Supporting information

Quantitative one-pot synthesis method for industrial azo pigments with recyclable wastewater

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Contents

1. Reagents and instruments

All of the chemicals were obtained from commercial sources. NMR spectra were recorded with a 400-MHz spectrometer for ^{1}H NMR and a 101-MHz instrument for ^{13}C NMR using TMS as an internal standard. Chemical shifts (δ) are reported relative to TMS (^{1}H NMR), $CDCl_3$ or DMSO-d_6 (^{13}C NMR). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared analyses (KBr pellet) were performed by FTIR spectroscopy. High resolution mass spectroscopy (HRMS) using a quadrupole time of flight mass analyzer with electrospray ionization was used to analyze reaction products. All aqueous reactions were conducted in 100-mL flasks (except for the 2.27-g-scale preparation which used 250-mL flasks). The reactions were agitated by a modified stirring rod.[1,2,3] The size of the granular PTFE was 30 pieces/g.

2. Synthesis of azo pigments

2.1 General procedure for the preparations of azo pigments

For products **1**-**6**, a mixture of the coupling component (1 g), aromatic primary amine (1.05 equiv), HCl (2 equiv), H_2O (3 mL), $NaNO_2$ (1.10 equiv, in 2 mL of H_2O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After thin-layer chromatography (TLC) indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification.

For products **7**-**25**, a mixture of aromatic primary amine (1.05 equiv), HCl (3 equiv), H_2O (3 mL), $NaNO_2$ (1.10 equiv, in 2 mL of H_2O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 20 min, the coupling component (1 g) was added. The reaction was continued until TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification.

2.2 Preparation of Pigment Red 4 (7) in 22.7 g scale

A mixture of 2-chloro-4-nitroaniline (1.05 equiv), HCl (3 equiv), H_2O (45 mL), $NaNO_2$ (1.10 equiv, in 5 mL of H_2O) and granular PTFE (12 g) was mechanically stirred (400 rpm) at rt. After 20 min, 2-naphthol (10 g) was added. The reaction was continued for 20 min and TLC was used to confirm the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (5 mL) and dried to give a quantitative yield of the product without further purification.

2.3 Wastewater and excess HCl recycling in the preparation of Pigment Yellow 1 (3)

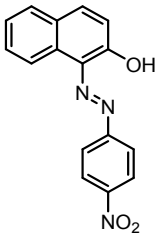
A mixture of acetoacetanilide (1 g), 4-methyl-2-nitroaniline (1.05 equiv), HCl (1.5 equiv), H_2O (8 mL), $NaNO_2$ (1.10 equiv, in 2 mL of H_2O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 45 min, TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were then filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification. The remaining mother liquid and PTFE from the above reaction and the washing water from the filtration were combined and then used in place of the initial H_2O in a second cycle. The amounts of acetoacetanilide, 4-methyl-2-nitroaniline, $NaNO_2$ and 2-naphthol were the same as for cycle 1 and the amount of added HCl was reduced to 1.1 equiv. In total, 11 cycles were conducted in this manner and all the reaction times from cycle 2-11 were 30 min with

quantitative yields. The combined volume of the mother liquid and washing water from the 11th cycle was 15.5 mL.

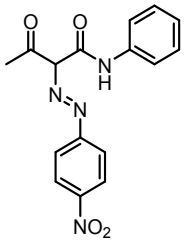
2.4 Wastewater and excess HCl recycling in the preparation of Pigment Red 3 (10)

A mixture of 4-methyl-2-nitroaniline (1.05 equiv), HCl (3 equiv), H_2O (8 mL), $NaNO_2$ (1.10 equiv, in 2 mL of H_2O) and granular PTFE (2.5 g) was mechanically stirred (400 rpm) at rt. After 20 min, 2-naphthol (1 g) was added. The reaction was continued for 60 min when TLC indicated the completion of the reaction. After stopping the reaction, the products were suspended in water while the granular PTFE precipitated on the bottom of the flask. The suspended products were filtered, washed with water (2 mL) and dried to give a quantitative yield of the product without further purification. The granular PTFE, mother liquid and washing water from the filtration were then combined and used in a second cycle. The amounts of 4-methyl-2-nitroaniline, $NaNO_2$ and 2-naphthol were the same as for cycle 1 and the amount of added HCl was reduced to 1.0 equiv. Altogether 11 cycles were conducted in this same way. All the reactions were complete in 60 min and had quantitative yields. After the 11th cycle, the combined volume of the mother liquid and washing water was 17 mL.

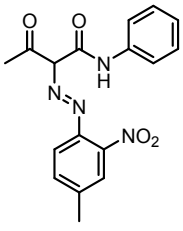
3. Analytic data of the products



1, Pigment Red 1:[4] 2.07 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 9.1 Hz, 3H), 7.53-7.59 (dd, *J* = 15.4, 7.6 Hz, 2H), 7.43-7.46 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 143.5, 133.0, 132.1, 129.8, 129.2, 128.6, 127.6, 126.4, 125.7, 122.5, 116.6. IR (KBr) *v*: 3480 (br.), 3087, 1593, 1501, 1331, 1106, 852, 748 cm^{-1}.

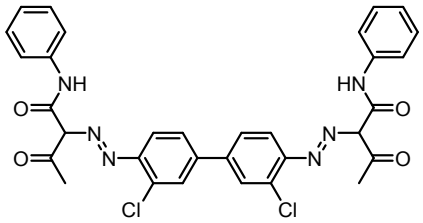


2, Pigment Yellow 4:[5] 1.85 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.90 (s, 1H), 11.35 (s, 1H), 8.31 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 2.63 (s, 3H). IR (KBr) *v*: 3250, 3087, 1665, 1598, 1516, 1337, 1249, 1106, 951, 852, 776 cm^{-1}. HRMS calcd for: $C_{16}H_{13}N_4O_4^-$ $[M-H]^-$: 325.0931, found: 325.0932.

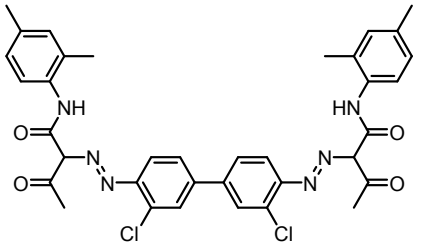


3, Pigment Yellow 1:[6] 1.93 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.81 (s, 1H), 11.30 (s, 1H), 8.08 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 2.64 (s,

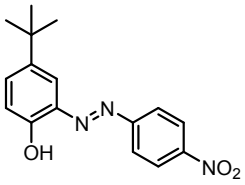
3H), 2.44 (s, 3H). IR (KBr) *v*: 3240, 3149, 1666, 1599, 1560, 1341, 1292, 1175, 771 cm^{-1}. HRMS calcd for: $C_{17}H_{15}N_4O_4^-$ $[M\text{-}H]^-$: 339.1088, found: 339.1088.



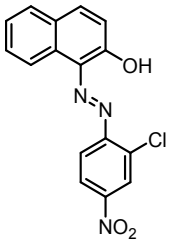
4, Pigment Yellow 12:[7] 1.79 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 15.08 (s, 2H), 11.41 (s, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.70-7.63 (m, 6H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.18 (d, *J* = 7.4 Hz, 2H), 2.64 (s, 6H). IR (KBr) *v*: 3135, 3058, 2242, 1665, 1597, 1553, 1512, 1445, 1244, 1178, 913, 753, 621, 435 cm^{-1}. HRMS calcd for: $C_{30}H_{23}Cl_2N_6O_3^{\bullet-}$ $[M\text{-}Ac\text{-}H]^{\bullet-}$: 585.1203, found: 585.1204.



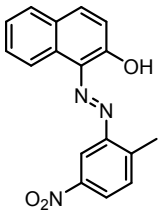
5, Pigment Yellow 13:[8] 1.68 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 15.13 (s, 2H), 11.21 (s, 2H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.63 (s, 1H), 7.52-7.57 (m, 3H), 7.03 (d, *J* = 16.2 Hz, 5H), 3.63 (s, 1H), 2.65 (s, 4H), 2.33 (dd, *J* = 19.6, 10.2 Hz, 13H). IR (KBr) *v*: 3241, 2916, 2216, 1713, 1667, 1598, 1512, 1228, 1182, 816, 619, 434 cm^{-1}. HRMS calcd for: $C_{34}H_{31}Cl_2N_6O_3^{\bullet-}$ $[M\text{-}Ac\text{-}H]^{\bullet-}$: 641.1829, found: 641.1831.



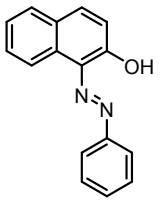
6, 2-(*p*-nitrodiazophenyl)-4-*tert*-butylphenol:[9] 2.01 g, >99%, ^1H NMR (400 MHz, DMSO-d_6, two isomers in a 80:20 ratio) δ 12.29 (s, 0.8H), 8.27 (d, *J* = 8.7 Hz, 1.6H), 8.14 (d, *J* = 8 Hz, 0.4H),7.84-7.93 (m, 2.2H), 7.43-7.59 (m, 0.6H), 7.37-7.39 (m, 1H), 7.26 (s, 0.4H), 6.89 (d, *J* = 8.7 Hz, 0.8H), 1.27 (s, 9 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.4, 154.2, 148.5, 142.7, 138.6, 133.3, 126.8, 126.3, 125.4, 124.0, 118.8, 117.8, 115.1, 112.8, 34.4, 34.1, 31.9, 31.4. IR (KBr) *v*: 3480 (br.), 3228, 2957, 1598, 1523, 1343, 1169, 1107, 857 cm^{-1}.



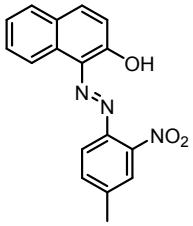
7, Pigment Red 4:[10] 2.29 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.1 Hz, 1H), 8.38 (d, *J* = 4.0 Hz, 1H), 8.27 (d, *J* = 9.0 Hz, 1H), 8.18 (d, *J* = 9.1 Hz, 1H), 7.70 (d, *J* = 9.7 Hz, 1H), 7.60-7.50 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 9.7 Hz, 1H). IR (KBr) *v*: 3480 (br.), 3094, 1621, 1510, 1336, 1197, 838, 510 cm^{-1}. HRMS calcd for: $C_{16}H_{10}ClN_3O_3^-$ $[M]^-$: 327.0466, found: 327.0469.



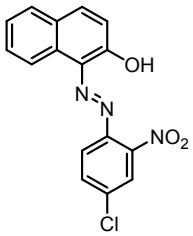
8, Pigment Orange 3:[11] 2.12 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.0 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 9.6 Hz, 1H), 7.56-7.63 (m, 2H), 7.43 (dd, *J* = 16.7, 8.0 Hz, 2H), 6.78 (d, *J* = 9.5 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 147.8, 142.8, 142.3, 134.1, 133.1, 131.7, 129.7, 128.9, 128.3, 126.9, 125.4, 122.2, 120.1, 110.2, 17.7. IR (KBr) *v*: 3480 (br.), 3099, 1616, 1519, 1344, 1149, 840, 742 cm^{-1}.



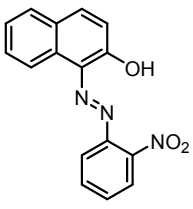
9, Sudan I:[12] 1.72 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 3H), 7.62-7.52 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.1, 133.6, 130.1, 129.6, 128.8, 128.6, 128.1, 127.4, 125.7, 124.8, 121.7, 118.5. IR (KBr) *v*: 3480 (br.), 3185, 1665, 1598, 1516, 1337, 1168, 852, 778 cm^{-1}.



10, Pigment Red 3:[13] 2.13 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 8.11 (s, 1H), 7.65 (d, *J* = 9.7 Hz, 1H), 7.53 (dd, *J* = 16.6, 8.8 Hz, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 9.7 Hz, 1H), 2.46 (s, 3H). IR (KBr) *v*: 3480 (br.), 3076, 1616, 1561, 1305, 1188, 1127, 749, 509 cm^{-1}. HRMS calcd for: $C_{17}H_{12}N_3O_3^-$ $[M-H]^-$: 306.0873, found: 306.0874.

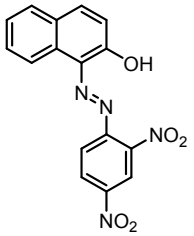


11, Pigment Red 6:[14] 2.28 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (t, *J* = 8 Hz, 2H), 8.30 (s, 1H), 7.67 (t, *J* = 10.2 Hz, 2H), 7.50-7.56 (m, 2H), 7.45 (t, *J* = 4 Hz, 1H), 6.70 (d, *J* = 8 Hz, 1H). IR (KBr) *v*: 3480 (br.), 3096, 1560, 1483, 1332, 1183, 832, 753, 507 cm^{-1}. HRMS calcd for: $C_{16}H_9ClN_3O_3^-$ $[M-H]^-$: 326.0327, found: 326.0322.

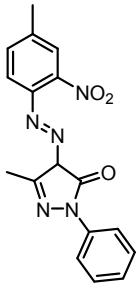


12, Pigment Orange 2:[4] 2.08 g, >99%, ^{1}H NMR (400 MHz, $CDCl_3$, two isomers in a 62:38 ratio) δ 8.45 (d, *J* = 8 Hz,

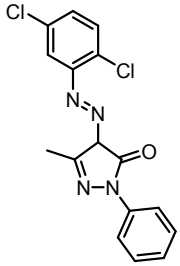
0.38H), 8.42 (d, *J* = 8 Hz, 0.38H), 8.31 (dd, *J* = 8.5, 1.4 Hz, 0.38H), 7.99 (d, *J* = 8.9 Hz, 0.62H), 7.90 (d, *J* = 7.7 Hz, 0.62H), 7.77-7.71 (m, 0.62H), 7.65 (d, *J* = 9.8 Hz, 0.38H), 7.57-7.48 (m, 1H), 7.46-7.20 (m, 4.62H), 7.16 (d, *J* = 8.4 Hz, 0.62H), 6.70 (d, *J* = 9.7 Hz, 0.38H). IR (KBr) *v*: 3480 (br.), 1604, 1567, 1485, 1310, 1187 cm^{-1}.



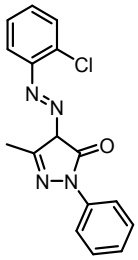
13, Pigment Orange 5:[15] 2.38 g, >99%, ^1H NMR (400 MHz, DMSO-d_6) δ 8.95 (d, *J* = 3.2 Hz, 1H), 8.66 (d, *J* = 9.4 Hz, 1H), 8.56 (dd, *J* = 9.4, 2.5 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 9.8 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.65-7.55 (m, 2H), 6.66 (d, *J* = 9.8 Hz, 1H). IR (KBr) *v*: 3480 (br.), 3104, 1610, 1593, 1526, 1492, 1340, 1176, 740 cm^{-1}. HRMS calcd for: $C_{16}H_9N_4O_5^-$ $[M-H]^-$: 337.0578, found: 337.0579.



