Silica supported palladium-phosphine as a reusable catalyst for Alkoxycarbonylation and Aminocarbonylation of aryl and heteroaryl iodides

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Supporting Information

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1. General information:

Materials and Methods:

All chemicals and reagents were purchased from Sigma Aldrich, S. D. fine chemical, Alfa Aesar and commercial suppliers. Solvents were purchased with high purity from commercial suppliers and used without purification. Reaction monitor by using Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm, was used for the mass analysis of the products. Products were purified by column chromatography on silca (100-200 mesh). The ^{1}H NMR spectrum was recorded on Bruker- 400 and 500 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. The ^{13}C NMR spectrum was recorded on Bruker-101 and 126 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. The *J* (coupling constant) values were described in Hz. Splitting patterns of proton are depicted as s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC-MS spectra, and/or ^{1}H and ^{13}C NMR spectra with those of authentic data.

2. General procedure for the synthesis of silica supported palladium phosphine complex.

2.1. Preparation of $PdCl_2$_$PPh_2Et@SiO_2$ (I)

The silica supported $PdCl_2$_PPh_2Et was prepared as, in 100 ml round bottom flask 0.372 g of $PdCl_2$ and 3.0 g of PPh_2EtSiO_2 (Aldrich 538019-5G, 2-diphenylphosphinoethyl functionalized silica, 0.7 mmol/g) were mixed, stirred and refluxed with acetonitrile under nitrogen atmosphere for 48 hours. The material showing yellow was filtered with 0.45 μm PTFE filter, washed with acetonitrile several time and dried at room temperature. The metal loading of $PdCl_2$_$PPh_2Et@SiO_2$ was 6.6 wt% as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.).

2.2. Preparation of $Pd(OAc)_2$_$PPh_2Et@SiO_2$ (II)

The silica supported $Pd(OAc)_2$_PPh_2Et was prepared as, in 100 mL round bottom flask 0.472 g of $Pd(OAC)_2$ and 3.0 g of PPh_2EtSiO_2 (Aldrich 538019-5G, 2-diphenylphosphinoethyl functionalized silica, 0.7 mmol/g) were mixed, stirred and refluxed with acetonitrile under nitrogen atmosphere for 48 hours. The material showing yellow was filtered with 0.45 μm PTFE filter, washed with acetonitrile several time and dried at room temperature. The metal loading of $Pd(OAc)_2$_$PPh_2Et@SiO_2$ was 6.4 wt % as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.).

3. General experimental procedure for the alkoxycarbonylation of aryl iodides:

To a 100 mL autoclave, aryl iodide (1 mmol), alcohol (5 mL), Pd catalyst (**I**) (0.5-1.0 mol%), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with nitrogen and finally pressurized with 0.5 MPa of carbon monoxide, and heated at 100 °C for 1-2 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was vented carefully, and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 × 10 mL) to remove any traces of product and catalyst if present. The catalyst was filtered, and the reaction mixture was evaporated under vacuum. The residue obtained was purified by column chromatography (silica gel, 100−200 mesh; petroleum ether/ethyl acetate, 95:05) to afford the desired product.

4. General experimental procedure for the aminocarbonylation of aryl iodides:

To a 100 mL autoclave, aryl iodide (1 mmol), amine (2 mmol), Pd catalyst (**I**) (0.5 - 1.0 mol%), toluene (8 mL), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 0.5 MPa of CO, and heated at 100 °C for 8 h (the ensuing procedure is the same as that discussed above for the alkoxycarbonylation reaction).

5. Characterization of fresh and spent $PdCl_2$_$PPh_2Et@SiO_2$ catalyst:

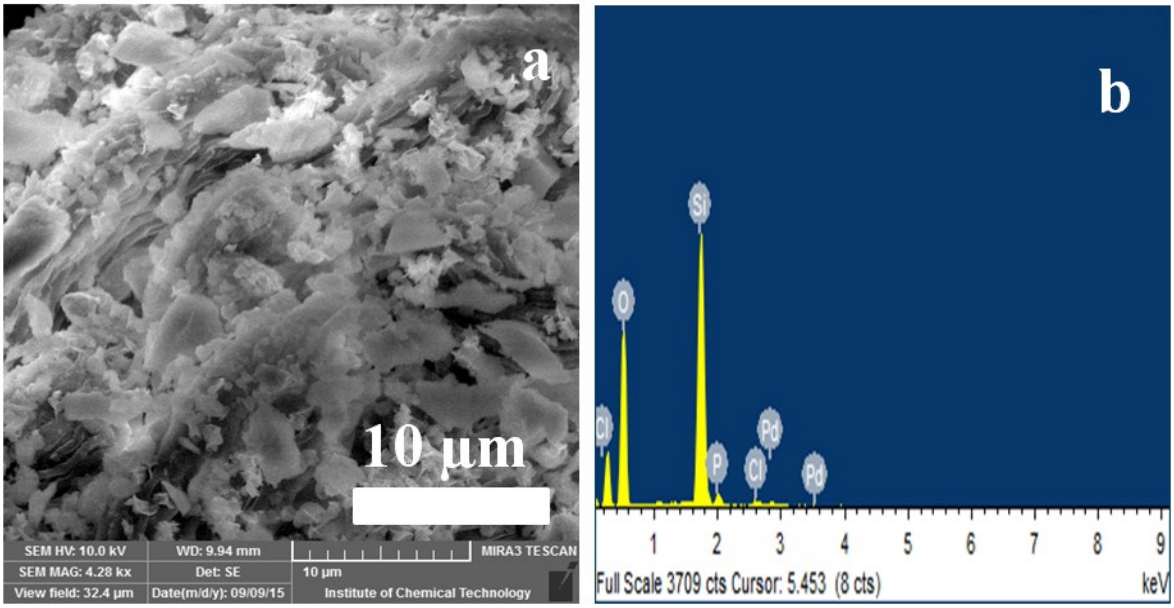


Figure S1 The (a) FEG-SEM (Scanning Electron Microscope) image and (b) EDS (Energy Dispersive X-Ray Spectroscopy) spectrum of fresh $PdCl_2$_$Ph_2PEt@SiO_2$ catalyst.

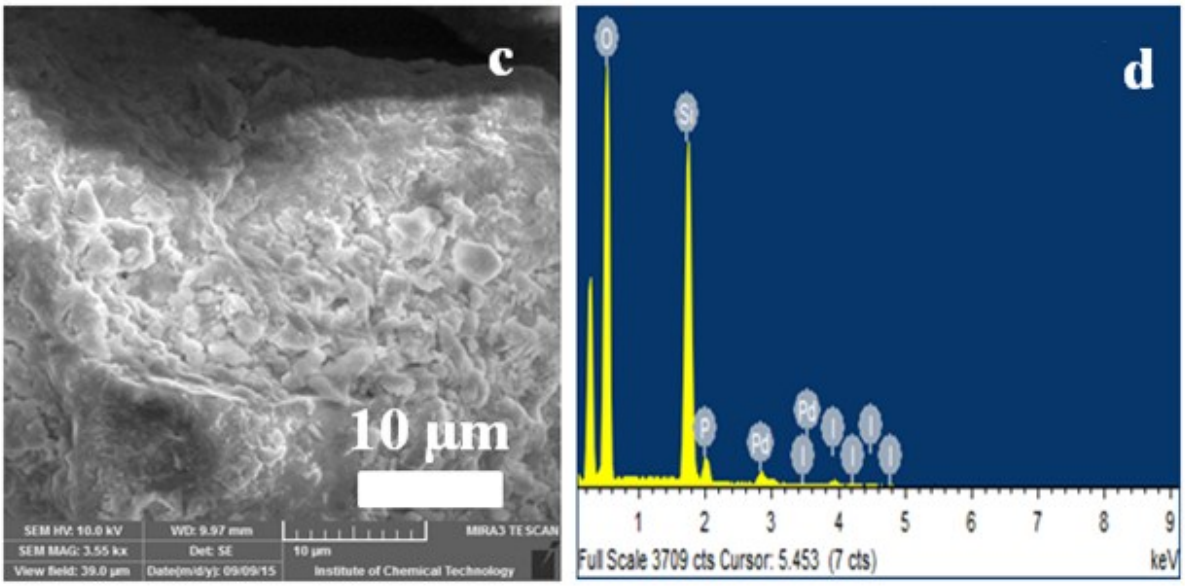


Figure S2 The (c) FEG-SEM image and (d) EDS spectrum of the 1st recycled $PdCl_2$_$Ph_2PEt@SiO_2$ catalyst.

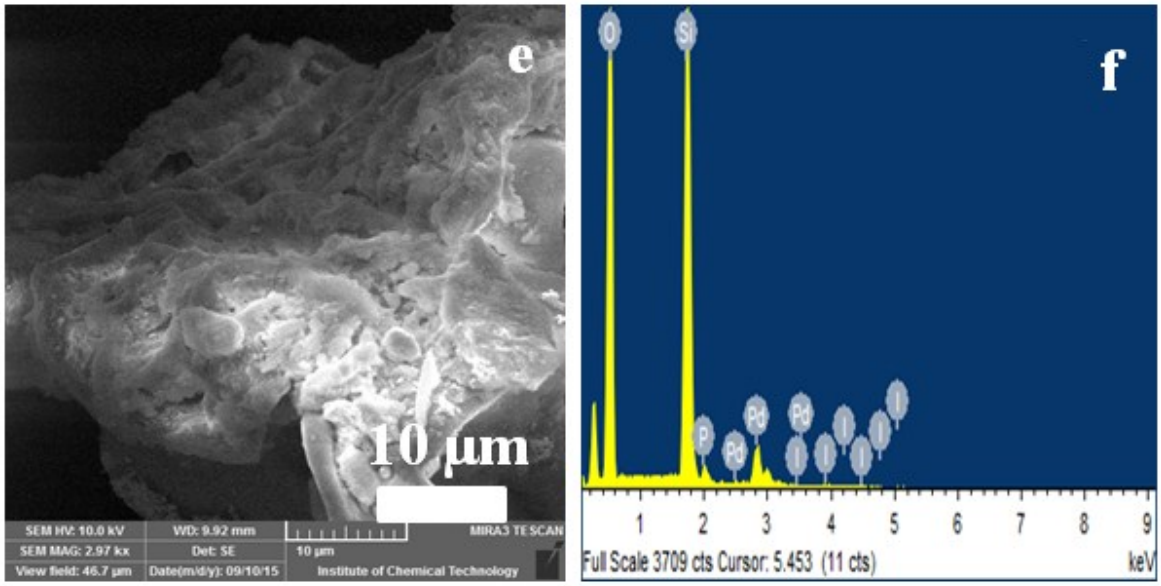


Figure S3 The (e) FEG-SEM image and (f) EDS spectrum images of the 4th recycled $PdCl_2$_$Ph_2PEt@SiO_2$ catalyst.

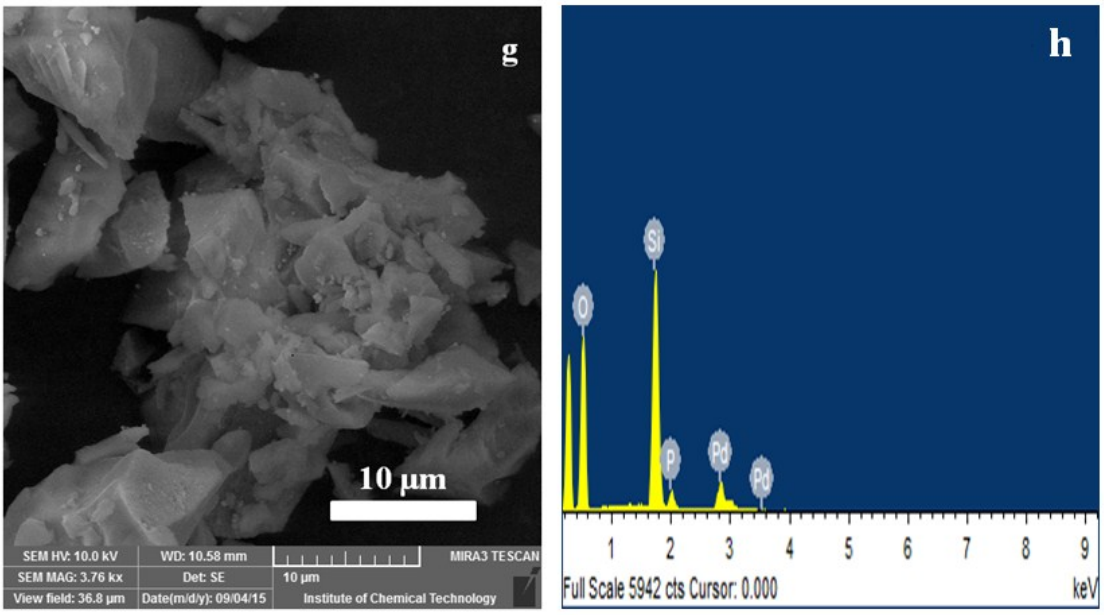


Figure S4 The (g) FEG-SEM image and (h) EDS spectrum images of fresh $Pd(OAc)_2$_$Ph_2PEt@SiO_2$ catalyst.

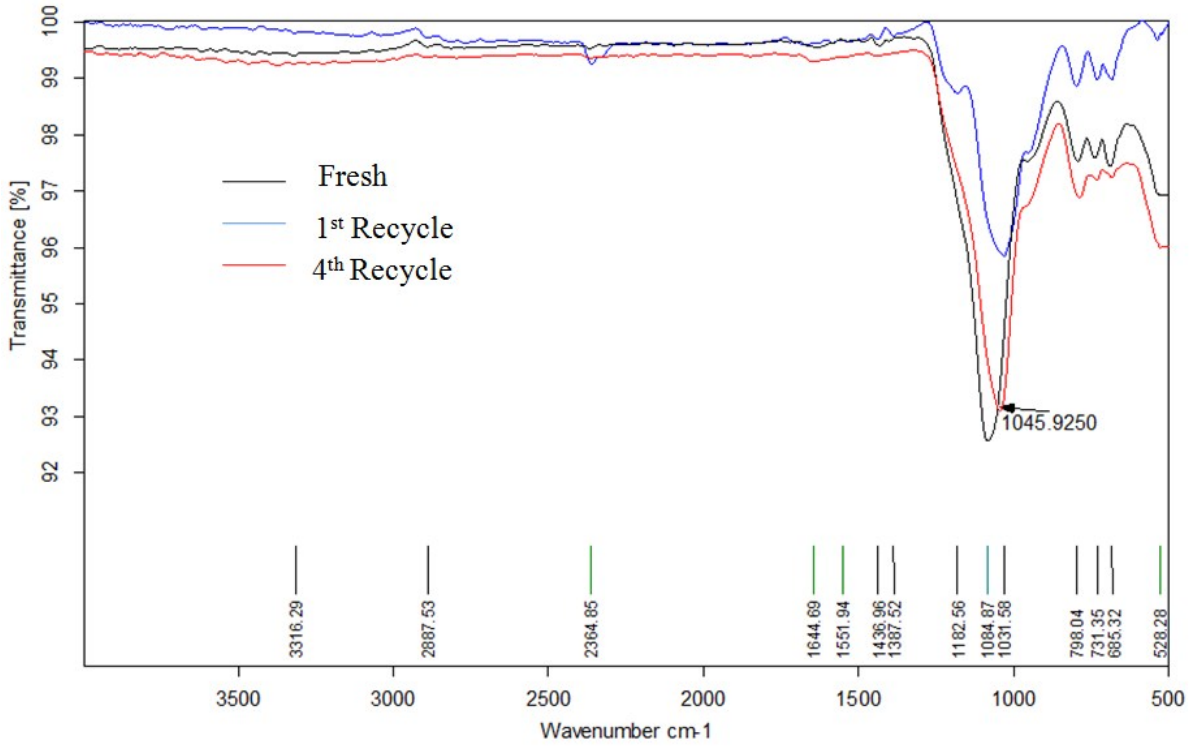
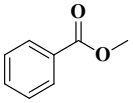


Figure S4 The FT-IR spectrum of fresh and spent recycled $PdCl_2$_$Ph_2PEt@SiO_2$ catalyst.

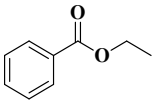
6. Spectral data of products:

Methyl Benzoate (2a)



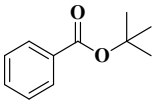
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.46 (tt, J = 6.9, 1.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 3.83 (d, J = 1.8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.92, 166.91, 132.82, 130.09, 129.48, 128.27, 51.92 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 136 [M^+] (36), 105 (100), 92 (4), 77 (61), 51 (19).

Ethyl Benzoate (2b)



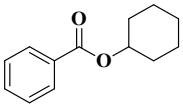
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 2H), 7.43 – 7.31 (m, 3H), 4.28 (qd, J = 7.1, 2.6 Hz, 2H), 1.29 (td, J = 7.1, 2.8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.36, 132.67, 130.42, 129.41, 128.19, 60.76, 14.18 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 150 [M^+] (23.19), 122 (34), 105 (100), 77 (50), 51 (22).

***tert*-butyl Benzoate (2c)**



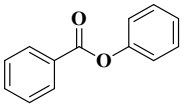
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.38 (t, J = 7.7 Hz, 2H), 1.59 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.82, 133.71, 130.16, 128.79, 128.47, 28.20 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 178 [M^+] (1), 123 (100), 105 (93), 77 (42), 56 (64), 55 (33), 51 (14), 41 (27).

Cyclohexyl Benzoate (2d)



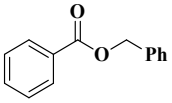
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.49 – 7.39 (dd, J = 15.1, 11.3 Hz, 3H), 5.04 (ddd, J = 12.7, 8.5, 3.8 Hz, 1H), 1.95 (dd, J = 12.2, 5.3 Hz, 1H), 1.81 – 1.79 (m, 1H), 1.62 – 1.56 (m, 2H), 1.49 – 1.27 (m, 6H); **^{13}C NMR** (126 MHz, cdcl$_3$) δ 166.05, 133.69, 132.70, 130.96, 129.52, 128.27, 73.07, 31.62, 25.47, 23.65 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 204 [M^+] (1), 177 (4), 123 (86.6), 105 (100), 82 (21), 77 (48), 67 (21), 55 (9), 41 (11).

Phenyl Benzoate (2e)



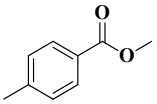
^{1}H NMR ((500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.3 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.31 (td, J = 7.7, 0.9 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H); **^{13}C NMR** (126 MHz, $cdcl_3$) δ 165.22, 150.97, 133.62, 130.19, 129.53, 128.60, 125.92, 121.75 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 198 [M^+] (4), 105 (100), 77 (40.5), 65 (4), 50 (11).

Benzyl Benzoate (2f)



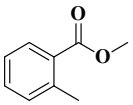
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, 2H, 8 Hz), 7.55-7.35 (m, 8H), 5.36 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.42, 136.01, 133.02, 130.08, 129.68, 128.58, 128.36, 128.23, 128.15, 66.68 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 212 [M^+] (16.90), 105 (100), 91(49.35), 77 (32.70), 65 (12), 51 (11.83).

Methyl 4-methylbenzoate (2g)



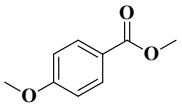
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 2H), 7.22 (dd, J = 7.9, 0.4 Hz, 2H), 3.89 (d, J = 0.7 Hz, 3H), 2.39 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.16, 143.53, 129.57, 129.04, 127.38, 77.35, 77.09, 76.84, 51.91, 21.60 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 150 [M^+] (49), 119 (100), 91 (53.96), 90 (24), 65 (21.86), 51 (4).

Methyl 2-methylbenzoate (2h)



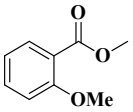
^{1}H NMR (500 MHz, CDC_3) δ 7.91 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.27 (dd, J = 5.6, 4.9 Hz, 2H), 3.90 (d, 3H), 2.61 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.10, 140.16, 131.95, 131.84, 131.66, 130.54, 125.67, 51.82, 29.70, 21.72 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 150 [M^+] (46), 135 (7), 119 (100), 118 (74), 91(77.4), 90 (24), 89 (14), 65 (25), 63 (10), 51 (5).

Methyl 4-methoxybenzoate (2i)



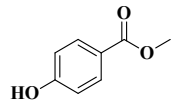
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (d, 2H, 8 Hz), 6.89-6.87 (d, 2H, 8Hz), 3.85 (s, 3H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.82, 163.26, 131.53, 122.50, 113.54, 55.35, 51.83 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 166 [M^+] (35.63), 135 (100), 107 (17.56), 92 (15.25), 77 (23.87), 63 (9).

Methyl 2-methoxybenzoate (2j)



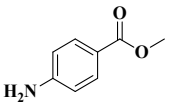
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 1H), 7.46 – 7.44 (m, 1H), 6.99 (dd, J = 7.4, 2.2 Hz, 2H), 3.89 (dd, J = 6.6, 1.2 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.72, 159.07, 133.54, 131.64, 120.10, 111.97, 111.61, 55.95, 52.02 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 166 [M^+] (24.3), 135 (100), 133 (44), 105 (16), 92 (20), 77 (47.5), 63 (10), 51 (7).

Methyl 4-hydroxybenzoate (2k)



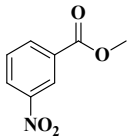
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (d, 2H, 8 Hz), 6.84-6.82 (d, 2H, 8Hz), 4.34 (bs, 1H), 3.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.60, 165.57, 135.60, 135.60, 124.87, 118.87, 55.60 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 152 [M^+] (37.6), 121 (100), 93 (27.3), 65 (23.4).

Methyl 4-aminobenzoate (2l)



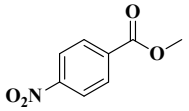
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (d, 2H, 8 Hz), 6.60-6.58 (d, 2H, 8Hz), 4.02 (bs, 2H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 167.26, 151.02, 131.55, 138.14, 113.74, 51.62 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 151 [M^+] (45), 120 (100), 92 (37), 65 (34), 39 (13).

Methyl 3-nitrobenzoate (2m)



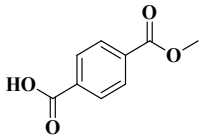
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.38-8.33 (dd, 3H, 8Hz), 3.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.92, 148.20, 135.25, 131.79, 129.62, 127.37, 124.55, 52.79 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 181 [M^+] (28), 150 (100), 135 (9), 120 (10), 104 (37.8), 76 (38), 50 (27), 39 (4).

Methyl 4-Nitrobenzoate (2n)



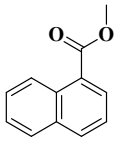
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 2H), 8.21 – 8.15 (m, 2H), 3.96 (d, J = 0.8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.15, 150.48, 135.44, 130.68, 123.51, 113.73, 77.31, 77.06, 76.80, 52.83 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 181 [M^+] (3), 180 (29), 164 (23.84), 150 (100), 120 (22.56), 104 (28.55), 92 (19.6), 76 (25.75), 50 (17).

4-(methoxycarbonyl)benzoic acid (2p)



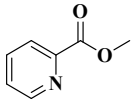
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.11 (d, 4H), 3.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.77, 170.62, 139.47, 137.47, 138.62, 133.30, 56.25 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 180 [M^+] (28.60), 149 (100), 121 (26.90), 76 (8.7), 65 (27.4), 50 (10.60), 40 (10.10).

Methyl 1-naphthoate (2r)



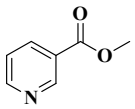
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 7.7, 1.6 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.54 – 7.51 (m, 2H), 7.50 (dd, J = 7.6, 4.7 Hz, 1H), 4.02 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.66, 132.20, 130.94, 130.06, 128.83, 128.26, 127.01, 125.16, 124.45, 123.97, 52.93 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 186 [M^+] (69), 155 (100), 127 (98.63), 101 (6), 77 (11), 63 (10), 51 (4).

Methyl picolinate (Table 3, entry 1)



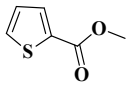
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (d, J = 4.7 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.51 – 7.49 (m, 1H), 4.02 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.69, 149.79, 147.86, 137.11, 127.01, 125.16, 52.93 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 137 [M^+] (4), 107 (30), 106 (11), 79 (100), 78 (69), 51 (22).

Methyl nicotinate (Table 3, entry 2)



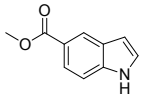
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.77 (s, 1H), 8.27-8.25 (d, J = 7.6 Hz, 1H), 7.37-8.35 (dd, J = 6.4, 3.1 Hz, 1H), 3.89 (s, 3H) ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 137 [M^+] (52.5), 136 (27.6), 106 (100), 78 (79), 51 (33), 50 (15).

Methyl thiophene-2-carboxylate (Table 3, entry 3)



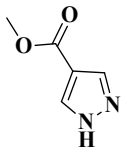
^{1}H NMR (500 MHz, $CDCl_3$): δ 87.87 – 7.71 (m, 1H), 7.63 – 7.48 (m, 1H), 7.14 – 7.02 (m, 1H), 3.88 (d, J = 0.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.69, 133.53, 133.46, 132.35, 127.73, 77.32, 77.06, 76.81, 52.14 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 142 [M^+] (46.67), 112 (8), 111 (100), 83 (18.62), 44 (6).

Methyl 1*H*-indole-5-carboxylate (Table 3, entry 4)



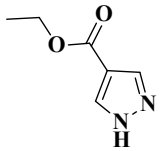
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (bs, 1H), 8.43 (s, 1H), 7.91-7.89 (dd, 1H, 8Hz), 7.39-7.37 (dd, 1H, 8Hz), 7.24 (s, 1H), 6.83 (s, 1H), 3.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.50, 138.46, 127.44, 125.71, 123.71, 123.24, 121.68, 110.85, 103.85, 51.94 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 175 [M^+] (63.90), 144 (100), 116(63.40), 89 (25.70), 63 (12.30), 58 (11.70).

Methyl 1*H*-pyrazole-4-carboxylate (Table 3, entry 5)



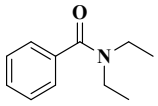
^{1}H NMR (400 MHz, DMSO-d6): δ 13.40 (bs, 1H, NH), 8.27 (s, 1H), 7.86 (s, 1H), 3.70 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d6): δ 163.98, 136.26, 114.13, 51.41 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 126 [M^+] (31), 96 (6.3), 95 (100), 68 (7), 39 (14.83), 31 (1).

Ethyl 1*H*-pyrazole-4-carboxylate (Table 3, entry 6)



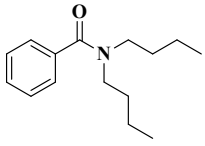
^{1}H NMR (400 MHz, DMSO-d6): δ 13.38 (bs, 1H, NH), 8.28 (s, 1H), 7.84 (s, 1H), 4.17 (q, 2H) 1.21 (t, 3H); **^{13}C NMR** (101 MHz, DMSO-d6): δ 163.11, 140.50,132.57, 113.96, 59.92, 14.73 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 140 [M^+] (17), 112 (41), 95 (100), 68 (9), 40 (8).

