Supporting Information

Visible light induced Knoevenagel condensation: A clean and efficient protocol using aqueous fruit extract of *Tamarindus indica* as catalyst

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Preparation of aqueous extract of tamarind juice

The raw tamarind fruits were purchased from the local market. The upper shell of unripped fruit and its inner grain were removed. The hard green material (pulp, 10 g) was boiled with water (50 mL), cooled and it was centrifuged using micro centrifuge (REMI RM-12C). The clear portion of the aqueous extract (pH=3) of the tamarind fruits was used as catalyst for the reactions.

General Method

Different aromatic and aliphatic aldehydes (**1a-v**) (10 mmol) or (**1w**) (5 mmol), malononitrile (10 mmol), and aqueous tamarind juice (5 mL, pH= 3) were taken in a round bottomed flask and irradiated with a 200 W tungsten lamp (Philips India Ltd). The reaction time varied from 2-7 min monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled and the crystalline products (**3a-t** and **3w**) so obtained was filtered, washed with water and dried in vacuo. In case of **3u** and **3v** the reaction mixture was extracted with ethyl acetate, dried over anhydrous sodium sulphate and chromatographed over silica gel to

obtained oily product **3u-v**. The Knoevenagel condensation products were isolated in excellent yields in essentially pure form.

NMR spectral data of all unknown compounds

*2-(3-Hydroxyphenylmethylene)malononitrile (**3a**)*: Yellow crystal, Yield: 92%, mp. 164 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.12 (s, 1H, OH), 8.44 (s, 1H, H-C=C), 7.35-7.44 (m, 3H), 7.08 (d, 7.5 Hz, 1H); Anal. Calcd. for $C_{10}H_6N_2O$, C, 70.58; H, 3.55; N, 16.46%, found C, 70.24; H, 3.88; N, 16.20%.

*2-(4-Benzoyloxyphenylmethylene)malononitrile (**3n**)*: Colorless crystal, Yield: 96%, mp. 152 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 7.8 Hz, 2H), 8.01 (d, 8.7 Hz, 2H), 7.78 (s, 1H, H-C=C), 7.66-7.78 (m, 1H), 7.54 (t, 7.5 Hz, 2H), 7.43 (d, 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 82.54 (=C<), 112.49 (CN), 113.61 (CN), 123.12, 128.41, 128.53, 128.75, 130.29 (-CH=), 132.37, 134.20, 155.56, 158.56, 164.24 (ester carbonyl); DEPT – 90 (75 MHz, $CDCl_3$): 123.11, 128.74, 130.28, 132.35, 134.18, 158.52; DEPT – 135 (75 MHz, $CDCl_3$): 123.11, 128.74, 130.28, 132.35, 134.18, 158.51; Anal. Calcd. for $C_{17}H_{10}N_2O_2$, C, 74.45; H, 3.67; N, 10.21%, found C, 74.15; H, 3.80; N, 10.41%.

*2-(4-Benzoyloxy-3-methoxyphenylmethylene)malononitrile (**3o**)*: Colorless crystal, Yield: 98%, mp. 140-141 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 8.7 Hz, 2H), 7.76 (s, 1H, H-C=C), 7.74 (d, 1.8 Hz, 1H), 7.64-7.69 (m, 1H), 7.53 (t, 7.5 Hz, 2H), 7.43 (dd, 8.7 and 1.8 Hz, 1H), 7.34 (d, 8.4 Hz, 1H), 3.89 (s, 3H, OMe); Anal. Calcd. for $C_{18}H_{12}N_2O_3$, C, 71.05; H, 3.97; N, 9.21%, found C, 70.89; H, 4.04; N, 9.45%.

*2-(3,4-Methylenedioxyphenylmethylene)malononitrile (**3p**)*: Yellow crystal, Yield: 96%, mp. 198 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.59 (s, 1H, H-C=C), 7.32 (dd, 8.1 and 1.5 Hz, 1H), 6.93 (d, 8.1 Hz, 1H), 6.12 (s, 2H, -O-CH_2-O-); Anal. Calcd. for $C_{11}H_6N_2O_2$, C, 66.67; H, 3.05; N, 14.14%, found C, 66.92; H, 3.19; N, 14.30%.

*2-(3-Indolylmethylene)malononitrile (**3r**)*: Yellow crystal, Yield: 82%, mp. 170-172 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.41 (m, 2H), 7.51 (d, 8.7 Hz, 1H), 7.75 (d, 8.4 Hz, 1H), 8.11 (s, 1H, H-C=C), 8.80 (d, 3.3 Hz, 1H), 9.13 (br. s, 1H, NH) ; Anal. Calcd. for $C_{12}H_7N_3$, C, 74.60; H, 3.65; N, 21.75%, found C, 74.43; H, 3.78; N, 21.88%.

2-[{p-3,3'-Bis(2-methylindolyl)methyl}phenylmethylene]malononitrile (***3t***): Pale-yellow crystal, Yield: 80%, mp. 320-322 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (br. s, 2H, NH), 7.80 (d, 8.7 Hz, 2H), 7.72 (s, 1H, H-C=C), 7.44 (d, 8.1 Hz, 2H), 7.28 (d, 9.0 Hz, 2H), 7.06 (t, 6.9 Hz, 2H), 6.84-6.93 (m, 4H), 6.04 (s, 1H, Ar-CH), 2.09 (s, 6H, Me); Anal. Calcd. for $C_{29}H_{22}N_4$, C, 81.67; H, 5.20; N, 13.14%, found C, 81.34; H, 5.41; N, 13.27%.

p-Bis-2-(phenylmethylene)malononitrile (***3w***): White crystal, Yield: 98%, mp. 298-300 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.63 (s, 2H, H-C=C), 8.09 (s, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 84.71 (=C<), 112.14 (CN), 113.80 (CN), 130.83 (-CH=), 135.32 (aromatic quarternary), 159.80 (aromatic –CH=); DEPT – 90 (75 MHz, DMSO-d_6): 130.83, 159.81; DEPT – 135 (75 MHz, DMSO-d_6): 130.84, 159.81; Anal. Calcd. for $C_{14}H_6N_4$, C, 73.04; H, 2.63; N, 24.34%, found C, 72.98, H, 2.76; N, 24.46%.

