Supporting Information

Synthesis of Alkyl Halides from Aldehydes via Deformylative Halogenation

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Table of contents

1. General Information 3

2. Procedures 3

2.1 General Procedure for Synthesis of DHP starting materials **1** 4

2.2 General Procedure for Synthesis of Brominated Products **2** 6

2.3 General Procedure for Synthesis of Chlorinated Products **3** 7

2.4 Gram-scale Synthesis of **2a** 7

2.5 Procedures for Selectivity Study 8

2.6 Procedure for Light On/Off Experiment 9

2.7 Procedure for Radical Quenching Experiment 9

2.8 Optimization of deformylative iodination of **1a** 10

2.9 General Procedure for Synthesis of Iodinated Products **4** 10

3. Experimental Data 11

3.1 Experimental Data for DHPs **1** 11

3.2 Experimental Data for Brominated Products **2** 23

3.3 Experimental Data for Chlorinated Products **3** 31

3.4 Experimental Data for Iodinated Products **4** 38

4. NMR Spectral Data 43

4.1 NMR Spectral Data for DHPs **1** 43

4.2 NMR Spectral Data for Brominated Products **2** 66

4.3 NMR Spectral Data for Chlorinated Products **3** 92

4.4 NMR Spectral Data for Iodinated Products **4** 112

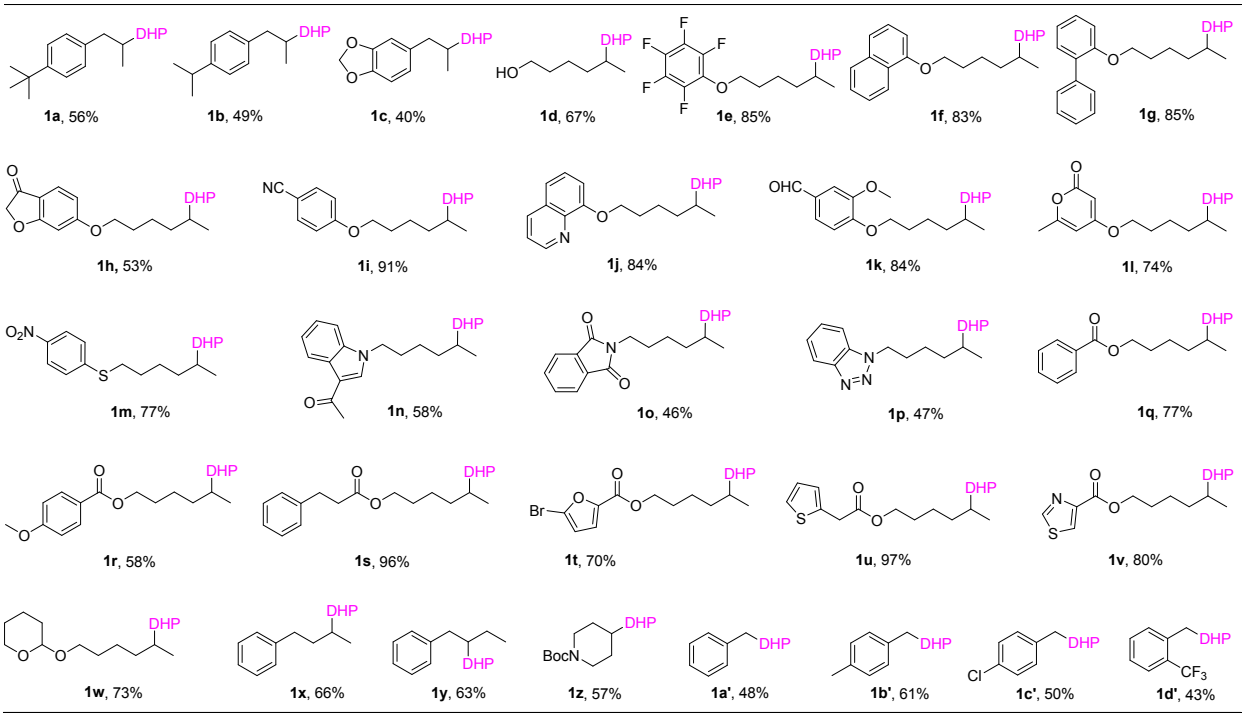
5. References Cited. 125

1. General Information

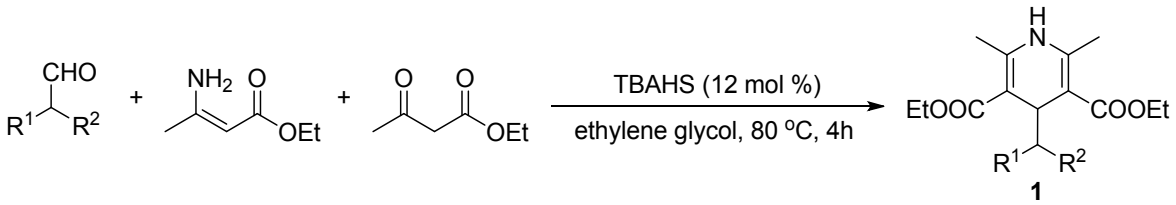
All commercial reagents were used without prior purification unless otherwise indicated. All reactions were performed under argon atmosphere. All reaction solvents were purified according to the method of Grubbs.[1] All compounds were purified by flash chromatography using a Teledyne Isco CombiFlash Rf 150 or preparative thin-layer chromatography (PTLC) on Analtech 1 mm silica gel GF plates. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 aluminum sheets. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ stain. ^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz, Varian Unity INOVA 500 MHz, and Varian VNMRS 700 MHz. ^{19}F NMR spectra were recorded on Varian MR-400 MHz. ^{1}H and ^{13}C NMR spectra are internally referenced to the residual solvent peaks (7.26 ppm and 77.16 ppm, respectively, for $CDCl_3$). ^{19}F NMR are internally referenced to $CFCl_3$ at δ 0.0 ppm. Data for ^{1}H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. High Resolution Mass Spectra were obtained using high-resolution mass spectrometer in the EI, ESI or APCI mode from Indiana University Bloomington Mass Spectral Facility.

2. Procedures

Synthesized DHP starting materials **1**: **1b**,[2] **1c**,[2] **1z**,[2] **1 a'**,[3] **1b'**[3] and **1c'**[3] are known compounds.

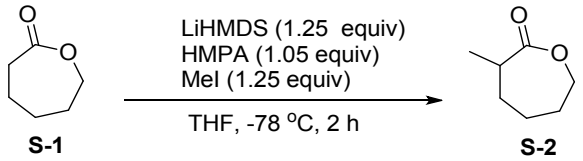


2.1 General procedure for synthesis of DHP starting materials 1



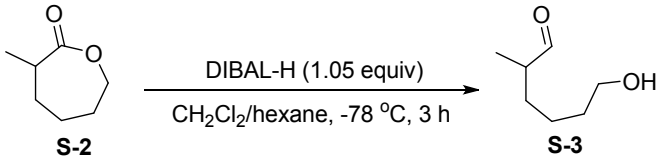
General procedure I: Over a solution of aldehyde (1 equiv), ethyl 3-aminocrotonate (1 equiv), and ethyl acetoacetate (1 equiv) in ethylene glycol (2.5 M) was added Bu_4NHSO_4 (12 mol %) in one portion. The vial was sealed and heated at 80 °C for 4 h. After consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel containing brine and extracted with EtOAc three times. After drying over anhydrous Na_2SO_4, it was filtered and taken to dryness. The crude reaction mixture was purified by flash column chromatography on silica gel to give DHP product **1**.

Synthesis of DHP starting material 1d



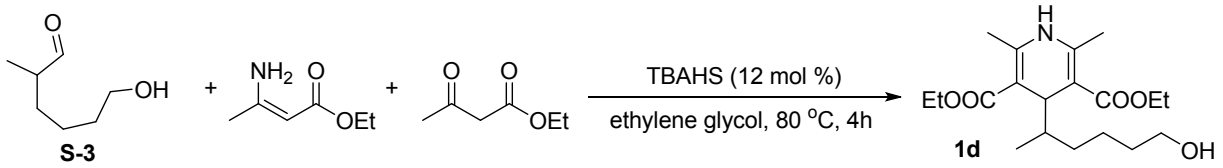
3-Methyloxepan-2-one (**S-2**)[4]

A solution of ε-caprolactone **S-1** (20.0 g, 176 mmol) in THF (60 mL) was added slowly to a solution of LiHMDS (220 mL, 1 mol/L in THF) in THF (100 mL) at -78 °C. After stirring for 50 min at -78 °C, HMPA (32.0 mL, 184 mmol) was added. After stirring for 10 min, MeI (13.7 mL, 220 mmol) was added dropwise. After stirring for 20 min, saturated aqueous NH_4Cl (40 mL) was added. The aqueous layer was extracted with Et_2O (3 × 100 mL). The combined extracts were washed with $Na_2S_2O_3$ (1 × 200 mL) and brine (1 × 200 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Purification by flash column chromatography on silica gel (0-10% EtOAc/hexane) gave lactone **S-2** as a colorless oil (6.8 g, 30%). The ^{1}H NMR spectral data match data previously reported.



6-Hydroxy-2-methylhexanal (**S-3**)[4b, 5]

To a stirred solution of the lactone **S-2** (6.4 g, 50 mmol) in a mixture of CH_2Cl_2 (120 mL) and hexane (120 mL) at -78 °C was slowly added DIBAH (52.5 mL, 1 mol/L in hexane), and the mixture was stirred for 3 h at the same temperature. After addition of Et_2O (80.0 mL) and water (50.0 mL) at 0 °C, the resulting mixture was stirred for 30 min at room temperature and then filtered through Celite. The filtrate was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give the aldehyde **S-3** as a pale yellowish oil which was used in the following reaction without purification.

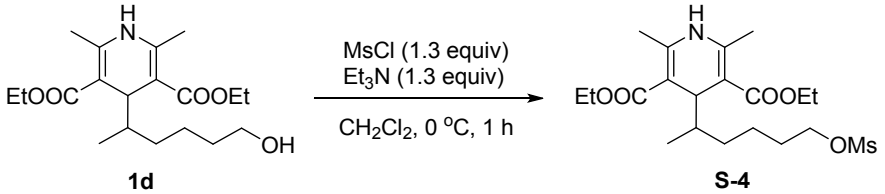


Diethyl 4-(6-hydroxyhexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1d**).[6]

The synthesis of **1d** was based on the <u>*general procedure I*</u>: Over a solution of **S-3** (5.9 g, 45 mmol), ethyl 3-aminocrotonate (5.8 g, 45 mmol), and ethyl acetoacetate (5.9 g, 45 mmol) in ethylene glycol (18 mL, 2.5 M) was added Bu_4NHSO_4 (1.4 g, 5.4 mmol, 12 mol %) in one portion. The vial was sealed and heated at 80 °C for 4 h. After complete consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc (40 mL). The solution was poured into a separatory funnel containing brine (60 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and

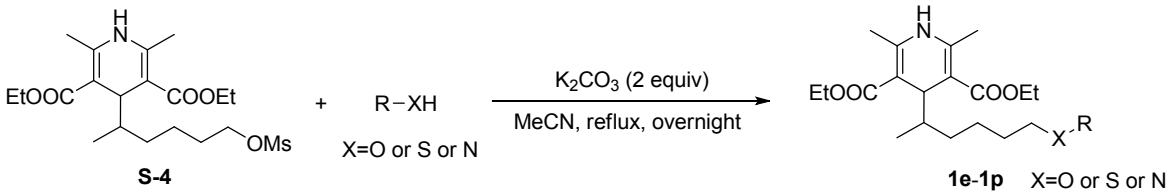
evaporated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (0-30% EtOAc/hexane) to give **1d** as a yellowish oil (10.7 g, 67% yield).

Synthesis of DHP starting materials 1e-1p



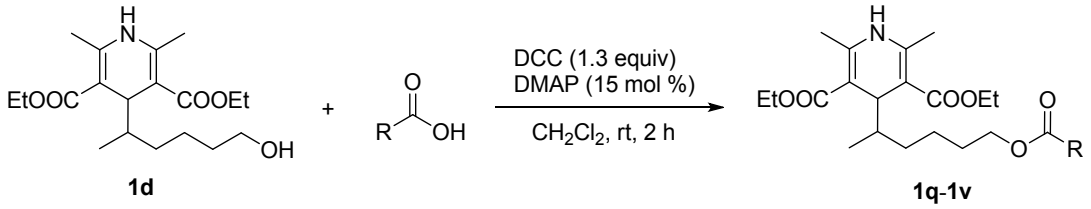
Diethyl 2,6-dimethyl-4-(6-((methylsulfonyl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**S-4**)

To a solution of the alcohol **1d** (4.3 g, 10 mmol) and triethylamine (1.8 mL, 13 mmol) in CH_2Cl_2 (20 mL) was added dropwise methanesulfonyl chloride (1.0 mL, 13 mmol) at 0 °C under argon. The reaction was stirred at 0 °C for 1 h. Then 2 M aq. NH_4Cl (20 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give **S-4** as a yellowish oil which was used in the following reaction without purification.



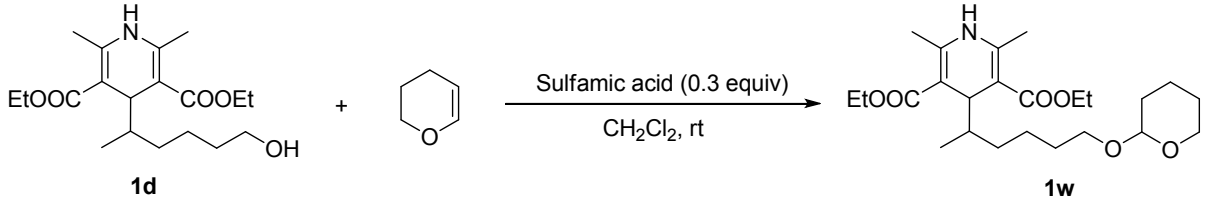
<u>*General procedure II*</u>: To a solution of **S-4** (431.5 mg, 1 mmol) in acetonitrile (4 mL) was added K_2CO_3 (276.4 mg, 2 mmol) and R-XH (1.2 mmol). The resulting mixture was refluxed overnight. After cool to rt the solvent was evaporated, and the residue was partitioned between ethyl acetate (4 mL) and water (4 mL), the aqueous layer was extracted with EtOAc (2 × 4 mL), and combined organic layers were washed with brine (4 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give **1e-1p**.

Synthesis of DHP starting materials 1q-1v



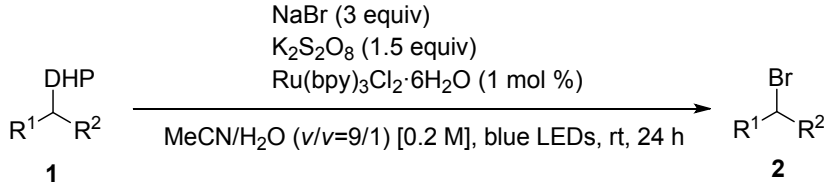
<u>*General procedure III*</u>: DMAP (244 mg, 2.0 mmol) was added to a stirred reaction mixture of **1d** (353.2 mg, 1 mmol), carboxylic acid (1 mmol), and DCC (268.2 mg, 1.3 mmol) in dry CH_2Cl_2 (2 mL) at room temperature. The reaction mixture was filtered after 2 h (TLC control), the precipitate was rinsed with CH_2Cl_2 (2 x 2 mL). The combined filtrates were evaporated to dryness. The crude mixture was purified by flash column chromatography on silica gel to give **1q-1v**.

Synthesis of DHP starting material 1w



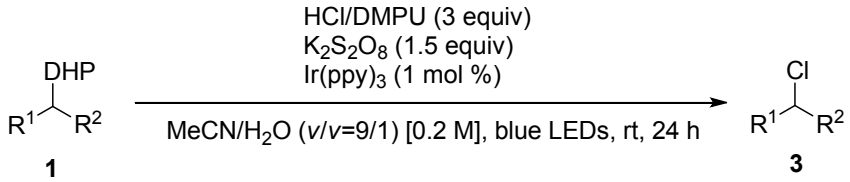
Procedure IV: To a stirred mixture of **1d** (353.2 mg, 1 mmol) and 3,4-dihydro-2H-pyran (109.2 mg, 1.3 mmol) in CH_2Cl_2, sulfamic acid (29.1 mg, 0.3 equiv) was added. The mixture was stirring at room temperature (15°C), and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was evaporated to dryness, and purified by flash column chromatography on silica gel to give **1w**.

2.2 General procedure for synthesis of brominated products 2



General procedure A: DHP **1** (0.1 mmol), NaBr (30.9 mg, 0.3 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.8 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, degassed solvent ($MeCN/H_2O$ = 450 µL/50 µL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was purified by either flash column chromatography on silica gel or preparative TLC to give **2**.

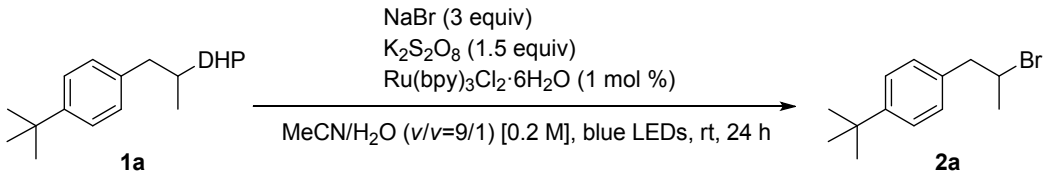
2.3 General procedure for synthesis of chlorinated products 3



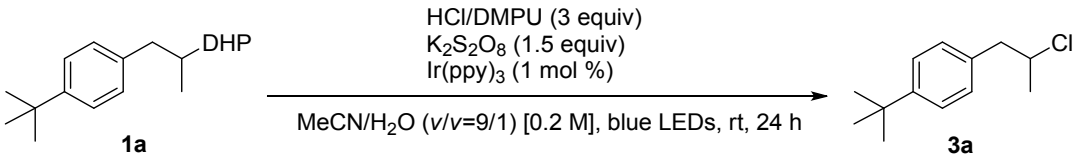
General procedure B: DHP **1** (0.1 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol) and $Ir(ppy)_3$ (0.7 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, HCl/DMPU (25.5 µL, 43% *w*/*w*, 0.3 mmol) and degassed solvent ($MeCN/H_2O$ = 450 µL/50 µL) was added under through syringe argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was

concentrated under reduced pressure and the crude product residue was purified by either flash column chromatography on silica gel or preparative TLC to give **3**.

2.4 Gram-scale synthesis of 2a and 3a



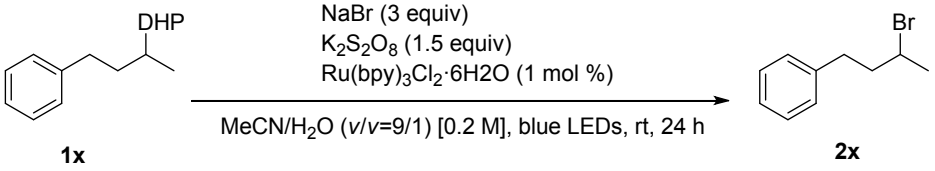
DHP **1a** (1.3 g, 3 mmol), NaBr (927.0 mg, 9 mmol), $K_2S_2O_8$ (1.2 g, 4.5 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (24.0 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, degassed solvent ($MeCN/H_2O$ = 13.5 mL/1.5 mL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was purified by flash column chromatography on silica gel to give **2a** in 79% isolated yield.



DHP **1a** (1.3 g, 3 mmol), $K_2S_2O_8$ (1.2 g, 4.5 mmol) and $Ir(ppy)_3$ (21.0 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, HCl/DMPU (765.0 µL, 43% *w*/*w*, 9 mmol) and degassed solvent ($MeCN/H_2O$ = 13.5 mL/1.5 mL) was added under through syringe argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was purified by flash column chromatography on silica gel to give **3a** in 67% isolated yield.

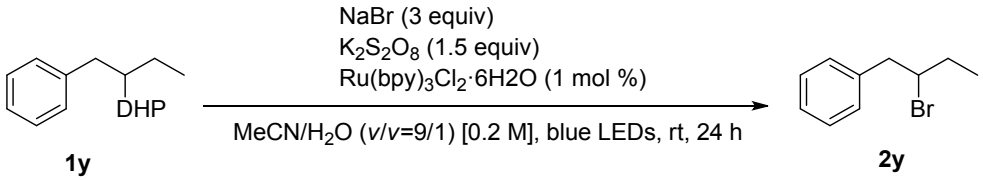
2.5 Procedures for selectivity study

Parallel experiment



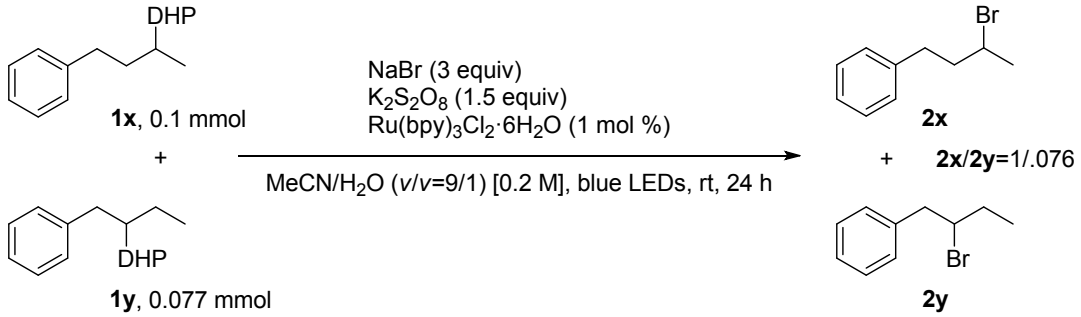
DHP **1x** (38.6 mg, 0.1 mmol), NaBr (30.9 mg, 0.3 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.8 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon.

Subsequently, degassed solvent (MeCN/H_2O = 450 μL/50 μL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was purified by flash column chromatography on silica gel to give **2x** in 81% isolated yield.



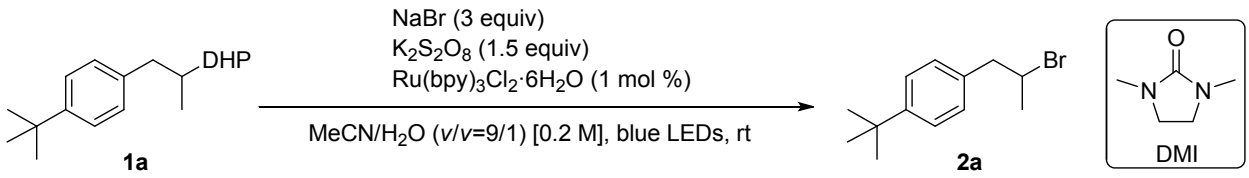
DHP **1y** (38.6 mg, 0.1 mmol), NaBr (30.9 mg, 0.3 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.8 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, degassed solvent (MeCN/H_2O = 450 μL/50 μL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was purified by flash column chromatography on silica gel to give **2y** in 81% isolated yield.

Crossover experiment



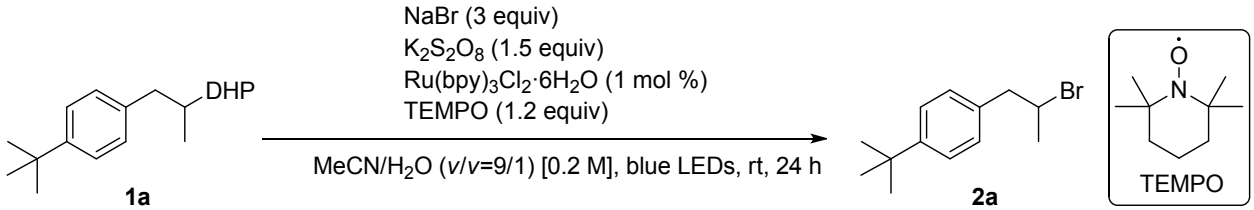
DHP **1x** (38.6 mg, 0.1 mmol), DHP **1y** (29.7 mg, 0.077 mmol), NaBr (61.8 mg, 0.6 mmol), $K_2S_2O_8$ (81.0 mg, 0.3 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1.6 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, degassed solvent (MeCN/H_2O = 900 μL/100 μL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product residue was analyzed by ^{1}H NMR to determine the ratio of **2x**/**2y** (1/0.76).

2.6 Procedure for light On/Off experiment



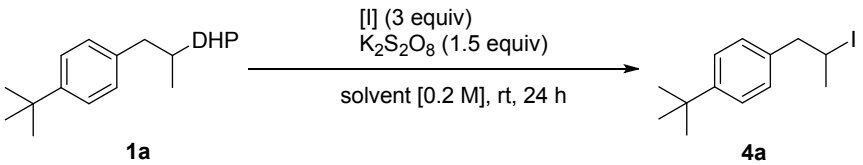
DHP **1a** (171.2 mg, 0.4 mmol), NaBr (123.6 mg, 1.2 mmol), $K_2S_2O_8$ (162.0 mg, 0.6 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3.2 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, internal standard DMI (45.6 mg, 0.4 mmol) and degassed solvent ($MeCN/H_2O$ = 1.8 mL/0.2 mL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 1 h at rt under irradiation of blue LEDs, then 50 µL of reaction solution was taken out through syringe under argon atmosphere and concentrated under reduced pressure, the crude mixture was analyzed by ^{1}H NMR to determine the yield of **2a**. Then the light source was removed, and the reaction was stirred in dark for another 1 h, then 50 µL of reaction solution was taken out through syringe under argon atmosphere and concentrated under reduced pressure, the crude mixture was analyzed by ^{1}H NMR to determine the yield of **2a**. This process repeated until 12 h (6 h under irradiation and 6 h in dark).

2.7 Procedure for radical quenching experiment



DHP **1a** (42.8 mg, 0.1 mmol), NaBr (30.9 mg, 0.3 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol), TEMPO (15.6 mg, 0.12 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.8 mg, 1 mol %) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar. Then the vail was capped and purged with three cycles of vacuum/argon. Subsequently, degassed solvent ($MeCN/H_2O$ = 450 µL/50 µL) was added through syringe under argon atmosphere. The reaction mixture was vigorously stirred for 24 h at rt under irradiation of blue LEDs. Then the vial was removed from the light source and the solid was filtered off. The filtrate was concentrated under reduced pressure, and the crude mixture was analyzed by ^{1}H NMR to determine the yield of **2a**.

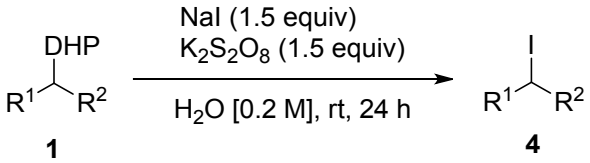
2.8 Optimization of deformylative iodination of 1a[a]



entry	[I]	Solvent	Yield(%)[b]
1	LiI	MeCN/H_2O (*v*/*v*=1:1)	99%
2	NaI	MeCN/H_2O (*v*/*v*=1:1)	99%
3	KI	MeCN/H_2O (*v*/*v*=1:1)	99%
4	HI	MeCN/H_2O (*v*/*v*=1:1)	99%
5	NaI	MeCN/H_2O (*v*/*v*=1:1)	99%
6	NaI	MeCN	0%
7	NaI	H_2O	99%
8	NaI	MeCN/H_2O (*v*/*v*=1:1)	99%[c]
9	NaI	MeCN/H_2O (*v*/*v*=1:1)	4%[d]
10	NaI	H_2O	99%[c],[e]

[a] Reaction conditions: **1a** (0.1 mmol), Iodide source [I] (0.3 mmol), $K_2S_2O_8$ (0.15 mmol), Solvent [0.5 ml], rt, 24 h, under air. [b]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Under air. [d] Without $K_2S_2O_8$. [e] 1.5 equiv of NaI.

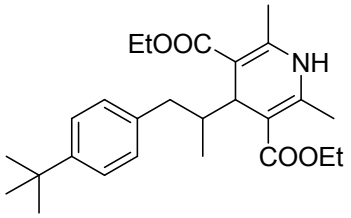
2.9 General procedure for synthesis of iodinated products 4



General procedure C: DHP **1** (0.1 mmol), $K_2S_2O_8$ (40.5 mg, 0.15 mmol), NaI (22.5 mg, 0.15 mmol) and H_2O (0.5 ml) were added to an oven-dried vial equipped with a PTFE-coated magnetic stir bar, and then the vail was capped. The reaction mixture was vigorously stirred for 24 h at rt under air. Then 2 ml of EtOAc was added and extracted with EtOAc(3 × 2ml). The organic layer was concentrated under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to give **4**.

3. Experimental Data

3.1 Experimental data for DHPs 1



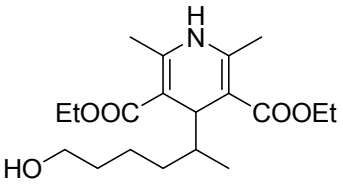
diethyl 4-(1-(4-(tert-butyl)phenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1a)

Prepared following *general procedure I* in 15 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow solid (3.6 g, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.57 (s, 1H), 4.27 – 4.13 (m, 5H), 2.76 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.31 (s, 6H), 2.11 – 2.06 (m, 1H), 1.78 – 1.70 (m, 1H), 1.33 – 1.26 (m, 15H), 0.65 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.5, 148.3, 144.9, 139.2, 128.8, 125.0, 102.1, 101.7, 59.8, 43.2, 38.9, 34.4, 31.6, 19.7, 19.6, 14.6, 14.5.

HRMS (ESI) m/z calcd. for $C_{26}H_{37}NO_4$ ([M + Na]$^+$) 450.2620, found 450.2618.



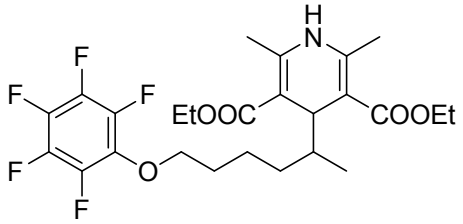
diethyl 4-(6-hydroxyhexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1d)

Prepared following *general procedure I* in 45 mmol scale. Purification by flash column chromatography (0–50% EtOAc/hexanes) provided the title compound as a yellow oil (10.7 g, 67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (s, 1H), 4.22 – 4.09 (m, 4H), 4.01 (d, *J* = 4.3 Hz, 1H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 6H), 1.74 (br, 1H), 1.52 – 1.46 (m, 2H), 1.41 – 1.26 (m, 10H), 1.00 – 0.93 (m, 1H), 0.71 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 168.6, 144.9, 144.7, 102.4, 101.2, 62.8, 59.8, 41.3, 37.7, 33.2, 32.5, 23.6, 19.5, 15.3, 14.5.

HRMS (ESI) m/z calcd. for $C_{19}H_{31}NO_5$ ([M + Na]$^+$) 376.2100, found 376.2098.



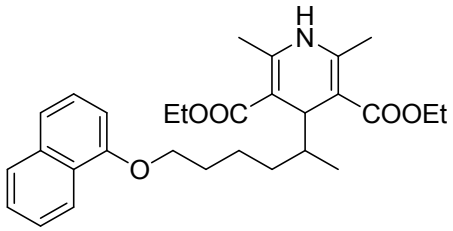
diethyl 2,6-dimethyl-4-(6-(perfluorophenoxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1e)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (441.3 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 4.20 – 4.04 (m, 6H), 3.97 (d, *J* = 4.4 Hz, 1H), 2.24 (s, 6H), 1.72 – 1.61 (m, 2H), 1.38 – 1.30 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H), 1.02 – 0.93 (m, 1H), 0.68 (d, *J* = 6.8 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -156.7 – -158.2 (m, 2F), -163.2 – -165.2 (m, 3F).

HRMS (ESI) m/z calcd. for $C_{25}H_{30}F_5NO_5$ ([M - H]$^-$) 518.1966, found 518.1960.



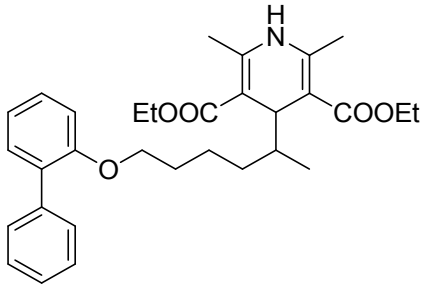
diethyl 2,6-dimethyl-4-(6-(naphthalen-1-yloxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1f)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (398.1 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 3H), 7.44 – 7.40 (m, 1H), 7.33 – 7.30 (m, 1H), 7.15 – 7.12 (m, 2H), 5.60 (s, 1H), 4.25 – 4.12 (m, 4H), 4.06 – 4.03 (m, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.85 – 1.73 (m, 2H), 1.58 – 1.27 (m, 10H), 1.12 – 1.03 (m, 1H), 0.76 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 169.0, 168.6, 157.2, 144.6, 134.8, 129.5, 129.0, 127.8, 126.8, 126.4, 123.5, 119.1, 106.7, 102.4, 101.5, 68.2, 59.8, 41.2, 38.0, 32.5, 29.7, 24.2, 19.5, 15.3, 14.6.

HRMS (ESI) m/z calcd. for $C_{29}H_{37}NO_5$ ([M + Na]$^+$) 502.2569, found 502.2566.

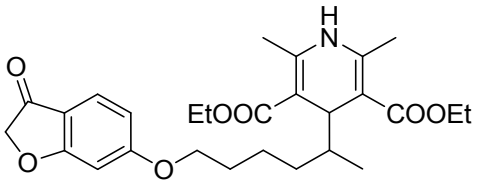


diethyl 4-(6-([1,1'-biphenyl]-2-yloxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1g)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (429.8mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.03 – 6.96 (m, 2H), 5.98 (s, 1H), 4.23 – 4.10 (m, 4H), 4.02 (d, *J* = 4.5 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.73 – 1.59 (m, 2H), 1.50 – 1.40 (m, 2H), 1.37 – 1.26 (m, 8H), 1.04 – 0.97 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 156.0, 145.0, 144.9, 138.7, 130.9, 130.8, 129.6, 128.6, 127.8, 126.7, 120.7, 112.5, 102.0, 101.1, 68.4, 59.6, 41.0, 37.9, 32.2, 29.5, 24.0, 19.3, 15.1, 14.4.



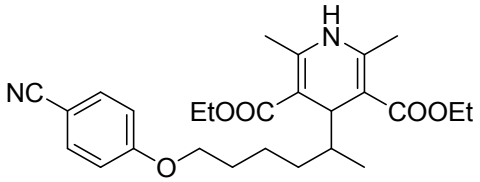
diethyl 2,6-dimethyl-4-(6-((3-oxo-2,3-dihydrobenzofuran-6-yl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1h)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (257.4mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 6.50 (s, 1H), 5.69 (s, 1H), 4.61 (s, 2H), 4.25 – 4.09 (m, 4H), 4.03 – 3.97 (m, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.79 – 1.68 (m, 2H), 1.53 – 1.26 (m, 10H), 1.08 – 0.99 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 176.7, 169.0, 168.6, 168.0, 144.8, 144.7, 125.1, 114.2, 112.2, 102.3, 101.3, 96.9, 75.7, 69.0, 59.8, 41.1, 37.9, 32.4, 29.3, 24.0, 19.5, 15.2, 14.5.

HRMS (ESI) m/z calcd. for $C_{27}H_{35}NO_7$ ([M + Na]$^+$) 508.2311, found 508.2306.



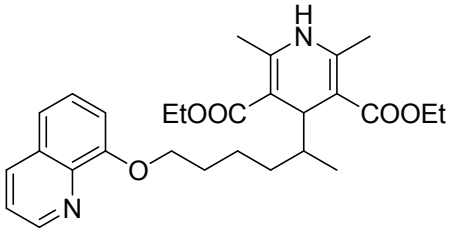
diethyl 4-(6-(4-cyanophenoxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1i)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (413.7mg, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.70 (s, 1H), 4.23 – 4.09 (m, 4H), 4.02 (d, *J* = 4.4 Hz, 1H), 3.96 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 6H), 1.79 – 1.66 (m, 2H), 1.52 – 1.26 (m, 10H), 1.07 – 1.00 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.5, 162.6, 144.8, 144.7, 134.0, 119.4, 115.3, 103.7, 102.3, 101.2, 68.6, 59.7, 41.2, 37.9, 32.5, 29.4, 24.0, 19.5, 15.2, 14.5.

HRMS (APCI) m/z calcd. for $C_{26}H_{34}N_2O_5$ ([M - H]$^-$) 453.2389, found 453.2383.



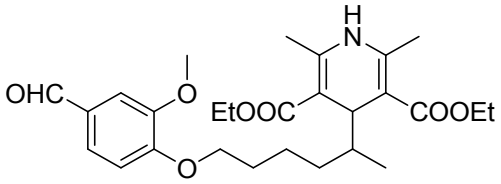
diethyl 2,6-dimethyl-4-(6-(quinoline-8-yloxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1j)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–60% EtOAc/hexanes) provided the title compound as a brown solid (403.7 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.49 – 7.31 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 4.30 – 4.05 (m, 6H), 4.01 (d, *J* = 4.4 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.00 – 1.82 (m, 2H), 1.57 – 0.99 (m, 10H), 1.15 – 1.03 (m, 1H), 0.76 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 168.6, 154.9, 149.0, 145.1, 145.0, 140.3, 135.9, 129.5, 126.8, 121.5, 119.3, 108.6, 101.7, 101.2, 69.0, 59.52, 59.49, 41.1, 37.9, 32.4, 29.4, 24.0, 19.14, 19.07, 15.6, 14.4, 14.2.

HRMS (APCI) m/z calcd. for $C_{28}H_{36}N_2O_5$ ([M + H]$^+$) 481.2702, found 481.2699.



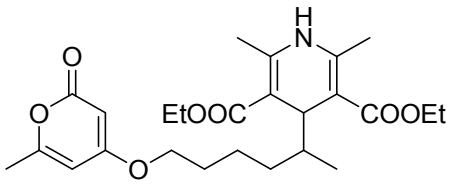
diethyl 4-(6-(4-formyl-2-methoxyphenoxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1k)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (409.6 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.40 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.59 (s, 1H), 4.23 – 4.11 (m, 4H), 4.06 (t, *J* = 7.0 Hz, 2H), 4.02 (d, *J* = 4.4 Hz, 1H), 3.91 (s, 3H), 2.28 (s, 6H), 1.88 – 1.75 (m, 2H), 1.54 – 1.26 (m, 10H), 1.10 – 1.00 (m, 1H), 0.74 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 169.0, 168.6, 154.4, 150.0, 144.8, 130.0, 126.9, 111.55, 109.4, 102.2, 101.3, 69.4, 59.7, 56.1, 41.1, 38.0, 32.4, 29.4, 24.0, 19.5, 15.2, 14.5.

HRMS (ESI) m/z calcd. for $C_{27}H_{37}NO_7$ ([M + Na]$^+$) 510.2468, found 510.2463.



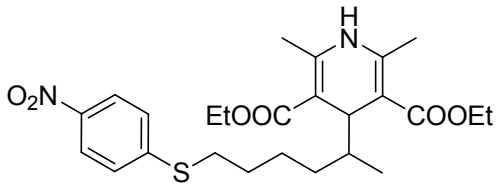
diethyl 2,6-dimethyl-4-(6-((6-methyl-2-oxo-2H-pyran-4-yl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1l)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (341.5 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.76 (s, 1H), 5.34 (s, 1H), 4.22 – 4.08 (m, 4H), 4.00 (d, *J* = 4.4 Hz, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 6H), 2.19 (s, 3H), 1.71 – 1.63 (m, 2H), 1.44 – 1.23 (m, 10H), 1.05 – 0.90 (m, 1H), 0.72 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 169.0, 168.6, 165.4, 162.1, 145.0, 102.1, 101.2, 100.9, 87.7, 69.0, 59.7, 41.0, 37.9, 32.1, 28.7, 23.8, 19.9, 19.5, 15.2, 14.6.

HRMS (ESI) m/z calcd. for $C_{25}H_{35}NO_7$ ([M - H]$^-$) 460.2335, found 460.2331.



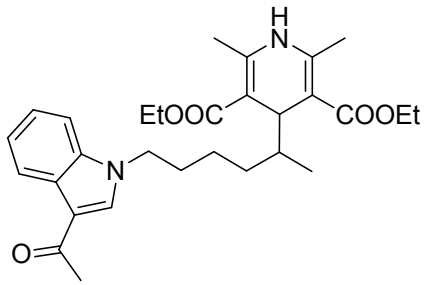
diethyl 2,6-dimethyl-4-(6-((4-nitrophenyl)thio)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1m)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow oil (377.8 mg, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 5.62 (s, 1H), 4.24 – 4.10 (m, 4H), 4.01 (d, *J* = 4.3 Hz, 1H), 3.02 – 2.93 (m, 2H), 2.28 (s, 6H), 1.68 – 1.62 (m, 2H), 1.52 – 1.23 (m, 10H), 1.04 – 0.97 (m, 1H), 0.72 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.5, 148.4, 145.0, 144.8, 126.1, 124.0, 102.3, 101.3, 59.8, 41.1, 38.0, 32.2, 32.1, 29.0, 27.0, 19.6, 15.2, 14.6.

HRMS (ESI) m/z calcd. for $C_{25}H_{34}N_2O_6S$ ([M + Na]$^+$) 513.2035, found 513.2031.



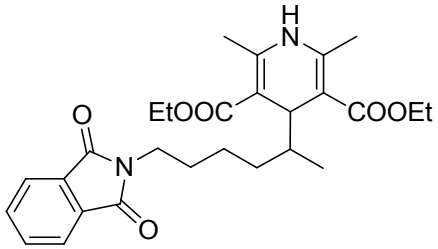
diethyl 4-(6-(3-acetyl-1H-indol-1-yl)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1n)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow solid (286.9 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 – 8.33 (m, 1H), 7.74 (s, 1H), 7.35 – 7.33 (m, 1H), 7.29 – 7.21 (m, 2H), 6.32 (s, 1H), 4.22 – 4.06 (m, 6H), 4.01 (d, *J* = 4.4 Hz, 1H), 2.51 (s, 3H), 2.27 (s, 6H), 1.83 – 1.76 (m, 2H), 1.42 – 1.20 (m, 10H), 1.05 – 0.98 (m, 1H), 0.71 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 169.0, 168.6, 145.2, 136.8, 135.2, 132.5, 126.3, 123.2, 122.5, 116.7, 111.7, 110.0, 101.7, 100.7, 59.6, 47.1, 40.9, 37.8, 32.0, 30.1, 27.6, 24.8, 19.3, 15.1, 14.4.

HRMS (ESI) m/z calcd. for $C_{29}H_{38}N_2O_5$ ([M + Na]$^+$) 517.2678, found 517.2675.



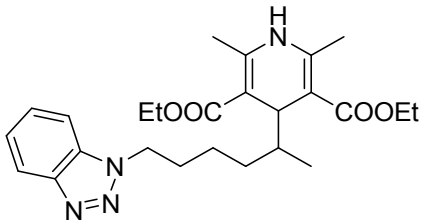
diethyl 4-(6-(1,3-dioxoisoindolin-2-yl)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1o)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow oil (222.0 mg, 46% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.71 – 7.67 (m, 2H), 5.62 (s, 1H), 4.23 – 4.09 (m, 4H), 3.98 (d, *J* = 4.6 Hz, 1H), 3.63 (t, *J* = 7.4 Hz, 2H), 2.27 (s, 6H), 1.63 – 1.53 (m, 2H), 1.42 – 1.24 (m, 10H), 1.04 – 0.96 (m, 1H), 0.71 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 168.5, 144.8, 144.7, 133.9, 132.4, 123.2, 102.3, 101.5, 59.7, 41.1, 38.3, 38.1, 32.2, 29.1, 25.1, 19.5, 15.3, 14.5.

HRMS (ESI) m/z calcd. for $C_{27}H_{34}N_2O_6$ ([M - H]$^-$) 481.2339, found 481.2334.



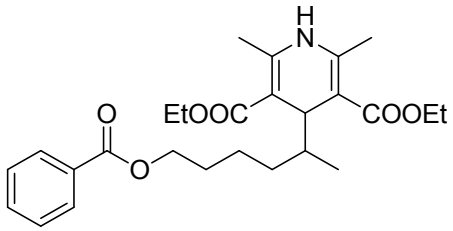
diethyl 4-(6-(1H-benzo[d][1,2,3]triazol-1-yl)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1p)

Prepared following *general procedure II* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow oil (213.6 mg, 47% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.34 – 7.30 (m, 1H), 6.28 (s, 1H), 4.57 (t, *J* = 7.3 Hz, 2H), 4.18 – 4.05 (m, 4H), 3.96 (d, *J* = 4.3 Hz, 1H), 2.25 (s, 6H), 1.97 – 1.85 (m, 2H), 1.39 – 1.21 (m, 10H), 1.01 – 1.95 (m, 1H), 0.66 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 168.6, 145.9, 145.2, 133.0, 127.2, 123.9, 119.9, 109.5, 101.8, 100.9, 59.6, 48.3, 40.9, 37.8, 31.9, 30.1, 24.8, 19.3, 15.2, 14.5.

HRMS (ESI) m/z calcd. for $C_{25}H_{34}N_4O_4$ ([M + Na]$^+$) 477.2478, found 477.2474.



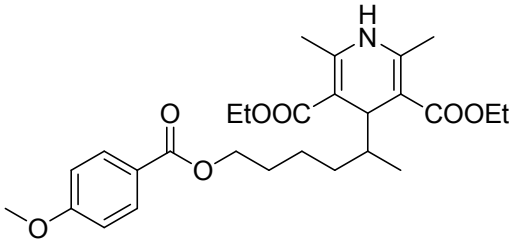
diethyl 4-(6-(benzoyloxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1q)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (352.3 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.3 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.46 – 7.37 (m, 2H), 5.53 (s, 1H), 4.30 – 4.10 (m, 6H), 4.02 (d, *J* = 4.4 Hz, 1H), 2.28 (s, 6H), 1.57 – 1.45 (m, 2H), 1.41 – 1.19 (m, 10H), 1.02 – 0.92 (m, 1H), 0.74 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.5, 166.8, 144.8, 144.6, 132.9, 130.7, 129.7, 128.5, 102.4, 101.4, 65.3, 59.8, 41.2, 38.0, 32.4, 29.2, 24.2, 19.6, 15.2, 14.6.

HRMS (APCI) m/z calcd. for $C_{26}H_{35}NO_6$ ([M - H]$^-$) 456.2386, found 456.2379.



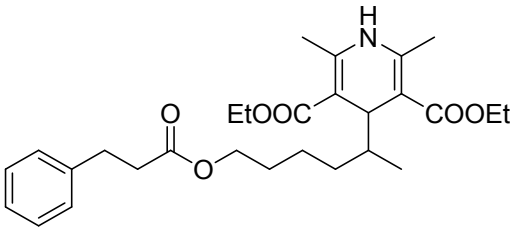
diethyl 4-(6-((4-methoxybenzoyl)oxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1r)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (282.8 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.03 (s, 1H), 4.26 – 4.06 (m, 6H), 4.00 (d, *J* = 4.3 Hz, 1H), 3.82 (s, 3H), 2.25 (s, 6H), 1.66 – 1.61 (m, 2H), 1.46 – 1.22 (m, 10H), 1.05 – 0.94 (m, 1H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 166.5, 163.3, 145.1, 144.9, 131.6, 123.0, 113.6, 102.0, 101.0, 65.0, 59.6, 55.5, 41.1, 37.8, 32.3, 29.2, 24.1, 19.3, 15.1, 14.5.

HRMS (ESI) m/z calcd. for $C_{27}H_{37}NO_7$ ([M - H]$^-$) 486.2492, found 486.2486.

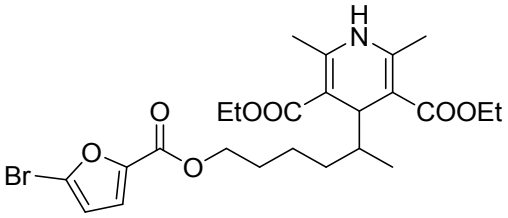


diethyl 2,6-dimethyl-4-(6-((3-phenylpropanoyl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1s)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (466.2 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 5H), 5.61 (s, 1H), 4.21 – 4.06 (m, 4H), 4.05 – 3.98 (m, 3H), 2.92 (t, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.26 (s, 6H), 1.57 – 1.45 (m, 2H), 1.42 – 1.22 (m, 10H), 1.02 – 0.92 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.0, 168.5, 144.8, 144.7, 140.7, 128.6, 128.4, 126.3, 102.3, 101.3, 64.9, 59.7, 41.1, 38.0, 36.1, 32.4, 31.1, 29.1, 24.0, 19.5, 15.2, 14.5.



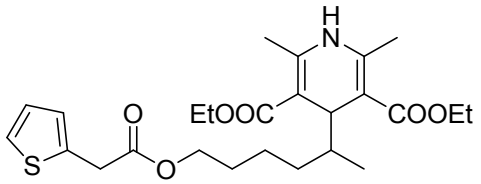
diethyl 4-(6-((5-bromofuran-2-carbonyl)oxy)hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1t)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow oil (368.5 mg, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 3.5 Hz, 1H), 6.06 (s, 1H), 4.26 – 4.06 (m, 6H), 3.98 (d, *J* = 4.4 Hz, 1H), 2.25 (s, 6H),1.69 – 1.58 (m, 2H), 1.39 – 1.22 (m, 10H), 1.03 – 0.94 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.6, 157.8, 146.5, 145.1, 145.0, 127.4, 120.0, 114.0, 102.0, 101.0, 65.5, 59.7, 41.1, 37.8, 32.3, 29.0, 23.9, 19.3, 15.1, 14.5.

HRMS (ESI) m/z calcd. for $C_{24}H_{32}BrNO_7$ ([M + Na]$^+$) 548.1081, found 548.1074.



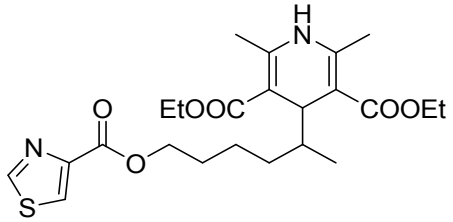
diethyl 2,6-dimethyl-4-(6-(2-(thiophen-2-yl)acetoxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1u)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow oil (463.3 mg, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 4.9 Hz, 1H), 6.95 – 6.92 (m, 2H), 5.76 (s, 1H), 4.24 – 4.06 (m, 6H), 3.99 (d, *J* = 4.4 Hz, 1H), 3.81 (s, 2H), 2.27 (s, 6H), 1.63 – 1.50 (m, 2H), 1.44 – 1.20 (m, 10H), 1.01 – 0.91 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.0, 168.6, 144.9, 144.8, 135.3, 127.0, 126.9, 125.1, 102.2, 101.2, 65.5, 59.7, 41.1, 37.9, 35.6, 32.3, 29.0, 23.9, 19.5, 15.2, 14.5.

HRMS (ESI) m/z calcd. for $C_{25}H_{35}NO_6S$ ([M + Na]$^+$) 500.2083, found 500.2080.



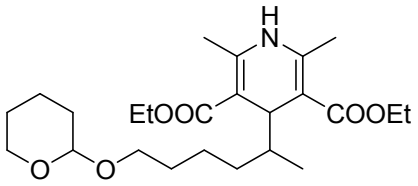
diethyl 2,6-dimethyl-4-(6-((thiazole-4-carbonyl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1v)

Prepared following *general procedure III* in 1 mmol scale. Purification by flash column chromatography (0–40% EtOAc/hexanes) provided the title compound as a yellow solid (371.7 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.23 (s, 1H), 5.78 (s, 1H), 4.33 (t, *J* = 7.8 Hz, 2H), 4.23 – 4.09 (m, 4H), 4.00 (d, *J* = 4.1 Hz, 1H), 2.27 (s, 6H), 1.78 – 1.65 (m, 2H), 1.46 – 1.23 (m, 10H), 1.07 – 0.94 (m, 1H), 0.72 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.6, 161.5, 153.5, 148.4, 144.9, 144.8, 127.3, 102.2, 101.3, 65.9, 59.7, 41.1, 38.0, 32.3, 29.2, 24.0, 19.5, 15.3, 14.5.

HRMS (ESI) m/z calcd. for $C_{23}H_{32}N_2O_6S$ ([M + Na]$^+$) 487.1879, found 487.1875.



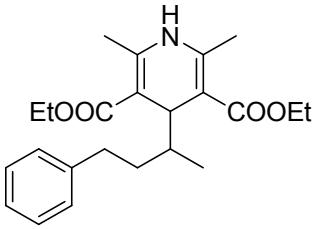
diethyl 2,6-dimethyl-4-(6-((tetrahydro-2H-pyran-2-yl)oxy)hexan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1w)

Prepared following *general procedure IV* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (319.4 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 4.53 (t, *J* = 4.1 Hz, 1H), 4.23 – 4.04 (m, 4H), 3.98 (d, *J* = 4.5 Hz, 1H), 3.86 – 3.65 (m, 2H), 3.49 – 3.29 (m, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.85 – 1.64 (m, 2H), 1.57 – 1.23 (m, 16H), 1.03 – 0.89 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 144.8, 144.6, 102.3, 101.4, 99.0, 67.8, 62.4, 59.7, 41.2, 38.0, 32.6, 30.9, 30.3, 25.6, 24.3, 19.8, 19.4, 15.2, 14.5.

HRMS (APCI) m/z calcd. for $C_{24}H_{39}NO_6$ ([M - H]$^-$) 436.2699, found 436.2692.



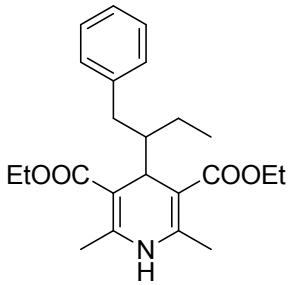
diethyl 2,6-dimethyl-4-(4-phenylbutan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1x)

Prepared following *general procedure I* in 0.5 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (127.2 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 5.88 (s, 1H), 4.25 – 4.14 (m, 4H), 4.11 (d, *J* = 4.4 Hz, 1H), 2.76 – 2.50 (m, 2H), 2.31 (s, 6H), 1.75 – 1.47 (m, 2H), 1.38 – 1.26 (m, 7H), 0.84 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.6, 145.0, 144.8, 143.2, 128.4, 128.2, 125.5, 102.0, 101.1, 59.7, 40.9, 37.9, 34.2, 33.9, 19.4, 15.2, 14.4.

HRMS (APCI) m/z calcd. for $C_{23}H_{31}NO_4$ ([M - H]$^-$) 384.2175, found 384.2170.



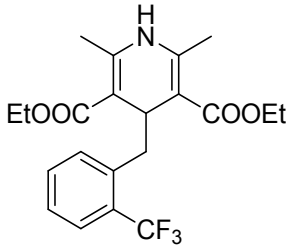
diethyl 2,6-dimethyl-4-(1-phenylbutan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1y)

Prepared following *general procedure I* in 0.5 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (123.3 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.13 – 7.06 (m, 3H), 5.88 (s, 1H), 4.28 (d, *J* = 3.7 Hz, 1H), 4.23 – 4.13 (m, 4H), 2.69 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 2.21 (dd, *J* = 13.7, 10.3 Hz, 1H), 1.57 – 1.53 (m, 1H), 1.30 – 1.26 (m, 6H), 1.14 – 1.06 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 168.4, 145.4, 144.9, 142.5, 129.1, 128.0, 125.4, 102.6, 101.1, 59.8, 50.4, 36.1, 35.0, 21.8, 19.5, 14.4, 12.0.

HRMS (APCI) m/z calcd. for $C_{23}H_{31}NO_4$ ([M - H]$^-$) 384.2175, found 384.2171.



diethyl 2,6-dimethyl-4-(2-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate (1d')

Prepared following *general procedure I* in 1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (176.9 mg, 43% yield).

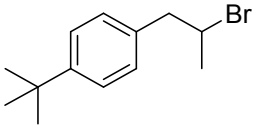
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.74 (s, 1H), 4.34 (t, *J* = 7.3 Hz, 1H), 4.02 – 3.90 (m, 2H), 3.87 – 3.75 (m, 2H), 2.74 (d, *J* = 7.2 Hz, 2H), 2.34 (s, 6H), 1.14 (t, *J* = 7.1 Hz, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.9 (s, 3F).

HRMS (ESI) m/z calcd. for $C_{21}H_{24}F_3NO_4$ ([M + Na]$^+$) 434.1551, found 434.1551.

3.2 Experimental data for brominated products 2

Products **2a** (CAS: 1310254-56-8), **2b** (CAS: 51259-03-1), **2c** (CAS: 5463-71-8),[7] **2d** (CAS: 34198-08-8),[8] **2s** (CAS: 180695-79-8),[8] **2t** (CAS: 100-39-0), **2u** (CAS: 104-81-4),[9] **2v** (CAS: 622-95-7)[10] and **2w** (CAS: 395-44-8) are known compounds.

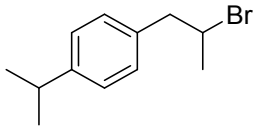


1-(2-bromopropyl)-4-(tert-butyl)benzene (2a)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–3% EtOAc/hexanes) provided the title compound as a colorless oil (23.5 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.35 – 4.26 (m, 1H), 3.23 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.03 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.70 (d, *J* = 6.6 Hz, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 135.6, 129.0, 125.5, 50.9, 47.2, 34.6, 31.5, 25.8.

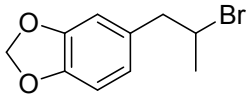


1-(2-bromopropyl)-4-isopropylbenzene (2b)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–3% EtOAc/hexanes) provided the title compound as a colorless oil (22.7 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.34 – 4.25 (m, 1H), 3.22 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.03 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.95 – 2.84 (m, 1H), 1.69 (d, *J* = 6.6 Hz, 3H), 1.26 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 136.0, 129.3, 126.6, 50.9, 47.3, 33.9, 25.8, 24.1.

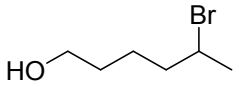


5-(2-bromopropyl)benzo[d][1,3]dioxole (2c)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (22.7 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 4.28 – 4.19 (m, 1H), 3.13 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.97 (dd, *J* = 14.1, 7.2 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.6, 132.4, 122.4, 109.7, 108.4, 101.1, 50.9, 47.3, 25.7.

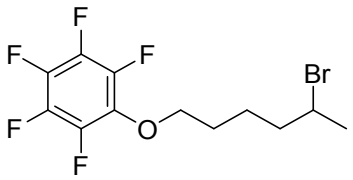


5-bromohexan-1-ol (2d)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a colorless oil (13.6 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 – 4.11 (m, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 1.89 – 1.75 (m, 2H), 1.72 (d, *J* = 6.7 Hz, 3H), 1.64 – 1.46 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 62.8, 51.8, 41.0, 32.2, 26.6, 24.2.



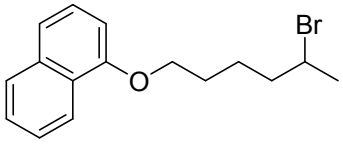
1-((5-bromohexyl)oxy)-2,3,4,5,6-pentafluorobenzene (2e)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (29.9 mg, 86% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 4.17 – 4.13 (m, 3H), 1.92 – 1.75 (m, 4H), 1.74 – 1.69 (m, 4H), 1.64 – 1.59 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -156.7 – -156.8 (m, 2F), -163.2 – -163.6 (m, 3F).

HRMS (EI) m/z calcd. for $C_{12}H_{12}BrF_5O$ $[M]^+$ 345.9992, found 345.9986.



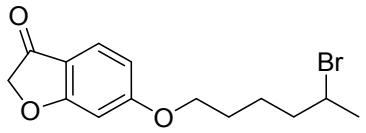
1-((5-bromohexyl)oxy)naphthalene (2f)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (23.6 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 3H), 7.45 – 7.41 (m, 1H), 7.35 – 7.31 (m, 1H), 7.16 – 7.13 (m, 2H), 4.23 – 4.14 (m, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.99 – 1.82 (m, 4H), 1.78 – 1.61 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 134.7, 129.5, 129.1, 127.8, 126.8, 126.5, 123.7, 119.1, 106.7, 67.8, 51.6, 41.0, 28.8, 26.6, 24.7.

HRMS (APCI) m/z calcd. for $C_{16}H_{19}BrO$ ($[M + H]^+$) 307.0698, found 307.0693.



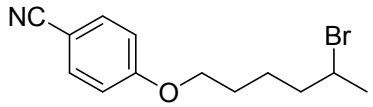
6-((5-bromohexyl)oxy)benzofuran-3(2H)-one (2g)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (19.4 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.53 (s, 1H), 4.62 (s, 2H), 4.19 – 4.09 (m, 1H), 4.04 (t, *J* = 6.2 Hz, 2H), 1.94 – 1.80 (m, 4H), 1.76 – 1.56 (m, 5H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 197.7, 176.7, 167.8, 125.2, 114.4, 112.2, 96.9, 75.7, 51.4, 40.8, 28.5, 26.6, 24.5.

HRMS (APCI) m/z calcd. for $C_{14}H_{18}BrO_3$ ([M + H]$^+$) 313.0439, found 313.0438.

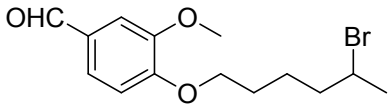


4-((5-bromohexyl)oxy)benzonitrile (2h)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by preparative thin-layer chromatography (15% EtOAc/hexanes) provided the title compound as a colorless oil (21.2 mg, 75% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.17 – 4.11 (m, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 1.92 – 1.79 (m, 4H), 1.74 – 1.68 (m, 4H), 1.63 – 1.58 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 162.4, 134.1, 119.4, 115.3, 104.0, 68.2, 51.4, 40.8, 28.5, 26.6, 24.5.



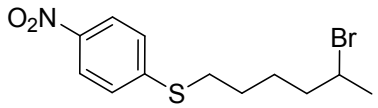
4-((5-bromohexyl)oxy)-3-methoxybenzaldehyde (2i)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (26.8 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.41 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 4.20 – 4.10 (m, 3H), 3.92 (s, 3H), 1.97 – 1.81 (m, 4H), 1.78 – 1.67 (m, 4H) 1.65 – 1.62 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 154.1, 150.0, 130.1, 126.9, 111.6, 109.4, 69.0, 56.2, 51.5, 40.8, 28.4, 26.6, 24.5.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}BrO_3$ ([M + H]$^+$) 315.0596, found 315.0590.



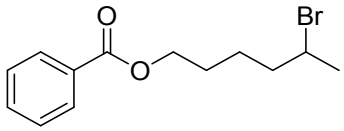
(5-bromohexyl)(4-nitrophenyl)sulfane (2j)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (26.7 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 4.17 – 4.08 (m, 1H), 3.04 (t, *J* = 7.0 Hz, 2H), 1.90 – 1.66 (m, 8H), 1.66 – 1.58 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.1, 126.3, 124.1, 51.2, 40.6, 31.9, 28.0, 27.2, 26.6.

HRMS (APCI) m/z calcd. for $C_{12}H_{16}BrNO_2S$ ([M + H]$^+$) 318.0163, found 318.0158.



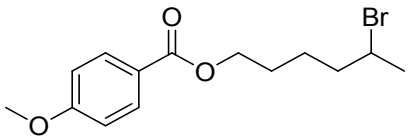
5-bromohexyl benzoate (2k)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (25.1 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 4.20 – 4.11 (m, 1H), 1.96 – 1.76 (m, 4H), 1.73 – 1.66 (m, 4H), 1.65 – 1.60 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 133.0, 130.6, 129.7, 128.5, 64.8, 51.4, 40.8, 28.3, 26.6, 24.5.

HRMS (APCI) m/z calcd. for $C_{13}H_{17}BrO_2$ ([M + H]$^+$) 285.0490, found 285.0486.



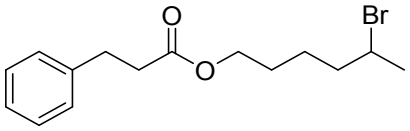
5-bromohexyl 4-methoxybenzoate (2l)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (24.6 mg, 78% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.30 (t, *J* = 7.7 Hz, 2H), 4.16 – 4.10 (m, 1H), 3.86 (s, 3H), 1.92 – 1.74 (m, 4H), 1.74 – 1.64 (m, 4H), 1.48 – 1.41 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 166.5, 163.4, 131.7, 122.9, 113.7, 55.6, 55.6, 51.5, 40.8, 28.3, 26.6, 24.5.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}BrO_3$ ([M + H]$^+$) 315.0596, found 315.0593.



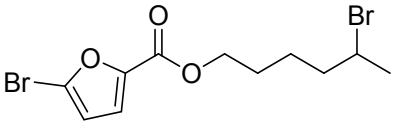
5-bromohexyl 3-phenylpropanoate (2m)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (29.4 mg, 94% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 4.13 – 4.06 (m, 3H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.70 (d, *J* = 6.7 Hz, 3H), 1.66 – 1.59 (m, 2H), 1.56 – 1.52 (m, 1H), 1.47 – 1.40 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 173.1, 140.6, 128.6, 128.4, 126.4, 64.3, 51.4, 40.7, 36.0, 31.1, 28.1, 26.6, 24.4.

HRMS (APCI) m/z calcd. for $C_{15}H_{21}BrO_2$ ([M + H]$^+$) 313.0803, found 313.0798.



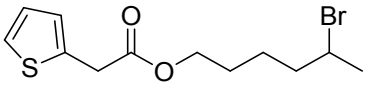
5-bromohexyl 5-bromofuran-2-carboxylate (2n)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (32.6 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 2H), 4.17 – 4.09 (m, 1H).1.92 – 1.59 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 146.5, 127.6, 120.1, 114.0, 65.0, 51.4, 40.7, 28.1, 26.6, 24.4.

HRMS (APCI) m/z calcd. for $C_{11}H_{14}Br_2O_3$ ([M + H]$^+$) 352.9388, found 352.9384.



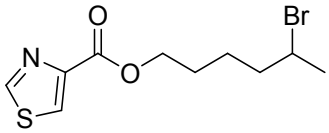
5-bromohexyl 2-(thiophen-2-yl)acetate (2o)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (22.6 mg, 74% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (d, *J* = 6.4 Hz, 1H), 6.98 – 6.94 (m, 2H), 4.14 – 4.08 (m, 3H), 3.84 (s, 2H), 1.86 – 1.74 (m, 2H), 1.70 – 1.63 (m, 5H), 1.61 – 1.56 (m, 1H), 1.49 – 1.43 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 170.6, 135.2, 127.0, 126.9, 125.2, 65.0, 51.4, 40.7, 35.7, 28.0, 26.6, 24.3.

HRMS (APCI) m/z calcd. for $C_{12}H_{17}BrO_2S$ ([M + H]$^+$) 305.0211, found 305.0205.



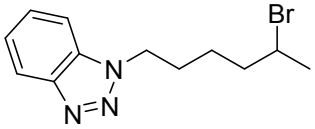
5-bromohexyl thiazole-4-carboxylate (2p)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a white solid (24.5 mg, 84% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.24 (s, 1H), 4.39 (t, *J* = 6.7 Hz, 2H), 4.16 – 4.11 (m, 1H), 1.91 – 1.78 (m, 4H), 1.72 – 1.64 (m, 4H), 1.60 – 1.53 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 161.4, 153.6, 148.2, 127.4, 65.4, 51.4, 40.7, 28.2, 26.6, 24.4.

HRMS (APCI) m/z calcd. for $C_{10}H_{14}BrNO_2S$ ([M + H]$^+$) 292.0007, found 292.0005.



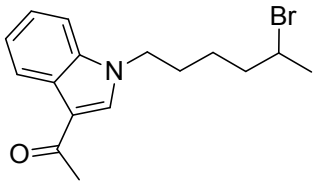
1-(5-bromohexyl)-1H-benzo[d][1,2,3]triazole (2q)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (23.1 mg, 82% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.39 – 7.37 (m, 1H), 4.66 (t, *J* = 7.1 Hz, 2H), 4.10 – 4.05 (m, 1H), 2.11 – 2.00 (m, 2H), 1.89 – 1.78 (m, 2H), 1.68 (d, *J* = 6.7 Hz, 3H), 1.64 – 1.59 (m, 1H), 1.52 – 1.46 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 146.2, 133.1, 127.4, 124.0, 120.3, 109.3, 51.0, 48.1, 40.5, 29.2, 26.6, 25.2.

HRMS (APCI) m/z calcd. for $C_{12}H_{16}BrN_3$([M + H]$^+$) 282.0606, found 282.0602.



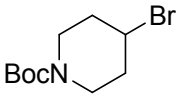
1-(1-(5-bromohexyl)-1H-indol-3-yl)ethenone (2r)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (15.8 mg, 49% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.39 – 8.37 (m, 1H), 7.75 (s, 1H), 7.36 – 7.34 (m, 1H), 7.32 – 7.29 (m, 2H), 4.18 (t, *J* = 7.2 Hz, 2H), 4.12 – 4.07 (m, 1H), 2.54 (s, 3H), 1.99 – 1.75 (m, 4H), 1.69 (d, *J* = 6.7 Hz, 3H), 1.65 – 1.58 (m, 1H), 1.52 – 1.46 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 193.1, 136.8, 134.8, 126.5, 123.4, 122.9, 122.7, 117.2, 109.9, 51.2, 47.1, 40.6, 29.4, 27.8, 26.6, 25.3.

HRMS (APCI) m/z calcd. for $C_{16}H_{20}BrNO$ ([M + H]$^+$) 322.0807, found 322.0805.

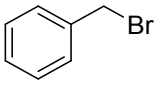


tert-butyl 4-bromopiperidine-1-carboxylate (2s)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (22.5 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 – 4.31 (m, 1H), 3.74 – 3.65 (m, 2H), 3.34 – 3.28 (m, 2H), 2.12 – 2.04 (m, 2H), 1.97 – 1.88 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 154.8, 80.0, 49.7, 35.8, 28.6.

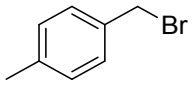


(bromomethyl)benzene (2t)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (14.2mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 4.51 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 129.2, 128.9, 128.6, 33.7.

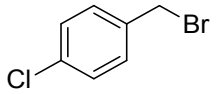


1-(bromomethyl)-4-methylbenzene (2u)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (15.2mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.49 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 135.0, 129.6, 129.1, 33.9, 21.4.

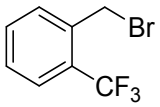


1-(bromomethyl)-4-chlorobenzene (2v)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (18.7 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 4.45 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.5, 130.5, 129.2, 32.5.



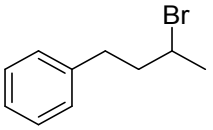
1-(bromomethyl)-2-(trifluoromethyl)benzene (2x)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (14.8 mg, 62% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.43 – 7.40 (m, 1H), 4.64 (s, 2H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 136.3, 132.7 (dd, *J* = 54.9, 35.3 Hz), 128.6 (dd, *J* = 43.9, 32.1 Hz), 126.4 (d, *J* = 35.8 Hz), 125.0, 123.4, 121.9, 28.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.5 (s, 3F).

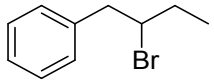


(3-bromobutyl)benzene (2y)

Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (17.3 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 – 7.19 (m, 3H), 4.14 – 4.02 (m, 1H), 2.90 – 2.71 (m, 2H), 2.19 – 1.99 (m, 2H), 1.73 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 128.7, 126.2, 51.1, 42.8, 34.1, 26.7.



(2-bromobutyl)benzene (2z)

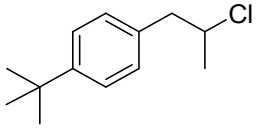
Prepared following *general procedure A* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (17.9 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 3H), 7.24 – 7.20 (m, 2H), 4.21 – 4.14(m, 1H), 3.25 – 3.13 (m, 2H), 1.95 – 1.73 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 129.3, 128.6, 126.9, 59.7, 45.5, 31.3, 12.2.

3.3 Experimental data for chlorinated products 3

Products **3a** (CAS: 1285188-17-1),[11] **3b** (CAS: 20914-98-1), **3c** (CAS: 4218-86-4),[12] **3d** (CAS: 85696-65-7) are known compounds.

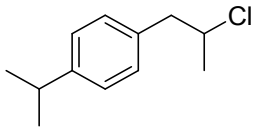


1-(tert-butyl)-4-(2-chloropropyl)benzene (3a)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (16.9 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.26 – 4.18 (m, 1H), 3.08 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.93 (dd, *J* = 13.9, 7.0 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 135.1, 129.1, 125.5, 58.8, 46.4, 34.6, 31.5, 24.8.

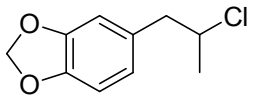


1-(2-chloropropyl)-4-isopropylbenzene (3b)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (16.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 4H), 4.25 – 4.17 (m, 1H), 3.07 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.95 – 2.86 (m, 2H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 135.4, 129.4, 126.6, 58.8, 46.5, 33.9, 24.8, 24.2.

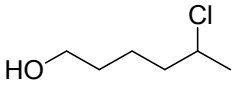


5-(2-chloropropyl)benzo[d][1,3]dioxole (3c)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (16.3 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 4.20 – 4.12 (m, 1H), 2.99 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.88 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.5, 131.9, 122.5, 109.8, 108.3, 101.1, 58.8, 46.5, 24.7.

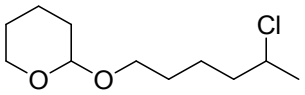


5-chlorohexan-1-ol (3d)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a colorless oil (10.7 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 – 4.00 (m, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.64 – 1.54 (m, 4H), 1.52 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.9, 58.9, 40.2, 32.3, 25.5, 23.1.



