Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

N-Heterocyclic Carbene Based Catalytic Platform for Hauser-Kraus Annulations

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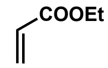
Contents:

1. General Information

All reactions were carried out in capped reaction vials with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. ^{1}H, ^{13}C NMR and ^{19}F NMR spectra were recorded were recorded on Varian Inova-400 spectrometers and Bruker-400 spectrometers. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.16 ppm) and are reported in terms of chemical shift (δ ppm). Infrared spectra were recorded on the React-IR 15 instrument from Mettler-Toledo Inc. MS data were measured using the AB Sciex QTRAP® 4500 LC-MS.

2. Commercially Available Reagents

Commercially available electron-deficient alkenes



11
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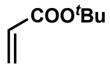

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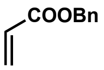

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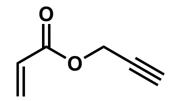

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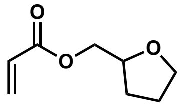

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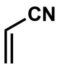

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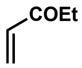

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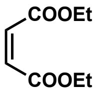

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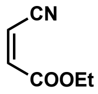

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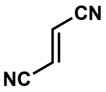

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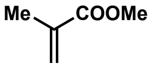

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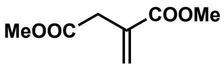

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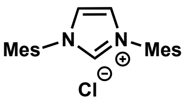
Commercially available *N*-heterocyclic carbene catalysts



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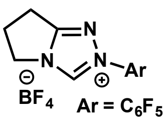

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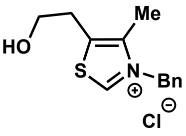

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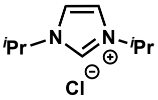

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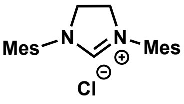

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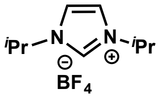
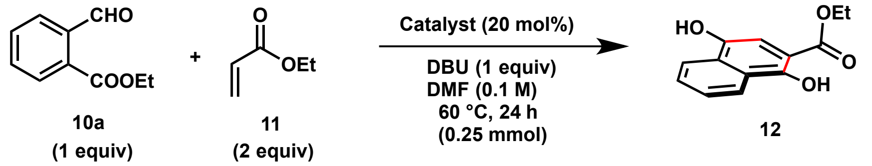


Combi-Blocks
CAS: 137581-18-1

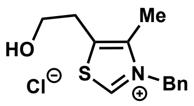
3. Optimizations and Control Experiments

Typical Procedure for Optimizations: In a flame dried microwave vial under Argon, *N*-heterocyclic carbene (NHC) catalyst and additive were diluted with DMSO (1 mL) and stirred for 5 min at 23 °C under an atmosphere of Ar. The mixture was treated with a solution of phthalaldehydate (0.25 mmol, 1 equiv) in DMSO (1 mL) from a separate vial, which was further rinsed with DMSO (0.5 mL). Ethyl acrylate and base were added sequentially via syringe into this mixture at 23 °C. Finally, the sealed microwave vial was submerged in an oil bath at the indicated temperature and stirred. The reaction progress was determined by TLC analysis. After completion, the reaction was cooled to 23 °C, diluted with *iso*-propyl acetate (20 mL) and quenched with 1M aqueous HCl (2 mL). The organic layer was washed with H_2O (10 mL X 2) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain the crude Hauser-Kraus Annulation product. The crude product was purified by silica gel chromatography (5% EtOAc/hexanes eluent) to afford the desired Hauser-Kraus Annulation product.

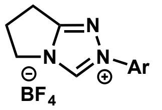
Table S1. Reaction Optimization: NHC Catalyst



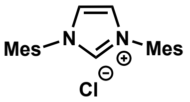
Results



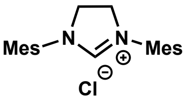
Cat. (A)
< 5% yield



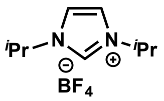
Cat. (B)
< 5% yield



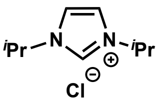
Cat. (C)
40% yield



Cat. (D)
< 5% yield

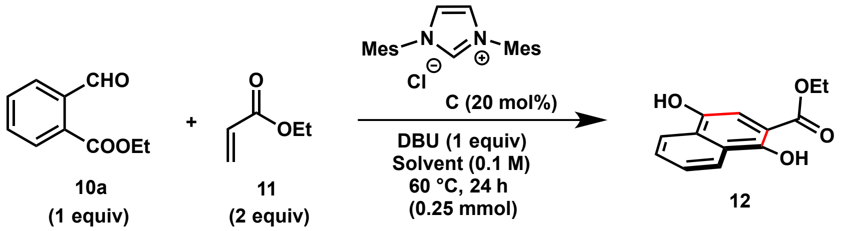


Cat. (E)
< 5% yield



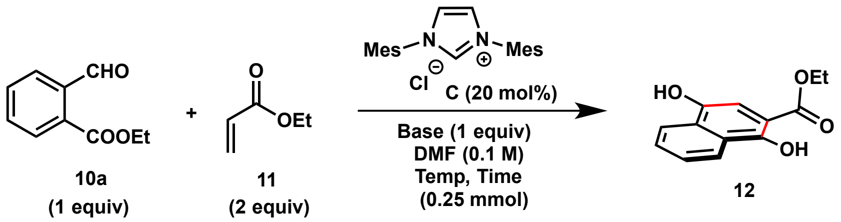
Cat. (F)
25% yield

Table S2. Reaction Optimization: Solvent



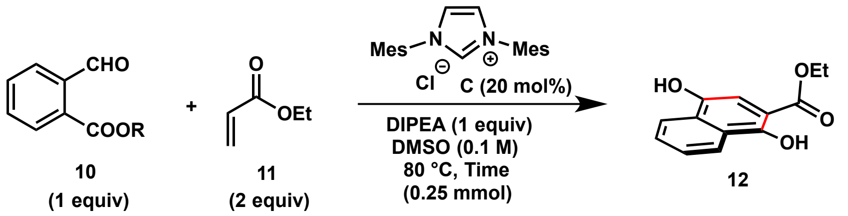
	Solvent	*Results*
1	DMF	40% NMR yield, > 95% conv.
2	THF	< 5% yield
3	PhMe	< 5% yield
4	DCE	< 5% yield
5	EtOH	< 5% yield
6	DMSO	45% NMR yield, 95% conv.

Table S3. Reaction Optimization: Base



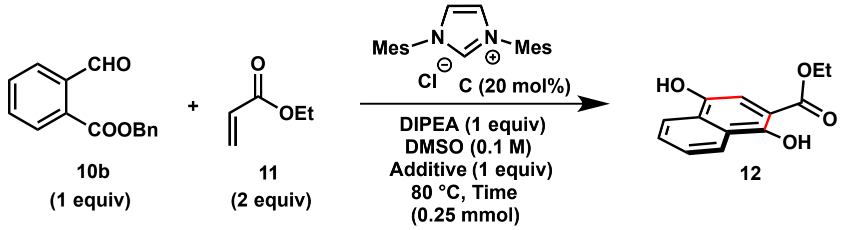
	Base	*Temp*	*Time*	*Results*
1	DBU	60 °C	6 h	40% NMR yield, > 95% conv.
2	Cs_2CO_3	60 °C	24 h	< 5% yield
3	Et_3N	60 °C	24 h	< 5% yield
4	KO^{t}Bu	60 °C	24 h	< 5% yield
5	DIPEA	80 °C	100 h	40% NMR yield, 55% conv.

Table S4. Reaction Optimization: Phthalaldehydate



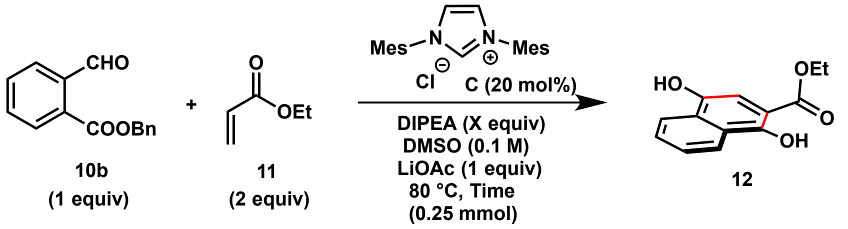
	R	*Time*	*Results*
1	Me	115 h	35% NMR yield, 60% conv.
2	Et	100 h	45% NMR yield, 60% conv.
3	Bn	90 h	60% NMR yield, 80% conv.

Table S5. Reaction Optimization: Additive



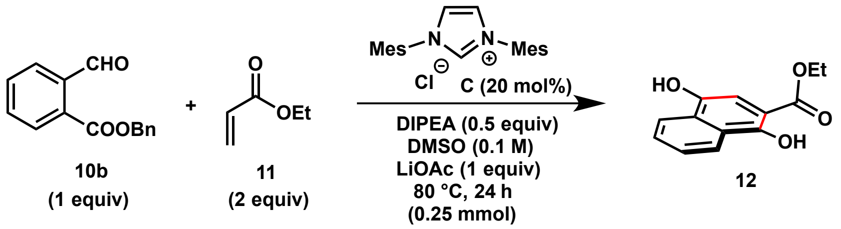
	Additive	*Time*	*Results*
1	$MgCl_2$	48 h	55% NMR yield, 95% conv.
2	LiCl	50 h	75% NMR yield, 95% conv.
3	LiOAc	12 h	80% NMR yield, 95% conv.

Table S6. Reaction Optimization: Equivalents of DIPEA



	DIPEA	*Time*	*Results*
1	1 equiv	12 h	80% NMR yield, 95% conv.
2	0.5 equiv	12 h	80% NMR yield, 95% conv.
3	No DIPEA	24 h	70% NMR yield, 95% conv.

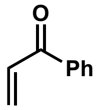
Table S7. Control Experiment: Necessity of NHC Catalyst



	Condition	*Results*
1	with NHC	80% NMR yield, 95% conv.
2	without NHC	< 5% yield

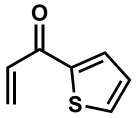
4. Synthesized Electron-Deficient Alkenes

1-Phenylprop-2-en-1-one (14r)



Following the literature procedure,[1] using 3-chloropropiophenone (1 g, 5.93 mmol, 1 equiv) and Et_3N (2 mL, 14.8 mmol, 2.5 equiv) in chloroform (10 mL), 1-Phenylprop-2-en-1-one **14r** was obtained as a colorless oil (0.55 g, 70% yield). The characterization spectra were consistent with those reported in the literature.[1]

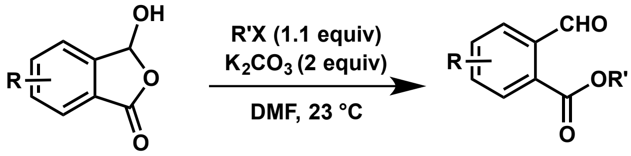
1-(Thiophen-2-yl)prop-2-en-1-one (14s)



Following the two-step literature procedure,[2] first, using 2-thiophenecarbonyl chloride (0.5 g, 3.41 mmol, 1 equiv), N,O-dimethylhydroxylamine hydrochloride (0.51 g, 5.2 mmol, 1.5 equiv) and Et_3N (1.2 mL, 8.5 mmol, 2.5 equiv) in CH_2Cl_2, N-methoxy-N-methylthiophene-2-carboxamide was obtained (0.56 g, 96% yield). Next, this product (0.5 g, 2.92 mmol, 1 equiv) was treated with allyl magnesium bromide (1 M in THF) (4.4 mL, 4.4 mmol, 1.5 equiv) to obtain 1-(thiophen-2-yl)prop-2-en-1-one **14s** as a yellow oil (310 mg, 77% yield). The characterization spectra were consistent with those reported in the literature.[3]

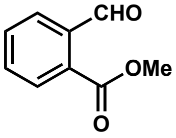
5. Synthesis and Characterization of Substituted Phthalaldehydate Substrates

General Procedure A:



According to a modified literature procedure,[4] a flame-dried round bottom flask was charged with substituted 3-hydroxy-1(3H)-isobenzofuranone (1 equiv) and K_2CO_3 (2 equiv). Under an argon atmosphere, anhydrous DMF (0.5 M) was added to the flask and the reaction mixture stirred at 23 °C for 15 min. R'X (1.1 equiv) was added via syringe at 23 °C and stirred for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc (20 mL) and washed with H_2O (10 mL x 2) and brine (10 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to yield the crude product. The crude product was purified by column chromatography on silica gel using EtOAc/Hexanes as an eluent to afford the desired protected ester product as a starting material for the catalytic Hauser-Kraus Annulation.

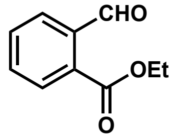
Methyl 2-formylbenzoate (S1)



Using 3-hydroxyisobenzofuran-1(3H)-one (0.5 g, 3.33 mmol, 1 equiv), methyl iodide (0.23 mL, 3.63 mmol, 1.1 equiv) and K_2CO_3 (0.92 g, 6.66 mmol, 2 equiv), following general procedure A, product **S1** was obtained as a light-yellow oil (0.51 g, 93% yield).

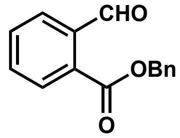
TLC R$_f$ = 0.6 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[4]

Ethyl 2-formylbenzoate (10a)



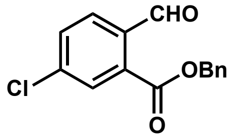
Using 3-hydroxyisobenzofuran-1(3H)-one (1 g, 6.66 mmol, 1 equiv), ethyl iodide (0.59 mL, 7.33 mmol, 1.1 equiv) and K_2CO_3 (1.84 g, 13.32 mmol, 2 equiv), following general procedure A, product **10a** was obtained as a clear oil (1.06 g, 90% yield). TLC R$_f$ = 0.6 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[4]

Benzyl 2-formylbenzoate (10b)



Using 3-hydroxyisobenzofuran-1(3H)-one (1 g, 6.66 mmol, 1 equiv), benzyl bromide (0.73 mL, 7.33 mmol, 1.1 equiv) and K_2CO_3 (1.84 g, 13.32 mmol, 2 equiv), following general procedure A, product **10b** was obtained as a clear oil (1.19 g, 93% yield). TLC R$_f$ = 0.55 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[4]

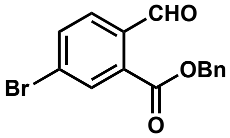
Benzyl 5-chloro-2-formylbenzoate (13e)



Using 6-chloro-3-hydroxyisobenzofuran-1(3H)-one (0.33 g, 1.76 mmol, 1 equiv), benzyl bromide (0.23 mL, 1.94 mmol, 1.1 equiv) and K_2CO_3 (0.49 g, 3.52 mmol, 2 equiv), following general procedure A, product **13e** was obtained as a clear oil (0.32 g, 66% yield). TLC R$_f$ = 0.6 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ

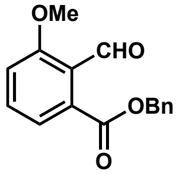
10.58 (s, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.61 (ddd, *J* = 8.4, 2.1, 0.8 Hz, 1H), 7.47 – 7.38 (m, 5H), 5.42 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 190.84, 165.02, 139.70, 135.41, 135.07, 133.59, 132.74, 130.66, 130.14, 128.96, 128.94, 128.78, 68.22. **React-IR** (CH_2Cl_2): 1716, 1423, 1265, 896, 703 cm^{-1}. **HRMS** calcd for [$C_{15}H_{11}ClO_3$, M + Na]+: 297.04, Found 296.98.

Benzyl 5-bromo-2-formylbenzoate (13f)



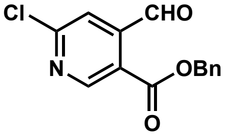
Using 6-bromo-3-hydroxyisobenzofuran-1(3H)-one (0.21 g, 0.92 mmol, 1 equiv), benzyl bromide (0.12 mL, 1.01 mmol, 1.1 equiv) and K_2CO_3 (0.26 g, 1.84 mmol, 2 equiv), following general procedure A, product **13f** was obtained as a colorless solid (0.22 g, 75% yield). TLC R*f* = 0.6 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.12 (d, *J* = 1.8 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.47 – 7.38 (m, 5H), 5.41 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 191.08, 164.91, 135.78, 135.02, 133.54, 133.51, 130.14, 128.95, 128.80, 128.15, 68.23. **React-IR** (CH_2Cl_2): 1720, 1585, 1254, 1096, 730, 701 cm^{-1}. **HRMS** calcd for [$C_{15}H_{11}BrO_3$, M + Na]+: 340.99, Found 340.92.

Benzyl 2-formyl-3-methoxybenzoate (13h)



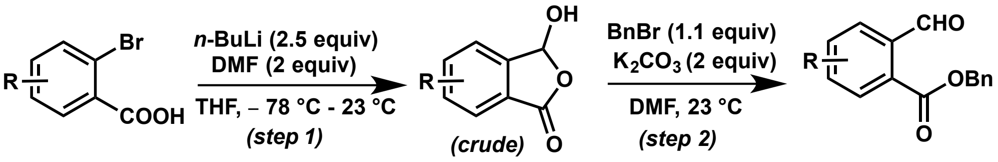
3-hydroxy-4-methoxyisobenzofuran-1(3H)-one (0.1 g, 0.54 mmol, 1 equiv) - synthesized via a known procedure,[5] benzyl bromide (0.07 mL, 0.6 mmol, 1.1 equiv) and K_2CO_3 (0.15 g, 1.08 mmol, 2 equiv), following general procedure A, product **13h** was obtained as a white solid (0.37 g, 65% yield). TLC R*f* = 0.5 (Hexane/EtOAc = 1:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.52 (dd, *J* = 8.5, 7.6 Hz, 1H), 7.43 – 7.30 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 9.4 Hz, 1H), 5.35 (s, 2H), 3.91 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 190.23, 168.33, 160.55, 135.60, 134.27, 133.78, 128.72, 128.70, 128.51, 124.75, 120.71, 114.21, 67.90, 56.26. **React-IR** (CH_2Cl_2): 1734, 1291, 1061, 731, 701 cm^{-1}. **HRMS** calcd for [$C_{16}H_{14}O_4$, M + Na]+: 293.09, Found 293.03.

