nBu_4NI-Catalyzed Unexpected Amide Bond Formation Between Aldehydes and Aromatic Tertiary Amines

Wenpeng Mai*, Ge Song, Jinwei Yuan, Liangru Yang, Gangchun Sun*,
Yongmei Xiao, Pu Mao and Lingbo Qu

Chemistry and Chemical Engineering School, Henan University of Technology, Zhengzhou Henan 450001, China

Email: maiwp@yahoo.com; sungangchun@163.com

Supporting Information

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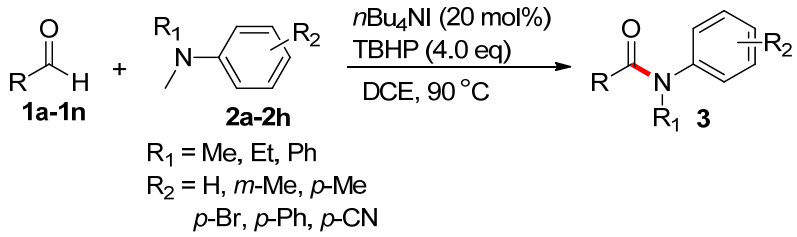
I. General Information

All experiments were carried out using common flask in Air. Aldehydes, aromatic tertiary amines, nBu$_4$NI and TBHP (70% in water) were purchased from commercial suppliers and used as received unless otherwise noted. All solvents and other commercially available reagents were purchased from Acros or TCI companies and used directly. Reactions were monitored by thin layer chromatography (TLC) (*Qingdao Haiyang Chemical Co. Ltd. Silica gel 60 F254)*. Products were detected using a UV/Vis lamp (254 nm). Column chromatography was performed on *Qingdao Haiyang Chemical Co. Ltd. Gel 60* (200–300 mesh). The ^{1}H and ^{13}C NMR spectras were obtained on a Bruker 400 MHz NMR Fourier transform spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm) multiplicity, and coupling constant (Hz). Hertz (Hz).The Spectra are referenced against the internal solvent ($CDCl_3$, δ 1H= 7.26 ppm, ^{13}C= 77.0 ppm; DMSO-d6, δ 1H= 2.50 ppm, ^{13}C= 40.0 ppm). Data is reported as follows: s= singlet, d= doublet, t= triplet, q=quartet and m= multiplet. ESI-MS spectra were recorded on a Bruker Esquire 3000. High resolution mass spectra (HR MS) were obtained on a Waters Micromass Q-Tof MicroTM instrument using the ESI technique.

II. Experimental Section

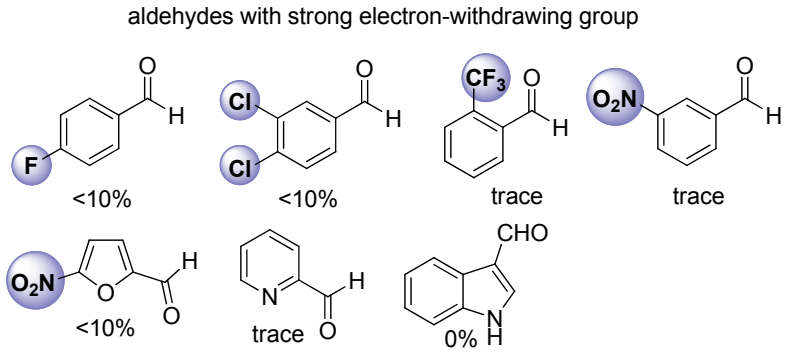
(a) General Procedure:



R$_1$ = Me, Et, Ph
R$_2$ = H, *m*-Me, *p*-Me
p-Br, *p*-Ph, *p*-CN

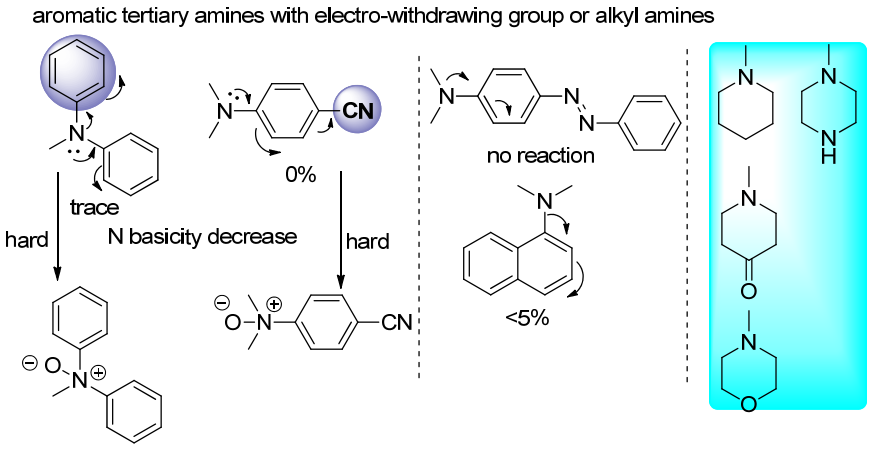
An 50 mL vial was charged with magnetic stir bar, aldehydes (**1**, 2.0 mmol), aromatic tertiary amines (**2**, 1.0 mmol), *n*Bu$_4$NI (0.2 mmol), TBHP 70 % in water (4.0 mmol), followed by DCE (3 mL). After stirring at 90℃ for 10 h, The reaction mixture was quenched with a saturated solution of Na_2SO_3 (for removal of excess TBHP) and extracted with CH_2Cl_2 (20ml×2). The combined organic phase was dried by Na_2SO_4 and then evaporated under reduced pressure. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of Ethyl acetate in Petroleum: 10 ~ 25%, v/v).

(b) Under the optimized conditions, the following substrates were ineffective in this transformation under current conditions.



Scheme S1

For aldehydes, we don't know why they do not work in this reaction until now.



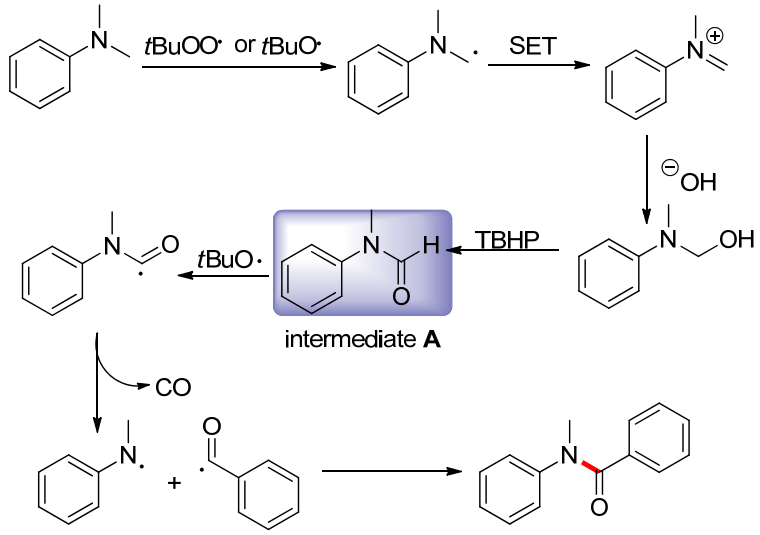
Scheme S2

For aromatic tertiary amines, its reactivity is related with N basicity due to the mechanism of previous reports and no reactivity is shown in alkyl amines.

(c) Mechanism studies

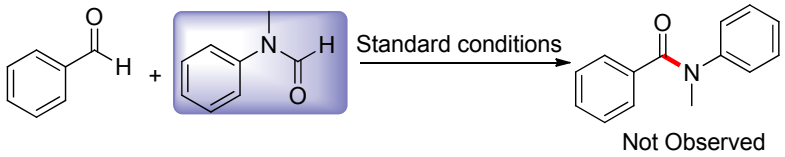
To clarify the mechanism of the reaction, we did some controlled experiments to investigate what processes involved in this transformation. At first, we thought aromatic tertiary amine was demethylated *via* CO release by radical due to our previous work (*Chem. Commun.*, 2012, **48**, 10117) and Wan's study (*Angew. Chem. Int. Ed*. 2012, **51**, 3231).

Hypothetical Mechanism I[1]:

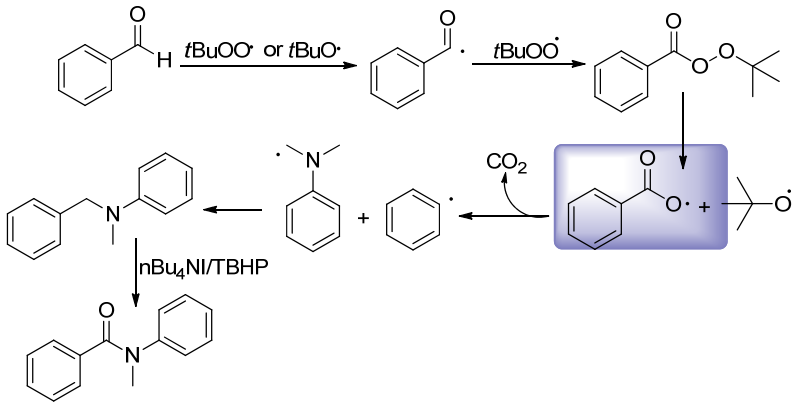


Scheme S3 hypothetical route Ⅰ

But when we used intermediate **A** in scheme S3 as substrate to react with benzaldehyde, no desired product was observed. So hypothetical mechanism I maybe incorrect.

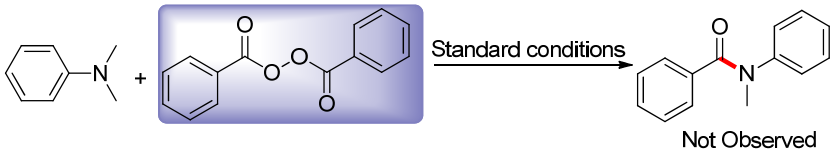


Hypothetical Mechanism II[2]:

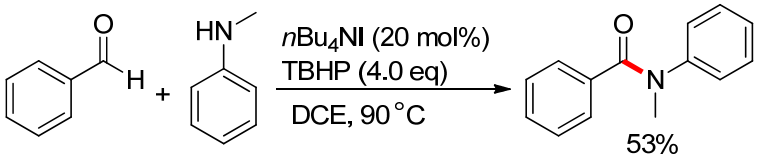


Scheme S4 hypothetical route Ⅱ

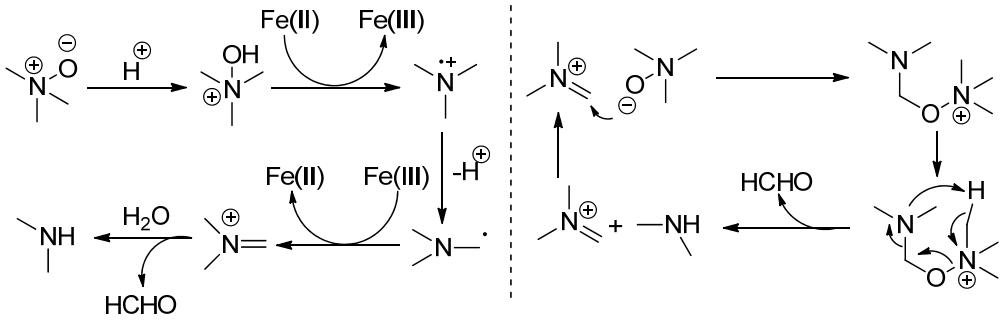
But when we used BPO as substrate to react with *N,N*-dimethylaniline, no desired product was observed. So hypothetical mechanism II maybe incorrect.



Then we thought demethylation of *N,N*-dimethylaniline in this process has great possibility. So we took *N*-methylaniline as substrate to react with benzaldehyde and obtained the good result.



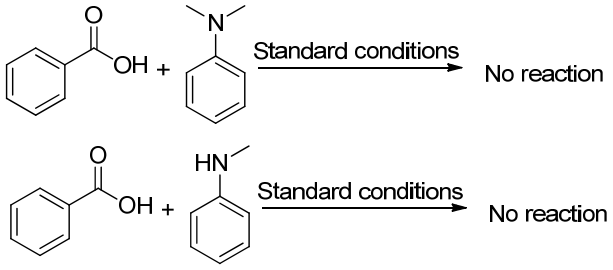
After having consulted papers, we found Thomas and Peter have reported N-demethylation of tertiary amine using the non-classical Polonovski reaction[3].

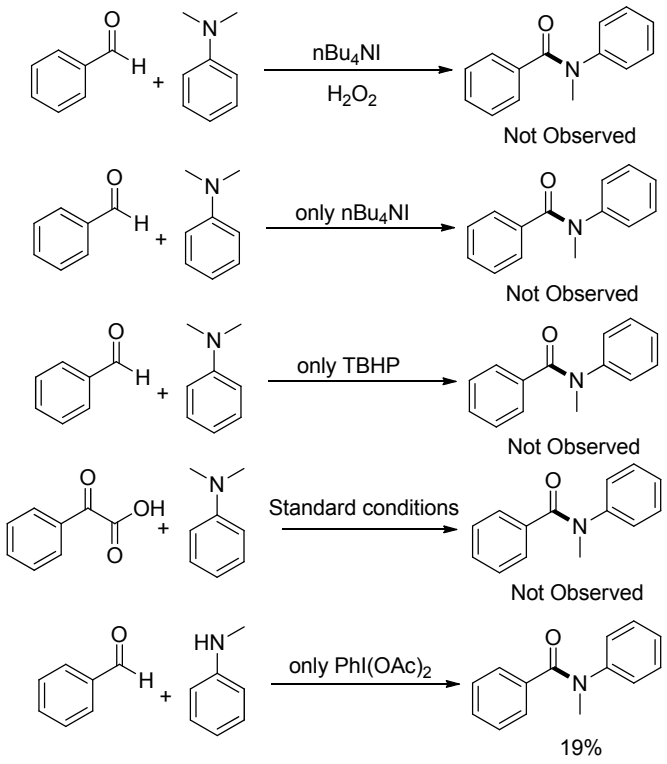


Peter's proposed mechanism of the iron salt-mediated Polonovski reaction

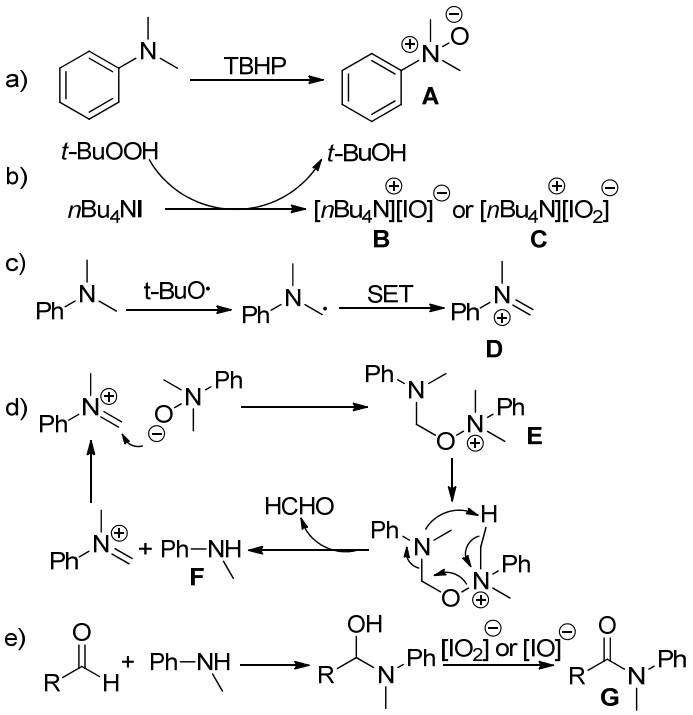
Thomas's mechanism of the autocatalytic deoxygenative demethylation reaction

After other controlled experiments as following, we seem to understand this transformation. On the basis of Thomas's and Peter's studies, we provide a proposed mechanism here.





Scheme S5 Investigations into the reaction mechanism.



Scheme S6 proposed mechanism

III References and Notes

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(9) Vorokov, M. G.; Tsyrendorzhieva, I. P.; Rakhlin, V. I. *Russ. J. Org. Chem,* **2008**, *44*, 481.
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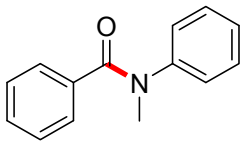
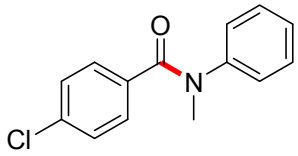
NMR Data of Products

N-Methyl-N-phenyl-benzamide (3aa) [6,7]



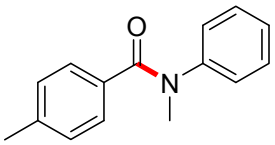
(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.27-7.32 (m, 2H), 7.21-7.26 (m, 6H), 7.04-7.19 (m, 2H), 3.52 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.7, 144.9, 135.9, 129.6, 129.2, 128.7, 127.7, 126.9, 126.5, 38.41

4-Chloro-N-methyl-N-phenyl-benzamide (3ba) [7]



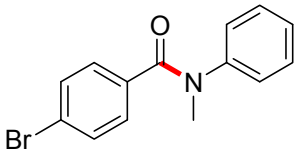
(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.24-7.28 (m, 4H), 7.14-7.21 (m, 3H), 7.04-7.06 (m, 2H), 3.51 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 169.5, 144.7, 135.7, 134.3, 130.3, 129.4, 128.0, 126.9, 126.8, 38.5

4-methyl-N-methyl-N-phenyl-benzamide (3ca)[6]



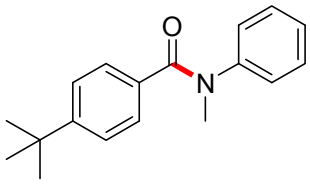
(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.14-7.28 (m, 5H), 7.05-7.07 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.51 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.7, 145.2, 139.8, 133.0, 129.1, 128.9, 128.4, 126.9, 126.3, 38.5, 21.3

4-Bromo-N-methyl-N-phenyl-benzamide (3da)[10]



^{1}H NMR (400MHz, $CDCl_3$) 7.27-7.33 (m, 2H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.196 (t, *J* = 8.4 Hz, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.51 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 169.5, 144.6, 134.8, 131.0, 130.4, 129.4, 126.9, 126.8, 124.1, 38.5

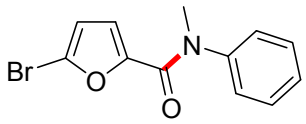
4-tert-Butyl-N-methyl-N-phenyl-benzamide (3ea)



(sticky yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.24-7.26 (m, 4H), 7.17-7.21 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 3.51 (s, 3H), 1.25 (s，9H).

