Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Carbene-catalyzed Acylation Reaction Promoted by an Unprecedented Oxidant CCl_3CN

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Supporting Information

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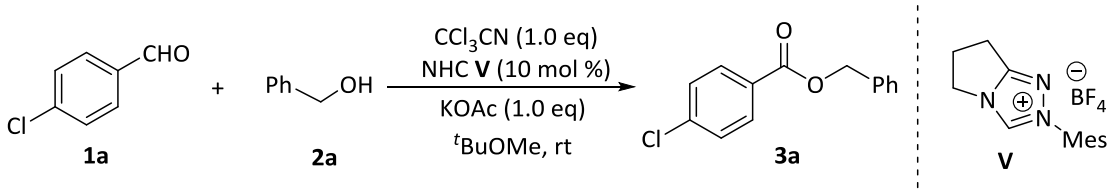
1. General information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Visualization on TLC was achieved by use of UV light (254 nm). Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). The enantiomeric excesses of products were determined by chiral phase HPLC analysis.

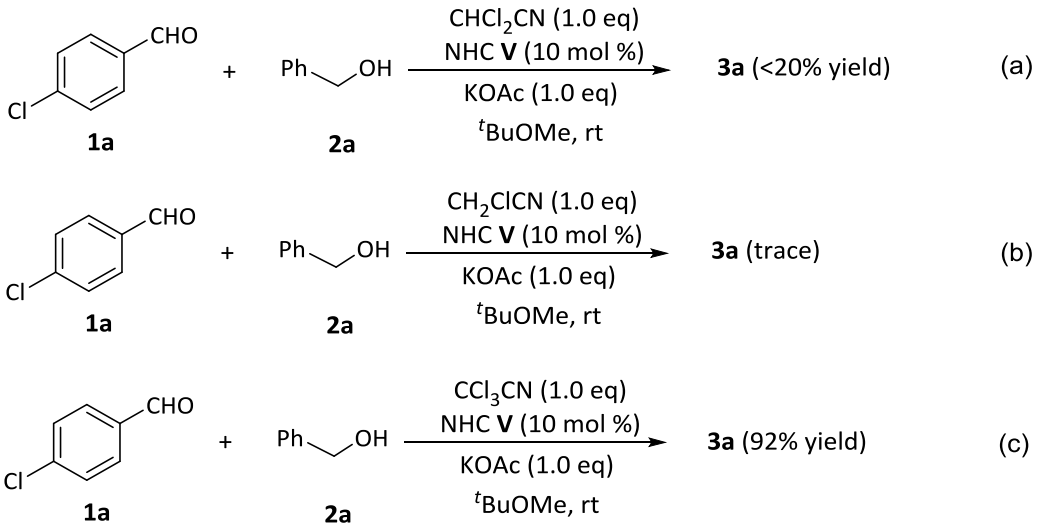
2. General procedure



To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added the azolium precatalyst **V** (3.2 mg, 0.01 mmol), aldehyde **1a** (14.1 mg, 0.10 mmol). phenylmethanol **2a** (10.8 mg, 0.10 mmol) and KOAc (9.8 mg, 0.10 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with Ar. After that CCl_3CN (14.4 mg, 10uL, 0.1 mmol) and anhydrous ^{t}BuOMe (1.0 mL) was added. The mixture was then stirred at room temperature until TLC indicated the fully consumed of the start materials. Subsequently, the reaction mixture was concentrated and directly purified through preparative thin layer chromatography on silica gel using EtOAc/hexane (1:20 to 1:10) as eluent to afford pure products **3a**.

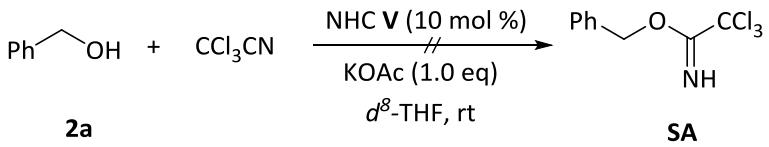
3. Control experiments and mechanistic study

3.1 Control experiments with $CHCl_2CN$, CH_2ClCN and CCl_3CN as the oxidants were performed, it showed that the electron-deficient nature of those nitriles was crucial in the transformation (Scheme S1).



Scheme S1

3.2 Under the strong base conditions, alcohol (e.g. phenylmethanol, **2a**) may react with CCl_3CN to give the benzyl 2,2,2-trichloroacetimidate[1] (**SA**, Scheme S2). However, mixed **2a** with cat. **V**, CCl_3CN, KOAc and d^8-THF, the crude NMR data showed that no signal changes observed (Figure S1). We concluded that **SA** may not be formed under the reaction condition.



Scheme S2

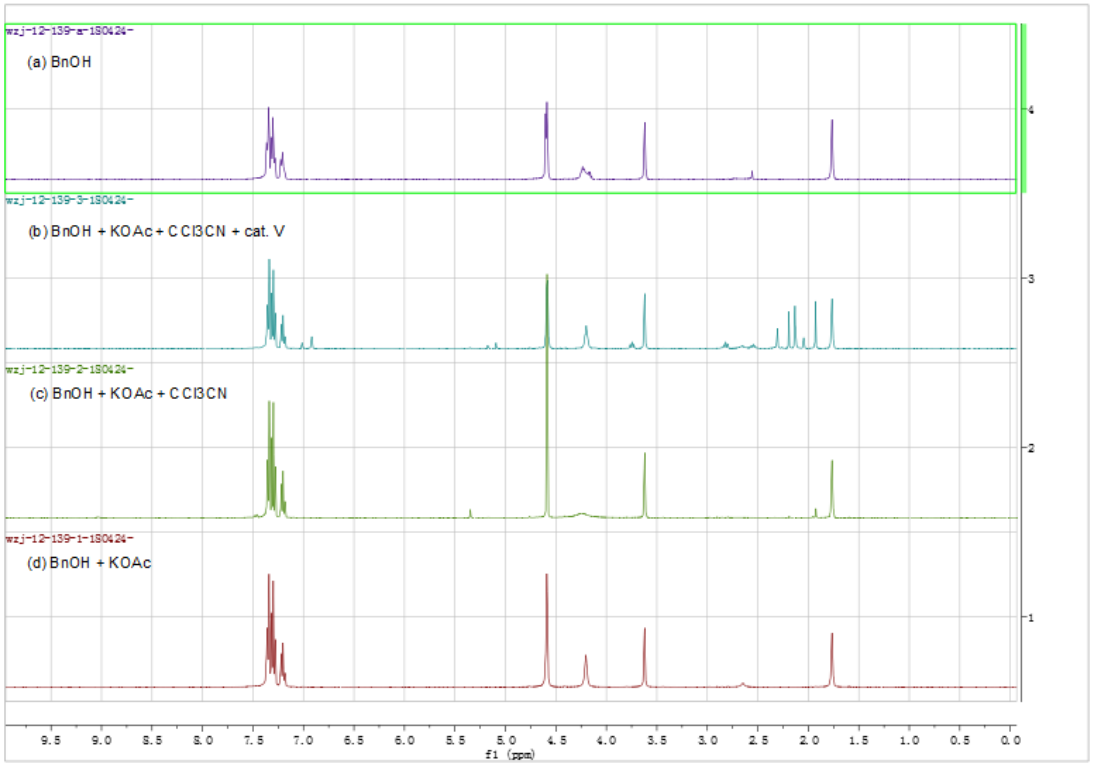
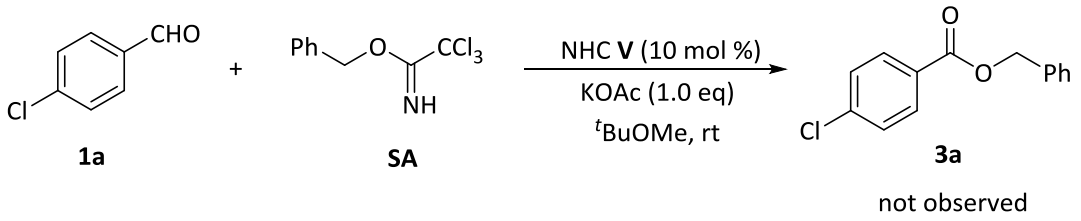


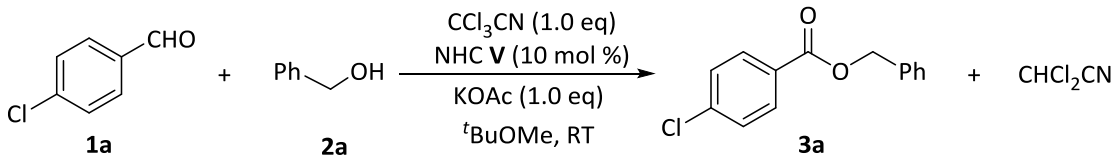
Figure S1 NMR control experiment in d^8-THF. (a) BnOH in d^8-THF; (b) BnOH, KOAc, CCl_3CN and cat. **V** in d^8-THF; (c) BnOH, KOAc and CCl_3CN in d^8-THF; (d) BnOH and KOAc in d^8-THF.

Furthermore, when **SA** (prepared according to the literature procedure[2]) was employed to react with **1a**, the desired product **3** was not observed (Scheme S3). Those results demonstrated that **SA** was not the intermediate for the reaction.



Scheme S3

3.3 When the standard reaction between **2a** and **1a** was finished (Scheme S4), $CHCl_2CN$ could be detected by GC-MS (Figure S2 and Figure S3).



Scheme S4

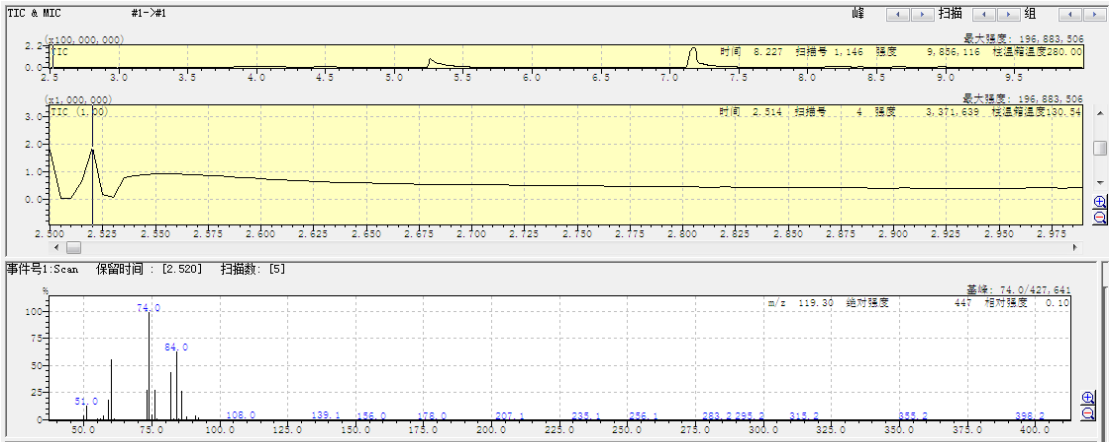


Figure S2 GC-MS spectrum of the reaction mixture

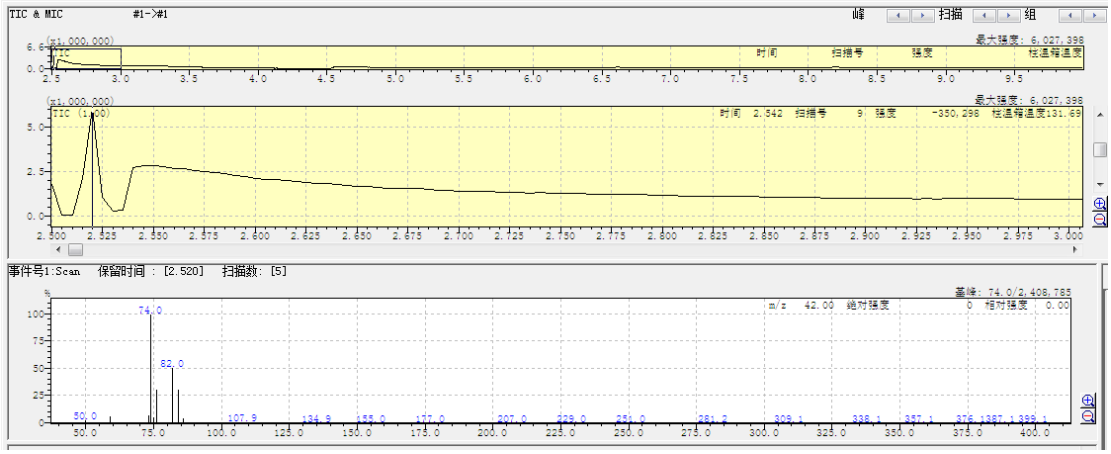
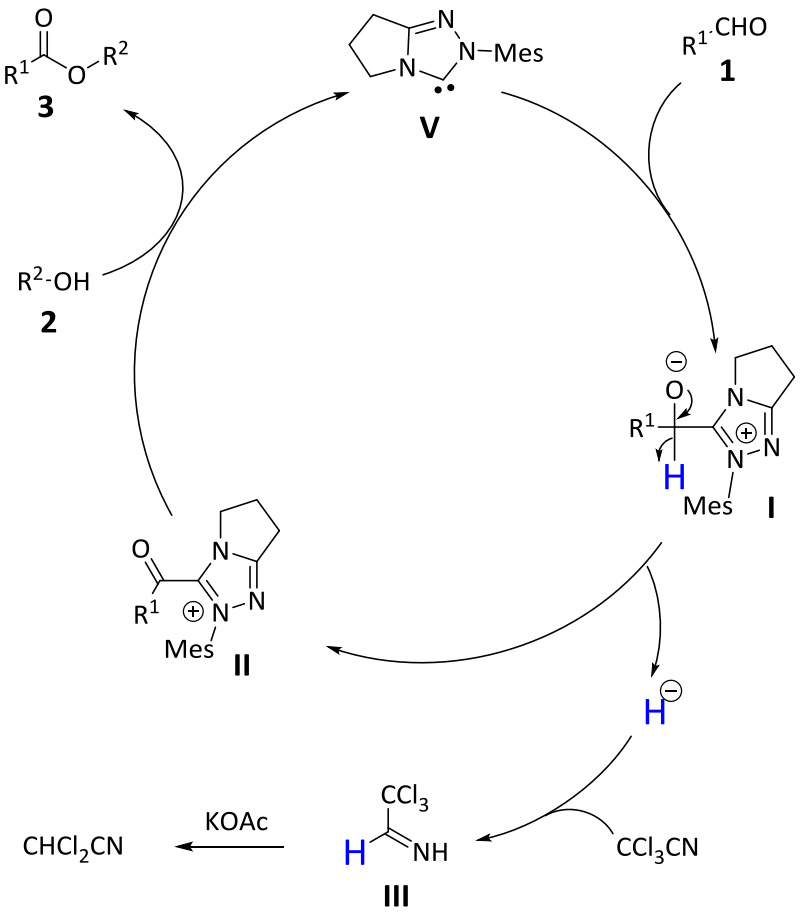


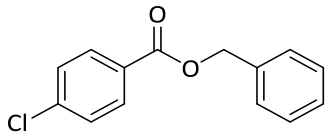
Figure S3 GC-MS spectrum of $CHCl_2CN$

Building upon above mechanistic studies, a plausible mechanism for this transformation is proposed as Scheme S5. The catalytic cycle is proposed to go through hydride transfer process. A hydride transfers from **I** to CCl_3CN to afford acyl azolium **II** and intermediate **III** (it was documented by Savkov that dichloroacetonitrile could undergo hydrogenation by triosmium dihydride cluster under mild conditions[3]). Dehydrochlorination of **III** leads to the byproduct $CHCl_2CN$[4]. Lastly, intermediate **II** reacts with nucleophile **2** to give the final product **3** along with the regeneration of catalyst **V** for next catalytic cycle.



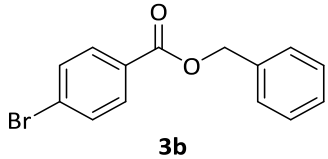
Scheme S5 Postulated mechanism

4. Characterization



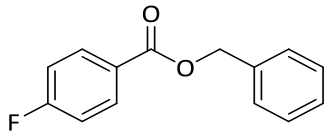
3a

Benzyl 4-chlorobenzoate (**3a**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 92% yield (22.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.38 (m, 7H), 5.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.5, 135.8, 131.1, 128.7, 128.7, 128.6, 128.4, 128.3, 67.0. HRMS (ESI): calcd for $C_{14}H_{12}ClO_2^+$ ($M+H^+$): 247.0526, found 247.0530.



3b

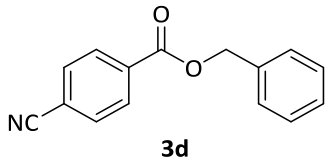
Benzyl 4-bromobenzoate (**3b**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 91% yield (26.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.60 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.48 – 7.36 (m, 5H), 5.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 135.8, 131.8, 131.3, 129.0, 128.7, 128.4, 128.3, 128.2, 67.0. HRMS (ESI): calcd for $C_{14}H_{12}BrO_2^+$ ($M+H^+$): 291.0015, found 291.0017.



3c

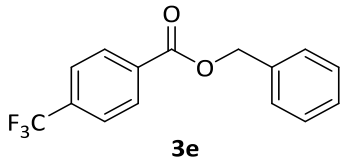
Benzyl 4-fluorobenzoate (**3c**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 88% yield (20.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.8, 5.5 Hz, 2H),

7.48 – 7.38 (m, 5H), 7.16 – 7.11 (m, 2H), 5.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, J_{C-F} = 253 Hz), 165.5, 135.9, 132.3 (d, J_{C-F} = 9 Hz), 128.7, 128.4, 128.2, 126.4 (d, J_{C-F} = 3 Hz), 115.6 (d, J_{C-F} = 22 Hz), 66.9. ^{19}F NMR (376 MHz, $CDCl_3$): -105.5. HRMS (ESI): calcd for $C_{14}H_{12}FO_2^+$ ($M+H^+$): 231.0816, found 231.0822.



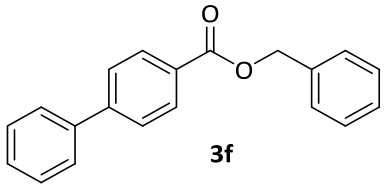
3d

Benzyl 4-cyanobenzoate (**3d**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 93% yield (22.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.48 – 7.39 (m, 5H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 135.3, 134.0, 132.3, 130.2, 128.8, 128.6, 128.4, 118.0, 116.5, 67.5. HRMS (ESI): calcd for $C_{15}H_{12}NO_2^+$ ($M+H^+$): 238.0863, found 238.0865.



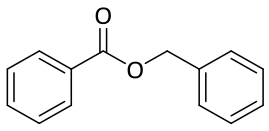
3e

Benzyl 4-(trifluoromethyl)benzoate (**3e**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 81% yield (22.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.50 – 7.39 (m, 5H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 134.5 (d, J_{C-F} = 33 Hz), 133.4, 130.1, 128.7, 128.5, 128.3, 125.4 (d, J_{C-F} = 4 Hz), 125.4 (d, J_{C-F} = 4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): -63.1. HRMS (ESI): calcd for $C_{15}H_{12}F_3O_2^+$ ($M+H^+$): 281.0784, found 281.0794.



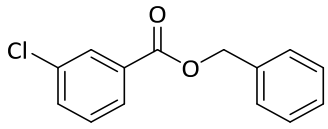
3f

Benzyl [1,1'-biphenyl]-4-carboxylate (**3f**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 83% yield (23.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.2 Hz, 2H), 7.69 (dd, J = 16.2, 7.9 Hz, 4H), 7.53 – 7.40 (m, 8H), 5.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.8, 140.0, 136.2, 130.3, 129.0, 128.9, 128.7, 128.3, 128.2, 127.3, 127.1, 66.7. HRMS (ESI): calcd for $C_{20}H_{17}O_2$+ ($M+H^+$): 289.1223, found 289.1227.



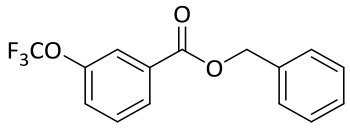
3g

Benzyl benzoate (**3g**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 71% yield (15.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 7.1 Hz, 2H), 7.59 – 7.57 (m, 1H), 7.50 – 7.38 (m, 7H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 136.1, 133.1, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7. HRMS (ESI): calcd for $C_{14}H_{13}O_2^+$ ($M+H^+$): 213.0910, found 213.0918.



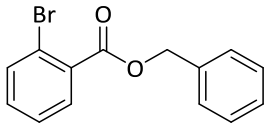
3h

Benzyl 3-chlorobenzoate (**3h**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 80% yield (19.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.37 (m, 6H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.7, 134.6, 133.1, 131.9, 129.8, 129.7, 128.7, 128.5, 128.3, 127.9, 67.1. HRMS (ESI): calcd for $C_{14}H_{12}ClO_2^+$ ($M+H^+$): 247.0520, found 247.0525.



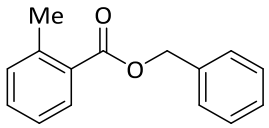
3i

benzyl 3-(trifluoromethoxy)benzoate (**3i**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 73% yield (21.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.95 (s, 1H), 7.53 – 7.37 (m, 7H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 149.2, 135.6, 132.2, 129.9, 128.7, 128.5, 128.3, 128.1, 125.5, 122.2, 119.1, 67.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9. HRMS (ESI): calcd for $C_{15}H_{12}F_3O_3^+$ ($M+H^+$): 297.0733, found 297.0739.



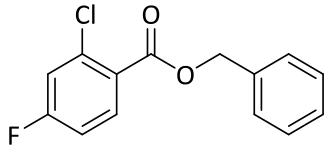
3j

Benzyl 2-bromobenzoate (**3j**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 78% yield (22.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.69 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.32 (m, 6H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.5, 134.4, 132.6, 132.1, 131.5, 128.6, 128.5, 128.4, 127.2, 121.8, 67.4. HRMS (ESI): calcd for $C_{14}H_{12}BrO_2^+$ ($M+H^+$): 291.0015, found 291.0017.



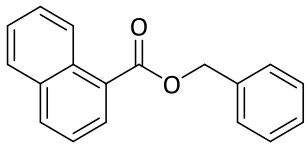
3k

Benzyl 2-methylbenzoate (**3k**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 68% yield (15.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.37 (m, 5H), 7.33 – 7.25 (m, 2H), 5.38 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 140.4, 136.2, 132.1, 131.7, 130.7, 129.7, 129.5, 128.6, 128.2, 125.7, 66.5, 21.8. HRMS (ESI): calcd for $C_{15}H_{15}O_2^+$ ($M+H^+$): 227.1067, found 227.1068.



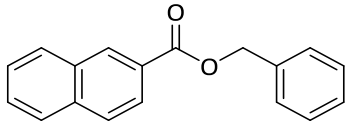
3l

Benzyl 2-chloro-4-fluorobenzoate (**3l**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 75% yield (19.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.8, 6.2 Hz, 1H), 7.49 – 7.36 (m, 5H), 7.22 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.06 – 7.02 (m, 1H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, $J_{C\text{-}F}$ =255 Hz), 164.5, 136.0, 135.7 (d, $J_{C\text{-}F}$ =44 Hz), 133.7 (d, $J_{C\text{-}F}$ =10 Hz), 128.7, 128.5, 128.1 (d, $J_{C\text{-}F}$ =69 Hz), 126.0 (d, $J_{C\text{-}F}$ =4 Hz), 118.7 (d, $J_{C\text{-}F}$ =25 Hz), 114.1 (d, $J_{C\text{-}F}$ =22 Hz), 67.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3. HRMS (ESI): calcd for $C_{14}H_{11}ClFO_2^+$ ($M+H^+$): 265.0426, found 265.0430.



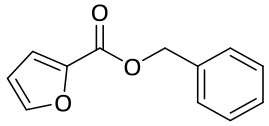
3m

Benzyl 1-naphthoate (**3m**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 79% yield (20.7 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.6 Hz, 1H), 8.27 (dd, *J* = 7.3, 1.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.64 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.55 (ddd, *J* = 15.4, 10.0, 4.5 Hz, 4H), 7.43 (ddd, *J* = 14.6, 5.1, 1.9 Hz, 3H), 5.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 136.1, 133.9, 133.5, 131.5, 130.4, 128.7, 128.6, 127.8, 127.0, 126.2, 125.8, 124.5, 66.8. HRMS (ESI): calcd for $C_{18}H_{15}O_2^+$ ($M+H^+$): 263.1067, found 263.1077.



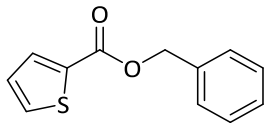
3n

Benzyl 2-naphthoate (**3n**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 84% yield (22.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.14 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.64 – 7.49 (m, 4H), 7.49 – 7.38 (m, 3H), 5.48 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 136.1, 135.6, 132.5, 131.3, 129.4, 128.7, 128.3, 128.3, 128.2, 127.8, 127.4, 126.7, 125.3, 66.9. HRMS (ESI): calcd for $C_{18}H_{15}O_2^+$ ($M+H^+$): 263.1067, found 263.1077.



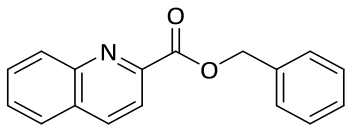
3o

Benzyl furan-2-carboxylate (**3o**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 88% yield (17.8 mg) as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 0.7 Hz, 1H), 7.47 – 7.37 (m, 5H), 7.23 (d, *J* = 3.2 Hz, 1H), 6.52 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.37 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.5, 144.6, 135.6, 128.6, 128.4, 128.4, 118.2, 117.9, 66.6. HRMS (ESI): calcd for $C_{12}H_{11}O_3^+$ ($M+H^+$): 203.0703, found 203.0707.



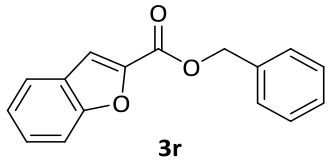
3p

Benzyl thiophene-2-carboxylate (**3p**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 87% yield (18.9 mg) as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.59 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.36 (m, 3H), 7.33 (dd, *J* = 5.1, 3.1 Hz, 1H), 5.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 136.1, 133.6, 133.0, 128.6, 128.3, 128.2, 128.0, 126.1, 66.4. HRMS (ESI): calcd for $C_{12}H_{11}O_2S^+$ ($M+H^+$): 219.0474, found 219.0479.



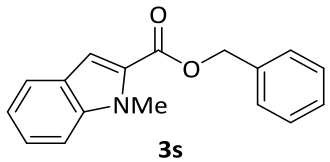
3q

Benzyl quinoline-2-carboxylate (**3q**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 97% yield (25.5 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.21 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.56 – 7.53 (m, 2H), 7.45 – 7.41 (m, 2H), 7.41 – 7.36 (m, 3H), 5.56 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 148.0, 147.7, 137.3, 135.7, 130.8, 130.3, 129.3, 128.6, 128.6, 128.5, 128.4, 127.5, 121.1, 67.7. HRMS (ESI): calcd for $C_{17}H_{14}NO_2^+$ ($M+H^+$): 264.1019, found 264.1018.



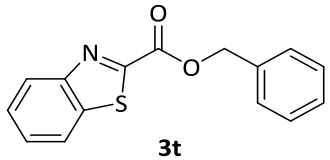
3r

Benzyl benzofuran-2-carboxylate (**3r**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 80% yield (20.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.45 (ddd, *J* = 18.4, 14.0, 7.4 Hz, 5H), 7.32 (t, *J* = 7.5 Hz, 1H), 5.45 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 155.8, 145.4, 135.4, 128.7, 128.5, 128.5, 127.7, 127.0, 123.8, 122.9, 114.2, 112.4, 67.1. HRMS (ESI): calcd for $C_{16}H_{13}O_3^+$ ($M+H^+$): 253.0859, found 253.0857.



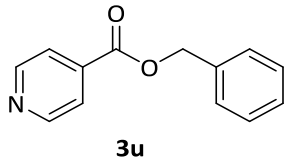
3s

Benzyl 1-methyl-1*H*-indole-2-carboxylate (**3s**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 64% yield (17.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 6.4, 1.4 Hz, 1H), 7.85 (s, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.50 – 7.310 (m, 6H), 5.41 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 137.2, 136.9, 135.4, 128.6, 128.1, 128.0, 127.0, 126.7, 122.8, 122.0, 121.7, 109.8, 65.4, 33.5. HRMS (ESI): calcd for $C_{17}H_{16}NO_2^+$ ($M+H^+$): 266.1176, found 266.1179.



3t

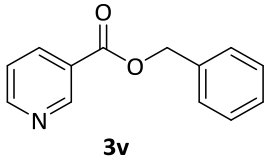
Benzyl benzo[*d*]thiazole-2-carboxylate (**3t**), the product was purified over silica gel by column chromatography (1:20 to 1: 6 EtOAc/hexane) and was obtained in 75% yield (20.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.53 (m, 4H), 7.45 – 7.37 (m, 3H), 5.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 158.1, 153.2, 136.8, 134.8, 128.8, 128.8, 128.7, 127.7, 127.1, 125.6, 122.1, 68.5. HRMS (ESI): calcd for $C_{15}H_{12}NO_2S^+$ ($M+H^+$): 270.0583, found 270.0588.



3u

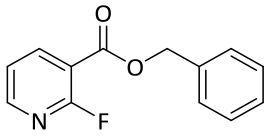
Benzyl isonicotinate (**3u**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 95% yield (20.2 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.89 (dd,

J = 4.4, 1.6 Hz, 1H), 7.48 – 7.37 (m, 2H), 5.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 150.7, 137.3, 135.3, 128.7, 128.7, 128.4, 122.9, 67.5. HRMS (ESI): calcd for $C_{13}H_{12}NO_2^+$ ($M+H^+$): 214.0863, found 214.0869.



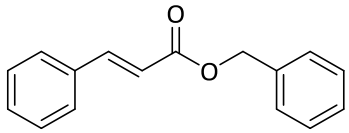
3v

Benzyl nicotinate (**3v**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 89% yield (19.0 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.80 (t, *J* = 1.6 Hz, 1H), 8.34 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.49 – 7.36 (m, 6H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.5, 151.1, 137.2, 135.5, 128.7, 128.5, 128.3, 126.1, 123.3, 67.1. HRMS (ESI): calcd for $C_{13}H_{12}NO_2^+$ ($M+H^+$): 214.0863, found 214.0868.



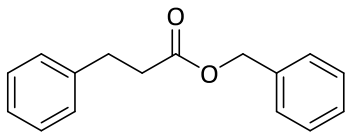
3w

Benzyl 2-fluoronicotinate (**3w**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 86% yield (19.9 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.41 (m, 2H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.33 – 7.30 (m, 1H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 4.0 Hz), 160.4, 151.8, 151.7, 143.3, 135.3, 128.7, 128.5, 128.3, 121.4 (d, *J* = 5.0 Hz), 67.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5, -61.5. HRMS (ESI): calcd for $C_{13}H_{11}FNO_2^+$ ($M+H^+$): 232.0768, found 232.0768.



3x

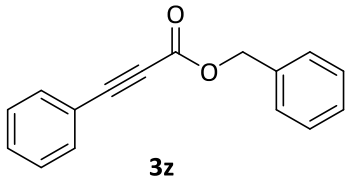
Benzyl cinnamate (**3x**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 41% yield (9.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.47 – 7.36 (m, 8H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.2, 136.1, 134.4, 130.4, 128.9, 128.6, 128.3, 128.3, 128.1, 117.9, 66.4. HRMS (ESI): calcd for $C_{16}H_{15}O_2^+$ ($M+H^+$): 239.1067, found 239.1066.



3y

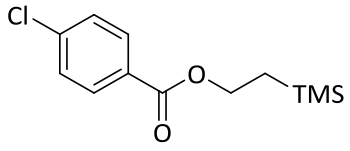
Benzyl 3-phenylpropanoate (**3y**), the product was purified over silica gel by column

chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 69% yield (16.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 7H), 7.25 – 7.21 (m, 3H), 5.15 (s, 2H), 3.01 (t, *J* = 7.8 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 140.4, 140.0, 129.3, 128.6, 128.5, 128.3, 128.2, 126.3, 66.5, 35.9, 31.0. HRMS (ESI): calcd for $C_{16}H_{17}O_2^+$ ($M+H^+$): 241.1223, found 241.1225.



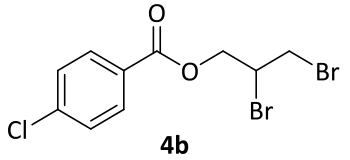
3z

Benzyl 3-phenylpropanoate (**3z**), the product was purified over silica gel by column chromatography (1:50 EtOAc/hexane) and was obtained in 23% yield (5.4 mg) as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.48 – 7.38 (m, 8H), 5.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 134.9, 133.0, 130.7, 128.9, 128.7, 128.6, 128.6, 119.6, 86.8, 80.5, 67.7. HRMS (ESI): calcd for C16H13O2$^+$ ($M+H^+$): 237.0916, found 237.0915.



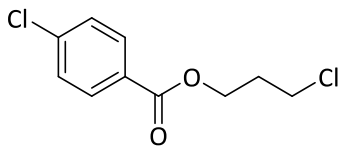
4a

2-(Trimethylsilyl)ethyl 4-chlorobenzoate (**4a**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 88% yield (22.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.44 (t, *J* = 8.4 Hz, 2H), 1.15 (t, *J* = 8.4 Hz, 2H), 0.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 139.2, 130.9, 129.1, 128.7, 63.5, 17.4, 1.0. HRMS (ESI): calcd for $C_{12}H_{18}ClO_2Si^+$ ($M+H^+$): 257.0765, found 257.0768.



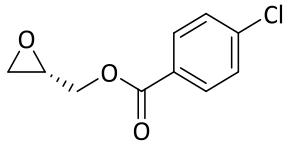
4b

2,3-Dibromopropyl 4-chlorobenzoate (**4b**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 78% yield (27.6 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 4.76 (ddd, *J* = 17.7, 12.2, 4.9 Hz, 2H), 4.49 (dt, *J* = 9.5, 4.8 Hz, 1H), 3.92 – 3.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 140.0, 131.2, 128.9, 127.8, 65.8, 46.8, 32.0. HRMS (ESI): calcd for $C_{10}H_{10}Br_2ClO_2^+$ ($M+H^+$): 354.8736, found 354.8736.



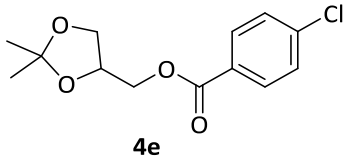
4c

3-Chloropropyl 4-chlorobenzoate (**4c**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 84% yield (19.5 mg) as a light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 4.50 (t, *J* = 6.1 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.26 (p, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.6, 131.0, 128.8, 128.5, 62.0, 41.2, 31.7. HRMS (ESI): calcd for $C_{10}H_{11}Cl_2O_2^+$ ($M+H^+$): 233.0136, found 233.0138.



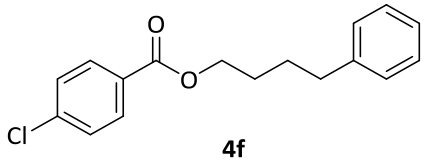
4d

(*S*)-Oxiran-2-ylmethyl 4-chlorobenzoate (**4d**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 74% yield (15.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 4.68 (dd, *J* = 12.3, 2.9 Hz, 1H), 4.17 (dd, *J* = 12.3, 6.4 Hz, 1H), 3.38 – 3.33 (m, 1H), 2.92 (t, *J* = 4.5 Hz, 1H), 2.75 (dd, *J* = 4.8, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.8, 131.2, 128.8, 128.1, 65.7, 49.4, 44.7. HRMS (ESI): calcd for $C_{10}H_{10}ClO_3^+$ ($M+H^+$): 213.0318, found 213.0322.



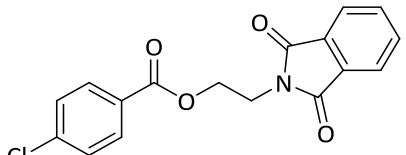
4e

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-chlorobenzoate (**4e**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 81% yield (21.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 4.50 – 4.34 (m, 3H), 4.17 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.88 (dd, *J* = 8.4, 5.8 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.7, 131.1, 128.8, 128.3, 109.9, 73.6, 66.3, 65.3, 26.8, 25.3. HRMS (ESI): calcd for $C_{13}H_{16}ClO_4^+$ ($M+H^+$): 271.0737, found 271.0739.



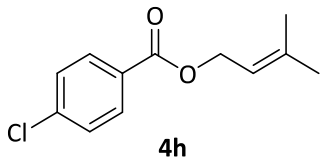
4f

4-phenylbutyl 4-chlorobenzoate (**4f**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 85% yield (24.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.31 (dd, *J* = 14.6, 7.4 Hz, 2H), 7.27 – 7.08 (m, 3H), 4.37 (t, *J* = 6.0 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 1.82 (dd, *J* = 7.4, 3.7 Hz, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.0, 139.3, 131.0, 128.9, 128.7, 128.4, 125.9, 65.1, 35.5, 28.3, 27.8. HRMS (ESI): calcd for $C_{17}H_{18}ClO_2^+$ ($M+H^+$): 289.0995, found 289.0999.



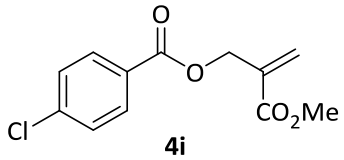
4g

2-(1,3-Dioxoisoindolin-2-yl)ethyl 4-chlorobenzoate (**4g**), the product was purified over silica gel by column chromatography (1:20 to 1: 5 EtOAc/hexane) and was obtained in 94% yield (30.9 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.88 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.50 – 7.34 (m, 2H), 4.64 – 4.45 (m, 2H), 4.13 (t, *J* = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 165.5, 139.6, 134.2, 132.0, 131.2, 131.1, 128.8, 128.2, 123.5, 62.6, 37.0. HRMS (ESI): calcd for $C_{17}H_{13}ClNO_4^+$ ($M+H^+$): 330.0533, found 330.0533.



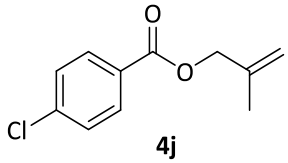
4h

3-Methylbut-2-en-1-yl 4-chlorobenzoate (**4h**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 82% yield (18.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 5.48 (t, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 2H), 1.81 (d, *J* = 8.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.5, 139.2, 131.0, 129.0, 128.7, 118.5, 62.1, 25.8, 18.1. HRMS (ESI): calcd for $C_{12}H_{14}ClO_2^+$ ($M+H^+$): 225.0682, found 225.0684.



4i

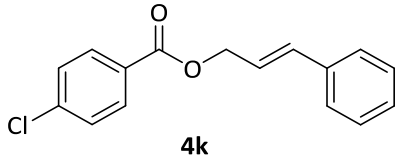
2-(Methoxycarbonyl)allyl 4-chlorobenzoate (**4i**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 83% yield (21.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.45 (s, 1H), 5.96 (d, *J* = 0.9 Hz, 1H), 5.08 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.1, 139.7, 135.2, 131.1, 128.8, 128.3, 127.8, 63.1, 52.1. HRMS (ESI): calcd for $C_{12}H_{12}ClO_4^+$ ($M+H^+$): 255.0424, found 255.0432.



4j

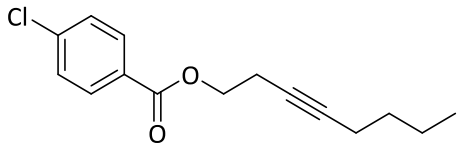
2-Methylallyl 4-chlorobenzoate (**4j**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 85% yield (17.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H),

7.45 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 29.7 Hz, 2H), 4.77 (s, 2H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.8, 139.5, 131.0, 128.8, 128.7, 68.4, 19.6. HRMS (ESI): calcd for $C_{11}H_{12}ClO_2^+$ ($M+H^+$): 211.0526, found 211.0531.



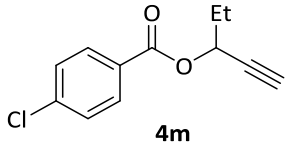
4k

Cinnamyl 4-chlorobenzoate (**4k**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 87% yield (23.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.42 (dt, *J* = 15.9, 6.5 Hz, 1H), 5.00 (dd, *J* = 6.5, 1.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.5, 136.1, 134.6, 131.1, 128.8, 128.7, 128.2, 126.7, 123.0, 65.8. HRMS (ESI): calcd for $C_{16}H_{14}ClO_2^+$ ($M+H^+$): 273.0682, found 273.0689.



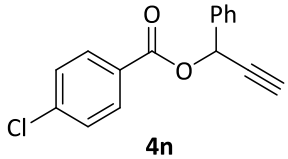
4l

Oct-3-yn-1-yl 4-chlorobenzoate (**4l**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 89% yield (23.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.40 (t, *J* = 6.9 Hz, 2H), 2.66 – 2.62 (m, 2H), 2.17 (dd, *J* = 7.9, 5.7 Hz, 2H), 1.50 – 1.34 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.4, 131.1, 128.7, 128.6, 82.3, 75.3, 63.6, 30.9, 21.9, 19.4, 18.4, 13.6. HRMS (ESI): calcd for $C_{15}H_{18}ClO_2^+$ ($M+H^+$): 265.0995, found 265.0993.



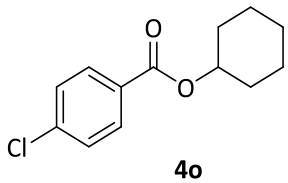
4m

Pent-1-yn-3-yl 4-chlorobenzoate (**4m**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 71% yield (15.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.56 (td, *J* = 6.4, 2.1 Hz, 1H), 2.52 (d, *J* = 2.1 Hz, 1H), 2.10 – 1.87 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 139.7, 131.2, 128.8, 128.3, 80.8, 73.9, 65.7, 28.0, 9.3. HRMS (ESI): calcd for $C_{12}H_{12}ClO_2^+$ ($M+H^+$): 223.0526, found 223.0528.



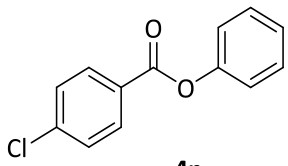
4n

1-Phenylprop-2-yn-1-yl 4-chlorobenzoate (**4n**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 68% yield (18.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 2H), 7.70 – 7.62 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (dt, *J* = 8.0, 6.5 Hz, 6H), 6.73 (d, *J* = 2.2 Hz, 1H), 2.72 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 136.6, 133.4, 129.9, 129.7, 129.6, 129.1, 128.8, 128.6, 128.4, 127.7, 80.3, 75.6, 65.8. HRMS (ESI): calcd for $C_{16}H_{12}ClO_2^+$ ($M+H^+$): 271.0526, found 271.0532.



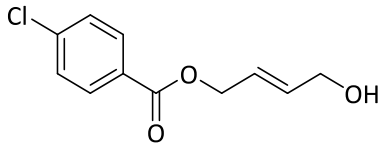
4o

Cyclohexyl 4-chlorobenzoate (**4o**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 80% yield (19.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 5.07 – 5.00 (m, 1H), 1.99 – 1.95 (m, 2H), 1.82 – 1.79 (m, 2H), 1.65 – 1.57 (m, 3H), 1.53 – 1.47 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 139.1, 130.9, 129.5, 128.6, 73.4, 31.6, 25.4, 23.7. HRMS (ESI): calcd for $C_{13}H_{16}ClO_2^+$ ($M+H^+$): 239.0839, found 239.0839.



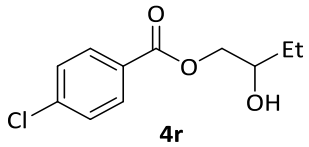
4p

Phenyl 4-chlorobenzoate (**4p**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 61% yield (14.2 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.31 (dd, *J* = 13.8, 6.4 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.8, 140.2, 131.6, 129.6, 129.0, 128.1, 126.1, 121.7. HRMS (ESI): calcd for $C_{13}H_{10}ClO_2^+$ ($M+H^+$): 233.0369, found 233.0369.



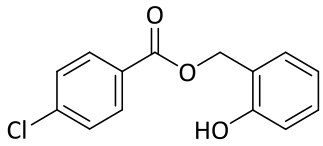
4q

(*E*)-4-Hydroxybut-2-en-1-yl 4-chlorobenzoate (**4q**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 92% yield (20.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.94 (dt, *J* = 12.9, 6.6 Hz, 1H), 5.77 (dt, *J* = 11.1, 7.0 Hz, 1H), 4.95 (d, *J* = 7.0 Hz, 2H), 4.35 (d, *J* = 6.5 Hz, 2H), 2.35 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.6, 133.7, 131.0, 128.8, 128.5, 125.4, 60.8, 58.5. HRMS (ESI): calcd for $C_{11}H_{12}ClO_3^+$ ($M+H^+$): 227.0475, found 227.0481.



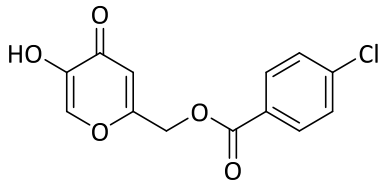
4r

2-Hydroxybutyl 4-chlorobenzoate (**4r**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 79% yield (18.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.40 (dd, *J* = 11.5, 3.3 Hz, 1H), 4.26 (dd, *J* = 11.5, 7.0 Hz, 1H), 3.93 (qd, *J* = 7.2, 3.4 Hz, 1H), 2.26 (s, 1H), 1.67 – 1.57 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 139.7, 131.1, 128.8, 128.4, 71.4, 69.0, 26.5, 9.8. HRMS (ESI): calcd for $C_{11}H_{14}ClO_3^+$ ($M+H^+$): 229.0631, found 229.0637.



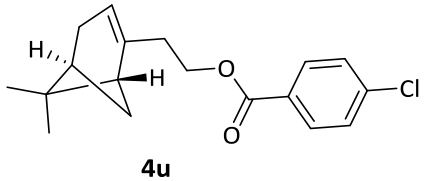
4s

2-Hydroxybenzyl 4-chlorobenzoate (**4s**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 89% yield (23.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.91 (s, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.38 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.34 – 7.25 (m, 1H), 6.98 (dd, *J* = 17.1, 7.9 Hz, 2H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 155.6, 140.2, 132.3, 131.4, 131.3, 128.9, 127.7, 121.5, 120.7, 117.9, 64.0. HRMS (ESI): calcd for $C_{14}H_{12}ClO_3^+$ ($M+H^+$): 263.0475, found 263.0478.



4t

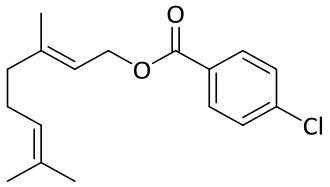
(5-Hydroxy-4-oxo-4*H*-pyran-2-yl)methyl 4-chlorobenzoate (**4t**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 79% yield (22.1 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.90 (s, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.61 (s, 1H), 5.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 164.7, 162.7, 145.9, 140.4, 137.8, 131.3, 129.1, 127.2, 111.2, 61.9. HRMS (ESI): calcd for $C_{13}H_{10}ClO_5^+$ ($M+H^+$): 281.0217, found 281.0222.



4u

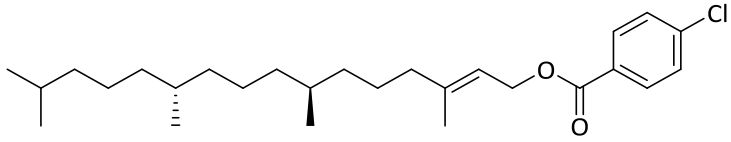
2-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 4-chlorobenzoate (**4u**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 71% yield (21.6 mg) as a white solid. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 5.38 (d, *J* = 1.2 Hz, 1H), 4.39 – 4.29 (m, 2H), 2.42 (ddd, *J* = 11.2, 10.8, 6.1 Hz, 3H), 2.26 (q, *J* = 17.6 Hz, 2H), 2.14 (t, *J* = 5.0 Hz, 2H), 1.30 (s, 4H), 1.19 (d, *J* = 8.5 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 144.1, 139.3, 130.9, 128.9, 128.7, 119.0, 63.5, 45.8, 40.7, 38.0, 36.0, 31.7, 31.4, 26.3, 21.2. HRMS (ESI): calcd for $C_{18}H_{22}ClO_2^+$ ($M+H^+$): 305.1308, found 305.1318.



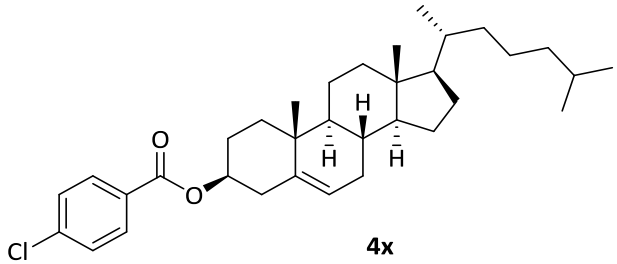
4v

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 4-chlorobenzoate (**4v**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 89% yield (26.0 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.48 (t, *J* = 6.5 Hz, 1H), 5.12 (s, 1H), 4.86 (d, *J* = 7.0 Hz, 2H), 2.21 – 2.07 (m, 4H), 1.79 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.7, 139.2, 131.9, 131.0, 129.0, 128.7, 123.7, 118.2, 62.1, 39.6, 26.3, 25.7, 17.7, 16.6. HRMS (ESI): calcd for $C_{17}H_{22}ClO_2^+$ ($M+H^+$): 293.1308, found 293.1316.



4w

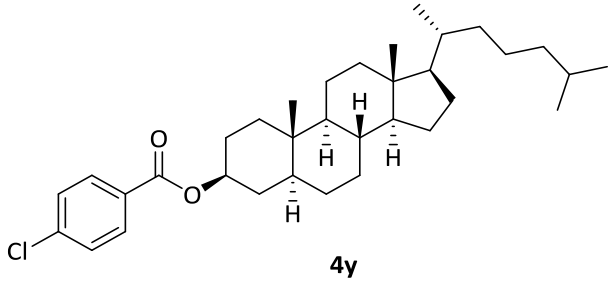
(7*S*,11*R*,*E*)-3,7,11,15-Tetramethylhexadec-2-en-1-yl 4-chlorobenzoate (**4w**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 81% yield (35.2 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 5.51– 5.44 (m, 1H), 4.86 (d, *J* = 6.7 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.78 (s, 3H), 1.60 – 1.39 (m, 20H), 1.37 – 0.89 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 143.2, 139.2, 131.0, 129.0, 128.6, 117.9, 62.1, 39.9, 39.4, 37.4, 37.3, 36.6, 32.8, 32.7, 28.0, 25.0, 24.8, 24.5, 22.7, 22.6, 19.7, 19.7. HRMS (ESI): calcd for $C_{27}H_{44}ClO_2^+$ ($M+H^+$): 435.3030, found 435.3037.



4x

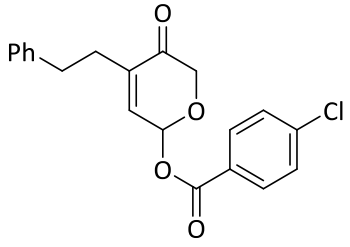
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-chlorobenzoate (**4x**), the product was purified over silica gel by column

chromatography (1:20 to 1: 4 EtOAc/hexane) and was obtained in 75% yield (39.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.44 (d, *J* = 4.1 Hz, 1H), 4.95 – 4.77 (m, 1H), 2.48 (d, *J* = 7.7 Hz, 2H), 2.11 – 1.70 (m, 3H), 1.68 – 1.13 (m, 20H), 1.10 (d, *J* = 10.2 Hz, 3H), 1.07 – 0.98 (m, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.89 (dd, *J* = 6.6, 1.6 Hz, 6H), 0.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 139.5, 139.1, 131.0, 129.3, 128.6, 122.9, 74.9, 56.7, 56.2, 50.1, 42.3, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 31.9, 29.7, 28.3, 28.0, 27.9, 24.3, 23.9, 22.8, 22.6. HRMS (ESI): calcd for $C_{34}H_{50}ClO_2^+$ ($M+H^+$): 525.3499, found 525.3497.



