benzoyl fluoride **9a** (Table 3, run 3).

Furthermore, the anodic behavior of the 4-(4-chlorophenyl)-1,3-diphenylspiropyrazoline-5,3′-thiochroman-4-one (**5b**) was similarly studied, and the results are shown in Table 3 (runs 4−6). Galvanostatic electrolysis of **5b** afforded mono- and difluorinated derivatives **9b** and **10b**, respectively, in equivalent yields (about 30%, each) (run 4). On the other hand, when the electrolysis was carried out under controlled potential condition at 1.10 V versus SSCE (the first oxidation potential of **5b**), the benzoyl fluoride derivative **9b** was obtained exclusively in 97% yield (Table 3, run 5). Constant potential elec-

TABLE 3. Anodic Fluorination of Spiropyrazoline-5,3′-thiochroman-4-one Derivative 5a,b



a: Ar = C_6H_5; **b**: Ar = 4-ClC_6H_4

run	substrate **5** Ar	charge passed F/mole	applied electrolysis[a]	yield %[b] **9**	**10**[c]	**11**[d]
1	C_6H_5	10	6 mA cm^{-2}	46	7	–
2	C_6H_5	8	+1.06 V[a]	89 (80)	–	–
3	C_6H_5	8	+1.83 V[a]	8	56	(71)
4	4-ClC_6H_4	10	6 mA cm^{-2}	32 (25)	30	(46)
5	4-ClC_6H_4	7	+1.1 V[a]	97 (95)	–	–
6	4-ClC_6H_4	8	+1.87 V[a]	15 (9)	65	(88)

[a] Versus SSCE, anode and cathode were Pt sheets (2 × 2 cm) using a divided cell. [b] Determined on the basis of ^{19}F NMR, and the values in parentheses indicate the isolated yields. [c] Unstable products and readily converted into 5-formylpyrazoles **11a**,**b** when left at room temperature or during the working up. Structures of **10a**,**b** were established by ^{19}F NMR. [d] Isolated yields after column chromatography of the crude reaction mixture.

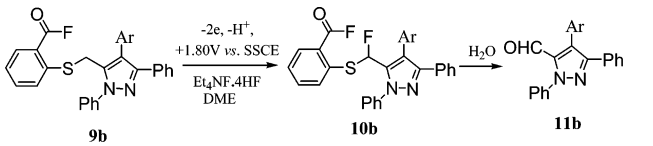
trolysis of compound **5b** at its second oxidation peak potential (E_p^{ox} = 1.87 V versus SCE) furnished the difluorinated derivative **10b** as the major product (65%) along with a minor yield of the benzoyl fluoride derivative **9b** (15%) (Table 3, run 6).

The fluorinated products **10a**,**b** are unstable under the purification conditions using silica gel chromatography; therefore their structures were identified on the basis of their ^{19}F NMR spectra [**10a**: δ −60.57 (d, 1F, J = 53.64 Hz), −136.45 (s, 1F). **10b**: δ −61.24 (d, 1F, J = 51.79 Hz), −135.10 (s, 1F)] of the crude reaction products. It is noted that compounds **10a**,**b** were completely converted into the 5-formylpyrazole derivatives **11a**,**b** when they were either passed through silica gel column chromatography or left at room temperature for 2 days in open air, and their isolated yields are shown in Table 3.

In addition, the oxidation peak potential of the benzoyl fluoride derivative **9b** was measured by cyclic voltammetry under the same conditions as described in Table 1. Compound **9b** showed two irreversible oxidation peaks at 1.80 and 2.10 V versus SSCE. Controlled potential electrolysis of **9b** at 1.80 V versus SSCE afforded the difluorinated product **10b** in 61% yield estimated by ^{19}F NMR of the crude product. Purification through silica gel column chromatography resulted in the formation of pure 5-formylpyrazole derivative **11b** in 86% yield as shown in Scheme 2.

