Supporting information

SalenCo(OAc)/chiral ionic liquid catalyzed the asymmetric cycloaddition of CO_2 to epoxides

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Experimental:

Materials and Instruments:

Propylene oxide (PO) and epichlorohydrin were refluxed over CaH_2, and fractionally distilled nuder a nitrogen atmosphere. Other epoxides were purchased from Aldrich company without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruke AM-300 spectrometer using TMS as an internal standard. MS spectra were measured with a Mariner TOF MS spectrometer. Molar rotation were measured with a Model 341 polarmeter. GC analyses of cyclic carbonates were carried out on Varian CP 3800 gas chromatograph equipped with FID detectors. For the determination of enantiomeric excess, Supelco-DEX series (225) chiral columns were used.

Preparation of chiral ionic liquid

The preparation of CIL is a simple reaction carried out by mixing the precise molar ratio of amino acid (10mmol) and fresh AgOH (10mmol), TBAB (10mmol) or substituted pyridinium iodide (10mmol) in water. The reaction mixture was stirred for 24h and followed by filtration. The filtrate was concentrated under reduced pressure by rotary evaporator and then was dried in vacuum drying oven at 80°C for 24h to afford the desired CIL product. The chiral ionic liquids were prepared by referring to the literature method.19,20 All compounds are viscous liquids at room temperature. The colour of the liquids range from colourless to orange. The CILs are soluble in epoxides, except for [dimetylpyridinium]$_2$[Tar] (Table 1, entries 23-27). The purity of CIL was depended on the molar ratio of acid and base (AgOH). If the ratio is accurate. The purity of CIL is good enough without purification process. The Jacobsen catalyst (^{t}Bu)2SalenCo(OAc) was synthesized by referring literature method and was very soluble in epoxide.

Coupling reaction of CO_2 and epoxides.

Epoxide (100mmol), catalyst SalenCo(OAc) (0.1mmol) and chiral ionic liquid (0.1mmol) were added to a 100 ml stainless autoclave equipped with a magnetic stir bar and pressurized with CO_2 to 100 psi. After a proper reaction time, the remainder mixture was fractionally distilled under reduced pressure or recrystallized with ethanol to obtain pure cyclic carbonate.

Analytical Data of New Compounds

[TBA][L-Ala], $[TBA]_2$[L-Glu], [TBA][L-Phe], [TBA][L-Thr], [TBA][L-His], [TBA][L-Pro], $[TBA]_2$[L-Tar], $[TBA]_2$[D-Tar] were identified by comparision of their physical and spectral data with those present in the literature.[1]

Compound 1.

1,4-dimetylpyridinium (L)-tartrate [1,4-dimetylpyridinium]$_2$[L-Tar]

Yield 98%. $[\alpha]_D^{22}$ +11.4 (c 5 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 8.58 (d, *J* = 6.3Hz, 2H，N-C*H*), 7.52 (d, *J* = 6.3Hz, 2H，N-CH -C*H*), 4.31 (m, 4H, N-CH_3, C*H*-COOH), 2.65 (s, 3H, -CH_3); $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 178.2, 159.6, 144.0, 128.4, 73.9, 47.3, 21.3. ESITOFMS Calcd for $[cation]^+$ $C_7H_{10}N$ requires *m/z* 108.2, found 108.1; Calcd for $[anion+2H]^+$ $C_4H_6O_6$ requires *m/z* 150.1, found 150.3.

Compound 2.

1,2-dimetylpyridinium (L)-tartrate [1,2-dimetylpyridinium]$_2$[L-Tar]

Yield 96%. $[\alpha]_D^{22}$ +12.8 (c 5 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 8.71 (d, *J* =

6.3Hz, 1H, N-C*H*), 8.40 (dd, J_1 = 8.4Hz, J_2 = 7.5Hz, 1H, N-CH-CH-C*H*), 7.93 (d, *J* = 8.4Hz, 1H, N-C(CH_3)-C*H*), 7.85 (dd, *J* = 6.9Hz, 1H, N-CH-C*H*), 4.38 (s, 1H, C*H*-COOH), 4.27 (s, 3H, N-CH_3), 2.82 (s, 3H, N-C-CH_3); $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 177.7, 156.2, 145.7, 145.1, 129.4, 125.3, 73.6, 45.5, 19.9. ESITOFMS Calcd for [cation]$^+$ $C_7H_{10}N$ requires *m/z* 108.2, found 108.2; Calcd for [anion+2H]$^+$ $C_4H_6O_6$ requires *m/z* 150.1, found 150.4.

Compound 3.

1,4-dimetylpyridinium (D)-tartrate [1,4-dimetylpyridinium]$_2$[D-Tar]

Yield 98%. $[\alpha]_D^{22}$ -11.5 (c 5 in H_20). ^1H NMR (300MHz; D_2O) δ [ppm] 8.58 (d, *J* = 6.3Hz, 2H，N-C*H*), 7.52 (d, *J* = 6.3Hz, 2H，N-CH -C*H*), 4.31 (m, 4H, N-CH_3, C*H*-COOH), 2.65 (s, 3H, -CH_3); $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 178.2, 159.6, 144.0, 128.4, 73.9, 47.3, 21.3. ESITOFMS Calcd for [cation]$^+$ $C_7H_{10}N$ requires *m/z* 108.2, found 108.1; Calcd for [anion+2H]$^+$ $C_4H_6O_6$ requires *m/z* 150.1, found 150.3.

.**Compound 4.**

1,2-dimetylpyridinium (D)-tartrate [1,2-dimetylpyridinium]$_2$[D-Tar]

Yield 96%. $[\alpha]_D^{22}$ -12.7 (c 5 in H_20). ^1H NMR (300MHz; D_2O) δ [ppm] 8.71 (d, *J* = 6.3Hz, 1H, N-C*H*), 8.40 (dd, J_1 = 8.4Hz, J_2 = 7.5Hz, 1H, N-CH-CH-C*H*), 7.93 (d, *J* = 8.4Hz, 1H, N-C(CH_3)-C*H*), 7.85 (dd, *J* = 6.9Hz, 1H, N-CH-C*H*), 4.38 (s, 1H, C*H*-COOH), 4.27 (s, 3H, N-CH_3), 2.82 (s, 3H, N-C-CH_3); $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 177.7, 156.2, 145.7, 145.1, 129.4, 125.3, 73.6, 45.5, 19.9. ESITOFMS Calcd for [cation]$^+$ $C_7H_{10}N$ requires *m/z* 108.2, found 108.2; Calcd for [anion+2H]$^+$ $C_4H_6O_6$ requires *m/z* 150.1, found 150.4.

Compound 5.

1-ethyl-2-metylpyridinium (L)-tartrate [1-ethyl-2-metylpyridinium]$_2$[L-Tar]

Yield 96%. $[\alpha]_D^{22}$ +11.3 (c 5 in H_20). ^1H NMR (300MHz; D_2O) δ [ppm] 8.68 (d, *J* = 6.3Hz, 1H, N-C*H*), 8.29 (dd, J_1 = 8.4Hz, J_2 = 7.5Hz, 1H, N-CH-CH-C*H*), 7.84 (d, *J* = 7.5Hz, 1H, N-C(CH_3)-C*H*), 7.66 (dd, J_1 = 7.2Hz, J_2 = 6.9Hz, 1H, N-CH-C*H*), 4.52 (q, *J* = 7.35Hz, 2H, N-CH_2), 4.21 (s, 1H, C*H*-COOH), 2.76 (s, 3H, N-C-CH_3), 1.49 (t, *J* = 7.2Hz, *J* = 7.5Hz, 3H, N-CH_2-CH_3). $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 178.1, 155.2, 145.0, 144.4, 130.1, 125.8, 73.8, 53.5, 19.4, 14.6. ESITOFMS Calcd for [cation]$^+$ $C_8H_{12}N$ requires *m/z* 122.2, found 122.3; Calcd for [anion+2H]$^+$ $C_4H_6O_6$ requires *m/z* 150.1, found 150.4.

Compound 6. Tetrabutylammonium L-aspartic acid [TBA][L-Asp]

Yield 87%. $[\alpha]_D^{22}$ -1.0 (c 10 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 3.52 (d, *J* = 9.9Hz,1H, COOH-C*H*-NH$_2$), 3.14 (m, 8H, TBA), 2.62 (d, 7.2Hz, 1H, COOH-C*H*(α)), 2.27 (d, 7.2Hz, 1H, COOH-C*H*(β)), 1.56 (m, 8H, TBA), 1.20 (m, 8H, TBA), 0.95 (m, 12H, TBA); $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 180.3, 179.5, 58.1, 53.6, 41.9, 23.2, 19.2, 12.9. ESITOFMS Calcd for [cation]$^+$ $C_{16}H_{36}N$ requires *m/z* 242.5, found 242.5, Calcd for [anion+2H]$^+$ $C_4H_7NO_4$ requires *m/z* 133.1, found 133.5.

