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1. General Considerations

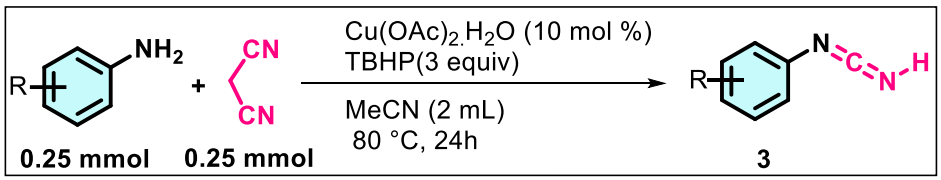
1.1.1 Reagent information:

Unless otherwise stated, all the catalytic reactions were carried out in a screw cap reaction tube with magnetic stirring under an air atmosphere. All the chemicals, like malononitrile, aromatic amine derivatives, and solvents, utilized in the experiments were purchased from commercial sources and used as received. For column chromatography, silica gel (100-200 mesh) was obtained from SRL Co. During elution, a petroleum ether and ethyl acetate mixture was used.

1.1.2 Analytical information:

^{1}H NMR, ^{13}C NMR spectroscopy, and HRMS were used to characterize all the isolated compounds. Copies of the ^{1}H NMR and ^{13}C NMR spectra were attached in this supporting information. All NMR spectra were recorded on a BRUKER 500 MHz and a BRUKER 400 MHz instrument. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to residual DMSO (2.51 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to DMSO-D6 (40.15 ppm). HRMS was recorded using an Agilent TOF/6500 series Q-TOF mass spectrometer.

1.1.3 General procedure for synthesis of carbodiimides from aromatic amines:



To perform the reaction, aromatic amine (0.25 mmol), malononitrile (0.25 mmol), $Cu(OAc)_2.H_2O$ (10 mol%), and TBHP (3 equiv.) in acetonitrile (2 mL) were added to a sealed reaction tube by syringe under an air atmosphere. The reaction mixture was stirred vigorously for 24 h in an air atmosphere in a preheated oil bath at 80 °C. Upon completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (EtOAc). The mixture was then filtered through a celite filter. The organic layer was collected and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ethyl acetate as the eluent.

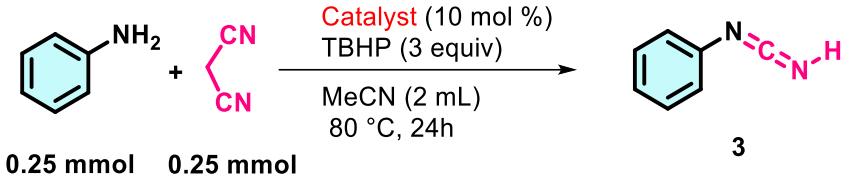
1.1.4 General procedure for scale-up reaction:

A round-bottomed flask was charged with aniline (0.45652 mL, 5 mmol), malononitrile (0.34648 mL, 5 mmol), $Cu(OAc)_2.H_2O$ (10 mol%), and TBHP (3 equiv.). The mixture was dissolved in 40 mL of acetonitrile and refluxed at 80 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (EtOAc). The mixture was then filtered through a celite filter. The organic layer was collected and dried over anhydrous Na_2SO_4. After filtration and evaporation of

the solvent, the crude mixture was purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ethyl acetate as the eluent.

2. Optimization of reaction conditions

Table S1: Optimization of Catalyst

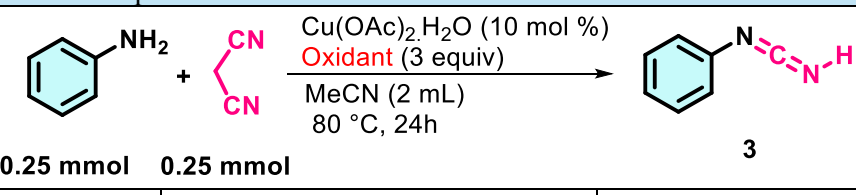


0.25 mmol 0.25 mmol 3

Sr. No	Catalyst	Isolated yield
1	CuCl	83 %
2	CuBr	70 %
3	CuI	20 %
4	$CuBr_2$	n.d.
5	$Cu(OAc)_2.H_2O$	92 %
6	$CuSO_4.5H_2O$	30 %
7	$CuCl_2.2H_2O$	40 %
8	$Cu(OTf)_2$	n.d.
9	CuPc	n.d.
10	CuO	50 %
11	$CuCrO_4$	60 %
12	-	n.d.

n.d. means not detected

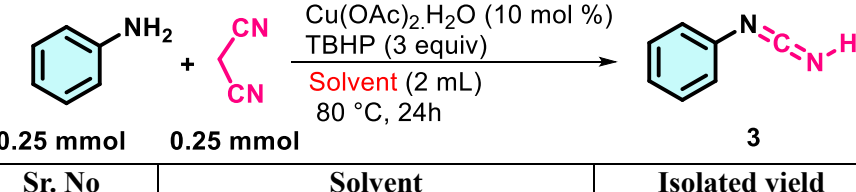
Table S2: Optimization of oxidant



0.25 mmol 0.25 mmol 3

Sr. No	Oxidant	Isolated yield
1	TBHP	92 %
2	DCP	50 %
3	BPO	45 %
4	TBPB	20 %
5	DTBP	67 %
6	CHP	72 %
7	H_2O_2	57 %
8	$(NH_4)_2S_2O_8$	n.d.
9	-	n.d.

Table S3: Optimization of solvent

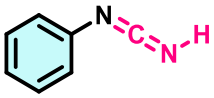


0.25 mmol 0.25 mmol 3

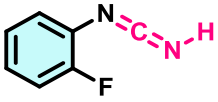
Sr. No	Solvent	Isolated yield
1	MeCN	92 %

2	DMF	< 5 %
3	DMSO	n.d.
4	Toluene	50 %
5	Dioxane	52 %
6	THF	55 %
7	*t*-BuOH	62 %
8	*t*-AmOH	65 %
9	EtOH	n.d.
10	TFE	n.d.
11	NMP	n.d.

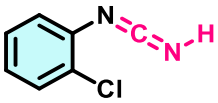
3. Characterization data



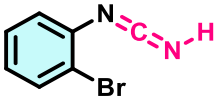
N-phenylmethanediimine (Table 2, entry 3a): Orange solid; **yield**: 92% (27.17 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.35 (s, 1H), 10.40 (d, *J* = 8.0 Hz, 2H), 10.21 – 10.15 (m, 2H), 9.90 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 153.0, 140.1, 129.2, 122.2, 118.6. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_7N_2$ is 119.0609 and found 119.0603.



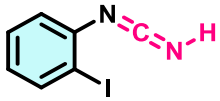
N-(2-fluorophenyl)methanediimine (Table 2, entry 3b): White solid; **yield**: 87% (29.60 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.11 (d, *J* = 2.6 Hz, 1H), 8.25 (td, *J* = 8.3, 1.7 Hz, 1H), 7.31 (ddd, *J* = 11.7, 8.2, 1.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 – 7.02 (m, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.4, 127.8, 125.0,124.9, 123.1, 123.0, 120.9, 115.5, 115.3. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6FN_2$ is 137.0515 and found 137.0509.



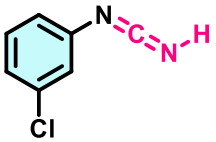
N-(2-chlorophenyl)methanediimine (Table 2, entry 3c): White solid; **yield**: 80% (30.51 mg); **^{1}H NMR** (500 MHz, DMSO) δ 8.98 (s, 1H), 8.01 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.24 (ddd, *J* = 8.5, 7.3, 1.5 Hz, 1H), 7.00 (td, *J* = 7.7, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 152.7, 136.2, 129.7, 127.9, 124.3, 123.2, 122.9. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6ClN_2$ is 153.0220 and found 153.0213.



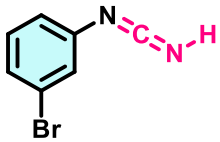
N-(2-bromophenyl)methanediimine (Table 2, entry 3d): Yellow solid; **yield**: 70% (34.48 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.89 (s, 1H), 7.94 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.35 (td, *J* = 8.3, 7.8, 1.6 Hz, 1H), 7.01 (td, *J* = 7.6, 1.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.8, 137.3, 133.0, 128.4, 125.1, 124.1, 114.5. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6BrN_2$ is 196.9714 and found 196.9708.



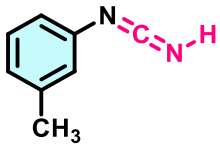
N-(2-iodophenyl)methanediimine (Table 2, entry 3e): White solid; **yield**: 50% (30.51 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.57 (s, 1H), 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.39 – 7.32 (m, 1H), 6.87 (td, *J* = 7.6, 1.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 153.2, 140.3, 139.4, 129.0, 126.0, 124.8, 92.9. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6IN_2$ is 244.9576 and found 244.9567.



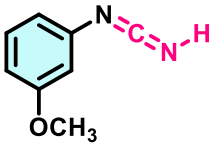
N-(3-chlorophenyl)methanediimine (Table 2, entry 3f): Light yellow solid; **yield**: 72% (27.46 mg); **1H NMR** (500 MHz, DMSO) δ 8.91 (s, 1H), 7.64 (s, 1H), 7.26 – 7.19 (m, 2H), 6.98 – 6.95 (m, 1H). **^{13}C NMR** (126 MHz, DMSO) δ 152.7, 141.4, 133.6, 130.8, 122.1, 118.2, 117.3. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6ClN_2$ is 153.0220 and found 153.0214.



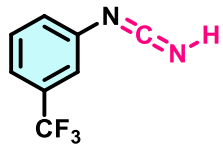
N-(3-bromophenyl)methanediimine (Table 2, entry 3g): Brown solid; **yield**: 76% (37.44 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.95 (s, 1H), 7.88 – 7.82 (m, 1H), 7.35 – 7.07 (m, 3H). **^{13}C NMR** (126 MHz, DMSO) δ 152.7, 136.2, 129.7, 127.9, 124.3, 123.2, 122.9. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6BrN_2$ is 196.9714 and found 196.9704.



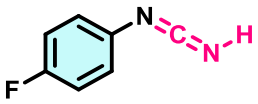
N-m-tolylmethanediimine (Table 2, entry 3h): Light brown solid; **yield**: 85% (28.09 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.62 (s, 1H), 7.36 (s, 1H), 7.30 – 7.24 (m, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 152.9, 140.1, 138.4, 129.0, 122.9, 119.1, 115.7, 21.7. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_8H_9N_2$ is 133.0766 and found 133.0762.



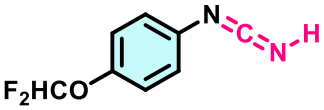
N-(3-methoxyphenyl)methanediimine (Table 2, entry 3i): Brown solid; **yield**: 78% (28.89 mg); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.61 (s, 1H), 7.16 – 7.10 (m, 2H), 6.90 (ddd, *J* = 8.1, 2.0, 0.9 Hz, 1H), 6.51 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 160.2, 152.9, 141.4, 130.0, 111.1, 107.7, 104.5, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_8H_9N_2O$ is 149.0715 and found 149.0709.



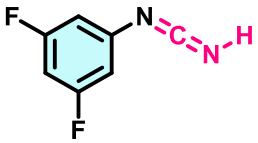
N-(3-(trifluoromethyl)phenyl)methanediimine (Table 2, entry 3j): Light brown solid; **yield**: 71% (33.04 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.19 (s, 1H), 8.02 (s, 1H), 7.57 (dd, *J* = 31.5, 8.0 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.9, 140.7, 130.3, 126.0, 123.2, 122.5, 118.8, 114.8. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_8H_6F_3N_2$ is 187.0483 and found 187.0476.



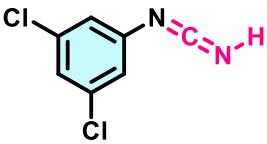
N-(4-fluorophenyl)methanediimine (Table 2, entry 3k): Yellow solid; **yield**: 65% (22.12 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.68 (s, 1H), 7.46 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.11 (t, *J* = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 153.1, 136.4, 120.5, 120.4, 120.3, 115.8, 115.6. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_6FN_2$ is 137.0515 and found 137.0511.



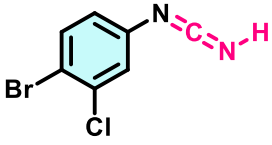
N-(4-(difluoromethoxy)phenyl)methanediimine (Table 2, entry 3l): Brown solid; **yield**: 70% (32.23 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.66 (s, 1H), 7.50 – 7.44 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 153.0, 140.1, 129.2, 122.2, 118.6, 23.8. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_8H_7F_2N_2O$ is 185.0526 and found 185.0518.



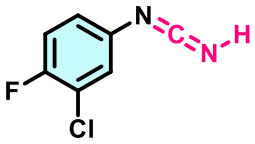
N-(3,5-difluorophenyl)methanediimine (Table 2, entry 3m): Brown solid**; yield**: 82% (31.59 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.26 (s, 1H), 7.23 – 7.15 (m, 2H), 6.83 (tt, *J* = 9.4, 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 164.3, 164.1, 161.9, 161.7, 152.4, 142.5, 142.4, 142.3, 101.9, 101.8, 101.7, 101.6, 97.9, 97.7, 97.4. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_5F_2N_2$ is 155.0421 and found 155.0413.



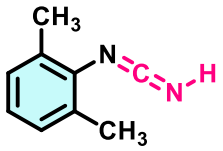
N-(3,5-dichlorophenyl)methanediimine (Table 2, entry 3n): White solid; **yield**: 74% (34.60 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.27 (s, 1H), 7.54 (d, *J* = 1.9 Hz, 2H), 7.21 – 7.19 (m, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.4, 142.2, 134.5, 121.8, 117.2. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_5Cl_2N_2$ is 186.9830 and found 186.9823.



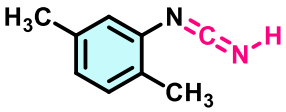
N-(4-bromo-3-chlorophenyl)methanediimine (Table 2, entry 3o): White solid; **yield**: 58% (33.56 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.14 (s, 1H), 7.87 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.28 (dd, *J* = 8.8, 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.5, 140.6, 134.2, 133.5, 120.0, 119.3, 113.5. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_5BrClN_2$ is 230.9325 and found 230.9315.



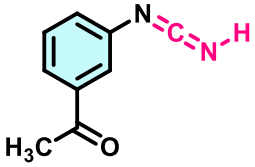
N-(3-chloro-4-fluorophenyl)methanediimine (Table 2, entry 3p): Light brown solid; **yield**: 54% (23.03 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.99 (s, 1H), 7.79 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.36 – 7.28 (m, 2H). **^{13}C** NMR (101 MHz, DMSO) δ 152.9, 151.7, 137.2, 137.1, 120.2, 119.7, 119.5, 119.2, 119.1, 117.4, 117.2**. HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_7H_5ClFN_2$ is 171.0125 and found 171.0118.



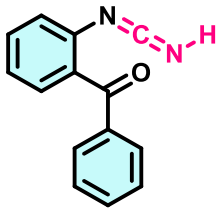
N-(2,6-dimethylphenyl)methanediimine (Table 2, entry 3q): Shiney green solid; **yield**: 47% (17.17 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.22 (s, 1H), 7.15 (q, *J* = 5.3 Hz, 2H), 6.24 (s, 1H), 2.13 (s, 3H), 2.11 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 149.6, 137.2, 136.3, 133.5, 128.9, 126.8, 112.8, 19.7, 18.4. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_9H_{11}N_2$ is 147.0922 and found 147.0916.



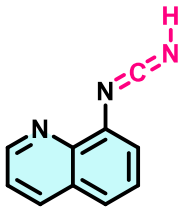
N-(2,5-dimethylphenyl)methanediimine (Table 2, entry 3r): Orange solid; **yield**: 50% (18.27 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.45 (s, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 2.31 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 152.5, 136.8, 134.9, 131.4, 128.2, 122.4, 112.8, 20.9, 17.6. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_9H_{11}N_2$ is 147.0922 and found 147.0916.



1-(3-((iminomethylene)amino)phenyl)ethane-1-one (Table 2, entry 3s): Brown solid; **yield**: 75% (30.03 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.97 (s, 1H), 8.09 (d, *J* = 2.5 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.62 – 7.58 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 2.57 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 198.1, 153.0, 140.4, 137.9, 129.6, 123.4, 122.5, 118.0, 27.2. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_9H_9N_2O$ is 161.0715 and found 161.0709.



((iminomethylene)amino)phenyl)(phenyl)methanone (Table 2, entry 3t): Brown solid; **yield**: 50% (27.78 mg); **^{1}H NMR** (400 MHz, DMSO) δ 9.37 (s, 1H), 8.17 – 8.02 (m, 3H), 7.59 – 7.46 (m, 3H), 7.38 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.26 (td, *J* = 7.4, 1.6 Hz, 2H). **13C NMR** (101 MHz, DMSO) δ 195.6, 154.8, 150.9, 134.7, 130.5, 130.3, 129.9, 129.0, 128.9, 128.6, 127.2, 124.5. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{14}H_{11}N_2O$ is 223.0871 and found 223.0862.



N-(quinoline-8-yl)methanediimine (Table 2, entry 3u): Pink solid; **yield**: 73% (30.87 mg); **^{1}H NMR** (400 MHz, DMSO) δ 8.88 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.58 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.16 (s, 2H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.78 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 154.6, 148.9, 136.7, 134.2, 126.8, 124.5, 116.0, 114.4, 112.8, 109.0. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{10}H_8N_3$ is 170.0718 and found 170.0710.