Benzyl 6-chloro-4-formylnicotinate (13k)



Using 6-chloro-1-hydroxyfuro[3,4-c]pyridin-3(1H)-one (0.1 g, 0.54 mmol, 1 equiv), benzyl bromide (0.07 mL, 0.6 mmol, 1.1 equiv) and K_2CO_3 (0.15 g, 1.08 mmol, 2 equiv), following general procedure A, product **13k** was obtained as a white solid (0.072 g, 48% yield). TLC R_f = 0.5 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 9.09 (s, 1H), 7.71 (s, 1H), 7.46 – 7.36 (m, 5H), 5.44 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 191.08, 164.91, 135.78, 135.02, 133.54, 133.51, 130.14, 128.95, 128.80, 128.15, 68.23. **React-IR** (CH_2Cl_2): 1720, 1544, 1118, 728, 701 cm^{-1}. **HRMS** calcd for [$C_{14}H_{10}ClNO_3$, M + Na]+: 298.03, Found 297.97.

General Procedure B:

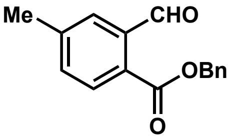


According to a modified literature procedure,[6] a flame-dried round bottom flask was charged with substituted 2-bromobenzoic acid (1.0 equiv). Under an argon atmosphere, anhydrous THF (0.5 M) was added to the flask, and the reaction mixture cooled to – 78 °C. *n*-BuLi (2.5 equiv, 2.5 M in hexanes) was added slowly via syringe, and the mixture was stirred for 30 min. At -78 °C, DMF (2 equiv) was added dropwise via syringe, and the reaction mixture was further stirred for overnight, allowing the reaction to slowly warm up to 23 °C. Saturated aqueous NH_4Cl was added to quench the reaction.

The mixture was extracted with EtOAc, washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was used directly for the next step without further purification.

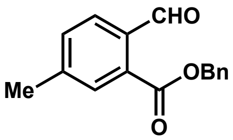
The crude product obtained from the above reaction was dissolved in anhydrous DMF and treated with K_2CO_3 (2 equiv). After stirring for 15 min, benzyl bromide (1.1 equiv) was added via syringe at 23 °C, and the reaction mixture was stirred for another 2-3 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc (20 mL), and the organic layer was washed with H_2O (10 mL x 2) and brine (10 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to yield the crude product. The crude product was purified by column chromatography on silica gel using EtOAc/Hexanes as an eluent to afford the desired protected ester product as a starting material for the catalytic Hauser-Kraus Annulation.

Benzyl 2-formyl-4-methylbenzoate (13a)



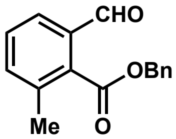
Following general procedure B, using 2-bromo-4-methylbenzoic acid (1.0 g, 4.65 mmol, 1 equiv), *n*-BuLi (4.65 mL, 11.63 mmol, 2.5 equiv, 2.5 M in hexanes), DMF (0.7 mL, 9.3 mmol, 2 equiv) in step 1 and K_2CO_3 (1.29 g, 9.3 mmol, 2 equiv), benzyl bromide (0.6 mL, 5.12 mmol, 1.1 equiv) in step 2, product **13a** was obtained as a clear oil (0.34 g, 29% yield over two steps). TLC $R_f = 0.65$ (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.64 (s, 1H), 7.37 – 7.24 (m, 6H), 5.3 (s, 2H), 2.35 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 192.64, 166.14, 143.56, 137.40, 135.54, 133.63, 130.83, 129.20, 128.93, 128.82, 128.65, 128.54, 128.44, 67.55, 21.57. **React-IR** (CH_2Cl_2): 1715, 1607, 1280, 1142, 1080, 697 cm^{-1}. **HRMS** calcd for [$C_{16}H_{14}O_3$, M + Na]+: 277.09, Found 277.03.

Benzyl 2-formyl-5-methylbenzoate (13b)



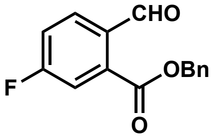
Following general procedure B, using 2-bromo-5-methylbenzoic acid (0.5 g, 2.32 mmol, 1 equiv), *n*-BuLi (2.32 mL, 5.8 mmol, 2.5 equiv, 2.5 M in hexanes), DMF (0.36 mL, 4.64 mmol, 2 equiv) in step 1 and K_2CO_3 (0.64 g, 4.64 mmol, 2 equiv), benzyl bromide (0.3 mL, 2.55 mmol, 1.1 equiv) in step 2, product **13b** was obtained as a clear oil (0.31 g, 61% yield over two steps). TLC $R_f = 0.65$ (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.47 – 7.35 (m, 6H), 5.41 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 191.81, 166.46, 144.24, 135.43, 134.54, 133.12, 132.29, 131.01, 128.84, 128.80, 128.70, 128.65, 67.75, 21.73. **React-IR** (CH_2Cl_2): 1719, 1607, 1305, 1192, 1077, 832, 701 cm^{-1}. **HRMS** calcd for [$C_{16}H_{14}O_3$, M + Na]+: 277.09, Found 277.04.

Benzyl 2-formyl-6-methylbenzoate (13c)



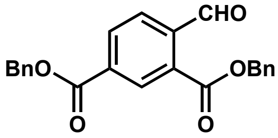
Following general procedure B, using 2-bromo-6-methylbenzoic acid (0.83 g, 3.85 mmol, 1 equiv), *n*-BuLi (3.85 mL, 9.63 mmol, 2.5 equiv, 2.5 M in hexanes), DMF (0.6 mL, 7.7 mmol, 2 equiv) in step 1 and K_2CO_3 (1.1 g, 7.7 mmol, 2 equiv), benzyl bromide (0.3 mL, 4.24 mmol, 1.1 equiv) in step 2, product **13c** was obtained as a clear oil (0.22 g, 23% yield over two steps). TLC $R_f = 0.65$ (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.69 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.41 – 7.34 (m, 3H), 5.43 (s, 2H), 2.35 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 190.83, 168.66, 136.38, 136.10, 135.34, 133.88, 133.53, 129.85, 129.23, 128.96, 128.74, 128.67, 67.89, 18.96. **React-IR** (CH_2Cl_2): 1732, 1273, 1256, 1176, 1073, 701 cm^{-1}. **HRMS** calcd for [$C_{16}H_{14}O_3$, M + Na]+: 277.09, Found 277.03.

Benzyl 5-fluoro-2-formylbenzoate (13d)



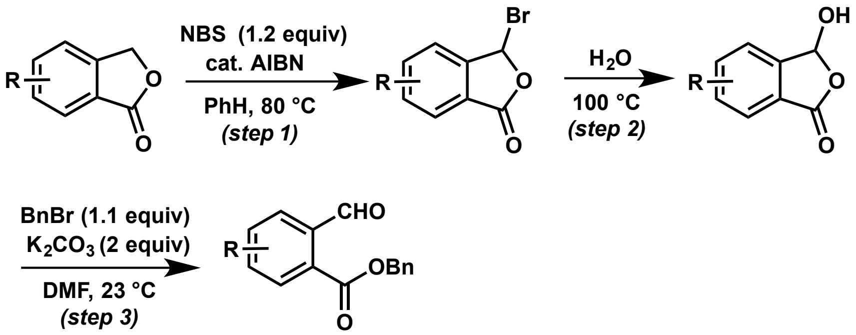
Following general procedure B, using 2-bromo-5-fluorobenzoic acid (0.5 g, 2.3 mmol, 1 equiv), *n*-BuLi (2.3 mL, 5.75 mmol, 2.5 equiv, 2.5 M in hexanes), DMF (0.36 mL, 4.6 mmol, 2 equiv) in step 1 and K_2CO_3 (0.64 g, 4.6 mmol, 2 equiv), benzyl bromide (0.3 mL, 2.53 mmol, 1.1 equiv) in step 2, product **13d** was obtained as a white solid (0.18 g, 31% yield over two steps). TLC R_f = 0.6 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.63 – 7.55 (m, 2H), 7.46 – 7.36 (m, 5H), 7.34 – 7.29 (m, 1H), 5.38 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 188.10, 166.26, 163.13, 160.56, 135.15, 134.17, 134.08, 128.83, 128.76, 128.46, 125.42, 125.39, 120.17, 119.96, 68.19. **^{19}F NMR** (376 MHz, CDCl3) δ -117.49 (dd, *J* = 9.9, 5.0 Hz). **React-IR** (CH_2Cl_2): 1713, 1457, 1285, 1142, 1006, 701 cm^{-1}. **HRMS** calcd for [$C_{15}H_{11}FO_3$, M + Na]+: 281.07, Found 281.01.

Dibenzyl 4-formylisophthalate (13i)



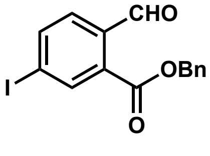
Following general procedure B, using 4-bromoisophthalic acid (1 g, 4 mmol, 1 equiv), *n*-BuLi (6.4 mL, 16 mmol, 4 equiv, 2.5 M in hexanes), DMF (0.62 mL, 8 mmol, 2 equiv) in step 1 and K_2CO_3 (1.1 g, 8 mmol, 2 equiv), benzyl bromide (0.52 mL, 4.4 mmol, 1.1 equiv) in step 2, product **13i** was obtained as a colorless solid (0.12 g, 10% yield over two steps). TLC R_f = 0.45 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.68 – 8.67 (m, 1H), 8.31 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.35 (m, 10H), 5.43 (s, 2H), 5.40 (s, 2H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 191.58, 165.42, 164.80, 140.37, 135.44, 135.14, 134.10, 133.48, 132.18, 131.91, 128.91, 128.85, 128.72, 128.69, 128.52, 68.11, 67.66. **React-IR** (CH_2Cl_2): 1756, 1591, 1201, 1005, 739, 701 cm^{-1}. **HRMS** calcd for [$C_{23}H_{18}O_5$, M + Na]+: 397.12, Found 397.10.

General Procedure C:



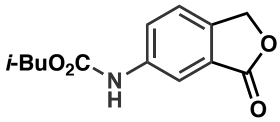
According to a modified literature procedure,[7] a flame-dried round bottom flask was charged with substituted phthalide (1.0 equiv), NBS (1.2 equiv) and catalytic AIBN (5 mol%). Under an argon atmosphere, benzene (0.2 M) was added to the flask and the reaction mixture refluxed at 85 °C for 12 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was cooled to 23 °C and concentrated under reduced pressure. The resulting bromo-phthalide crude product was directly used in the next step without purification. H_2O was added to the crude mixture and refluxed for 4 h at 100 °C. The resultant crude mixture was diluted with ethyl acetate and extracted three times with additional ethyl acetate. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to yield the crude product. The unpurified hydroxy-phthalide product was then subjected to K_2CO_3 (2 equiv), benzyl bromide (1.1 equiv) and dry DMF conditions (general procedure A) to yield the corresponding crude formyl-benzoate product. The crude product was purified by column chromatography on silica gel using EtOAc/Hexanes as an eluent to afford the desired protected ester product as a starting material for the catalytic Hauser-Kraus Annulation.

Benzyl 2-formyl-5-iodobenzoate (13g)



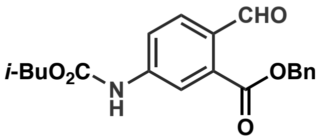
Following general procedure C, using 2-bromo-5-chlorobenzoic acid (0.25 g, 1.04 mmol, 1 equiv), NBS (0.22 g, 1.25 mmol, 1.2 equiv), AIBN (8.5 mg, 0.052 mmol, 5 mol%), benzene (5 mL) in step 1 and H_2O (20 mL), step 2 and K_2CO_3 (0.64 g, 4.64 mmol, 2 equiv), benzyl bromide (0.3 mL, 2.55 mmol, 1.1 equiv) in step 3, product **13g** was obtained as a white solid (0.16 g, 42% yield over three steps). TLC R_f = 0.5 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 8.32 (d, *J* = 1.7 Hz, 1H), 8.00 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.35 (m, 5H), 5.41 (s, 2H). ^{13}**C NMR** (400 MHz, $CDCl_3$) δ 191.34, 164.78, 141.73, 139.30, 136.25, 135.03, 133.18, 129.85, 128.92, 128.91, 128.78, 100.53, 68.18. **React-IR** (CH_2Cl_2): 1735, 1511, 1204, 1159, 701 cm^{-1}. **HRMS** calcd for [$C_{15}H_{11}IO_3$, M + Na]+: 388.98, Found 388.90.

Carbamate S2



According to reported procedure,[4] commercially available 6-aminoisobenzofuran-1(3H)-one (0.75 g, 5 mmol, 1 equiv) was treated with isobutyl chloroformate (0.97 mL, 7.5 mmol, 1.5 equiv), DMAP (61 mg, 0.5 mmol, 10 mol%) in DCM (15 mL) to obtain carbamate **S2** (0.87 g, 70% yield).

Benzyl 2-formyl-5-((isobutoxycarbonyl)amino)benzoate (13j)

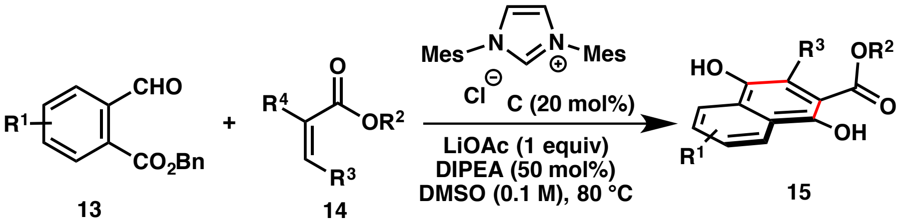


Following general procedure C, using synthesized carbamate **S2** (0.45 g, 1.8 mmol, 1 equiv), NBS (0.39 g, 2.2 mmol, 1.2 equiv), AIBN (15 mg, 0.09 mmol, 5 mol%), benzene (5 mL) in step 1 and H_2O (20 mL), step 2 and K_2CO_3 (0.5 g, 3.6 mmol, 2 equiv), benzyl bromide (0.24 mL, 2 mmol, 1.1 equiv) in step 3, product **13j** was obtained as a clear liquid (0.24 g, 38% yield over three steps). TLC R_f = 0.35 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 2.3 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.39 – 7.25 (m, 5H), 6.91 (s, 1H), 5.33 (s, 2H), 3.91 (d, *J* = 6.7 Hz, 2H), 1.97 – 1.85 (m, 1H), 0.9 (s, 3H), 0.88 (s, 3H). ^{13}**C NMR**

(400 MHz, $CDCl_3$) δ 190.76, 166.01, 153.17, 142.78, 135.36, 133.89, 131.54, 130.49, 128.88, 128.76, 128.68, 120.99, 119.34, 72.13, 67.93, 28.02, 19.13. **React-IR** (CH_2Cl_2): 1738, 1525, 1212, 1059, 701 cm^{-1}. **HRMS** calcd for $[C_{20}H_{21}NO_5, M + Na]^+$: 378.14, Found 378.07.

6. General Procedure for Catalytic Hauser-Kraus Annulation

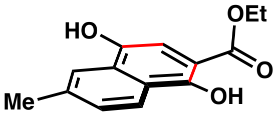
General Procedure D:



In a flame dried microwave vial under Argon, 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride **C** (IMes-NHC) (17 mg, 0.05 mmol, 20 mol%) and oven-dried lithium acetate (16.5 mg, 0.25 mmol, 1 equiv) were diluted with 1 mL DMSO and stirred for 5 min at 23 °C. The mixture was treated with a solution of substituted benzyl phthalaldehydate **13** (0.25 mmol, 1 equiv) in DMSO (1 mL) from a separate vial, which was further rinsed with DMSO (0.5 mL). DIPEA (22 µl, 0.125 mmol, 50 mol%) and electron-deficient alkene **14** (0.5 mmol, 2 equiv) were added sequentially into this mixture at 23 °C. The sealed microwave vial was submerged in an oil bath at 80 °C and stirred for 12-24 h. Once the reaction was determined to be complete by TLC analysis, the reaction was cooled to 23 °C, diluted with *iso*-propyl acetate (20 mL) and quenched with 1 M HCl (2 mL). The organic layer was washed with H_2O (10 mL x 2) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain the crude Hauser-Kraus product. The crude product was purified by silica gel chromatography using EtOAc/hexanes as an eluent to afford the desired Hauser-Kraus Annulation product.

