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New Indole Derivatives. Synthesis of 3-Acyl-1-carbethoxy-2-trifluoromethanesulfonylindoles and of Substituted 2-vinylindoles.

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Abstract. 3-Acyl-1-carbethoxy-2-trifluoromethanesulfonylindoles **6** and 3-acyl-2-vinylindoles **7** are synthesized from 3-[(1-chloro)alkylidene]indol-2(3H)-ones **2** via 1-carbethoxy-3-[(1-dimethylamino) alkylidene]indol-2(3H)-ones **4**.

Indoles bearing unsaturated groups at position 2 are of great interest as they are present as subunits in biologically active and naturally occuring compounds.[1]

An efficient entry to some rapresentatives of this class has been recently reported starting from a 2-(tributylstannyl)-1H-indole via Pd-catalyzed reaction with a variety of organic halides.[2] An alternative route for the synthesis of these important compounds may be, in principle, also the Pd-catalyzed reaction between a 2-indolyltriflate and organostannanes derivatives.

The importance of aryl triflates in transition metal catalyzed cross-coupling reactions with a variety of organometallic reagents, e.g. organostannanes,[3] is well known. Despite the great potential interest, the synthesis and reactivity of heteroaryltriflates has been considered only occasionally.[4] In the indole field, the synthesis[5] and reactivity[6] of the 1-(phenylsulfonyl)indol-3-yl trifluoromethane sulfonate have been reported. A single example exist of 2-indolyltriflate. The synthesis of 1-(trifluoromethanesulfonyl)indol-2-yl trifluoromethanesulfonate is known,[7] but its reaction with organostannane derivatives has not been considered.

In the present paper, we report on a new synthesis of the previously unknown 3-acyl-1-carbethoxy-2-trifluoromethanesulfonylindoles **6**, starting from the 3-[(1-hydroxy)alkylidene] indol-2(3H)-ones **1**.

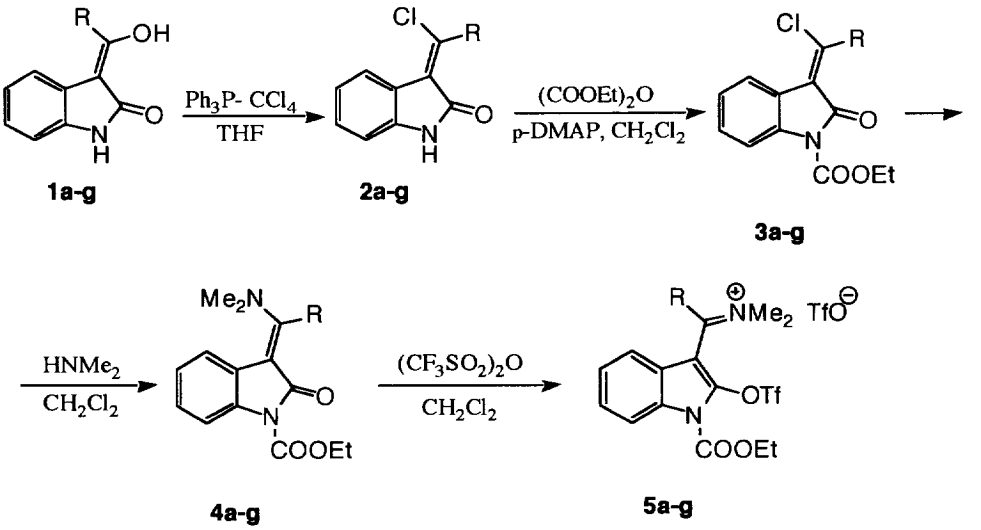
Compounds **1** are easily prepared by condensation of the indol-2(3H)-one, with the appropriate ester following the reported methods.[8-10] The 3-[(1-chloro)alkylidene]indol-2(3H)-ones **2** are prepared, from compounds **1**, by reaction with Ph_3P-CCl_4 in anhydrous THF.[11]

Compounds **3a-c** are prepared from **2a-c** by reaction with ethyl chloroformate and triethylamine,whereas **3d-g** are obtained from **2d-g**, by reaction with ethyl pyrocarbonate in the presence of p-dimethylamino pyridine. The use of the pyrocarbonate allows to avoid the competing formation of the corresponding 2-ethoxycarbonyloxy-3-ethynylindoles.[11]

The stereochemistry of compounds **3a-g** is assumed to be the same of the starting compounds **2a-g**. A complete elucidation of the stereochemistry of compounds **2** has been already published.[11]

The reaction of the chloroderivatives **3a-g** with ethanolic dimethylamine, in dichloromethane, affords the corresponding dimethylamino compounds **4a-g** in high yield. Evidence (see later) strongly favours the indicated configuration (Scheme 1).

