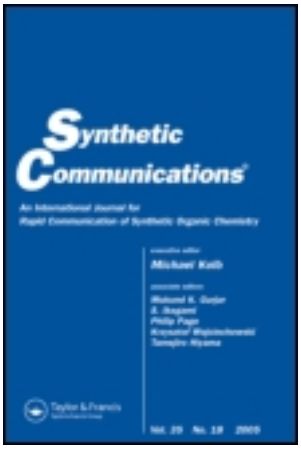

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Free Radical Cyclization of 1,3-Dicarbonyl Compounds Mediated by Manganese(III) Acetate with Alkynes and Synthesis of Tetrahydrobenzofurans, Naphthalene, and Trifluoroacetyl Substituted Aromatic Compounds

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Free Radical Cyclization of 1,3-Dicarbonyl Compounds Mediated by Manganese(III) Acetate with Alkynes and Synthesis of Tetrahydrobenzofurans, Naphthalene, and Trifluoroacetyl Substituted Aromatic Compounds

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Abstract: Furan derivatives were obtained from radical cyclizations of 1,3-dicarbonyl compounds mediated by $Mn(OAc)_3$ with phenyl acetylene **2a** (14–66% yields). Naphthalene derivates **4a** and **4b** were produced in the treatments with **2a**. In addition to these, trifluoroacetyl substituted naphthalene **4c**, benzofuran **4d**, and benzothien **4e** were obtained in the reactions of trifluoromethyl-1,3-dicarbonyls **(1 g–i)** with **2a**.

Keywords: Benzofuran, benzothien, 1,3-dicarbonyl, free radical cyclization, furan, manganese(III) acetate, naphthalene, trifluoroacetyl

It is widely known that the C–C bond is obtained by transition metal salts–mediated oxidative addition of organic compounds to unsaturated systems.[1] $Mn(OAc)_3$ is used effectively as a mediator in the inter- and intramolecular cyclizations for the synthesis of furans,[2–6] dihydrofurans,[7–9] lactones,[4] and natural products.[10–13] The addition of α-carbon radical generated in carbonyl compounds using $Mn(OAc)_3$ and cerium(IV) amonniumnitrate (CAN) to aromatics was first reported by Heiba et al.[14] Malonylation and nitromethylation of aromatic compounds are also known.[15–17]

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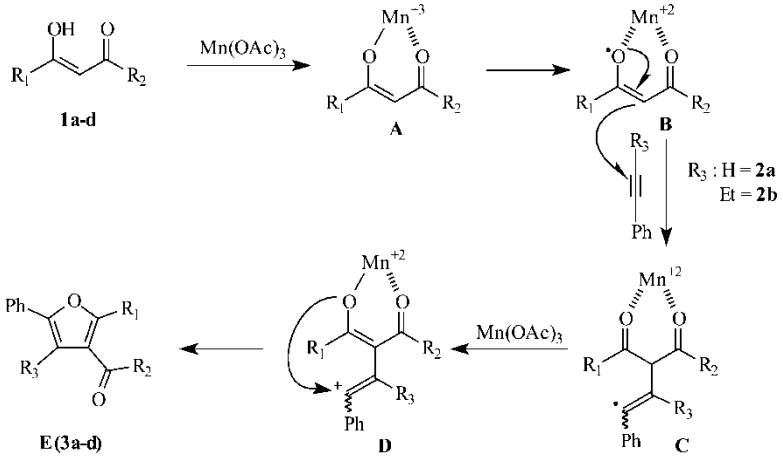
Many furans show biological activities, and furan derivatives are useful synthetic intermediates used in the synthesis of photochromic molecules, food additives, and pharmaceuticals.[18–20] Additionally, fluorinated molecules are widespread in pharmaceutical applications such as proteaz and phosphodiestereaz inhibitors, antiparasitic agents, anticancer compunds, antibacterials, and anastetics.[21,22] Here we studied $Mn(OAc)_3$-mediated addition of various 1,3-dicarbonyl compounds to alkynes and obtained furan, tetrahydrobenzofurans, naphthalens, and trifluoroacetyl substituted aromatic compounds, which are worth consideration.

