Supplementary Information

Synthesis of new ethyl cyanoacetate analogs catalyzed by nano-Fe_3O_4@EA

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1. FT-IR, NMR and elemental analysis data

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Ethyl 2-cyano-3-(4-((phenylsulfonyl)oxy)phenyl)acrylate (**3a**)

FT- IR (KBr): 3415 (aromatic C-H stretch), 2985 (aliphatic C-H stretch), 2216 (C-N stretch), 1737 (C=O stretch), 1610, 1446 (aromatic C=C stretch), 1151, 1201 (SO_2 stretch), 746 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ; 8.39 (s, 1H), 8.02 (d, *J*=8.7 Hz, 2H), 7.83-7.94 (m, 3H), 7.70 (t, *J*=7.5 Hz, 2H), 4.32 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.30 (t, 3H, CH_3) ppm; ^{13}C NMR: 14.42, 62.95, 104.07, 115.80, 123.41, 128.70, 130.45, 133.20, 134.51, 135.81, 152.16, 153.89, 162.00 ppm. MS (ESI+): *m/z* = 358.300 $[M+ H]^+$.

Ethyl 2-cyano-3-(4-(tosyloxy)phenyl)acrylate (**3b**)

FT- IR (KBr): 3417 (aromatic C-H stretch), 2218 (CN stretch), 1720 (C=O stretch), 1610, 1194 (aromatic C=C stretch), 1348, 1182 (SO_2 stretch), 707 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ; 8.40 (s, 1H), 8.08 (d, *J*=8.4 Hz, 2H), 7.81 (d, *J*=7.8 Hz, 2H), 7.77 (d, *J*= 8.1 Hz, 2H), 7.29 (d, *J*=8.4 Hz, 2H), 4.33 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.32 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.44, 21.68, 62.69, 104.00, 115.83, 123.41, 128.74, 130.87, 131.62, 133.21, 146.67, 152.27, 153.94, 162.03 ppm. MS (ESI+): *m/z* = 394.020 $[M+ Na]^+$.

Ethyl 2-cyano-3-(2-(tosyloxy)phenyl)acrylate (**3c**)

FT- IR (KBr): 3415 (aromatic C-H stretch), 2981 (aliphatic C-H stretch), 2227 (C-N stretch), 1706 (C=O stretch), 1610, 1448 (aromatic C=C stretch), 1170, 1193 (SO_2 stretch), 715 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ; 7.97 (dd, J_1=2.1 Hz, J_2=6.6 Hz, 1H), 7.87 (s, 1H), 7.77 (td, J_1=1.5 Hz, J_2=6.6 Hz, 1H), 7.55-7.62 (m, 3H), 7.73 (dd, J_1=0.6 Hz, J_2=7.5 Hz, 1H), 7.83 (d, *J*=8.1 Hz, 1H), 4.34 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.35 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.43, 21.58, 63.12, 105.82, 114.62, 124.87, 125.90, 128.75, 128. 80, 129.59, 130.24, 131.21, 134.99, 147.16, 148.01, 148.11, 161.22 ppm. . MS (ESI+): *m/z* = 372.238 $[M+ H]^+$.

Ethyl 2-cyano-3-(2-((phenylsulfonyl)oxy)phenyl)acrylate (**3d**)

FT- IR (KBr): 3023 (aromatic C-H stretch), 2982 (aliphatic C-H stretch), 2222 (C-N stretch), 1735 (C=O stretch), 1619, 1450 (aromatic C=C stretch), 1160, 1193 (SO_2 stretch), 742 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ; 8.03 (dd, J_1=1.2 Hz, J_2=6.6 Hz, 1H), 7.95 (s, 1H), 7.82-7.87 (m, 1H), 7.73-7.79 (m, 3H), 7.57-767 (m, 3H), 7.45 (d, *J*=8.4 Hz, 1H), 4.33 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.34 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.42, 63.11, 106.06, 114.80, 124.70, 125.77, 128.71, 128.80, 129.65, 130.70, 133.59, 135.08, 136.06, 148.03, 148.07, 161.22 ppm. MS (ESI+): *m/z* = 380.096 $[M+ Na]^+$.

Ethyl 2-cyano-3-(3-(tosyloxy)phenyl)acrylate (**3e**)

FT- IR (KBr): 3064 (aromatic C-H stretch), 2989 (aliphatic C-H stretch), 2219 (C-N stretch), 1726 (C=O stretch), 1606, 1442 (aromatic C=C stretch), 1174, 1190 (SO_2 stretch), 717 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ; 8.40 (s, 1H), 8.01

(d, *J*=7.8 Hz, 1H), 7.82 (s, 1H), 7.78 (d, *J*=8.4 Hz, 2H), 7.62 (t, *J*=7.8 Hz, 1H), 7.49 (d, *J*=8.1 Hz, 2H), 7.27 (dd, J_1=1.5 Hz, J_2=6.6 Hz, 1H), 4.34 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.32 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.43, 21.67, 63.03, 104.79, 115.54, 124.33, 127.03, 128.71, 130.19, 130.86, 131.50, 131.53, 133.62, 146.59, 149.69, 153.67, 161.88 ppm. MS (ESI+): *m*/*z* = 394.200 $[M+ Na]^+$.

Ethyl 2-cyano-3-(3-methoxy-4-(tosyloxy)phenyl)acrylate (**3f**)

FT- IR (KBr): 3039 (aromatic C-H stretch), 2941 (aliphatic C-H stretch), 2230 (C-N stretch), 1726 (C=O stretch), 1614, 1448 (aromatic C=C stretch), 1117, 1187 (SO_2 stretch), 754 (aromatic C-H out of plane bending) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ; 8.39 (s, 1H), 7.83-7.89 (m, 3H), 7.67-7.76 (m, 4H), 7.37 (d, *J*=8.4 Hz, 1H), 4.34 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 3.55 (s, 3H, OCH_3), 1.32 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.45, 56.28, 62.97, 104.10, 115.93, 116.26, 123.78, 124.88, 128.66, 130.05, 131.95, 135.36, 135.54, 140.87, 151.94, 154.26, 162.04 ppm. MS (ESI+): *m*/*z* = 424.109 $[M+ Na]^+$.

Ethyl 2-cyano-3-(3-methoxy-4-((phenylsulfonyl)oxy)phenyl)acrylate (**3g**)

FT- IR (KBr): 3056 (aromatic C-H stretch), 2945 (aliphatic C-H stretch), 2230 (C-N stretch), 1746 (C=O stretch), 1613, 1468 (aromatic C=C stretch), 1116, 1174 (SO_2 stretch), 820 (aromatic C-H out of plane bending) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ; 8.39 (s, 1H), 7.77 (d, *J*=2.4 Hz, 2H), 7.75 (s, 1H), 7. (dd, J_1=1.8 Hz, J_2=6.6 Hz, 1H), 7.49 (t, *J*=8.4 Hz, 2H), 7.34 (d, *J*=8.1 Hz, 1H), 4.34 (q, J_1=6.9 Hz, J_2=7.2 Hz, 2H, CH_2), 1.32 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.34, 14.45, 21.65, 24.96, 56.30, 62.39, 62.97, 104.10, 115.58, 115.94, 116.26, 123.78, 124.78, 128.71, 130.46, 131.86, 132.43, 140.98, 146.40, 152.01, 154.29, 162.05, 164.80 ppm. MS (ESI+): *m*/*z* = 409.994 $[M+ Na]^+$.

Ethyl 2-cyano-3-(3-methoxy-2-((phenylsulfonyl)oxy)phenyl)acrylate (**3h**)

FT- IR (KBr): 3064 (aromatic C-H stretch), 2941 (aliphatic C-H stretch), 2230 (C-N stretch), 1711 (C=O stretch), 1613, 1445 (aromatic C=C stretch), 1157 (SO_2 stretch), 751 (aromatic C-H out of plane bending) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ; 8.12 (s, 1H), 7.84 (t, *J*=8.1 Hz, 3H), 7.71 (s, 1H), 7.61 (t, *J*=7.5 Hz, 2H), 7.53 (t, *J*=8.1 Hz, 1H), 7.44 (dd, J_1=0.9 Hz, J_2=7.8 Hz, 1H), 4.27 (q, J_1=3.3 Hz, J_2=7.2 Hz, 2H, CH_2), 3.64 (s, 1H), 1.32 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.38, 56.61, 63.07, 106.30, 115.05, 118.37, 120.50, 127.36, 128.65, 129.20, 130.32, 135.32, 135.60, 137.40, 148.87, 149.69, 152.98, 161.33 ppm. MS (ESI+): *m*/*z* = 388.100 $[M+ H]^+$.

Ethyl 3-(2-bromo-5-((phenylsulfonyl)oxy)phenyl)-2-cyanoacrylate (**3i**)

FT- IR (KBr): 3061 (aromatic C-H stretch), 2982 (aliphatic C-H stretch), 2232 (C-N stretch), 1718 (C=O stretch), 1617, 1449 (aromatic C=C stretch), 1111, 1193 (SO_2 stretch), 749 (aromatic C-H out of plane bending) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ; 8.13 (d, *J*=2.4 Hz, 1H), 7.96 (dd, J_1=2.4 Hz, J_2=7.8 Hz, 1H), 7.86 (t, *J*=7.5 Hz, 2H), 7.78 (d, *J*=7.2 Hz, 2H), 7.66 (t, *J*=7.5 Hz, 2H), 7.42 (t, *J*=9.0 Hz, 1H), 4.33 (q, J_1=3.3 Hz, J_2=7.2 Hz, 2H, CH_2), 1.35 (t, *J*=7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR: 14.41, 63.26, 107.65, 120.99, 126.81, 127.96, 128.78, 130.83, 132.09, 133.36, 136.23, 137.30, 146.65, 147.06, 160.85 ppm. MS (ESI+): *m*/*z* = 459.967 $[M+ Na]^+$.

