Supporting Information

Silver-Promoted Decarboxylative Amidation of α-Keto Acids with Amines

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1. General Information and Materials.

All the reactions were conducted in oven-dried Schlenk tubes. All solvents were obtained from commercial suppliers and used without further purification. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer in $CDCl_3$ and $(CD_3)_2SO$. Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz).

2. Preparation of substrates.

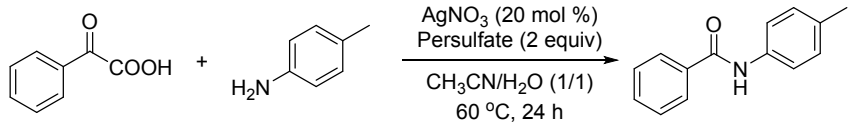
Benzoylformic acid, 3,3-dimethyl-2-oxobutanoic acid and pyruvic acid were obtained from commercial suppliers. The other α-keto acids were prepared from oxidation of corresponding methyl ketones by SeO_2 according to the reported procedure. (K. Wadhwa, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, 38, 4434.)

3. General procedure for decarboxylative amidation.

α-keto acid (0.25 mmol), amine (0.375 mmol), AgOTf (0.5 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The solvents CH_3CN (1.3 mL) and H_2O (0.7 mL) were added under air atmosphere. The reaction mixture was stirred at 60 ^{o}C for 24 h. After 24 h, the mixture was quenched with saturated sodium bicarbonate (10 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate).

4. Investigation of the key reaction parameters

4.1 The study of persulfates



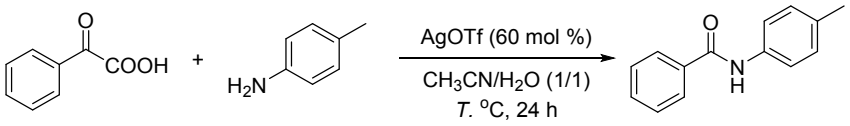
0.25 mmol 0.375 mmol

entry	Catalyst (0.2 equiv)	Persulfate (2 equiv)	Temp. (^{o}C)	Time (h)	Yield (%)
1	$AgNO_3$	$K_2S_2O_8$	60	24	9
2	$AgNO_3$	$Na_2S_2O_8$	60	24	11
3	$AgNO_3$	$(NH_4)_2S_2O_8$	60	24	10
4	$AgNO_3$	-	60	24	8

Firstly, we examined various persulfates like $K_2S_2O_8$, $Na_2S_2O_8$, and $(NH_4)_2S_2O_8$ with $AgNO_3$

(entry 1-3). Interesting, the control experiment without persulfate (entry 4) gave the similar yield with those experiments added persulfate. So it suggest that 2 equiv of persulfate did not lead to a high yield.

4.2 The study of temperature

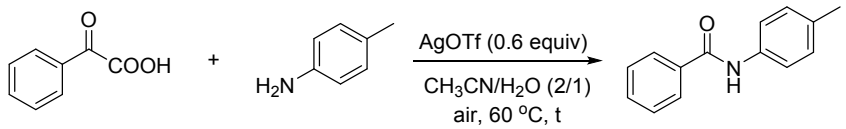


0.25 mmol 0.375 mmol

entry	Catalyst (0.6 equiv)	Temp. (°C)	Time (h)	Yield (%)
1	AgOTf	rt	24	trace
2	AgOTf	40	24	27
3	AgOTf	60	24	50
4	AgOTf	80	24	39

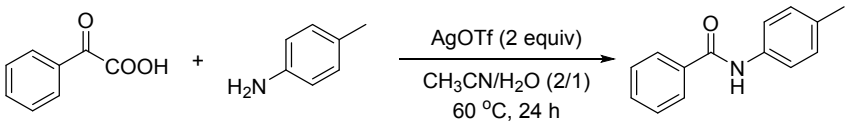
These experiments under different temperature were conducted (entries 1-4). And the results released that 60 °C was the most suitable temperature.

4.3 The study of reaction time



entry	Time (h)	Yield (%)
1	12	50
2	24	55
3	36	56

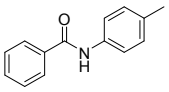
4.4 Protection atomosphere



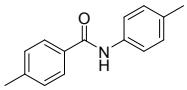
0.25 mmol 0.375 mmol

entry	Catalyst (2.0 equiv)	Atomosphere	Time (h)	Yield (%)
1	AgOTf	N_2	24	16
2	AgOTf	air	24	87
3	AgOTf	O_2	24	89

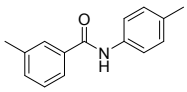
5. Characterization of products.



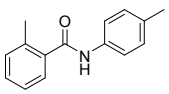
N-(p-tolyl)benzamide (**3a**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 87% yield as a white solid (45.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 6.5 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.69, 135.36, 135.04, 134.15, 131.62, 129.49, 128.64, 126.99, 120.35, 20.86.



4-methyl-N-(p-tolyl)benzamide (**3b**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 79% yield as a white solid (44.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.60, 142.10, 135.47, 133.97, 132.16, 129.46, 129.30, 126.99, 120.28, 21.42, 20.85.

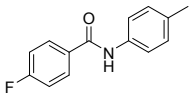


3-methyl-N-(p-tolyl)benzamide (**3c**).[2] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 75% yield as a white solid (44.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.67 (s, 1H), 7.62 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 3.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.88, 138.50, 135.43, 135.02, 134.02, 132.33, 129.45, 128.47, 127.75, 123.92, 120.32, 21.29, 20.84.

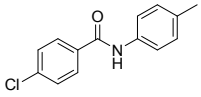


2-methyl-N-(p-tolyl)benzamide (**3d**).[2] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 48% yield as a white solid (27.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H), 2.34 (s, 3H). ^{13}C

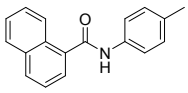
NMR (151 MHz, $CDCl_3$) δ 167.92, 136.56, 136.37, 135.41, 134.18, 131.19, 130.15, 129.54, 126.57, 125.84, 119.92, 20.87, 19.78.



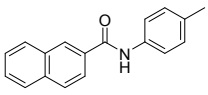
4-fluoro-N-(p-tolyl)benzamide (**3e**).[3] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 46% yield as a white solid (26.4 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.19 (s, 1H), 8.03 (dd, *J* = 8.3, 5.7 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 164.21, 164.00 (d, *J* = 248.8 Hz), 136.54, 132.68, 131.45 (d, *J* = 2.9 Hz), 130.32 (d, *J* = 9.0 Hz), 129.00, 120.42, 115.28 (d, *J* = 21.8 Hz), 20.50.



4-chloro-N-(p-tolyl)benzamide (**3f**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 66% yield as a white solid (40.5 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.24 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 164.19, 136.44, 136.29, 133.70, 132.78, 129.56, 129.00, 128.40, 120.43, 20.50.

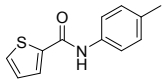


N-(p-tolyl)-1-naphthamide (**3g**).[4] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 43% yield as a white solid (28.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, J = 7.4 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.56 (dd, J = 12.5, 5.6 Hz, 4H), 7.48 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.41, 135.46, 134.32, 133.73, 130.90, 130.07, 129.60, 129.56, 128.37, 127.28, 126.53, 125.28, 125.00, 124.71, 120.03, 20.91.

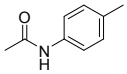


N-(p-tolyl)-2-naphthamide (**3h**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 80% yield as a white solid (52.3 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.39 (s, 1H), 8.59 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.04

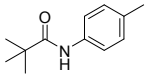
(s, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 165.38, 136.72, 134.21, 132.62, 132.36, 132.09, 129.03, 128.92, 127.96, 127.87, 127.74, 127.65, 126.80, 124.46, 120.38, 20.51.



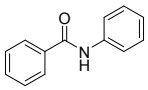
N-(p-tolyl)thiophene-2-carboxamide (**3i**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 57% yield as a yellow solid (31.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.62 (d, J = 3.4 Hz, 1H), 7.52 (d, J = 4.8 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.13 – 7.09 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.83, 139.36, 135.00, 134.30, 130.52, 129.58, 128.33, 127.75, 120.31, 20.88.



N-(p-tolyl)acetamide (**3j**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 5:1), obtained in 49% yield as a white solid (18.3 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 9.83 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.23 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 167.99, 136.83, 131.79, 129.02, 118.96, 23.94, 20.43.

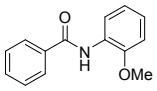


N-(p-tolyl)pivalamide (**3k**).[3] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 20:1), obtained in 61% yield as an off-white solid (29.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.39, 135.45, 133.72, 129.37, 120.02, 39.48, 27.62, 20.79.

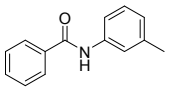


N-phenylbenzamide (**3l**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 56% yield as a white solid (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.75, 137.88, 134.96, 131.82, 129.07, 128.76, 126.99, 124.56,

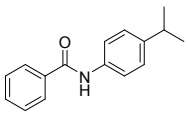
120.19.



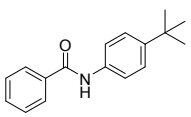
N-(2-methoxyphenyl)benzamide (**3m**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 60% yield as a colorless liquid (34.1 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 9.44 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 164.95, 151.46, 134.50, 131.62, 128.50, 127.46, 126.81, 125.71, 124.28, 120.20, 111.36, 55.71.



N-(m-tolyl)benzamide (**3n**).[2] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 77% yield as a white solid (40.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.73, 138.95, 137.83, 135.03, 131.70, 128.83, 128.69, 126.98, 125.33, 120.89, 117.31, 21.45.

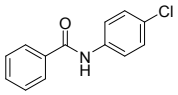


N-(4-isopropylphenyl)benzamide (**3o**).[3] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 66% yield as a white solid (39.5 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.19 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.86 (hept, *J* = 6.8 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 165.31, 143.72, 136.91, 135.02, 131.44, 128.34, 127.60, 126.29, 120.45, 32.93, 23.98.

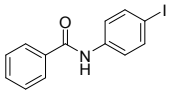


N-(4-(tert-butyl)phenyl)benzamide (**3p**).[1] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 72% yield as a white solid (45.6 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.20 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.70 (d,

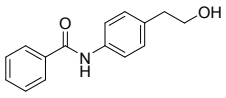
J = 8.5 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 165.32, 145.96, 136.60, 135.01, 131.45, 128.34, 127.61, 125.19, 120.13, 34.05, 31.21.



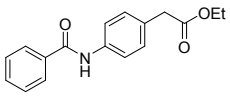
N-(4-chlorophenyl)benzamide (**3q**).[3] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 50% yield as a white solid (29.0 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.39 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 165.69, 138.17, 134.72, 131.74, 128.55, 128.45, 127.70, 127.28, 121.85.



N-(4-iodophenyl)benzamide (**3r**).[3] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 40% yield as a white solid (32.3 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 10.34 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 165.65, 139.05, 137.27, 134.72, 131.72, 128.43, 127.68, 122.45, 87.35.

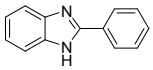


N-(4-(2-hydroxyethyl)phenyl)benzamide (**3s**).[5] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 3:1), obtained in 84% yield as a yellow solid (47.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.55 (dd, *J* = 13.1, 7.7 Hz, 3H), 7.48 (t, *J* = 6.7 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.86 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.84, 136.26, 134.93, 134.84, 133.57, 131.87, 130.13, 129.64, 128.78, 128.44, 127.03, 120.70, 119.40, 63.62, 38.57.

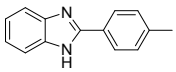


ethyl 2-(4-benzamidophenyl)acetate (**3t**). Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 10:1), obtained in 37% yield as a white solid (26.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* =

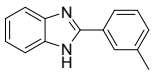
8.1 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.60, 165.70, 136.89, 134.90, 131.84, 130.33, 129.90, 128.77, 127.01, 120.38, 60.91, 40.86, 14.16.



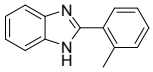
2-phenyl-1H-benzo[d]imidazole (**4a**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 80% yield as a yellow solid (38.8 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.58 (s, 1H), 8.30 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.4 Hz, 3H), 7.35 – 7.31 (m, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 154.57, 135.60, 132.04, 132.00, 130.30, 130.17, 129.18, 128.75, 127.84, 123.38, 115.08.



2-(p-tolyl)-1H-benzo[d]imidazole (**4b**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 83% yield as a yellow solid (40.5 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.83 (s, 1H), 8.08 (d, J = 8.1 Hz, 2H), 7.64 (s, 1H), 7.51 (s, 1H), 7.35 (d, J = 7.9 Hz, 2H), 7.19 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 151.36, 143.80, 139.52, 134.93, 129.48, 127.44, 126.36, 22.29, 21.52, 118.68, 111.16, 20.95.

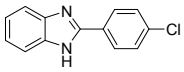


2-(m-tolyl)-1H-benzo[d]imidazole (**4c**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 87% yield as a white solid (45.3 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.67 (s, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 6.3 Hz, 3H), 7.21 (dt, *J* = 14.0, 7.2 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 151.98, 143.74, 137.06, 134.45, 131.32, 130.09, 129.49, 129.36, 126.02, 122.41, 121.45, 118.97, 111.31, 21.14.

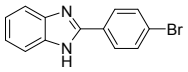


2-(o-tolyl)-1H-benzo[d]imidazole (**4d**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 86% yield as a white solid (44.8 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.94 (s, 1H), 8.06 (s, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 42.9 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.21 (s, 2H), 2.40 (s,

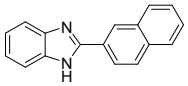
3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 151.40, 138.21, 132.09, 130.53, 130.14, 128.89, 127.07, 123.64, 115.14, 21.12.



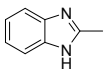
2-(4-chlorophenyl)-1H-benzo[d]imidazole (**4e**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 84% yield as a yellow solid (48.0 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.98 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.21 (dq, *J* = 14.5, 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 150.36, 134.77, 129.24, 129.06, 128.32, 122.62, 119.14, 111.62.



2-(4-bromophenyl)-1H-benzo[d]imidazole (**4f**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 83% yield as a yellow solid (56.7 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 13.01 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 14.5, 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 150.20, 143.76, 135.02, 131.99, 129.38, 128.35, 123.25, 122.74, 121.81, 118.97, 111.42.

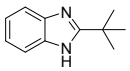


2-(naphthalen-2-yl)-1H-benzo[d]imidazole (**4g**).[6] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 4:1), obtained in 90% yield as a yellow solid (55.0 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ13.09 (s, 1H), 8.76 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 6.2 Hz, 1H), 7.98 (d, *J* = 6.6 Hz, 1H), 7.65 (s, 1H), 7.63 – 7.53 (m, 3H), 7.24 (s, 2H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 151.23, 133.43, 132.79, 129.81, 128.49, 128.39, 127.74, 127.59, 127.04, 126.86, 125.79, 123.92, 122.20, 115.11.



2-methyl-1H-benzo[d]imidazole (**4h**).[7] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 50:1), obtained in 60% yield as a white solid (19.8 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 12.33 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 159.27,

154.97, 131.95, 129.37, 127.91, 123.09, 115.26, 20.62.



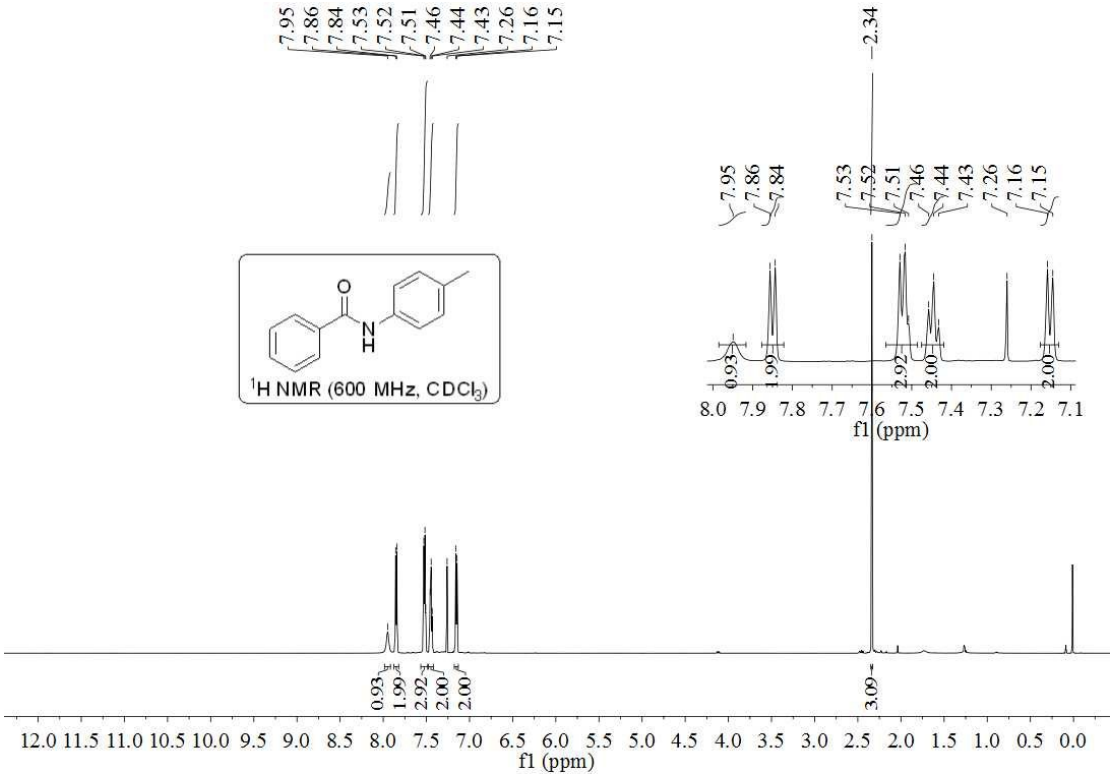
2-(tert-butyl)-1H-benzo[d]imidazole (**4i**).[7] Following general procedure, the product was purified by flash column chromatography on silica gel (PE/EA = 50:1), obtained in 90% yield as a wihte solid (39.2 mg). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ12.06 (s, 1H), 7.47 (s, 2H), 7.10 (dd, *J* = 5.8, 3.0 Hz, 2H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 162.32, 140.04, 121.23, 119.07, 33.25, 29.33.

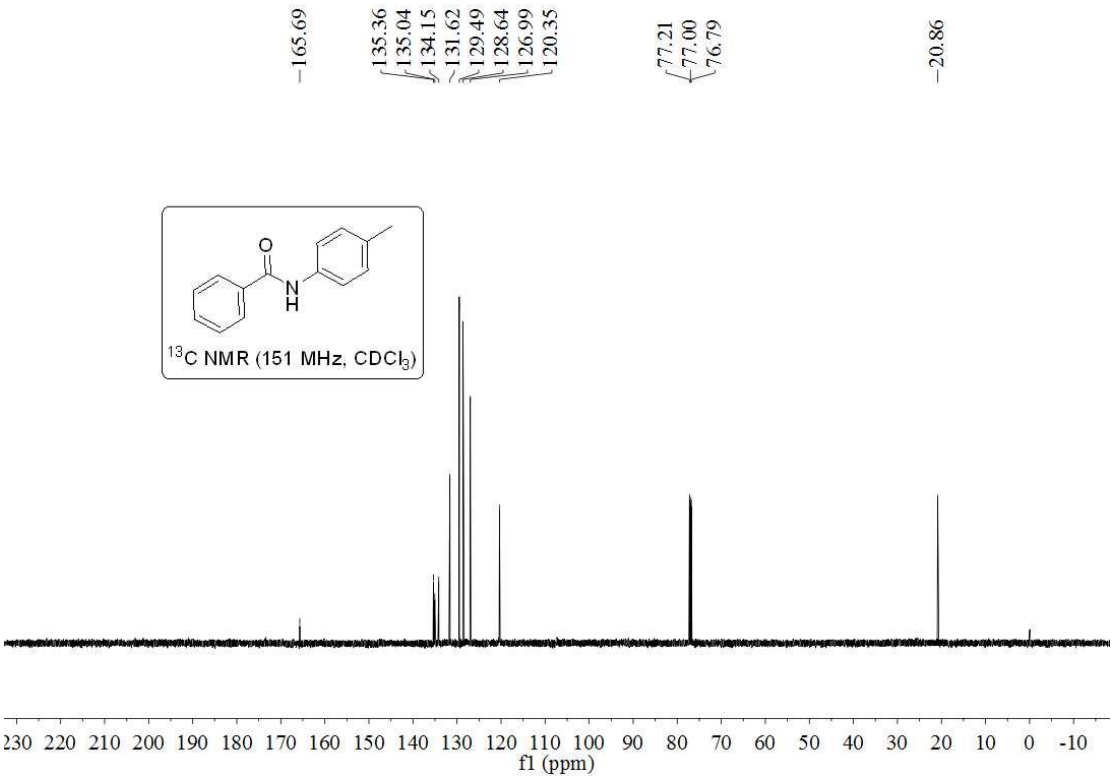
Reference:

1. J. Liu, Q. Liu, H. Yi, C. Qin, R. Bai, X. Qi, Y. Lan and A. Lei, *Angew. Chem., Int. Ed.*, 2014, **53**, 502.
2. J. Du, K. Luo and X. Zhang, *RSC Adv.*, 2014, **4**, 54539.
3. W. T. Xu, B. Huang, J. J. Dai, J. Xu and H. J. Xu, *Org. Lett.*, 2016, **18**, 3114.
4. W. W. Fang, Q. Y. Deng, M. Z. Xu and T. Tu, *Org. Lett.*, 2013, **15**, 3678.
5. Y. J. Kang, H. A. Chung, J. J. Kim and Y. J. Yoon, *Synthesis*, 2002, 733.
6. D. Mahesh, P. Sadhu and T. Punniyamurthy, *J. Org. Chem.*, 2015, **80**, 1644.
7. J. Huang, Y. He, Y. Wang and Q. Zhu, *Chem. Eur. J.*, 2012, **18**, 13964.

