# Preparation of Pyrrole-2-carboxylates with Electron-Withdrawing Groups at the 4-Position

Hidemitsu Uno,[a]* Masanori Tanaka,[a] Takashi Inoue,[a] Noboru Ono[b]

[a] Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho 2–5, Matsuyama 790–8577, Japan

[b] Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2–5, Matsuyama 790–8577, Japan

Fax +81(89)9279670; E-mail: uno@dpc.ehime-u.ac.jp

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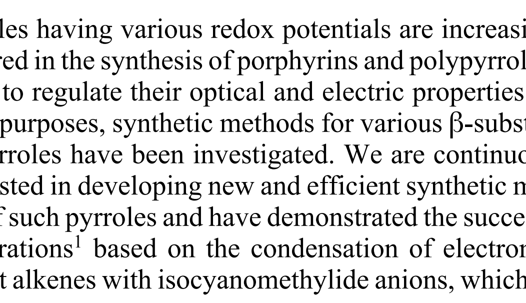
**Abstract:** Reaction of α-trifluoromethyl, α-cyano, and α-ethoxycarbonyl alkenyl sulfones with ethyl isocyanoacetate in the presence of a base gave 4-substituted pyrrole-2-carboxylates in moderate to good yields.

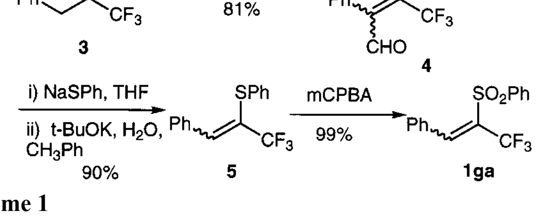
**Key words:** pyrrole-2-carboxylate, trifluoromethyl, Barton–Zard reaction, alkenyl sulfones

Pyrroles having various redox potentials are increasingly required in the synthesis of porphyrins and polypyrroles in order to regulate their optical and electric properties. For these purposes, synthetic methods for various β-substituted pyrroles have been investigated. We are continuously interested in developing new and efficient synthetic methods of such pyrroles and have demonstrated the successful preparations[1] based on the condensation of electron-deficient alkenes with isocyanomethylide anions, which was initially reported by Barton and Zard.[2] In this pyrrole synthesis, nitroalkenes are commonly employed because the nitro group can act both as a powerful stabilizer of the intermediate anion and as a good nucleofuge in the aromatization forming a pyrrole ring. Vinyl sulfones can be employed instead of the nitro compounds,[3] although the sulfonyl group is less effective as the anion stabilizer. From a synthetic viewpoint, however, the sulfonyl compounds are more desirable as they are more accessible than the corresponding nitro compounds. When another electron-withdrawing group is substituted, the sulfonyl group would be sufficient to stabilize the anion. This is found to be the case for α-trifluoromethyl, α-cyano, and α-ethoxycarbonyl alkenyl sulfones. In this paper, we would like to report a new and facile method for 4-trifluoromethyl-, 4-ethoxycarbonyl-, and 4-cyano-substituted pyrroles **2** from the sulfones **1** (Eq 1).