4. NMR Spectra of the Synthesized Compounds

Table 2, entry 3a

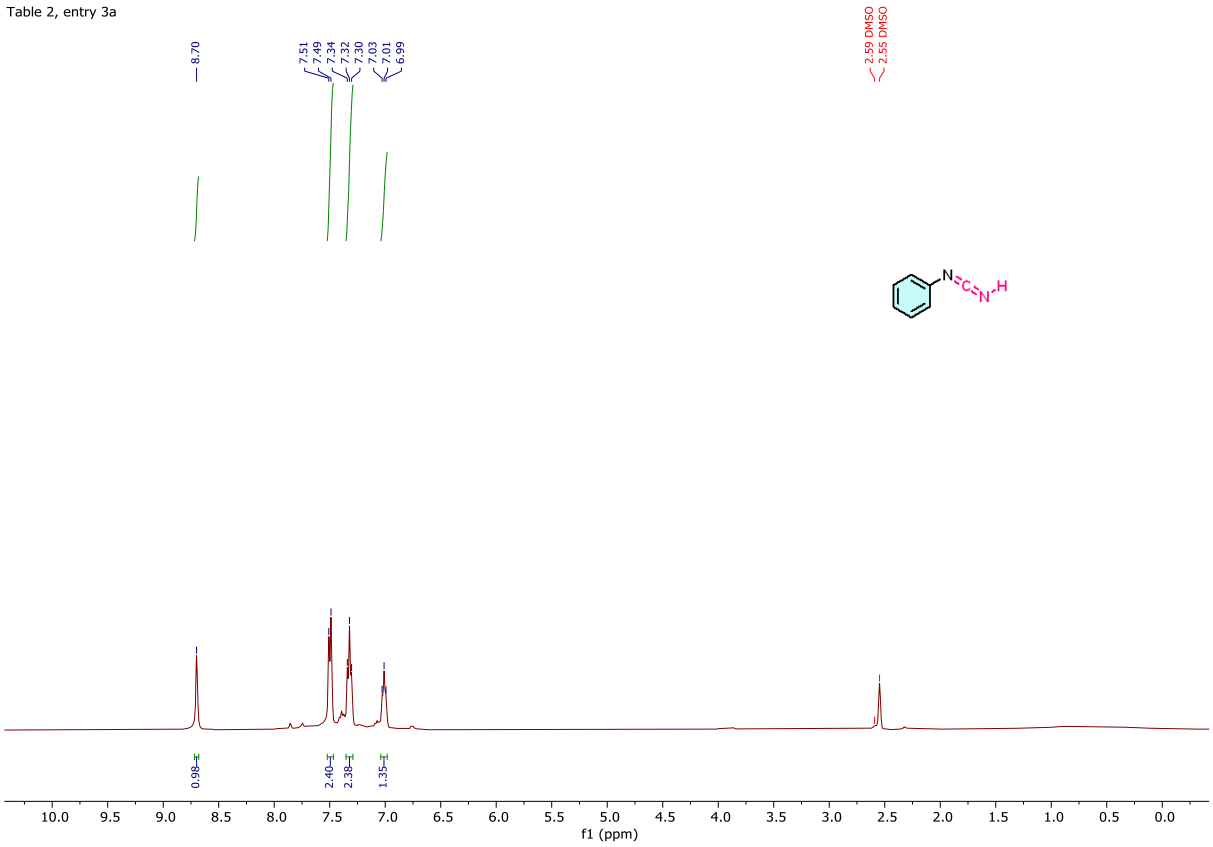


Table 2, entry 3a

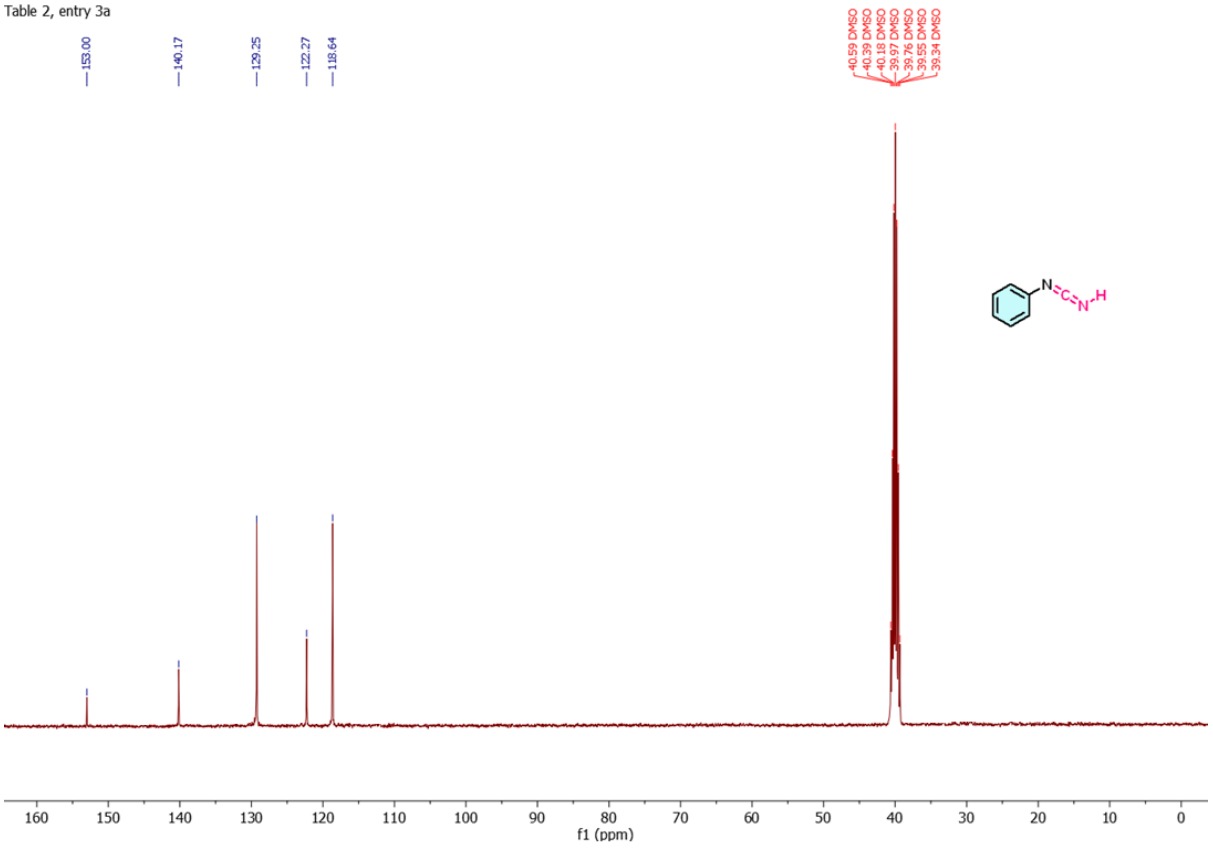


Table 2, entry 3b

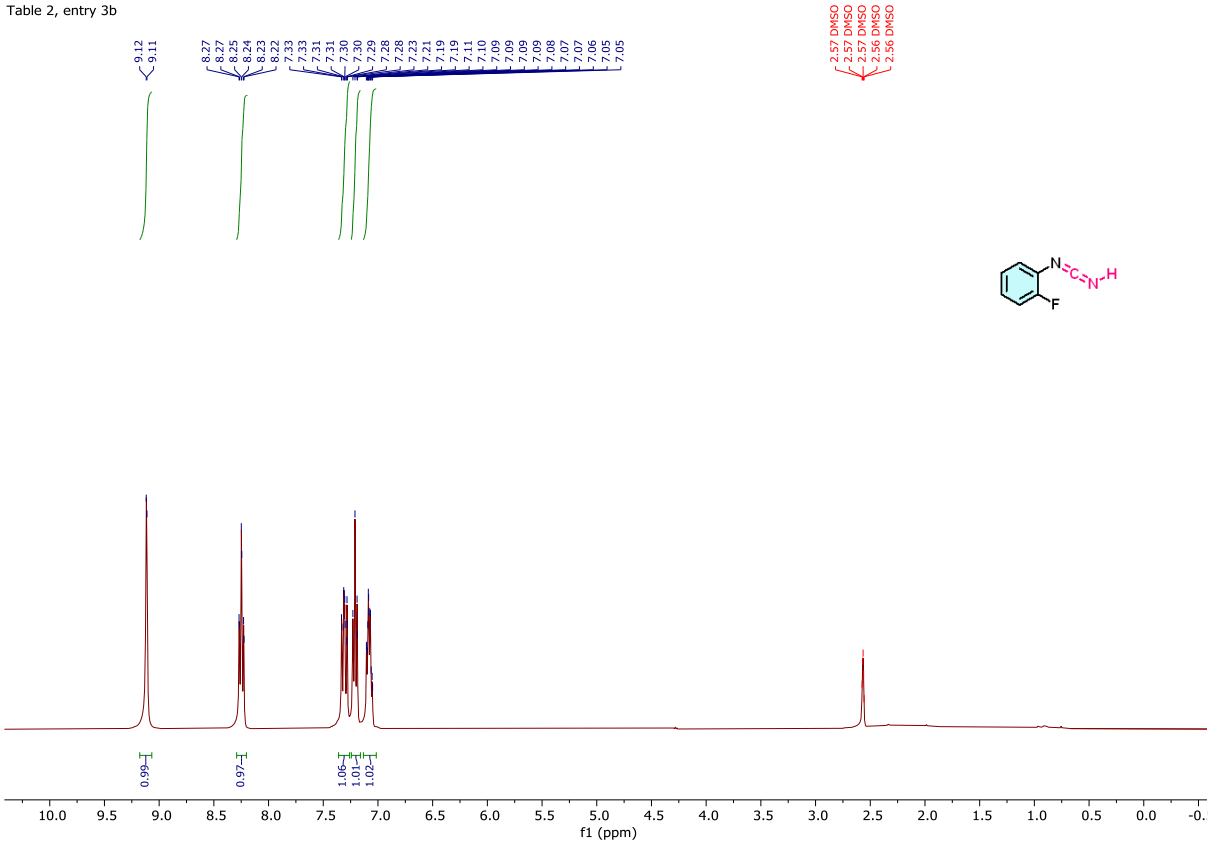


Table 2, entry 3b

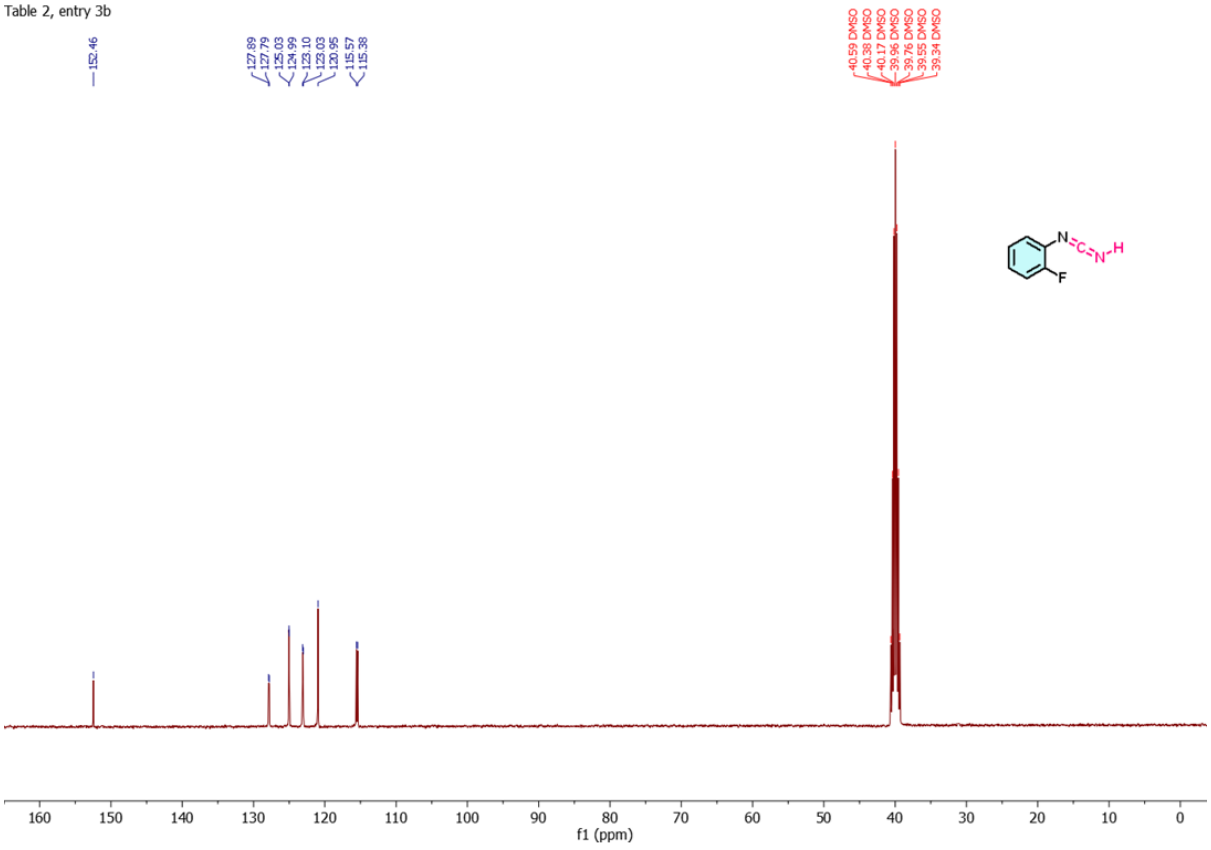


Table 2, entry 3c

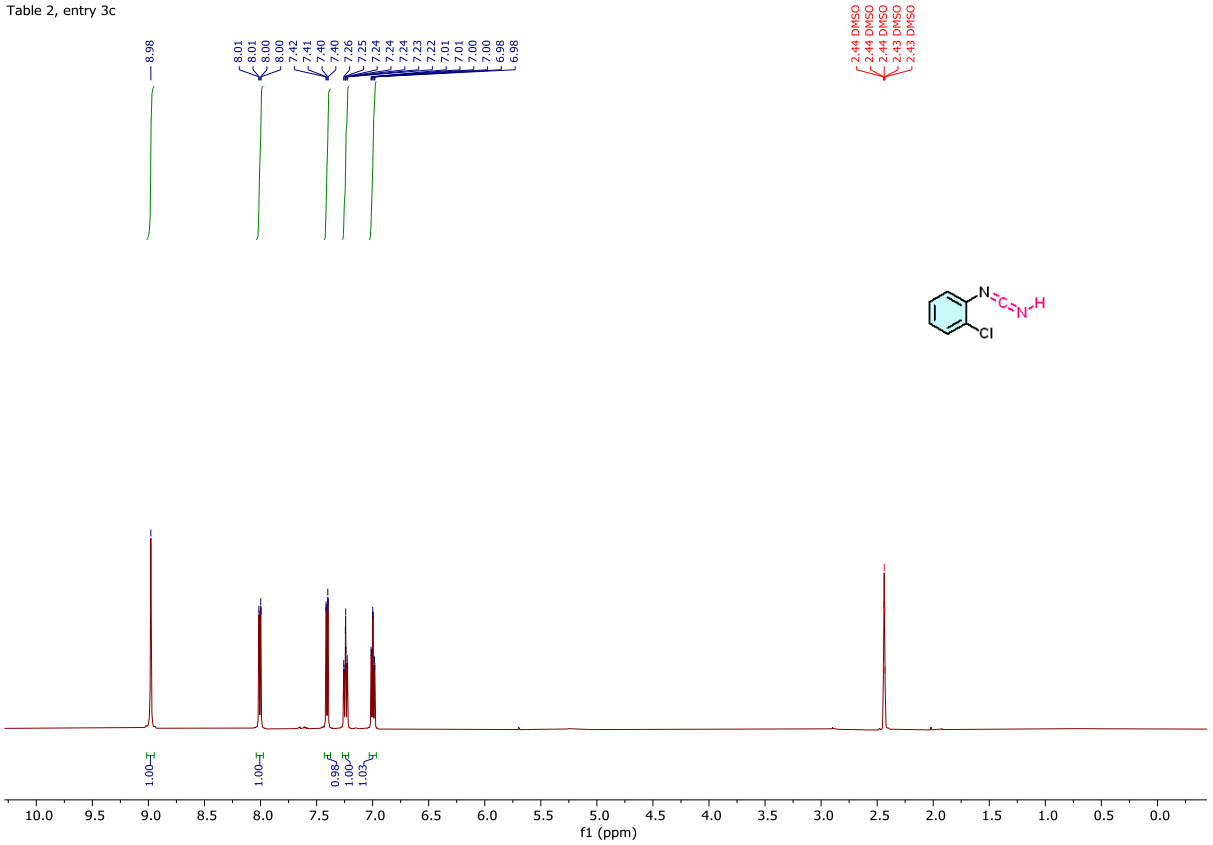


