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Enantioselective synthesis of (*R*)-(+)-α-lipoic acid via proline-catalyzed sequential α-aminoxylation and HWE olefination of aldehyde

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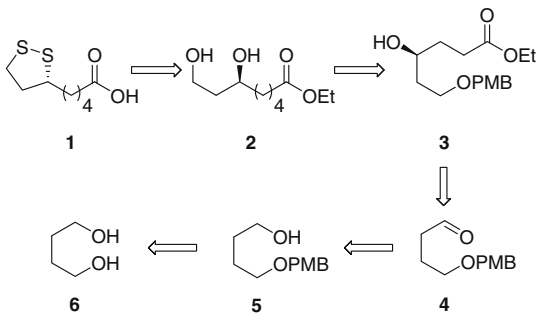
ABSTRACT

An efficient enantioselective synthesis of (*R*)-(+)-α-lipoic acid is described, in high optical purity (>97% ee), using L-proline-catalyzed sequential α-aminoxylation and Horner–Wadsworth–Emmons olefination of aldehyde as the key step.

α-Lipoic acid is an important growth factor for a variety of micro-organisms, and also a co-factor for the multi-enzyme complex that catalyzes oxidative decarboxylation of α-keto acids.[1] Reed and co-workers reported the isolation of α-lipoic acid in 1951 from liver residue.[1] Although the chemical structure of α-lipoic acid was determined,[1,2] its absolute configuration *R* was not known till Golding's synthesis of complementary enantiomer from *S*-malic acid.[3] Since then a number of (±)-α-lipoic acid syntheses have been documented in the literature.[4] Lipoic acid and its derivatives are highly active as anti-HIV and anti-tumor agents. The *R*-(+)-enantiomer is more effective than the *S*-(−)-enantiomer in enhanced insulin-stimulated glucose transport and non-oxidative and oxidative glucose metabolism.[5] In this context, the development of enantioselective methods for the preparation of enantiomerically pure lipoic acid is of particular interest from the standpoint of pharmaceutical and organic chemistry. Several asymmetric syntheses of **1** have been reported, which include (i) the stereospecific synthesis from chiral building blocks or using chiral auxilaries;[6] (ii) the enzymatic reduction of prochiral ketones;[7] (iii) the enzymatic resolution of racemic mixtures;[8] (iv) the asymmetric organometallic catalytic methods.[9] Recently, L-proline-catalyzed aldol reaction was used for the synthesis of (*R*)-α-lipoic acid **1**, but it involves destroying one of the chiral centers.[10] Some of these methods are not amenable to scale up, due to large number of steps coupled with low yields.

The area of asymmetric organocatalysis is rapidly developing and attracts scientific community around the world. In the recent years organocatalytic asymmetric synthesis has provided several new methods for obtaining chiral building blocks.[11] In this context, proline, the only natural amino acid with a secondary amine functionality, an abundant, inexpensive amino acid available in both enantiomeric forms, has emerged as a 'universal catalyst'.[11] Proline has high utility, especially in enantioselective aldol reaction,[12] Mannich reaction,[13] Diels–Alder cycloaddition,[14] Michael addition,[15] and α-functionalization of aldehydes[16] among many others. Proline-catalyzed sequential transformations[17] is an emerging research field in organic synthesis.

Optically active α-hydroxyaldehydes are important intermediates in organic synthesis.[18] The more prominent, well-established methods of enantioselective α-oxygenations include the use of Davis oxaziridine,[19a] Sharpless dihydroxylation of enol ethers,[19b] manganese-salen epoxidation of enol ethers,[19c] and Shi epoxidation of enol ethers.[19d] Recently, L-proline-catalyzed α-aminoxylation of aldehydes[16] has also been found to be an excellent asymmetric method for chiral α-hydroxyaldehydes. The reaction has several advantages from a practical point of view, which include inexpensive and commercially available proline as the catalyst, commercial availability of both forms of proline, low catalyst loadings (5–20 mol %), and good to excellent yield of enantiomerically enriched alcohols. In continuation with our work of organocatalytic asymmetric synthesis of biologically active compounds,[20] in this Letter, we wish to report the organocatalytic enantioselective approach to synthesis of (*R*)-(+)-α-lipoic acid by using a L-proline-catalyzed sequential aminoxylation-HWE olefination reaction of aldehyde[17d] as the key step.