| 1 | R$^1$ | R$^2$ | R$^3$ | 2 |
|---|---|---|---|---|
| **1a** | CO$_2$Et | Ph | 4-MeC$_6$H$_4$ | **2a** |
| **1b** | CO$_2$Et | 4-MeC$_6$H$_4$ | 4-MeC$_6$H$_4$ | **2b** |
| **1c** | CO$_2$Et | 4-ClC$_6$H$_4$ | 4-MeC$_6$H$_4$ | **2c** |
| **1d** | CO$_2$Et | 4-MeOC$_6$H$_4$ | 4-MeC$_6$H$_4$ | **2d** |
| **1e** | CN | Ph | 4-MeC$_6$H$_4$ | **2e** |
| **1f** | CN | 4-MeC$_6$H$_4$ | 4-MeC$_6$H$_4$ | **2f** |
| **1ga** | CF$_3$ | Ph | Ph | **2g** |
| **1gb** | CF$_3$ | Ph | $n$-C$_6$H$_{13}$ | **2g** |
| **1h** | CF$_3$ | 4-MeC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | **2h** |
| **1i** | CF$_3$ | 4-ClC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | **2i** |
| **1j** | CF$_3$ | 4-MeOC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | **2j** |
| **1k** | CF$_3$ | 4-O$_2$NC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | **2k** |
| **1*l*** | CF$_3$ | 2,6-Cl$_2$C$_6$H$_3$ | $n$-C$_6$H$_{13}$ | **2*l*** |
| **1m** | CF$_3$ | C$_6$F$_5$ | $n$-C$_6$H$_{13}$ | **2m** |
| **1n** | CF$_3$ | 2-thienyl | $n$-C$_6$H$_{13}$ | **2n** |
| **1o** | CF$_3$ | CO$_2$Et | $n$-C$_6$H$_{13}$ | **2o** |
| **1p** | CF$_3$ | CN | $n$-C$_6$H$_{13}$ | **2p** |
| **1q** | CF$_2$CF$_3$ | Ph | $n$-C$_6$H$_{13}$ | |
| **1r** | CF$_2$CF$_3$ | 4-MeC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | |
| **1s** | CF$_2$CF$_3$ | 4-ClC$_6$H$_4$ | $n$-C$_6$H$_{13}$ | |

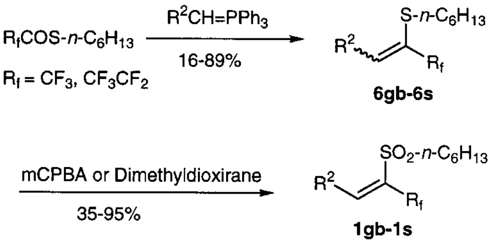
Although α-toluenesulfonyl-substituted acryl derivatives (**1a–1f**) were easily prepared by the Knoevenagel reaction,[4] preparation of vinyl sulfones with a perfluoroalkyl group is rare probably due to the failure of condensation of trifluoroethyl sulfones with aldehydes.[5] A potent route to α-trifluoromethyl α,β-unsaturated sulfones is oxidation of the corresponding sulfides. One reported method[6] for such a sulfide is based on the Vilsmeier reaction of a trifluoromethyl ketone (Scheme 1) and we started to prepare **1ga** from trifluoroacetic acid. Thus, 1,1,1-trifluoro-3-phenylacetone (**3**)[7], prepared from trifluoroacetic acid and the benzyl Grignard reagent in 77%, was treated with DMF and phosphoryl chloride to give 3-chloro-4,4,4-trifluoro-2-phenylbut-2-enal (**4**) as a mixture of stereoisomers. Substitution of the chloride with phenylthiolate followed by decarbonylation with in situ-generated KOH gave α-trifluoromethyl vinyl sulfide (**5**), which was then successfully oxidized to give the sulfone **1ga** (*E*/*Z* = 4:1) by an excess amount of *m*-chloroperbenzoic acid (mCPBA). Although the overall yield is quite good, there is no common intermediate for the preparation of variously β-sub-



**Scheme 1**

stituted sulfones in this route and we must start from the first step of the Grignard reaction every time.

Recently, Bégué et al. reported the preparation of α-trifluoromethyl vinyl sulfides based on the Wittig reaction with *S*-alkyl trifluorothioacetate.[8] This method is quite attractive for our purpose. Thus, a variety of sulfides were prepared by this method and oxidized with mCPBA to the corresponding sulfones (**1gb–1o**; Scheme 2 and Table 1). Similarly, α-pentafluoroethyl sulfones **1q–1s** were prepared from *S*-hexyl pentafluorothiopropionate. As no **1p** could be obtained by using mCPBA probably due to the decomposition of labile **1p** during the reaction and purification, dimethyldioxirane[9] was used instead of mCPBA and **1p** was used immediately after short silica gel column chromatography.