Scheme 1



1a-g **2a-g** **3a-g** **4a-g** **5a-g**

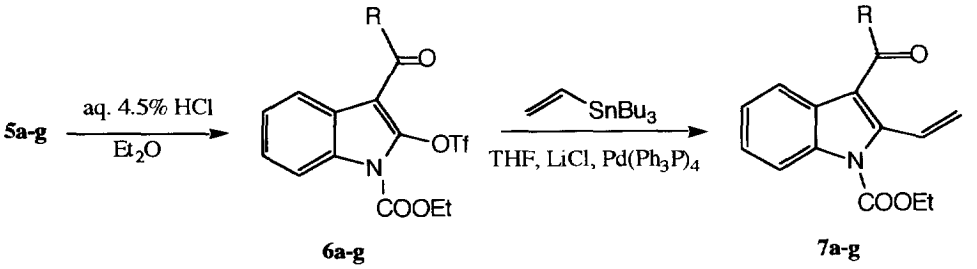
1-5	R	1-5	R	1-5	R
a	H	**b**	COOEt	**c**	$CH(OMe)_2$
d	CH_2Ph	**e**	CH_2OMe	**f**	Me
g	Et				

The key synthetic step of our synthesis is the reaction of the dimethylamino compounds **4a-g** with the trifluoromethanesulfonyl anhydride in dichloromethane or in dichloromethane-diethyl ether solution. From this reaction, the iminium salts **5a-g** are obtained as pure products directly by crystallization from the reaction mixture (Scheme 1, Table 1). The hydrolysis of the salts **5a-g** to the 3-acyl-1-carbethoxy-2-trifluoromethane sulfonylindoles **6a-g** is achieved with 4.5% HClaq.-Et_2O (Scheme 2, Table 1). The reaction of the 2-indolyltriflates **6a-g**, in THF and in the presence of $Pd(Ph_3P)_4$ and LiCl, with vinyltributyltin affords, in good yield, the corresponding 2-vinyl derivatives **7a-g** (Scheme 2, Table 1).

The successful preparation of the triflates **6** from the salts **5** suggested to us the possibility to obtain 2-indolyltriflates of the type A (Scheme 3) from the iminium salts **5d-g**, were allylic acid hydrogens are present, by reaction with triethylamine. When a dichloromethane solution of the salts **5f,g** is treated with triethylamine,

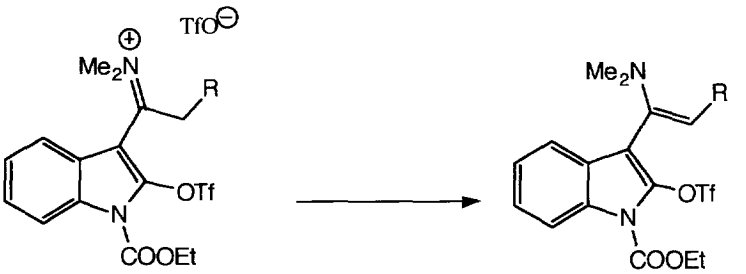
the new deep yellow compounds **8f,g** are obtained in good yield (Scheme 4). From **8d,e** only intractable tars are obtained.