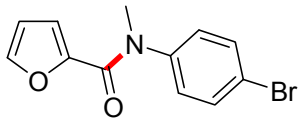
^{13}C NMR (100MHz, $CDCl_3$) 170.6, 152.9, 145.2, 132.8, 129.1, 128.7, 126.8, 126.3, 124.6, 38.6, 34.7, 31.1. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{18}H_{21}NNaO^+$: 290.1521, found: 290.1525

5-Bromo-furan-2-carboxylic acid methyl-phenyl-amide (3fa)



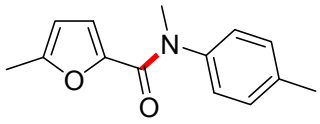
^{1}H NMR (400MHz, $CDCl_3$) 7.39-7.45 (m, 3H), 7.21-7.24 (m, 2H), 6.15 (d, *J* = 3.6 Hz, 1H), 5.85 (d, *J* = 3.6 Hz, 1H), 3.44 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 158.2, 148.9, 143.7, 129.7, 128.1, 127.4, 125.3, 118.6, 112.9, 38.5. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{12}H_{10}BrNNaO_2^+$: 301.9793, found: 301.9801

Furan-2-carboxylic acid (4-bromo-phenyl)-methyl-amide (3gd)



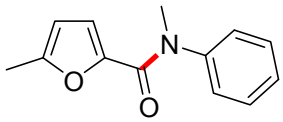
(yellow solid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.52-7.57 (m, 2H), 7.33 (s, 1H), 7.07-7.12 (m, 2H), 6.29 (d, *J* = 3.6 Hz, 1H), 6.15 (d, *J* = 3.6 Hz, 1H) 3.43 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 159.2, 144.4, 143.3, 132.7, 128.9, 123.8, 121.3, 116.8, 111.1, 38.4. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{12}H_{10}BrNNaO_2^+$: 301.9793, found: 301.9797

5-Methyl-furan-2-carboxylic acid methyl-p-tolyl-amide (3hc)



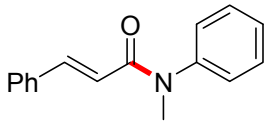
^{1}H NMR (400MHz, $CDCl_3$) 7.23 (d, *J* = 8.0 Hz, 2H), 7.10-7.12 (m, 2H), 5.80 (d, *J*= 3.2 Hz, 1H), 5.55 (d, *J* = 3.2 Hz, 1H), 3.40 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 159.6, 154.8, 145.4, 141.8, 137.8, 130.2, 127.4, 117.7, 107.4, 38.5, 21.1, 13.6. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{14}H_{15}NNaO_2^+$: 252.1000, found: 252.1003

5-Methyl-furan-2-carboxylic acid methyl-phenyl-amide (3ha)



^{1}H NMR (400MHz, $CDCl_3$) 7.35-7.44 (m, 3H), 7.22-7.24 (m, 2H), 5.80 (d, *J* = 3.6 Hz, 1H), 5.65 (d, *J* = 3.6 Hz, 1H), 3.44 (s, 3H), 2.21 (s, 3H) . **^{13}C NMR (100MHz, $CDCl_3$)** 159.5, 154.8, 144.4, 129.6, 129.5, 127.8, 127.5, 117.8, 107.5, 38.4, 13.6. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{13}H_{13}NNaO_2^+$: 238.0844, found: 238.0851

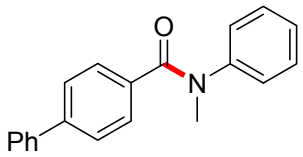
N-Methyl-3,N-diphenyl-acrylamide (3ia)[8]



^{1}H NMR (400MHz, $CDCl_3$) 7.7 (d, *J* = 15.6 Hz, 1H), 7.44-7.48 (m, 2H),

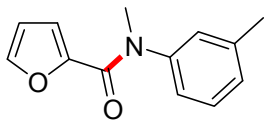
7.37-7.41 (m, 1H), 7.29-7.33 (m, 5H), 7.25-7.27 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.44 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)** 166.2, 143.6, 141.7, 135.2, 129.6, 129.5, 128.7, 127.9, 127.6, 127.3, 118.8, 37.6

Biphenyl-4-carboxylic acid methyl-phenyl-amide (3ja)[6]



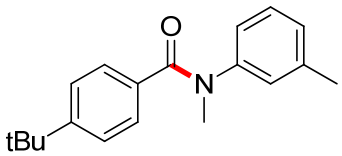
(pale yellow liquid) **^{1}H NMR (400MHz, CDCl$_3$)** 7.55 (d, *J* = 7.2 Hz, 2H), 7.39-7.44 (m, 6H), 7.33-7.38 (m, 1H), 7.25-7.27 (m, 2H), 7.15-7.21 (m, 1H), 7.09-7.11 (m, 2H), 3.55 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)** 170.4, 145.0, 142.3, 140.1, 134.7, 129.4, 129.3, 128.8, 127.7, 127.1, 126.9, 126.5, 126.4, 38.5

Furan-2-carboxylic acid methyl-m-tolyl-amide (3gb)



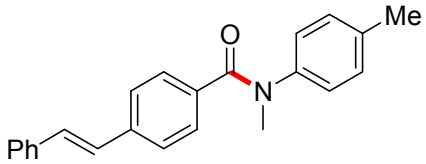
(white solid) **^{1}H NMR (400MHz, CDCl$_3$)** 7.36 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.21 (d, *J* = 3.6 Hz, 1H), 5.79 (d, *J* = 3.6 Hz, 1H), 3.43 (s, 3H), 2.38 (s, 3H). **^{13}C NMR (100MHz, CDCl$_3$)** 159.3, 147.0 144.2, 144.0, 139.7, 129.4, 128.7, 128.0, 124.4, 116.2, 110.9, 38.5, 21.3. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{13}H_{13}NNaO_2^+$: 238.0844, found: 238.0846

4-tert-Butyl-N-methyl-N-m-tolyl-benzamide (3eb)



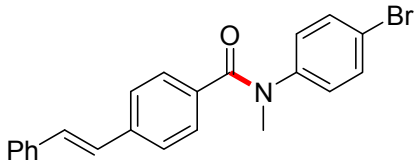
(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.25-7.28 (m, 2H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6Hz, 1H), 6.90 (s, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.49 (s, 3H) , 2.27 (s, 3H), 1.25 (s, 9H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.6, 152.8, 145.0, 139.0, 132.9, 128.8, 128.7, 127.3, 127.1, 124.6, 124.0, 38.6, 34.7, 31.1, 21.2. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{19}H_{23}NNaO^+$: 304.1677, found: 304.1675

N-Methyl-4-styryl-N-p-tolyl-benzamide (3kc)



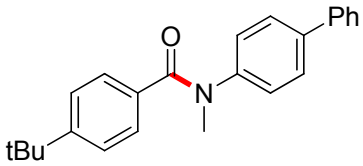
(pale yellow solid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.50 (d, *J* = 7.6 Hz 2H), 7.32-7.38 (m, 6H), 7.05 (m, 6H), 3.50 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.3, 142.4, 138.4, 137.0, 136.4, 134.9 129.9, 129.8, 129.3, 128.7, 127.9, 127.8, 126.7, 126.6, 125.7, 38.6, 21.0. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{23}H_{21}NNaO^+$: 350.1521, found: 350.1516

N-(4-Bromo-phenyl)-N-methyl-4-styryl-benzamide (3kd)



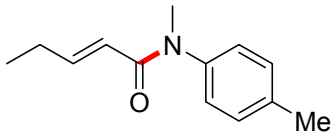
(colorless liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.57 (d, *J* = 8.8 Hz, 1H), 7.49-7.51 (t, *J* = 8.8 Hz, 2H), 7.35-7.40 (m, 6H), 7.30-7.32 (m, 1H), 6.94-7.14 (m, 5H), 3.50 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.2, 144.1, 138.9, 136.9, 134.3, 132.7, 132.4, 130.3, 129.3, 128.7, 128.4, 128.0, 127.6, 126.7, 126.0, 123.8, 38.4. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{22}H_{18}BrNNaO^+$: 414.0469, found: 414.0460

N-Biphenyl-4-yl-4-tert-butyl-N-methyl-benzamide (3ee)



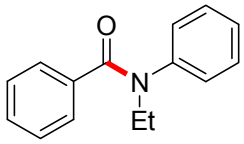
(sticky yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.57 (d, *J* = 8.4Hz 2H), 7.51 (dt, *J* = 8.8 Hz, *J'* = 2.4Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.38 (tt, *J* = 1.2 Hz, J' = 7.2 Hz, 1H), 7.30-7.32 (m, 2H), 7.21-7.28 (m, 2H), 7.13-7.16 (m, 2H), 3.55 (s, 3H), 1.25 (s, 9H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.7, 153.1, 144.4, 140.0, 139.0, 132.8, 128.9, 128.8, 127.7, 127.5, 127.0, 126.9, 124.8, 38.6, 34.7, 31.1. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{24}H_{25}NNaO^+$: 366.1834, found: 366.1838

Pent-2-enoic acid methyl-p-tolyl-amide (3lc)



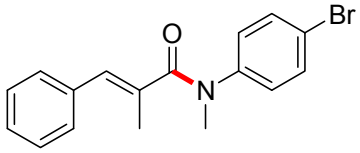
(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.21-7.24 (m, 2H), 7.06-7.09 (m, 2H), 6.91-6.98 (m, 1H), 5.77 (d, *J* = 15.2 Hz, 1H), 3.33 (s, 3H), 2.40 (s, 3H), 2.08 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 166.4, 147.2, 141.2, 137.2, 130.1, 130.0, 127.1, 120.5, 37.4, 25.3, 21.0, 12.6. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{13}H_{17}NNaO^+$: 226.1208, found: 226.1215

N-Ethyl-N-phenyl-benzamide (3af)[9]



^{1}H NMR (400MHz, $CDCl_3$) 7.26 (t, *J* = 7.6 Hz, 2H), 7.21-7.25 (m, 3H), 7.14-7.18 (m, 3H), 7.05 (d, *J* = 7.2 Hz, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 170.2, 143.2, 136.3, 129.4, 129.1, 128.7, 127.9, 127.7, 126.6, 45.4, 13.0

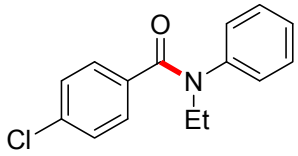
N-(4-Bromo-phenyl)-2,N-dimethyl-3-phenyl-acrylamide (3md)



(yellow liquid) **^{1}H NMR (400MHz, $CDCl_3$)** 7.51 (d, *J* = 8.8 Hz 2H), 7.31

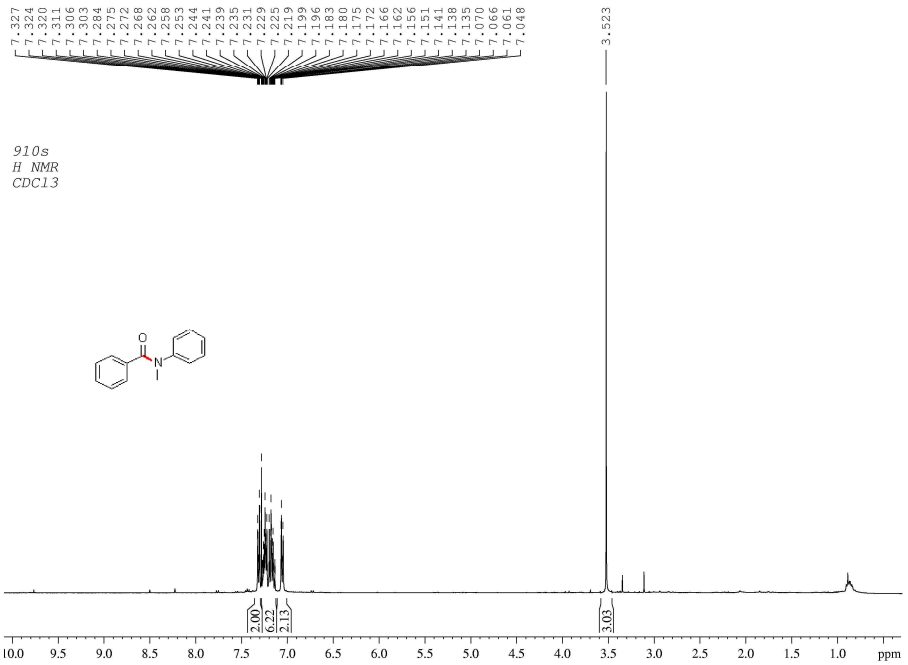
(d, J = 7.6 Hz, 2H), 7.25-7.27 (m, 1H), 7.10 (d, J = 6.8 Hz, 4H), 6.64 (s, 1 H), 3.41 (s, 3H), 1.86 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 173.1, 143.9, 135.9, 134.1, 133.2, 132.4, 128.9, 128.3, 128.0, 127.6, 120.2, 37.8, 16.3. **ESI-HRMS**: $[M+Na]^+$ m/z calcd for $C_{17}H_{16}BrNNaO^+$: 352.0313, found: 352.0309

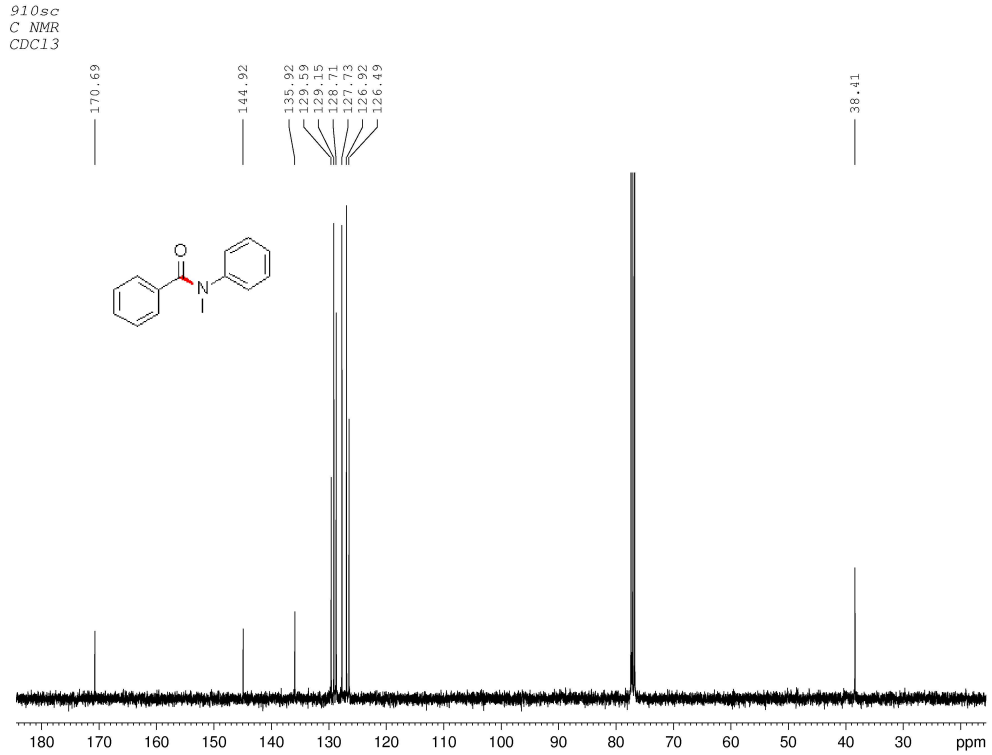
4-Chloro-N-ethyl-N-phenyl-benzamide (3bf)[9]

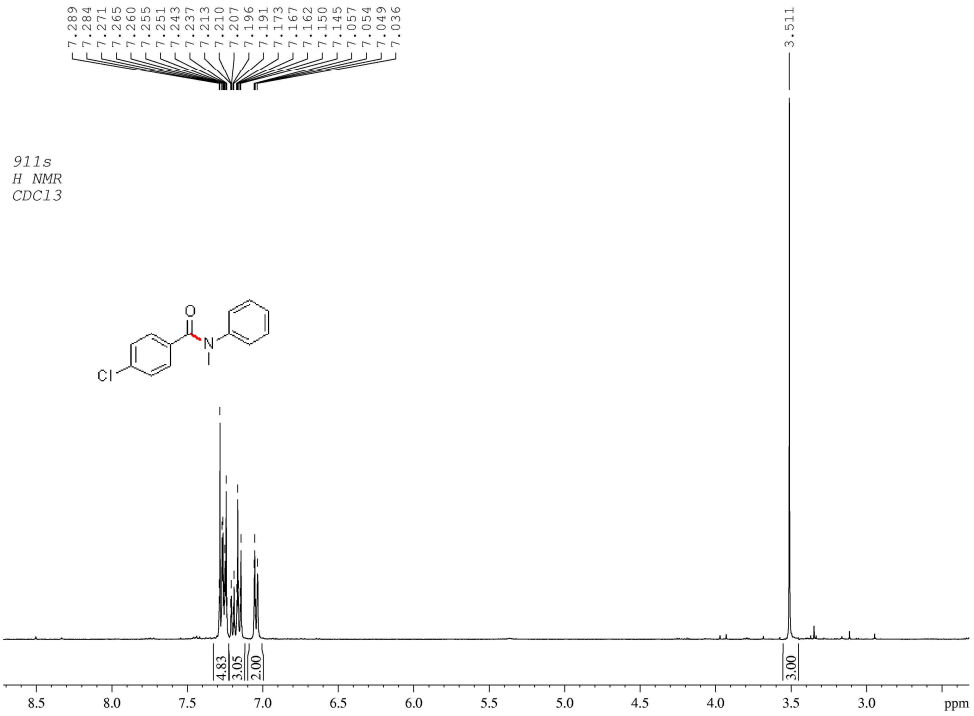


^{1}H NMR (400MHz, $CDCl_3$) 7.21-7.28 (m, 4H), 7.17-7.21 (m, 1H), 7.15 (d, J = 7.2 Hz, 2H), 7.04 (d, J = 7.2Hz, 2H), 4.00 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100MHz, $CDCl_3$)** 169.0, 143.0, 135.5, 134.7, 130.2, 129.3, 128.0, 127.9, 126.9, 45.5, 12.9.