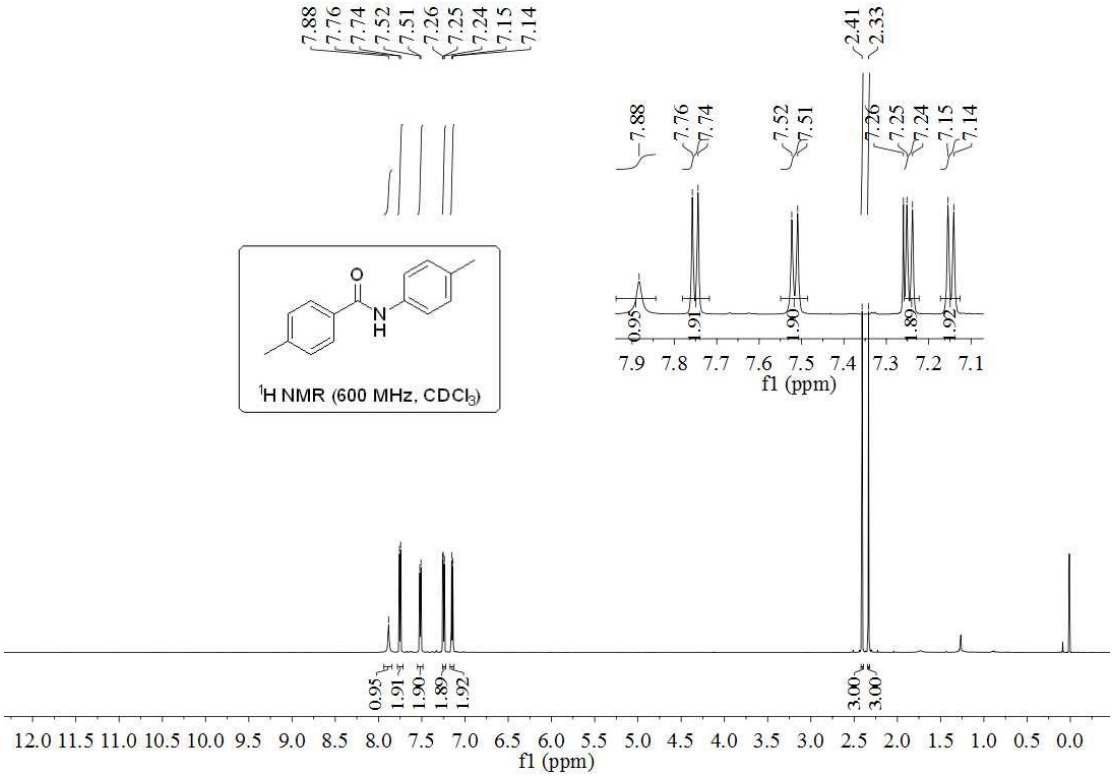
6. ^{1}H NMR and ^{13}C NMR spectra of products.

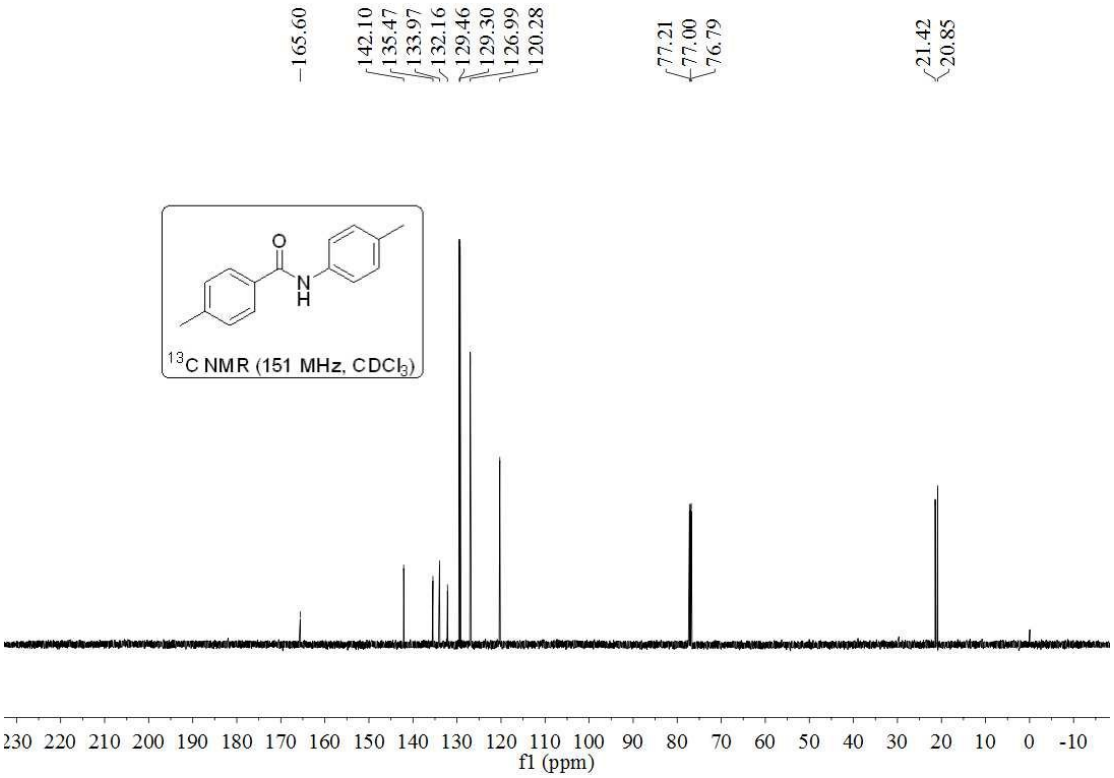
N-(p-tolyl)benzamide (3a)



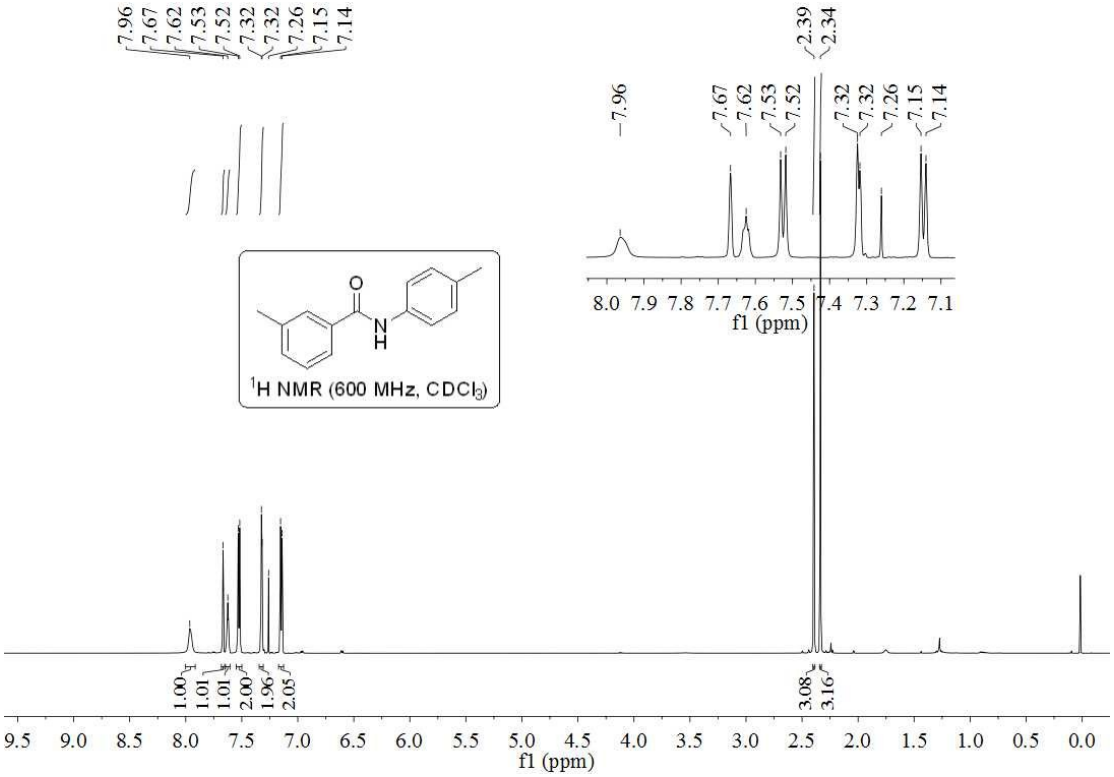


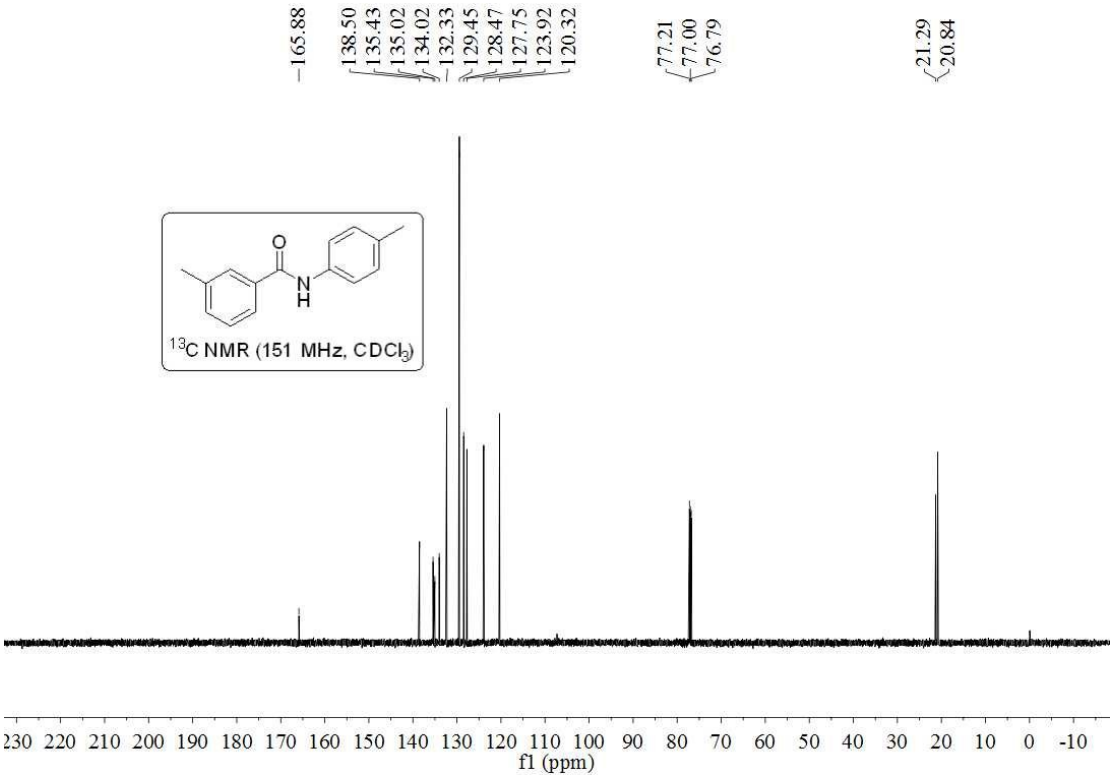
4-methyl-N-(p-tolyl)benzamide (3b)



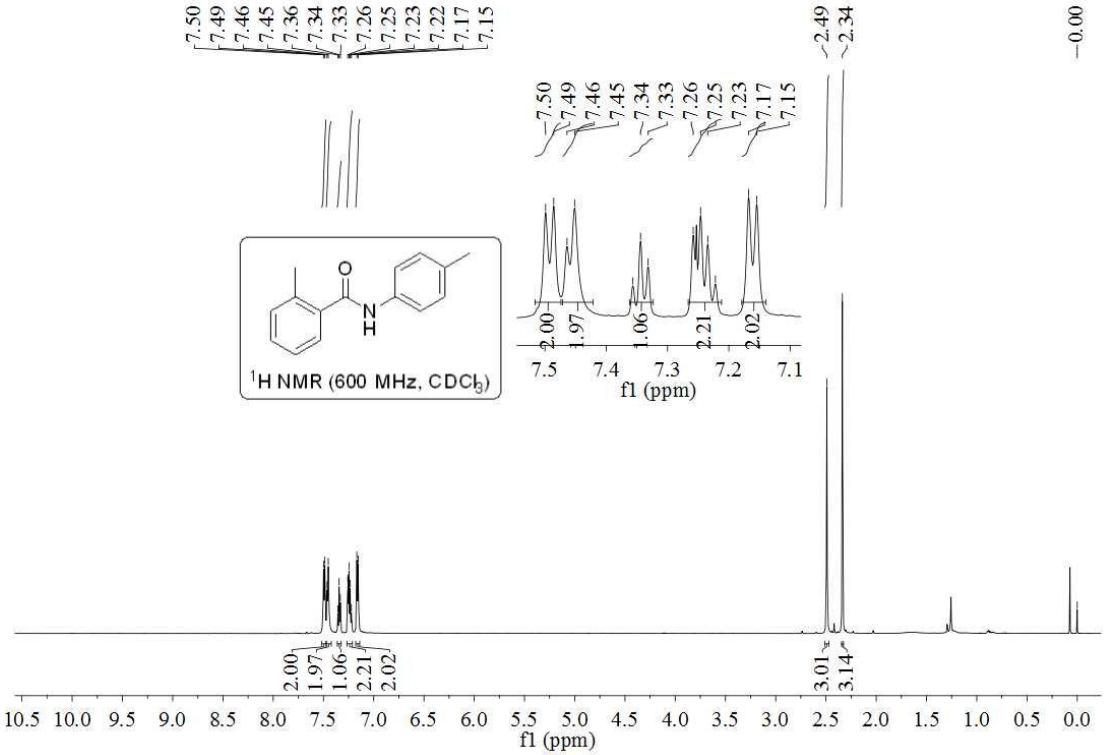


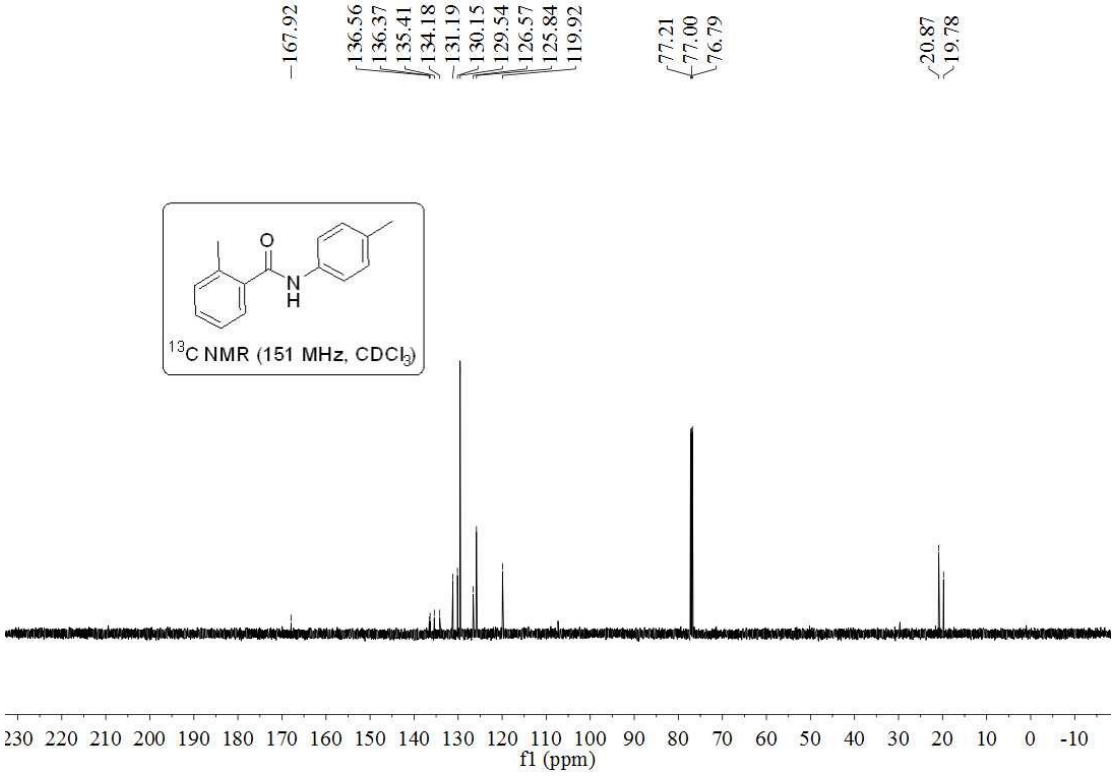
3-methyl-N-(p-tolyl)benzamide (3c)



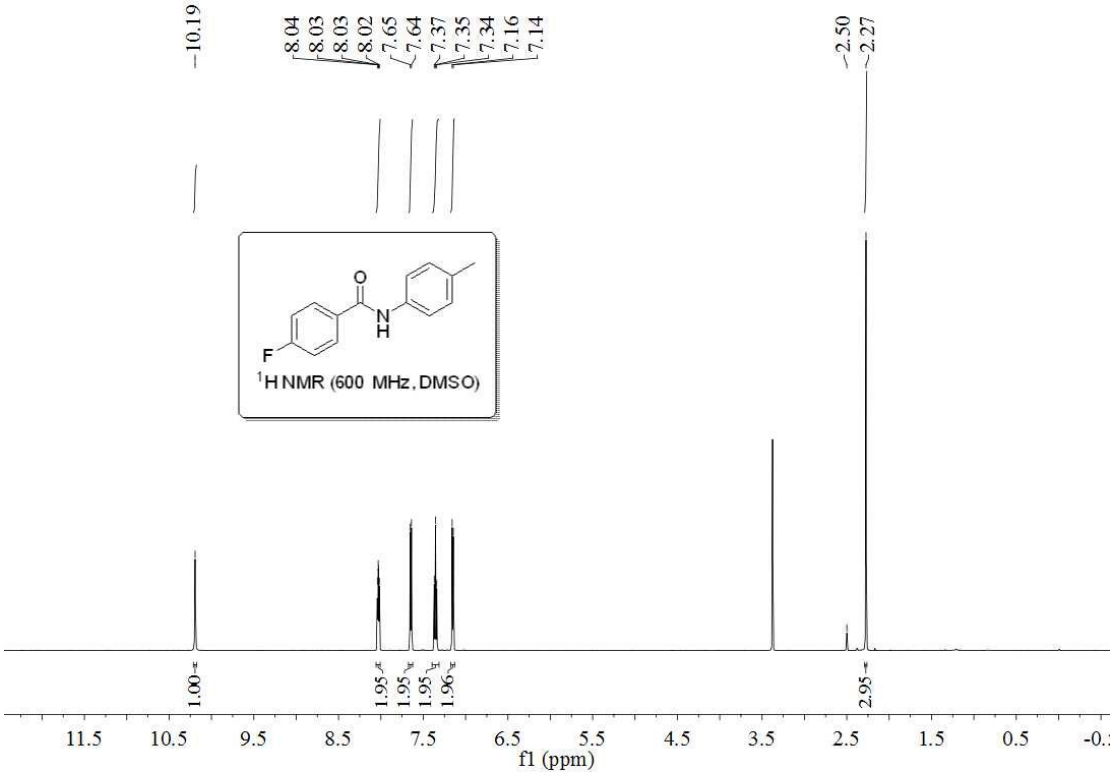


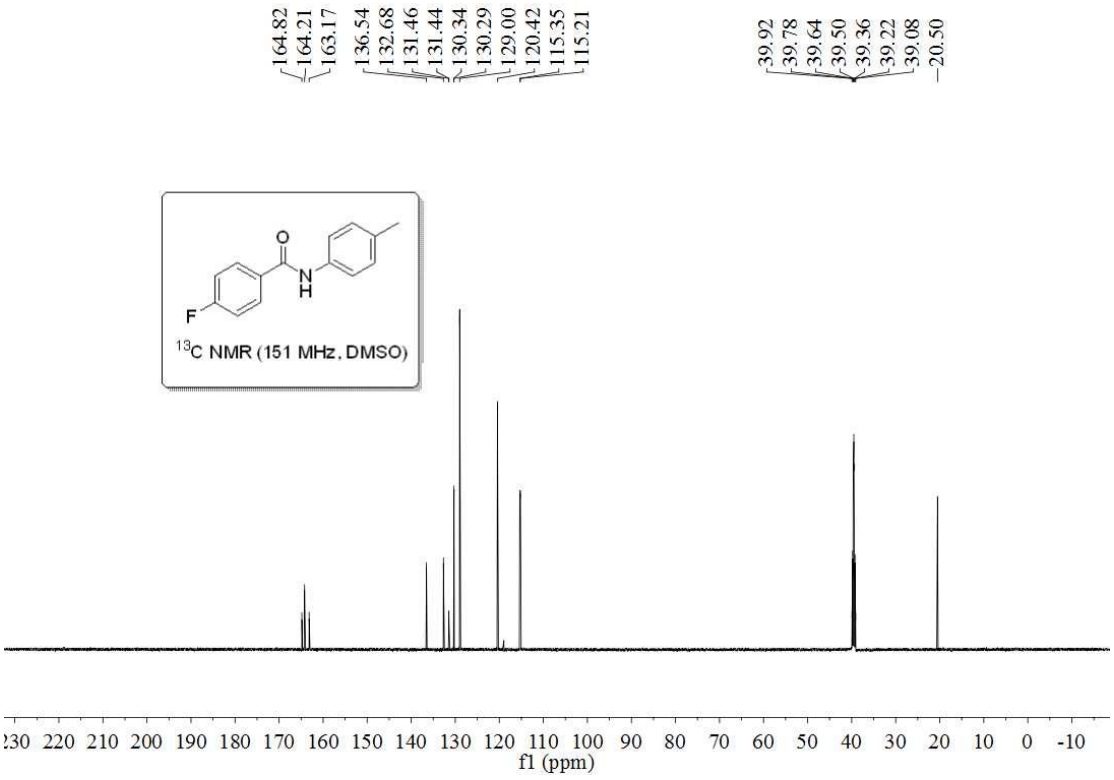
2-methyl-N-(p-tolyl)benzamide (3d)



