SUPPORTING INFORMATION

Efficient and Selective *N*-Methylation of Nitroarenes under Mild Reaction Conditions

Elena Pedrajas, Iván Sorribes*, Eva Guillamón, Kathrin Junge, Matthias Beller* and Rosa Llusar*

1. Catalyst characterization.

Figure SI1. ^{1}H NMR spectrum of the complex $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ ($3(BF_4)$) in CD_2Cl_2

Figure SI2. ^{13}C NMR spectrum of the complex $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ ($3(BF_4)$) in CD_2Cl_2.

Figure SI3. ESI mass spectrum of the complex $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ ($3(BF_4)$) in CH_3CN at 20 V.

Figure SI4. Cyclic Voltammogram recorded on a CH_2Cl_2 solution containing 3^+ (a) and 1^+ (b) at scan rate of 100mV/s (*vs* Ag/AgCl).

2. Conditions optimization for the *N*-methylation of *p*-nitrotoluene (1a).

Table SI1. Screening of silanes.

Table SI2. Influence of the solvent on the catalytic *N*-methylation of 1a.

3. ESI mass spectra from the reaction mixture during the *N*-methylation of 1a.

Figure SI5. ESI mass spectrum from the *N*-methylation reaction after 8 hours.

Figure SI6. ESI mass spectrum from the mixture of $[Mo_3S_4Cl_3(dmen)_3](BF_4)$ ($1(BF4)$) (0.003 mmol) and $Pt(PPh_3)_4$ (2) (0.001 mmol) in THF after 10 minutes stirring at room temperature.

4. Reaction pathway investigation.

Scheme SI1. Proposed pathways for the direct *N*-methylation of nitroarenes with formic acid.

5. Characterization data of isolated products.

6. References

7. ^{1}H NMR and ^{13}C NMR spectra of isolated products.

1. Catalyst characterization

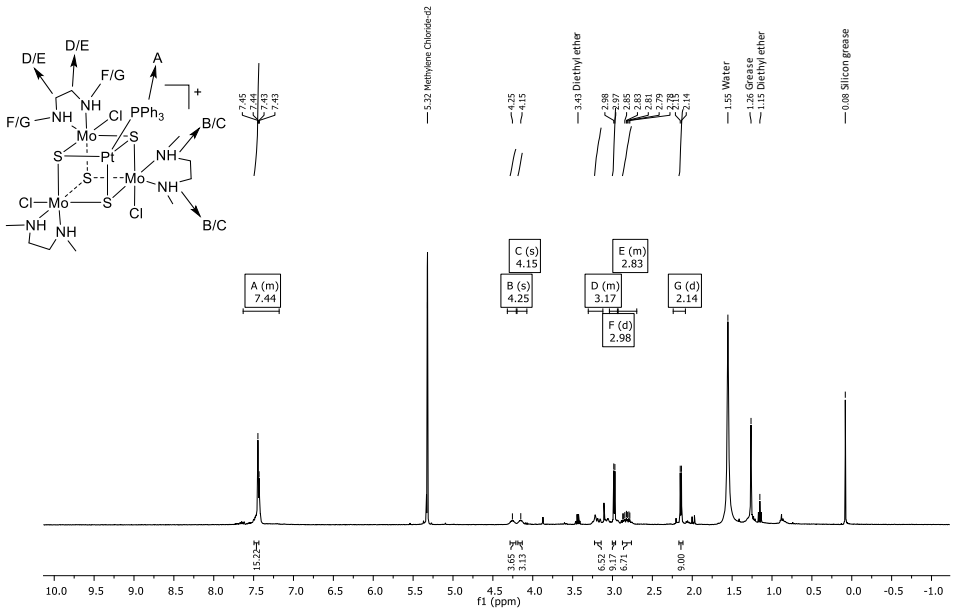


Figure SI1. ^{1}H NMR spectrum of the $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ (**3**(BF_4)) complex in CD_2Cl_2.

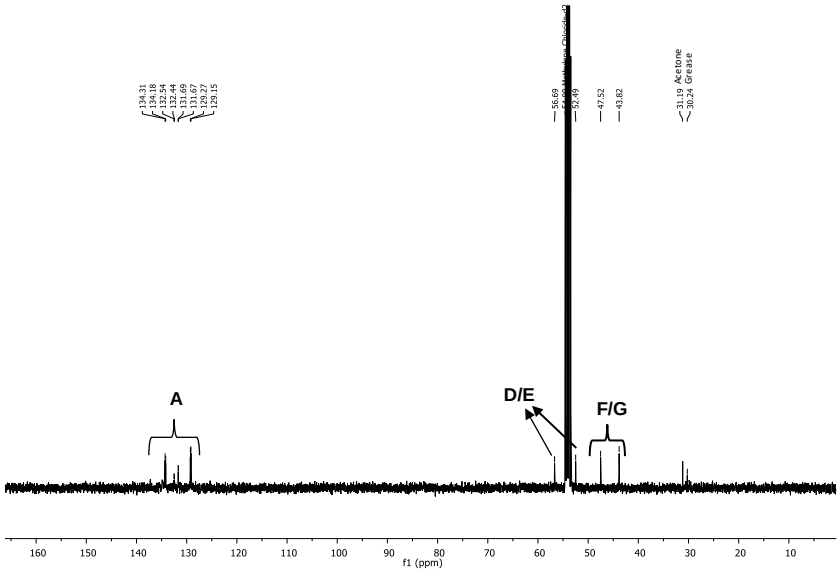


Figure SI2. ^{13}C NMR spectrum of the $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ (**3**(BF_4)) complex in CD_2Cl_2.

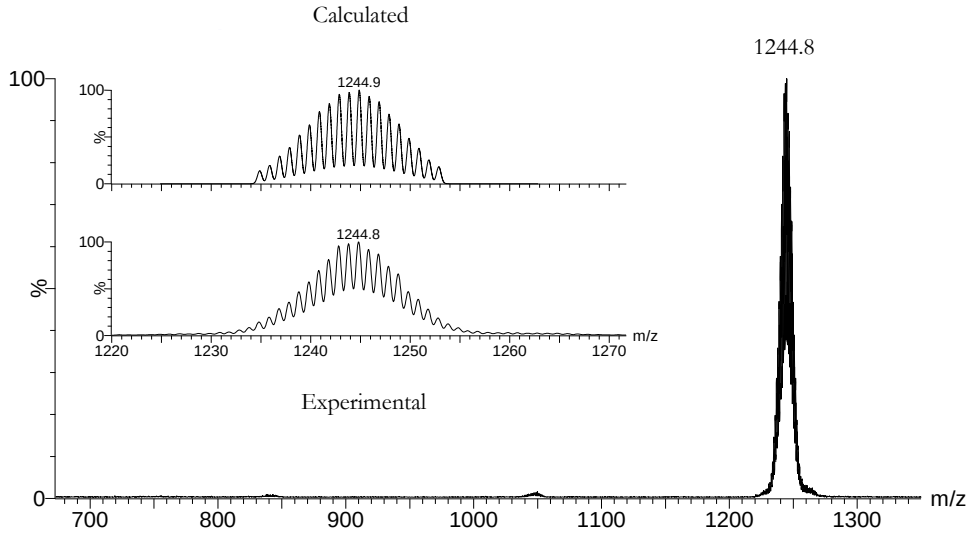


Figure SI3. ESI mass spectrum of the $[Mo_3Pt(PPh_3)S_4Cl_3(dmen)_3](BF_4)$ complex (**3**(BF_4)) in CH_3CN at 20 V.

