Room temperature diazotization and coupling reaction using DES-Ethanol system: A green approach towards the synthesis of monoazo pigments

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Supporting Information

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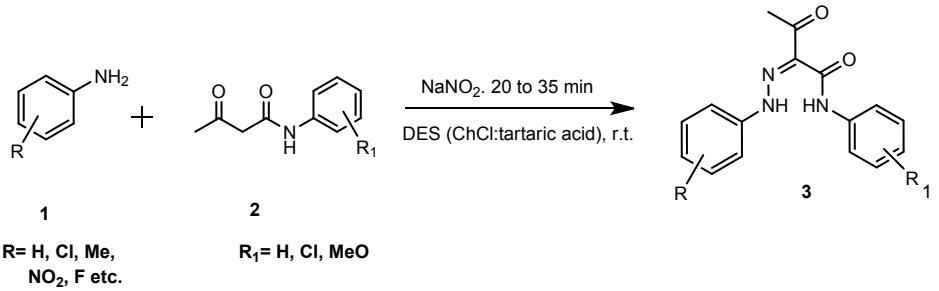
1. SYNTHESIS OF DERIVATIVES

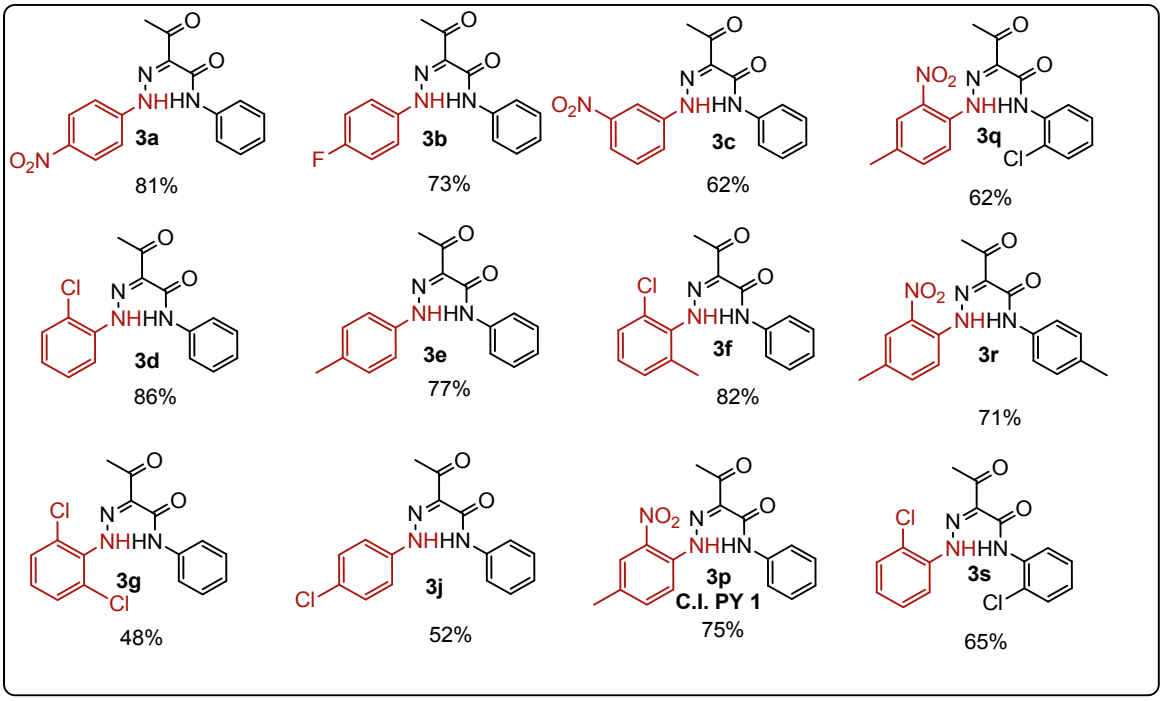
The versatility of DES with different amines and couplers was studied further following the optimized conditions, anilines (1 eq.), acetoacetanilide (1 eq.), $NaNO_2$ (1.1 eq.), DES (0.5 eq.)



and ethanol at room temperature. (Scheme ES 1).

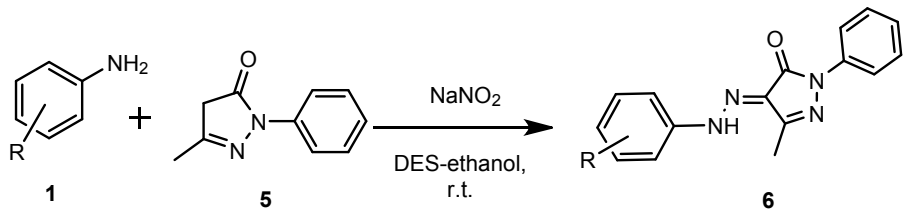
Scheme ES 1 Synthesis of monoazo arylide pigments (yellow pigments) of various anilines at room temperature using DES.

The optimized protocol was successfully employed for the synthesis of various monoazo

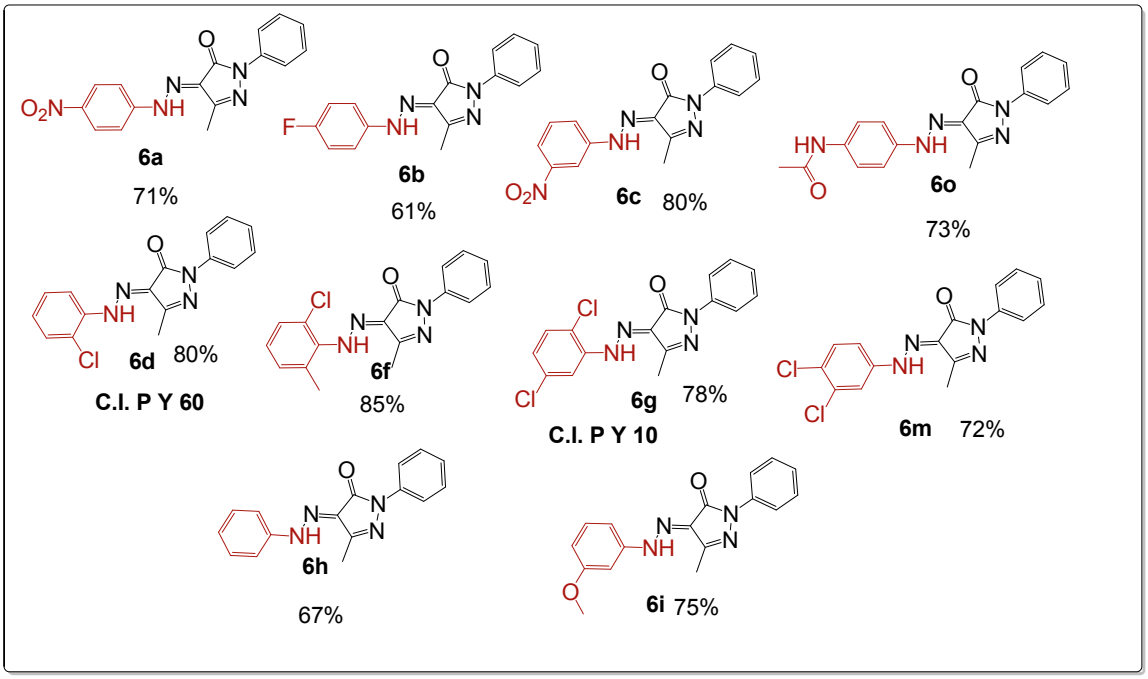


arylide (yellow) pigments by coupling diazonium salt with acetoacetanilide derivatives (figure ES 1).

Figure ES 1 Synthesis of monoazo arylide pigments (yellow pigments) of various anilines at room temperature using DES.



Various aromatic amines were coupled with 1-methyl-5-phenyl pyrazolone to give corresponding monoazo orange pigments (Scheme ES 2).

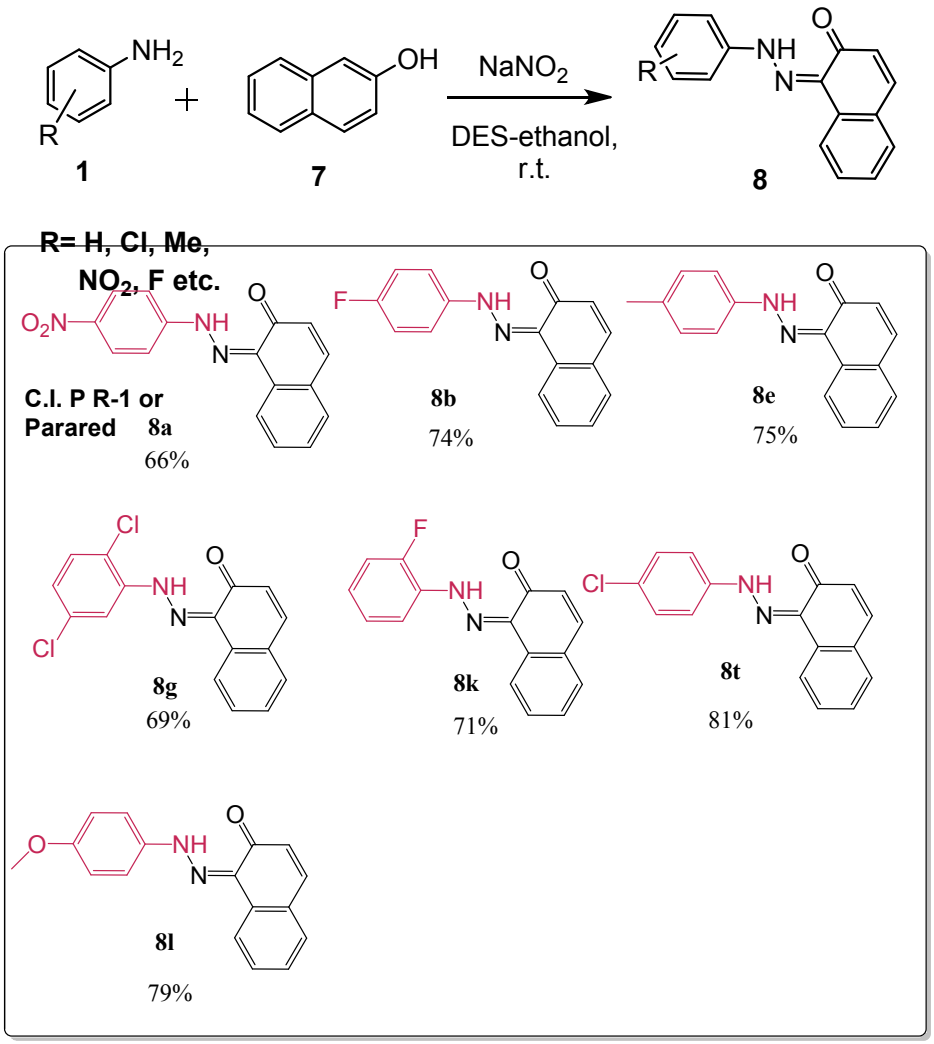


Scheme ES 2 Synthesis of monoazo pyrazolone pigments at room temperature.

The results obtained from coupling with 3-methyl-1-phenyl pyrazolone are depicted in figure ES 2.

Figure ES 2 Synthesis of monoazo pyrazolone (orange) pigments at room temperature.

Similarly, aniline derivatives are coupled with β-hydroxy naphthalene to give β-naphthol pigments (Scheme ES 3, Figure ES 3)



Scheme ES 3 Synthesis of monoazo β-naphthol pigments at room temperature**.**

Figure ES 3 Synthesis of monoazo β-naphthol pigments at room temperature.

2. RECYCLING STUDY OF CHOLINE CHLORIDE: TARTARIC ACID (DES)

2-chloroaniline (5 g, 0.039 moles) was taken in 2.5 mL ethanol containing DES (0.5 eq.), 0.039 moles (2.7 g) of $NaNO_2$ was added to the mixture and stirred for 20 min at room temperature. Then 6.92 g of acetoacetanilide (0.0156 moles) was added to the diazotized mixture and reaction mass stirred for 20 min. The product was precipitated by adding water into reaction mass and separated by filtration. The deep eutectic solvent was recovered from the filtrate by

evaporating the water phase at 80 °C under vacuum. The recycled deep eutectic solvent was used for the next batch and recycled again. (ES Table 1)

Table 1 Recycling of deep eutectic solvent for room temperature diazotization of 2-chloroaniline and subsequent coupling reaction[a].

Entry	Cycle	Yield[b] (%)
1	Fresh	86
2	1st recycle	80
3	2nd recycle	73
4	3rd recycle	72
5	4th recycle	72

[a]**Reaction conditions:** 2-chloroacniline, $NaNO_2$, acetoacetanilide, ChCl: tartaric acid (DES), ethanol, room temeparture, [b] isolate yield.

3. EXPERIMENTAL

3.1 General

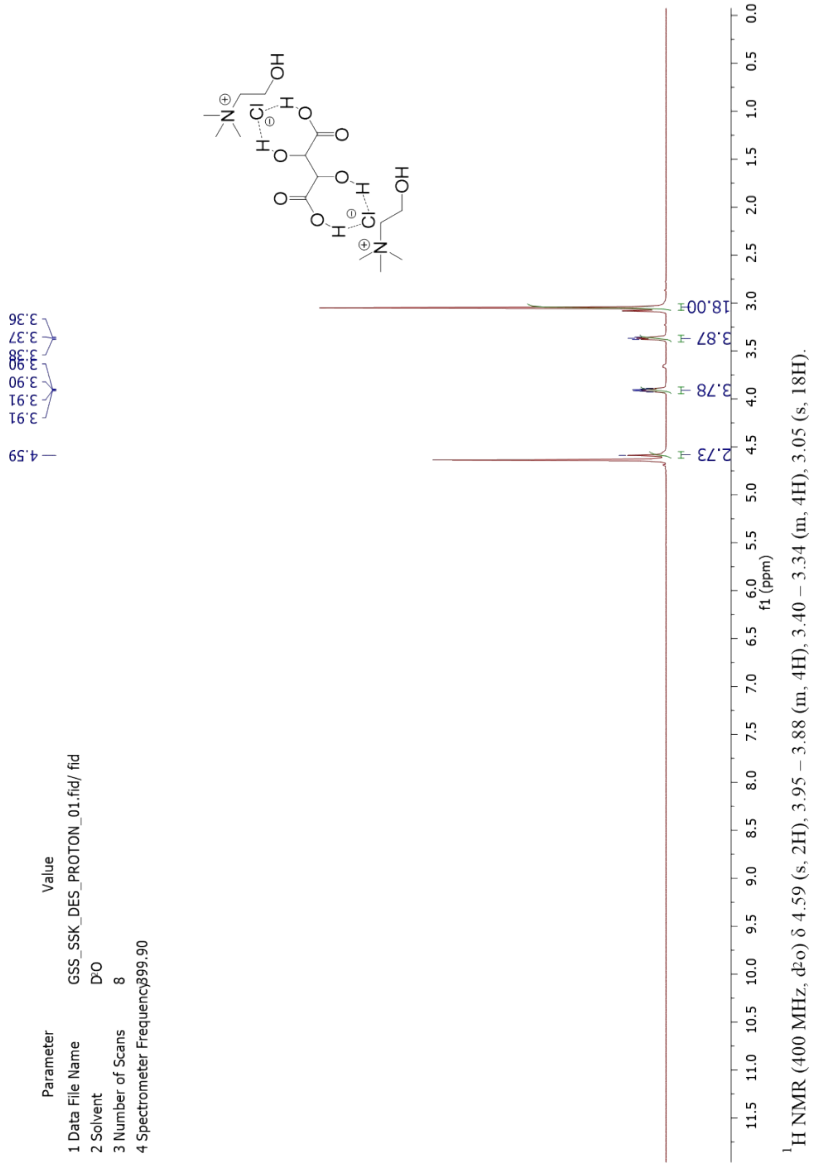
All the solvents and chemicals were procured from S D Fine Chemicals (India) and were used without further purification. All products are well characterized by 1H NMR spectrometry. The 1H NMR spectroscopic data were recorded on 400 and 500 MHz instruments in CDCl3 and DMSO-d6 as a solvent and chemical shifts are expressed in δ ppm using TMS as an internal standard.

3.2 Synthesis of DES

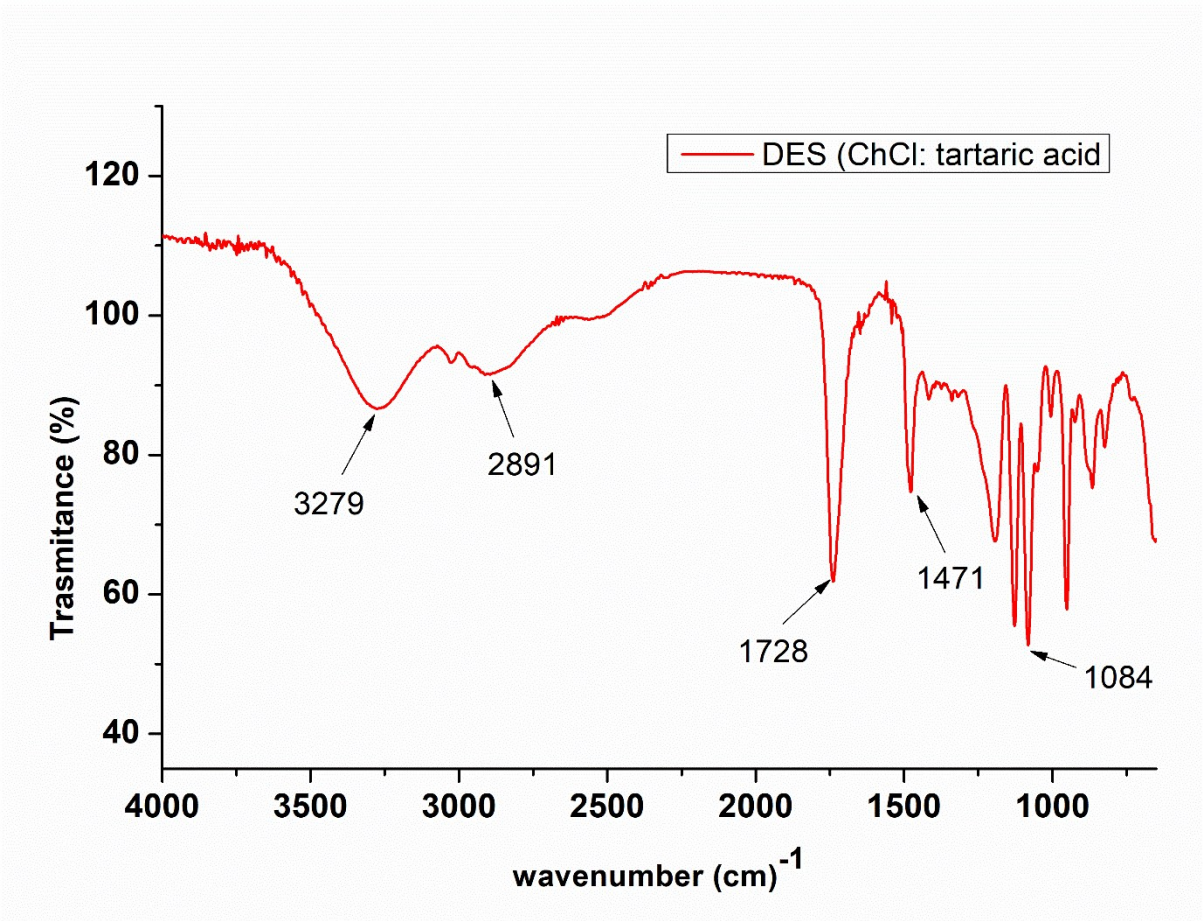
The synthesis of deep eutectic solvent has been carried out using method reported in the literature1. It is prepared by the mixing of choline chloride (20 g, 14.3 mmol) and tertaric acid (10.8 g, 7.2 mmol) in the ratio of 1:0.5. The two solids are then heated slowly and maintained at 80 °C for 60 min resulting in the formation of eutectic solvent with 100% atom economy. The liquid is allowed to cool till it attains room temperature and is used for diazotization reaction without further purification.

^{1}H NMR (400 MHz, D_2O) δ 4.59 (s, 2H), 3.95 – 3.88 (m, 4H), 3.40 – 3.34 (m, 4H), 3.05 (s, 18H). IR: 3279, 2891, 1728, 1471, 1084 cm^{-1}.

3.2a. ^{1}H NMR of DES:



3.2b. IR Spectra of DES:

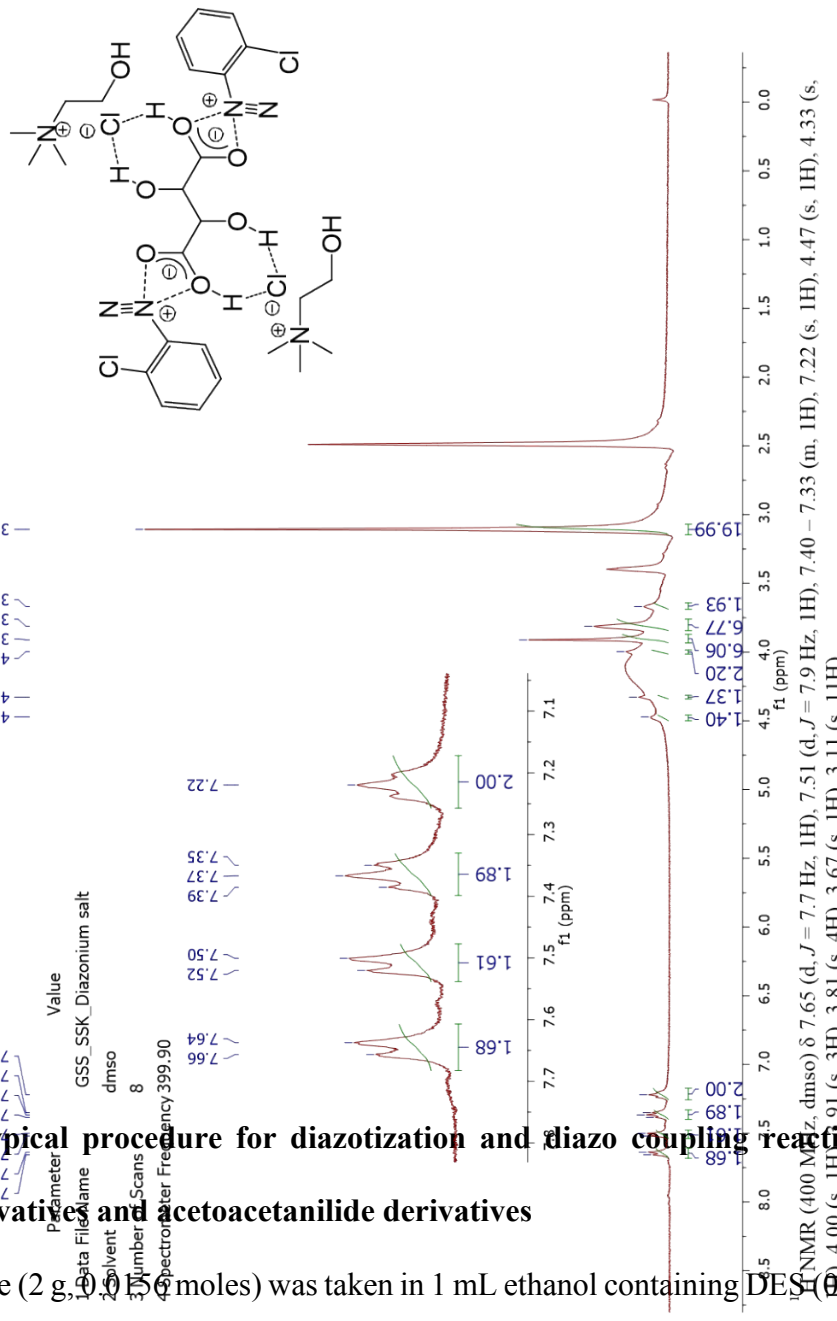


3.3 Synthesis of arene diazonium salt

In 10 mL of ethanol containing 1 mL of DES, 2-chloroaniline (2g, 0.0156 moles) was taken. Then $NaNO_2$ (1.13g, 0.0164 moles) was added to the mixture and stirred for 10 min at room temperature to carry out diazotization. The diazonium salt is isolated by filtration.

Reddish yellowish solid, ^{1}H NMR (400 MHz, DMSO D_6) δ 7.65 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.22 (s, 1H), 4.47 (s, 1H), 4.33 (s, 1H), 4.00 (s, 1H), 3.91 (s, 3H), 3.81 (s, 4H), 3.67 (s, 1H), 3.11 (s, 11H).

3.3a. ^{1}H NMR of arene diazonium salt:



3.4 A typical procedure for diazotization and diazo coupling reaction of aniline derivatives and acetoacetanilide derivatives

2-chloroaniline (2 g, 0.0156 moles) was taken in 1 mL ethanol containing DES (0.5 eq.), 0.0156 moles (1.08 g) of NaNO2 was added to the mixture and stirred for 20 min at room temperature. Then 2.77 g of acetoacetanilide (0.0156 moles) was added to the diazotized mixture and reaction mass stirred for 20 min. The product was precipitated by adding water into reaction

mass and separated by filtration. The crude product was then recrystallized with ethanol to yield 86% pure product.

3.5. Spectral Data:

1. **2-(2-(2-Chlorophenyl)hydrazono)-3-oxo-N-phenylbutanamide**[1]**:** Yellow solid, mp: 158-160 °C, Yield: 86%, ^{1}H NMR (400 MHz, DMSO d_6) δ 14.56 (s, 1H), 11.23 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.18 (dd, J = 13.0, 7.0 Hz, 2H), 2.53 (s, 3H), ^{13}C NMR (101 MHz, DMSO d_6) δ 199.43, 162.27, 138.39, 137.24, 129.91, 129.24, 129.21, 128.59, 126.13, 125.28, 120.99, 116.32, 26.52, HRMS (m/z) for ($C_{16}H_{14}ClN_3O_2$): 316.0830 (M+H).
2. **2-(2-(4-Nitrophenyl)hydrazono)-3-oxo-N-phenylbutanamide**[1]**:** Yellow Solid, mp: 212-214 °C, Yield: 81%, ^{1}H NMR (400 MHz, DMSO d_6) δ 12.79 (s, 1H), 10.81 (s, 1H), 8.24 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.3 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 7.14 (d, J = 7.0 Hz, 1H), 2.49 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.63, 162.23, 146.56, 144.20, 136.59, 129.10, 128.55, 125.79, 125.35, 121.02, 115.40, 26.28, HRMS (m/z) for ($C_{16}H_{14}N_5O_4$): 327.1076 (M+H).
3. **3-Oxo-N-phenyl-2-(2-(p-tolyl)hydrazono)butanamide**[1,2]**:** Yellow Solid, mp: 162-164 °C, Yield: 77%, ^{1}H NMR (400 MHz, DMSO D6) δ 13.76 (s, 1H), 12.90 (s, 1H), 7.57 (d, J = 7.7 Hz, 2H), 7.30 (m, 4H), 7.17 (dd, J = 12.0, 8.2 Hz, 3H), 6.86 (d, J = 7.8 Hz, 2H), 2.29 (s, 3H), 2.19 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.90, 163.89, 137.94, 129.92, 129.65, 128.89, 124.77, 124.22, 120.86, 120.05, 115.08, 20.88, 16.79.
4. **2-(2-(3-Nitrophenyl)hydrazono)-3-oxo-N-phenylbutanamide**[1]**:** Yellow Solid, mp: 188-190 °C, Yield: 62%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.04 (s, 1H), 10.89 (s, 1H), 8.32 (s, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.9 Hz, 3H), 7.36 (t, J = 7.7 Hz, 2H), 7.13 (t, J = 7.1 Hz, 1H), 2.50 (s, 3H), ^{13}C NMR (101 MHz,

$CDCl_3$) δ 199.54, 162.50, 149.37, 142.90, 136.73, 130.46, 129.07, 127.63, 125.18, 121.21, 120.96, 119.23, 110.33, 26.22, HRMS (m/z) for ($C_{16}H_{14}N_5O_4$): 327.1056 (M+H).

5. **2-(2-(4-Chlorophenyl)hydrazono)-3-oxo-N-phenylbutanamide:**[2,3] Yellow Solid, mp: 157-159 °C, Yield: 52%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.55 (s, 1H), 11.08 (s, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.1 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, DMSO d_6) δ 168.36, 162.86, 145.41, 138.07, 129.44, 124.69, 122.60, 120.58, 116.67, 116.35, 116.04, 16.89.

6. **2-(2-(4-Fluorophenyl)hydrazono)-3-oxo-N-phenylbutanamide[4]:** Yellow Solid, mp: 170-172 °C, Yield: 73%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.44 (s, 1H), 12.49 (s, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.21 (dd, J = 16.0, 7.8 Hz, 4H), 7.10 (m, 1H), 2.19 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.86, 163.78,163.58, 137.55, 128.96, 124.51, 121.77, 120.87, 116.13, 115.74, 16.89.

7. **N-(2-chlorophenyl)-2-(2-(2-chlorophenyl)hydrazono)-3-oxobutanamide[1]:** Yellow Solid, mp: 168-170 °C, Yield: 65%, ^{1}H NMR (400 MHz, DMSO d_6) δ 11.79 (s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.55 (s, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.18 (dd, J = 18.0, 7.9 Hz, 2H), 2.53 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.36, 162.50, 138.51, 134.55, 129.86, 129.38, 127.99, 127.44, 125.49, 125.18, 124.43, 122.56, 122.11, 115.90, 26.11.

8. **N-(2-chlorophenyl)-2-(2-(4-methyl-2-nitrophenyl)hydrazono)-3-oxobutanamide:** Yellow Solid, mp: 235-237 °C, Yield: 62%, ^{1}H NMR (400 MHz, DMSO d_6) δ 11.71 (s, 1H), 8.40 (d, J = 7.2 Hz, 1H), 8.24 (s, 1H), 8.06 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 6.9 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.0 Hz, 1H), 2.58 (s, 2H), 2.39 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.17, 172.20, 162.87,

137.48, 136.98 129.52, 128.95, 128.27, 127.42, 126.79, 126.37, 125.36, 124.87, 120.97, 26.31, 18.47, HRMS (m/z) for ($C_{17}H_{15}ClN_4O_4$): 375.0827 (M+H).

9. **2-(2-(4-methyl-2-nitrophenyl)hydrazono)-3-oxo-N-(p-tolyl)butanamide:**[3,5] Yellow Solid, mp: 228-230 °C, Yield: 71%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 2.65 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.97, 161.22, 136.68, 135.49, 134.15, 130.38, 129.75, 128.57, 126.68, 125.79, 125.02, 122.17, 116.96, 26.44, 20.55, 18.13.

10. **2-(2-(2-Chloro-6-methylphenyl)hydrazono)-3-oxo-N-phenylbutanamide**: Yellow Solid, mp: 125-127 °C, Yield: 82%, ^{1}H NMR (400 MHz, DMSO d_6) δ 14.43 (s, 1H), 11.27 (s, 1H), 7.62 (d, J = 7.7 Hz, 2H), 7.36 (m, 3H), 7.29 (d, J = 7.4 Hz, 1H), 7.15 (dd, J = 13.6, 7.4 Hz, 2H), 2.50 (s, 3H), 2.40 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.60, 162.71, 137.14, 131.41, 130.93, 128.95, 127.82, 127.28, 126.10, 124.96, 124.71, 120.95, 26.46, 20.64, HRMS (m/z) for ($C_{17}H_{16}ClN_3O_2$): 330.1008 (M+H).

11. **2-(2-(2,6-Dichlorophenyl)hydrazono)-3-oxo-N-phenylbutanamide:** Yellow Solid, mp: 172-174 °C, Yield: 48%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.97 (s, 1H), 11.13 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.58 (dd, J = 7.7, 6.4 Hz, 3H), 7.37 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 8.1 Hz, 1H), 7.16 (d, J = 6.8 Hz, 1H), 2.42 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.17, 172.20, 162.87, 137.48, 136.98 129.52, 128.95, 128.27, 127.42, 126.79, 126.37, 125.36, 124.87, 120.97, 26.31, 18.47.

12. **5-Methyl-2-phenyl-4-(2-phenylhydrazono)-2,4-dihydro-3H-pyrazol-3-one**[6]**:** Orange Solid, mp: 155-157 °C, Yield: 67%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.58 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 5.7 Hz, 6H), 7.20 (t, J = 6.8 Hz, 2H), 2.36 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.75, 148.52, 141.13, 138.03, 129.63, 128.87, 128.49,

125.76, 125.10, 118.53, 115.78, 11.74 (s), HRMS (m/z) for ($C_{16}H_{14}N_4O$): 279.1222 (M+H).

13. **5-Methyl-4-(2-(4-nitrophenyl)hydrazono)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one[6]:** Orange Solid, mp: 188-190 °C, Yield: 71%, ^{1}H NMR (500 MHz, DMSO d_6) δ 13.22 (s, 1H), 8.29 (d, J = 9.1 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 9.1 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 2.31 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.21, 148.58, 146.15, 144.44, 137.53, 131.59, 128.98, 125.68, 118.53, 115.33, 11.77, HRMS (m/z) for ($C_{16}H_{13}N_5O3$): 322.0979 (M-H).