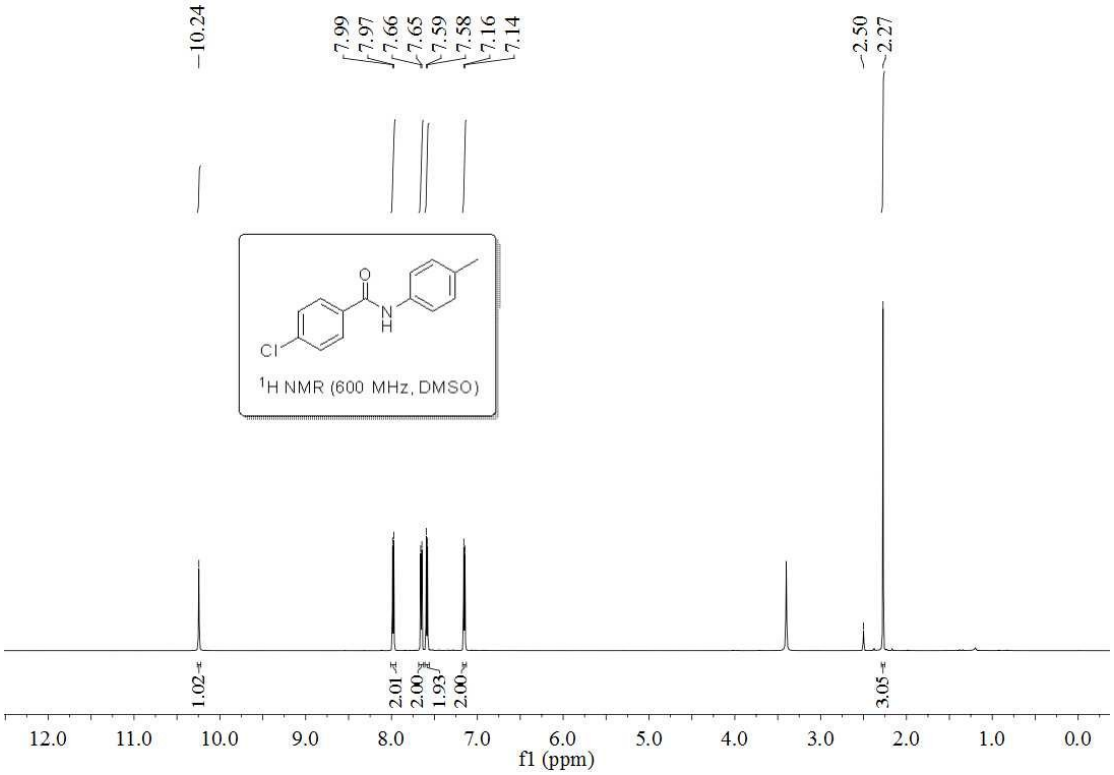


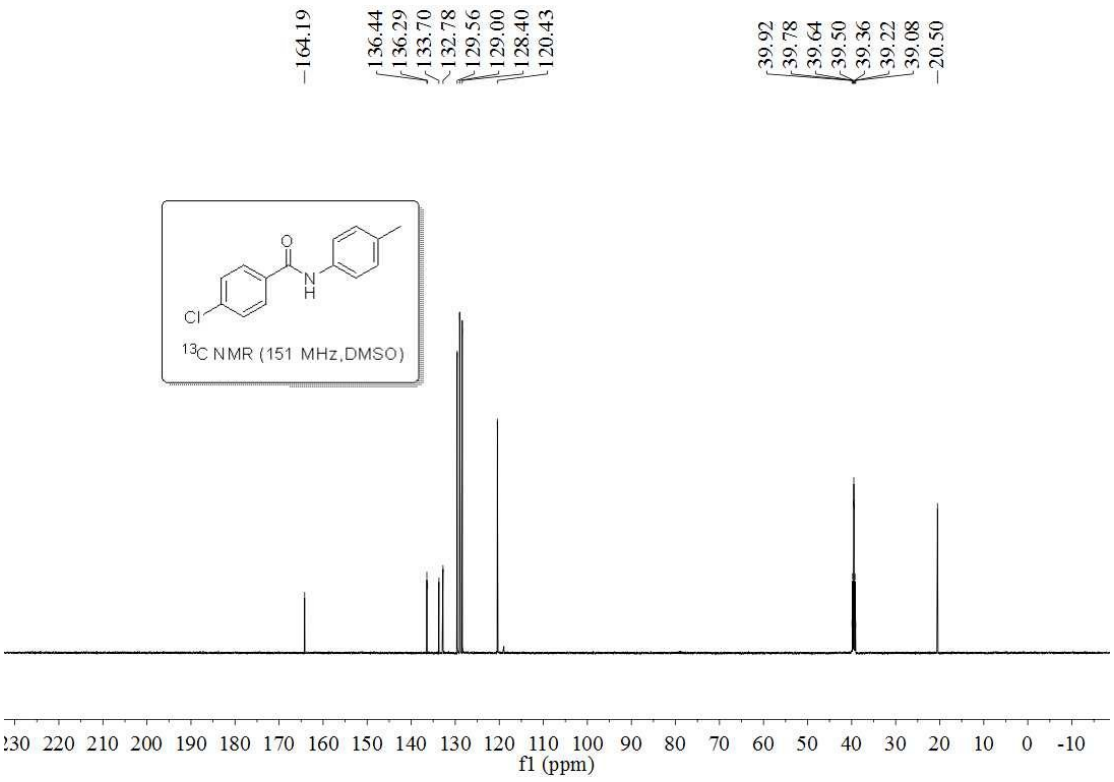
4-fluoro-N-(p-tolyl)benzamide (3e)



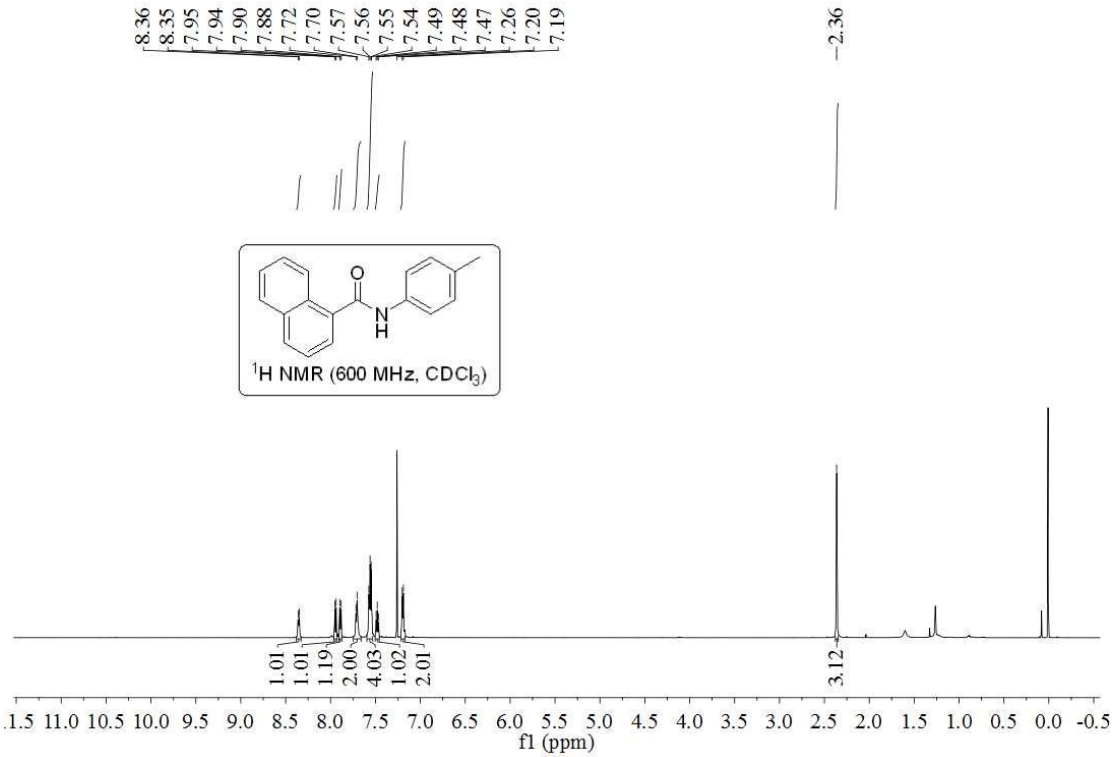


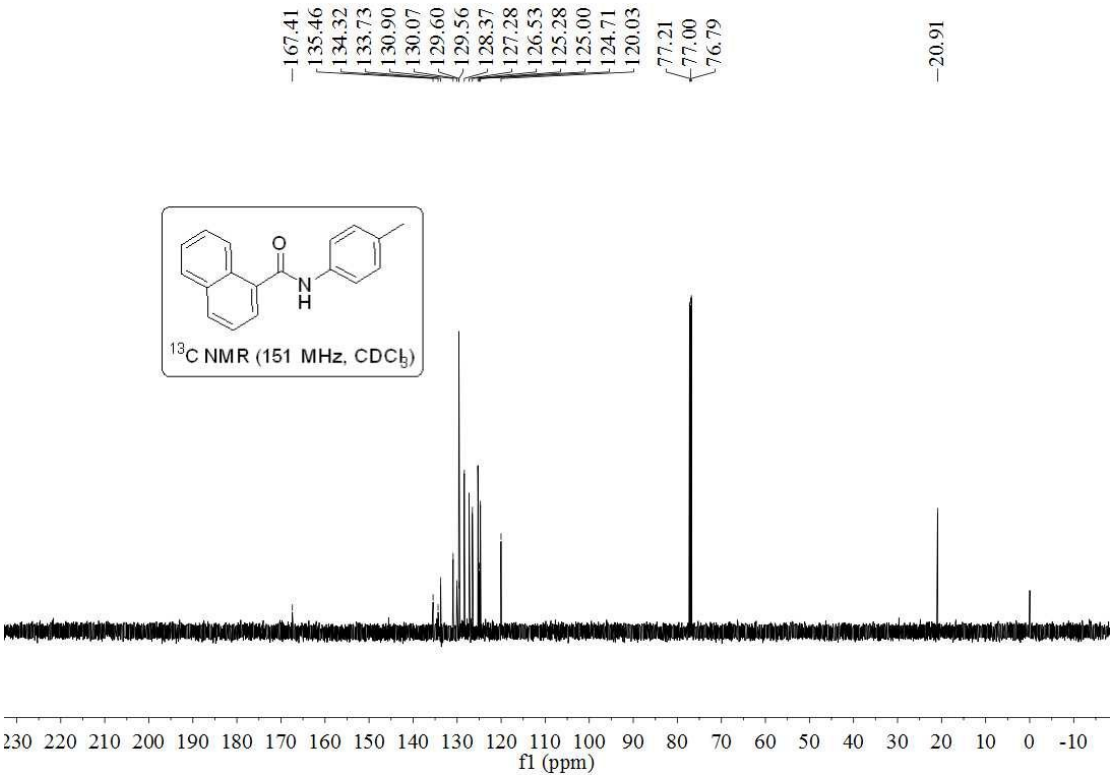
4-chloro-N-(p-tolyl)benzamide (3f)



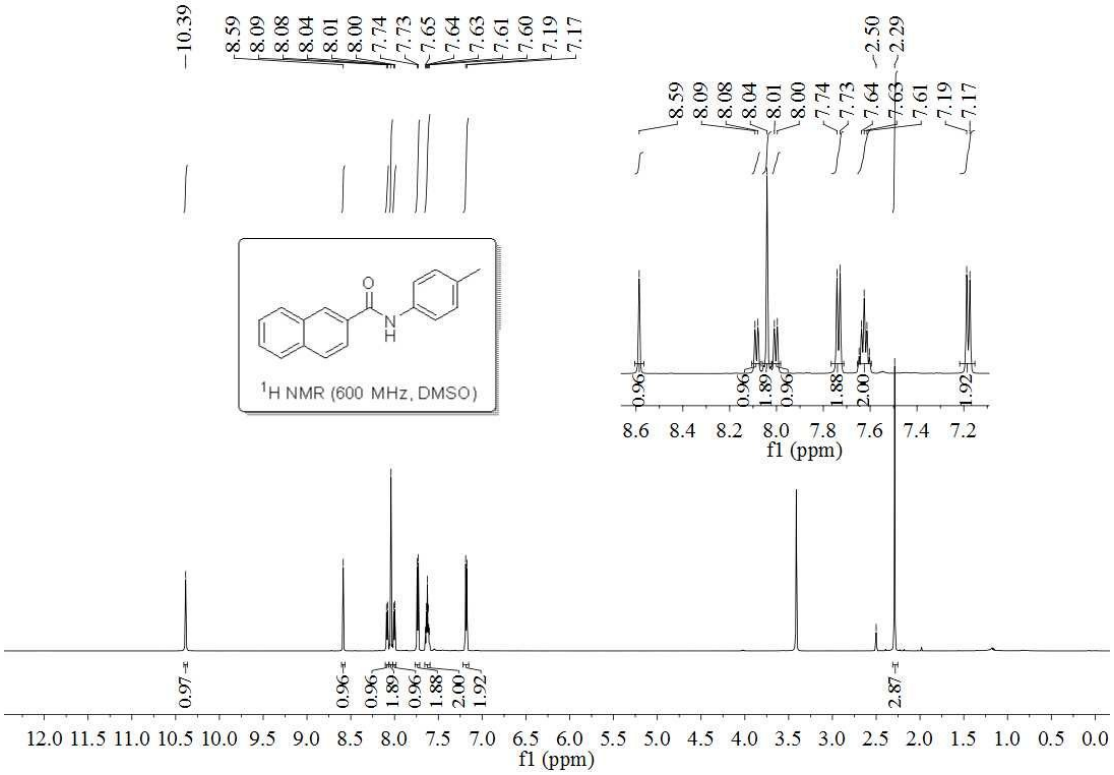


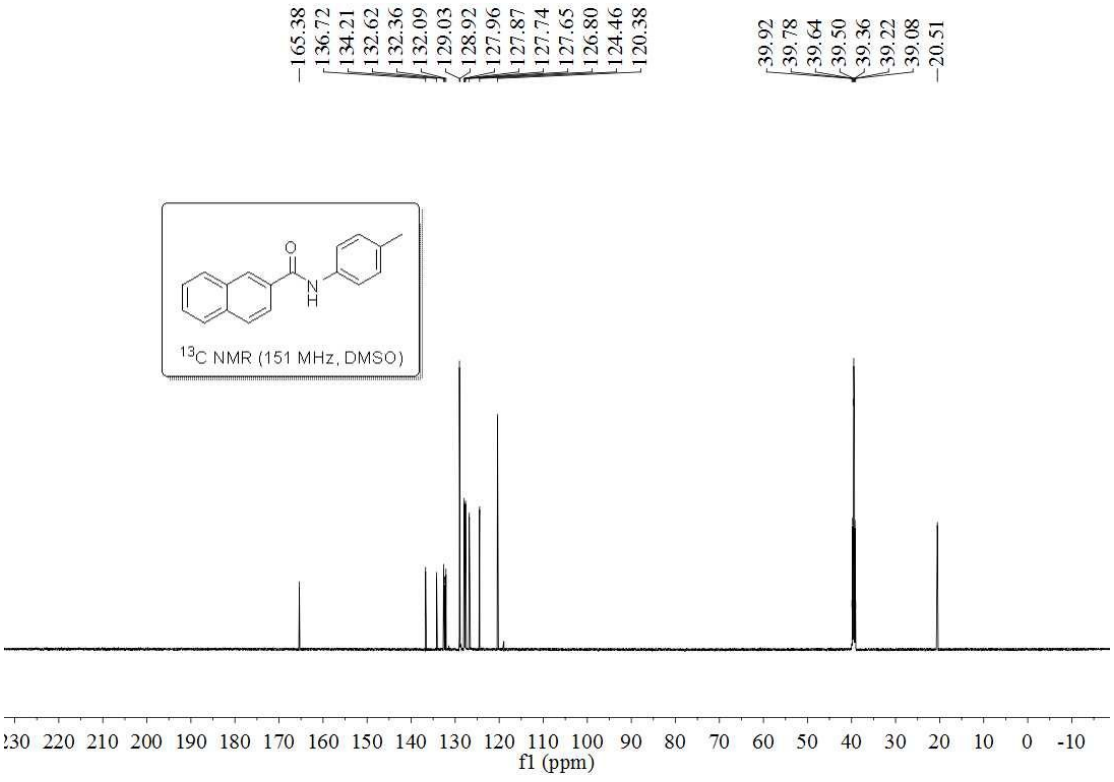
N-(p-tolyl)-1-naphthamide (3g)



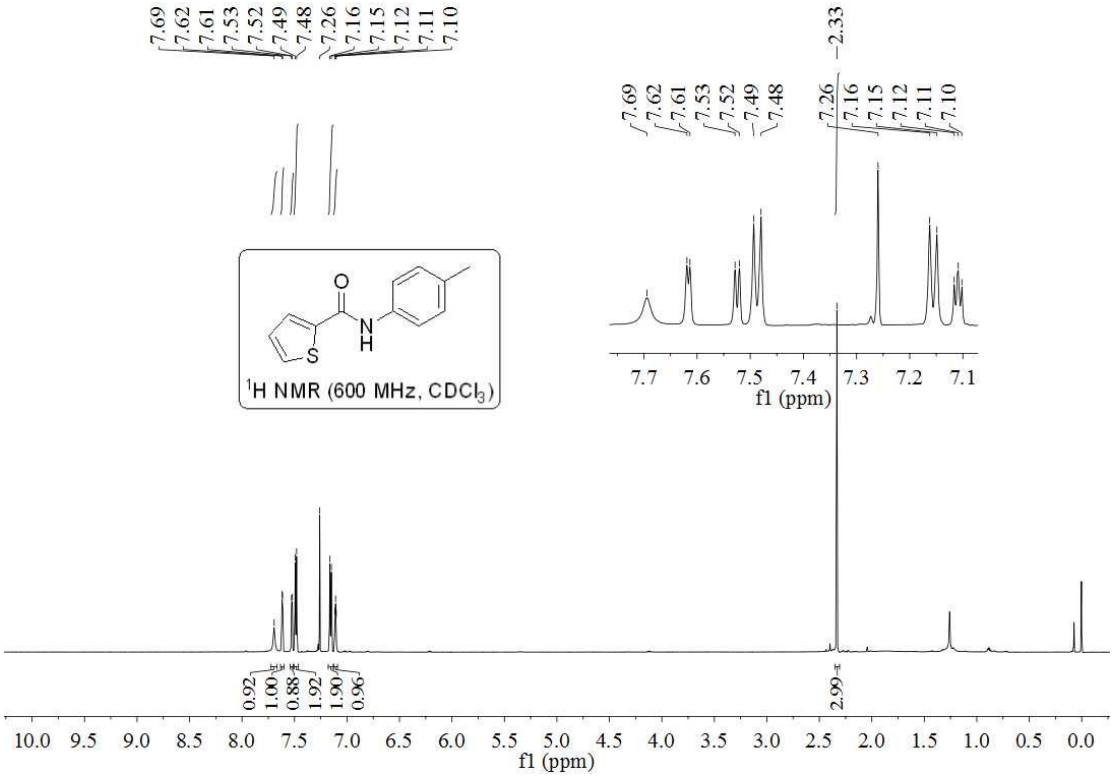


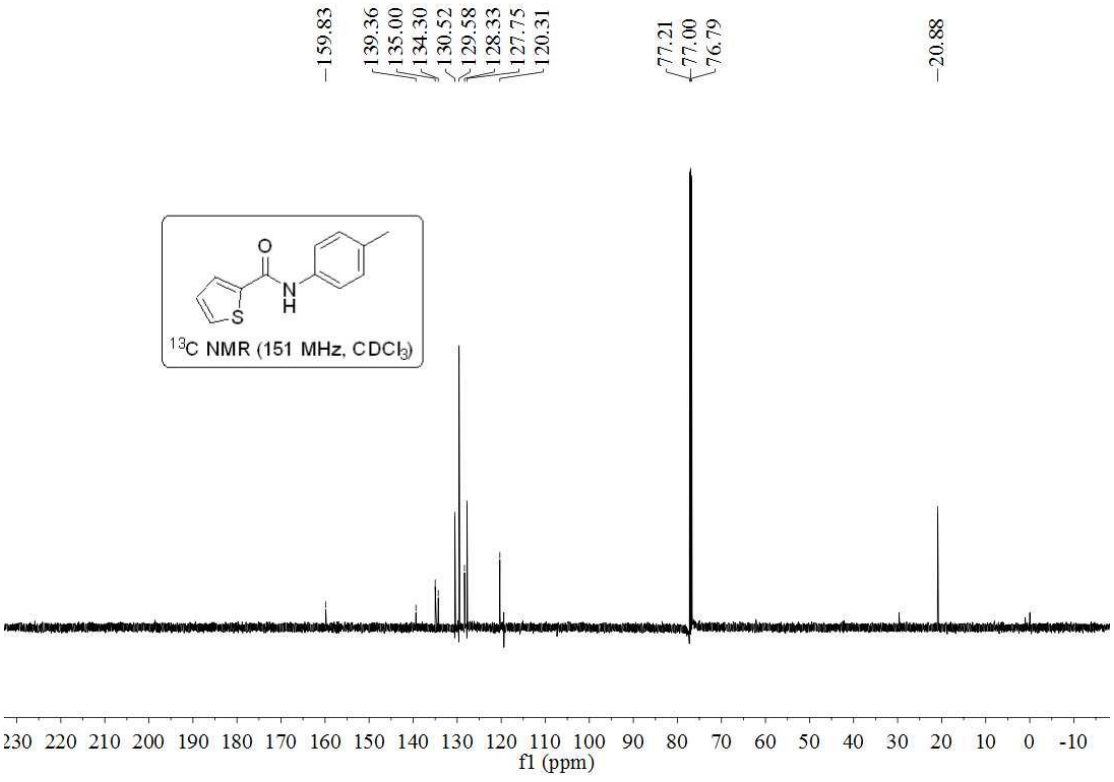
N-(p-tolyl)-2-naphthamide (3h)