Compound 7. Tetrabutylammonium lactic acid [TBA][L-Lac]

Yield 96%. $[\alpha]_D^{22}$ -0.3 (c 10 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 3.95 (d, *J* = 5.4Hz, 1H, COOH-C*H*), 2.97 (m, 8H, TBA), 1.40 (m, 8H, TBA)**,** 1.23-1.08 (m, 11H, TBA, COOH-C*H*$_3$), 0.97 (m, 12H, TBA). $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 175.9, 67.8, 57.9, 23.0, 19.9, 19.0, 12.8. ESITOF-MS Calcd for [cation]$^+$ $C_{16}H_{36}N$ requires *m/z* 242.5, found 242.2; Calcd for [anion+H]$^+$ $C_3H_6O_3$ requires *m/z* 90.1, found 90.4.

Compound 8. Tetrabutylammonium L-lysine [TBA][L-Lys]

Yield 85%. $[\alpha]_D^{22}$ +0.5 (c 5 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 3.35 (m, 1H, COOH-C*H*), 3.27(m, 8H,TBA), 2.94 (t, J_1 = 7.5H, J_2 = 7.2Hz, NH$_2$-C*H*$_2$), 1.71 (m, 12H, TBA, NH$_2$-CH$_2$-C*H*$_2$, NH$_2$-CH$_2$-CH$_2$-CH$_2$-C*H*$_2$,), 1.28-1.21 (m, 10H, TBA, NH$_2$-CH$_2$-CH$_2$-C*H*$_2$), 1.01 (t, J_1 = 7.5Hz, J_2 = 7.2Hz, 12H). $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 182.7, 58.1, 57.4, 39.7, 33.8, 23.2, 22.1, 19.2, 16.9, 12.9. ESITOF-MS Calcd for [cation]$^+$ $C_{16}H_{36}N$ requires *m/z* 242.5, found 242.3, Calcd for [anion+H]$^+$ $C_6H_{14}N_2O_2$ requires *m/z* 146.2, found 146.4.

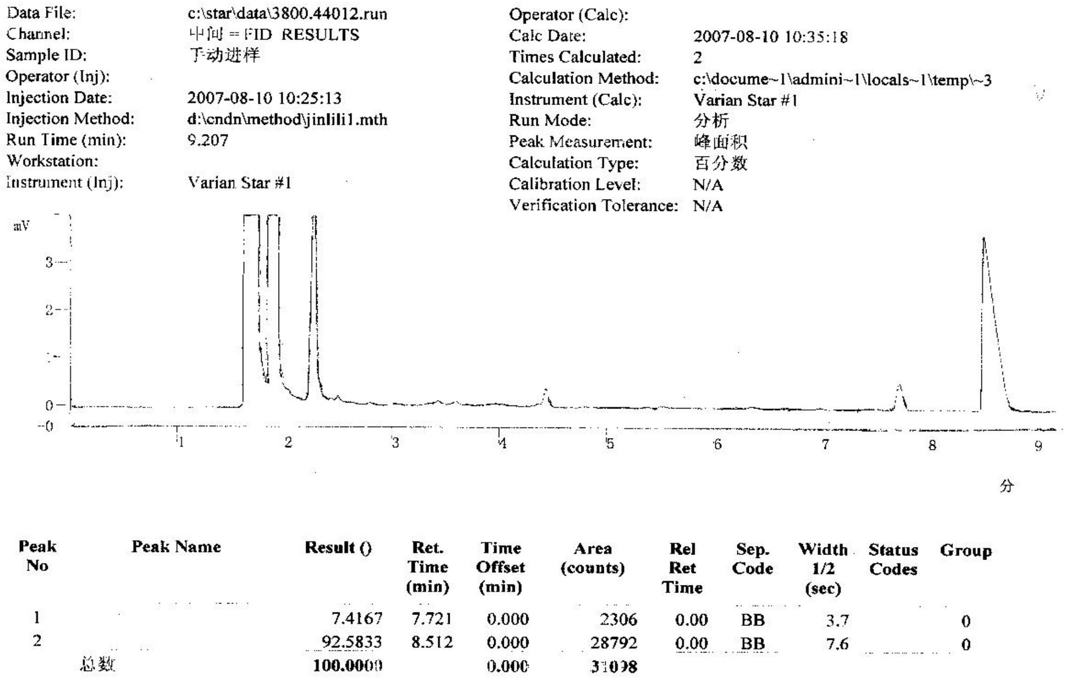
Compound 9. Tetrabutylammonium L-leucine [TBA][L-Leu]

Yield 82%. $[\alpha]_D^{22}$ -0.5 (c 5 in H_20). ^{1}H NMR (300MHz; D_2O) δ [ppm] 5.27(d, *J* = 3.2Hz, 1H, COOH-C*H*), 3.28 (m, 8H, TBA), 1.63-1.42 (m, 10H, -C*H*$_2$-CH-(CH$_3$)$_2$), 1.40 (m, 9H, TBA ,-CH$_2$-C*H*-(CH$_3$)$_2$), 1.00-0.87 (m, 18H, TBA, -C*H*$_3$). $^{13}C\{^1H\}$ NMR (D_2O) δ [ppm] 182.5, 58.2, 54.4, 43.4, 24.7, 23.3, 22.5, 21.5，19.3. ESITOF-MS Calcd for [cation]$^+$ $C_{16}H_{36}N$ requires *m/z* 242.5, found 242.3, Calcd for [anion+H]$^+$

$C_6H_{13}NO_2$ requires *m/z* 131.2, found 131.6.

REFERENCE

[1] C. R.Allen, P. L. Richard, A. J. Ward, L. G. A. Water, A. F. Masters, T. Maschmeyer. Tetrahedron Lett., 2006, 47, 7367.



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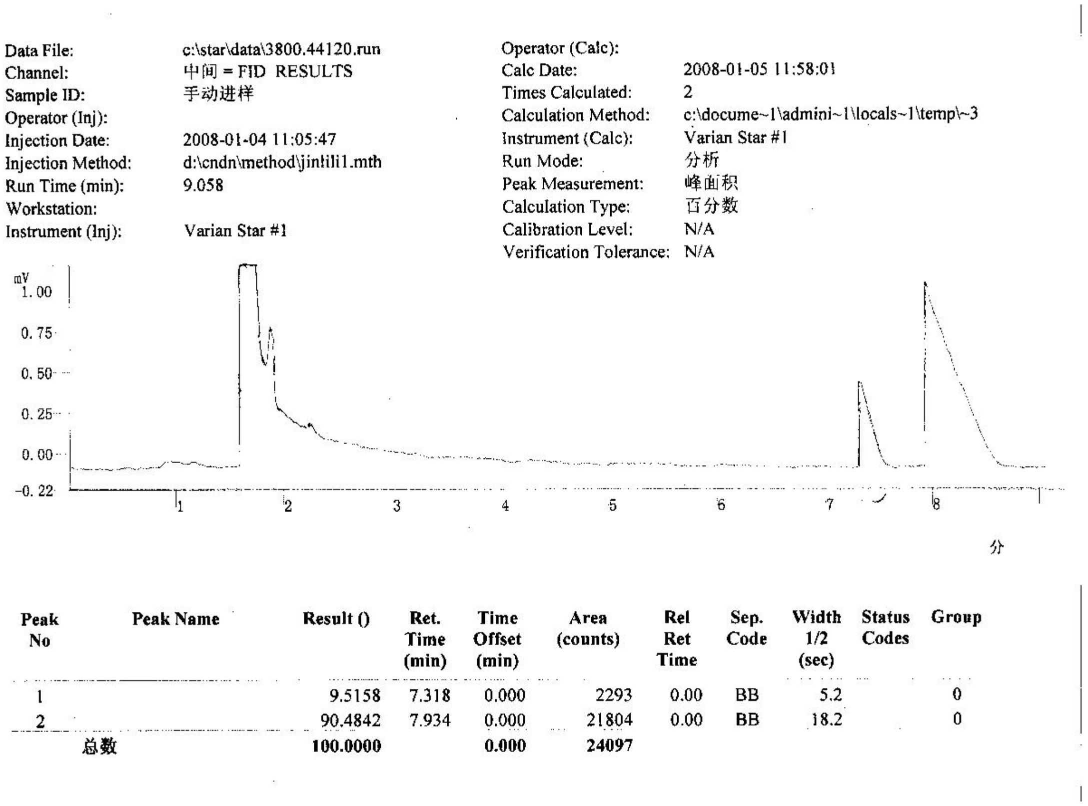
GC of PC catalyzed by (*R*,*R*)-1/[TBA][L-Ala] at 0°C(Table 1, Entry 2)