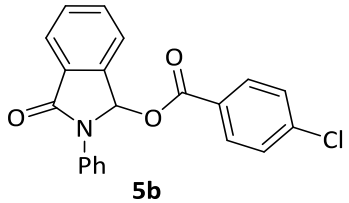
4y

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-chlorobenzoate (**4y**), the product was purified over silica gel by column chromatography (1:20 to 1: 4 EtOAc/hexane) and was obtained in 79% yield (41.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 5.04 – 4.88 (m, 1H), 1.99 (dd, *J* = 18.9, 9.1 Hz, 2H), 1.89 – 1.44 (m, 9H), 1.42 – 0.98 (m, 20H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.92 – 0.85 (m, 9H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.1, 130.9, 129.4, 128.6, 74.7, 56.4, 56.3, 54.3, 44.7, 42.6, 40.0, 39.5, 36.8, 36.2, 35.8, 35.5, 34.1, 32.0, 29.7, 28.7, 28.3, 28.0, 27.6, 24.2, 23.9, 22.8. HRMS (ESI): calcd for $C_{34}H_{52}ClO_2^+$ ($M+H^+$): 527.3656, found 527.3661.



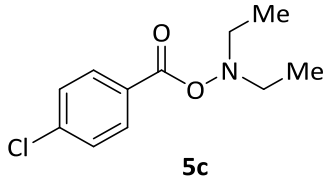
5a

5-Oxo-4-phenethyl-5,6-dihydro-2*H*-pyran-2-yl 4-chlorobenzoate (**5a**), the product was purified over silica gel by column chromatography (1:20 to 1: 8 EtOAc/hexane) and was obtained in 83% yield (29.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (dd, *J* = 10.0, 4.5 Hz, 2H), 7.21 (t, *J* = 8.1 Hz, 3H), 6.65 (dd, *J* = 28.8, 3.7 Hz, 2H), 4.59 (d, *J* = 17.1 Hz, 1H), 4.31 (d, *J* = 17.1 Hz, 1H), 2.88 – 2.79 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 164.3, 140.6, 140.3, 139.4, 137.1, 131.3, 129.0, 128.5, 128.5, 127.7, 126.2, 88.7, 67.4, 33.8, 29.9. HRMS (ESI): calcd for $C_{20}H_{18}ClO_4^+$ ($M+H^+$): 357.0894, found 357.0895.



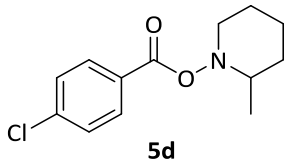
5b

3-Oxo-2-phenylisoindolin-1-yl 4-chlorobenzoate (**5b**), the product was purified over silica gel by column chromatography (1:20 to 1: 4 EtOAc/hexane) and was obtained in 68% yield (24.7 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.5, 2.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.82 (s, 1H), 7.74 – 7.71 (m, 1H), 7.71 – 7.62 (m, 4H), 7.45 – 7.38 (m, 4H), 7.25 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.6, 140.4, 140.3, 136.3, 133.2, 132.0, 131.3, 130.8, 129.3, 129.0, 127.3, 126.2, 124.2, 124.2, 122.0, 82.5. HRMS (ESI): calcd for $C_{21}H_{15}ClNO_3^+$ ($M+H^+$): 364.0740, found 364.0740.



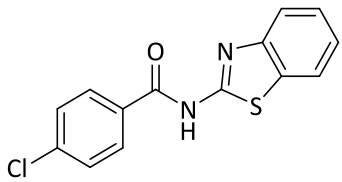
5c

O-(4-Chlorobenzoyl)-*N*,*N*-diethylhydroxylamine (**5c**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 83% yield (18.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.04 (q, *J* = 7.1 Hz, 4H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 139.5, 130.9, 128.8, 127.6, 53.5, 11.9. HRMS (ESI): calcd for $C_{11}H_{15}ClNO_2^+$ ($M+H^+$): 228.0791, found 228.0795.



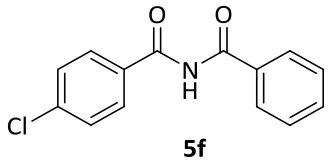
5d

2-Methylpiperidin-1-yl 4-chlorobenzoate (**5d**), the product was purified over silica gel by column chromatography (1:20 to 1: 10 EtOAc/hexane) and was obtained in 72% yield (18.2 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.58 – 3.55 (m, 1H), 2.86 (d, *J* = 2.8 Hz, 1H), 2.86 – 2.70 (m, 1H), 1.92 – 1.47 (m, 5H), 1.42 – 1.24 (m, 1H), 1.18 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 139.4, 130.8, 128.7, 128.0, 62.6, 58.0, 33.7, 25.6, 23.8, 19.9. HRMS (ESI): calcd for $C_{13}H_{17}ClNO_2^+$ ($M+H^+$): 254.0948, found 254.0946.



5e

N-(Benzo[*d*]thiazol-2-yl)-4-chlorobenzamide (**5e**), following the general procedure, Cs_2CO_3 was used as base, the product was purified over silica gel by column chromatography (1:20 to 1: 4 EtOAc/hexane) and was obtained in 73% yield (21.0 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.92 – 7.84 (m, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 160.0, 147.6, 139.6, 131.9, 130.4, 129.4, 129.3, 126.3, 124.3, 121.5, 120.6. HRMS (ESI): calcd for $C_{14}H_{10}ClN_2OS^+$ ($M+H^+$): 289.0202, found 289.0203.

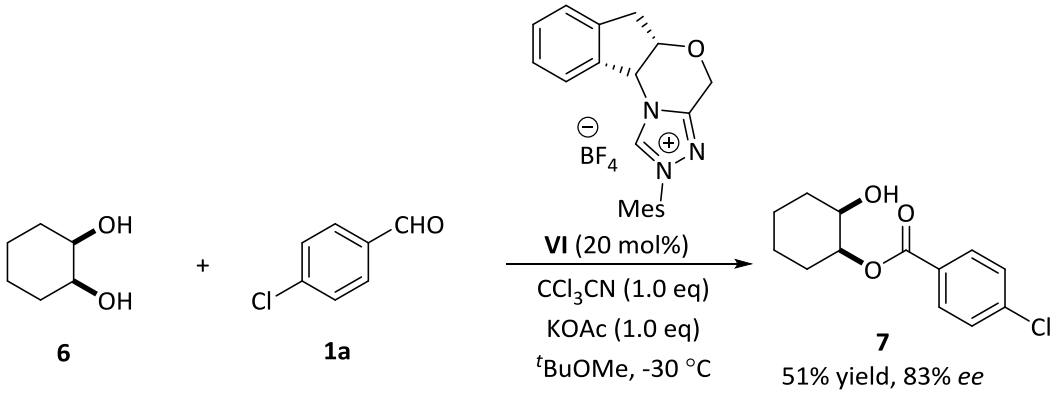


5f

N-Benzoyl-4-chlorobenzamide (**5f**), following the general procedure, NaH was used as base, the product was purified over silica gel by column chromatography (1:20 to 1: 6 EtOAc/hexane) and was obtained in 69% yield (17.9 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 139.6, 133.3, 133.0, 131.7, 129.6, 129.1, 129.0, 128.0. HRMS (ESI): calcd for $C_{14}H_{11}ClNO_2^+$ ($M+H^+$): 260.0478, found 260.0478.

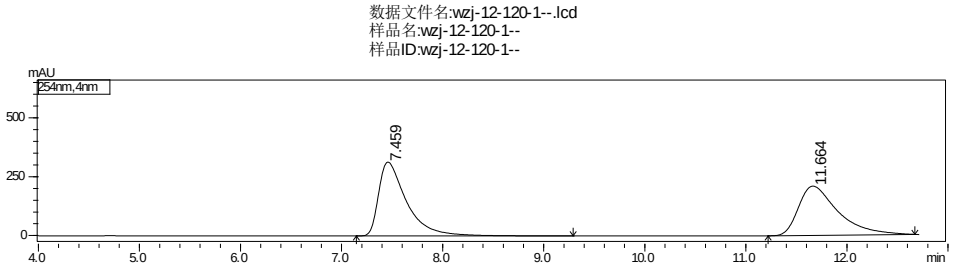
5. Application to the desymmetrization of *cis*-diols

5.1 Desymmetrization reaction of 1,2-diols

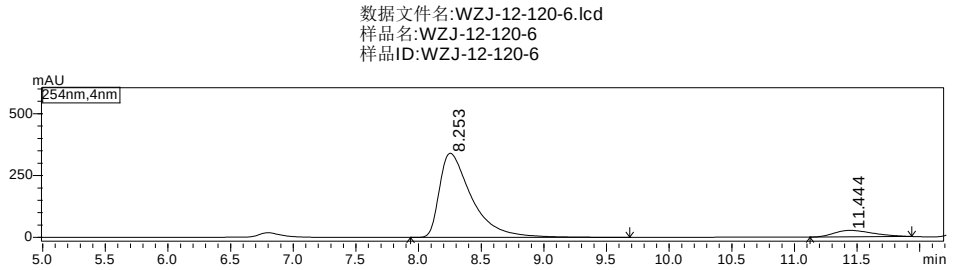


To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added the azolium precatalyst **VI** (8.4 mg, 0.02 mmol), *cis*-cyclohexane-1,2-diol **6** (11.6 mg, 0.10 mmol) and KOAc (9.8 mg, 0.10 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with Ar. Then CCl_3CN (14.4 mg, 10uL, 0.1 mmol) and ^{t}BuOMe (0.8 mL) were added. After that the Schlenk tube was cooled to -30 ℃, aldehyde **1a** (14.1 mg, 0.10 mmol) in anhydrous ^{t}BuOMe (0.2 mL) was added slowly. The mixture was then stirred at that temperature overnight. Subsequently, the reaction mixture was quenched with drops of water, concentrated and directly purified through preparative thin layer chromatography on silica gel (1:20 to 1: 10 EtOAc/hexane) to

afford pure products **7** with 51% yield (13.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 5.23 (dt, *J* = 5.7, 2.5 Hz, 1H), 3.99 (t, *J* = 3.2 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.91 – 1.80 (m, 5H), 1.78 – 1.64 (m, 2H). HRMS (ESI): calcd for $C_{13}H_{16}ClO_3^+$ ($M+H^+$): 255.0788, found 255.0790. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.5, 131.0, 128.9, 128.8, 74.9, 69.6, 30.4, 27.4, 21.8, 21.5. HPLC analysis: (Chiralpak OJ-H, isopropanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm): t_R (major) = 8.3 min, t_R (minor) = 11.4 min, *ee* =83%.

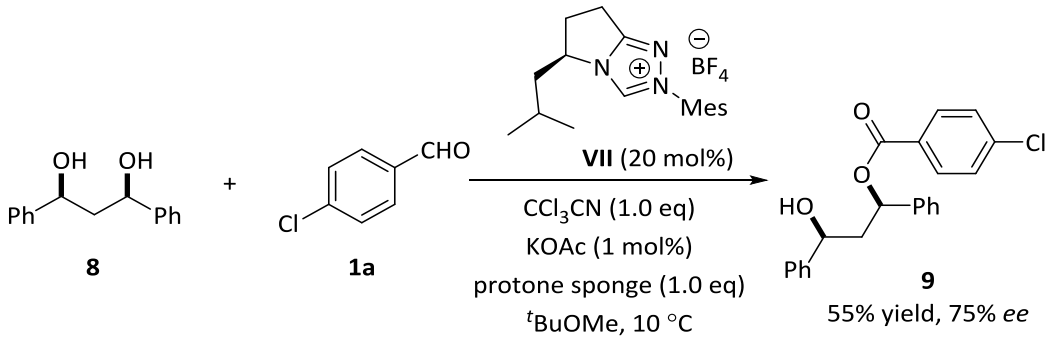


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.459	6047910	313655	51.509	59.971
2	11.664	5693507	209359	48.491	40.029
Total		11741417	523014	100.000	100.000



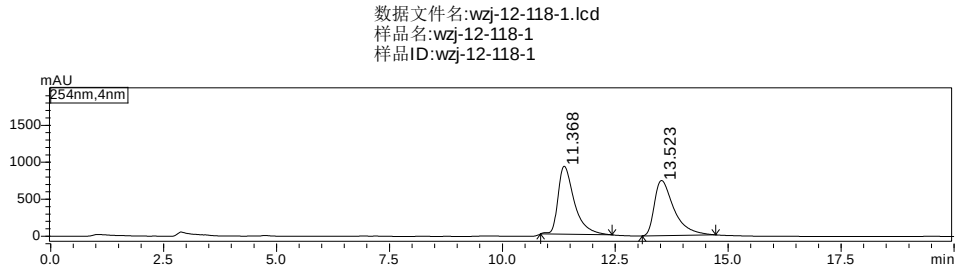
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.253	6111844	340631	91.512	92.865
2	11.444	566868	26172	8.488	7.135
Total		6678713	366803	100.000	100.000

5.2 Desymmetrization reaction of 1,3-diols

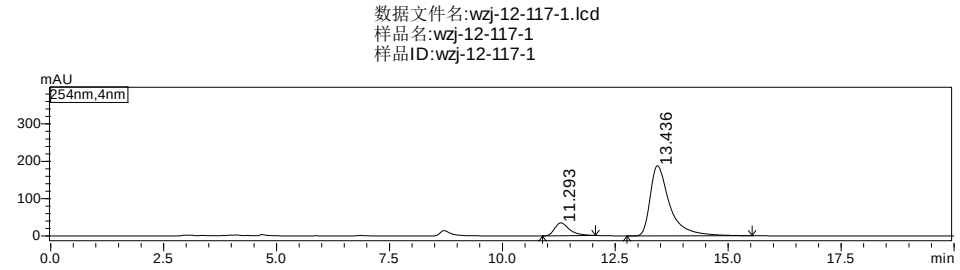


To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added the azolium precatalyst **VII** (7.5 mg, 0.02 mmol), *cis*-1,3-diphenylpropane-1,3-diol **8** (22.8 mg, 0.10 mmol), KOAc (1.0 mg, 0.01 mmol) and proton sponge (30.1 mg, 0.1

mmol). The Schlenk tube was closed with a septum, evacuated and refilled with Ar. Then CCl_3CN (14.4 mg, 10uL, 0.1 mmol) and ^{t}BuOMe (0.8 mL) were added. After that the Schlenk tube was cooled to 10 ℃, aldehyde **1a** (14.1 mg, 0.10 mmol) in anhydrous ^{t}BuOMe (0.2 mL) was added slowly. The mixture was then stirred at that temperature overnight. Subsequently, the reaction mixture was quenched with drops of water, concentrated and directly purified through preparative thin layer chromatography on silica gel (1:20 to 1: 10 EtOAc/hexane) to afford pure products **9** with 55% yield (20.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.44 (m, 4H), 7.40 – 7.36 (m, 6H), 7.36 – 7.33 (m, 1H), 7.32 – 7.26 (m, 1H), 6.34 (dd, *J* = 10.3, 3.3 Hz, 1H), 4.82 (dd, *J* = 9.7, 3.4 Hz, 1H), 2.87 – 2.64 (m, 1H), 2.45 (ddd, *J* = 14.1, 10.3, 3.5 Hz, 1H), 2.31 (ddd, *J* = 14.5, 9.8, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 143.6, 140.2, 139.7, 131.2, 128.8, 128.7, 128.6, 128.5, 128.2, 127.8, 126.4, 125.8, 74.2, 70.6, 46.6. HRMS (ESI): calcd for $C_{22}H_{20}ClO_3^+$ ($M+H^+$): 367.1101, found 367.1108. HPLC analysis: (Chiralpak AD-H, isopropanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): t_R (minor) = 11.3 min, t_R (major) = 13.4 min, *ee* =75%.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.368	23098271	919363	50.696	55.256
2	13.523	22464153	744477	49.304	44.744
Total		45562424	1663839	100.000	100.000

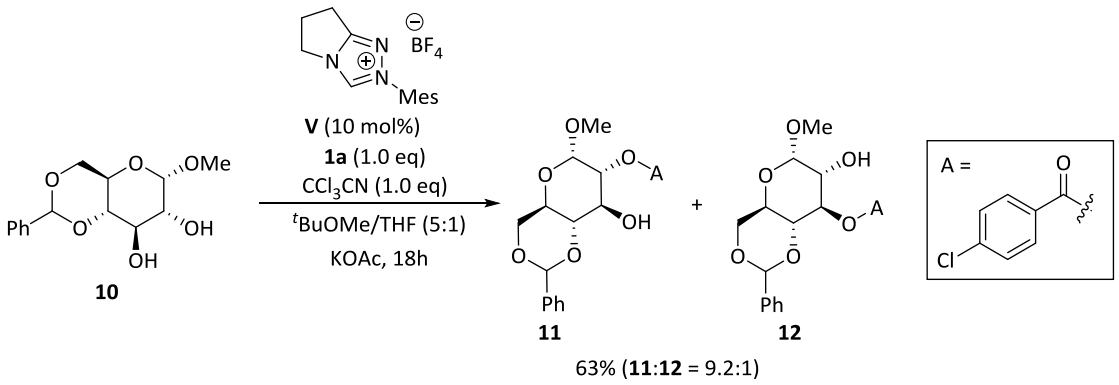


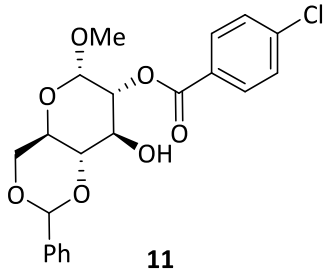
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.293	791102	34641	12.291	15.557
2	13.436	5645322	188032	87.709	84.443
Total		6436423	222674	100.000	100.000

6. Application to the acylation of carboxhydrates

General procedure. To a flame-dried Schlenk reaction tube equipped with a magnetic

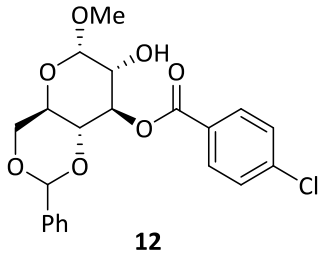
stir bar, was added the corresponding azolium precatalyst (**V**/**VIII**, 0.01 mmol), aldehyde **1a** (14.1 mg, 0.10 mmol). carboxhydrates **10/13/16** (28.2 mg, 0.10 mmol) and KOAc (9.8 mg, 0.10 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with Ar. After that CCl_3CN (14.4 mg, 10uL, 0.1 mmol), anhydrous ^{t}BuOMe (1.0 mL) and THF (0.2 mL) was added. The mixture was then stirred at room temperature until TLC indicated the fully consumed of the start materials. Subsequently, the reaction mixture was concentrated and directly purified through preparative thin layer chromatography on silica gel (1:10 to 1: 2 EtOAc/hexane) to afford pure products as white solid.





11

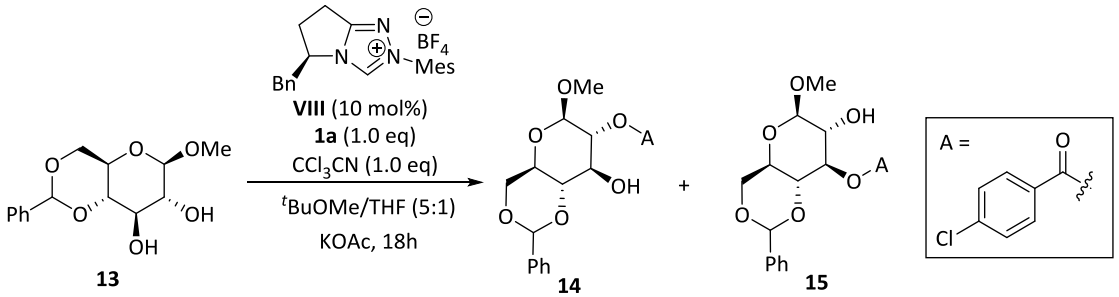
According to the general procedure, **11** was obtained with 23.9 mg as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.54 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.46 – 7.40 (m, 5H), 5.60 (s, 1H), 5.07 (dt, *J* = 9.3, 3.8 Hz, 2H), 4.38 – 4.33 (m, 2H), 3.93 (td, *J* = 9.9, 4.7 Hz, 1H), 3.82 (t, *J* = 10.2 Hz, 1H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.42 (s, 3H), 2.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.9, 137.0, 131.4, 129.4, 128.8, 128.4, 128.0, 126.3, 102.1, 97.7, 81.5, 74.2, 68.9, 68.8, 62.1, 55.5. HRMS (ESI): calcd for $C_{21}H_{22}ClO_7^+$ ($M+H^+$): 421.1054, found 421.1053.

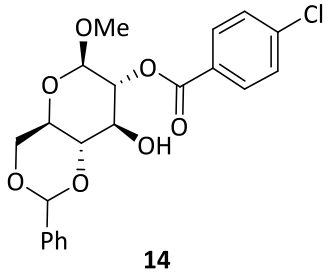


12

According to the general procedure, **12** was obtained with 2.6 mg as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.42 (m, 4H), 7.34 – 7.32

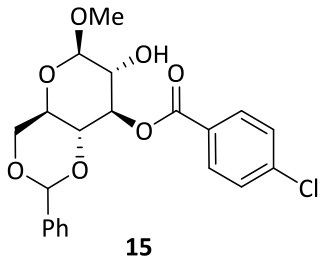
(m, 3H), 5.58 (dd, *J* = 18.4, 8.8 Hz, 2H), 4.89 (d, *J* = 3.8 Hz, 1H), 4.37 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.97 (td, *J* = 9.9, 4.8 Hz, 1H), 3.84 –3.74 (m, 3H), 3.53 (s, 3H), 2.32 (d, *J* = 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.6, 136.9, 131.3, 129.1, 128.7, 128.4, 128.2, 126.1, 100.6, 100.2, 78.8, 73.3, 72.0, 69.0, 62.8, 55.7. HRMS (ESI): calcd for $C_{21}H_{22}ClO_7^+$ ($M+H^+$): 421.1054, found 421.1056.





14

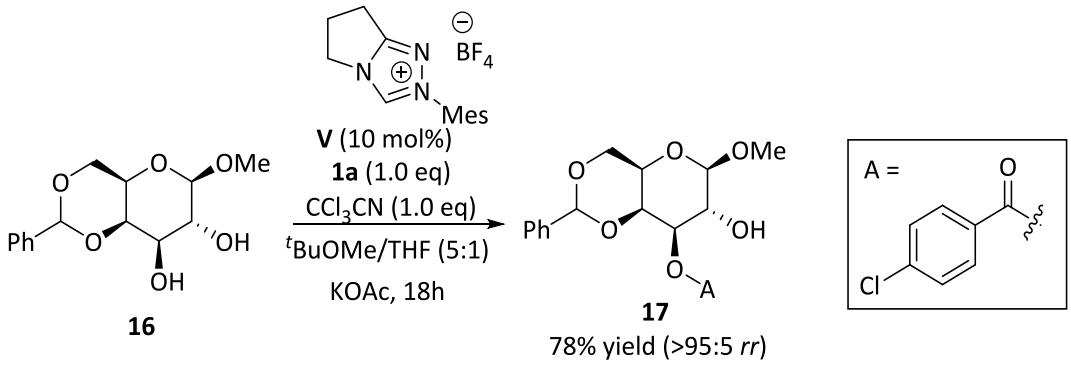
According to the general procedure with cat. **VIII**, **14** was obtained with 27.5 mg as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.53 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.40 (m, 3H), 5.60 (s, 1H), 5.20 (dd, *J* = 9.0, 8.0 Hz, 1H), 4.62 (d, *J* = 7.9 Hz, 1H), 4.43 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.07 (t, *J* = 9.0 Hz, 1H), 3.86 (t, *J* = 10.3 Hz, 1H), 3.69 (t, *J* = 9.3 Hz, 1H), 3.62 – 3.53 (m, 4H), 2.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 139.8, 136.9, 131.3, 129.4, 128.8, 128.4, 128.1, 126.3, 102.3, 102.0, 80.9, 74.8, 72.4, 68.6, 66.2, 57.2. HRMS (ESI): calcd for $C_{21}H_{22}ClO_7^+$ ($M+H^+$): 421.1054, found 421.1054.

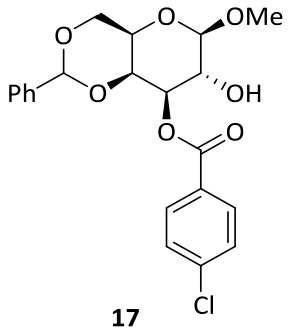


15

According to the general procedure with cat. **VIII**, **15** was obtained with 2.7 mg as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.43 (dd, *J* = 9.1, 2.2 Hz, 4H), 7.40 – 7.32 (m, 3H), 5.55 (s, 1H), 5.49 (t, *J* = 9.4 Hz, 1H), 4.48 (d, *J* = 7.6 Hz, 1H), 4.44 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.84 (dt, *J* = 13.3, 9.9 Hz, 2H), 3.76 – 3.71 (m, 1H), 3.65 – 3.60 (m, 4H), 2.71 (d, *J* = 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 139.8, 136.8, 131.4, 129.1, 128.8, 128.2, 128.1, 126.1, 104.6, 101.5,

78.6, 74.5, 73.6, 68.7, 66.6, 57.7. HRMS (ESI): calcd for $C_{21}H_{22}ClO_7^+$ ($M+H^+$): 421.1054, found 421.1052.





According to the general procedure, **17** was obtained with 32.7 mg as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.49 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 5.0, 1.6 Hz, 3H), 5.55 (s, 1H), 5.16 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.54 (dd, *J* = 14.7, 7.1 Hz, 1H), 4.40 (t, *J* = 9.9 Hz, 2H), 4.20 – 4.11 (m, 2H), 3.63 (s, 3H), 3.61 (s, 1H), 2.41 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.8, 137.6, 131.3, 128.9, 128.8, 128.1, 128.1, 126.1, 104.1, 100.8, 74.4, 73.6, 69.0, 68.7, 66.6, 57.3. HRMS (ESI): calcd for $C_{21}H_{22}ClO^+$ ($M+H^+$): 421.1054, found 421.1059.

7. References

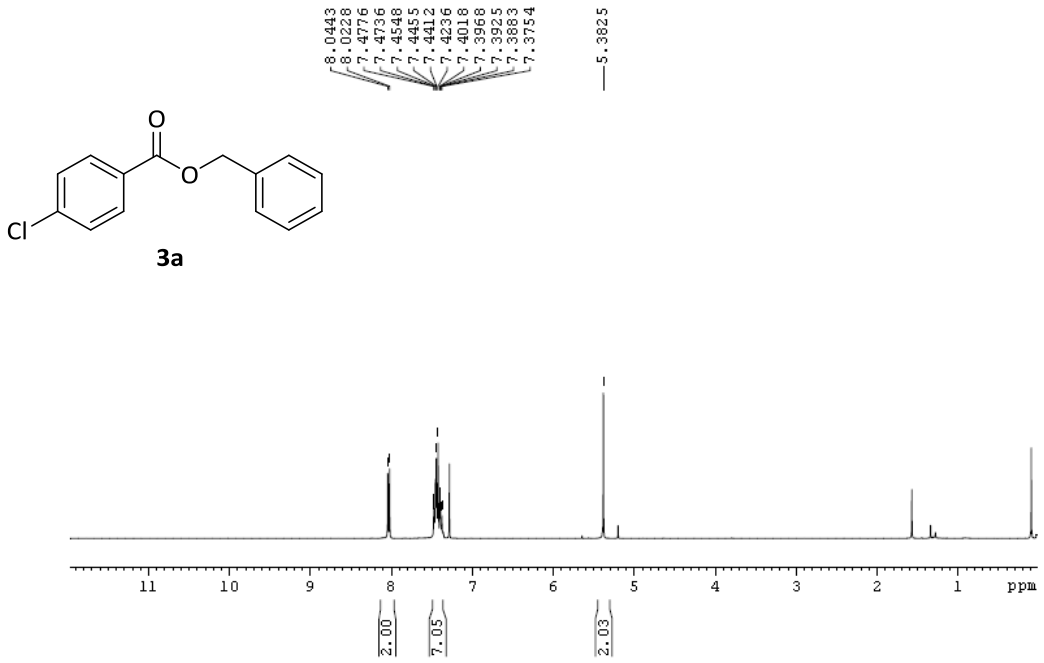
(1) (a) J. C. Grivas, A. Taurins, *Can. J. Chem*. 1958, **36**, 771–774. (b) R. R. Schmidt, M. Hoffmann, *Tetrahedron Lett*. 1982, **23**, 409–412; (c) R. R. Schmidt, J. Michel, *Angew. Chem. Int. Ed*. 1980, **19**, 731–732.

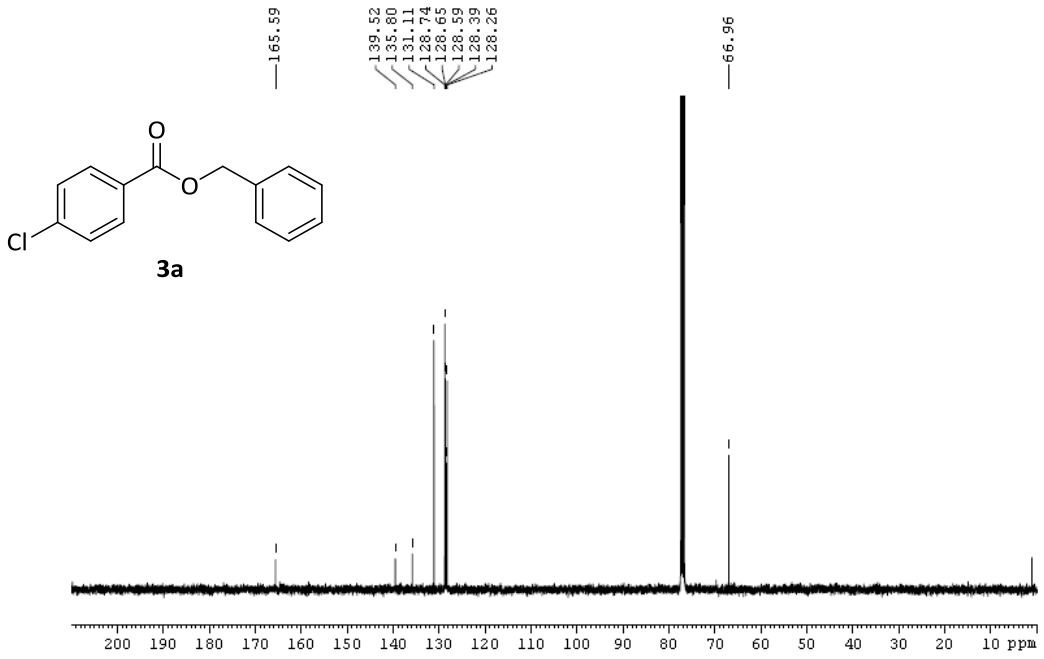
(2) (a) F. C. Schaefer, G. A. Peters, *J. Org. Chem*. 1961, **26**, 412–418; (b) P. Eckenberg, U. Groth, T. Huhn, N. Richter, C. Schmeck, *Tetrahedron*, 1993, **49**, 1619–1624.

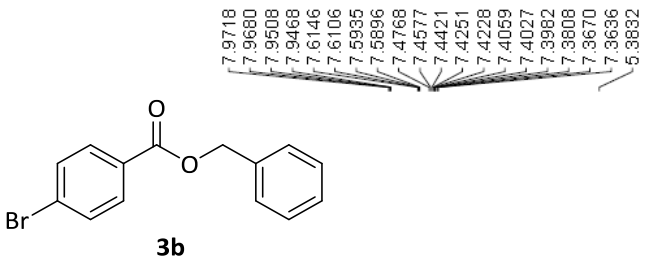
(3) B. Y. Savkov, A. V. Virovets, V. A. Maksakov, *J. Mol. Struc*. 2017, **1141**, 115–118.

(4) (a) D. Borrmann, R. Wegler, *Chem. Ber*. 1967, **100**, 1814–1816; (b) H. Hamana, T. Sugasawa, *Chem. Lett*. 1985, 571–574; (c) K. A. Tehrani, S. Stas, B. Lucas, N. De Kimpe, *Tetrahedron* 2009, **65**, 1957–1966.

8. Copies of ^{1}H and ^{13}C NMR spectra



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7.6146
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7.5935
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7.4768
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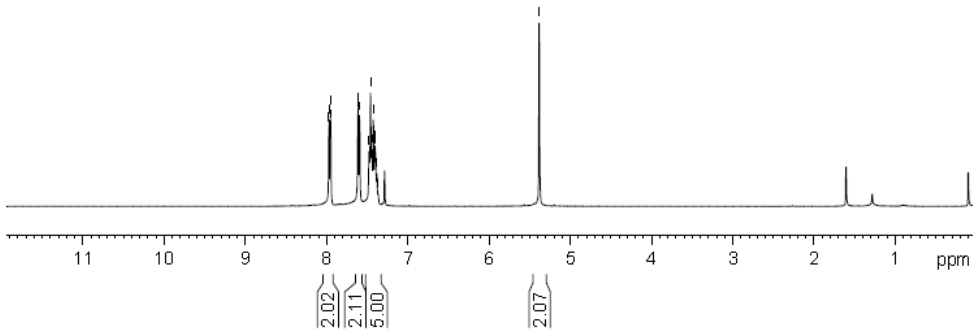
7.4421
7.4251
7.4228
7.4059
7.4027
7.3982
7.3808
7.3670
7.3636
5.3832
O
O
Br

3b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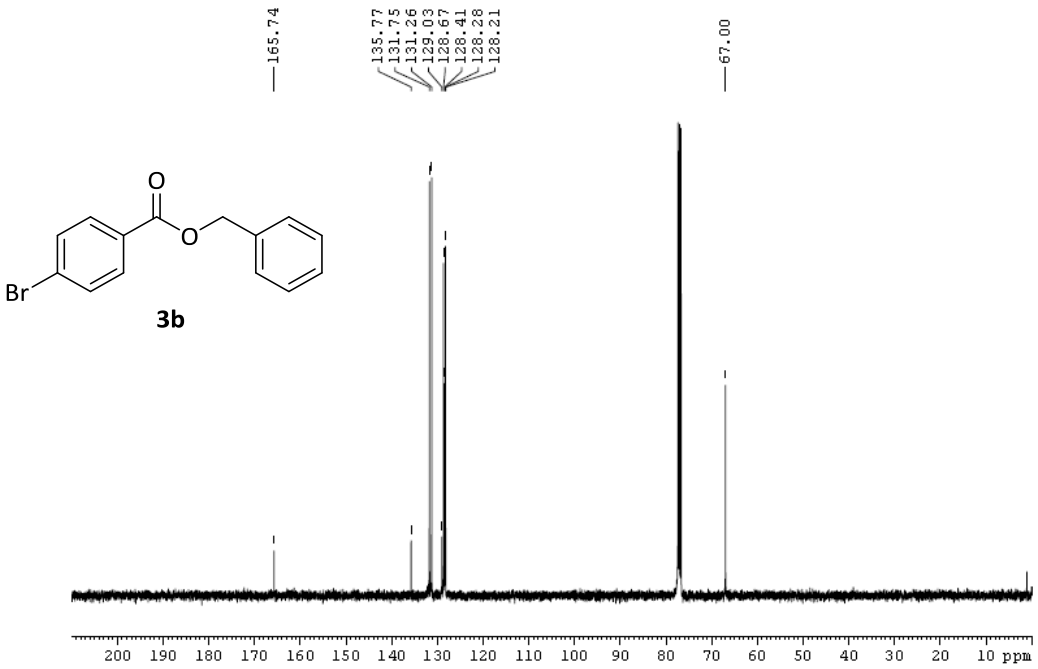
9
8
7
6
5
4
3
2
1
ppm
2.02
2.11
5.00
2.07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131.75
131.26
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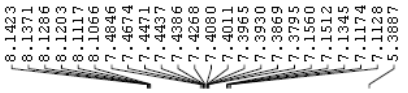
128.67
128.41
128.28
128.21
67.00
O
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

3b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8.1286
8.1203
8.1117
8.1066
7.4846
7.4674
7.4471
7.4437
7.4386
7.4268
7.4080
7.4011
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7.3869
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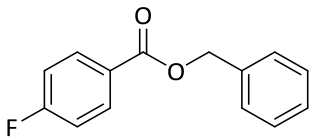
7.1560
7.1512
7.1345
7.1174
7.1128
5.3887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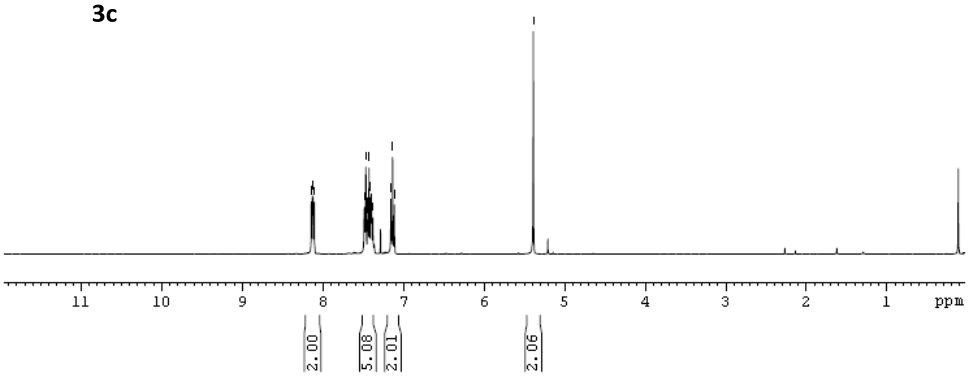
O
F

3c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9
8
7
6
5
4
3
2
1
ppm
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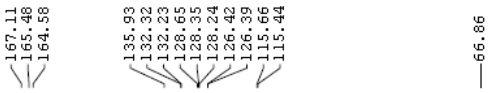
5.08
2.01
2.06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165.48
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132.23
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126.42
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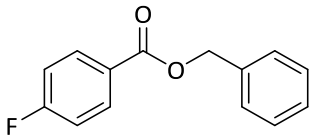
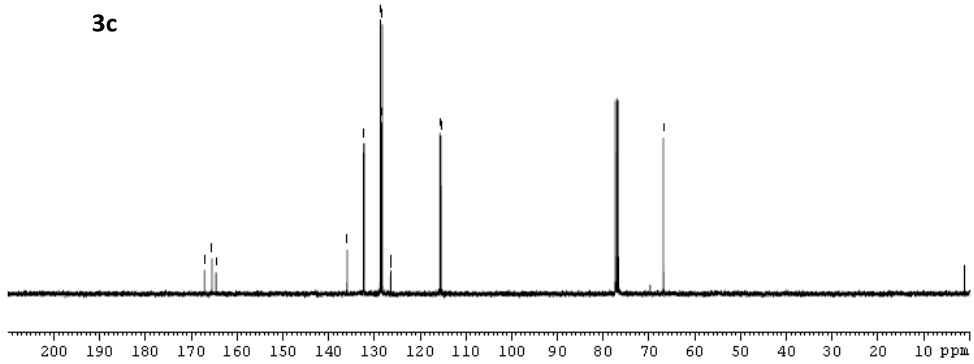
115.66
115.44
66.86


O
O
F

3c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170
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150
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120
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90
80
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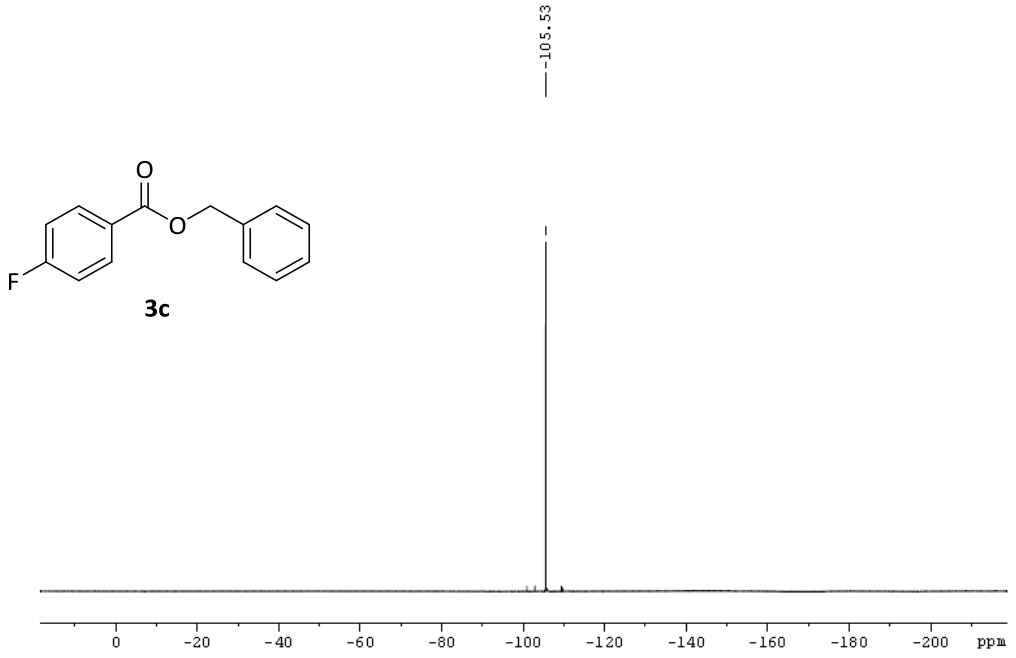
60
50
40
30
20
10 ppm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O
O
F
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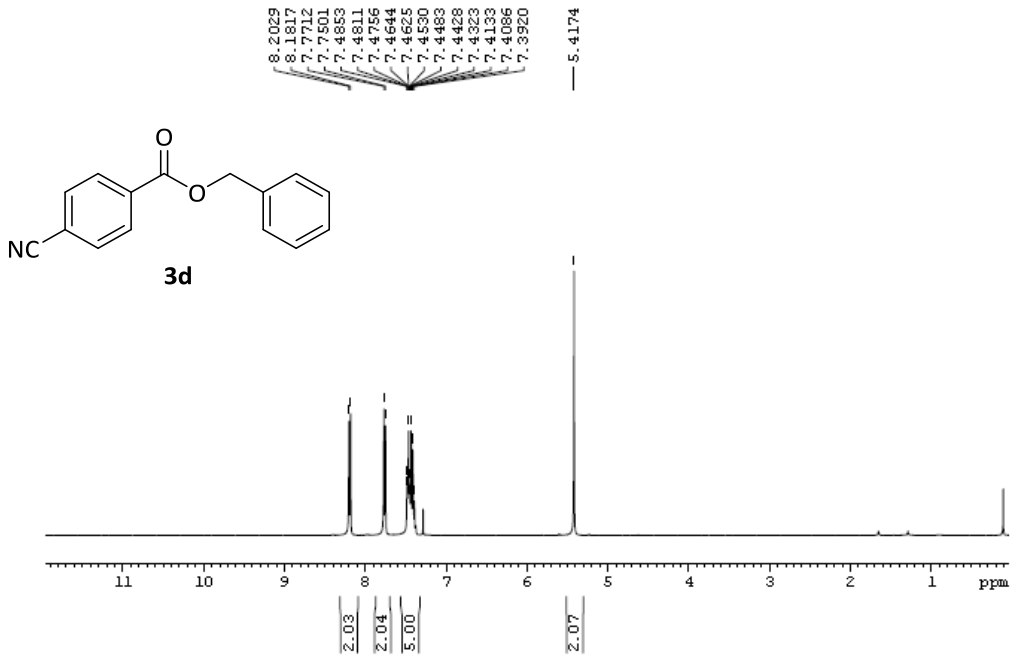
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

3c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7.4756
7.4644
7.4625
7.4530
7.4483
7.4428
7.4323
7.4133
7.4086
7.3920
5.4174
O
O
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9
8
7
6
5
4
3
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ppm
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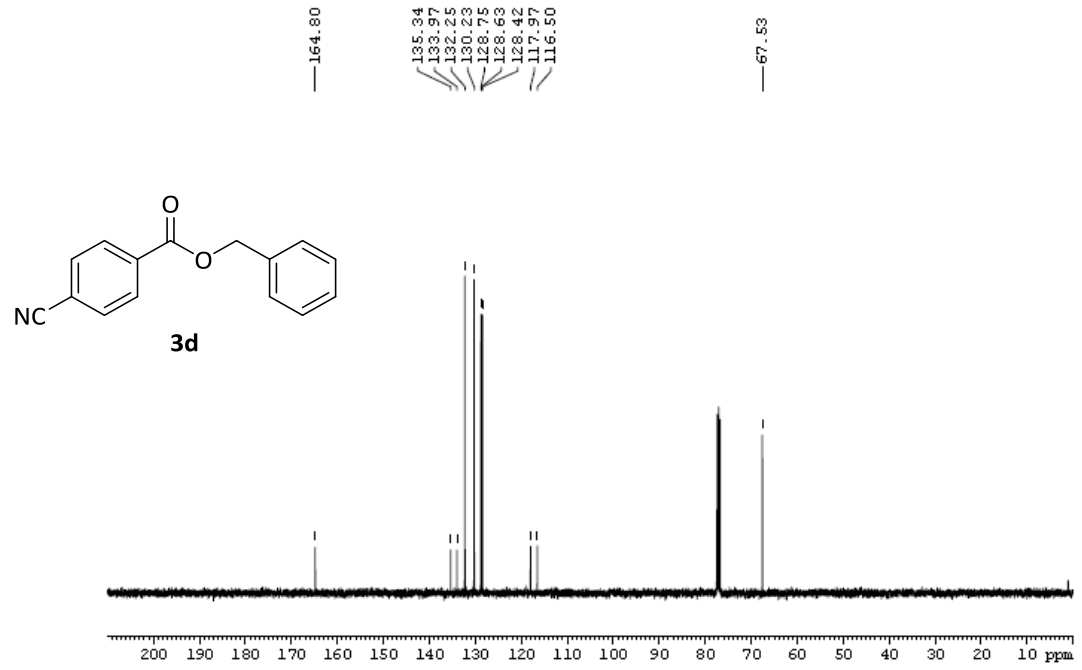
2.04
5.00
2.07

3d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133.97
132.25
130.23
128.75
128.63
128.42
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116.50
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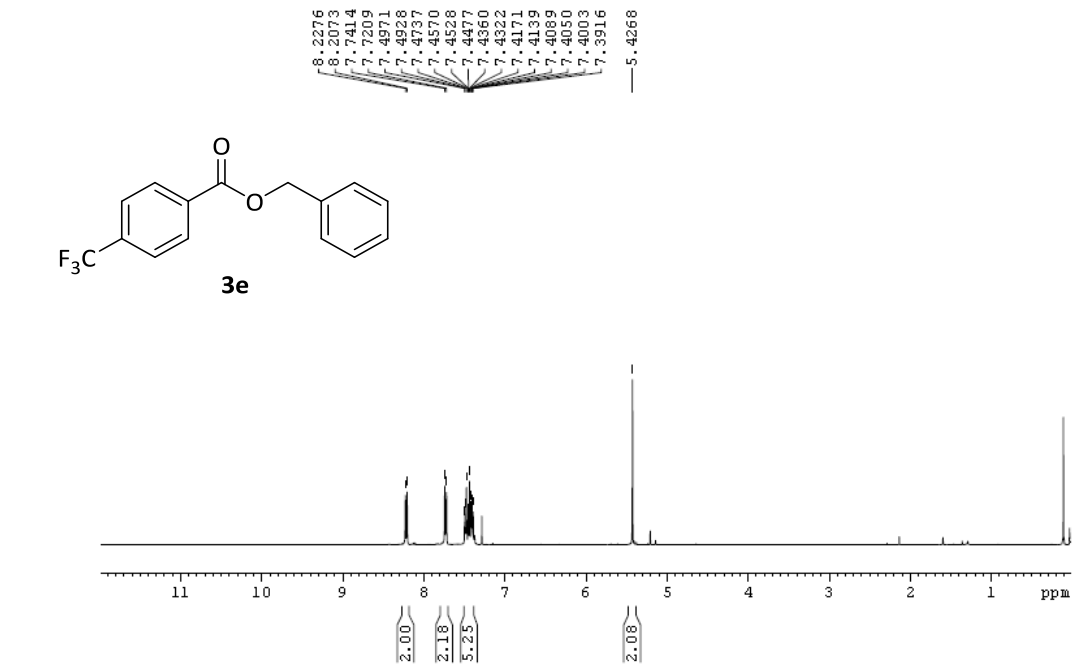
O
NC
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3d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7.4360
7.4322
7.4171
7.4139
7.4089
7.4050
7.4003
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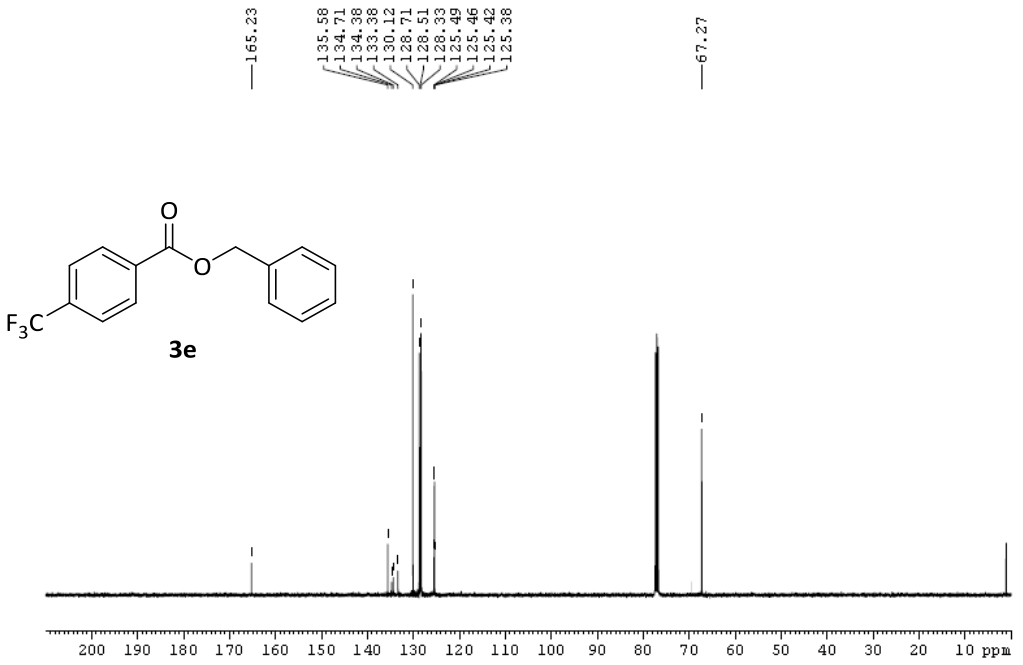
O
O
F3C
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.18
5.25
2.08