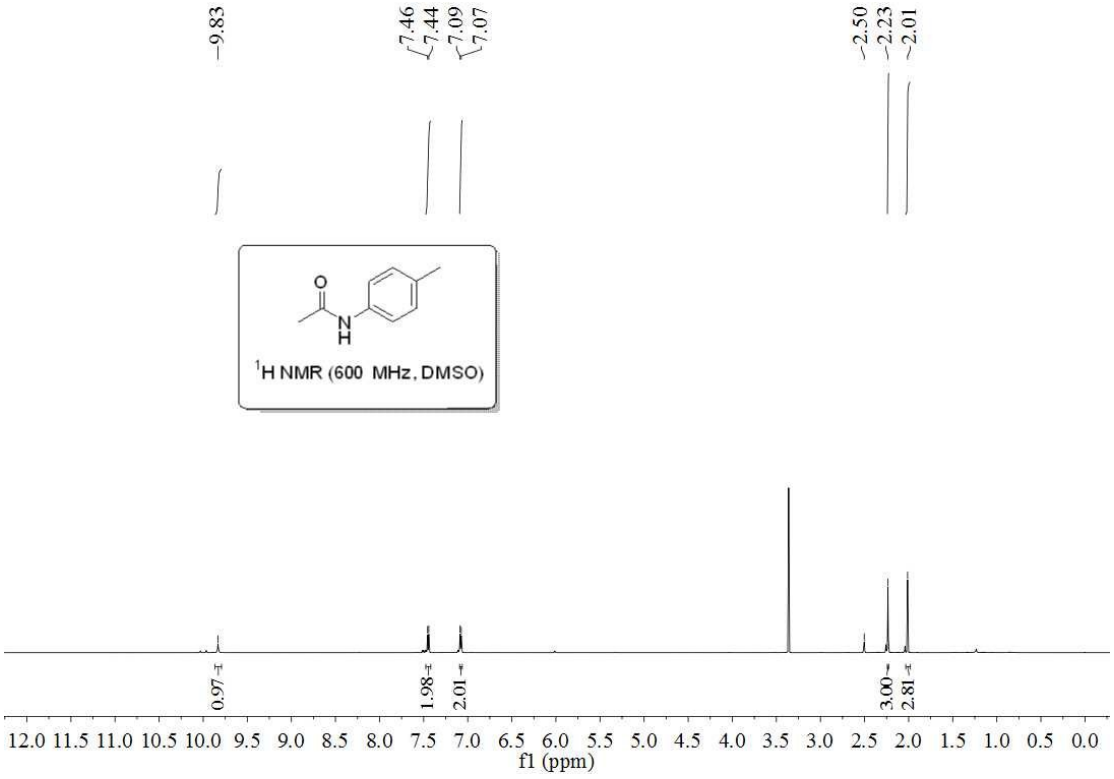


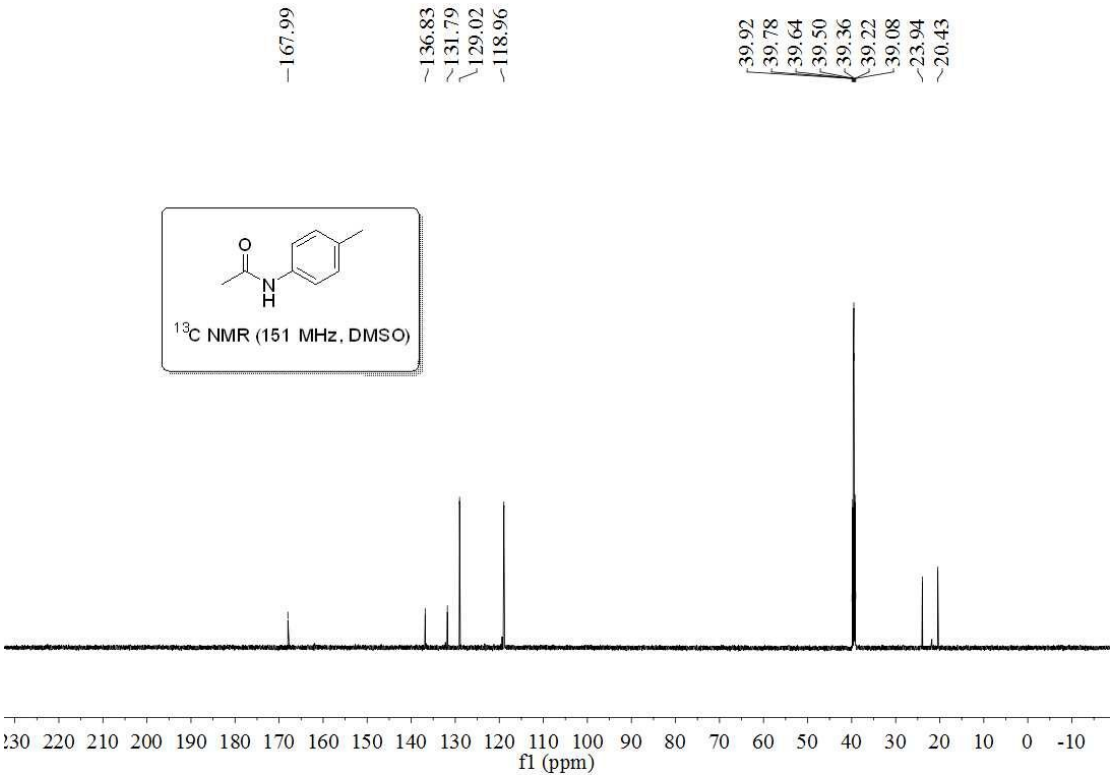
N-(p-tolyl)thiophene-2-carboxamide (3i)



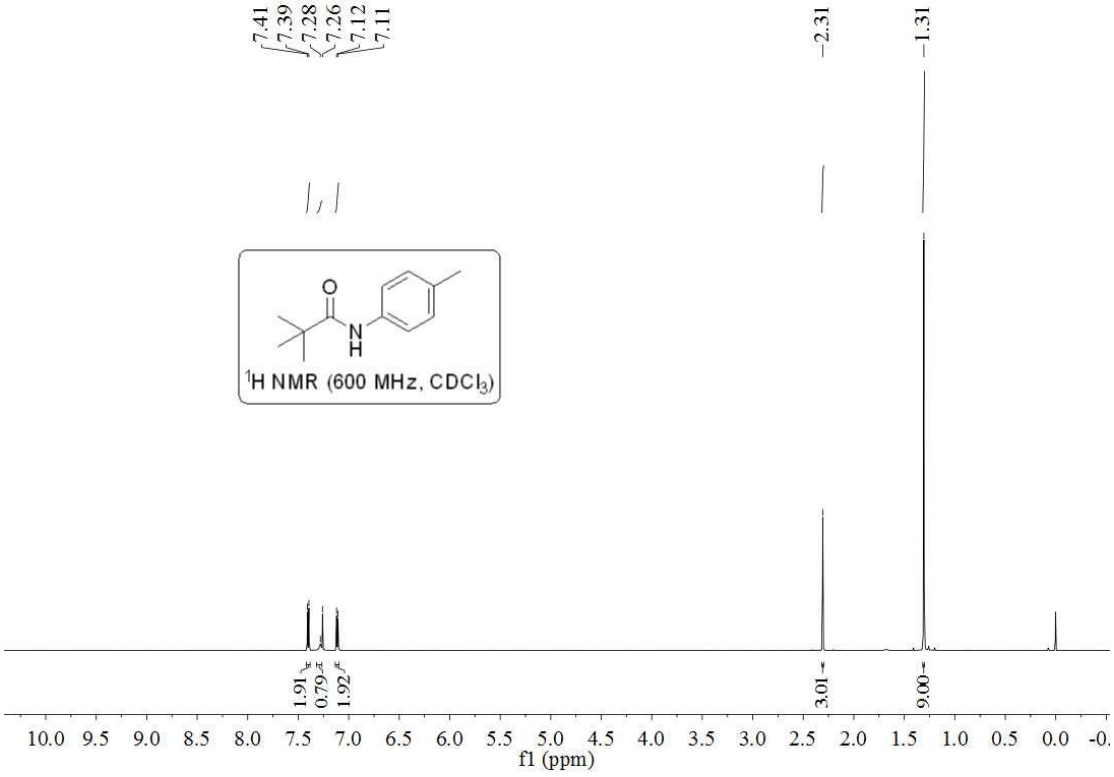


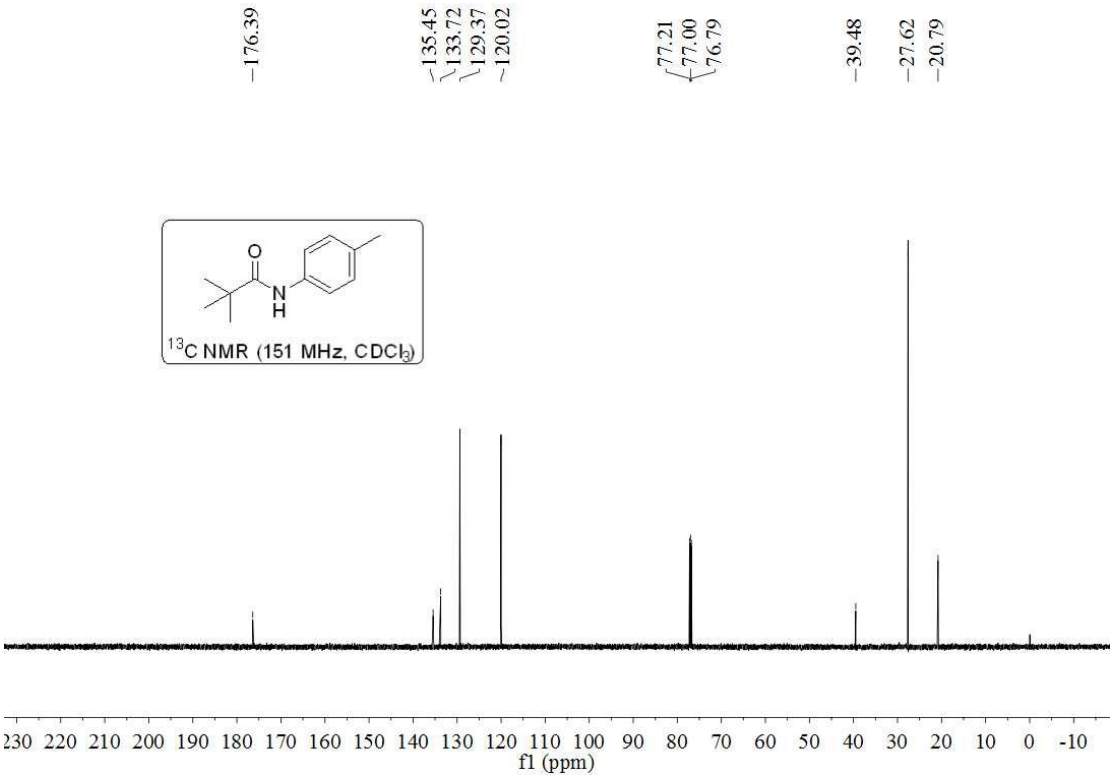
N-(p-tolyl)acetamide (3j)



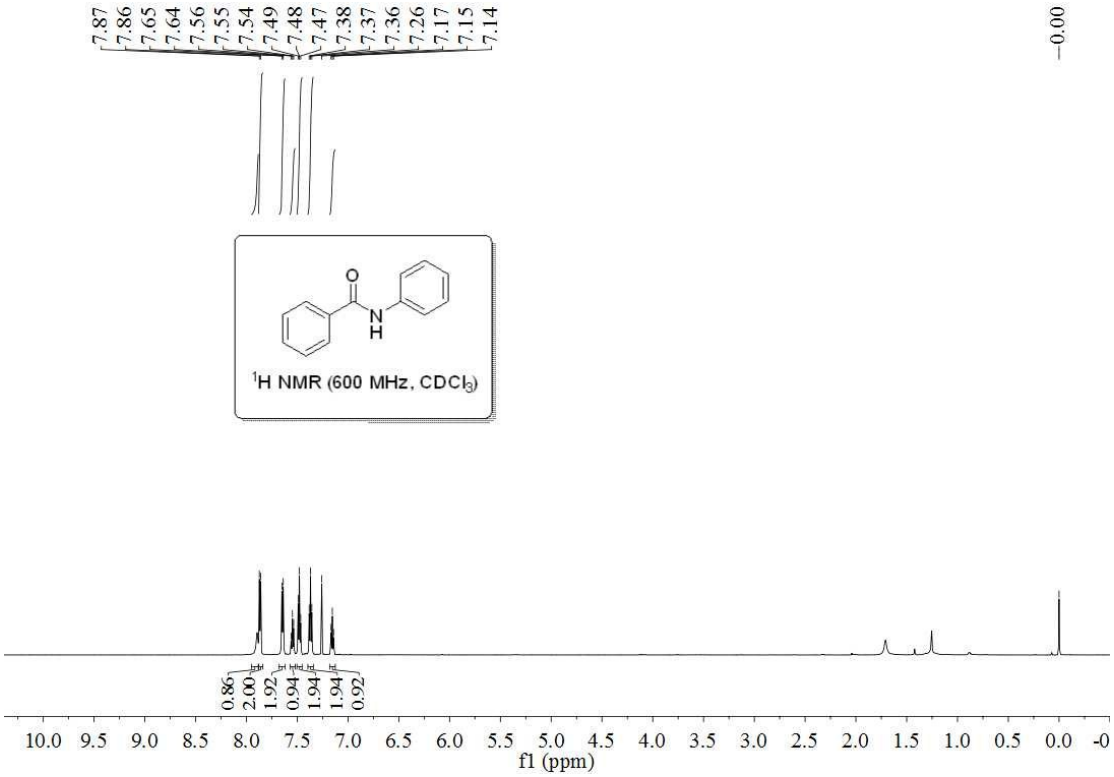


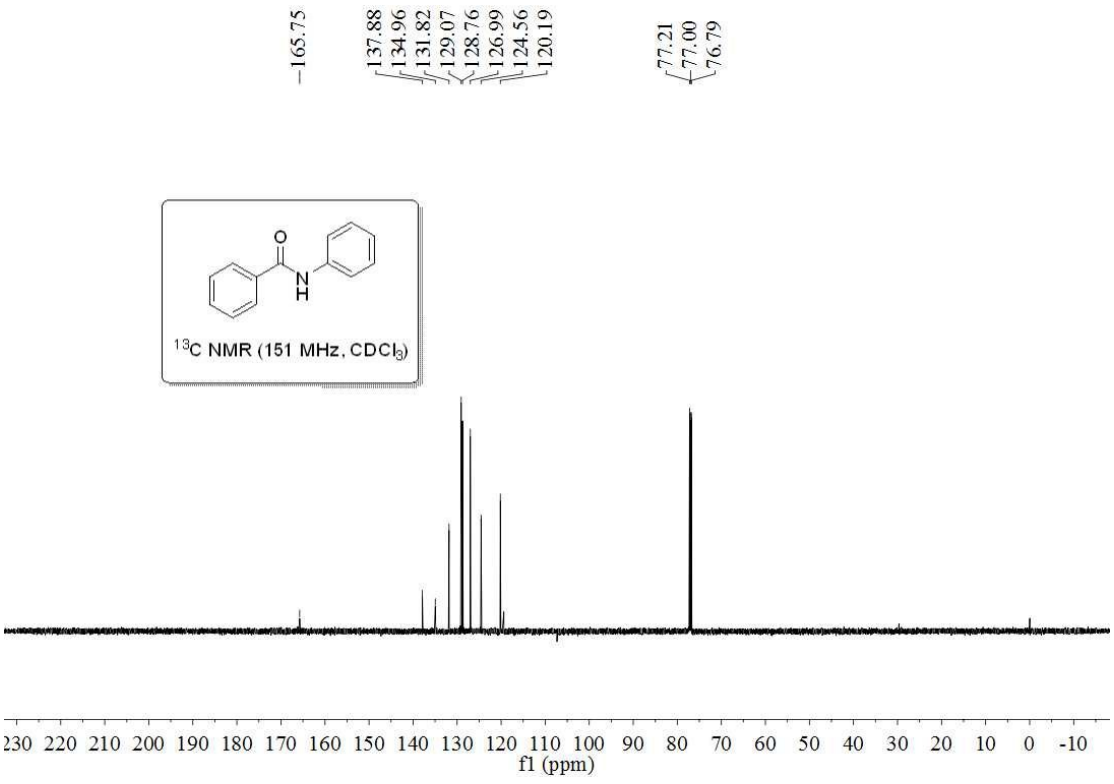
N-(p-tolyl)pivalamide (3k)



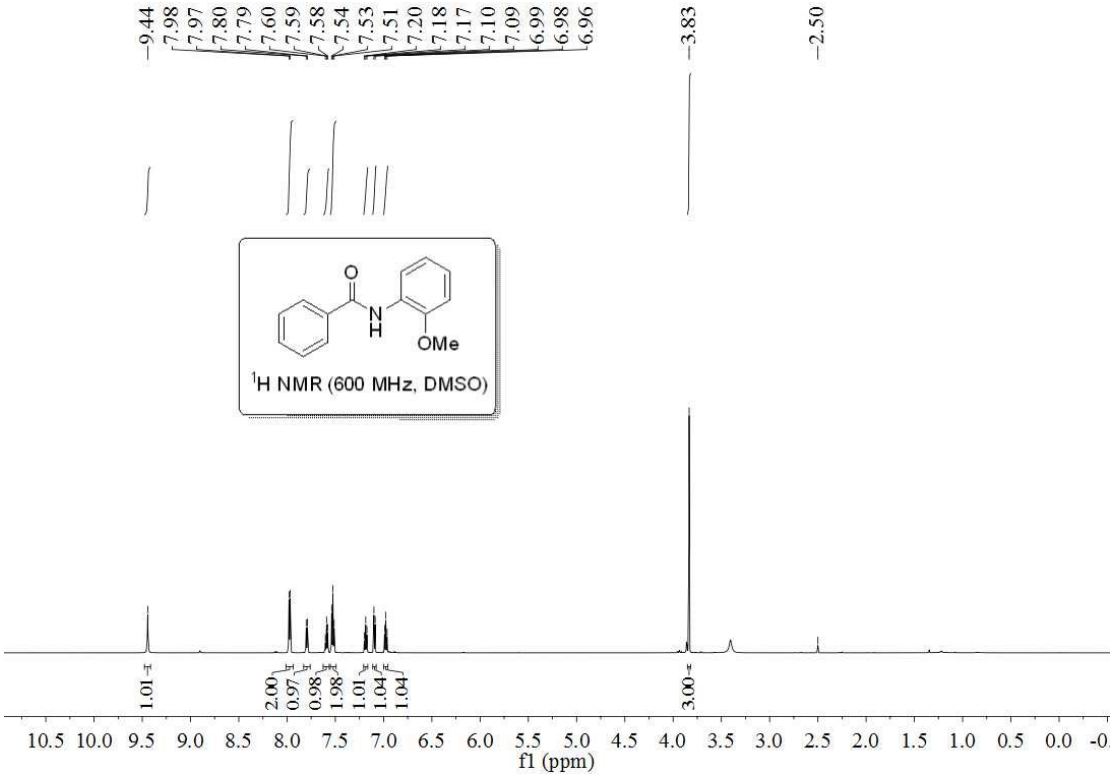


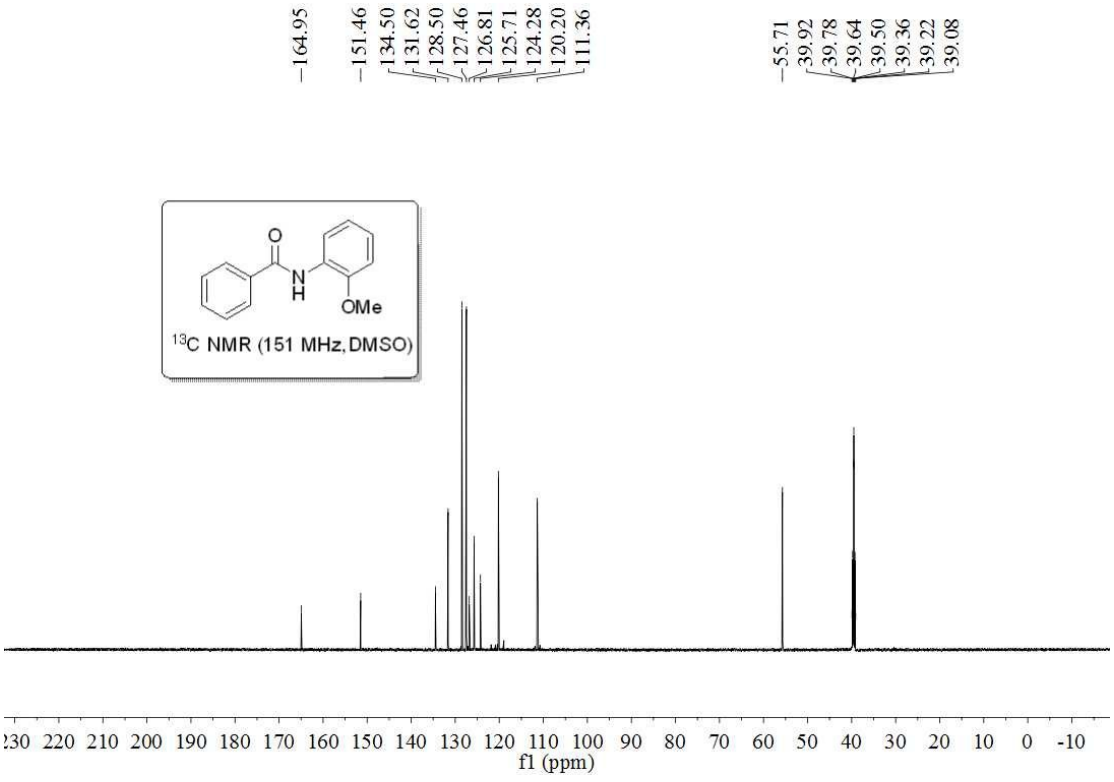
N-phenylbenzamide (3l)