IV. NMR Spectrum Copies



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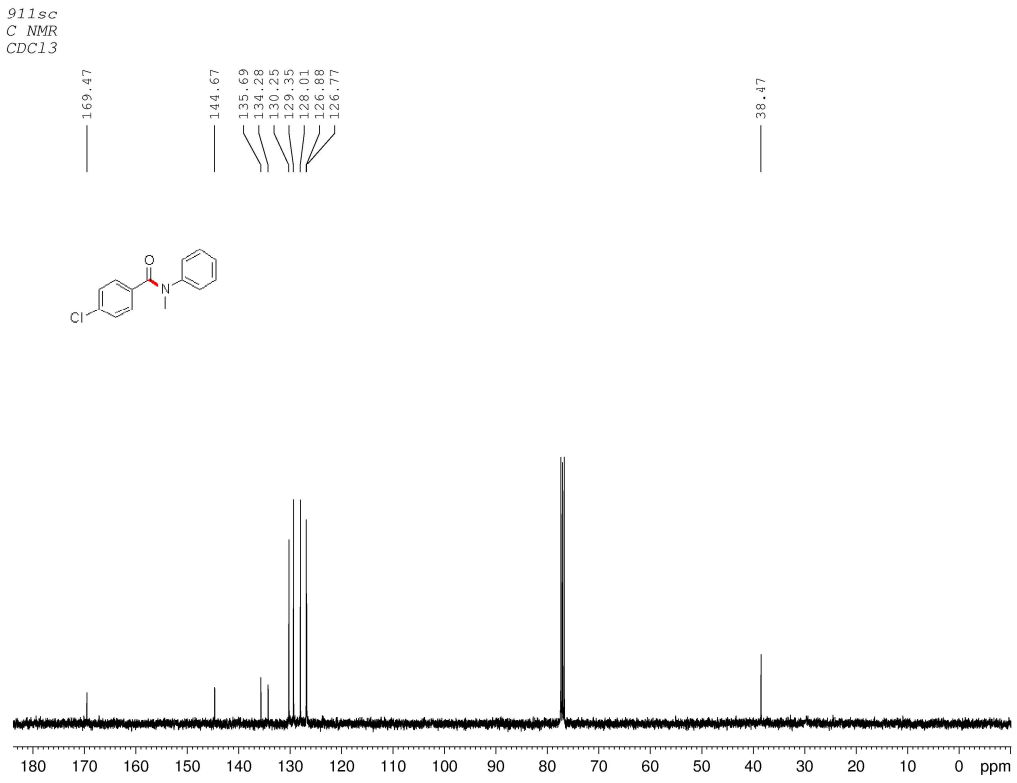
7.271
7.265
7.260
7.255
7.251
7.243
7.237
7.213
7.210
7.207
7.196
7.191
7.173
7.167
7.162
7.150
7.145
7.057
7.054
7.049
7.036
3.511
911s
H NMR
CDCl3
O
N
Cl
4.83
3.05
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm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CDCl3
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135.69
134.28
130.25
129.35
128.01
126.88
126.77
38.47
O
N
Cl
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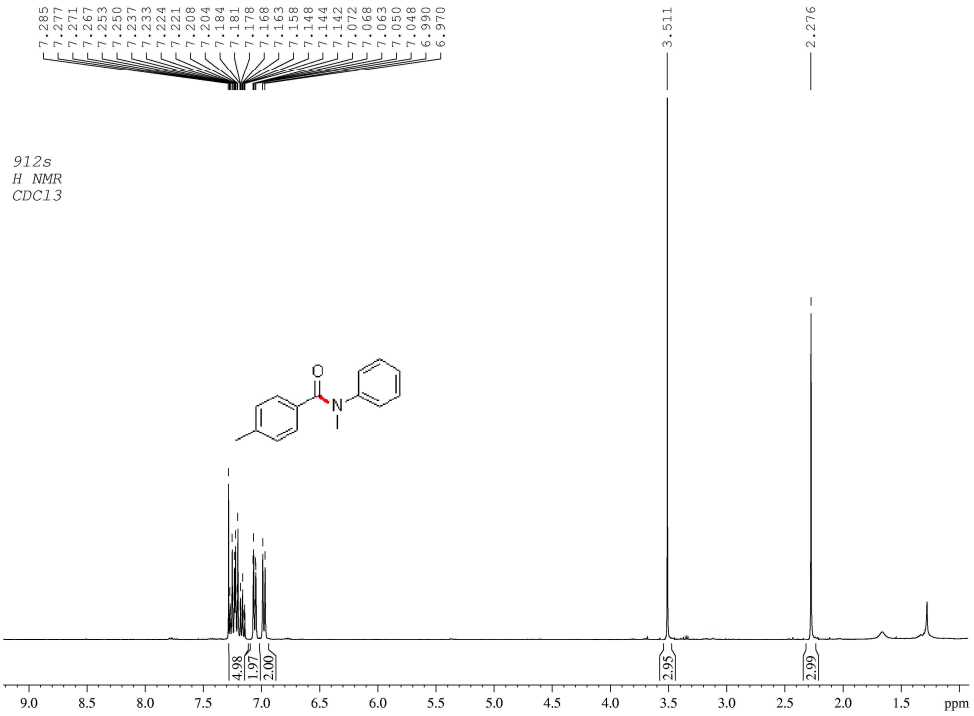
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.237
7.233
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7.204
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7.181
7.178
7.168
7.163
7.158
7.148
7.144
7.142
7.072
7.068
7.063
7.050
7.048
6.990
6.970
3.511
2.276
912s
H NMR
CDC13
O
N
4.98
1.97
2.00
2.95
2.99
9.0
8.5
8.0
7.5
7.0
6.5
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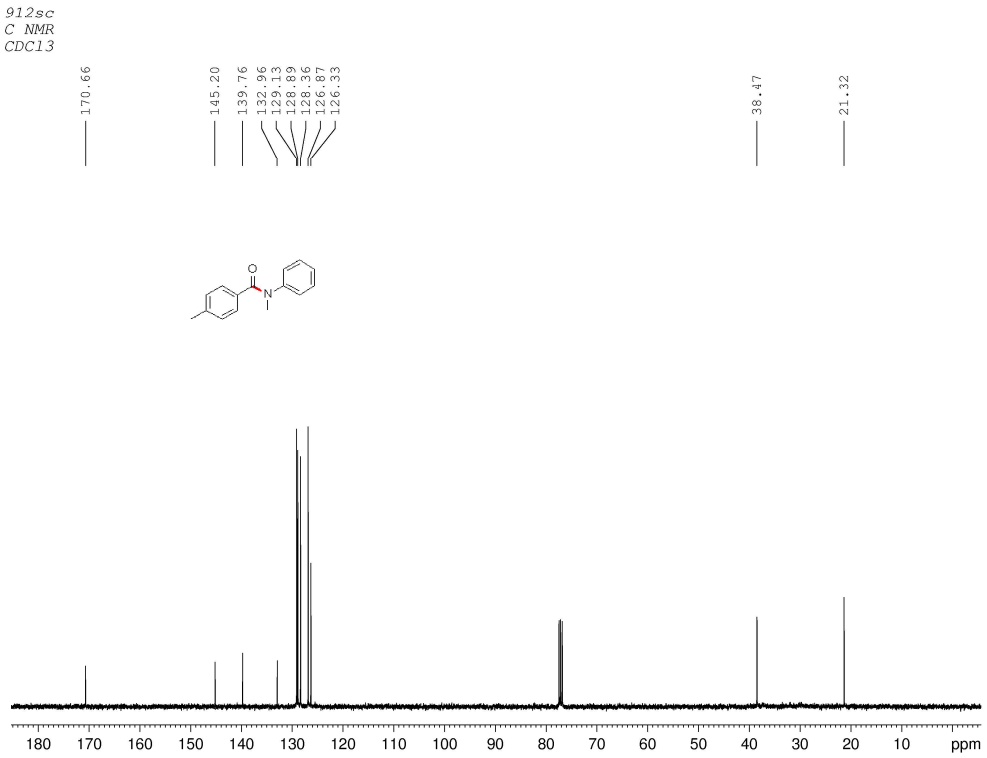
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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C NMR
CDC13
170.66
145.20
139.76
132.96
129.13
128.89
128.36
126.87
126.33
38.47
21.32
O
N
180
170
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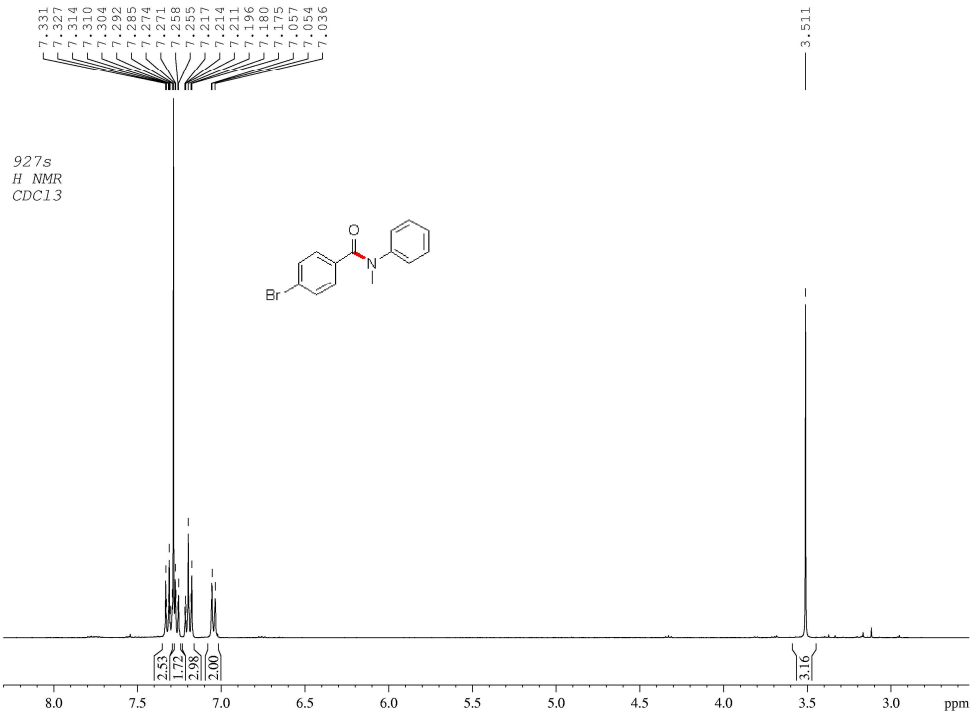
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.314
7.310
7.304
7.292
7.285
7.274
7.271
7.258
7.255
7.217
7.214
7.211
7.196
7.180
7.175
7.057
7.054
7.036
3.511
927s
H NMR
CDC13
O
N
Br
2.53
1.72
2.98
2.00
3.16
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7.0
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6.0
5.5
5.0
4.5
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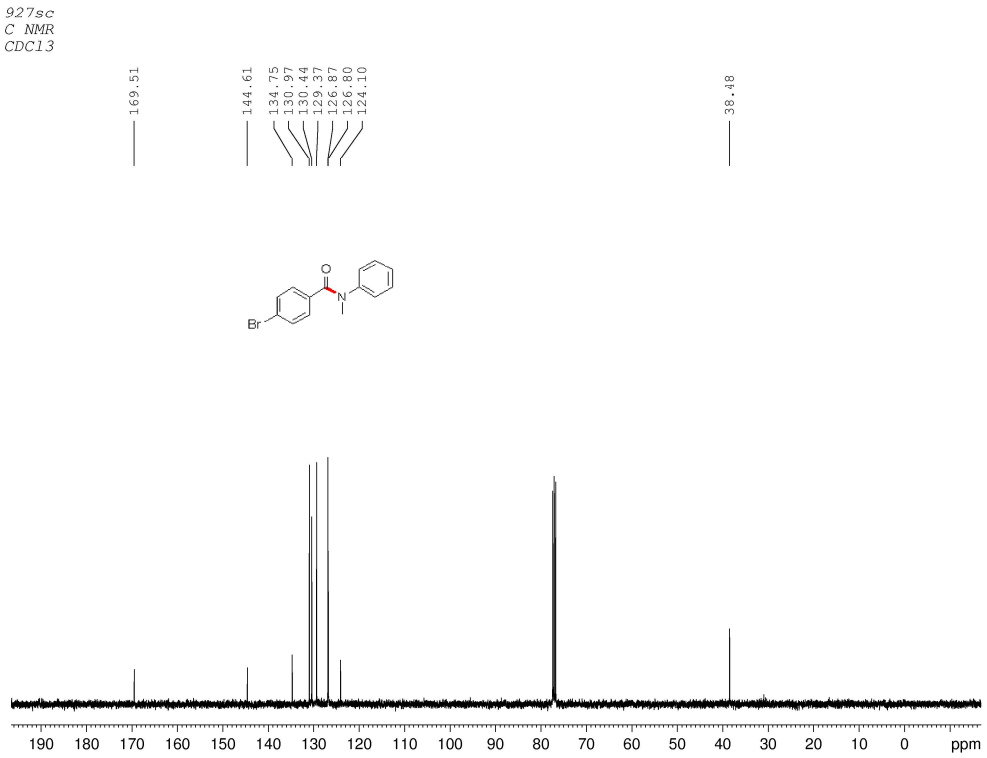
3.5
3.0
ppm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C NMR
CDC13
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134.75
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130.44
129.37
126.87
126.80
124.10
38.48
O
N
Br
190
180
170
160
150
140
130
120
110
100
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80
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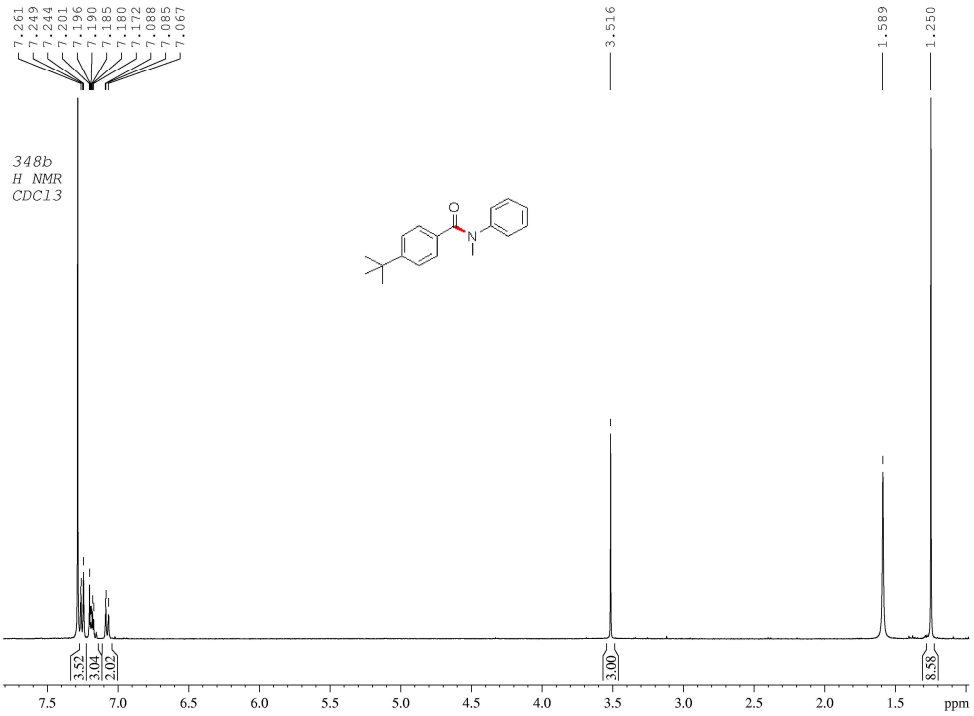
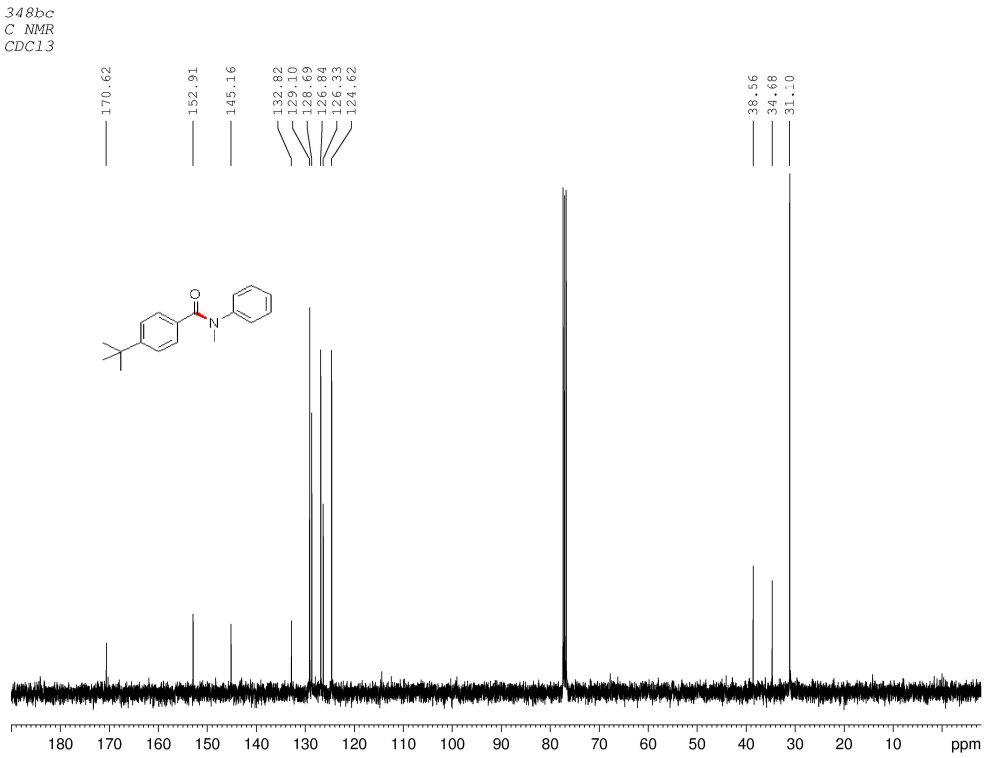
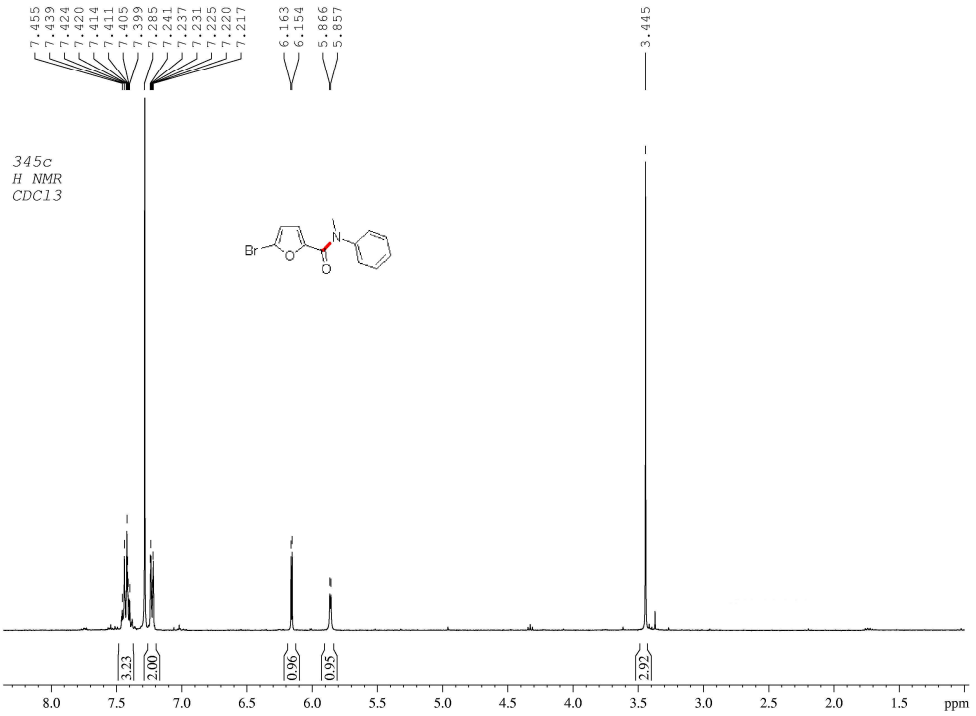
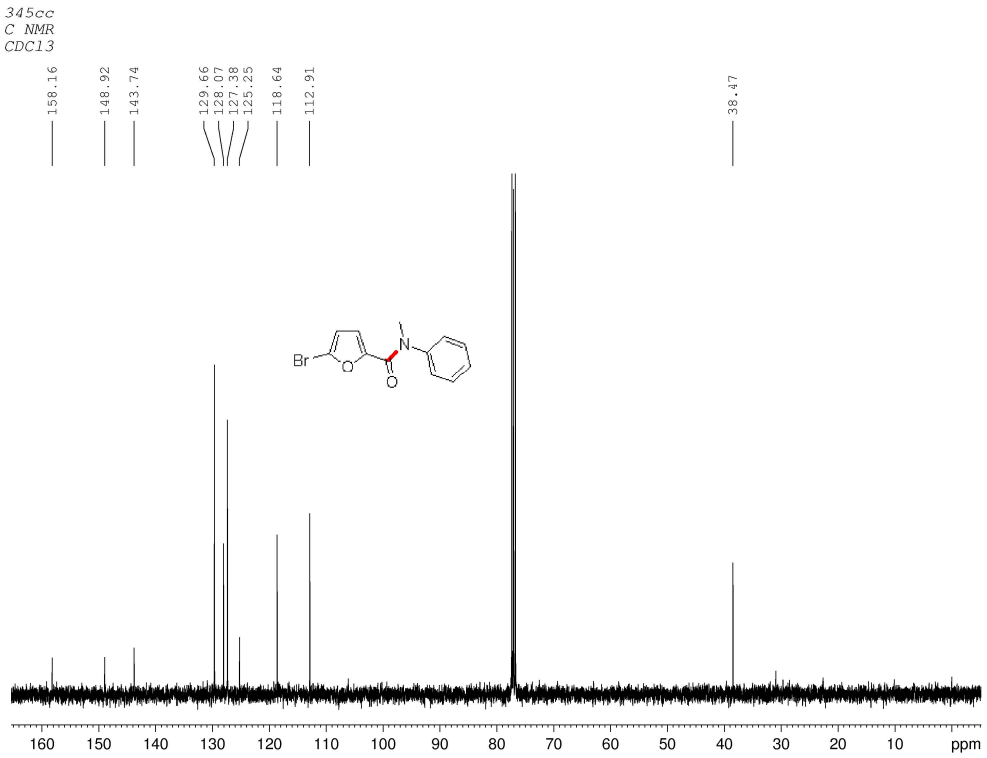
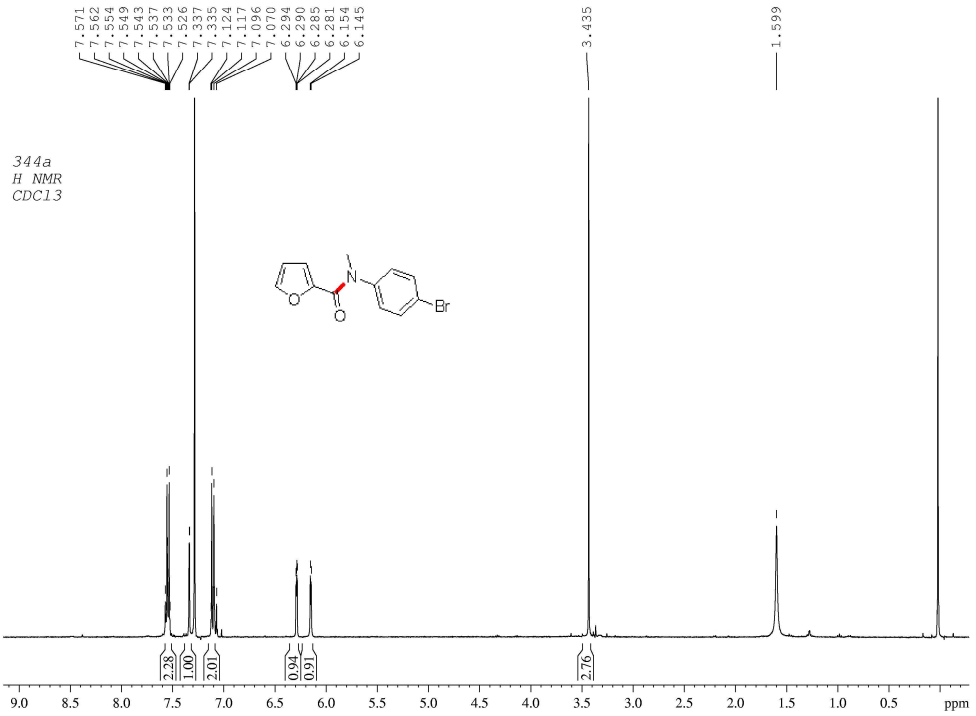
60
50
40
30
20
10
0
ppm