***N*,*N*-diethylbenzamide (3a)**



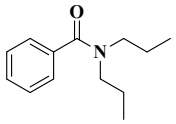
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 5H), 3.48 (s, 2H), 3.19 (s, 2H), 1.18 (s, 3H), 1.04 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.28, 137.13, 129.05, 128.33, 126.17, 77.43, 77.11, 76.79, 43.24, 39.19, 14.15, 12.84.; **GC-MS** (EI, 70 eV): *m/z* (%) = 177 [M^+] (11), 176 (33), 105 (100), 77 (40), 51 (9).

***N*,*N*-dibutylbenzamide (3b)**



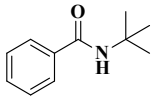
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 3.49 (s, 2H), 3.18 (s, 2H), 1.65 (s, 2H), 1.43 (dd, J = 20.4, 12.6 Hz, 4H), 1.13 (d, J = 6.7 Hz, 2H), 0.98 (s, 3H), 0.79 (d, J = 6.5 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.65, 137.19, 129.85, 128.95, 128.25, 128.14, 126.35, 48.71, 44.40, 30.72, 29.56, 20.23, 19.66, 13.87, 13.54, 13.54 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 233 (9) $[M]^+$, 232 (11), 190 (8), 148 (5), 134 (4), 105 (100), 77 (26), 51 (4), 40 (13).

***N*,*N*-dipropylbenzamide (3c)**



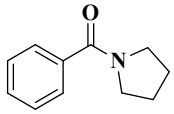
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 3H), 7.30 (dd, J = 7.3, 4.6, 2.3 Hz, 2H), 3.41 (s, 2H), 3.11 (s, 2H), 1.65 (d, J = 6.8 Hz, 2H), 1.48 (d, J = 6.8 Hz, 2H), 0.93 (t, J = 6.4 Hz, 3H), 0.70 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.76, 137.31, 128.96, 126.37, 50.63, 46.22, 21.85, 20.65, 11.40, 10.97 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 204 [M^+] (11.64), 176 (5.71), 134 (6.88), 105 (100), 77 (34.64), 51 (6.69), 39 (36.08).

***N*-(*tert*-butyl)benzamide (3d)**



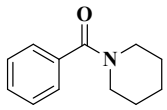
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.68 (d, 2H, 8Hz), 7.44-7.36 (m, 3H), 5.95 (s, 1H), 1.45 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.90, 135.85, 131.05, 128.43, 126.66, 51.57, 28.83 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 177 [M^+] (11), 162 (12), 122 (14.9), 105 (100), 77 (44), 51 (13), 41 (8).

Phenyl(pyrrolidin-1-yl)methanone (3e)



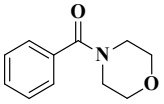
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.36 – 7.32 (m, 3H), 3.59 (t, J = 7.0 Hz, 2H), 3.37 (t, J = 6.6 Hz, 2H), 1.90 (dd, J = 13.7, 6.5 Hz, 2H), 1.82 (dd, J = 13.1, 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.70, 137.11, 129.74, 128.19, 127.00, 49.58, 46.14, 26.33, 24.41 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 175 [M^+] (3), 174 (17), 156 (9), 146 (10), 105 (100), 95 (8), 77 (68), 56 (13), 51 (27), 41 (13).

Phenyl(piperidin-1-yl)methanone (3f)



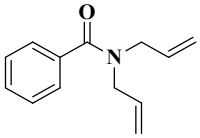
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 3.66 (s, 2H), 3.29 (s, 2H), 1.62 (s, 4H), 1.46 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.28, 136.40, 129.32, 128.36, 126.71, 48.73, 43.07, 26.50, 25.58, 24.53 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 188 [M^+] (73.80), 160 (2.19), 105 (100), 84(10), 77 (67.40), 51 (19.09).

Morpholino(phenyl)methanone (3g)



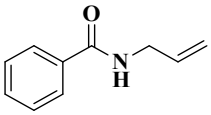
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 5H), 3.83 – 3.38 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.43, 135.15, 129.85, 128.51, 127.01, 66.80, 48.17, 42.50, 20.65; **GC-MS** (EI, 70 eV): *m/z* (%) = 191 [M^+] (8), 190 (25.58), 176 (7), 105 (100), 91 (5), 86 (12), 77 (48), 56 (14), 51 (14).

***N*,*N*-diallylbenzamide (3h)**



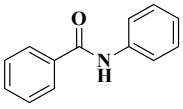
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 – 7.39 (m, 2H), 7.37 – 7.33 (m, 3H), 5.85 (s, 1H), 5.70 (s, 1H), 5.26 – 5.22 (d, *J* = 20.0 Hz, 1H), 5.19 (d, *J* = 1.0 Hz, 2H), 5.14 (s, 1H), 4.10 (s, 2H), 3.80 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 171.76, 136.15, 133.13, 132.69, 129.31, 128.33, 126.52, 117.61, 50.71, 46.92 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 201 [M^+] (3), 160 (9), 105 (100), 96 (6), 51 (11.25), 41 (10), 39 (8).

***N*-allylbenzamide (3i)**



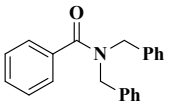
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.82 – 7.70 (m, 2H), 7.50 – 7.41 (m, 1H), 7.37 (td, *J* = 7.0, 1.0 Hz, 2H), 6.63 (s, 1H), 5.96 – 5.80 (m, *J* = 16 Hz, 1H), 5.24 – 5.09 (m, *J* = 16 Hz 2H), 4.02 (tt, *J* = 10 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* 167.56, 134.36, 134.12, 131.44, 128.49, 126.95, 116.49, 42.40 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 161 [M^+] (9), 146 (7), 105 (100), 77 (51), 56 (7), 51 (16), 39 (4).

***N*-phenylbenzamide (3j)**



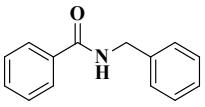
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.95 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.47 (dd, *J* = 11.1, 4.0 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.14 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 165.83, 137.91, 134.97, 131.84, 129.09, 128.77, 127.03, 124.58, 120.24; **GC-MS** (EI, 70 eV): *m/z* (%) = 197 [M^+] (43.6), 105 (100), 91 (6), 77 (48), 65 (9), 51 (13.83).

***N*,*N*-dibenzylbenzamide (3k)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.38 – 7.31 (m, 8H), 7.29 (t, J = 7.0 Hz, 4H), 7.13 (d, J = 5.7 Hz, 2H), 4.70 (s, 2H), 4.39 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.26, 136.09, 129.65, 128.84, 128.71, 128.55, 128.39, 127.65, 127.51, 127.01, 126.68, 51.50, 46.81 ppm; **GC-MS** (EI, 70 eV): *m/z* (%) = 301 [M^+] (8.1), 210 (31.20), 105 (100), 91(16.40), 77 (30.32), 65 (5.96), 51 (4).

***N*- benzylbenzamide (3l)**

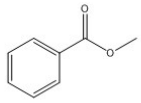


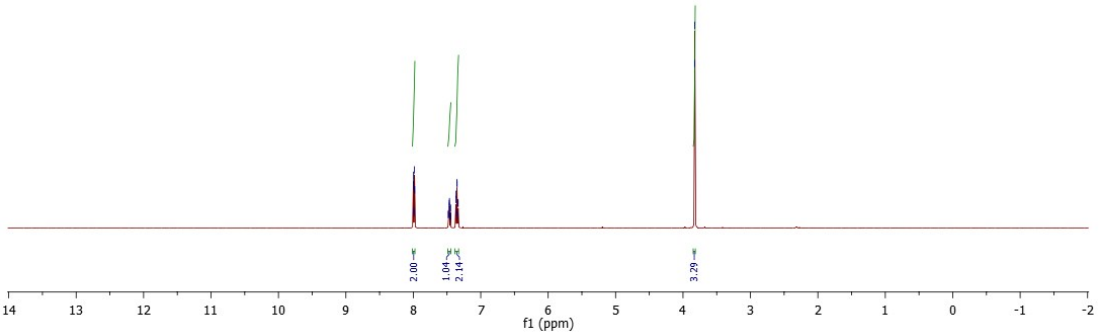
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.49 –7.23 (m, 8H), 6.67 (bs, 1H), 4.62 (d, J = 5.7 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.44, 138.21, 134.34, 131.54, 128.76, 128.57, 127.88, 127.57, 126.99, 44.09, 29.71; **GC-MS** (EI, 70 eV): *m/z* (%) = 211 [M^+] (56), 210 (21), 106 (28), 105 (100), 91 (10), 77 (59), 51 (14).

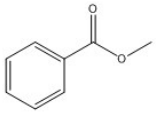
7. References

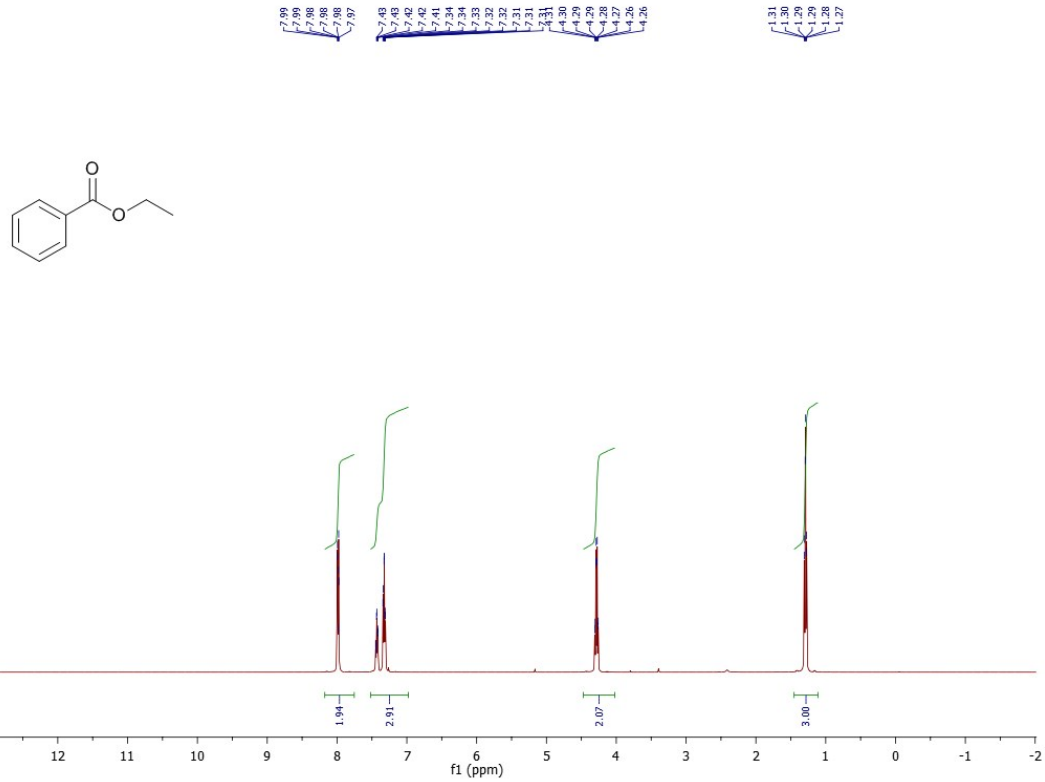
1. X. F. Wu, C. Darcel, *Eur. J. Org. Chem*., 2009, 1147.
2. N. Samuel, K. L. Hull, *Org. Lett*., 2015 17, 3236.
3. J. D. Moore, R. J. Byrne, P. Vedantham, D. L. Flynn, P. R. Hanson, *Org. Lett*., 2003, 5, 4241.
4. S. D. Sarkar, S. Grimme, A. Studer, *J. Am. Chem. Soc*., 2010, 132, 1190.
5. W. Han, F. Jin, Q. Zhou, *Synthesis,* 2015, 47, 1861.
6. Y. Yamamoto, *Adv. Synth. Catal*., 2010, 352, 478.
7. J. A. Walker, C. Bazaral, T. Leavey, P. G. Dormer, J. A. Murry, *Org. Lett.,* 2004, 6, 2100.
8. J. Liu, J. Chen, C. Xia, *J. Catal*., 2008, 253, 56.
9. W. J. Ang, L.-C. Lo and Y. Lam, *Tetrahedron*, 2014, 70, 8545.
10. T. T. Dang, Y. Zhu, J. S. Y. Ngiam, S. C. Ghosh, A. Chen, A. M. Seayad, *ACS Catal*., 2013, 3, 1410.
11. A. S. Prasad, B. Satyanarayana, *J. Mol. Catal. A: Chem*., 2013, 370, 209.
12. Y, Lei, L. Wu, X. Zhang, M. Hui, Y. Gu, Li. Guangxing, *J. Mol. Catal. A: Chem*., 2015, 398, 169.
13. M. V. Khedkar, T. Sasaki and B. M. Bhanage, *ACS Catal*., 2013, 3, 293.
14. H. Mei, J. Hu, S. Xiao, Y. Lei, G. Li, *Appl. Catal., A,* 2014, 475, 40.
15. E. D. Anderson and D. L. Boger, *J. Am. Chem. Soc*., 2011, 133 (31), 12285.
16. P. Toto, J. Chenault, A. E. Hakmaoui, M. Akssira, G. Guillaumet, *Synth. Commun*., 2008, 38, 674.

