Supporting Information

Copper catalysis: Ligand-controlled selective *N*-methylation or *N*-formylation of amines with CO_2 and phenylsilane

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1. General Experimental Section

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, and the results were consistent with those reported in the literature. NMR spectra were determined on Bruker 400 in $CDCl_3$ or C_6D_6. ^{1}H NMR spectra was recorded on 400 MHz spectrometers using $CDCl_3$ as solvent referenced to tetramethylsilane (TMS, 0 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^{1}H NMR peaks were labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, were reported in Hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m × 0.25 μm) using a flame ionization detector.

Unless otherwise noted, carbon dioxide (99.999%), commercially available Cu salts, ligands all secondary amines were obtained from Aladdin, Alfa Aesar and Heowns and used as received. Hydrosilanes were abtained from Energy. All operations were carried out by using standard high vacuum and Schlenk technique unless otherwise noted.

2. General experimental Procedure

General procedure for reductive functionalization of CO_2 with amines to formylamines

Under inert atmosphere (Ar/N_2), a 10 mL Schlenk flask was charged successively with $Cu_2(OH)_2CO_3$ (3.3 mg, 3 mol%), Ph_2CyP (15.6 mg, 12 mol%), *N*-methylaniline (54 µL, 0.5 mmol), CH_3CN (2 mL) and phenylsilane (0.2 mL, 1.5 mmol). The reaction mixture was stirred at 60 ^{o}C for the desired time under an atmosphere of CO_2 (99.999%). After the reaction, 1,3,5-trimethyoxybenzene (40.0 mg) was added as an internal standard and then a sample was taken for GC or ^{1}H NMR analysis to determine the conversion and yield. To identify the structure of the formylated product, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether-EtOAc) to afford the corresponding formamide.

General procedure for reductive functionalization of CO_2 with amines to methylamines

Under inert atmosphere (Ar/N_2), a 10 mL Schlenk flask was charged successively with $Cu_2(OH)_2CO_3$ (3.3 mg, 3 mol%), DPPB (12.8 mg, 6 mol%), *N*-methylaniline (54 µL, 0.5 mmol), CH_3CN (2 mL) and phenylsilane (0.2 mL, 1.5 mmol). The reaction mixture was stirred at 60 ^{o}C for the desired time under an atmosphere of CO_2 (99.999%). After the reaction, 1,3,5-trimethyoxybenzene (40.0 mg) was added as an internal standard and then a sample was taken for GC or ^{1}H NMR analysis to determine the conversion and yield. To identify the structure of the methylated product, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether-EtOAc) to afford the corresponding methylamine.

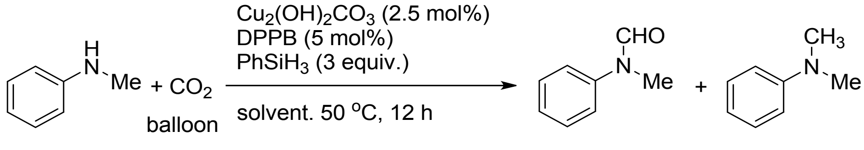
General procedure for preparing $[Cu(DPPB)_2]_2CO_3$ and $[Cu(Ph_2CyP)_2]_2CO_3$

$[Cu(DPPB)_2]_2CO_3$: 1.71 g (4 mmol) DPPB was dissolved in 150 mL H_2O–iso-propanol (5:7) and then 0.22 g (1 mmol) $Cu_2(OH)_2CO_3$ was added. The mixture was heated and stirred at the temperature of 70 °C for 24 hrs. After that, the resulting turquoise green precipitate was collected on a filter, washed with Et_2O and dried in vacuo. ESI-MS (m/z): $[CuC_{56}H_{56}P_4]_2^{2+}$ 915.26 (calculated), 915.34 (found).

$[Cu(Ph_2CyP)_2]_2CO_3$: 1.07 g (4 mmol) Ph_2CyP was dissolved in 150 mL H_2O–iso-propanol (5:7) and then 0.22 g (1 mmol) $Cu_2(OH)_2CO_3$ was added. The mixture was heated and stirred at the temperature of 70 °C for 24 hrs. Then the resulting turquoise green precipitate was collected on a filter, washed with Et_2O and dried in vacuo. ESI-MS (m/z): $[CuC_{36}H_{42}P_2]_2^{2+}$ 600.21 (calculated), 600.15 (found).

3. Screening Results

Table S1. Optimization of the solvent[a]

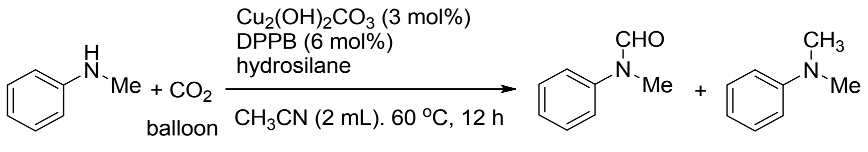


1a **2a** **3a**

Entry	Solvent/mL	Conv[b]/%	Yield[b]/%	
			2a	**3a**
1	CH_3CN (2)	90	11	77
2	PhMe (2)	87	27	14
3	*n*Bu_2O (2)	90	26	27
4	CH_3CN (1)	89	11	35
5	CH_3CN (3)	99	61	29

[a] Reaction condition: **1a** (54 μL, 0.5 mmol), $Cu_2(OH)_2CO_3$ (2.7 mg, 2.5 mol%), DPPB (10.5 mg, 5 mol%), $PhSiH_3$ (0.2 mL, 3 equiv.), CO_2 balloon, 50 °C for 12 h. [b] Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard.

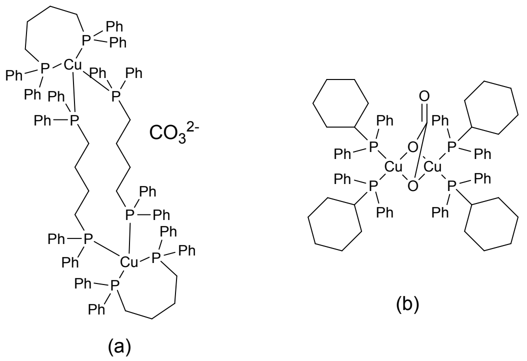
Table S2. Optimization of the hydrosilane[a]



Entry	Silane /eq	Conv[b]/%	Yield[b]/%	
			2a	**3a**
1	$PhSiH_3$(3)	99	6	93
2	Ph_2SiH_2(4.5)	90	18	72
3	PMHS(9)	<1	trace	trace
4	EtO_3SiH(9)	<1	trace	trace
5	$PhSiH_3$(2)	86	14	54

[a] Reaction condition: **1a** (54 μL, 0.5 mmol), $Cu_2(OH)_2CO_3$ (3.3 mg, 3 mol%), DPPB (12.8 mg, 6 mol%), CH_3CN (2 mL), CO_2 balloon, 60 °C for 12 h. [b] Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard.

4. Proposed Structure Active Catalyst and the



Scheme S1. Proposed structure for (a) $[Cu(DPPB)_2]_2CO_3$ and (b) $[Cu(Ph_2CyP)_2]_2CO_3$.

5. Verification of the interaction between allyl-group and copper

The interaction between Cu and C=C is also identified by DFT calculation. As shown in this figure, for *N*-allyl formanilide, both of the C=O in formyl group and C=C can coordinate to Cu, but methyl group in *N*-ethylformanilide cannot coordinate to Cu.

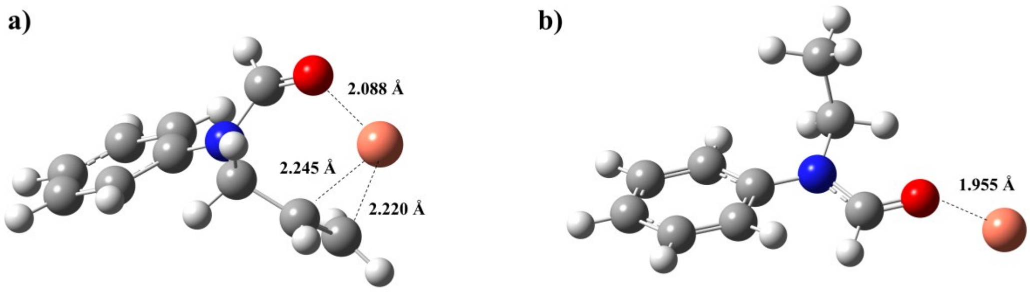
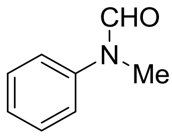


Figure S1. Interaction between copper and different substrates (Copper: orange; Oxygen: red; Nitrogen: blue; Carbon: gray; a: interaction between Cu and *N*-allyl formanilide; b: interaction between Cu and *N*-ethylformanilide)

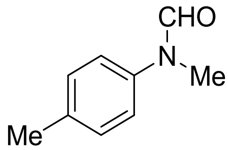
6. Characterization Data for the Products

_N_-Methylformanilide (2a)[1]



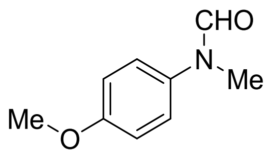
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 3.33 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.21, 142.03, 129.49, 126.26, 122.21, 31.90 ppm. GC-MS (EI, 70 eV) m/z (%) 135.15 (70.68), 106.10 (100.00), 94.10 (30.45), 79.10 (20.54), 77.10 (42.48), 66.05 (21.05).

_N_,4'-Dimethylformanilide (2b)[2]



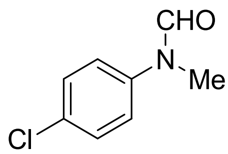
Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 3.30 (s, 3H), 2.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.34, 139.62, 136.33, 130.10, 122.50, 32.18, 20.82 ppm. GC-MS (EI, 70 eV) m/z (%) 149.20 (76.70), 120.15 (100.00), 108.10 (42.15), 91.10 (33.92), 65.10 (21.58).

_N_-Methyl-4-methoxylformanilde (2c)[2]



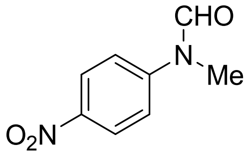
Brown oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.10 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H), 3.27 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.28, 158.11, 135.06, 124.47, 114.58, 55.38, 32.50 ppm. GC-MS (EI, 70 eV) m/z (%) 165.15 (100.00), 124.15 (62.20), 122.15 (95.98), 94.10 (33.80), 65.10 (21.69).

_N_-(4-Chlorophenyl)-_N_-methylformamide (2d)[2]



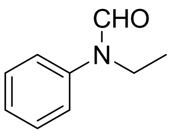
Yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.39 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 3.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.94, 140.68, 131.97, 129.71, 123.46, 32.01 ppm. GC-MS (EI, 70 eV) m/z (%) 169.10 (54.97), 142.10 (31.49), 140.10 (100.00), 128.10 (44.0), 77.10 (26.63).

***N*-(4-Nirophenyl)-*N*-methylformamide (2e)**



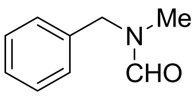
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.31 (d, J = 9.1 Hz, 2H), 7.34~7.32 (m, 2H), 3.40 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.45 , 147.49 , 145.03 , 125.42 , 120.40 , 31.40 ppm. GC-MS (EI, 70 eV) m/z (%) 180.10 (55.01), 151.10 (100.00).

***N*-Ethyl-*N*-phenyl-formamide (2f)[2]**



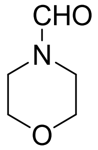
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 3.86 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.13, 140.89, 129.71, 126.94, 124.34, 40.17, 13.14 ppm. GC-MS (EI, 70 eV) m/z (%) 150.06 (22.86), 149.04 (76.16), 121.06 (97.60), 120.18 (19.42), 107.13 (10.49), 106.18 (100.00).

N-Benzyl-N-methylformamide (2h)[3]



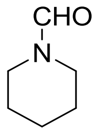
Purple oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 0.57H), 8.07 (s, 0.43H), 7.30~7.11 (m, 5H), 4.44 (s, 0.86H), 4.30 (s, 1.14H,), 2.76 (s, 1.26H), 2.69 (s, 1.74H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.78, 162.61, 136.06, 135.80, 128.93, 128.72, 128.27, 128.12, 127.67, 127.43, 53.50, 47.77, 29.74, 29.47 ppm. GC-MS (EI, 70 eV) m/z (%) 149.10 (100.00), 134.15 (17.80), 106.10 (29.35), 91.10 (57.23), 79.10 (28.00).

4-Morpholine carbaldehydede (2i)[2]



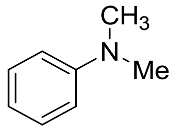
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 3.75 – 3.63 (m, 4H), 3.62 – 3.53 (m, 2H), 3.49 – 3.31 (m, 2H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 67.18, 66.39, 45.75, 40.55 ppm. GC-MS (EI, 70 eV) m/z (%) 115.15 (100.00), 100.10 (77.82), 86.10 (51.09), 85.10 (22.02).

Piperidine-1-carbaldehyde (2j)[3]



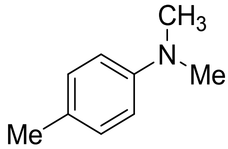
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.55 – 3.43 (m, 2H), 3.38 – 3.28 (m, 2H), 1.70 (p, J = 5.7 Hz, 2H), 1.63 – 1.50 (m, 4H) ppm. 13C NMR (101 MHz, CDCl3) δ 160.43 , 46.36, 40.10 , 26.00 , 24.53 , 24.08 ppm. GC-MS (EI, 70 eV) m/z (%) 113.15 (100.00), 112.15 (30.57), 98.10 (36.95), 84.15 (50.88), 70.10 (20.83).

***N,N*-Dimethylaniline (3a)[1]**



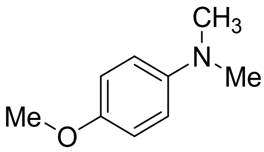
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 8.8, 7.3 Hz, 2H), 6.85 – 6.62 (m, 3H), 2.94 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.58, 129.03, 116.60, 112.62, 40.61 ppm. GC-MS (EI, 70 eV) m/z (%) 121.15 (81.29), 120.15 (100.00), 77.05 (29.56).

***N,N*-Dimethyl-*p*-toluidine (3b)[1]**



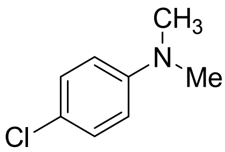
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 8.2 Hz, 2H), 2.89 (s, 6H), 2.25 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.77, 129.54, 126.09, 113.19, 41.05, 20.22 ppm. GC-MS (EI, 70 eV) m/z (%) 35.20 (77.14), 134.15 (100.00), 91.10 (22.96).

4-Methoxy-*N,N*-dimethylaniline (3c)[1]



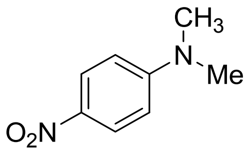
White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.88 – 6.81 (m, 2H), 6.79 – 6.72 (m, 2H), 3.76 (s, 3H), 2.86 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.12, 145.52, 115.04, 114.60, 55.72, 41.92 ppm. GC-MS (EI, 70 eV) m/z (%) 151.25 (59.49), 136.20 (100.00).

4-Chloro-N,N-dimethylaniline (3d)[1]



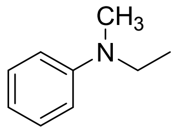
Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 2.92 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.10, 128.75, 121.36, 113.59, 40.64 ppm. GC-MS (EI, 70 eV) m/z (%) 157.10 (25.27), 156.10 (39.00), 155.10 (82.99), 154.10 (100.00).

4-Nitro-*N,N*-dimethylaniline (3e)[4]



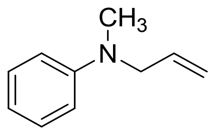
Yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 2.12 (s, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.13, 135.95, 125.11, 110.29, 40.32 ppm. GC-MS (EI, 70 eV) m/z (%) 166.25 (100), 136.25 (60.88), 119.20 (48.22), 105.20 (32.98), 104.20 (33.69), 79.15 (31.13), 77.10 (68.33).

***N*-Ethyl-*N*-methylaniline (3f)[1]**



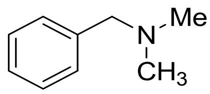
Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.7 Hz, 2H), 6.84 – 6.52 (m, 3H), 3.39 (q, J = 7.0 Hz, 2H), 2.89 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.05, 129.11, 115.97, 112.33, 46.75, 37.38, 11.13 ppm. GC-MS (EI, 70 eV) m/z (%) 135.15 (31.98), 120.15 (100.00), 77.05 (33.12).