Scheme 2

Table 1 Preparation of Sulfides **6** and Sulfones **1**

| Conditions[a] | Sulfide | | | Conditions[a] | Sulfone | |
|---|---|---|---|---|---|---|
| | **6** | Yield/% | *E*/*Z*[b] | | **1**[c] | Yield/% |
| A | **6gb** | 62 | <5/>95 | B | **1gb** | 76 |
| A | **6h** | 79 | 14/86 | B | **1h** | 60 |
| A | **6i** | 89 | 17/83 | B | **1i** | 95 |
| A | **6j** | 43 | <5/>95 | B | **1j** | 57 |
| A | **6k** | 66 | 10/90 | B | **1k**[d] | 35 |
| C | **6l** | 16 | <5/>95 | B | **1l** | 44 |
| A | **6m** | 30 | <5/>95 | B | **1m** | 87 |
| A | **6n** | 73 | <5/>95 | B | **1n** | 93 |
| D | **6o** | 63 | <5/>95 | B | **1o** | 83 |
| D | **6p** | 83 | 11/89 | E | **1p** | 89 |
| F | **6q** | 44 | <5/>95 | B | **1q** | 77 |
| F | **6r** | 49 | <5/>95 | B | **1r** | 83 |
| F | **6s** | 51 | 13/87 | B | **1s** | 87 |

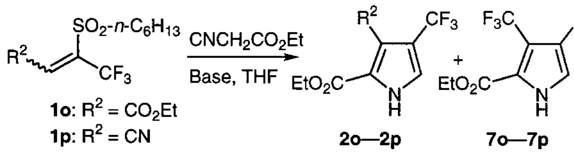
[a] A: Phosphonium salt (1.1 equiv), $CF_3COS$-*n*-$C_6H_{13}$, NaH, HMDSA (cat), THF, r.t., overnight; B: mCPBA (3 equiv), $CHCl_3$, r.t., overnight; C: Phosphonium salt (1.1 equiv), $CF_3COS$-*n*-$C_6H_{13}$, NaH, HMDSA (cat), THF, reflux, 72 h; D: Phosphorane (2 equiv), $CF_3COS$-*n*-$C_6H_{13}$, $CH_2Cl_2$, r.t. overnight; E: Dimethyldioxirane (3 equiv), acetone, r.t., overnight; F: Phosphonium salt (1.1 equiv), $CF_3CF_2COS$-*n*-$C_6H_{13}$, NaH, HMDSA (cat), THF, r.t., overnight.

[b] Stereosiomeric ratio was estimated by $^1H$ NMR spectra of the chromatographed or recrystallized material.

[c] The corresponding (*Z*)-sulfides were employed as the starting materials and only the *Z* isomers of sulfones were obtained.

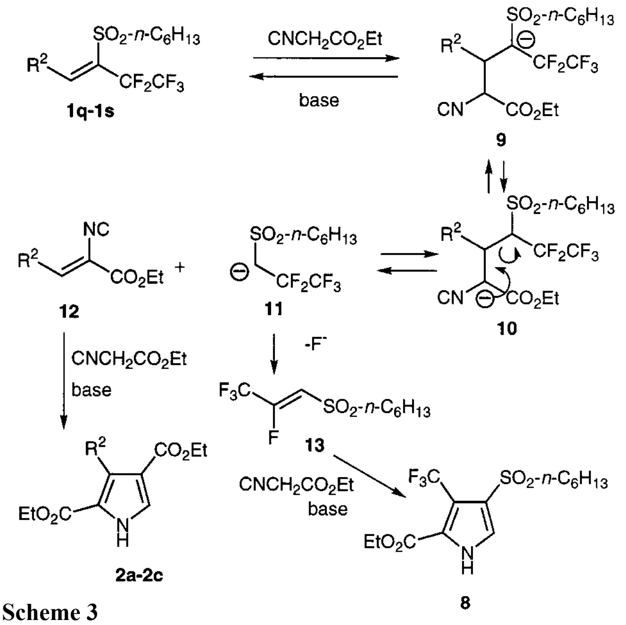
[d] A stereoisomeric mixture of **6k** (*E*/*Z* = 1/2) was used for the oxidation.

