Electronic Supporting Information (ESI)-1

Atmospheric Pressure Aminocarbonylation of Aryl Iodides using Palladium Nanoparticles Supported on MOF-5

Tuan T. Dang, Zhu Yinghuai, Subhash C. Ghosh, Chen Anqi, Christina L. L. Chai, Abdul M. Seayad*
Institute of Chemical and Engineering Sciences (ICES), 8 Biomedical Grove, #07-01 Neuros, Singapore 138665. Fax: 65-64642102; Tel: 65-67998527; E-mail: abdul_seayad@ices.a-star.edu.sg

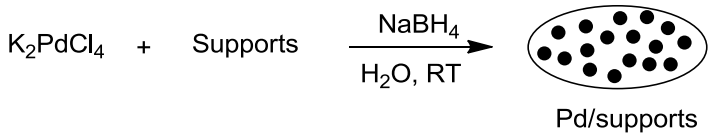
CONTENTS

General:

Materials. The chemicals were purchased from Aldrich or Alfa Aesar or Stem and are used as received unless mentioned. The solvents used were from Glass Contour solvent purification system.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker 400 MHz. Chemical shifts for protons were reported in parts per million (ppm) that are referenced to residual protium in the NMR solvent ($CHCl_3$: 7.26). Chemical shifts for carbon were given in ppm that also referenced to the carbon resonances of the solvent ($CDCl_3$: 77.16). Data are presented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constants (*J*) in Hertz (Hz). GC analysis was obtained from Agilent 6890N series instrument using a the HP-5 capillary column. HRMS (Thermo Finnigan MAT95XP), ICP analysis (Varian VISTA-MPX), BET surface area measurements (Qunatachrome AS-1 or micrometric ASAP2520), XRD (Bruker, D8 ADVANCE), SEM (JEOL JSM 6700F), TEM (FEI Tecnai TF 20ST/STEM), etc., were carried out using ICES central facility

1. Preparation of Pd nanoparticles on various supports



General procedure:

K_2PdCl_4 (97.92 mg, 0.3 mmol) was dissolved in 50 mL H_2O to form an orange solution. 1.0 g of the support (Al_2O_3, SiO_2, Florisil, Celite, 4 Å molecular sieve) was added into the solution, and the mixture was stirred for 30 minutes at room temperature. A solution of $NaBH_4$ in 30 mL water (3.0 mmol, excess) was added dropwise into the reaction mixture under vigorous stirring. The colour of mixture turned to gray immediately. After stirring about 60 minutes, the solid was isolated by filtration, washed 3 times with water (20 mL) and 3 times with methanol followed by dry ether (20 mL) and dried under vacuum at 100°C.[1] Pd on support (3.0 wt%) was obtained as a gray powder, and kept under nitrogen atmosphere. The palladium loadings of sample were determined by ICP-AES method.

2. Synthesis of Pd nanoparticle on MOF-5 with different Pd loadings

MOF-5 was prepared according to the procedure of Shu and coworkers.[2] The preparation was carried out under strict anhydrous conditions and the palladium nanoparticles (PdNPs) were supported on the surface of MOF-5 using a simple modified procedure as that for the preparation of PdNPs/Fe_3O_4 in water.[1] In the present case, the adsorbed K_2PdCl_4 was reduced using $NaBH_4$ in dry DMF instead of water.

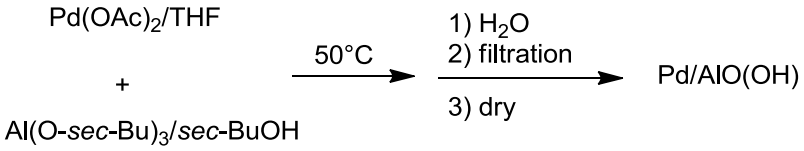
General procedure:

K_2PdCl_4 (16.32 mg, 0.05 mmol) was dissolved in 30 mL dry DMF to form an orange solution. MOF-5 (1.0 g) was added to the solution, the mixture was sonicated for five minutes and stirred for 30 minutes at room temperature. A solution of $NaBH_4$ in DMF (0.25 mmol, excess) was added dropwise into the reaction mixture under vigorous stirring. The colour of mixture turned to gray immediately. After stirring for about 60 minutes under argon atmosphere, the solid was isolated by filtration, washed with DMF (3x20 mL) followed by dry ether (3x20 mL), and dried under vacuum at 100°C. Pd-MOF-5 (0.5 wt%) was obtained as a gray powder, and stored under nitrogen

[1] K. V. S. Ranganath, J. Kloesges, A. H. Schäfer and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 7786.
[2] S. Gao, N. Zhao, M. Shu, S. Che, *Appl. Catal. A: Gen.*, 2010, **388**, 196.

atmosphere. The palladium loading was determined by ICP method. (The same procedure was applied for the preparation of Pd-MOF-5 (0.25 wt %, 1.0 wt% and 3.0 wt %).

3. Preparation of Pd nanoparticle on AlO(OH)



This Pd/AlO(OH) catalyst was prepared according to a protocol described in the literature.[3] $Pd(OAc)_2$ (115 mg, 0.512 mmol) was dissolved in THF (1 mL) to form a brown solution and stirred under air for 30 minutes. Al(O-*sec*-Bu)$_3$ (4.00 g, 16.2 mmol) and *sec*-BuOH (1 mL) were added to the reaction mixture with vigorously stirring and the mixture was heated at 50 °C for 20 min. Water (3 mL) was added to the reaction mixture and the solid was isolated by filtration, washed with acetone and dry ether, and dried at 120 °C under vacuum. Pd/AlO(OH) was obtained as gray powder, and stored under nitrogen atmosphere. The palladium loading was evaluated by ICP method.

4. Evaluation of Pd loadings on MOF-5 by ICP-AES method

Samples	**Pd wt % (ICP method)**
Pd/4Å-MS (3 wt%)	2.76
Pd/SiO_2 (3 wt%)	2.82
Pd/Al_2O_3 (3 wt%)	2.84
Pd/Florisil (3 wt%)	2.78
Pd/Celite (3 wt%)	2.77
Pd/AlO(OH) (3 wt%)	2.79
Pd/MOF-5 (3 wt%)	2.86
Pd/MOF-5 (1 wt%)	0.94
Pd/MOF-5 (0.5 wt%)	0.45
Pd/MOF-5 (0.25 wt%)	0.19

[3] Park, J. *et al. Org. Lett.* 2007, **9**, 3417.

5. XRD patterns of MOF-5 and Pd/MOF-5

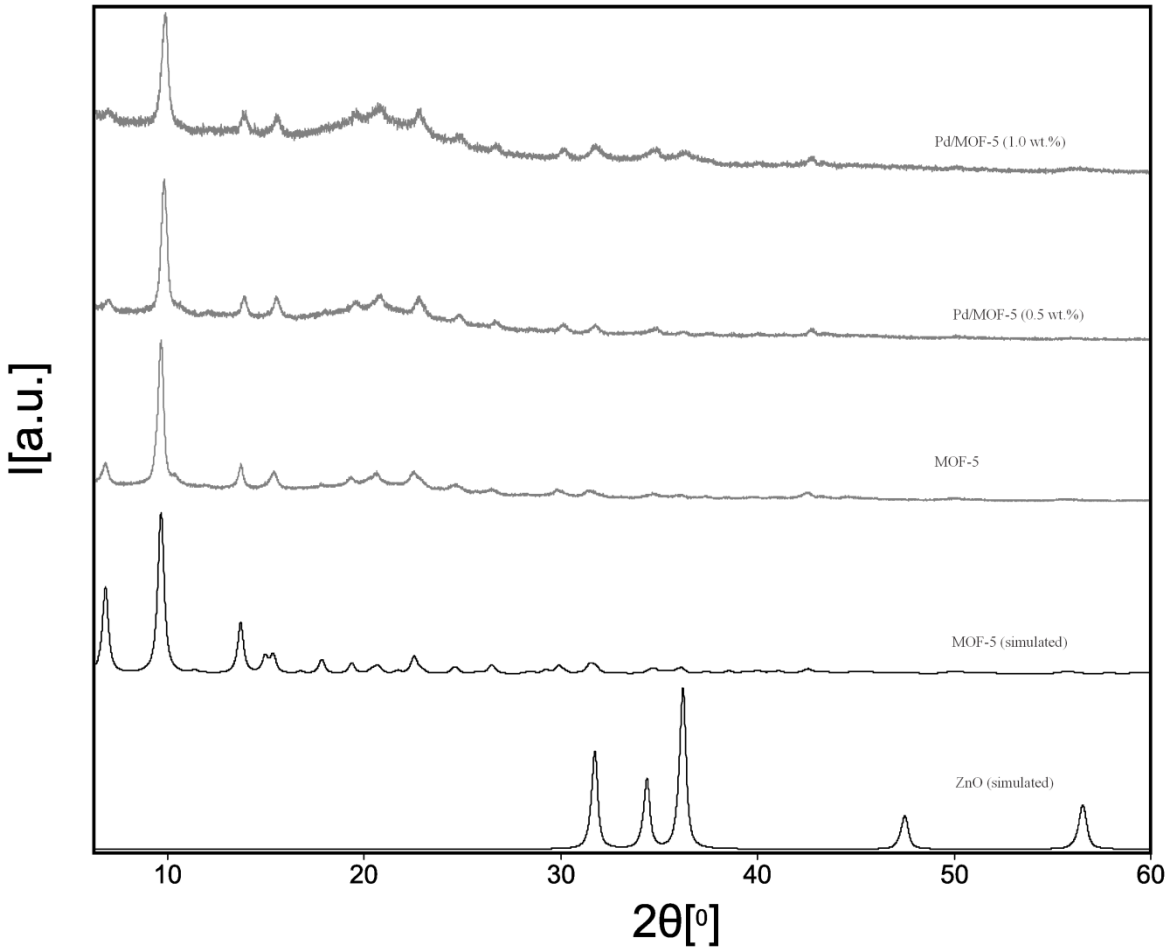


Figure 1: XRD patterns of MOF-5 & Pd/MOF-5 (0.5 & 1 wt%) together with MOF-5 Simulated and ZnO Simulated.

The comparison between simulated MOF-5 and simulated ZnO patterns clearly indicate that there is no significant ZnO content in the observed patterns and all crystalline peaks observed for PdMOF-5 can be compared with MoF-5. The reduced intensity of the the (1 0 2) reflection at 7° in 2θ may indicate a partial collapse of the MOF framework, but can also be explained by preferred orientation as can other discrepancies between calculated and observed intensities. All samples were measured in an airtight sample holder with a Poly(methyl methacrylate) cupola. The amorphous hump at 20-22° is mainly due to diffuse scattering at the cupola and is naturally more pronounced with less crystalline samples. However, we cannot exclude a partial collapse of the MOF-5framework and the formation of some amorphous phase.

6. SEM and TEM images

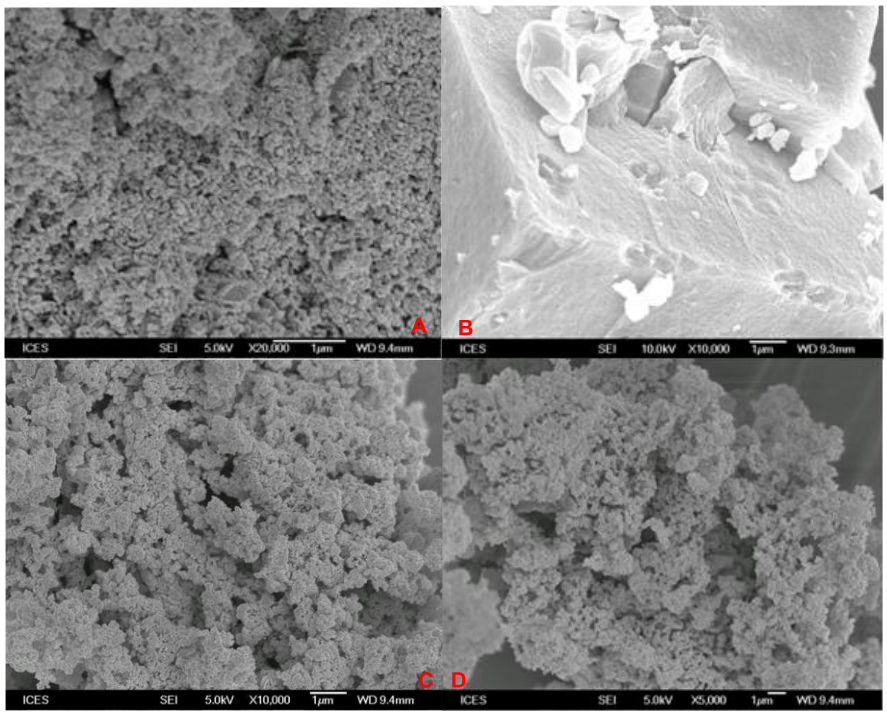


Figure 2: SEM images of MOF-5 (A & B) and Pd/MOF-5 (1 wt%, C) and Pd/MOF-5 (0.5 wt%, D)

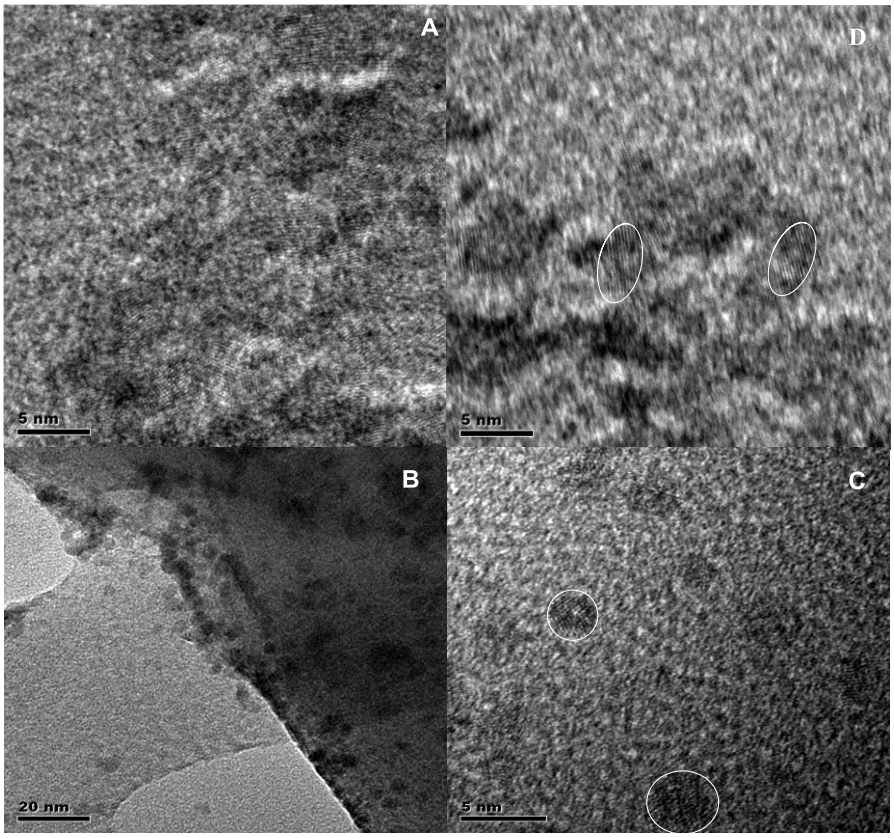


Figure 3: HR-TEM images of Pd/MOF-5 (3 wt% (A); 1 wt% (B); 0.5 wt% (C) and 0.25 wt% (B)

7. Surface area of catalysts (BET & Langmuir)

Table 1: Suface area (m^2/g) evaluated by BET and Langmuir methods

Samples	BET	Langmuir
MOF-5	718	1043
Pd/MOF-5 (3 wt%)	452	828
Pd/MOF-5 (1 wt%)	506	737
Pd/MOF-5 (0.5 wt%)	582	838
Pd/MOF-5 (0.25 wt%)	550	751

Particle size distribution

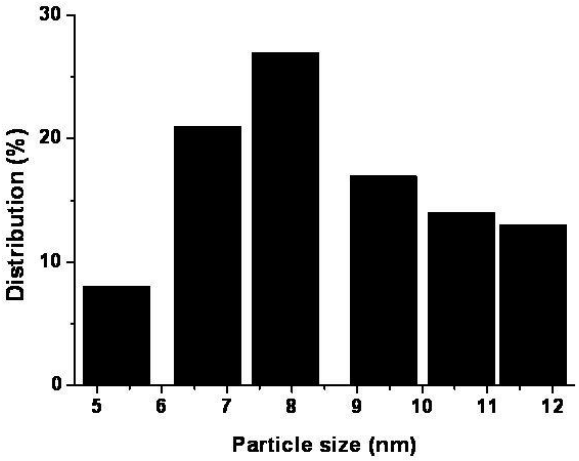
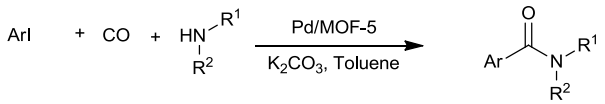


Figure 4: Particle size distribution of 0.5wt% Pd/MOF

8. Aminocarbonylation of iodoarenes

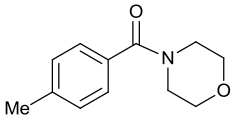


General procedure of aminocarbonylation:

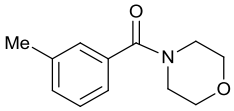
Toluene (dry) (1 mL) was added to a mixture of 15 mg of 0.5 wt% Pd/MOF-5 (0.25 mol % of Pd), 4-iodotoluene (53.8 mg, 0.25 mmol), morpholine (34.8 mg, 0.4 mmol) and K_2CO_3 (51.8 mg, 0.375 mmol), in a 50 mL Hi-Vac valve_schlenk tube. The Schlenk tube was evacuated and then filled with carbon monoxide gas from a balloon at room temperature. The reaction mixture was heated at 120°C. After the desired reaction time, the reaction mixture was cooled to room temperature to isolate the product. The catalyst was removed by filtration and washed

three times with DCM (30 mL). The organic solvents were removed by evaporation and the crude product was purified by column chromatography using gradient elution with EtOAc:Hexane (10:1-1:1).

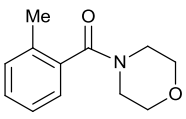
Characterization of amides



N-(4-Toluoyl)morpholine (3a):[4] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 49.7 mg (0.242 mmol, 97%) N-(4-Toluoyl)morpholine as an yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ= 2.37 (s, 3H), 3.37-3.90 (m, 8H), 7.59 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.7, 42.9, 48.6, 67.2, 127.4, 129.4, 132.6, 140.4, 171.0. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{15}NO_2$: 206.1182. Found: 206.1186.



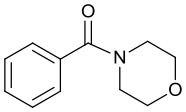
N-(3-Toluoyl)morpholine (3b):[2] The general procedure was followed by using 3-iodotoluene (53.8 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 48.2 mg (0.235 mmol, 94%) N-(3-Toluoyl)morpholine as an yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ= 2.37 (s, 3H), 3.32-3.90 (m, 8H), 7.16 (d, *J* = 4.7 Hz, 1H), 7.22-7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.4, 42.5, 48.2, 66.9, 124.0, 127.7, 128.4, 130.6, 135.3, 138.5, 170.8. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{15}NO_2$: 206.1182. Found: 206.1184.



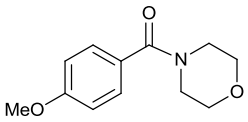
N-(2-Toluoyl)morpholine (3c):[3] The general procedure was followed by using 2-iodotoluene (53.8 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 36.9 mg (0.18 mmol, 72%) N-(2-

[4] K. Ekoue-Kovi, C. Woft, *Org. Lett.* 2007, **9**, 3429.

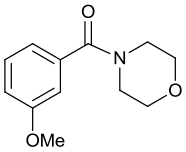
Toluoyl)morpholine as anyellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ= 2.31 (s, 3H) 3.24 (br d, *J* = 4.5 Hz, 2H), 3.57, (br t, *J* = 4.5 Hz, 2H), 3.75-3.84 (br m, 4H), 7.14-7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 19.1, 42.0, 47.4, 67.1, 125.9, 126.1, 129.2, 130.6, 134.3, 135.8, 170.3. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{15}NO_2$: 206.1182. Found: 206.1183.



N-Benzoylmorpholine (3d):[2] The general procedure was followed by using iodobenzene (51.1 mg, 0.25 mmol), morpholine (34.8 mg, 0.4 mmol) and K_2CO_3 (51.8 mg, 0.375 mmol), in a 50 mL Hi-Vac valve_schlenk tube. The Schlenk tube was evacuated and then filled with carbon monoxide gas from a balloon at room temperature. The reaction was carried out in 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexan 1:6-1:2) gave 46.8 mg (0.245 mmol, 98%) of a yellow crystal. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.32-3.93 (m, 8H), 7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.8, 48.5, 67.2, 127.3, 128.9, 130.2, 135.5, 170.7. HR-MS $(M+H)^+$ m/z Calcd for $C_{11}H_{12}N_2O_4$: 259.0707. Found: 259.0701.



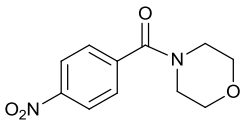
N-(4-Methoxybenzoyl)morpholine (3e):[5] The general procedure was followed by using 4-methoxytoluene (58.5 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 41.4 mg (0.19 mmol, 75%) N-(4-Methoxybenzoyl)morpholine as an yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.45-3.80 (m, 8H), 3.81 (s, 3H), 6.88 (d, J = 8.4 Hz, 2H), 7.35 (dd, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.6, 48.2, 55.4, 67.0, 113.8, 129.3, 161.0, 170.5. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{15}NO_3$: 222.1125. Found: 222.1122.



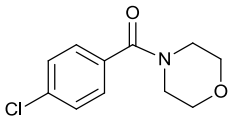
N-(3-Methoxybenzoyl)morpholine (3f):[1] The general procedure was followed by using 3-methoxytoluene (58.5 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 46.4 mg (0.21 mmol, 84%) N-(3-Methoxybenzoyl)morpholine as an yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ =

[5] K. Shimizu, K. Ohshima, A. Satsuma, *Chem. Eur. J.* 2009, **15**, 9977.

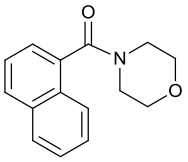
3.32-3.81 (m, 8H), 3.75 (s, 3H), 6.89 (m, 3H), 7.24 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.5, 48.2, 55.4, 66.9, 112.5, 115.6, 119.1, 129.7, 136.6, 159.7, 170.2. HR-MS $(M+H)^+$ m/z Calcd for $C_{12}H_{15}NO_3$: 222.1125. Found: 222.1120.



N-(4-Nitrobenzoyl)morpholine (3g):[1] The general procedure was followed by using 4-iodo-1-nitrobenzene (62.3 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 46.0 mg (0.195 mmol, 78%) N-(4-Nitrobenzoyl)morpholine as yellow crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.25-3.98 (m, 8H), 7.57 (d, J = 6.9 Hz, 2H), 8.27 (d, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.7, 48.1, 66.8, 124.1, 128.2, 141.5, 148.6, 168.1. HR-MS $(M+H)^+$ m/z Calcd for $C_{11}H_{12}N_2O_4$: 237.0876. Found: 237.0873.