Scheme 2



6a-g **7a-g**

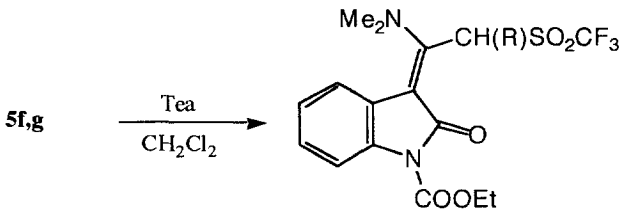
Scheme 3



5d-g **A**

d R = Ph **e** R = OMe **f** R = H **g** R = Me

Scheme 4

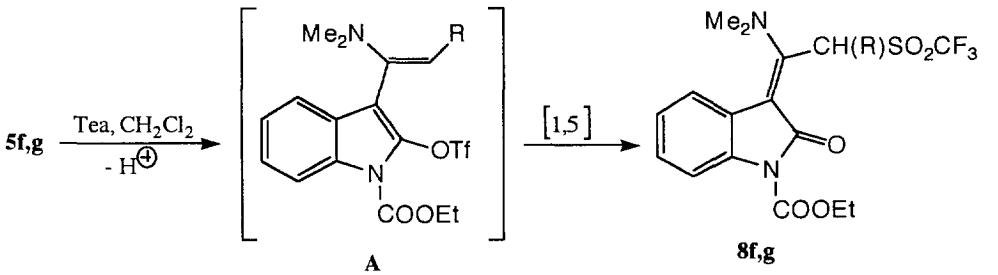


8f,g

The structure of new compounds is assigned on the basis of analytical and spectroscopic data. In the ^{1}H-nmr spectrum of compound **8f**, the allylic methylene hydrogens give rise to a broad singlet at 5.78 δ, whereas in compound **8g** the allylic hydrogen gives a quartet at 7.76 δ. All these hydrogens exchange easily with D_2O. The presence of the quartet at 7.76 δ suggests to us E stereochemistry for compound **8g**, and hence for compound **8f**. This was verified by NOE experiments that confirm the proximity of the aromatic hydrogen in position 4 with the methyl hydrogens of the dimethylamino group in compound **8g**. This result allows also to hypothesize E stereochemistry for all compounds **4**. The formation of compounds **8** from the corresponding

iminium salts **5**, suggest the formation of an intermediate 3-vinylindole A, from which the final compound arise via an [1,5] shift of the trifluoromethylsulfonyl group (Scheme 5). The spectral data of new compounds are reported in Table 2.

Scheme 5



EXPERIMENTAL

Melting points were determined on a Buchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 instrument, in nujol mull for solids and as liquid film for oils. ^{1}H-NMR were recorded on a Varian Gemini 200 spectrometer in $CDCl_3$ solution unless otherwise stated. Colomn chromatography was performed on Kieselgel Merck 60, 0.063-0.2 mm. Evaporation was carried out under vacuum in a rotary evaporator.

Compounds **1a**,[12] **1b**,[8] **1d**,[10] **1e**,[9] **1f**,[8] **1g**,[9] **2a**,[13] **2d-g**,[11] and **3d**[11] were prepared according to the literature procedure.

3-[(2,2-Dimethoxy-1-hydroxy)ethylidene]indol-2(3H)-one ***1c.***

Indol-2(3H)-one (5.34g, 40 mmol) was added under stirring, to a warm NaOEt solution, prepared from Na (1.84 g, 80 mmol) and absolute EtOH (60 mL).

To this solution, methyl dimethoxyacetate (8 mL, 65 mmol) was then added. The mixture was refluxed under stirring for 2h and the formed sodium salt filtered after cooling at 0°C for 30 min. A water (90 mL) solution of the sodium salt was acidified with 16% HCl, the acid filtered and crystallized (Table 1).

Compounds ***2b,c*** *from Compounds* ***1b,c.***

The compound **1** (10 mmol) was dissolved in anhydrous THF (70 mL) and Ph_3P (5.25 g, 20 mmol) and CCl_4 (5 mL) were added. The solution was heated to reflux for the reported time (Table 1). The residue obtained from the solvent evaporation, was purified by silica gel column chromatography and crystallized (Table 1).

Compounds ***3a-c*** *from Compounds* ***2a-c.***

The compound **3** (10 mmol) was suspended in CH_2Cl_2 (50 mL) and then ethyl chloformate (1.44 mL, 15 mmol) was added. The stirred reaction mixture was cooled at 5°C and a solution of Et_3N (2.3 mL, 20 mmol) in CH_2Cl_2 (10 mL) was added. After being warmed for the reported time (Table 1), the reaction mixture was

washed with H_2O (50 mL). The organic layer was dried (Na_2SO_4), filtered and evaporated. The residue was purified by crystallization (Table 1).

*Compounds **3d-g** from Compounds **2d-g**.*

The compound **3** (10 mmol) was dissolved in CH_2Cl_2 (70 mL) and diethyl pyrocarbonate (2.2 mL, 20 mmol) and p-dimethylaminopyridine (50 mg) were added. After 10 min at room temperature, the mixture was evaporated, the residue purified by silica gel column chromatography and crystallized (Table 1).

