



Enantioselective synthesis of hyperparathyroidism agent Cinacalcet hydrochloride

N S Ganesh, K V L D Spandana & A Venkat Narsaiah*

Organic Synthesis Laboratory, Fluoro-Agrochemicals Department,
CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India
E-mail: vnakkirala@iict.res.in; vnakkirala2001@yahoo.com

Received 8 October 2021; accepted (revised) 22 April 2022

A simple and efficient route has been developed for enantioselective synthesis of hyperparathyroidism agent (*R*)-Cinacalcet. The synthesis started from commercially available trifluoromethyl benzaldehyde and 1-(naphthalen-1-yl) ethanone and completed in 8 steps with an overall yield 18.5%. The key reactions involved are Corey-Bakshi-Shibata chiral reduction and reductive amination.

Keywords: Wittig reaction, CBS-reduction, oxidation, reductive amination, hyperparathyroidism

Hyperparathyroidism (HPT) is the most common cause of hypercalcemia and diagnosed in most individuals as an asymptomatic stage without signs or symptoms. HPT is a condition characterized by the over secretion of parathyroid hormone (PTH), a result of the failure of calcium receptors on parathyroid glands^{1,2}. Calcimimetics are the agents that mimic the action of calcium to increase the sensitivity of these receptors to calcium, which inhibits the release of parathyroid hormone and lowers PTH levels. Cinacalcet (Sensipar, Mimpara, Figure 1) is a calcimimetic agent and the first active pharmaceutical ingredient approved by US FDA for the treatment of secondary hyperthyroidism in patients with chronic kidney disease placed on dialysis and for the treatment of elevated calcium levels in the patients with parathyroid carcinoma^{3,4}. The active ingredient is the (*R*)-enantiomer and the pharmaceutical importance of Cinacalcet was attracted many synthetic chemists and led to its synthesis in different ways⁵⁻¹², but most of the reports are in the form of patents¹³⁻¹⁹.

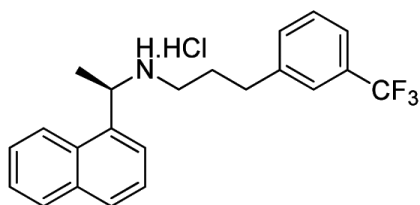
Results and Discussion

As part of our regular research program, in synthesis of biologically active molecules²⁰⁻²⁵, herein, we report, an enantioselectivity synthesis of hyperparathyroidism agent Cinacalcet. Retrosynthetic analysis shows that the target molecule (**1**) synthesis was started from 3-(trifluoro methyl) benzaldehyde (**2**) and 1-(naphthalen-1-yl) ethanone (**3**).

As mentioned in the retrosynthetic analysis (Scheme I), one of the fragments was started from commercially available, 3-(trifluoromethyl) benzaldehyde. The aldehyde (**2**) was subjected to Wittig reaction with two carbonylides, in CH₂Cl₂ at RT to afford, (*E*)-ethyl-3-[3(trifluoromethyl) phenylacrylate (**4**) in 97% yield^{26,27}. The obtained olefin was treated with Pd/C under hydrogen atmosphere at RT to achieve, ethyl-3-[3(trifluoromethyl) phenyl] propanoate in quantitative yield²⁸. The saturated ester (**5**) on hydrolysis with NaBH₄ in presence of LiBr in methanol at low temperature resulted, 3-[3(trifluoromethyl) phenyl]propan-1-ol (**6**) in 82% (Ref. 29). Thus obtained alcohol on oxidation with Dess-Martin Periodinane in CH₂Cl₂ at RT afforded, 3-[3(trifluoromethyl) phenyl] propanal (**7**) in very good yields as shown in the Scheme II^{30,31}.

