Ytterbium(III) bis(perfluorooctanesulfonyl)imide catalyzed one-pot synthesis of tetrahydrobenzo[*b*]pyrans in fluorous biphase system

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Ytterbium(III) bis(perfluorooctanesulfonyl)imide [$Yb(NPf_2)_3$] has been prepared, and used as an efficient catalyst for the synthesis of 4*H*-benzo[*b*]pyran derivatives by a one-pot three-component condensation of aldehydes, active methylene compounds, and dimedone in a fluorous biphase system (FBS). The reaction proceeds smoothly and affords the corresponding 4*H*-benzo[*b*]pyrans in moderate to excellent yields. The catalyst is selectively dissolved in the fluorous phase, can be recovered simply by phase separation and reused several times without any obvious decrease of activity.

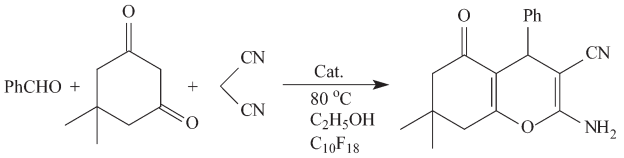
Keywords: fluorous biphase system, Lewis acid catalyst, bis(perfluorooctanesulfonyl)imide, ytterbium, three component reaction, 4*H*-benzo[*b*]pyrans

4*H*-Benzo[*b*]pyran and its derivatives are of considerable interest because of their wide range of biological and pharmacological activities,[1] such as spasmolytic, diuretic, anti-coagulant, anti-cancer and anti-anaphylactic activities.[2–4] The pharmacological activities exhibited by these compounds are mainly due to the presence of the heterocyclic ring system. They can be used as cognitive enhancers for the treatment of neurodegenerative disease including Alzheimer's disease, AIDS-associated dementia and Down's syndrome, as well as for the treatment of schizophrenia and myoclonus.[5] A number of 2-amino-4*H*-pyran derivatives are useful as photoactive materials.[6] Furthermore, these compounds can be employed as cosmetics, pigments[7] and utilised as potential biodegradable agrochemicals.[8] In view of their wide utility, researchers have synthesised the 4*H*-benzo[*b*]pyran unit using different methods involving microwave,[9] ultrasonic irradiation[10] or the use of hexadecyltrimethylammonium salts,[11] KF-alumina,[12] rare earth perfluorooctanoates,[13] (S)-proline,[14] Mg/La mixed oxide,[15] PEG_{1000}-based dicationic acidic ionic liquid,[16] basic quaternary ammonium salts,[17] PF_6,[18] [b_{mim}^+][BF_4^-][19] as catalysts in one-pot reactions. Each of the above methods has its own merits, while some are disadvantaged by limitations such as harsh reaction conditions, low yields, tedious work-up protocols, or poor catalyst recyclability. Consequently, the development of a catalyst for the efficient synthesis of 4*H*-enzo[*b*]pyrans in one step still remains attractive to researchers.

During the last decade, fluorinated Lewis acid catalysts in a variety of synthetic reactions have been recognised because of their strong Lewis acidity and the characteristic that they can be immobilised in a fluorous solvent. Recently, the value of the fluorous phase-separation and fluorous catalyst recyclability under fluorous biphase system (FBS) has been recognised.[20] We have introduced $Yb(NPf_2)_3$ as an efficient Lewis acid catalyst for the allylation of 1,3-dicarbonyl compounds[21] in FBS. A key factor to accomplish the catalytic processes was was believed to be the use of a sufficiently long perfluorinated ligand $–N(SO_2C_8F_{17})_2$, whose structural characteristic can coordinate with a variety of metal cations to obtain the desired Lewis acid catalysts with appropriate catalytic activity, as well as the selective immobilisation in the fluorous phase.[22] This report describes a very efficient one-pot three-component synthesis of tetrahydrobenzo[*b*]pyrans catalysed by the Lewis acid catalyst $Yb(NPf_2)_3$ in FBS.

First of all, we began to examine the catalytic activities of different rare earth complexes to optimise the conditions for reaction of benzaldehyde, dimedone and malononitrile in a biphase of co-solvent ethanol and perfluorodecalin ($C_{10}F_{18}$, *cis*- and *trans*-mixture) (Table 1). Among these catalysts, $Yb(NPf_2)_3$ showed the best catalytic activity in this reaction. We also found that an increased yield could be obtained when the catalyst loading was increased from 0.2 to 1 mol%, but further increasing the amount of catalyst (over 1 mol%) did not provide further improvements (Table 1, entries 3–6). When the reaction was completed, the fluorous layer containing the catalyst could be separated easily by decantation at room temperature and used five times with yields of products ranging from 88 to 92% (Table 1, entry 5).

