Supporting Information

Zinc-catalyzed transamidation and esterification of *N*-benzoyl cytosine *via* C–N bond cleavage

Sujeet Gaware,[a] Rana Chatterjee,[a] Anant R. Kapdi[b] and Rambabu Dandela*[a]

[a]*Department of Chemistry, Institute of Chemical Technology- Indian Oil Odisha Campus, IIT Kharagpur Extension Centre, Mouza Samantpuri, Bhubaneswar, Odisha-751013, India*

[b]*Department of Chemistry, Institute of Chemical Technology, Nathalal Parekh Road, Matunga, Mumbai-400019, India*

E-mail: r.dandela@iocb.ictmumbai.edu.in

Table of contents

1. Experimental Section

1.1. General Information

All starting materials and commercial reagent were purchased from Alfa Aesar, Sigma Aldrich, Avra, Spectrochem, TCI. Thin Layer Chromatography plates were visualized by exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed by using iodine chamber. Thin-layer chromatography was performed using pre-coated plates. Column chromatography was performed in 120 to 200 mesh size silica gel. The reactions were carried out in round bottom flask and sealed tube. NMR spectra were recorded by Bruker Advance 400 spectrometer (^{1}H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts for ^{1}H NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Similarly, ^{13}C NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). The ^{1}H NMR and ^{13}C NMR of the known products were compared with literature reports.

1.2. General procedure for the synthesis of *N*-benzoyl cytosine (1):

In a clean dry three-neck round bottom flask purge nitrogen for 2 min and add benzoic Acid (249 mg, 1.02 equiv., 2.02 mmol) and 10 ml of DMF. Add 4-Dimethylaminopyridine (50 mg, 20 mo%) *N,N*-Diisopropylethylamine (1043 ul, 6 mmol, 3 equiv.) and 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxide hexafluorophosphate (HATU) (767 mg, 1.01equiv., 2.02 mmol) in the mixture. During addition, nitrogen purging was monitored and maintained carefully. After 15 min of stirring at room temperature, cytosine (222mg, 2 mmol) was added gradually to the reaction mass and continued the reactions for 12 hr at rt. After the completion of the reaction, a milky white precipitate was observed. Then the reaction mixture was poured into 50 ml of ice water to quench the DMF. Finally, filter the mixture and wash out the crude product with chilled methanol and dry the product.

1.3. Synthesis of amides from *N*-benzoyl cytosine (3a):

In a clean dry round bottom flask *N*-benzoyl cytosine (108 mg, 0.5 mmol) with 3 mL DMF. Was taken and then $Zn(OTf)_2$ (18 mg, 10 Mol %) was added to the mixture. In continued stirring for 2 min, then add *n*-butyl amine (292 mg, 4 mmol) was mixed into the reaction mixture. After that, di-*tert*-butyl peroxide (365 ul, 4 eq, 2 mmol) was added and the reaction mixture was stirred at refluxed conditions for 12 hr at 100 ^{o}C. The reaction was monitored by

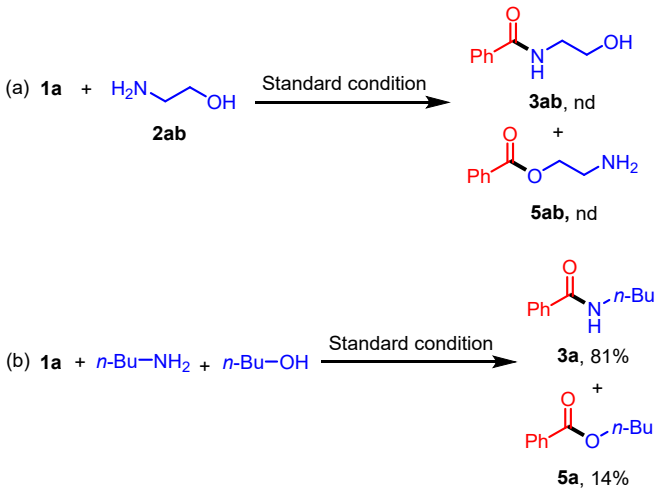
TLC, after completion of the reaction, the mixture was poured into the ice water to quench DMF and then extracted product crude was washed with ethyl acetate/water and dried over anhydrous $NaSO_4$ followed by concentrating under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel (*n*-Hexane/EtOAc) to afford the desired amide **3a**.

1.3. Synthesis of ester from *N*-benzoyl cytosine (5a):

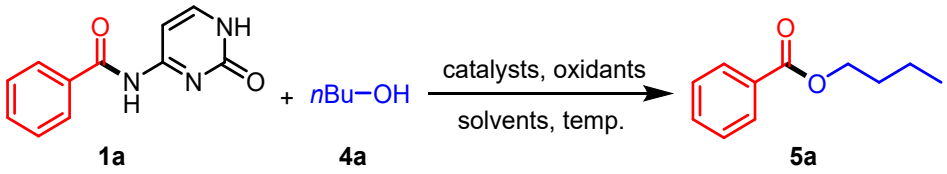
In a clean dry round bottom flask *N*-benzoyl cytosine (108 mg, 0.5 mmol) with 3 mL DMF. Was taken and then $Zn(OTf)_2$ (18 mg, 10 Mol %) was added to the mixture. In continued stirring for 2 min, then add *n*-butanol (296 mg, 4 mmol) was mixed into the reaction mixture. After that, di-*tert*-butyl peroxide (365 ul, 4 eq, 2 mmol) was added and the reaction mixture was stirred at refluxed conditions for 12 hr at 100 °C. The reaction was monitored by TLC, after completion of the reaction, the mixture was poured into the ice water to quench DMF and then extracted product crude was washed with ethyl acetate/water and dried over anhydrous $NaSO_4$ followed by concentrating under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel (*n*-Hexane/EtOAc) to afford the desired amide **5a**.

1.5. Selectivity in transamidation and esterification

Furthermore, we were interested to check the selectivity of the present methods towards the noted nucleophiles. At first, we have carried out the reaction with ethanolamine having both amnio and hydroxy centres. Interestingly, the experiment did not show any fruitful conversion and provide the expected amide or ester. Later, the reaction was investigated with a primary amine and alcohol in 1:1 ratio. Notably, *n*-butyl amine worked faster in the competition to afford the corresponding amide in 81% yield while only 14% of ester was formed.



1.6 Optimization of the reaction conditions with alcohol.[a,b]



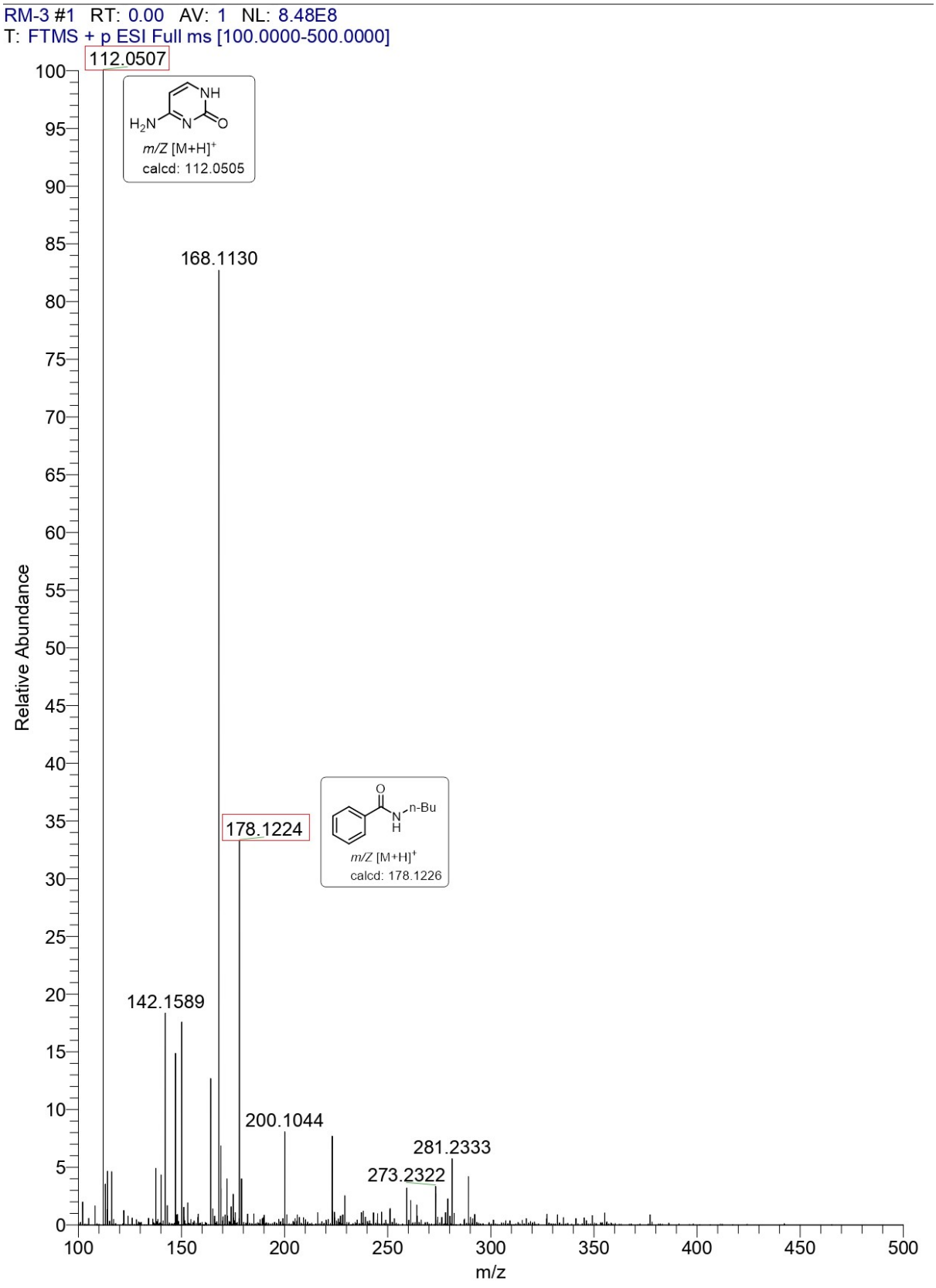
1a **4a** **5a**

Entry	Catalyst (mol%)	Oxidant (euqiv.)	Solvent (mL)	Yield (%)
1	Ag(OTf) (10)	DTBP (4)	DMF	22
2	$Zn(OTf)_2$ (10)	DTBP (4)	DMF	84
3	$Zn(OTf)_2$ (10)	TBHP (4)	DMF	41
4	$Zn(OTf)_2$ (10)	*m*CPBA (4)	DMF	32
5	$Zn(OTf)_2$ (10)	DTBP (4)	DMSO	29
6	$Zn(OTf)_2$ (10)	DTBP (4)	MeCN	18
7	$Zn(OTf)_2$ (10)	DTBP (4)	1,4-Dioxane	trace
8	$Zn(OTf)_2$ (20)	DTBP (4)	DMF	85
9	-	DTBP (4)	DMF	nr
10	$Zn(OTf)_2$ (10)	DTBP (2)	DMF	46

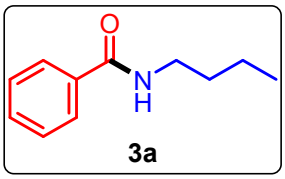
[a]Reaction conditions: Amide (**1**, 1.0 mmol), alcohols (**4**, 4.0 mmol), $Zn(OTf)_2$ (10 mol%), DTBP (4 equiv.), DMF (3 mL) refluxed at 100 ℃ for 12 h. [b]Isolated yield

2. Characterization data

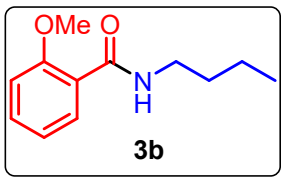
2.1. HRMS data and spectra:



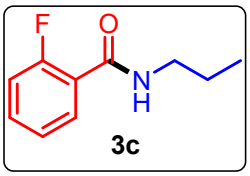
2.2. ^{1}H and ^{13}C data of compounds:



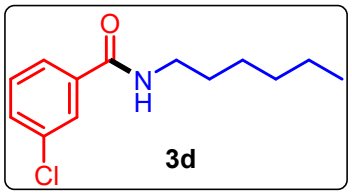
***N*-Butylbenzamide (3a)[1]:** Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.34 (m, 2H), 6.45 (s, 1H), 3.44 – 3.38 (m, 2H), 1.61 – 1.52 (m, 2H), 1.42 – 1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.76, 134.87, 131.38, 128.58, 126.99, 39.93, 31.80, 20.25, 13.89.



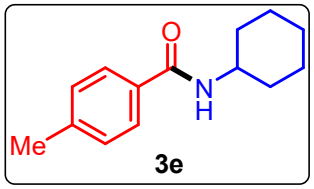
***N*-Butyl-2-methoxybenzamide (3b)[1]:** Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 41.0 Hz, 2H), 7.33 (q, *J* = 5.6, 3.1 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 3.37 (d, *J* = 6.8 Hz, 2H), 1.51 (t, *J* = 7.7 Hz, 2H), 1.33 (q, *J* = 7.8 Hz, 2H), 0.87 (q, *J* = 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.10, 157.34, 132.44, 131.97, 121.69, 121.07, 111.27, 55.84, 39.33, 31.56, 20.14, 13.69.



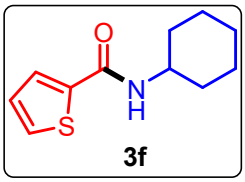
2-Fluoro-N-propylbenzamide (3c)[2]: White gummy; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 1H), 7.39 (dq, *J* = 12.6, 7.3, 5.2 Hz, 1H), 7.18 (td, *J* = 7.9, 2.8 Hz, 1H), 7.04 (ddd, *J* = 11.8, 8.1, 2.8 Hz, 1H), 6.67 (s, 1H), 3.38 (q, *J* = 6.5, 5.2 Hz, 2H), 1.62 – 1.54 (m, 2H), 0.97 – 0.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.24, 160.82, 158.37, 132.09, 131.99, 131.08, 131.06, 123.78, 123.75, 115.03, 114.78, 40.74, 28.68, 21.75, 10.40.



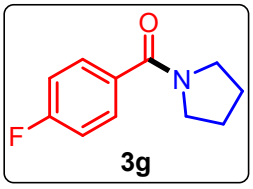
3-Chloro-*N*-hexylbenzamide (3d): Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 6.59 (s, 1H), 3.33 (d, *J* = 7.8 Hz, 2H), 1.50 (q, *J* = 7.8 Hz, 2H), 1.24 (d, *J* = 18.7 Hz, 6H), 0.79 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 136.67, 134.61, 131.24, 129.77, 127.31, 125.04, 40.30, 31.49, 29.54, 26.67, 22.54, 13.99.



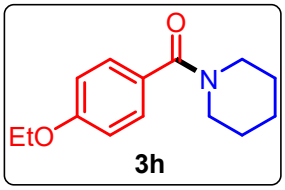
***N*-Cyclohexyl-4-methylbenzamide (3e)[3]:** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 5.9 Hz, 2H), 5.93 (s, 1H), 3.97 – 3.84 (m, 1H), 2.31 (s, 3H), 1.95 (d, *J* = 11.9 Hz, 2H), 1.62 (dd, *J* = 38.7, 11.0 Hz, 3H), 1.35 (q, *J* = 12.8 Hz, 2H), 1.16 (q, *J* = 12.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 141.57, 132.26, 129.14, 126.84, 48.60, 33.27, 25.61, 24.94, 21.41.



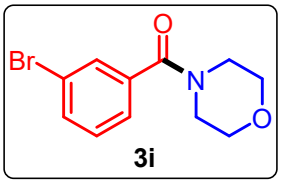
***N*-Cyclohexylthiophene-2-carboxamide (3f)[4]:** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 20.2 Hz, 2H), 6.98 (d, *J* = 5.1 Hz, 1H), 5.87 (s, 1H), 3.86 (q, *J* = 10.3 Hz, 1H), 1.94 (d, *J* = 12.2 Hz, 2H), 1.67 (d, *J* = 13.5 Hz, 2H), 1.57 (d, *J* = 13.3 Hz, 1H), 1.33 (q, *J* = 12.9 Hz, 2H), 1.15 (p, *J* = 11.2, 10.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.00, 139.54, 129.53, 127.74, 127.50, 48.78, 33.22, 25.54, 24.92.



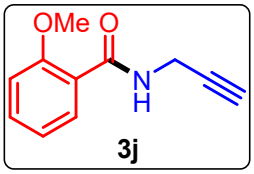
(4-Fluorophenyl)(pyrrolidin-1-yl)methanone (3g)[5]: Yellow solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.49 (d, *J* = 78.6 Hz, 4H), 1.97 – 1.77 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78, 164.77, 162.28, 133.32, 133.29, 129.56, 129.48, 115.45, 115.24, 49.80, 46.42, 26.52, 24.52.



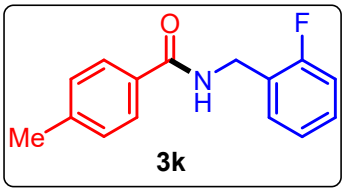
(4-Ethoxyphenyl)(piperidin-1-yl)methanone (3h)[6]: Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 6.7 Hz, 2H), 3.53 (s, 3H), 2.79 (d, *J* = 4.3 Hz, 2H), 1.73 – 1.55 (m, 5H), 1.40 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.28, 159.87, 128.78, 128.33, 114.07, 63.45, 38.53, 24.59, 14.69.



(3-Bromophenyl)(morpholino)methanone (3i)[7]: Yellow liqiod; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.22 (d, *J* = 11.2 Hz, 2H), 3.72 – 3.29 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.47, 137.23, 132.78, 130.13, 130.01, 125.52, 122.54, 66.63, 38.47.

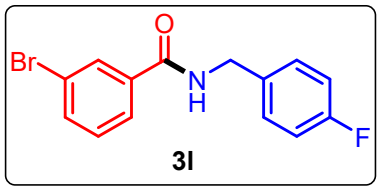


2-Methoxy-N-(prop-2-yn-1-yl)benzamide (3j)[8]: Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.92 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.04 – 6.96 (m, 1H), 6.95 – 6.88 (m, 1H), 4.22 – 4.14 (m, 2H), 3.90 (d, *J* = 2.7 Hz, 3H), 3.36 (d, *J* = 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.72, 156.58, 132.12, 131.27, 120.26, 119.77, 110.40, 79.05, 70.20, 54.98, 28.34.

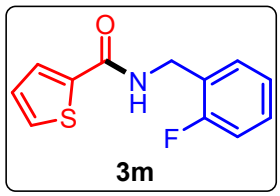


***N*-(2-Fluorobenzyl)benzamide (3k)[9]:** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.16 (dd, *J* = 21.1, 6.0 Hz, 3H), 7.00 (dt, *J* = 21.2, 8.4 Hz, 2H), 6.53 (s, 1H), 4.59 (d, *J* = 4.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.41, 162.34, 159.89, 142.03, 131.41, 130.41, 130.37, 129.36, 129.28,

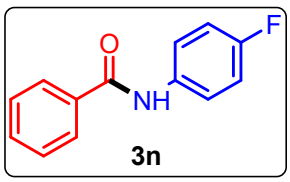
129.24, 127.01, 125.39, 125.25, 124.39, 124.36, 115.50, 115.29, 38.05, 38.01, 21.45. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.01.



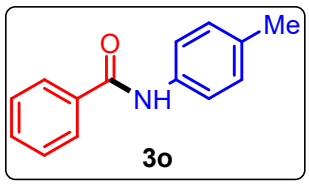
3-Bromo-*N*-(4-fluorobenzyl)benzamide (3l): Pale yellow solid, m.p.: 137-139 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.11 (m, 3H), 6.96 (s, 1H), 6.89 (dt, *J* = 10.0, 5.0 Hz, 2H), 4.43 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 163.43, 160.99, 136.23, 134.53, 133.84, 133.81, 130.28, 130.13, 129.54, 129.45, 125.67, 122.74, 115.66, 115.45, 43.41. HRMS Calcd m/z $[M+H]^+$: 308.0081. Found: 308.0101.



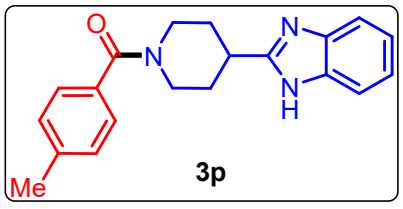
***N*-(2-Fluorobenzyl)thiophene-2-carboxamide (3m):** White solid, m.p.: 121-124 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 3.4 Hz, 1H), 7.39 (d, *J* = 4.2 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.08 – 6.95 (m, 3H), 6.36 (s, 1H), 4.59 (d, *J* = 5.7 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.33, 161.85, 159.88, 138.62, 130.52, 130.47, 130.10, 129.50, 129.42, 128.24, 127.64, 125.11, 124.97, 124.44, 124.40, 115.52, 115.31, 38.00, 37.96. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.04. HRMS Calcd m/z $[M+H]^+$: 236.0540. Found: 236.0551.



***N*-(4-Fluorophenyl)benzamide (3n)[10]:** Off white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.31 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.81 (dt, *J* = 7.9, 3.6 Hz, 2H), 7.64 – 7.51 (m, 3H), 7.20 (td, *J* = 8.7, 2.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 165.94, 159.97, 157.58, 136.02, 136.00, 135.30, 132.04, 128.86, 128.09, 122.70, 122.63, 115.74, 115.52. ^{19}F NMR (377 MHz, DMSO) δ -118.93.;

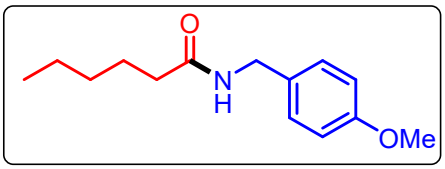


***N*-(p-Tolyl)benzamide (3o)[10]:** White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 8.01 – 7.93 (m, 2H), 7.73 – 7.65 (m, 2H), 7.63 – 7.49 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 165.82, 137.14, 135.56, 133.07, 131.88, 129.45, 128.80, 128.07, 120.89, 20.96.

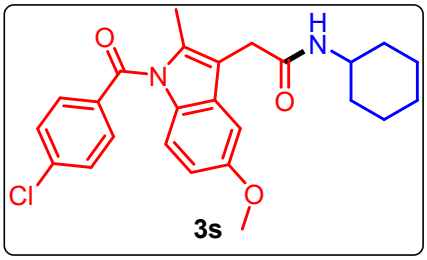


(4-(1*H*-Benzo[d]imidazol-2-yl)piperidin-1-yl)(p-tolyl)methanone (3p): Pale yellow solid, m.p. 152-155 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.13 (dt, *J* = 5.7, 3.4 Hz, 2H), 3.38 (s, 2H), 3.19 (tt, *J* = 7.7, 3.6 Hz, 2H), 2.51 (s, 1H),

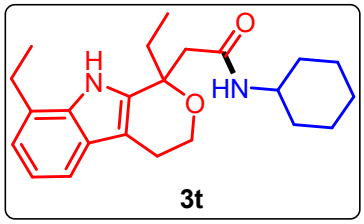
2.35 (d, J = 2.9 Hz, 3H), 2.04 (s, 2H), 1.82 (t, J = 12.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 169.65, 157.72, 139.50, 133.87, 129.38, 127.27, 121.74, 49.08, 36.22, 30.92, 21.36. HRMS Calcd m/z $[M+H]^+$: 320.1757. Found: 320.1765.



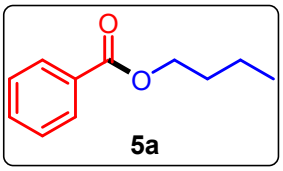
N-(4-methoxybenzyl)hexanamide (3q)[11]**:** ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (t, J = 5.9 Hz, 1H), 7.11 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.13 (d, J = 5.9 Hz, 2H), 3.68 (s, 3H), 2.05 (t, J = 7.4 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.20 (dddd, J = 14.3, 12.8, 6.5, 3.3 Hz, 4H), 0.81 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.52, 158.65, 132.23, 129.03, 114.16, 55.57, 41.91, 35.84, 31.43, 25.54, 22.41, 14.43.



2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-cyclohexylacetamide (3s): White solid, m.p: 154-157 °C; ^{1}H NMR (400 MHz, DMS-d_6) δ 8.06 – 7.95 (m, 1H), 7.66 (p, J = 8.5 Hz, 4H), 7.13 (s, 1H), 6.93 (d, J = 9.0 Hz, 1H), 6.70 (d, J = 8.9 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 1H), 3.47 (s, 2H), 2.22 (s, 3H), 1.79 – 1.59 (m, 4H), 1.54 (d, J = 11.9 Hz, 1H), 1.22 (d, J = 14.5 Hz, 5H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.76, 168.32, 156.00, 138.00, 135.41, 134.78, 131.59, 131.41, 130.74, 129.51, 115.27, 114.98, 111.73, 102.41, 55.90, 48.06, 32.97, 31.76, 25.69, 24.99, 13.82. HRMS Calcd m/z $[M+H]^+$: 439.1783. Found: 439.1791.

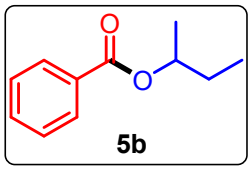


N-cyclohexyl-2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetamide (3t): White solid, m.p: 169-172°C; ^{1}H NMR (400 MHz, DMSO-D_6) δ 10.52 (s, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.23 (d, J = 7.3 Hz, 1H), 6.90 (d, J = 9.3 Hz, 2H), 3.95 (s, 2H), 3.54 (d, J = 10.7 Hz, 1H), 2.94 – 2.75 (m, 4H), 2.75 – 2.56 (m, 4H), 2.50 (s, 2H), 2.09 – 1.91 (m, 2H), 1.65 (q, J = 13.5, 12.2 Hz, 4H), 1.26 (t, J = 7.7 Hz, 5H), 0.68 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.04, 137.36, 134.84, 126.89, 126.59, 120.04, 119.19, 115.86, 107.27, 75.89, 60.29, 47.66, 44.59, 32.80, 32.64, 30.95, 25.66, 24.85, 24.82, 24.19, 22.44, 14.78, 8.23. HRMS Calcd m/z $[M+H]^+$: 369.2537. Found: 369.2544

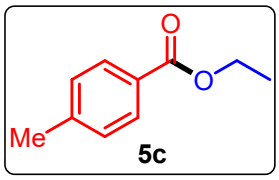


Butyl benzoate (5a)[12]**:** Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 7.1 Hz, 2H), 4.22 (p, J = 4.5 Hz, 2H), 1.64 (p, J = 7.8 Hz, 2H), 1.37 (q, J = 7.5,

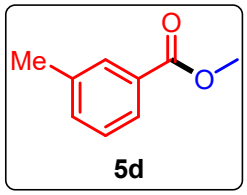
7.1 Hz, 2H), 0.88 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.62, 132.76, 130.56, 129.52, 128.29, 64.78, 30.79, 19.28, 13.74.



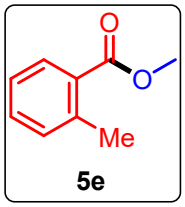
***sec*-Butyl benzoate (5b)**[13]**:** Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.0, 2.6 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 5.09 – 4.94 (m, 1H), 1.62 (ddt, J = 26.6, 14.0, 6.0 Hz, 2H), 1.27 – 1.21 (m, 3H), 0.88 (td, J = 7.8, 2.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.23, 132.68, 130.95, 129.50, 128.27, 72.83, 28.96, 19.55, 9.73.



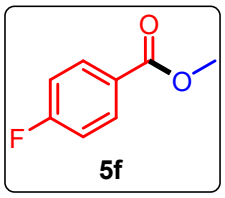
Ethyl 4-methylbenzoate (5c)[12]**:** Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.31 – 4.18 (m, 2H), 2.28 (s, 3H), 1.28 (dq, J = 7.4, 2.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 143.38, 129.56, 129.01, 127.80, 60.71, 21.58, 14.33.



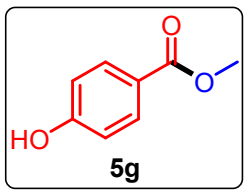
Methyl 3-methylbenzoate (5d)[14]**:** White liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 11.3 Hz, 2H), 7.30 – 7.19 (m, 2H), 3.81 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.27, 138.12, 133.65, 130.12, 128.25, 126.71, 52.00, 21.23.



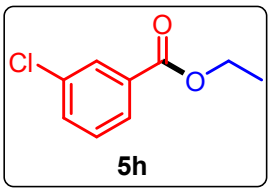
Methyl 2-methylbenzoate (5e)[14]**:** White gummy; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.31 (td, J = 7.6, 2.4 Hz, 1H), 7.16 (d, J = 7.5 Hz, 2H), 3.80 (d, J = 2.0 Hz, 3H), 2.52 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.09, 140.17, 131.94, 131.67, 130.56, 129.59, 125.68, 51.78, 21.69.