Condensation reaction of sulfones **1** with 2 equivalents of ethyl isocyanoacetate was carried out in THF at room temperature for 3 h (Table 2). *t*-Butyliminotris(pyrrolidino)phosphrane (BTPP)[10] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can be employed with the similar efficiency, though BTPP gave somewhat better yields (runs 7–12). Although potasium *t*-butoxide was reported to be the efficient base in the reaction of cyclohexenyl sulfone,[3a] no aimed pyrrole was obtained in the reaction of **1gb** (run 13). In the cases of **1o** and **1p**, regioisomeric mixtures were obtained (**2o**:**7o** = 5:6; **2p**:**7p** = 1:2). Even the corresponding sulfide **6o** reacted with the isocyanoacetate to give **2o**. Regiochemical determination was unambiguously done by $^1H$ NMR analysis based on the long-range coupling between the trifluoromethyl group and the pyrrole α-proton in **2o**, since the similar coupling was observed in other **2** compounds. The reactions of pentafluoroethyl sulfones **1q–1s** gave trifluoromethylated pyrrole **8** in low yields accompanied with a comparable amount of diethyl 3-arylpyrrole-2,4-dicarboxylates (**2a–2c**) and pentafluoroethyl derivatives could not be detected even in the reaction mixture by $^{19}F$ NMR analysis (runs 24–26).



(2)

A probable route to **8** and **2a–2c** is illustrated in Scheme 3. The Michael addition of the isocyanoacetate anion to the vinyl sulfones would give the sulfone-stabilized anion **9**. In the cases of trifluoromethyl vinyl sulfones, the similar anions to **9** underwent the ring closure between the anionic carbon and isocyano carbon, while the anion **9** would be then equilibrated with enolate **10** probably due to interference toward the nucleophilic ring closure by the



Scheme 3

very bulky pentafluoroethyl group. The enolate **10** would decompose to 2,2,3,3,3-pentafluoropropyl anion **11** and α-isocyano α,β-unsaturated ester **12**. The former would lose a β-fluoride to provide 2,3,3,3-tetrafluoropropenyl sulfone **13**. The α,β-unsaturated ester **12** and sulfone **13** would then react with ethyl isocyanoacetate to afford the observed products **8** and **2a–2c**.

Melting points are uncorrected. NMR spectra were obtained with a JEOL GSX-270 or JMN-400 spectrometer at ambient temperature by using $CDCl_3$ as a solvent and TMS and $CFCl_3$ as internal standards for $^1H$, $^{13}C$, and $^{19}F$. Mass spectra and HRMS were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: EI (electron impact, 20 eV; 70 eV for HRMS; high boiling perfluorokerosine as a standard) and CI (chemical ionization, 70 eV, isobutane as CI gas). Column chromatography and TLC analysis were carried out using C-200 (Wakogel) and Kieselgel 60 $F_{254}$ (Merk), respectively. $Et_2O$ and THF were freshly distilled from sodium benzophenone ketyl. $CH_2Cl_2$ was distilled from $CaH_2$ under an inert atmosphere. Other commercially available materials were used without further purification. General procedures used in this paper are as follows. Satisfactory microanalyses (C, ±0.4; H, ±0.2; N, ±0.13) or HRMS were found for all compounds.

**Table 2** Preparation of Pyrroles **2**

| Run | Sulfone | Base[a] | Products | Yield % | Run | Sulfone | Base[a] | Products | Yield % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | A | **2a** | 81 | 17 | **1k** | A | **2k** | 61 |
| 2 | **1b** | A | **2b** | 87 | 18 | **1l** | A | **2l** | 60 |
| 3 | **1c** | A | **2c** | 98 | 19 | **1m** | A | **2m** | 51 |
| 4 | **1d** | A | **2d** | 94 | 20 | **1n** | A | **2n** | 49 |
| 5 | **1e** | A | **2e** | 95 | 21 | **1o** | A | **2o** | 34 |
| 6 | **1f** | A | **2f** | 88 | | | | **7o** | 40 |
| 7 | **1ga** | A | **2g** | 20 | 22 | **6o** | A | **2o** | 15 |
| 8 | **1ga** | B | **2g** | 70 | 23 | **1p** | A | **2p** | 19 |
| 9 | **1gb** | C | **2g** | 42 | | | | **7p** | 11 |
| 10 | **1bg** | D | **2g** | 56 | 24 | **1q** | A | **8** | 21 |
| 11 | **1gb** | A | **2g** | 57 | | | | **2a** | 23 |
| 12 | **1gb** | E | **2g** | 79 | 25 | **1r** | A | **8** | 26 |
| 13 | **1gb** | F | **2g** | 0 | | | | **2b** | 30 |
| 14 | **1h** | A | **2h** | 40 | 26 | **1s** | A | **8** | 18 |
| 15 | **1i** | A | **2i** | 47 | | | | **2c** | 27 |
| 16 | **1j** | A | **2j** | 40 | | | | | |

[a] A: 4 equivs of DBU; B: 4 equivs of BTPP; C: 1.3 equivs of DBU; D. 2.7 equivs of DBU; E 1.3 equivs of BTPP; F: 1.3 equivs of *t*-BuOK.