2. FT-IR Spectra

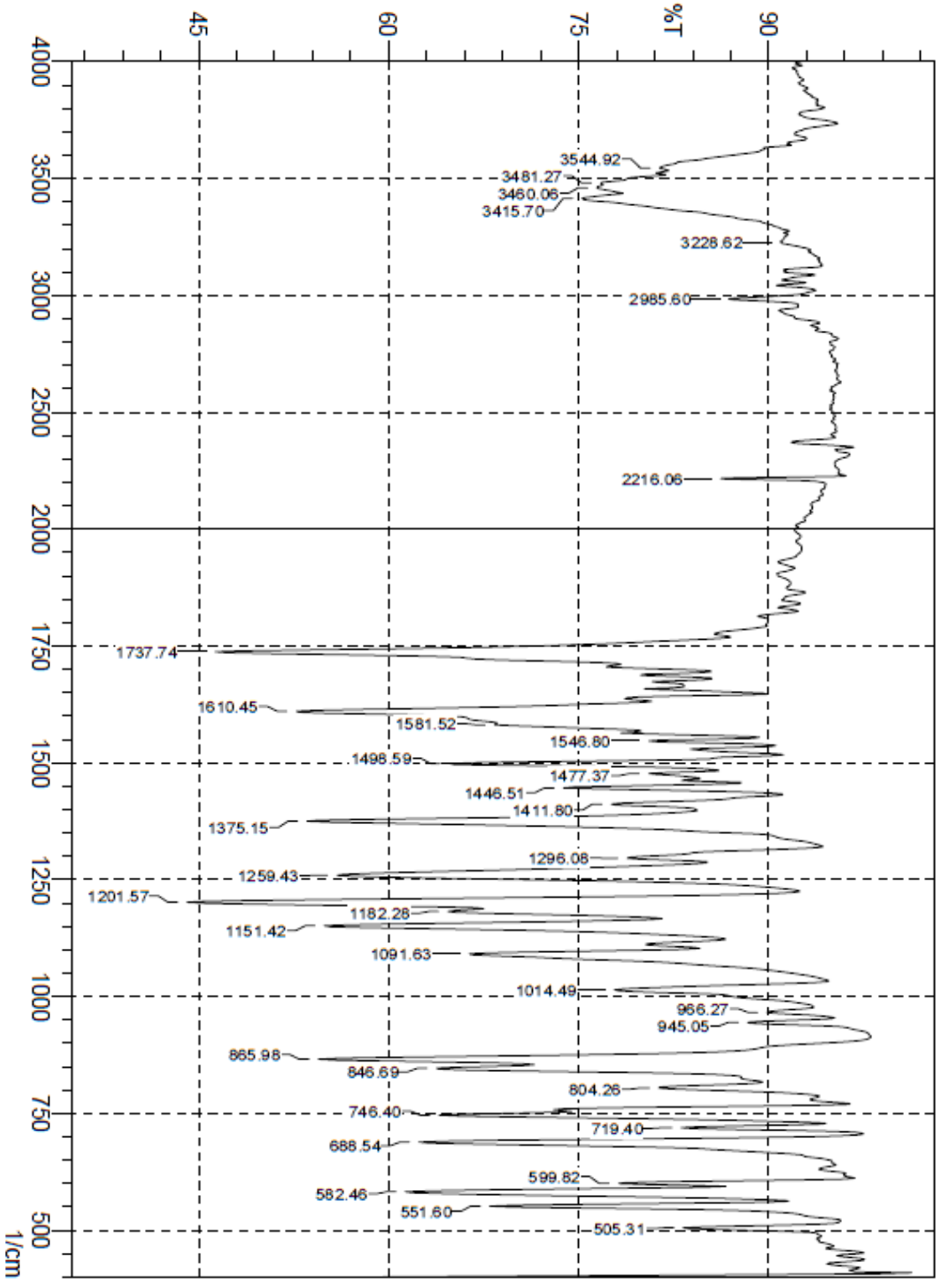

Figure S1 FT-IR spectrum of compound **3a**

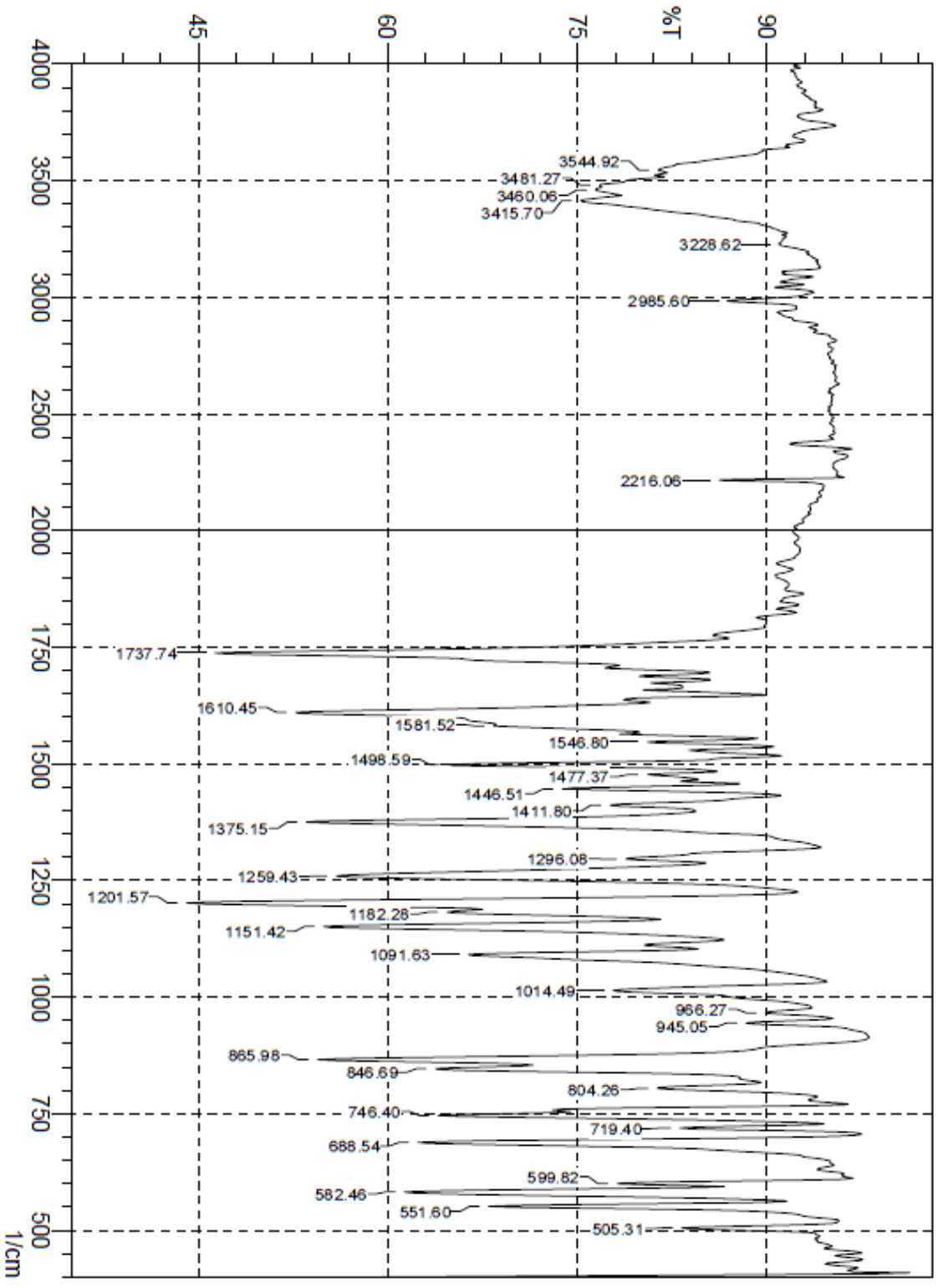

Figure S2 FT-IR spectrum of compound **3b**

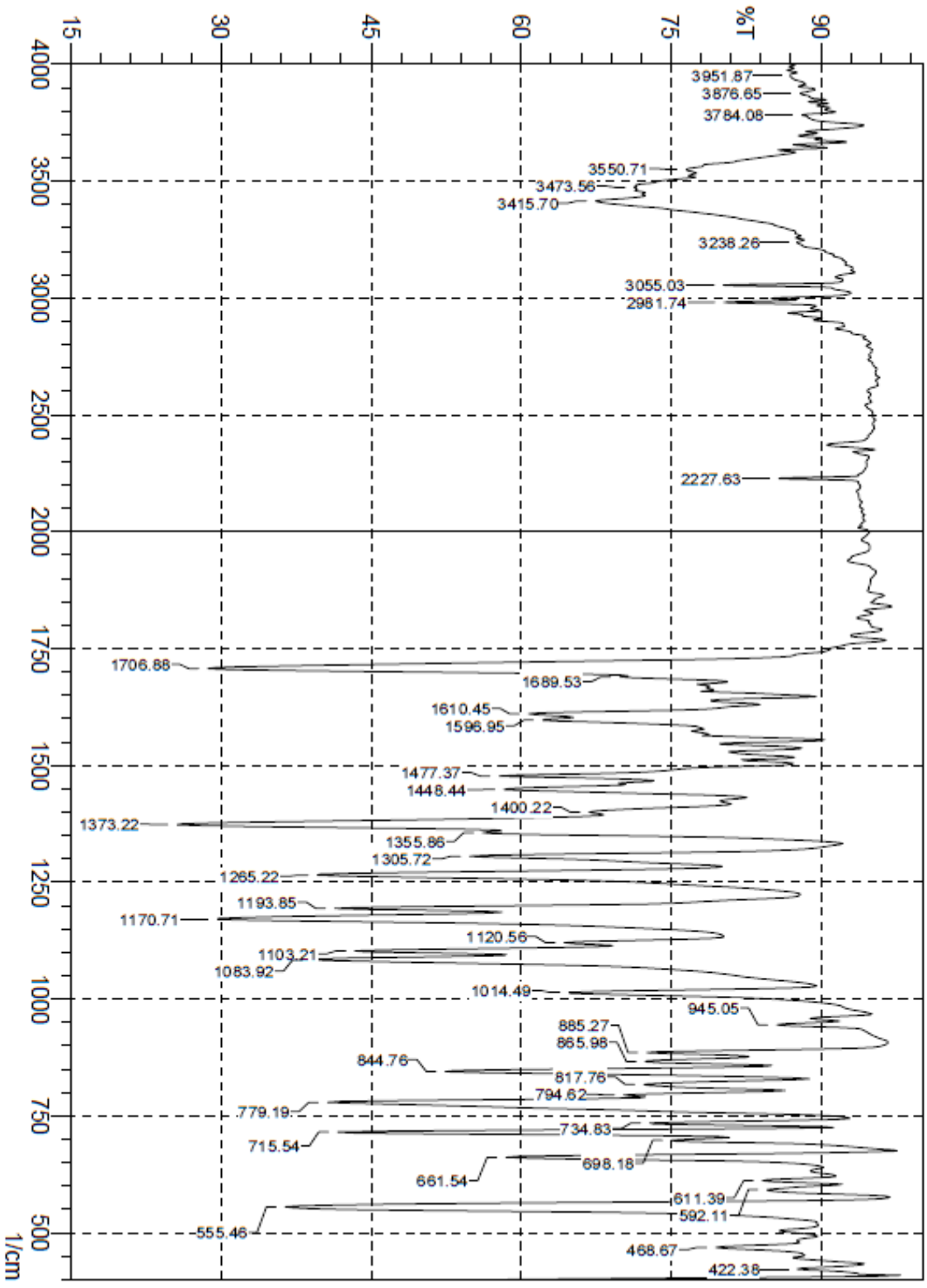

Figure S3 FT-IR spectrum of compound **3c**

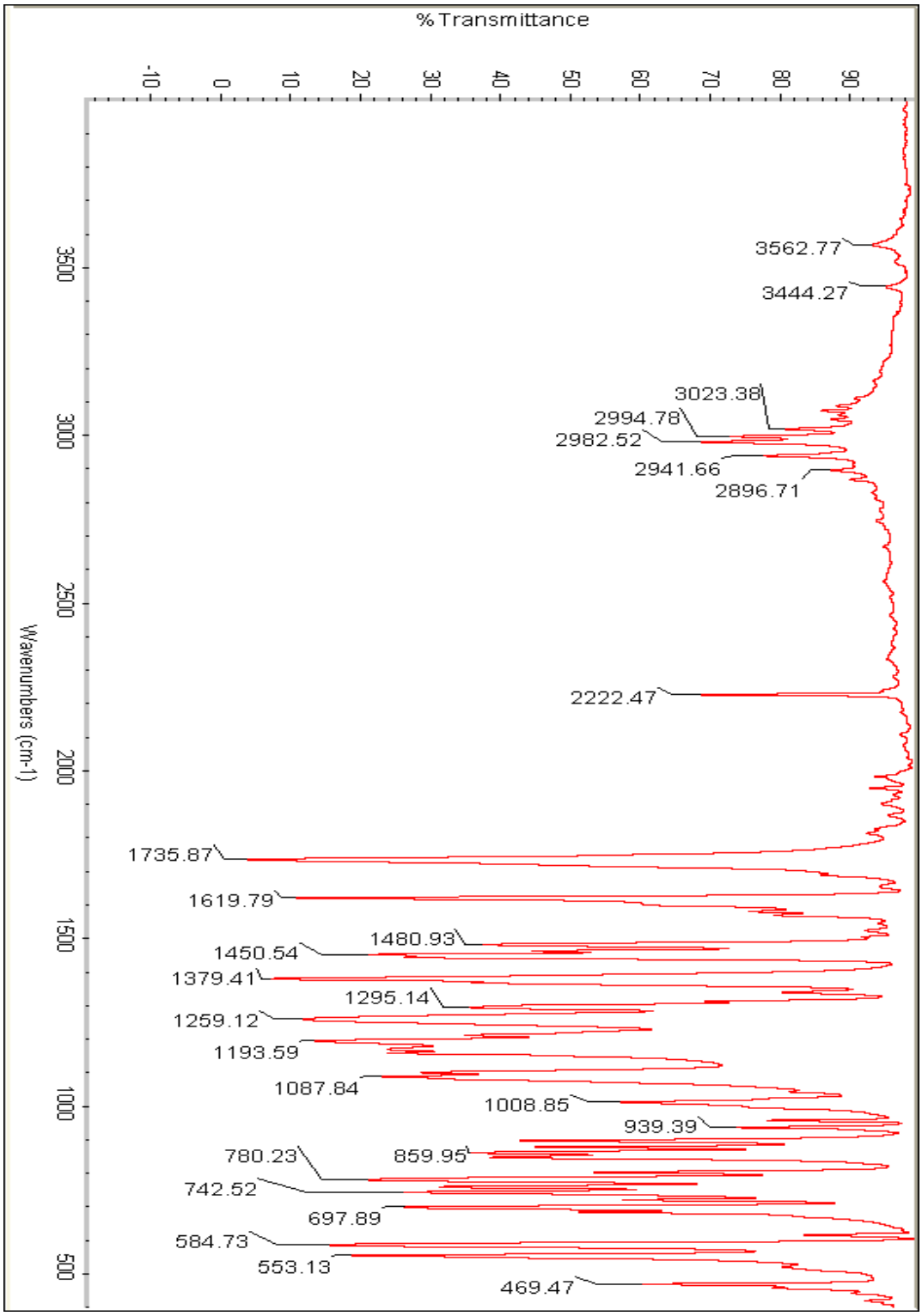

Figure S4 FT-IR spectrum of compound **3d**