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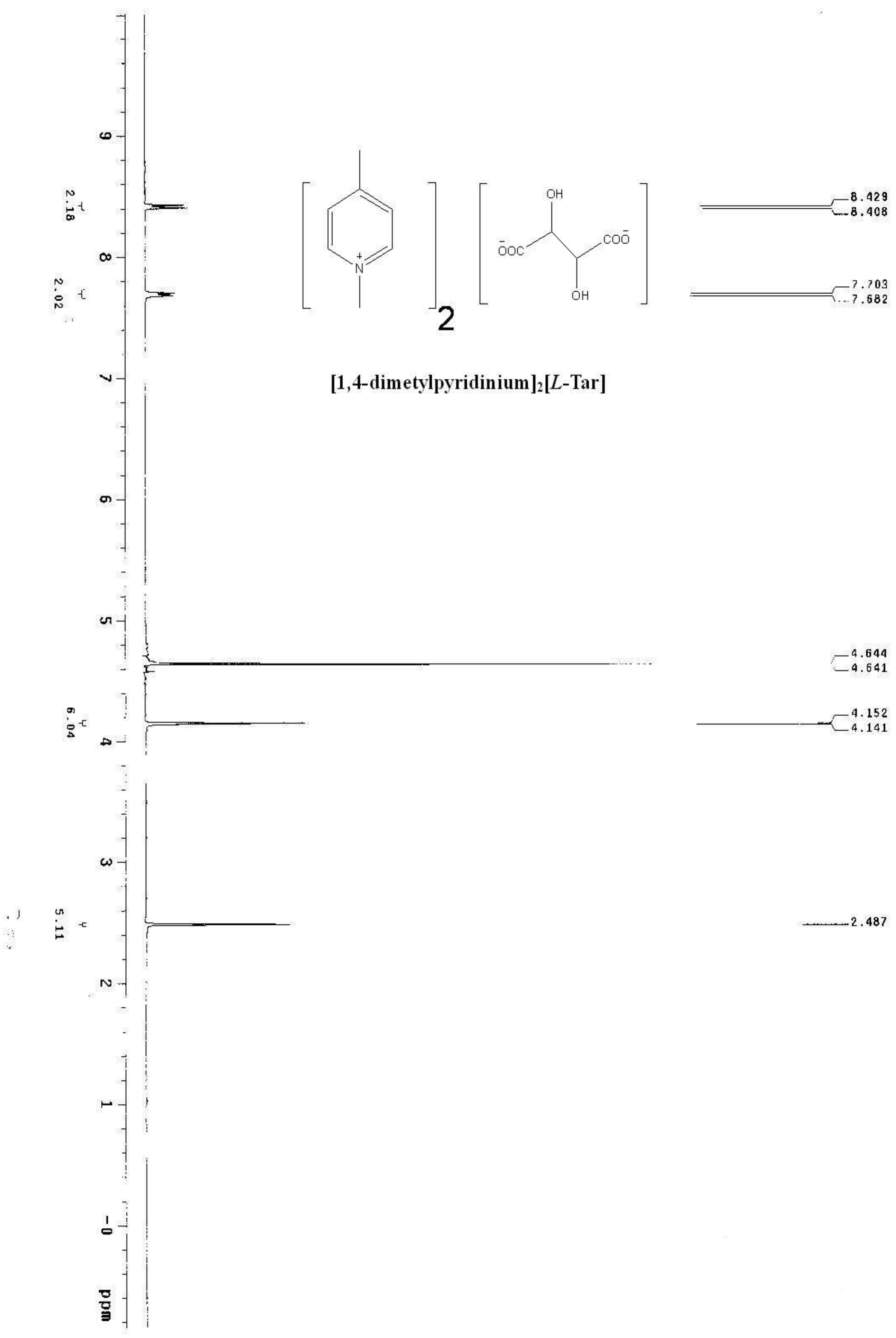
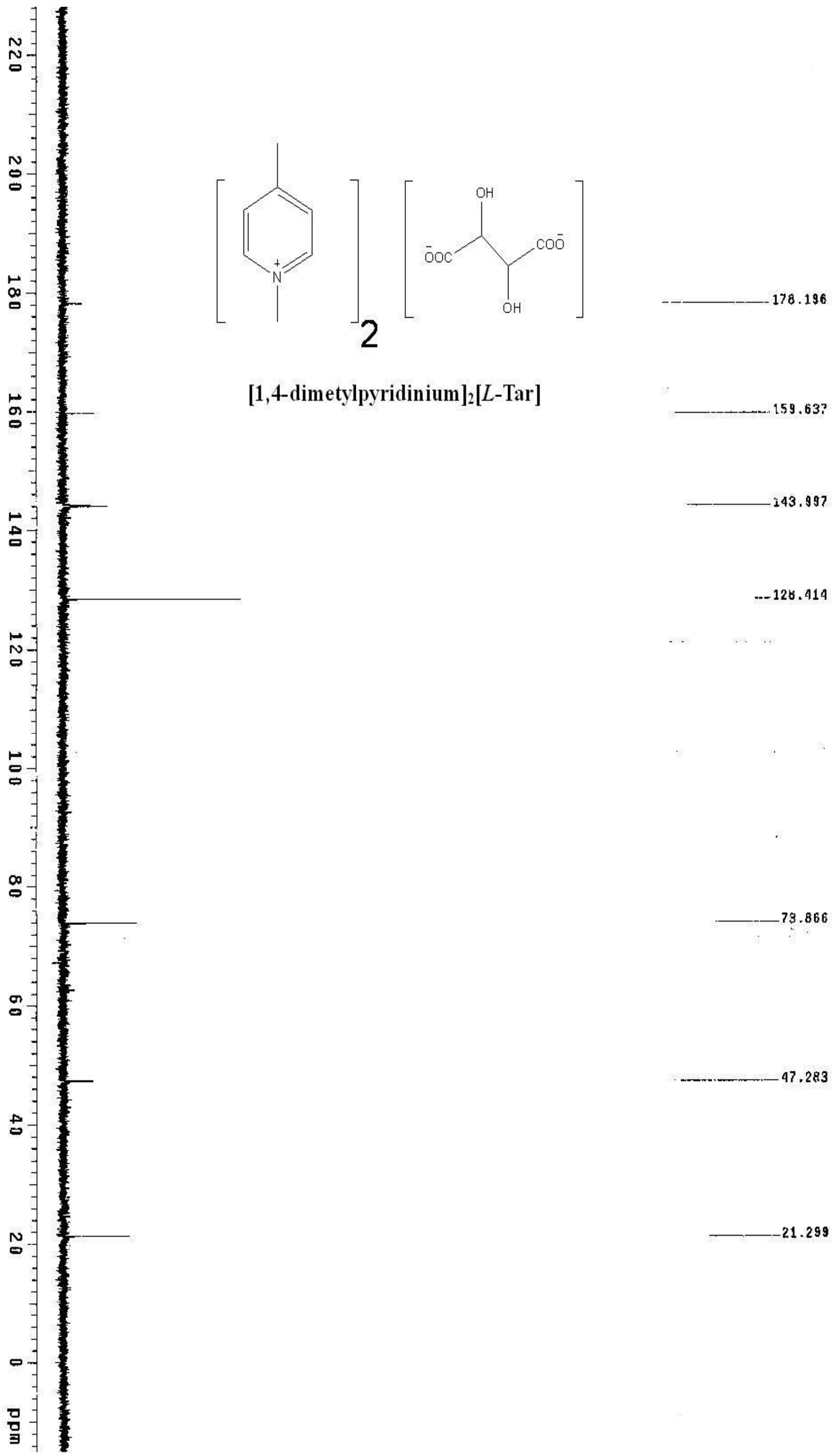
GC of PC catalyzed by (*R*,*R*)-1/[TBA][D-Pro] at 0 ^{o}C (Table 1, Entry 12)