**Table 3** Selected Spectroscopic Data for Sulfones

| Compound | Mp (°C) | NMR/δ in ppm | | | | IR/cm$^{-1}$ | | EI-MS *m*/*z* |
|---|---|---|---|---|---|---|---|---|
| | | Vinylic[a] | $R_f$[b] | C2[a] | C3[a] | $SO_2$ | Others | |
| (*E*)-**1a** | 77–78 | 7.94 | – | 131.5 | 143.0 | 1316, 1150 | 1722, 1622 | (331, 285, 266)[c] |
| (*E*)-**1b** | 107 | 7.90 | – | 129.7 | 143.2 | 1316, 1148 | 1724, 1606 | 344, 280, 189 |
| (*E*)-**1c** | 138–140 | 7.89 | – | 130.1 | 141.8 | 1314, 1148 | 1722 | 364, 209, 181 |
| (*E*)-**1d** | 88 | 7.89 | – | 131.9 | 143.2 | 1318, 1150 | 1720, 1598 | 360, 203, 132 |
| (*E*)-**1e** | 123 | 8.21 | – | 114.9 | 151.0 | 1328, 1160 | 2216, 1594 | (284, 155, 128)[c] |
| (*E*)-**1f** | 153–155 | 8.17 | – | 113.4 | 151.0 | 1328, 1156 | 2212, 1588 | 297, 155, 142 |
| (*Z*)-**1ga** | 40–70[d] | 7.84 (1.6) | –61.16 (1.6) | 131.2 (33) | 148.7 (3) | 1328, 1153 | 1267, 1172 | 312, 156, 125 |
| (*E*)-**1ga** | 40–70[d] | 8.43 | –55.48 | 134.6 (34) | 146.2 (6) | – | – | – |
| **1gb** | oil | 7.92 | –61.23 (0.9) | 131.5 (30) | 145.7 (6) | 1334, 1148 | 1266, 1148 | 320, 171, 151 |
| **1h** | oil | 7.84 | –60.93 | 130.1 (30) | 135.6 (6) | 1332, 1158 | 1268, 1192 | 334, 184, 139 |
| **1i** | oil | 7.84 | –61.21 | 131.8 (30) | 144.7 (6) | 1336, 1160 | 1262, 1160 | 354, 205, 133 |
| **1j** | oil | 7.76 | –60.45 (1.6) | 127.8 (30) | 145.0 (6) | 1332, 1158 | 1598, 1264, 1184 | 350, 202, 200 |
| (*Z*)-**1k** | 77[e] | 8.08 | –61.62 (1.6) | 134.4 (31) | 144.4 (5) | 1336, 1148 | 1524, 1348, 1182 | (366, 336, 316)[c] |
| (*E*)-**1k** | – | 8.25 | –55.46 | – | – | – | – | – |
| **1l** | oil | 7.75 | –61.66 | 135.4 (31) | 142.4 (5) | 1342, 1155 | 1646, 1270, 1172 | (389, 353, 269)[c] |
| **1m** | oil | 7.55 | –61.45 | 138.4 (32) | 131.9 (m) | 1344, 1160 | 1664, 1270, 1132 | (411, 327, 192)[c] |
| **1n** | oil | 7.86 (1.5) | –60.24 | 122.4 (31) | 137.9 (6) | 1334, 1154 | 1606, 1270, 1140 | (327, 307, 178)[c] |
| **1o**[f] | oil | 7.18 | –63.06 | 136.3 (33) | 137.7 (5) | 1342, 1156 | 1744, 1272, 1180 | (317, 271, 215)[c] |
| **1p**[f] | oil | 6.84 (1.5) | –63.10 (1.5) | 147.5 (34) | 115.9 (69) | 1336, 1149 | 2231, 1270, 1186 | (270, 186)[c] |
| **1q**[f] | oil | 7.39 | –82.90, –107.92 | 131.2 (22) | 149.4 (9) | 1334, 1152 | 1212, 1192, 1060 | 370, 221, 105 |
| **1r**[f] | oil | 7.68 | –82.90, –107.58 | 129.8 (23) | 149.3 (8) | 1334, 1152 | 1216, 1186, 1060 | 384, 234, 151 |
| **1s**[f] | oil | 7.81 | –82.99, –108.24 | 131.6 (22) | 148.5 (9) | 1336, 1152 | 1216, 1194, 1062 | 404, 255, 133 |