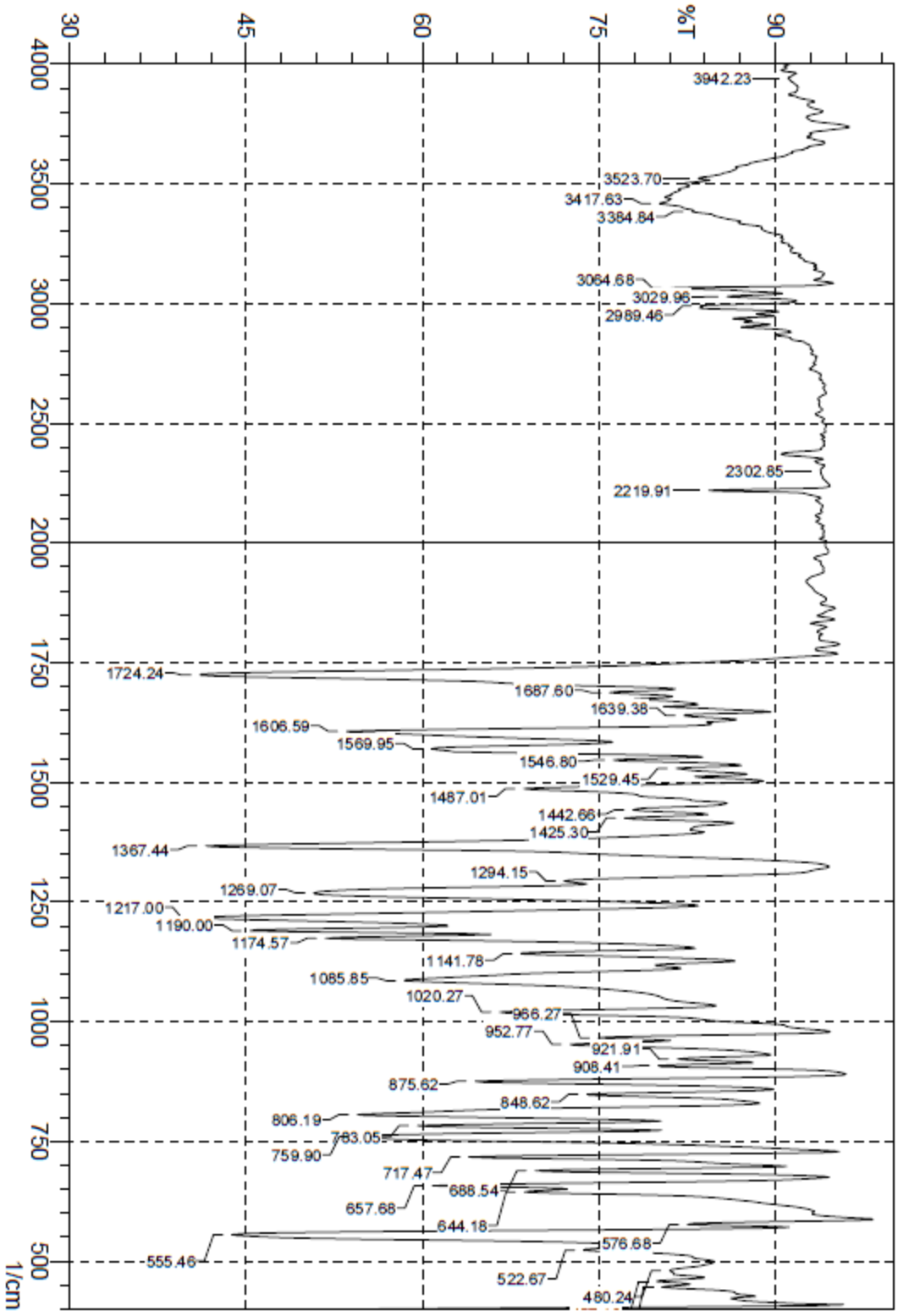

Figure S6 FT-IR spectrum of compound **3e**

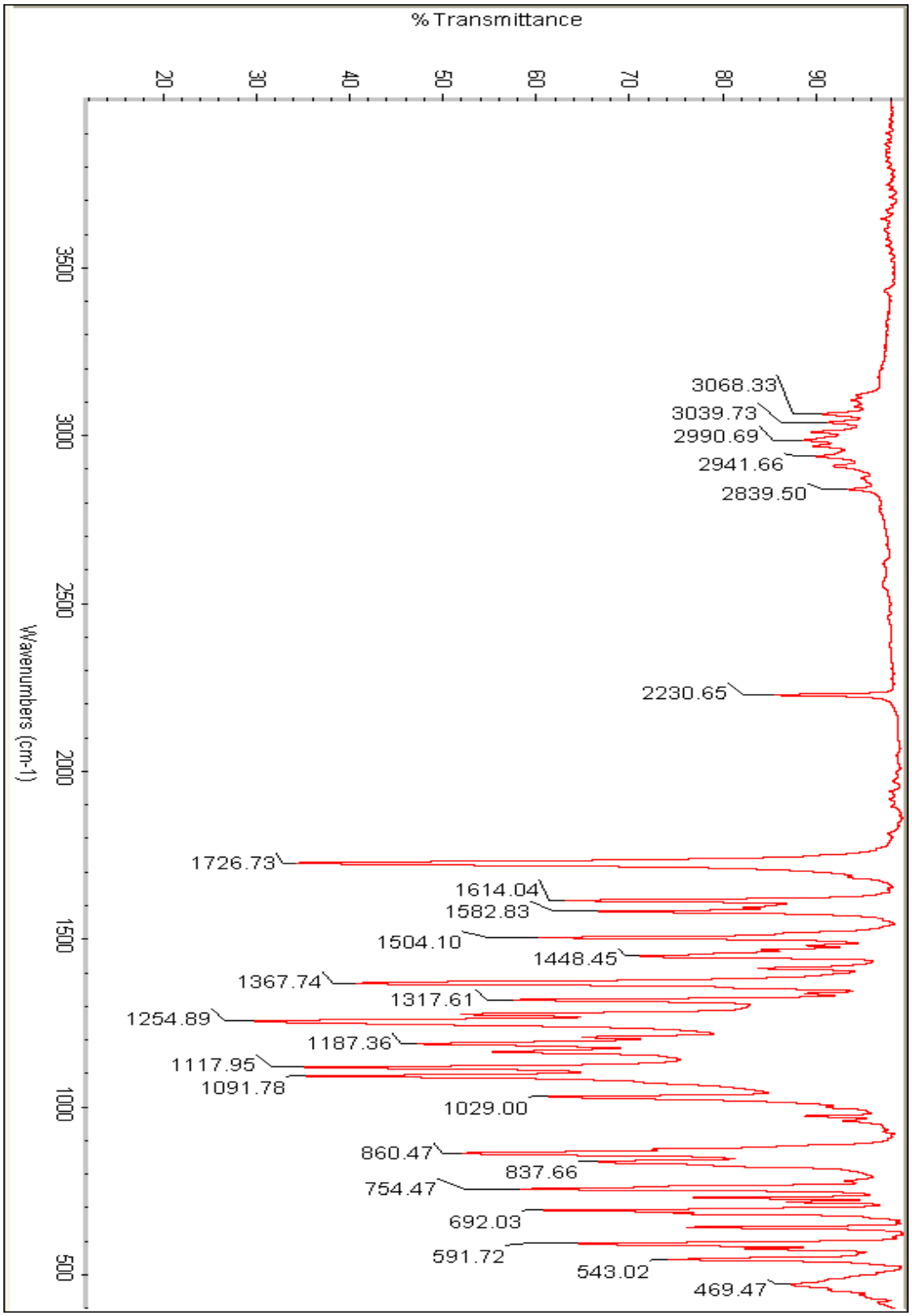

Figure S7 FT-IR spectrum of compound **3f**

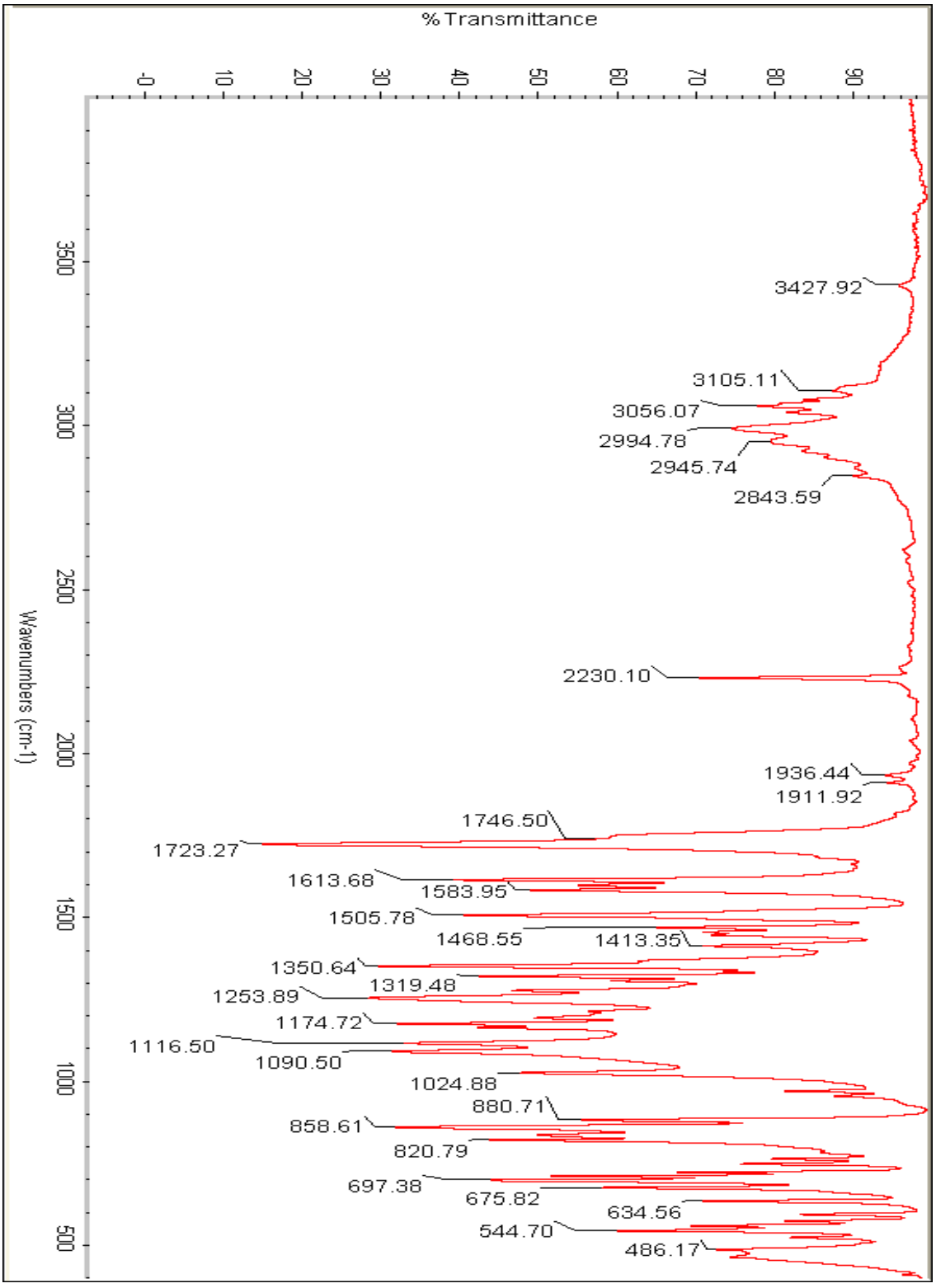

Figure S8 FT-IR spectrum of compound **3g**

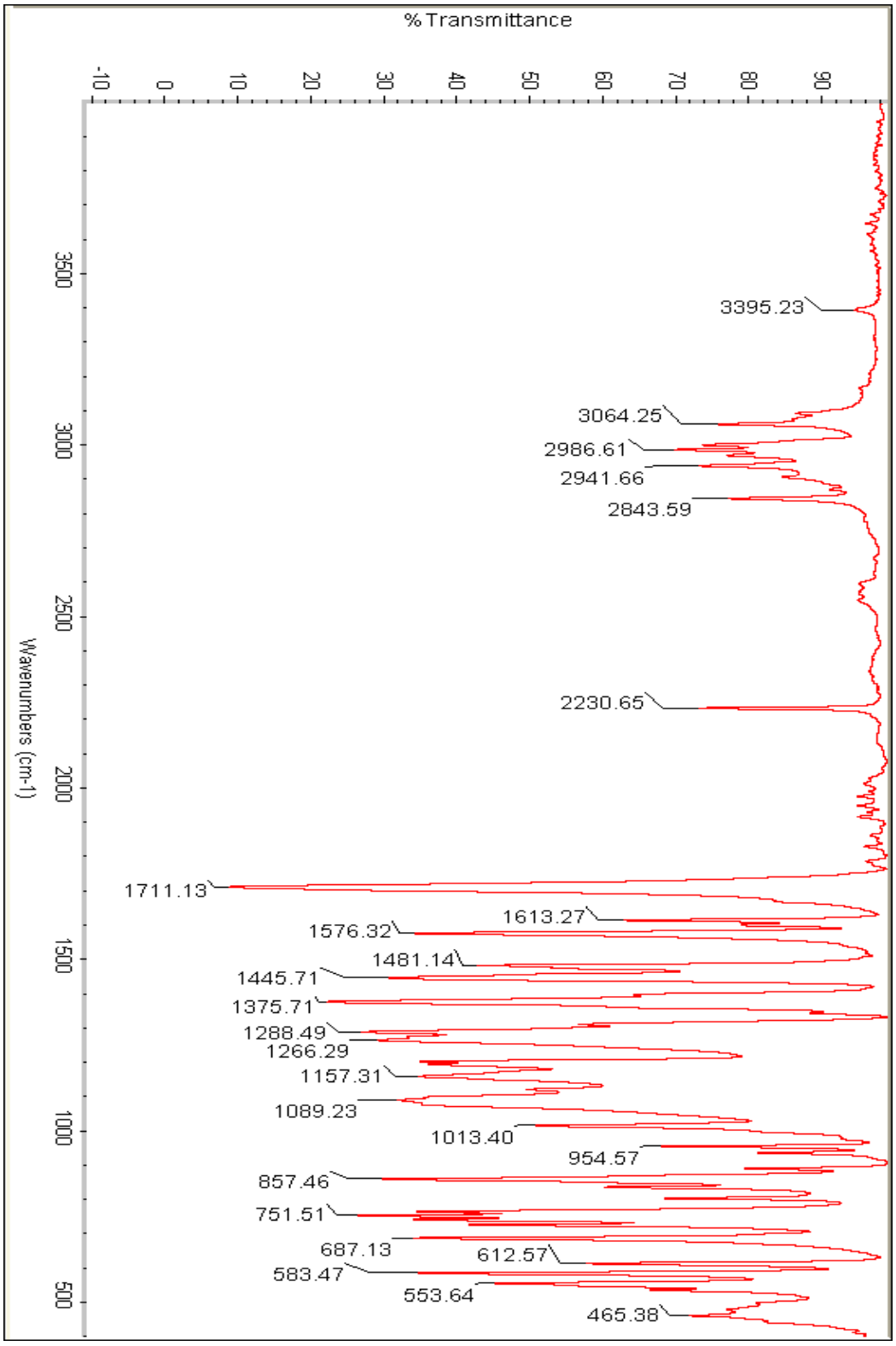

Figure S9 FT-IR spectrum of compound **3h**