Methyl 4-fluorobenzoate (5f)[13]**:** White liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dq, J = 6.7, 3.2 Hz, 2H), 7.09 (td, J = 7.7, 6.4, 4.5 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 166.06, 164.46, 132.12, 132.03, 126.42, 126.39, 115.55, 115.33, 52.09.

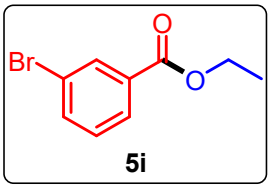


Methyl 4-hydroxybenzoate (5g)[15]**:** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 6.29 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 160.25, 131.96, 122.37, 115.29, 52.06.

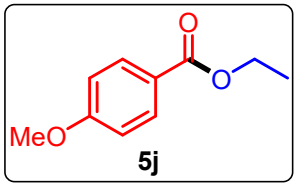


Ethyl 3-chlorobenzoate (5h)[16]**:** White gummy; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.28 (q, J = 5.6, 3.4 Hz, 1H), 4.31 (q, J = 7.6 Hz, 2H), 1.39 – 1.28

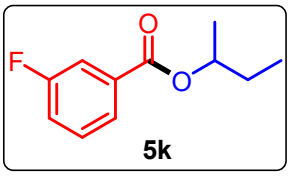
(m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.24, 134.41, 132.75, 132.21, 129.59, 129.55, 127.62, 61.31, 14.22.



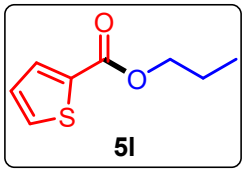
Ethyl 3-bromobenzoate (5i)[16]**:** Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 8.2, 3.5 Hz, 1H), 4.26 (dt, *J* = 7.4, 3.4 Hz, 2H), 1.27 (t, *J* = 3.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.11, 165.09, 135.67, 132.47, 129.86, 128.08, 122.37, 61.33, 14.26.



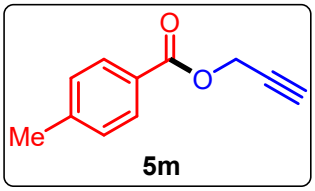
Ethyl 4-methylbenzoate (5j)[17]**:** Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 6.81 (d, *J* = 9.9 Hz, 2H), 4.29 – 4.20 (m, 2H), 3.73 (s, 3H), 1.33 – 1.23 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 163.26, 131.51, 122.93, 113.53, 60.60, 55.34, 14.35.



***sec*-Butyl 3-fluorobenzoate (5k):** Yellow gummy; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 9.5 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.16 (t, *J* = 8.2 Hz, 1H), 5.01 (d, *J* = 6.5 Hz, 1H), 1.70 – 1.56 (m, 2H), 1.25 (d, *J* = 5.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.08, 165.05, 163.78, 161.33, 133.17, 133.09, 129.92, 129.84, 125.23, 125.20, 119.81, 119.60, 116.49, 116.26, 73.38, 28.89, 19.47, 9.67. HRMS Calcd m/z $[M+H]^+$: 197.0972. Found: 197.0981.



Propyl thiophene-2-carboxylate (5l)[18]**:** Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 3.6 Hz, 1H), 7.44 (d, *J* = 4.2 Hz, 1H), 6.99 (q, *J* = 4.1 Hz, 1H), 4.16 (dt, *J* = 7.4, 3.0 Hz, 2H), 1.68 (qd, *J* = 7.5, 2.6 Hz, 2H), 0.92 (td, *J* = 7.9, 2.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 134.11, 133.20, 132.14, 127.66, 66.64, 22.11, 10.40.



Prop-2-yn-1-yl 4-methylbenzoate (5m)[19]**:** Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.6 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 2H), 4.83 (s, 2H), 4.19 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.87, 144.10, 129.86, 129.16, 126.68, 98.93, 74.89, 52.29, 21.69.

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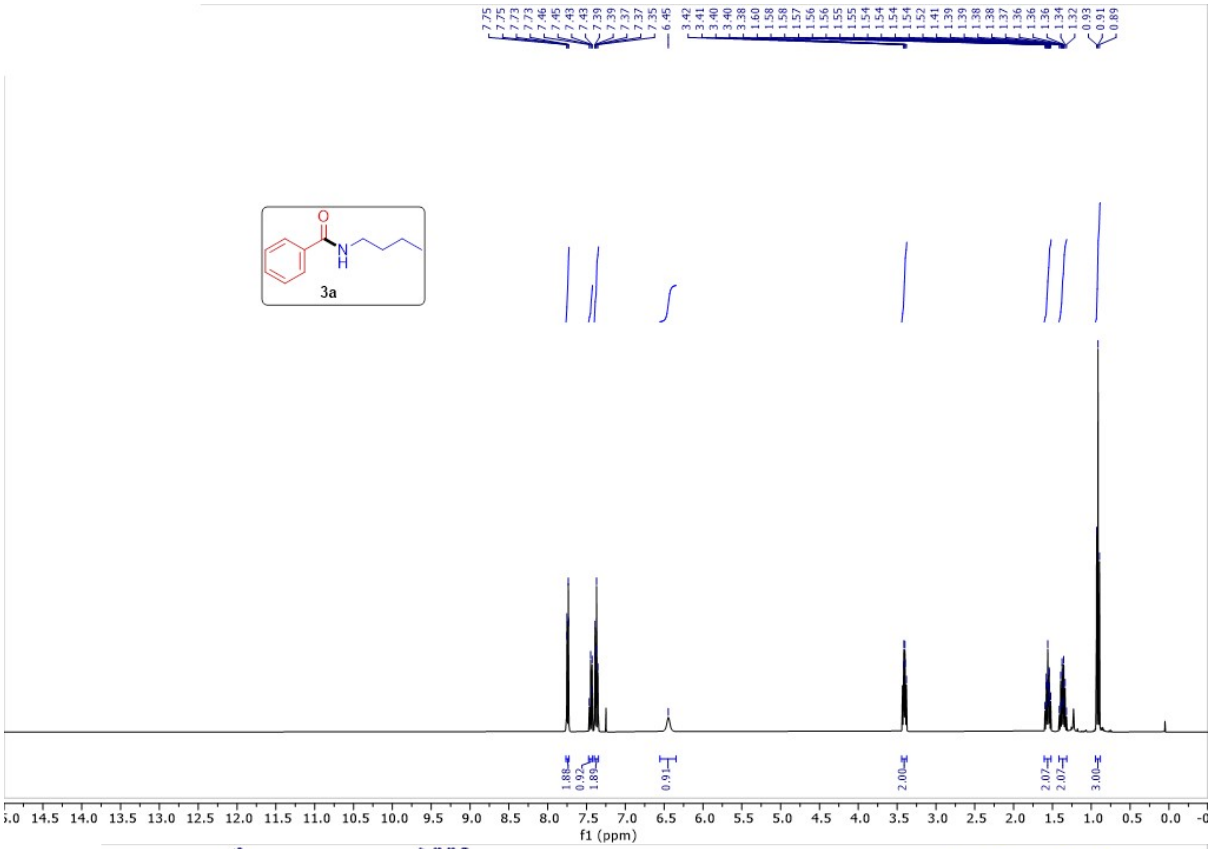
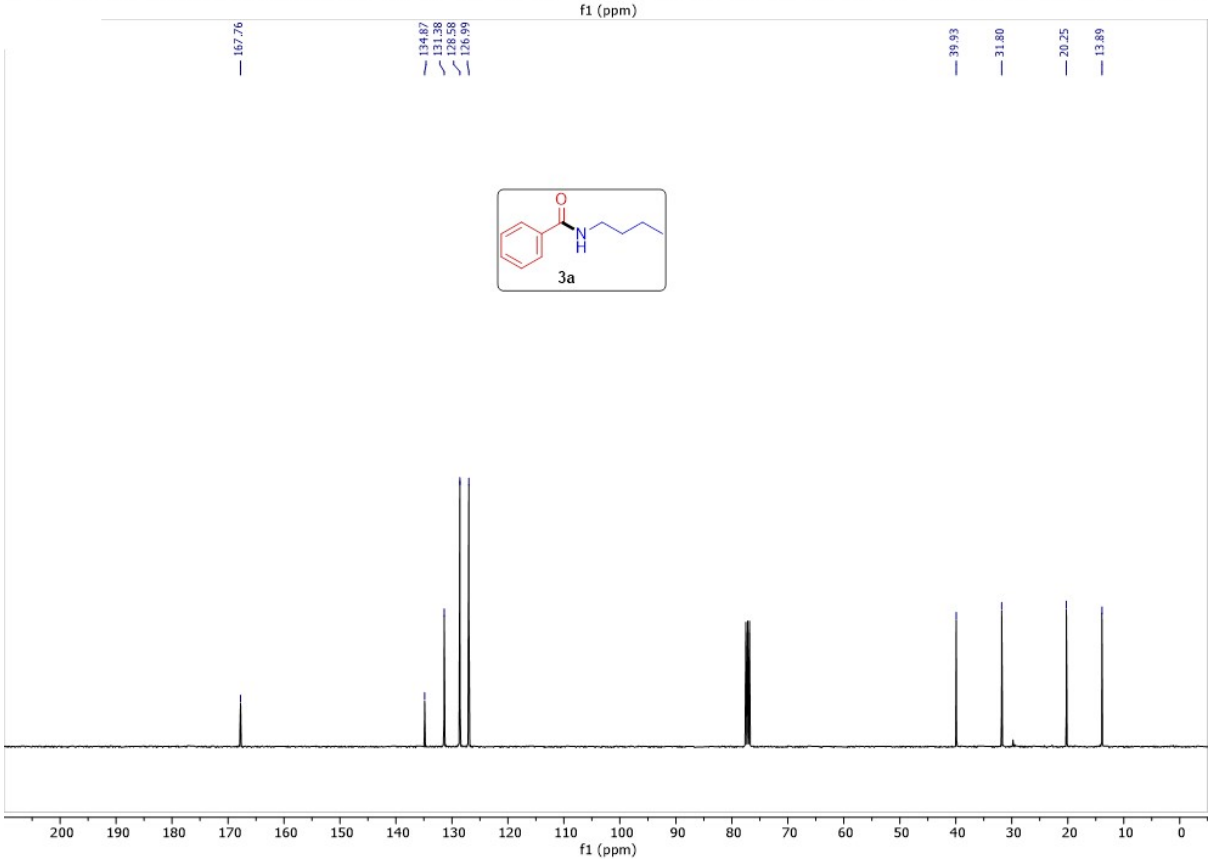
^{1}H and ^{13}C NMR Spectra of Compounds





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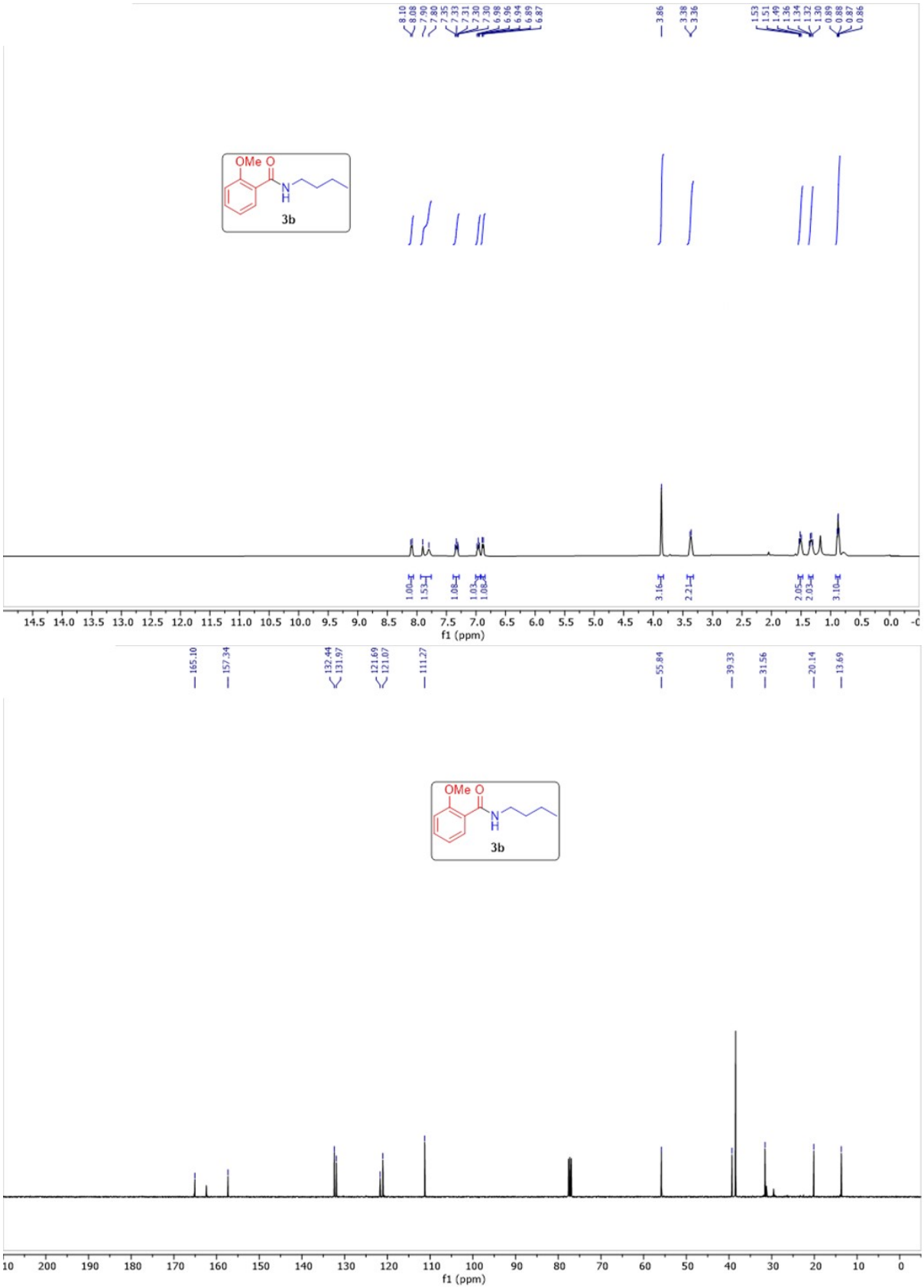

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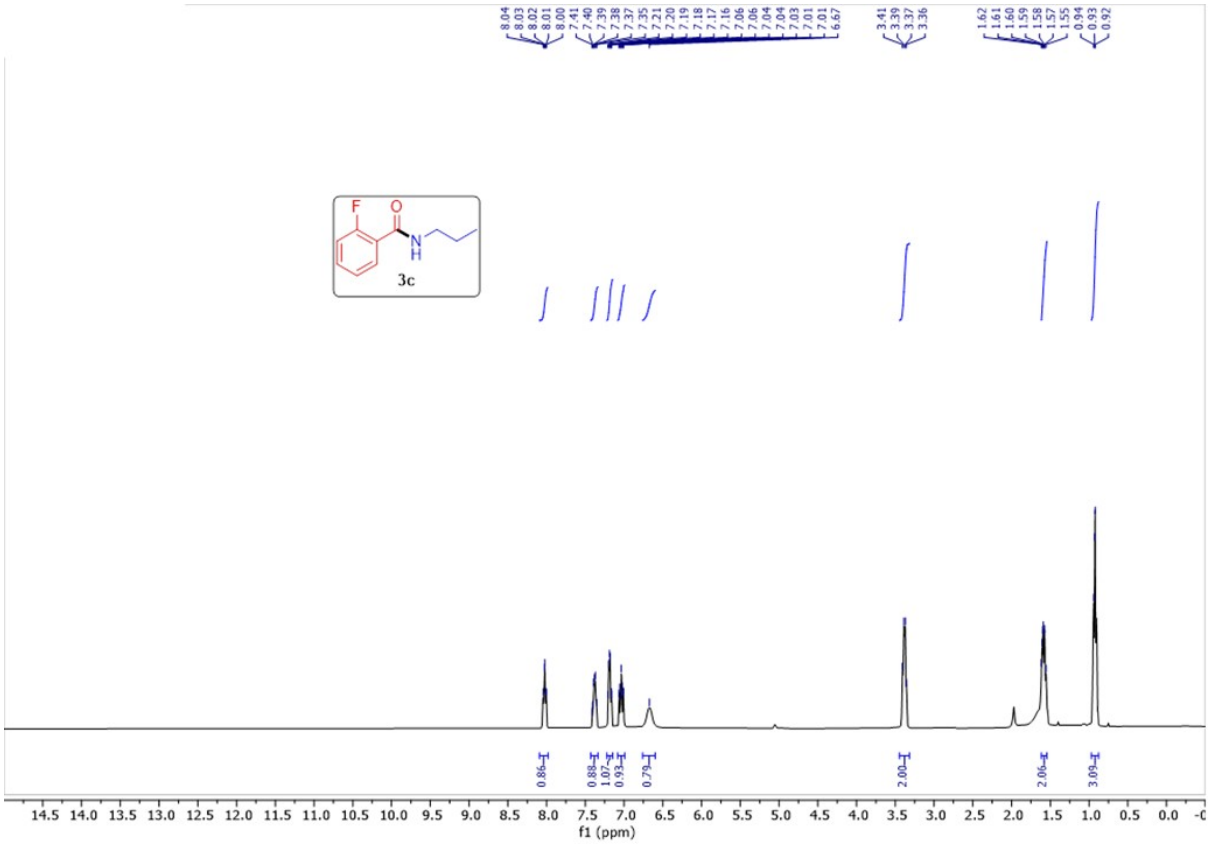

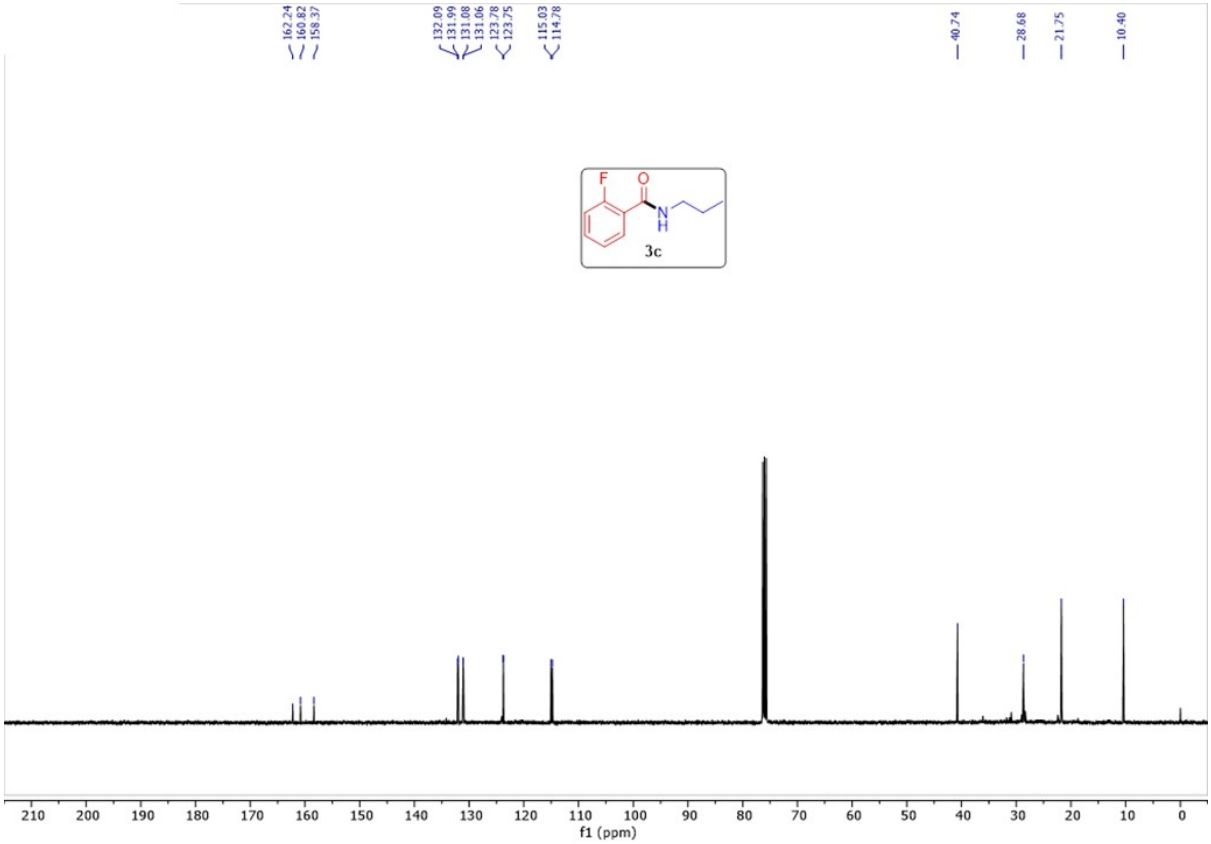

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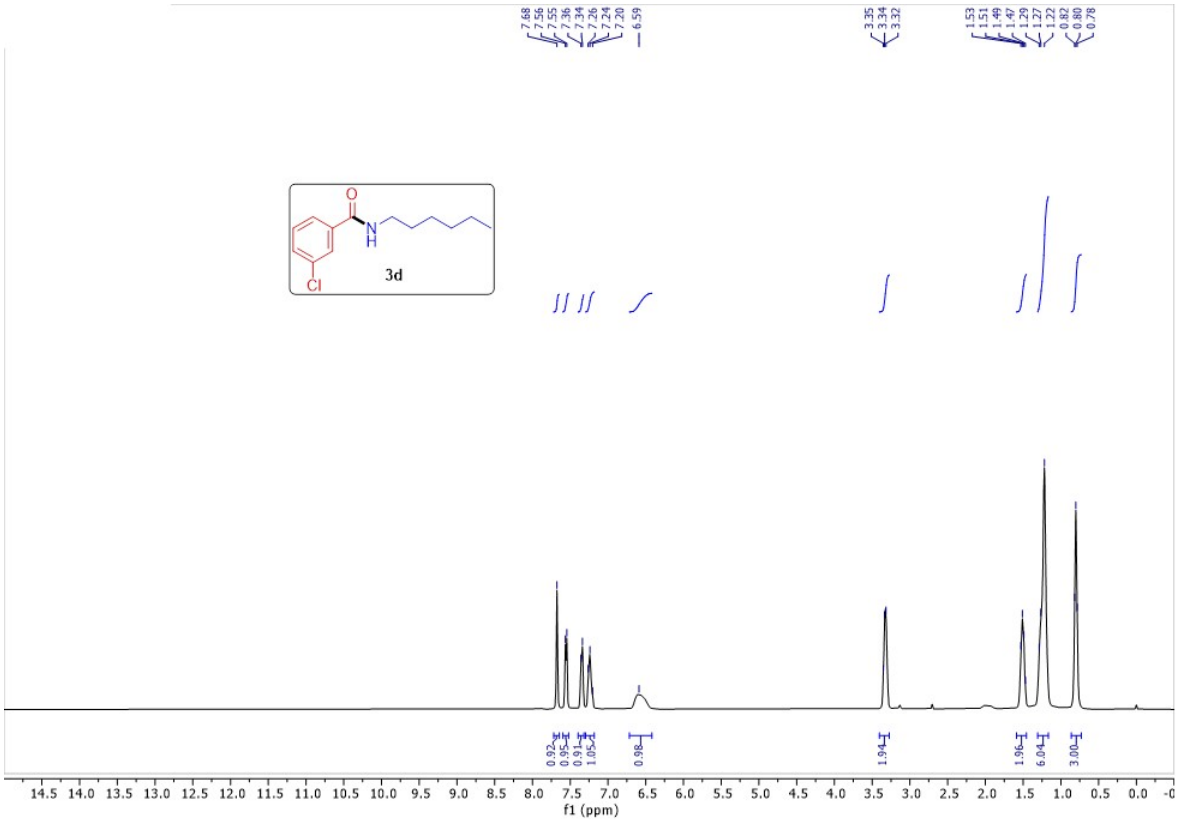
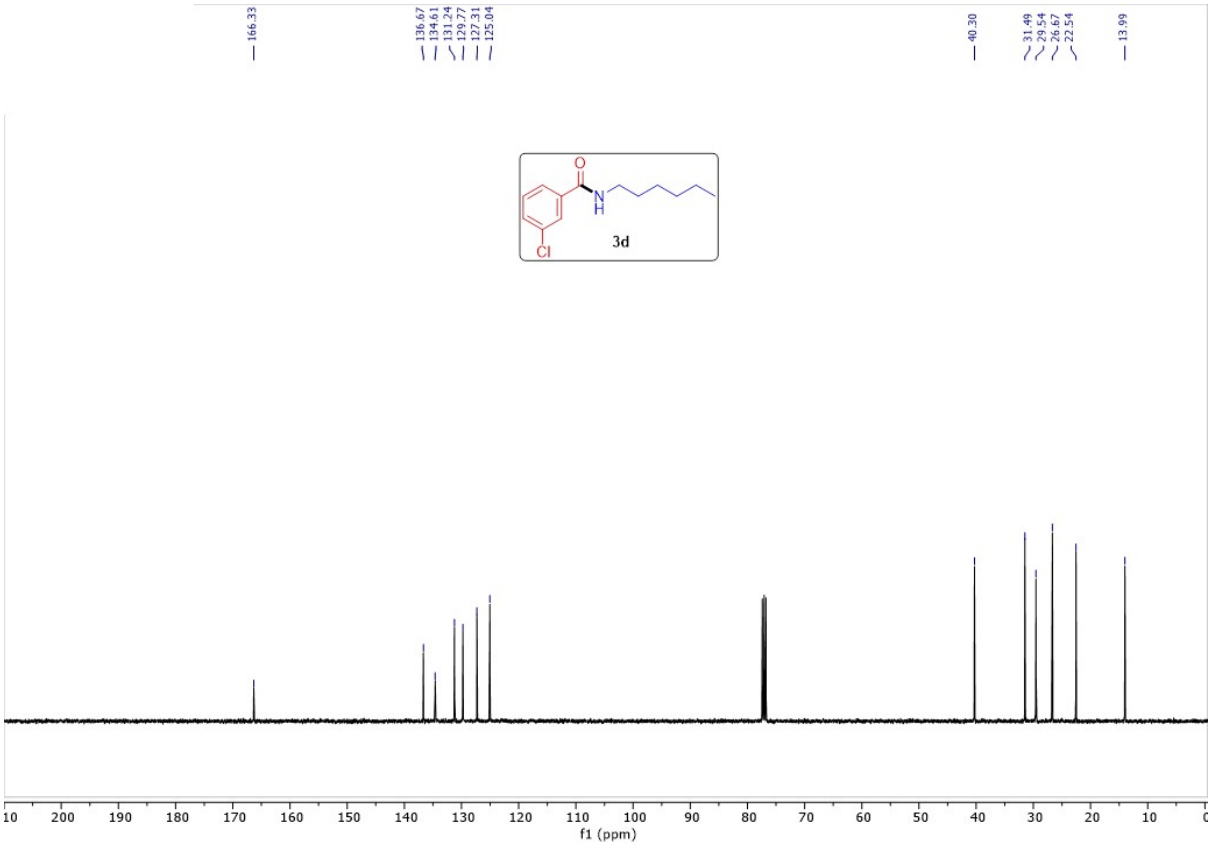
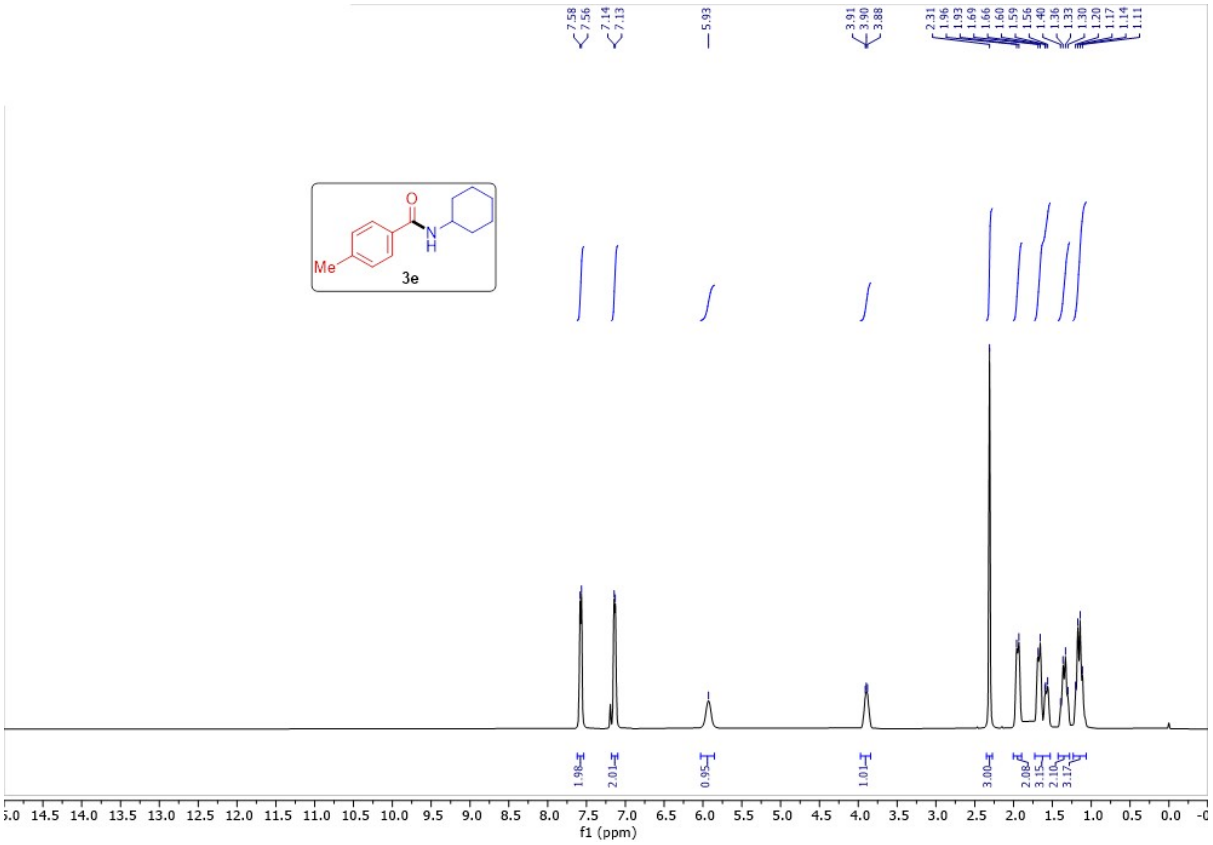
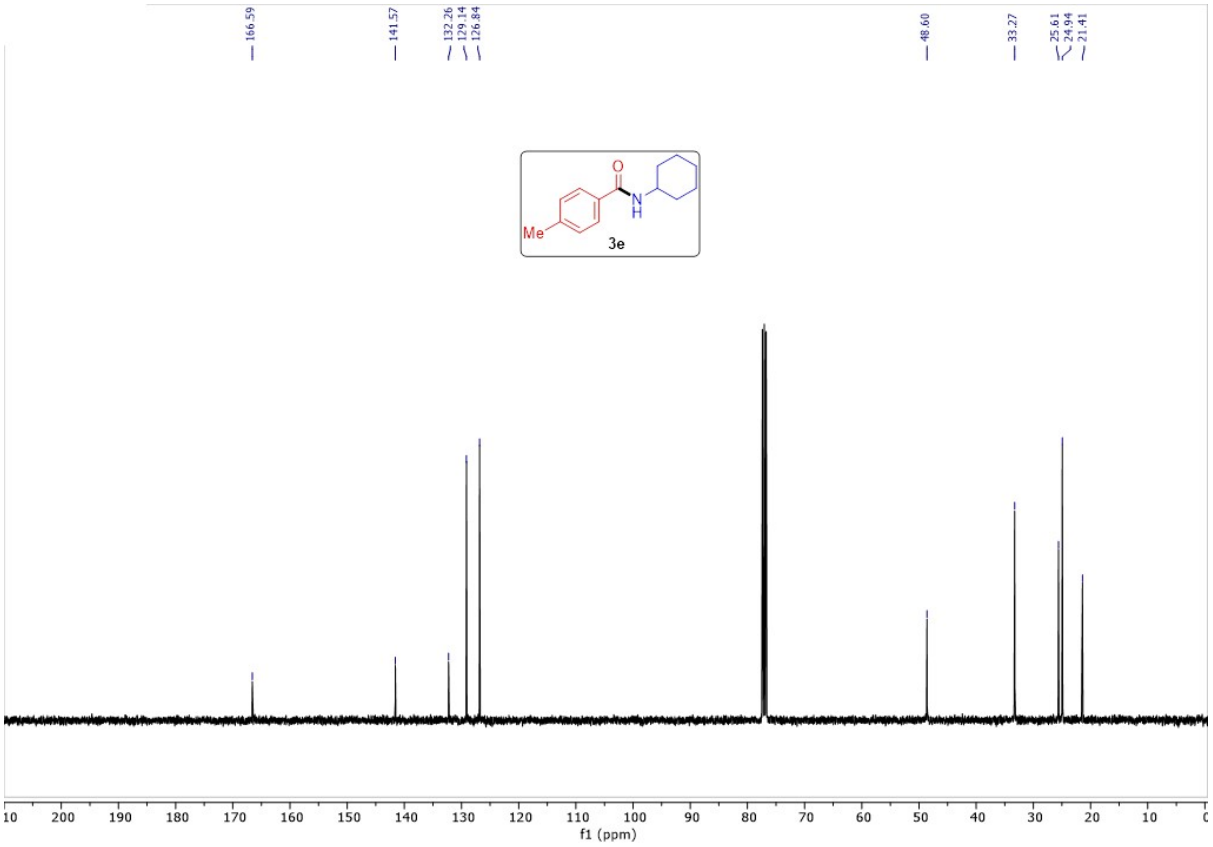