[a] Numerals in the parentheses are the coupling constants (Hz) with $CF_3$ fluorine atoms.

[b] Numerals in the parentheses are the coupling constants (Hz) with $H^5$.

[c] Spectra were measured under CI conditions.

[d] *E*/*Z* (4/1) mixture.

[e] *E*/*Z* (1/2) mixture.

[f] The position numbering is not done by the IUPAC nomenclature rule but based on Eq 1.

**Table 4** Selected Spectroscopic Data for Pyrroles

| Compound | Mp (°C) | NMR/δ in ppm | | | | | | IR/cm$^{-1}$ | | EI-MS *m*/*z* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | α-H[a] | $R_f$[b] | C2[a] | C3[a] | C4[a] | C5[a] | NH | C=O and Others | |
| **2a** | 113–115 | 7.57 | – | 120.8 | 132.4 | 116.7 | 127.3 | 3288 | 1688 | 287, 242, 196 |
| **2b** | 94 | 7.56 | – | 120.9 | 132.6 | 116.8 | 127.1 | 3280, 3140 | 1704, 1674 | 301, 255, 205 |
| **2c** | 117–120 | 7.59 | – | 120.7 | 131.0 | 116.7 | 127.1 | 3260, 3132 | 1706, 1674 | 321, 275, 230 |
| **2d** | 105 | 7.57 | – | 120.7 | 132.2 | 116.6 | 127.2 | 3292 | 1692 | 317, 271, 226 |
| **2e** | 153–154 | 7.33 | – | 119.7 | 133.7 | 96.4 | 128.4 | 3268 | 2228, 1692 | 321, 275, 230 |
| **2f** | 159–161 | 7.31 | – | 119.5 | 133.9 | 96.4 | 128.4 | 3272 | 2224, 1724 | 254, 208, 139 |
| **2g** | 107 | 7.28 | –56.05 | 121.2 | 129.2 (3) | 116.4 (36) | 121.4 (6) | 3296 | 1686, 1298, 1114 | 283, 237, 140 |
| **2h** | 130 | 7.27 | –55.93 | 121.0 | 129.4 (3) | 116.2 (36) | 121.6 (5) | 3320, 3292 | 1680, 1298, 1110 | 297, 251, 154 |
| **2i** | 128 | 7.27 | –56.00 | 121.2 | 127.7 (3) | 116.3 (35) | 121.7 (5) | 3384 | 1702, 1280, 1136 | 317, 271, 208 |
| **2j** | 118–120 | 7.25 | –56.03 | 121.1 | 129.0 (3) | 116.3 (35) | 121.5 (5) | 3300 | 1702, 1290, 1118 | 313, 267, 170 |
| **2k** | 167 | 7.34 | –56.00 | 121.4 | 126.4 (3) | 116.4 (36) | 121.8 (5) | 3356, 3140 | 1702, 1520, 1348 | 328, 282, 237 |
| **2l** | 128–129 | 7.23 | –58.66 | 121.6 | 123.0 (3) | 115.9 (37) | 122.2 (5) | 3270 | 1691, 1300, 1117 | (352, 316, 288)[c] |
| **2m** | 158–159 | 7.40 | –58.52 | 123.0 | 111.1 (br) | 117.3 (37) | 122.5 (5) | 3280 | 1700, 1298, 1120 | 373, 327, 230 |
| **2n** | 116 | 7.28 | –56.73 | 122.4 | 121.0 (3) | 117.3 (35) | 121.6 (6) | 3260 | 1680, 1294, 1116 | 289, 243, 146 |
| **2o** | 91–93 | 7.23 | –57.75 | 122.8 | 119.3 (3) | 115.5 (38) | 121.5 (5) | 3368, 3172 | 1742, 1714, 1308 | 279, 234, 188 |
| **2p** | 185–186 | 7.31 | –59.04 | 129.4 | 95.7 (2) | 119.7 (39) | 122.6 (br) | 3236, 3134 | 2244, 1720, 1314 | 232, 204, 186 |
| **3o** | 124–126 | 7.49 | –54.56 | 123.3 (4) | 116.5 (40) | 117.5 (2) | 126.5 | 3367, 3172 | 1741, 1712, 1308 | (280, 260,212)[c] |
| **3p** | 112–115 | 7.45 | –56.55 | 122.2 (5) | 119.4 (39) | 95.3 (3) | 128.5 | 3162, 3102 | 1712, 1631, 1306 | (233, 187, 152)[c] |
| **8** | oil | 7.59 | –53.19 | 125.0 (4) | 115.2 (40) | 124.0 | 128.1 | 3380 | 1743, 1324, 1139 | (356, 336)[c] |