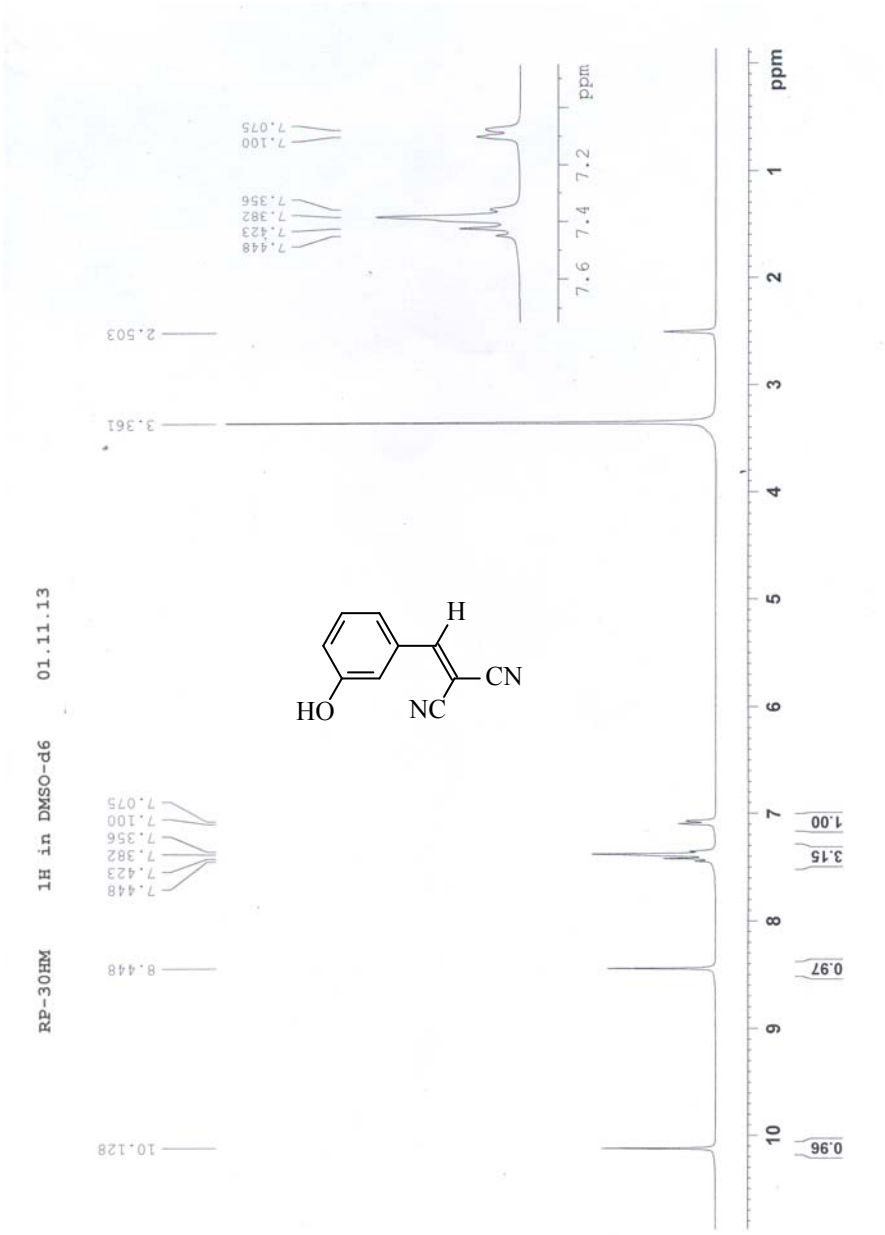

Fig. 1. ^{1}H NMR spectrum of compound **3a** in DMSO-d_6 (300 MHz)

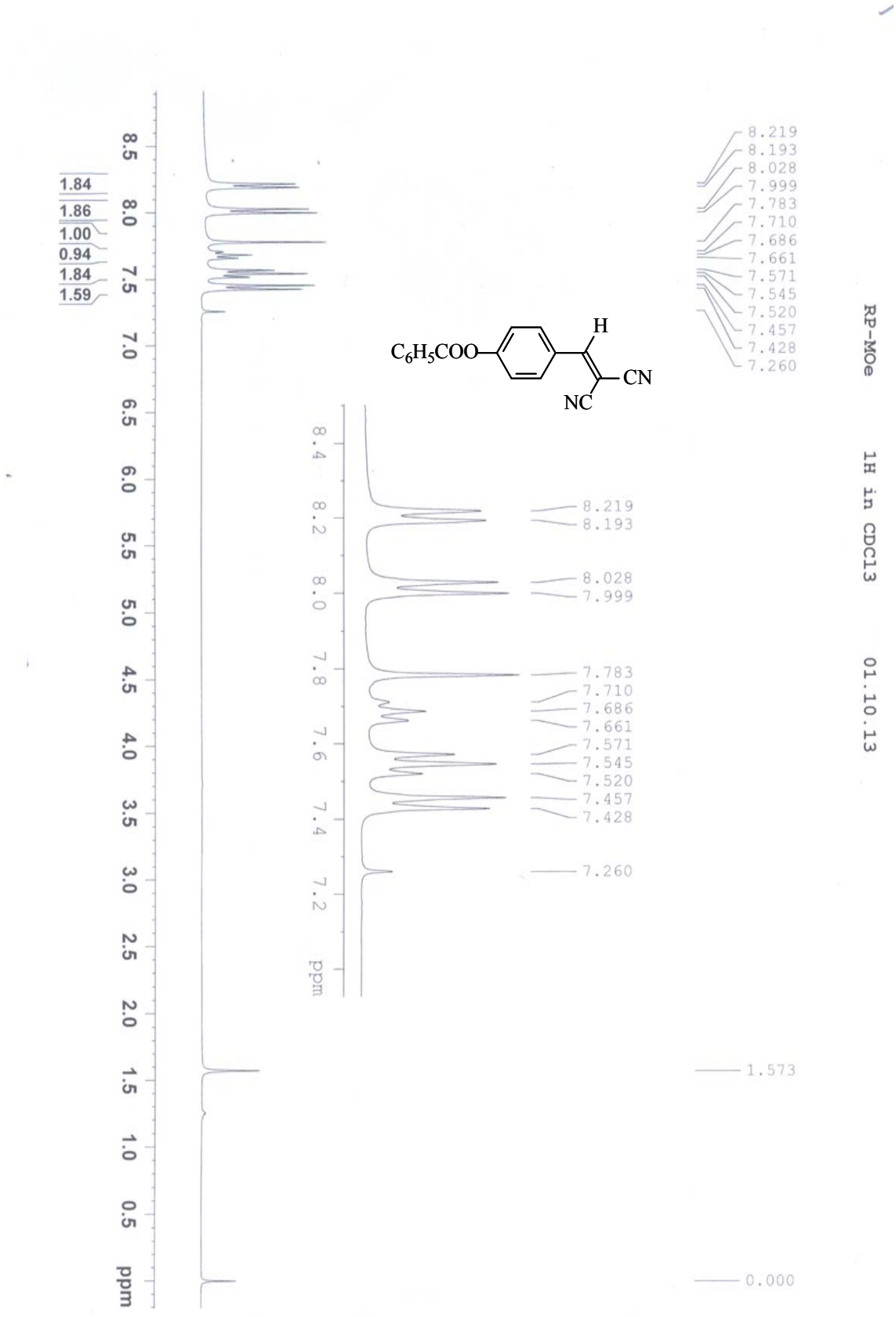

Fig. 2. ^{1}H NMR spectrum of compound **3n** in $CDCl_3$ (300 MHz)