8. List ^{1}H NMR and ^{13}C NMR of products





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7.99
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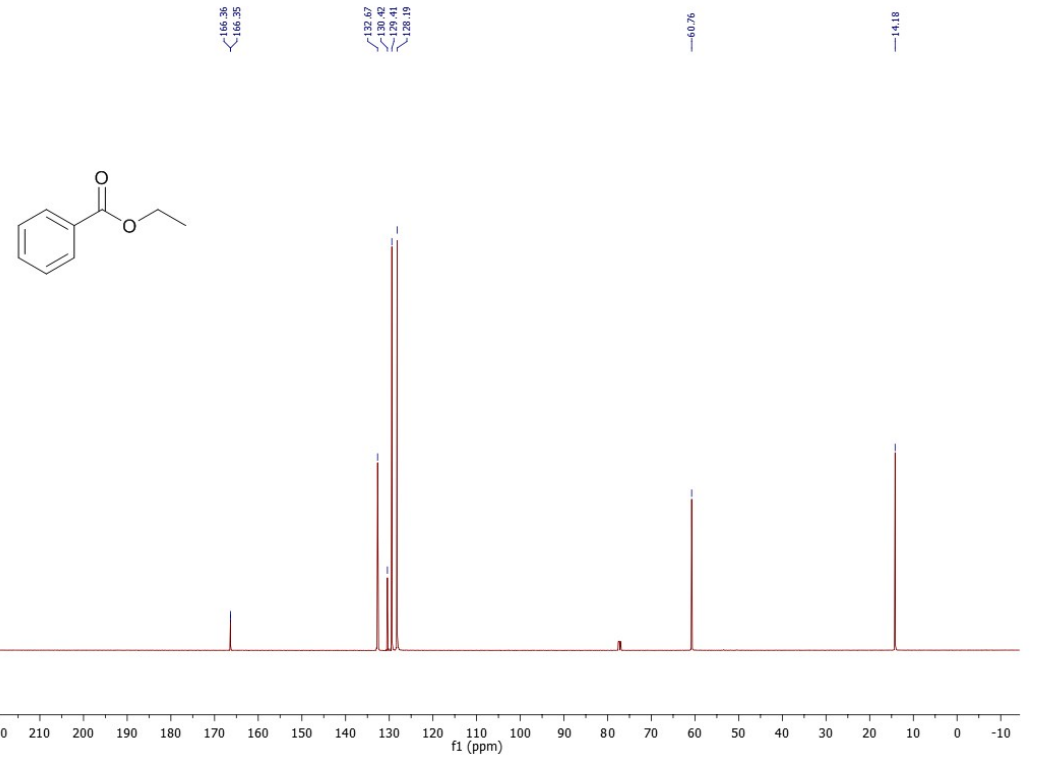
7.31
7.31
7.31
4.30
4.29
4.29
4.28
4.27
4.26
4.26
1.31
1.30
1.29
1.29
1.28
1.27
1.94
2.91
2.07
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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166.35
132.67
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128.19
60.76
14.18
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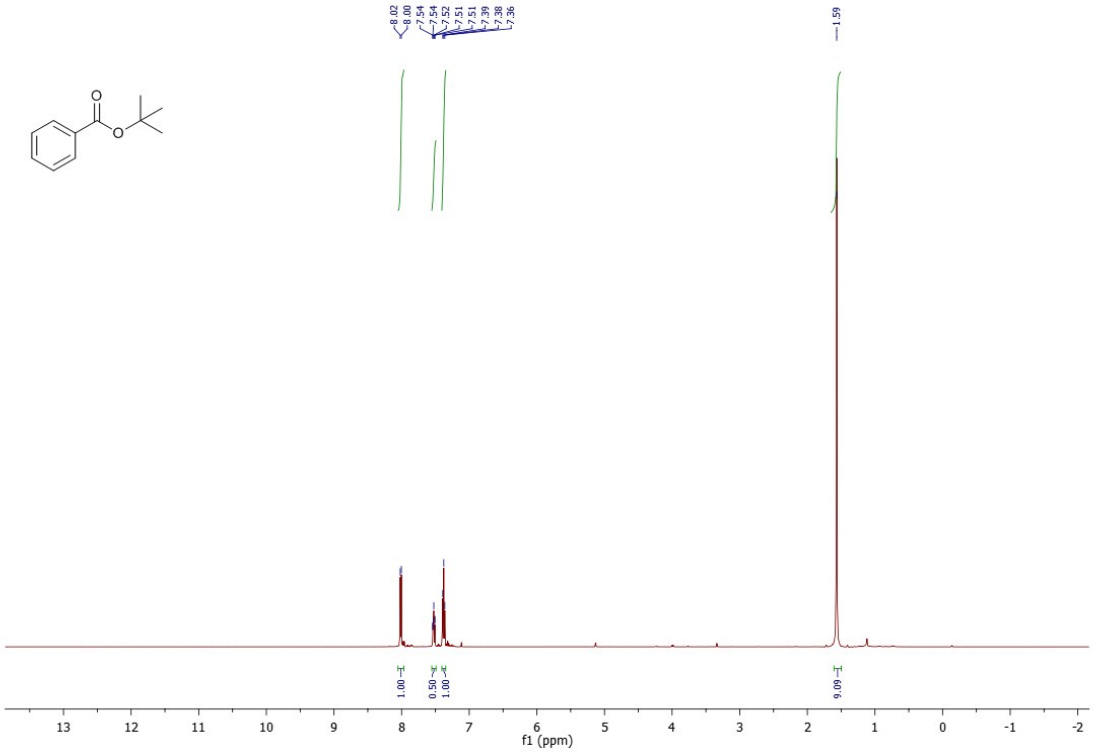
f1 (ppm)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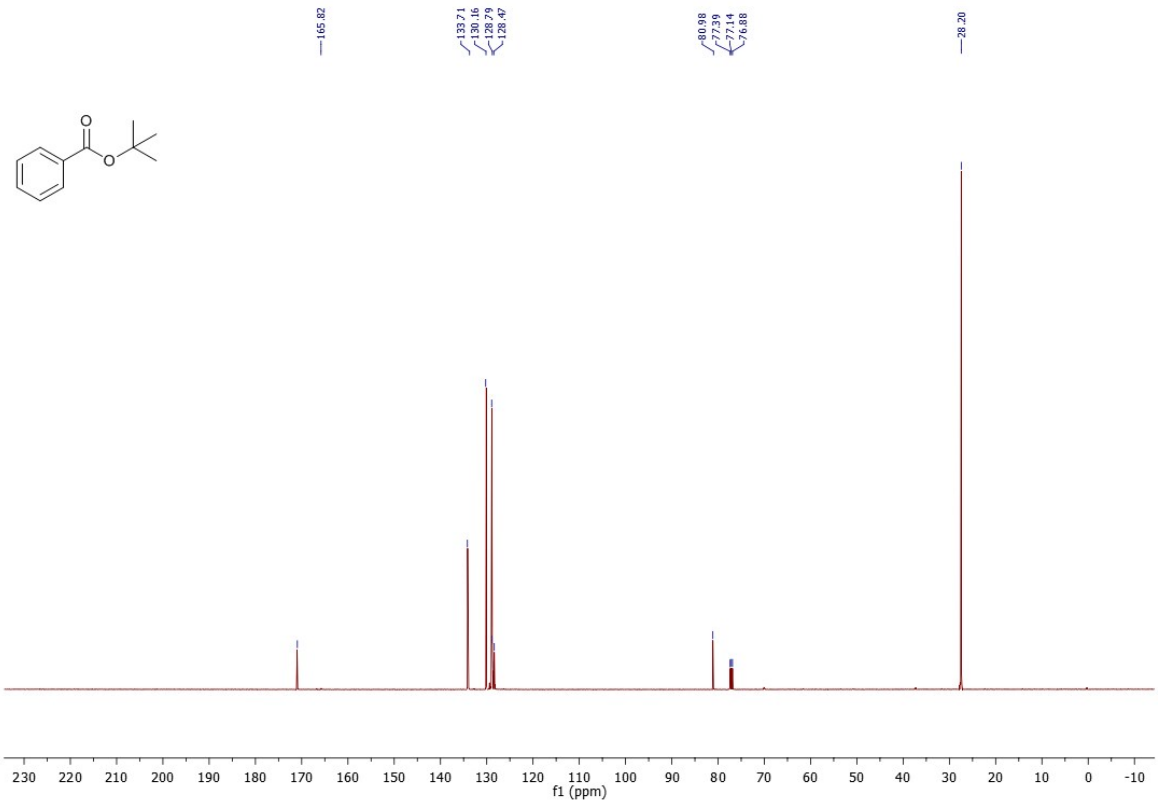
7.52
7.52
7.51
7.51
7.39
7.38
7.36
1.59
1.00
0.50
1.00
9.09
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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77.14
76.88
28.20
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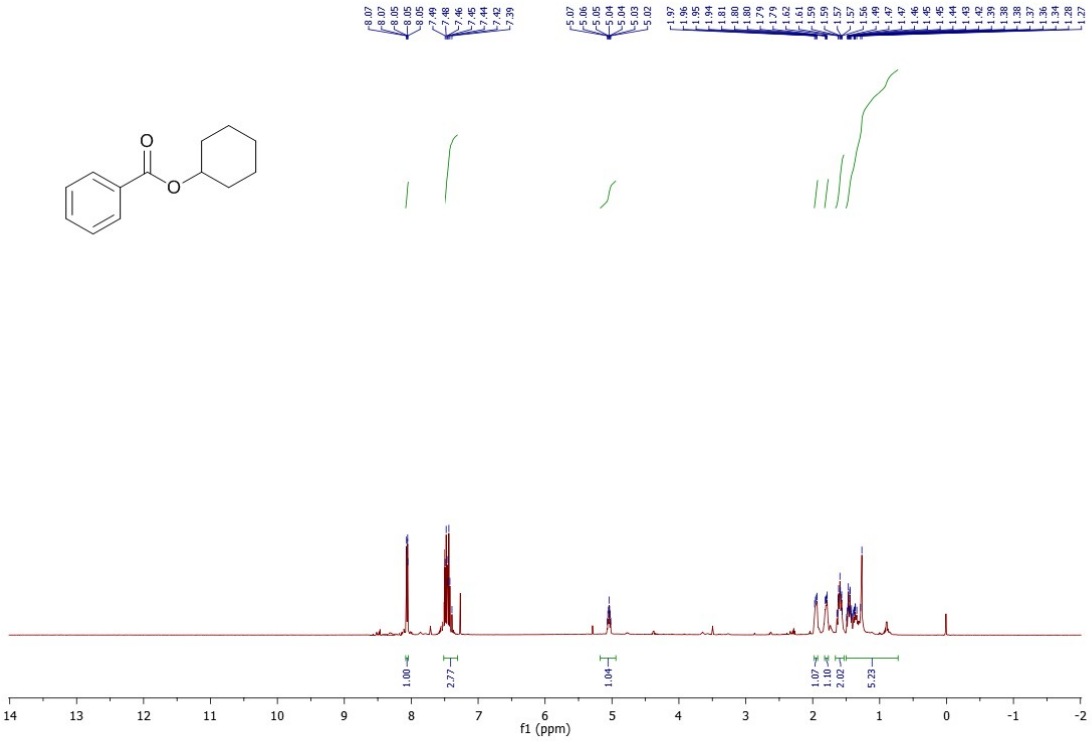
f1 (ppm)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1.34
1.28
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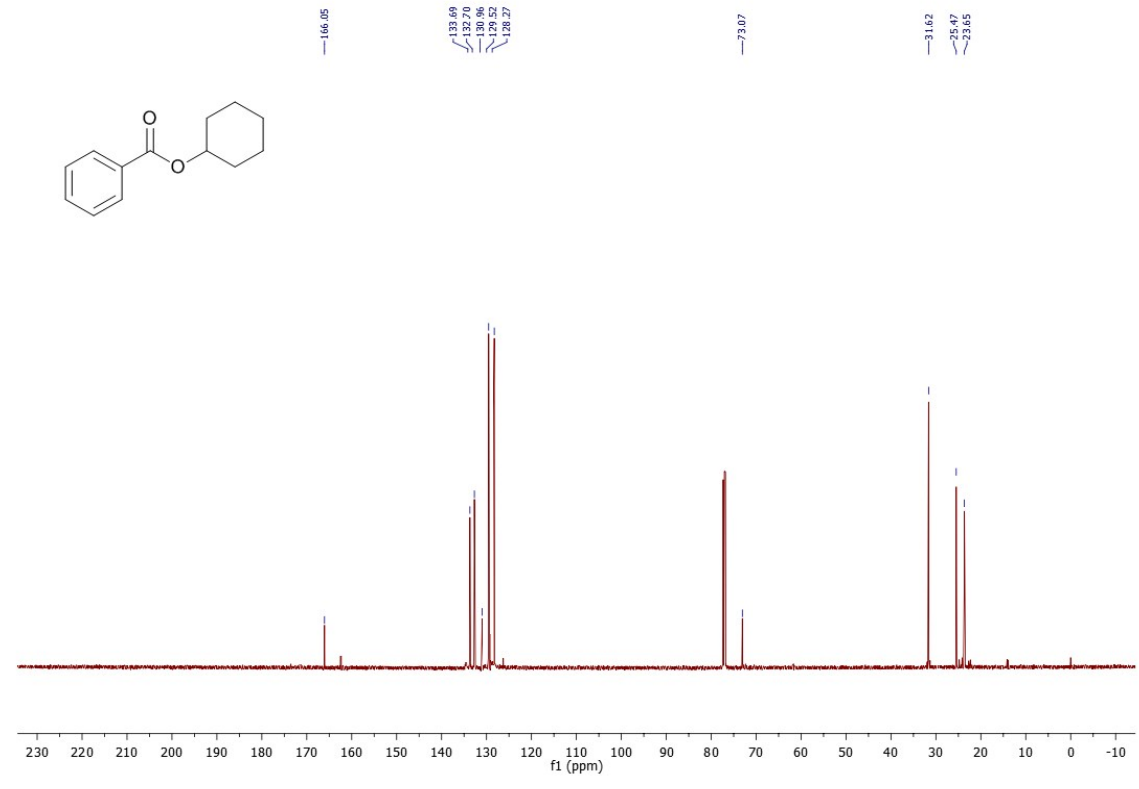
O
O
1.00
2.77
1.04
1.07
1.10
2.02
5.23
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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133.69
132.70
130.86
129.52
128.27
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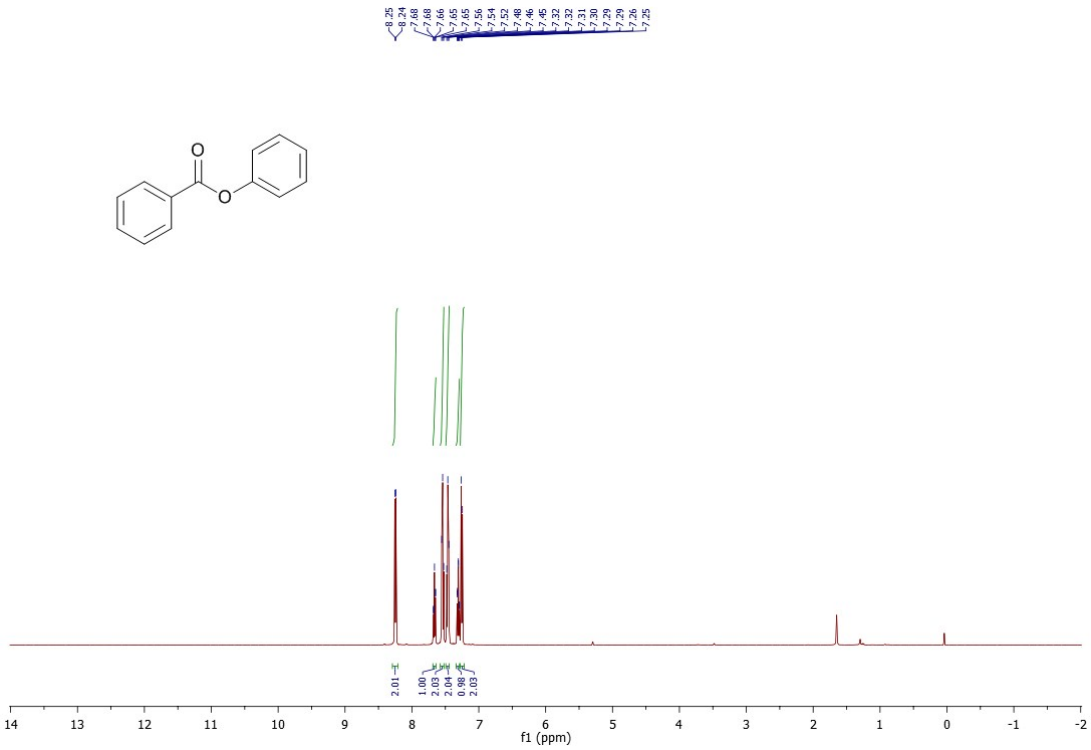
31.62
25.47
23.65
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.24
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7.65
7.56
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7.52
7.48
7.46
7.45
7.32
7.31
7.30
7.29
7.29
7.26
7.25
O
O
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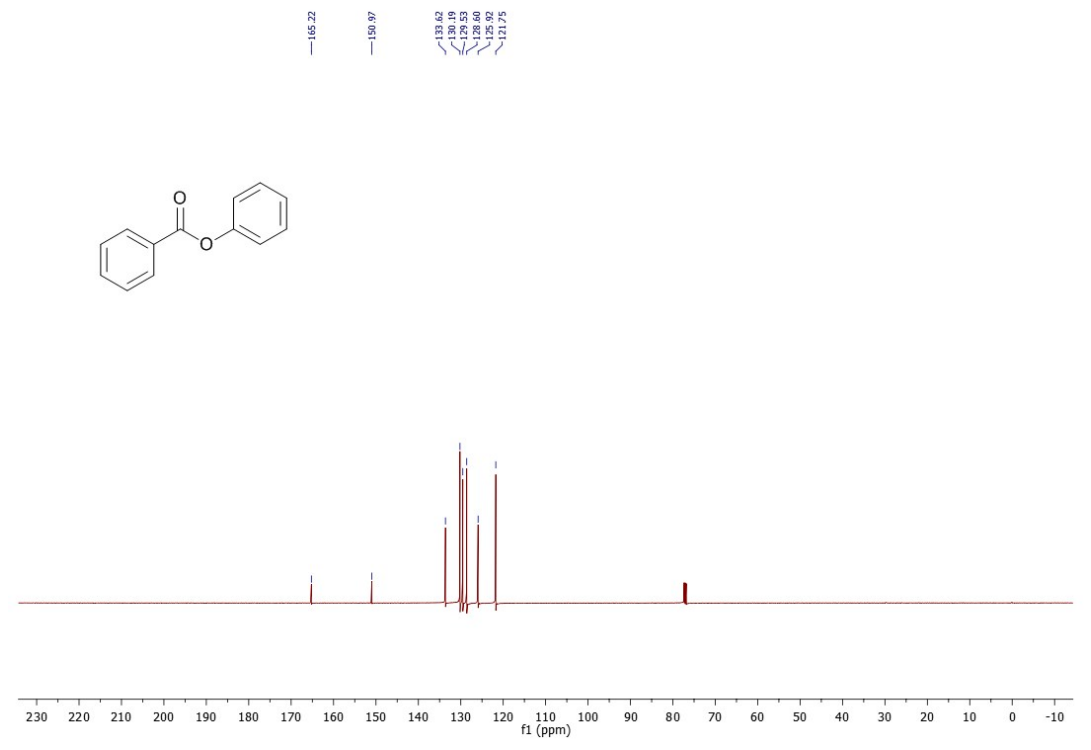
1.00
2.03
2.04
0.98
2.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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150.97
133.62
130.19
129.53
128.60
125.92
121.75
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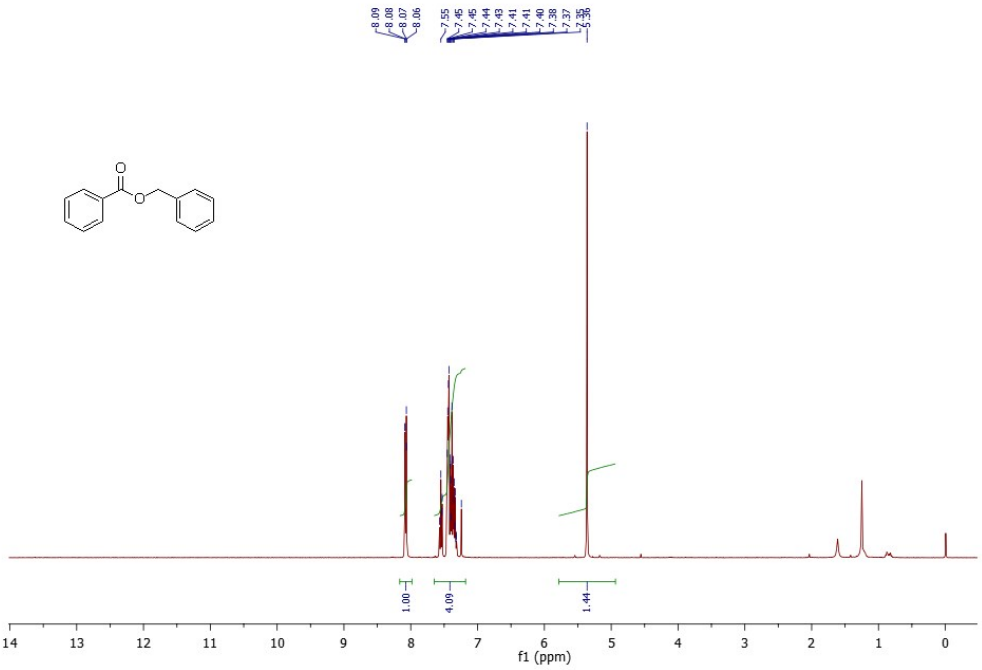
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.08
8.07
8.06
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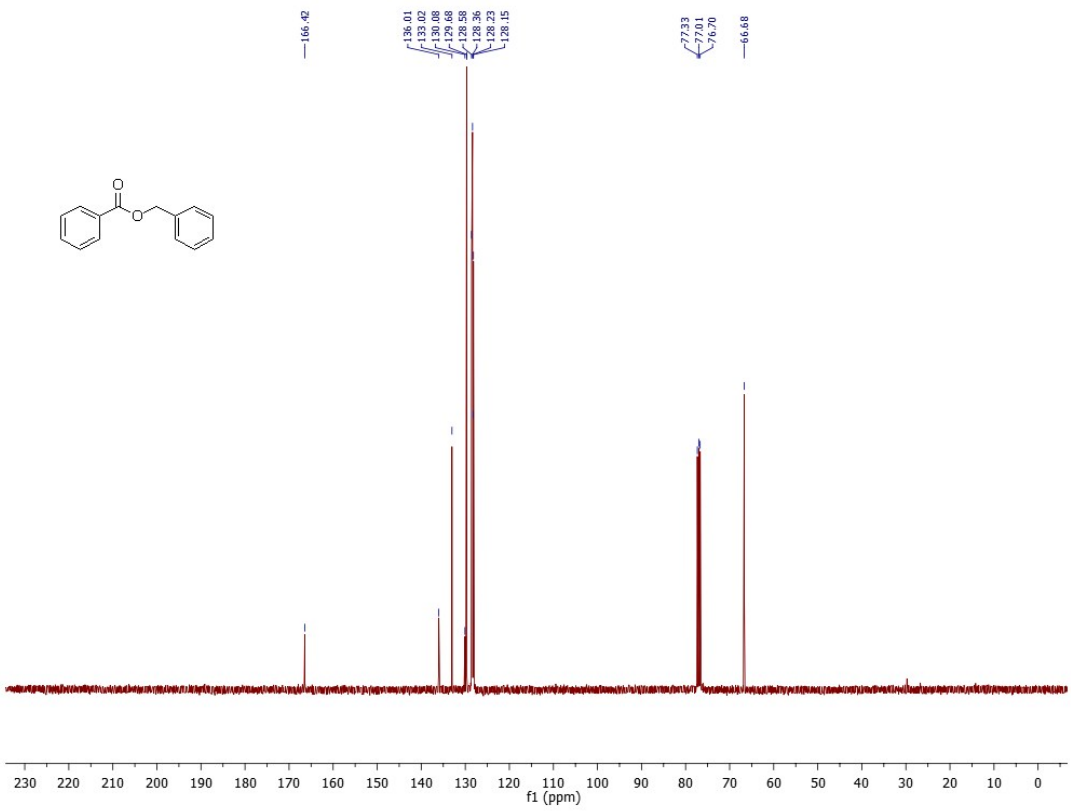
7.45
7.45
7.44
7.43
7.41
7.41
7.40
7.38
7.37
5.36
1.00
4.09
1.44
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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136.01
133.02
130.08
129.68
128.58
128.36
128.23
128.15
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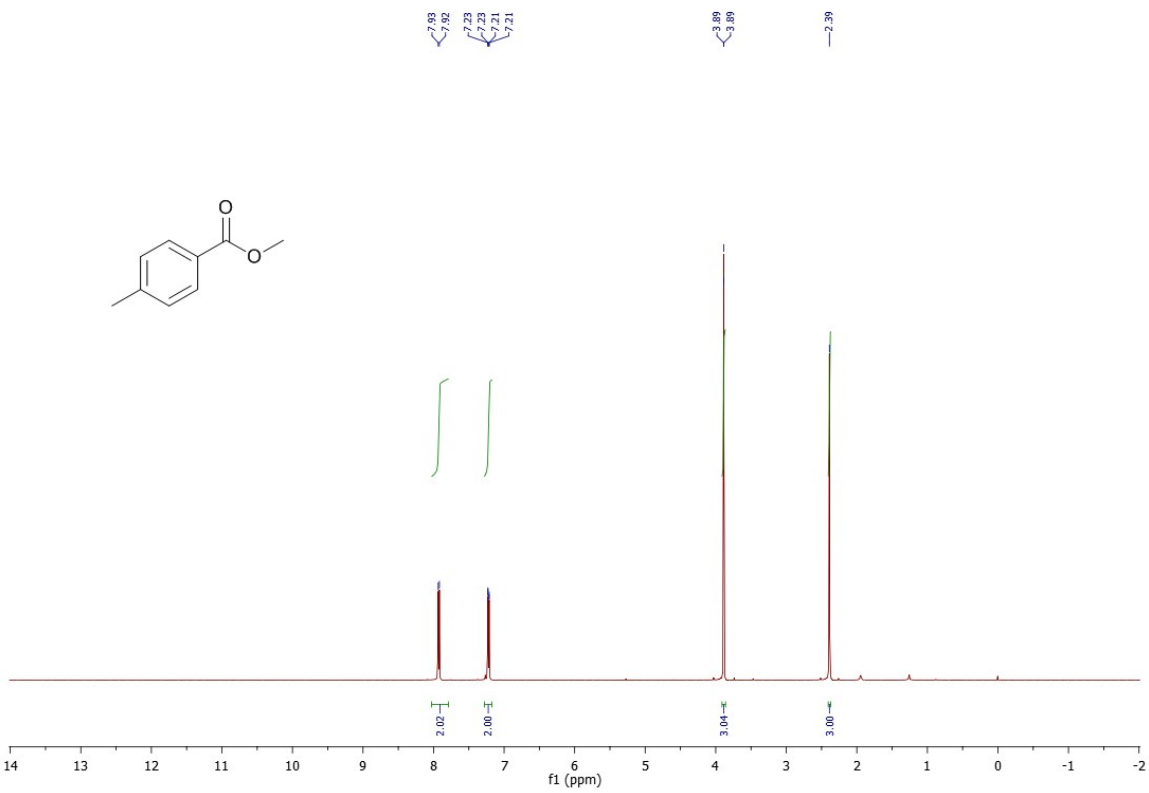
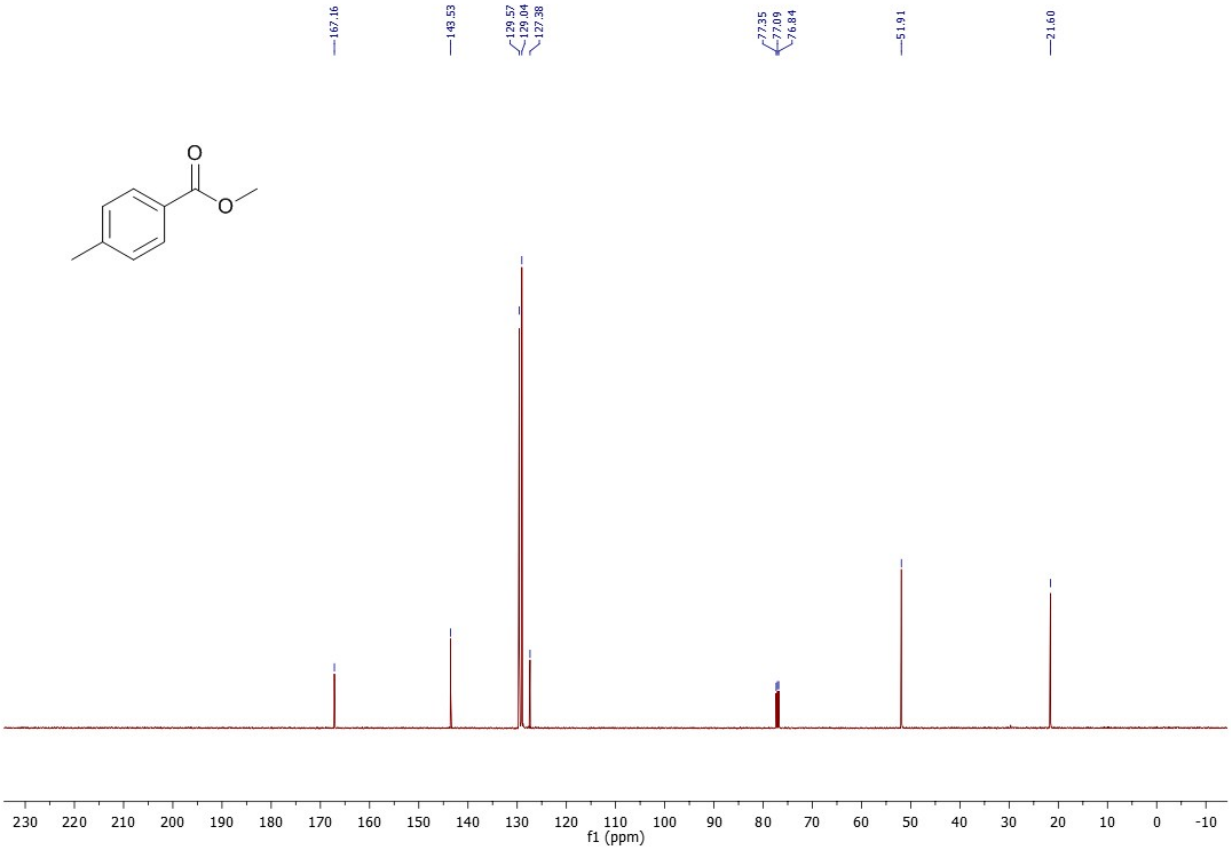
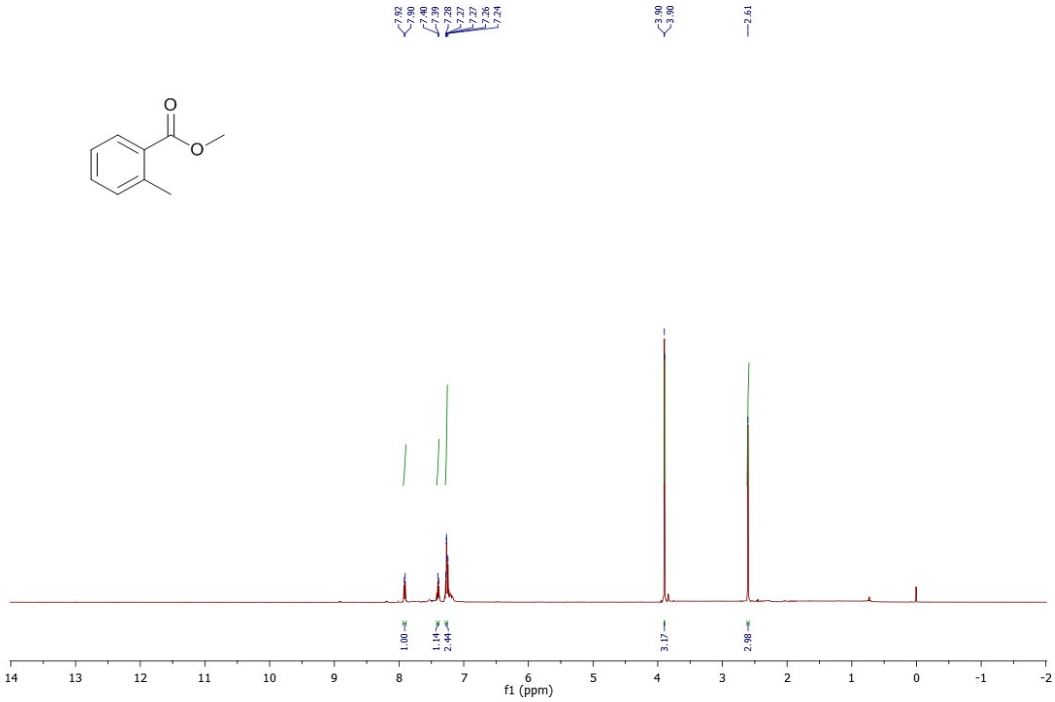
77.01
76.70
66.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.93
7.92
7.23
7.23
7.21
7.21
3.89
3.89
2.39
O
O
2.02
2.00
3.04
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


167.16
143.53
129.57
129.04
127.38
77.35
77.09
76.84
51.91
21.60
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.92
7.90
7.40
7.39
7.28
7.27
7.27
7.26
7.24
3.90
3.90
2.61
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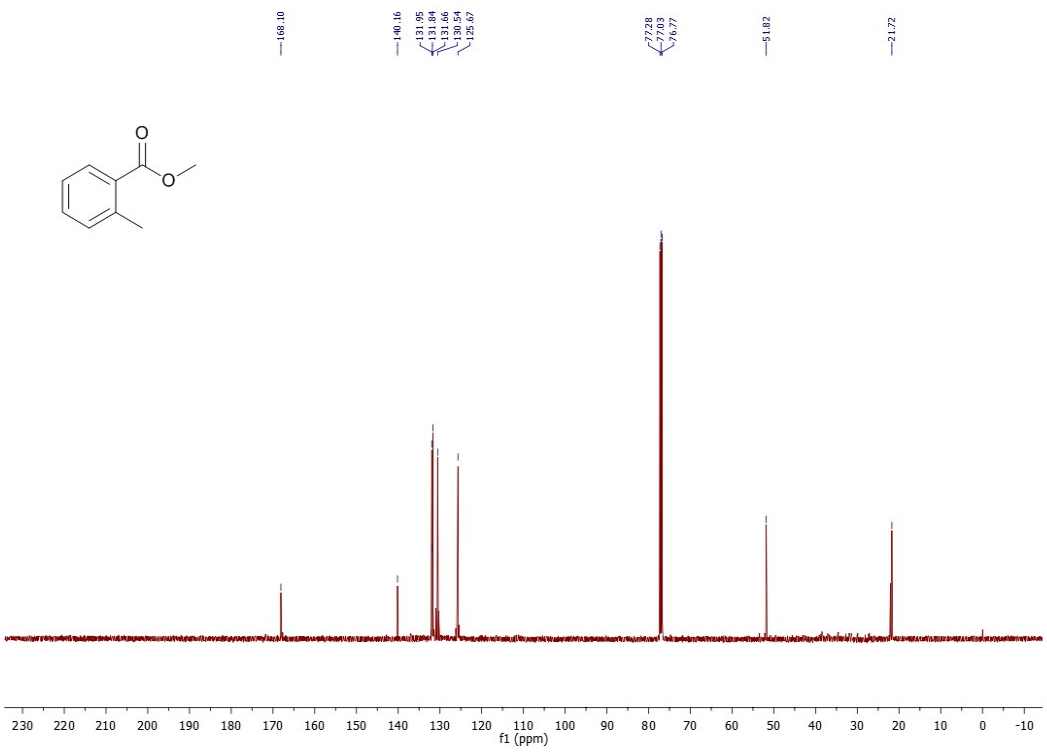
1.14
2.44
3.17
2.98
f1 (ppm)