Table 1 Effect of different catalysts on the condensation of benzaldehyde, dimedone, and malononitrile[a]



Entry	Catalyst	Amount of catalyst /mol%	Yield /%[b]
1	$Yb(OTf)_3$	1	73
2	$Yb(OPf)_3$	1	82
3	$Yb(NPf_2)_3$	0.2	68
4	$Yb(NPf_2)_3$	0.5	81
5	$Yb(NPf_2)_3$[c]	1	92, 92, 90, 88, 88
6	$Yb(NPf_2)_3$	1.2	91
7	$La(NPf_2)_3$	1	67
8	$Nd(NPf_2)_3$	1	63
9	$Sm(NPf_2)_3$	1	71
10	$Gd(NPf_2)_3$	1	75
11	$Y(NPf_2)_3$	1	81
12	$Er(NPf_2)_3$	1	83

[a] Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), ethanol (2 mL), $C_{10}F_{18}$ (2 mL), 80 °C, 4 h.
[b] Isolated yields.
[c] Catalyst was reused in five times.

In order to make the reaction more accessible, we explored different co-solvent systems taking a general organic solvent. In each case, the substrates were mixed together with 5 mol% $Yb(NPf_2)_3$ agitated with 2 mL co-solvent and 2 mL $C_{10}F_{18}$. The results are shown in Table 2. It is important to note that the use of a polar co-solvent such as ethanol, methanol or acetonitrile resulted in higher product yield, and ethanol as co-solvent was the most efficient. We assumed that the difference in solubility of the catalyst and the substrates in polar or non-polar solvents would have an influence on their effective miscibility.

In order to generalise this method, aldehydes **1**, 5,5-dimethyl-1,3-cyclohexanedione (dimedone) **2**, and malononitrile or ethyl cyanoacetate **3** (see Table 3) were subjected to the

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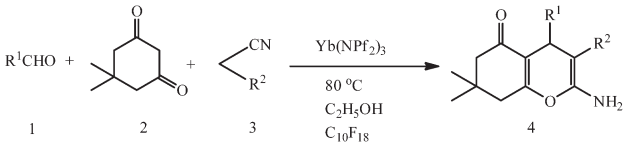
Table 2 Effect of co-solvents on the condensation of benzaldehyde, dimedone, and malononitrile catalysed by $Yb(NPf_2)_3$[a]

Entry	Co-solvent	Temperature /°C	Yield /% [b]
1	95% C_2H_5OH	80	84
2	C_2H_5OH	80	92
3	CH_3OH	65	83
4	H_2O	80	35
5	PhMe	80	62
6	CH_3CN	80	71

[a]Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), $Yb(NPf_2)_3$ (0.01 mmol), $C_{10}F_{18}$ (2 mL), 4 h.
[b]Isolated yields.

Table 3 $Yb(NPf_2)_3$ catalysed the preparation of tetrahydrobenzo[*b*]pyrans[a]



Entry	R^1	R^2	Time /h	Product	Yield /%[b]
1	C_6H_5	CN	4	**4a**	92
2	4-$CH_3C_6H_4$	CN	5	**4b**	80
3	4-$CH_3OC_6H_4$	CN	5	**4c**	86
4	4-BrC_6H_4	CN	3	**4d**	96
5	4-ClC_6H_4	CN	3	**4e**	96
6	2,4-$Cl_2C_6H_3$	CN	3	**4f**	89
7	3-$NO_2C_6H_4$	CN	3	**4g**	82
8	4-$NO_2C_6H_4$	CN	3	**4h**	80
9	4-HOC_6H_4	CN	3	**4i**	88
10	$CH_3(CH_2)_5$	CN	24	**4j**	37
11	2-Furyl	CN	3	**4k**	83
12	2-Thienyl	CN	3	**4l**	85
13	C_6H_5	$CO_2C_2H_5$	6	**4m**	71
14	4-ClC_6H_4	$CO_2C_2H_5$	5	**4o**	93
15	4-$NO_2C_6H_4$	$CO_2C_2H_5$	5	**4p**	81
16	2,4-$Cl_2C_6H_3$	$CO_2C_2H_5$	5	**4q**	87