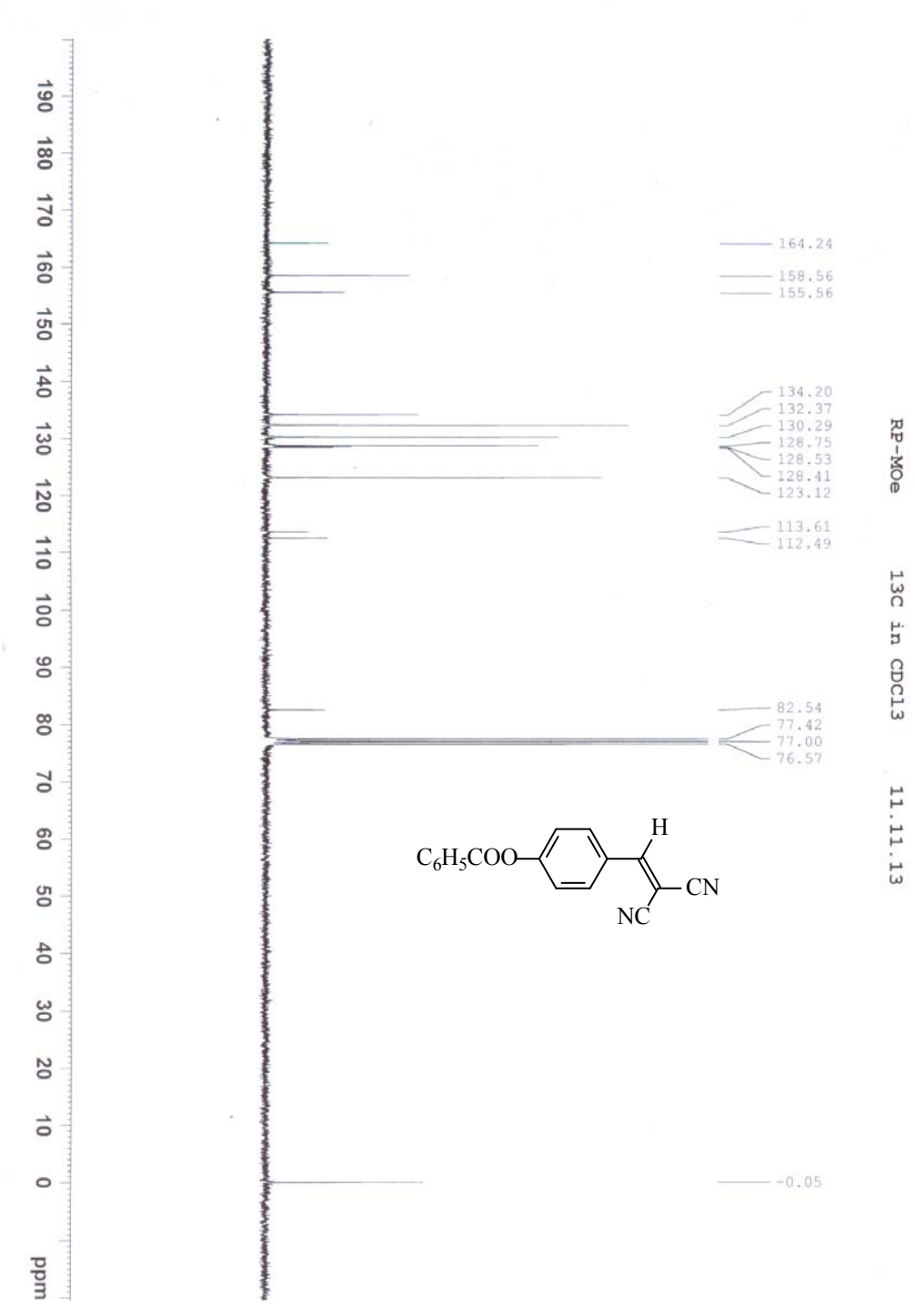

Fig. 3. ^{13}C NMR spectrum of compound **3n** in $CDCl_3$ (75 MHz)

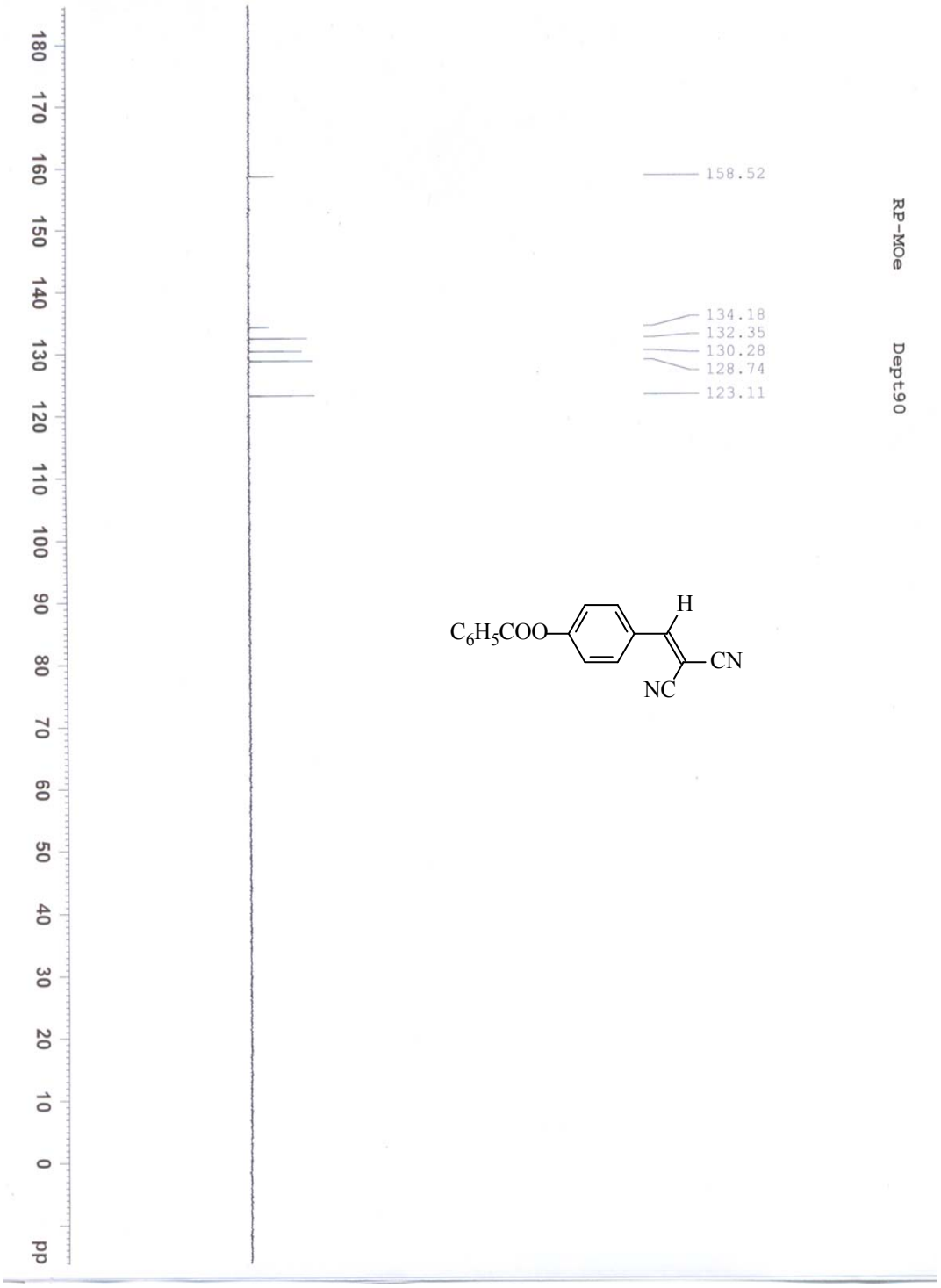

Fig. 4. DEPT-90 spectrum of compound **3n** in $CDCl_3$ (75 MHz)