3e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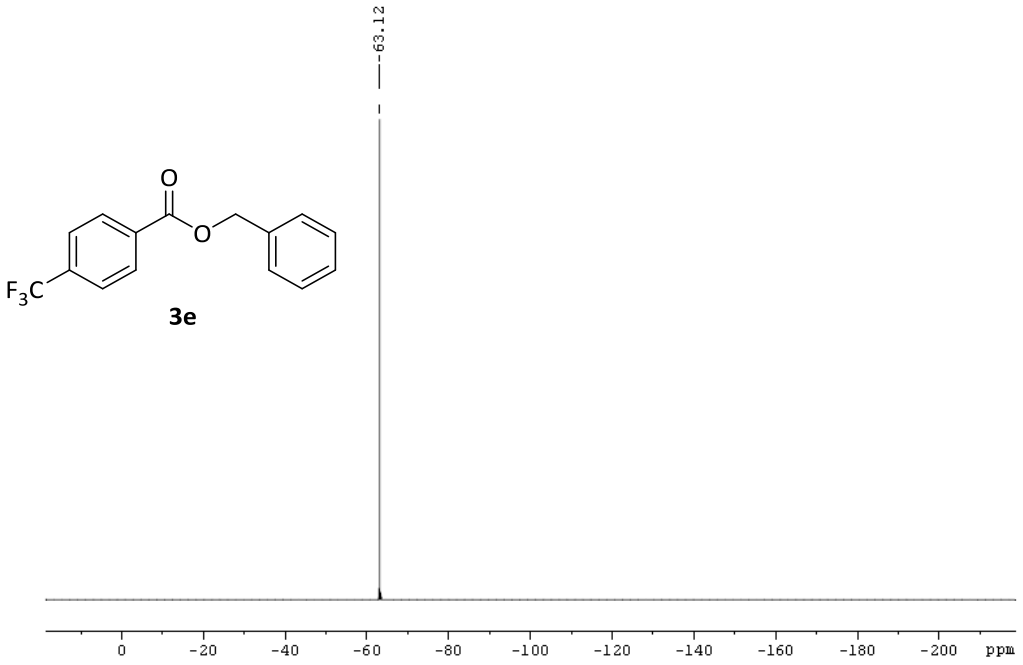
O
O
F3C
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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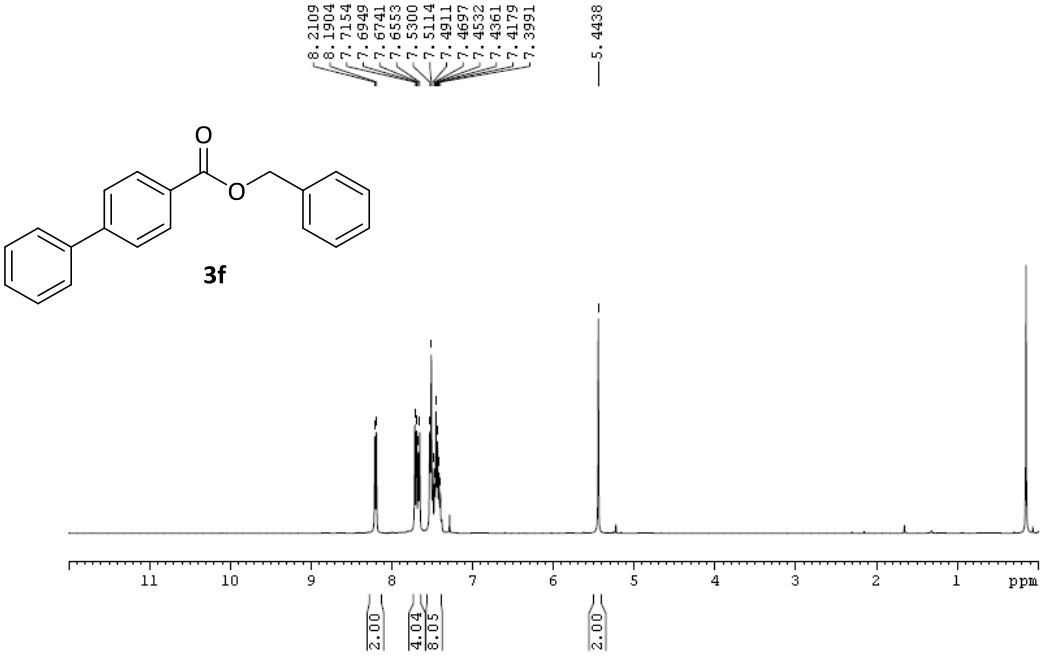
O
O
F3C
3e
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm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7.4361
7.4179
7.3991
5.4438
O
O
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9
8
7
6
5
4
3
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ppm
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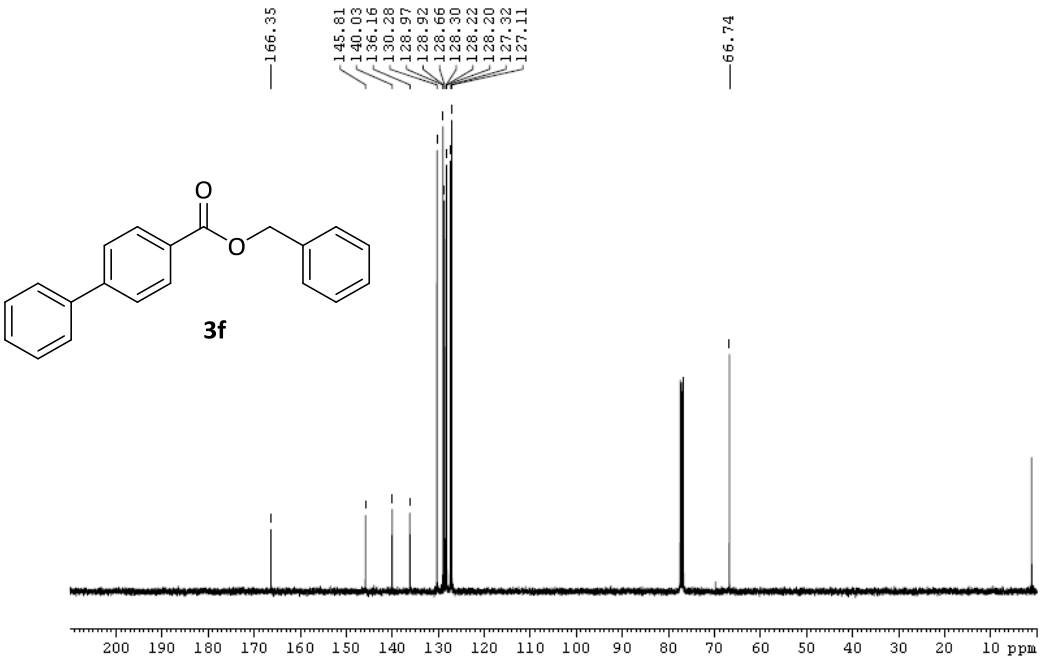
4.04
8.05
2.00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127.11
66.74
O
O
3f
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140
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80
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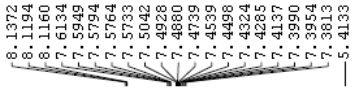
50
40
30
20
10 ppm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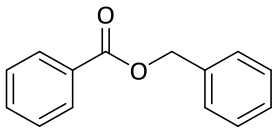
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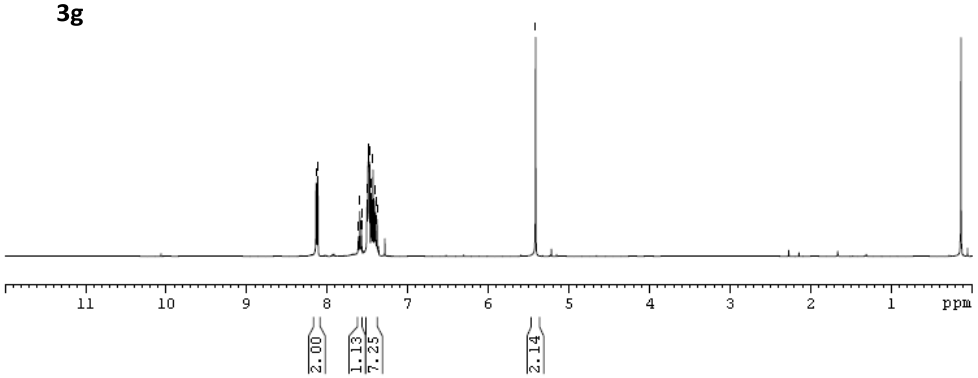
O

3g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7
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5
4
3
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1
ppm
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7.25
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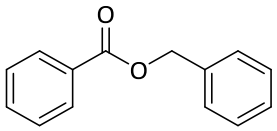
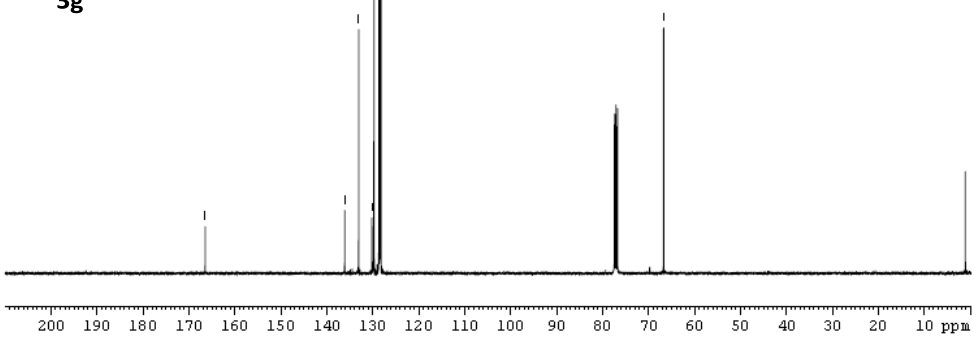
66.71


O
O

3g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140
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120
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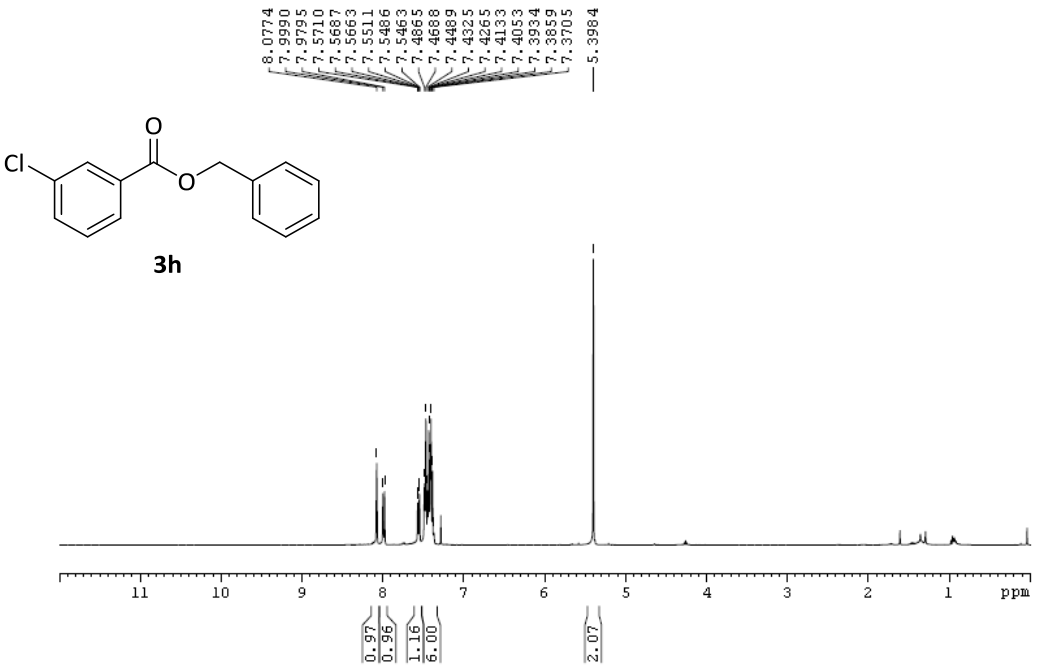
100
90
80
70
60
50
40
30
20
10 ppm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7.4688
7.4489
7.4325
7.4265
7.4133
7.4053
7.3934
7.3859
7.3705
5.3984
Cl
O
O
3h
11
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6
5
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ppm
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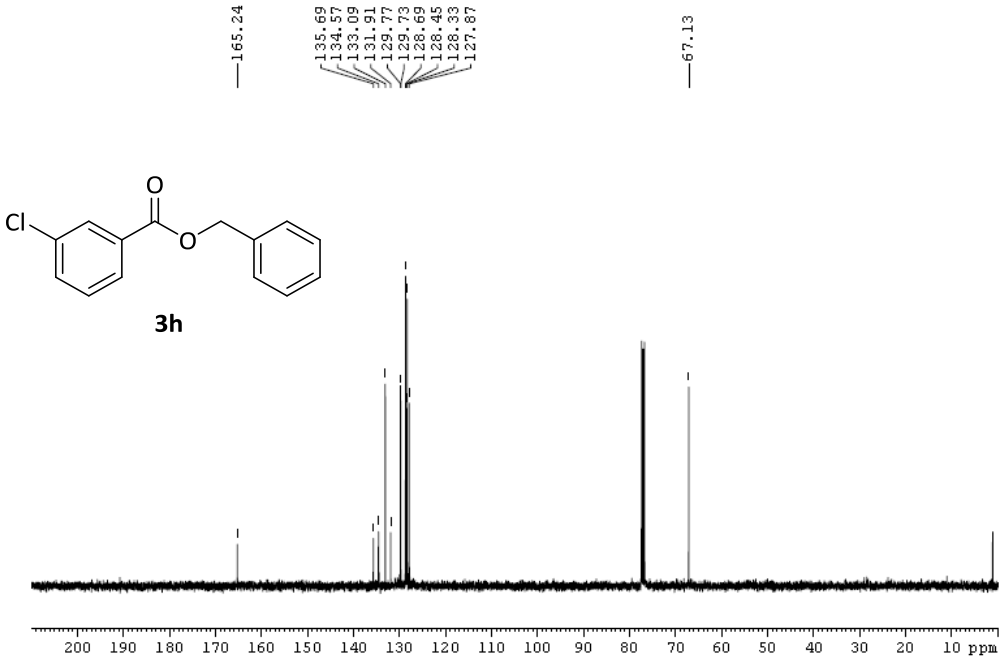
6.00
2.07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128.45
128.33
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Cl
O
O
3h
200
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180
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160
150
140
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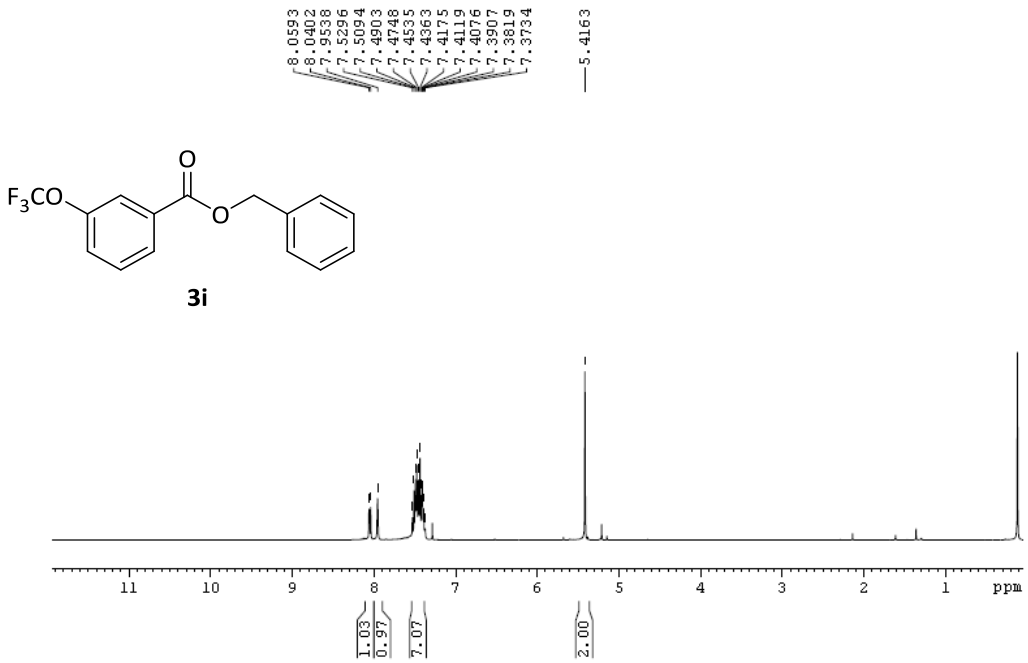
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.4175
7.4119
7.4076
7.3907
7.3819
7.3734
5.4163
O
F3CO
O
3i
11
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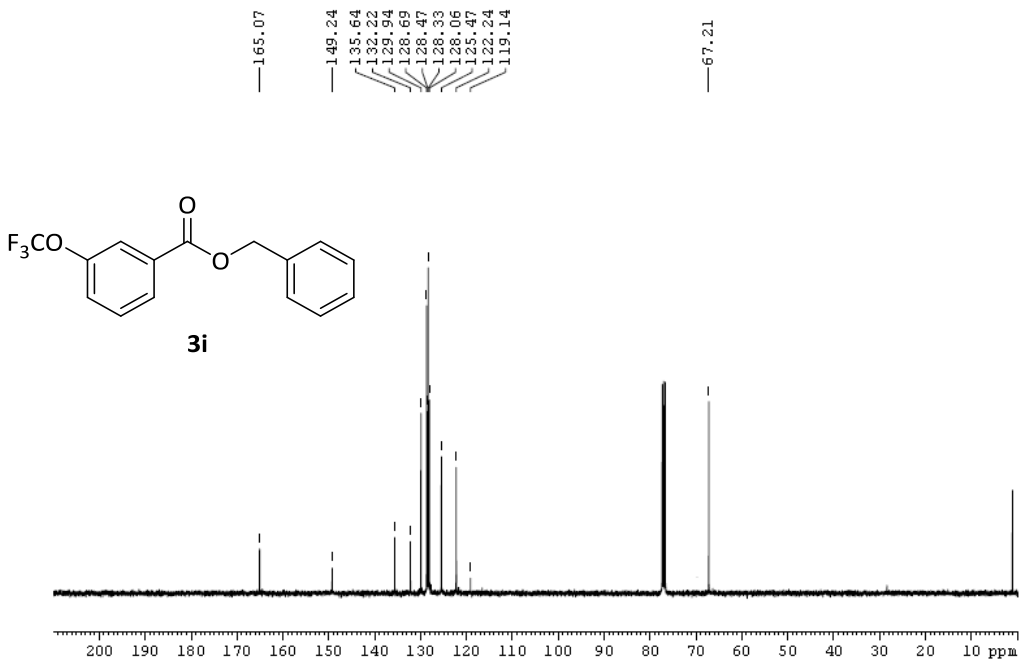
9
8
7
6
5
4
3
2
1
ppm
1.03
0.97
7.07
2.00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122.24
119.14
67.21
O
F3CO
O
3i
200
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180
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120
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80
70
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50
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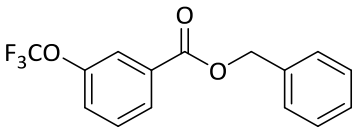
30
20
10 ppm


O
F3CO
O

3i

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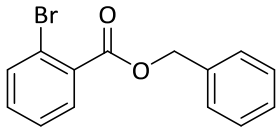
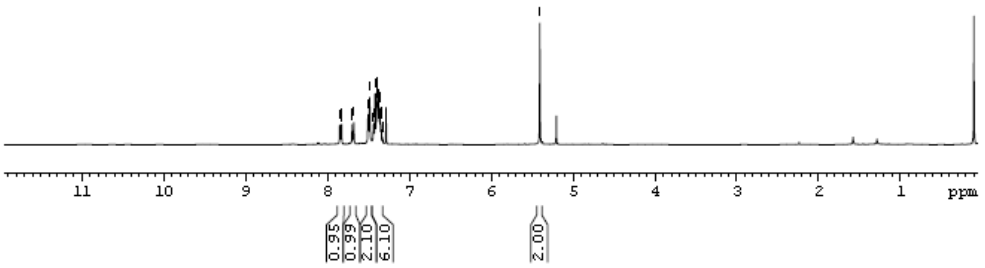

Br
O
O

3j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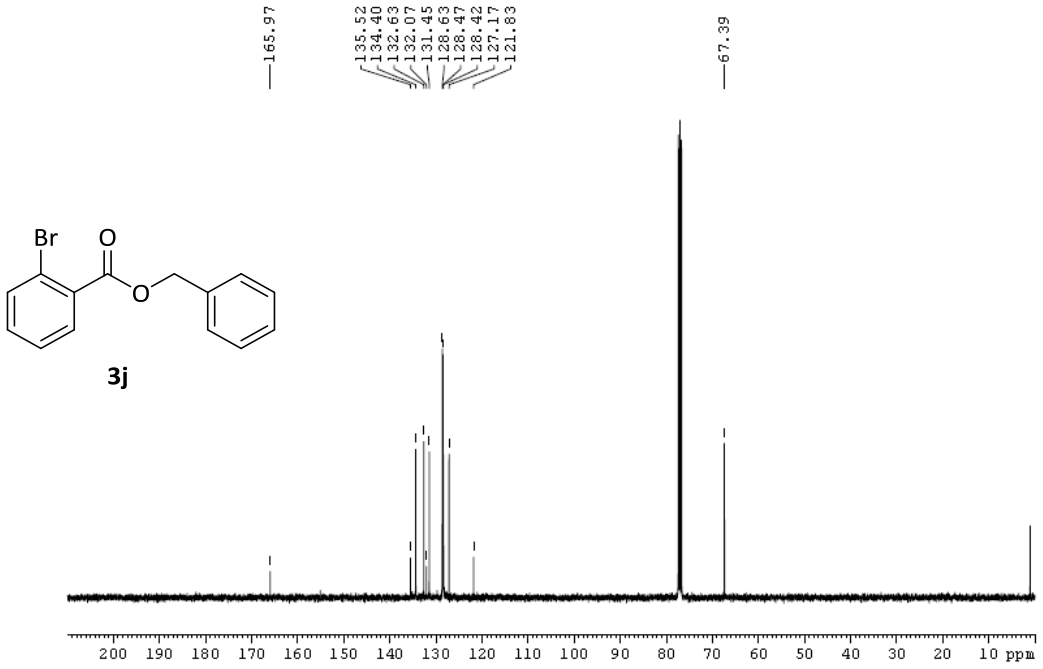
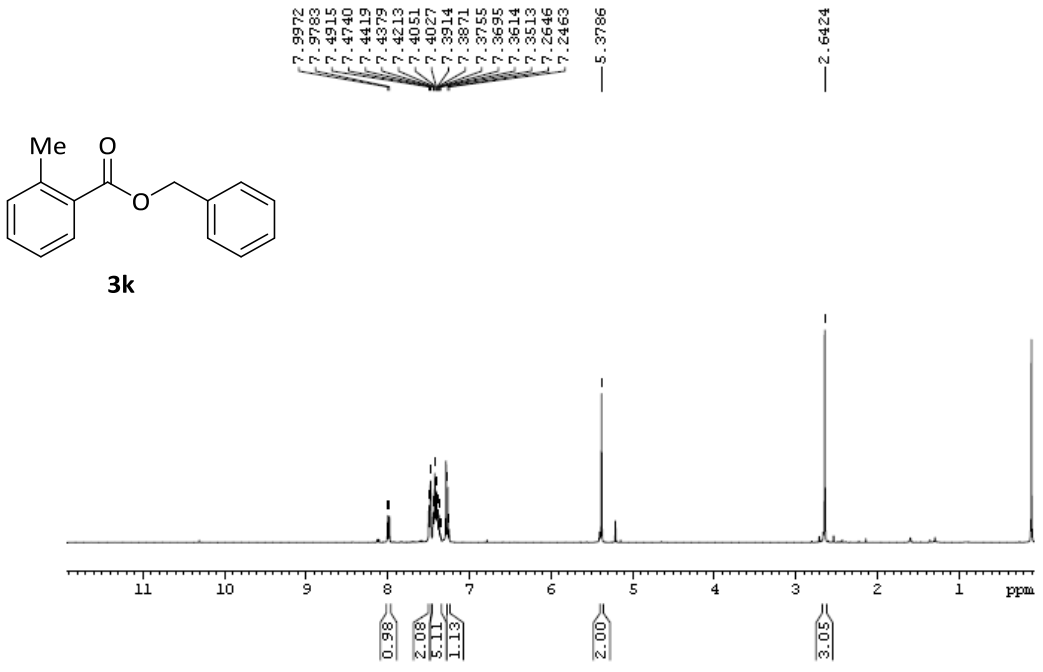
10
9
8
7
6
5
4
3
2
1
ppm
0.95
0.99
2.10
6.10
2.00


165.97
135.52
134.40
132.63
132.07
131.45
128.63
128.47
128.42
127.17
121.83
67.39
Br
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3j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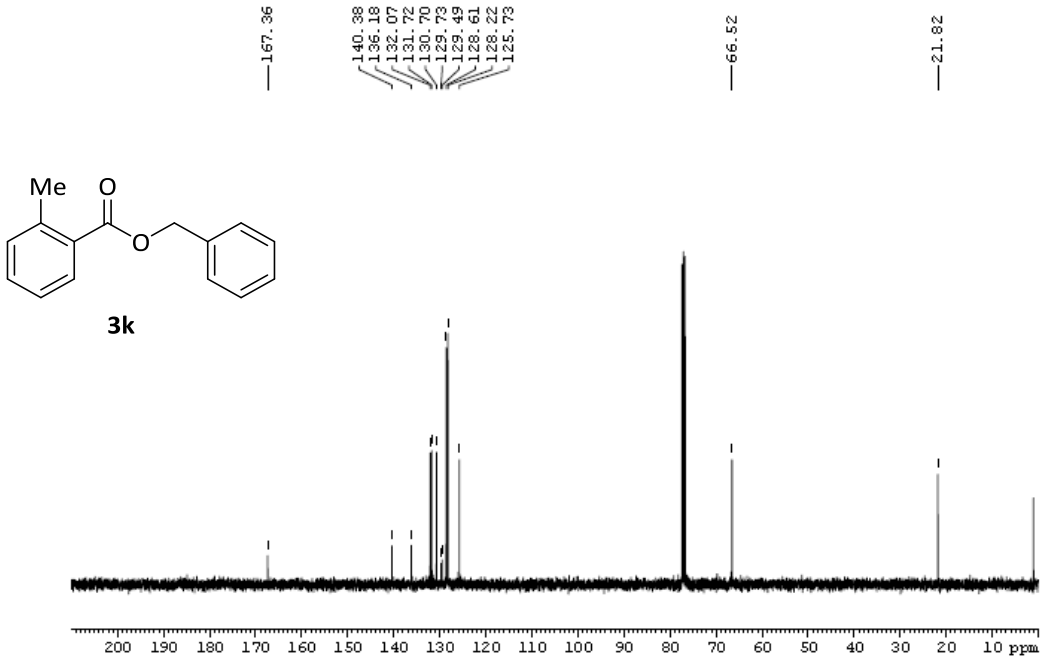
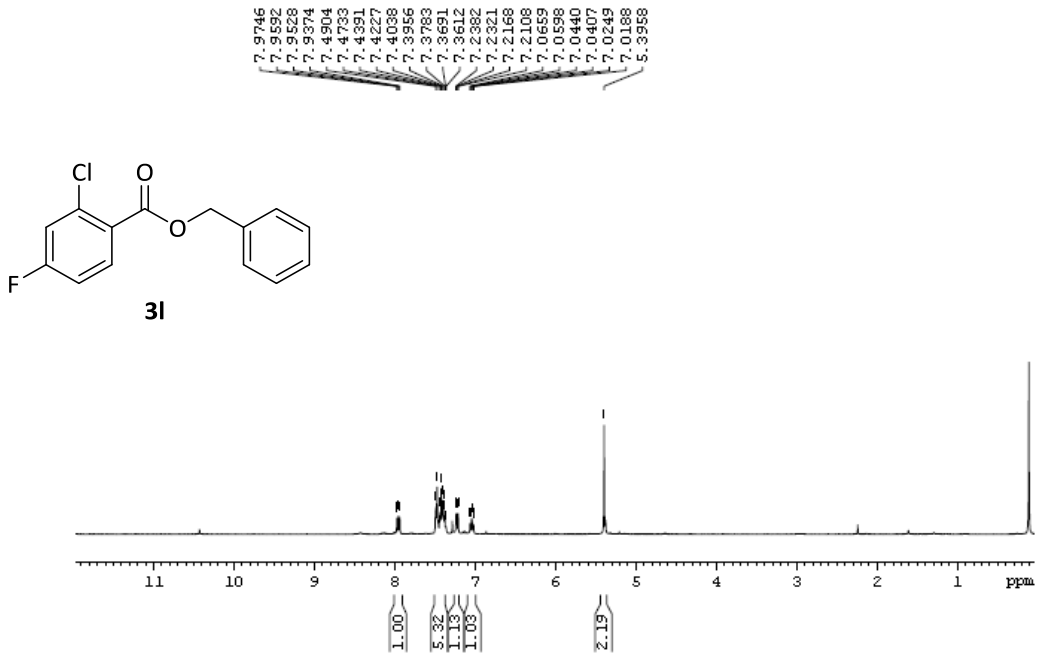
7.9783
7.4915
7.4740
7.4419
7.4379
7.4213
7.4051
7.4027
7.3914
7.3871
7.3755
7.3695
7.3614
7.3513
7.2646
7.2463
5.3786
2.6424
Me
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
0.98
2.08
5.11
1.13
2.00
3.05

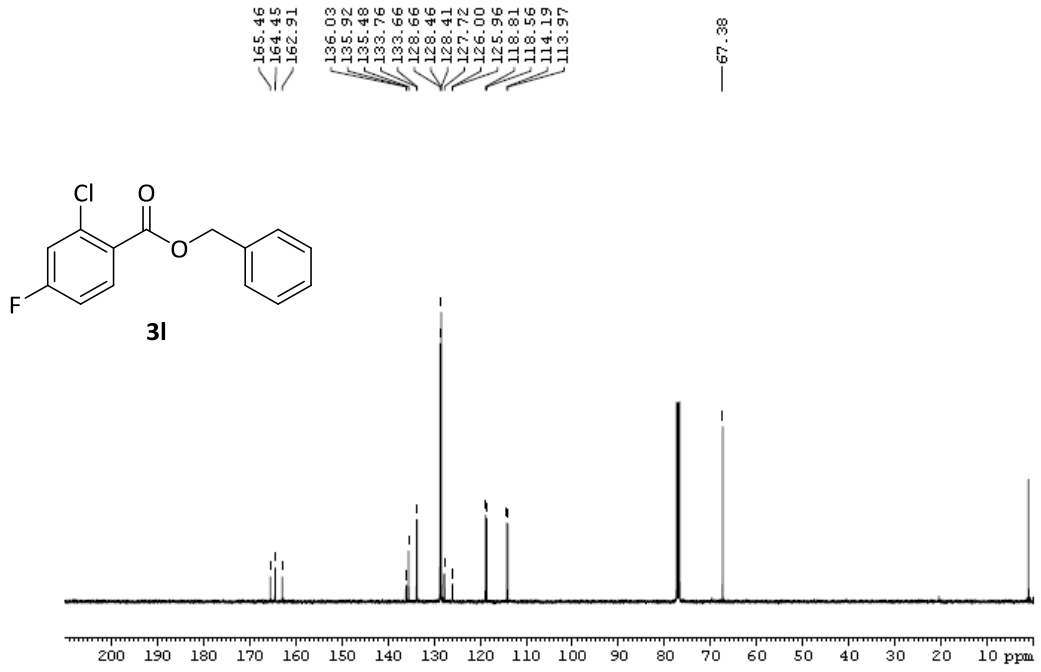
3k


167.36
140.38
136.18
132.07
131.72
130.70
129.73
129.49
128.61
128.22
125.73
66.52
21.82
Me
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3k


7.9746
7.9592
7.9528
7.9374
7.4904
7.4733
7.4391
7.4227
7.4038
7.3956
7.3783
7.3691
7.3612
7.2382
7.2321
7.2168
7.2108
7.0659
7.0598
7.0440
7.0407
7.0249
7.0188
5.3958
Cl
O
O
F
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
5.32
1.13
1.03
2.19

3l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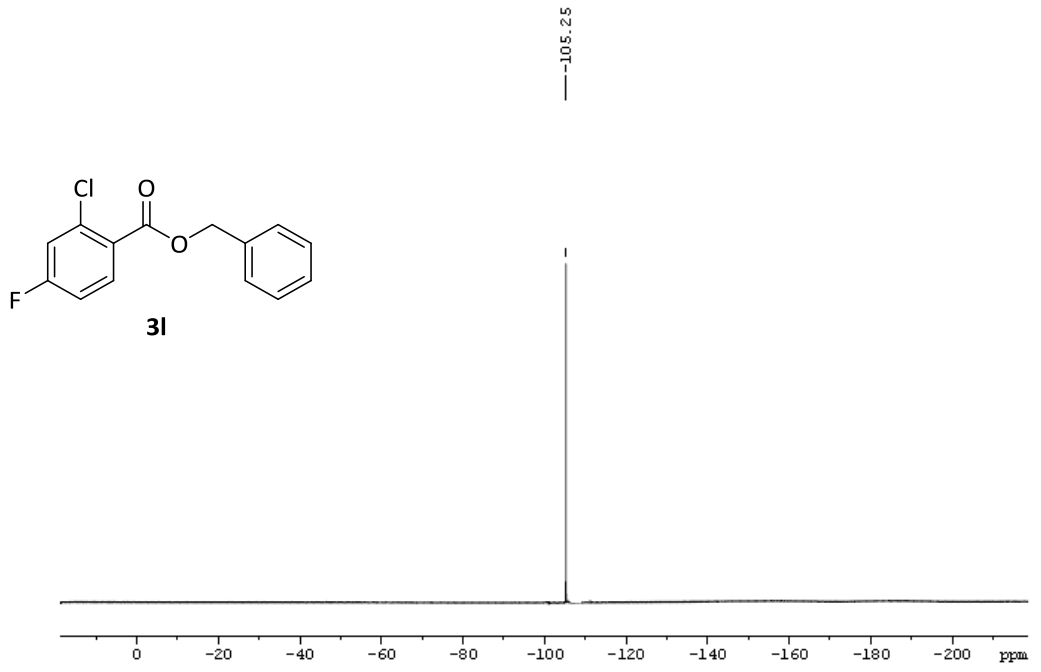
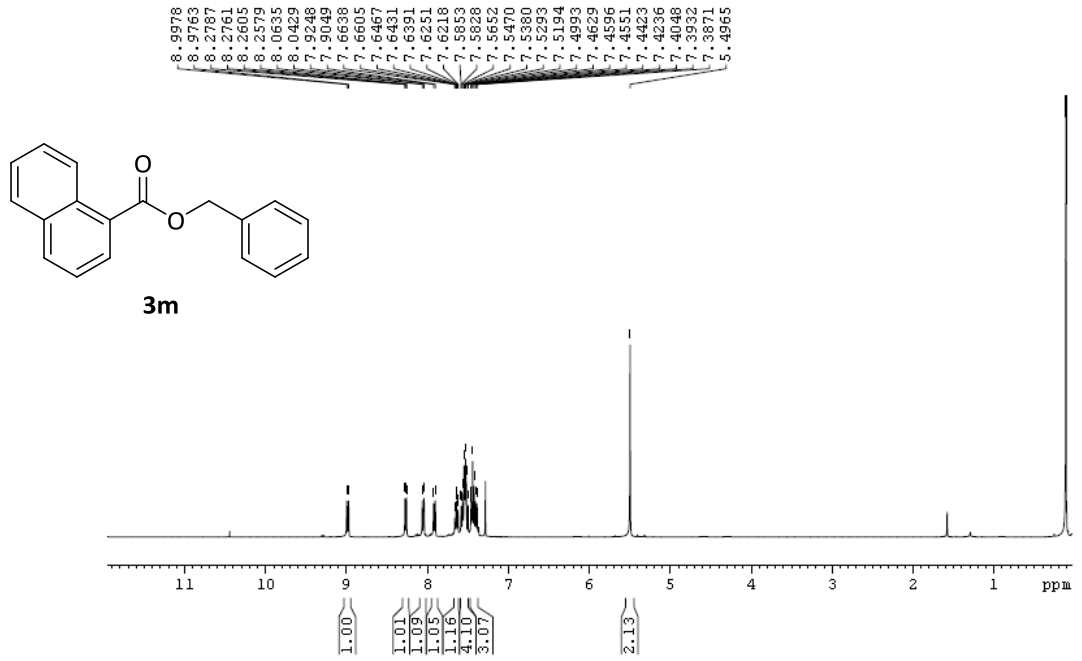
164.45
162.91
136.03
135.92
135.48
133.76
133.66
128.66
128.46
128.41
127.72
126.00
125.96
118.81
118.56
114.19
113.97
67.38
Cl
O
O
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3l


-105.25
Cl
O
O
F
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3l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8.9763
8.2787
8.2761
8.2605
8.2579
8.0635
8.0429
7.9248
7.9049
7.6638
7.6605
7.6467
7.6431
7.6391
7.6251
7.6218
7.5853
7.5828
7.5652
7.5470
7.5380
7.5293
7.5194
7.4993
7.4629
7.4596
7.4551
7.4423
7.4236
7.4048
7.3932
7.3871
5.4965
O
O
3m
11
10
9
8
7
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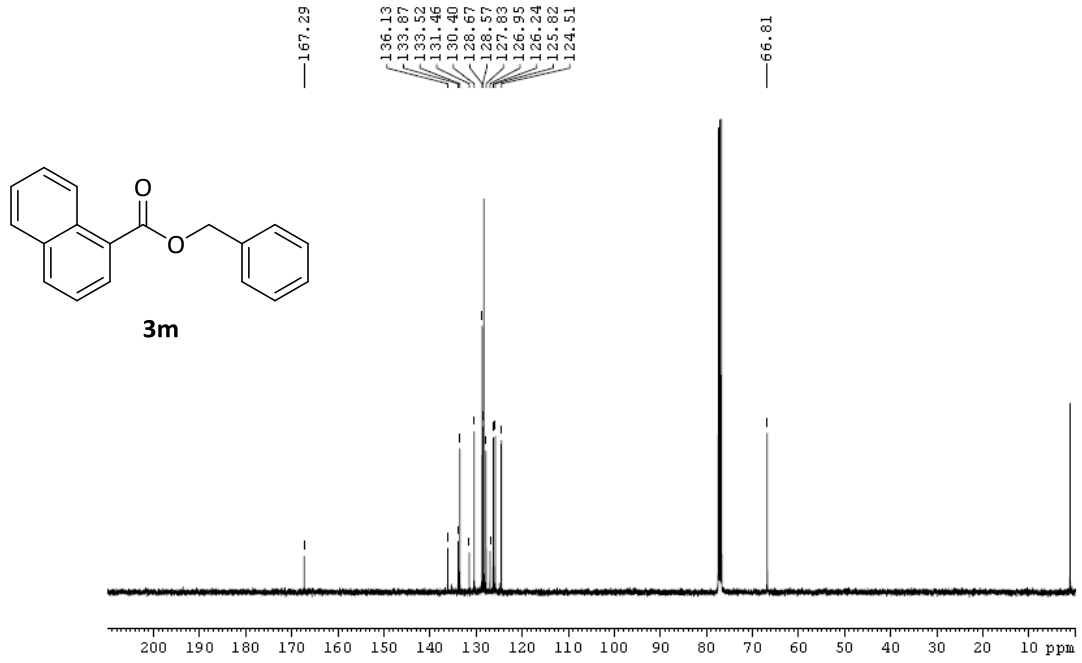
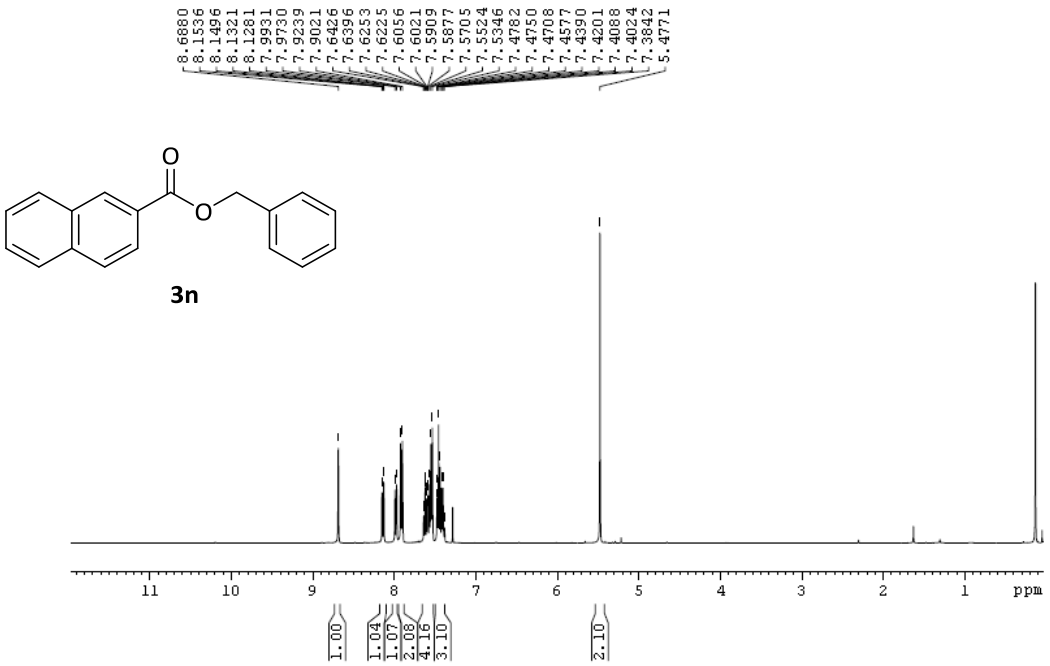
1.09
1.05
1.16
4.10
3.07
2.13


167.29
136.13
133.87
133.52
131.46
130.40
128.67
128.57
127.83
126.95
126.24
125.82
124.51
66.81
O
O
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.1536
8.1496
8.1321
8.1281
7.9931
7.9730
7.9239
7.9021
7.6426
7.6396
7.6253
7.6225
7.6056
7.6021
7.5909
7.5887
7.5705
7.5524
7.5346
7.4782
7.4750
7.4708
7.4577
7.4390
7.4201
7.4088
7.4024
7.3842
5.4771
O
O
3n
11
10
9
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3
2
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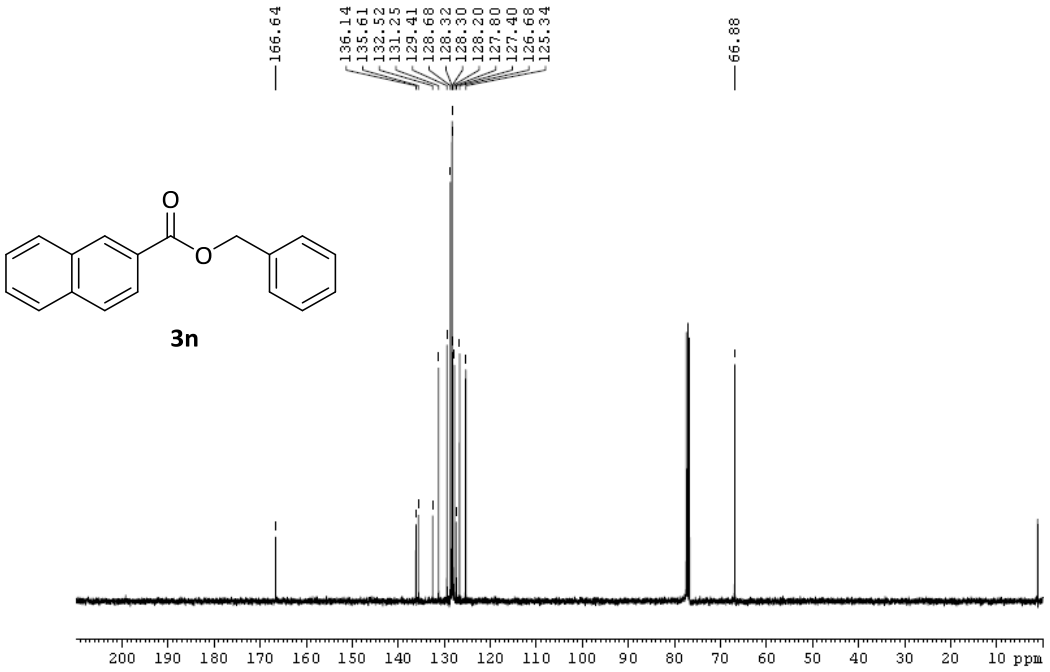
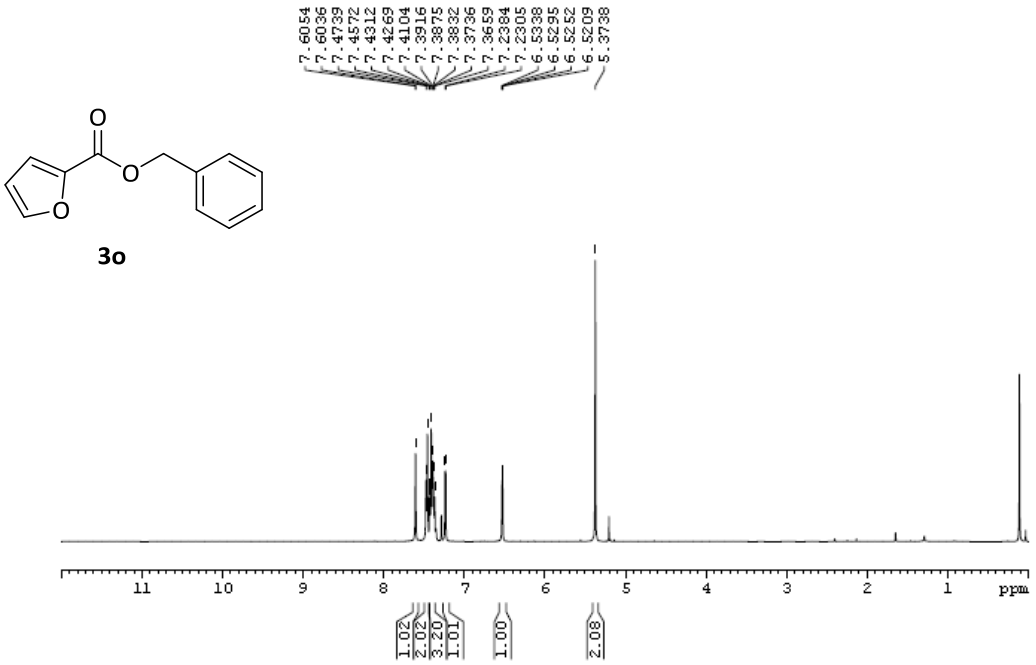
1.04
1.07
2.08
4.16
3.10
2.10


166.64
136.14
135.61
132.52
131.25
129.41
128.68
128.32
128.30
128.20
127.80
127.40
126.68
125.34
66.88
O
O
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.6054
7.6036
7.4739
7.4572
7.4312
7.4269
7.4104
7.3916
7.3875
7.3832
7.3736
7.3659
7.2384
7.2305
6.5338
6.5295
6.5252
6.5209
5.3738
O
O
O
3o
11
10
9
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5
4
3
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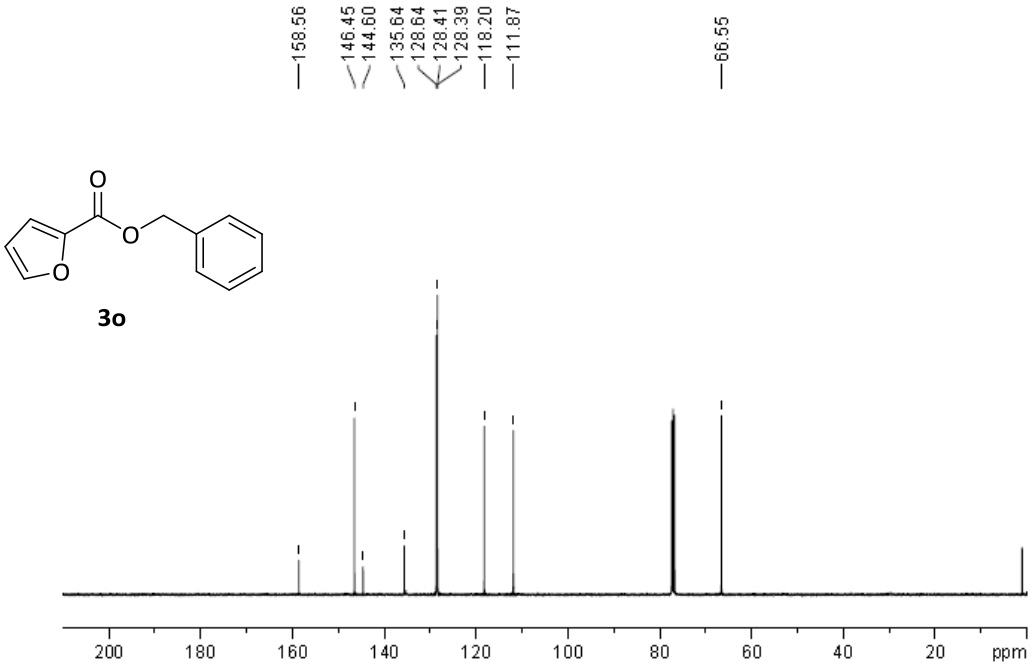
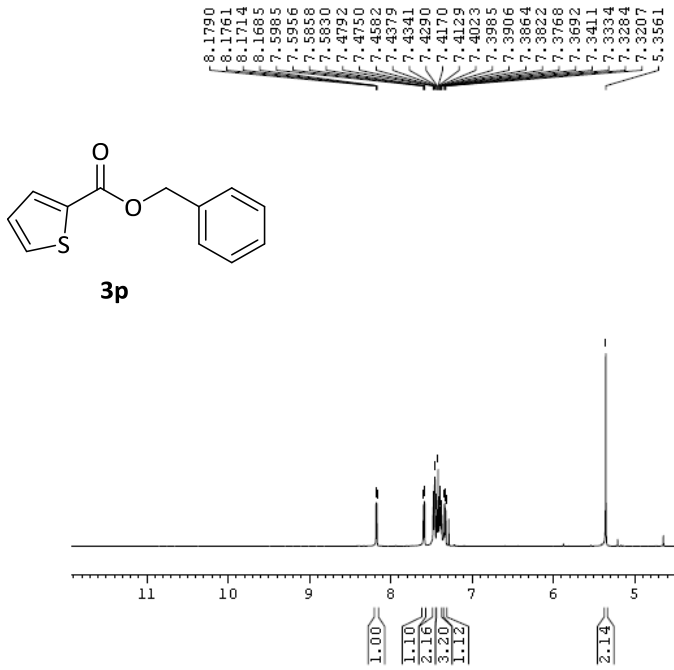
ppm
1.02
2.02
3.20
1.01
1.00
2.08


158.56
146.45
144.60
135.64
128.64
128.41
128.39
118.20
111.87
66.55
O
O
O
3o
200
180
160
140
120
100
80
60
40
20
ppm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8.1761
8.1714
8.1685
7.5985
7.5956
7.5858
7.5830
7.4792
7.4750
7.4582
7.4379
7.4341
7.4290
7.4170
7.4129
7.4023
7.3985
7.3906
7.3864
7.3822
7.3768
7.3692
7.3411
7.3334
7.3284
7.3207
5.3561
O
O
S
3p
11
10
9
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4
3
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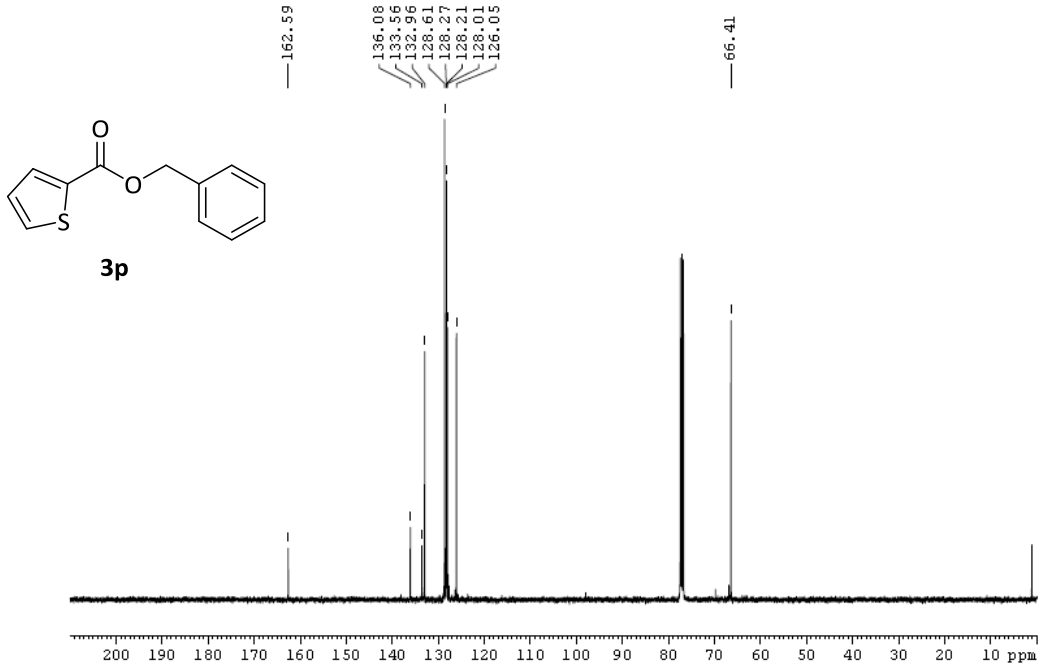
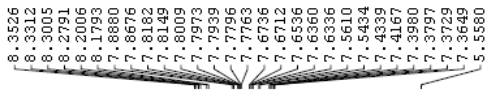
1.00
1.10
2.16
3.20
1.12
2.14