[a] Numerals in the parentheses are the coupling constants (Hz) with $CF_3$ fluorine atoms.

[b] Numerals in the parentheses are the coupling constants (Hz) with $H^5$.

[c] Spectra were measured under CI conditions.

### Sulfide 6

To a suspension of phosphonium salt (20 mmol) and NaH (60% oil dispersion, 20 mmol) in anhyd THF (100 mL) was added with stirring a catalytic amount (0.1 mL) of hexamethyldisilazane (HMDSA) followed by *S*-ethyl perfluorothioacetate (20 mmol) at r.t. After the mixture was stirred overnight, hexane (200 mL) was added and the mixture was filtered through a short pad of silica gel, which is washed with hexane (200 mL). The combined filtrate was again filtered through a short pad of silica gel and then the solvent was evaporated. The residual oil was purified by silica gel column chromatography (EtOAc/hexane). In all cases except for **6k**, the *Z*-isomers of **6** were eluted first and obtained as oil in a pure form. The last few fractions of **6** were gradually contaminated with the *E*-isomers of **6**. The yields combining all fractions of **6** and the isomeric ratios calculated by the NMR are listed in Table 1. In the next step, the pure *Z*-isomers of **6** were used in order to simplify the spectroscopic determination, although the oxidation of stereoisomeric mixtures of **6** could be carried out with similar efficiency. In the case of **6k**, the stereoisomers did not separate even on TLC.

### Oxidation of Sulfide with mCPBA

To a stirred solution of sulfide **5** or **6** (5 mmol) in $CHCl_3$ (25 mL) was added mCPBA (15 mmol) over 5 min at r.t. and the mixture was stirred overnight. To the resulting suspension was added aq $Na_2S_2O_3$ (1 M, 20 mL) and the solvent was removed in vacuo at r.t. The white powdery *m*-chlorobenzoic acid was triturated with toluene/hexane (1:4, 30 mL), filtered, and washed with toluene/hexane (1:4, 2 × 10 mL). The combined organic phase was washed with sat. $NaHCO_3$ (5 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by chromatography on silica gel (EtOAc/hexane) or recrystallization. Selected spectoscopic data are tabulated in Table 3.

### Reaction of 1 with Ethyl Isocyanoacetate

To a solution of sulfone (**1**, 3 mmol) and ethyl isocyanoacetate (0.66 mL, 6 mmol) in anhyd THF (6 mL) was added DBU (1.79 mL, 12 mmol) at r.t. After the mixture was stirred for 3 h, aq HCl (1 M, 15 mL) was added and the mixture was extracted with EtOAc (3 × 30 mL). The organic phase was washed with $H_2O$ (3 × 30 mL) and brine (30 mL), dried ($Na_2SO_4$) and concentrated. The residue was chromatographed on silica gel (EtOAc/hexane). Selected spectroscopic data are tabulated in Table 4.

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