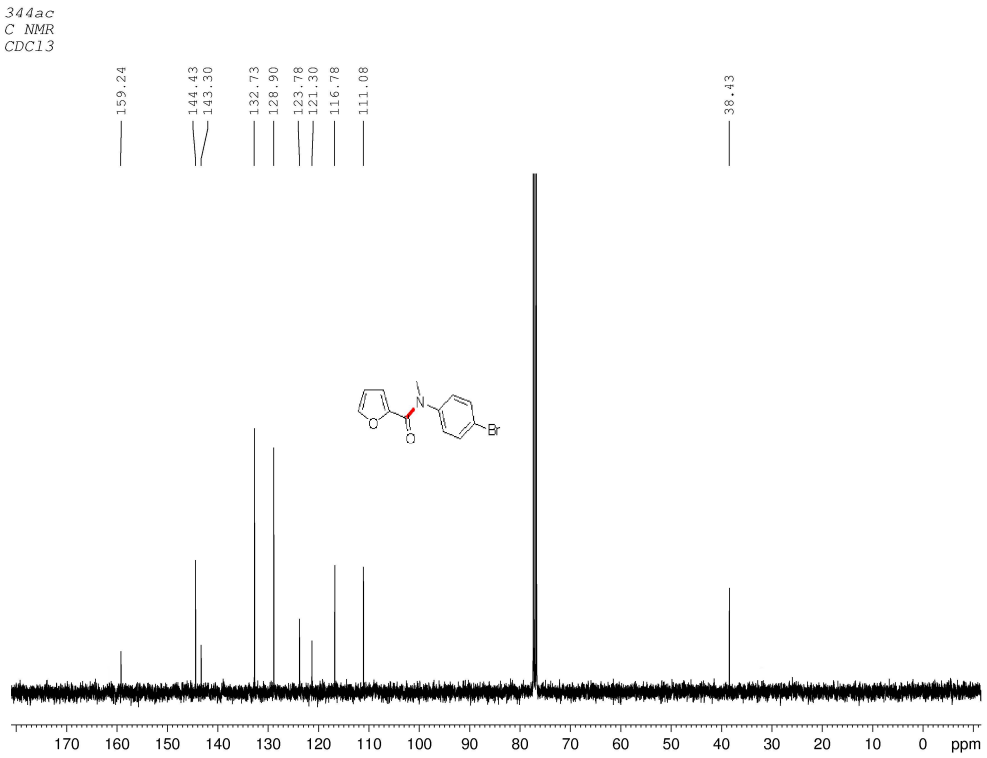


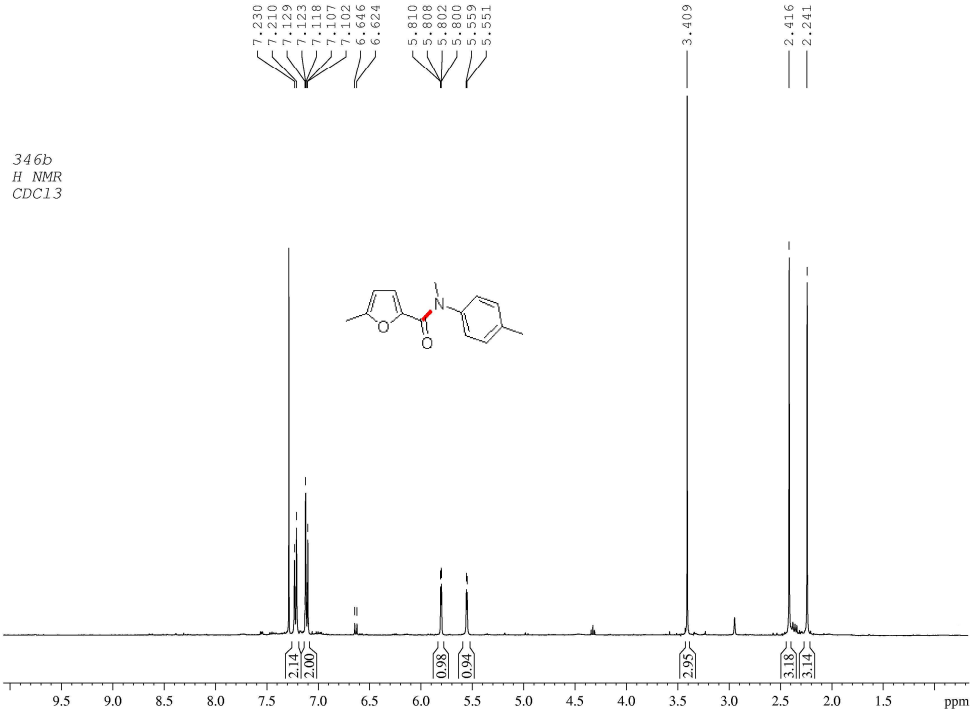








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7.123
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7.102
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5.808
5.802
5.800
5.559
5.551
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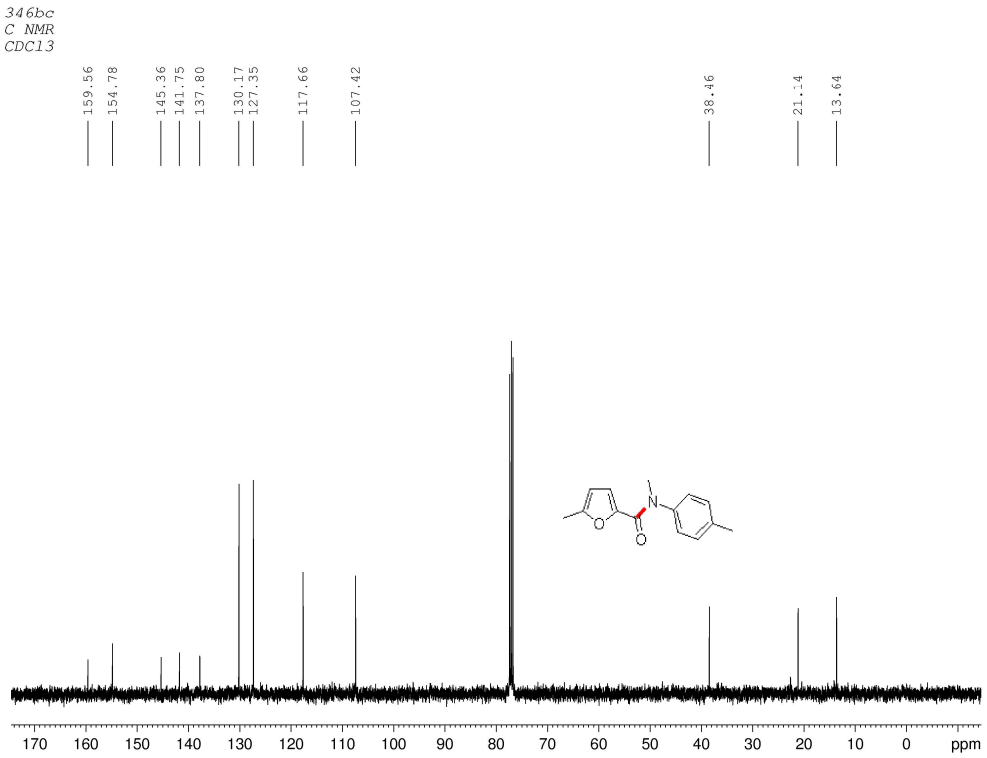
2.416
2.241
2.14
2.00
0.98
0.94
2.95
3.18
3.14
ppm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117.66
107.42
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21.14
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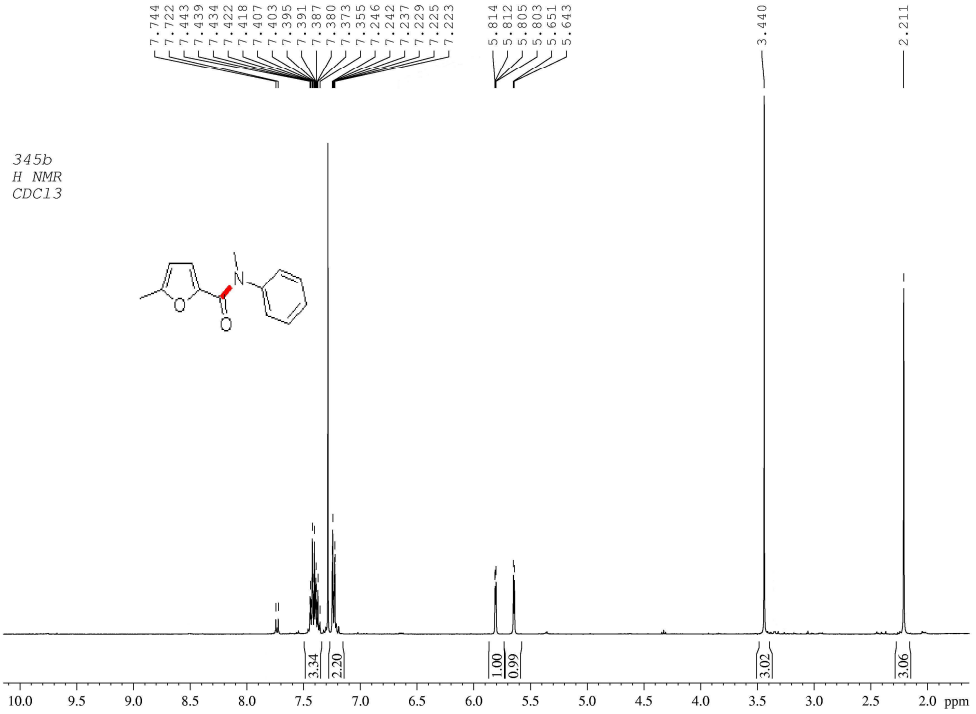
ppm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7.439
7.434
7.422
7.418
7.407
7.403
7.395
7.391
7.387
7.380
7.373
7.355
7.246
7.242
7.237
7.229
7.225
7.223
5.814
5.812
5.805
5.803
5.651
5.643
3.440
2.211
345b
H NMR
CDC13
O
N
O
3.34
2.20
1.00
0.99
3.02
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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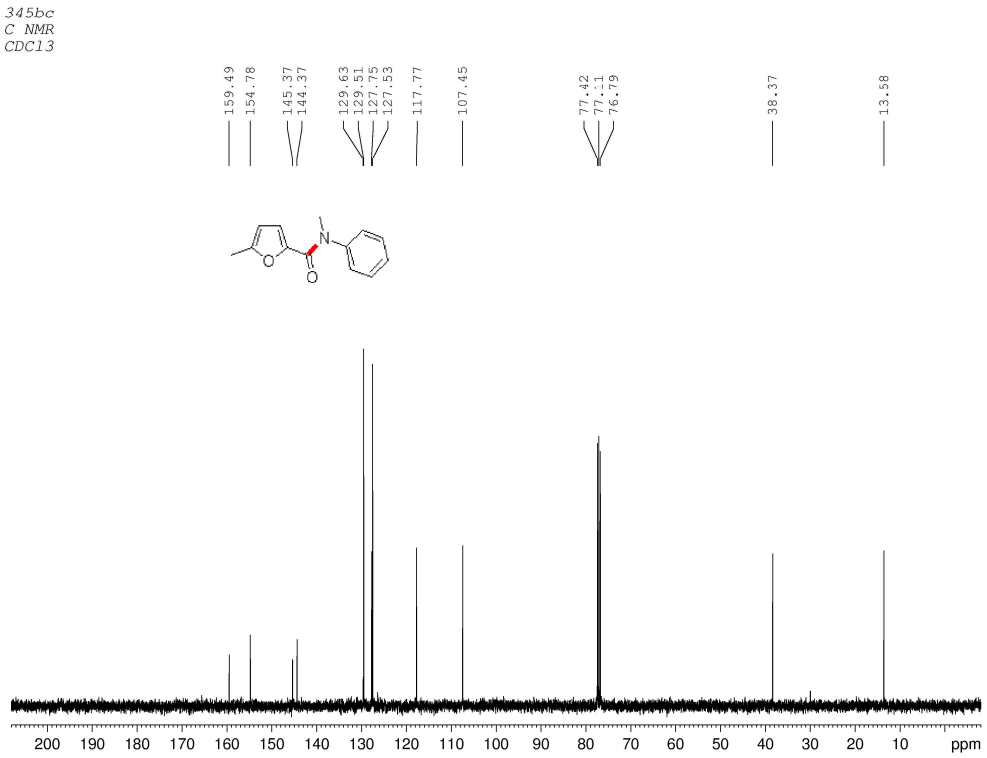
4.0
3.5
3.0
2.5
2.0 ppm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C NMR
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129.63
129.51
127.75
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117.77
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76.79
38.37
13.58
O
N
O
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150
140
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110
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80
70
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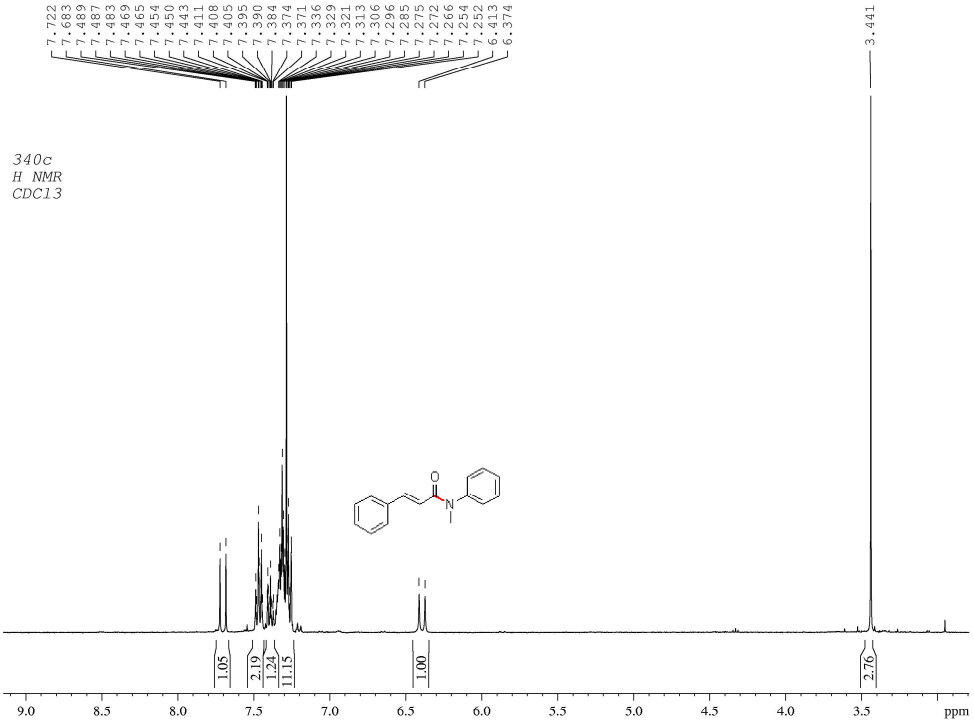
30
20
10
ppm