168.10
140.16
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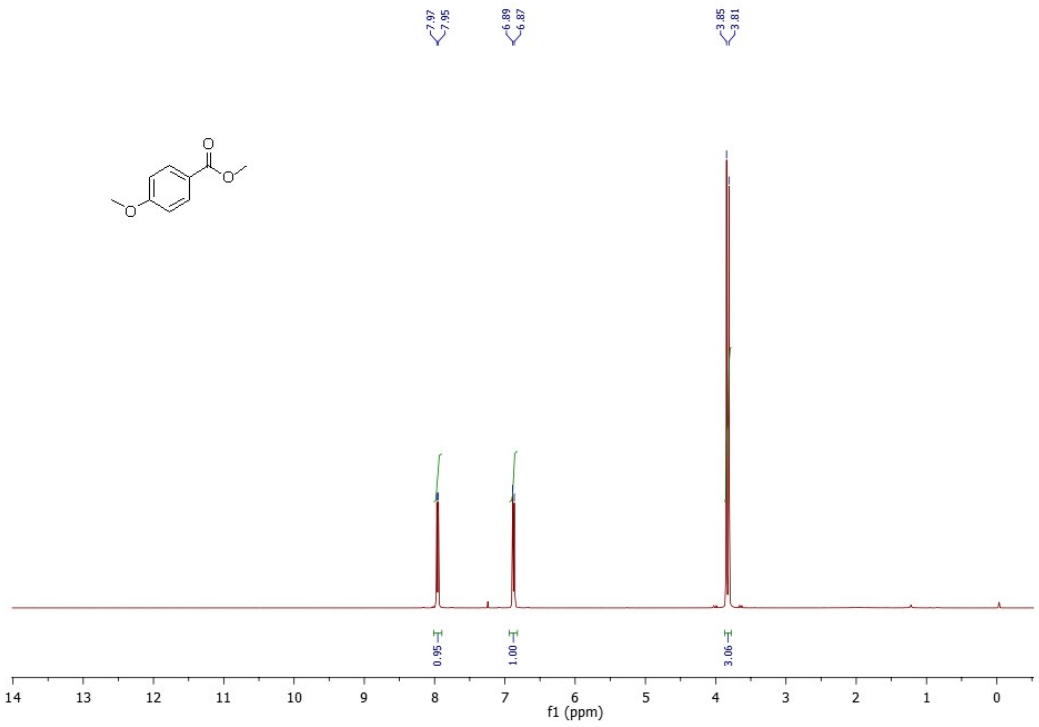
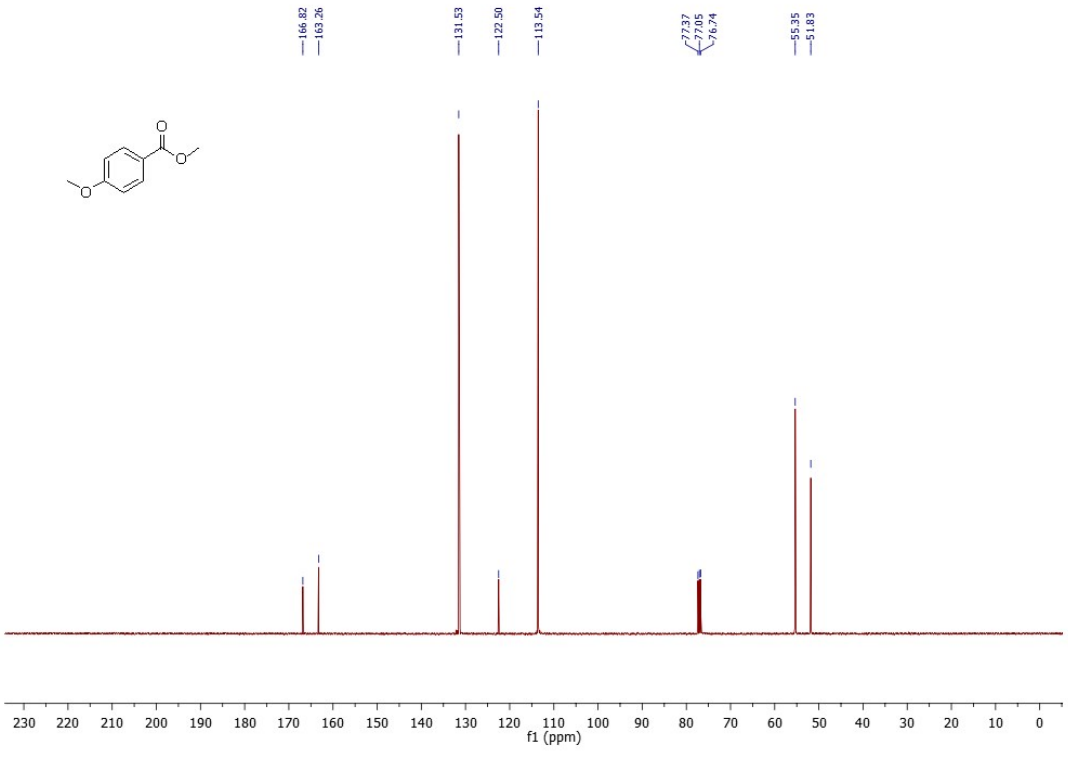
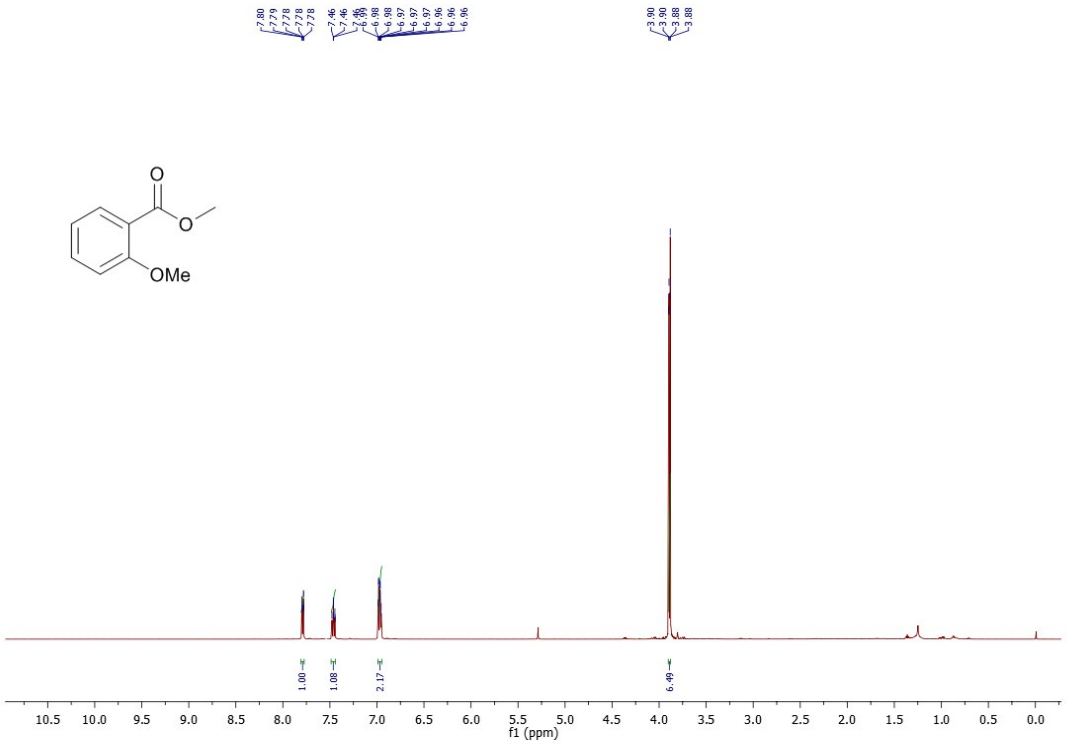
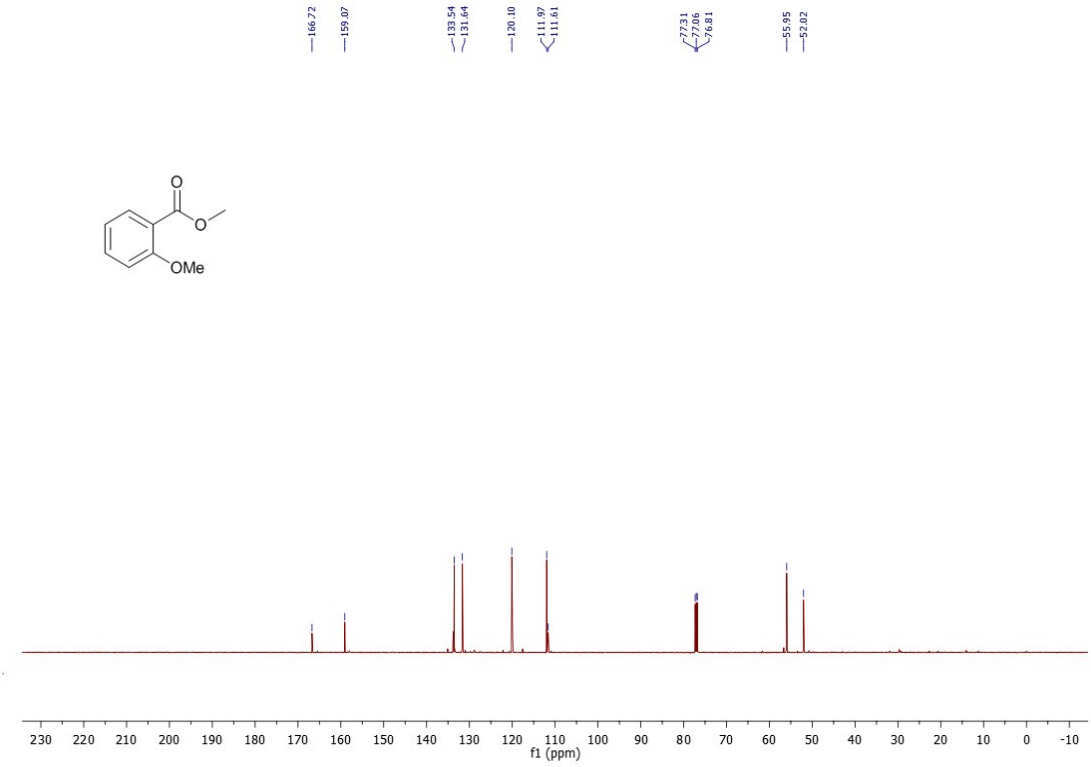
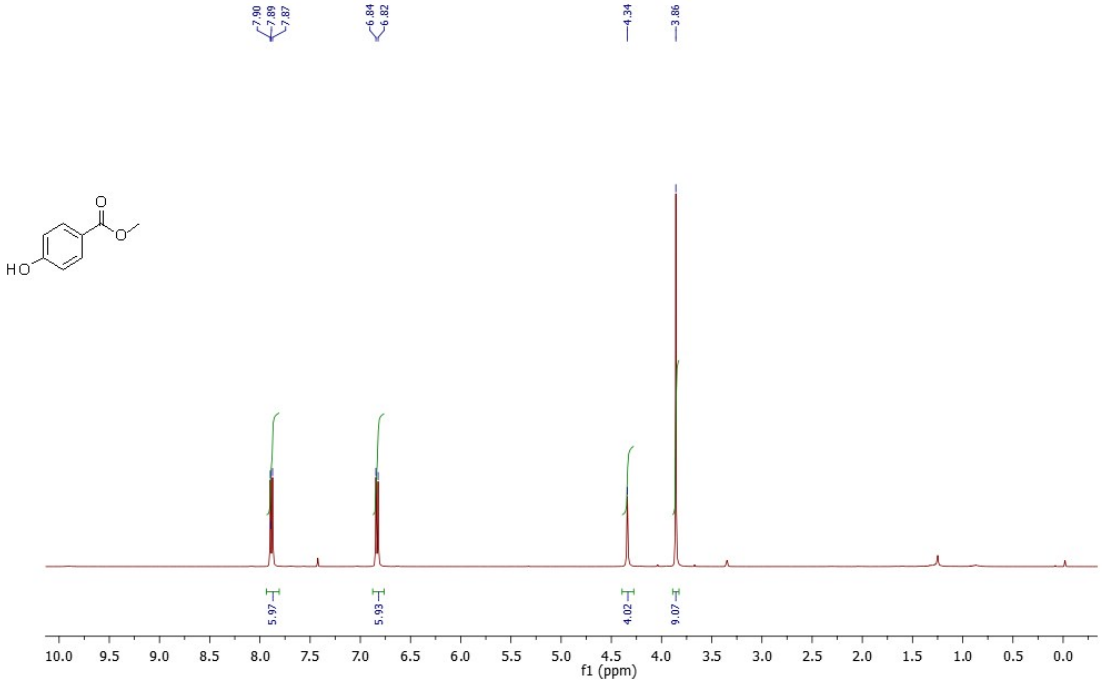
131.66
130.54
125.67
77.28
77.03
76.77
51.82
21.72
f1 (ppm)

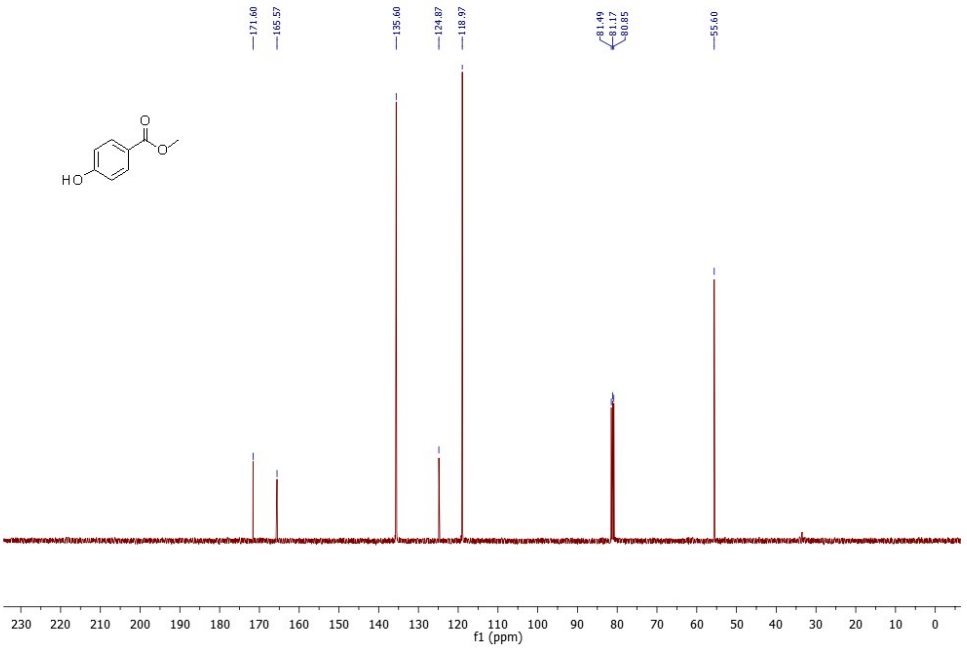

7.97
7.95
6.89
6.87
3.85
3.81
0.95
1.00
3.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

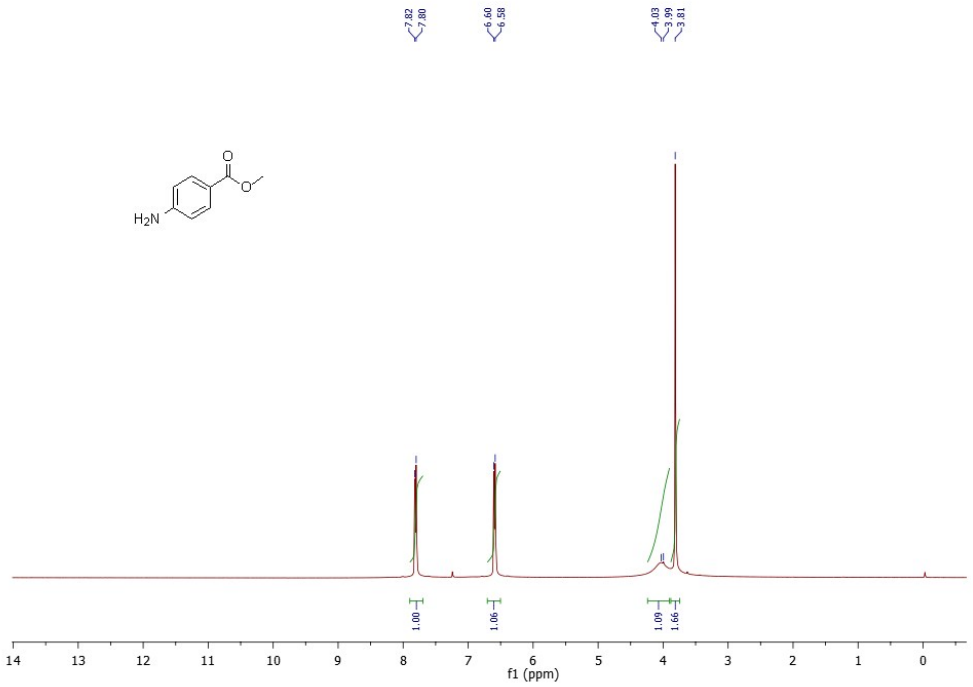

166.82
163.26
131.53
122.50
113.54
77.37
77.05
76.74
55.35
51.83
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

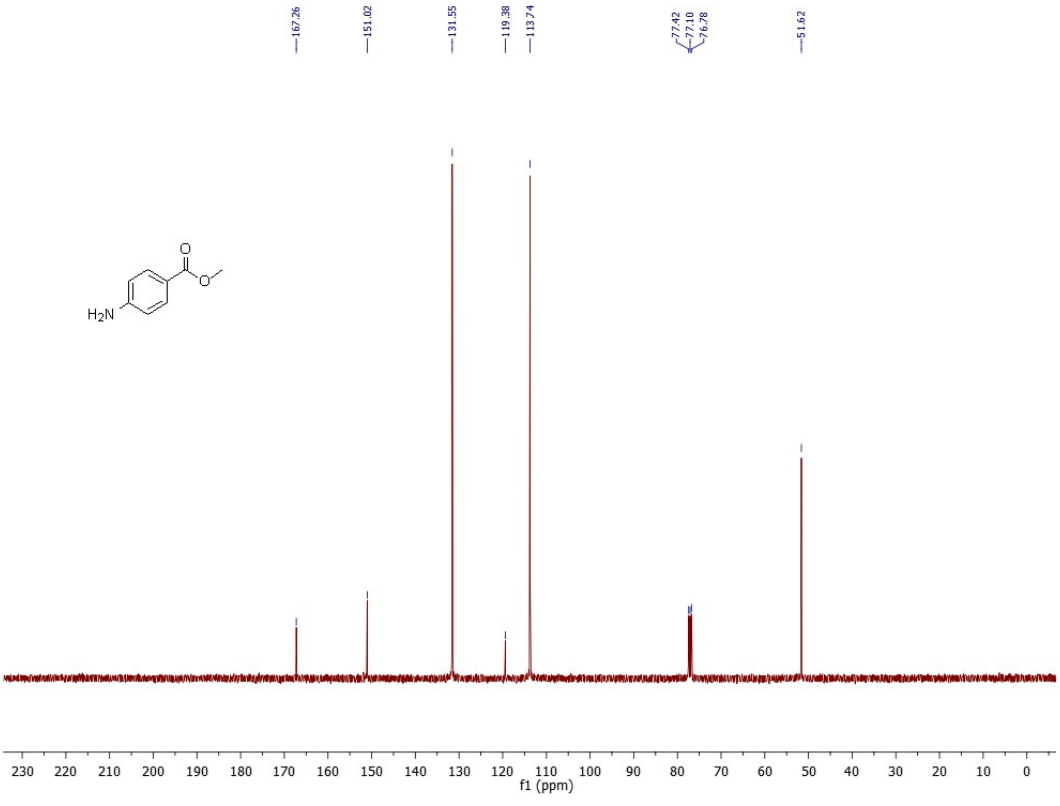

7.80
7.79
7.78
7.78
7.78
7.78
7.46
7.46
6.98
6.98
6.98
6.97
6.97
6.97
6.96
6.96
6.96
3.90
3.90
3.88
3.88
O
O
OMe
1.00
1.08
2.17
6.49
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

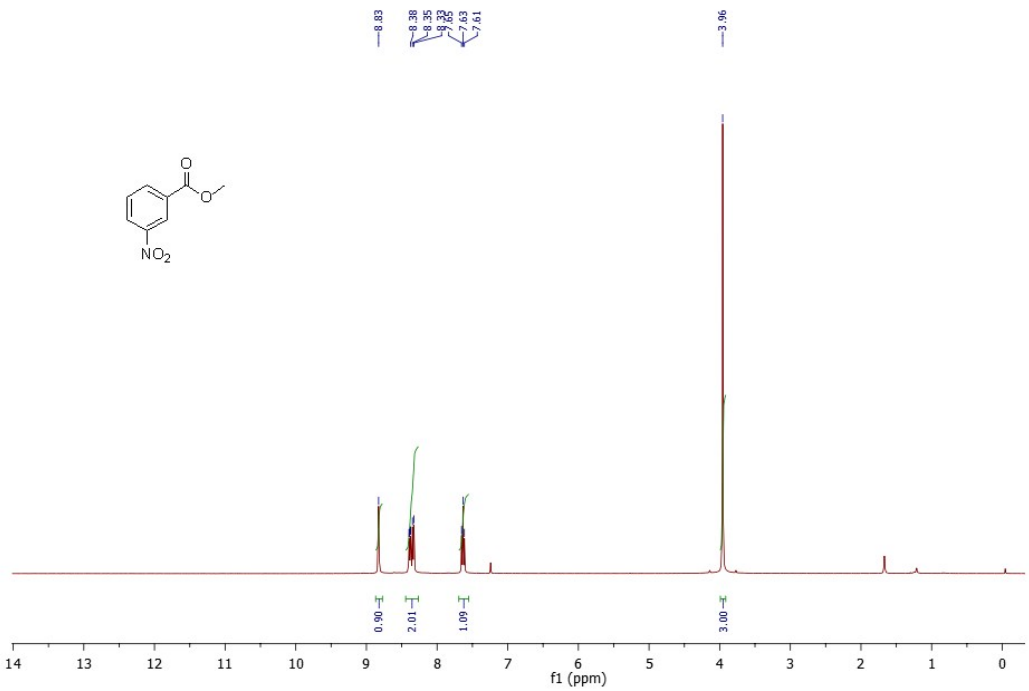

166.72
159.07
133.54
131.64
120.10
111.97
111.61
77.31
77.06
76.81
55.95
52.02
O
O
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

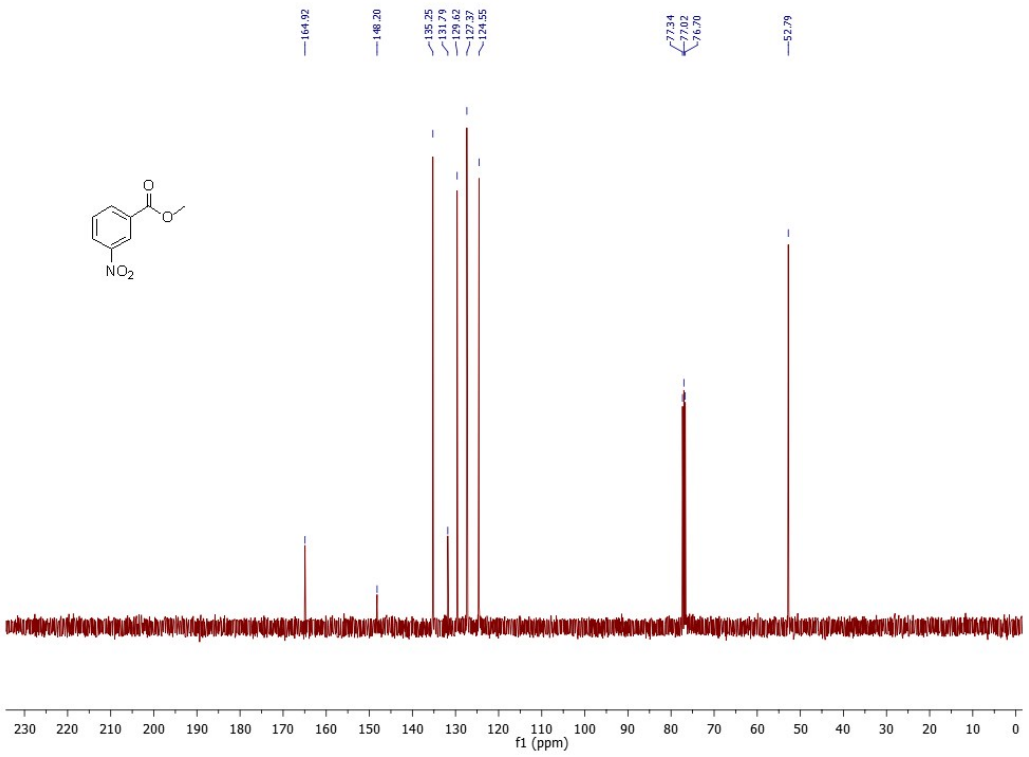

7.90
7.89
7.87
6.84
6.82
4.34
3.86
HO
O
O
5.97
5.93
4.02
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.60
165.57
135.60
124.87
118.97
81.49
81.17
80.85
55.60
HO
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.82
7.80
6.60
6.58
4.03
3.99
3.81
O
O
H2N
1.00
1.06
1.09
1.66
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


167.26
151.02
131.55
119.38
113.74
77.42
77.10
76.78
51.62
O
O
H2N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.83
8.38
8.35
8.33
7.65
7.63
7.61
3.96
O
O
NO2
0.90
2.01
1.09
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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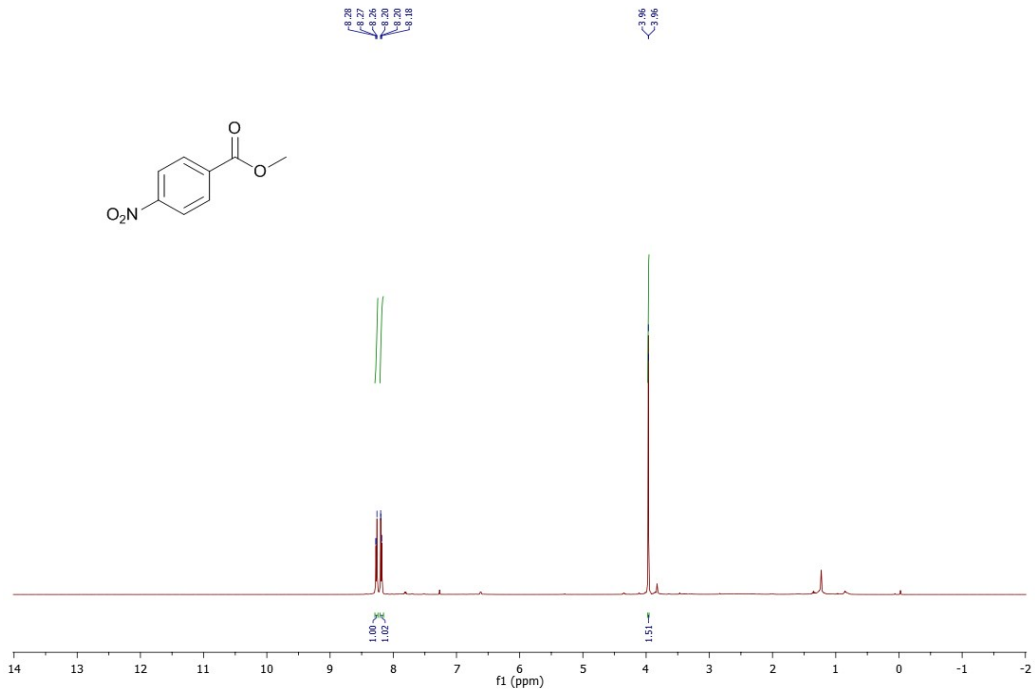
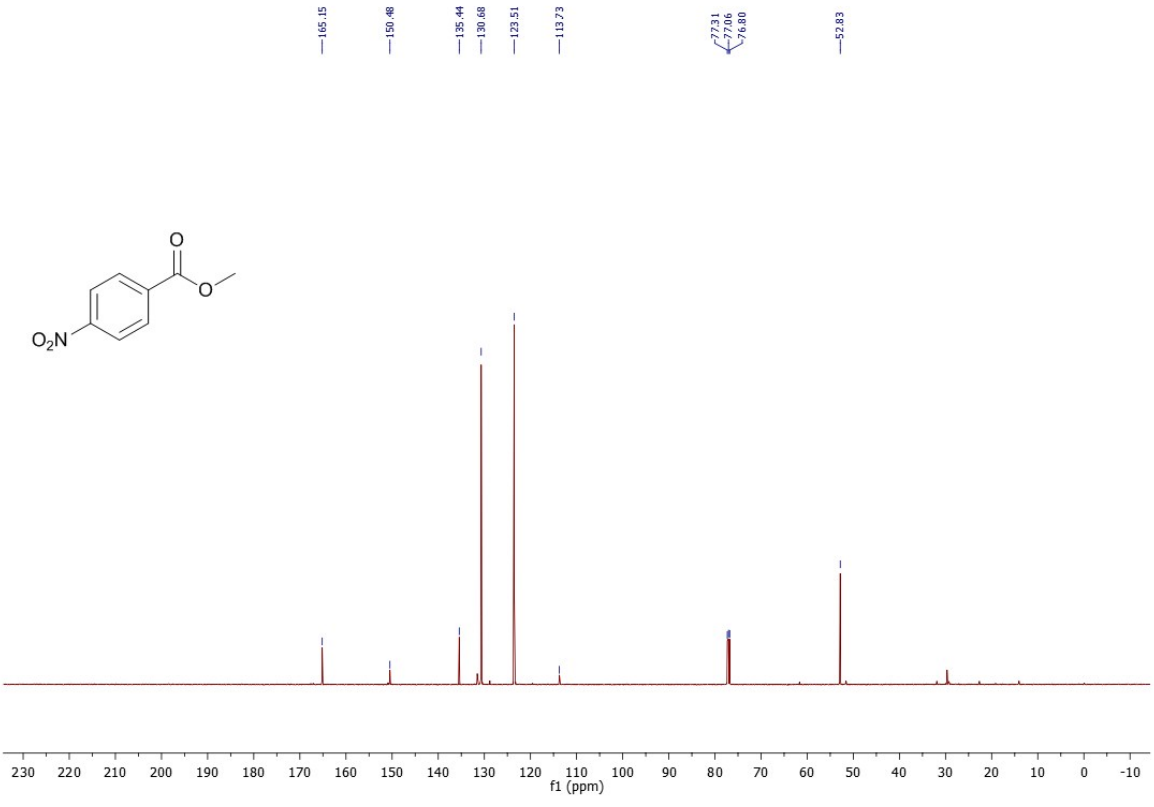
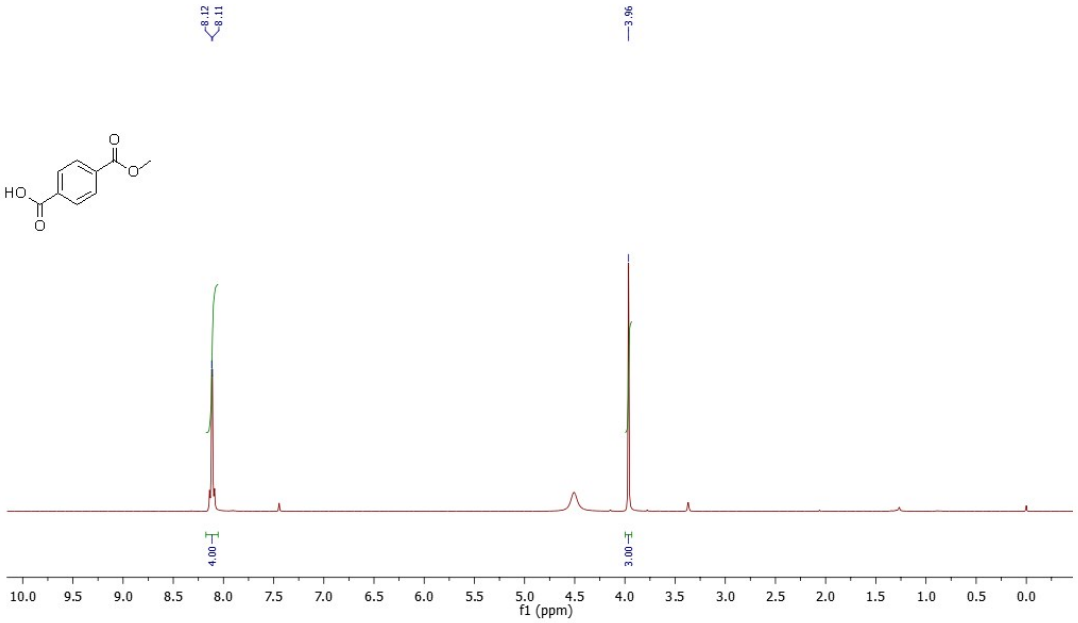
148.20
135.25
131.79
129.62
127.37
124.55
77.34
77.02
76.70
52.79
O
O
NO2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.28
8.27
8.26
8.20
8.20
8.18
3.96
3.96
O
O
O2N
1.00
1.02
1.51
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