*Compounds **4a-g** from Compounds **3a-g**.*

The compound **3** (10 mmol) was dissolved in CH_2Cl_2 (40 mL) and dimethylamine in EtOH (33%) (5.4 mL, 30 mmol) was then added. After 5 min, the reaction mixture was washed with water. the organic layer was dried (Na_2SO_4), filtered and evaporated. The residue was crystallized (Table 1).

*Compounds **5a-g** from Compounds **4a-g**.*

The compound **4** (10 mmol) was dissolved in a CH_2Cl_2-Et_2O mixture [for **4a,b,f** CH_2Cl_2 (20 mL), Et_2O (20 mL); for **4c,g** CH_2Cl_2 (10 mL), Et_2O (30 mL); for **4d,e** CH_2Cl_2 (5 mL), Et_2O (40 mL)]. To the solution, cooled at 0-5 °C, the trifluoromethanesulfonic anhydride (2.2 mL, 13 mmol) was then added. After 20 min at 0-5 °C, the crystallized product was filtered and washed with Et_2O.

*Compounds **6a-g** from Compounds **5a-g**.*

The finely powdered salt **5** (5 mmol) was suspended in Et_2O (30 mL) and then 4.5% HCl (40 mL) was added. The mixture was stirred to the complete salt solution. The organic layer was dried (Na_2SO_4), filtered and evaporated. The residue was crystallized or purified by silica gel column chromatography (Table 1).

*3-Acyl-1-ca; bethoxy-2-vinylindoles **7a-g** from **6a-g**.*

Compound **6** (1 mmol) was dissolved in anhydrous THF (15 mL). To this solution, LiCl (135 mg, 3.2 mmol), $Pd[(Ph)_3P]_4$ (23 mg, 0.02 mmol) and vinyltributyltin (0.32 mL, 1.1 mmol) were then added. After the reported time (Table 1), the reaction mixture was evaporated, the residue purified by silica gel column chromatography and crystallized (Table 1).

*Compounds **8f,g** from Compounds **5f,g**.*

Compound **5** (1 mmol) was dissolved in CH_2Cl_2 (20 mL) and, after cooling at 0-5 °C, triethylamine (0.28 mL, 2 mmol) was added under stirring. The reaction mixture was then evaporated, purified by silica gel column chromatography and crystallized (Table 1).

Table 1. New Compounds Prepared

Product[a]	Reaction Time (h)	Yield (%)	Eluent[b]	mp(°C) (solvent)
1c	2	84	--	146-148 (acetone-Et_2O)
2b	3	75	Hx-Et_2O (1:1)	159-160 (Et_2O-Hx)
2c	4	60	CH_2Cl_2-Et_2O (20:1)	118-120 (Et_2O)
3a	0.5	78	Hx-CH_2Cl_2 (1:1)	115-117 (CH_2Cl_2-Et_2O)
3b	0.5	89	Hx-CH_2Cl_2 (1:1)	90-92 (Et_2O-Hx)
3c	0.5	88	--	97-99 (Et_2O)
3e	0.5	93	Hx-CH_2Cl_2 (1:1)	67-69 (Et_2O-Hx)
3f	0.5	91	Hx-CH_2Cl_2 (1:1)	97-99 (Et_2O-Hx)
3g	0.5	81	Hx-CH_2Cl_2 (1:1)	69-70 (Et_2O-Hx)
4a	0.1	95	--	74-75 (Et_2O)
4b	0.1	92	--	106 (Et_2O-Hx)
4c	0.1	97	--	oil
4d	0.1	92	--	105-107 (Et_2O)
4e	0.1	95	--	oil
4f	0.1	79	--	125-127 (CH_2Cl_2-Et_2O)
4g	0.1	95	--	73-75 (Et_2O-Hx)
5a	1	89	--	132 dec.
5b	0.5	86	--	115-117 dec.
5c	1	81	--	125-126 dec.
5d	1	85	--	128-130 dec.
5e	0.5	83	--	99-100 dec.
5f	1	91	--	128-129 dec.
5g	1	90	--	119-121 dec.
6a	0.5	83	Hx-CH_2Cl_2 (1:2)	88-90 (Et_2O-Hx)
6b	0.1	97	--	60-61 (pentane)
6c	0.5	88	--	45-46 (Hx)
6d	0.5	88	Hx-CH_2Cl_2 (1.5:1)	75-77 (Hx)
6e	0.5	67	Hx-CH_2Cl_2 (1:2)	98-99 (Et_2O-Hx)
6f	0.3	91	Hx-CH_2Cl_2 (1:1)	103-104 (Et_2O-Hx)
6g	0.3	92	Hx-CH_2Cl_2 (1:1)	82-83 (Et_2O-Hx)
7a	1.5[c]	65	Hx-CH_2Cl_2 (1:2)	93-94 (Et_2O-Hx)
7b	1.5[c]	82	Hx-CH_2Cl_2 (1:1)	78-79 (Hx)