We report a one-step synthesis of tetrahydrobenzofuran, naphthalens, and trifluoroacetyl substituted organic compounds by $Mn(OAc)_3$-mediated radical cyclization of 1,3-dicarbonyls **(1a–i)** with **2a** and **2b** (molar ratio 2 : 3 : 1, respectively). The best product yields were obtained at 80 °C in HOAc. After workup, all new products purified with preparative TLC were characterized by IR; ^1H, ^{19}F, and ^{13}C NMR; MS; and microanalysis, and the other products were characterized by ^1H NMR. All spectroscopic data are given in the experimental section.

In the radical cyclization, 1,3-dicarbonyls without aromatic groups **(1a–d)** and 1,3-dicarbonyls **(1e–i)** containing aromatic groups such as phenyl, 2-furyl, and 2-thienyl were used. Furan and tetrahydrobenzofurans were obtained in the $Mn(OAc)_3$-mediated treatments of **1a–d** with **2a** and **2b**. Recommended reaction mechanism is given in Scheme 1, and the results of the experiment are given in Table 1.

According to this mechanism, $Mn(OAc)_3$ with the enole forms of 1,3-dicarbonyls **(1a–d)** forms Mn(III)-enolate complex **A.** In this structure, Mn^{+3} is reduced to Mn^{+2} and an oxo radical **B** forms. Oxo radical changes into α-carbon radical, which is more stable, and this radical is added to



Scheme 1.

Table 1. Synthesis of furan and benzofuran derivatives

Entry	1,3-Dicarbonyl	R_1	R_2	Alkyne	Product and yield (%)[a]
1	**1a**	Me	OEt	**2a**	**3a** (14)
2	**1b**	$-CH_2CH_2CH_2-$		**2a**	**3b** (66)
3	**1b**	$-CH_2CH_2CH_2-$		**2b**	**3c** (50)
4	**1c**	$-CH_2CHPhCH_2-$		**2b**	**3d** (38)
5	**1d**	$-CH_2C(CH_3)_2CH_2-$		**2b**	**3e** (60)

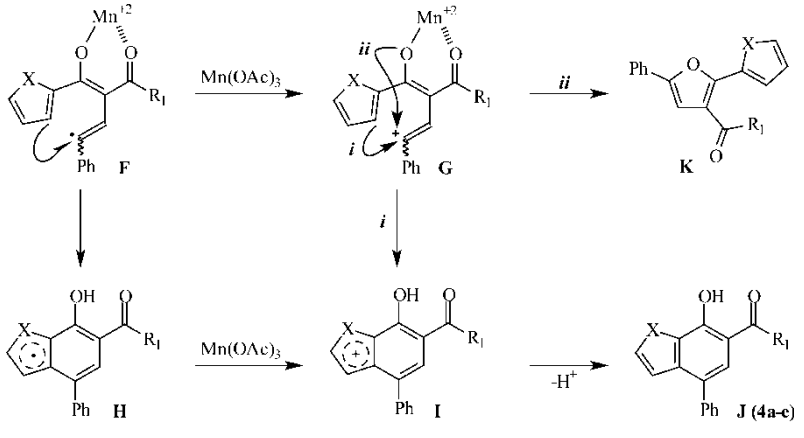
[a]Yield of isolated product based on the alkynes.

alkyne (**2a, 2b**), so **C** intermediate product gains. This intermediate product is oxidized to carbocation **D** with the equivalent $Mn(OAc)_3$, and furan derivatives **E (3a–d)** form intramolecular cyclization of oxanion.