Scheme 1. Retrosynthetic analysis of (*R*)-(+)-α-lipoic acid **1**.

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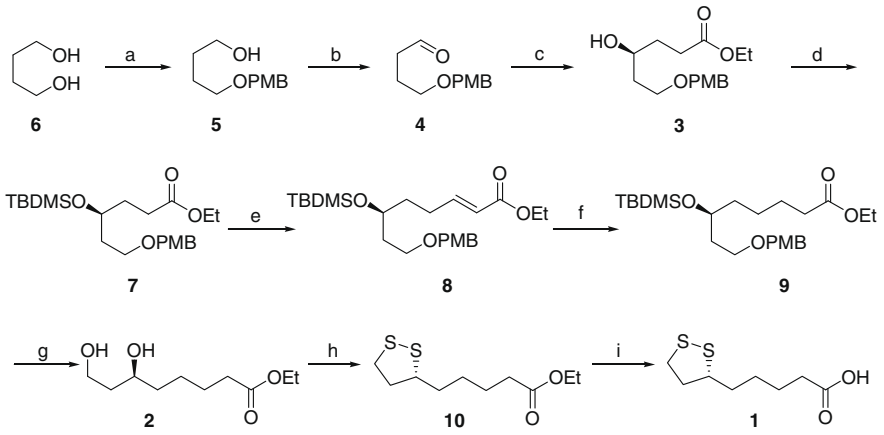
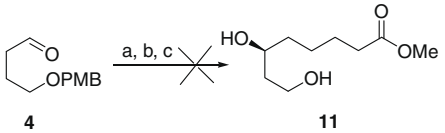


Scheme 2. Reagents and conditions: (a) 4-methoxybenzyl chloride, NaH, THF/DMF (1:1), 0 °C to rt overnight, 79%; (b) IBX, DMSO, rt, 2 h, 94%; (c) (i) PhNO, L-proline, DMSO, rt, 20 min then triethylphosphonoacetate, LiCl, DBU, CH_3CN, 0 °C, 45 min; (ii) 10% Pd/C, H_2, EtOAc, 4 h, 58% (for two steps); (d) TBDMSCl, imidazole, 4-DMAP, CH_2Cl_2, 0 °C to rt overnight, 89%; (e) DIBAL-H (2 M in toluene), CH_2Cl_2, −78 °C, 2 h then triethylphosphonoacetate, LiCl, DBU, CH_3CN, 0 °C, 45 min, 82%; (f) 10% Pd/C, H_2, EtOAc, rt, 4 h, 94%; (g) $TiCl_4$, CH_2Cl_2, 0 °C, 1 h, 87%; (h) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 4 h then Na_2S, sulfur, DMF, 80 °C, 24 h, 85%; (i) 1 M ethanolic KOH, rt, 24 h, 76%.

From retrosynthetic analysis (Scheme 1), it was envisaged that the key intermediate **3** could be derived from the aldehyde **4** using L-proline-catalyzed sequential α-aminoxylation and HWE olefination to install required chirality.