^{1}H NMR of compound 1



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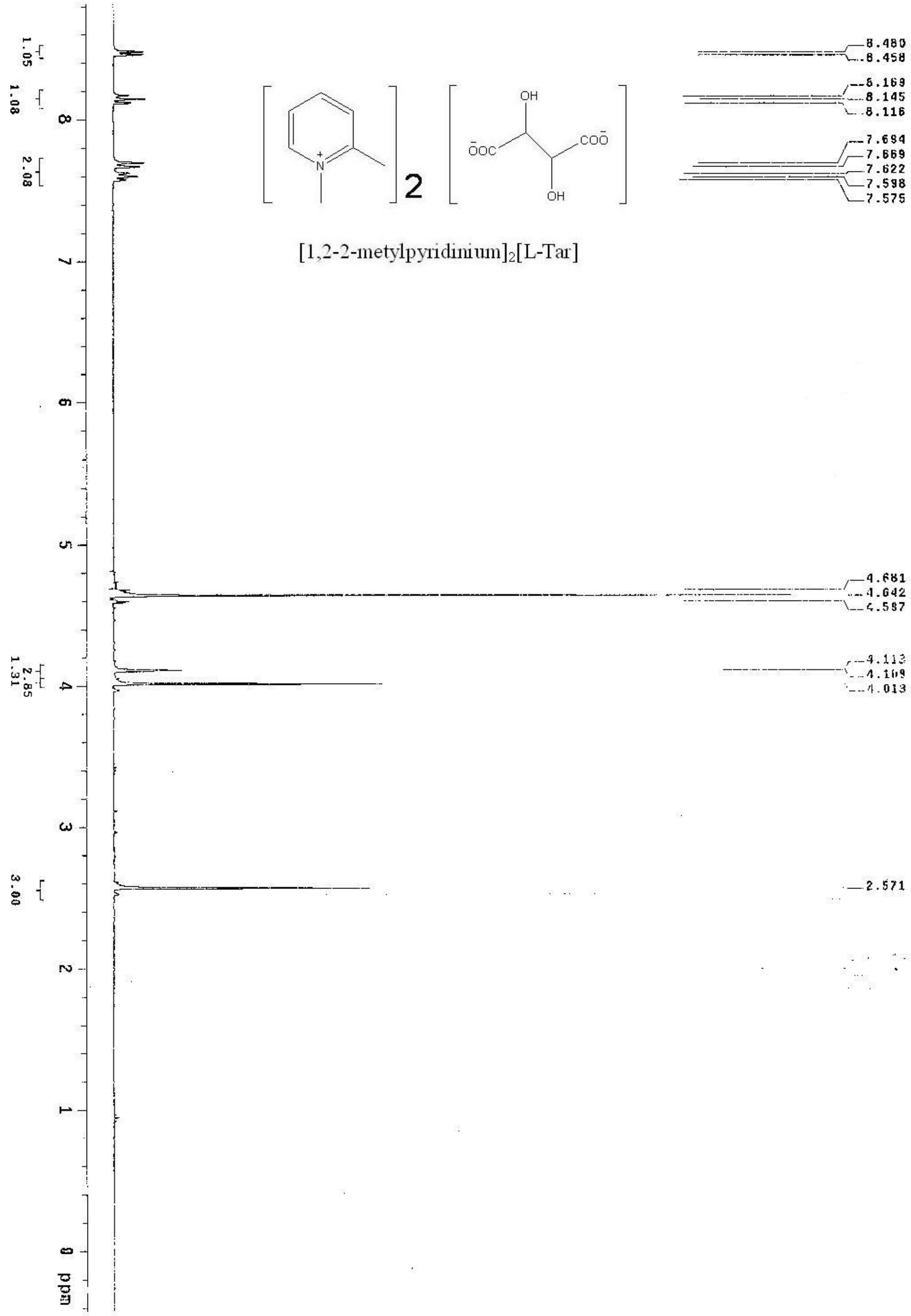

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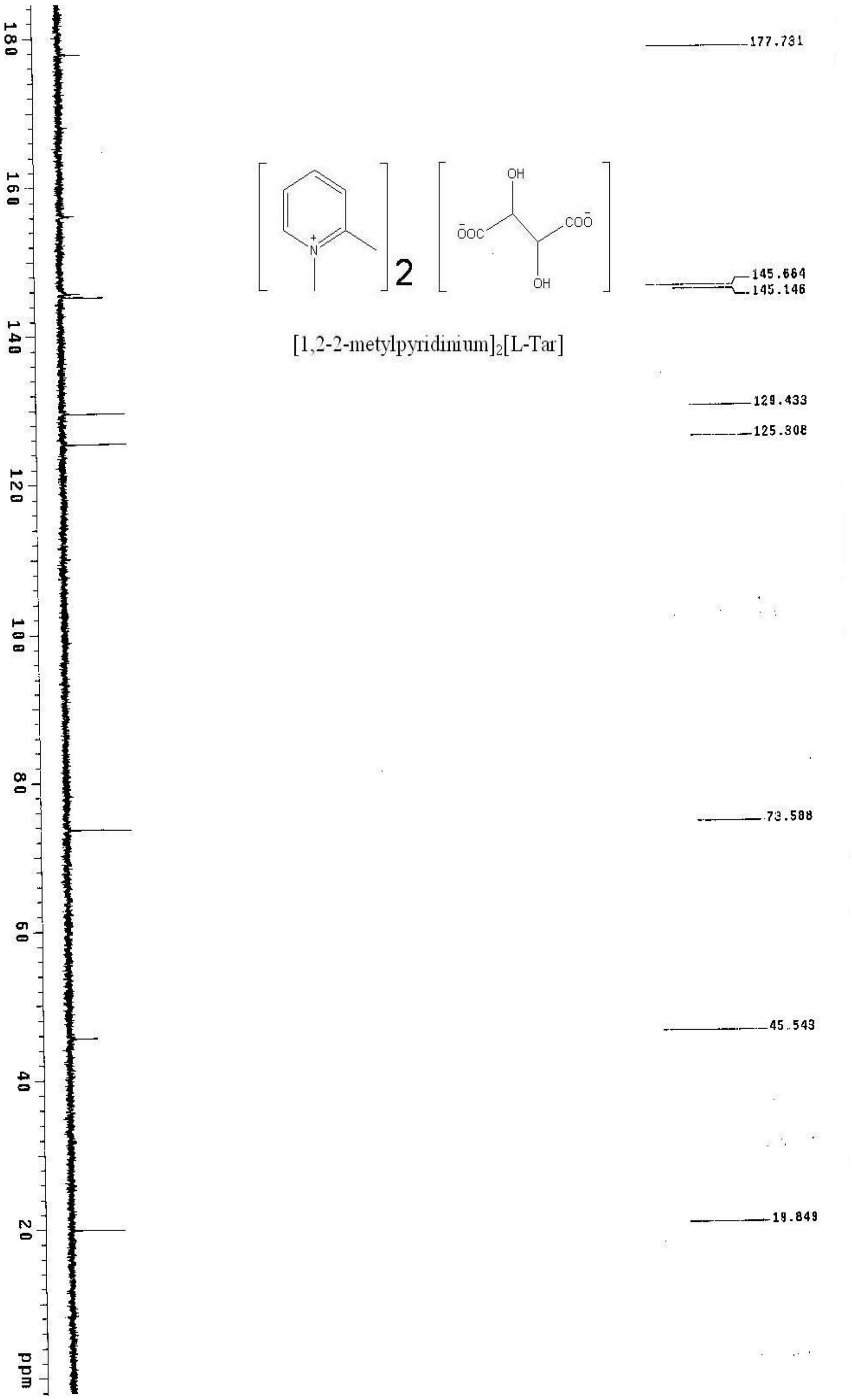