7.722
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7.465
7.454
7.450
7.443
7.411
7.408
7.405
7.395
7.390
7.384
7.374
7.371
7.336
7.329
7.321
7.313
7.306
7.296
7.285
7.275
7.272
7.266
7.254
7.252
6.413
6.374
3.441
340c
H NMR
CDC13
O
N
1.05
2.19
1.24
11.15
1.00
2.76
9.0
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4.5
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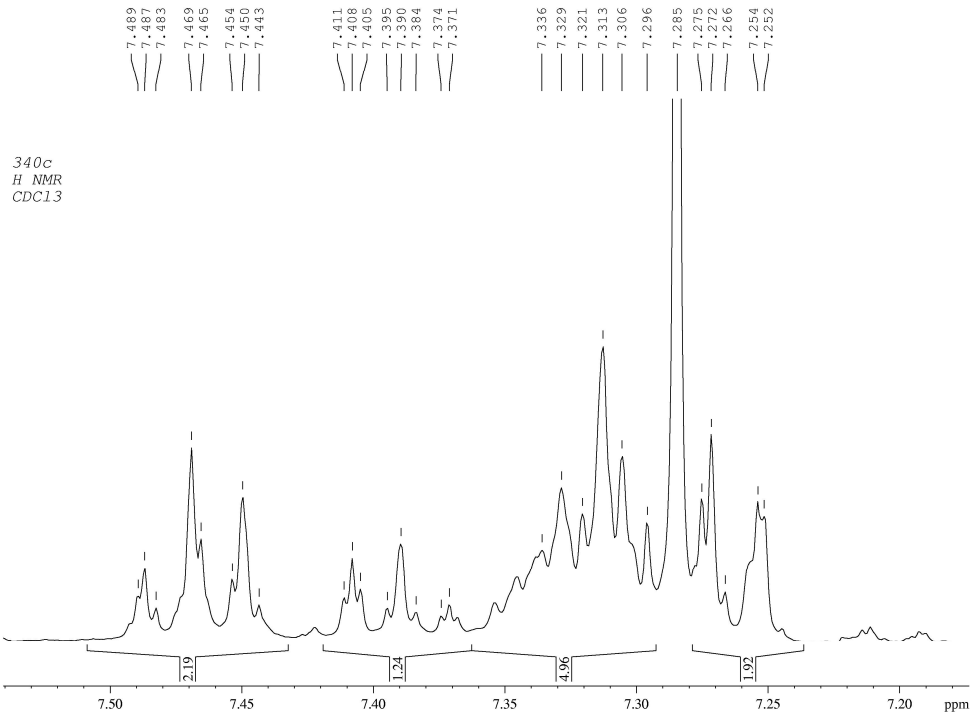
ppm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7.405
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7.390
7.384
7.374
7.371
7.336
7.329
7.321
7.313
7.306
7.296
7.285
7.275
7.272
7.266
7.254
7.252
340c
H NMR
CDC13
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4.96
1.92
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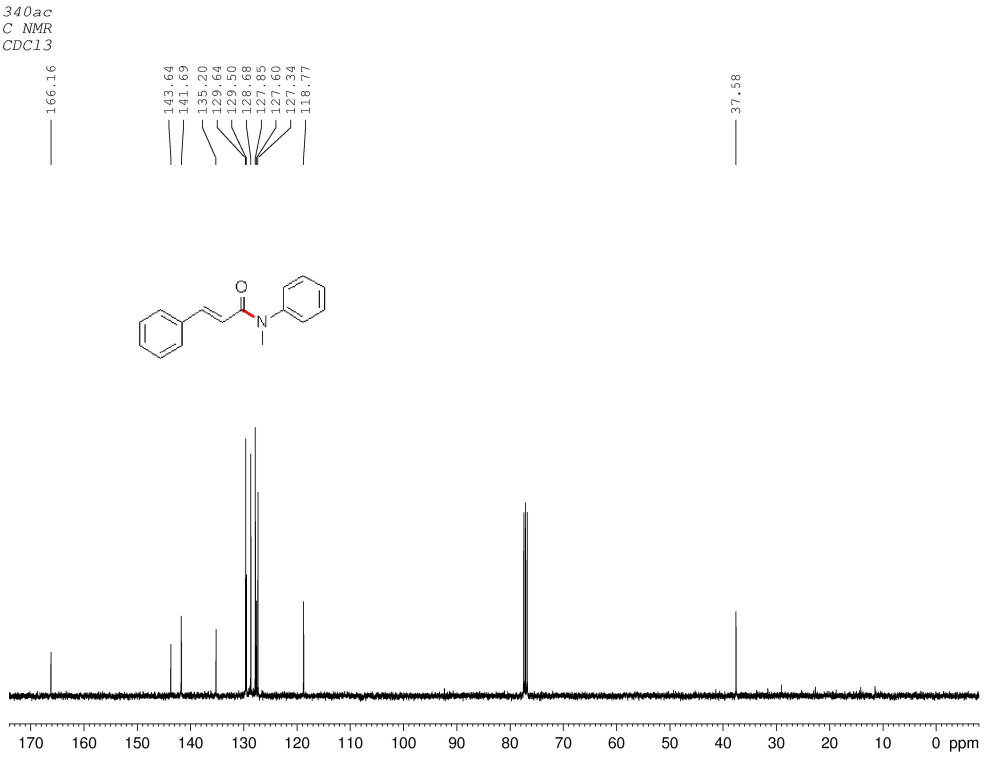
7.40
7.35
7.30
7.25
7.20
ppm