***N*-Allyl-*N*-methylaniline (3g)[4]**



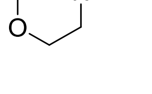
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 6.74 – 6.68 (m, 3H), 5.89 – 5.80 (m, 1H), 5.18 – 5.13 (m, 2H), 3.92 (d, J = 4.9 Hz, 2H), 2.93 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.43, 133.75, 129.07, 116.36, 116.12, 112.40, 55.23, 37.97 ppm. GC-MS (EI, 70 eV) m/z (%) 148.08 (70.11), 147.15 (100.00), 146.26 (25.67), 120.28 (34.38).

***N*,*N*-dimethyl-Benzenemethanamine (3h)[1]**



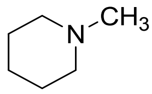
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 3.42 (s, 2H), 2.24 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.82, 129.10, 128.22, 127.03, 54.40, 45.35 ppm. GC-MS (EI, 70 eV) m/z (%) 135.25 (66.41), 134.25 (54.64), 91.15 (100), 65.10 (36.51).

4-Methylmorpholine (3i)[5]



Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 – 3.61 (m, 4H), 2.41 (s, 4H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.67, 55.20, 46.23 ppm. GC-MS (EI, 70 eV) m/z (%) 101.15 (100.00), 100.15 (36.36), 71.10 (60.10).

1-Methylpiperidine (3j)[6]

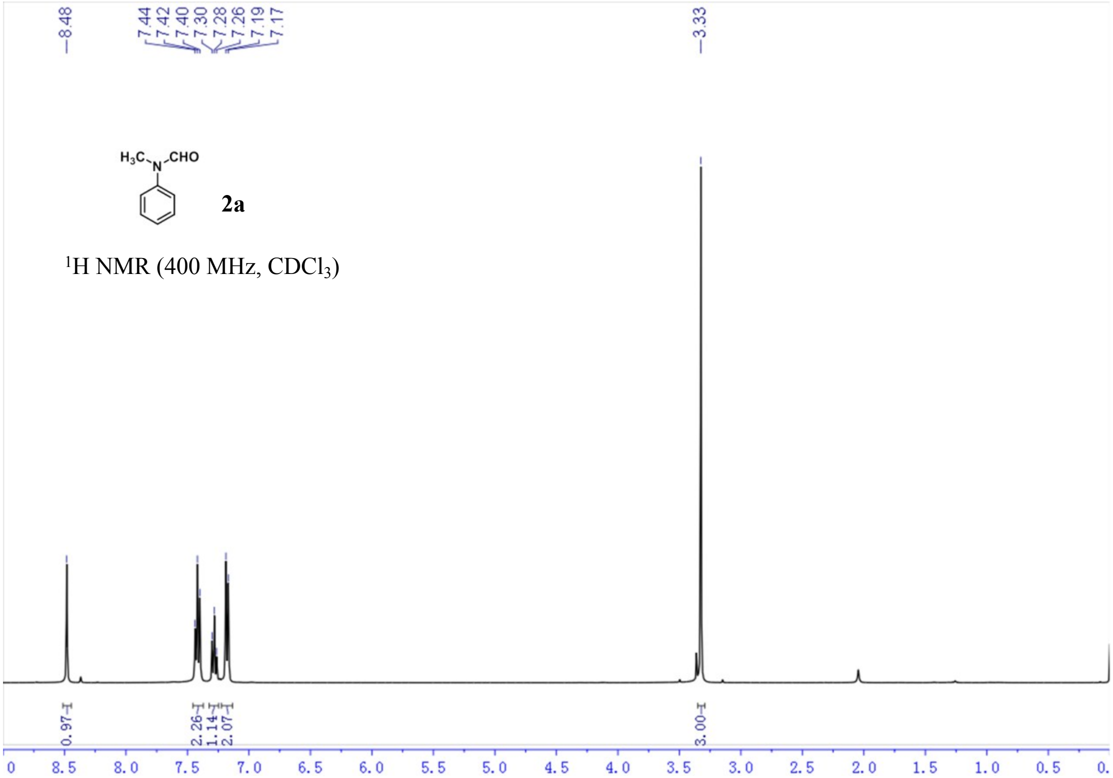


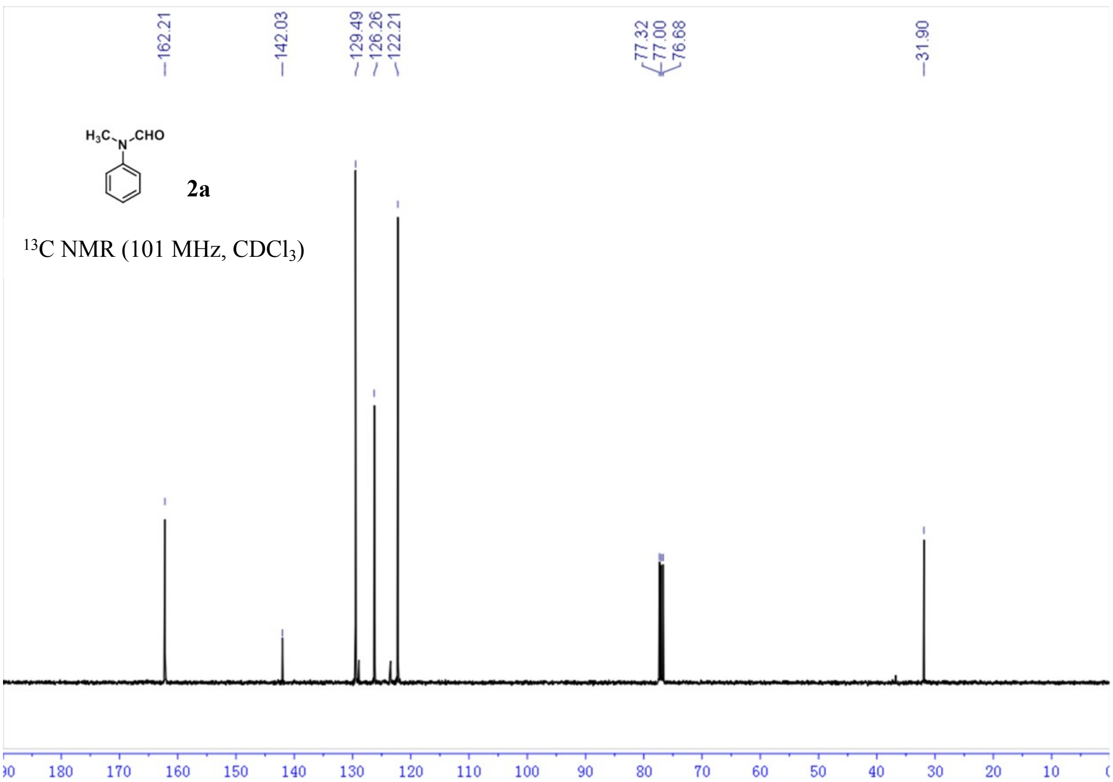
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 4H), 2.24 (s, 3H), 1.68 – 1.51 (m, 4H), 1.41 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.46, 46.86, 25.95, 23.70 ppm. GC-MS (EI, 70 eV) m/z (%) 99.15 (42.36), 98.15 (100.00), 71.10 (22.54).

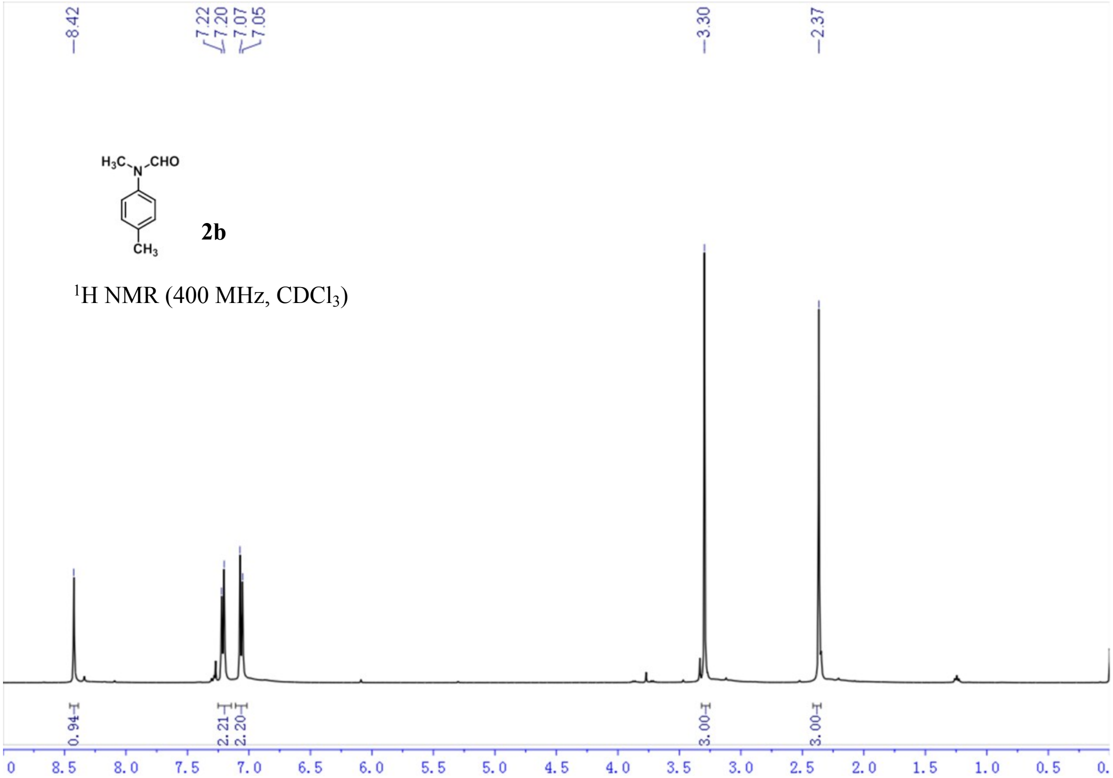
Reference:

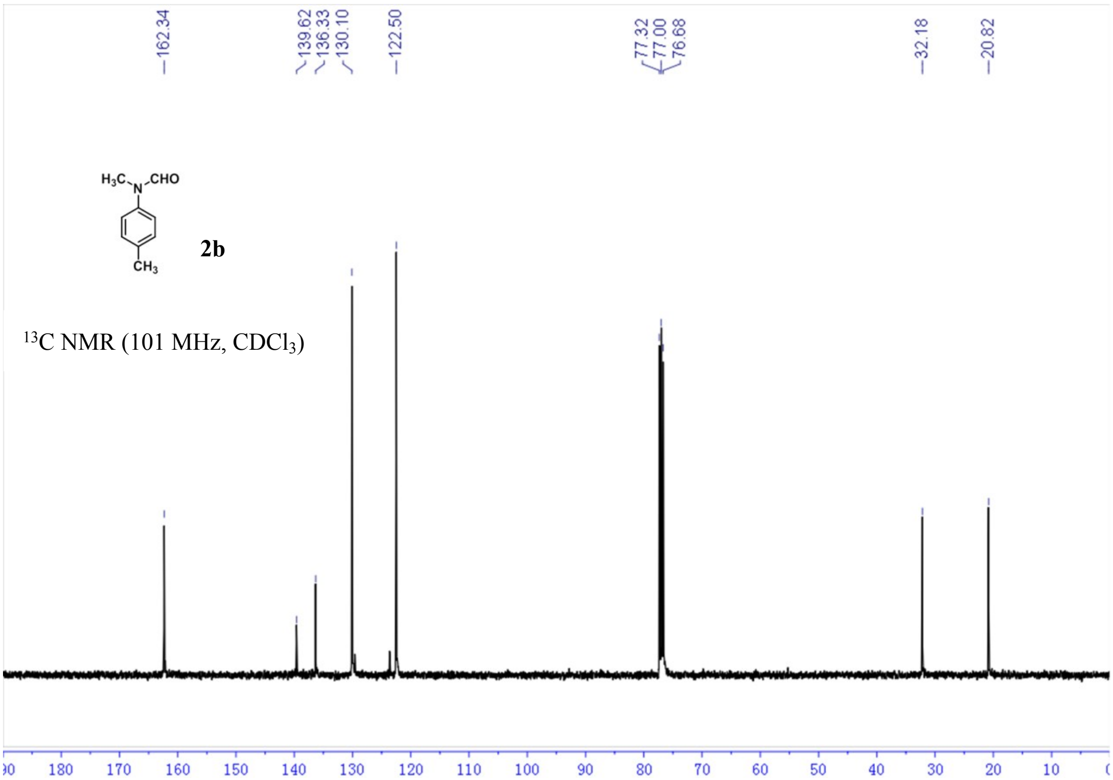
1. Z. Yang, B. Yu, H. Zhang, Y. Zhao, G. Ji, Z. Ma, X. Gao and Z. Liu, *Green Chem.*, 2015, **17**, 4189.
2. T. X. Zhao, G. W. Zhai, J. Liang, P. Li, X. B. Hu and Y. T. Wu, *Chem. Comm.*, 2017, **53**, 8046.
3. Z. Ke, Y. Zhang, X. Cui and F. Shi, *Green Chem.*, 2016, **18**, 808
4. H. Niu, L. Lu, R. Shi, C. W. Chiang, A. Lei, *Chem. Comm.*, 2017, **53**, 1148.
5. M. Y. Wang, N. Wang, X. F. Liu, C. Qiao, and L. N. He, *Green Chem.*, 2018, **20**, 1564.
6. C. Qiao, X. F. Liu, X. Liu, L. N. He, *Org. Lett.*, 2017, **19**, 1490.