14. **5-Methyl-4-(2-(3-nitrophenyl)hydrazono)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:**[3] Orange Solid, mp: 184-186 °C, Yield: 80%, ^{1}H NMR (500 MHz, DMSO d_6) δ 13.21 (s, 1H), 8.44 (t, J = 2.0 Hz, 1H), 8.04 (dd, J = 8.1, 1.6 Hz, 1H), 7.99 (dd, J = 8.1, 1.9 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 8.2 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.21a (t, J = 7.4 Hz, 1H), 2.29 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 148.55, 142.47, 137.65, 130.51, 128.95, 125.48, 121.12, 119.58, 118.55, 110.24, 11.83.

15. **4-(2-(2-Chlorophenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:3** Orange Solid, mp: 188-190 °C, Yield: 80%, 1H NMR (500 MHz, DMSO d6) δ 13.61 (s, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.48 (dt, J = 13.7, 8.3 Hz, 3H), 7.24 (m, 2H), 2.32 (s, 3H), 13C NMR (101 MHz, CDCl3) δ 157.45, 148.39, 137.89, 130.40, 129.82, 128.89, 128.04, 125.71, 125.23, 121.76, 118.62, 115.77, 11.78, HRMS (m/z) for ($C_{16}H_{13}ClN_4O$): 313.0830 (M+H).

16. **4-(2-(4-Fluorophenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:** Orange Solid, mp: 153-155 °C, Yield: 61%, ^{1}H NMR (500 MHz, DMSO d_6) δ 13.26 (s, 1H), 7.91 (dd, J = 8.6, 1.0 Hz, 2H), 7.68 (m, 2H), 7.45 (m, 2H), 7.30 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 2.29 (s, 3H), ^{13}C NMR (101 MHz, $CDCL_3$) δ 161.76, 159.32, 157.76,

148.43, 137.96, 137.44, 128.89, 125.18, 118.55, 117.20, 116.68, 116.45, 11.73, HRMS (m/z) for ($C_{16}H_{13}FN_4O$): 297.1130 (M+H).

17. **2-(2-(4-Methyl-2-nitrophenyl)hydrazono)-3-oxo-N-phenylbutanamide:**[7] Yellow Solid, mp: 252-254 °C, Yield: 75%, ^{1}H NMR (400 MHz, DMSO D6) δ 11.10 (s, 1H), 8.19 (s, 1H), 8.02 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.34 (s, 2H), 7.12 (s, 1H), 2.55 (s, 3H), 2.37 (s, 3H).

18. **4-(2-(3-Methoxyphenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:**[3] Orange Solid, mp: 148-150 °C, Yield: 75%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.54 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 8.1 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.02 (s, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 3.85 (s, 3H), 2.36 (s, 3H), ^{13}C NMR (101 MHz, $cdcl_3$) δ 160.87, 157.75, 148.54, 142.38, 130.49, 128.89, 125.16, 118.58, 111.64, 108.53, 101.21, 55.44, 11.77.

19. **4-(2-(3,4-Dichlorophenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:**[3] Orange Solid, mp: 170-172 °C, Yield: 72%, ^{1}H NMR (500 MHz, DMSO d_6) δ 13.10 (s, 1H), 7.89 (m, 3H), 7.63 (dt, J = 8.8, 5.6 Hz, 2H), 7.45 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), ^{13}C NMR (101 MHz, $cdcl_3$) δ 157.52, 148.45, 140.64, 137.74, 133.93, 131.21, 128.92, 125.35, 118.50, 117.09, 115.00, 11.77.

20. **4-(2-(2-Chloro-6-methylphenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:**[3] Orange Solid, mp: 182-184 °C, Yield: 85%, ^{1}H NMR (500 MHz, DMSO d_6) δ 13.37 (s, 1H), 7.91 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.9 Hz, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.22 (m, 2H), 2.52 (s, 3H), 2.26 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.27, 148.50, 137.97, 135.87, 131.34, 128.89, 127.76, 126.18, 125.15, 118.68, 21.05, 11.77.

21. **4-(2-(2,5-Dichlorophenyl)hydrazono)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one:**[3] Orange Solid, mp: 200-202 °C, Yield: 78%, ^{1}H NMR (500 MHz, DMSO d_6) δ

13.57 (s, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.74 (d, J = 2.4 Hz, 1H), 7.37 (m, 3H), 7.15 (t, J = 7.4 Hz, 1H), 7.09 (dd, J = 8.6, 2.4 Hz, 1H), 2.32 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.29, 148.41, 138.83, 137.66, 134.21, 130.69, 128.93, 125.37, 119.70, 118.61, 115.68, 11.83.

22. **4-(2-(3-Methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4-ylidene)hydrazinyl)benzenesulfonic acid:** Orange Solid, mp: 310-312 °C, Yield: 78%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.25 (s, 3H), 7.88 (d, J = 7.7 Hz, 4H), 7.62 (d, J = 8.6 Hz, 4H), 7.52 (d, J = 8.6 Hz, 4H), 7.42 (t, J = 8.0 Hz, 4H), 7.18 (t, J = 7.4 Hz, 2H), 2.28 (s, 6H), HRMS (m/z) for ($C_{16}H_{14}N_4O_4S$): 359.0786 (M+H).

23. **N-(4-(2-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4H-pyrazol-4 ylidene)hydrazinyl)phenyl)acetamide:** Orange Solid, mp: 189-190 °C, Yield: 73%, ^{1}H NMR (400 MHz, DMSO d_6) δ 13.31 (s, 1H), 10.03 (s, 1H), 7.87 (s, 2H), 7.42 (dd, J = 113.0, 66.7 Hz, 7H), 2.24 (s, 3H), 1.99 (s, 3H), ^{13}C NMR (101 MHz, DMSO d_6) δ 168.67, 157.15, 148.70, 138.47, 136.84, 129.40, 125.13, 120.32, 117.63, 24.43, 12.05, HRMS (m/z) for ($C_{18}H_{17}N_5O_2$): 336.1435 (M+H).

24. **1-(2-(4-Fluorophenyl)hydrazono)naphthalen-2(1H)-one:**[8,9] Red Solid, mp: 138-140 °C, Yield: 74%, ^{1}H NMR (500 MHz, DMSO d_6) δ 8.63 (d, J = 8.3 Hz, 1H), 8.01 (ddd, J = 12.8, 7.2, 5.0 Hz, 3H), 7.84 (d, J = 7.8 Hz, 1H), 7.63 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.48 (m, 1H), 7.41 (m, 2H), 7.04 (d, J = 9.3 Hz, 1H), ^{13}C NMR (101 MHz, $cdcl_3$) δ 161.75, 159.31, 157.77, 148.42, 137.95, 137.43, 128.88, 128.89, 125.19, 118.54, 117.21, 116.69, 116.46. HRMS (m/z) for ($C_{16}H_{11}FN_2O$): 267.0880 (M+H)

25. **1-(2-(2,5-Dichlorophenyl)hydrazono)naphthalen-2(1H)-one:** Reddish- brown solid, mp: 138-140 °C, Yield: 69%, ^{1}H NMR (400 MHz, DMSO d_6) δ 8.49 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 2.3 Hz, 1H), 7.94 (d, J = 9.5 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.61 (dd, J = 20.6, 8.0 Hz, 2H), 7.47 (d, J = 7.0 Hz, 1H), 7.32 (d, J = 6.4 Hz, 1H), 6.77 (d, J = 9.5 Hz,

1H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.28, 148.42, 138.82, 137.67, 134.20, 131.31, 130.68, 128.92, 125.36, 119.71, 118.62, 115.67.

26. **1-(2-(*p*-Tolyl)hydrazono)naphthalen-2(1H)-one:**[9] Reddish- Brown solid, mp: 145-147 °C, Yield: 75%, ^{1}H NMR (500 MHz, DMSO d_6) δ 8.56 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 9.4 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.62 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.47 (m, 1H), 7.41 (dd, J = 13.4, 7.2 Hz, 2H), 7.28 (td, J = 7.4, 1.1 Hz, 1H), 6.93 (d, J = 9.4 Hz, 1H), 3.31 (s, 4H), ^{13}C NMR (101 MHz, DMSO d_6) δ 135.55, 126.34, 124.13, 123.87, 123.21, 122.60, 122.24, 121.00, 120.42, 116.89, 110.99, 12.80, HRMS (m/z) for ($C_{17}H_{14}N_2O$): 263.0573 (M+H).

27. **1-(2-(4-chlorophenyl)hydrazono)naphthalen-2(1H)-one:**[10] Reddish- Brown solid, mp: 153-155 °C, Yield: 81%, ^{1}H NMR (400 MHz, DMSO d_6) δ 8.52 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 9.7 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 3H), 7.45 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 9.4 Hz, 1H), ^{13}C NMR (101 MHz, $cdcl_3$) δ 157.44, 148.38, 137.88, 130.41, 129.83, 128.88, 128.69, 128.03, 125.72, 125.21, 121.77, 118.61, 115.78.

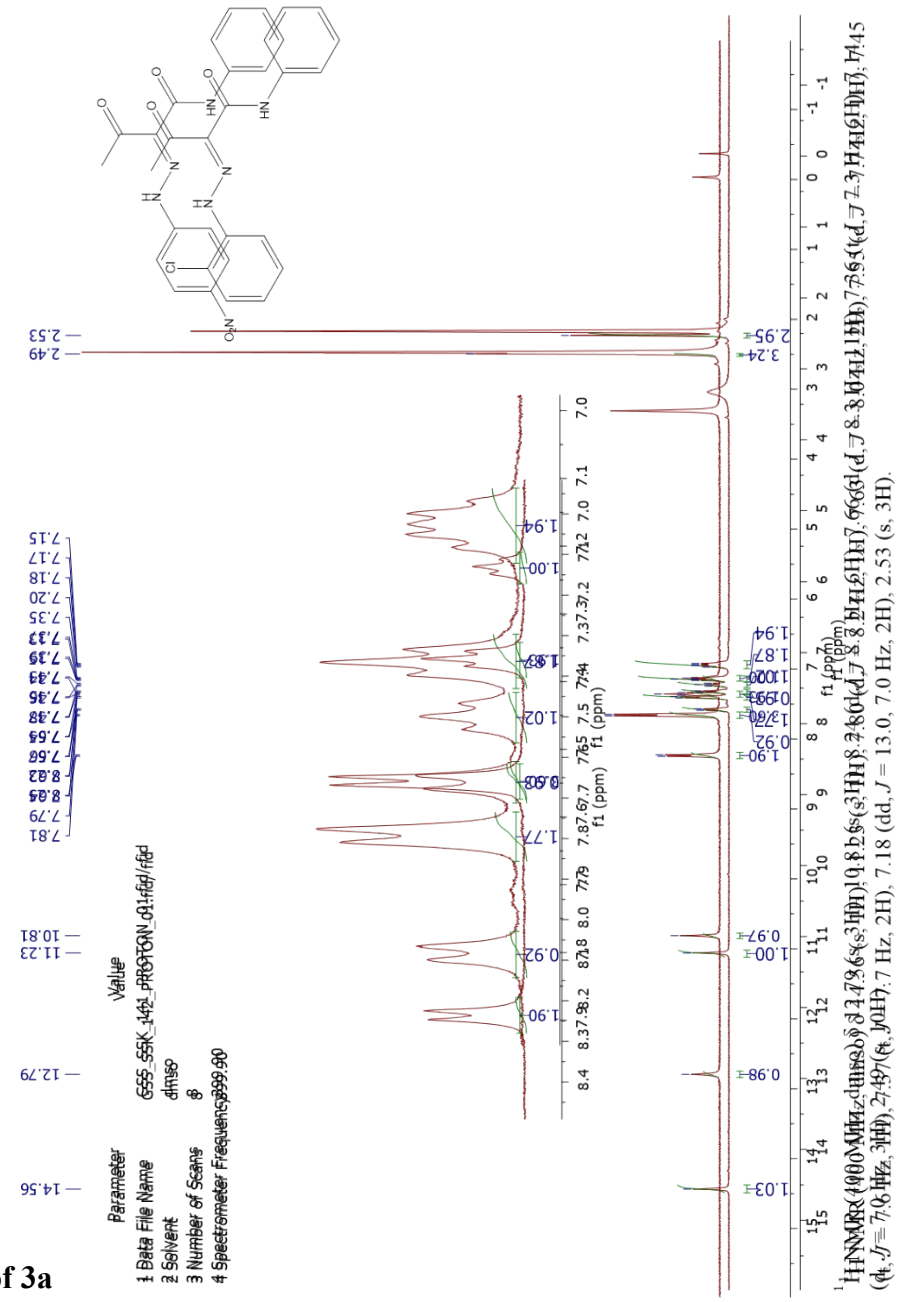
28. **1-(2-(2-Fluorophenyl)hydrazono)naphthalen-2(1H)-one:** Reddish- Brown solid, mp: 150-152 °C, Yield: 71%, ^{1}H NMR (500 MHz, DMSO d_6) δ 8.55 (d, J = 8.2 Hz, 1H), 8.14 (t, J = 8.8 Hz, 1H), 7.99 (d, J = 9.5 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.47 (ddd, J = 11.3, 9.7, 5.3 Hz, 2H), 7.40 (m, 2H), 6.91 (d, J = 9.4 Hz, 1H), ^{13}C NMR (101 MHz, $cdcl_3$) δ 173.51, 155.18, 152.69, 140.75, 133.38, 131.10, 128.99, 128.69, 128.16, 127.38, 126.11, 125.33, 121.82, 117.08, 116.12, HRMS (m/z) for ($C_{16}H_{11}FN_2O$): 267.0686 (M+H).

29. **1-(2-(4-Methoxyphenyl)hydrazono)naphthalen-2(1H)-one:**[11] Red Solid, mp: 158-160 °C, Yield: 81%, ^{1}H NMR (500 MHz, DMSO d_6) δ 8.71 (d, J = 8.2 Hz, 1H), 7.99 (dt, J = 4.8, 3.0 Hz, 3H), 7.88 (d, J = 7.9 Hz, 1H), 7.64 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 7.47 (m,

1H), 7.15 (m, 3H), 3.87 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.46, 160.60, 141.71, 136.72, 133.27, 129.49, 128.20, 124.76, 122.18, 121.98, 121.56, 114.74, 55.59, HRMS (m/z) for ($C_{17}H_{14}N_2O_2$): 302.0524 (M+23).

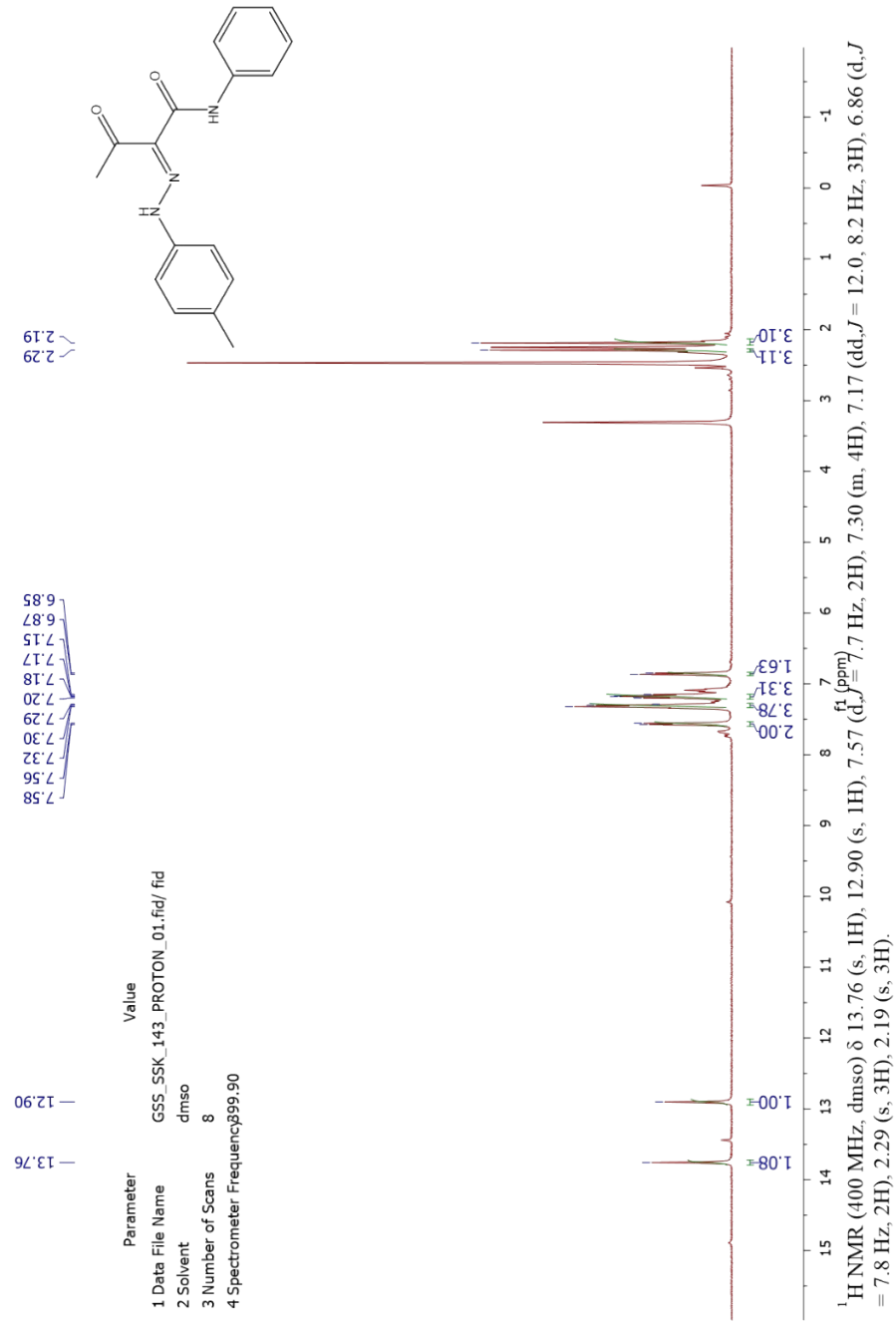
3.6. ^{1}H NMR of of mono azo pigments

^{1}H NMR of 3d



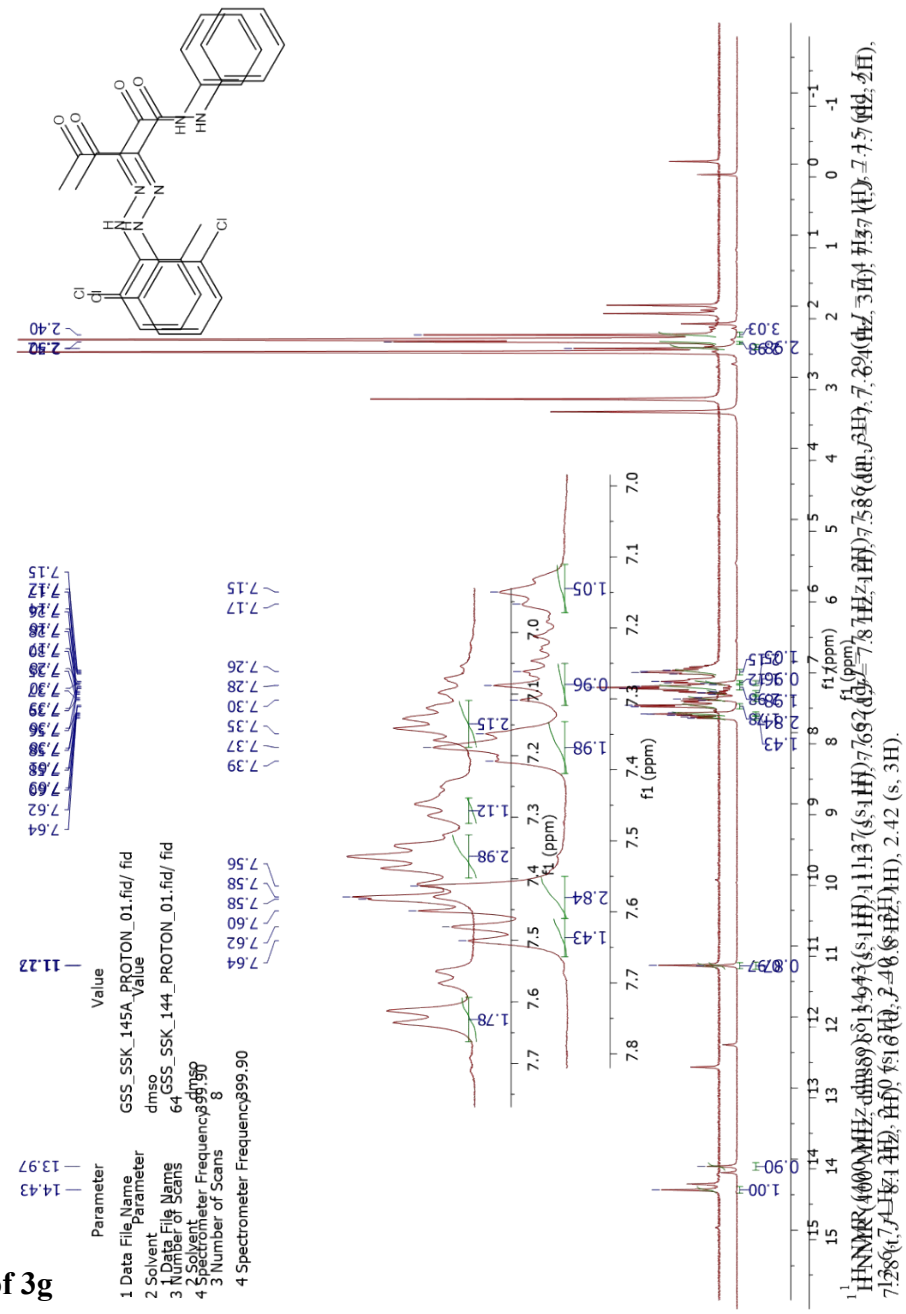
^{1}H NMR of 3a

^{1}H NMR of 3e



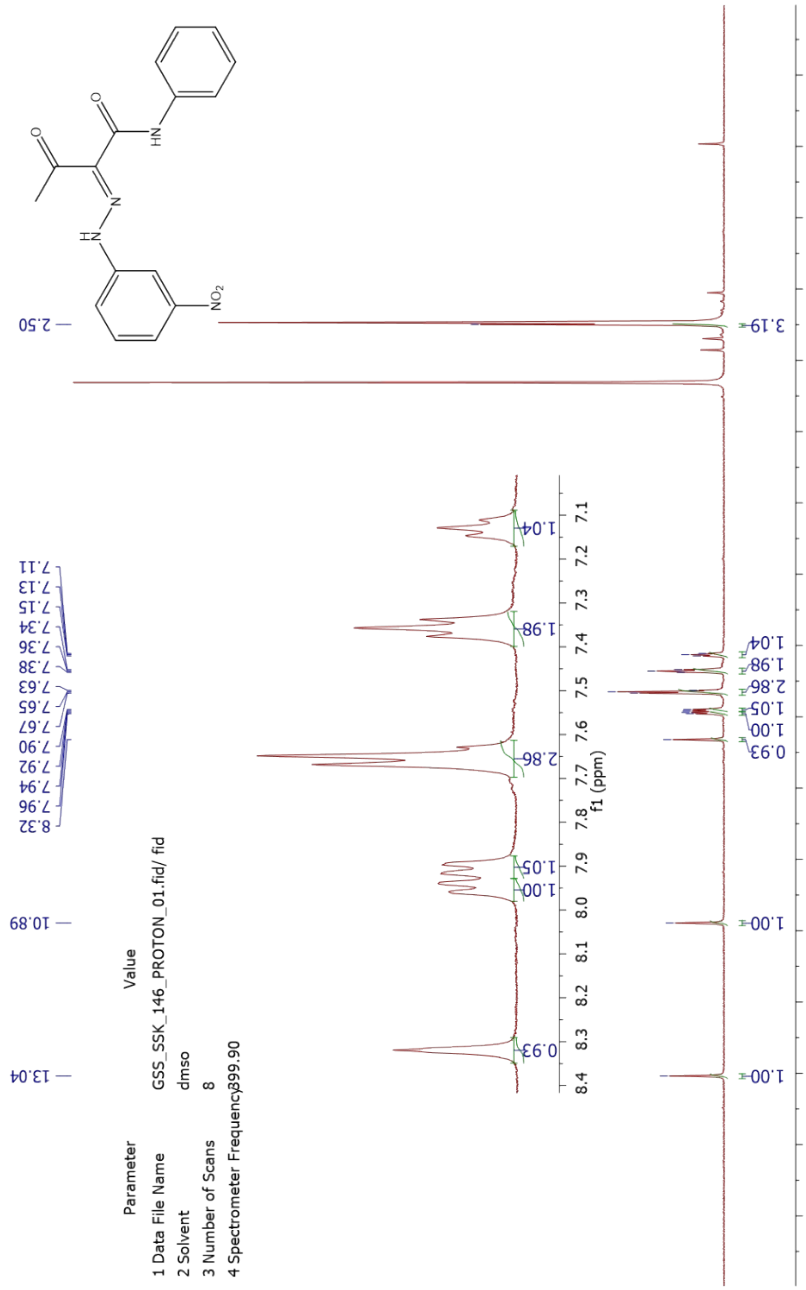
^{1}H NMR (400 MHz, dmso) δ 13.76 (s, 1H), 12.90 (s, 1H), 7.57 (d, J = 7.7 Hz, 2H), 7.30 (m, 4H), 7.17 (dd, J = 12.0, 8.2 Hz, 3H), 6.86 (d, J = 7.8 Hz, 2H), 2.29 (s, 3H), 2.19 (s, 3H).

^{1}H NMR of 3f



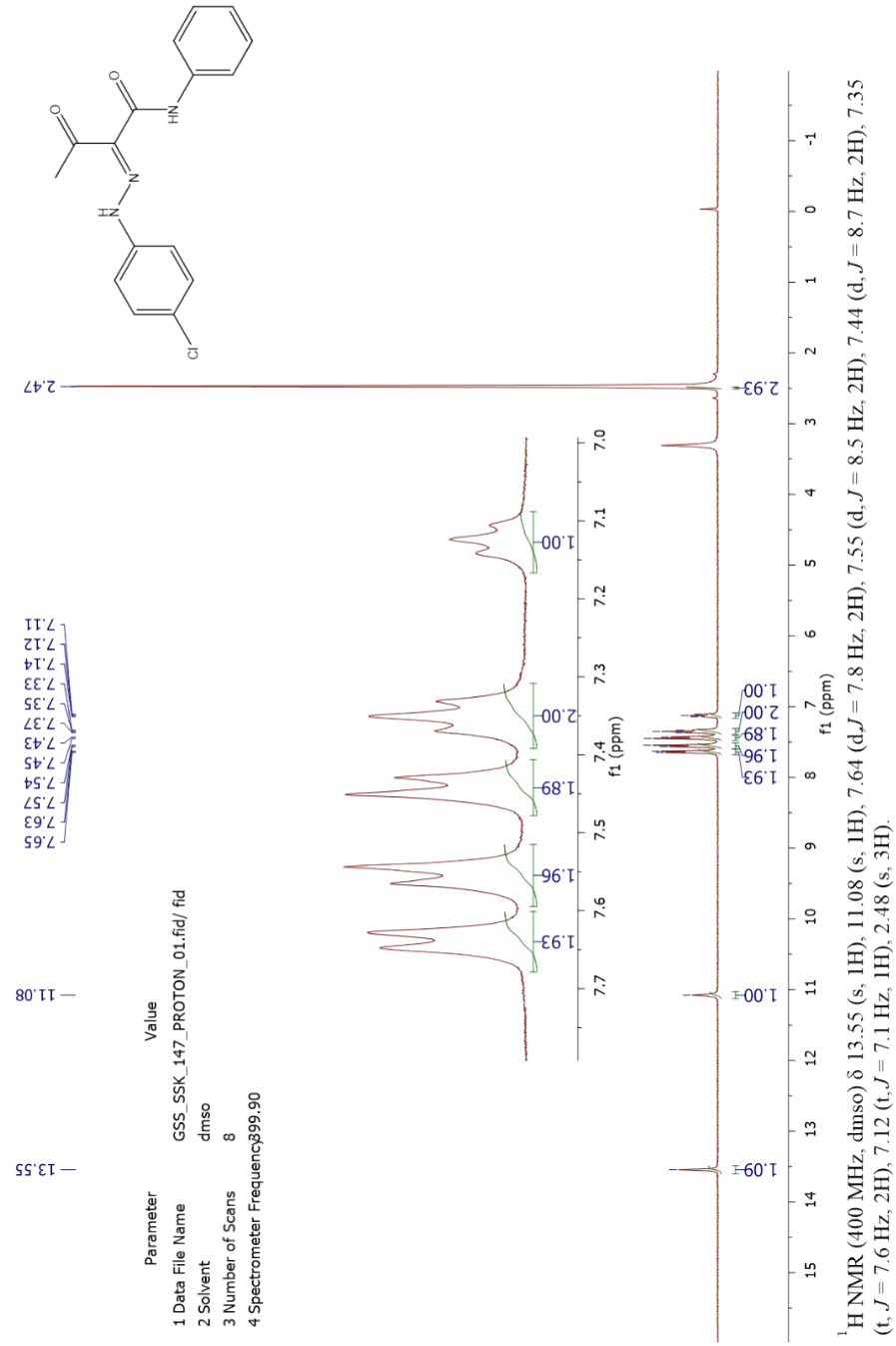
^{1}H NMR of 3g

^{1}H NMR of 3c



^{1}H NMR (400 MHz, dmso) δ 13.04 (s, 1H), 10.89 (s, 1H), 8.32 (s, 1H), 7.95 (d,J = 7.5 Hz, 1H), 7.91 (d,J = 8.1 Hz, 1H), 7.65 (t,J = 7.9 Hz, 3H), 7.36 (t,J = 7.7 Hz, 2H), 7.13 (t,J = 7.1 Hz, 1H), 2.50 (s, 3H).

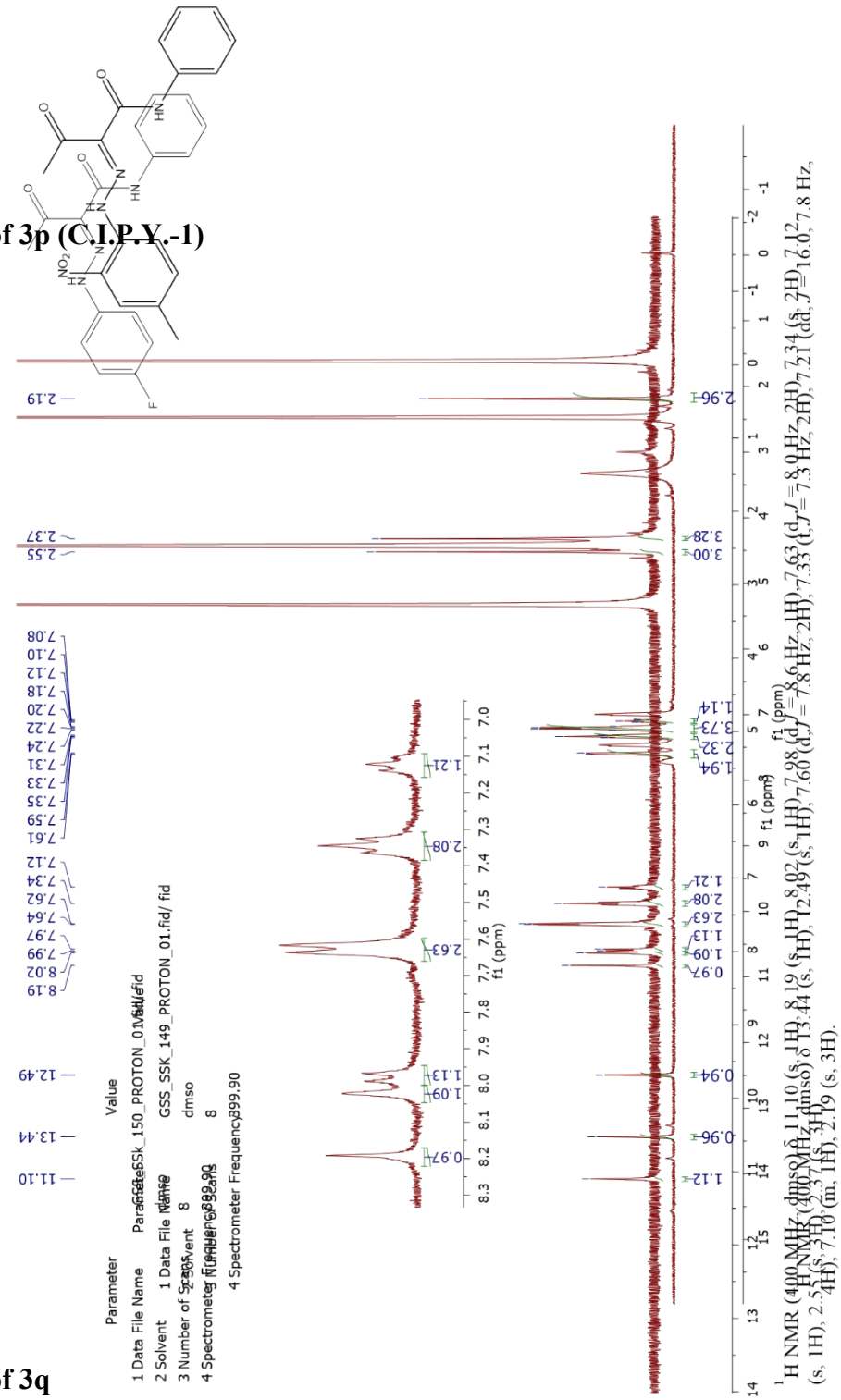
^{1}H NMR of 3j



^{1}H NMR (400 MHz, dmso) δ 13.55 (s, 1H), 11.08 (s, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.1 Hz, 1H), 2.48 (s, 3H).