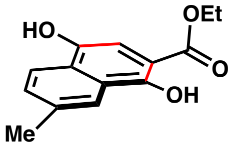
7. Characterization of Hauser-Kraus Annulation Products

Ethyl 1,4-dihydroxy-6-methyl-2-naphthoate (15a)



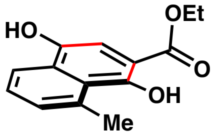
Following the general procedure D, using **13a** (64 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15a** was obtained as a yellow solid (36.2 mg, 59% yield). TLC $R_f = 0.4$ (Hexane/EtOAc = 2:1, v/v). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.28 (d, $J = 8.5$ Hz, 1H), 7.89 (s, 1H), 7.41 – 7.38 (m, 1H), 7.09 (s, 1H), 5.03 (s, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 2.55 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H). ^{13}**C NMR** (400 MHz, $CDCl_3$) 170.88, 155.92, 142.92, 139.53, 129.29, 128.55, 124.04, 123.86, 121.02, 105.57, 103.96, 61.44, 22.21, 14.40.δ **React-IR** (CH_2Cl_2): 2913, 2834, 1701, 1544, 1249, 731 cm^{-1}. **HRMS** calcd for [$C_{14}H_{14}O_4$, M + Na]+: 269.09, Found 269.10.

Ethyl 1,4-dihydroxy-7-methyl-2-naphthoate (15b)



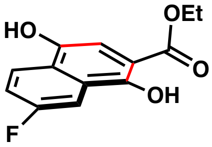
Following the general procedure D, using **13b** (64 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15b** was obtained as a yellow solid (32 mg, 52% yield). TLC $R_f = 0.4$ (Hexane/EtOAc = 2:1, v/v). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.18 – 8.17 (m, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.48 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.06 (s, 1H), 4.43 (q, $J = 7.1$ Hz, 2H), 2.55 (s, 3H), 1.44 (t, $J = 7.2$ Hz, 3H). ^{13}**C NMR** (400 MHz, $CDCl_3$) δ 170.91, 155.44, 143.40, 136.48, 131.21, 127.21, 125.93, 123.24, 121.69, 104.78, 104.50, 61.49, 21.89, 14.43. **React-IR** (CH_2Cl_2): 2909, 2834, 1701, 1544, 1249, 701 cm^{-1}. **HRMS** calcd for [$C_{14}H_{14}O_4$, M + Na]+: 269.09, Found 269.06.

Ethyl 1,4-dihydroxy-8-methyl-2-naphthoate (15c)



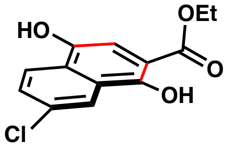
Following the general procedure D, using **13c** (64 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15c** was obtained as a yellow solid (25.3 mg, 41% yield). TLC R_f = 0.4 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.18 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.12 (s, 1H), 4.94 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 171.42, 159.23, 143.09, 138.60, 130.75, 129.76, 128.82, 125.16, 119.83, 105.61, 104.66, 61.51, 25.21, 14.39. **React-IR** (CH_2Cl_2): 2916, 2831, 1678, 1500, 1265, 701 cm^{-1}. **HRMS** calcd for [$C_{14}H_{14}O_4$, M + Na]+: 269.09, Found 269.08.

Ethyl 7-fluoro-1,4-dihydroxy-2-naphthoate (15d)



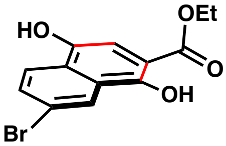
Following the general procedure D, using **13d** (65 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15d** was obtained as a yellow solid (38 mg, 60% yield). TLC R_f = 0.4 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.29 – 7.23 (m, 2H), 6.43 (d, *J* = 24.9 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.58, 160.11, 157.70, 153.98, 153.94, 142.78, 127.76, 127.72, 126.00, 125.90, 121.22, 121.18, 117.78, 117.70, 113.92, 113.70, 108.38, 108.35, 106.87, 106.85, 61.83, 14.32. **^{19}F NMR** (376 MHz, CDCl3) δ -122.00 (ddd, *J* = 24.8, 14.6, 5.4 Hz). **React-IR** (CH_2Cl_2): 2913, 2835, 1670, 1400, 1211, 701 cm^{-1}. **HRMS** calcd for [$C_{13}H_{11}FO_4$, M + Na]+: 251.06, Found 251.07.

Ethyl 7-chloro-1,4-dihydroxy-2-naphthoate (15e)



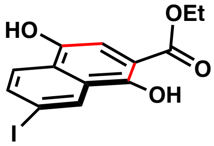
Following the general procedure D, using **13e** (69 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15e** was obtained as a yellow solid (45 mg, 68% yield). TLC R_f = 0.4 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.36 (d, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.57 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.11 (s, 1H), 5.01 (br, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (400 MHz, $CDCl_3$) δ 170.52, 154.64, 143.30, 132.82, 129.75, 127.17, 126.58, 123.81, 123.27, 105.84, 105.72, 61.77, 14.40. **React-IR** (CH_2Cl_2): 2913, 2835, 1701, 1543, 1246, 701 cm^{-1}. **HRMS** calcd for [$C_{13}H_{11}ClO_4$, M + Na]+: 289.03, Found 289.06.

Ethyl 7-bromo-1,4-dihydroxy-2-naphthoate (15f)



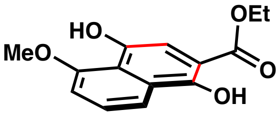
Following the general procedure D, using **13f** (80 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15f** was obtained as a yellow solid (58 mg, 74% yield). TLC R_f = 0.35 (Hexane/EtOAc = 2:1, v/v). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.54 (d, *J* = 2.0 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.70 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.12 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (400 MHz, $CDCl_3$) δ 170.49, 154.54, 143.37, 132.28, 127.41, 126.91, 126.52, 123.88, 120.96, 105.88, 105.82, 61.78, 14.40. **React-IR** (CH_2Cl_2): 2913, 2834, 1656, 1246, 701 cm^{-1}. **HRMS** calcd for [$C_{13}H_{11}BrO_4$, M + Na]+: 332.98, Found 332.97.

Ethyl 7-iodo-1,4-dihydroxy-2-naphthoate (15g)



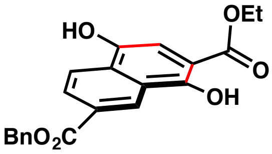
Following the general procedure D, using **13g** (92 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15g** was obtained as a yellow solid (74 mg, 82% yield). TLC R_f = 0.35 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 11.32 (s, 1H), 10.01 (s, 1H), 8.55 (d, *J* = 1.7 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.13 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (400 MHz, DMSO-d$_6$) δ 169.81, 151.18, 145.25, 136.75, 131.52, 127.58, 126.35, 124.35, 106.02, 104.70, 92.95, 61.66, 14.05. **React-IR** (CH_2Cl_2): 2910, 2854, 1701, 1288, 701 cm^{-1}. **HRMS** calcd for [$C_{13}H_{11}IO_4$, M + Na]+: 380.97, Found 380.97.

Ethyl 1,4-dihydroxy-5-methoxy-2-naphthoate (15h)



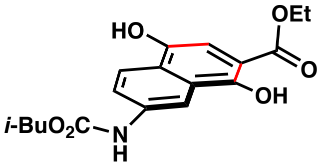
Following the general procedure D, using **13h** (68 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15h** was obtained as a yellow foamy solid (55 mg, 84% yield). TLC R_f = 0.5 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 11.46 (s, 1H), 8.82 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.18 (s, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.06 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (400 MHz, CDCl$_3$) δ 170.83, 155.81, 153.30, 146.01, 127.34, 125.97, 119.07, 117.81, 108.13, 106.87, 106.73, 61.59, 56.41, 14.34. **React-IR** (CH_2Cl_2): 2912, 2834, 1669, 1402, 1220, 873, 701 cm^{-1}. **HRMS** calcd for [$C_{14}H_{14}O_5$, M + H]+: 263.08, Found 263.04.

7-Benzyl 2-ethyl 1,4-dihydroxynaphthalene-2,7-dicarboxylate (15i)



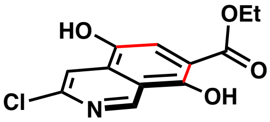
Following the general procedure D, using **13i** (93.6 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15i** was obtained as a yellow solid (41 mg, 45% yield). TLC R_f = 0.2 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 9.16 (d, *J* = 1.7 Hz, 1H), 8.26 – 8.16 (m, 2H), 7.52 – 7.49 (m, 2H), 7.46 – 7.34 (m, 3H), 7.24 (s, 1H), 5.44 (s, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), s1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.47, 166.38, 156.49, 143.14, 136.16, 131.06, 128.80, 128.72, 128.49, 128.47, 128.04, 127.19, 125.16, 122.33, 108.27, 105.61, 67.13, 61.79, 14.41, 14.26. **React-IR** (CH_2Cl_2): 2912, 2834, 1719, 1543, 1245, 727 cm^{-1}. **HRMS** calcd for [$C_{21}H_{18}O_6$, M + Na]+: 389.11, Found 389.03.

Ethyl 1,4-dihydroxy-7-(3-methylbutanamido)-2-naphthoate (15j)



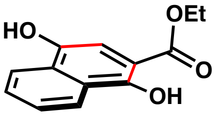
Following the general procedure D, using **13j** (89 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15j** was obtained as a yellow solid (34 mg, 39% yield). TLC R_f = 0.2 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 8.22 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.02 (s, 1H), 6.85 (br, 1H), 5.04 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.01 (d, *J* = 6.6 Hz, 2H), 2.03 – 1.97 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.0 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.78, 155.08, 153.97, 143.39, 136.55, 126.36, 125.51, 123.20, 121.78, 111.68, 105.31, 104.22, 71.81, 61.54, 28.13, 19.22, 14.41. **React-IR** (CH_2Cl_2): 2913, 2835, 1737, 1523, 1210, 730, 701 cm^{-1}. **HRMS** calcd for [$C_{18}H_{21}NO_6$, M + Na]+: 370.14, Found 370.06.

Ethyl 3-chloro-5,8-dihydroxyisoquinoline-7-carboxylate (15k)



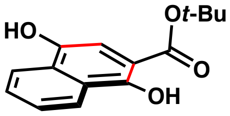
Following the general procedure D, using **13k** (69 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **15k** was obtained as a yellow solid (25 mg, 38% yield). TLC $R_f = 0.3$ (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.42 (s, 1H), 10.36 (s, 1H), 9.37 (d, *J* = 0.8 Hz, 1H), 7.93 (d, *J* = 0.8 Hz, 1H), 7.35 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (400 MHz, DMSO-d_6) δ 169.05, 152.95, 149.00, 147.95, 143.62, 133.71, 119.12, 114.53, 109.98, 107.04, 61.88, 14.02. **React-IR** (CH_2Cl_2): 2967, 2755, 1701, 1609, 722, 701 cm^{-1}. **HRMS** calcd for [$C_{12}H_{10}ClNO_4$, M + Na]+: 290.03, Found 290.07.

Ethyl 1,4-dihydroxy-2-naphthoate (12)



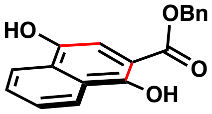
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and ethyl acrylate **11** (55 µl, 0.5 mmol, 2 equiv), product **12** was obtained as a yellow solid (42 mg, 72% yield). TLC $R_f = 0.2$ (Hexane/EtOAc = 2:1, v/v).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.65 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.11 (s, 1H), 5.18 (s, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.83, 155.71, 143.34, 129.11, 129.04, 126.48, 125.72, 124.07, 121.80, 105.39, 104.69, 61.58, 14.38. **React-IR** (CH_2Cl_2): 2916, 2876, 1664, 1247, 731 cm^{-1}. **HRMS** calcd for [$C_{13}H_{12}O_4$, M + H]+: 233.07, Found 233.04.

tert-Butyl 1,4-dihydroxy-2-naphthoate (15l)



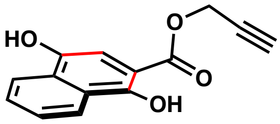
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and *tert*-butyl acrylate **14l** (73 µl, 0.5 mmol, 2 equiv), product **15l** was obtained as a yellow oil (40 mg, 62% yield). TLC R*f* = 0.4 (Hexane/EtOAc = 2:1, v/v).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.37 (s, 1H), 7.08 (s, 1H), 1.64 (s, 9H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.41, 155.67, 143.04, 128.87, 128.77, 128.48, 126.35, 125.83, 124.03, 121.68, 105.99, 82.87, 28.42. **React-IR** (CH_2Cl_2): 2950, 2916, 2842, 2369, 1256, 701. **HRMS** calcd for [$C_{15}H_{16}O_4$, M + Na]+: 283.1, Found 283.08.

Benzyl 1,4-dihydroxy-2-naphthoate (15m)



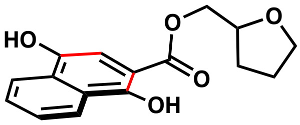
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and benzyl acrylate **14m** (77 µl, 0.5 mmol, 2 equiv), product **15m** was obtained as a light yellow solid (46 mg, 63% yield). TLC R*f* = 0.4 (Hexane/EtOAc = 2:1, v/v).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.55 (s, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.35 (m, 5H), 7.13 (s, 1H), 5.41 (s, 2H), 5.03 (s, 1H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.55, 155.96, 143.41, 135.52, 129.24, 129.12, 128.87, 128.71, 128.47, 126.56, 125.72, 124.13, 121.83, 105.24, 104.46, 67.15. **React-IR** (CH_2Cl_2): 2916, 2876, 2368, 1667, 1096, 728. **HRMS** calcd for [$C_{18}H_{14}O_4$, M + Na]+: 317.09, Found 317.02.

Prop-2-yn-1-yl 1,4-dihydroxy-2-naphthoate (15n)



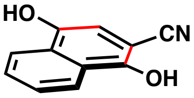
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and propargyl acrylate **14n** (55 µl, 0.5 mmol, 2 equiv), product **15n** was obtained as a yellow solid (47 mg, 78% yield). TLC R_f = 0.45 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, CDCl$_3$) δ 11.32 (s, 1H), 8.41 – 8.39 (m, 1H), 8.15 – 8.12 (m, 1H), 7.67 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.38– 7.37 (m, 1H), 7.12 (s, 1H), 4.98 (d, *J* = 2.4 Hz, 1H), 4.98 (d, *J* = 2.4 Hz, 2H), 4.72 (br, 1H), 2.57 (t, *J* = 2.4 Hz, 1H). ^{13}**C NMR** (400 MHz, CDCl$_3$) δ 169.90, 156.18, 143.53, 129.46, 128.75, 127.19, 126.67, 124.18, 121.90, 105.00, 103.88, 75.76, 65.61, 52.87. **React-IR** (CH_2Cl_2): 2949, 2931, 2368, 1240, 729. **HRMS** calcd for [$C_{14}H_{10}O_4$, M + Na]+: 265.06, Found 265.

(Tetrahydrofuran-2-yl)methyl 1,4-dihydroxy-2-naphthoate (15o)



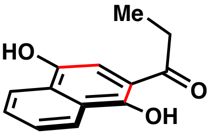
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and tetrahydrofurfuryl acrylate **14o** (73 µl, 0.5 mmol, 2 equiv), product **15o** was obtained as a light yellow solid (45 mg, 63% yield). TLC R_f = 0.25 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, CDCl$_3$) δ 11.40 (s, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.57 – 7.53 (m, 1H), 7.11 (s, 1H), 5.55 (s, 1H), 4.49 – 4.43 (m, 1H), 4.36 – 4.29 (m, 2H), 4.02 – 3.96 (m, 1H), 3.91 – 3.86 (m, 1H), 2.16 – 2.08 (m, 1H), 2.05 – 1.92 (m, 2H), 1.79 – 1.70 (m, 1H). ^{13}**C NMR** (400 MHz, CDCl$_3$) δ 170.58, 155.69, 143.57, 129.15, 129.13, 126.46, 125.64, 124.03, 121.89, 105.17, 104.37, 68.78, 67.11, 29.85, 28.15, 25.90. **React-IR** (CH_2Cl_2): 2950, 2875, 2368, 1244, 742. **HRMS** calcd for [$C_{16}H_{16}O_5$, M + Na]+: 311.1, Found 311.03.

1,4-Dihydroxy-2-naphthonitrile (15p)



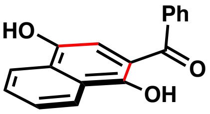
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and acrylonitrile **14p** (33 µl, 0.5 mmol, 2 equiv), product **15p** was obtained as a beige solid (39 mg, 85% yield). TLC R_f = 0.15 (Hexane/EtOAc = 2:1, v/v).^{1}**H NMR** (400 MHz, DMSO-d_6) δ 10.52 (s, 1H), 10.16 (s, 1H), 8.25 – 8.22 (m, 1H), 8.14 – 8.12 (m, 1H), 7.68 – 7.60 (m, 2H), 6.73 (s, 1H). ^{13}**C NMR** (400 MHz, DMSO-d_6) δ 151.05, 146.58, 128.24, 128.01, 126.85, 125.81, 122.94, 122.49, 118.03, 106.22, 93.41. **React-IR** (CH_2Cl_2): 2925, 2865, 2274, 1321, 732. **HRMS** calcd for [$C_{11}H_7NO_2$, M + Na]+: 208.05, Found 208.02.