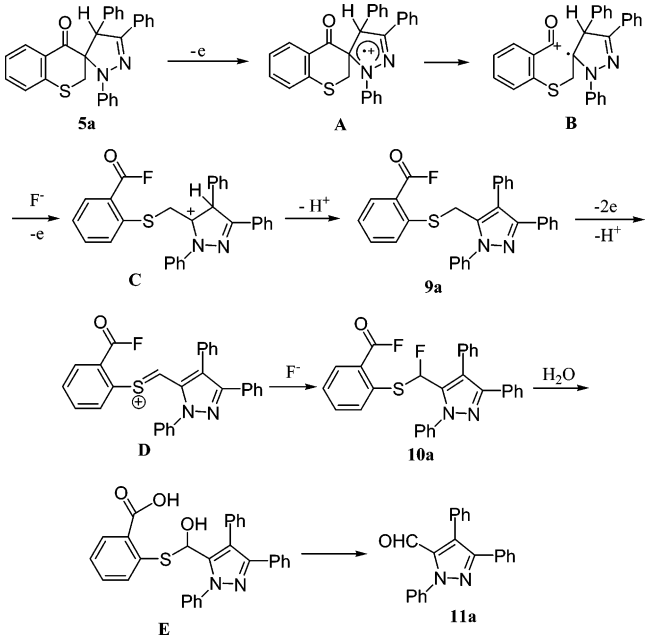
A plausible mechanism for the anodic formation of the benzoyl fluoride derivative **9a** and the aldehyde derivative **11a** from the spiroheterocycle **5a** is depicted in Scheme 3. Since the spiroheterocycles have oxidation potentials (ca. 1 V versus SSCE) much lower than those of thiochromanones and chromanones (ca. ∼1.7−2 V versus SSCE),[15,16] the initial electron transfer seems to take place at the pyrazole ring. The resulting radical

SCHEME 2



E_p^{ox} 1.80 and 2.10 V vs. SSCE

SCHEME 3



cation **A** undergoes cleavage of the carbon−carbon bond between the carbonyl−carbon and the spirocarbon to form a benzoyl cation at one terminal and a pyrazolinyl radical at the other terminal of the intermediate **B**. The benzoyl cation of **B** reacts with a fluoride ion, and the pyrazolinyl radical is subsequently oxidized to give the corresponding cation **C**, which undergoes deprotonation to give pyrazole derivative **9a**. In the electrolysis at the second oxidation peak potential, further anodic oxidation of compound **9a** took place to form the difluorinated derivative **10a** via the cationic intermediate **D**. The fluorine atom α to the sulfur in compound **10a** can be easily nucleophilically attacked by a hydroxide ion from the moisture to form the thioacetal intermediate **E**, which is easily converted into the corresponding 5-formylpyrazole derivative **11a** (Scheme 3).

Chemical evidence for the presence of the acyl fluoride moiety in the electrolytic products **6a**,**b** and **9a**,**b** was further confirmed by their treatment with methanol to give the corresponding methyl esters **12a**,**b** and **13a**,**b**, respectively (Table 4).

Previously, Yoneda at al. reported anodic fluorination of alkyl aldehydes to provide acyl fluorides selectively.[18] However, in the case of aromatic aldehydes, the aromatic ring fluorination always took place as a side reaction. On the contrary, in our case, the benzene ring was not fluorinated at all.

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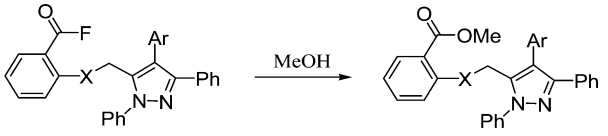
TABLE 4. Esterification of Acyl Fluorides 6a,b and 9a,b



6(9) **12(13)**

a: Ar = C_6H_5; **b**: Ar = 4-ClC_6H_4

run	X	substrate	product	yield %[a]
1	O	**6a**	**12a**	94
2	O	**6b**	**12b**	98
3	S	**9a**	**13a**	83
4	S	**9b**	**13b**	85

[a] Isolated yields.

In summary, we have shown the first example of the electrochemical synthesis of aroyl fluorides through anodic fluorination accompanied with ring opening of spiroheterocycles.

Experimental Section

Hydrazonoyl chloride **1**,[19] 3-benzylidene derivatives of chromanones **2a**,**b**, and thiochromanones **3a**,**b**[20] were prepared according to the procedures described in the literature.