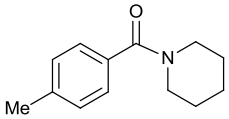


N-(4-Chlorobenzoyl)morpholine (3h):[1] The general procedure was followed by using 4-chloro-1-iodotoluene (59.6 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 54.1 mg (0.24 mmol, 96%) N-(4-Chlorobenzoyl)morpholine as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.30-3.88 (m, 8H), 7.25-7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.7, 48.2, 66.9, 128.7, 128.9, 133.7, 136.1, 169.5. HR-MS $(M+Na)^+$ m/z Calcd for $C_{11}H_{12}NO_2Cl$: 248.6613. Found: 248.6619.

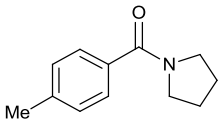


N-(1-Naphthoyl)morpholine (3i):[2] The general procedure was followed by using 1-iodonaphthalene (63.5 mg, 0.25 mmol) and morpholine (34.8 mg, 0.4 mmol) for 8h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:6-1:2) gave 49.9 mg (0.207 mmol, 83%) of product as yellow crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.25-3.99 (m, 8H), 7.45 (m, 3H), 7.81 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 42.8, 48.4, 67.0, 124.3,

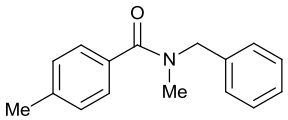
126.9, 127.1, 127.3, 127.9, 128.5, 128.6, 132.7, 132.8, 133.8, 170.5. HR-MS $(M+H)^+$ m/z Calcd for $C_{15}H_{15}NO_2$: 242.1182. Found: 242.1185.



(4-Methyl-phenyl)-piperidin-1-yl-methanone (3j):[6] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and pyperidine (34.2 mg, 0.4 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 48.2 mg (0.237 mmol, 95%) of product as a colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.49-1.82 (br m, 6H), 2.37 (s, 3H), 3.36 (br s, 2H), 3.69 (br s, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 7.8, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.5, 24.8, 25.7, 26.7, 43.3, 49.0, 127.0, 129.1, 133.7, 139.5, 170.6. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{17}NO$: 203.1315. Found: 204.1384.



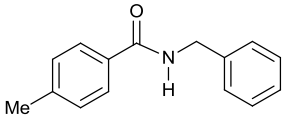
N-(4-Toluoyl)pyrrolidine (3k):[1] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), pyrrolidine (53.25 mg, 0.75 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 39.7 mg (0.21 mmol, 84%) of product as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.85-2.00 (m, 4H), 2.36 (s, 3H), 3.42(t, J = 6.4 Hz, 2H), 3.63 (t, J = 7.1 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 7.8 Hz,2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.5, 24.6, 26.5, 46.3, 49.8, 127.3, 128.9, 134.4, 140.1, 169.9. HR-MS $(M+Na)^+$ m/z Calcd for $C_{12}H_{15}NO$: 212.1052. Found: 212.1054.



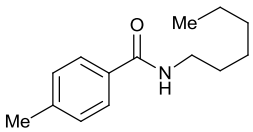
4-Methyl-N-benzyl-N-methylbenzamide (3l):[7], The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and N-methyl-1-benzylamine (48.4 mg, 0.4 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 47.8 mg (0.20 mmol, 80%) of product as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.36 (s,

[6] Y. Jo, J. Ju, J. Choe, K. H. Song and S. Lee, *J. Org. Chem.*, 2009, **74**, 6358.
[7] S. Y. Seo, T. J. Marks, *Org. Lett*., 2008, **10**, 317.

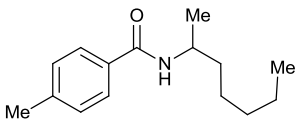
6H), 2.87 (bs, 3H), 3.01 (bs, 3H), 4.53 (bs, 2H), 4.75 (bs, 2H), 7.12-7.39 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.5, 33.3, 37.2, 51.0, 55.3, 127.3, 127.8.128.4, 128.7, 129.0, 129.3, 129.9, 133.4, 137.2, 139.8, 171.8, 172.5. HR-MS $(M+H)^+$ m/z Calcd for $C_{16}H_{17}NO$: 240.1307. Found: 240.1373.



4-Methyl-*N*-benzylbenzamide (3m):[3] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and benzylamine (42.8 mg, 0.4 mmol) for 12h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 41.1 mg (0.183 mmol, 73%) of product as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.39 (s, 3H), 4.63 (d, *J* = 6.3Hz, 2H), 6.43 (br s, 1H), 7.21 (d, *J* = 6.3 Hz, 2H), 7.24-7.35 (m, 5H), 7.69 (d, *J* = 6.3Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 21.9, 44.4, 127.3, 127.9, 128.3, 129.1, 129.6, 131.8, 138.6, 142.3, 167.6. HR-MS $(M+Na)^+$ m/z Calcd for $C_{15}H_{15}NO$: 248.1052. Found: 248.1046.

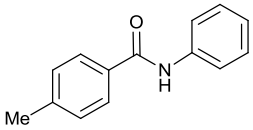


4-Methyl-*N*-hexylbenzamide (3n):[3] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and hexylamine (34.2 mg, 0.4 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 46.03 mg (0.21 mmol, 84%) of product as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.87 (t, *J* = 6.9 Hz, 3H), 1.28-1.35 (m, 6H), 1.58 (m, 2H), 2.37 (s, 3H), 3.40 (m, 2H), 6.31 (br, s, 1H) 7.20 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 14.12, 21.5, 22.7, 26.8, 29.8, 31.6, 40.2, 126.9, 129.2, 132.1, 141.7, 167.6. HR-MS $(M+Na)^+$ m/z Calcd for $C_{14}H_{21}NO$: 242.1518. Found: 242.1513.

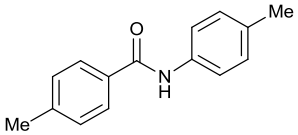


N-(heptan-2-yl)-4-methylbenzamide (3o):[3] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol) and heptan-2-amine (46.2 mg, 0.4 mmol) for 12h at 120 °C. Purification by flash chromatography (EtOAc:Hexane 1:8-1:2) gave 47.8 mg (0.205 mmol, 82%) of product as white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.87 (m, 3H), 1.22 (d,

J = 6.6 Hz, 3H), 1.23-1.38 (m, 6H), 0.51 (m, 2H), 2.39 (s, 3H), 4.18 (m, 1H), 5.85 (br, s, 1H) 7.21 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 14.2, 21.2, 21.6, 22.7, 25.9, 31.9, 37.2, 45.8, 126.9, 129.3, 130.5, 132.4, 141.7, 166.9. HR-MS $(M)^+$ m/z Calcd for $C_{15}H_{23}NO$: 233.1780. Found: 233.2030.

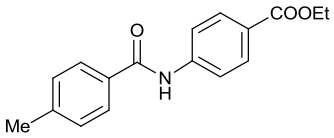


4-methyl-N-phenylbenzamide (3p)[8]: The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), aniline (37.2 mg, 0.4 mmol) and Pd/MOF-5 (30 mg, 1.0 wt%) for 24h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 44.8 mg (0.212 mmol, 85%) of product as white solid. mp 145- 146°C; ^{1}H NMR ($CDCl_3$, 300MHz) δ = 1.49 (s, 3H), 6.17(m, 1H), 6.42 (m, 4H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 9.22 (s, 1H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 21.98, 121.3, 124.5, 128.7, 133.0, 140.2, 142.5, 166.3. HR-MS $(M+H)^+$ m/z Calcd for $C_{14}H_{13}NO$: 212.0997. Found: 212.1070.

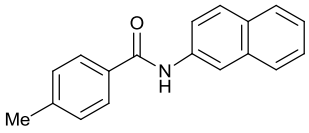


4-methyl-N-(p-tolyl)benzamide (3q):[9] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), 4-methylaniline (42.8 mg, 0.4 mmol) and Pd/MOF-5 (30 mg, 1.0 wt%) for 24h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 41.6 mg (0.185 mmol, 74%) of product as white solid; ^{1}H NMR($CDCl_3$, 300MHz) δ = 2.33 (s, 3H), 2.41 (s, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H) 7.82 (br s, 1H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 21.0, 21.6, 120.4, 127.1, 129.5, 129.7, 132.3, 134.2, 135.6, 142.4, 165.7. HR-MS $(M+Na)^+$ m/z Calcd for $C_{15}H_{15}NO$: 248.1050. Found: 248.1044.

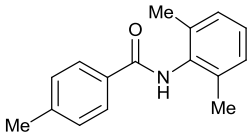
[8] S. Hitomi, T. Junko, H. Yoshio, S. Naofumi, O. Atsuhiro, *Chem. Lett.*, **1983**, 449.
[9] X.-F., Wu, *et al*. *Tetrahedron Lett.*, 2011, **52**, 3702.



Ethyl 4-(4-methylbenzamido)benzoate (3r): The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), ethyl-4-aminobenzoate (66.1 mg, 0.4 mmol) and Pd/MOF-5 (30 mg, 1.0 wt%) for 24h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 50.2 mg (0.177 mmol, 53%) of product as white solid; ^{1}H NMR($CDCl_3$, 300MHz) δ = 1.40 (t, *J* = 7.1 Hz, 3H), 2.43 (s, 3H), 4.37 (q, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.92 (br s, 1H), 8.07 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 14.5, 21.7, 61.0, 119.2, 126.2, 127.2, 129.7, 131.0, 131.8, 142.3, 143.0, 165.8, 166.1. HR-MS $(M+H)^+$ m/z Calcd for $C_{17}H_{17}NO_3$: 284.1213. Found: 284.1286.



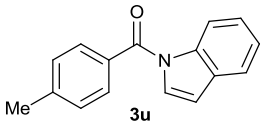
4-methyl-N-(naphthalen-2-yl)benzamide (3s):[10] The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), naphthalen-2-amine (57.2 mg, 0.4 mmol) and Pd/MOF-5 (30 mg, 1.0 wt%) for 36h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 43.06 mg (0.165 mmol, 66%) of product as white solid; ^{1}H NMR($CDCl_3$, 300MHz) δ = 2.44 (s, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.40-7.51 (m, 2H), 7.59 (dd, *J* = 8.8 Hz, 1H), 7.82 (m, 5H), 7.96 (br s, 1H), 8.34 (d, *J* = 1.9 Hz, 2H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 21.7, 117.1, 120.2, 125.2, 126.7, 127.2, 127.7, 127.9, 129.0, 129.7, 130.9, 132.2, 135.6, 142.7, 165.9. HR-MS $(M+Na)^+$ m/z Calcd for $C_{18}H_{15}NO$: 284.1057. Found: 284.1051.



N-(2,6-dimethylphenyl)-4-methylbenzamide (3t): The general procedure was followed by using 4-iodotoluene (53.8 mg, 0.25 mmol), 2,6-dimethylaniline (90.8 mg, 0.75 mmol) and Pd/MOF-5 (30 mg, 1.0 wt%), for 36h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 31.7 mg (0.133 mmol, 53%) of product as white solid; ^{1}H

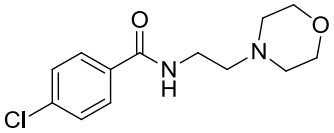
[10] C. I. Chiriac, *Revue Roumaine de Chimie*, 1982, **27**, 747.

NMR($CDCl_3$, 300MHz) δ = 2.27 (s, 3H), 2.44 (s, 3H), 7.12 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.38 (br s, 1H), 7.82 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 18.6, 21.6, 127.4, 128.4, 129.6, 134.1, 135.7, 142.5, 159.4, 165.9. HR-MS $(M+Na)^+$ m/z Calcd for $C_{16}H_{17}NO$: 262.1199. Found: 262.1193.



3u

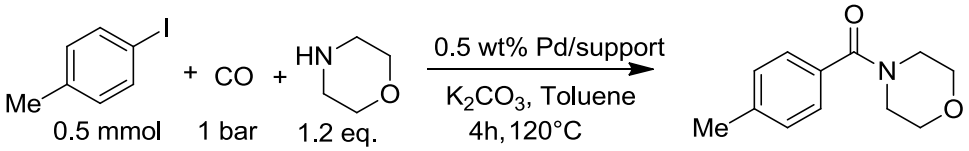
(1H-indol-1-yl)(*p*-tolyl)methanone(3u): The general procedure was followed by using, 4-iodotoluene (53.8 mg, 0.25 mmol), indole (46.8 mg, 0.4 mmol) and Pd/MOF-5 (30 mg, 0.5 wt%) for 24h at 120°C. Purification by flash chromatography (EtOAc:Hexane 1:20-1:10) gave 47.6 mg (0.202 mmol, 81%) of product as white solid; ^{1}H NMR($CDCl_3$, 300MHz) δ = 2.46 (s, 3H), 6.61 (d, *J* = 3.7 Hz, 1H), 7.32-7.39 (m, 5H), 7.60 (d, *J* = 7.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 8.38 (m, 1H); ^{13}C NMR（$CDCl_3$, 75 MHz）δ = 21.8, 108.4, 116.5, 121.0, 123.9, 124.9, 127.8, 129.4, 129.6, 131.0, 131.8, 136.2, 142.8, 168.9. HR-MS $(M+Na)^+$ m/z Calcd for $C_{16}H_{13}NO$: 258.0904. Found: 235.0898.

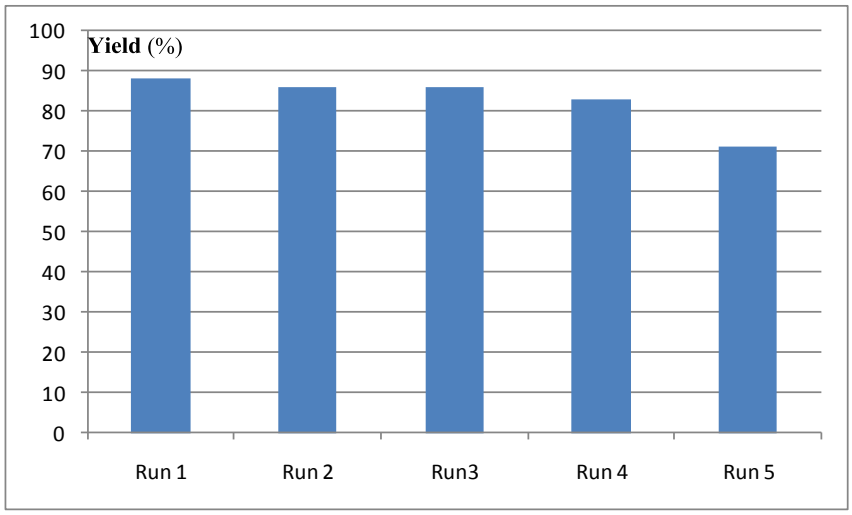


4-chloro-N-(2-morpholinoethyl)benzamide (*Moclobemide*®) 6: Toluene (dry) (6 mL) was added to a mixture of Pd/MOF-5 (60 mg, 0.5 wt%), 4-chloro-1-iodotoluene (238.5 mg, 1.0 mmol), 2-morpholinoethanamine (195.3 mg, 1.5 mmol) and K_2CO_3 (207 mg, 1.5 mmol), in a 50 mL Parr reactor. The Parr reactor was purged 3 times with N_2 and then filled with carbon monoxide gas at 20 PSI at room temperature. The reaction was carried out in 24h at 120 °C. Purification by flash chromatography (EtOAc:Hexan 1:6-3:1) gave 253 mg (0.94 mmol, 94%) of a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.48 (m, 4H), 2.57 (t, *J* = 6.0 Hz, 2H), 3.49-3.54 (dd, *J* = 11.3, 5.7 Hz, 2H), 3.70 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.69 (dd, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 36.2, 53.4, 56.9, 67.1, 128.5, 128.9, 133.1, 137.7, 166.4. HR-MS $(M+H)^+$ m/z Calcd for $C_{13}H_{18}ClN_2O_2$: 269.1051. Found: 269.1058.

9. Recycle study

Recycle studies with aminocarbonylation of p-iodotoluene and morpholine were carried out in pressure reactor (HEL CAT-7 reactor with 10mL vial capacity and the reaction mixture was magnetically agitated) at 2 atm of CO. After each run, the solid particles were allowed settle and the supernatant liquid was removed by a syringe, wash with toluene and charged with fresh substrates, solvent and 1 equivalent of base under an argon blanket before starting the aminocarbonylation. After the 5th run, it was difficult to separate the solids from the liquid as it took long time to settle down and no further recycle was carried out.





In order to estimate the Pd leaching, ICP analysis was carried out using the filtrate of standard aminocarbonylation of *p*-iodotoluene with morpholine using 30 mg of Pd/MOF-5 (0.5 wt%) in HEL reactor at 1 bar.

Pd leaching analysis by ICP AES:

Experiment	Pd leaching, ppm
Run 1	1.22
Run 2	1.26
Run 3	0.92
Run 4	1.02
Run 5	1.36

Electronic Supplementary Material (ESI) for Chemical Communications

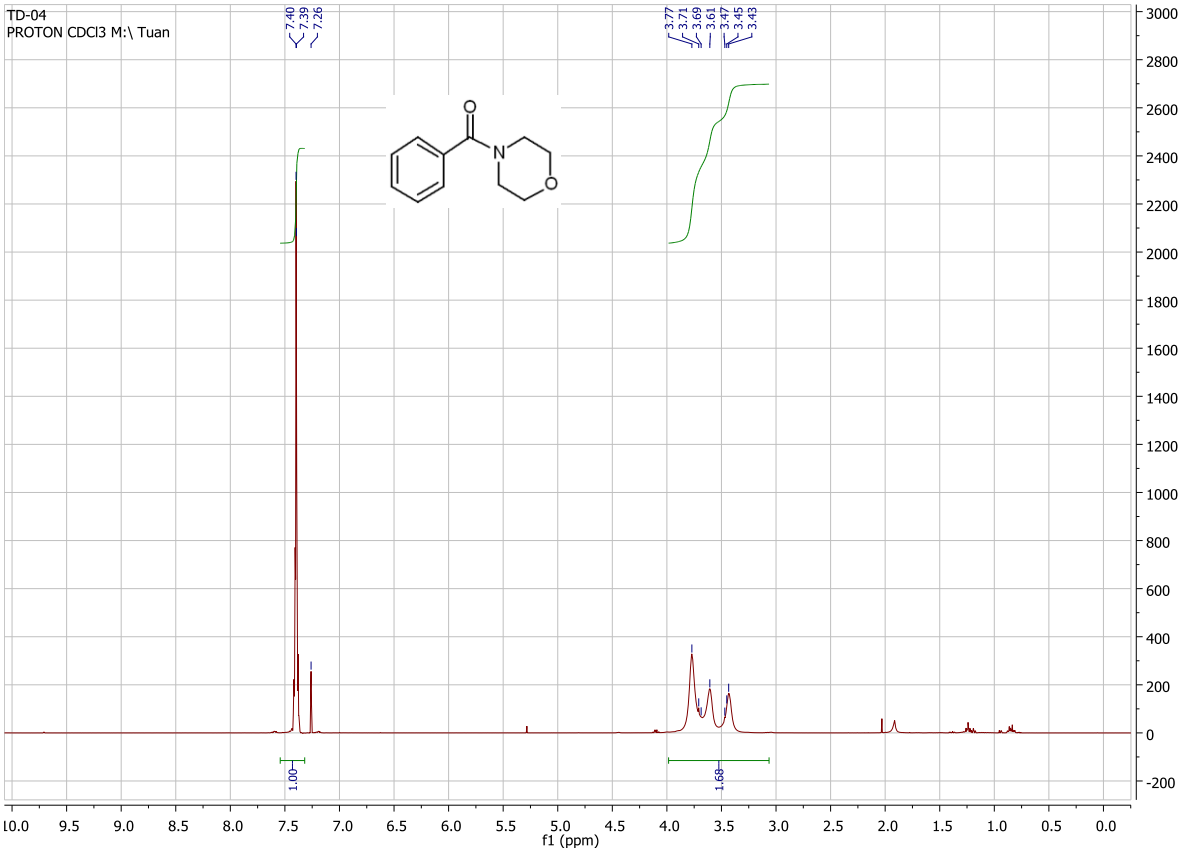
Electronic Supporting Information (ESI)-2

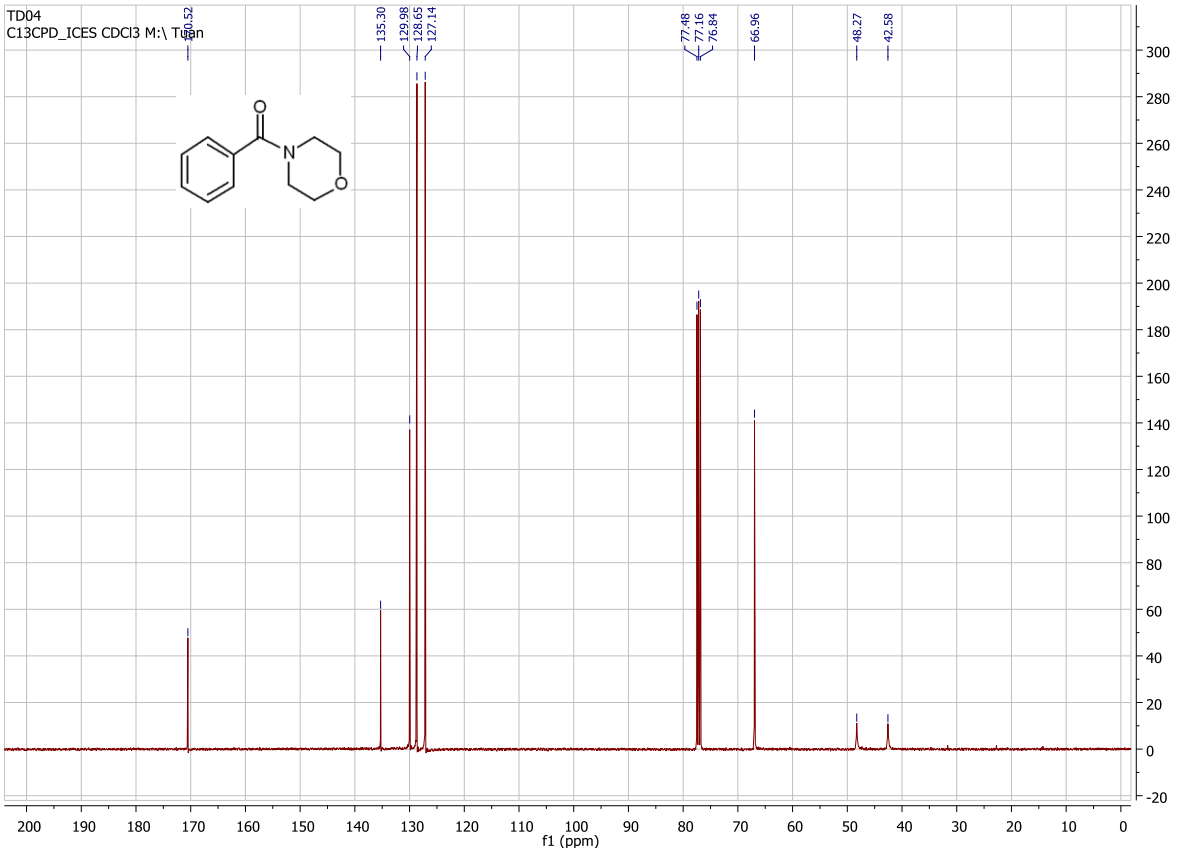
Atmospheric Pressure Aminocarbonylation of Aryl Iodides using Palladium Nanoparticles Supported on MOF-5

