Electronic Supplementary Information

Representative spectral data for:

Solvent-free mechanochemical synthesis of arylcyanomethylenequinone oximes from phenylacetonitriles and 4-unsubstituted nitroaromatic compounds using KF/nano-γ-Al_2O_3 as catalyst

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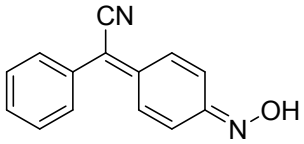
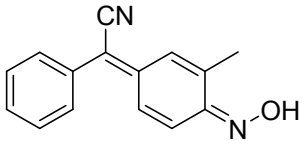


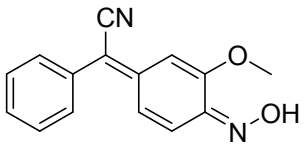
3a

***α*-[4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3a):** Yield: 1.84 g (83%). Orange powder, m.p.: 158.9-159.4 °C (Lit.,[S4] 160-161 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.85 (brs, 1H, =N-OH), 7.56-7.47 (m, 5H, ArH), 7.42-7.19 (m, 2H, ArH), 7.07-6.87 (m, 2H, ArH). IR (KBr), v (cm^{-1}): 3224.8, 3067.6, 3022.2, 2192.9, 1510.2, 1442.7, 1343.3, 992.3, 758.9, 698.2. m/z (EI$^-$): 221 (M-1, 100), 222 (14).



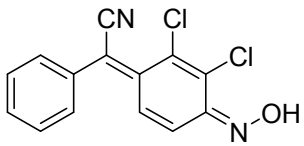
3b

***α*-[3-methyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3b)**: Yield: 2.01 g (85%). Orange powder, m.p.: 160.4-161.9 °C (Lit.,[S5] 161 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.76 (s, 1H, =N-OH), 7.55-7.46 (m, 5H, ArH), 7.40-7.27 (dd, J_1=J_2=10Hz, 1H, ArH), 7.24-6.80 (m, 2H, ArH), 2.13 (d, J=48.8Hz, 3H, CH_3). IR (KBr), v (cm^{-1}): 3267.2, 3157.3, 2924.8, 2199.7, 1558.4, 1514.0, 1440.7, 1000.0, 757.0, 740.6. m/z (EI$^-$): 235 (M-1, 100), 236 (7).



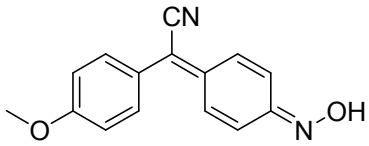
3c

***α*-[3-methoxyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3c)**: Yield: 2.17 g (86%). Orange powder, m.p.: 185.3-186.5 °C (Lit.,[S5] 186 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.81 (s, 1H, =N-OH), 7.59-7.44 (m, 5H, ArH), 7.37-7.23 (dd, J_1= J_2=10Hz, 1H, ArH), 7.17-6.84 (m, 1H, ArH), 6.42-6.29 (dd, J_1=1.6Hz, J_2=1.2Hz, 1H, ArH), 3.78 (d, J=76Hz, 3H, OCH_3). IR (KBr), v (cm^{-1}): 3145.7, 3058.9, 2982.7, 2338.5, 2193.9, 1613.3, 1556.4, 1416.6, 1213.1, 1010.6, 837.0, 693.4. m/z (EI$^-$): 251 (M-1, 100), 252 (7).



3d

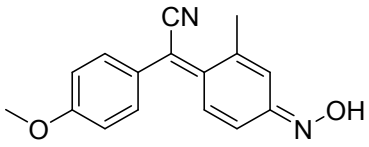
***α*-[2,3-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3d)**: Yield: 2.27 g (78%). Yellow powder, m.p.: 167.9-168.8 °C (Lit.,[S5] 168 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.52 (s, 1H, =N-OH), 7.57-7.42 (m, 5H, ArH), 7.22 (d, J=10.4Hz, 1H, ArH), 6.77 (d, J=10.4Hz, 1H, ArH). IR (KBr), v (cm^{-1}): 3193.9, 3029.0, 2197.7, 1562.2, 1506.3, 1489.9, 1396.4, 1331.8, 1034.7, 820.7, 697.2. m/z (EI$^-$): 289 (M-1, 100), 291 (71), 293 (18).



3e

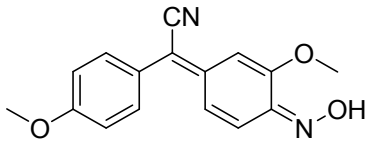
4-methoxyl-*α*-[4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3e): Yield: 2.25 g (89%). Yellow powder, m.p.: 162.7-164.1 °C (Lit.,[S4] 161 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.68 (brs, 1H, =N-

OH), 6.85-7.49 (m, 8H, ArH), 3.83 (s, 3H, OCH_3). IR (KBr), *v* (cm^{-1}): 3252.0, 2964.6, 2198.9, 1597.1, 1508.3, 1257.6, 1180.4, 979.8, 842.9. m/z (EI^-): 251 (M-1, 100), 252 (8).



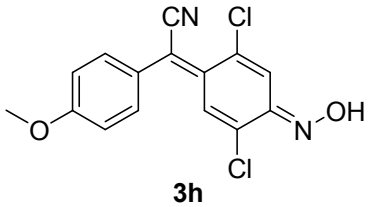
3f

4-methoxyl-*α*-[2-methyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3f): Yield: 2.02 g (76%). Yellow powder, m.p.: 172.9-174.0 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.52 (s, 1H, =N-OH), 7.39-7.32 (m, 2H, ArH), 7.17-7.01 (m, 3H, ArH), 6.89-6.65 (m, 2H, ArH), 3.83 (s, 3H, OCH_3), 2.55 (d, J=16Hz, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 160.42, 150.58, 142.85, 137.66, 134.27, 131.87, 130.89, 128.93, 128.05, 121.55, 119.98, 117.71, 115.03, 109.44, 55.87, 23.09. IR (KBr), *v* (cm^{-1}): 3244.3, 3076.5, 2966.5, 2189.2, 1602.9, 1573.9, 1510.3, 1269.2, 1180.4, 827.5. HRMS (ESI) calcd for $C_{16}H_{14}N_2O_2$+H^+: 267.2798 found 267.2801.



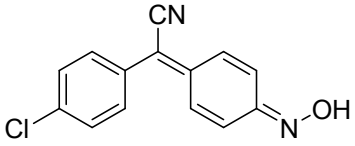
3g

4-methoxyl-*α*-[3-methoxyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3g): Yield: 2.60 g (92%). Orange powder, m.p.: 192.5-193.9 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.73 (s, 1H, =N-OH), 7.53 (d, J=8Hz, 1H, ArH), 7.39 (d, J=8Hz, 1H, ArH), 7.33-7.22 (dd, J_1= J_2=10Hz, 1H, ArH), 7.14-6.86 (m, 3H, ArH), 3.83 (s, 3H, OCH_3), 3.78 (d, J=62.8Hz, 3H, OCH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 160.32, 155.75, 145.72, 142.30, 131.65, 131.40, 127.95, 125.66, 120.00, 119.06, 115.15, 107.86, 101.82, 99.82, 55.84, 55.63. IR (KBr), *v* (cm^{-1}): 3424.4, 3218.0, 3148.6, 2363.6, 2193.9, 1613.3, 1557.4, 1507.3, 1254.6, 1015.5, 835.1. HRMS (ESI) calcd for $C_{16}H_{14}N_2O_3$+H^+: 283.2788 found 283.2792.



3h

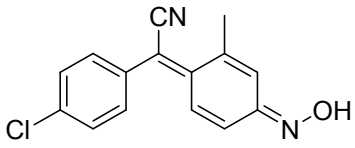
4-methoxyl-*α*-[2,5-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene] benzeneacetonitrile (3h): Yield: 2.41 g (75%). Orange powder, m.p.: 169.0-171.4 °C (Lit.,[S5] 178 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.56 (s, 1H, =N-OH), 7.48-7.35 (m, 3H, ArH), 7.12-7.01 (dd, J_1= J_2=8.8Hz, 2H, ArH), 6.90 (s, 1H, ArH), 3.85 (s, 3H, OCH_3). IR (KBr), *v* (cm^{-1}): 3184.5, 3066.8, 2968.5, 2200.8, 1600.9, 1537.3, 1506.4, 1259.5, 1028.1, 835.2, 752.2. m/z (EI^-): 319 (M-1, 100), 321 (69), 323 (11).



3i

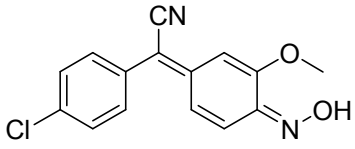
4-chloro-*α*-[4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3i): Yield: 2.31 g (90%). Yellow powder, m.p.: 188.1-189.6 °C (Lit.,[S4] 188-189 °C). ^{1}H NMR

(DMSO-d_6, 400 MHz), δ (ppm): 12.88 (s, 1H, =N-OH), 7.62-6.88 (m, 8H, ArH). IR (KBr), v (cm^{-1}): 3182.6, 2200.8, 1541.1, 1519.9, 1398.4, 1093.6, 1008.8, 829.4. m/z (EI^-): 255 (M-1, 100), 257 (31).



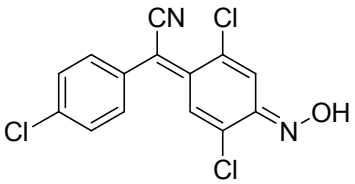
3j

4-chloro-α-[2-methyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3j): Yield: 1.92 g (71%). Light yellow powder, m.p.: 179.2-180.3 °C (Lit.,[S5] 173 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.63 (d, J=24 Hz, 1H, =N-OH), 7.46-7.61 (m, 4H, ArH), 7.10-7.37 (m, 1H, ArH), 6.63-6.82 (m, 2H, ArH), 2.58-2.54 (dd, J_1= J_2=1.2Hz, 2H, CH_3), 1.57-1.53 (dd, J_1= J_2=0.8Hz, 1H, CH_3). IR (KBr), v (cm^{-1}): 3159.4, 3039.8, 2883.6, 2195.0, 1587.4, 1558.5, 1491.0, 1398.4, 1006.8, 829.4, 765.7. m/z (EI^-): 269 (M-1, 100), 271 (28).



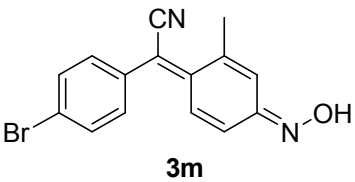
3k

4-chloro-α-[3-methoxyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3k): Yield: 2.44 g (85%). Light yellow powder, m.p.: 202.3-204.4 °C (Lit.,[S5] 205 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.88 (brs, 1H, =N-OH), 7.62-7.56 (m, 3H, ArH), 7.47 (d, J=8.4 Hz, 1H, ArH), 7.37 (d, J=10 Hz, 1H, ArH), 7.23 (d, J=10.4 Hz, 1H, ArH), 7.16-6.82 (m, 1H, ArH), 6.4-6.25 (dd, J_1=J_2=1.6Hz, 1H, ArH), 3.79 (d, J=66.8Hz, 3H, OCH_3). IR (KBr), v (cm^{-1}): 3219.2, 3076.5, 2920.2, 2197.0, 1612.5, 1560.4, 1450.3, 1421.5, 1213.2, 1014.6, 835.2. m/z (EI^-): 285 (M-1, 100), 287 (27).



3l

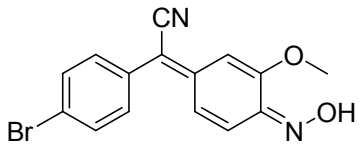
4-chloro-α-[2,5-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3l): Yield: 2.64 g (81%). Light yellow powder, m.p.: 182.6-183.1 °C (Lit.,[S5] 184 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.73 (d, J=8.8Hz, 1H, =N-OH), 7.63-7.36 (m, 5H, ArH), 6.80 (s, 1H, ArH). IR (KBr), v (cm^{-1}): 3200.0, 3080.3, 2197.0, 1579.7, 1537.3, 1055.1, 1037.7, 833.3, 765.7. m/z (EI^-): 323 (93), 325 (M, 100), 327 (25).



3m

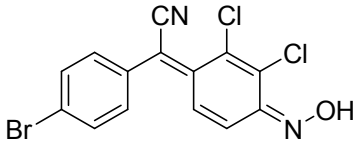
4-bromo-α-[2-methyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3m): Yield: 2.71 g (86%). Yellow powder, m.p.: 166.3-167.3 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.66 (d, J=22.8Hz, 1H, =N-OH), 7.73-7.66 (m, 2H, ArH), 7.41-7.09 (m, 3H, ArH), 6.95-6.62 (m, 2H, ArH), 2.55 (d, J=15.6Hz, 2H, CH_3), 1.55 (d, J=14.8Hz, 1H, CH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 143.90,

137.54, 135.17, 132.61, 132.50, 132.42, 130.42, 127.38, 123.26, 121.08, 120.33, 118.20, 108.15, 23.00, 22.26. IR (KBr), v (cm^{-1}): 3249.8, 3088.8, 2198.7, 1581.5, 1558.4, 1395.4, 1077.2, 1001.0, 818.7, 788.8. HRMS (ESI) calcd for $C_{15}H_{11}BrN_2O+H^+$: 316.0136 found 316.0139.



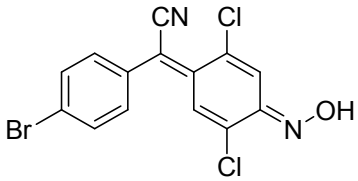
3n

4-bromo-α-[3-methoxyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3n): Yield: 2.65 g (80%). Orange powder, m.p.: 205.6-207.4 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.88 (s, 1H, =N-OH), 7.73-7.70 (m, 2H, ArH), 7.54 (d, J=8.4Hz, 1H, ArH), 7.40 (d, J=8.4Hz, 1H, ArH), 7.37-7.24 (dd, J_1=J_2=10 Hz, 1H, ArH), 7.15-6.82 (m, 1H, ArH), 6.40-6.25 (dd, J_1=J_2=1.6 Hz, 1H, ArH), 3.79 (d, J=65.6 Hz, 3H, OCH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 156.33, 145.69, 143.84, 132.67, 132.55, 132.21, 131.92, 127.80, 125.34, 123.02, 119.60, 106.46, 101.66, 99.46, 55.80. IR (KBr), v (cm^{-1}): 3212.2, 3075.3, 2195.8, 1612.4, 1582.5, 1419.5, 1212.2, 1013.5, 837.0, 802.3, 733.9. HRMS (ESI) calcd for $C_{15}H_{11}BrN_2O_2+H^+$: 332.0126 found 332.0128.



3o

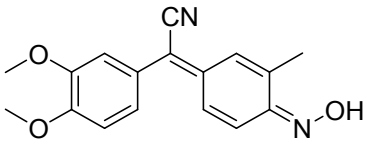
4-bromo-α-[2,3-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3o): Yield: 2.59 g (70%). Orange powder, m.p.: 182.1-184.3 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.63 (brs, 1H, =N-OH), 7.76-7.66 (m, 2H, ArH), 7.47-7.40 (m, 2H, ArH), 7.19 (d, J=10Hz, 1H, ArH), 6.75 (d, J=10.4Hz, 1H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 148.21, 139.88, 135.11, 134.80, 132.73, 132.59, 132.39, 131.95, 128.83, 128.64, 124.13, 119.50, 118.03, 111.58. IR (KBr), v (cm^{-1}): 3191.4, 3137.4, 2197.0, 1579.8, 1507.4, 1484.3, 1391.7, 1080.2, 1040.6, 1007.9, 870.9, 824.6, 758.1. HRMS (ESI) calcd for $C_{14}H_7BrCl_2N_2O+H^+$: 369.9106 found 369.9111.



3p

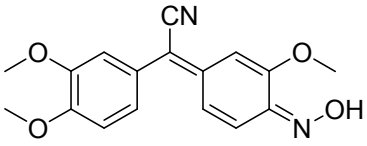
4-bromo-α-[2,5-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3p): Yield: 2.78 g (75%). Orange powder, m.p.: 181.6-183.5 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.76 (s, 1H, =N-OH), 7.75 (d, J=8.4Hz, 2H, ArH), 7.47 (d, J=8Hz, 3H, ArH), 6.81 (s, 1H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 146.42, 139.16, 134.33, 132.85, 132.79, 132.74, 132.46, 132.42, 131.92, 126.88, 124.40, 121.14, 119.01, 111.27. IR (KBr), v (cm^{-1}): 3197.2, 3082.4, 2197.0, 1576.9, 1539.3, 1479.5, 1279.8, 1054.1, 1037.8, 950.0, 890.2, 829.4, 762.9. HRMS (ESI) calcd

for $C_{14}H_7BrCl_2N_2O+H^+$: 369.9106 found 369.9113.