4-Aryl-1,3-diphenylspiropyrazoline-5,3′-thiochroman 4-ones 5a,b. To a mixture of the hydrazonoyl chloride **3** (2 mmol) and the appropriate (*E*)-3-arylidenethiochroman-4-one **2a** or **2b** (2 mmol) in dry benzene (20 mL), triethylamine (0.2 mL) was added, and the reaction mixture was refluxed for 30−36 h. After the reaction was complete, it was left to cool to room temperature. The solvent was removed under reduced pressure, and the residue was triturated with methanol to give yellow precipitates that were collected by filtration, washed with methanol, and dried. The products were further purified by recrystallization from dioxane/water to afford the corresponding spiroheterocycles **5a**,**b**.

1,3,4-Triphenylspiropyrazoline-5,3′-thiochroman-4-one (5a): Yield (79%); mp 160−161 °C; IR (KBr) ν 1681 (C=O), 1583 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.88 (d, 1H, J = 13.52 Hz), 4.31 (d, 1H, J = 13.52 Hz), 4.83 (s, 1H), 6.96 (m, 1H), 7.17−7.57 (m, 17H), 8.14 (d, 1H, J = 7.83 Hz); ^{13}C NMR δ 30.51, 60.75, 75.73, 118.93, 121.72, 125.28, 126.09, 126.87, 128.12, 128.20, 128.27, 128.40, 128.60, 128.64, 131.15, 131.38, 133.88, 134.66, 140.85, 143.14, 149.10, 189.47. MS *m/z*, 447 (M^+ + 1), 446 (M^+), 341, 310, 233, 206, 178, 154, 107, 69. For $C_{29}H_{22}N_2OS$ calcd: C, 78.00; H, 4.97; N, 6.27; S, 7.18. Found: C, 78.13; H, 5.03; N, 6.16; S, 7.11%.

4-(4-Chlorophenyl)-1,3-diphenylspiropyrazoline-5,3′-thiochroman-4-one (5b): Yield (83%); mp 163−164 °C; IR (KBr) ν 1687 (C=O), 1594 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (d, 1H, J = 13.68 Hz), 4.31 (d, 1H, J = 13.68 Hz), 4.80 (s, 1H), 6.97 (m, 1H), 7.17−7.28 (m, 12H), 7.39−7.54 (m, 4H), 8.13 (d, 1H, J = 7.75 Hz); ^{13}C NMR δ 30.54, 59.91, 75.79, 119.18, 122.02, 125.40, 126.03, 126.91, 128.22, 128.48, 128.63, 128.69, 131.08, 131.21, 133.21, 133.98, 134.14, 140.59, 143.04, 148.78, 189.09. MS *m/z*, 483 (M^+ + 2), 482 (M^+ + 1), 481 (M^+), 375, 344, 281, 207, 178, 142, 77. For $C_{29}H_{21}ClN_2OS$ calcd: C, 72.41; H, 4.40; N, 5.82; S, 6.67. Found: C, 72.60; H, 4.58; N, 5.89; S, 6.71%.

The 4-aryl-1,3-diphenylspiropyrazoline-5,3′-chroman-4-ones **4a**,**b** were prepared at room temperature using the similar procedure that was used in the synthesis of compounds **5a**,**b**, and the spectral data of the products **4a**,**b** were in complete accordance with those reported in the literature.[17]

Anodic Fluorination of 4-Aryl-1,3-diphenylspiropyrazoline-5,3′-chroman (thiochroman)-4-ones 4a,b and 5a,b. Electrolysis was conducted with platinum electrodes (2 × 2 cm^2) in 0.3 M solution of a fluoride salt in dimethoxyethane or acetonitrile (20 mL) containing the appropriate spiroheterocycle **4a**,**b** or **5a**,**b** (1 mmol). The electrolysis was performed in a divided or an undivided cell under a nitrogen atmosphere at room temperature. A constant current (6 mA cm^{-2}) or controlled potential electrolyte was applied until the starting substrate was completely consumed (monitored by TLC and GC−MS). After the electrolysis, the solution was passed through a short column of silica gel using ethyl acetate as an eluent. The eluents were evaporated under reduced pressure, and then the yield of the fluorinated product was calculated by means of ^{19}F NMR by using a known amount of monofluorobenzene as an internal standard. The yields were calculated on the basis of the integral ratios between the monofluorobenzene and the fluorinated products. The products were purified by column chromatography using ethyl acetate/hexane mixture (1:5) as an eluent.