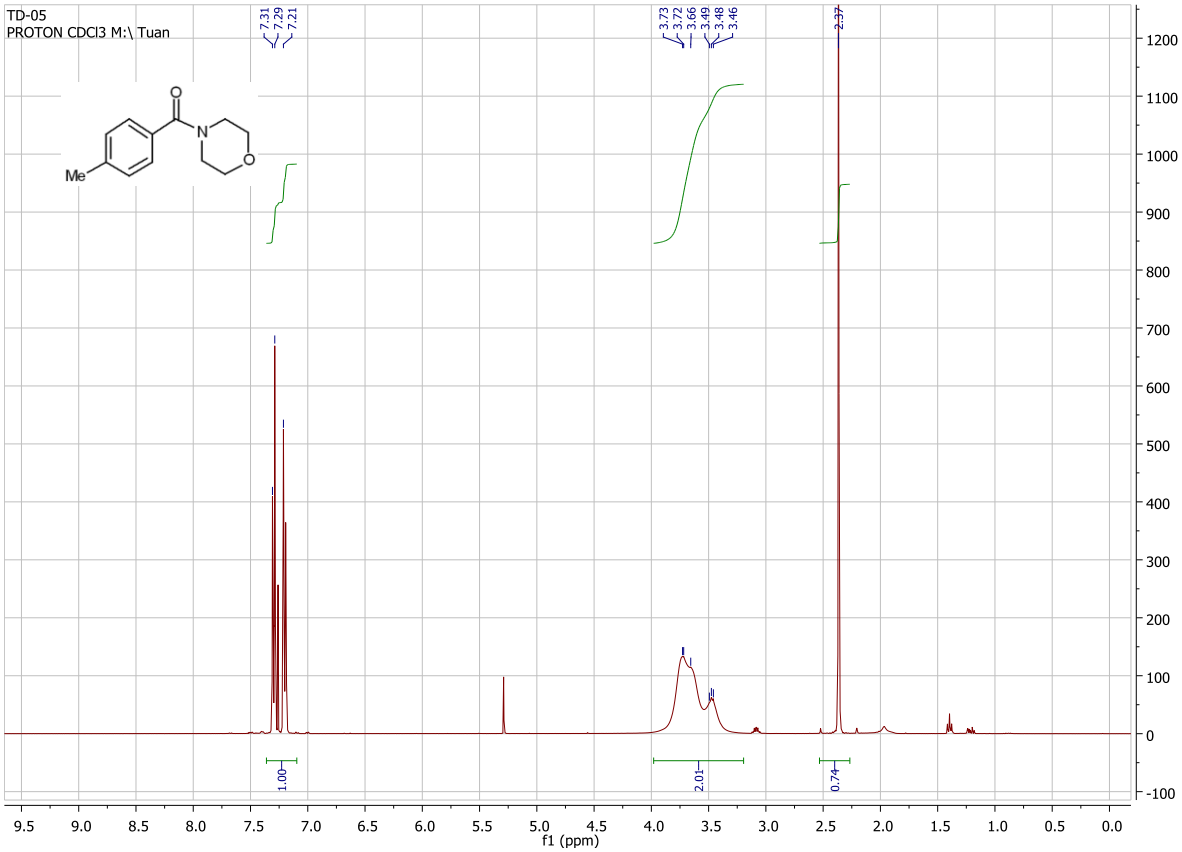
Tuan T. Dang, Zhu Yinghuai, Subhash C. Ghosh, Chen Anqi, Christina L. L. Chai, Abdul M. Seayad*