340ac
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141.69
135.20
129.64
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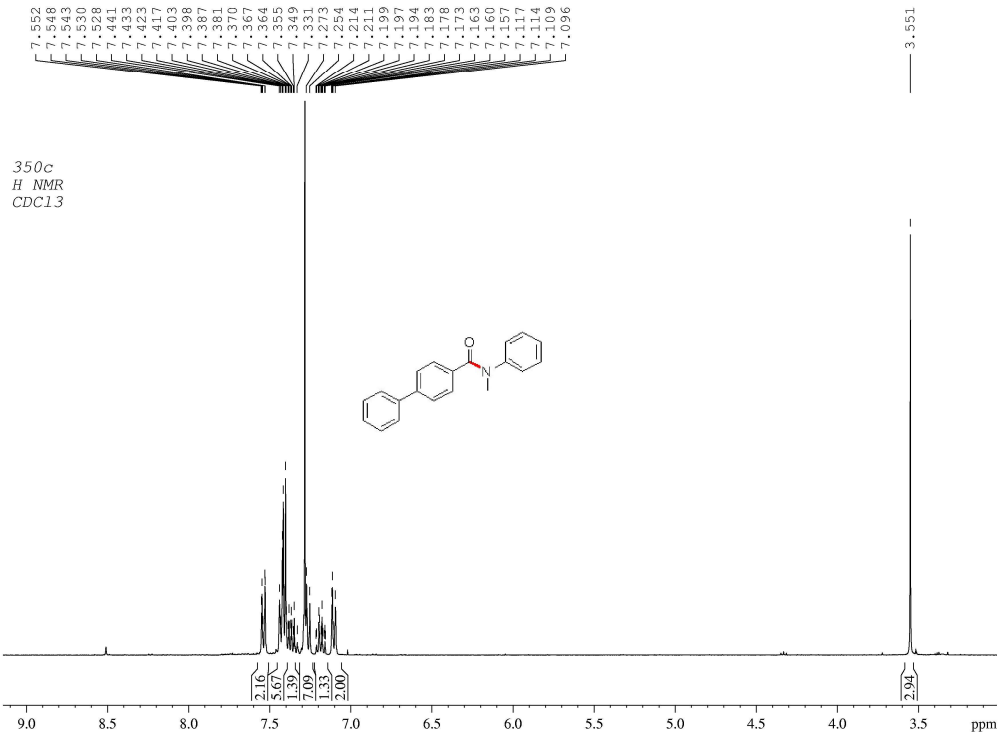
127.60
127.34
118.77
37.58
O
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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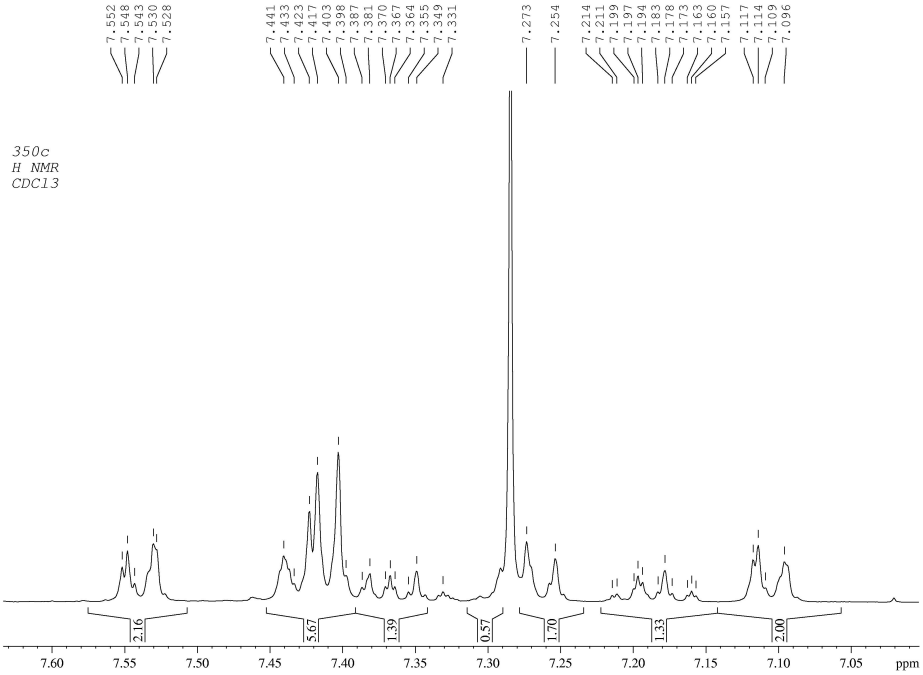
7.381
7.370
7.367
7.364
7.355
7.349
7.331
7.273
7.254
7.214
7.211
7.199
7.197
7.194
7.183
7.178
7.173
7.163
7.160
7.157
7.117
7.114
7.109
7.096
3.551
350c
H NMR
CDC13
O
N
2.16
5.67
1.39
7.09
1.33
2.00
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm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7.387
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7.163
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7.157
7.117
7.114
7.109
7.096
350c
H NMR
CDC13
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5.67
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0.57
1.70
1.33
2.00
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7.45
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7.35
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7.20
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7.10
7.05
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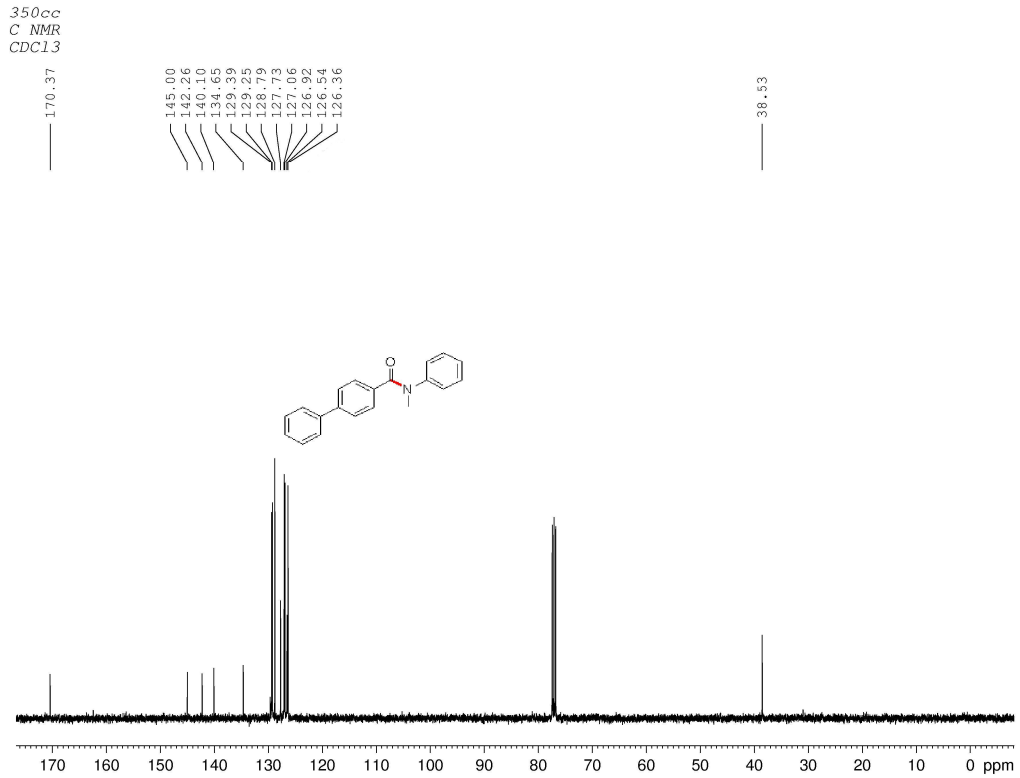
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C NMR
CDC13
170.37
145.00
142.26
140.10
134.65
129.39
129.25
128.79
127.73
127.06
126.92
126.54
126.36
38.53
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160
150
140
130
120
110
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90
80
70
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50
40
30
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10
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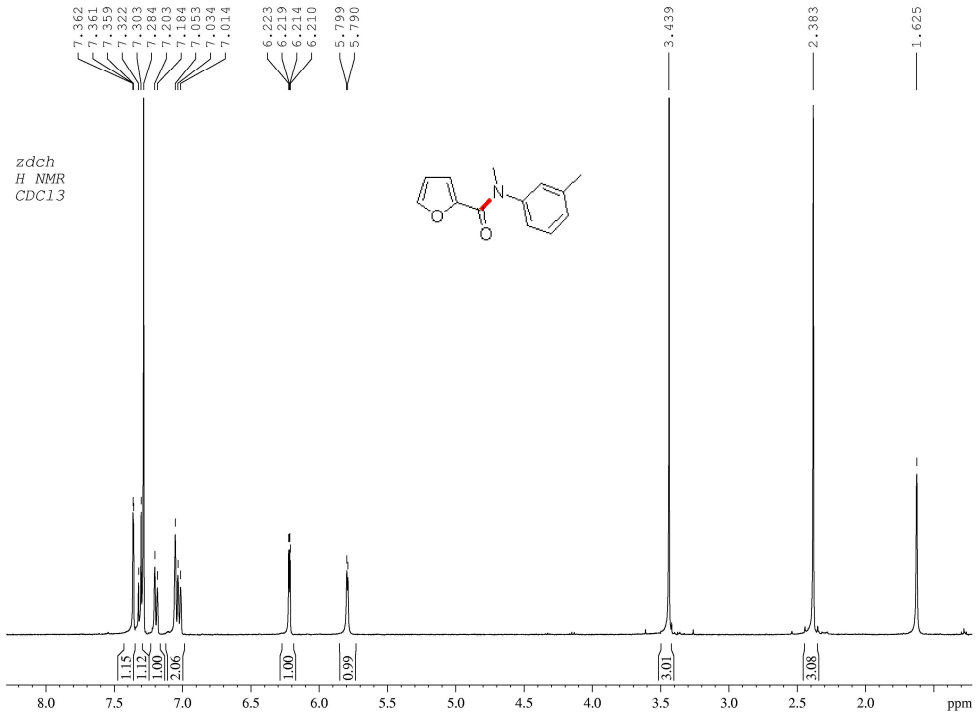
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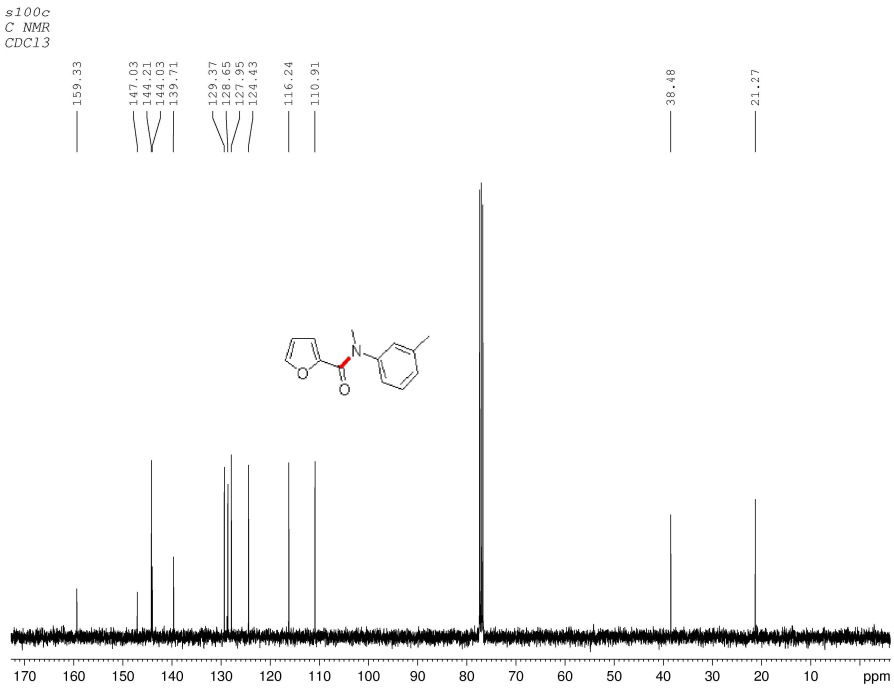
7.361
7.359
7.322
7.303
7.284
7.203
7.184
7.053
7.034
7.014
6.223
6.219
6.214
6.210
5.799
5.790
3.439
2.383
1.625
zdch
H NMR
CDC13
1.15
1.13
1.00
2.06
1.00
0.99
3.01
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm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C NMR
CDC13
159.33
147.03
144.21
144.03
139.71
129.37
128.65
127.95
124.43
116.24
110.91
38.48
21.27
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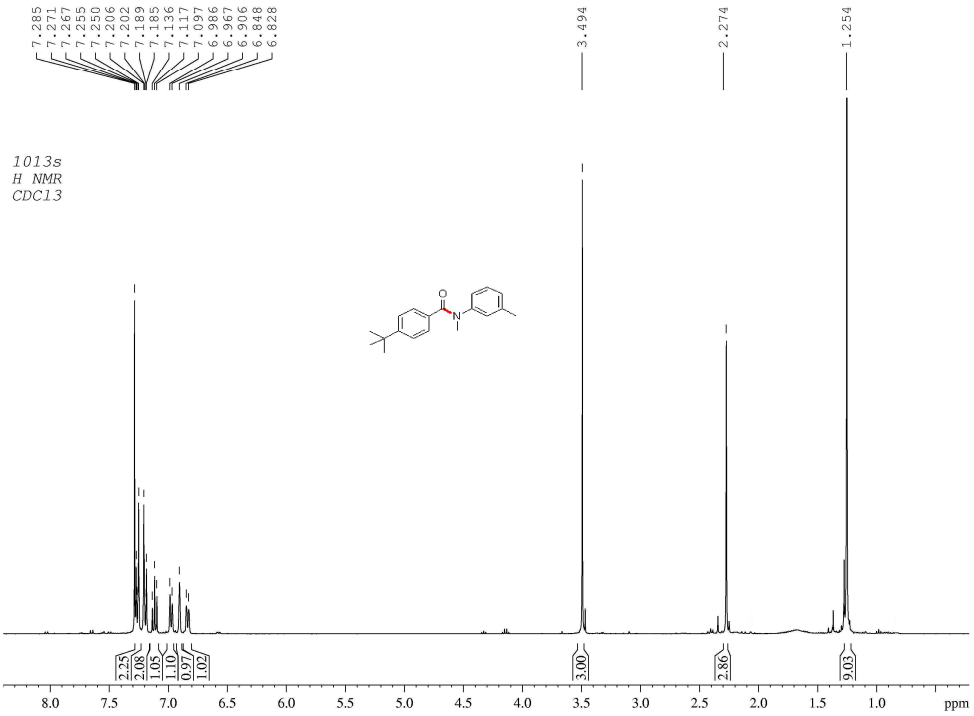
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.285
7.271
7.267
7.255
7.250
7.206
7.202
7.189
7.185
7.136
7.117
7.097
6.986
6.967
6.906
6.848
6.828
3.494
2.274
1.254
1013s
H NMR
CDC13
2.25
2.08
1.05
1.10
0.97
1.02
3.00
2.86
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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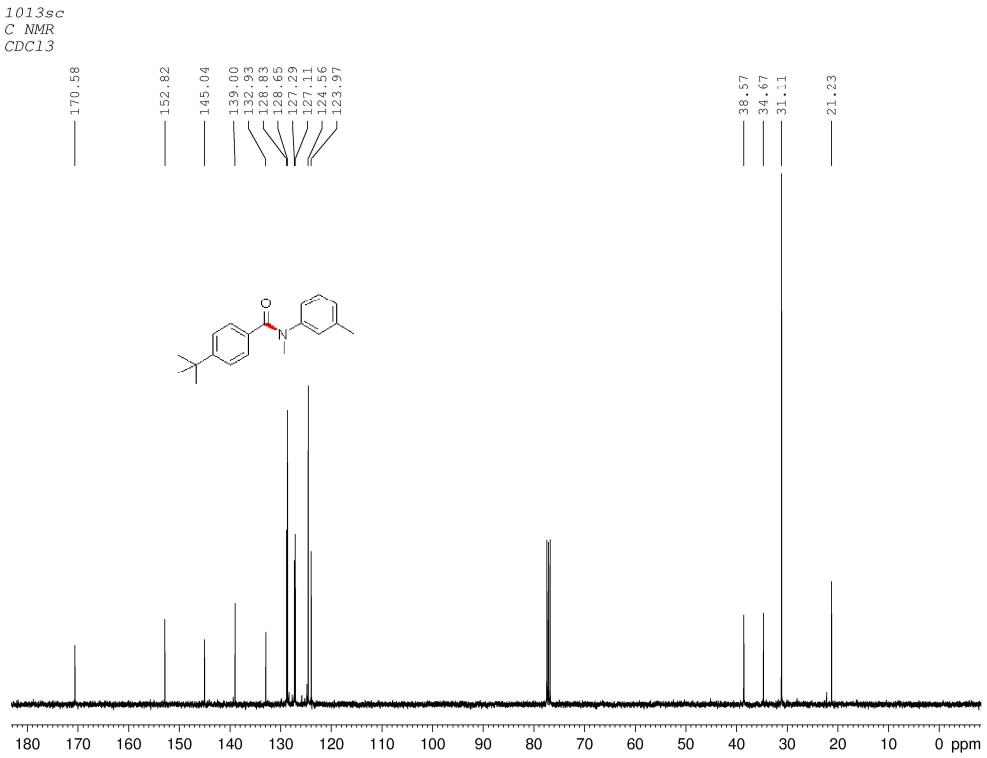
3.0
2.5
2.0
1.5
1.0
ppm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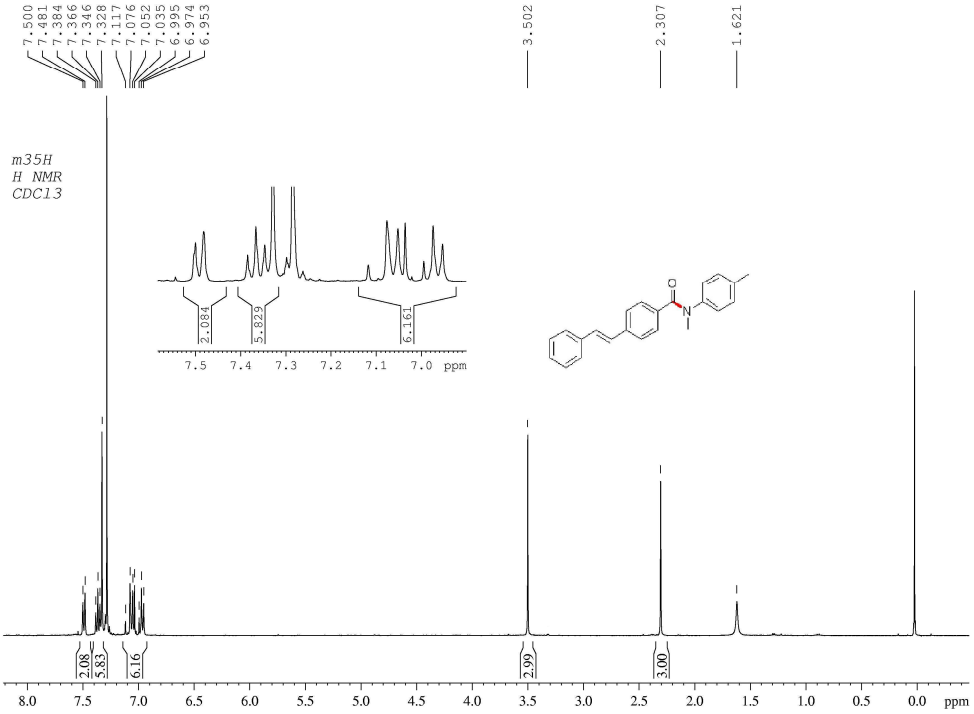
C NMR
CDC13
170.58
152.82
145.04
139.00
132.93
128.83
128.65
127.29
127.11
124.56
123.97
38.57
34.67
31.11
21.23
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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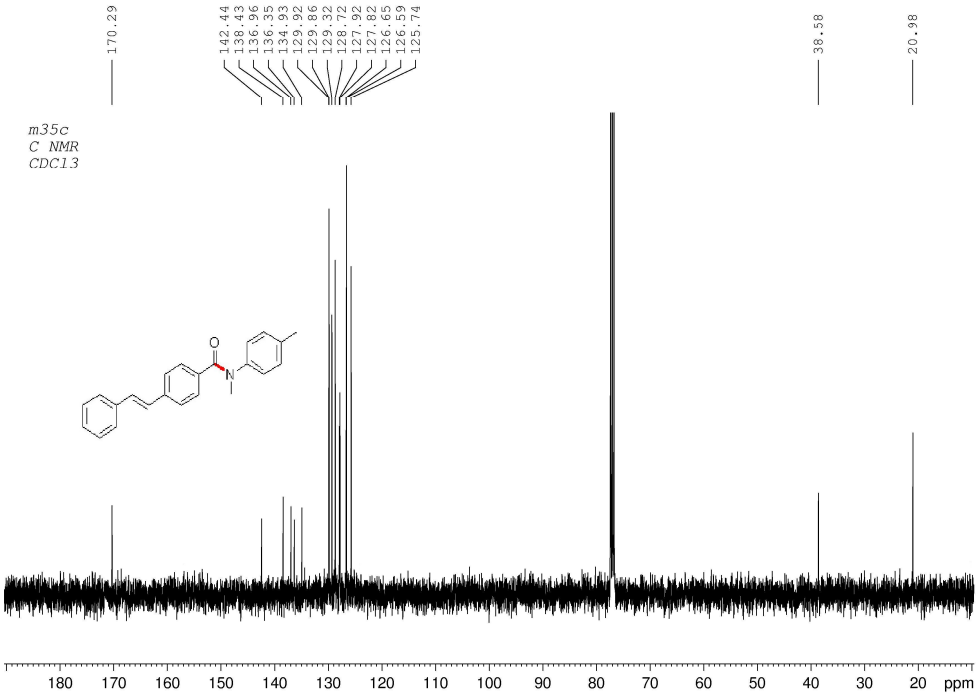
7.384
7.366
7.346
7.328
7.117
7.076
7.052
7.035
6.995
6.974
6.953
3.502
2.307
1.621
m35H
H NMR
CDC13
2.084
5.829
6.161
7.5 7.4 7.3 7.2 7.1 7.0 ppm
O
N
2.08
5.83
6.16
2.99
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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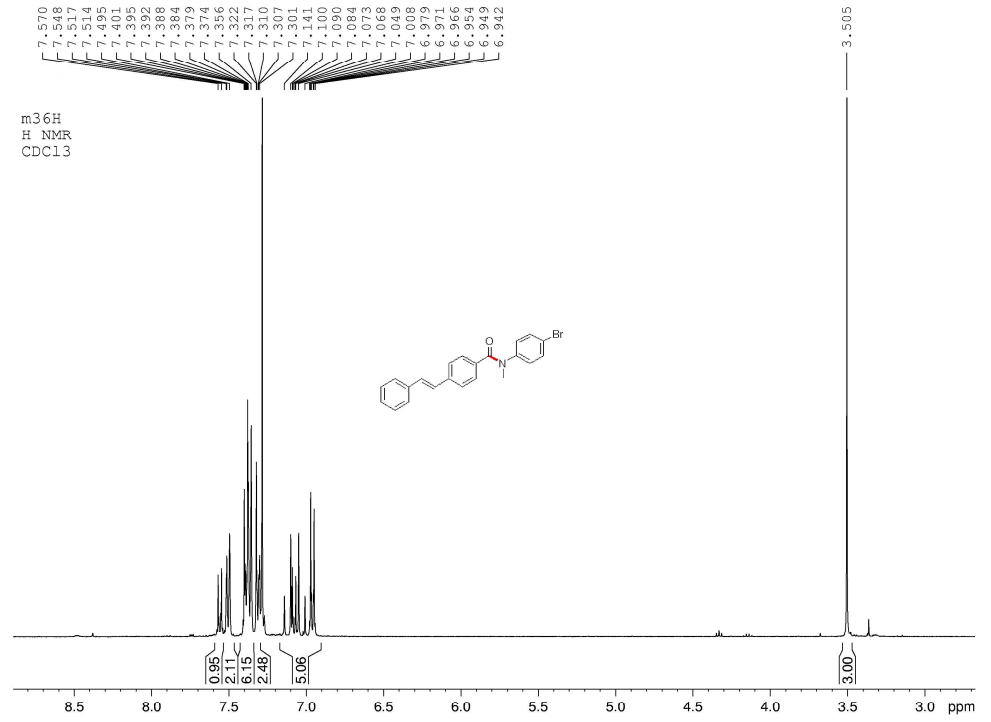
142.44
138.43
136.96
136.35
134.93
129.92
129.86
129.32
128.72
127.92
127.82
126.65
126.59
125.74
38.58
20.98
m35c
C NMR
CDC13
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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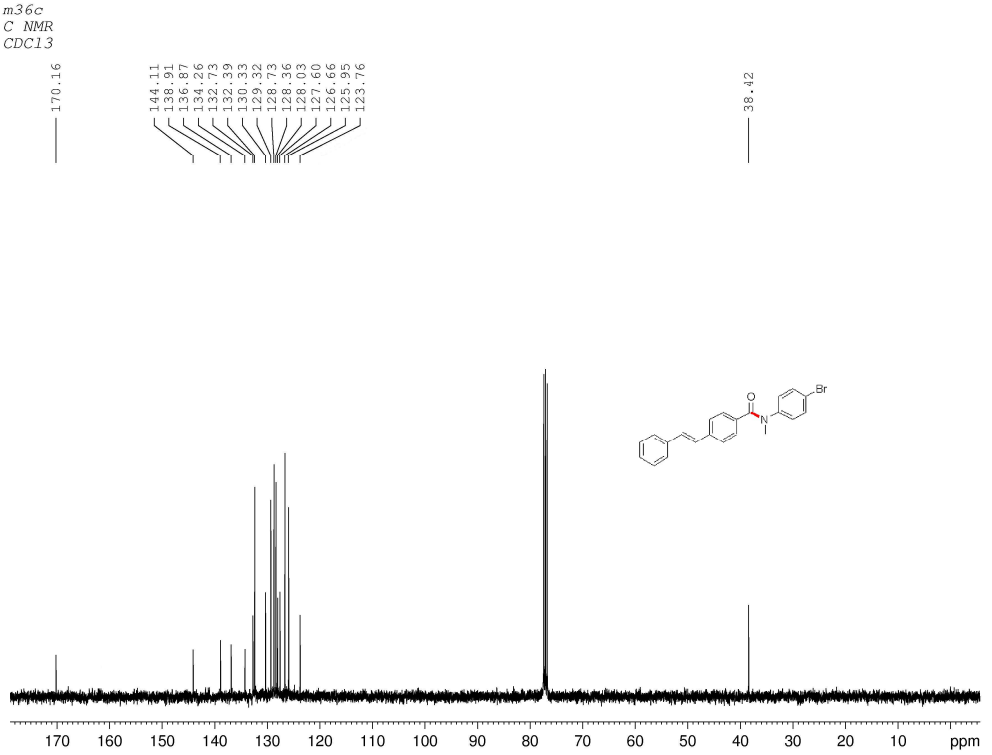
7.548
7.517
7.514
7.495
7.401
7.395
7.392
7.388
7.384
7.379
7.374
7.356
7.322
7.317
7.310
7.307
7.301
7.141
7.100
7.090
7.084
7.073
7.068
7.049
7.008
6.979
6.971
6.966
6.954
6.949
6.942
3.505
m36H
H NMR
CDCl3
Br
O
N
0.95
2.11
6.15
2.48
5.06
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