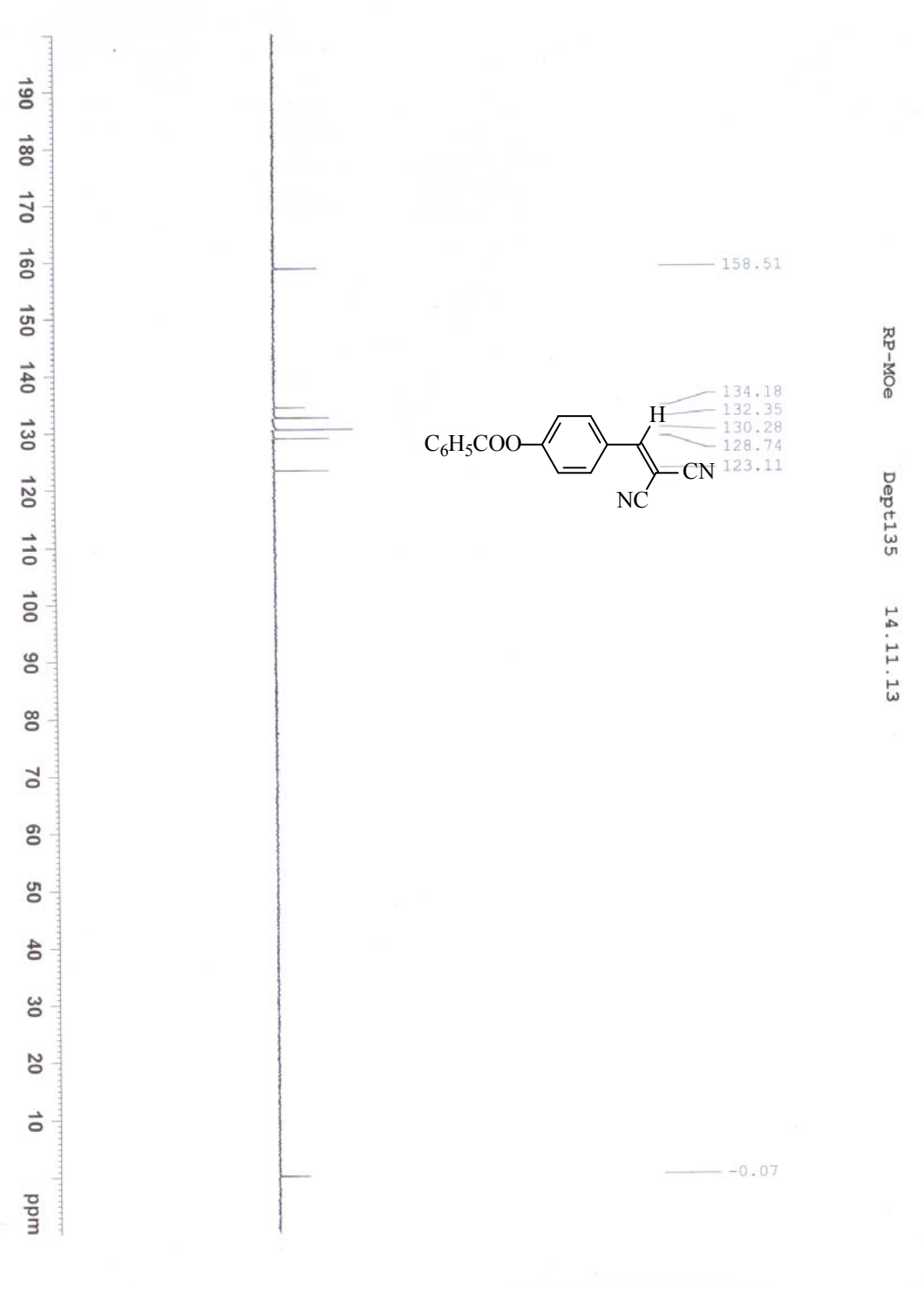

Fig. 5. DEPT-135 spectrum of compound **3n** in $CDCl_3$ (75 MHz)

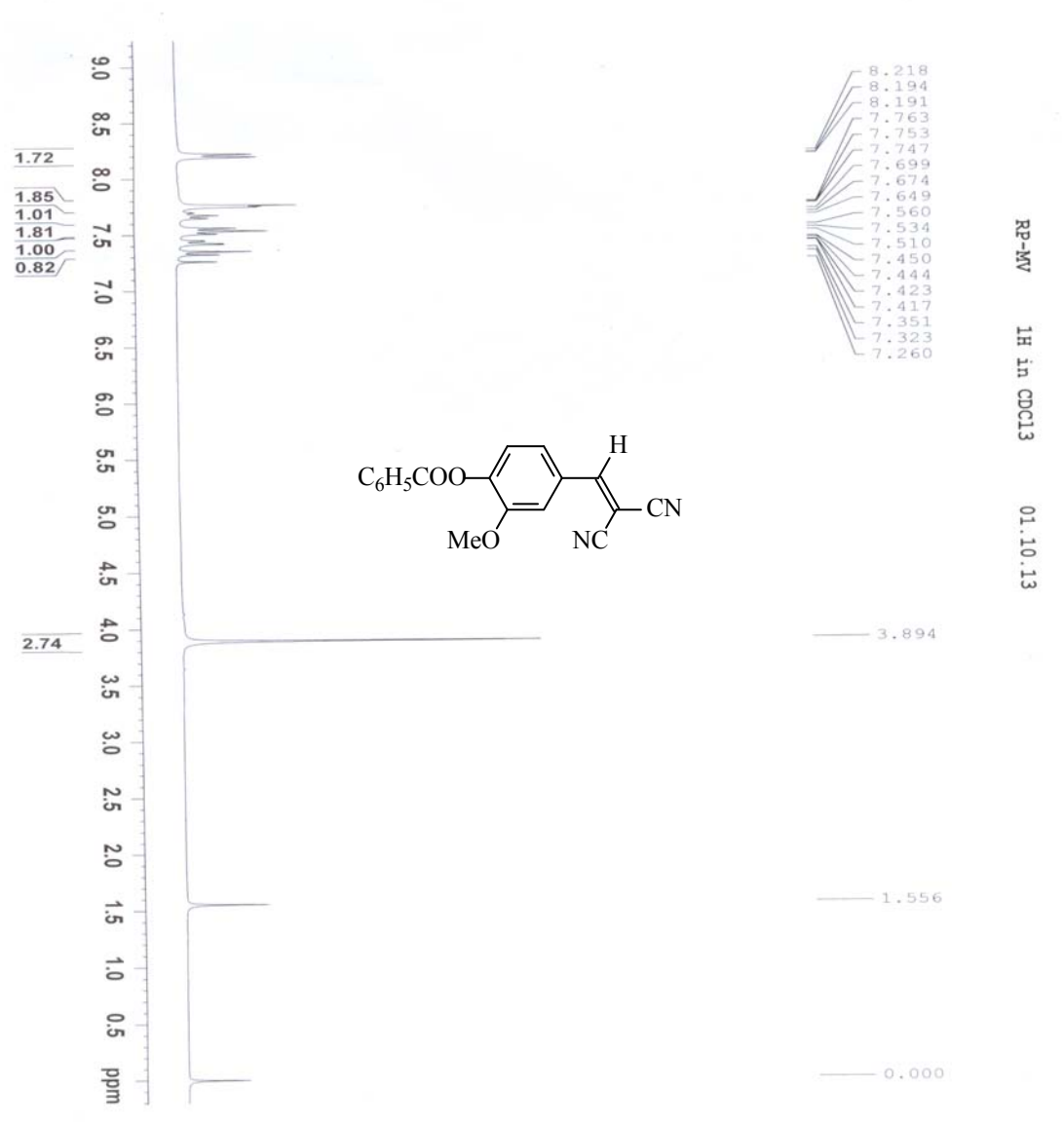

Fig. 6. ^{1}H NMR spectrum of compound **3o** in $CDCl_3$ (300 MHz)