14, Pigment Orange 6:[16] 1.95 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 14.79 (s, 1H), 8.10 (s, 1H), 8.07 (d, *J* = 12 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H). IR (KBr) *v*: 3021, 1664, 1560, 1512, 1329, 1154, 771 cm^{-1}. HRMS calcd for: $C_{17}H_{14}N_5O_3^-$ $[M-H]^-$: 336.1091, found: 336.1099.

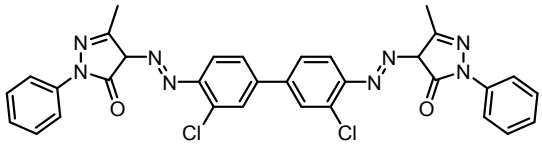


15, Pigment Yellow 10:[17] 1.98 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 13.68 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.82 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 8 Hz, 1H), 7.08 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.40 (s, 3H). IR (KBr) *v*: 3064, 1662, 1556, 1498, 1251, 1154, 719 cm^{-1}. HRMS calcd for: $C_{16}H_{11}Cl_2N_4O^-$ $[M-H]^-$: 345.0304, found: 345.0309.

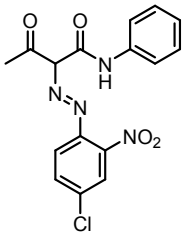


16, Pigment Yellow 60:[18] 1.80 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 13.77 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J*

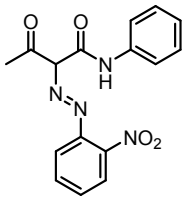
= 8.2 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 3H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 2.38 (s, 3H). IR (KBr) *v*: 3019, 1658, 1551, 1501, 1340, 1256, 1155, 749, 665 cm^{-1}. HRMS calcd for: $C_{16}H_{12}ClN_4O^-$ $[M-H]^-$: 311.0694, found: 311.0693.



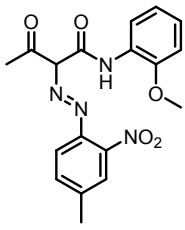
17, Pigment Orange 13:[19] 1.79 g, >99%, ^1H NMR (400 MHz, $CDCl_3$) δ 13.88 (s, 2H), 7.95 (dd, *J* = 17.7, 8.4 Hz, 6H), 7.66 (s, 2H), 7.58 (d, *J* = 7.9 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 5H), 2.42 (s, 6H). IR (KBr) *v*: 3062, 2921, 1662, 1546, 1499, 1458, 1369, 1337, 1154, 1073, 998, 870, 653, 593 cm^{-1}. HRMS calcd for: $C_{32}H_{23}Cl_2N_8O_2^-$ $[M-H]^-$: 621.1316, found: 621.1317.



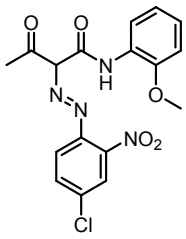
18, Pigment Yellow 6:[5] 2.1 g, >99%, ^1H NMR (400 MHz, $CDCl_3$, two isomers in a 70:30 ratio) δ 15.86 (s, 0.7H), 11.23 (s, 0.7H), 11.12 (s, 0.3H), 8.37 (s, 0.3H), 8.28 (s, 0.7H), 8.24 (s, 0.3H), 8.04 (d, *J* = 9.1 Hz, 0.7H), 7.85 (d, *J* = 9.0 Hz, 0.3H), 7.60-7.70 (m, 3H), 7.44 (s, 0.3H), 7.36-7.41 (m, 1.7H), 7.16-7.19 (m, 1H), 2.64 (s, 3H). IR (KBr) *v*: 3304, 1665, 1491, 1341, 1280, 1169, 904, 760 cm^{-1}. HRMS calcd for: $C_{16}H_{12}ClN_4O_4^-$ $[M-H]^-$: 359.0542, found: 359.0541.



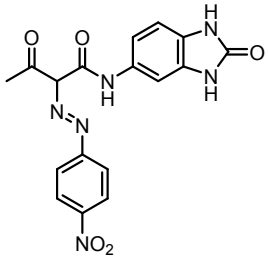
19, Pigment Yellow 5:[5] 1.89 g, >99%, ^1H NMR (400 MHz, $CDCl_3$, two isomers in a 60:40 ratio) δ 15.82 (s, 0.4H), 11.27 (s, 0.4H), 11.18 (s, 0.6H), 8.44 (s, 0.6H), 8.22-8.28 (m, 1H), 8.07 (d, *J*=8.5 Hz, 0.4H), 7.87 (d, *J*=8.5 Hz, 0.6H), 7.65-7.73 (m, 3H), 7.34-7.42 (m, 2.6H), 7.24 (d, *J*=8.0 Hz, 0.4H), 7.16 (t, *J*=8.5 Hz, 1H), 7.04 (t, *J*=7.8 Hz, 0.6H), 2.61 (s, 1.8H), 1.62 (s, 1.2H). IR (KBr) *v*: 3249, 1673, 1604, 1493, 1145, 768, 622 cm^{-1}. HRMS calcd for: $C_{16}H_{13}N_4O_4^-$ $[M-H]^-$: 325.0931, found: 325.0936.



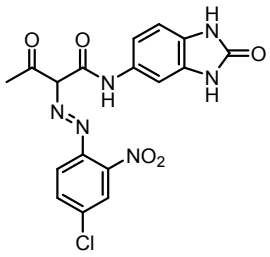
20, Pigment Yellow 203:[20] 1.79 g, >99%, ^1H NMR (400 MHz, $CDCl_3$, two isomers in a 70:30 ratio) δ 15.83 (s, 0.67H), 11.66 (s, 0.7H), 11.09 (s, 0.3H), 8.55 (d, *J* = 7.9 Hz, 0.7H), 8.43 (d, *J* = 7.7 Hz, 0.3H), 8.07 (s, 0.7H), 8.02 (s, 0.3H), 7.96 (d, *J* = 8.6 Hz, 0.7H), 7.79 (d, *J* = 8.6 Hz, 0.3H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.16-7.12 (m, 1H), 6.97-7.01 (m, 1H), 6.91-6.93 (m, 1H), 3.98 (s, 3H), 2.63 (s, 2.3H), 2.41 (s, 3.4H). IR (KBr) *v*: 3310, 3080, 1676, 1503, 1343, 1170, 1027, 803, 760 cm^{-1}. HRMS calcd for: $C_{18}H_{17}N_4O_5^-$ $[M-H]^-$: 369.1193, found: 369.1196.



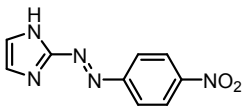
21, Pigment Yellow 73:[6] 1.89 g, >99%,[1]H NMR (400 MHz, $CDCl_3$, two isomers in a 65:35 ratio) δ 15.90 (s, 0.89H), 11.63 (s, 0.65H), 11.11 (s, 0.35H), 8.54 (d, *J* = 8.0 Hz, 0.65H), 8.43 (d, *J* = 7.9 Hz, 0.35H), 8.28 (s, 0.65H), 8.24 (s, 0.35H), 8.04 (d, *J* = 9.1 Hz, 0.6H), 7.87 (d, *J* = 9.1 Hz, 0.4H), 7.61-7.67 (m, 1.0H), 7.10-7.14 (m, 1H), 6.98-7.03 (m, 1H), 6.92-6.94 (m, 1H), 3.98 (s, 3H), 2.64 (s, 3H). IR (KBr) *v*: 3260, 3119, 1674, 1497, 1280, 1142, 799, 755 cm^{-1}. HRMS calcd for: $C_{17}H_{14}ClN_4O_5^-$ $[M-H]^-$: 389.0647, found: 389.0648.



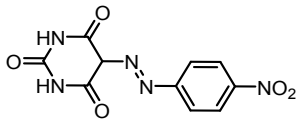
22, Pigment Orange 62:[21] 1.64 g, >99%, ^{1}H NMR (400 MHz, DMSO-d_6 , two isomers in a 75:25 ratio) δ 13.06 (s, 0.75H), 11.67 (s, 0.25H), 10.54-10.84 (m, 2.75H), 9.99 (s, 0.25H), 8.27 (d, *J* = 8.7 Hz, 1.75H), 8.19 (d, *J* = 8.6 Hz, 0.5H), 7.70 (d, *J* = 8.7 Hz, 1.5H), 7.58 (d, *J* = 12 Hz, 0.75H), 7.39 (d, *J* = 8.6 Hz, 0.5H), 7.23 (d, *J* = 8.3 Hz, 0.25H), 7.05 (d, *J* = 8.3 Hz, 0.75H), 6.87-6.95 (m, 1H). 2.59 (s, 3H). IR (KBr) *v*: 3280, 3125, 1709, 1501, 1337, 1162, 1108, 853, 808, 707 cm^{-1}. HRMS calcd for: $C_{17}H_{13}N_6O_5^-$ $[M-H]^-$: 381.0942, found: 381.0940.



23, Pigment Orange 36:[22] 1.79 g, >99%, ^{1}H NMR (400 MHz, DMSO-d_6 , two isomers in a 50:50 ratio) δ 14.95 (s, 0.64H), 11.44 (s, 0.5H), 10.98 (s, 0.5H), 10.63-10.68 (m, 1.5H), 10.56 (s, 0.5H), 10.03 (s, 0.5H), 8.27-8.29 (m, 1H), 8.13-8.15 (m, 1H), 7.91-7.96 (m, 1H), 7.76-7.79 (m, 0.5H), 7.53-7.61 (m, 1H), 7.24 (d, *J* = 8.5 Hz, 0.5H), 7.04-7.07 (m, 0.5H), 6.85-6.95 (m, 1H), 2.59 (s, 3H). IR (KBr) *v*: 3210, 1711, 1495, 1342, 1282, 1194, 1143, 805, 709 cm^{-1}. HRMS calcd for: $C_{17}H_{12}ClN_6O_5^-$ $[M-H]^-$: 415.0552, found: 415.0544.

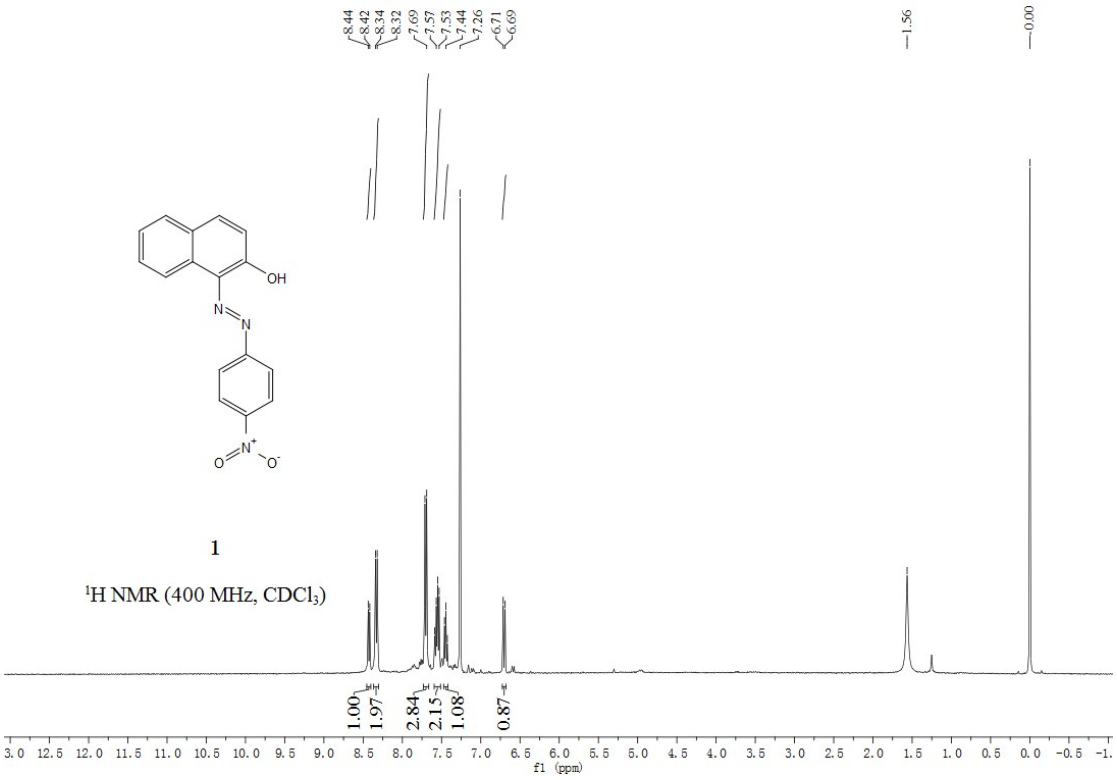


24, 2-(*p*-Nitrophenylazo)imidazole:[23] 3.99 g, >99%, ^{1}H NMR (400 MHz, DMSO-d_6 , two isomers in a 90:10 ratio) δ 13.34 (s, 0.9H), 12.99 (s, 0.1H), 8.43 (d, *J* = 8.7 Hz, 1.8H), 8.39 (d, *J* = 8.8 Hz, 0.2H), 8.04 (d, *J* = 8.7 Hz, 1.8H), 7.96 (d, *J* = 8.7 Hz, 0.2H), 7.71 (d, *J* = 8.7 Hz, 0.2H), 7.51 (d, *J* = 35.4 Hz, 1.8H). ^{13}CNMR (101 MHz, DMSO-d_6) δ 155.9, 155.2, 148.7, 133.7, 125.6, 123.6, 123.2, 122.1, 101.2. IR (KBr) *v*: 3019, 2986, 2880, 2772, 1595, 1520, 1336, 1097, 903, 855, 783 cm^{-1}.