5-(2-Fluorocarbonyl)phenoxymethyl-1,3,4-triphenylpyrazole (6a): mp 158−159 °C; ^1H NMR ($CDCl_3$) δ 4.94 (s, 2H), 6.80 (d, 1H, J = 8.41 Hz), 7.06 (dd, 1H, J = 7.75, 7.58 Hz), 7.25−7.57 (m, 14H), 7.79 (d, 2H, J = 7.75 Hz), 7.95 (d, 1H, J = 7.91 Hz); ^{19}F NMR δ −128.84 (s); ^{13}C NMR (DEPT) δ 60.31 (CH_2), 113.47, 121.12, 124.84, 127.31, 127.67, 128.10, 128.51, 129.17, 130.15, 133.82, 133.88, 136.32 (CH), 114.08, 123.75, 132.35, 132.59, 134.97, 139.20, 149.60, 154.74 (d, J = 343.18 Hz), 159.08 (C). MS (*m/z*): 448 (M^+), 343, 309, 231, 204, 193, 168, 149, 77, 58. Anal. Calcd for $C_{29}H_{21}FN_2O_2$: C, 77.66; H, 4.77; N, 6.25. Found: C, 77.31; H, 4.82; N, 6.24.

4-(4-Chlorophenyl)-5-(2-fluorocarbonyl)phenoxymethyl-1,3-diphenylpyrazole (6b): mp 163 °C; ^1H NMR ($CDCl_3$): δ 4.90 (s, 2H), 6.84 (d, 1H, J = 8.24 Hz), 7.09 (t, 1H, J = 7.58 Hz), 7.29−7.54 (m, 13H), 7.76 (d, 2H, J = 8.08 Hz), 7.98 (d, 1H, J = 7.91 Hz); ^{19}F NMR δ −128.76 (s); ^{13}C NMR (DEPT) δ 60.26 (CH_2), 113.35, 121.31, 124.82, 127.86, 128.12, 128.25, 128.78, 129.24, 131.41, 133.92, 136.40 (CH), 114.14, 122.61, 130.87, 132.33, 133.39, 134.99, 139.04, 149.63, 154.66 (d, J = 343.18 Hz), 159.01 (C). MS (*m/z*): 484 (M^+ + 2), 482 (M^+), 358, 343, 308, 265, 204, 180, 123, 105, 77, 58. Anal. Calcd. for $C_{29}H_{20}ClFN_2O_2$: C, 72.12; H, 4.17; N, 5.80. Found: C, 71.99; H, 4.31; N, 5.80.

5-(2-Fluorocarbonyl)phenylthiomethyl-1,3,4-triphenylpyrazole (9a): mp 126−127 °C; ^1H NMR ($CDCl_3$) δ 4.16 (s, 2H), 7.12 (d, 1H, J = 8.08 Hz), 7.18−7.48 (m, 15H), 7.72 (d, 2H, J = 7.42 Hz), 7.96 (d, 1H, J = 7.75 Hz); ^{19}F NMR δ −136.45 (s); ^{13}C NMR (DEPT) δ 27.17 (CH_2), 124.71, 125.45, 126.61, 127.23, 127.58, 127.98, 128.07, 128.38, 128.54, 129.21, 130.14, 133.12, 134.58 (CH), 132.60, 132.65, 134.85, 139.27, 143.87, 143.99, 149.86, 155.30 (d, J = 343.74 Hz), (C). MS (*m/z*): 464 (M^+), 327, 309, 281, 221, 207, 147, 95, 69. Anal. Calcd for $C_{29}H_{21}FN_2OS$: C, 74.98; H, 4.56; N, 6.03; S, 6.90. Found: C, 74.81; H, 4.42; N, 6.21; S, 6.83.