1-(1,4-dihydroxynaphthalen-2-yl)propan-1-one (15q)



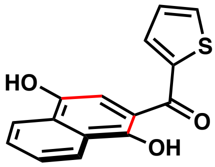
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and ethyl vinyl ketone **14q** (50 µl, 0.5 mmol, 2 equiv), product **15q** was obtained as a light yellow solid (14 mg, 25% yield). TLC R_f = 0.6 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[8]

(1,4-dihydroxynaphthalen-2-yl)(phenyl)methanone (15r)



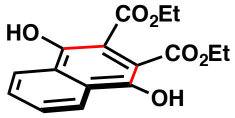
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and phenyl vinyl ketone **14r** (66 µl, 0.5 mmol, 2 equiv), product **15r** was obtained as a yellow solid (32 mg, 48% yield). TLC R_f = 0.5 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[9]

(1,4-Dihydroxynaphthalen-2-yl)(thiophen-2-yl)methanone (15s)



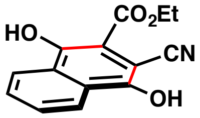
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and 1-(Thiophen-2-yl)prop-2-en-1-one **14s** (69 mg, 0.5 mmol, 2 equiv), product **15s** was obtained as a red solid (24 mg, 35% yield). TLC R_f = 0.35 (Hexane/EtOAc = 2:1, v/v). The characterization spectra were consistent with those reported in the literature.[10]

Diethyl 1,4-dihydroxynaphthalene-2,3-dicarboxylate (15v)



Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and diethyl maleate **14v** (81 µl, 0.5 mmol, 2 equiv), product **15v** was obtained as a light yellow solid (56 mg, 74% yield). TLC R_f = 0.5 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.41 (s, 2H), 8.35 (dd, J = 6.3, 3.3 Hz, 2H), 7.69 (dd, J = 6.3, 3.3 Hz, 2H), 4.37 (q, J = 7.2 Hz, 4H), 1.36 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 170.38, 152.36, 129.52, 127.93, 124.04, 103.69, 61.86, 14.26. **React-IR** (CH_2Cl_2): 2950, 2916, 2368, 1663, 1231, 704. **HRMS** calcd for [$C_{16}H_{16}O_6$, M + Na]+: 327.09, Found 327.02.

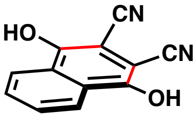
Ethyl 3-cyano-1,4-dihydroxy-2-naphthoate (15w)



Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and Ethyl *cis*-(*β*-cyano)acrylate **14w** (63 mg, 0.5 mmol, 2 equiv), product **15w** was obtained as a light yellow solid (53 mg, 83% yield). TLC R_f = 0.2 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 8.46 – 8.41 (m, 1H), 8.31 – 8.27 (m, 1H), 7.79 – 7.72 (m, 2H), 6.47 (br, 1H), 4.56 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H).

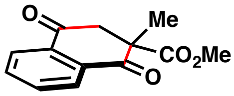
^{13}C NMR (400 MHz, $CDCl_3$) δ 169.26, 156.96, 152.70, 130.62, 130.03, 127.82, 127.01, 124.50, 123.34, 116.56, 100.73, 88.21, 62.95, 14.03. **React-IR** (CH_2Cl_2): 2916, 2875, 2367, 1247, 728. **HRMS** calcd for [$C_{14}H_{11}NO_4$, M + Na]+: 280.07, Found 280.01.

1,4-Dihydroxynaphthalene-2,3-dicarbonitrile (15x)



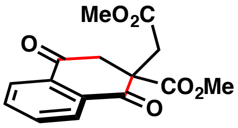
Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and fumaronitrile **14x** (39 mg, 0.5 mmol, 2 equiv), product **15x** was obtained as off white solid (27 mg, 51% yield). TLC R_f = 0.5 ($MeOH/CH_2Cl_2$ = 1:9, v/v). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.48 (br, 2H), 8.34 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.84 (dd, *J* = 6.4, 3.3 Hz, 2H). **^{13}C NMR** (400 MHz, DMSO-d_6) δ 153.30, 130.01, 127.99, 123.72, 115.48, 91.81. **React-IR** (CH_2Cl_2): 2952, 2880, 2366, 1250, 704. **HRMS** calcd for [$C_{12}H_6N_2O_2$, M + Na]+: 233.04, Found 233.05.

Methyl 2-methyl-1,4-dioxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (15y)



Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and methyl methacrylate **14y** (54 µl, 0.5 mmol, 2 equiv), product **15y** was obtained as a yellow oil (35 mg, 60% yield). TLC R_f = 0.4 (Hexane/EtOAc = 2:1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.77 – 7.22 (m, 2H), 3.64 (s, 3H), 3.49 (d, *J* = 16.3 Hz, 1H, diastereotopic), 2.90 (d, *J* = 16.4 Hz, 1H, diastereotopic), 1.6 (s, 3H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 194.07, 193.53, 171.44, 135.04, 134.64, 134.57, 134.12, 127.71, 126.72, 57.10, 53.36, 47.83, 20.92. **React-IR** (CH_2Cl_2): 2916, 2875, 2368, 1704, 728. **HRMS** calcd for [$C_{13}H_{12}O_4$, M + Na]+: 255.07, Found 255.01.

Methyl 2-(2-methoxy-2-oxoethyl)-1,4-dioxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (15z)

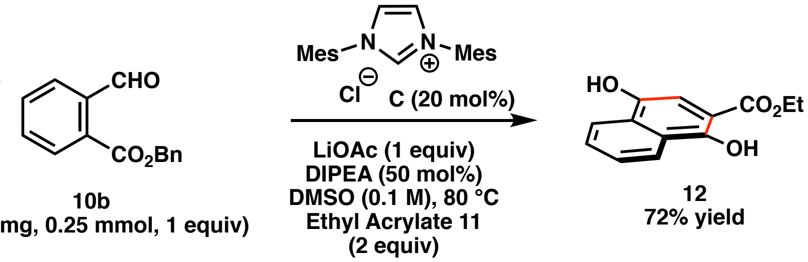


Following the general procedure D, using **10b** (60 mg, 0.25 mmol, 1 equiv) and dimethyl itaconate **14z** (70 µl, 0.5 mmol, 2 equiv), product **15z** was obtained as a light yellow oil (52 mg, 72% yield). TLC R_f = 0.15 (Hexane/EtOAc = 2:1, v/v).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.78 – 7.71 (m, 2H), 3.69 (s, 3H), 3.61 (s, 3H), 3.43 (d, *J* = 16.4 Hz, 1H, diastereotopic), 3.30 (d, *J* = 16.4 Hz, 1H, diastereotopic), 3.23 (d, *J* = 17.5 Hz, 1H, diastereotopic), 3.15 (d, *J* = 17.5 Hz, 1H, diastereotopic). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 192.95, 191.71, 170.98, 169.70, 135.45, 134.90, 134.36, 133.66, 127.86, 126.65, 58.60, 53.68, 52.24, 45.30, 38.17. **React-IR** (CH_2Cl_2): 2916, 2748, 2342, 1702, 727, 703. **HRMS** calcd for [$C_{15}H_{14}O_6$, M + Na]+: 313.08, Found 313.01.

8. Mechanistic Experiments and NMR Studies

A

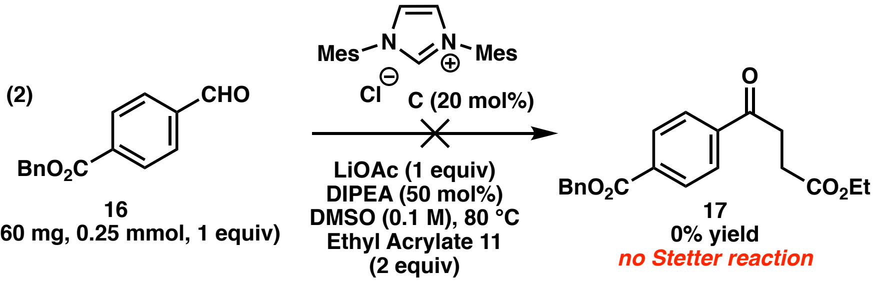
(1)



10b
(60 mg, 0.25 mmol, 1 equiv)

12
72% yield

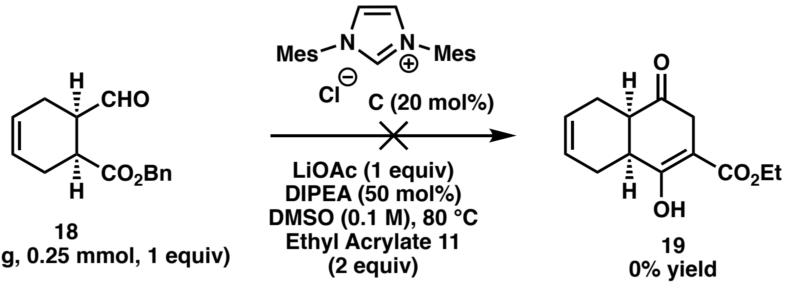
(2)



16
(60 mg, 0.25 mmol, 1 equiv)

17
0% yield
no Stetter reaction

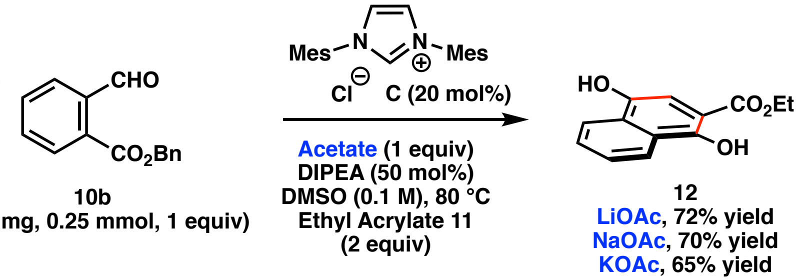
(3)



18
(61 mg, 0.25 mmol, 1 equiv)

19
0% yield
no Stetter reaction/ Dieckman condensation

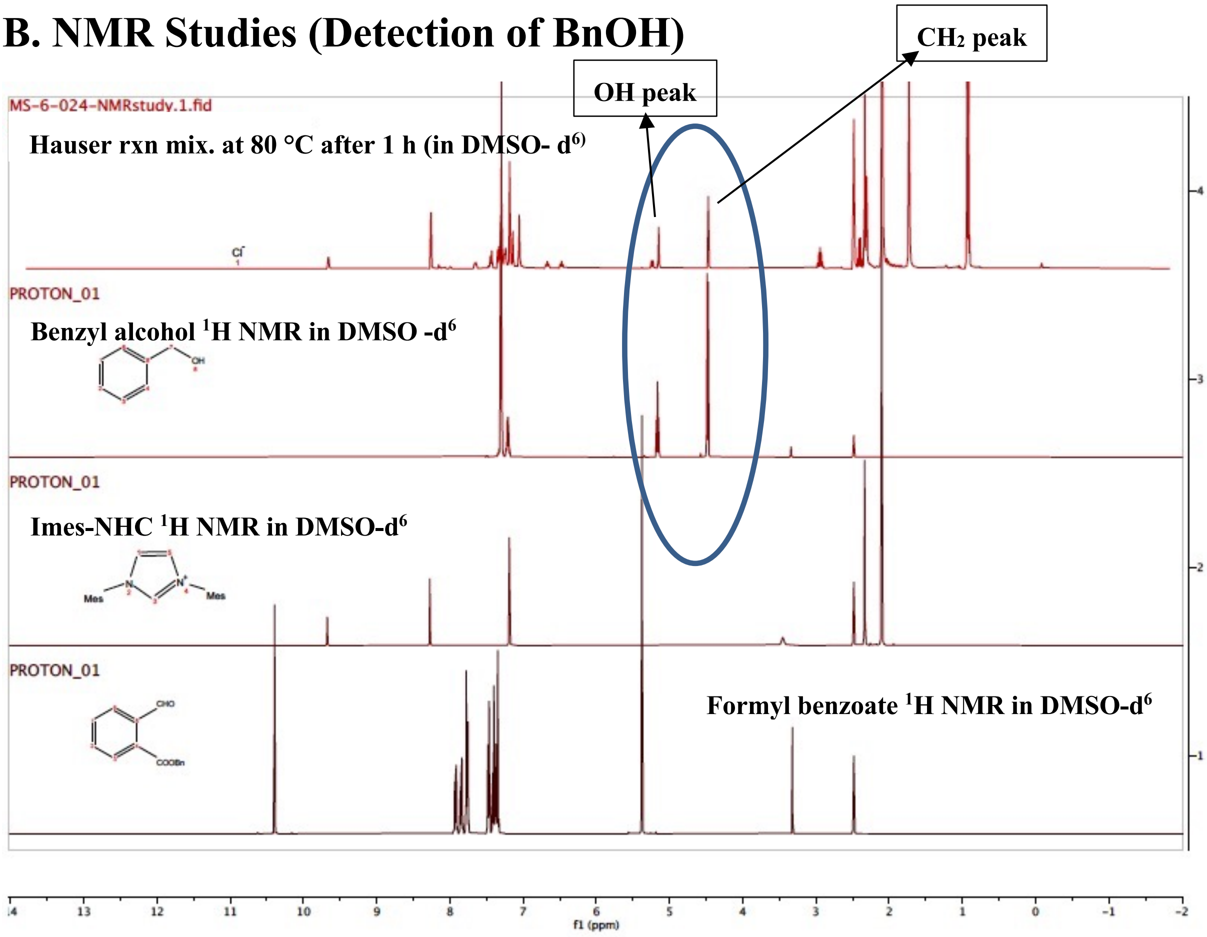
(4)



10b
(60 mg, 0.25 mmol, 1 equiv)

12
LiOAc, 72% yield
NaOAc, 70% yield
KOAc, 65% yield
NH_4OAc, <5% yield

B. NMR Studies (Detection of BnOH)



9. Initial Rate Study Using ^{1}H NMR

Typical Procedure for VT-NMR Initial Rate Study of Catalytic Hauser-Kraus Annulation: In an oven dried NMR tube, a stock solution of reagents (benzyl phthalaldehydate **10b**, benzyl acrylate, Imes-NHC **C**, LiOAc, DIPEA) in DMSO along with the internal standard (trimethoxybenzene) were added, except for the one variable component. The concentration of this variable component was modified in each VT-NMR experiment (80 °C). The progress of the reaction was recorded every 3 minutes over 30 min to obtain stacked NMR spetra. The spetcra were analyzed, and a graph of product formation vs. time created by integrating the product peak with respect to the internal standard (trimethoxybenzene). The slope of each run (obtained via trend-line fitting in Microsoft Excel) was plotted against the concentration of the variable component. Then, the initial rate of the reaction and the rate order of the catalytic Hauser-Kraus Annulation with respect to the variable component was determined.

Experiment 1 (Formyl-benzoate rate study)

Stock solution 1 [S1]: in 2 mL of DMSO

Formyl benzoate = 0.5 mmol = 120 mg

Trimethoxybenzene = 0.1 mmol = 16.8 mg

Stock solution 2 [S2]: in 3 mL DMSO

Acrylate = 3 mmol = 0.46 mL

NHC = 0.3 mmol = 102 mg

LiOAC = 1.5 mmol = 99 mg

DIPEA = 0.75 mmol = 130 µl

Run 1: 0.5 mL [S1] + 0.5 mL [S2] + 1.5 mL neat DMSO

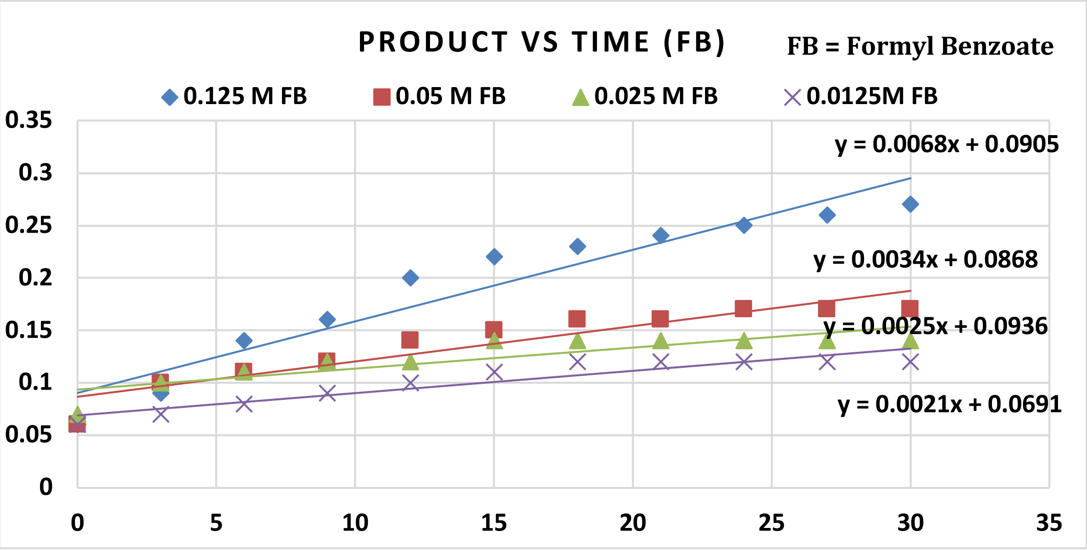
Run 2: 0.2 mL [S1] + 0.5 mL [S2] + 1.8 mL neat DMSO