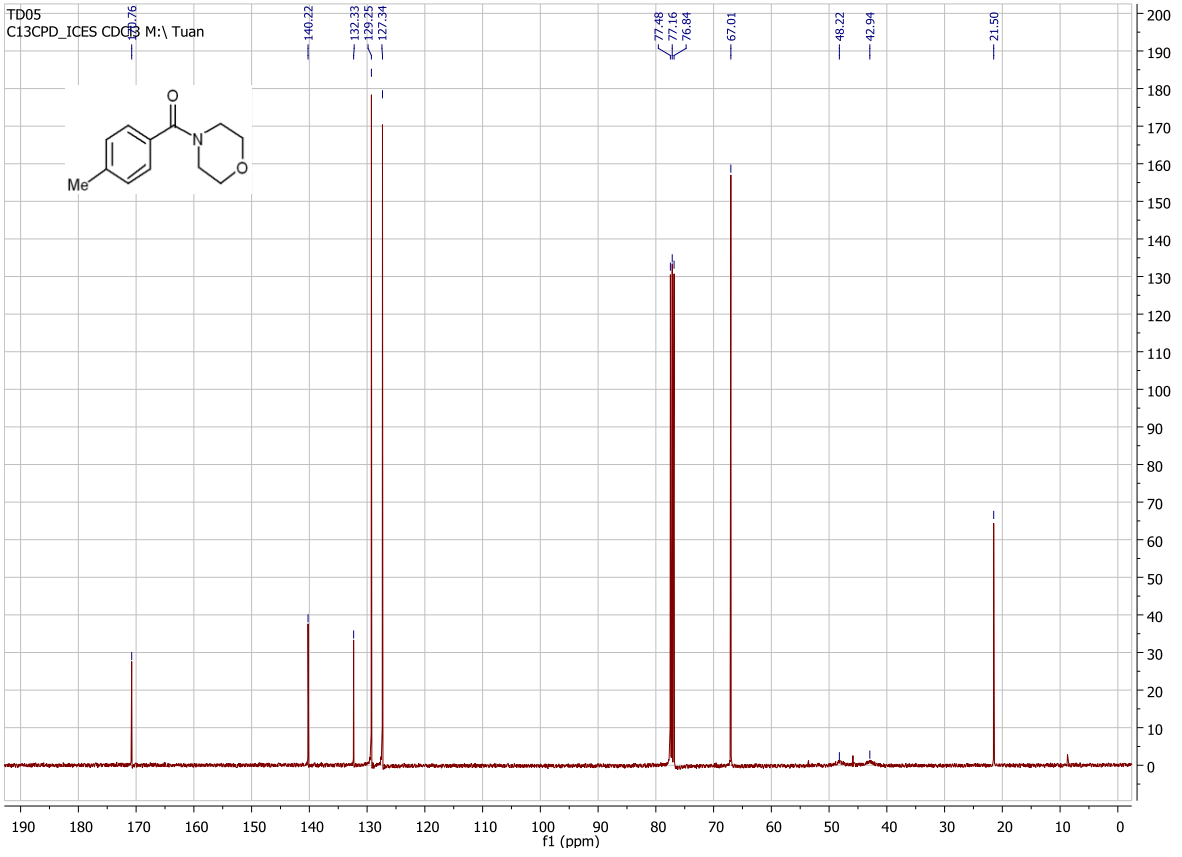
Content

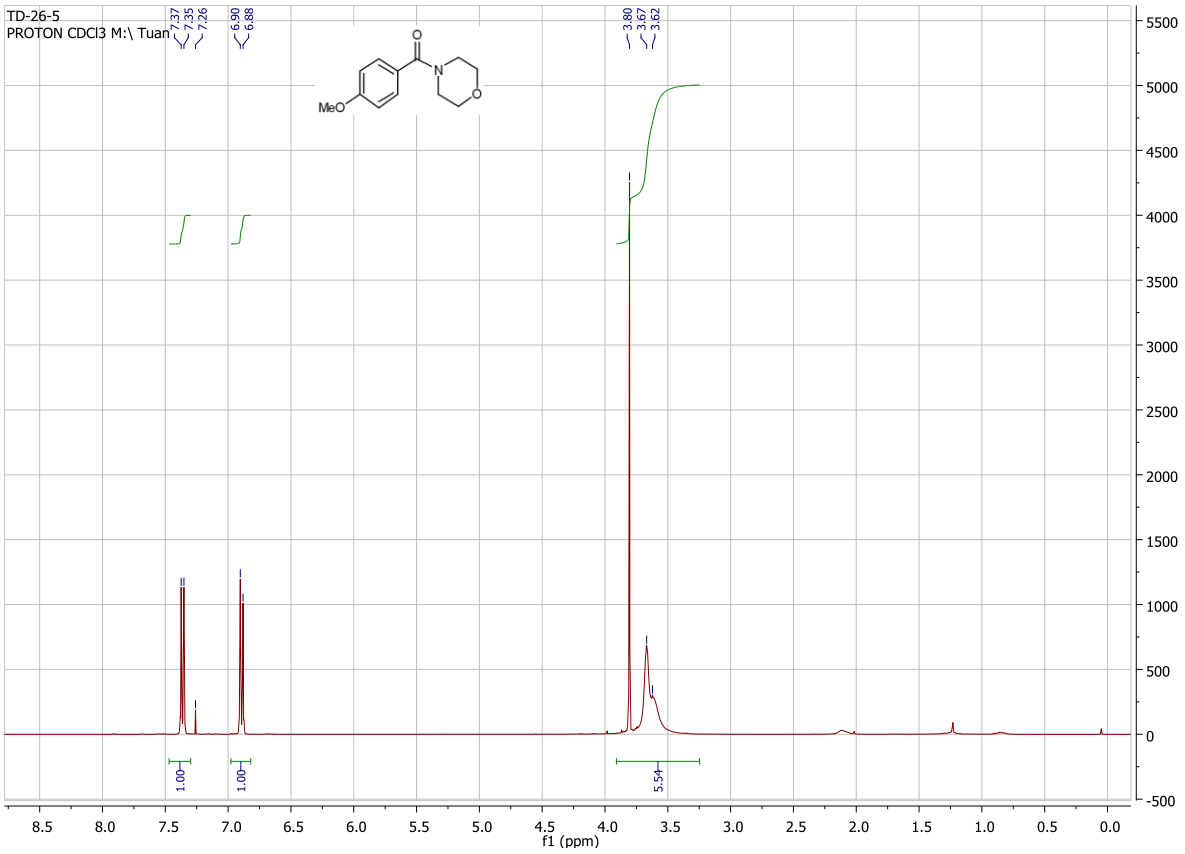
Supporting NMR Data

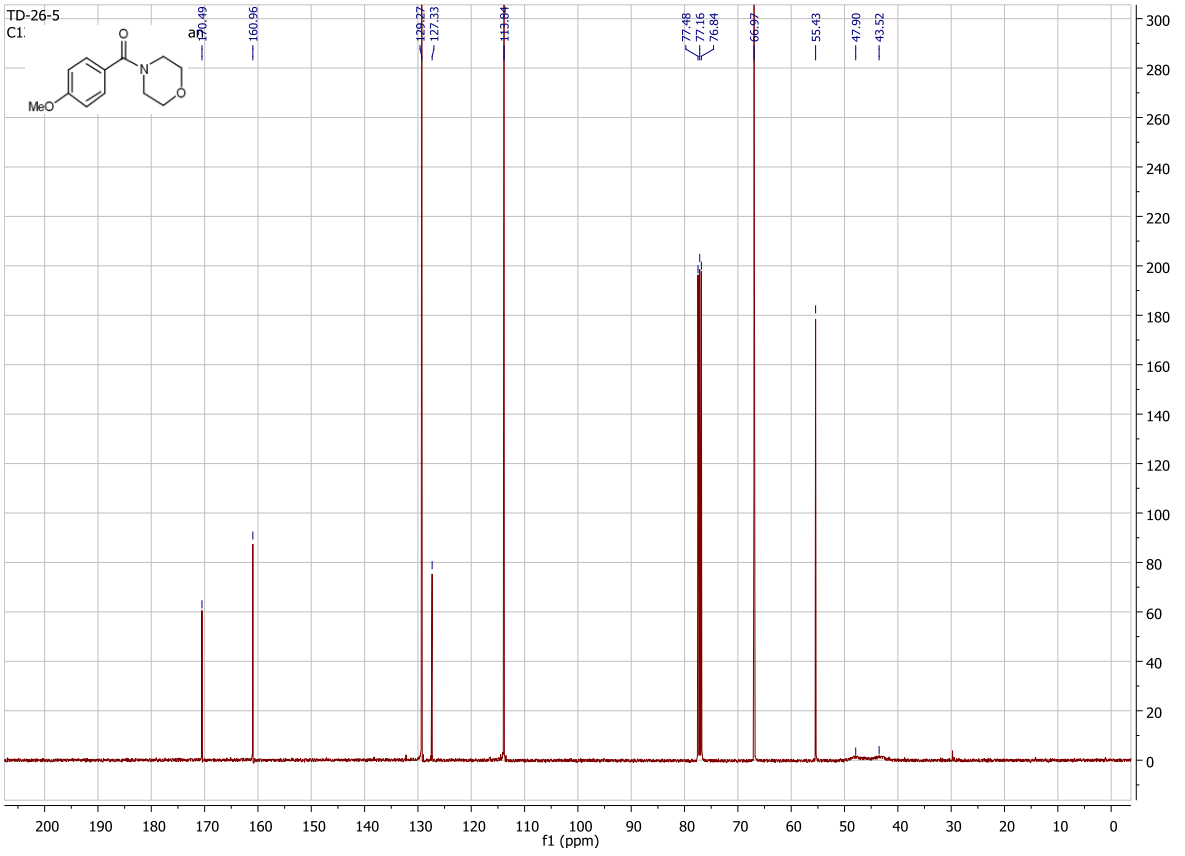


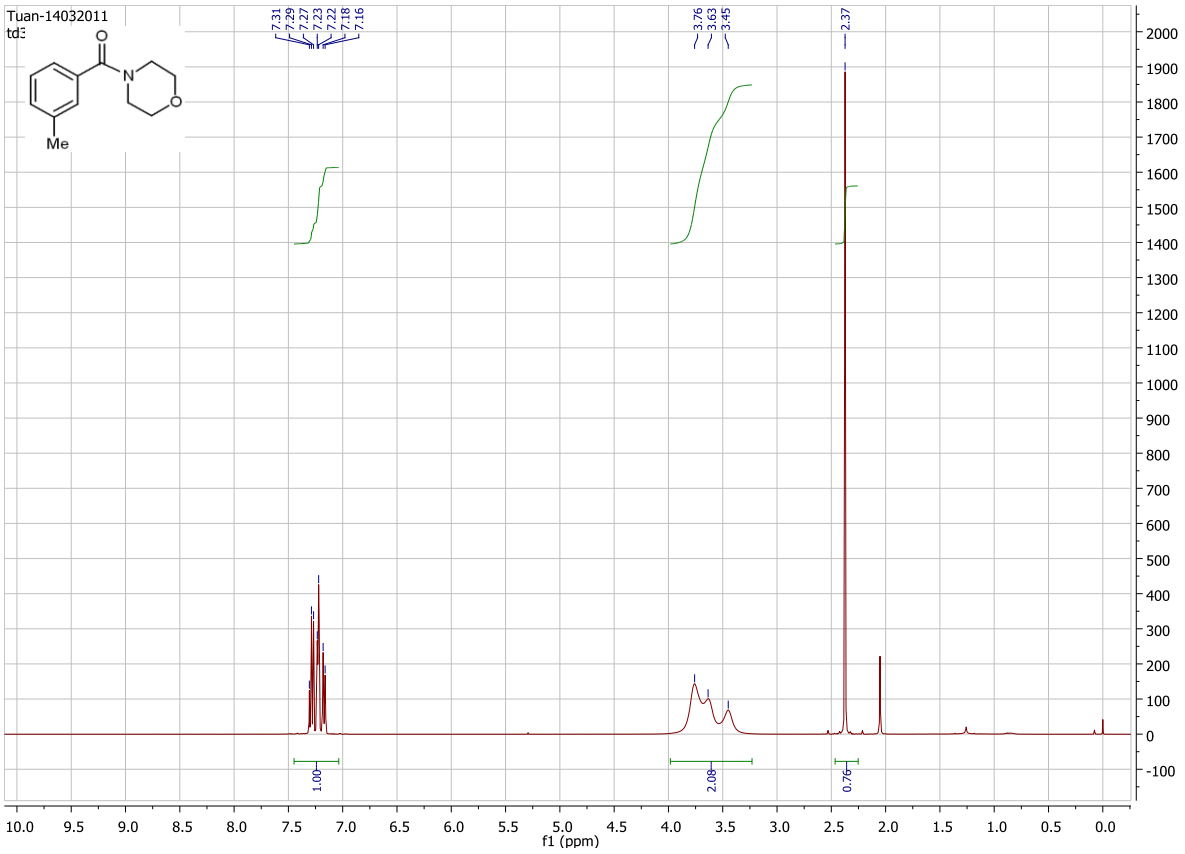


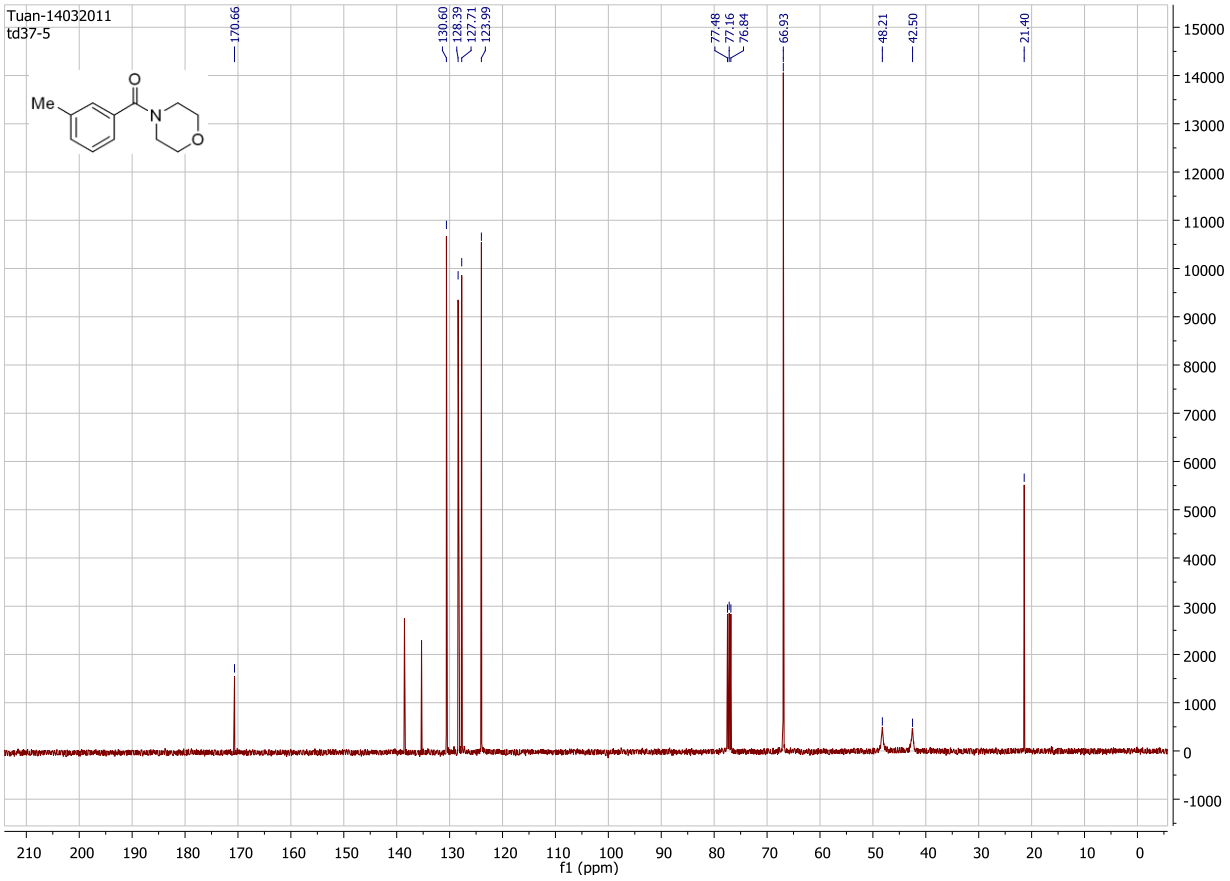


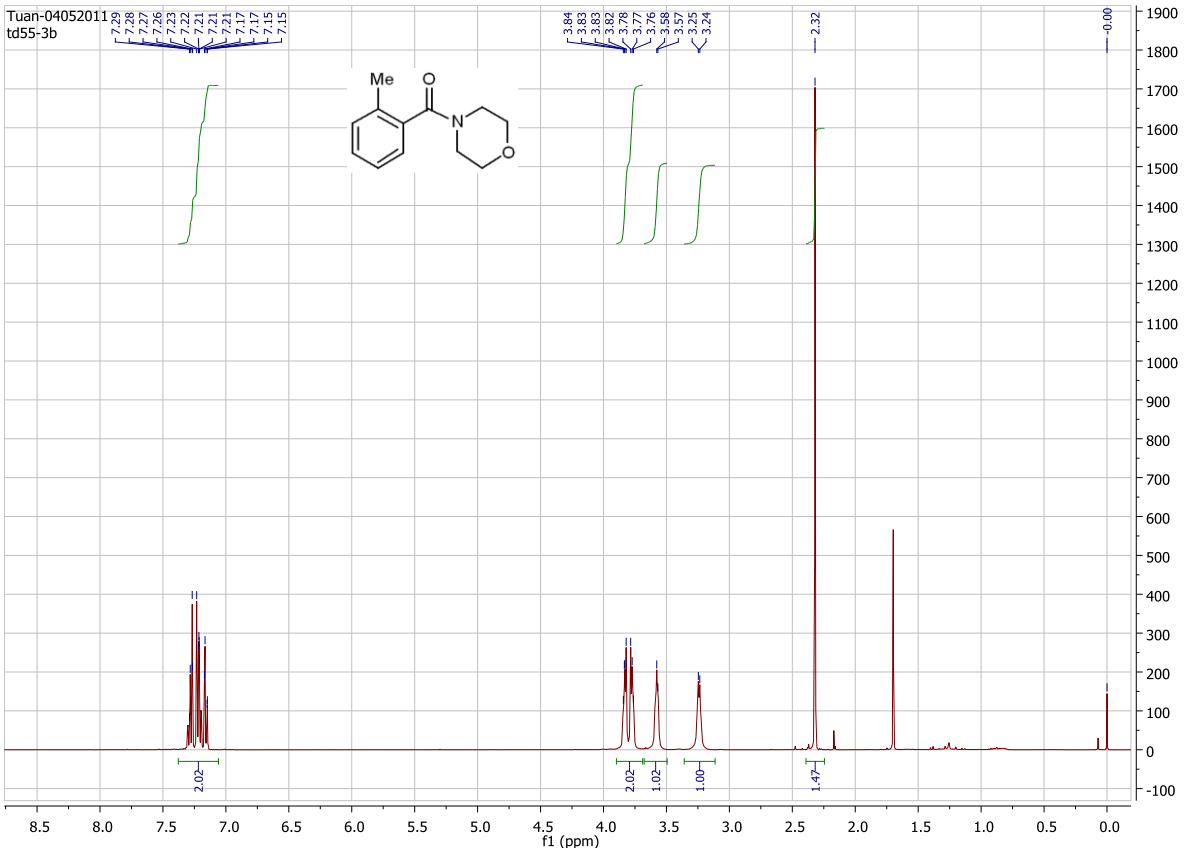


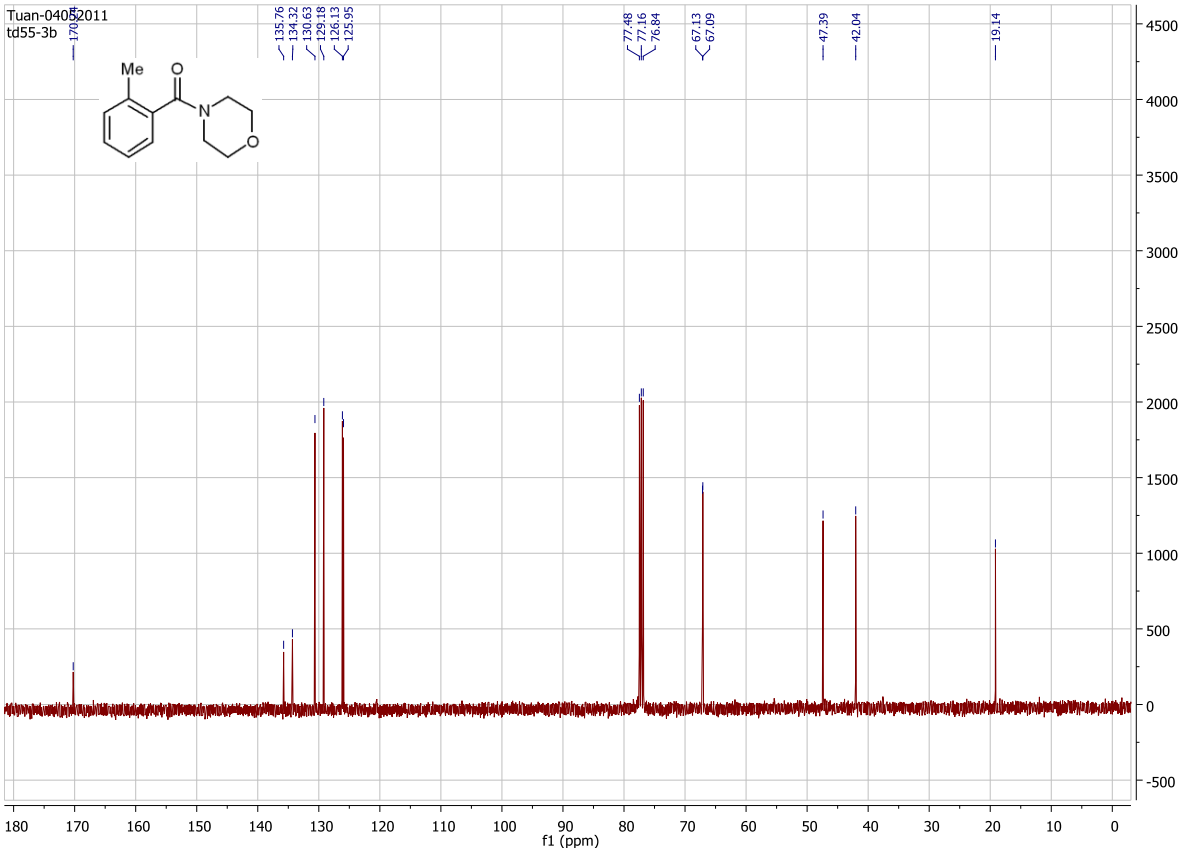


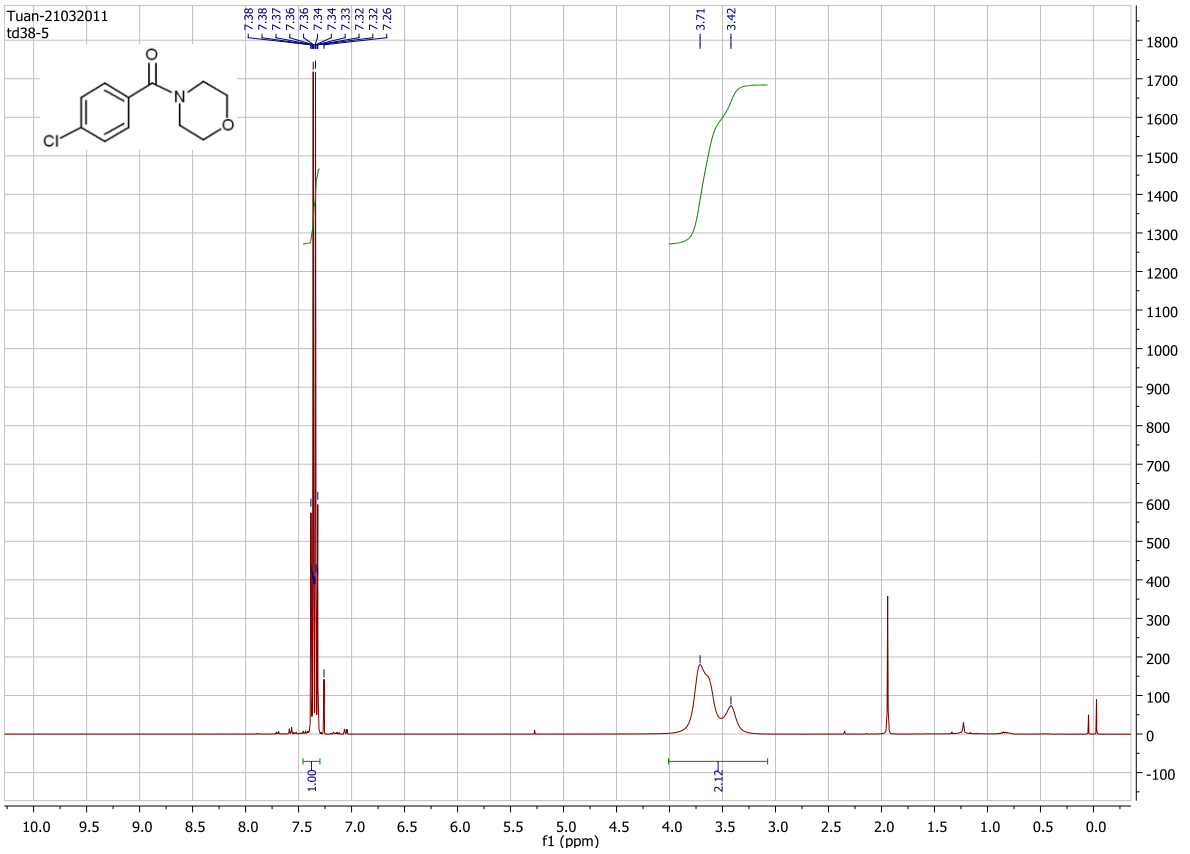


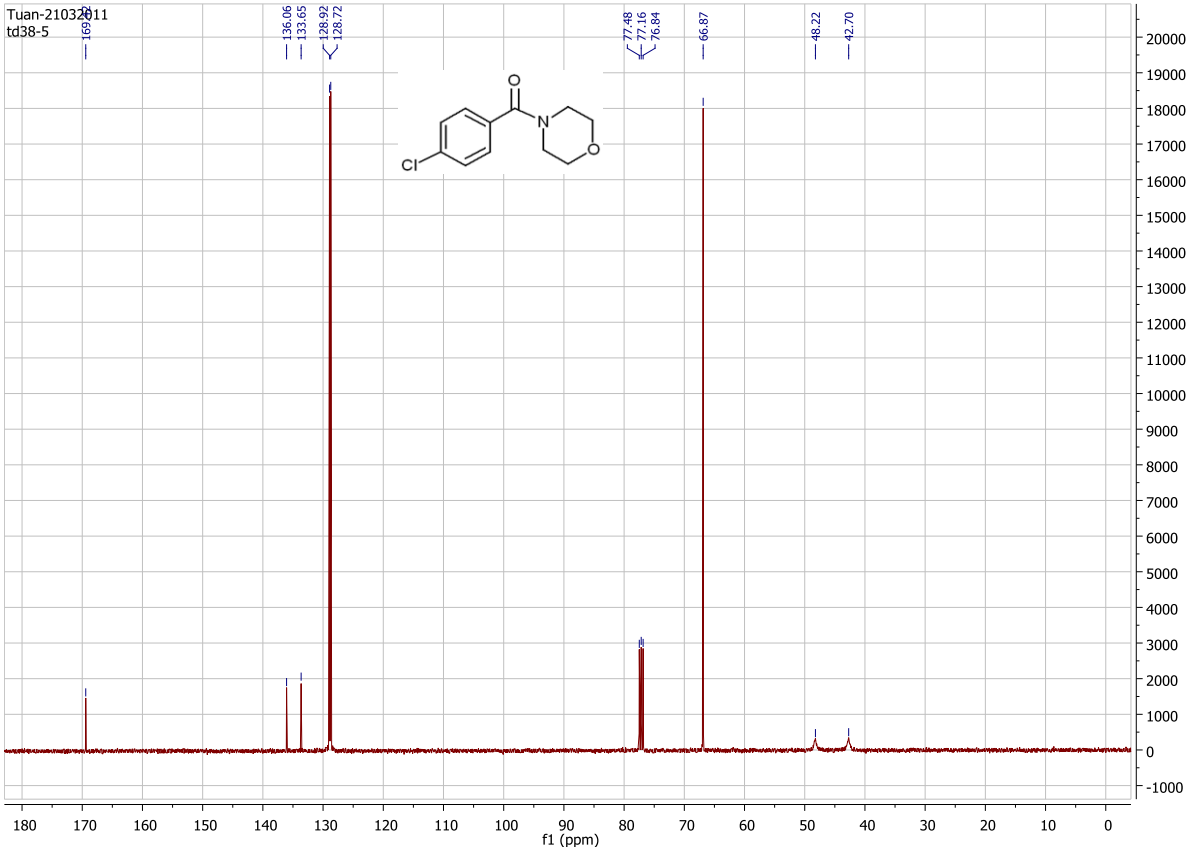

Tuan-14032011
td3
7.31
7.29
7.27
7.23
7.22
7.18
7.16
3.76
3.63
3.45
2.37
Me
1.00
2.08
0.76
f1 (ppm)

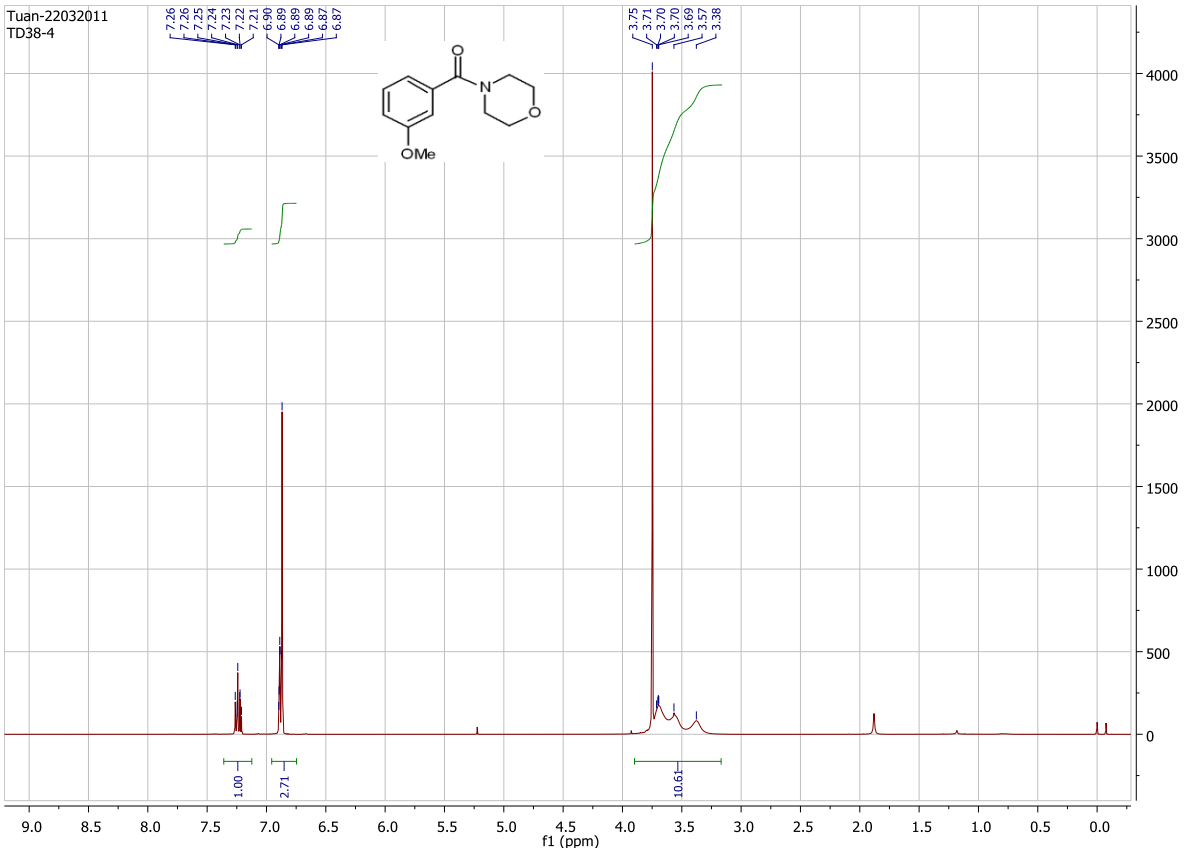

Tuan-14032011
td37-5
170.66
130.60
128.39
127.71
123.99
77.48
77.16
76.84
66.93
48.21
42.50
21.40
Me
f1 (ppm)