^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





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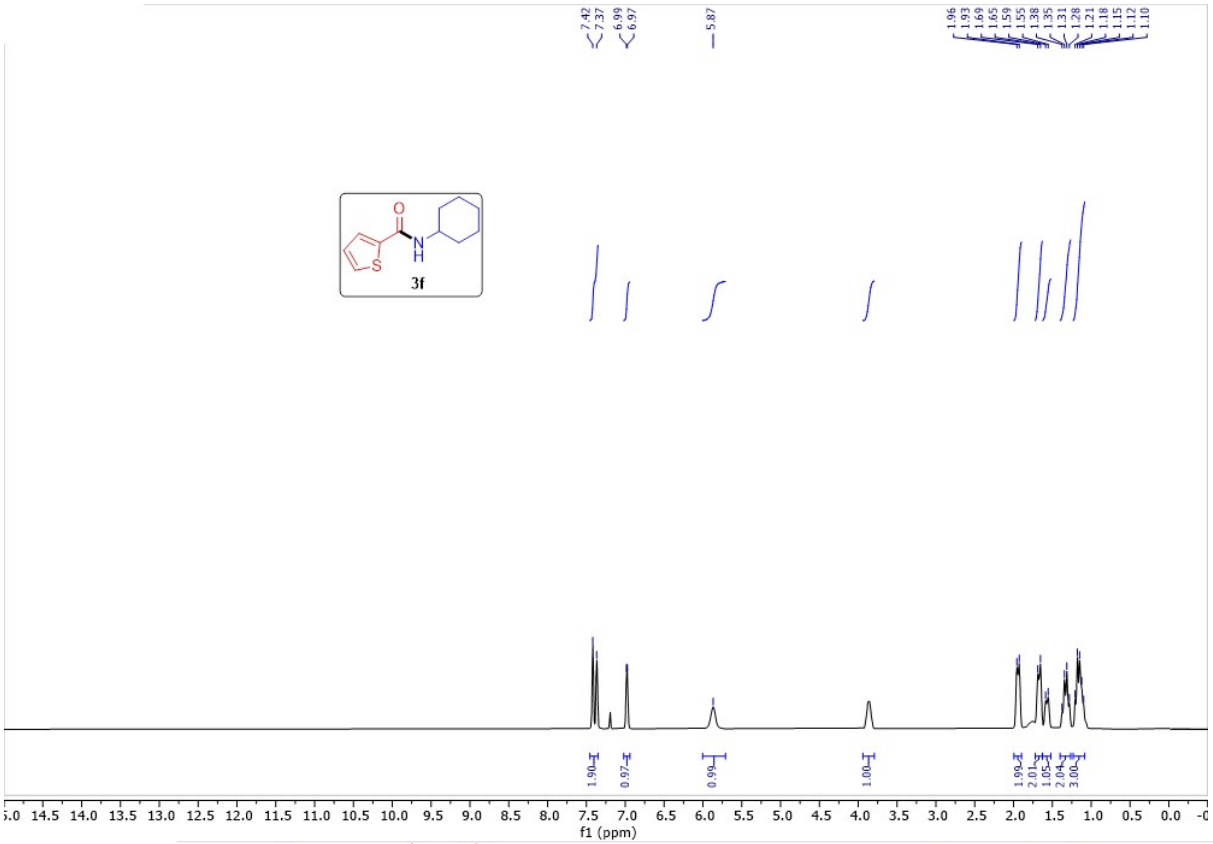
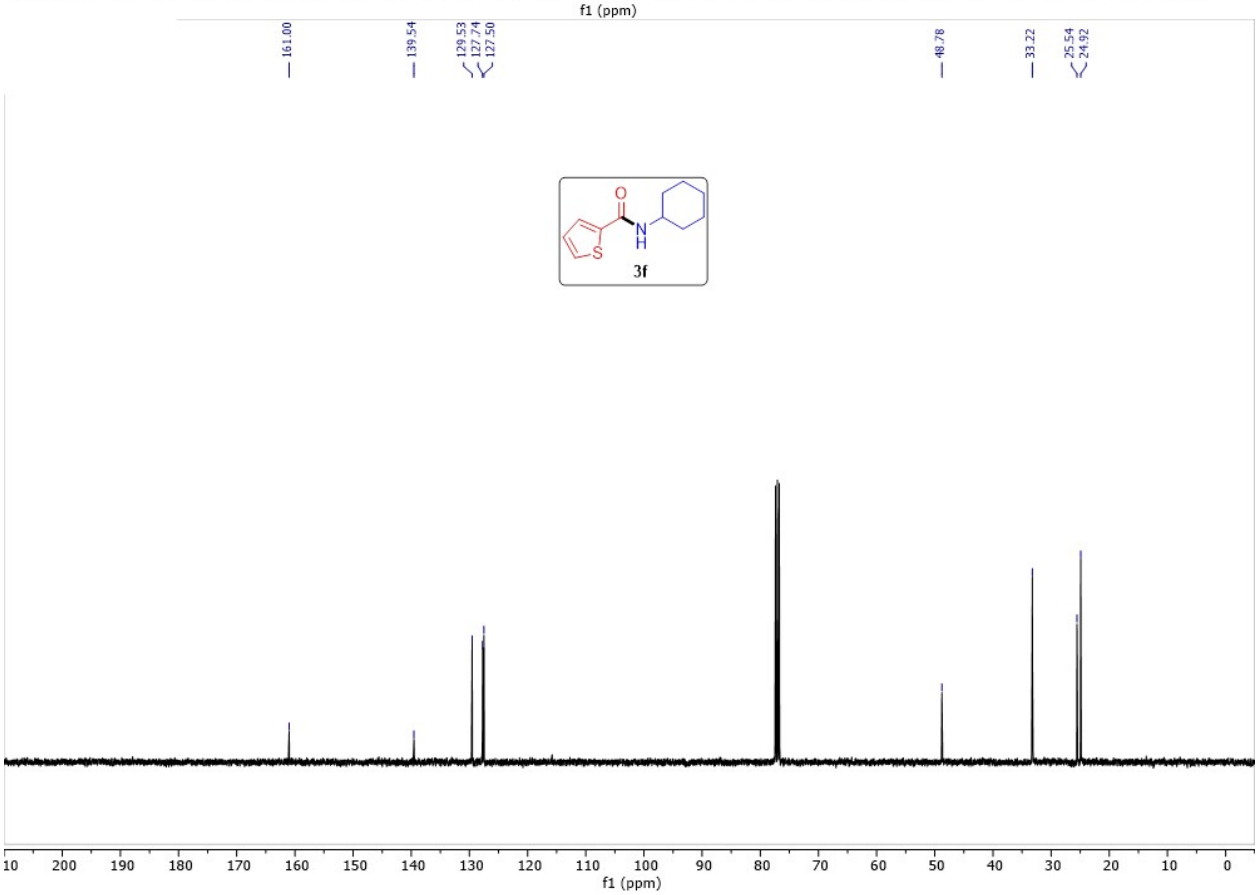
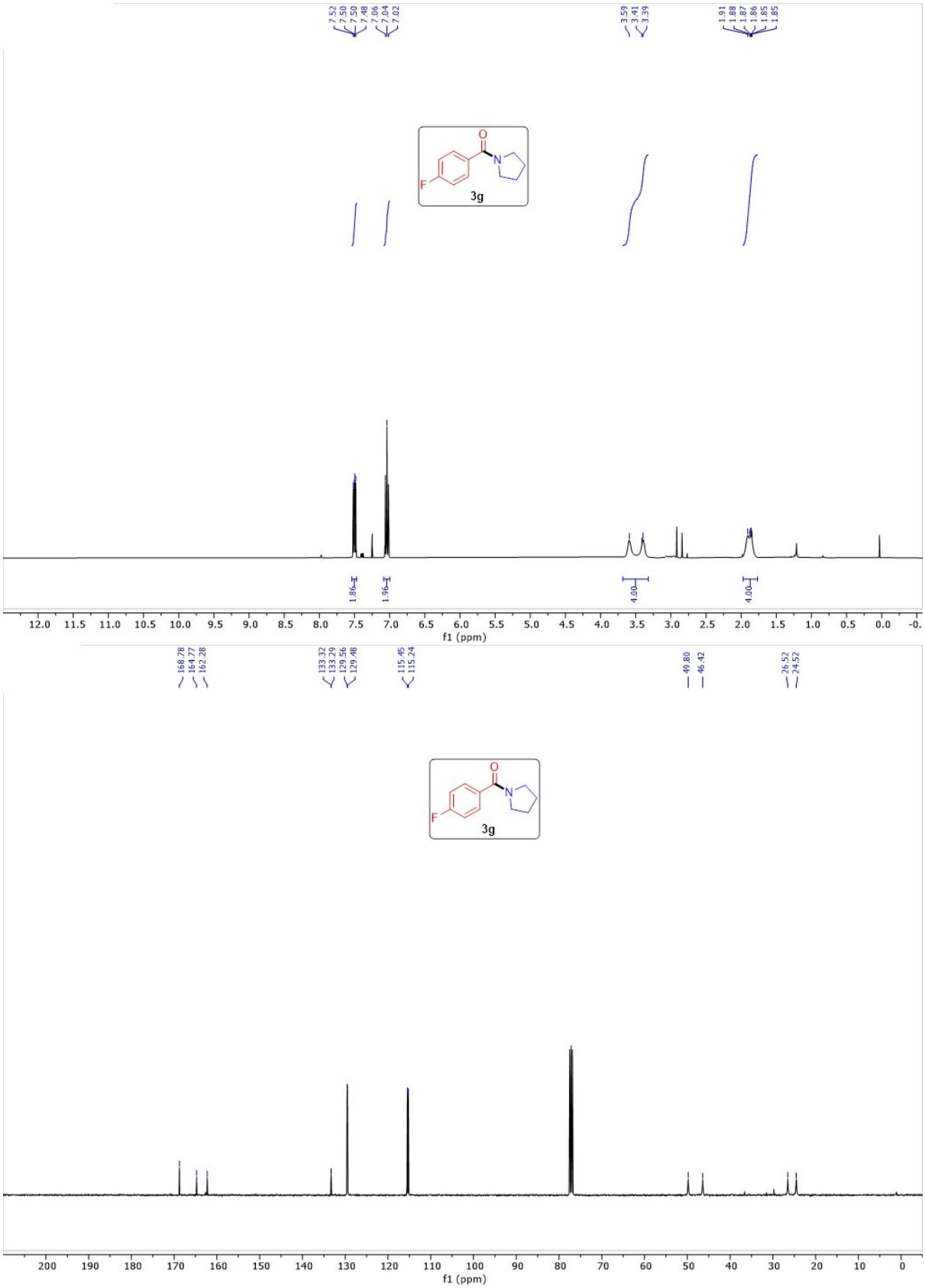
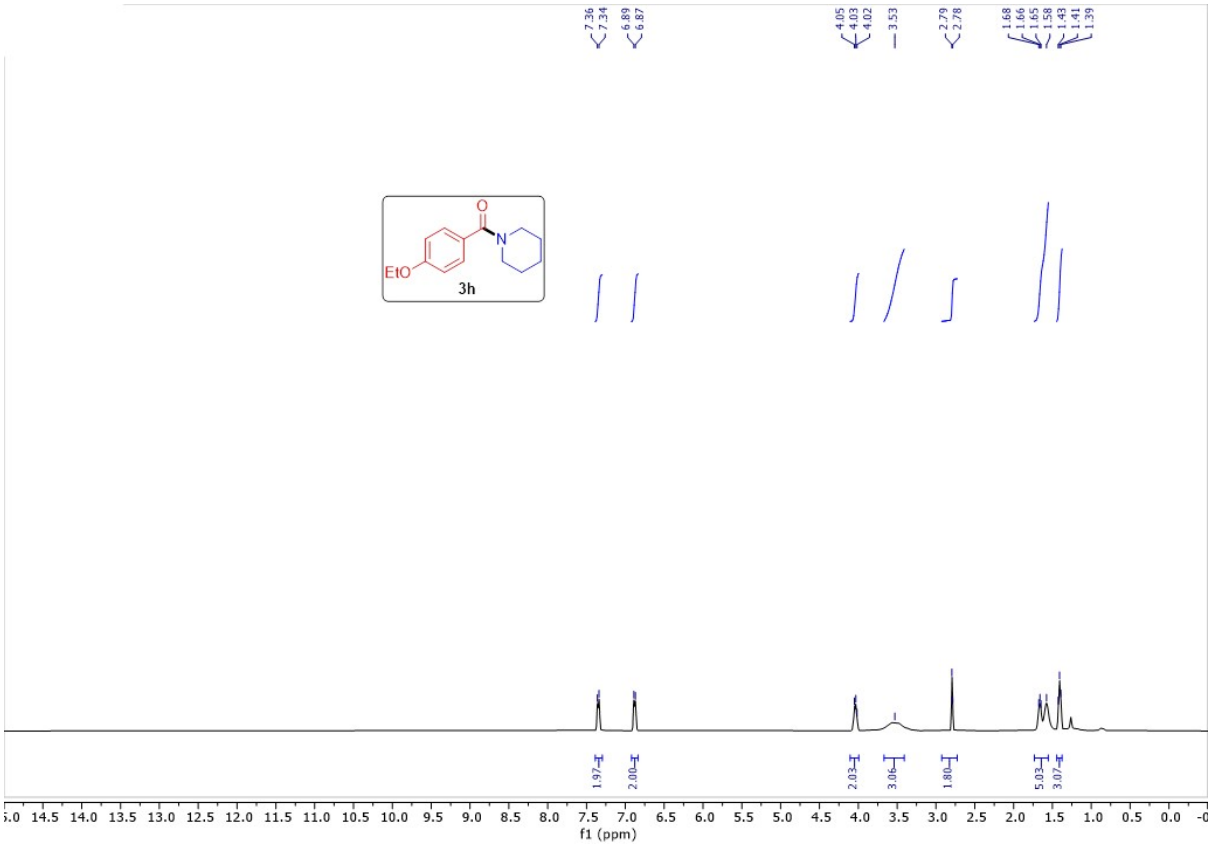


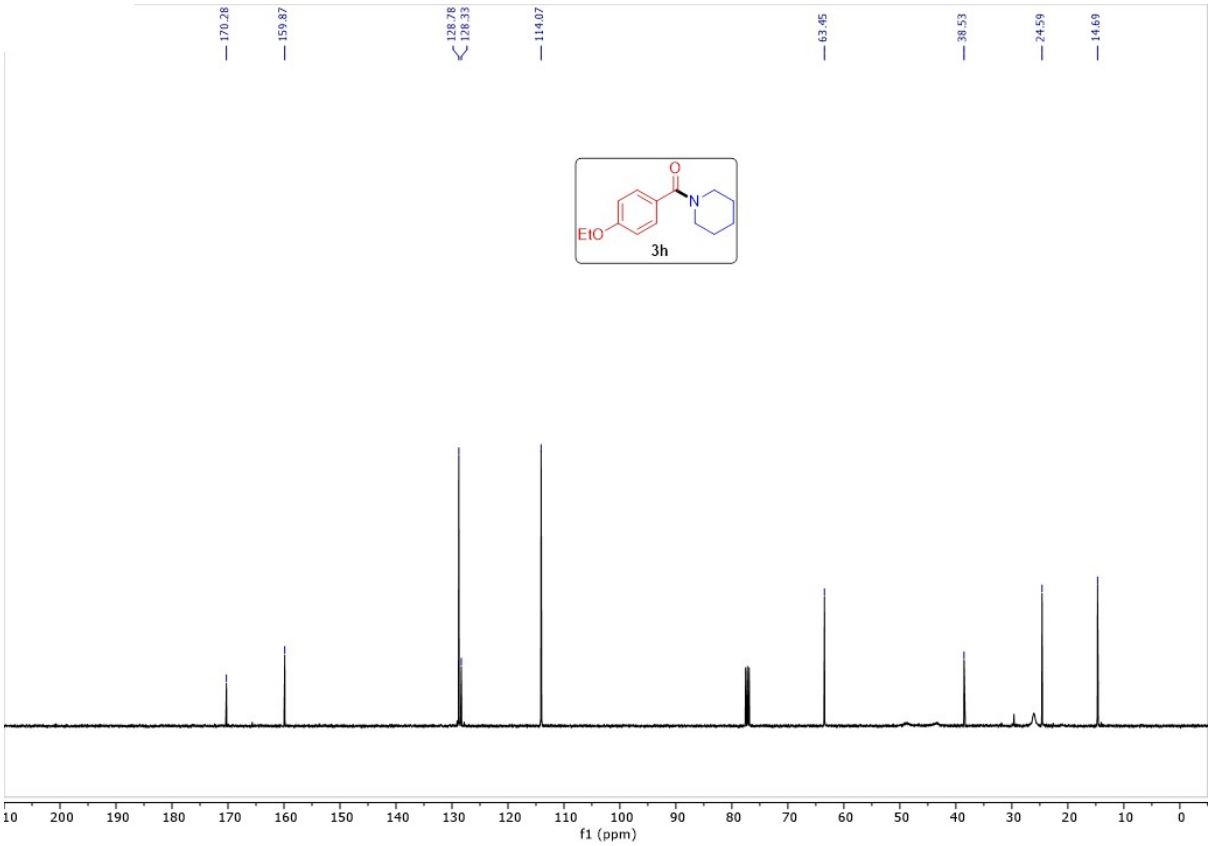


^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





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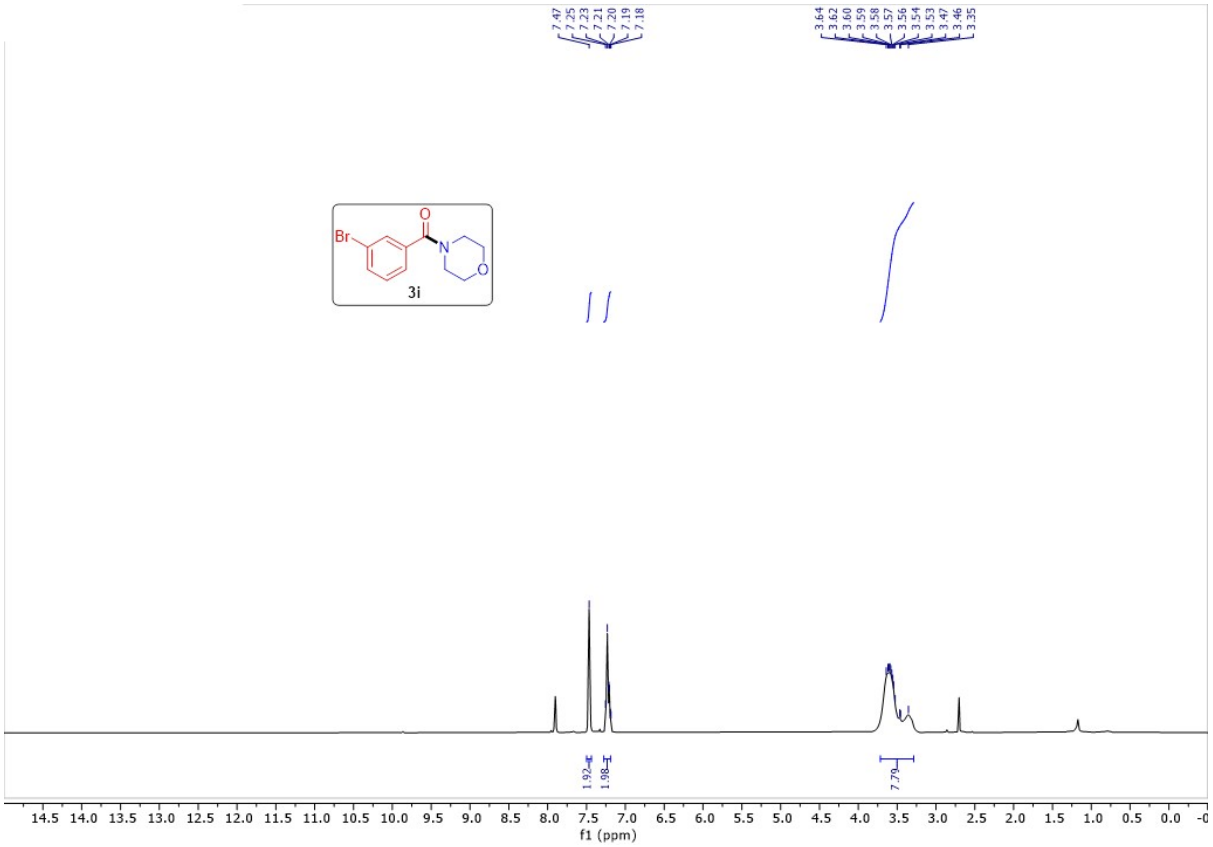