Run 3: 0.1 mL [S1] + 0.5 mL [S2] + 1.9 mL neat DMSO

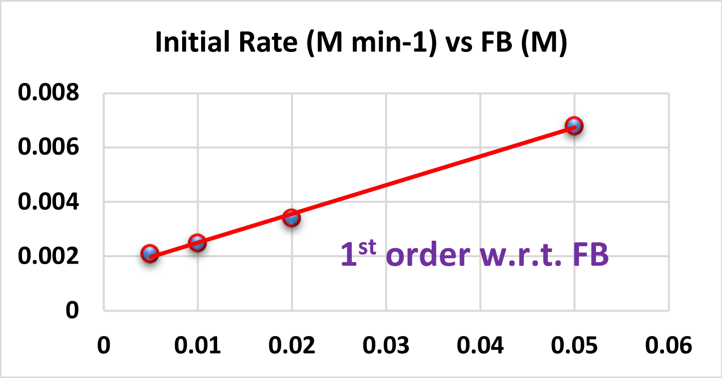
Run 4: 0.05 mL [S1] + 0.5 mL [S2] + 1.95 mL neat DMSO

VT- NMR data

Time (min)	Run 1 0.125M	Run 2 0.05M	Run 3 0.025 M	Run 4 0.0125 M
0	0.06	0.06	0.07	0.06
3	0.09	0.1	0.1	0.07
6	0.14	0.11	0.11	0.08
9	0.16	0.12	0.12	0.09
12	0.2	0.14	0.12	0.1
15	0.22	0.15	0.14	0.11
18	0.23	0.16	0.14	0.12
21	0.24	0.16	0.14	0.12
24	0.25	0.17	0.14	0.12
27	0.26	0.17	0.14	0.12
30	0.27	0.17	0.14	0.12



FB Conc. (M)	Slope (M min^{-1})
0.125	0.0068
0.05	0.0034
0.025	0.0025
0.0125	0.0021



Experiment 2 (Acrylate rate study)

Stock solution 1 [S1]: in 4 mL of DMSO

Acrylate = 1 mmol = 0.153 mL

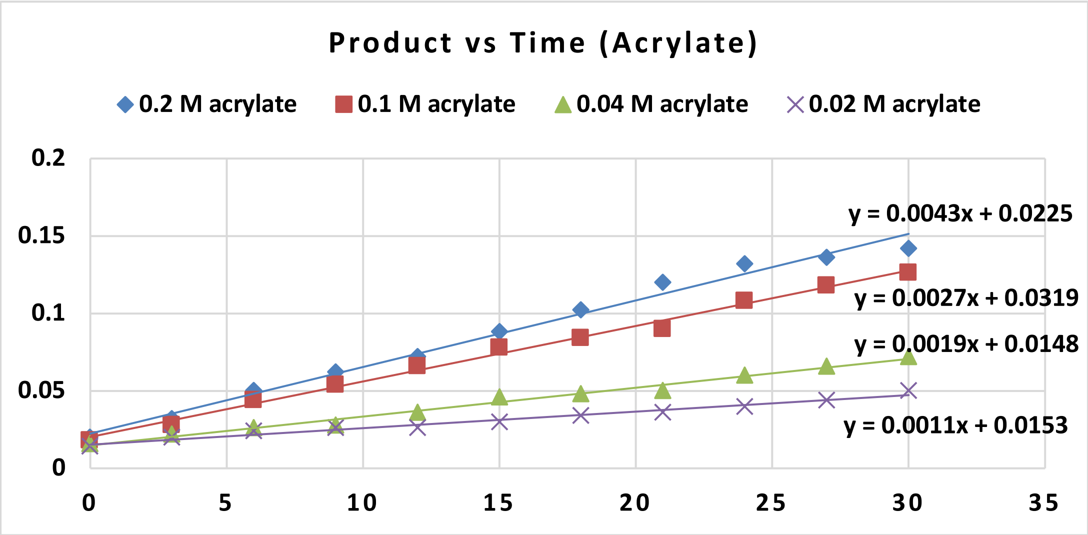
Stock solution 2 [S2]: in 3 mL DMSO

Formyl-benzoate = 1.5 mmol = 360 mg
NHC = 0.3 mmol = 102 mg
LiOAC = 1.5 mmol = 99 mg
DIPEA = 0.75 mmol = 130 µl
Trimethoxybenzene = 0.1 mmol = 16.8 mg

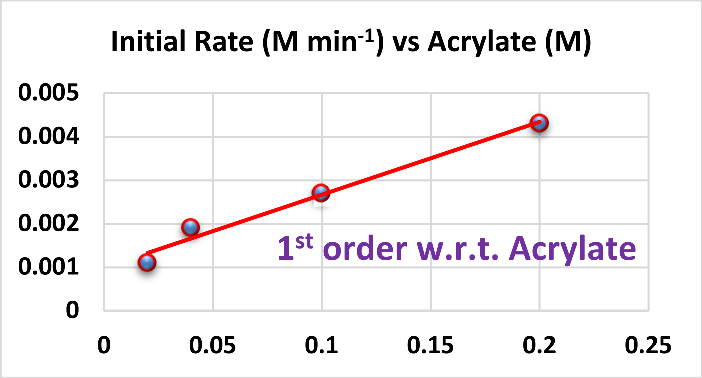
Run 1: 2 mL [S1] + 0.5 mL [S2]
Run 2: 1 mL [S1] + 0.5 mL [S2] + 1 mL neat DMSO
Run 3: 0.4 mL [S1] + 0.5 mL [S2] + 1.6 mL neat DMSO
Run 4: 0.2 mL [S1] + 0.5 mL [S2] + 1.8 mL neat DMSO

VT- NMR data

Time (min)	Run 1 0.2 M	Run 2 0.1M	Run 3 0.04 M	Run 4 0.02 M
0	0.02	0.018	0.016	0.014
3	0.032	0.028	0.022	0.02
6	0.05	0.044	0.026	0.024
9	0.062	0.054	0.028	0.026
12	0.072	0.066	0.036	0.026
15	0.088	0.078	0.046	0.03
18	0.102	0.084	0.048	0.034
21	0.12	0.09	0.05	0.036
24	0.132	0.108	0.06	0.04
27	0.136	0.118	0.066	0.044
30	0.142	0.126	0.072	0.05



Acylate Conc. (M)	Slope (M min^{-1})
0.2	0.0043
0.1	0.0027
0.04	0.0019
0.02	0.0011



Experiment 3 (NHC rate study)

Stock solution 1 [S1]: in 0.4 mL of DMSO

NHC = 0.1 mmol = 34.1 mg

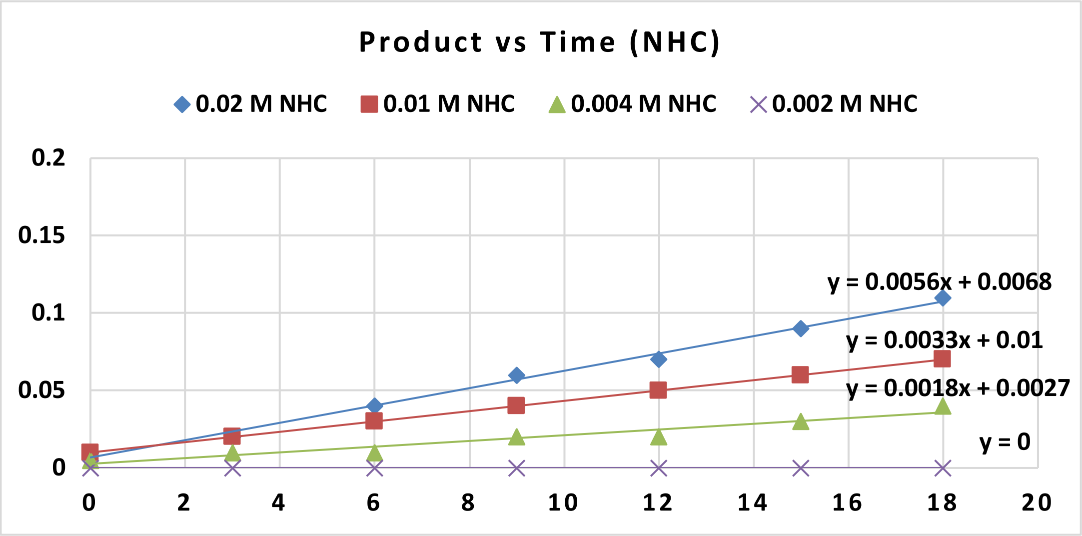
Stock solution 2 [S2]: in 2.5 mL DMSO

Formyl-benzoate = 1.25 mmol = 300 mg
Acrylate = 2.5 mmol = 0.38 mL
LiOAC = 1.25 mmol = 82.5 mg
DIPEA = 0.625 mmol = 108 µl
Trimethoxybenzene = 0.25 mmol = 42 mg

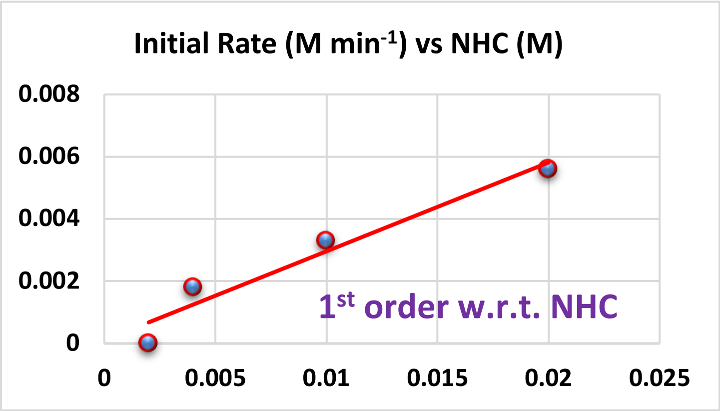
VT- NMR data

Time (min)	Run 1 0.02 M	Run 2 0.01M	Run 3 0.004 M	Run 4 0.002 M
0	0.01	0.01	0.005	0
3	0.02	0.02	0.01	0
6	0.04	0.03	0.01	0
9	0.06	0.04	0.02	0
12	0.07	0.05	0.02	0
15	0.09	0.06	0.03	0
18	0.11	0.07	0.04	0

Run 1: 0.2 mL [S1] + 0.5 mL [S2] + 1.8 mL neat DMSO
Run 2: 0.1 mL [S1] + 0.5 mL [S2] + 1.9 mL neat DMSO
Run 3: 0.04 mL [S1] + 0.5 mL [S2] + 1.96 mL neat DMSO
Run 4: 0.02 mL [S1] + 0.5 mL [S2] + 1.98 mL neat DMSO



NHC Conc. (M)	Slope $(M\ min^{-1})$
0.02	0.0056
0.01	0.033
0.004	0.0018
0.002	0



Experiment 4 (LiOAc rate study)

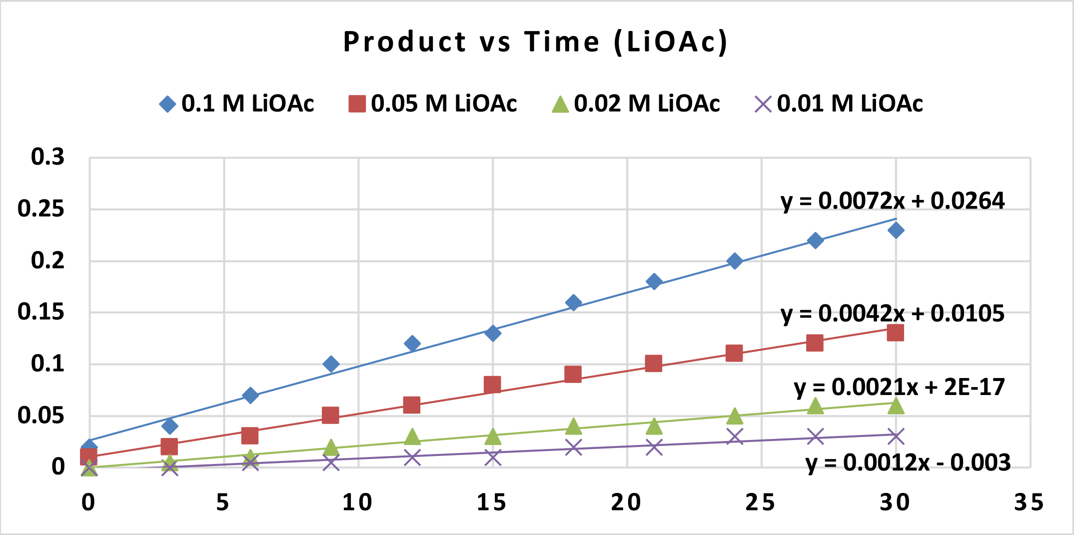
Stock solution 1 [S1]: in 2 mL of DMSO
LiOAC = 0.5 mmol = 33 mg

Stock solution 2 [S2]: in 2.5 mL DMSO
Formyl-benzoate = 1.25 mmol = 300 mg
Acrylate = 2.5 mmol = 0.38 mL
NHC = 0.25 mmol = 85 mg
DIPEA = 0.625 mmol = 108 µl
Trimethoxybenzene = 0.25 mmol = 42 mg

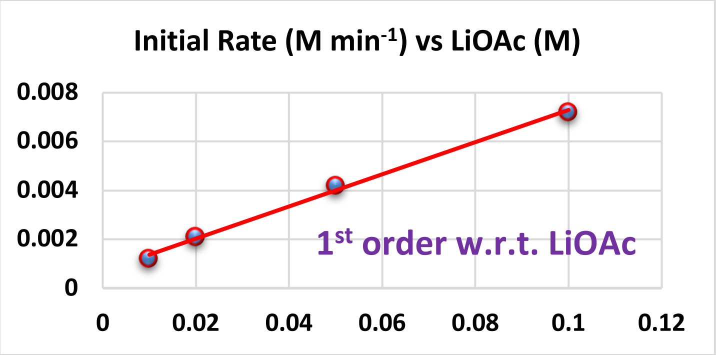
Run 1: 1 mL [S1] + 0.5 mL [S2] + 1 mL neat DMSO
Run 2: 0.5 mL [S1] + 0.5 mL [S2] + 1.5 mL neat DMSO
Run 3: 0.2 mL [S1] + 0.5 mL [S2] + 1.8 mL neat DMSO
Run 4: 0.1 mL [S1] + 0.5 mL [S2] + 1.9 mL neat DMSO

VT- NMR data

Time (min)	Run 1 0.1 M	Run 2 0.05M	Run 3 0.02 M	Run 4 0.01 M
0	0.02	0.01	0	0
3	0.04	0.02	0.005	0
6	0.07	0.03	0.01	0.005
9	0.1	0.05	0.02	0.005
12	0.12	0.06	0.03	0.01
15	0.13	0.08	0.03	0.01
18	0.16	0.09	0.04	0.02
21	0.18	0.1	0.04	0.02
24	0.2	0.11	0.05	0.03
27	0.22	0.12	0.06	0.03
30	0.23	0.13	0.06	0.03



LiOAc Conc. (M)	Slope (M min^{-1})
0.1	0.0072
0.05	0.0042
0.02	0.0021
0.01	0.0012



Experiment 5 (DIPEA rate study)

Stock solution 1 [S1]: in 4 mL of DMSO

DIPEA = 0.5 mmol = 87 µl

Stock solution 2 [S2]: in 2.5 mL DMSO

Formyl-benzoate = 1.25 mmol = 300 mg

Acrylate = 2.5 mmol = 0.38 mL

LiOAC = 1.25 mmol = 82.5 mg

NHC = 0.25 mmol = 85 mg

Trimethoxybenzene = 0.25 mmol = 42 mg

Run 1: 1 mL [S1] + 0.5 mL [S2] + 1 mL neat DMSO

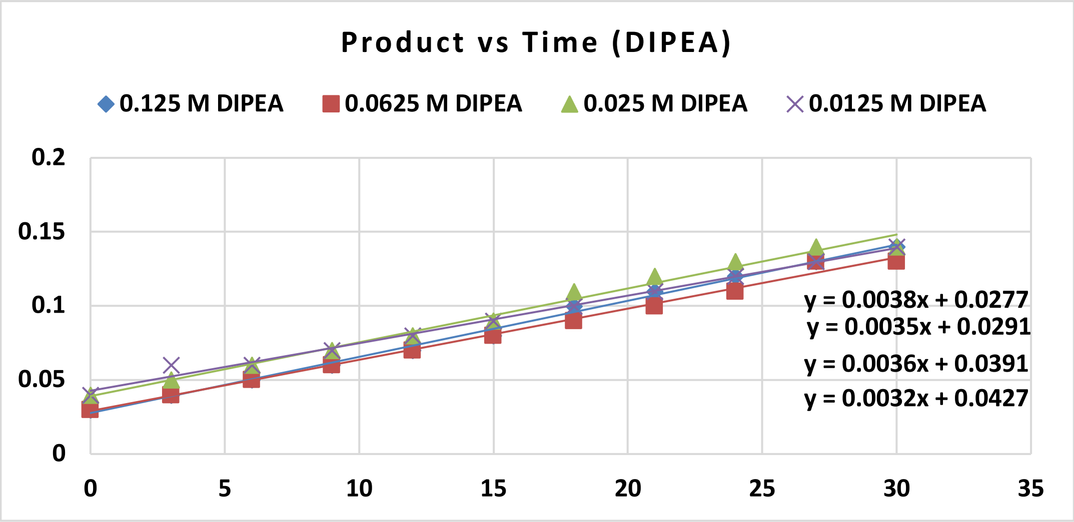
Run 2: 0.5 mL [S1] + 0.5 mL [S2] + 1.5 mL neat DMSO

Run 3: 0.2 mL [S1] + 0.5 mL [S2] + 1.8 mL neat DMSO

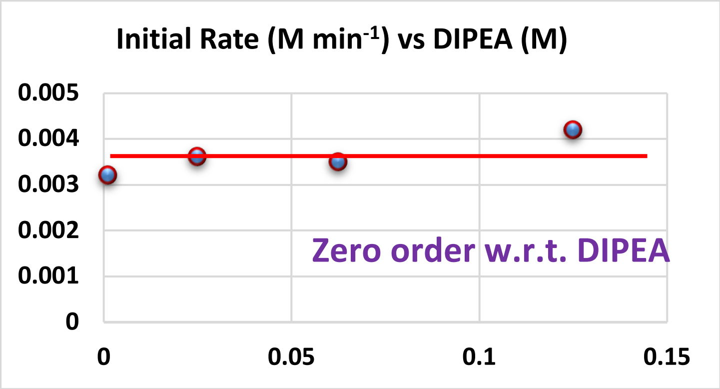
Run 4: 0.1 mL [S1] + 0.5 mL [S2] + 1.9 mL neat DMSO

VT- NMR data

Time (min)	Run 1 0.125 M	Run 2 0.063M	Run 3 0.025 M	Run 4 0.013 M
0	0.03	0.03	0.04	0.04
3	0.04	0.04	0.05	0.06
6	0.05	0.05	0.06	0.06
9	0.06	0.06	0.07	0.07
12	0.07	0.07	0.08	0.08
15	0.08	0.08	0.09	0.09
18	0.1	0.09	0.11	0.1
21	0.11	0.1	0.12	0.11
24	0.12	0.11	0.13	0.12
27	0.13	0.13	0.14	0.13
30	0.14	0.13	0.14	0.14



DIPEA Conc. (M)	Slope ($M\ min^{-1}$)
0.125	0.0038
0.0625	0.0035
0.025	0.0036
0.0125	0.0032



10. References

(1) Chanthamath, S.; Takaki, S.; Shibatomi, K.; Iwasa, S. Highly Stereoselective Cyclopropanation of α,β -Unsaturated Carbonyl Compounds with Methyl (Diazoacetoxy) acetate Catalyzed by a Chiral Ruthenium (II) Complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 5818–5821.