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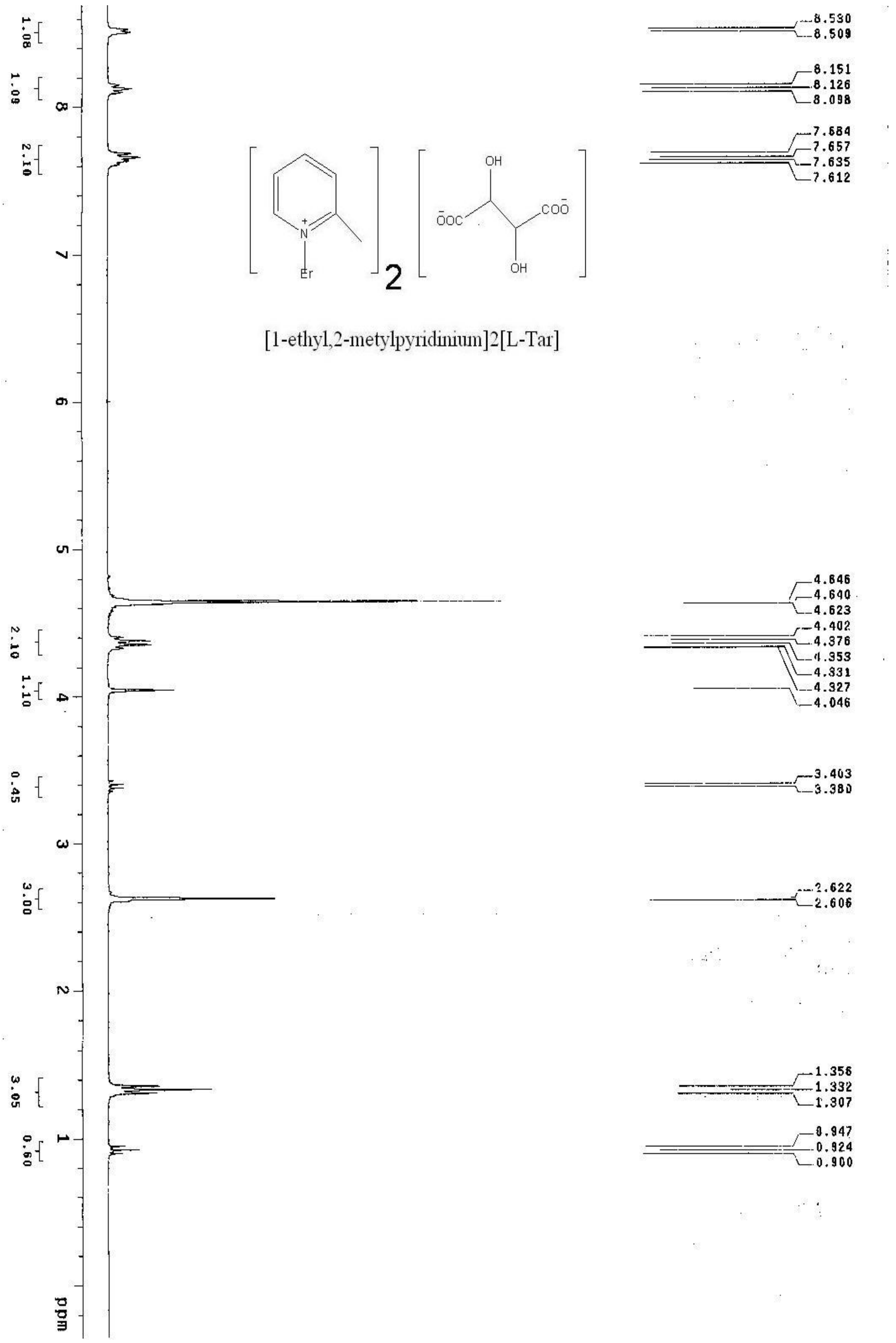

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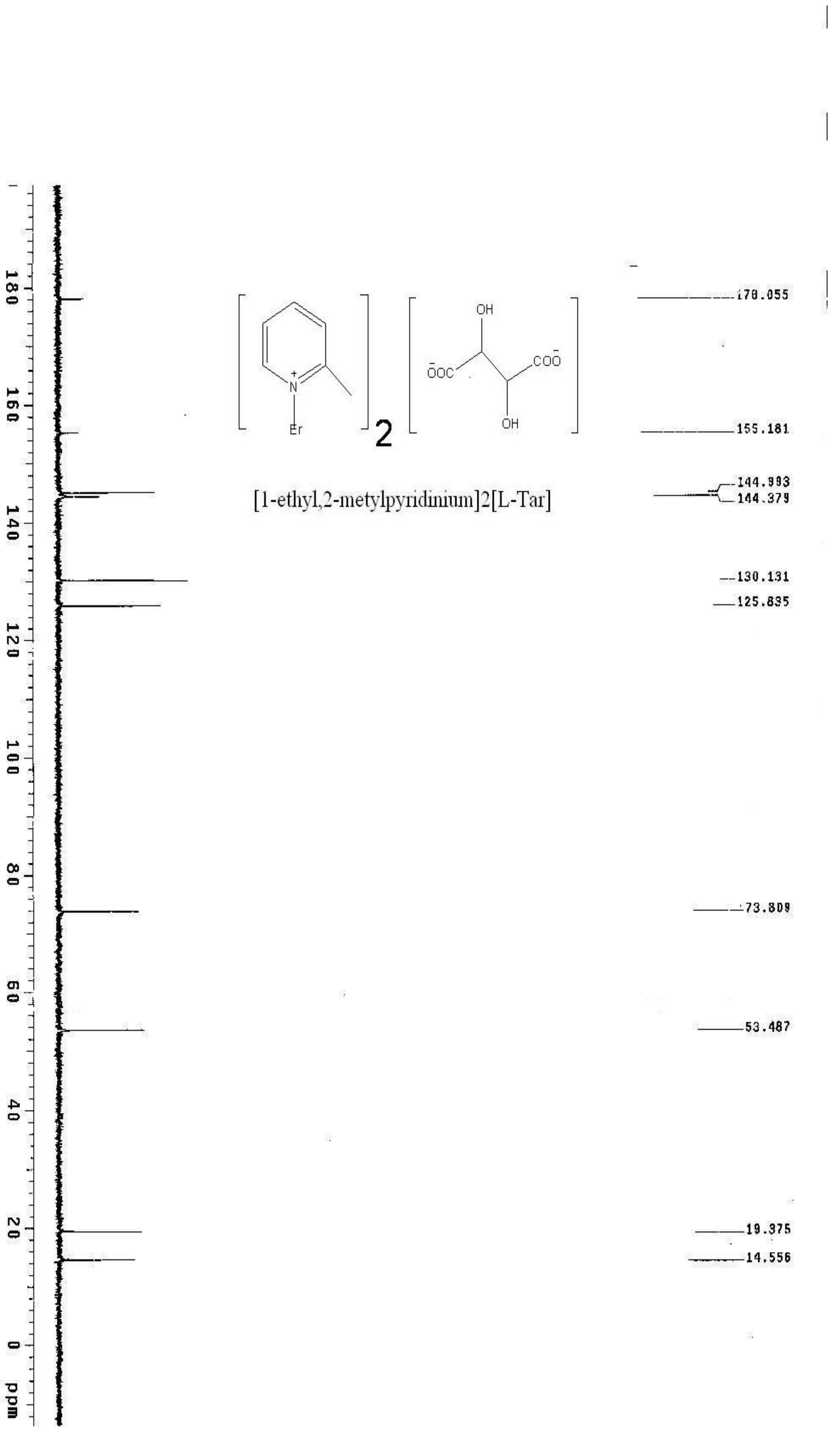