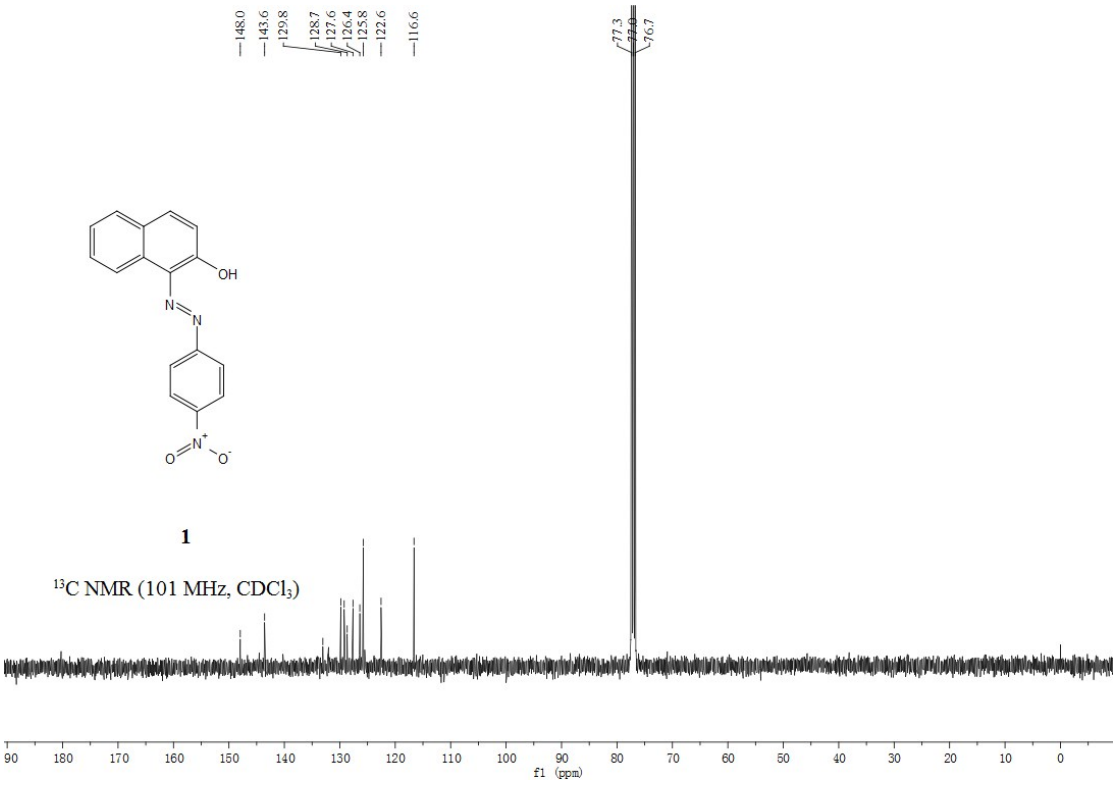
25, 5-(*p*-nitrophenylazo)barbituric acid:[24] 2.18 g, >99%, ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.94 (s, 1H), 11.65 (s, 1H), 11.43 (s, 1H), 8.30-8.33 (m, 2H), 7.79 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.1, 159.9, 150.21, 147.4, 144.31, 126.1, 121.3, 117.2. IR (KBr) *v*: 3461, 3067, 2833, 1734, 1517, 1445, 1340, 1237, 1107, 850, 804, 513cm^{-1}.

4. ^{1}H NMR and ^{13}C NMR spectra for all compounds



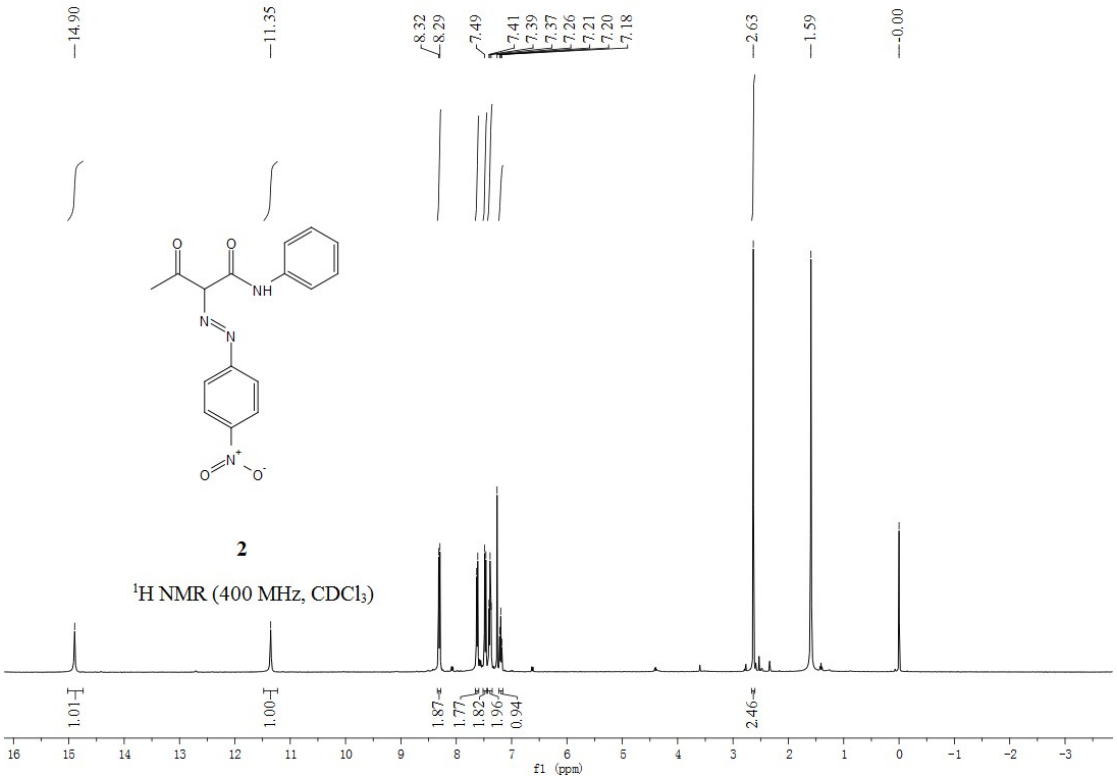
1

^{1}H NMR (400 MHz, $CDCl_3$)



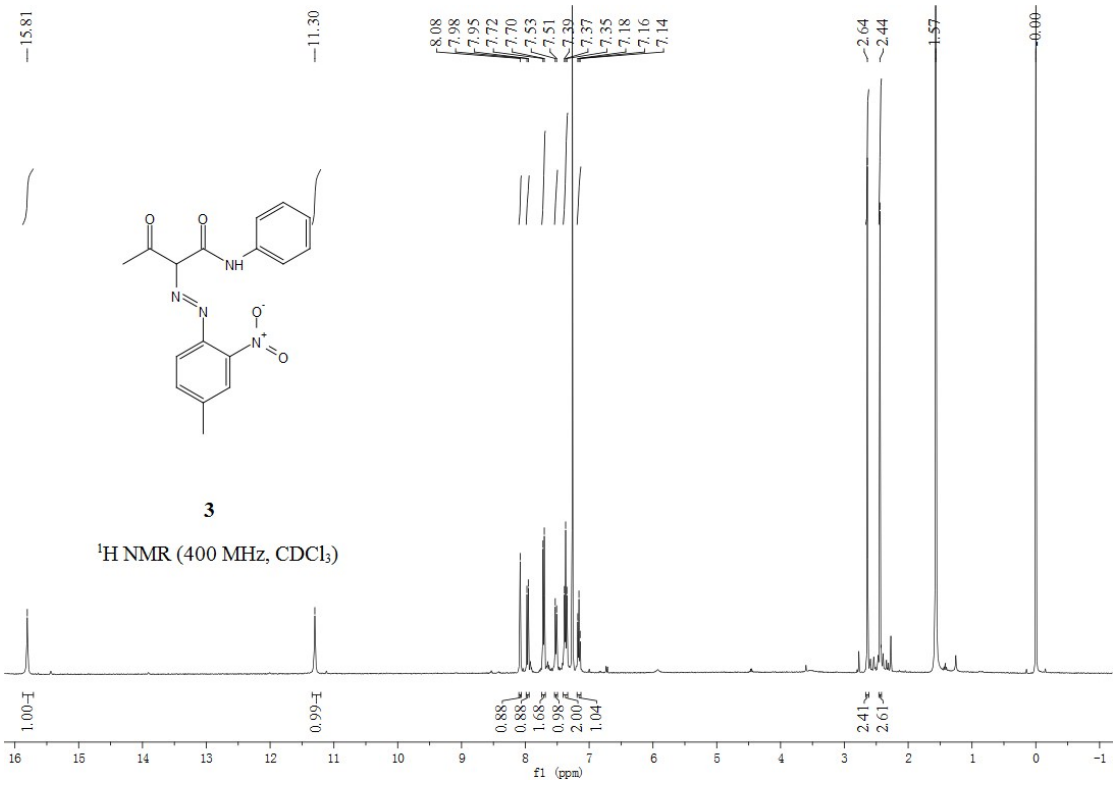
1

^{13}C NMR (101 MHz, $CDCl_3$)



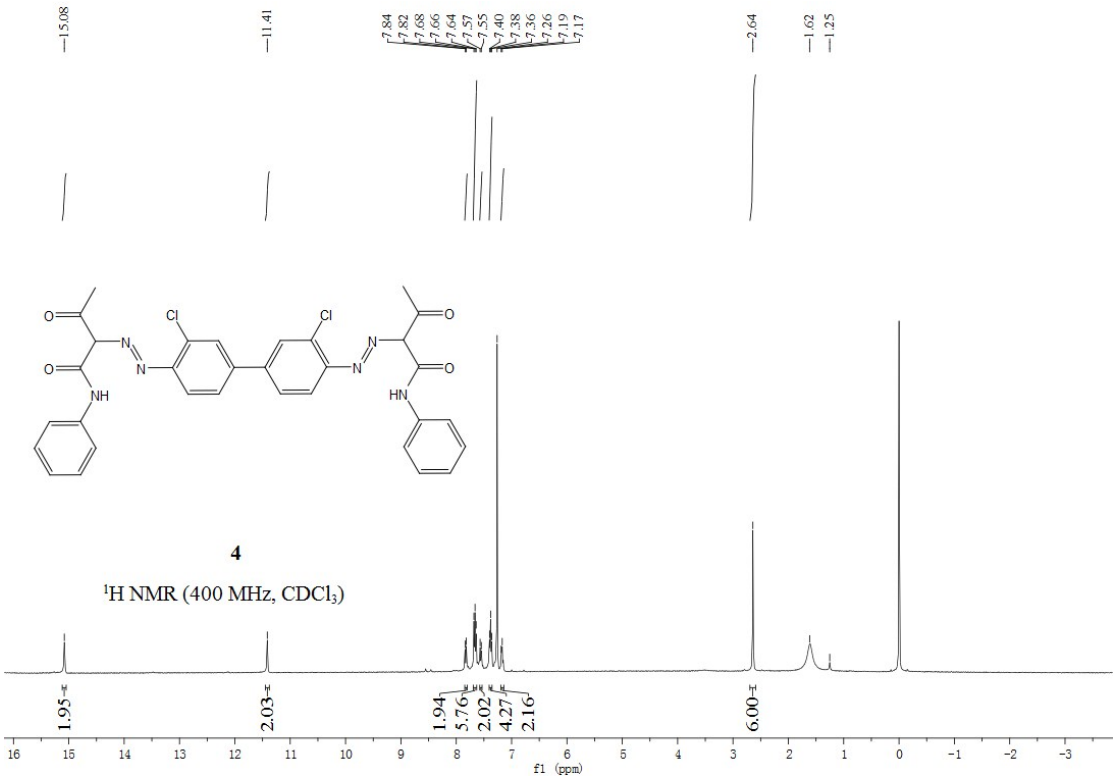
2

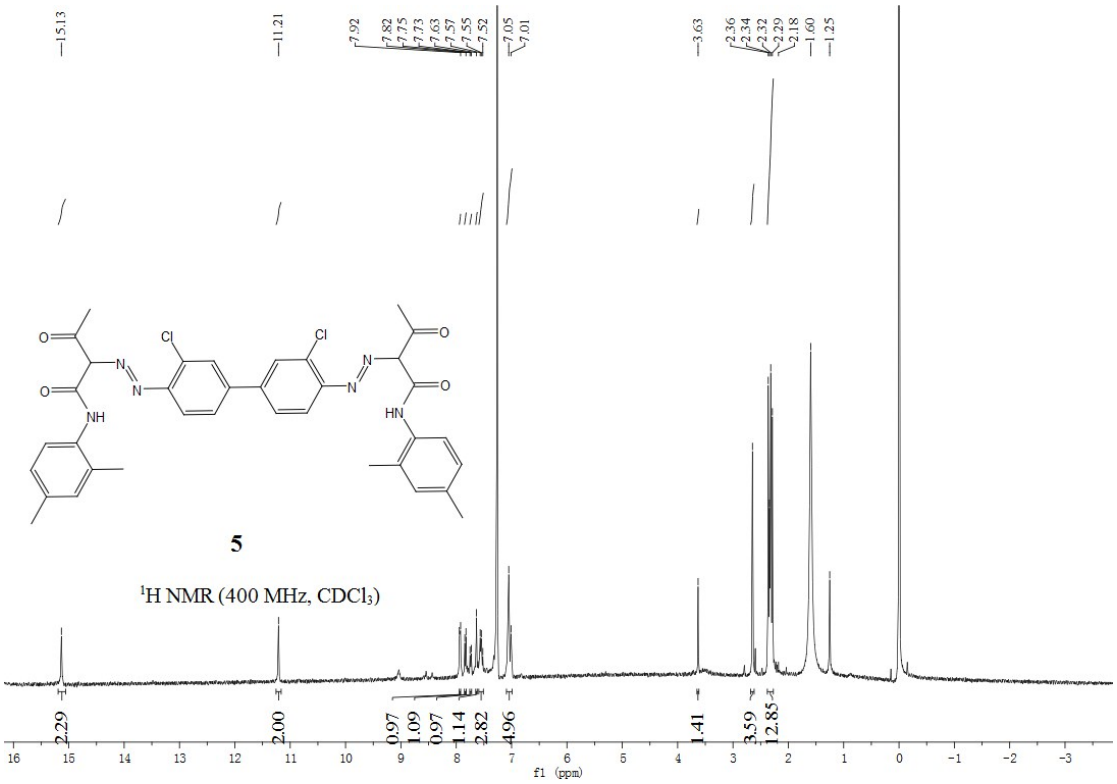
^{1}H NMR (400 MHz, $CDCl_3$)