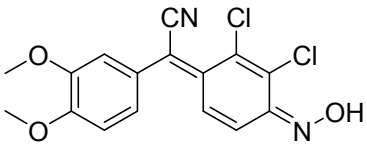
3q

3,4-dimethoxyl-*α*-[3-methyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3q): Yield: 2.58 g (87%). Orange powder, m.p.: 181.2-182.0 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.64 (s, 1H, =N-OH), 7.37-6.89 (m, 6H, ArH), 3.82 (d, J=3.2Hz, 3H, OCH_3), 3.80 (d, J=2Hz, 3H, OCH_3), 2.13 (d, J=37.6Hz, 1H, CH_3). ^{13}C NMR(DMSO-d_6, 100 MHz), δ (ppm): 150.86, 150.33, 149.31, 141.57, 138.85, 129.58, 127.42, 126.09, 125.61, 123.16, 119.45, 113.17, 112.41, 109.98. IR (KBr), v (cm^{-1}): 3248.1, 3014.7, 2935.7, 2197.0, 1595.1, 1518.0, 1261.5, 1143.8, 989.5, 852.5, 806.3. HRMS (ESI) calcd for $C_{17}H_{16}N_2O_3$+Na^+: 319.2643 found 319.2637.



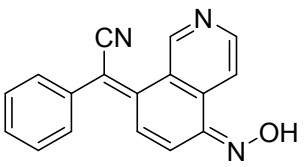
3r

3,4-dimethoxyl-*α*-[3-methoxyl-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3r): Yield: 2.75 g (88%). Orange powder, m.p.: 187.4-187.7 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.71 (s, 1H, =N-OH), 7.32-7.21 (dd, J_1= J_2=10Hz, 1H, ArH), 7.15-7.05 (m, 3H, ArH), 6.99-6.92 (m, 1H, ArH), 6.39 (s, 1H, ArH), 3.85-3.71 (m, 9H, OCH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 155.72, 150.12, 145.74, 142.34, 127.96, 125.85, 122.94, 119.00, 112.36, 108.10, 101.84, 100.09, 56.19, 56.08, 56.05, 55.76, 55.67. IR (KBr), v (cm^{-1}): 3142.0, 3010.9, 2935.7, 2189.2, 1593.2, 1556.6, 1514.1, 1460.1, 1423.5, 1257.6, 1219.0, 995.3, 862.2, 814.0. HRMS (ESI) calcd for $C_{17}H_{16}N_2O_4$+Na^+: 335.2633 found 335.2628.



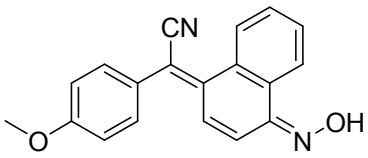
3s

3,4-dimethoxyl-*α*-[2,3-dichloro-4-(hydroxyimino)-2,5-cyclohexadien-1-ylidene]benzeneacetonitrile (3s): Yield: 2.49 g (71%). Deep red powder, m.p.: 196.9-198.5 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.41 (s, 1H, =N-OH), 7.39-7.04 (m, 4H, ArH), 6.90 (d, J=10.4Hz, 1H, ArH), 3.84 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 56.21, 112.48, 113.36, 113.84, 117.45, 119.82, 123.89, 127.86, 129.07, 129.55, 134.34, 138.84, 148.30, 149.34, 150.90. IR (KBr), v (cm^{-1}): 3120.6, 3021.3, 2942.2, 2190.0, 1597.9, 1572.8, 1514.2, 1444.6, 1266.2, 1075.2, 823.5, 725.2. HRMS (ESI) calcd for $C_{16}H_{12}Cl_2N_2O_3$+Na^+: 373.1829 found 373.1834.



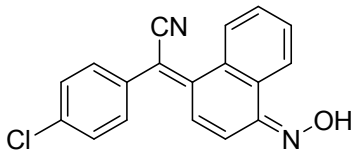
5a

***α*-[5-(hydroxyimino)-8-isoquinolyl]benzeneacetonitrile (5a)**: Yield: 1.91 g (70%). Brown powder, m.p.: 232.4-236.4 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 13.03 (s, 1H, =N-OH), 9.97-7.95 (m, 4H, ArH), 7.66-6.97 (m, 6H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 150.39, 149.36, 148.08, 146.09, 140.24, 138.17, 134.69, 131.87, 130.37, 129.78, 129.49, 124.30, 121.16, 119.16, 116.53, 112.20, 109.69. IR (KBr), ν (cm^{-1}): 3130.5, 2187.3, 1606.7, 1539.2, 1437.0, 1398.4, 991.4, 808.2, 700.2. HRMS (ESI) calcd for $C_{17}H_{11}N_3O+H^+$: 274.2733 found 274.2735.



5b

4-methoxyl-*α*-[4-(hydroxyimino)-1(4H)-naphthalenylidene] benzeneacetonitrile (5b): Yield: 2.15 g (71%). Yellow powder, m.p.: 191.9-194.2 °C (Lit.,[S5] 193-194 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.43 (d, J=8.8Hz, 1H, =N-OH), 8.78-8.80 (m, 1H, ArH), 8.12-8.27 (m, 1H, ArH), 7.63-7.66 (m, 1H, ArH), 7.30-7.50 (m, 4H, ArH), 7.00-7.19 (m, 3H, ArH), 3.83 (d, J=8.0Hz, 3H, OCH_3). IR (KBr), ν (cm^{-1}): 3244.3, 2916.4, 2193.1, 1604.8, 1508.3, 1261.5, 1174.7, 960.6, 823.6, 760.1. m/z (EI$^-$): 301 (M-1, 100), 302 (10).

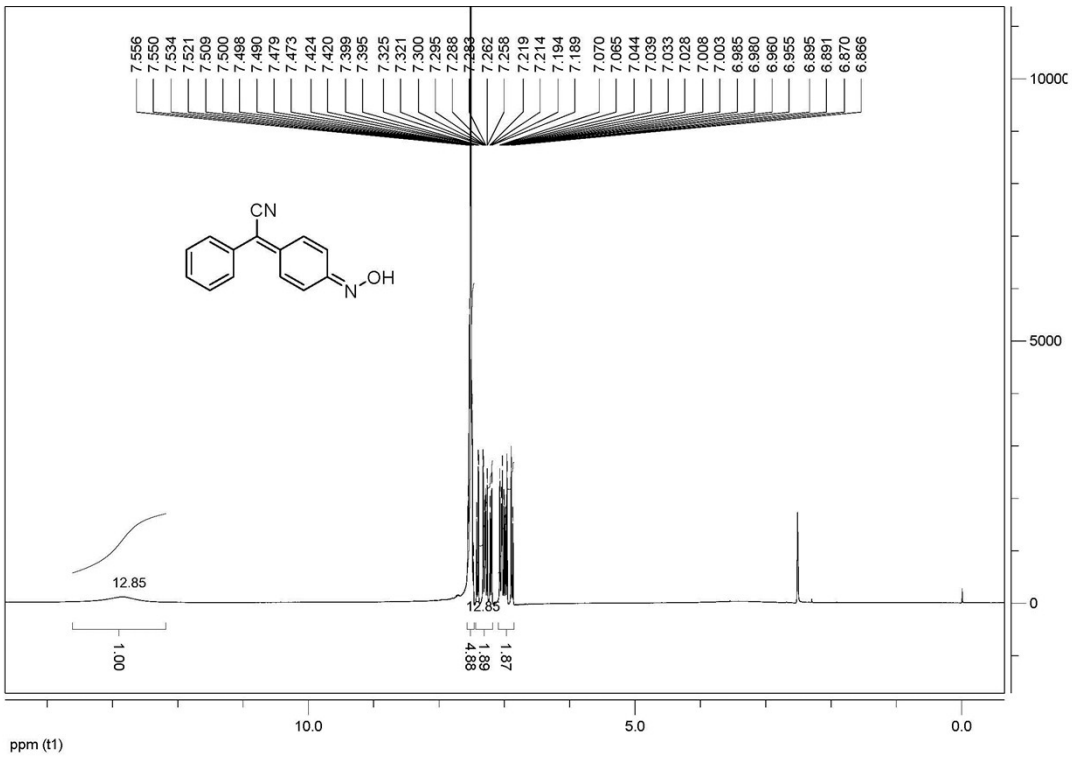


5c

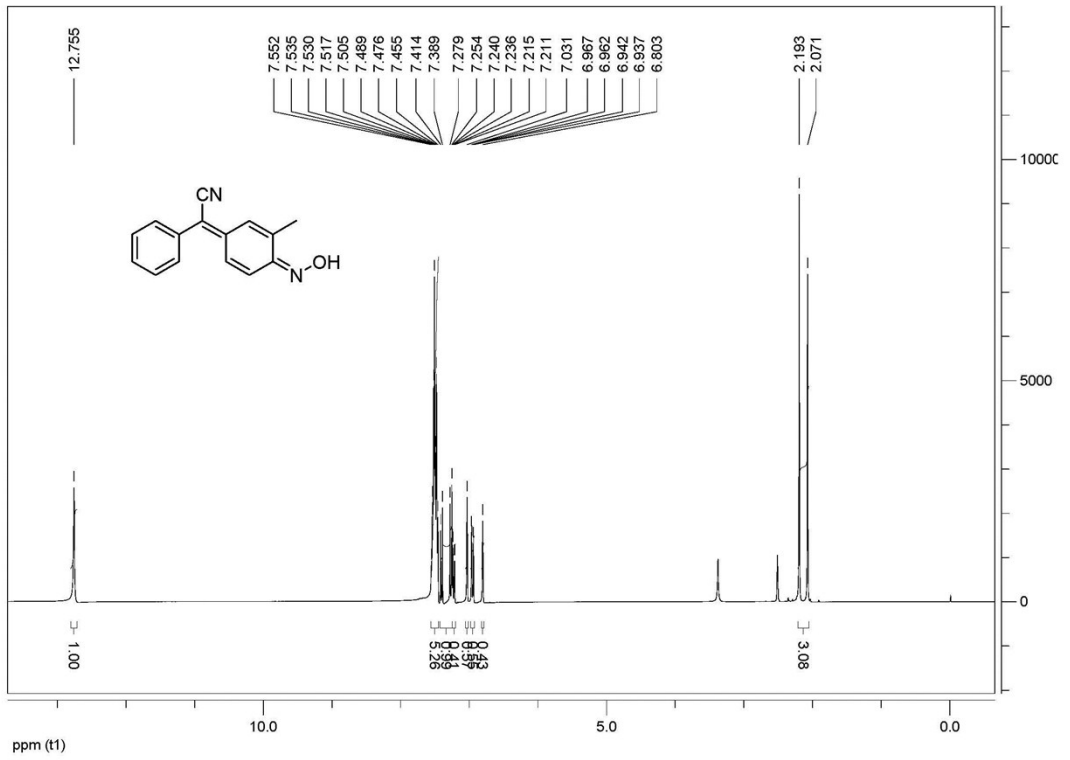
4-chloro-*α*-[4-(hydroxyimino)-1(4H)-naphthalenylidene] benzeneacetonitrile (5c): Yield: 2.48 g (75%). Light yellow powder, m.p.: 195.3-197.6 °C (Lit.,[S5] 195-196 °C). ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 12.54 (d, J=12.4Hz, 1H, =N-OH), 8.81-8.79 (m, 1H, ArH), 8.28-8.14 (m, 1H, ArH), 7.68-6.92 (m, 8H, ArH). IR (KBr), ν (cm^{-1}): 3240.4, 3009.0, 2193.1, 1587.4, 1506.4, 1487.1, 1398.4, 1091.7, 958.6, 825.5, 754.2. m/z (EI$^-$): 305 (M-1, 100), 307 (27).

2. The NMR spectra of products (3a to 3s, 5a to 5c)

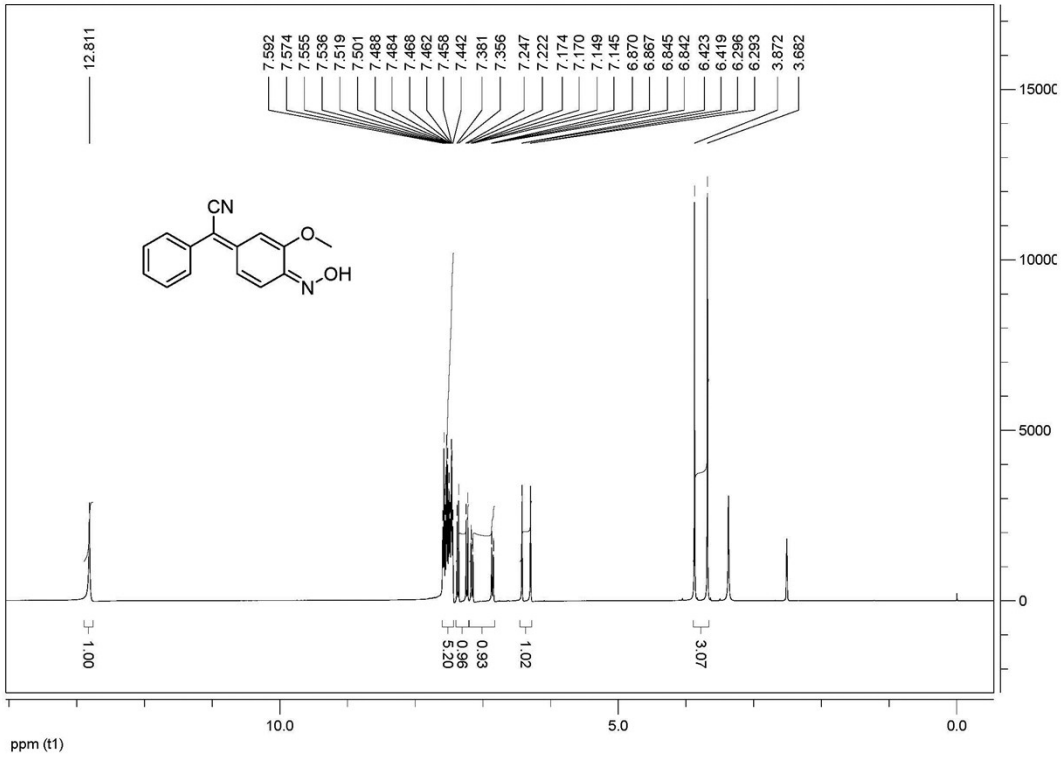
3a ^{1}H NMR(400MHz, d_6-DMSO)



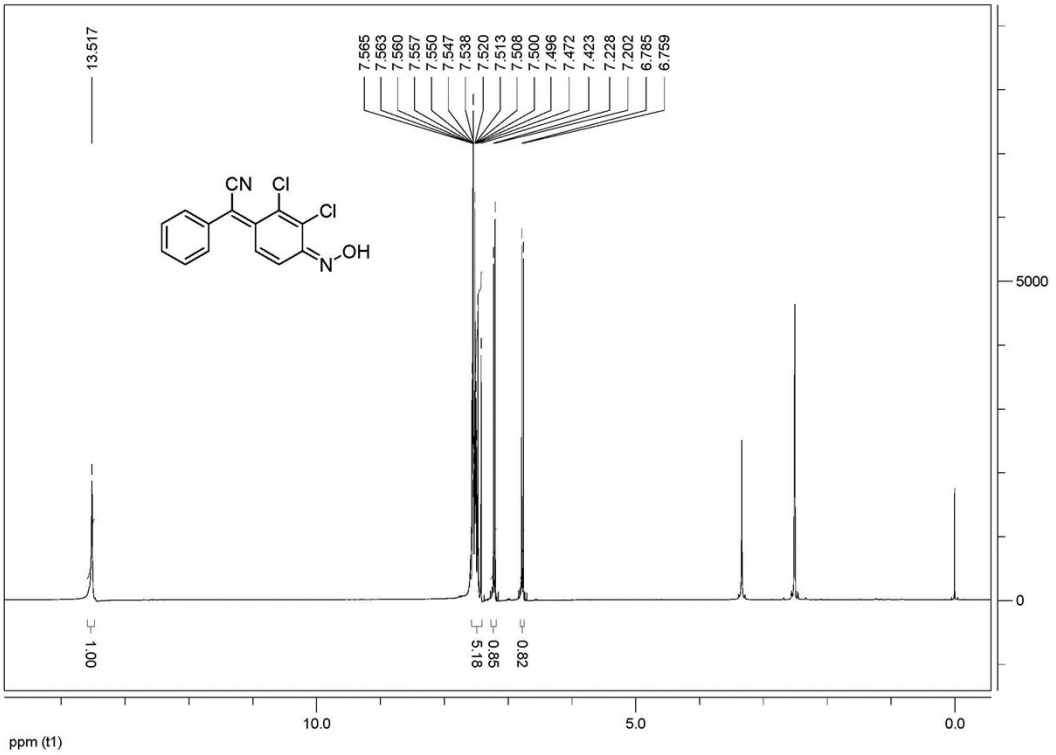
3b ^{1}H NMR(400MHz, d_6-DMSO)