Reaction conditions: [a]Aldehyde (1 mmol), dimedone (1 mmol), malononitrile or ethyl cyanoacetate (1 mmol), $Yb(NPf_2)_3$ (0.01 mmol), ethanol (2 mL), $C_{10}F_{18}$ (2 mL), 80 °C.
[b]Isolated yields.

biphase system of ethanol and $C_{10}F_{18}$ at 80 °C in the presence of a catalytic amount of $Yb(NPf_2)_3$ (Table 3). Both aldehydes having electron-withdrawing and electron-donating groups on the aromatic ring can undergo the reaction to afford the corresponding 4*H*-benzo[*b*]pyrans in moderate to excellent yields (71–96%). The position of the substituents on the aromatic ring also did not show obvious effects on the yields. Longer reaction times were required for the condensation with ethyl cyanoacetate.

In summary, rare earth bis(perfluorooctanesulfonyl)imide complexes $RE(NPf_2)_3$, especially $Yb(NPf_2)_3$ proved to be effective catalysts for the synthesis of 4*H*-benzo[*b*]pyrans by the condensation of aldehydes, malononitrile or ethyl cyanoacetate, and dimedone in FBS. The current methodology has the advantages of operational simplicity, mild reaction conditions, moderate to excellent yields of products and reusability of the catalyst.

Experimental

Melting points were determined in a capillary tube and are uncorrected. ^{1}H NMR and ^{19}F- NMR spectra were recorded using a Bruker Advance RX300 spectrometer. IR spectra were recorded on a Bomem MB154S IR analyser. UV-Vis spectra were obtained on a UV-1601 apparatus. Mass spectra were obtained with a Hewlett Packard 5989A spectrometer. Inductively coupled plasma (ICP) spectra were measured on Ultima2C apparatus. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Commercially available reagents were used without further purification.

Bis(perfluorooctanesulfonyl)imide:[23,24] Ammonia gas (300 mmol) was added into perfluorooctanesulfonyl fluoride (50 g, 99.6 mmol) at -20 °C. After stirring at –20 °C for about 1 h, stirring was continued at room temperature for another 1 h. The solid product was acidified to pH about 2 with 2M HCl followed by addition of Et_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_4, the solvent removed under reduced pressure, and the residue dried *in vacuo* at 80 °C for 16 h to give $C_8F_{17}SO_2NH_2$ (87% yield). Then the mixture of perfluorooctanesulfonyl fluoride (45.7 g, 91 mmol), perfluorooctanesulfonamide (43.4 g, 87 mmol) and Et_3N (76 mL) was stirred under reflux for 23 h. The lower brown fluorous layer was washed with 4M HCl to yield a brown solid which was dried *in vacuo* at 70 °C for 6 h to afford $(C_8F_{17}SO_2)_2N\ HNEt_3$. Free $(C_8F_{17}SO_2)_2NH$ was obtained in 50% yield, using acidic ion exchange resin column.

$Yb(NPf_2)_3$: To a stirried solution of bis(perfluorooctanesulfonyl)imide (0.883 g, 0.9 mmol) in 10 mL H_2O, ytterbium(III) chloride (0.083 g, 0.3 mmol) was added and the mixture was stirred for 1 h under reflux. Then the water was removed under reduced pressure at 80 °C for 16 h to afford a white powder of ytterbium(III) bis(perfluoroctanesulfonyl)imide in 98% yield. Anal. Calcd for $C_{48}O_{12}N_3F_{102}S_6Yb$: Yb, 5.56. C, 18.52; N, 1.35. Found: Yb: 5.60, C: 18.45; N, 1.41%. ^{19}F NMR (300 MHz, α,α,α-trifluorotoluene): δ –81.8 (CF_3), –115.2 (α–CF_2), –121.2 (β-CF_2), –122.6 (3×CF_2), –123.4 (γ–CF_2), –126.9 (θ-CF_2). IR(cm^{-1}): 3475, 1651, 1338, 1207, 1153, 1084, 987, 945, 806, 740, 628. UV-vis (EtOH) λ (nm): 210.