m36c
C NMR
CDCl3
170.16
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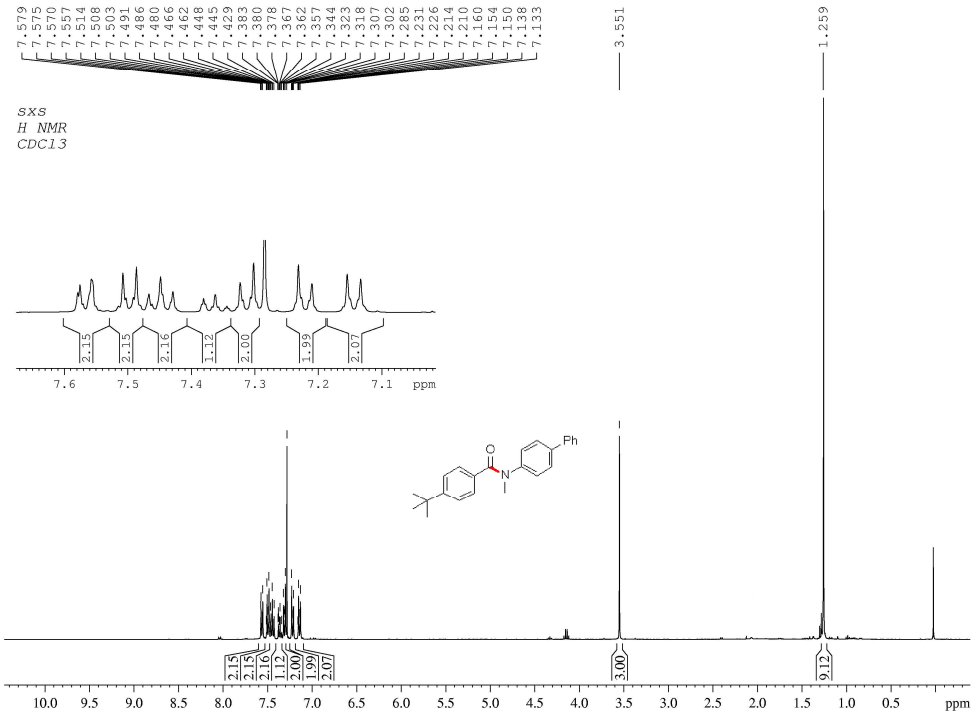
138.91
136.87
134.26
132.73
132.39
130.33
129.32
128.73
128.36
128.03
127.60
126.66
125.95
123.76
38.42
Br
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.570
7.557
7.514
7.508
7.503
7.491
7.486
7.480
7.466
7.462
7.448
7.445
7.429
7.383
7.380
7.378
7.367
7.362
7.357
7.344
7.323
7.318
7.307
7.302
7.285
7.231
7.226
7.214
7.210
7.160
7.154
7.150
7.138
7.133
3.551
1.259
sxs
H NMR
CDC13
2.15
2.15
2.16
1.12
2.00
1.99
2.07
7.6
7.5
7.4
7.3
7.2
7.1
ppm
Ph
O
N
3.00
9.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
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2.0
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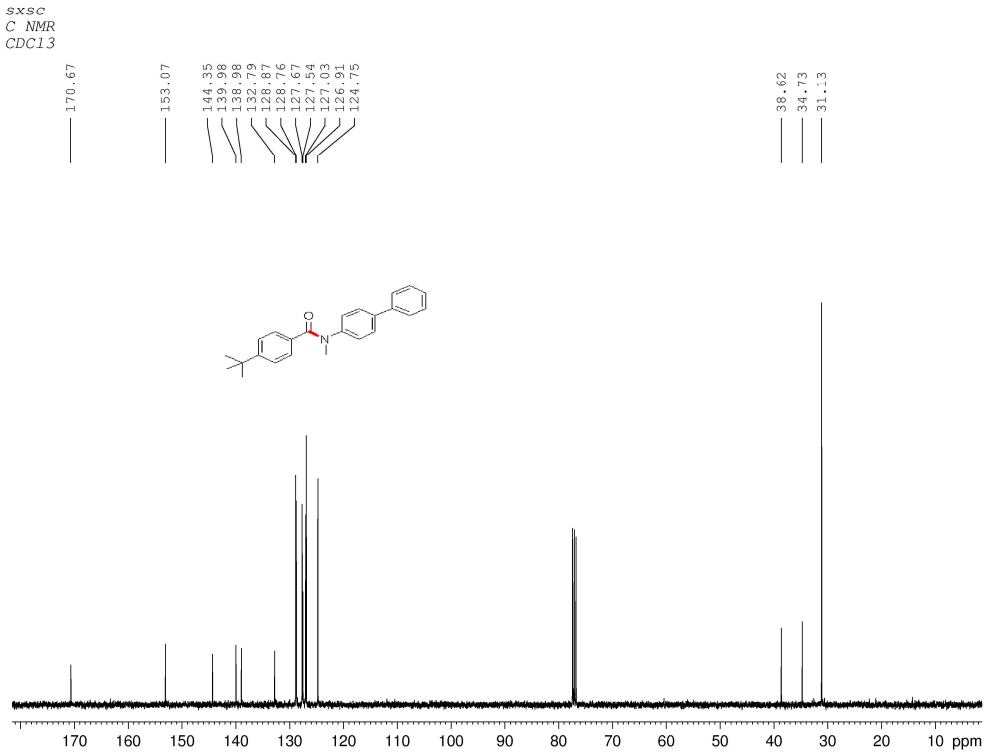
1.0
0.5
ppm


sxsc
C NMR
CDC13
170.67
153.07
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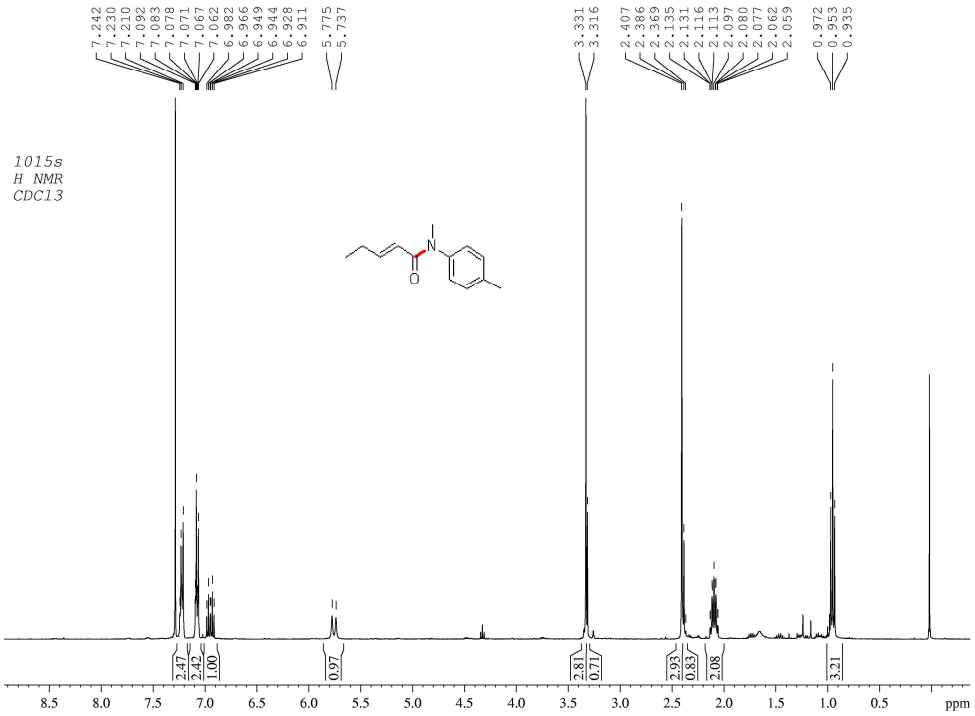
139.98
138.98
132.79
128.87
128.76
127.67
127.54
127.03
126.91
124.75
38.62
34.73
31.13
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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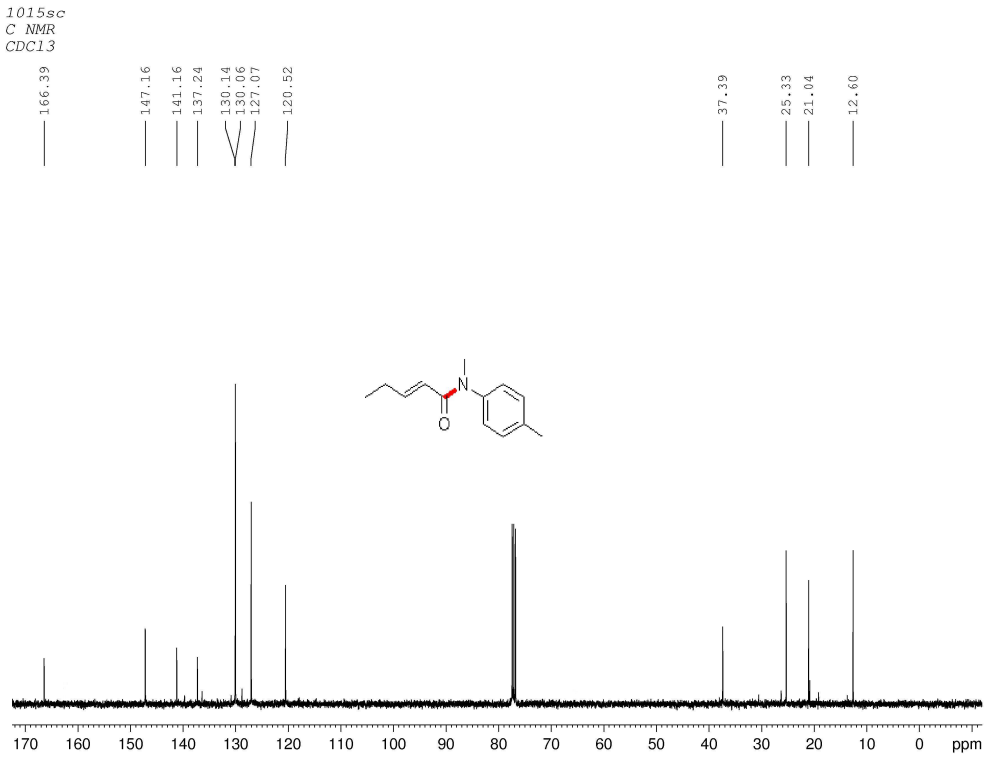
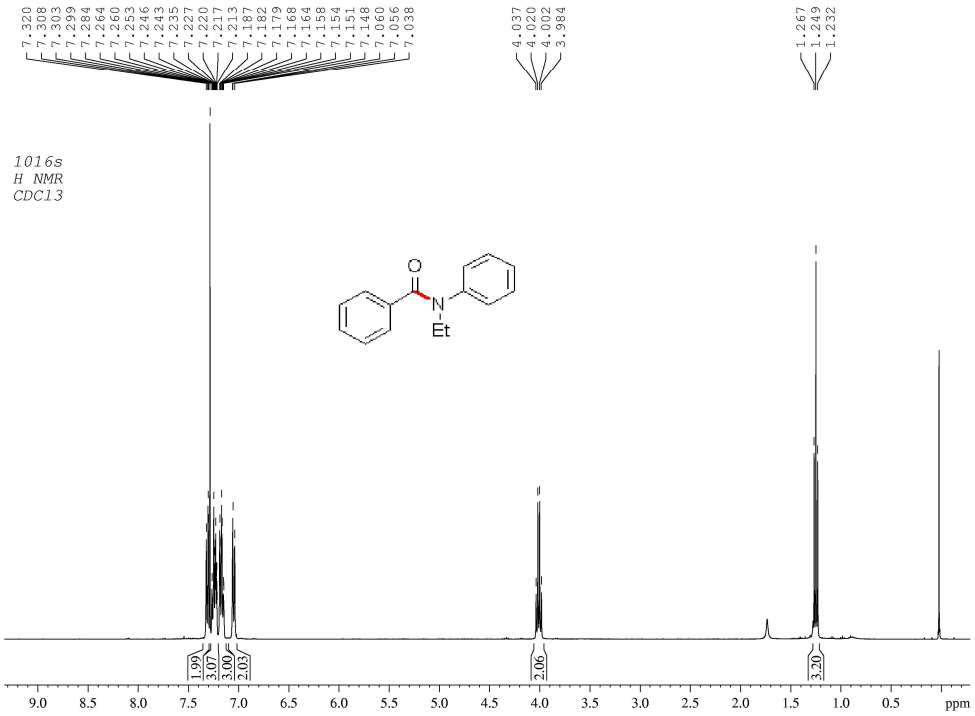
H NMR
CDC13
7.242
7.230
7.210
7.092
7.083
7.078
7.071
7.067
7.062
6.982
6.966
6.949
6.944
6.928
6.911
5.775
5.737
3.331
3.316
2.407
2.386
2.369
2.135
2.131
2.116
2.113
2.097
2.080
2.077
2.062
2.059
0.972
0.953
0.935
2.47
2.42
1.00
0.97
2.81
0.71
2.93
0.83
2.08
3.21
ppm


1015sc
C NMR
CDC13
166.39
147.16
141.16
137.24
130.14
130.06
127.07
120.52
37.39
25.33
21.04
12.60
ppm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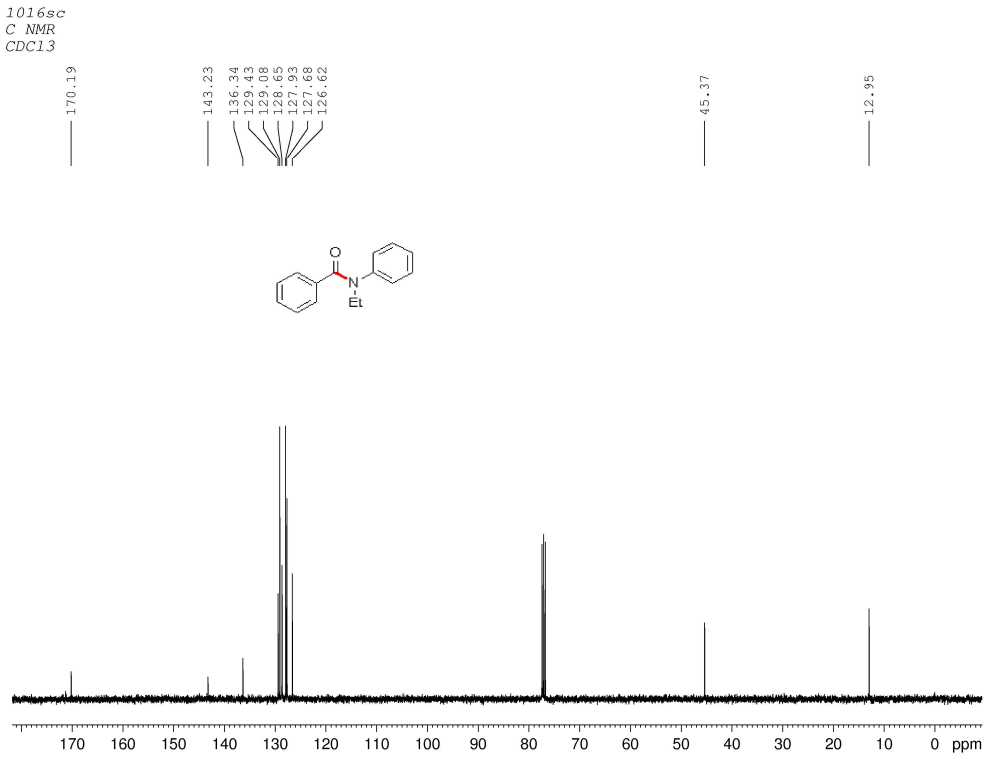
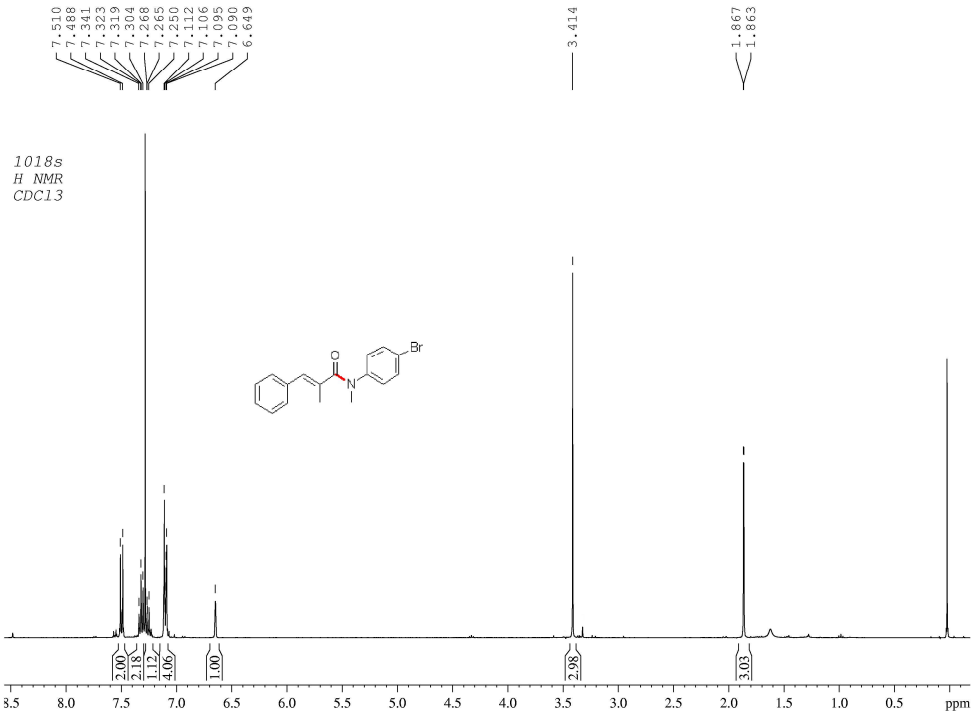
7.308
7.303
7.299
7.284
7.264
7.260
7.253
7.246
7.243
7.235
7.227
7.220
7.217
7.213
7.187
7.182
7.179
7.168
7.164
7.158
7.154
7.151
7.148
7.060
7.056
7.038
4.037
4.020
4.002
3.984
1.267
1.249
1.232
1016s
H NMR
CDC13
O
N
Et
1.99
3.07
3.00
2.03
2.06
3.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