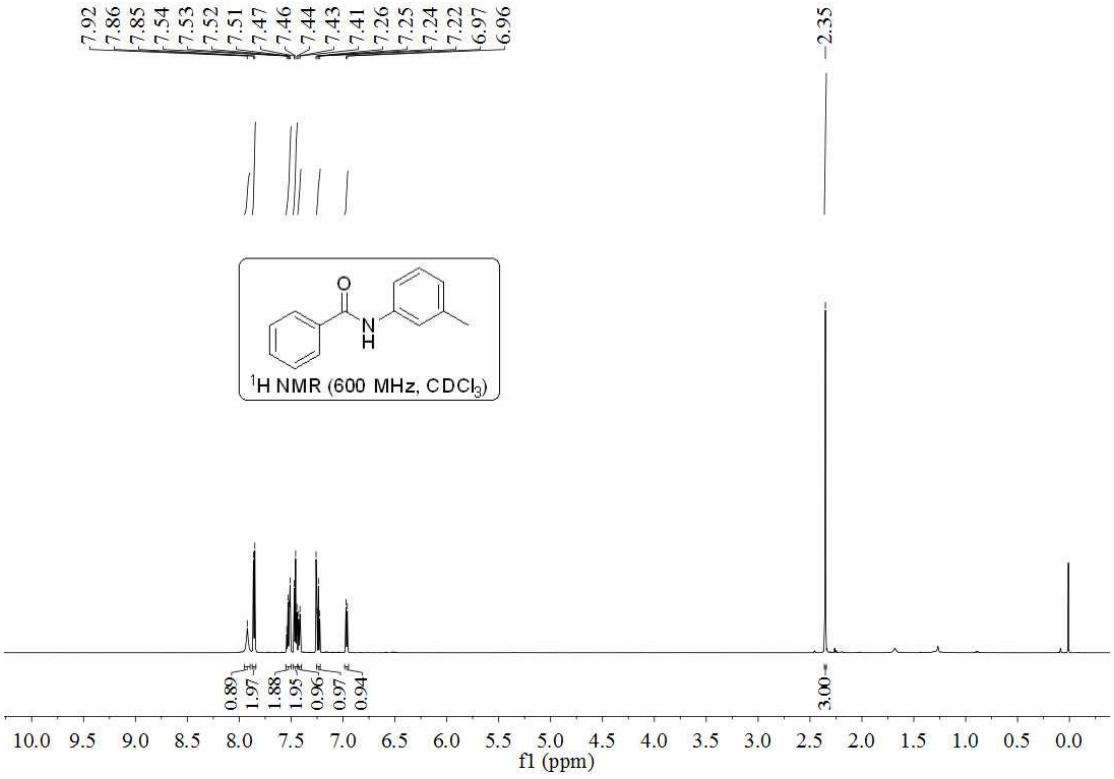


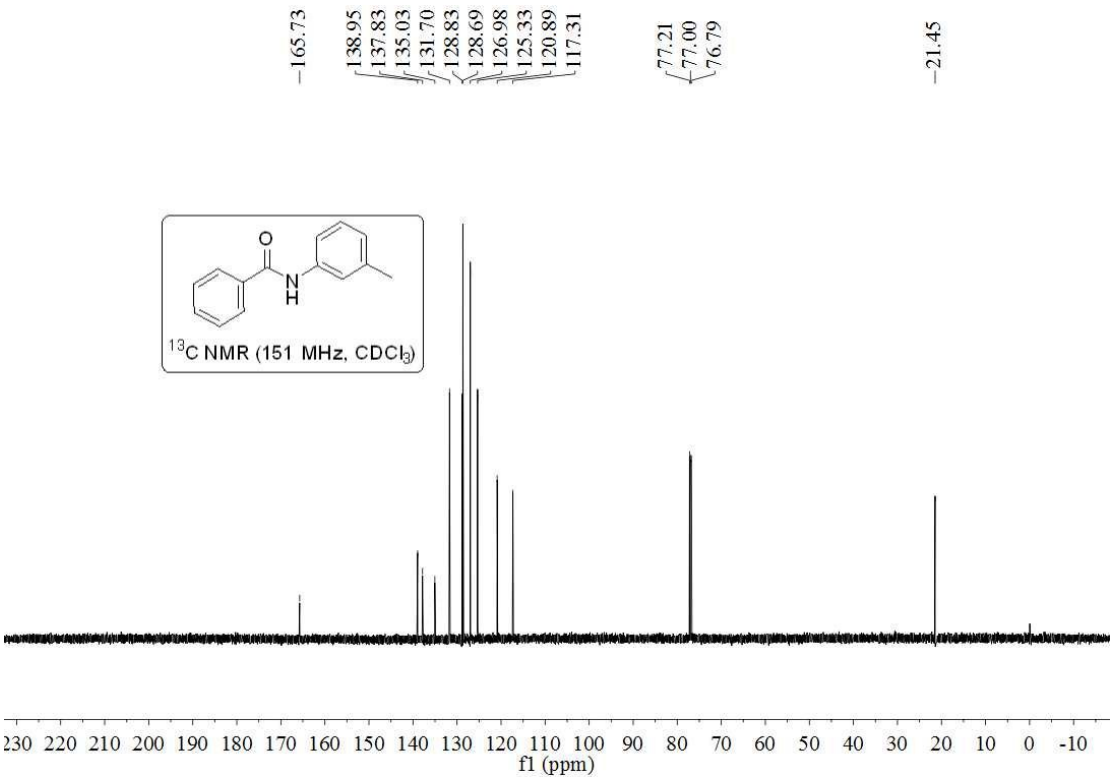
N-(2-methoxyphenyl)benzamide (3m)



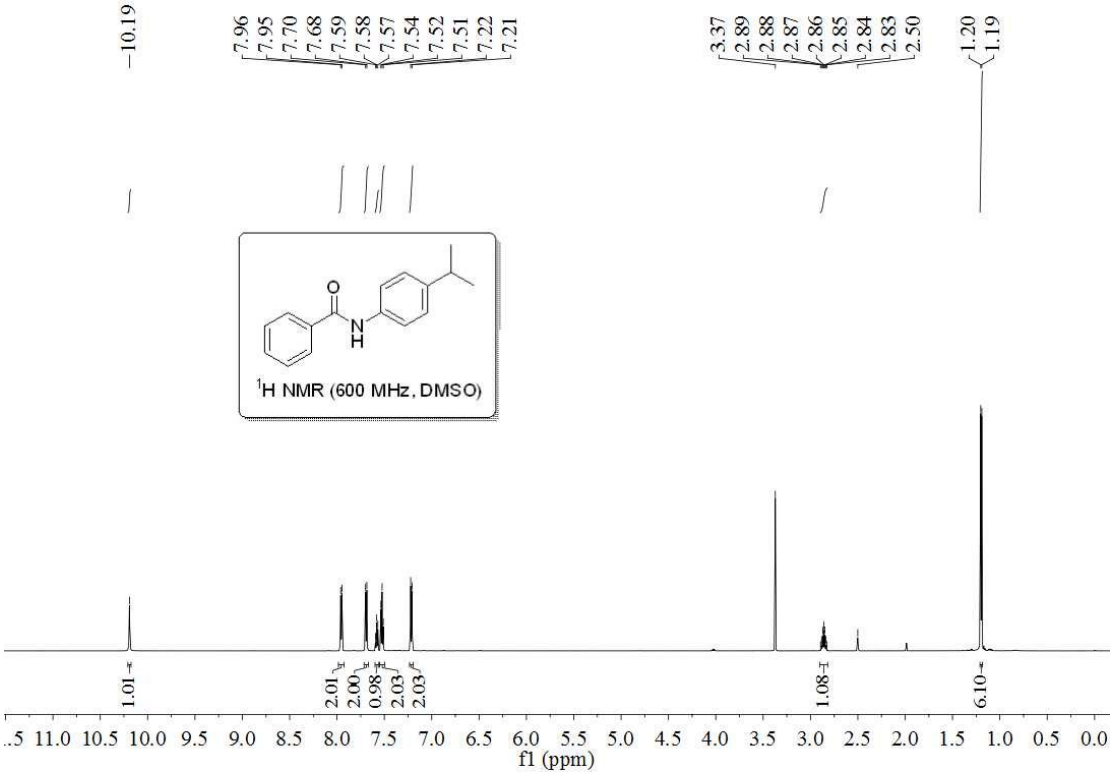


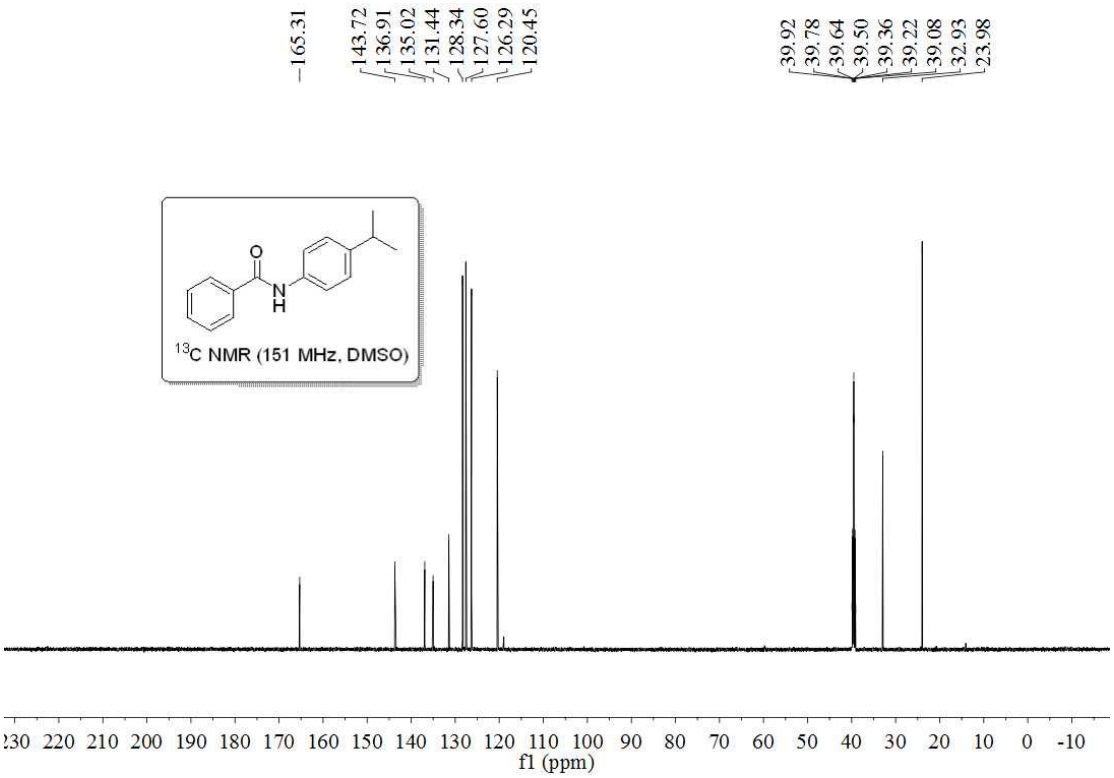
N-(m-tolyl)benzamide (3n)



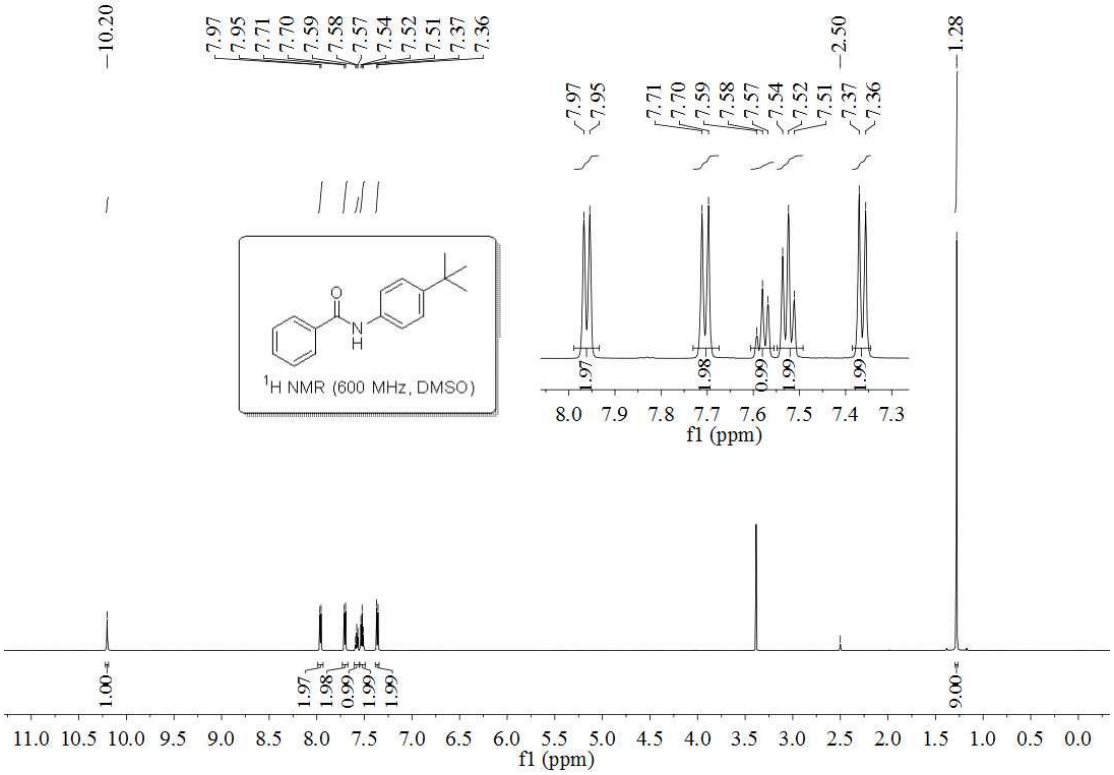


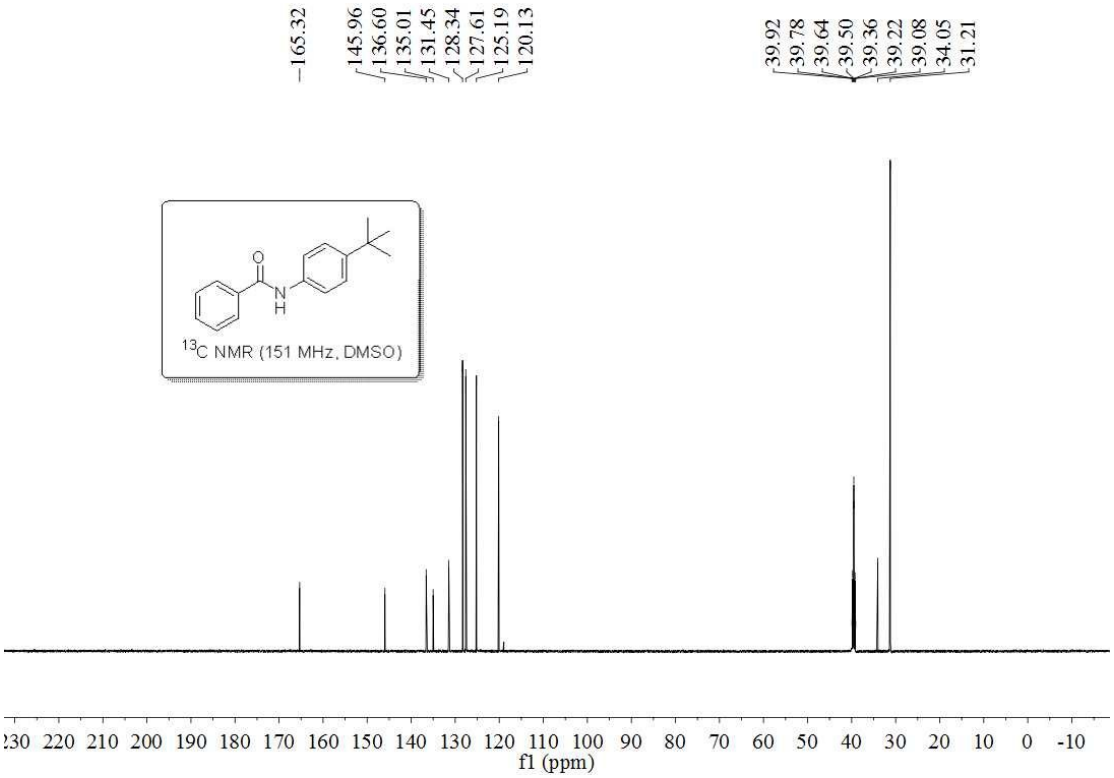
N-(4-isopropylphenyl)benzamide (3o)