Synthesis of tetrahydrobenzo[b]pyrans; general procedure

A mixture of aldehyde (1 mmol), malononitrile (or ethyl cyanoacetate) (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (0.140 g, 1 mmol) and $Yb(NPf_2)_3$ (0.031g, 1 mol%) in a biphase of ethanol (2 mL) and $C_{10}F_{18}$ (2 mL) was stirred at 80 °C for an appropriate time. When the reaction was completed as indicated by TLC, the mixture was cooled to room temperature, the lower fluorous phase containing the catalyst was separated and reused in the subsequent recycling reaction. The upper phase was cooled in a refrigerator overnight; the solid product which had crystallised was filtered off, washed with H_2O and purified by recrystallisation from EtOH (95%).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzo[b]pyran (**4a**): White solid. m.p: 226–228 °C (lit.[13] 227–229 °C). IR (KBr) ν: 3396, 3325, 2199, 1664, 1214, 1036 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.04 (s, 3H), 1.11 (s, 3H), 2.19 (d, 1H, *J* = 16.1 Hz), 2.24 (d, 1H, *J* = 16.1 Hz), 2.45 (s, 2H), 4.40 (s, 1H), 4.53 (s, 2H), 7.18–7.27 (m, 5H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-tolylphenyl)-4H-benzo[b]pyran (**4b**): White solid. m.p. 208–210 °C (lit.[12] 208–210 °C). IR (KBr) ν: 3426, 3330, 2193, 1678, 1140, 1041 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.07 (s, 3H), 1.11 (s, 3H), 2.25 (s, 5H), 2.43 (s, 2H), 4.36 (s, 1H), 4.53 (s, 2H), 7.15–7.30 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-methoxyphenyl)-4H-benzo[b]pyran (**4c**): White solid. m.p. 192–193 °C (lit.[12] 198–200 °C). IR (KBr) ν: 3378, 3315, 2193, 1687, 1655, 1141, 1034 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.02 (s, 3H), 1.11 (s, 3H), 2.25 (s, 2H), 2.45 (s, 2H), 3.81 (s, 3H), 4.37 (s, 1H), 4.51 (s, 2H), 7.13–7.28 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-bromophenyl)-4H-benzo[b]pyran (**4d**): White solid. m.p. 201–203 °C (lit. [14]: 203–205 °C). IR (KBr) ν: 3392, 3328, 2192, 1682, 1214, 1039 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.02 (s, 3H), 1.12 (s, 3H), 2.25 (s, 2H), 2.45 (s, 2H), 4.35 (s, 1H), 4.71 (s, 2H), 7.12–7.41 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-chlorophenyl)-4H-benzo[b]pyran (**4e**): White solid. m.p. 215–217 °C (lit.[12] 207–209 °C). IR (KBr) ν: 3370, 3324, 2178, 1674, 1215, 1014 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.02 (s, 3H), 1.13 (s, 3H), 2.25 (s, 2H), 2.47 (s, 2H), 4.40 (s, 1H), 4.62 (s, 2H), 7.17–7.35 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(2′,4′-chlorophenyl)-4H-benzo[b]pyran (**4f**): White solid. m.p. 115–117 °C (lit.[13] 115-117 °C). IR (KBr) ν: 3363, 3156, 2966, 2192, 1686, 1607, 1473, 1040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 1.06 (s, 3H), 1.10 (s,