Our approach started with commercially available butane-1,4-diol **6** as illustrated in Scheme 2. The mono hydroxyl protection of **6** with *p*-methoxybenzyl chloride and NaH gave alcohol **5** in 79% yield. Alcohol **5** was oxidized with IBX to aldehyde **4** in 94% yield and subsequently subjected to modified MacMillan protocol[17d] (sequential L-proline-catalyzed α-aminoxylation-HWE olefination) and then hydrogenation to obtain chiral γ-hydroxy ester **3** in 58% yield over two steps. The enantiopurity of γ-hydroxy ester **3** was 97%, determined by chiral HPLC analysis.[21] In order to avoid interference of hydroxyl group during chain elongation, it was protected with TBDMSCl and imidazole to obtain silyl ether **7** in 89% yield. The ester **7** was then reduced to aldehyde with DIBAL-H at −78 °C and subjected to HWE olefination to obtain α,β-unsaturated ester **8** in 82% yield. The α,β-unsaturated ester **8** on hydrogenation with 10% Pd/C afforded saturated ester **9** in 94% yield. The next task was deprotection of *p*-methoxybenzyl ether and silyl ether. For the purpose of deprotection of both the protecting groups, we subjected ester **9** to $TiCl_4$ in CH_2Cl_2 at 0 °C for 30 min and obtained dihydroxy ester **2** in 87% yield. The dihydroxy ester **2**, a well known key intermediate in the synthesis of α-lipoic acid, was efficiently converted to dimesylate derivative by treatment with mesyl chloride and triethyl amine. The dimesylate derivative on treatment with Na_2S and elemental sulfur in DMF at 80 °C afforded ethyl lipoate **10**. Ethyl lipoate **10** on hydrolysis using 1 M ethanolic KOH furnished the target (*R*)-(+)-α-lipoic acid **1** in 76% yield.

To reduce the number of steps and to increase the efficacy of synthesis we subjected aldehyde **4** to Hayashi's protocol[16a] (L-proline-catalyzed α-aminoxylation) followed by Wittig reaction[22] with (*E*)-methyl-4-(triphenylphosphoranylidene)but-2-enoate and the resultant material after workup was subjected to Pd/C-catalyzed hydrogenation. But to our disappointment it resulted in a complex reaction mixture instead of the desired dihydroxy ester **11** (Scheme 3). We obtained similar results for Wittig reaction at lower temperatures. If this reaction would have worked then this synthesis would have been much shorter than the present synthesis.



Scheme 3. Reagents and conditions: (a) PhNO, L-proline, CH_3CN, −20 °C, 24 h; (b) (*E*)-methyl-4-(triphenylphosphoranylidene)but-2-enoate, CH_2Cl_2, rt, 12 h; (c) 10% Pd/C, H_2, EtOAc, 6 h.

The analytical data of all new compounds are in good agreement with proposed structures[23] and that of **1** is in good agreement with the literature data.[24]

In conclusion, we have achieved a short and efficient synthesis of (*R*)-(+)-α-lipoic acid (overall yield 16.6%) by employing proline-catalyzed sequential α-aminoxylation-HWE olefination of aldehyde. Excellent yields, simple and environmentally friendly procedures, and easy availability of the starting materials are some of the salient features of this approach.