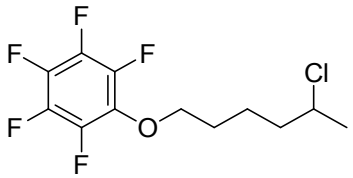
2-((5-chlorohexyl)oxy)tetrahydro-2H-pyran (3e)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (11.9 mg, 54% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 4.57 (t, *J* = 3.1 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.88 – 3.85 (m, 1H), 3.77 – 3.73 (m, 1H), 3.52 – 3.49 (m, 1H), 3.41 – 3.38 (m, 1H), 1.85 – 1.79 (m, 1H), 1.76 – 1.69 (m, 3H), 1.64 – 1.46 (m, 11H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 99.1, 67.5, 62.5, 58.9, 40.3, 30.9, 29.4, 25.6, 25.5, 23.6, 19.8.

HRMS (APCI) m/z calcd. for $C_{11}H_{21}ClO_2$ ([M + H]$^+$) 221.1308, found 221.1302.



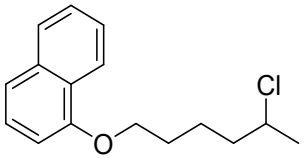
1-((5-chlorohexyl)oxy)-2,3,4,5,6-pentafluorobenzene (3f)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (20.9 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (t, *J* = 6.1 Hz, 2H), 4.09 – 4.01 (m, 1H), 1.84 – 1.58 (m, 6H), 1.54 (d, *J* = 6.5 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -157.0 – -157.1 (m, 2F), -163.5 – -163.9 (m, 3F).

HRMS (EI) m/z calcd. for $C_{12}H_{12}ClF_5O$ $[M]^+$ 302.0497, found 302.0487.



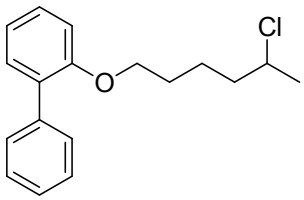
1-((5-chlorohexyl)oxy)naphthalene (3g)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (19.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 3H), 7.45 – 7.41 (m, 1H), 7.35 – 7.31 (m, 1H), 7.16 – 7.13 (m, 2H), 4.13 – 4.04 (m, 3H), 1.92 – 1.66 (m, 6H), 1.54 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 134.7, 129.5, 129.1, 127.8, 126.8, 126.5, 123.7, 119.1, 106.7, 67.8, 58.8, 40.2, 28.9, 25.5, 23.6.

HRMS (EI) m/z calcd. for $C_{16}H_{19}ClO$ $[M]^+$ 262.1124, found 262.1130.



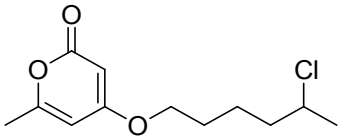
2-((5-chlorohexyl)oxy)-1,1'-biphenyl (3h)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (18.5 mg, 64% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.34 – 7.29 (m, 3H), 7.04 – 7.02 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.99 – 3.95 (m, 3H), 1.77 – 1.59 (m, 5H), 1.53 – 1.48 (m, 1H), 1.46 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 156.0, 138.7, 131.1, 129.8, 129.6, 128.8, 128.6, 128.1, 127.9, 127.0, 120.9, 112.5, 68.2, 58.8, 40.0, 28.8, 25.5, 23.5.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}ClO$ ([M + H]$^+$) 289.1359, found 289.1354.



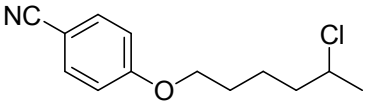
4-((5-chlorohexyl)oxy)-6-methyl-2H-pyran-2-one (3i)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (18.1 mg, 74% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 5.77 (s, 1H), 5.37 (s, 1H), 4.06 – 4.01 (m, 1H), 3.94 (t, *J* = 6.3 Hz, 2H), 2.20 (s, 3H), 1.84 – 1.72 (m, 4H), 1.69 – 1.64 (m, 1H), 1.57 – 1.52 (m, 4H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 170.7, 165.2, 162.2, 100.7, 87.8, 68.6, 58.5, 39.9, 28.1, 25.5, 23.2, 19.9.

HRMS (APCI) m/z calcd. for $C_{12}H_{17}ClO_3$ ([M + H]$^+$) 245.0944, found 245.0942.



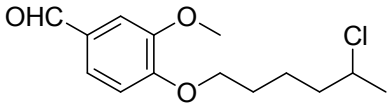
4-((5-chlorohexyl)oxy)benzonitrile (3j)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by preparative thin-layer chromatography (15% EtOAc/hexanes) provided the title compound as a colorless oil (21.2 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.09 – 4.00 (m, 3H), 1.89 – 1.56 (m, 6H), 1.53 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 134.1, 119.4, 115.3, 104.0, 68.2, 58.6, 40.1, 28.7, 25.5, 23.4.

HRMS (APCI) m/z calcd. for $C_{13}H_{16}ClNO$ ([M + H]$^+$) 238.0999, found 238.0995.



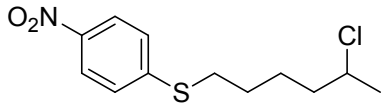
4-((5-chlorohexyl)oxy)-3-methoxybenzaldehyde (3k)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (22.5 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 4.09 – 4.02 (m, 1H), 3.93 (s, 3H), 1.97 – 1.85 (m, 2H), 1.84 – 1.59 (m, 4H), 1.53 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 154.2, 150.0, 130.1, 126.9, 111.6, 109.4, 69.0, 58.6, 56.2, 40.1, 28.6, 25.5, 23.4.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}ClO_3$ ([M + H]$^+$) 271.1101, found 271.1101.



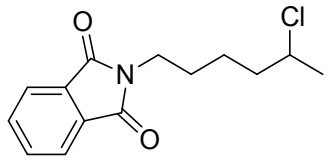
(5-chlorohexyl)(4-nitrophenyl)sulfane (3l)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (19.4 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 4.07 – 3.99 (m, 1H), 3.04 (t, *J* = 7.0 Hz, 2H), 1.81 – 1.67 (m, 5H), 1.65 – 1.58 (m, 1H), 1.52 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.1, 126.3, 124.1, 58.5, 39.8, 32.0, 28.2, 26.1, 25.5.

HRMS (APCI) m/z calcd. for $C_{12}H_{16}ClNO_2S$ ([M + H]$^+$) 274.0669, found 274.0663.



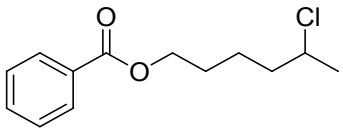
2-(5-chlorohexyl)isoindoline-1,3-dione (3m)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by preparative thin-layer chromatography (15% EtOAc/hexanes) provided the title compound as a colorless oil (23.4 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.72 – 7.70 (m, 2H), 4.05 – 3.97 (m, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 1.78 – 1.67 (m, 4H), 1.57 – 1.53 (m, 1H), 1.51 – 1.39 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 134.1, 132.3, 123.4, 58.6, 39.9, 37.9, 28.2, 25.5, 24.1.

HRMS (APCI) m/z calcd. for $C_{14}H_{16}ClNO_2$ ([M + H]$^+$) 266.0948, found 266.0938.



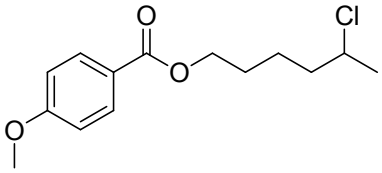
5-chlorohexyl benzoate (3n)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (19.3 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 4.09 – 4.01 (m, 1H), 1.85 – 1.56 (m, 6H), 1.53 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 133.0, 130.6, 129.7, 128.5, 64.8, 58.6, 40.0, 28.4, 25.5, 23.4.

HRMS (APCI) m/z calcd. for $C_{13}H_{17}ClO_2$ ([M + H]$^+$) 241.0995, found 241.0990.



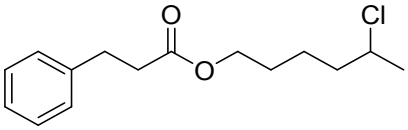
5-chlorohexyl 4-methoxybenzoate (3o)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (22.2 mg, 82% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.30 (t, *J* = 7.6 Hz, 2H), 4.07 – 4.03 (m, 1H), 3.86 (s, 3H), 1.83 – 1.73 (m, 4H), 1.71 – 1.64 (m, 1H), 1.57 – 1.52 (m, 1H), 1.52 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 166.5, 163.4, 131.6, 122.9, 113.7, 64.5, 58.6, 55.5, 40.0, 28.4, 25.5, 23.4.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}ClO_3$ ([M + H]$^+$) 271.1101, found 271.1098.



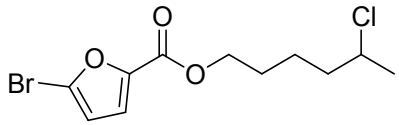
5-chlorohexyl 3-phenylpropanoate (3p)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (22.8 mg, 85% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H) 7.22 – 7.16 (m, 3H), 4.08 (t, *J* = 6.6 Hz, 2H), 4.03 – 3.98 (m, 1H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.73 – 1.68 (m, 2H), 1.66 – 1.57 (m, 2H), 1.55 – 1.52 (m, 1H), 1.50 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.39 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 173.1, 140.6, 128.4, 126.4, 64.4, 58.6, 40.0, 36.0, 31.1, 28.2, 25.5, 23.2.

HRMS (APCI) m/z calcd. for $C_{15}H_{21}ClO_2$ ([M + H]$^+$) 269.1308, found 269.1304.



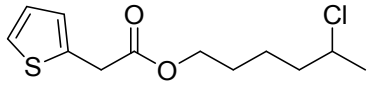
5-chlorohexyl 5-bromofuran-2-carboxylate (3q)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (24.5 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 3.5 Hz, 1H), 6.45 (d, *J* = 3.5 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 4.08 – 4.00 (m, 1H), 1.81 – 1.74 (m, 4H), 1.73 – 1.57 (m, 2H), 1.52 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 146.5, 127.6, 120.1, 114.0, 65.1, 58.6, 39.9, 28.3, 25.5, 23.3.

HRMS (APCI) m/z calcd. for $C_{11}H_{14}BrClO_3$ ([M + H]$^+$) 308.9893, found 308.9879.



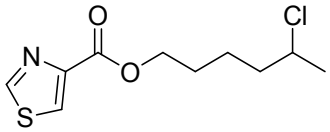
5-chlorohexyl 2-(thiophen-2-yl)acetate (3r)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (20.1 mg, 77% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.1 Hz, 1H), 6.98 – 6.92 (m, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 4.03 – 3.98 (m, 1H), 3.84 (s, 2H), 1.73 – 1.64 (m, 4H), 1.60 – 1.56 (m, 1H), 1.50 (d, *J* = 6.5 Hz, 3H), 1.48 – 1.43 (m, 1H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 170.6, 135.3, 126.9, 126.9, 125.2, 65.1, 58.6, 39.9, 35.7, 28.2, 25.5, 23.2.

HRMS (APCI) m/z calcd. for $C_{12}H_{17}ClO_2S$ ([M + H]$^+$) 261.0716, found 261.0710.



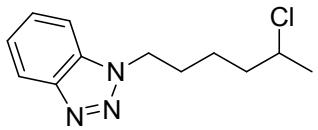
5-chlorohexyl thiazole-4-carboxylate (3s)

Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a white solid (16.3 mg, 66% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.24 (s, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 4.06 – 4.01 (m, 1H), 1.87 – 1.76 (m, 4H), 1.70 – 1.64 (m, 1H), 1.57 – 1.53 (m, 1H), 1.52 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 161.5, 153.6, 148.3, 127.4, 65.4, 58.6, 40.0, 28.3, 25.5, 23.3.

HRMS (APCI) m/z calcd. for $C_{10}H_{14}ClNO_2S$ ([M + H]$^+$) 248.0512, found 248.0509.



1-(5-chlorohexyl)-1H-benzo[d][1,2,3]triazole (3t)

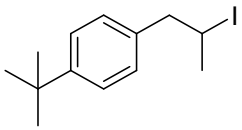
Prepared following *general procedure B* in 0.1 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (16.6 mg, 70% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.48(m, 2H), 7.40 – 7.35 (m, 1H), 4.66 (t, *J* = 7.7 Hz, 2H), 4.01 – 3.96 (m, 1H), 2.10 – 2.00 (m, 2H), 1.77 – 1.74 (m, 2H), 1.64 – 1.59 (m, 1H), 1.52 – 1.45 (m, 4H).

HRMS (APCI) m/z calcd. for $C_{12}H_{16}ClN_3$ ([M + H]$^+$) 238.1111, found 238.1108.

3.4 Experimental data for iodide products 4

Products **4m** (CAS: 35424-56-7)[13] is known compounds.



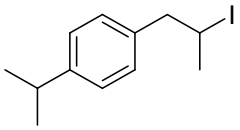
1-(tert-butyl)-4-(2-iodopropyl)benzene (4a)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (28.8 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 4.25 – 4.45 (m, 1H), 3.31 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.04 (dd, *J* = 14.0, 7.9 Hz, 1H) 1.89 (d, *J* = 6.9 Hz, 3H), 1.32 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 136.7, 128.8, 125.5, 49.3, 34.6, 31.5, 28.7, 28.2.

HRMS (EI) m/z calcd. for $C_{13}H_{19}I$ [M]$^+$ 302.0531, found 302.0533.



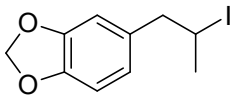
1-(2-iodopropyl)-4-isopropylbenzene (4b)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (25.0 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.44 – 4.26 (m, 1H), 3.30 (dd, *J* = 14.1, 6.9 Hz, 1H), 3.04 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.90 (m, 1H), 1.90 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 137.1, 129.0, 126.6, 49.4, 33.9, 28.9, 28.2, 24.1.

HRMS (EI) m/z calcd. for $C_{12}H_{17}I$ $[M]^+$ 288.0375, found 288.0374.



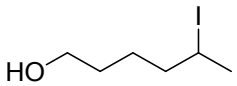
5-(2-iodopropyl)benzo[d][1,3]dioxole (4c)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (25.3 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.94 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 1H), 3.20 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.96 (dd, *J* = 14.2, 7.4 Hz, 1H), 1.89 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.5, 133.6, 122.2, 109.4, 108.3, 101.1, 49.3, 29.0, 28.1.

HRMS (EI) m/z calcd. for $C_{10}H_{11}IO_2$ $[M]^+$ 289.9804, found 289.9801.



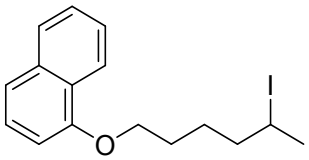
5-iodohexan-1-ol (4d)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a colorless oil (16.4 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 – 4.10 (m, 1H), 3.66 (t, *J* = 5.7 Hz 2H), 1.93 (d, *J* = 6.8 Hz, 3H), 1.91 – 1.80 (m, 1H), 1.74 – 1.30 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.8, 42.7, 32.0, 30.4, 29.1, 26.2.

HRMS (APCI) m/z calcd. for $C_6H_{13}IO$ ($[M + H]^+$) 229.0089, found 229.0084.



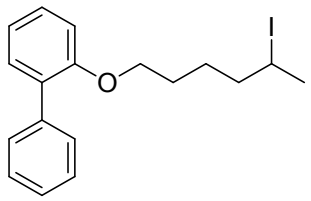
1-((5-iodohexyl)oxy)naphthalene (4e)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a brown oil (28.6 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.68 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.06 (m, 2H), 4.33 – 4.17 (m, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.96 (d, *J* = 6.9 Hz, 3H), 1.93 – 1.52 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 134.7, 129.5, 129.1, 127.8, 126.8, 126.5, 123.7, 119.1, 106.7, 67.8, 42.7, 30.2, 29.1, 28.5, 26.6.

HRMS (APCI) m/z calcd. for $C_{16}H_{19}ClO$ ([M + H]$^+$) 354.0481, found 354.0480.



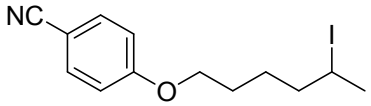
2-((5-iodohexyl)oxy)-1,1'-biphenyl (4f)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a colorless oil (36.5 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.22 – 4.07 (m, 1H), 3.98 (t, *J* = 6.2 Hz, 2H), 1.88 (d, *J* = 6.8 Hz, 3H), 1.85 – 1.42 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 138.7, 131.1, 131.2, 129.7, 128.7, 128.00, 126.9, 121.0, 112.6, 68.2, 42.6, 30.4, 29.0, 28.5, 26.6.

HRMS (APCI) m/z calcd. for $C_{18}H_{21}IO$ ([M + NH_4]$^+$) 398.0981, found 398.0976.



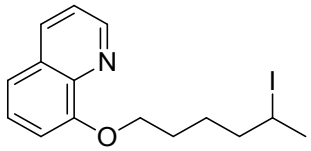
4-((5-iodohexyl)oxy)benzonitrile (4g)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by preparative thin-layer chromatography (20% EtOAc/hexanes) provided the title compound as a colorless oil (20.0 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.29 – 4.11 (m, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 1.94 (d, *J* = 6.8 Hz, 3H), 1.92 – 1.50 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 42.5, 29.9, 29.0, 28.3, 26.5.

HRMS (APCI) m/z calcd. for $C_{13}H_{16}INO$ ([M + H]$^+$) 330.0355, found 330.0351.



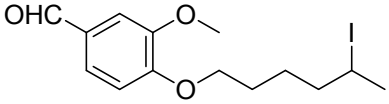
8-((5-iodohexyl)oxy)quinoline (4h)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–30% EtOAc/hexanes) provided the title compound as a yellow oil (32.0 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.32 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.33 – 4.15 (m, 3H), 2.20-1.50 (m, 6H), 1.93 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 149.4, 140.5, 136.1, 129.6, 126.8, 121.7, 119.7, 108.9, 68.8, 42.7, 30.3, 29.1, 28.3, 26.6.

HRMS (APCI) m/z calcd. for $C_{15}H_{18}INO$ ([M + H]$^+$) 356.0511, found 356.0509.



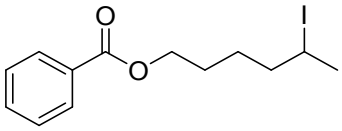
4-((5-iodohexyl)oxy)-3-methoxybenzaldehyde (4i)

Prepared following *general procedure C* in 0.184 mmol scale. Purification by flash column chromatography (0–20% EtOAc/hexanes) provided the title compound as a colorless oil (49.5 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 4.25 – 4.10 (m, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 3.90 (s, 3H), 2.02 – 1.46 (m, 6H), 1.89 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 154.1, 149.9, 130.1, 126.8, 111.6, 109.4, 68.9, 56.1, 42.5, 30.0, 29.0, 28.2, 26.5.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}IO_3$ ([M + H]$^+$) 363.0457, found 363.0455.



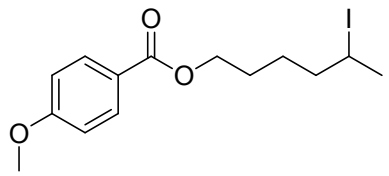
5-iodohexyl benzoate (4j)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (28.6 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 4.27 – 4.11 (m, 1H), 1.94 (d, *J* = 6.8 Hz, 3H) 1.92 – 1.45 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 133.0, 130.5, 129.7, 128.5, 64.8, 42.5, 30.0, 29.1, 28.0, 26.5.

HRMS (APCI) m/z calcd. for $C_{13}H_{17}IO_2$ ([M + H]$^+$) 333.0351, found 333.0346.



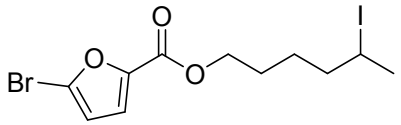
5-iodohexyl 4-methoxybenzoate (4k)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (29.4 mg, 80% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 4.24 – 4.11 (m, 1H), 3.85 (s, 3H), 1.93 (d, *J* = 6.8 Hz, 3H), 1.92 – 1.48 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 163.4, 131.7, 122.9, 113.7, 64.5, 55.6, 42.5, 30.1, 29.1, 28.0, 26.5.

HRMS (APCI) m/z calcd. for $C_{14}H_{19}IO_3$ ([M + H]$^+$) 363.0457, found 363.0454.



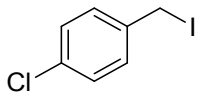
5-iodohexyl 5-bromofuran-2-carboxylate (4l)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–10% EtOAc/hexanes) provided the title compound as a colorless oil (30.0 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.24 – 4.11 (m, 1H), 1.93 (d, *J* = 6.9 Hz, 3H), 1.92 – 1.44 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 146.5, 127.6, 120.1, 114.3, 65.0, 42.4, 29.9, 29.1, 27.9, 26.3.

HRMS (APCI) m/z calcd. for $C_{11}H_{14}BrIO_3$ ([M + H]$^+$) 400.9249, found 400.9244.



1-(iodomethyl)-4-chlorobenzene (4m)

Prepared following *general procedure C* in 0.1 mmol scale. Purification by flash column chromatography (0–5% EtOAc/hexanes) provided the title compound as a brown solid (11.6 mg, 45% yield).

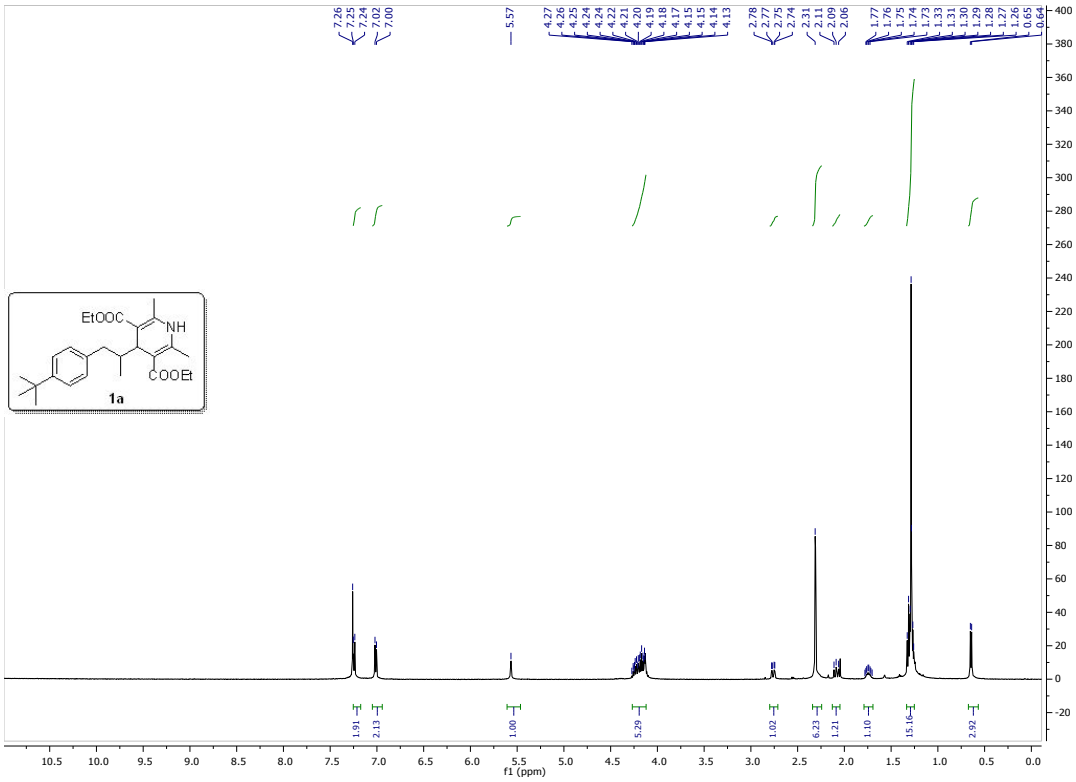
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.41 (s, 2H).

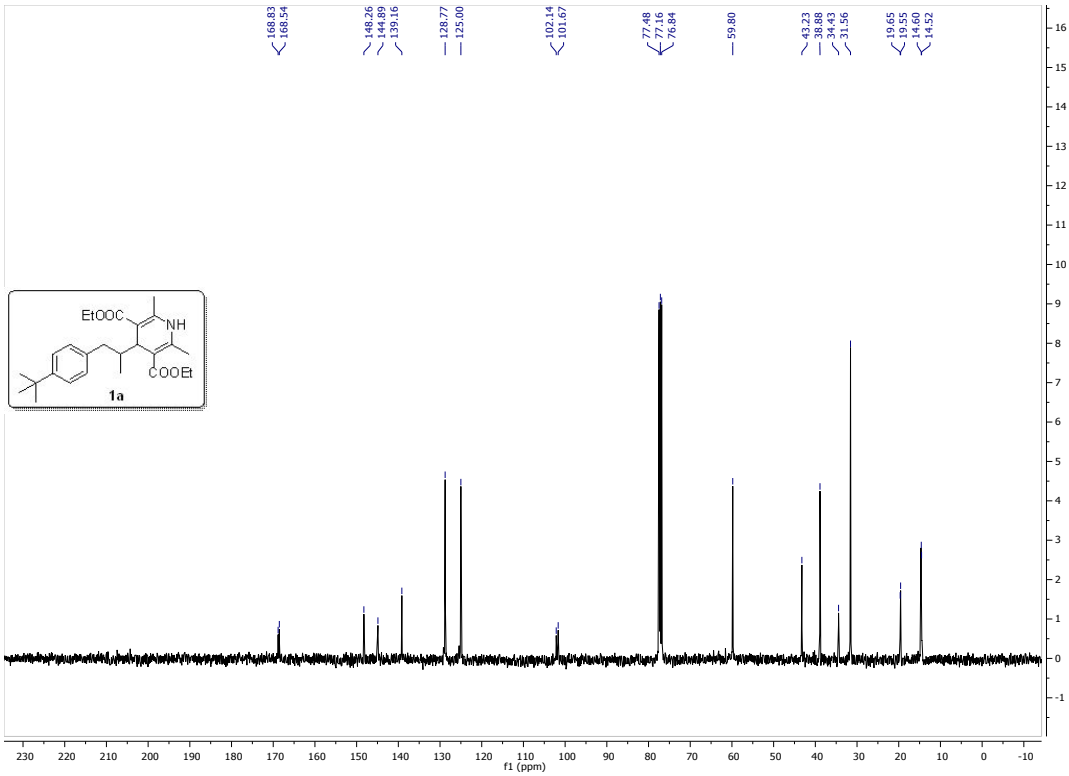
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 133.8, 130.2, 129.2, 4.4.

HRMS (EI) m/z calcd. for C_7H_6ClI $[M]^+$ 251.9203, found 251.9199.

4. NMR Spectral Data

4.1 NMR spectral data for DHPs 1

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43.23
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EtOOC
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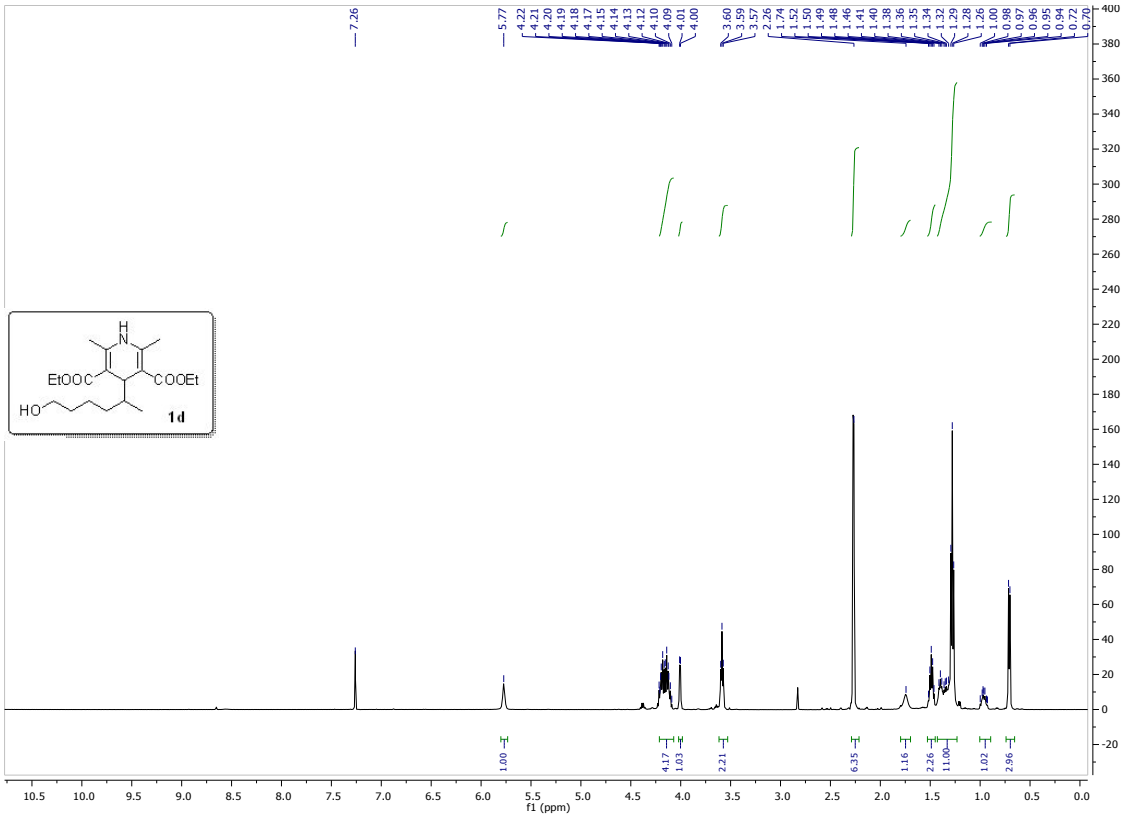
1a
f1 (ppm)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1.36
1.35
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1.29
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N
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HO
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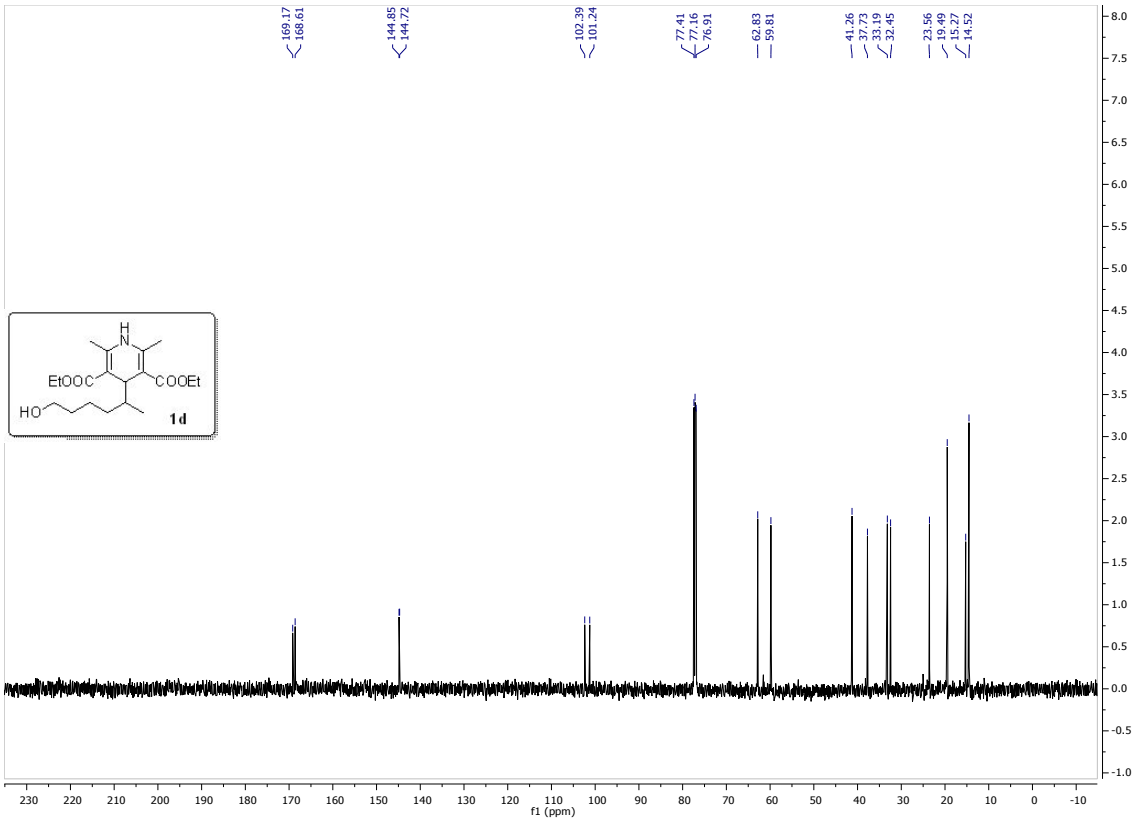
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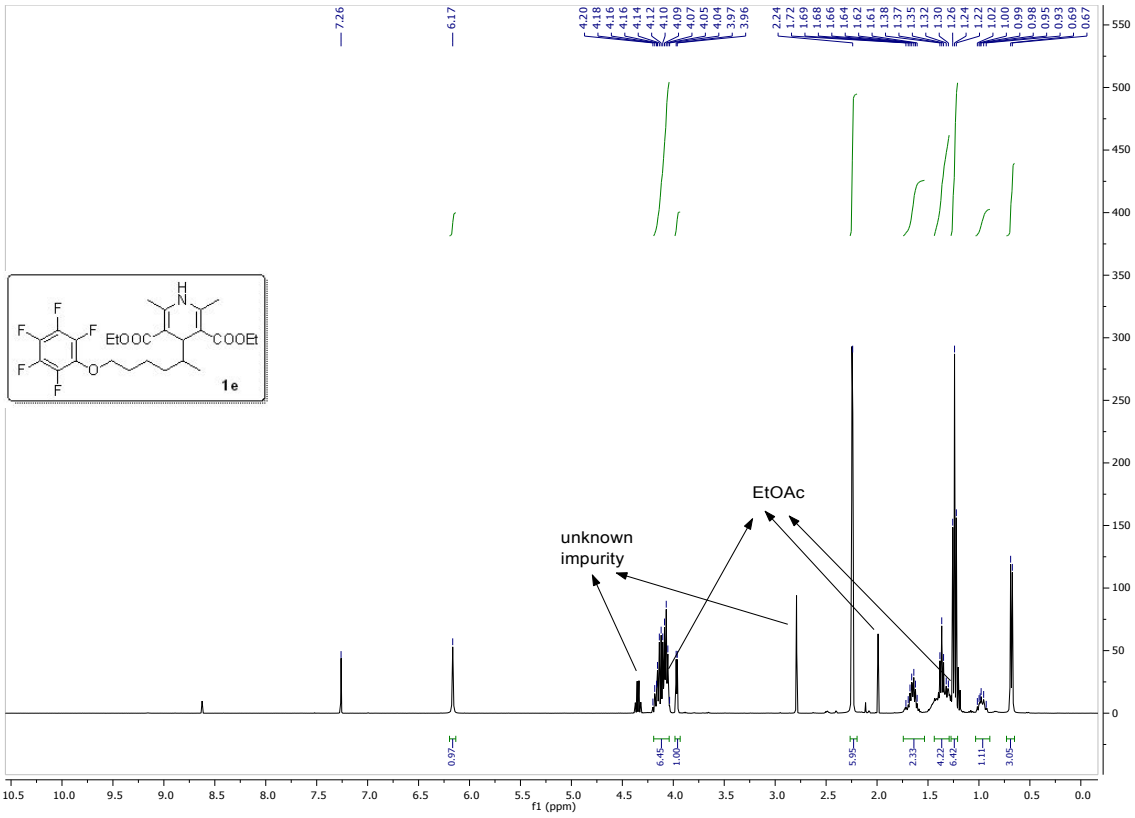
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1.38
1.37
1.35
1.32
1.30
1.26
1.24
1.22
1.02
1.00
0.99
0.98
0.95
0.93
0.69
0.67
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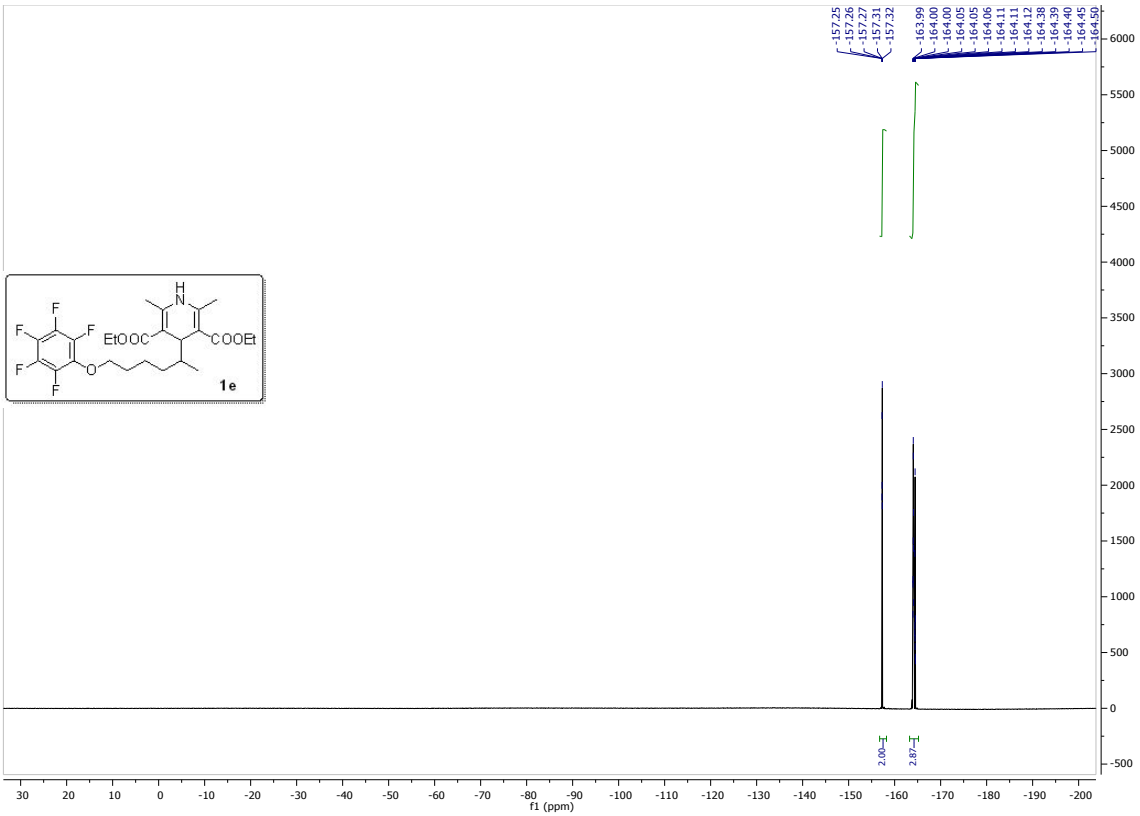
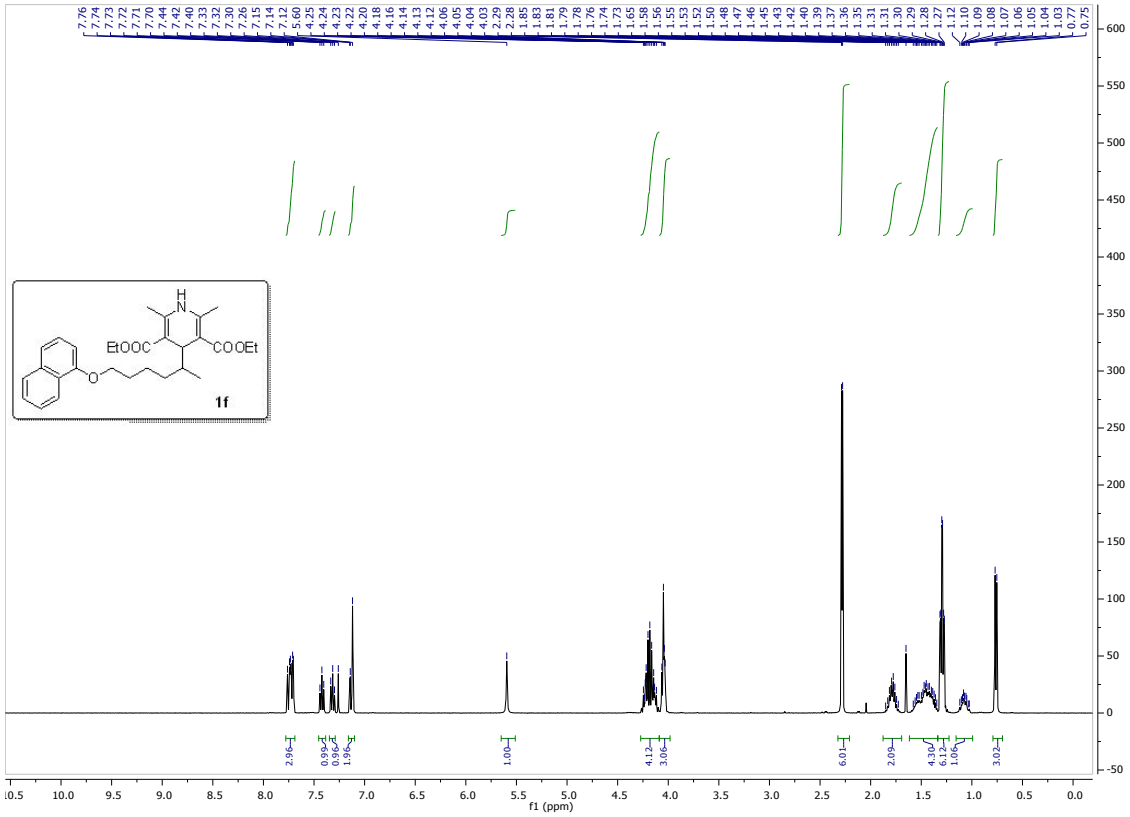
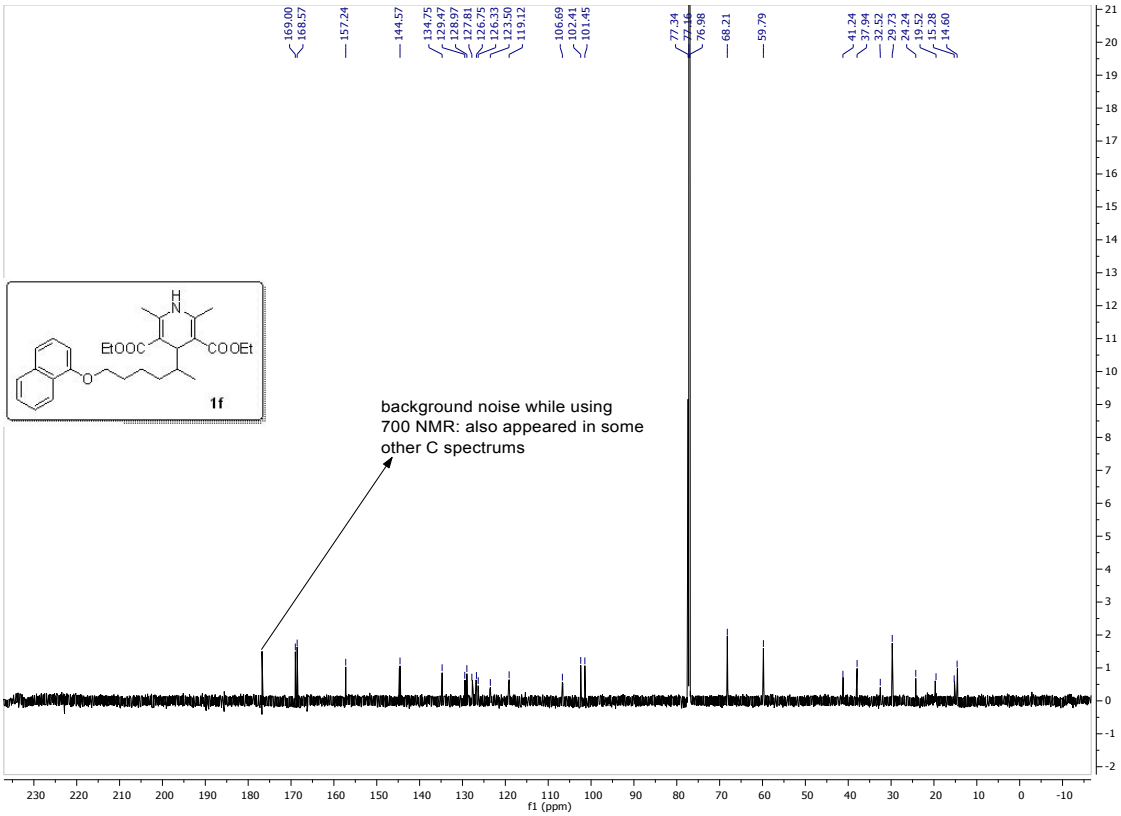
COOEt
1e
EtOAc
unknown
impurity
0.97
6.45
1.00
5.95
2.33
4.22
6.42
1.11
3.05
f1 (ppm)


1e
EtOOC
COOEt
f1 (ppm)


1f
EtOOC
COOEt
f1 (ppm)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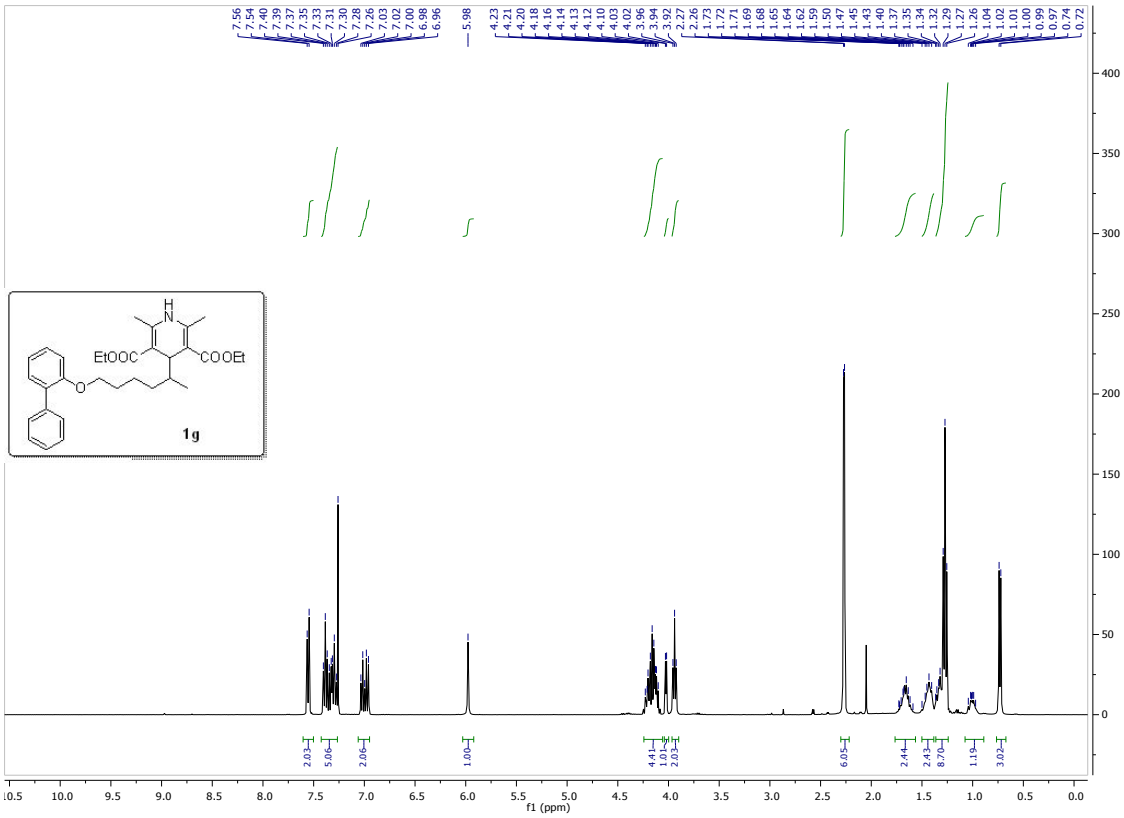
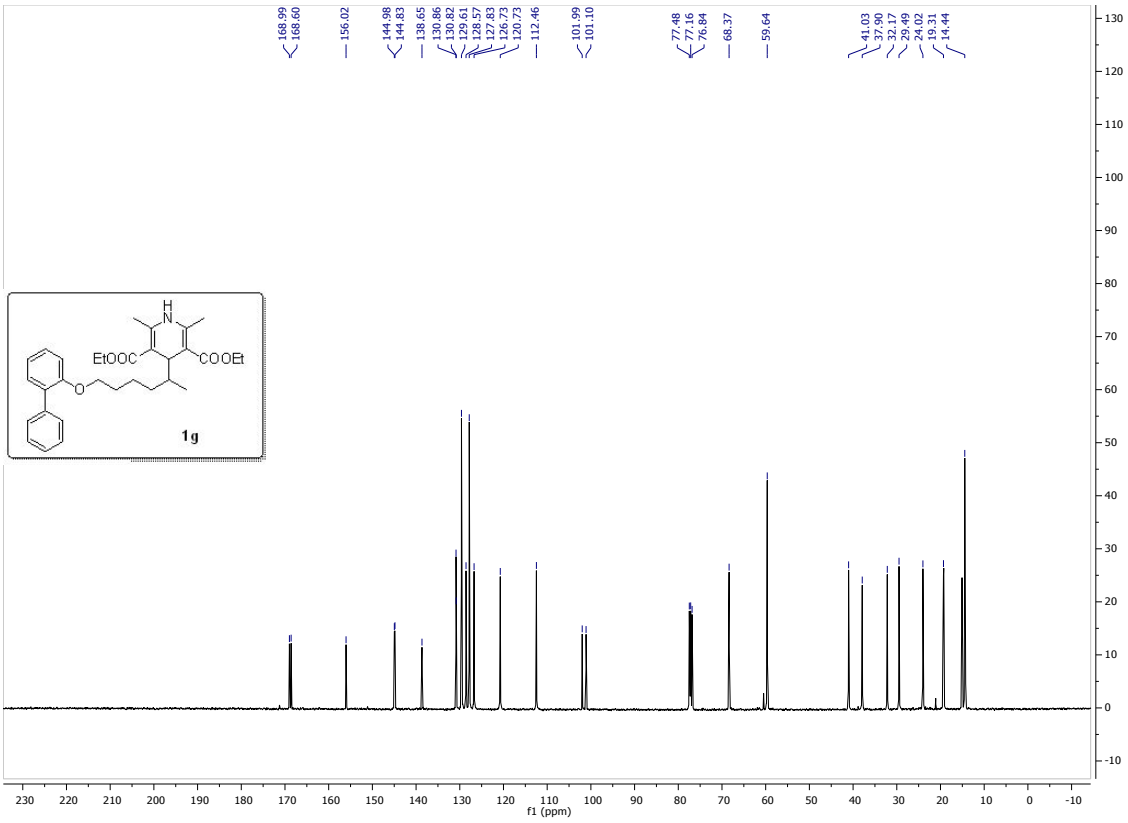
144.57
134.75
129.47
128.97
127.81
126.75
126.33
123.50
119.12
106.69
102.41
101.45
77.34
77.16
76.98
68.21
59.79
41.24
37.94
32.52
29.73
24.24
19.52
15.28
14.60
EtOOC
COOEt
1f
background noise while using
700 NMR: also appeared in some
other C spectrums
f1 (ppm)


7.56
7.54
7.40
7.39
7.37
7.35
7.33
7.31
7.30
7.28
7.26
7.03
7.02
7.00
6.98
6.96
5.98
4.23
4.21
4.20
4.18
4.16
4.14
4.13
4.12
4.10
4.03
4.02
3.96
3.94
3.92
2.27
2.26
1.73
1.72
1.71
1.69
1.68
1.65
1.64
1.62
1.59
1.50
1.47
1.45
1.43
1.40
1.37
1.35
1.34
1.32
1.29
1.27
1.26
1.04
1.02
1.01
1.00
0.99
0.97
0.74
0.72
EtOOC
COOEt
1g
2.03
5.06
2.06
1.00
4.41
1.01
2.03
6.05
2.44
2.43
8.70
1.19
3.02
f1 (ppm)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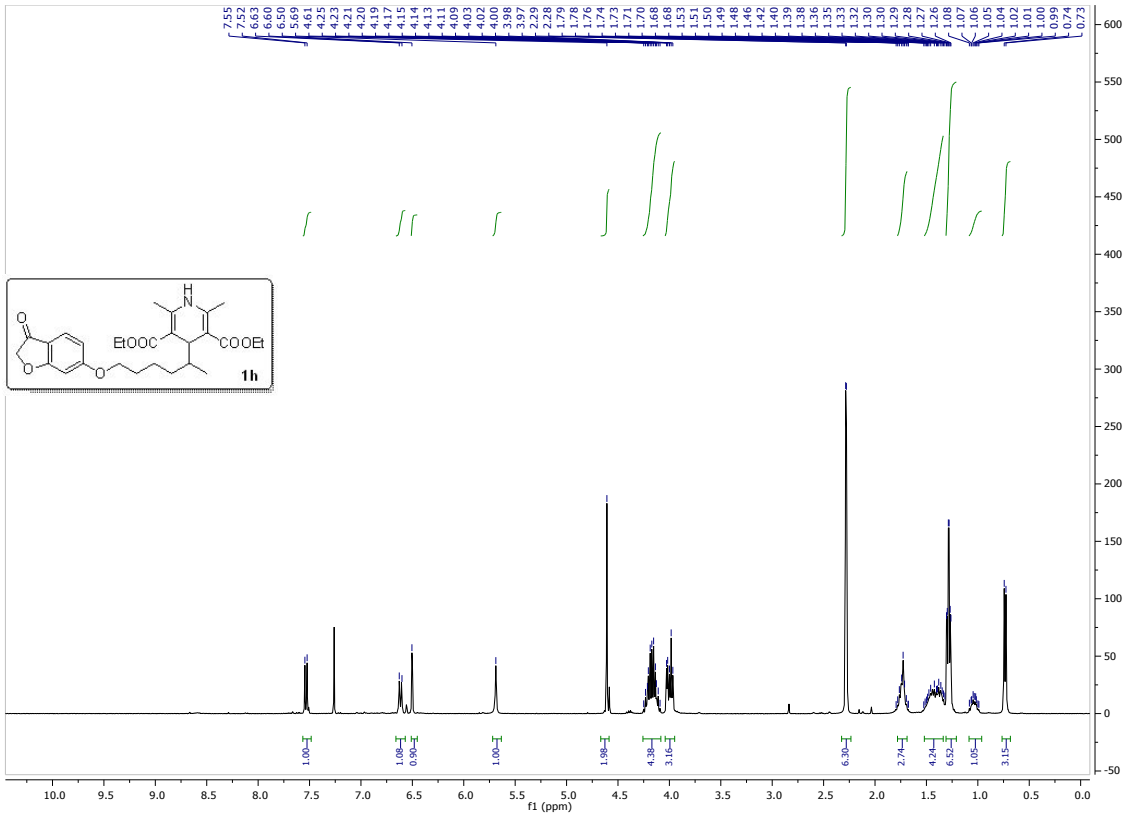
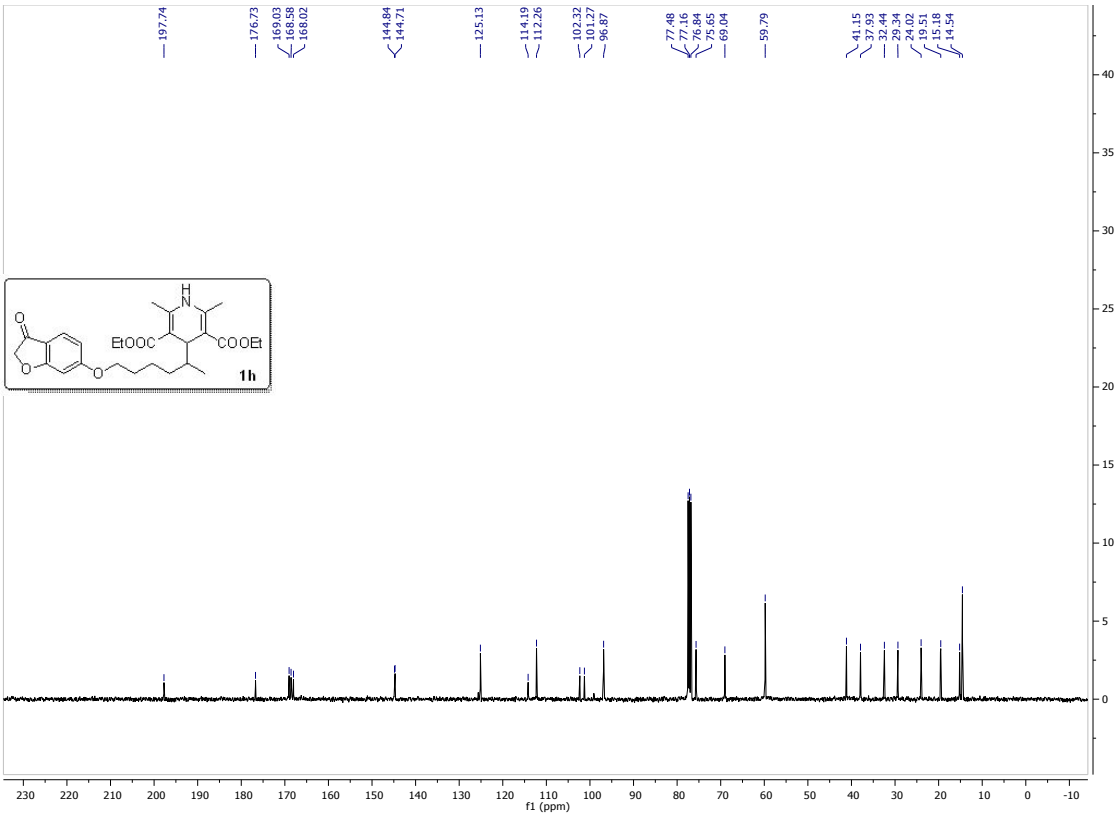
168.60
156.02
144.98
144.83
138.65
130.86
130.82
129.61
128.57
127.83
126.73
120.73
112.46
101.99
101.10
77.48
77.16
76.84
68.37
59.64
41.03
37.90
32.17
29.49
24.02
19.31
14.44
EtOOC
COOEt
1g
f1 (ppm)


EtOOC
COOEt
1h
1.00
1.08
0.98
1.00
1.98
4.38
3.16
6.30
2.74
4.24
6.52
1.05
3.15
f1 (ppm)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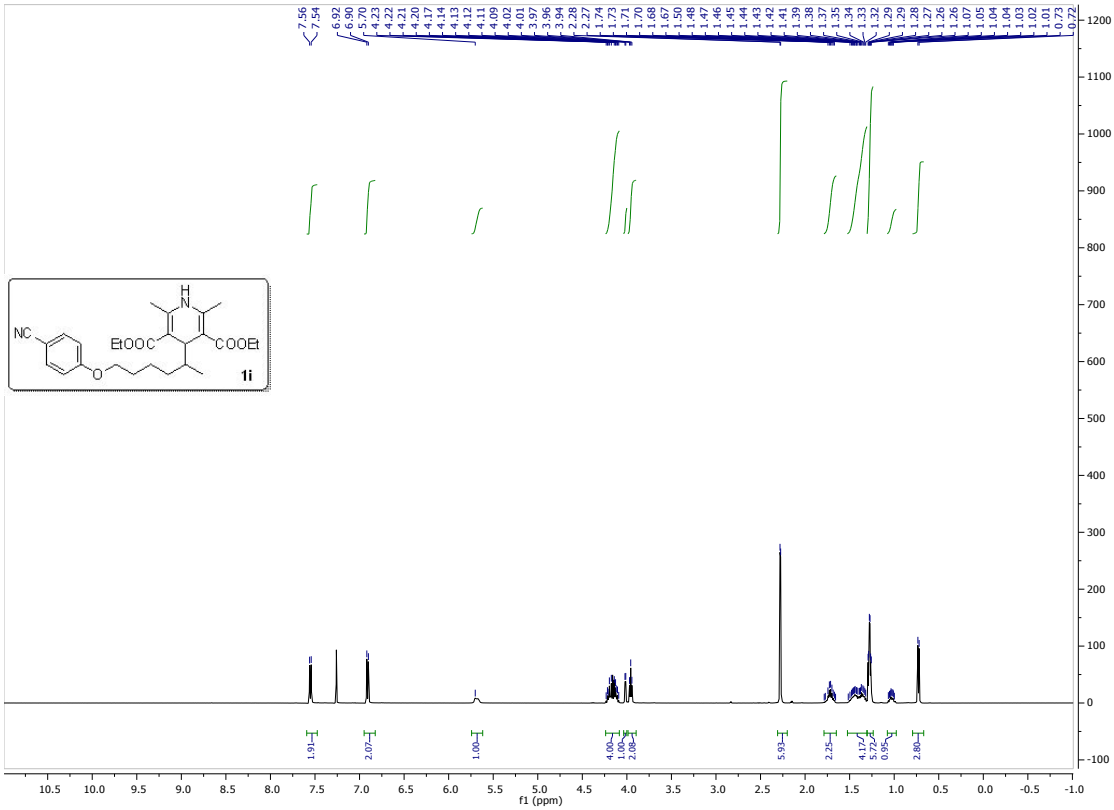
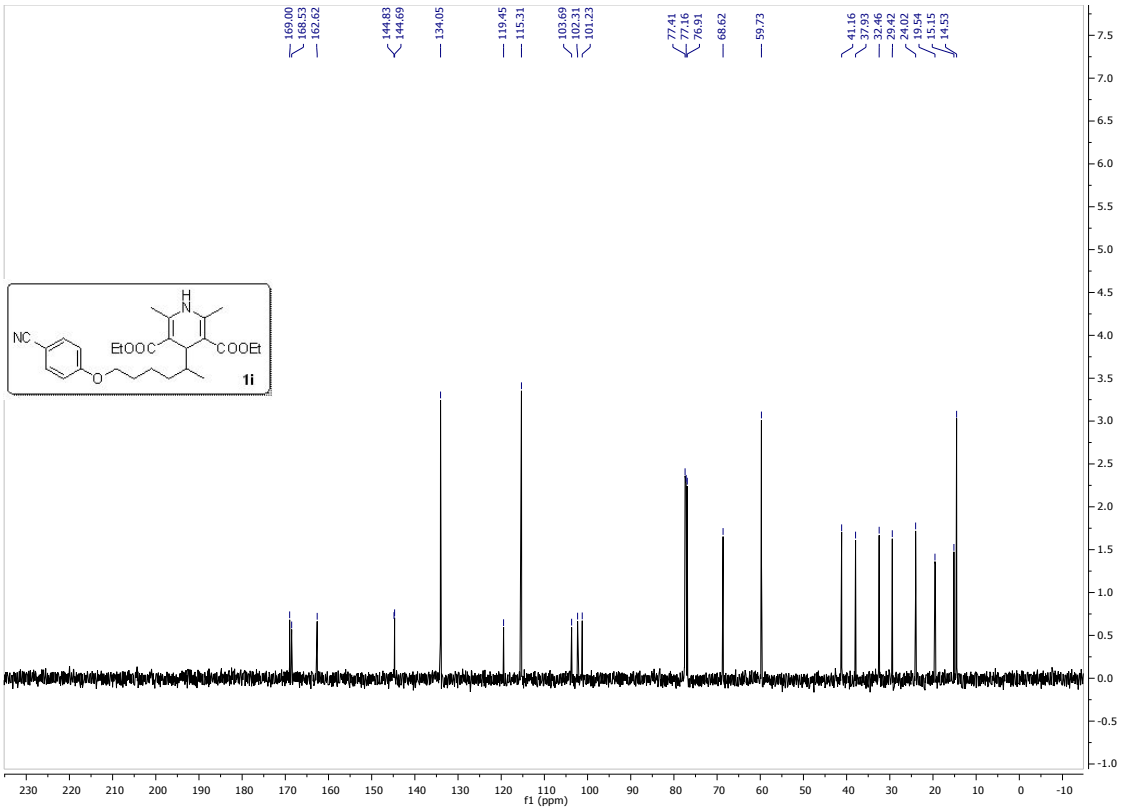
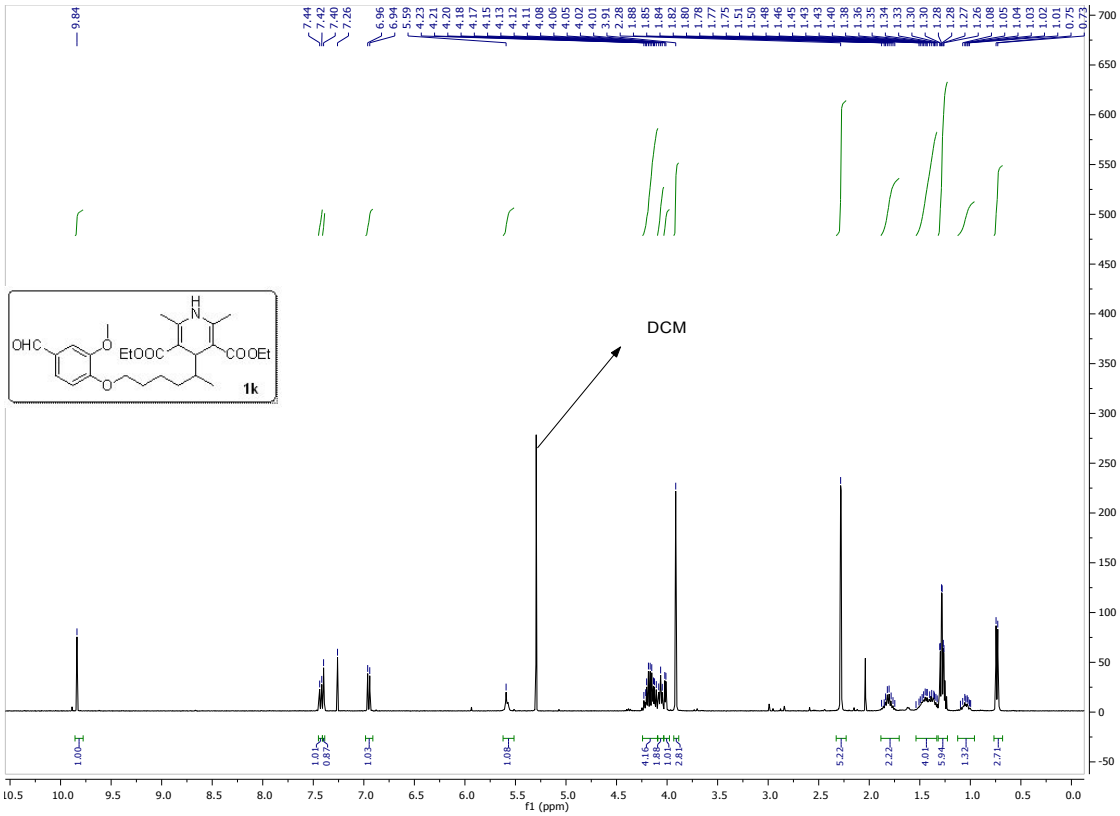
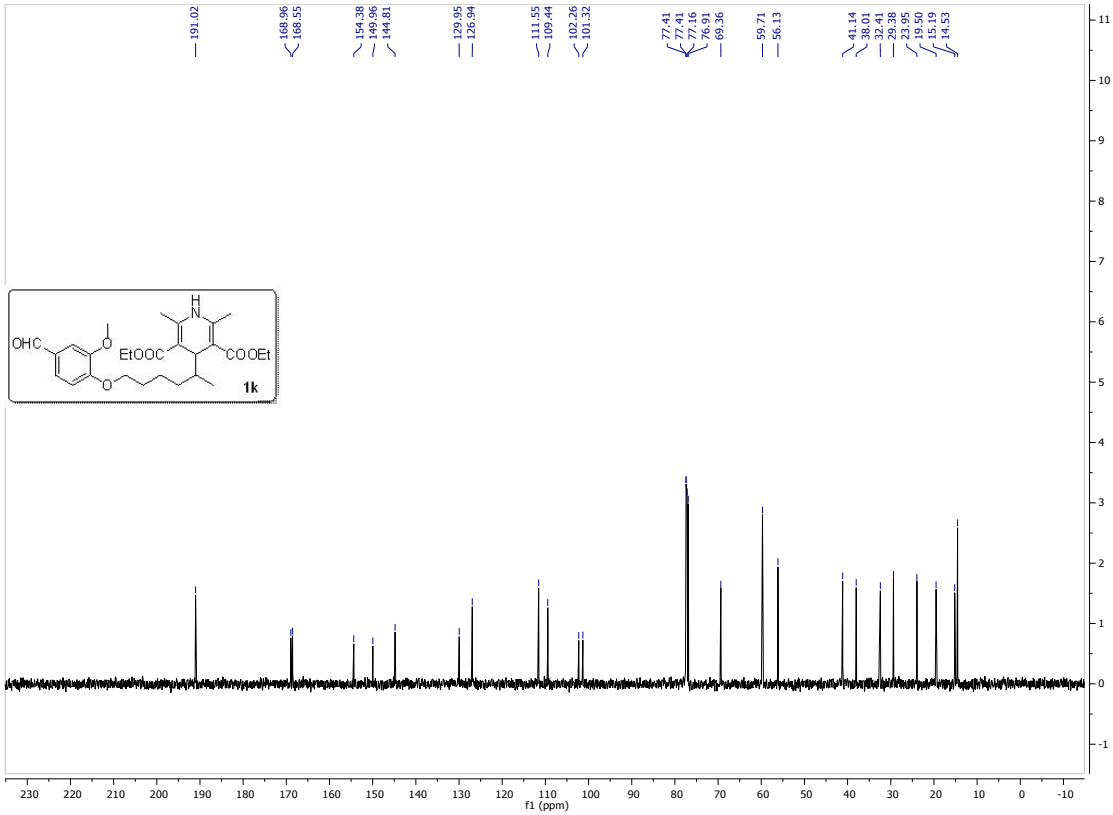
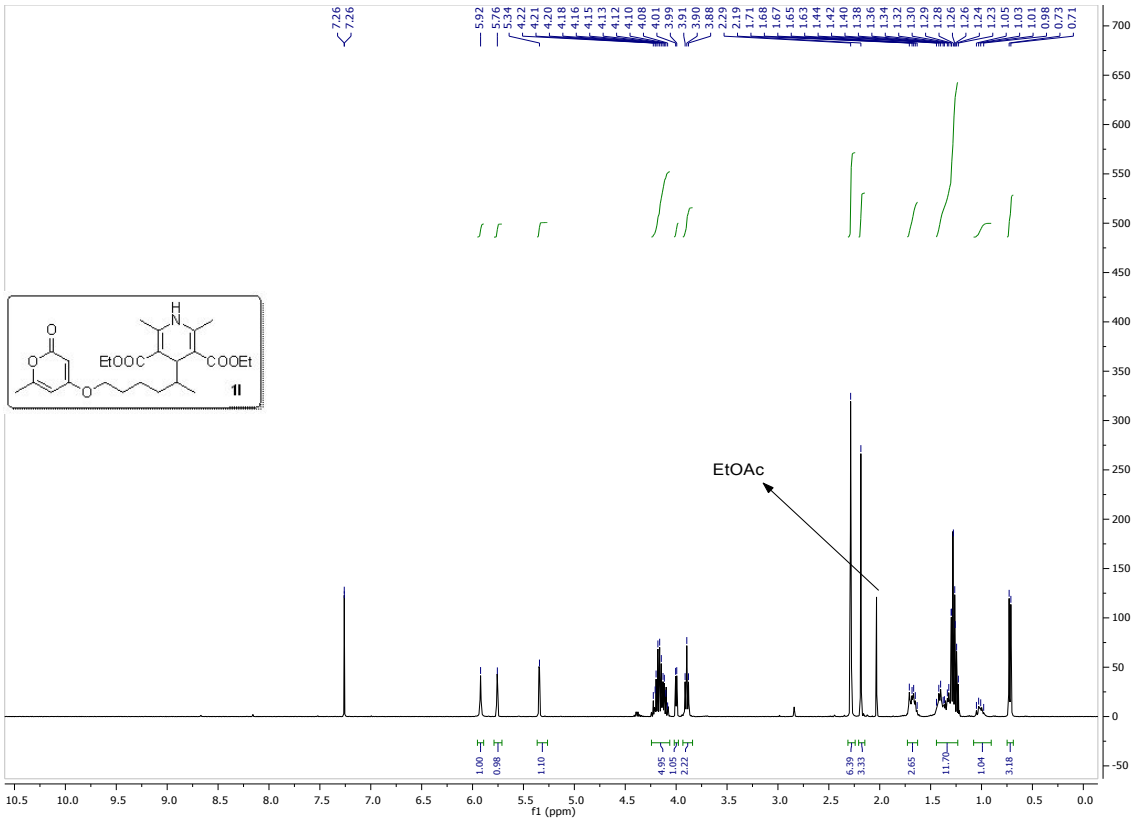
176.73
169.03
168.58
168.02
144.84
144.71
125.13
114.19
112.26
102.32
101.27
96.87
77.48
77.16
76.84
75.65
69.04
59.79
41.15
37.93
32.44
29.34
24.02
19.51
15.18
14.54
EtOOC
COOEt
1h
f1 (ppm)