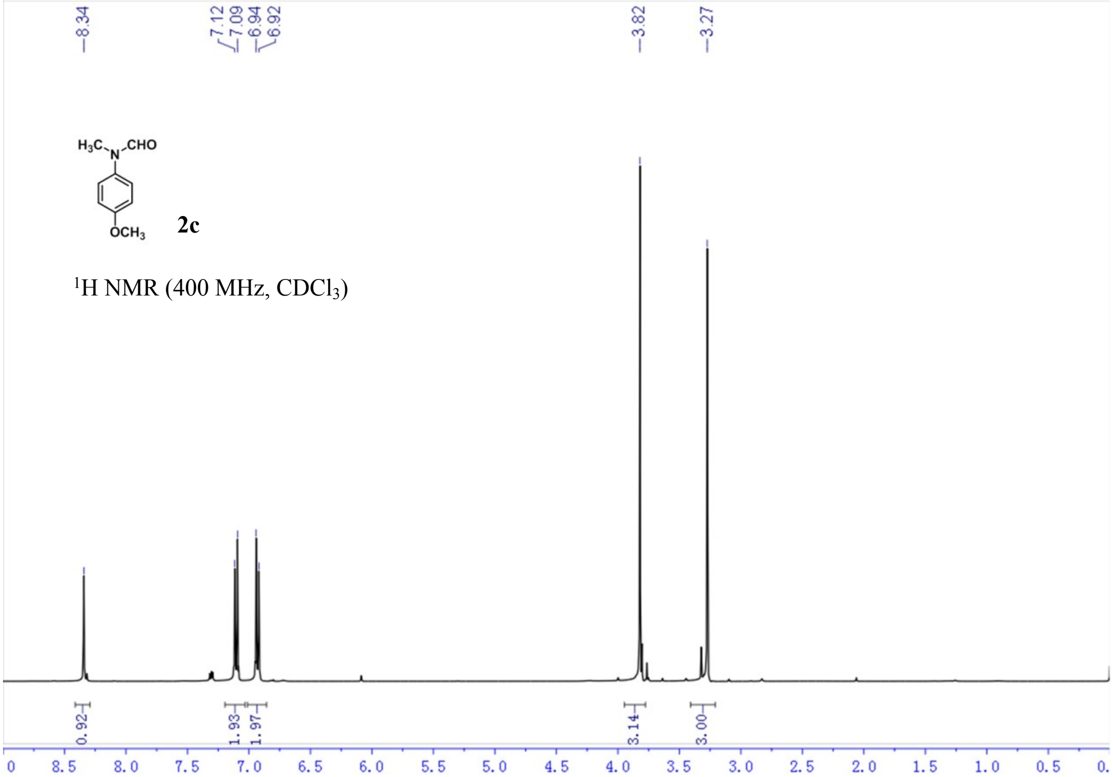
7. NMR Spectral Copies of the Products



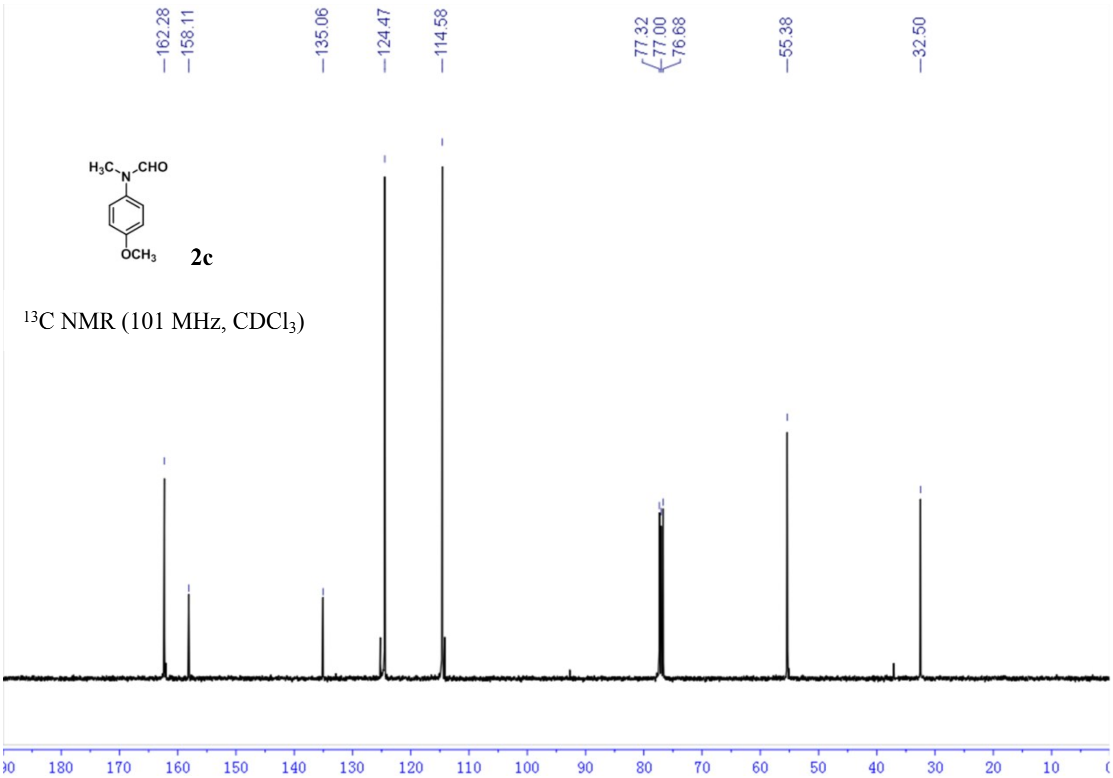



8.42
7.22
7.20
7.07
7.05
3.30
2.37
2b
^{1}H NMR (400 MHz, CDCl$_3$)
0.94
2.21
2.20
3.00
3.00

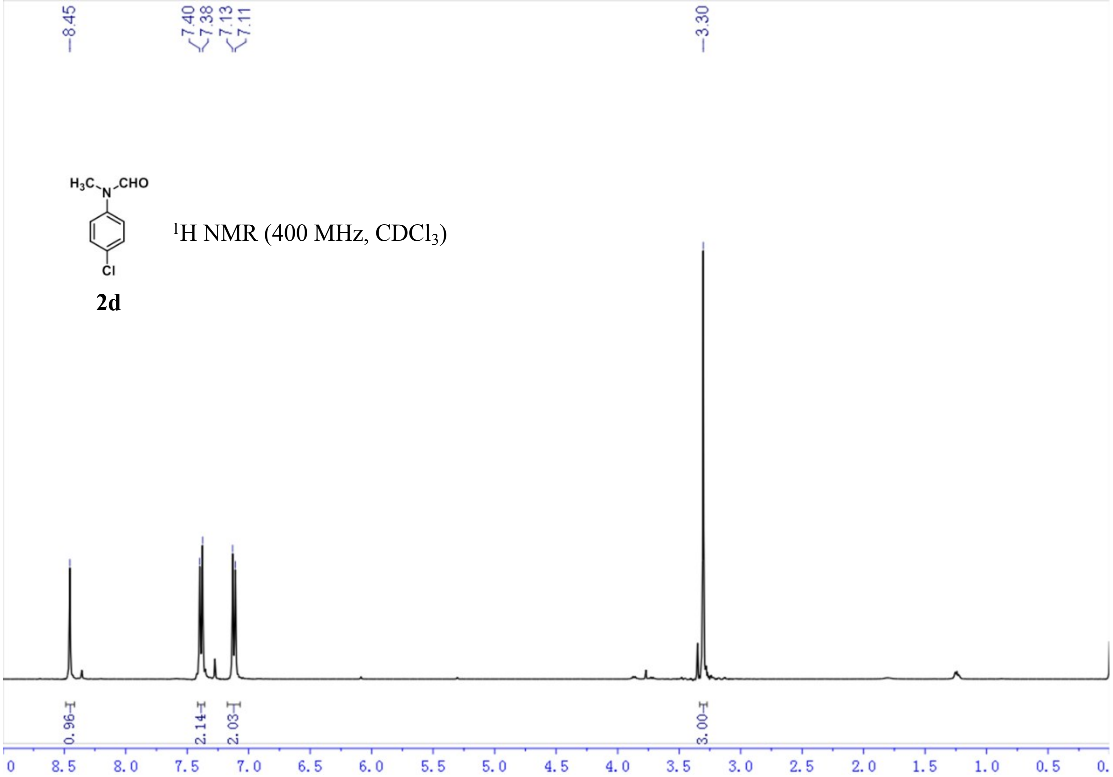

162.34
139.62
136.33
130.10
122.50
77.32
77.00
76.68
32.18
20.82
2b
^{13}C NMR (101 MHz, CDCl$_3$)

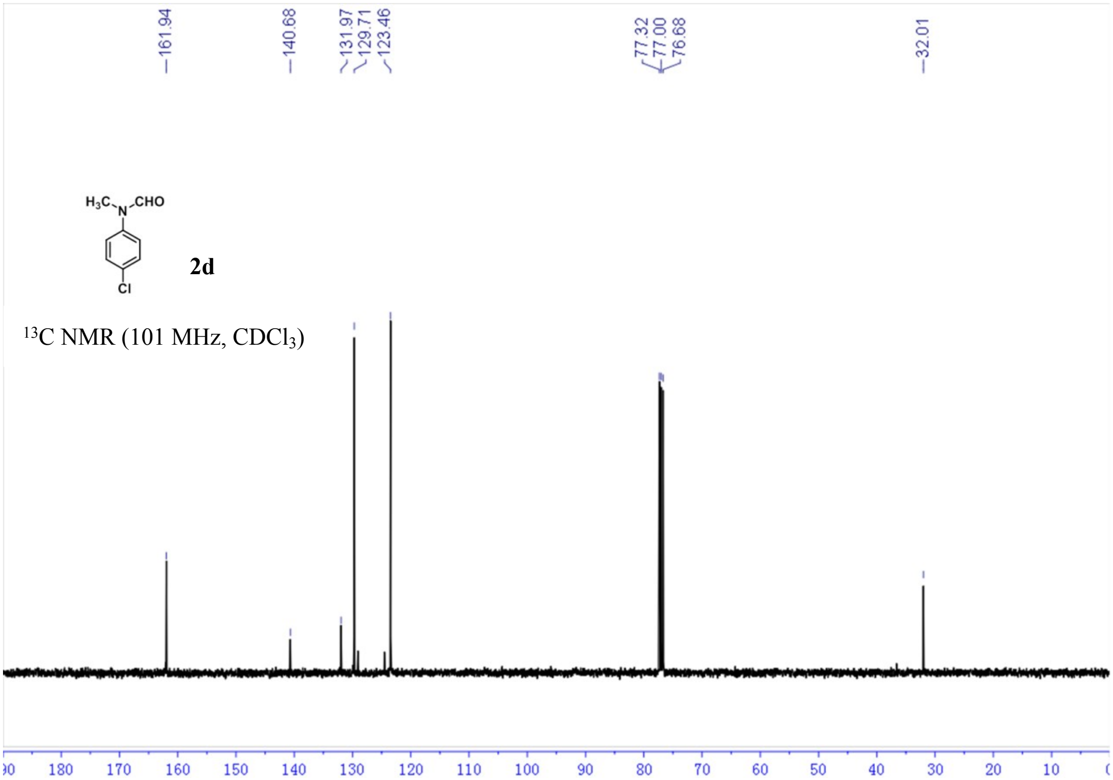


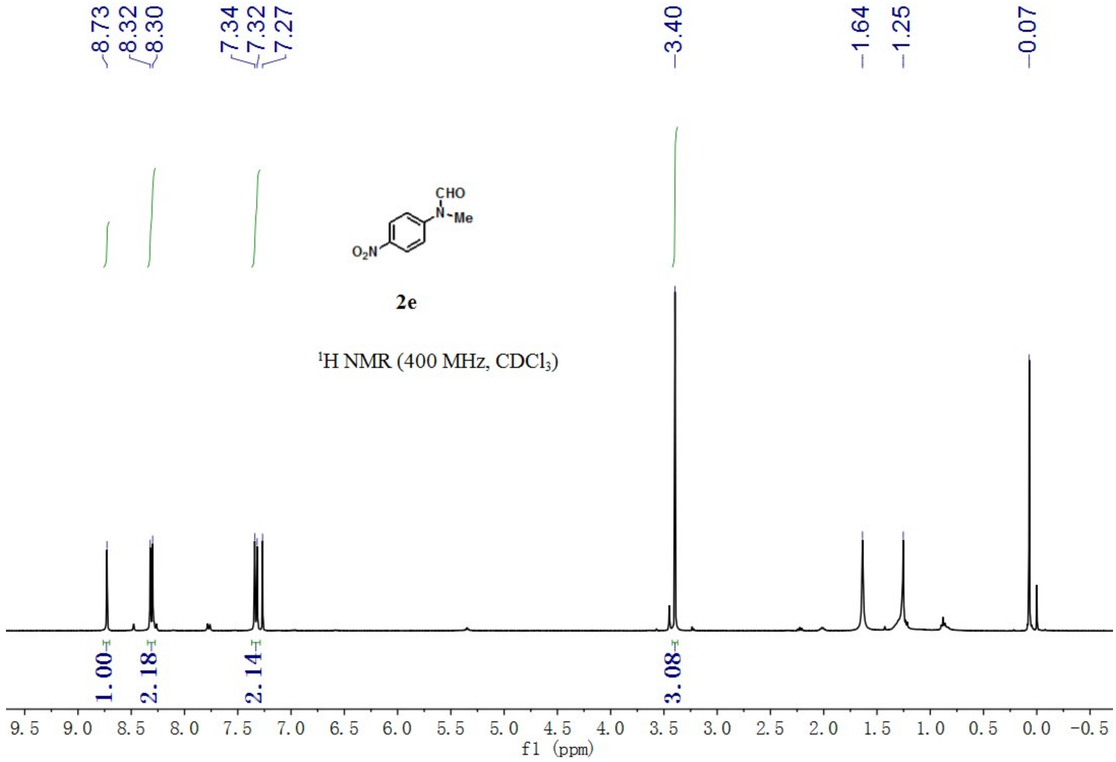
8.34
7.12
7.09
6.94
6.92
3.82
3.27
H3C N CHO
OCH3
2c
1H NMR (400 MHz, CDCl3)
0.92
1.93
1.97
3.14
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

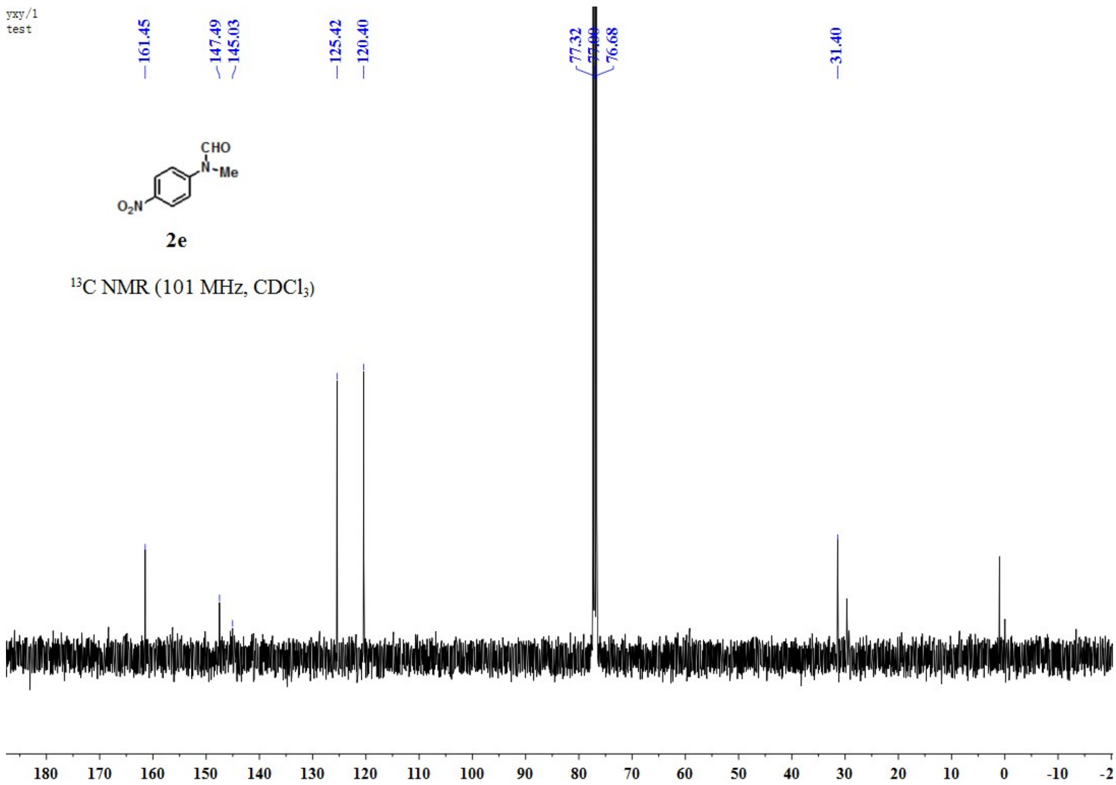


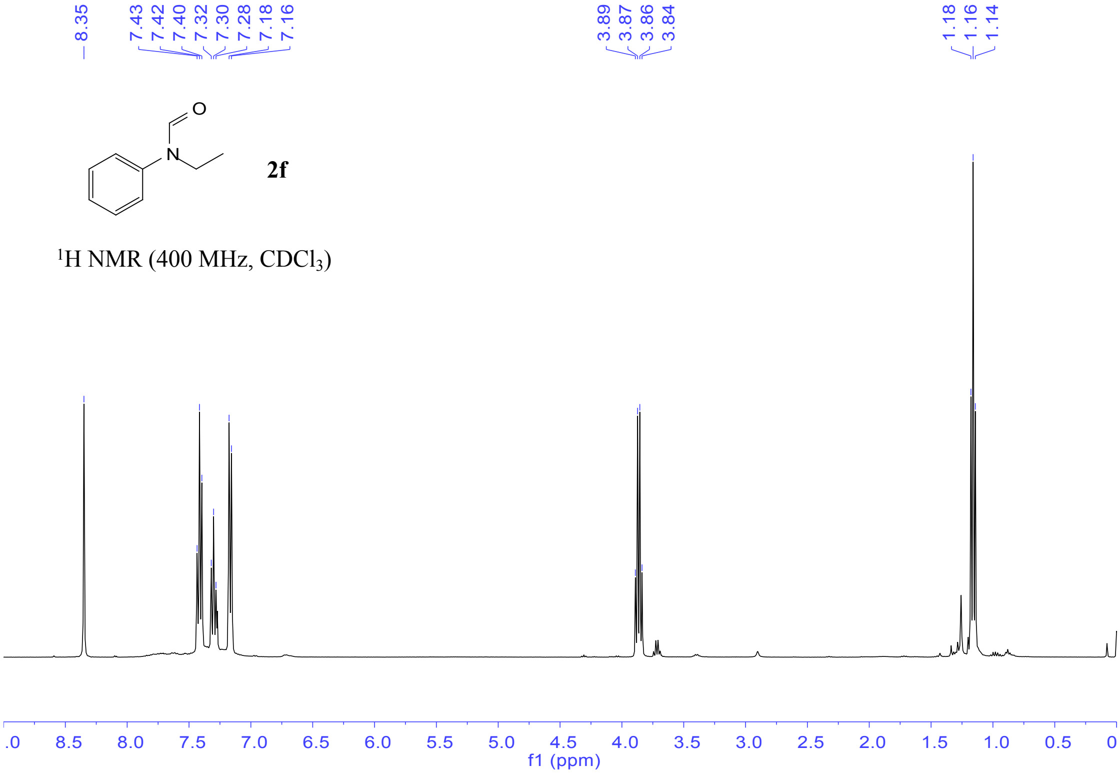
162.28
158.11
135.06
124.47
114.58
77.32
77.00
76.68
55.38
32.50
H3C N CHO
OCH3
2c
13C NMR (101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.45
7.40
7.38
7.13
7.11
3.30
H3C N CHO
Cl
1H NMR (400 MHz, CDCl3)
2d
0.96
2.14
2.03
3.00