162.59
136.08
133.56
132.96
128.61
128.27
128.21
128.01
126.05
66.41
O
O
S
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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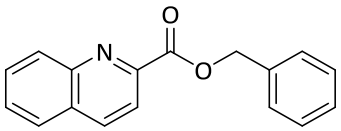
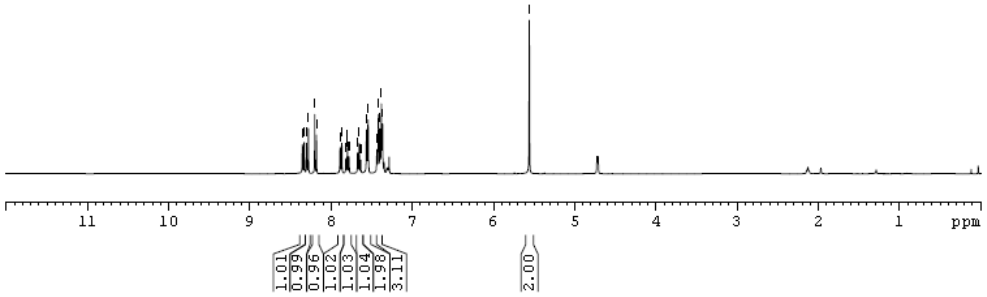
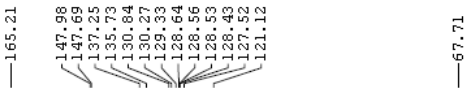
8.3312
8.3005
8.2791
8.2006
8.1793
7.8880
7.8676
7.8182
7.8149
7.8009
7.7973
7.7939
7.7796
7.7763
7.6736
7.6712
7.6536
7.6360
7.6336
7.5610
7.5434
7.4339
7.4167
7.3980
7.3797
7.3729
7.3649
5.5580


O
N
O

3q


11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
0.99
0.96
1.02
1.03
1.04
1.98
3.11
2.00


165.21
147.98
147.69
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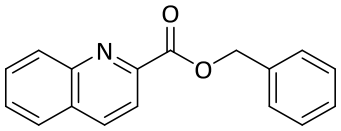
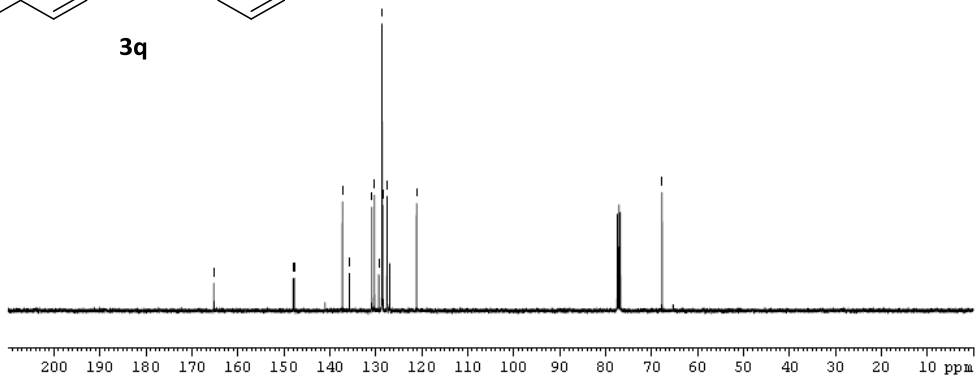
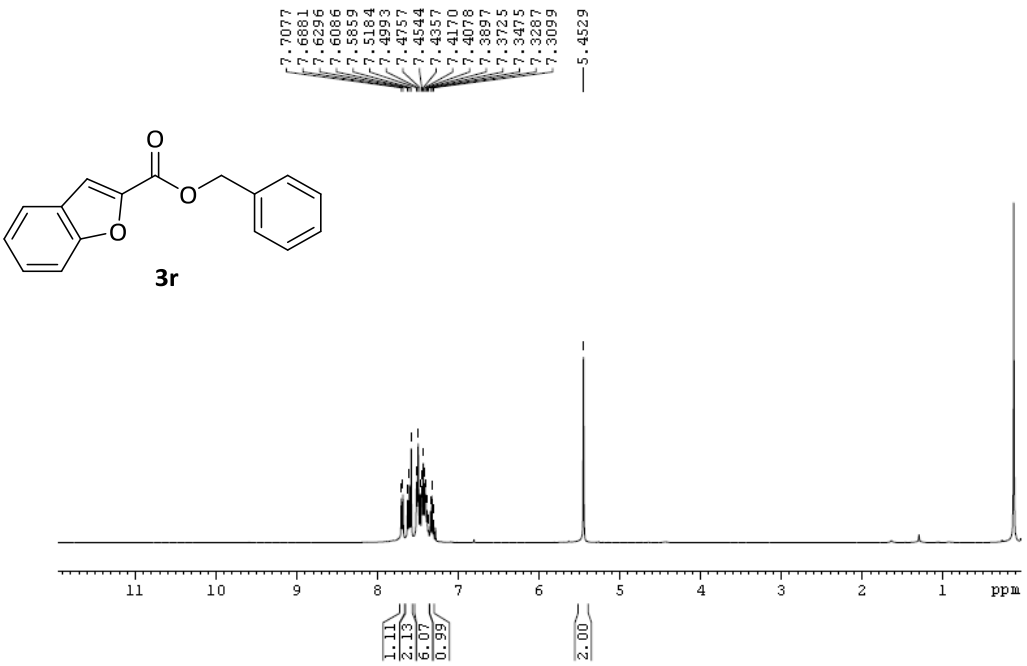
135.73
130.84
130.27
129.33
128.64
128.56
128.53
128.43
127.52
121.12
67.71


O
N
O

3q


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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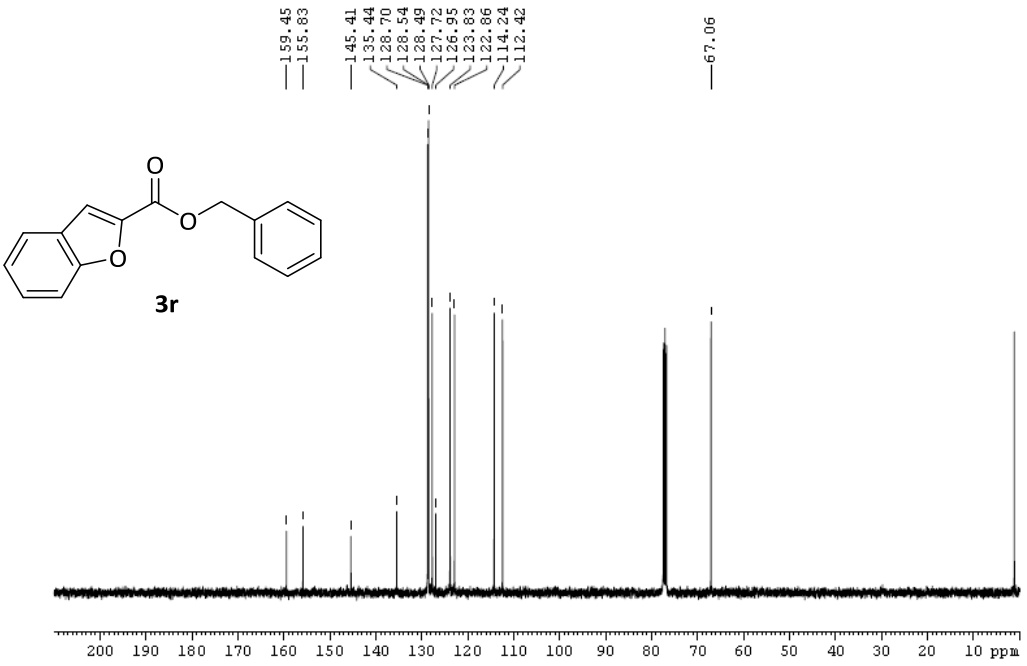
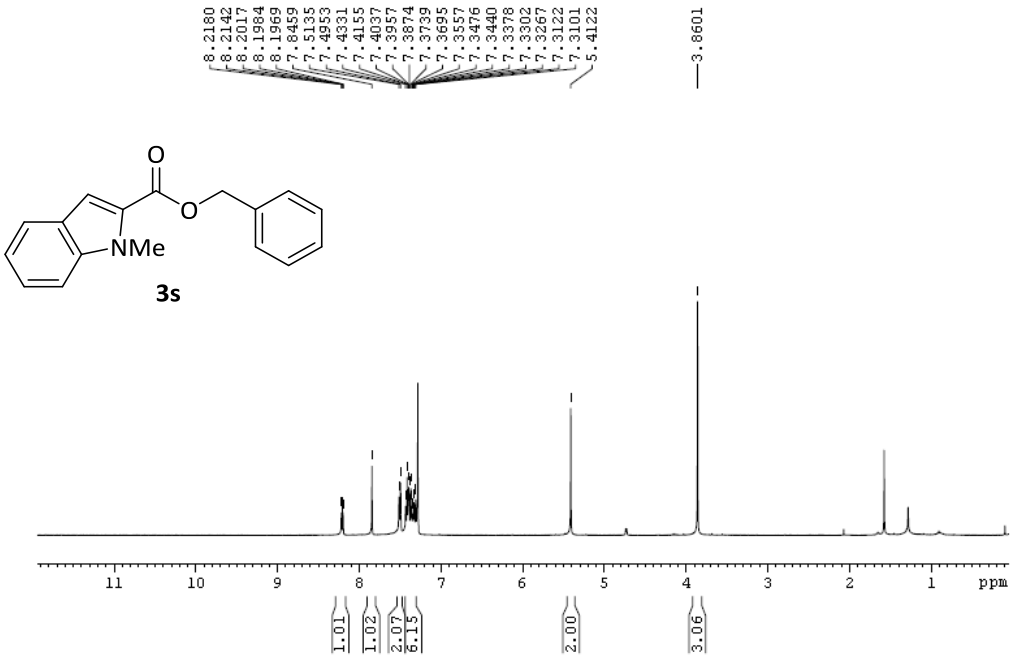
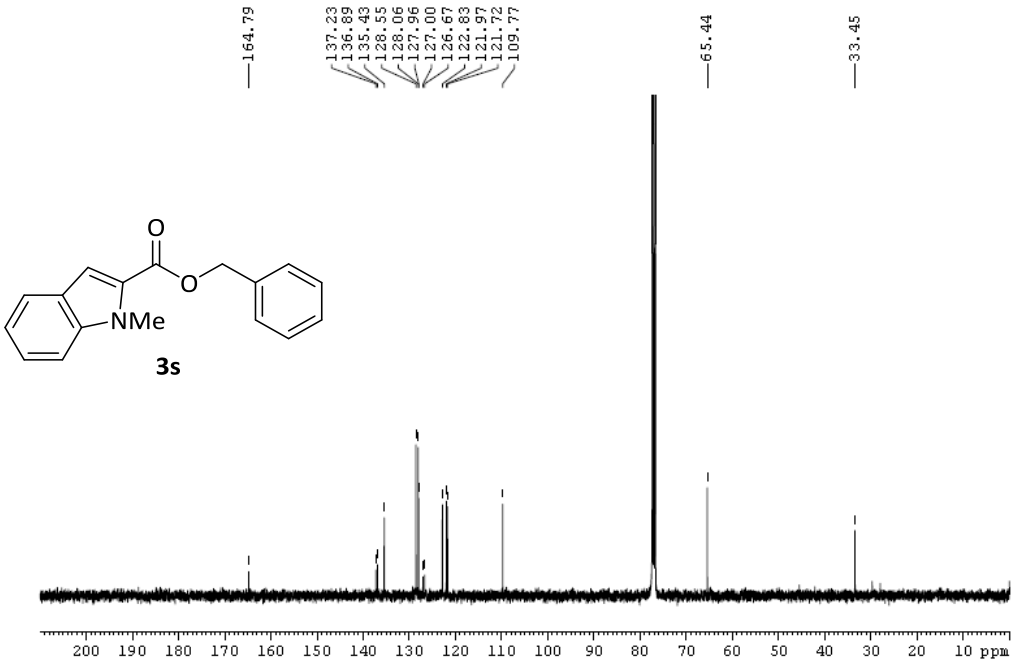
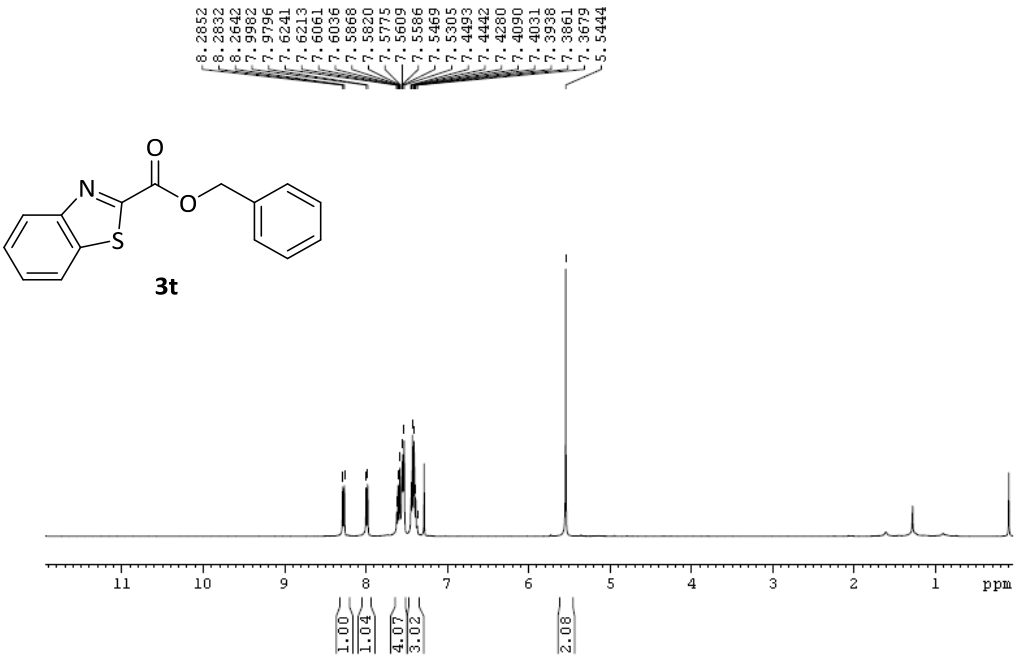
7.6296
7.6086
7.5859
7.5184
7.4993
7.4757
7.4544
7.4357
7.4170
7.4078
7.3897
7.3725
7.3475
7.3287
7.3099
5.4529
O
O
O
3r
11
10
9
8
7
6
5
4
3
2
1
ppm
1.11
2.13
6.07
0.99
2.00


159.45
155.83
145.41
135.44
128.70
128.54
128.49
127.72
126.95
123.83
122.86
114.24
112.42
67.06
O
O
O
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.2180
8.2142
8.2017
8.1984
8.1969
7.6459
7.5135
7.4953
7.4331
7.4155
7.4037
7.3957
7.3874
7.3739
7.3695
7.3557
7.3476
7.3440
7.3378
7.3302
7.3267
7.3122
7.3101
5.4122
3.8601
O
O
NMe
3s
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.02
2.07
6.15
2.00
3.06


164.79
137.23
136.89
135.43
128.55
128.06
127.96
127.00
126.67
122.83
121.97
121.72
109.77
65.44
33.45
O
O
NMe
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.2832
8.2642
7.9982
7.9796
7.6241
7.6213
7.6061
7.6036
7.5868
7.5820
7.5775
7.5609
7.5586
7.5469
7.5305
7.4493
7.4442
7.4280
7.4090
7.4031
7.3938
7.3861
7.3679
5.5444
O
N
O
S
3t
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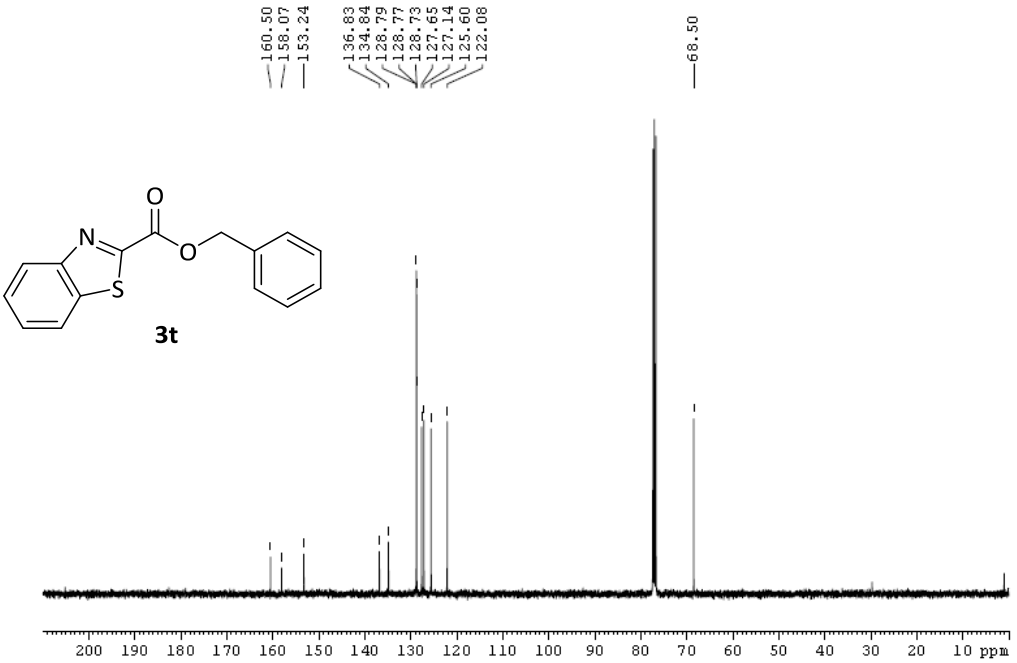
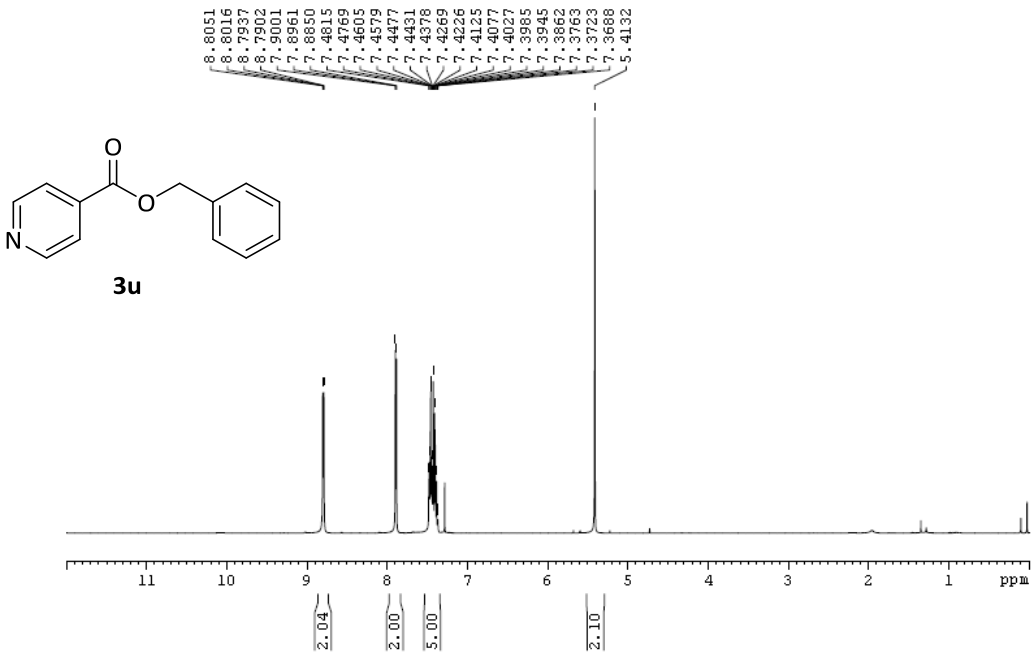
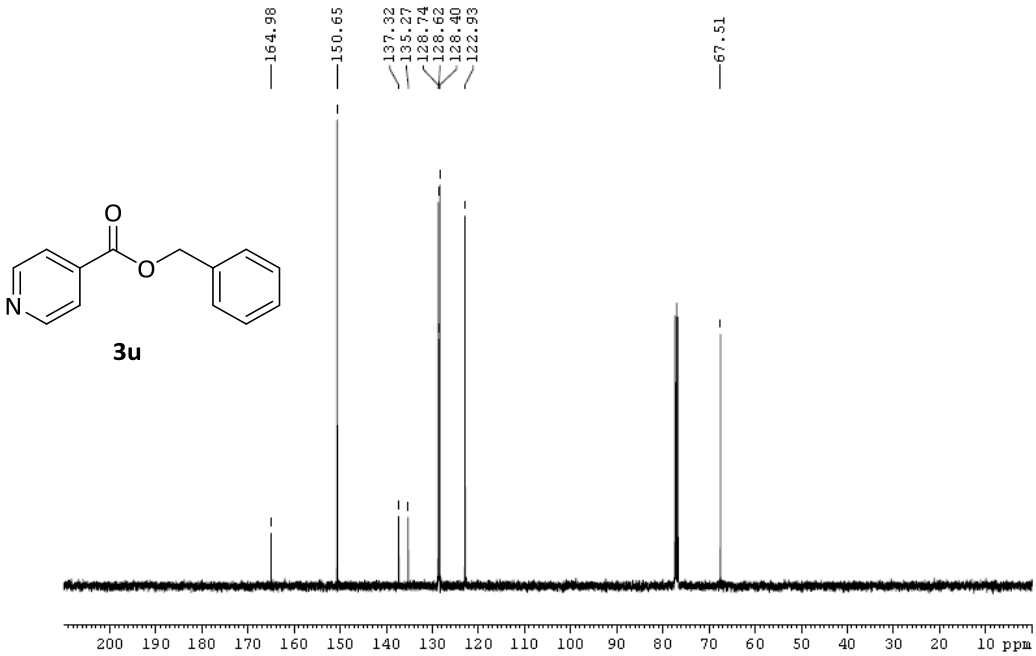
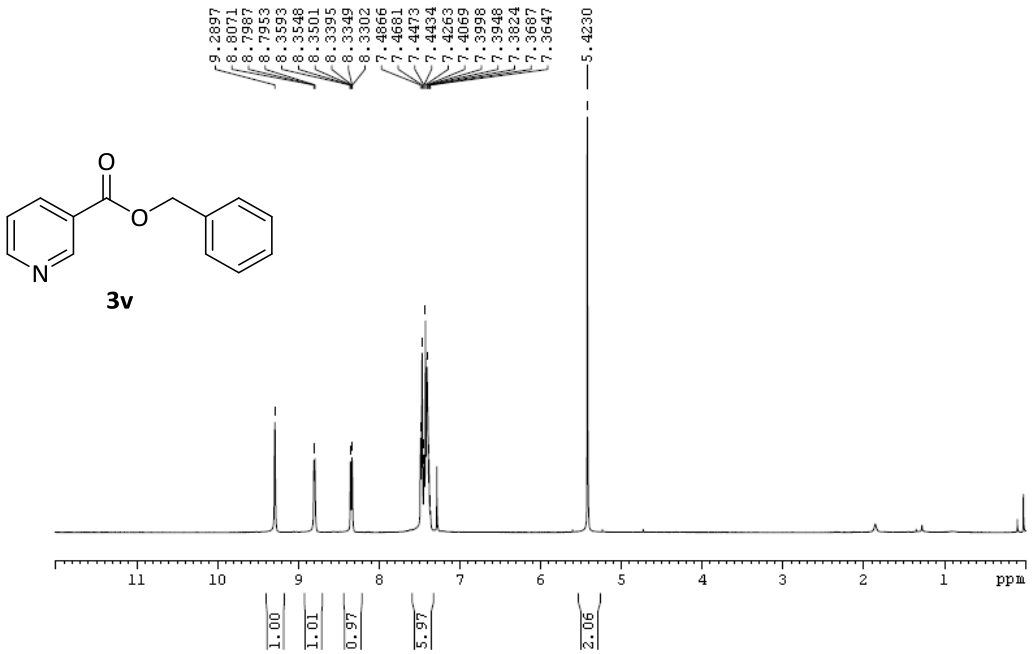
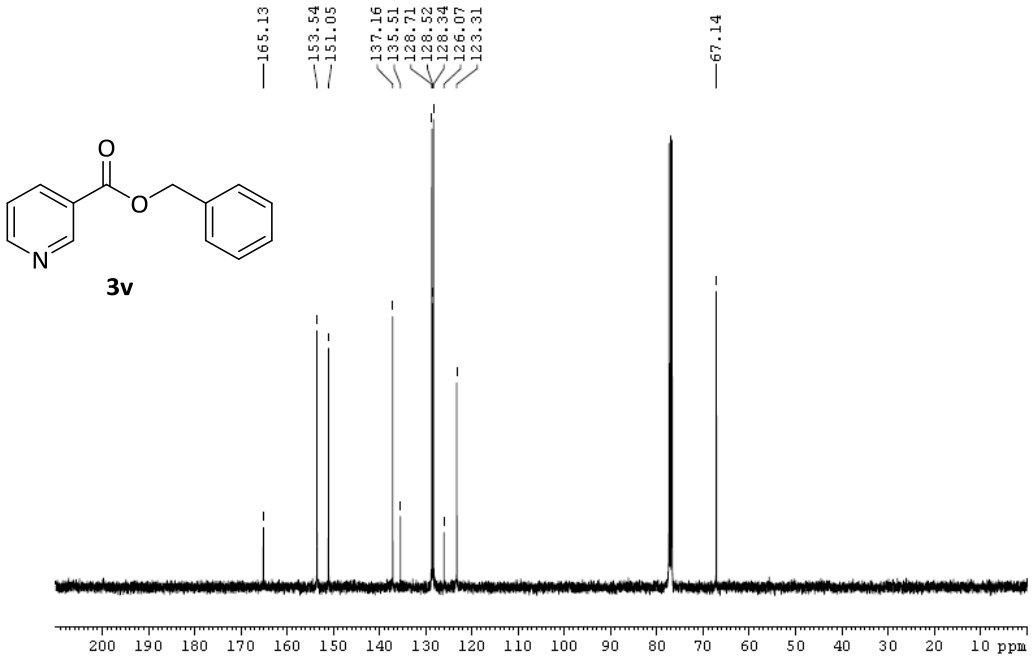
ppm
1.00
1.04
4.07
3.02
2.08

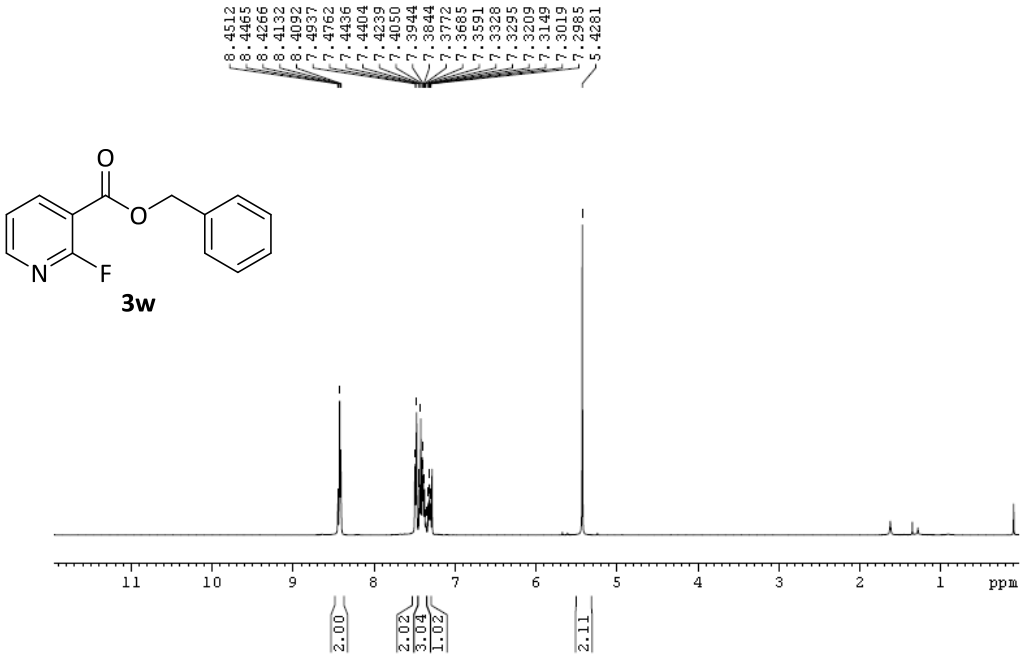

160.50
158.07
153.24
136.83
134.84
128.79
128.77
128.73
127.65
127.14
125.60
122.08
68.50
O
N
O
S
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

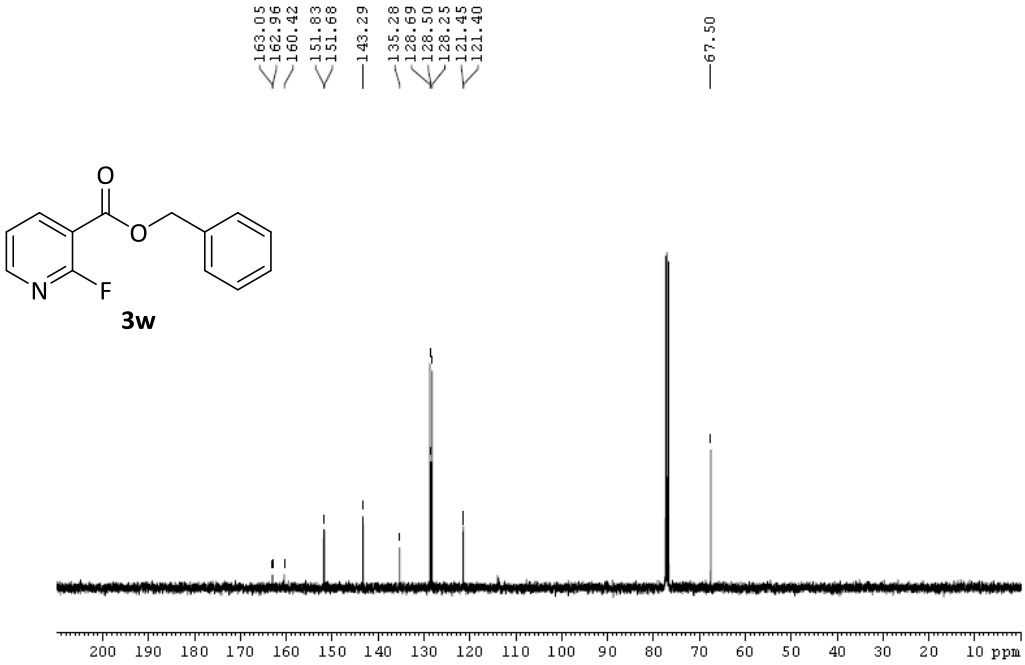

8.8051
8.8016
8.7937
8.7902
7.9001
7.8961
7.8850
7.4815
7.4769
7.4605
7.4579
7.4477
7.4431
7.4378
7.4269
7.4226
7.4125
7.4077
7.4027
7.3985
7.3945
7.3862
7.3763
7.3723
7.3688
5.4132
O
O
N
3u
11
10
9
8
7
6
5
4
3
2
1
ppm
2.04
2.00
5.00
2.10

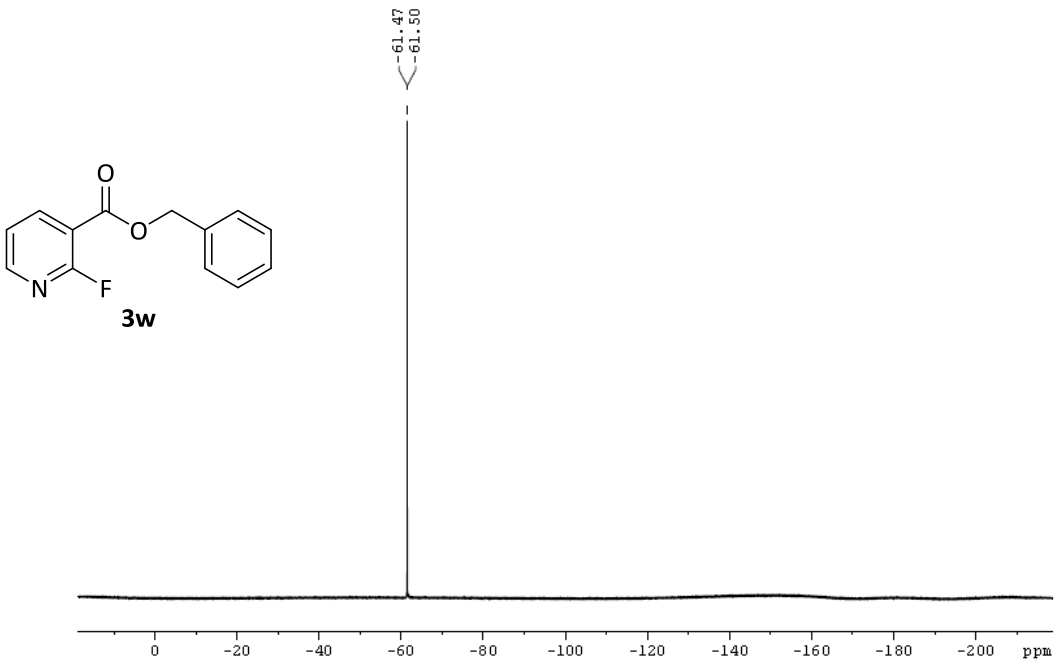

164.98
150.65
137.32
135.27
128.74
128.62
128.40
122.93
67.51
O
O
N
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


9.2897
8.8071
8.7987
8.7953
8.3593
8.3548
8.3501
8.3395
8.3349
8.3302
7.4866
7.4681
7.4473
7.4434
7.4263
7.4069
7.3998
7.3948
7.3824
7.3687
7.3647
5.4230
O
O
N
3v
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
0.97
5.97
2.06

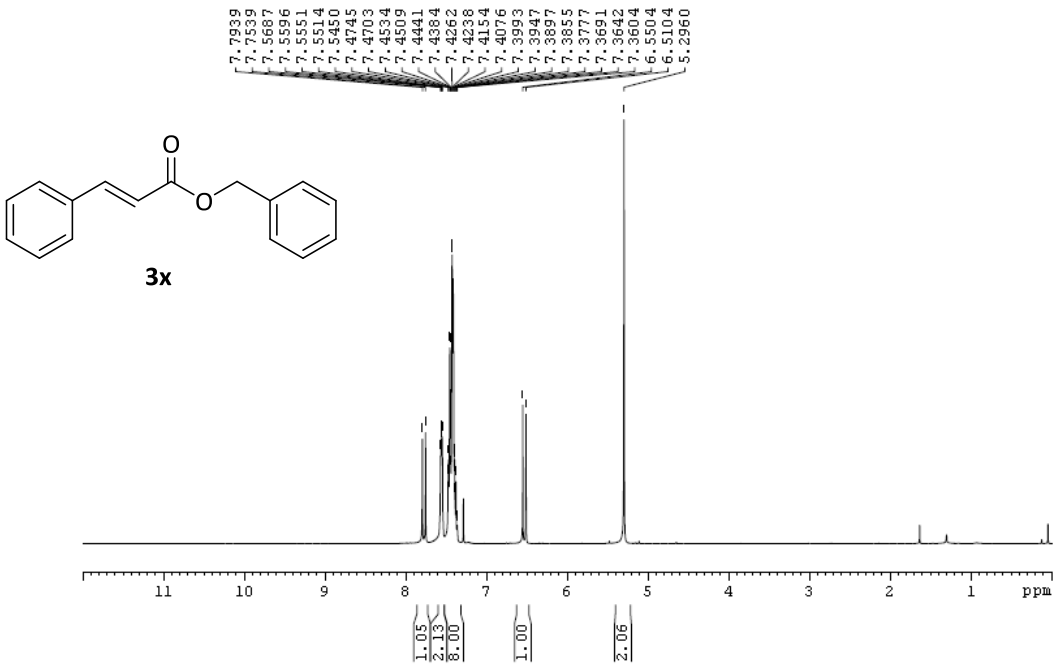

165.13
153.54
151.05
137.16
135.51
128.71
128.52
128.34
126.07
123.31
67.14
O
O
N
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.4512
8.4465
8.4266
8.4132
8.4092
7.4937
7.4762
7.4436
7.4404
7.4239
7.4050
7.3944
7.3844
7.3772
7.3685
7.3591
7.3328
7.3295
7.3209
7.3149
7.3019
7.2985
5.4281
O
O
N
F
3w
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.02
3.04
1.02
2.11

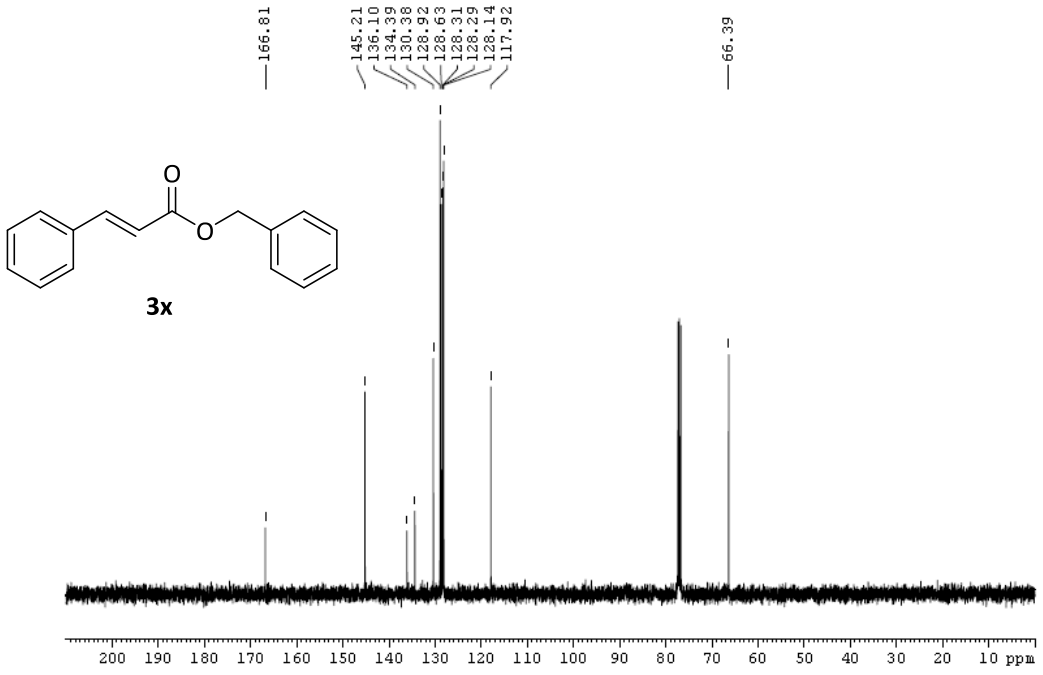

163.05
162.96
160.42
151.83
151.68
143.29
135.28
128.69
128.50
128.25
121.45
121.40
67.50
O
O
N
F
3w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


-61.47
-61.50
O
O
N
F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

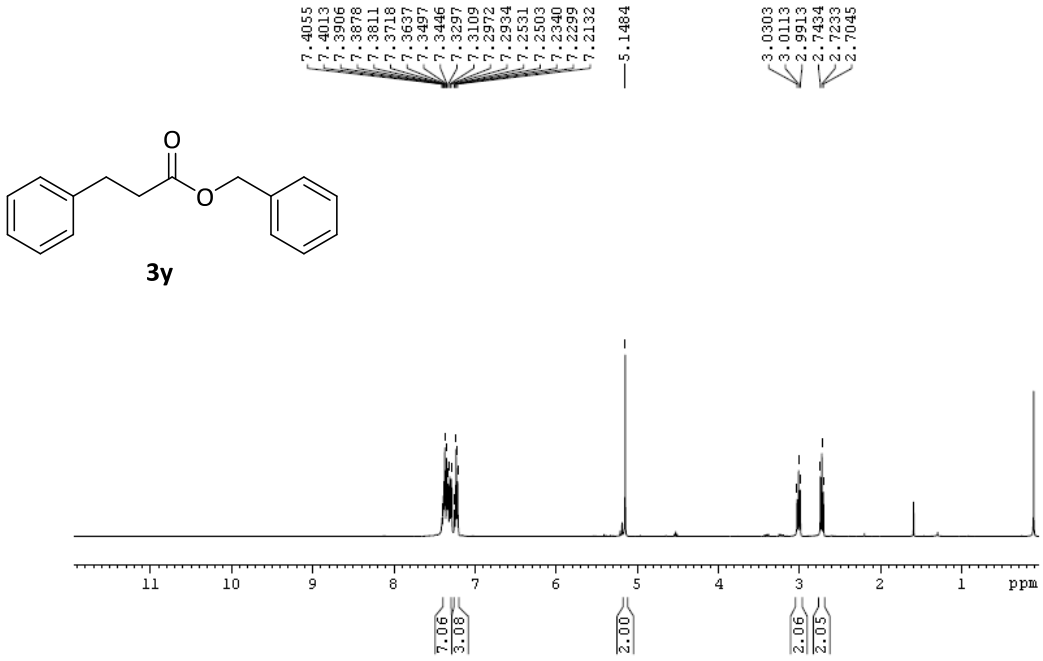
3w


7.7939
7.7539
7.5687
7.5596
7.5551
7.5514
7.5450
7.4745
7.4703
7.4534
7.4509
7.4441
7.4384
7.4262
7.4238
7.4154
7.4076
7.3993
7.3947
7.3897
7.3855
7.3777
7.3691
7.3642
7.3604
6.5504
6.5104
5.2960
O
O
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
2.13
8.00
1.00
2.06

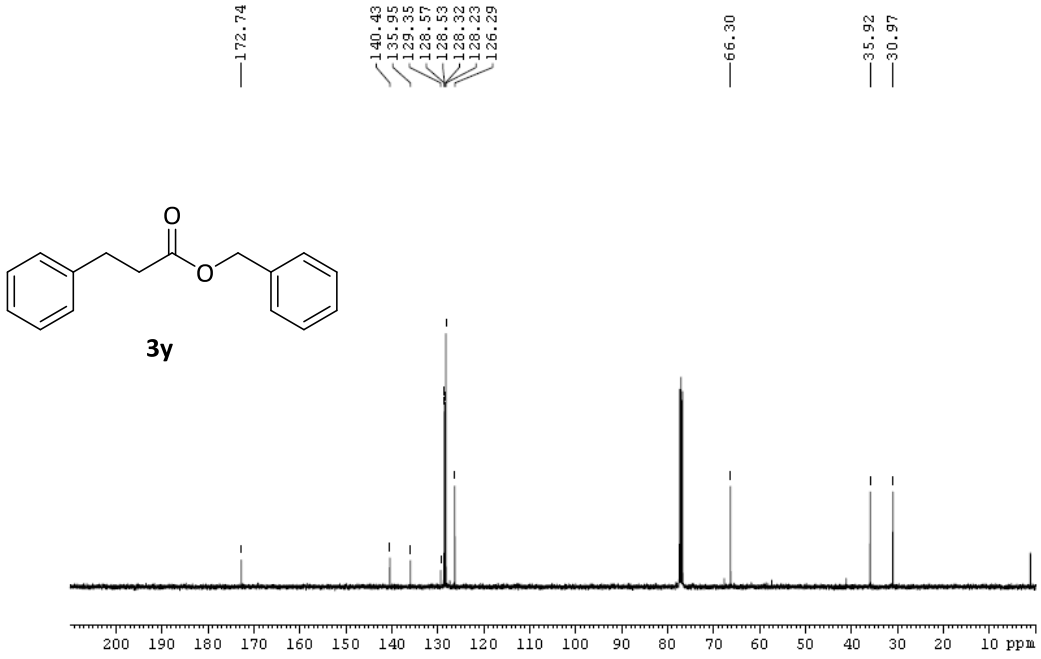
3x

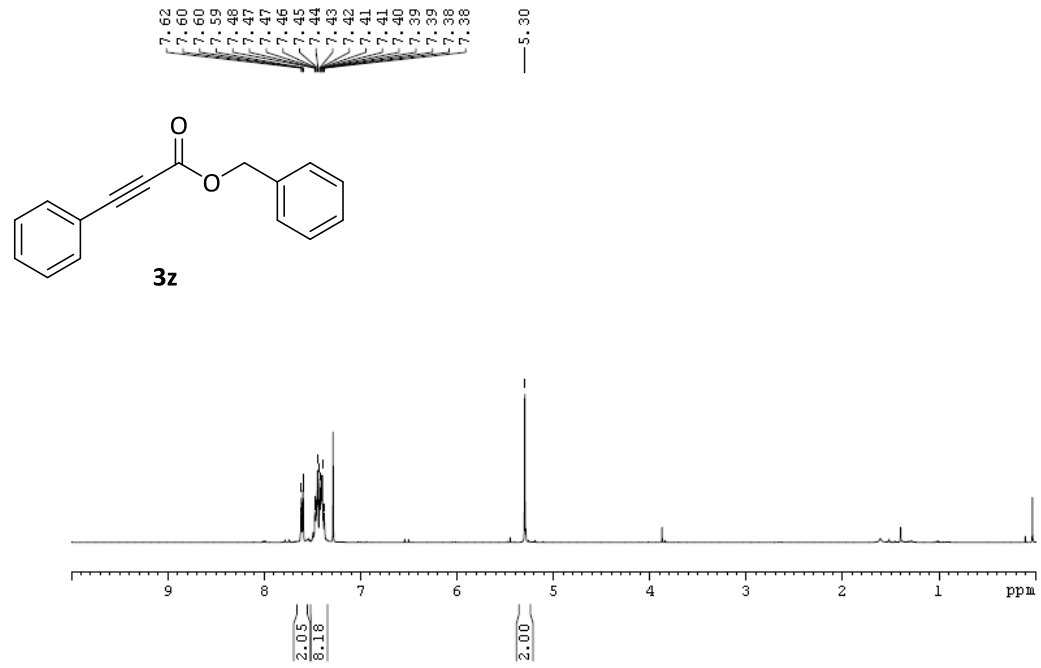

166.81
145.21
136.10
134.39
130.38
128.92
128.63
128.31
128.29
128.14
117.92
66.39
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

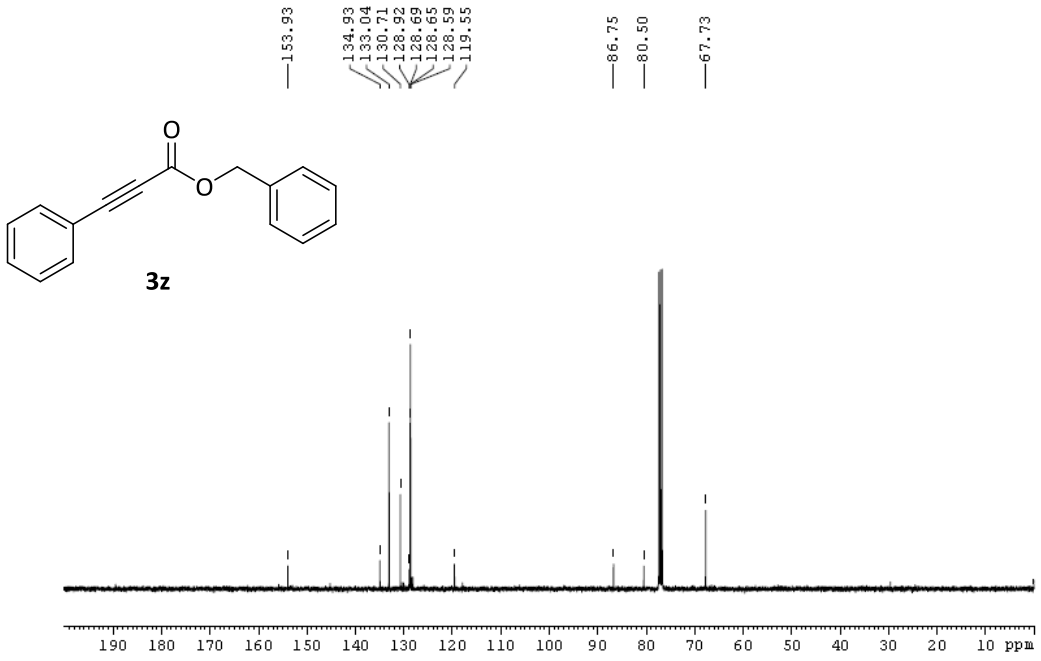
3x

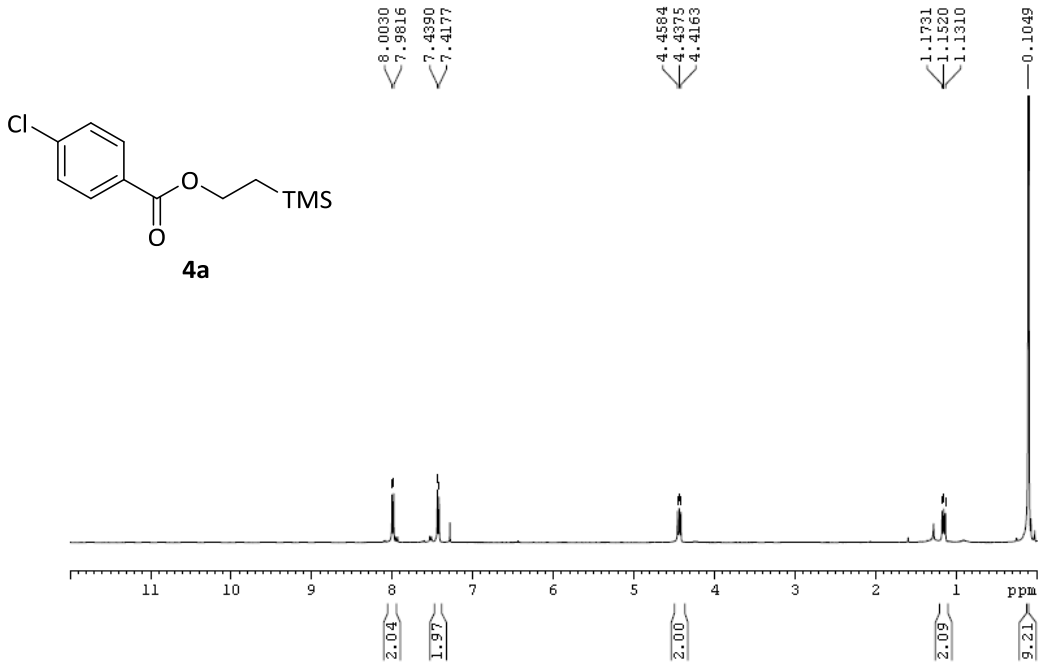

7.4055
7.4013
7.3906
7.3878
7.3811
7.3718
7.3637
7.3497
7.3446
7.3297
7.3109
7.2972
7.2934
7.2531
7.2503
7.2340
7.2299
7.2132
5.1484
3.0303
3.0113
2.9913
2.7434
2.7233
2.7045
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
7.06
3.08
2.00
2.06
2.05