Table 2, entry 3c

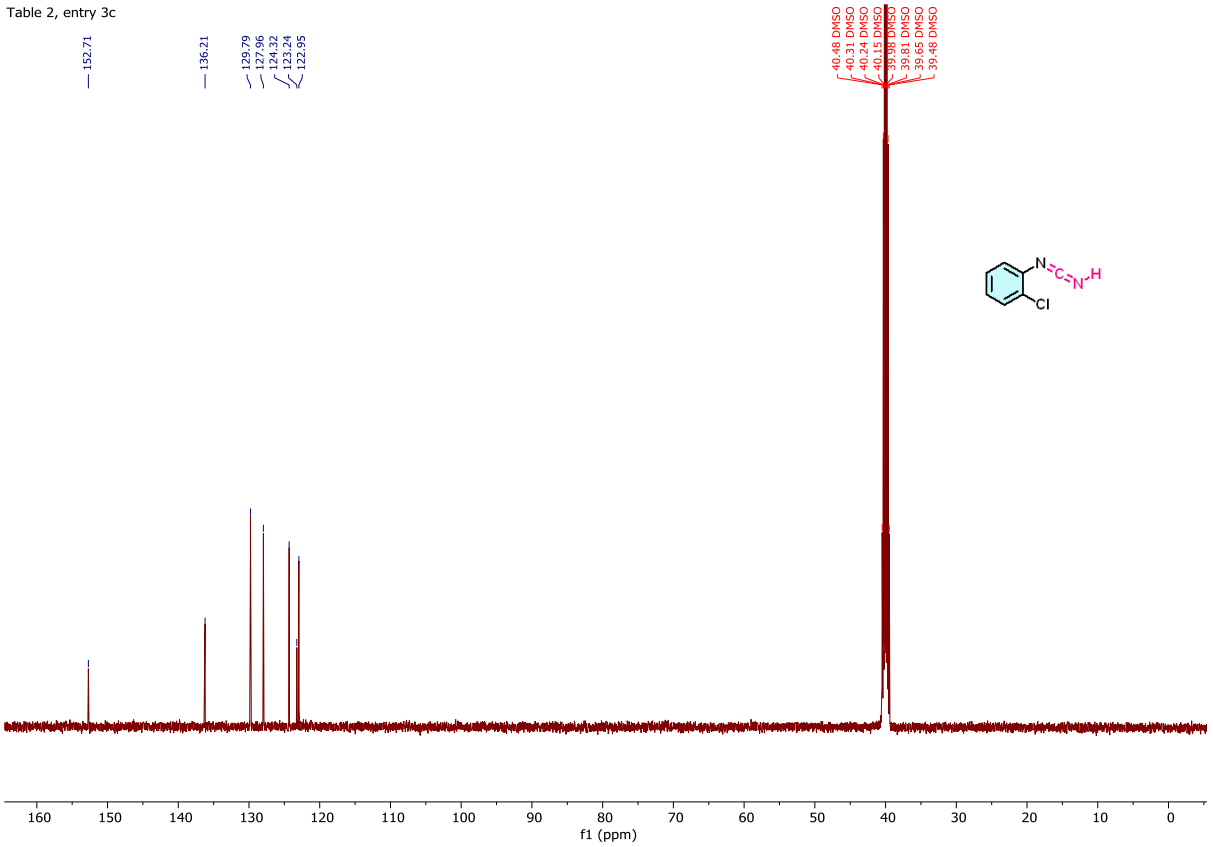


Table 2, entry 3d

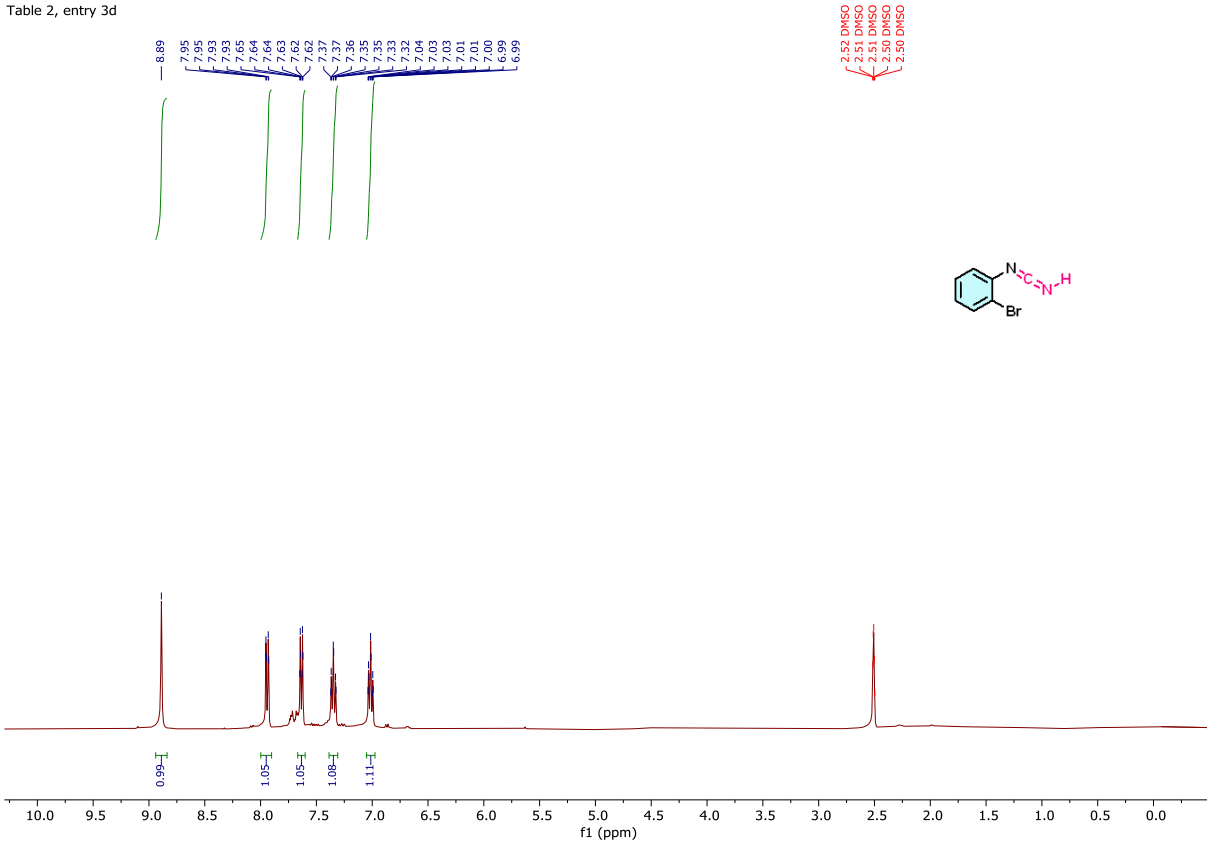


Table 2, entry 3d

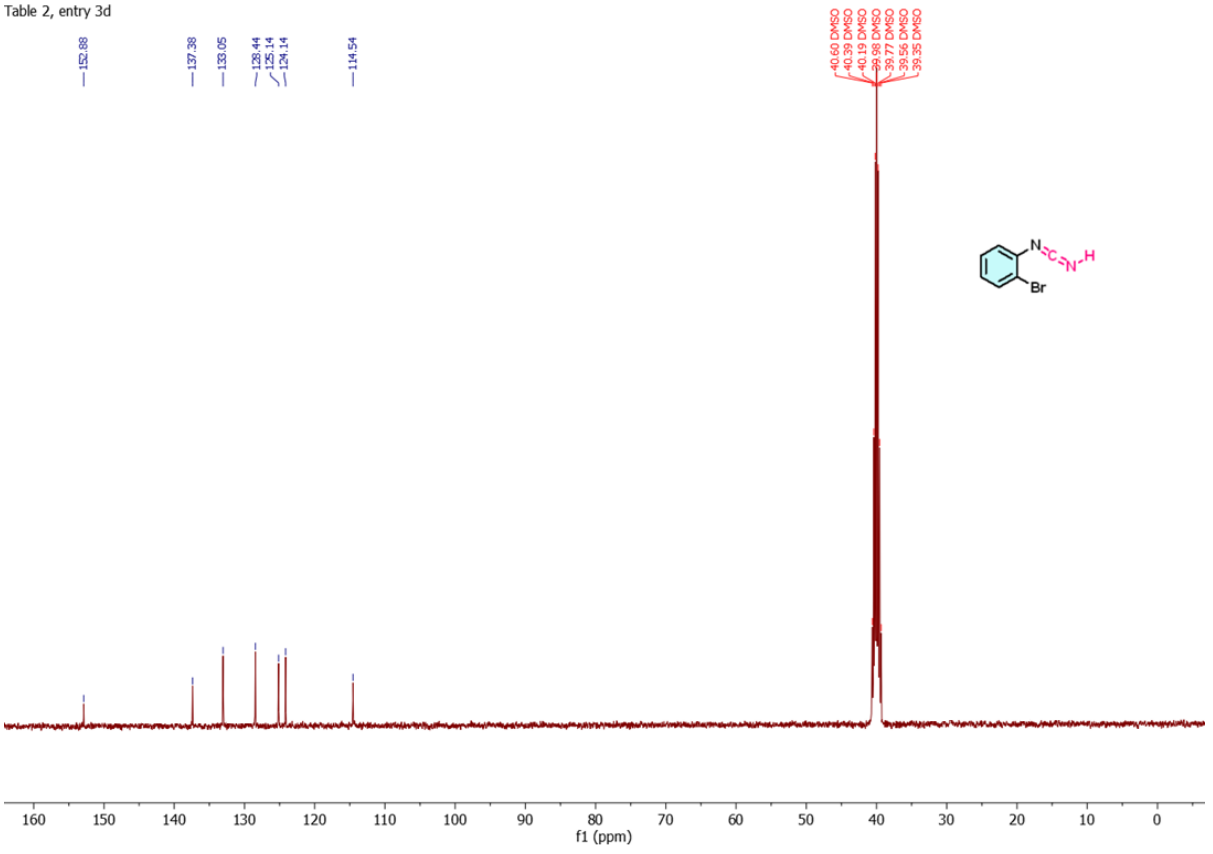
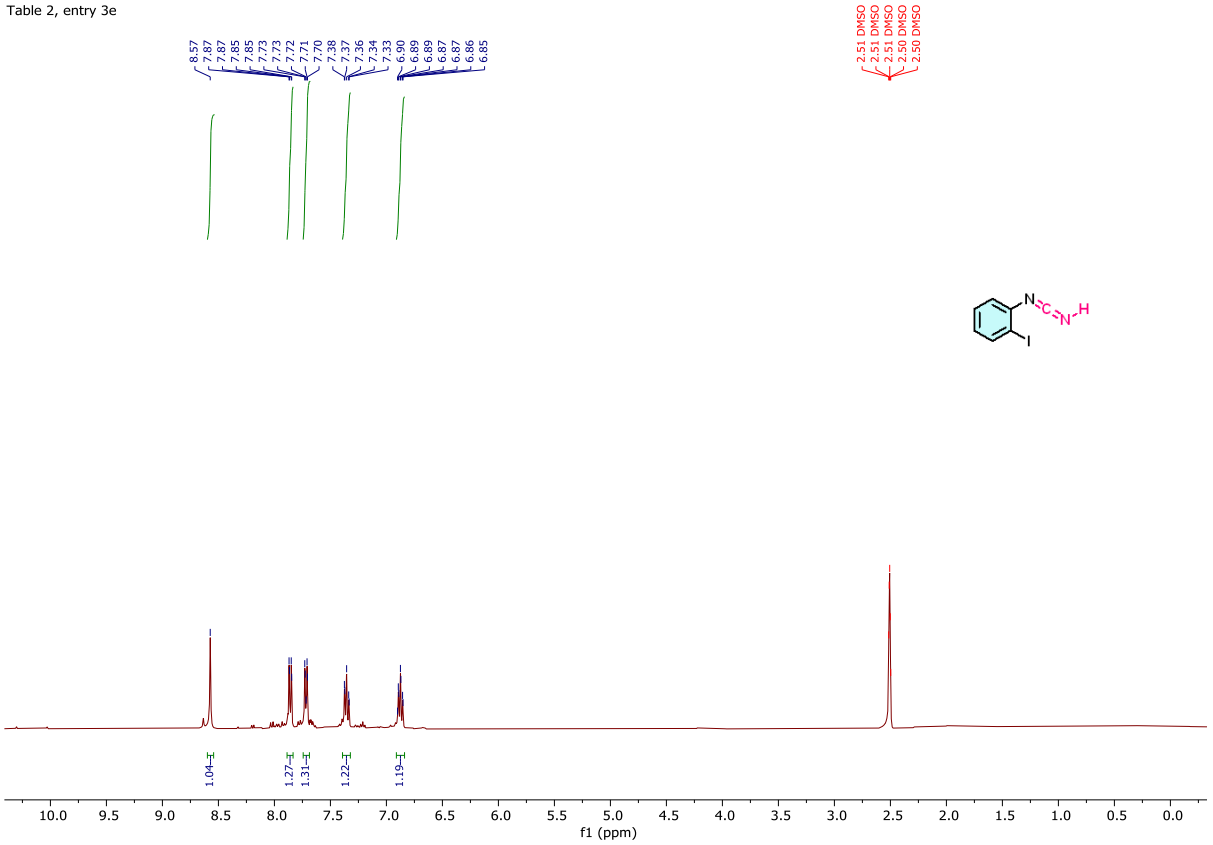


Table 2, entry 3e



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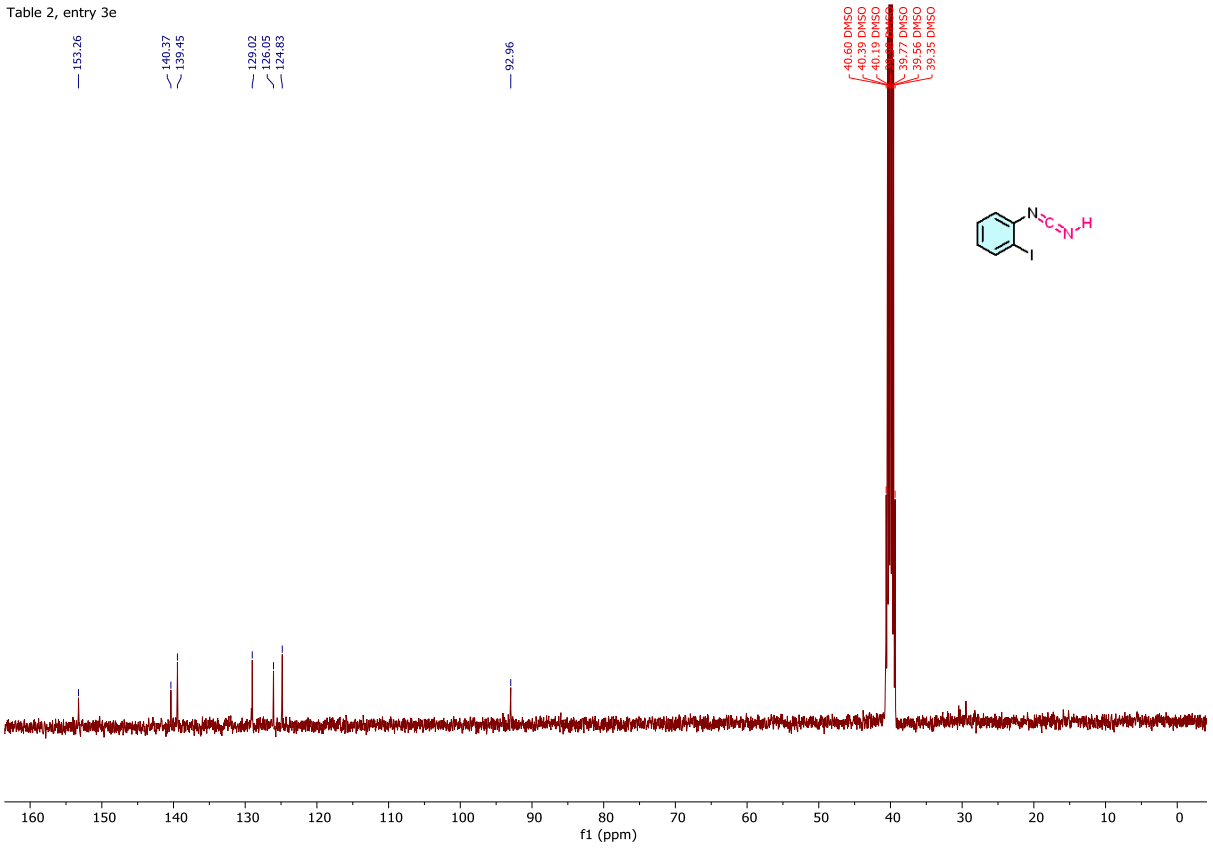