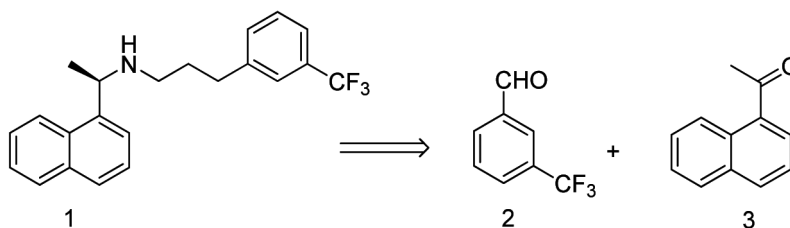
The other fragment was synthesized from achiral ketone, 1-(naphthalen-1-yl)ethanone (**3**), which on enantioselective reduction with boranedimethyl sulfide in presence of a chiral ligand, (*S*)-methyl-CBS-oxazaborolidine complex³², at -40°C in dry THF for 2h to afford, (*S*)-1-(naphthalen-1-yl) ethanol (**8**) in 65% yield and with excellent enantioselectivity and the observed optical rotation of compound, $[\alpha]_D^{27} = -72.2^\circ$ (c 1, methanol). The chiral alcohol was mesylated (**9**) by reacting with methanesulfonyl chloride and triethyl amine in CH₂Cl₂ at 0°C and followed by reaction with NaN₃ at acetonitrile reflux for 5h to afford, the inverted configuration product,

(*R*)-1-(1-azidoethyl) naphthalene (**10**) in 70% yield³³, with excellent enantioselectivity and the observed optical rotation of compound, $[\alpha]_D^{27} = 13.6^\circ$ (c 0.3, CHCl_3). The azido compound on reduction with $\text{Zn-NH}_4\text{Cl}$ in $\text{Et.OH-H}_2\text{O}$ solvent mixture at 60°C afforded, (*R*)-1-(naphthalen-1-yl)ethanamine (**11**)³⁴ in 92% yield as shown in the Scheme III and the observed optical rotation of compound, $[\alpha]_D^{27} = 51.6^\circ$ (c 2, EtOH).

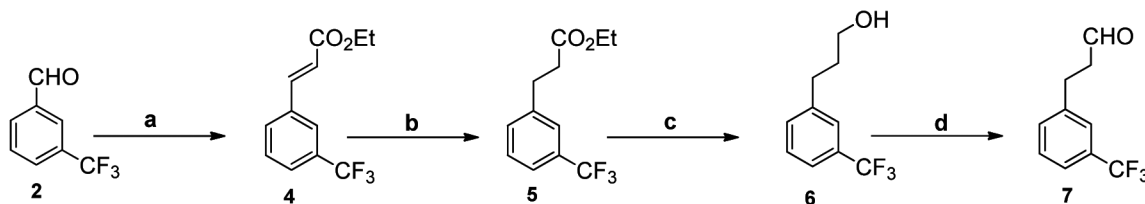


1

Figure 1

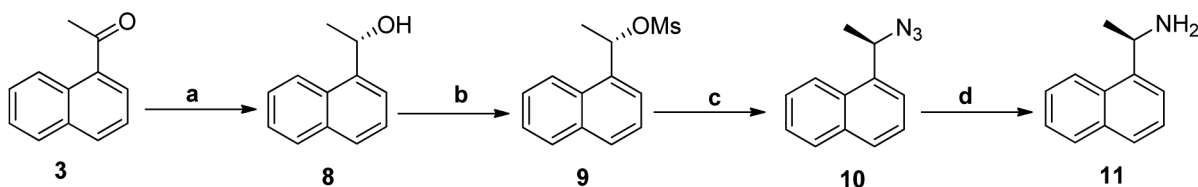


Scheme I



Reagents and Conditions: (a) Wittig, DCM, RT, 3 h, 97%, (b) Pd/C , H_2 , RT, 6 h, 98%, (c) NaBH_4 , MeOH, LiBr , 0°C - RT, 6 h, 82%, (d) DMP, DCM, 0°C - RT, 1 h, 71%.

Scheme II



Reagents and Conditions: (a) (*R*)-CBS, BH_3 , DMS complex, THF, -40°C , 2 h, 65%, (b) MsCl , TEA, DCM, 0°C - RT, 1 h, (c) NaN_3 , CH_3CN , 80°C , 5 h, 70%, (d) Zn , NH_4Cl , $\text{EtOH-H}_2\text{O}$, 50°C , 1 h, 92%.