4-(4-Chlorophenyl)-5-(2-fluorocarbonyl)phenylthiomethyl-1,3-diphenylpyrazole (9b): mp 140−141 °C; ^1H NMR ($CDCl_3$) δ 4.13 (s, 2H), 7.14 (d, 1H, J = 8.08 Hz), 7.20−7.31 (m, 8H), 7.40−7.49 (m, 6H), 7.71 (dd, 2H, J = 8.08, 1.48 Hz), 7.97 (dd, 1H, J = 7.91, 1.48 Hz); ^{19}F NMR δ −136.27 (s); ^{13}C NMR δ 27.13, 120.66, 121.20, 122.07, 124.90, 125.41, 126.59, 126.65, 127.76, 127.97, 128.16, 128.18, 128.49, 128.80, 129.24, 131.16, 131.39, 132.32, 133.16, 133.24, 134.64, 134.90, 139.08, 143.54, 143.66, 149.88, 155.31 (d, J = 343.74 Hz). MS (*m/z*): 500 (M^+ + 2), 498 (M^+), 343, 308, 204, 180, 77, 58. Anal. Calcd for $C_{29}H_{20}ClFN_2OS$: C, 69.80; H, 4.04; N, 5.61; S, 6.43. Found: C, 69.44; H, 4.06; N, 5.73; S, 6.43.

5-Formyl-1,3,4-triphenylpyrazole (11a): mp 122−123 °C; ^1H NMR ($CDCl_3$) δ 7.17−7.22 (m, 3H), 7.32−7.35 (m, 5H), 7.39−7.42 (m, 5H), 7.49−7.51 (m, 2H), 9.66 (s, 1H); ^{13}C NMR (DEPT) δ 125.67, 128.02, 128.11, 128.24, 128.49, 128.79, 130.58, 180.09 (CH), 128.91, 130.18, 131.47, 136.45, 139.36, 150.04 (C). MS (*m/z*): 324 (M^+), 220, 188, 155, 124, 84. Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.25; H, 4.88; N, 8.56.

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4-(4-Chlorophenyl)-1,3-diphenyl-5-formylpyrazole (11b): mp 130−131 °C; ^{1}H NMR ($CDCl_3$) δ 7.31−7.35 (m, 5H), 7.38−7.41 (m, 2H), 7.46−7.57 (m, 7H), 9.76 (s, 1H); ^{13}C NMR (DEPT) δ 125.72, 128.11, 128.31, 128.37, 128.39, 128.76, 128.98, 131.90, 179.89 (CH), 126.75, 128.82, 131.27, 134.39, 136.52, 139.09, 150.23 (C). MS (*m/z*): 360 (M^+ + 2), 359 (M^+ + 1), 358 (M^+), 329, 227, 190, 165, 123, 77. Anal. Calcd for $C_{22}H_{15}ClN_2O$: C, 73.64; H, 4.21; N, 7.81. Found: C, 73.49; H, 3.97; N, 7.87.

Esterification of the Acyl Fluorides 6a,b and 9a,b. A mixture of the appropriate acyl fluoride derivatives **6a**,**b** or **9a**,**b** (0.3 mmol) in methanol (3 mL) was heated at 60 °C for 1 h and then left to cool. The solvent was evaporated under vacuum, and the residue was further purified by being passed through silica gel column chromatography using ethyl acetate/hexane (1:5) as an eleunt.

5-(2-Methoxycarbonyl)phenoxymethyl-1,3,4-triphenylpyrazole (12a): mp 116−117 °C (EA/hexane); ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 4.78 (s, 2H), 6.67 (d, 1H, J = 8.24 Hz), 6.91 (dd, 1H, J = 7.42, 7.26 Hz), 7.19−7.35 (m, 12H), 7.44−7.48 (m, 2H), 7.70−7.79 (m, 3H); ^{13}C NMR (DEPT) δ 52.16 (CH_3), 60.23 (CH_2), 113.42, 120.94, 124.47, 127.12, 127.60, 127.81, 128.07, 128.41, 129.11, 130.04, 131.57, 133.07 (CH), 121.14, 123.62, 132.34, 132.68, 135.43, 139.28, 149.51, 156.58, 166.60 (C). MS (*m/z*): 461 (M^+ + 1), 460 (M^+), 309, 154, 136, 77, 69. Anal. Calcd for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 6.08. Found: C, 78.08; H, 5.45; N, 5.99.