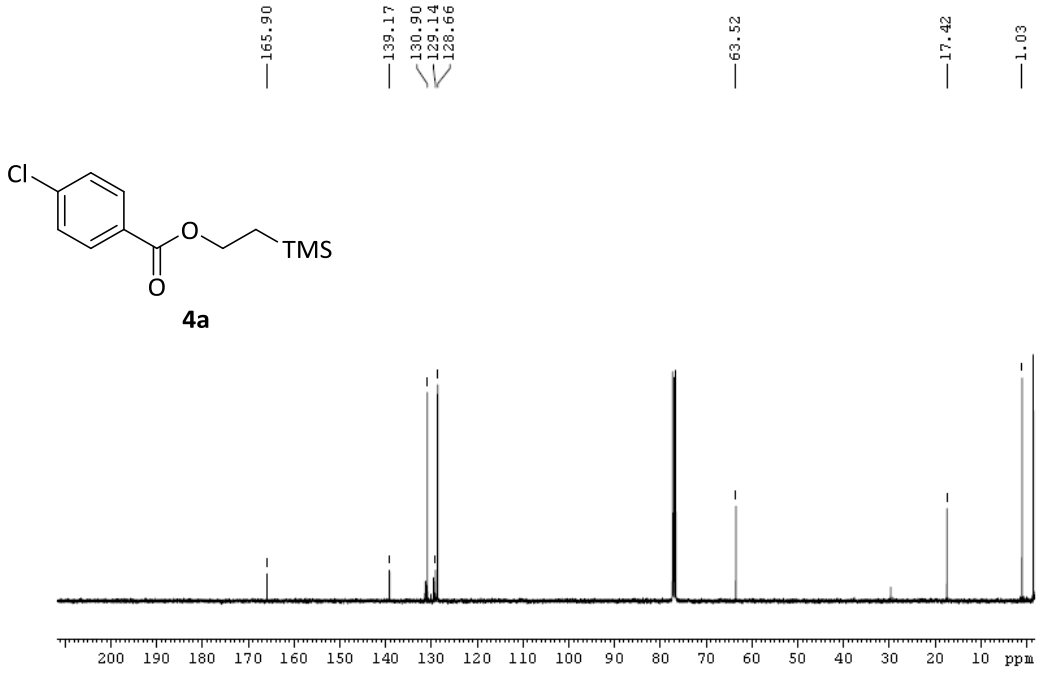
3y


172.74
140.43
135.95
129.35
128.57
128.53
128.32
128.23
126.29
66.30
35.92
30.97
O
O
3y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

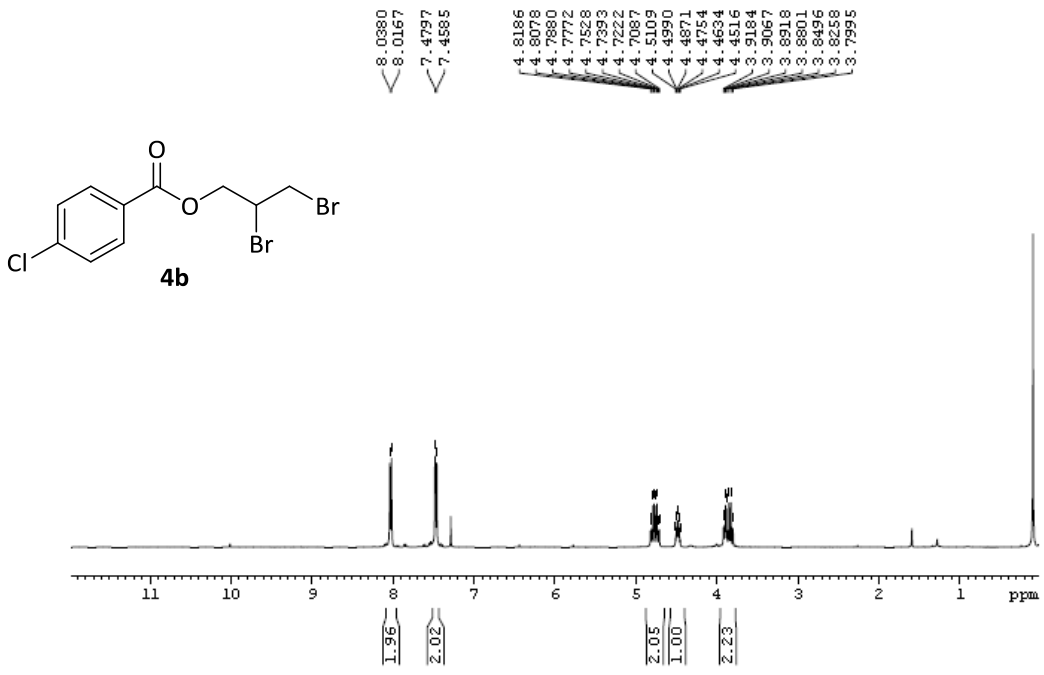

7.62
7.60
7.60
7.59
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
5.30
O
O
3z
9 8 7 6 5 4 3 2 1 ppm
2.05
8.18
2.00


153.93
134.93
133.04
130.71
128.92
128.69
128.65
128.59
119.55
86.75
80.50
67.73
O
O
3z
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

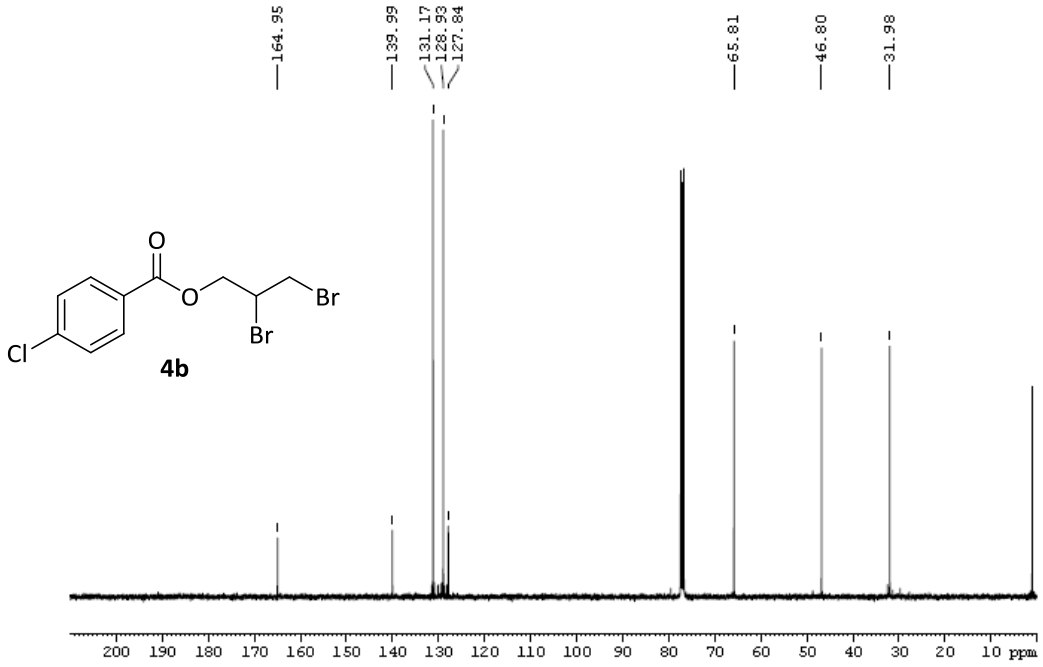

8.0030
7.9816
7.4390
7.4177
4.4584
4.4375
4.4163
1.1731
1.1520
1.1310
0.1049
Cl
O
O
TMS
4a
11 10 9 8 7 6 5 4 3 2 1 ppm
2.04
1.97
2.00
2.09
9.21


165.90
139.17
130.90
129.14
128.66
63.52
17.42
1.03
Cl
O
O
TMS
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

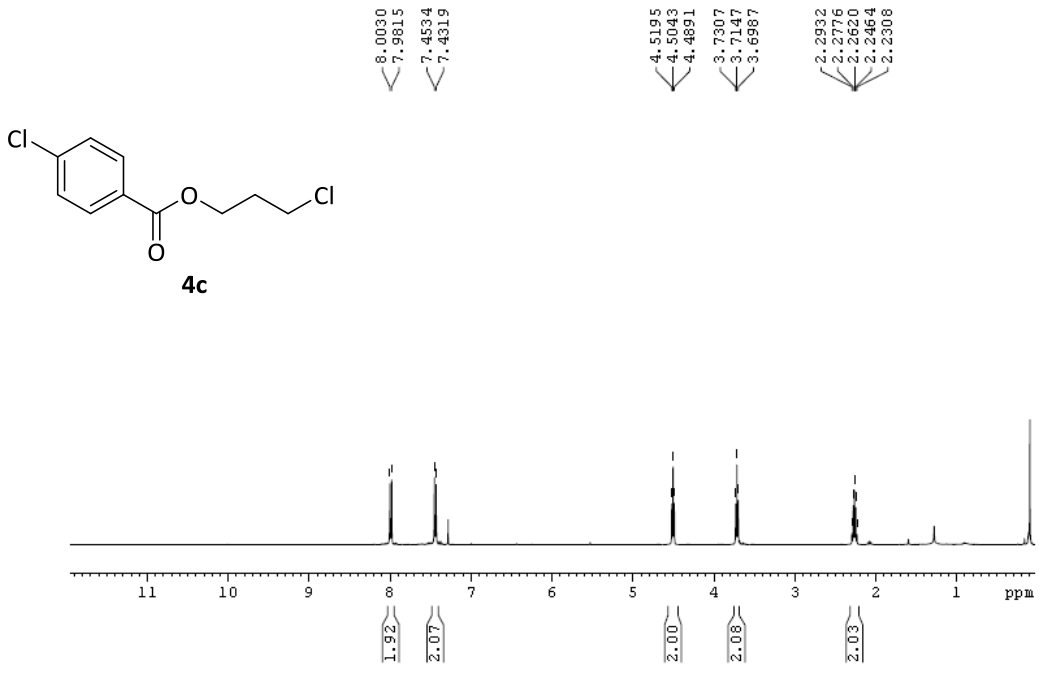
4a


8.0380
8.0167
7.4797
7.4585
4.8186
4.8078
4.7880
4.7772
4.7528
4.7393
4.7222
4.7087
4.5109
4.4990
4.4871
4.4754
4.4634
4.4516
3.9184
3.9067
3.8918
3.8801
3.8496
3.8258
3.7995
O
O
Br
Br
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
2.02
2.05
1.00
2.23

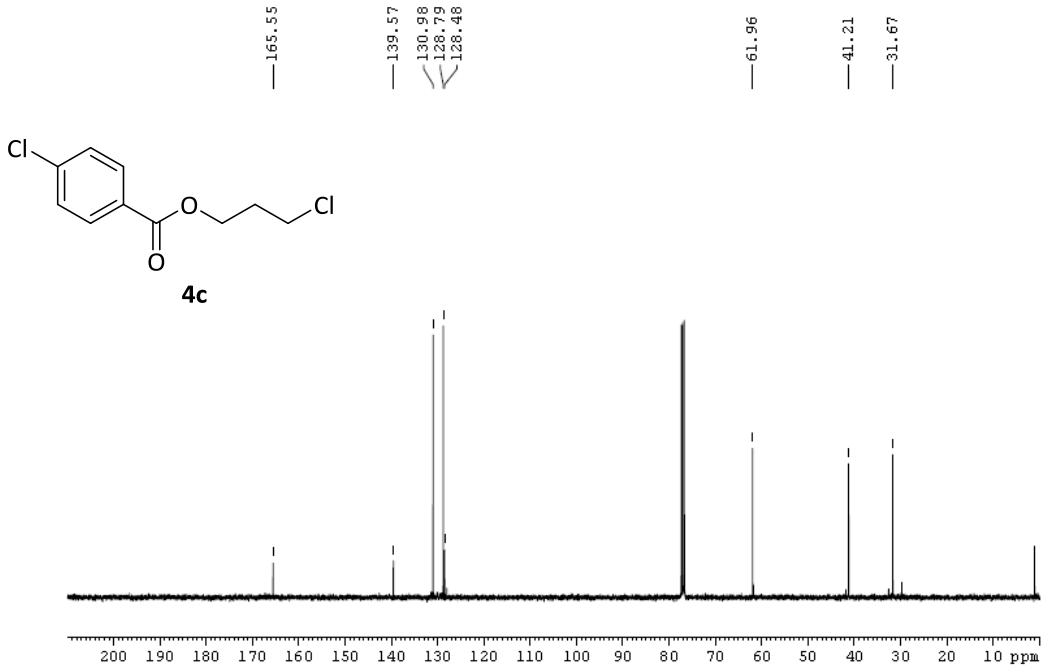
4b


164.95
139.99
131.17
128.93
127.84
65.81
46.80
31.98
O
O
Br
Br
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

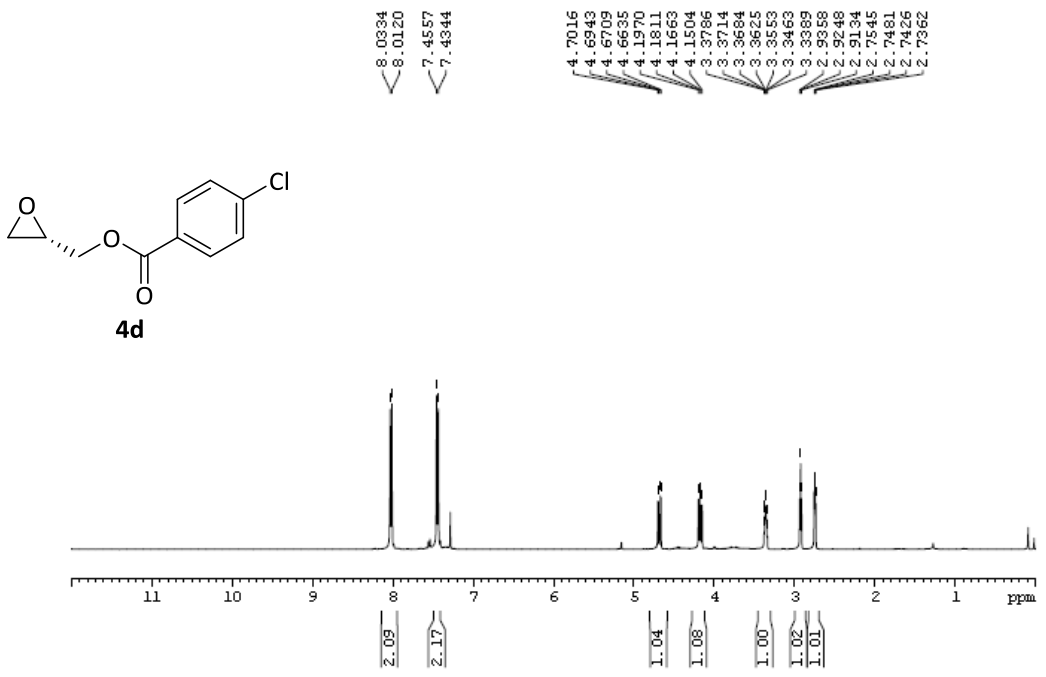
4b


8.0030
7.9815
7.4534
7.4319
4.5195
4.5043
4.4891
3.7307
3.7147
3.6987
2.2932
2.2776
2.2620
2.2464
2.2308
Cl
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.92
2.07
2.00
2.08
2.03

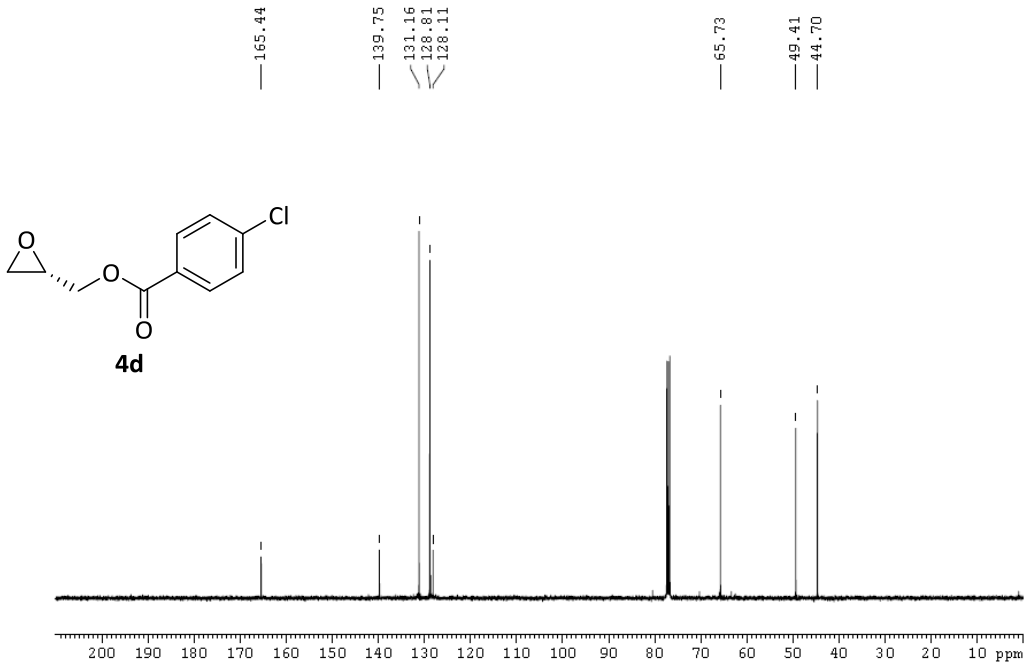
4c


165.55
139.57
130.98
128.79
128.48
61.96
41.21
31.67
Cl
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

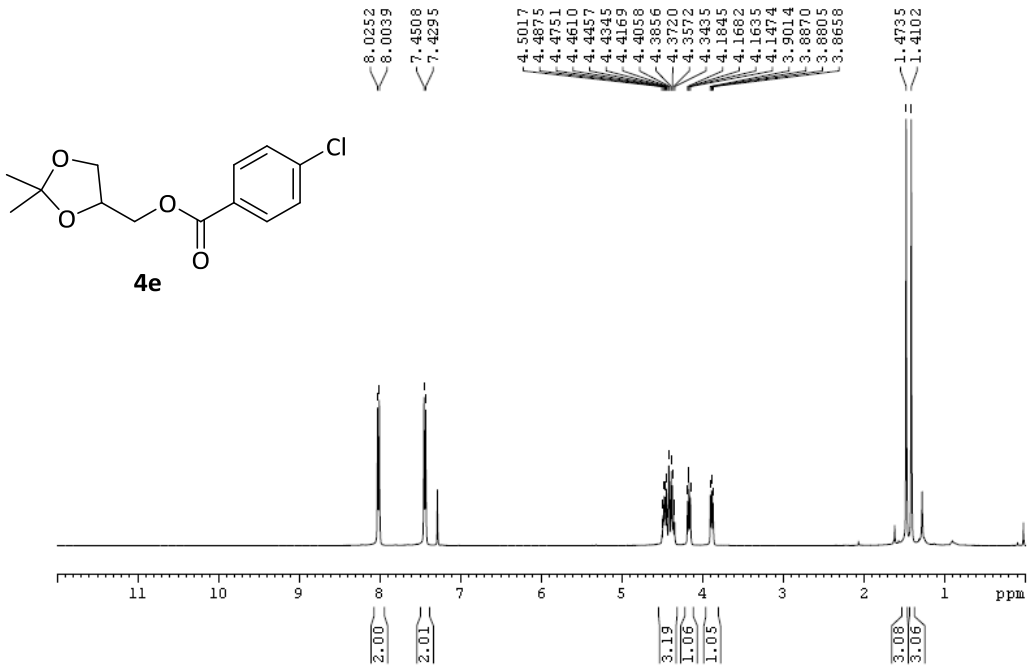
4c


8.0334
8.0120
7.4557
7.4344
4.7016
4.6943
4.6709
4.6635
4.1970
4.1811
4.1663
4.1504
3.3786
3.3714
3.3684
3.3625
3.3553
3.3463
3.3389
2.9358
2.9248
2.9134
2.7545
2.7481
2.7426
2.7362
O
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.09
2.17
1.04
1.08
1.00
1.02
1.01

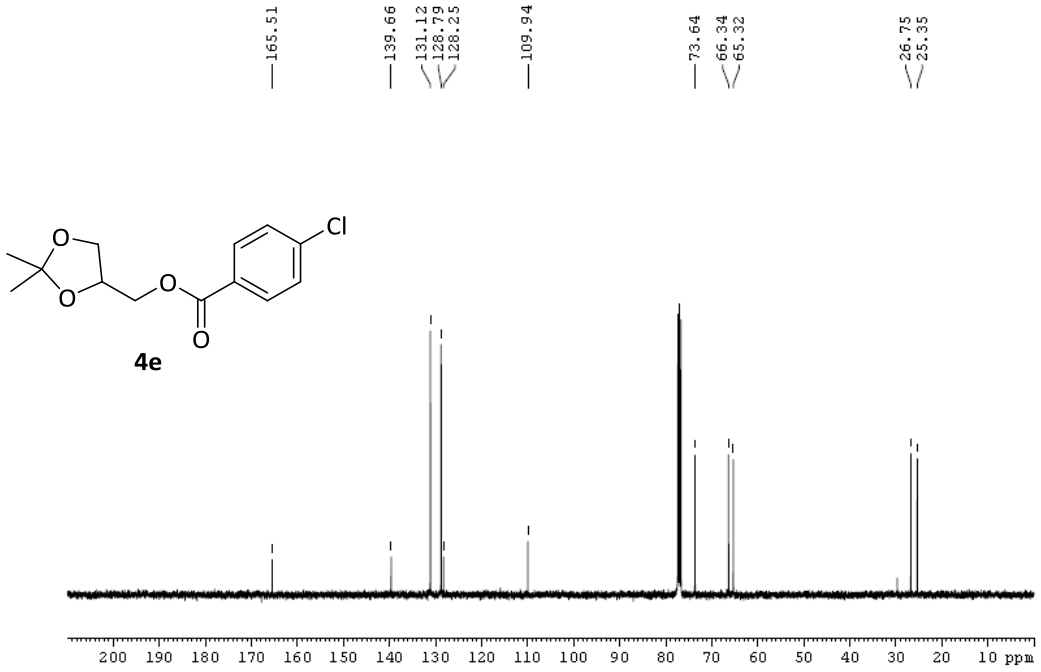
4d


165.44
139.75
131.16
128.81
128.11
65.73
49.41
44.70
Cl
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

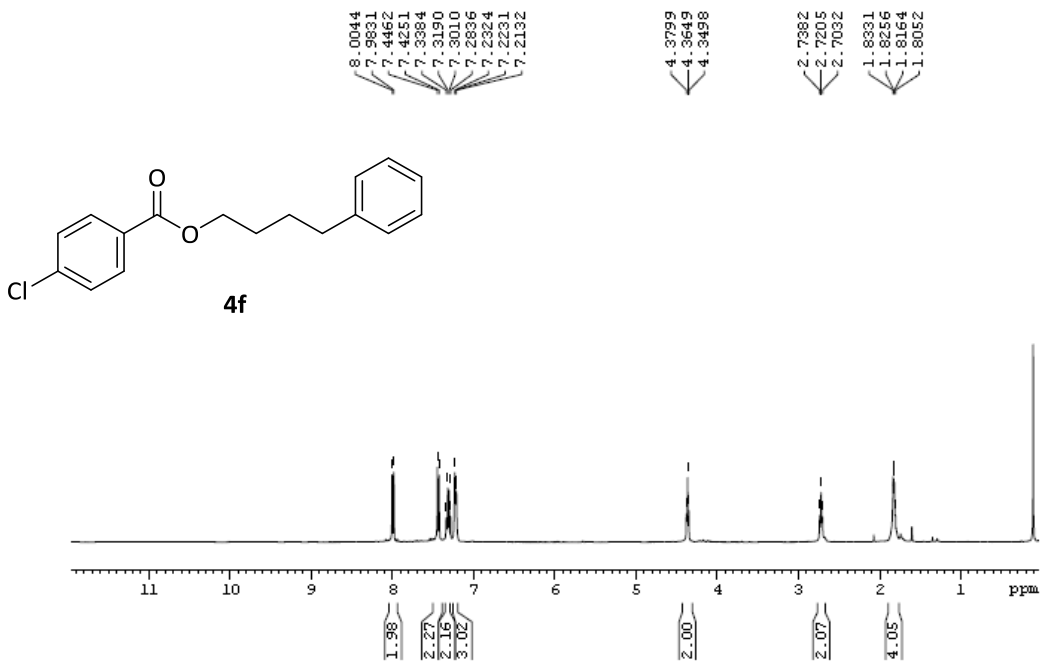
4d


8.0252
8.0039
7.4508
7.4295
4.5017
4.4875
4.4751
4.4610
4.4457
4.4345
4.4169
4.4058
4.3856
4.3720
4.3572
4.3435
4.1845
4.1682
4.1635
4.1474
3.9014
3.8870
3.8805
3.8658
1.4735
1.4102
Cl
O
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.01
3.19
1.06
1.05
3.08
3.06

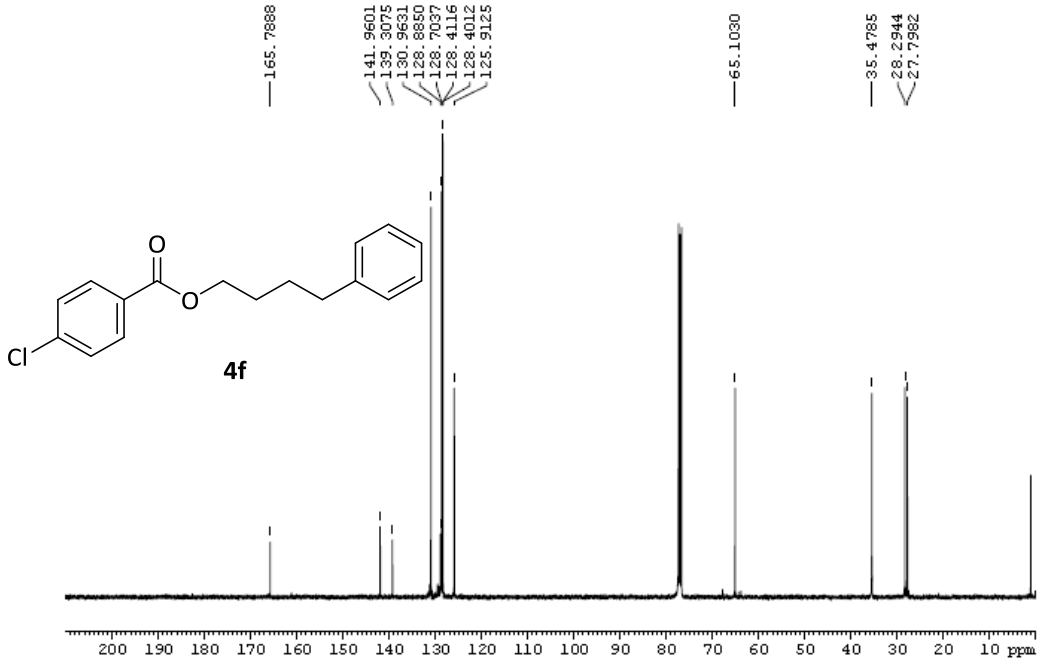
4e

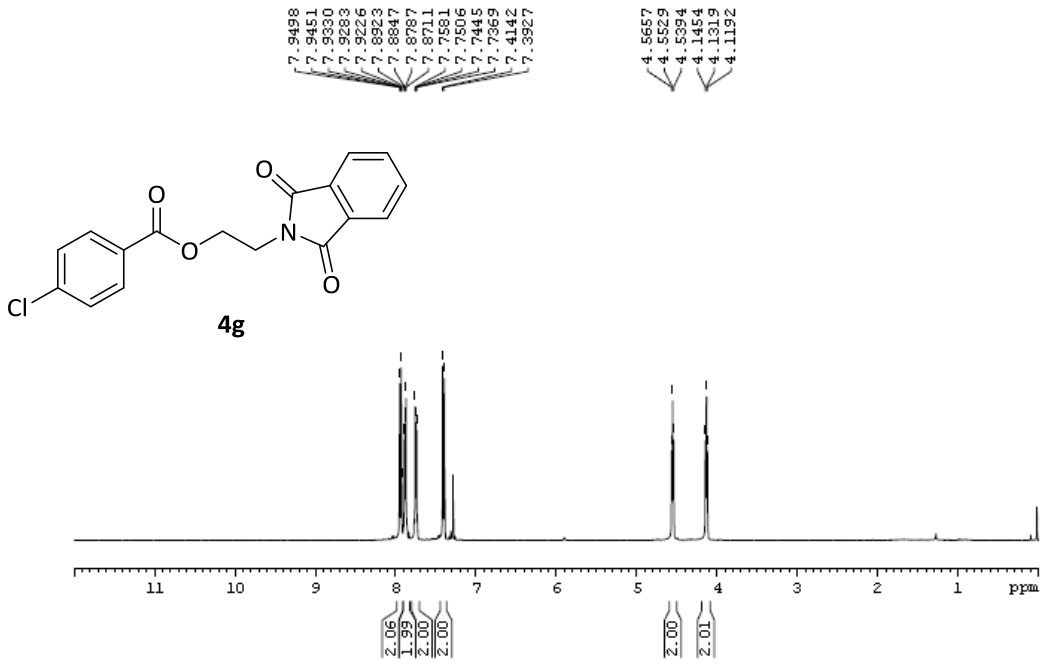

165.51
139.66
131.12
128.79
128.25
109.94
73.64
66.34
65.32
26.75
25.35
Cl
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

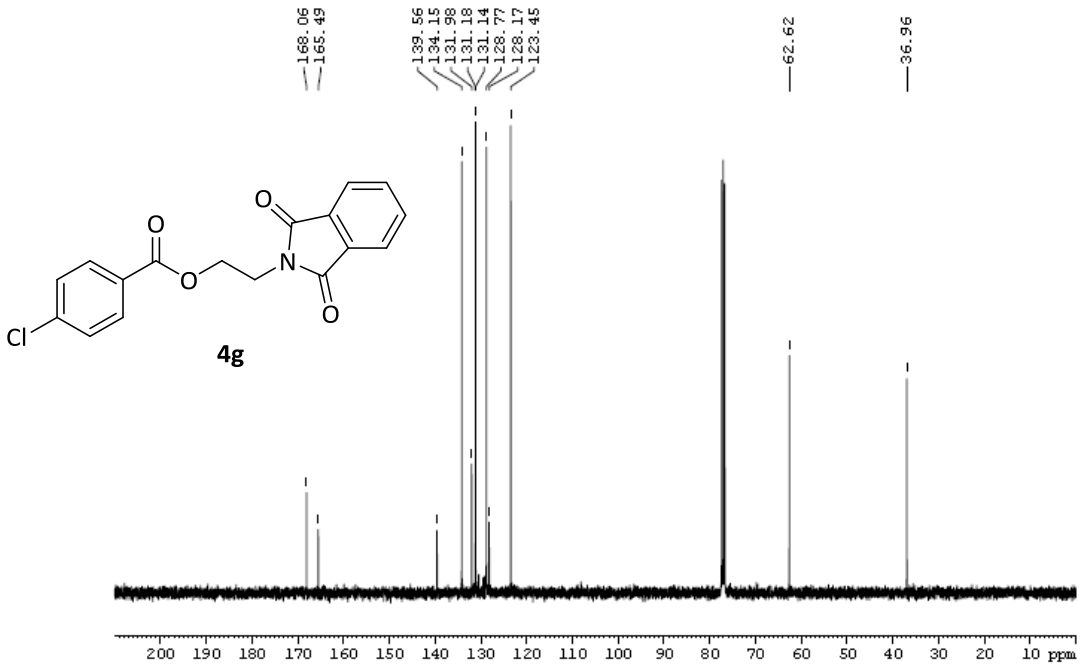
4e


8.0044
7.9831
7.4462
7.4251
7.3384
7.3190
7.3010
7.2836
7.2324
7.2231
7.2132
4.3799
4.3649
4.3498
2.7382
2.7205
2.7032
1.8331
1.8256
1.8164
1.8052
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.98
2.27
2.16
3.02
2.00
2.07
4.05

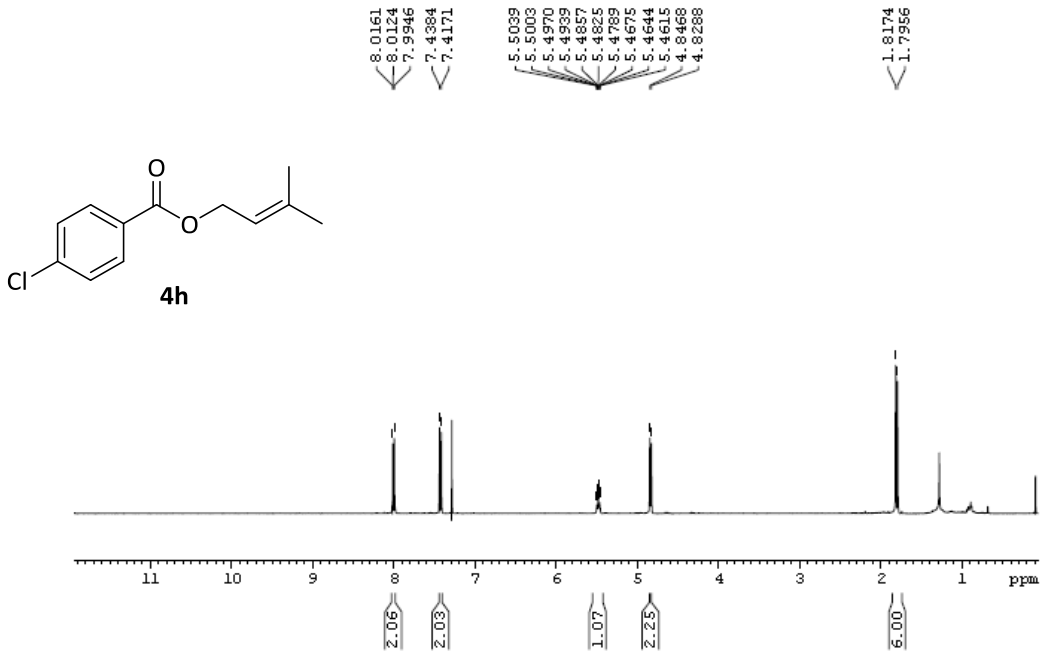
4f


165.7888
141.9601
139.3075
130.9631
128.8850
128.7037
128.4116
128.4012
125.9125
65.1030
35.4785
28.2944
27.7982
O
O
Cl
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

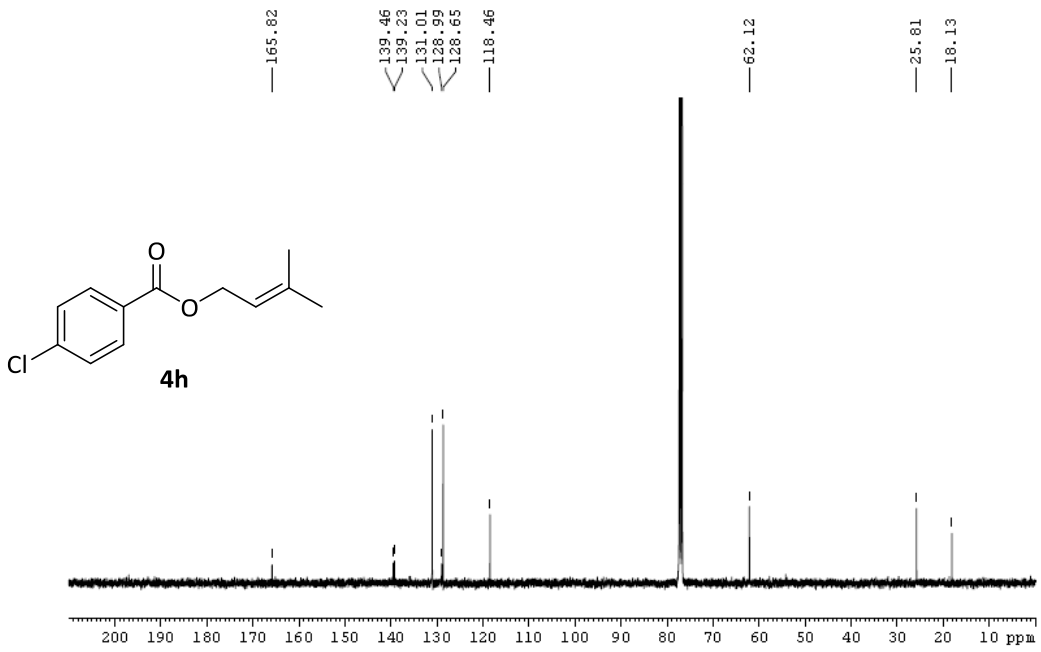

7.9498
7.9451
7.9330
7.9283
7.9226
7.8923
7.8847
7.8787
7.8711
7.7581
7.7506
7.7445
7.7369
7.4142
7.3927
4.5657
4.5529
4.5394
4.1454
4.1319
4.1192
O
O
N
O
O
Cl
4g
11 10 9 8 7 6 5 4 3 2 1 ppm
2.06
1.99
2.00
2.00
2.00
2.01

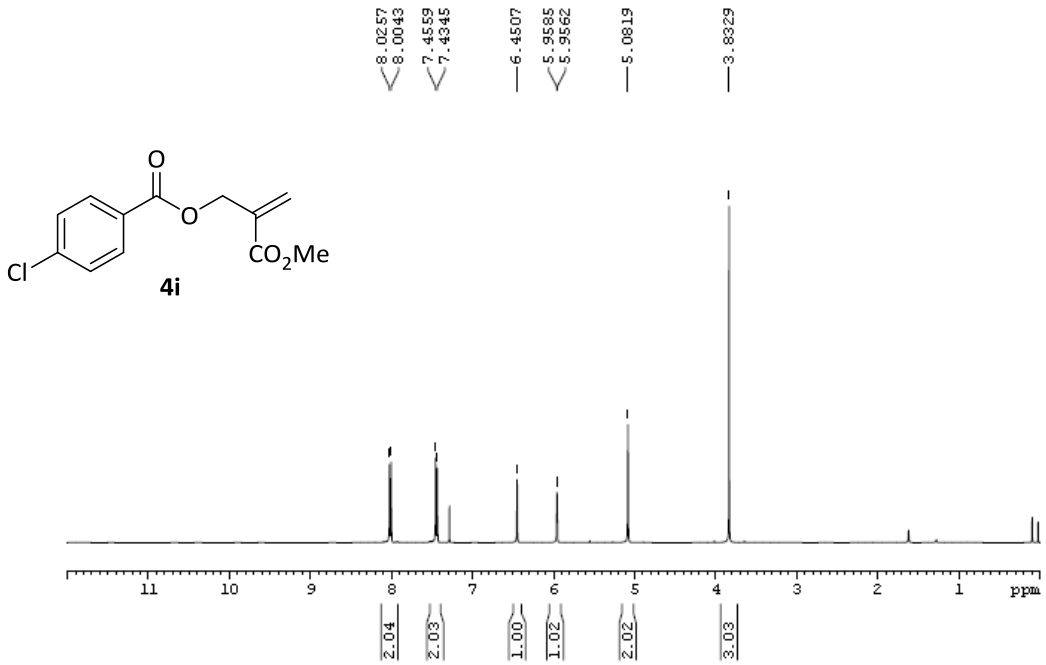

168.06
165.49
139.56
134.15
131.98
131.18
131.14
128.77
128.17
123.45
62.62
36.96
O
O
N
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

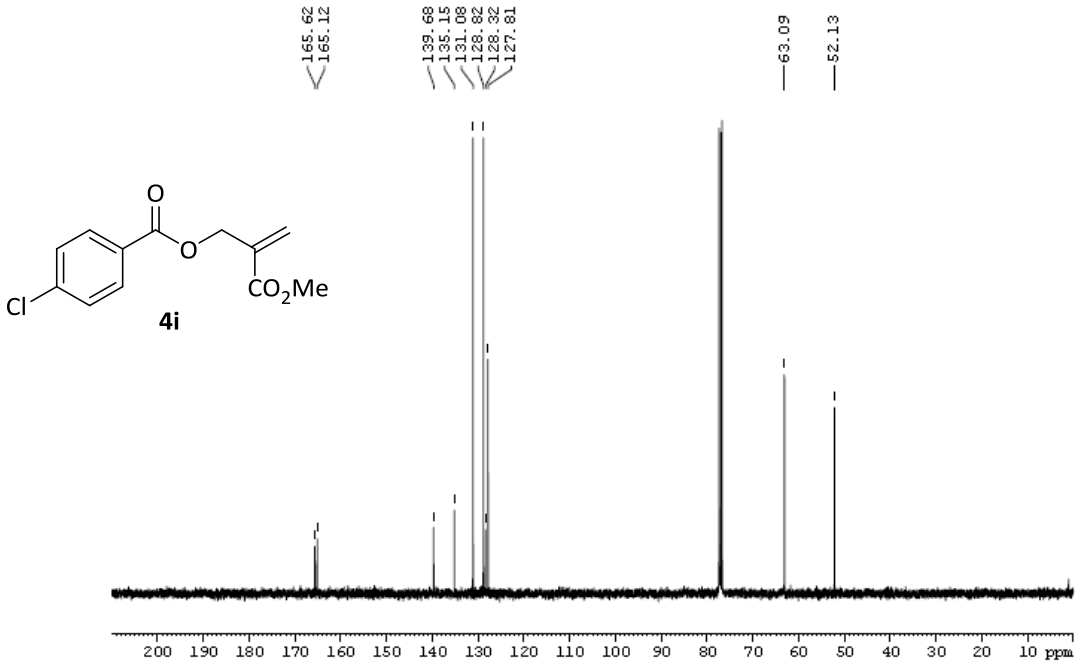
4g


8.0161
8.0124
7.9946
7.4384
7.4171
5.5039
5.5003
5.4970
5.4939
5.4857
5.4825
5.4789
5.4675
5.4644
5.4615
4.8468
4.8288
1.8174
1.7956
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.06
2.03
1.07
2.25
6.00

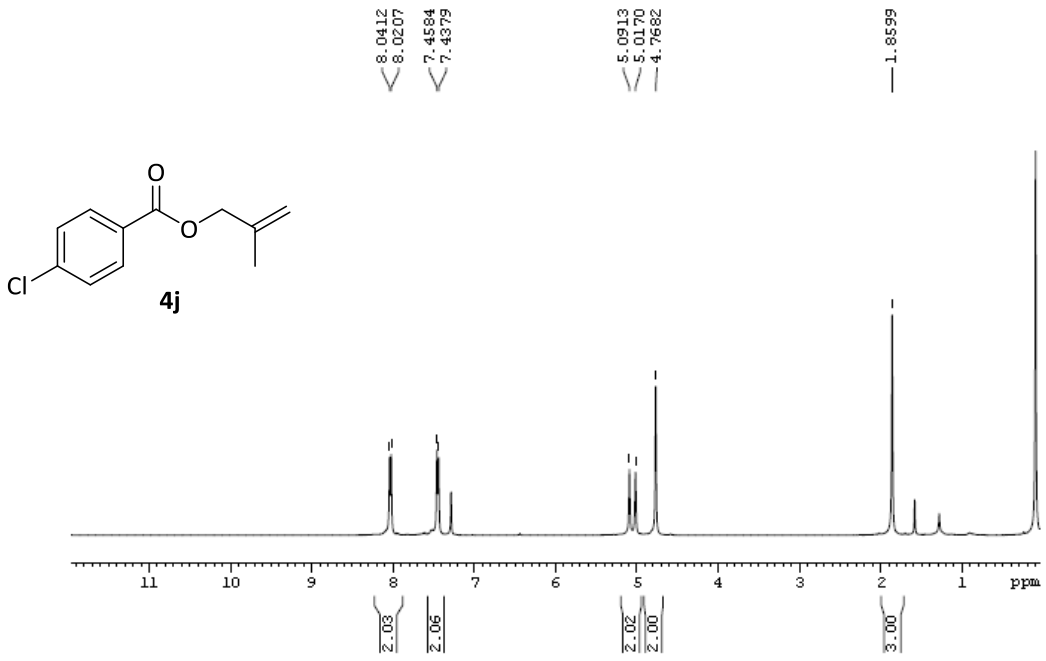
4h


165.82
139.46
139.23
131.01
128.99
128.65
118.46
62.12
25.81
18.13
O
O
Cl
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

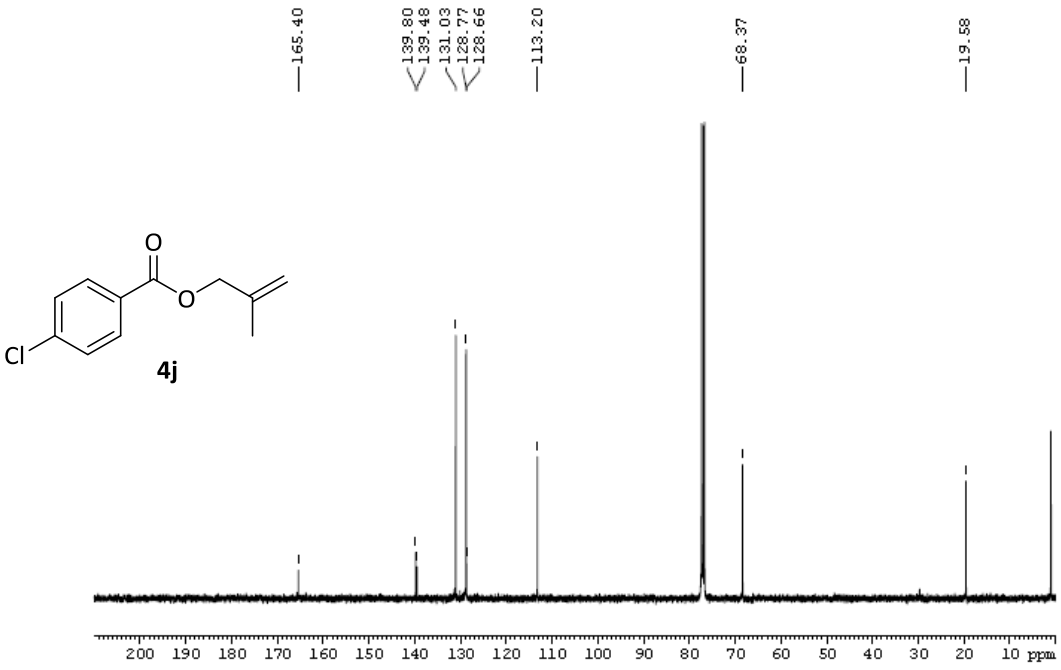

8.0257
8.0043
7.4559
7.4345
6.4507
5.9585
5.9562
5.0819
3.8329
O
O
CO2Me
Cl
4i
11 10 9 8 7 6 5 4 3 2 1 ppm
2.04
2.03
1.00
1.02
2.02
3.03


165.62
165.12
139.68
135.15
131.08
128.82
128.32
127.81
63.09
52.13
O
O
Cl
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

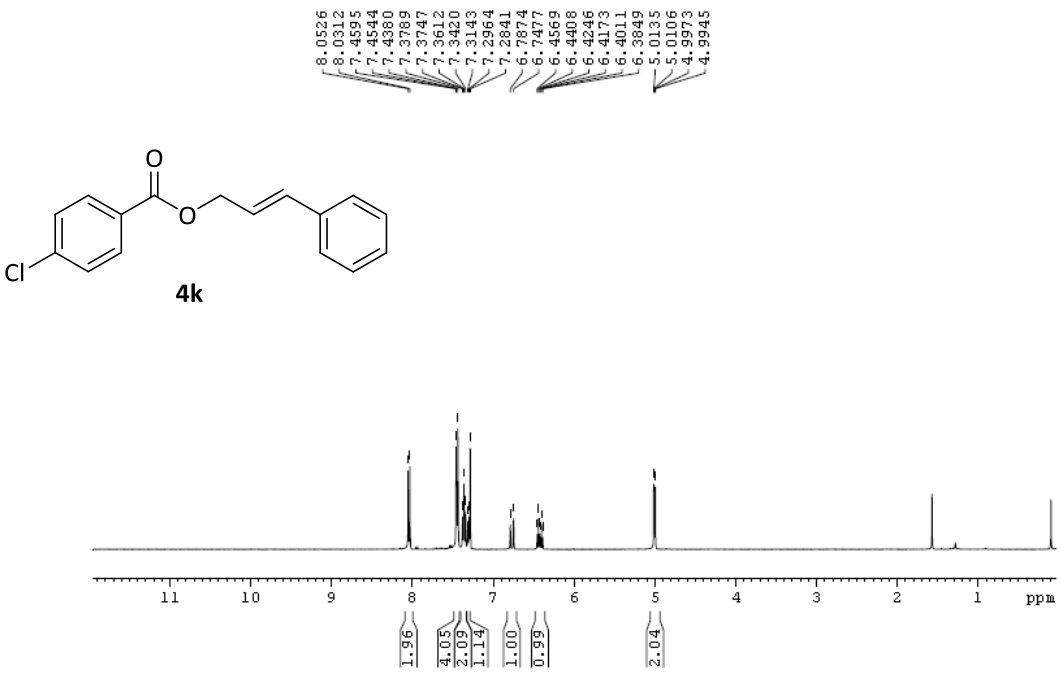
4i


8.0412
8.0207
7.4584
7.4379
5.0913
5.0170
4.7682
1.8599
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.03
2.06
2.02
2.00
3.00

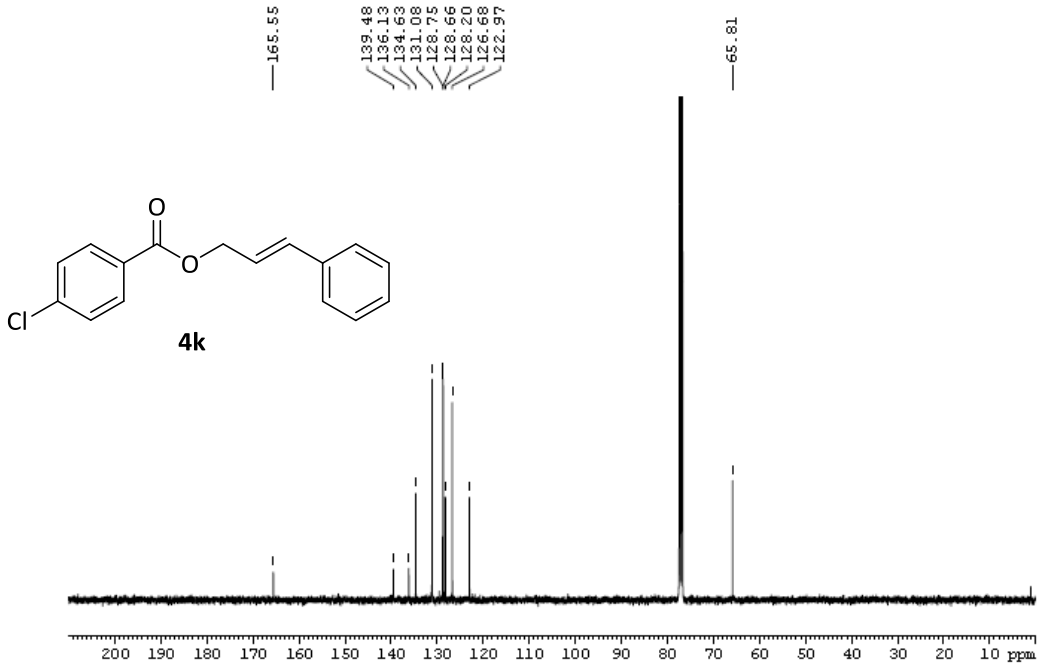
4j


165.40
139.80
139.48
131.03
128.77
128.66
113.20
68.37
19.58
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