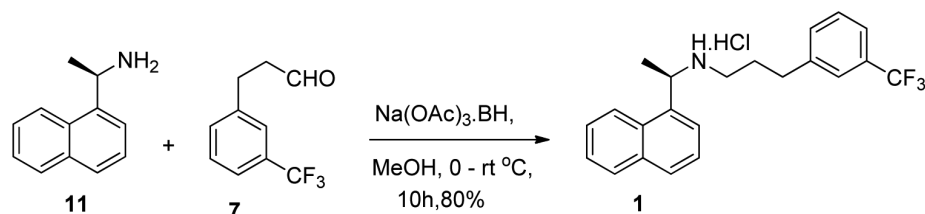
Scheme III

The reductive amination has been carried out by the condensation of equimolar amounts of the aldehyde fragment, 3-[3(trifluoromethyl) phenyl] propanal (**7**) and the chiral amine fragment, (*R*) -1-(naphthalen-1-yl) ethanamine (**10**) in presence of sodium triacetoxy borohydride [$\text{Na(OAc)}_3 \cdot \text{BH}$]³⁵ in methanol at RT to afford the target molecule, (*R*)-*N*-[1(naphthalen-1-yl) ethyl]-3[3(trifluoromethyl) phenyl]propan-1- amine (**1**) in 80% yield as shown in the Scheme IV.

The observed optical rotation of the compound, $[\alpha]_D^{27} = -27^\circ$ (c 1, MeOH). All the products were characterized by their ^1H and ^{13}C NMR, IR, mass spectroscopy and optical rotation data and compared with literature reports.

Experimental Section

All the air and moisture sensitive reactions were carried out under nitrogen atmosphere. Oven-dried glass apparatus were used to perform all the reactions.



Scheme IV

Freshly distilled anhydrous solvents were used for air and moisture sensitive reactions. Commercially available reagents were used as received. Purification of compounds was carried out *via* column chromatography by using silica gel (60-120 mesh) packed in glass columns. ^1H and ^{13}C NMR were recorded in CDCl_3 on 400 MHz and 500 MHz spectrometers, using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FT-RT 240-c spectrophotometer using KBr / Thin Film optics. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. Optical rotation values were recorded on Horiba sepa300 polarimeter. High resolution mass spectra (HRMS) [ESI⁺] were obtained using either a TOF or a double focusing spectrometer.

(E)-Ethyl-3-[3-(trifluoromethyl)phenyl]acrylate, 4

To a stirred solution of trifluoromethyl benzaldehyde (2 g, 11.5 mmol) in benzene (20 mL) was added Wittig ylide (4.78 g, 13.8 mmol) and refluxed for 3 h. After completion of the reaction, solvent was removed under reduced pressure and the residue was dissolved in water and extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with ethyl acetate-hexane (5:95) mixture to obtain pure product **4**, as yellow liquid (2.74 g, 97%).

IR (neat): ν 2985, 1716, 1643, 1336, 1314, 1196, 1169, 981 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.77 (s, 1H), 7.72 (d, 1H, $J = 6.4$ Hz), 7.67 (d, 1H, $J = 6.4$ Hz), 7.63 (d, 1H, $J = 7.7$ Hz), 7.50 (t, 1H, $J = 7.7$ Hz), 6.50 (d, 1H, $J = 16$ Hz), 4.28 (q, 2H, $J = 6.0$ Hz), 1.35 (t, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3): δ 166.1, 142.4, 134.9, 130.7, 129.1, 126.2, 124.2, 119.9, 60.4, 13.9 ppm.; EIMS m/z (%): $\text{M}^+ 245$ (10), 229 (10), 213 (80), 181 (100), 167 (10), 143 (10), 119 (10).

Ethyl-3-[3-(trifluoromethyl)phenyl]propanoate, 5

To a mixture of (*E*)-ethyl-3[3(trifluoromethyl)

phenyl] acrylate (2g, 8.2 mmol) in ethyl acetate (20 mL) was added Pd/C (50 mg, 10%) and stirred under hydrogen atmosphere (25 psi) for 8 h. Then filtered on celite bed and washed with ethyl acetate (2×10 mL). The combined filtrate was concentrated under reduced pressure to afford, product **5**, as colorless liquid (2g, 98%).