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References and notes

1. Reed, L. J.; Gunsalus, I. C.; DeBusk, B. G.; Hornberger, C. S., Jr. *Science* **1951**, *114*, 93.
2. (a) Reed, L. J.; Gunsalus, I. C.; Schnakenberg, G. H. F.; Soper, Q. F.; Boaz, H. E.; Kern, S. F.; Parke, T. V. *J. Am. Chem. Soc.* **1953**, *75*, 1267; (b) Reed, L. J.; DeBusk, B. G.; Hornberger, C. S.; Gunsalus, I. C. *J. Am. Chem. Soc.* **1953**, *75*, 1271.
3. Brookes, M. H.; Golding, B. T.; Howes, D. A.; Hudson, A. T. *J. Chem. Soc., Chem. Commun.* **1983**, 1051.
4. (a) Segre, A.; Viterbo, R.; Parisi, G. *J. Am. Chem. Soc.* **1957**, *79*, 3503; (b) Tsuji, J.; Yasuda, H.; Mandai, T. *J. Org. Chem.* **1978**, *43*, 3606; (c) Chavan, S. P.; Kale, R. R.; Pasupathy, K. *Synlett* **2005**, 1129; (d) Chavan, S. P.; Shivsankar, K.; Pasupathy, K. *Synthesis* **2005**, 1297.
5. Streeper, R. S.; Henriksen, E. J.; Tritschler, H. J. *Am. J. Physiol.* **1997**, 273.
6. (a) Elliott, J. D.; Steele, J.; Johnson, W. S. *Tetrahedron Lett.* **1985**, *26*, 2535; (b) Rama Rao, A. V.; Garyali, K.; Gurjar, M. K.; Ravindranathan, T. *Carbohydr. Res.* **1986**, *148*, 51; (c) Rama Rao, A. V.; Mysorekar, S. V.; Gurjar, M. K.; Yadav, J. S. *Tetrahedron Lett.* **1987**, *28*, 2183; (d) Menon, R. B.; Kumar, M. A.; Ravindranathan, T. *Tetrahedron Lett.* **1987**, *28*, 5313; (e) Brookes, M. H.; Golding, B. T. *J. Chem. Soc., Perkin Trans.1* **1988**, 9; (f) Wei, Z.; Lan, H.-Q.; Zheng, J.-F.; Huang, P.-Q. *Synth. Commun.* **2009**, *39*, 691.
7. (a) Gopalan, A. S.; Jacobs, H. K. *Tetrahedron Lett.* **1989**, *30*, 5705; (b) Gopalan, A. S.; Jacobs, H. K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1897; (c) Dasaradhi, L.; Fadnavis, N. W.; Bhalerao, U. T. *J. Chem. Soc., Chem. Commun.* **1990**, 729; (d) Bezbarua, M.; Saikia, A. K.; Barua, N. C.; Kalita, D. *Synthesis* **1996**, 1289.
8. (a) Adger, B.; Bes, M. T.; Grogan, G.; McCague, R.; Pedragosa-Moreau, S.; Roberts, S. M.; Villa, R.; Wan, P. W. H.; Willetts, A. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1563; (b) Bes, M. T.; Villa, R.; Roberts, S. M.; Wan, P. W. H.; Willetts, A. *J. Mol. Catal. B: Enzym.* **1996**, *1*, 127; (c) Santosh Laxmi, Y. R.; Iyenger, D. S. *Synthesis* **1996**, 594; (d) Adger, B.; Bes, M. T.; Grogan, G.; McCague, R.; Pedragosa-Moreau, S.; Roberts, S. M.; Villa, R.; Wan, P. W. H.; Willetts, A. J.

Bioorg. Med. Chem. **1997**, *5*, 253; (e) Fadnavis, N. W.; Babu, R. L.; VadiVel, S. K.; Deshpande, A. A.; Bhalerao, U. T. *Tetrahedron: Asymmetry* **1998**, *9*, 4109; (f) Schwarz-Linek, U.; Krödel, A.; Ludwig, F.-A.; Schuleze, A.; Rissom, S.; Kragl, U.; Tishkov, V. I.; Vogel, M. *Synthesis* **2001**, 947.