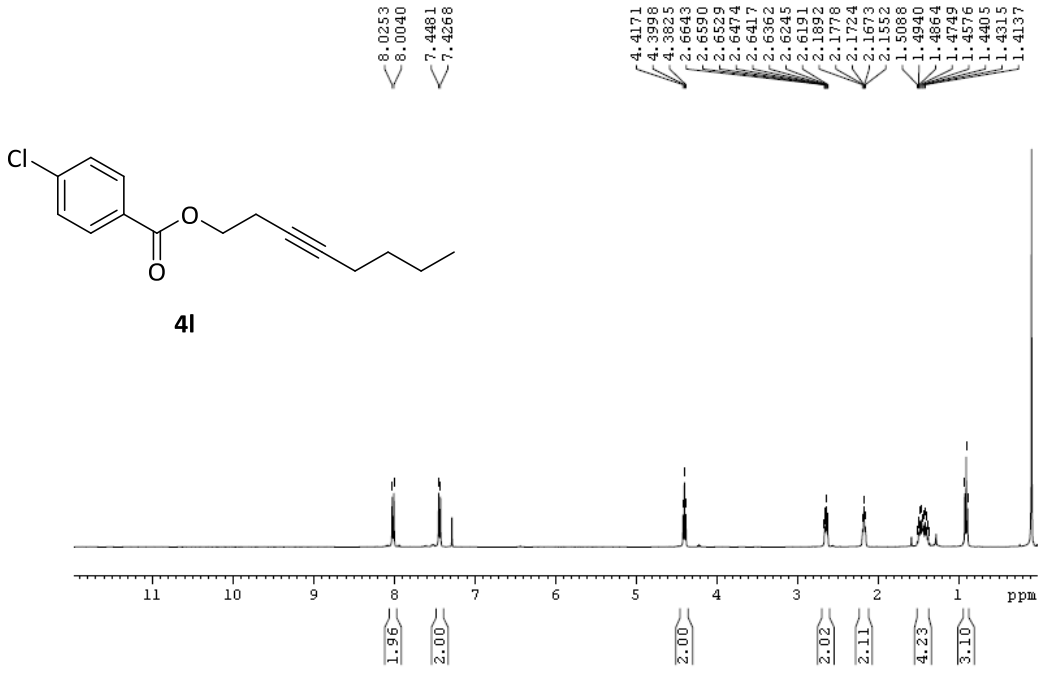
4j


8.0526
8.0312
7.4595
7.4544
7.4380
7.3789
7.3747
7.3612
7.3420
7.3143
7.2964
7.2841
6.7874
6.7477
6.4569
6.4408
6.4246
6.4173
6.4011
6.3849
5.0135
5.0106
4.9973
4.9945
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
4.05
2.09
1.14
1.00
0.99
2.04

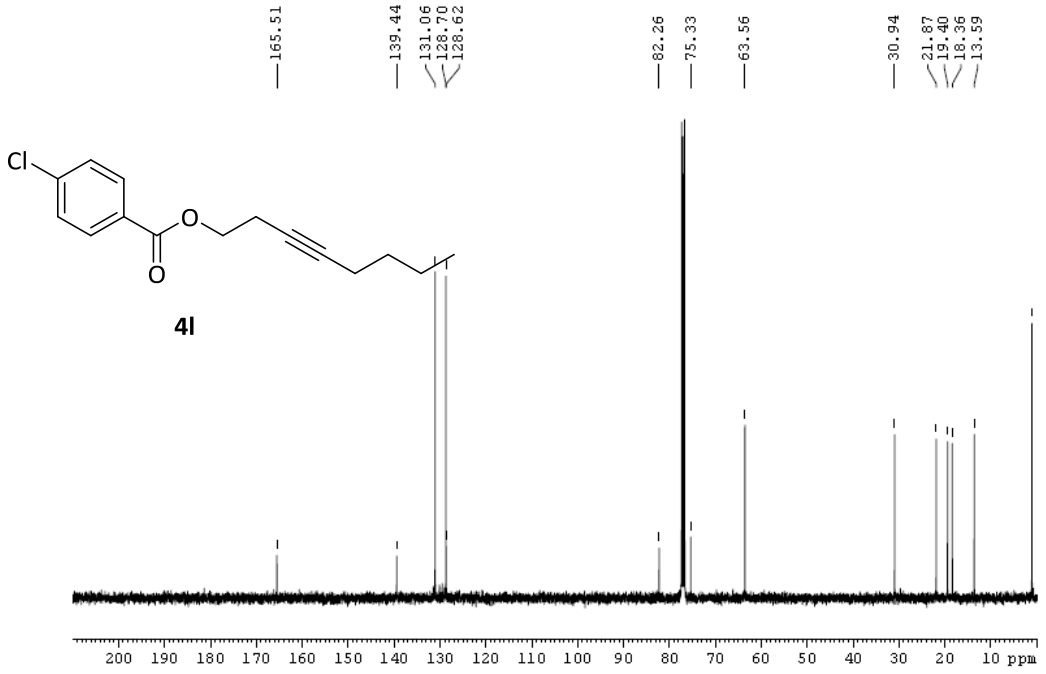
4k


165.55
139.48
136.13
134.63
131.08
128.75
128.66
128.20
126.68
122.97
65.81
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

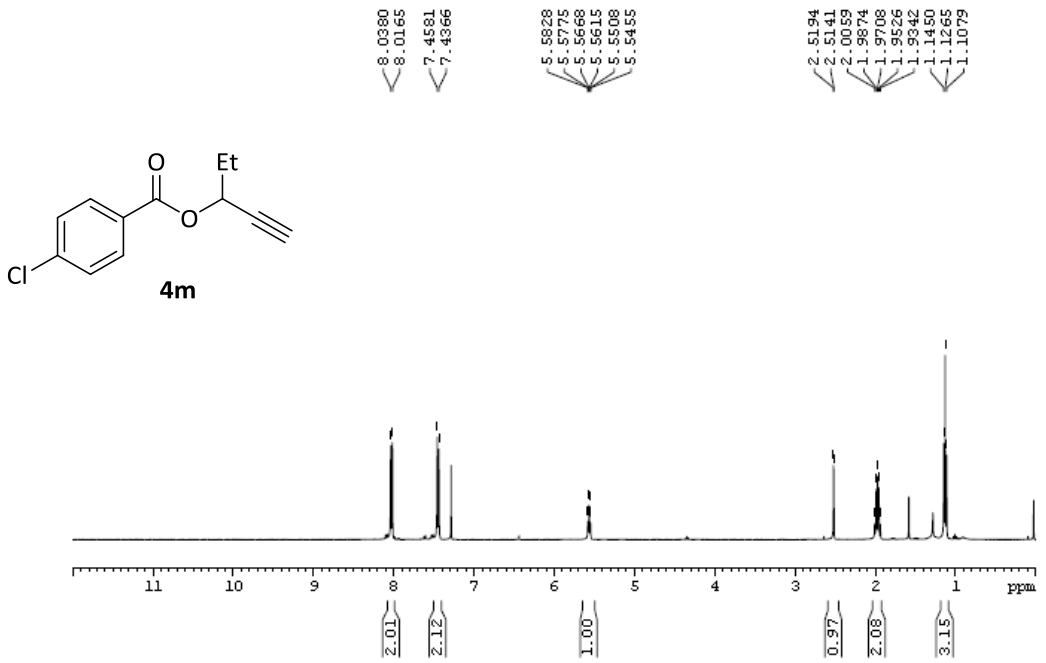
4k


8.0253
8.0040
7.4481
7.4268
4.4171
4.3998
4.3825
2.6643
2.6590
2.6529
2.6474
2.6417
2.6362
2.6245
2.6191
2.1892
2.1778
2.1724
2.1673
2.1552
1.5088
1.4940
1.4864
1.4749
1.4576
1.4405
1.4315
1.4137
Cl
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
2.00
2.00
2.02
2.11
4.23
3.10

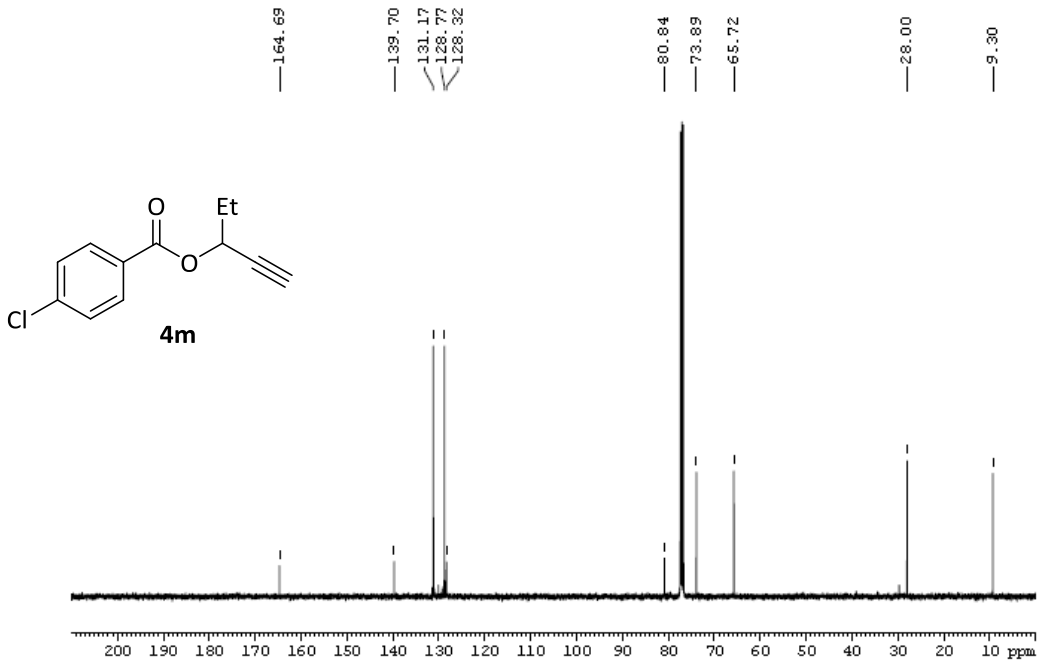
4l


165.51
139.44
131.06
128.70
128.62
82.26
75.33
63.56
30.94
21.87
19.40
18.36
13.59
Cl
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

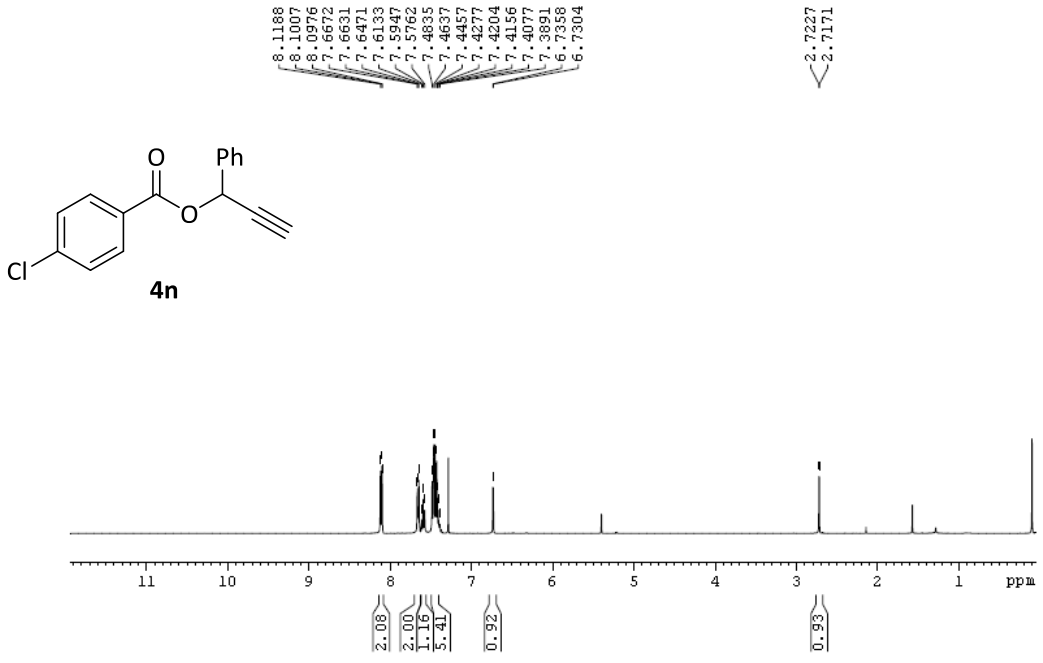
4l


8.0380
8.0165
7.4581
7.4366
5.5828
5.5775
5.5668
5.5615
5.5508
5.5455
2.5194
2.5141
2.0059
1.9874
1.9708
1.9526
1.9342
1.1450
1.1265
1.1079
O
Et
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.01
2.12
1.00
0.97
2.08
3.15

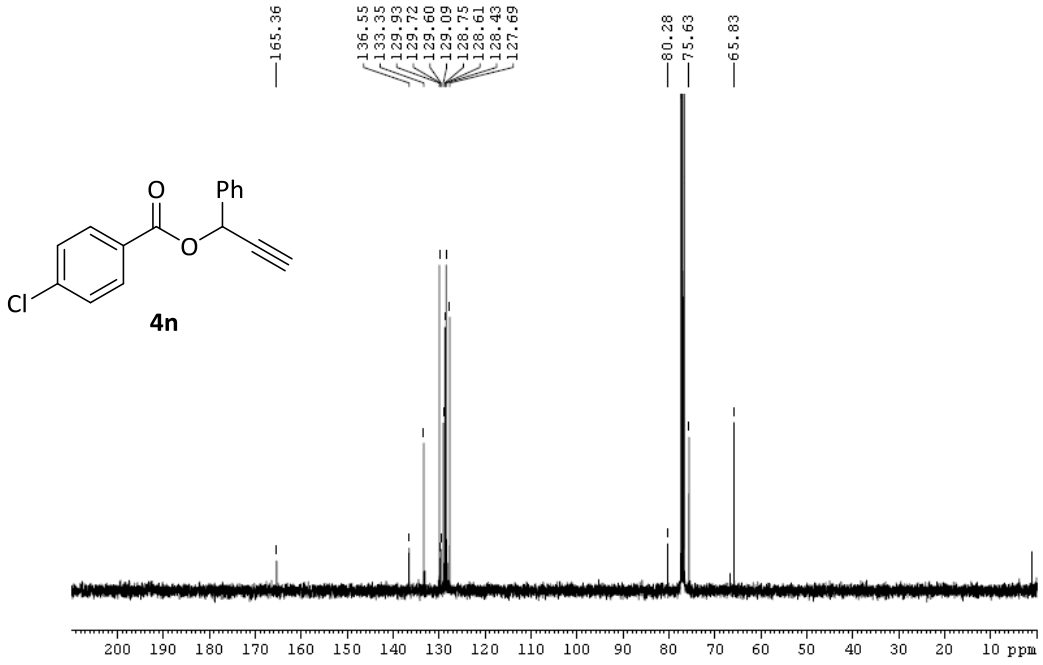
4m


164.69
139.70
131.17
128.77
128.32
80.84
73.89
65.72
28.00
9.30
O
Et
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

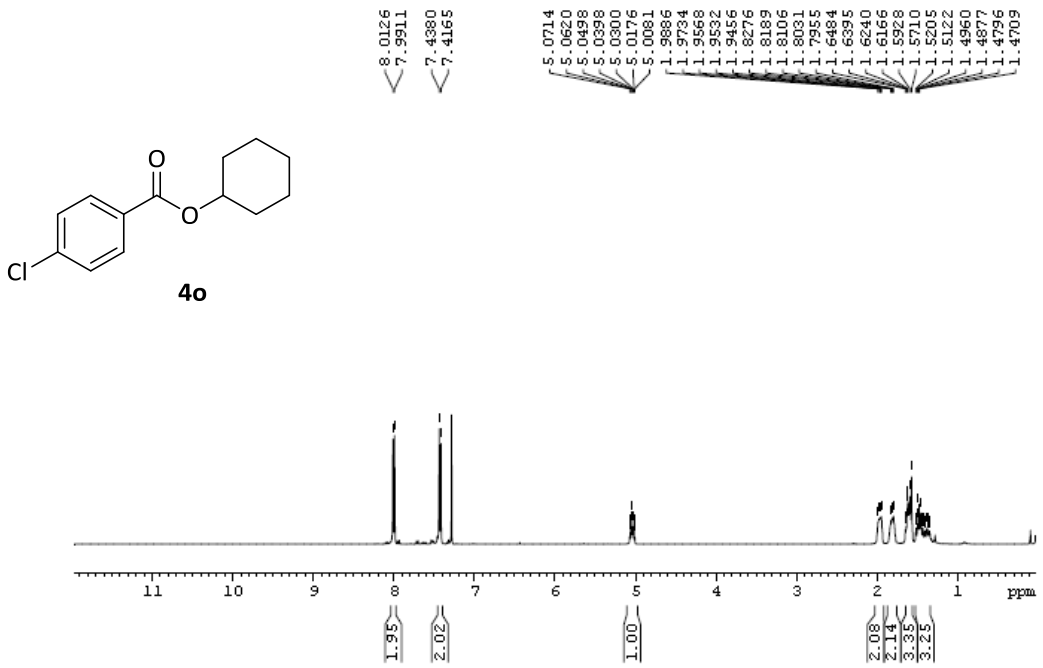
4m


8.1188
8.1007
8.0976
7.6672
7.6631
7.6471
7.6133
7.5947
7.5762
7.4835
7.4637
7.4457
7.4277
7.4204
7.4156
7.4077
7.3891
7.7358
7.7304
2.7227
2.7171
O
Ph
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.08
2.00
1.16
5.41
0.92
0.93

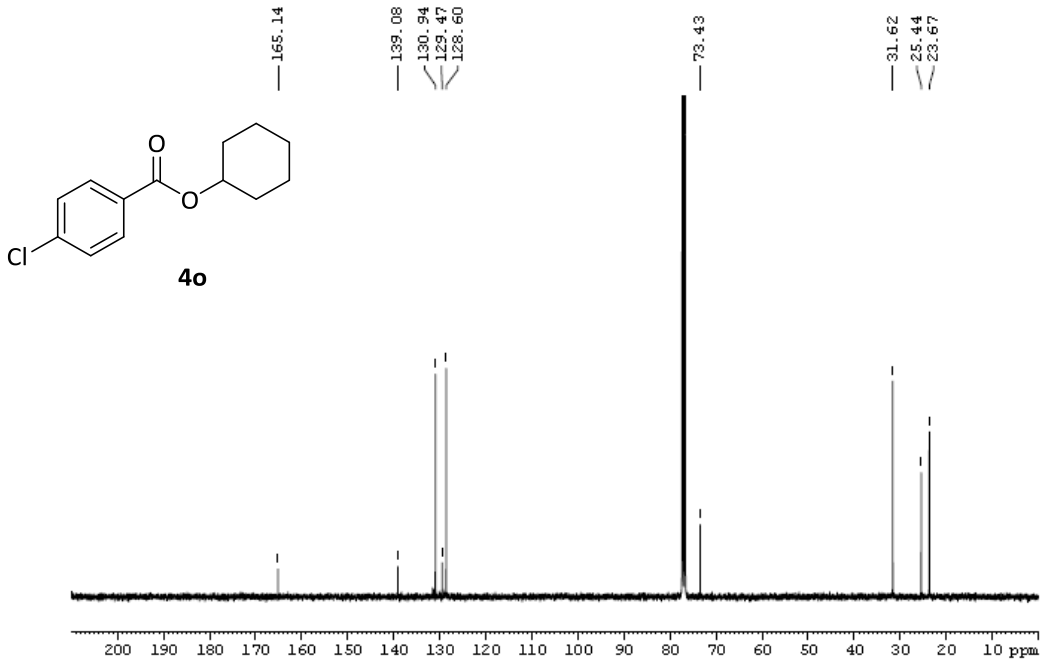
4n


165.36
136.55
133.35
129.93
129.72
129.60
129.09
128.75
128.61
128.43
127.69
80.28
75.63
65.83
O
Ph
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

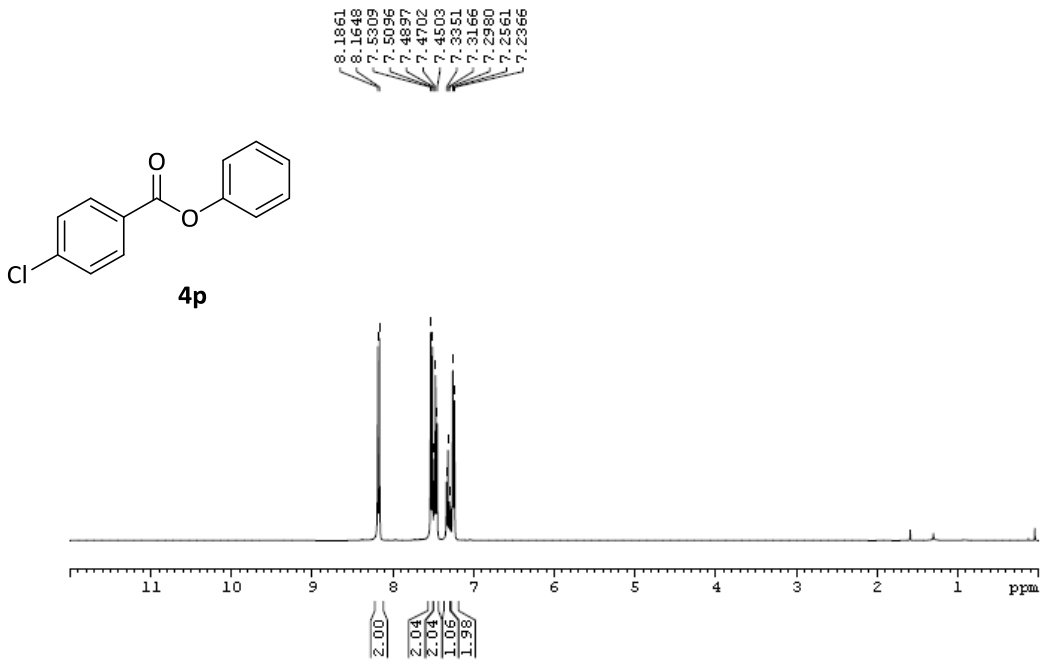
4n


8.0126
7.9911
7.4380
7.4165
5.0714
5.0620
5.0498
5.0398
5.0300
5.0176
5.0081
1.9886
1.9734
1.9568
1.9532
1.9456
1.8276
1.8189
1.8106
1.8031
1.7955
1.6484
1.6395
1.6240
1.6166
1.5928
1.5710
1.5205
1.5122
1.4960
1.4877
1.4796
1.4709
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.95
2.02
1.00
2.08
2.14
3.35
3.25

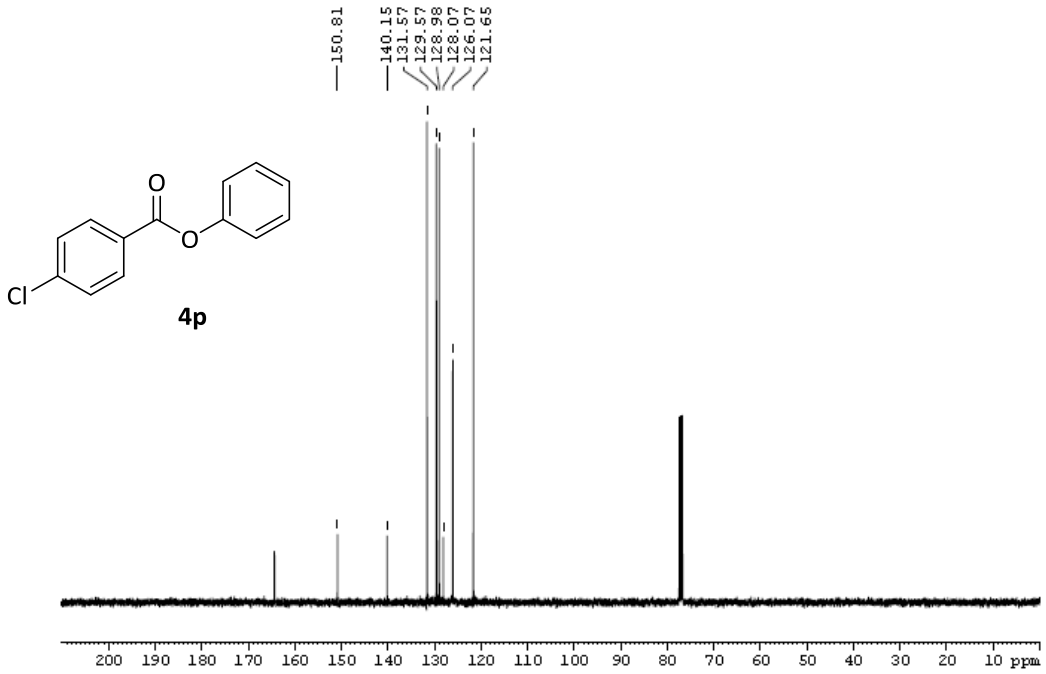
4o


165.14
139.08
130.94
129.47
128.60
73.43
31.62
25.44
23.67
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

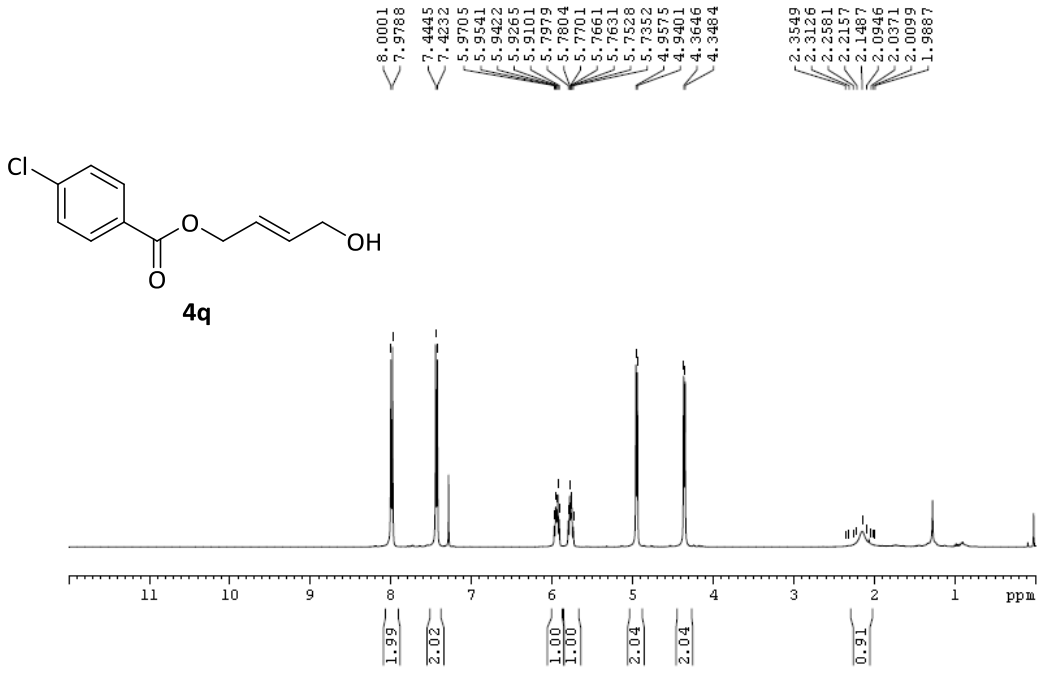
4o


8.1861
8.1648
7.5309
7.5096
7.4897
7.4702
7.4503
7.3351
7.3166
7.2980
7.2561
7.2366
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.04
2.04
1.06
1.98

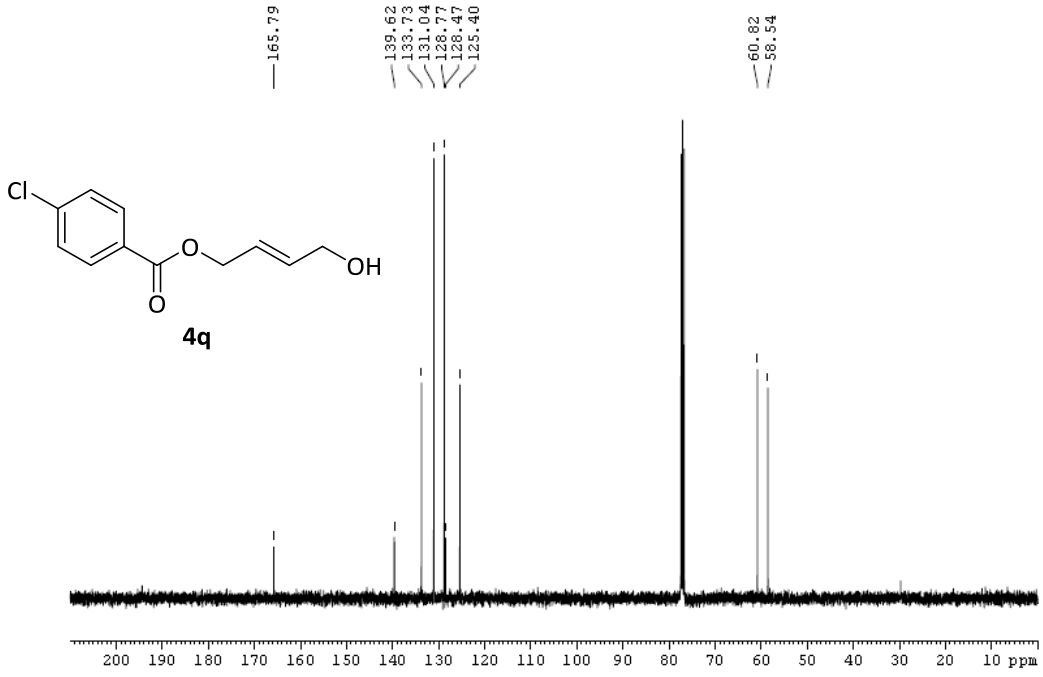
4p


150.81
140.15
131.57
129.57
128.98
128.07
126.07
121.65
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

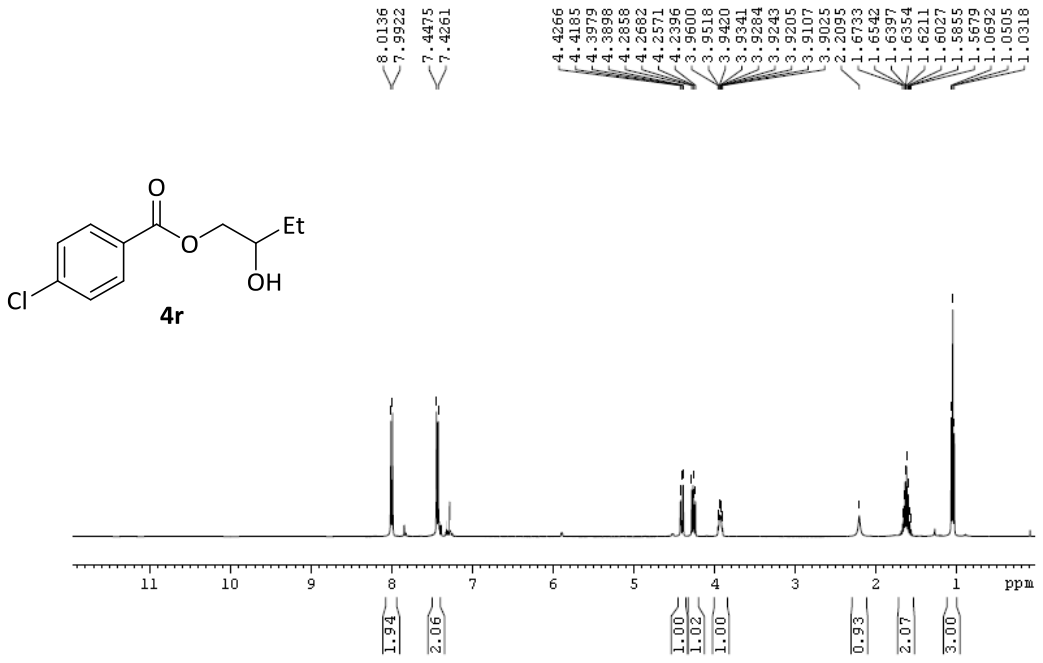
4p


8.0001
7.9788
7.4445
7.4232
5.9705
5.9541
5.9422
5.9265
5.9101
5.7979
5.7804
5.7701
5.7661
5.7631
5.7528
5.7352
4.9575
4.9401
4.3646
4.3484
2.3549
2.3126
2.2581
2.2157
2.1487
2.0946
2.0371
2.0099
1.9887
Cl
O
O
OH
11 10 9 8 7 6 5 4 3 2 1 ppm
1.99
2.02
1.00
1.00
2.04
2.04
0.91

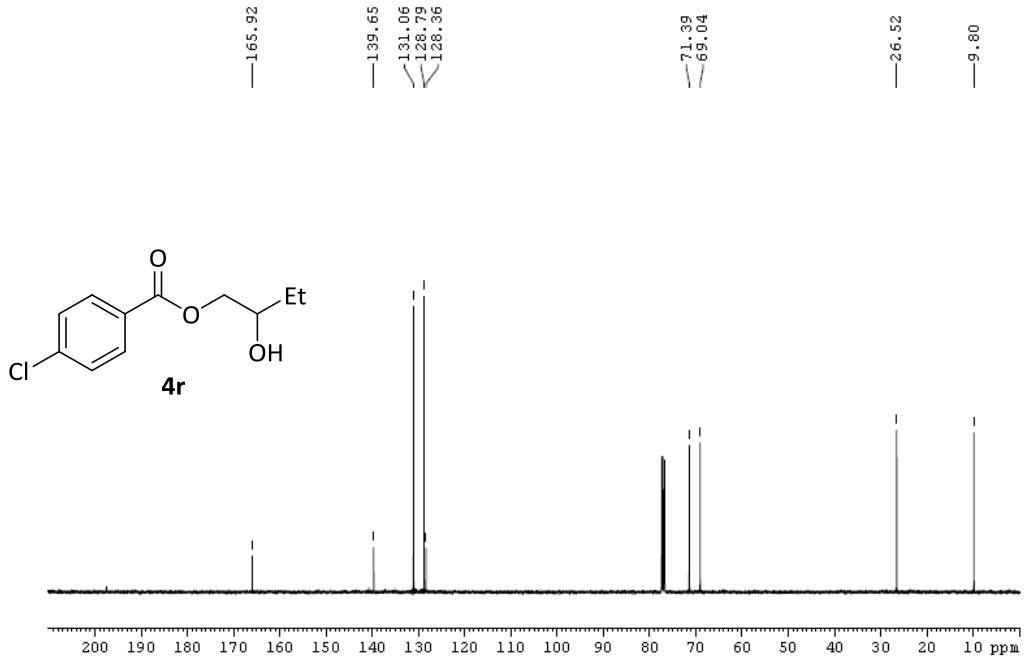
4q


165.79
139.62
133.73
131.04
128.77
128.47
125.40
60.82
58.54
Cl
O
O
OH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

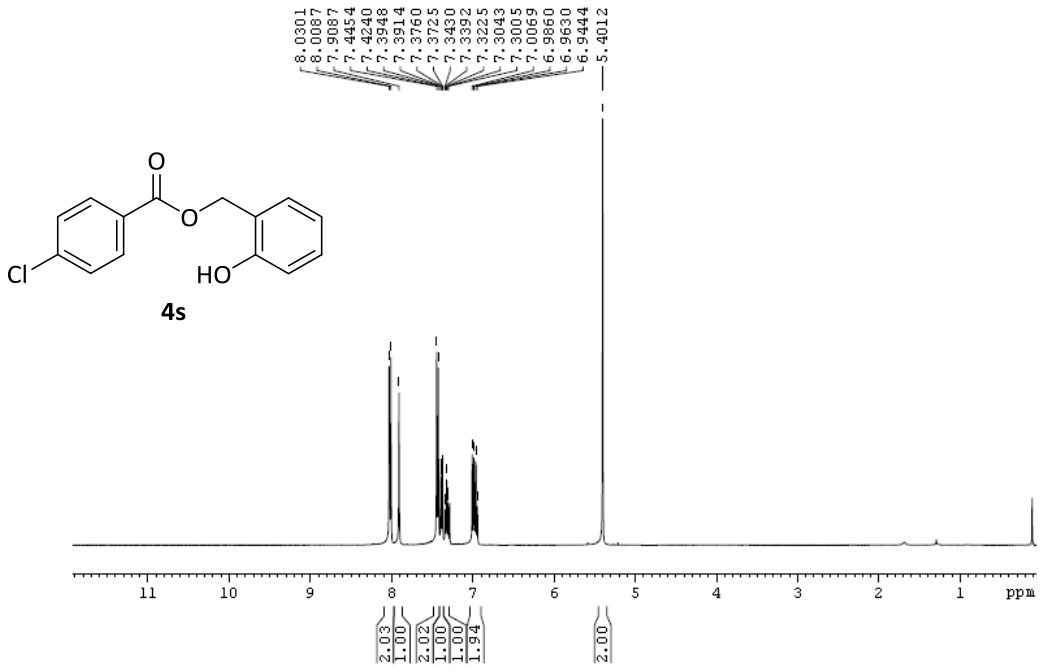
4q


8.0136
7.9922
7.4475
7.4261
4.4266
4.4185
4.3979
4.3898
4.2858
4.2682
4.2571
4.2396
3.9600
3.9518
3.9420
3.9341
3.9284
3.9243
3.9205
3.9107
3.9025
2.2095
1.6733
1.6542
1.6397
1.6354
1.6211
1.6027
1.5855
1.5679
1.0692
1.0505
1.0318
O
O
Et
OH
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.94
2.06
1.00
1.02
1.00
0.93
2.07
3.00

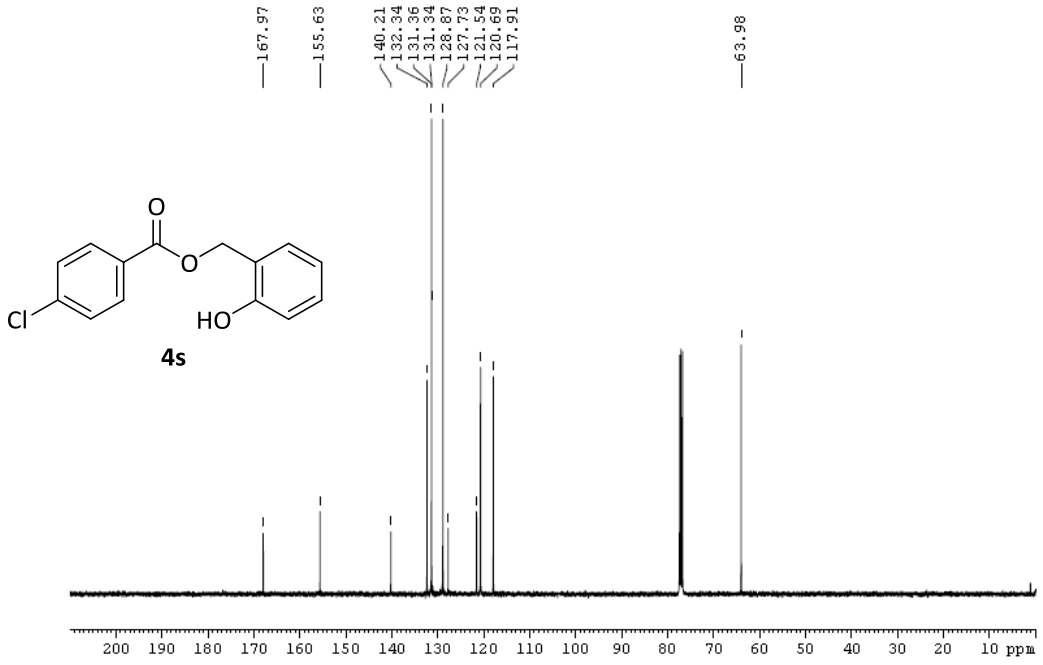
4r


165.92
139.65
131.06
128.79
128.36
71.39
69.04
26.52
9.80
O
O
Et
OH
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

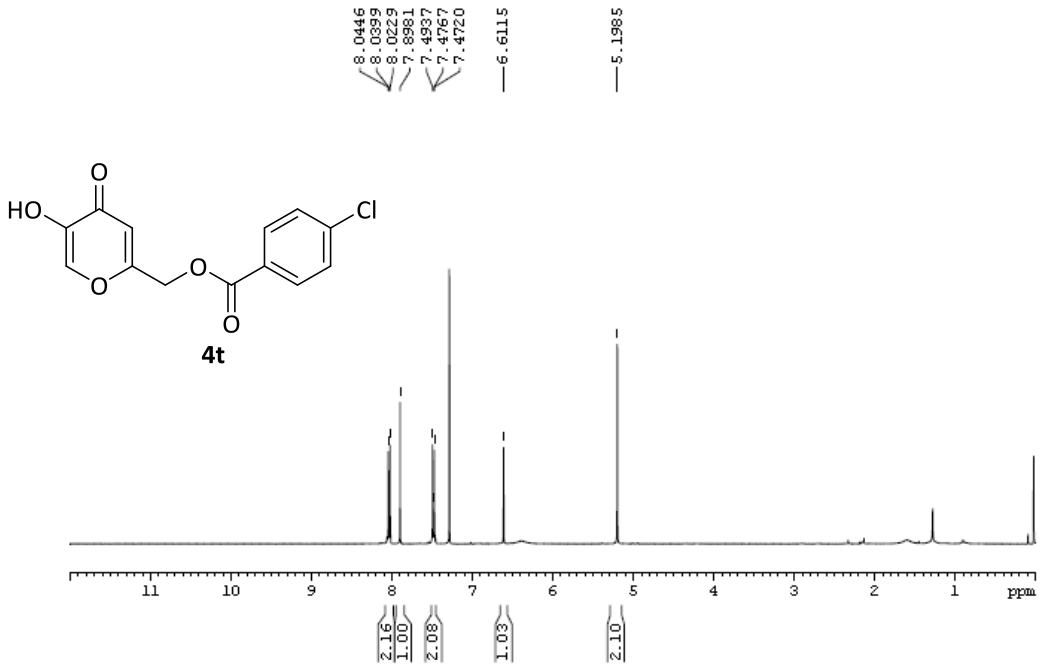
4r


8.0301
8.0087
7.9087
7.4454
7.4240
7.3948
7.3914
7.3760
7.3725
7.3430
7.3392
7.3225
7.3043
7.3005
7.0069
6.9860
6.9630
6.9444
5.4012
O
O
Cl
HO
11 10 9 8 7 6 5 4 3 2 1 ppm
2.03
1.00
2.02
1.00
1.00
1.94
2.00

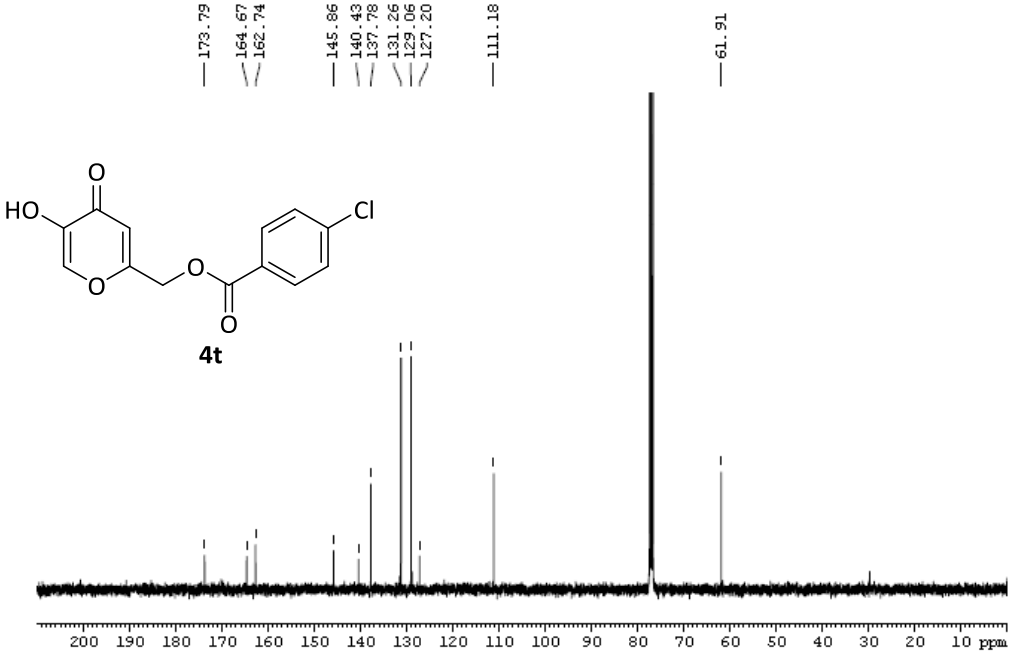
4s


167.97
155.63
140.21
132.34
131.36
131.34
128.87
127.73
121.54
120.69
117.91
63.98
O
O
Cl
HO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

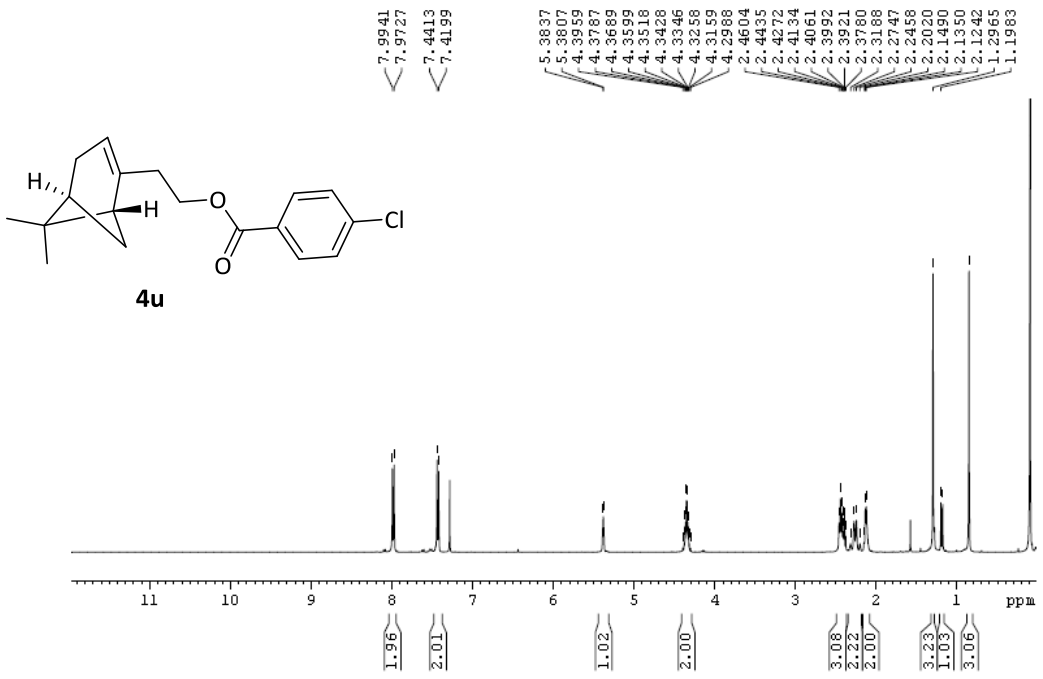
4s


8.0446
8.0399
8.0229
7.8981
7.4937
7.4767
7.4720
6.6115
5.1985
O
HO
O
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.16
1.00
2.08
1.03
2.10

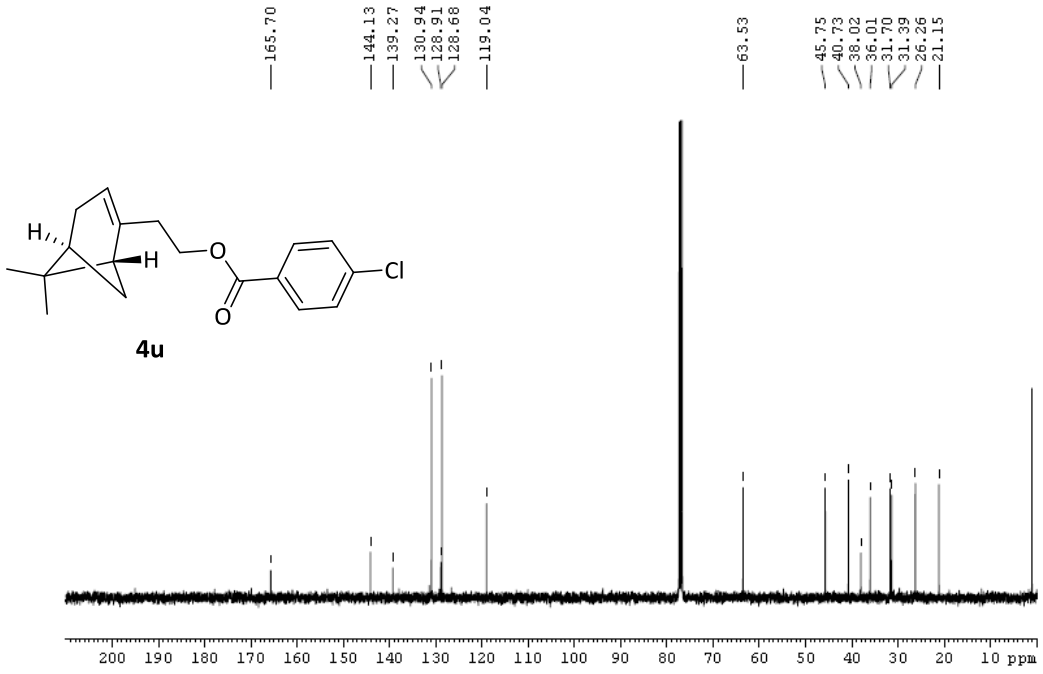
4t


173.79
164.67
162.74
145.86
140.43
137.78
131.26
129.06
127.20
111.18
61.91
HO
O
O
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

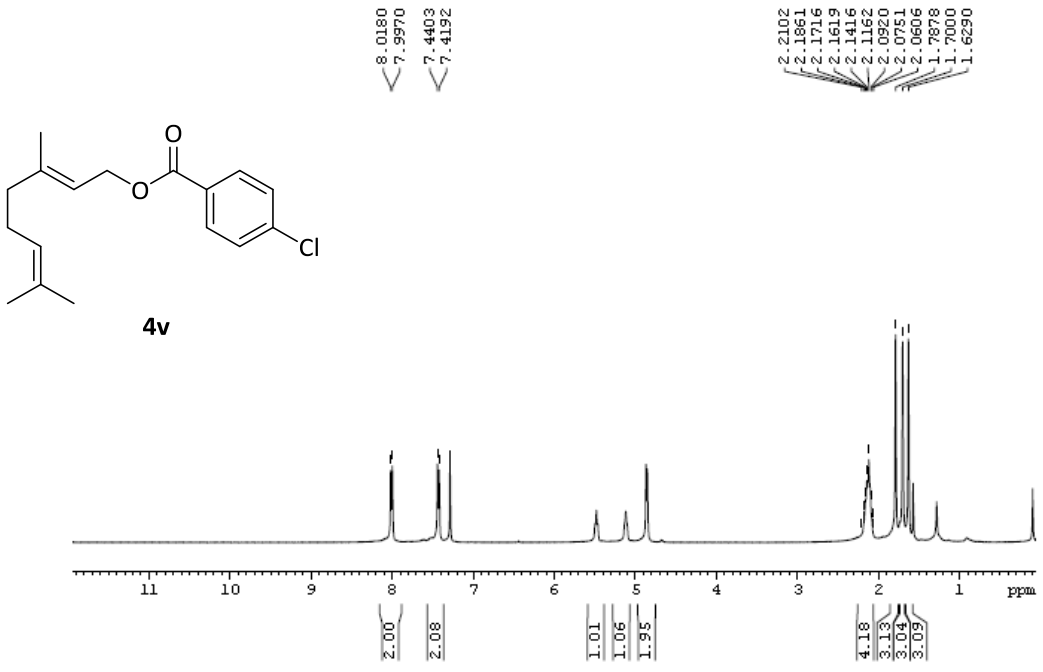
4t


7.9941
7.9727
7.4413
7.4199
5.3837
5.3807
4.3959
4.3787
4.3689
4.3599
4.3518
4.3428
4.3346
4.3258
4.3159
4.2988
2.4604
2.4435
2.4272
2.4134
2.4061
2.3992
2.3921
2.3780
2.3188
2.2747
2.2458
2.2020
2.1490
2.1350
2.1242
1.2965
1.1983
H
H
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
2.01
1.02
2.00
3.08
2.22
2.00
3.23
1.03
3.06