IR (neat): ν 2985, 1735, 1449, 1329, 1163, 1074, 702 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.45 - 7.51 (m, 3H), 7.38 - 7.43 (m, 1H), 4.13 (q, 2H, $J = 7.5$ Hz), 3.05 (t, 2H, $J = 7.5$ Hz), 2.64 (t, 2H, $J = 7.5$ Hz), 1.22 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3): δ 172.4, 141.5, 131.7, 128.9, 125.0, 123.0, 60.6, 35.5, 30.6, 14.0 ppm.; HRMS(ESI): m/z [M^+]⁺ caclcd for $\text{C}_{12}\text{H}_{14}\text{O}_2\text{F}_3$: 247.0940: found: 247.0935, C12 H17 O2 N F3 = 264.12059.

3-[3-(Trifluoromethyl) phenyl] propan-1-ol, 6

To a stirred solution of ethyl-3[3(trifluoromethyl)phenyl] propanoate (1.85g, 7.5 mmol) in methanol (20 mL) was added NaBH_4 (0.55g, 15 mmol) followed by LiBr (0.78 g, 9 mmol) at 0°C and allowed to stir at RT for 5h. After completion of the reaction, solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with ethyl acetate-hexane (3:7) mixture to obtain, alcohol **6** as colorless liquid (1.25g, 82%).

IR (neat): ν 3351, 2942, 2870, 1614, 1597, 1450, 1331, 1200, 1163, 1074, 920, 702 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.45 - 7.50 (m, 2H), 7.32 - 7.43 (m, 2H), 3.68 (t, 2H, $J = 6.4$ Hz), 2.78 (t, 2H, $J = 7.6$ Hz), 1.85 - 1.95 (m, 2H), 1.48 (brs, 1H); ^{13}C NMR (CDCl_3): δ 142.6, 131.8, 130.7, 128.7, 125.0, 122.7, 61.8, 33.9, 31.8 ppm.; HRMS (ESI): m/z [M^+]⁺ caclcd for $\text{C}_{10}\text{H}_{13}\text{ONF}_3$: 204.0991: found: 204.0994.

3-[3-(Trifluoromethyl) phenyl] propanal, 7

To a stirred solution of 3[3(trifluoromethyl)phenyl] propan-1-ol (0.5g, 2.45 mmol) in dry CH_2Cl_2 (5 mL) was added DMP (1.2 g, 2.9 mmol) at RT and stirred

for 1h. After completion, the reaction mixture was quenched by adding water and extracted with CH_2Cl_2 (2×15 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, the crude compound was purified by column chromatography using silica gel (60-120 mesh) by eluting with ethyl acetate-hexane (1:9) mixture to yield, aldehyde **7**, as yellow liquid (0.35 g, 71%).

IR (neat): ν 2971, 2845, 1675, 1516, 1489, 1373, 1261, 1103, 885, 761 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 9.80 (s, 1H), 7.22 - 7.26 (m, 2H), 7.18 - 7.20 (m, 2H), 3.10 (t, 2H, $J = 6.4$ Hz), 2.80 (t, 2H, $J = 7.6$ Hz).

(S)-1-(Naphthalen-1-yl)ethanol, **8**

To a stirred solution of 1-(naphthalen-1-yl) ethanone (2 g, 11.76 mmol) in dry THF (20 mL) was added *R*-(-)-2-methyl-CBS-oxazoborolidine (3.8 mL, 3.8 mmol, 1M, toluene) at -40°C and stirred for 30 minutes, then added $\text{BH}_3 \cdot \text{DMS}$ (1.22 mL, 12.9 mmol) at the same temperature and continued stirring for 1h. The reaction mixture was quenched by adding methanol (0.1 mL, 5 mL ether) followed by saturated NaHCO_3 (15 mL). The solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (2×15 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography by eluting with ethyl acetate-hexane (2:8) mixture to yield, chiral alcohol **8** as colorless, low melting solid, (1.3 g, 65%). $[\alpha]_{\text{D}}^{27} = -72.2^\circ$ (c 1, methanol). $^{13}\text{C NMR}$ (CDCl_3): δ 136.1, 133.9, 130.5, 128.9, 128.7, 126.4, 125.7, 125.2, 123.5, 123.0, 57.5, 20.6; EIMS m/z (%): 198 (M+1, 10), 197 (25), 168 (30), 155 (100), 77 (20), 63 (10).