(2) Firth, J. D.; Craven, P. G. E.; Lilburn, M.; Pahl, A.; Marsden, S. P.; Nelson, A. A Biosynthesis-Inspired Approach to Over Twenty Diverse Natural Product-Like Scaffolds. *Chem. Commun.* **2016**, *52*, 9837–9840.

(3) Tiwari, P. K.; Aidhen, I. S. Weinreb Amide Based Building Block for Convenient Access to Vinyl Ketones. *Synlett* **2013**, *24*, 1777–1780.

(4) Mirabdolbaghi, R.; Dudding, T. An Indium-Mediated Allylative/Trans Esterification DFT-Directed Approach to Chiral $C_{(3)}$-Functionalized Phthalides. *Org. Lett.* **2012**, *14*, 3748–3751.

(5) Maresh, J.; Zhang, J.; Tzeng, Y.-L.; Goodman N. A.; Lynn D. G. Rational Design of Inhibitors of VirA-VirG Two-Component Signal Transduction. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3281–3286.

(6) Meng, J.-L.; Jiao, T.-Q.; Chen, Y.-H.; Fu R.; Zhang S.-S.; Zhao, Q.; Feng, C.-G.; Lin, G.-Q. Synthesis of Chiral isoindolinones via Asymmetric Propargylation Lactamization Cascade. *Tet. Lett.* **2018**, *59*, 1564–1567.

(7) Beck, D. E.; Abdelmalak, M.; Lv, W.; Reddy P. V. N.; Tender G. S.; O'Neill, E.; Agama, K.; Marchand, C.; Pommier, Y.; Cushman M. Discovery of Potent Indenoisoquinoline Topoisomerase I Poisons Lacking the 3-Nitro Toxixophore. *J. Med. Chem.* **2015**, *58*, 3997–4015.

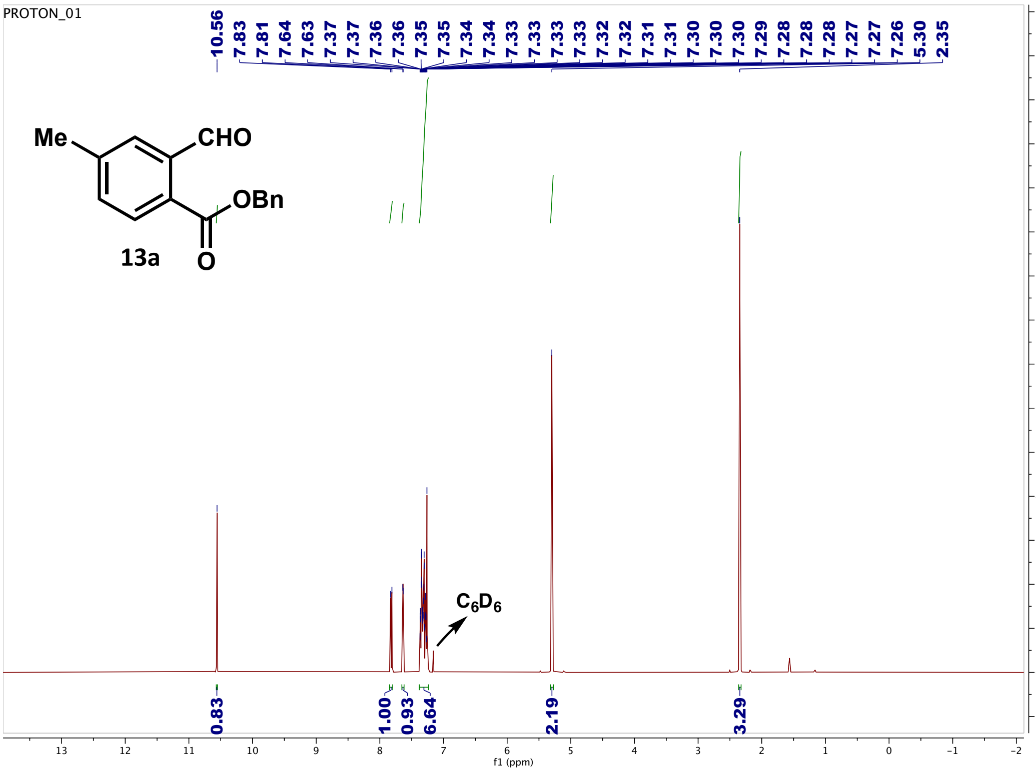
(8) Sun, F.-G.; Huang, X.-L.; Song, Y. Diastereoselective Synthesis of 4-Hydroxytetralones via a Cascade Stetter-Aldol Reaction Catalyzed by N-Heterocyclic Carbenes. *J. Org. Chem.* **2010**, *75*, 273–276.

(9) Oelgemoller, M.; Schiel, C.; Frohlich, R.; Mattay, J. The "Photo-Friedel-Crafts Acylation" of 1,4-Naphthoquinones. *Eur. J. Org. Chem.* **2002**, 2465–2474.

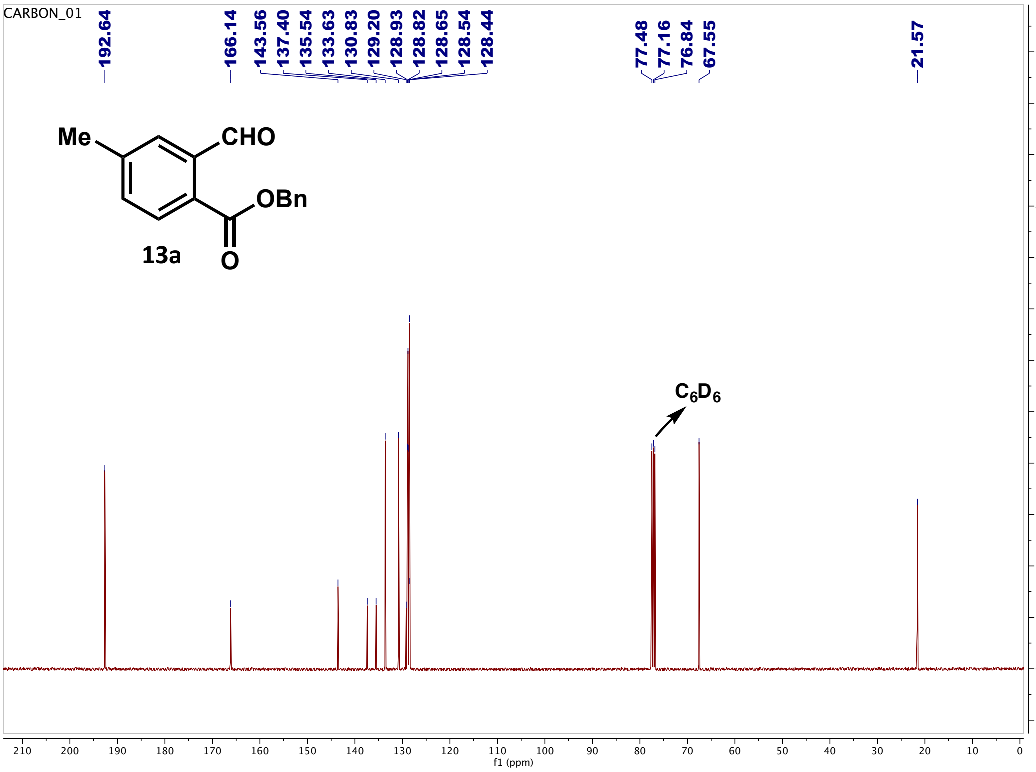
(10) Mitchell, L. J.; Lewis, W.; Moody, C. J. Solar Photochemistry: Optimisation of the Photo Friedel-Crafts Acylation of Naphthoquinones. *Green. Chem.* **2013**, *15*, 2830–2842.

11. NMR spectra

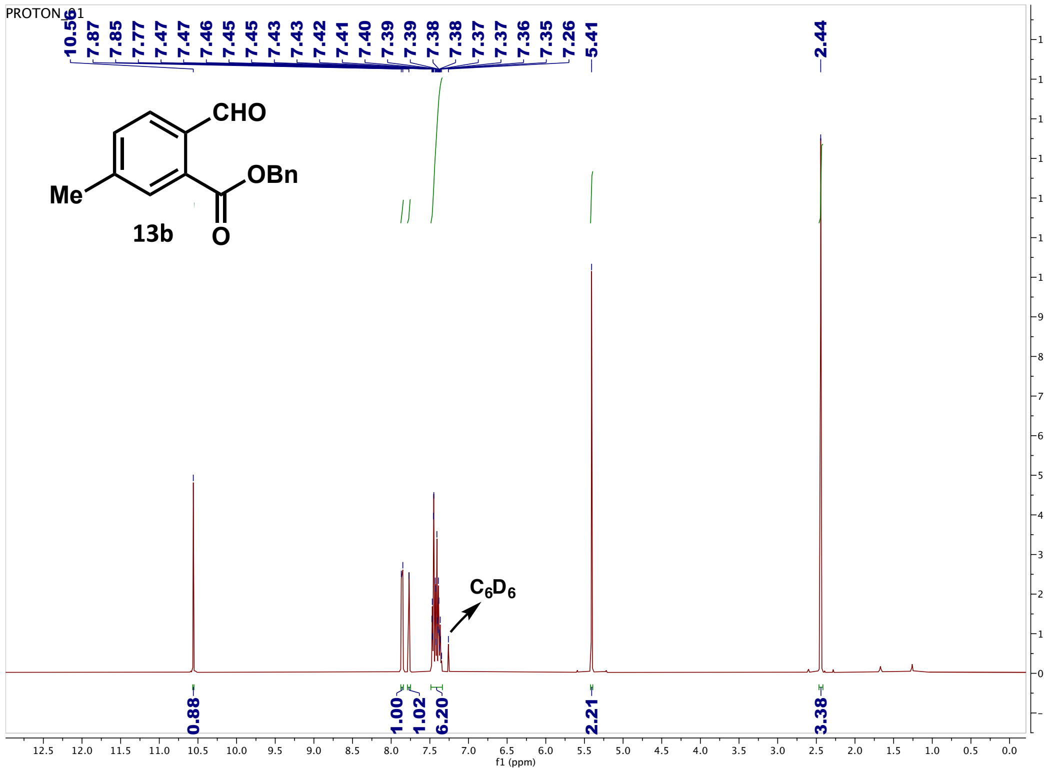
^{1}H NMR (C_6D_6, 400 MHz)



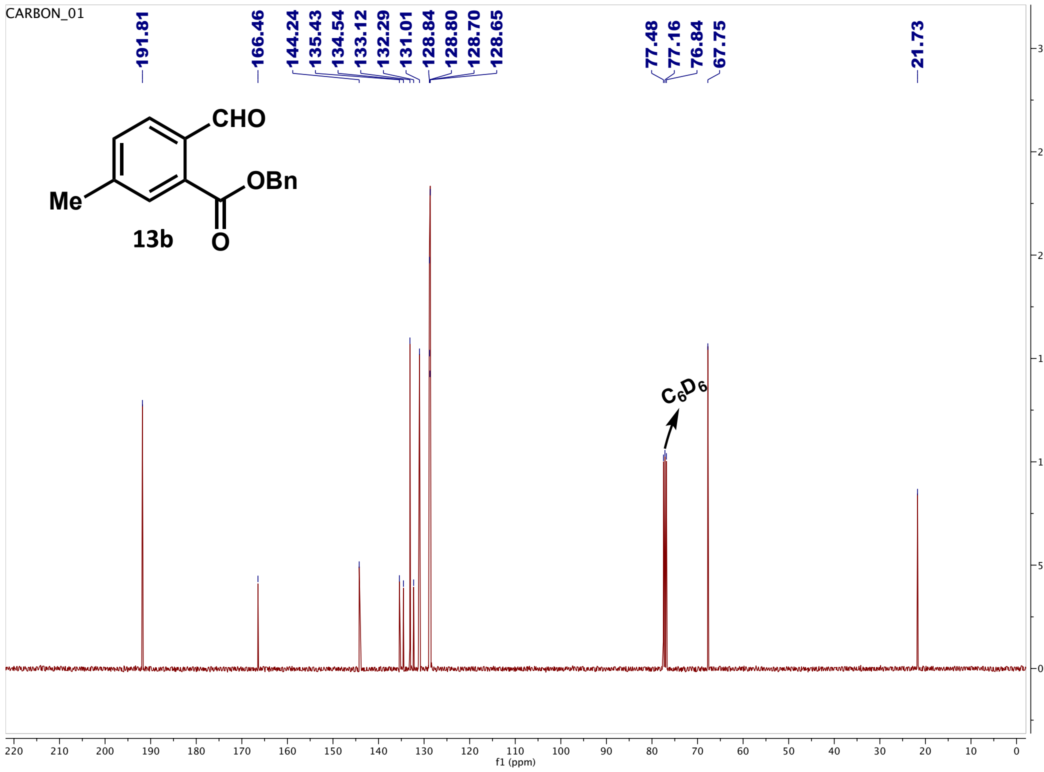
^{13}C NMR (C_6D_6, 100 MHz)



^{1}H NMR (C_6D_6, 400 MHz)



^{13}C NMR (C_6D_6, 100 MHz)



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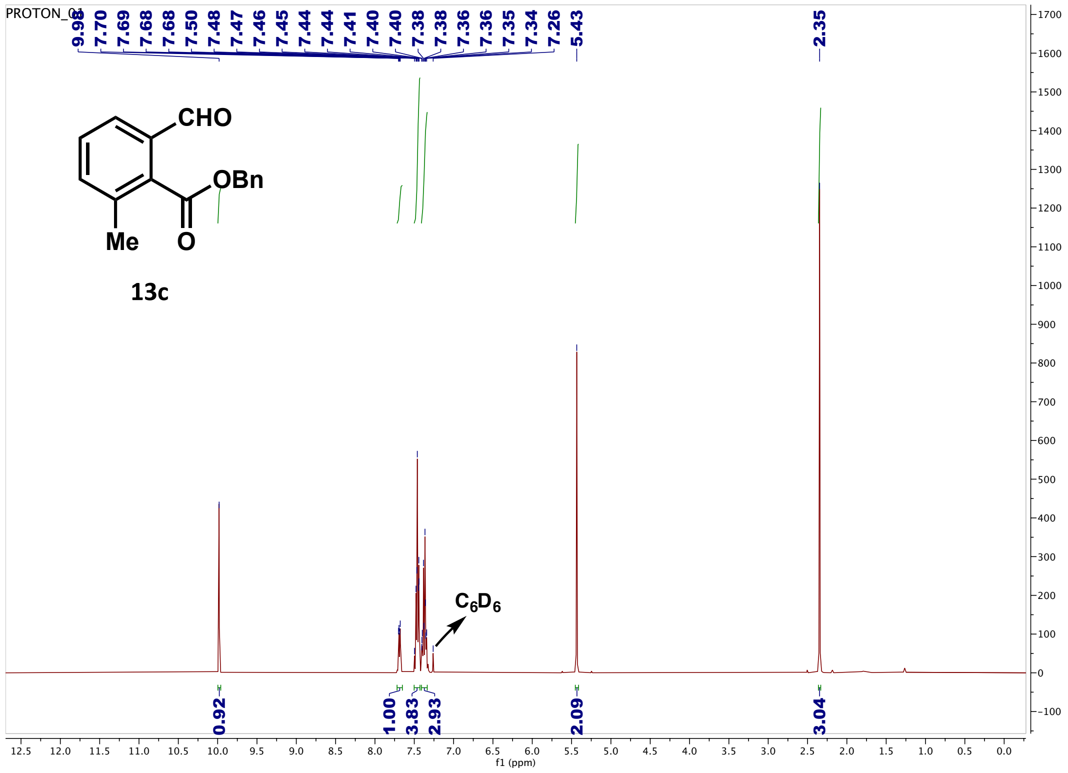

