Electronic Supplementary Material (ESI) for Catalysis Science & Technology

P_2O_5/SiO_2 as an efficient heterogeneous catalyst for the synthesis of heterocyclic alkene derivatives under thermal solvent-free conditions

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Experimental

Reagents

All starting materials were purchased from Sigma-Aldrich, were of commercial grade and used without further purification. The purity of all compounds was checked by TLC on glass plates coated with silica gel (E-Merck G_{254}). P_2O_5 and SiO_2 were purchased from Merck.

Apparatus and instruments

Melting points were determined on a Riechert Thermover instrument and are uncorrected. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-300 and Bruker Avance 400 Spectrometer. TMS was used as an internal standard and chemical shift values were in δ (ppm). The microanalytical data were collected on an Elementar vario EL III elemental analyzer. FT-IR spectra were obtained using a Perkin–Elmer spectrometer and done on KBr disc. The spectra were recorded in the 400–4000 cm^{-1} wave-number range. Mass spectra were obtained on a Jeol-SX-120 (FAB) and Micromass Quattro II (ESI). X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 10–70° (scan rate of 4° min^{-1}) on a Rigaku Miniflex X-ray diffractometer with Ni-filtered Cu Kα radiation at a wavelength of 1.54060°A. The SEM-EDX analysis was obtained using a JEOL JSM-6510 scanning electron microscope equipped with energy dispersive X-ray spectrometer (acc. voltage: 20 kV) at different magnification and transmission electron microscope (TEM) using JEM-2100 F model (acc. voltage: 200 kV) with magnification up to 100000x. Thermogravimetric/differential thermal analyses (TG/DTA) were obtained with a DTG-60H, with a heating rate of 25 °C min^{-1} from 100 to 1000 °C under N_2 atmosphere, and the differential scanning calorimetry (DSC) data was obtained with DSC-60 (Simultaneous DTA-TG Apparatus), Shimadzu (TGA) instrument with a heating rate of 20 °C min^{-1} from 0 to 500 °C under N_2 atmosphere. The X-ray single crystal diffraction of the compound **3a** was

performed on a BRUKER AXS SMART APEX diffractometer with a CCD area detector (MoKα = 0.71073 Å, monochromator: graphite).

Synthesis of the P_2O_5/SiO_2 catalyst

P_2O_5/SiO_2 was prepared by mixing P_2O_5 (1 mmol, 0.142 g) and 2 g of dried Silica Gel 60 (0.125–0.250 mm, previously heated at 120 ˚C for 24 h) in a mortar and grinding with a pestle to obtain a homogenous mixture as a white powder (2.142 g). This reagent is stable and can be kept at room temperature for months without losing its activity.[1]

General procedure for the Knoevenagel reaction

A mixture of 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde **1** (1.00 mmol), active methylene compounds **2a–k** (1.00 mmol), **2l-n** (2.00 mmol), and 0.05g of P_2O_5/SiO_2 (*7% w/w*)[2] were mixed thoroughly using a mortar and pestle. The reaction mixture was then transferred to an open Pyrex 100 mL beaker and heated at 80 ˚C for the given time (Table 8). After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and added ethyl acetate (5 mL). The reaction mixture was filtered to remove the catalyst and concentrated to furnish pure products **3a-n** (Scheme 2).

2.5. Spectral data of compounds

2.5.1. 5-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-1,3-dimethyl-2, 4, 6-pyrimidinetrione (3a)

Shining yellow crystals; m.p. 207–209 °C (lit. 208-210 °C); IR (KBr) cm^{-1}: 740, 1219, 1338, 1520, 1587, 1664, 1730, 2849, 3089. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H, CH_3), 3.42 (s, 3H, N–CH_3), 3.45 (s, 3H, N–CH_3), 7.32–7.84 (m, 5H, Ar–H), 8.48 (s, 1H, –CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 27.7, 28.3, 115.9, 124.4, 126.7, 127.6, 136.9, 139.1, 144.9, 150.6, 151.7, 159.8, 165.2. FAB-MS: (*m/z*) 358. Anal. calc. for $C_{17}H_{15}N_4O_3Cl$: C, 56.93; H, 4.18; N, 15.61. Found: C, 56.99; H, 4.16; N, 15.56.