161.94
140.68
131.97
129.71
123.46
77.32
77.00
76.68
32.01
H3C N CHO
Cl
2d
13C NMR (101 MHz, CDCl3)

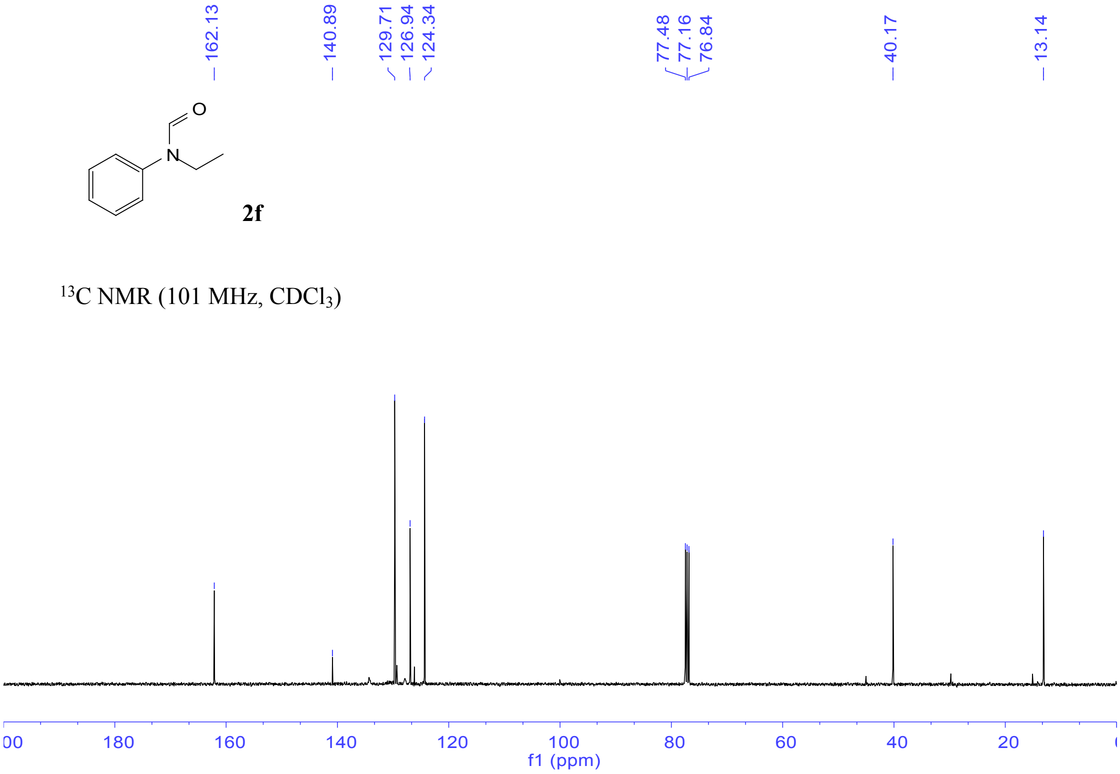

8.73
8.32
8.30
7.34
7.32
7.27
3.40
1.64
1.25
0.07
CHO
N
Me
O_2N
2e
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
2.18
2.14
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


yxy/1
test
161.45
147.49
145.03
125.42
120.40
77.32
77.00
76.68
31.40
CHO
N
Me
O_2N
2e
^{13}C NMR (101 MHz, $CDCl_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2



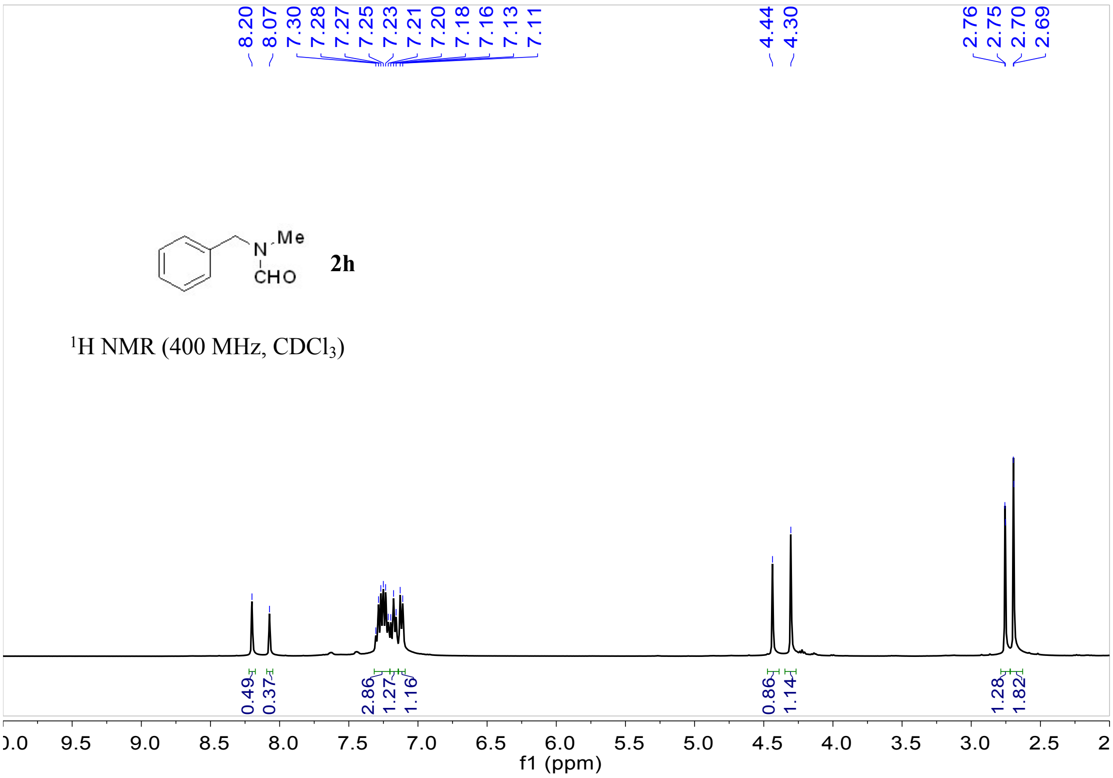
2f

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

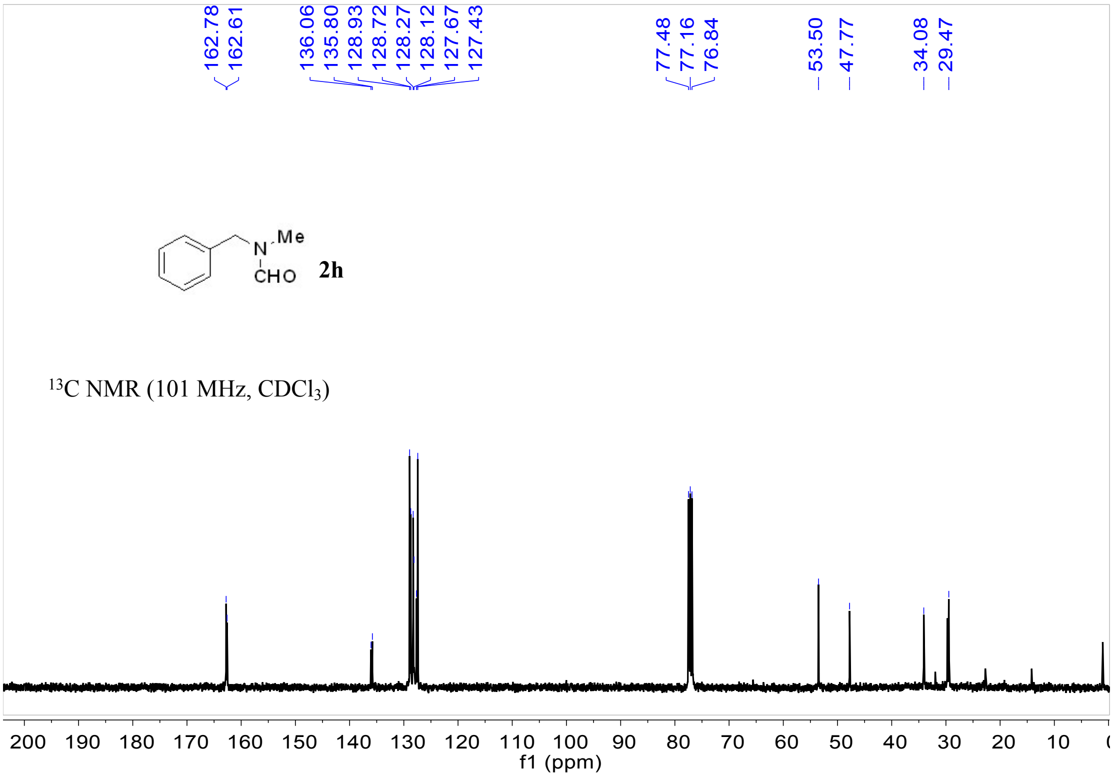


2f

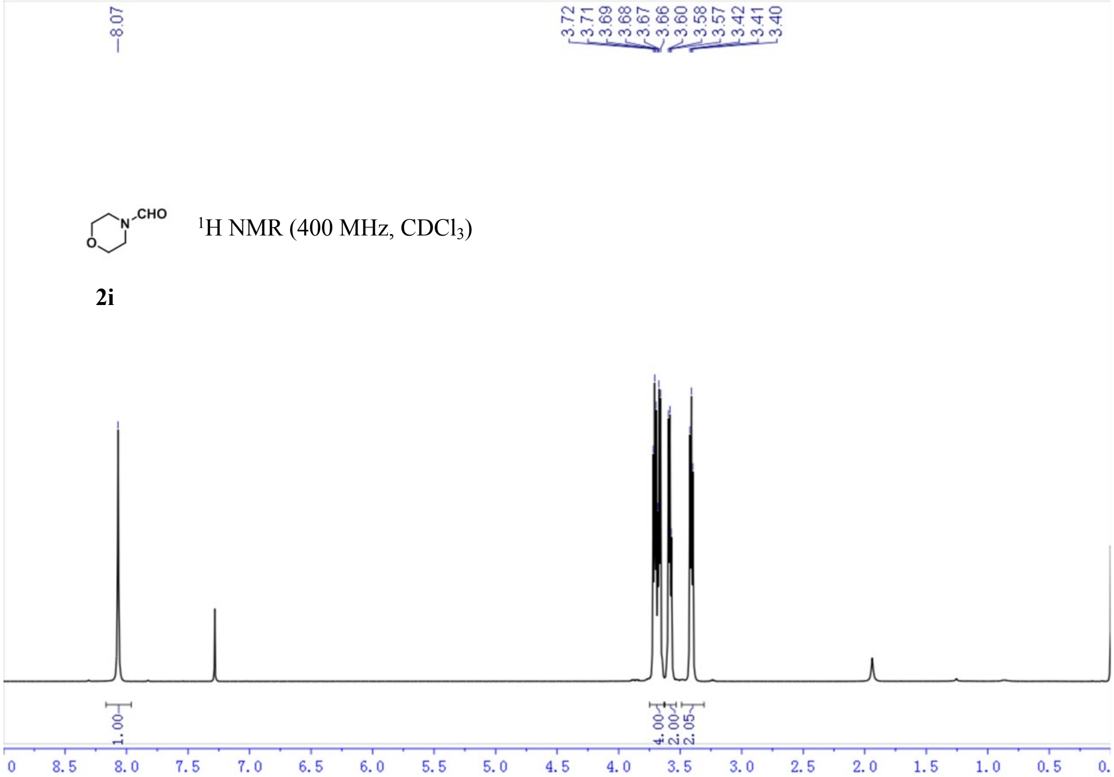
^{13}C NMR (101 MHz, $CDCl_3$)