^{1}H NMR of 3b

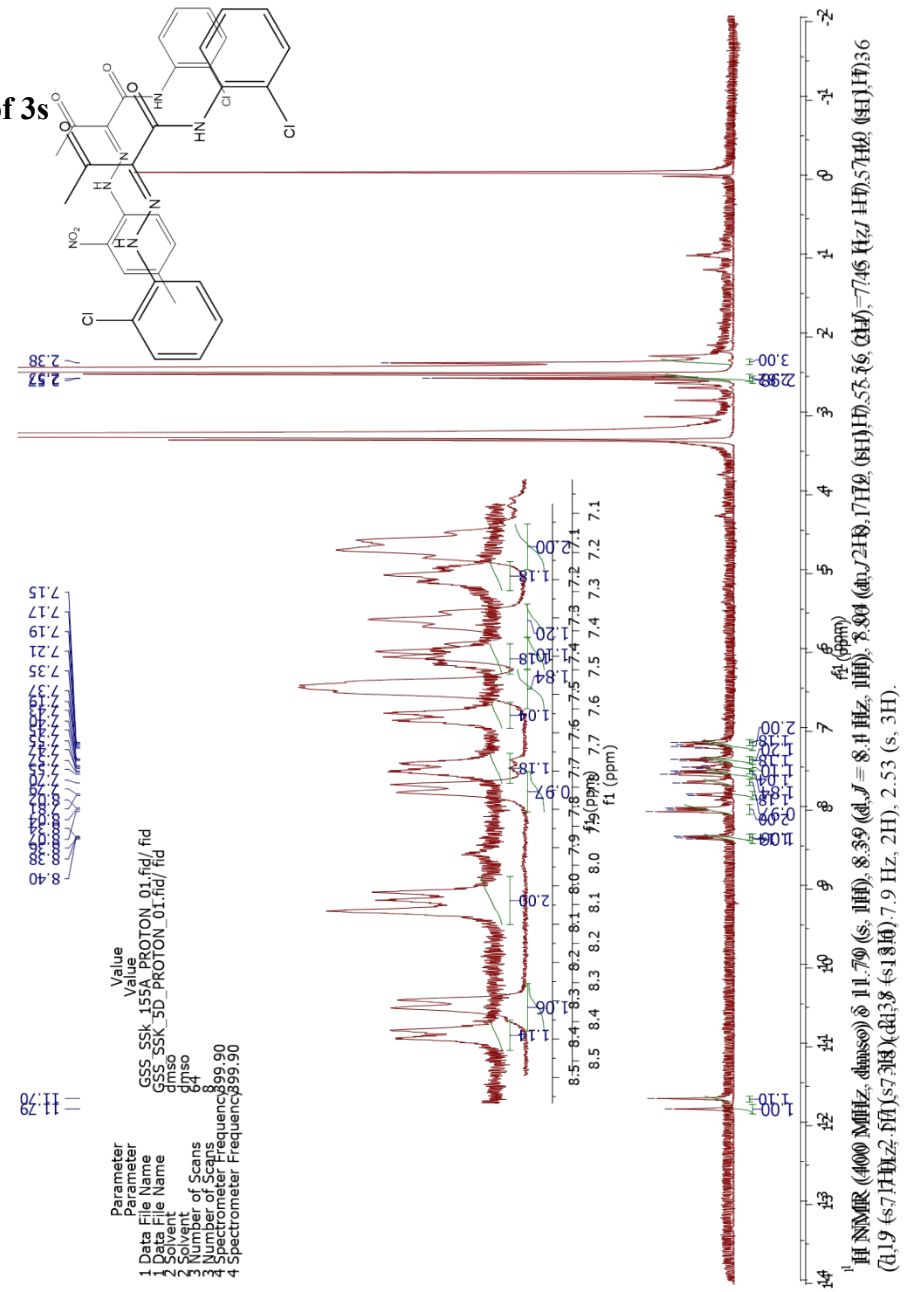
^{1}H NMR of 3p (C.I.P.Y.-1)



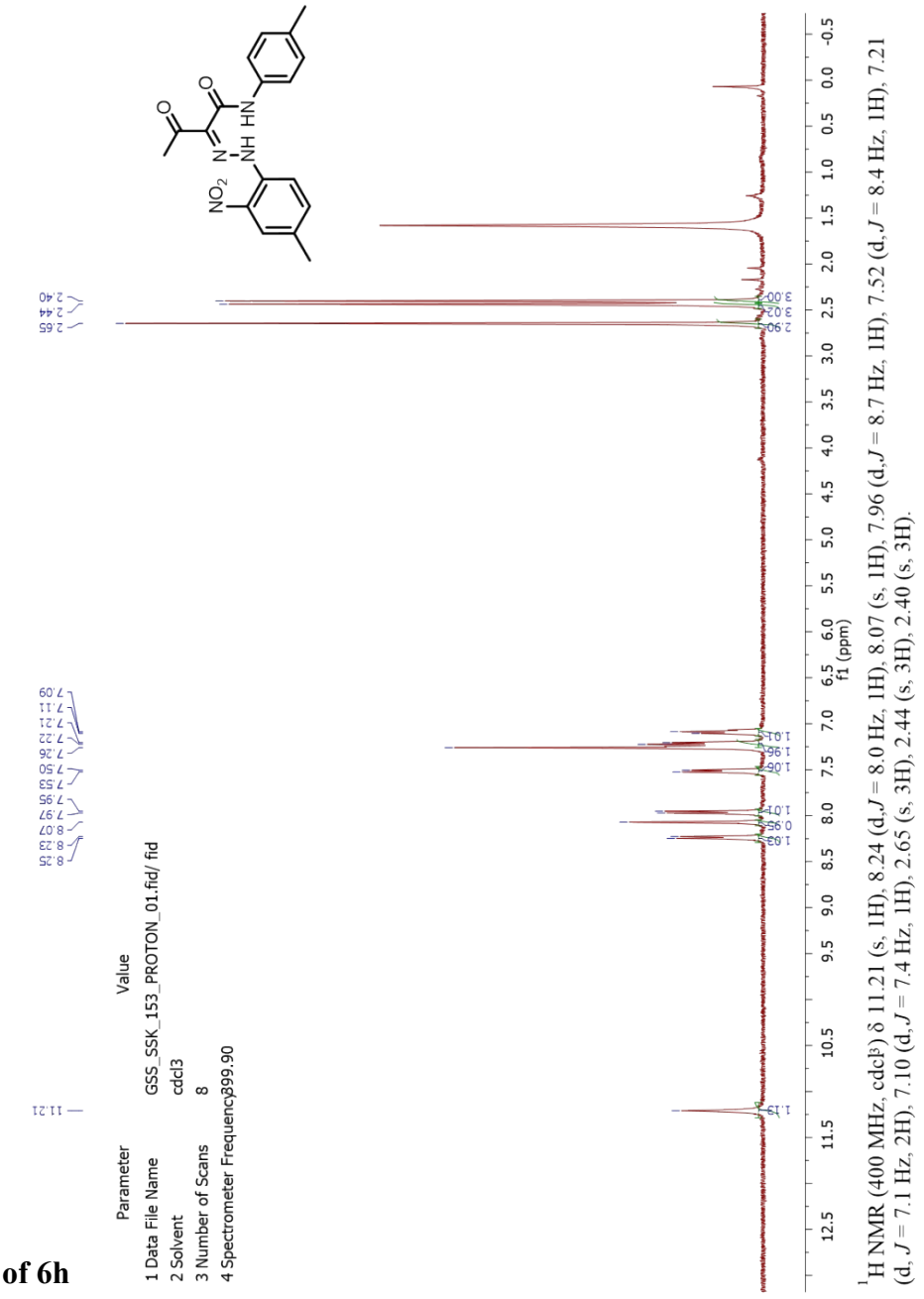
^{1}H NMR (400 MHz, dmso) δ 11.10 (s, 1H), 8.19 (s, 1H), 8.02 (s, 1H), 13.44 (s, 1H), 12.49 (s, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.34 (s, 2H), 7.21 (dd, J = 16.0, 7.8 Hz, 4H), 7.10 (m, 1H), 2.19 (s, 3H).

^{1}H NMR of 3q

^{1}H NMR of 3s



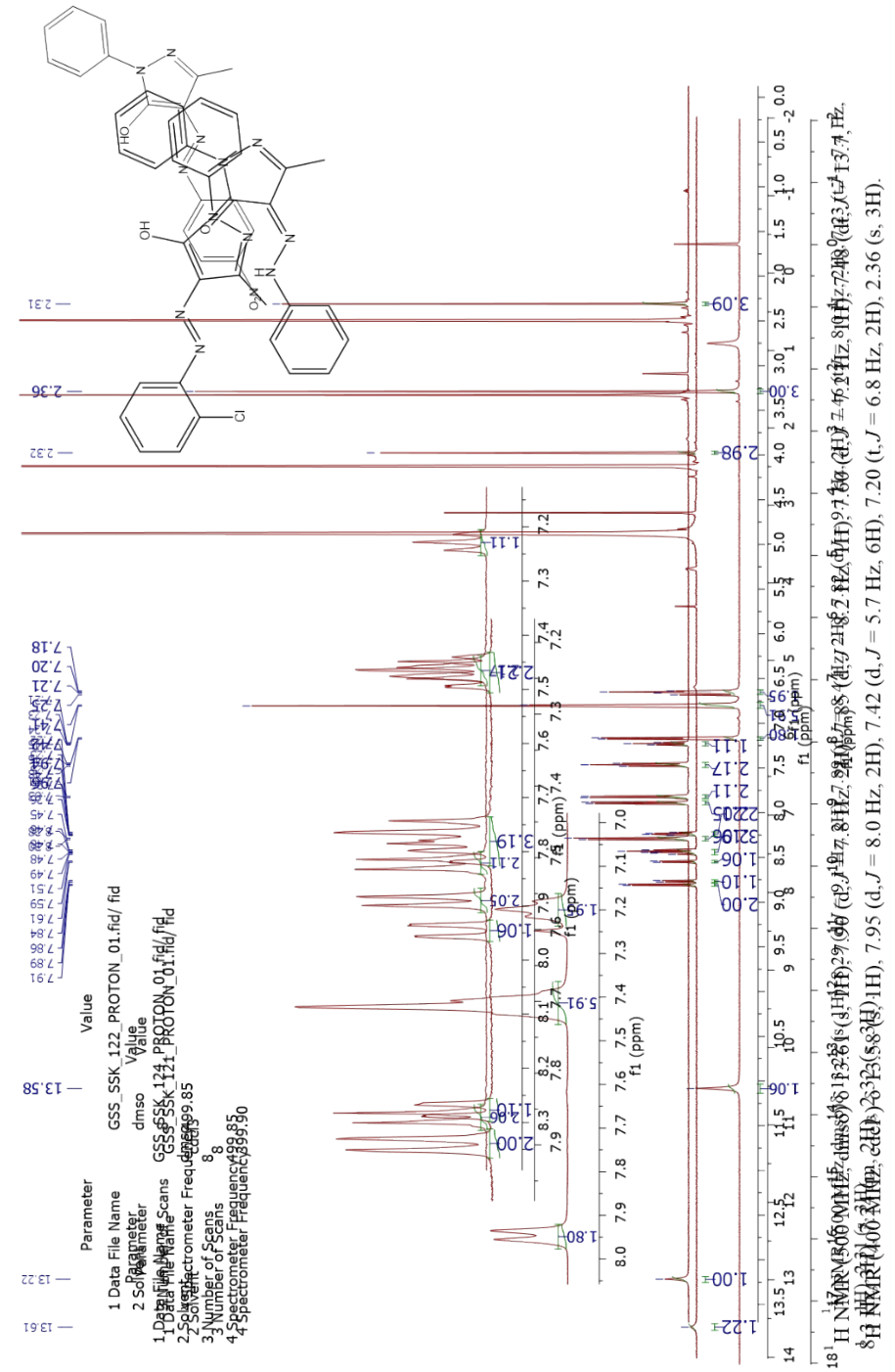
^{1}H NMR of 3r



^{1}H NMR (400 MHz, cdcl^3) δ 11.21 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 7.1 Hz, 2H), 7.10 (d, J = 7.4 Hz, 1H), 2.65 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H).

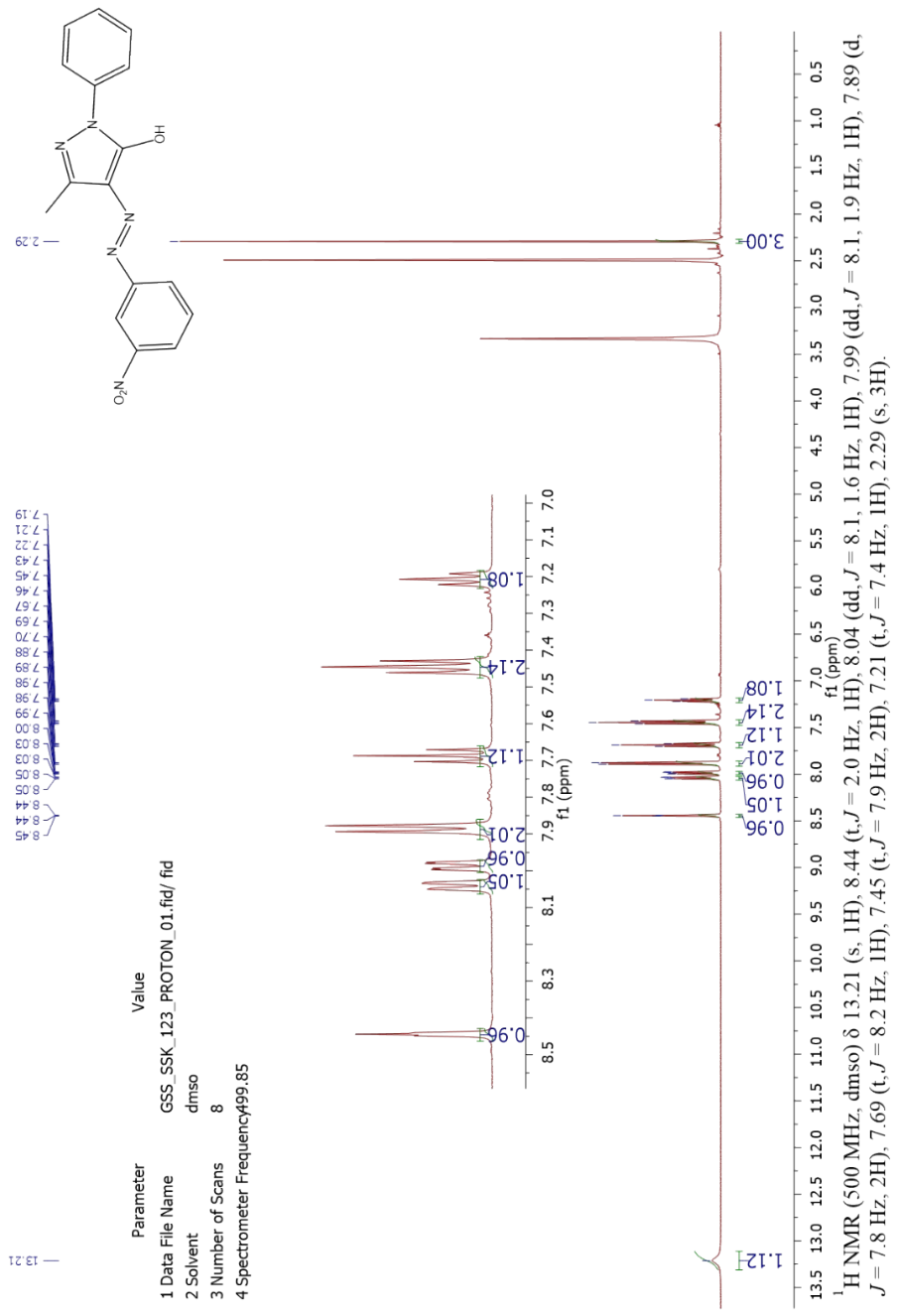
^{1}H NMR of 6h

^{1}H NMR of 6a



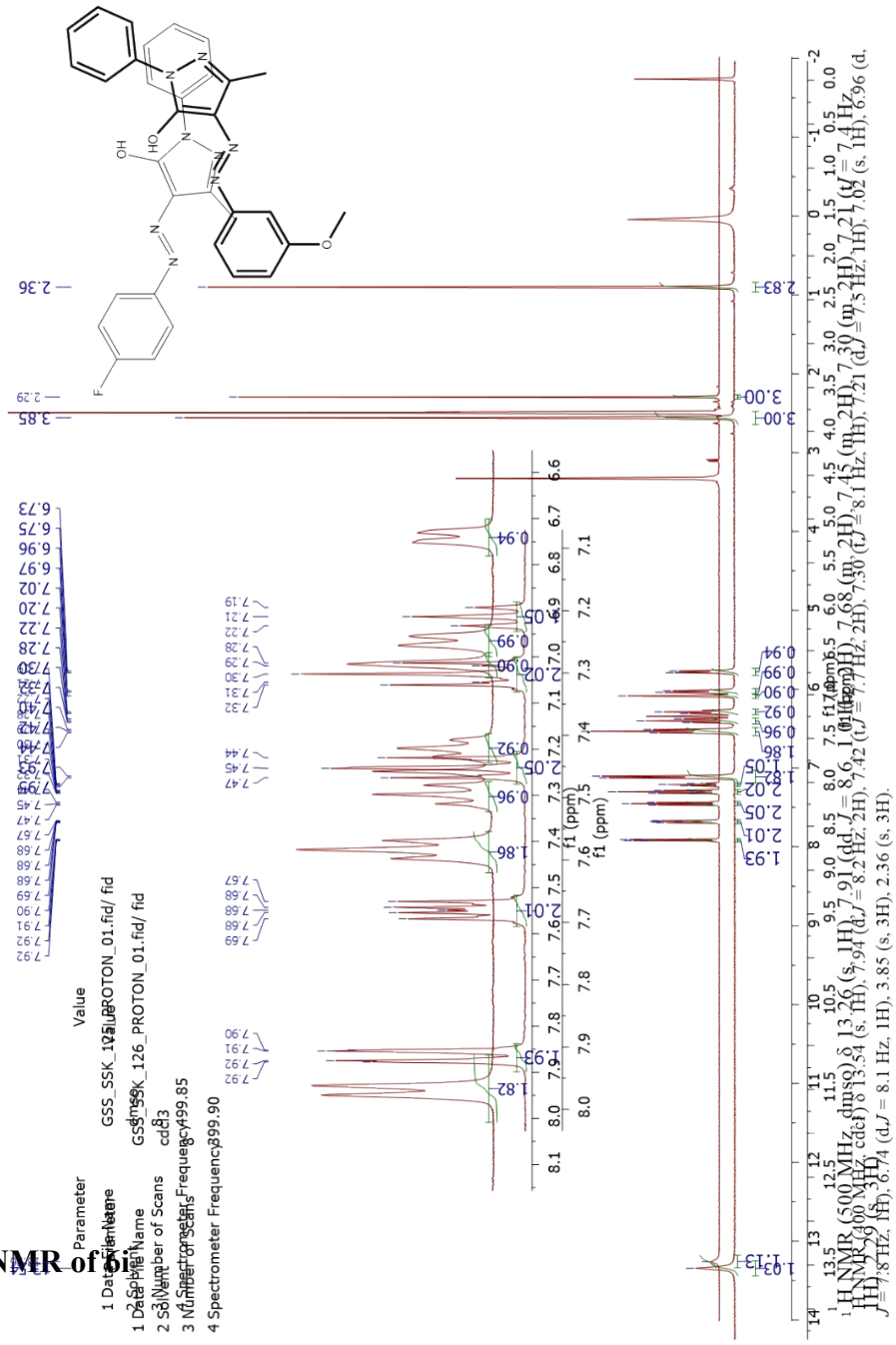
^{1}H NMR of 6d

^{1}H NMR of 6c



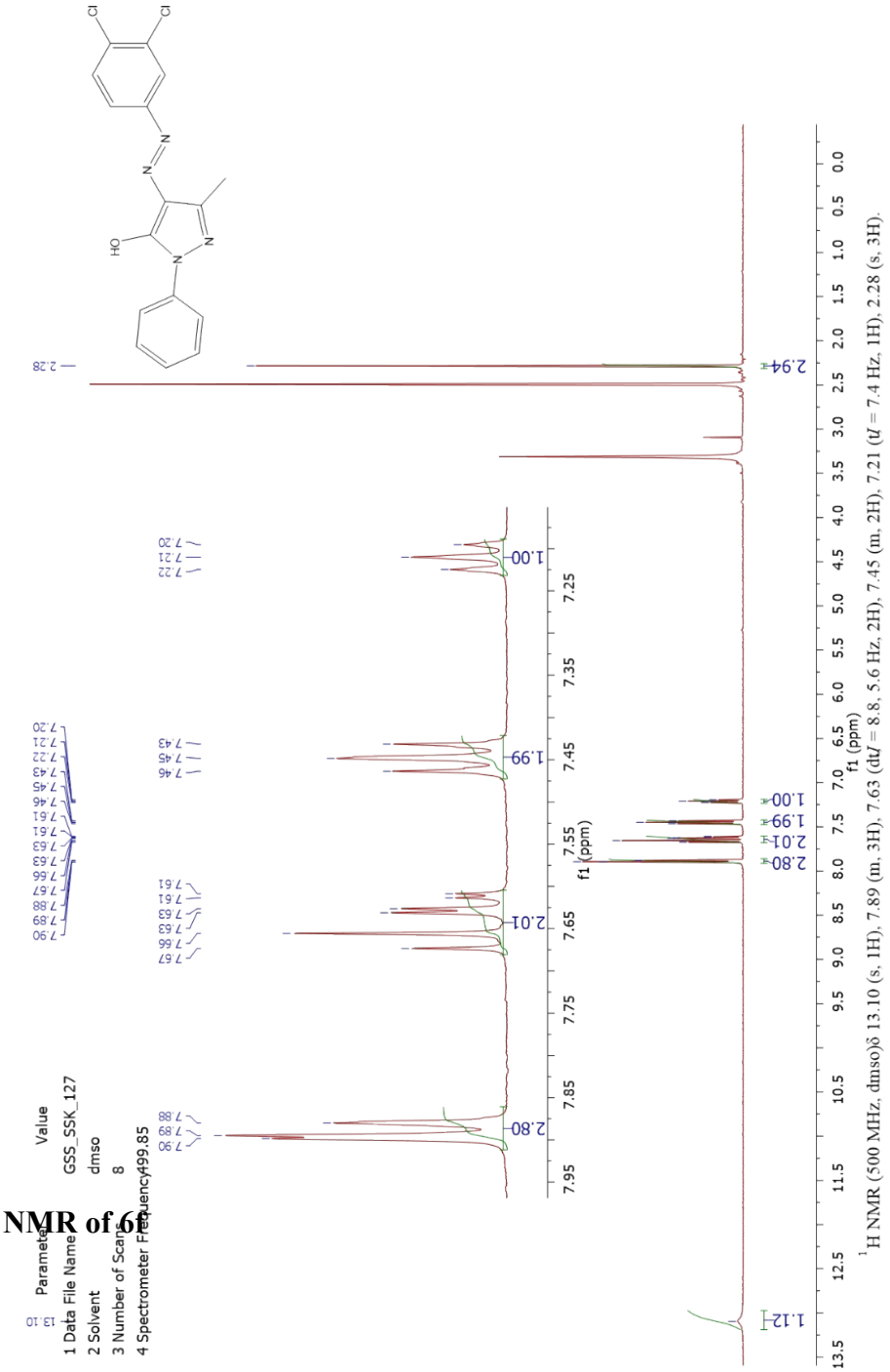
^{1}H NMR (500 MHz, dmso) δ 13.21 (s, 1H), 8.44 (t, J = 2.0 Hz, 1H), 8.04 (dd, J = 8.1, 1.6 Hz, 1H), 7.99 (dd, J = 8.1, 1.9 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 8.2 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 2.29 (s, 3H).

^{1}H NMR of 6b

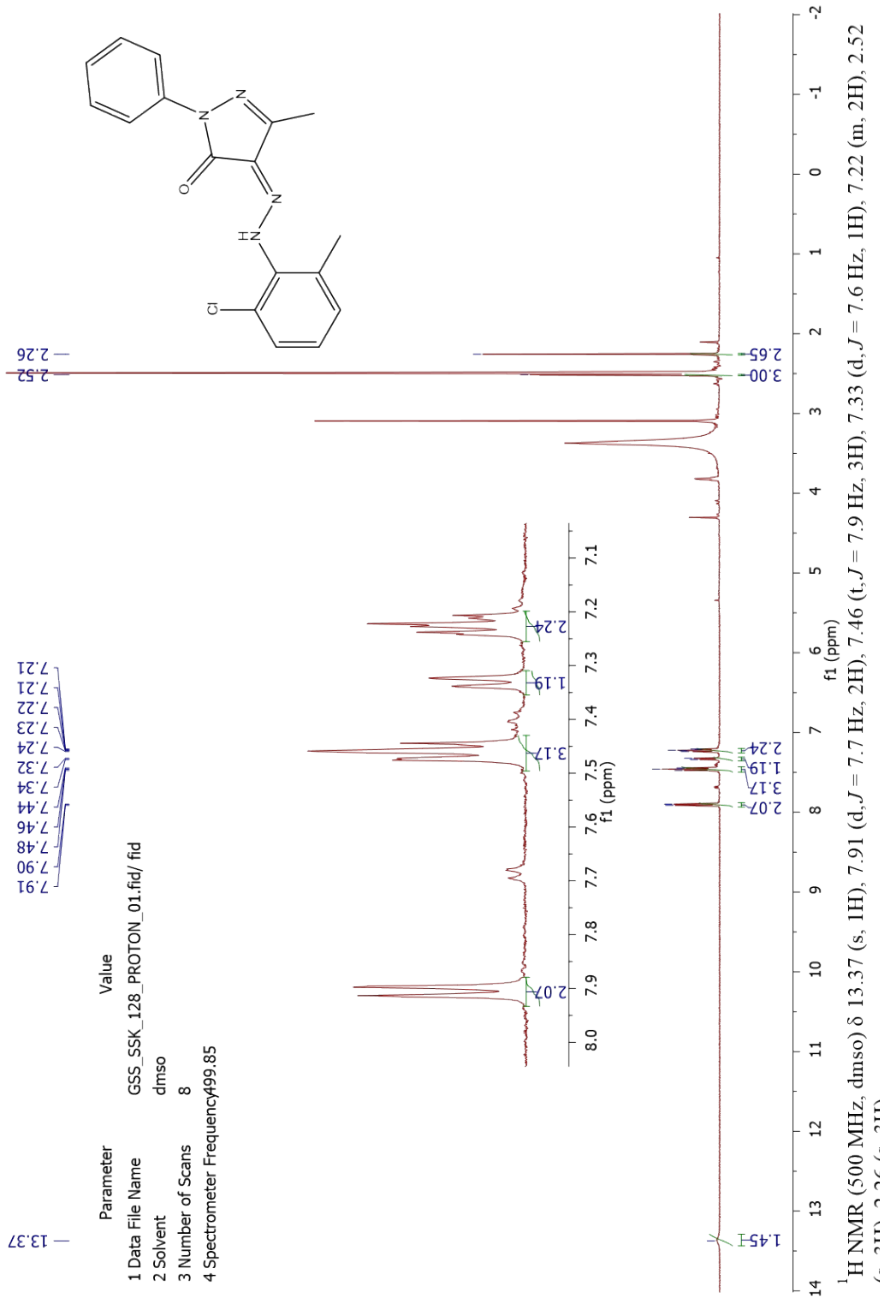


^{1}H NMR of 6i

^{1}H NMR of 6m

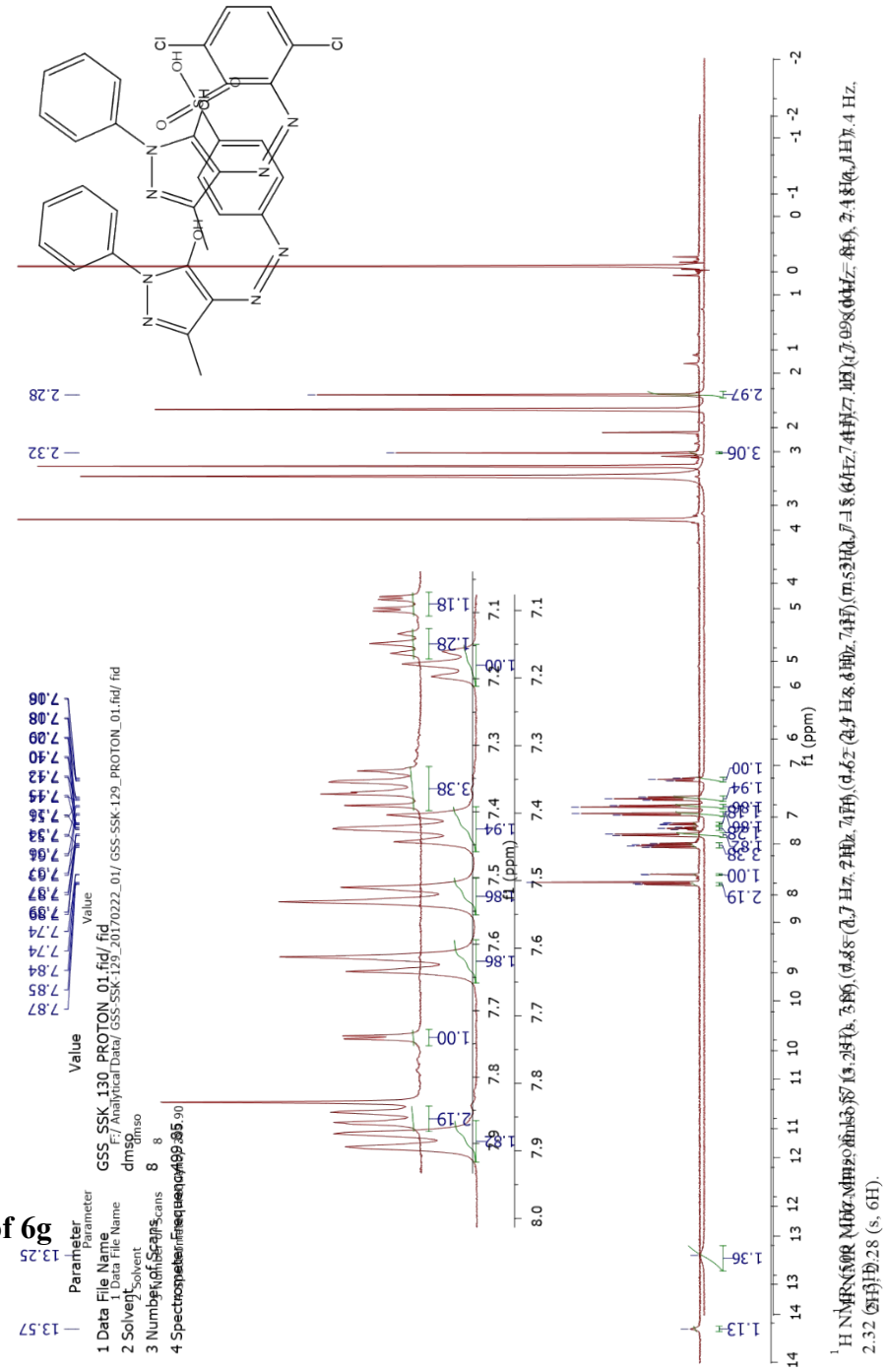


^{1}H NMR of 6n



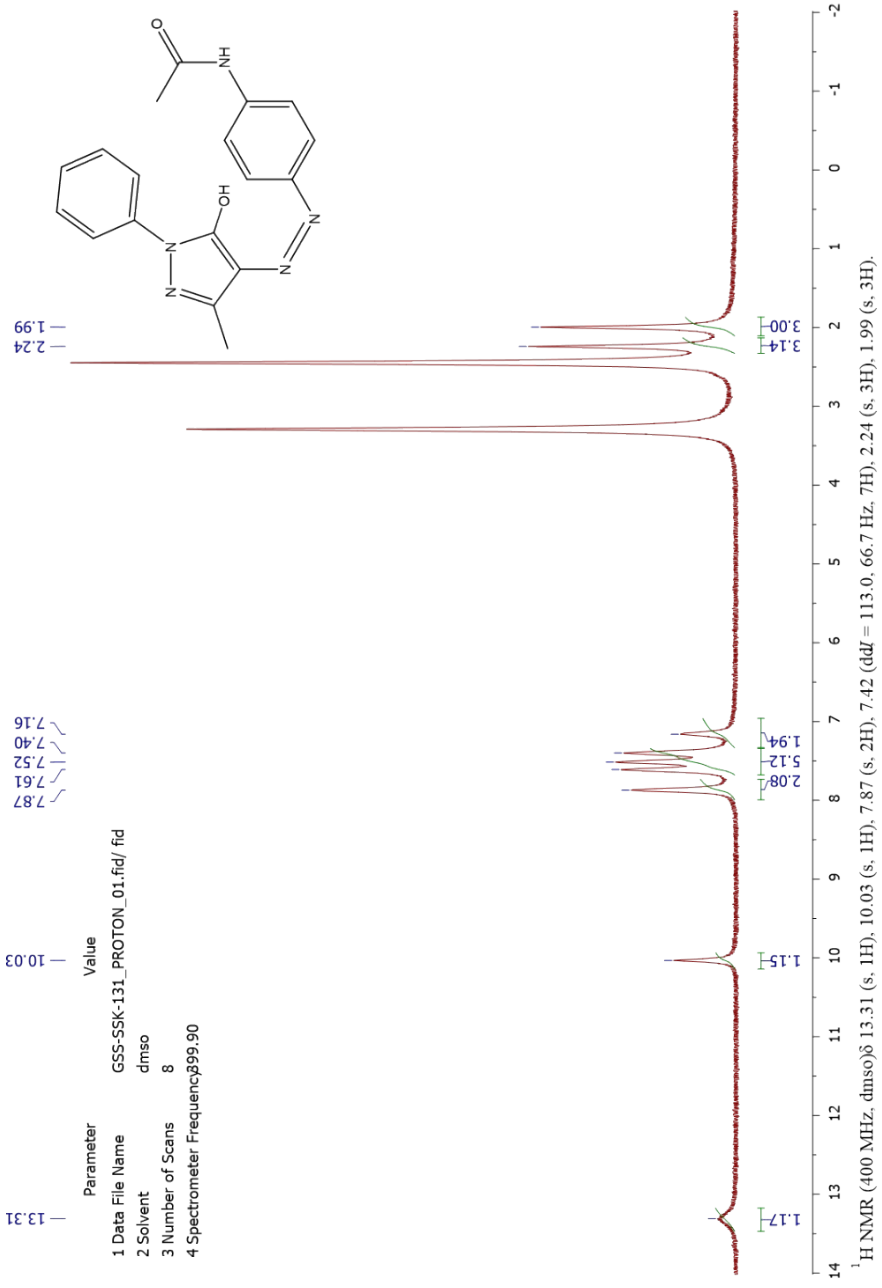
^{1}H NMR (500 MHz, dmso) δ 13.37 (s, 1H), 7.91 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.9 Hz, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.22 (m, 2H), 2.52 (s, 3H), 2.26 (s, 3H).