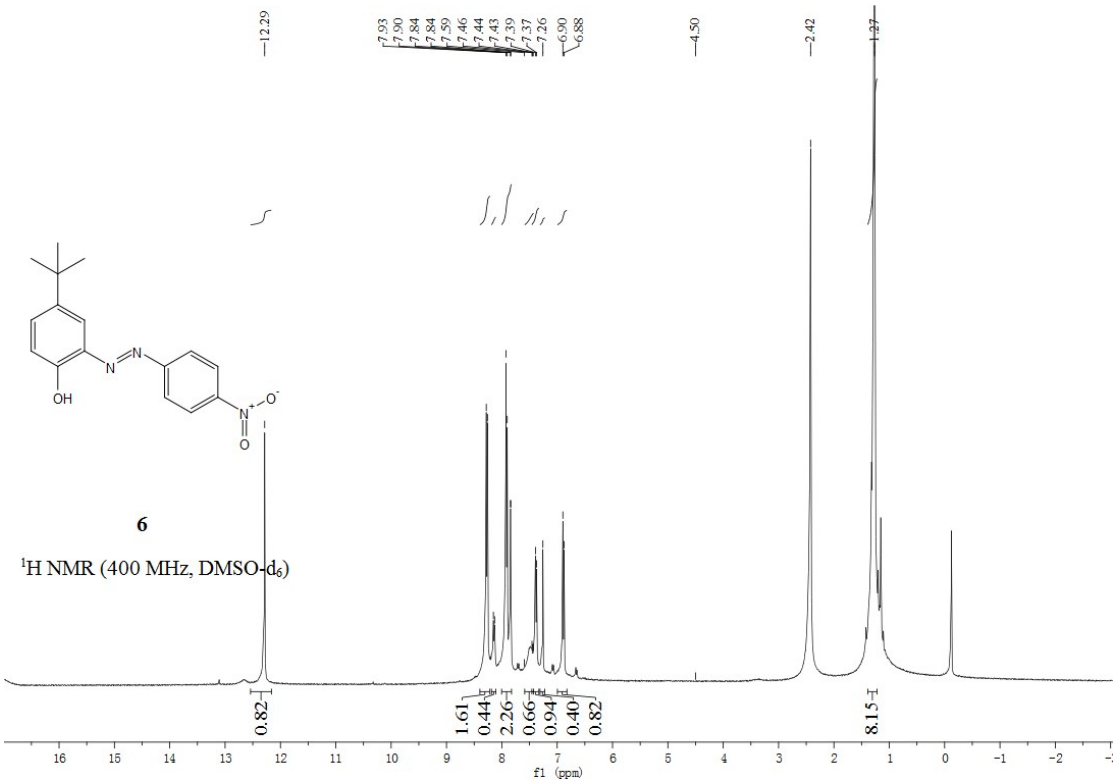


3

^{1}H NMR (400 MHz, $CDCl_3$)

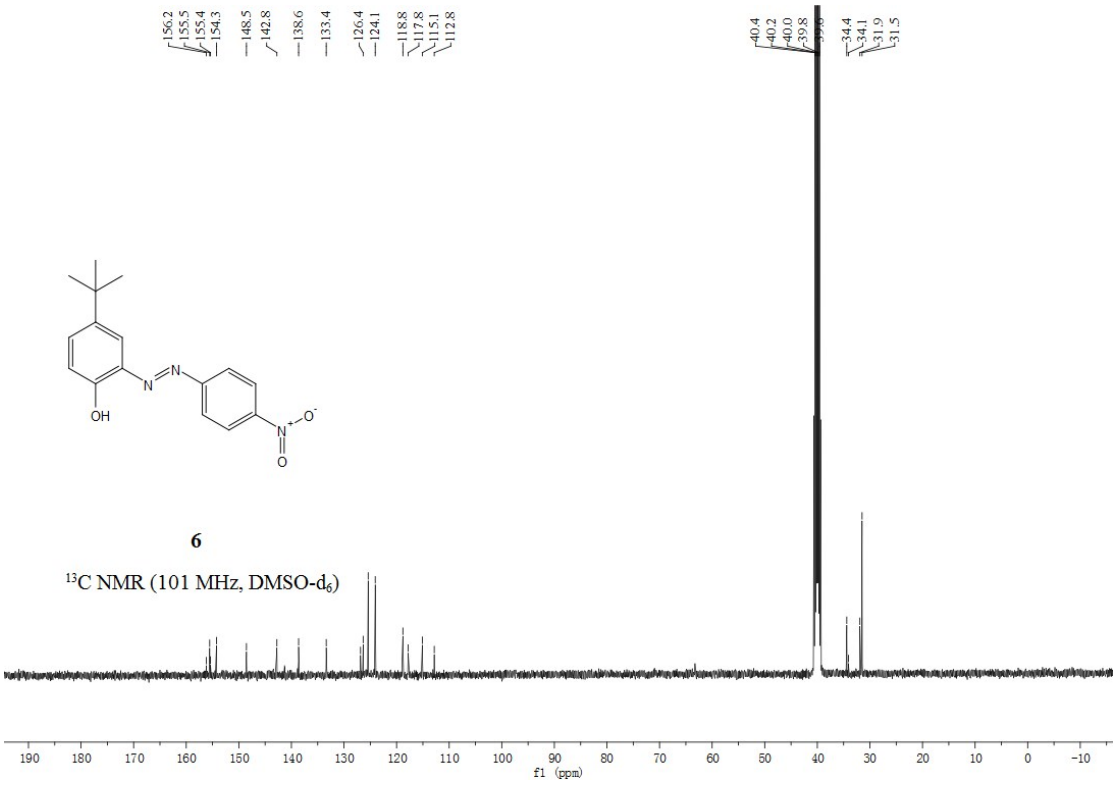

15.08
11.41
7.84
7.82
7.68
7.66
7.64
7.57
7.55
7.40
7.38
7.36
7.26
7.19
7.17
2.64
1.62
1.25
Cl
Cl
O
O
N
N
NH
HN
4
1H NMR (400 MHz, CDCl3)
1.95
2.03
1.94
5.76
2.02
4.27
2.16
6.00
f1 (ppm)


15.13
11.21
7.92
7.82
7.75
7.73
7.63
7.57
7.55
7.52
7.05
7.01
3.63
2.36
2.34
2.32
2.29
2.18
1.60
1.25
Cl
Cl
O
O
N
N
NH
HN
5
1H NMR (400 MHz, CDCl3)
2.29
2.00
0.97
1.09
0.97
1.14
2.82
4.96
1.41
3.59
12.85
f1 (ppm)



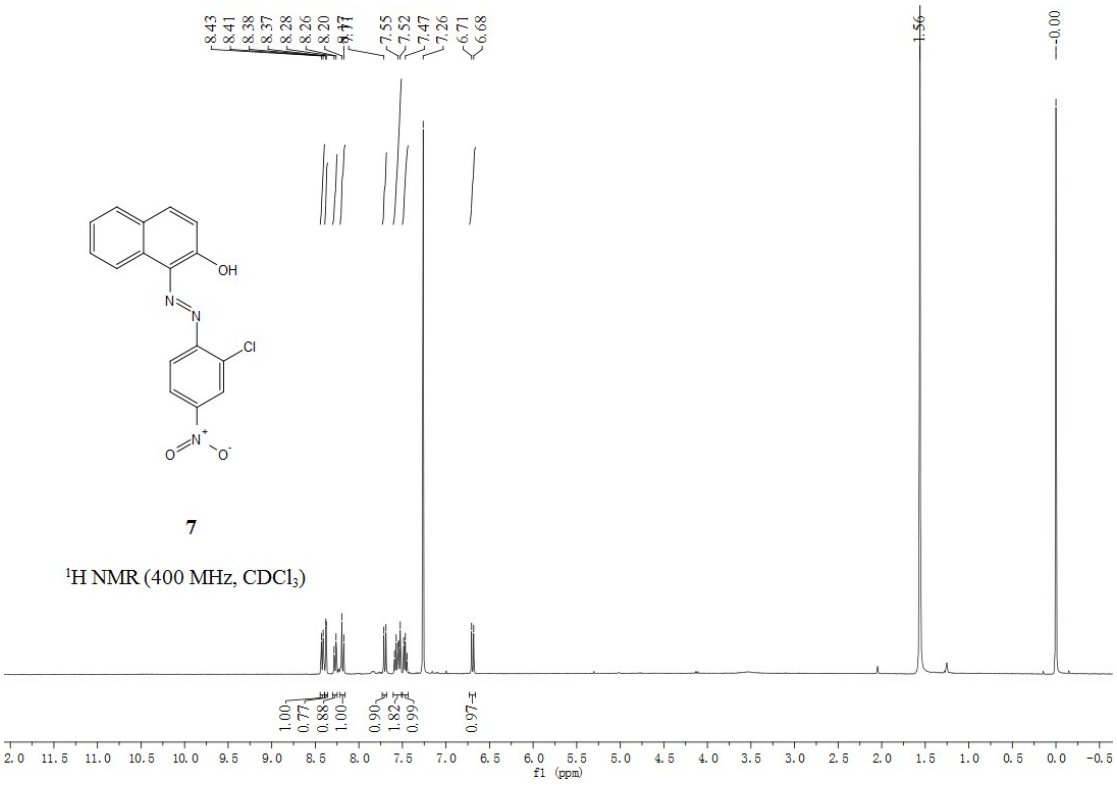
6

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



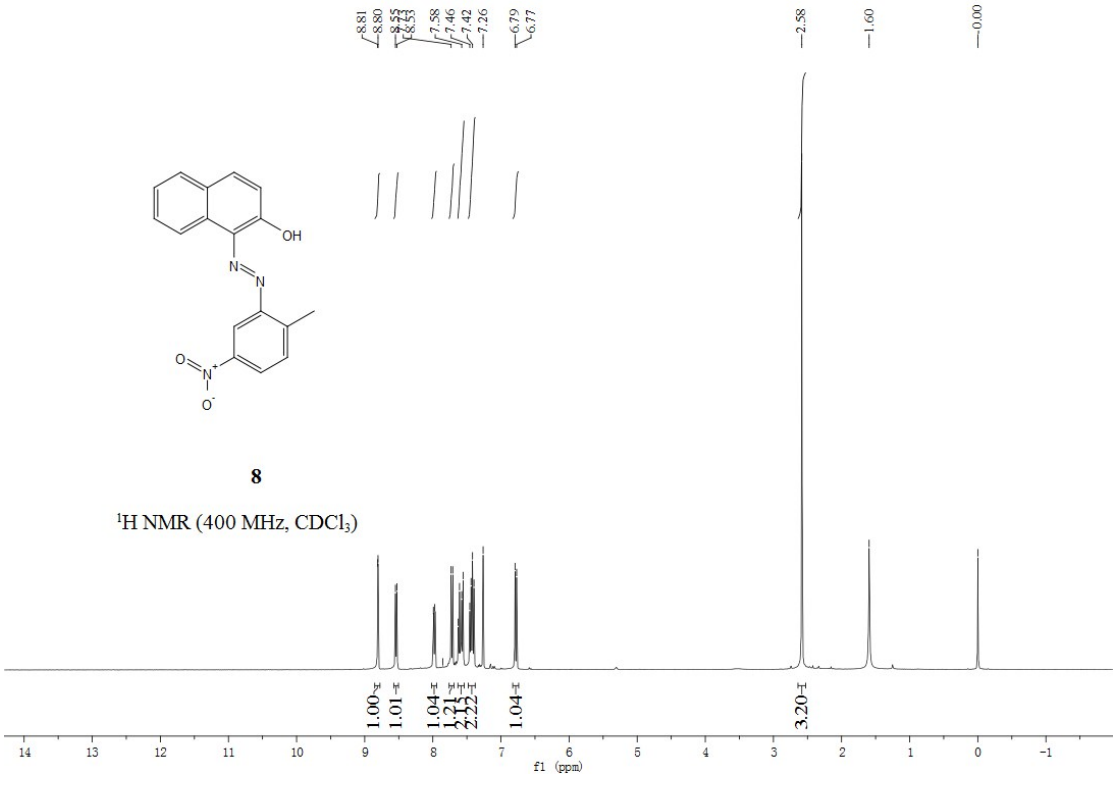
6

^{13}C NMR (101 MHz, DMSO-d_6)



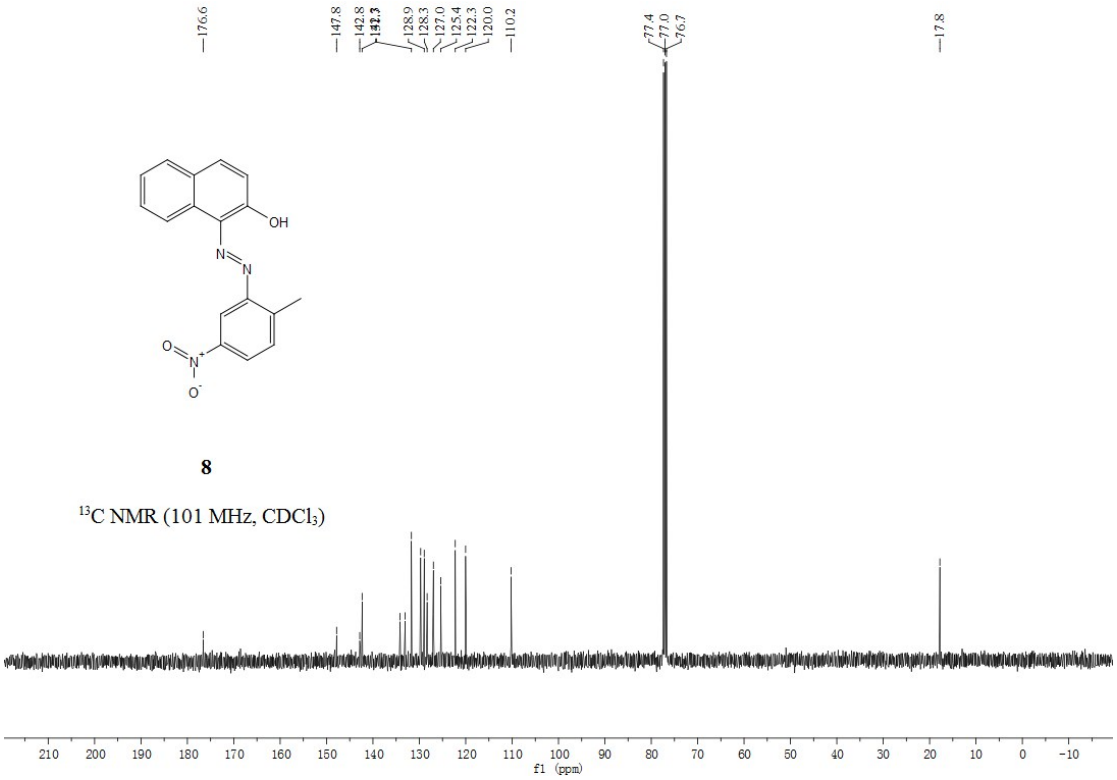
7

^{1}H NMR (400 MHz, $CDCl_3$)