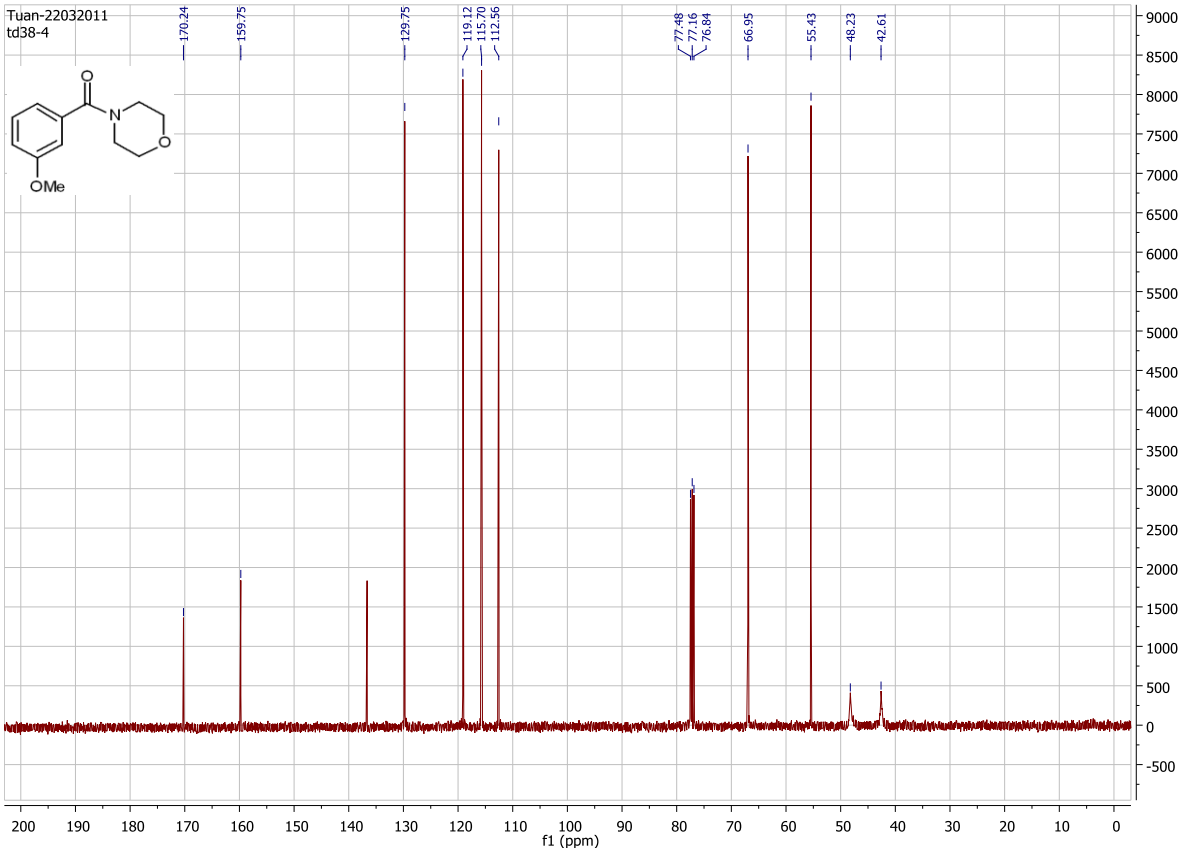


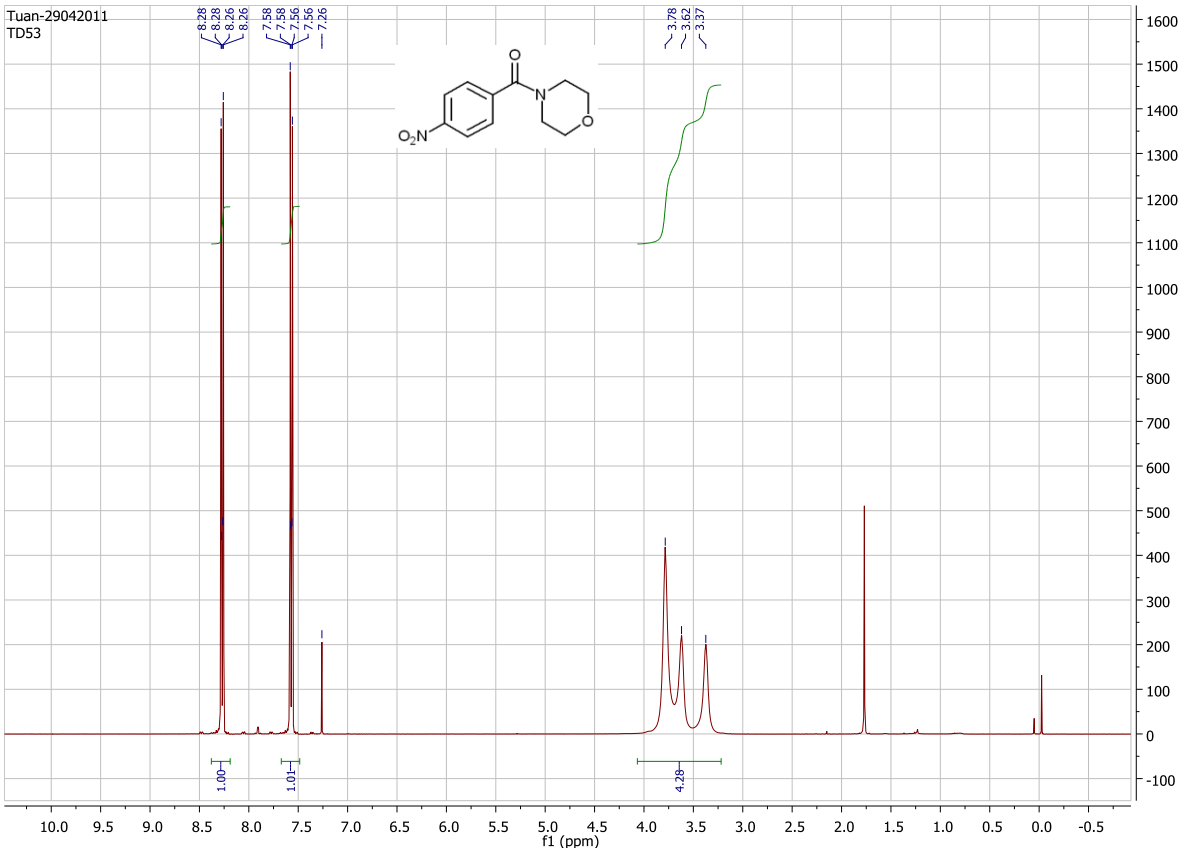


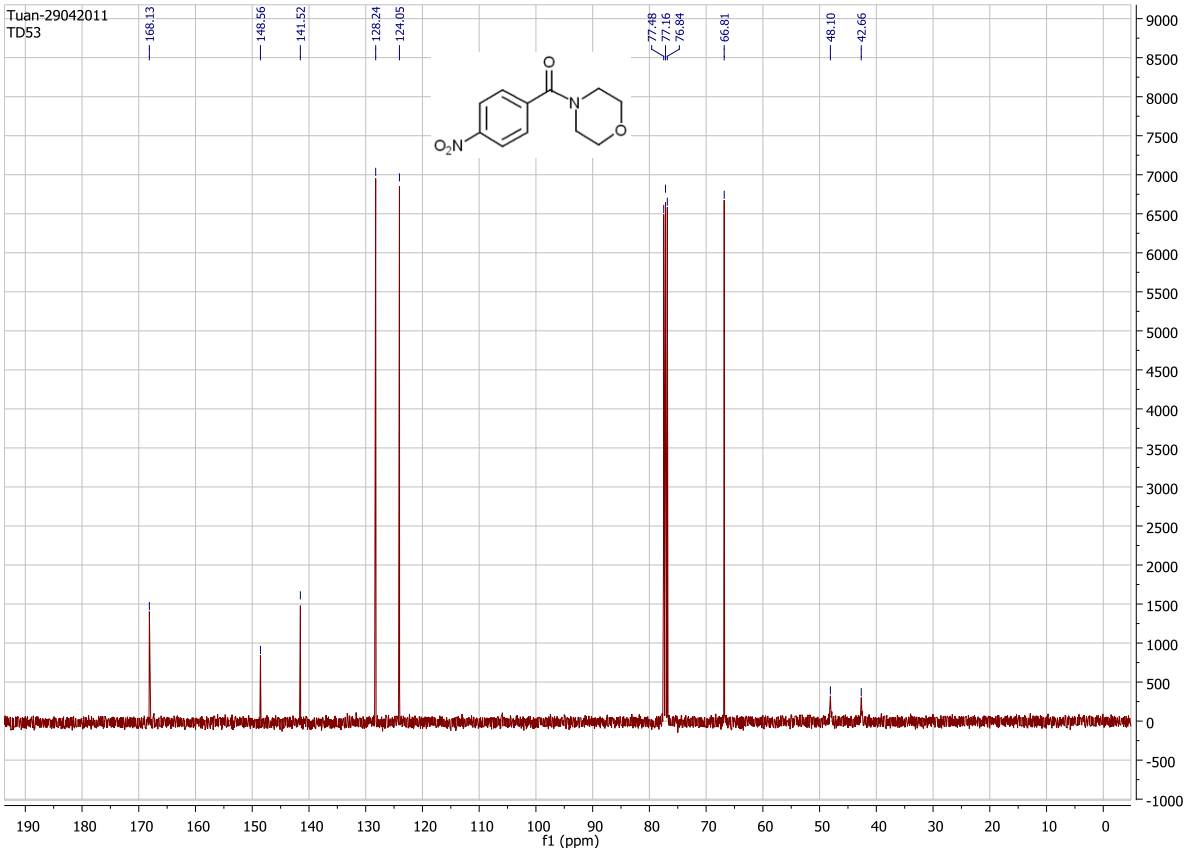


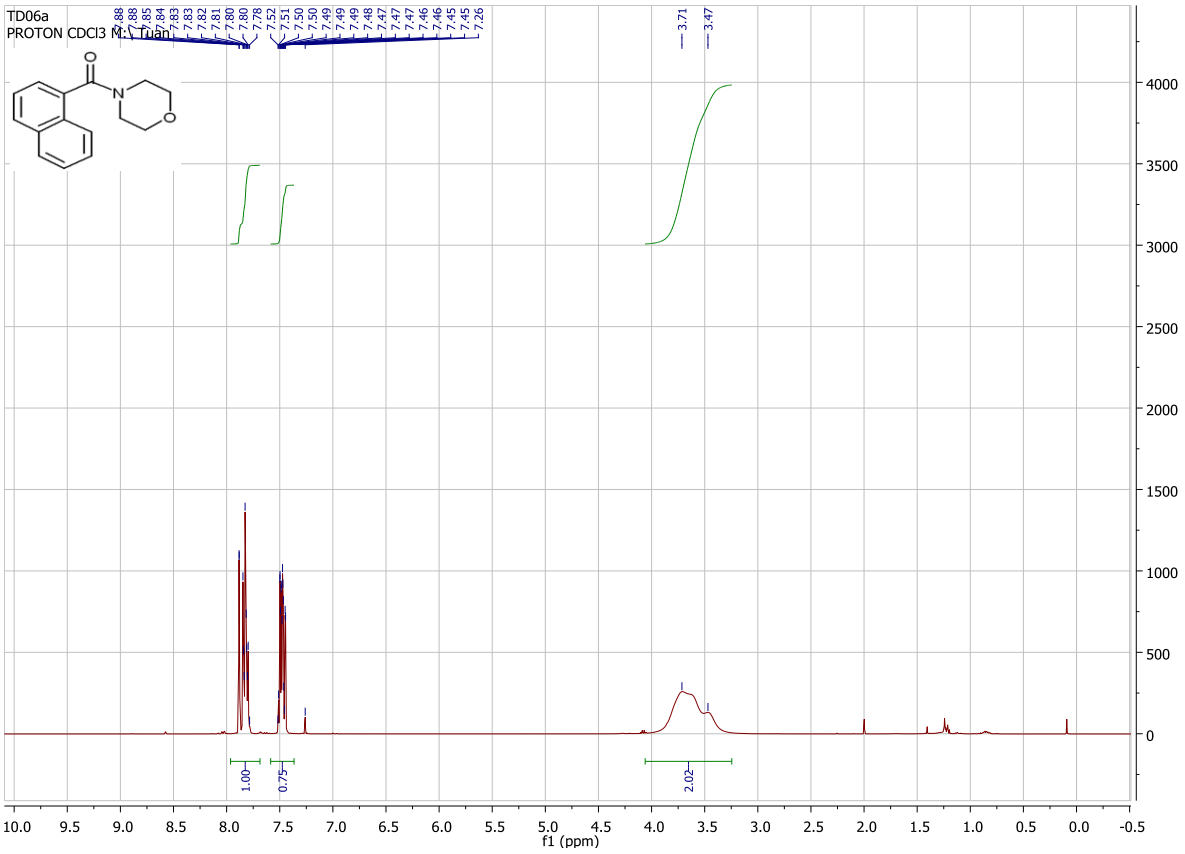


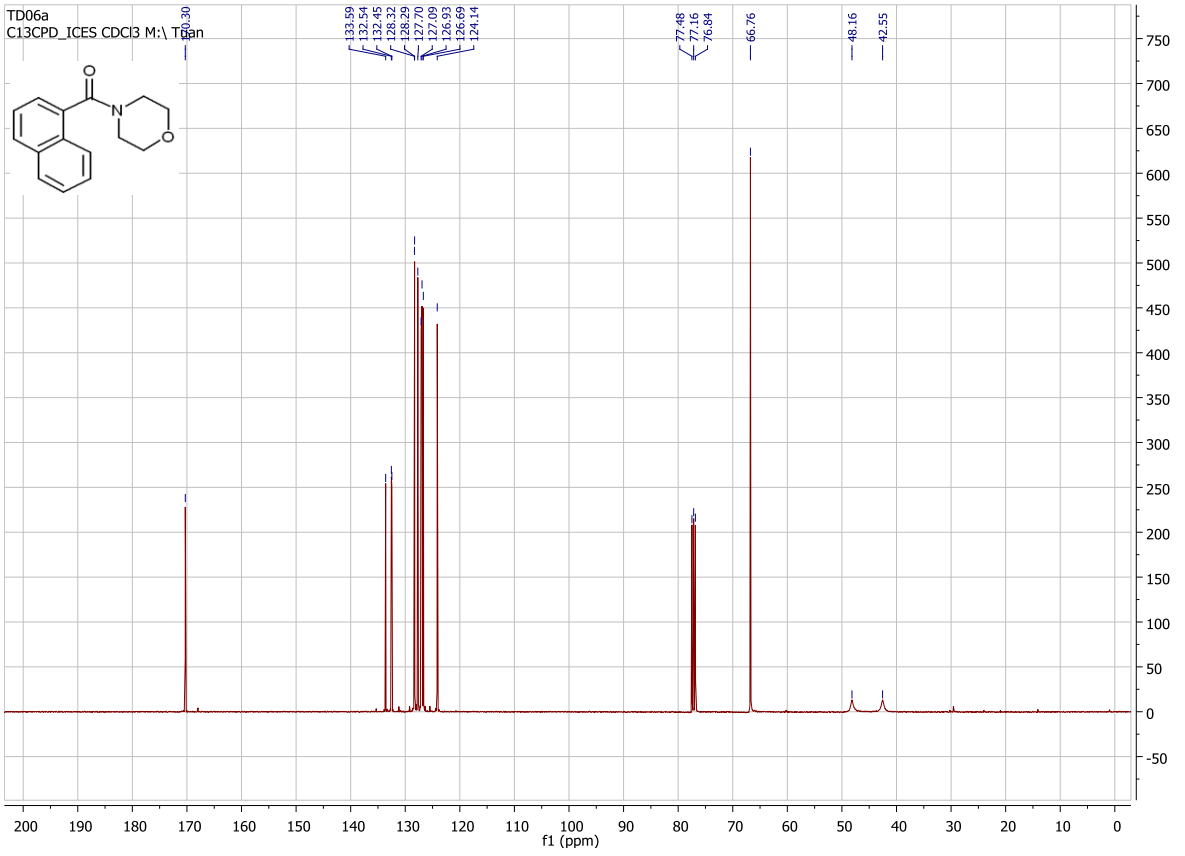

Tuan-22032011
TD38-4
7.26
7.26
7.25
7.24
7.23
7.22
7.21
6.90
6.89
6.89
6.89
6.87
6.87
3.75
3.71
3.70
3.70
3.69
3.57
3.38
OMe
1.00
2.71
10.61
f1 (ppm)

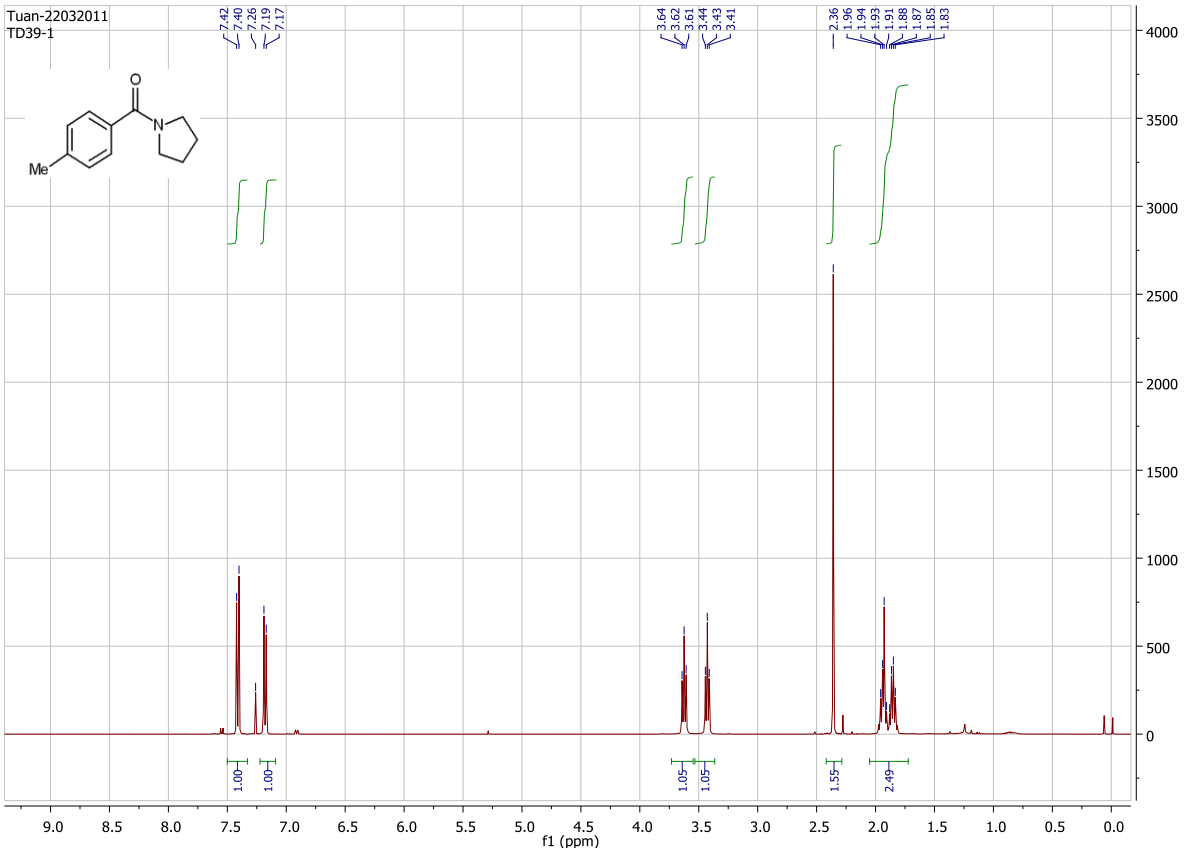

Tuan-22032011
td38-4
170.24
159.75
129.75
119.12
115.70
112.56
77.48
77.16
76.84
66.95
55.43
48.23
42.61
OMe
f1 (ppm)

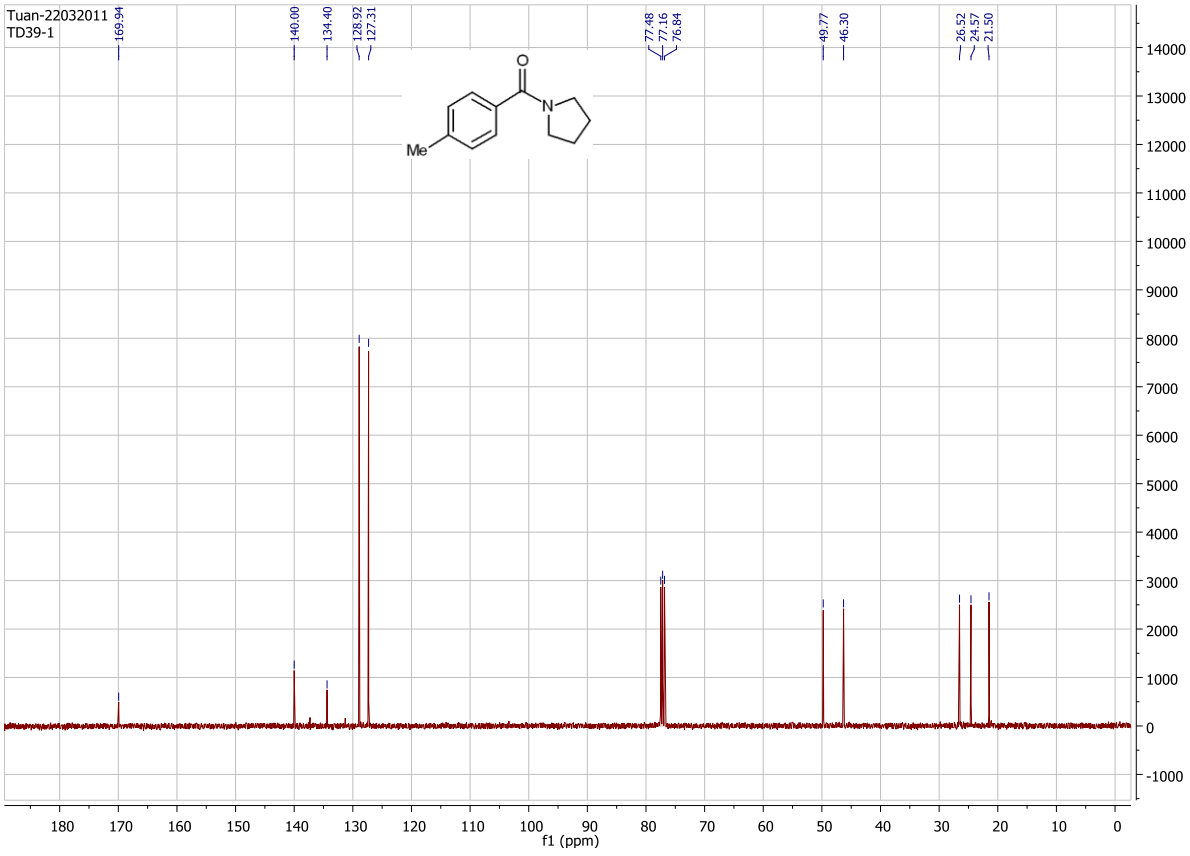

Tuan-29042011
TD53
8.28
8.28
8.26
8.26
7.58
7.58
7.56
7.56
7.26
3.78
3.62
3.37
1.00
1.01
4.28
f1 (ppm)

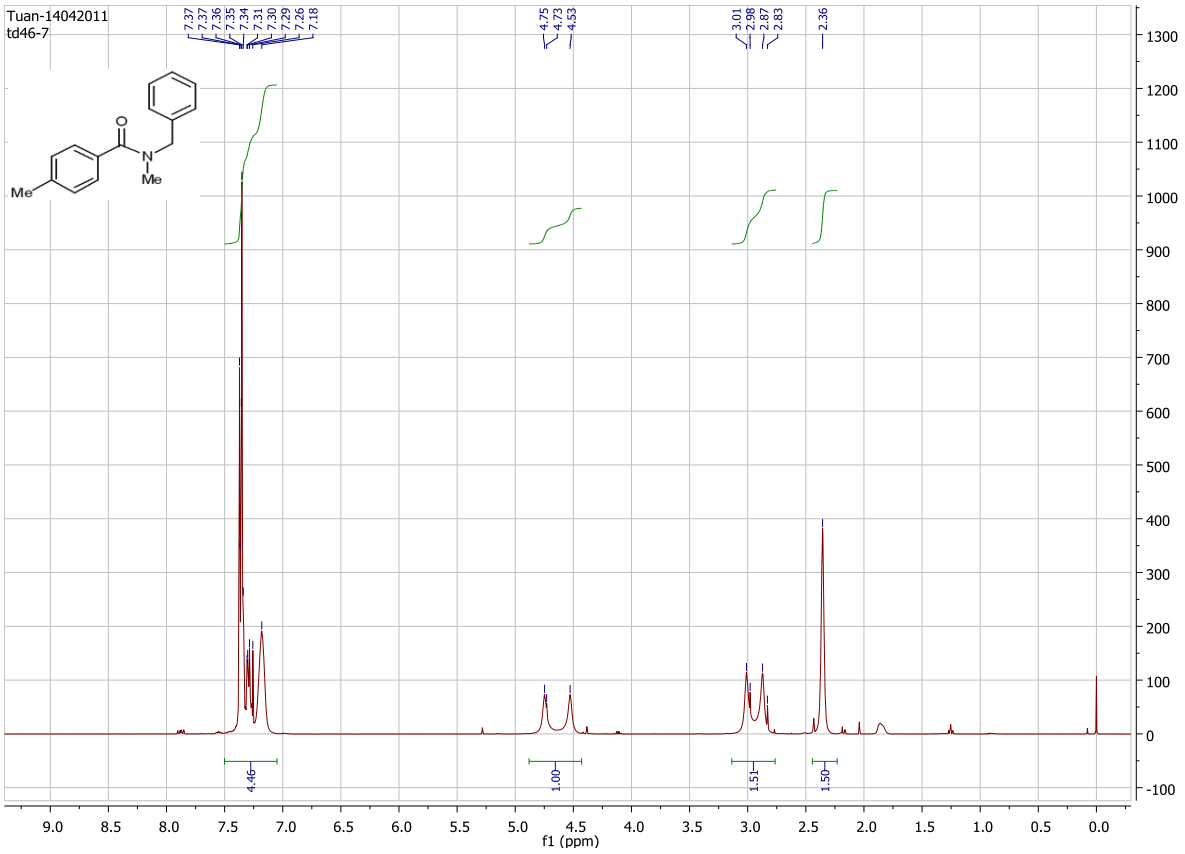

Tuan-29042011
TD53
168.13
148.56
141.52
128.24
124.05
77.48
77.16
76.84
66.81
48.10
42.66
f1 (ppm)