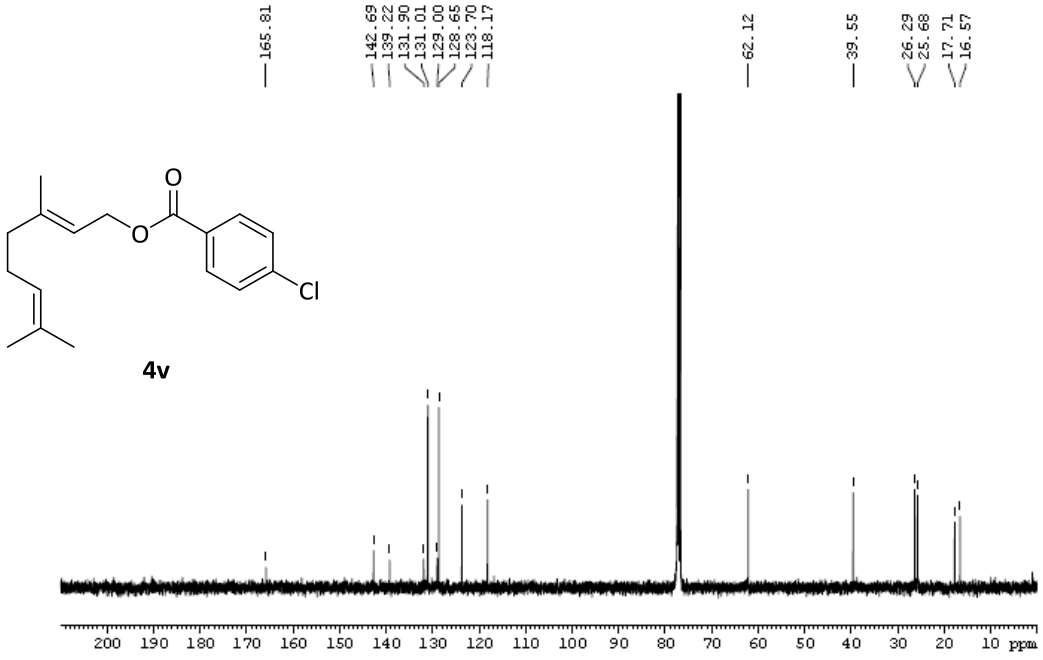
4u


165.70
144.13
139.27
130.94
128.91
128.68
119.04
63.53
45.75
40.73
38.02
36.01
31.70
31.39
26.26
21.15
H
H
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

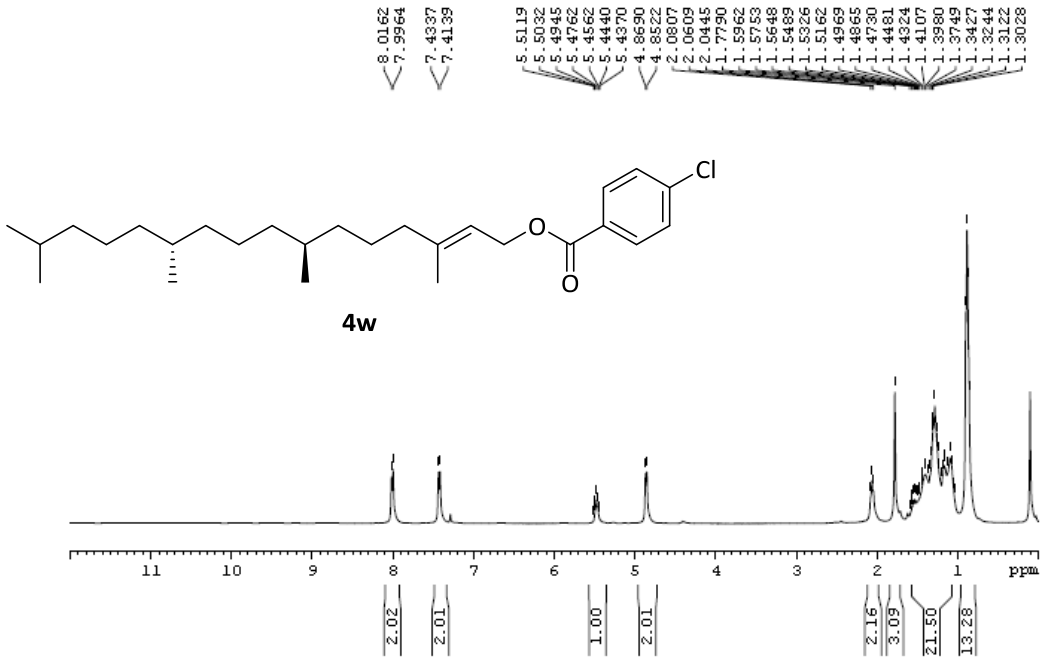
4u


8.0180
7.9970
7.4403
7.4192
2.2102
2.1861
2.1716
2.1619
2.1416
2.1162
2.0920
2.0751
2.0606
1.7878
1.7000
1.6290
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.08
1.01
1.06
1.95
4.18
3.13
3.04
3.09

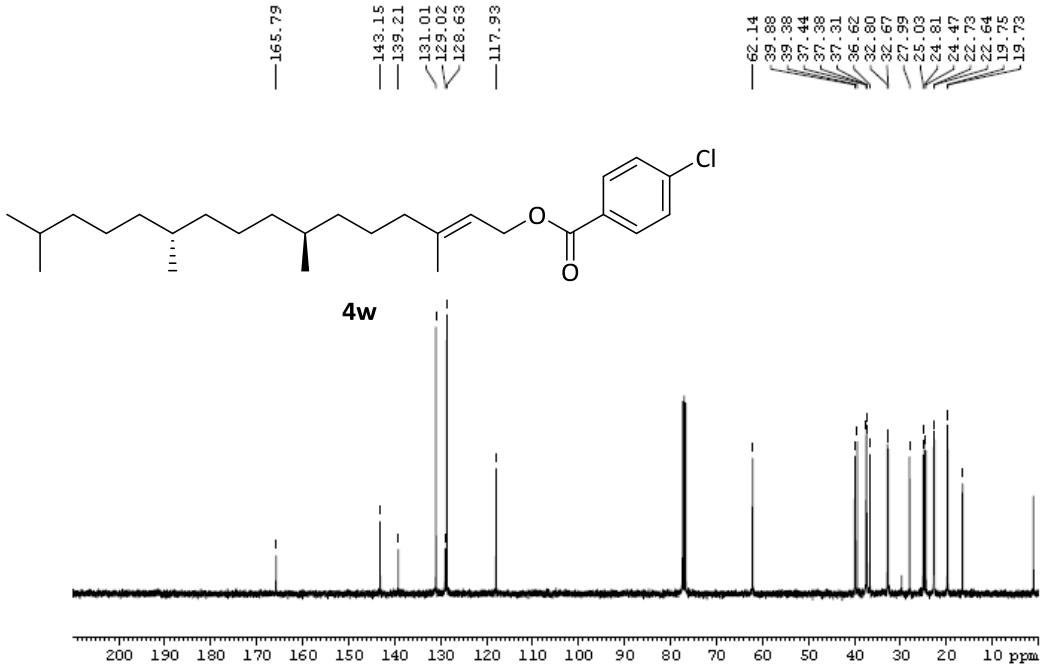
4v

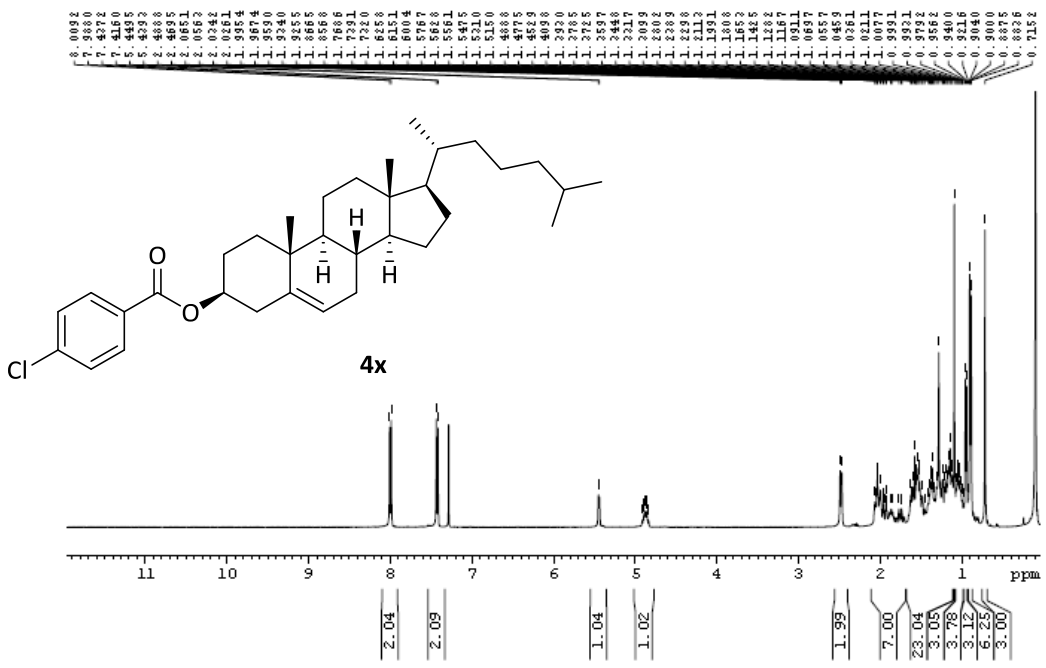

165.81
142.69
139.22
131.90
131.01
129.00
128.65
123.70
118.17
62.12
39.55
26.29
25.68
17.71
16.57
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

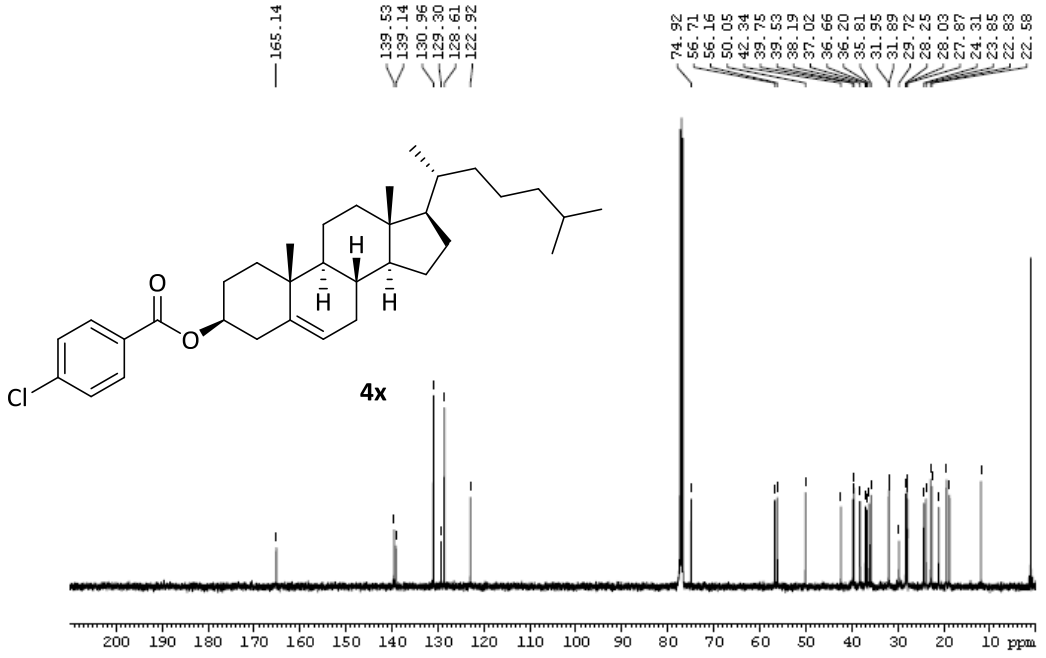
4v

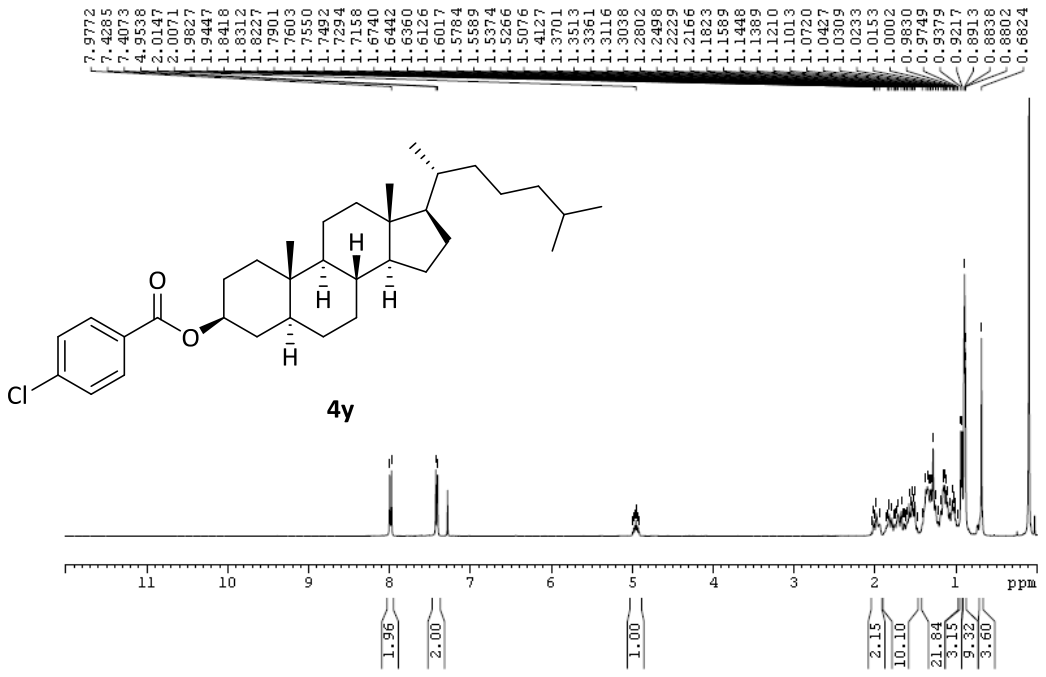

8.0162
7.9964
7.4337
7.4139
5.5119
5.5032
5.4945
5.4762
5.4562
5.4440
5.4370
4.8690
4.8522
2.0807
2.0609
2.0445
1.7790
1.5962
1.5753
1.5648
1.5489
1.5326
1.5162
1.4969
1.4865
1.4730
1.4481
1.4324
1.4107
1.3980
1.3749
1.3427
1.3244
1.3122
1.3028
Cl
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
2.02
2.01
1.00
2.01
2.16
3.09
21.50
13.28

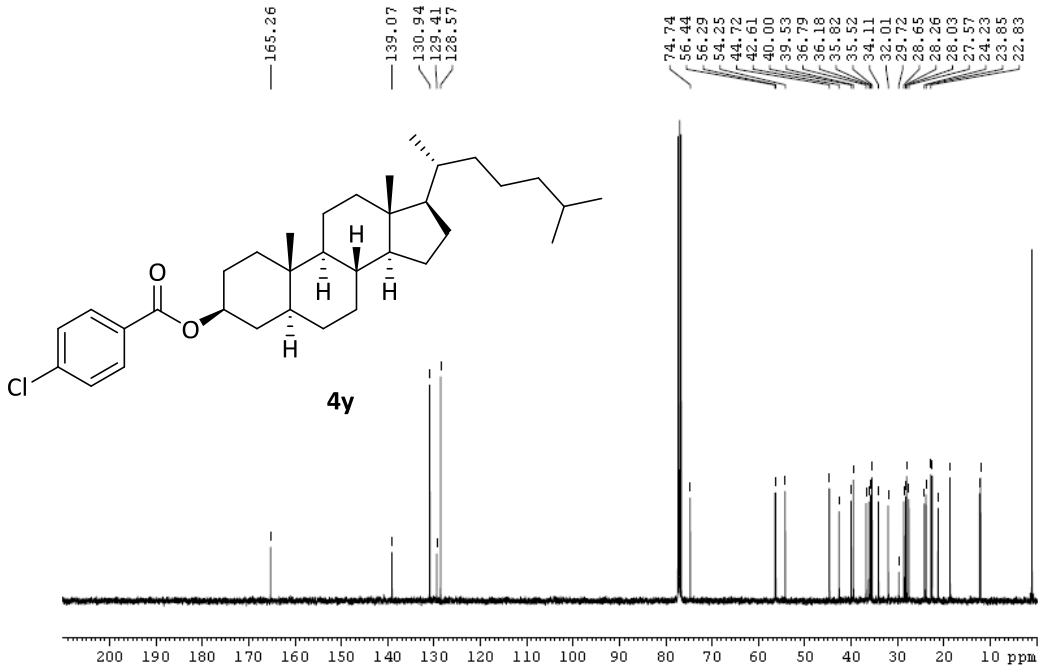
4w

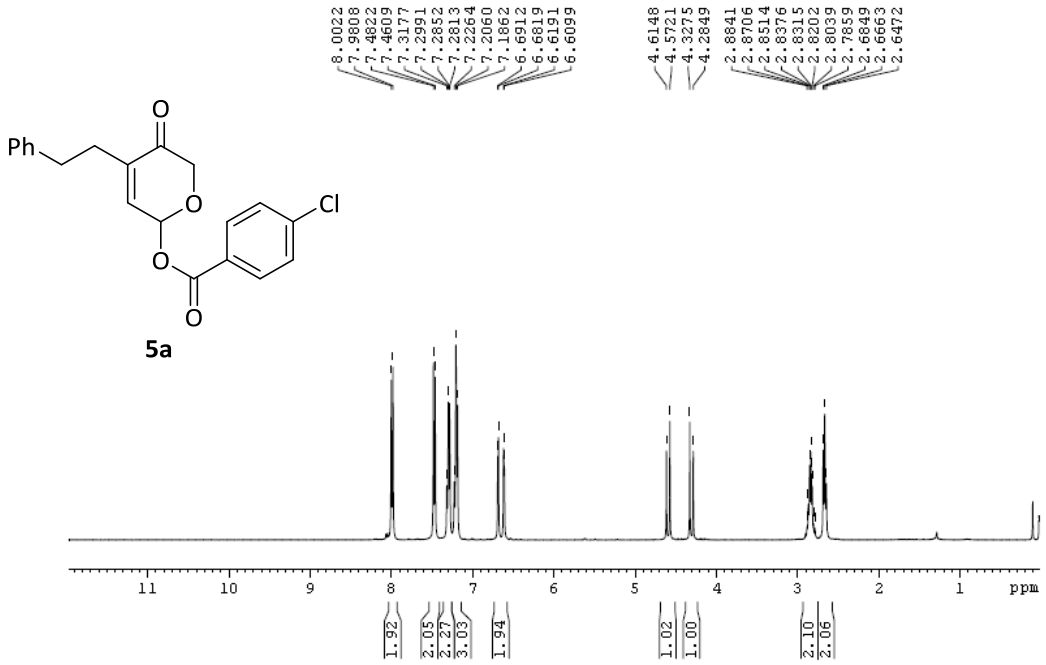

165.79
143.15
139.21
131.01
129.02
128.63
117.93
62.14
39.88
39.38
37.44
37.38
37.31
36.62
32.80
32.67
27.99
25.03
24.81
24.47
22.73
22.64
19.75
19.73
Cl
O
O
4w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

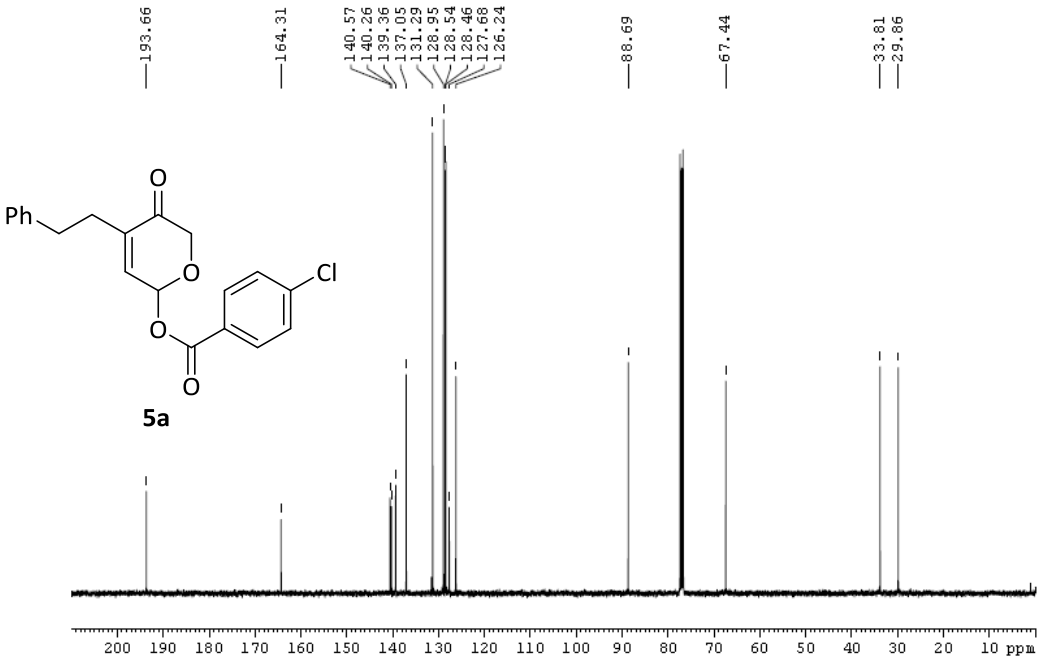

H
H
H
O
O
Cl
4x
11 10 9 8 7 6 5 4 3 2 1 ppm
2.04
2.09
1.04
1.02
1.99
7.00
23.04
3.05
3.78
3.12
6.25
3.00


165.14
139.53
139.14
130.96
129.30
128.61
122.92
74.92
56.71
56.16
50.05
42.34
39.75
39.53
38.19
37.02
36.66
36.20
35.81
31.95
31.89
29.72
28.25
28.03
27.87
24.31
23.85
22.83
22.58
Cl
O
O
H
H
H
4x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

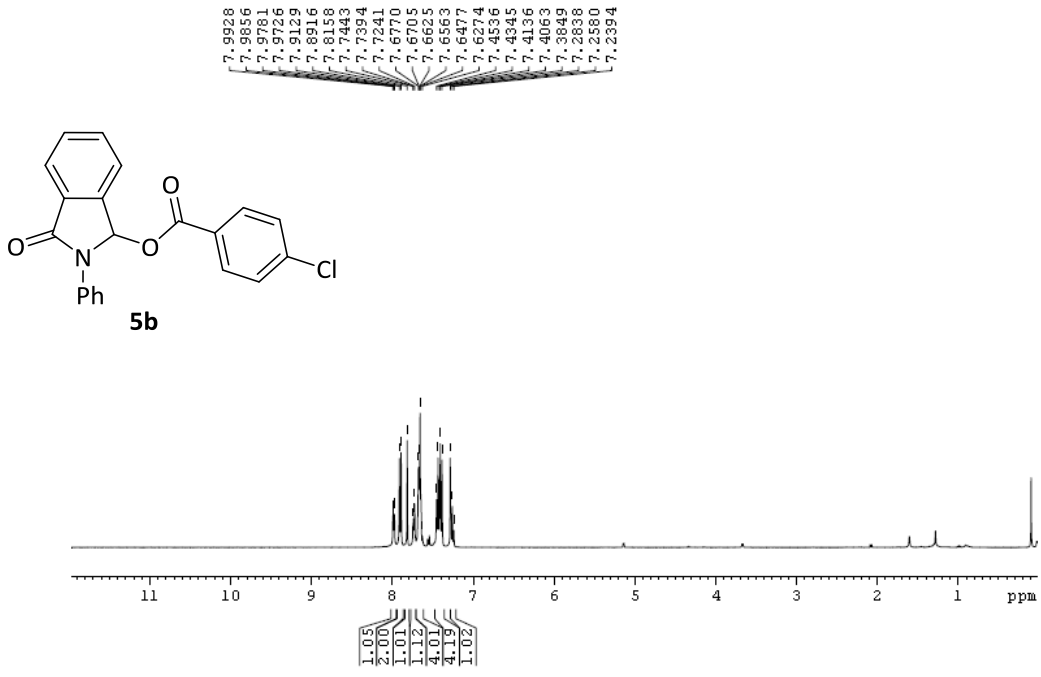

7.9772
7.4285
7.4073
4.9538
2.0147
2.0071
1.9827
1.9447
1.8418
1.8312
1.8227
1.7901
1.7603
1.7550
1.7492
1.7294
1.7158
1.6740
1.6442
1.6360
1.6126
1.6017
1.5784
1.5589
1.5374
1.5266
1.5076
1.4127
1.3701
1.3513
1.3361
1.3116
1.3038
1.2802
1.2498
1.2229
1.2166
1.1823
1.1589
1.1448
1.1389
1.1210
1.1013
1.0720
1.0427
1.0309
1.0233
1.0153
1.0002
0.9830
0.9749
0.9379
0.9217
0.8913
0.8838
0.8802
0.8824
Cl
O
O
H
H
H
H
4y
11 10 9 8 7 6 5 4 3 2 1 ppm
1.96
2.00
1.00
2.15
10.10
21.84
3.15
9.32
3.60


165.26
139.07
130.94
129.41
128.57
74.74
56.44
56.29
54.25
44.72
42.61
40.00
39.53
36.79
36.18
35.82
35.52
34.11
32.01
29.72
28.65
28.26
28.03
27.57
24.23
23.85
22.83
Cl
O
O
H
H
H
H
4y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

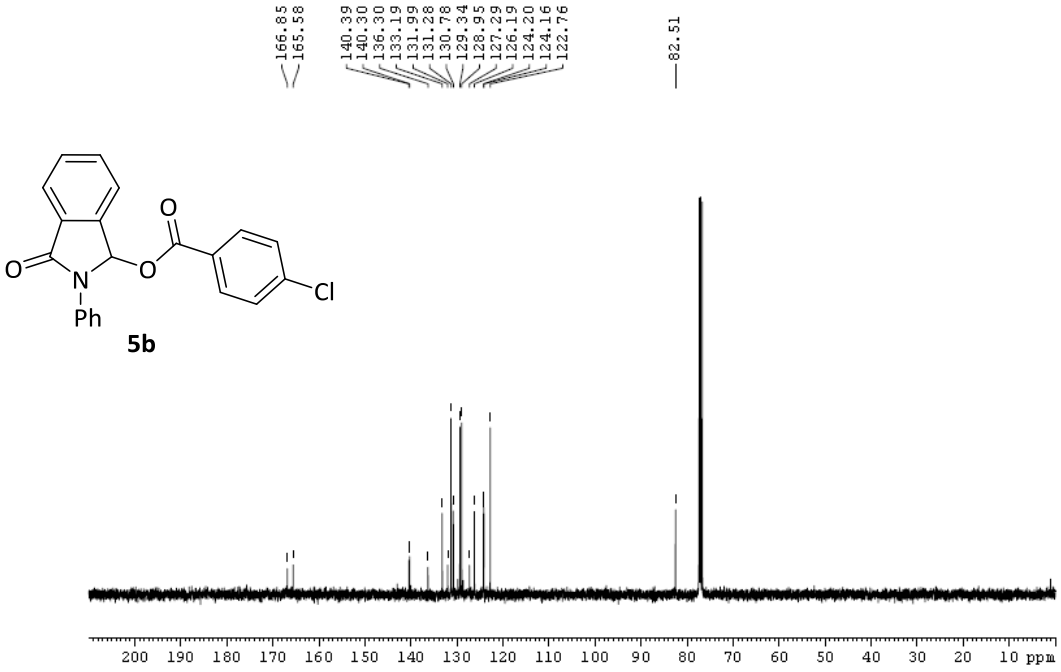

8.0022
7.9808
7.4822
7.4609
7.3177
7.2991
7.2852
7.2813
7.2264
7.2060
7.1862
6.6912
6.6819
6.6191
6.6099
4.6148
4.5721
4.3275
4.2849
2.8841
2.8706
2.8514
2.8376
2.8315
2.8202
2.8039
2.7859
2.6849
2.6663
2.6472
Ph
O
O
O
O
Cl
5a
11 10 9 8 7 6 5 4 3 2 1 ppm
1.92
2.05
2.27
3.03
1.94
1.02
1.00
2.10
2.06


193.66
164.31
140.57
140.26
139.36
137.05
131.29
128.95
128.54
128.46
127.68
126.24
88.69
67.44
33.81
29.86
Ph
O
O
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

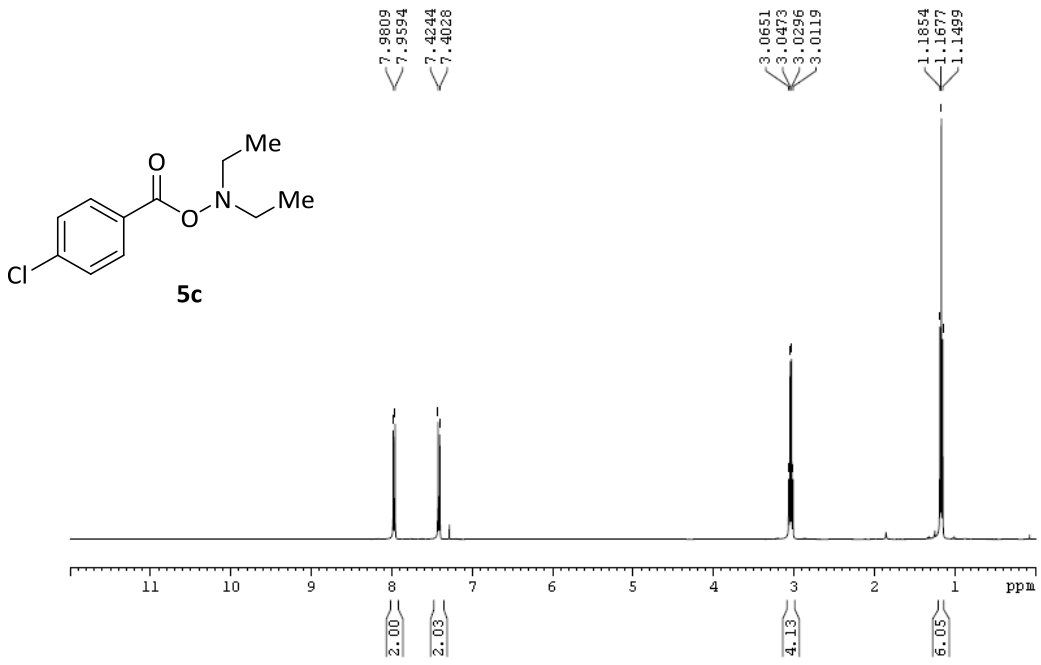
5a


7.9928
7.9856
7.9781
7.9726
7.9129
7.8916
7.8158
7.7443
7.7394
7.7241
7.6770
7.6705
7.6625
7.6563
7.6477
7.6274
7.4536
7.4345
7.4136
7.4063
7.3849
7.2838
7.2580
7.2394
O
O
N
Ph
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
1.05
2.00
1.01
1.12
4.01
4.19
1.02

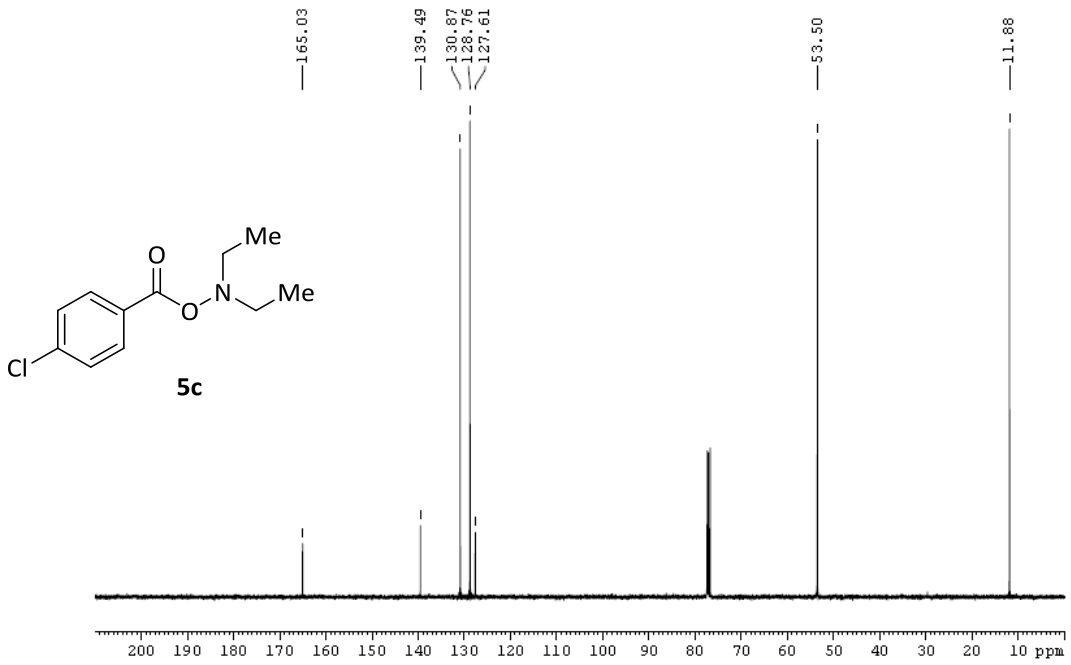
5b


166.85
165.58
140.39
140.30
136.30
133.19
131.99
131.28
130.78
129.34
128.95
127.29
126.19
124.20
124.16
122.76
82.51
O
O
N
Ph
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

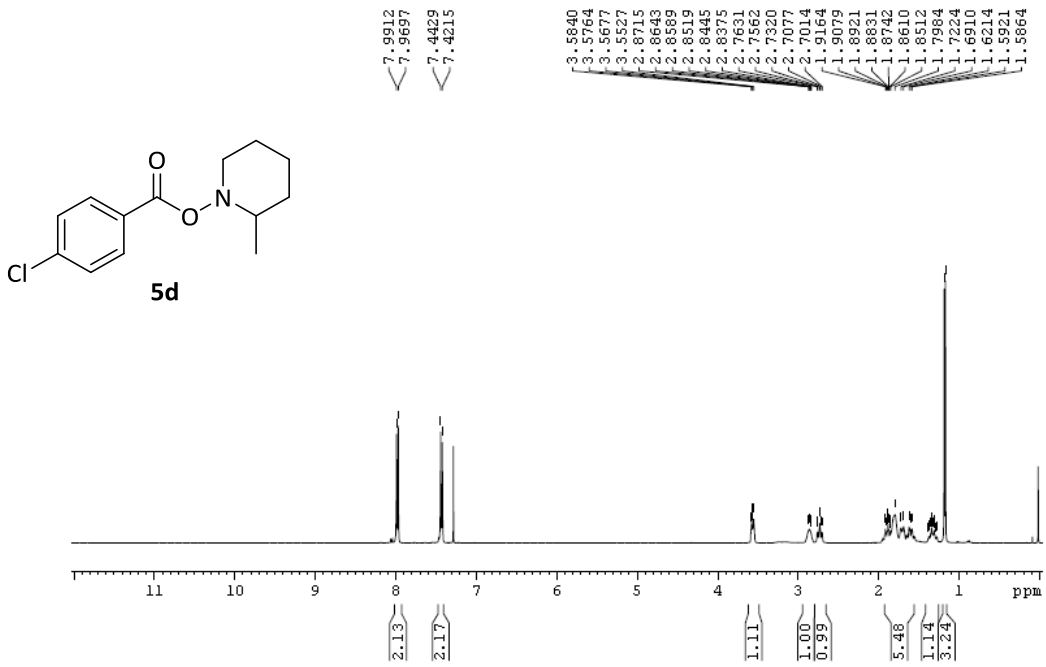
5b


7.9809
7.9594
7.4244
7.4028
3.0651
3.0473
3.0296
3.0119
1.1854
1.1677
1.1499
Me
O
N
Me
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.03
4.13
6.05

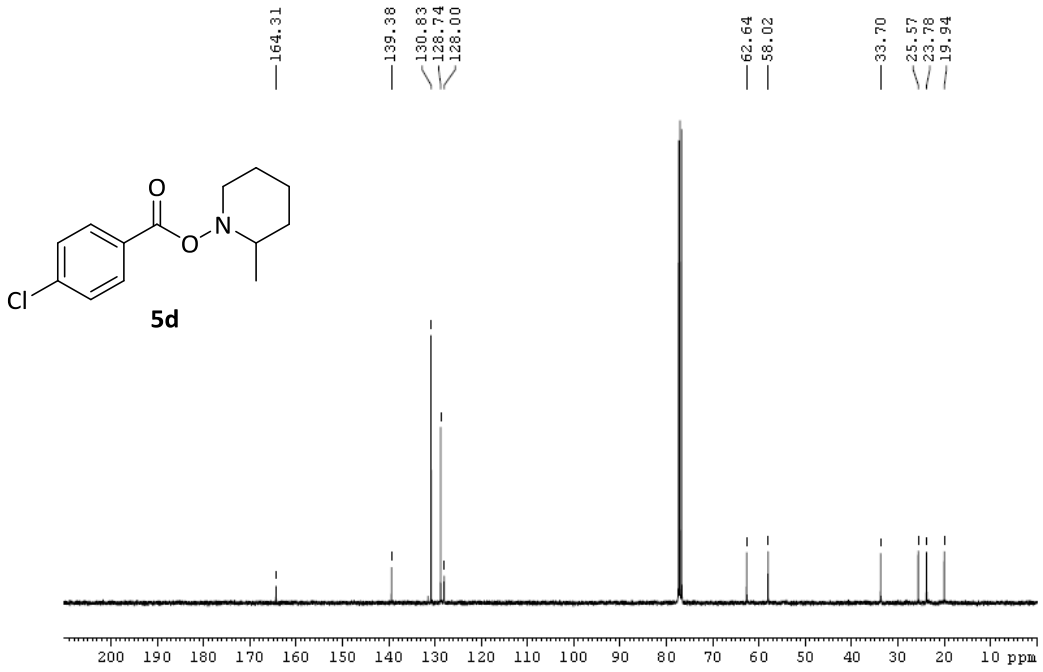
5c


165.03
139.49
130.87
128.76
127.61
53.50
11.88
O
N
O
Me
Me
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

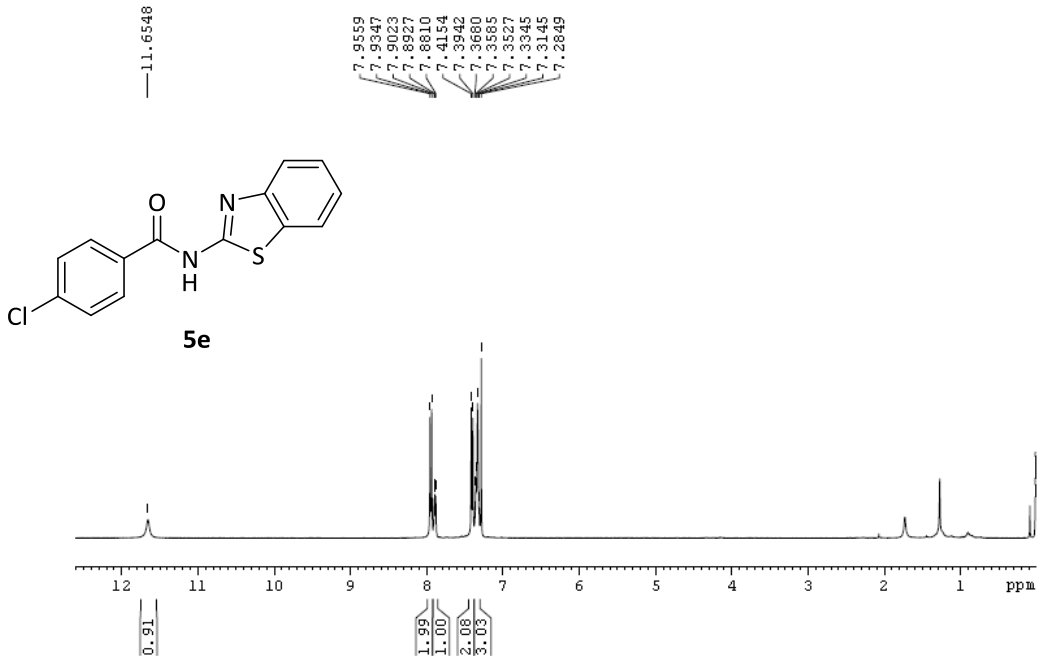
5c


7.9912
7.9697
7.4429
7.4215
3.5840
3.5764
3.5677
3.5527
2.8715
2.8643
2.8589
2.8519
2.8445
2.8375
2.7631
2.7562
2.7320
2.7077
2.7014
1.9164
1.9079
1.8921
1.8831
1.8742
1.8610
1.8512
1.7984
1.7224
1.6910
1.6214
1.5921
1.5864
O
N
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.13
2.17
1.11
1.00
0.99
5.48
1.14
3.24

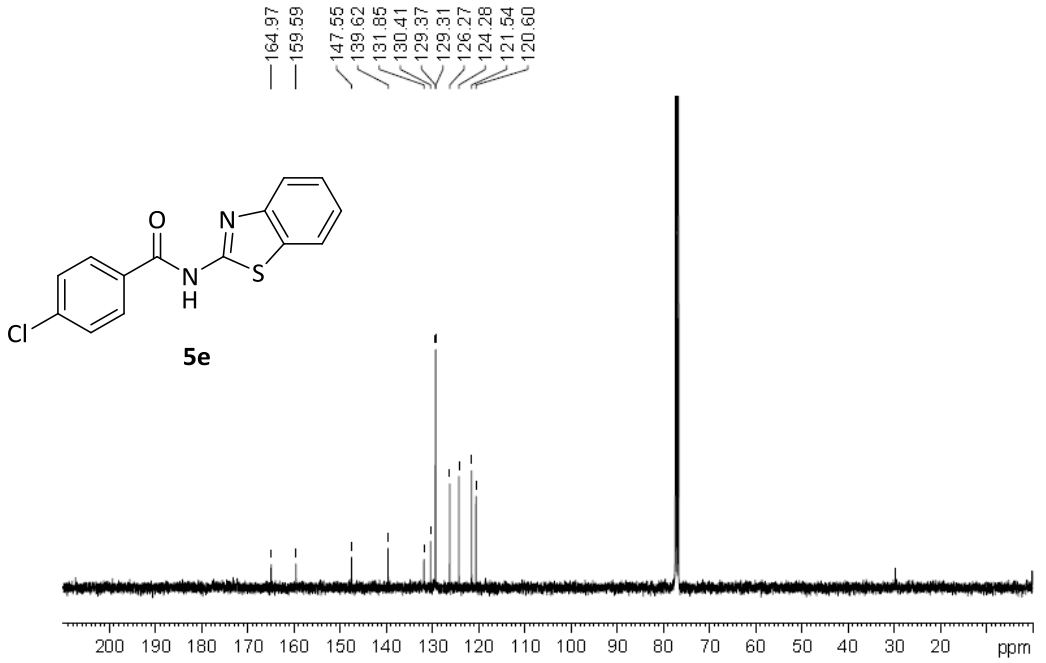
5d


164.31
139.38
130.83
128.74
128.00
62.64
58.02
33.70
25.57
23.78
19.94
O
O
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

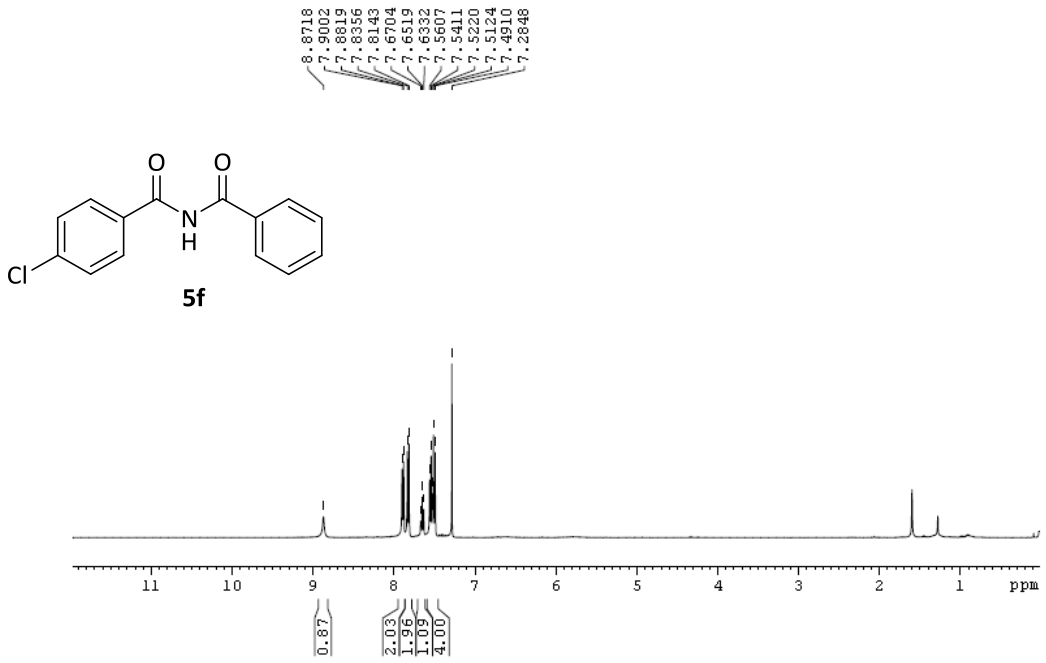
5d


11.6548
7.9559
7.9347
7.9023
7.8927
7.8810
7.4154
7.3942
7.3680
7.3585
7.3527
7.3345
7.3145
7.2849
O
N
N
H
S
Cl
12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.91
1.99
1.00
2.08
3.03

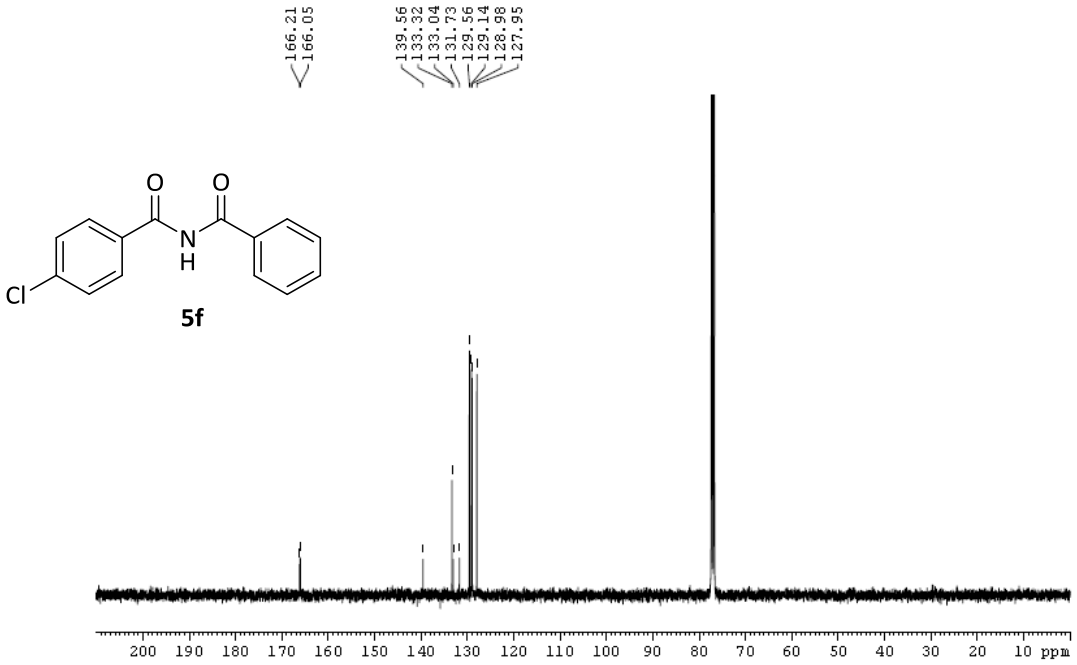
5e


164.97
159.59
147.55
139.62
131.85
130.41
129.37
129.31
126.27
124.28
121.54
120.60
O
N
N
H
S
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

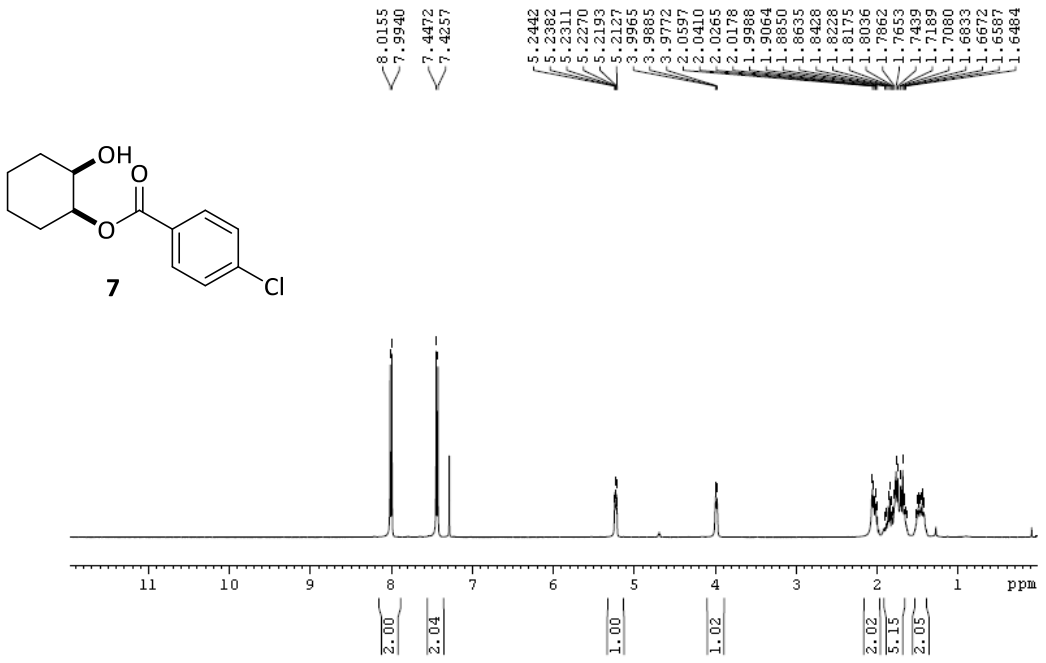
5e


8.8718
7.9002
7.8819
7.8356
7.8143
7.6704
7.6519
7.6332
7.5607
7.5411
7.5220
7.5124
7.4910
7.2848
O
O
N
H
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
0.87
2.03
1.96
1.09
4.00