^{1}H NMR of 6n

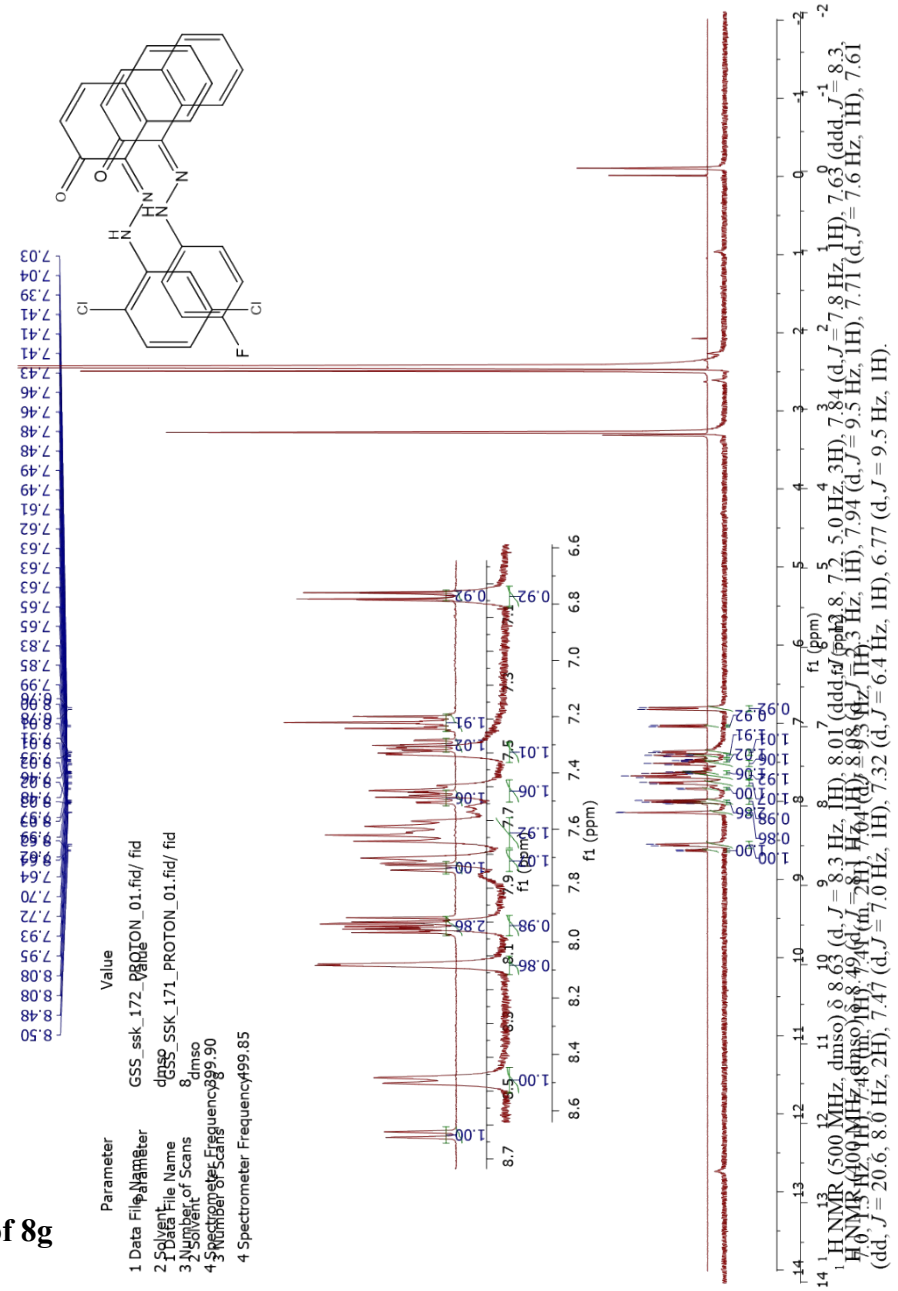


^{1}H NMR of 6g

^{1}H NMR of 6o

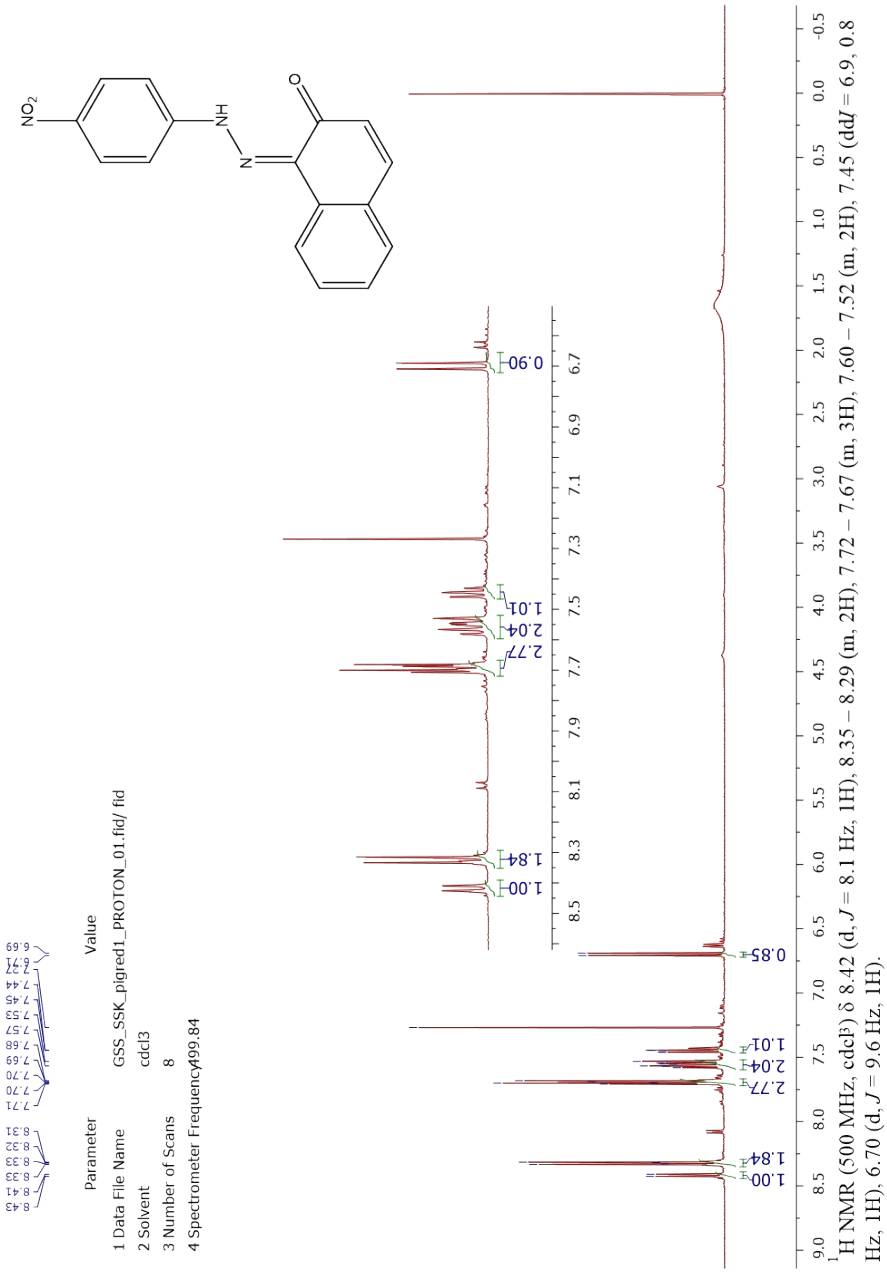

13.31
10.03
7.87
7.61
7.52
7.40
7.16
2.24
1.99
1.17
1.15
2.08
5.12
1.94
3.14
3.00
Parameter Value
1 Data File Name GSS-SSK-131_PROTON_01.fid/ fid
2 Solvent dmso
3 Number of Scans 8
4 Spectrometer Frequency 399.90
^{1}H NMR (400 MHz, dmso) δ 13.31 (s, 1H), 10.03 (s, 1H), 7.87 (s, 2H), 7.42 (dd, J = 113.0, 66.7 Hz, 7H), 2.24 (s, 3H), 1.99 (s, 3H).

^{1}H NMR of 8b



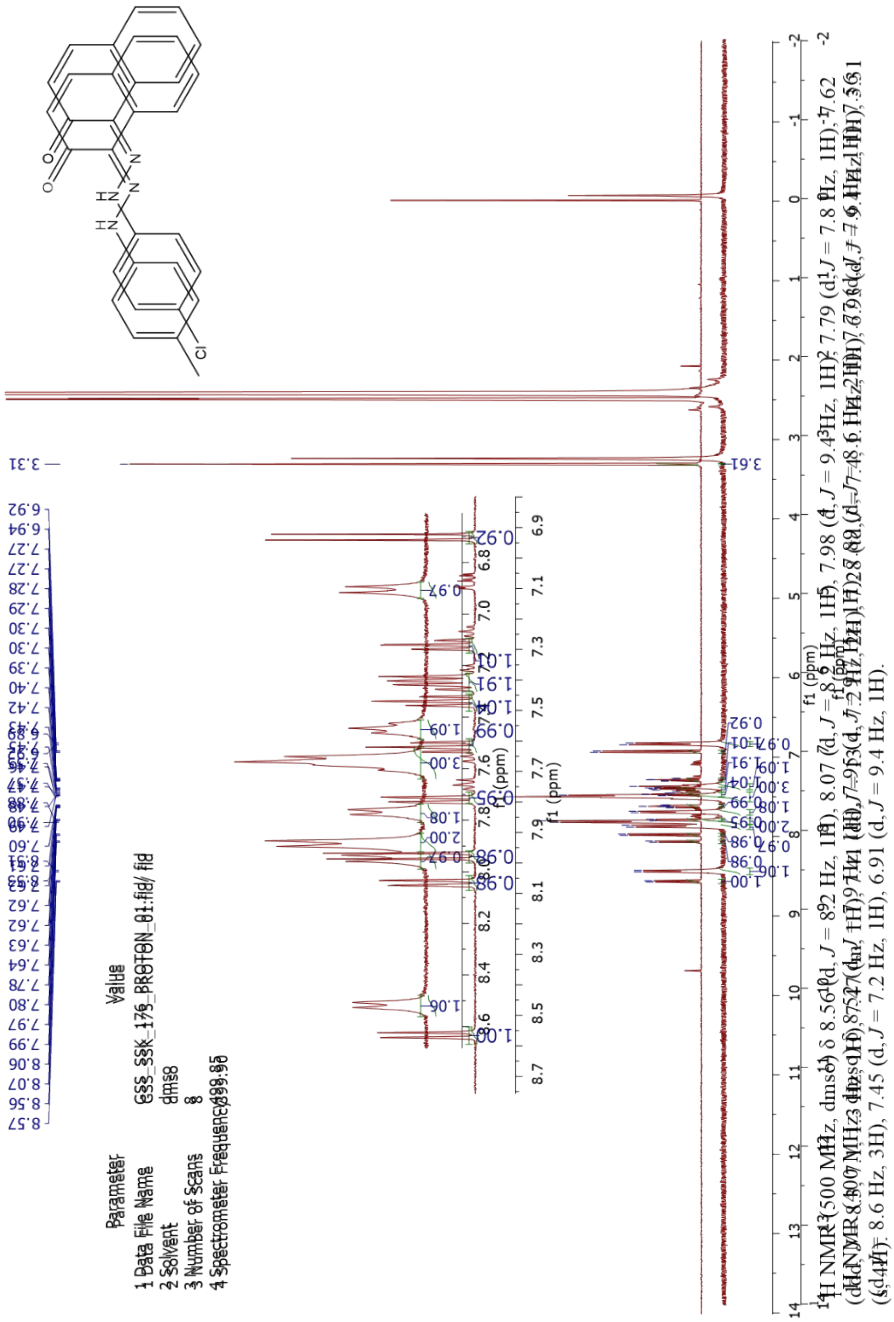
^{1}H NMR of 8g

^{1}H NMR of 8a



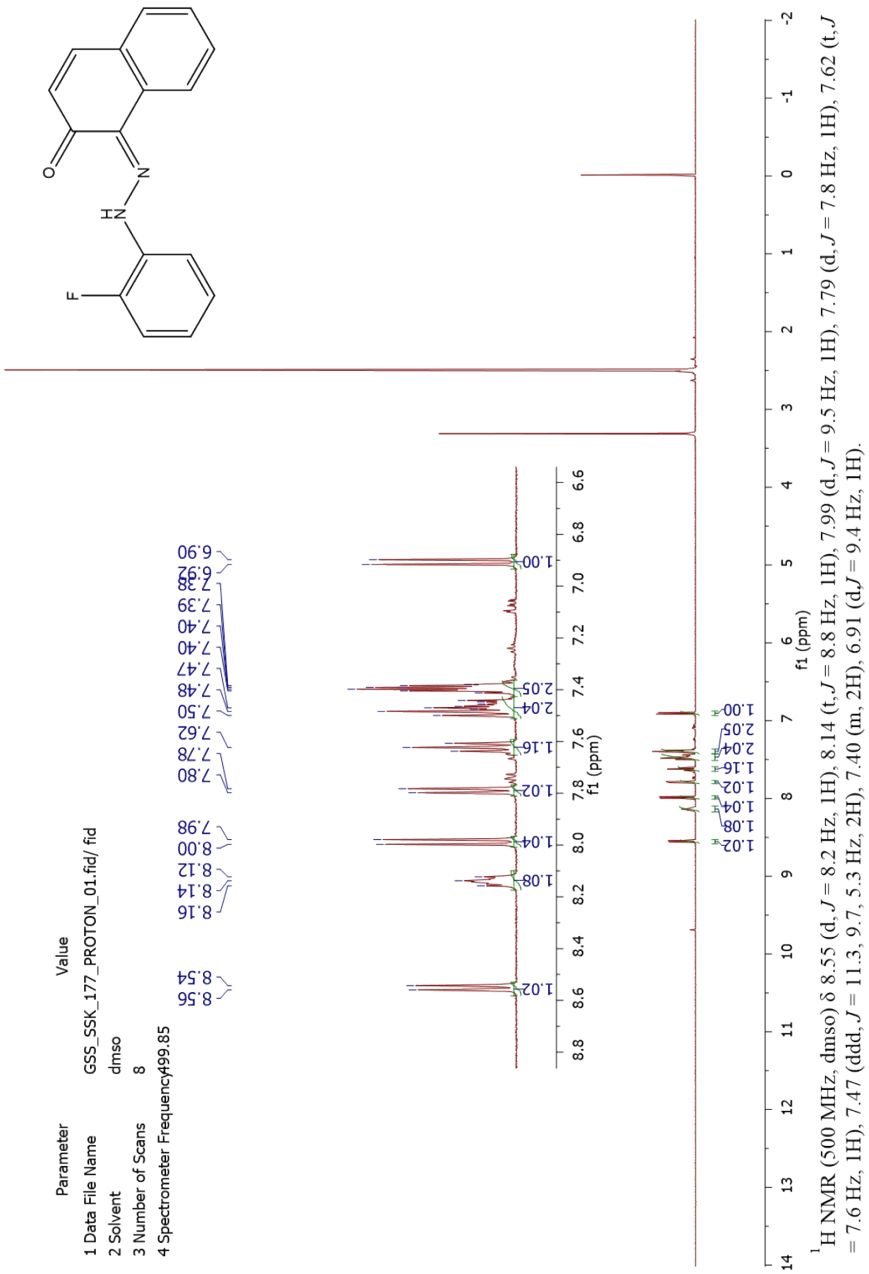
^{1}H NMR (500 MHz, cdcl$_3$) δ 8.42 (d, J = 8.1 Hz, 1H), 8.35 – 8.29 (m, 2H), 7.72 – 7.67 (m, 3H), 7.60 – 7.52 (m, 2H), 7.45 (dd$J$ = 6.9, 0.8 Hz, 1H), 6.70 (d, J = 9.6 Hz, 1H).

^{1}H NMR of 8j



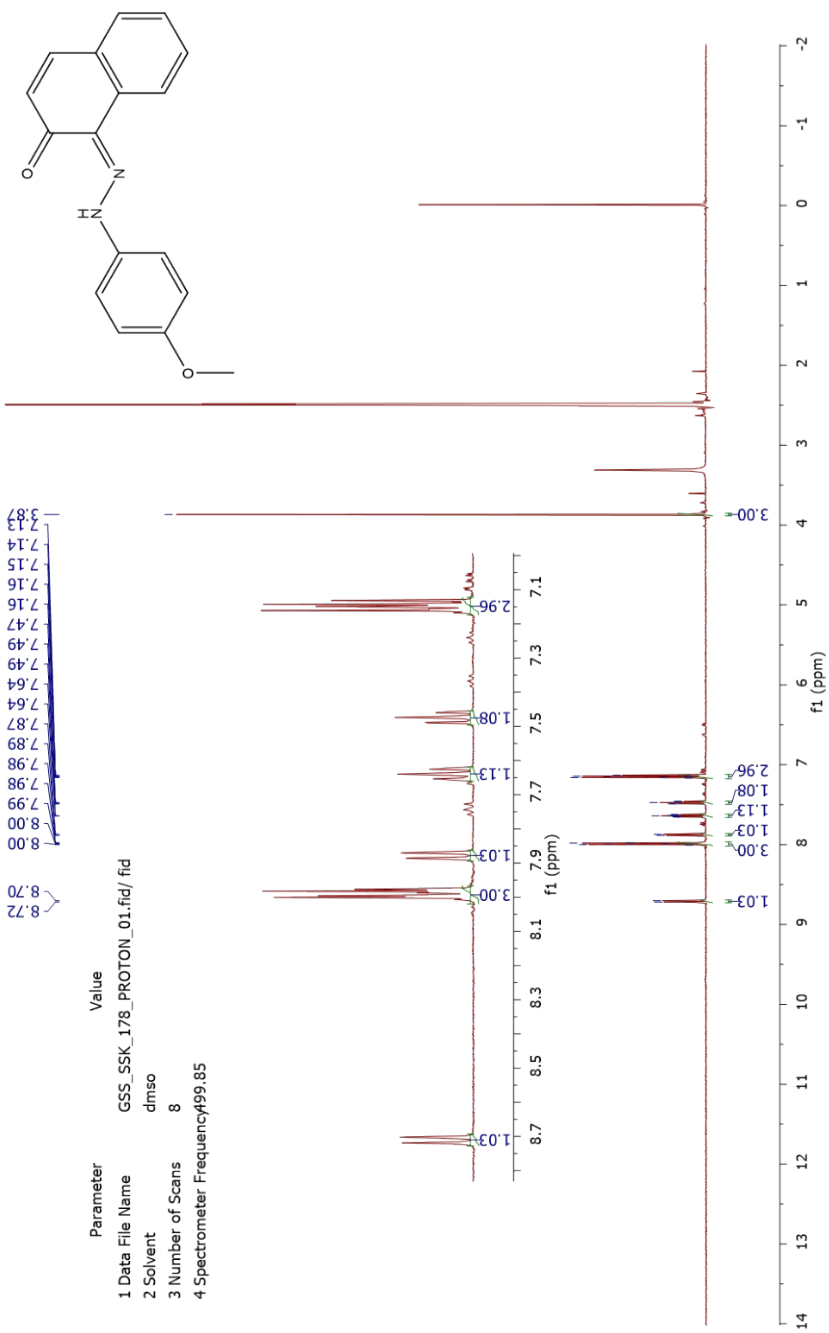
^{1}H NMR of 8e

^{1}H NMR of 8k



^{1}H NMR (500 MHz, dmso) δ 8.55 (d, J = 8.2 Hz, 1H), 8.14 (t, J = 8.8 Hz, 1H), 7.99 (d, J = 9.5 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.47 (ddd, J = 11.3, 9.7, 5.3 Hz, 2H), 7.40 (m, 2H), 6.91 (d, J = 9.4 Hz, 1H).

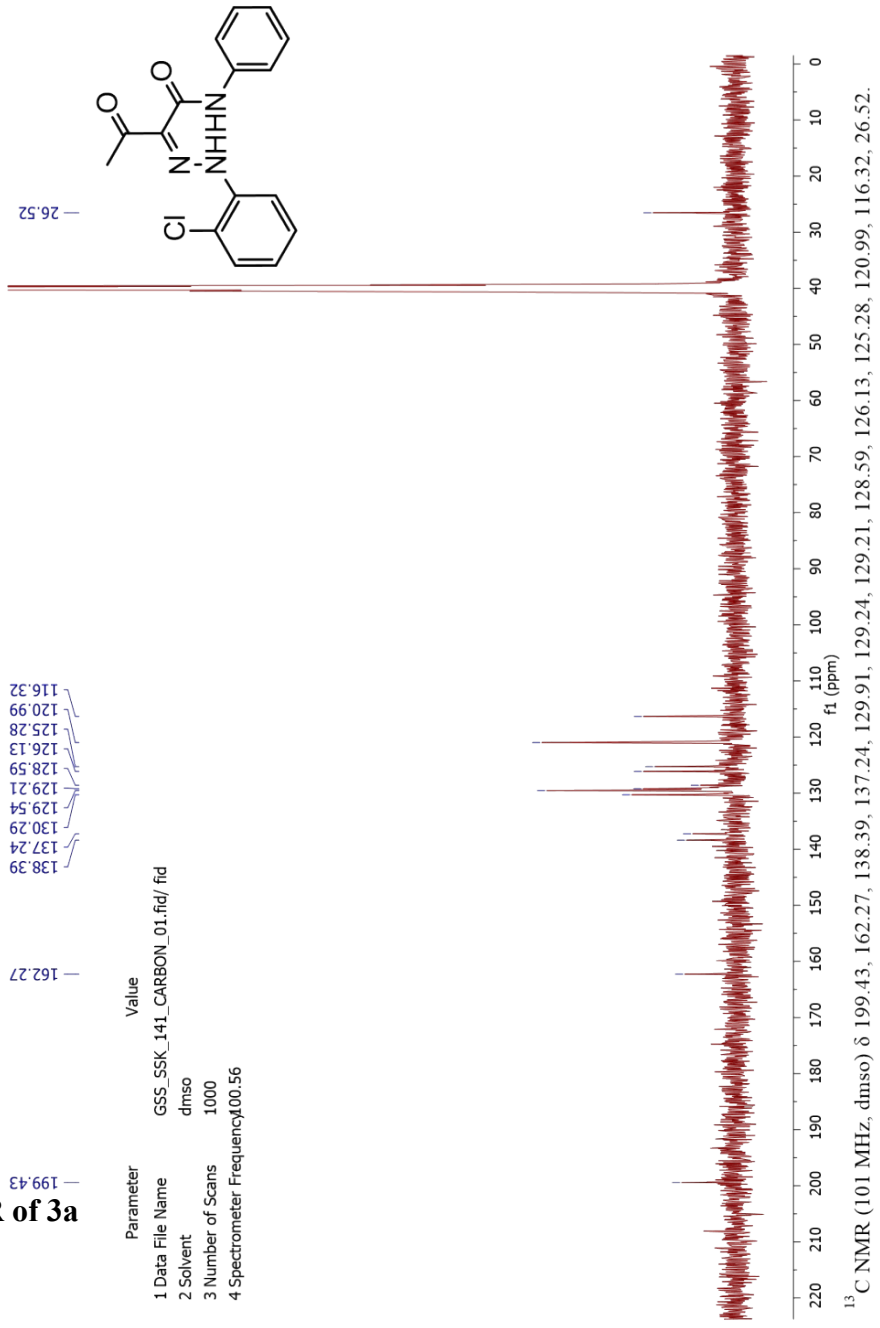
^{1}H NMR of 8l



^{1}H NMR (500 MHz, dmso) δ 8.71 (d, J = 8.2 Hz, 1H), 7.99 (dt, J = 4.8, 3.0 Hz, 3H), 7.88 (d, J = 7.9 Hz, 1H), 7.64 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H), 7.47 (m, 1H), 7.15 (m, 3H), 3.87 (s, 3H).

3.7. ^{13}C NMR of monoazo pigments:

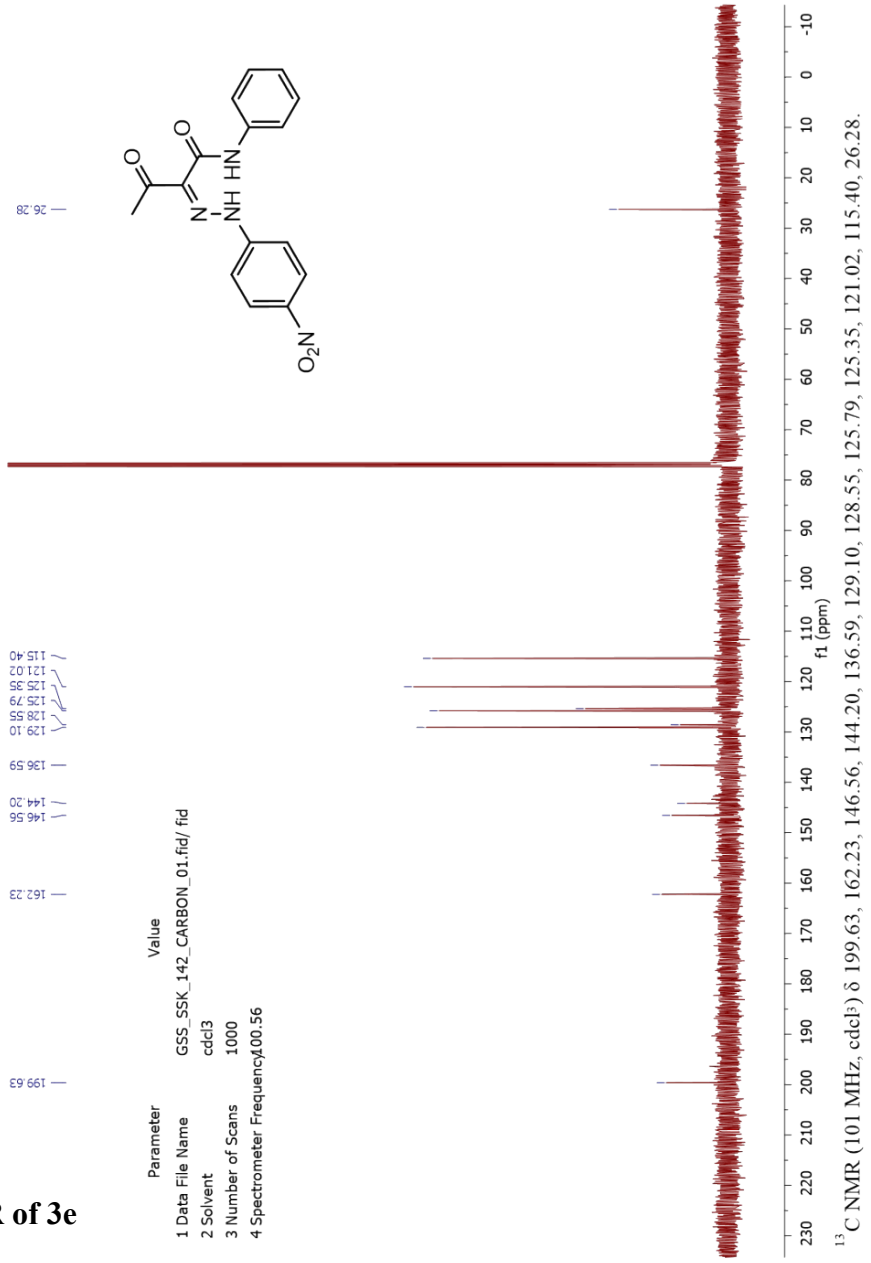
^{13}C NMR of 3d



^{13}C NMR (101 MHz, dmso) δ 199.43, 162.27, 138.39, 137.24, 129.91, 129.24, 129.21, 128.59, 126.13, 125.28, 120.99, 116.32, 26.52.