7c	1.5[c]	89	Hx-CH_2Cl_2 (1:2)	54-55 (Hx)
7d	0.5[d]	90	Hx-CH_2Cl_2 (1:2)	44-45 (Hx)
7e	1[d]	76	CH_2Cl_2-Et_2O (30:1)	49-50 (Hx)
7f	0.5[d]	92	Hx-CH_2Cl_2 (1:1)	36 (Hx)
7g	0.5[d]	82	--	71-73 (Et_2O-Hx)
8f	0.1	65	CH_2Cl_2-Et_2O (20:1)	174-176 (CH_2Cl_2-Et_2O)
8g	0.1	84	--	129-131 (CH_2Cl_2-Et_2O)

[a] Satisfactory microananyses obtained: C $\pm$ 0.21, H $\pm$ 0.14, N $\pm$ 0.17. [b] Hx: hexane. [c] The reaction was carried out at room temperature. [d] The reaction was carried out at 50 °C.

Table 2. Spectral Data of New Compounds

Product	IR (Nujol or film) ν cm^{-1}	^{1}H-NMR δ, J (Hz)
1c	3280,1680, 1645	3.50 (6H, s), 5.37 (1H, s), 6.98 (1H, m), 7.07 (1H, m), 7.18 (1H, m), 7.61 (1H, m), 8.72 (1H, bs)[a]
2b	3175, 3125, 1717, 1701	1.41 (3H, t, 7.2), 4.45 (2H, q, 7.2), 6.85 (1H, d, 7.9), 7.07 (1H, dt, 1.1, 7.7), 7.32 (1H, dt, 1.2, 7.7), 7.97 (1H, d, 7.7), 8.07 (1H, bs)[a]
2c	3250, 1702, 1605	3.54 (6H, s), 6.70 (1H, s), 6.86 (1H, d,7.7), 7.08 (1H, dt, 1.1, 7.7), 7.31 (1H, dt, 1.2, 7.7), 8.02 (1H, bs)[a], 8.20 (1H, d, 8.0)
3a	1757, 1735, 1720sh	1.46 (3H, t, 7.1), 4.50 (2H, q, 7.1), 7.24 (1H, m), 7.42 (1H, m), 7.97 (1H, bd, 7.7), 8.10 (1H, bd, 7.7)
3b	1755, 1722, 1620	1.43 (6H, m), 4.45 (4H, m), 7.24 (1H, dt, 1.1, 7.7), 7.46 (1H, dt, 1.4, 7.8), 7.98 (1H, bd, 7.7), 8.13 (1H, dd, 1.4, 7.7)
3c	1749, 1737, 1617	1.46 (3H, t, 7.1), 3.52 (6H, s), 4.49 (2H, q, 7.1), 6.60 (1H, s), 7.21 (1H, bt, 7.7), 7.40 (1H, bt, 7.7), 7.40 (1H, bt, 7.7), 7.91 (1H, d, 8.2), 8.33 (1H, d, 7.8)
3e	1790, 1740, 1619	1.46 (3H, t, 7.1), 3.44 (3H, s), 4.49 (2H, q, 7.1), 5.00 (2H, s), 7.22 (1H, t, 7.5), 7.40 (1H, t, 8.0), 7.94 (1H, d, 8.2), 8.32 (1H, d, 7.2)
3g	1743, 1730, 1610	1.31 (3H, t, 7.4), 1.48 (3H, t, 7.2), 3.38 (2H, q, 7.4), 4.51 (2H, q, 7.2), 7.20 (1H, t, 8.2), 7.37 (1H, t, 7.7), 7.96 (1H, d, 7.9), 8.28 (1H, d, 8.1)