9. (a) Bulman Page, P. C.; Rayner, C. M.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1986**, 1408; (b) Bulman Page, P. C.; Rayner, C. M.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1615; (c) Zimmer, R.; Hain, U.; Berndt, M.; Gewald, R.; Reissig, H.-U. *Tetrahedron: Asymmetry* **2000**, *11*, 879; (d) Upadhya, T. T.; Nikalje, M. D.; Sudalai, A. *Tetrahedron Lett.* **2001**, *42*, 4891; (e) Zimmer, R.; Peritz, A.; Czerwonka, R.; Schefzig, L.; Reissig, H.-U. *Eur. J. Org. Chem.* **2002**, 3419; (f) Chavan, S. P.; Praveen, C.; Ramakrishna, G.; Kalkote, U. R. *Tetrahedron Lett.* **2004**, *45*, 6027; (g) Bose, D. S.; Fatima, L.; Rajender, S. *Synthesis* **2006**, 1863.
10. Zhang, S.; Chen, X.; Zhang, J.; Wang, W.; Duan, W. *Synthesis* **2008**, 383.
11. (a) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3726; (b) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138; (c) Houk, K.N., List, B., Eds., Acc. Chem. Res. 2004, 37.; (d) List, B., Bolm, C., Eds., Adv. Synth. Catal. 2004, 346.; (e)*Asymmetric Organocatalysis*; Berkessel, A., Gröger, H., Eds.; Wiley-VCH: Weinheim, 2005; (f) List, B.; Seayad, J. *Org. Biomol. Chem.* **2005**, *3*, 719.
12. List, B.; Lerner, R. A.; Barbas, C. F., III *J. Am. Chem. Soc.* **2000**, *122*, 2395.
13. (a) List, B. *J. Am. Chem. Soc.* **2000**, *122*, 9336; (b) Barbas, C. F., III *J. Am. Chem. Soc.* **2002**, *124*, 1842.
14. (a) Ramachary, D. B.; Chowdari, N. S.; Barbas, C. F., III *Synlett* **2003**, 1910; (b) Sabitha, G.; Fatima, N.; Reddy, E. V.; Yadav, J. S. *Adv. Synth. Catal.* **2005**, *347*, 1353.
15. Hechavarria Fonseca, M. T.; List, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3958.
16. (a) Hayashi, Y.; Yamaguchi, J.; Hibino, K.; Shoji, M. *Tetrahedron Lett.* **2003**, *44*, 8293; (b) Zhong, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4247; (c) Hayashi, Y.; Yamaguchi, J.; Sumiya, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2003**, *43*, 1112; (d) List, B. *J. Am. Chem. Soc.* **2002**, *125*, 5656; (e) Brown, S. P.; Brochu, M. P.; Sinz, C. J.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 10808; (f) Cordova, A.; Sunden, H.; Bøgevig, A.; Johansson, M.; Himo, F. *Chem. Eur. J.* **2004**, *10*, 3673.
17. (a) Chowdari, N. S.; Ramachary, D. B.; Barbas, C. F., III *Org. Lett.* **2003**, *5*, 1685; (b) Zhong, G. *Chem. Commun.* **2004**, 606; (c) Zhong, G.; Yu, Y. *Org. Lett.* **2004**, *6*, 1637; (d) Mangion, I. K.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 3696; (e) Kumaran, S.; Shaw, D. M.; Longbottom, D. A.; Ley, S. V. *Org. Lett.* **2005**, *7*, 4189; (f) Kotkar, S. P.; Chavan, V. B.; Sudalai, A. *Org. Lett.* **2007**, *9*, 1001.
18. (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1983**, *13*, 1; (b) Hanneseian, S. *Total Synthesis of Natural Products: The Chiron Approach*; Pergamon Press: New York, 1983. Chapter 2; (c) Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447.
19. (a) Davis, F. A.; Bang-Chi, C. *Chem. Rev.* **1992**, *92*, 919; (b) Morikawa, K.; Park, J.; Andersson, P. G.; Hashiyama, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 8463; (c) Adam, W.; Fell, R. T.; Stegmann, V. R.; Saha-Moller, C. R. *J. Am. Chem. Soc.* **1996**, *118*, 708; (d) Zhu, Y.; Tu, H.; Shi, Y. *Tetrahedron Lett.* **1998**, *39*, 7819.
20. Panchgalle, S. P.; Gore, R. G.; Chavan, S. P.; Kalkote, U. R. *Tetrahedron: Asymmetry* **2009**, *20*, 1767.