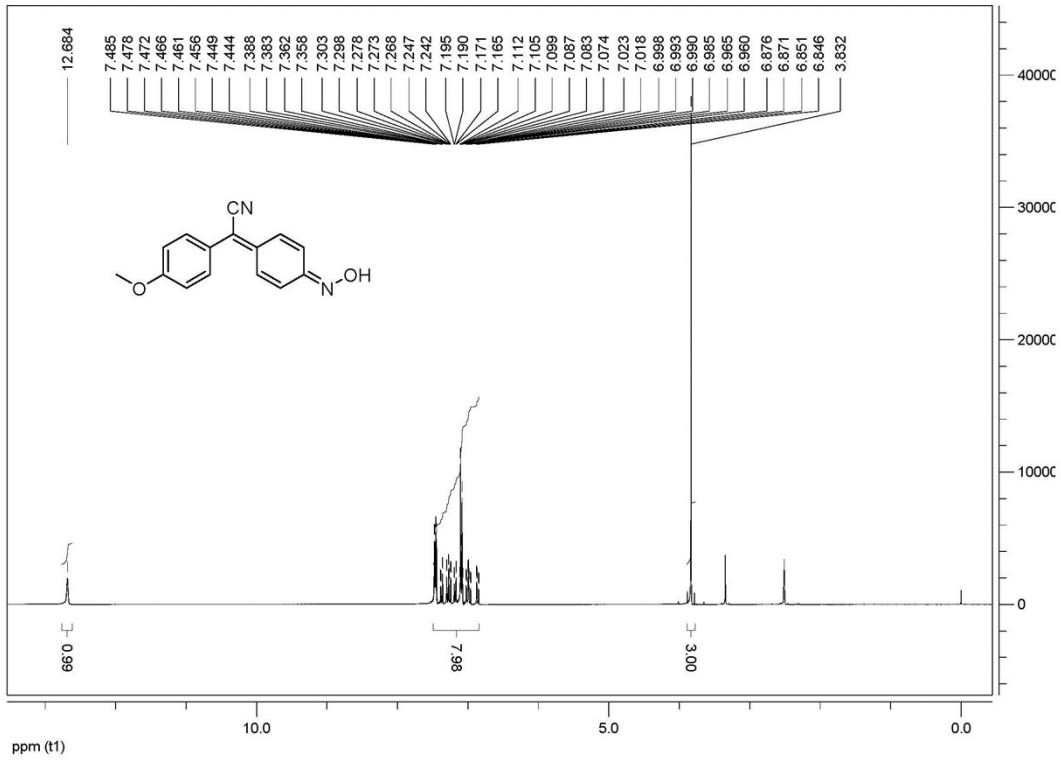
3c ^{1}H NMR(400MHz, d_6-DMSO)



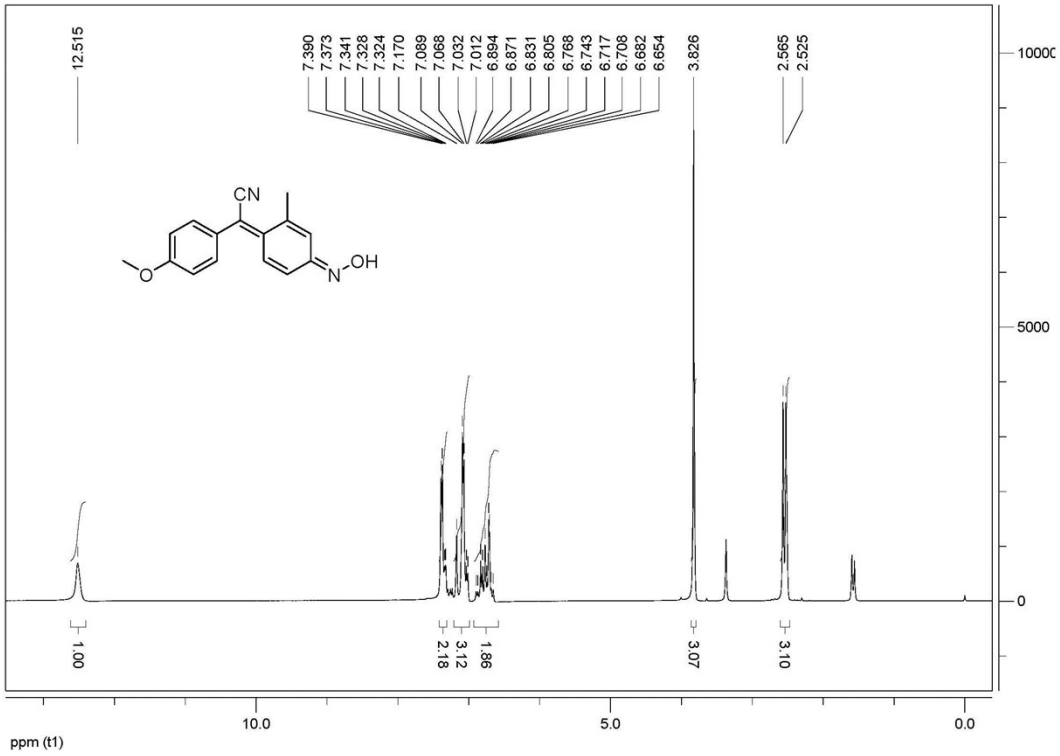
3d ^{1}H NMR(400MHz, d_6-DMSO)



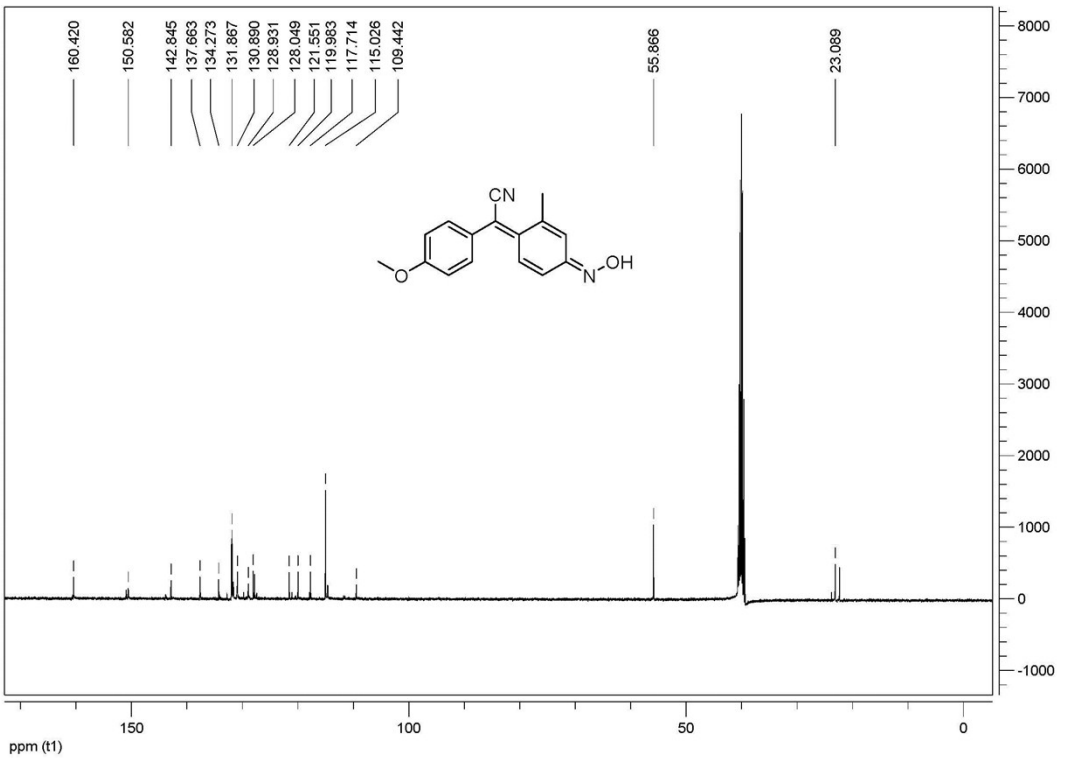
3e ^{1}H NMR(400MHz, d_6-DMSO)



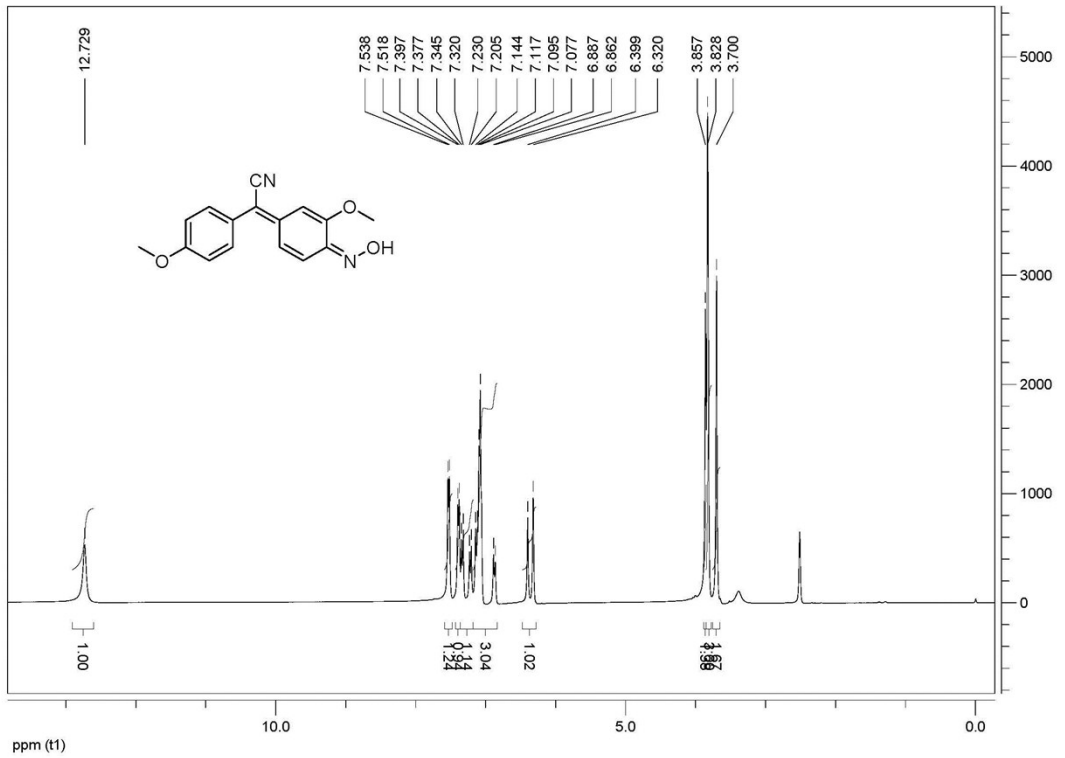
3f ^{1}H NMR(400MHz, d_6-DMSO)



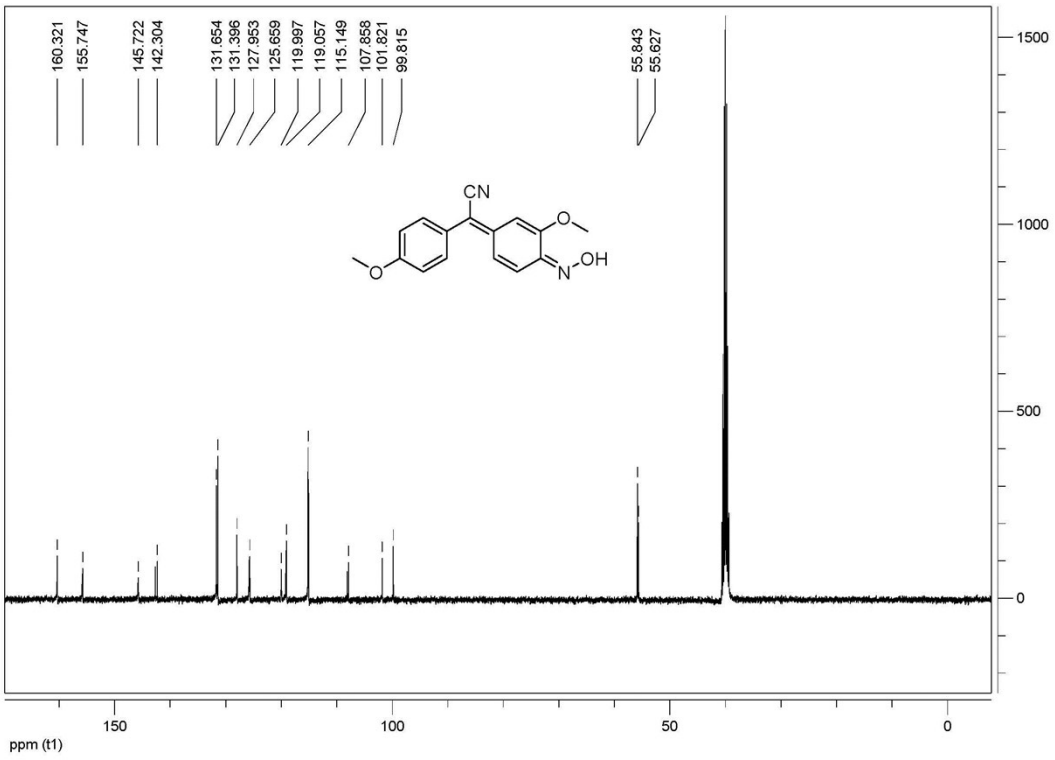
3f ^{13}C NMR(100MHz, d_6-DMSO)



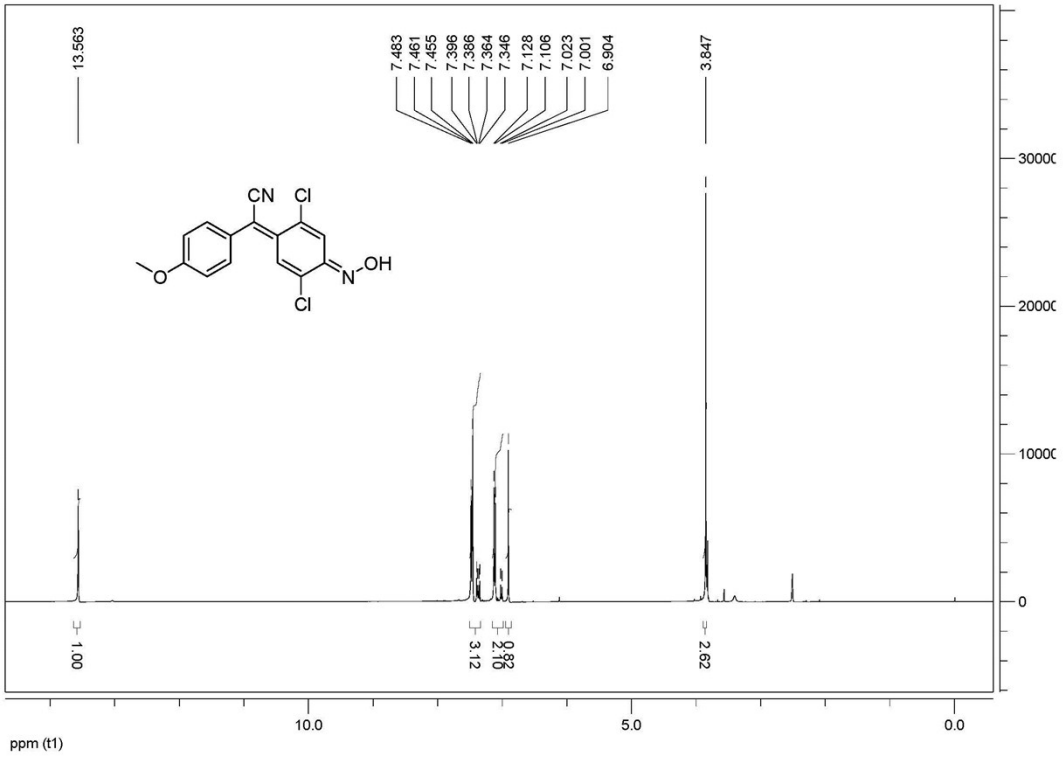
3g ^{1}H NMR(400MHz, d_6-DMSO)