2.5.2. 5-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-2,4,6- pyrimidinetrione (3b)

Bright yellow crystals; m.p. >300 °C (lit. >300°C); IR (KBr) cm^{-1}: 734, 1207, 1381, 1528, 1572, 1679, 1724, 3067, 3095, 3195. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.29 (s, 3H, CH_3), 7.31–7.82 (m, 5H, Ar–H), 8.12 (s, 1H, –CH=C), 11.05 (s, 1H, NH), 11.36 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 12.4, 115.7, 123.3, 127.7, 128.7, 136.9, 138.7, 143.2, 150.0, 151.4, 162.2, 165.6. ESI-MS: (*m/z*) 330.20. Anal. calc. for $C_{15}H_{11}N_4O_3Cl$: C, 54.49; H, 3.32; N, 16.94. Found: C, 54.56; H, 3.36; N, 16.87.

2.5.3. 5-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-2-mercapto-4,6-pyrimidinedione (3c)

Pale yellow solid; m.p. >300 °C(lit. >300 °C); IR (KBr) cm^{-1}: 729, 1007, 1347, 1501, 1618, 1674, 3047, 3089, 3124. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.32 (s, 3H, CH_3), 7.34–7.84 (m, 5H, Ar–H), 8.22 (s, 1H, –CH=C), 11.12 (s, 1H, NH), 11.43(s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 12.6, 115.3, 122.3, 127.7, 128.9,136.2, 138.4, 141.2, 150.0, 151.8, 163.6, 172.1. ESI-MS: (*m/z*) 346.15. Anal. calc. for $C_{15}H_{11}N_4O_2SCl$: C, 51.97; H, 3.17; N, 16.15. Found: C, 51.99; H, 3.13; N, 16.07.

2.5.4. 2-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-1,3-indanedione (3d)

Pale greenish crystals; m.p. 198–202 °C (lit. 199-202 °C); IR (KBr) cm^{-1}: 732, 1213, 1343, 1521, 1623, 1689, 3065. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 7.45–8.04 (m, 9H, Ar–H), 7.80 (s, 1H, –CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 122.9, 123.3, 128.0, 128.2, 131.6, 135.0, 135.3, 137.2, 138.9, 141.9, 152.1, 188.5, 189.4. FAB-MS: (*m/z*) 349. Anal. calc. for $C_{20}H_{13}N_2O_2Cl$: C, 68.89; H, 3.72; N, 8.03. Found: C, 68.96; H, 3.77; N, 8.08.

2.5.5. 2-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-1, 4-benzothiazine-3-one (3e)

Greenish yellow solid; m.p. 115–116 °C (lit. 114-116 °C); IR (KBr) cm^{-1}: 727, 1209, 1351, 1517, 1597, 1653, 3053, 3185. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3) 7.12–8.02 (m, 10H, Ar–H + CH=C), 9.61 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 115.21, 126.18, 129.19, 129.38, 134.43, 136.96, 151.74, 191.38. FAB-MS: (*m/z*) 368. Anal. calc. for $C_{19}H_{14}N_3OSCl$: C, 62.06; H, 3.80; N, 11.42. Found: C, 62.08; H, 3.83; N, 11.39.

2.5.6. 5-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-2,2-dimethyl-1, 3-dioxane-4, 6-dione (3f)

Pale yellow crystals; m.p: 241–243 °C (lit. 240-242 °C); IR (KBr) cm^{-1}: 729, 1217, 1347, 1525, 1582, 1725. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6H, 2 CH3), 2.52 (s, 3H, CH_3), 7.00–7.73 (m, 6H, Ar–H + CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 27.94, 117.01, 125.11, 128.49, 129.18, 133.03, 136.916, 153.14, 191.84. FAB-MS: (*m/z*) 347. Anal. calc. for $C_{17}H_{15}N_2O_4Cl$: C, 58.90; H, 4.32; N, 8.07. Found: C, 58.94; H, 4.35; N, 8.03.