Table 2, entry 3f

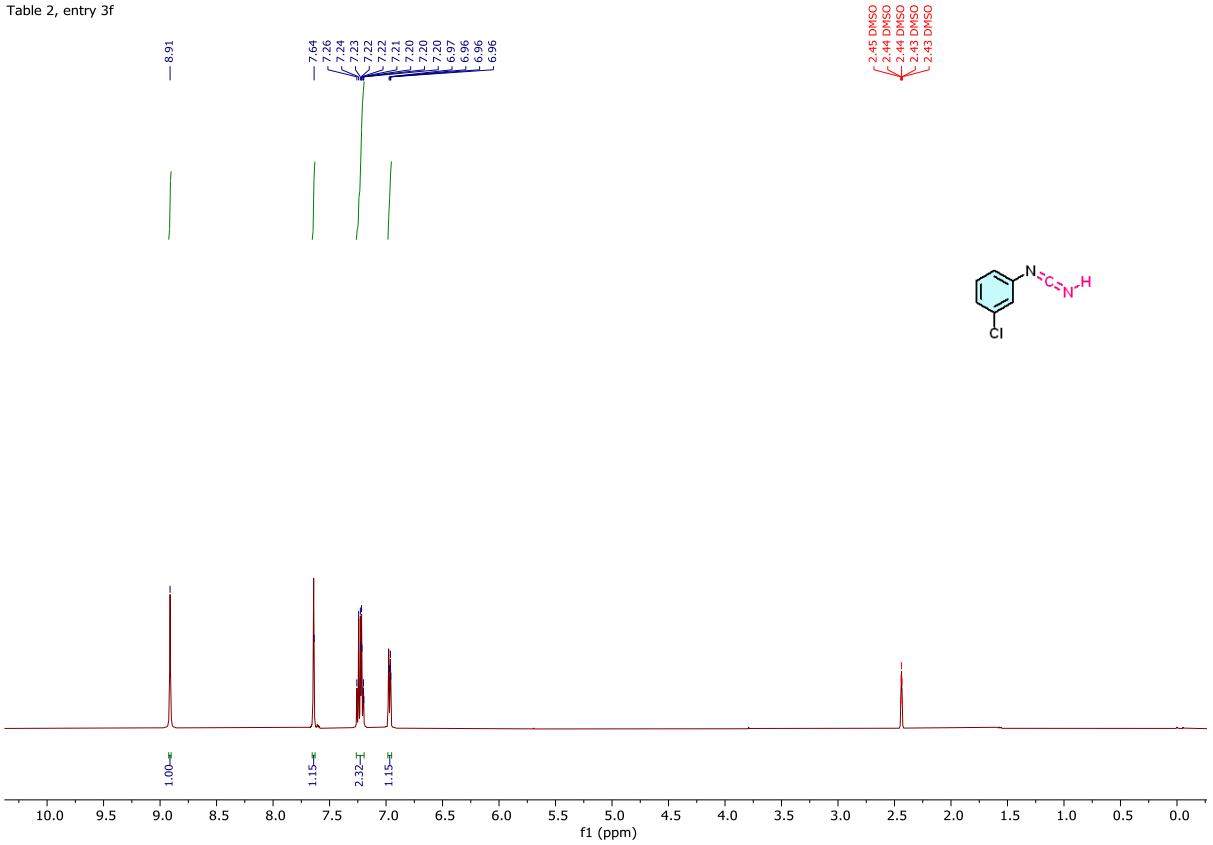


Table 2, entry 3f

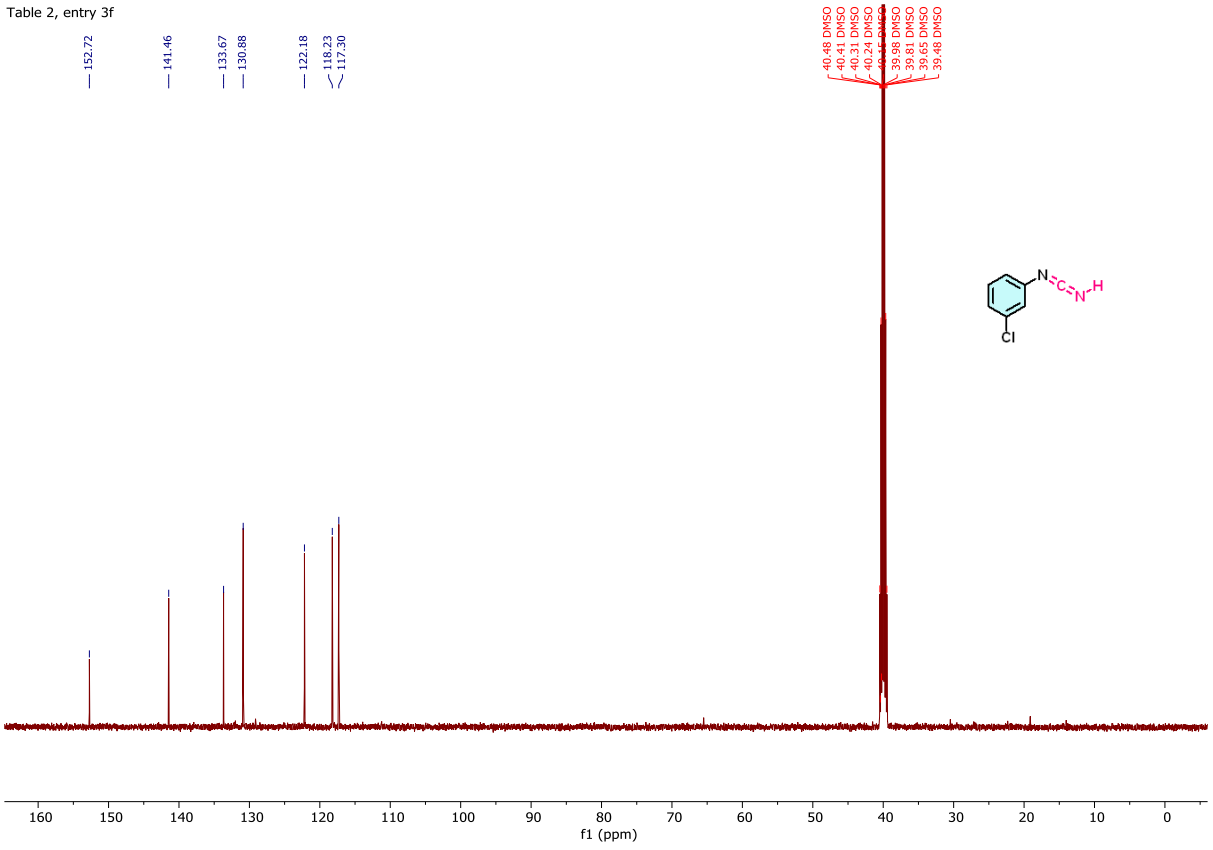


Table 2, entry 3g

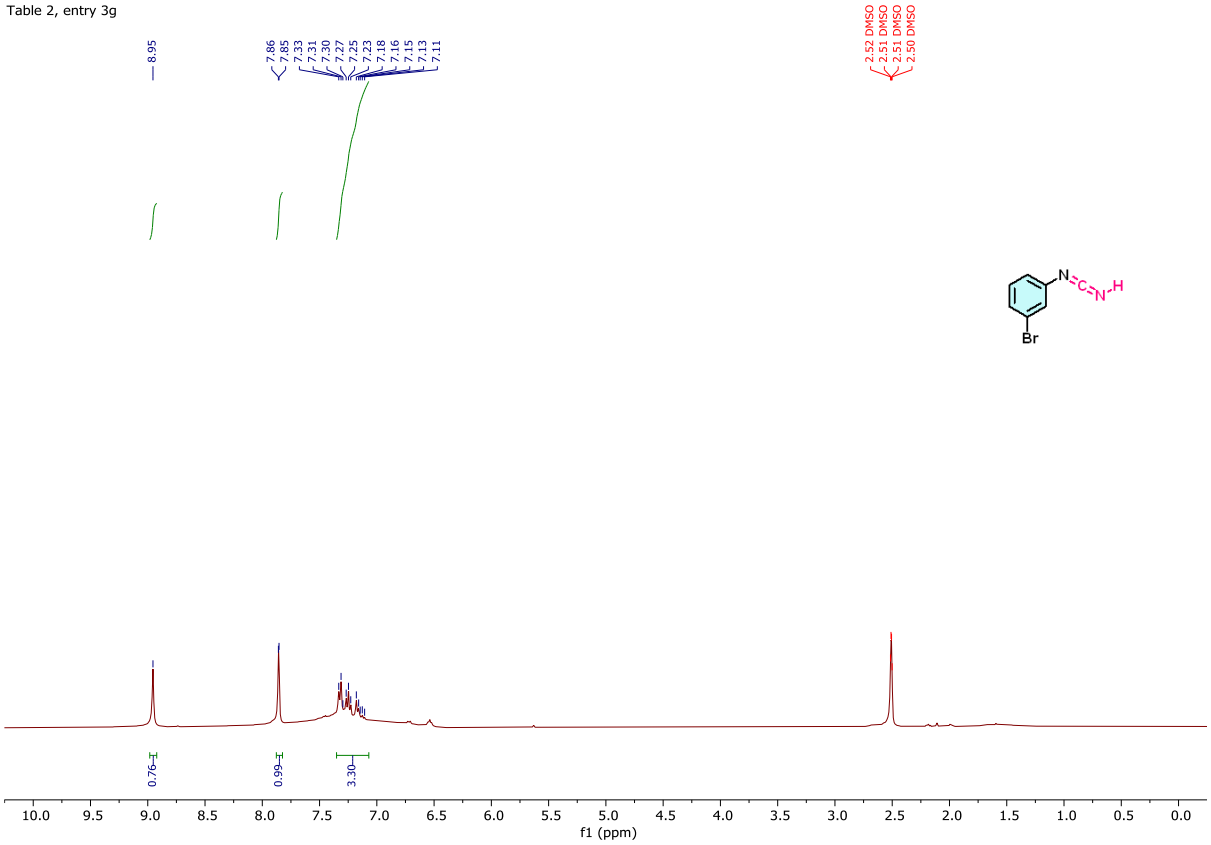


Table 2, entry 3g

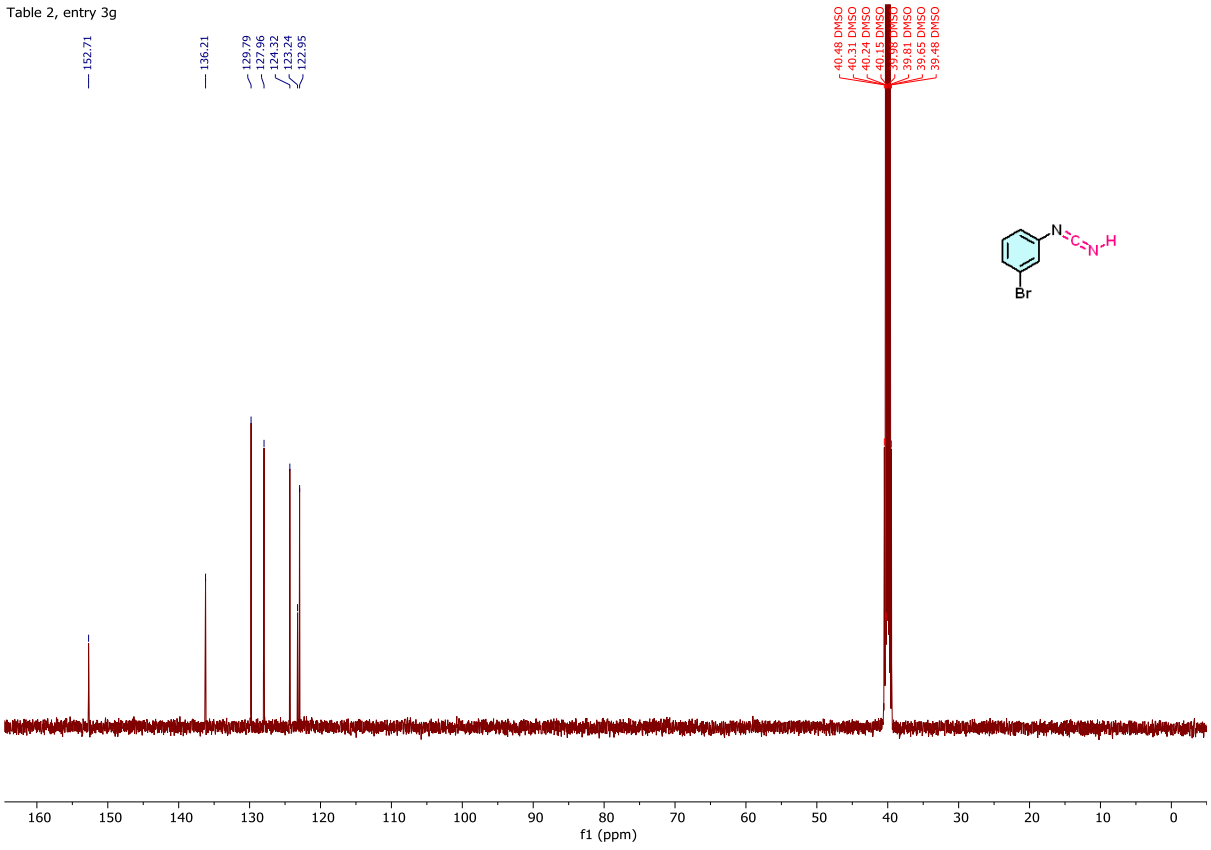
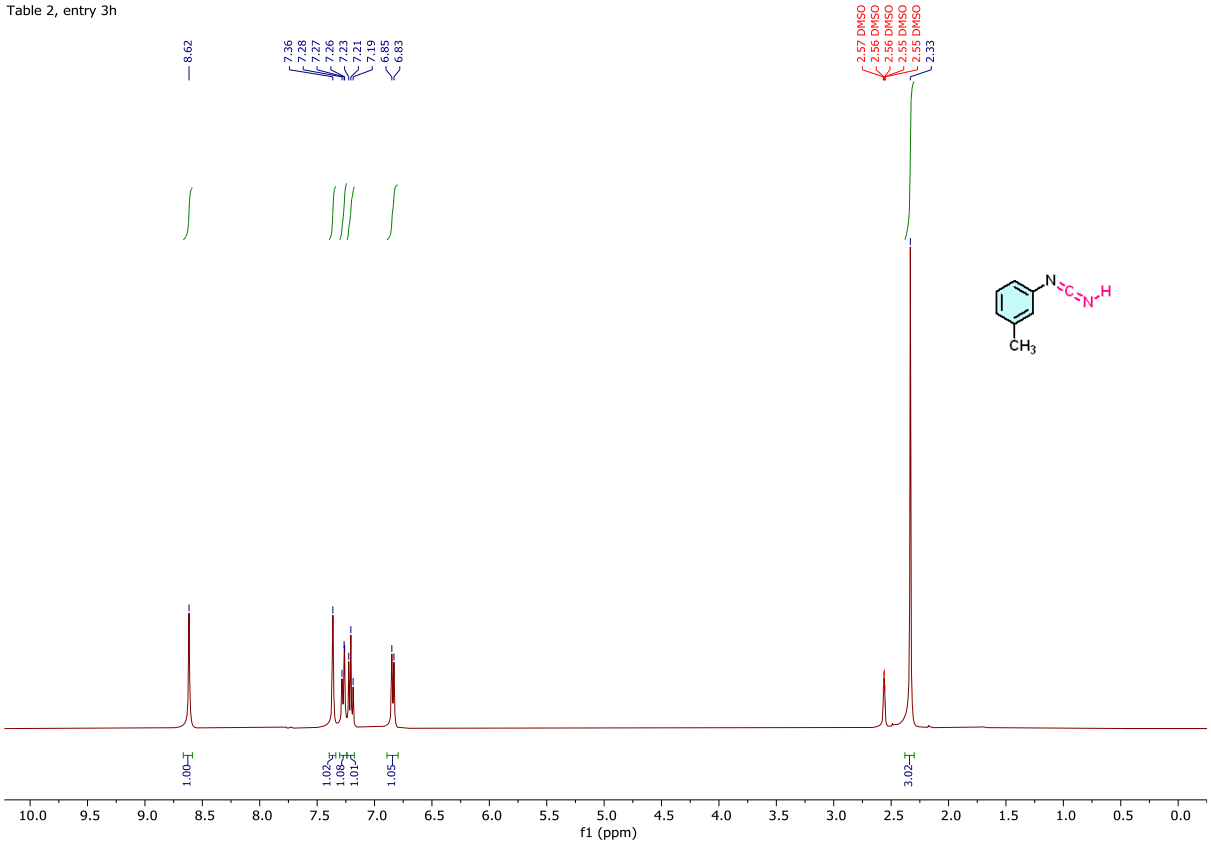


Table 2, entry 3h



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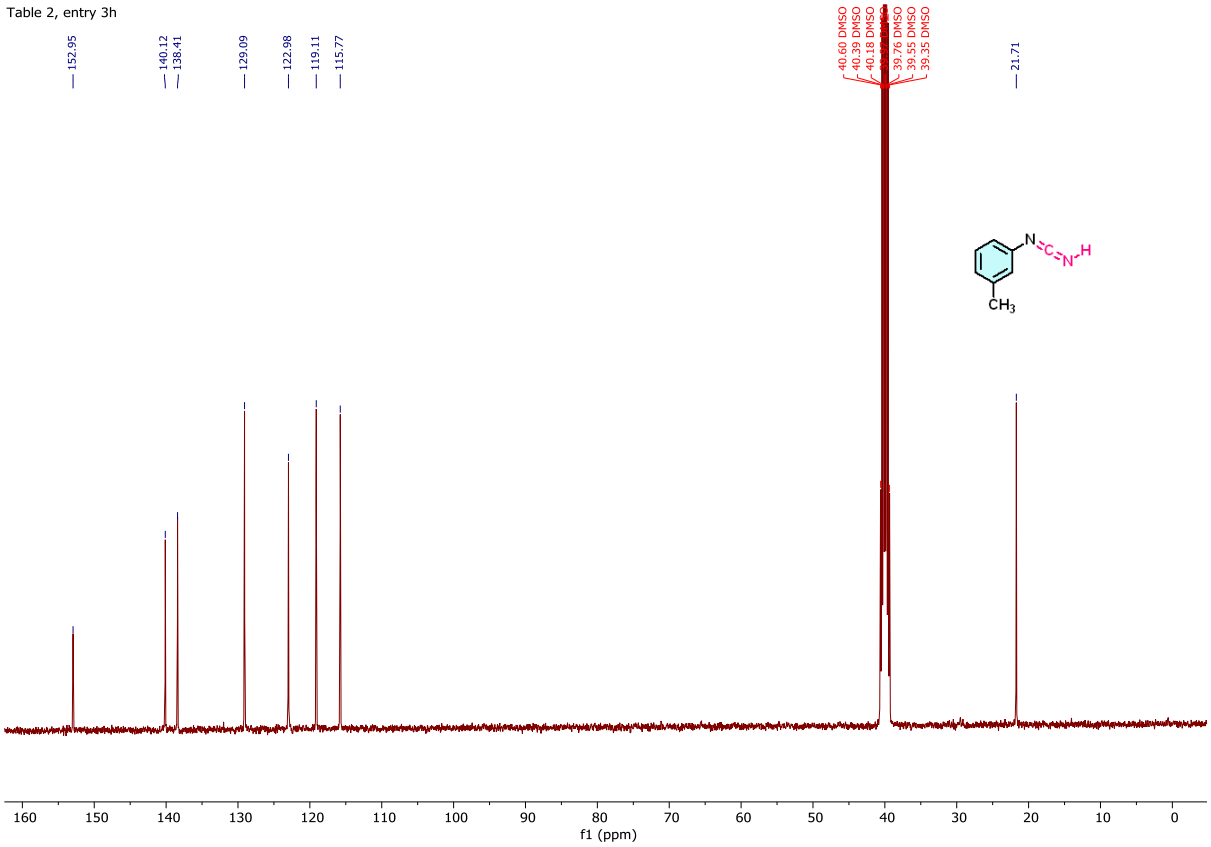


table 2, entry 3i

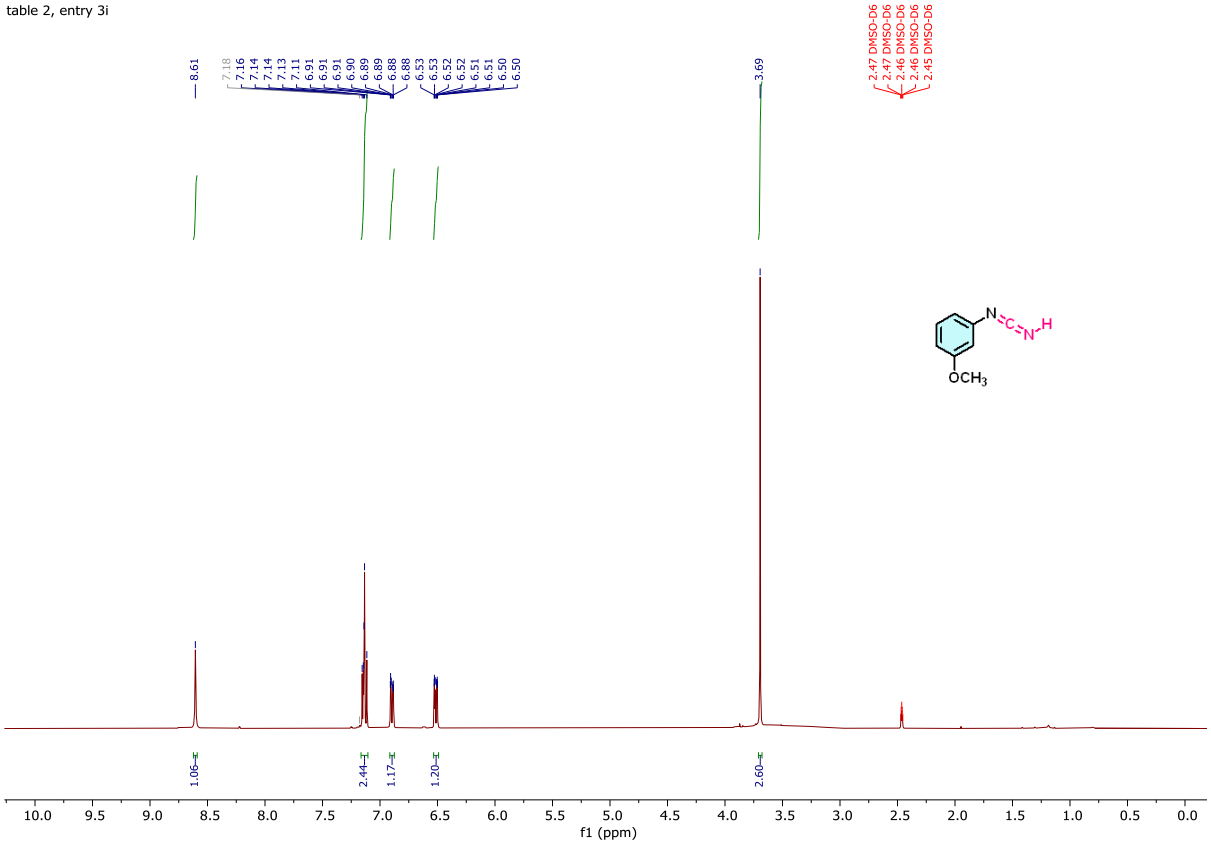
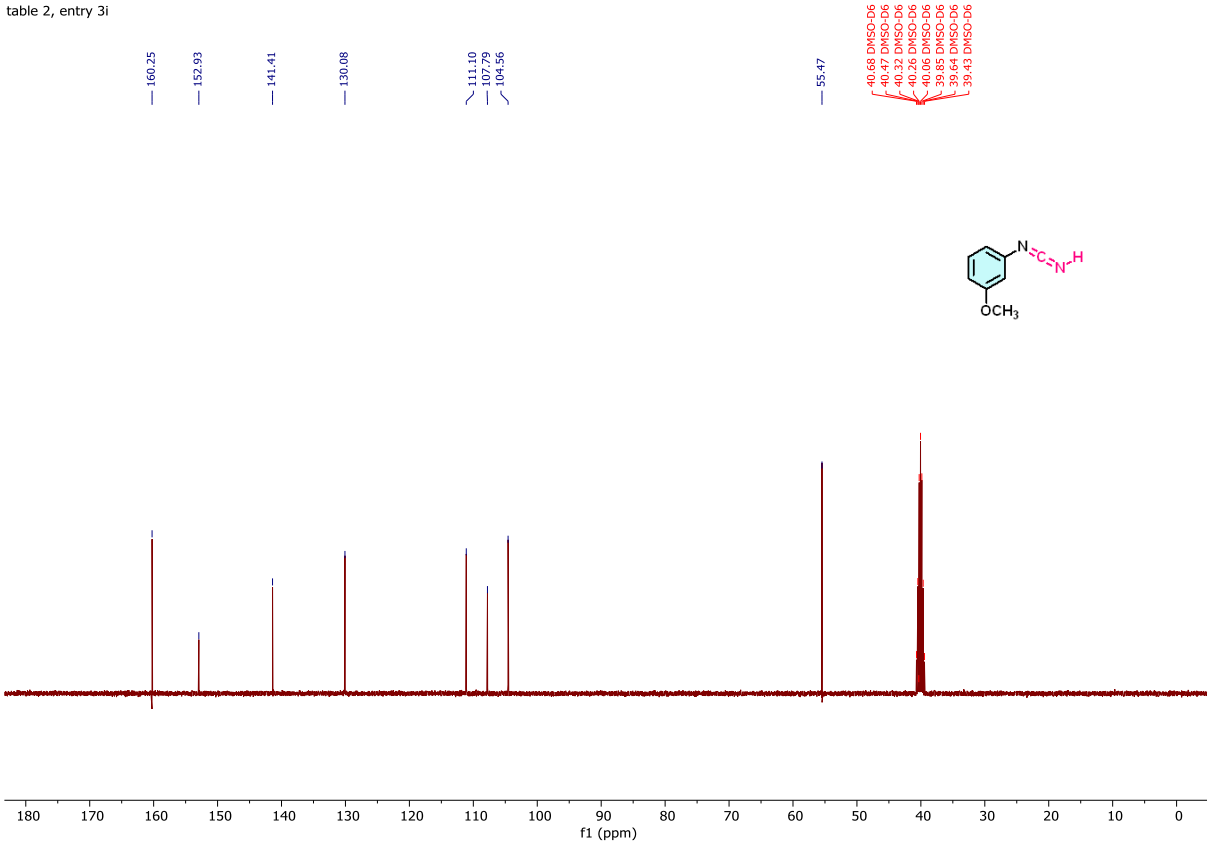