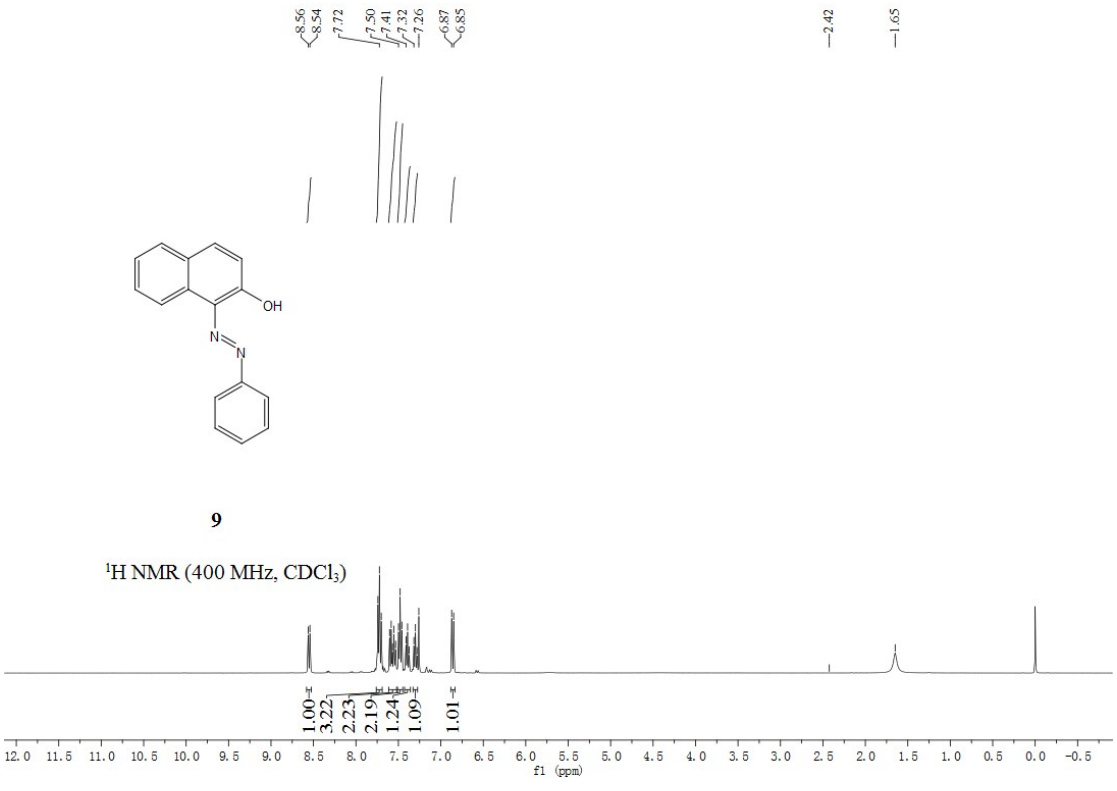
8

^{1}H NMR (400 MHz, $CDCl_3$)



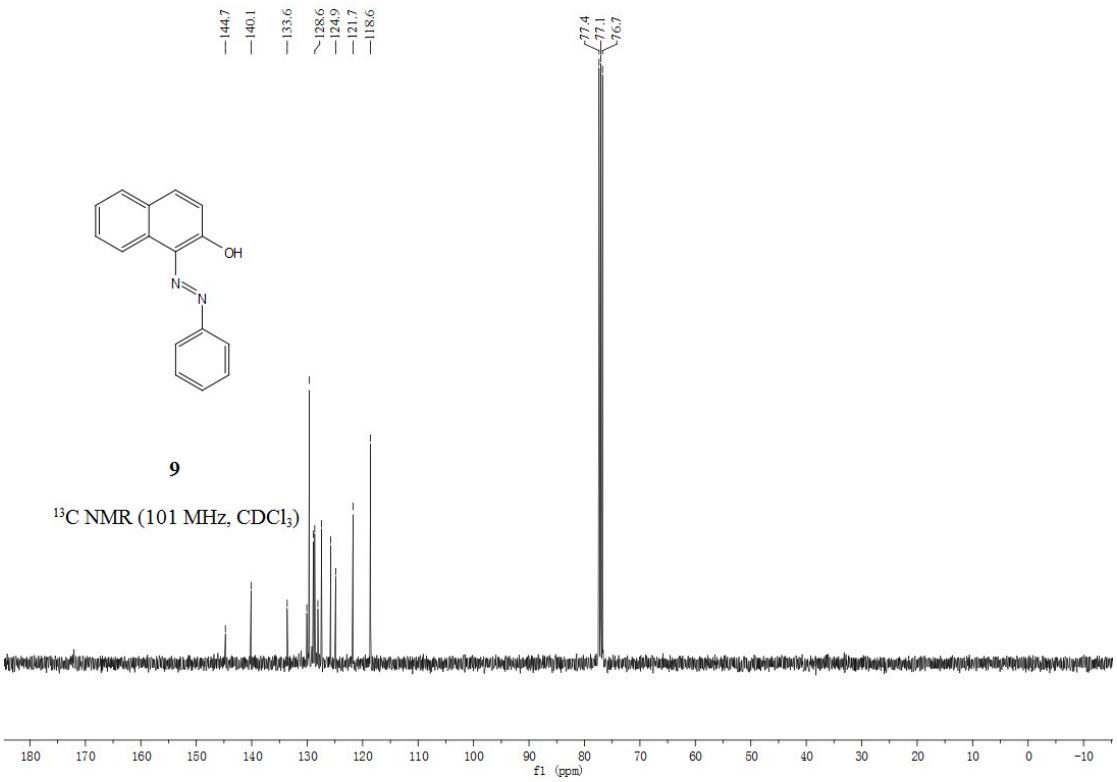
8

^{13}C NMR (101 MHz, $CDCl_3$)



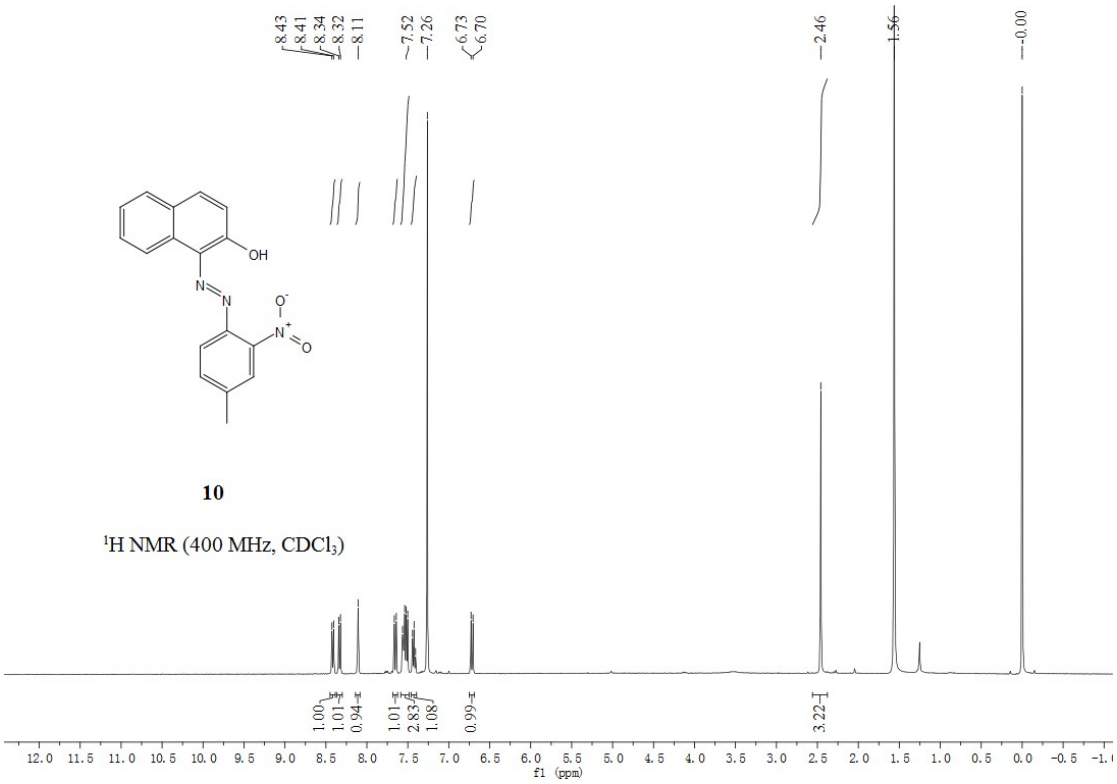
9

^{1}H NMR (400 MHz, $CDCl_3$)



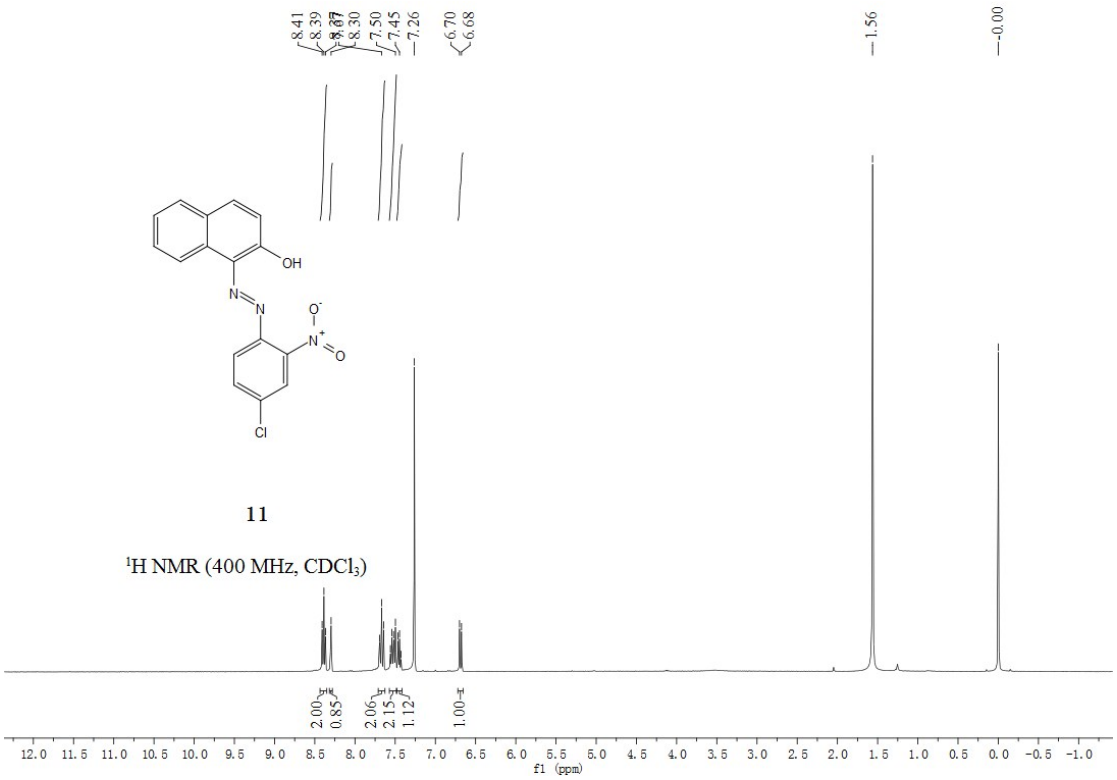
9

^{13}C NMR (101 MHz, $CDCl_3$)



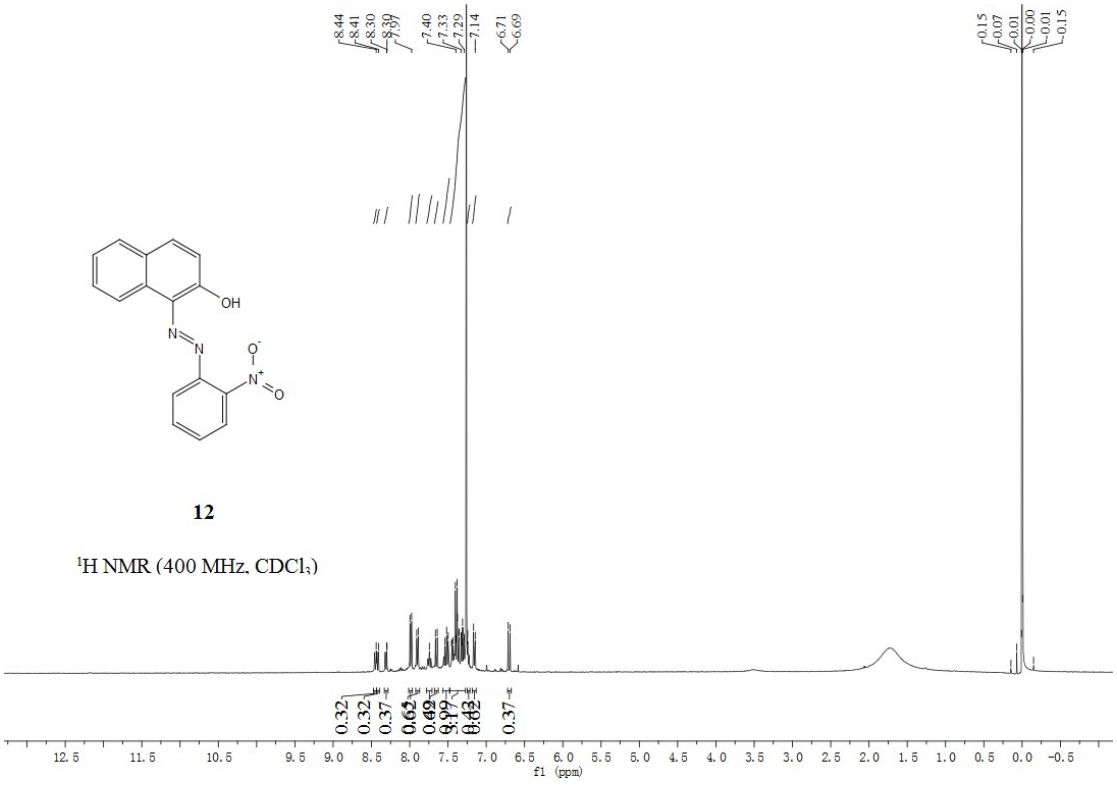
10

^{1}H NMR (400 MHz, $CDCl_3$)