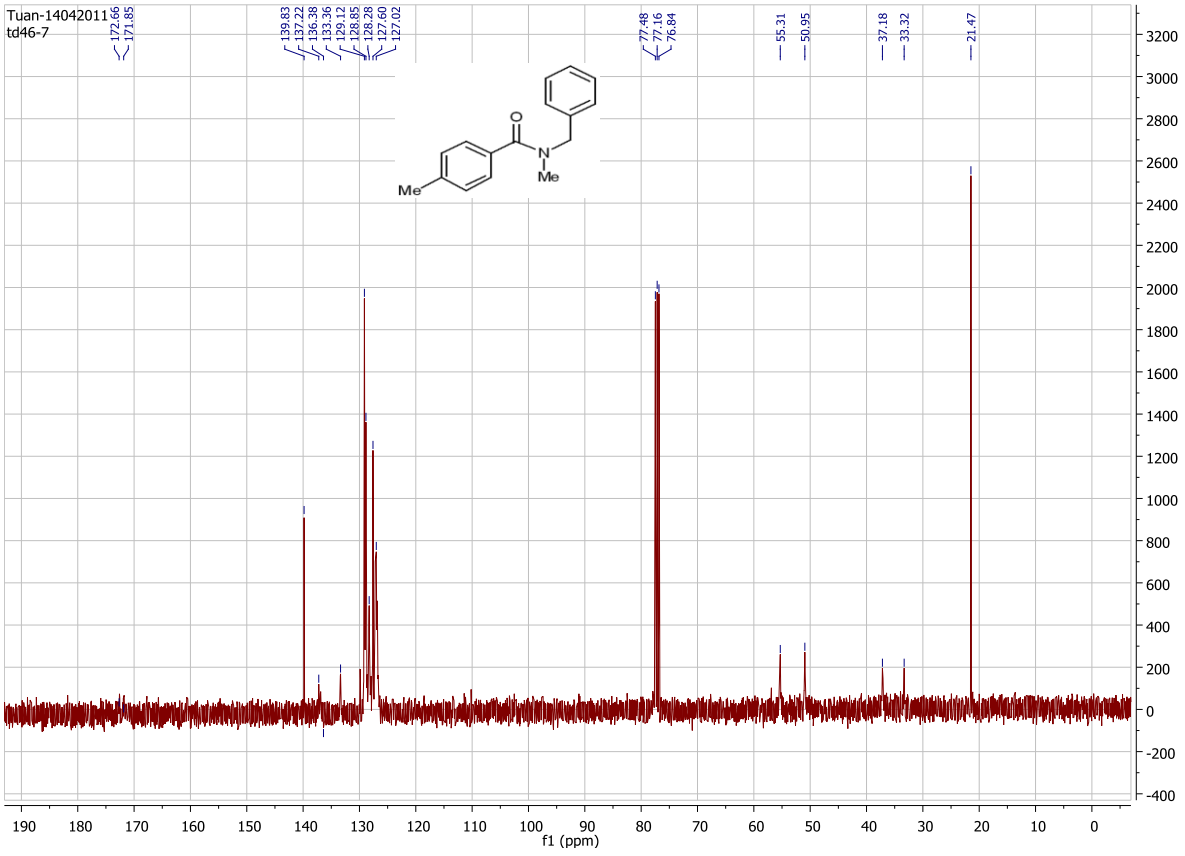


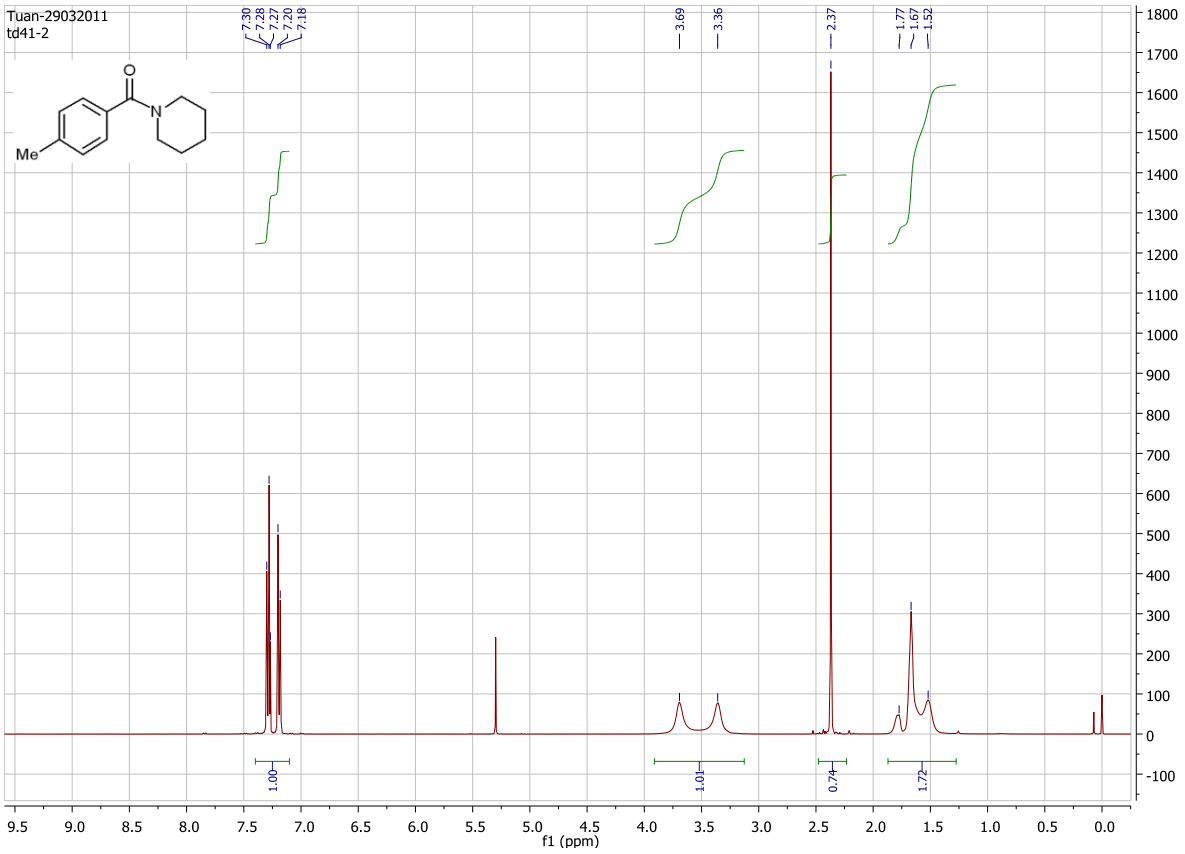


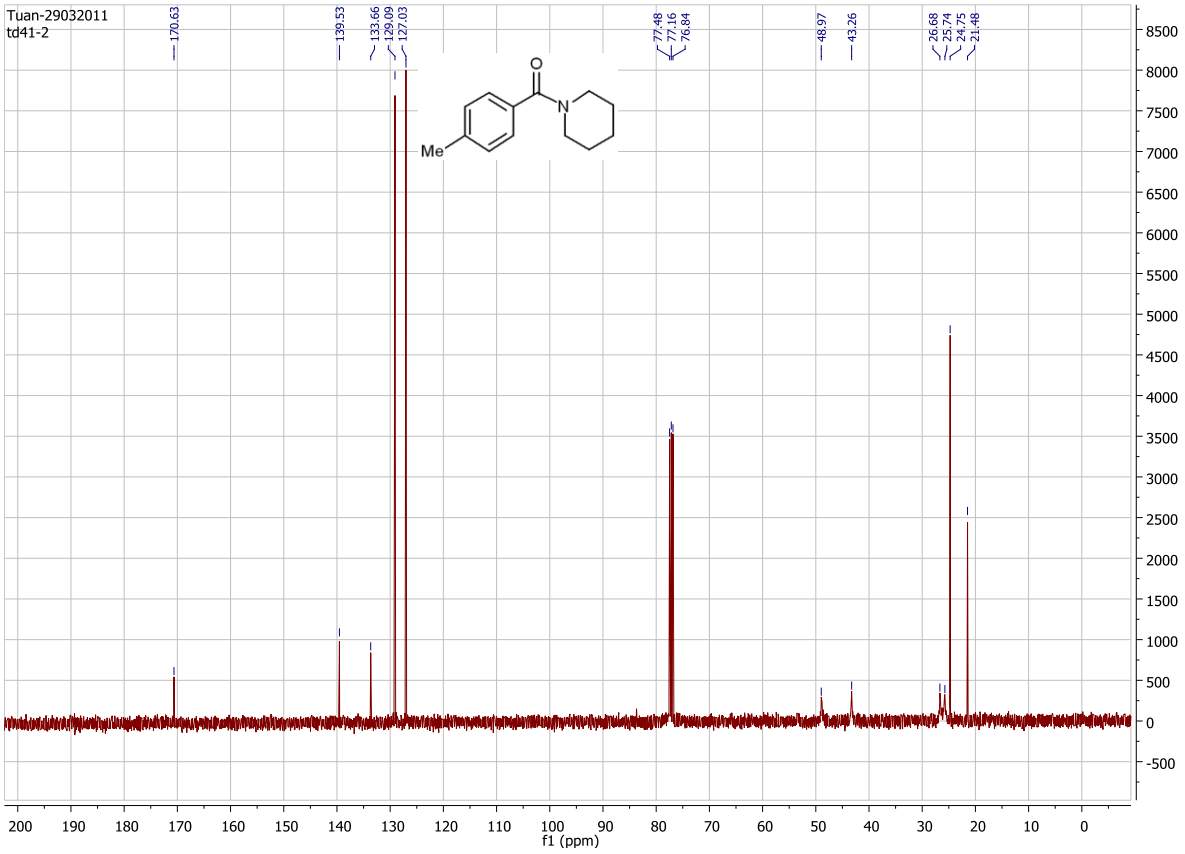


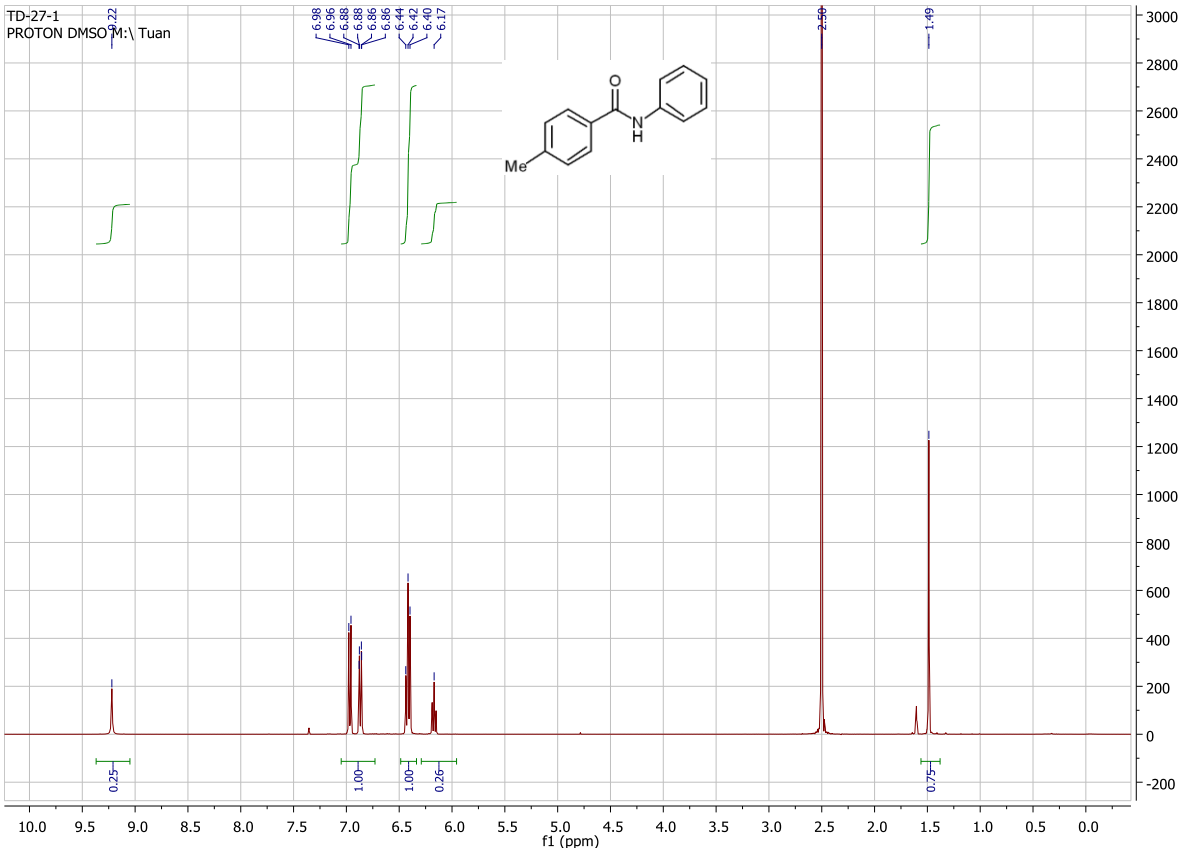


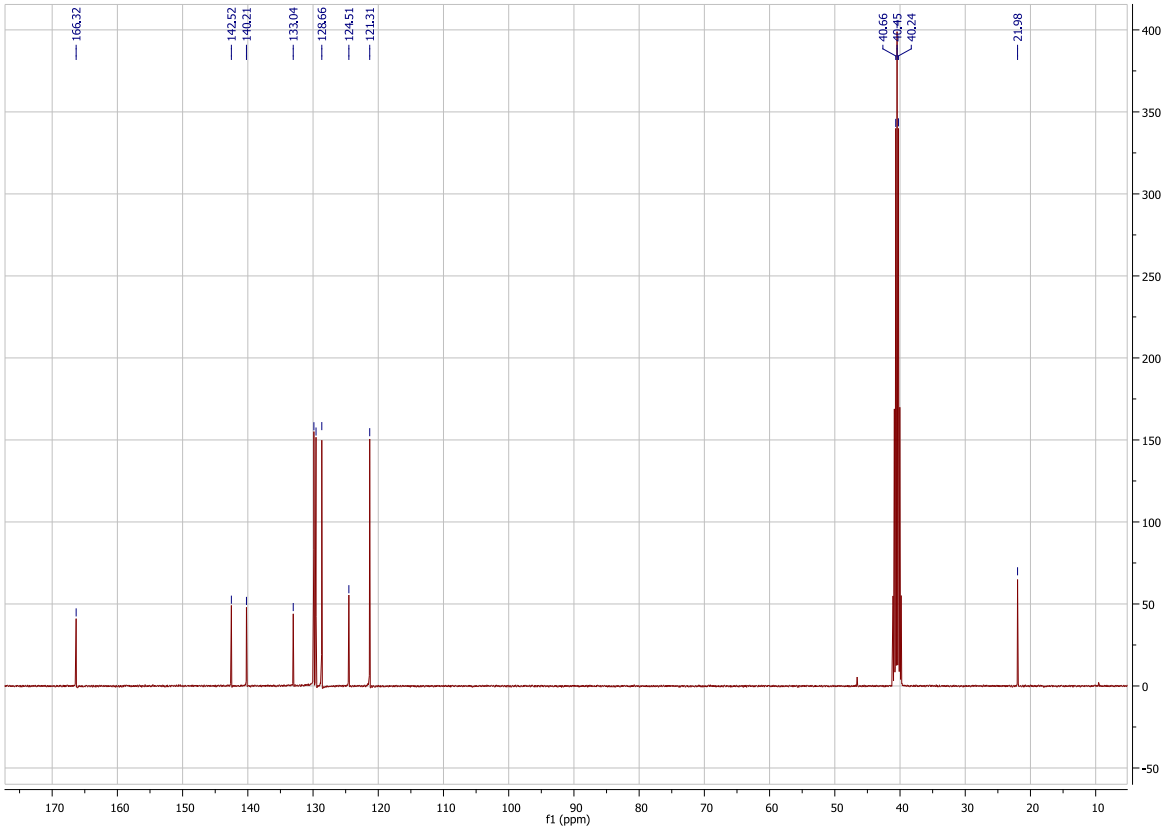


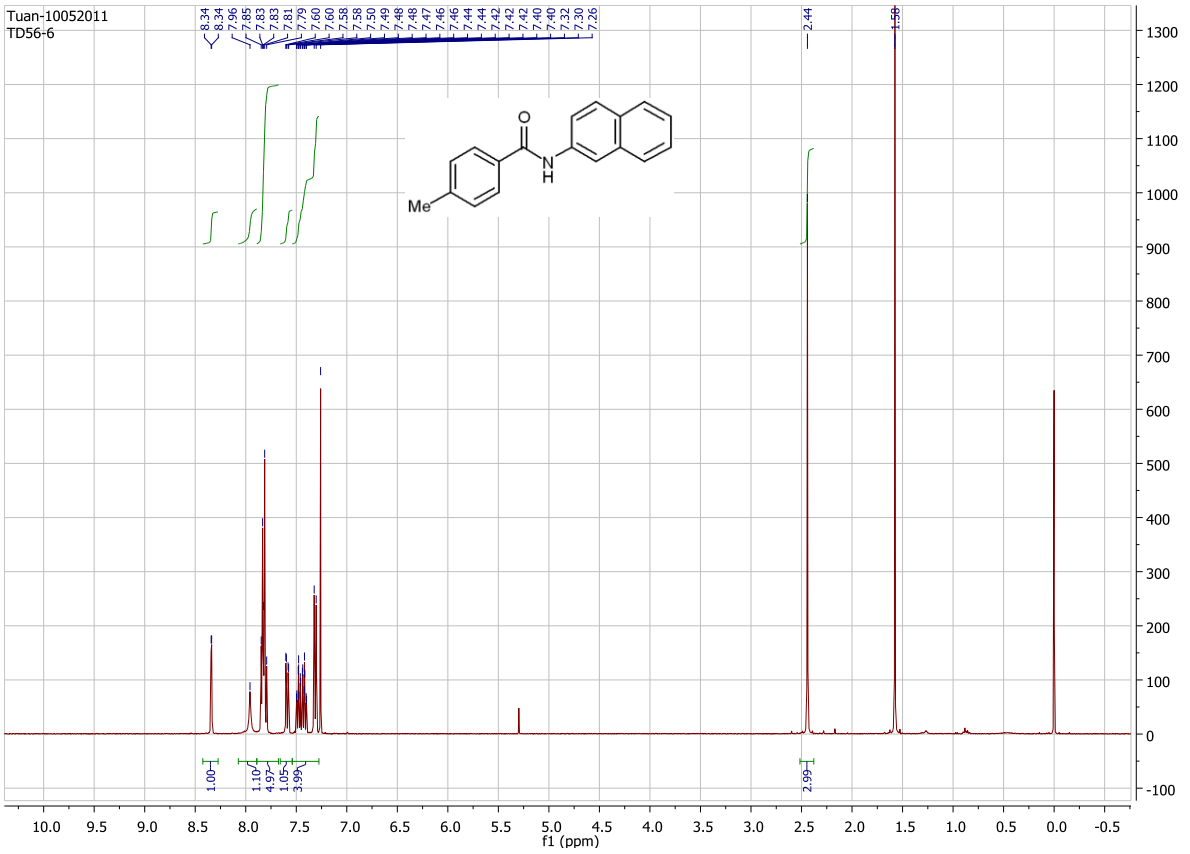


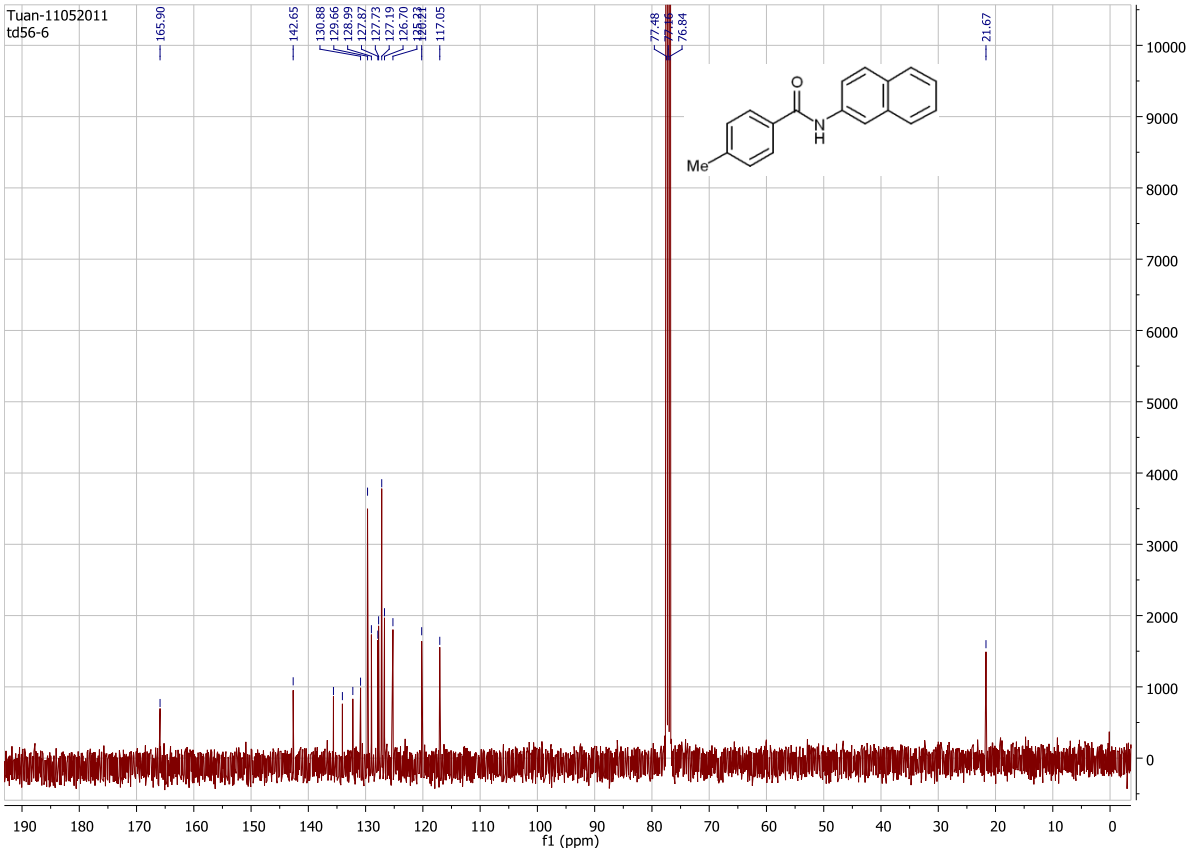


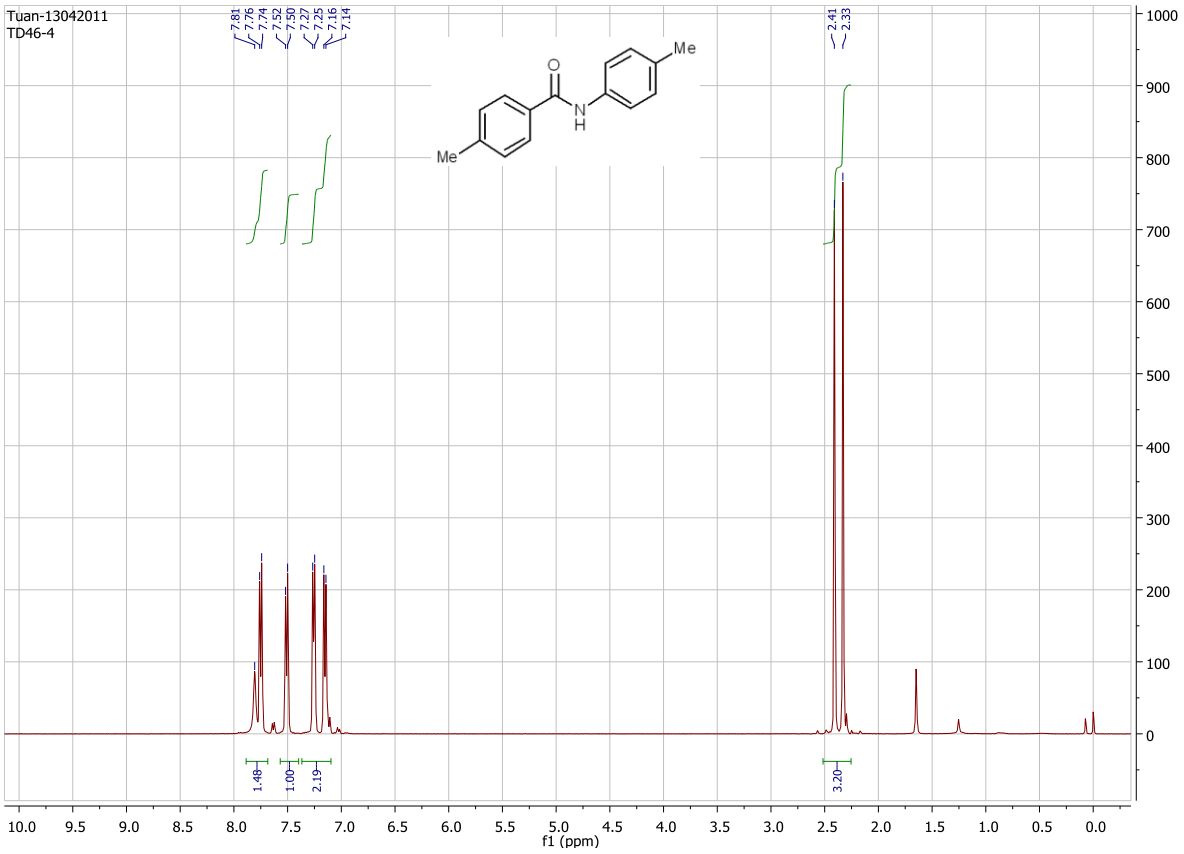


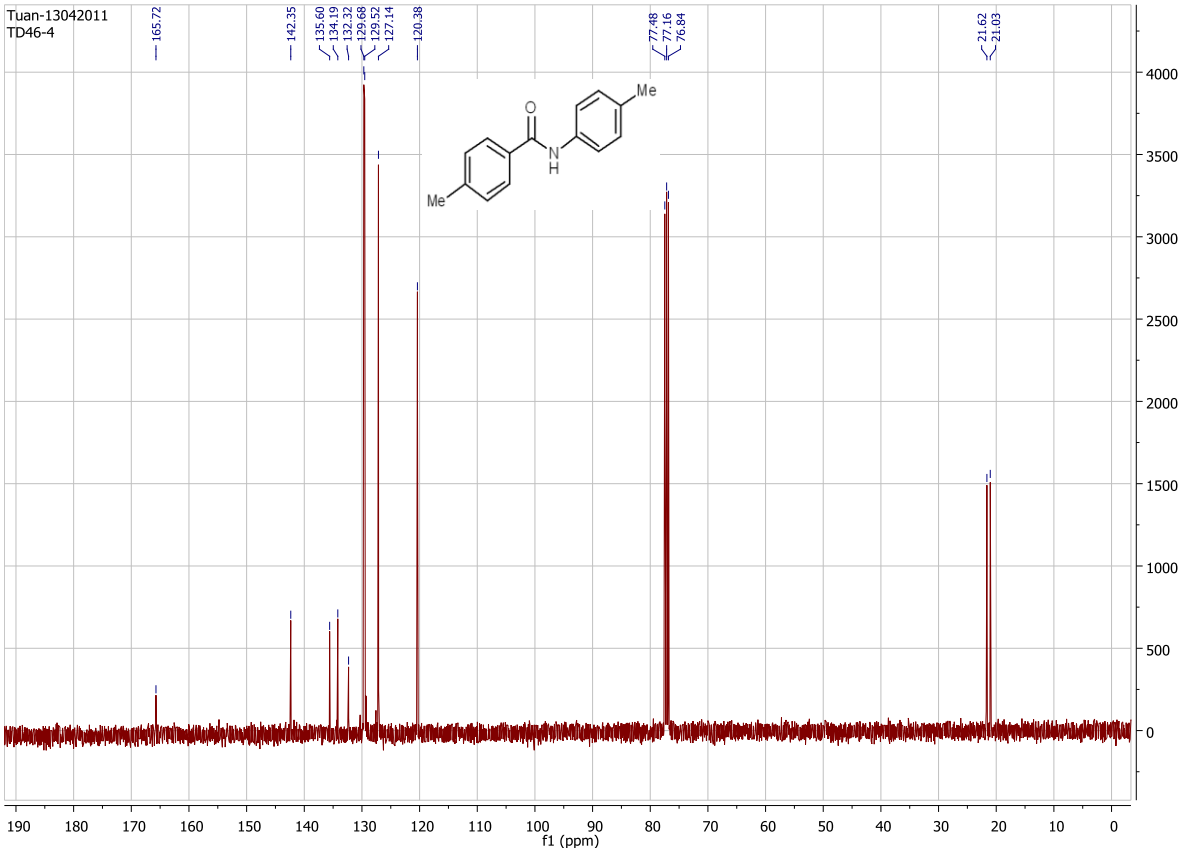


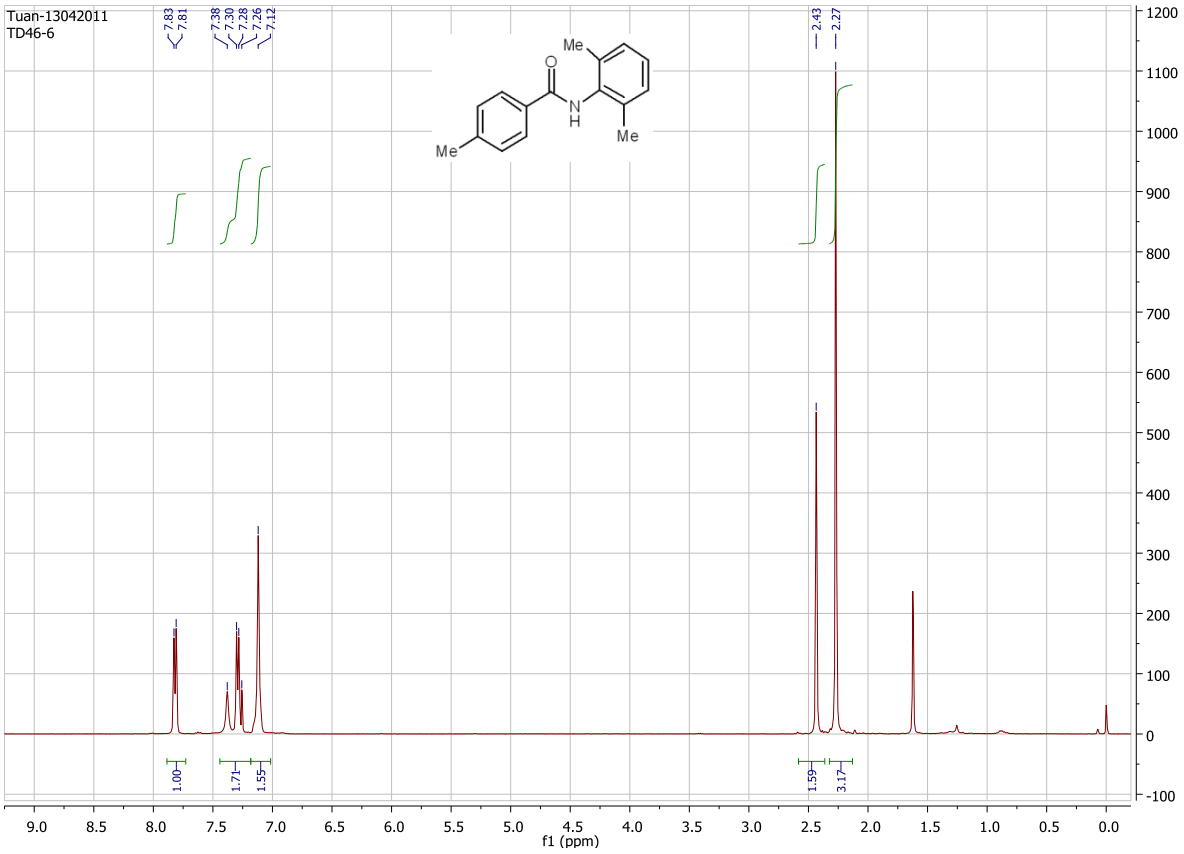


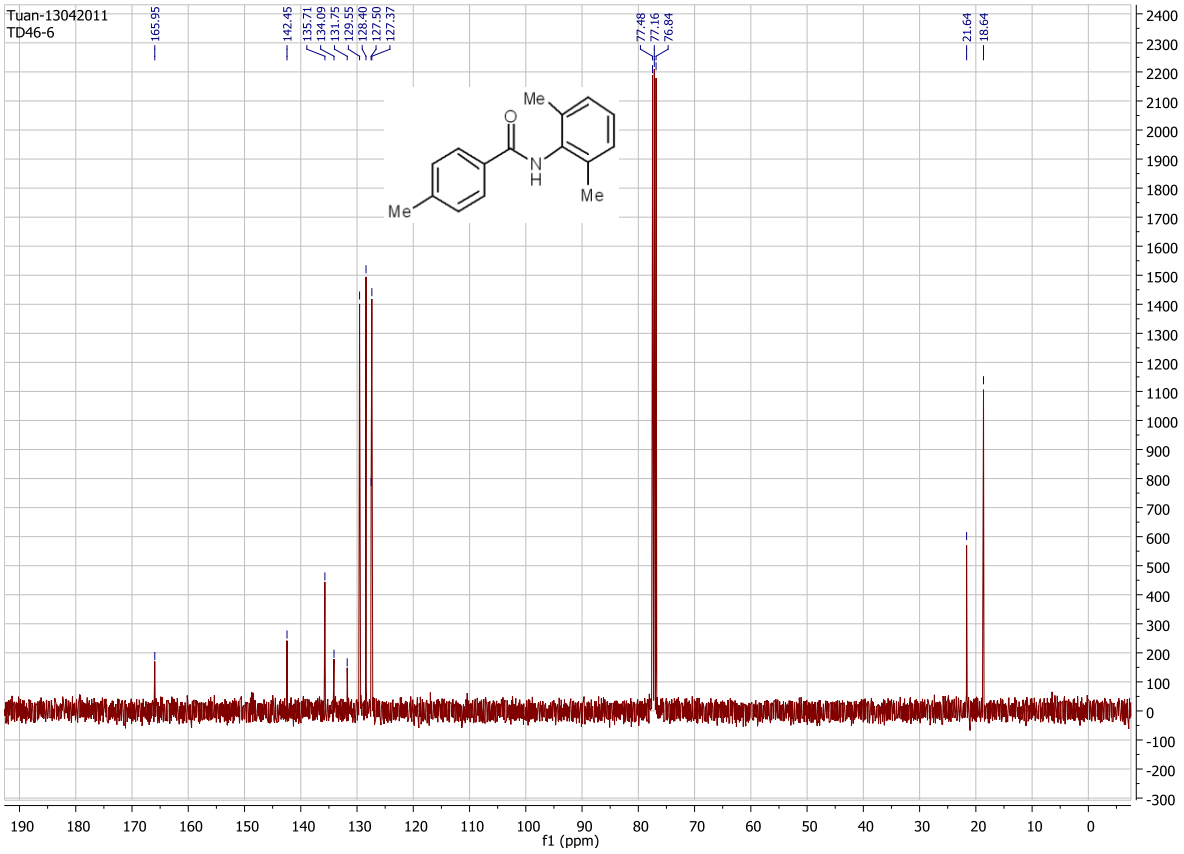


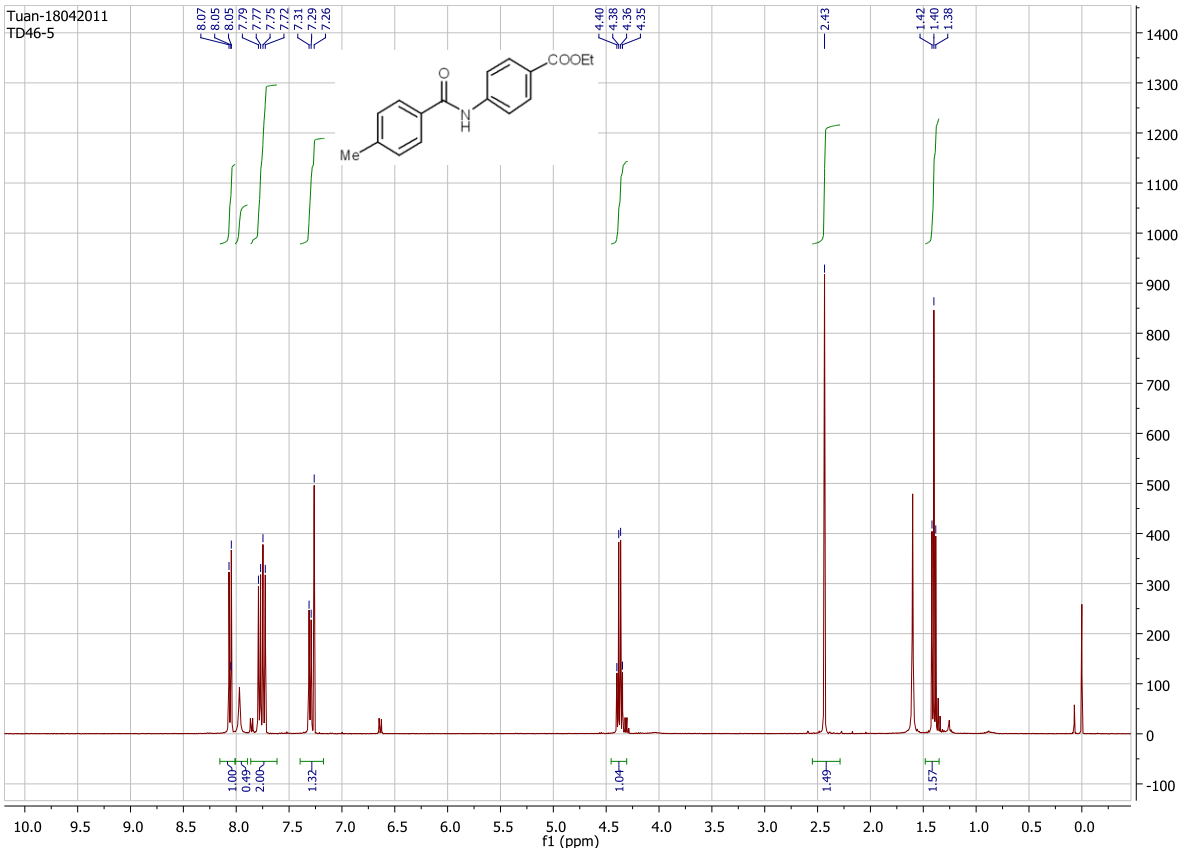


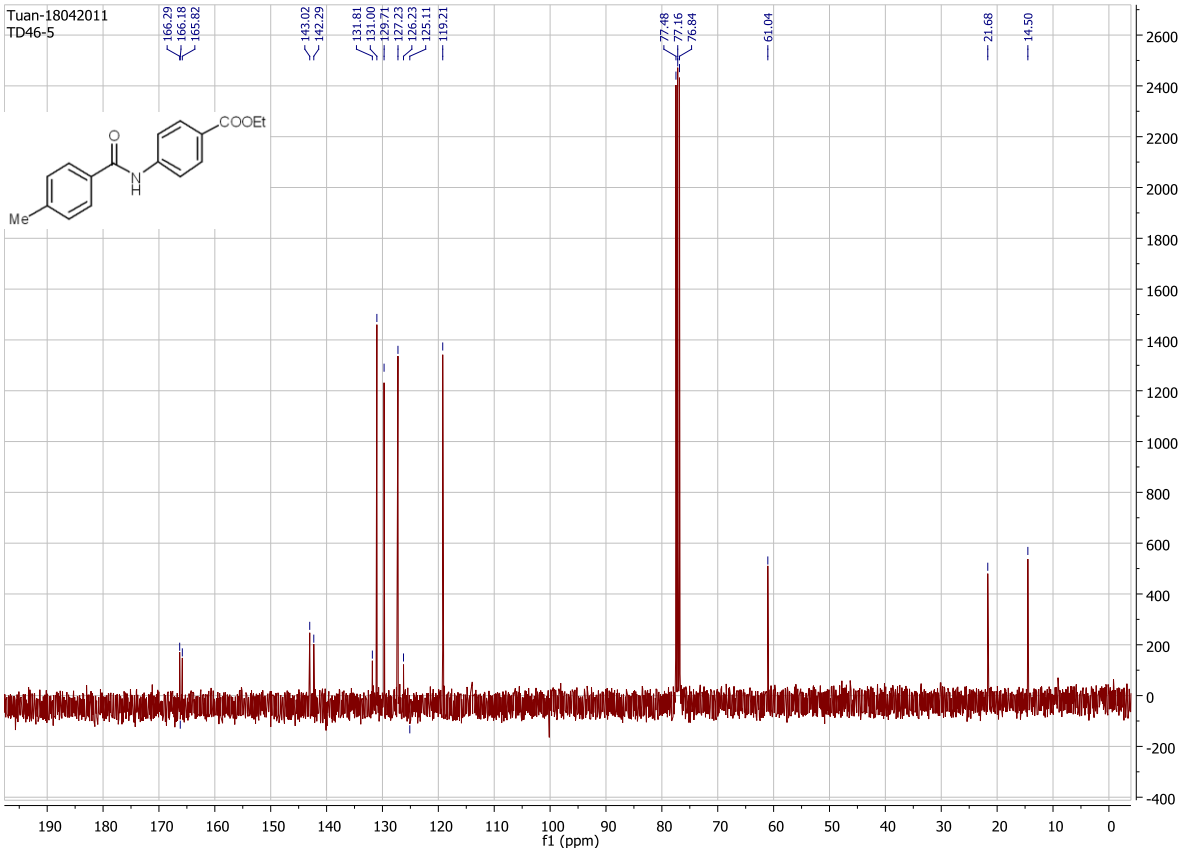