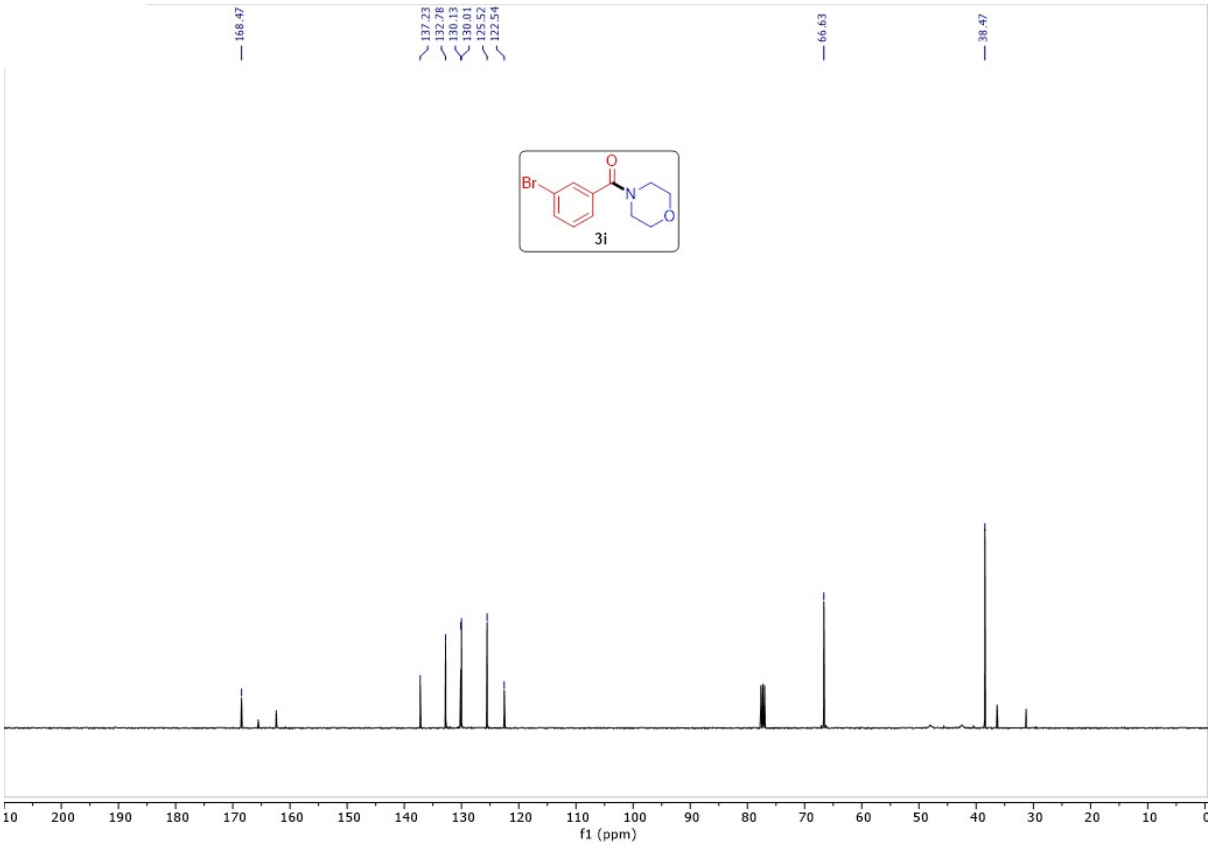

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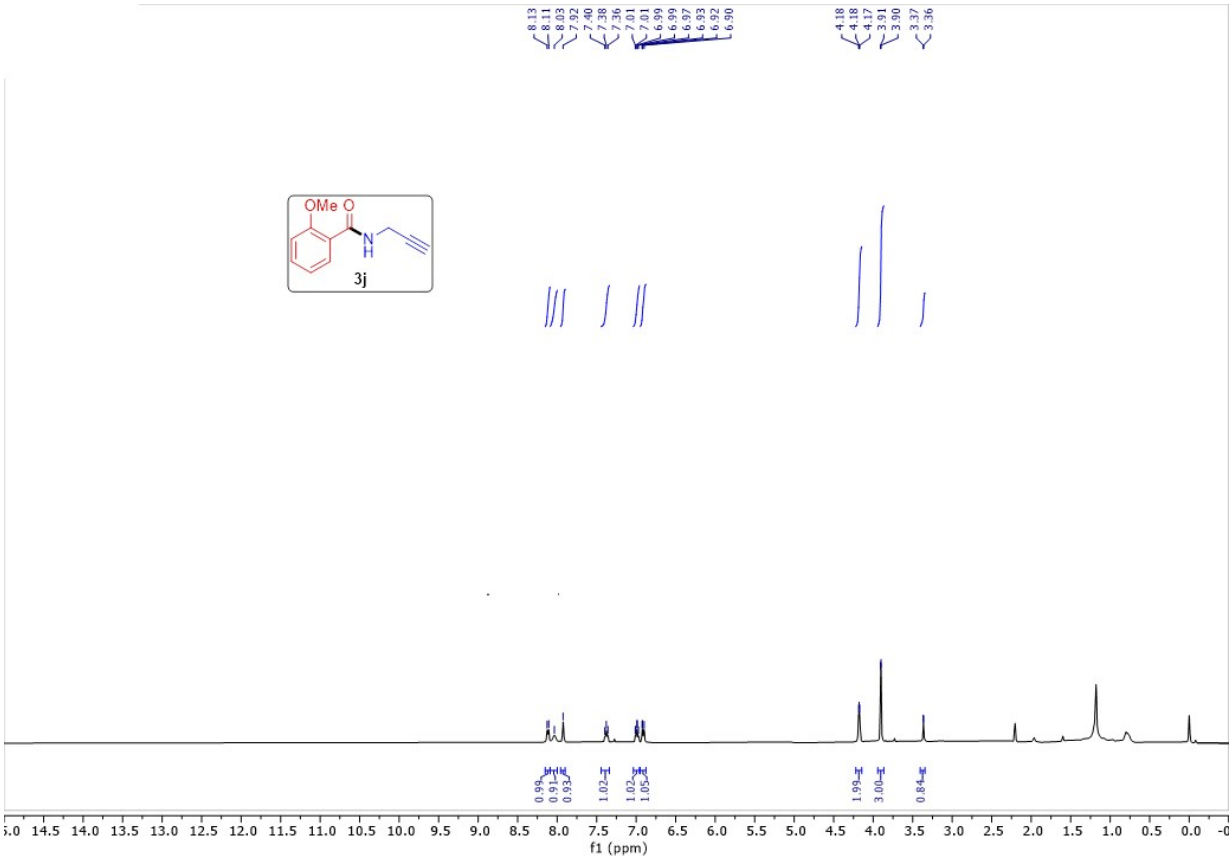
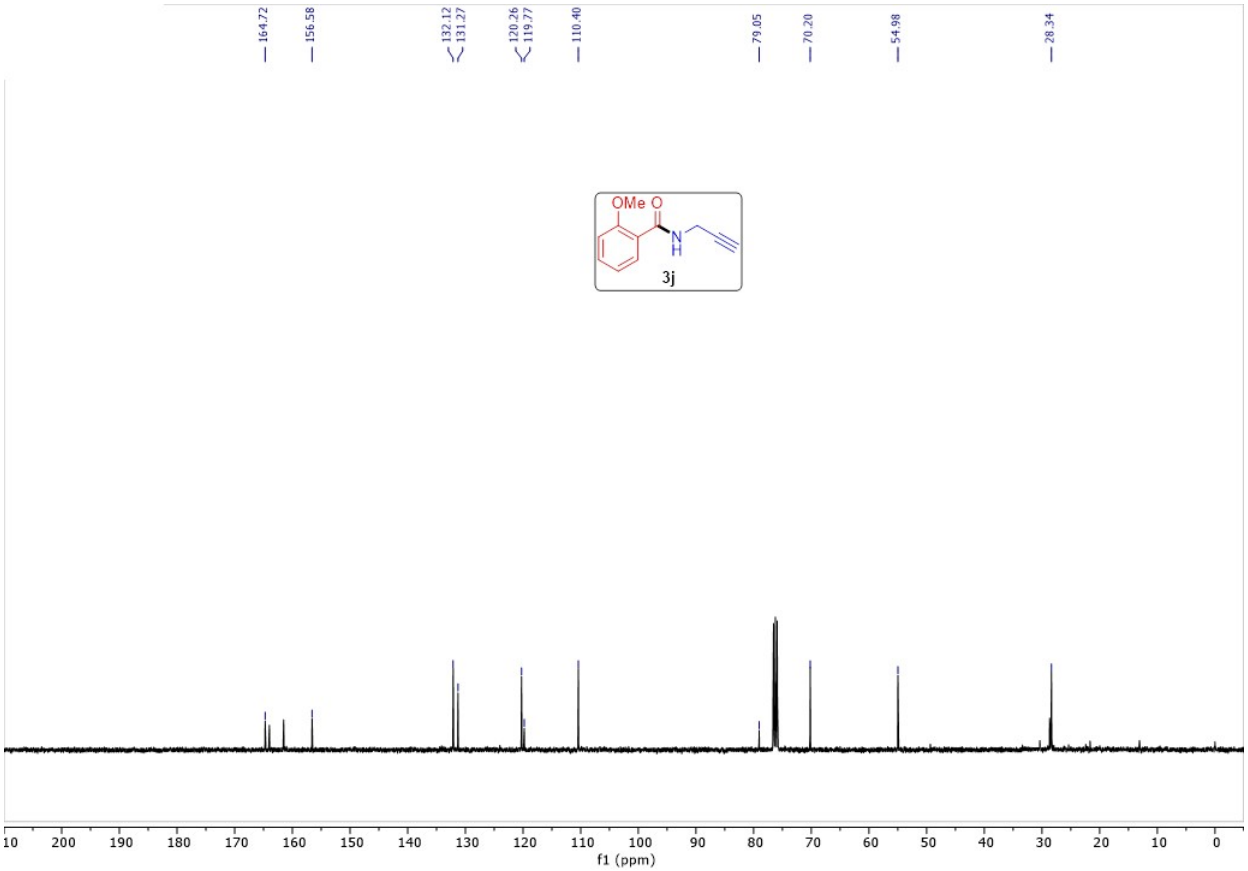
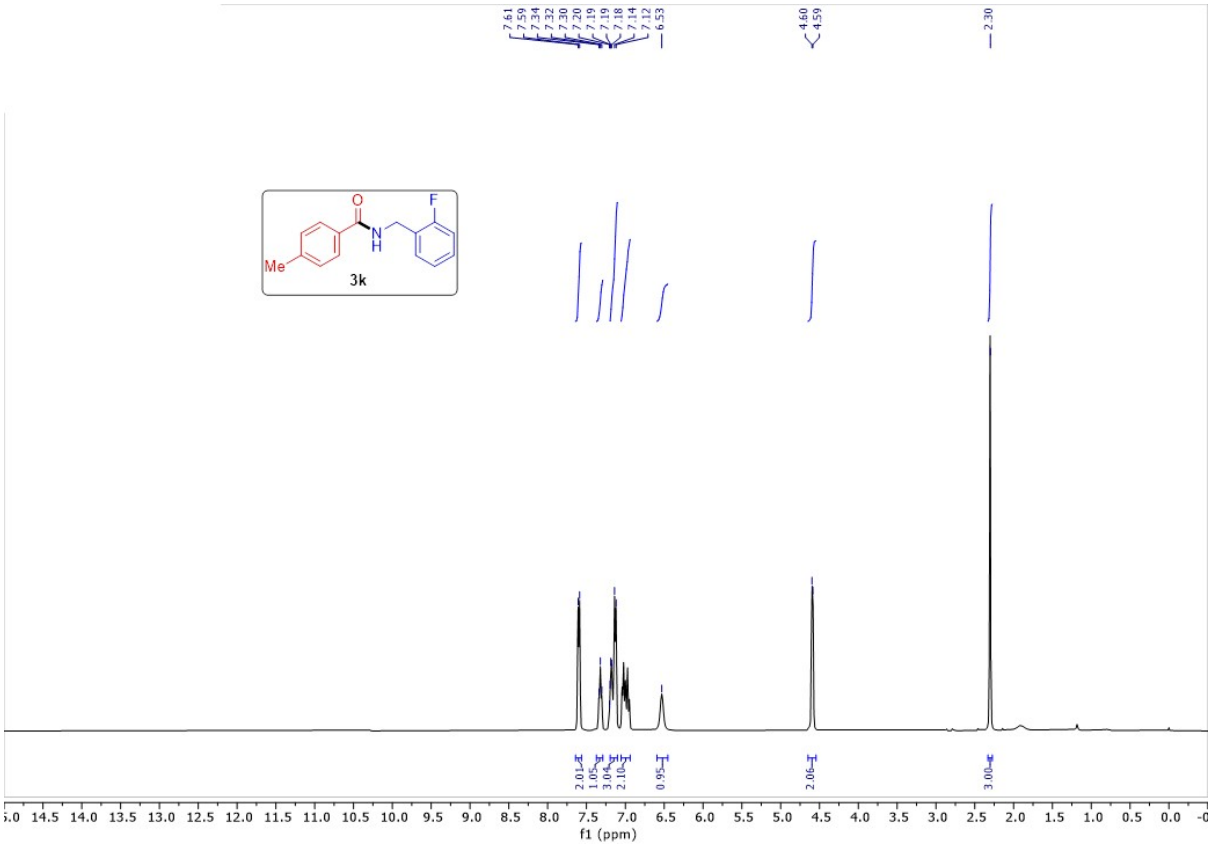
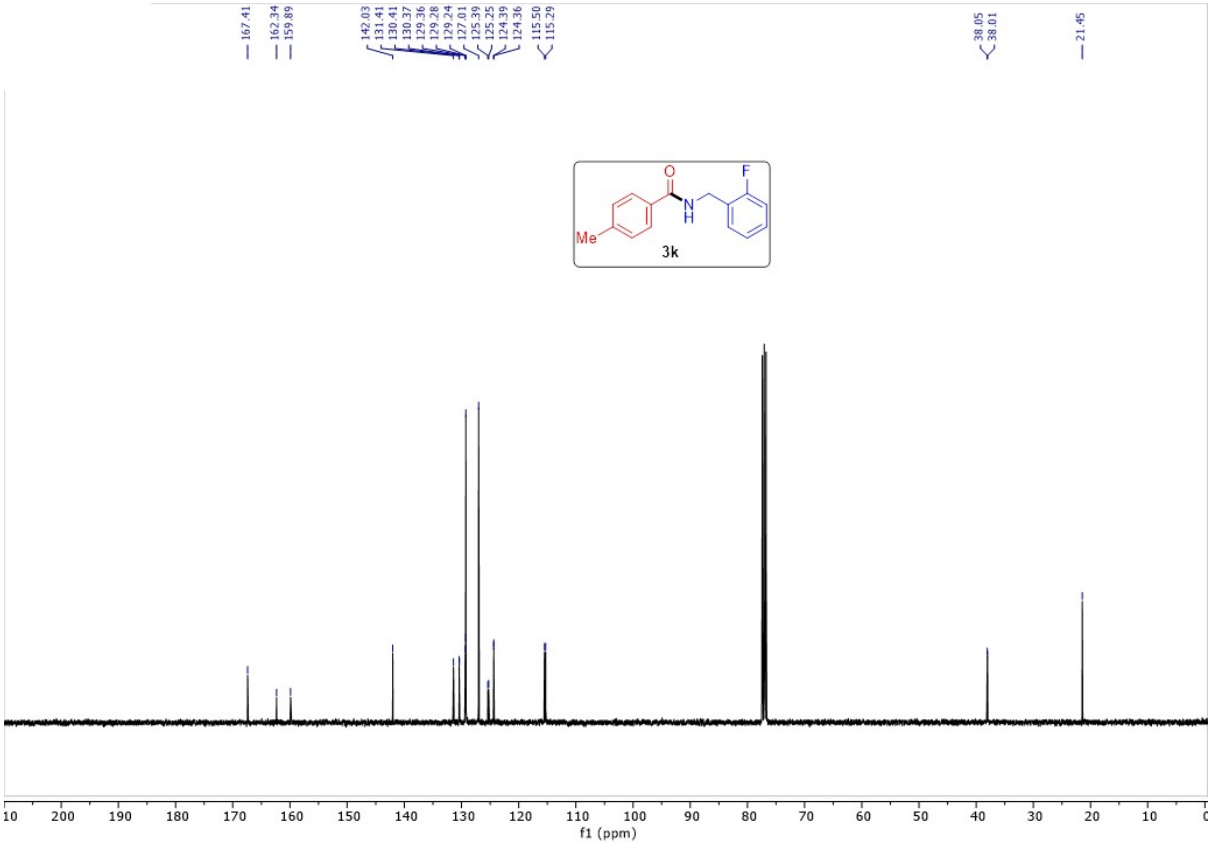




^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





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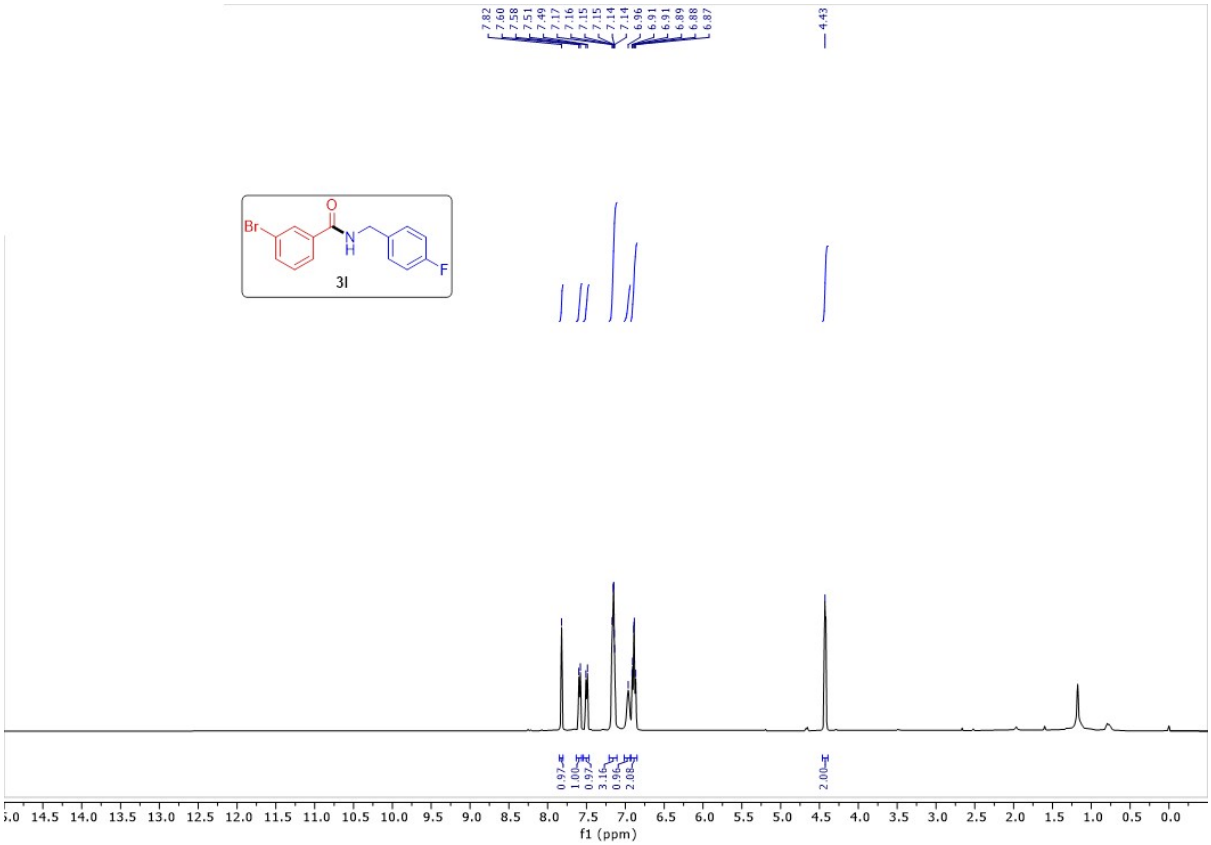

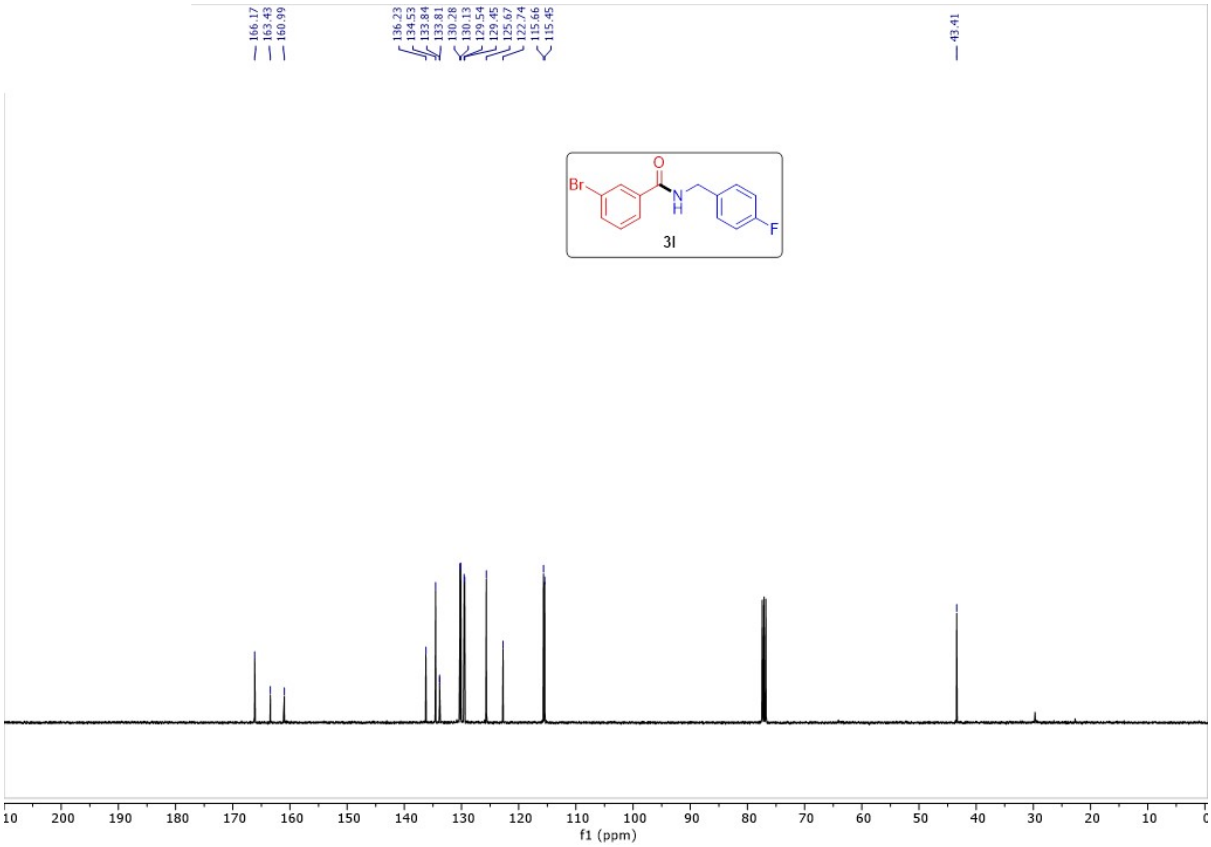

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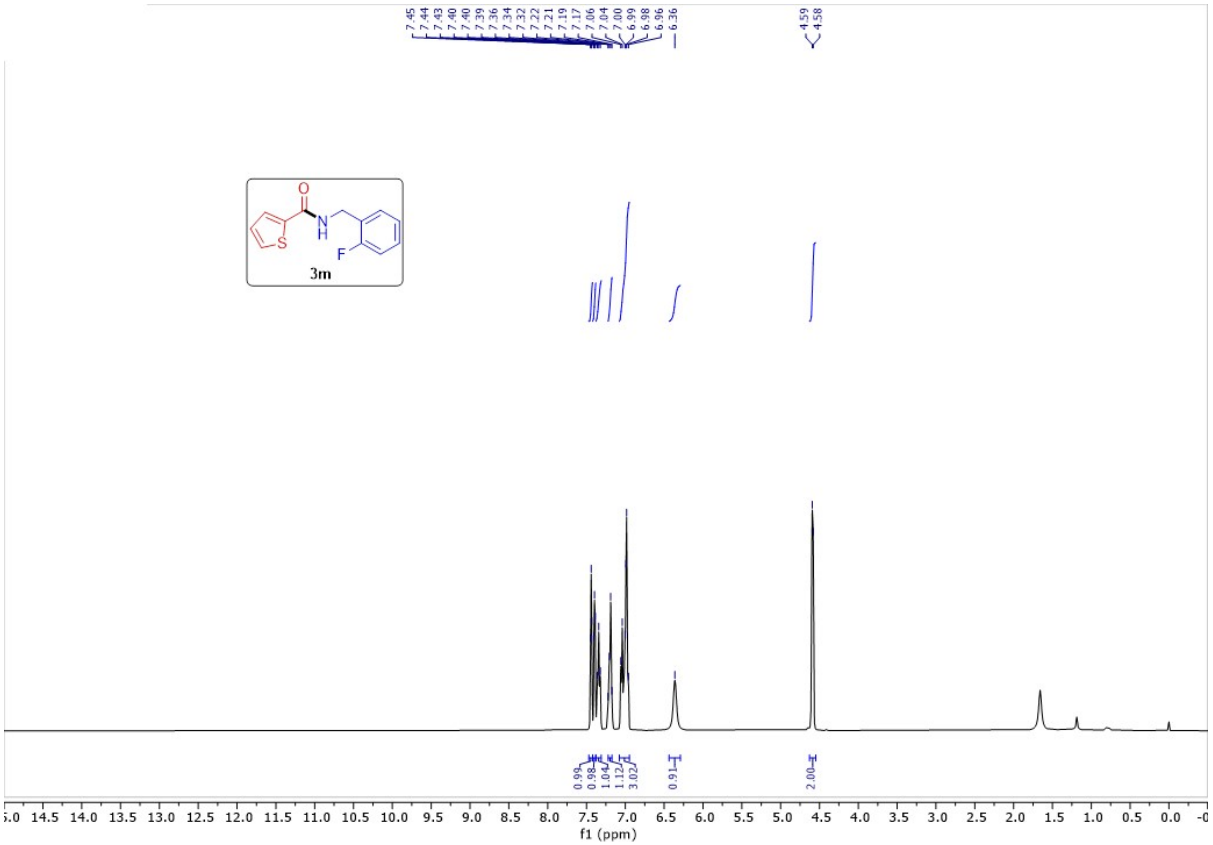