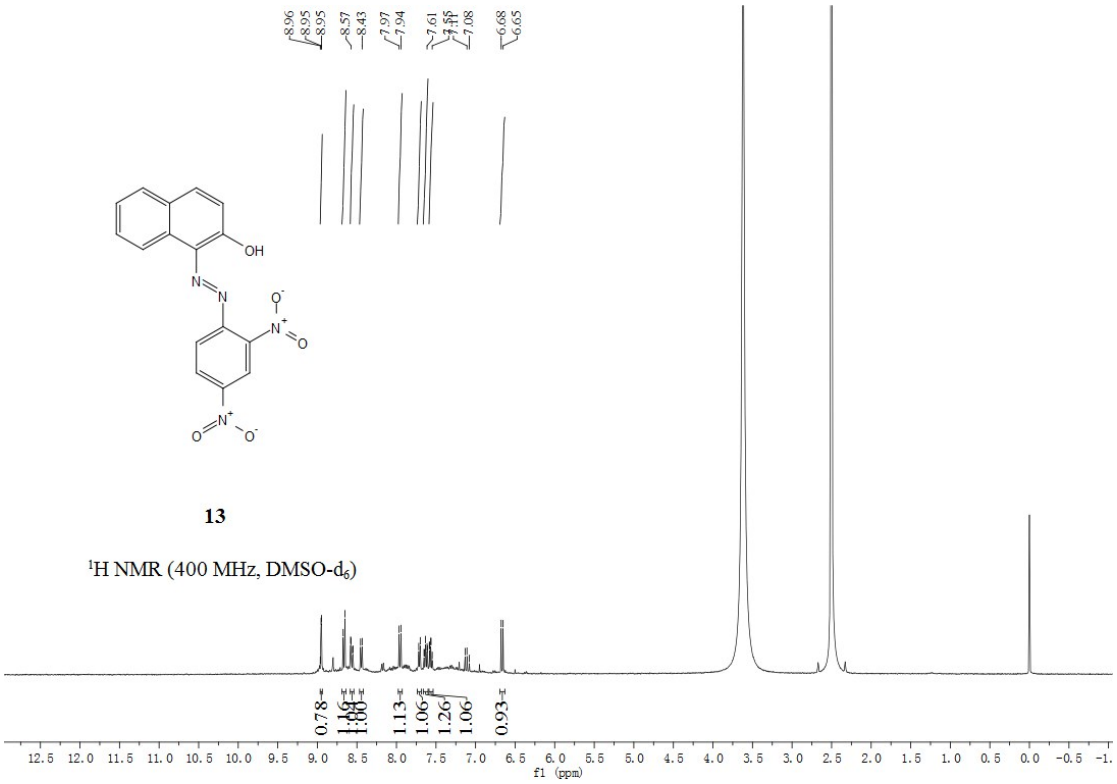
11

^{1}H NMR (400 MHz, $CDCl_3$)



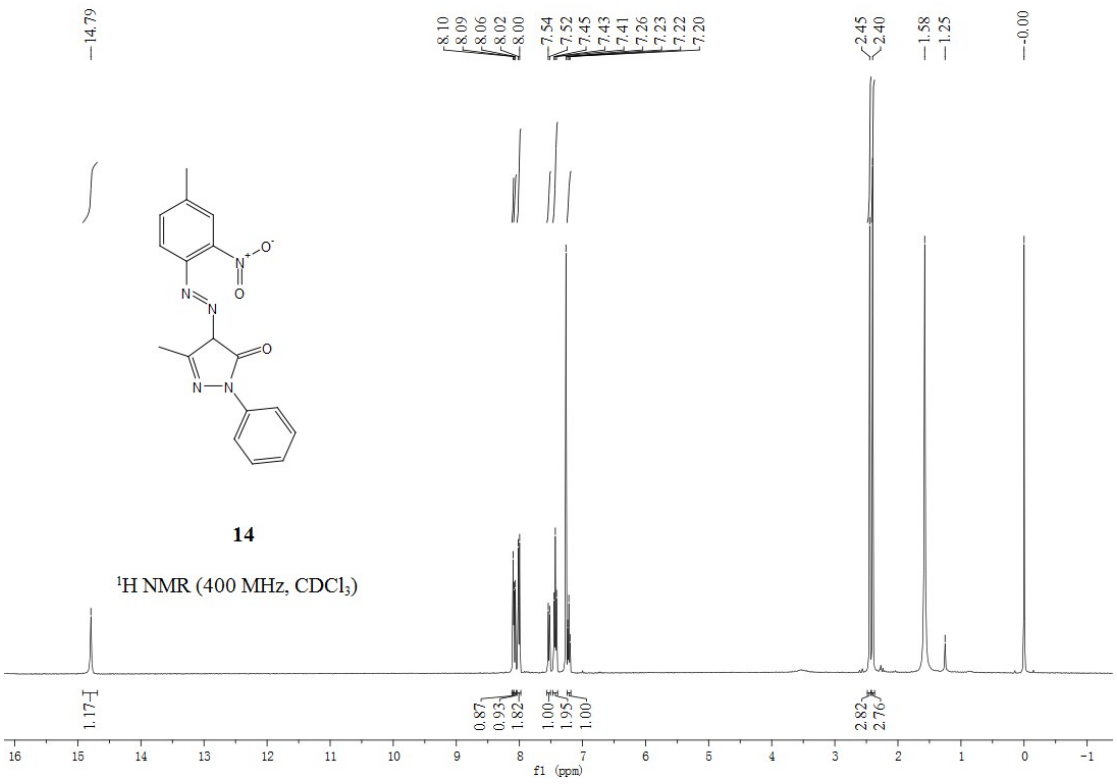
12

^{1}H NMR (400 MHz, $CDCl_3$)



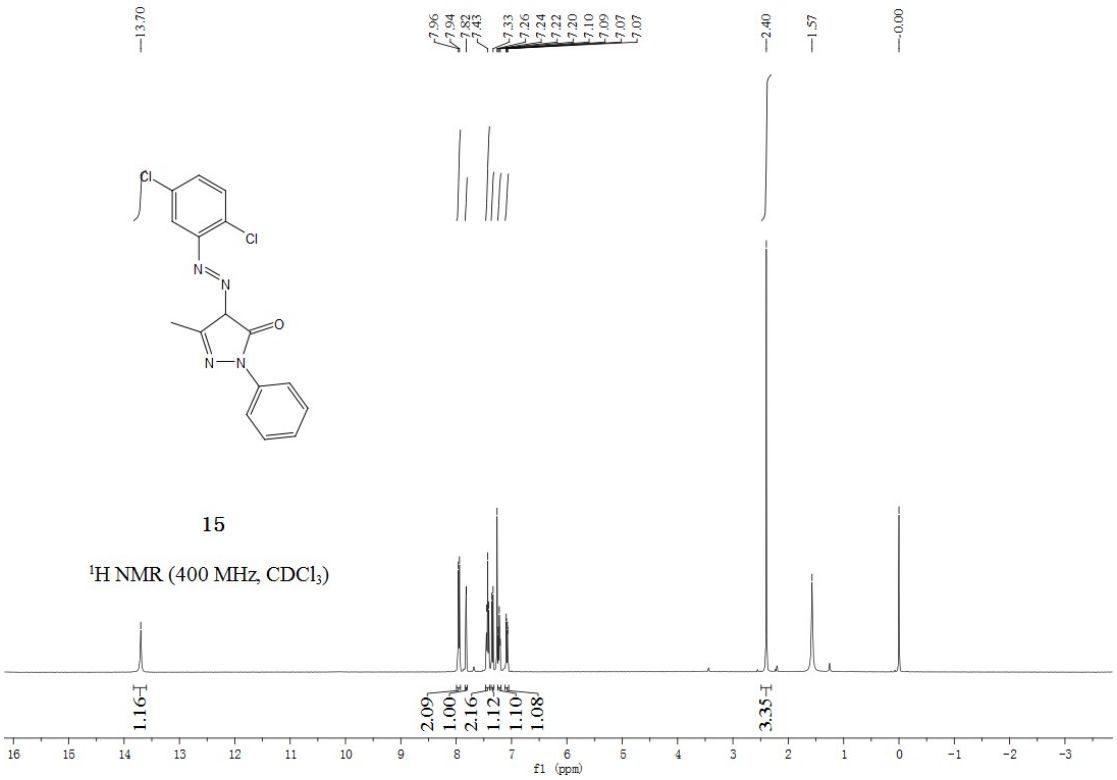
13

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



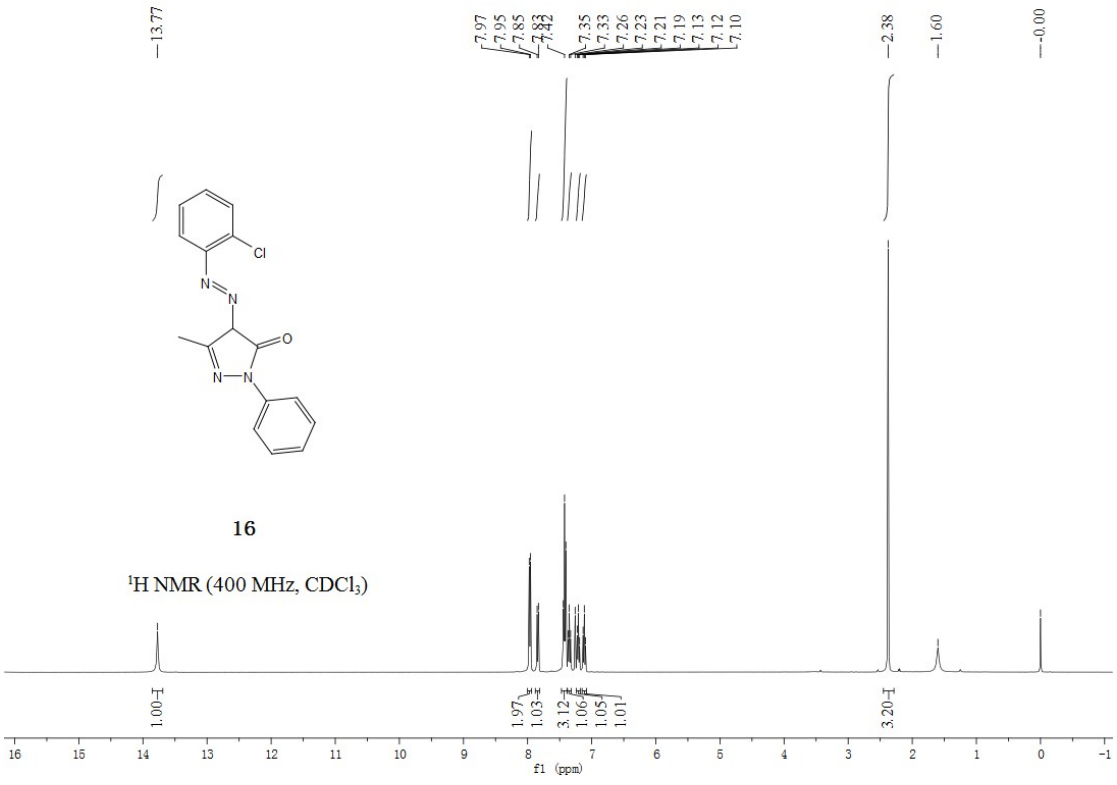
14

^{1}H NMR (400 MHz, $CDCl_3$)



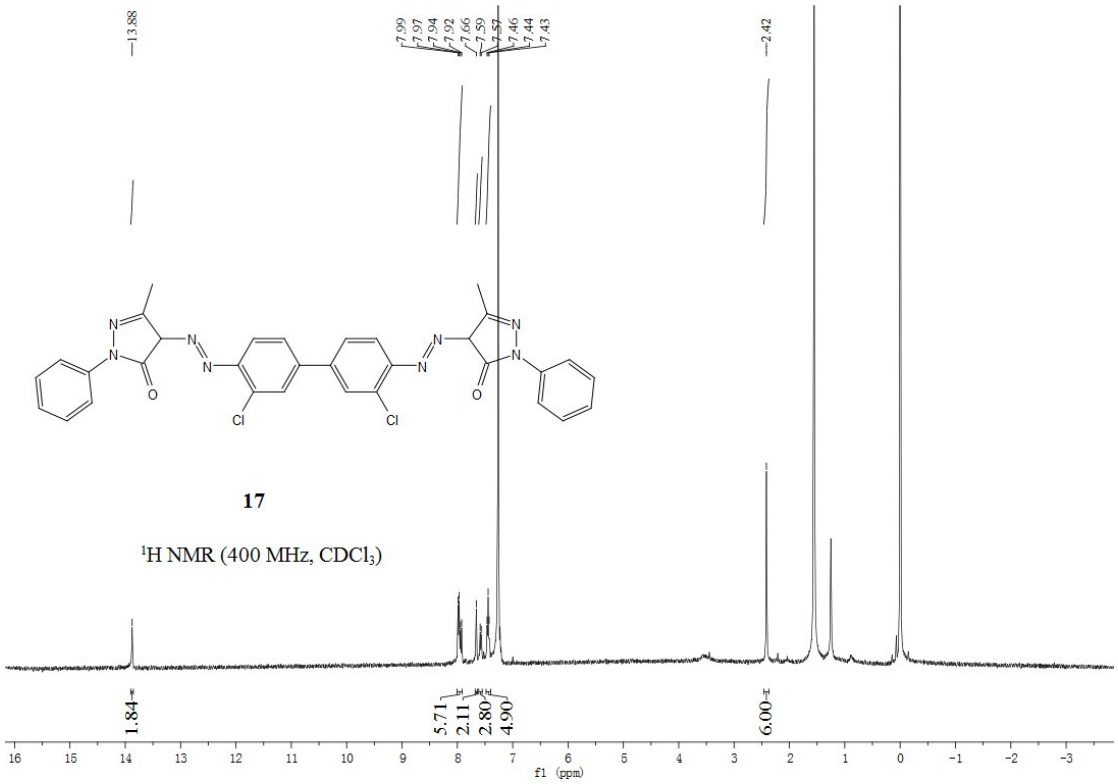
15

^{1}H NMR (400 MHz, $CDCl_3$)



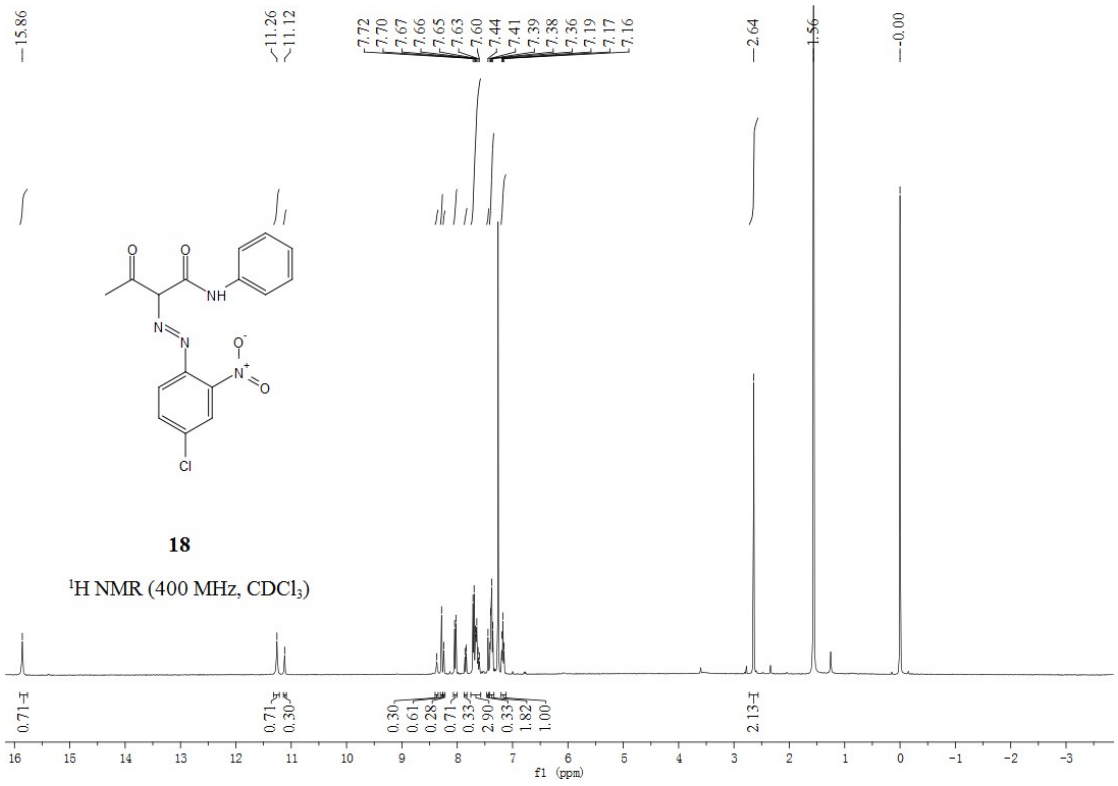
16

^{1}H NMR (400 MHz, $CDCl_3$)