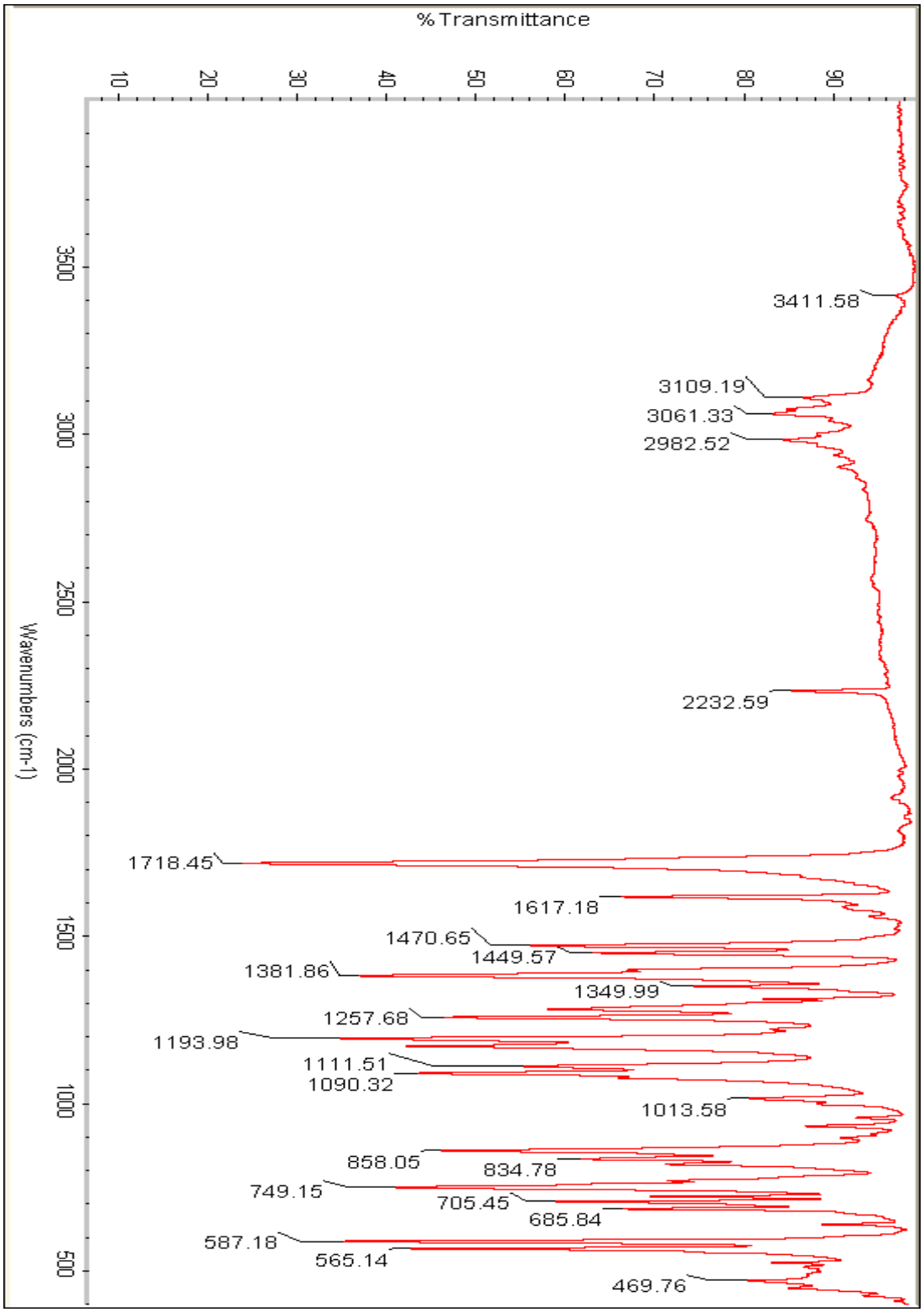

Figure S10 FT-IR spectrum of compound **3i**

3. [1]HNMR Spectra

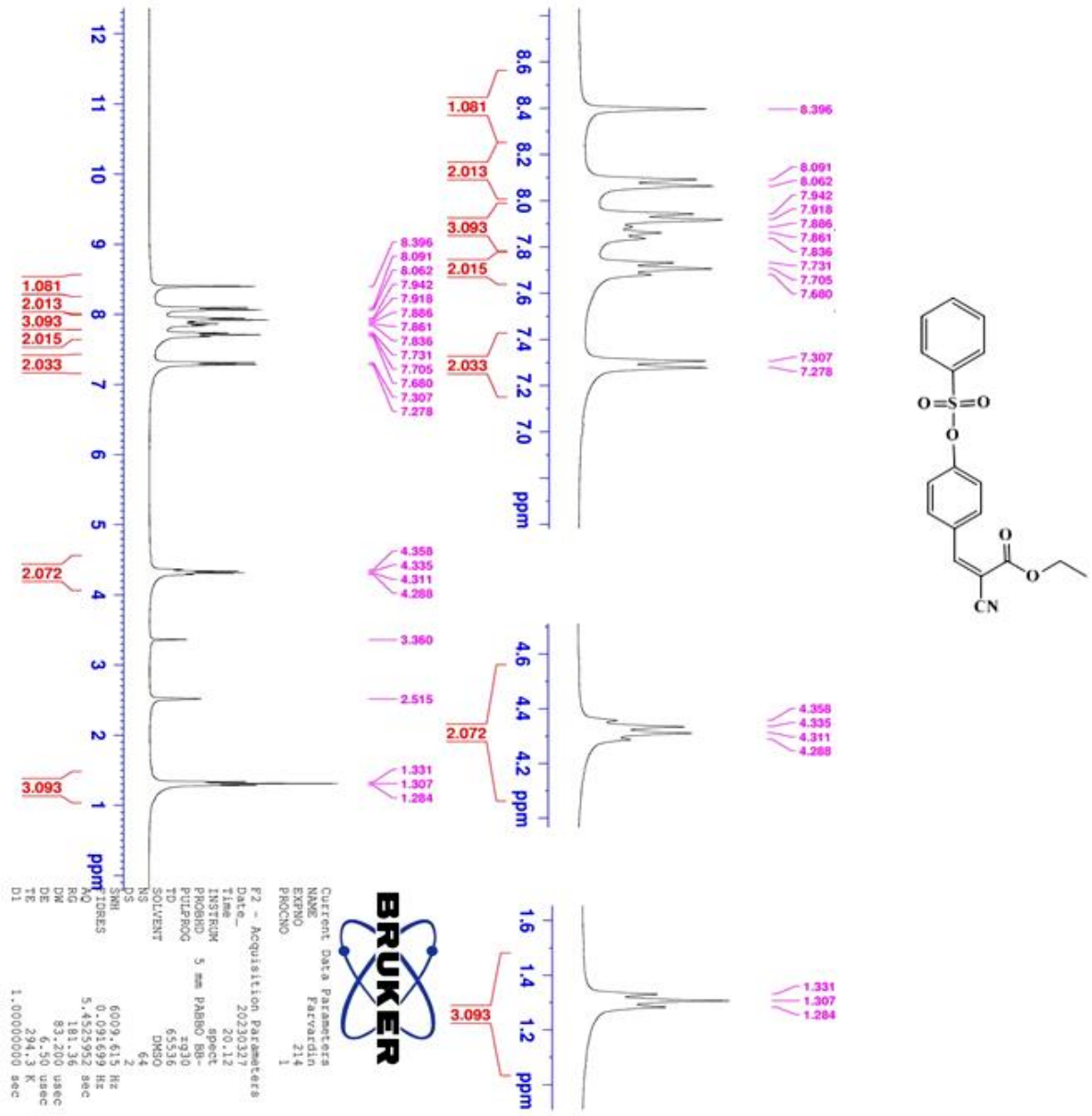

Figure S11 [1]HNMR spectrum of compound **3a**

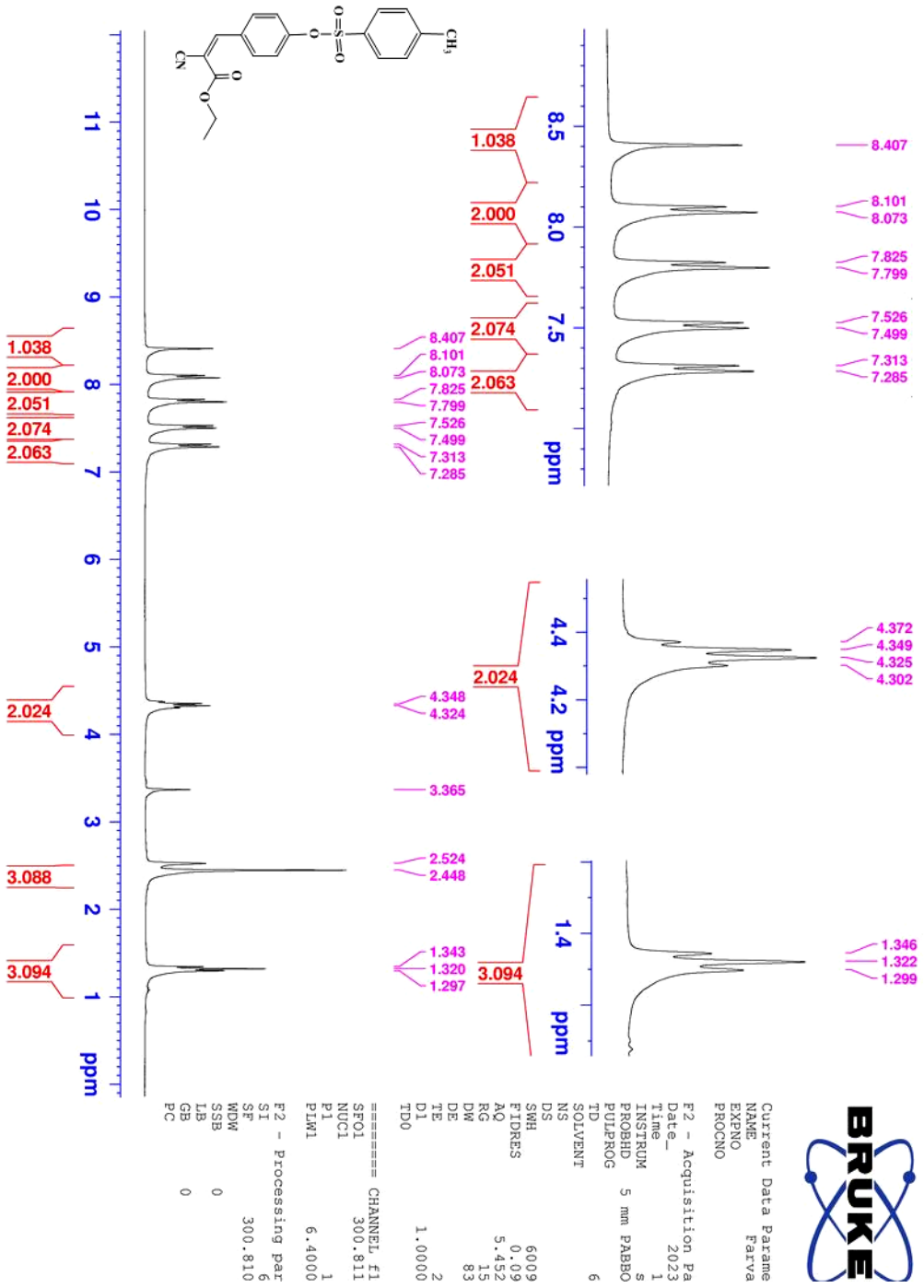

Figure S12 [1]HNMR spectrum of compound **3b**

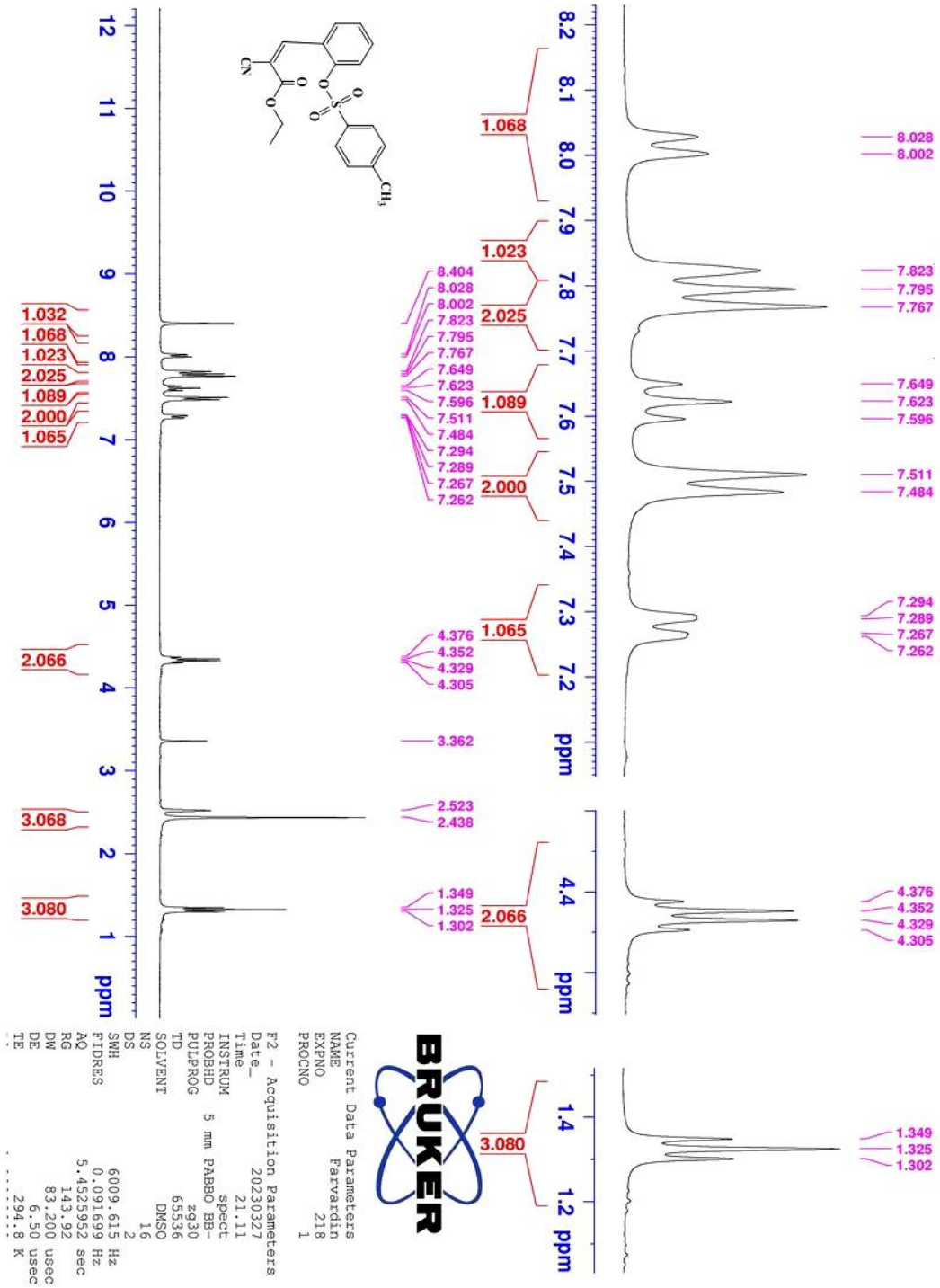