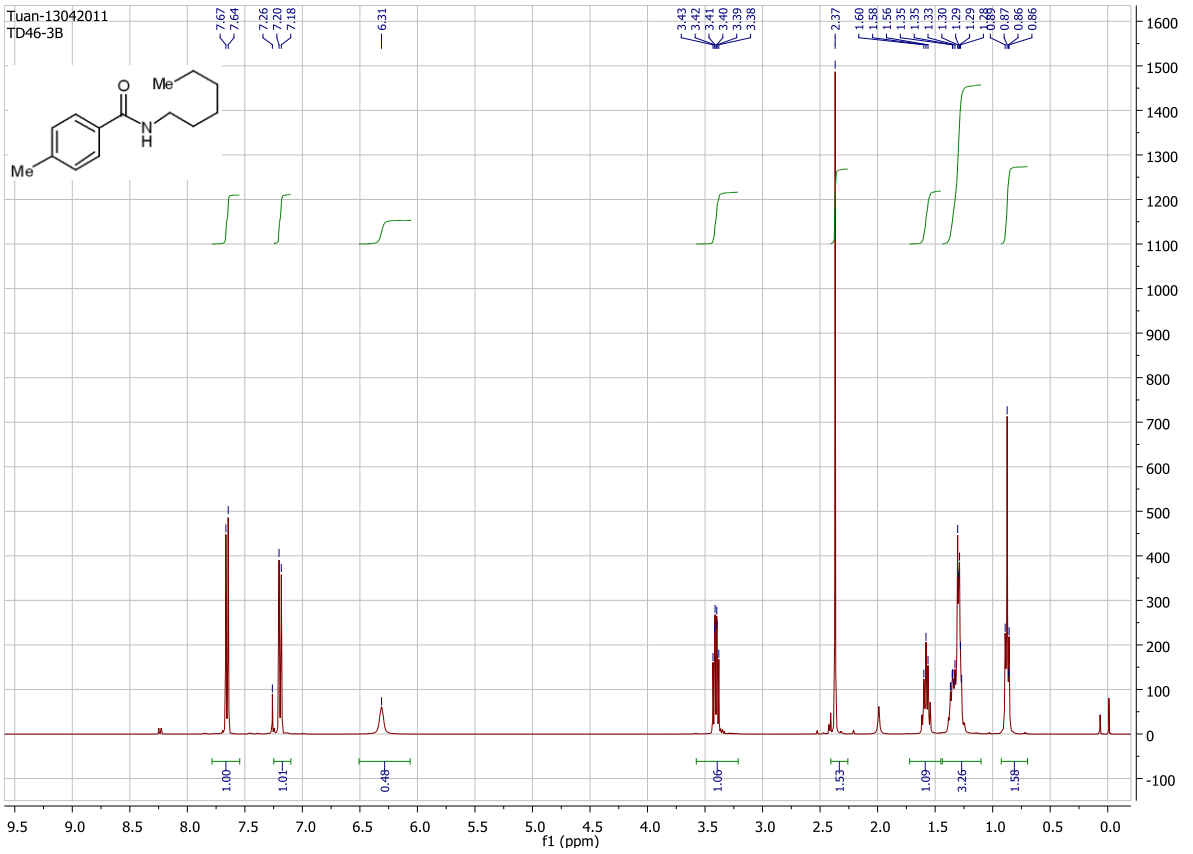


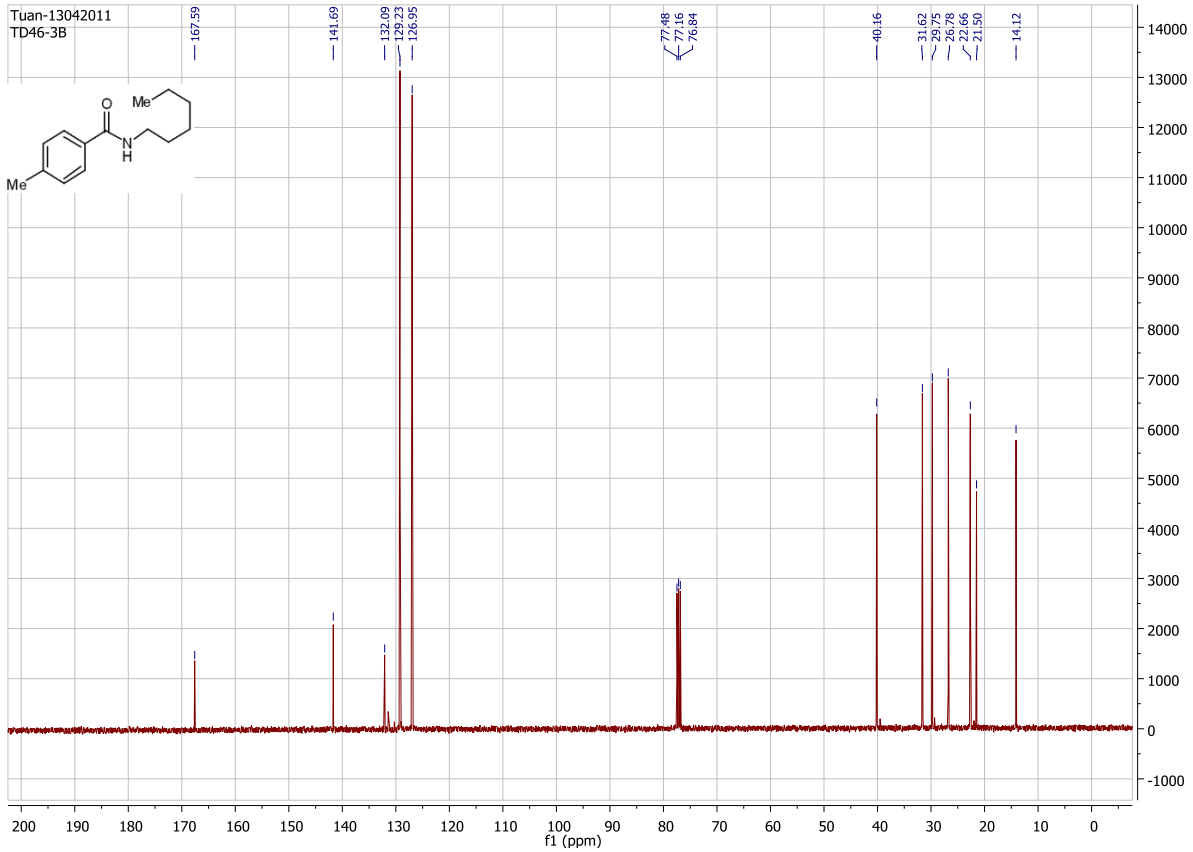


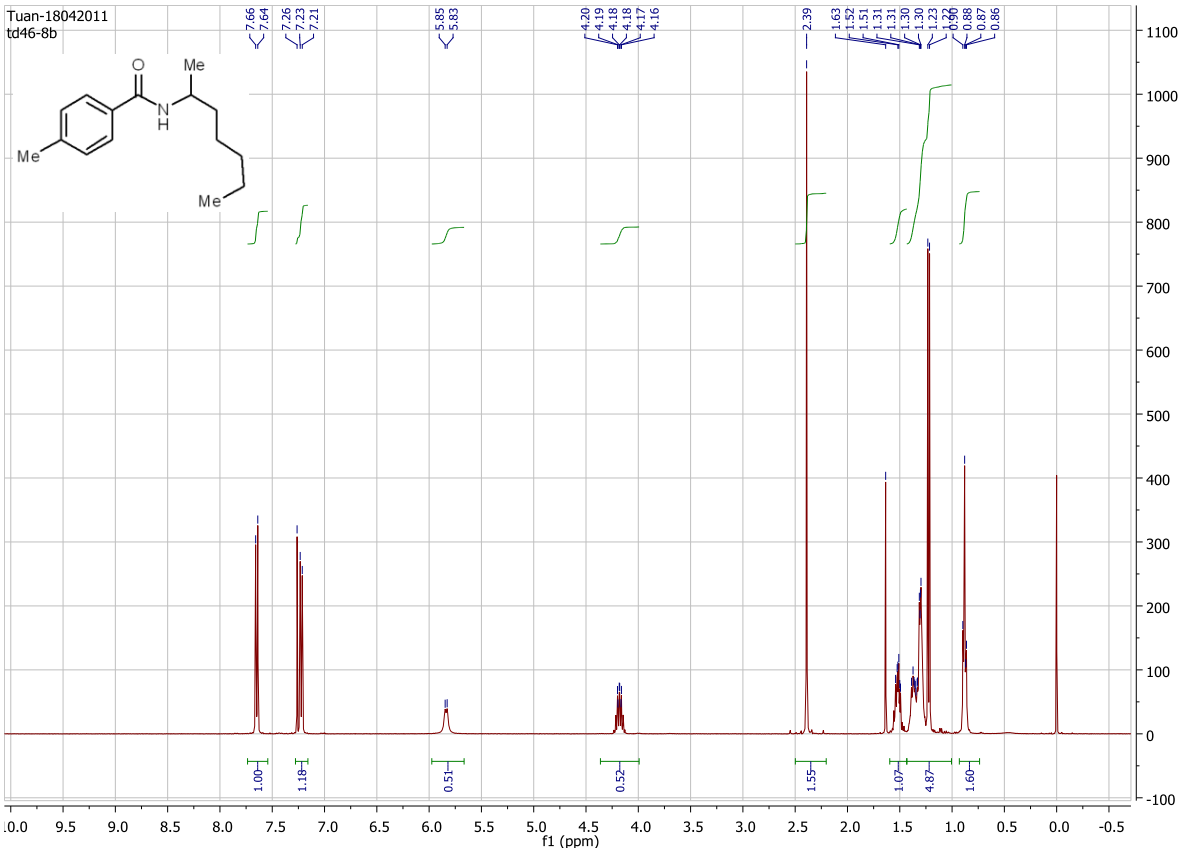


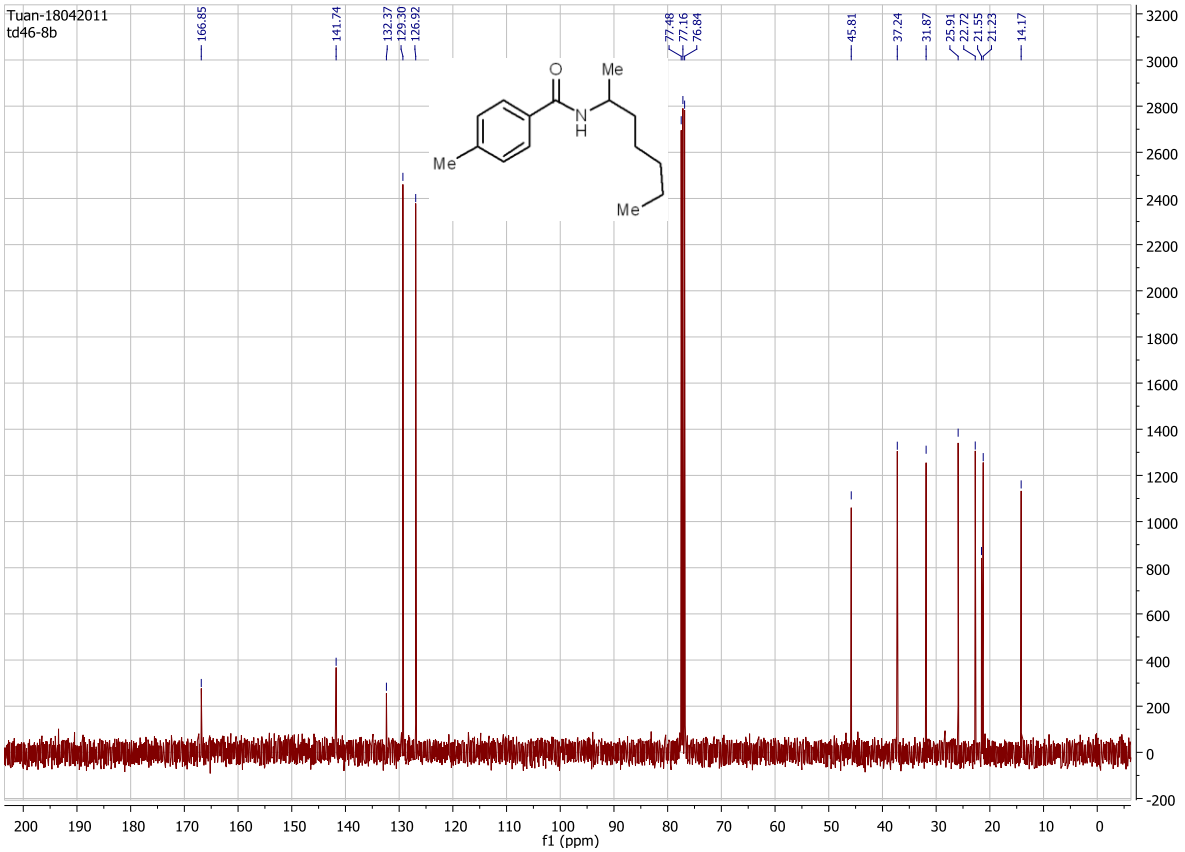


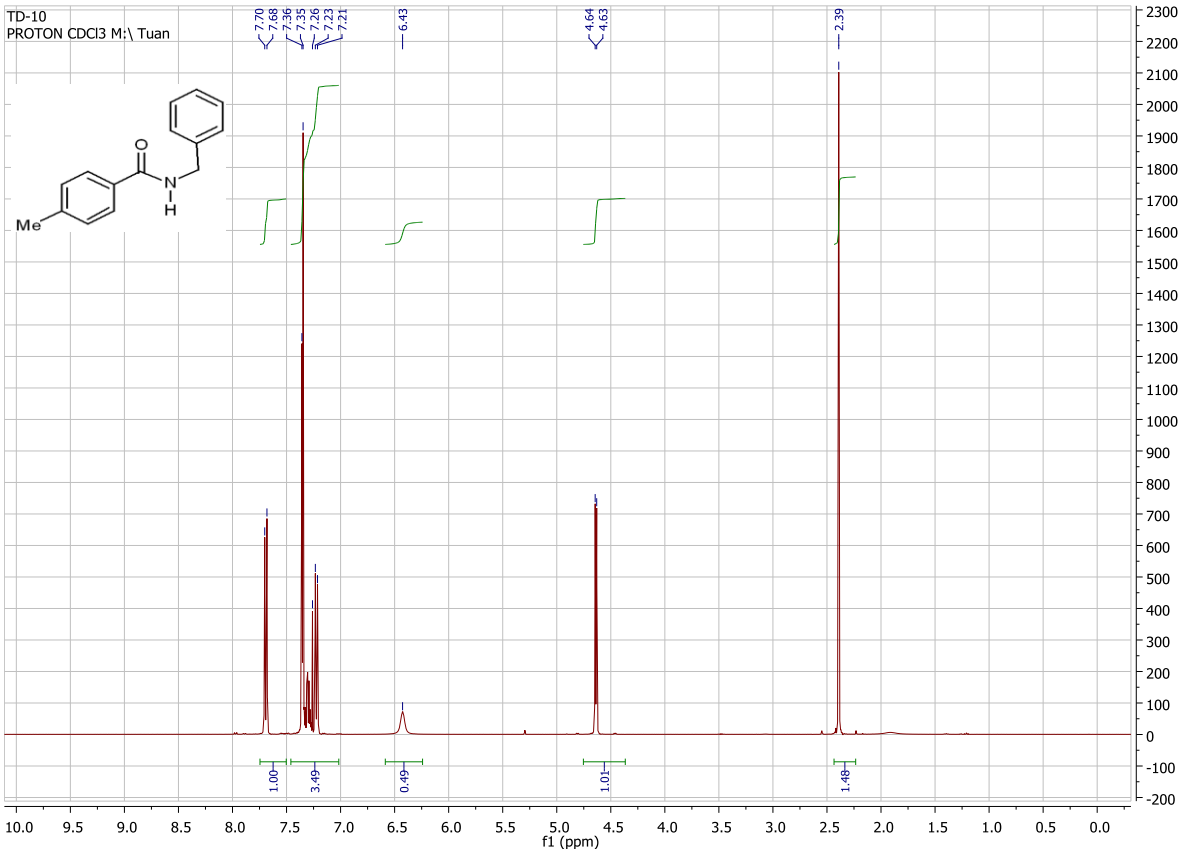


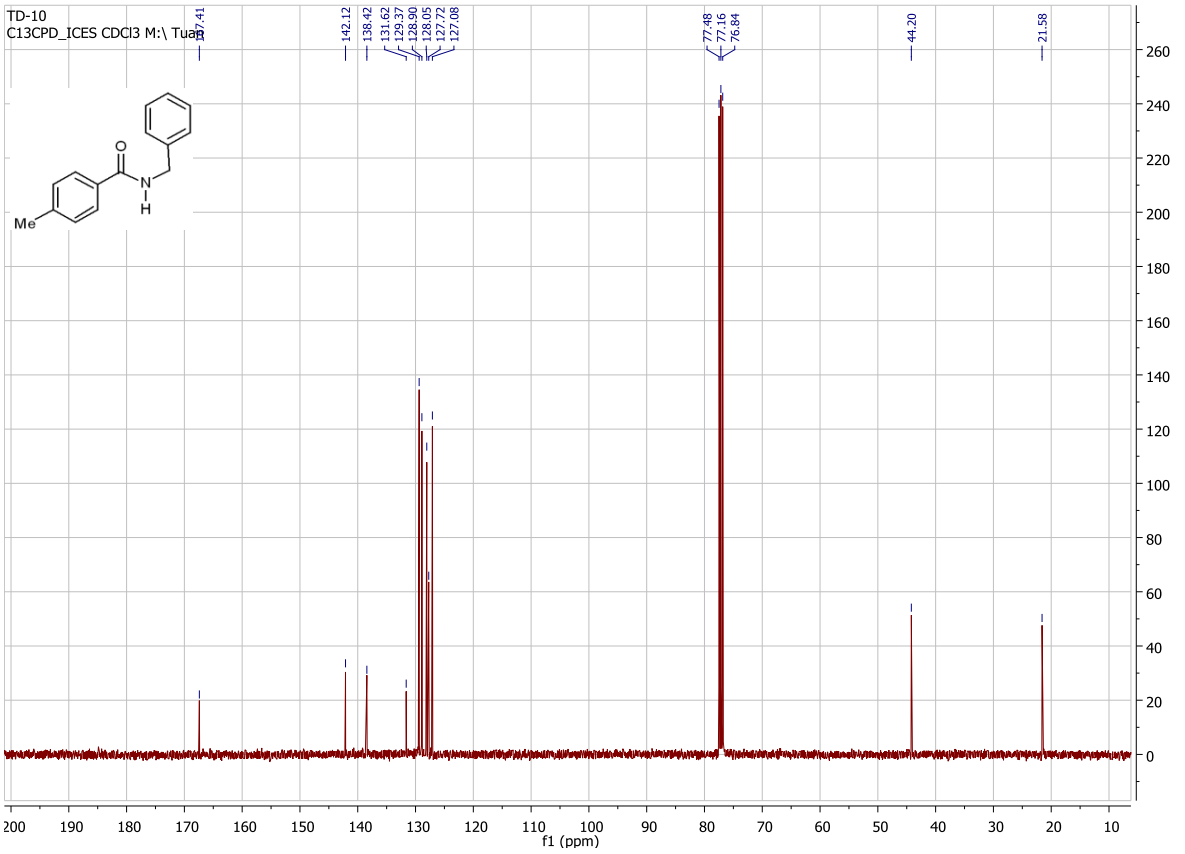

Tuan-13042011
TD46-3B
7.67
7.64
7.26
7.20
7.18
6.31
3.43
3.42
3.41
3.40
3.39
3.38
2.37
1.60
1.58
1.56
1.35
1.33
1.30
1.29
1.28
0.89
0.87
0.86
0.86
Me
O
N
H
Me
1.00
1.01
0.48
1.06
1.53
1.09
3.26
1.58
f1 (ppm)

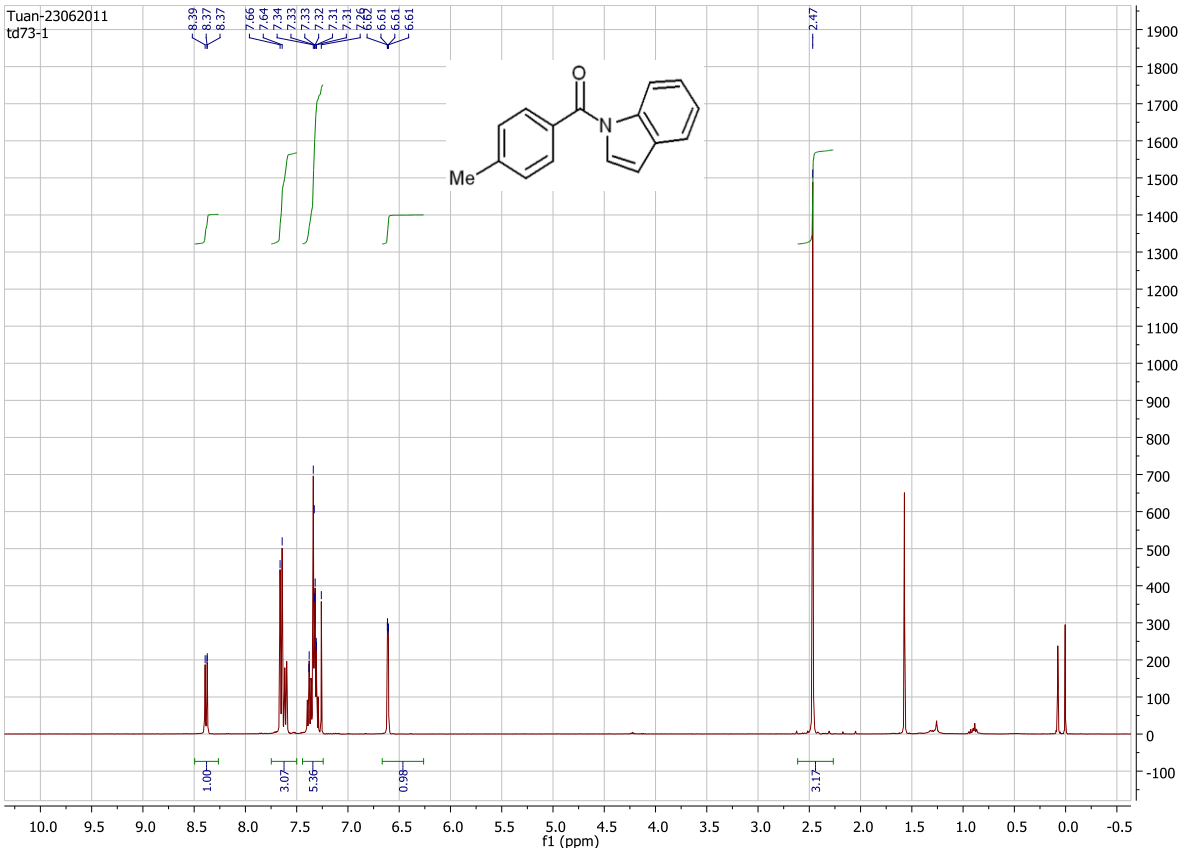

Tuan-13042011
TD46-3B
167.59