165.15
150.48
135.44
130.68
123.51
113.73
77.31
77.06
76.80
52.83
O
O
O2N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.11
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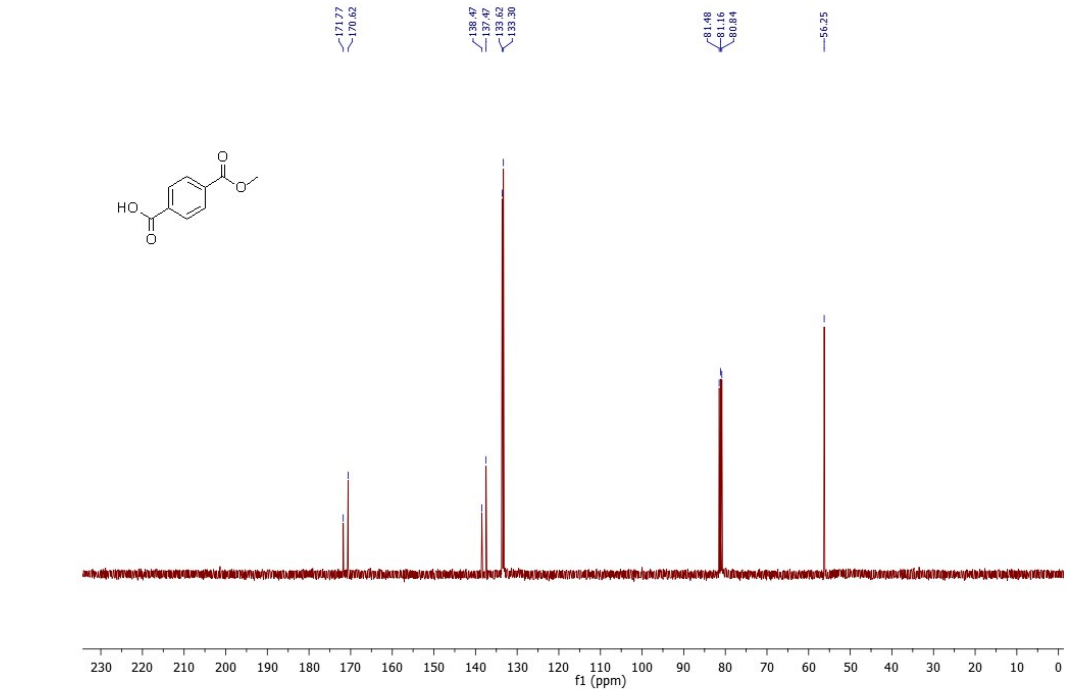
HO
O
O
O
4.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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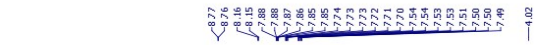
170.62
138.47
137.47
133.62
133.30
81.48
81.16
80.84
56.25
HO
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.86
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7.85
7.74
7.73
7.73
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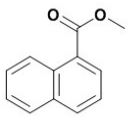
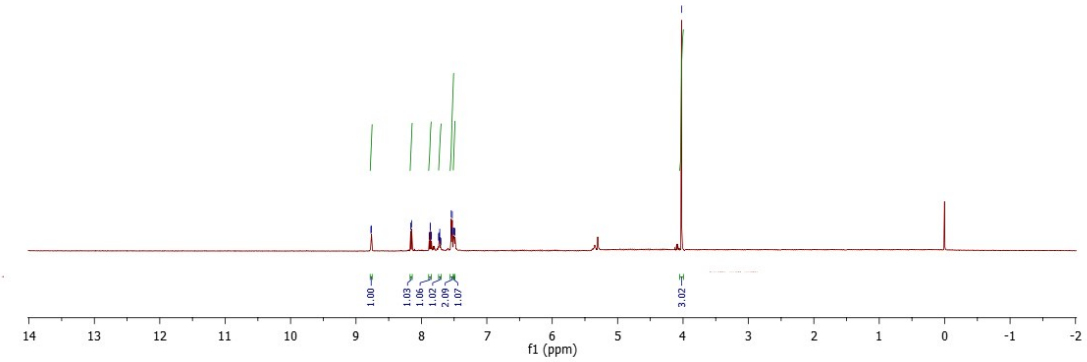
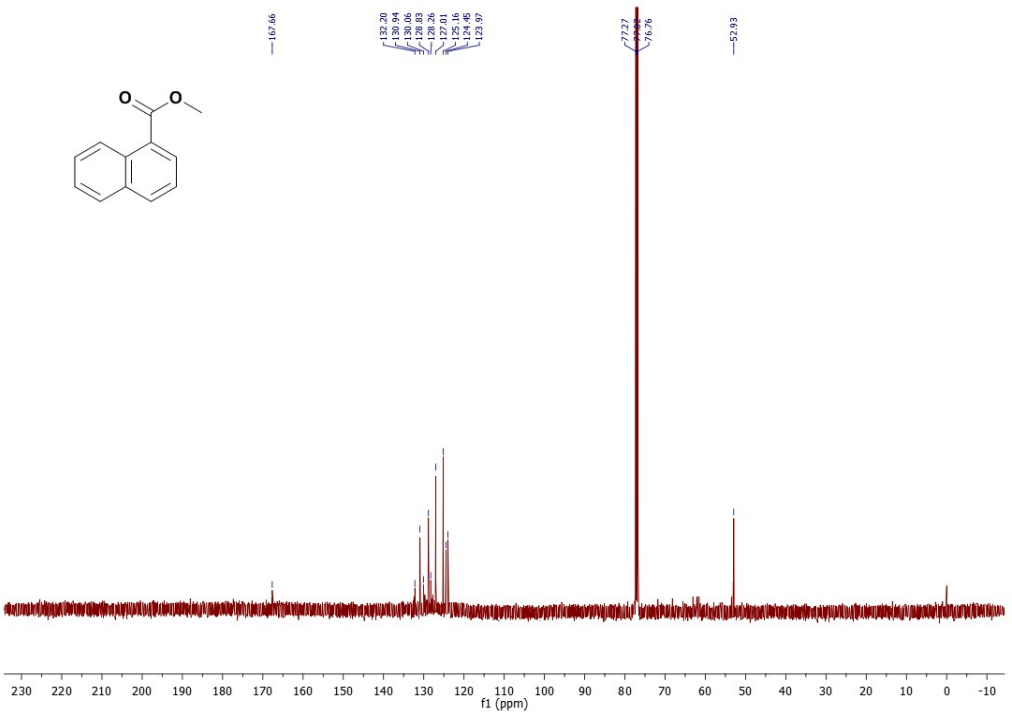
7.70
7.54
7.54
7.53
7.53
7.51
7.50
7.50
7.49
4.02


O
O


1.00
1.03
1.06
1.02
2.09
1.07
3.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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128.26
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125.16
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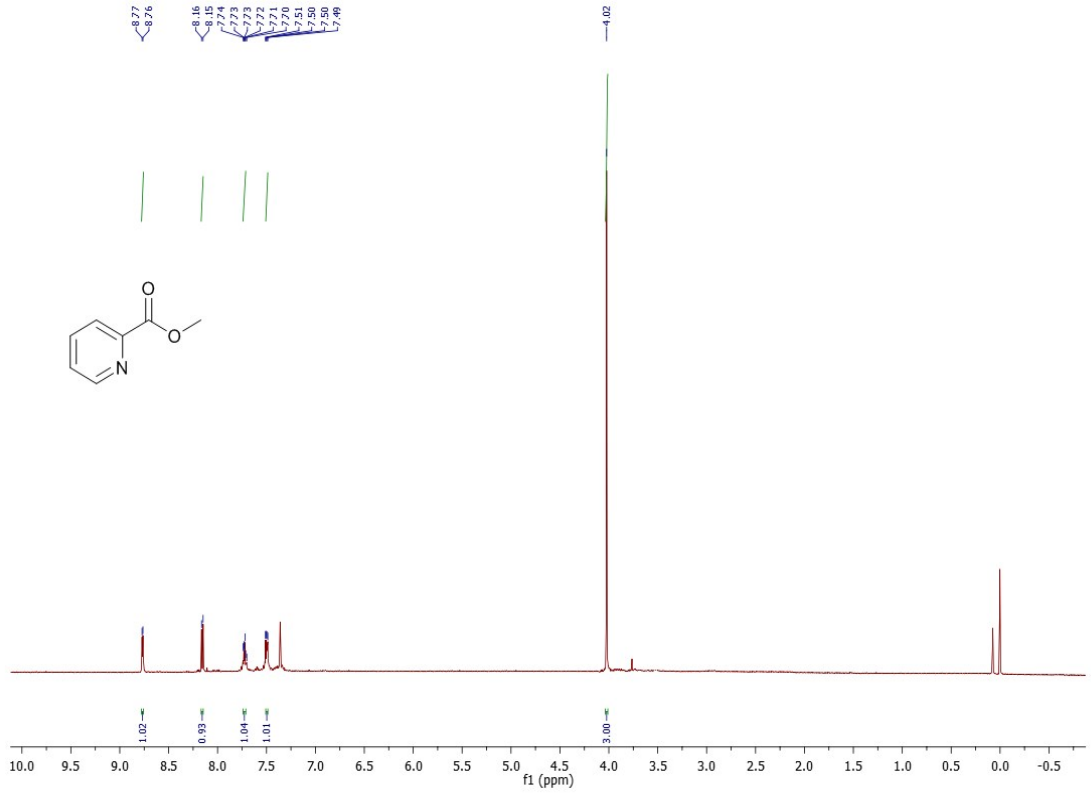
123.97
77.27
77.02
76.76
52.93
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

O
O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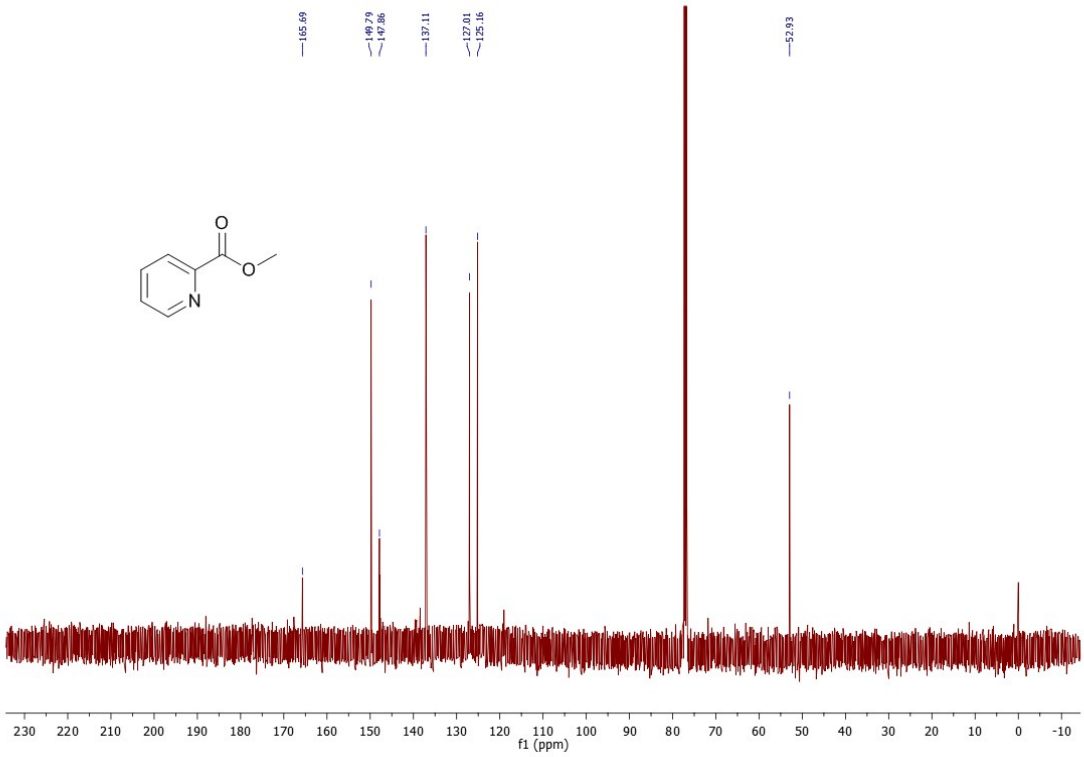
7.73
7.72
7.71
7.70
7.51
7.50
7.50
7.49
4.02
O
O
N
1.02
0.93
1.04
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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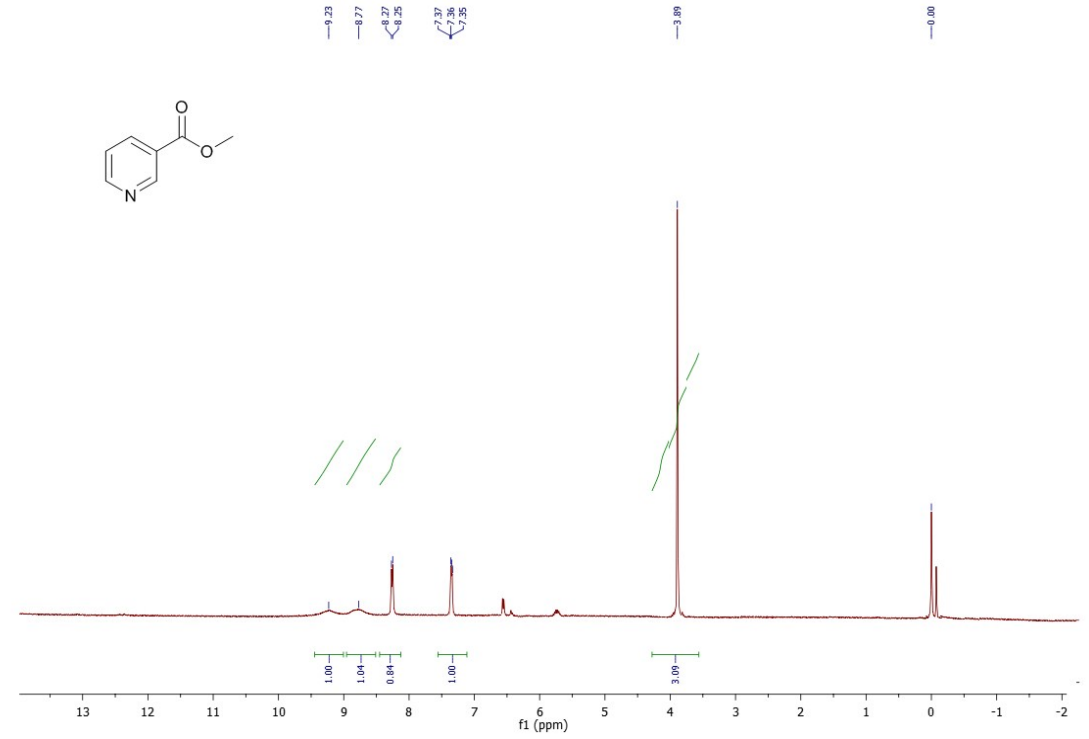
149.79
147.86
137.11
127.01
125.16
52.93
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.27
8.25
7.37
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7.35
3.89
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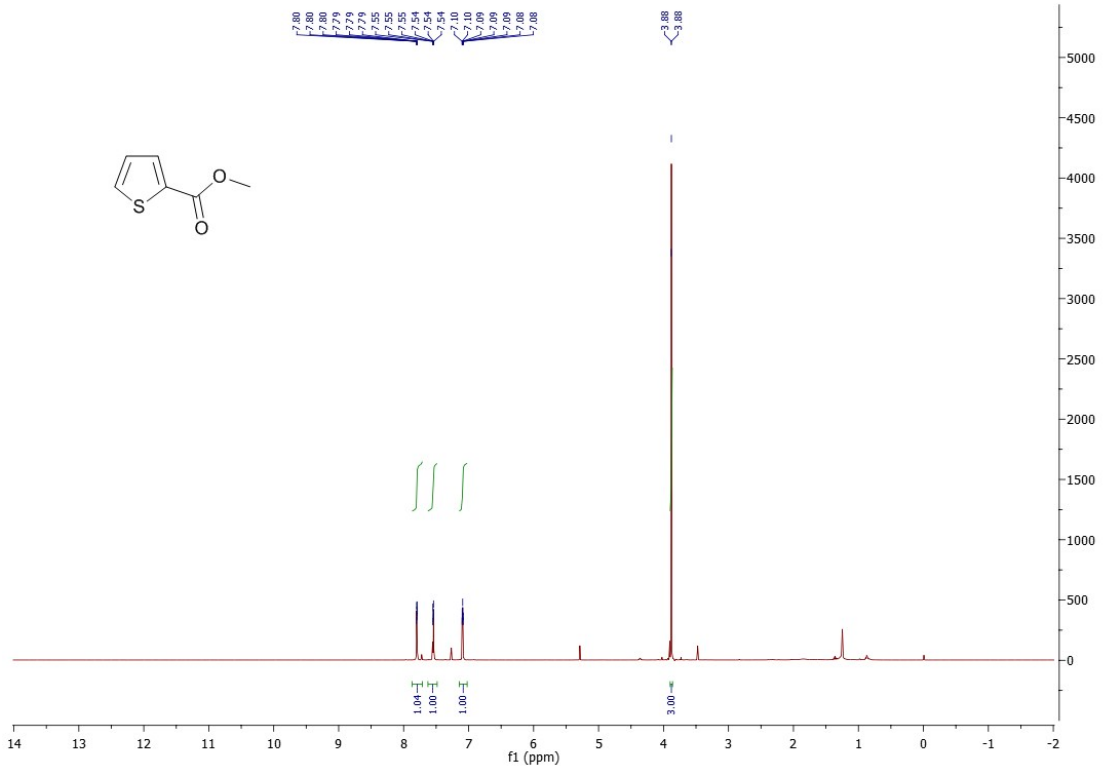
O
O
N
1.00
1.04
0.84
1.00
3.09
f1 (ppm)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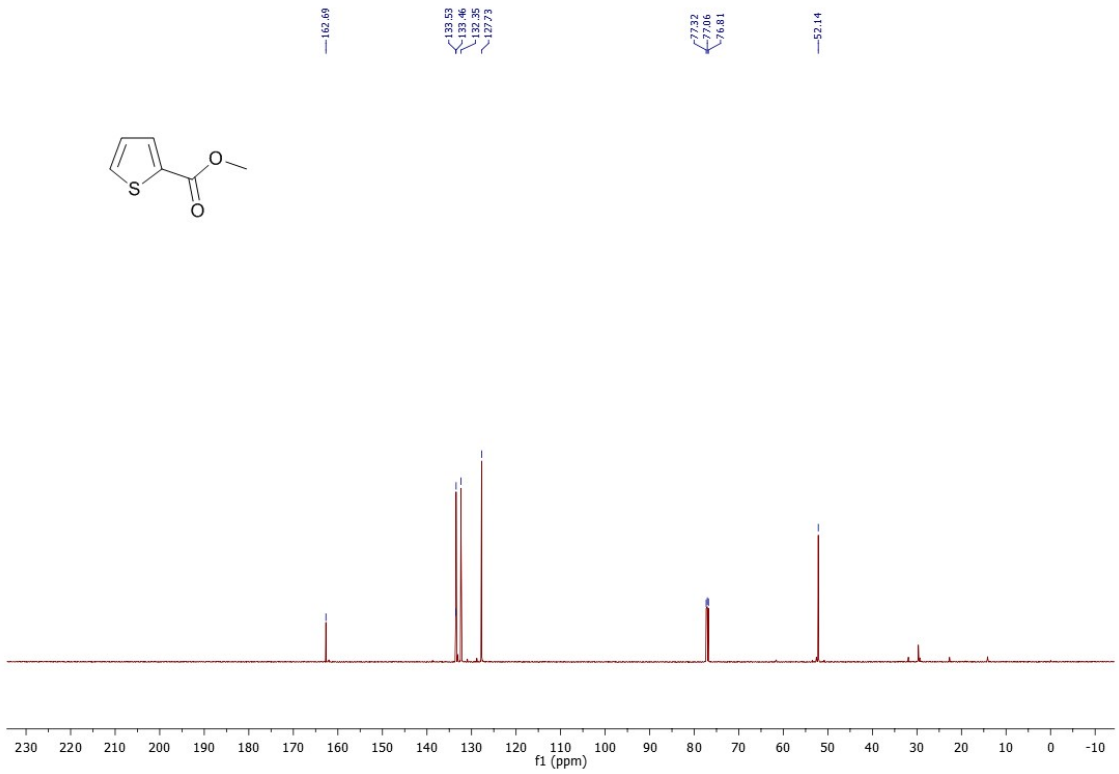
7.79
7.55
7.55
7.54
7.54
7.54
7.10
7.09
7.09
7.09
7.08
7.08
3.88
3.88
S
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.04
1.00
1.00
3.00
f1 (ppm)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133.46
132.35
127.73
77.32
77.06
76.81
52.14
S
O
O
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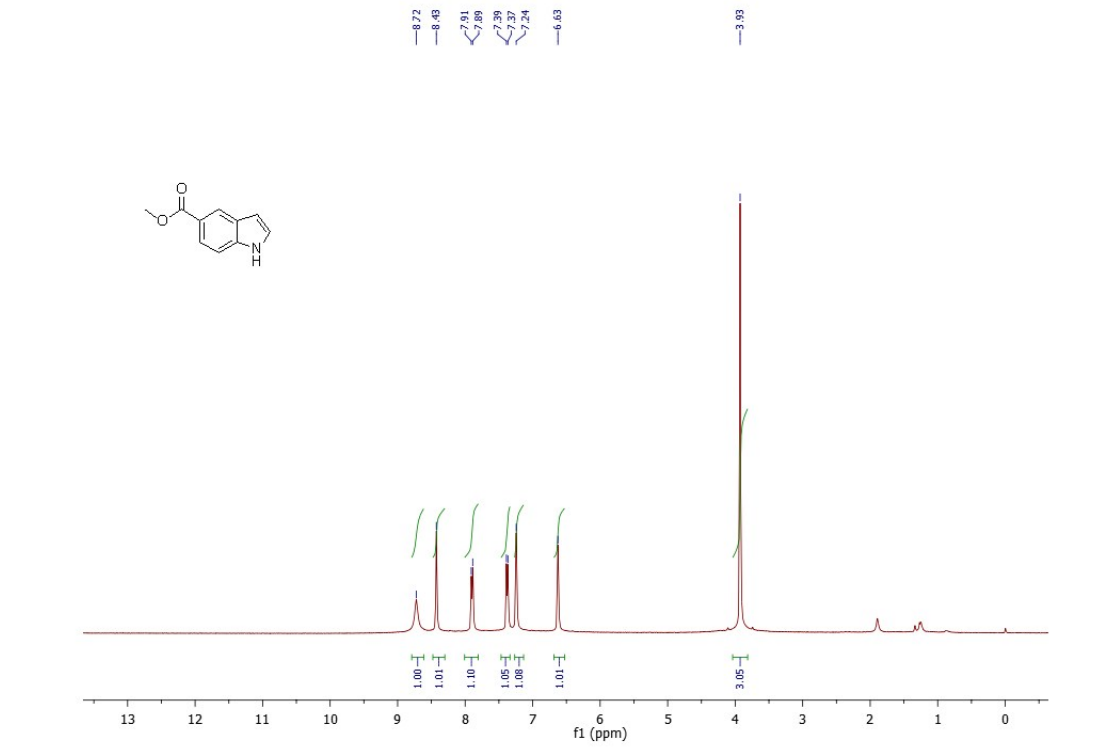
f1 (ppm)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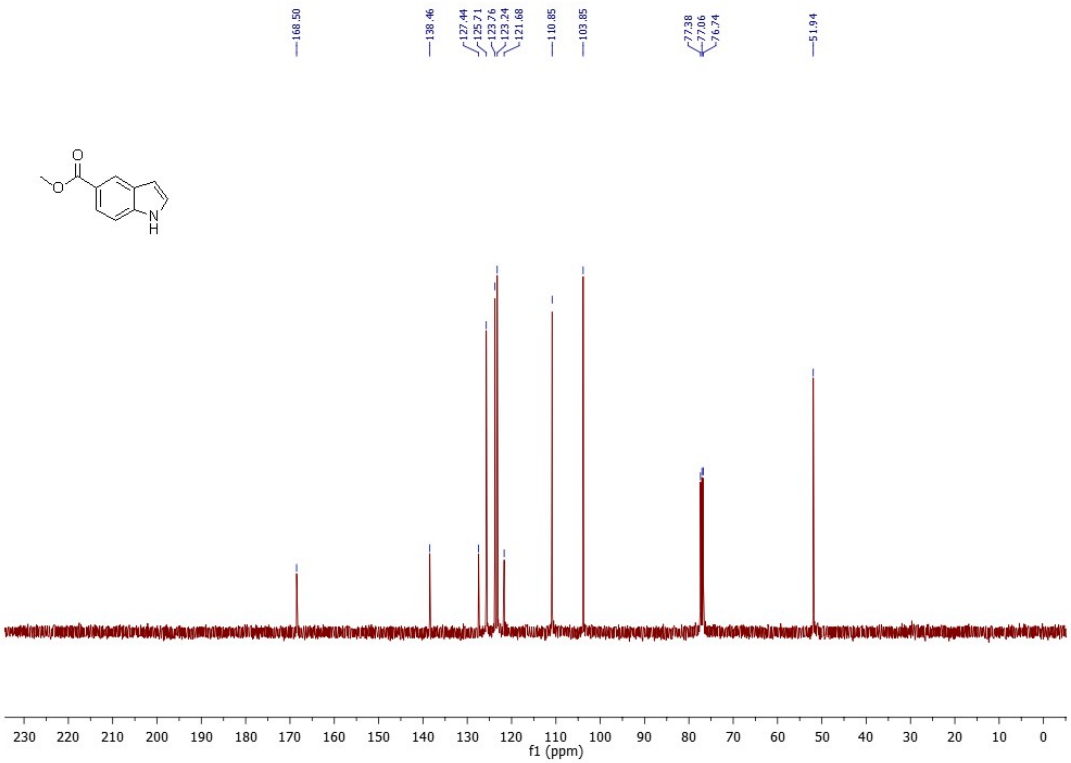
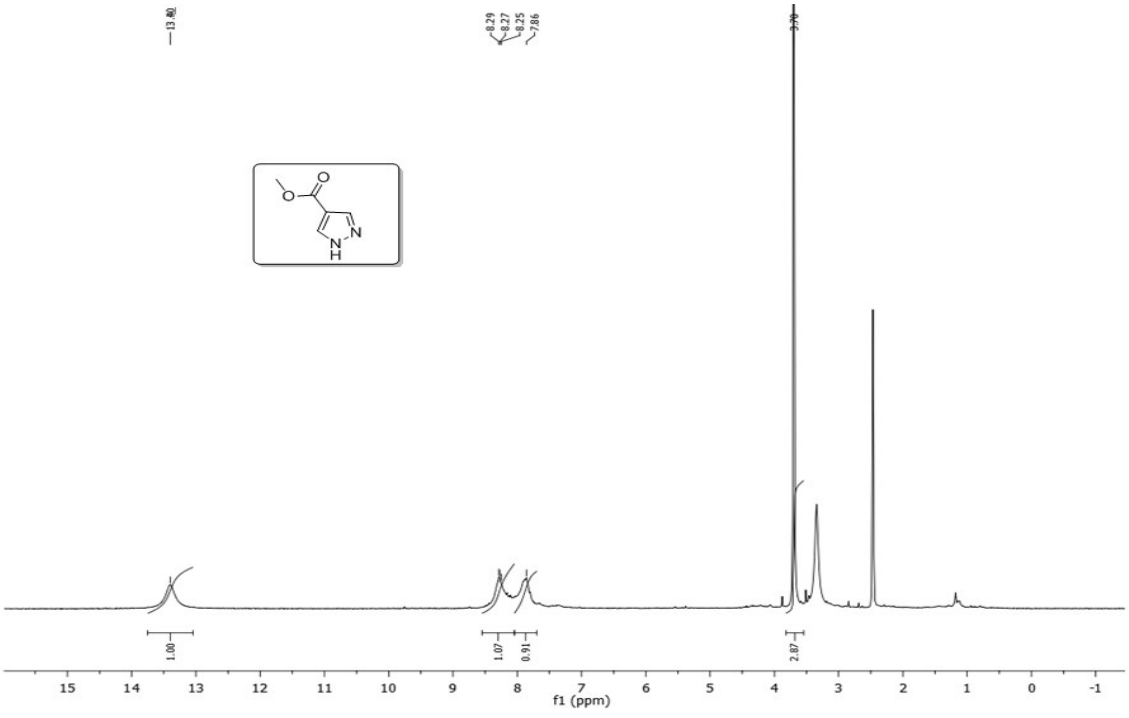
8.43
7.91
7.89
7.39
7.37
7.24
6.63
3.93
O
O
N
H
1.00
1.01
1.10
1.05
1.08
1.01
3.05
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