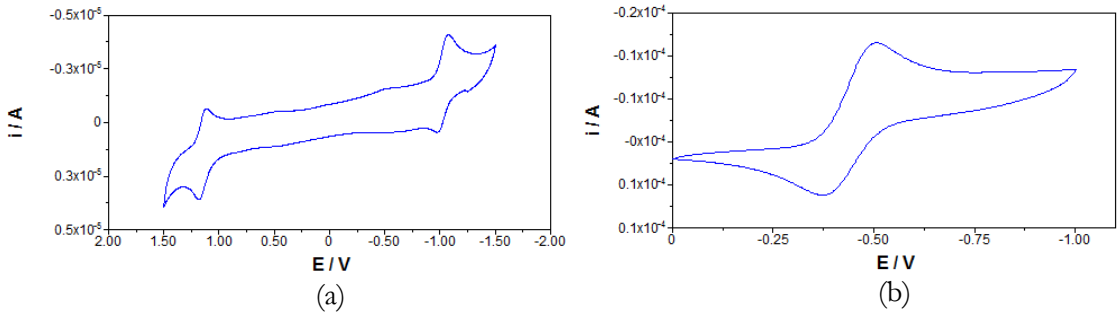
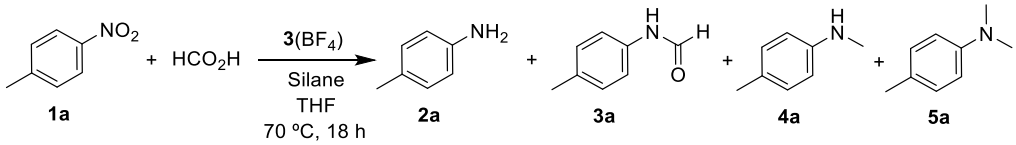


Figure SI4. Cyclic Voltammogram recorded on a CH_2Cl_2 solution containing $\mathbf{3}^+$ (a) and 1^+ (b) at scan rate of 100 mV/s (*vs* Ag/AgCl).

2. Conditions optimization for the *N*-methylation of *p*-nitrotoluene (1a).

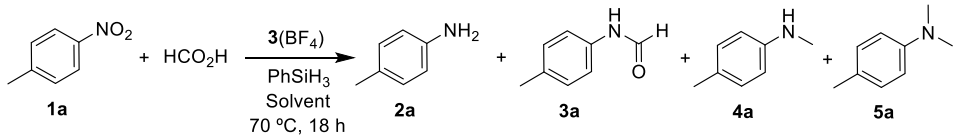
Table SI1. Screening of silanes.[a]



Entry	Silane	Conversion [%][b]	Yield **2a** [%][b]	Yield **3a** [%][b]	Yield **4a** [%][b]	Yield **5a** [%][b]
1	$PhSiH_3$	>99	1	0	2	97
2	Ph_2SiH_2	34	4	6	2	16
3	$PhMe_2SiH$	0	0	0	0	0
4	Et_3SiH	0	0	0	0	0
5	PHMS	21	3	0	1	6

[a]Reaction conditions: **1a** (0.1 mmol), HCO_2H (8.5 equiv.), Silane (10 equiv.), Catalyst (3 mol%), THF (2 mL), 18 h, 70ºC. [b] Determined by GC analysis using *n*-hexadecane as an internal standard.

Table SI2. Influence of the solvent on the catalytic *N*-methylation of **1a**.[a]



Entry	Solvent	Conversion [%][b]	Yield **2a** [%][b]	Yield **3a** [%][b]	Yield **4a** [%][b]	Yield **5a** [%][b]
1[c]	MeCN	50	10	1	5	4
2	MeOH	6	0	0	0	4
3[c]	Toluene	99	41	5	13	13
4	THF	>99	1	0	2	97

[a]Reaction conditions: **1a** (0.1 mmol), HCO_2H (8.5 equiv.), $PhSiH_3$ (10 equiv.), Catalyst (3 mol%), Solvent (2 mL), 18 h, 70ºC. [b] Determined by GC analysis using hexadecane as an internal standard. [c] The urea intermediate 1,3-dimethyl-1,3-di-*p*-tolylurea is detected by GC-Mass.

3. ESI mass spectra from the reaction mixture during the *N*-methylation of 1a.

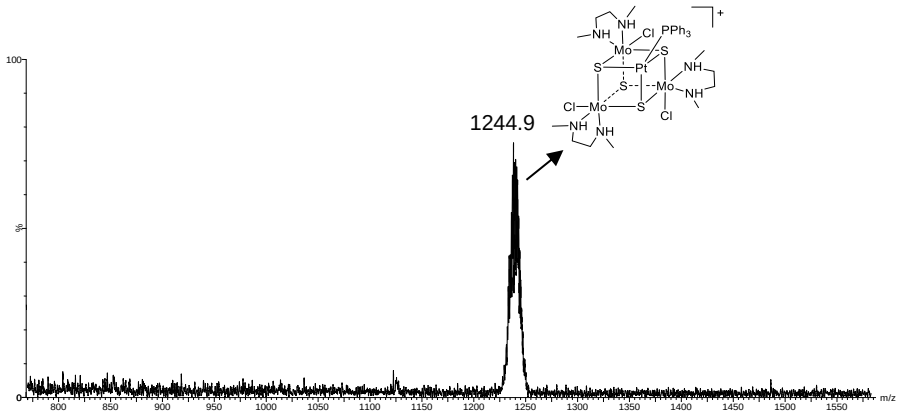


Figure SI5. ESI mass spectrum from the *N*-methylation reaction after 8 hours.

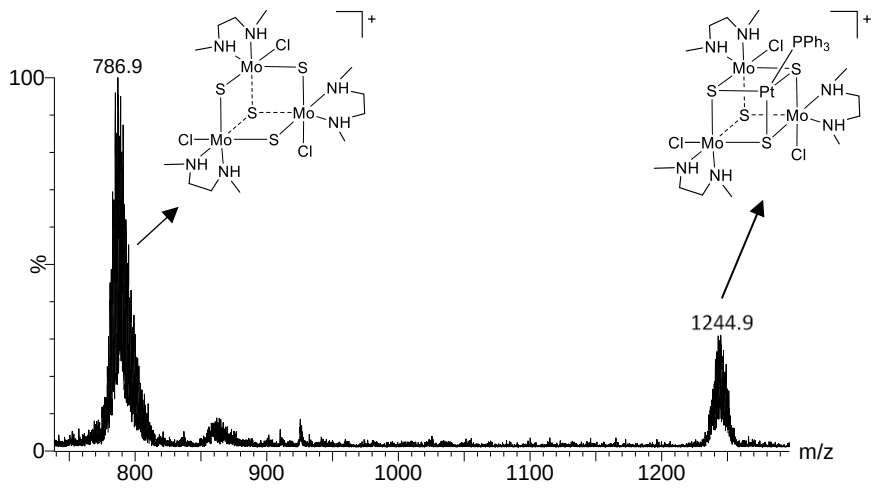
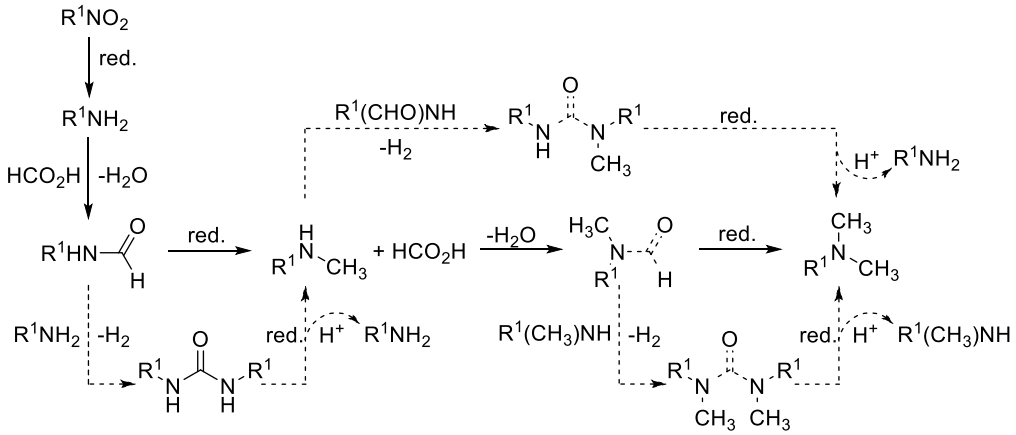