4a	1709, 1690	DMSO: 1.34 (3H, t, 7.1), 3.40 (6H, m), 4.34 (2H, q, 7.1), 7.02 (2H, m), 7.40 (1H, m), 7.65 (1H, m), 7.81 (1H, s)
4b	1723, 1710	1.24-1.45 (6H, m), 3.14 (3H, s), 3.26 (3H, s), 4.45 (4H, m), 6.86-7.19 (3H, m), 7.90 (1H, m)
4c	1758, 1718, 1685	1.47 (3H, t, 7.1), 3.26 (3H, s), 3.45 (6H, s), 3.54 (3H, s), 4.51 (2H, q, 7.1), 5.61 (1H, s), 6.68 (1H, m), 7.05 (2H, m), 7.89 (1H, m)
4d	1756, 1714, 1696	1.47 (3H, t, 7.1), 3.20 (6H, bs), 4.36 (2H, bs), 4.51 (2H, q, 7.1), 6.90-7.39 (8H, m), 7.93 (1H, d, 9.2)
4e	1752, 1710, 1685	1.49 (3H, t, 7.1), 3.35 (6H, m), 3.53 (3H, s), 4.49 (2H, q, 7.1), 4.50 (2H, s), 7.05 (3H, m), 7.88 (1H, m)
4f	1700, 1680	1.45 (3H, t, 7.2), 2.59 (3H, s), 3.30 (6H, bs), 4.48 (2H, q, 7.2), 7.06 (3H, m), 7.92 (1H, m)
4g	1710, 1690	1.31 (3H, t, 7.6), 1.46 (3H, t, 7.0), 3.02 (2H, q, 7.6), 3.28 (6H, s) 4.50 (2H, q, 7.0), 7.09 (3H, m), 7.93 (1H, m)
5a	1758, 1678	1.55 (3H, t, 7.2), 3.80 (3H, s), 4.10 (3H, s), 4.66 (2H, q, 7.2), 7.51-7.63 (2H, m), 8.04 (1H, m), 8.19 (1H, m), 9.26 (1H, s)
5b	1760, 1738, 1642	1.39 (3H, t, 7.1), 1.55 (3H, t, 7.1), 3.95 (3H, s), 4.15 (3H, s), 4.56 (2H, q, 7.1), 4.66 (2H, q, 7.1), 7.59 (2H, m), 7.96 (1H, m), 8.23 (1H, m)
5c	1761, 1658	1.55 (3H, t, 7.0), 3.41 (3H, s), 3.64 (3H, s), 3.76 (3H, s), 4.14 (3H, s), 4.64 (2H, q, 7.0), 5.70 (1H, s), 7.55 (2H, m), 8.00 (1H, m), 8.21 (1H, s)
5d	1749, 1643	1.49 (3H, t, 7.2), 3.80 (3H, s), 4.16 (3H, s), 4.30 and 4.83 (2H, AB, 17.2), 4.58 (2H, m), 7.08-7.20 (5H, m), 7.48 (2H, m), 8.04 (2H, m)
5e	1750, 1643	1.53 (3H, t, 7.1), 3.38 (3H, s), 3.72 (3H, s), 3.93 (3H, s), 4.64 (2H, q, 7.1), 4.86 and 5.02 (2H, AB, 18.2), 7.49 (2H, m), 7.88 (1H, m), 8.19 (1H, m)
5f	1760, 1643	1.54 (3H, t, 7.1), 2.97 (3H, s), 3.55 (3H, s),3.89 (3H, s), 4.63 (2H, q, 7.1), 7.54 (2H, m), 8.00 (1H, m), 8.19 (1H, m)
5g	1740, 1655	1.25 (3H, t, 7.5), 1.54 (3H, t, 7.1), 3.09 (1H, m), 3.44 (1H, m), 3.73 (3H, s), 4.00 (3H, s), 4.65 (2H, q, 7.1), 7.56 (2H, m), 8.06 (1H, m), 8.20 (1H, m)
6a	1760, 1676	1.54 (3H, t, 7.2), 4.65 (2H, q, 7.2), 7.48 (2H, m), 8.18 (1H, m), 8.32 (1H, m), 10.20 (1H, s)
6b	1748, 1730, 1660	1.44 (3H, t, 7.2), 1.53 (3H, t, 7.2), 4.45 (2H, q, 7.2), 4.62 (2H, q, 7.2), 7.47 (2H, m), 8.06 (1H, m), 8.18 (1H, m)
6c	1740, 1697	1.52 (3H, t, 7.2), 3.49 (6H, s), 4.60 (2H, q, 7.2), 5.20 (1H, s), 7.44 (2H, m), 8.09 (1H, m), 8.17 (1H, m)