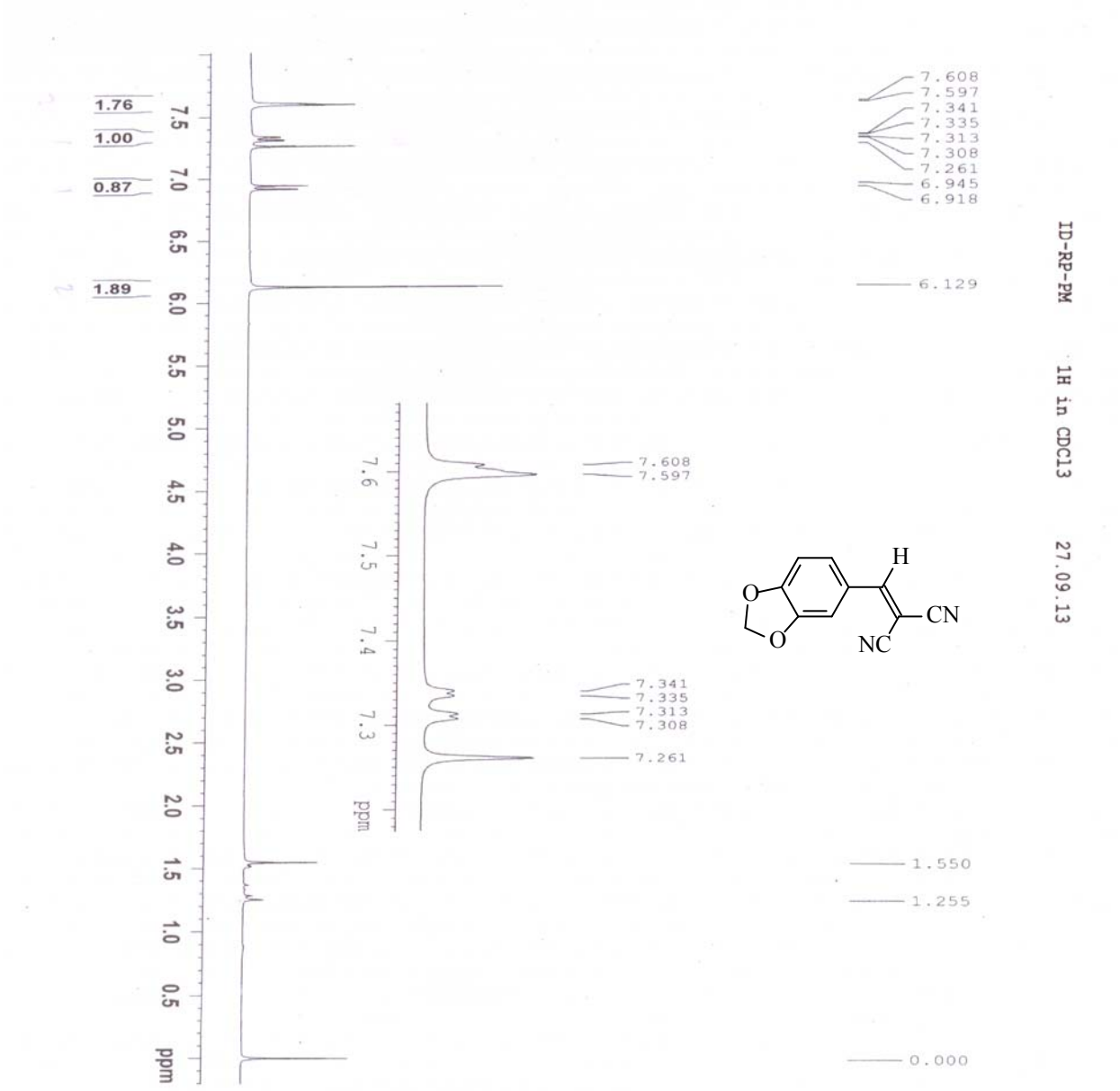

Fig. 7. ^{1}H NMR spectrum of compound **3p** in $CDCl_3$ (300 MHz)