We obtained **3a**[23–25] (14%) in the treatment of **1a** with **2a** with moderate yield, and the radical cyclization of **1b** with **2a** and **2b** gave tetrahydrobenzofurans **3b**[26] (66%) and **3c** (50%), respectively. Additionally, the reaction of **1d** with **2b** gave **3e** (60%) with a better yield. Because **2b** is more sterically hindered than **2a**, the reaction of **1b** with **2b** formed tetrahydrobenzofuran with lower yields than that of **2a** (entries 2, 3).

In the $Mn(OAc)_3$-mediated radical cyclizations of 1,3-dicarbonyl compounds **(1e–i)** containing aromatic groups with **2a**, we obtained benzofuran, benzothien, and naphthalene derivatives. The recommended reaction mechanism for formation of these compounds is given in Scheme 2 and the results of experiment are given in Table 2.

Intermediate product **F**, which is formed by the addition of α-carbon radical generated by 1,3-dicarbonyl compounds containing aromatic group



Scheme 2.

Table 2. Synthesis of benzothien, benzofuran, and naphthalene derivatives

Entry	1,3-Dicarbonyl	X	R_1	Product and yield (%)[a]
1	**1e**	–CH=CH–	Me	**4a** (44)
2	**1f**	–CH=CH–	Ph	**4b** (30)
3	**1g**	–CH=CH–	CF_3	**4c** (42)
4	**1h**	O	CF_3	**4d** (38)
5	**1i**	S	CF_3	**4e** (45)

[a]Yield of isolated product based on the alkynes.

(1e–i) mediated $Mn(OAc)_3$ to **2a**, can follow two ways. First, **H**, which is formed by the addition of the radical to aromatic group as electrophilic radical, produces carbocation intermediate product **I** by oxidizing the equivalent $Mn(OAc)_3$. **J (4a–e)** compounds are formed by removing a H^+ from this structure. Second, **F** is oxidized to carbocation **G** by the equivalent $Mn(OAc)_3$ directly, and this intermediate product can form **I** following path ***i*** or furans **K** following path ***ii***. Yet, furans were not formed in the treatments of **1e–i** with **2a** in our study. For this reason we believe that this mechanism forms **4a–e** compounds following the first way.

Although **4a**[27,28] was obtained with 44% yield, in the reaction of **1e** with **2a**, the treatment of **1f** with **2a** gave naphthalene derivative **4b**[28] with a lower yield (30%). Trifluoroacetyl substituted naphthalene (**4c**, 42%), benzofuran (**4d**, 38%), and benzothien (**4e**, 45%) compounds were obtained in the treatments of trifluoromethyl-1,3-dicarbonyls containing different aromatic groups **(1g–i)** with **2a**. Unknown products formed in the treatments of **1e–i** with **2b**.

Compounds **4a–c** were characterized by spectroscopic techniques and microanalysis. The characteristic coupling of these compounds in ^1H, ^{13}C, and ^{19}F NMR spectra are given later. The peaks at 12–14 ppm (s, -OH) in ^1H NMR spectra of **4a–e** disappeared during D_2O exchanges. Although H-5 protons of **4a** and **4b** appear as a singlet, the protons H-3 of **4c** and H-5 of **4d** and **4e** appear as quartet ($^4J_{H\text{-}F} = 2$ Hz) because of the coupling with CF_3. Similarly, the peak of $-CF_3$ in ^{19}F NMR spectra of **4c–e** resonated as a doublet ($^4J_{F\text{-}H} = 2$ Hz). The chemical shift values of carbonyl groups at **4a** and **4b** in ^{13}C NMR spectra were 205 ppm (s), and 202 ppm (s), respectively. Additionally, these values of the carbonyl groups at **4c–e** were 185–189 ppm quartet ($^2J_{C\text{-}F} = 35$ Hz).