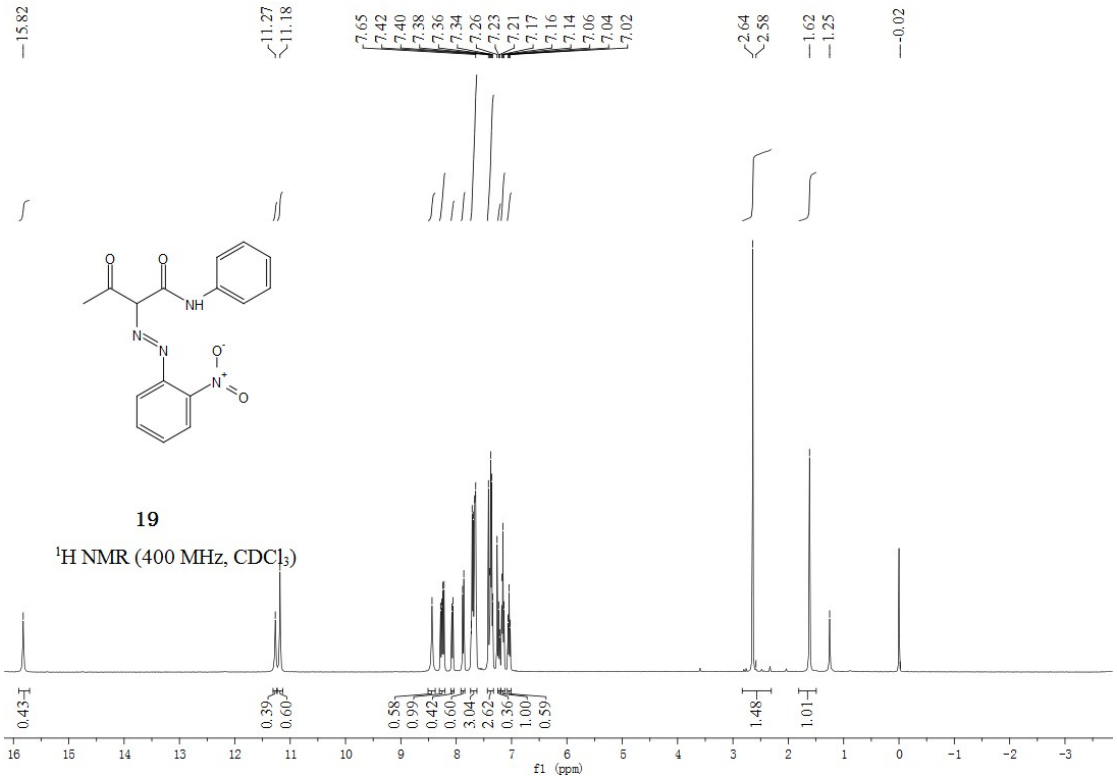
17

^{1}H NMR (400 MHz, $CDCl_3$)



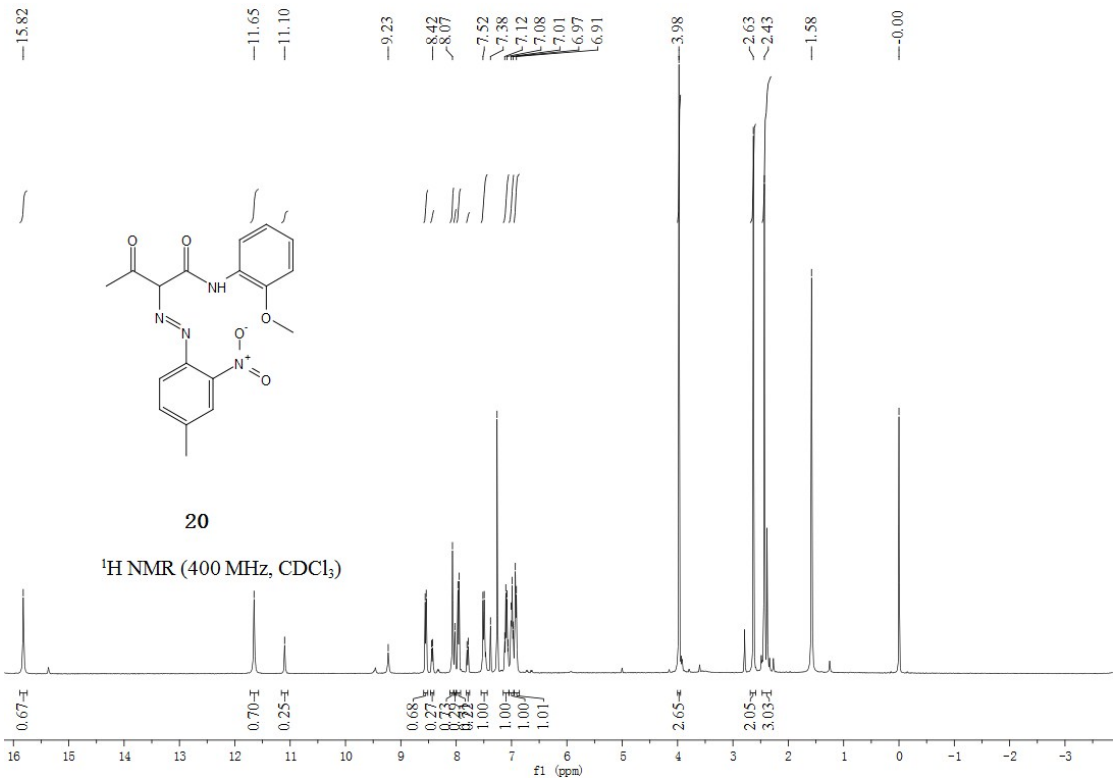
18

^{1}H NMR (400 MHz, $CDCl_3$)



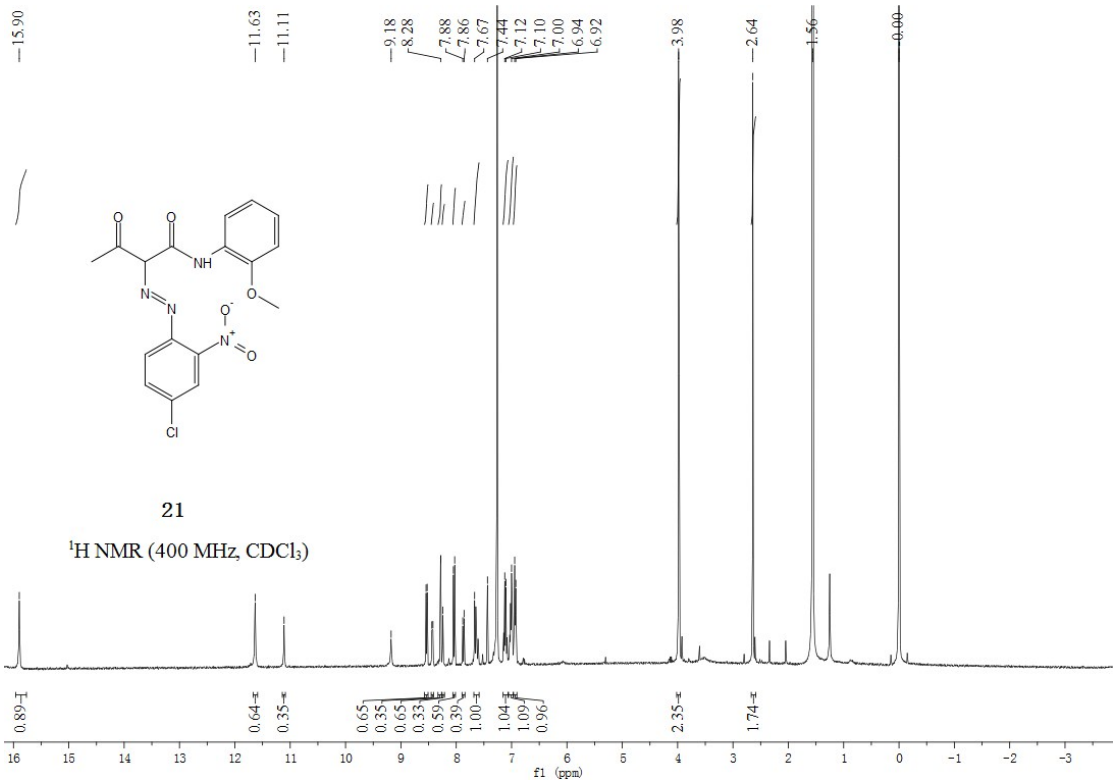
19

^{1}H NMR (400 MHz, $CDCl_3$)



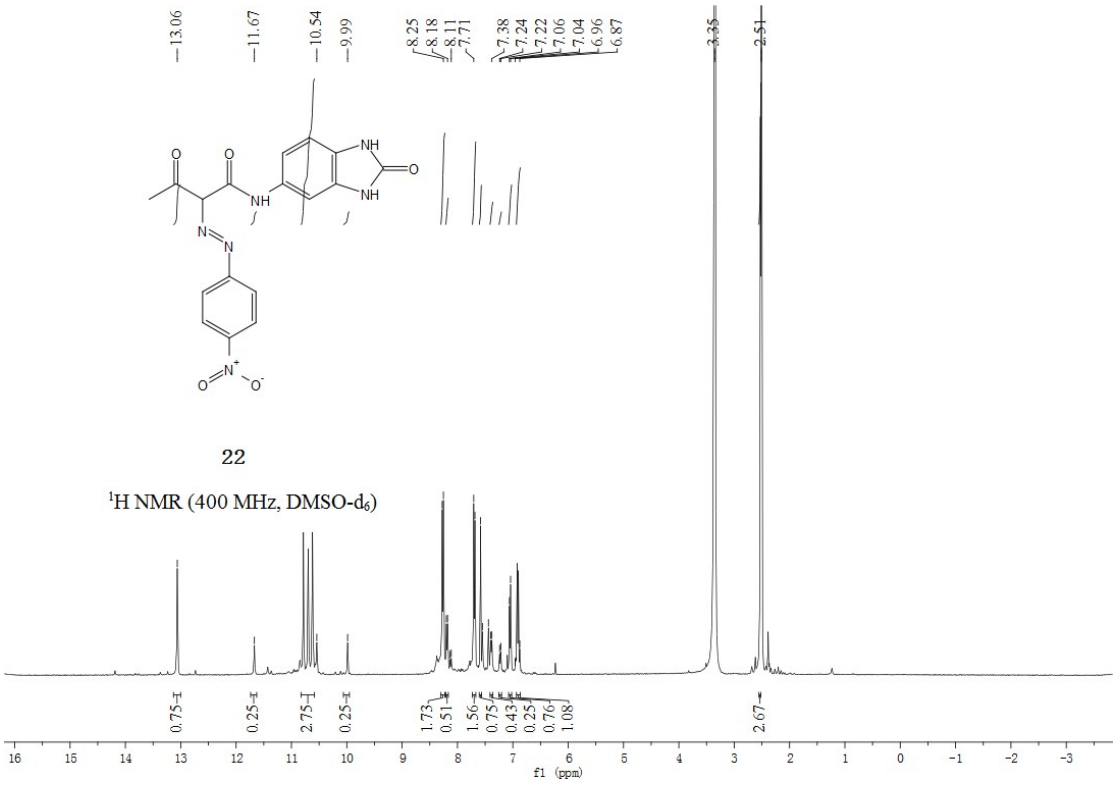
20

^{1}H NMR (400 MHz, $CDCl_3$)



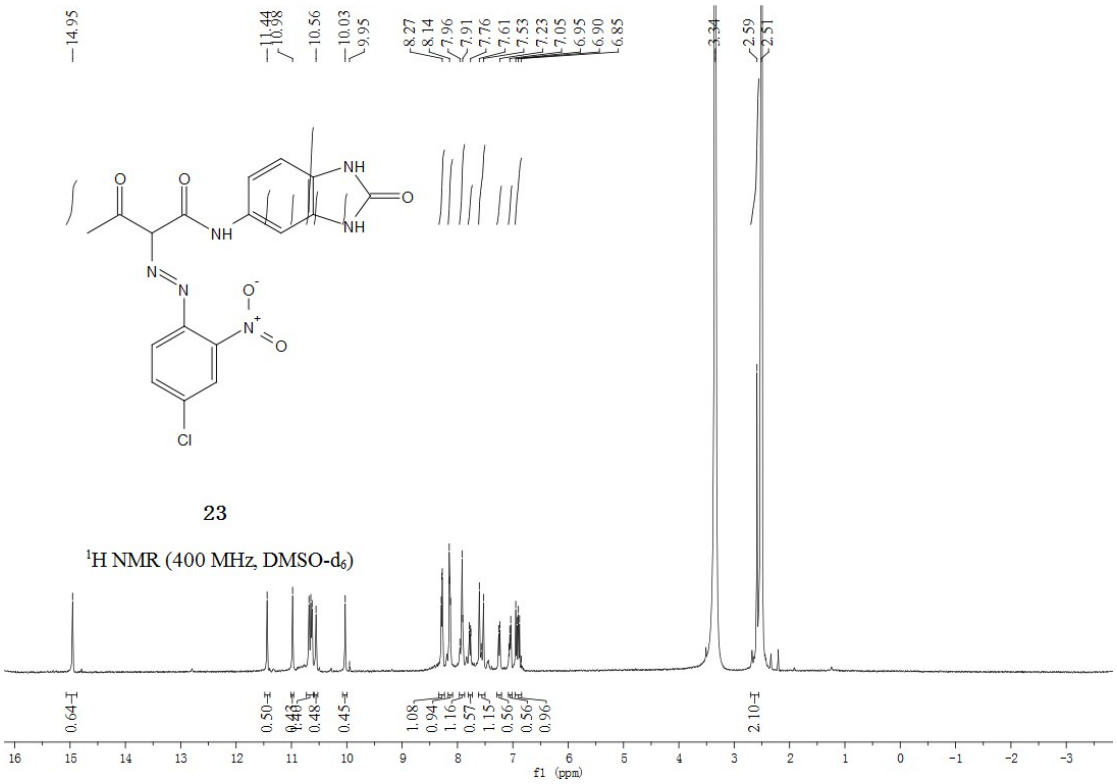
21

^{1}H NMR (400 MHz, $CDCl_3$)