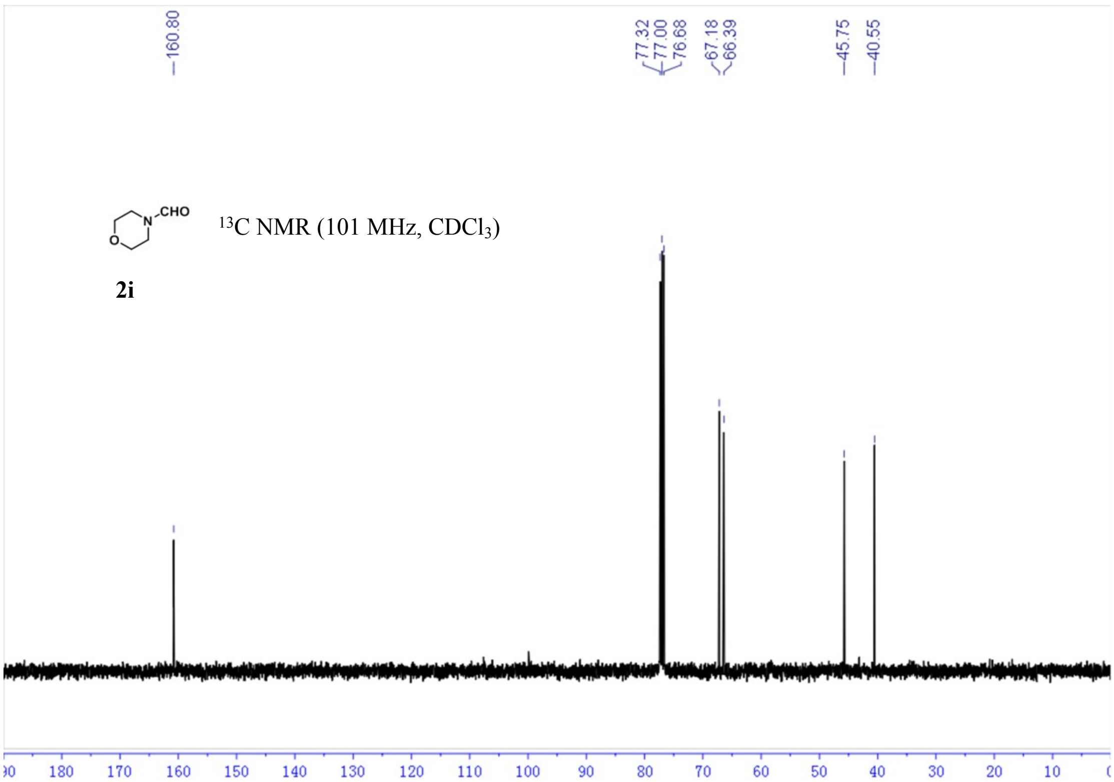


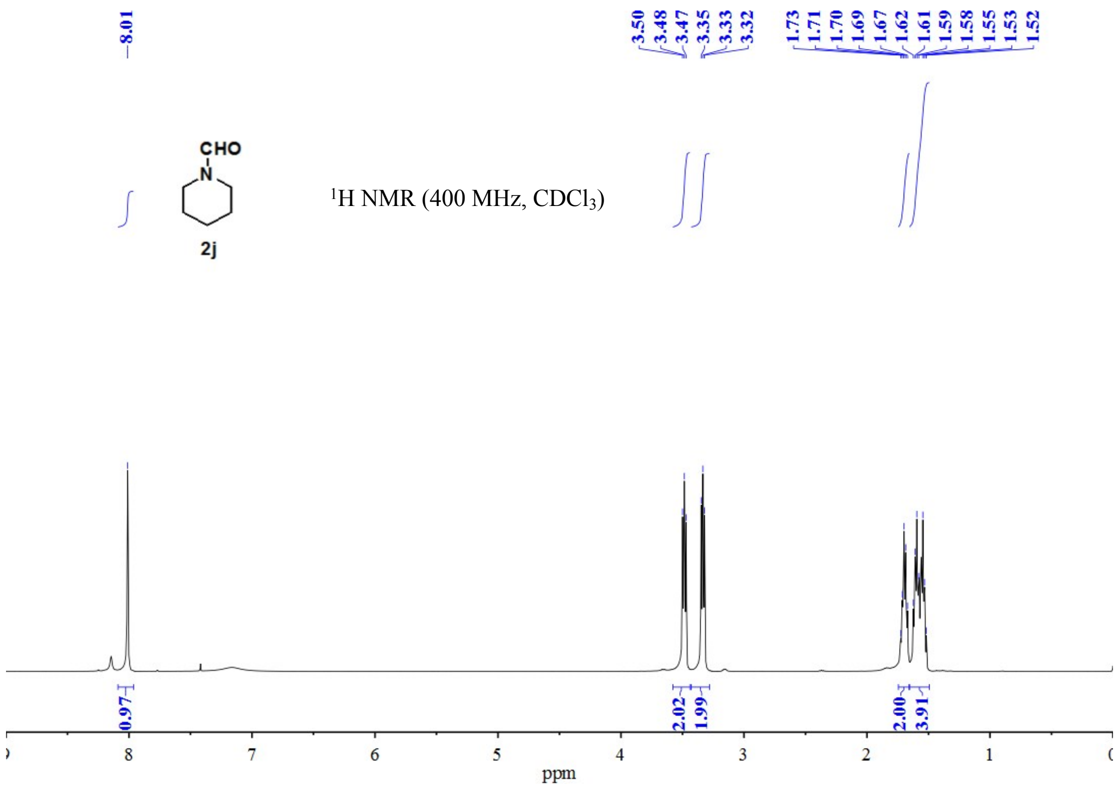
8.20
8.07
7.30
7.28
7.27
7.25
7.23
7.21
7.20
7.18
7.16
7.13
7.11
4.44
4.30
2.76
2.75
2.70
2.69
Me
N
CHO
2h
1H NMR (400 MHz, CDCl3)
0.49
0.37
2.86
1.27
1.16
0.86
1.14
1.28
1.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

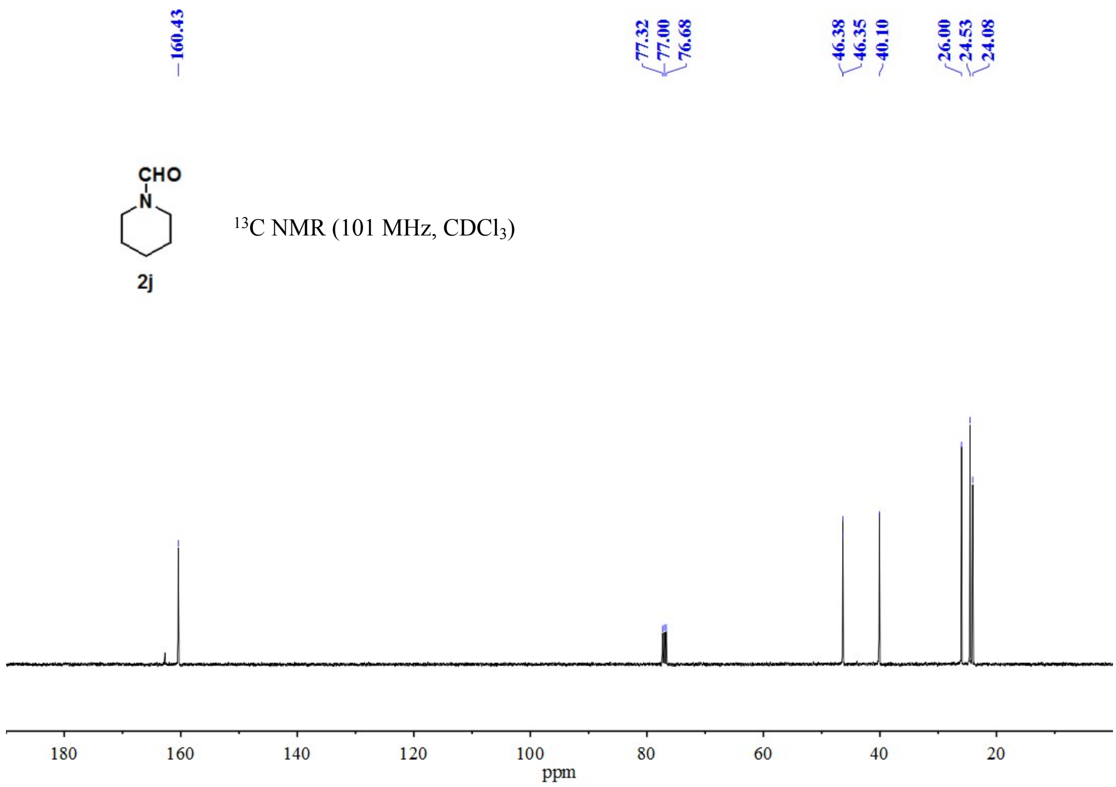


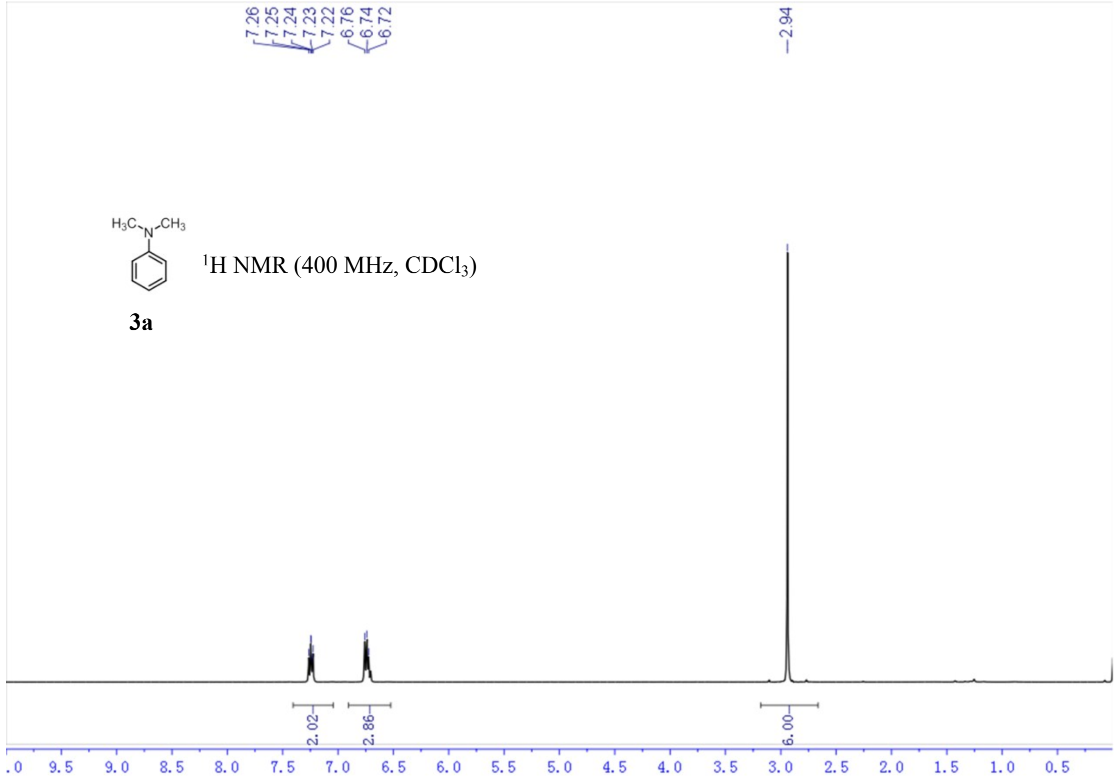
162.78
162.61
136.06
135.80
128.93
128.72
128.27
128.12
127.67
127.43
77.48
77.16
76.84
53.50
47.77
34.08
29.47
Me
N
CHO
2h
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

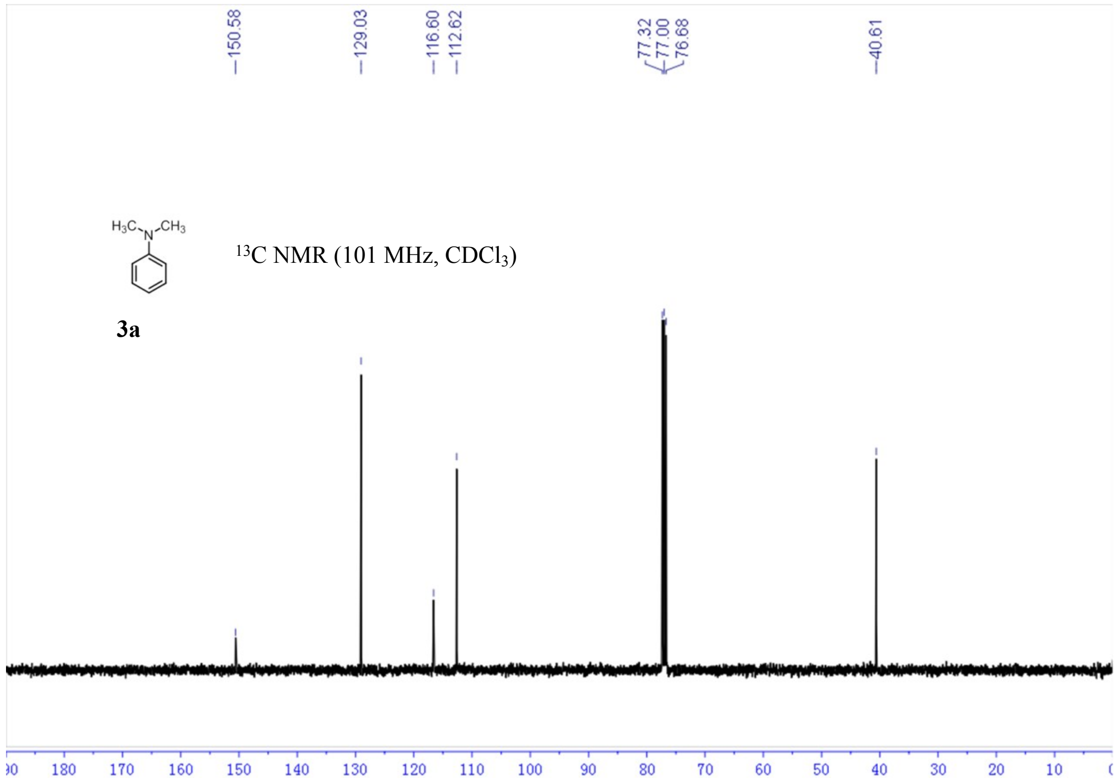

8.07
3.72
3.71
3.69
3.68
3.67
3.66
3.60
3.58
3.57
3.42
3.41
3.40
CHO
N
O
1H NMR (400 MHz, CDCl3)
2i
1.00
4.00
2.00
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

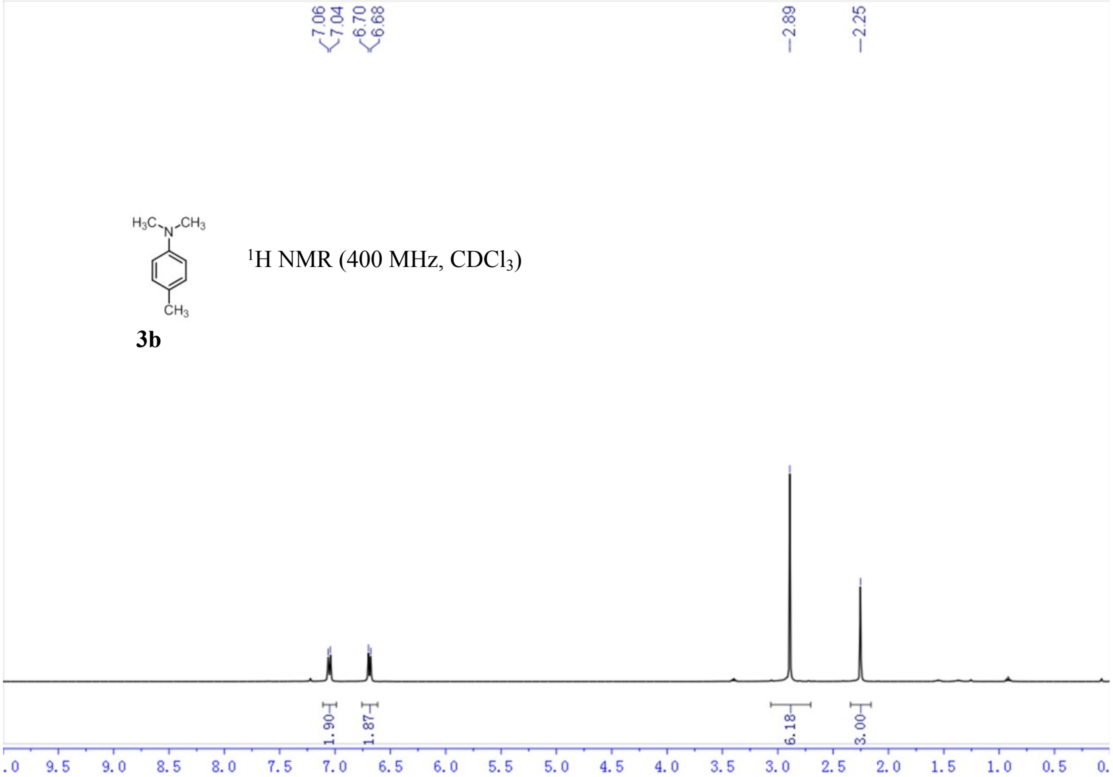

160.80
77.32
77.00
76.68
67.18
66.39
45.75
40.55
CHO
N
O
13C NMR (101 MHz, CDCl3)
2i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

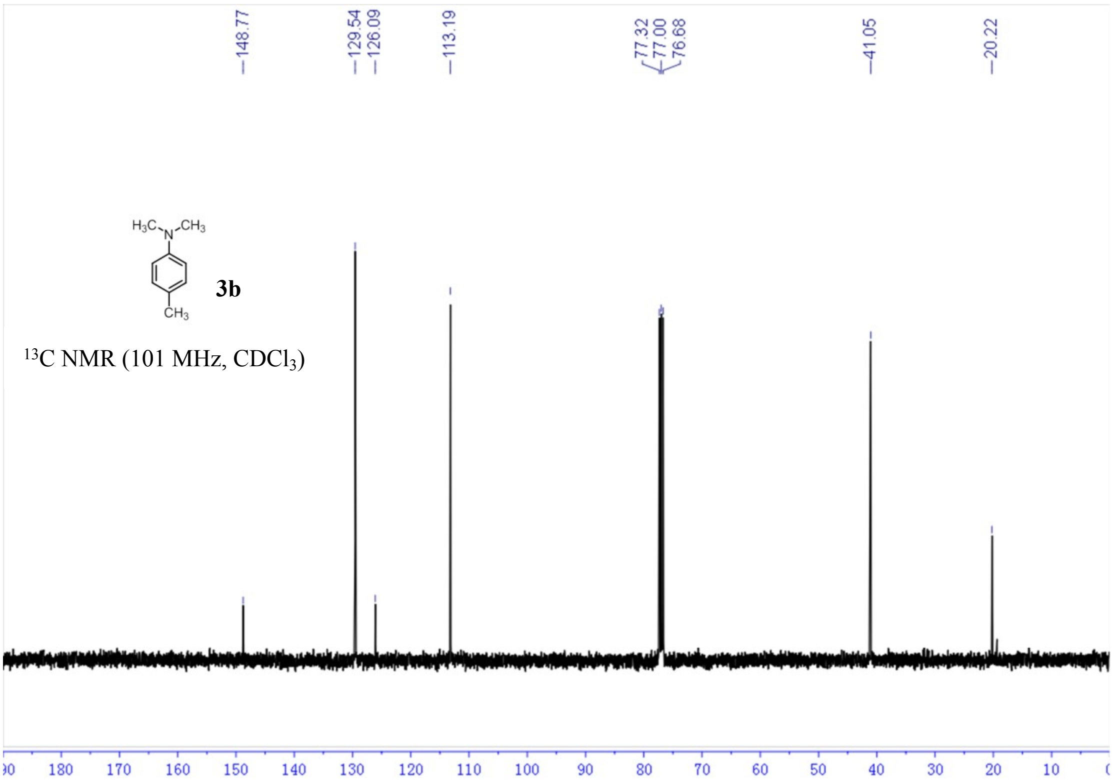

8.01
3.50
3.48
3.47
3.35
3.33
3.32
1.73
1.71
1.70
1.69
1.67
1.62
1.61
1.59
1.58
1.55
1.53
1.52
CHO
N
2j
^{1}H NMR (400 MHz, $CDCl_3$)
0.97
2.02
1.99
2.00
3.91
8
7
6
5
4
3
2
1
ppm