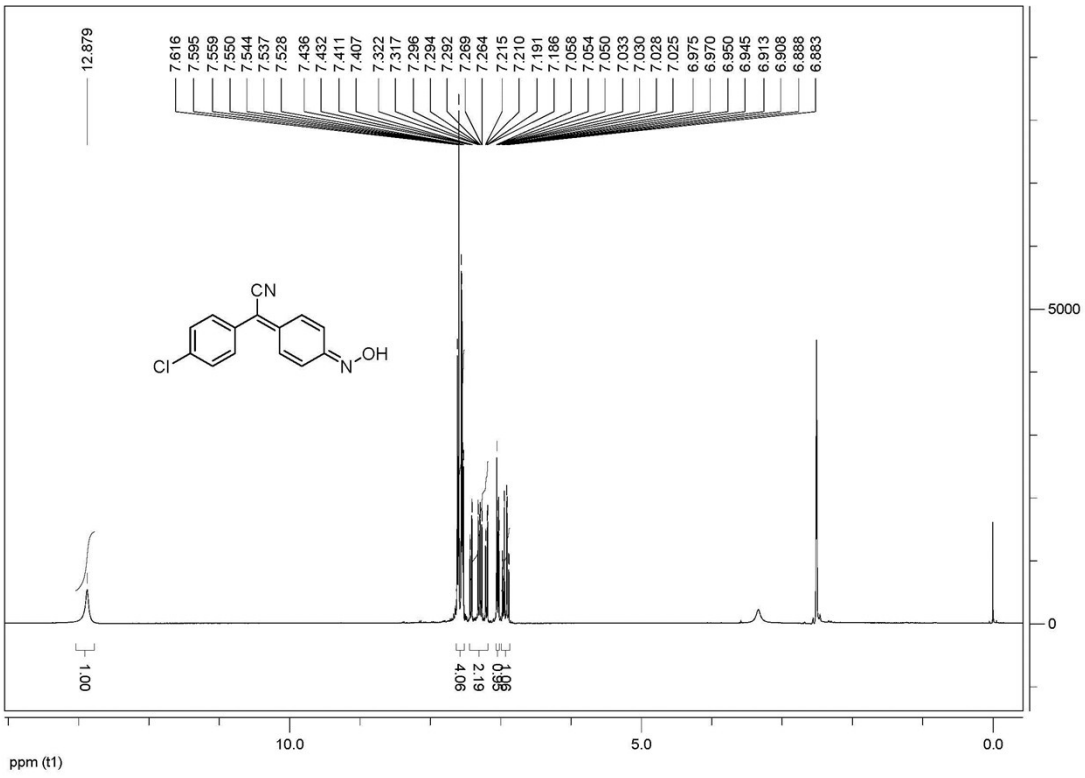
3g ^{13}C NMR(100MHz, d_6-DMSO)



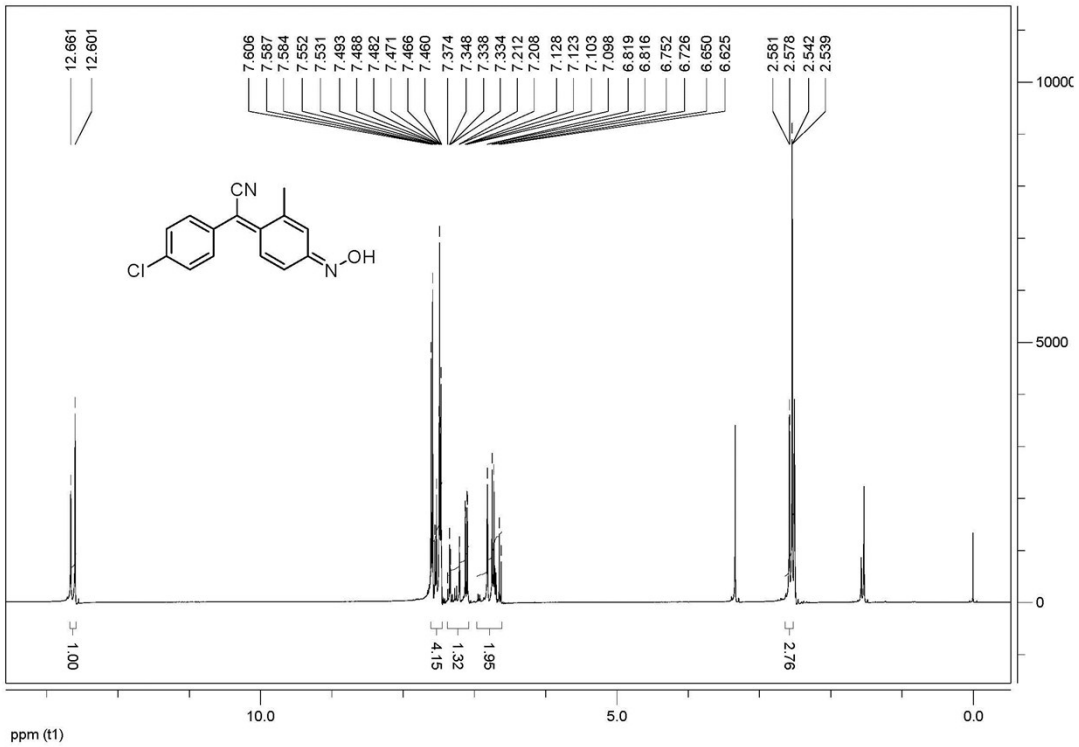
3h ^{1}H NMR(400MHz, d_6-DMSO)



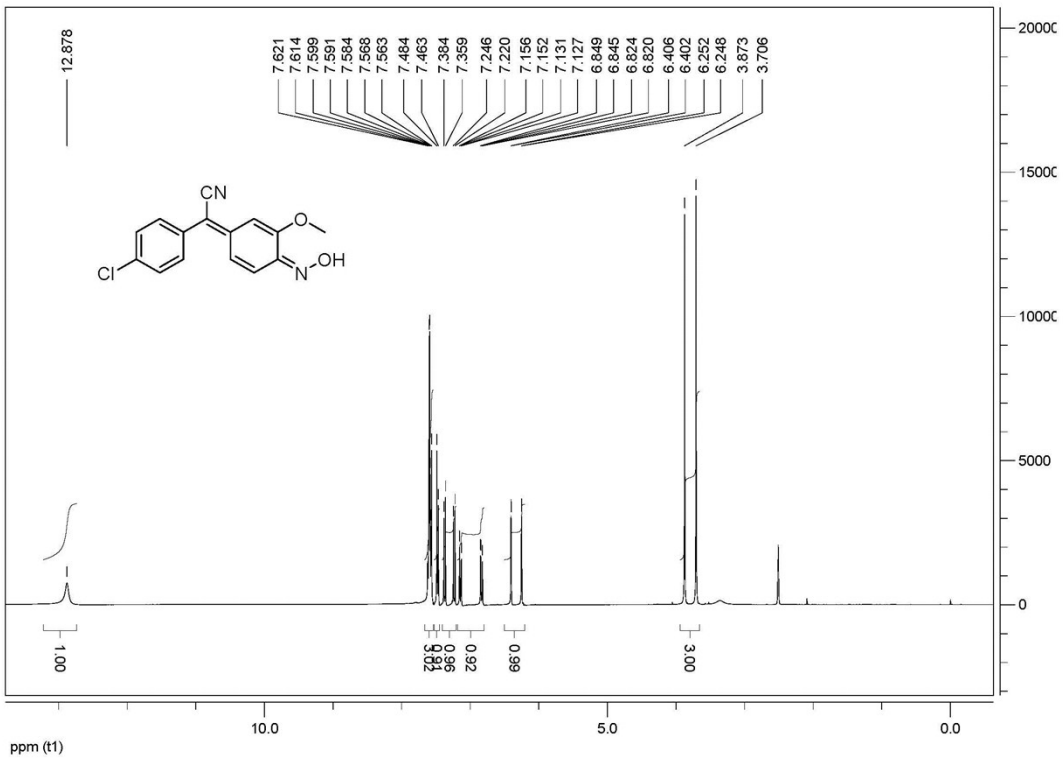
3i ^{1}H NMR(400MHz, d_6-DMSO)



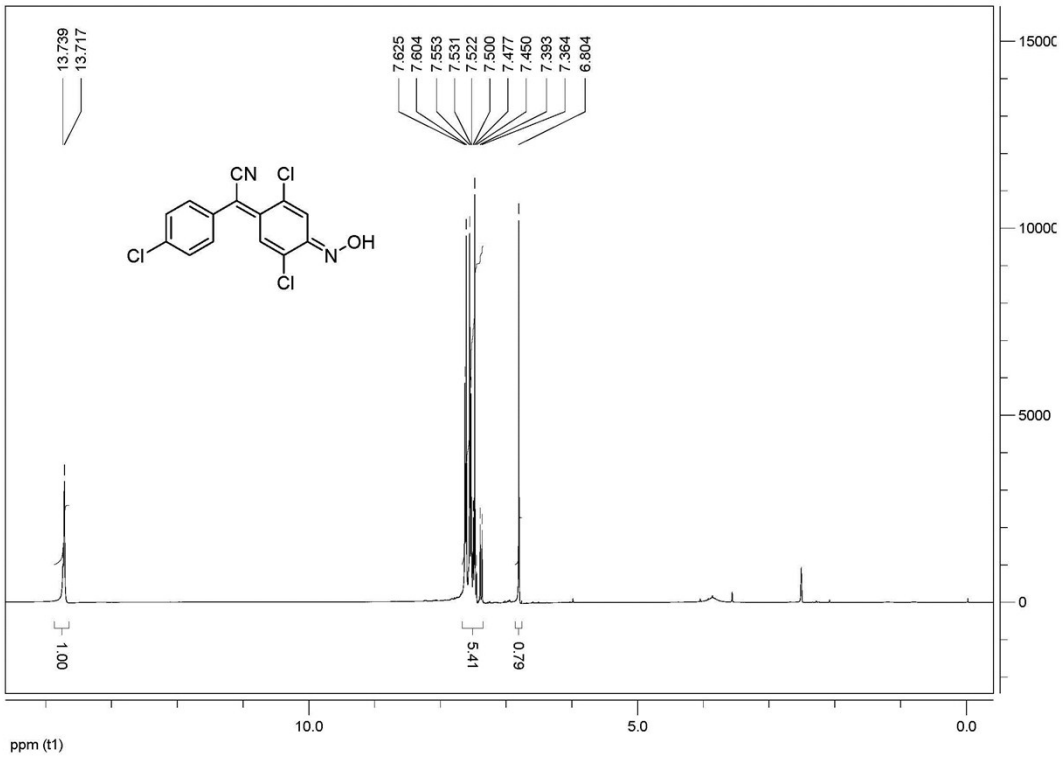
3j ^{1}H NMR(400MHz, d_6-DMSO)



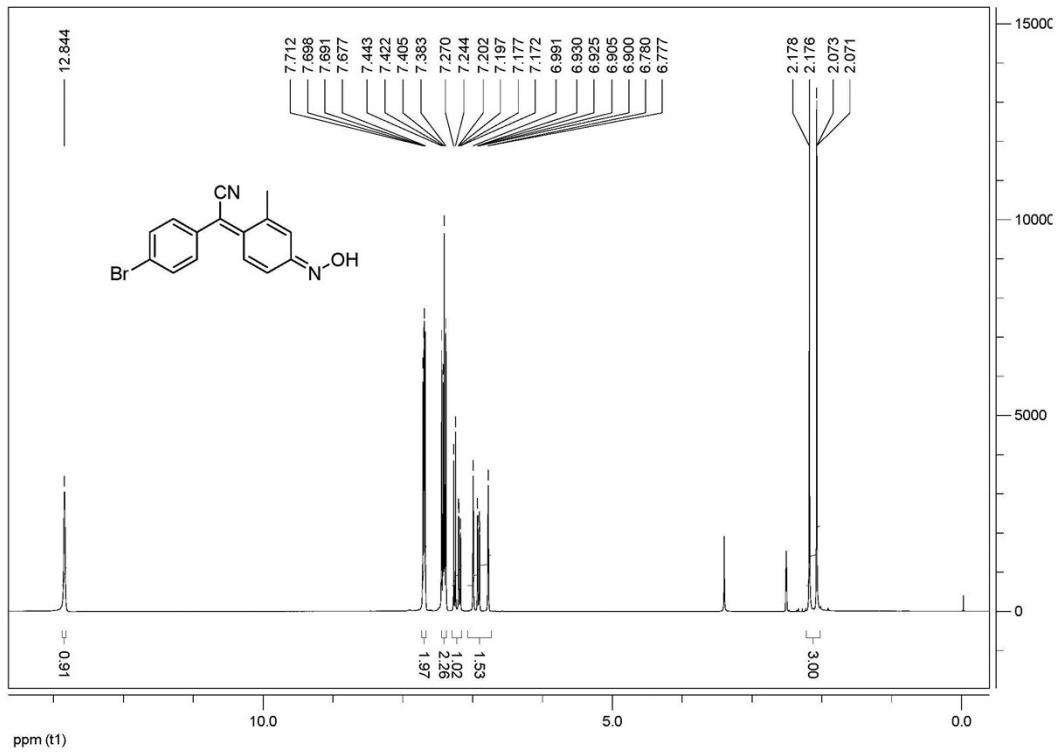
3k ^{1}H NMR(400MHz, d_6-DMSO)



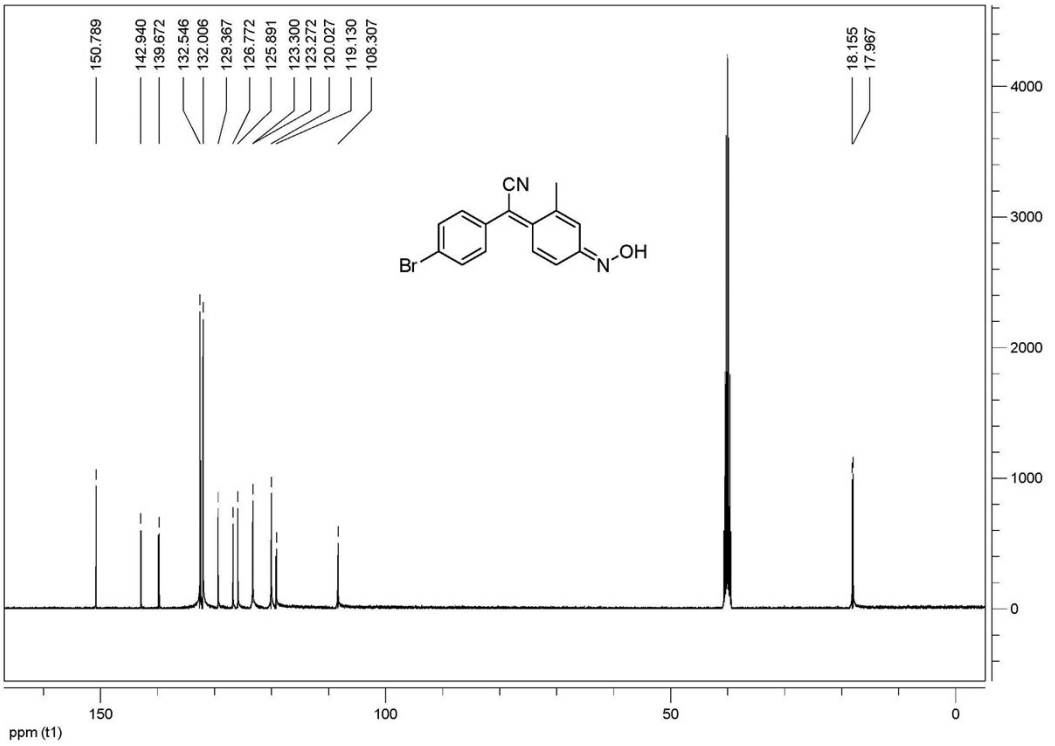
3l ^{1}H NMR(400MHz, d_6-DMSO)