IR (neat): ν 3380, 2973, 2927, 1510, 1370, 1109, 777 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.12 (d, 1H, $J = 8.3$ Hz), 7.84 - 7.91 (m, 1H), 7.78 (d, 1H, $J = 7.5$ Hz), 7.67 (d, 1H, $J = 7.5$ Hz), 7.44 - 7.58 (m, 3H), 5.67 (q, 1H, $J = 6.9$ Hz), 1.67 (d, 3H, $J = 6.9$ Hz); $^{13}\text{C NMR}$ (CDCl_3): δ 141.3, 133.8, 130.2, 128.9, 127.9, 126.0, 125.5, 123.1, 121.9, 67.1, 24.3 ppm.; EIMS m/z (%): 195 (M+23, 10), 172 (M^+ , 10), 155 (30).

(R)-1-(1-Azidoethyl) naphthalene, **10**

To a stirred solution of 1-(naphthalen-1-yl) ethanol (1 g, 5.8 mmol) in dry CH_2Cl_2 (10 mL) was added triethylamine (1.5g, 14.5mmol) followed by methane sulfonyl chloride (1g, 8.7 mmol) at 0°C and continued stirring for 30 minutes and confirmed the completion of reaction by TLC. Then the reaction mixture was diluted by adding CH_2Cl_2 (20 mL) and washed with water, brine, dried over Na_2SO_4 and concentrated. The afforded, mesyl compound (**9**) was used for further process without purification.

To a stirred mixture of the above mesyl compound **9** (1.5 g, 6 mmol) in acetonitrile (15 mL) was added sodium azide (0.78g, 12 mmol) and refluxed for 5h and solvent was evaporated under vacuum and residue was extracted with ethyl acetate (2×15 mL). The combined organic layers was washed with brine, dried over Na_2SO_4 and concentrated. Crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with ethylacetate-hexane (1:9) mixture. Pure product **10** was obtained as brown liquid, 1.2g (70%). $[\alpha]_{\text{D}}^{27} = 13.6^\circ$ (c 0.3, CHCl_3).

IR (neat): ν 3051, 2980, 2101, 1597, 1510, 1449, 1376, 1247, 980, 777 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.10 (d, 1H, $J = 8.3$ Hz), 7.89 (d, 1H, $J = 9.0$ Hz), 7.82 (d, 1H, $J = 8.12$ Hz), 7.43 - 7.61 (m, 4H), 5.34 (q, 1H, $J = 7.5$ Hz), 1.72 (d, 3H, $J = 7.8$ Hz); $^{13}\text{C NMR}$ (CDCl_3): δ 136.1, 133.9, 130.5, 128.9, 128.7, 126.4, 125.7, 125.2, 123.5, 123.0, 57.5, 20.6; EIMS m/z (%): 198 (M+1, 10), 197 (25), 168 (30), 155 (100), 77 (20), 63 (10).

(R)-1-(Naphthalen-1-yl)-ethanamine, **11**

To a stirred solution of 1-azidonaphthalene (1g, 5m mol) in ethanol-water (10 mL, 3:1) mixture was added ammonium chloride (0.7 g, 12.5 mmol) and Zinc dust (0.5 g, 7.5 mmol) and stirred for 1h at 60°C . After completion of reaction, the reaction mixture was filtered by sintered funnel and the filtrate was concentrated under reduced pressure, the residue was extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on neutral alumina by eluting with methanol-chloroform (1:9) mixture. Product **11** obtained as brown liquid, 0.8g (92%). $[\alpha]_{\text{D}}^{27} = 51.6^\circ$ (c 2, EtOH). $^{13}\text{C NMR}$ (CDCl_3): δ 143.0, 133.9, 130.7, 129.0, 127.3, 126.0, 125.6, 125.4, 122.9, 121.4, 46.5, 24.7 ppm.; EIMS m/z (%): 172 (M+1, 10), 155 (25).