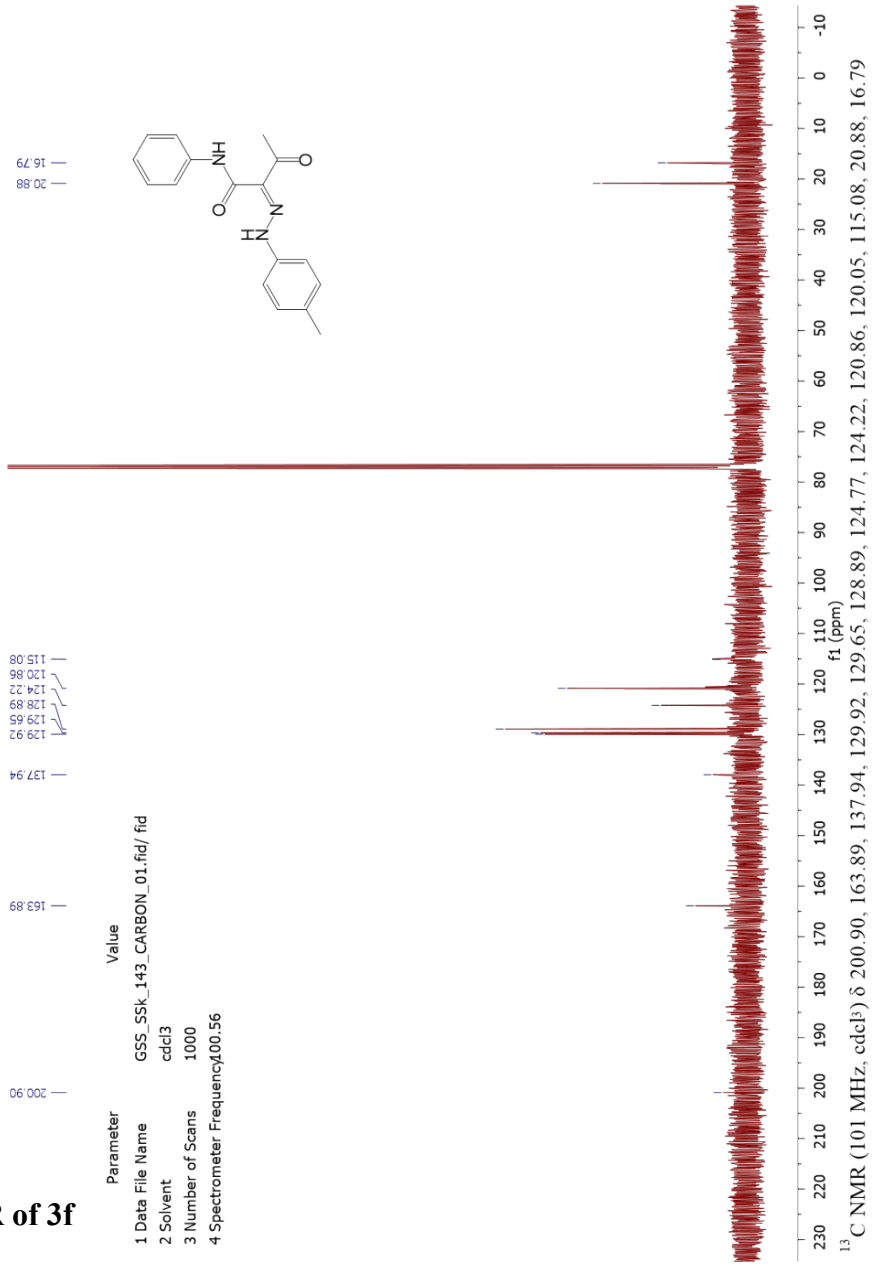
^{13}C NMR of 3a

^{13}C NMR of 3e

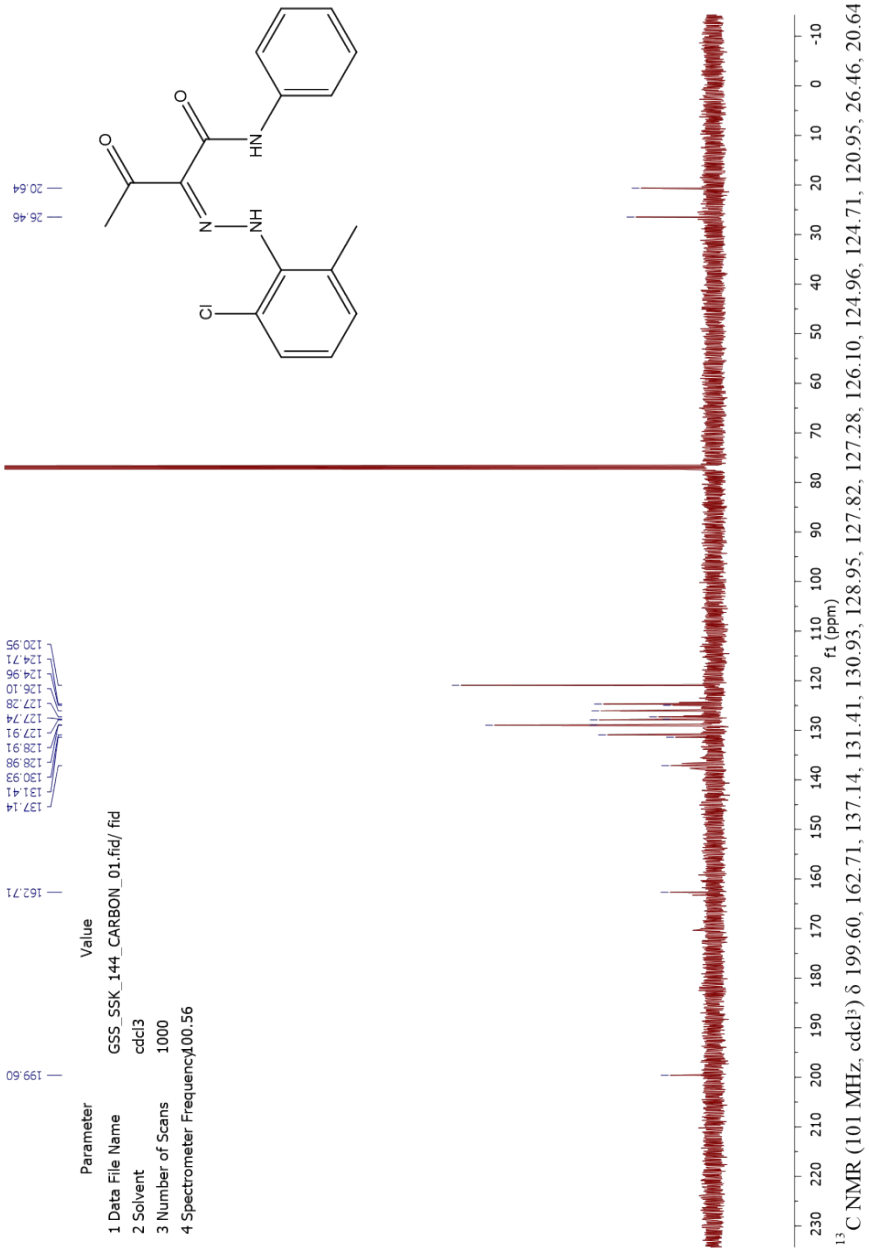


^{13}C NMR (101 MHz, cdcl$_3$) δ 199.63, 162.23, 146.56, 144.20, 136.59, 129.10, 128.55, 125.79, 125.35, 121.02, 115.40, 26.28.

^{13}C NMR of 3f

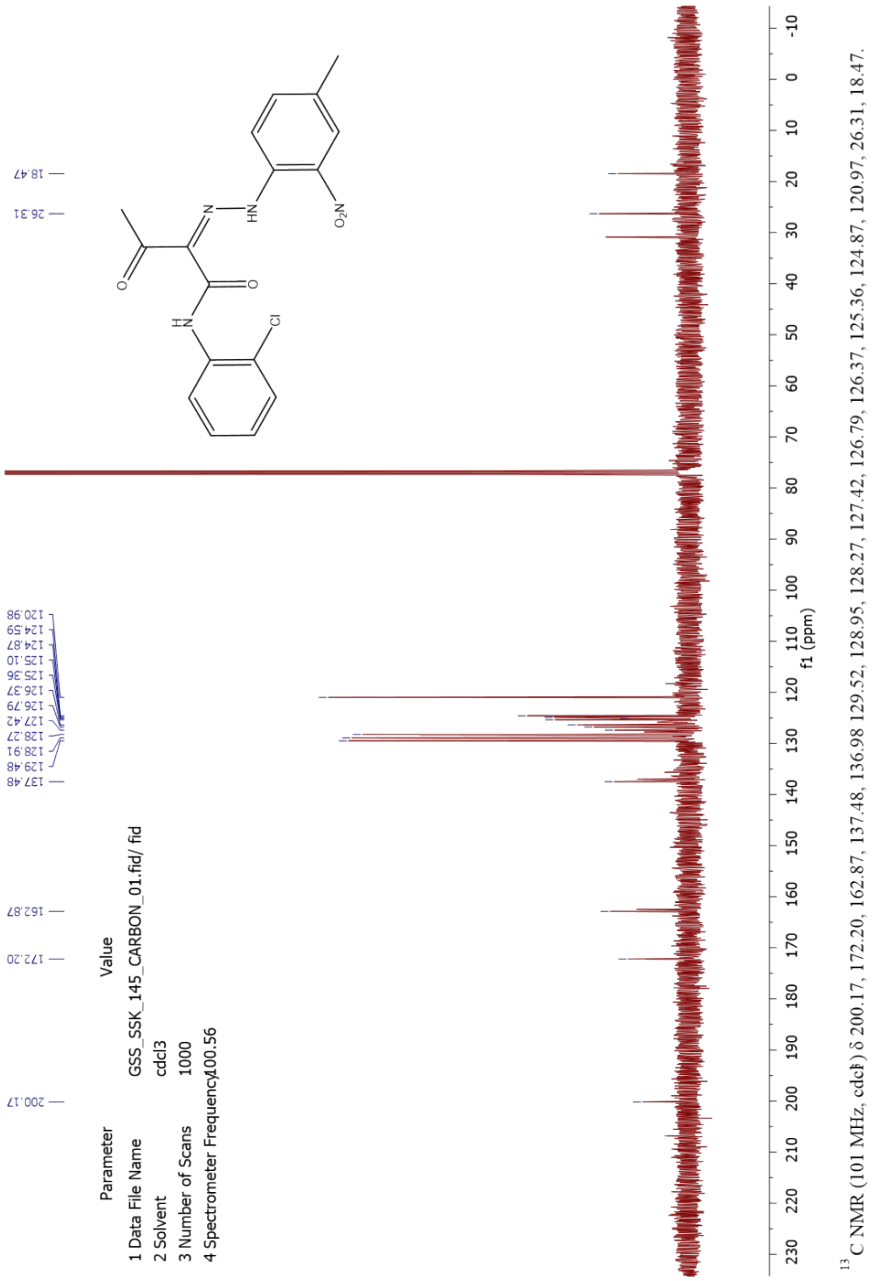


^{13}C NMR (101 MHz, cdcl$_3$) δ 200.90, 163.89, 137.94, 129.92, 129.65, 128.89, 124.77, 124.22, 120.86, 120.05, 115.08, 20.88, 16.79



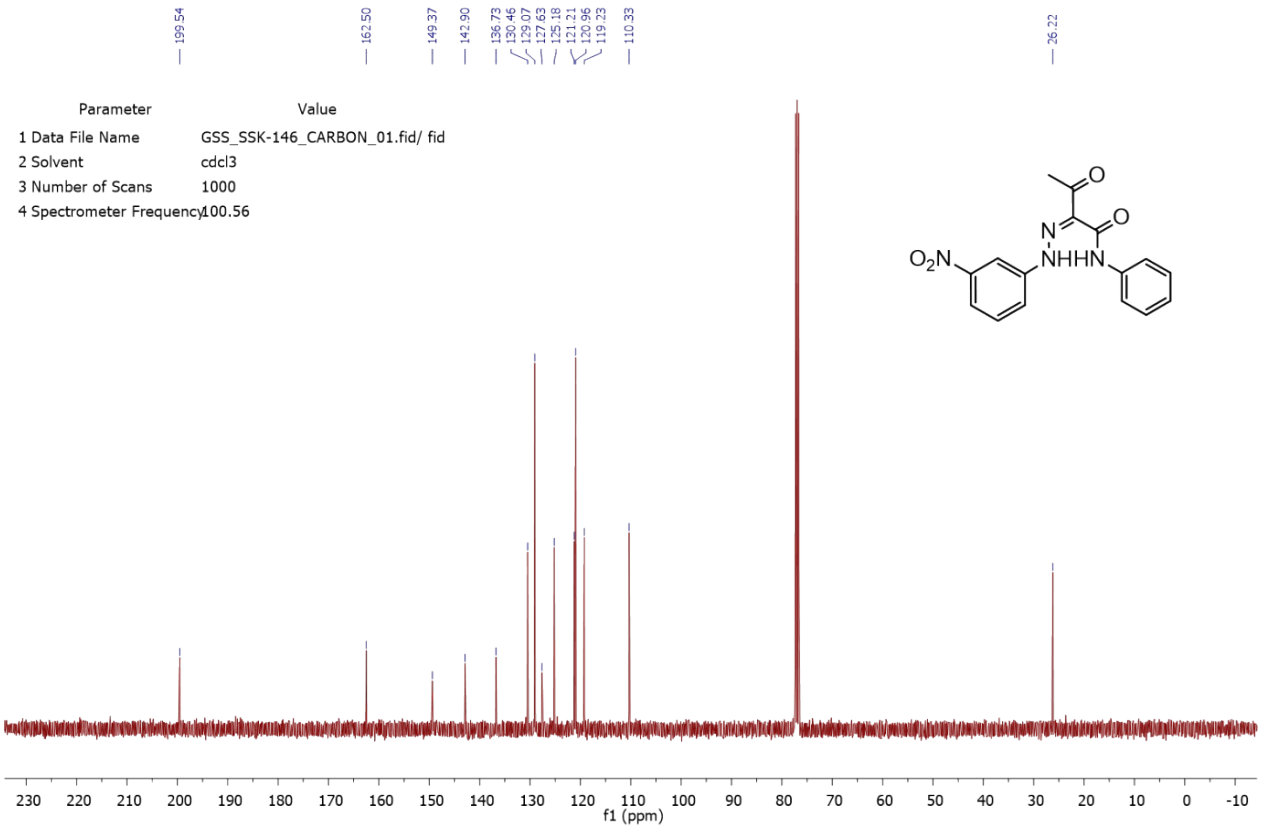
^{13}C NMR (101 MHz, cdcl^3) δ 199.60, 162.71, 137.14, 131.41, 130.93, 128.95, 127.82, 127.28, 126.10, 124.96, 124.71, 120.95, 26.46, 20.64

^{13}C NMR of 3q



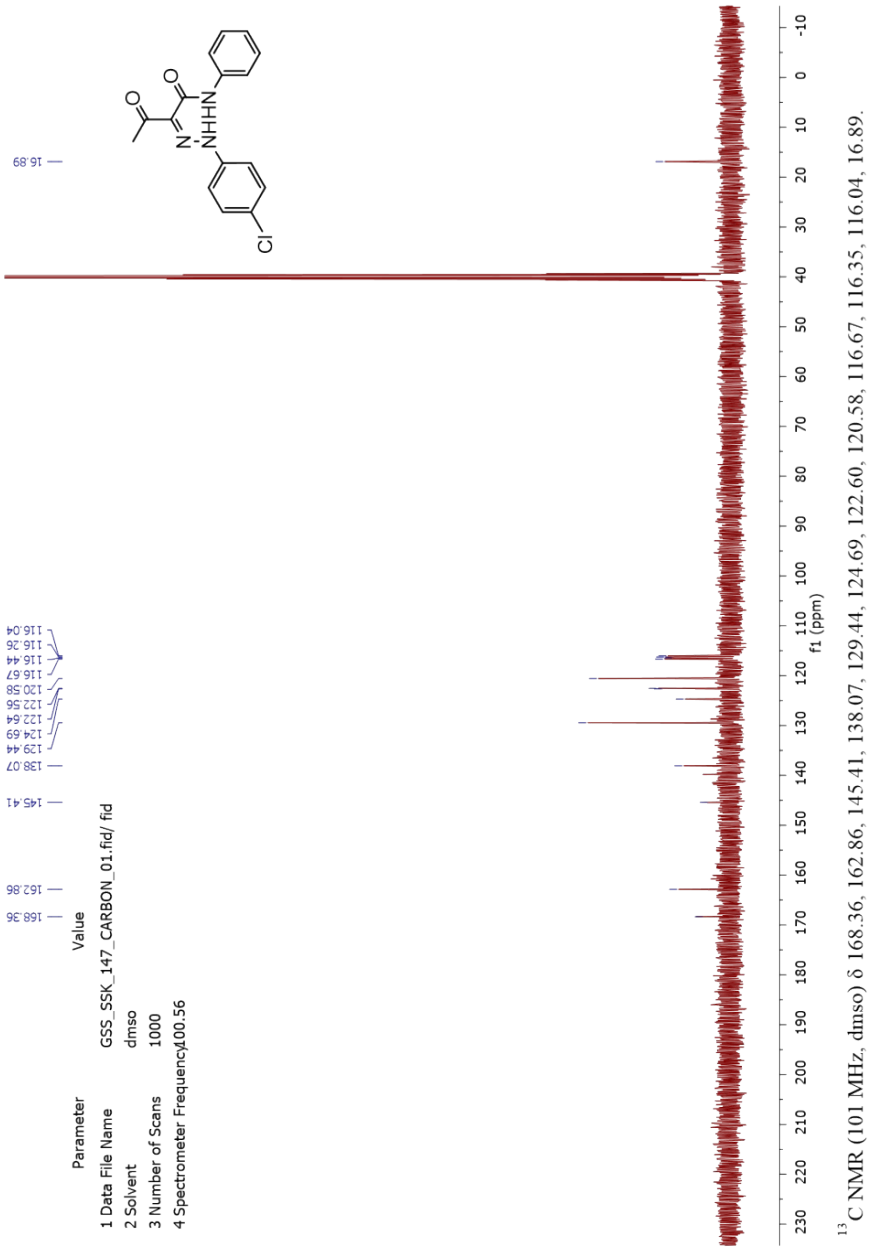
^{13}C NMR (101 MHz, cdcl) δ 200.17, 172.20, 162.87, 137.48, 136.98 129.52, 128.95, 128.27, 127.42, 126.79, 126.37, 125.36, 124.87, 120.97, 26.31, 18.47.

^{13}C NMR of 3c



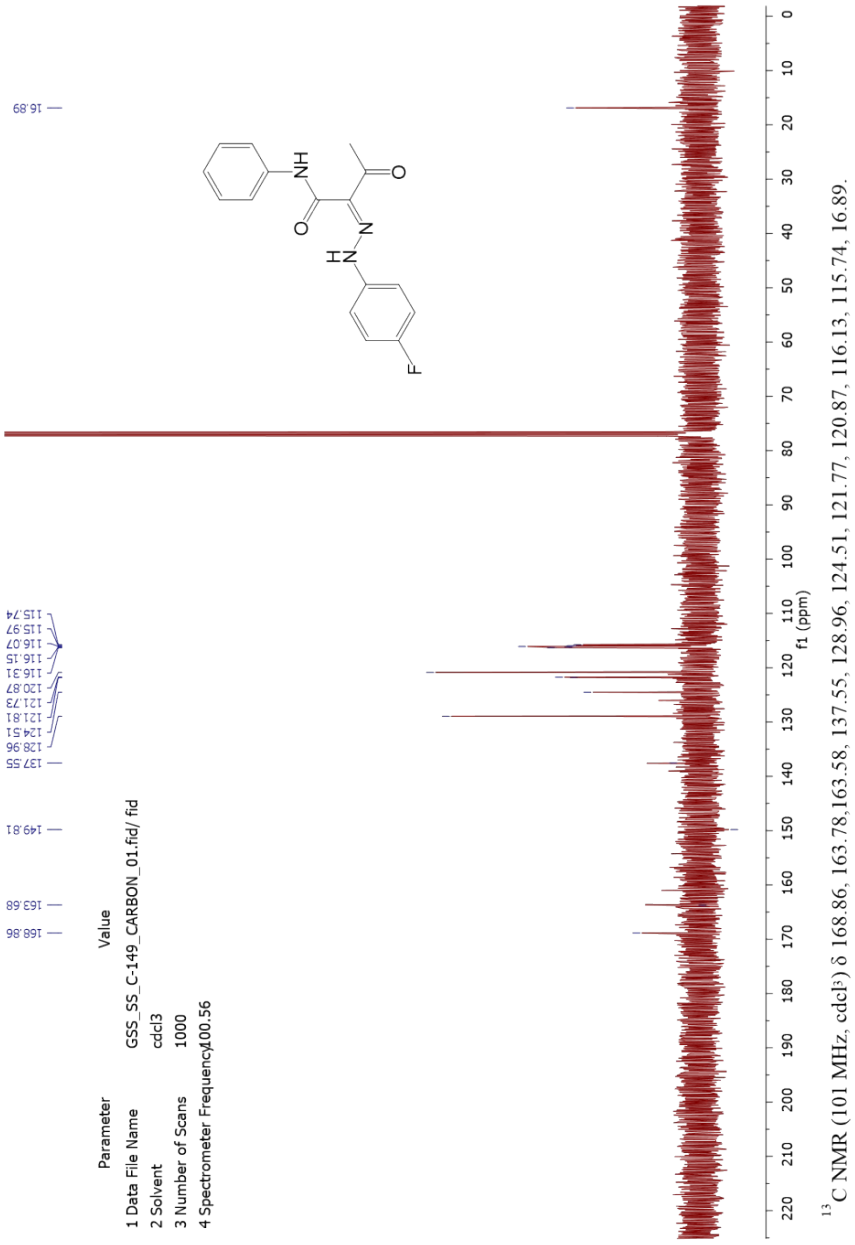
^{13}C NMR (101 MHz, cdcl$_3$) δ 199.54, 162.50, 149.37, 142.90, 136.73, 130.46, 129.07, 127.63, 125.18, 121.21, 120.96, 119.23, 110.33, 26.

^{13}C NMR of 3j



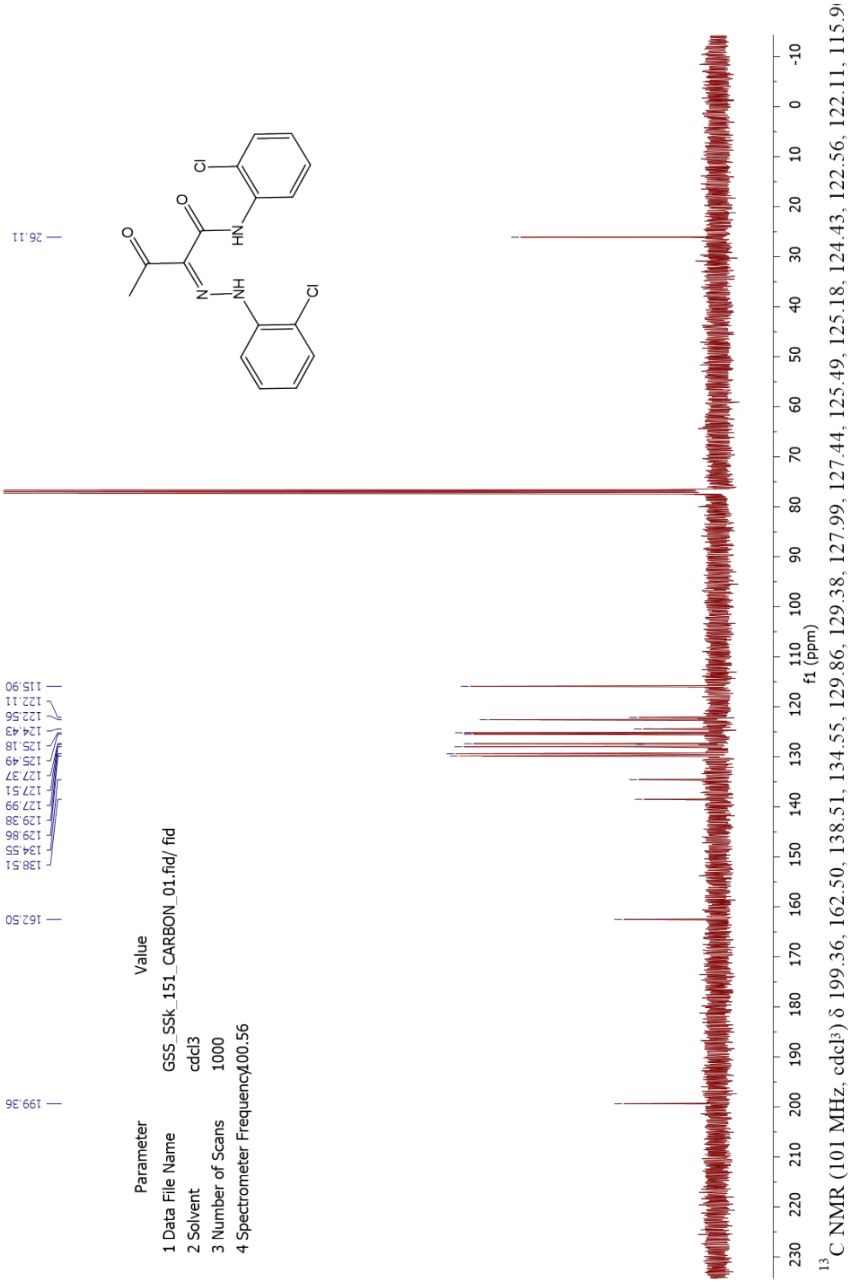
^{13}C NMR (101 MHz, dmso) δ 168.36, 162.86, 145.41, 138.07, 129.44, 124.69, 122.60, 120.58, 116.67, 116.35, 116.04, 16.89.

^{13}C NMR of 3b



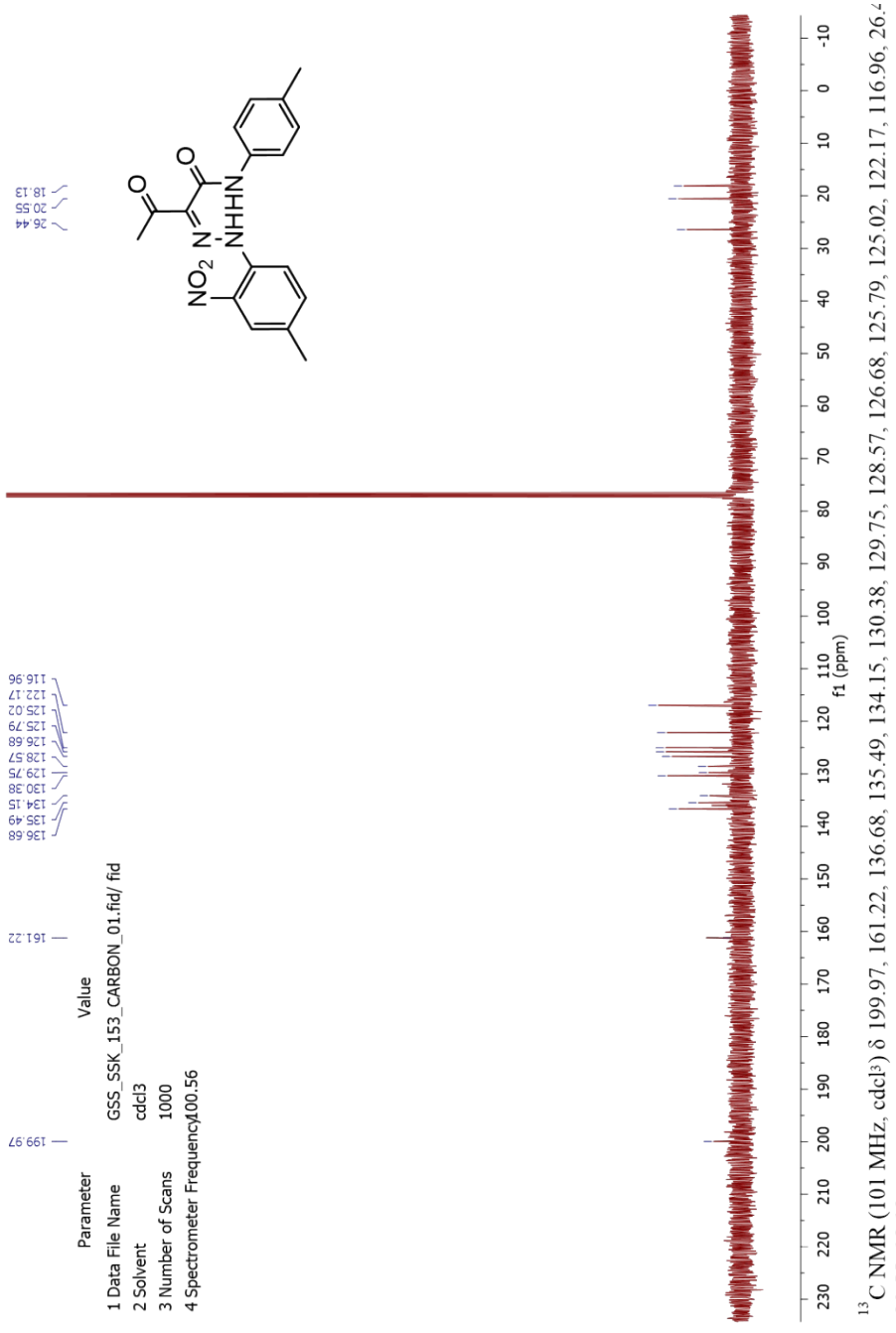
^{13}C NMR (101 MHz, cdcl^{3}) δ 168.86, 163.78,163.58, 137.55, 128.96, 124.51, 121.77, 120.87, 116.13, 115.74, 16.89.

^{13}C NMR of 3s



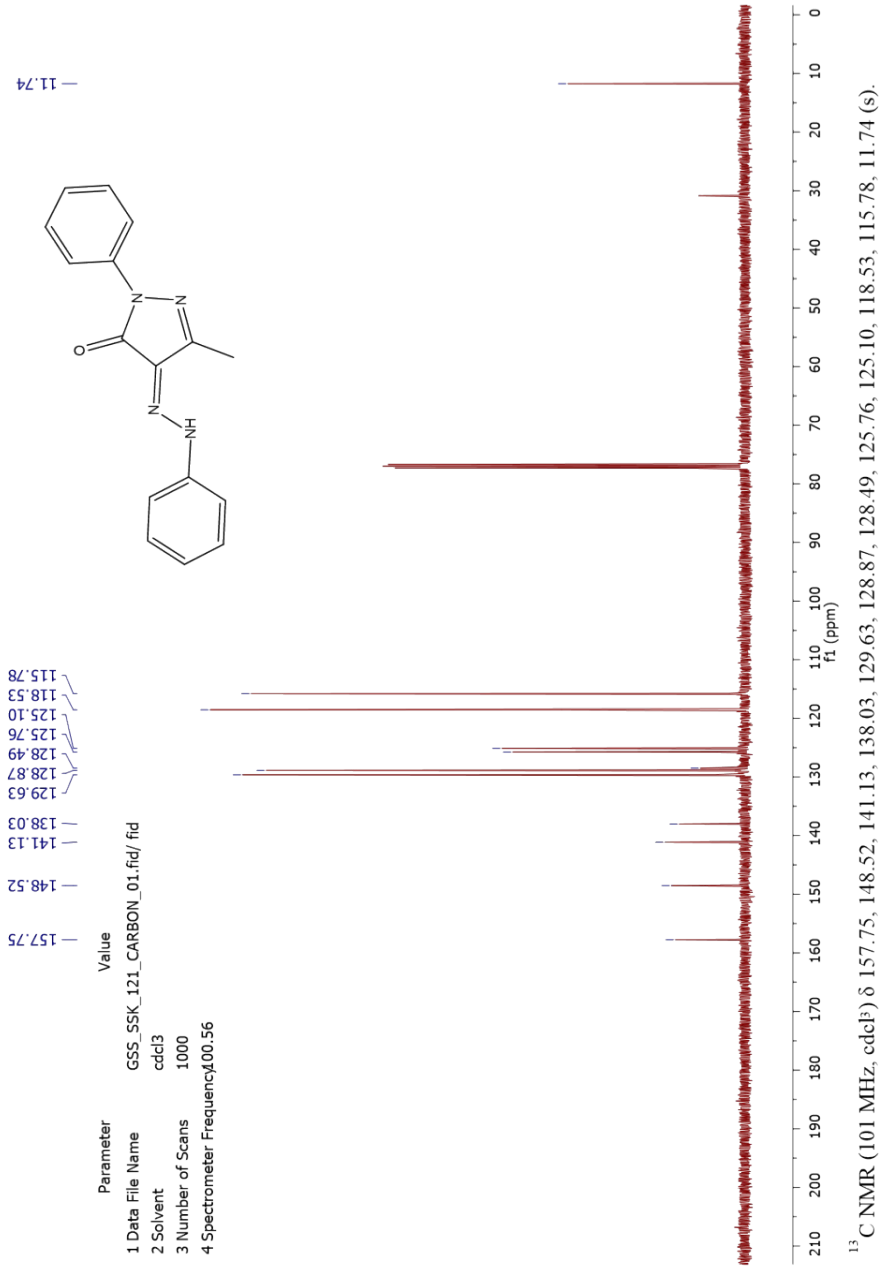
^{13}C NMR (101 MHz, cdcl^{3}) δ 199.36, 162.50, 138.51, 134.55, 129.86, 129.38, 127.99, 127.44, 125.49, 125.18, 124.43, 122.56, 122.11, 115.9
26.11.

^{13}C NMR of 3r



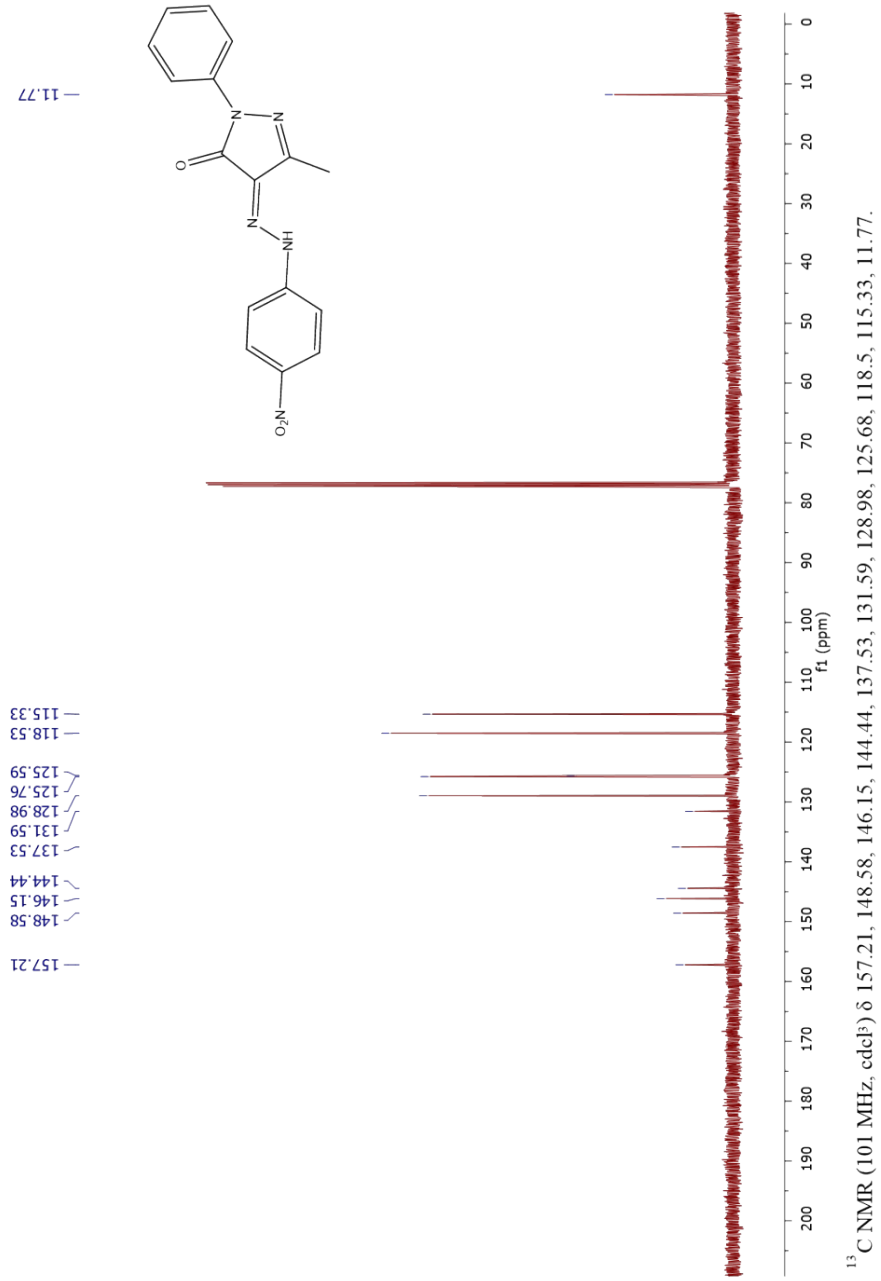
^{13}C NMR (101 MHz, cdcl$_3$) δ 199.97, 161.22, 136.68, 135.49, 134.15, 130.38, 129.75, 128.57, 126.68, 125.79, 125.02, 122.17, 116.96, 26.4
20.55, 18.13.