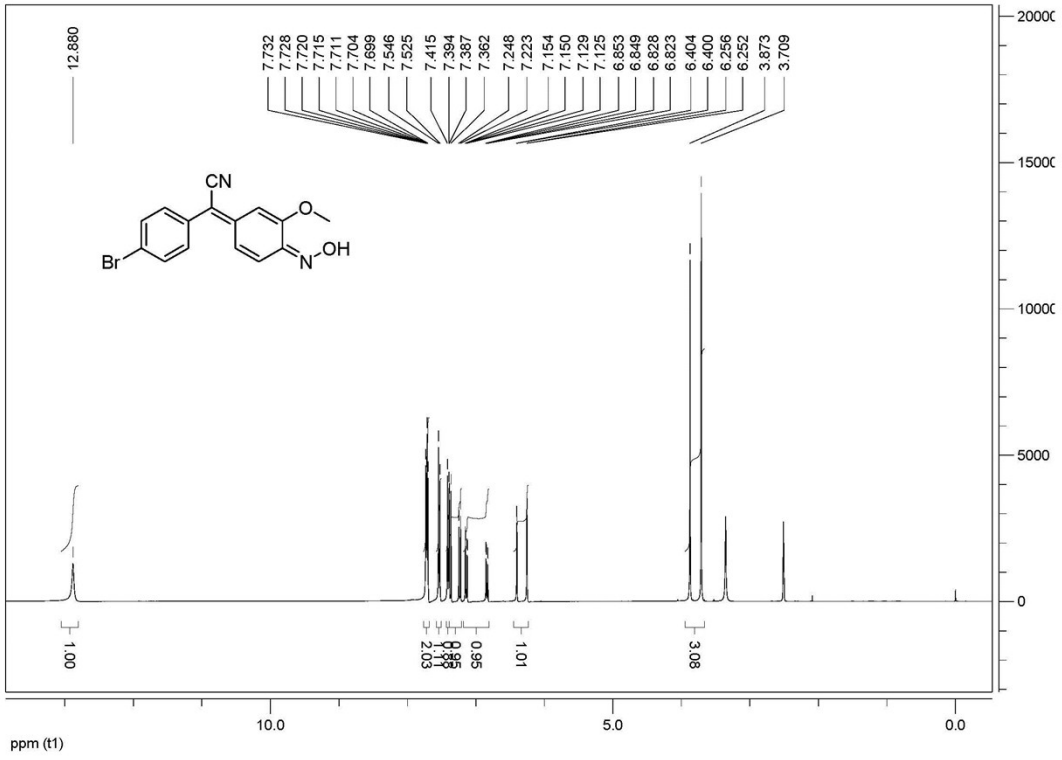
3m ^{1}H NMR(400MHz, d_6-DMSO)



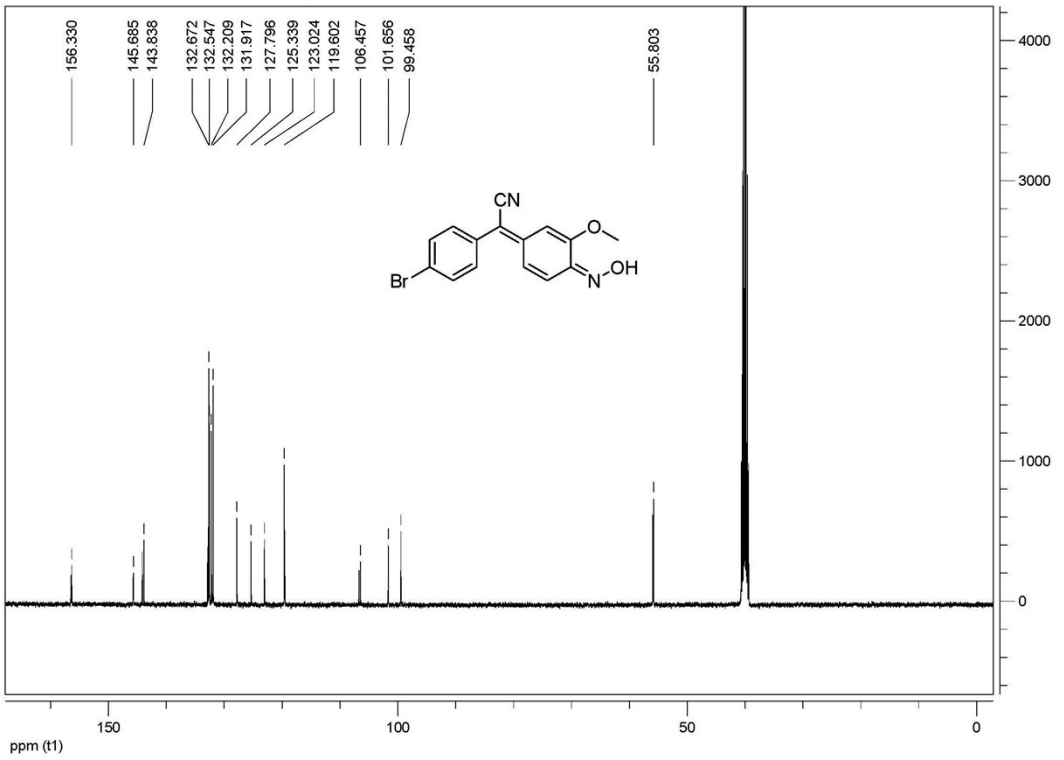
3m ^{13}C NMR(100MHz, d_6-DMSO)



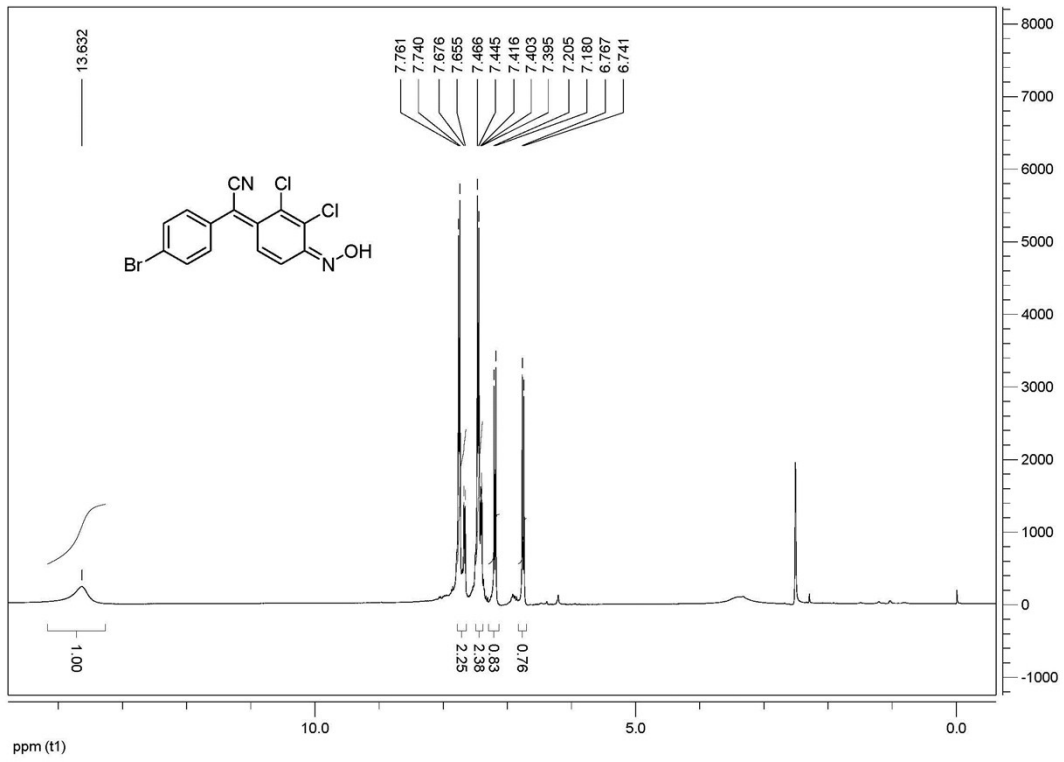
3n ^{1}H NMR(400MHz, d_6-DMSO)



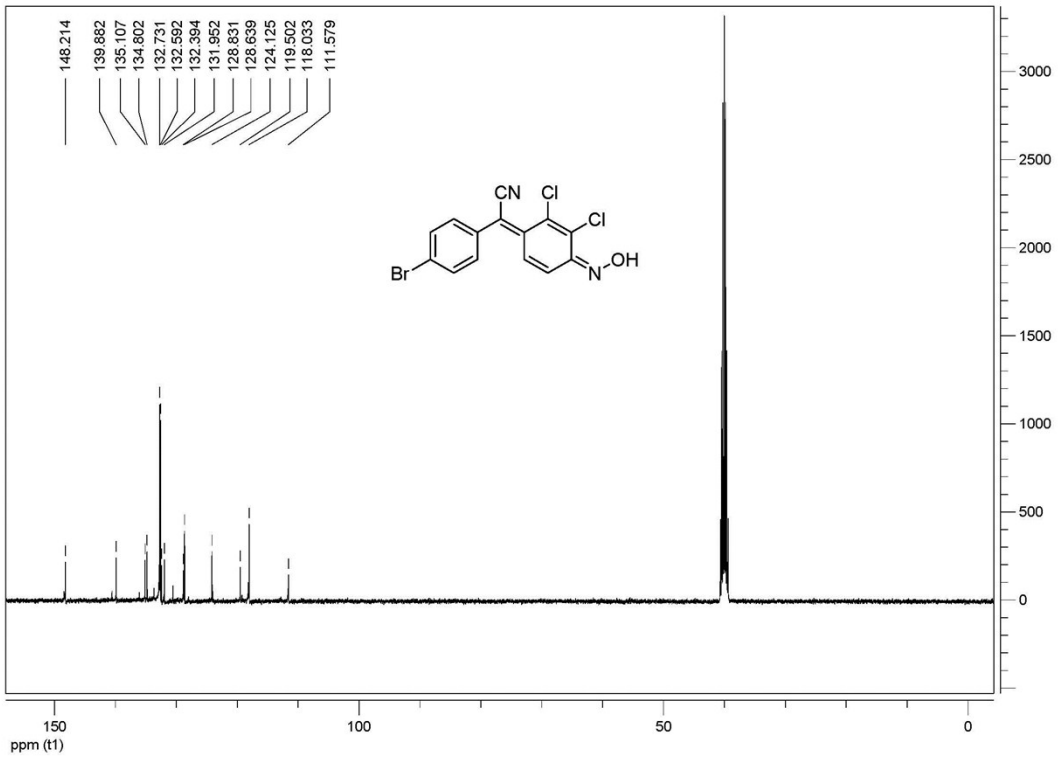
3n ^{13}C NMR(100MHz, d_6-DMSO)



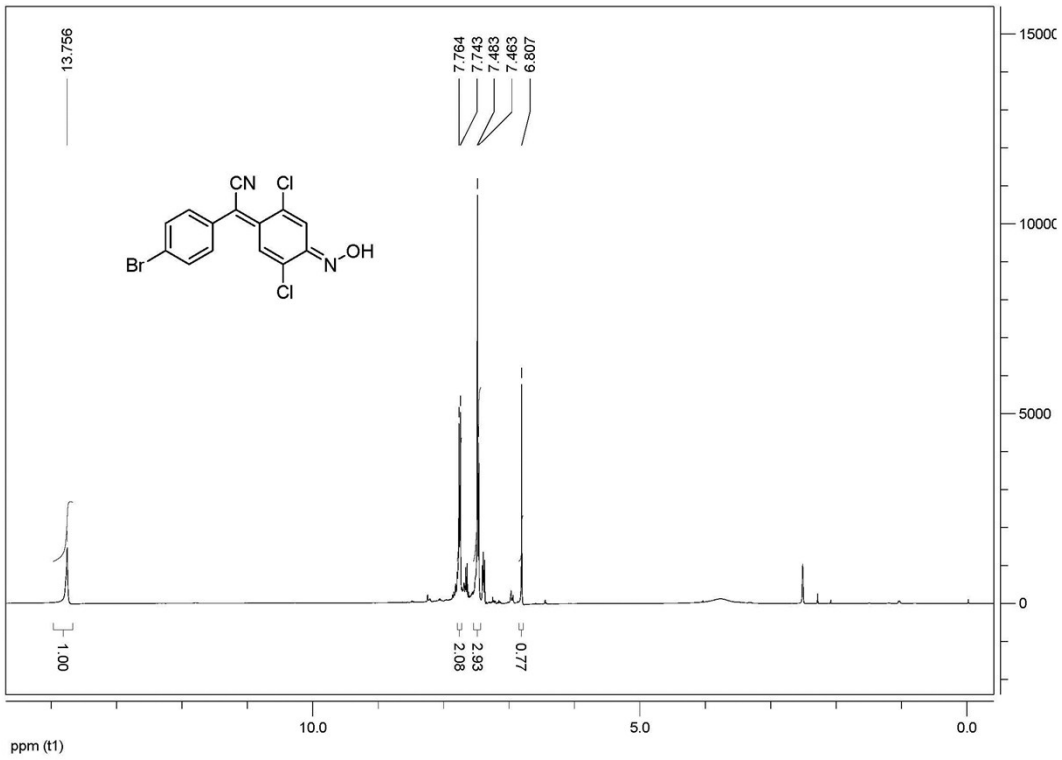
3o ^{1}H NMR(400MHz, d_6-DMSO)



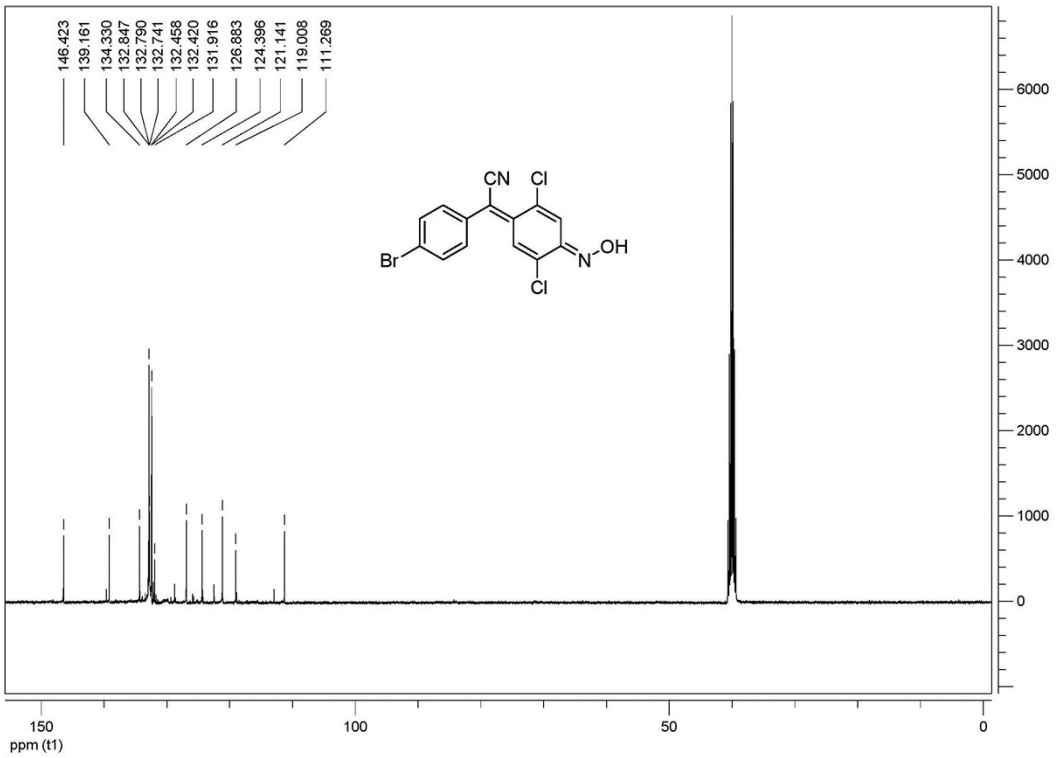
3o ^{13}C NMR(100MHz, d_6-DMSO)