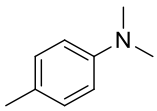
Figure SI6. ESI mass spectrum from the mixture of $[Mo_3S_4Cl_3(dmen)_3](BF_4)$ (**1**(BF4)) (0.003 mmol) and $Pt(PPh_3)_4$ **(2)** (0.001 mmol) in THF after 10 minutes stirring at room temperature.

4. Reaction pathway investigation.

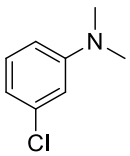


Scheme SI1. Proposed pathways for the direct *N*-methylation of nitroarenes with formic acid in the presence of the heterobimetallic $\mathbf{3}^{+}$ catalyst.

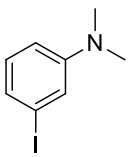
5. Characterization data of isolated products.



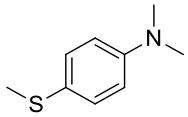
N,N,4-trimethylaniline:[1] ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.03 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 2.88 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 149.53, 130.00, 126.39, 113.56, 41.43, 20.48; MS (EI): m/z (rel. Int) 135.



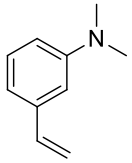
3- Chloro-N,N-dimethylaniline:[1] ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.13 (t, J = 8.1 Hz, 1H), 6.70 – 6.56 (m, 3H), 2.94 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.26, 135.31, 130.50, 116.33, 112.51, 111.04, 40.69; MS (EI): m/z (rel. Int) 155.



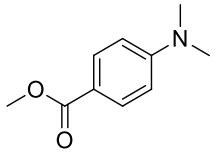
3-iodo-N,N-dimethylaniline:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 – 7.02 (m, 2H), 6.96 – 6.91 (m, 1H), 6.69 – 6.65 (m, 1H), 2.93 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.68, 130.51, 125.33, 121.21, 111.70, 95.67, 40.45; MS (EI): m/z (rel. Int) 247.



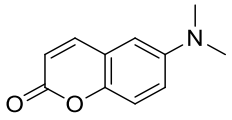
N,N-dimethyl-4-(methylthio)aniline: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (d, J = 9.0 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 2.81 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 134.63, 131.47, 128.45, 113.83, 41.02, 19.24; MS (EI): m/z (rel. Int) 167.



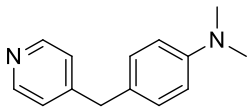
N,N-dimethyl-3-vinylaniline: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.23 (t, J = 7.6 Hz, 1H), 6.88 – 6.77 (m, 2H), 6.77 – 6.65 (m, 2H), 5.78 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 3.00 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 151.61, 138.84, 138.39, 129.65, 115.06, 113.46, 112.88, 111.08, 40.94; MS (EI): m/z (rel. Int) 147.



Methyl 4-(dimethylamino)benzoate: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.76 (d, J = 9.1 Hz, 2H), 6.56 (d, J = 9.1 Hz, 2H), 3.72 (s, 3H), 2.92 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.72, 153.99, 131.58, 117.44, 111.22, 51.79, 40.39; MS (EI): m/z (rel. Int) 179.



6-(dimethylamino)-2H-chromen-2-one: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 9.1 Hz, 1H), 6.97 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.70 (d, *J* = 3.0 Hz, 1H), 6.32 (d, *J* = 9.5 Hz, 1H), 2.96 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 161.52, 148.05, 146.58, 144.03, 119.58, 117.42, 117.22, 116.97, 109.50, 41.01; MS (EI): *m*/*z* (rel. Int) 189.