^{13}C NMR of 6h



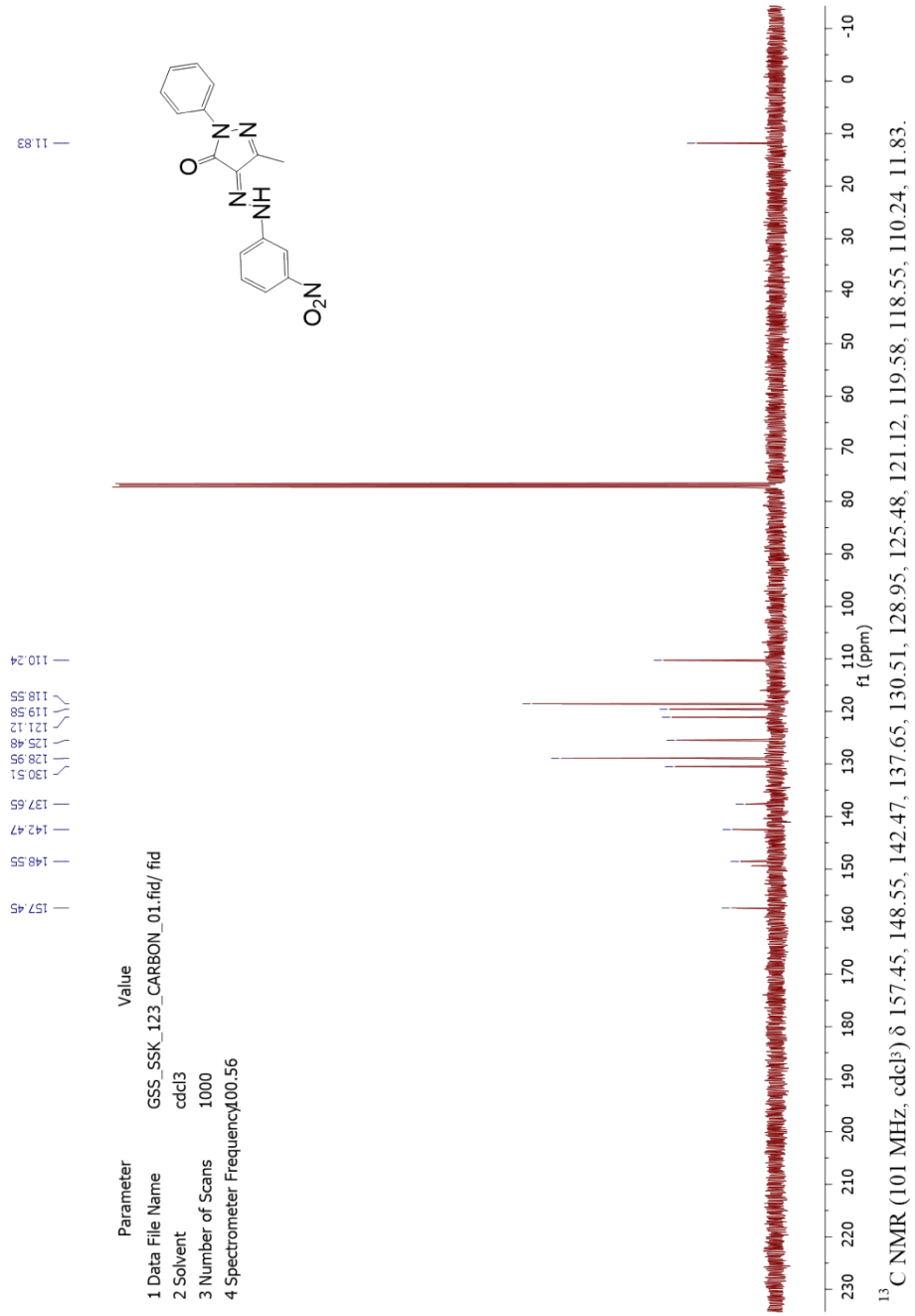
^{13}C NMR (101 MHz, cdcl^3) δ 157.75, 148.52, 141.13, 138.03, 129.63, 128.87, 128.49, 125.76, 125.10, 118.53, 115.78, 11.74 (s).

^{13}C NMR of 6a



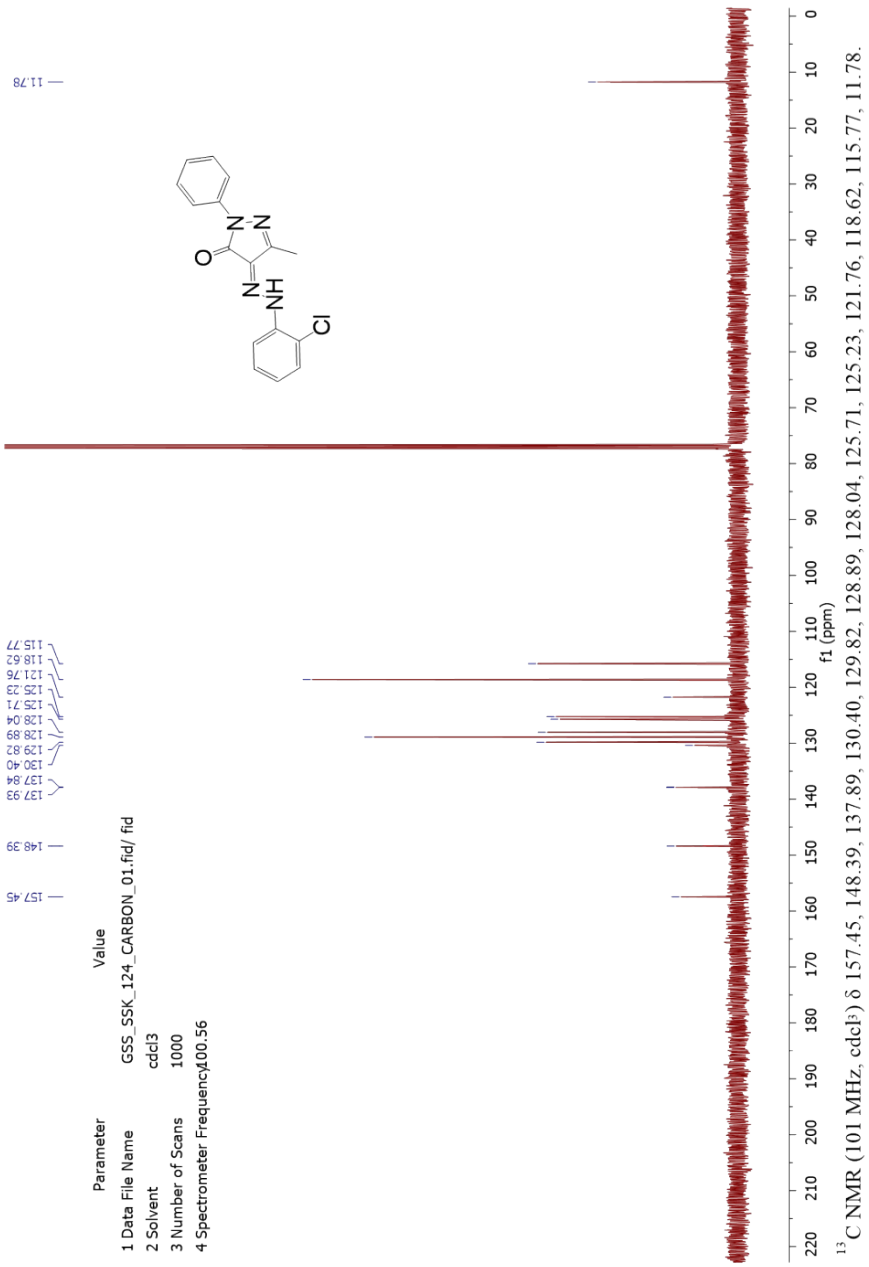
^{13}C NMR (101 MHz, cdcl^{3}) δ 157.21, 148.58, 146.15, 144.44, 137.53, 131.59, 128.98, 125.68, 118.5, 115.33, 11.77.

^{13}C NMR of 6c



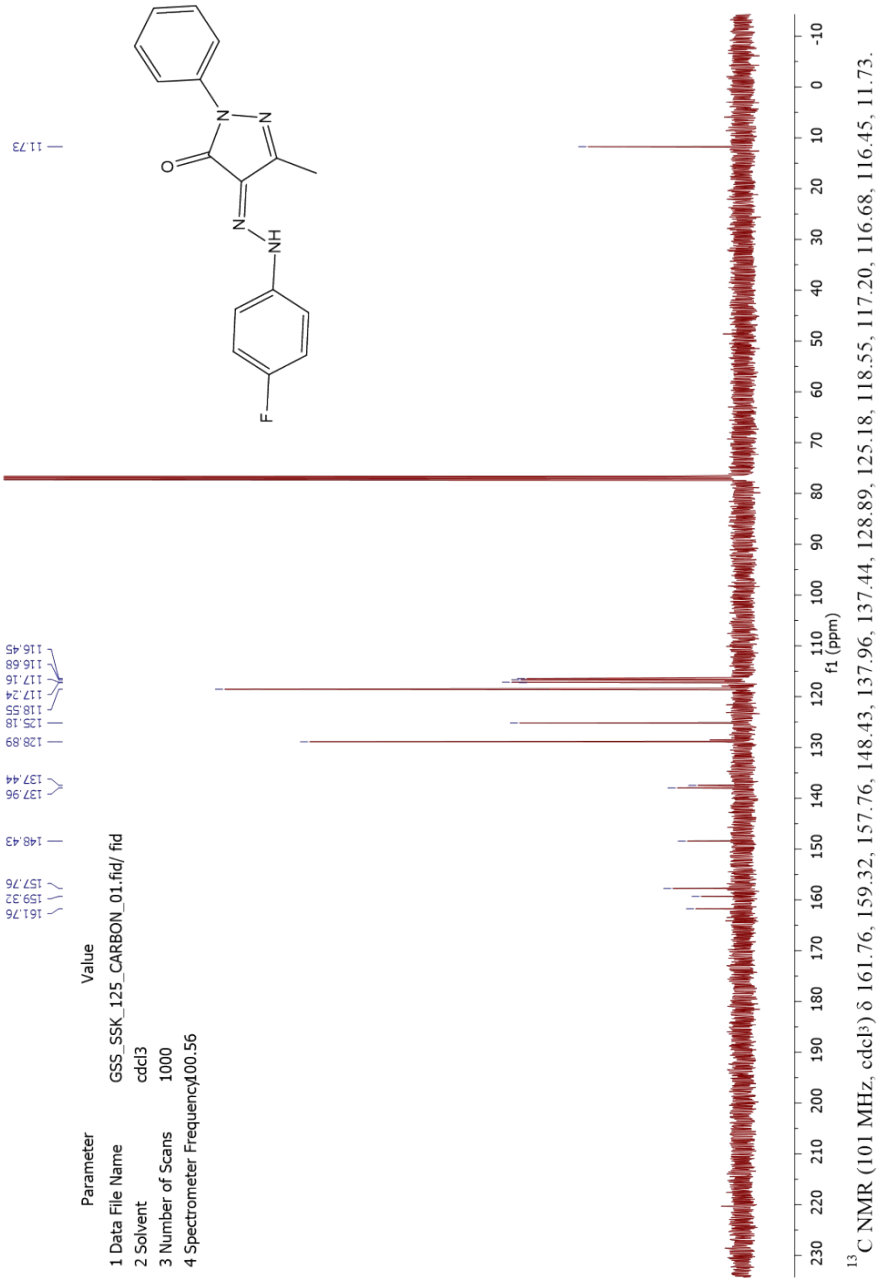
^{13}C NMR (101 MHz, cdcl^3) δ 157.45, 148.55, 142.47, 137.65, 130.51, 128.95, 125.48, 121.12, 119.58, 118.55, 110.24, 11.83.

^{13}C NMR of 6d



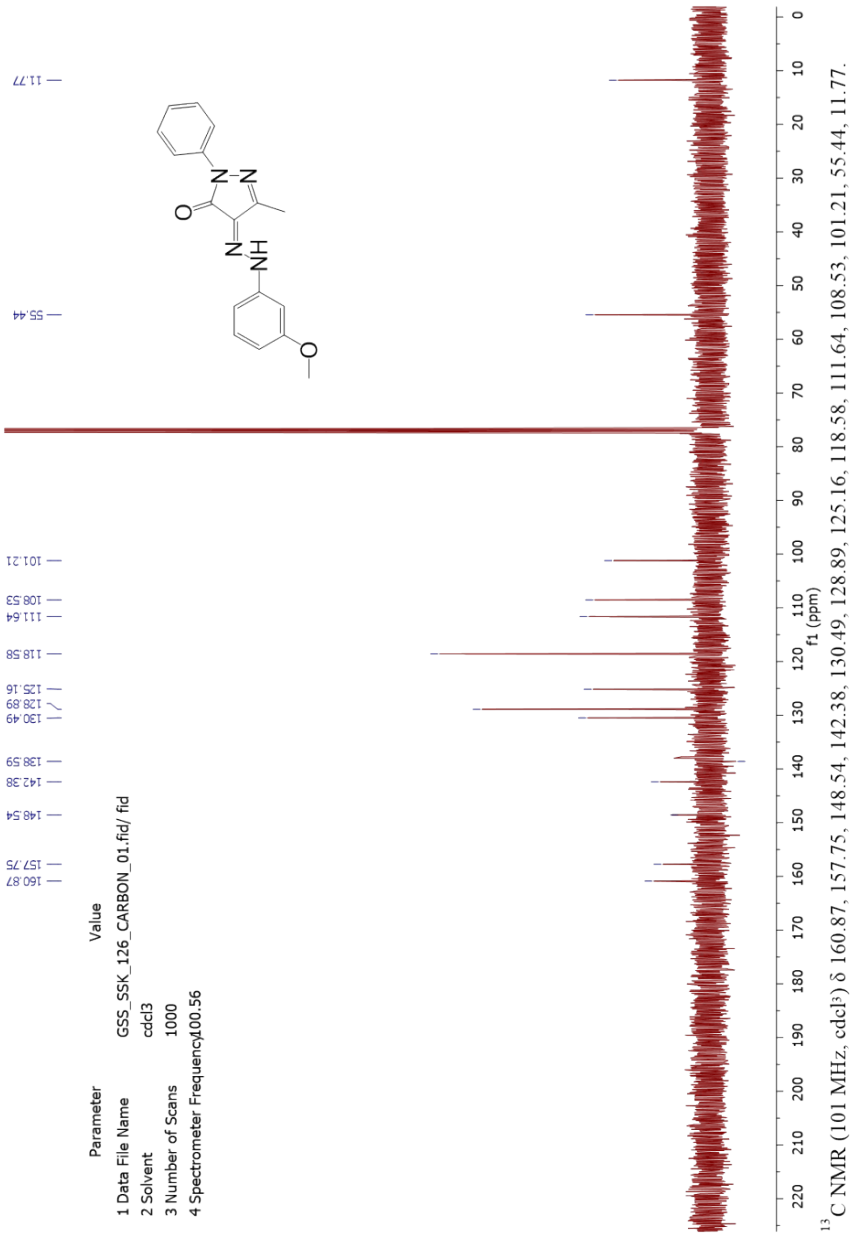
^{13}C NMR (101 MHz, cdcl^{3}) δ 157.45, 148.39, 137.89, 130.40, 129.82, 128.89, 128.04, 125.71, 125.23, 121.76, 118.62, 115.77, 11.78.

^{13}C NMR of 6b



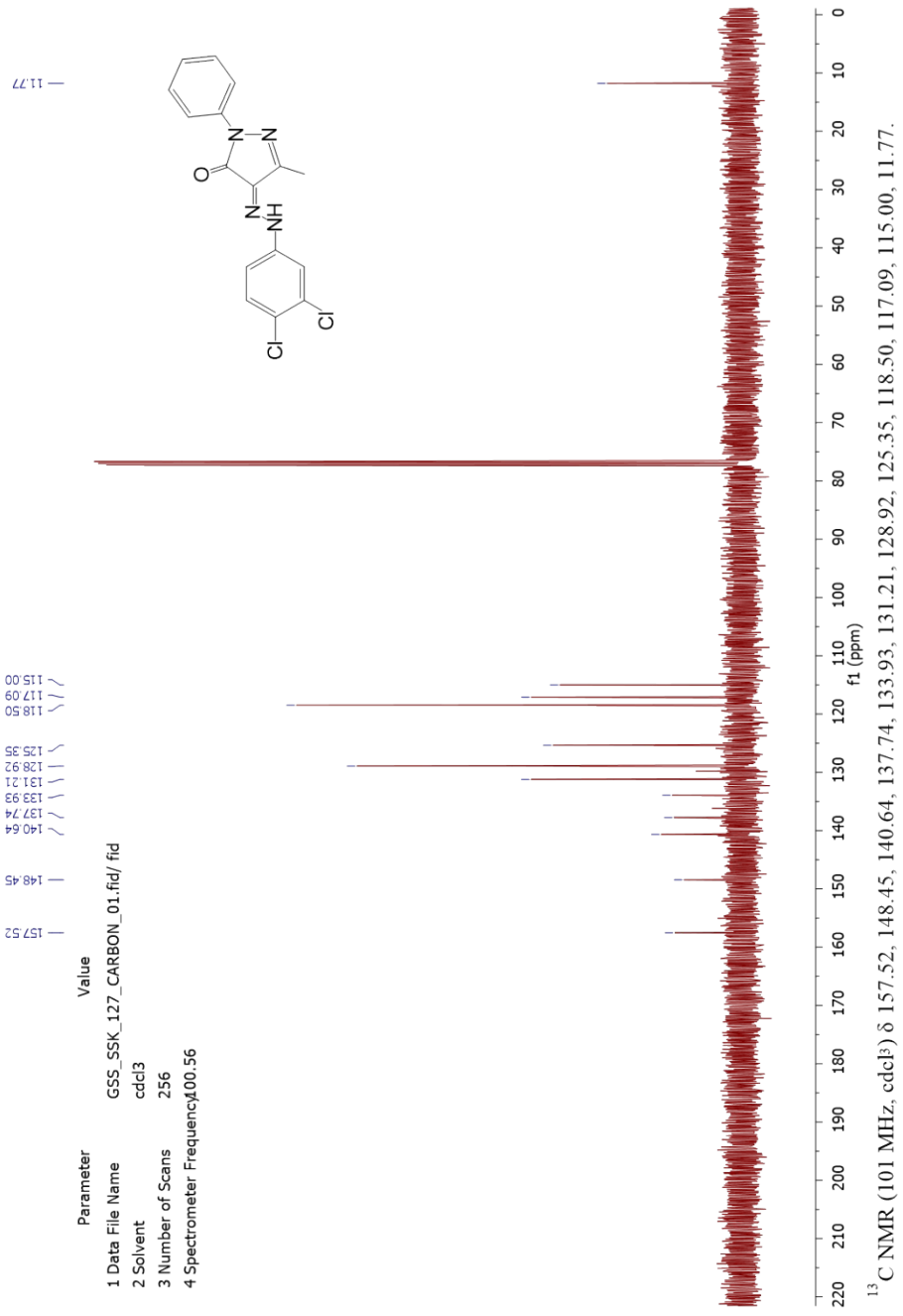
^{13}C NMR (101 MHz, cdcl$_3$) δ 161.76, 159.32, 157.76, 148.43, 137.96, 137.44, 128.89, 125.18, 118.55, 117.20, 116.68, 116.45, 11.73.

^{13}C NMR of 6i



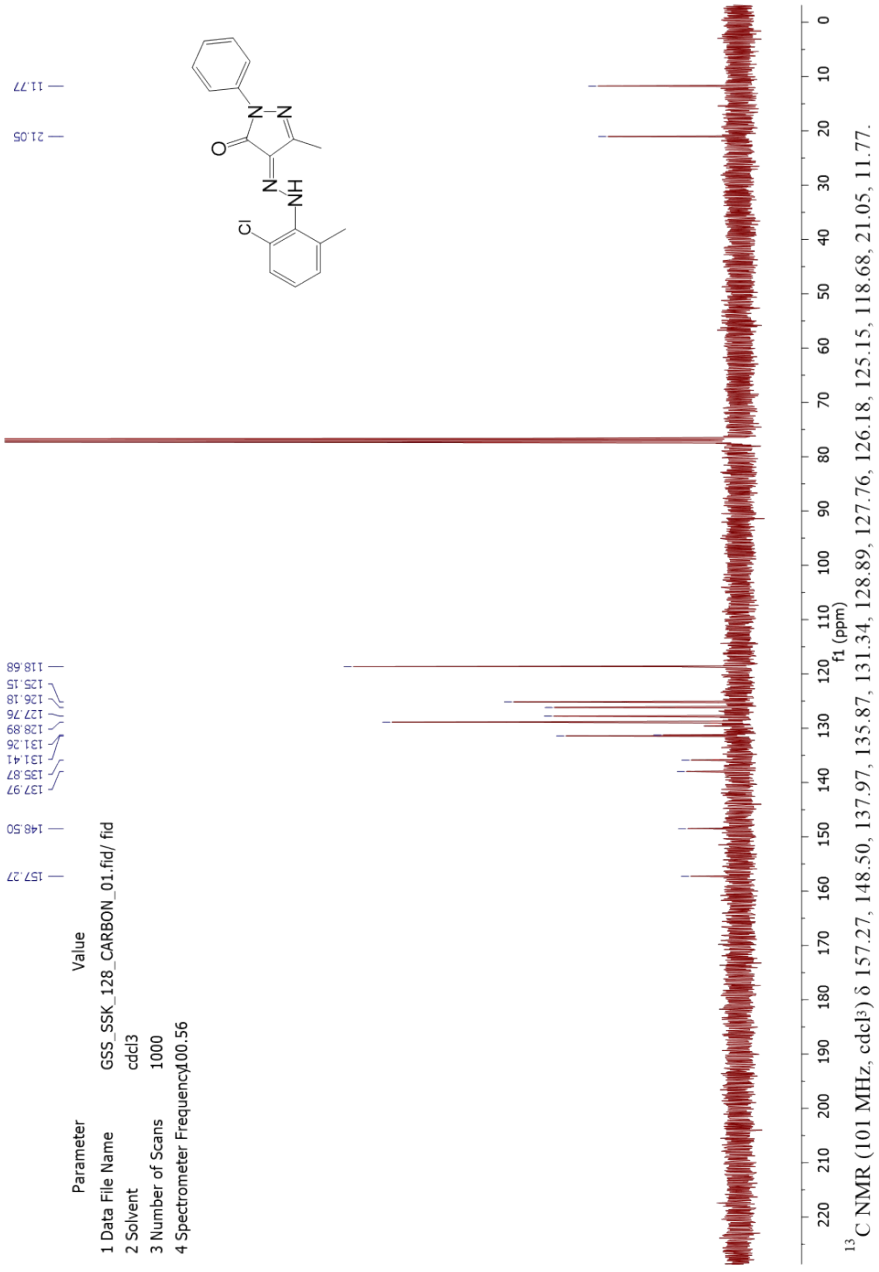
^{13}C NMR (101 MHz, cdcl$_3$) δ 160.87, 157.75, 148.54, 142.38, 130.49, 128.89, 125.16, 118.58, 111.64, 108.53, 101.21, 55.44, 11.77.

^{13}C NMR of 6m



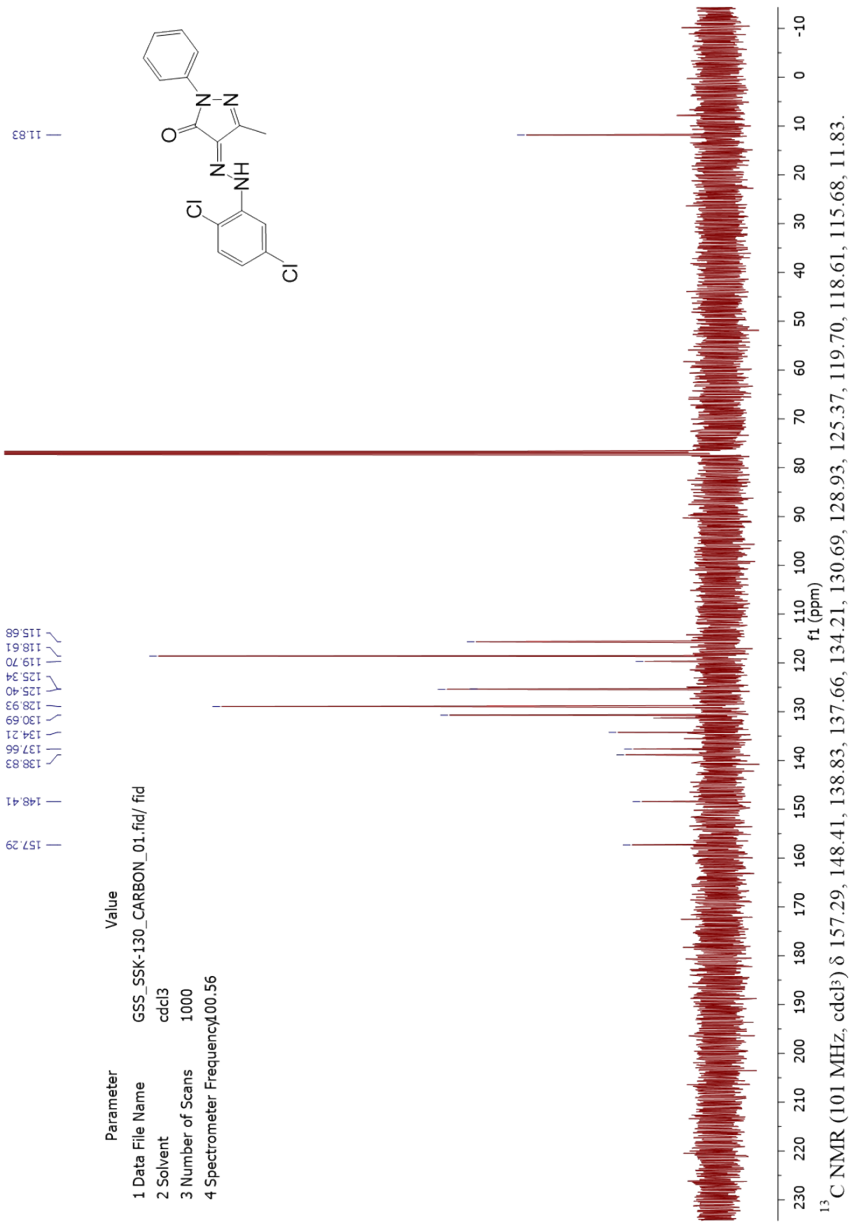
^{13}C NMR (101 MHz, cdcl$_3$) δ 157.52, 148.45, 140.64, 137.74, 133.93, 131.21, 128.92, 125.35, 118.50, 117.09, 115.00, 11.77.

^{13}C NMR of 6f



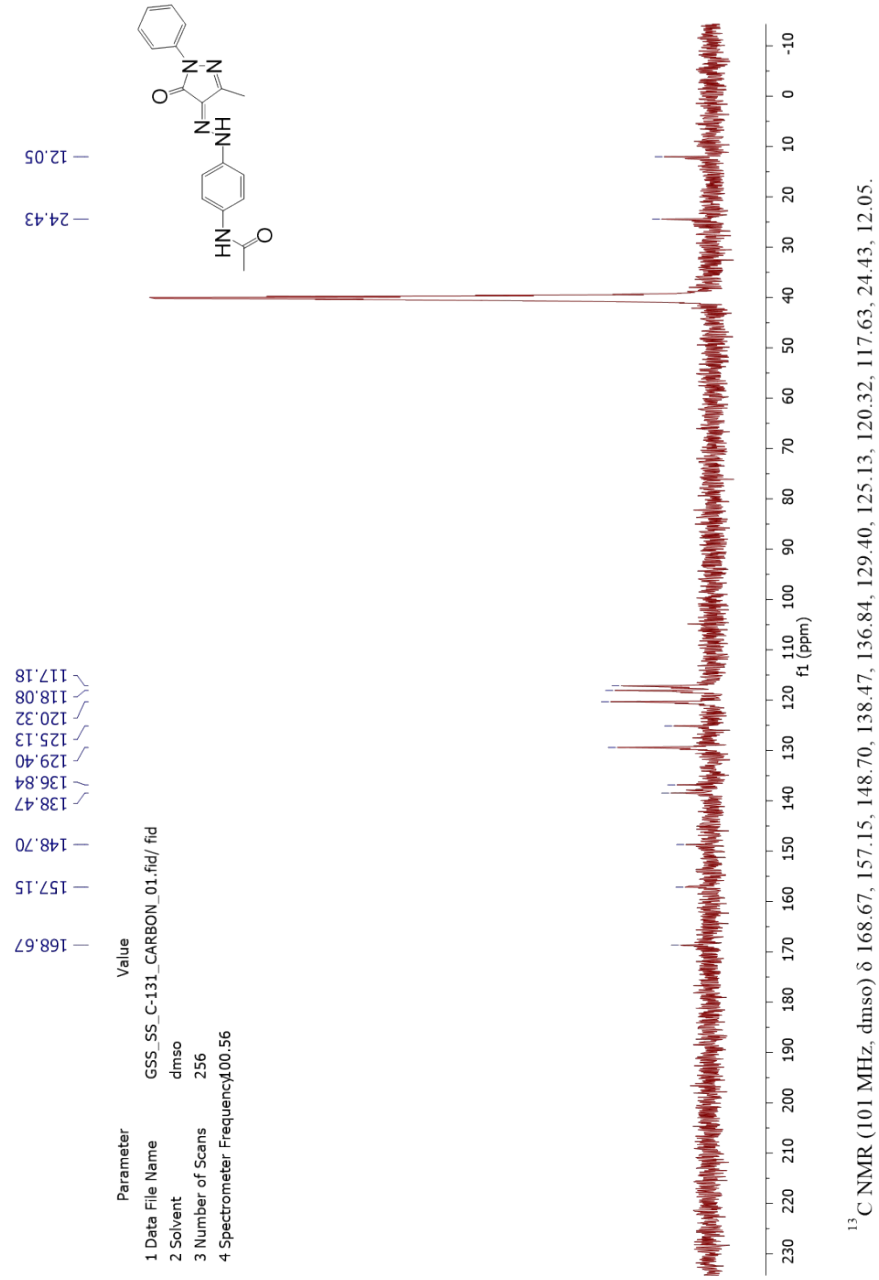
^{13}C NMR (101 MHz, cdcl$_3$) δ 157.27, 148.50, 137.97, 135.87, 131.34, 128.89, 127.76, 126.18, 125.15, 118.68, 21.05, 11.77.