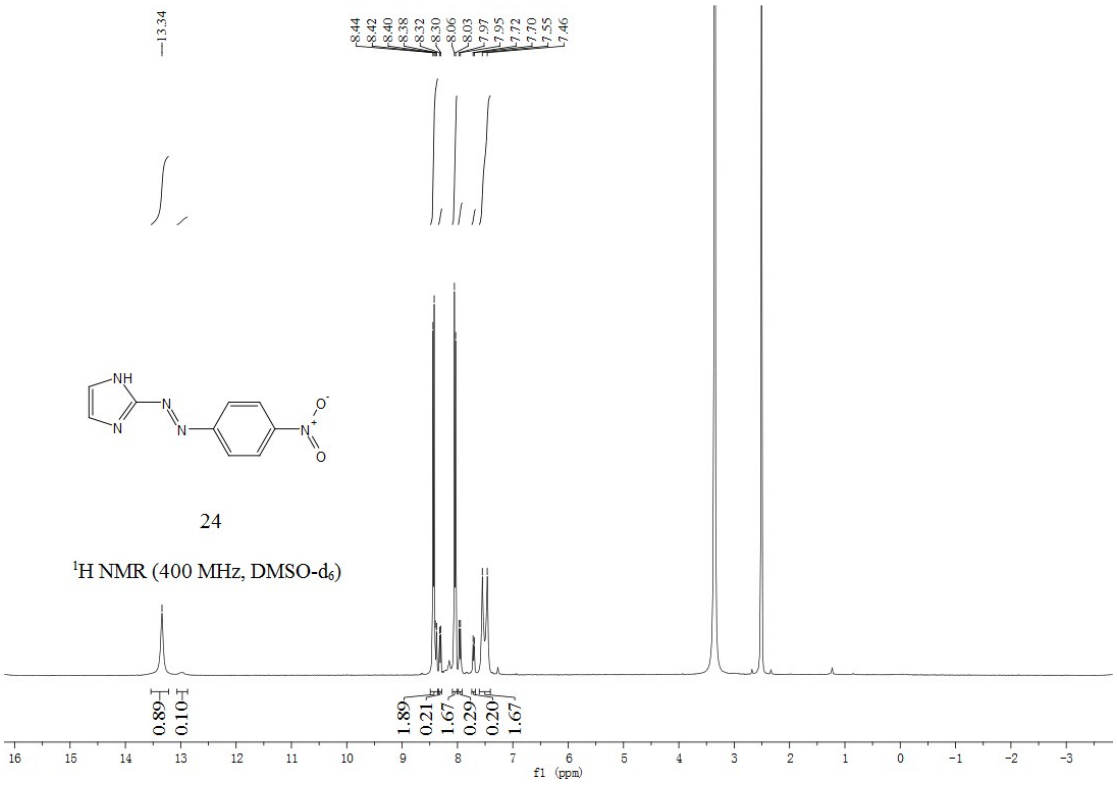
22

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



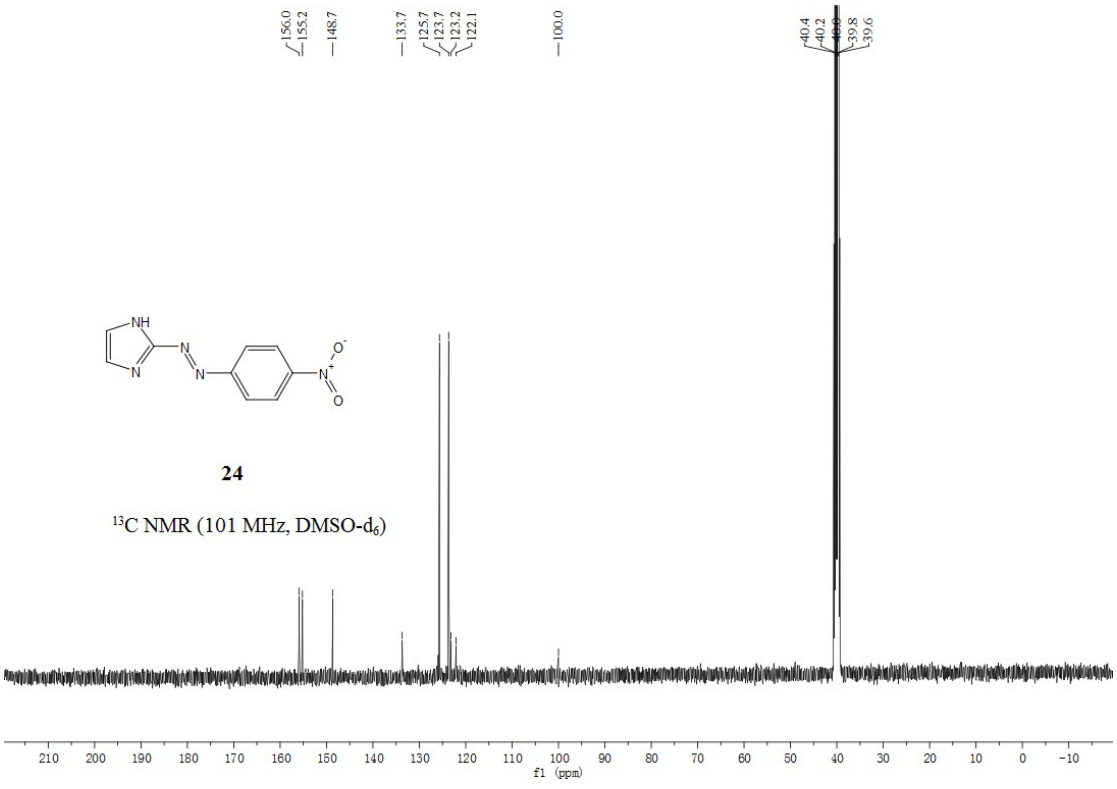
23

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



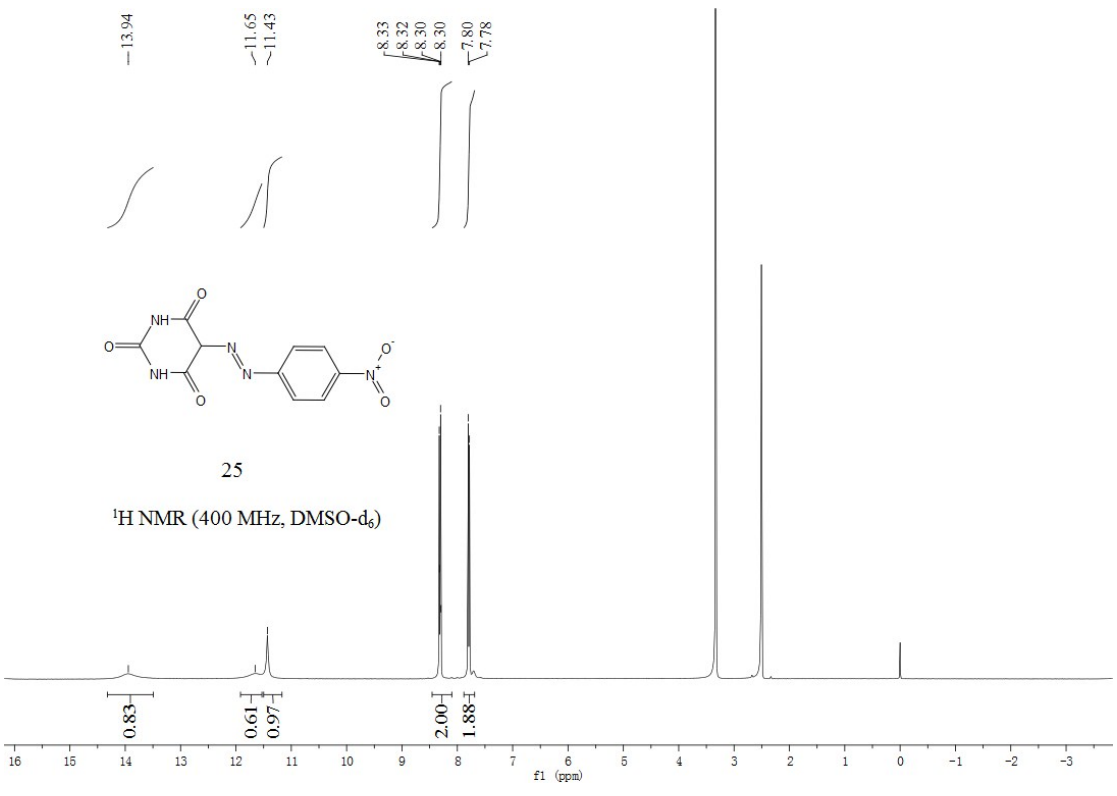
24

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



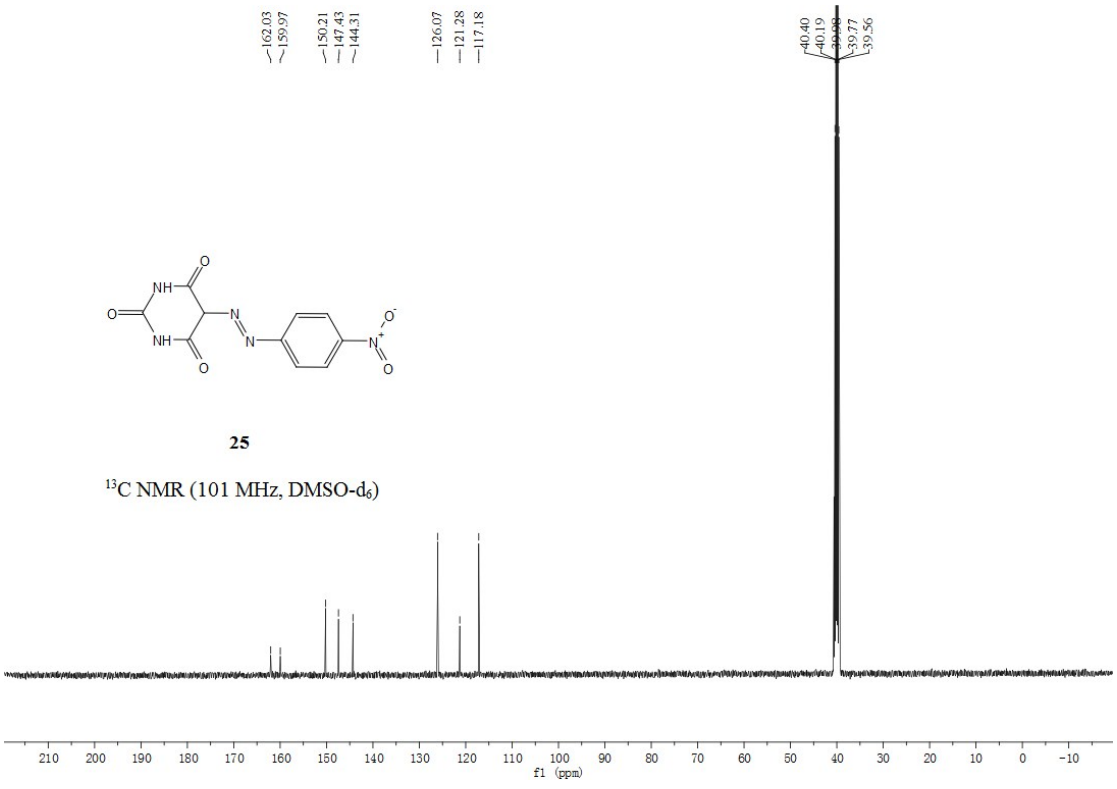
24

^{13}C NMR (101 MHz, DMSO-d_6)



25

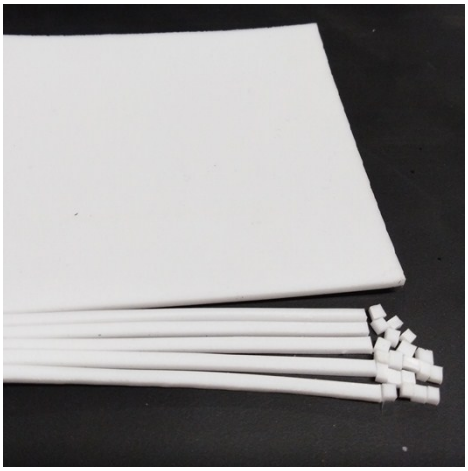
^{1}H NMR (400 MHz, DMSO-d_6)


162.03
159.97
150.21
147.43
144.31
126.07
121.28
117.18
40.40
40.19
39.98
39.77
39.56
NH
O
NH
O
N
N
O
N
O
O
25
13C NMR (101 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

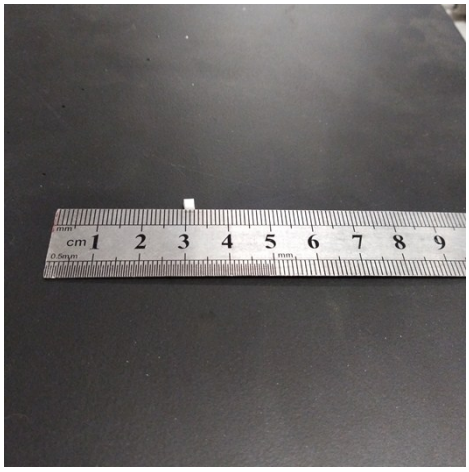
5. Pictures of the granular PTFE

Polytetrafluoroethylene (PTFE) has many unique properties including no self-coagulation, no electrostatic effect, a low friction coefficient, and tolerances to acids, bases, reducing and oxidizing reagents.[25,26] PTFE plate (10 cm x 10 cm x 2 mm, Picture 1) was cut into wires (Picture 2) and then into granules (*ca*. 2 mm x 2-3 mm x 2-3 mm, Pictures 3 and 4).

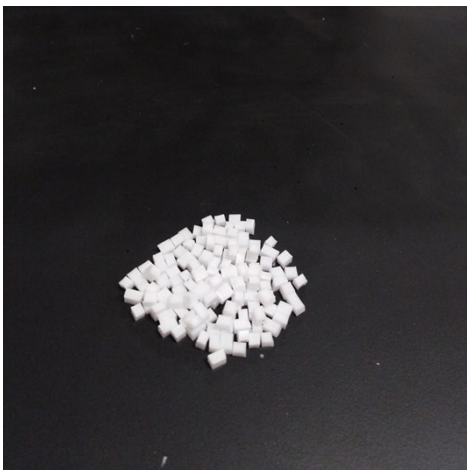
Picture 1



Picture 2



Picture 3



Picture 4

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