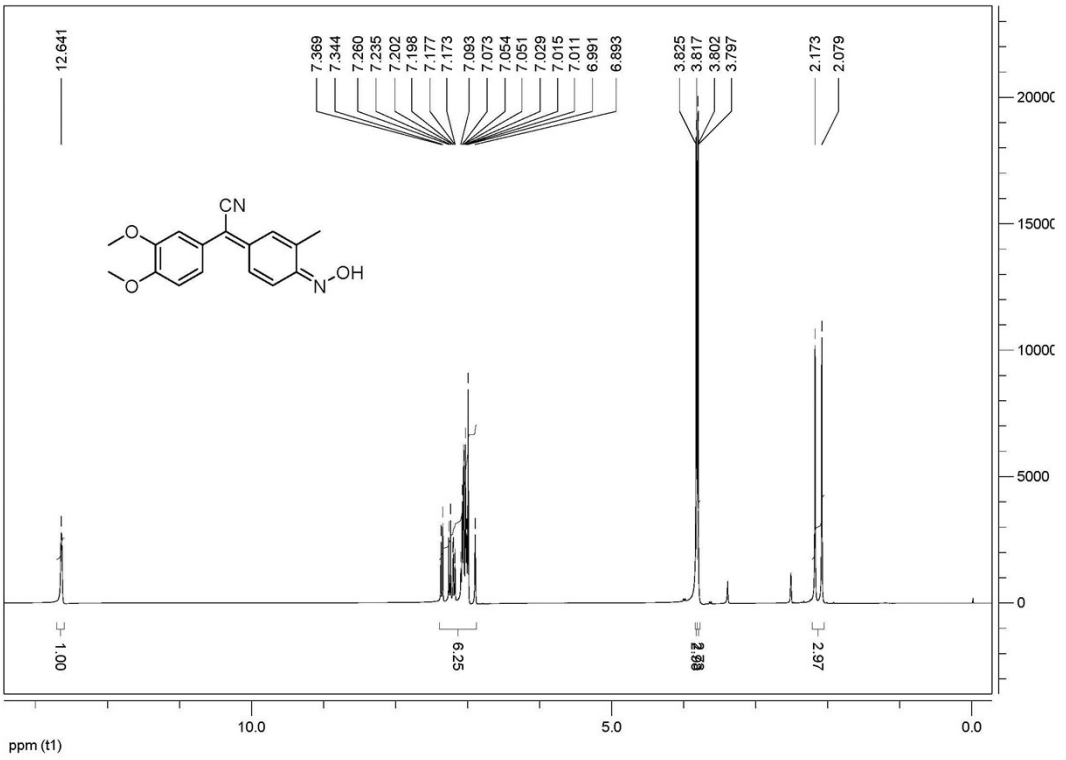
3p ^{1}H NMR(400MHz, d_6-DMSO)



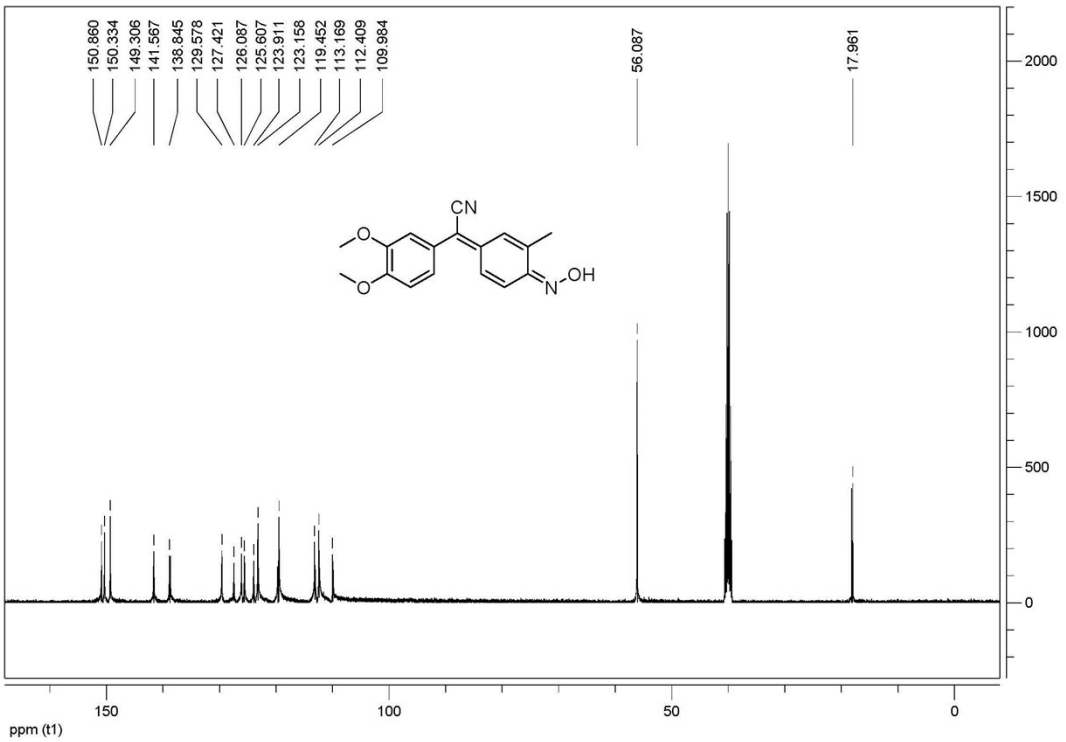
3p ^{13}C NMR(100MHz, d_6-DMSO)



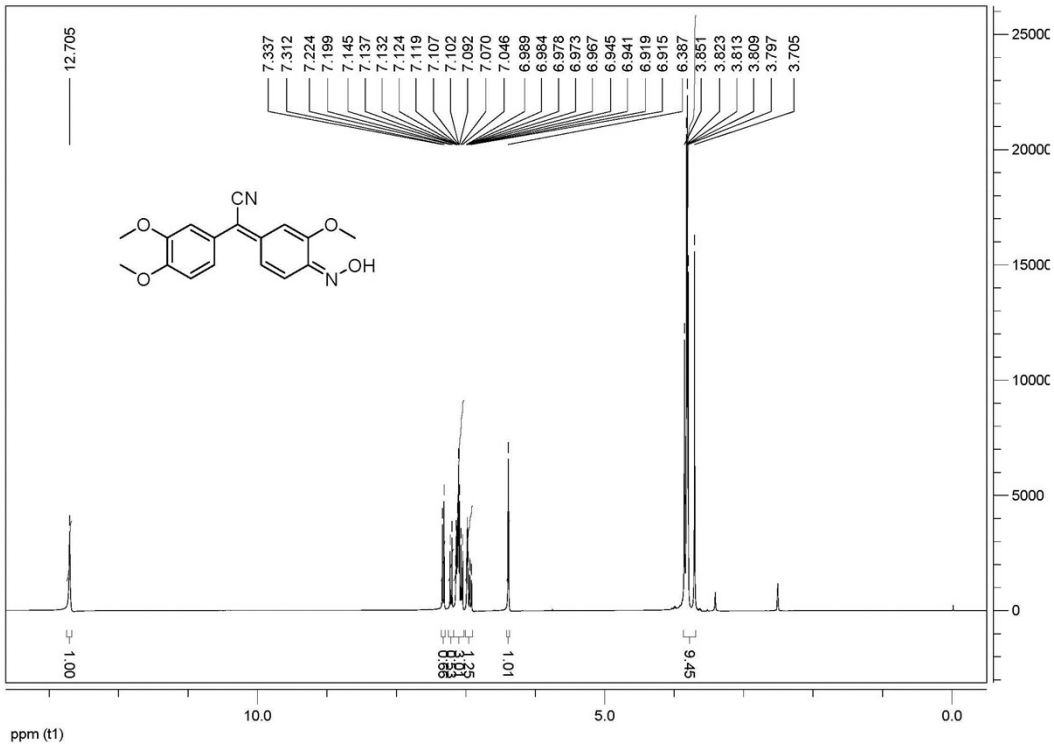
3q ^{1}H NMR(400MHz, d_6-DMSO)



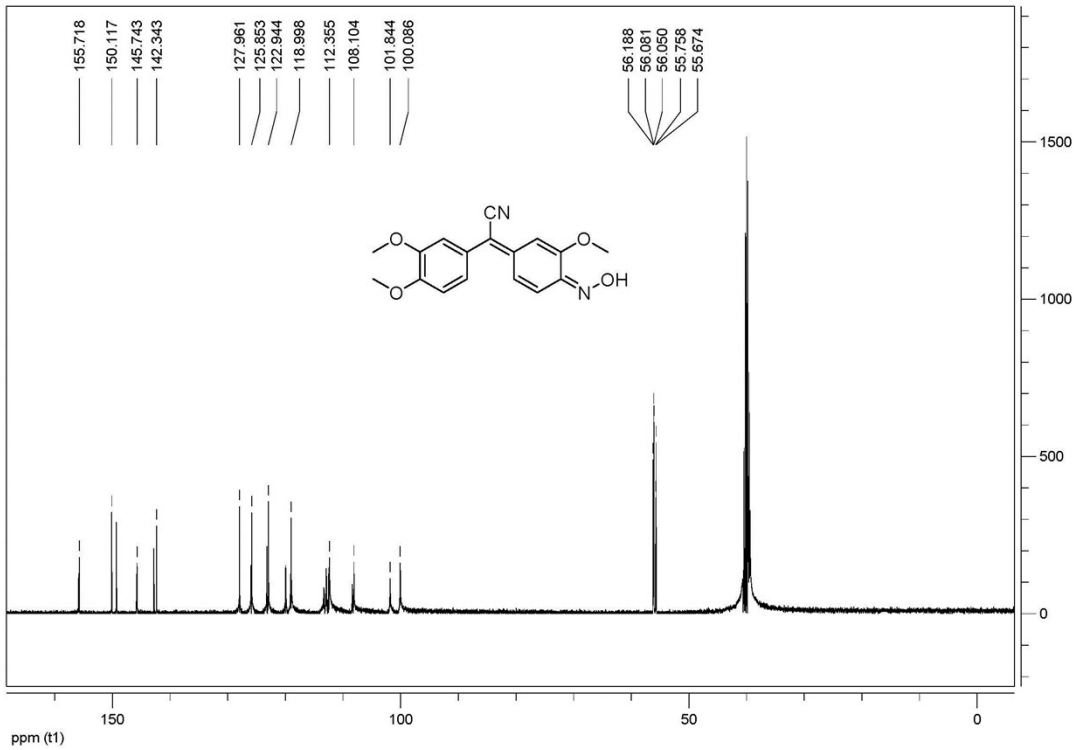
3q ^{13}C NMR(100MHz, d_6-DMSO)



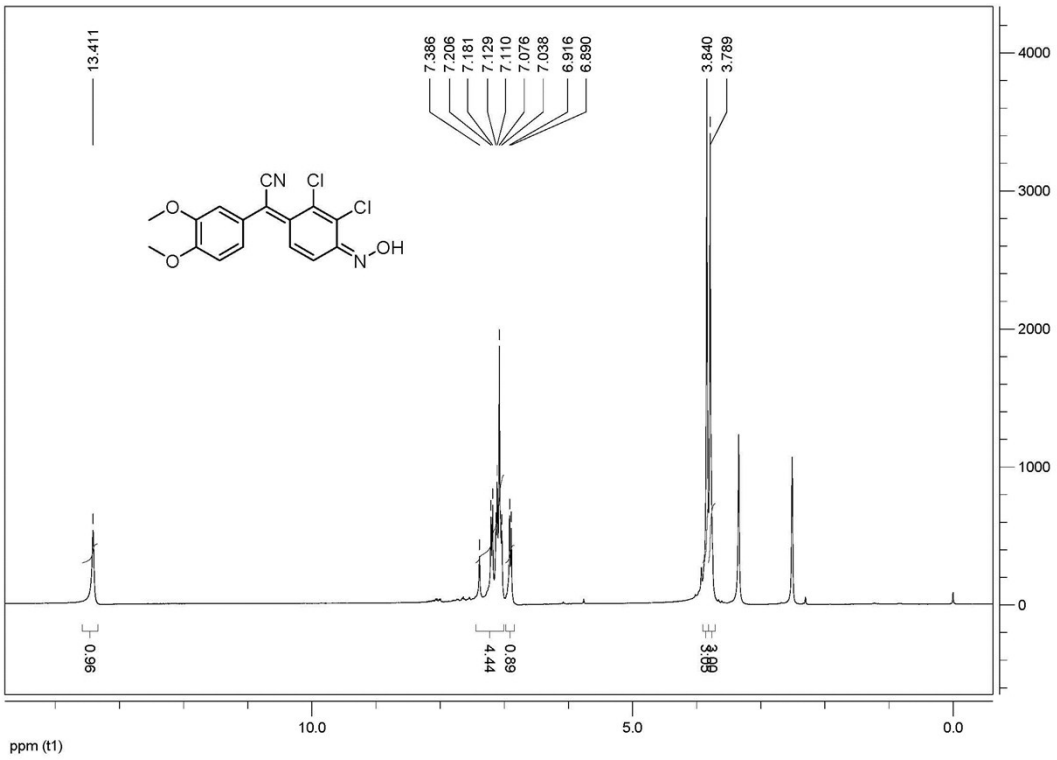
3r ^{1}H NMR(400MHz, d_6-DMSO)



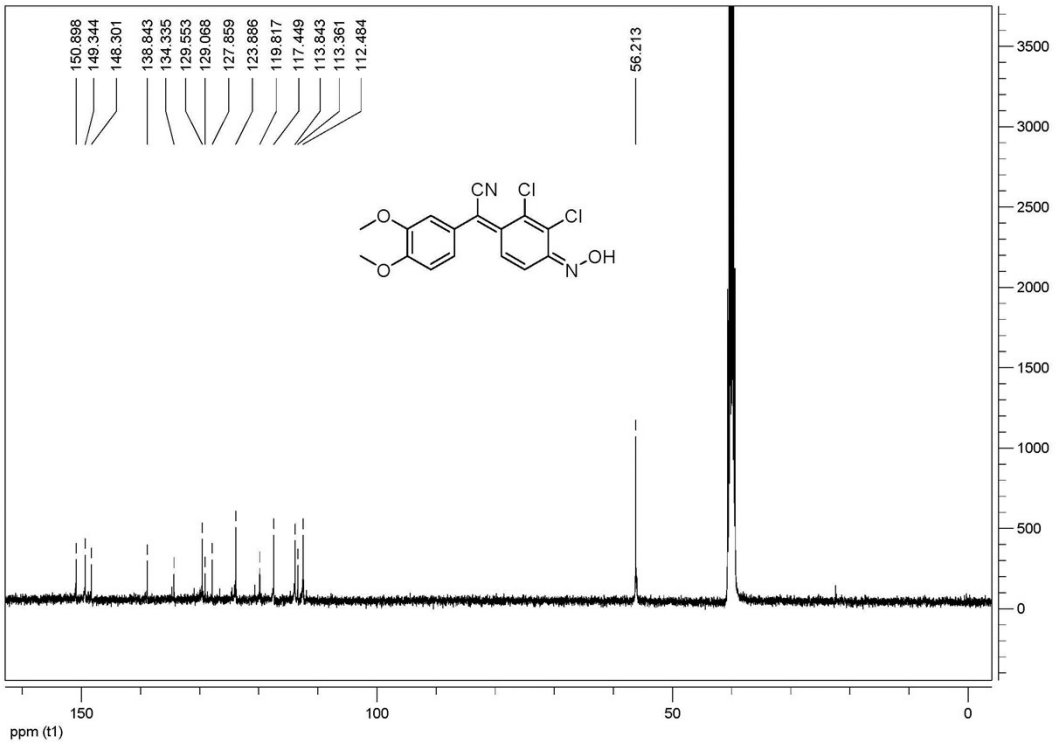
3r ^{13}C NMR(100MHz, d_6-DMSO)