EXPERIMENTAL

Melting points were determined on Gallencamp capillary melting-point apparatus. IR spectra (KBr disc, $CHCl_3$) were obtained with a Matson 1000

FT-IR in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. ^{1}H (400 MHz), ^{19}F (376 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX 400-MHz high-performance digital FT-NMR, in $CDCl_3$ solution using TMS as internal standard. The electron impact mass spectra (EIMS 70 eV) were measured on Shimadzu GC-17A/GC-MS-QP5000 spectrophotometer. Microanalyses were performed on a Leco 932 CHNS-O instrument.

Manganese(III) acetate dihydrate (98%) was prepared by an electrochemical method according to the literature.[29] All the alkynes and trifluoromethyl-1,3-dicarbonyl compounds were purchased from ABCR; the other 1,3-dicarbonyl compounds and preparative silica gel (PF 254–366 nm) were purchased from Merck.

General Procedure

A solution of manganese(III) acetate (6 mmol, 1.61 g) in 30 mL of glacial acetic acid was heated under nitrogen atmosphere at 80 °C until it dissolved. After $Mn(OAc)_3$ was dissolved completely, the solution was cooled down to 50 °C. A solution of 1,3-dicarbonyl compound (4 mmol) and alkyne (2 mmol) in 5 mL of acetic acid was added to this mixture. The reaction finished when the dark brown color of the solution disappeared. Acetic acid was evaporated out under reduced pressure. Water was added to the residue and extraction was performed with $CHCl_3$ or EtOAc (3×20 mL). The combined organic extracts were neutralized with satd. $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by TLC (silica gel PF 254–366 nm) eluting with hexane–EtOAc (4 : 1).

2-Methyl-5-phenyl-furan-3-carboxylicacid ethylester (3a): yellow oil; ^{1}H NMR, δ (ppm): 1.39 (t, 3H, $J = 7.1$ Hz), 2.67 (s, 3H), 4.34 (q, 2H, $J = 7.1$ Hz), 6.91 (s, 1H), 7.28 (tt, 1H, $J = 7.4$ and 1.2 Hz), 7.40 (td, 2H, $J = 7.4$ and 1.5 Hz), 7.66 (dd, 2H, $J = 8.3$ and 1.2 Hz).

2-Phenyl-6,7-dihydro-5H-benzofuran-4-one (3b): colorless solid, mp 135–136 °C; IR, υ_{max}: 3080–3050, 2970, 1675 (C═O), 1600, 1450–1380, 1130 cm^{-1}; ^{1}H NMR, δ (ppm): 2.23 (m, 2H), 2.56 (t, 2H, $J = 6.4$ Hz), 2.98 (t, 2H, $J = 6.3$ Hz), 6.91 (s, 1H), 7.31 (t, 1H, $J = 7.5$ Hz), 7.41 (t, 2H, $J = 7.5$ Hz), 7.67 (d, 2H, $J = 7.5$ Hz); ^{13}C NMR, δ (ppm): 22.9, 23.8, 38.0, 101.2, 123.3, 124.3, 128.4, 129.2, 130.2, 154.6, 167.1, 194.9 (C═O); MS (m/z, %): 213 (M^{+1}, 0.2), 212 (M^{+}, 2.71), 104 ($COC_6H_5^{+}$, 19.98), 76 ($C_6H_5^{+}$, 28.87), 50 (100), 41 (68.86); anal. calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66; found: C, 79.30; H, 5.68.

3-Ethyl-2-phenyl-6,7-dihydro-5H-benzofuran-4-one (3c): colorless solid, mp 88–90 °C IR, υ_{max}: 3050, 2980, 1685 (C═O), 1450, 1070–1020 cm^{-1};