168.50
138.46
127.44
125.71
123.76
123.24
121.68
110.85
103.85
77.38
77.06
76.74
51.94
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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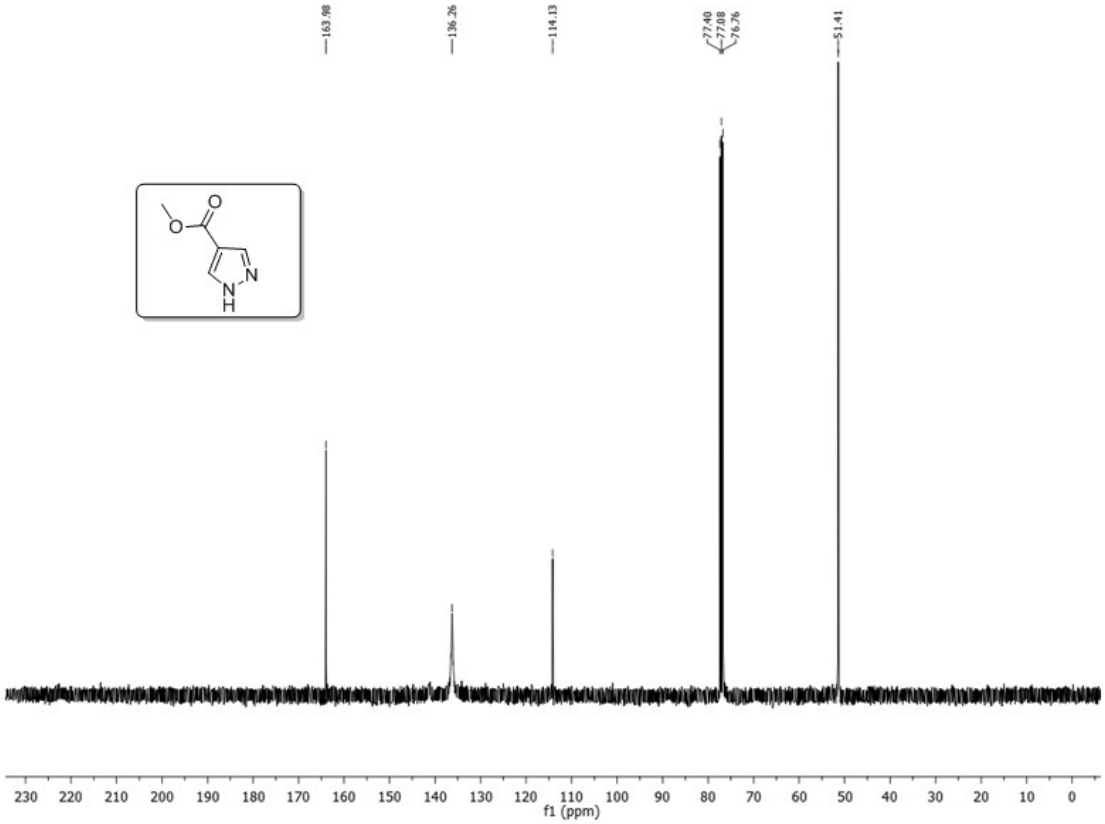
8.29
8.27
8.25
7.86
3.70
1.00
1.07
0.91
2.87
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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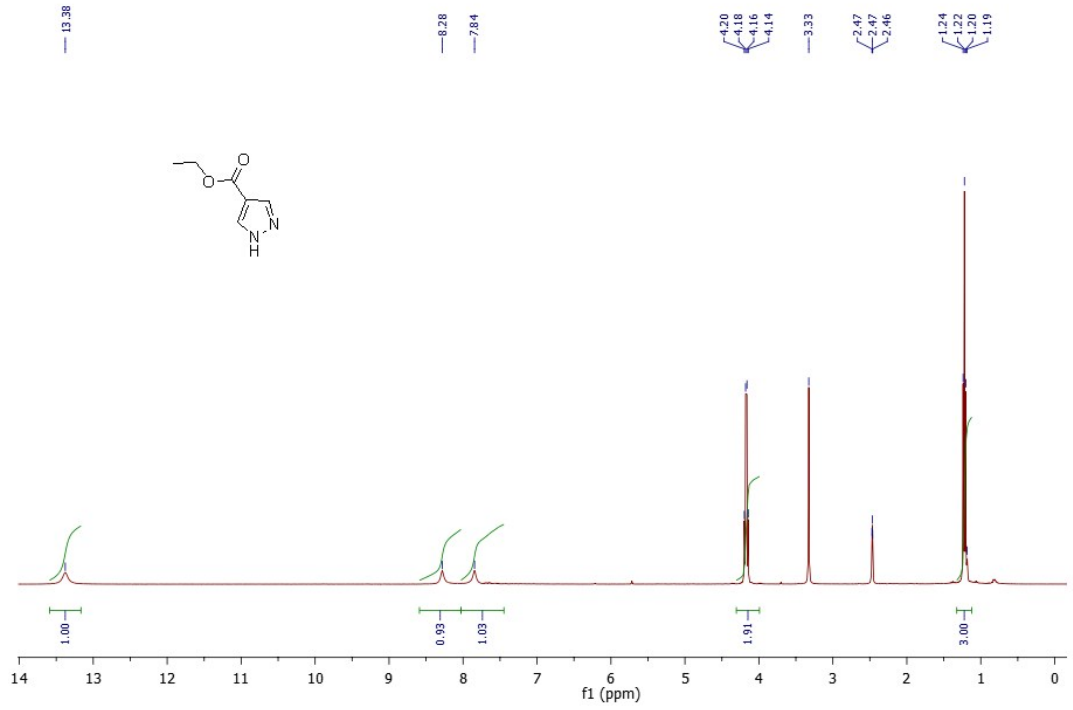
136.26
114.13
77.40
77.08
76.76
51.41
O
O
N
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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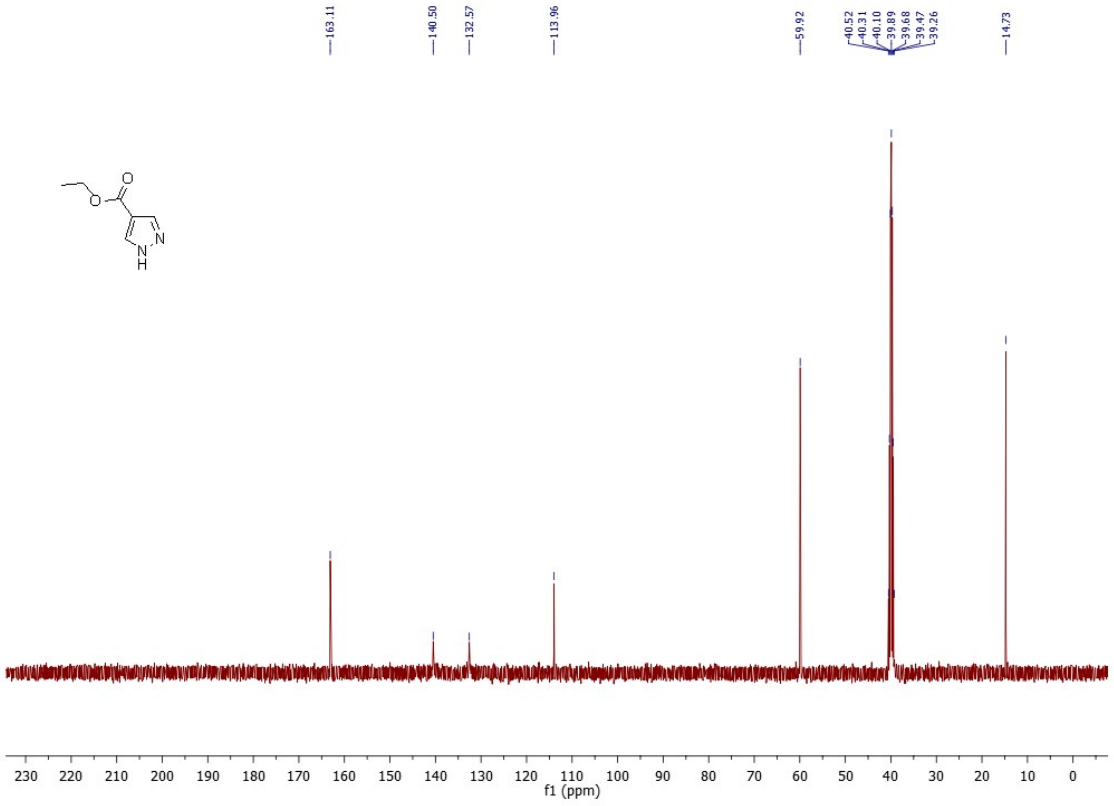
7.84
4.20
4.18
4.16
4.14
3.33
2.47
2.47
2.46
1.24
1.22
1.20
1.19
O
O
N
N
H
1.00
0.93
1.03
1.91
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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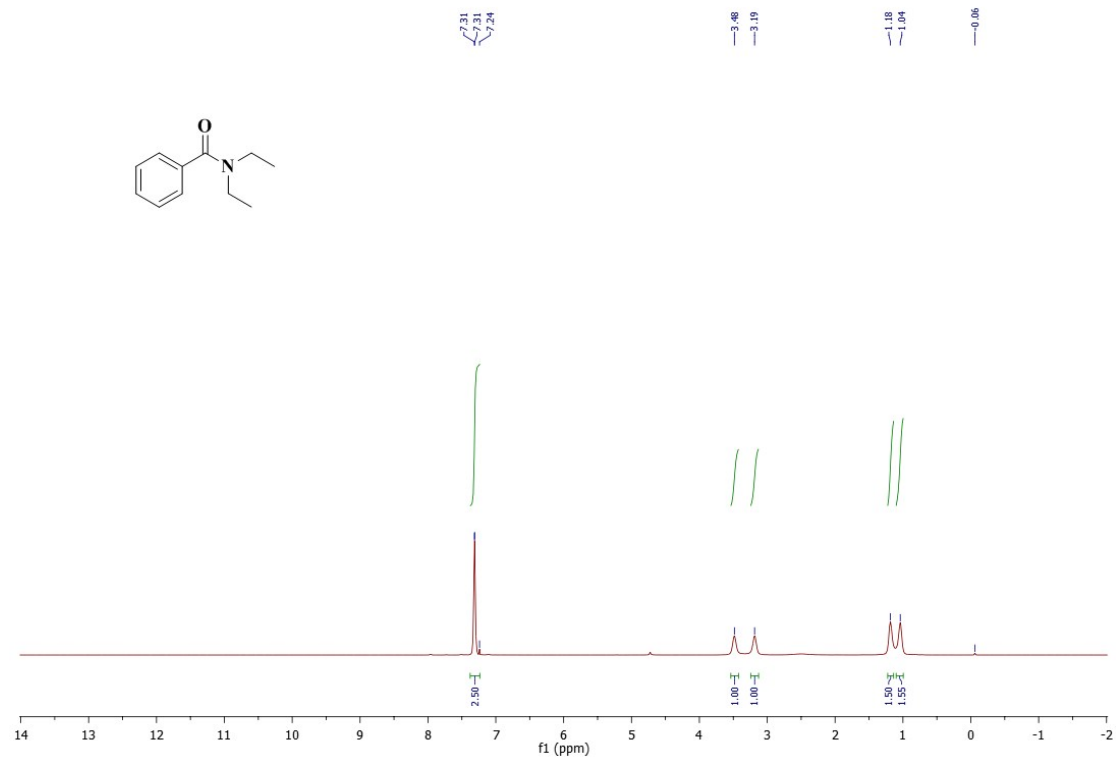
140.50
132.57
113.96
59.92
40.52
40.31
40.10
39.89
39.68
39.47
39.26
14.73
O
O
N
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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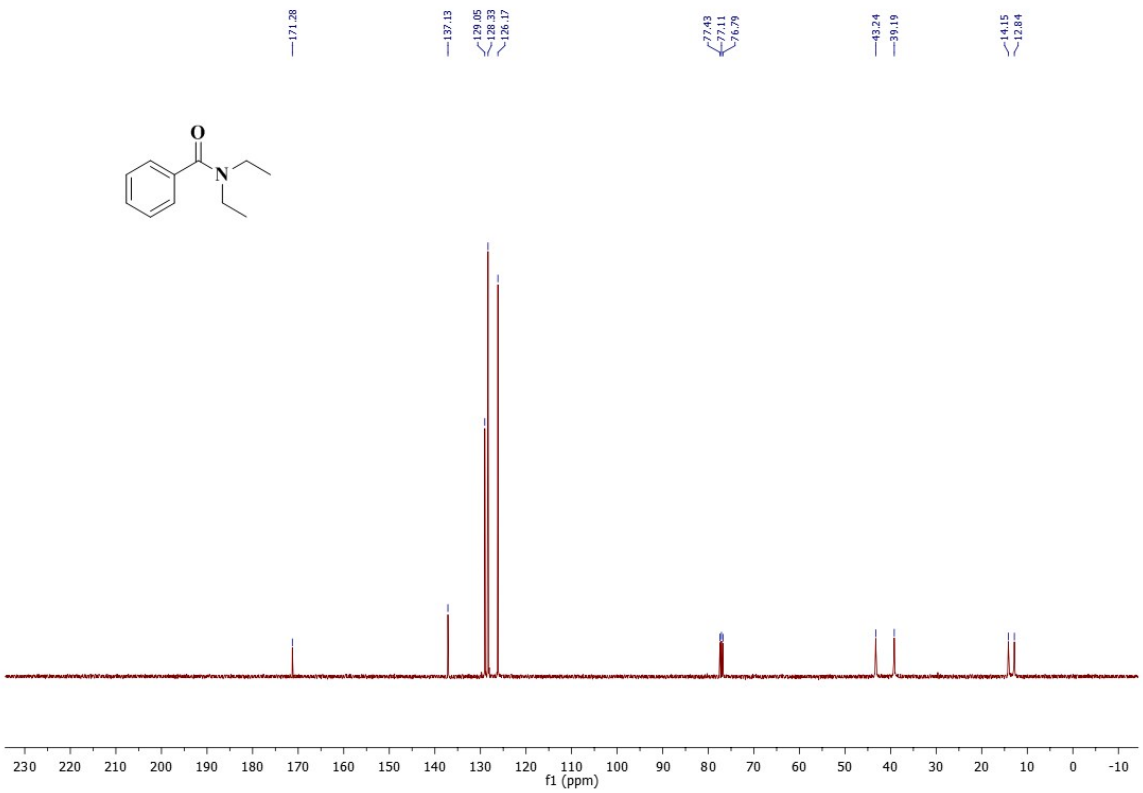
7.31
7.24
3.48
3.19
1.18
1.04
0.06
O
N
2.50
1.00
1.00
1.50
1.55
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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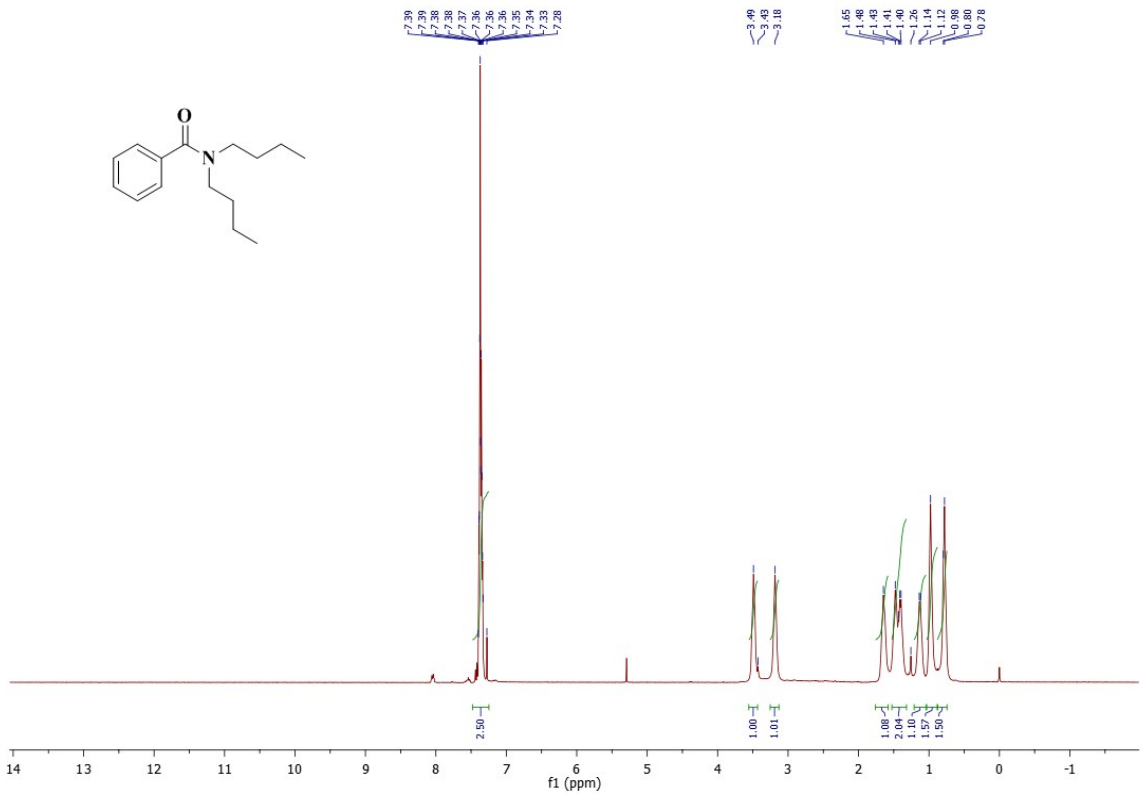
77.11
76.79
43.24
39.19
14.15
12.84
O
N
f1 (ppm)