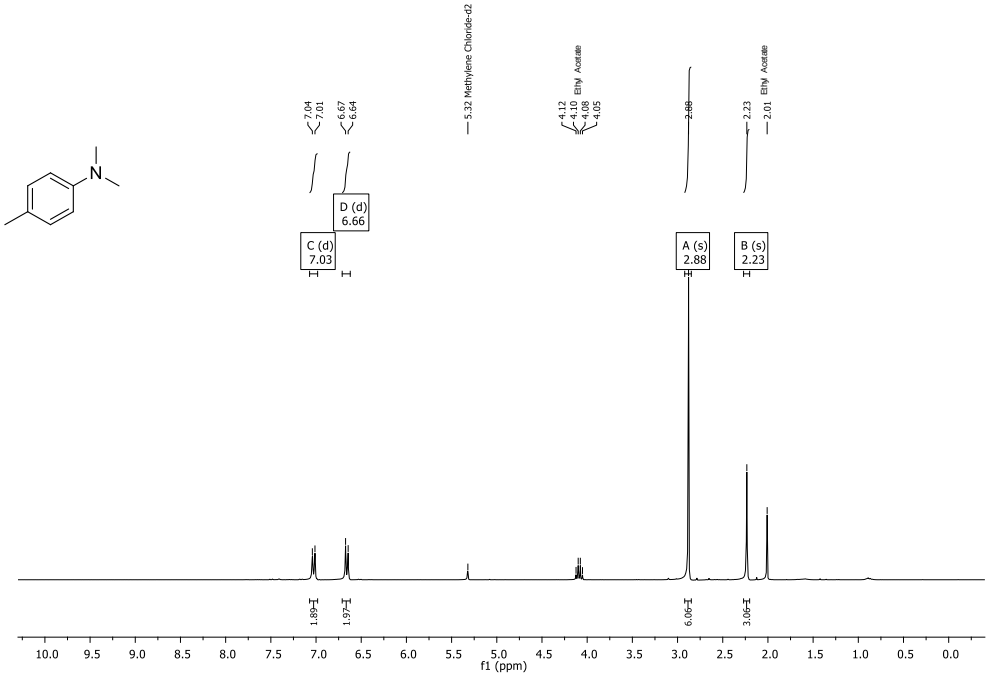


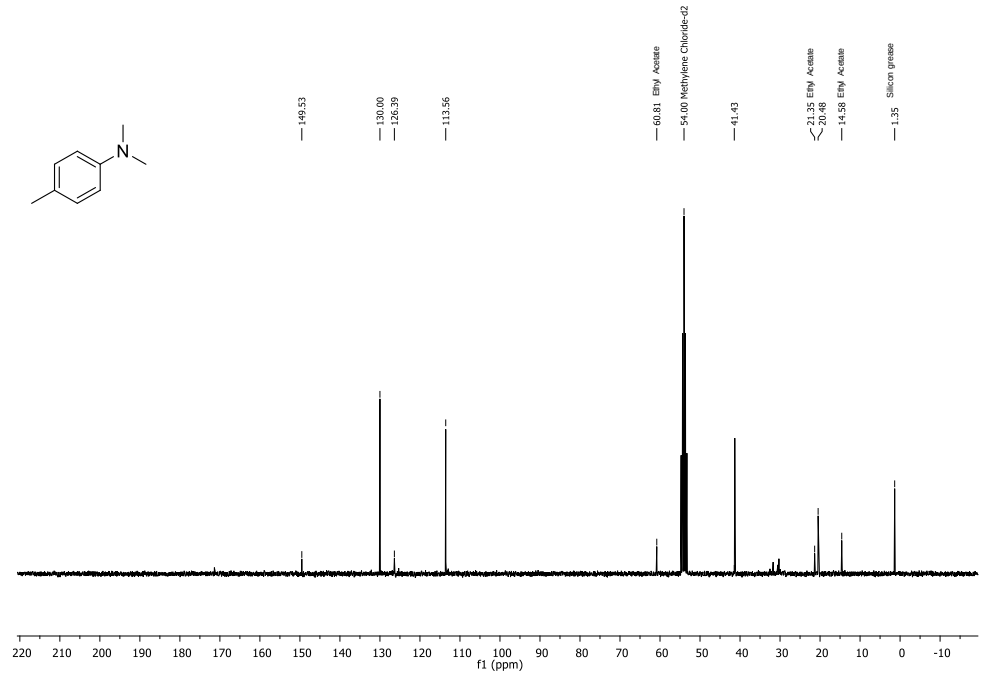
N,N-dimethyl-4-(pyridin-4-ylmethyl)aniline: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.41 – 8.36 (m, 2H), 7.08 – 7.02 (m, 4H), 6.73 – 6.66 (m, 2H), 3.85 (s, 2H), 2.92 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.97, 149.95, 130.13, 128.27, 127.42, 124.59, 113.39, 41.02, 40.77; MS (EI): *m*/*z* (rel. Int) 212.

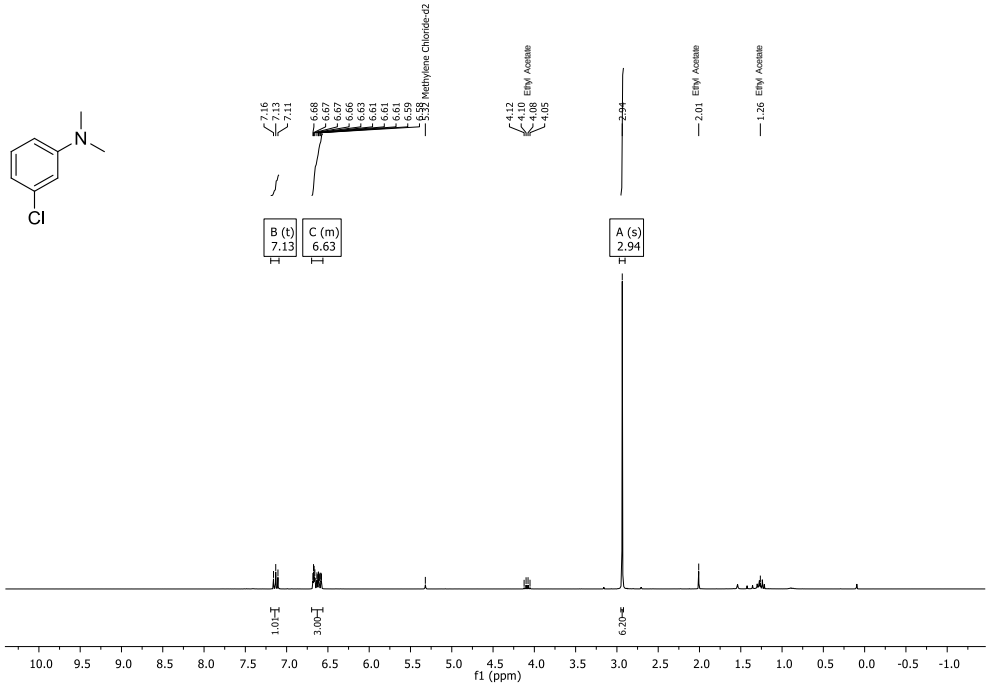
6. References.

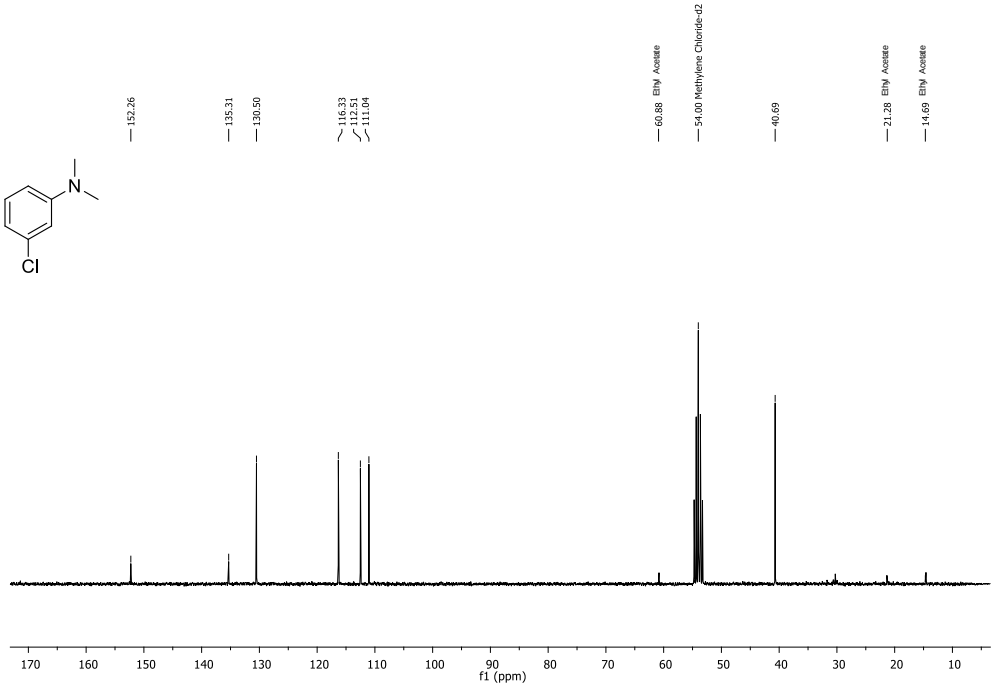
[1] X. Jiang, C. Wang, Y. Wei, D. Xue, Z. Liu and J. Xiao, *Chem. Eur. J.* **2014**, *20*, 58–63.