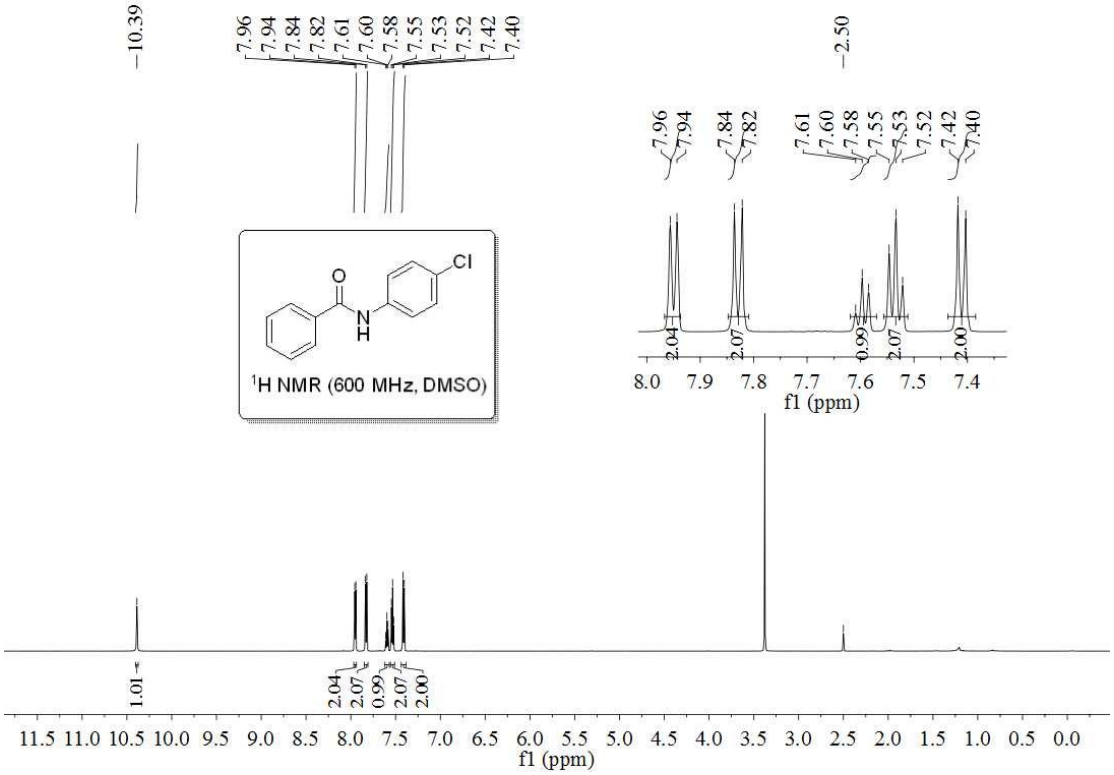


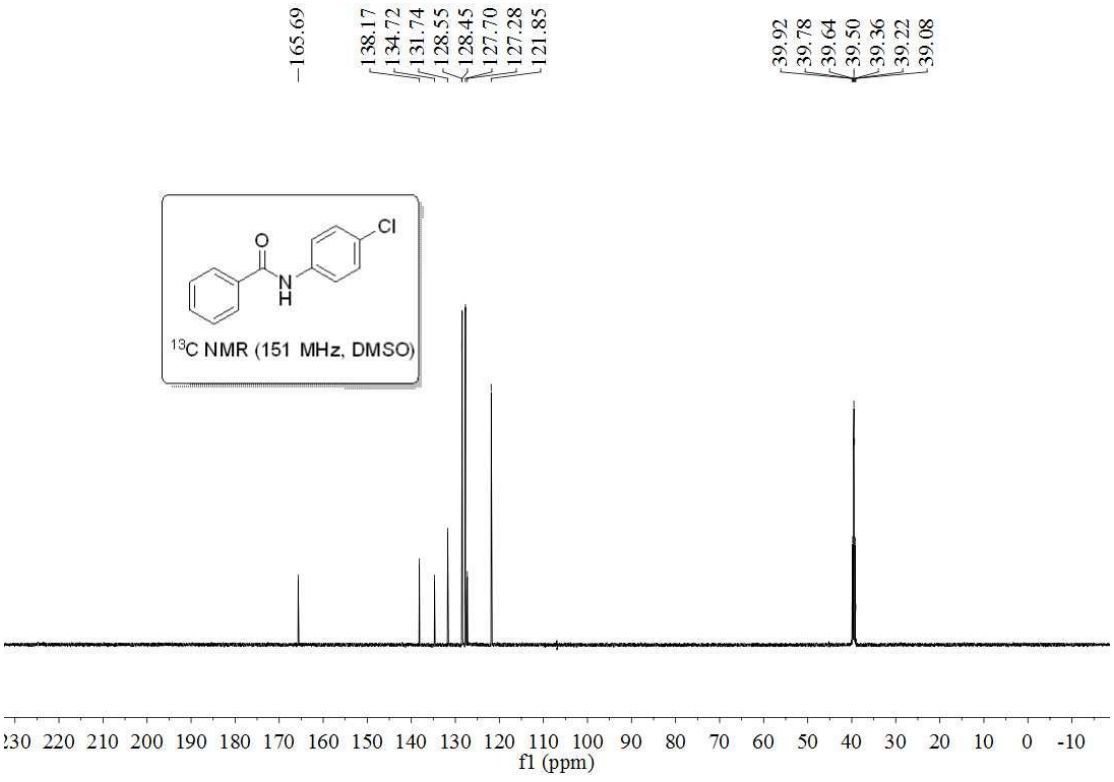
N-(4-(tert-butyl)phenyl)benzamide (3p)



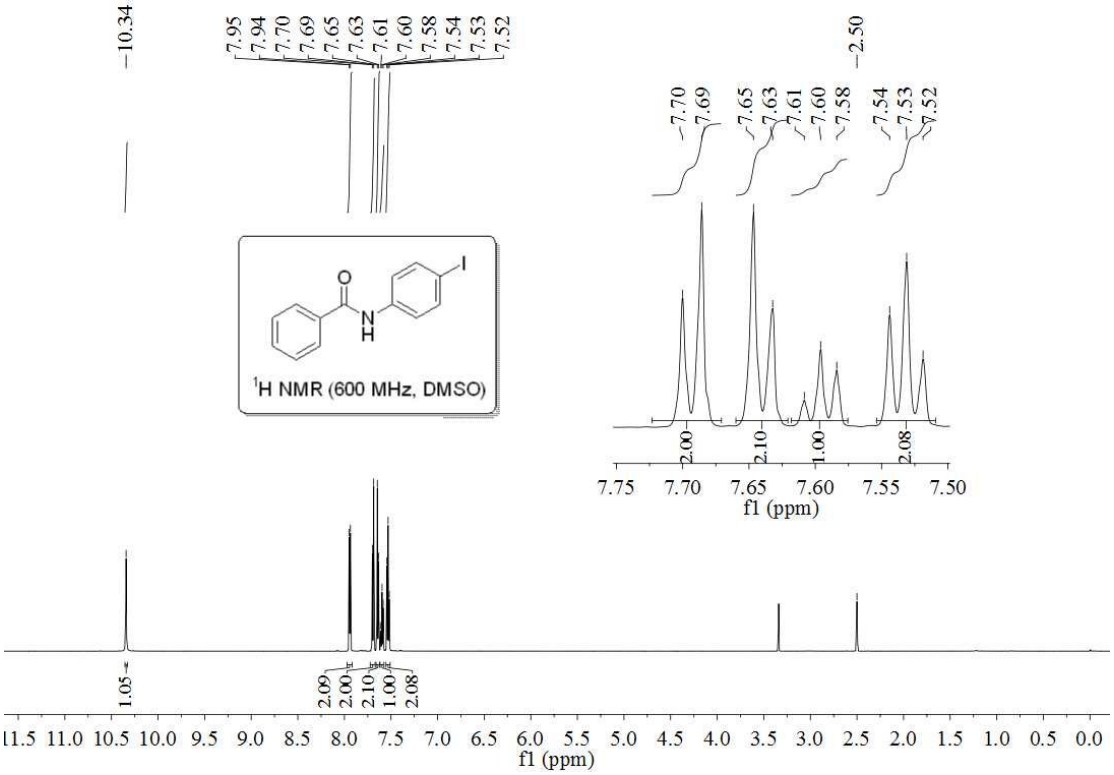


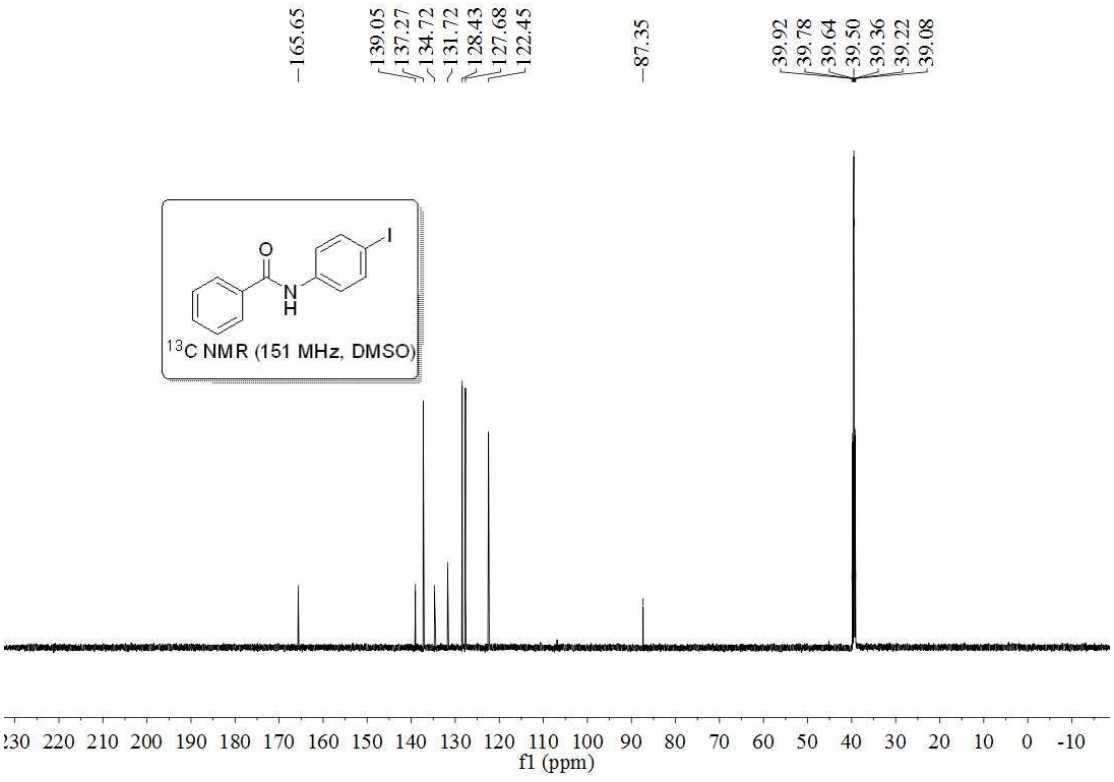
N-(4-chlorophenyl)benzamide (3q)



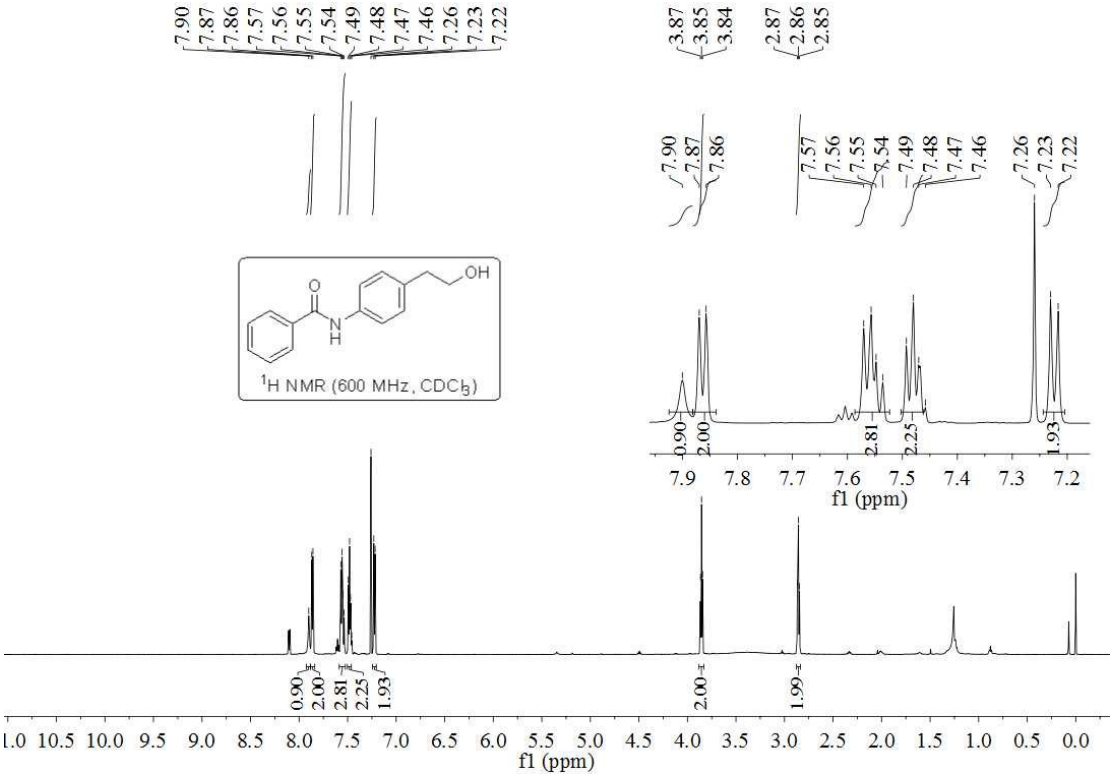


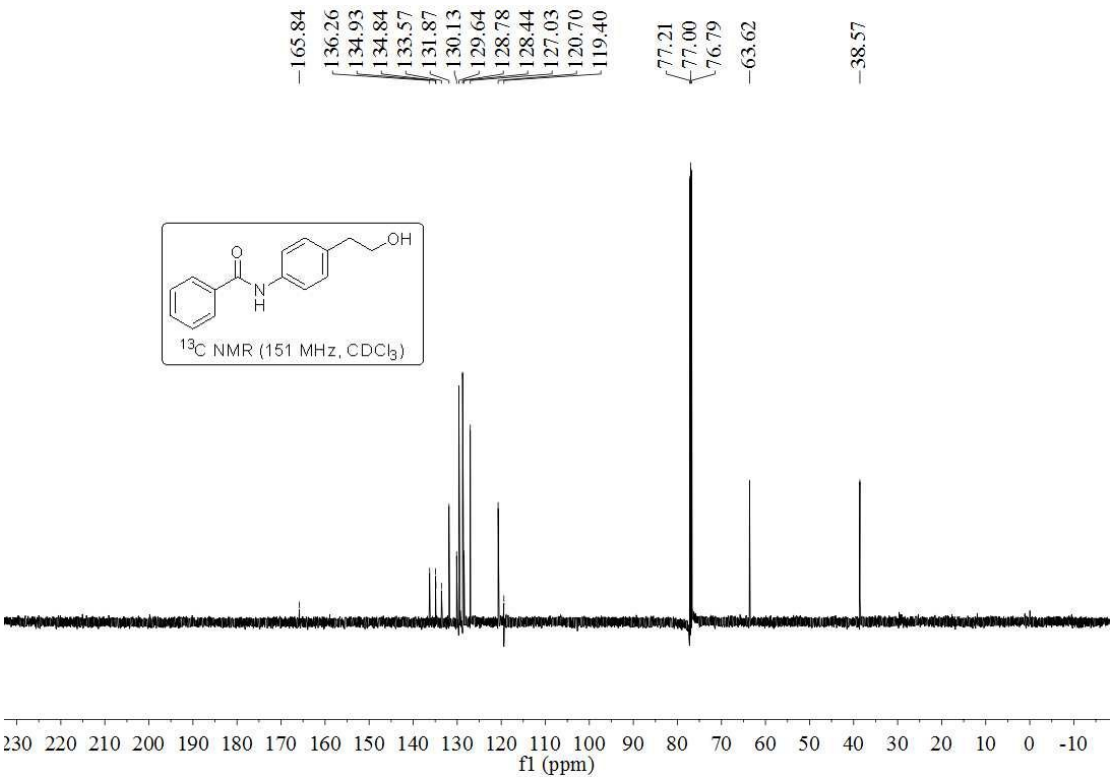
N-(4-iodophenyl)benzamide (3r)



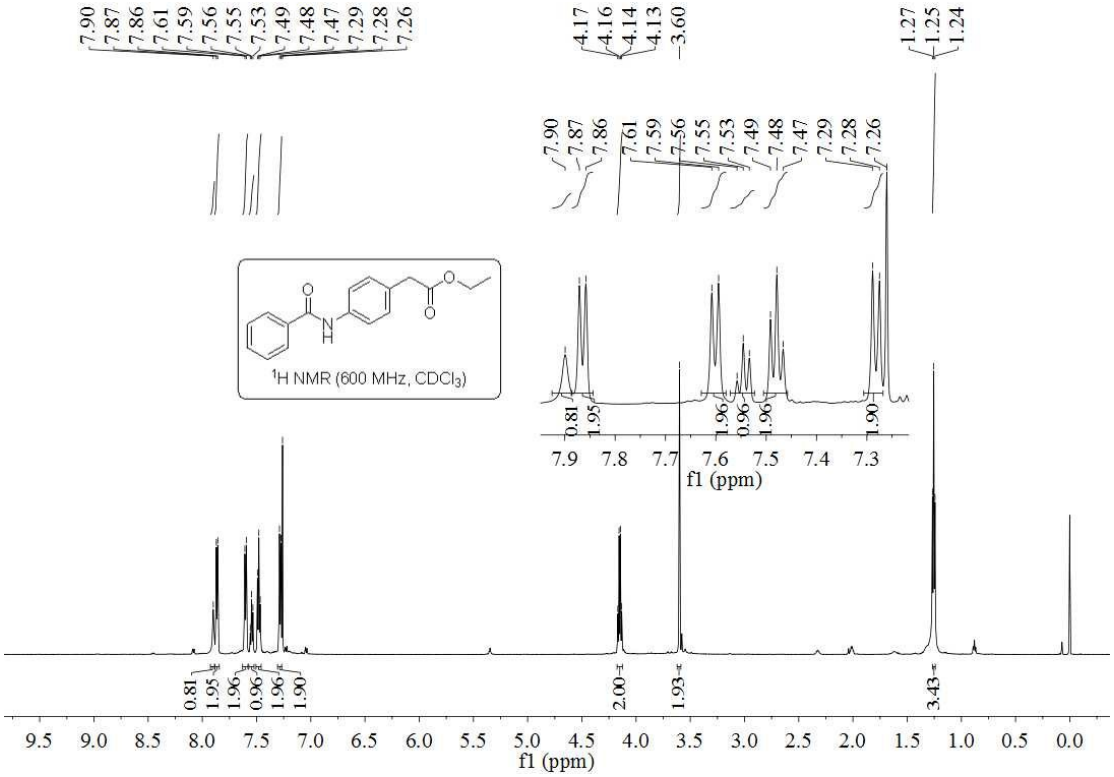


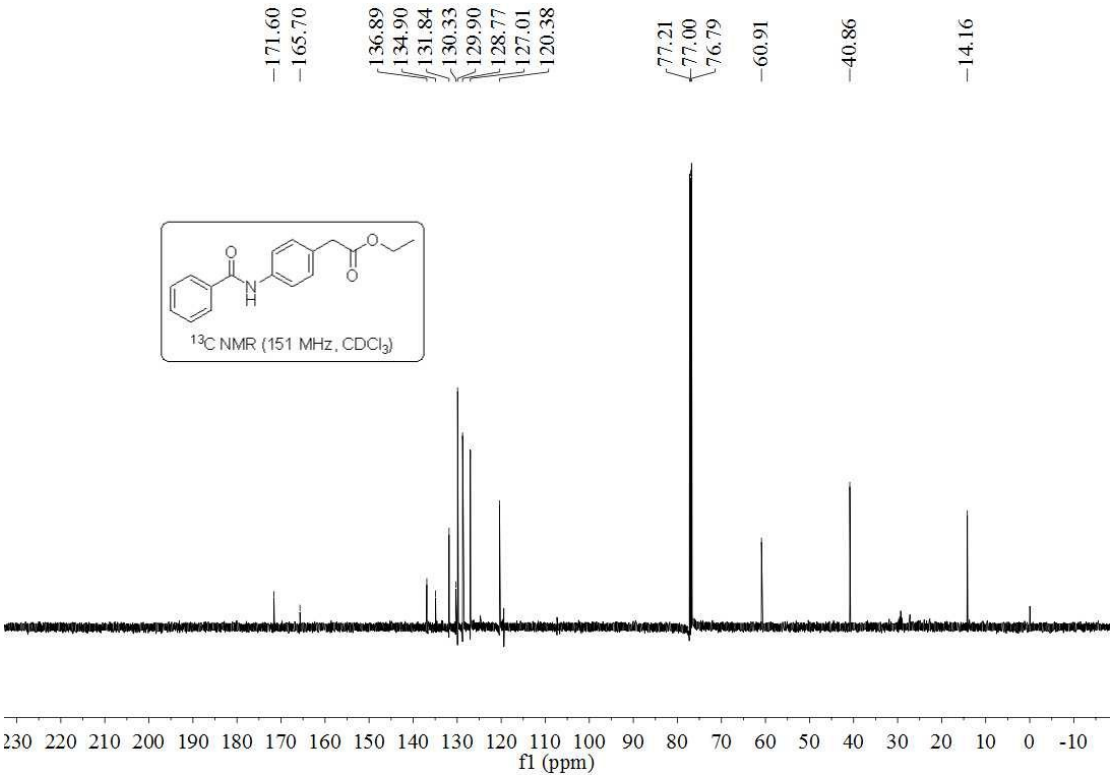
N-(4-(2-hydroxyethyl)phenyl)benzamide (3s)