IR (neat): ν 3185, 3049, 2925, 1596, 1510, 1449, 1246, 1168, 1027, 777 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.11 (d, 1H, $J = 8.3$ Hz), 7.88 (d, 1H, $J = 7.6$ Hz), 7.76 (d, 1H, $J = 8.3$ Hz), 7.67 (d, 1H, $J = 6.7$ Hz), 7.42 - 7.58 (m, 3H), 5.01 (q, 1H, $J = 7.5$ Hz), 1.89 (brs, 2H), 1.59 (d, 3H, $J = 6.8$ Hz); $^{13}\text{C NMR}$ (CDCl_3): δ 143.0, 133.9, 130.7, 129.0, 127.3, 126.0, 125.6, 125.4, 122.9, 121.4, 46.5, 24.7 ppm.; EIMS m/z (%): 172 (M+1, 10), 155 (25).

(R)-N-[1-(Naphthalen-1-yl)ethyl]-3-[3-(trifluoromethyl)phenyl]propan-1-amine, **1**

To a stirred solution of 3-[3-(trifluoromethyl)phenyl]propanal (0.8g, 4 mmol) in methanol (10 mL) was added (*R*)-1-(naphthalen-1-yl)-ethanamine (0.68g, 4m mol) and sodium triacetoxy borohydride (1.27 g, 6 mmol)

followed by acetic acid (0.25 mL, 4 mmol). The resulting mixture was stirred at RT for 10h. After confirming the completion of reaction by TLC, the reaction mixture was quenched with 1N NaOH. Then, solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate (2×10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, concentrated under vacuum. Crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with ethyl acetate-hexane (1:1) mixture. Pure product, obtained as brown sticky material, 1.1 g (80%), which was crystallized with hydrochloric methanol and filtered the obtained white solid. $[\alpha]_D^{27} = -27^\circ$ (c 1, MeOH). Mp. 175 - 177°C (Lit.178 - 184°C).

IR (KBr): ν 3158, 2962, 2750, 1599, 1587, 1450, 1326, 1129, 1070, 774 cm⁻¹; ¹H NMR (DMSO-d₆): δ 8.12 (dd, 2H, $J = 7.2, 8.0$ Hz), 7.84 - 7.97 (m, 2H), 7.51 - 7.64 (m, 4H), 7.25 - 7.44 (m, 4H), 5.08 - 5.18 (m, 1H), 2.69 - 2.76 (m, 2H), 2.67 (t, 2H, $J = 7.0$ Hz), 2.08 - 2.25 (m, 2H), 1.88 (d, 3H, $J = 6.6$ Hz); ¹³C NMR (DMSO): δ 140.6, 133.2, 13 1.2, 131.1, 129.9, 128.6, 128.3, 126.7, 125.7, 125. 2, 124.3, 122.4, 121.0, 52.6, 44.8, 31.9, 26.7, 20.3 ppm.; HRMS (ESI): m/z [M⁺H]⁺ caclcd for C₂₂H₂₂ONF₃: 358.1763; found: 358.1777.

Conclusion

In conclusion, we have achieved the enantio selective synthesis of (*R*)-Cinacalcet (**1**) success fully. The synthesis was started from a commercially available 3-(trifluoromethyl) benzaldehyde (**2**) and 1-(naphthalen-1-yl)ethanone (**3**). The synthesis was completed within 8 steps with an overall yield 18.5%.

Supplementary Information

Supplementary information is available in the website <http://nopr.niscair.res.in/handle/123456789/58776>.

Acknowledgements

Authors are thankful to DST-SERB-EEQ/2018/001311 for financial support and NSG is thankful to CSIR-New Delhi, for providing fellowship.

IICT Communication No: IICT/Pubs./2021/295.