table 2, entry 3i



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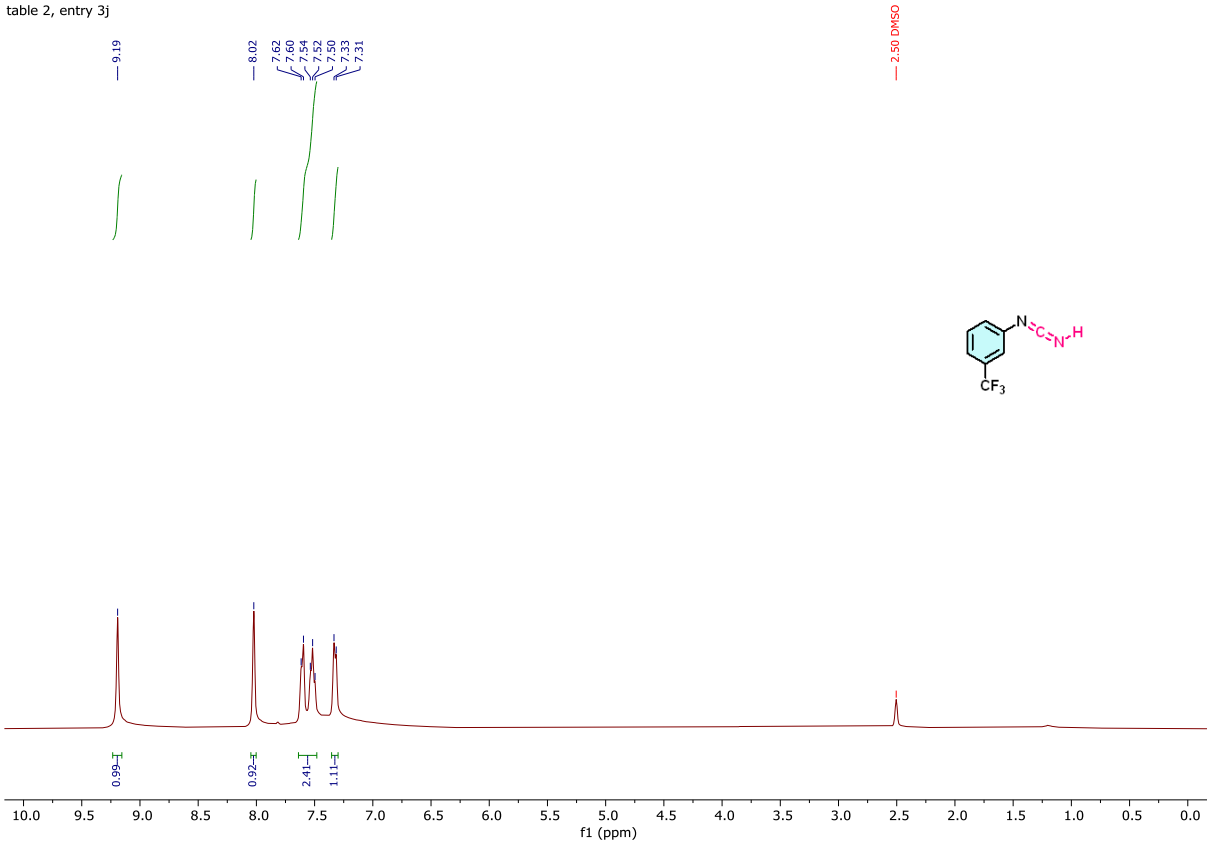
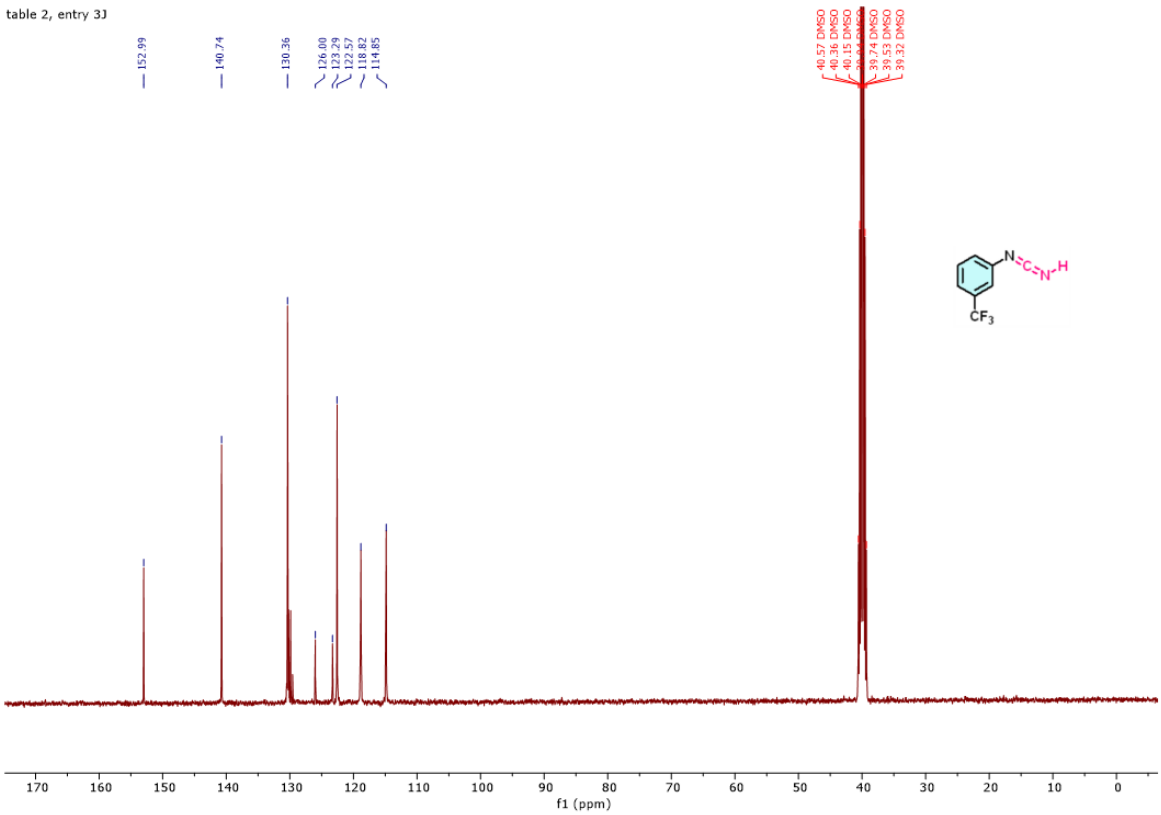


table 2, entry 3J



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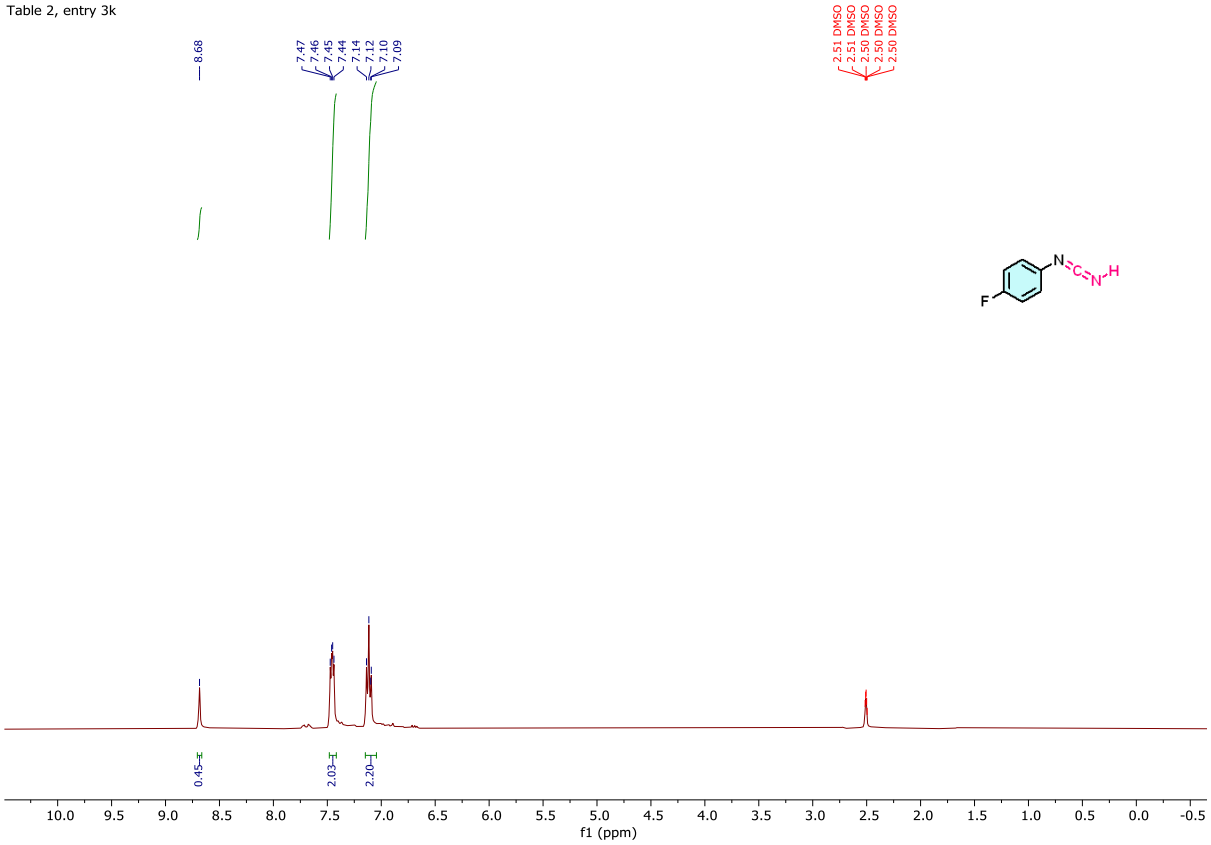

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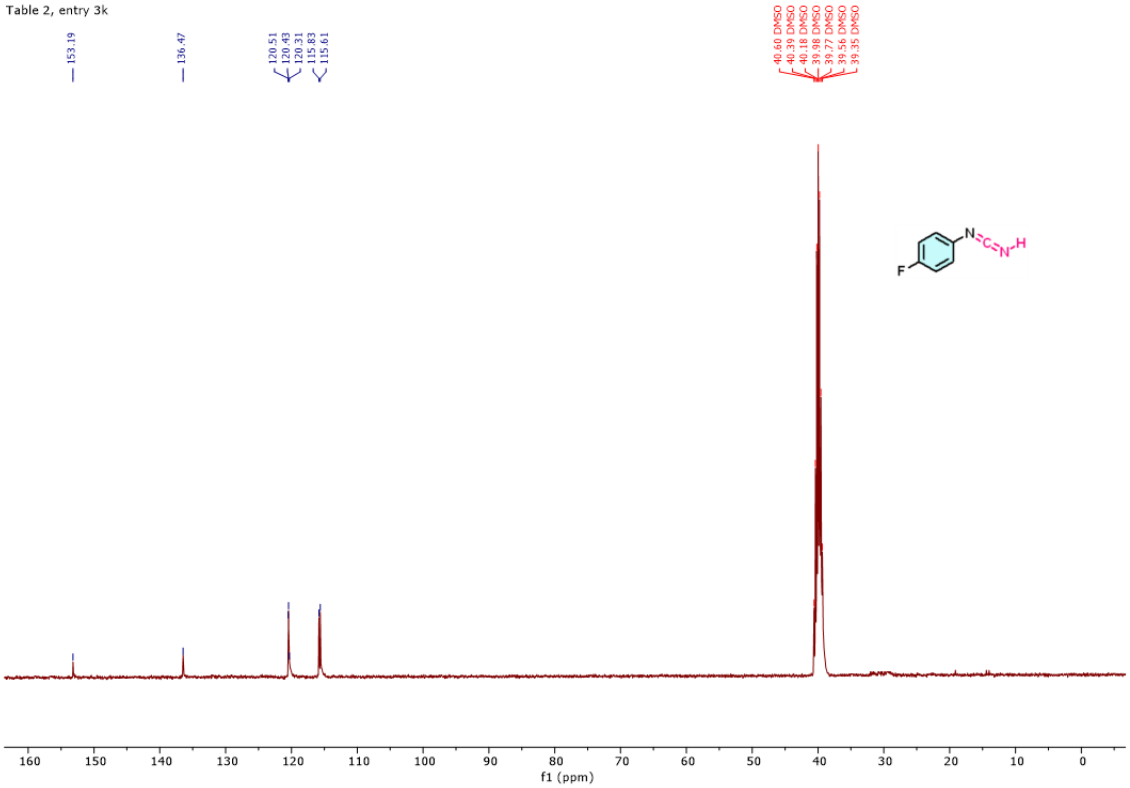

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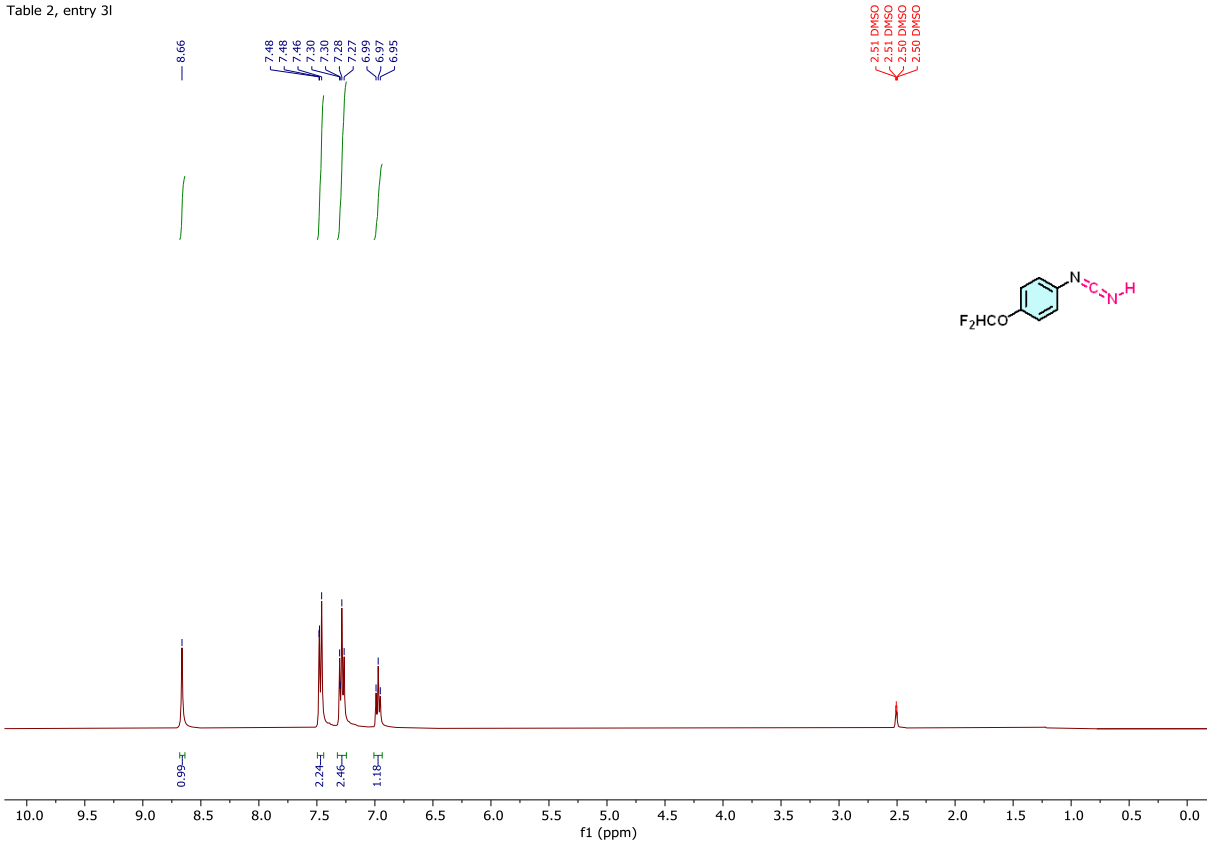