2.5.7. 4-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-3-methyl-1-phenylpyrazol-5-one (3g)

White powder; m.p. 186–189 °C (lit. 186-188 °C); IR (KBr) cm^{-1}: 736, 1219, 1353, 1529, 1602, 1730, 3056. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.4 (s, 6H, $2CH_3$), 4.93 (s, 1H, –CH=C), 7.23–7.76 (m, 10H, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 30.92, 119.04, 127.08, 128.69, 129.11, 133.23, 136.76, 154.71, 176.23. FAB-MS: (*m/z*) 376. Anal. calc. For $C_{21}H_{17}N_4OCl$: C, 66.96; H, 4.51; N, 14.86. Found: C, 66.92; H, 4.49; N, 14.83.

2.5.8. 3-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)-2-phenyl-acrylic acid (3h)

White crystalline solid; m.p. 160-163 °C; IR (KBr) cm^{-1}: 762, 1211, 1373, 1528, 1599, 1679, 2867, 3063. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3H, CH_3), 7.43–7.59 (m, 10H,

Ar–H), 9.97 (s, 1H, –CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 117.41, 125.18, 129.19, 129.28, 133.43, 136.96, 151.74, 183.84. ESI-MS: (*m/z*) 339.6. Anal. calc. for $C_{19}H_{15}N_2O_2Cl$: C, 67.31; H, 4.42; N, 8.26. Found: C, 67.29; H, 4.39; N, 8.24.

2.5.9. Ethyl-3-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)-2-cyanoacrylate (3i)

White crystals; m.p: 75–79 °C (lit. 75-78 °C); IR (KBr) cm^{-1}: 729, 1217, 1347, 1525, 1582, 1720, 2220. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (t, 3H, CH3), 2.35 (s, 3H, CH_3), 4.29 (q, 2H, CH_2), 7.40 (m, 5H, Ar–H), 8.10 (s, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 14.10, 61.84, 114.60, 118.44, 127.98, 129.19, 129.58, 132.30, 136.61, 153.64, 166.29. FAB-MS: (*m/z*) 316. Anal. calc. for $C_{16}H_{14}N_3O_2Cl$: C, 60.86; H, 4.47; N, 13.31. Found: C, 61.01; H, 4.53; N, 13.00.

2.5.10. 2-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl)methylene-malononitrile (3j)

Yellow crystals; m.p: 195–199 °C (lit. 195-197 °C); IR (KBr) cm^{-1}: 729, 1217, 1347, 1525, 1582, 2215. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 7.78 (m, 6H, Ar–H + CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 114.53, 117.36, 125.12, 129.76, 129.99, 133.13, 136.00, 151.21. FAB-MS: (*m/z*) 368.71. Anal. calc. for $C_{14}H_9N_4Cl$: C, 62.57; H, 3.38; N, 20.85. Found: C, 62.21; H, 3.40; N, 20.96.

2.5.11. 3-(5-Chloro-3-methyl-1-phenylpyrazol-4-yl))-2-phenylacrylonitrile (3k)

Yellow crystals; m.p: 76–79 °C (lit. 76-78 °C); IR (KBr) cm^{-1}: 729, 1217, 1347, 1525, 1582, 2222. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H, CH_3), 7.45 (m, 11H, Ar–H + CH=C). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.84, 114.98, 119.41, 125.87, 127.19, 128.28, 134.43, 135.36, 153.14. FAB-MS: (*m/z*) 319.87. Anal. calc. for $C_{14}H_9N_4Cl$: C, 71.34; H, 4.41; N, 13.14. Found: C, 70.98; H, 4.21; N, 12.85.

2.5.12. 4-(4-hydroxy-6-methyl-2-oxo-2H-pyran-2-one-3-yl)-3, 7-dimethyl-1-phenylpyrazolo [3,4:2,3]-4H-pyrano [3,2-b] pyran-5-one (3l)

White crystalline solid; m.p. 259-261 °C (lit. 260-262 °C); IR (KBr) cm^{-1}: 723, 1207, 1355, 1517, 1642, 1726, 3059, 3442. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 6H, $2CH_3$), 2.29 (s, 3H, CH_3), 4.53 (S, 1H, CH), 6.01 (s, 2H, H-5), 7.068-7.62 (m, 5H, Ar-H), 10.49 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.15, 103.45, 121.23, 128.17, 134.11, 136.21, 166.51, 182.10. FAB-MS: (*m/z*) 418. Anal. calc. for $C_{23}H_{18}N_2O_6$: C, 66.02; H, 4.30; N, 6.69. Found: C, 66.23; H, 4.55; N, 6.40.