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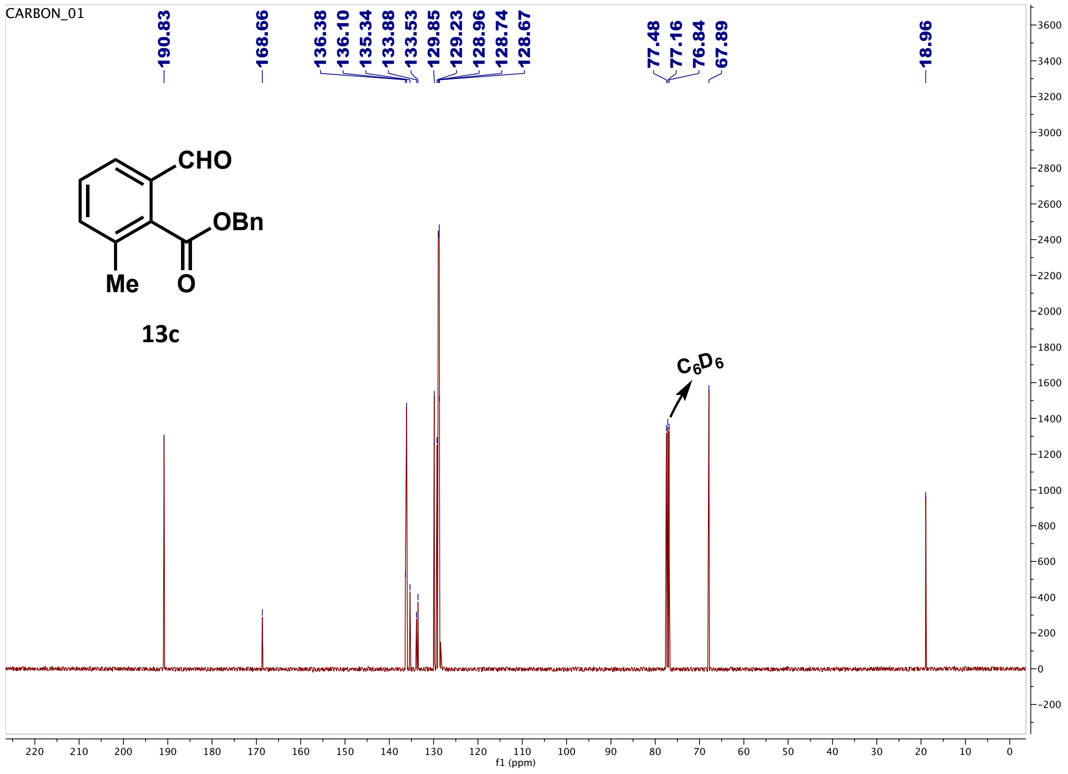

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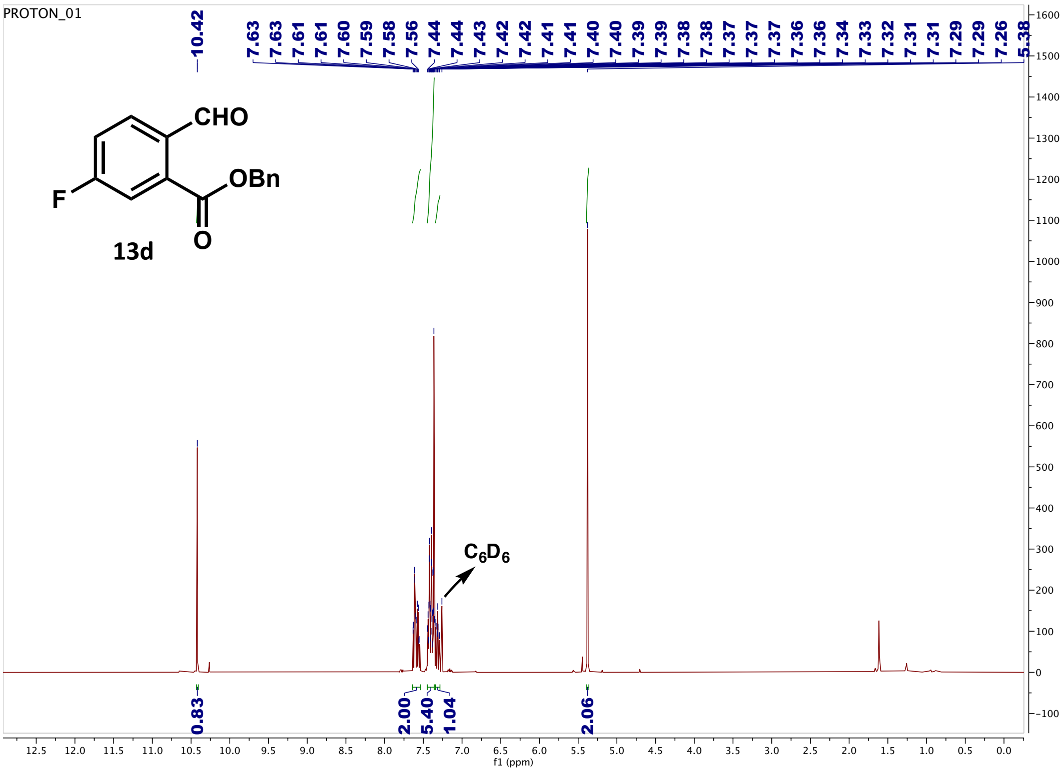

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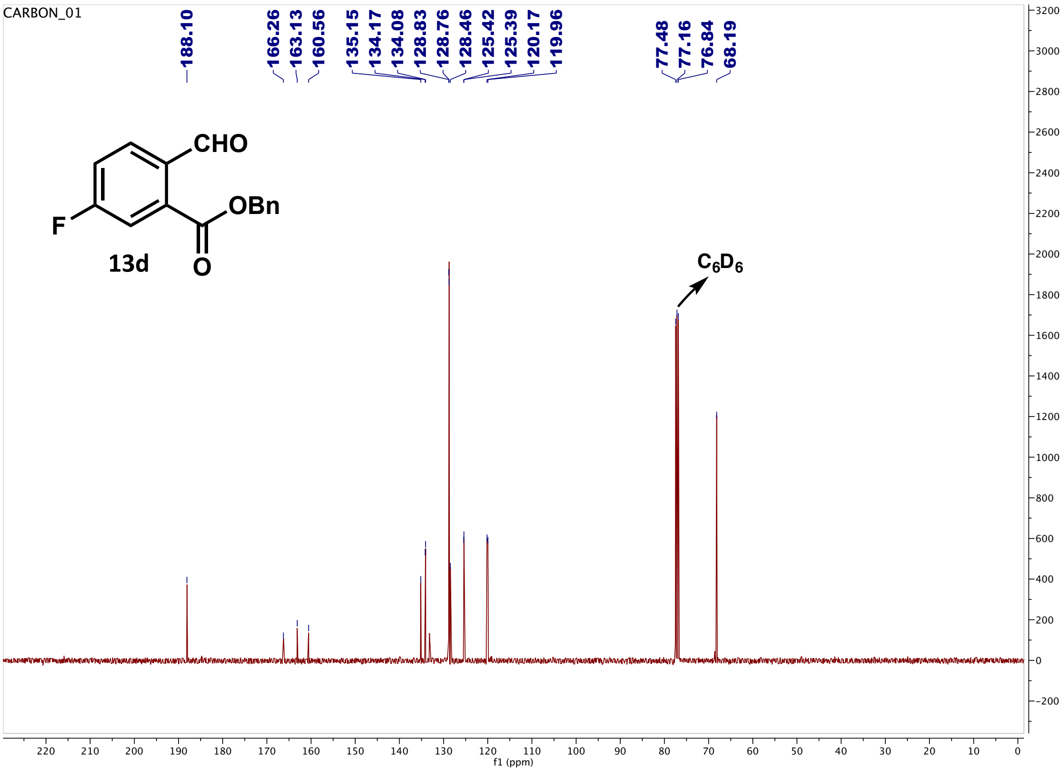

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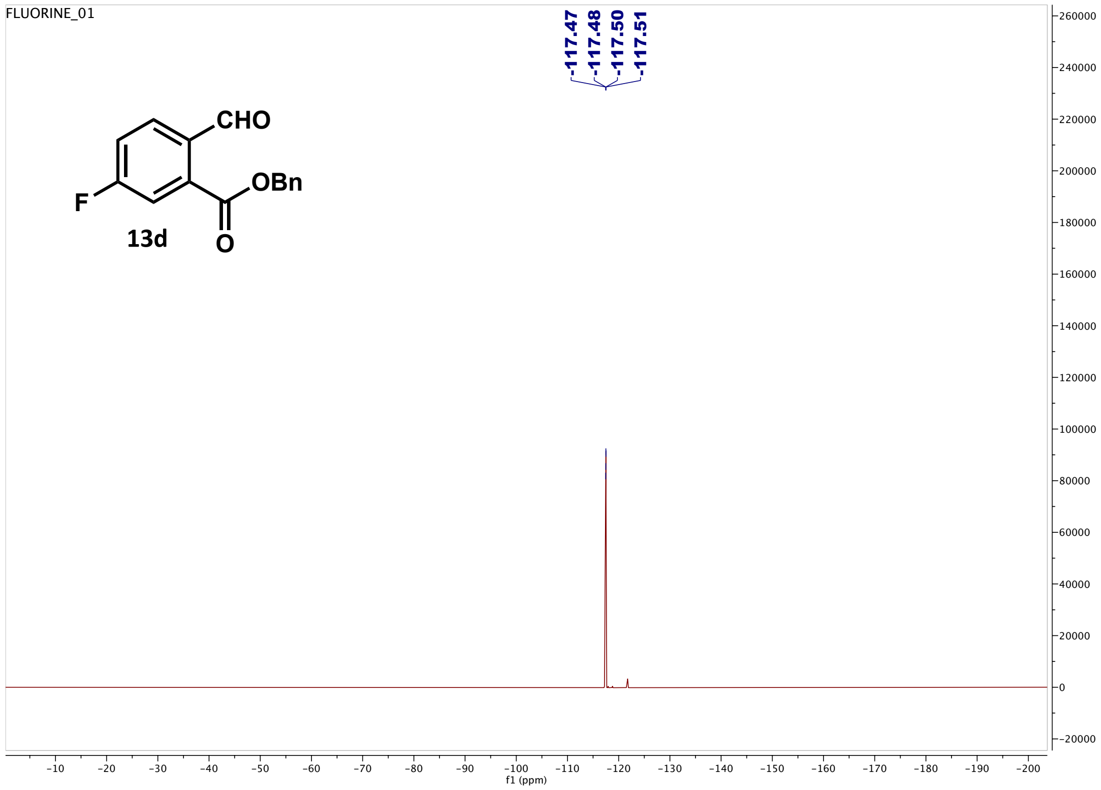

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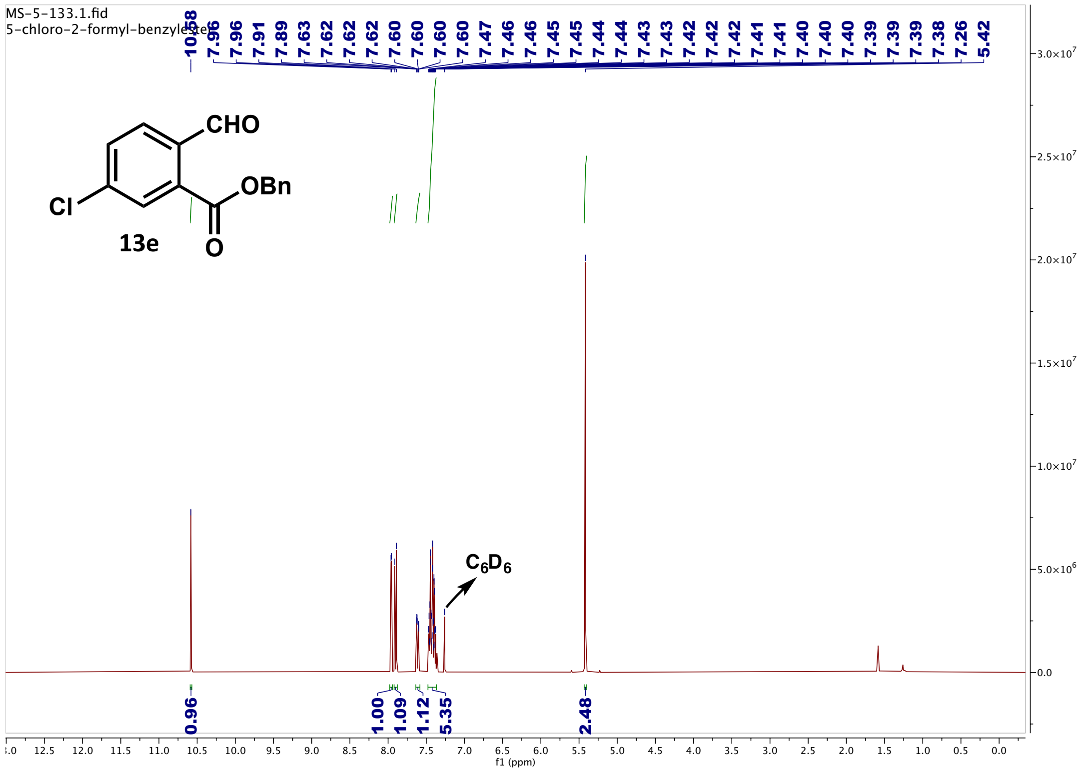

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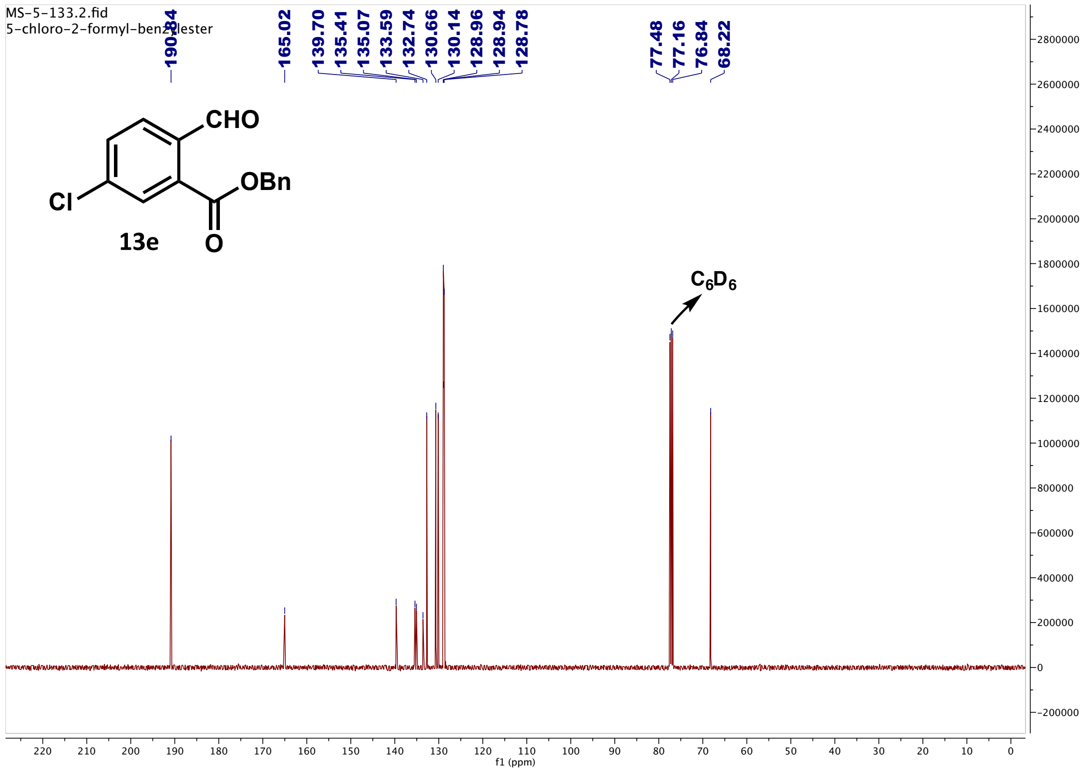