4-(4-Chlorophenyl)-5-(2-methoxycarbonyl)phenoxymethyl-1,3-diphenylpyrazole (12b): mp 120−121 °C; ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H), 4.86 (s, 2H), 6.79 (d, 1H, J = 8.24 Hz), 7.03 (dd, 1H, J = 7.41, 7.26 Hz), 7.25−7.55 (m, 14H), 7.83 (d, 2H, J = 7.42 Hz); ^{13}C NMR (DEPT) δ 52.19 (CH_3), 60.21 (CH_2), 113.37, 121.12, 124.46, 124.76, 127.79, 127.96, 128.15, 128.70, 129.17, 131.34, 131.63, 133.16 (CH), 122.46, 128.08, 130.86, 132.41, 133.34, 135.46, 139.11, 149.54, 156.51, 166.44 (C). MS (*m/z*): 496 (M^+ + 2), 495 (M^+ + 1), 494 (M^+), 391, 343, 307, 289, 197, 154, 136, 69. Anal. Calcd. for $C_{30}H_{23}ClN_2O_3$: C, 72.80; H, 4.68; N, 5.66. Found: C, 72.64; H, 4.59; N, 5.44.

5-(2-Methoxycarbonyl)phenylthiomethyl-1,3,4-triphenylpyrazole (13a): mp 110−111 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 4.03 (s, 2H), 6.99 (d, 1H, J = 8.08 Hz), 7.06 (dd, 1H, J = 7.58, 7.42 Hz), 7.16−7.40 (m, 14H), 7.67 (d, 2H, J = 7.42 Hz), 7.82 (d, 1H, J = 7.58 Hz); ^{13}C NMR (DEPT) δ 52.18 (CH_3), 27.62 (CH_2), 124.55, 125.31, 126.68, 127.04, 127.50, 127.99, 128.02, 128.14, 128.41, 129.09, 130.11, 130.96, 132.23 (CH), 121.64, 128.10, 132.70, 135.63, 139.30, 140.03, 149.75, 166.54 (C). MS (*m/z*): 477 (M^+ + 1), 476 (M^+), 325, 309, 259, 231, 197, 154, 135. Anal. Calcd for $C_{30}H_{24}N_2O_2S$: C, 75.60; H, 5.08; N, 5.88; S, 6.73. Found: C, 75.41; H, 5.15; N, 5.69; S, 6.71.

4-(4-Chlorophenyl)-5-(2-methoxycarbonyl)phenylthiomethyl-1,3-diphenylpyrazole (13b): mp 117−118 °C; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 4.01 (s, 2H), 7.02 (d, 1H, J = 7.92 Hz), 7.10 (dd, 1H, J = 7.75, 7.42 Hz), 7.19−7.39 (m, 13H), 7.67 (d, 2H, J = 7.58 Hz), 7.85 (d, 1H, J = 7.75 Hz); ^{13}C NMR (DEPT) δ 52.24 (CH_3), 27.57 (CH_2), 124.84, 125.41, 126.74, 127.99, 128.11, 128.26, 128.39, 128.78, 129.27, 131.16, 131.49, 132.31 (CH), 120.37, 127.66, 131.24, 132.45, 132.99, 135.65, 139.16, 139.79, 149.80, 166.50 (C). MS (*m/z*): 512 (M^+ + 2), 511 (M^+ + 1), 510 (M^+), 308, 229, 194, 135, 77. Anal. Calcd for $C_{30}H_{23}ClN_2O_2S$: C, 70.51; H, 4.54; N, 5.48; S, 6.27. Found: C, 70.52; H, 4.49; N, 5.42; S, 6.31.

X-ray Crystallography of Compound 6b. X-ray diffraction measurements of compound **6b** were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −60 °C. Crystal data for **6b**: $C_{29}H_{20}O_2ClF$, fw = 482.94, monoclinic, space group $P2_1/n$, a = 16.1589(7) Å, b = 8.0433(2) Å, c = 18.0403(7) Å, β = 93.1640(10)°, V = 2341.1(2) Å^3, Z = 4, d_{calcd} = 1.37 g·cm^{-3}, μ = 2.01 cm^{-1}, R1 = 0.051 for the 2879 unique data with $F > 4\sigma(F)$ (wR2 = 0.149 for all 4967 data) and 316 parameters.

Acknowledgment. We thank Prof. M. Akita of the Tokyo Institute of Technology for X-ray analysis. K.M.D. is greatly indebted to the JSPS for awarding him a postdoctoral fellowship (1999−2001).

Supporting Information Available: General part, general experimental method, X-ray data, and cyclic voltammograms of **4a**, **4b**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0507587