^{1}H NMR, δ (ppm): 1.30 (t, 3H, $J = 7.4$ Hz), 2.21 (m, 2H), 2.53 (t, 2H, $J = 6.5$ Hz), 2.90 (m, 4H), 7.33 (tt, 1H, $J = 7.4$ and 1.7 Hz), 7.45 (td, 2H, $J = 7.5$ and 1.7 Hz), 7.61 (dd, 2H, $J = 7.5$ and 1.4 Hz); ^{13}C NMR, δ (ppm): 14.9, 18.1, 22.9, 24.0, 30.1, 38.9, 121.8, 121.9, 126.3, 127.9, 129.0, 131.0, 148.9, 166.7, 195.7 (C═O); MS, (m/z, %): 241 (MH^+, 9.67), 240 (M^+, 68.02), 225 (M^+-CH_3, 8.14), 105 ($C_6H_5CO^+$, 31.69), 77 ($C_6H_5^+$, 100.00), 41.08 (52.62); Anal. calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6,71; found: C, 79.94; H, 6.74.

3-Ethyl-2,6-diphenyl-6,7-dihydro-5H-benzofuran-4-one (3d): colorless solid, mp 138–139 °C; IR, υ_{max}: 3000, 2980, 1685 (C═O), 1450, 1060 cm^{-1}; ^{1}H NMR, δ (ppm): 1.33 (t, 3H, $J = 7.4$ Hz), 2.80 (m, 2H), 2.94 (q, 2H, $J = 7.4$ Hz), 3.12 (dd, 1H, $J = 17.1$ and 11.1 Hz), 3.24 (dd, 1H, $J = 17.1$ and 5.3 Hz), 3.62 (m, 1H), 7.40–7.50 (m, 8H, arom.), 7.62 (dd, 2H, $J = 7.9$ and 1.3 Hz); ^{13}C NMR, δ (ppm): 14.9, 18.1, 31.8, 41.6, 46.2, 121.8, 126.4, 127.2, 127.6, 128.1, 129.1, 129.3, 130.9, 143.0, 149.5, 165.9, 194.2 (C═O); MS, (m/z, %): 317 (MH^+, 2.35), 316 (M^+, 11.04), 211 (M^+-C_6H_5CO, 6.98), 183 ($M^+-C_6H_5CO-C_2H_5$, 12.66), 105 ($C_6H_5CO^+$, 27.60), 102 (89.61), 77 ($C_6H_5^+$, 100.00); anal. calcd. for $C_{22}H_{20}O_2$: C, 83.54; H, 6.33; found: C, 83.62; H, 6.36.

3-Ethyl-6,6-dimethyl-2-phenyl-6,7-dihydro-5H-benzofuran-4-one (3e): pale yellow oil; IR, υ_{max}: 3050, 2980, 1685 (C═O), 1450, 1070–1020 cm^{-1}; ^{1}HNMR, δ (ppm): 1.18 (s, 6H, -CH_3), 1.29 (t, 3H, $J = 7.4$ Hz, -CH_3), 2.41 (s, 2H), 2.79 (s, 2H), 2.89 (q, 2H, $J = 7.4$ Hz, -CH_2), 7.33 (t, 1H, $J = 7.3$ Hz), 7.44 (t, 2H, $J = 7.6$ Hz), 7.6 (dd, 2H, $J = 7.7$ and 1.1 Hz); ^{13}C NMR, δ (ppm): 14.9, 18.0, 26.8, 29.0, 35.5, 38.3, 53.1, 121.6, 126.2, 127.4, 129.0, 130.5, 134.0, 149.3, 166.1, 195.5 (C═O); MS, (m/z, %): 269 (MH^+, 1.06), 268 (M^+, 4.92), 165 (M^+-2CH_3 $-C_6H_5$, 1.68), 152 ($M^+-3CH_3-C_6H_5$, 1.25), 104 ($COC_6H_5^+$, 17.97), 77 ($C_6H_5^+$, 54.11), 41 (100.00); anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51; found: C, 80.51; H, 7.48.