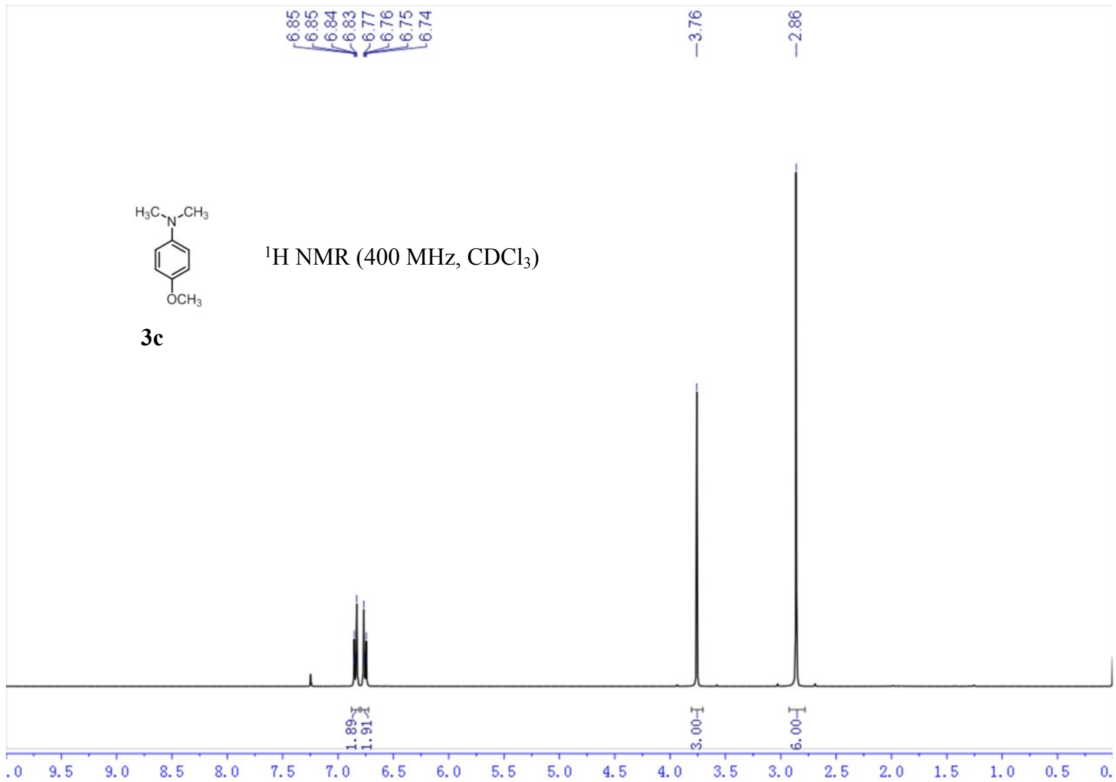

160.43
77.32
77.00
76.68
46.38
46.35
40.10
26.00
24.53
24.08
CHO
N
2j
^{13}C NMR (101 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
ppm


7.26
7.25
7.24
7.23
7.22
6.76
6.74
6.72
2.94
H3C N CH3
1H NMR (400 MHz, CDCl3)
3a
2.02
2.86
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

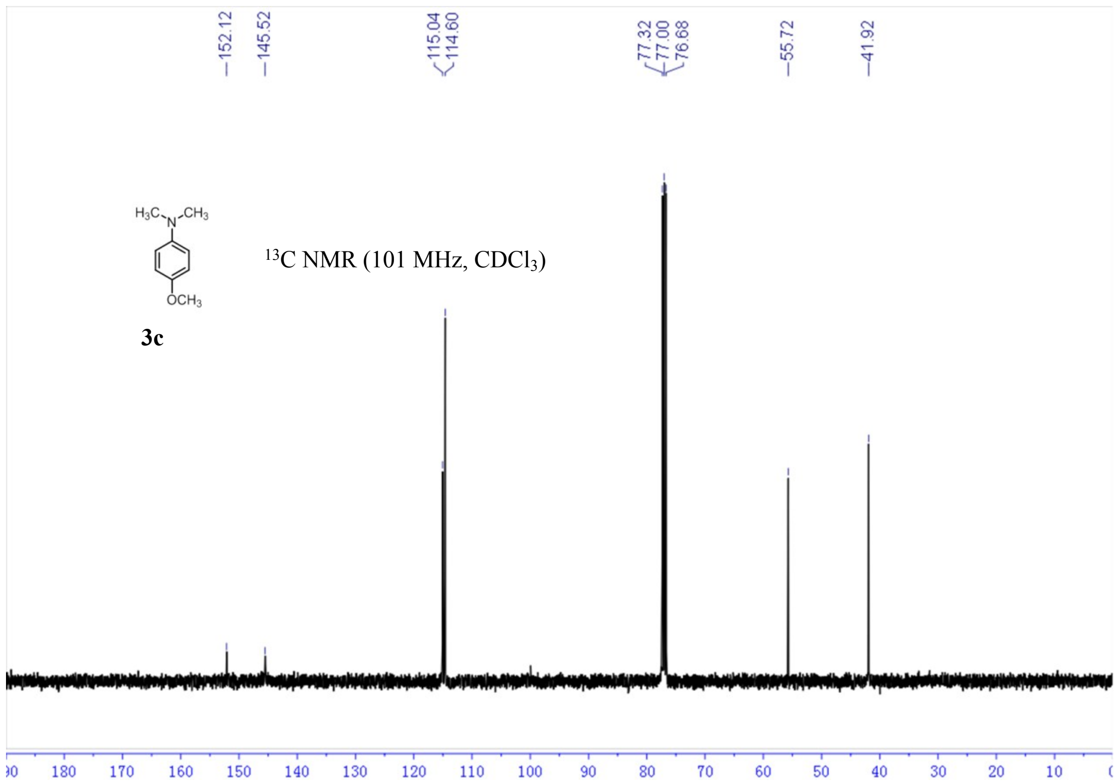

150.58
129.03
116.60
112.62
77.32
77.00
76.68
40.61
H3C N CH3
13C NMR (101 MHz, CDCl3)
3a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.06
7.04
6.70
6.68
2.89
2.25
H3C N CH3
CH3
1H NMR (400 MHz, CDCl3)
3b
1.90
1.87
6.18
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

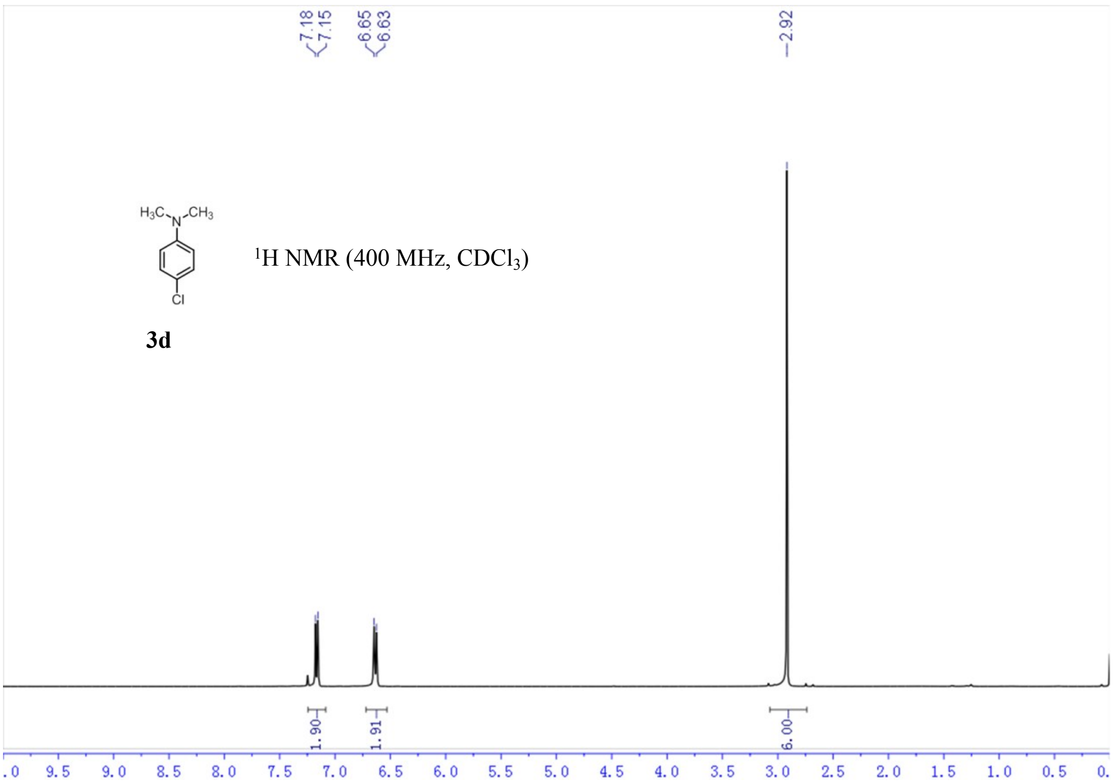

148.77
129.54
126.09
113.19
77.32
77.00
76.68
41.05
20.22
H3C N CH3
CH3
3b
13C NMR (101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

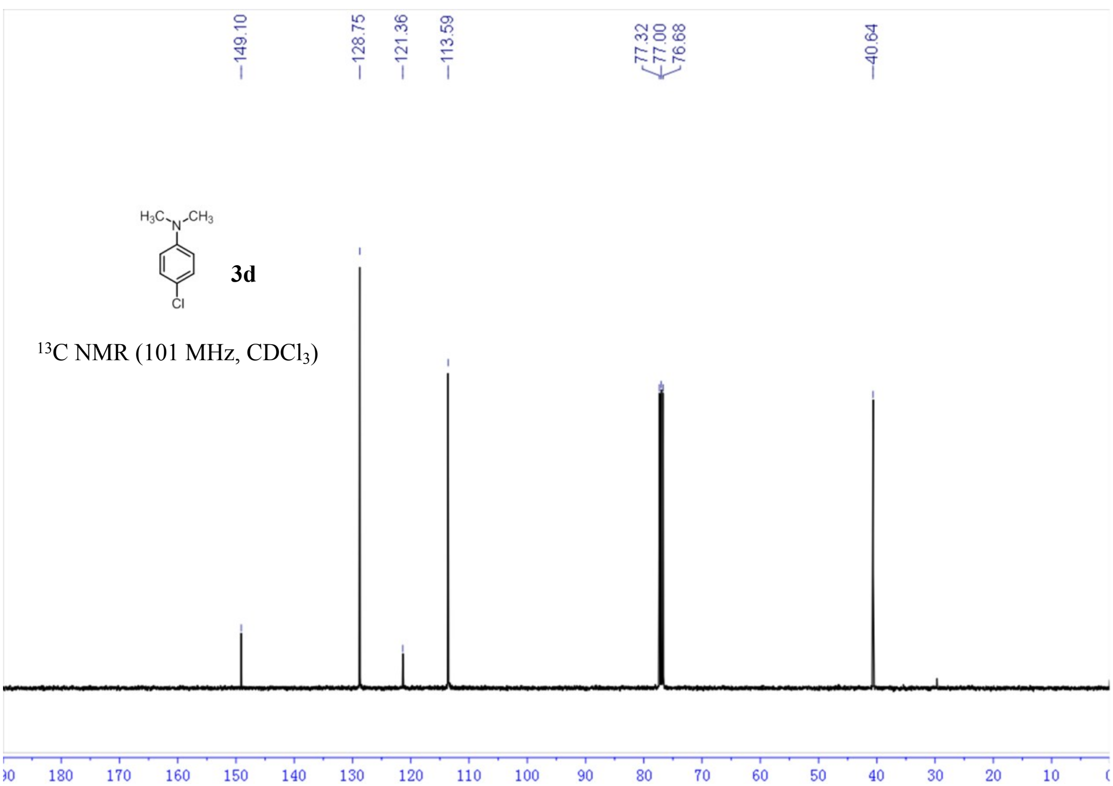


3c
^{1}H NMR (400 MHz, $CDCl_3$)
6.85
6.85
6.84
6.83
6.77
6.76
6.75
6.74
3.76
2.86
1.89
1.91
3.00
6.00



3c
^{13}C NMR (101 MHz, $CDCl_3$)
152.12
145.52
115.04
114.60
77.32
77.00
76.68
55.72
41.92