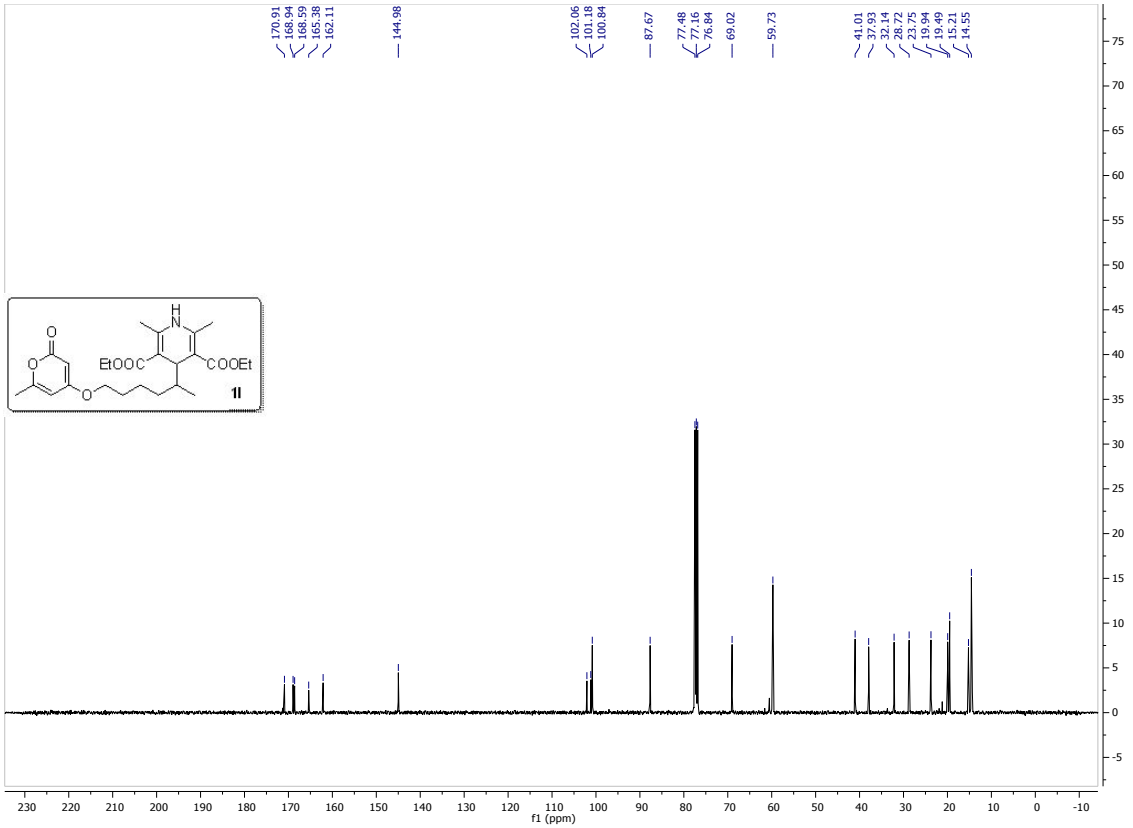

NC
EtOOC
COOEt
1i
f1 (ppm)

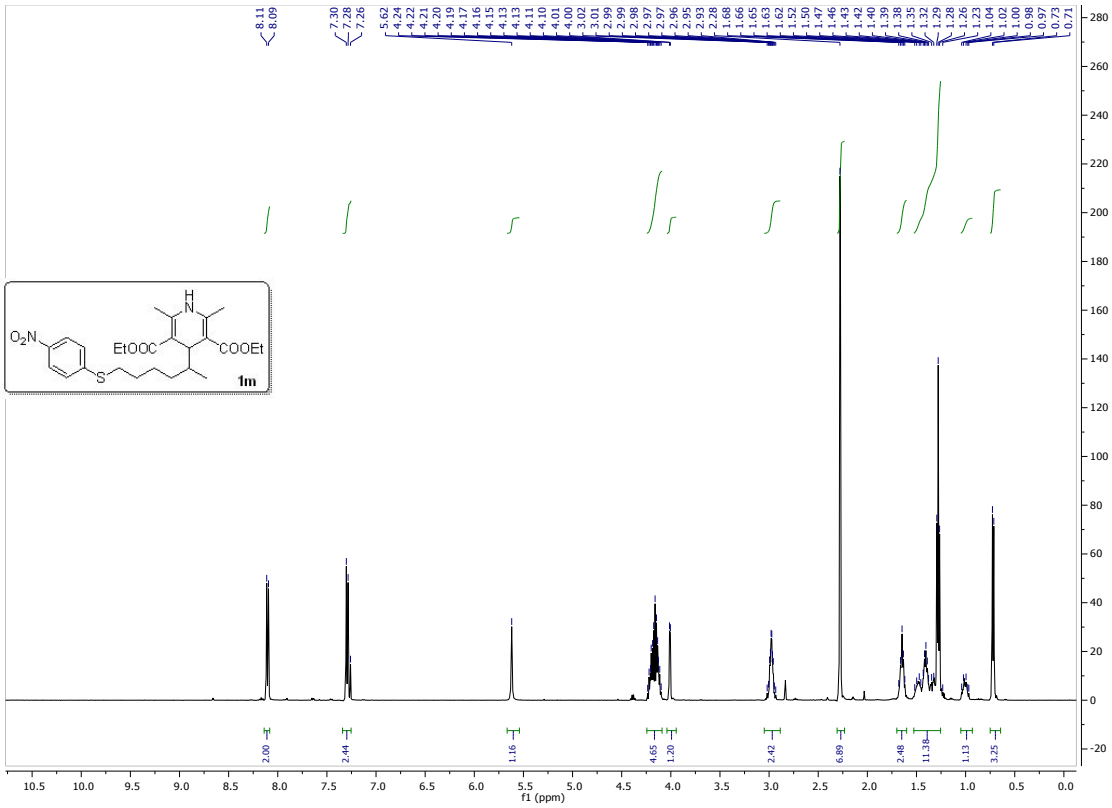

169.00
168.53
162.62
144.83
144.69
134.05
119.45
115.31
103.69
102.31
101.23
77.41
77.16
76.91
68.62
59.73
41.16
37.93
32.46
29.42
24.02
19.54
15.15
14.53
NC
EtOOC
COOEt
H
N
O
1i
f1 (ppm)

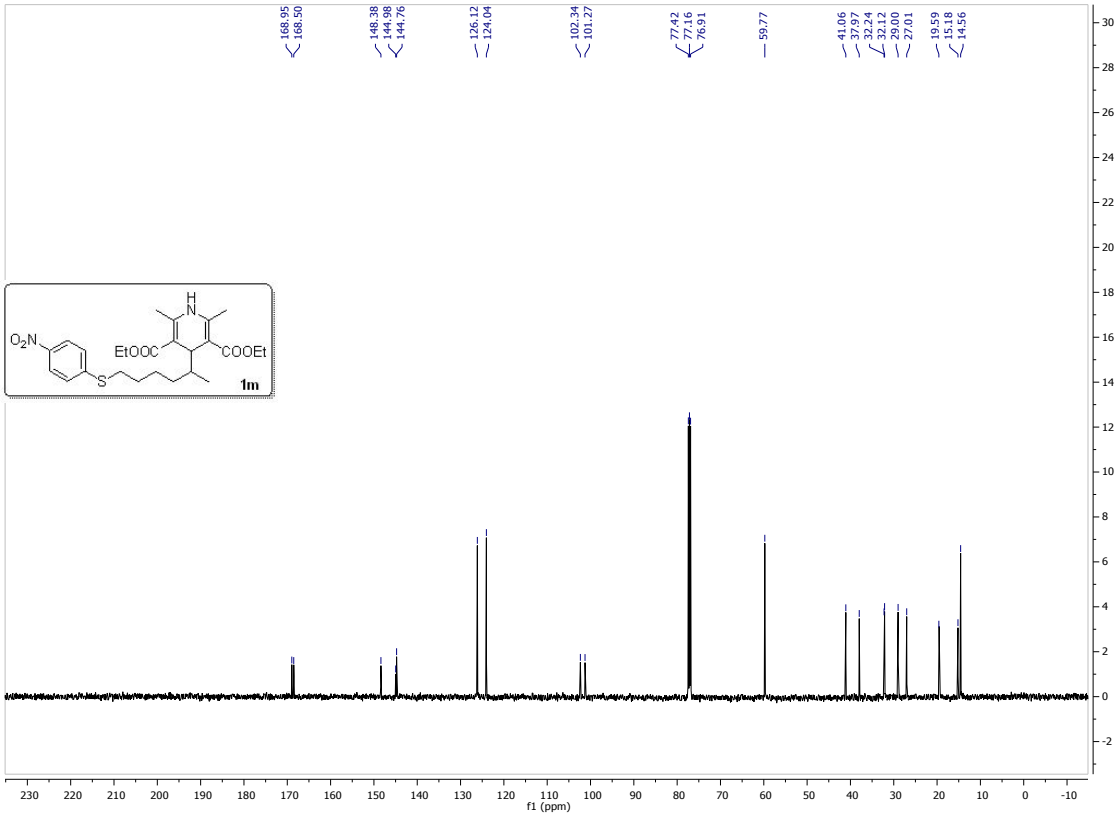

DCM
1k
f1 (ppm)


1k
f1 (ppm)


EtOAc
1l
f1 (ppm)


1l
f1 (ppm)


8.11
8.09
7.30
7.28
7.26
5.62
4.24
4.22
4.21
4.20
4.19
4.17
4.16
4.15
4.13
4.11
4.10
4.01
4.00
3.02
3.01
2.99
2.99
2.98
2.97
2.97
2.96
2.95
2.93
2.28
2.68
1.66
1.65
1.63
1.62
1.52
1.50
1.47
1.46
1.43
1.42
1.40
1.39
1.38
1.35
1.32
1.29
1.28
1.26
1.23
1.04
1.02
1.00
0.98
0.97
0.73
0.71
2.00
2.44
1.16
4.65
1.20
2.42
6.89
2.48
11.38
1.13
3.25
f1 (ppm)
O2N
EtOOC
COOEt
S
H
N
1m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168.50
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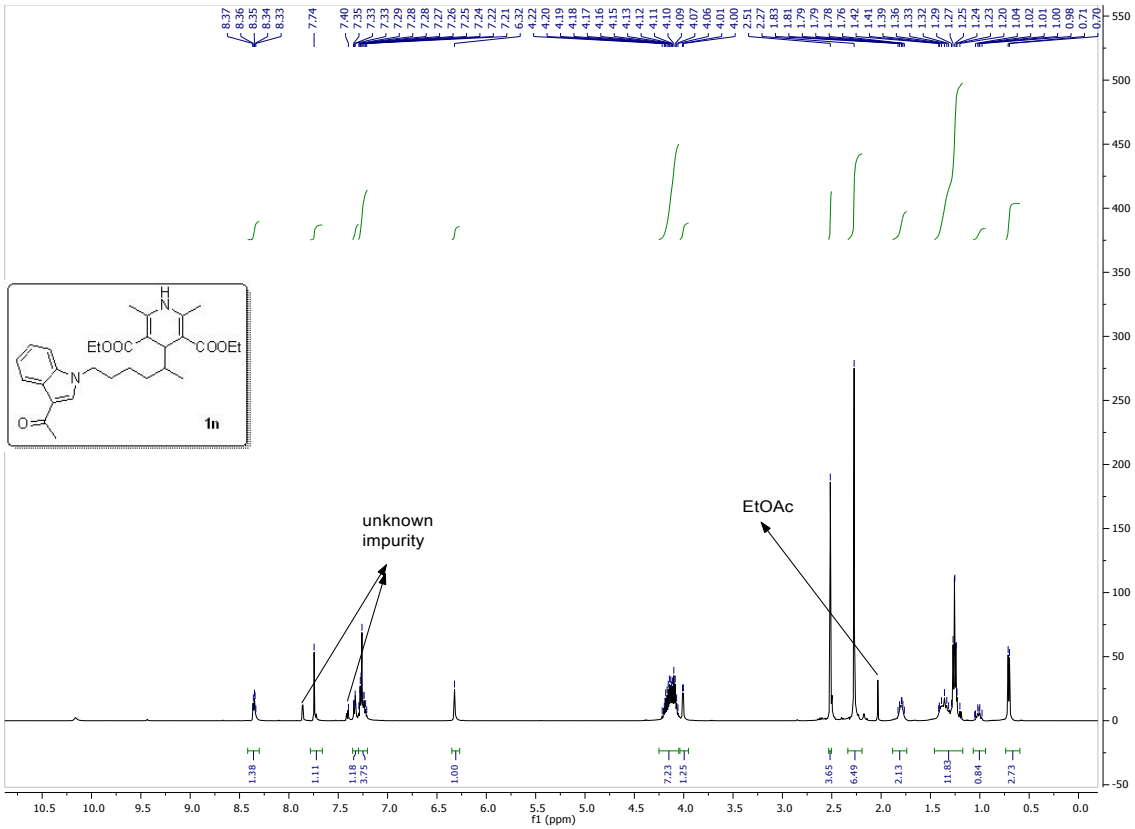
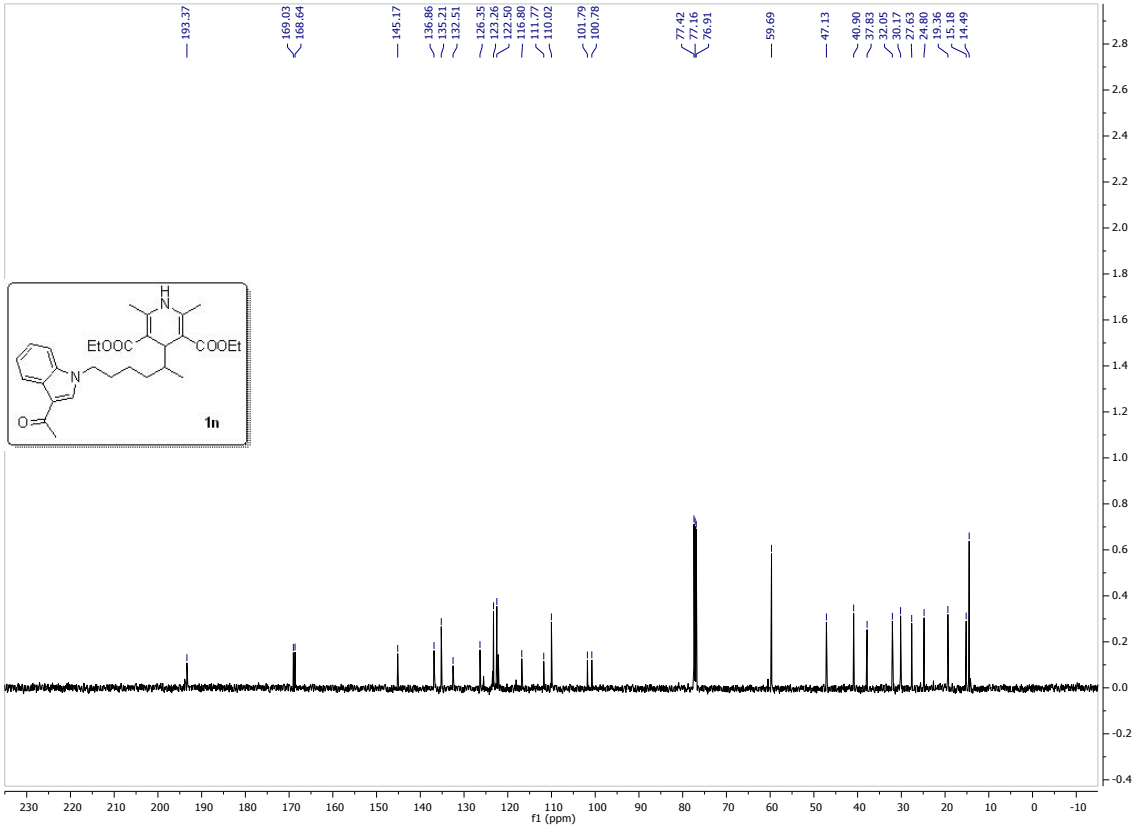
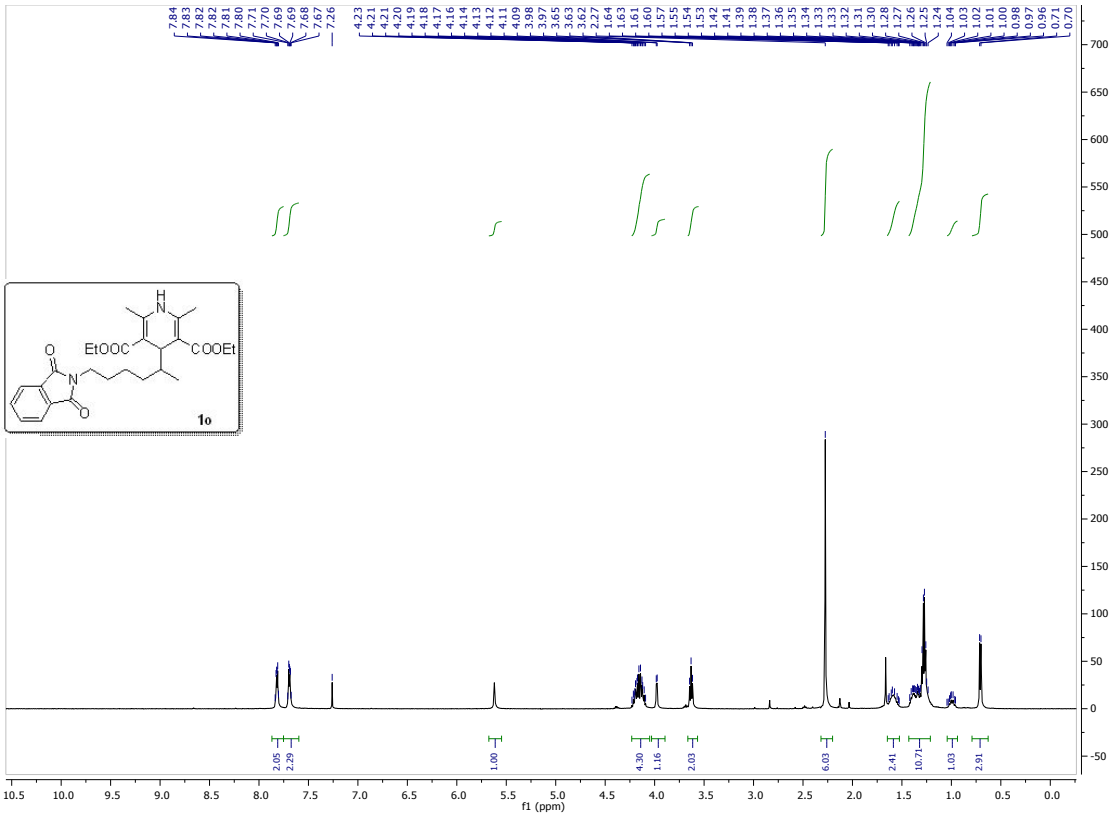
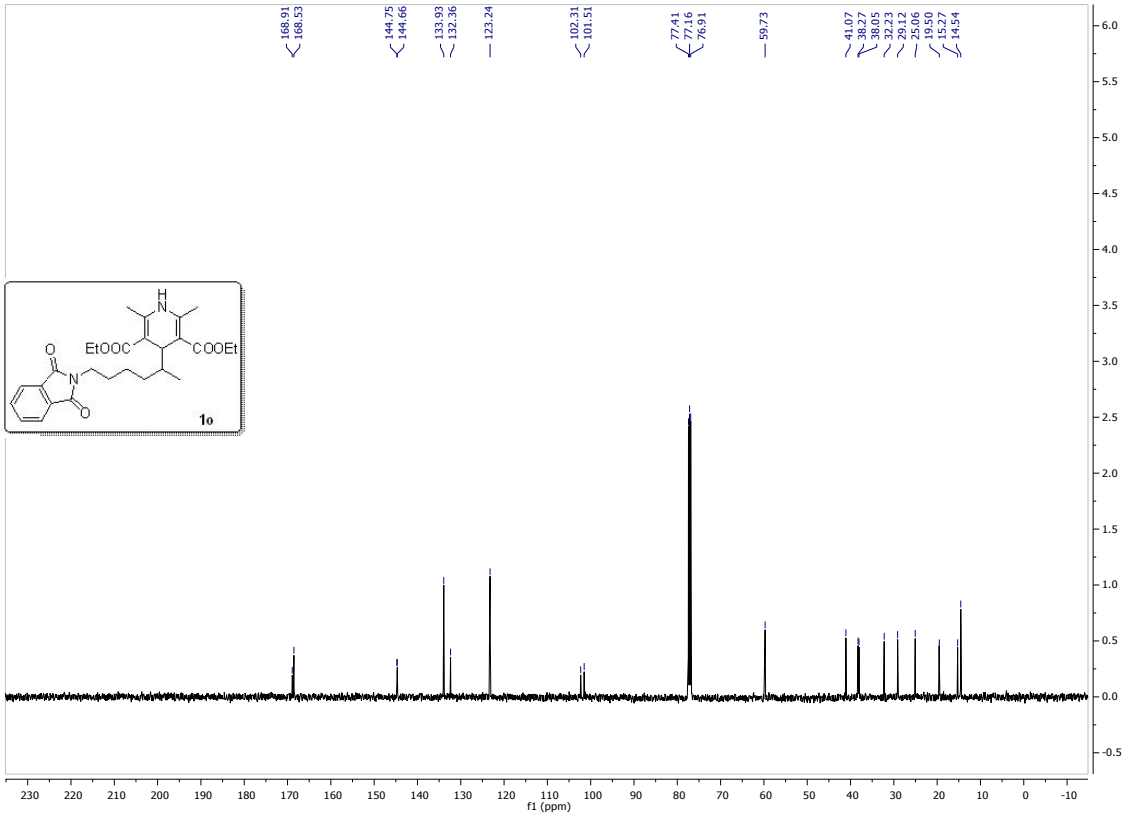
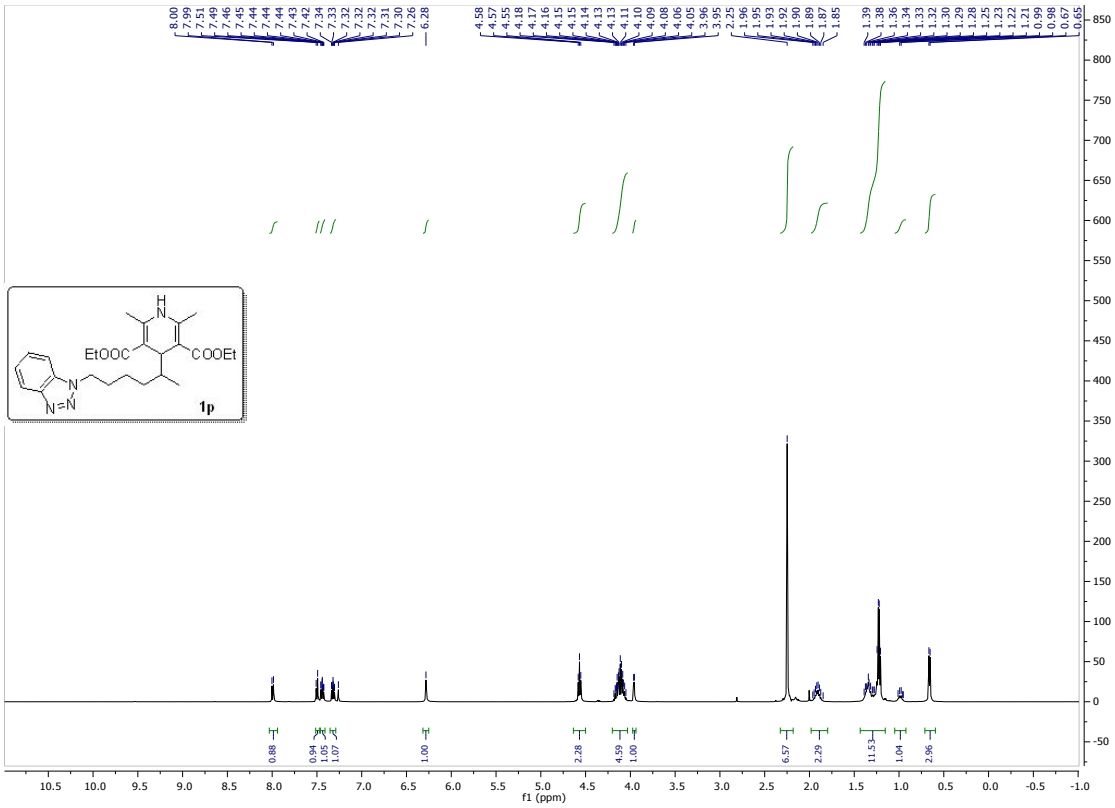
144.76
126.12
124.04
102.34
101.27
77.42
77.16
76.91
59.77
41.06
37.97
32.24
32.12
29.00
27.01
19.59
15.18
14.56
f1 (ppm)
O2N
EtOOC
COOEt
S
H
N
1m

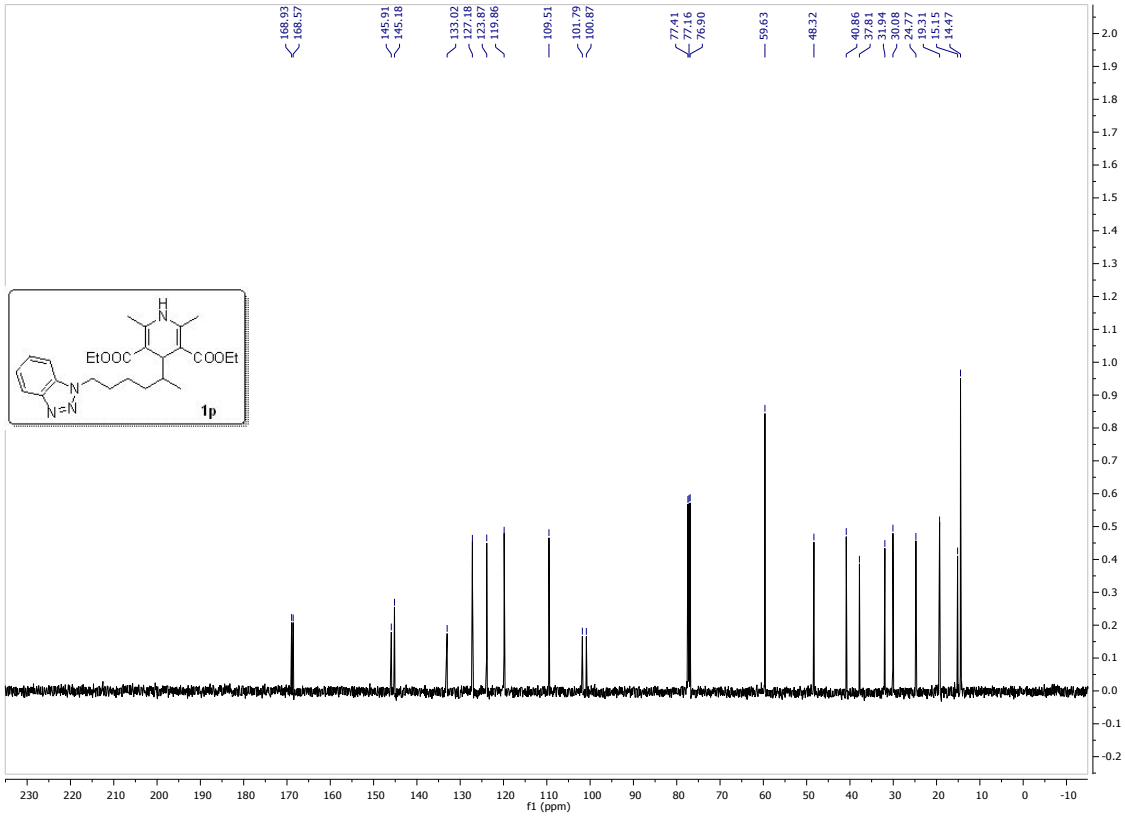

unknown
impurity
EtOAc
EtOOC
COOEt
1n
f1 (ppm)

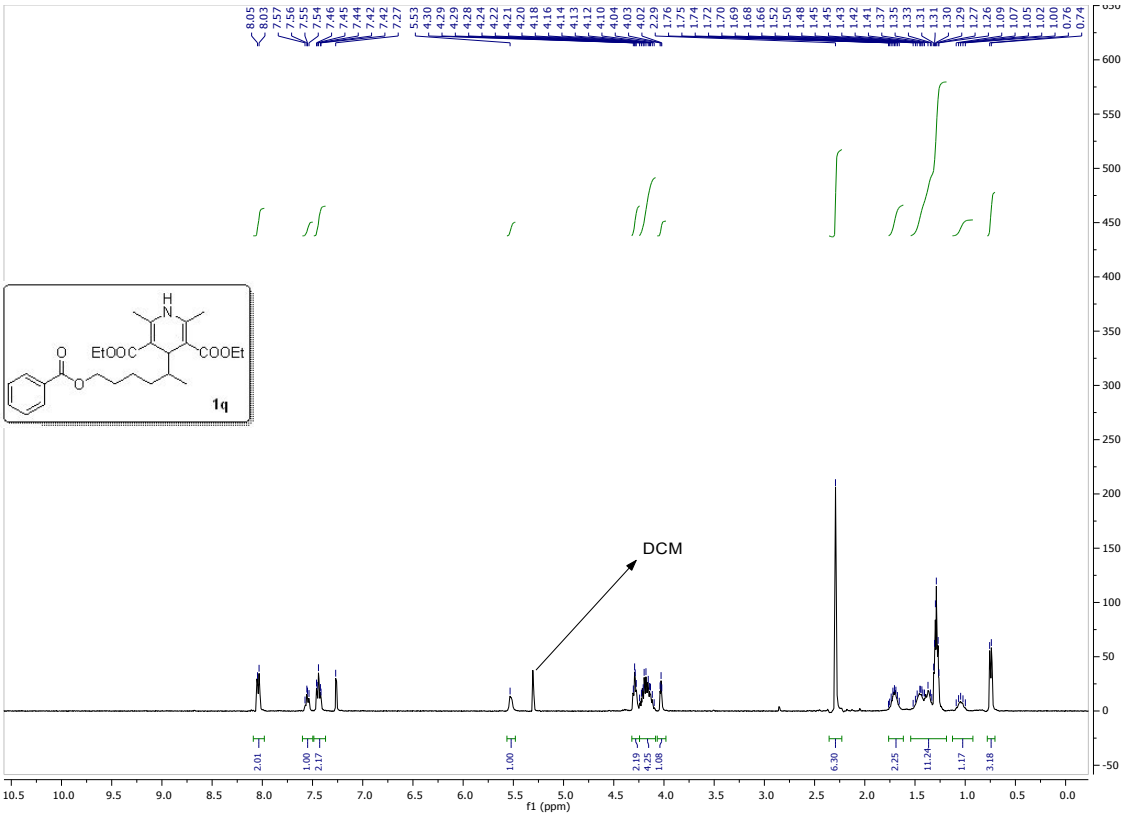

EtOOC
COOEt
1n
f1 (ppm)

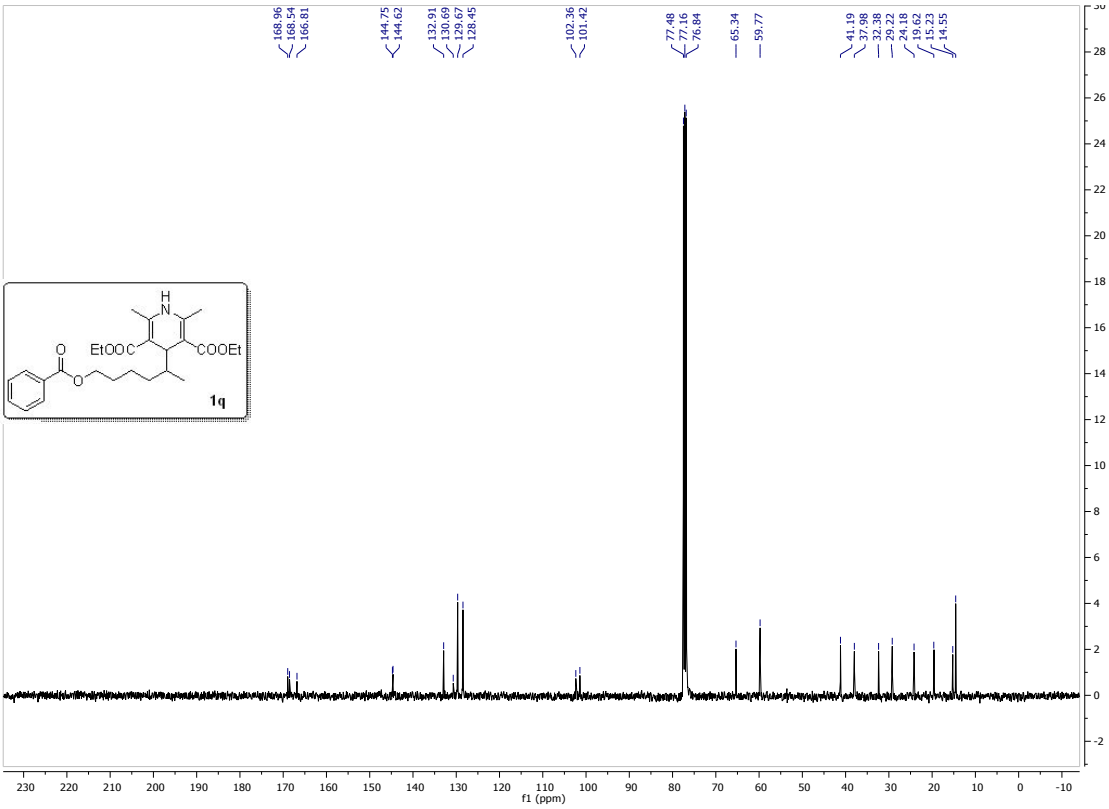

1o
f1 (ppm)

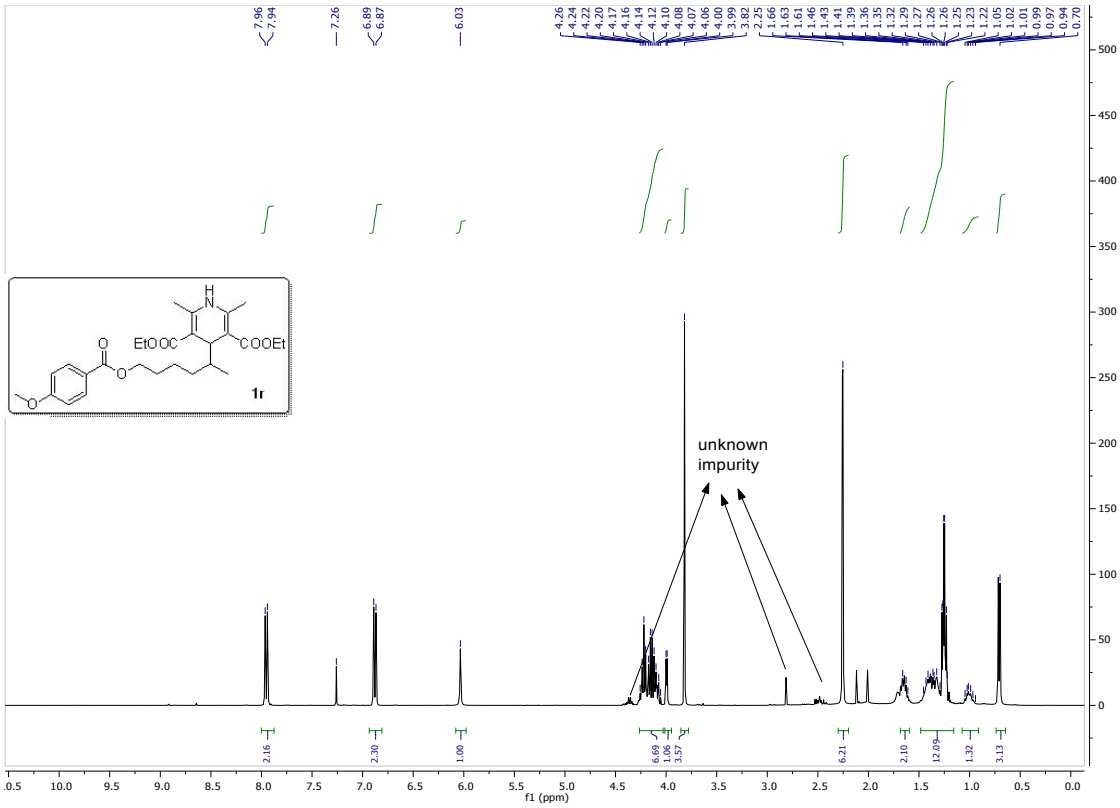

1o
f1 (ppm)

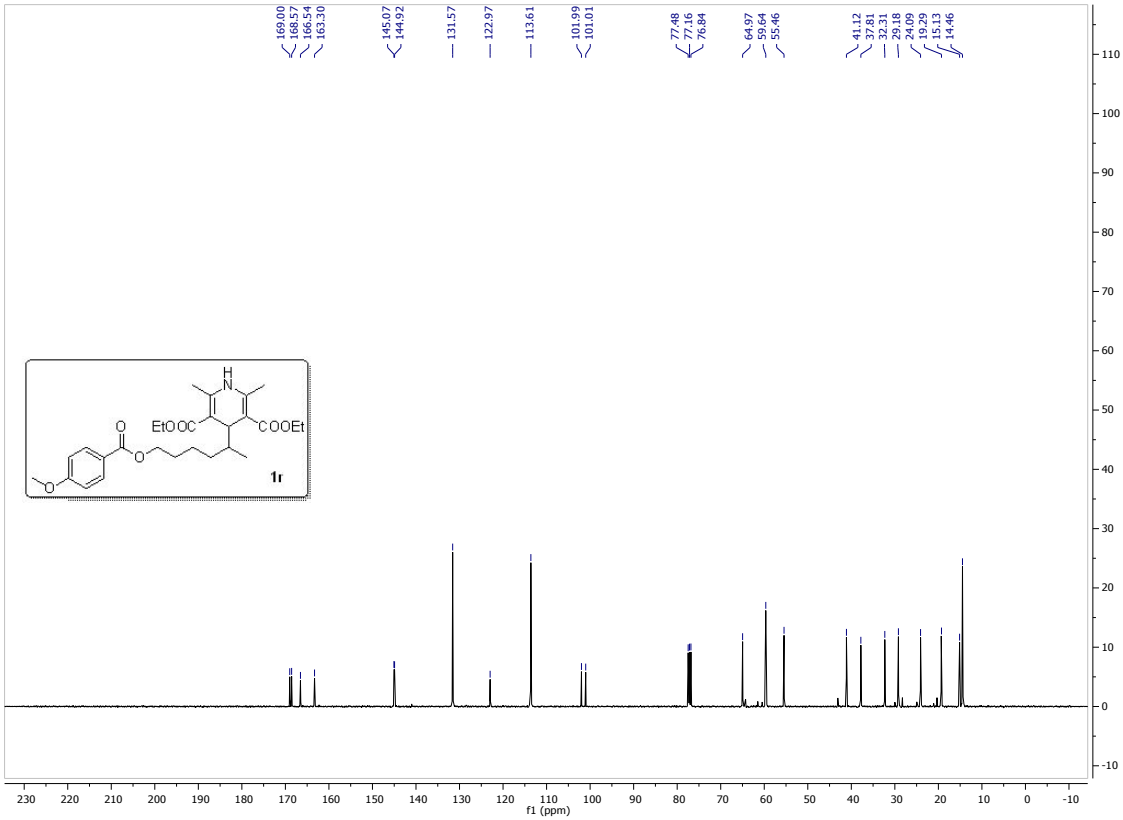

EtOOC
COOEt
1p
f1 (ppm)


EtOOC
COOEt
1p
f1 (ppm)


DCM
1q
f1 (ppm)


1q
f1 (ppm)


7.96
7.94
7.26
6.89
6.87
6.03
4.26
4.24
4.22
4.20
4.17
4.16
4.14
4.12
4.10
4.08
4.07
4.06
4.00
3.99
3.82
2.25
1.66
1.63
1.61
1.46
1.43
1.41
1.39
1.36
1.35
1.32
1.29
1.27
1.26
1.26
1.25
1.23
1.22
1.05
1.02
1.01
1.01
0.99
0.97
0.94
0.70
unknown
impurity
2.16
2.30
1.00
6.69
1.06
3.57
6.21
2.10
12.09
1.32
3.13
f1 (ppm)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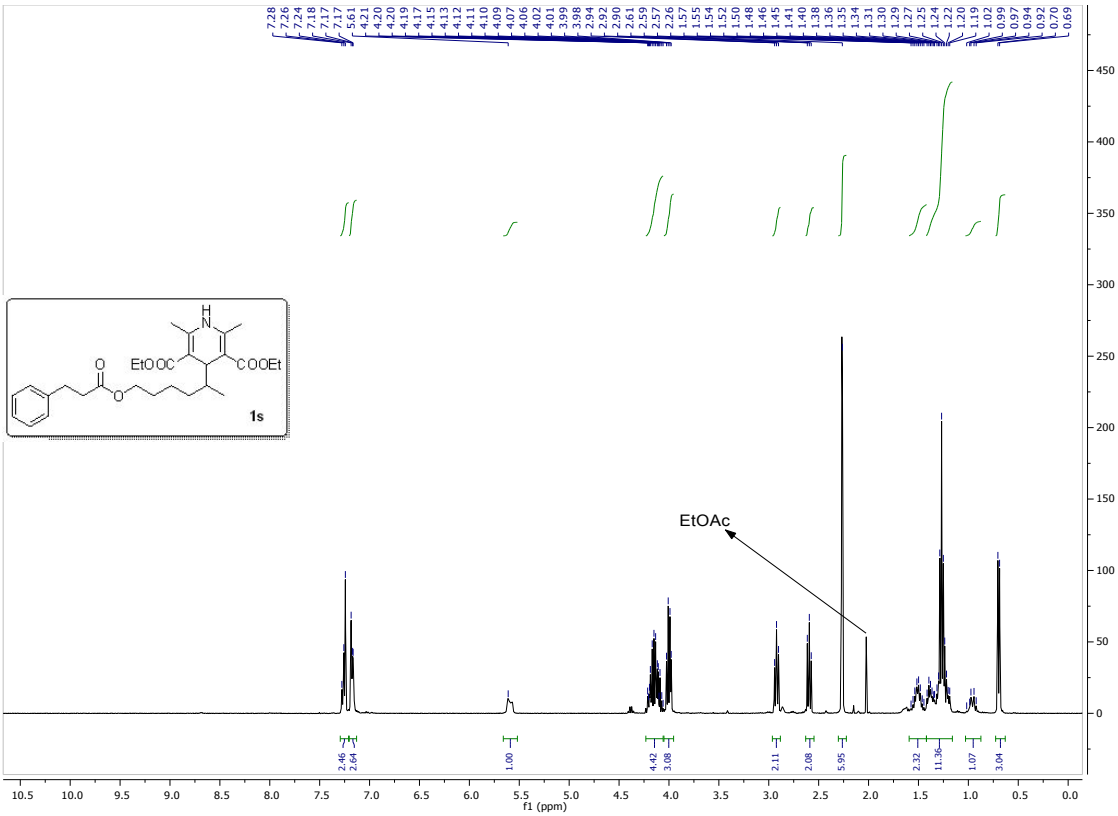
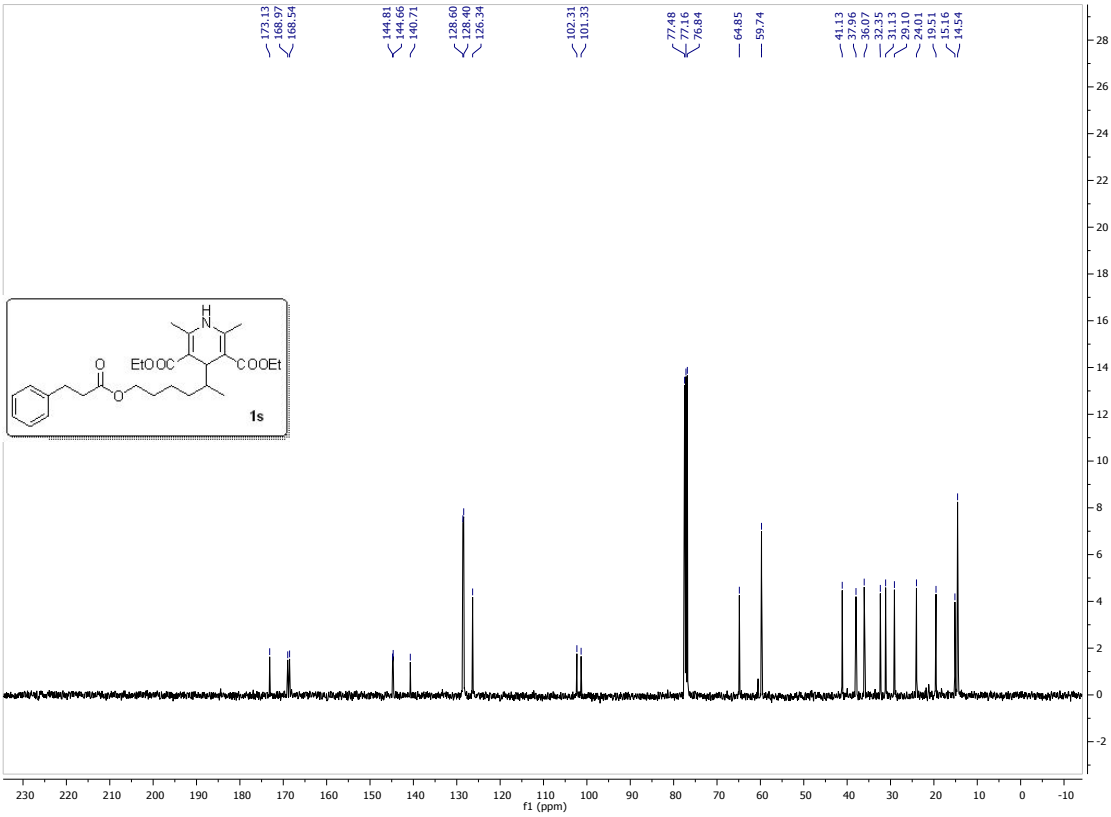
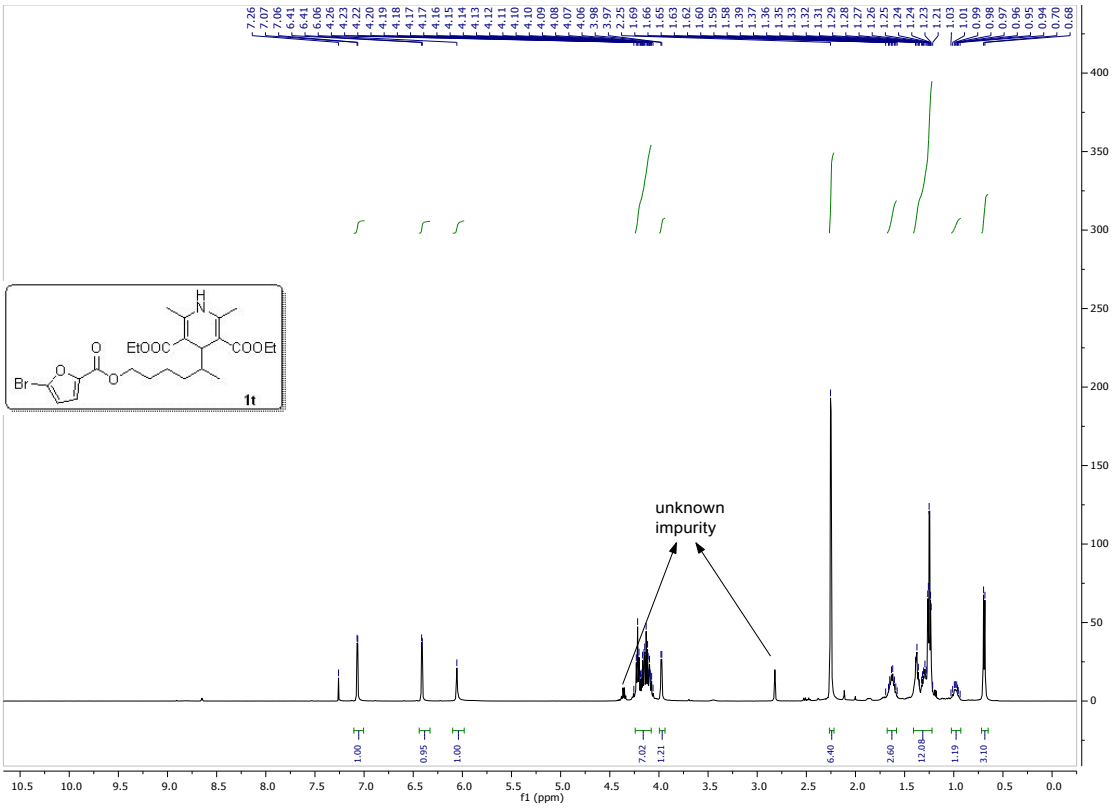
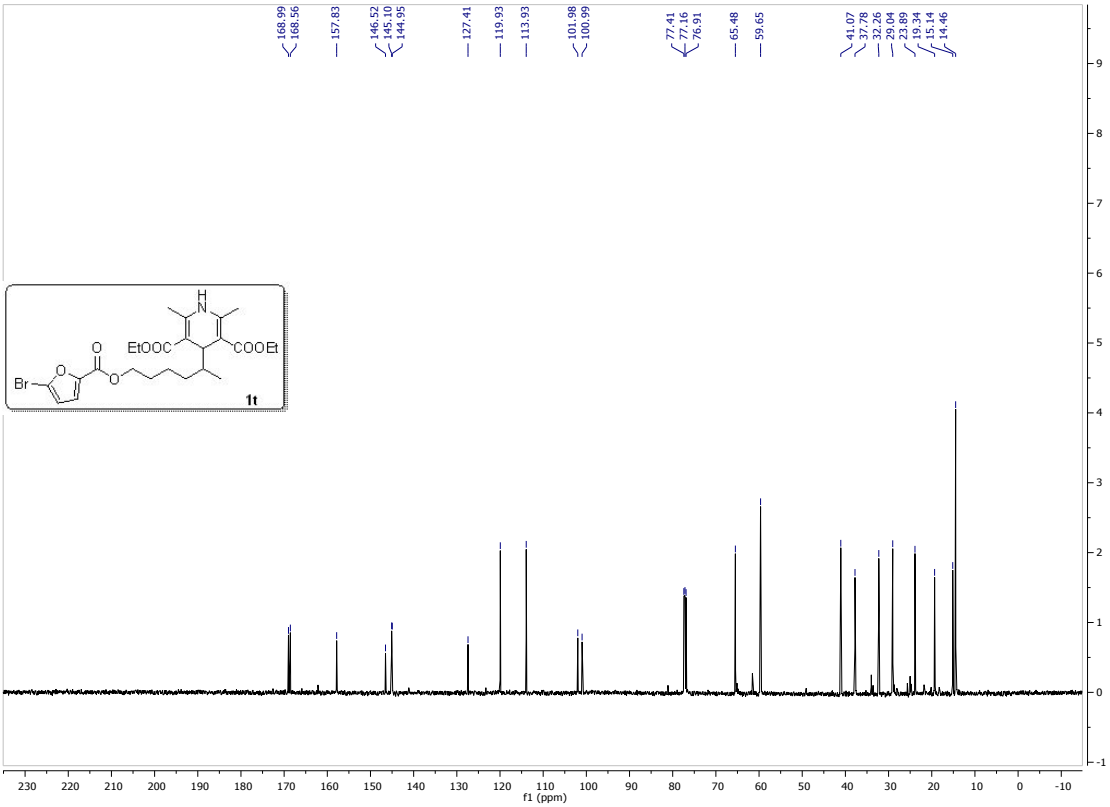
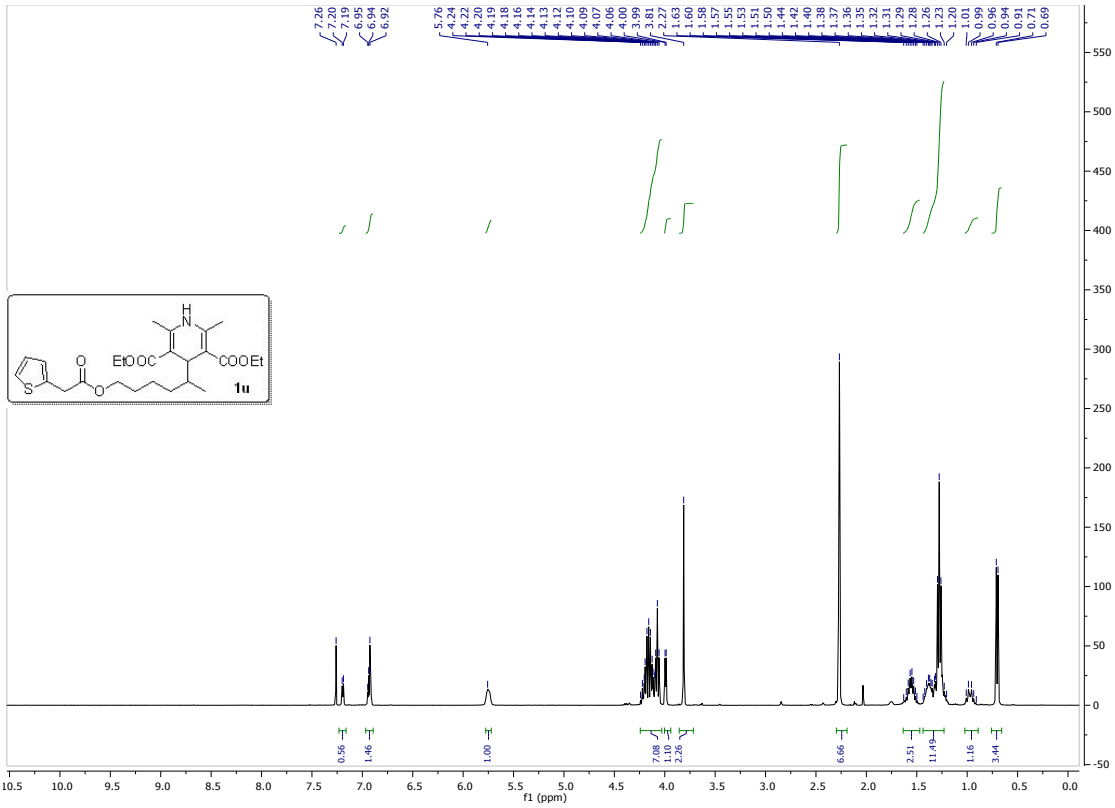
166.54
163.30
145.07
144.92
131.57
122.97
113.61
101.99
101.01
77.48
77.16
76.84
64.97
59.64
55.46
41.12
37.81
32.31
29.18
24.09
19.29
15.13
14.46
f1 (ppm)

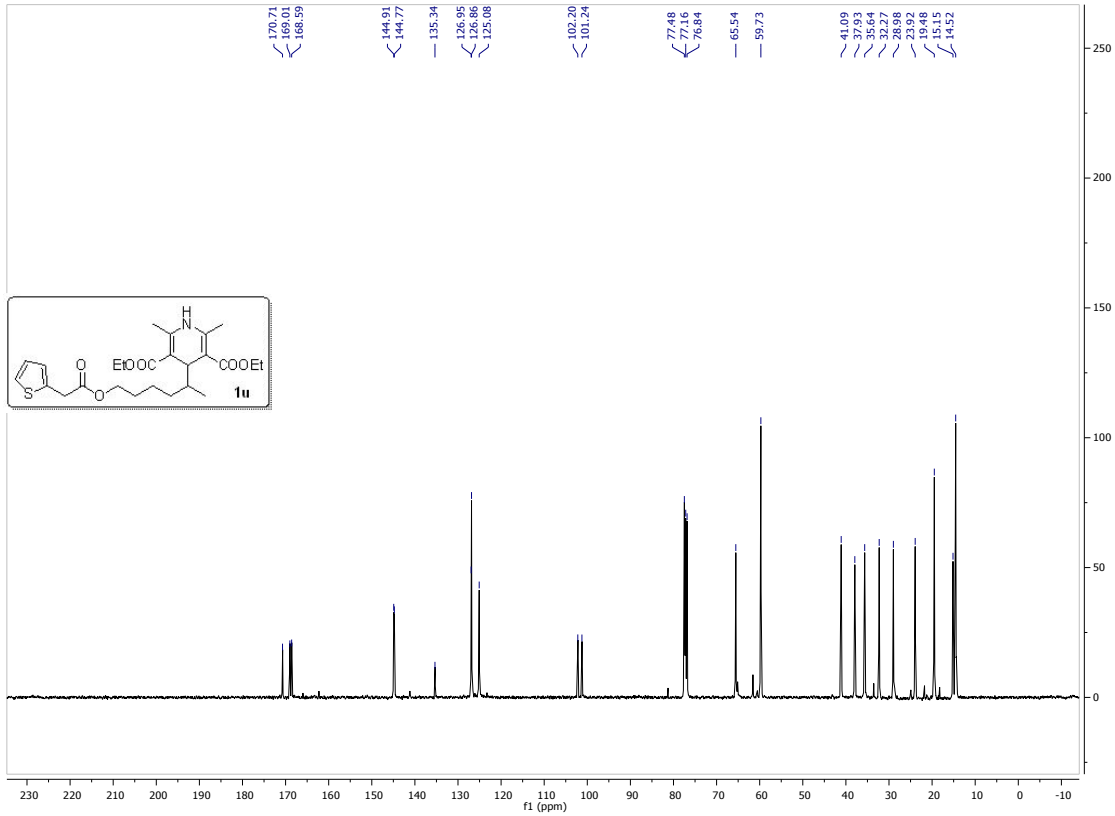

EtOAc
1s
f1 (ppm)

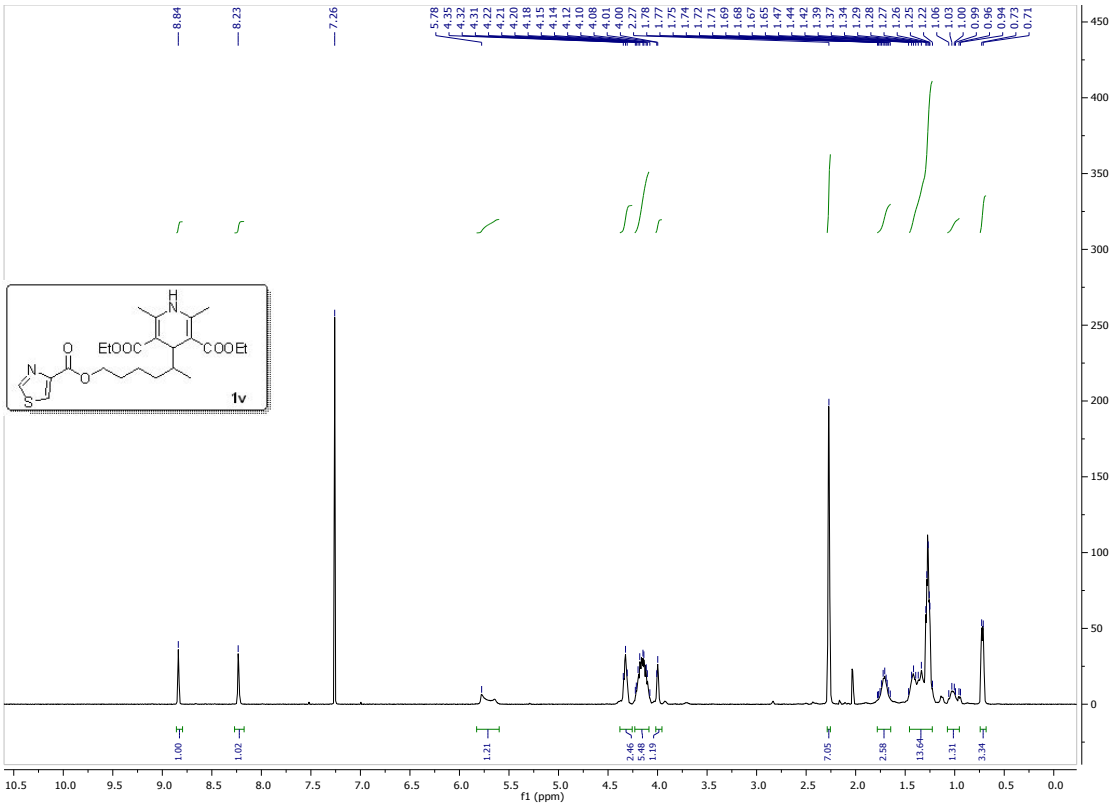

1s
f1 (ppm)

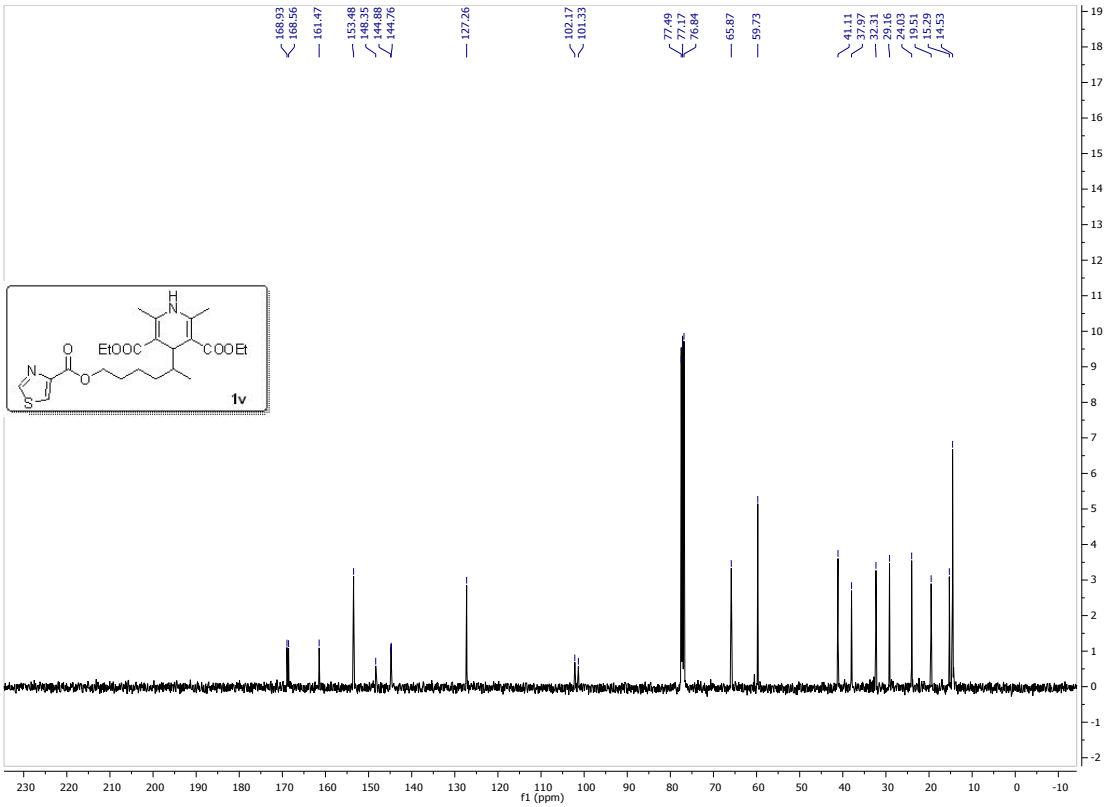

unknown
impurity
1t
f1 (ppm)

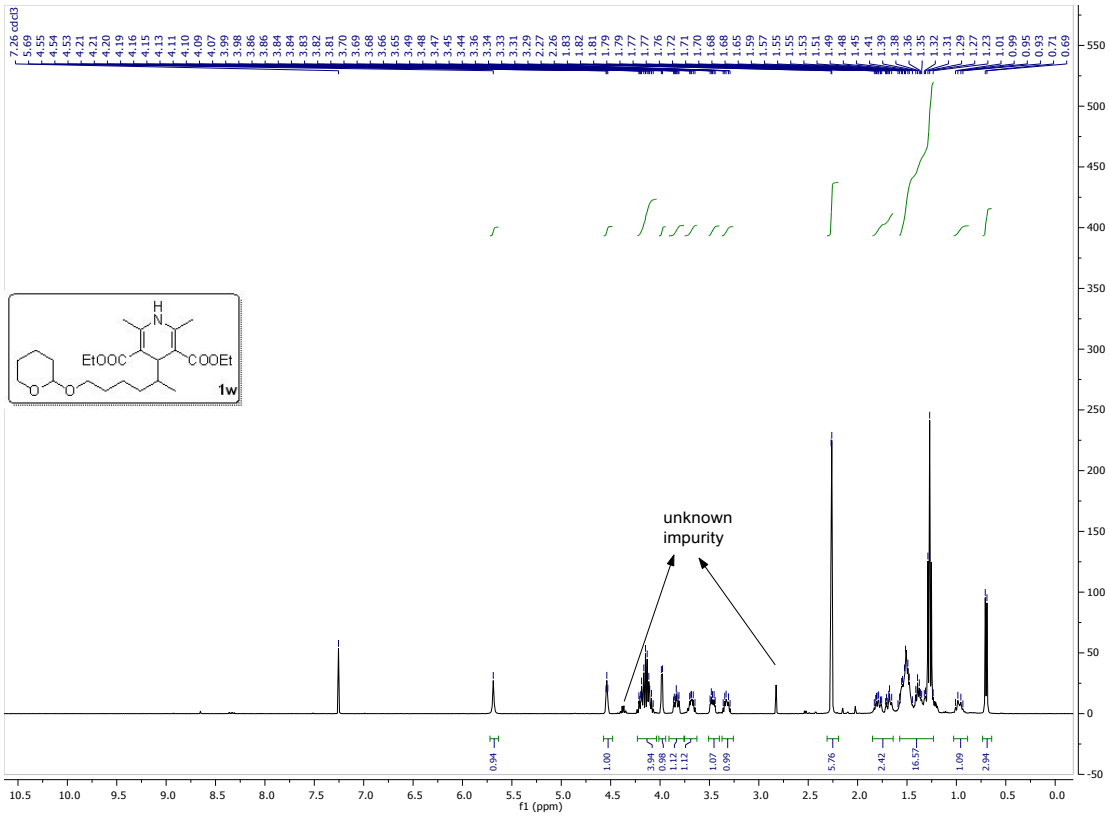

1t
f1 (ppm)

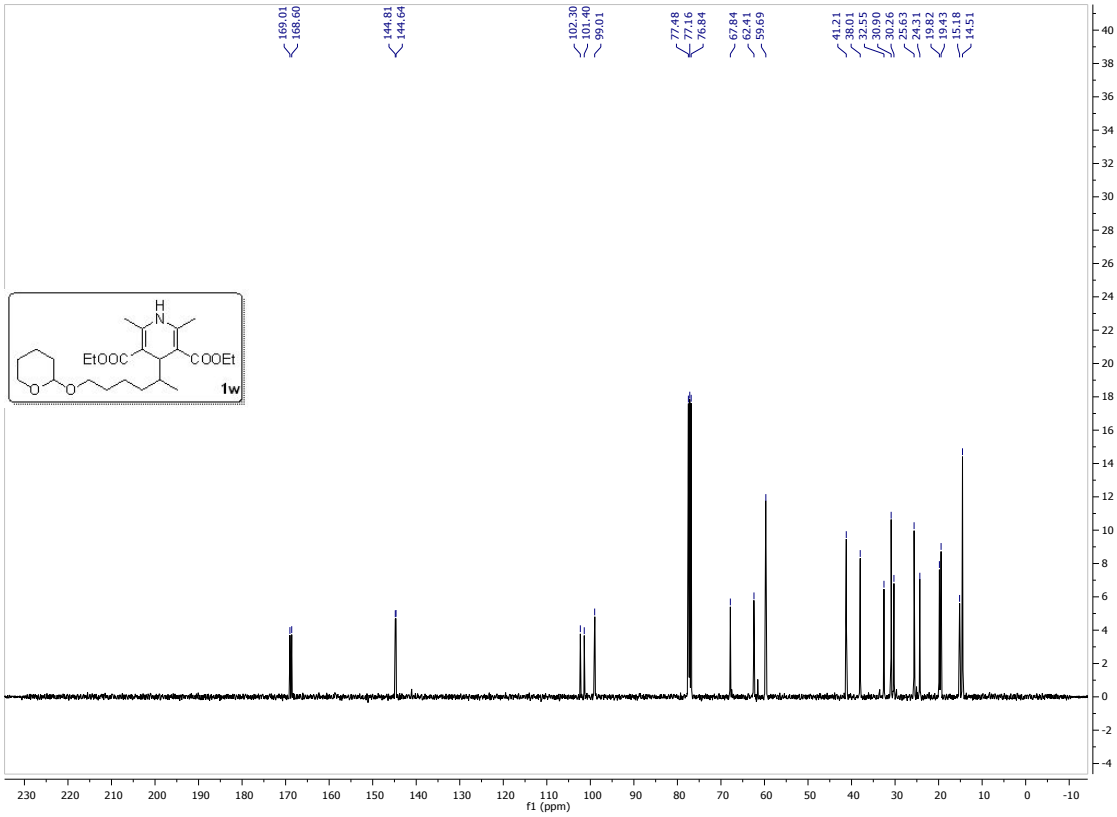

7.26 7.20 7.19 6.95 6.94 6.92
5.76 4.24 4.22 4.20 4.19 4.18 4.16 4.14 4.13 4.12 4.10 4.09 4.07 4.06 4.00 3.99 3.81 2.27 1.63 1.60 1.58 1.57 1.55 1.53 1.51 1.50 1.44 1.42 1.40 1.38 1.37 1.36 1.35 1.32 1.31 1.29 1.28 1.26 1.23 1.20 1.01 0.99 0.96 0.94 0.91 0.71 0.69
0.56 1.46 1.00 7.08 1.10 2.26 6.66 2.51 11.49 1.16 3.44
f1 (ppm)
EtOOC
COOEt
1u

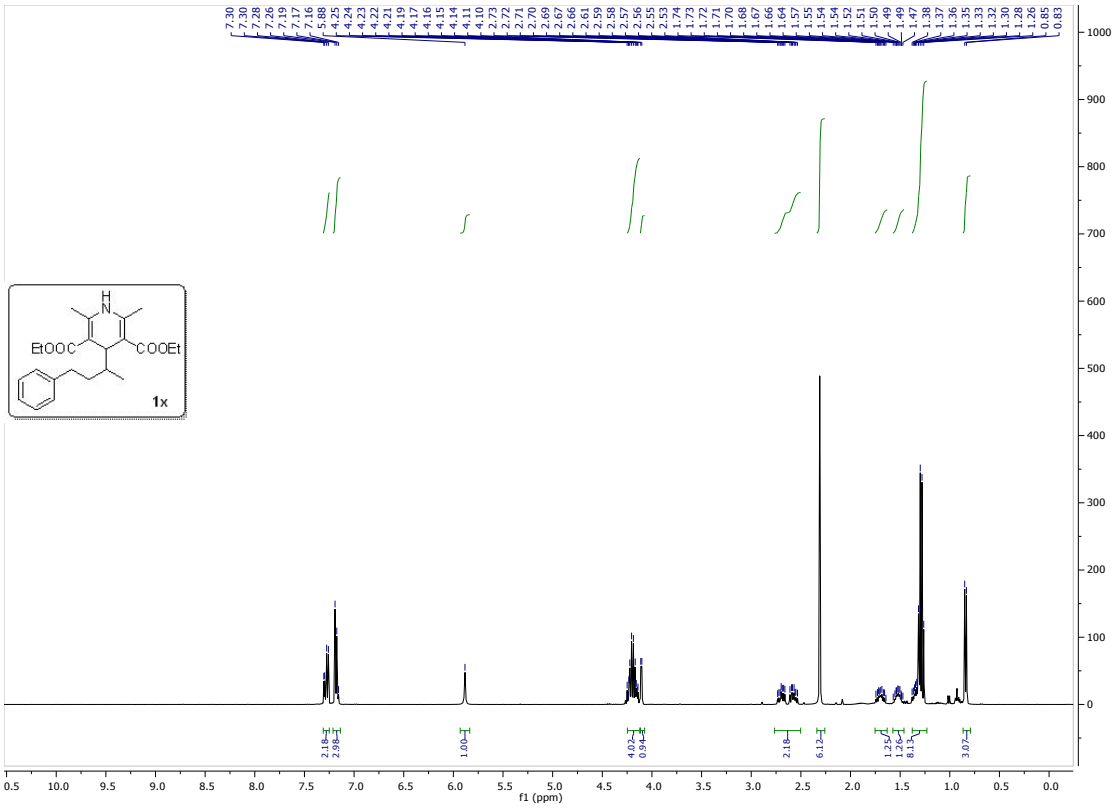

170.71 169.01 168.59
144.91 144.77
135.34
126.95 126.86 125.08
102.20 101.24
77.48 77.16 76.84
65.54
59.73
41.09 37.93 35.64 33.77 28.98 23.92 19.48 15.15 14.52
f1 (ppm)
EtOOC
COOEt
1u