3H), 2.27 (s, 2H), 2.45 (s, 2H), 4.56 (s, 1H), 4.89 (s, 2H), 7.13–7.39 (m, 3H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(3′-nitrophenyl)-4H-benzo[b]pyran (**4g**): White solid. m.p. 210–212 °C (lit.[13] 204–205 °C). IR (KBr) ν: 3324, 3212, 2185, 1679, 1211, 1037 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.01 (s, 3H), 1.12 (s, 3H), 2.26 (s, 2H), 2.51 (s, 2H), 4.51 (s, 1H), 4.68 (s, 2H), 7.15–7.39 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-nitrophenyl)-4H-benzo[b]pyran (**4h**): White solid. m.p. 177–178 °C (lit.[13] 171–172 °C). IR (KBr) ν: 3408, 3321, 2187, 1673, 1216, 1039 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.01 (s, 3H), 1.12 (s, 3H), 2.25 (s, 2H), 2.47 (s, 2H), 4.53 (s, 1H), 4.68 (s, 2H), 7.41–8.15 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-hydroxyphenyl)-4H-benzo[b]pyran (**4i**): White solid. m.p. 208–210 °C (lit.[13] 208–210 °C). IR (KBr) ν: 3357, 3250, 3163, 2191, 1664, 1558 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.05 (s, 3H), 1.10 (s, 3H), 2.23 (s, 2H), 2.45 (s, 2H), 4.31 (s, 1H), 4.75 (s, 1H), 5.34 (s, 2H), 6.75–7.13 (m, 4H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-heptyl-4H-benzo[b]pyran (**4j**): White solid. m.p. 187–189 °C(lit.[18] 185–187 °C). IR (KBr) ν: 3387, 3319, 2185, 1681, 1146, 1040 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.86 (s, 3H), 1.08 (s, 3H), 1.10 (s, 3H), 1.14–1.26 (m, 10H), 2.28 (s, 2H), 2.29–2.35 (m, 2H), 3.41 (s, 1H), 4.46 (s, 2H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(2′-furyl)-4H-benzo[b]pyran (**4k**): White solid. m.p. 218–220 °C (lit.[12] 218–220 °C). IR (KBr) ν: 3405, 3295, 3051, 2993, 2978, 2243, 1680, 1600, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.01 (s, 3H), 1.10 (s, 3H), 2.28 (s, 2H), 2.51 (s, 2H), 4.44 (s, 1H), 4.75 (s, 2H), 6.18–7.37 (m, 3H).

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(2′-thienyl)-4H-benzo[b]pyran (**4l**): White solid. m.p. 224–226 °C (lit.[19] 224–226 °C). IR (KBr) ν: 3322, 3208, 2964, 2199, 1679, 1603, 1541, 1466, 758, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.08 (s, 3H), 1.13 (s, 3H), 2.28 (s, 2H), 2.44 (s, 2H), 4.61 (s, 1H), 4.79 (s, 2H), 6.92–7.14 (m, 3H).

2-Amino-3-ethylcarboxylate-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzo[b]pyran (**4m**): White solid. m.p. 155–157 °C (lit.[14] 155–157 °C). IR (KBr) ν: 3403, 3290, 2956, 1693, 1655, 1606, 1524, 835, 796, 769, 725, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.96 (s, 3H), 1.09 (s, 3H), 1.16 (t, 3H, J = 7.1 Hz), 2.18 (s, 2H), 2.41 (s, 2H), 4.02 (q, 2H, J = 7.2 Hz), 4.71 (s, 1H), 6.11 (s, 2H), 7.16–7.25 (s, 5H).

2-Amino-3-ethylcarboxylate-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-chlorophenyl)-4H- benzo[b]pyran (**4o**): White solid. m.p. 150–152 °C (lit.[14] 153–155 °C). IR (KBr) ν: 3480, 3327, 2976, 1684, 1660, 1525, 919, 857, 842 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.98 (s, 3H), 1.08 (s, 3H), 1.14 (t, 3H, J = 7.1 Hz), 2.17 (s, 2H), 2.42 (s, 2H), 4.06 (q, 2H, J = 7.2 Hz), 4.69 (s, 1H), 6.21 (s, 2H), 7.13–7.27 (s, 4H).

2-Amino-3-ethylcarboxylate-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(4′-nitrophenyl)4H- benzo[b]pyran (**4p**): White solid. m.p. 183–185 °C (lit.[14] 183–185 °C). IR (KBr) ν: 3476, 3338, 1687, 1659 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) 0.98 (s, 3H), 1.10 (s, 3H), 1.15 (t, 3H, J = 7.2 Hz), 2.19 (s, 2H), 2.47 (s, 2H), 4.05 (q, 2H, J = 7.2 Hz), 4.81 (s, 1H), 6.28 (s, 2H), 7.46 (d, 2H, J = 8.8 Hz), 8.01 (d, 2H, J = 8.8Hz).

2-Amino-3-ethylcarboxylate-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-(2′,4′-chlorophenyl)-4H- benzo[b]pyran (**4q**): White solid. m.p. 176–178 °C (lit.[14] 172–174 °C). IR (KBr) ν: 3426, 3313, 2959, 1696, 1650, 1614, 867, 847, 804, 758 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.02 (s, 3H), 1.12 (s, 3H), 1.16 (t, 3H, J = 7.2 Hz), 2.15 (s, 2H), 2.47 (s, 2H), 4.06 (q, 2H, J = 7.2 Hz), 4.98 (s, 1H), 6.21 (s, 2H), 7.16 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.35 (s, 1H).

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