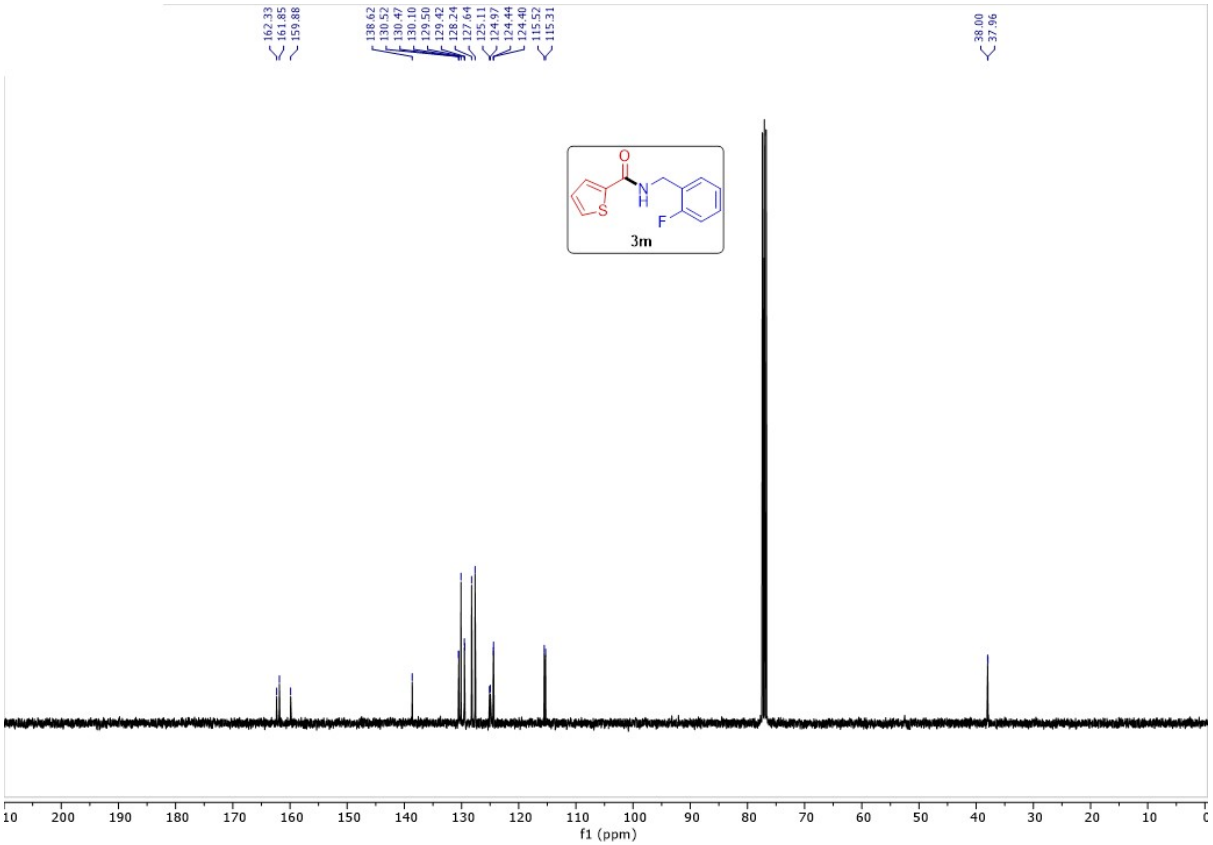

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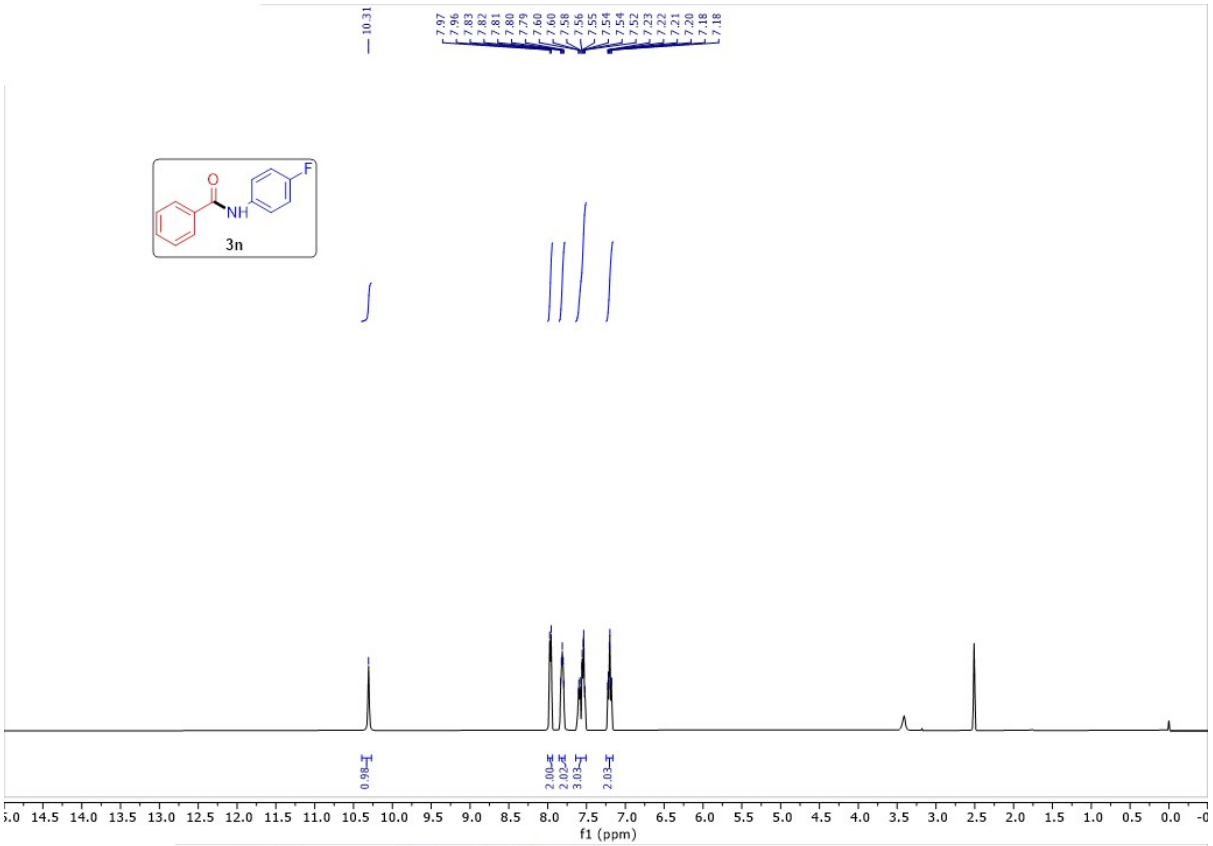
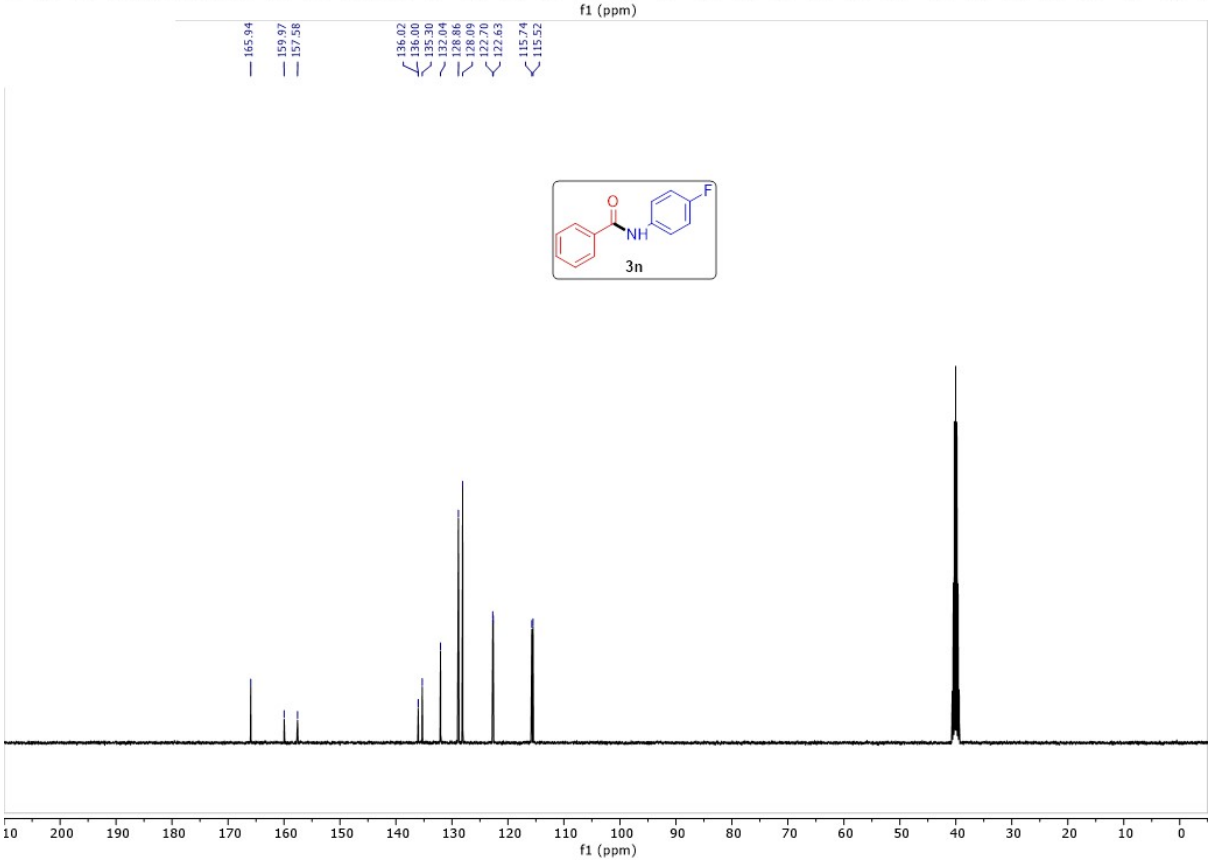
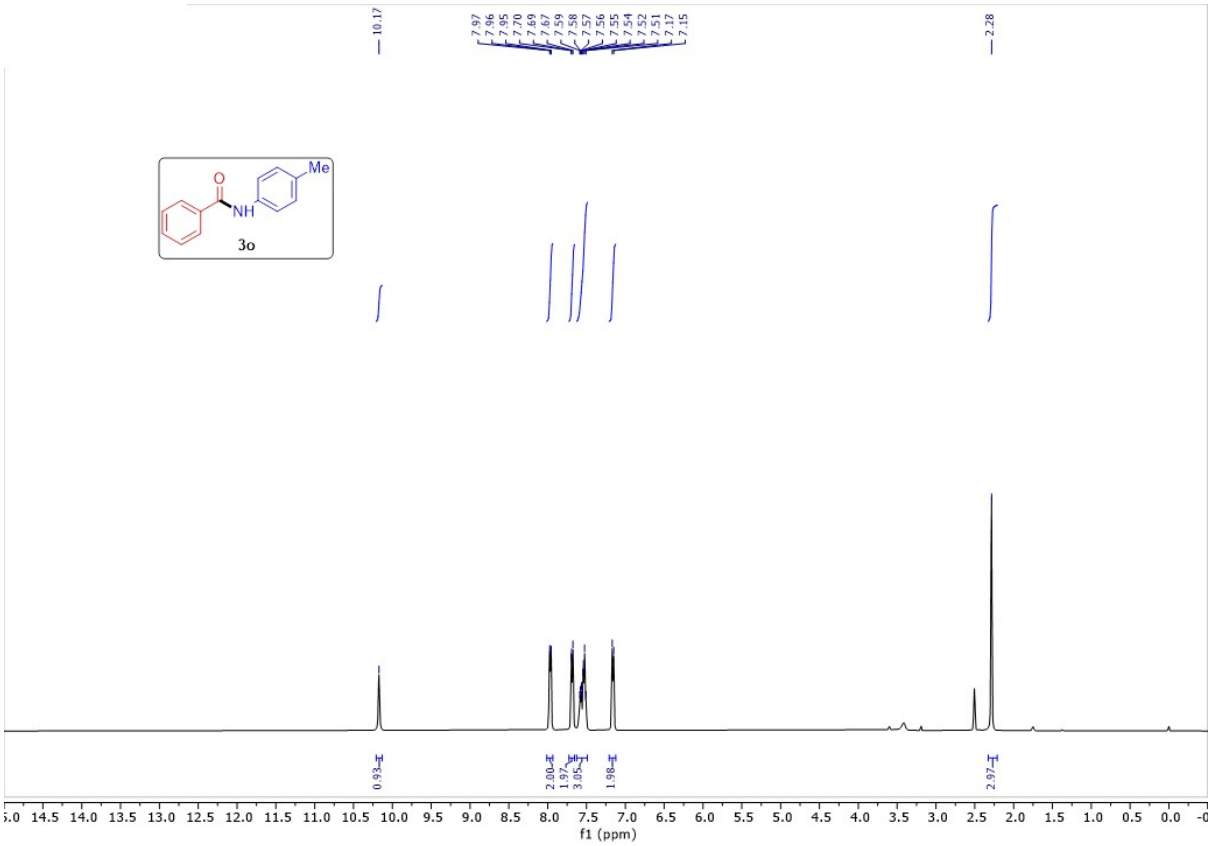
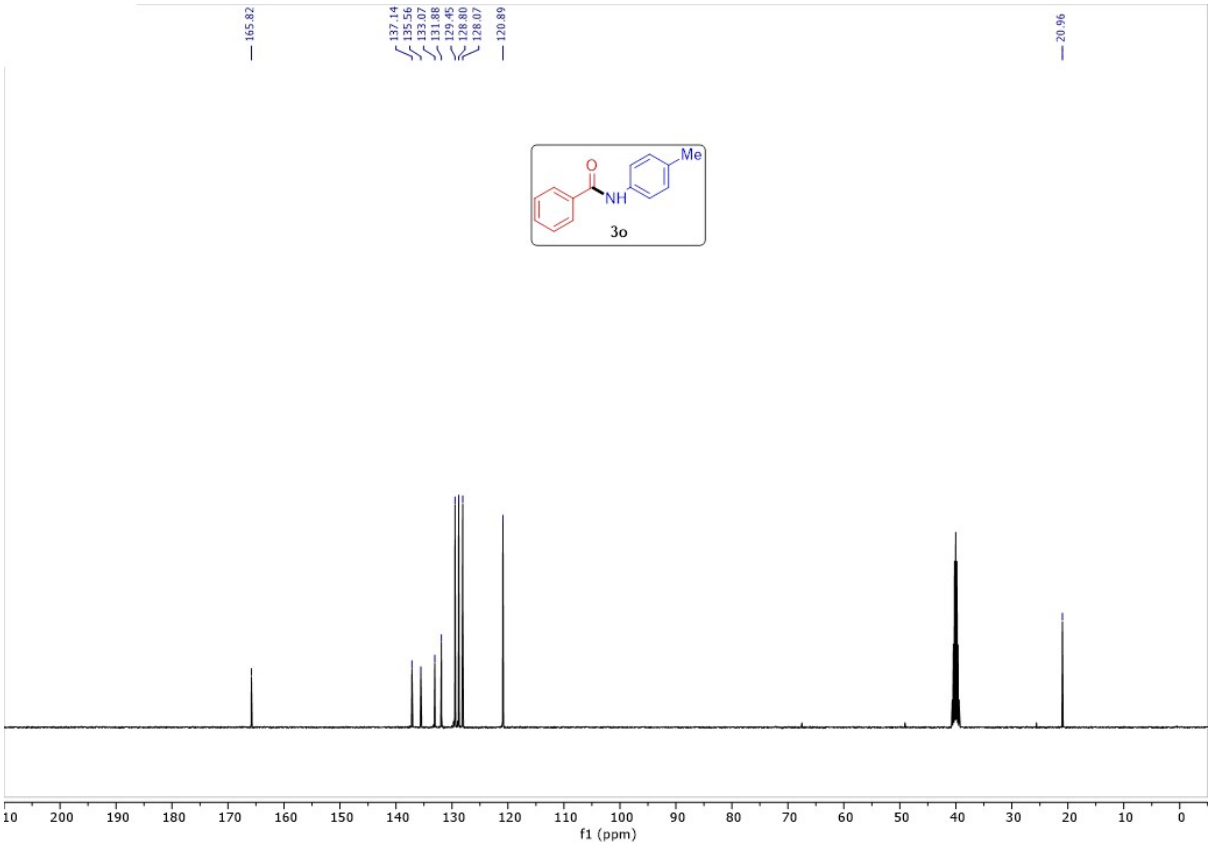


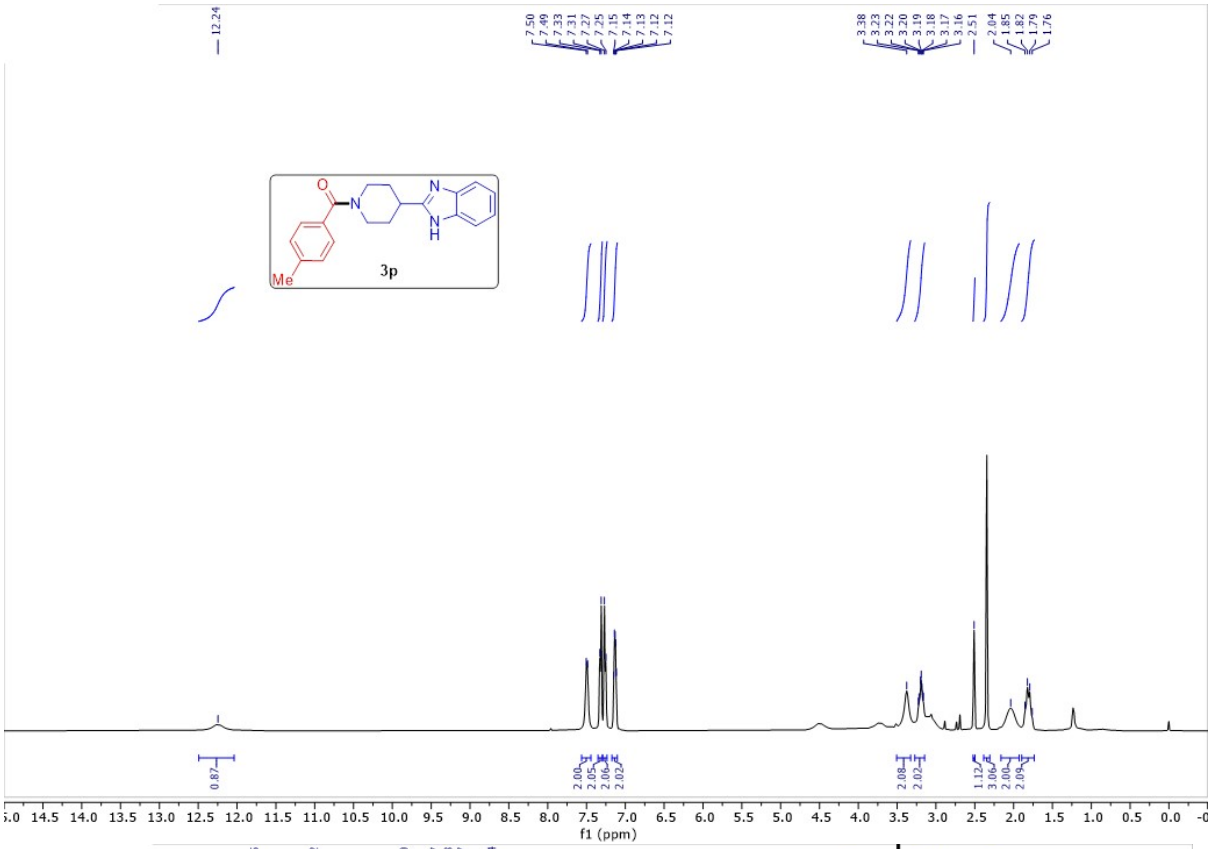


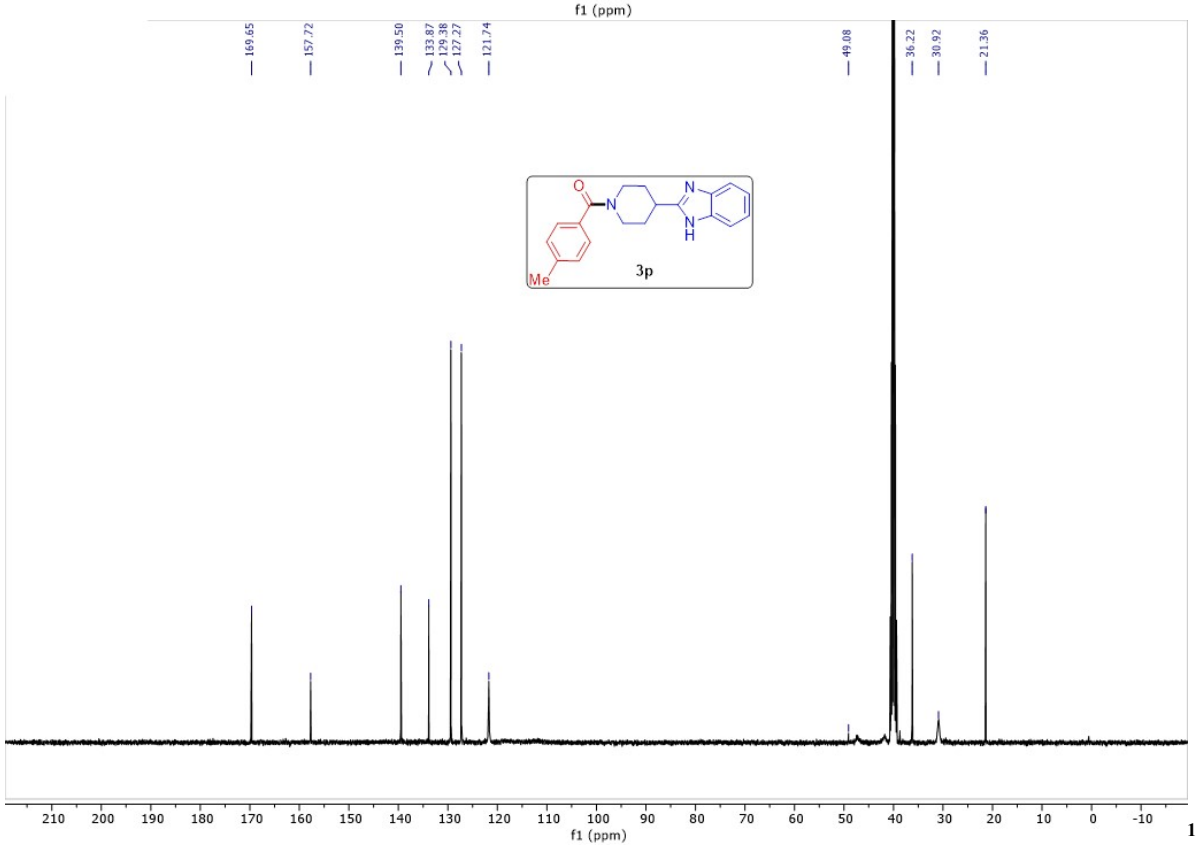
^{1}H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)



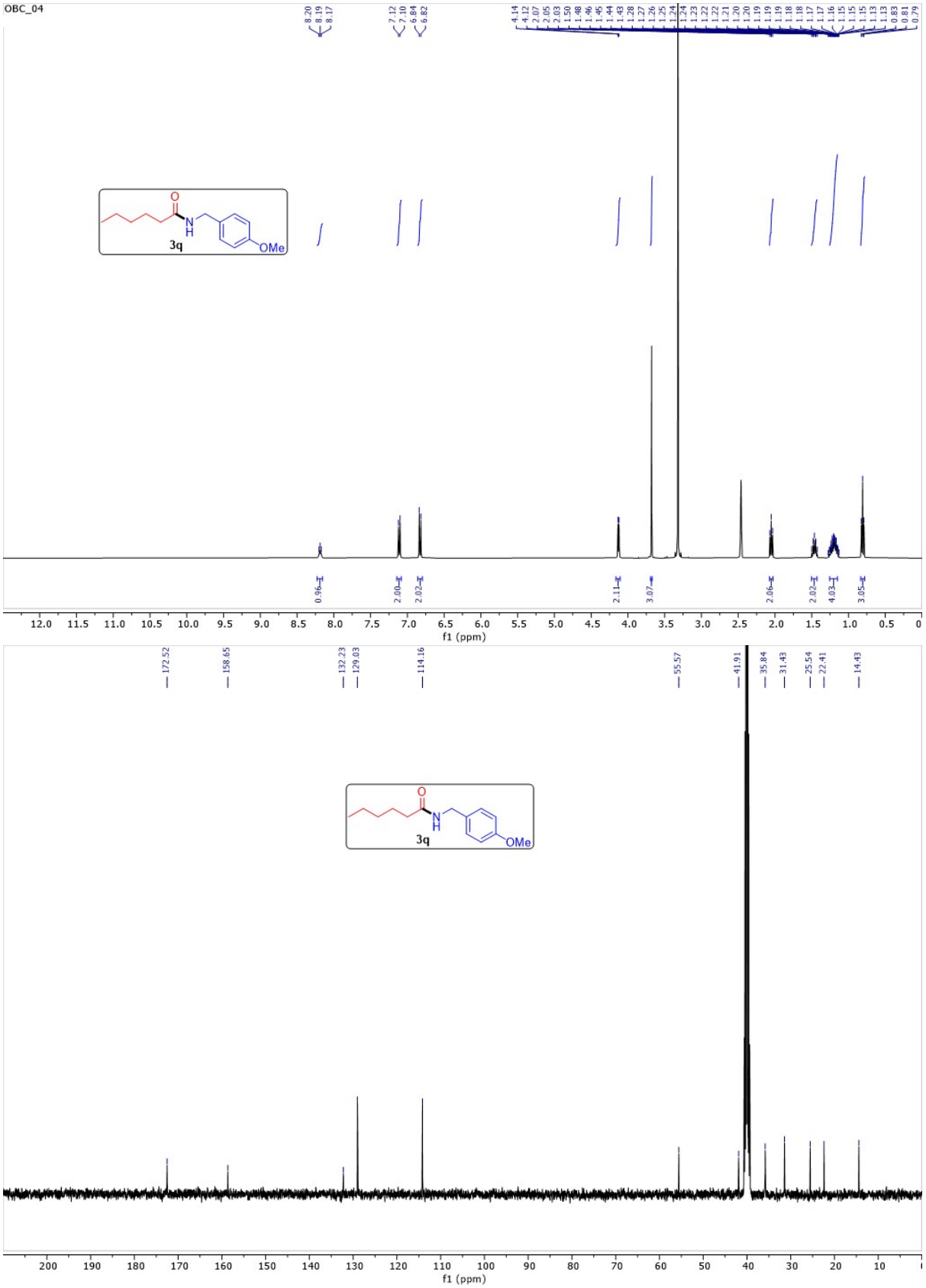


^{1}H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)

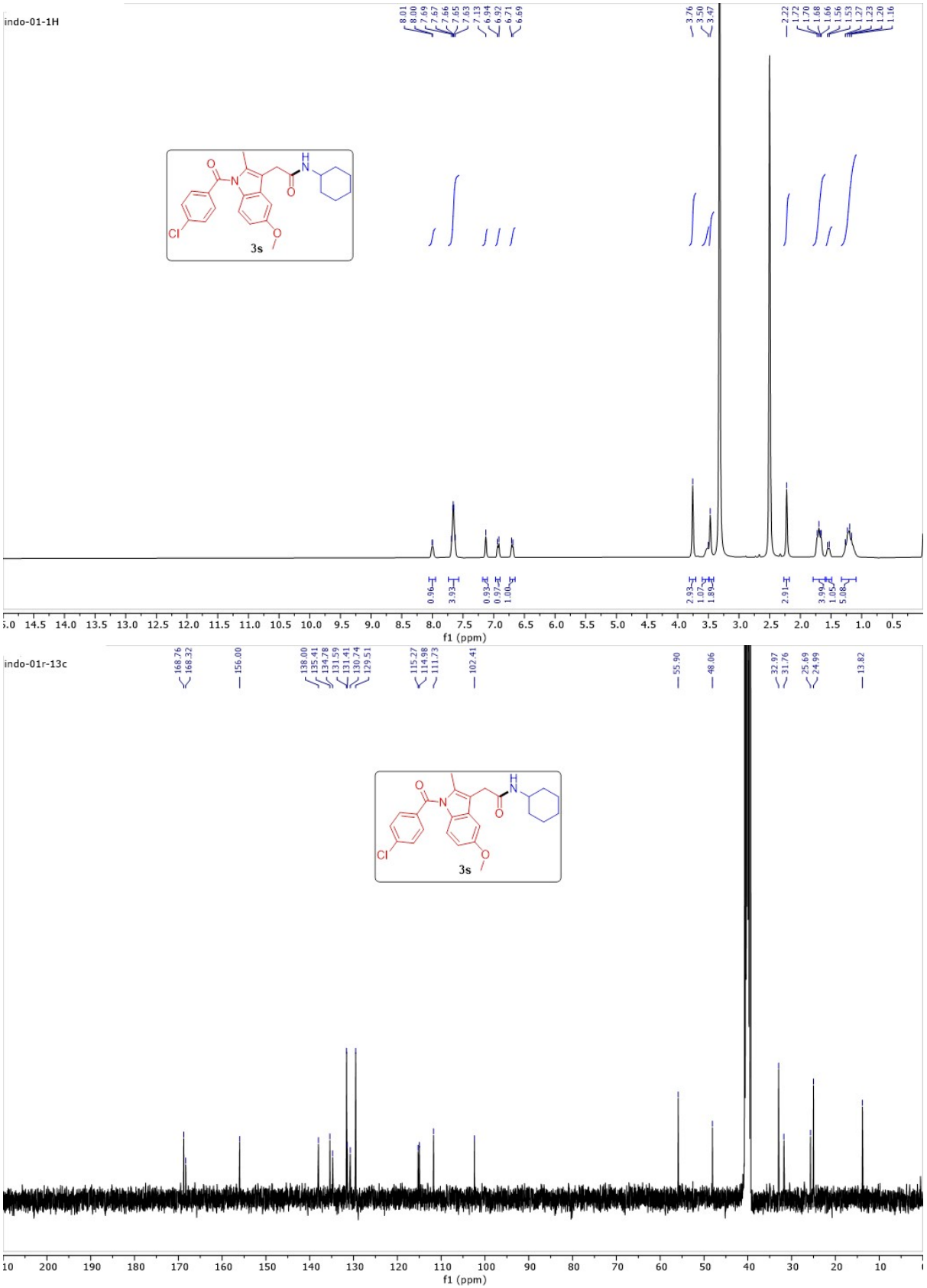




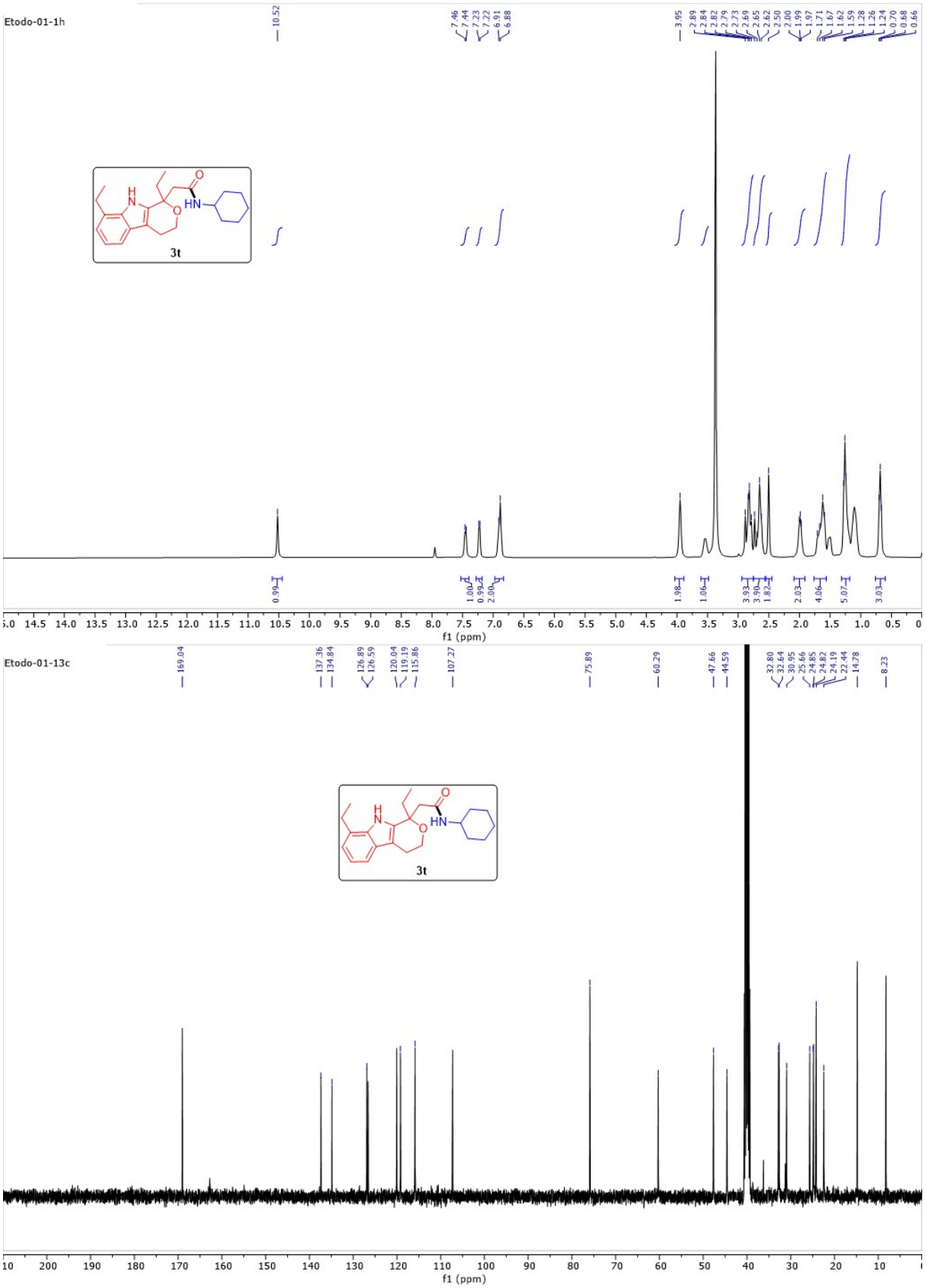
H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)