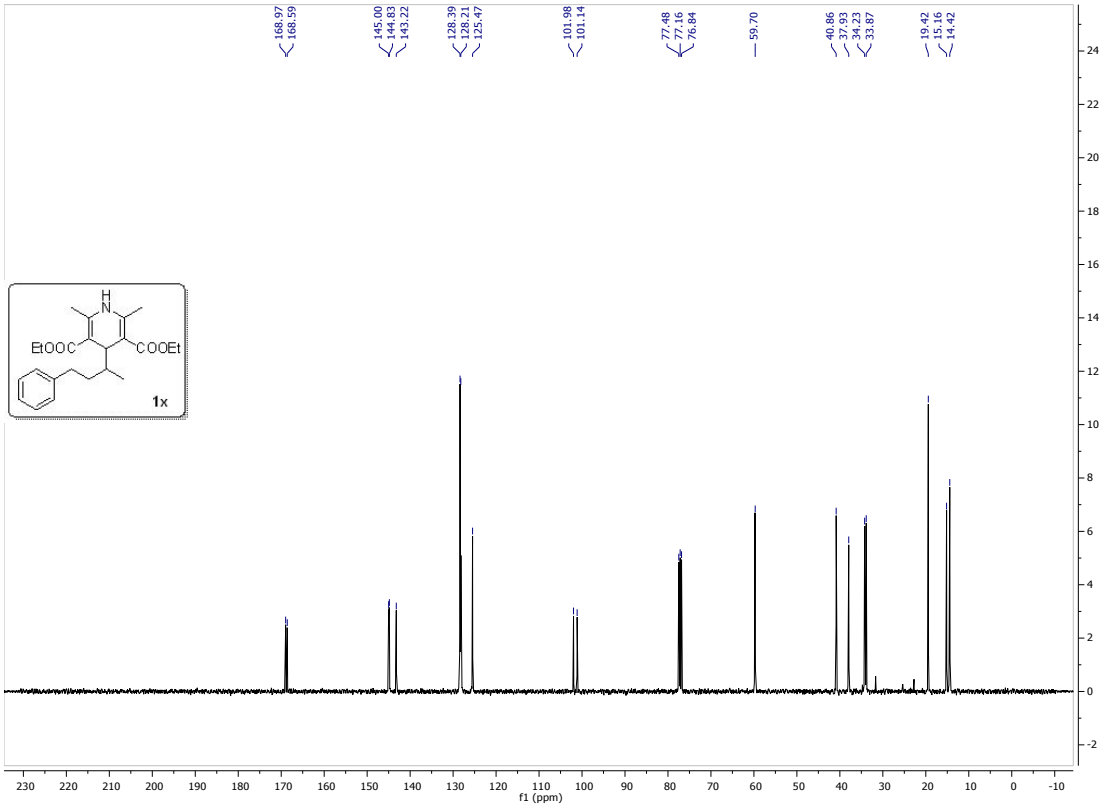

8.84
8.23
7.26
1.00
1.02
1.21
2.46
5.48
1.19
7.05
2.58
13.64
1.31
3.34
f1 (ppm)
EtOOC
COOEt
1v

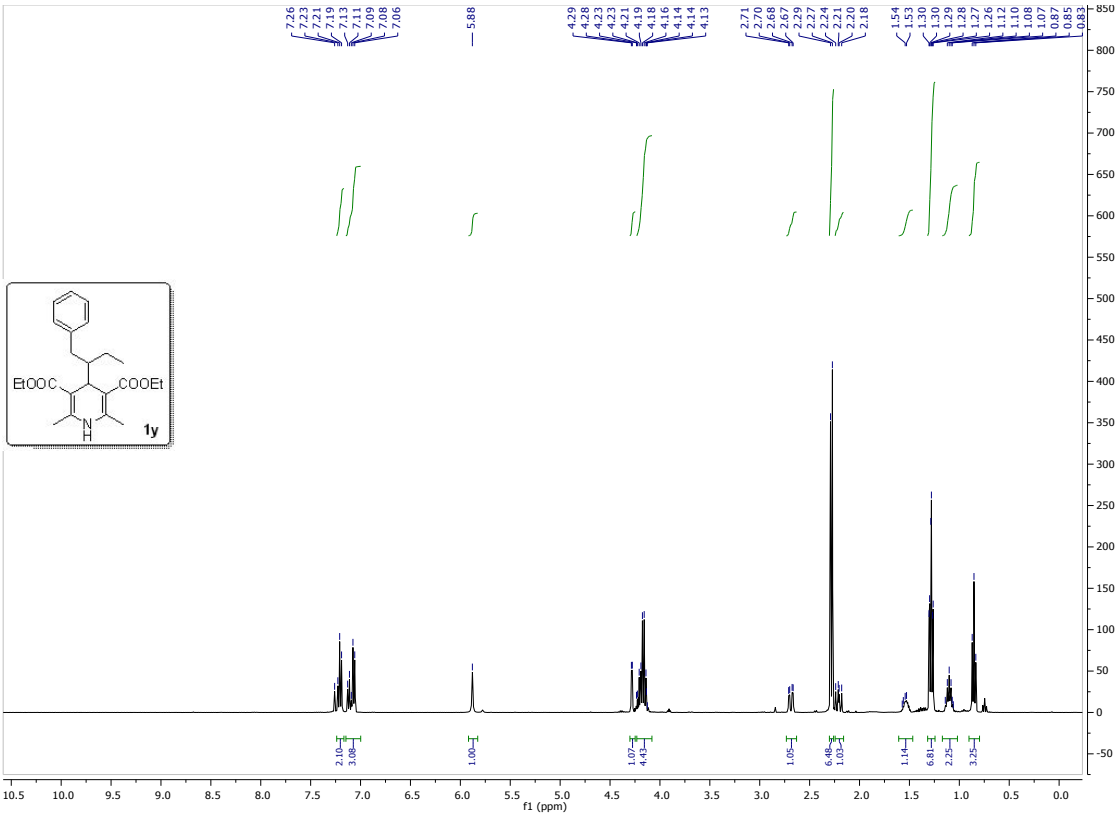

168.93
168.56
161.47
153.48
143.35
144.88
144.76
127.26
102.17
101.33
77.49
77.17
76.84
65.87
59.73
41.11
37.97
32.31
29.16
24.03
19.51
15.29
14.53
f1 (ppm)
EtOOC
COOEt
1v

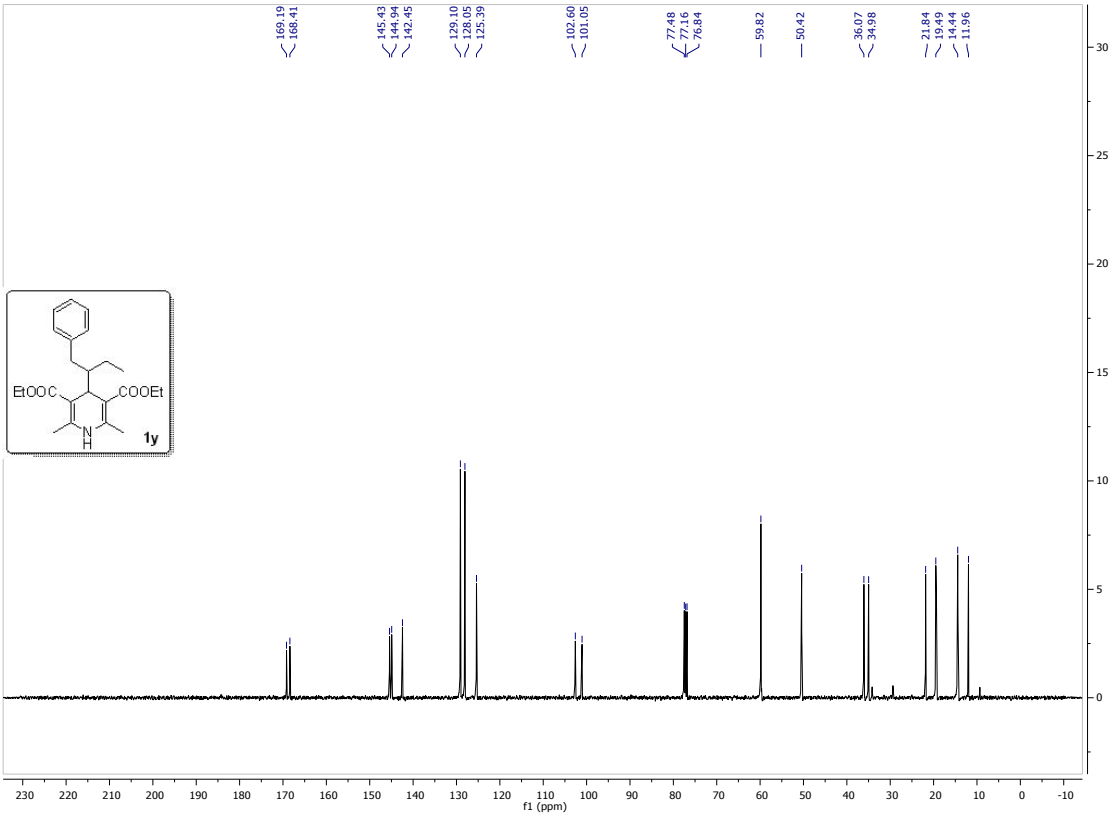

7.26 cdcl3
EtOOC
COOEt
1w
unknown
impurity
f1 (ppm)

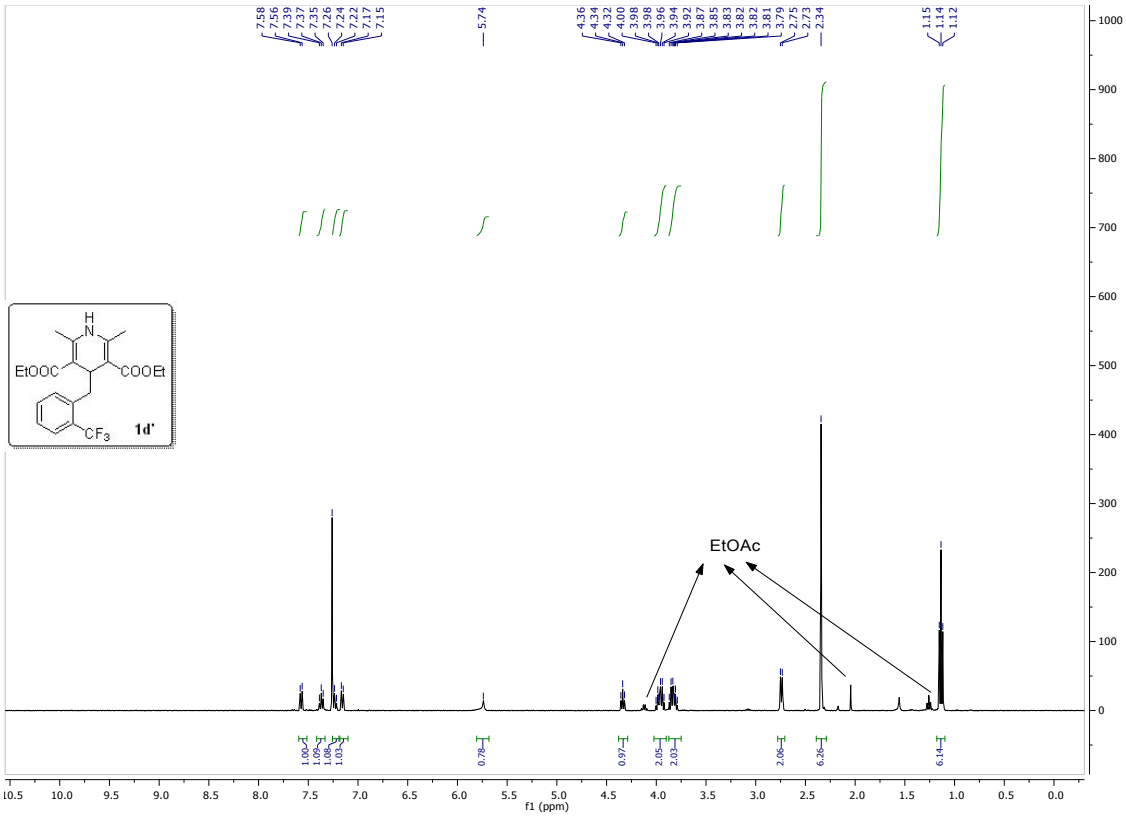

169.01
168.60
144.81
144.64
102.30
101.40
99.01
77.48
77.16
76.84
67.84
62.41
59.69
41.21
38.01
32.55
30.90
30.26
25.63
24.31
19.82
19.43
15.18
14.51
EtOOC
COOEt
1w
f1 (ppm)

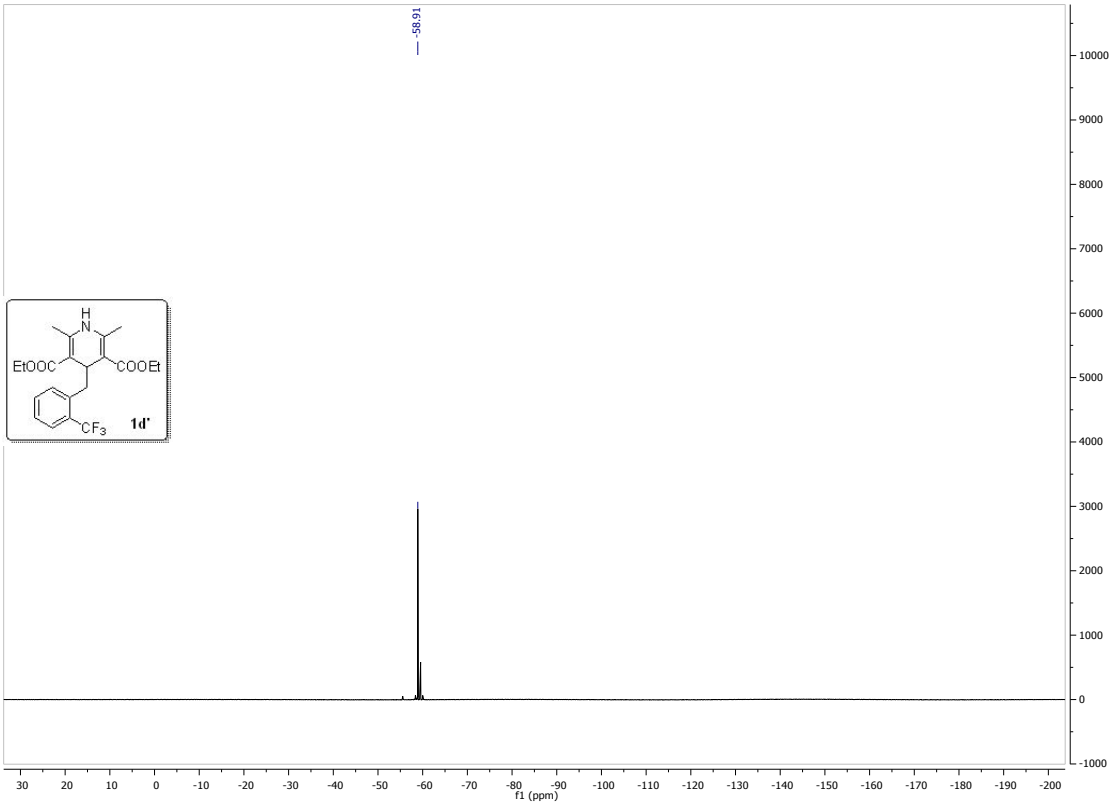

7.30 7.30 7.28 7.26 7.19 7.17 7.16 5.88 4.25 4.24 4.23 4.22 4.21 4.19 4.17 4.16 4.15 4.14 4.11 4.10 2.73 2.72 2.71 2.70 2.69 2.67 2.66 2.61 2.59 2.58 2.57 2.56 2.55 2.53 1.74 1.73 1.72 1.71 1.70 1.68 1.67 1.66 1.64 1.57 1.55 1.54 1.54 1.52 1.51 1.50 1.49 1.49 1.47 1.38 1.37 1.36 1.35 1.33 1.32 1.30 1.28 1.26 0.85 0.83
H
N
EtOOC
COOEt
1x
2.18 2.98 1.00 4.02 0.94 2.18 6.12 1.25 1.26 8.13 3.07
f1 (ppm)


168.97 168.59 145.00 144.83 143.22 128.39 128.21 125.47 101.98 101.14 77.48 77.16 76.84 59.70 40.86 37.93 34.23 33.87 19.42 15.16 14.42
H
N
EtOOC
COOEt
1x
f1 (ppm)

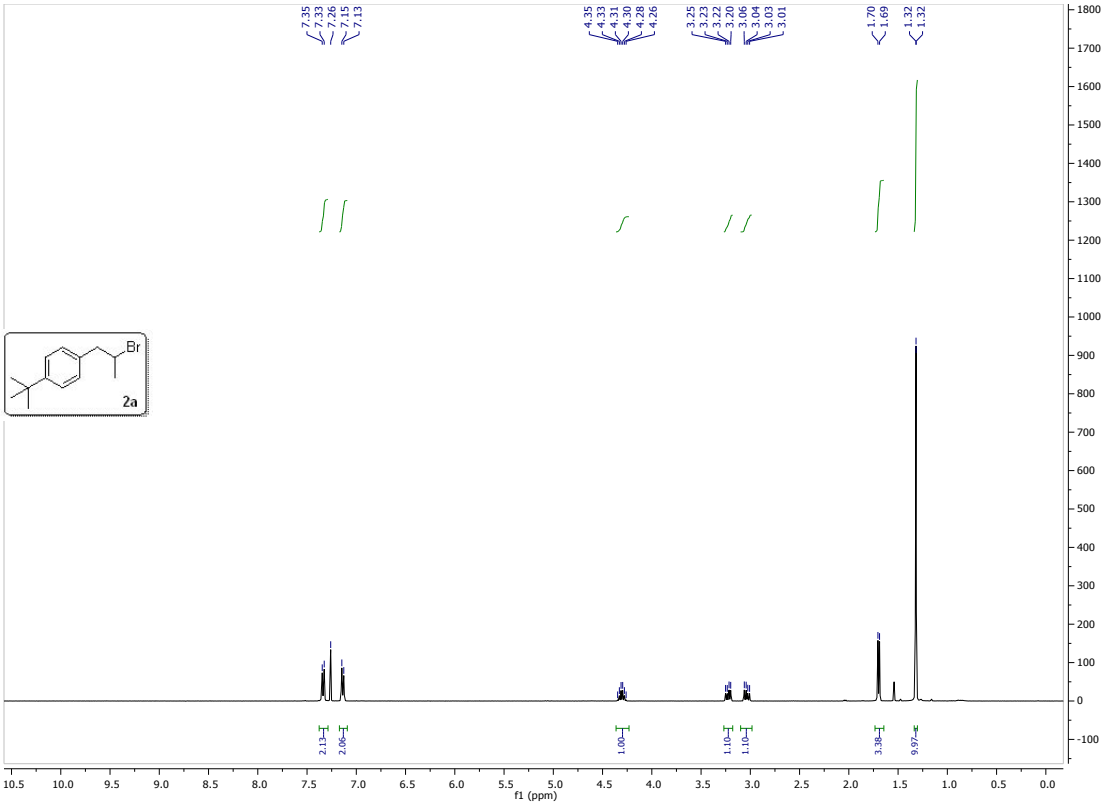

EtOOC
COOEt
N
H
1y
f1 (ppm)

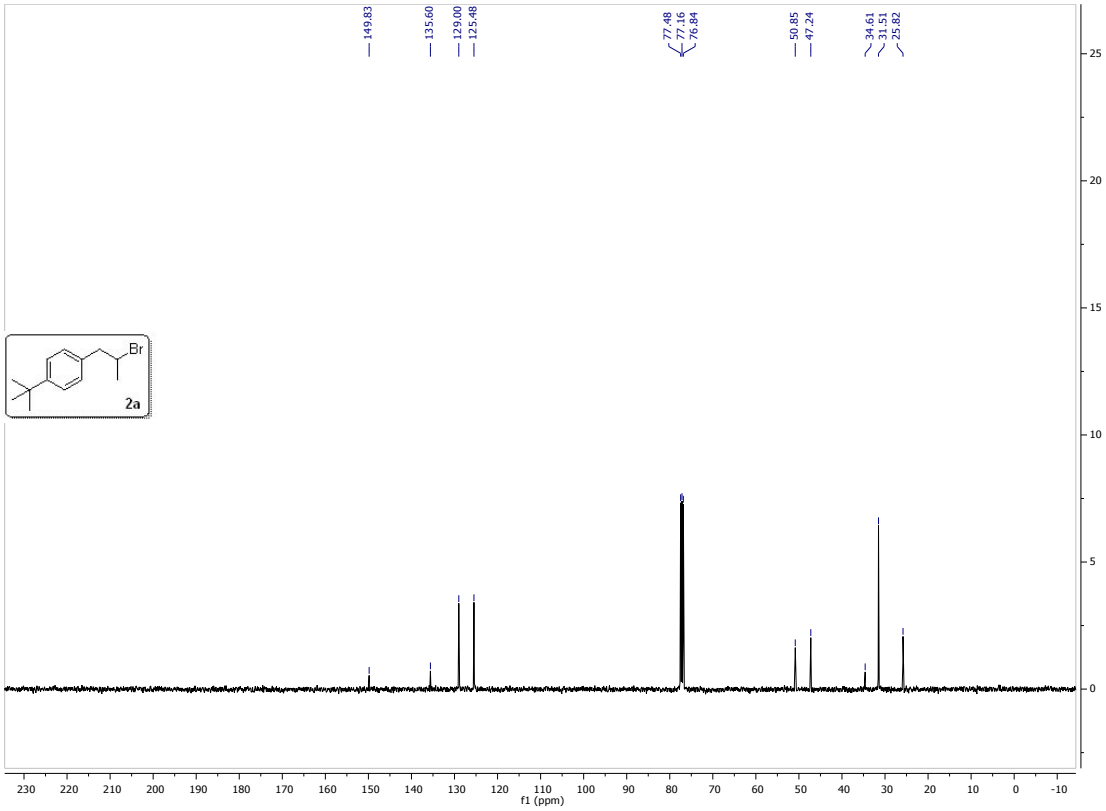

EtOOC
COOEt
N
H
1y
f1 (ppm)

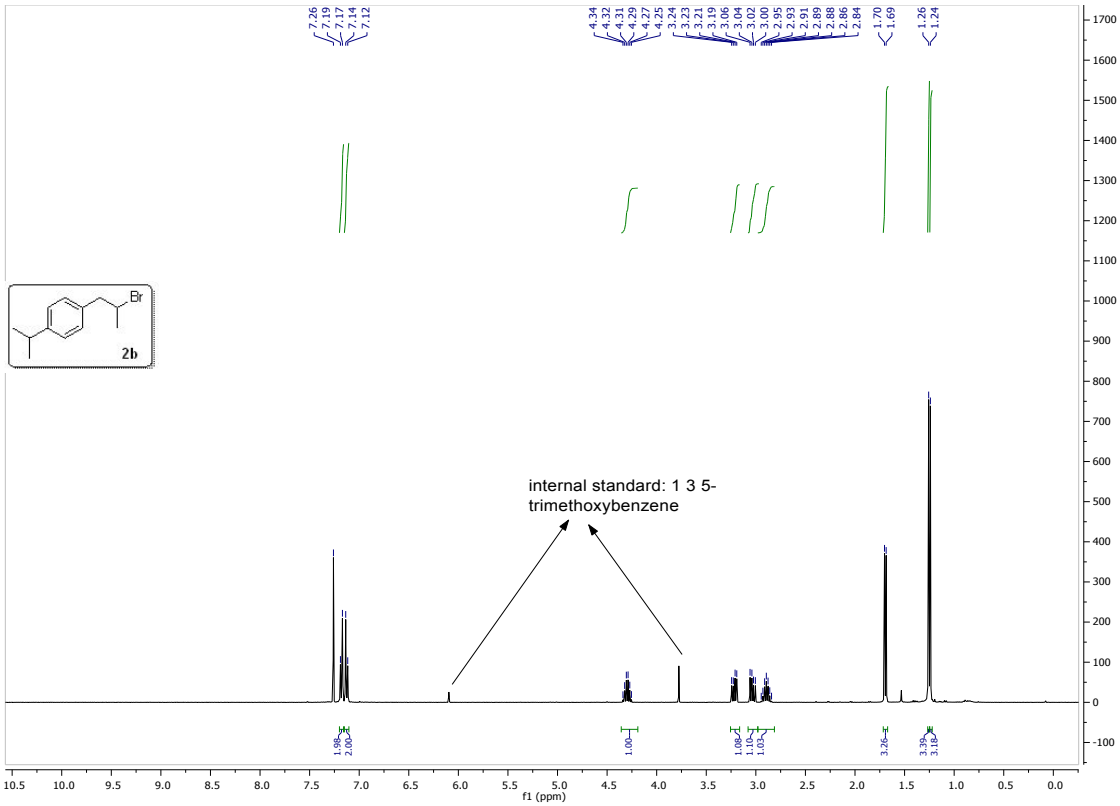

EtOAc
1d'
f1 (ppm)

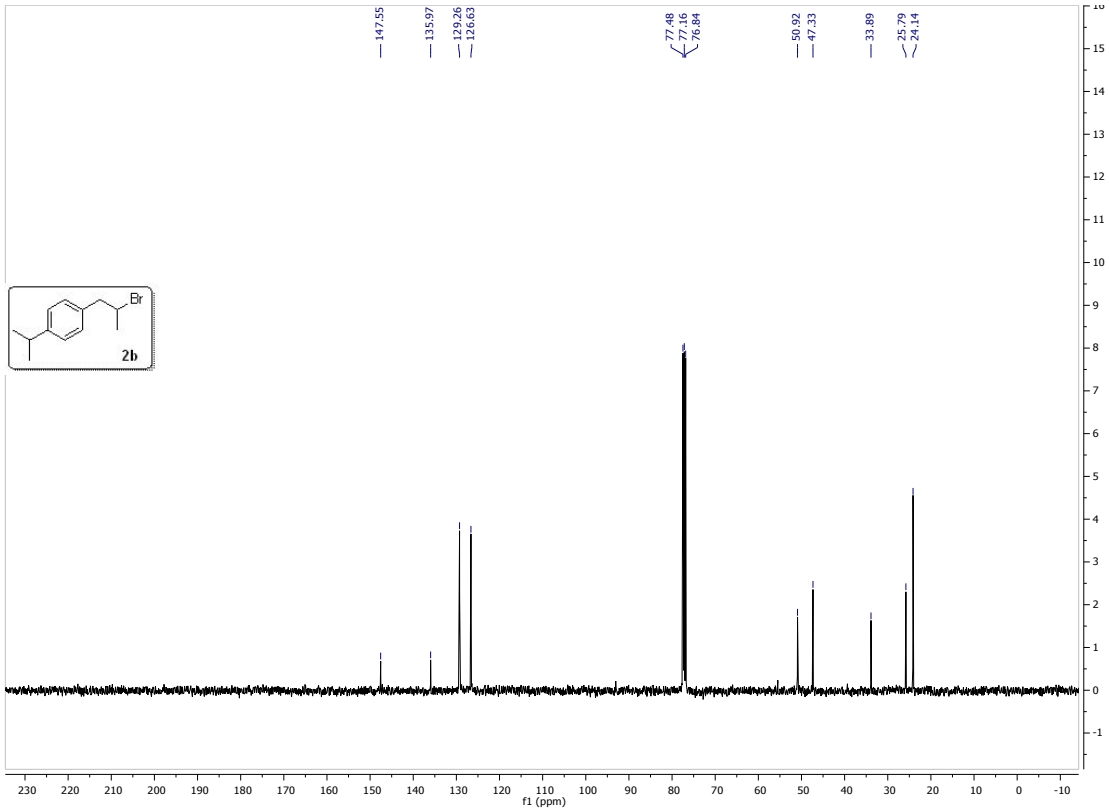

-58.91
1d'
f1 (ppm)

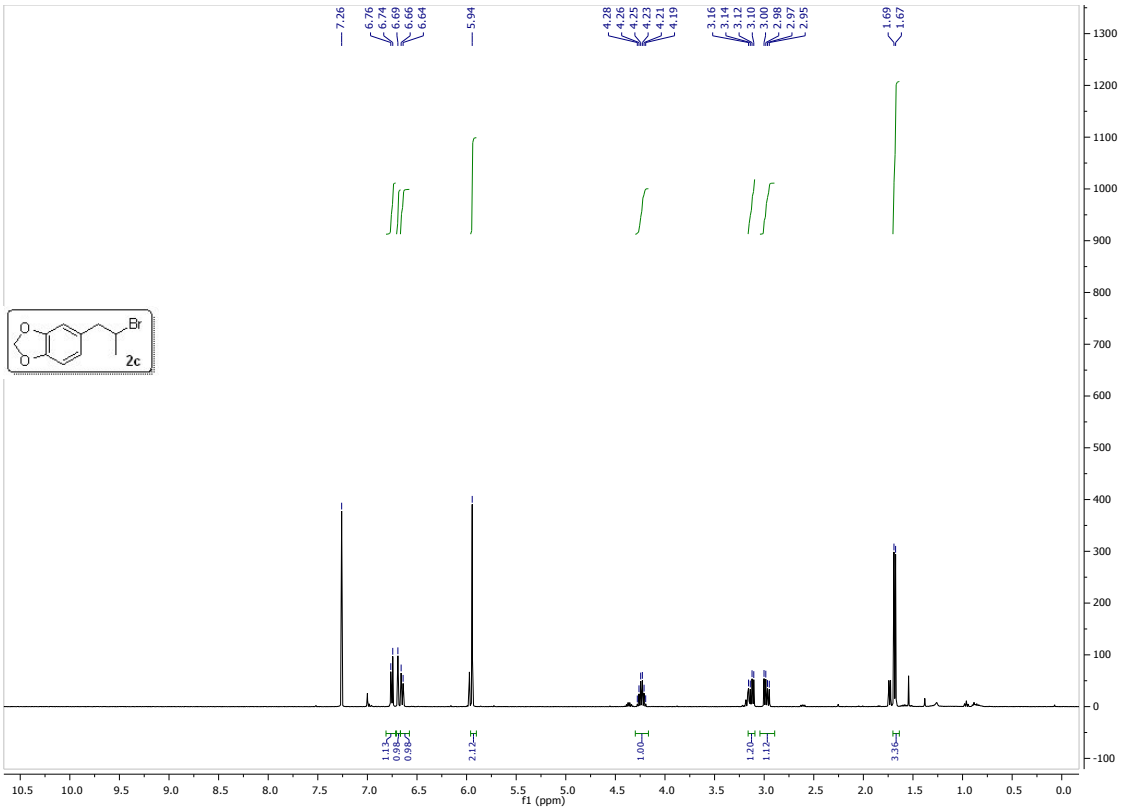
4.2 NMR spectral data for brominated products 2

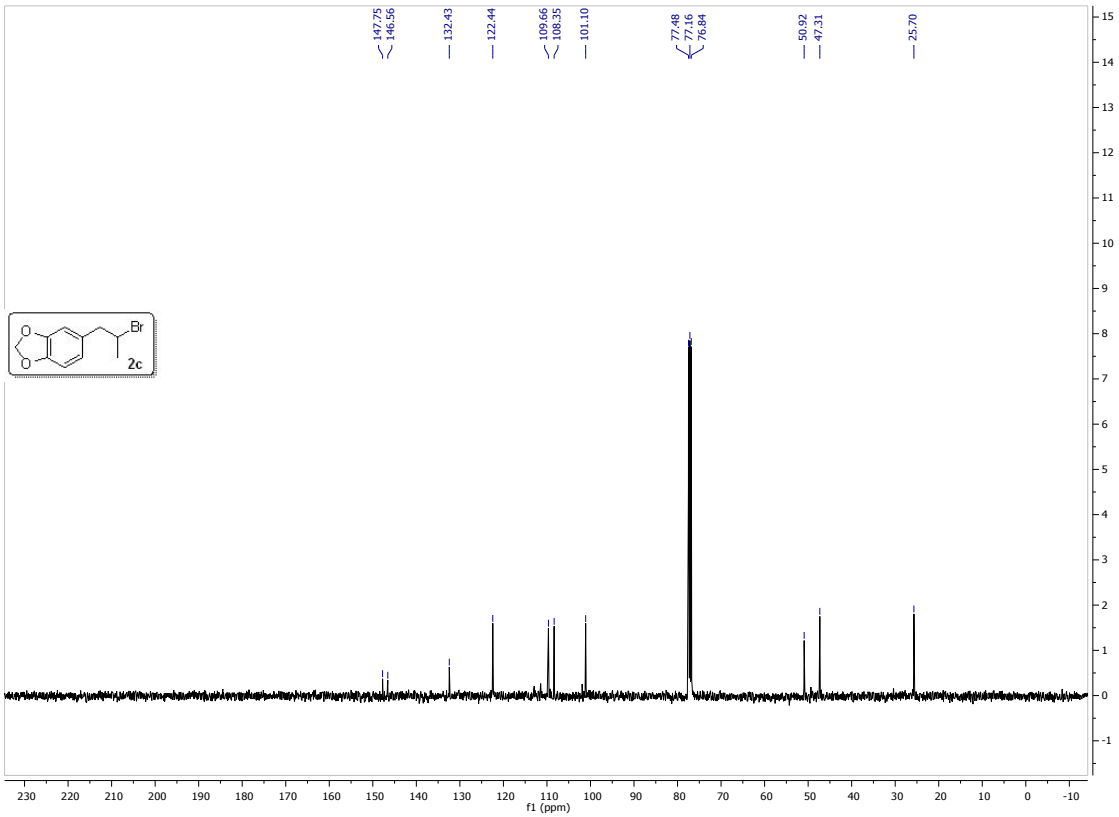


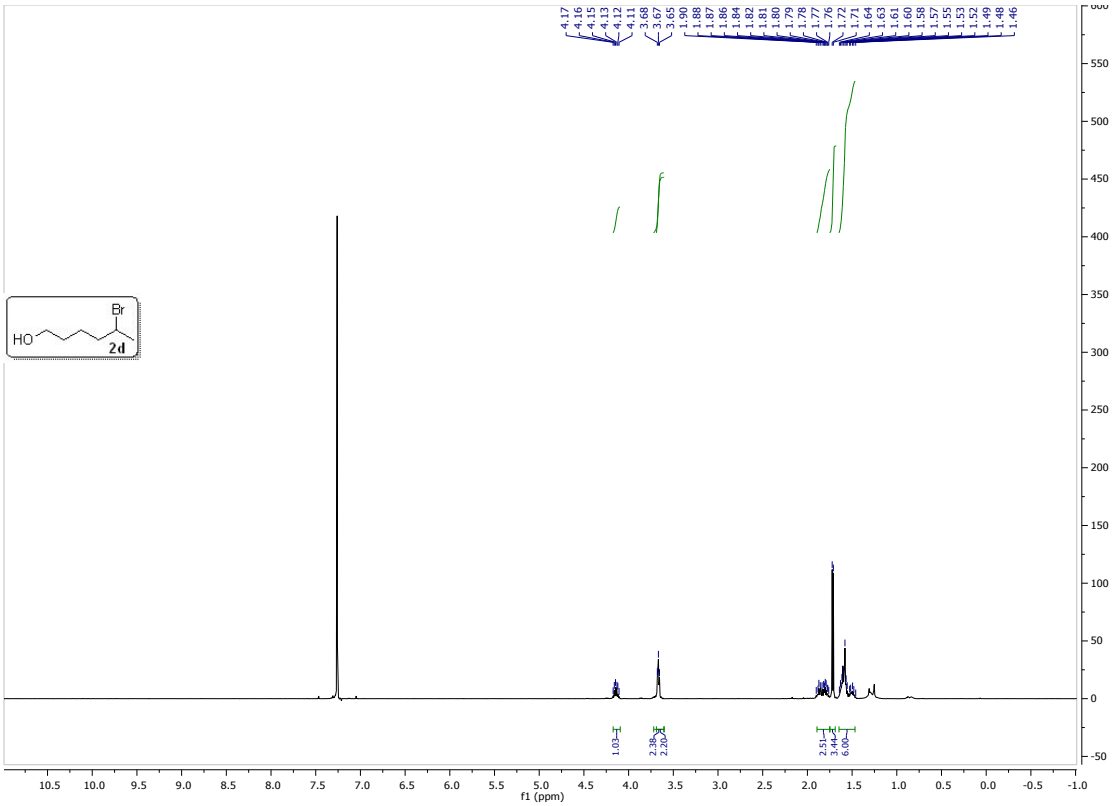


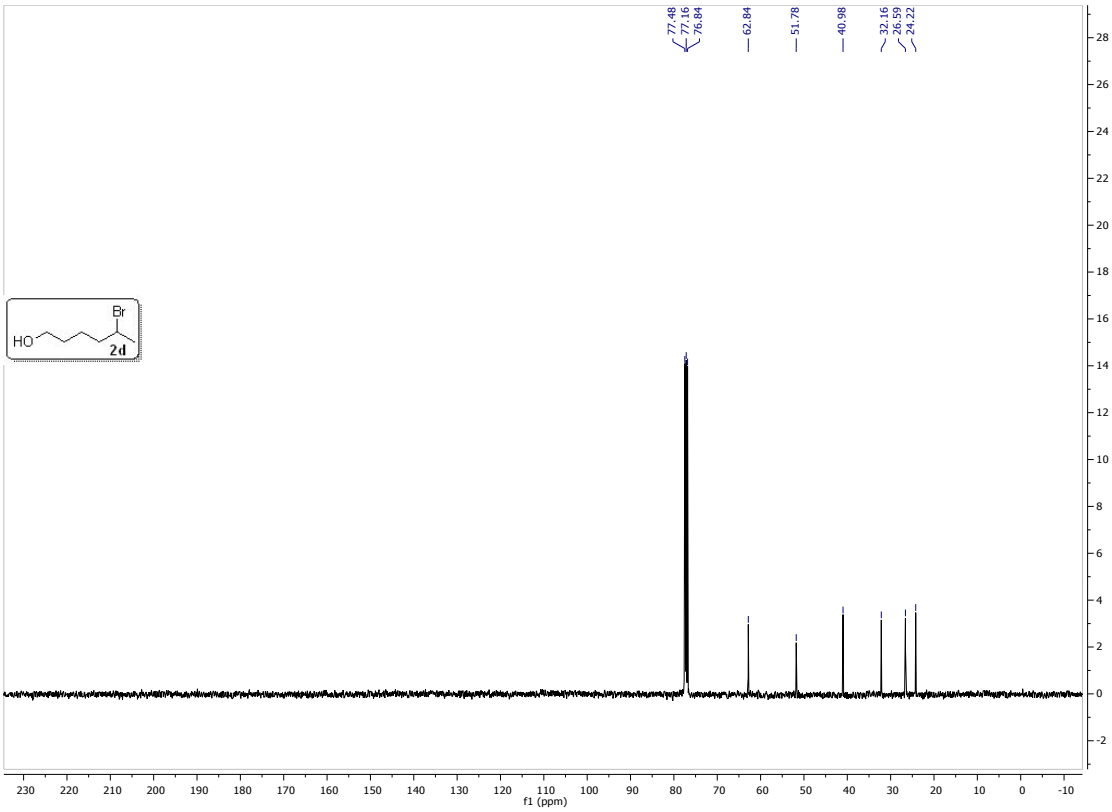

2b
Br
internal standard: 1 3 5-
trimethoxybenzene
f1 (ppm)

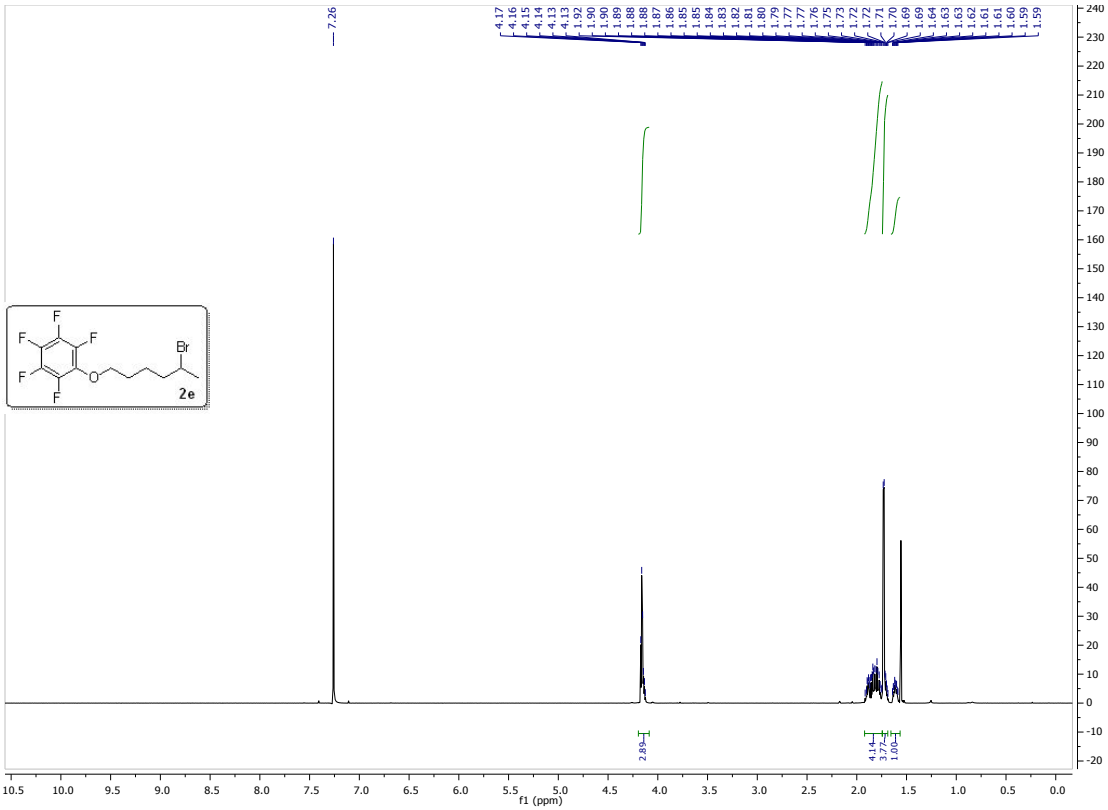

2b
Br
f1 (ppm)

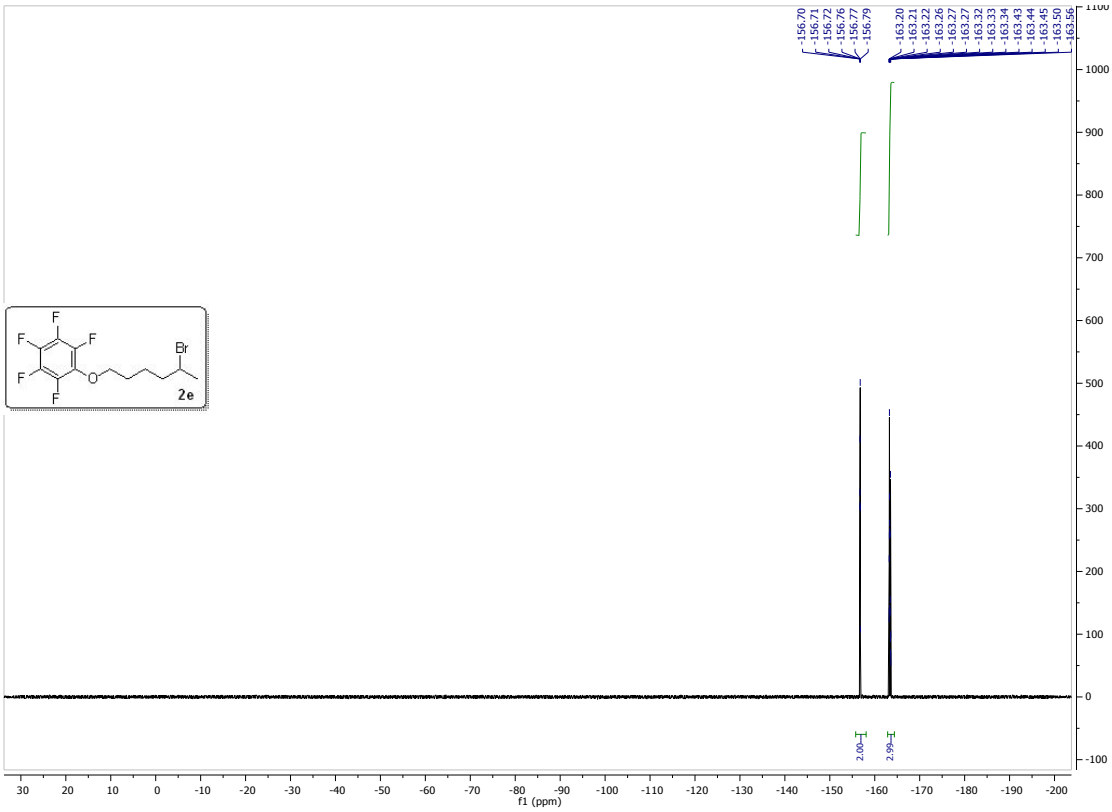

7.26
6.76
6.74
6.69
6.66
6.64
5.94
4.28
4.26
4.25
4.23
4.21
4.19
3.16
3.14
3.12
3.10
3.00
2.98
2.97
2.95
1.69
1.67
1.13
0.98
0.98
2.12
1.00
1.20
1.12
3.36
f1 (ppm)
Br
2c

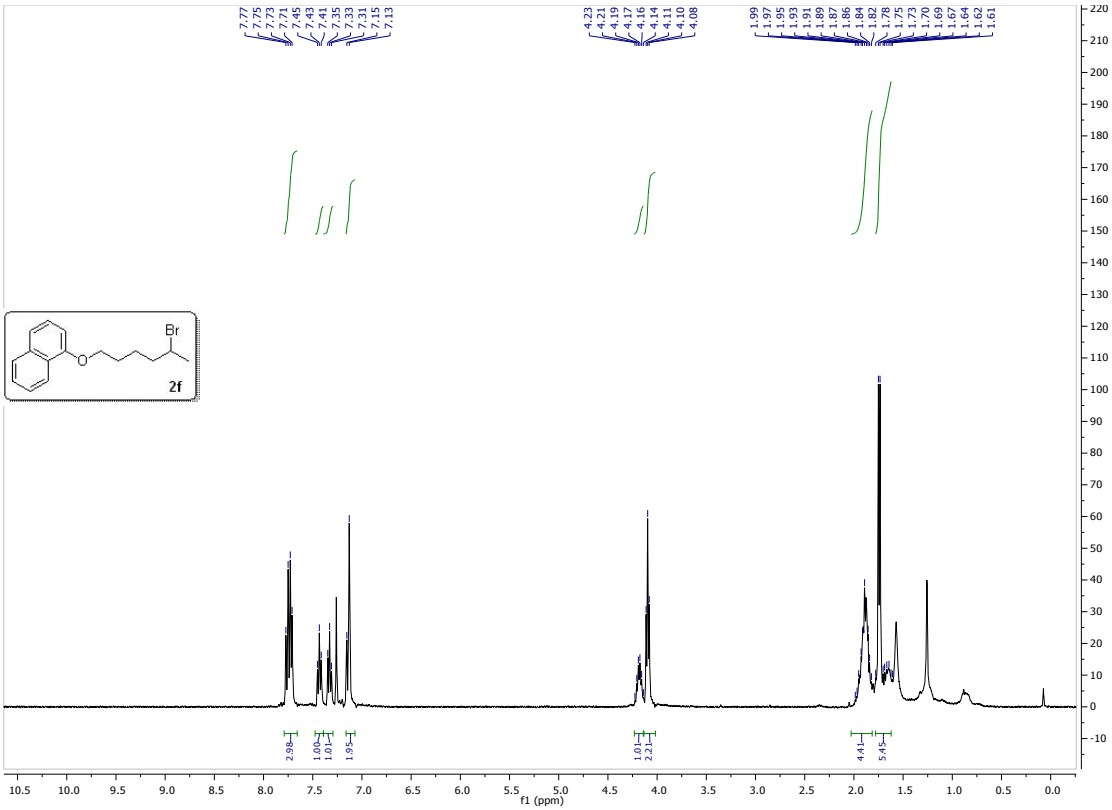

147.75
146.56
132.43
122.44
109.66
108.35
101.10
77.48
77.16
76.84
50.92
47.31
25.70
f1 (ppm)
Br
2c

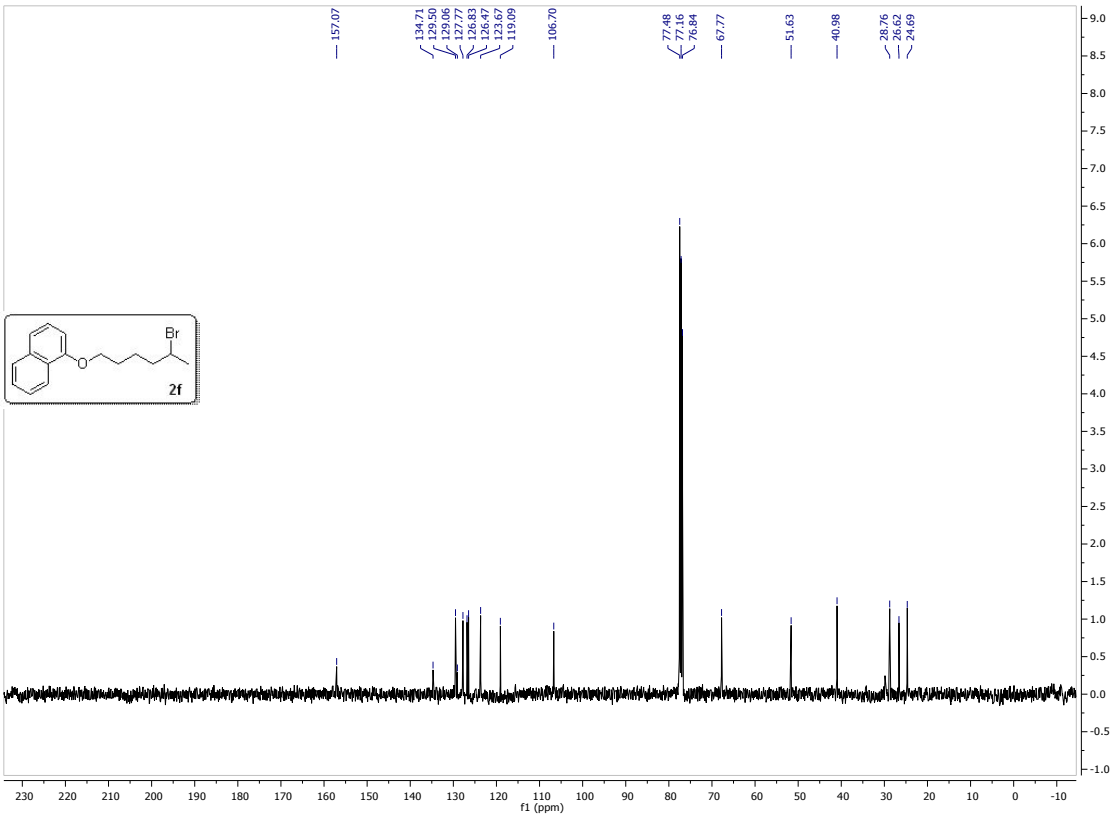

4.17
4.16
4.15
4.13
4.12
4.11
3.68
3.67
3.65
1.90
1.88
1.87
1.86
1.84
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.72
1.71
1.64
1.63
1.61
1.60
1.58
1.57
1.55
1.53
1.52
1.49
1.48
1.46
Br
HO
2d
1.03
2.38
2.20
2.51
3.44
6.00
f1 (ppm)

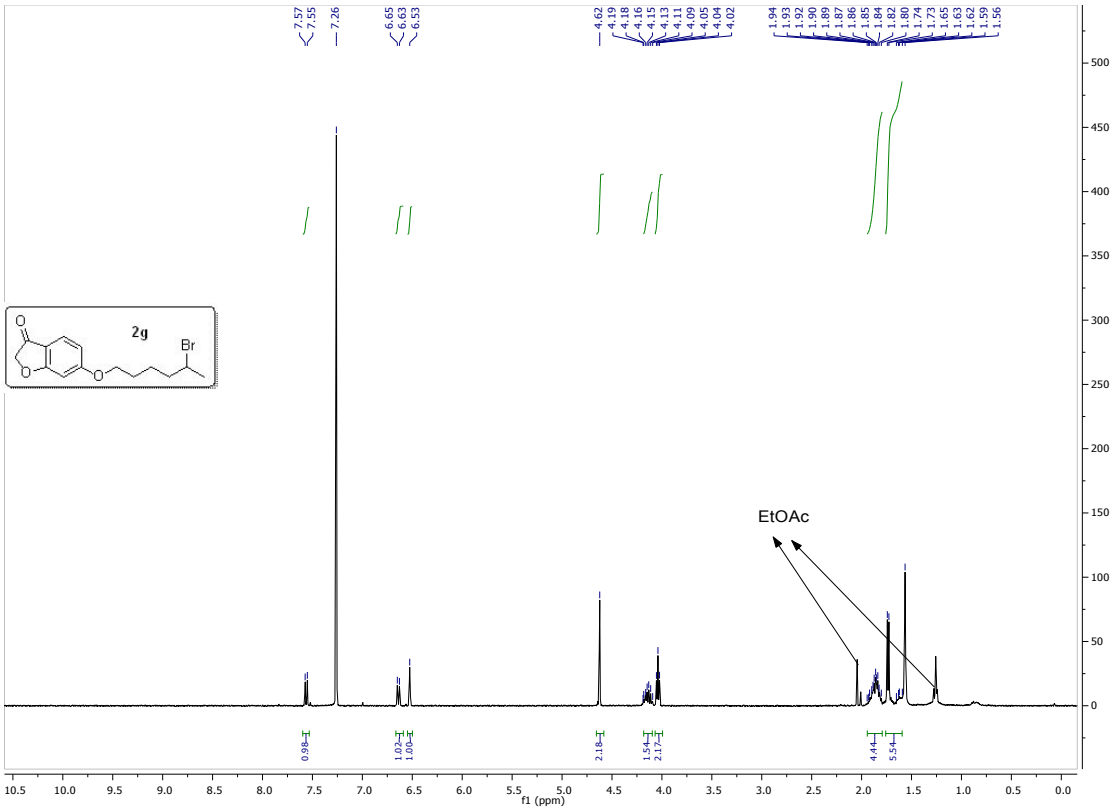

77.48
77.16
76.84
62.84
51.78
40.98
32.16
26.59
24.22
Br
HO
2d
f1 (ppm)

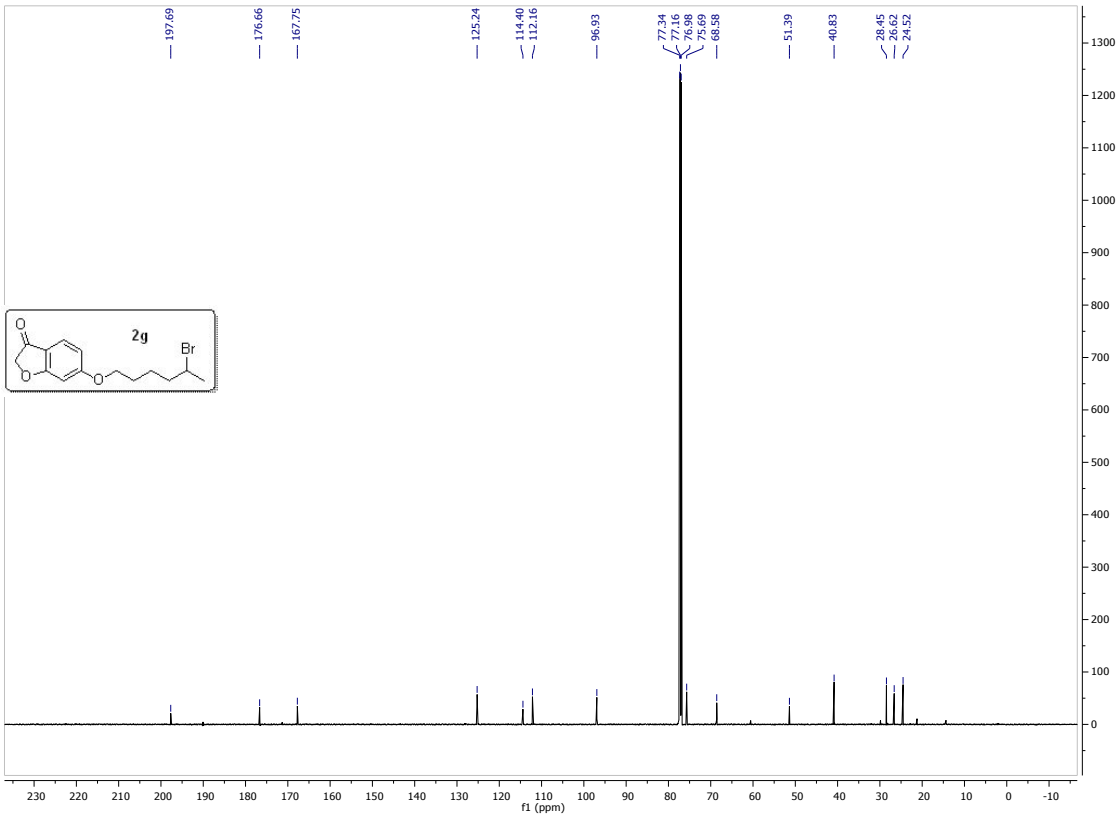

7.26
4.17
4.16
4.15
4.14
4.13
4.13
1.92
1.90
1.90
1.89
1.88
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.77
1.77
1.76
1.75
1.73
1.72
1.72
1.71
1.70
1.69
1.69
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.59
2.89
4.14
3.77
1.00
F
F
F
F
F
Br
O
2e
f1 (ppm)

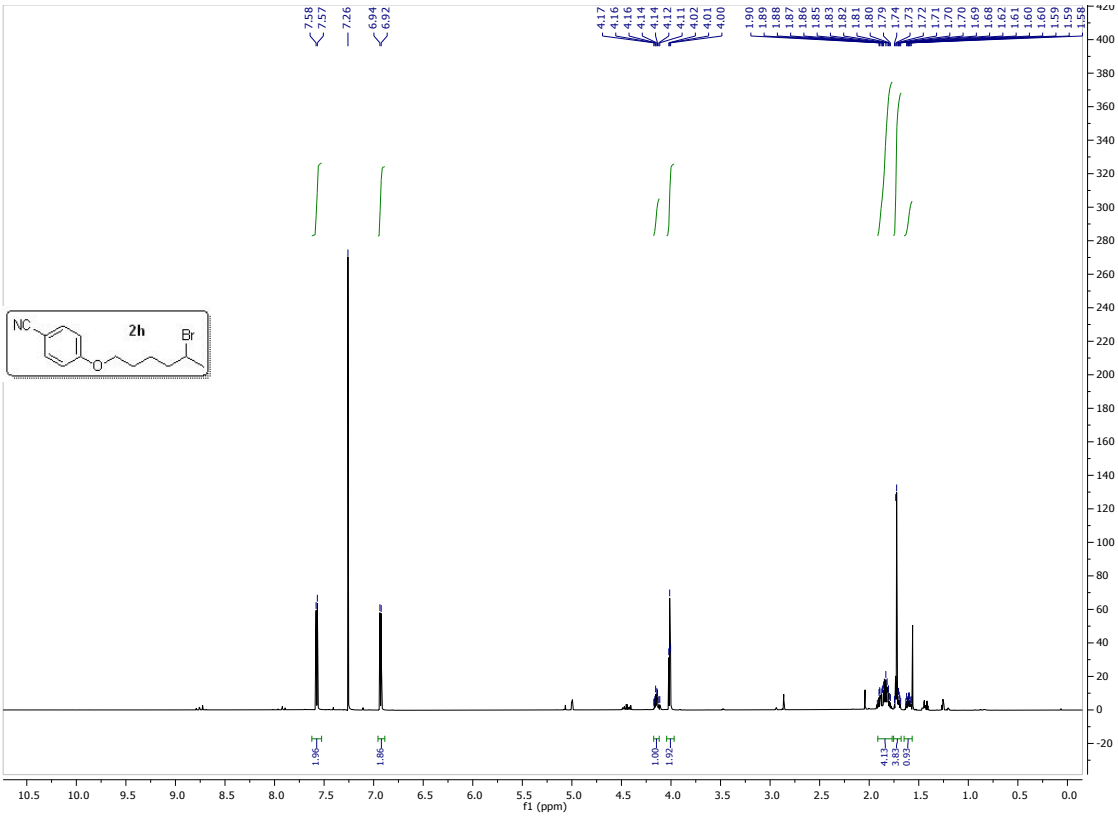

-156.70
-156.71
-156.72
-156.76
-156.77
-156.79
-163.20
-163.21
-163.22
-163.26
-163.27
-163.27
-163.32
-163.33
-163.34
-163.43
-163.44
-163.45
-163.50
-163.56
2.00
2.99
F
F
F
F
F
Br
O
2e
f1 (ppm)

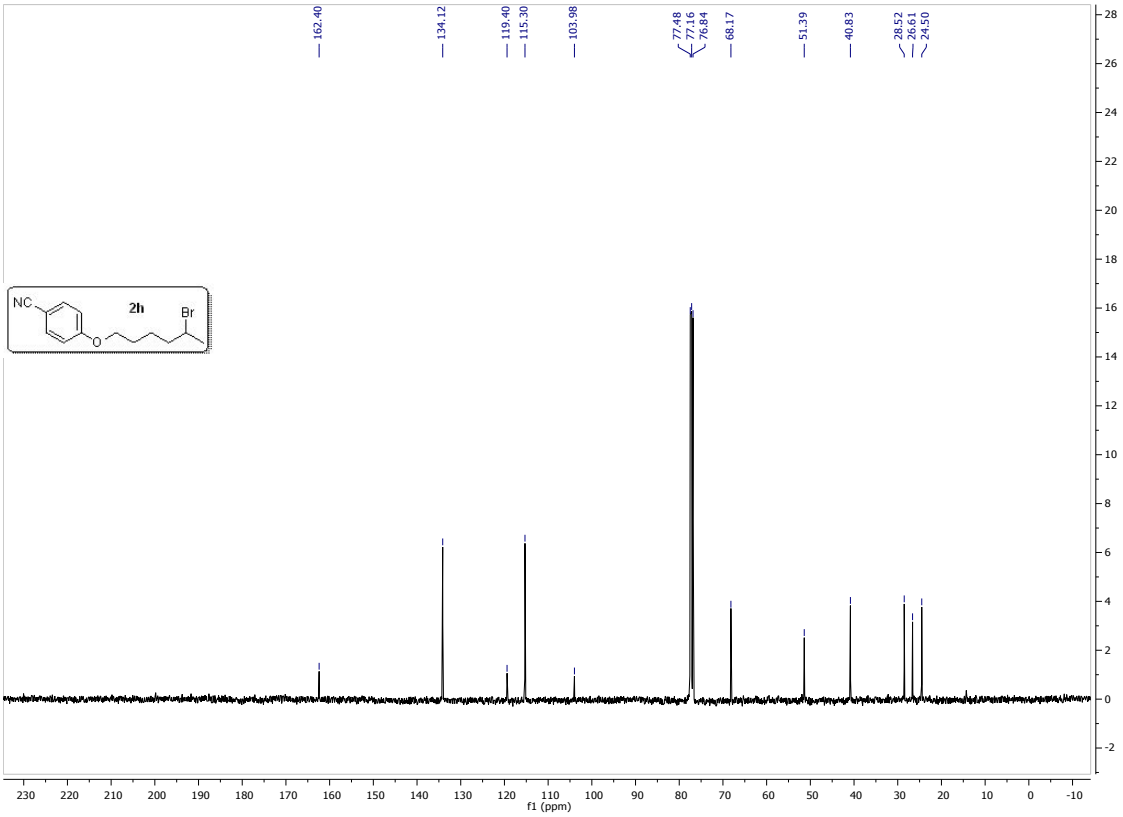

7.77
7.75
7.73
7.71
7.45
7.43
7.41
7.35
7.33
7.31
7.15
7.13
4.23
4.21
4.19
4.17
4.16
4.14
4.11
4.10
4.08
1.99
1.97
1.95
1.93
1.91
1.89
1.87
1.86
1.84
1.82
1.78
1.75
1.73
1.70
1.69
1.67
1.64
1.62
1.61
Br
O
2f
2.98
1.00
1.01
1.95
1.01
2.21
4.41
5.45
f1 (ppm)

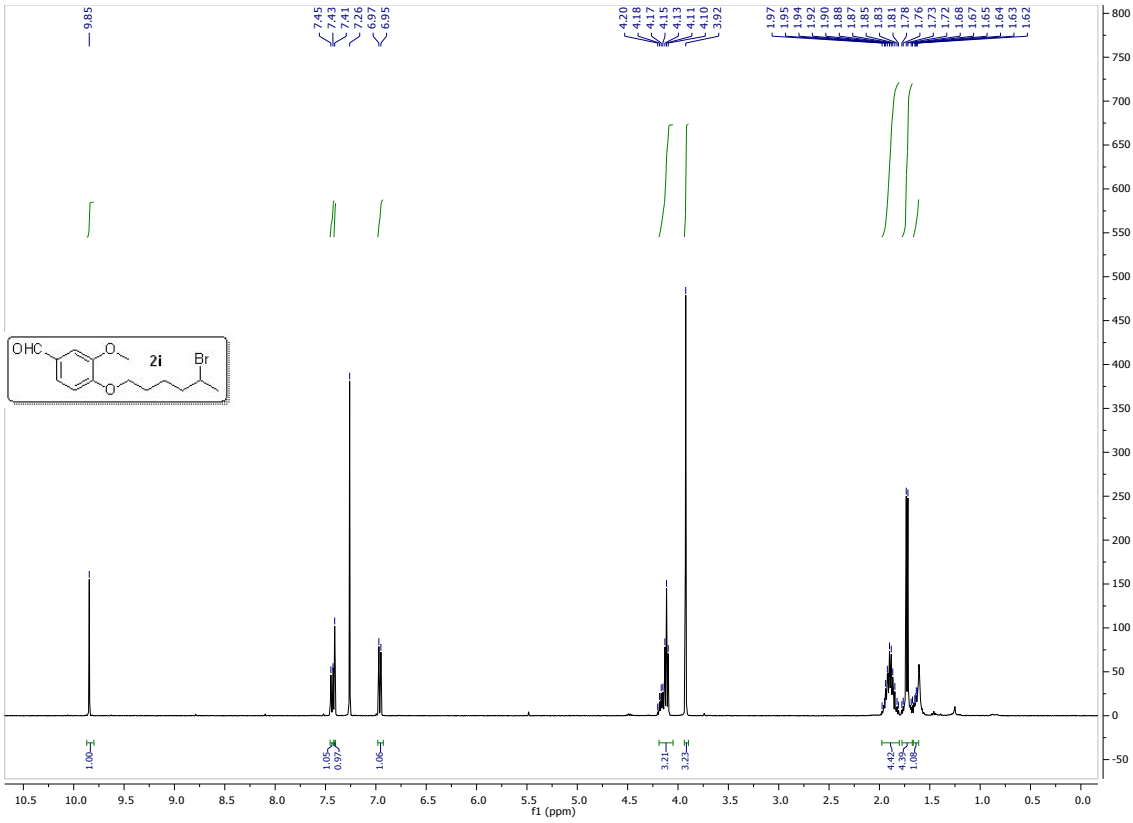

157.07
134.71
129.50
129.06
127.77
126.83
126.47
123.67
119.09
106.70
77.48
77.16
76.84
67.77
51.63
40.98
28.76
26.62
24.69
Br
O
2f
f1 (ppm)

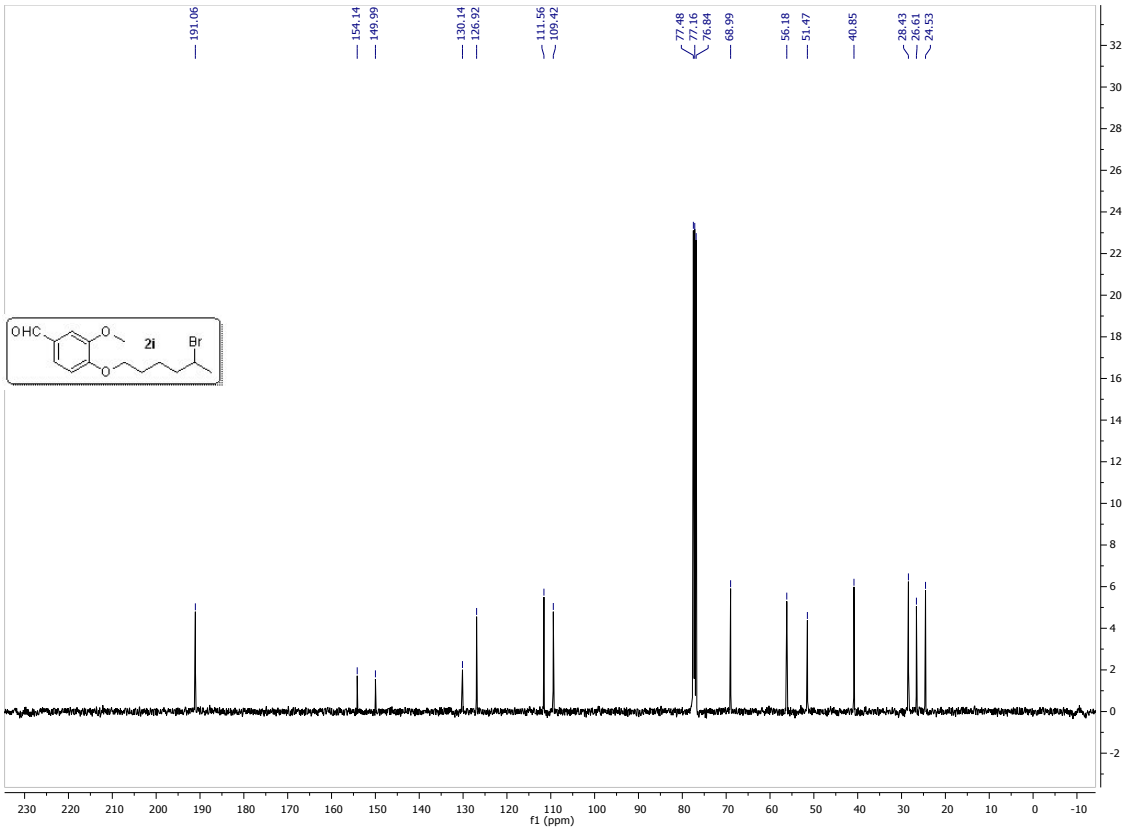

7.57
7.55
7.26
6.65
6.63
6.53
4.62
4.19
4.18
4.16
4.15
4.13
4.11
4.09
4.05
4.04
4.02
1.94
1.93
1.92
1.90
1.89
1.87
1.86
1.85
1.84
1.82
1.80
1.74
1.73
1.65
1.63
1.62
1.59
1.56
2g
Br
EtOAc
0.98
1.02
1.00
2.18
1.54
2.17
4.44
5.54
f1 (ppm)

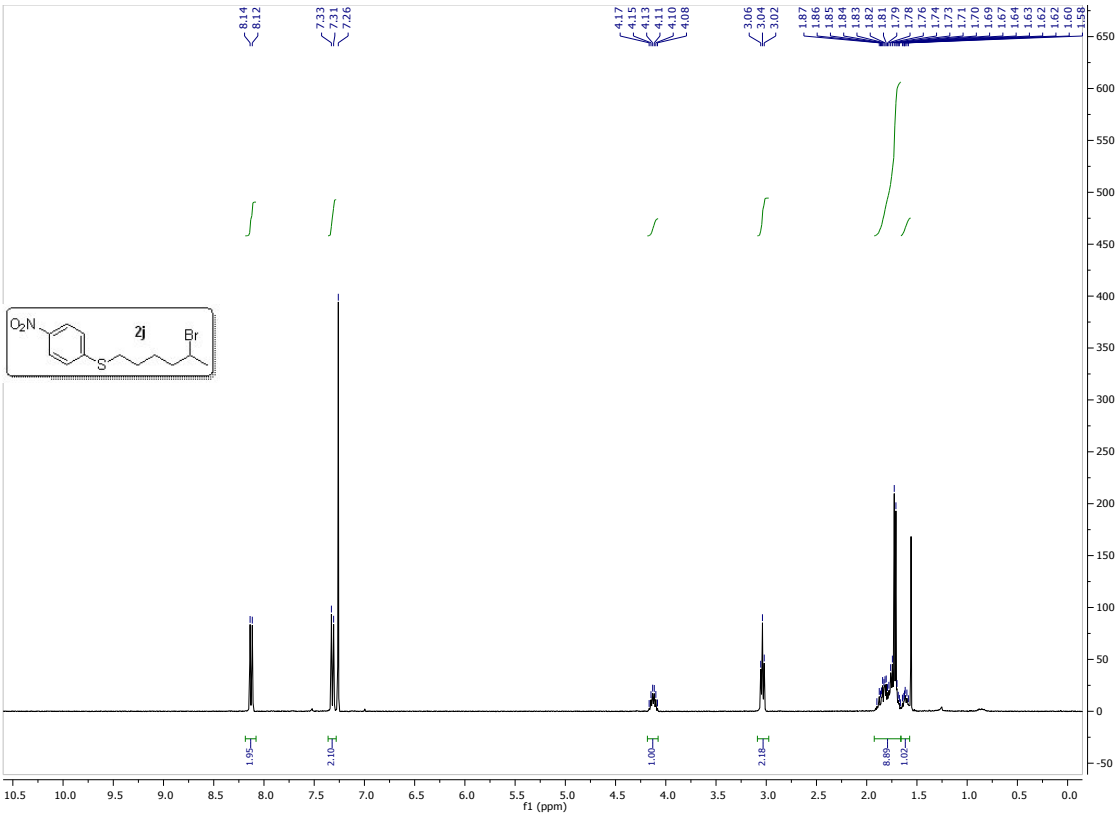

197.69
176.66
167.75
125.24
114.40
112.16
96.93
77.34
77.16
76.98
75.69
68.58
51.39
40.83
28.45
26.62
24.52
2g
Br
f1 (ppm)