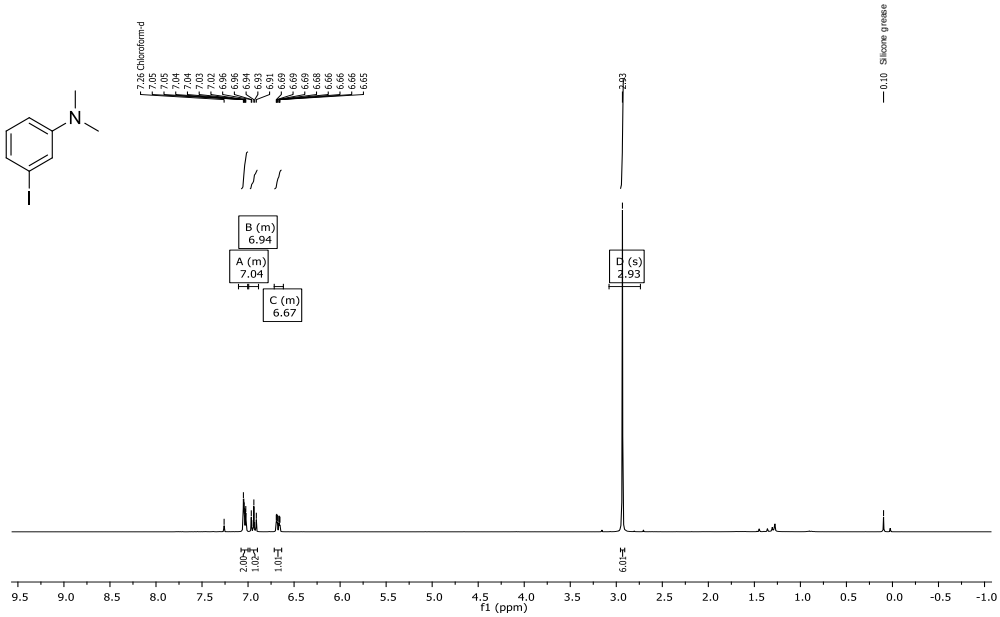
7. ^{1}H NMR and ^{13}C NMR spectra of isolated products.