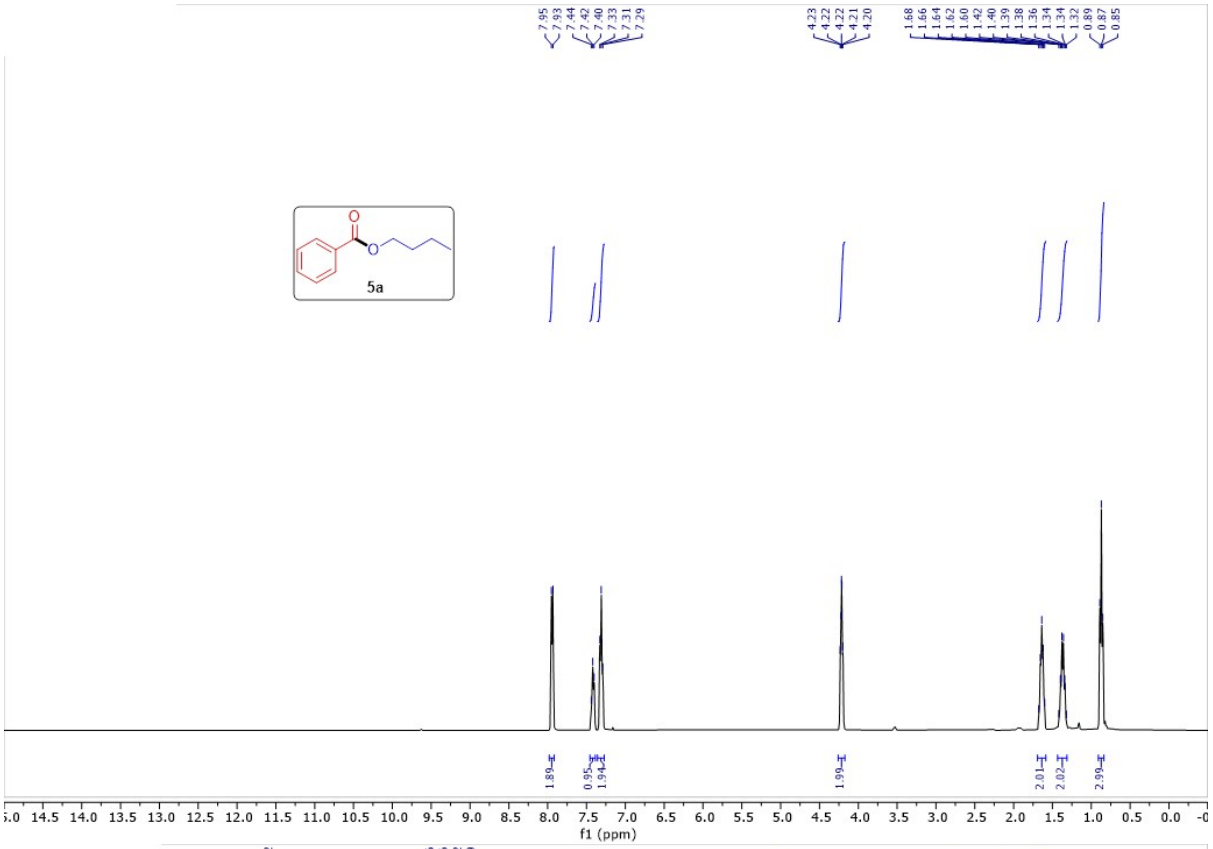
^{1}H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)

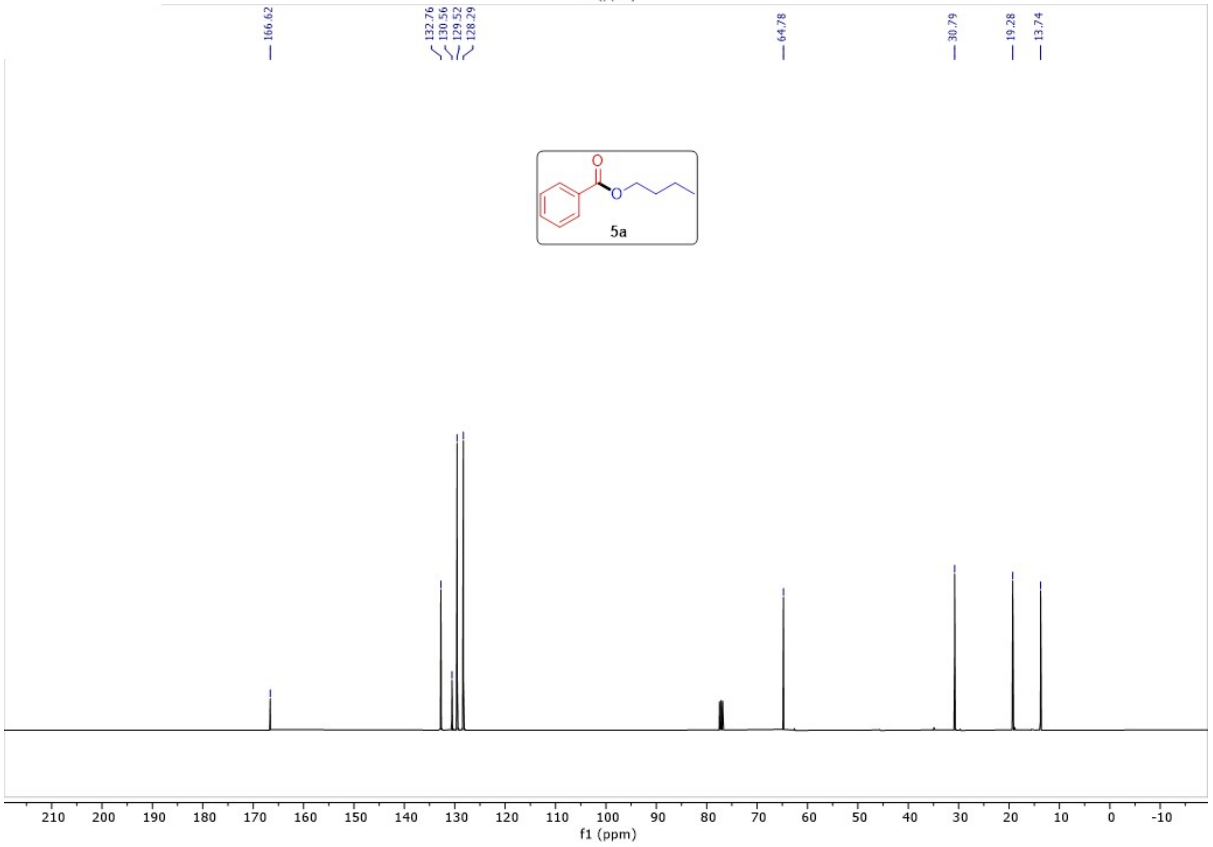


^{1}H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)

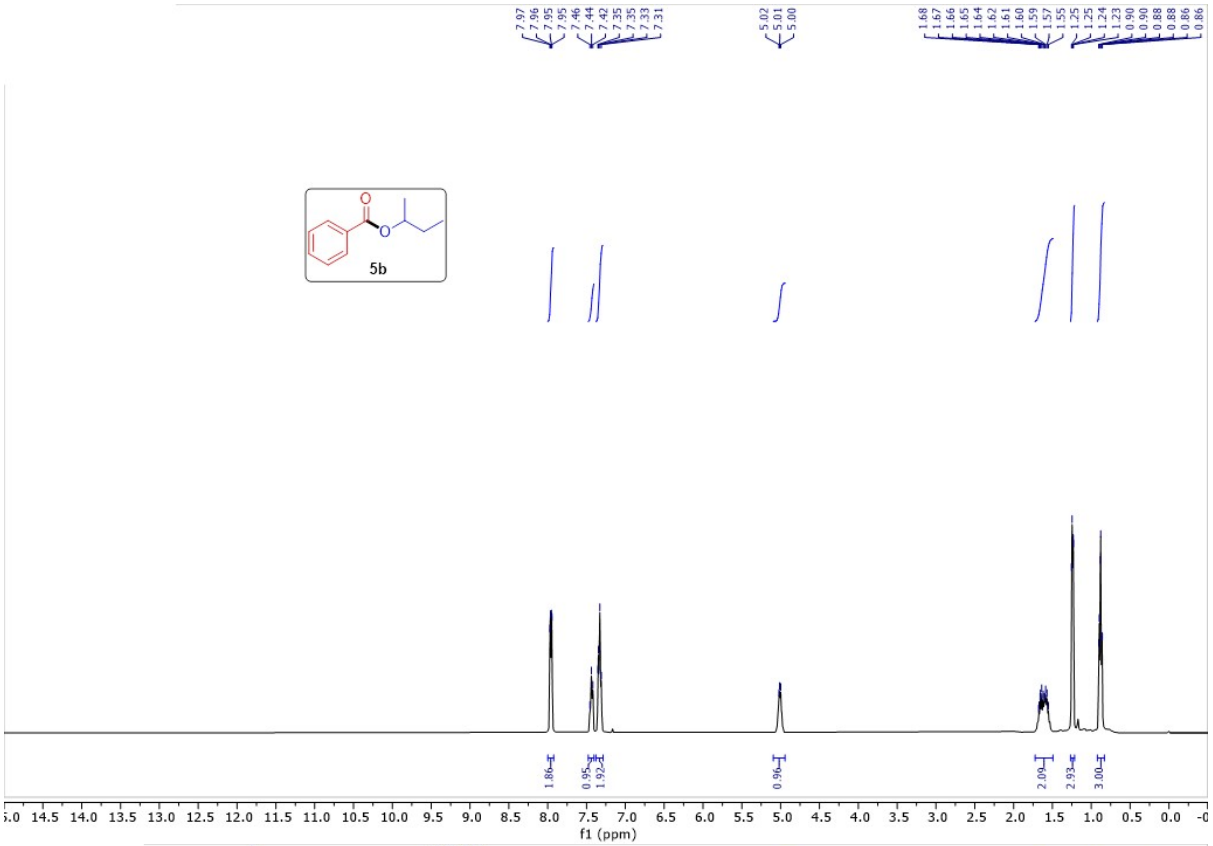


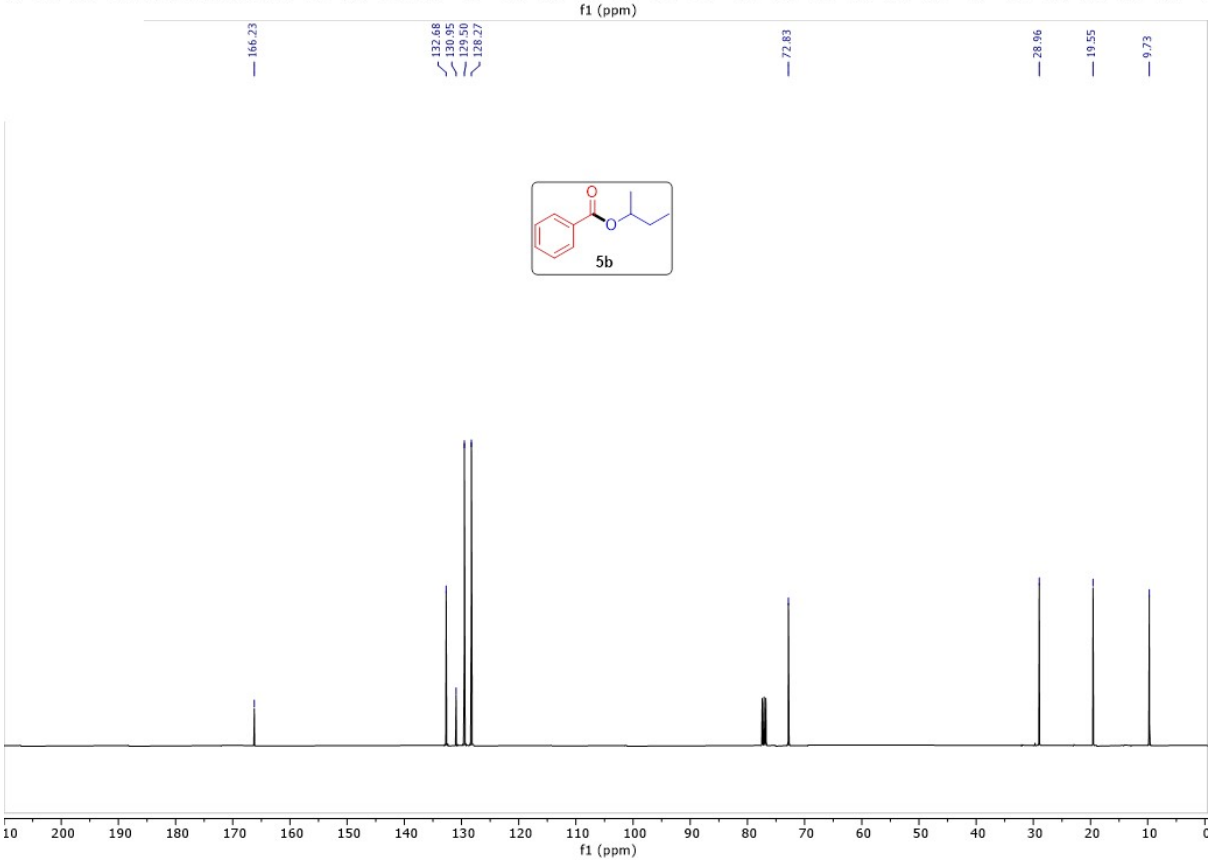
^{1}H (400 MHz, DMSO-d_6); **^{13}C** (101 MHz, DMSO-d_6)



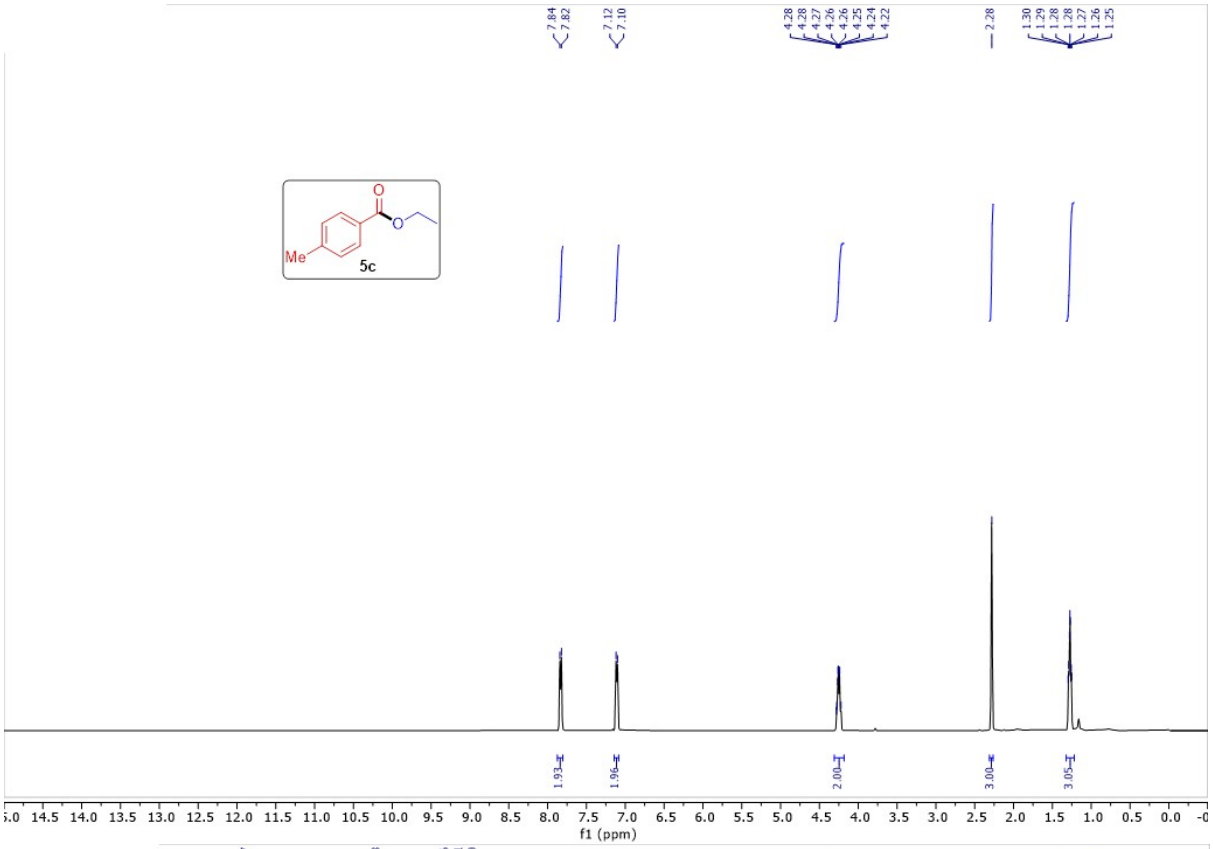


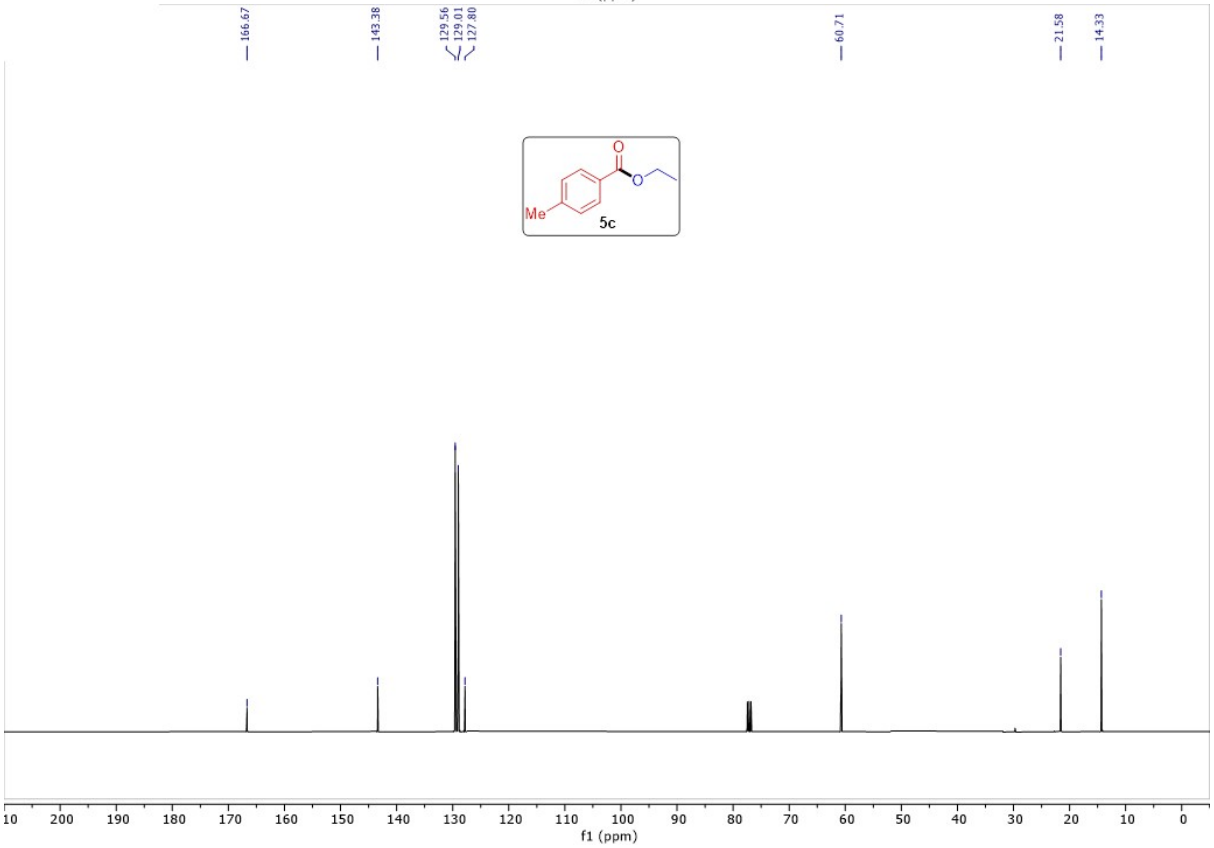
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



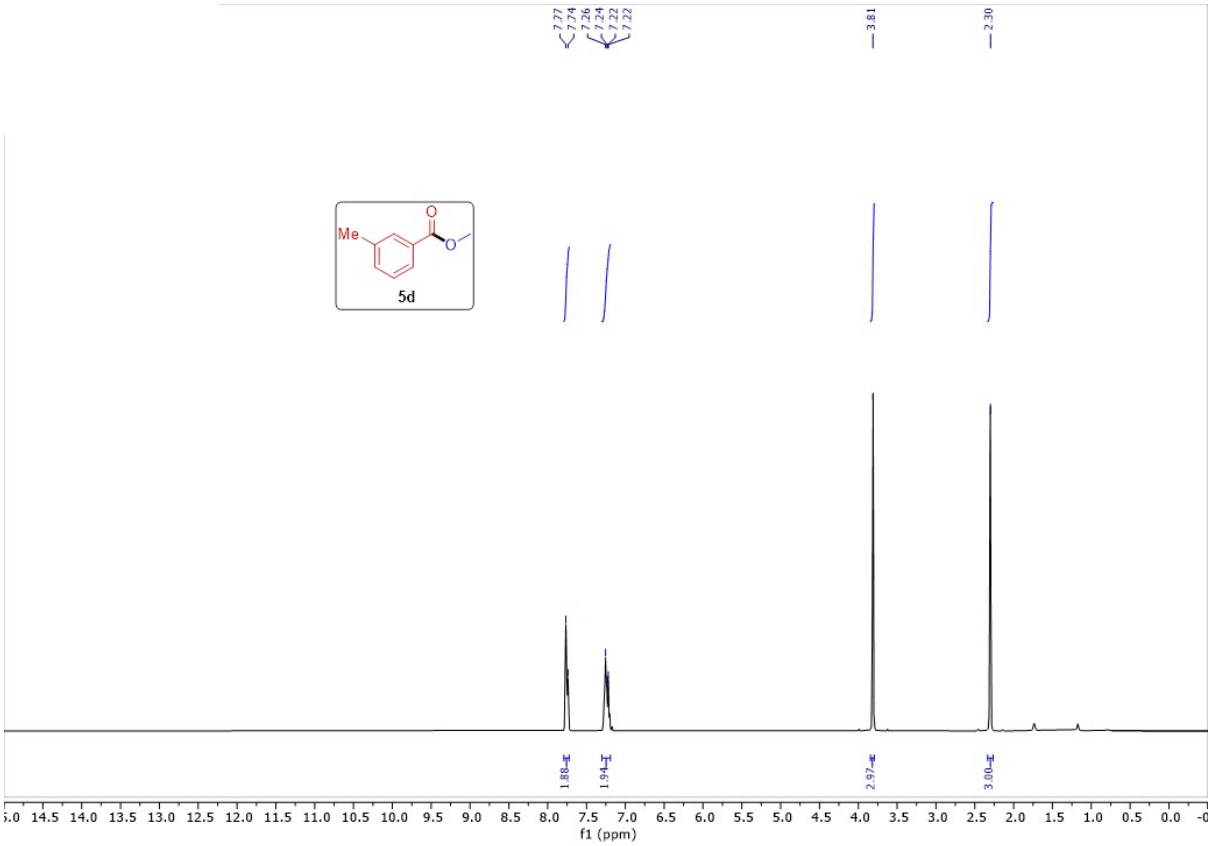


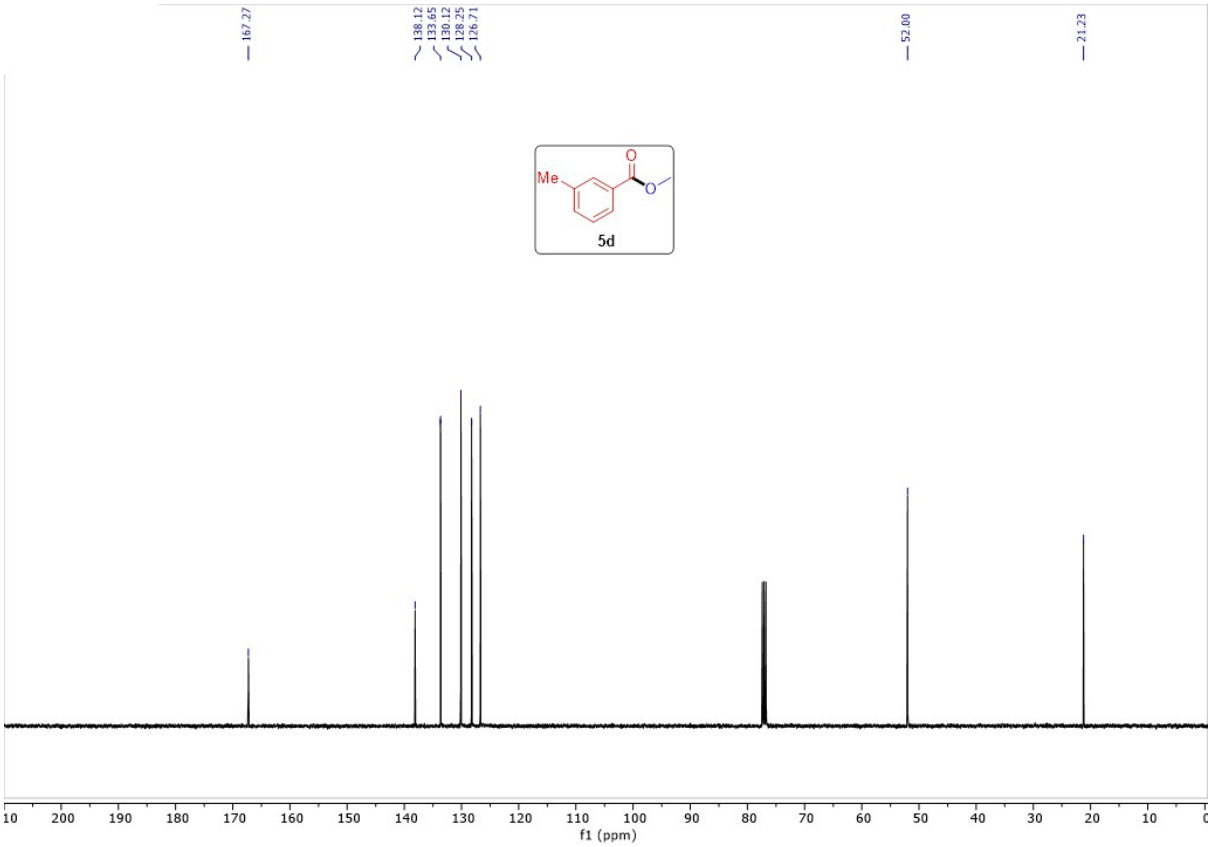
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