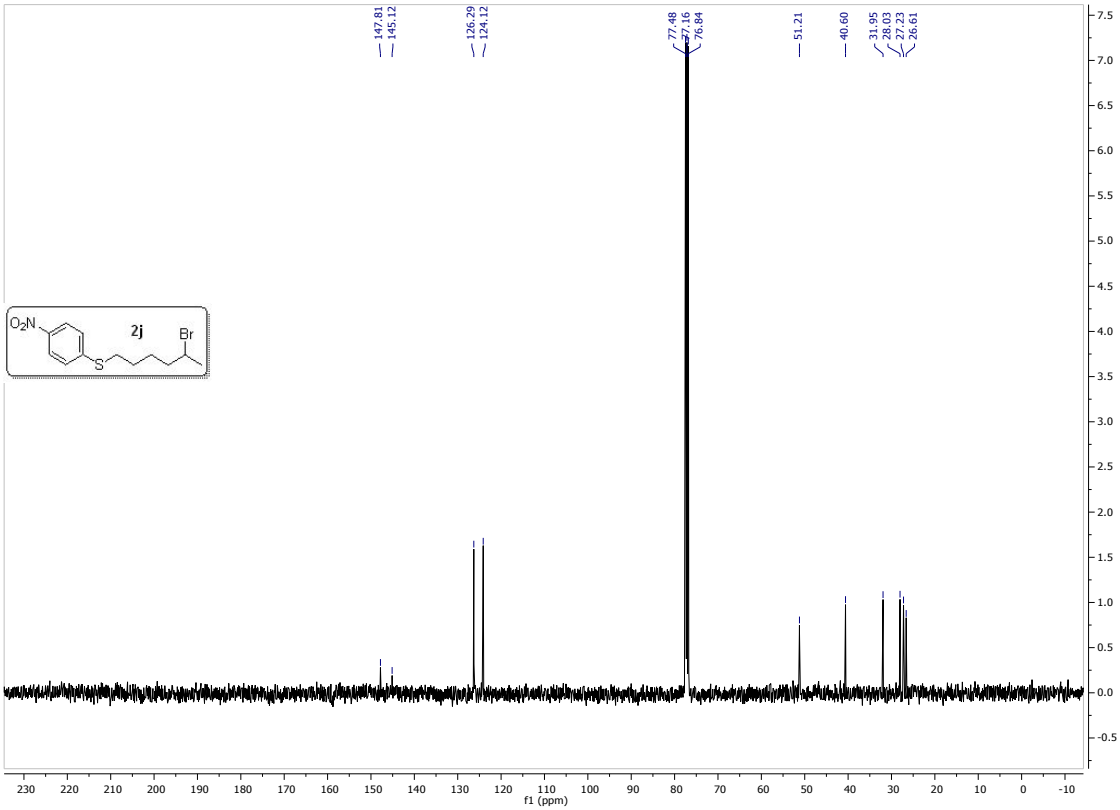

7.58
7.57
7.26
6.94
6.92
4.17
4.16
4.16
4.14
4.14
4.12
4.11
4.02
4.01
4.00
1.90
1.89
1.88
1.87
1.86
1.85
1.83
1.82
1.81
1.80
1.79
1.74
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.62
1.61
1.60
1.60
1.59
1.59
1.58
NC
2h
Br
O
1.96
1.86
1.00
1.92
4.13
3.83
0.93
f1 (ppm)

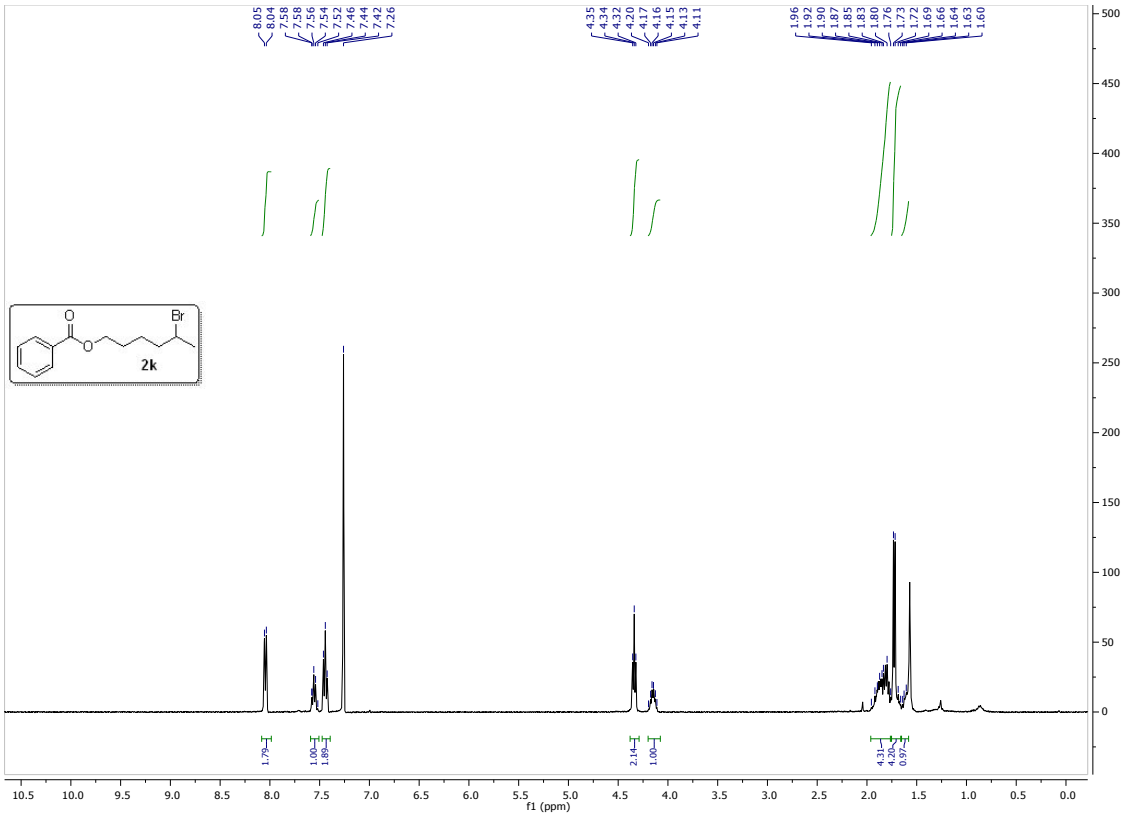

162.40
134.12
119.40
115.30
103.98
77.48
77.16
76.84
68.17
51.39
40.83
28.52
26.61
24.50
NC
2h
Br
O
f1 (ppm)

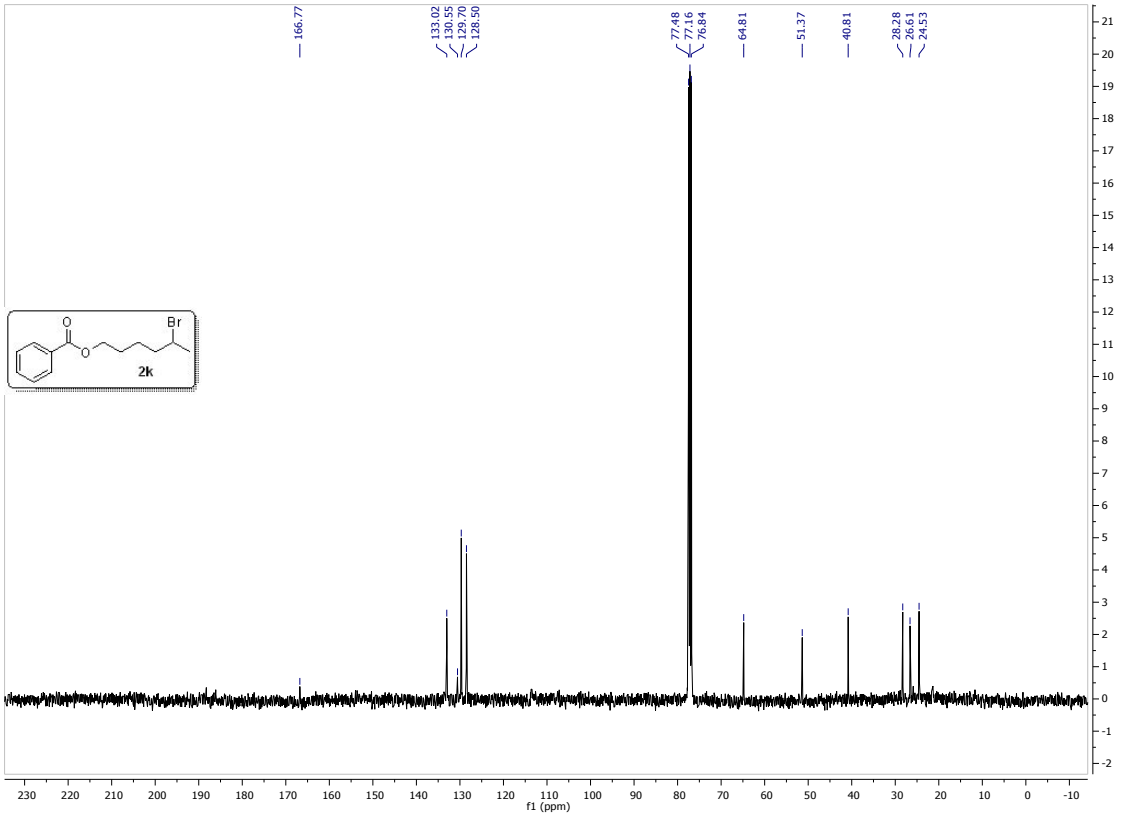

9.85
7.45
7.43
7.41
7.26
6.97
6.95
4.20
4.18
4.17
4.15
4.13
4.11
4.10
3.92
1.97
1.95
1.94
1.92
1.90
1.88
1.87
1.85
1.83
1.81
1.78
1.76
1.73
1.72
1.68
1.67
1.65
1.64
1.63
1.62
OHC
O
2i
Br
O
1.00
1.05
0.97
1.06
3.21
3.23
4.42
4.39
1.08
f1 (ppm)

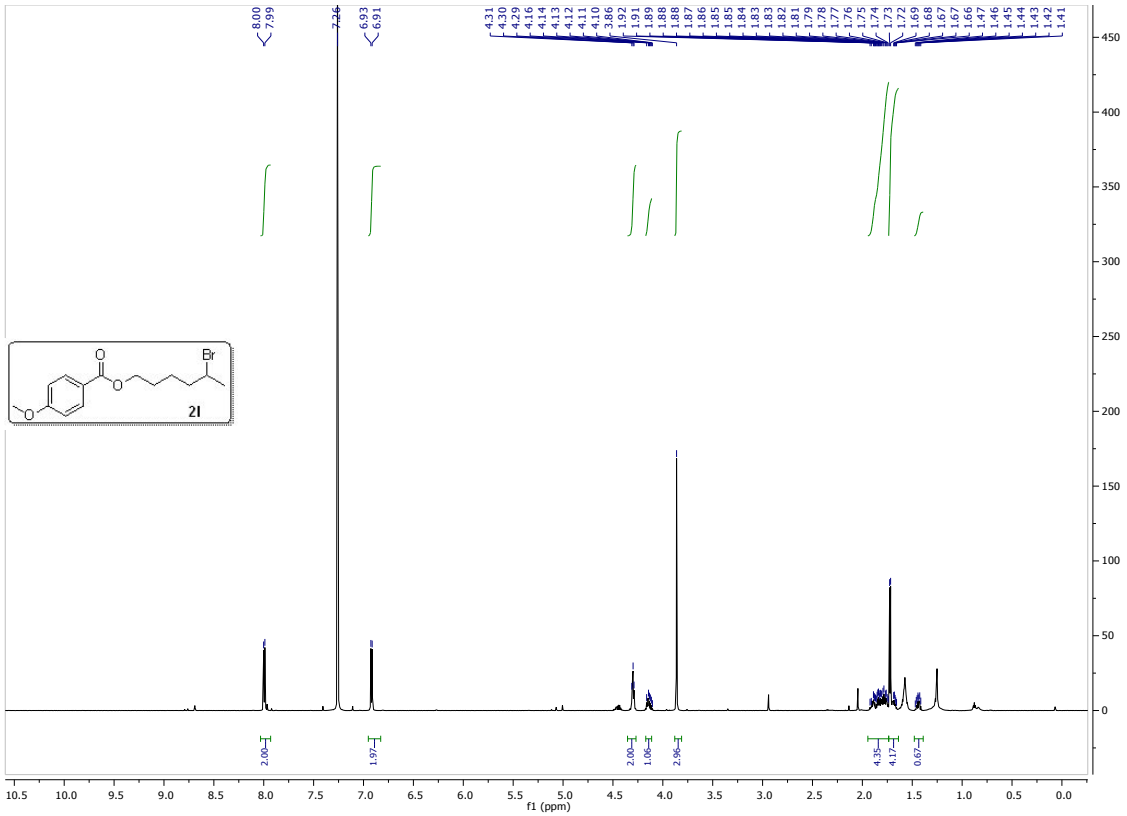

191.06
154.14
149.99
130.14
126.92
111.56
109.42
77.48
77.16
76.84
68.99
56.18
51.47
40.85
28.43
26.61
24.53
OHC
O
2i
Br
O
f1 (ppm)

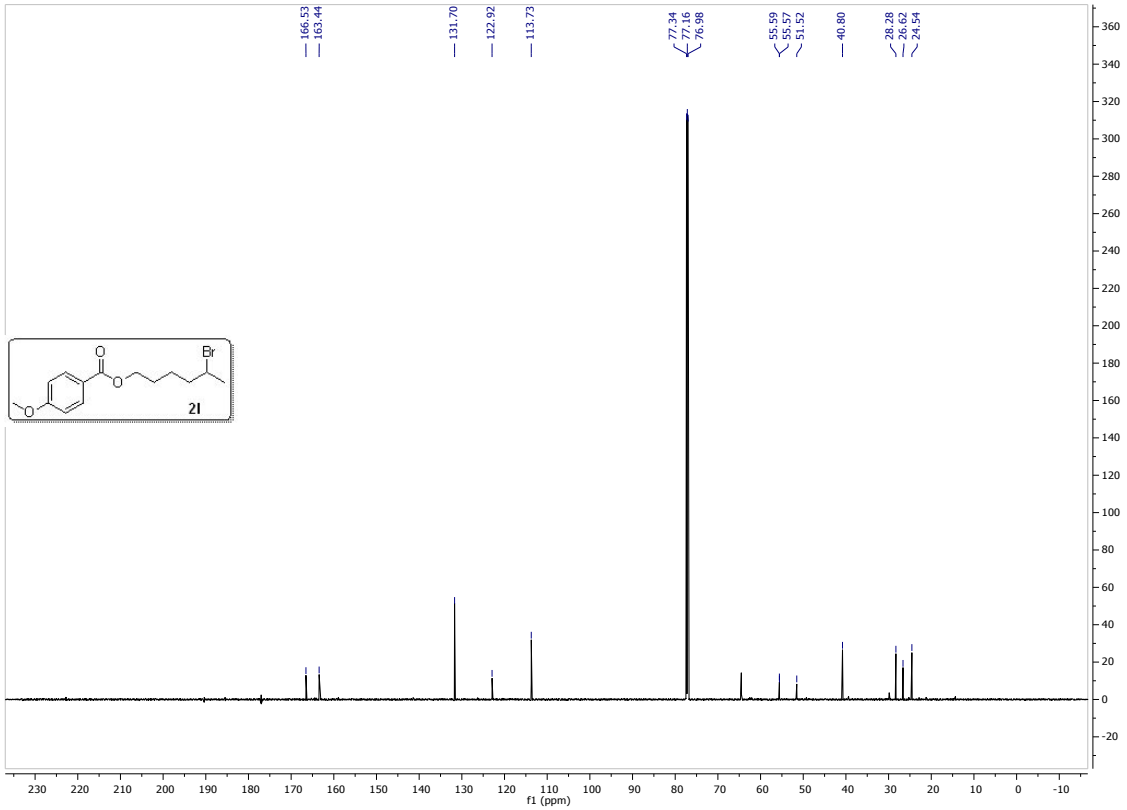

8.14
8.12
7.33
7.31
7.26
4.17
4.15
4.13
4.11
4.10
4.08
3.06
3.04
3.02
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.79
1.78
1.76
1.74
1.73
1.71
1.70
1.69
1.67
1.64
1.63
1.62
1.62
1.60
1.58
O2N
2j
Br
S
1.95
2.10
1.00
2.18
8.89
1.02
f1 (ppm)

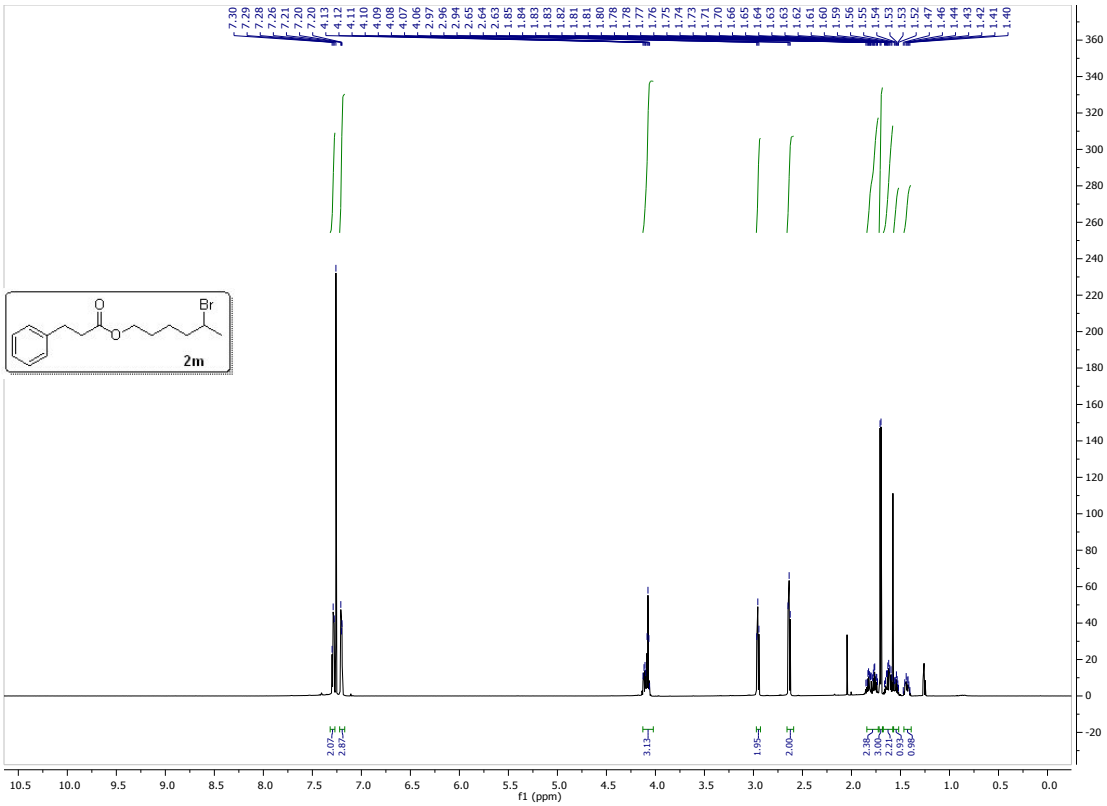

147.81
145.12
126.29
124.12
77.48
77.16
76.84
51.21
40.60
31.95
28.03
27.23
26.61
O2N
2j
Br
S
f1 (ppm)

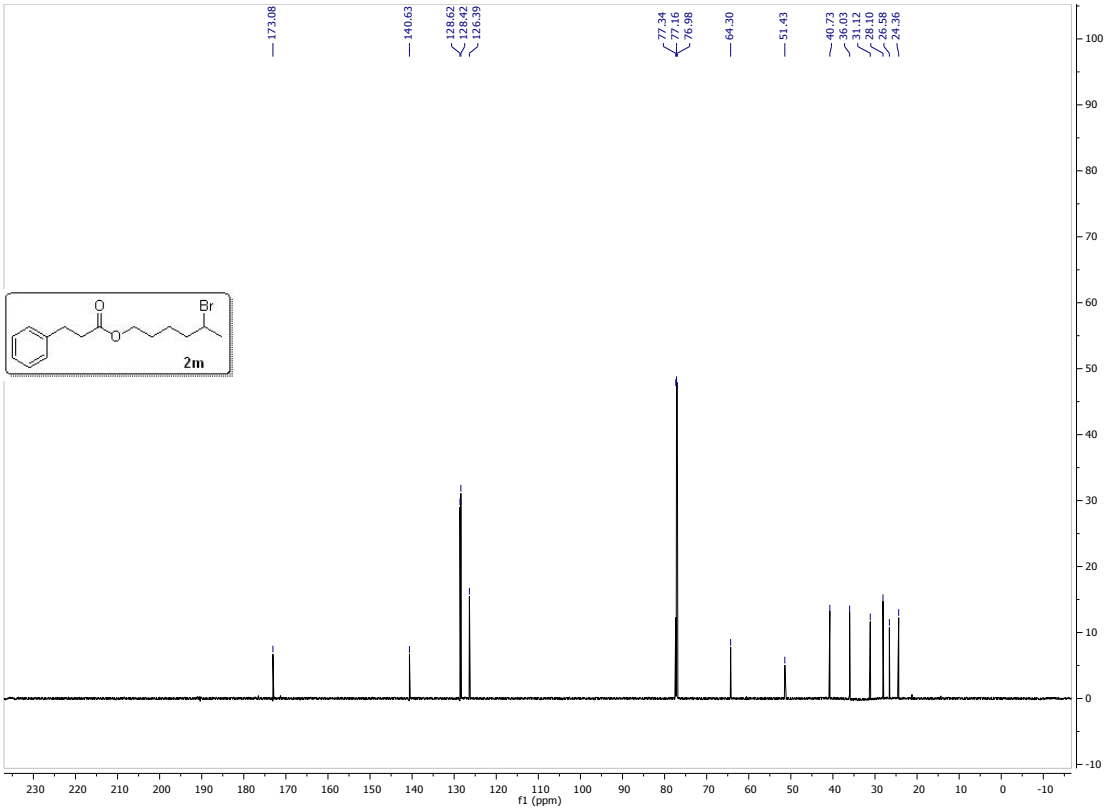

8.05
8.04
7.58
7.58
7.56
7.54
7.52
7.46
7.44
7.42
7.26
4.35
4.34
4.32
4.20
4.17
4.16
4.15
4.13
4.11
1.96
1.92
1.90
1.87
1.85
1.83
1.80
1.76
1.75
1.72
1.69
1.66
1.64
1.63
1.60
O
Br
O
2k
1.79
1.00
1.89
2.14
1.00
4.31
4.20
0.97
f1 (ppm)

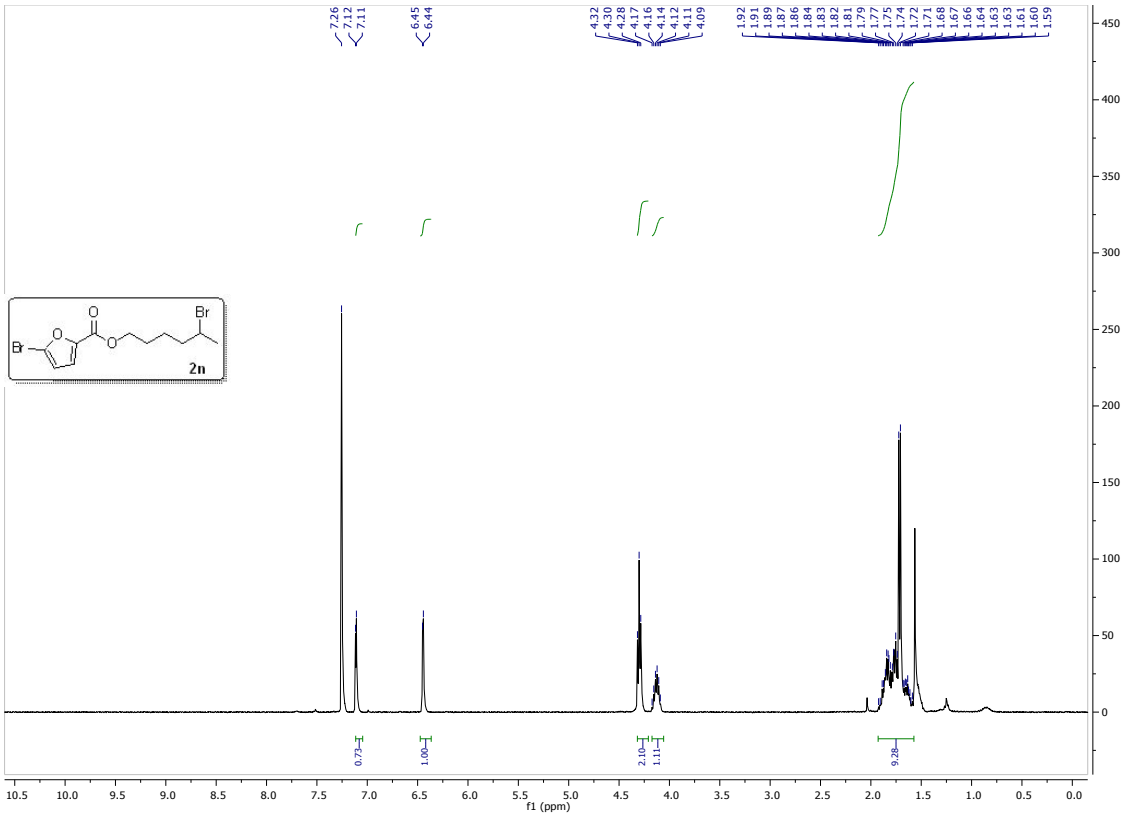

166.77
133.02
130.55
129.70
128.50
77.48
77.16
76.84
64.81
51.37
40.81
28.28
26.61
24.53
O
Br
O
2k
f1 (ppm)

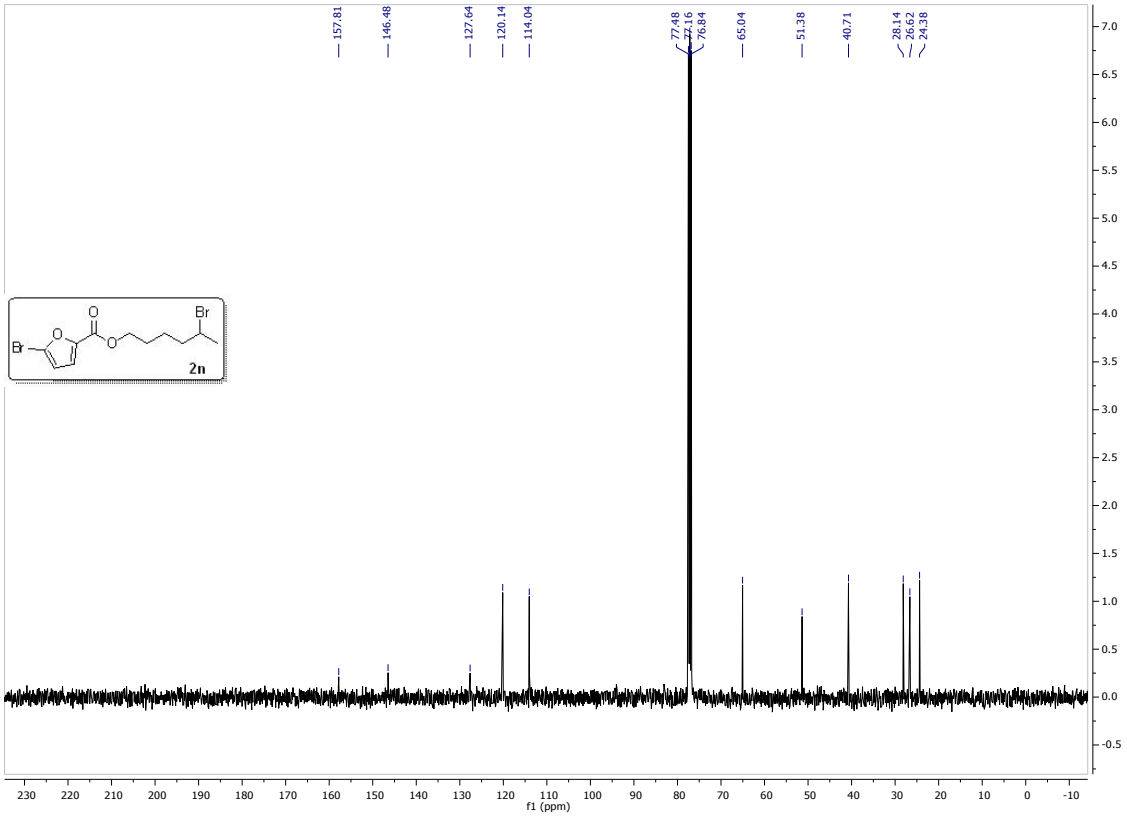

8.00
7.99
7.26
6.93
6.91
4.31
4.30
4.29
4.16
4.14
4.13
4.12
4.11
4.11
4.10
3.86
3.92
1.91
1.89
1.88
1.88
1.88
1.87
1.86
1.85
1.85
1.85
1.84
1.83
1.83
1.82
1.81
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.69
1.68
1.67
1.67
1.66
1.47
1.46
1.45
1.44
1.43
1.42
1.41
2.00
1.97
2.00
1.06
2.96
4.35
4.17
0.67
f1 (ppm)
O
Br
O
O
2l

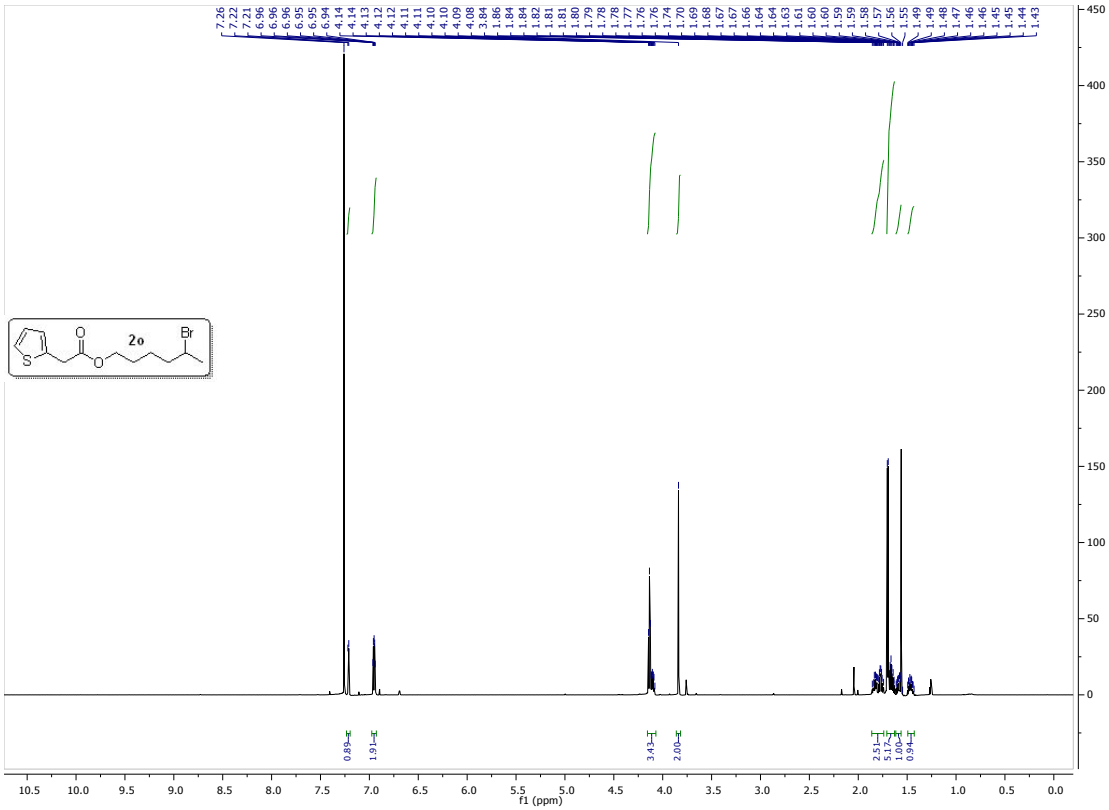

166.53
163.44
131.70
122.92
113.73
77.34
77.16
76.98
55.59
55.57
51.52
40.80
28.28
26.62
24.54
f1 (ppm)
O
Br
O
O
2l

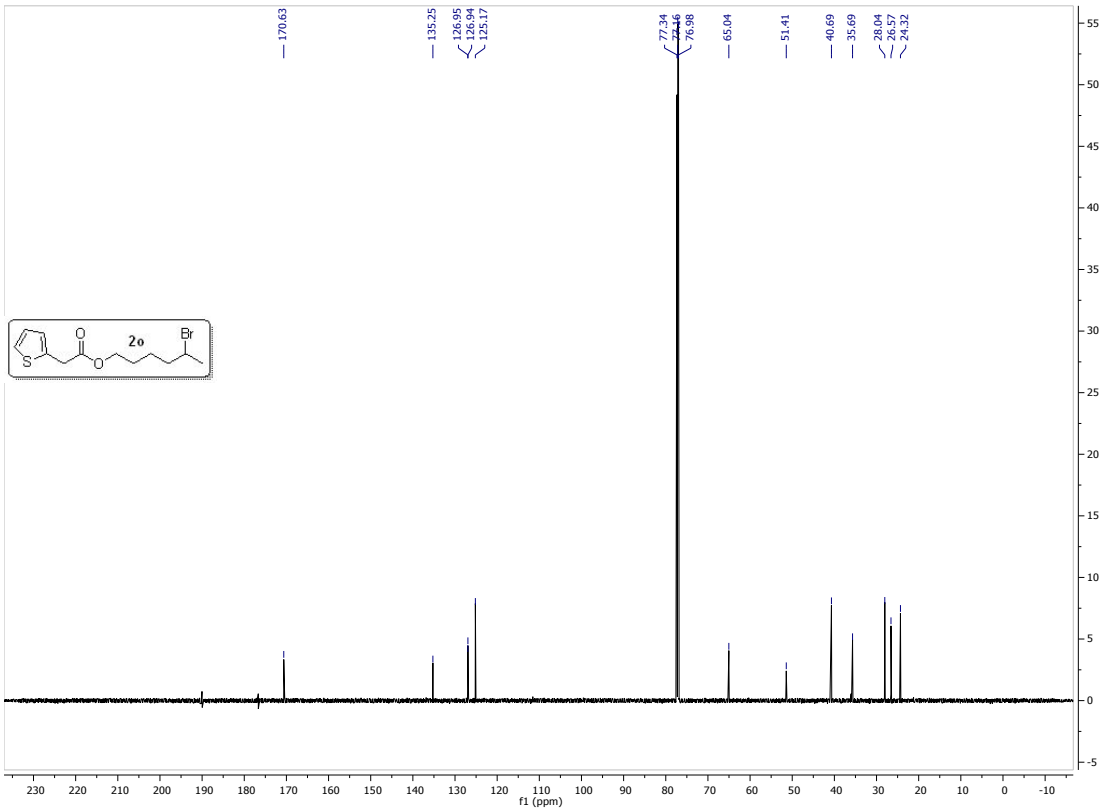

2m
f1 (ppm)

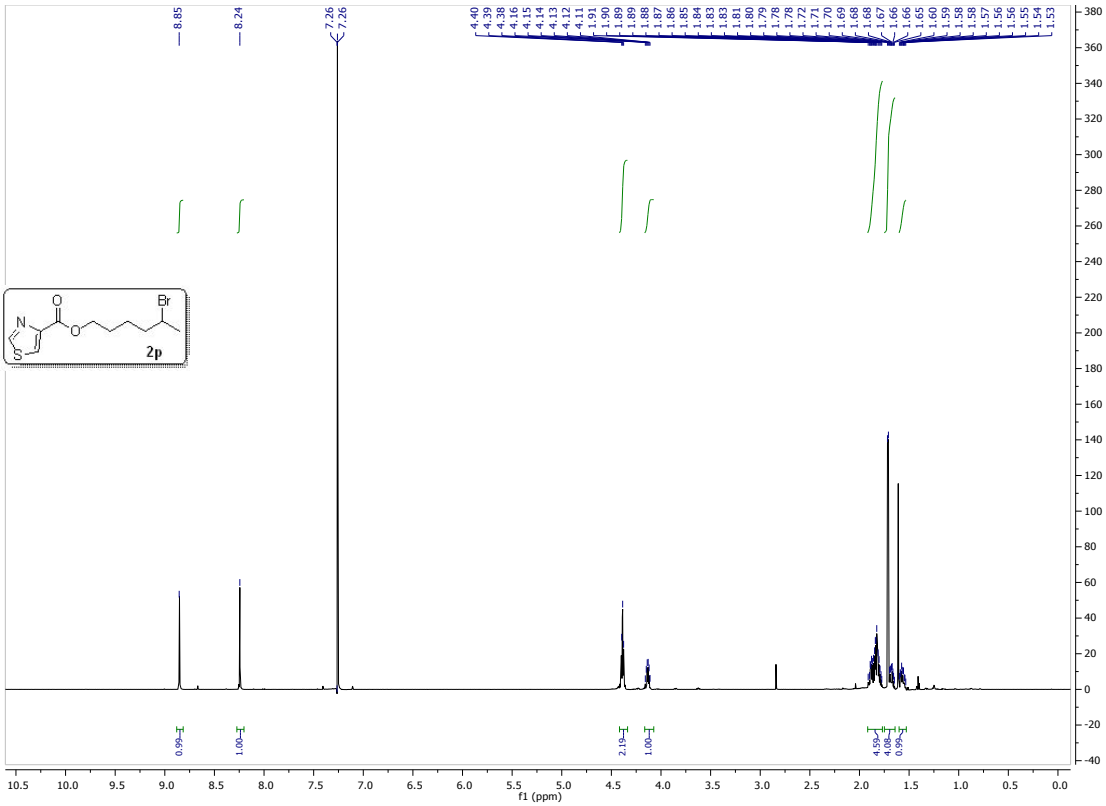

2m
f1 (ppm)

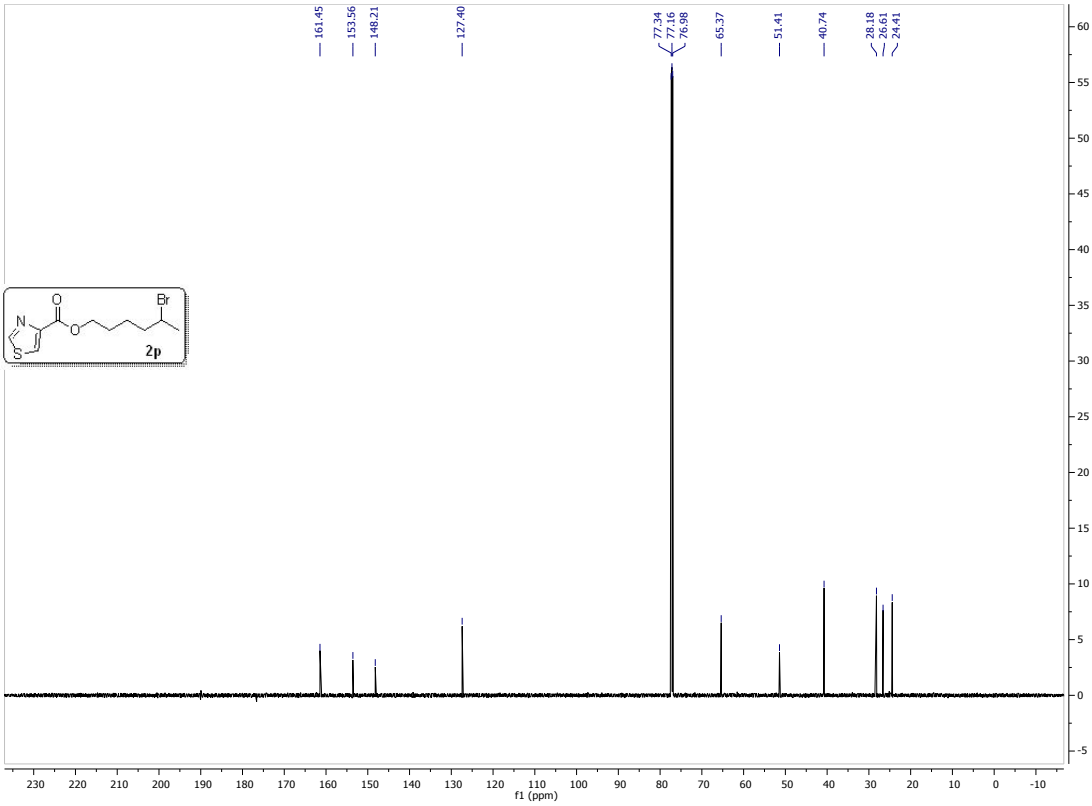

7.26
7.12
7.11
6.45
6.44
4.32
4.30
4.28
4.17
4.16
4.14
4.12
4.11
4.09
1.92
1.91
1.89
1.87
1.86
1.84
1.83
1.82
1.81
1.79
1.77
1.75
1.74
1.72
1.71
1.68
1.67
1.66
1.64
1.63
1.63
1.61
1.60
1.59
0.73
1.00
2.10
1.11
9.28
f1 (ppm)
2n

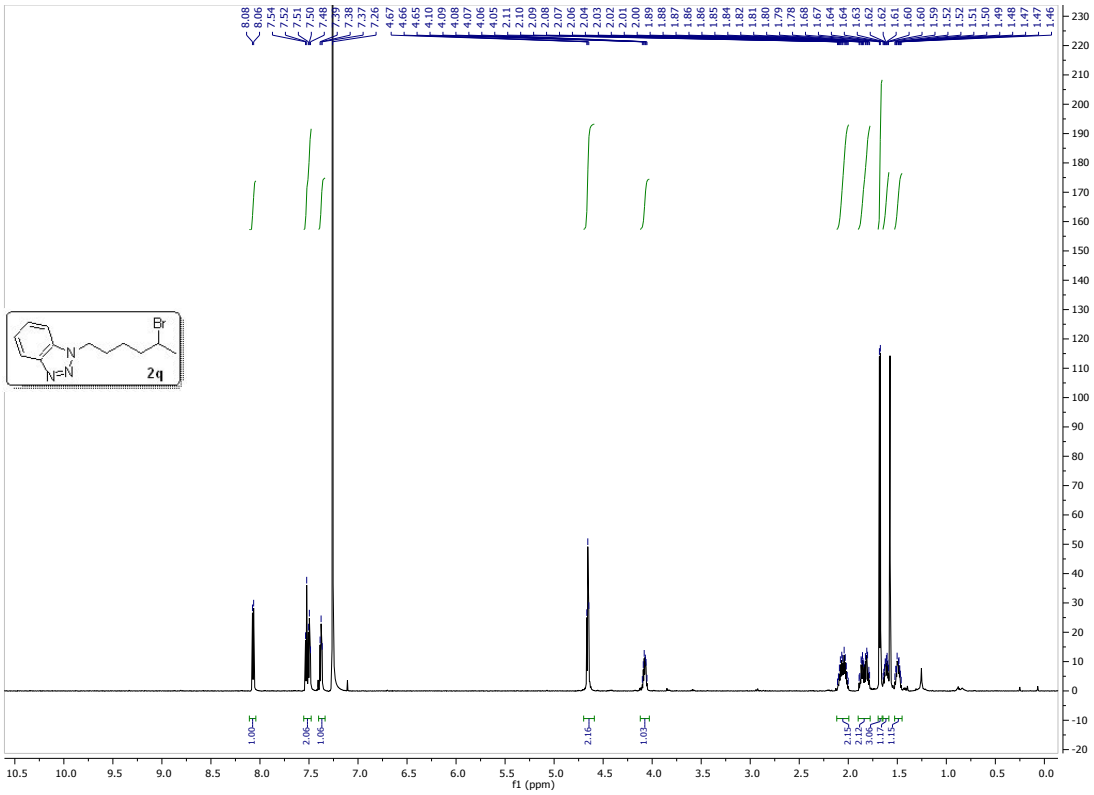

157.81
146.48
127.64
120.14
114.04
77.48
77.16
76.84
65.04
51.38
40.71
28.14
26.62
24.38
f1 (ppm)
2n

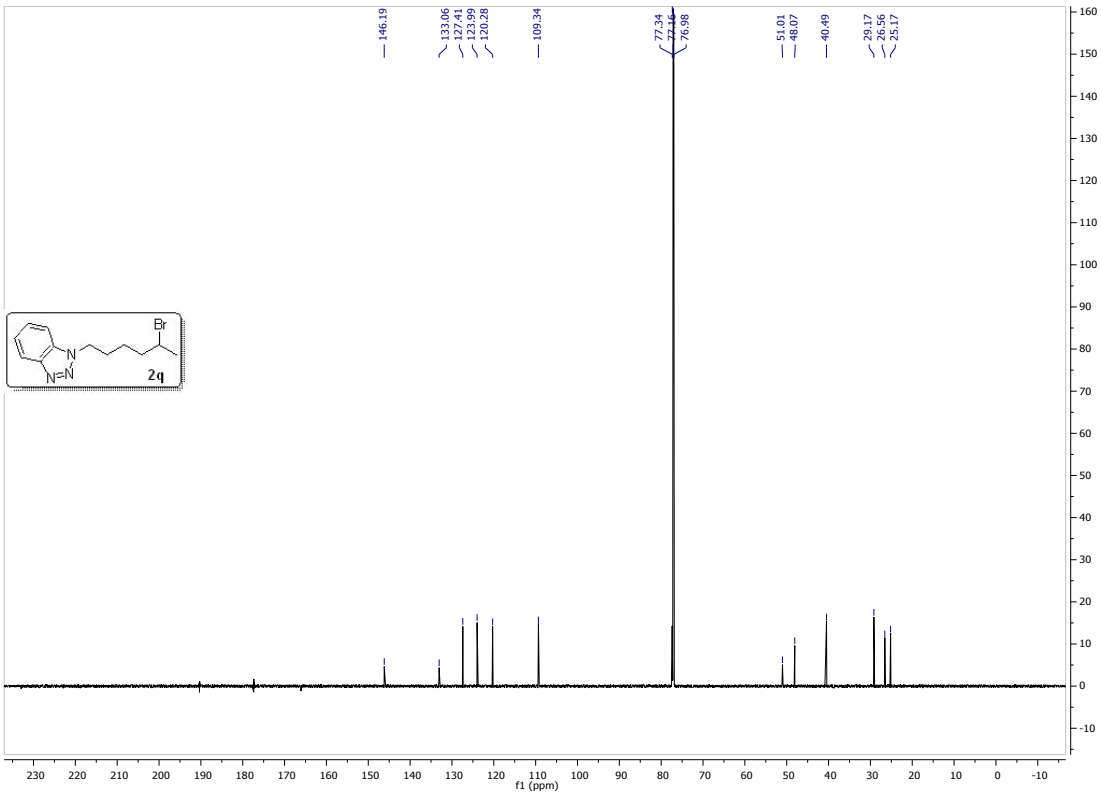

2o
Br
f1 (ppm)

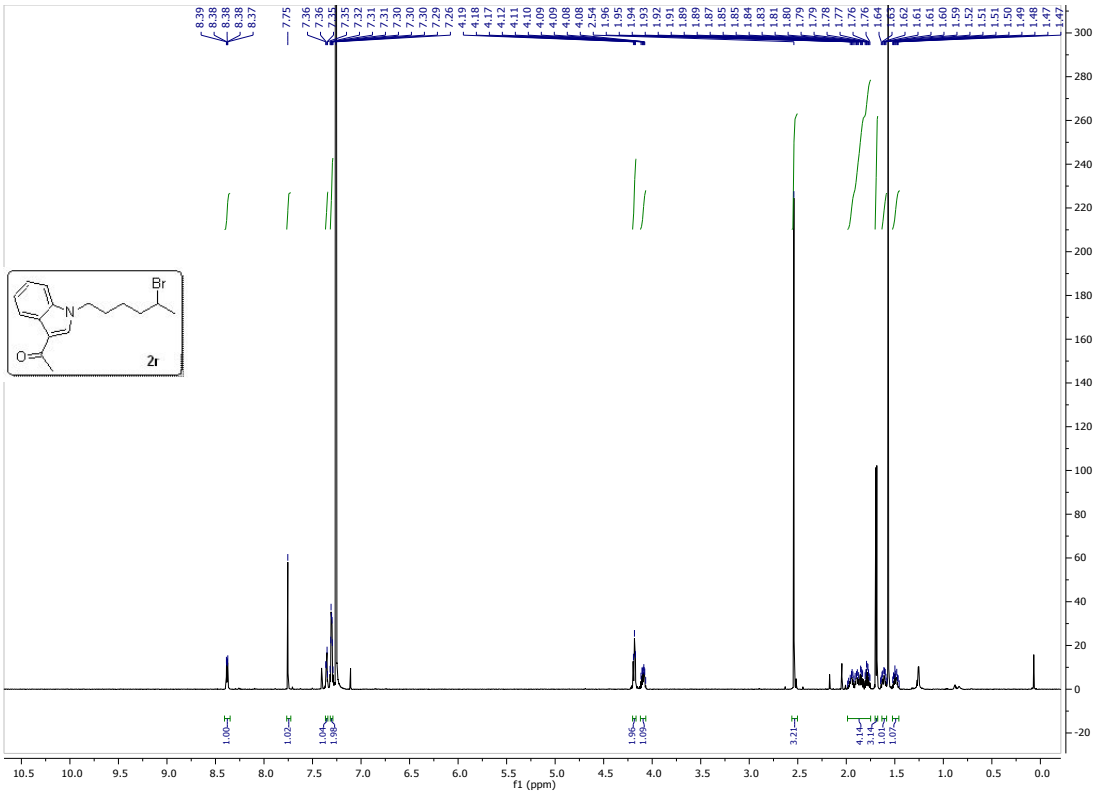

2o
Br
f1 (ppm)

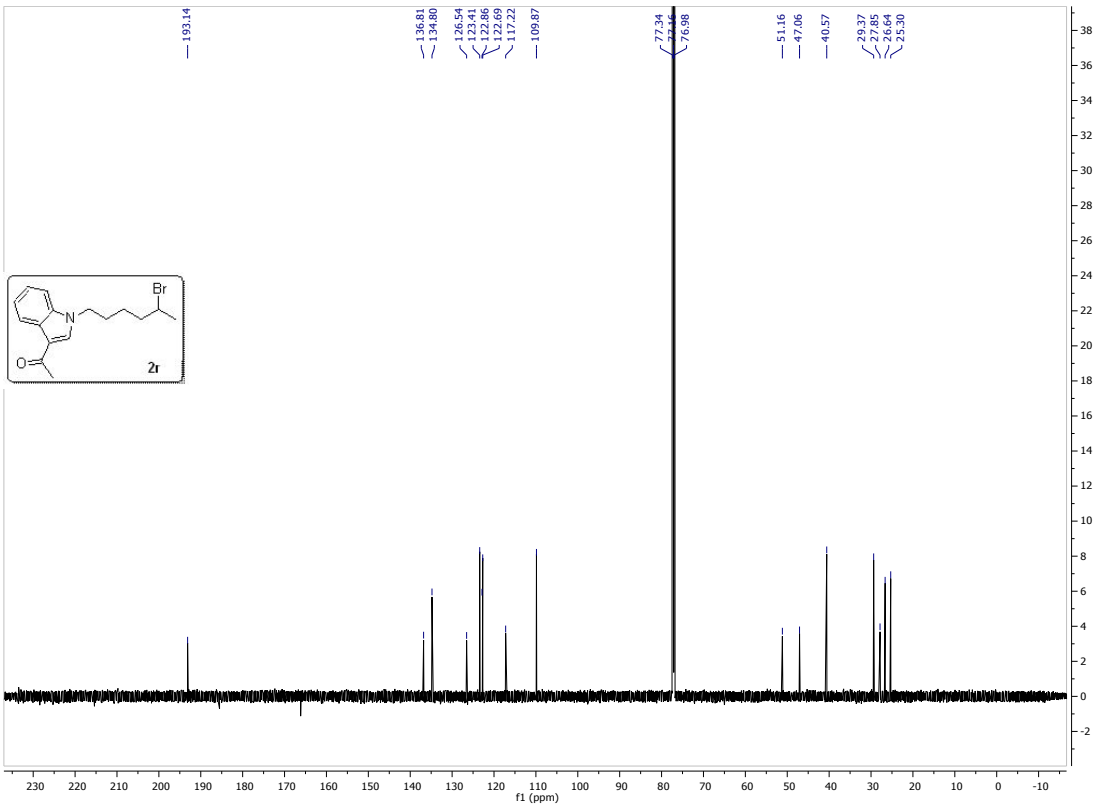

8.85
8.24
7.26
7.26
4.40
4.39
4.38
4.16
4.15
4.14
4.13
4.12
4.11
1.91
1.90
1.89
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.83
1.81
1.80
1.79
1.78
1.78
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.66
1.65
1.60
1.59
1.58
1.58
1.57
1.56
1.56
1.55
1.54
1.53
0.99
1.00
2.19
1.00
4.59
4.08
0.99
f1 (ppm)
2p

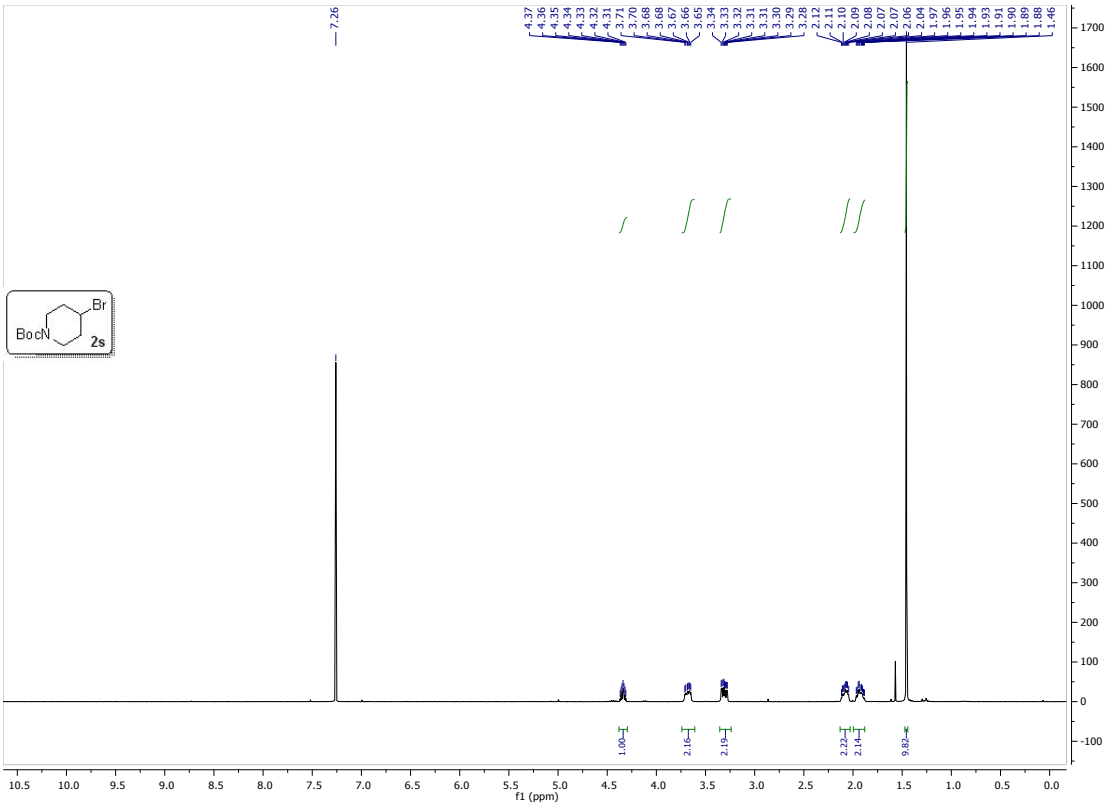

161.45
153.56
148.21
127.40
77.34
77.16
76.98
65.37
51.41
40.74
28.18
26.61
24.41
f1 (ppm)
2p

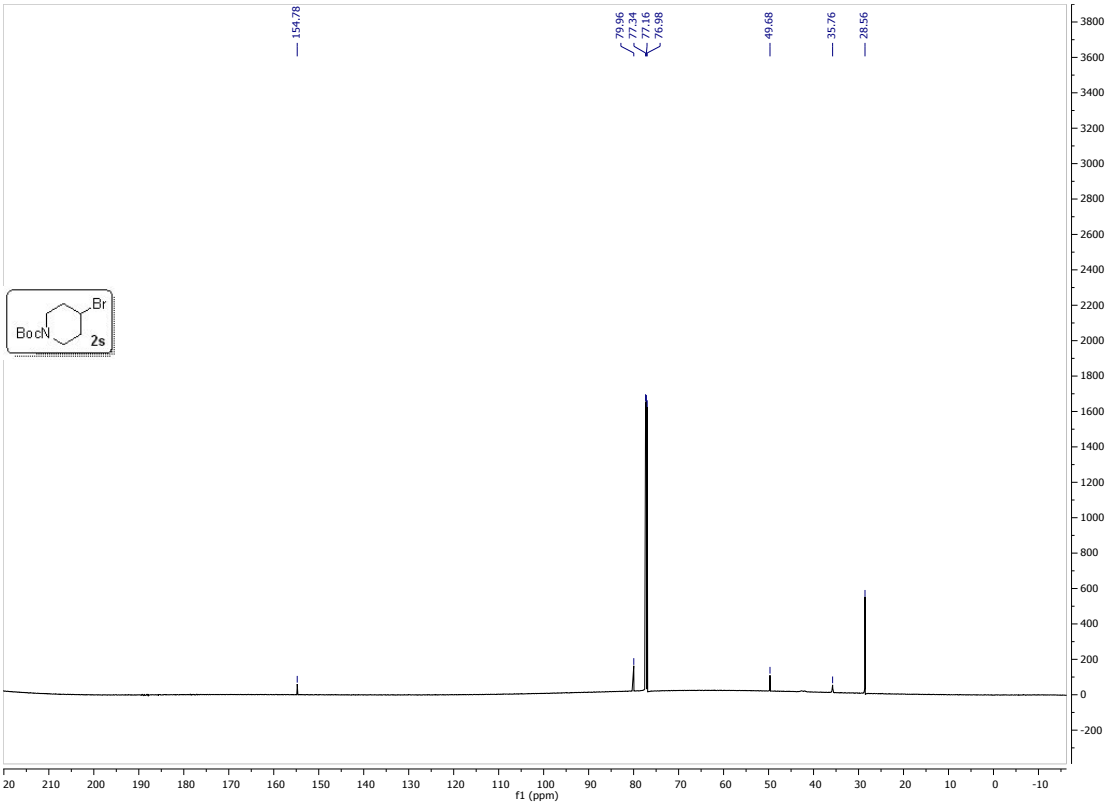

Br
N
N=N
2q
f1 (ppm)

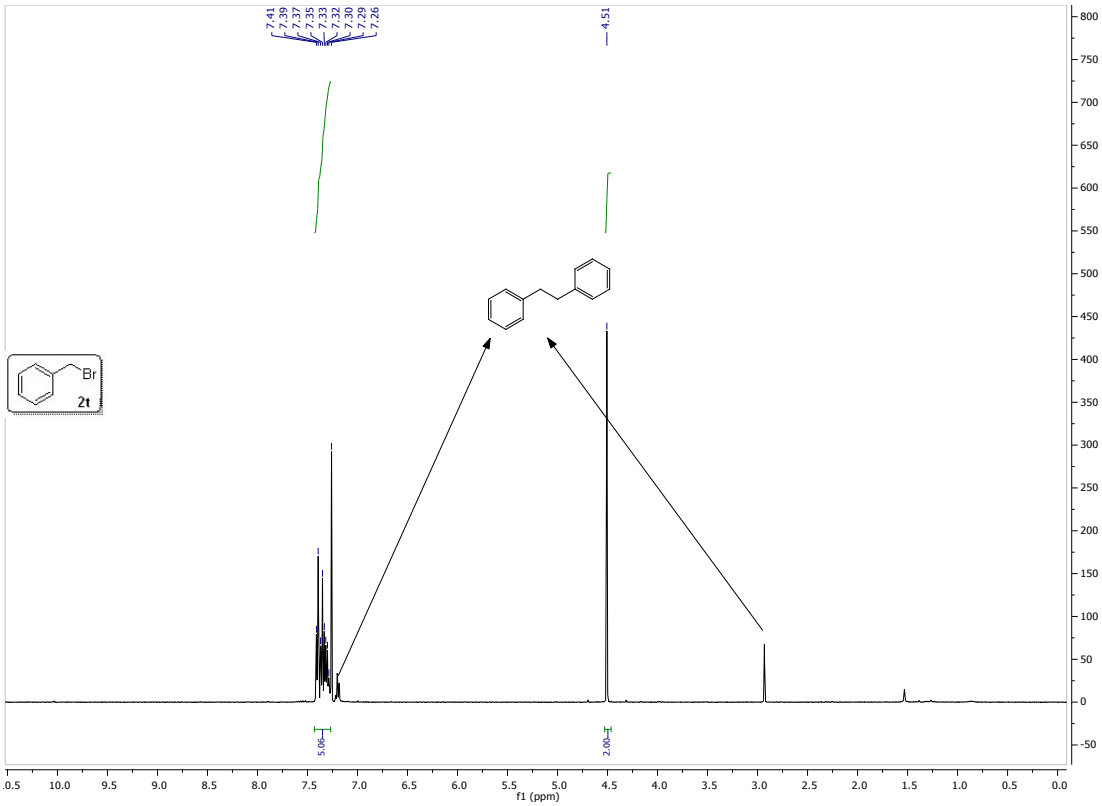

146.19
133.06
127.41
123.99
120.28
109.34
77.34
77.16
76.98
51.01
48.07
40.49
29.17
26.56
25.17
Br
N
N=N
2q
f1 (ppm)

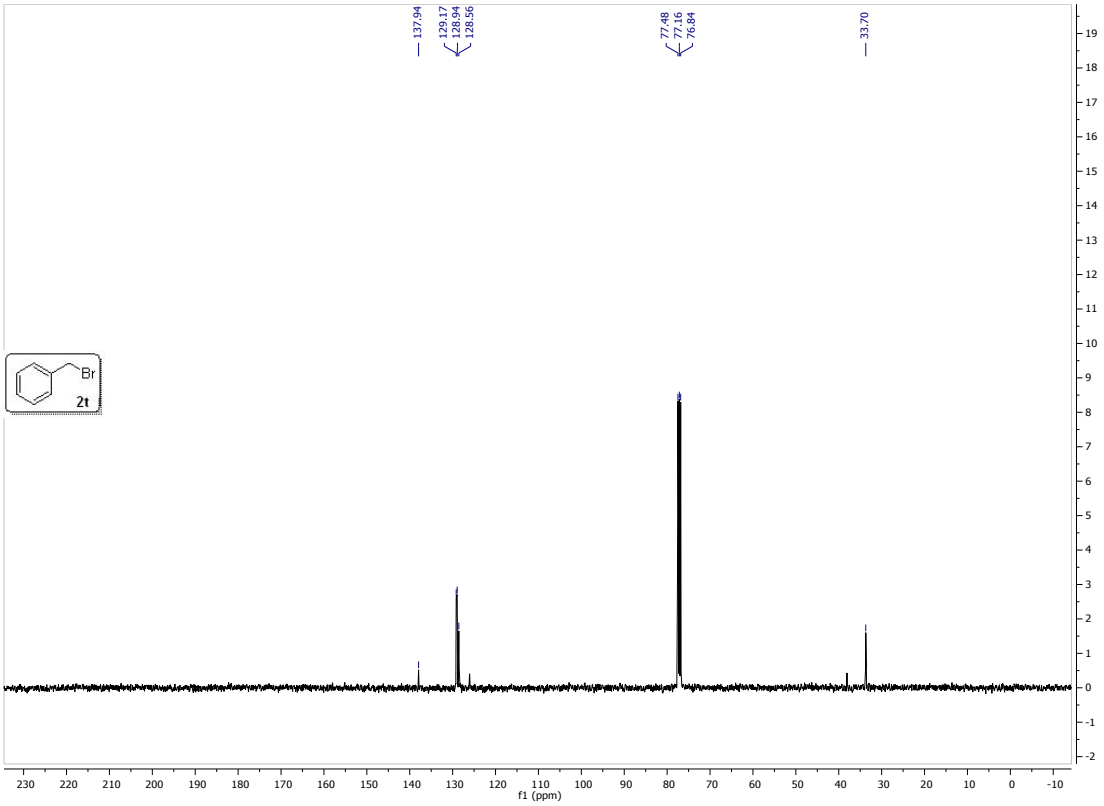

Br
N
O
2r
f1 (ppm)

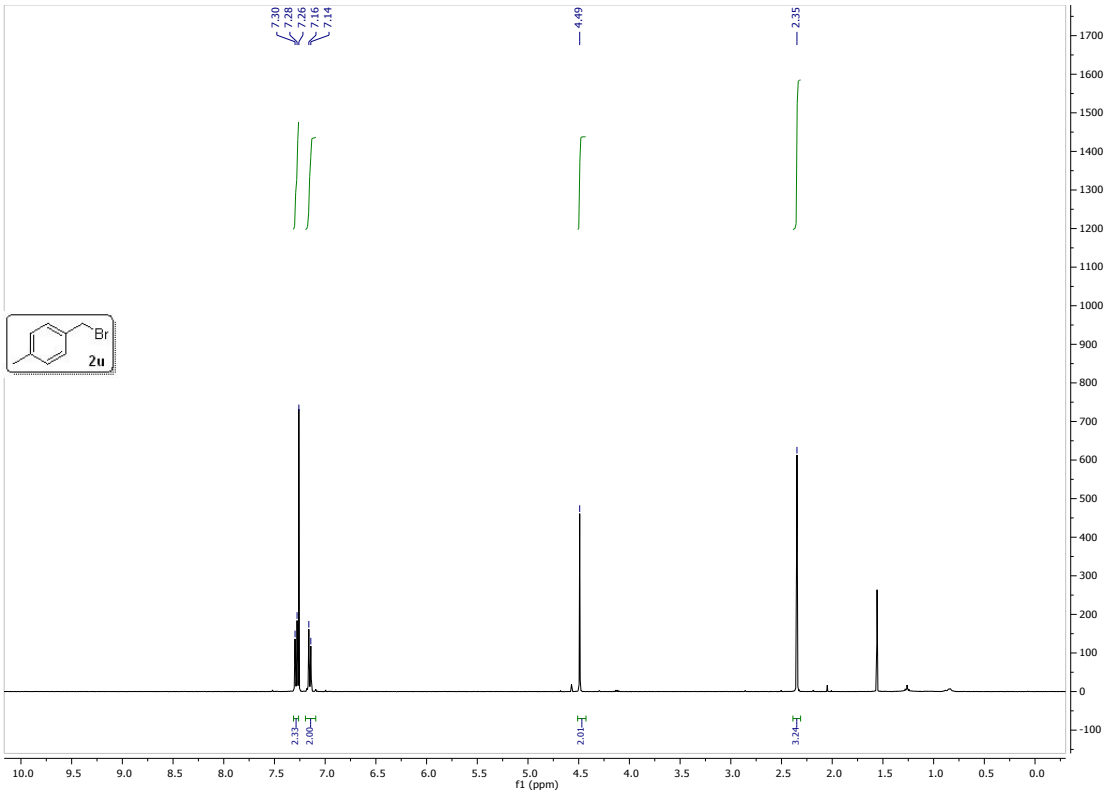

Br
N
O
2r
f1 (ppm)

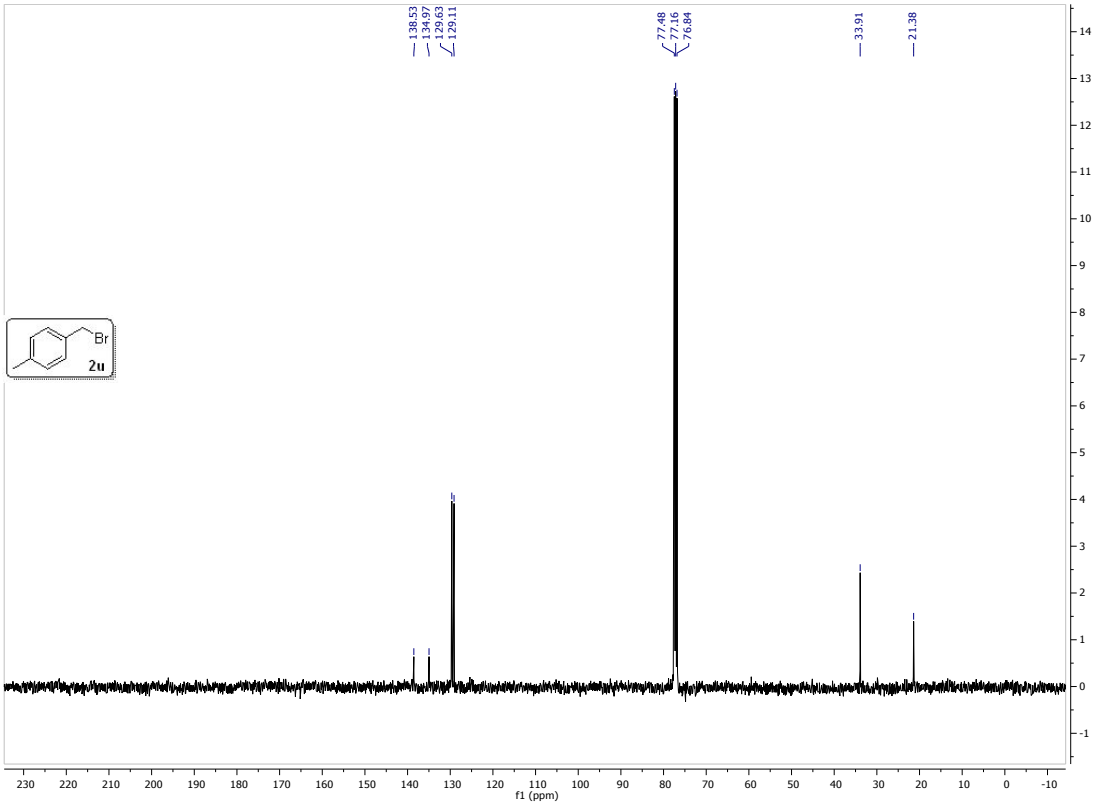

7.26
4.37
4.36
4.35
4.34
4.33
4.32
4.31
3.71
3.70
3.68
3.68
3.67
3.66
3.65
3.34
3.33
3.32
3.31
3.31
3.30
3.29
3.28
2.12
2.11
2.10
2.09
2.08
2.07
2.07
2.06
2.04
2.04
1.97
1.96
1.95
1.94
1.93
1.91
1.90
1.89
1.88
1.46
1.00
2.16
2.19
2.22
2.14
9.82
Br
BocN
2s
f1 (ppm)

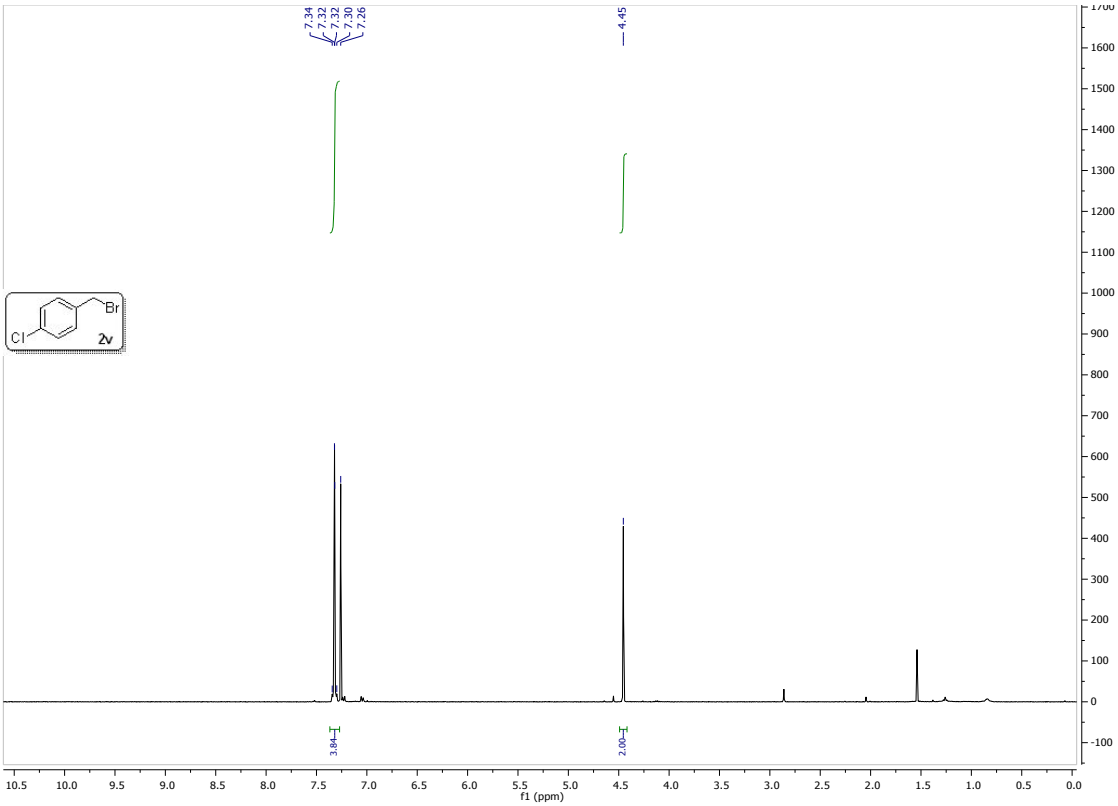

154.78
79.96
77.34
77.16
76.98
49.68
35.76
28.56
Br
BocN
2s
f1 (ppm)