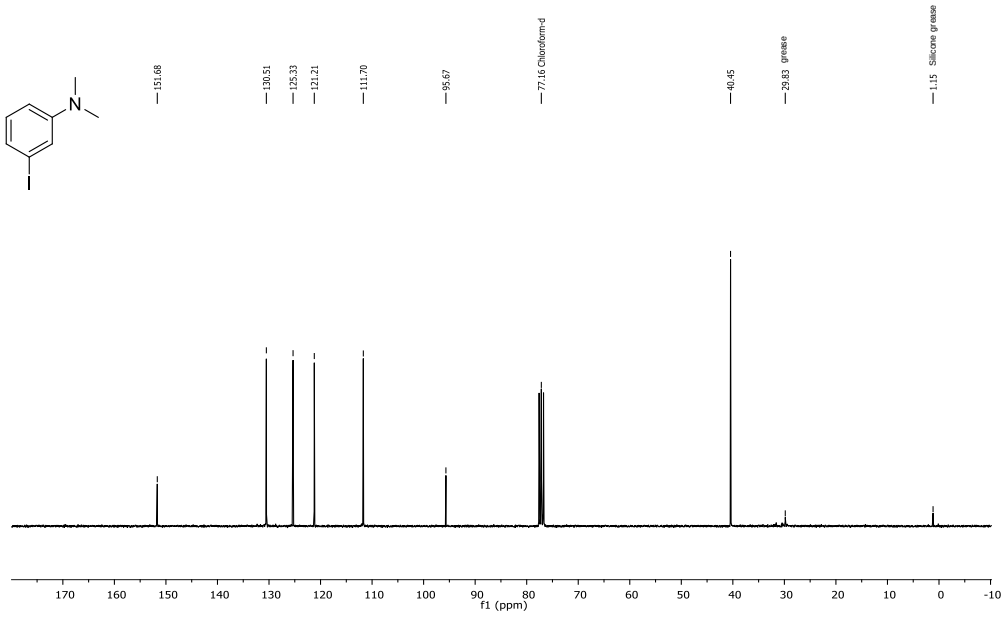


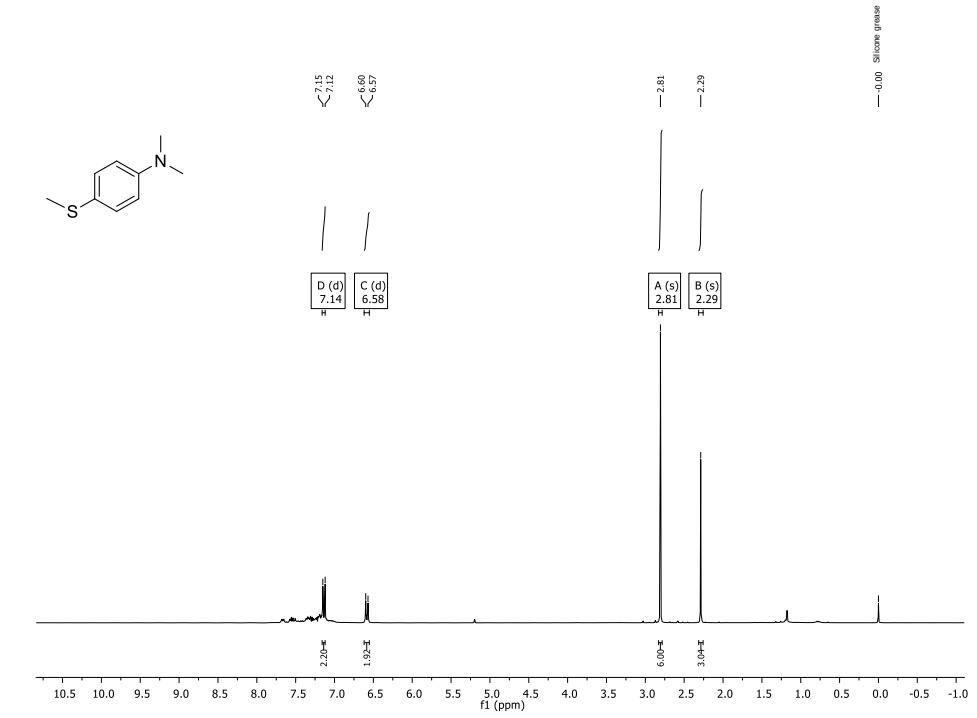


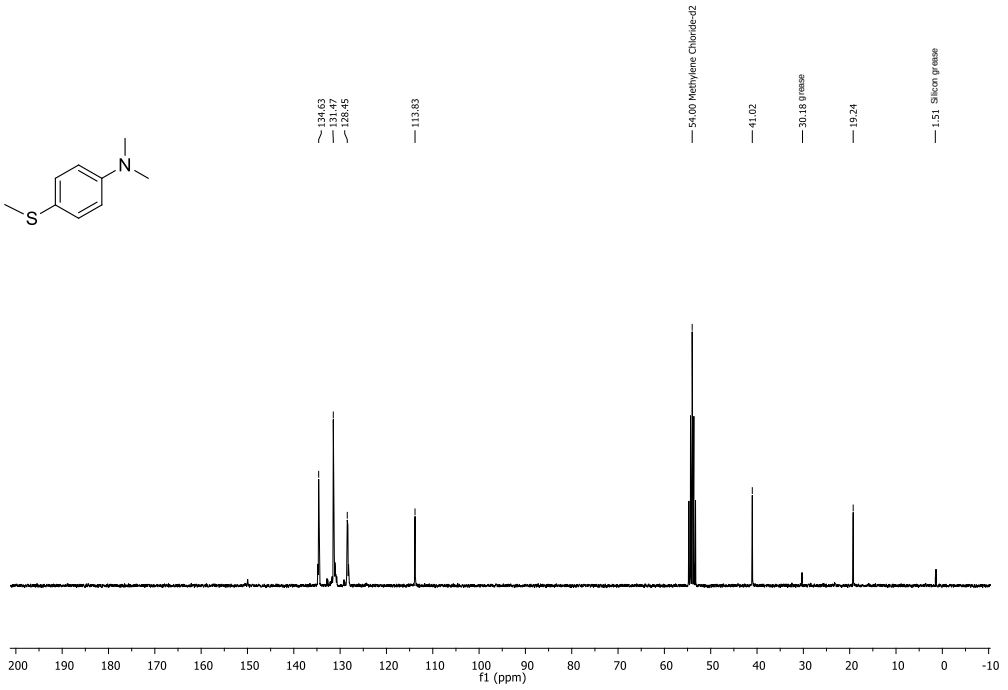

7.16
7.13
7.11
6.68
6.67
6.67
6.66
6.65
6.61
6.61
6.61
6.59
5.32 Methylene Chloride-d2
4.12
4.10 Ethyl Acetate
4.08
4.05
2.94
2.01 Ethyl Acetate
1.26 Ethyl Acetate
B (t)
7.13
C (m)
6.63
A (s)
2.94
1.01
3.00
6.20
f1 (ppm)

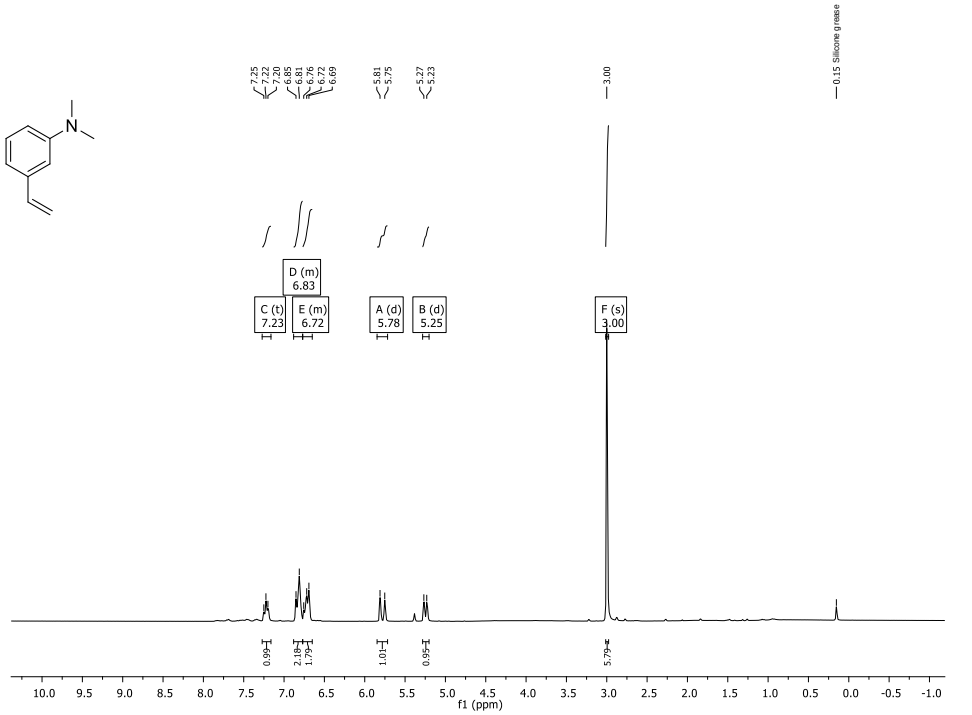

152.26
135.31
130.50
116.33
113.51
111.04
60.88 Ethyl Acetate
54.00 Methylene Chloride-d2
40.69
21.28 Ethyl Acetate
14.69 Ethyl Acetate
f1 (ppm)