7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.33
7.28
3.49
3.43
3.18
1.65
1.48
1.43
1.41
1.40
1.26
1.14
1.12
0.98
0.80
0.78
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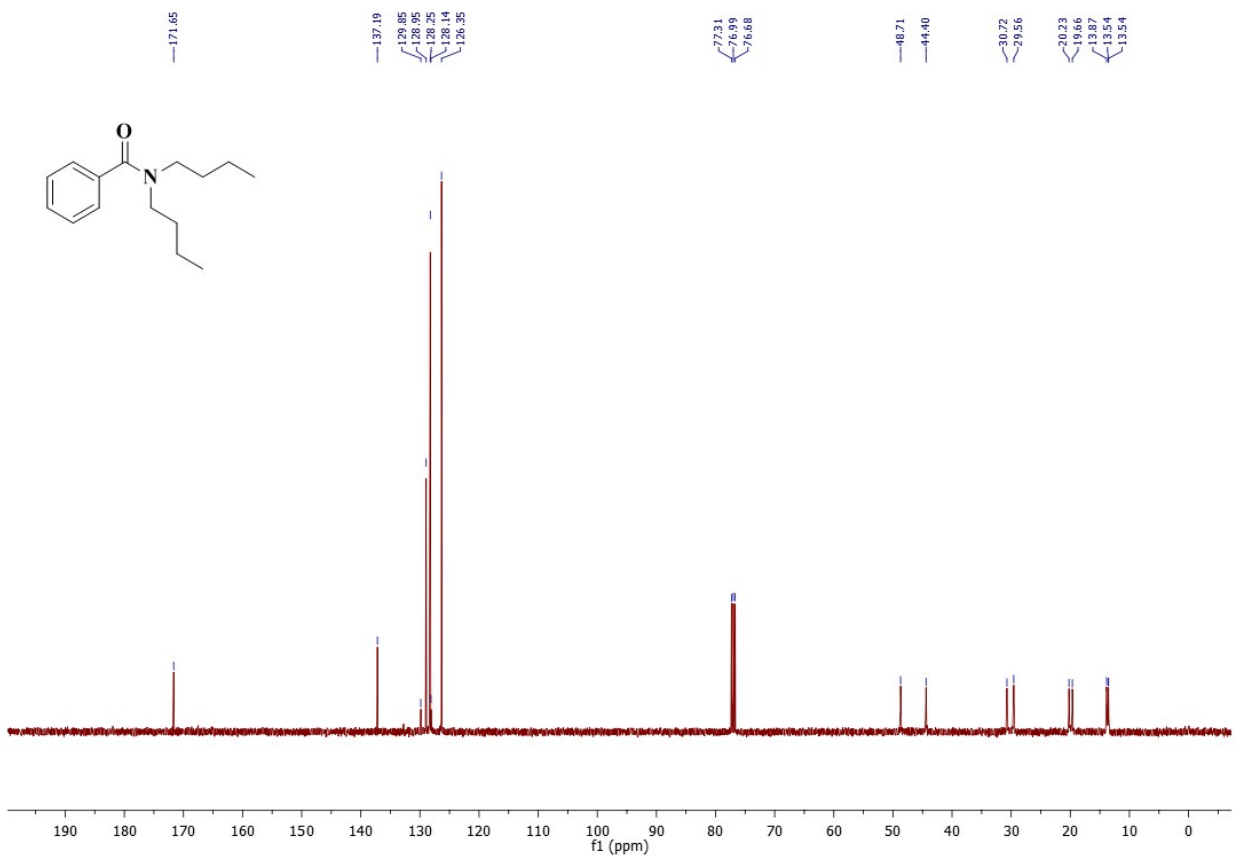
1.00
1.01
1.08
2.04
1.10
1.57
1.50
O
N
f1 (ppm)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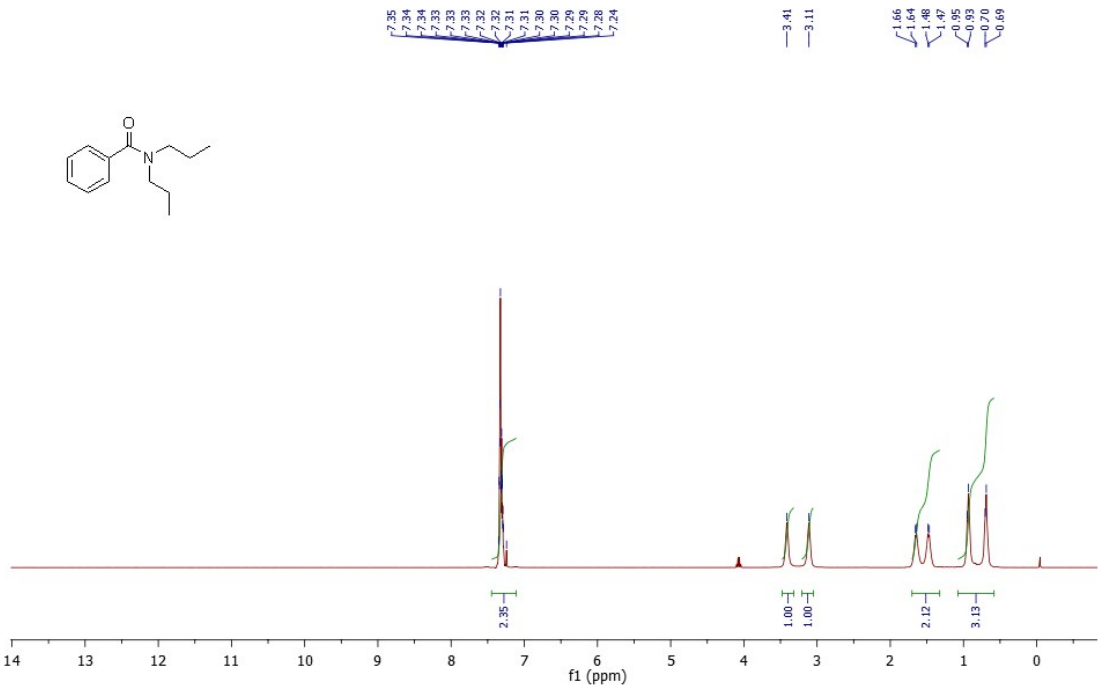
129.85
128.95
128.25
128.14
126.35
77.31
76.99
76.68
48.71
44.40
30.72
29.56
20.23
19.66
13.87
13.54
13.54
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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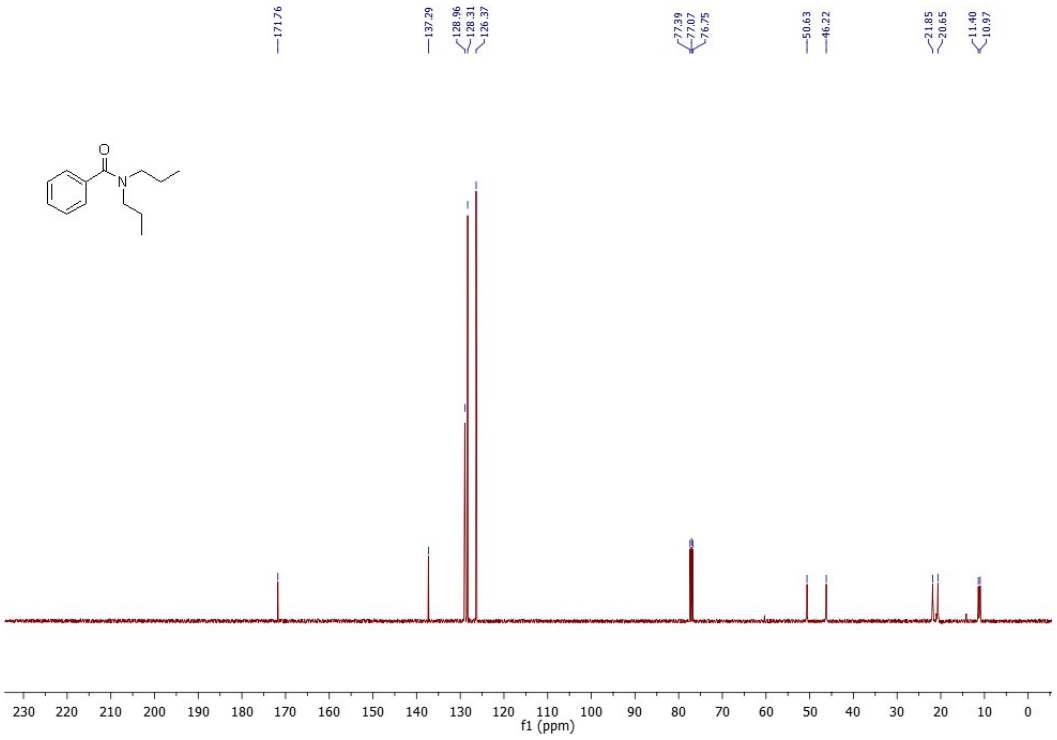
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.24
3.41
3.11
1.66
1.64
1.48
1.47
0.95
0.93
0.70
0.69
O
N
2.35
1.00
1.00
2.12
3.13
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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137.29
128.96
128.31
126.37
77.39
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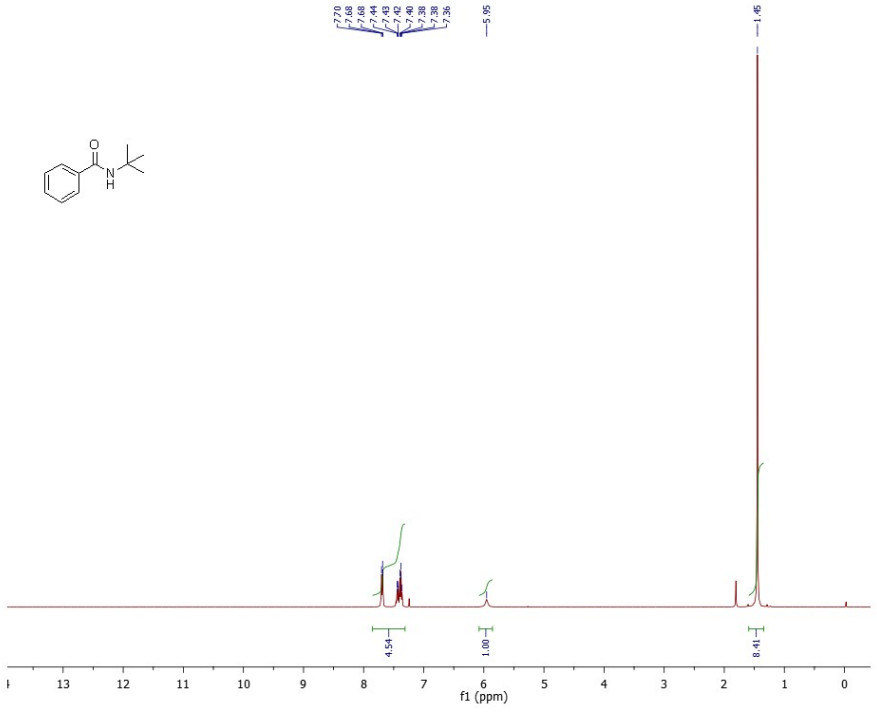
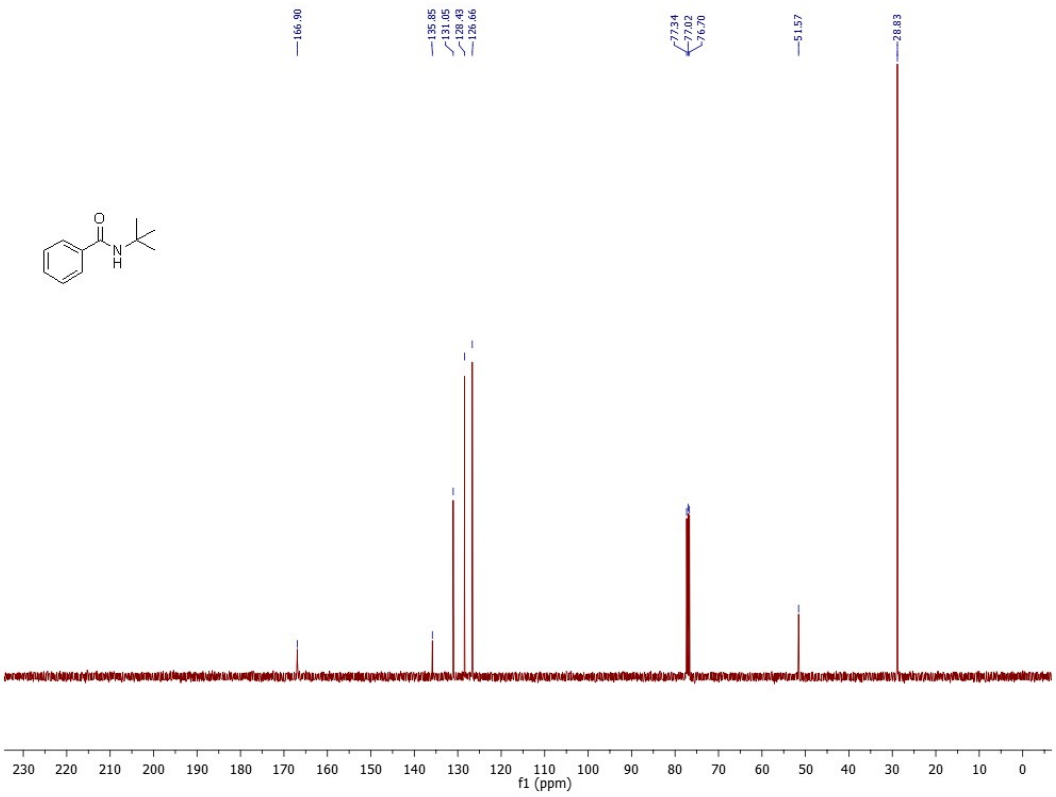
76.75
50.63
46.22
21.85
20.65
11.40
10.97
O
N
f1 (ppm)


7.70
7.68
7.66
7.44
7.43
7.42
7.40
7.38
7.38
7.36
5.95
1.45
O
N
H
4.54
1.00
8.41
f1 (ppm)


166.90
135.85
131.05
128.43
126.66
77.34
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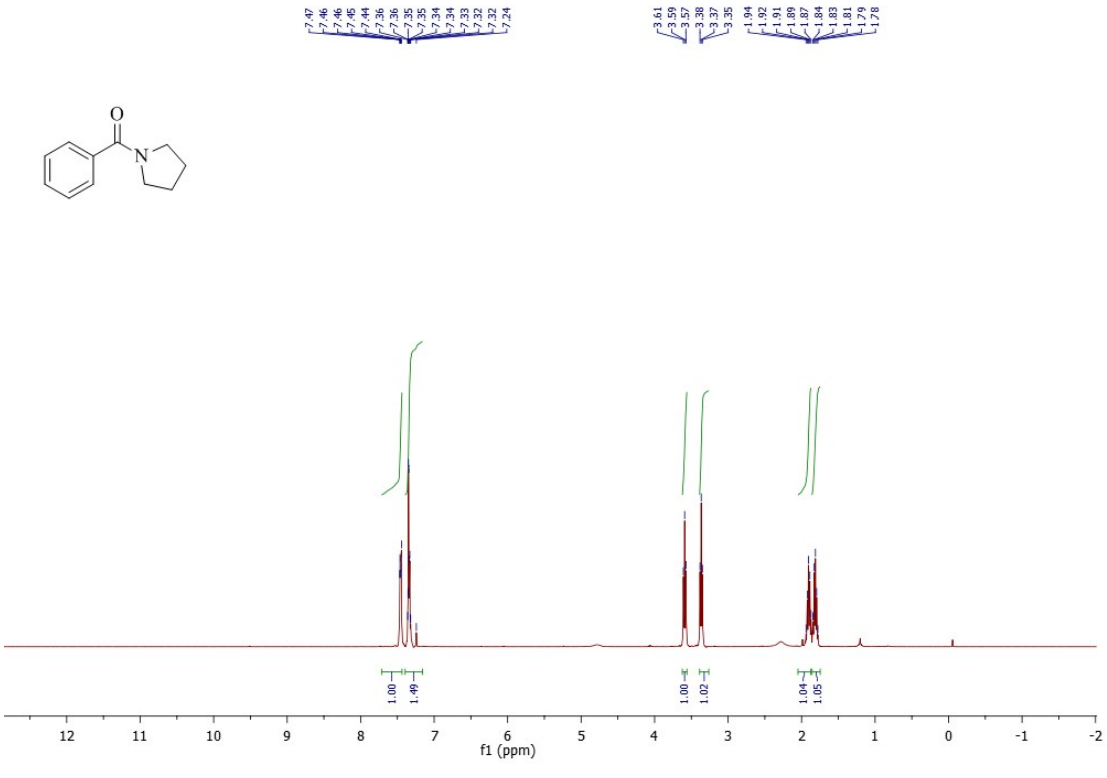
76.70
51.57
28.83
O
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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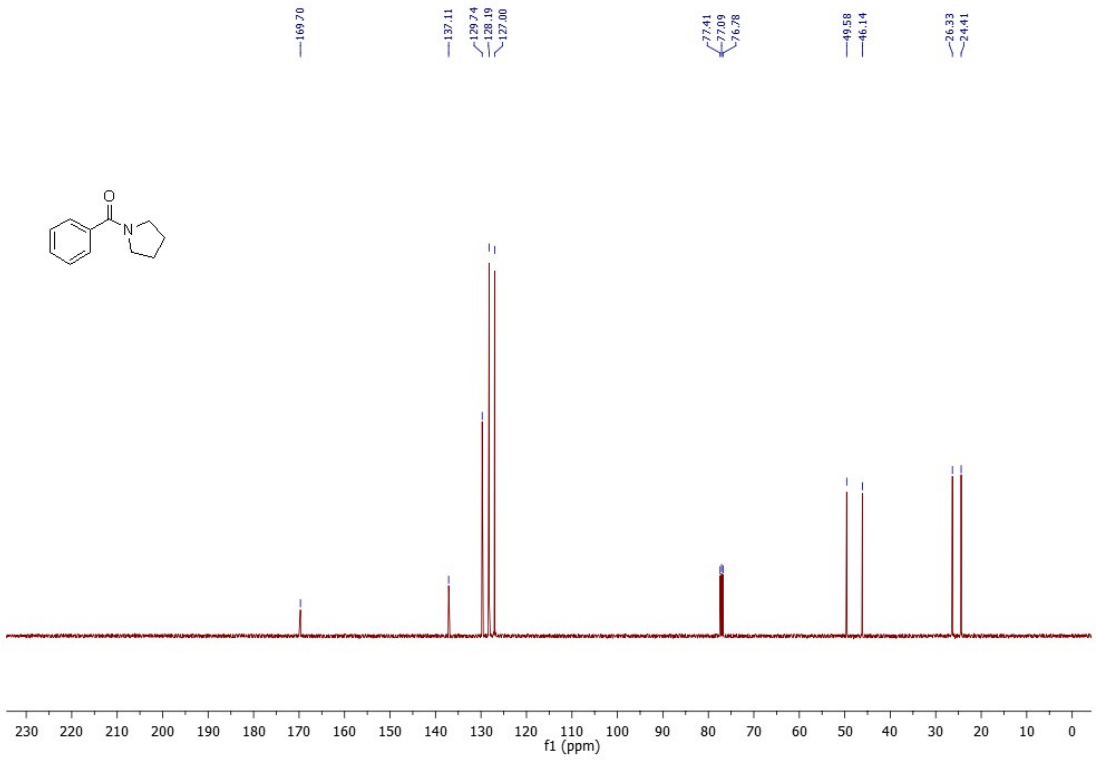
7.46
7.45
7.45
7.44
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.24
3.61
3.59
3.57
3.38
3.37
3.35
1.94
1.92
1.91
1.89
1.87
1.84
1.83
1.81
1.79
1.78
O
N
1.00
1.49
1.00
1.02
1.04
1.05
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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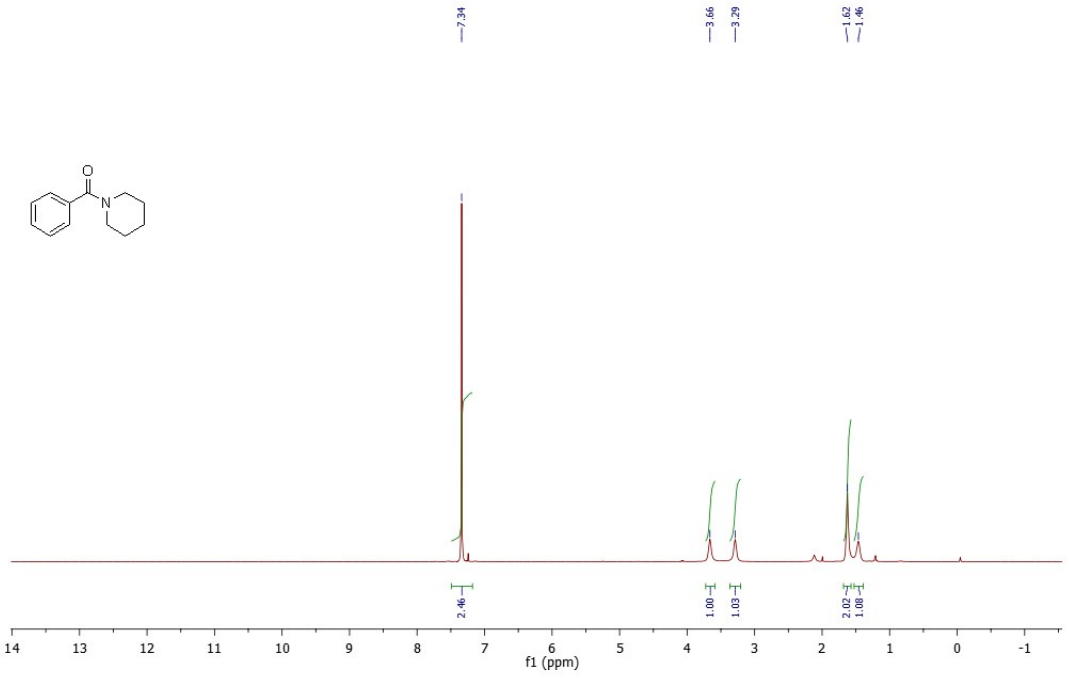
137.11
129.74
128.19
127.00
77.41
77.09
76.78
49.58
46.14
26.33
24.41
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.66
3.29
1.62
1.46
O
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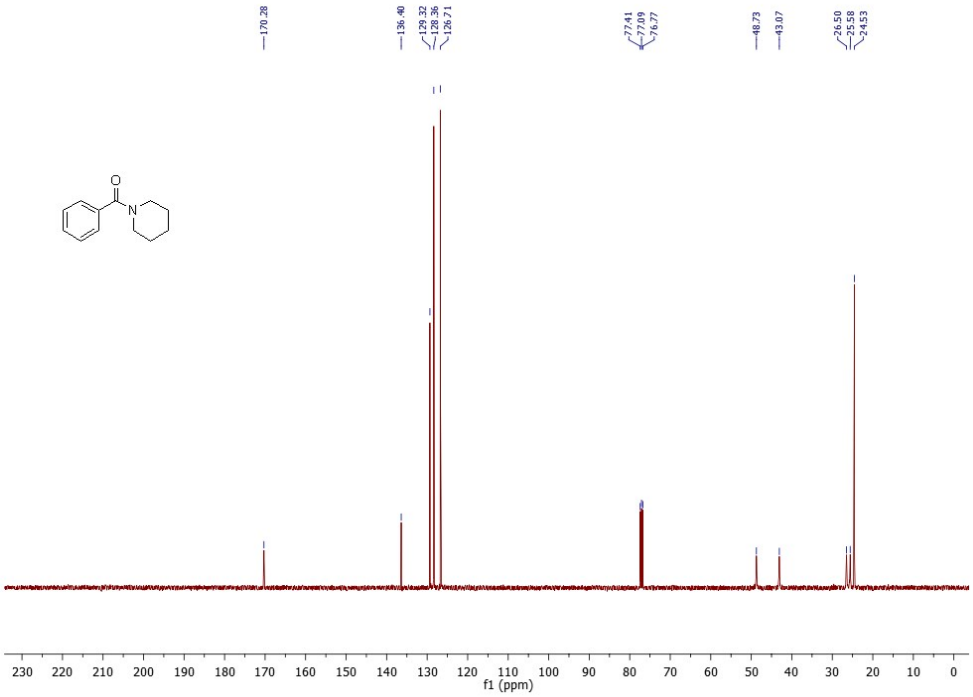
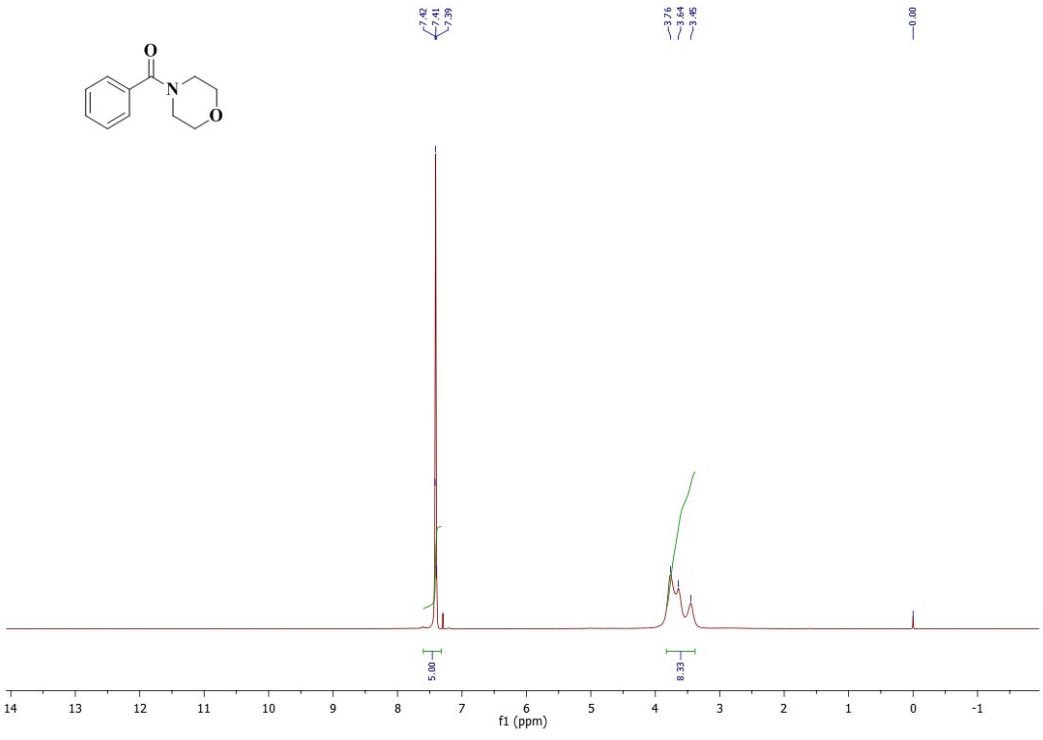
2.46
1.00
1.03
2.02
1.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