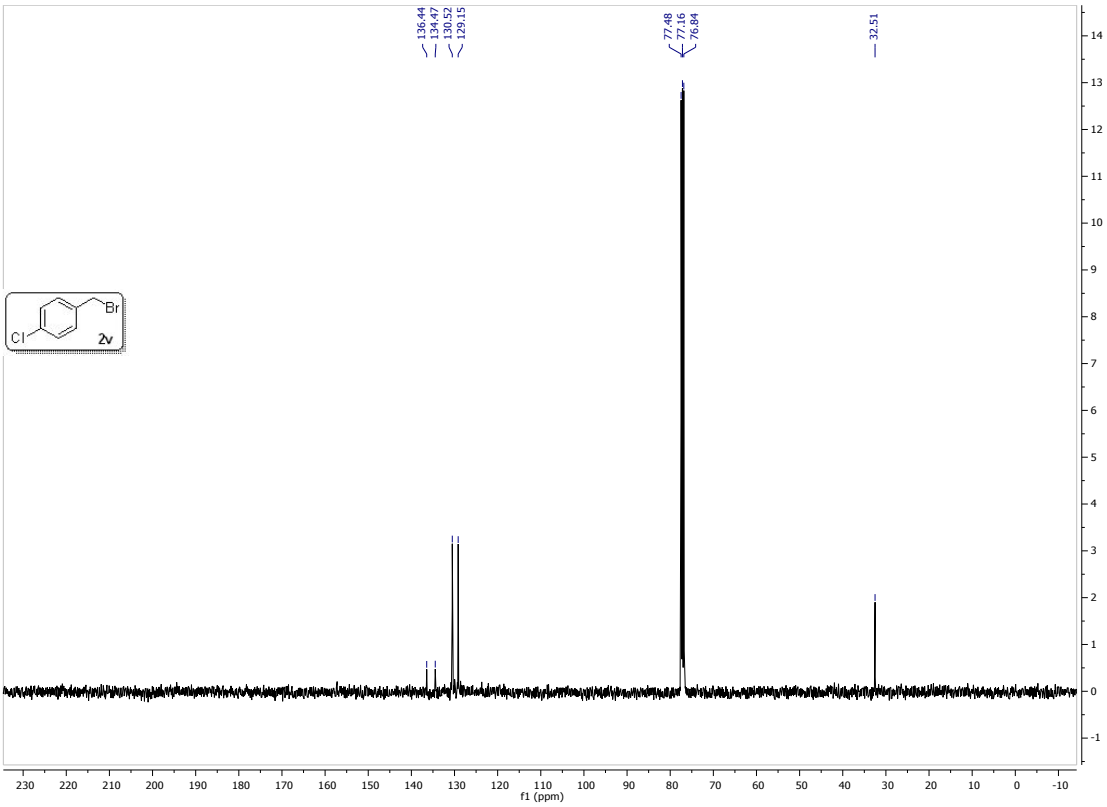

7.41
7.39
7.37
7.35
7.33
7.32
7.30
7.29
7.26
4.51
Br
2t
5.06
2.00
f1 (ppm)

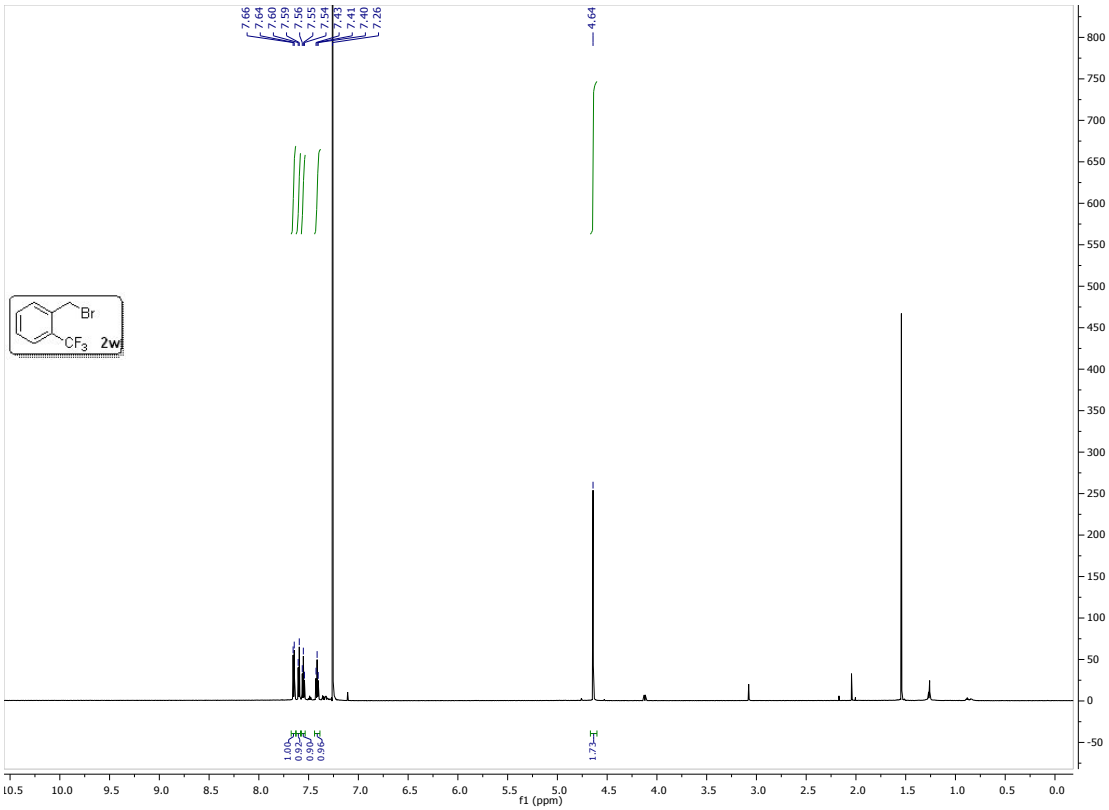

137.94
129.17
128.94
128.56
77.48
77.16
76.84
33.70
Br
2t
f1 (ppm)

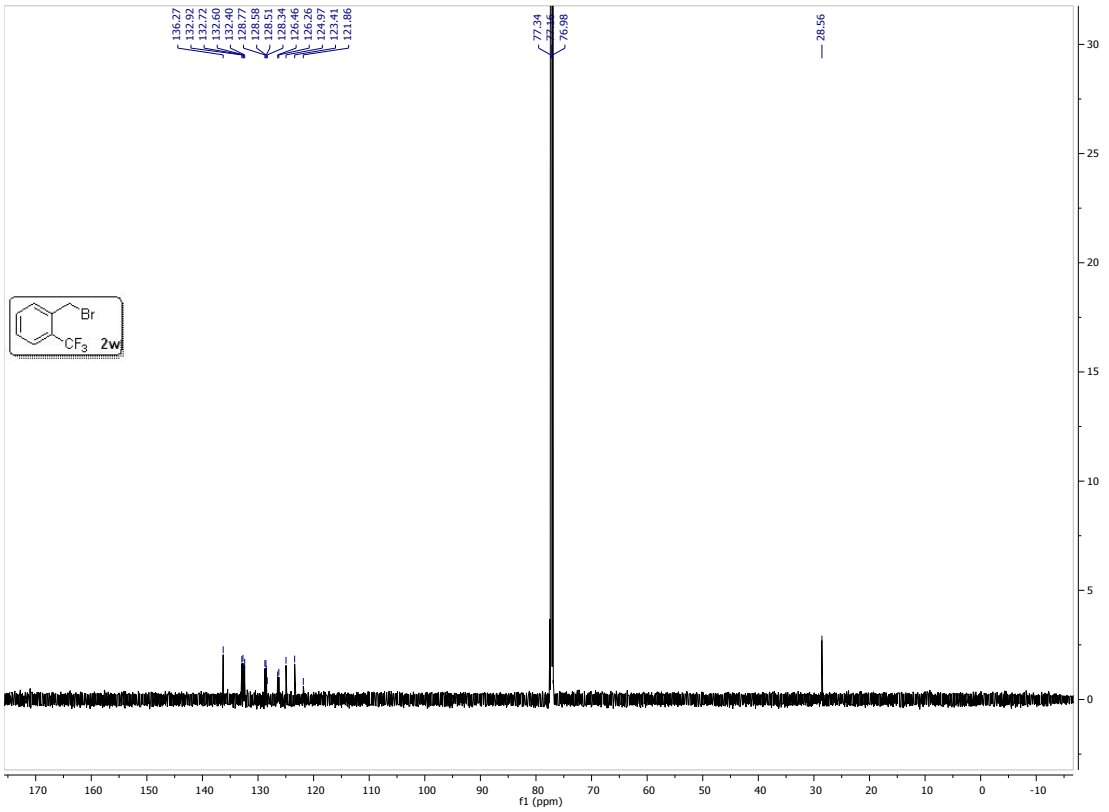

7.30
7.28
7.26
7.16
7.14
4.49
2.35
Br
2u
2.33
2.00
2.01
3.24
f1 (ppm)

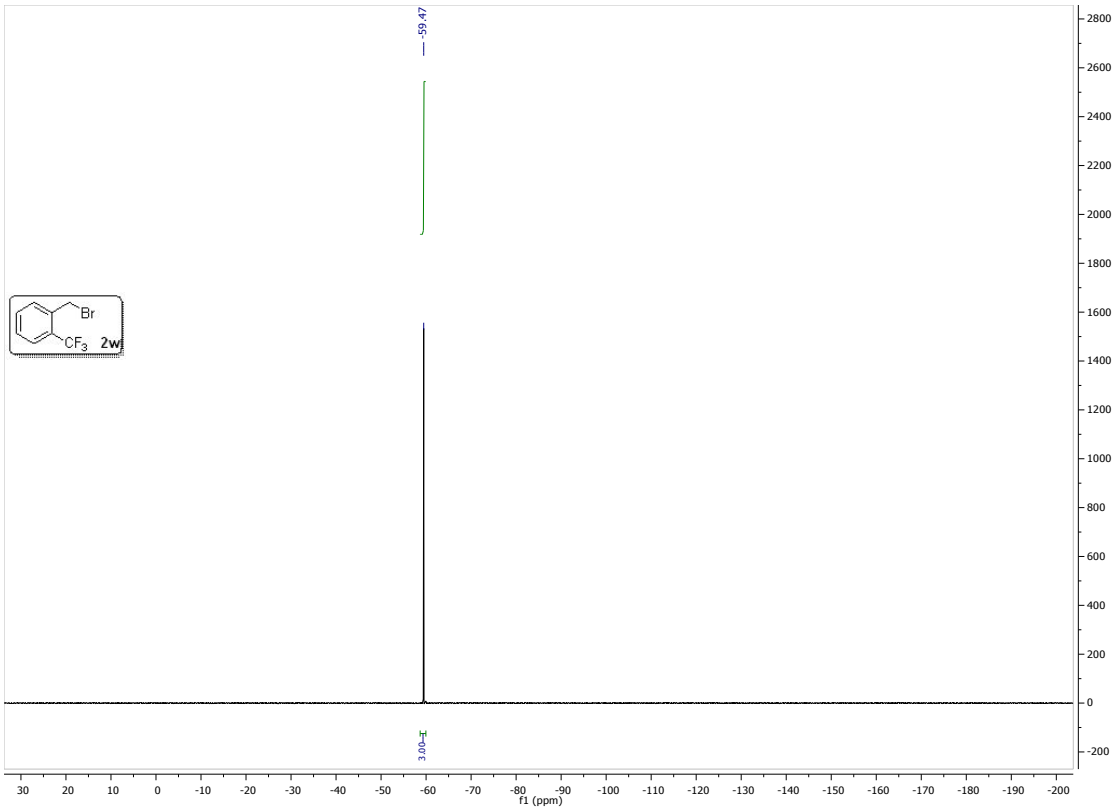

138.53
134.97
129.63
129.11
77.48
77.16
76.84
33.91
21.38
Br
2u
f1 (ppm)

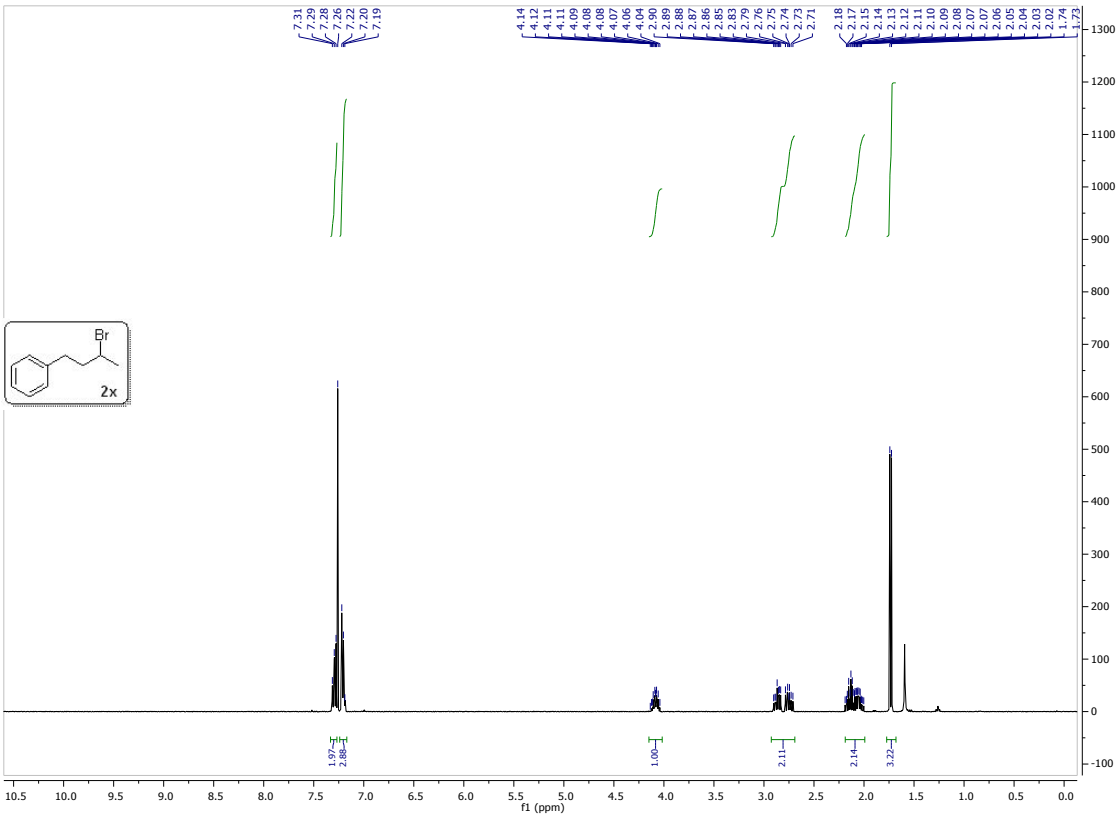

7.34
7.32
7.32
7.30
7.26
4.45
Br
Cl
2v
3.94
2.00
f1 (ppm)

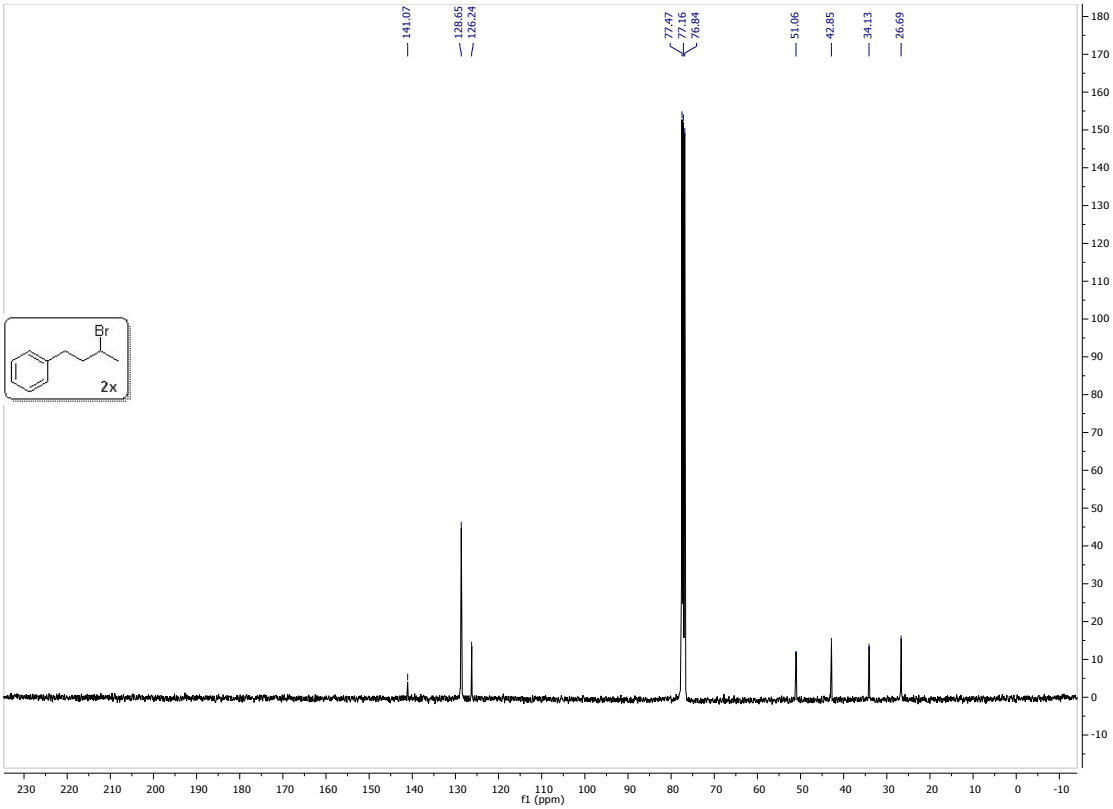

136.44
134.47
130.52
129.15
77.48
77.16
76.84
32.51
Br
Cl
2v
f1 (ppm)

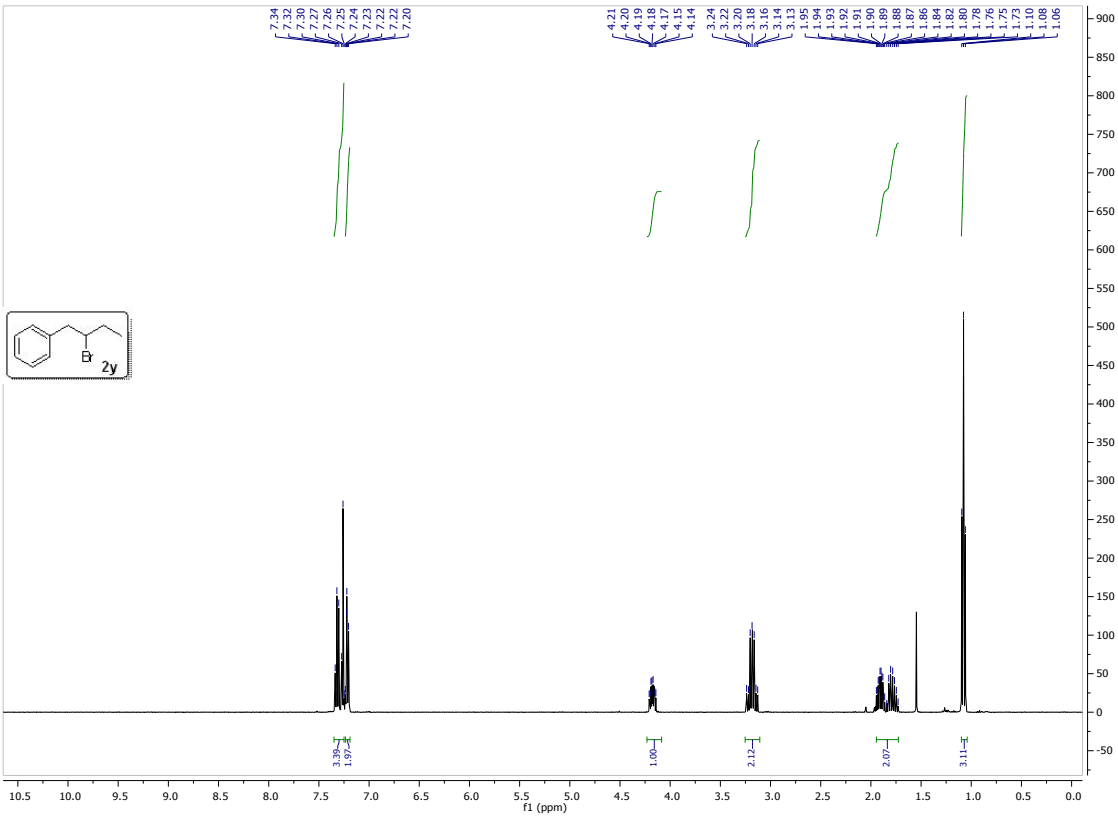

7.66
7.64
7.60
7.59
7.56
7.55
7.54
7.43
7.41
7.40
7.26
4.64
Br
CF3
2w
1.00
0.92
0.90
0.96
1.73
f1 (ppm)

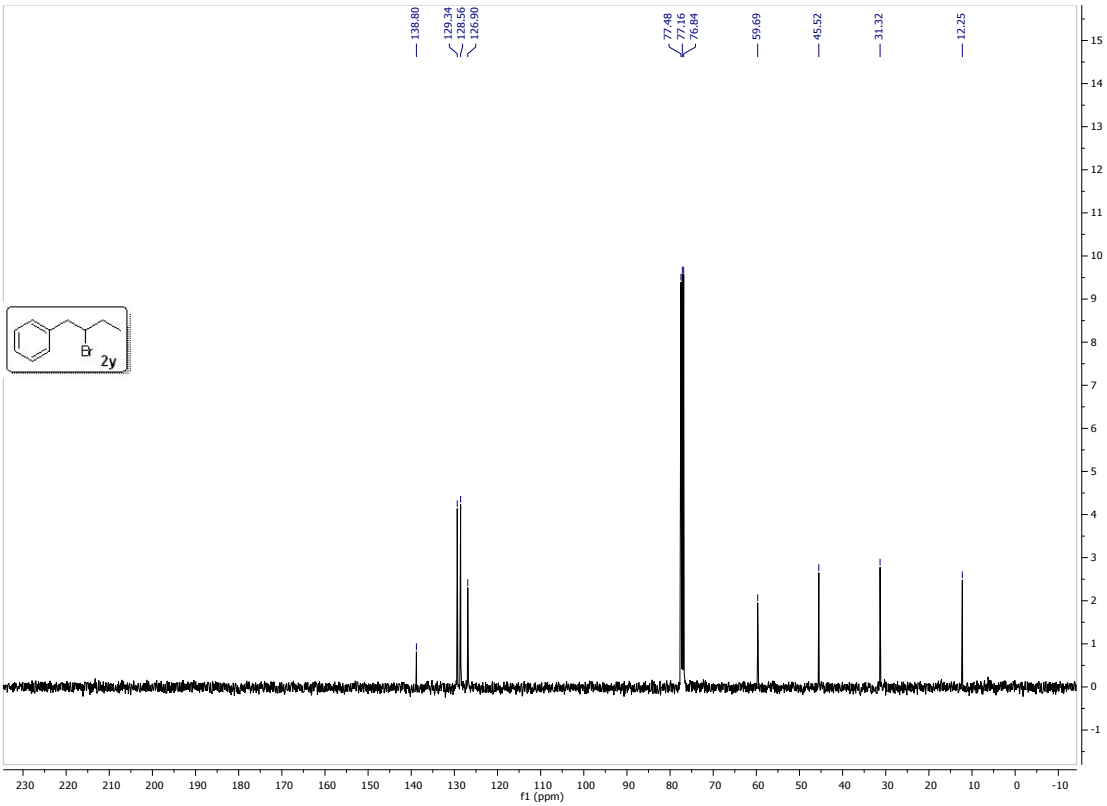

136.27
132.92
132.72
132.60
132.40
128.77
128.58
128.51
128.34
126.46
126.26
124.07
123.41
121.86
77.34
77.16
76.98
28.56
Br
CF3
2w
f1 (ppm)


-59.47
Br
CF3
2w
3.00
f1 (ppm)

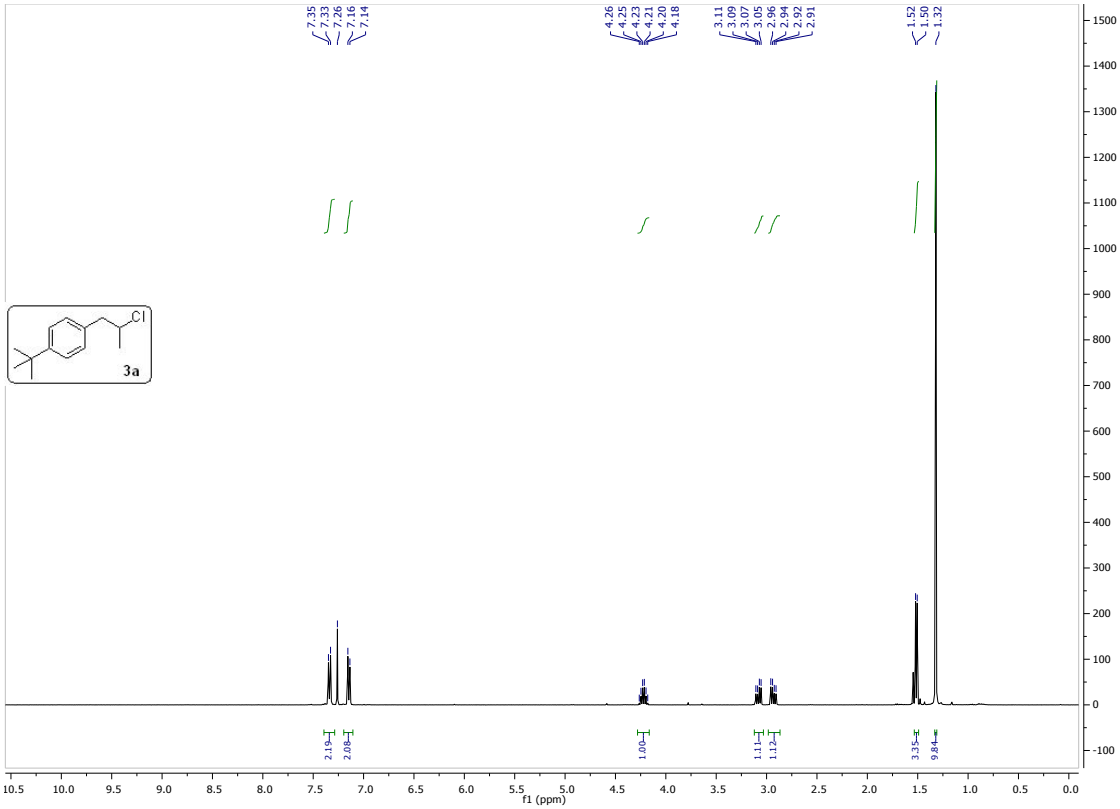

Br
2x
1.97
2.88
1.00
2.11
2.14
3.22
f1 (ppm)

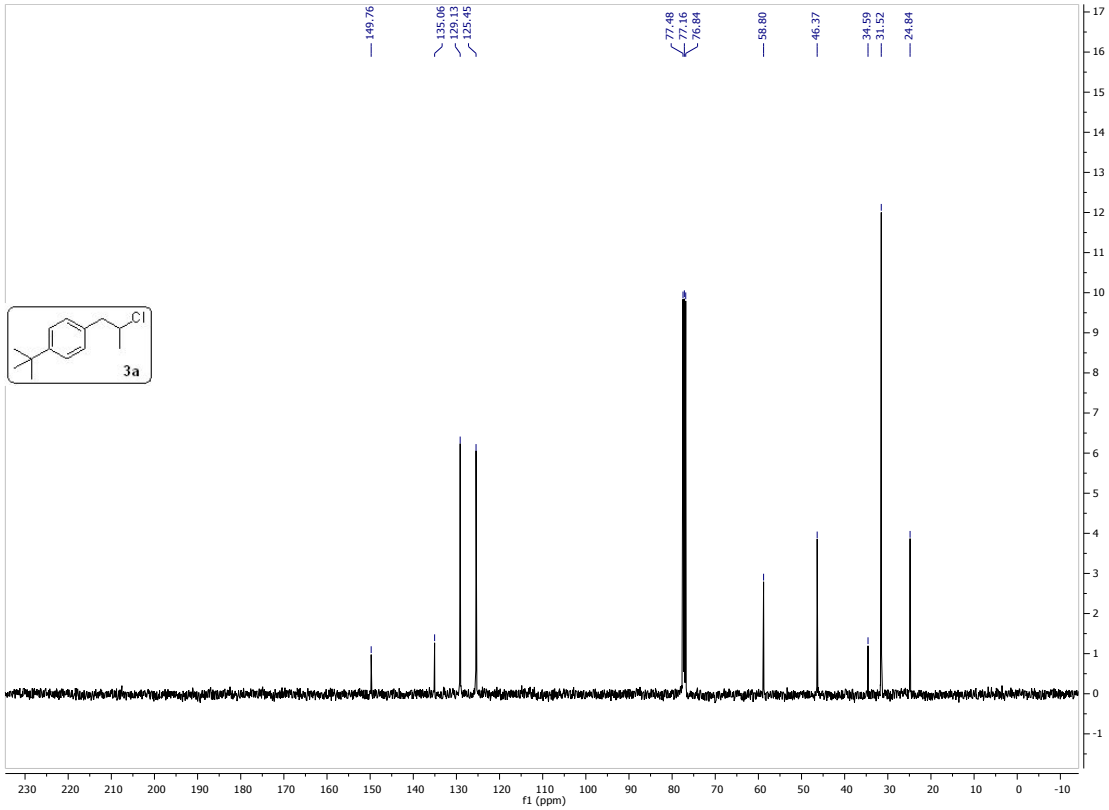

141.07
128.65
126.24
77.47
77.16
76.84
51.06
42.85
34.13
26.69
Br
2x
f1 (ppm)

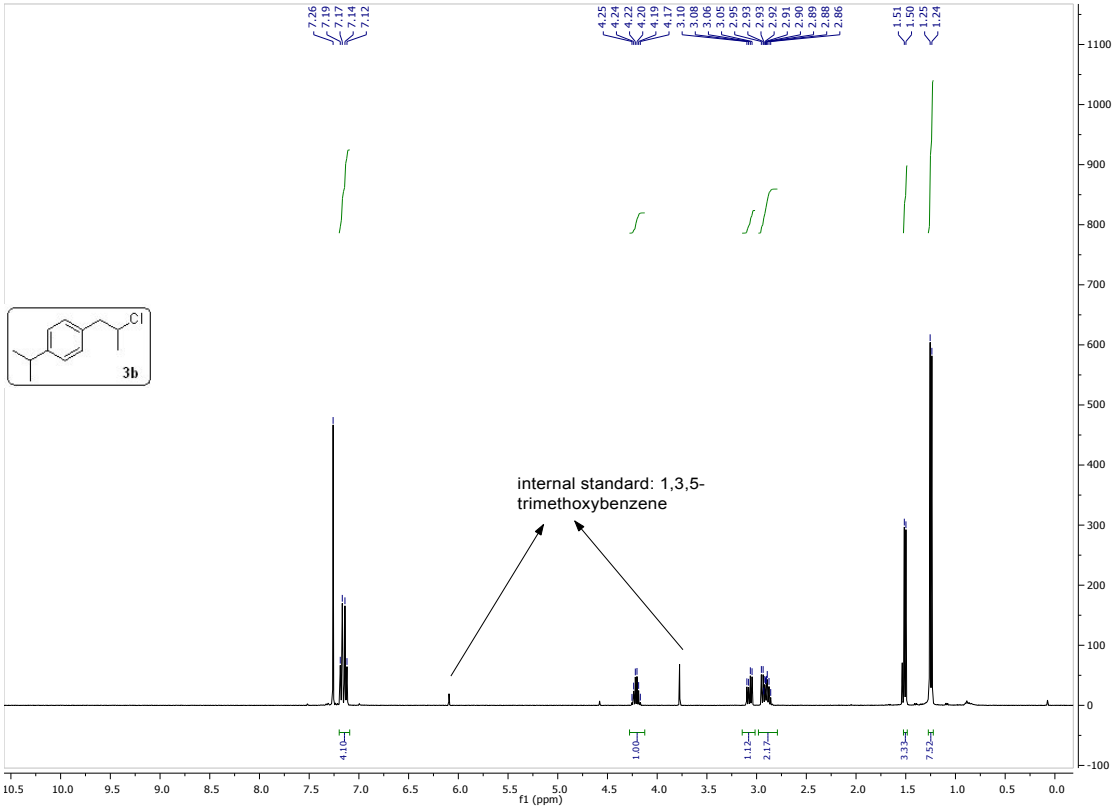

7.34
7.32
7.30
7.27
7.26
7.25
7.24
7.23
7.22
7.20
4.21
4.20
4.19
4.18
4.17
4.15
4.14
3.24
3.22
3.20
3.18
3.16
3.14
3.13
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.88
1.87
1.86
1.84
1.82
1.80
1.78
1.76
1.75
1.73
1.10
1.08
1.06
Br
2y
3.39
1.97
1.00
2.12
2.07
3.11
f1 (ppm)

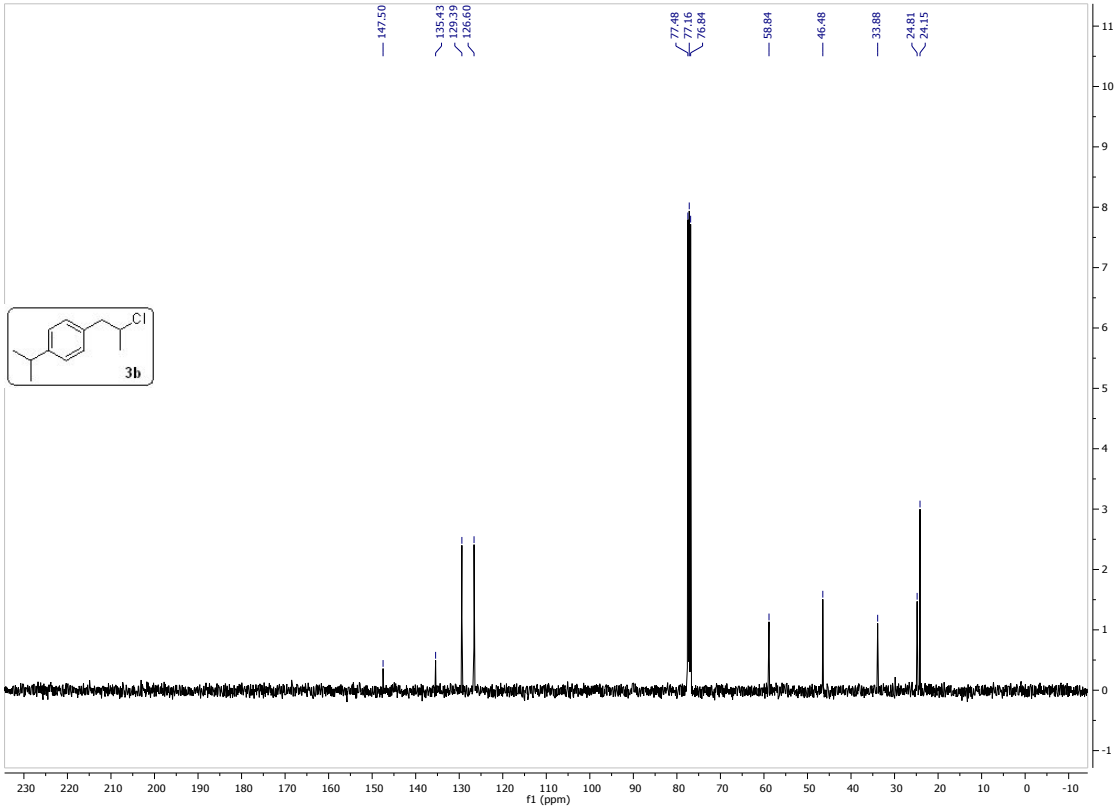

138.80
129.34
128.56
126.90
77.48
77.16
76.84
59.69
45.52
31.32
12.25
Br
2y
f1 (ppm)

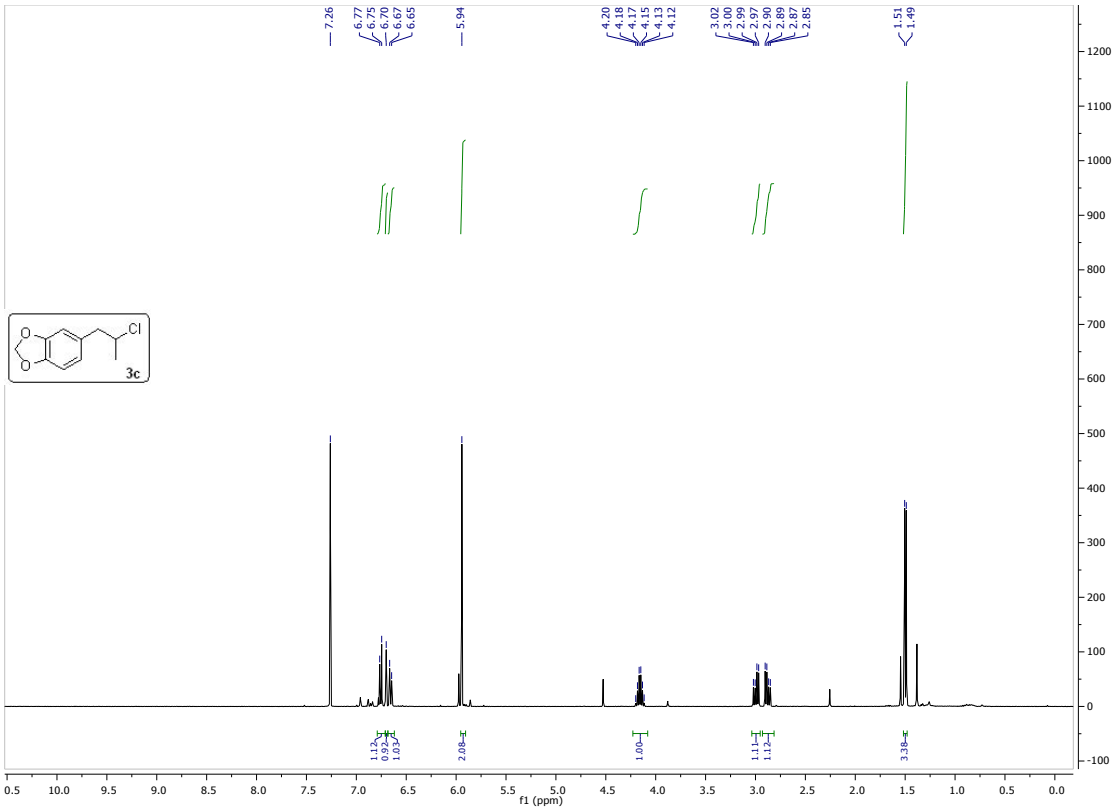
4.3 NMR spectral data for chlorinated products 3

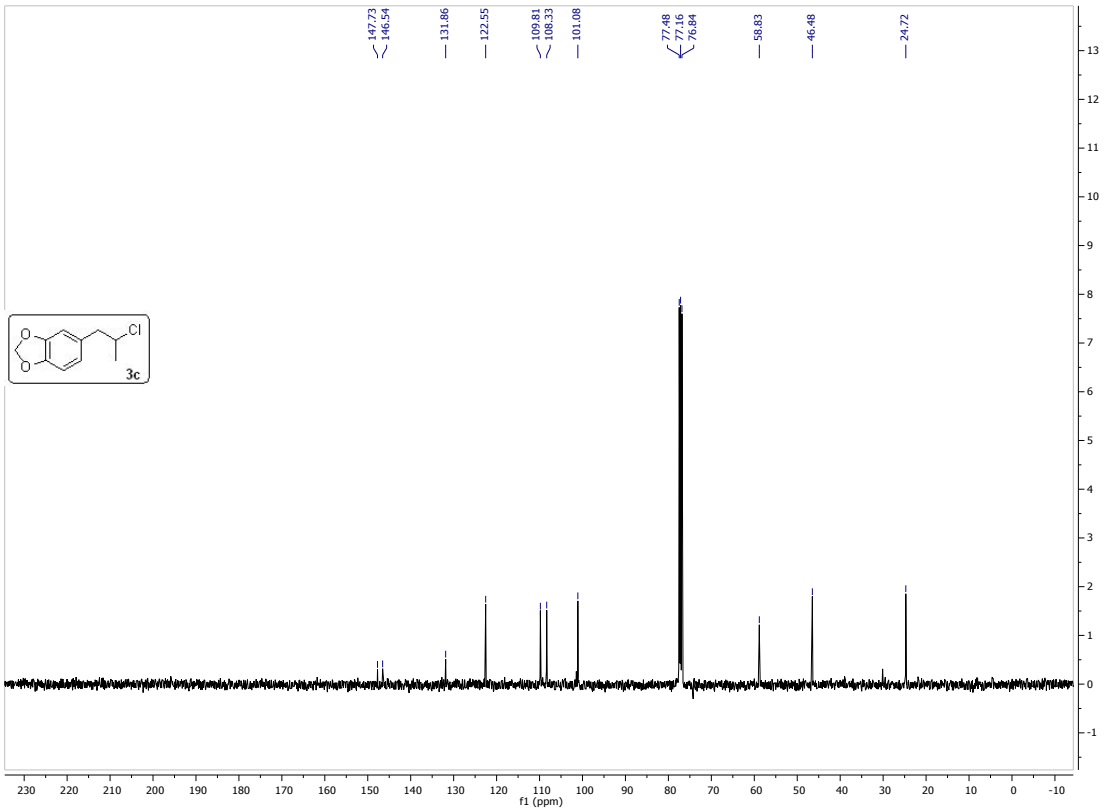


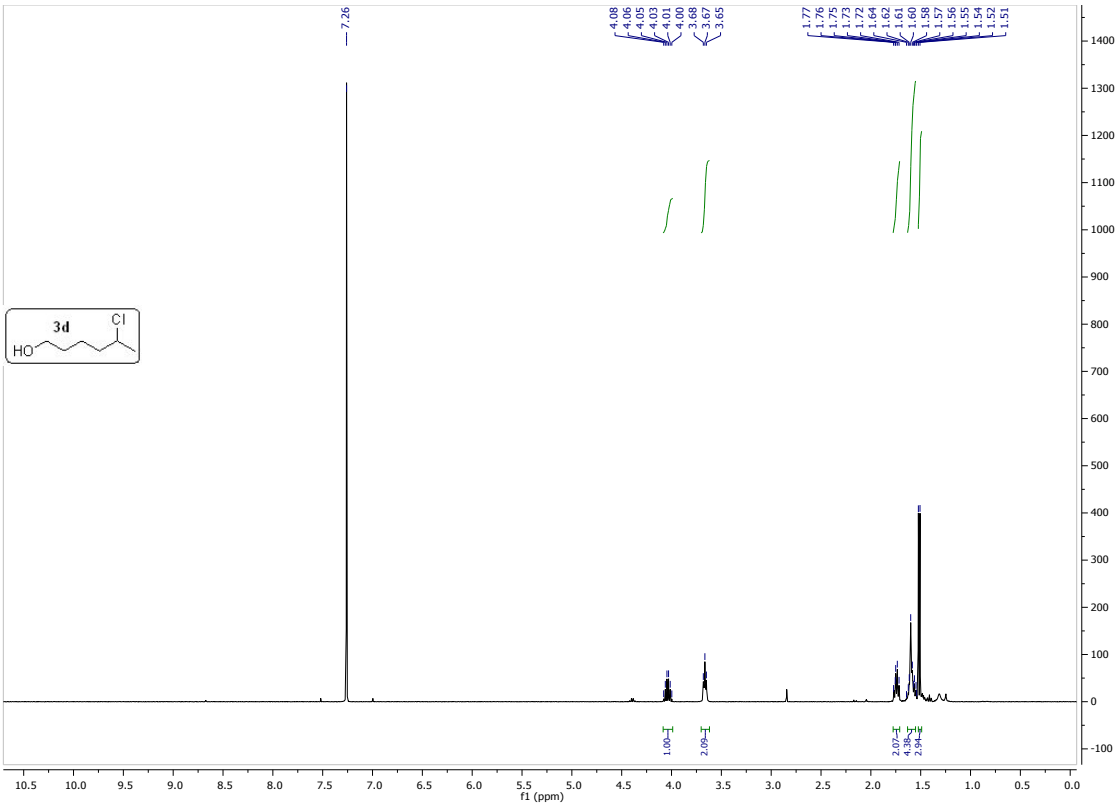


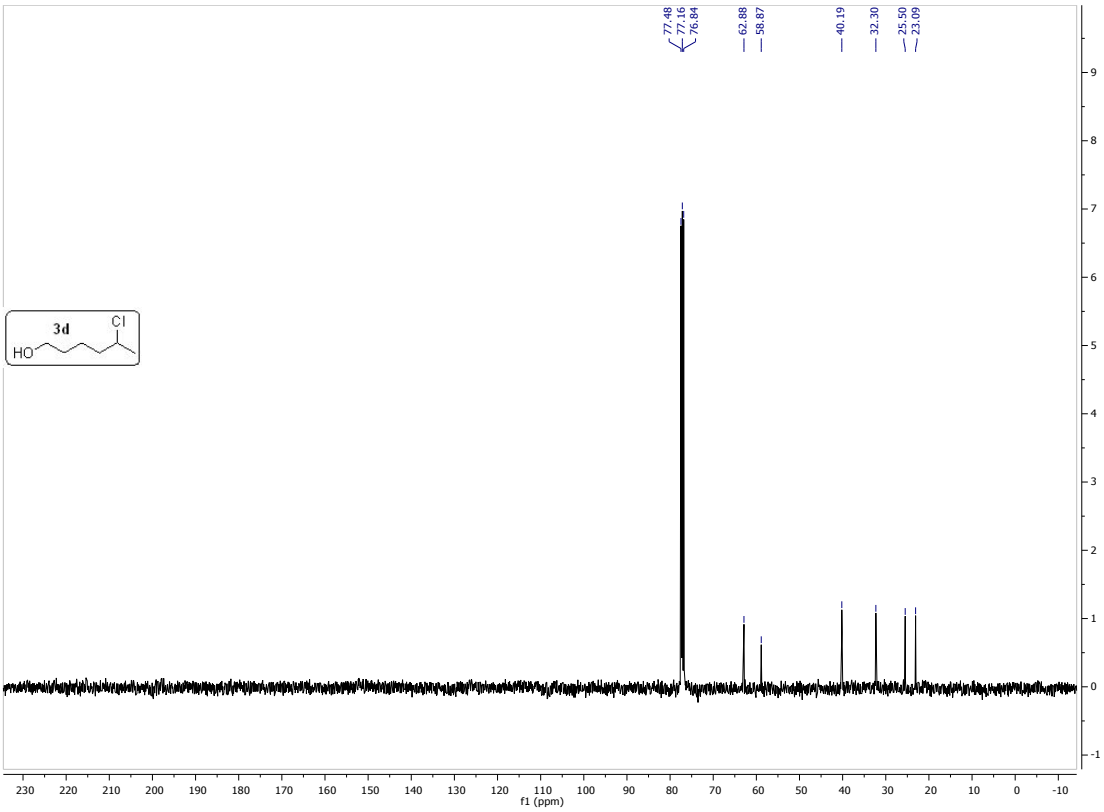

3b
internal standard: 1,3,5-trimethoxybenzene
f1 (ppm)

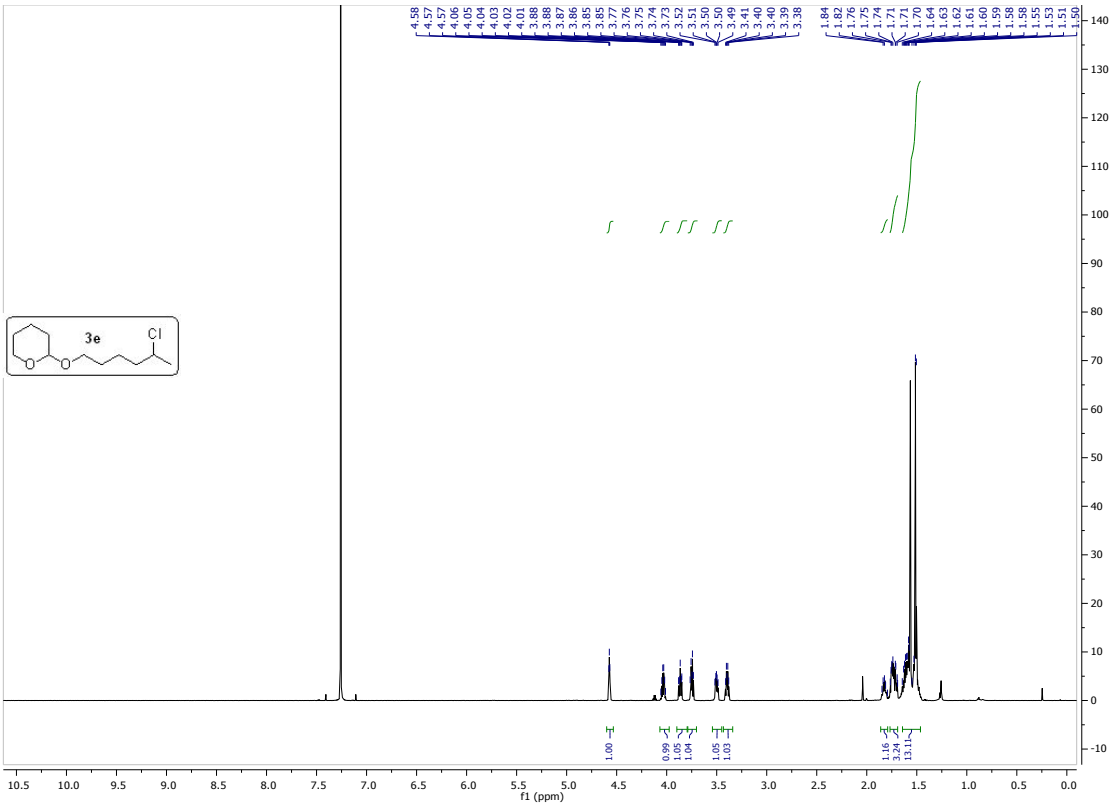

3b
f1 (ppm)

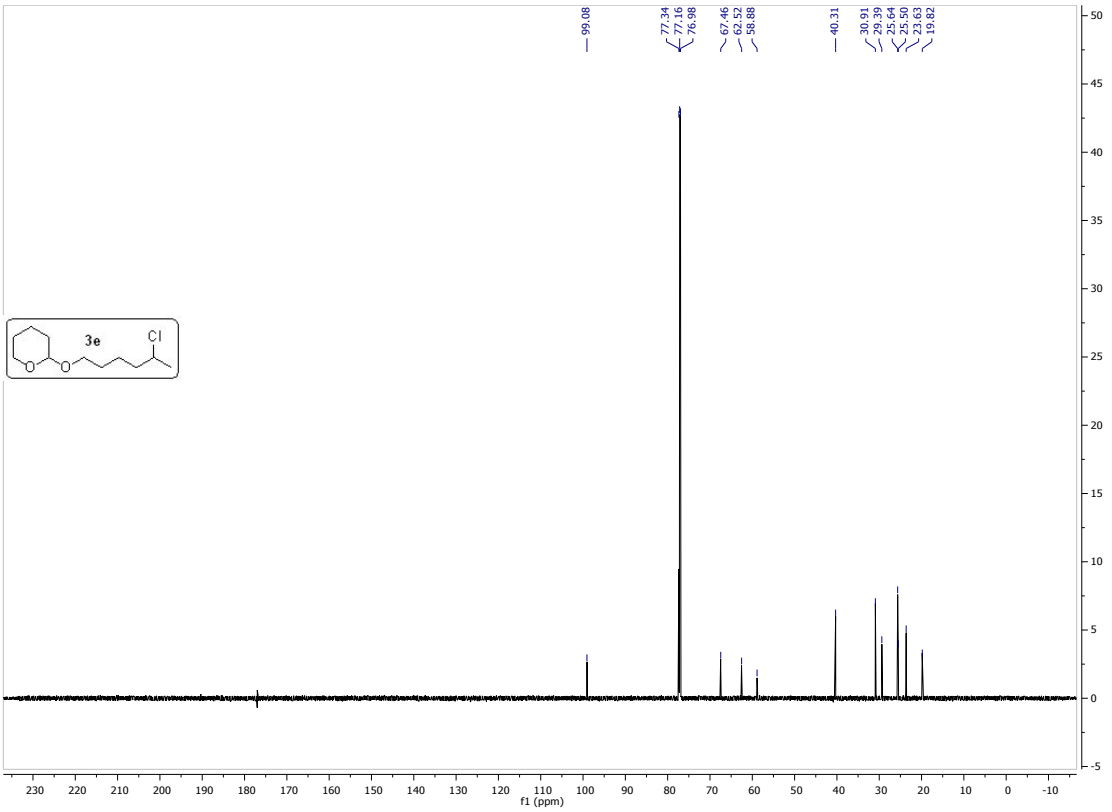

7.26
6.77
6.75
6.70
6.67
6.65
5.94
4.20
4.18
4.17
4.15
4.13
4.12
3.02
3.00
2.99
2.97
2.90
2.89
2.87
2.85
1.51
1.49
Cl
3c
1.12
0.92
1.03
2.08
1.00
1.11
1.12
3.38
f1 (ppm)

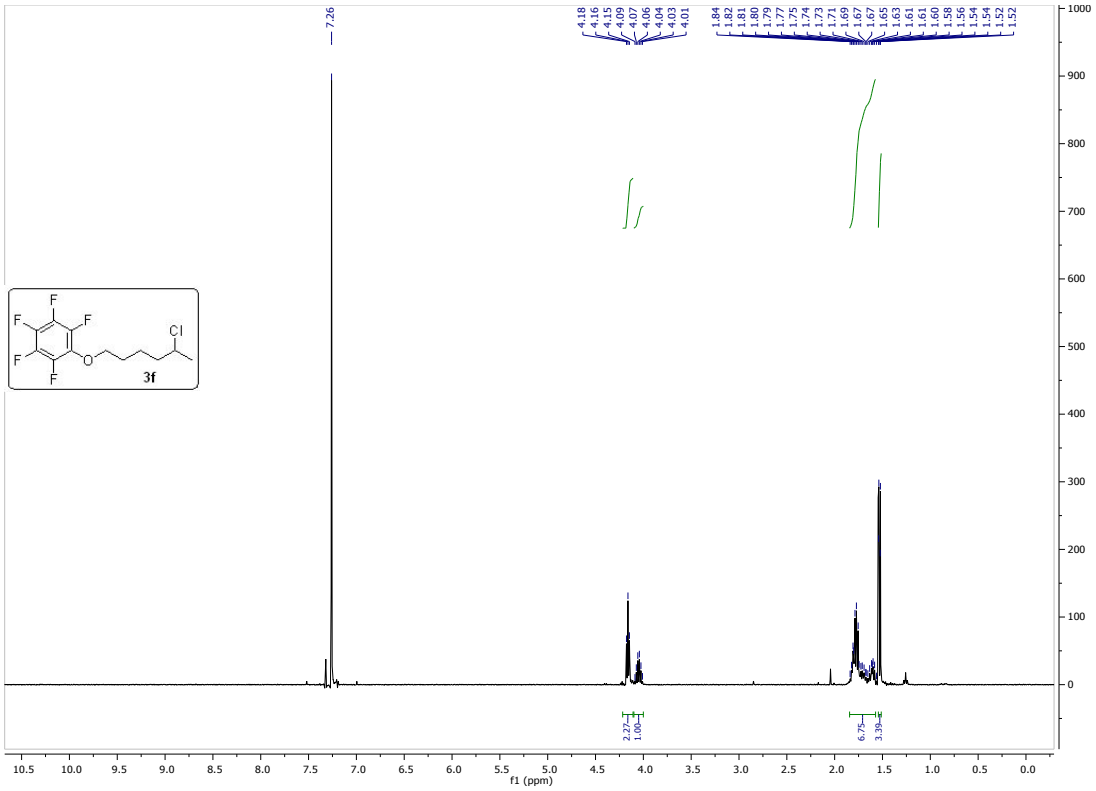

147.73
146.54
131.86
122.55
109.81
108.33
101.08
77.48
77.16
76.84
58.83
46.48
24.72
Cl
3c
f1 (ppm)

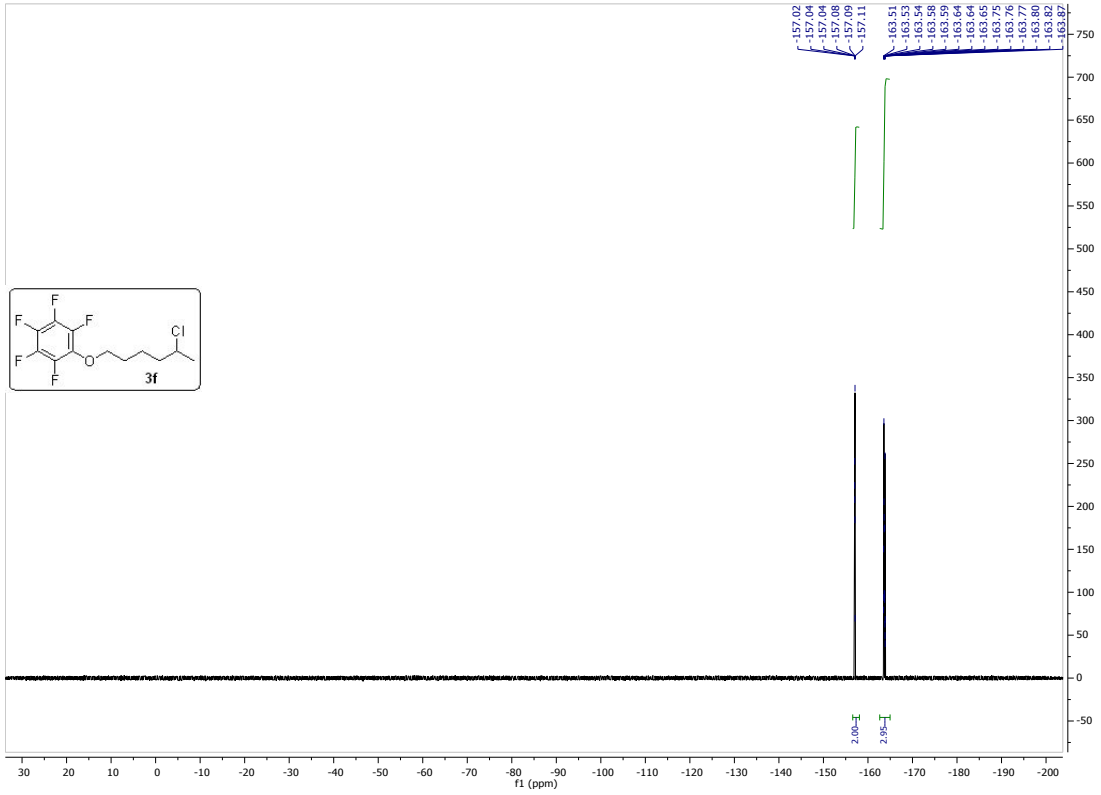

3d
HO
Cl
7.26
4.08
4.06
4.05
4.03
4.01
4.00
3.68
3.67
3.65
1.77
1.76
1.75
1.73
1.72
1.64
1.62
1.61
1.60
1.58
1.57
1.56
1.55
1.54
1.52
1.51
1.00
2.09
2.07
4.38
2.94
f1 (ppm)

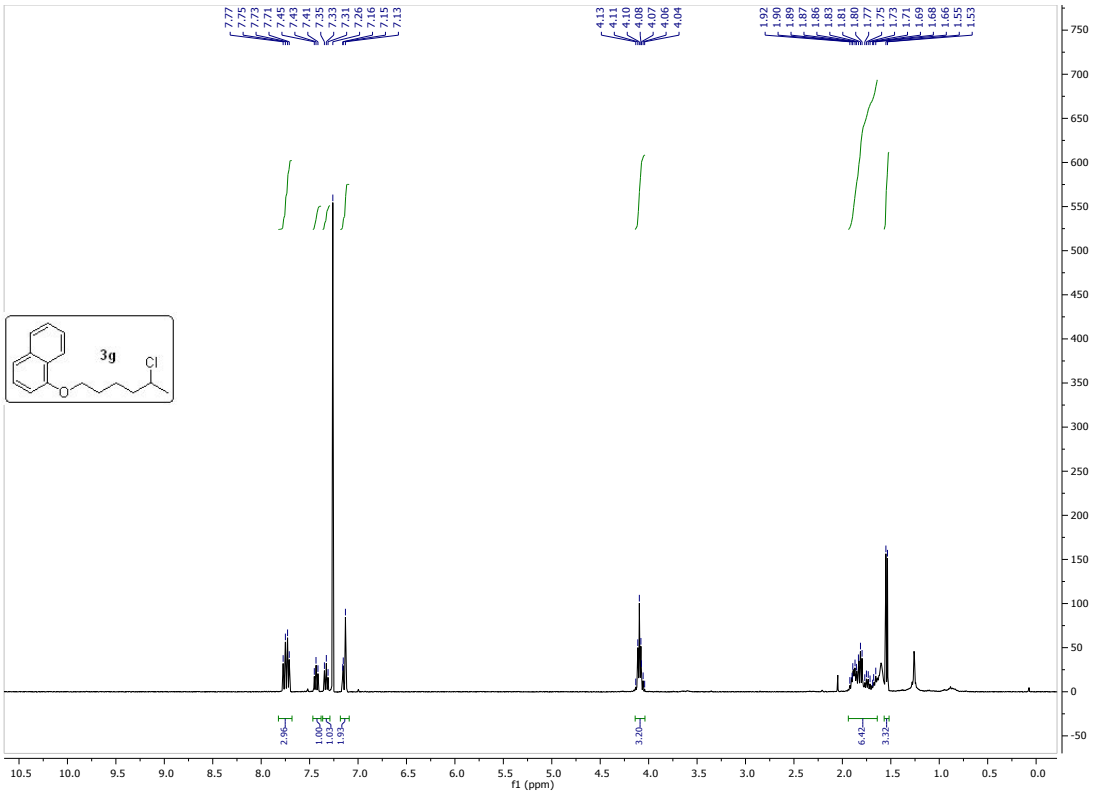

3d
HO
Cl
77.48
77.16
76.84
62.88
58.87
40.19
32.30
25.50
23.09
f1 (ppm)

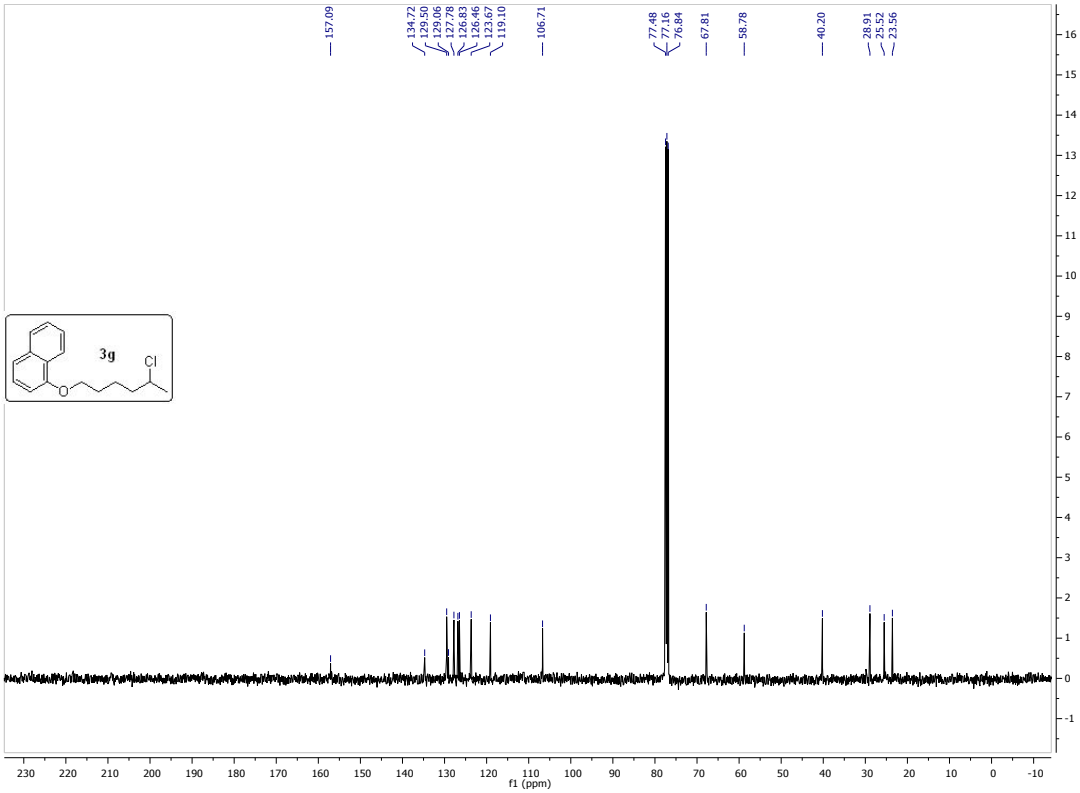

3e
Cl
f1 (ppm)

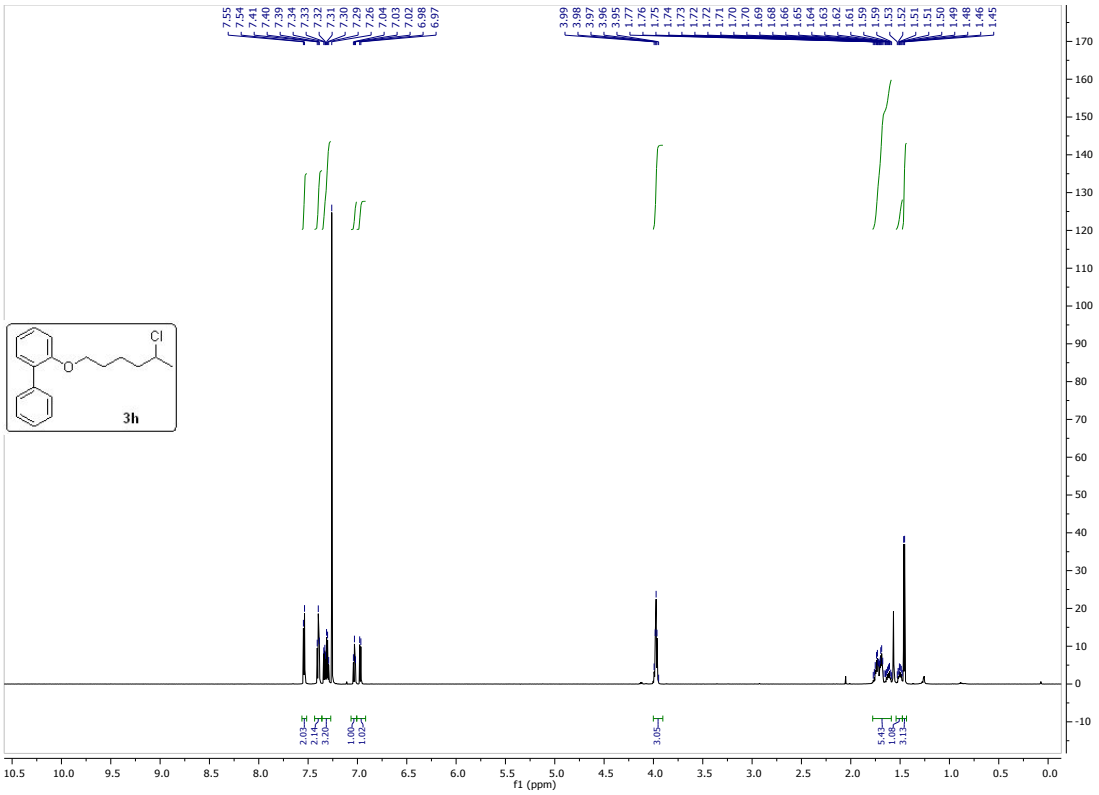

3e
Cl
f1 (ppm)

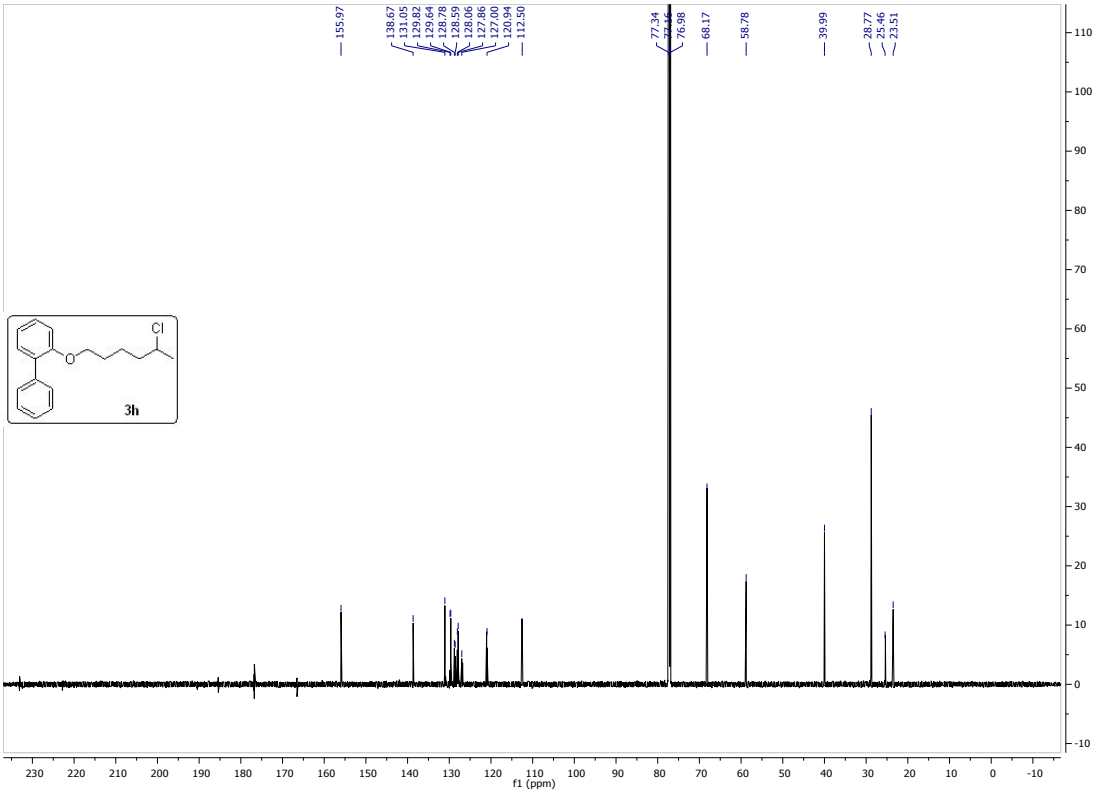

7.26
4.18 4.16 4.15 4.09 4.07 4.06 4.04 4.03 4.01
1.84 1.82 1.81 1.80 1.79 1.77 1.75 1.74 1.73 1.71 1.69 1.67 1.65 1.63 1.61 1.61 1.60 1.58 1.56 1.54 1.54 1.52 1.52
2.27
1.00
6.75
3.39
f1 (ppm)
3f

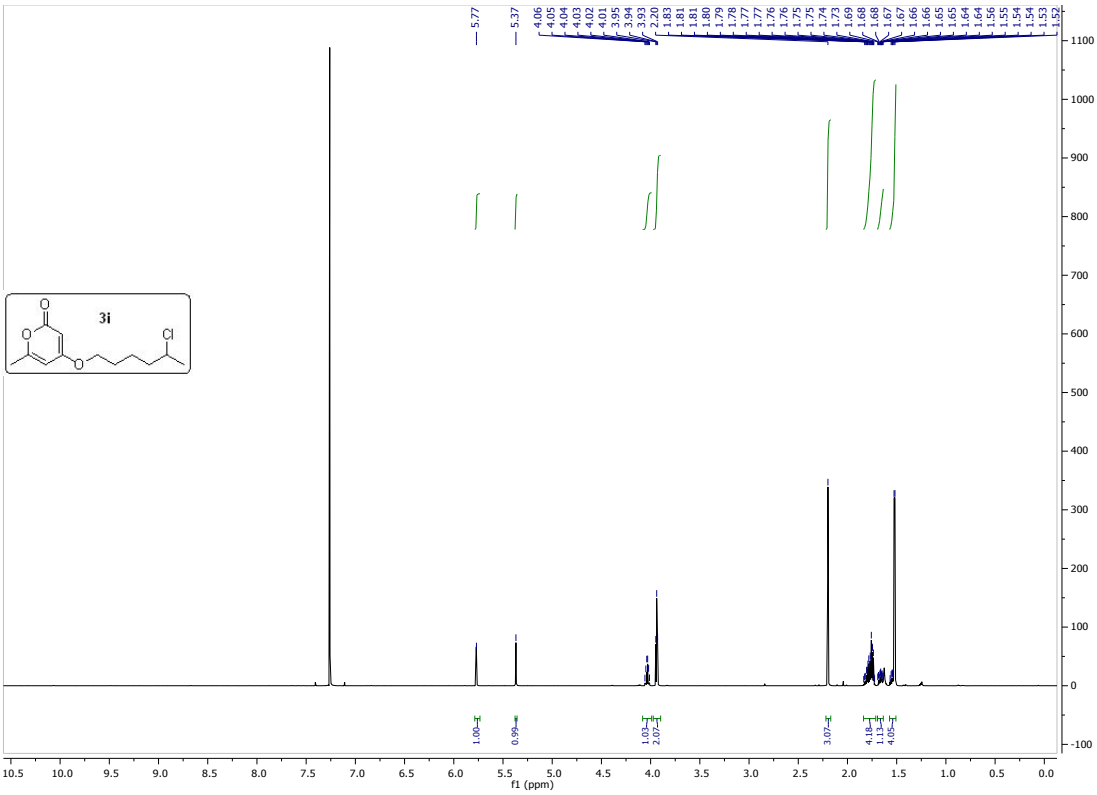

157.02 157.04 157.04 157.08 157.09 157.11
163.51 163.53 163.54 163.58 163.59 163.64 163.64 163.65 163.75 163.76 163.77 163.80 163.82 163.87
2.00
2.95
f1 (ppm)
3f