7.18
7.15
6.65
6.63
2.92
H_3C N CH_3
Cl
^{1}H NMR (400 MHz, $CDCl_3$)
3d
1.90
1.91
6.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.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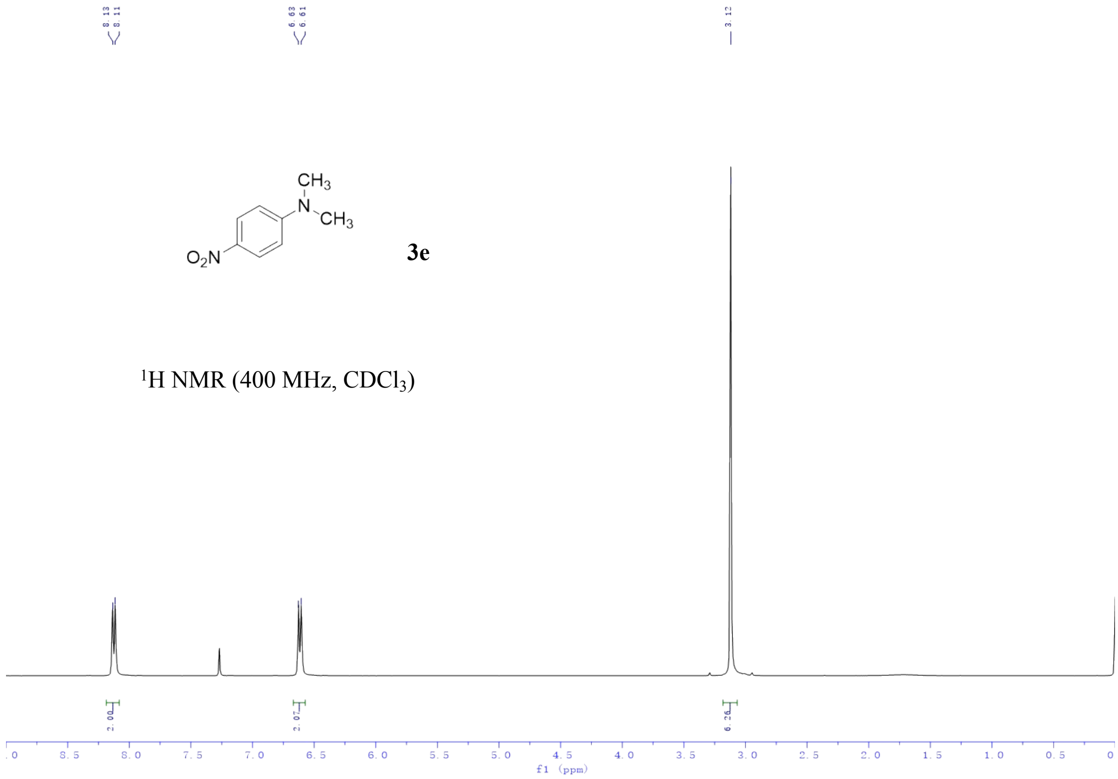
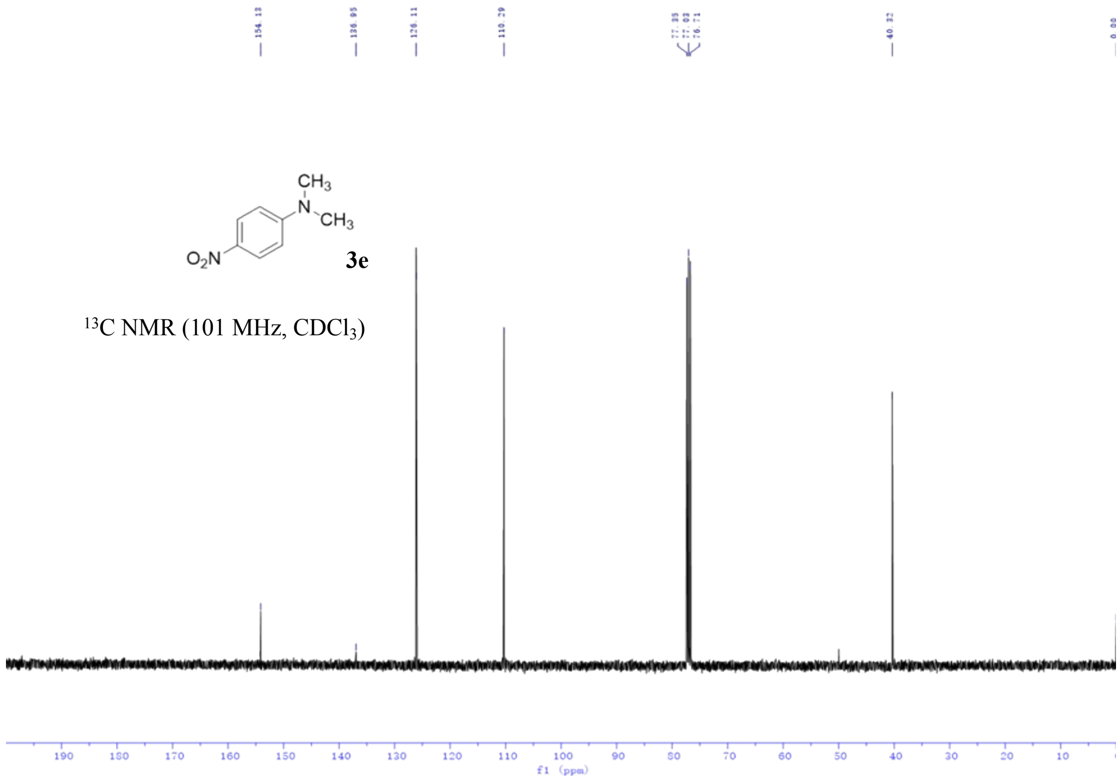
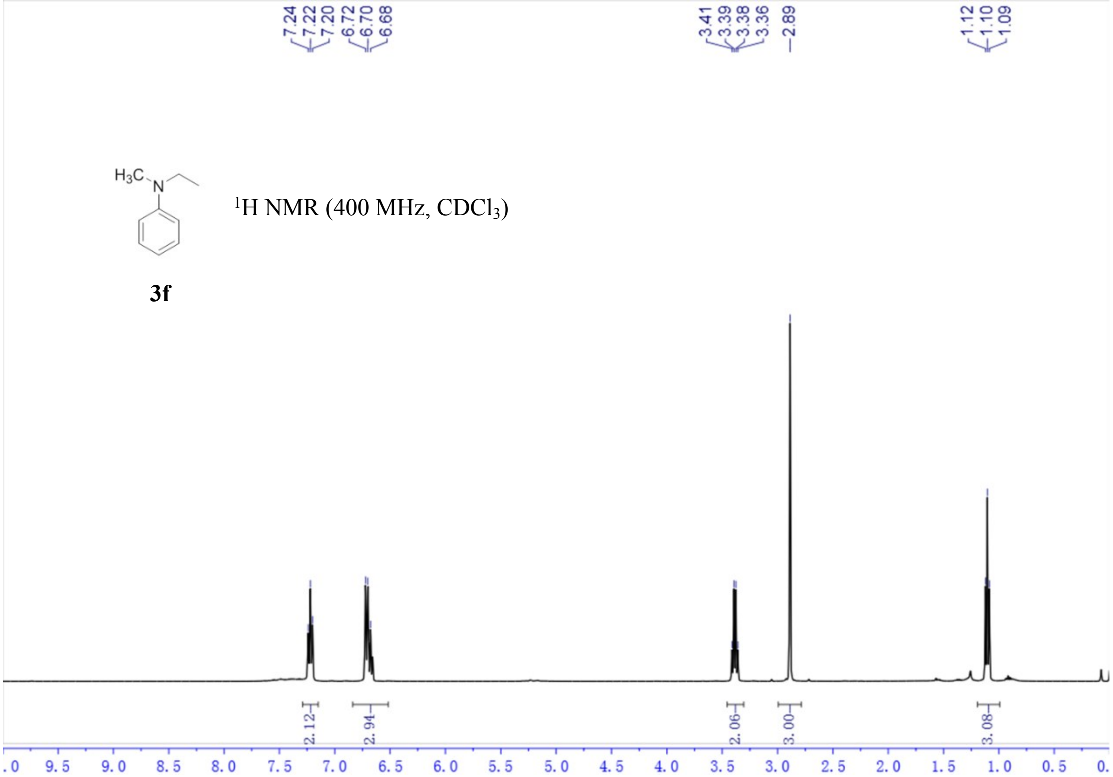
128.75
121.36
113.59
77.32
77.00
76.68
40.64
H_3C N CH_3
Cl
3d
^{13}C NMR (101 MHz, $CDCl_3$)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10



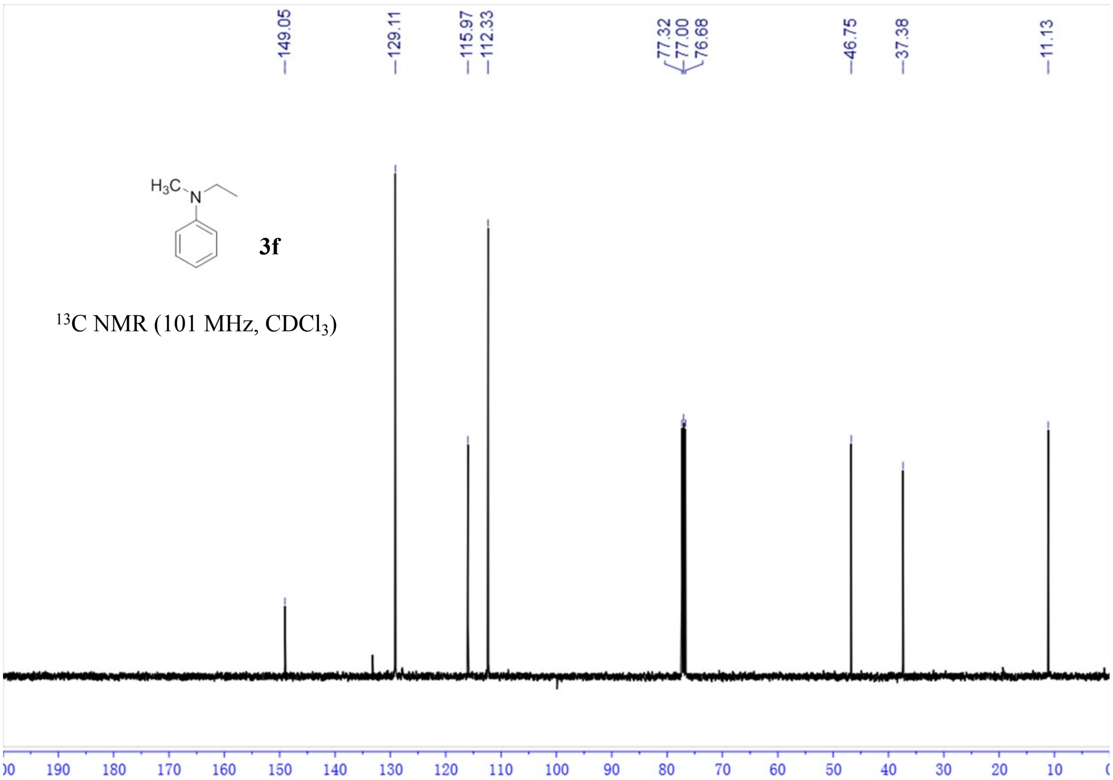
8.13
8.11
6.63
6.61
3.12
CH3
N
CH3
O2N
3e
1H NMR (400 MHz, CDCl3)
2.00
2.07
6.26
f1 (ppm)



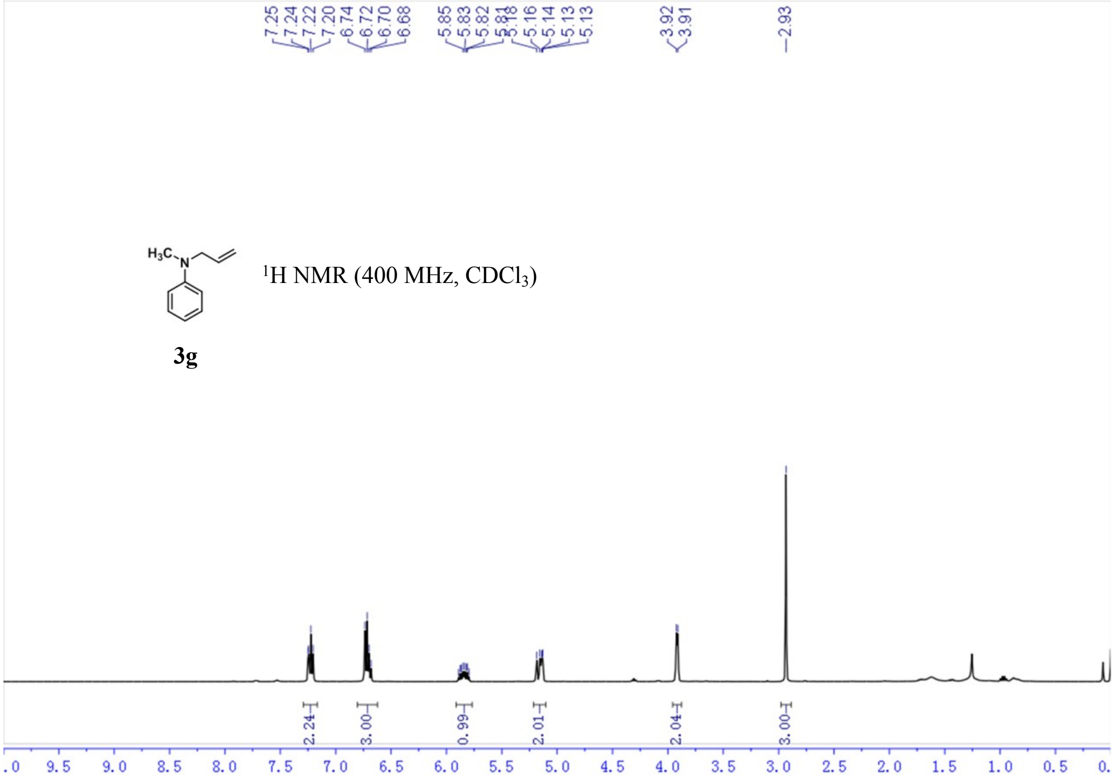
154.13
136.95
126.11
110.29
77.35
77.03
76.71
40.32
0.00
CH3
N
CH3
O2N
3e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

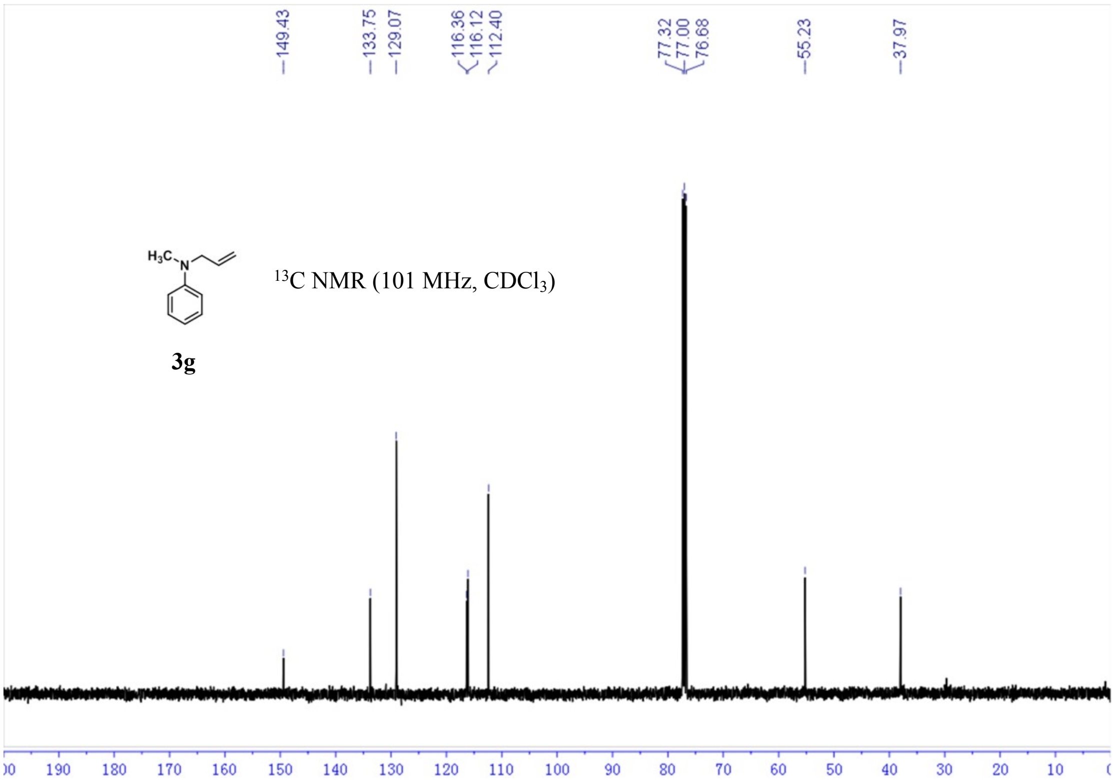


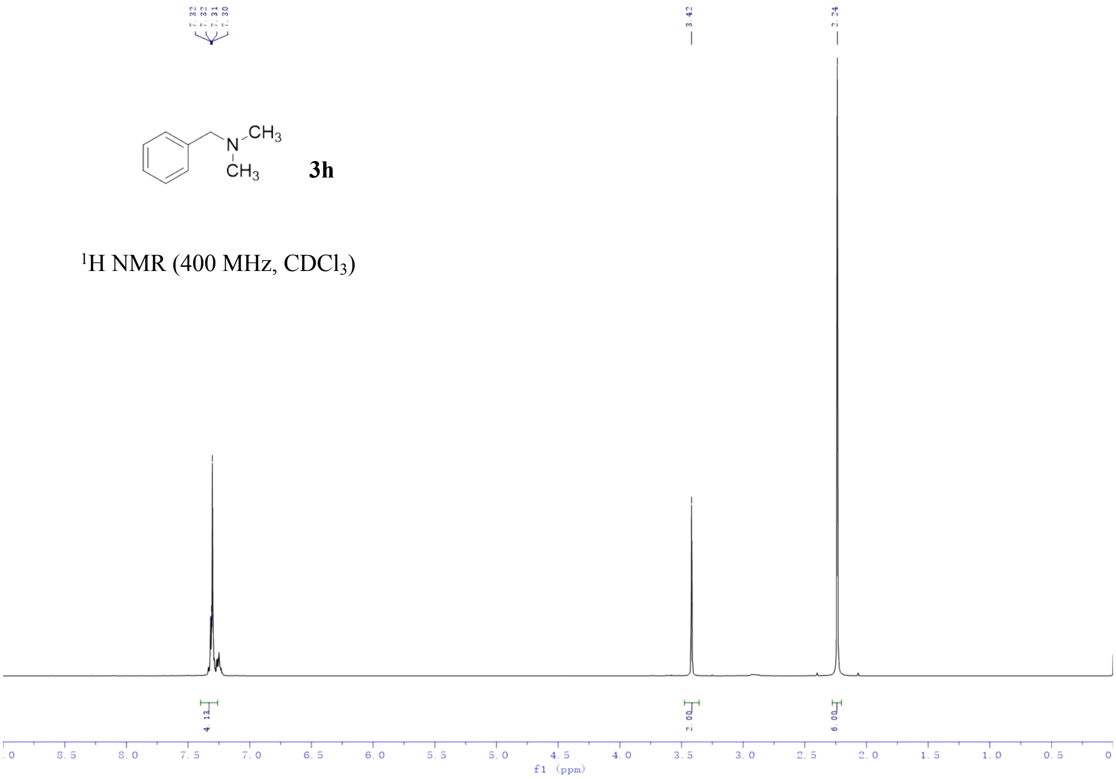
7.24
7.22
7.20
6.72
6.70
6.68
3.41
3.39
3.38
3.36
2.89
1.12
1.10
1.09
H3C
N
1H NMR (400 MHz, CDCl3)
3f
2.12
2.94
2.06
3.00
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