2.5.13. 4-(4-hydroxy-6,7-dimethyl-2-oxo-2H-1-benzopyran-2-one-3-yl)-3-methyl-1-phenylpyrazolo [3,4:2,3]-4H-pyrano [3,2-b]-7,8-dimethyl-1-benzopyran-5-one (3m)

Orange powder; m.p: >300 °C; IR (KBr) cm^{-1}: 758, 1203, 1377, 1572, 1619, 1726, 3052, 3377. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.34, 2.39, 2.43 (s, 15H, CH_3), 7.07 (s, 1H, CH), 7.34-8.35 (m, 9H, Ar-H), 8.20. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.13, 103.85, 120.47, 128.57, 133.11, 136.57, 166.52, 183.17. ESI- MS: (*m/z*) 547.6. Anal. calc. for $C_{33}H_{26}N_2O_6$: C, 72.59; H, 4.76; N, 5.12. Found: C, 72.56; H, 4.73; N, 5.10.

2.5.14. 4-(4-hydroxy-2-oxo-2H-1-benzopyran-2-one-3-yl)-3-methyl-1-phenylpyrazolo [3,4:2,3]-4H-pyrano [3,2-b]-1-benzopyran-5-one (3n)

White crystalline solid; m.p: 269-271 °C (lit. 270 °C); IR (KBr) cm^{-1}: 735, 1213, 1356, 1518, 1659, 1729, 3062, 3451. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.62 (s, 3H, CH_3), 4.75 (s, 1H, CH), 7.25-7.79 (m, 11H, Ar-H), 8.20 (d, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.13, 102.15, 122.34, 128.65, 133.09, 136.34, 165.35, 181.07. FAB-MS: (*m/z*) 491. Anal. calc. for $C_{29}H_{18}N_2O_6$: C, 71.02; H, 3.67; N, 5.71. Found: C, 71.35; H, 3.95; N, 5.40.

References

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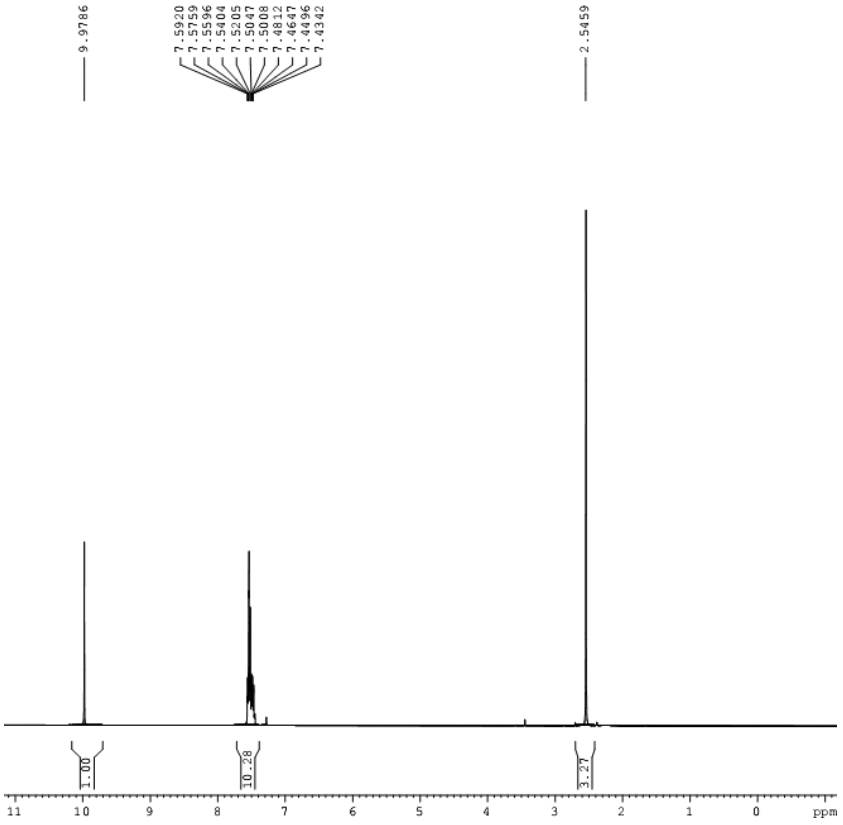
2 Shaterian H R, Ranjbar M, Azizi K (2011) Chin J Chem 29:1635.