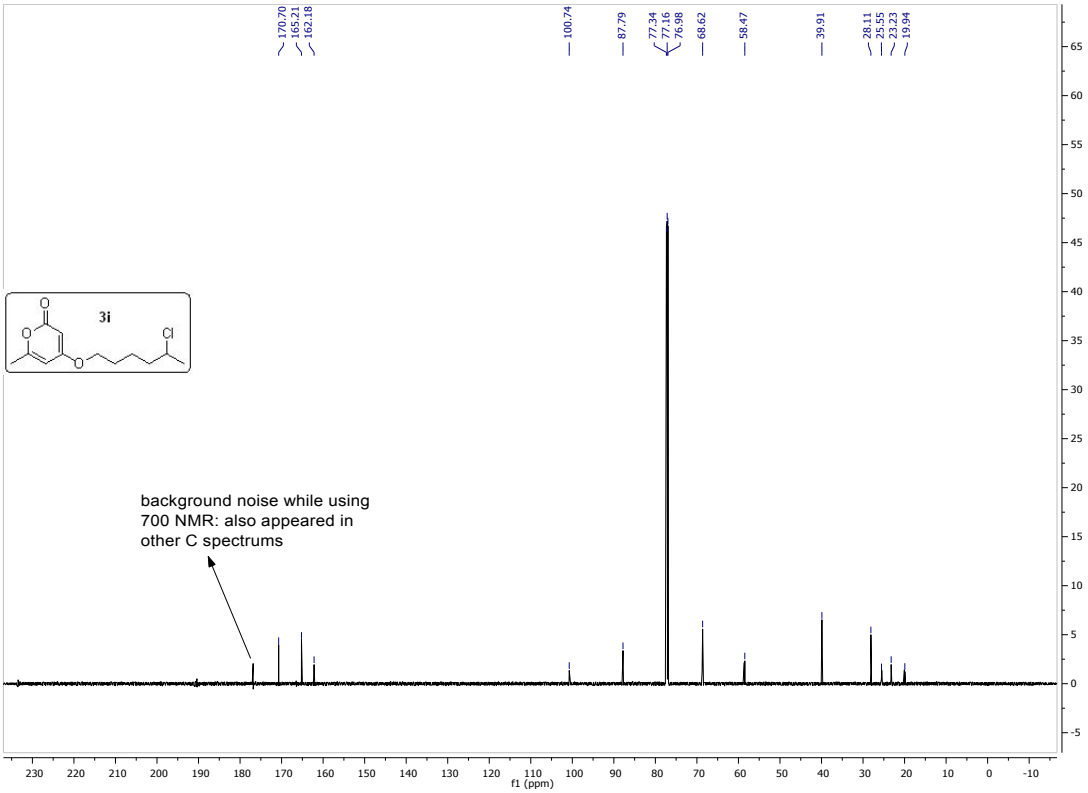

7.77
7.75
7.73
7.71
7.45
7.43
7.41
7.35
7.33
7.31
7.26
7.16
7.15
7.13
4.13
4.11
4.10
4.08
4.07
4.06
4.04
1.92
1.90
1.89
1.87
1.86
1.85
1.83
1.81
1.80
1.77
1.75
1.73
1.71
1.69
1.68
1.66
1.55
1.53
3g
Cl
O
2.96
1.00
1.03
1.93
3.20
6.42
3.32
f1 (ppm)

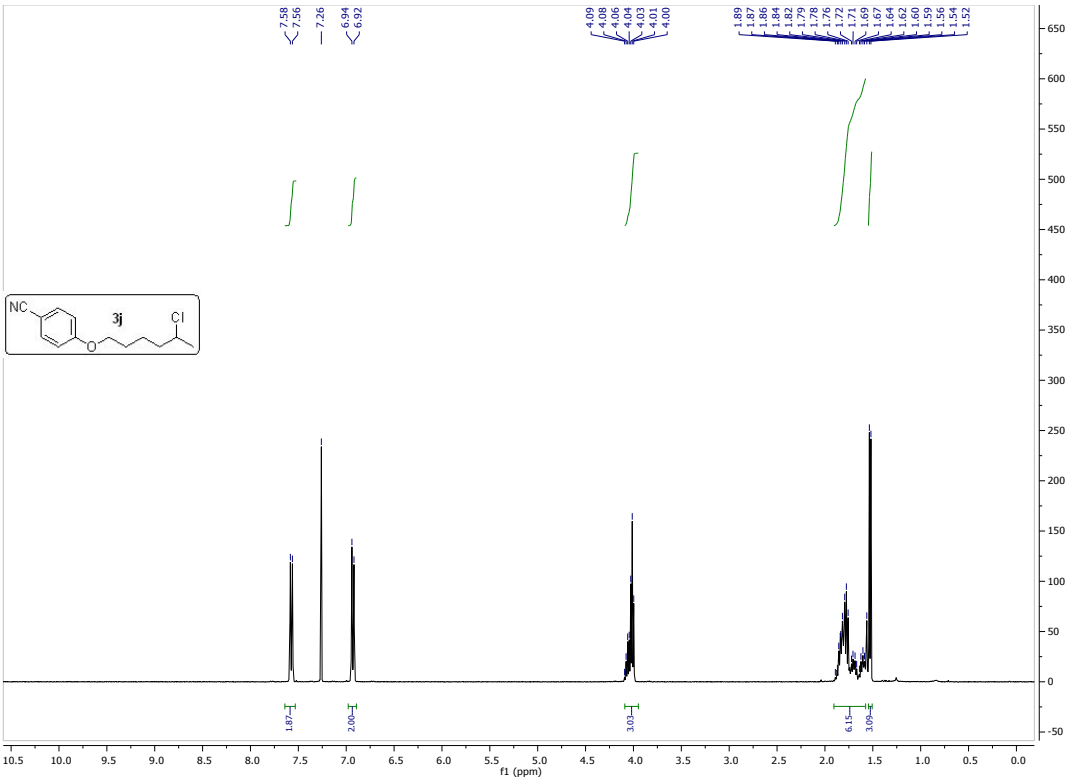

157.09
134.72
129.50
129.06
127.78
126.83
126.46
123.67
119.10
106.71
77.48
77.16
76.84
67.81
58.78
40.20
28.91
25.52
23.56
3g
Cl
O
f1 (ppm)

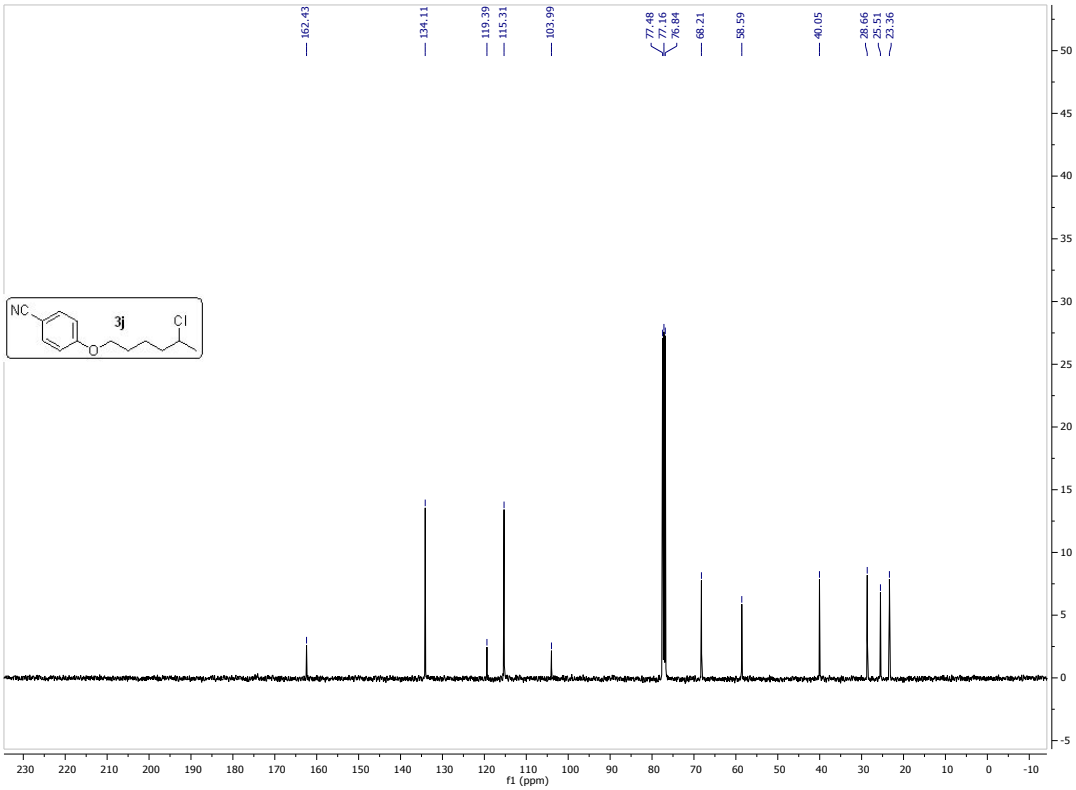

7.55 7.54 7.41 7.40 7.39 7.34 7.33 7.32 7.31 7.30 7.29 7.26 7.04 7.03 7.02 6.98 6.97
3.99 3.98 3.97 3.96 3.95 1.77 1.76 1.75 1.74 1.73 1.72 1.72 1.72 1.71 1.70 1.70 1.69 1.68 1.66 1.65 1.64 1.63 1.62 1.61 1.59 1.59 1.55 1.52 1.51 1.51 1.50 1.49 1.48 1.46 1.45
Cl
O
3h
2.03
2.14
3.20
1.00
1.02
3.05
5.43
1.08
3.13
f1 (ppm)

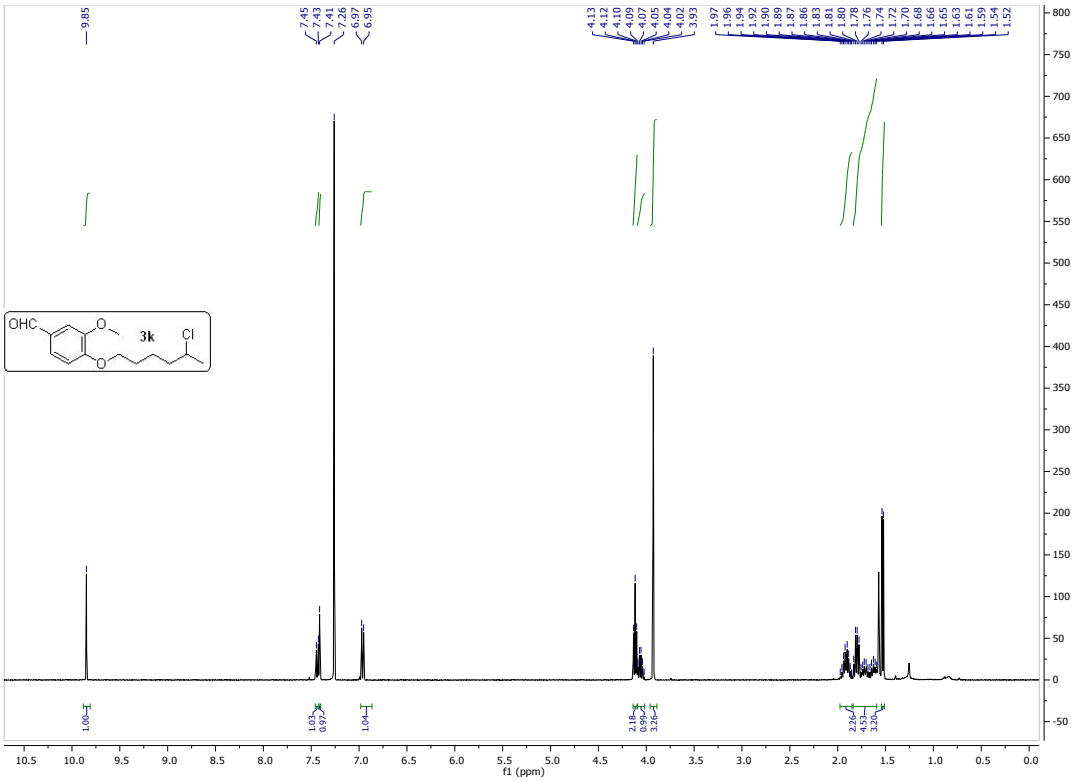

155.97
138.67
131.05
129.82
129.64
128.78
128.59
128.06
127.86
127.00
120.94
112.50
77.34
77.16
76.98
68.17
58.78
39.99
28.77
25.46
23.51
Cl
O
3h
f1 (ppm)

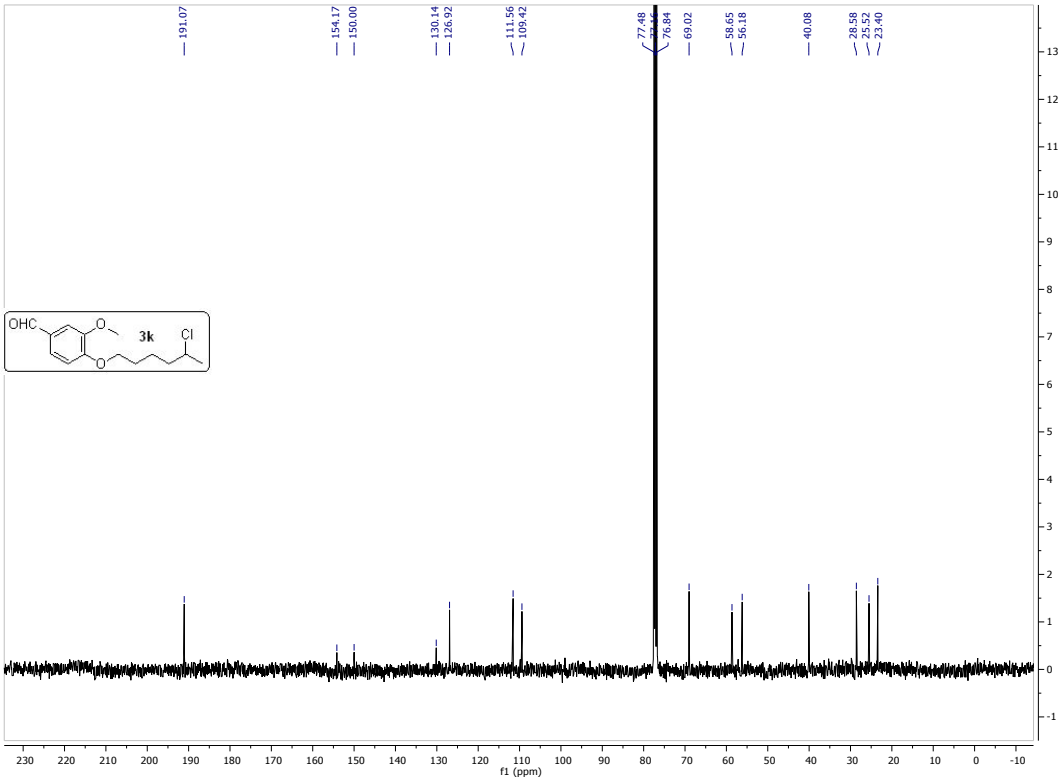

3i
f1 (ppm)

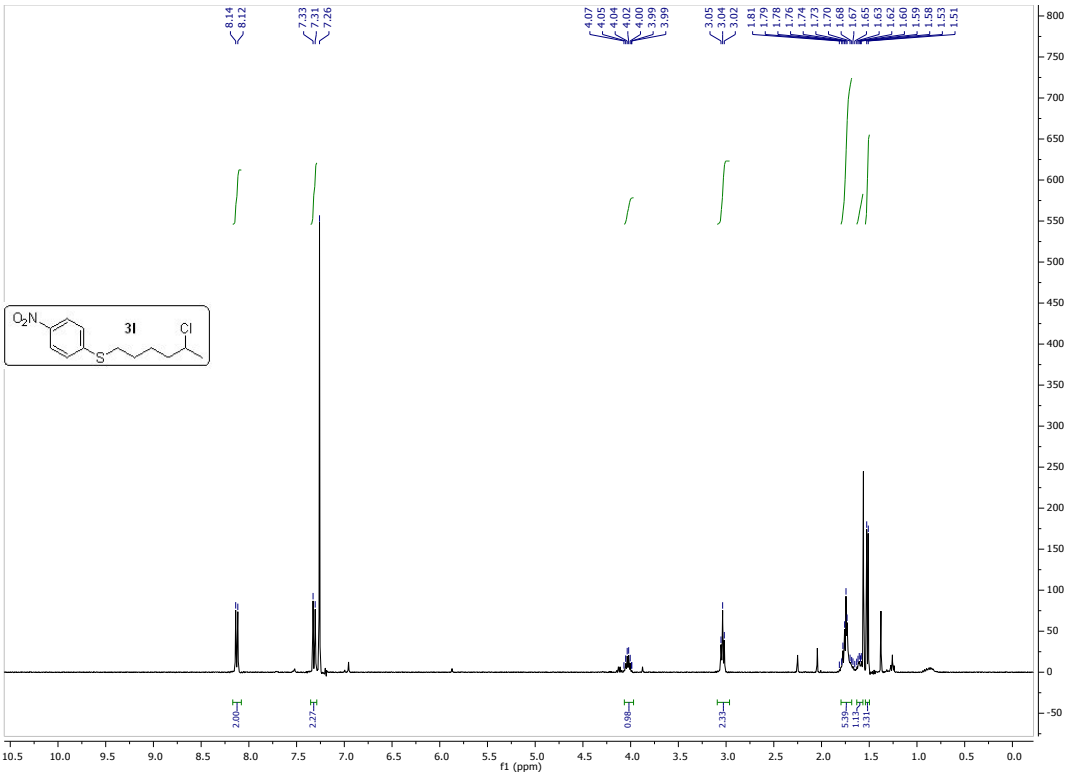

3i
background noise while using 700 NMR: also appeared in other C spectrums
f1 (ppm)

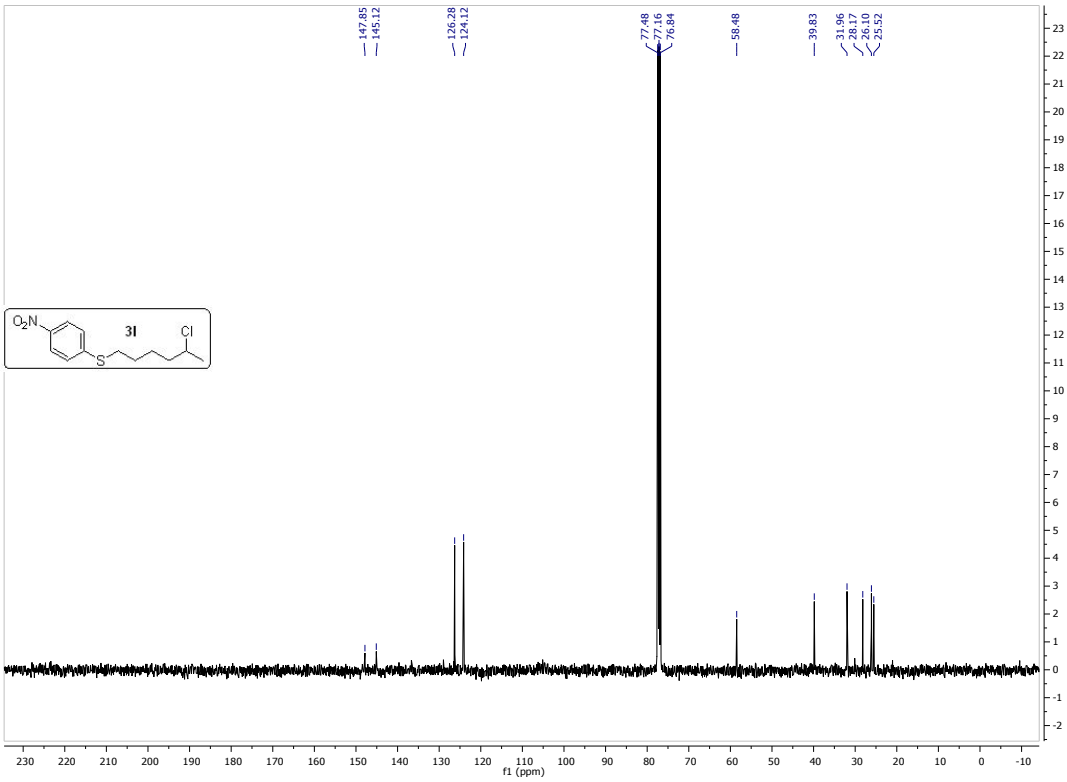

7.58
7.56
7.26
6.94
6.92
4.09
4.08
4.06
4.04
4.03
4.01
4.00
1.89
1.87
1.86
1.84
1.82
1.79
1.78
1.76
1.72
1.71
1.69
1.67
1.64
1.62
1.60
1.59
1.56
1.54
1.52
NC
3j
Cl
O
1.87
2.00
3.03
6.15
3.09
f1 (ppm)

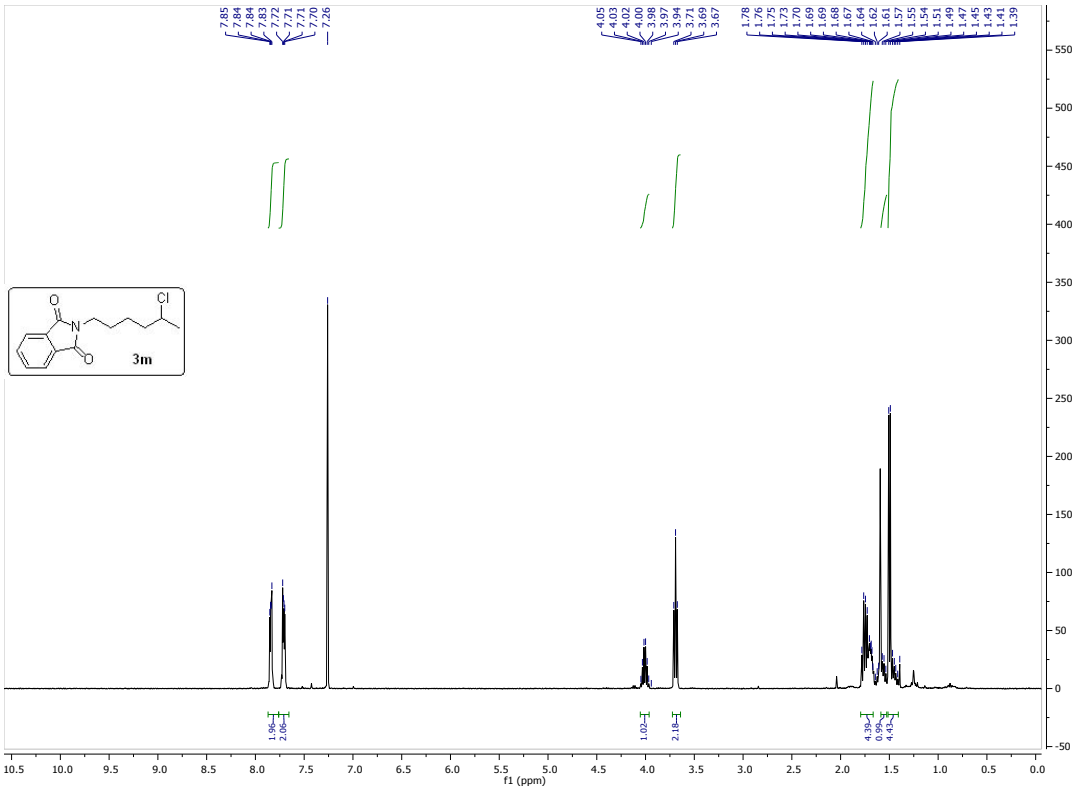

162.43
134.11
119.39
115.31
103.99
77.48
77.16
76.84
68.21
58.59
40.05
28.66
25.51
23.36
NC
3j
Cl
O
f1 (ppm)

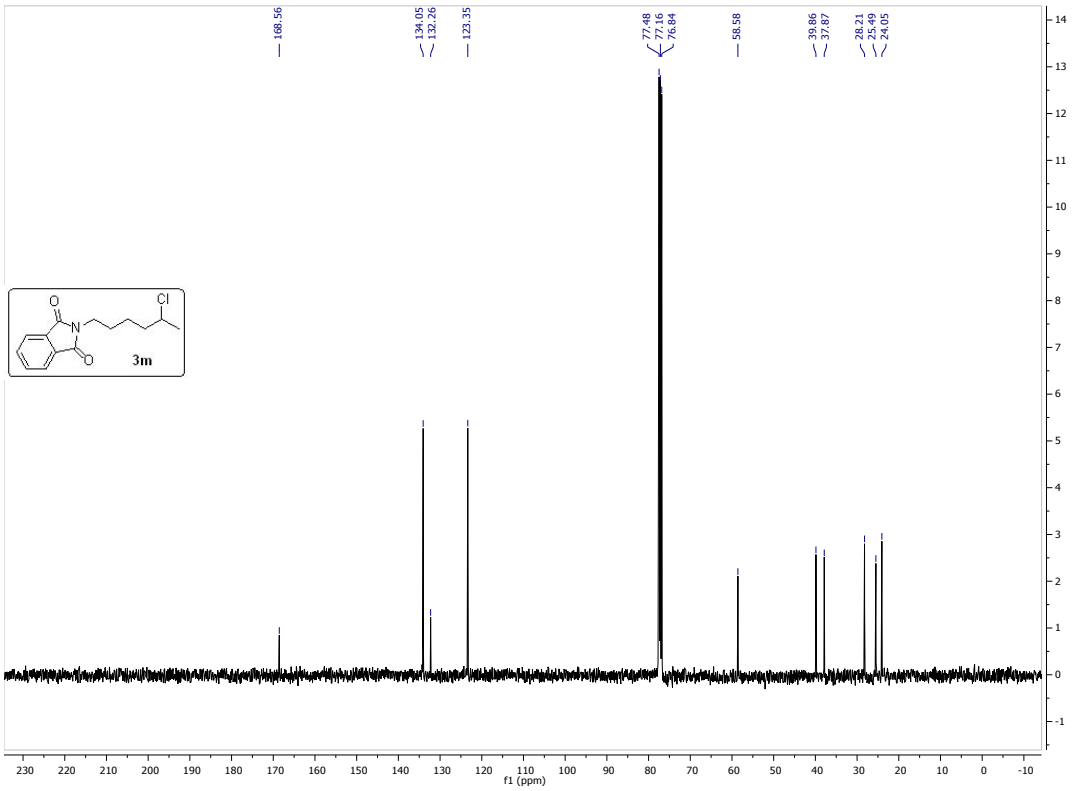

9.85
7.45
7.43
7.41
7.26
6.97
6.95
4.13
4.12
4.10
4.09
4.07
4.05
4.04
4.02
3.93
1.97
1.96
1.94
1.92
1.90
1.89
1.87
1.86
1.83
1.81
1.80
1.78
1.76
1.74
1.72
1.70
1.68
1.66
1.65
1.63
1.61
1.59
1.54
1.52
OHC
O
O
3k
Cl
1.00
1.03
0.97
1.04
2.18
0.99
3.26
2.26
4.33
3.10
f1 (ppm)

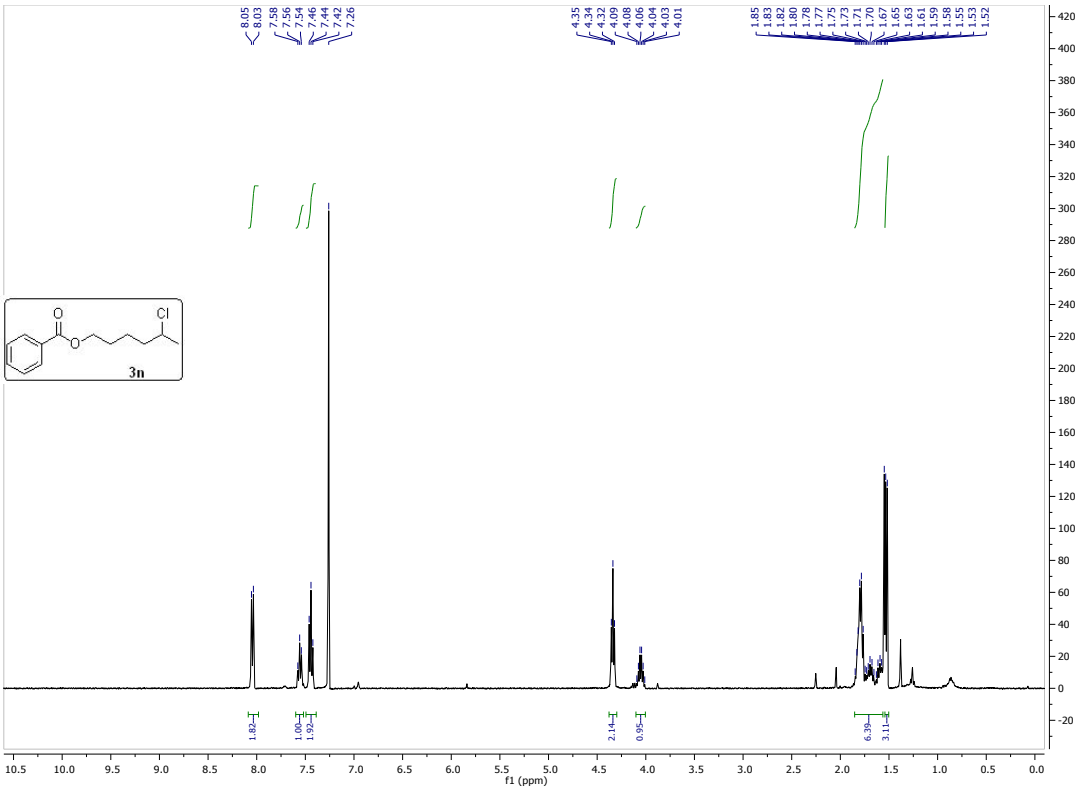

191.07
154.17
150.00
130.14
126.92
111.56
109.42
77.48
76.84
69.02
58.65
56.18
40.08
28.58
25.52
23.40
OHC
O
O
3k
Cl
f1 (ppm)

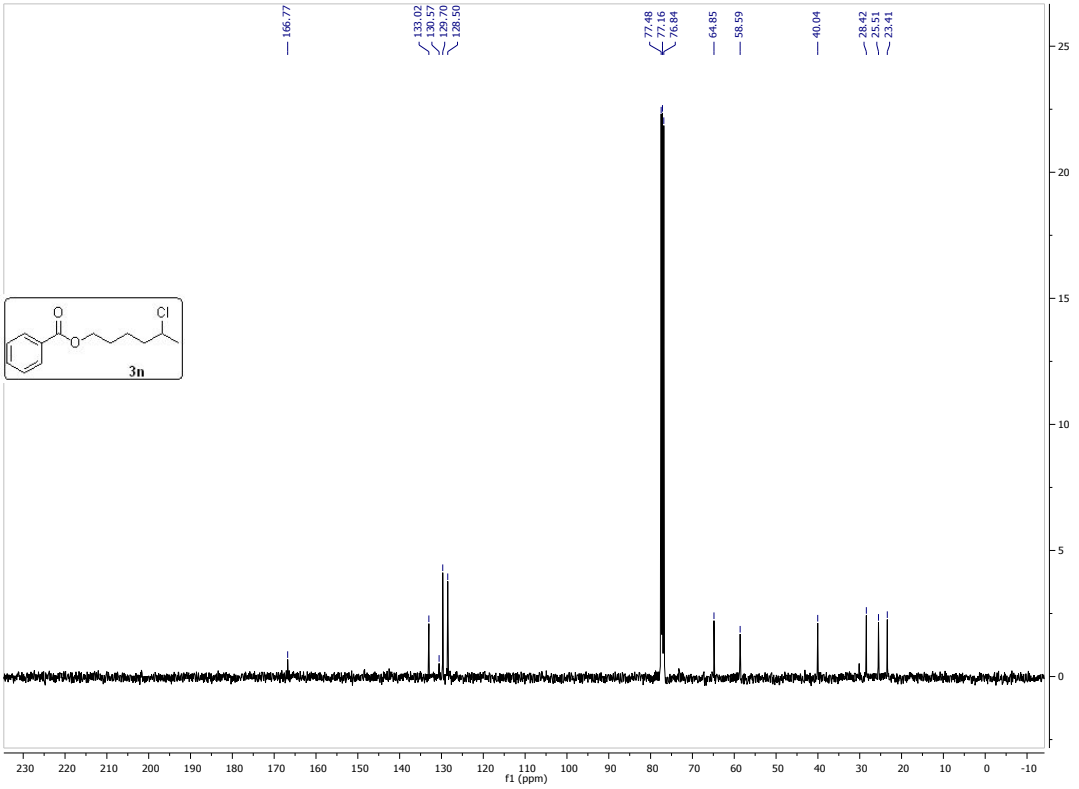

8.14
8.12
7.33
7.31
7.26
4.07
4.05
4.04
4.02
4.00
3.99
3.99
3.05
3.04
3.02
1.81
1.79
1.78
1.76
1.74
1.73
1.70
1.68
1.67
1.65
1.63
1.62
1.60
1.59
1.58
1.55
1.51
O2N
3l
Cl
S
2.00
2.27
0.98
2.33
5.39
1.13
3.31
f1 (ppm)

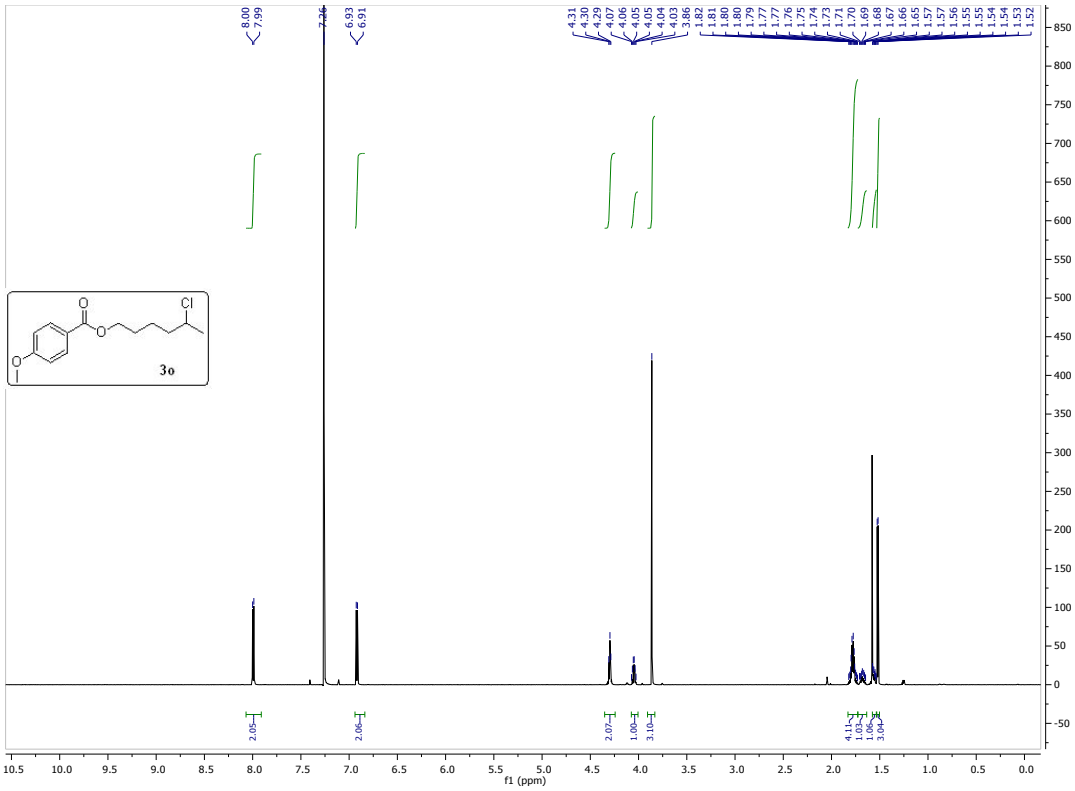

147.85
145.12
126.28
124.12
77.48
77.16
76.84
58.48
39.83
31.96
28.17
26.10
25.52
O2N
3l
Cl
S
f1 (ppm)

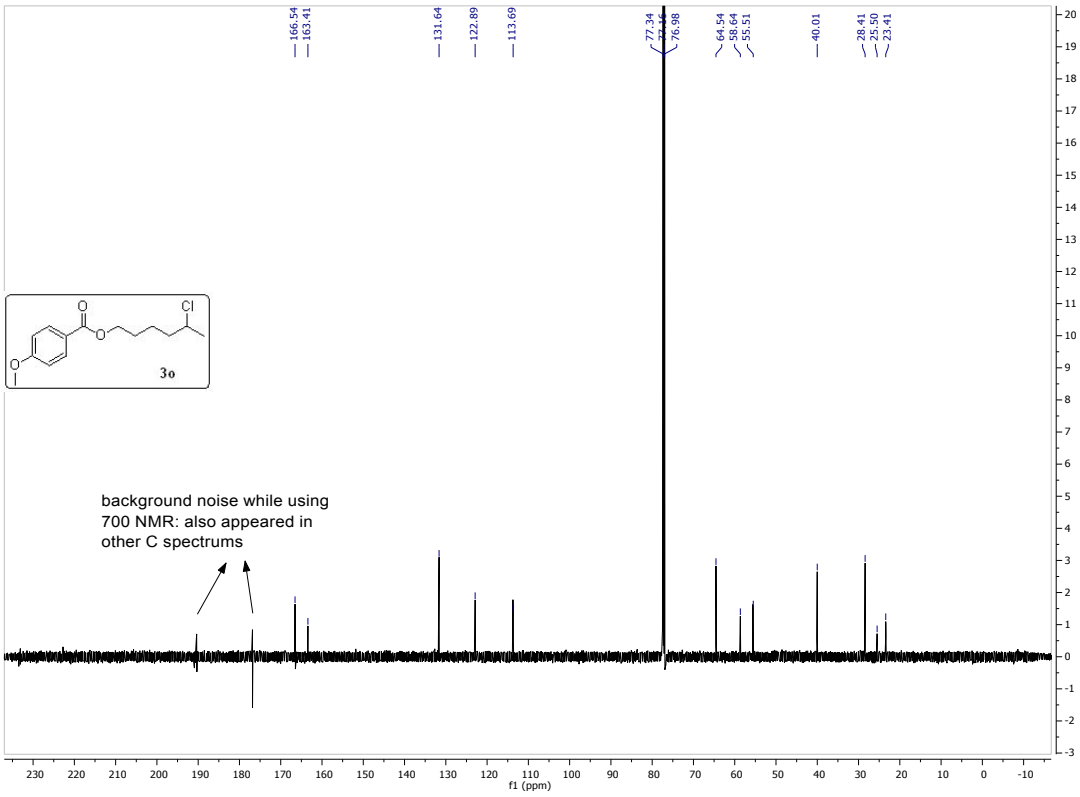

7.85
7.84
7.84
7.83
7.72
7.71
7.71
7.70
7.26
4.05
4.03
4.02
4.00
3.98
3.97
3.94
3.71
3.69
3.67
1.78
1.76
1.75
1.73
1.70
1.69
1.68
1.67
1.64
1.62
1.61
1.57
1.55
1.54
1.51
1.49
1.47
1.45
1.43
1.41
1.39
Cl
3m
1.96
2.06
1.02
2.18
4.39
0.99
4.45
f1 (ppm)

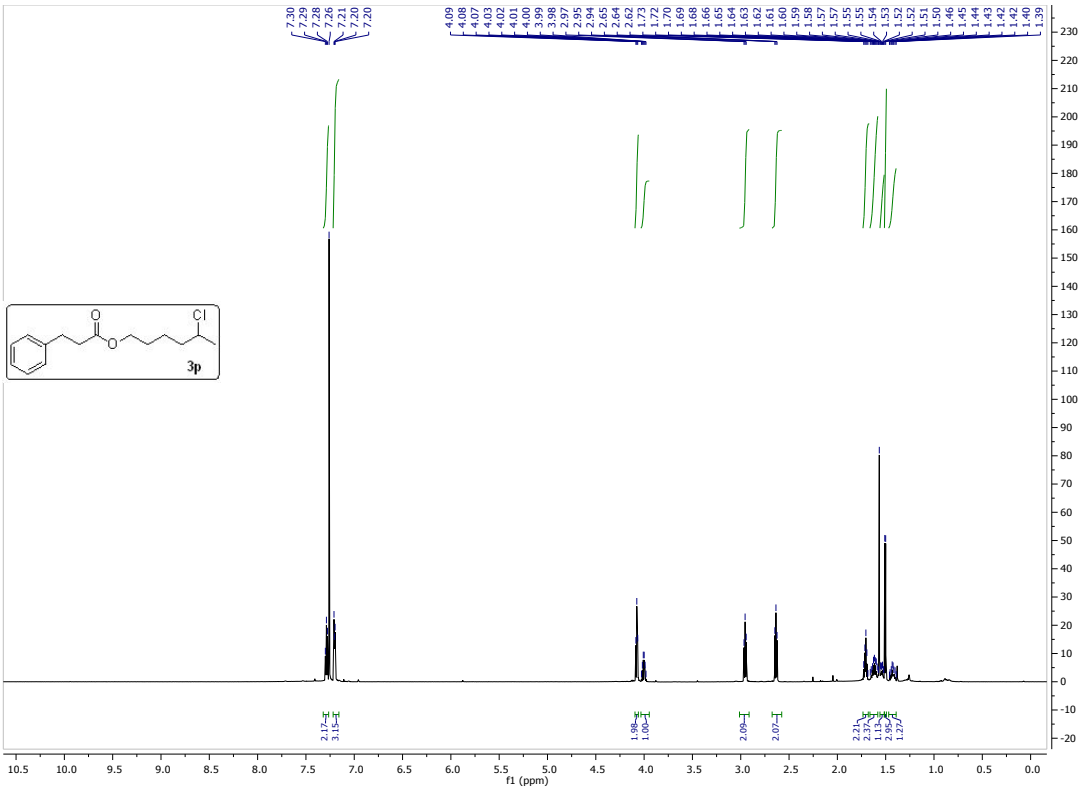

168.56
134.05
132.26
123.35
77.48
77.16
76.84
58.58
39.86
37.87
28.21
25.49
24.05
Cl
3m
f1 (ppm)

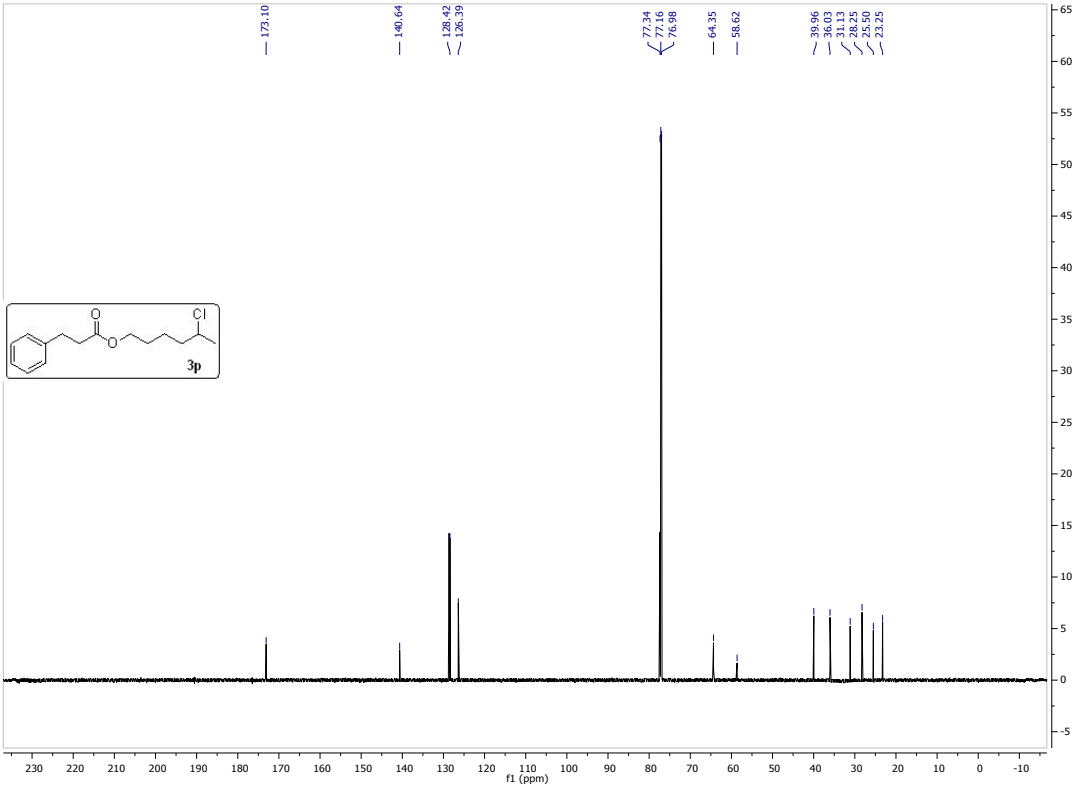

8.05
8.03
7.58
7.56
7.54
7.46
7.44
7.42
7.26
4.35
4.34
4.32
4.09
4.08
4.06
4.04
4.03
4.01
1.85
1.83
1.82
1.80
1.78
1.77
1.75
1.73
1.71
1.70
1.67
1.65
1.63
1.61
1.59
1.58
1.55
1.53
1.52
1.82
1.00
1.92
2.14
0.95
6.39
3.11
f1 (ppm)
3n

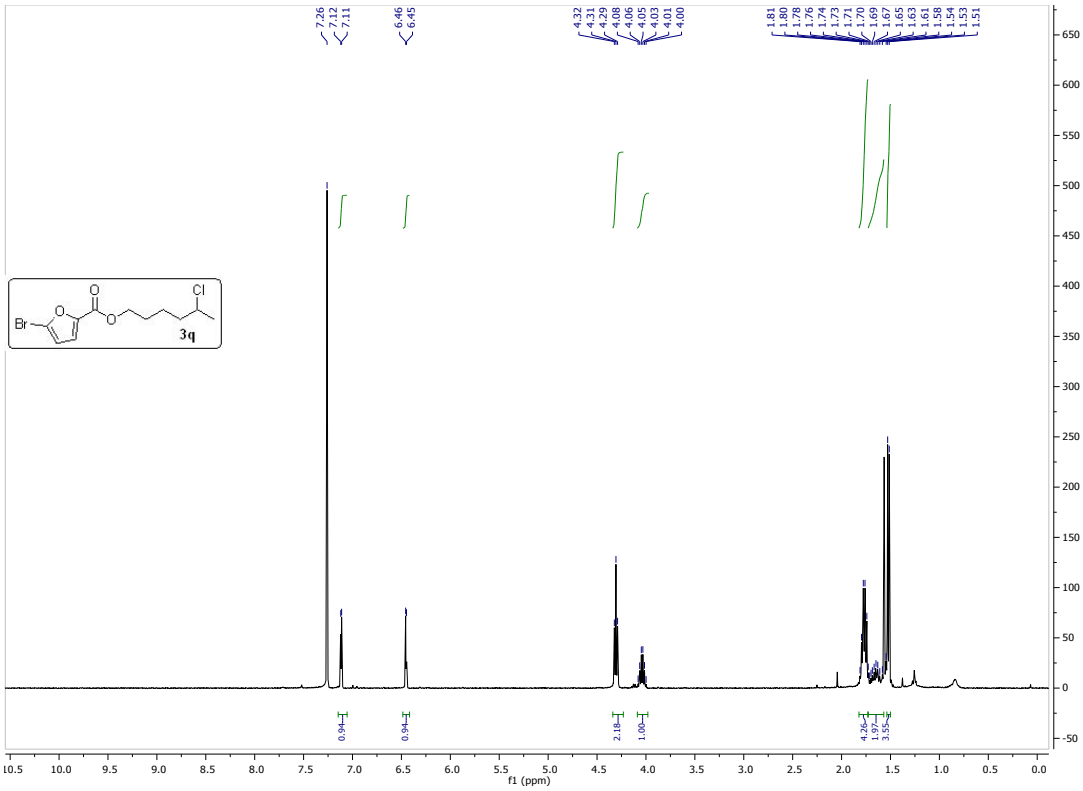

166.77
133.02
130.57
129.70
128.50
77.48
77.16
76.84
64.85
58.59
40.04
28.42
25.51
23.41
f1 (ppm)
3n

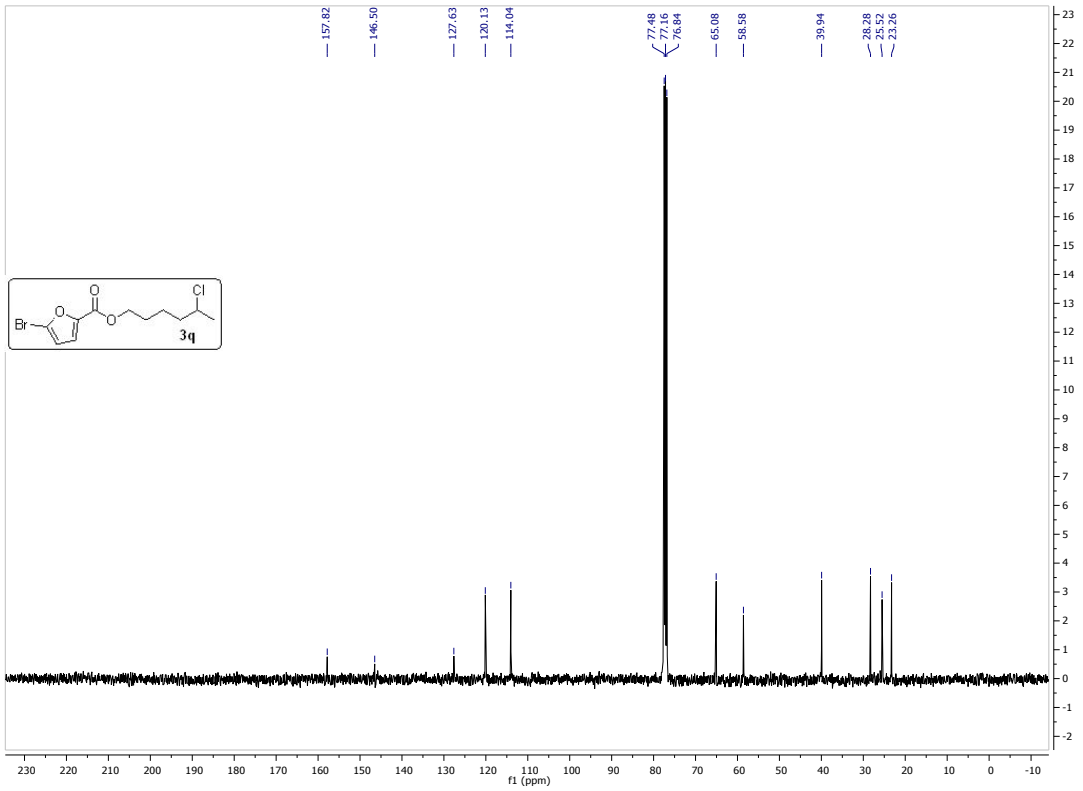

3o
f1 (ppm)

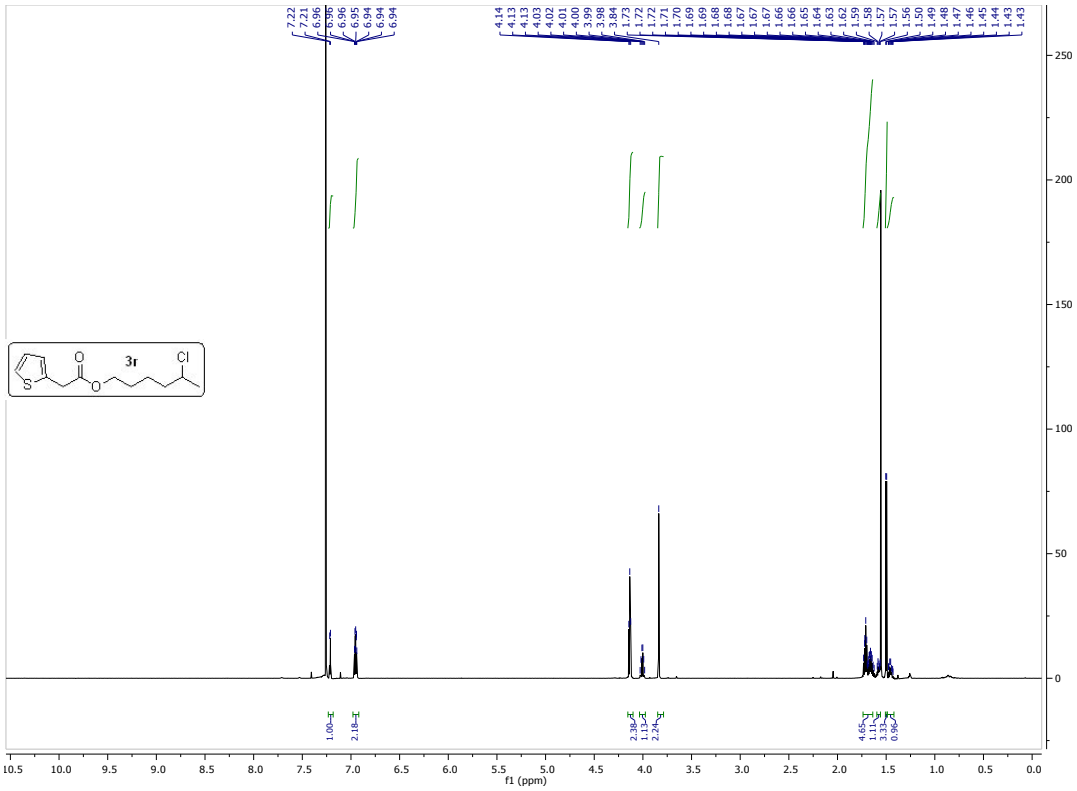

3o
background noise while using
700 NMR: also appeared in
other C spectrums
f1 (ppm)

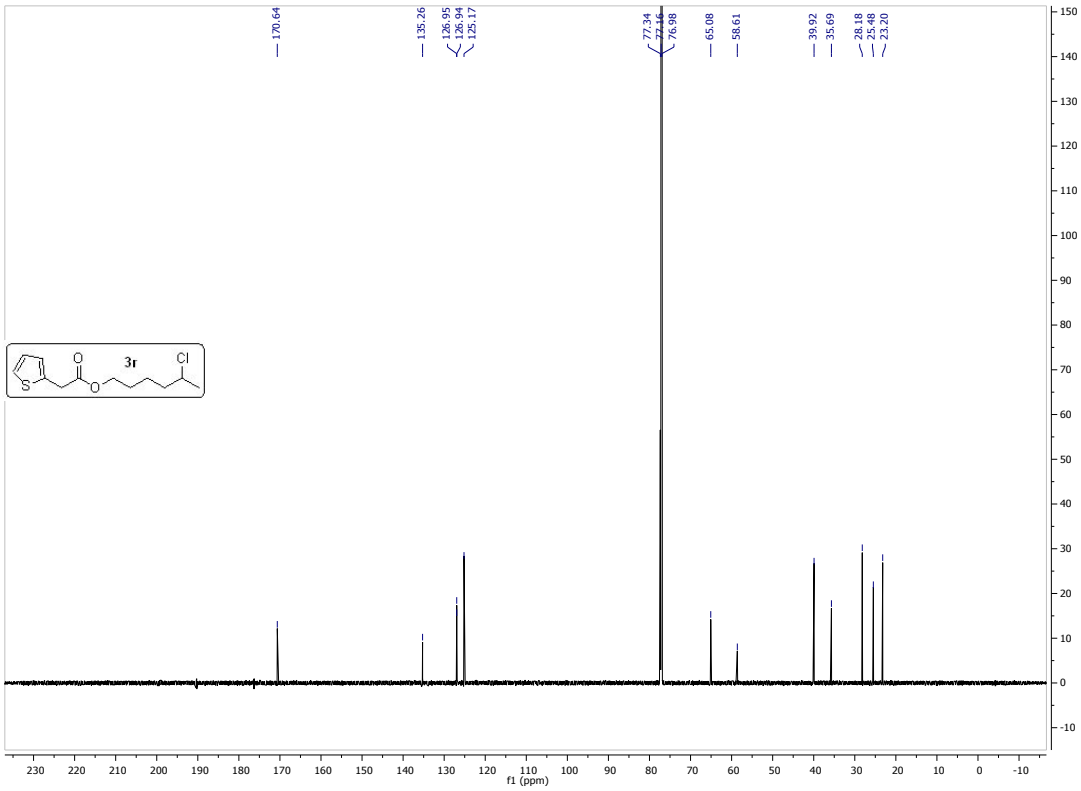

3p
f1 (ppm)

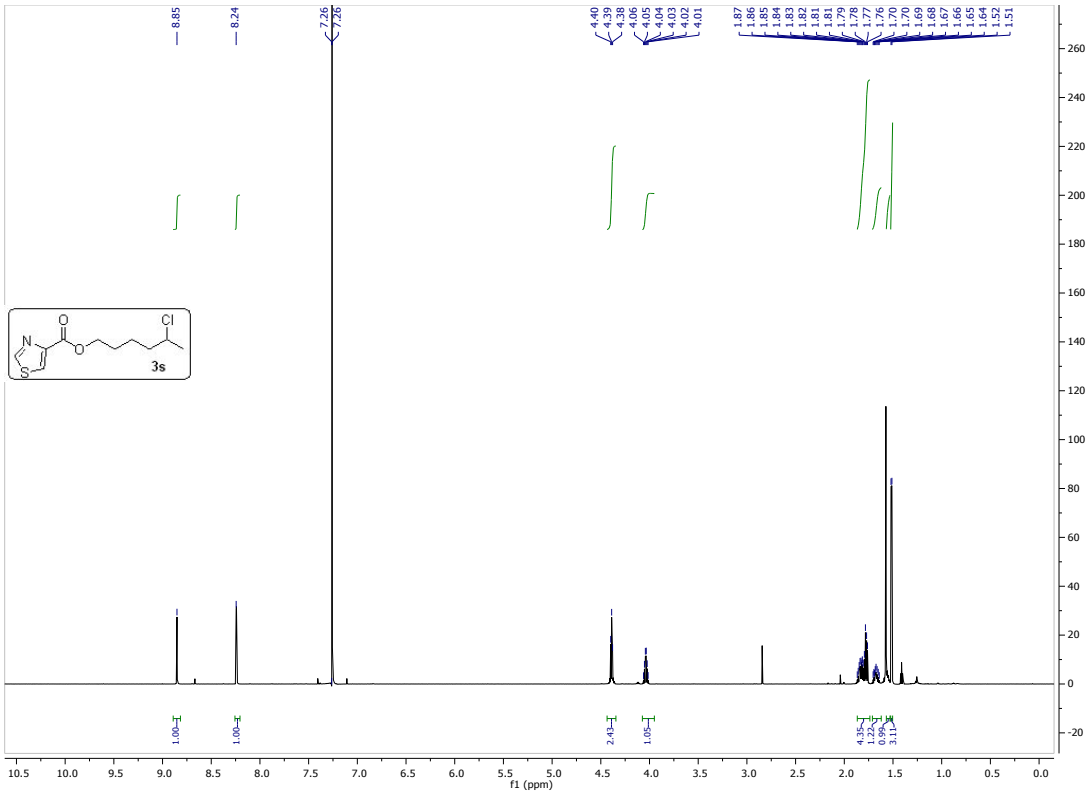

3p
f1 (ppm)

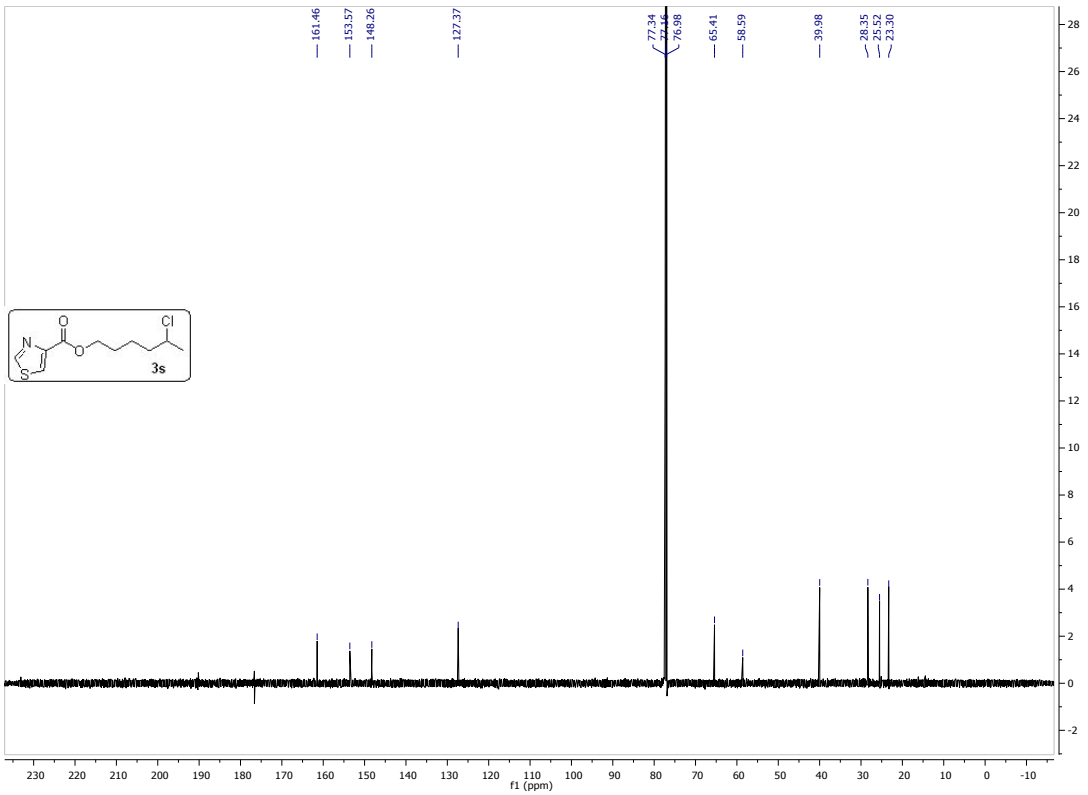

7.26
7.12
7.11
6.46
6.45
4.32
4.31
4.29
4.08
4.06
4.05
4.03
4.01
4.00
1.81
1.80
1.78
1.76
1.74
1.73
1.71
1.70
1.69
1.67
1.65
1.63
1.61
1.58
1.54
1.53
1.51
0.94
0.94
2.18
1.00
4.26
1.97
3.55
f1 (ppm)
Br
Cl
3q

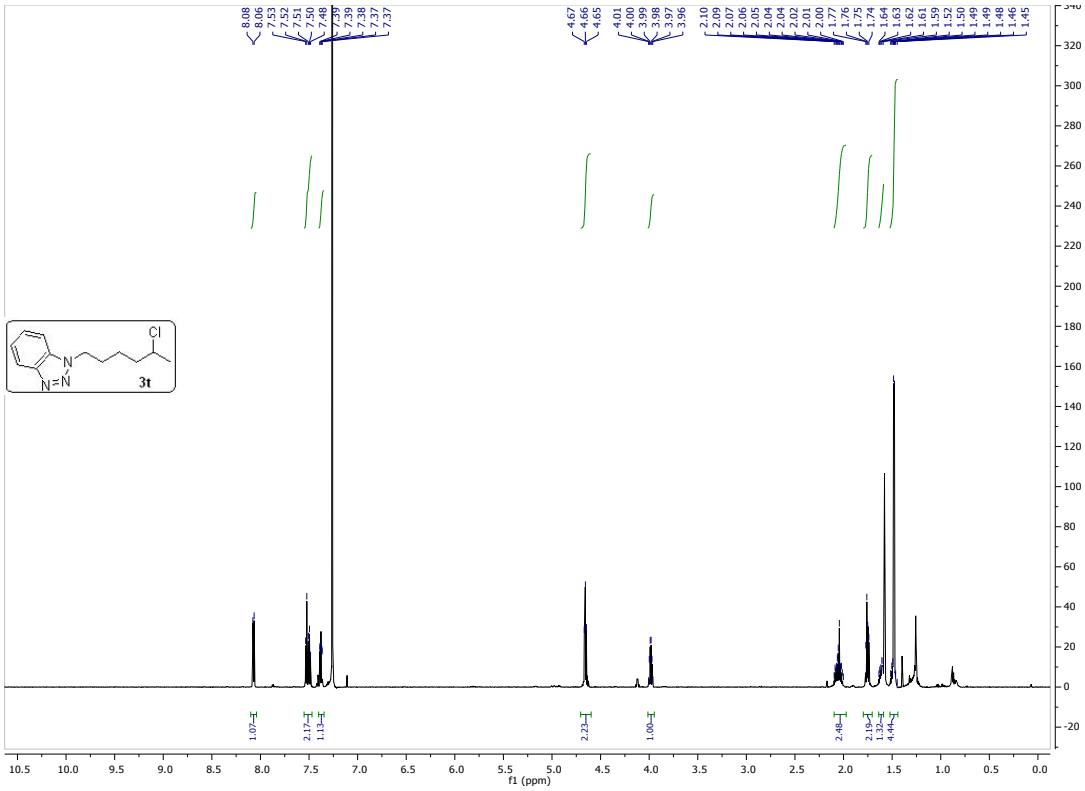

157.82
146.50
127.63
120.13
114.04
77.48
77.16
76.84
65.08
58.58
39.94
28.28
25.52
23.26
f1 (ppm)
Br
Cl
3q

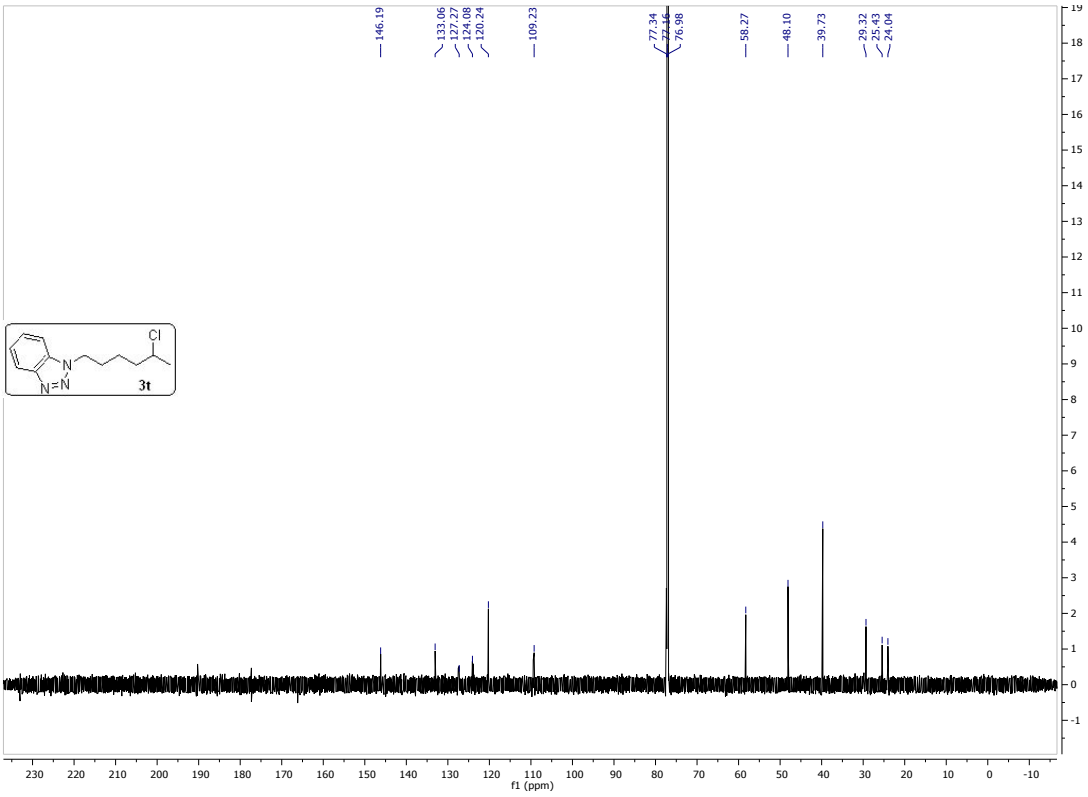

3r
Cl
f1 (ppm)


3r
Cl
f1 (ppm)

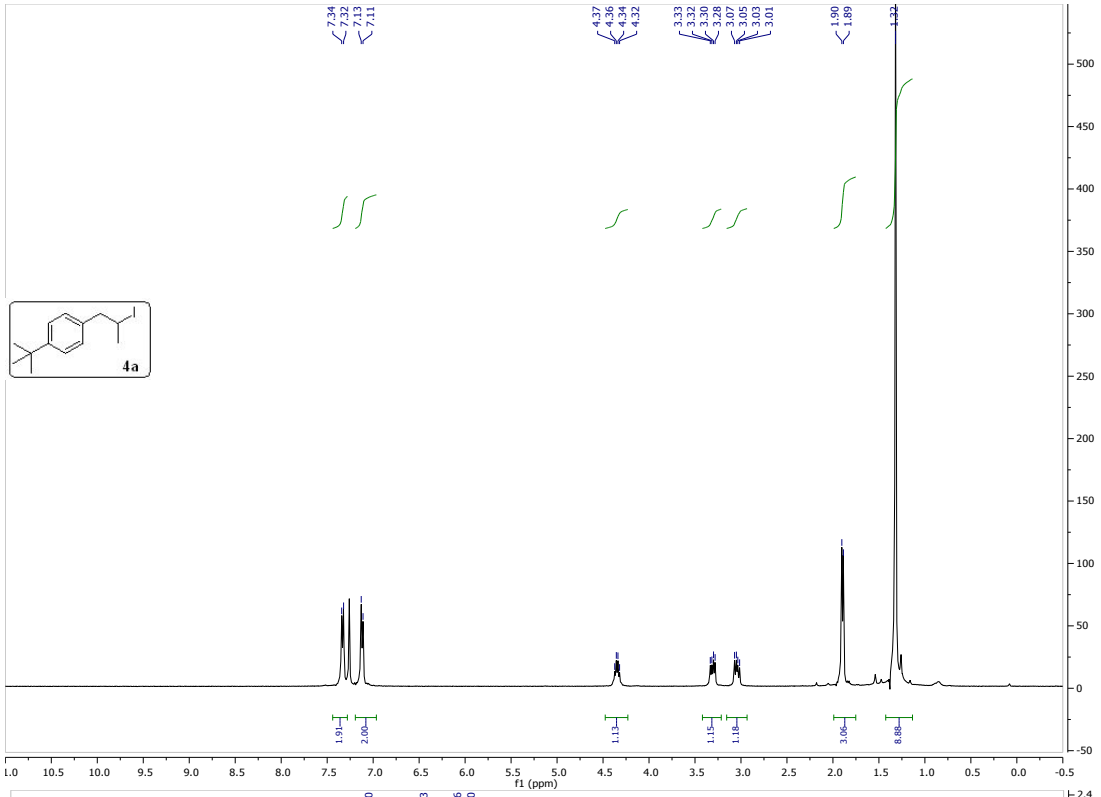

8.85
8.24
7.26
4.40
4.39
4.38
4.06
4.05
4.04
4.03
4.02
4.01
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.52
1.51
3s
1.00
1.00
2.43
1.05
4.35
1.72
0.99
3.11
f1 (ppm)