References

- Franceschini N, Joy M S & Kshirsagar A, *Expert Opin Invest Drugs*, 12 (2007) 1413.
- Herbert S C, *Annu Rev Med*, 57 (2006) 349.
- Sorbera L A, Castaner R M & Bayes M, *Drugs Future*, 27 (2002) 831.
- Nagano N, *Pharmacol Ther*, 109 (2006) 339.
- Shinde G B, Niphade N C, Deshmukh S P, Toche R B & Mathad V T, *Org Proc Res Dev*, 15 (2011) 455.
- Kumar G B, Maloyesh B, Bhaskar B S & Rajendra A, *Synth Commun*, 38 (2008) 1512.
- Tamura M & Kochi J, *J Am Chem Soc*, 93 (1971) 1487.
- Cahiez G, Habiak V, Duplais C & Moyeux A, *Angew Chem Int Ed*, 46 (2007) 4364.
- Arava V R, Gorentla L N & Dubey P K, *Beil J Org Chem*, 8 (2012) 1366.
- Thiel O R, Bernard C, Tormos W, Brewin A, Hirotani S, Murakami K, Saito K, Larsen R D, Martinelli M J & Reider P J, *Tetrahedron Lett*, 49 (2008) 13.
- Xicota B M, Leiva R, Escolano C & Vazquez S, *Synthesis*, 48 (2016) 783.
- Marx L, Lombardia N R, Fernberger J F, Kroutil W, Mateos A I B, Gallego F L, Moris F, Sabin J G & Berglund P, *Adv Synth Catal*, 360 (2018) 2157.
- Vanwagenen B C, Moe S T, Balandrin M F, del Mar E G & Nemeth E F, *US Patent* (NPS Pharmaceuticals) (2001) 6211244.
- Nemeth E F, Vanwagenen B C, Balandrin M F, del Mar E G & Moe S T, *US Patent* (NPS Pharmaceuticals) (2000) 6011068.
- Reddy B P, Reddy K R, Reddy D M, Reddy R R, Reddy J M & Krishna B V, *PCT Int Appl* WO2012007954 (2012).
- Sebastian S, Sarma S R, Murthy K R & Pradhan N S, *US Patent* 020110178326A1 (2011).
- Ferrari M, Ghezz M & Bonaldi M, *US Patent* 020110105799A1 (2011).
- Allegrini P, Attolino E & Rossi D, *US Patent* 020110124917A1 (2011).
- Thiel O, Bernard C, Larsen R, Martinelli J M & Raza M T, *PCT Int Appl* WO200900247A3 (2008).
- Anil T, Karunakar B & Narsaiah A V, *Arkivoc*, v (2019) 307.
- Anil T, Karunakar B & Narsaiah A V, *SynOpen*, 3 (2019) 49.
- Karunakar B, Anil T & Narsaiah A V, *SynOpen*, 3 (2019) 26.
- Karunakar B, Anil T & Narsaiah A V, *ChemistrySelect*, 4 (2019) 5531.
- Ganesh N S, Nagalatha G & Narsaiah A V, *Nat Prod Res*, 34 (2020) 2173.
- Nagalatha G, Ganesh N S & Narsaiah A V, *Tetrahedron Lett*, xx (2021) ASAP.
- Wittig G & Schollkopf U, *Chem Ber*, 87 (1954) 1318.
- Reddy A R, Wadavrao S B, Yadav J S & Narsaiah A V, *Helv Chim Acta*, 98 (2015) 1009.
- Tungler A, Tarnai T, Hegediis L & Fodor K, *Platinum Metals Rev*, 42 (1998) 108.
- Laib T & Zhu J, *Synlett*, 9 (2000) 1363.
- Dess D B & Martin J C, *J Org Chem*, 48 (1983) 4155.
- Yadav J S, Reddy B V S, Basak A K & Narsaiah A V, *Tetrahedron*, 60 (2004) 2131.
- Corey E J, Shibata S & Bakshi R K, *J Org Chem*, 53 (1988) 2861.
- Wadavrao S B, Ashritha N & Narsaiah A V, *Synthesis*, 45 (2013) 3383.
- Lin W, Zhang X, He Z, Jin Y, Gong L & Mi A, *Synth Commun*, 32 (2002) 3279.
- Abdel-Magid A F, Carson K G, Harris B D, Maryanoff C A & Shah R D, *J Org Chem*, 61 (1996) 3849.