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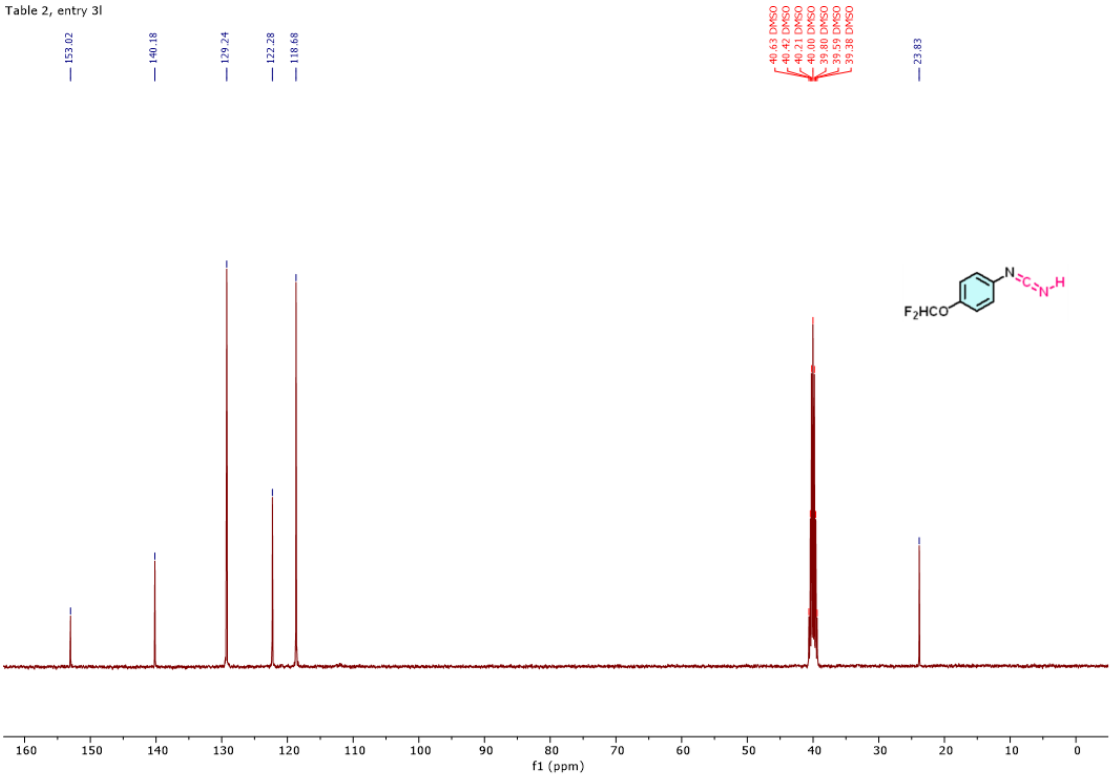

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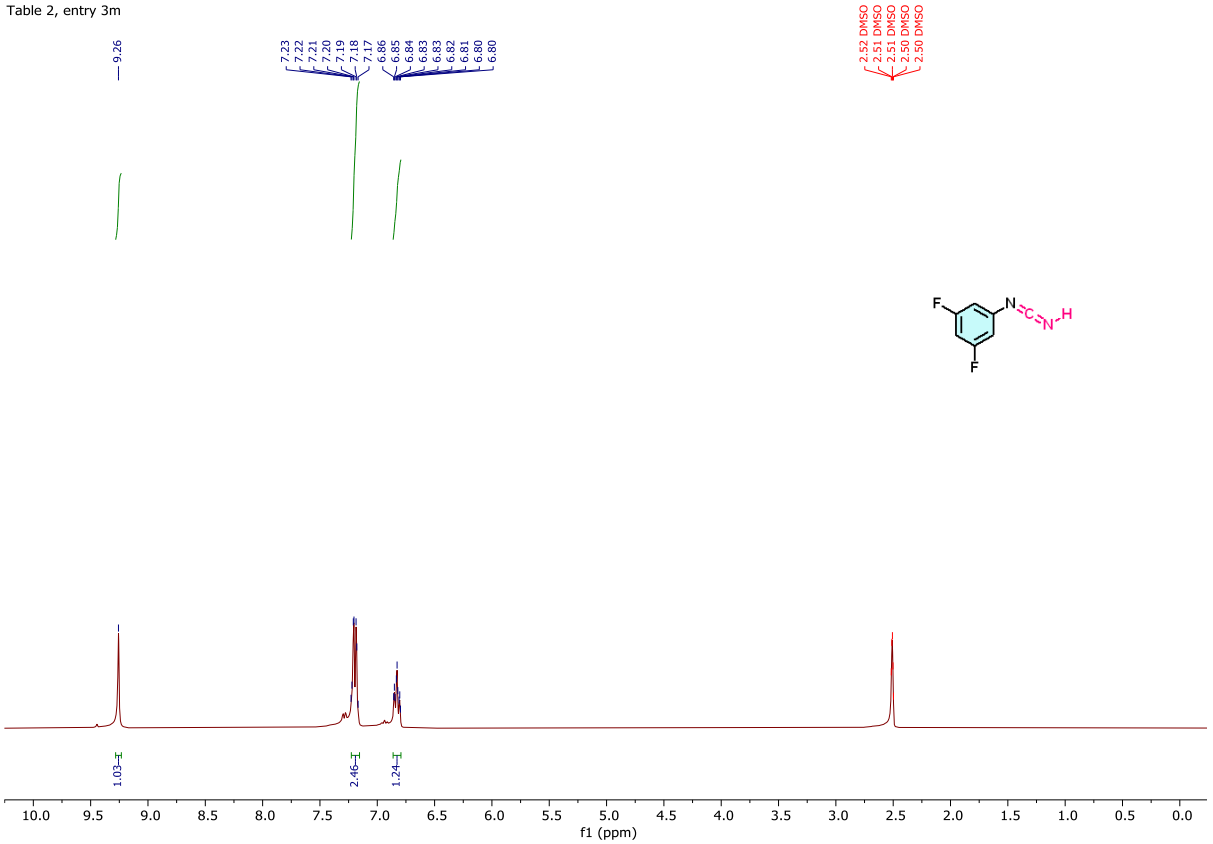
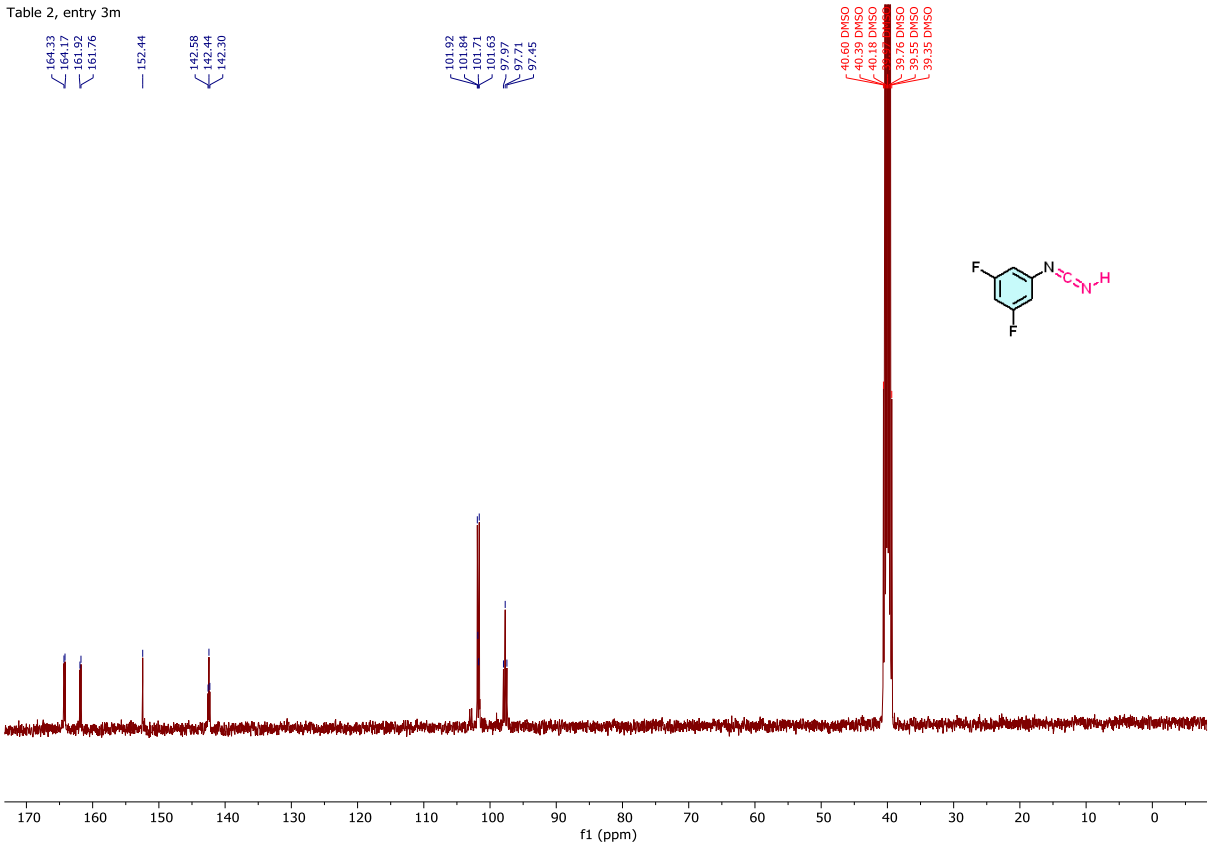


Table 2, entry 3m



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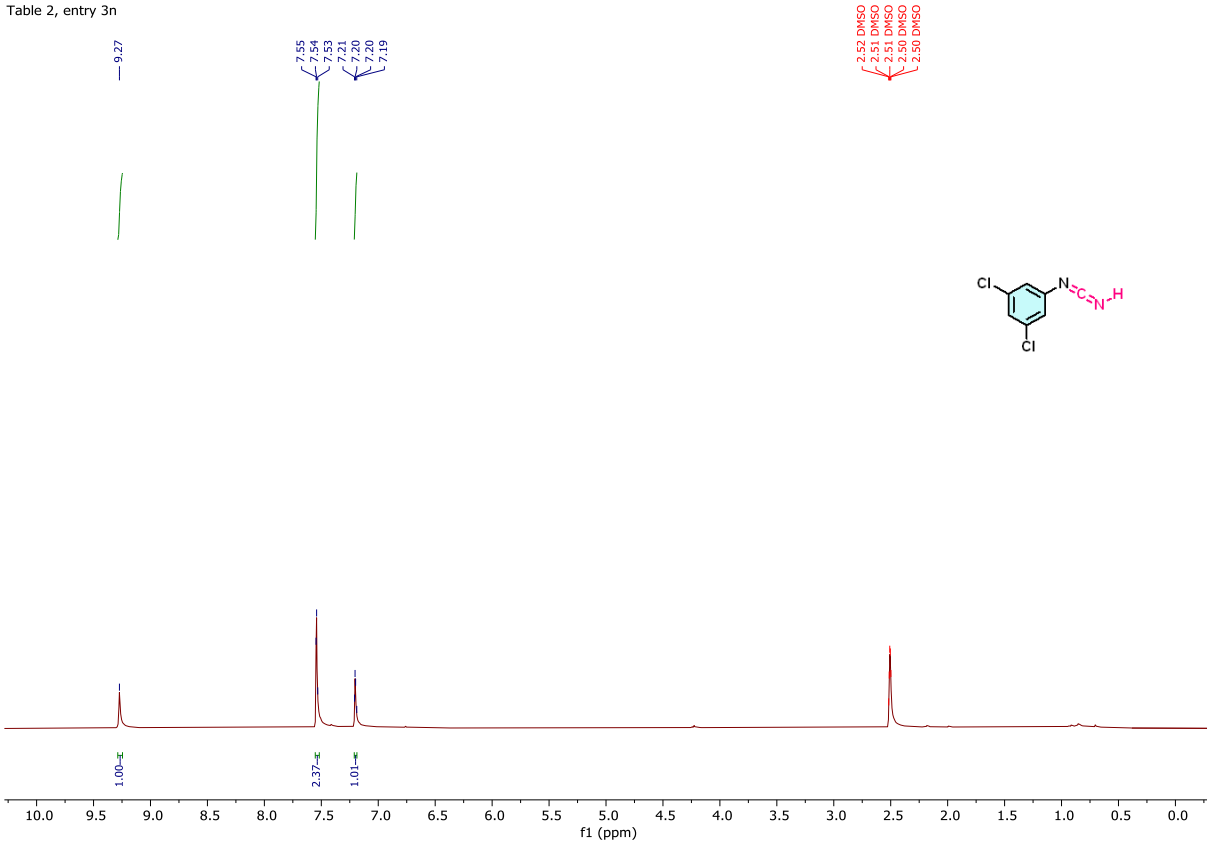

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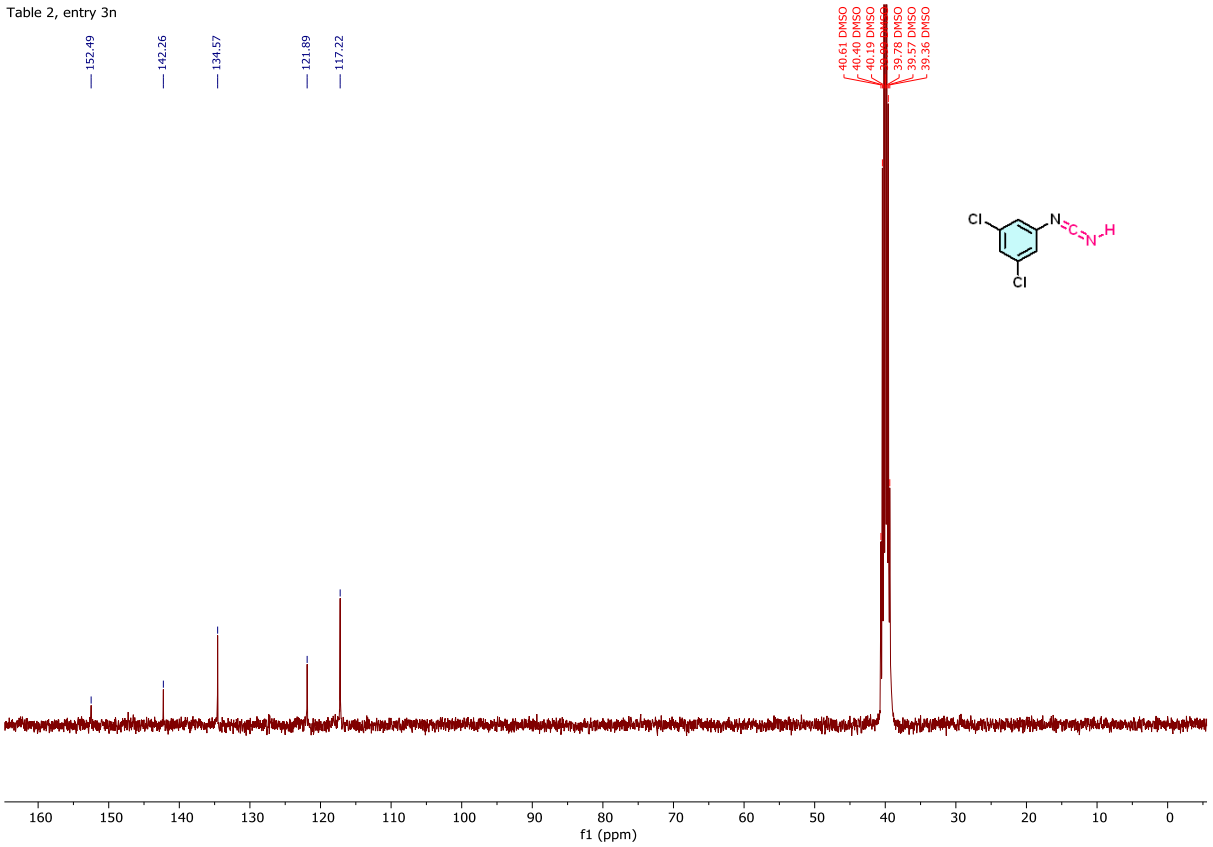

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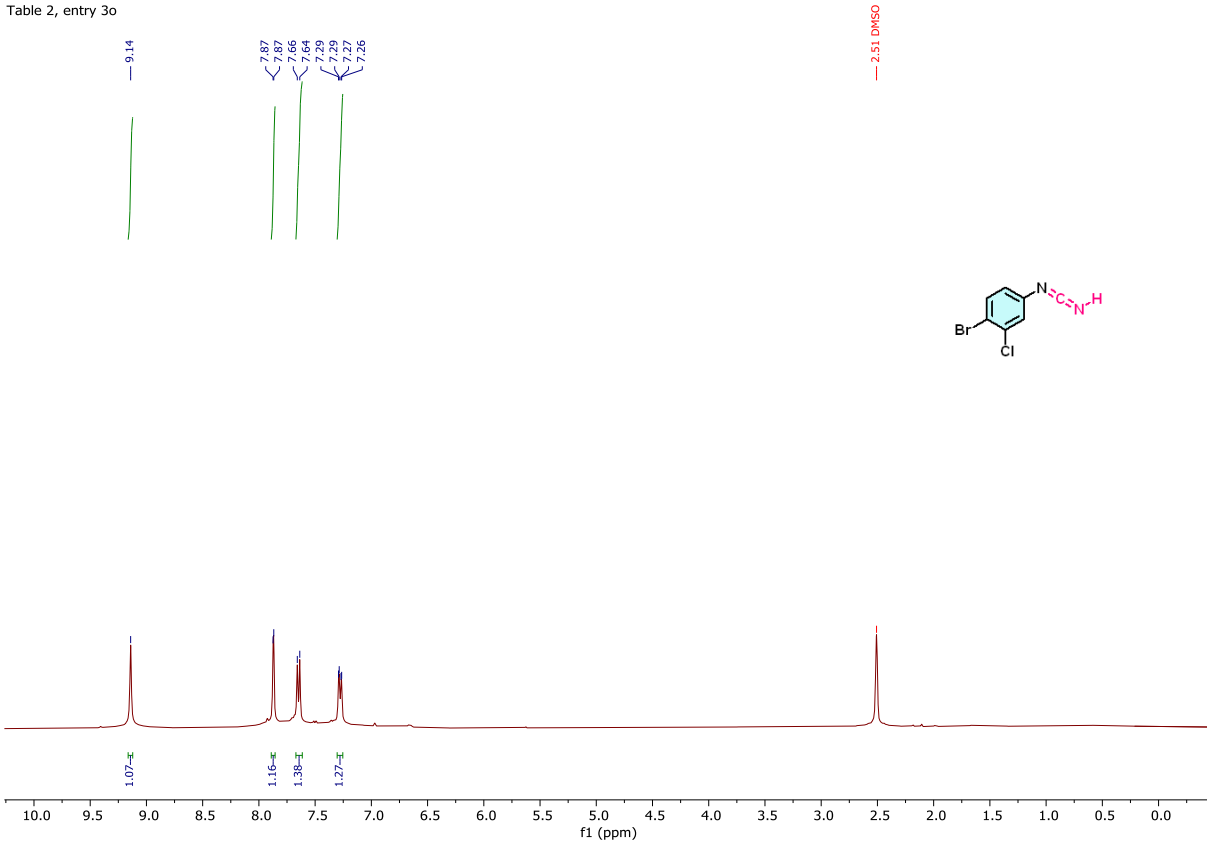