Figure S13 [1]HNMR spectrum of compound **3c**

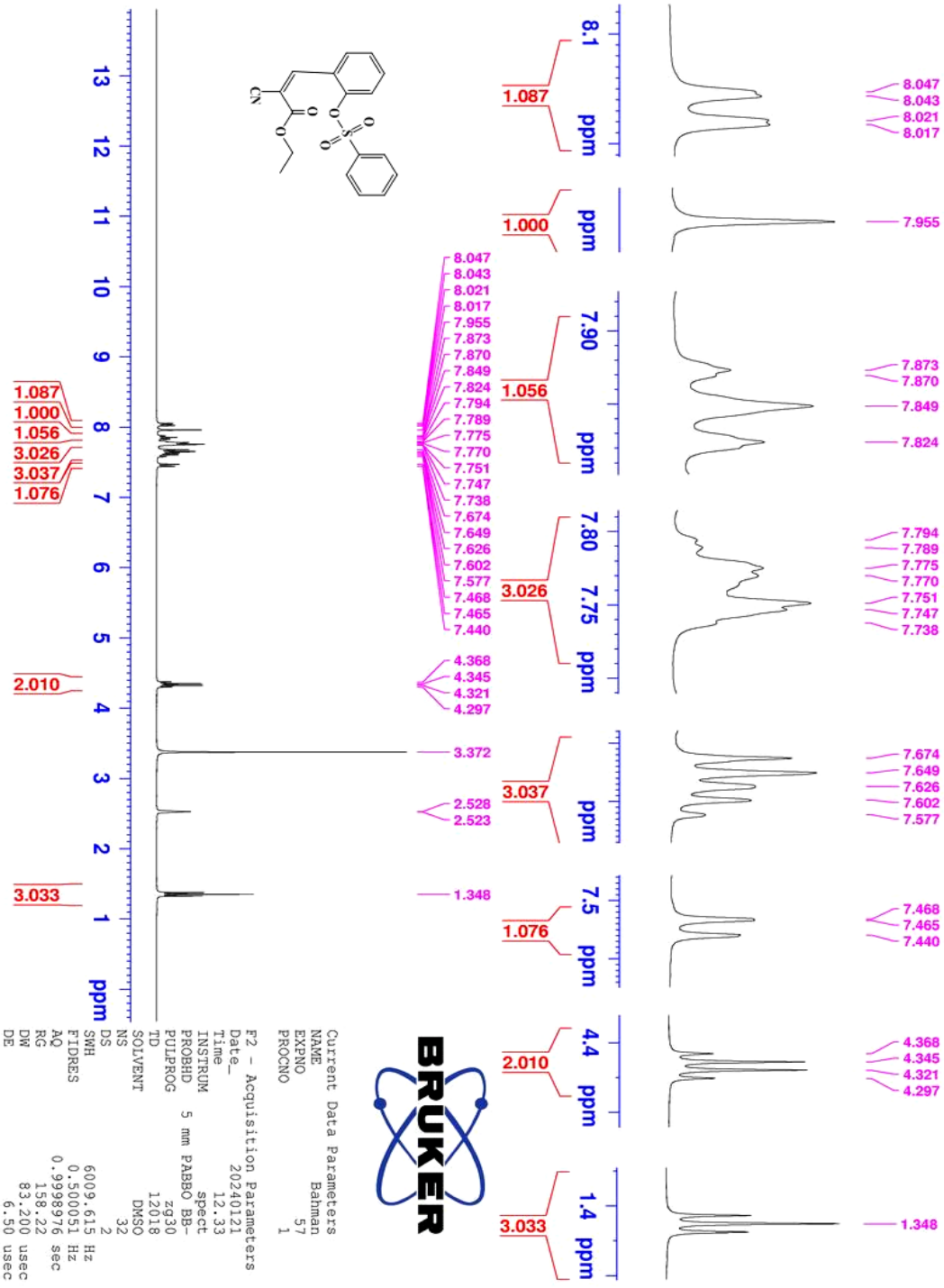

Figure S14 [1]HNMR spectrum of compound **3d**

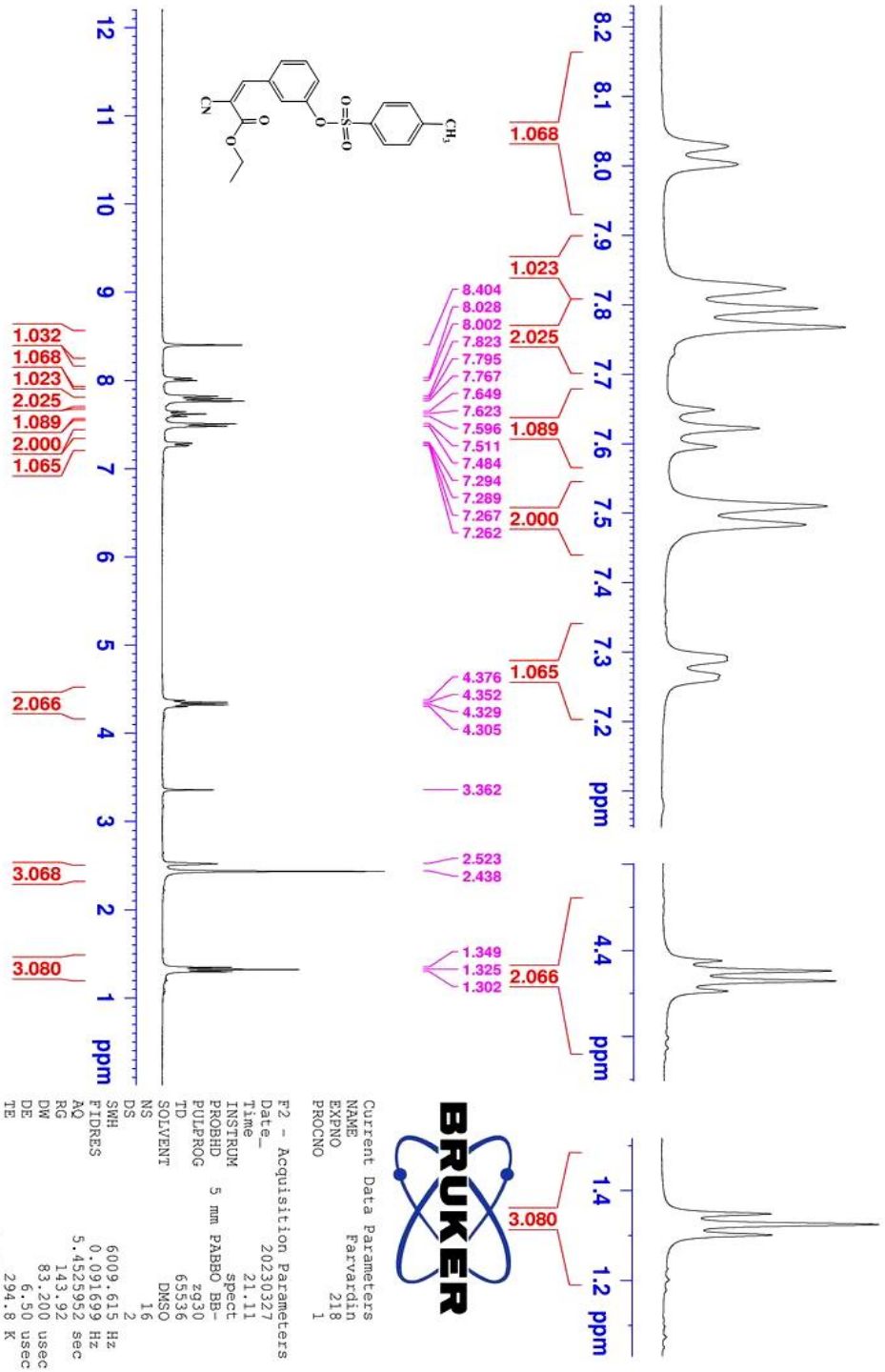

Figure S15 [1]HNMR spectrum of compound **3e**

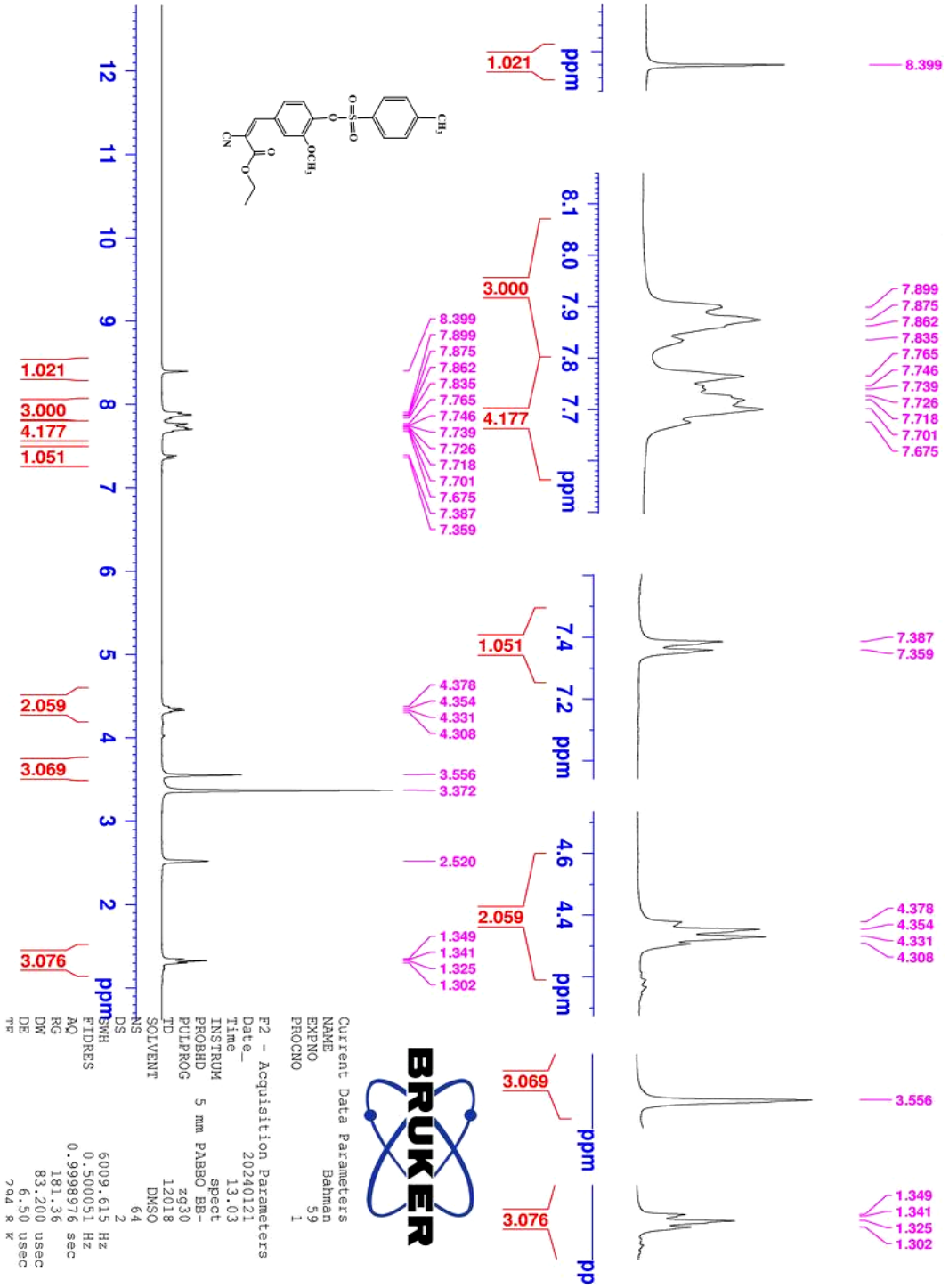

Figure S16 [1]HNMR spectrum of compound **3f**

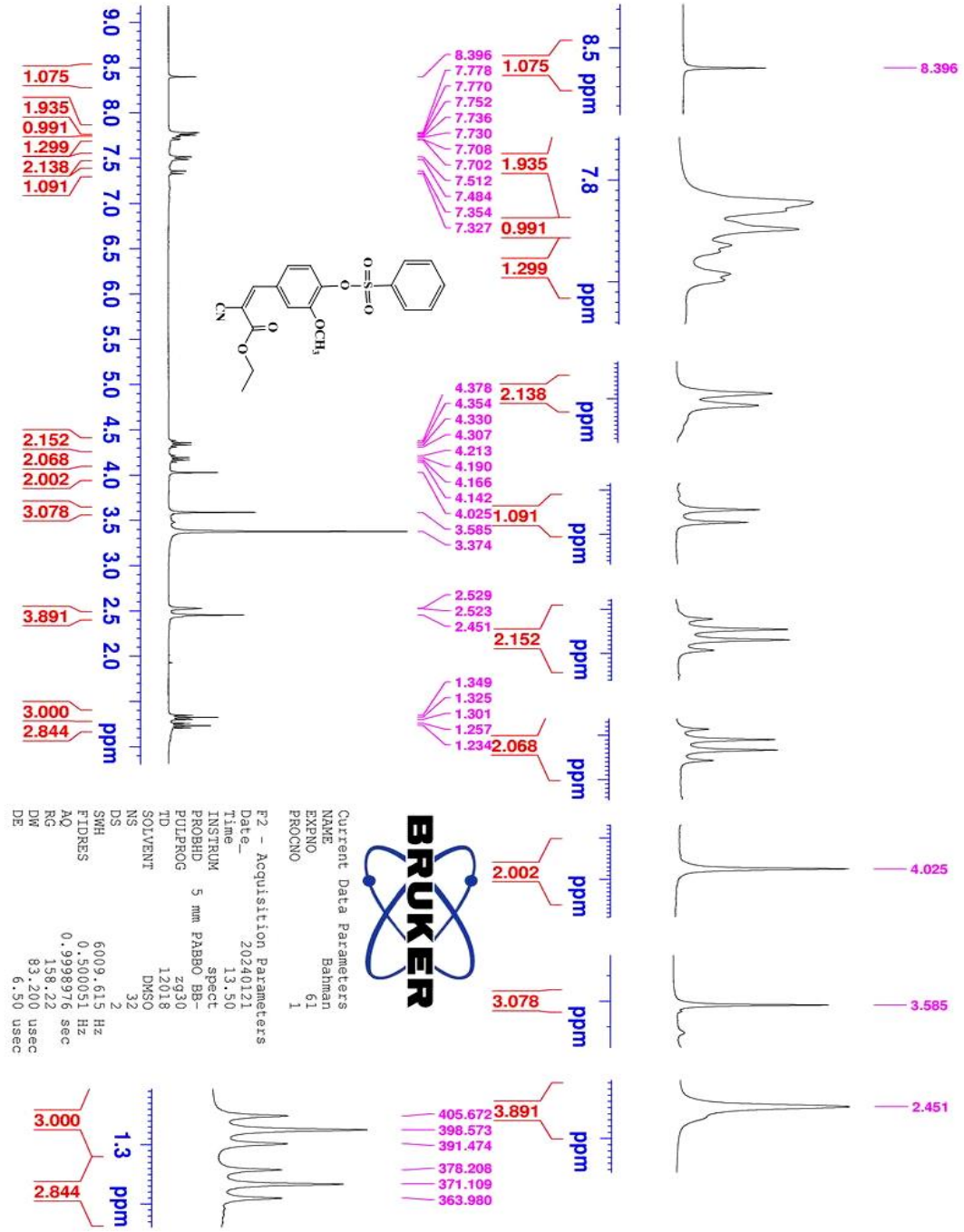