21. Chiral HPLC analysis at 230 nm, t_R = 17.37 min, t_S = 18.79 min on Chiralcel OD-H (250 × 4.6 mm) column using 2-propanol/petroleum ether (80:20) as mobile phase with 0.5 mL/min flow rate.
22. Buchta, E.; Andree, F. *Chem. Ber.* **1960**, *93*, 1349.
23. *All new compounds were characterized and gave satisfactory analytical data. Compound* **3**: yellow oil, $[\alpha]_D^{25}$ −41.6 (*c* 1.12, $CHCl_3$); ee >97%; IR ($CHCl_3$) ν_{max} 3453, 2997, 1733 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ ppm 1.24 (t, 3H), 1.69–1.81 (m, 4H), 2.36–2.50 (m, 2H), 3.12 (br s, 1H), 3.58–3.63 (m, 1H), 3.66–3.71 (m, 1H), 3.76–3.83 (m, 1H), 3.79 (s, merged, 3H), 4.11 (q, 2H), 4.43 (s, 2H), 6.85 (d, *J* = 8.54, 2H), 7.22 (d, *J* = 8.54, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 30.5, 32.1, 36.3, 55.2, 60.3, 68.7, 70.5, 72.9, 113.7, 129.3, 129.8, 159.2, 174.0 ppm. Elemental Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.79; H, 8.14. *Compound* **7**: yellow oil; $[\alpha]_D^{25}$ −68.3 (*c* 1.21, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ ppm 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.27 (t, *J* = 7.15 Hz, 3H), 1.74–1.79 (m, 3H), 1.81–1.87 (m, 1H), 2.37 (t, *J* = 7.70 Hz, 2H), 3.52 (t, *J* = 6.33 Hz, 2H), 3.83 (s, 3H), 3.89–3.94 (m, 1H), 4.14 (q, 2H), 4.44 (q, 2H), 6.89 (d, *J* = 8.53, 2H), 7.27 (d, *J* = 8.53, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −4.6, −4.5, 14.1, 17.9, 25.8, 29.7, 32.0, 36.7, 55.2, 60.2, 66.5, 68.2, 72.6, 113.7, 129.2, 130.5, 159.0, 173.8 ppm. *Compound* **8**: colorless oil; $[\alpha]_D^{25}$ −29.71 (*c* 1.19, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ ppm 0.05 (s, 6H), 0.88 (s, 9H), 1.29 (t, *J* = 7.19 Hz, 3H), 1.57–1.64 (m, 1H), 1.70–1.83 (m, 3H), 2.20–2.26 (m, 1H), 2.34–2.40 (m, 1H), 3.52 (t, *J* = 7.78 Hz, 2H), 3.82 (s, 3H), 3.88–3.92 (m, 2H), 4.19 (q, 2H), 4.42 (dd, *J* = 9.79, 11.54 Hz, 2H), 5.81 (d, *J* = 15.56 Hz, 1H), 6.90 (d, *J* = 8.53 Hz, 2H), 6.99 (dt, *J* = 6.77, 15.56 Hz, 1H), 7.26 (d, *J* = 8.53 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.6, 14.2, 18.0, 25.8, 29.7, 32.0, 36.8, 55.2, 60.1, 66.5, 68.6, 72.6, 113.7, 121.1, 129.2, 130.4, 149.2, 159.0, 173.8 ppm. *Compound* **9**: yellow oil; $[\alpha]_D^{25}$ −41.5 (*c* 0.95, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ ppm 0.04 (s, 6H), 0.87 (s, 9H), 1.26 (t, *J* = 7.32 Hz, 3H), 1.34–1.43 (m, 2H), 1.54–1.85 (m, 5H), 2.25–2.40 (m, 2H), 3.50 (t, *J* = 6.57 Hz, 2H), 3.81 (s, 3H), 3.85–3.89 (m, 1H), 4.10 (q, *J* = 7.32 Hz, 2H), 4.41 (dd, *J* = 2.53, 11.62 Hz, 2H), 6.86 (d, *J* = 8.72 Hz, 2H), 7.24 (d, *J* = 8.72 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.6, 14.2, 18.0, 25.8, 29.7, 32.0, 34.3, 36.8, 37.1, 55.2, 60.1, 66.8, 69.1, 72.6, 113.7, 129.2, 130.6, 159.0, 173.7 ppm; LC–MS: *m*/*z* = 461.17 (M^++Na).
24. *Analytical data for (R)-(+)-α-lipoic acid*: yellow solid; mp 48 °C; $[\alpha]_D$ +103.18 (*c* 0.86, benzene); IR ($CHCl_3$) ν_{max} 3018, 2934, 1701 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ ppm 1.43–1.56 (m, 2H), 1.66–1.76 (m, 4H), 1.88–1.96 (m, 1H), 2.38 (t, *J* = 7.28 Hz, 2H), 2.43–2.51 (m, 1H), 3.09–3.22 (m, 2H), 3.35–3.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 28.6, 33.7, 34.5, 38.4, 40.1, 56.2, 179.5 ppm. Elemental Anal. Calcd for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84; S, 31.8. Found: C, 46.49; H, 6.89; S, 31.79.