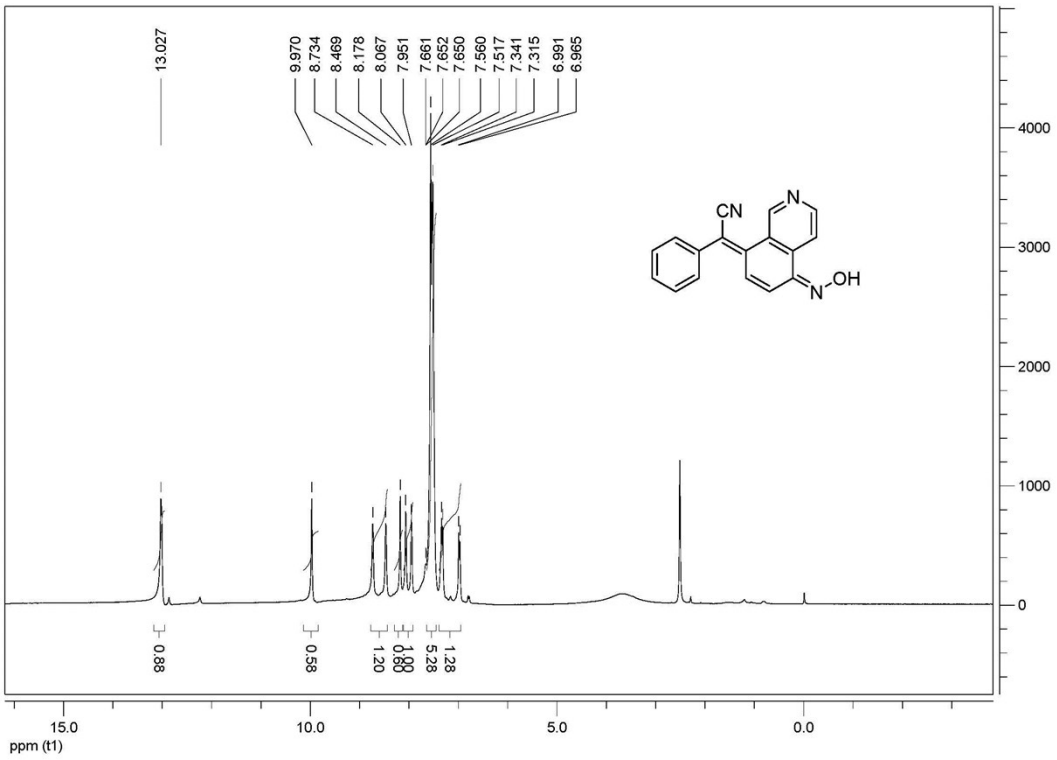
3s ^{1}H NMR(400MHz, d_6-DMSO)



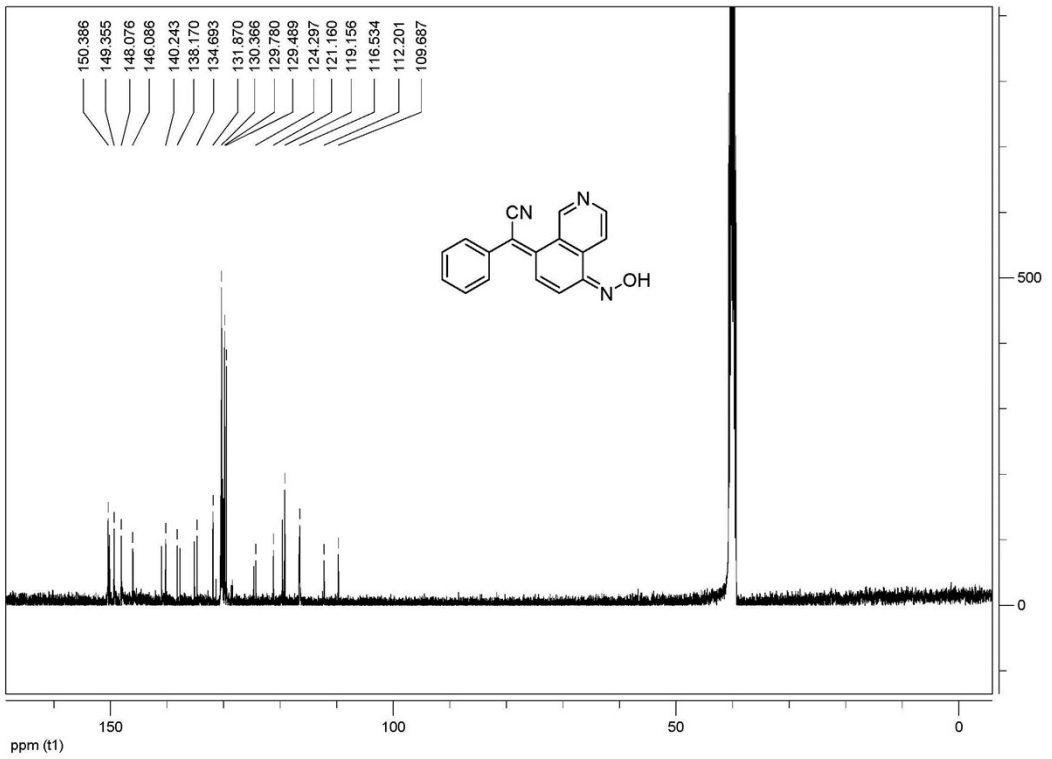
3s ^{13}C NMR(100MHz, d_6-DMSO)



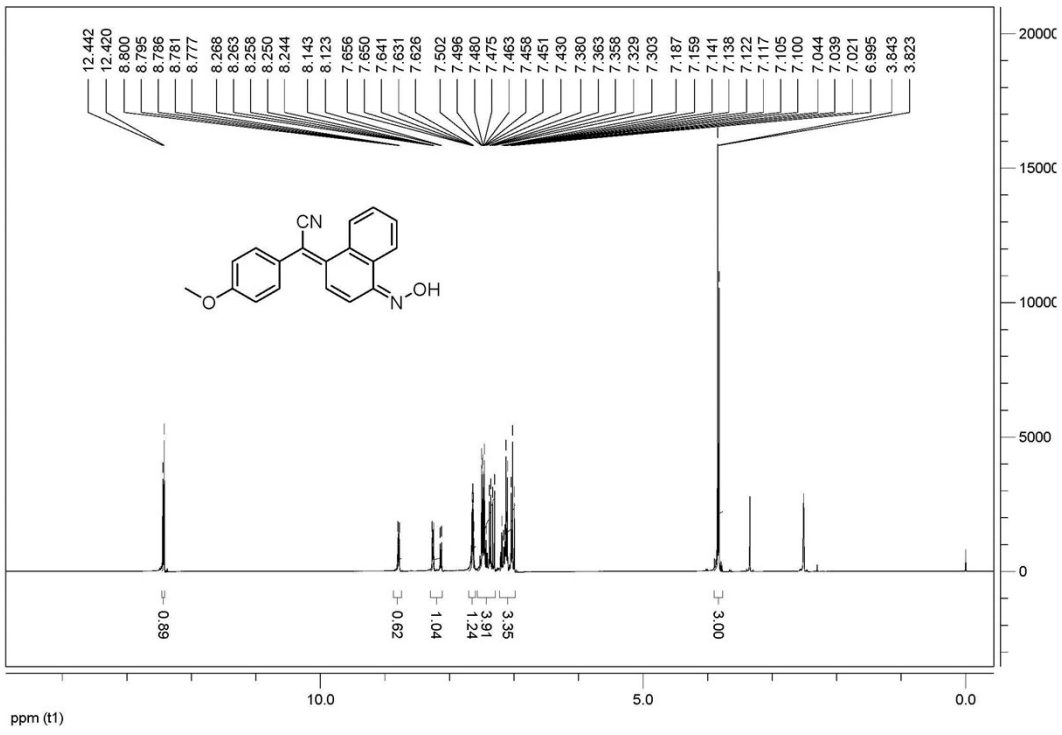
5a ^{1}H NMR(400MHz, d_6-DMSO)



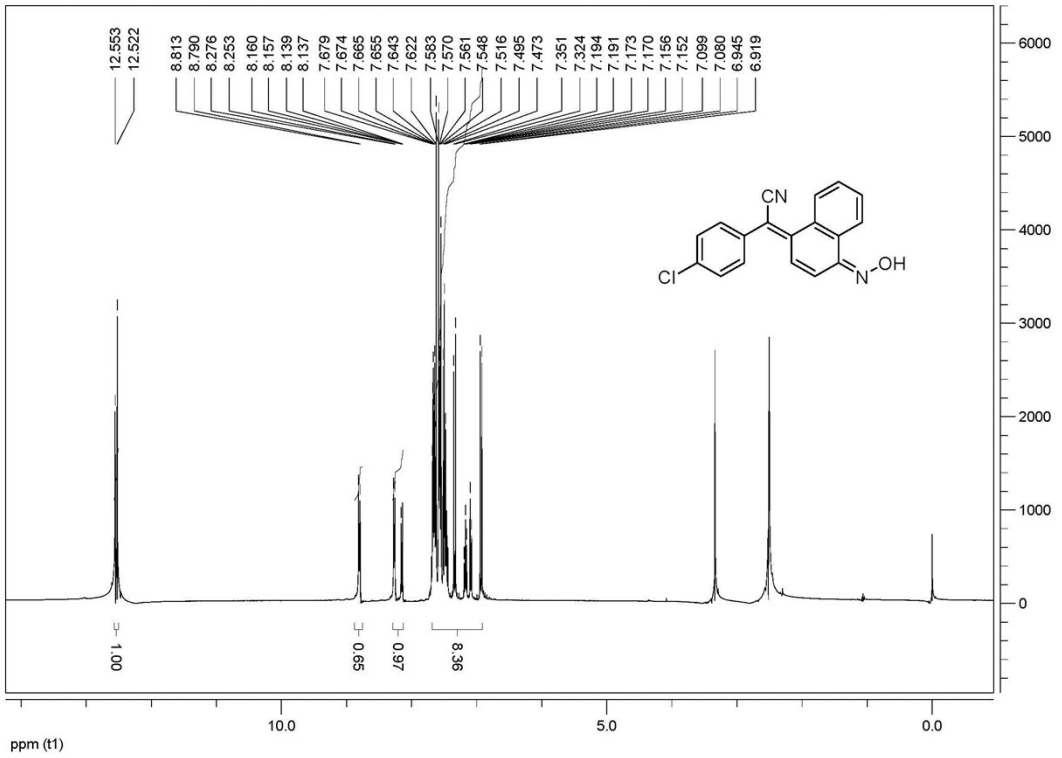
5a ^{13}C NMR(100MHz, d_6-DMSO)



5b ^{1}H NMR(400MHz, d_6-DMSO)



5c ^{1}H NMR(400MHz, d_6-DMSO)



3. X-ray diffraction of 3b

For the compound **3b**, an Oxford CrysAlisPro diffractometer with a CCD area detector was employed for data collection using Mo-*K*α radiation (λ = 0.71073 Å). By using the CRYSALISPRO software[S1] the data collection and reduction were performed. The structures were solved by direct methods (SHELXS-97[S2]) and refined by fullmatrix least-squares on F^2 (SHELXL[S2]) and finally checked using the PLATON software[S3] integrated in the WinGX software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected based on gaussian integration over a multifaceted crystal model. All DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

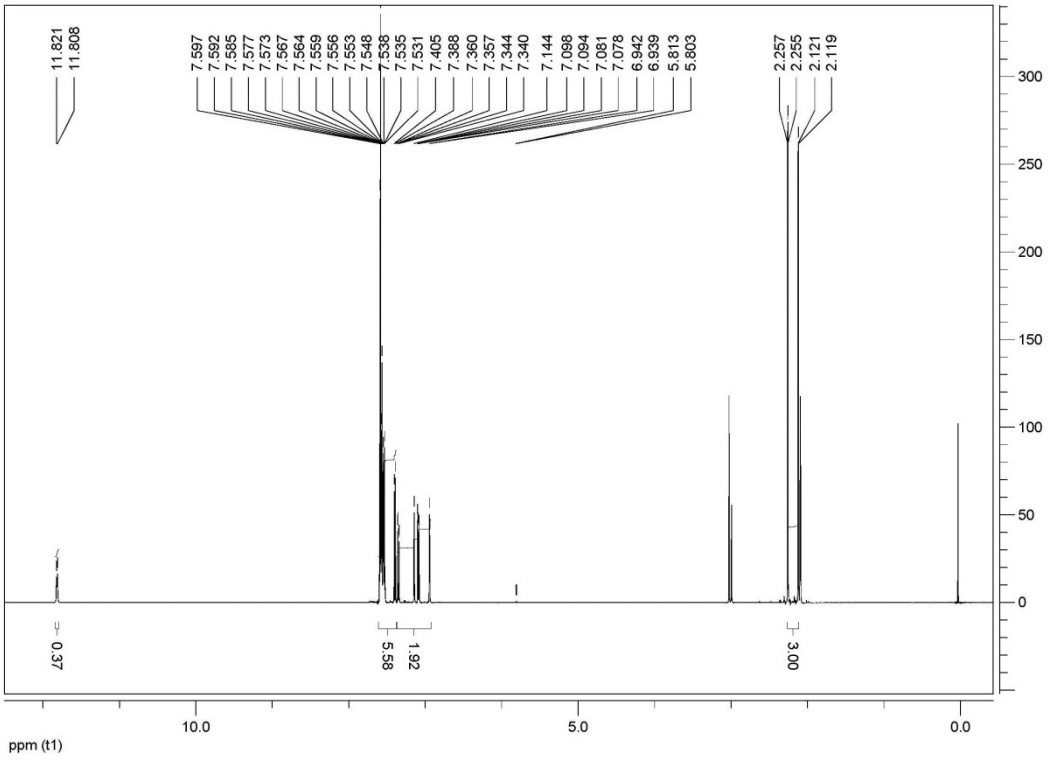
Table S1 Crystallographic data and refinement parameters of compound **3b**

Empirical formula	$C_{15}H_{12}N_2O$
Formula weight	236.27
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 6.958(5) Å α= 90°.
	b = 3.937(3) Å β= 91.278(9)°
	c = 45.96(3) Å γ= 90°.

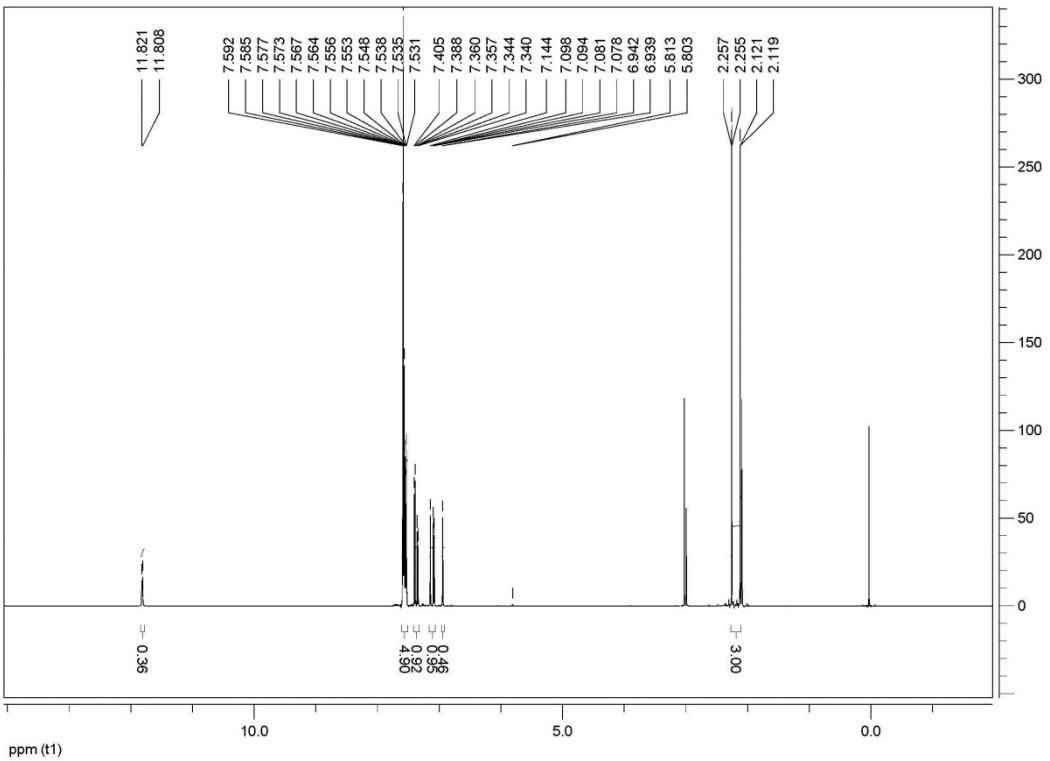
Volume	1258.6(16) $Å^3$
Z	4
Density (calculated)	1.247 mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	496
Crystal size	0.54 x 0.12 x 0.10 mm^3
Theta range for data collection	1.773 to 27.410°
Index ranges	-8<=h<=8, -5<=k<=5, -59<=l<=52
Reflections collected	9322
Independent reflections	2791 [R(int) = 0.0501]
Completeness to theta = 25.242°	99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.992 and 0.982
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2791 / 204 / 250
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0784, wR2 = 0.2199
R indices (all data)	R1 = 0.1307, wR2 = 0.2605
Extinction coefficient	0.028(7)
Largest diff. peak and hole	0.345 and -0.280 $e.Å^{-3}$