Figure S17 [1]HNMR spectrum of compound **3g**

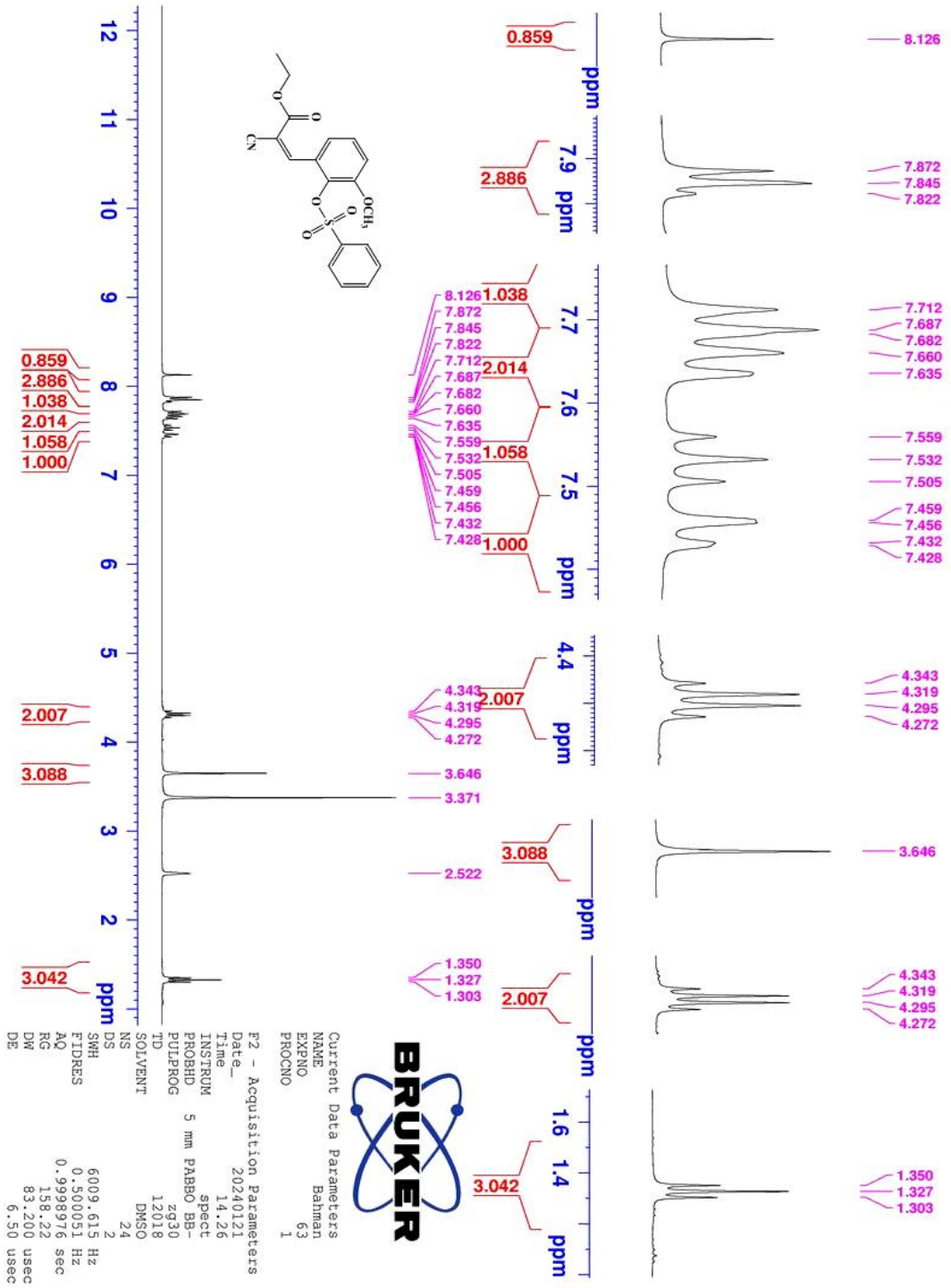

Figure S18 [1]HNMR spectrum of compound **3h**

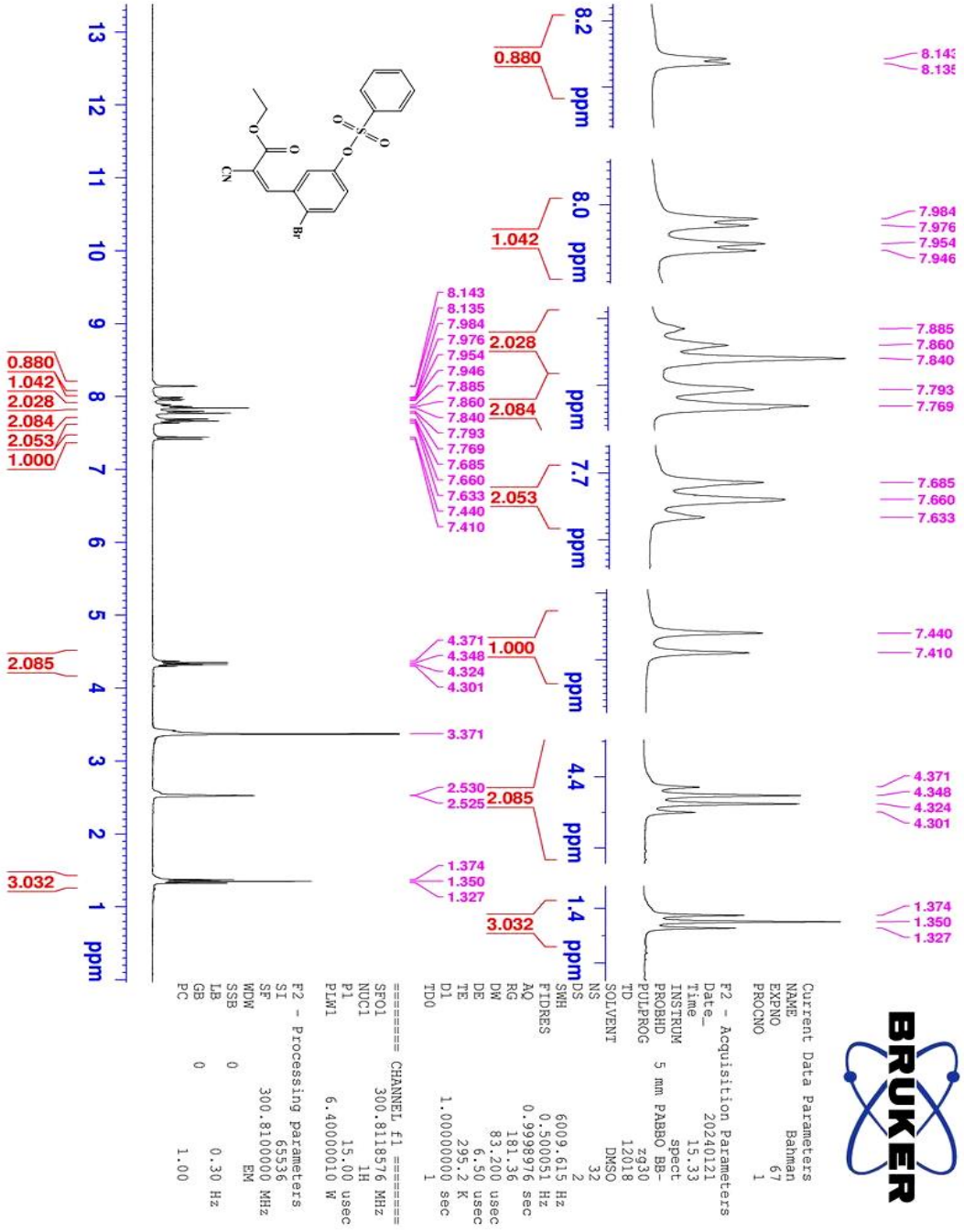

Figure S19 [1]HNMR spectrum of compound **3i**

4. ^{13}CNMR Spectra

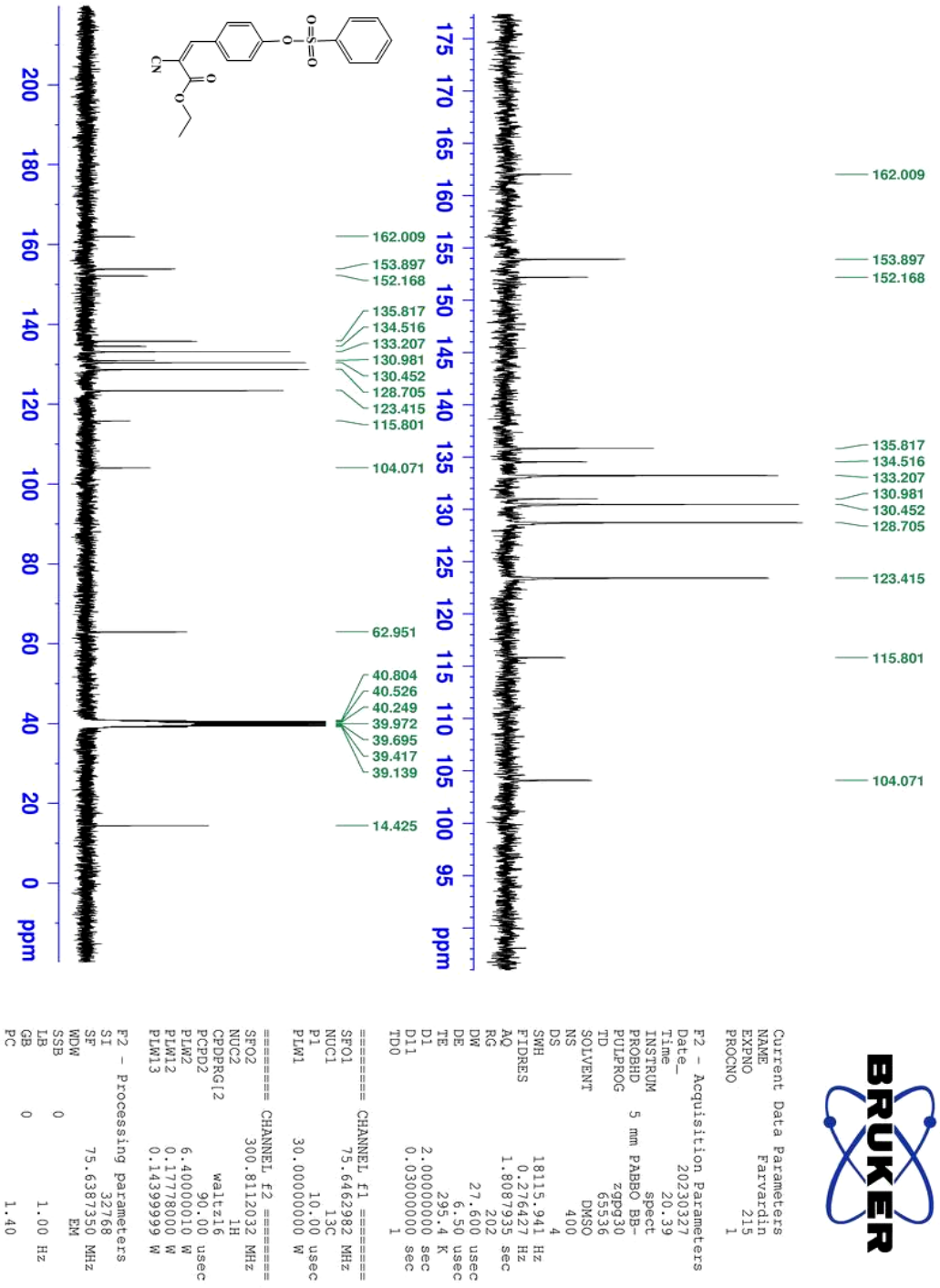

Figure S20 ^{13}CNMR spectrum of compound **3a**

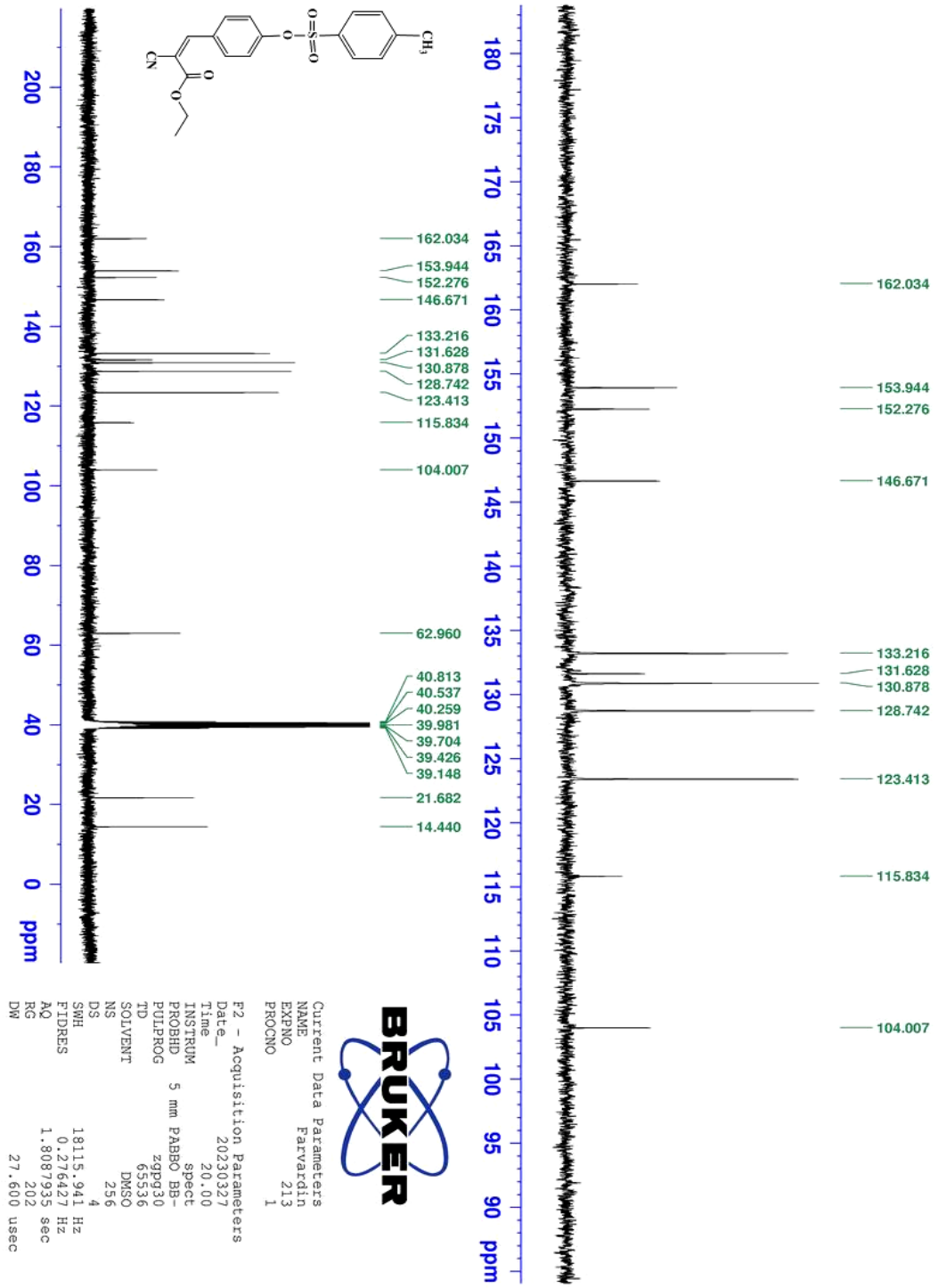