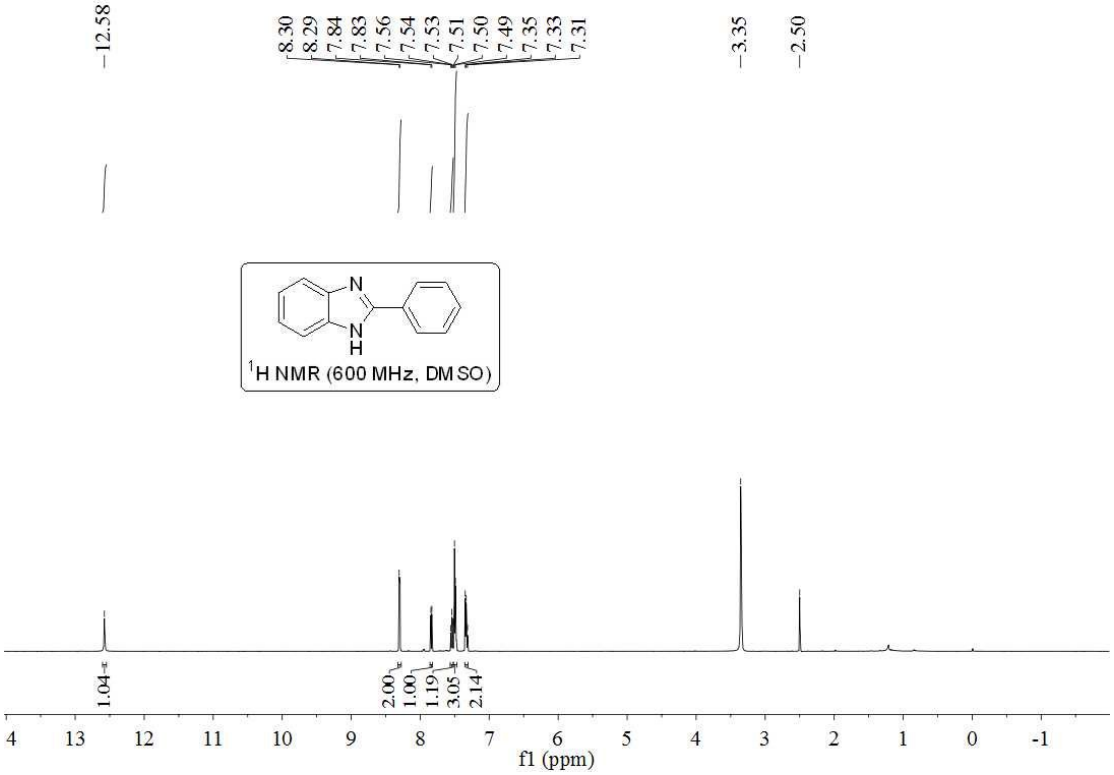


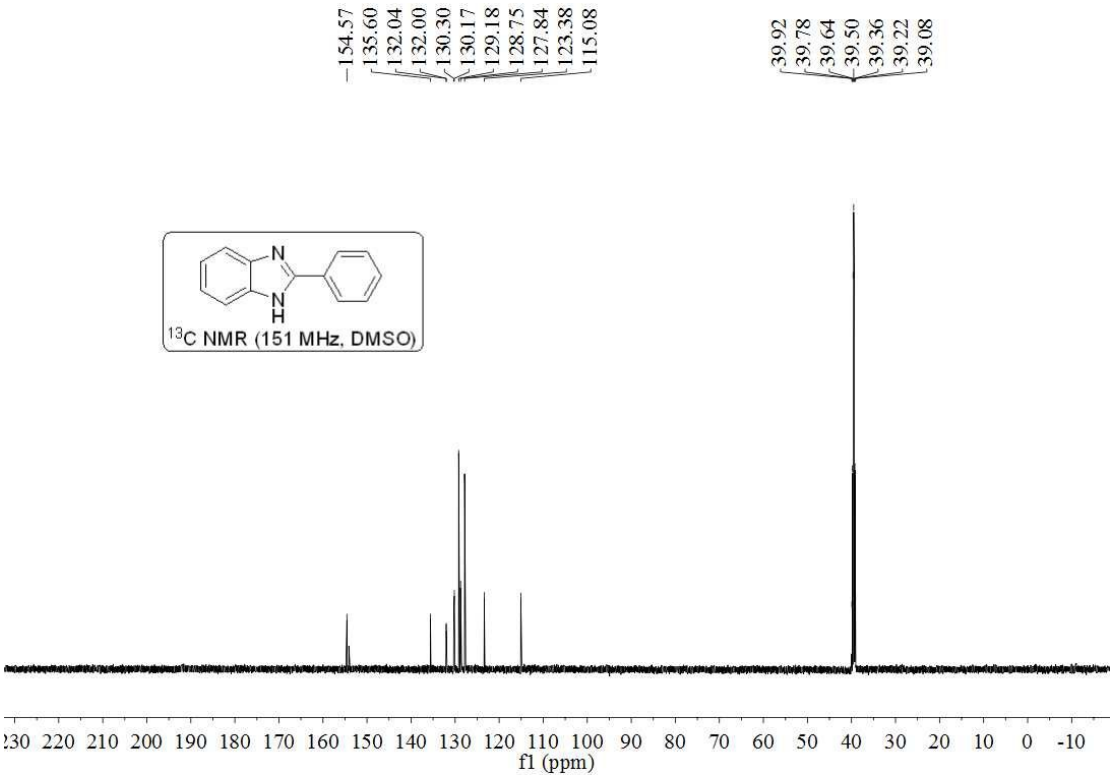
ethyl 2-(4-benzamidophenyl)acetate (3t)



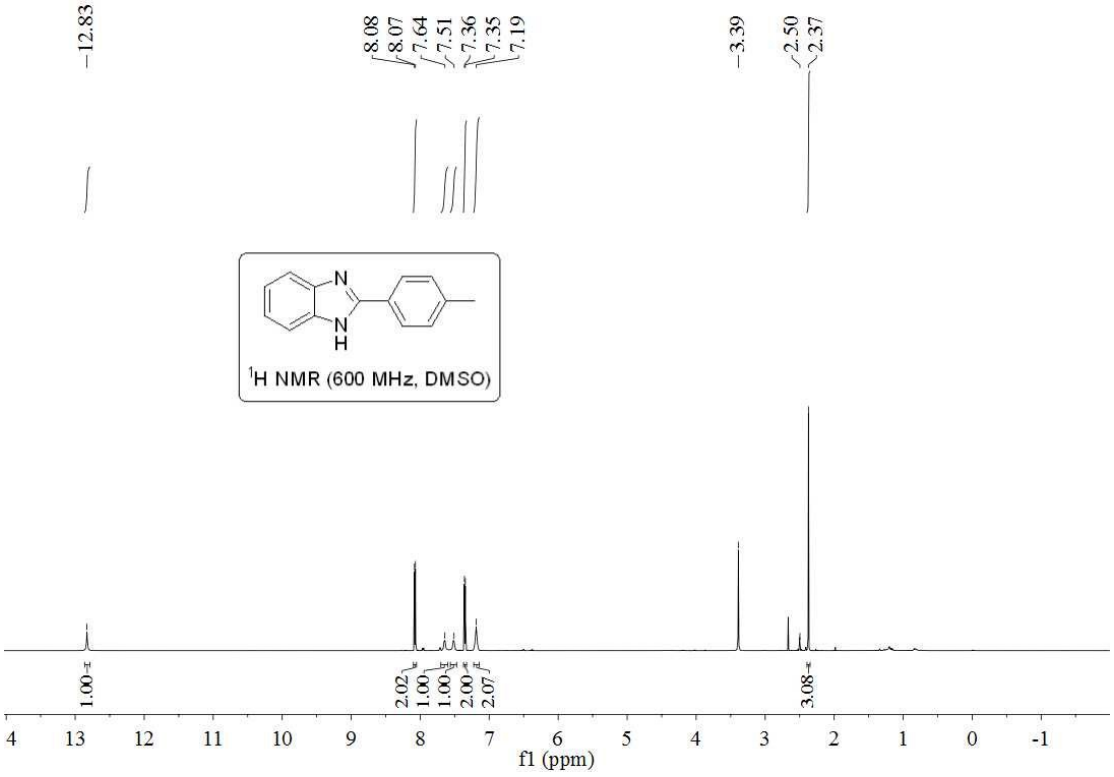


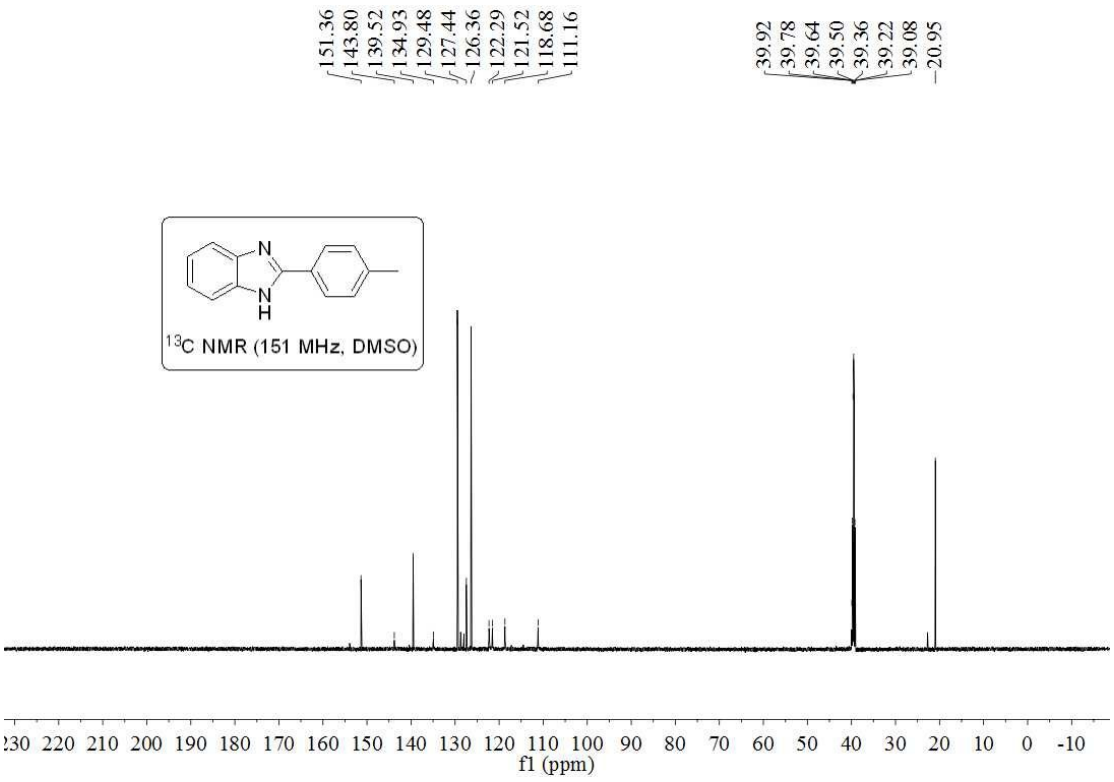
2-phenyl-1H-benzo[d]imidazole (4a)



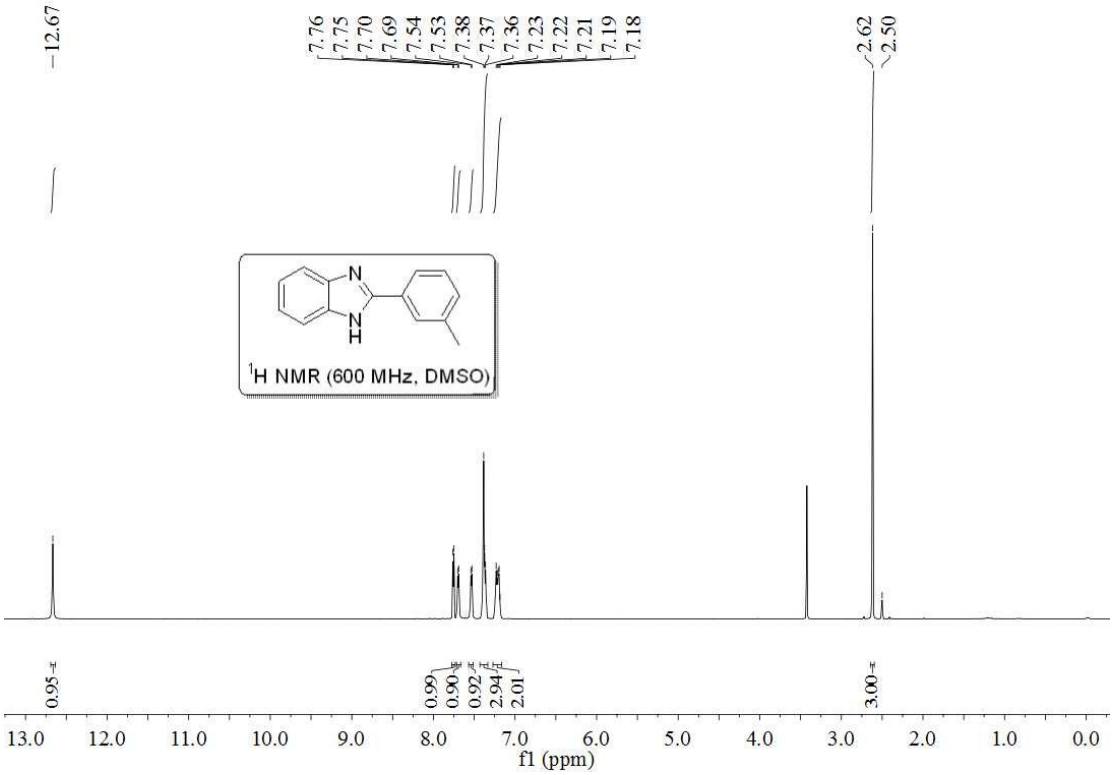


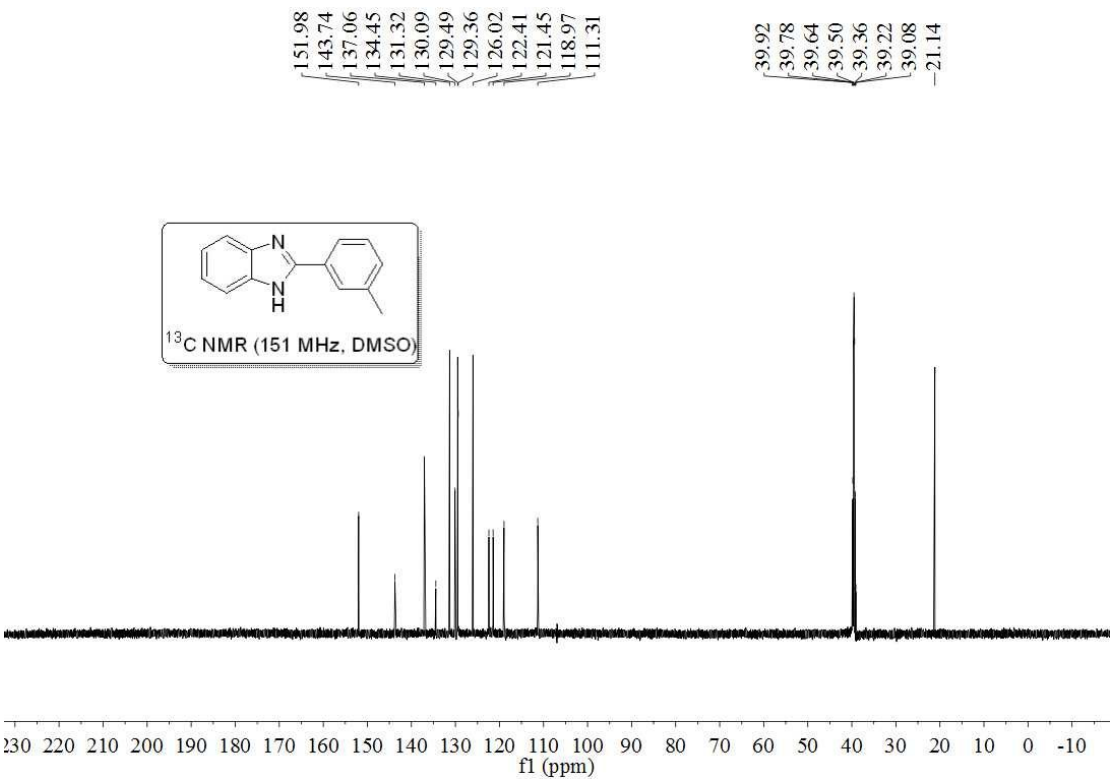
2-(p-tolyl)-1H-benzo[d]imidazole (4b)



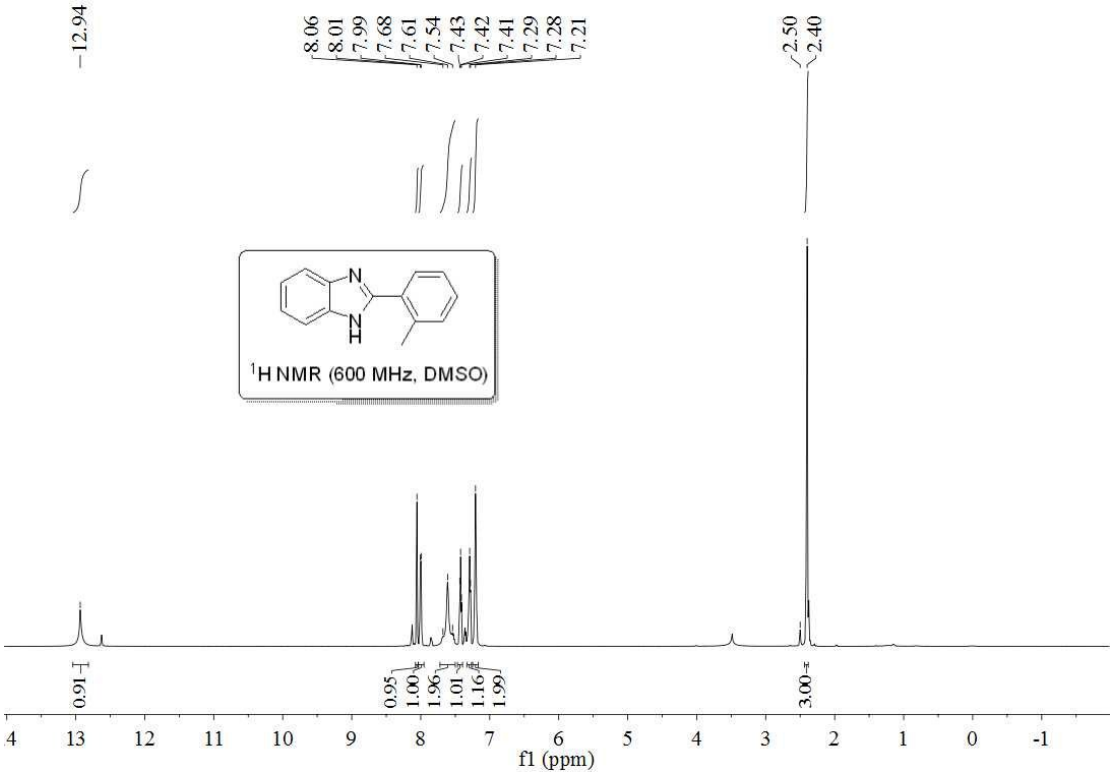


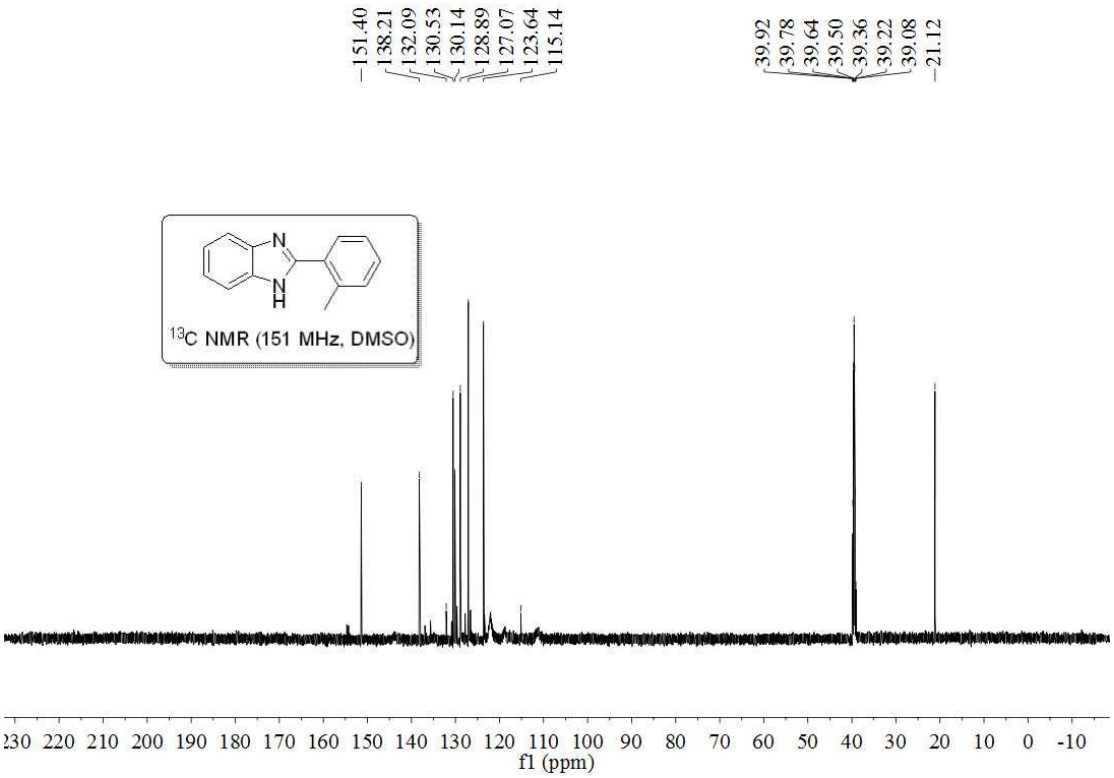
2-(m-tolyl)-1H-benzo[d]imidazole (4c)