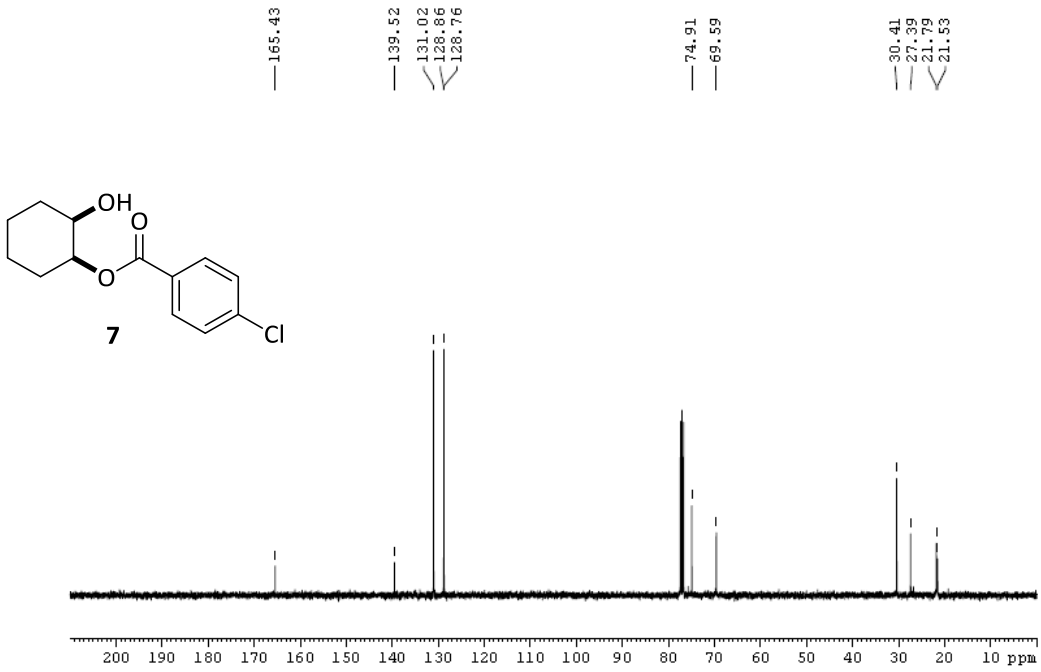
5f

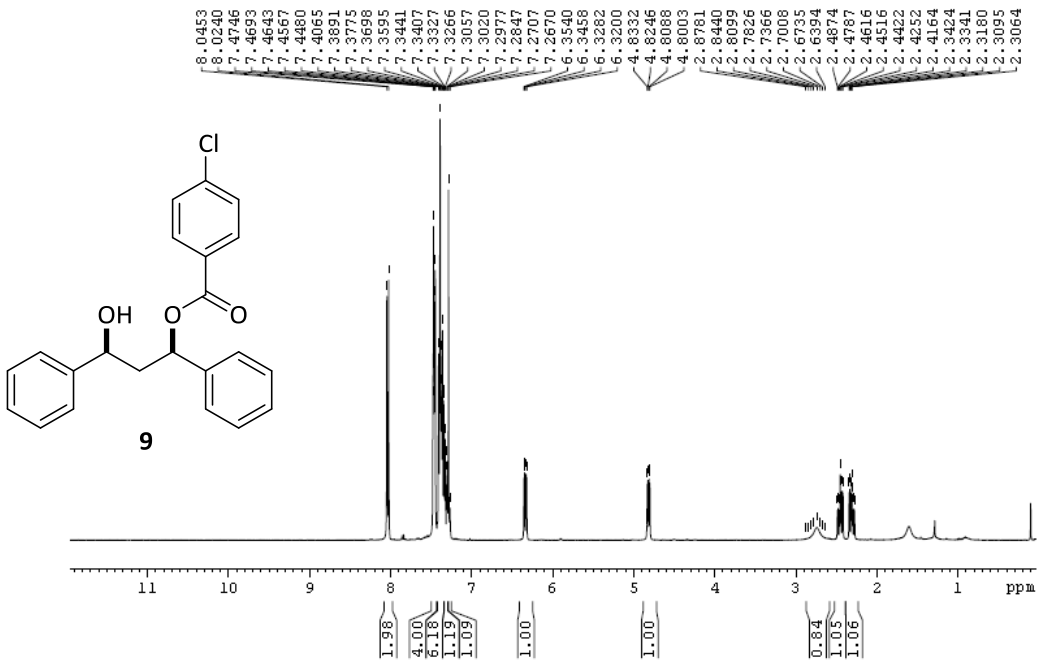

166.21
166.05
139.56
133.32
133.04
131.73
129.56
129.14
128.98
127.95
O
O
N
H
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

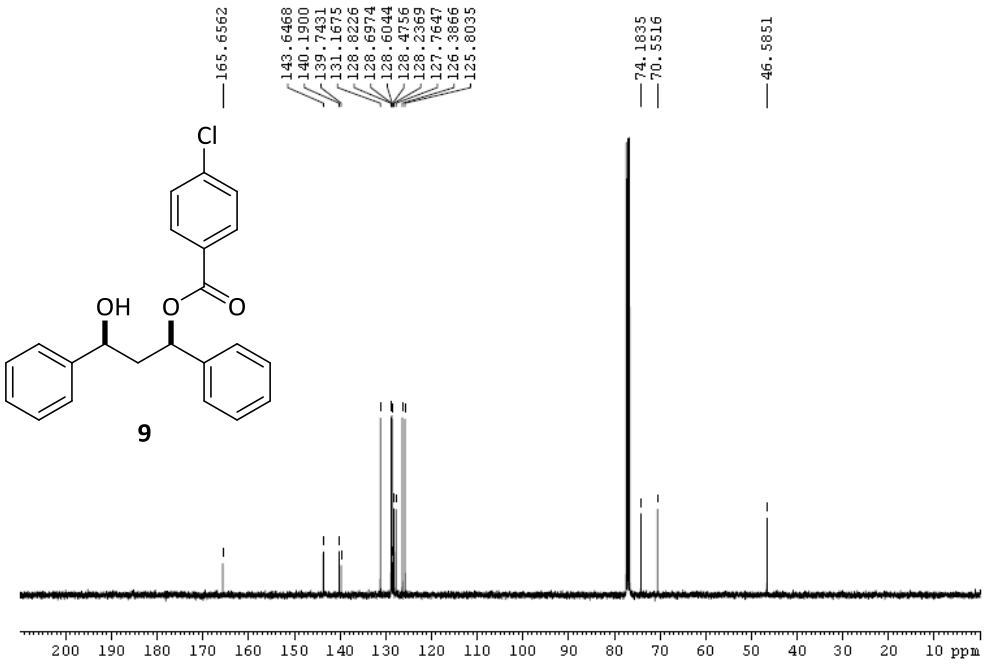
5f

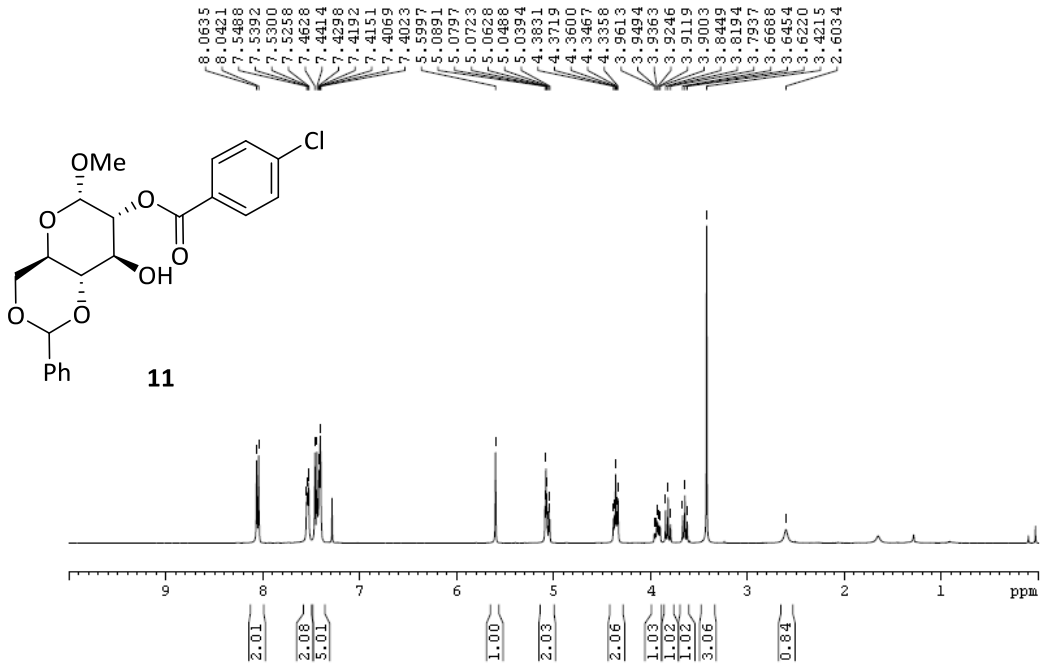

8.0155
7.9940
7.4472
7.4257
5.2442
5.2382
5.2311
5.2270
5.2193
5.2127
3.9965
3.9885
3.9772
2.0597
2.0410
2.0265
2.0178
1.9988
1.9064
1.8850
1.8635
1.8428
1.8228
1.8175
1.8036
1.7862
1.7653
1.7439
1.7189
1.7080
1.6833
1.6672
1.6587
1.6484
OH
O
O
Cl
11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.04
1.00
1.02
2.02
5.15
2.05

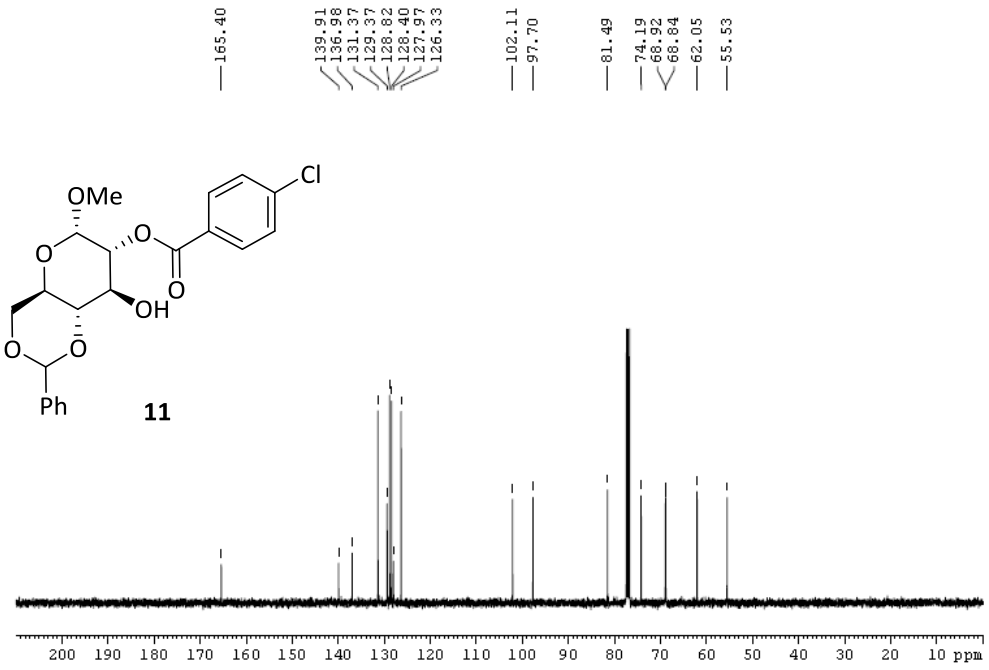
7

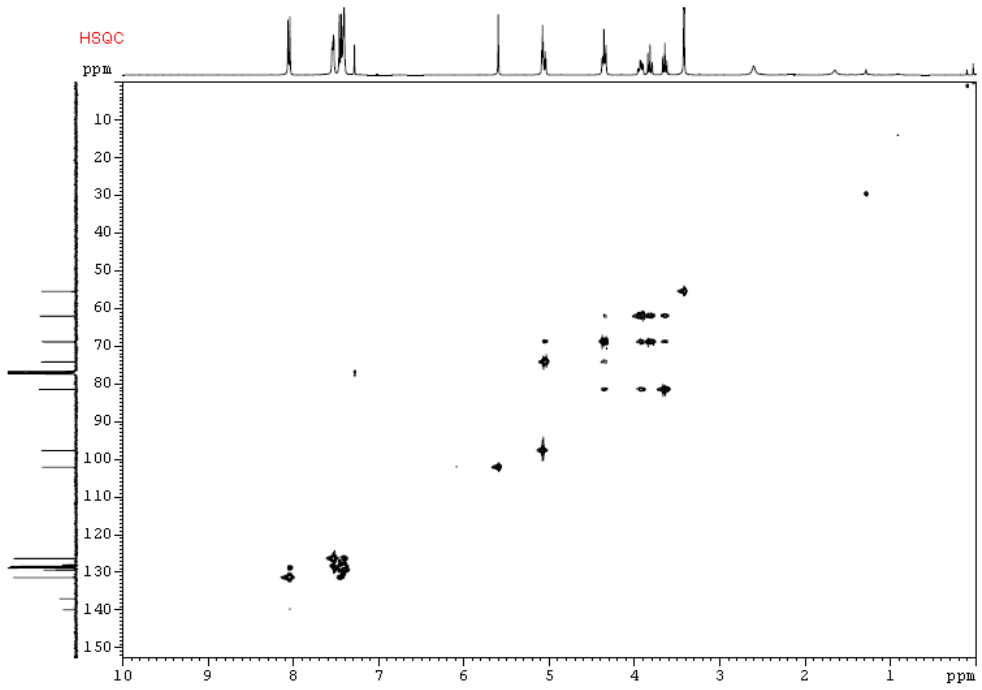

165.43
139.52
131.02
128.86
128.76
74.91
69.59
30.41
27.39
21.79
21.53
OH
O
O
Cl
7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

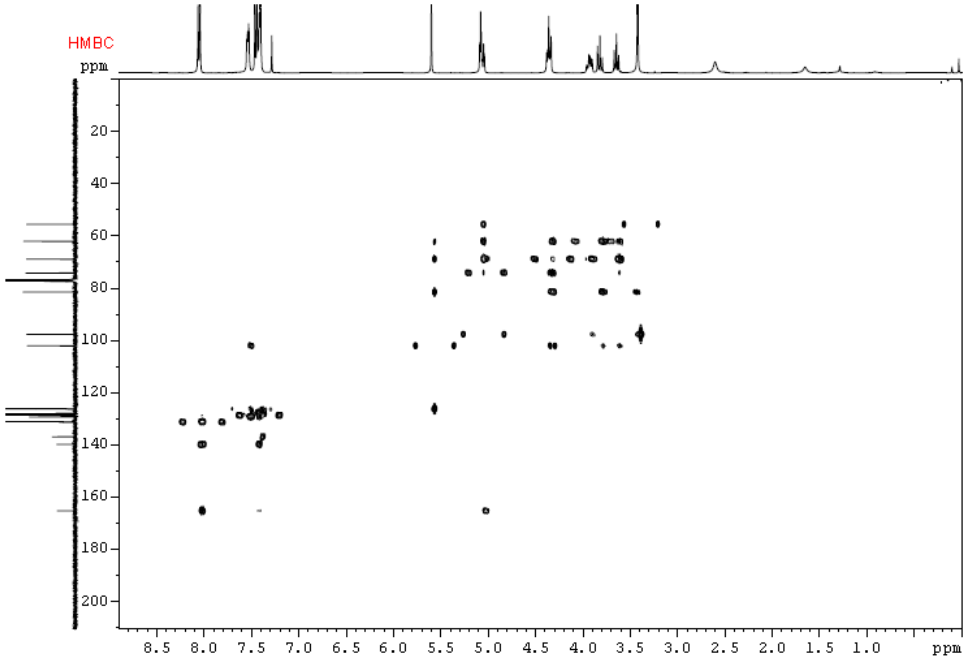

8.0453
8.0240
7.4746
7.4693
7.4643
7.4567
7.4480
7.4065
7.3891
7.3775
7.3698
7.3595
7.3441
7.3407
7.3327
7.3266
7.3057
7.3020
7.2977
7.2847
7.2707
7.2670
6.3540
6.3458
6.3282
6.3200
4.8332
4.8246
4.8088
4.8003
2.8781
2.8440
2.8099
2.7826
2.7366
2.7008
2.6735
2.6394
2.4874
2.4787
2.4616
2.4516
2.4422
2.4252
2.4164
2.3424
2.3341
2.3180
2.3095
2.3064
Cl
OH
O
O
9
11 10 9 8 7 6 5 4 3 2 1 ppm
1.98
4.00
3.18
1.19
1.09
1.00
1.00
0.84
1.05
1.06

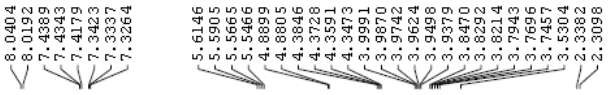

165.6562
143.6468
140.1900
139.7431
131.1675
128.8226
128.6974
128.6044
128.4756
128.2369
127.7647
126.3866
125.8035
74.1835
70.5516
46.5851
Cl
OH
O
O
9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

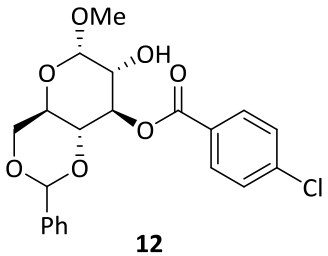

8.0635
8.0421
7.5488
7.5392
7.5300
7.5258
7.4628
7.4414
7.4298
7.4192
7.4151
7.4069
7.4023
5.5997
5.0891
5.0797
5.0723
5.0628
5.0488
5.0394
4.3831
4.3719
4.3600
4.3467
4.3358
3.9613
3.9494
3.9363
3.9246
3.9119
3.9003
3.8449
3.8194
3.7937
3.6688
3.6454
3.6220
3.4215
2.6034
OMe
Cl
O
O
O
OH
O
O
Ph
11
9 8 7 6 5 4 3 2 1 ppm
2.01
2.08
5.01
1.00
2.03
2.06
1.03
1.02
1.02
3.06
0.84


165.40
139.91
136.98
131.37
129.37
128.82
128.40
127.97
126.33
102.11
97.70
81.49
74.19
68.92
68.84
62.05
55.53
OMe
Cl
O
O
O
OH
O
O
Ph
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

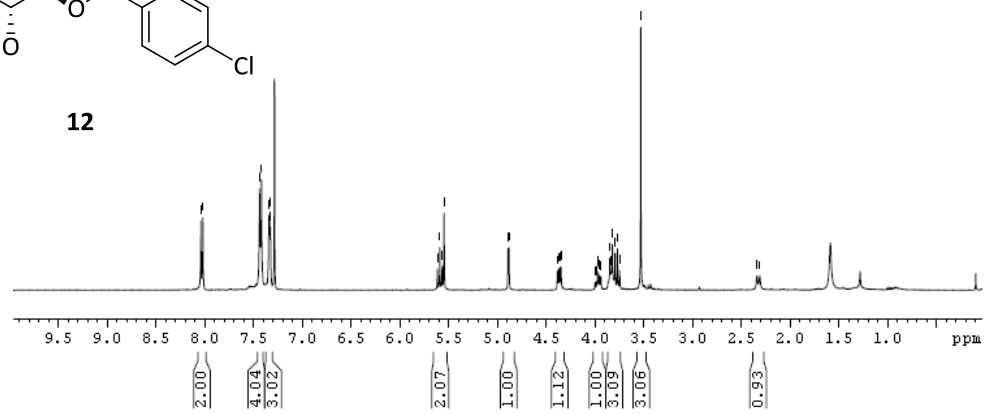

HSQC
ppm
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
10 9 8 7 6 5 4 3 2 1 ppm

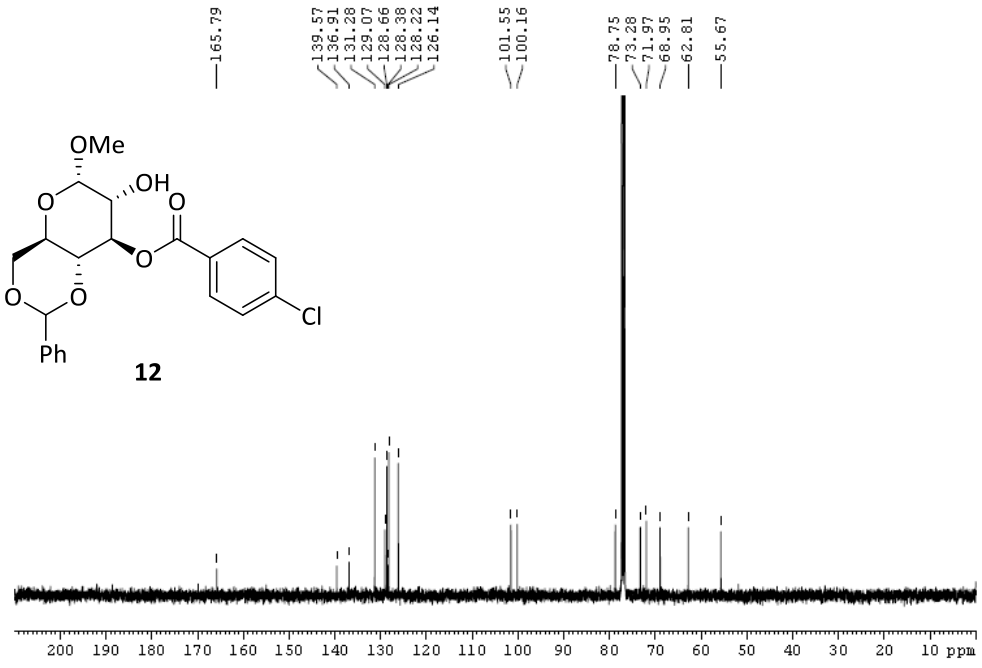

HMBC
ppm
20
40
60
80
100
120
140
160
180
200
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


8.0404
8.0192
7.4389
7.4343
7.4179
7.3423
7.3337
7.3264
5.6146
5.5905
5.5665
5.5466
4.8899
4.8805
4.3846
4.3728
4.3591
4.3473
3.9991
3.9870
3.9742
3.9624
3.9498
3.9379
3.8470
3.8292
3.8214
3.7943
3.7696
3.7457
3.5304
2.3382
2.3098

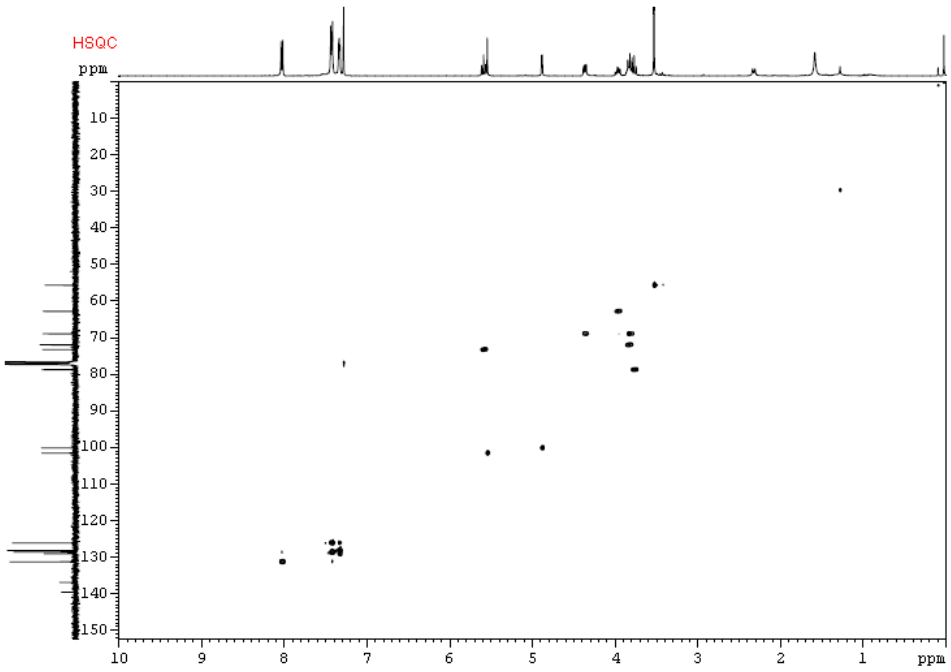

OMe
OH
O
O
O
O
O
Cl
Ph

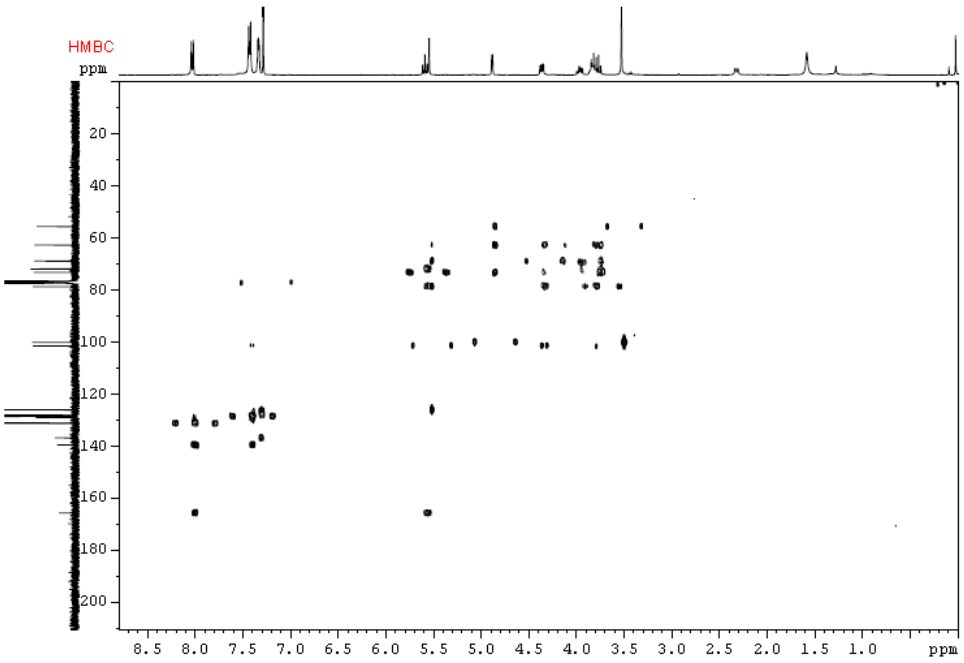
12

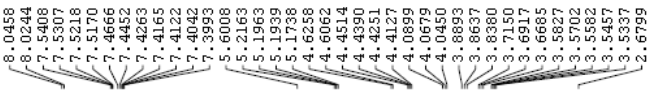

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
2.00
4.04
3.02
2.07
1.00
1.12
1.00
3.09
3.06
0.93


165.79
139.57
136.91
131.28
129.07
128.66
128.38
128.22
126.14
101.55
100.16
78.75
73.28
71.97
68.95
62.81
55.67
OMe
OH
O
O
O
O
O
Cl
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

12


HSQC
ppm
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
10 9 8 7 6 5 4 3 2 1 ppm


HMBC
ppm
20
40
60
80
100
120
140
160
180
200
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
ppm


8.0458
8.0244
7.5408
7.5307
7.5218
7.5170
7.4666
7.4452
7.4263
7.4165
7.4122
7.4042
7.3993
5.6008
5.2163
5.1963
5.1939
5.1738
4.6258
4.6062
4.4514
4.4390
4.4251
4.4127
4.0899
4.0679
4.0450
3.8893
3.8637
3.8380
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3.6917
3.6685
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3.5702
3.5582
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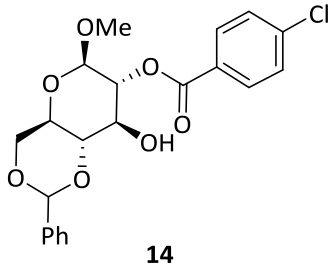
3.5337
2.6799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Cl
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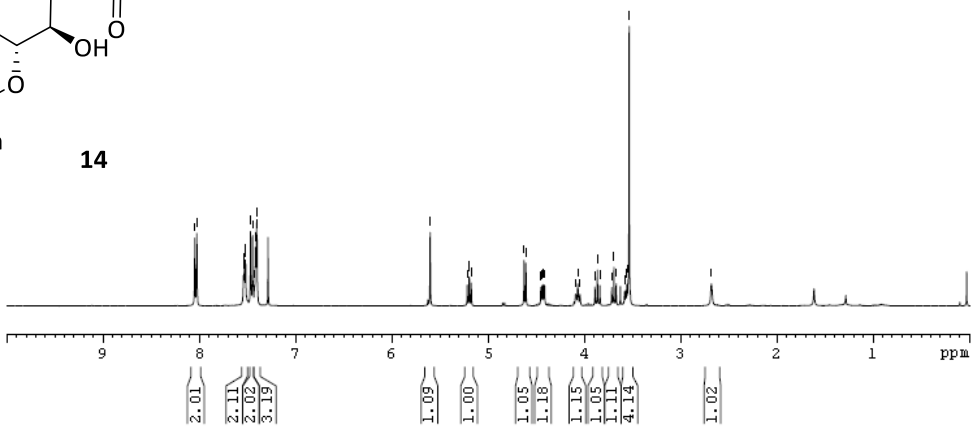
O
O
OH
O
O
Ph

14


9
8
7
6
5
4
3
2
1
ppm
2.01
2.11
2.02
3.19
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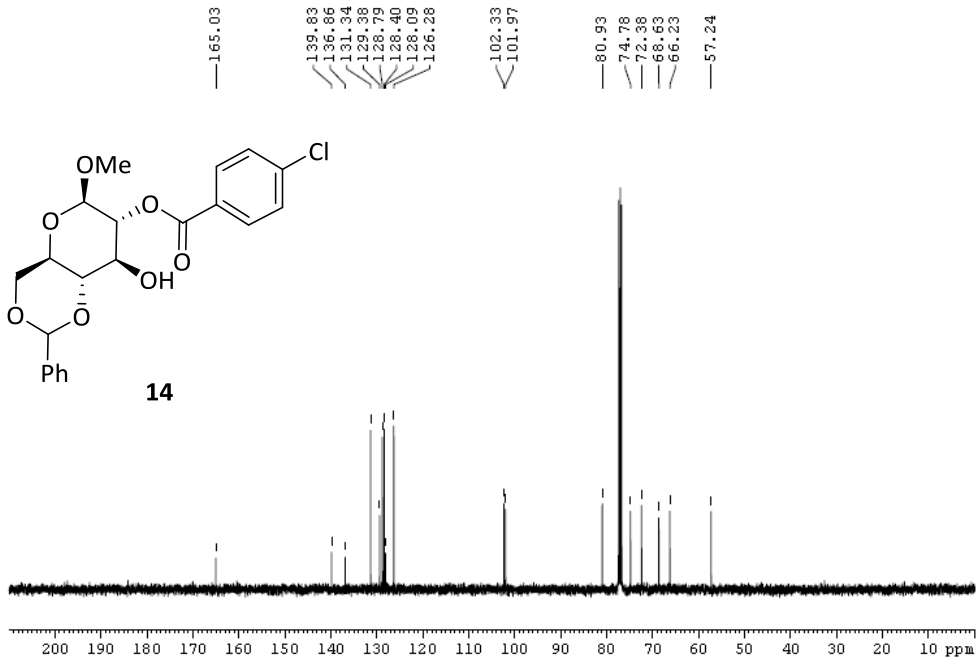
1.00
1.05
1.18
1.15
1.05
1.11
4.14
1.02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139.83
136.86
131.34
129.38
128.79
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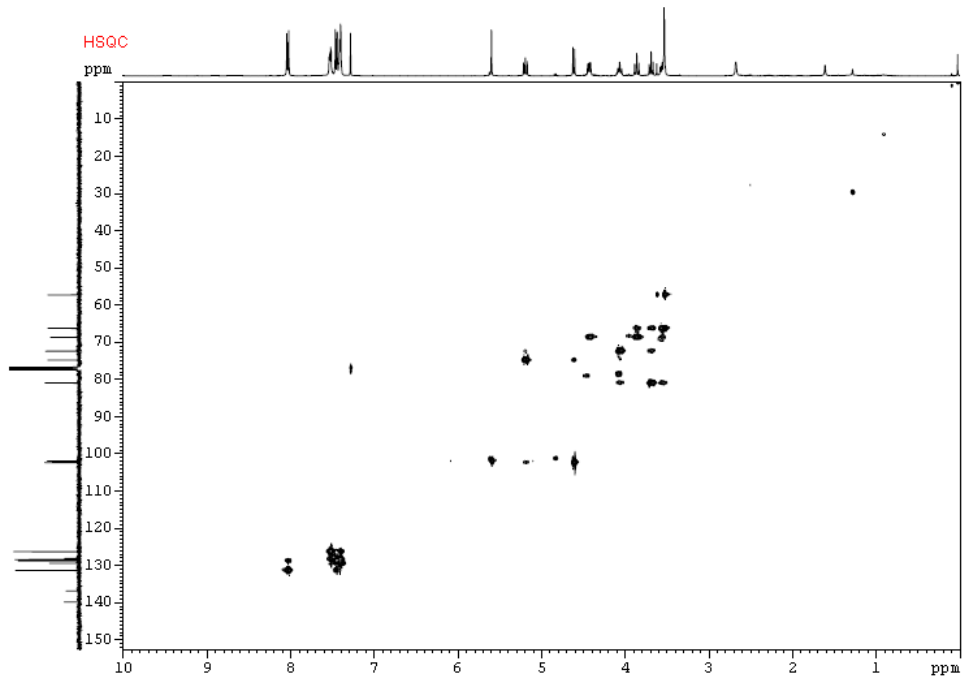
128.09
126.28
102.33
101.97
80.93
74.78
72.38
68.63
66.23
57.24
OMe
Cl
O
O
O
OH
O
O
Ph
14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


HSQC
ppm
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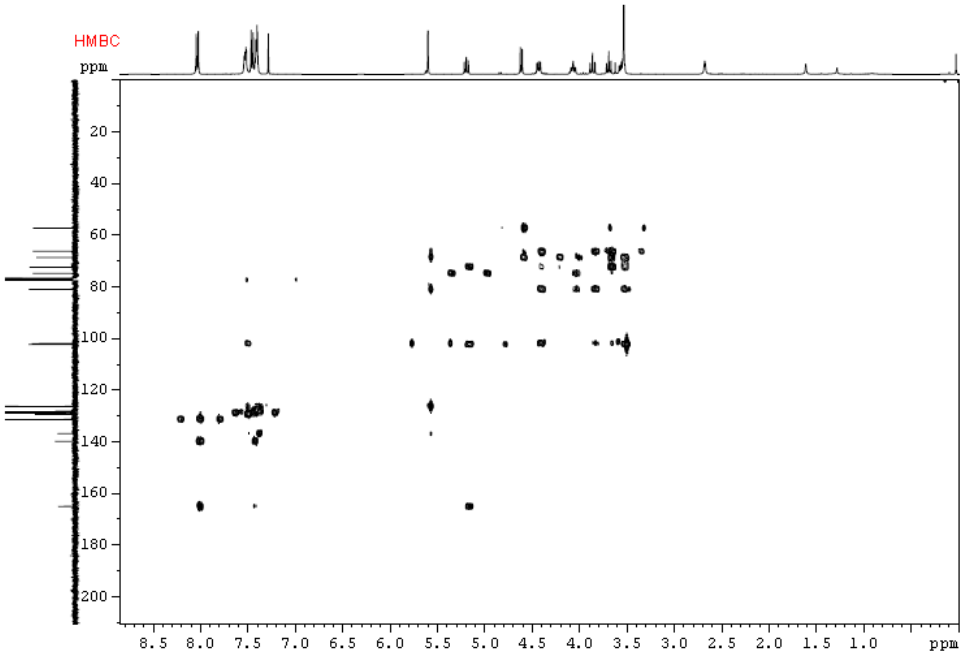
HMBC
ppm
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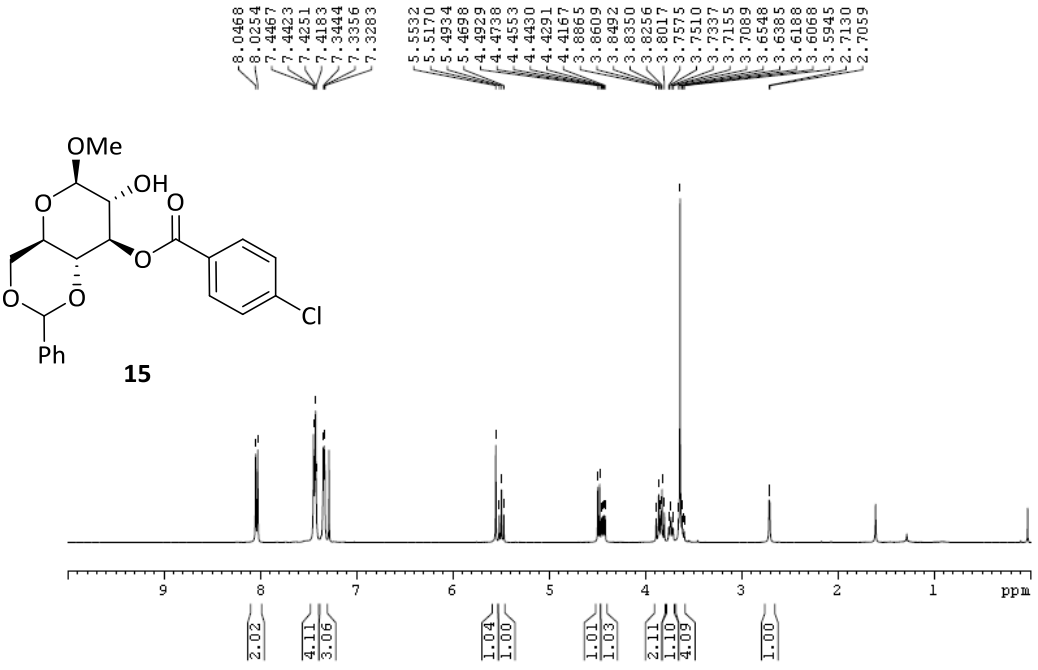
40
60
80
100
120
140
160
180
200
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm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7.3283
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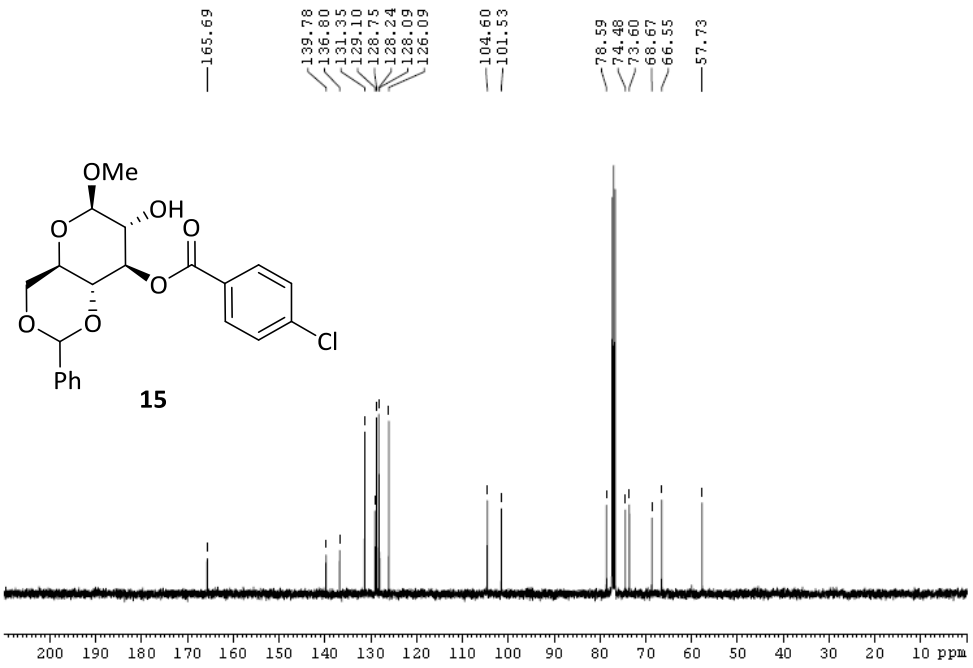
5.5170
5.4934
5.4698
4.4929
4.4738
4.4553
4.4430
4.4291
4.4167
3.8865
3.8609
3.8492
3.8350
3.8256
3.8017
3.7575
3.7510
3.7337
3.7155
3.7089
3.6548
3.6385
3.6188
3.6068
3.5945
2.7130
2.7059
OMe
OH
O
O
O
O
O
Cl
Ph
15
9
8
7
6
5
4
3
2
1
ppm
2.02
4.11
3.06
1.04
1.00
1.01
1.03
2.11
1.10
4.09
1.00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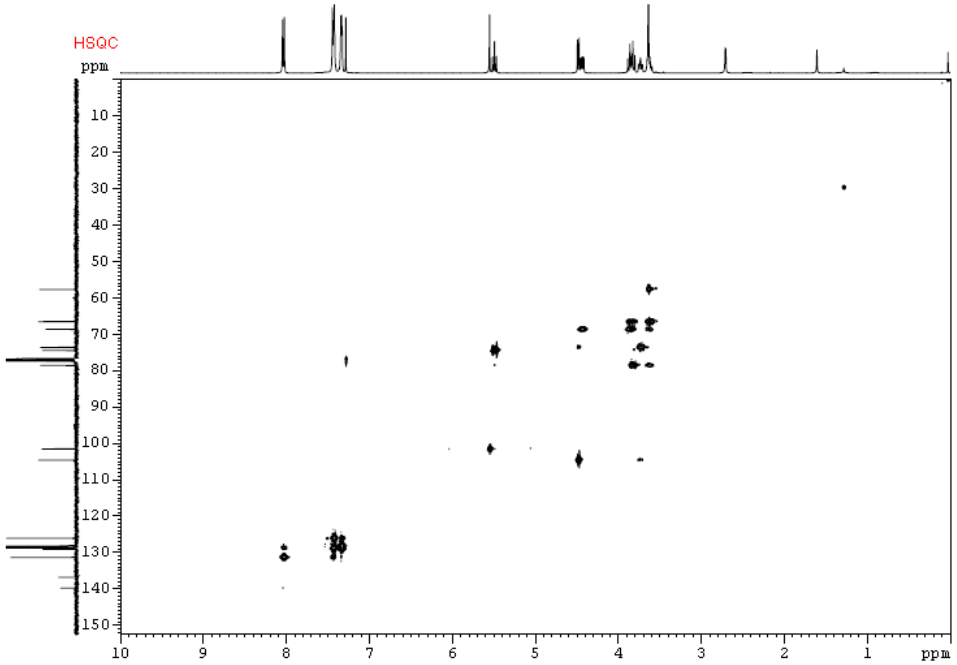
139.78
136.80
131.35
129.10
128.75
128.24
128.09
126.09
104.60
101.53
78.59
74.48
73.60
68.67
66.55
57.73
OMe
OH
O
O
O
O
O
Cl
Ph
15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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ppm
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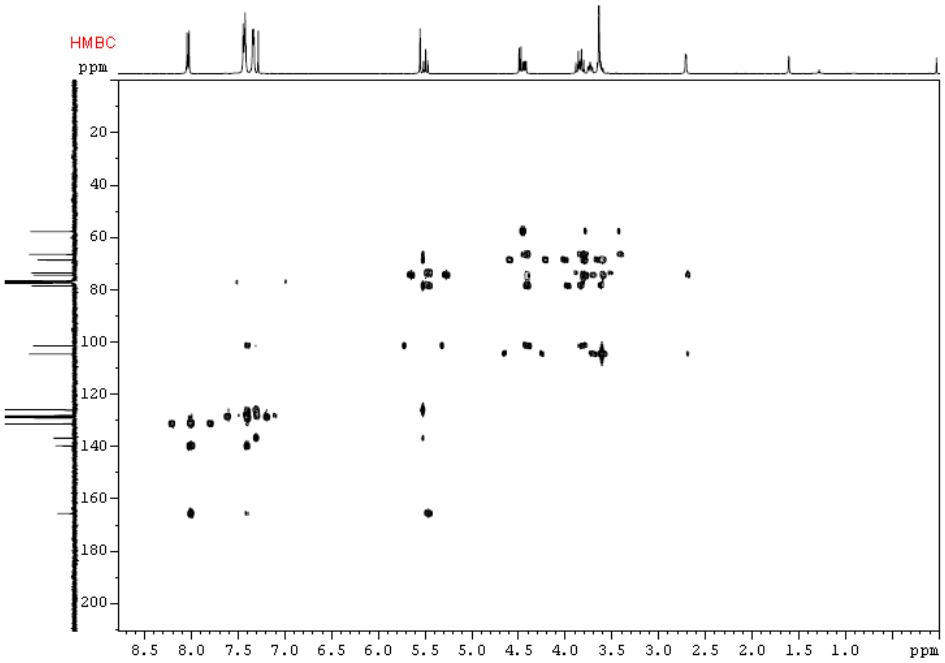
10 9 8 7 6 5 4 3 2 1 ppm


HMBC
ppm
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40
60
80
100
120
140
160
180
200
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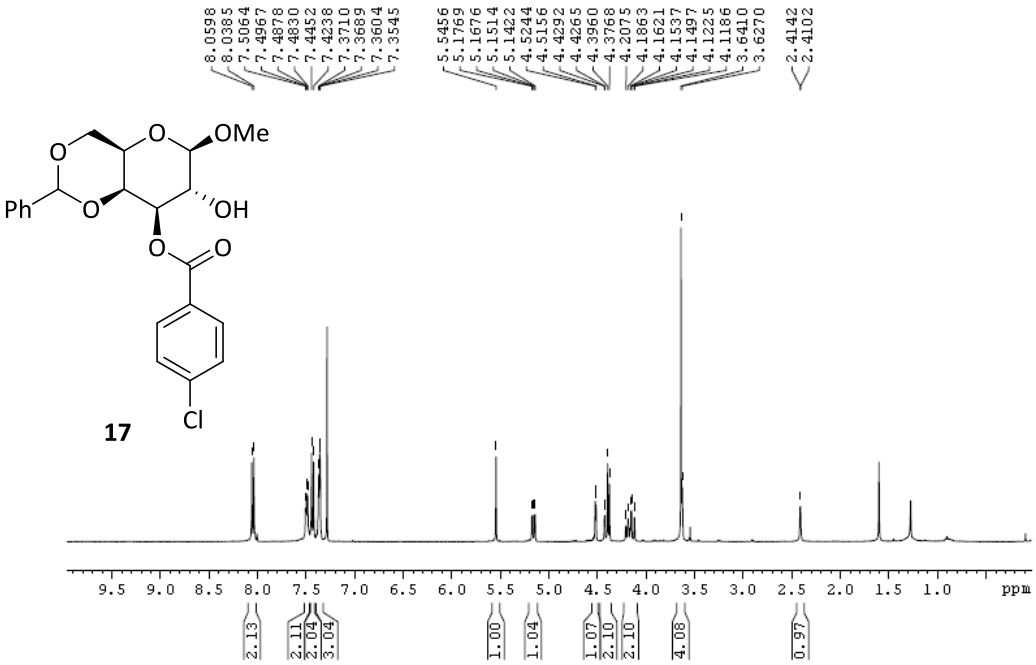
ppm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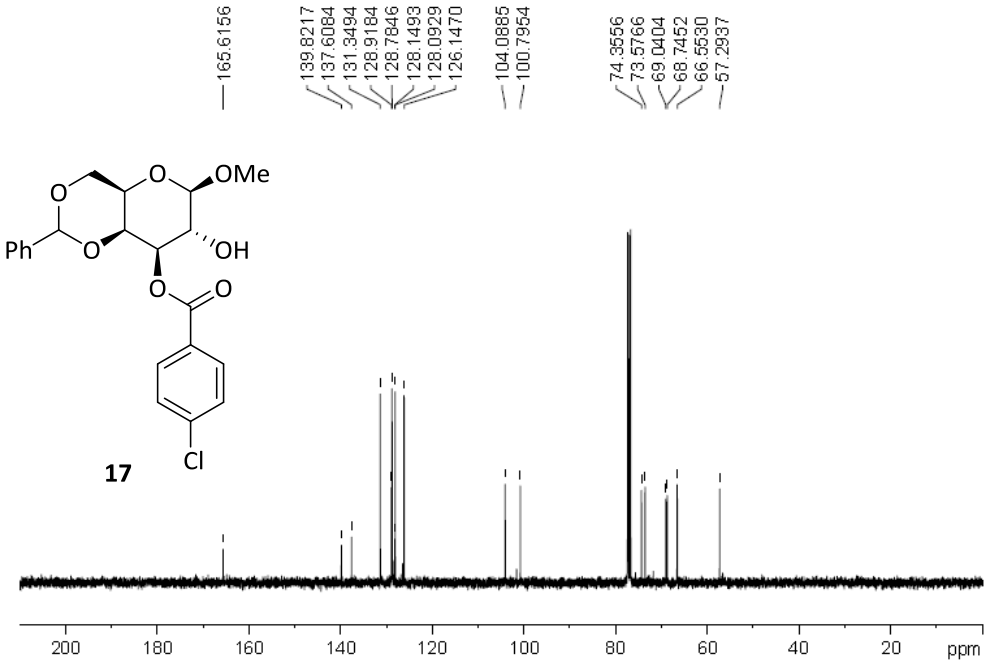
7.4238
7.3710
7.3689
7.3604
7.3545
5.5456
5.1769
5.1676
5.1514
5.1422
5.5244
4.5156
4.4292
4.4265
4.3960
4.3768
4.2075
4.1863
4.1621
4.1537
4.1497
4.1225
4.1186
3.6410
3.6270
2.4142
2.4102
O
O
OMe
Ph
O
OH
O
O
Cl
17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
2.13
2.11
2.04
3.04
1.00
1.04
1.07
2.10
2.10
4.08
0.97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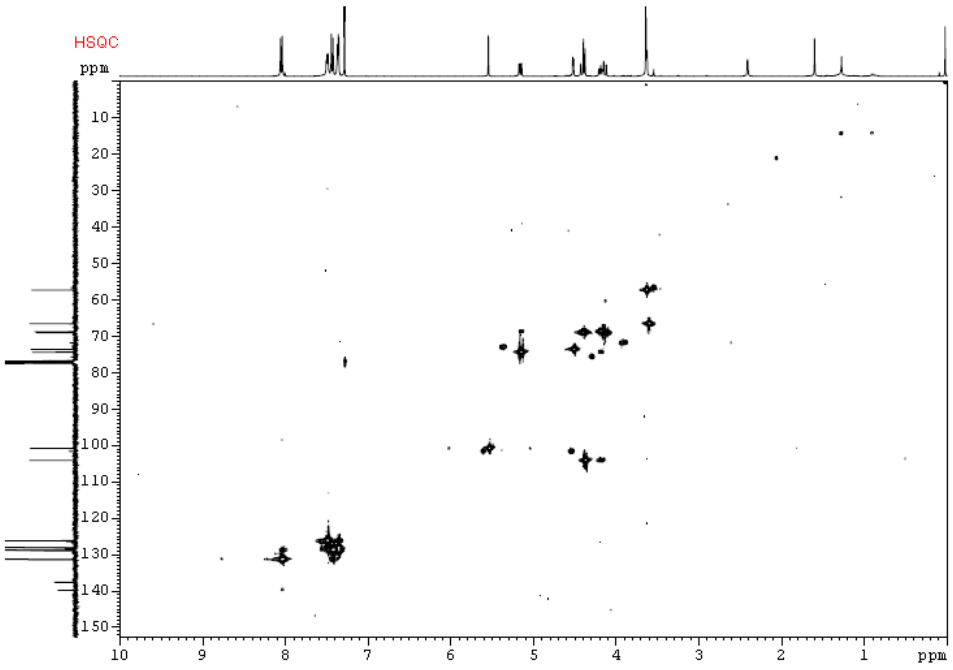
128.1493
128.0929
126.1470
104.0885
100.7954
74.3556
73.5766
69.0404
68.7452
66.5530
57.2937
OMe
OH
Ph
O
Cl
17
200
180
160
140
120
100
80
60
40
20
ppm


HSQC
ppm
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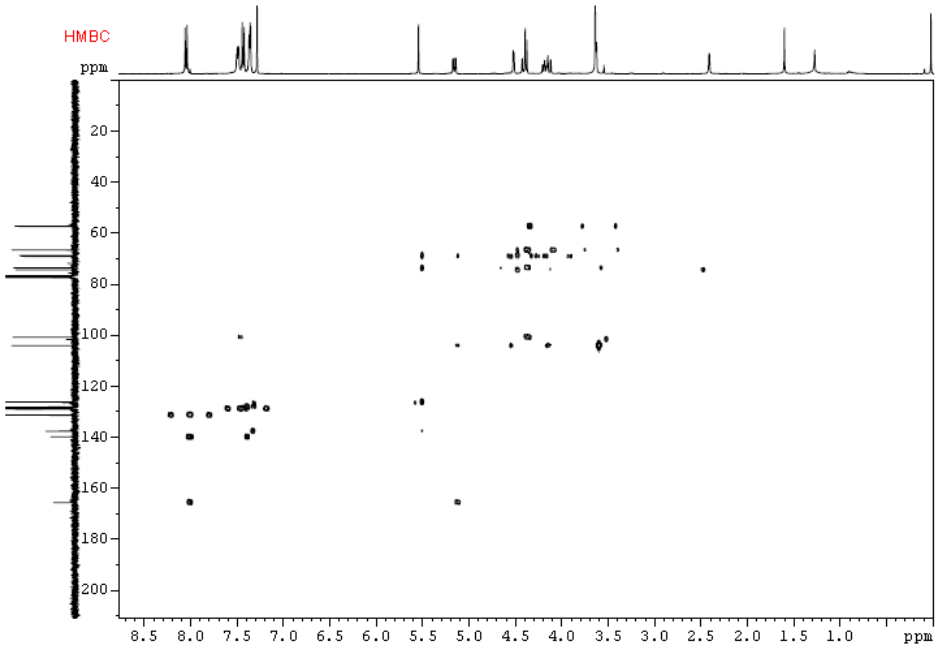
20
30
40
50
60
70
80
90
100
110
120
130
140
150
10
9
8
7
6
5
4
3
2
1
ppm


HMBC
ppm
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60
80
100
120
140
160
180
200
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
ppm