1-(1-Hydroxy-4-phenyl-naphthalen-2-yl)-ethanone (4a): pale yellow solid, mp: 181–182 °C; IR, υ_{max}: 3020, 1635 (C═O), 1600, 1500, 1450–1400, 1250 cm^{-1}; ^{1}H NMR, δ (ppm): 2.73 (s, 3H, -CH_3), 7.45 (m, 5H), 7.55 (m, 3H), 7.78 (dd, 1H, $J = 7.7$ and 1.7 Hz), 8.57 (dd, 1H, $J = 7.6$ and 1.7 Hz), 13.98 (s, 1H, -OH); ^{13}C NMR, δ (ppm): 27.8, 113.6, 125.6, 126.2, 126.4, 126.7, 128.2, 129.3, 130.7, 131.0, 131.8, 136.7, 140.9, 162.7, 205.3 (C═O); MS, (m/z, %): 263 (MH^+, 17.89), 262 (M^+, 100.00), 247 (M^+-CH_3, 63.60), 220 (M^+-CH_3CO, 1.94), 202 ($M^+-OH-CH_3CO$, 5.20), 189 (32.64), 186 ($M^+-C_6H_5$, 7.64), 77 ($C_6H_5^+$, 2.56), 43 (CH_3CO^+, 100.00); anal. calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38; found: C, 82.34; H, 5.41.

(1-Hydroxy-4-phenyl-naphthalen-2-yl)-phenyl-methanone (4b): yellow solid, mp 159–160 °C; IR, υ_{max}: 3030, 1615 (C═O), 1600, 1500,

1450–1380, 1250 cm^{-1}; ^1H NMR, δ (ppm): 7.42–7.62 (m, 11H), 7.76 (dd, 2H, $J = 7.6$ and 1.6 Hz), 7.85 (dd, 1H, $J = 7.1$ and 2.5 Hz), 8.65 (dd, 1H, $J = 7.2$ and 2.6 Hz), 13.98 (s, 1H, –OH); ^{13}C NMR, δ (ppm): 113.0, 125.6, 126.4, 126.8, 128.1, 128.1, 128.6, 129.3, 129.3, 129.6, 129.9, 131.0, 131.3, 131.4, 132.6, 136.6, 139.0, 140.8, 164.2, 202.4 (C═O); MS, (m/z, %): 325 (MH^+, 2.82), 324 (M^+, 18.83), 246 (M^+ -C_6H_5, 4.90), 218 (M^+ -COC_6H_5, 1.91), 189 (22.22), 105 ($COC_6H_5^+$, 46.91), 77 ($C_6H_5^+$, 100.00); anal. calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97; found: C, 85.09; H, 5.04.

2,2,2-Trifluoro-1-(1-hydroxy-4-phenyl-naphthalen-2-yl)-ethanone (4c): pale yellow solid, mp 92–93 °C; ^1H NMR, δ (ppm): 7.49 (m, 5H), 7.61 (m, 2H), 7.68 (td, 1H, $J = 7.6$ and 1.8 Hz), 7.81 (dd, 1H, $J = 7.2$ and 1.1 Hz), 8.59 (dd, 1H, $J = 8.4$ and 1.1 Hz), 12.90 (s, 1H, –OH); ^{13}C NMR, δ (ppm): 107.94, 117.12 (q, $^1J_{C\text{-}F} = 289$ Hz), 123.53, 125.20, 125.35, 126.50, 126.86, 127.96, 128.81, 130.27, 132.21, 132.65, 137.02, 139.45, 165.96, 184.23 (q, $^2J_{C\text{-}F} = 35.5$ Hz); ^{19}F NMR, δ (ppm): −69.6 (d, $^5J_{F\text{-}H} = 2$ Hz, $-CF_3$); MS, (m/z, %): 317 (MH^+, 13.31), 316 (M^+, 72.78), 246 (M^+ $-CF_3$, 85.39), 219 (M^+ $-COCF_3$, 8.28), 189 (60.00), 105 ($C_6H_5CO^+$, 12.09), 94 ($C_6H_5OH^+$, 100.00), 77 ($C_6H_5^+$, 12.15), 69.05 (CF_3^+, 29.07), 43 (CH_3CO^+, 33.67); anal. calcd. for $C_{18}H_{11}F_3O_2$: C, 68.36; H, 3.51; found: C, 68.40; H, 3.44.