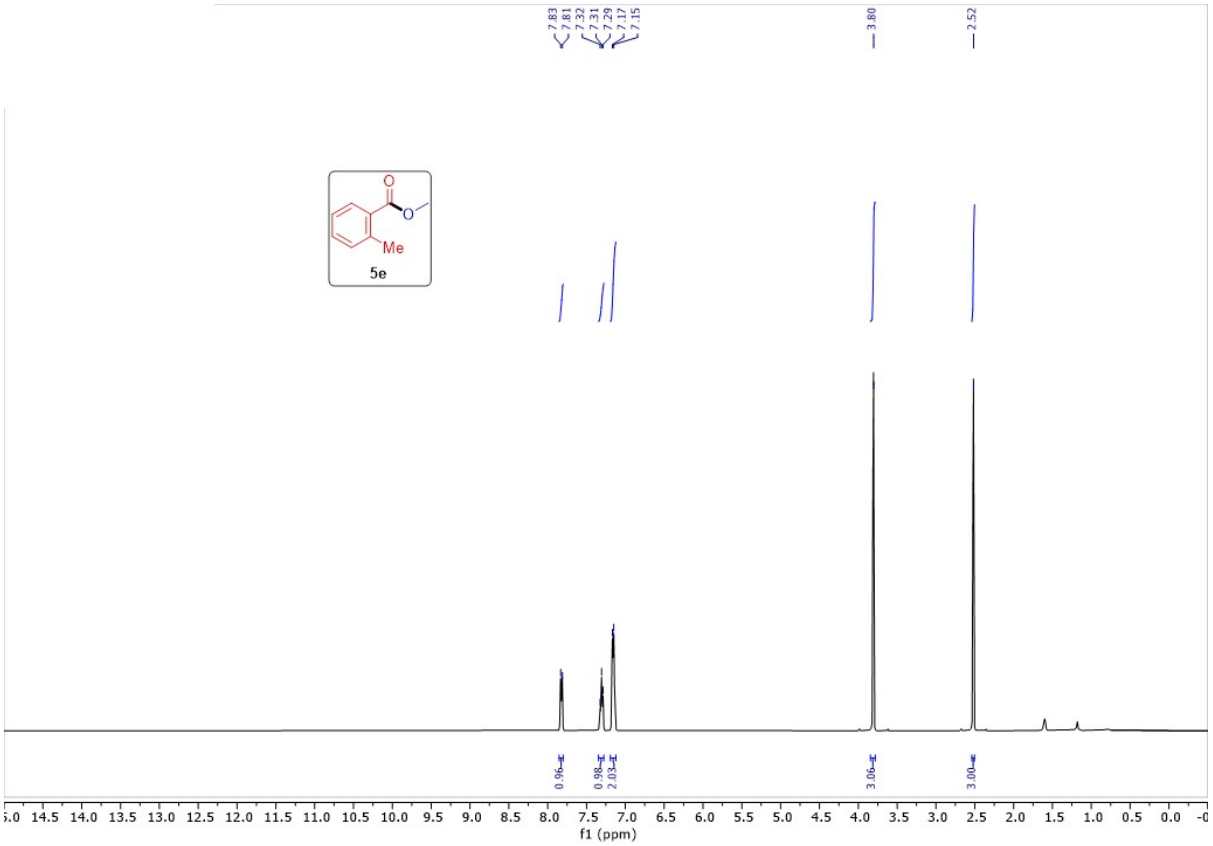


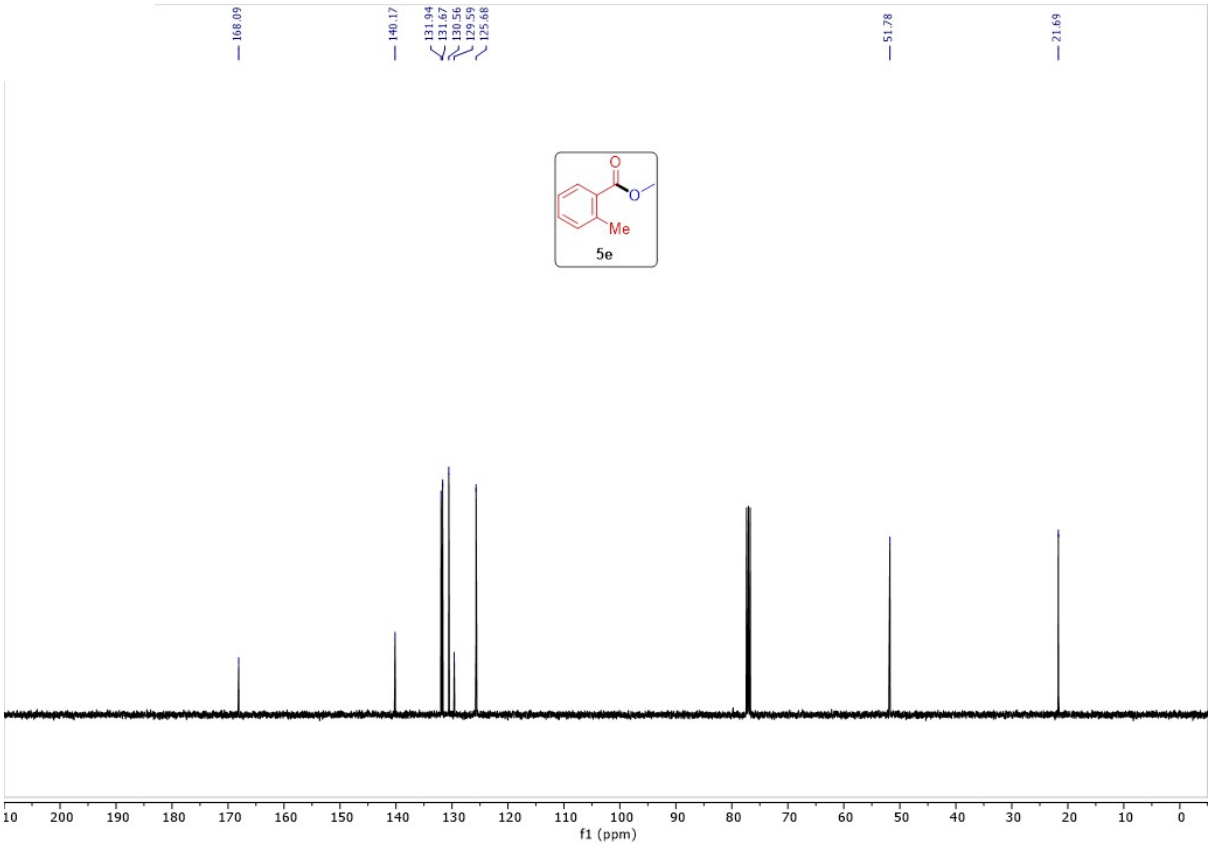
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



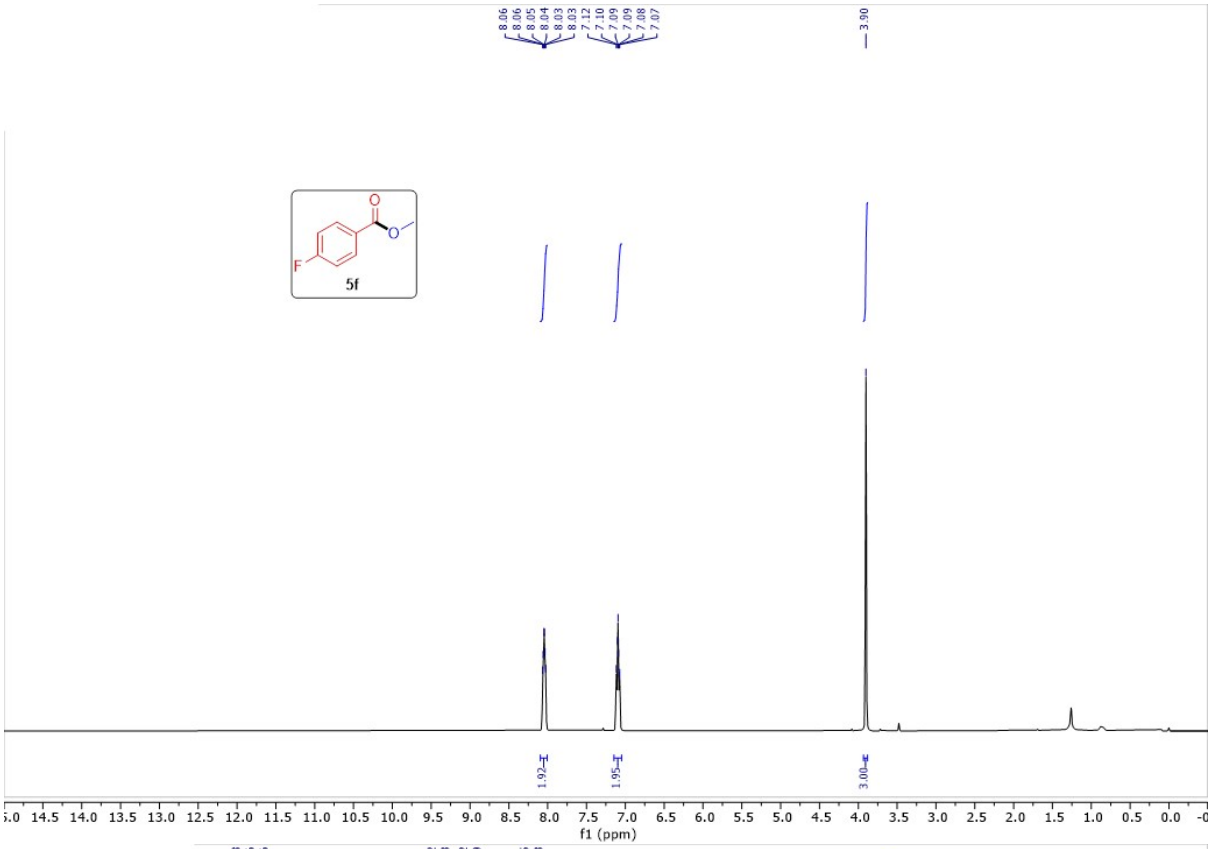


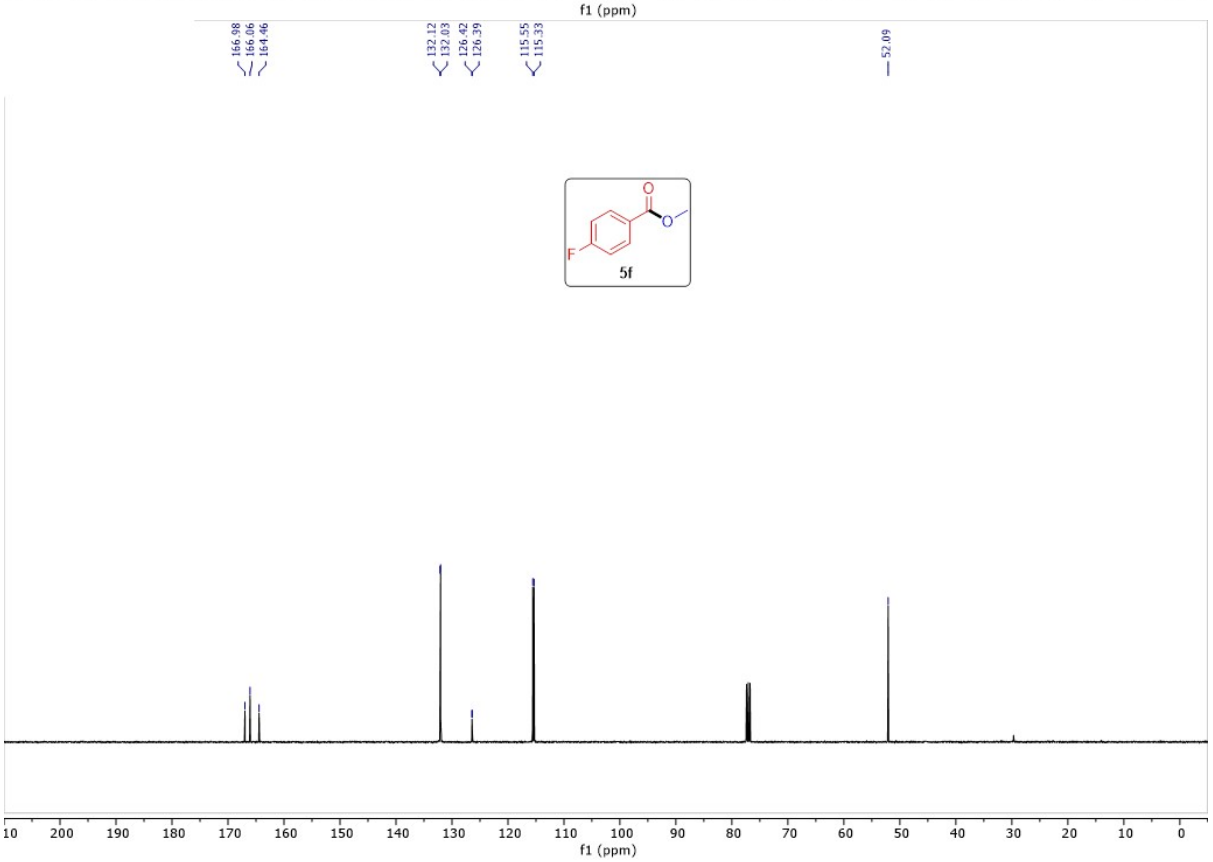
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



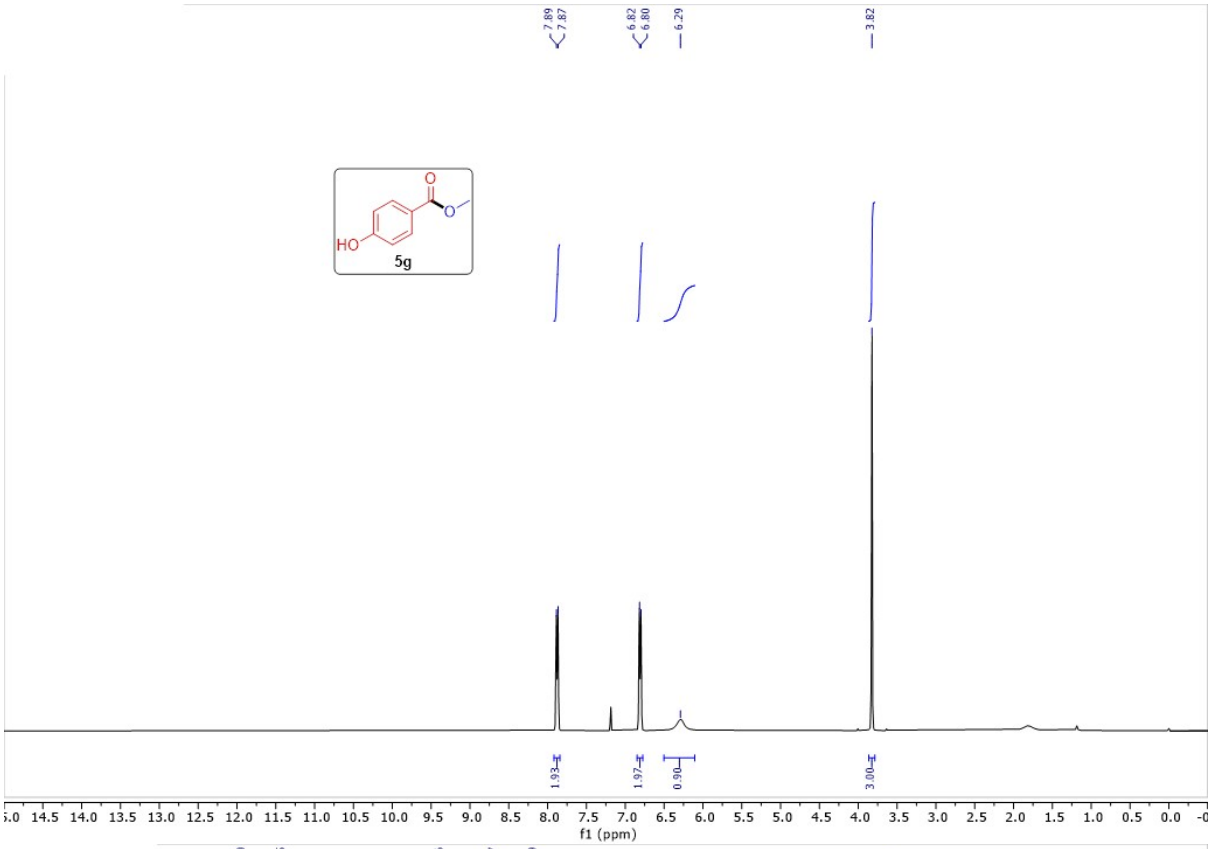


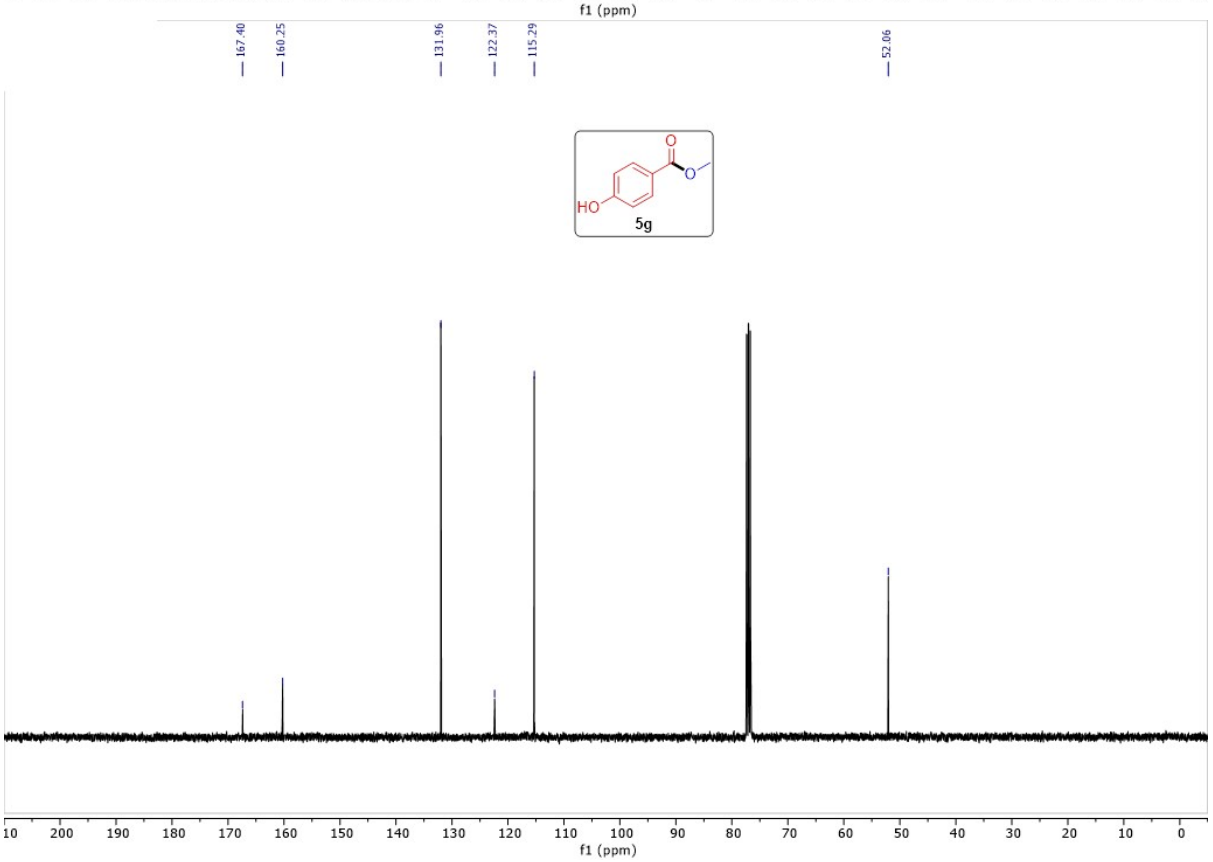
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



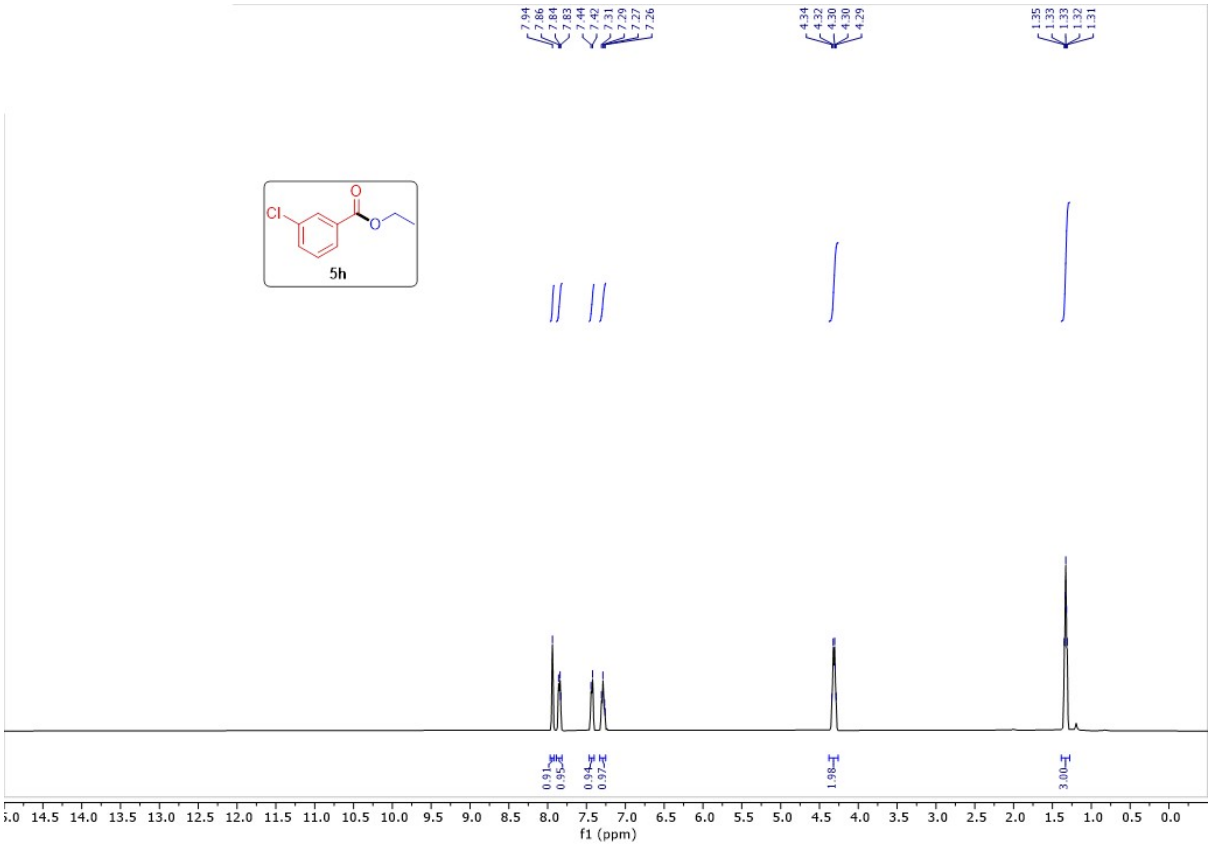


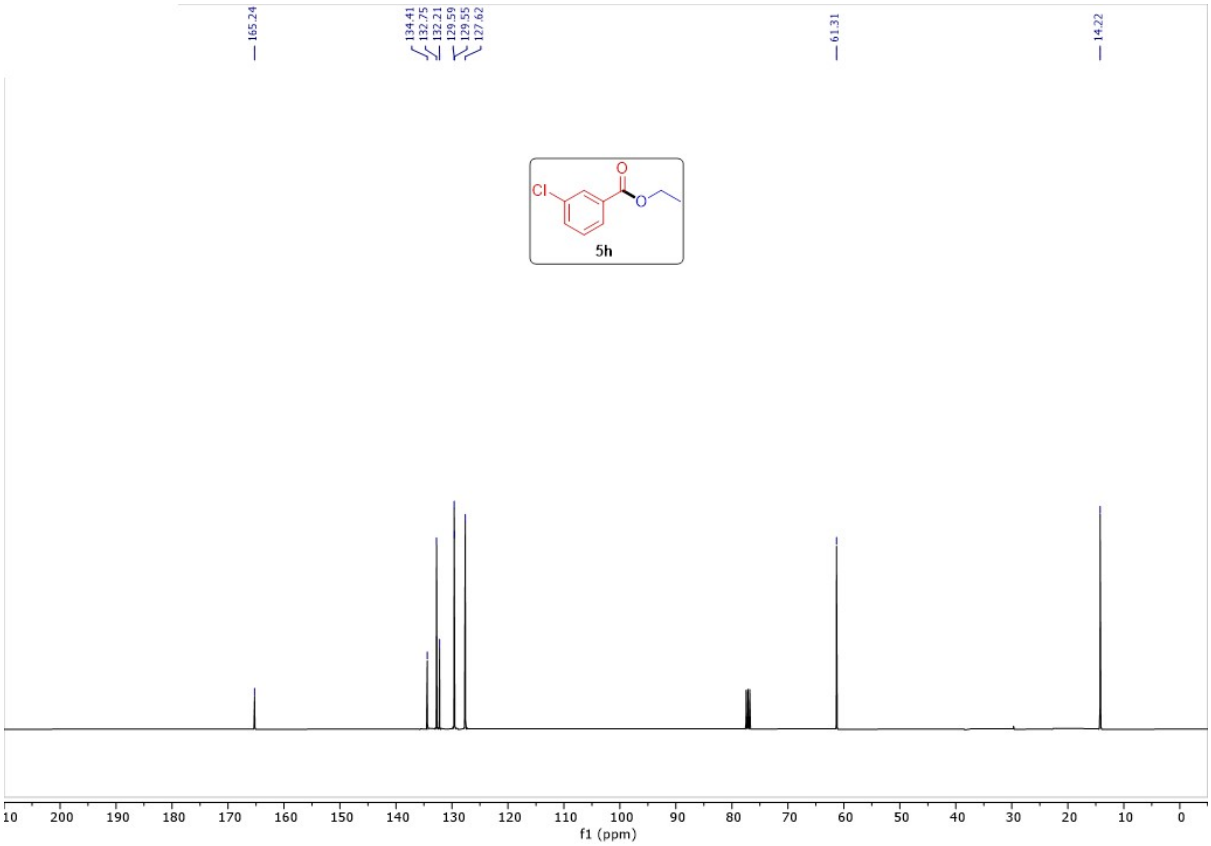
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



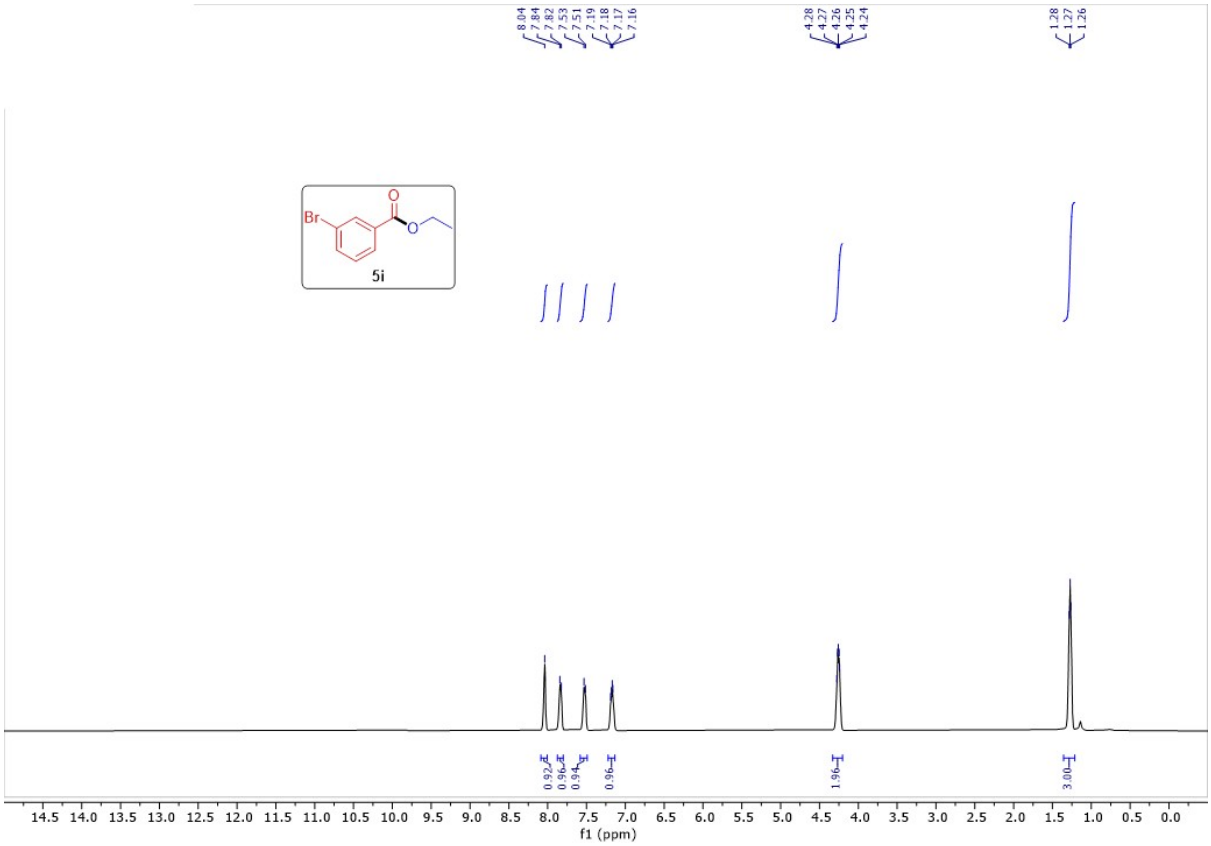


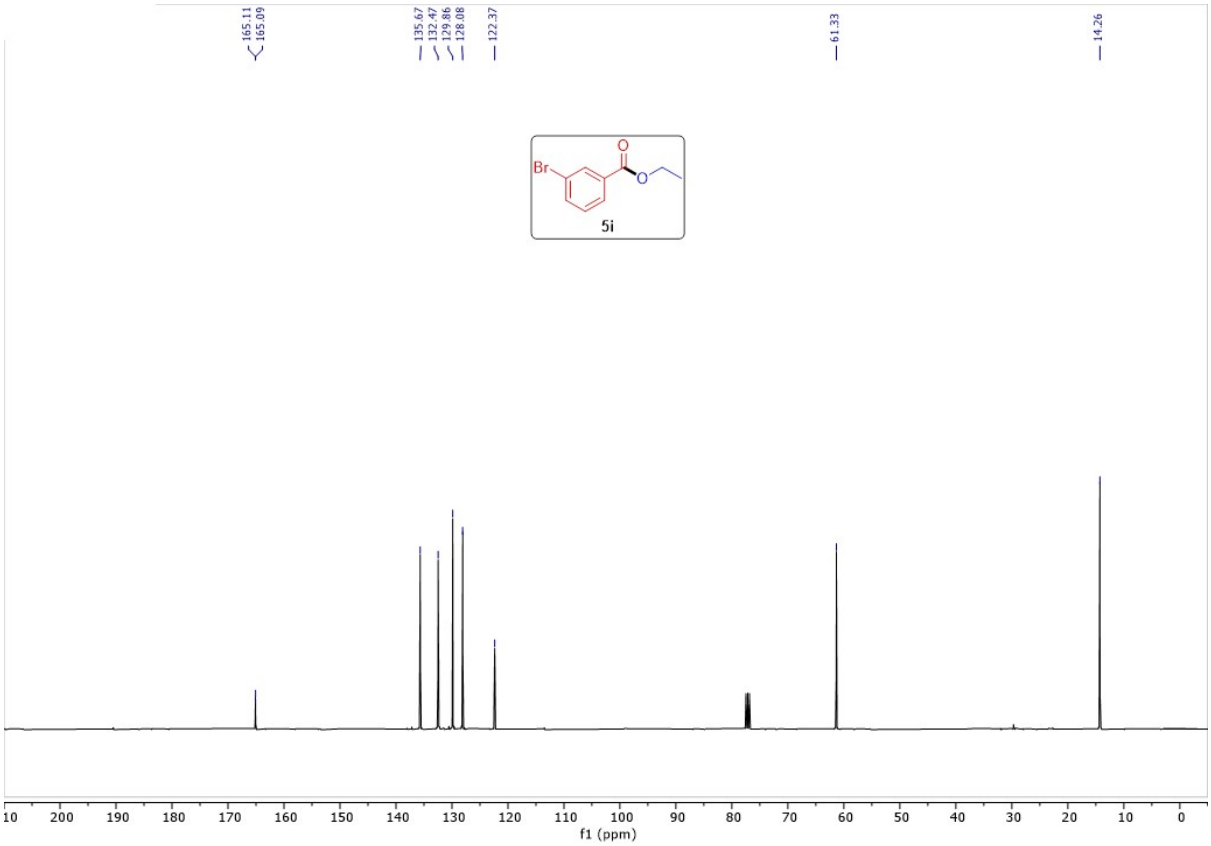
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)