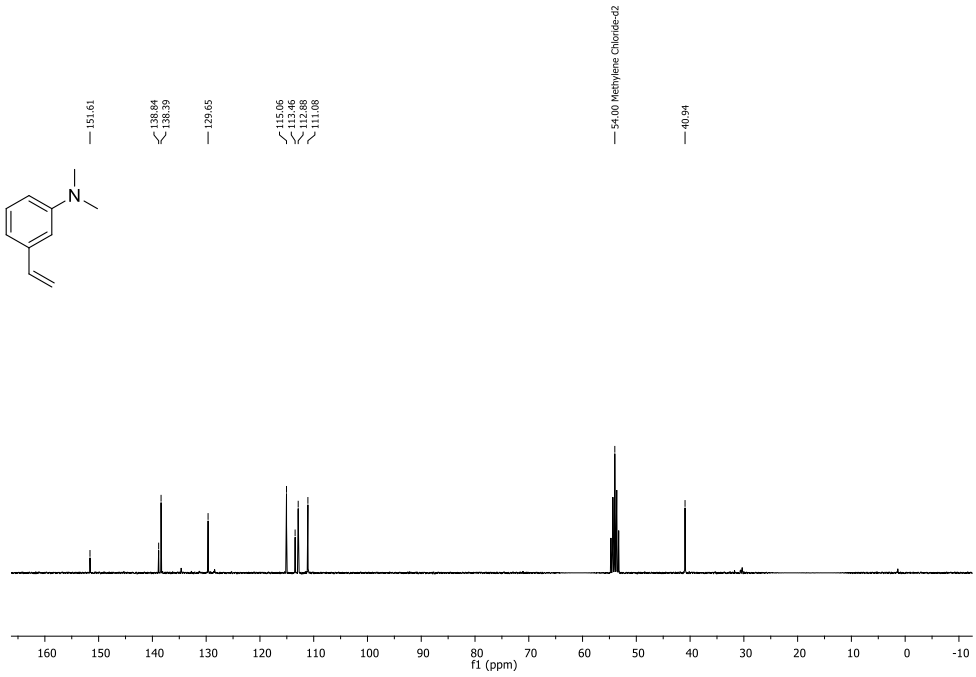

7.26 Chloroform-d
2.93
0.10 Silicone grease
B (m) 6.94
A (m) 7.04
C (m) 6.67
D (s) 2.93
2.00
1.02
1.01
6.01
f1 (ppm)

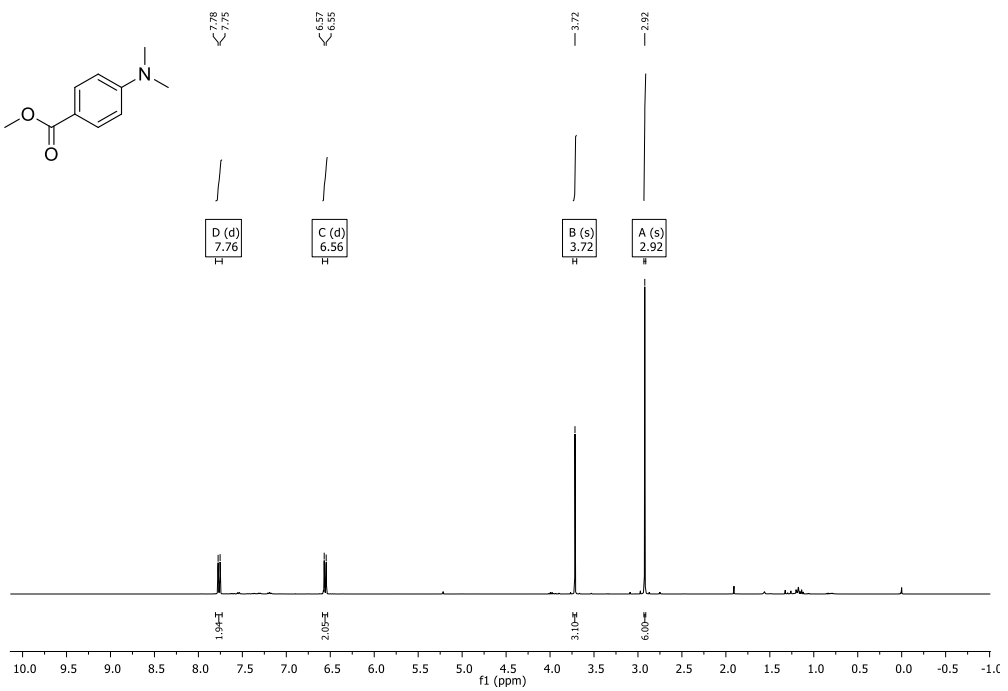

151.68
130.51
125.33
121.21
111.70
95.67
77.16 Chloroform-d
40.45
29.83 grease
1.15 Silicone grease
f1 (ppm)

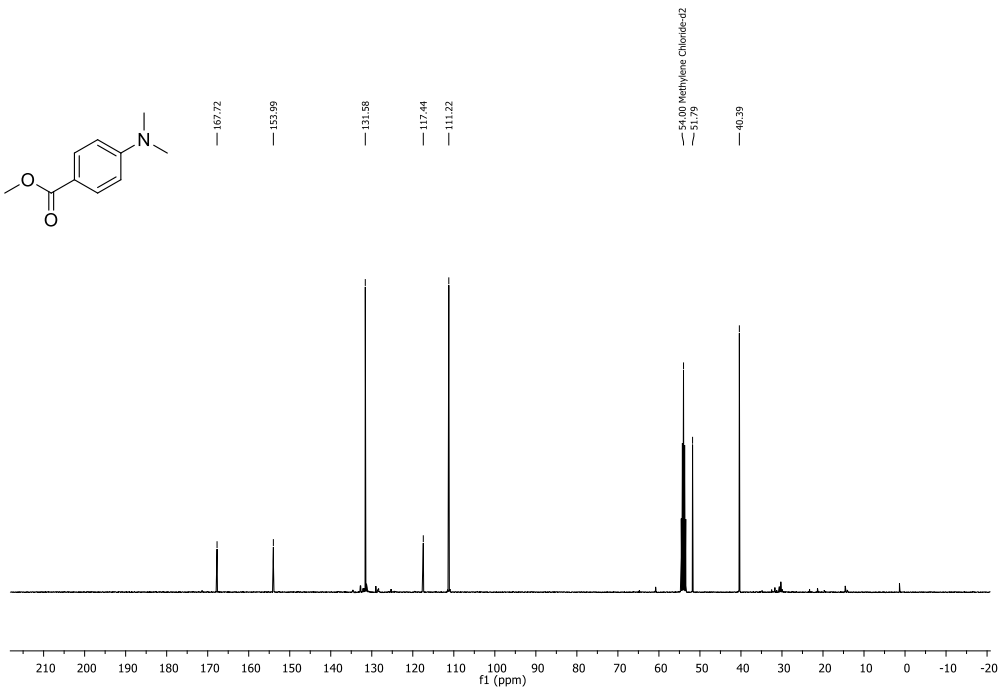

7.15
7.12
6.60
6.57
2.81
2.29
-0.00
Silicone grease
D (d)
7.14
H
C (d)
6.58
H
A (s)
2.81
H
B (s)
2.29
H
2.20
1.92
6.00
3.04
f1 (ppm)

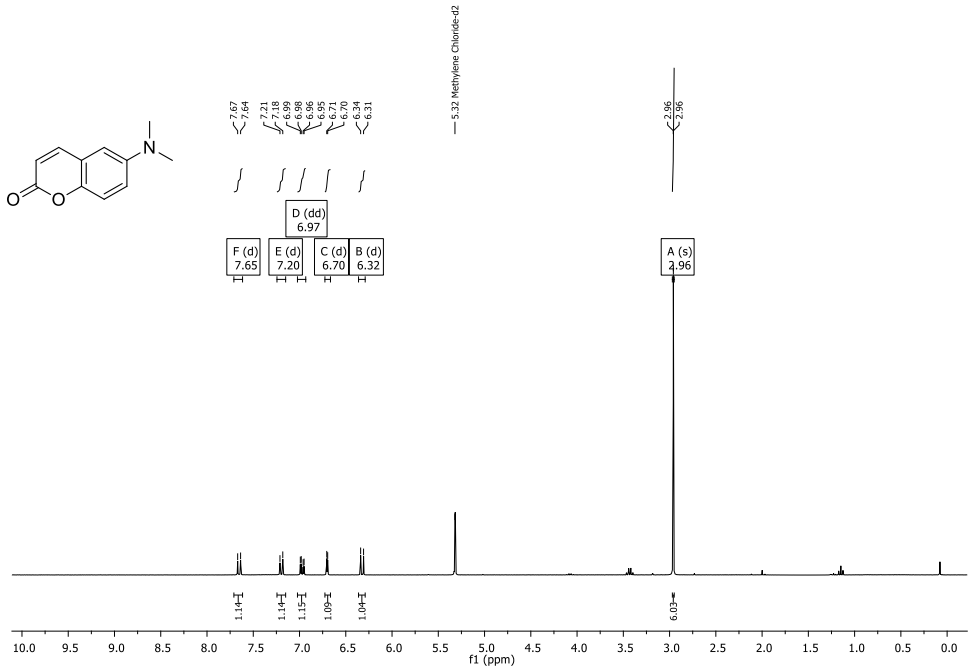

134.63
131.47
128.45
113.83
54.00 Methylene Chloride-d2
41.02
30.18 grease
19.24
1.51 Silicon grease
f1 (ppm)