^{1}H NMR of 3h



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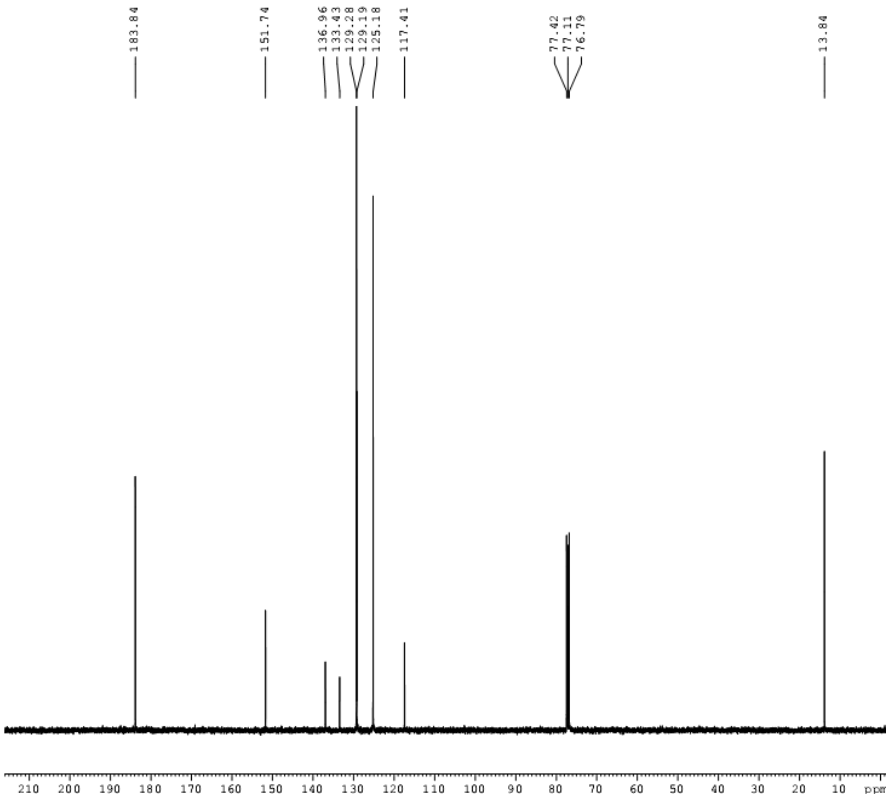

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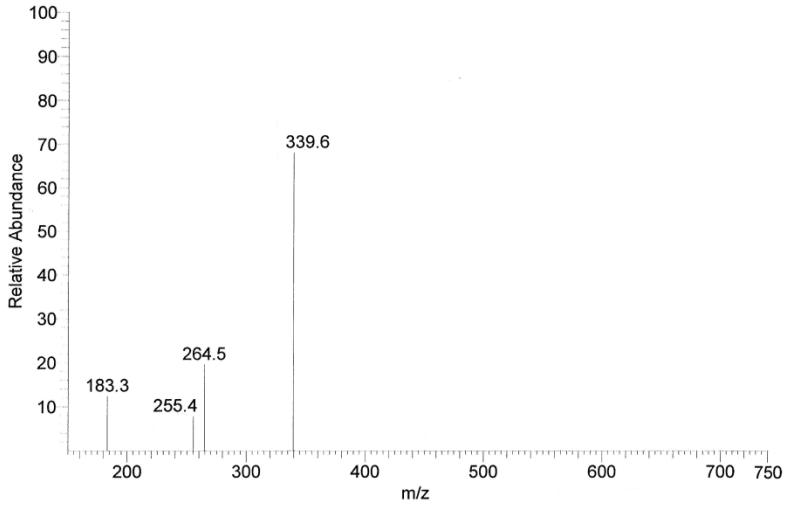