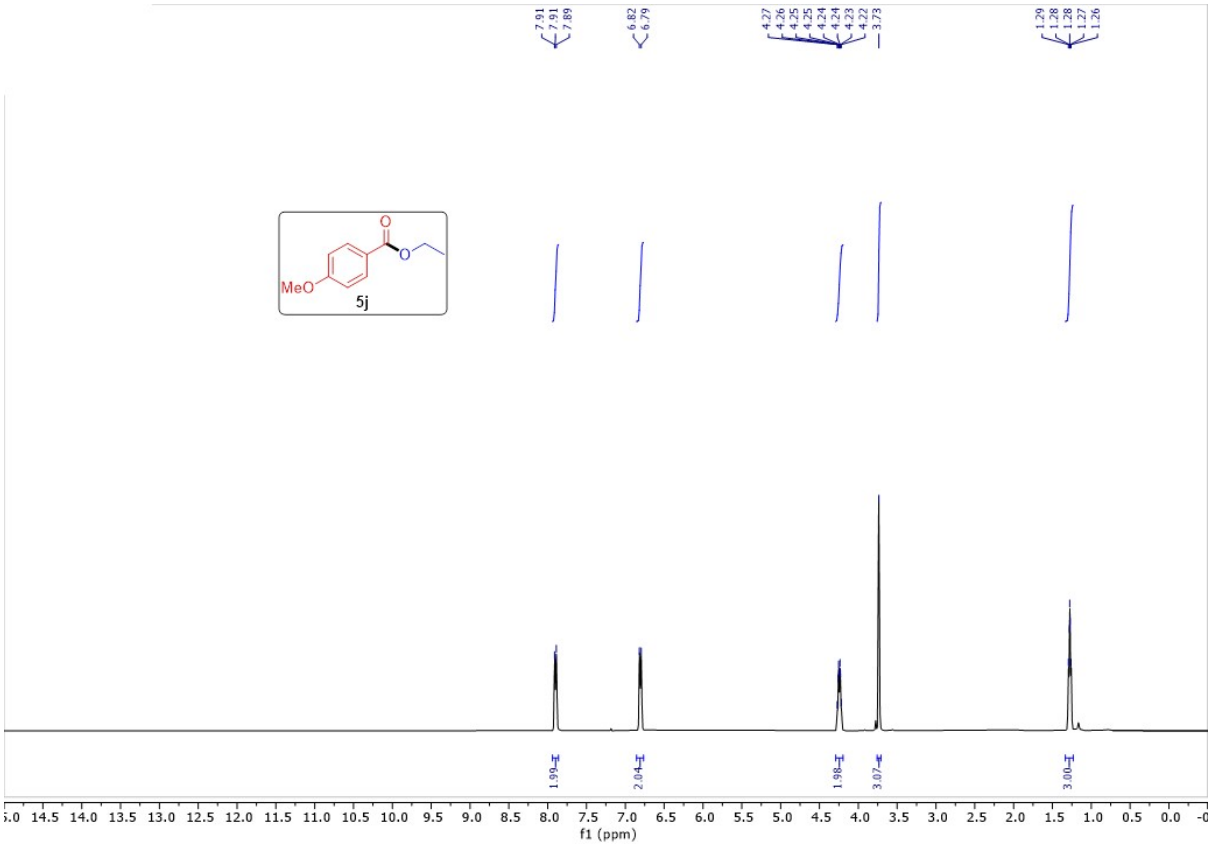


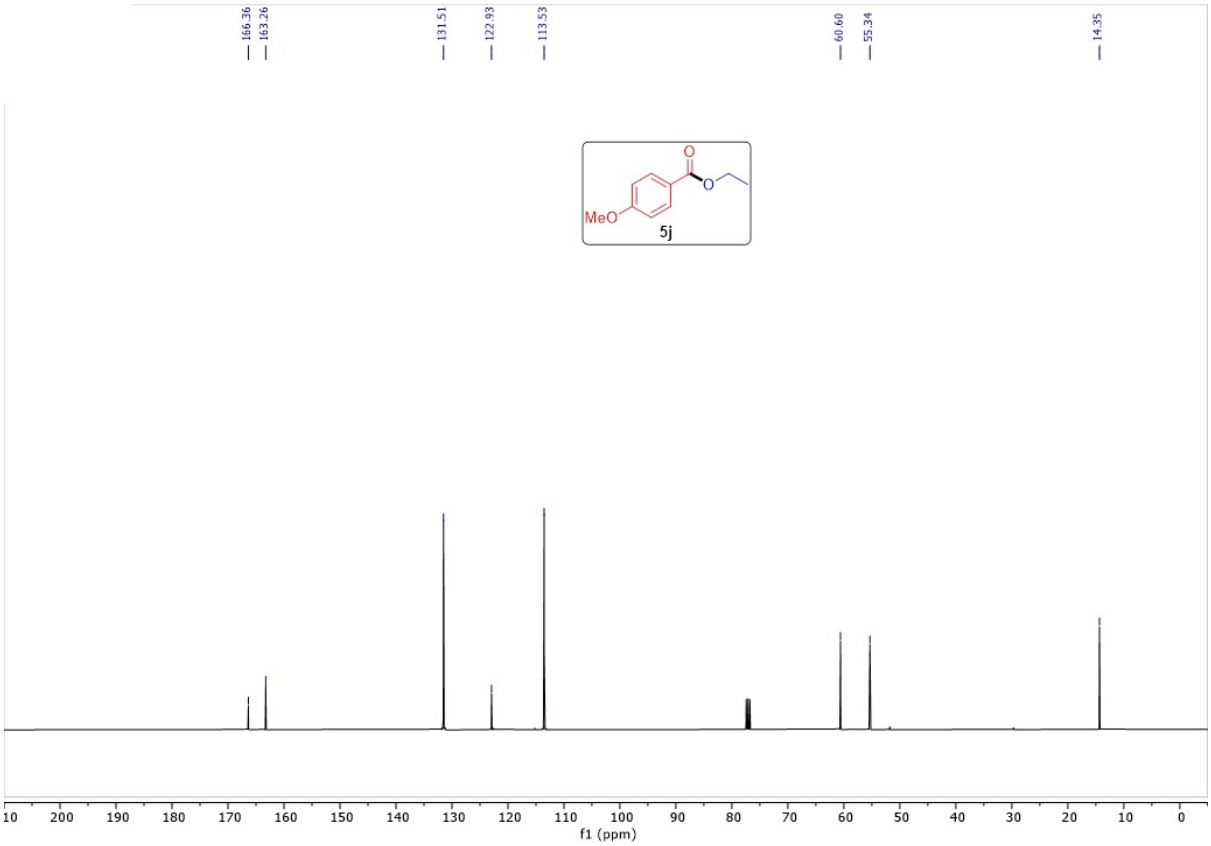
^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





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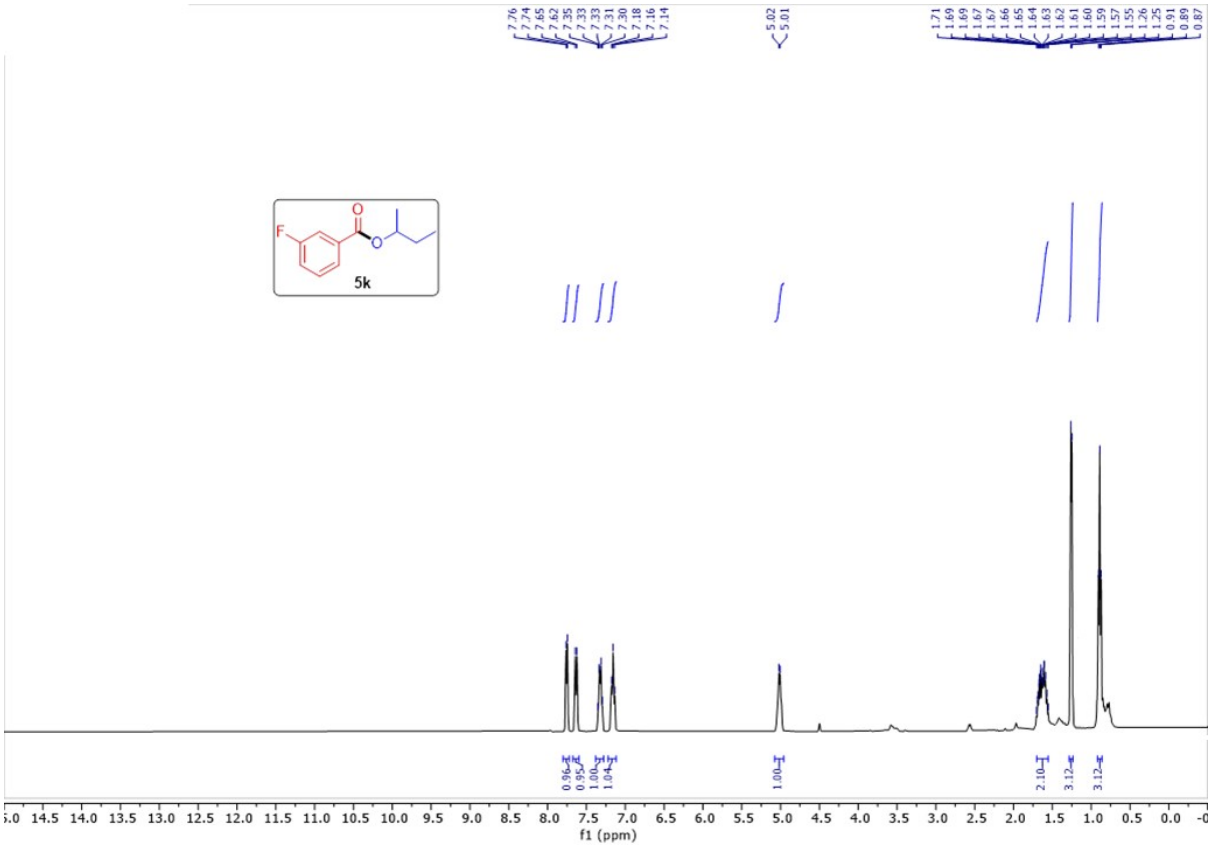

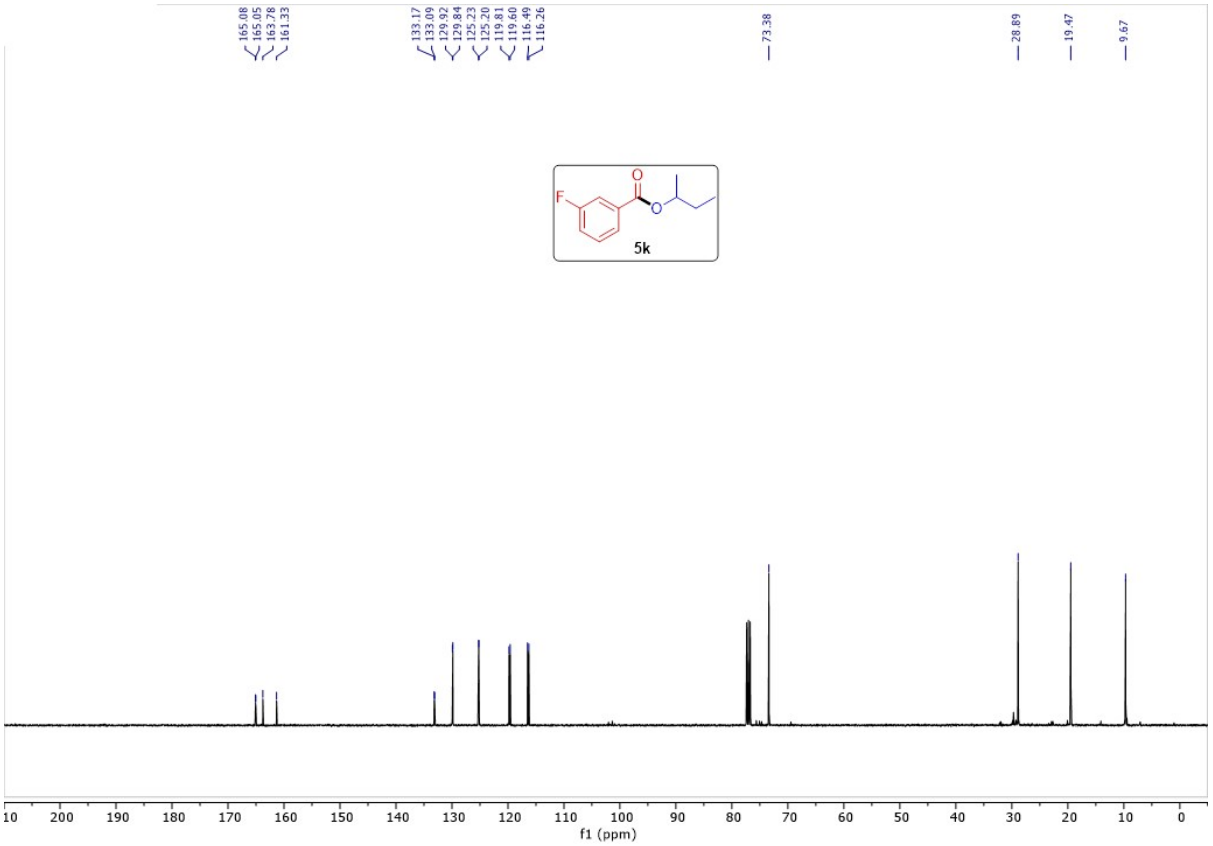

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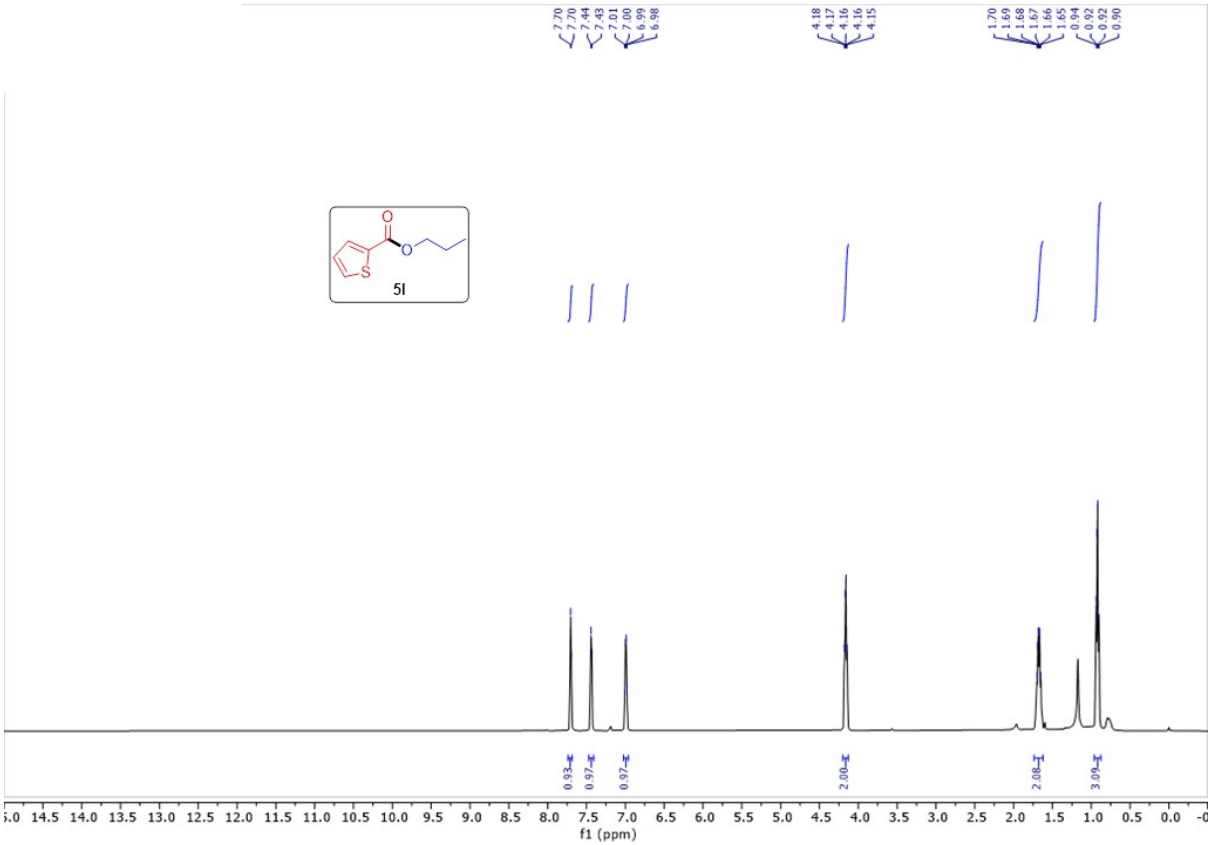
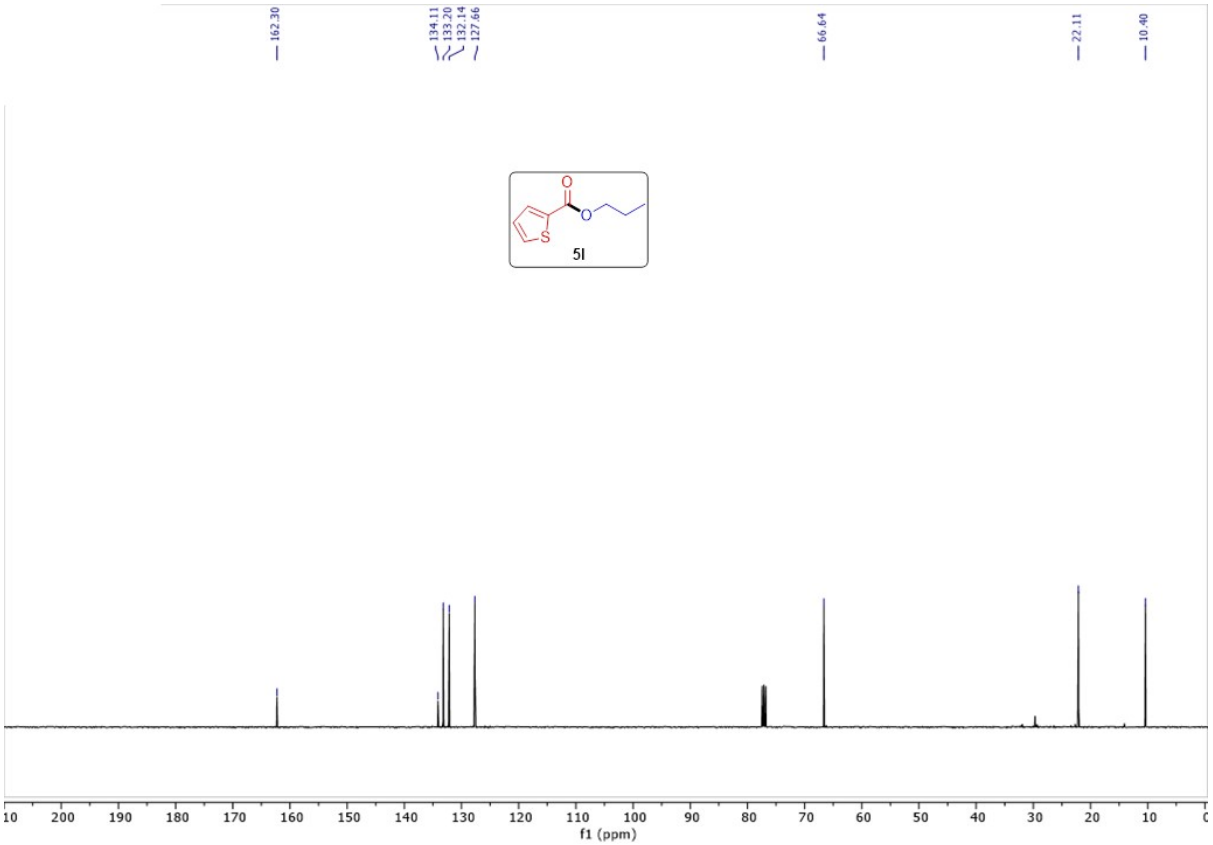
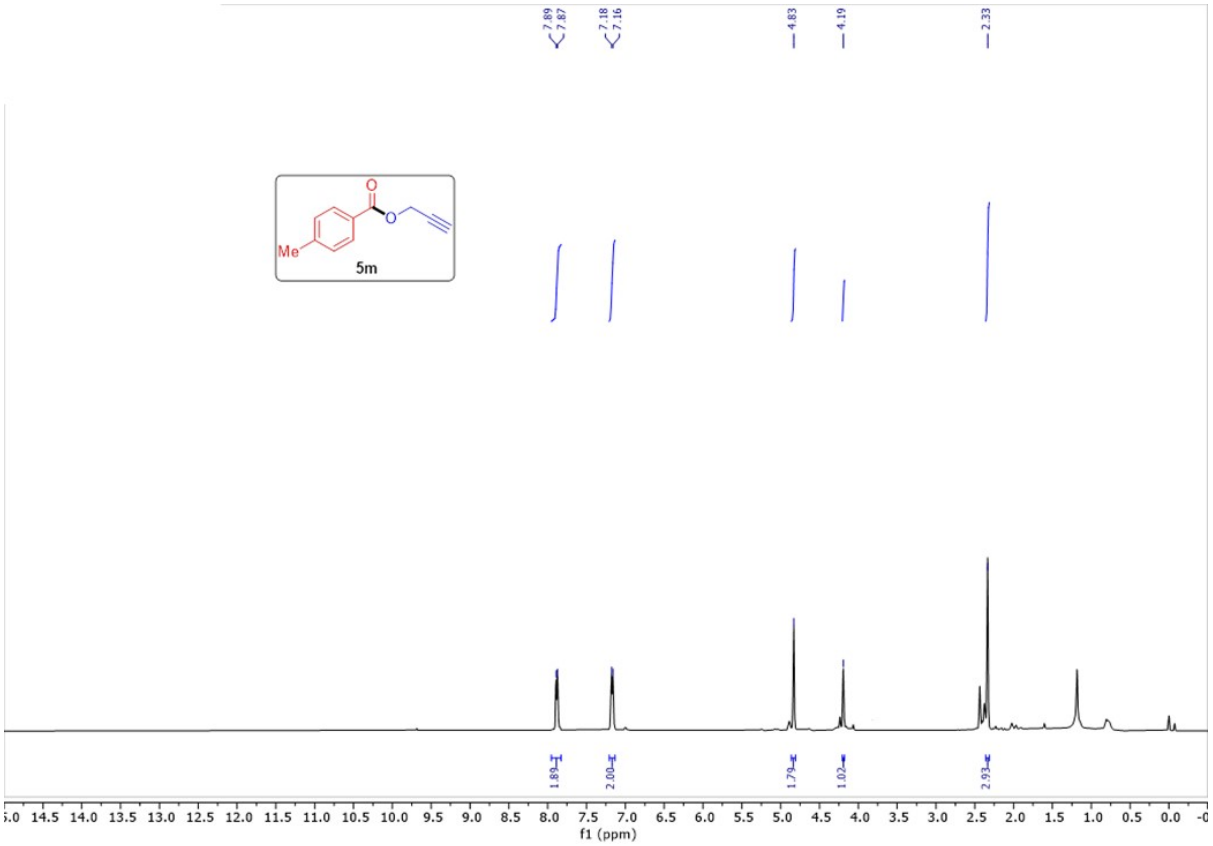
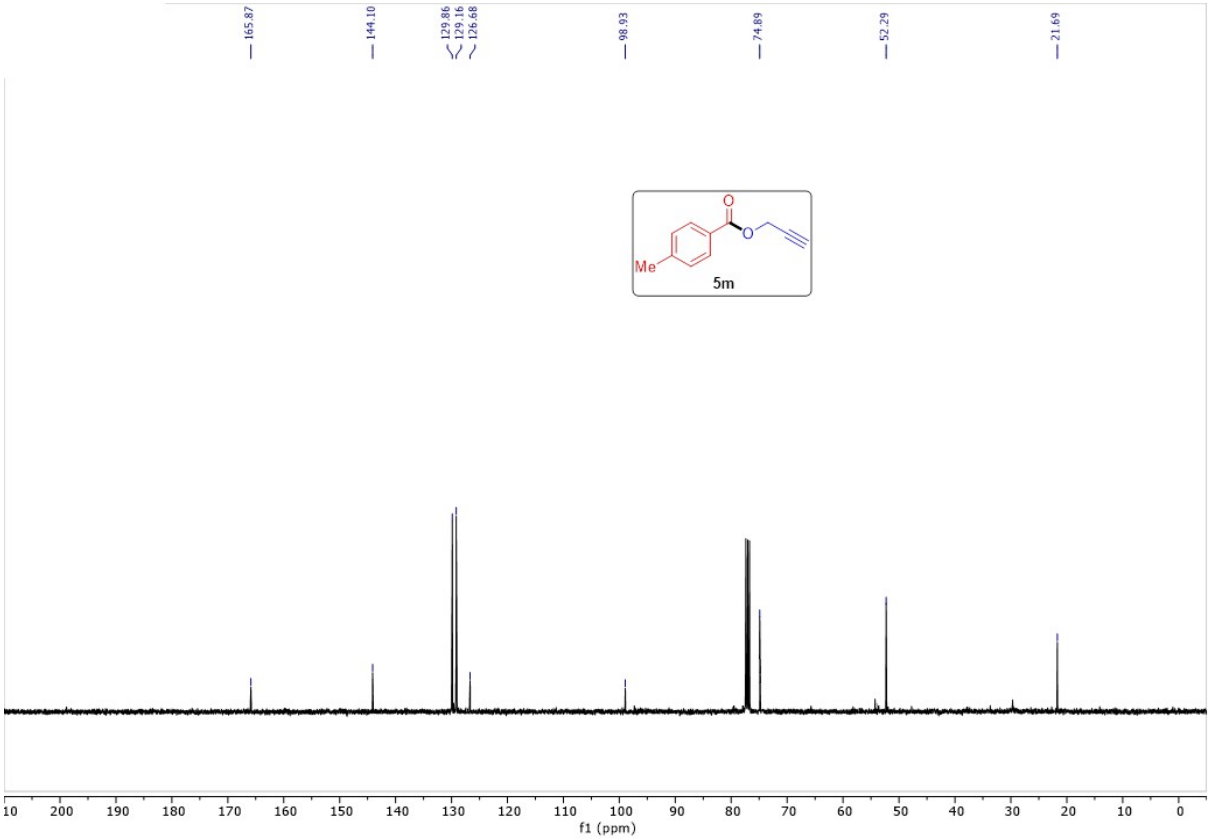




^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)





^{1}H (400 MHz, $CDCl_3$); **^{13}C** (101 MHz, $CDCl_3$)