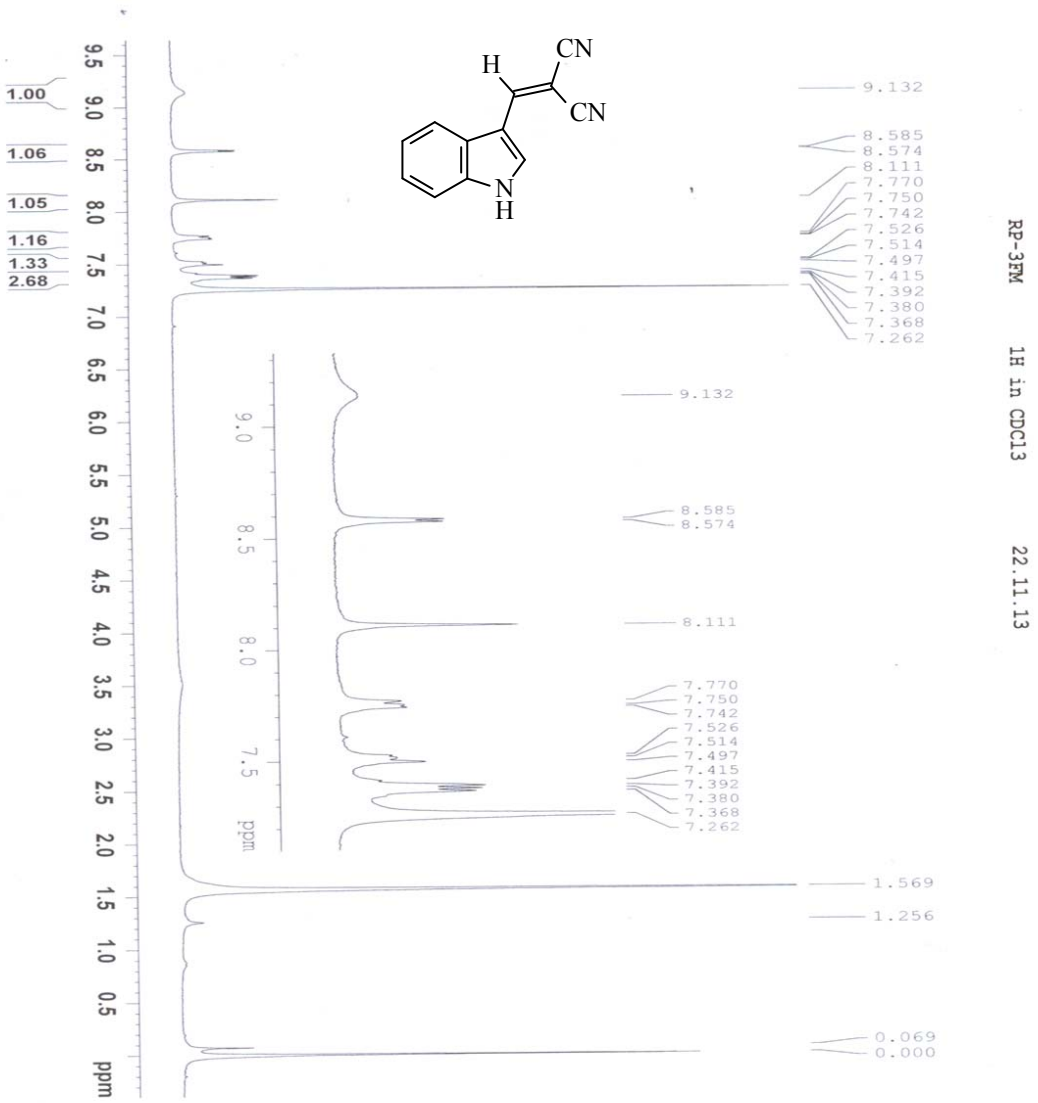

Fig. 8. ^{1}H NMR spectrum of compound **3r** in $CDCl_3$ (300 MHz)

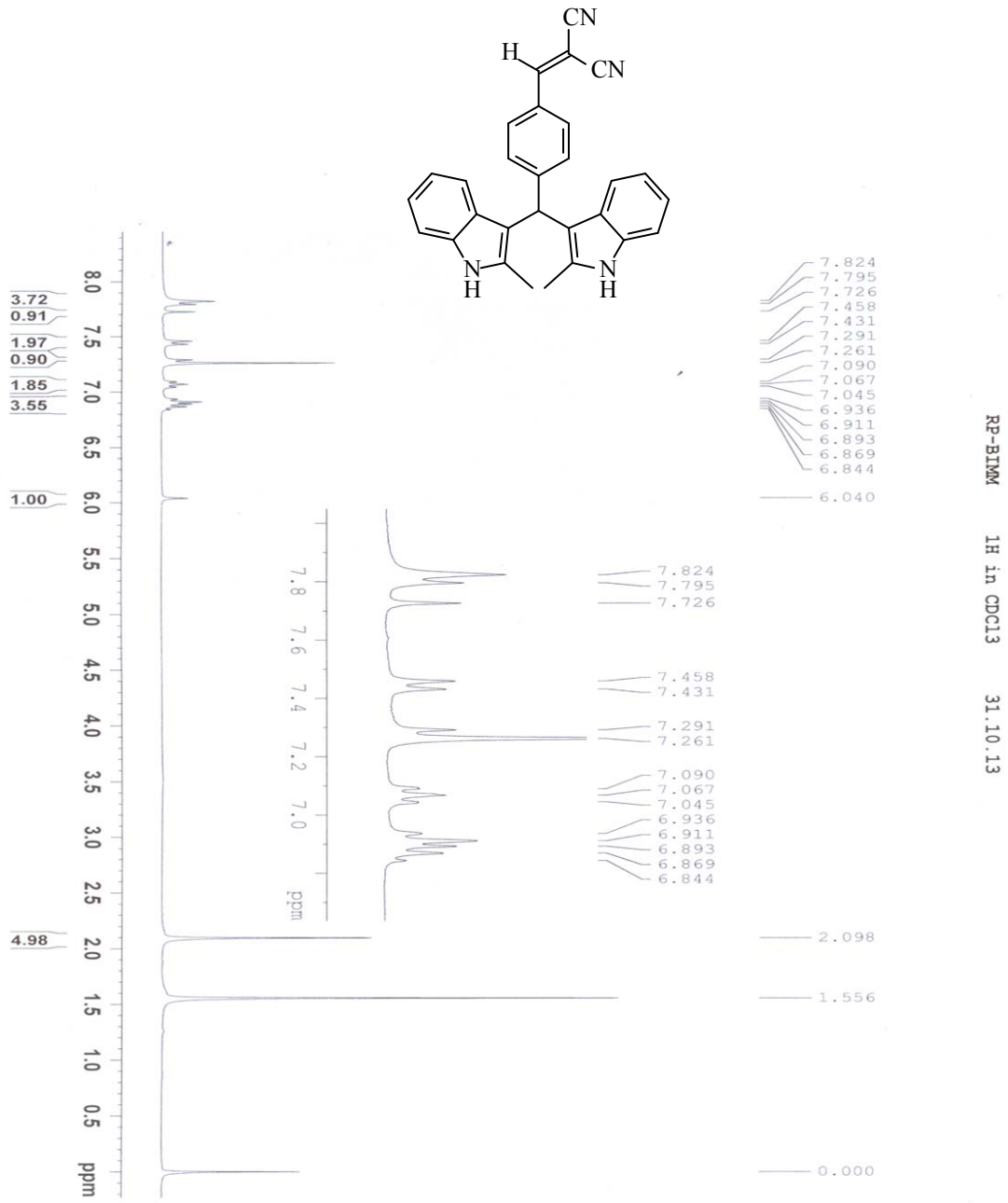

Fig. 9. ^{1}H NMR spectrum of compound **3t** in $CDCl_3$ (300 MHz)