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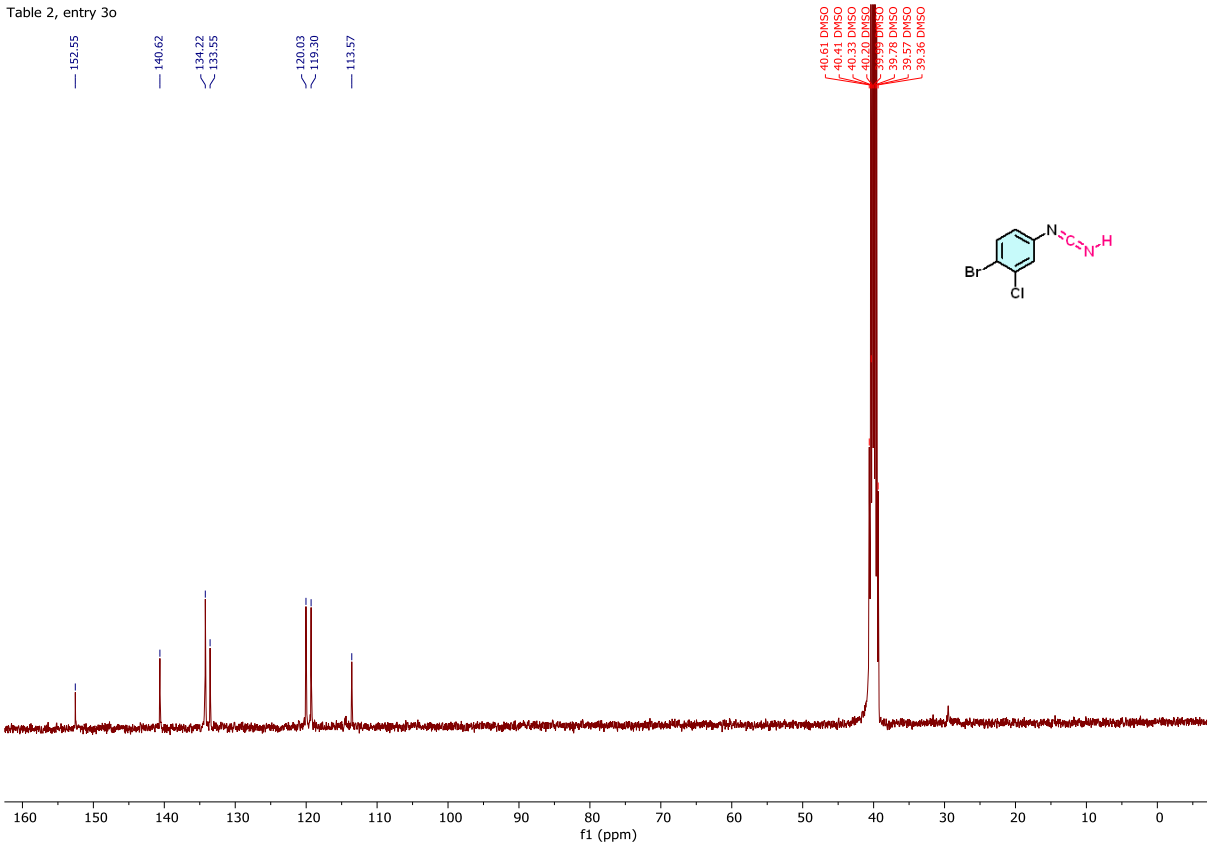
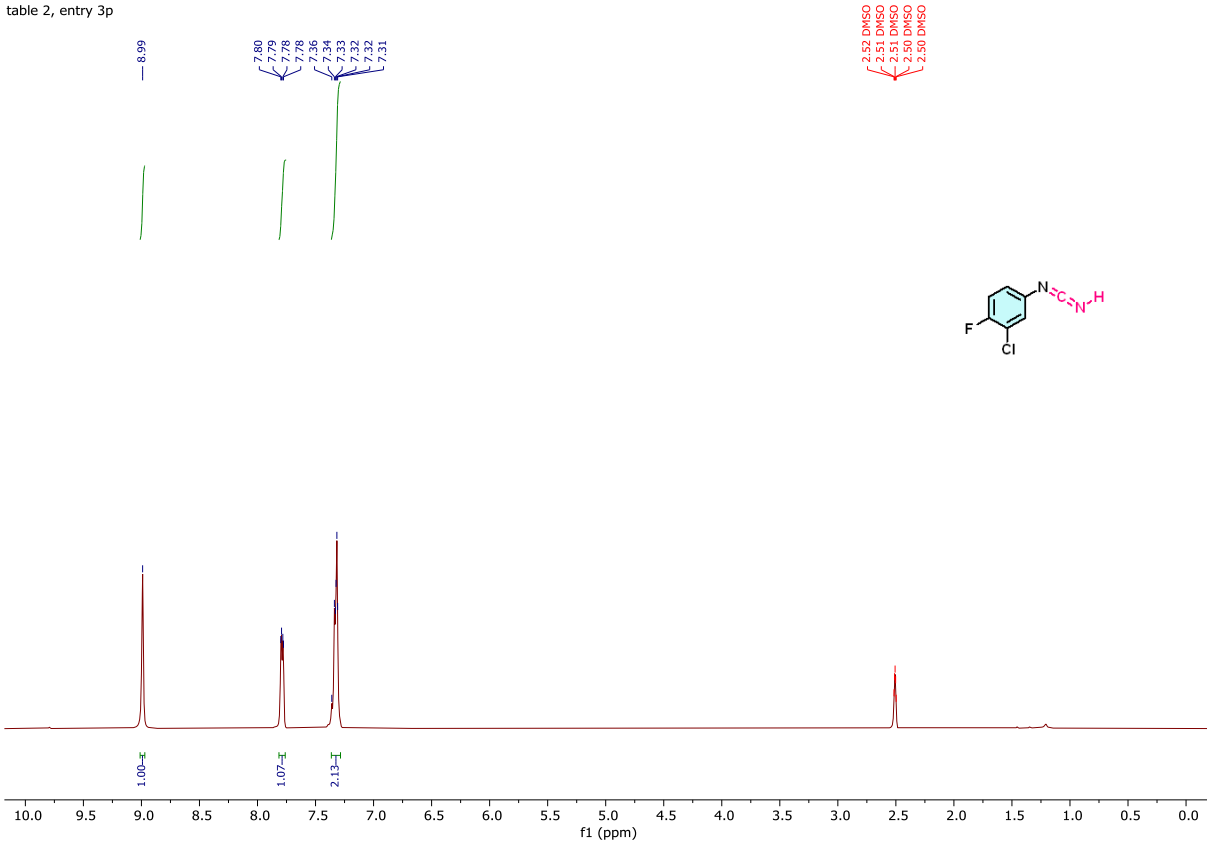


table 2, entry 3p



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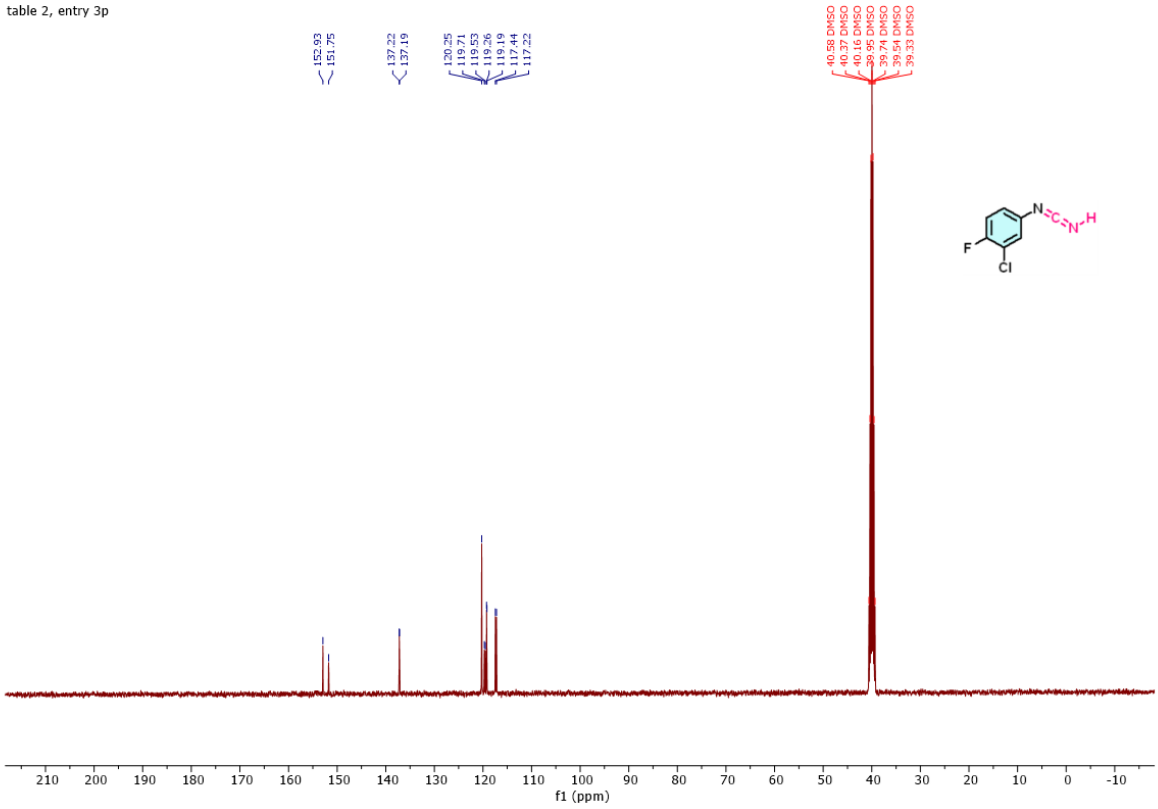

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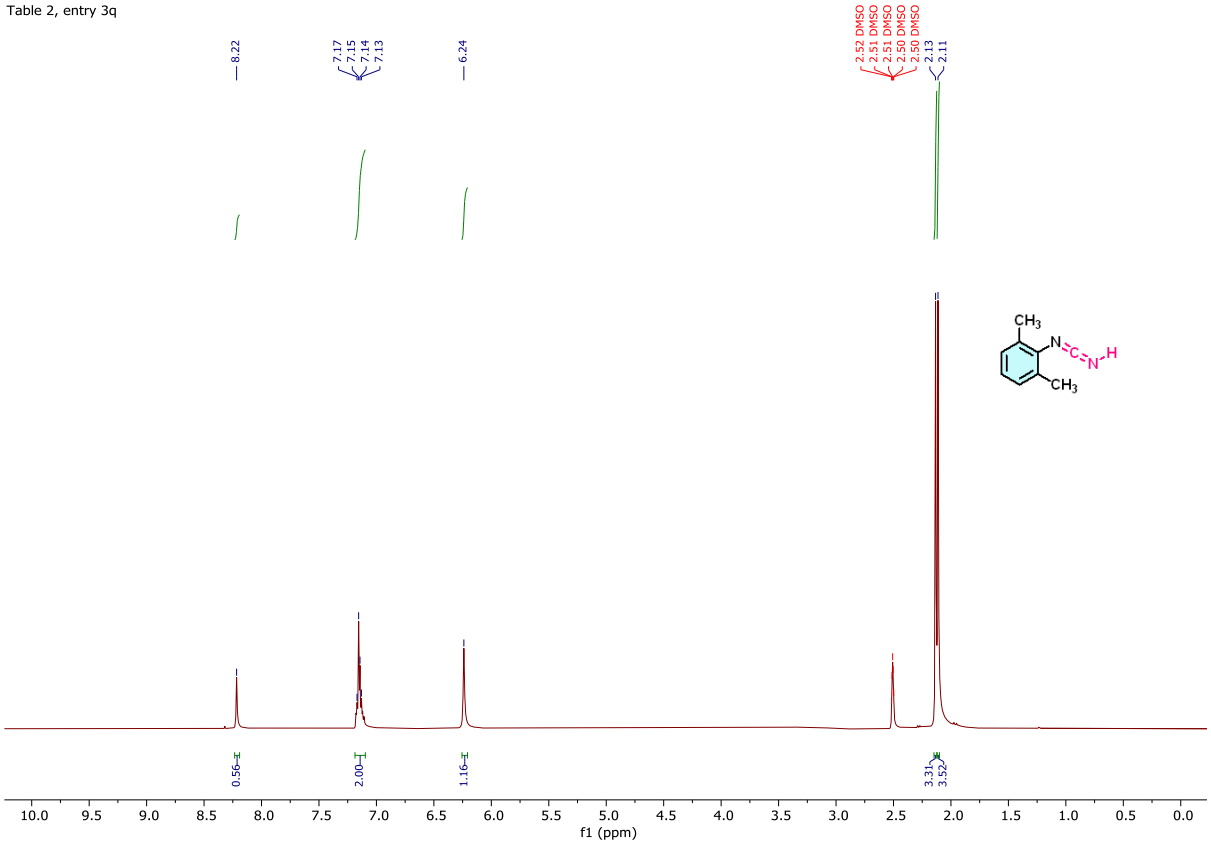
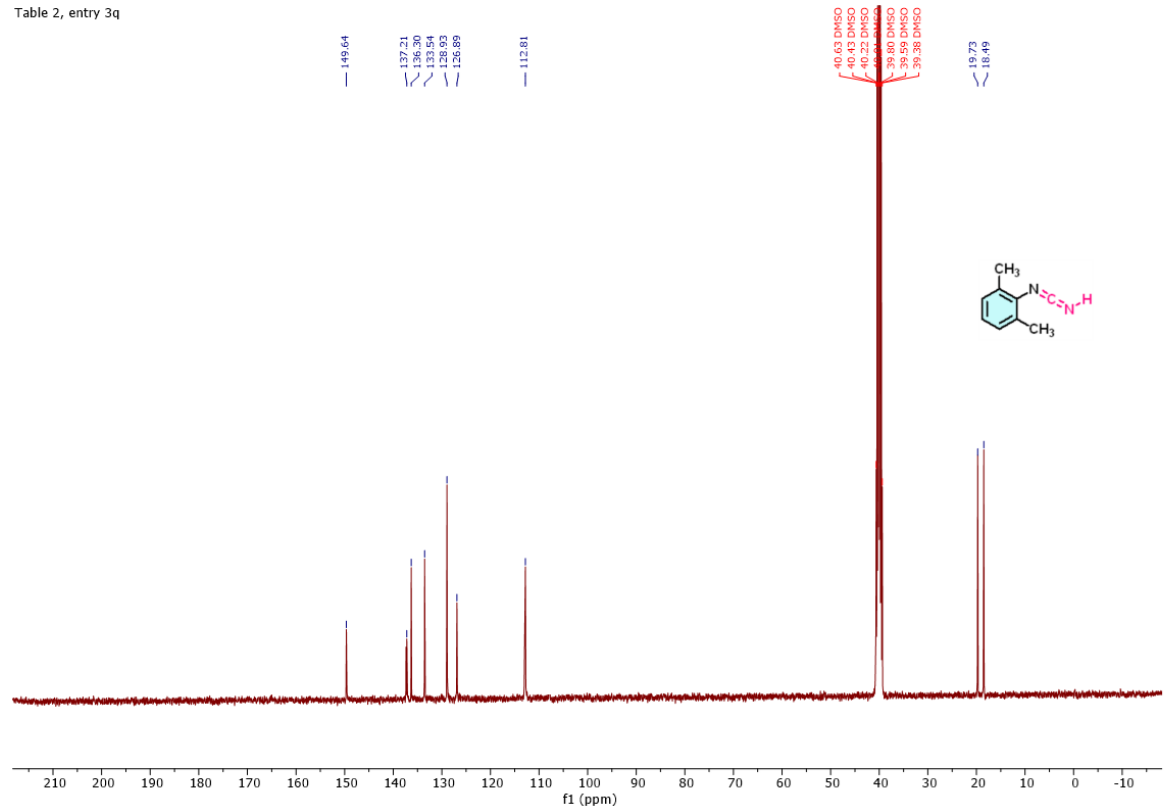


Table 2, entry 3q



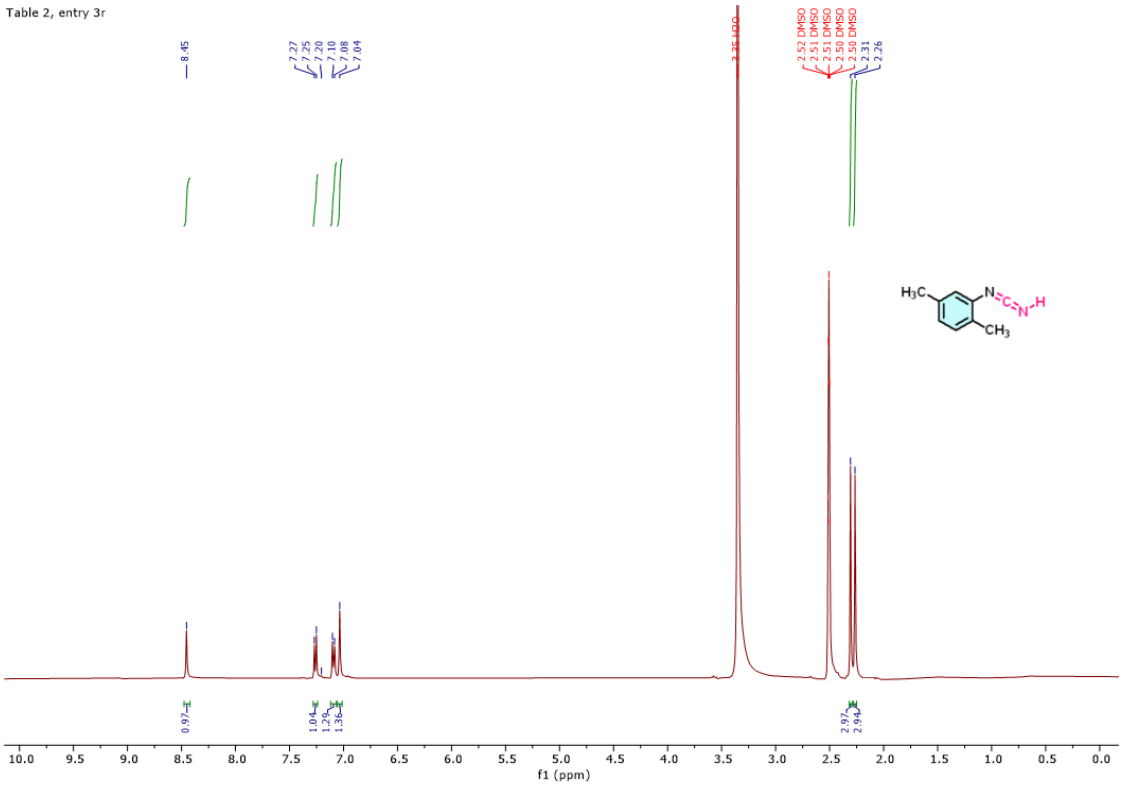


Table 2, entry 3r
8.45
7.27
7.25
7.20
7.10
7.08
7.04
2.35 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.31
2.26
0.97
1.04
1.29
1.36
2.97
2.94
f1 (ppm)