6d	1758, 1670	1.53 (3H, t, 7.2), 4.29 (2H, s), 4.62 (2H, q, 7.2), 7.22-7.52 (7H, m), 8.06 (1H,m), 8.15 (1H, m)
6e	1741, 1690	1.52 (3H, t, 7.1), 3.52 (3H, s), 4.58 (2H, s), 4.61 (2H, q, 7.1), 7.46 (2H, m), 7.98 (1H, m), 8.18 (1H, m)
6f	1755, 1675	1.52 (3H, t, 7.0), 2.57 (3H, s), 4.61 (2H, q, 7.0), 7.45 (2H, m), 8.14 (2H, m)
6g	1746, 1678	1.26 (3H, t, 7.2), 1.52 (3H, t, 7.1), 3.01 (2H, q, 7.2), 4.60 (2H, q, 7.1), 7.45 (2H, m), 8.04 (1H, dd, 2.0, 7.3), 8.18(1H, dd, 1.6, 7.2)
7a	1741, 1657	1.53 (3H, t, 7.1), 4.58 (2H, q, 7.1), 5.65 (1H, dd, 1.5, 17.2), 5.84 (1H, dd, 1.5, 11.2), 7.18 (1H, dd, 11.2, 17.2), 7.39 (2H, m), 8.10 (1H, m), 8.42 (1H, m), 10.08 (1H, s)
7b	1737, 1638	1.36 (3H, t, 7.2), 1.52 (3H, t, 7.2), 4.29 (2H, q, 7.2), 4.57 (2H, q, 7.2), 5.47 (1H, dd, 1.3, 17.2), 5.62 (1H, dd, 1.3, 11.1), 7.15 (1H, dd, 11.1, 17.2), 7.40 (2H, m), 8.12 (1H, m), 8.22 (1H, m)
7c	1738, 1668	1.51 (3H, q, 7.2), 3.39 (6H, s), 4.54 (2H, q, 7.2), 5.35 (1H, s), 5.50 (1H, dd, 1.5, 17.4), 5.63 (1H, dd, 1.5, 11.2), 7.20-7.41 (3H, m), 7.98-8.10 (2H, m)
7d	1740, 1642	1.51 (3H, t, 7.2), 4.20 (2H, s), 4.53 (2H, q, 7.2), 5.53 (1H, dd, 1.6, 17.4), 5.71 (1H, dd, 1.6, 11.1), 7.16-7.40 (8H, m), 7.91 (1H, m), 8.07 (1H, m)
7e	1740, 1660	1.51 (3H, t, 7.1), 3.43 (3H, s), 4.44 (2H, s), 4.54 (2H, q, 7.1), 5.52 (1H, dd, 1.5, 17.3), 5.63 (1H, dd, 1.5, 11.2), 7.18-7.40 (3H, m), 7.98-8.10 (2H, m)
7f	1740, 1638	1.51 (3H, t, 7.2), 2.53 (3H, s), 4.54 (2H, q, 7.2), 5.53 (1H, dd, 1.6, 17.3), 5.70 (1H, dd, 1.6, 11.2), 7.18-7.40 (4H, m), 8.07 (1H, m)
7g	1738, 1642	1.16 (3H, t, 7.4), 1.50 (3H, t, 7.0), 2.86 (2H, q, 7.4), 4.54 (2H, q, 7.0), 5.47 (1H, dd, 1.5, 17.3), 5.64 (1H, dd, 1.5, 11.2), 7.18-7.40 (3H, m), 7.95 (1H, m), 8.08 (1H, m)
8f	1747, 1645	1.46 (3H, t, 7.1), 3.22 (6H, s), 4.49 (2H, q, 7.1), 5.78 (2H, bs)[a], 6.94 (1H, m), 7.19 (2H, m), 7.90 (1H, m)
8g	1711, 1679	1.47 (3H, t, 7.1), 1.84 (3H, d, 7.1, s after D_2O), 3.21 (6H, s), 4.50 (2H, q, 7.1), 6.80 (1H, m), 7.19 (2H, m), 7.76 (1H, q, 7.1)[a], 7.90 (1H, m)

[a] Exchange with D_2O.

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