^{13}C NMR of 6g



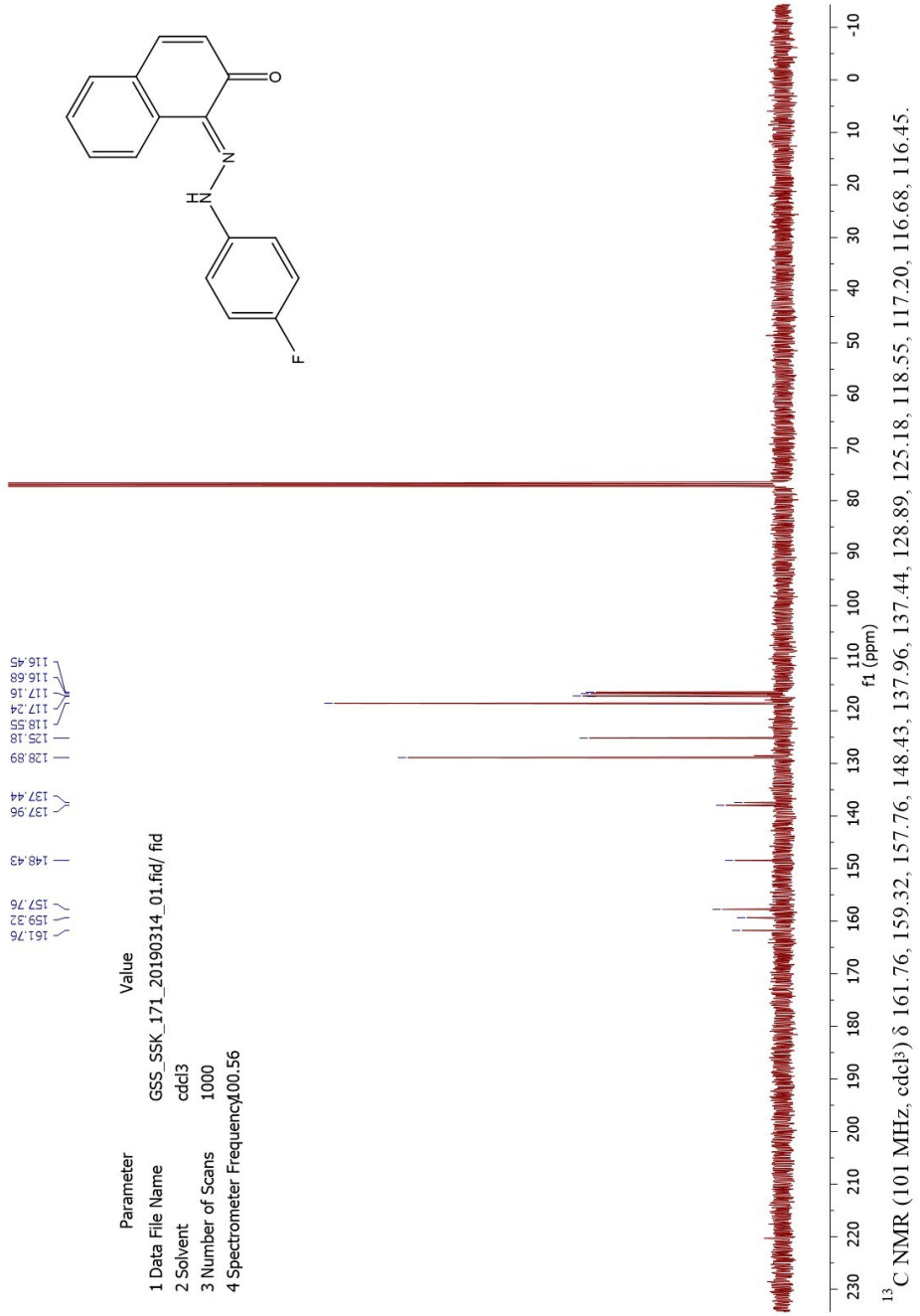
^{13}C NMR (101 MHz, cdcl^3) δ 157.29, 148.41, 138.83, 137.66, 134.21, 130.69, 128.93, 125.37, 119.70, 118.61, 115.68, 11.83.

^{13}C NMR of 6o



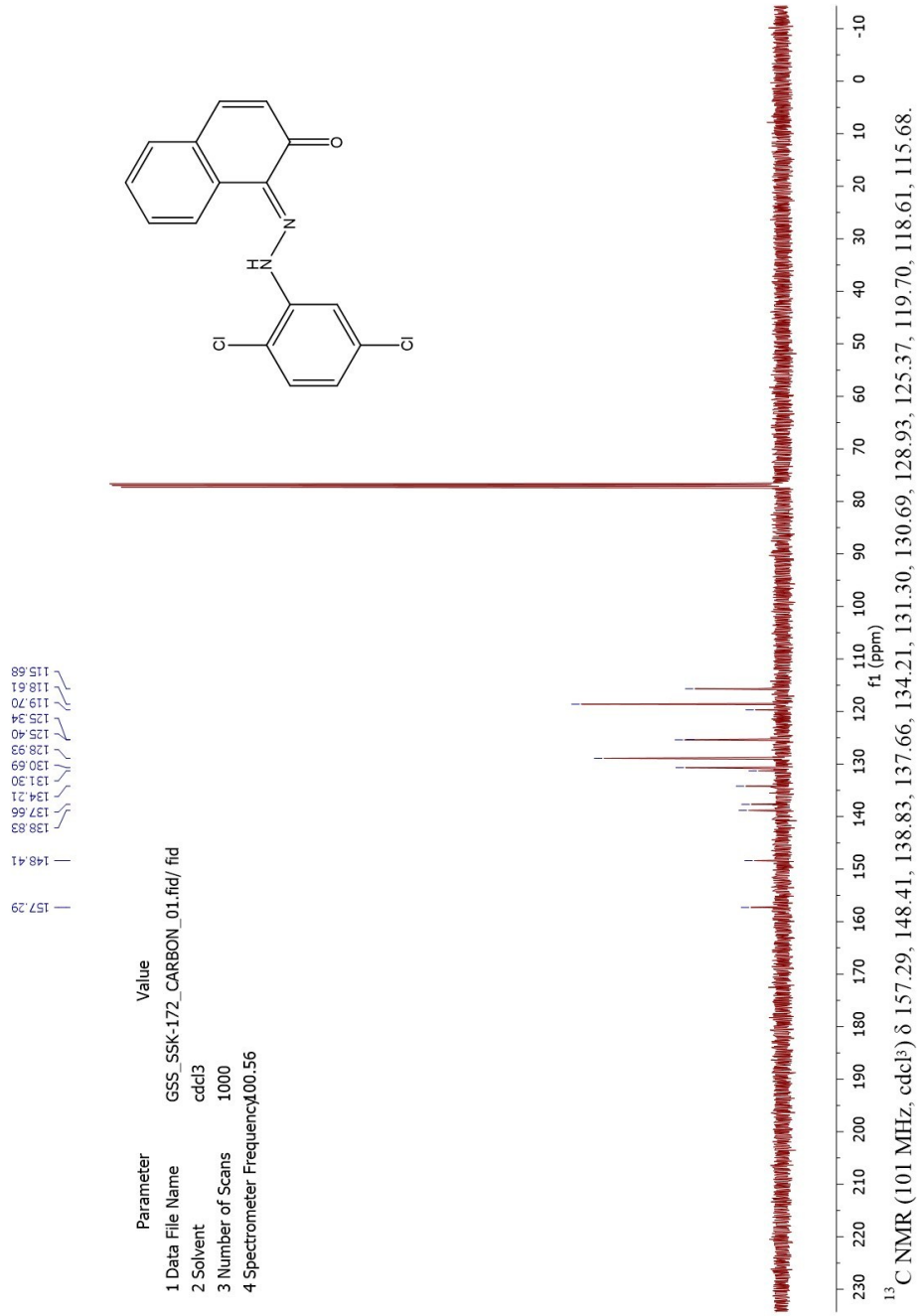
^{13}C NMR (101 MHz, dmso) δ 168.67, 157.15, 148.70, 138.47, 136.84, 129.40, 125.13, 120.32, 117.63, 24.43, 12.05.

^{13}C NMR of 8b



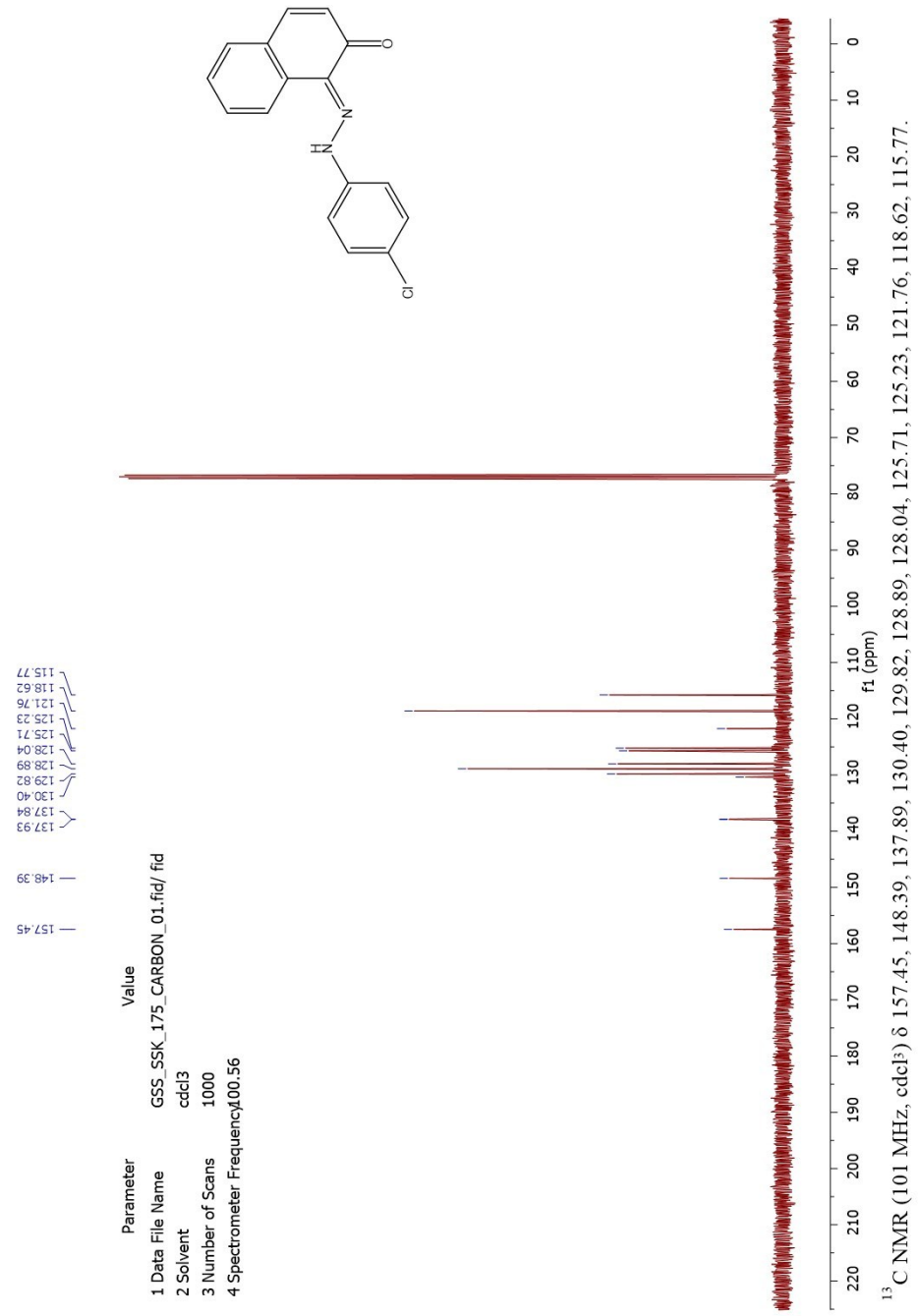
^{13}C NMR (101 MHz, cdcl^3) δ 161.76, 159.32, 157.76, 148.43, 137.96, 137.44, 128.89, 125.18, 118.55, 117.20, 116.68, 116.45.

^{13}C NMR of 8g



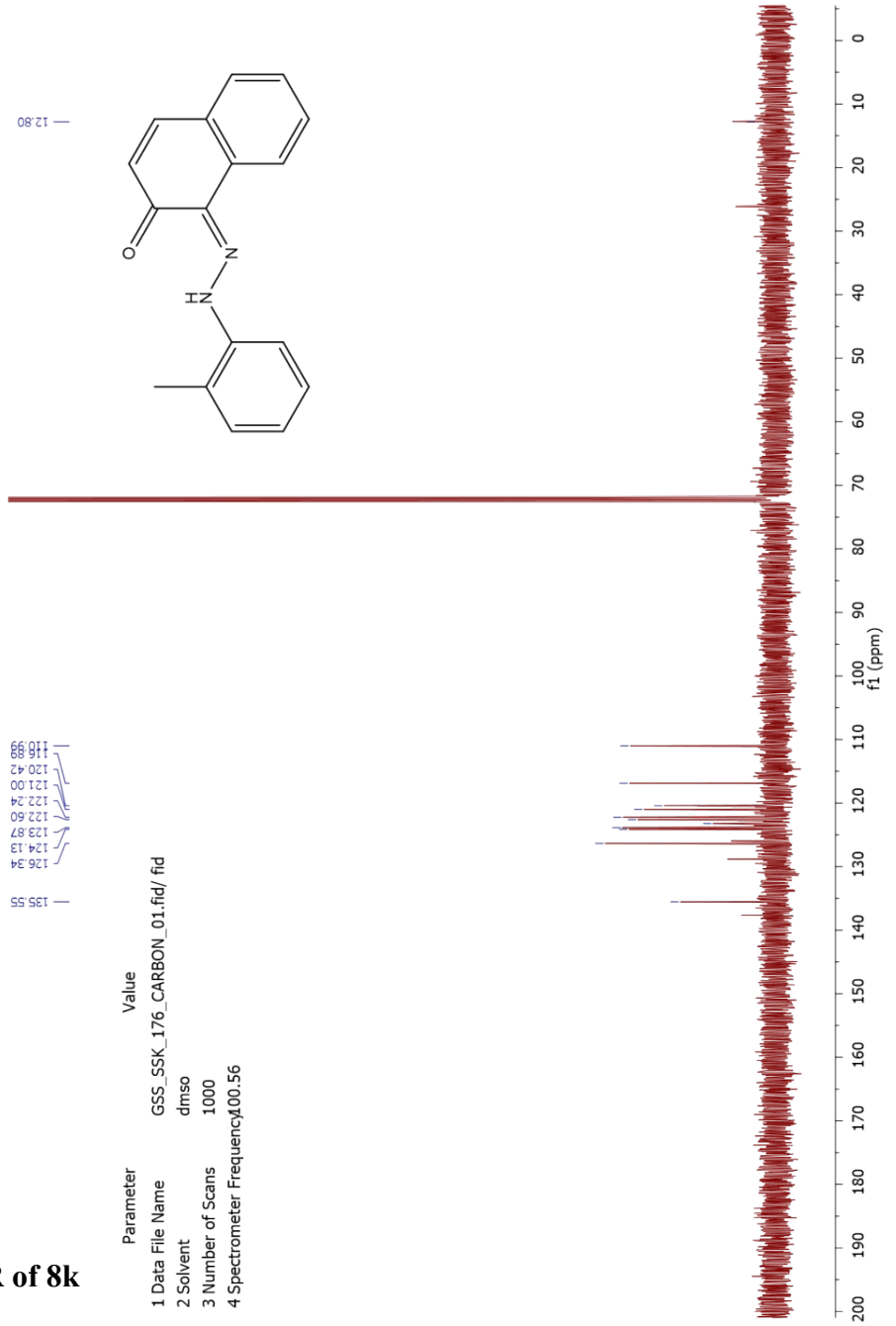
^{13}C NMR (101 MHz, cdcl^3) δ 157.29, 148.41, 138.83, 137.66, 134.21, 131.30, 130.69, 128.93, 125.37, 119.70, 118.61, 115.68.

^{13}C NMR of 8j

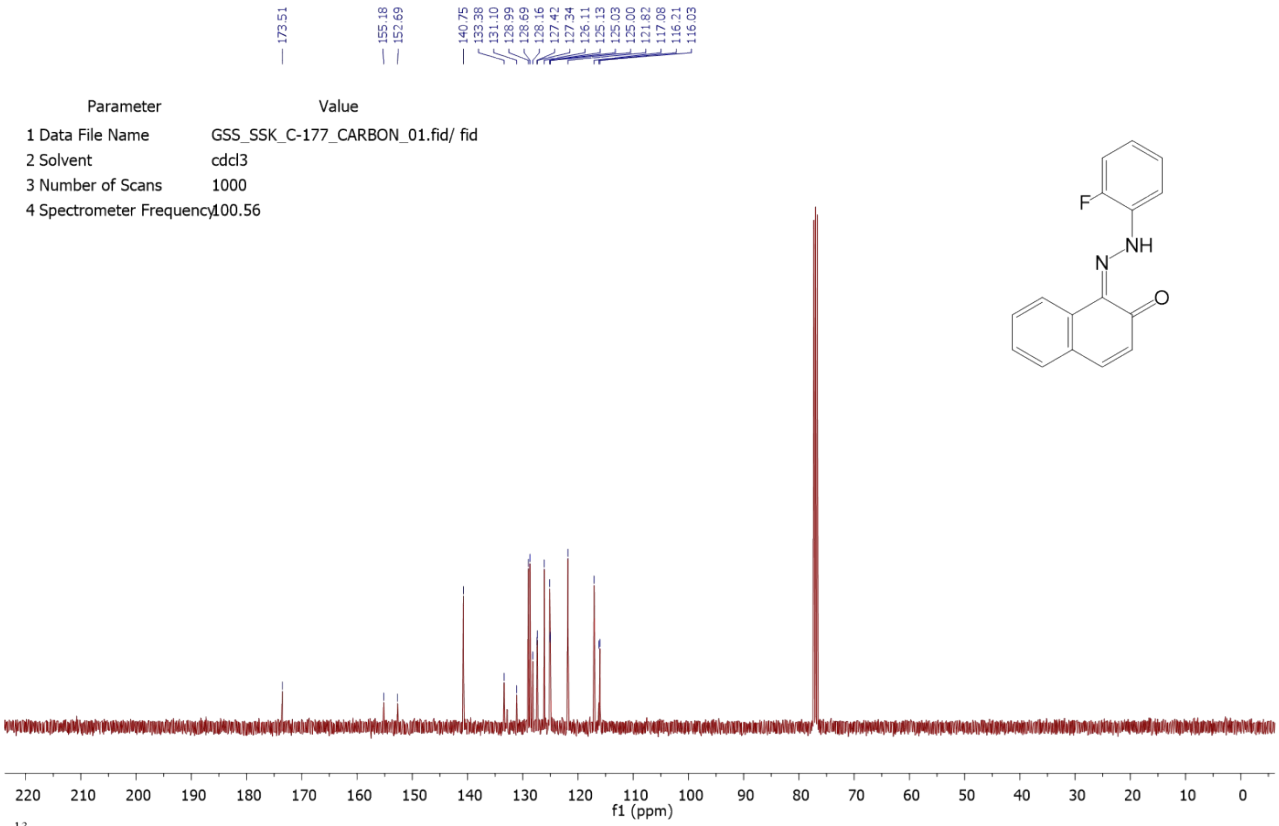


^{13}C NMR (101 MHz, cdcl$_3$) δ 157.45, 148.39, 137.89, 130.40, 129.82, 128.89, 128.04, 125.71, 125.23, 121.76, 118.62, 115.77.

^{13}C NMR of 8e

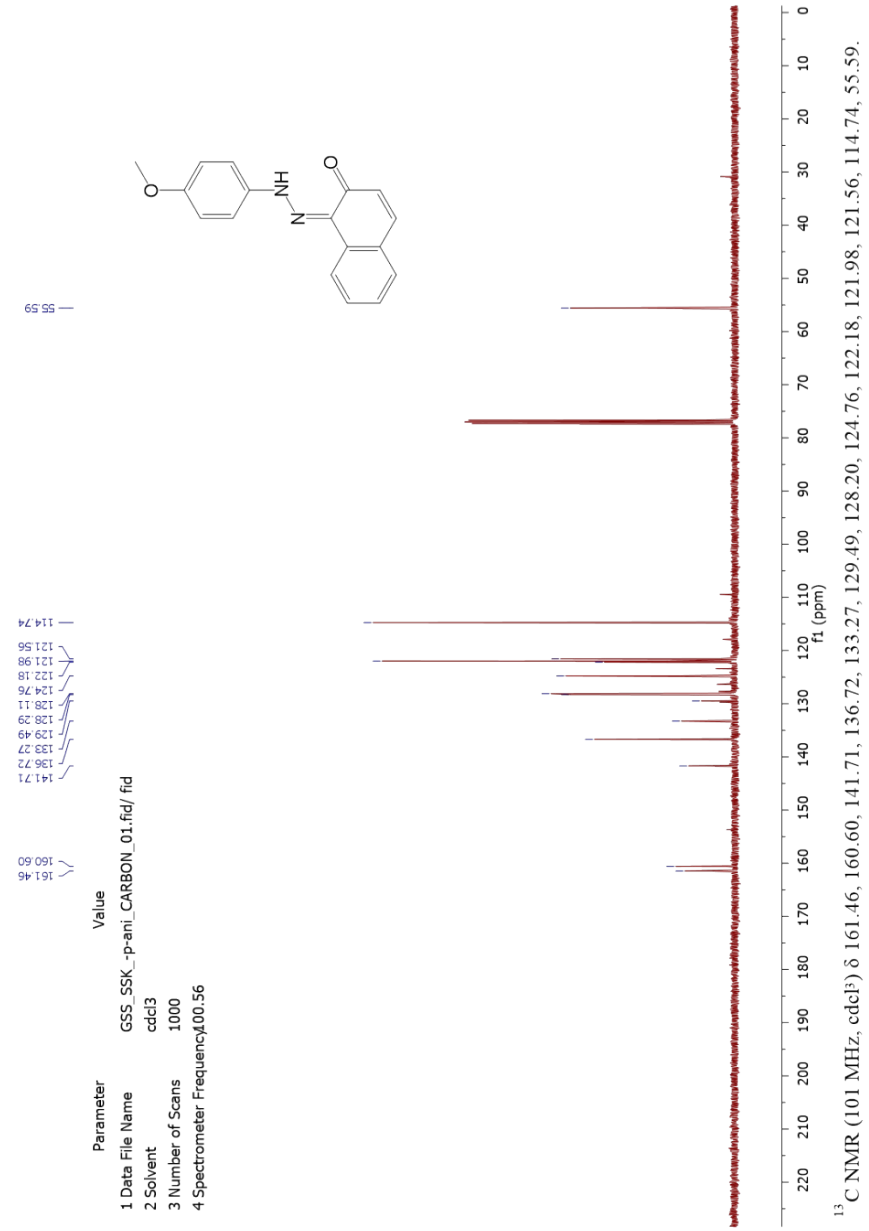


^{13}C NMR of 8k



^{13}C NMR (101 MHz, cdcl$_3$) δ 173.51, 155.18, 152.69, 140.75, 133.38, 131.10, 128.99, 128.69, 128.16, 127.38, 126.11, 125.33, 121.82, 117.08, 116.12

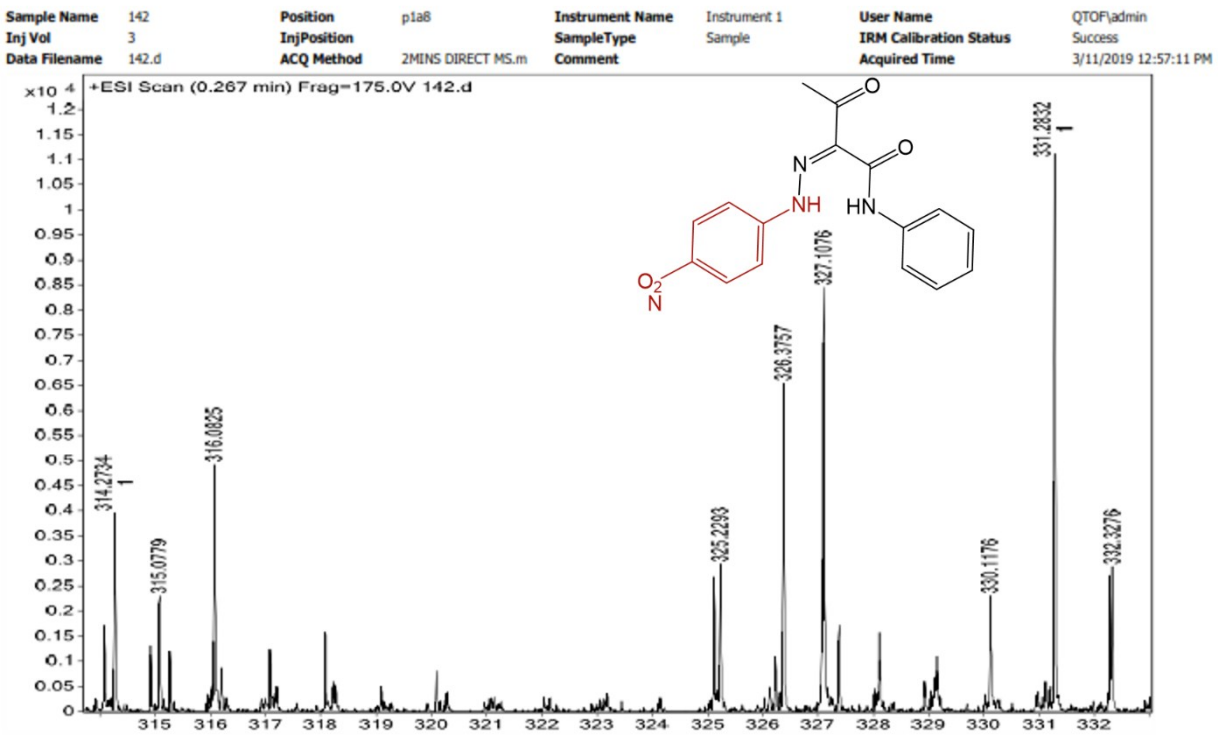
^{13}C NMR of 8l



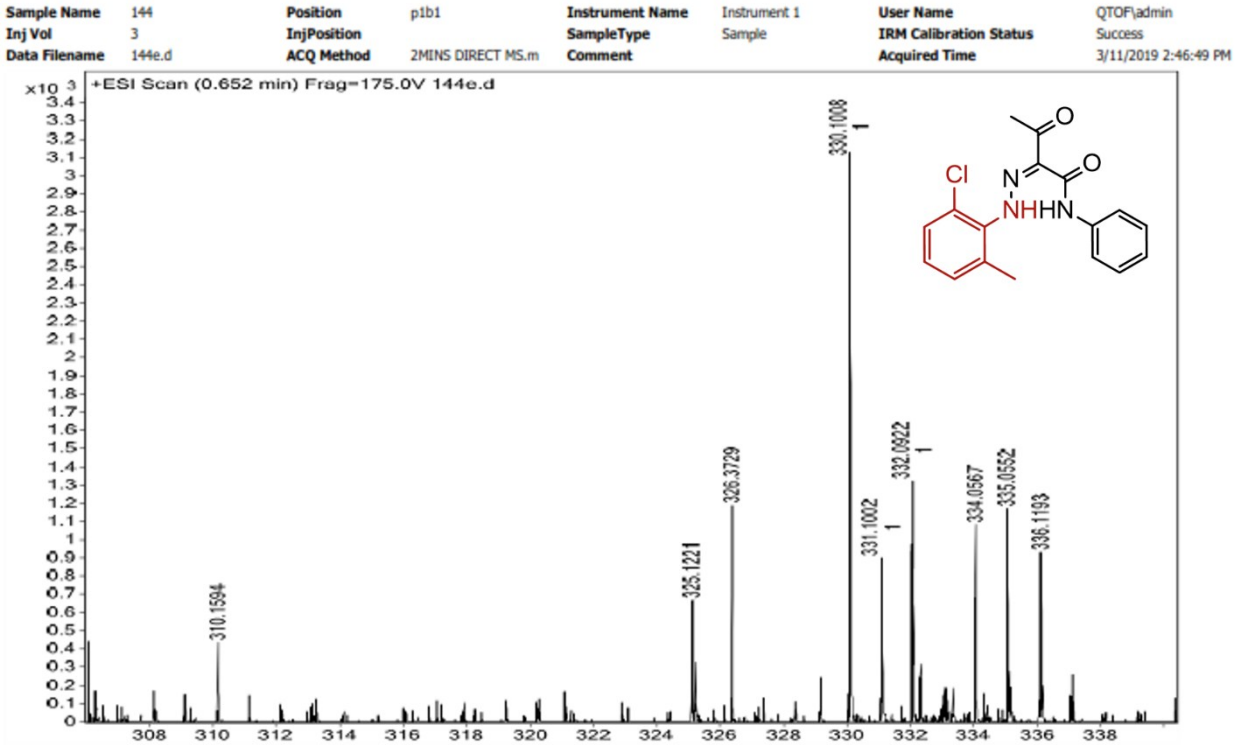
^{13}C NMR (101 MHz, cdcl^3) δ 161.46, 160.60, 141.71, 136.72, 133.27, 129.49, 128.20, 124.76, 122.18, 121.98, 121.56, 114.74, 55.59.

3.8. HRMS spectra of monoazo pigments

HRMS spectra of 3a

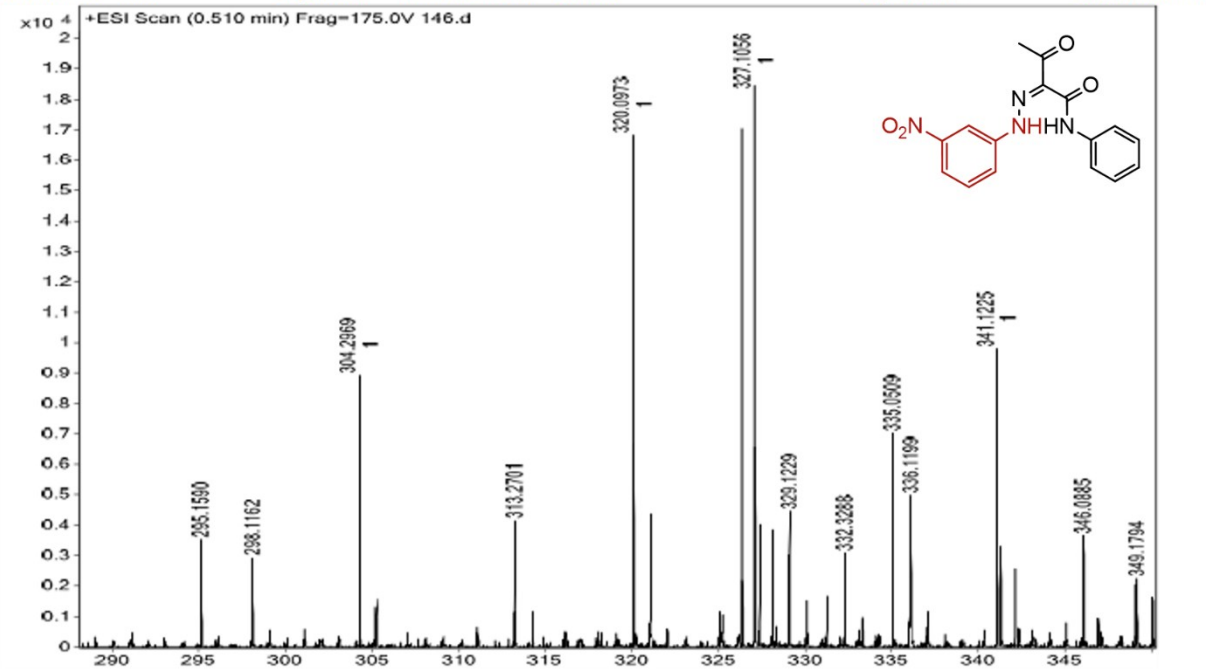


HRMS spectra of 3f



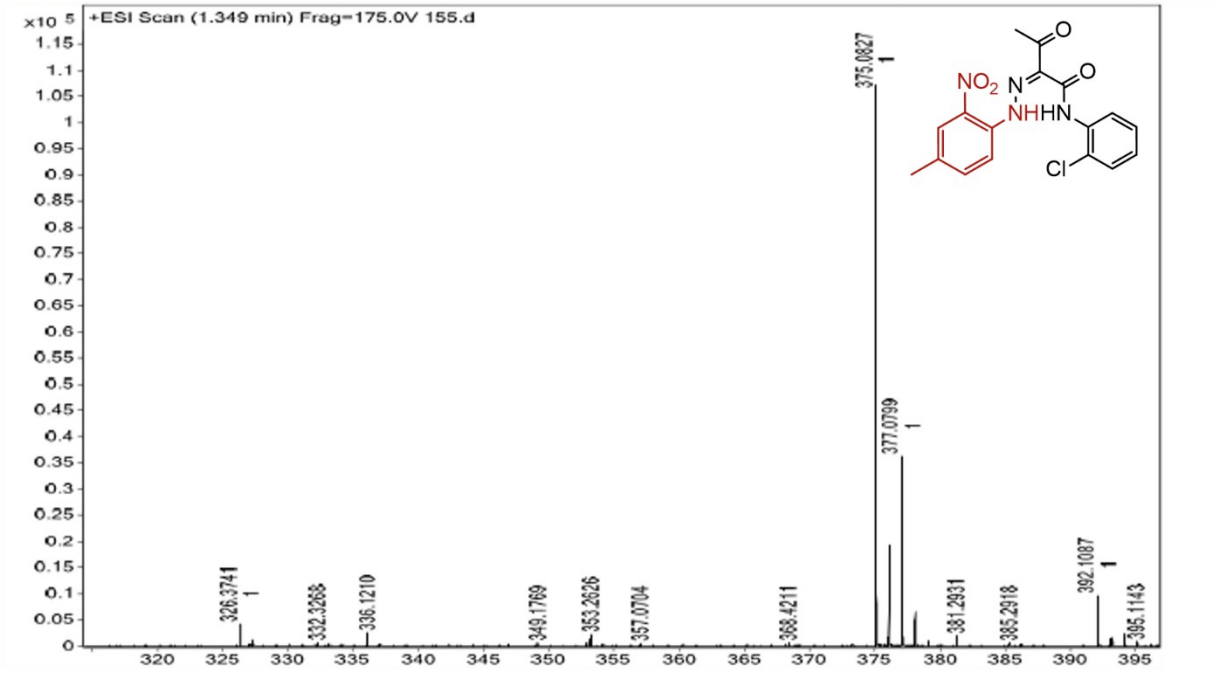
HRMS spectra of 3c

Sample Name	146	**Position**	p1a9	**Instrument Name**	Instrument 1	**User Name**	QTOF\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	146.d	**ACQ Method**	2MINS DIRECT MS.m	**Comment**		**Acquired Time**	3/11/2019 2:36:31 PM