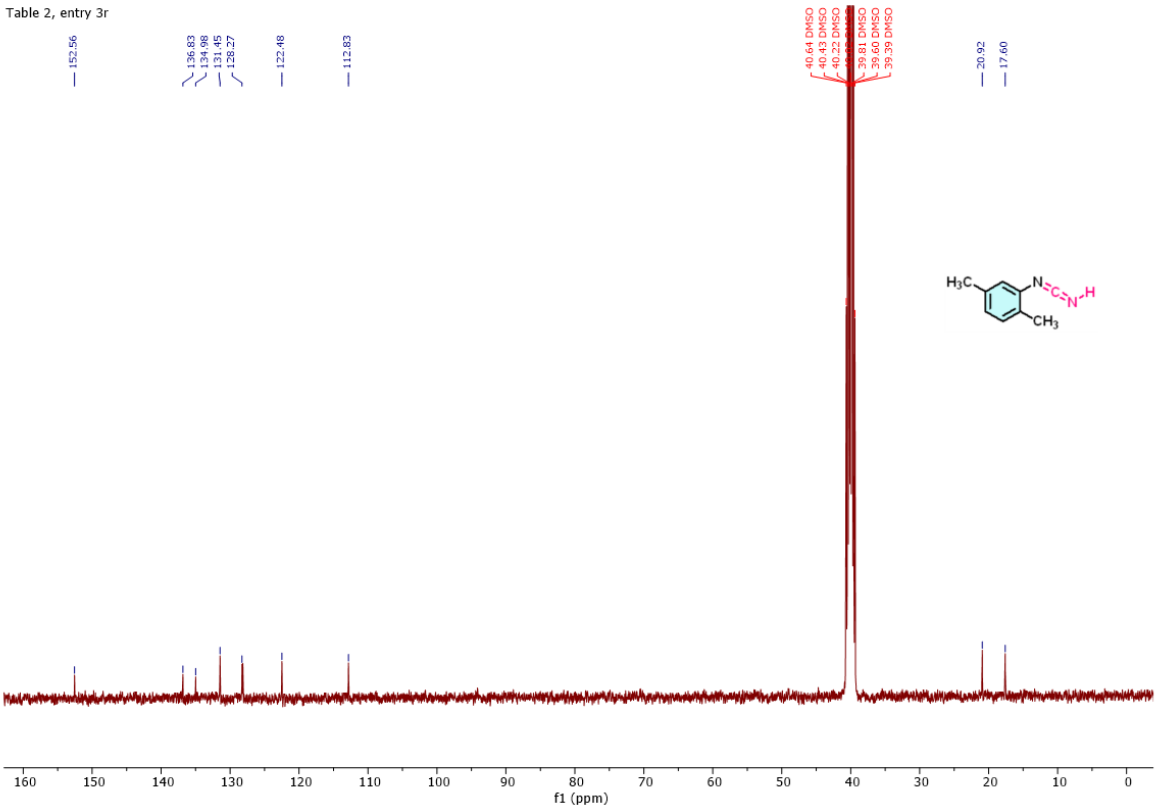
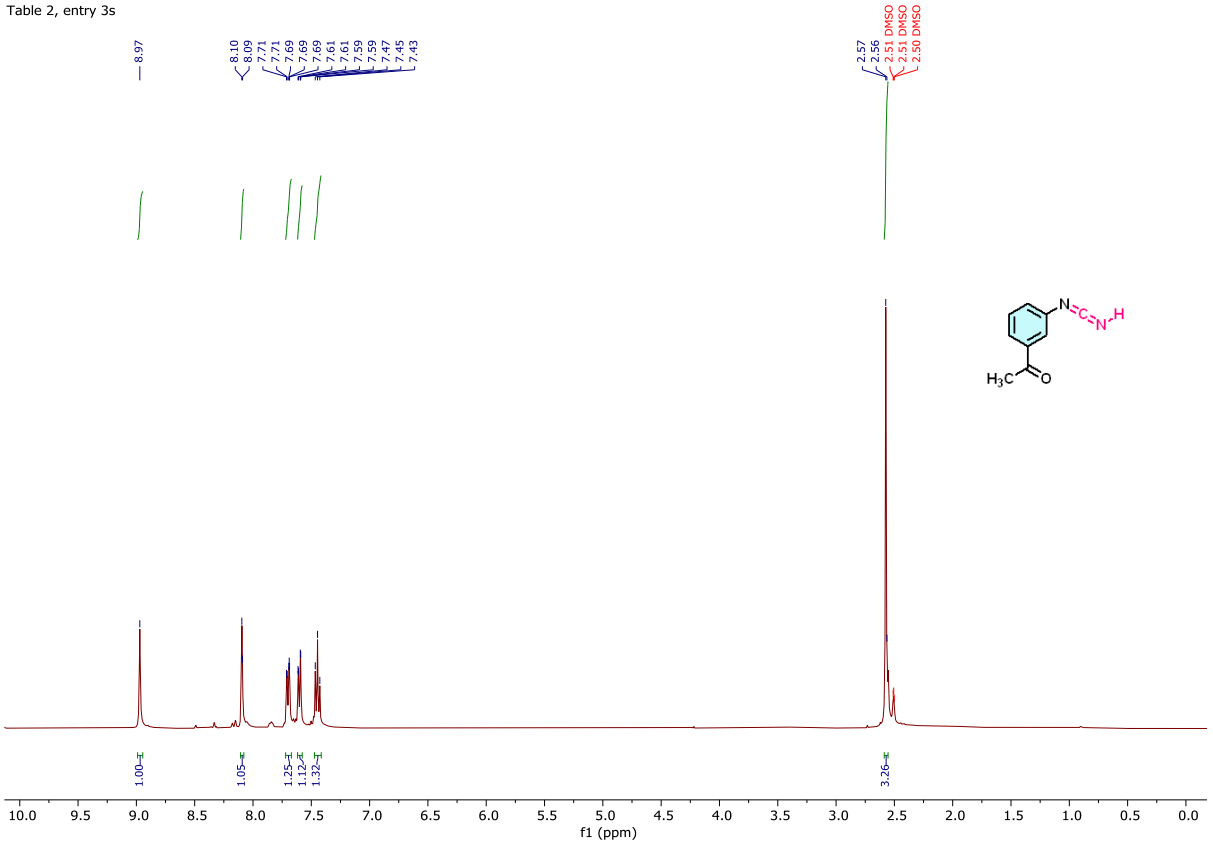


Table 2, entry 3r
152.56
136.83
134.98
131.45
128.27
122.48
112.83
40.64 DMSO
40.43 DMSO
40.22 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO
20.92
17.60
f1 (ppm)

Table 2, entry 3s



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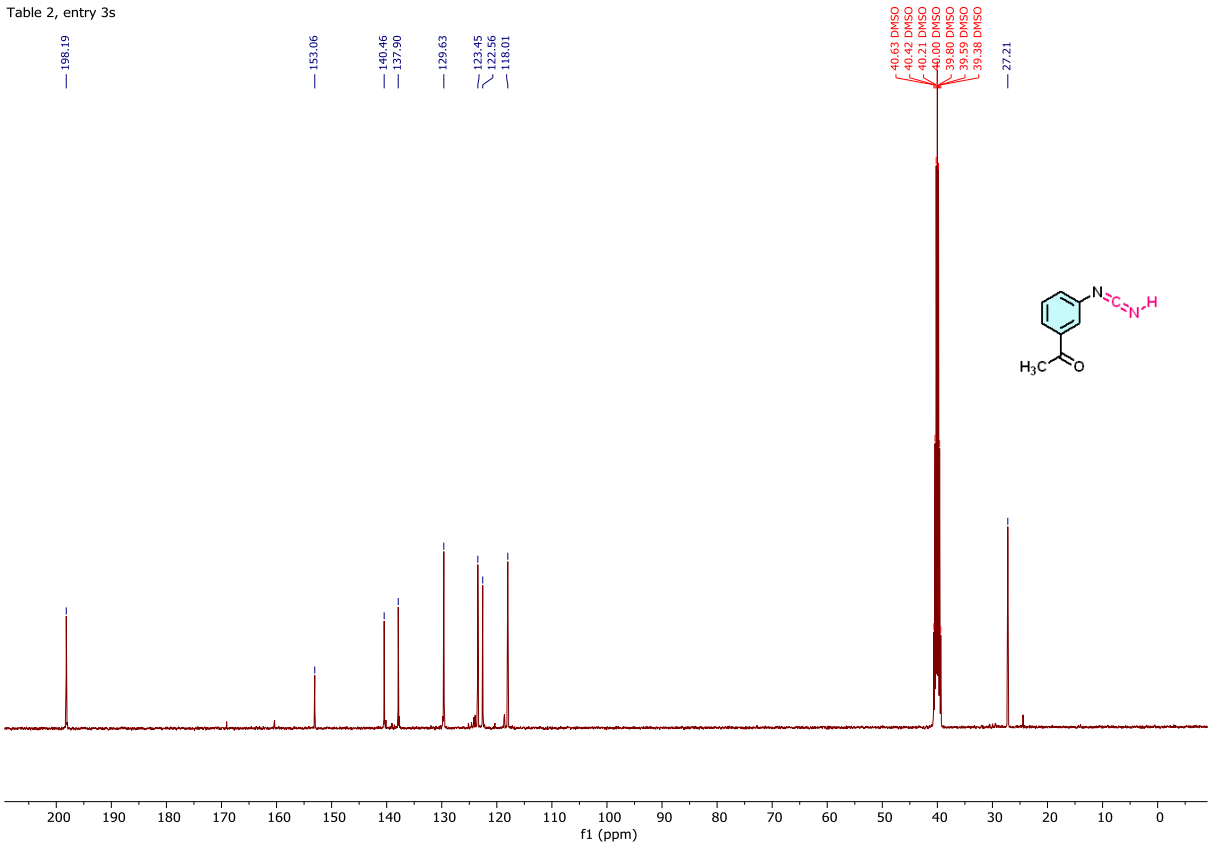

Table 2, entry 3t

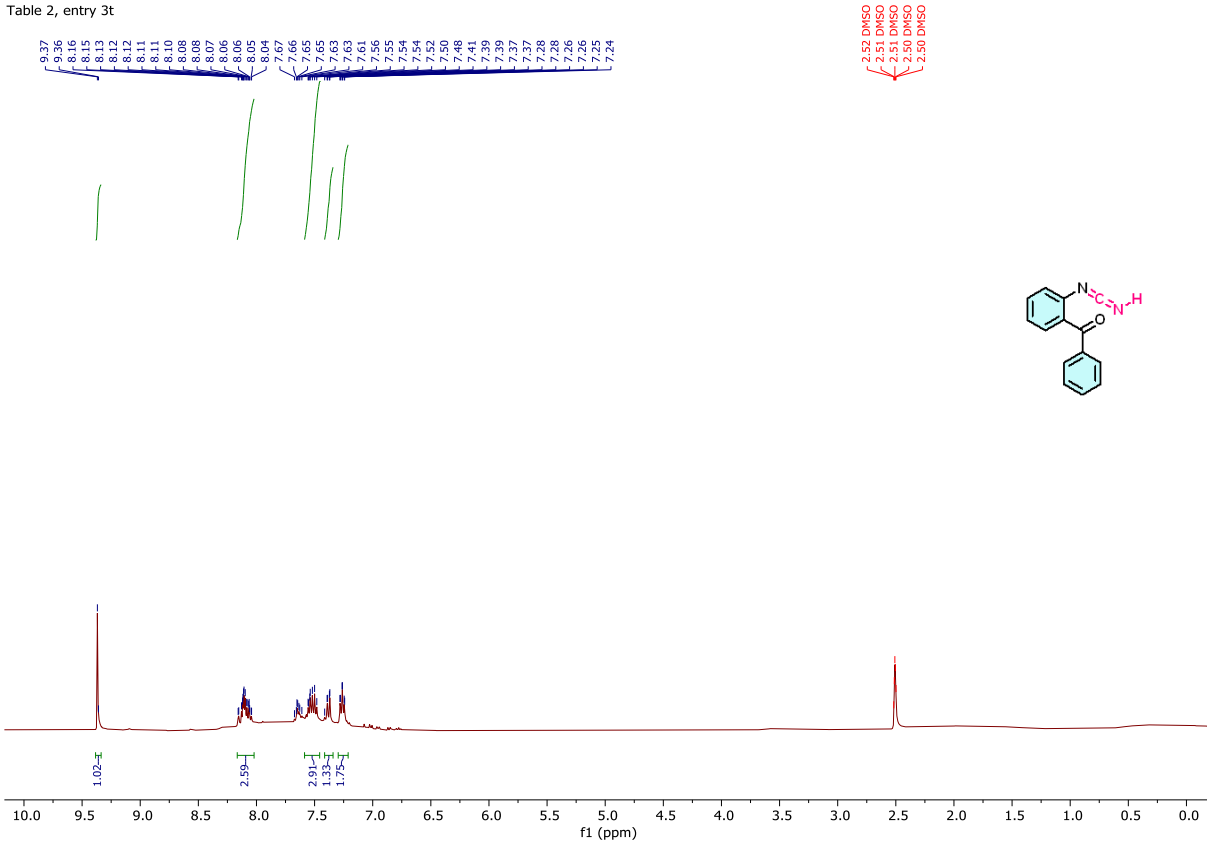

Table 2, entry 3t

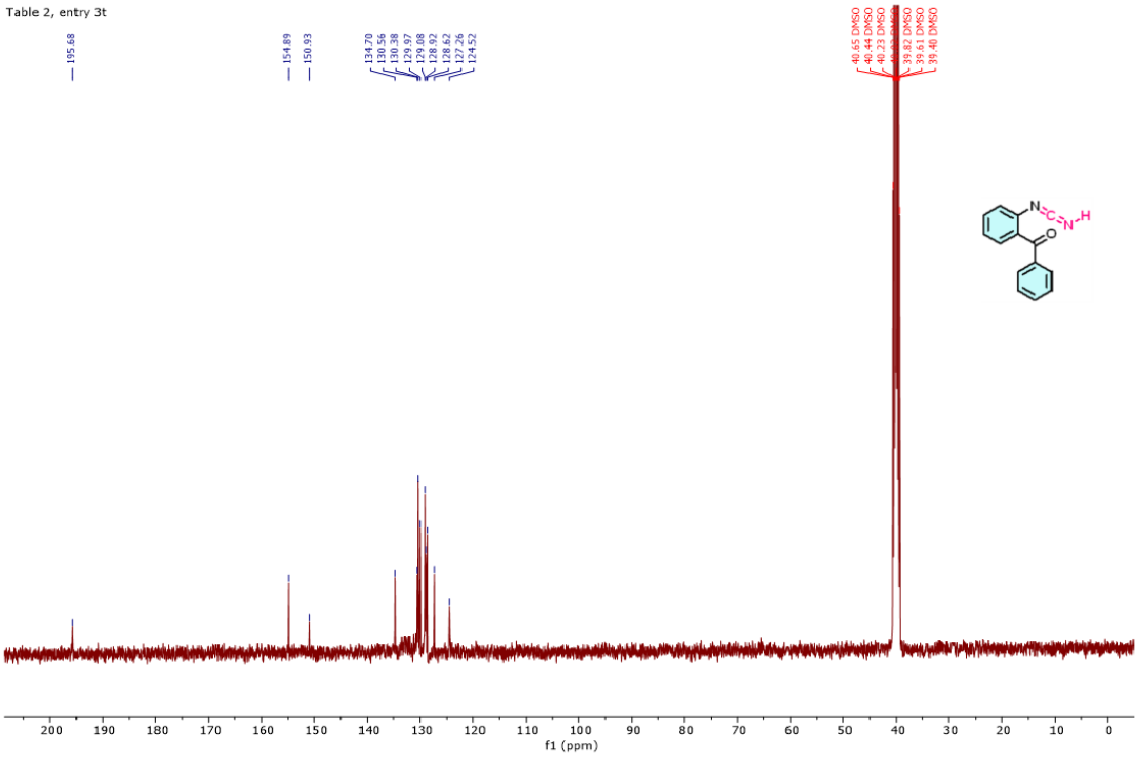

Table 2, entry 3u

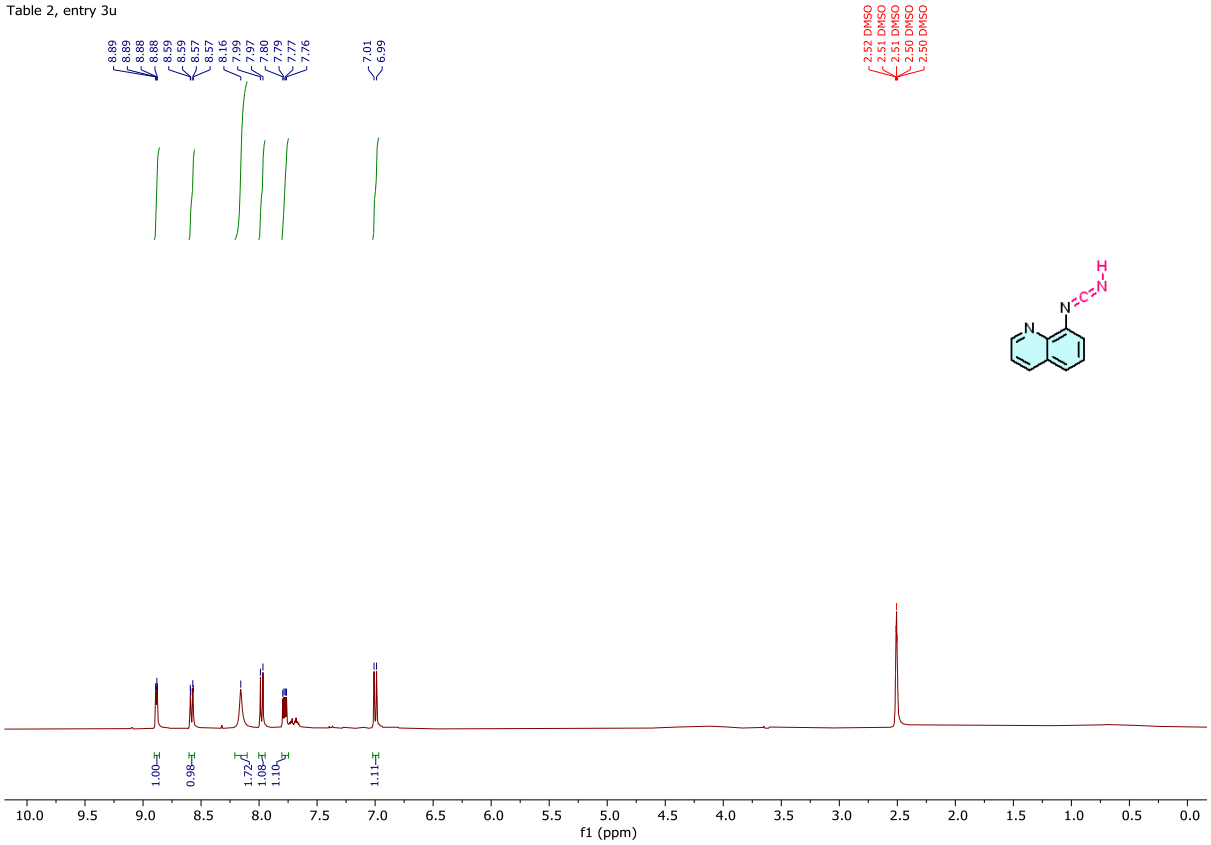

Table 2, entry 3u