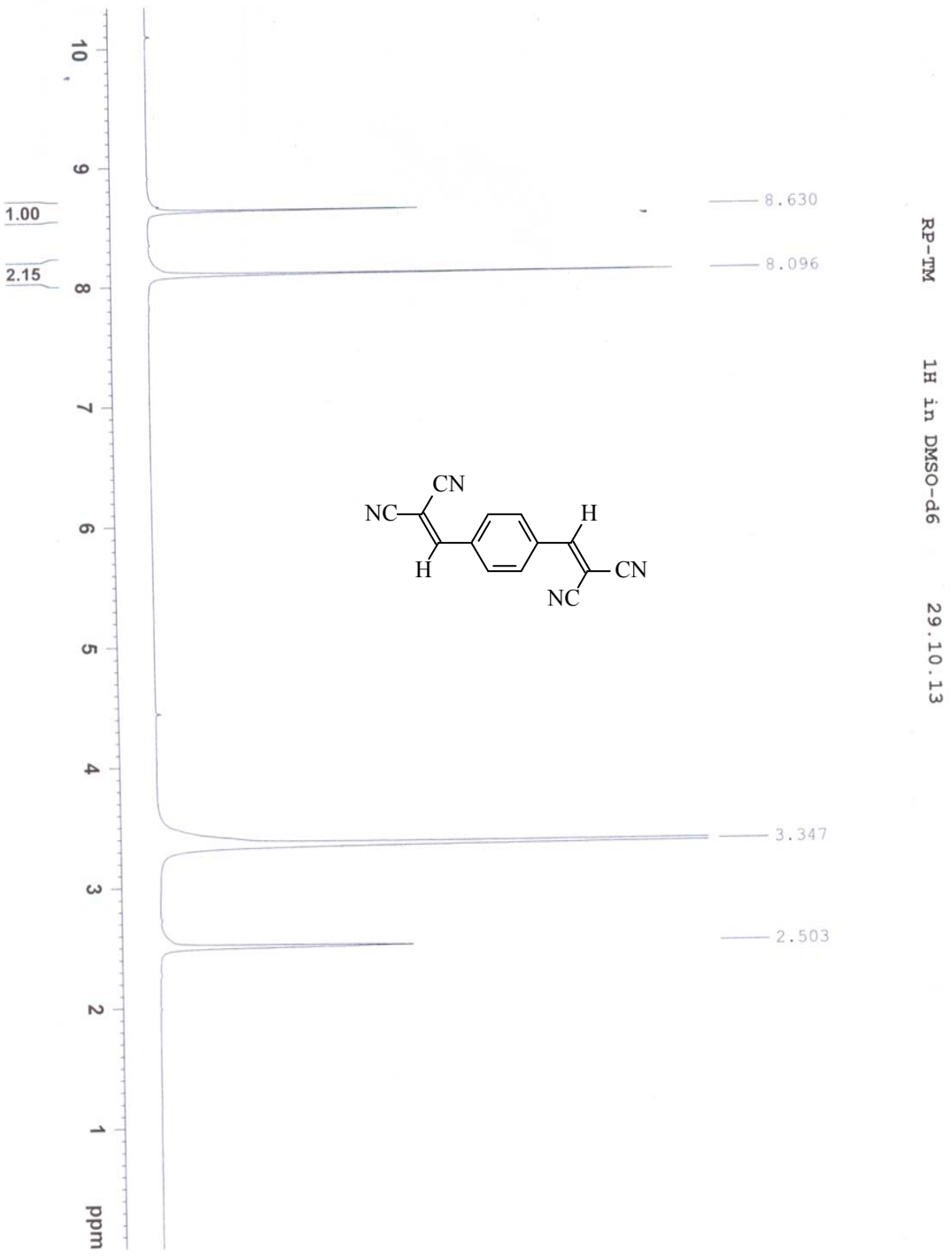

Fig. 10. ^{1}H NMR spectrum of compound **3w** in DMSO-d_6 (300 MHz)

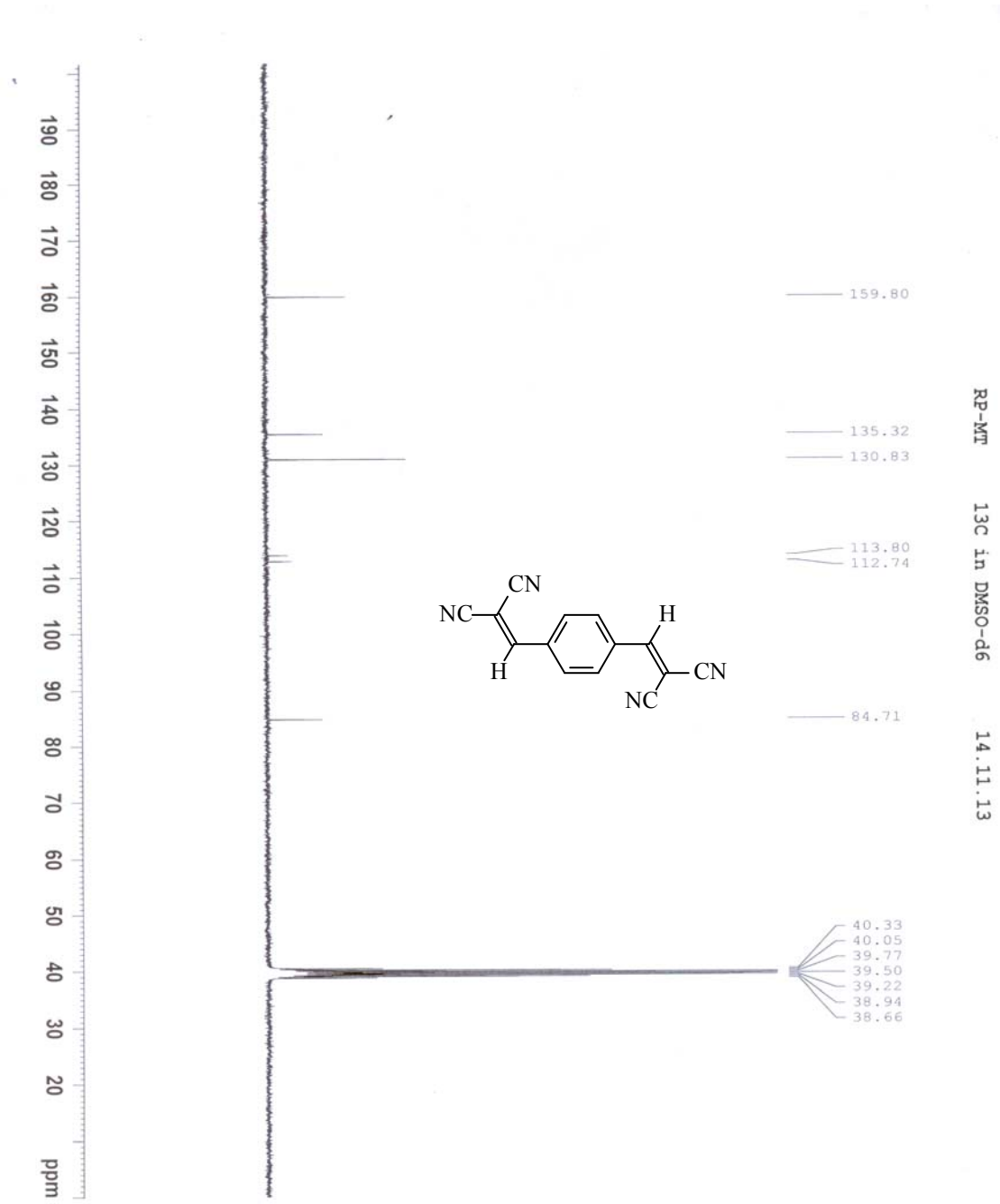

Fig. 11. ^{13}C NMR spectrum of compound **3w** in $CDCl_3$ (75 MHz)