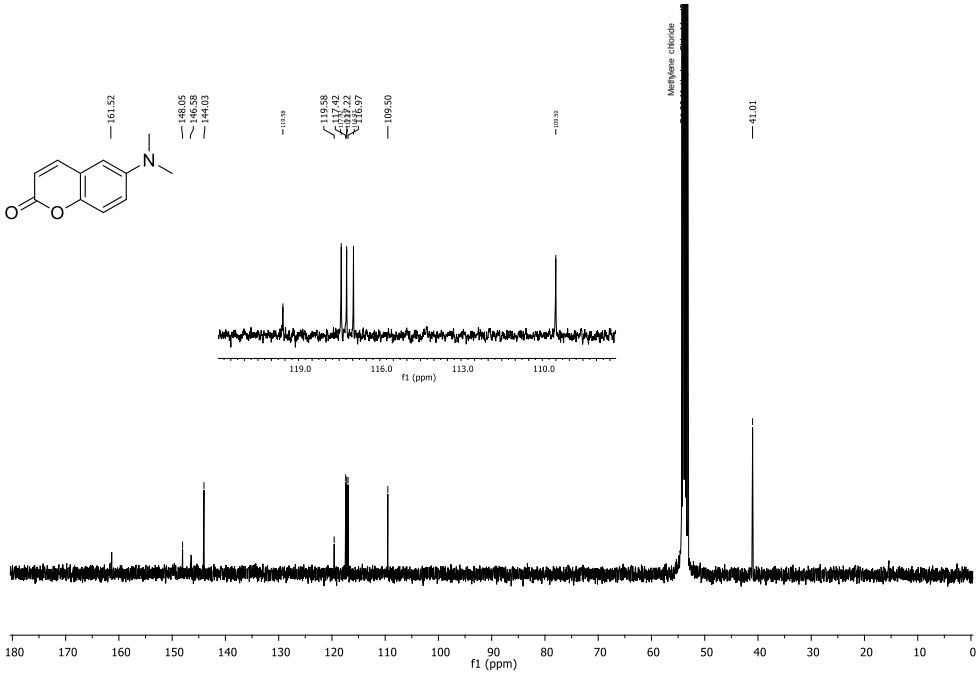

7.25
7.22
7.20
6.85
6.81
6.76
6.72
6.69
5.81
5.75
5.27
5.23
3.00
0.15 Silicone grease
D (m)
6.83
C (t)
7.23
E (m)
6.72
A (d)
5.78
B (d)
5.25
F (s)
3.00
0.99
2.18
1.79
1.01
0.95
5.79
f1 (ppm)

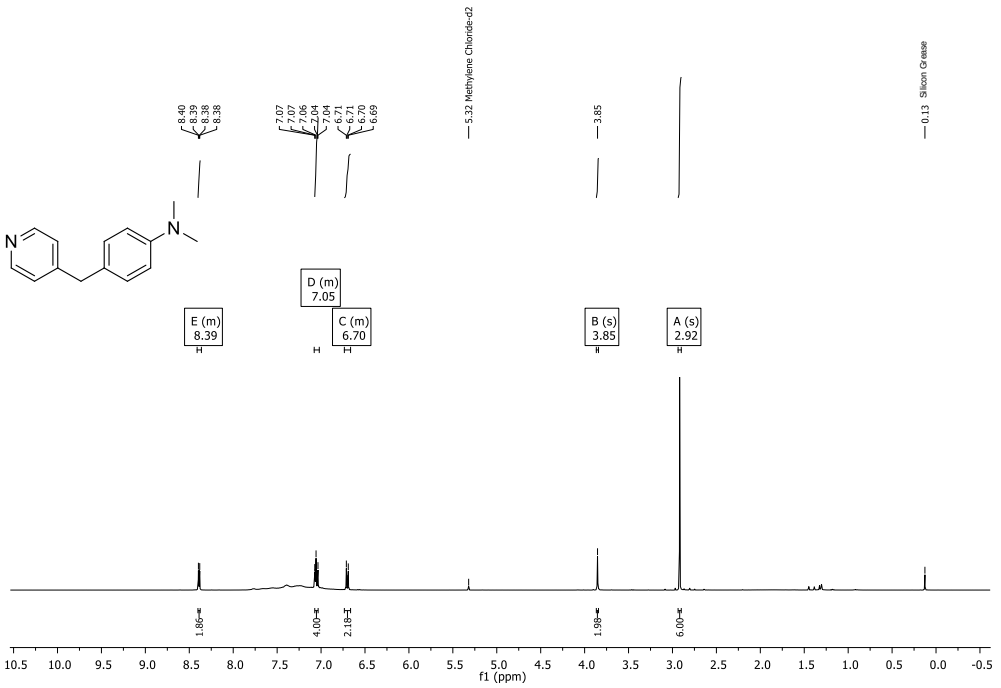

151.61
138.84
138.39
129.65
115.06
113.46
112.88
111.08
54.00 Methylene Chloride-d2
40.94
f1 (ppm)

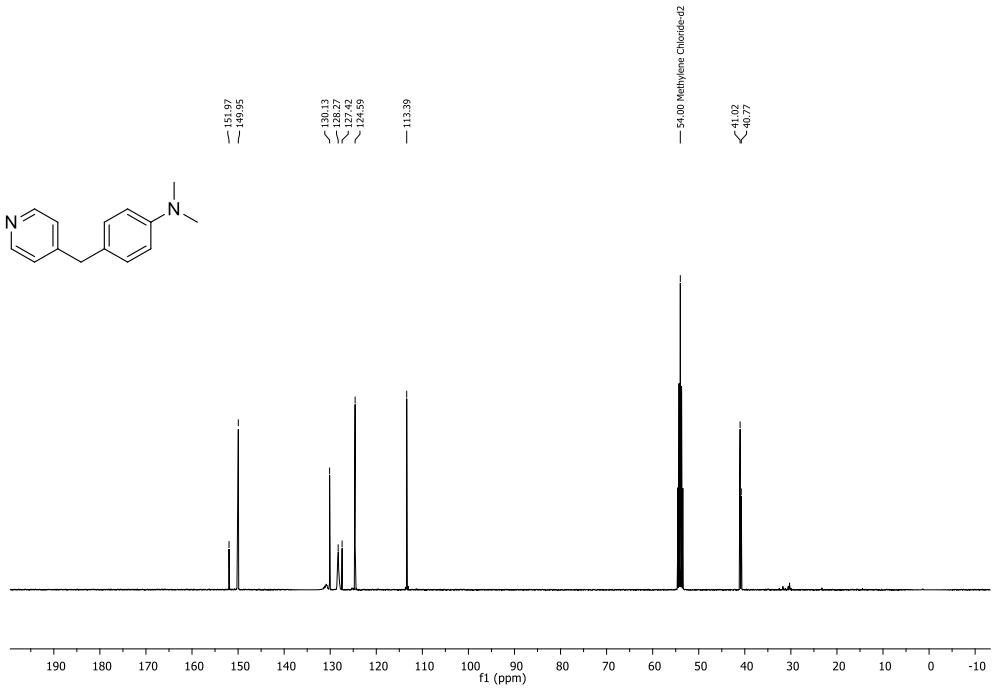

7.78
7.75
6.57
6.55
3.72
2.92
D (d)
7.76
C (d)
6.56
B (s)
3.72
A (s)
2.92
1.94
2.05
3.10
6.00
f1 (ppm)


167.72
153.99
131.58
117.44
111.22
54.00 Methylene Chloride-d2
51.79
40.39
f1 (ppm)


7.67
7.64
7.21
7.18
6.99
6.98
6.96
6.95
6.71
6.70
6.34
6.31
5.32 Methylene Chloride-d2
2.96
2.96
D (dd)
6.97
F (d)
7.65
E (d)
7.20
C (d)
6.70
B (d)
6.32
A (s)
2.96
1.14
1.14
1.15
1.09
1.04
6.03
f1 (ppm)


161.52
148.05
146.58
144.03
119.58
117.42
117.22
116.97
109.50
Methylene chloride
41.01
119.0
116.0
113.0
110.0
f1 (ppm)
f1 (ppm)


8.40
8.39
8.38
8.38
7.07
7.07
7.06
7.04
7.04
6.71
6.71
6.70
6.69
5.32 Methylene Chloride-d2
3.85
0.13 Silicon Grease
N
N
D (m)
7.05
E (m)
8.39
C (m)
6.70
B (s)
3.85
A (s)
2.92
1.86
4.00
2.18
1.98
6.00
10.5 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 -0.5
f1 (ppm)


151.97
149.95
130.13
128.27
127.42
124.59
113.39
54.00 Methylene Chloride-d2
41.02
40.77
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)