4. The variable-temperature ^{1}H NMR spectra of 3b in acetone-d_6 (25 °C to -50 °C)

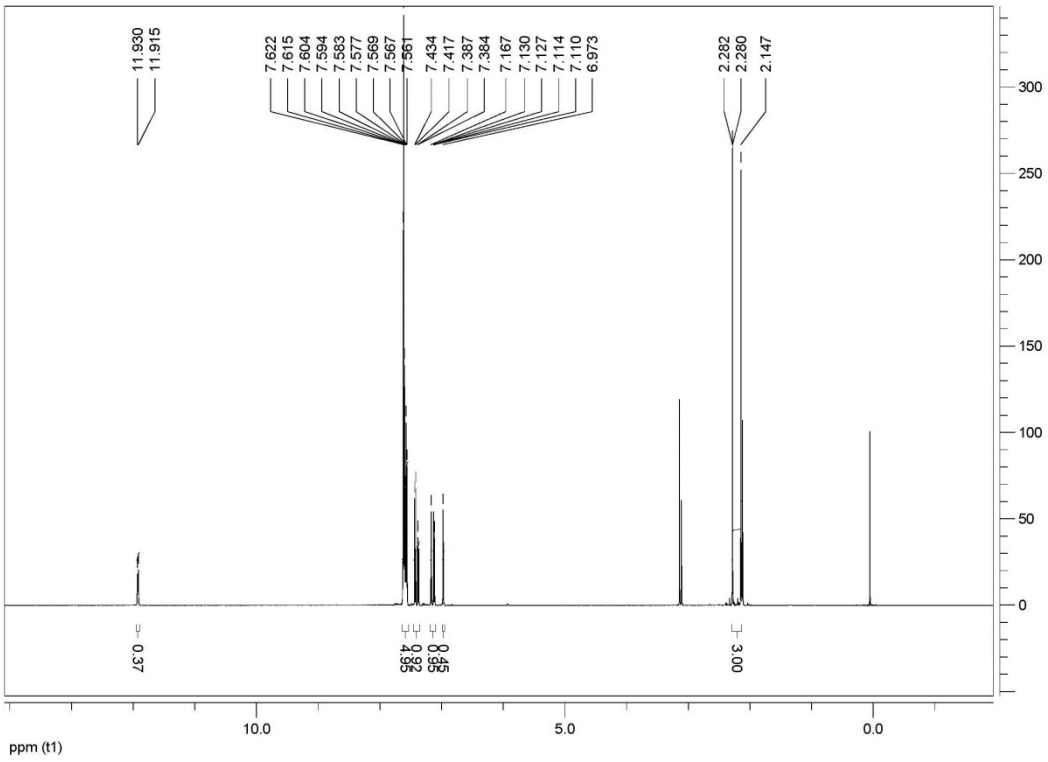
a. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at 25 °C



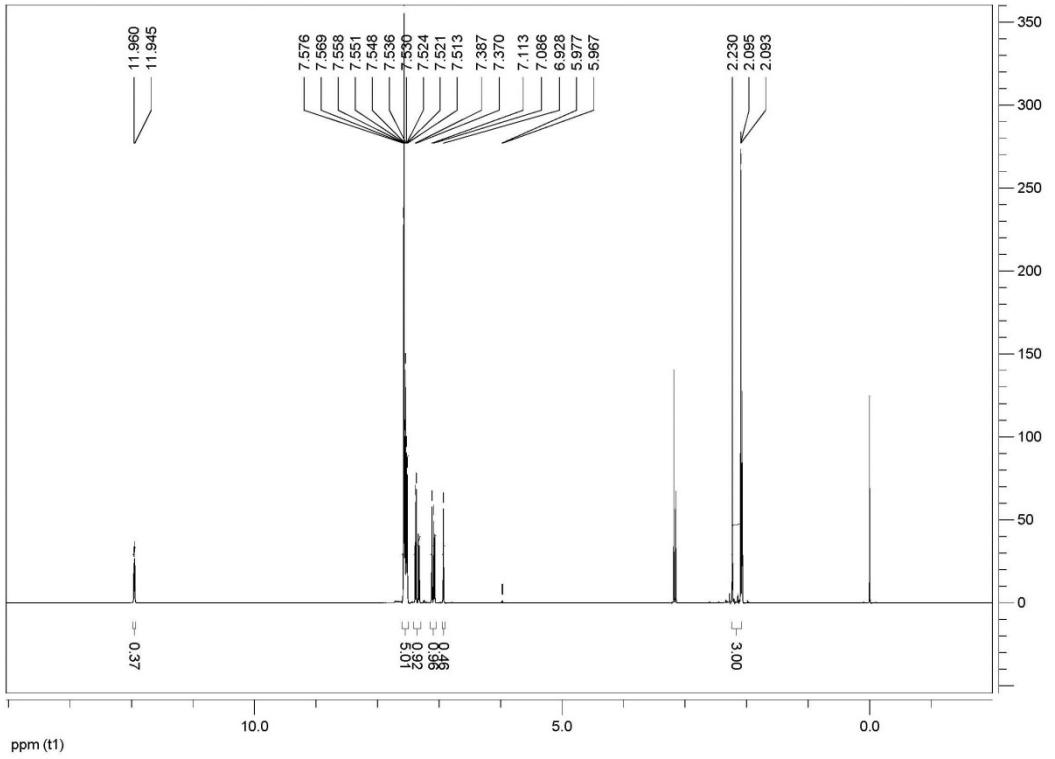
b. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at 10 °C



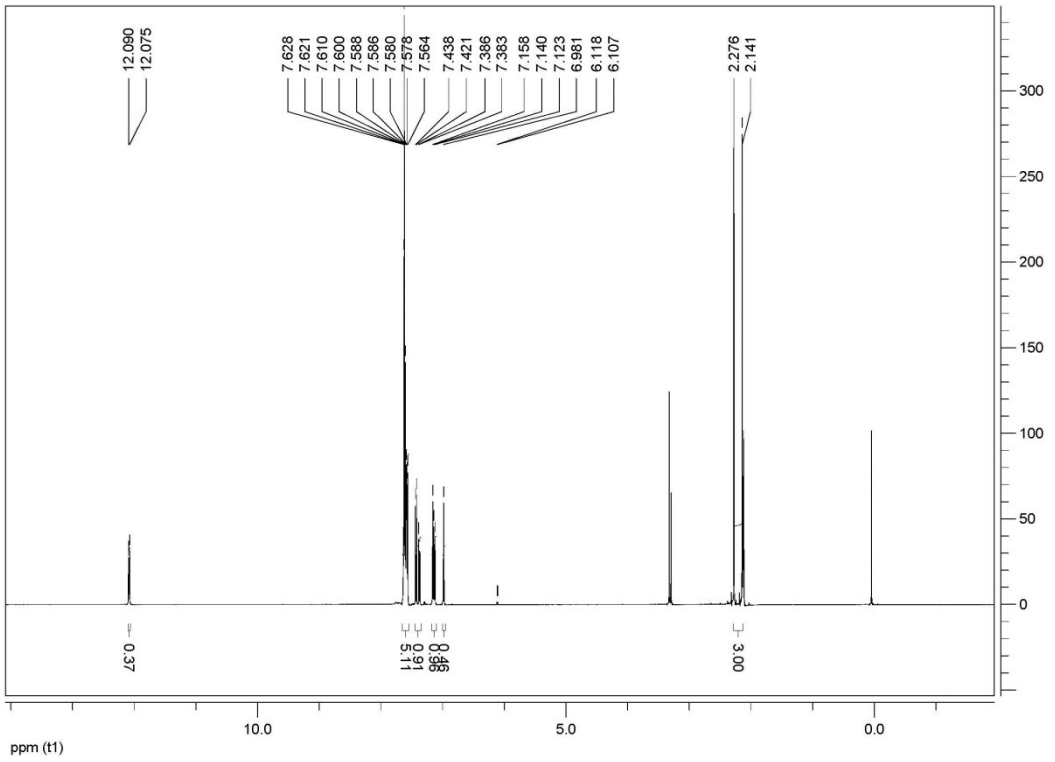
c. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at 0 °C



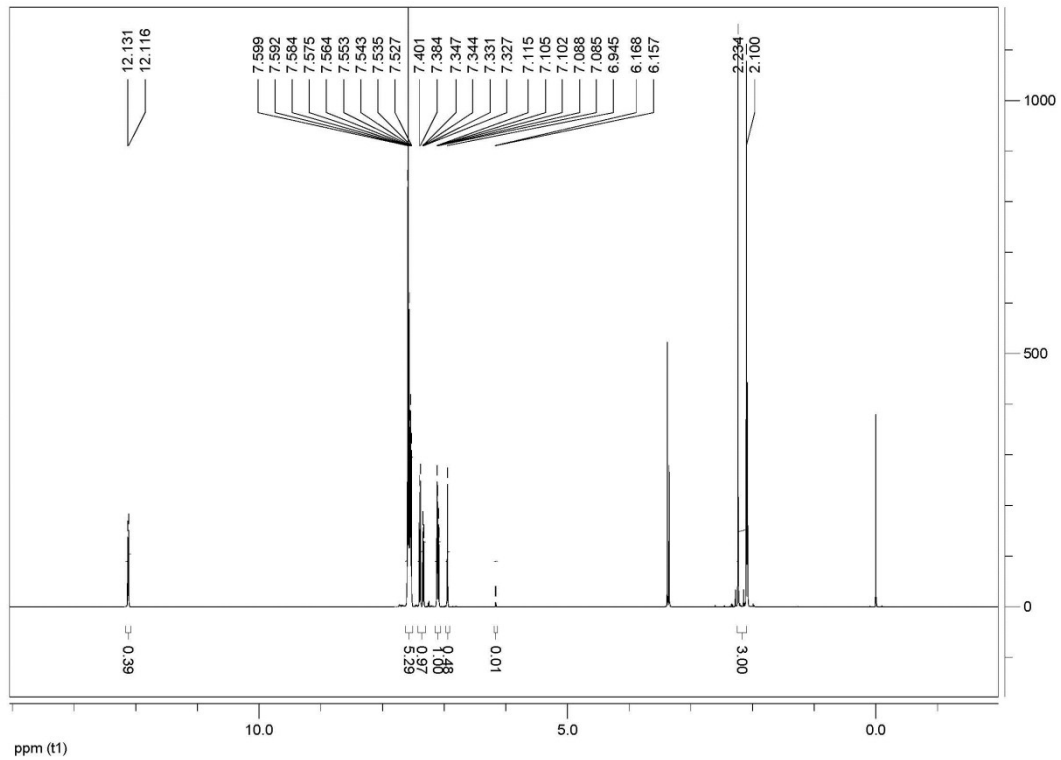
d. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at -10 °C



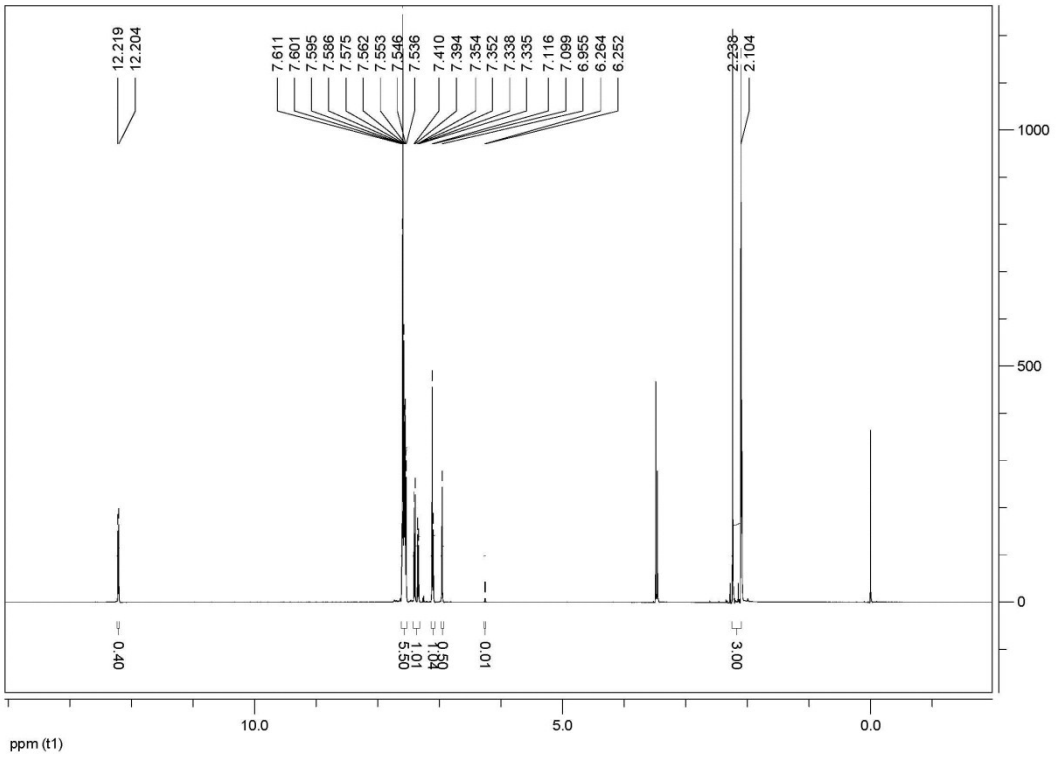
e. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at -20 °C



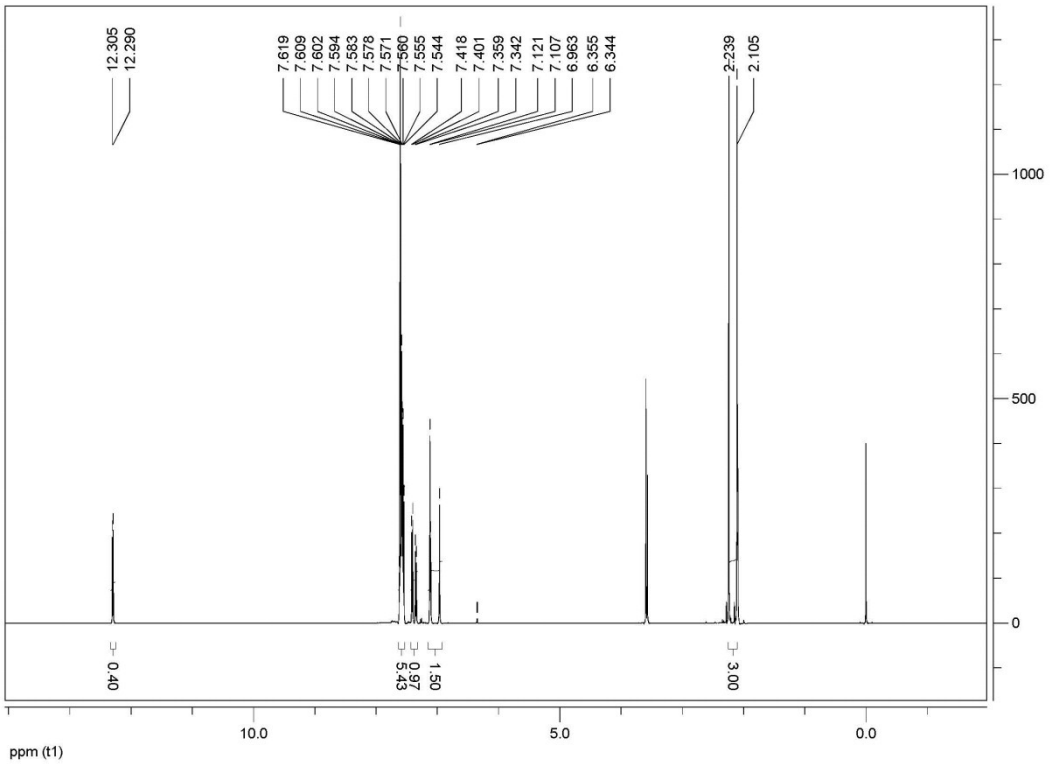
f. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at -30 °C



g. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at -40 °C



h. ^{1}H NMR(400MHz, acetone-d_6) spectra of **3b** at -50 °C



5. References

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