170.28
136.40
129.32
128.36
126.71
77.41
77.09
76.77
48.73
43.07
26.50
25.58
24.53
f1 (ppm)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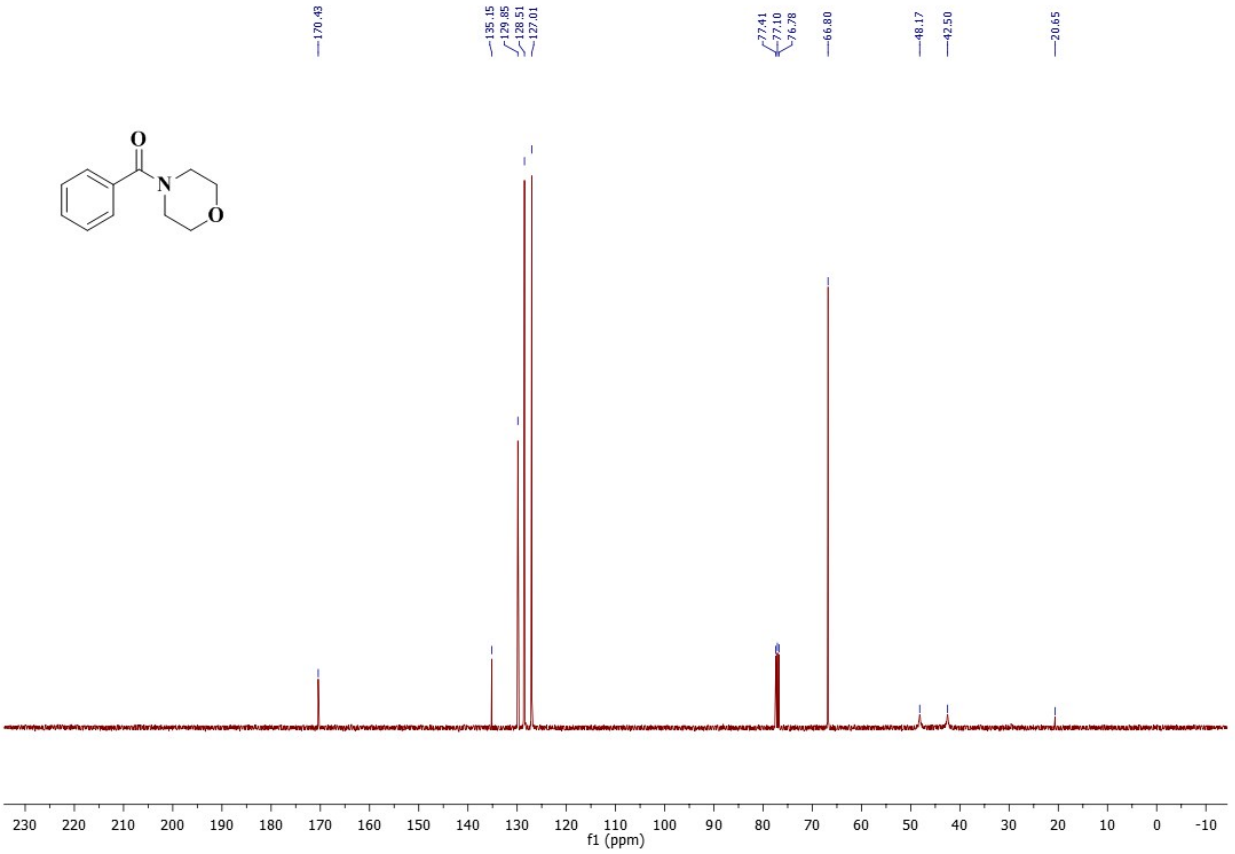
7.41
7.39
3.76
3.64
3.45
0.00
5.00
8.33
f1 (ppm)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128.51
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77.10
76.78
66.80
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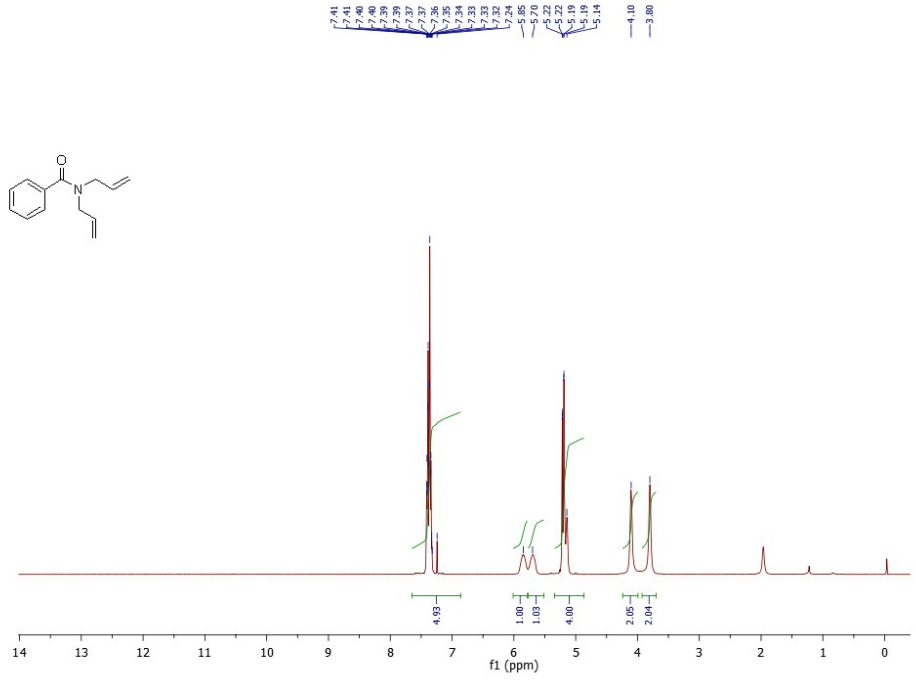
42.50
20.65
O
N
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.33
7.33
7.32
7.24
5.85
5.70
5.22
5.19
5.19
5.14
4.10
3.80
O
N
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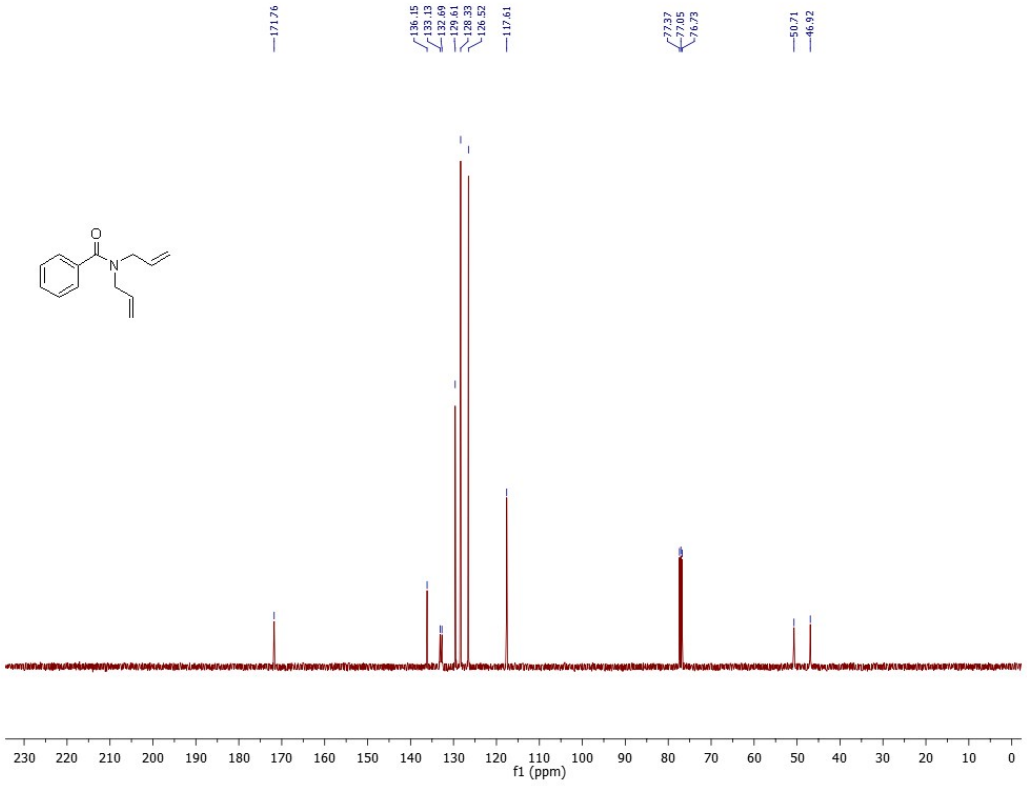
1.00
1.03
4.00
2.05
2.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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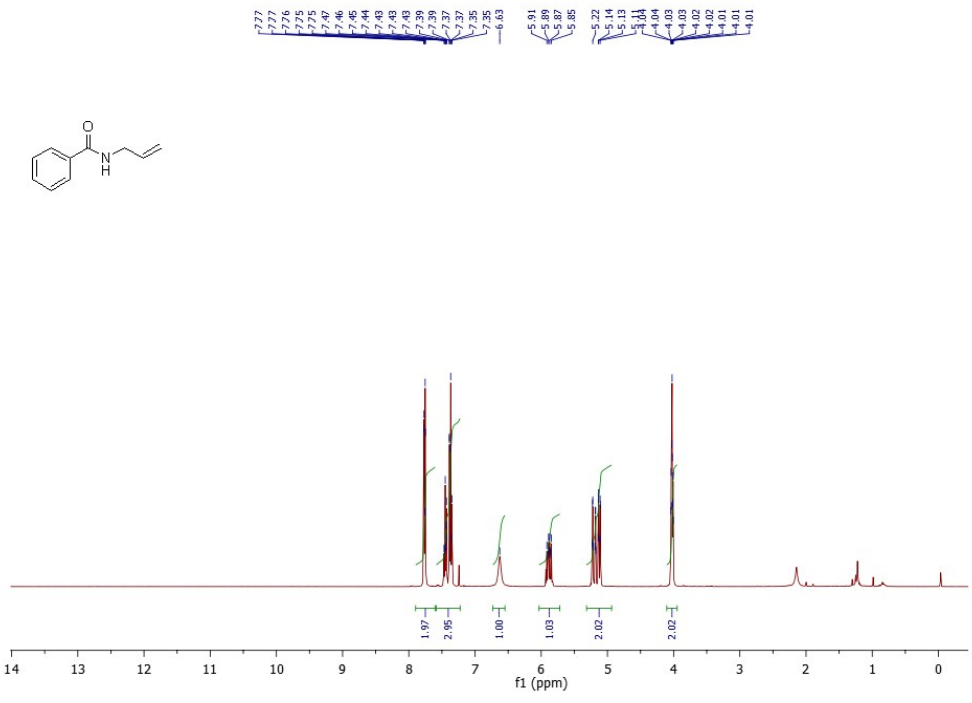
76.73
50.71
46.92
O
N
f1 (ppm)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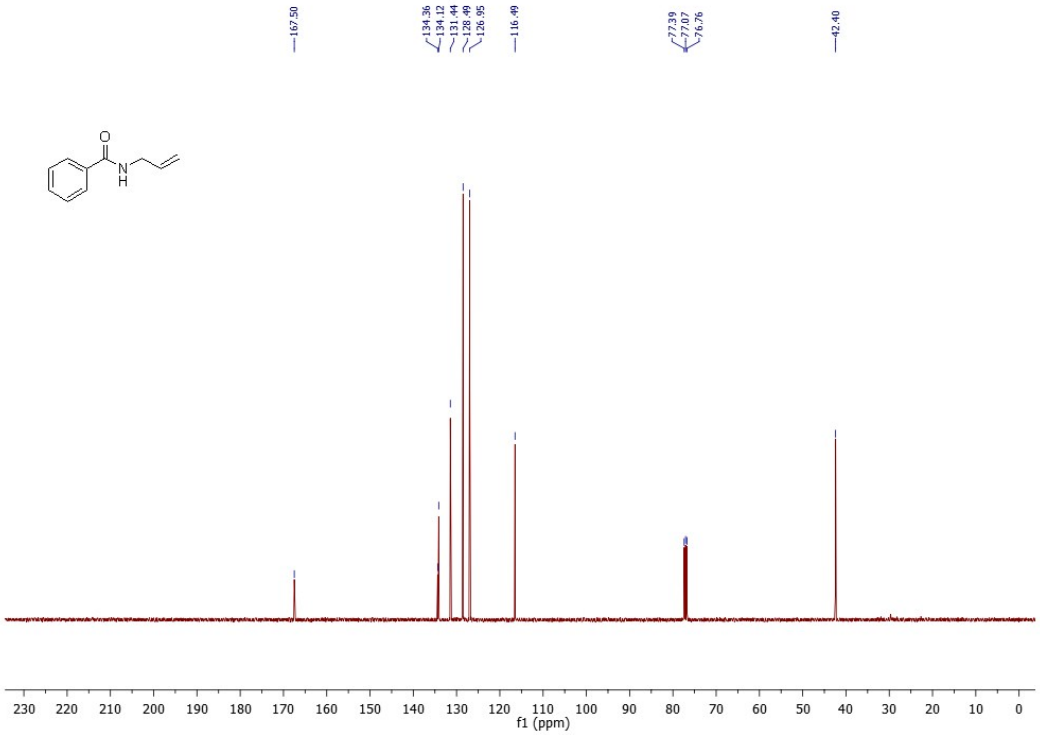
7.39
7.37
7.37
7.35
6.63
5.91
5.89
5.87
5.85
5.22
5.14
5.13
4.04
4.03
4.03
4.02
4.02
4.01
4.01
4.01
O
N
H
1.97
2.95
1.00
1.03
2.02
2.02
f1 (ppm)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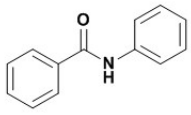
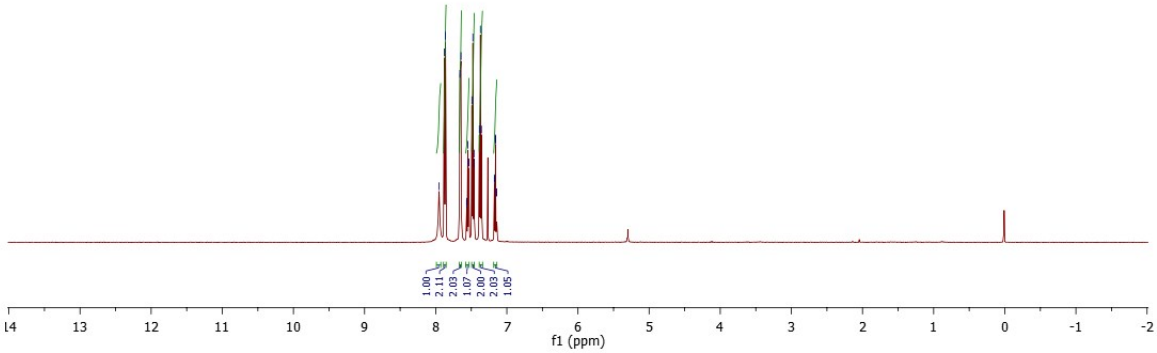
131.44
128.49
126.95
116.49
77.39
77.07
76.76
42.40
O
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.95
7.88
7.86
7.66
7.64
7.57
7.56
7.55
7.54
7.53
7.49
7.48
7.46
7.46
7.39
7.37
7.36
7.18
7.17
7.16
7.16
7.16
7.15
7.14


O
N
H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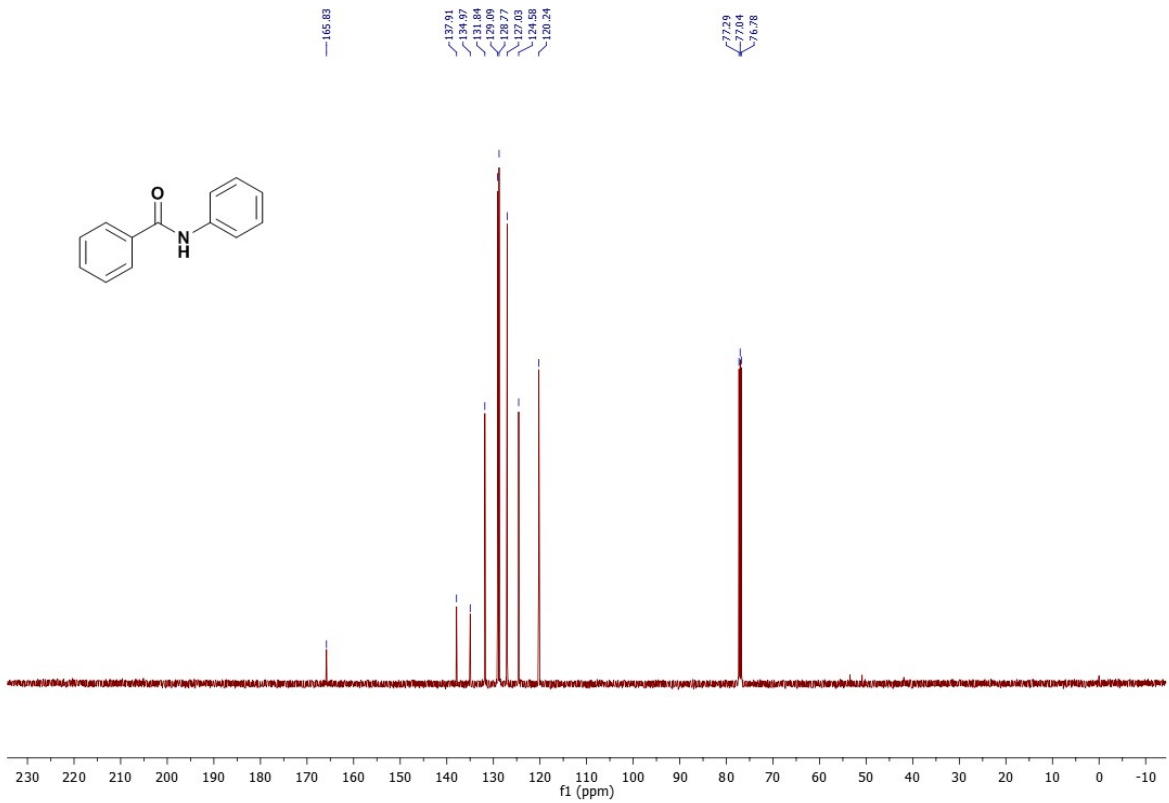
2.11
2.03
1.07
2.00
2.03
1.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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128.77
127.03
124.58
120.24
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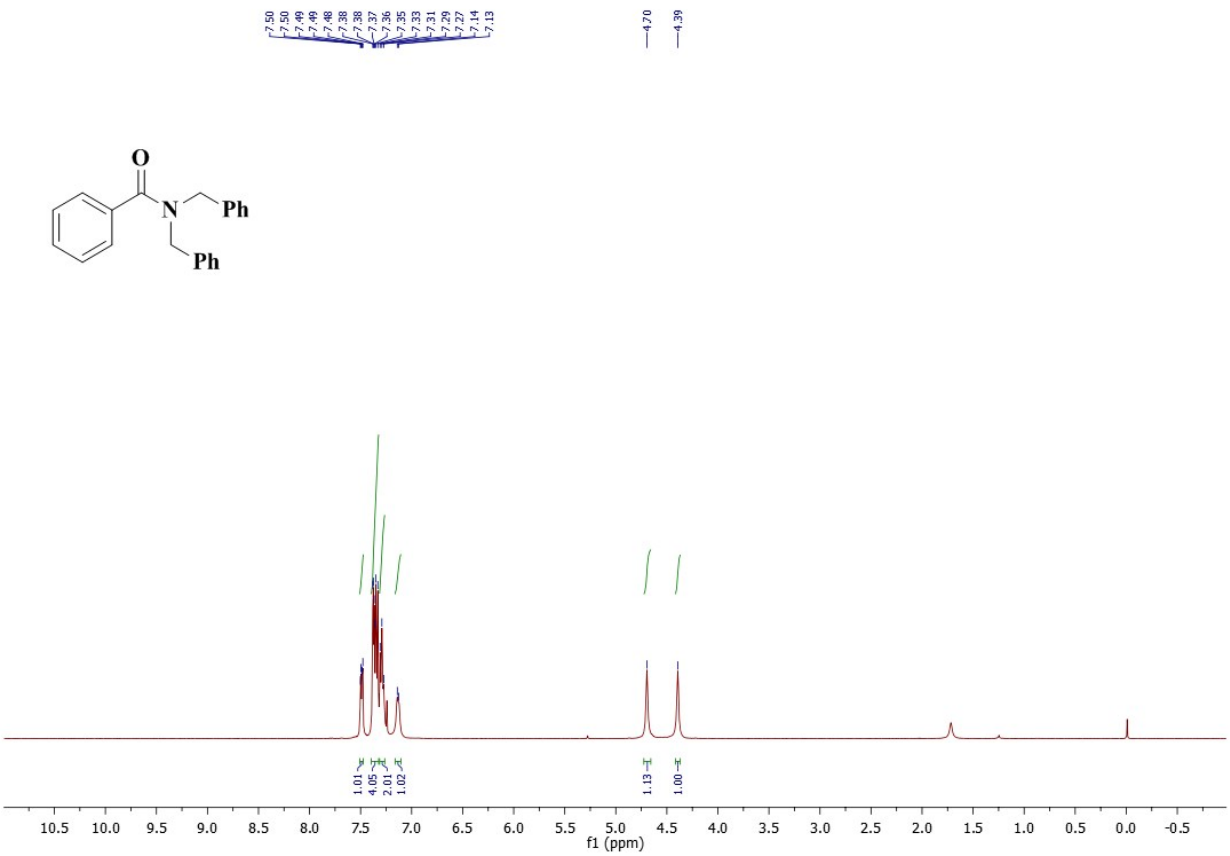
77.04
76.78
O
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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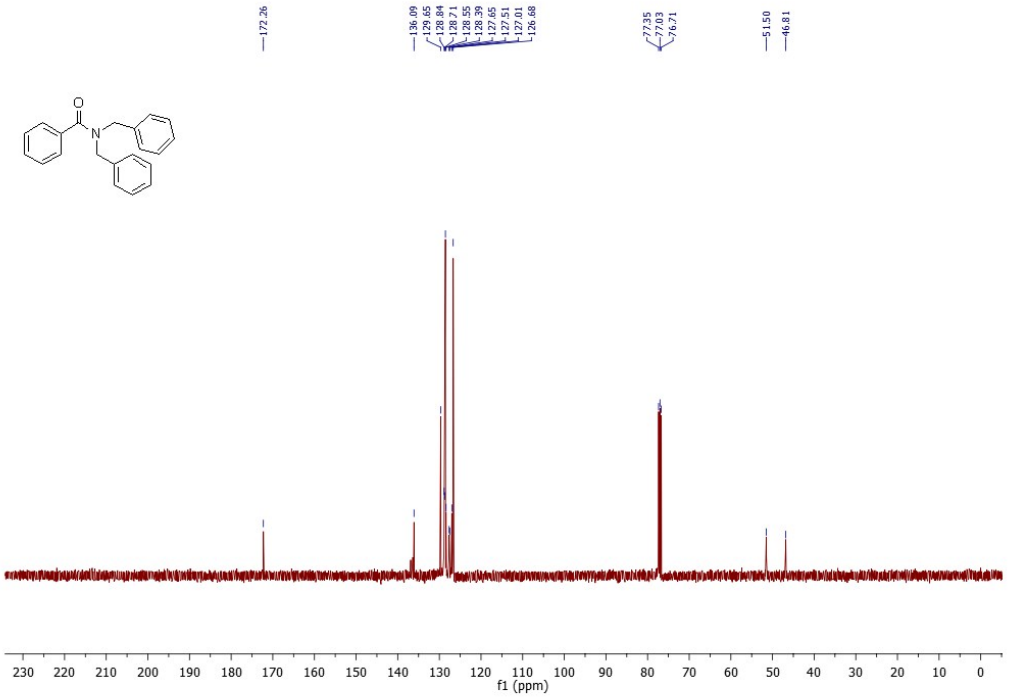
7.50
7.49
7.49
7.48
7.38
7.37
7.36
7.35
7.33
7.31
7.29
7.27
7.14
7.13
4.70
4.39
O
N
Ph
Ph
1.01
4.05
2.01
1.02
1.13
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.39
127.65
127.51
127.01
126.68
77.35
77.03
76.71
51.50
46.81
O
N
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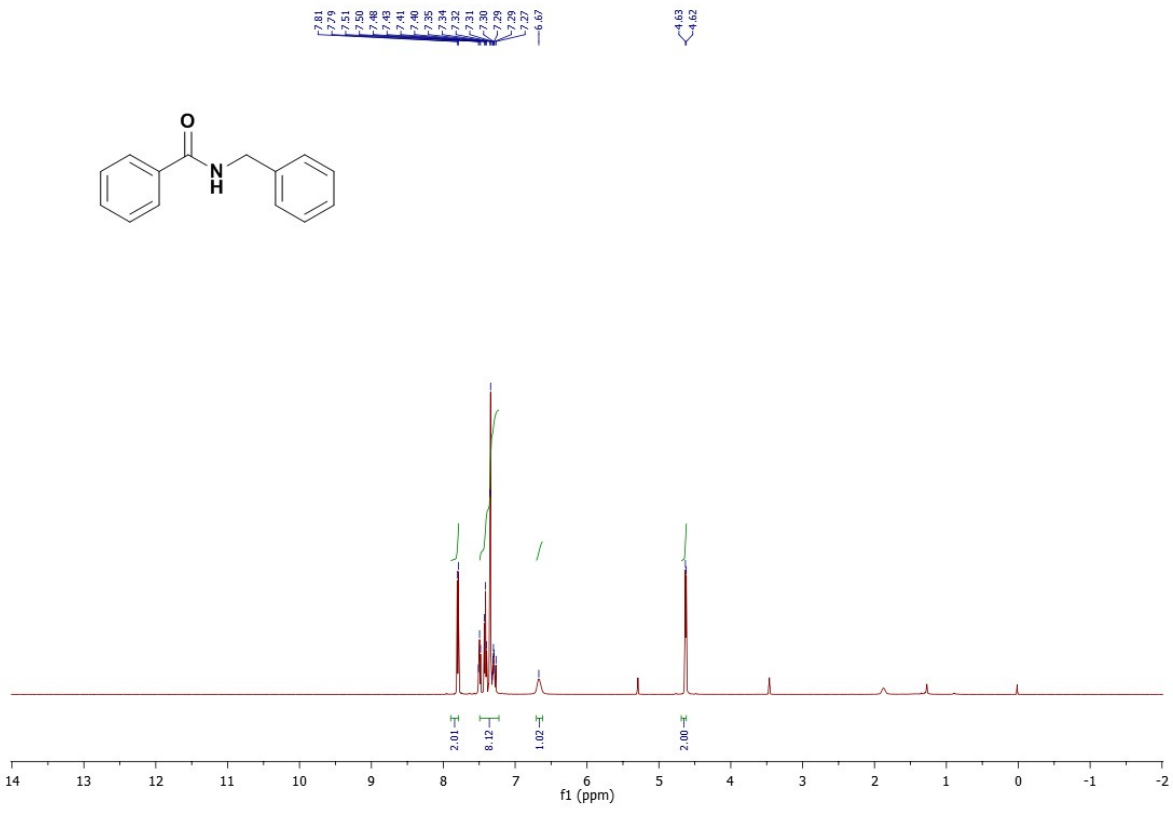
f1 (ppm)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7.79
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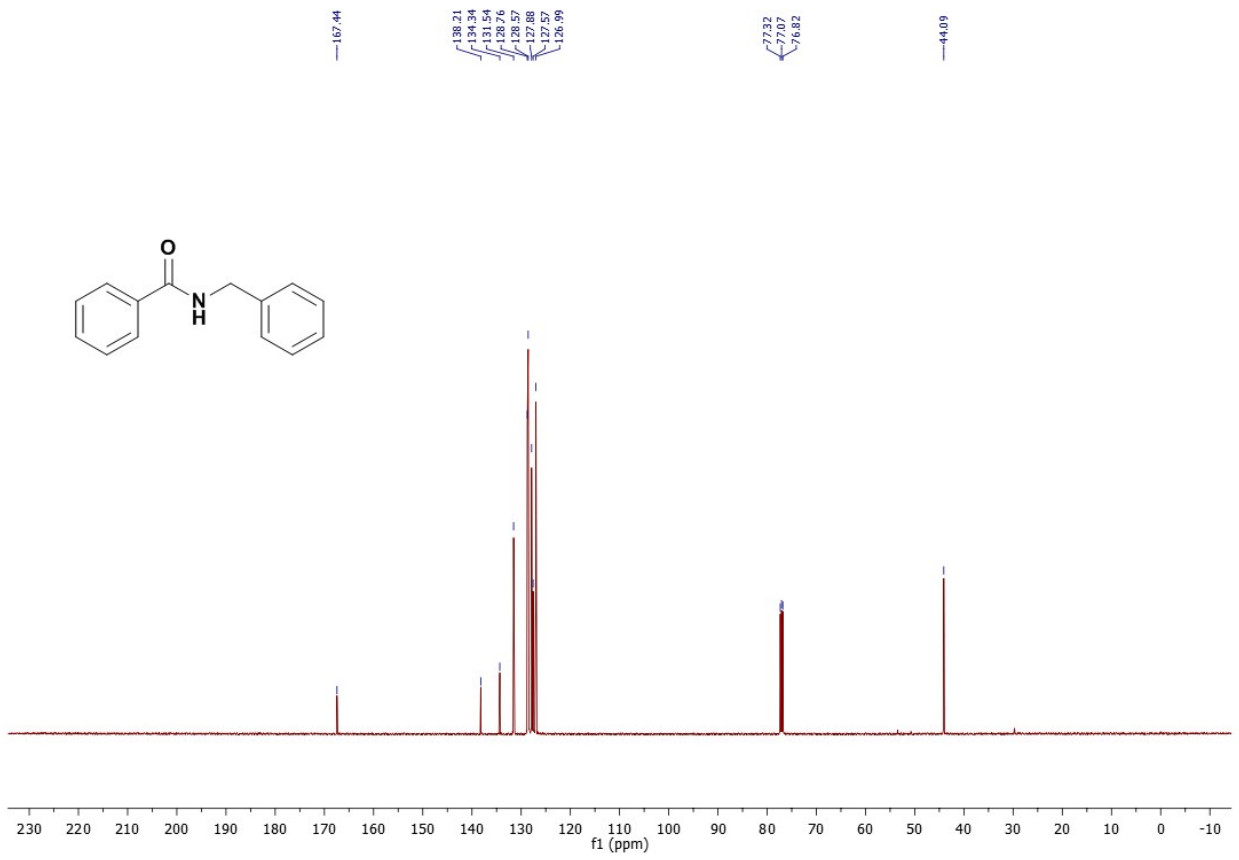
7.41
7.40
7.35
7.34
7.32
7.31
7.30
7.29
7.29
7.27
6.67
4.63
4.62
O
N
H
2.01
8.12
1.02
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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131.54
128.76
128.57
127.88
127.57
126.99
77.32
77.07
76.82
44.09
O
N
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)