1016sc
C NMR
CDC13
170.19
143.23
136.34
129.43
129.08
128.65
127.93
127.68
126.62
45.37
12.95
O
N
Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.488
7.341
7.323
7.319
7.304
7.268
7.265
7.250
7.112
7.106
7.095
7.090
6.649
3.414
1.867
1.863
1018s
H NMR
CDCl3
Br
O
N
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1.12
4.06
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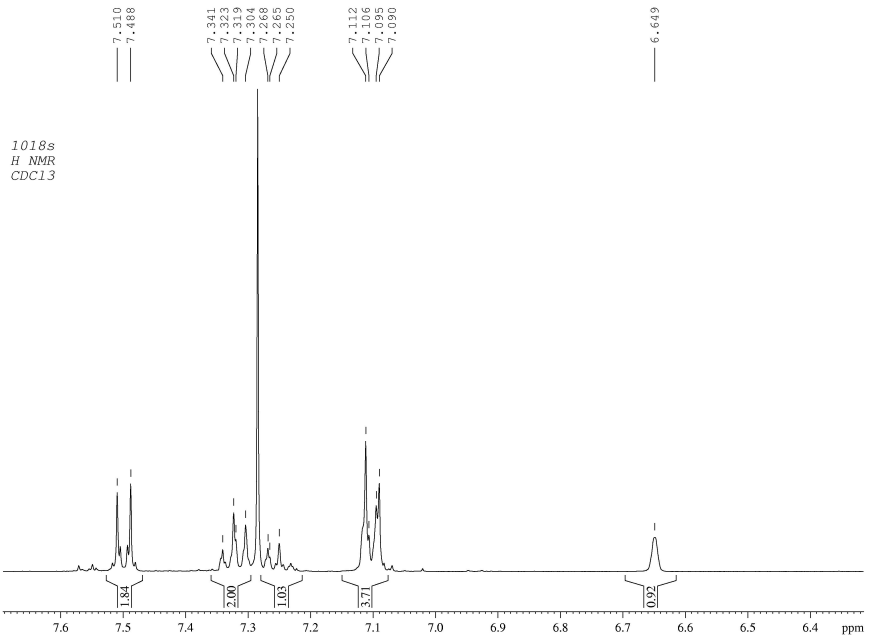
3.03
ppm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7.488
7.341
7.323
7.319
7.304
7.268
7.265
7.250
7.112
7.106
7.095
7.090
6.649
1018s
H NMR
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1.03
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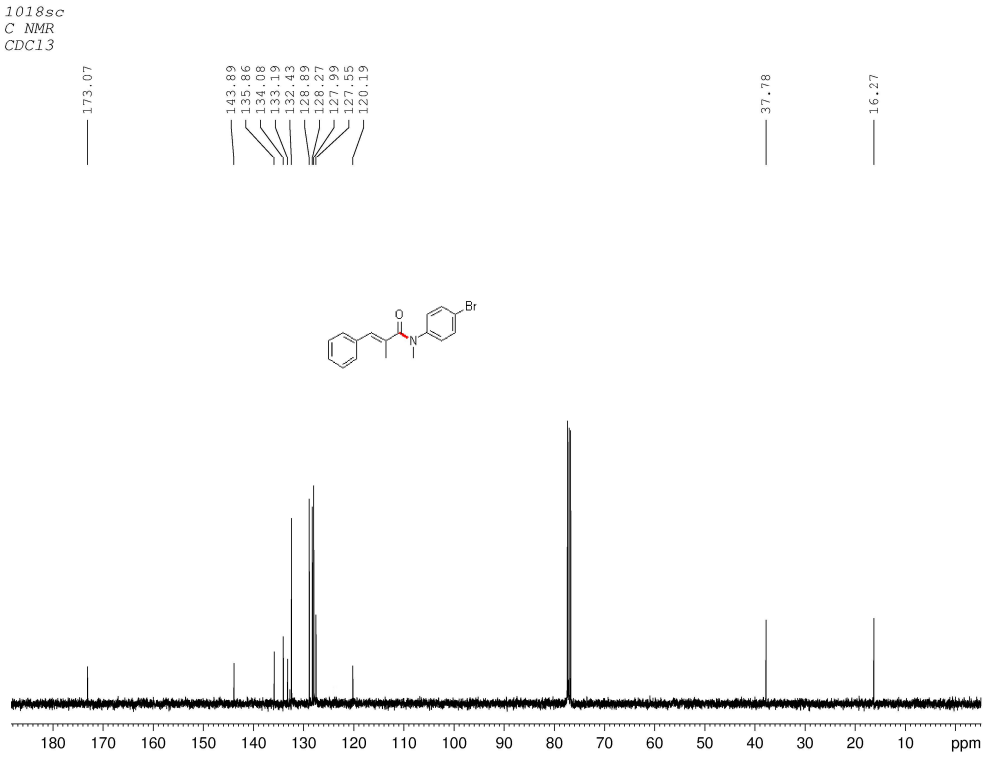
ppm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C NMR
CDC13
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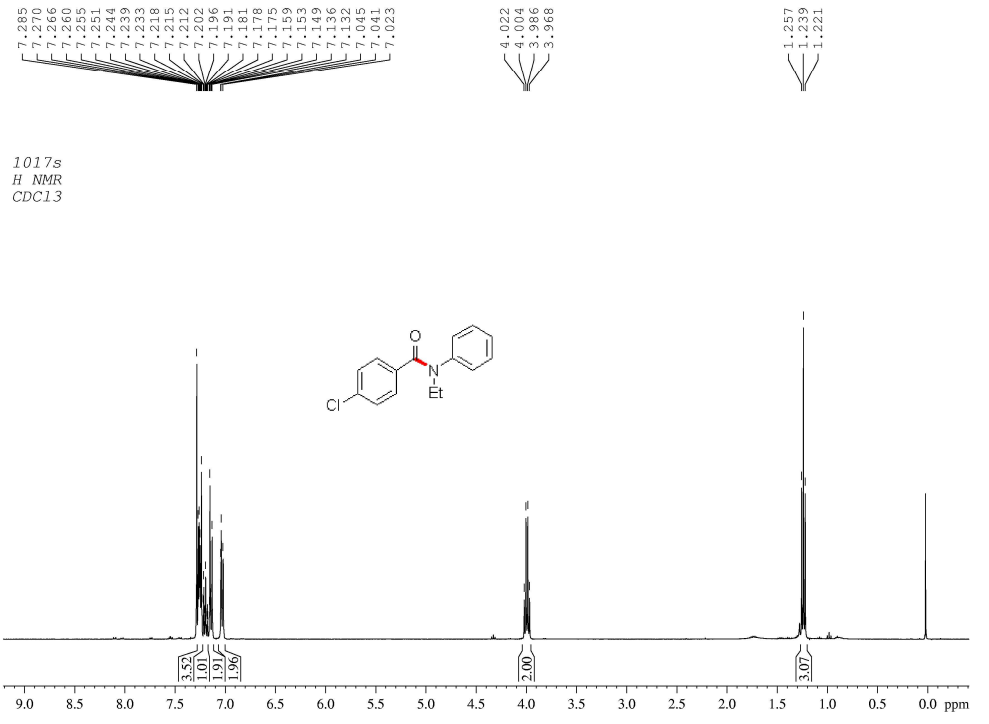
134.08
133.19
132.43
128.89
128.27
127.99
127.55
120.19
37.78
16.27
O
N
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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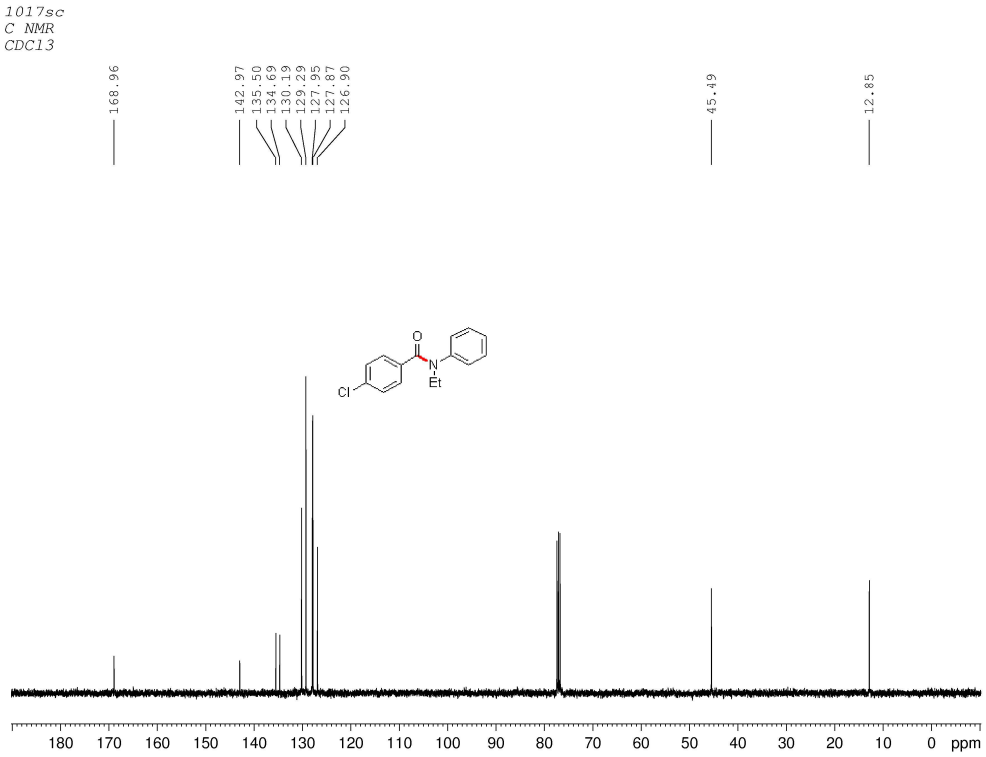
7.270
7.266
7.260
7.255
7.251
7.244
7.239
7.233
7.218
7.215
7.212
7.202
7.196
7.191
7.181
7.178
7.175
7.159
7.153
7.149
7.136
7.132
7.045
7.041
7.023
4.022
4.004
3.986
3.968
1.257
1.239
1.221
1017s
H NMR
CDC13
O
N
Et
Cl
3.52
1.01
1.91
1.96
2.00
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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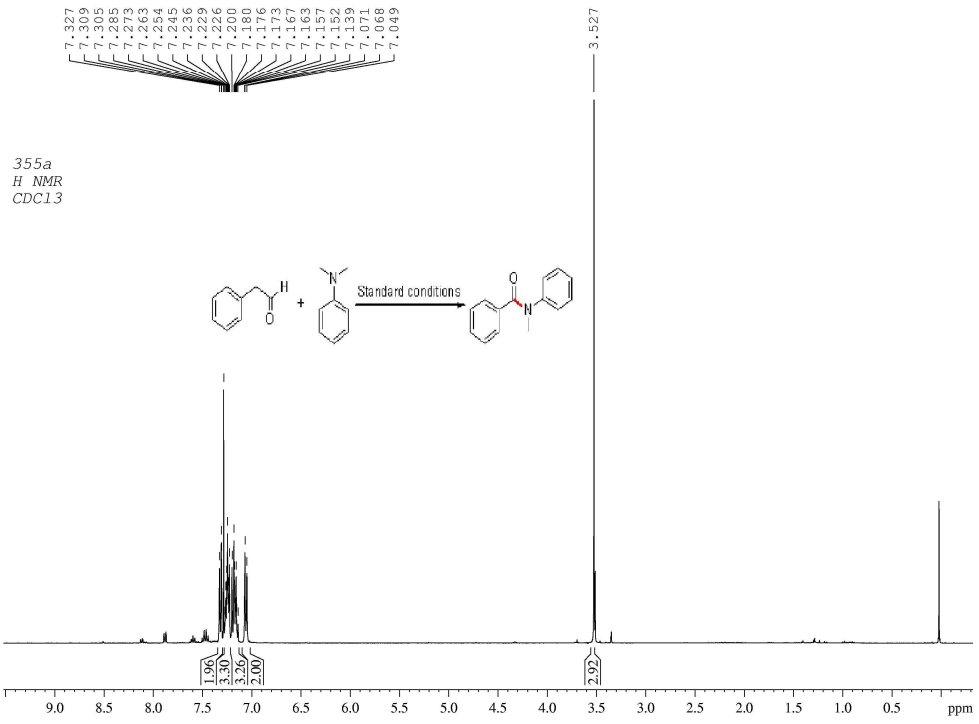
C NMR
CDC13
168.96
142.97
135.50
134.69
130.19
129.29
127.95
127.87
126.90
45.49
12.85
Cl
O
N
Et
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.327
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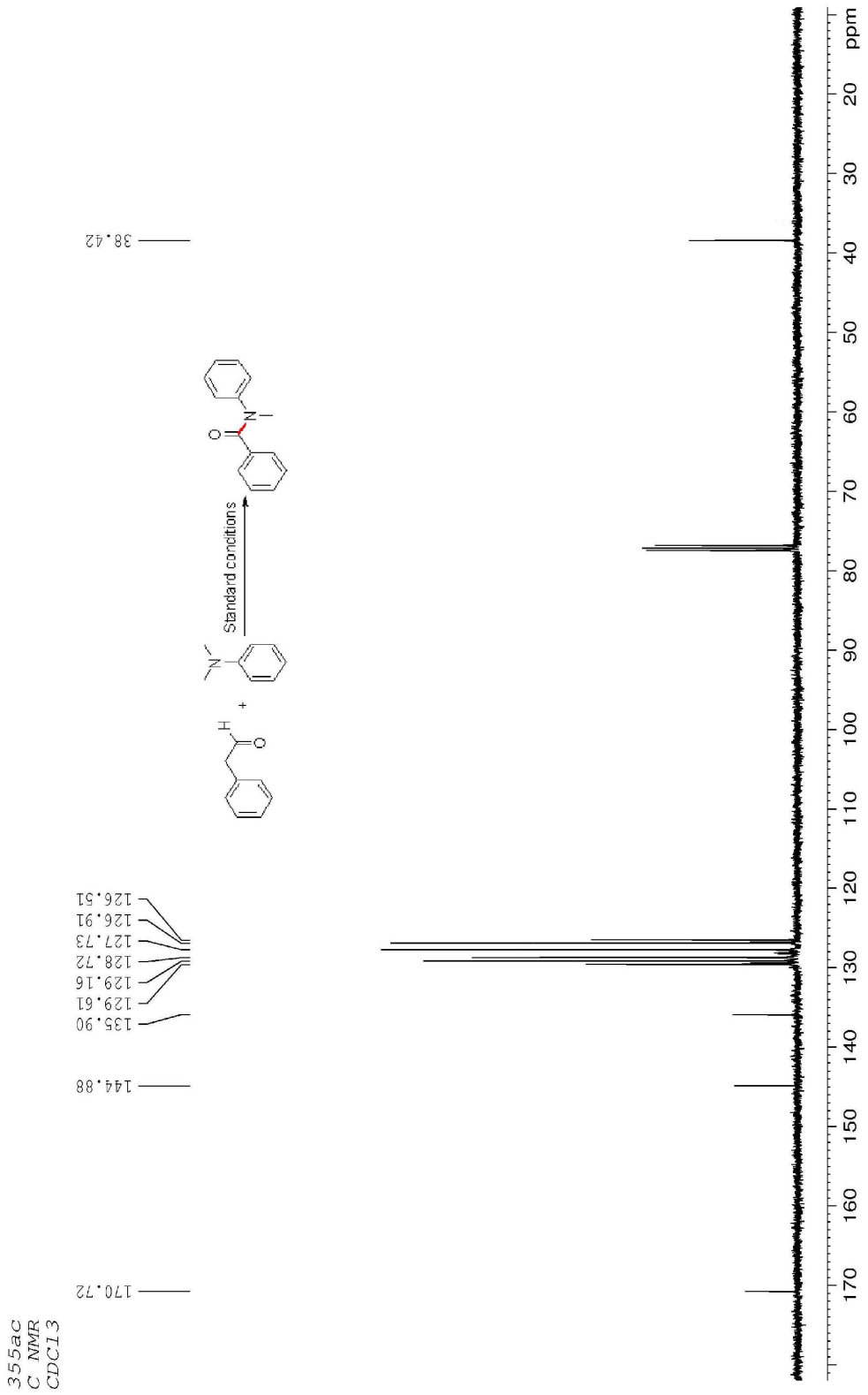
7.305
7.285
7.273
7.263
7.254
7.245
7.236
7.229
7.226
7.200
7.180
7.176
7.173
7.167
7.163
7.157
7.152
7.139
7.071
7.068
7.049
3.527
355a
H NMR
CDC13
Standard conditions
1.96
3.30
3.26
2.00
2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


355ac
C NMR
CDC13
170.72
144.88
135.90
129.61
129.16
128.72
127.73
126.91
126.51
38.42
Standard conditions
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170