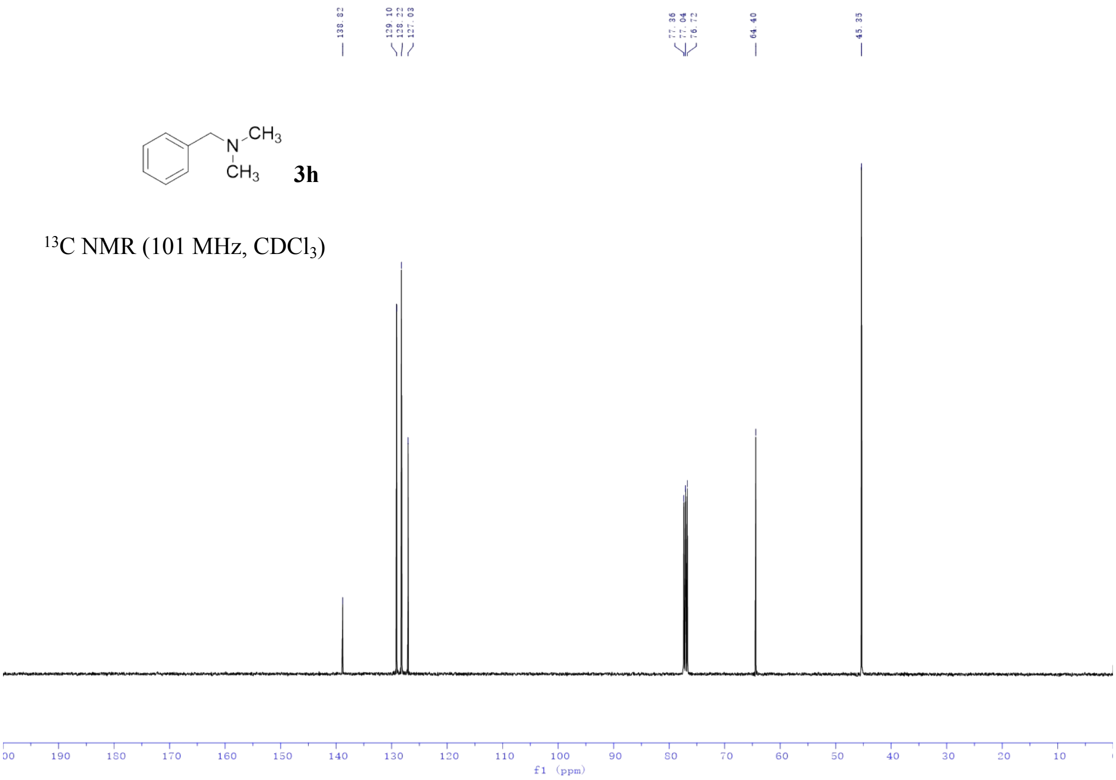


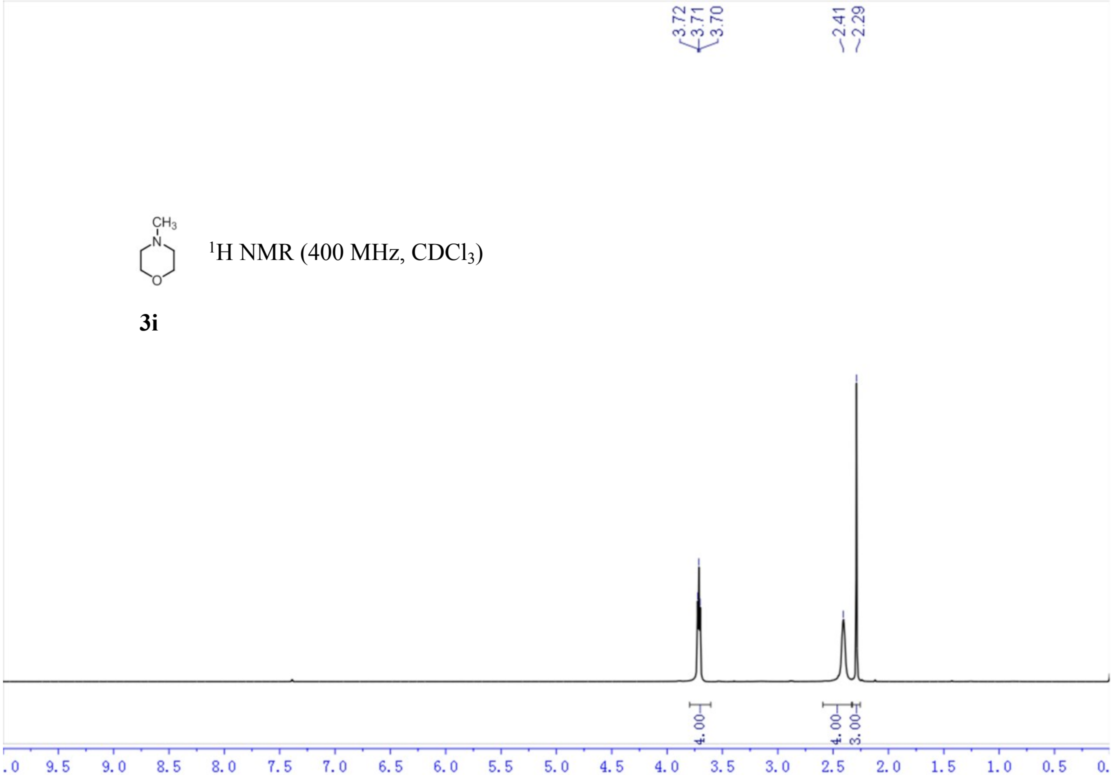
149.05
129.11
115.97
112.33
77.32
77.00
76.68
46.75
37.38
11.13
H3C
N
3f
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

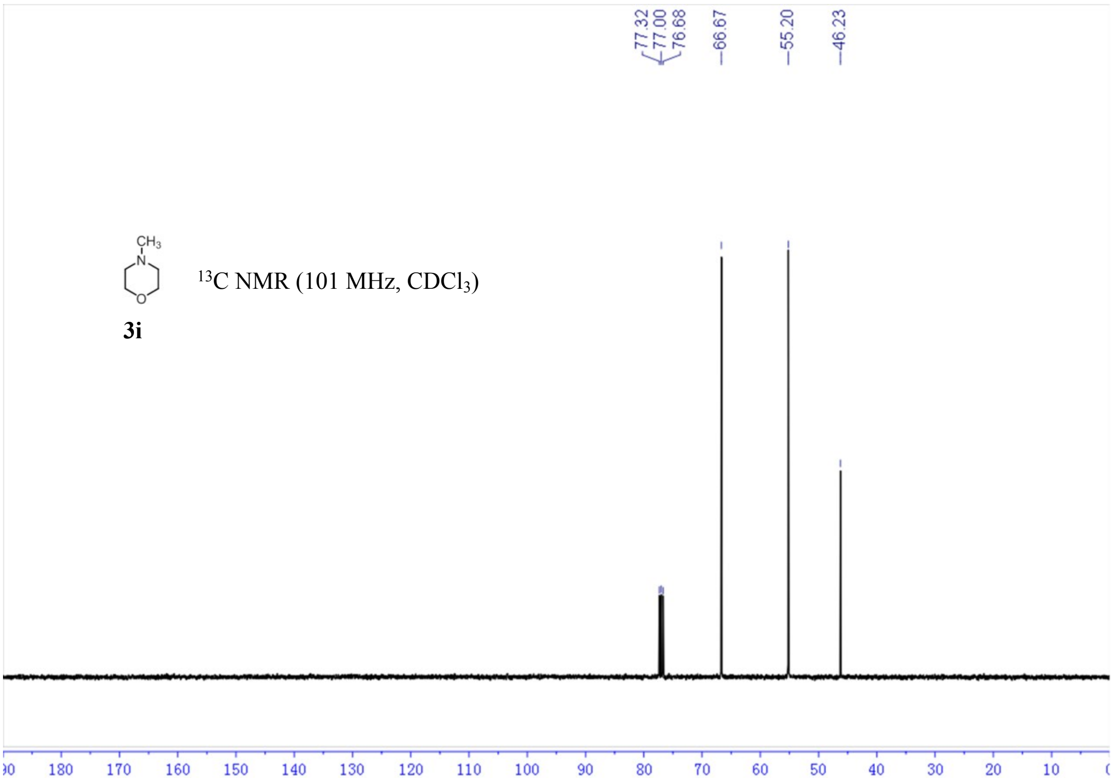

7.25
7.24
7.22
7.20
6.74
6.72
6.70
6.68
5.85
5.83
5.82
5.81
5.18
5.16
5.14
5.13
5.13
3.92
3.91
2.93
H_3C
N
^1H NMR (400 MHz, $CDCl_3$)
3g
2.24
3.00
0.99
2.01
2.04
3.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

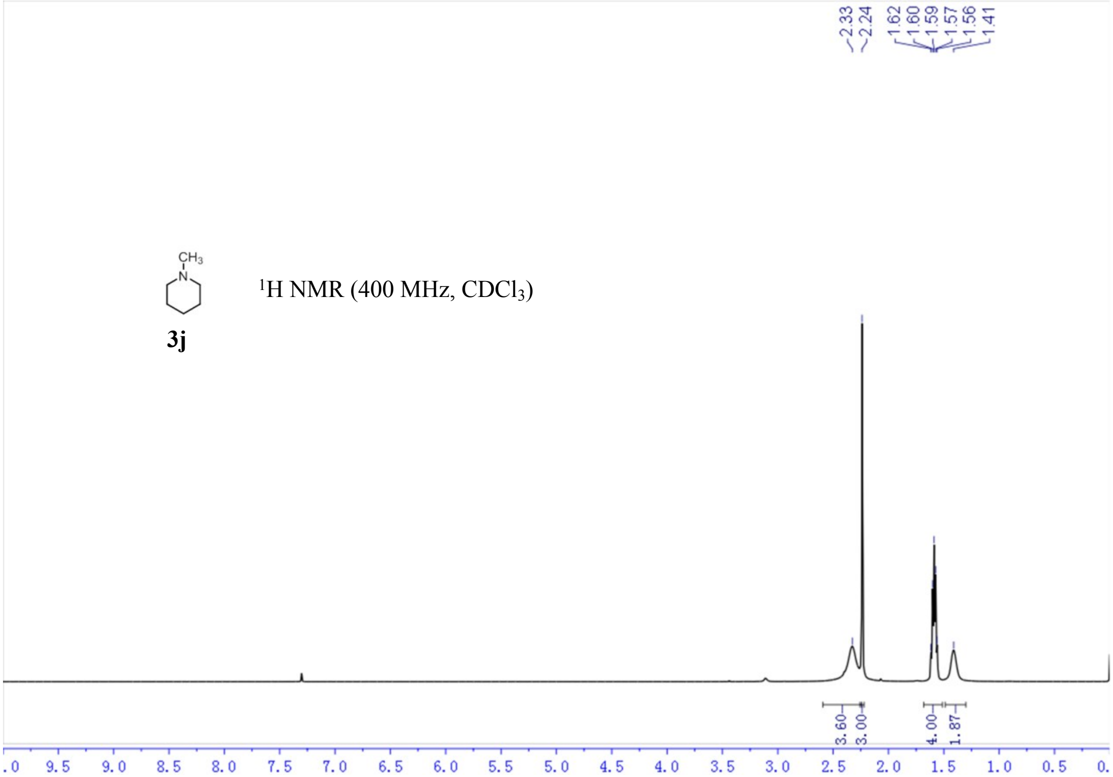

149.43
133.75
129.07
116.36
116.12
112.40
77.32
77.00
76.68
55.23
37.97
H_3C
N
^{13}C NMR (101 MHz, $CDCl_3$)
3g
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (

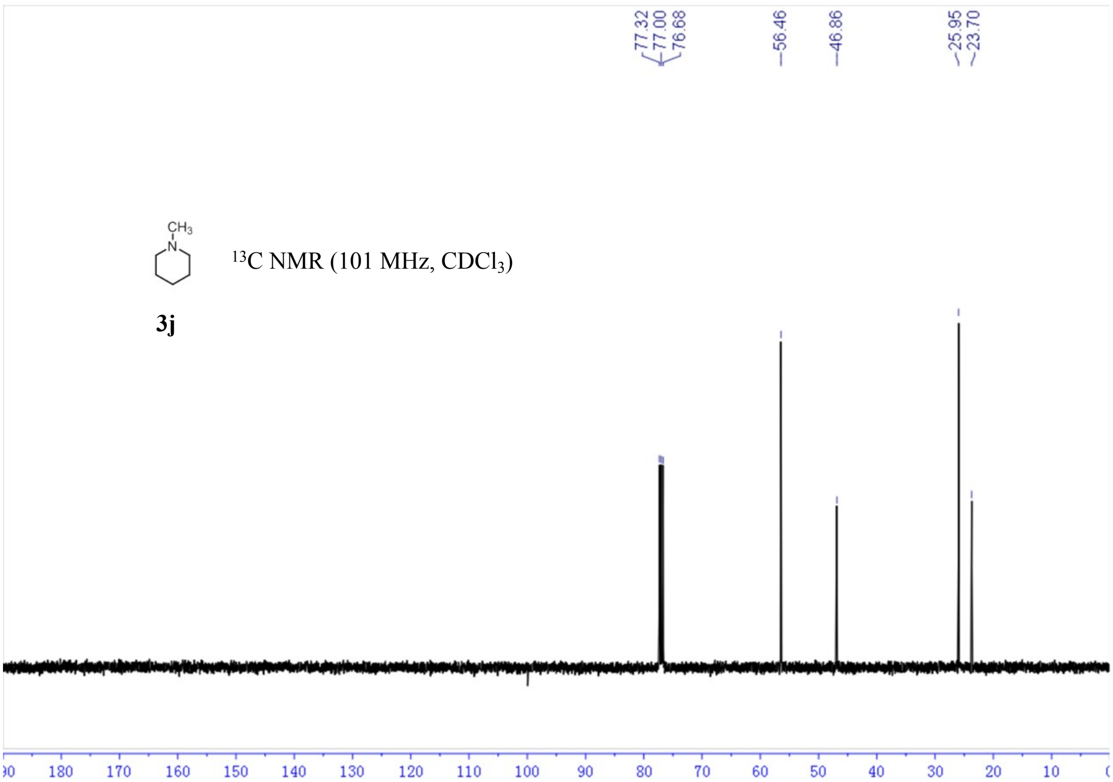

7.32
7.32
7.31
7.30
3.42
2.24
3h
^{1}H NMR (400 MHz, $CDCl_3$)
4.13
2.00
6.00
f1 (ppm)


138.82
129.10
128.22
127.03
77.36
77.04
76.72
64.40
45.35
3h
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


3.72
3.71
3.70
2.41
2.29
CH3
N
O
1H NMR (400 MHz, CDCl3)
3i
4.00
4.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


77.32
77.00
76.68
66.67
55.20
46.23
CH3
N
O
13C NMR (101 MHz, CDCl3)
3i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


2.33
2.24
1.62
1.60
1.59
1.57
1.56
1.41
CH3
N
1H NMR (400 MHz, CDCl3)
3j
3.60
3.00
4.00
1.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


77.32
77.00
76.68
56.46
46.86
25.95
23.70
CH3
N
13C NMR (101 MHz, CDCl3)
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0