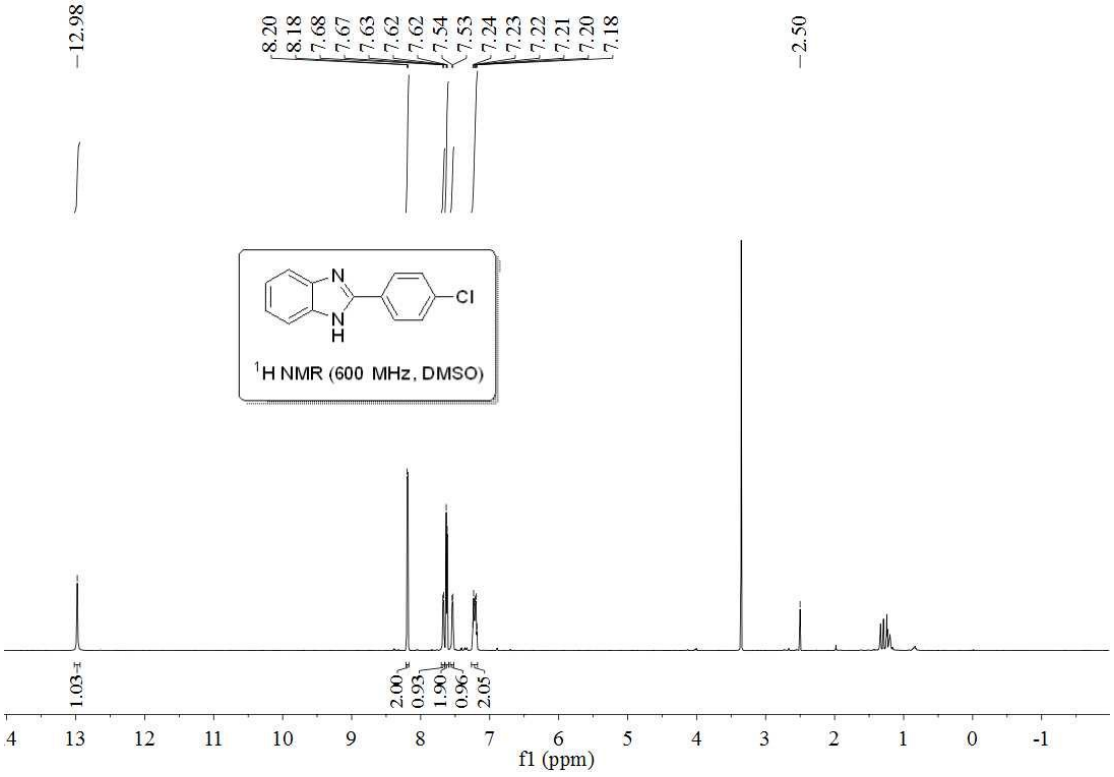


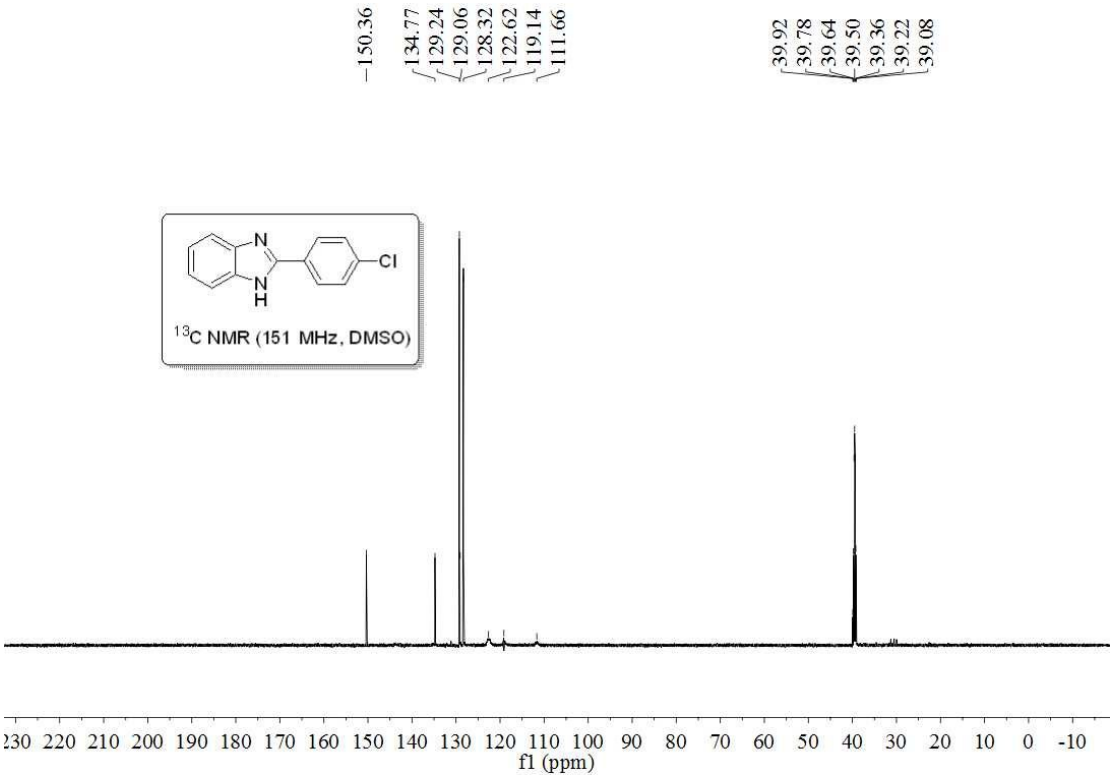
2-(o-tolyl)-1H-benzo[d]imidazole (4d)



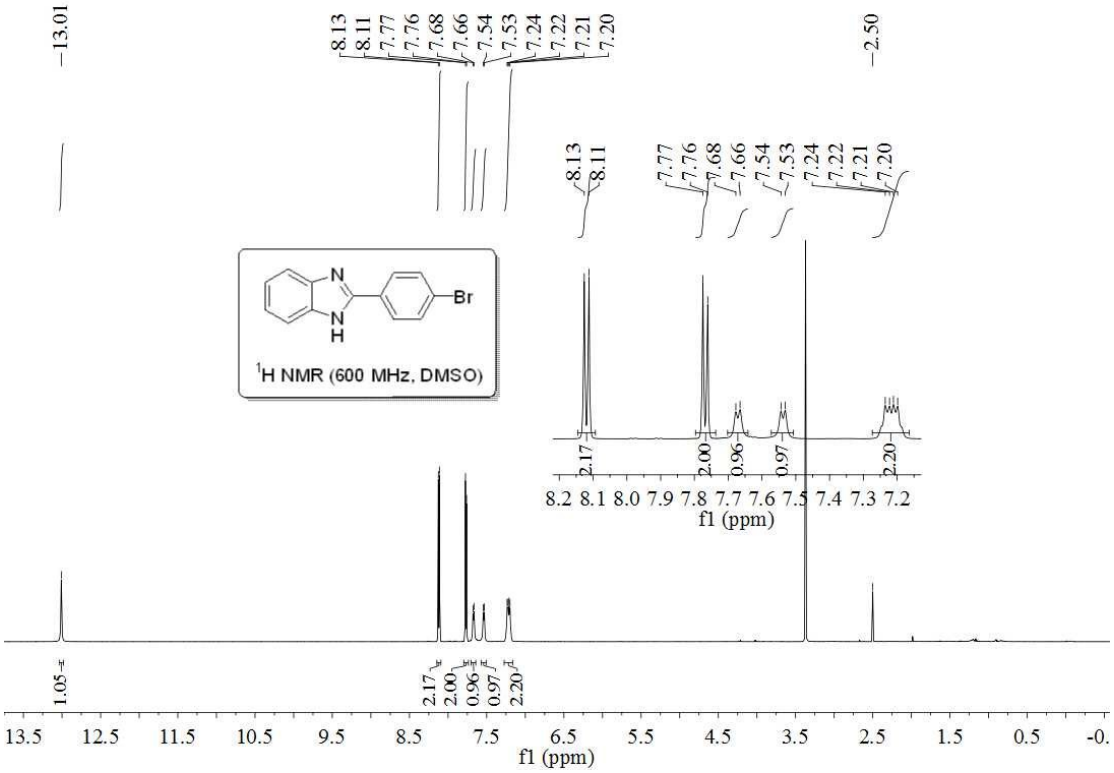


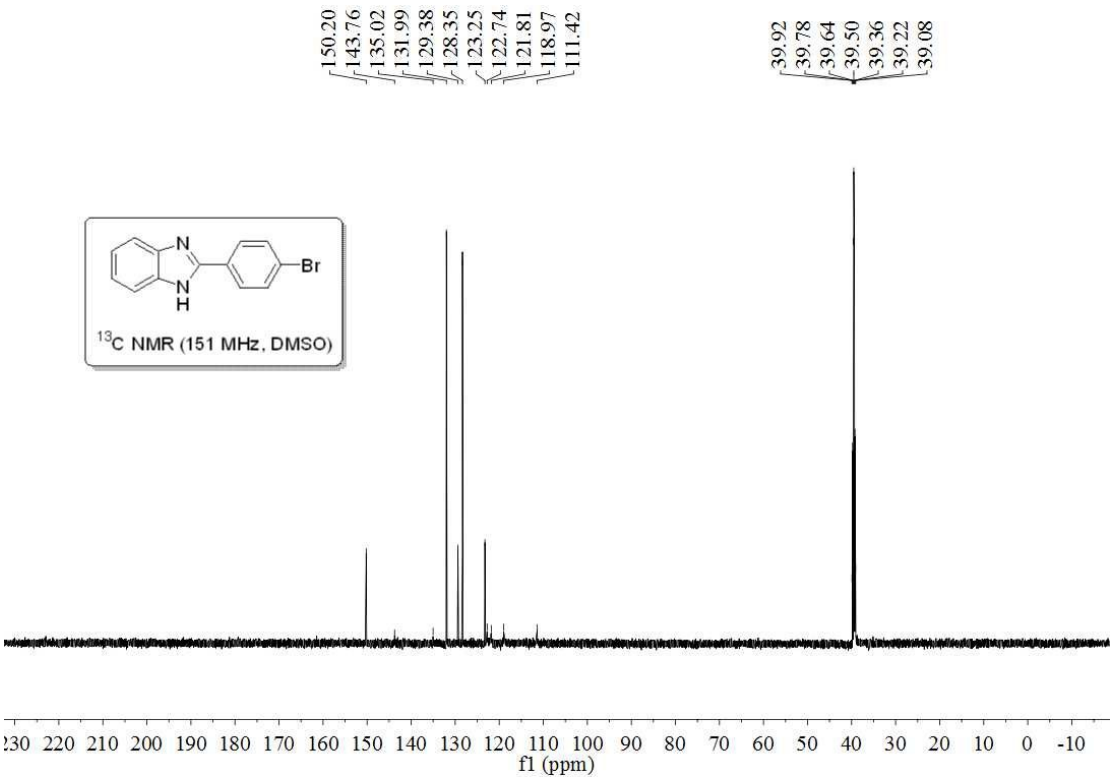
2-(4-chlorophenyl)-1H-benzo[d]imidazole (4e)



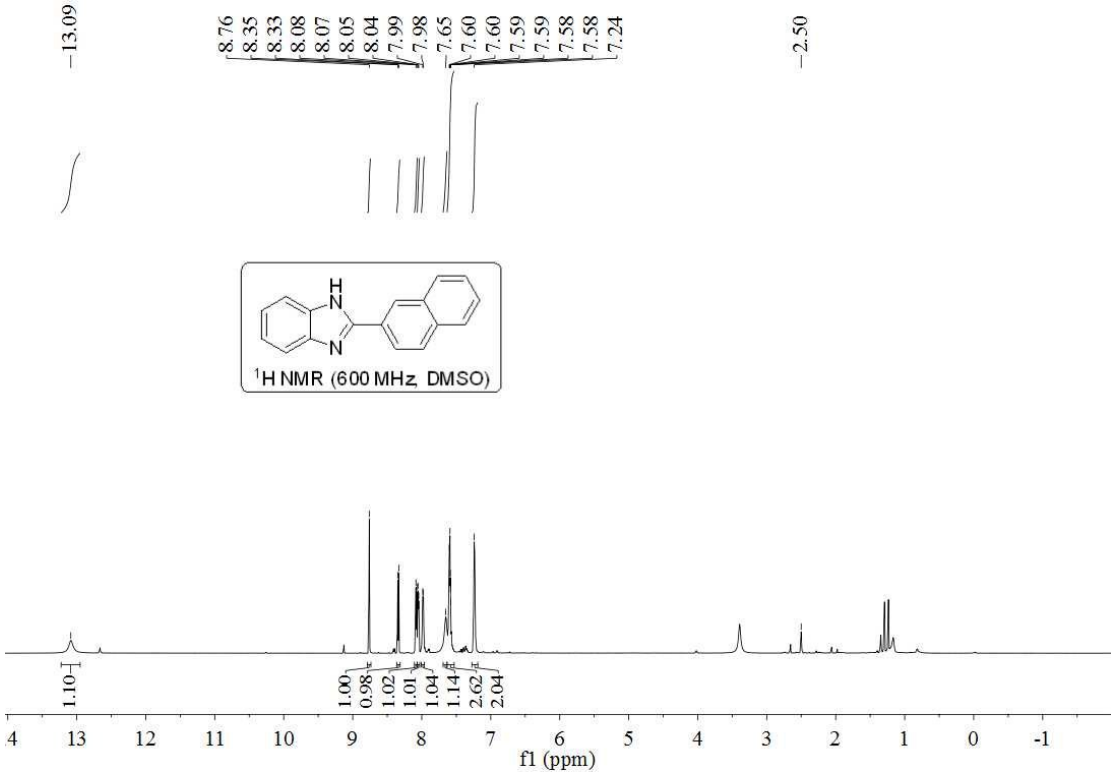


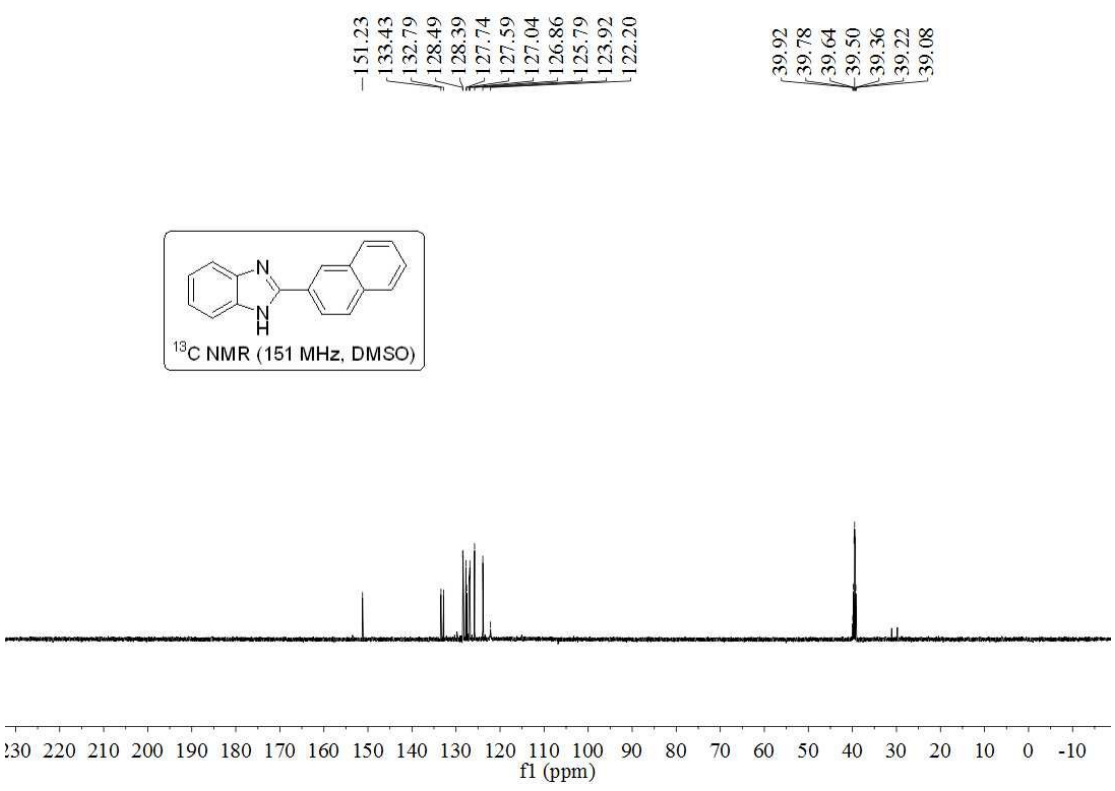
2-(4-bromophenyl)-1H-benzo[d]imidazole (4f)



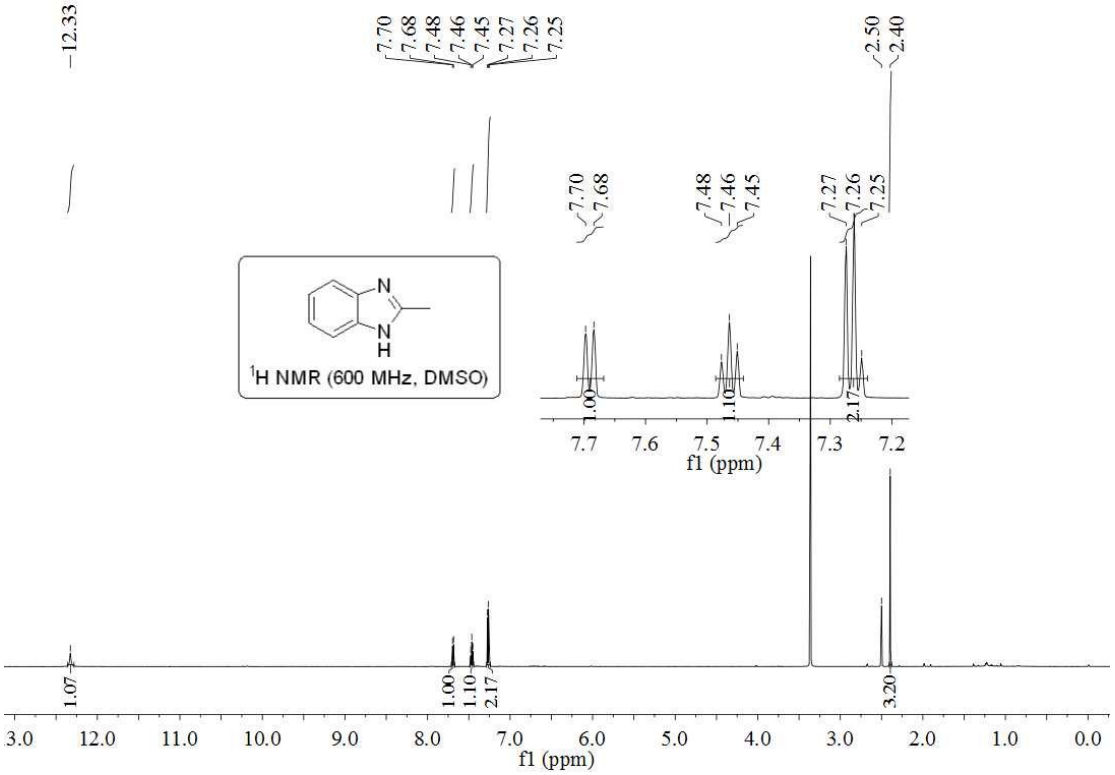


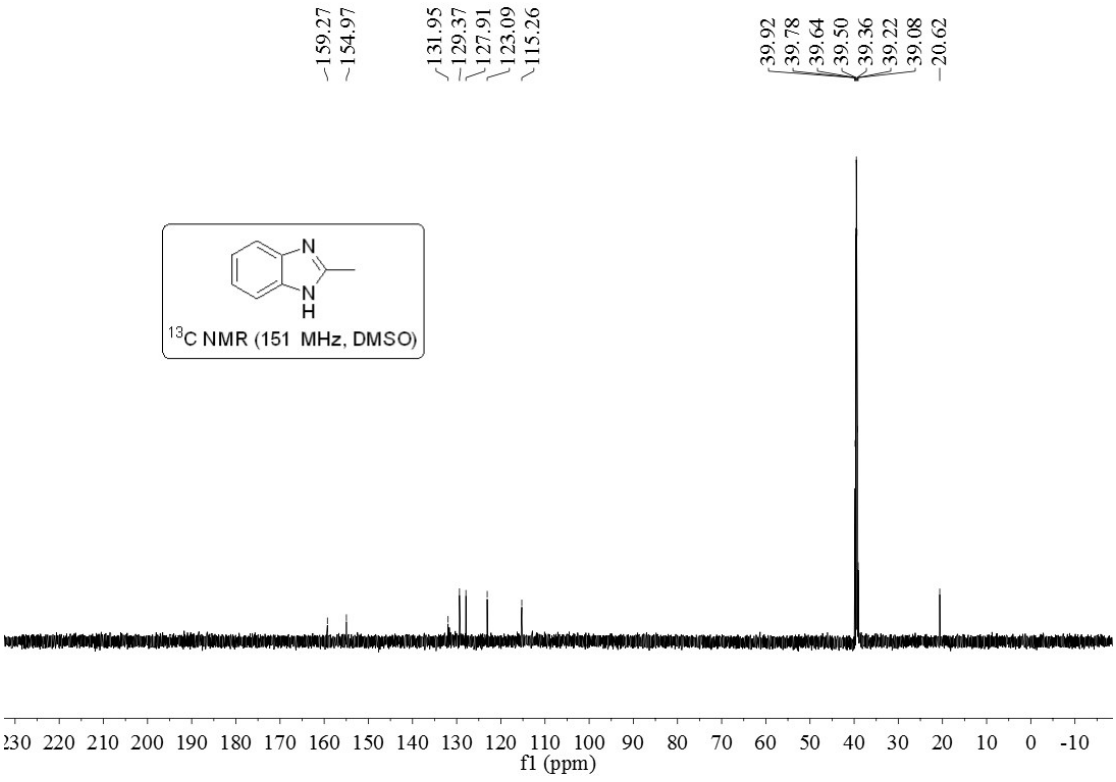
2-(naphthalen-2-yl)-1H-benzo[d]imidazole (4g)





2-methyl-1H-benzo[d]imidazole (4h)





2-(tert-butyl)-1H-benzo[d]imidazole (4i)