2,2,2-Trifluoro-1-(4-hydroxy-7-phenyl-benzofuran-5-yl)-ethanone (4d): pale yellow solid, mp: 103–104 °C; IR, υ_{max}: 3030, 1615 (C═O), 1600, 1250, 750, 703 cm^{-1}; ^1HNMR, δ (ppm): 7.00 (d, 1H, $J = 2.0$ Hz), 7.44 (tt, 1H, $J = 7.1$ and 1.4 Hz), 7.52 (m, 4H), 7.68 (q, 1H, $^5J_{H\text{-}F} = 2.1$ Hz, H-5), 7.93 (d, 1H, $J = 2.0$ Hz), 11.78 (s, 1H); ^{13}C NMR, δ (ppm): 107.6, 110.3, 116.6 (q, $^1J_{C\text{-}F} = 289.8$ Hz, CF_3), 123.21 (q, $^4J_{C\text{-}F} = 3.7$ Hz, C-5), 127.0, 127.9, 128.2, 135.9, 139.2, 128.8, 150.3, 184.5 (d, $^2J_{C\text{-}F} = 35.9$ Hz, C═O); ^{19}F NMR, δ (ppm): −69.7 (d, $^5J_{F\text{-}H} = 2.2$ Hz, $-CF_3$); MS, (m/z, %): 307 (MH^+, 7.23), 306 (M^+, 45.76), 237 (M^+ -CF_3, 100.00), 209 (M^+ -$COCF_3$, 6.66), 118 (M^+ $-OH$ $-COCF_3$ -C_6H_5, 37.40), 97 ($COCF_3^+$, 4.14), 77 ($C_6H_5^+$, 21.09), 69 (CF_3^+, 7.57); anal. calcd. for $C_{16}H_9F_3O_3$: C, 62.75; H, 2.96; found: C, 62.81; H, 2.88.

2,2,2-Trifluoro-1-(4-hydroxy-7-phenyl-benzo[b]thiophen-5-yl)-ethanone (4e): yellow solid, mp 102–103 °C; IR, υ_{max}: 3030, 1600 (C═O), 1600, 1250, 745, 700 cm^{-1}; ^1H NMR, δ (ppm): 7.51 (m, 2H), 7.54 (m, 4H), 7.71 (q, 1H, $^5J_{H\text{-}F} = 2.2$ Hz, H-5), 7.86 (d, 1H, $J = 5.4$ Hz), 12.13 (s, 1H, –OH); ^{13}C NMR, δ (ppm): 109.3, 117.5 (q, $^1J_{C\text{-}F} = 289.5$ Hz, $-CF_3$), 125.4, 126.4 (q, $^4J_{C\text{-}F} = 3.8$ Hz, C-5), 128.7, 129.6, 129.8, 131.4, 135.4, 140.1, 147.3, 161.6, 185.1 (q, $^2J_{C\text{-}F}$ =35.5 Hz, C═O); ^{19}F NMR, δ (ppm): −70.51 (d, $^5J_{F\text{-}H} = 2.0$ Hz, $-CF_3$); MS, (m/z, %): 323 (MH^+, 18.36), 322 (M^+, 100.00), 303 (M^+ $-H_2O$, 1.99), 253 (M^+ $-CF_3$, 99.42), 225 (M^+ $-COCF_3$, 3.61), 195 (42.30), 152 (19.58), 97 ($COCF_3^+$, 39.21), 77 ($C_6H_5^+$, 5.59), 69 (CF_3^+, 12.10); anal. calcd. for $C_{16}H_9F_3O_2S$: C, 59.63; H, 2.81; S, 9.95; found: C, 59.67; H, 2.88; S, 9.87.

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