141.69
132.09
129.23
126.95
77.48
77.16
76.84
40.16
31.62
29.75
26.78
22.66
21.50
14.12
Me
O
N
H
Me
f1 (ppm)

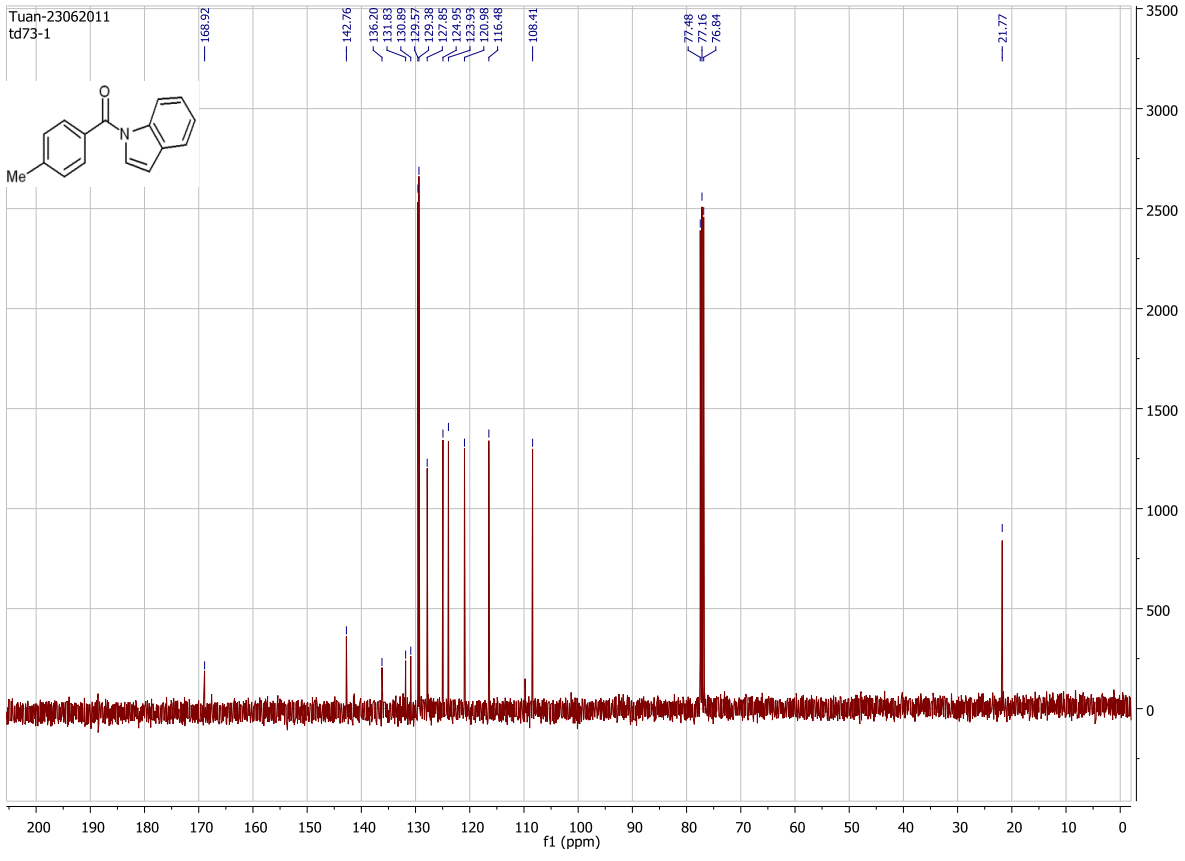


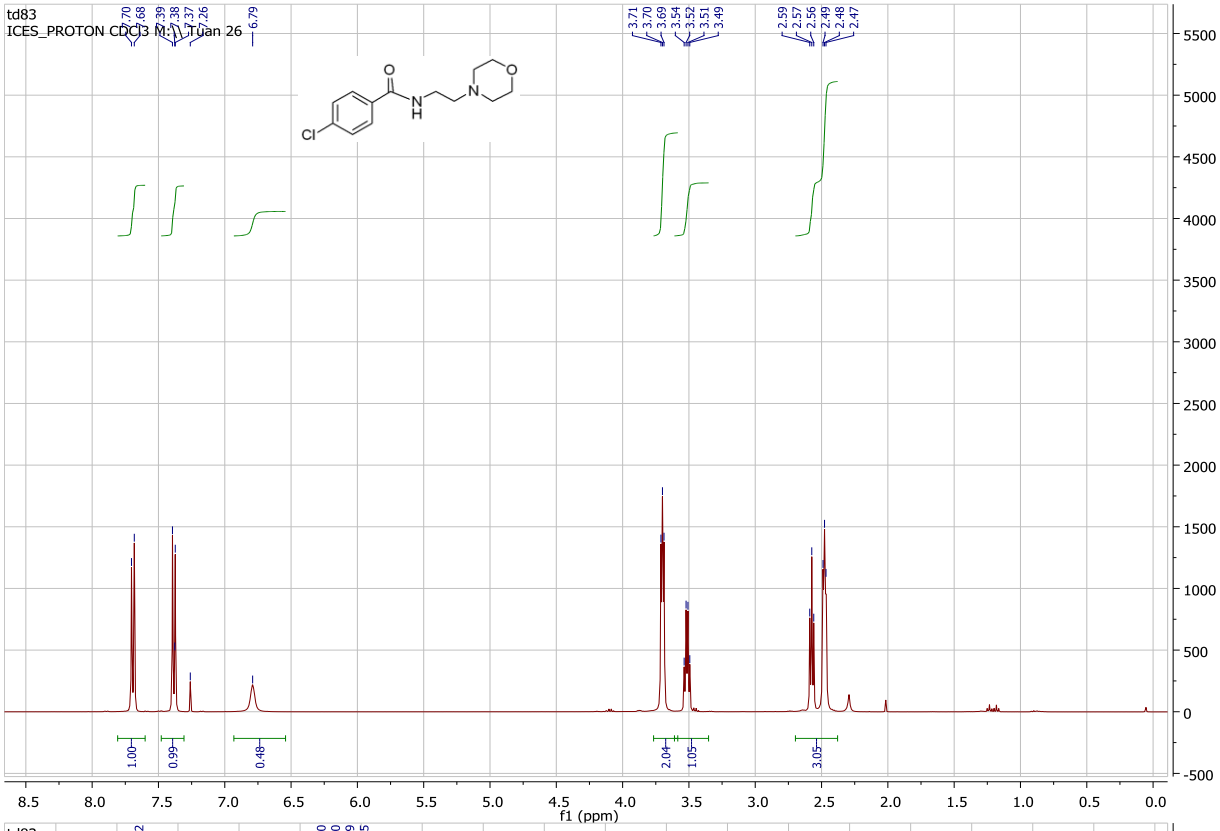


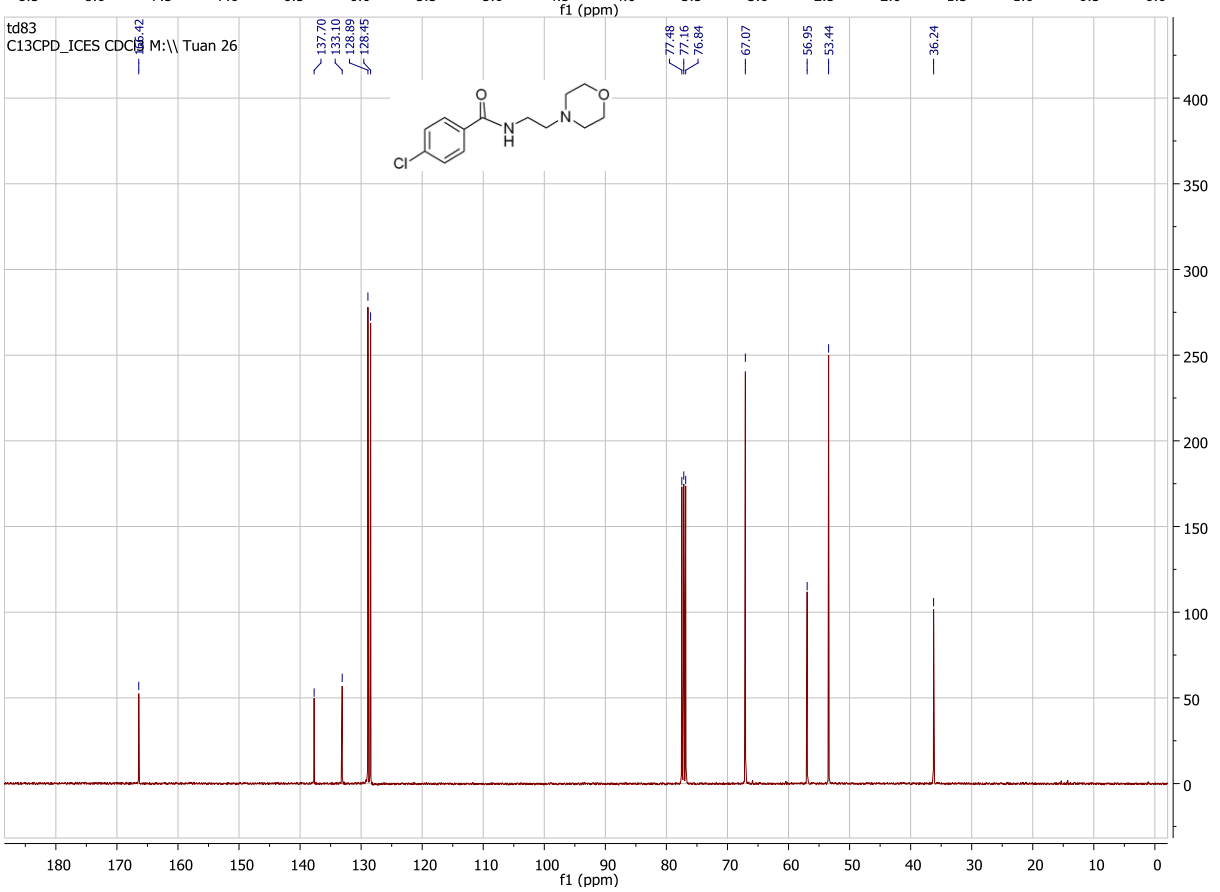









td83
ICES_PROTON CDCl3 M:\\ Tuan 26
7.70
7.68
7.39
7.38
7.37
7.26
6.79
3.71
3.70
3.69
3.54
3.52
3.51
3.49
2.59
2.57
2.56
2.49
2.48
2.47
1.00
0.99
0.48
2.04
1.05
3.05
f1 (ppm)


td83
C13CPD_ICES CDCl3 M:\\ Tuan 26
165.42
137.70
133.10
128.89
128.45
77.48
77.16
76.84
67.07
56.95
53.44
36.24
f1 (ppm)