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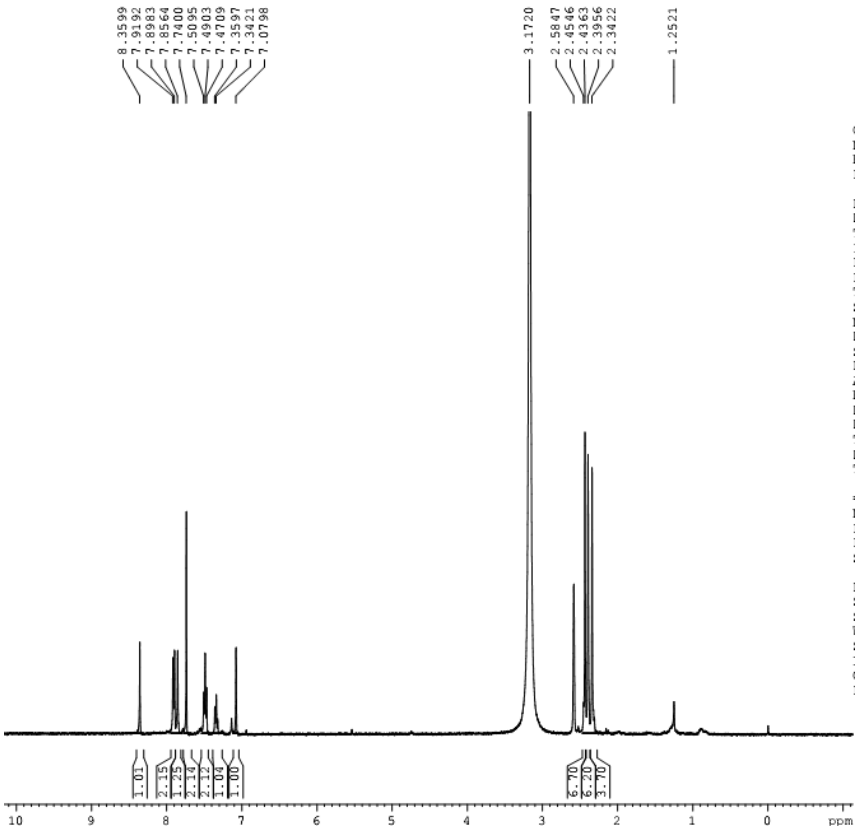

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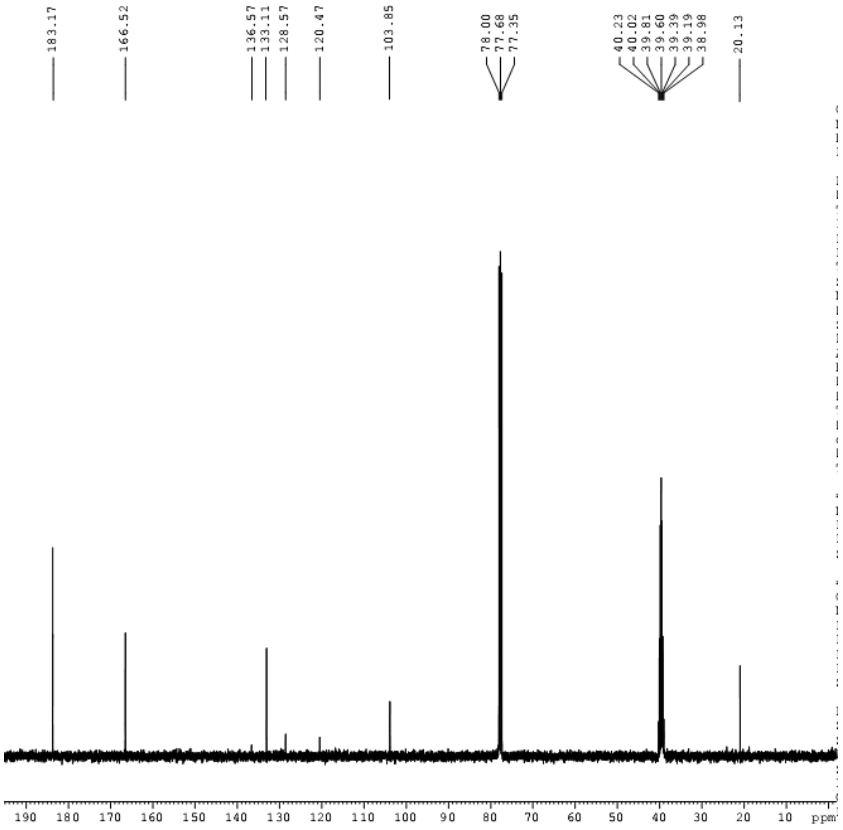

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