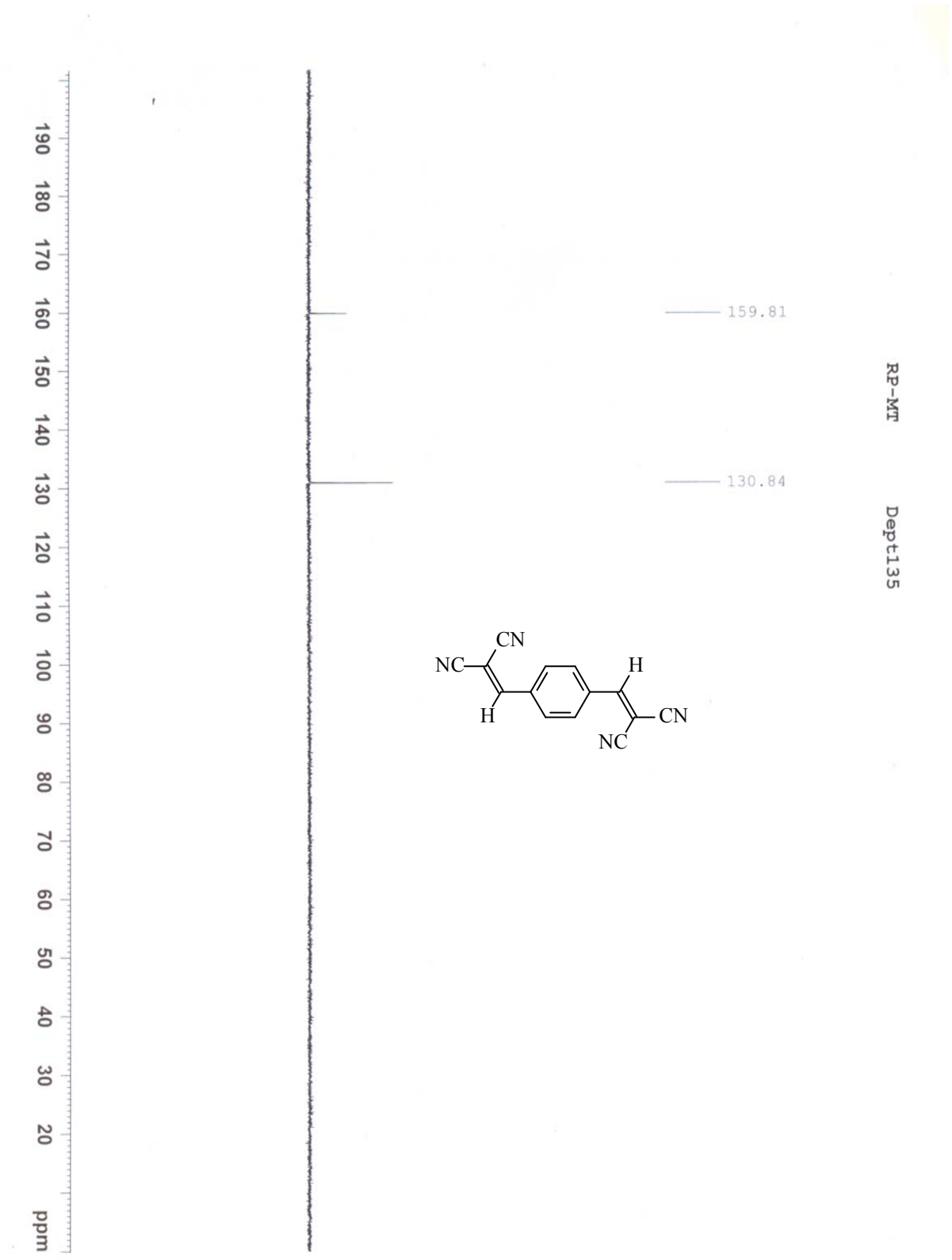

Fig. 12. DEPT-135 spectrum of compound **3w** in $CDCl_3$ (75 MHz)

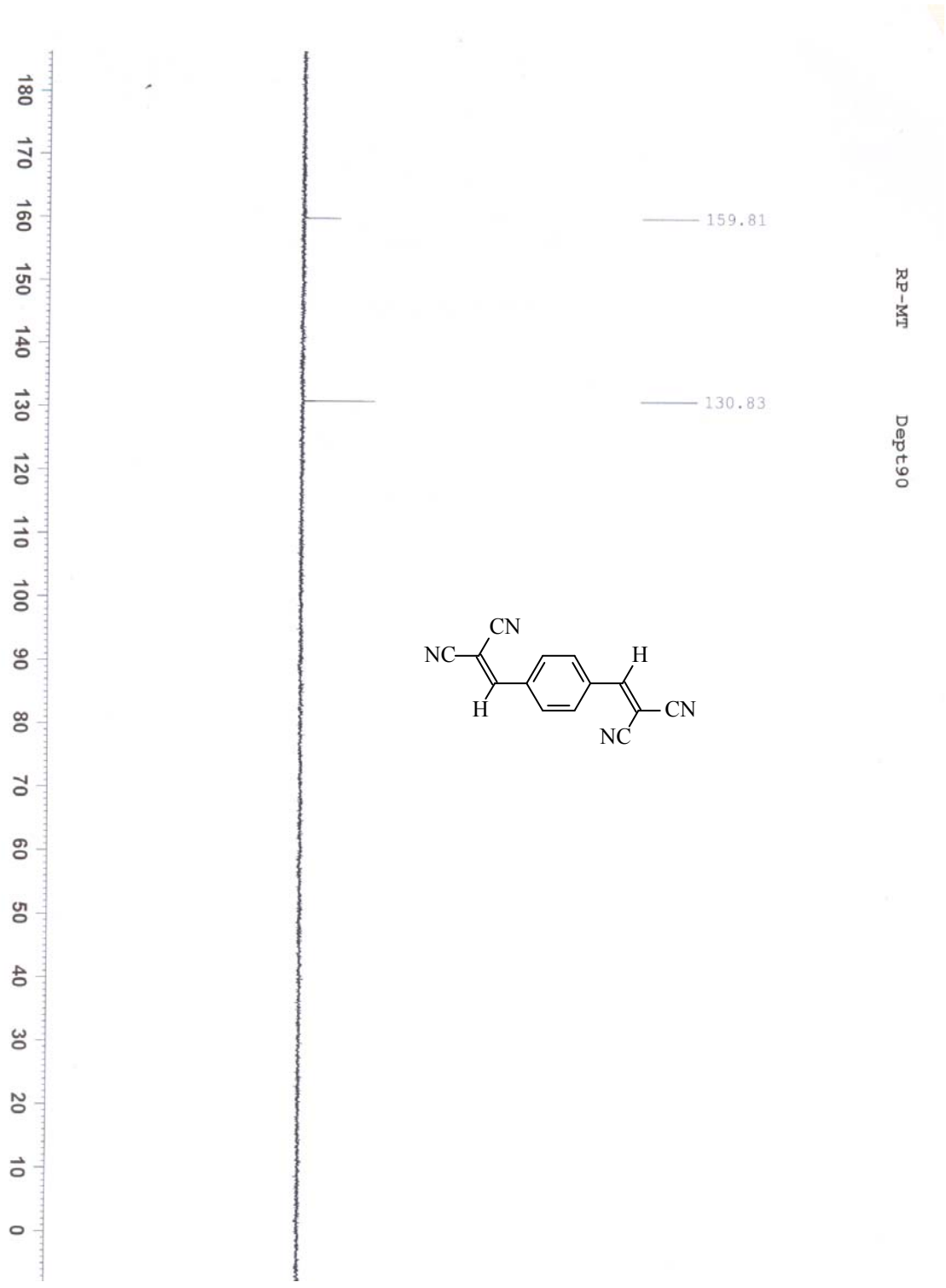

Fig. 13. DEPT-90 spectrum of compound **3w** in $CDCl_3$ (75 MHz)