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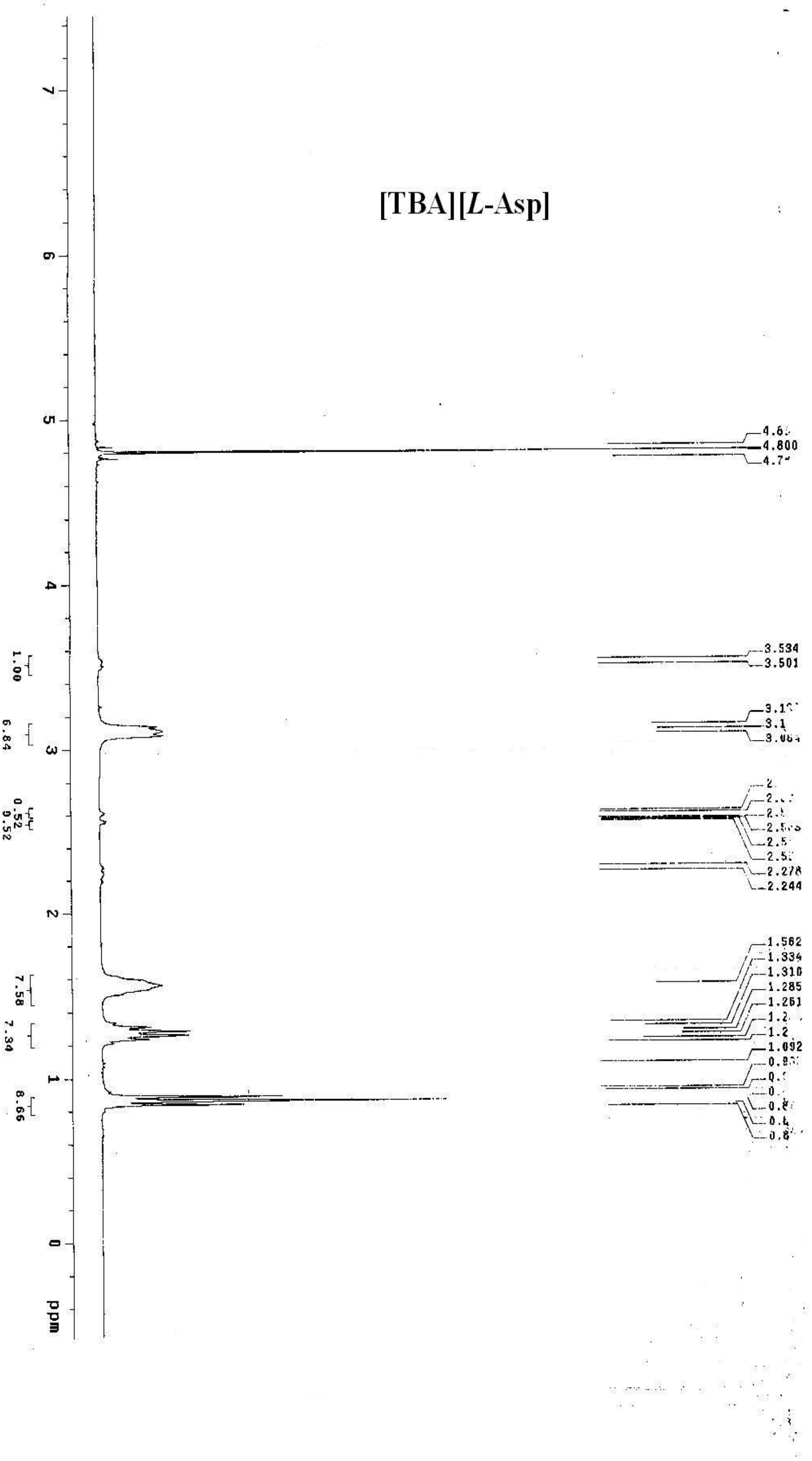
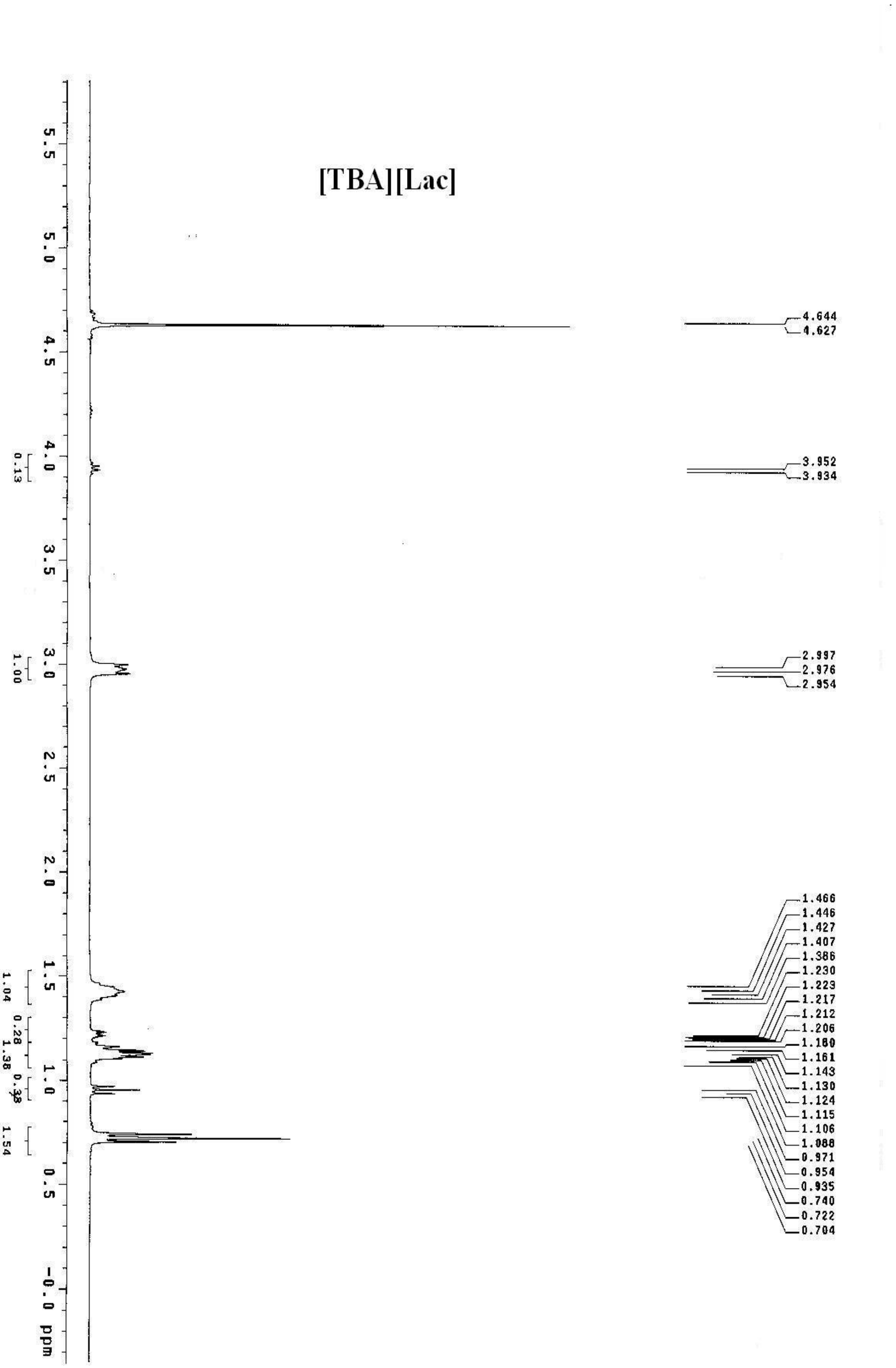


^{1}H NMR of compound 6

^{13}C NMR of compound 6



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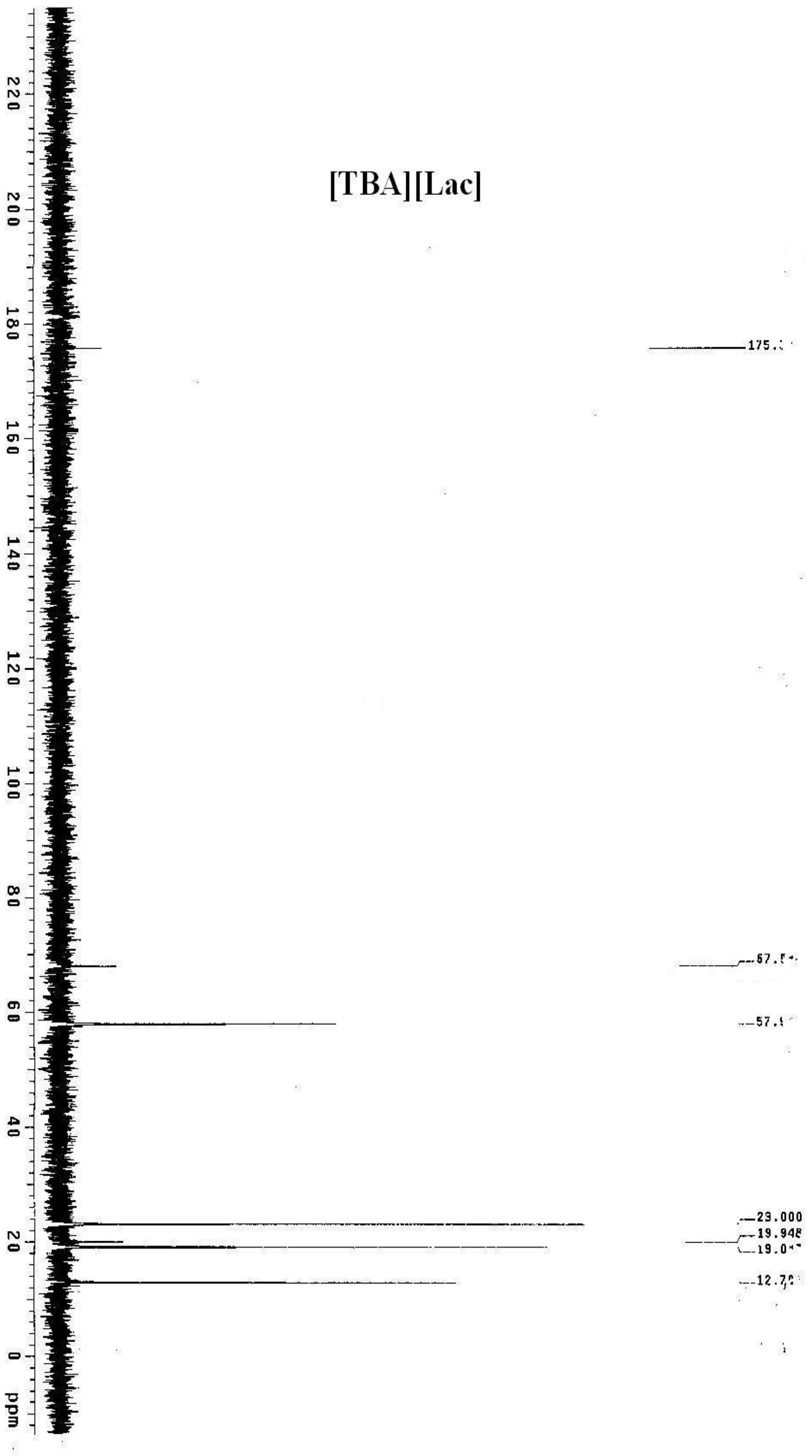