Figure S21 ^{13}CNMR spectrum of compound **3b**

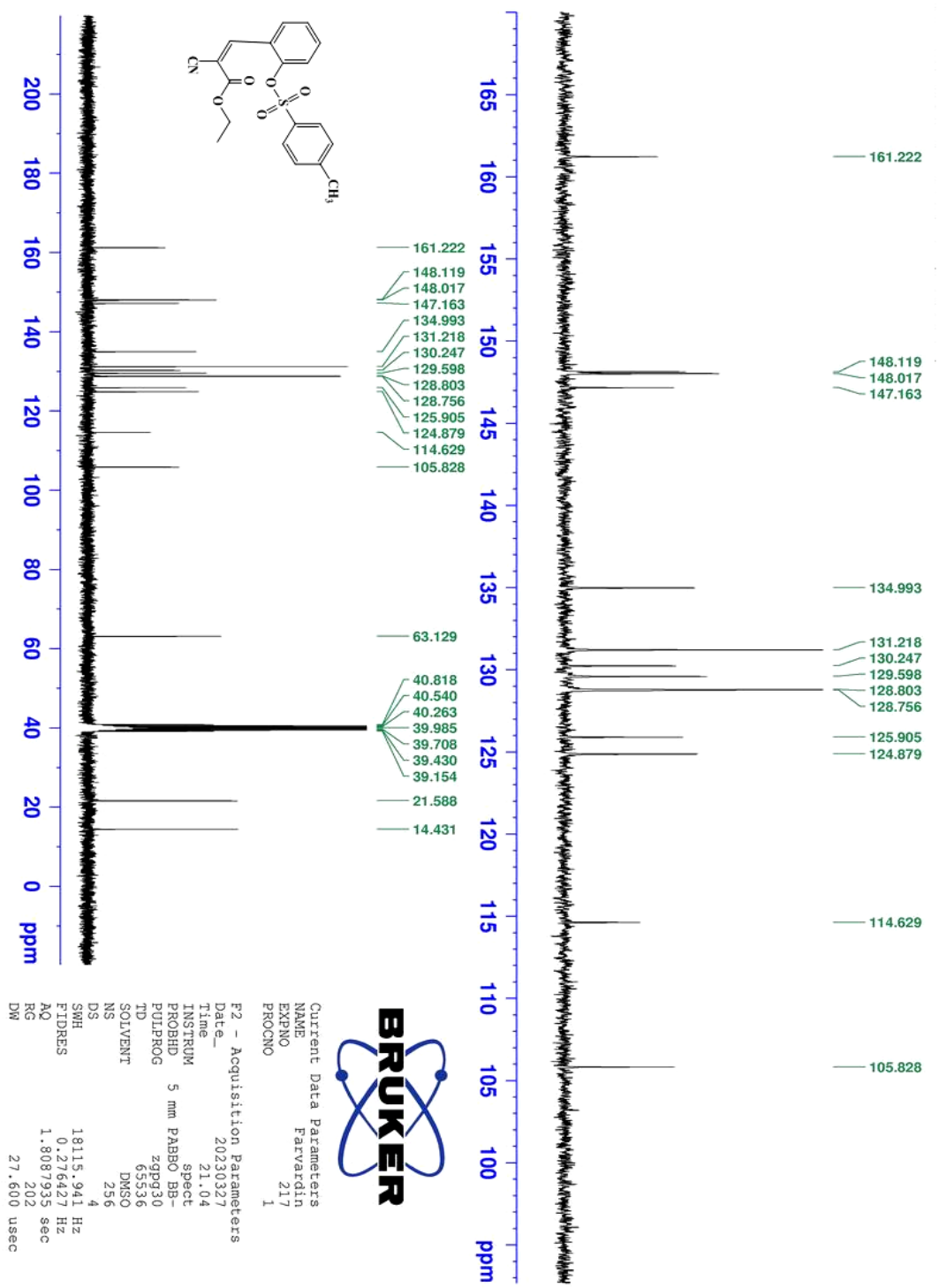

Figure S22 ^{13}CNMR spectrum of compound **3c**

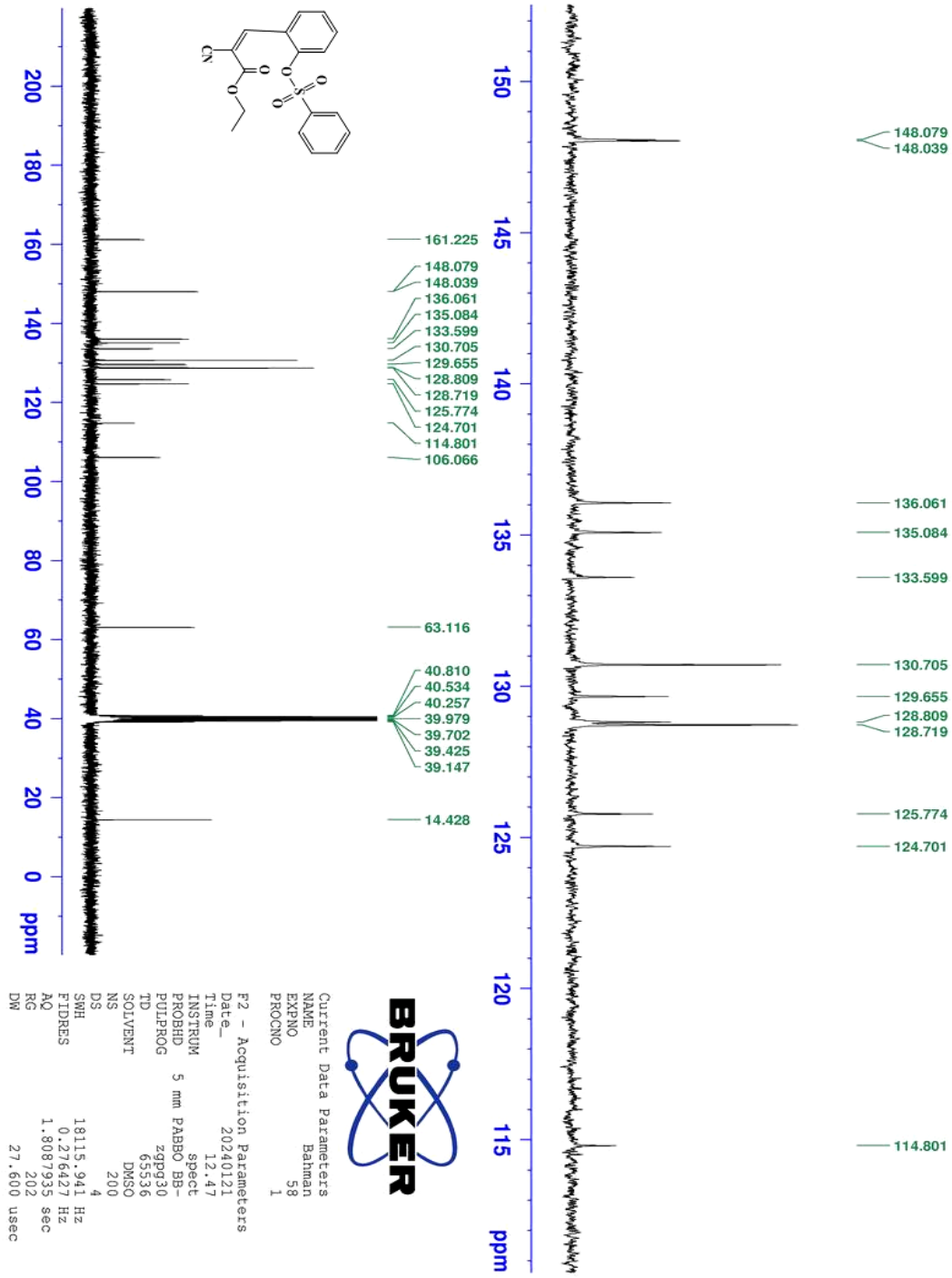

Figure S23 ^{13}CNMR spectrum of compound **3d**

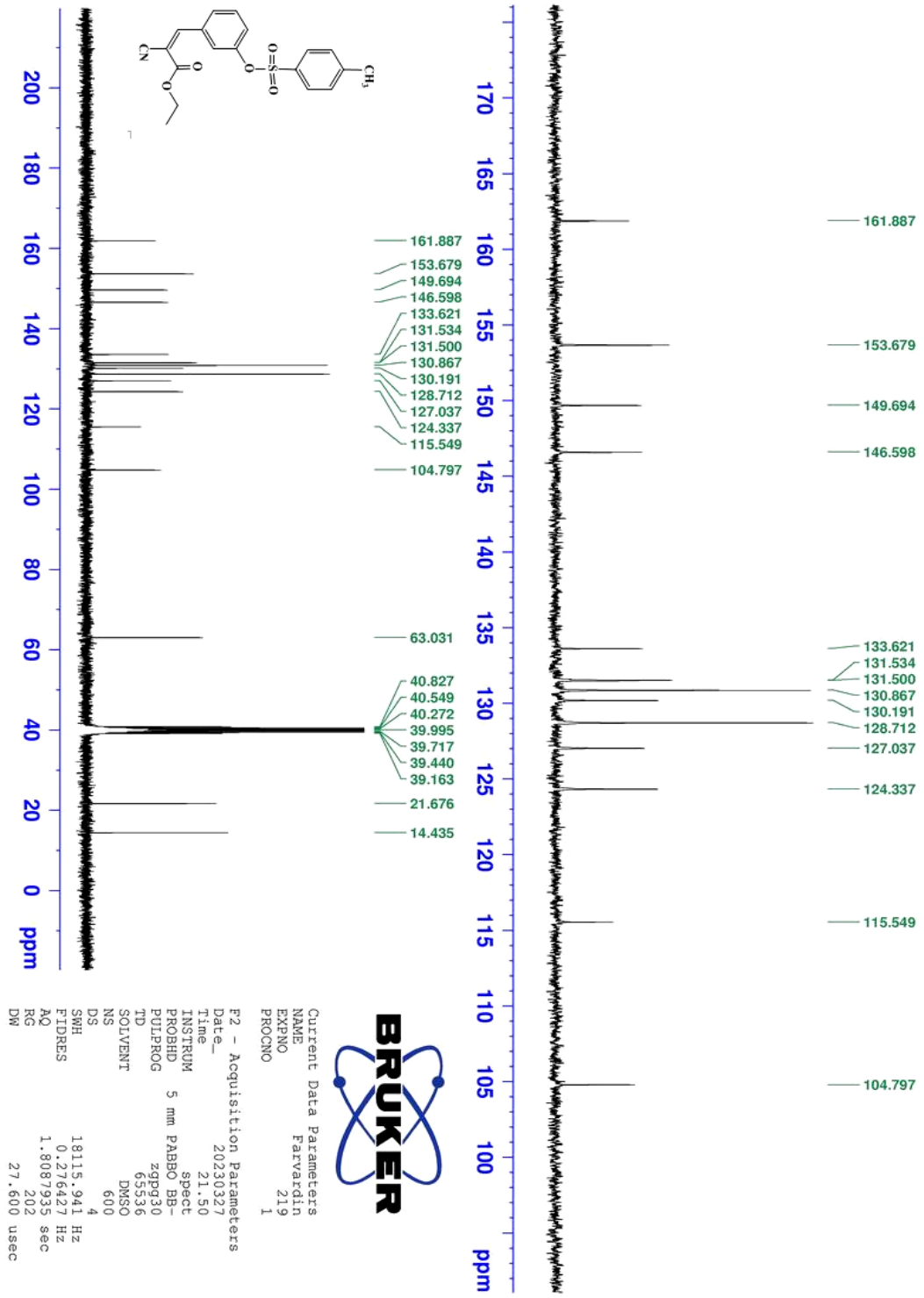

Figure S24 ^{13}CNMR spectrum of compound **3e**