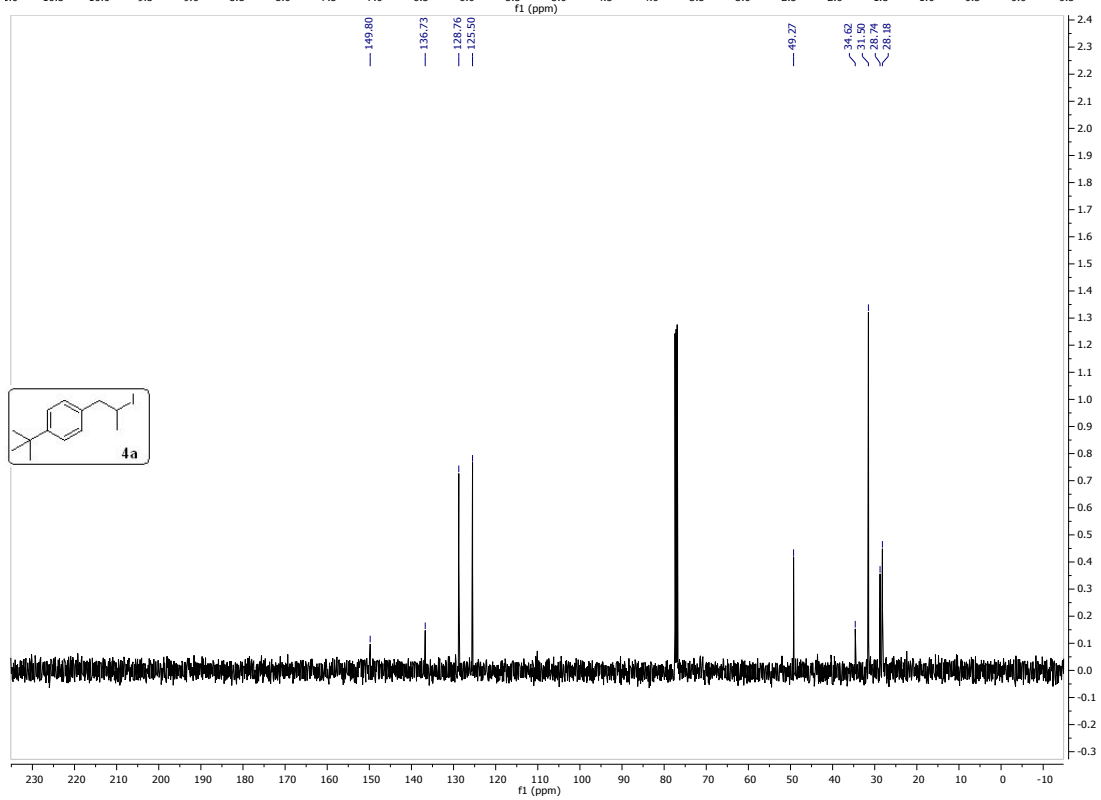

161.46
153.57
148.26
127.37
77.34
77.16
76.98
65.41
58.59
39.98
28.35
25.52
23.30
3s
f1 (ppm)

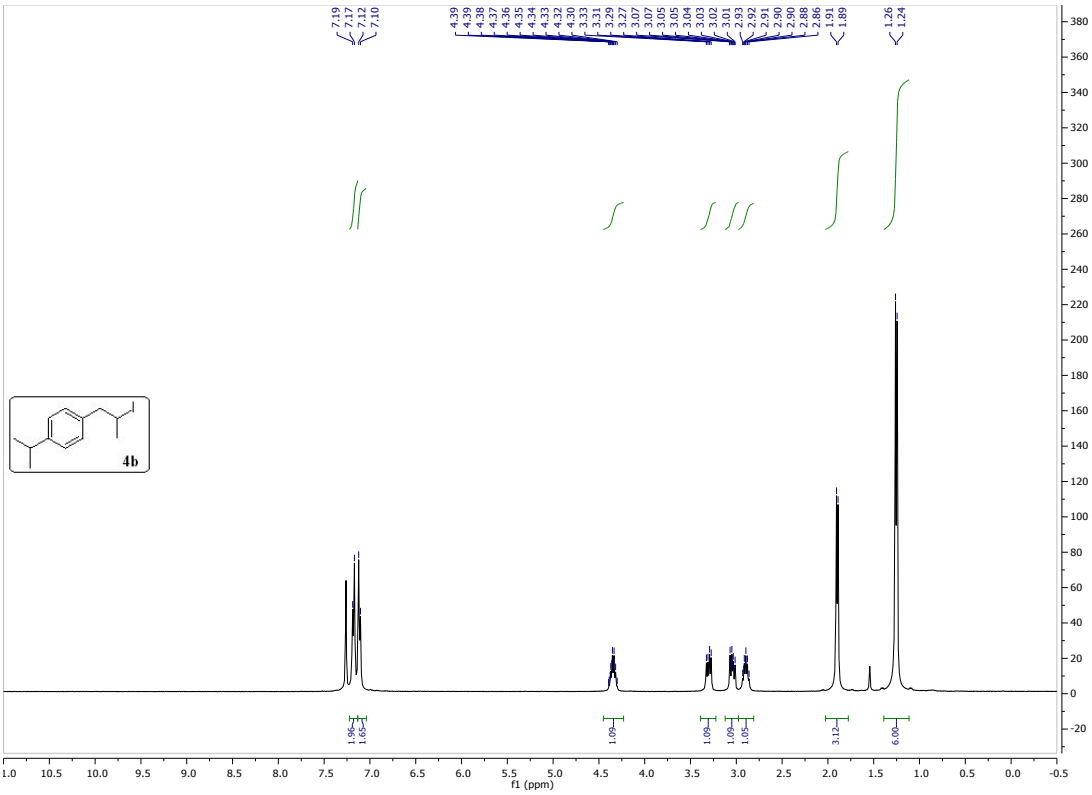

8.08
8.06
7.53
7.52
7.51
7.50
7.48
7.39
7.38
7.37
7.37
4.67
4.66
4.65
4.01
4.00
3.99
3.98
3.97
3.96
2.10
2.09
2.07
2.06
2.05
2.04
2.04
2.02
2.01
2.00
1.77
1.76
1.75
1.74
1.64
1.63
1.62
1.61
1.59
1.52
1.50
1.49
1.49
1.48
1.46
1.45
Cl
N
N=N
3t
1.07
2.17
1.13
2.23
1.00
2.48
2.19
1.32
4.44
f1 (ppm)

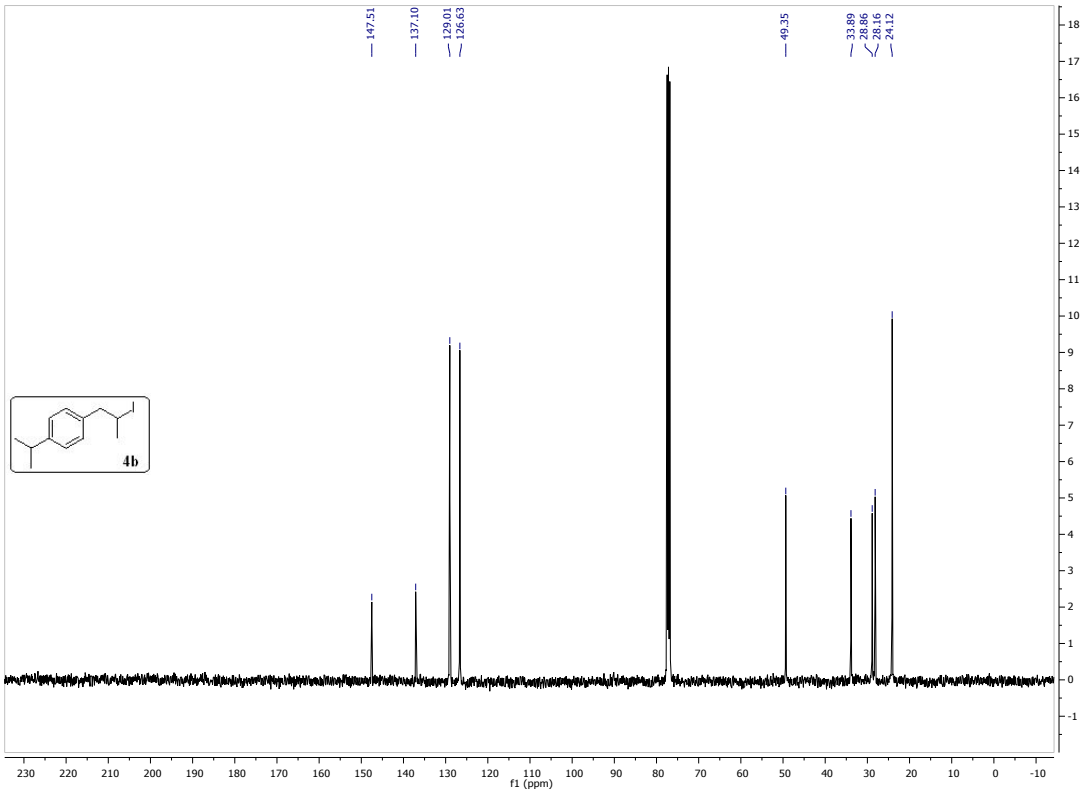

146.19
133.06
127.27
124.08
120.24
109.23
77.34
77.16
76.98
58.27
48.10
39.73
29.32
25.43
24.04
Cl
N
N=N
3t
f1 (ppm)

4.4 NMR spectral data for iodide products 4






7.19
7.17
7.12
7.10
4.39
4.39
4.38
4.37
4.36
4.35
4.34
4.33
4.32
4.30
3.33
3.31
3.29
3.27
3.07
3.07
3.05
3.05
3.04
3.03
3.02
3.01
2.93
2.92
2.91
2.90
2.90
2.88
2.86
1.91
1.89
1.26
1.24
4b
1.96
1.65
1.09
1.09
1.09
1.05
3.12
6.00
f1 (ppm)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137.10
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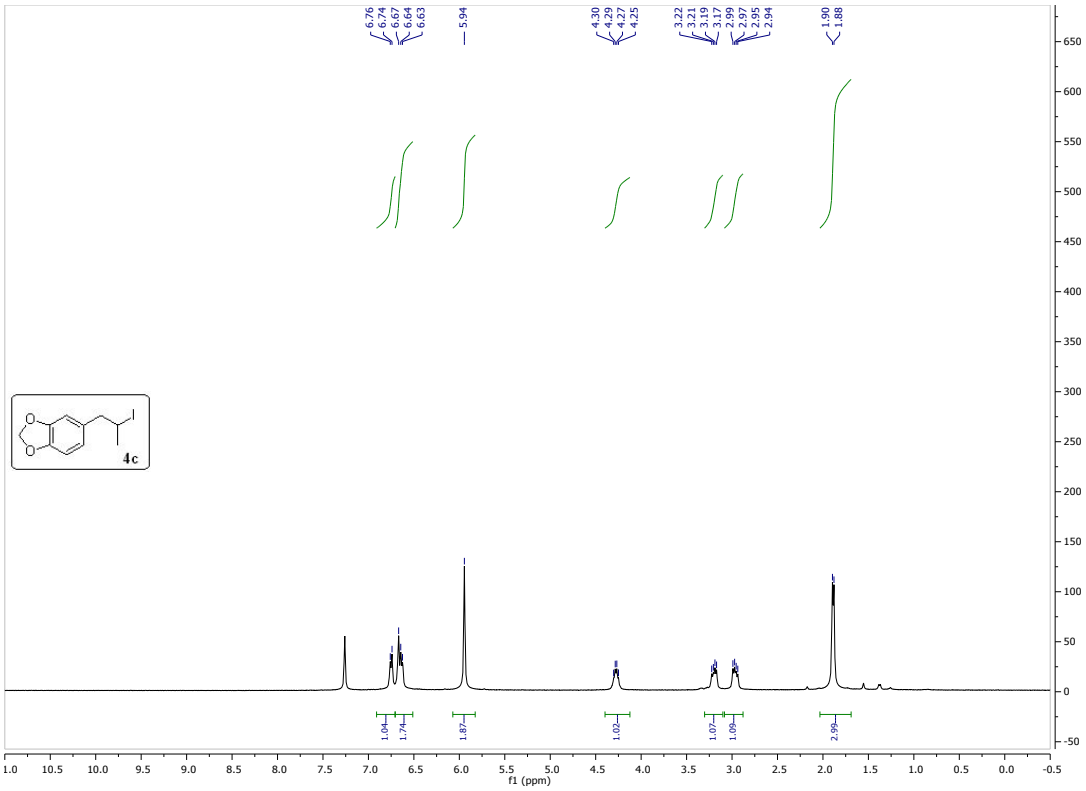
126.63
49.35
33.89
28.86
28.16
24.12
4b
f1 (ppm)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6.67
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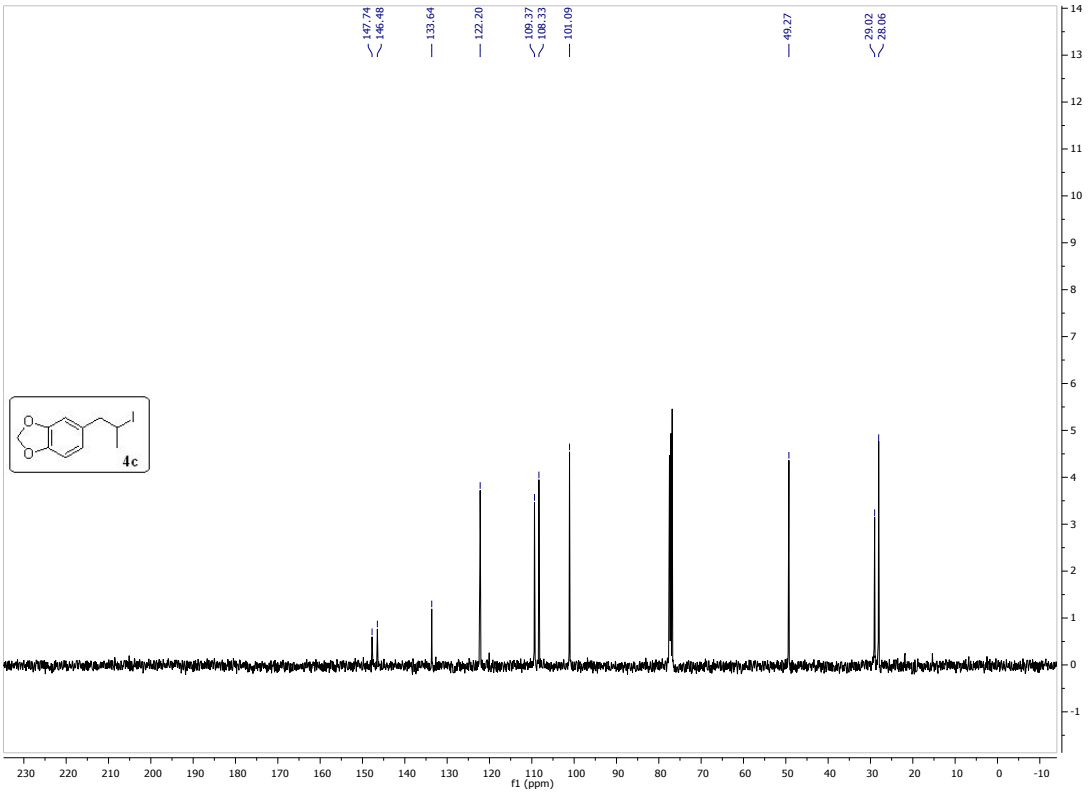
6.63
5.94
4.30
4.29
4.27
4.25
3.22
3.21
3.19
3.17
2.99
2.97
2.95
2.94
1.90
1.88
4c
1.04
1.74
1.87
1.02
1.07
1.09
2.99
f1 (ppm)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101.09
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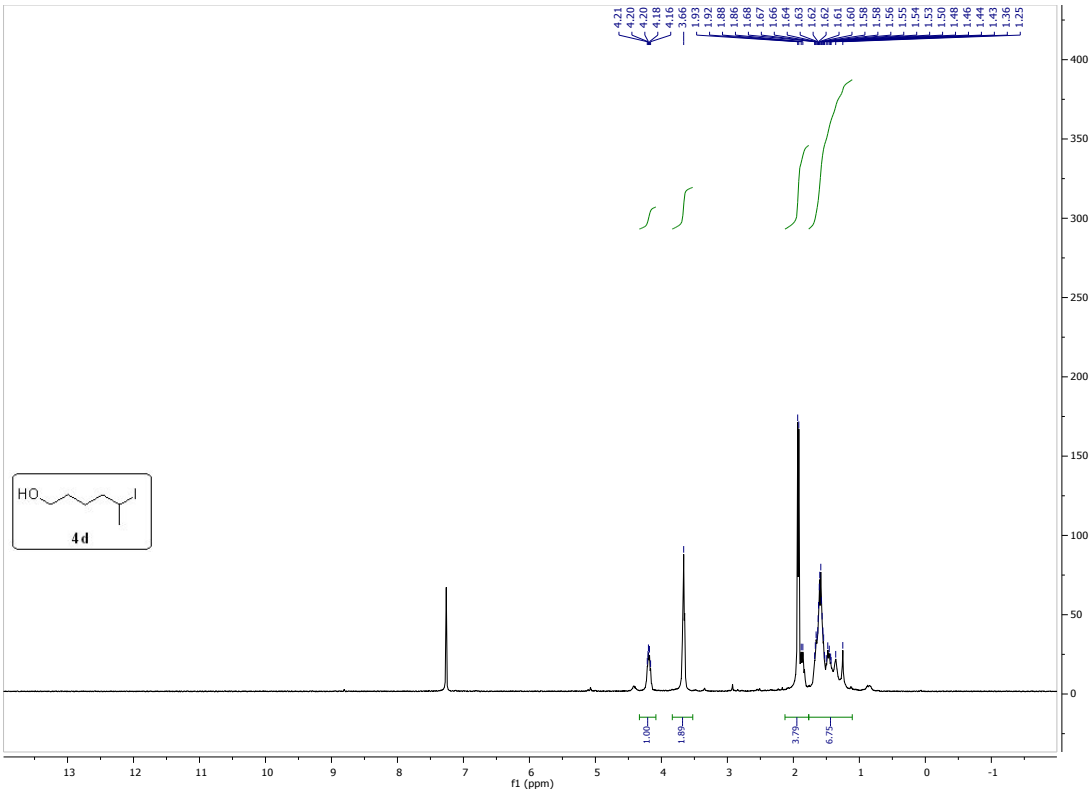
4c
f1 (ppm)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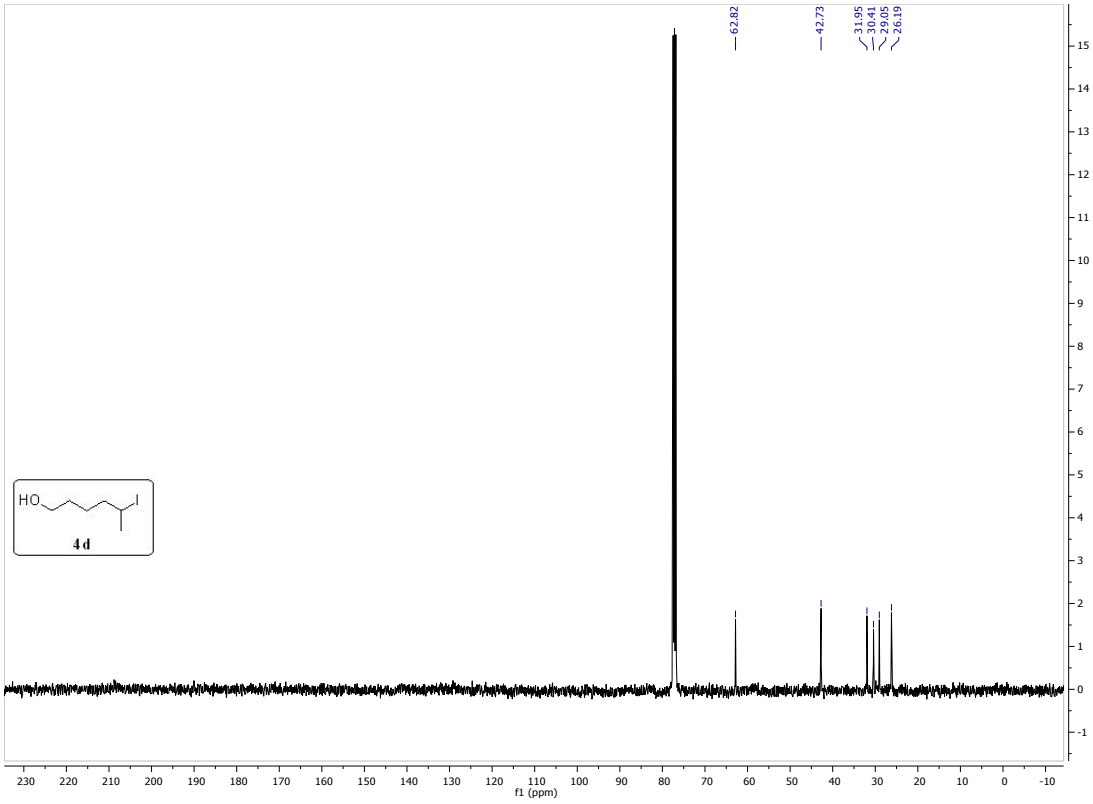
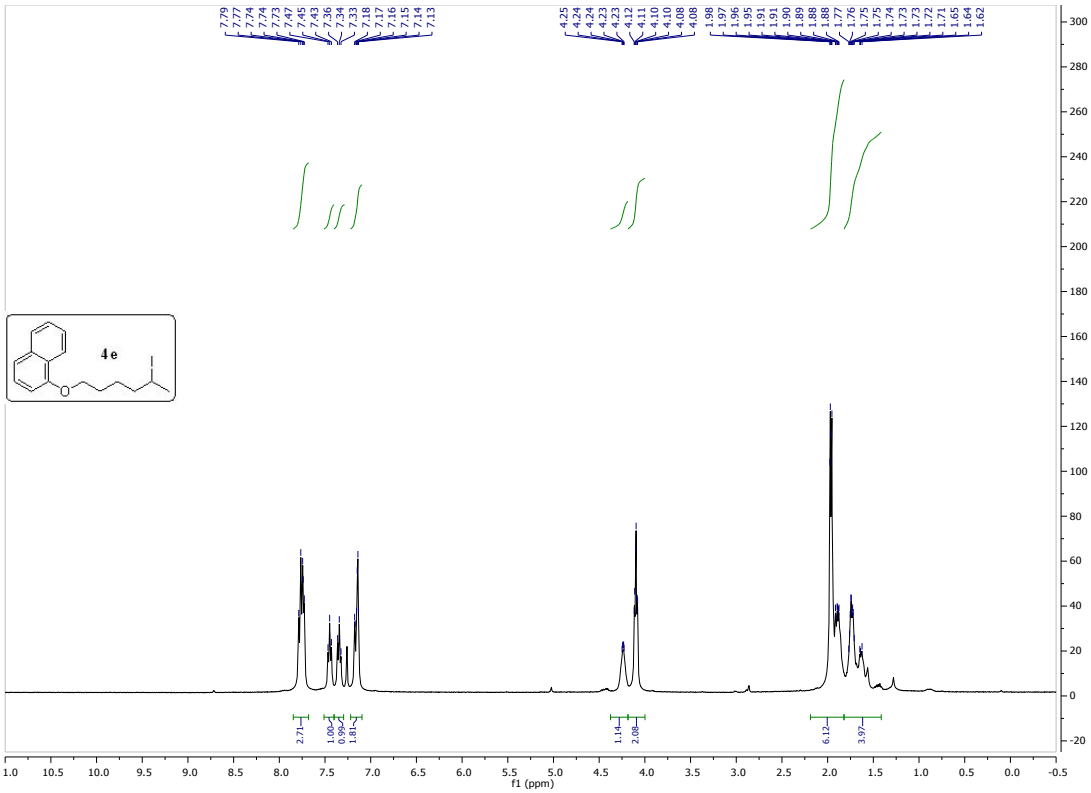
4.20
4.20
4.18
4.16
3.66
1.93
1.92
1.88
1.86
1.68
1.67
1.66
1.64
1.63
1.62
1.62
1.61
1.60
1.58
1.58
1.56
1.55
1.54
1.53
1.50
1.48
1.46
1.44
1.43
1.36
1.25
HO
I
4 d
1.00
1.89
3.79
6.75
f1 (ppm)


62.82
42.73
31.95
30.41
29.05
26.19
HO
I
4 d
f1 (ppm)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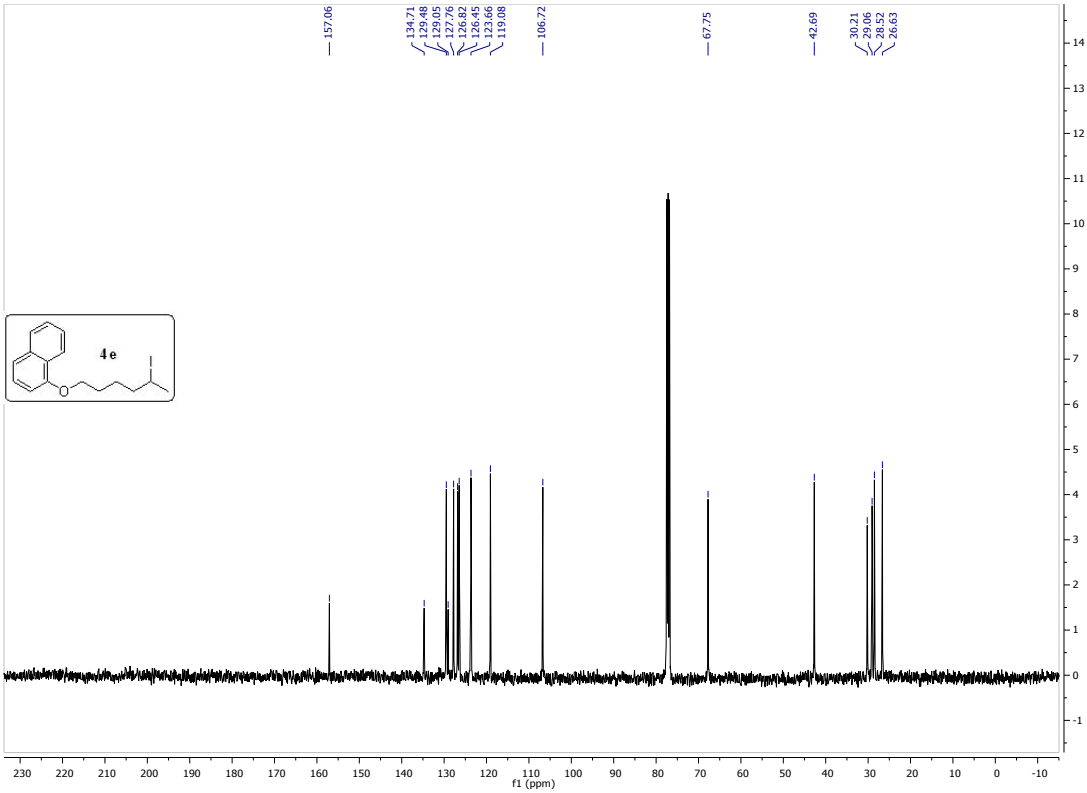
f1 (ppm)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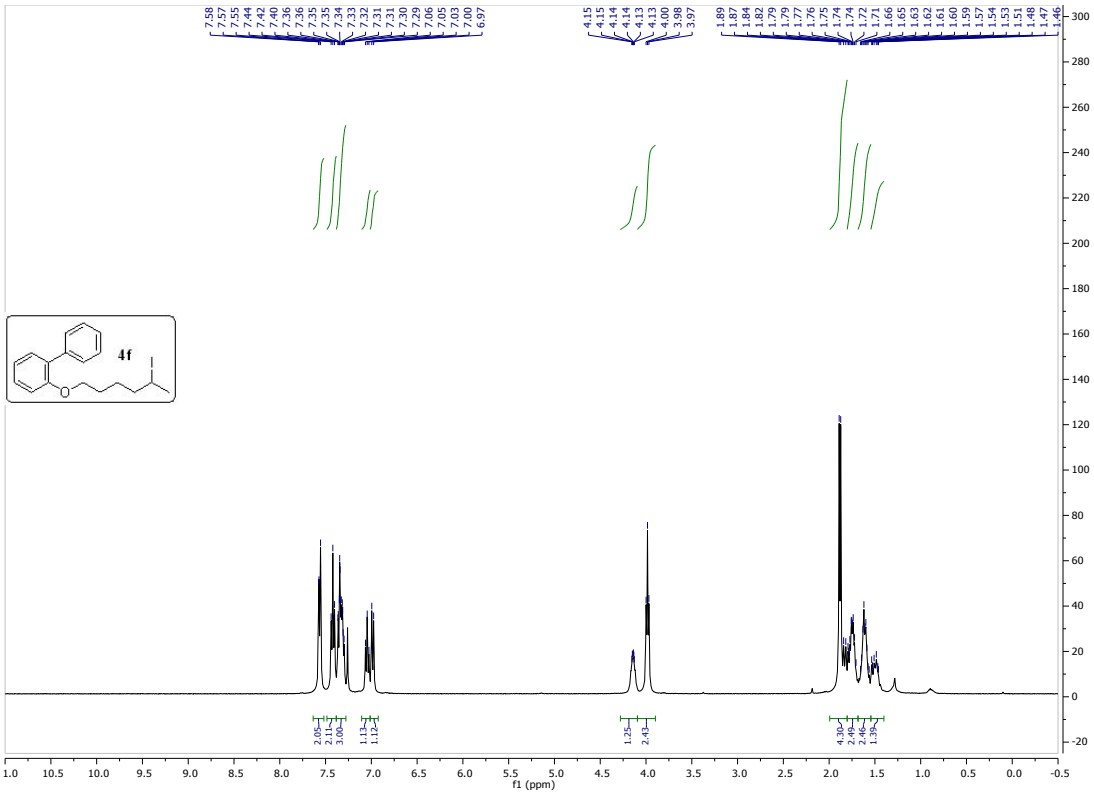
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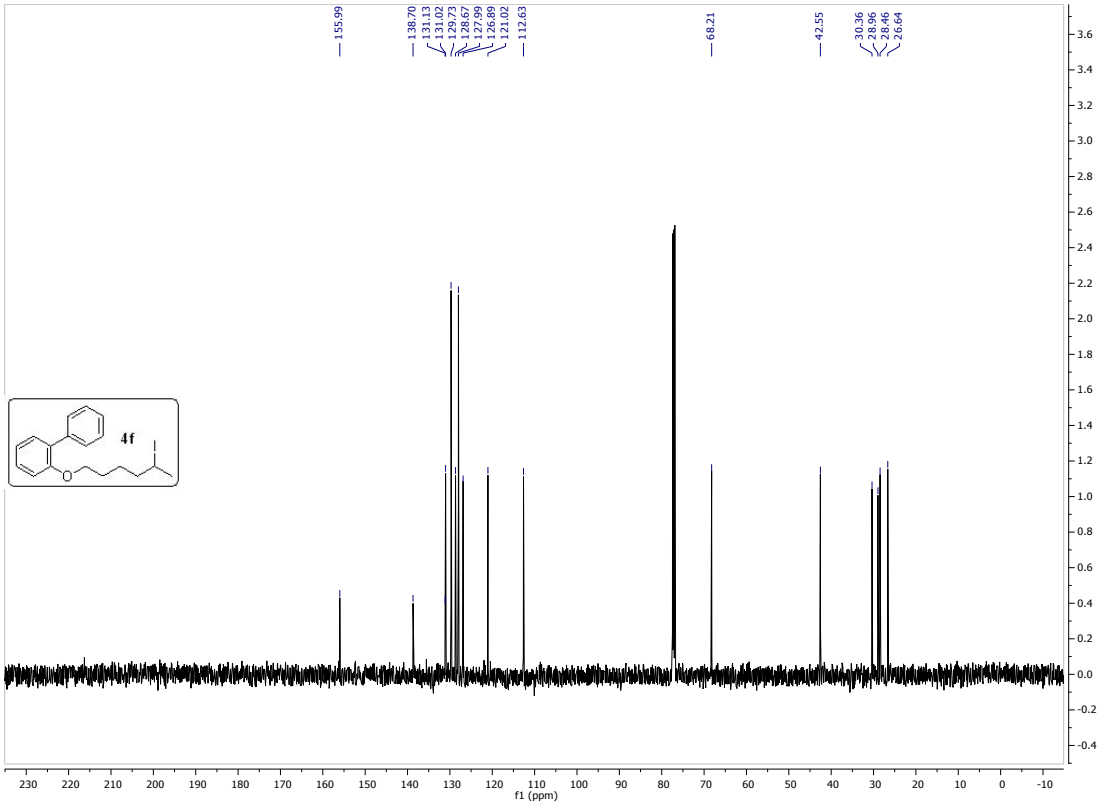
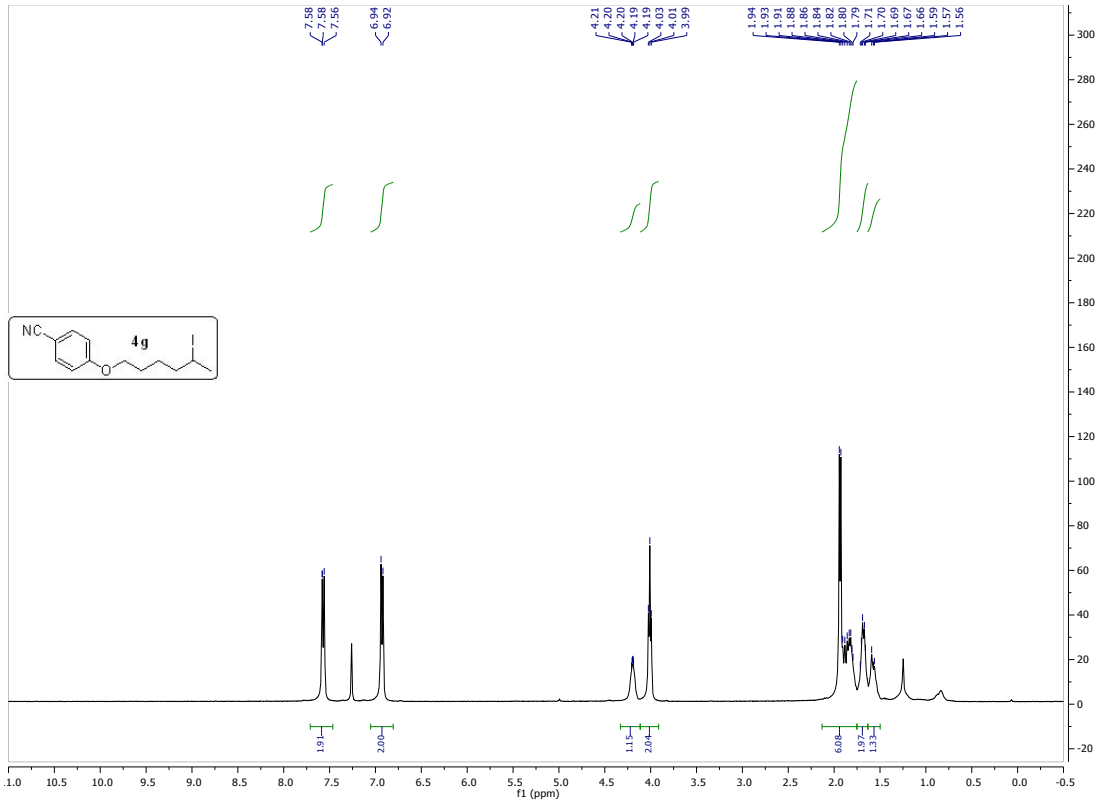
f1 (ppm)


4f
f1 (ppm)


7.58
7.58
7.56
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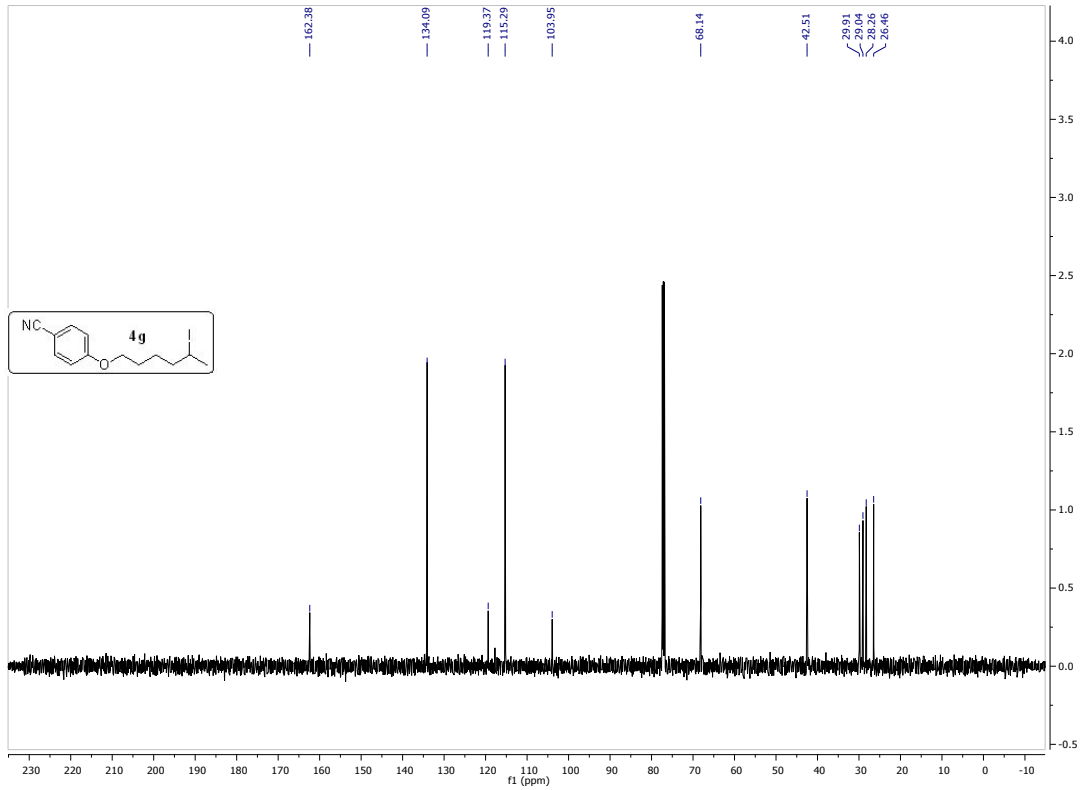
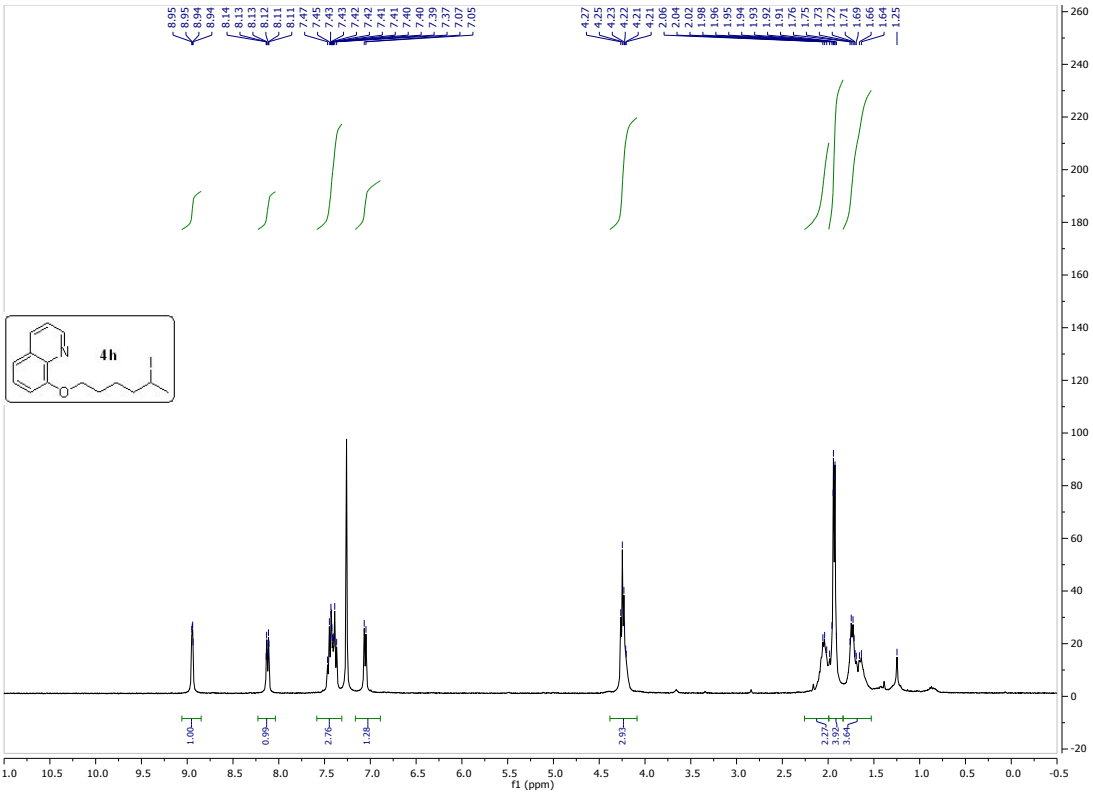
6.92
4.21
4.20
4.20
4.19
4.19
4.03
4.01
3.99
1.94
1.93
1.91
1.88
1.86
1.84
1.82
1.80
1.79
1.71
1.70
1.69
1.67
1.66
1.59
1.57
1.56
NC
4g
1.91
2.00
1.15
2.04
6.08
1.97
1.33
f1 (ppm)


162.38
134.09
119.37
115.29
103.95
68.14
42.51
29.91
29.04
28.26
26.46
NC
4g
f1 (ppm)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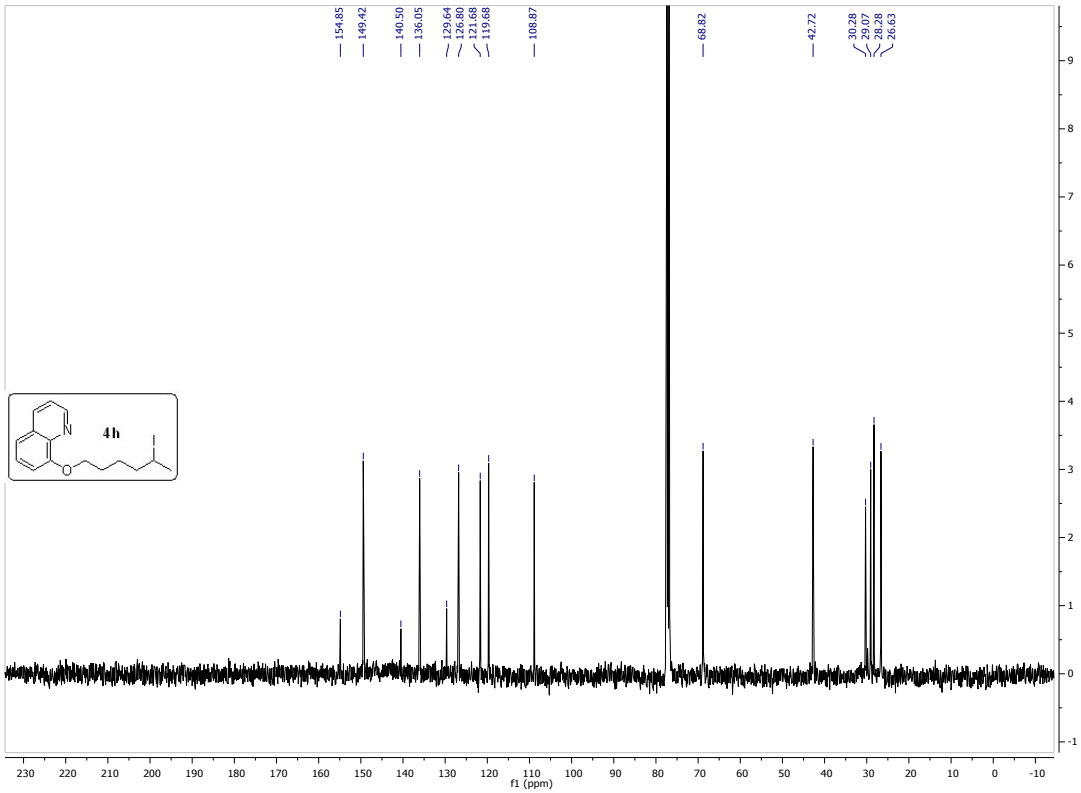
8.95
8.94
8.94
8.14
8.13
8.13
8.12
8.11
8.11
7.47
7.45
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.07
7.05
4.27
4.25
4.23
4.22
4.21
4.21
2.06
2.04
2.02
1.98
1.96
1.95
1.94
1.93
1.92
1.91
1.76
1.75
1.73
1.72
1.71
1.71
1.69
1.66
1.64
1.25
4h
1.00
0.99
2.76
1.28
2.93
2.27
3.92
3.64
f1 (ppm)


154.85
149.42
140.50
136.05
129.64
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119.68
108.87
68.82
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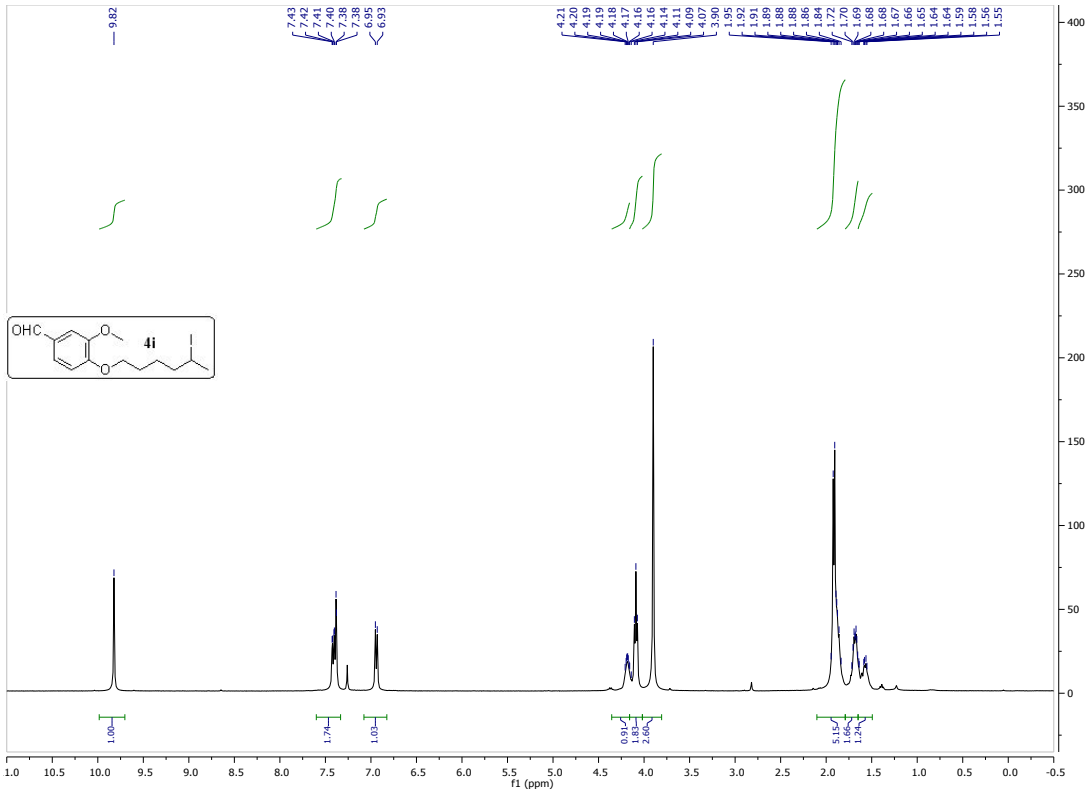
30.28
29.07
28.28
26.63
4h
f1 (ppm)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7.42
7.41
7.40
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7.38
6.95
6.93
4.21
4.20
4.19
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4.18
4.17
4.16
4.16
4.14
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1.86
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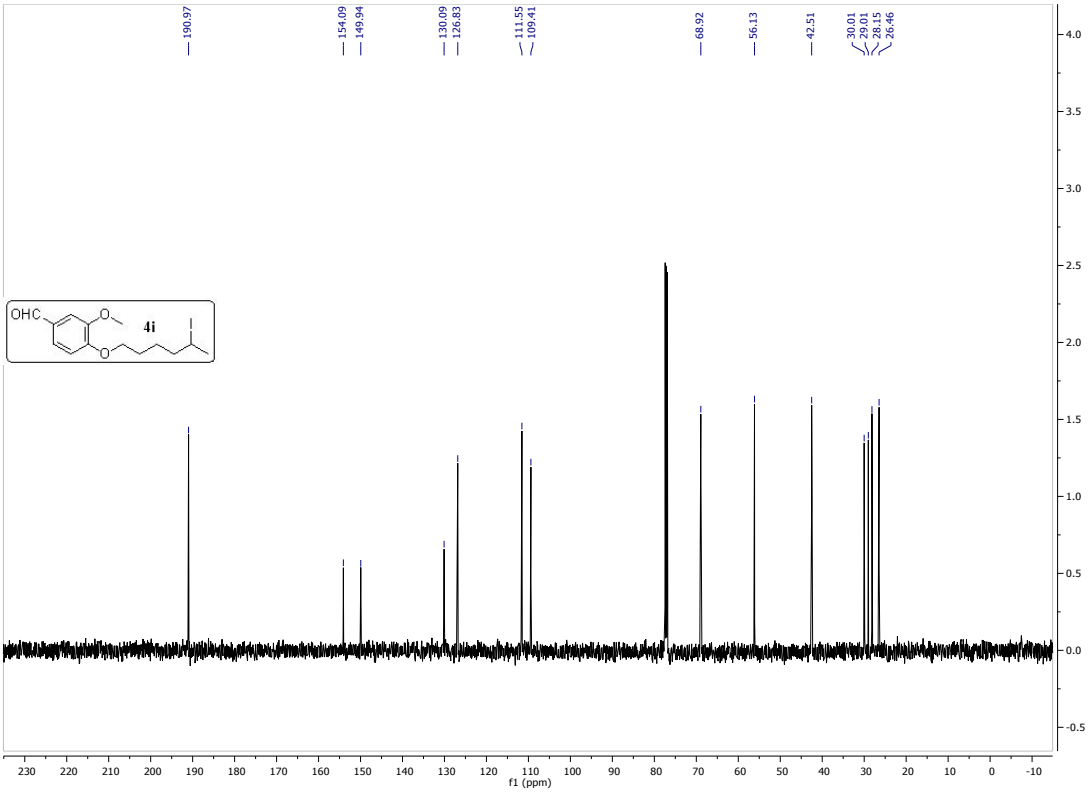
1.69
1.68
1.68
1.67
1.66
1.65
1.64
1.64
1.59
1.58
1.56
1.55
OHC
4i
1.00
1.74
1.03
0.91
1.83
2.86
5.15
1.66
1.24
f1 (ppm)


190.97
154.09
149.94
130.09
126.83
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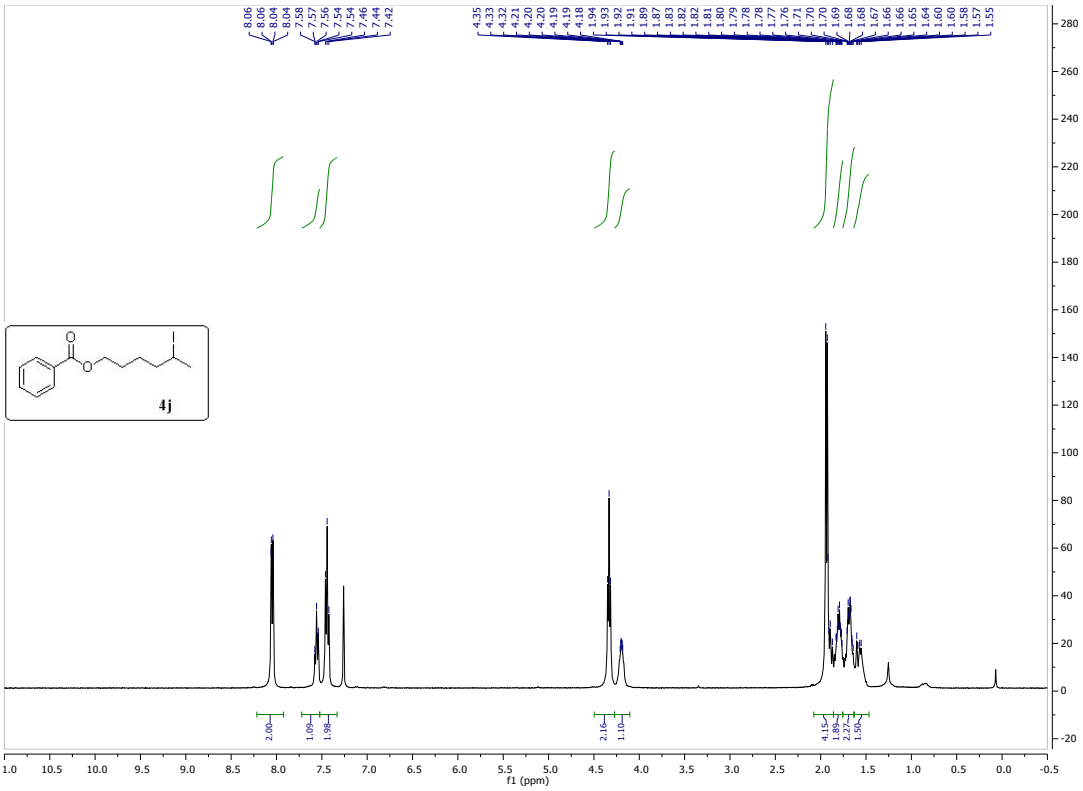
109.41
68.92
56.13
42.51
30.01
29.01
28.15
26.46
OHC
4i
f1 (ppm)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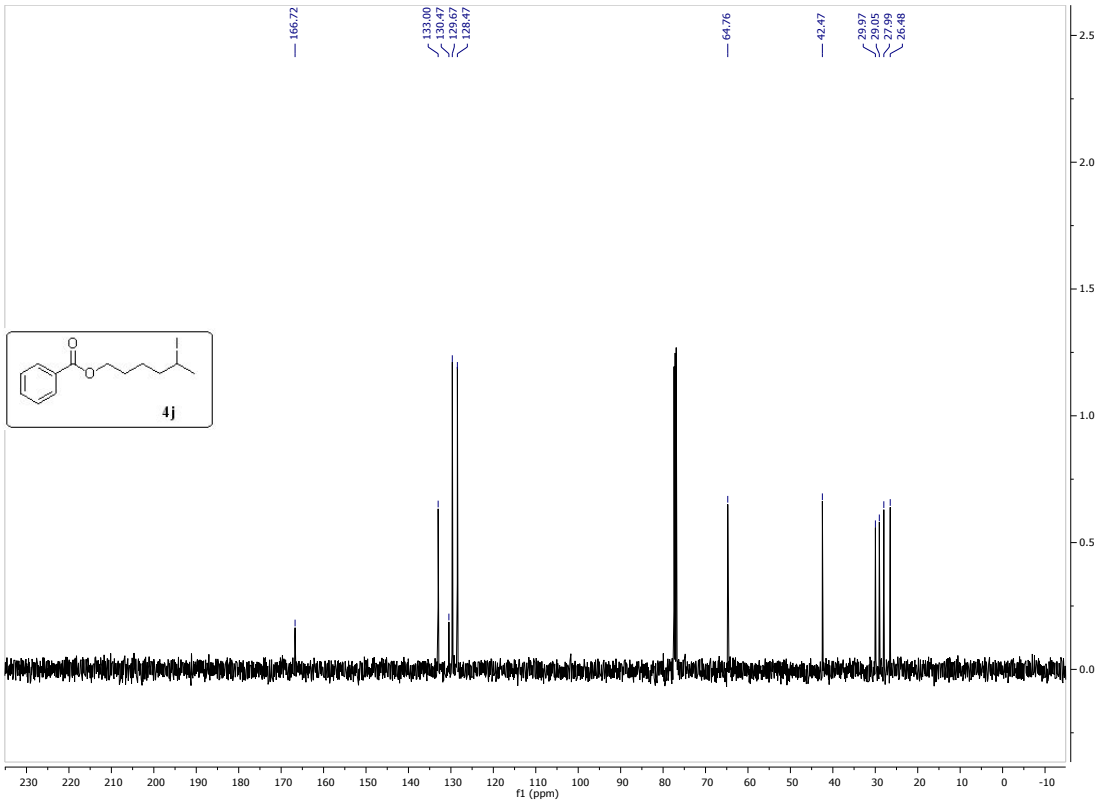
f1 (ppm)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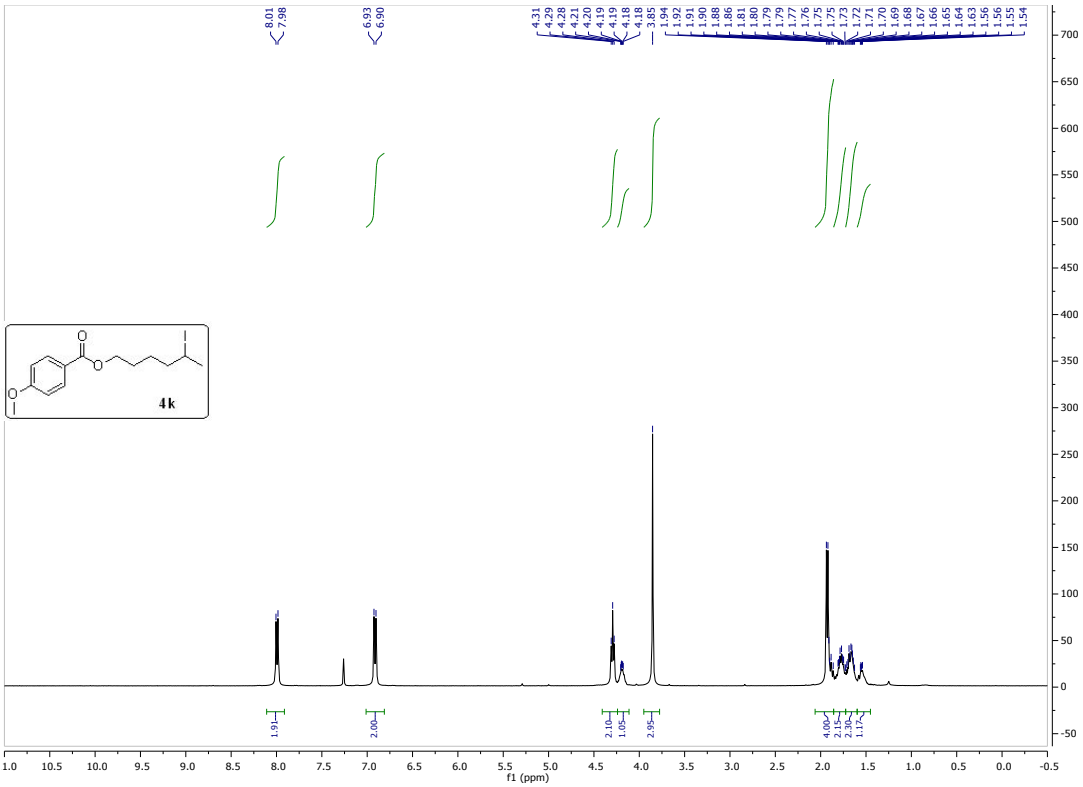
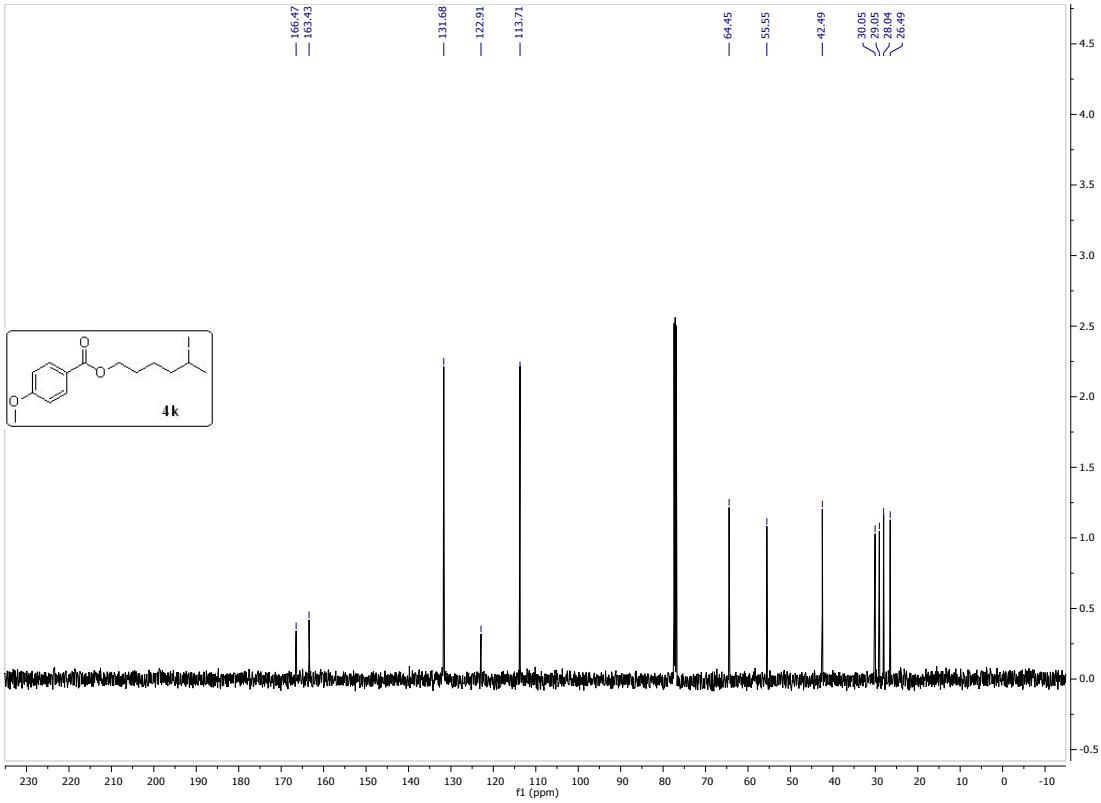
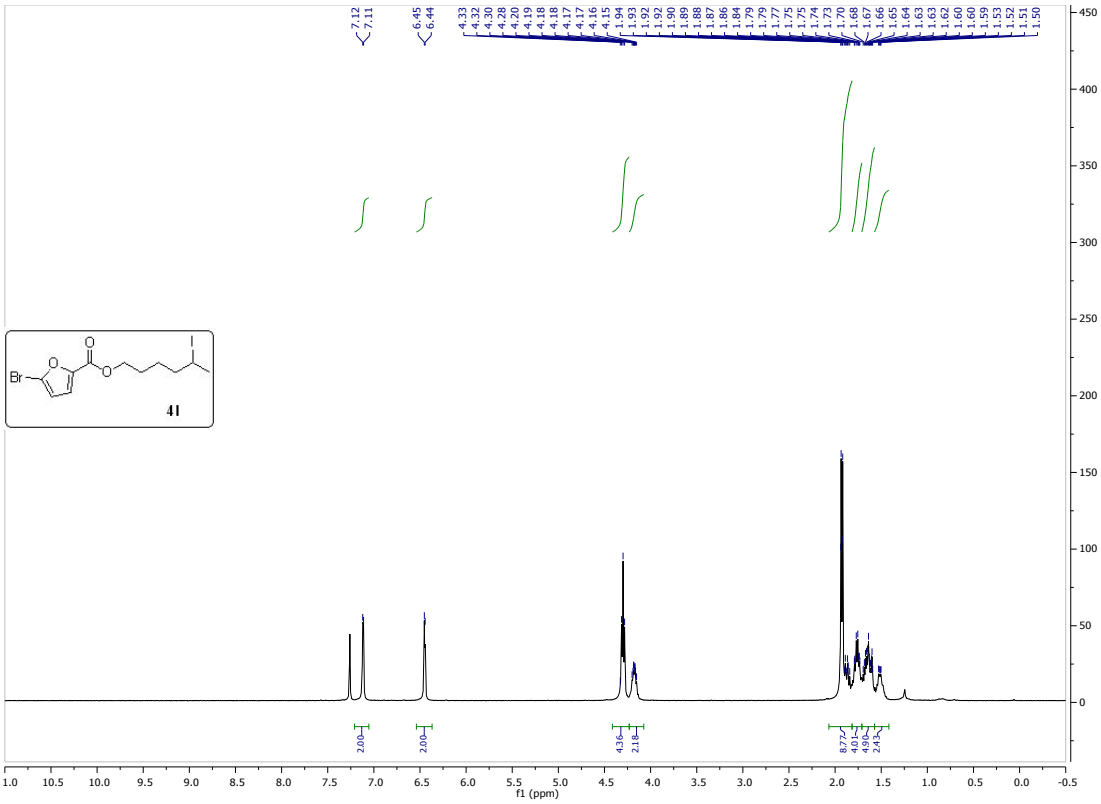
f1 (ppm)


4k
f1 (ppm)


4k
f1 (ppm)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6.45
6.44
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4.32
4.30
4.28
4.20
4.19
4.18
4.18
4.17
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4.16
4.15
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1.93
1.92
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1.88
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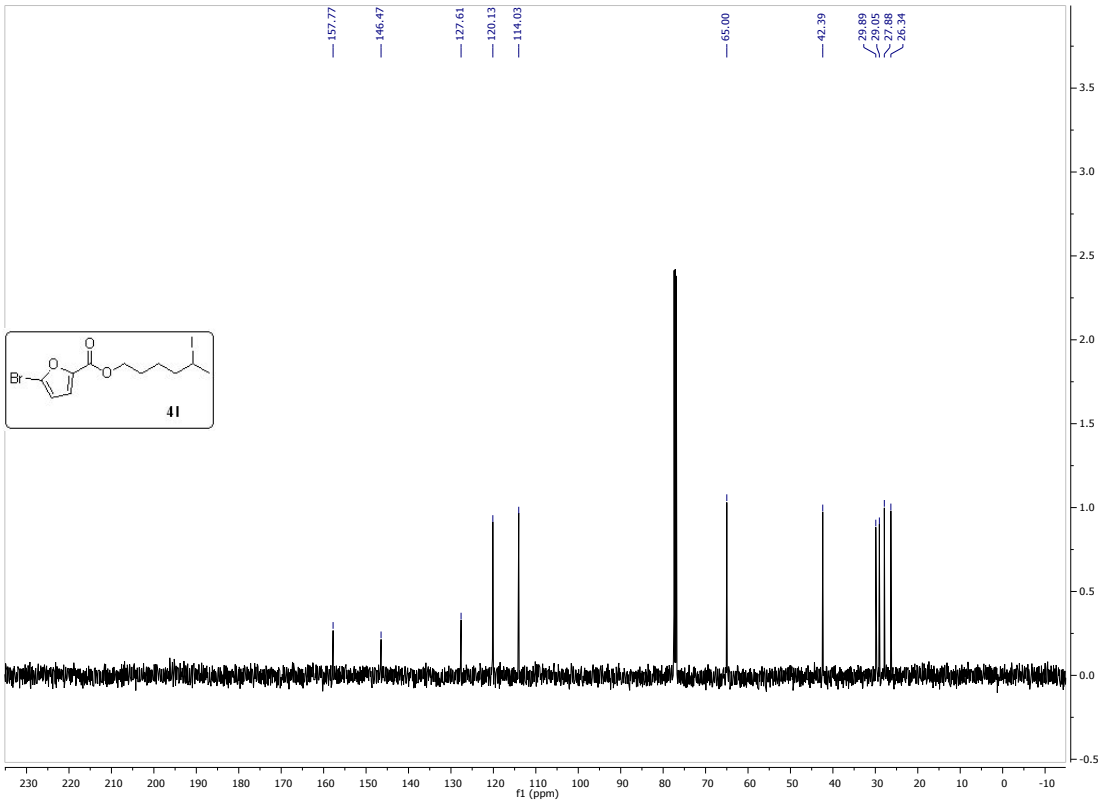
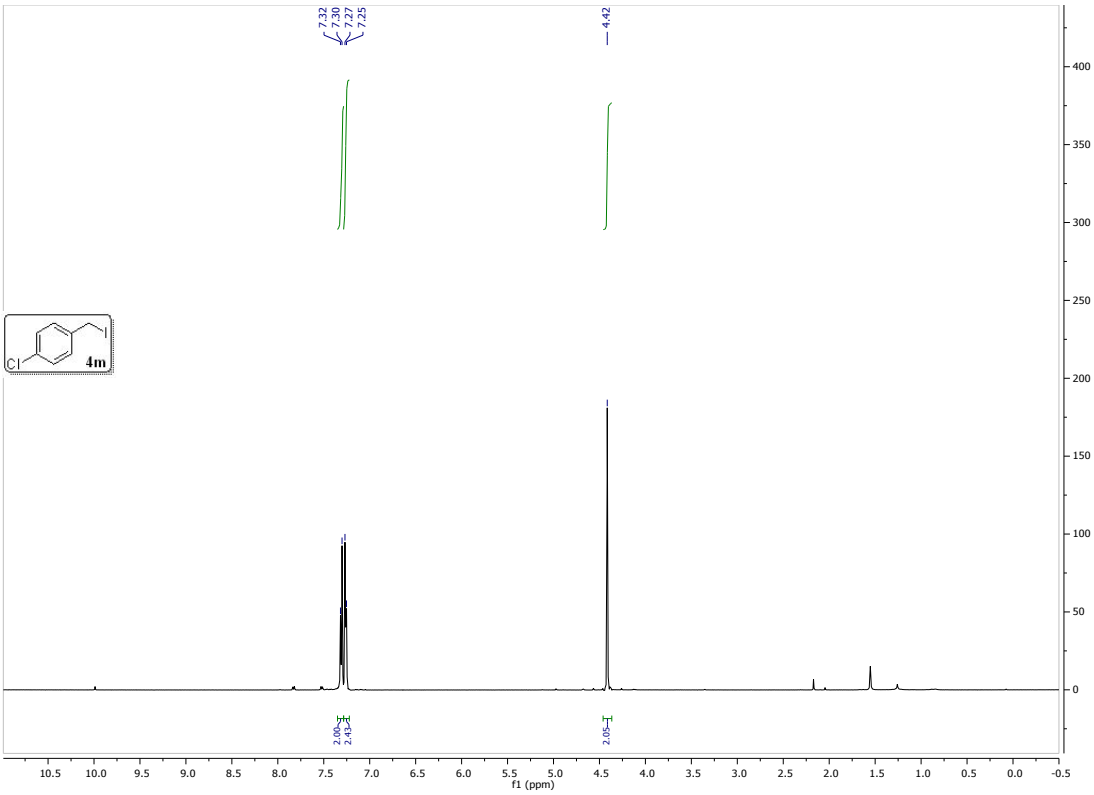
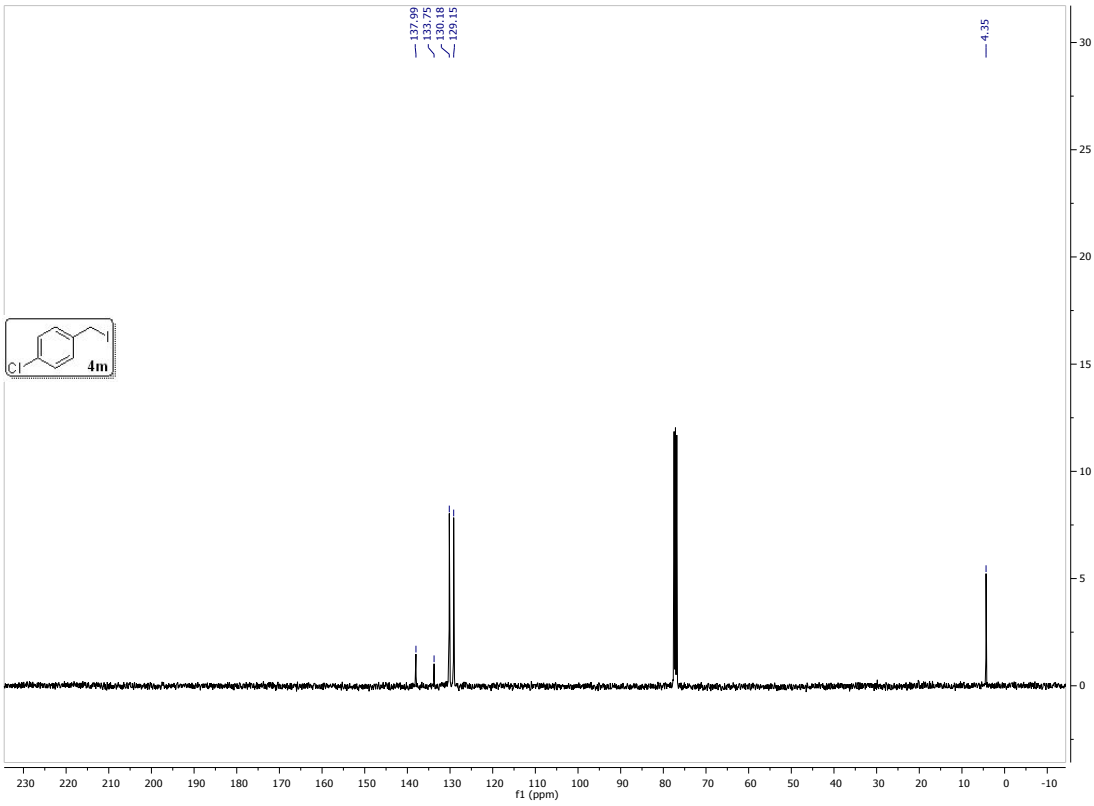
1.79
1.77
1.75
1.75
1.74
1.73
1.70
1.68
1.67
1.66
1.65
1.64
1.63
1.63
1.62
1.60
1.60
1.59
1.53
1.52
1.51
1.50
2.00
2.00
4.36
2.18
8.77
4.01
4.90
2.43
f1 (ppm)
Br
O
O
O
I
41


157.77
146.47
127.61
120.13
114.03
65.00
42.39
29.89
29.55
27.88
26.34
f1 (ppm)
Br
O
O
O
I
41


7.32
7.30
7.27
7.25
4.42
4m
Cl
2.00
2.43
2.05
f1 (ppm)


137.99
133.75
130.18
129.15
4.35
4m
Cl
f1 (ppm)

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