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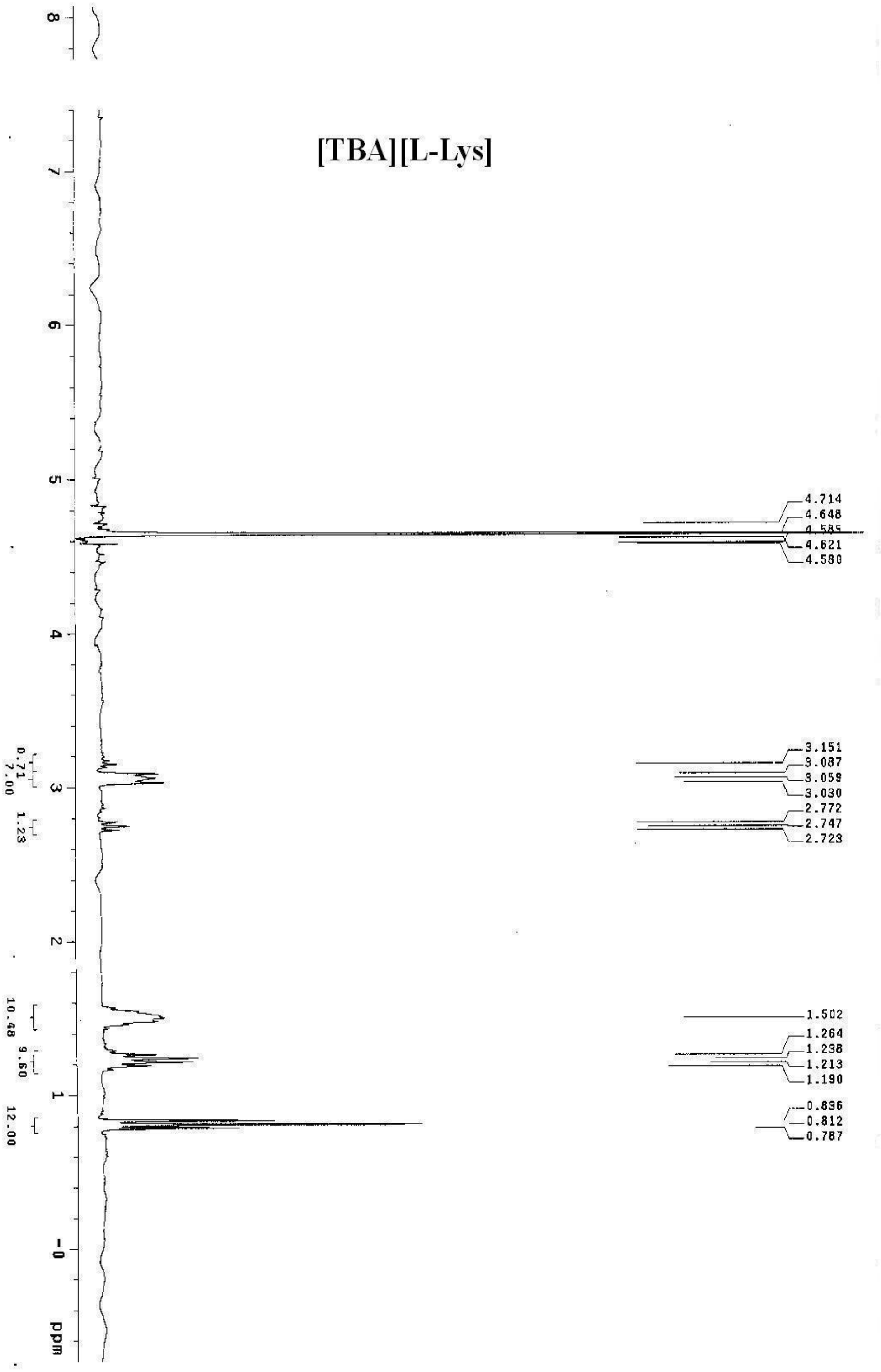

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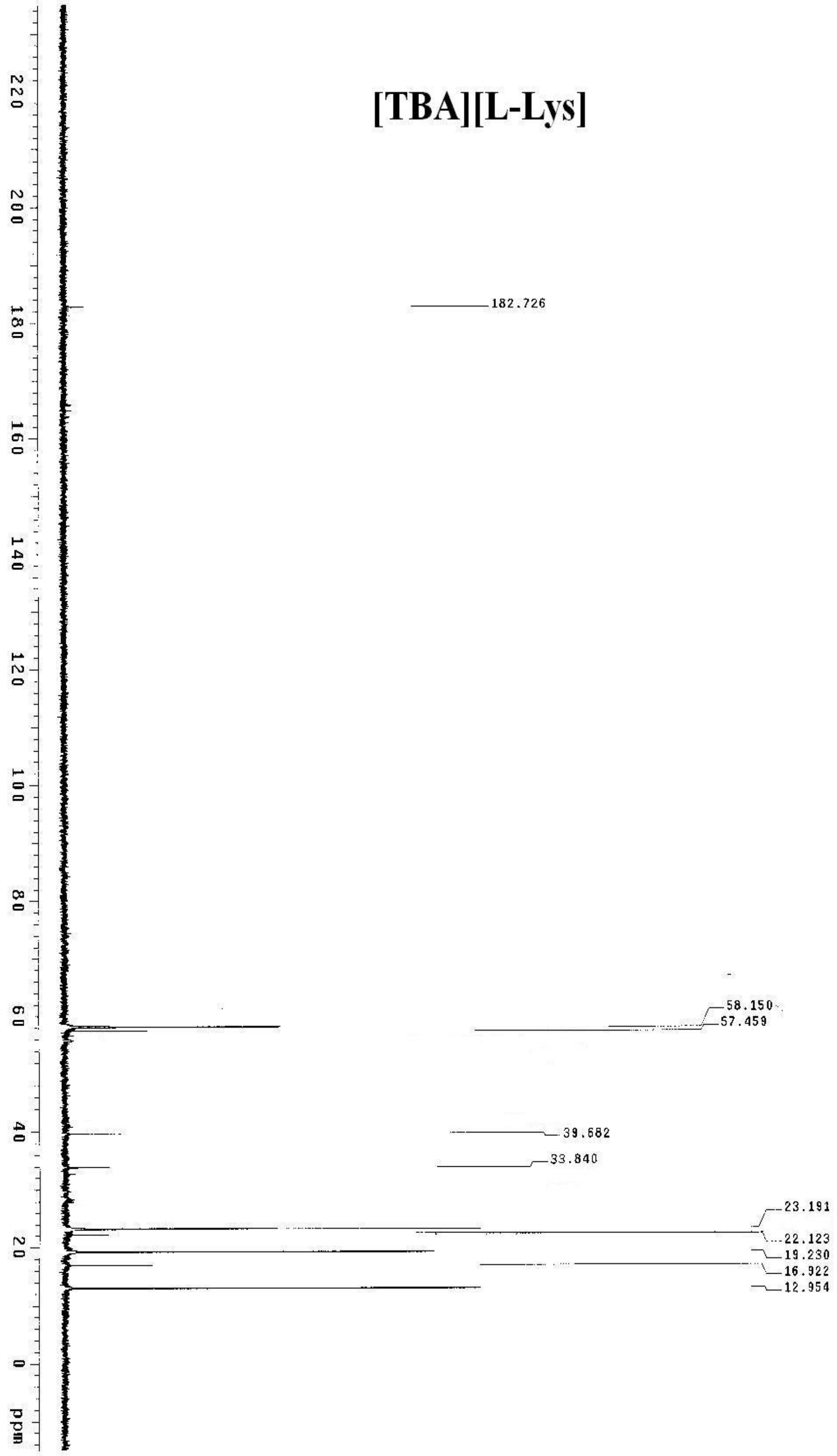