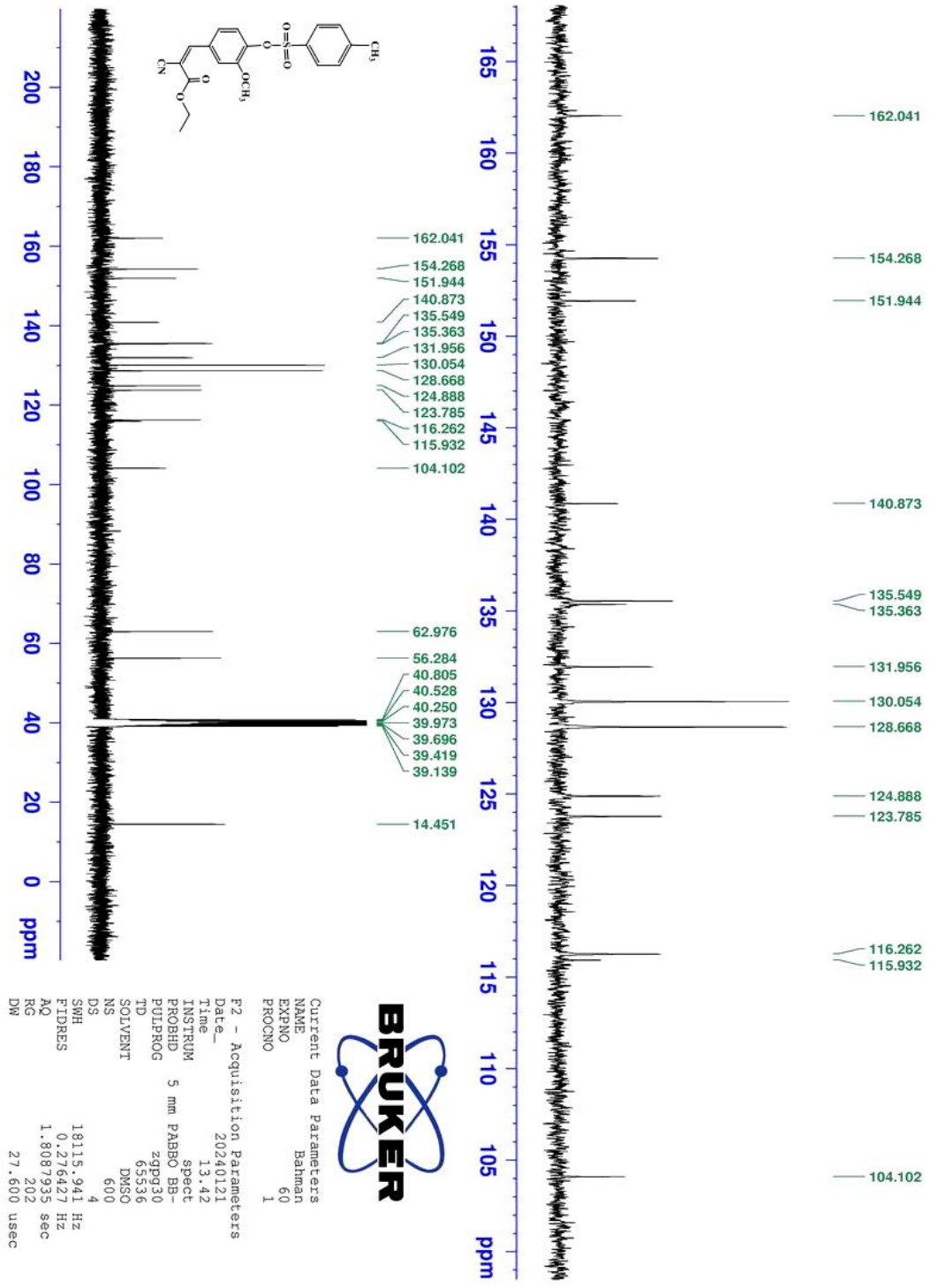

Figure S25 ^{13}CNMR spectrum of compound **3f**

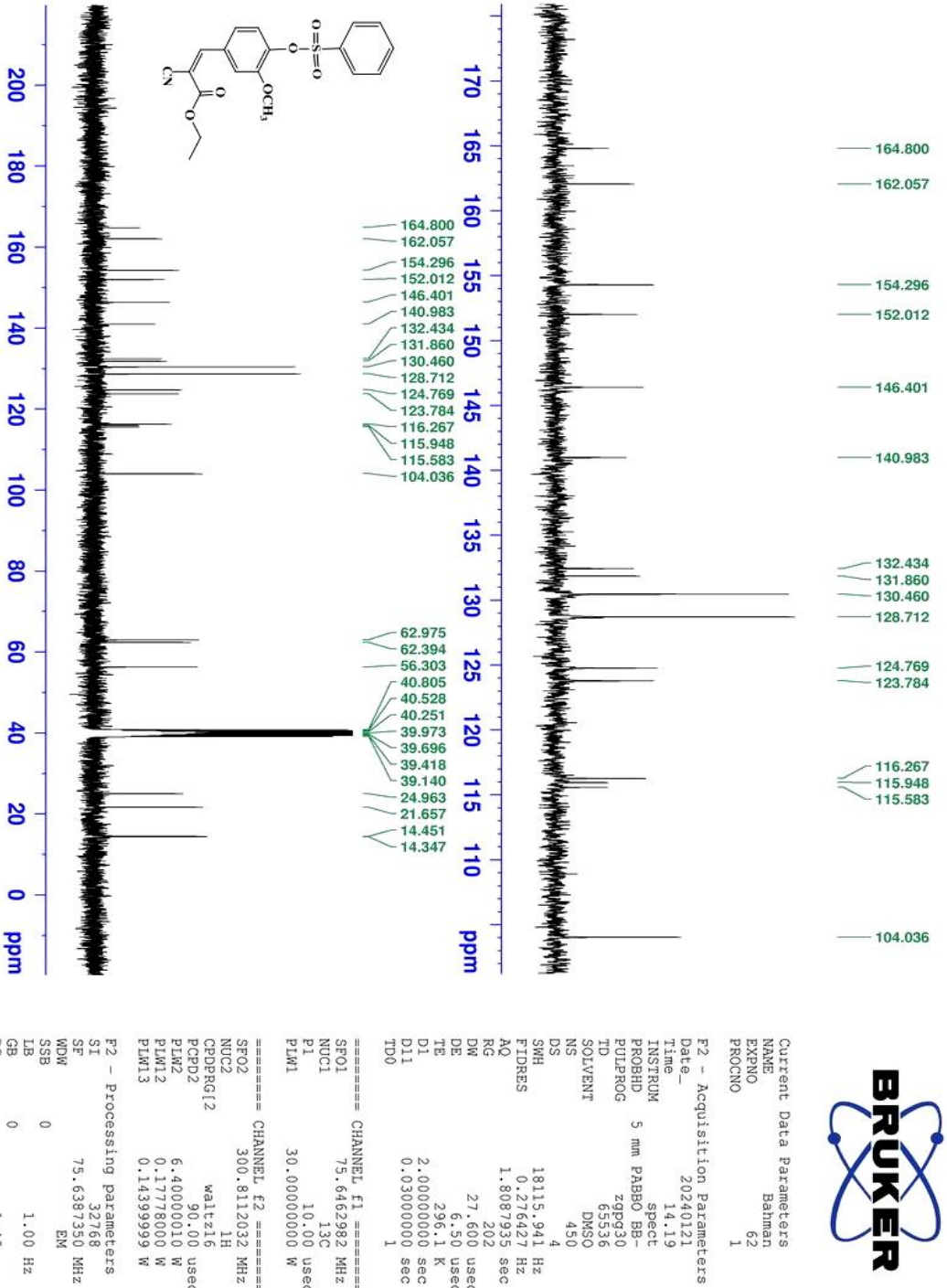

Figure S26 ^{13}CNMR spectrum of compound **3g**

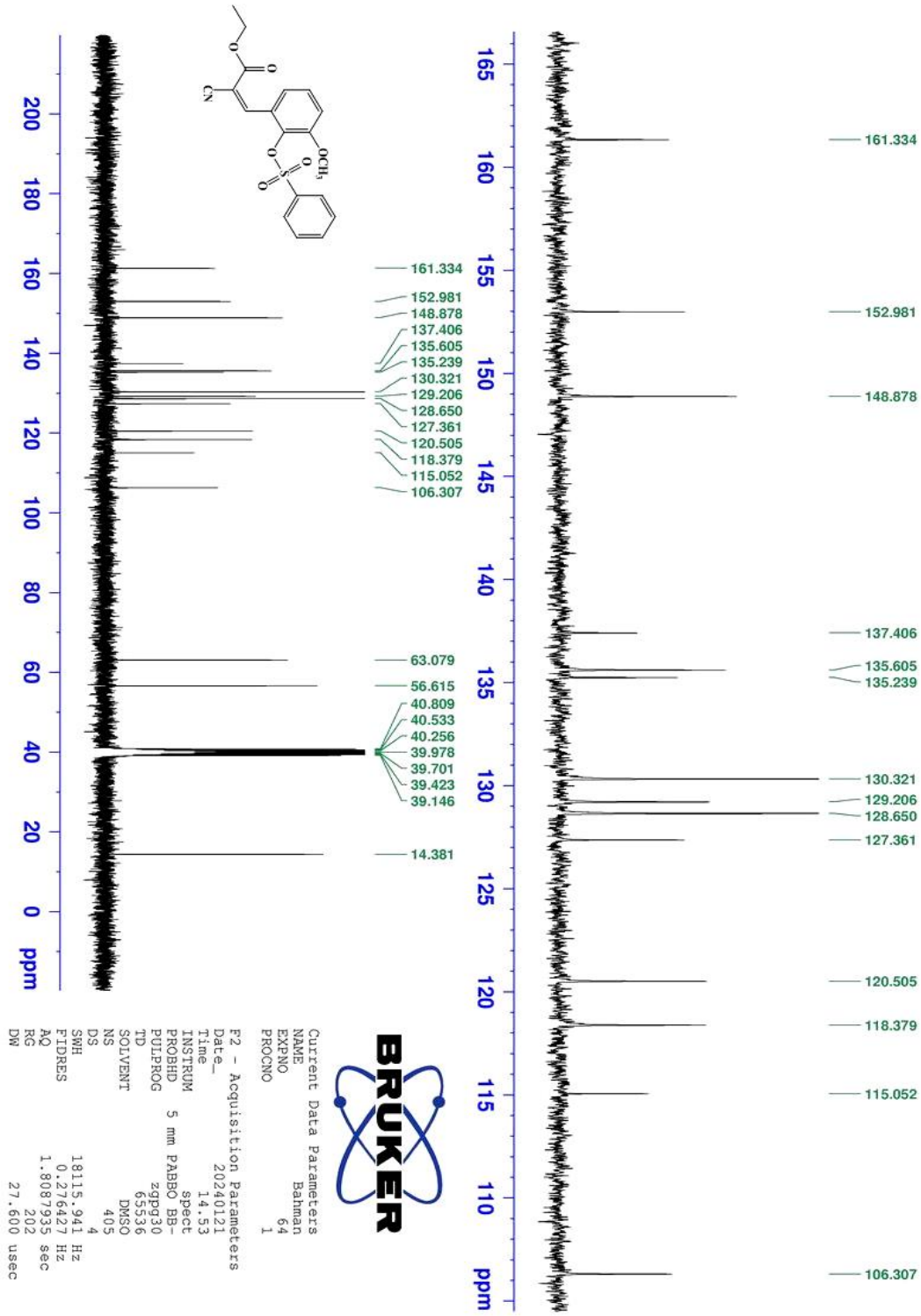

Figure S27 ^{13}CNMR spectrum of compound **3h**

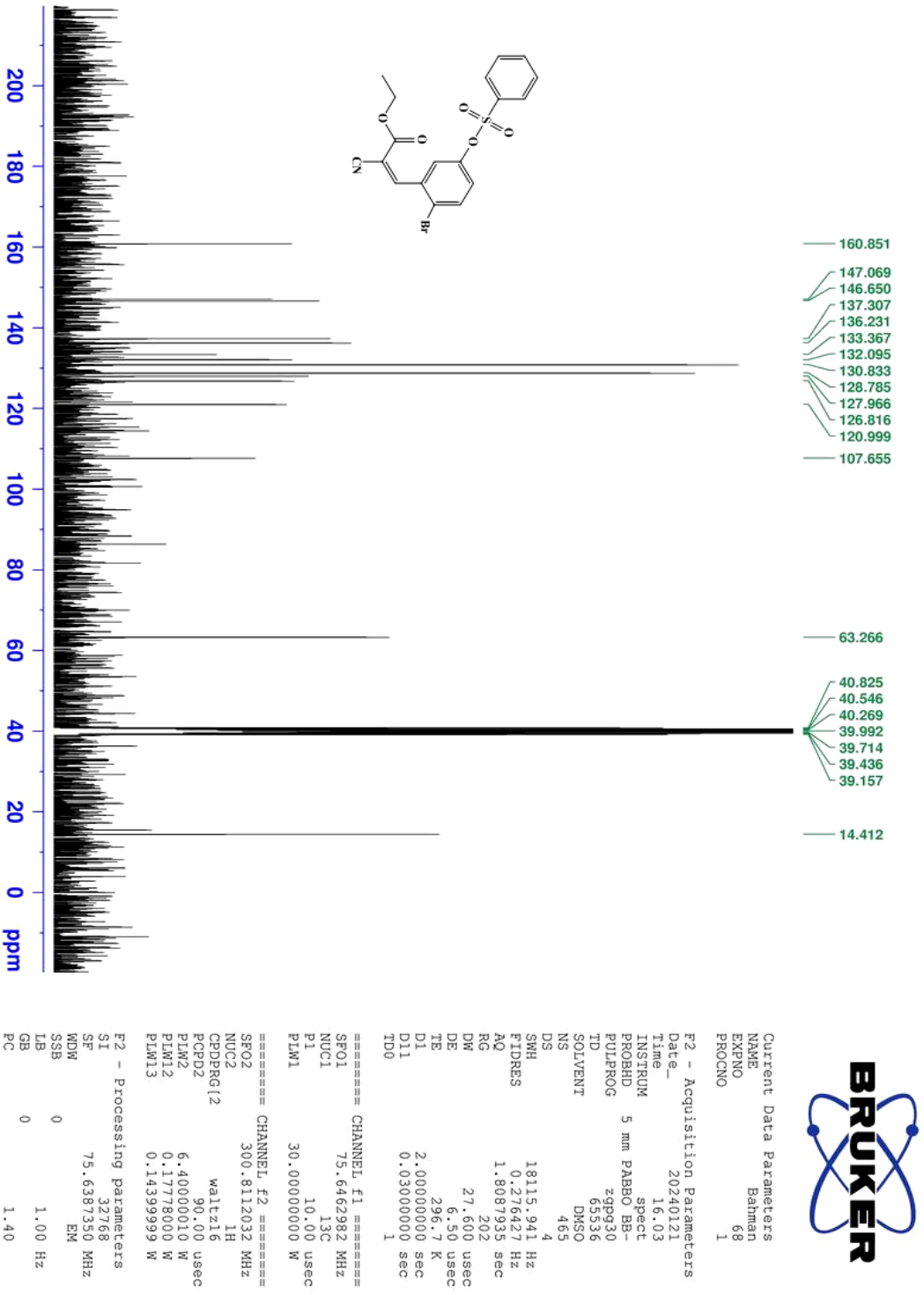

Figure S28 ^{13}CNMR spectrum of compound **3i**