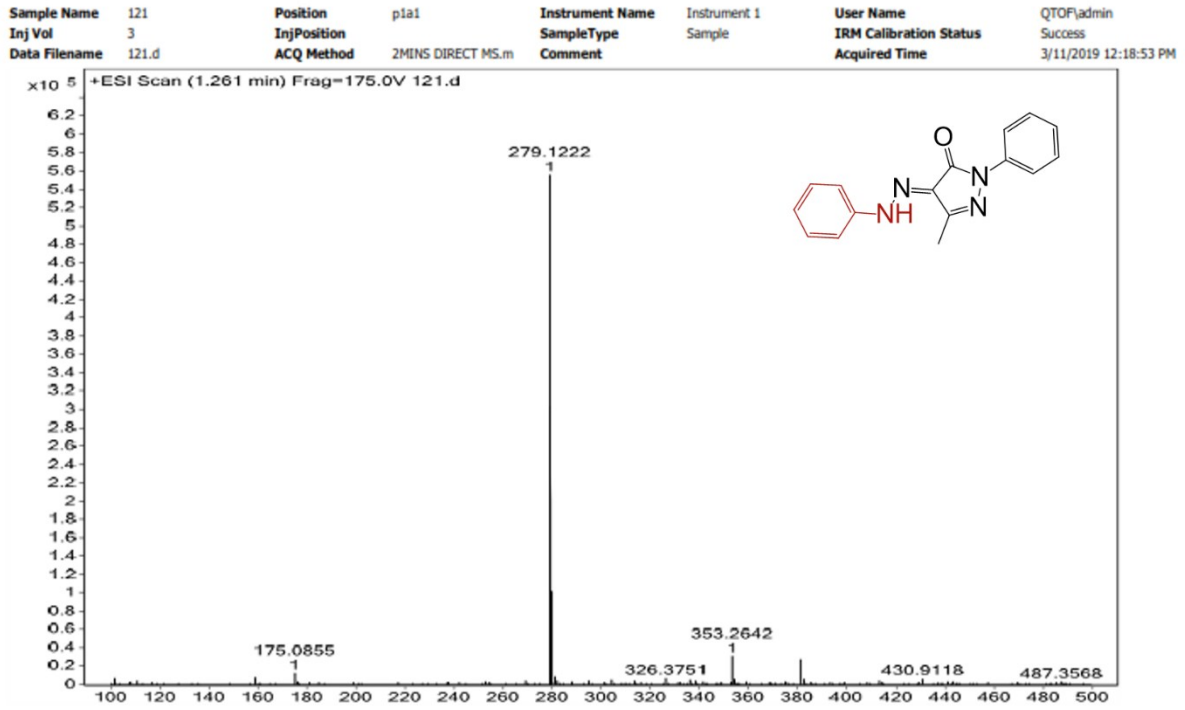


HRMS spectra of 3q

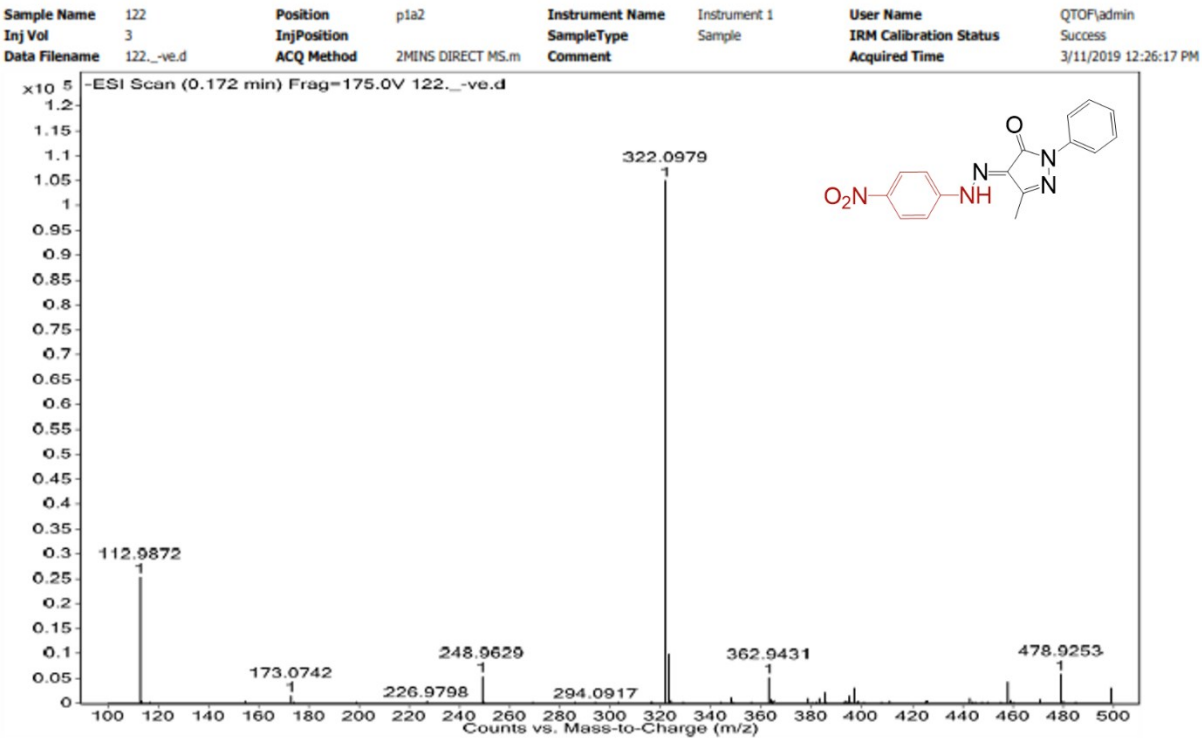
Sample Name	155	**Position**	p1b2	**Instrument Name**	Instrument 1	**User Name**	QTOF\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	155.d	**ACQ Method**	2MINS DIRECT MS.m	**Comment**		**Acquired Time**	3/11/2019 2:52:00 PM



HRMS spectra of 6h

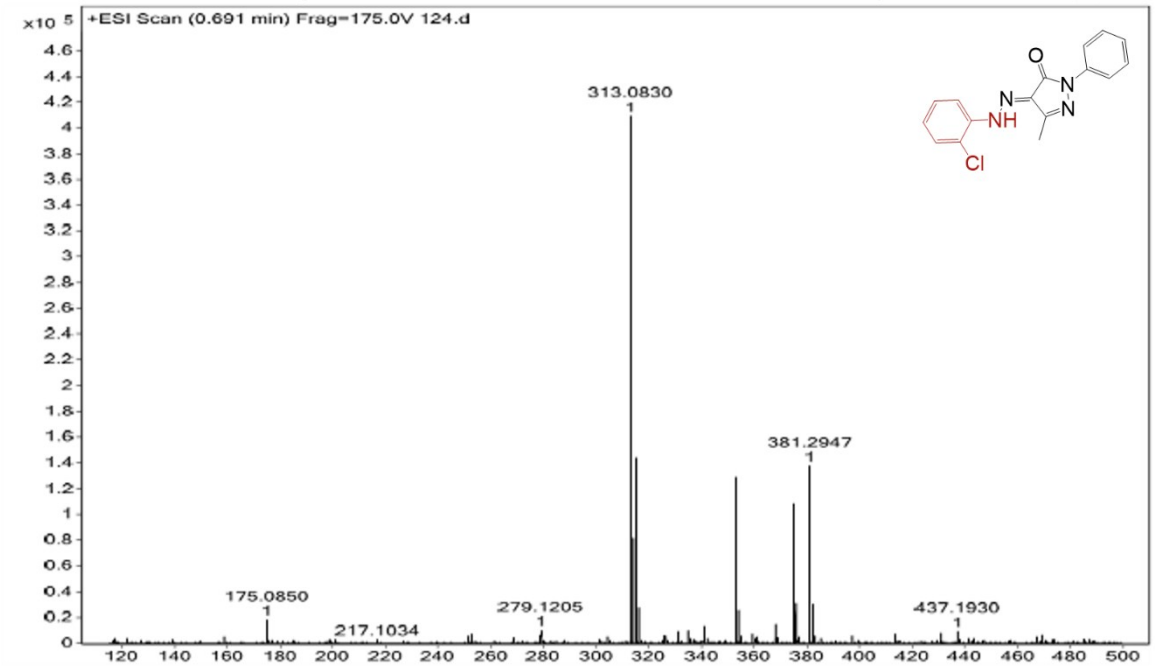


HRMS spectra of 6a



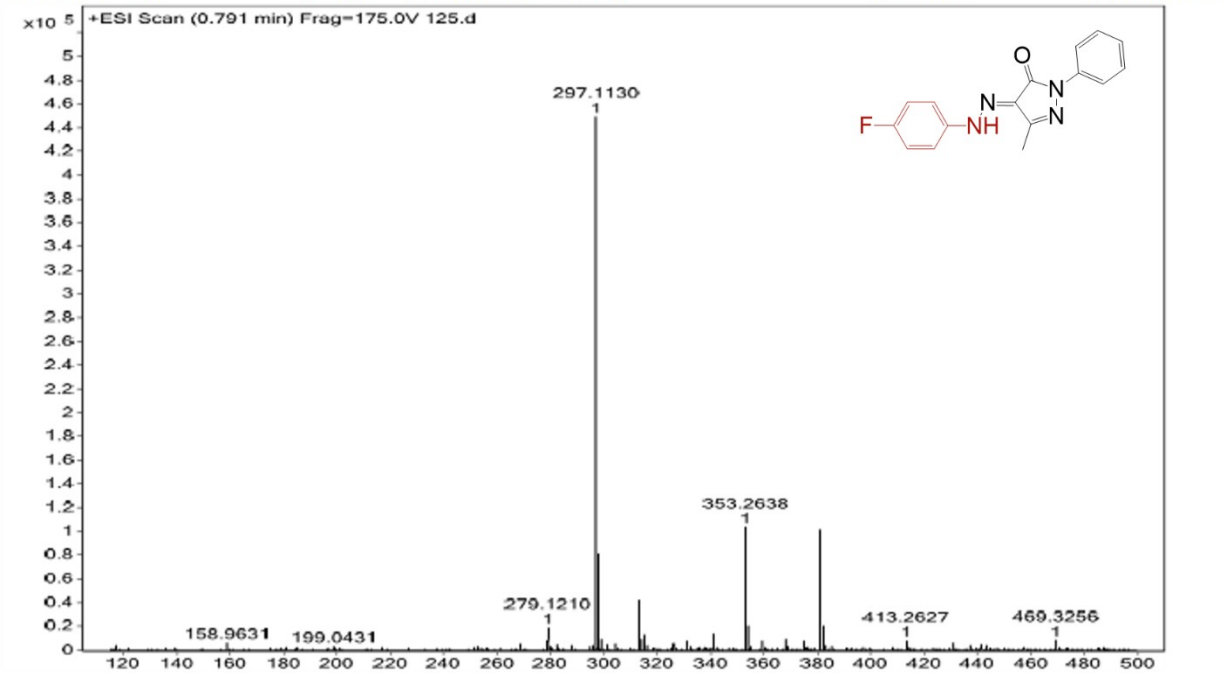
HRMS spectra of 6d

Sample Name	124	**Position**	p1a3	**Instrument Name**	Instrument 1	**User Name**	QTOF\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	124.d	**ACQ Method**	2MINS DIRECT MS.m	**Comment**		**Acquired Time**	3/11/2019 12:31:49 PM

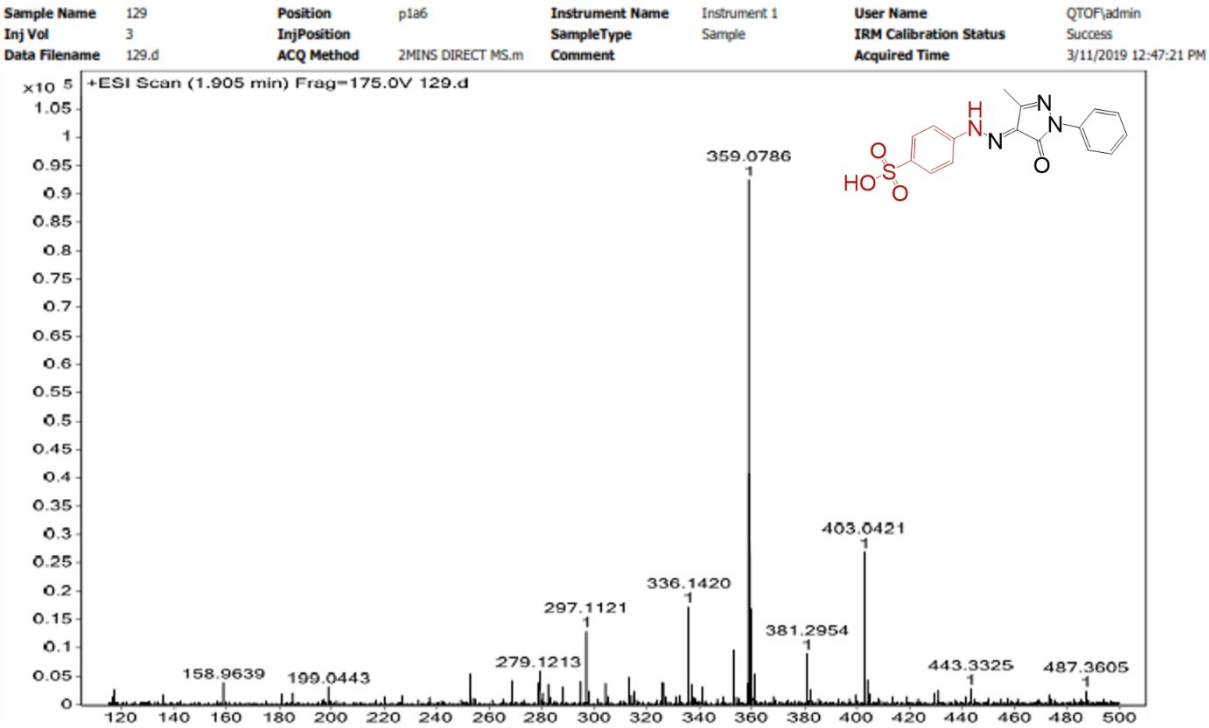


HRMS spectra of 6b

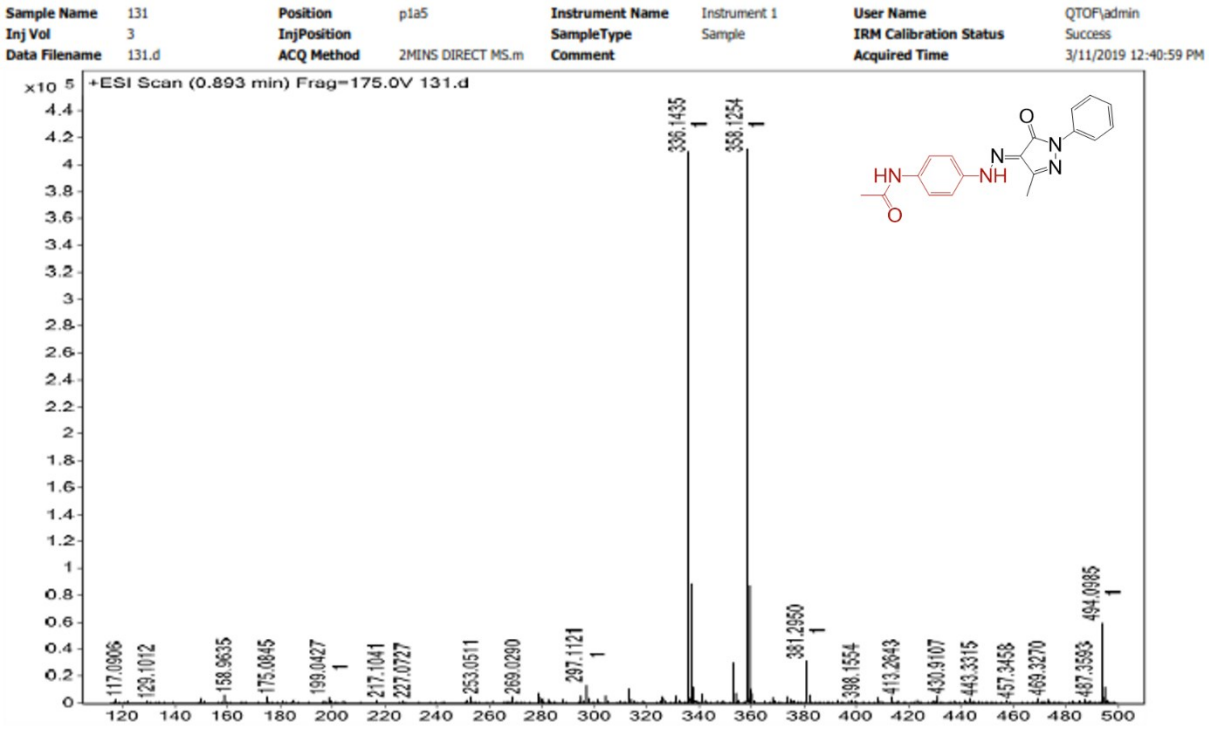
Sample Name	125	**Position**	p1a4	**Instrument Name**	Instrument 1	**User Name**	QTOF\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	125.d	**ACQ Method**	2MINS DIRECT MS.m	**Comment**		**Acquired Time**	3/11/2019 12:34:40 PM



HRMS spectra of 6n

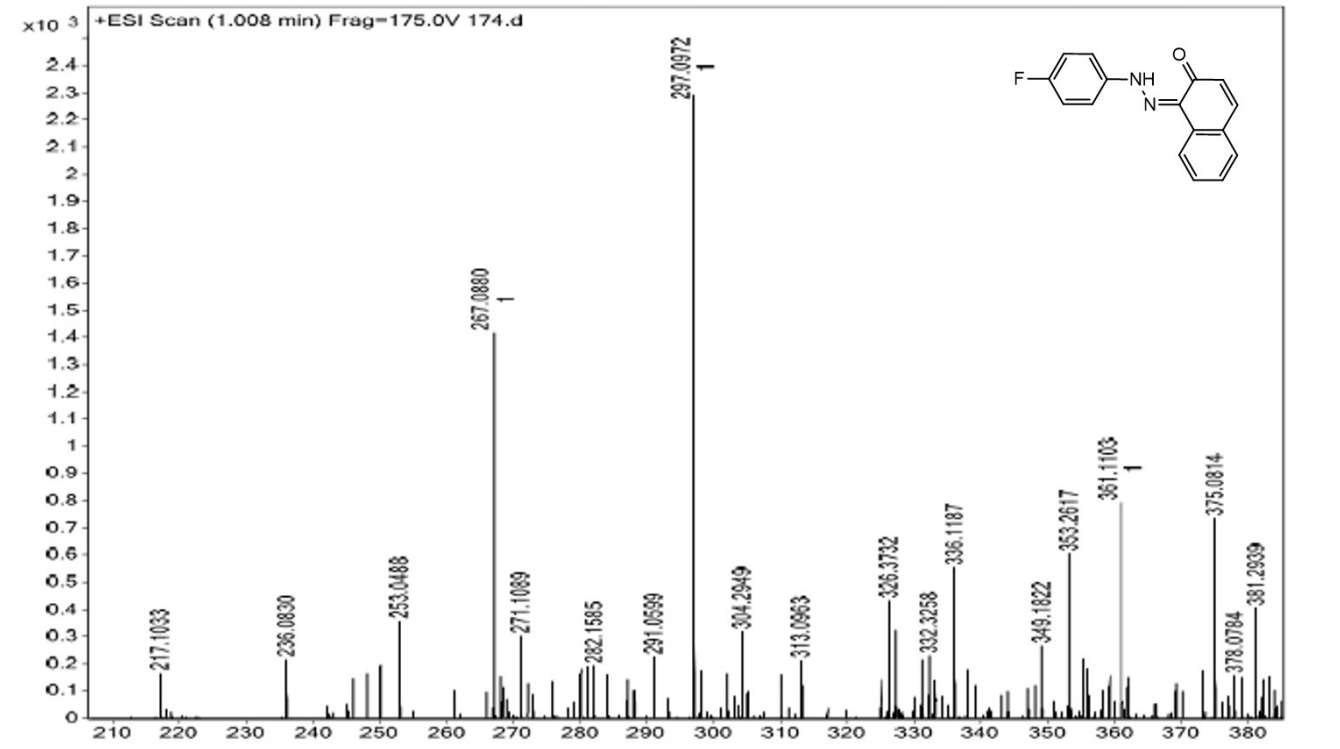


HRMS spectra of 6o



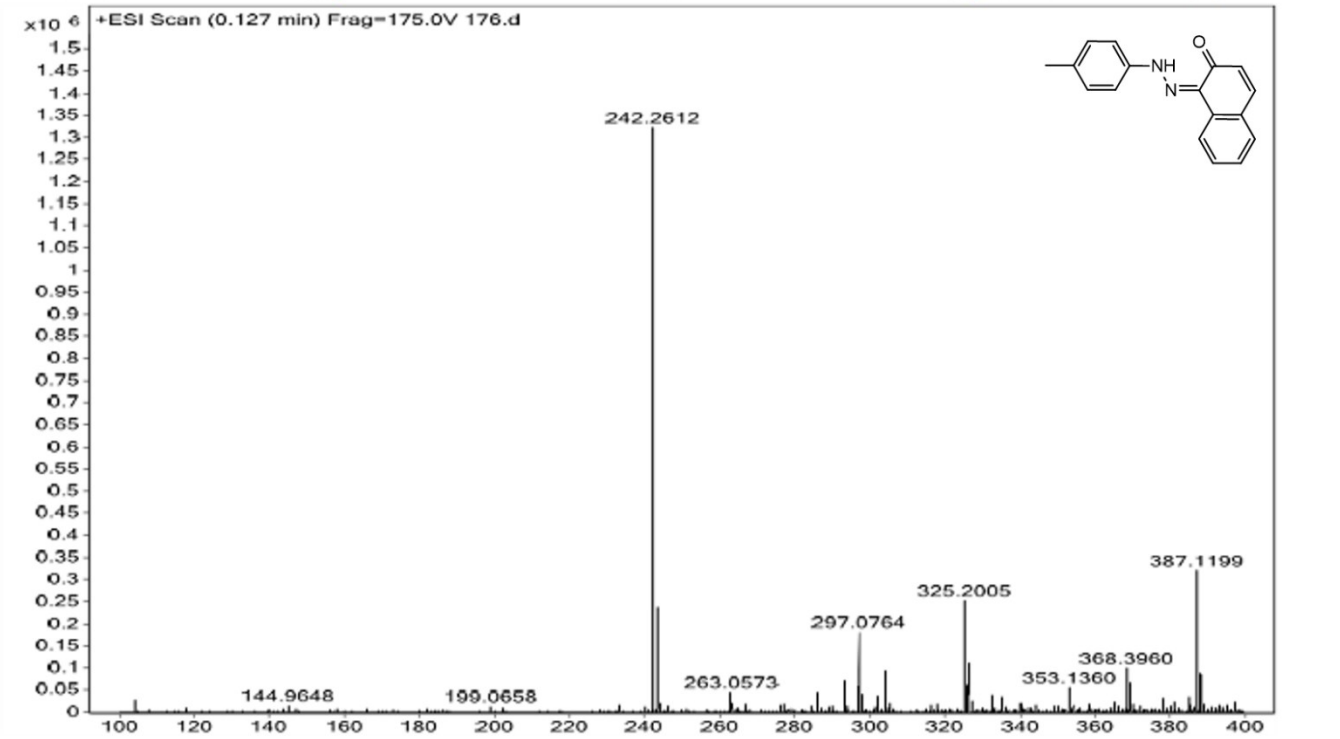
HRMS spectra of 8a

Sample Name	174	**Position**	p1b3	**Instrument Name**	Instrument 1	**User Name**	QTOF\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	174.d	**ACQ Method**	2MINS DIRECT MS.m	**Comment**		**Acquired Time**	3/11/2019 2:59:35 PM



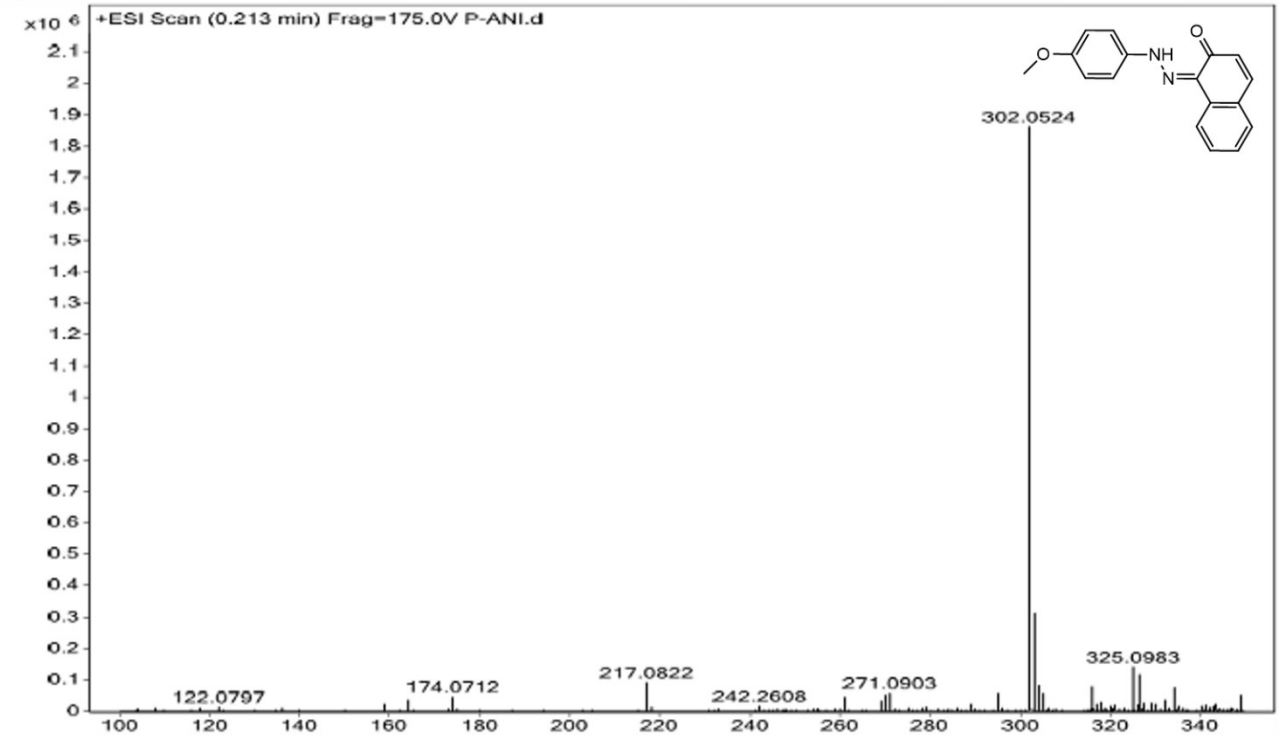
HRMS spectra of 8e

Sample Name	176	**Position**	P1A3	**Instrument Name**	QTOF	**User Name**	LCMSQTOF-PC\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	176.d	**ACQ Method**	2min-test.m	**Comment**		**Acquired Time**	4/16/2019 3:26:21 PM



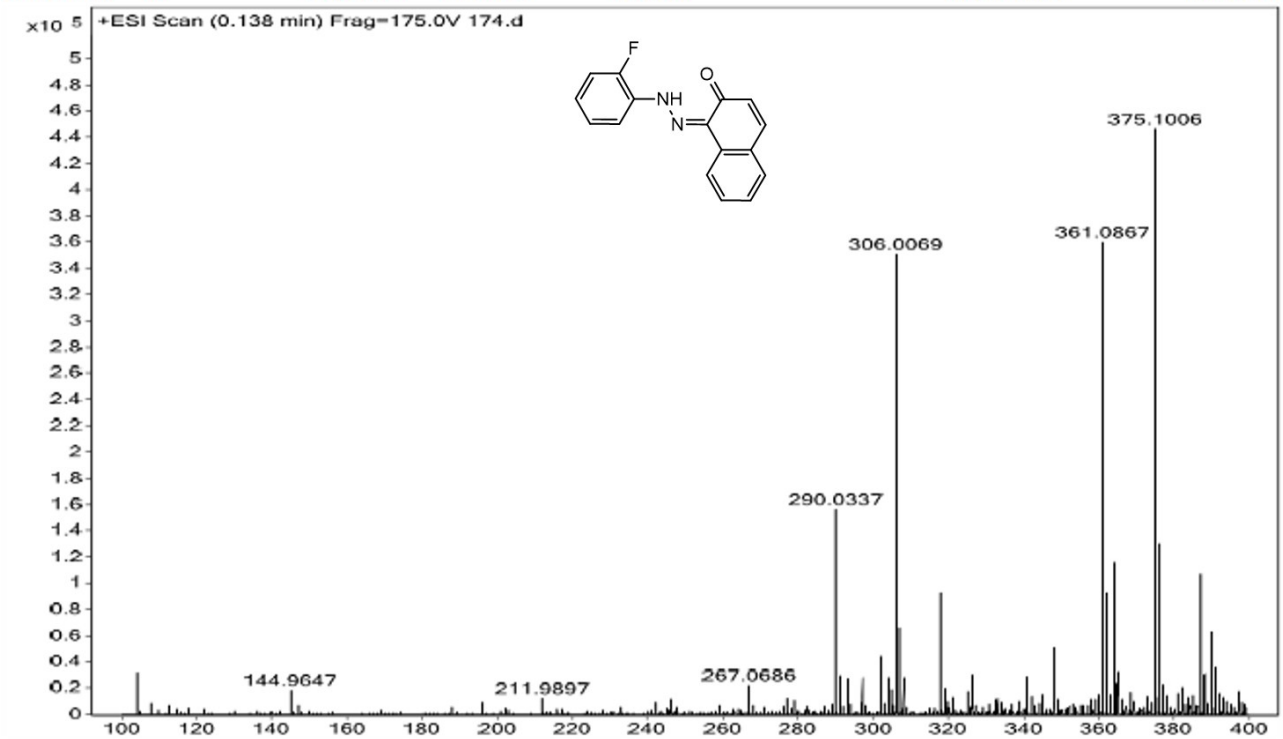
HRMS spectra of 8l

Sample Name	P-ANI	**Position**	P1A5	**Instrument Name**	QTOF	**User Name**	LCMSQTOF-PC\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	P-ANI.d	**ACQ Method**	2min-test.m	**Comment**		**Acquired Time**	4/16/2019 3:40:08 PM



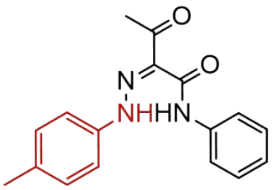
HRMS spectra of 8k

Sample Name	174	**Position**	p1a2	**Instrument Name**	QTOF	**User Name**	LCMSQTOF-PC\admin
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	174	**ACQ Method**	2min-test.m	**Comment**		**Acquired Time**	4/16/2019 3:18:54 PM



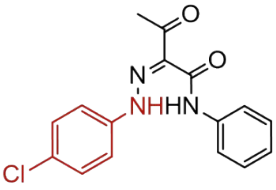
4. Drawdowns of some selected compounds:

Mass Tone



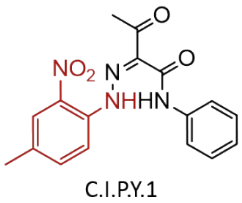
Reduced Tone

Mass Tone



Reduced Tone

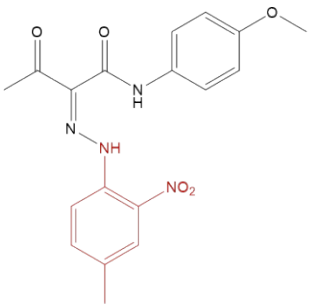
Mass Tone



C.I.P.Y.1

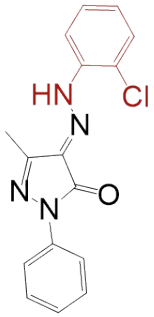
Reduced Tone

Mass Tone



Reduced Tone

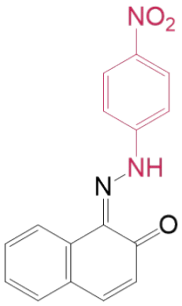
Mass Tone



124

Reduced Tone

Mass Tone



C.I.P.R. 1 or
Para Red

Reduced Tone

5. REFERENCES:

1 P. N. Jain, Renuka K., Pandey, *J. Indian Chem. Soc.*, 1989, **66**, 350–352.

2 R. N. Malhas, N. A. Al-Awadi and O. M. E. El-Dusouqui, *Int. J. Chem. Kinet.*, 2007, **39**, 82–91.

3 K. Hunger, P. Mischke, W. Rieper and S. Zhang, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

4 Z. Li, D. Lv, X. Li and S. Wang, *Dye. Pigment.*, 2016, **128**, 246–255.

5 P. N. Jain, Renuka K., Pandey, *J. Indian Chem. Soc.*, 1990, **67**, 350–351.

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