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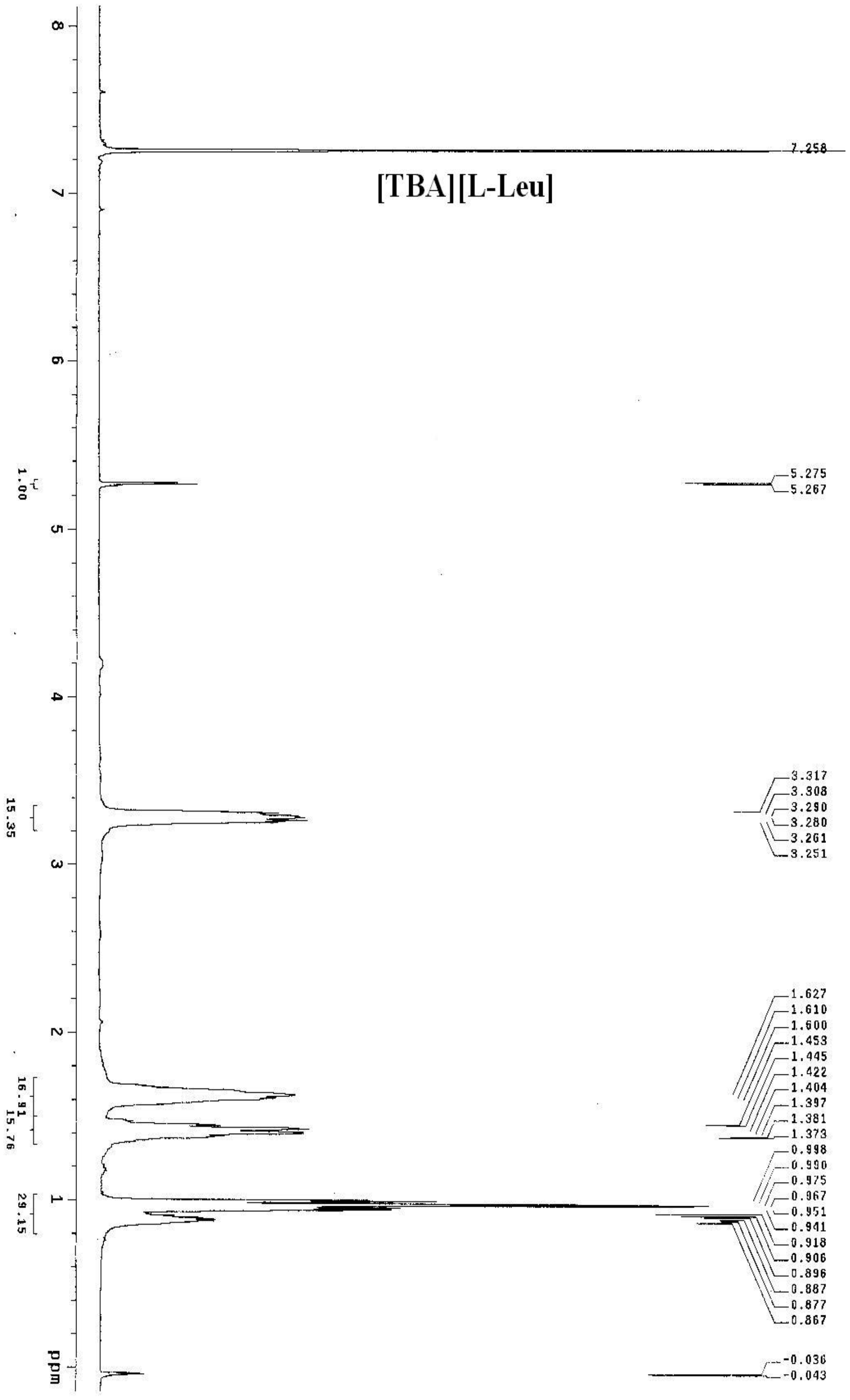
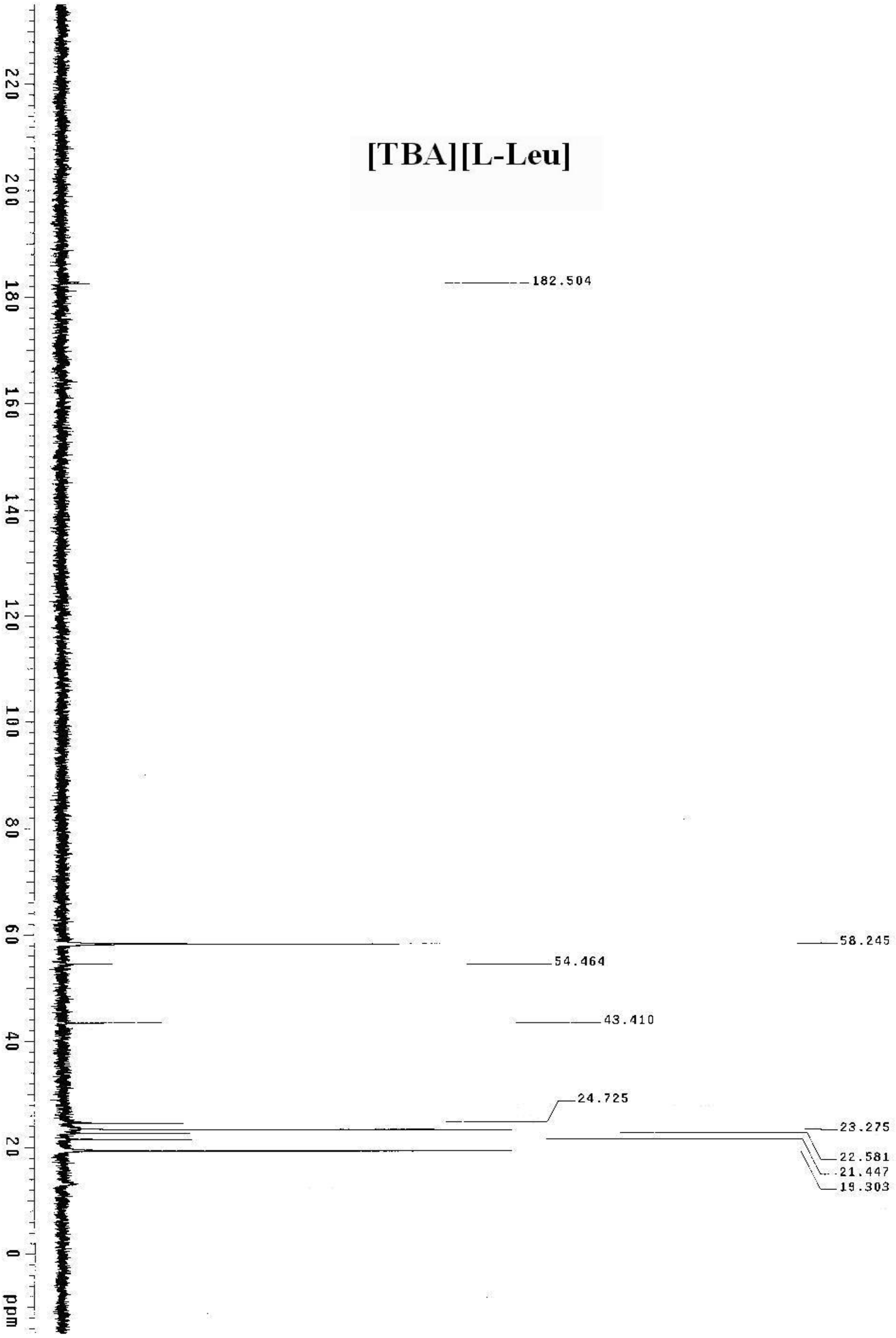


^{1}H NMR of compound 9



^{13}C NMR of compound 9