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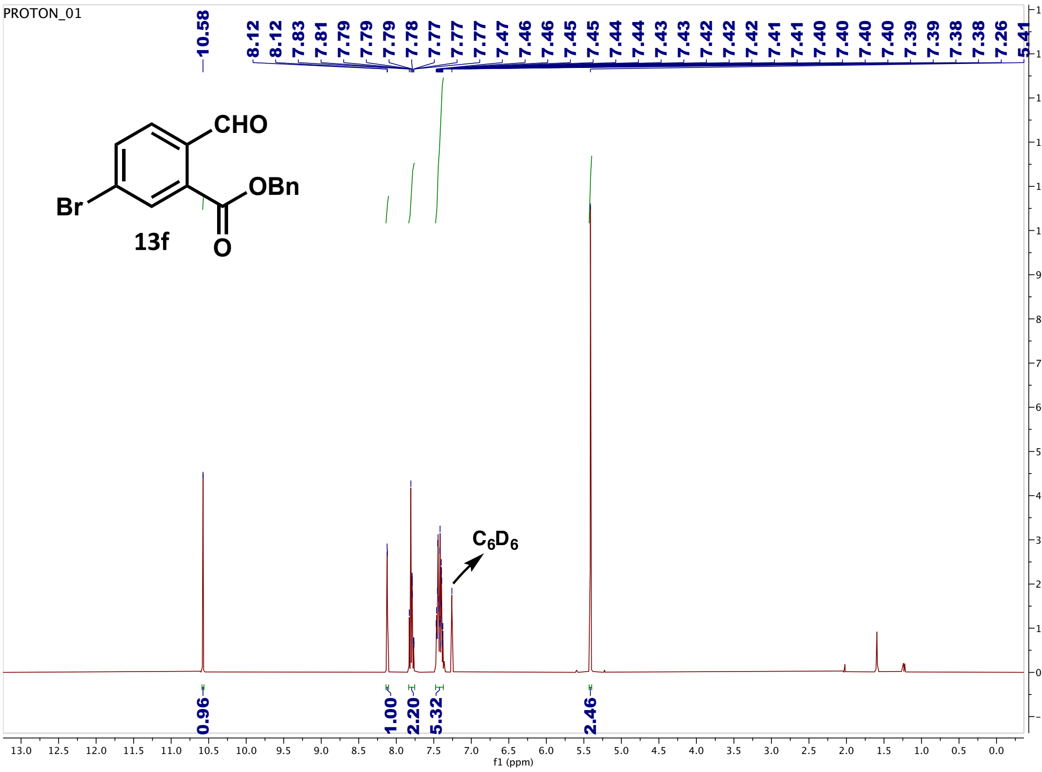

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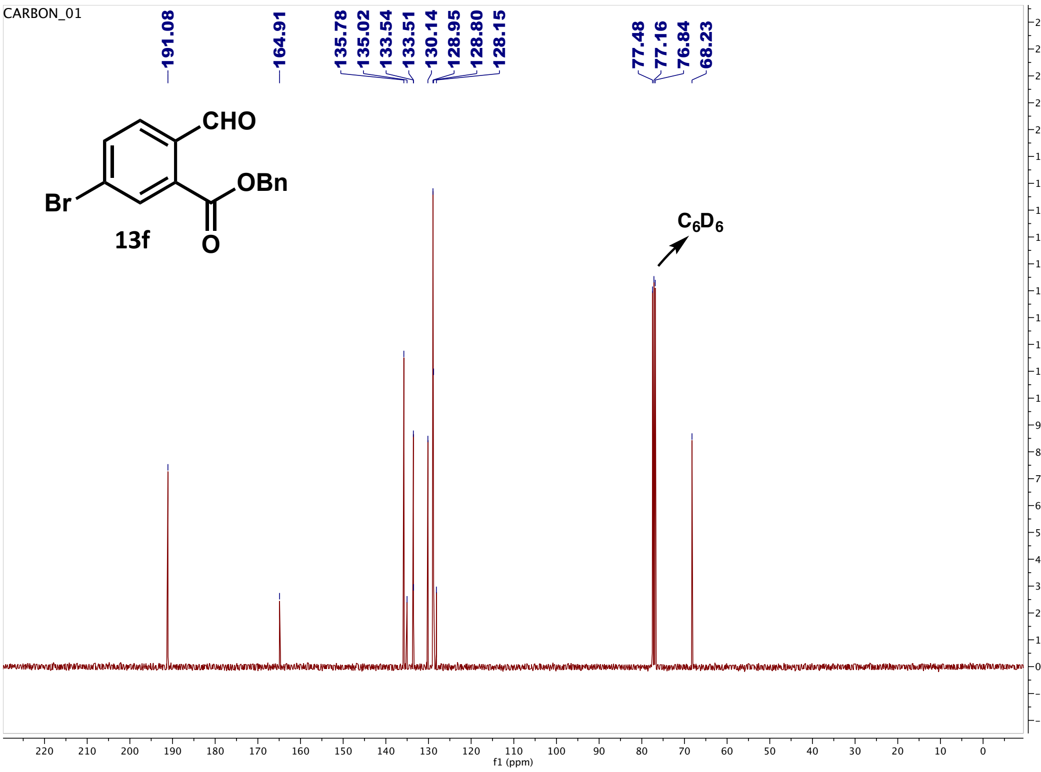

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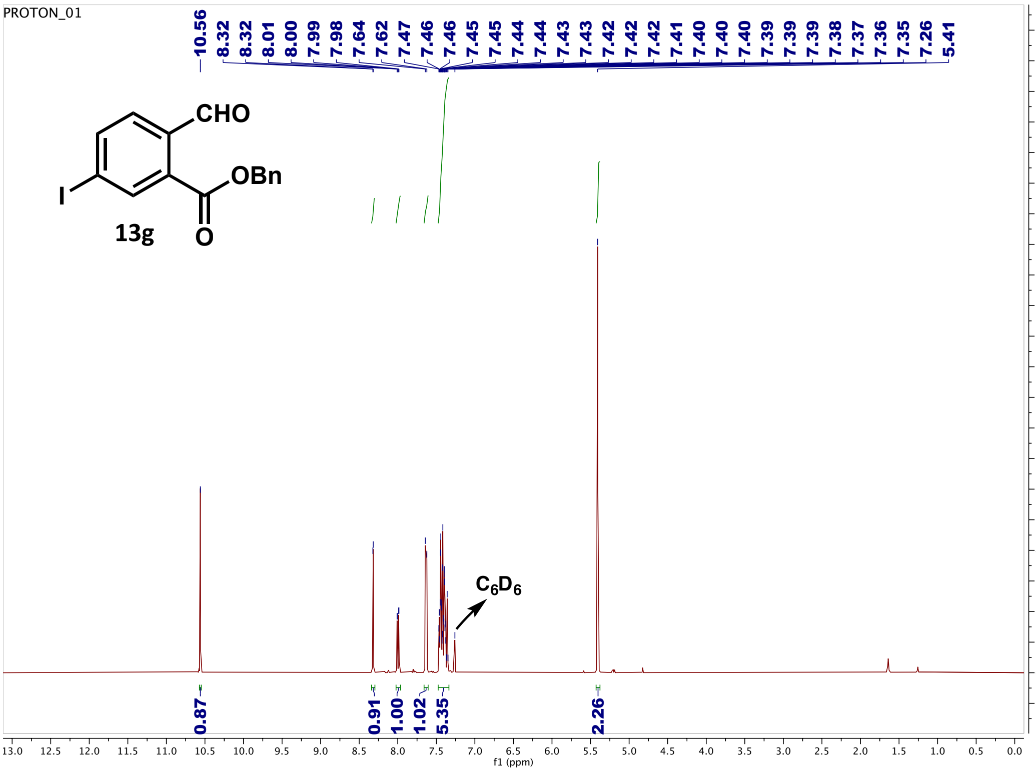

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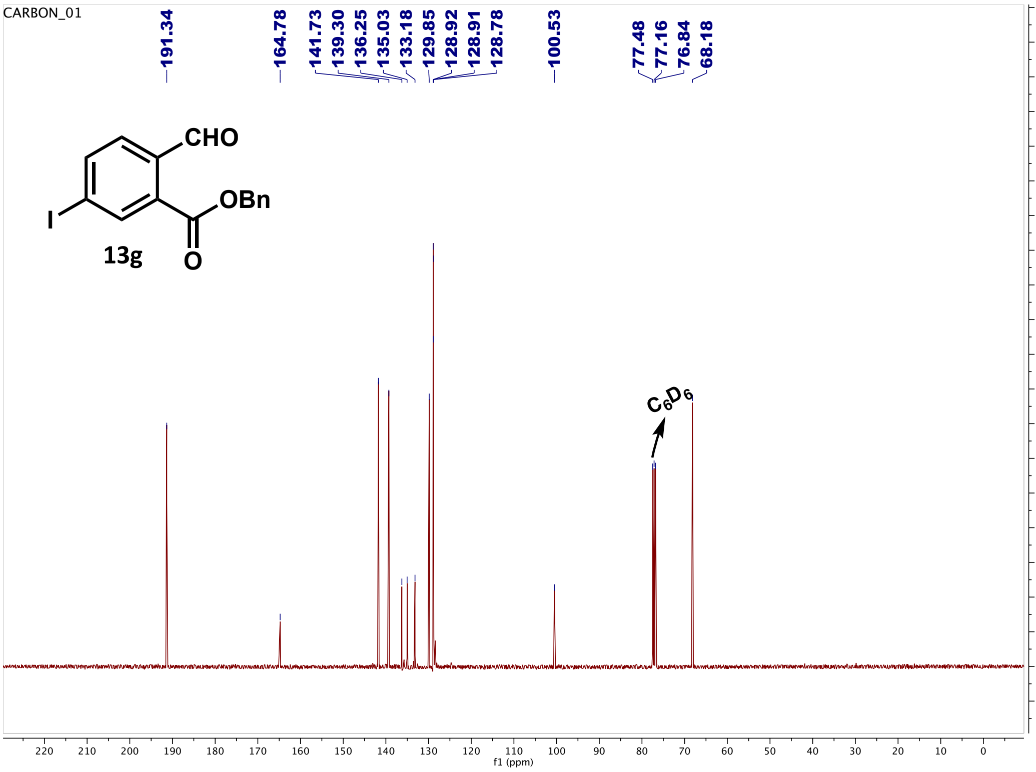

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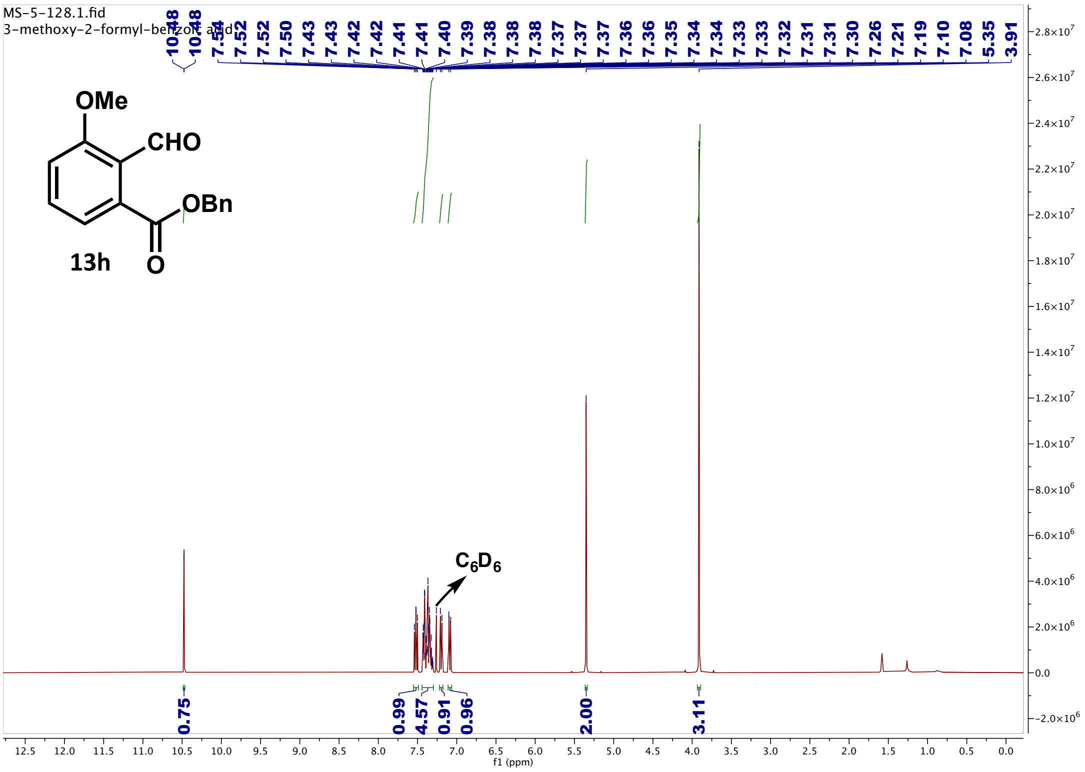

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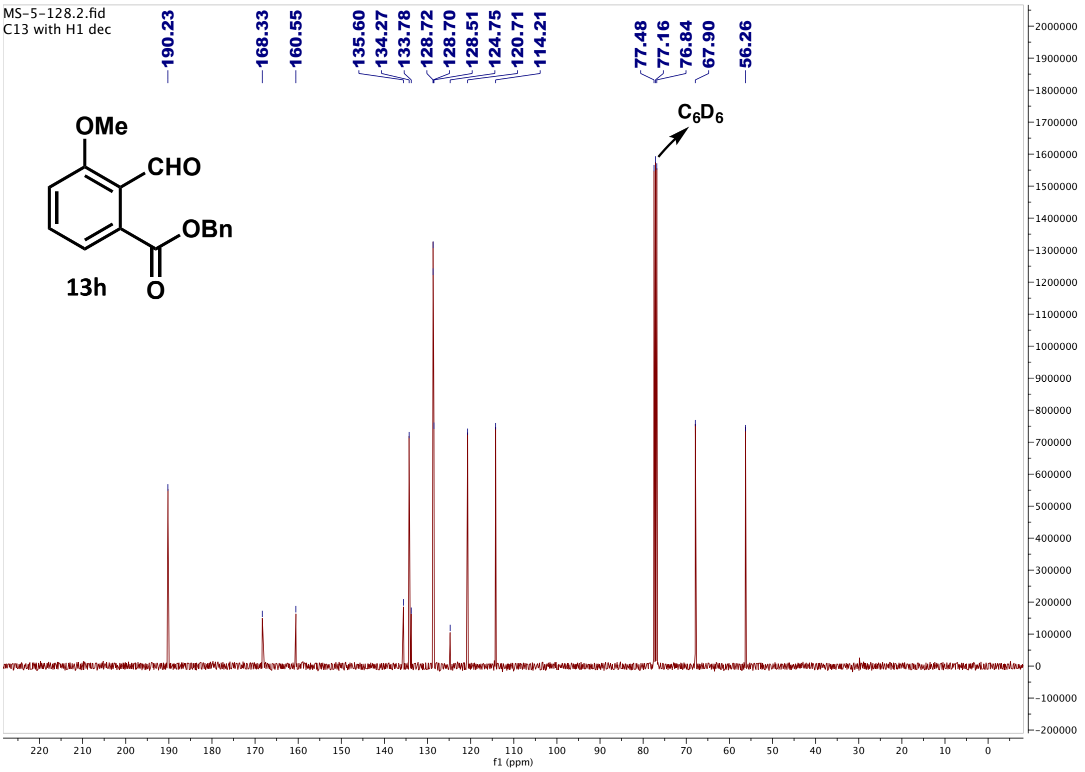

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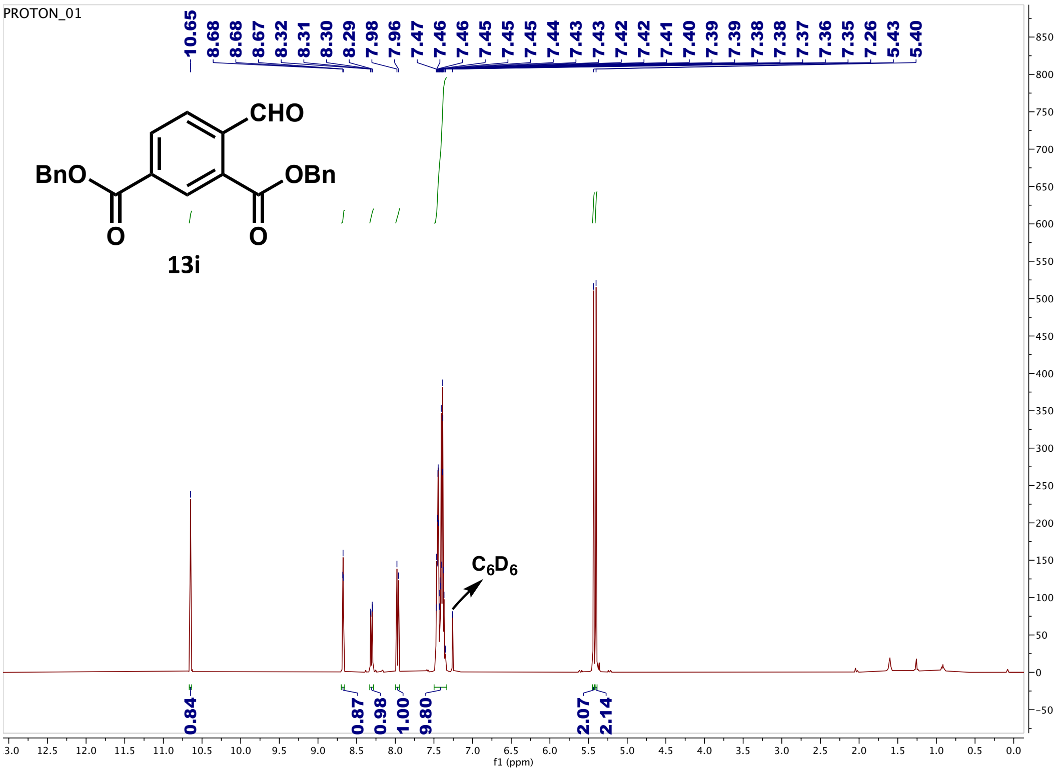

13i

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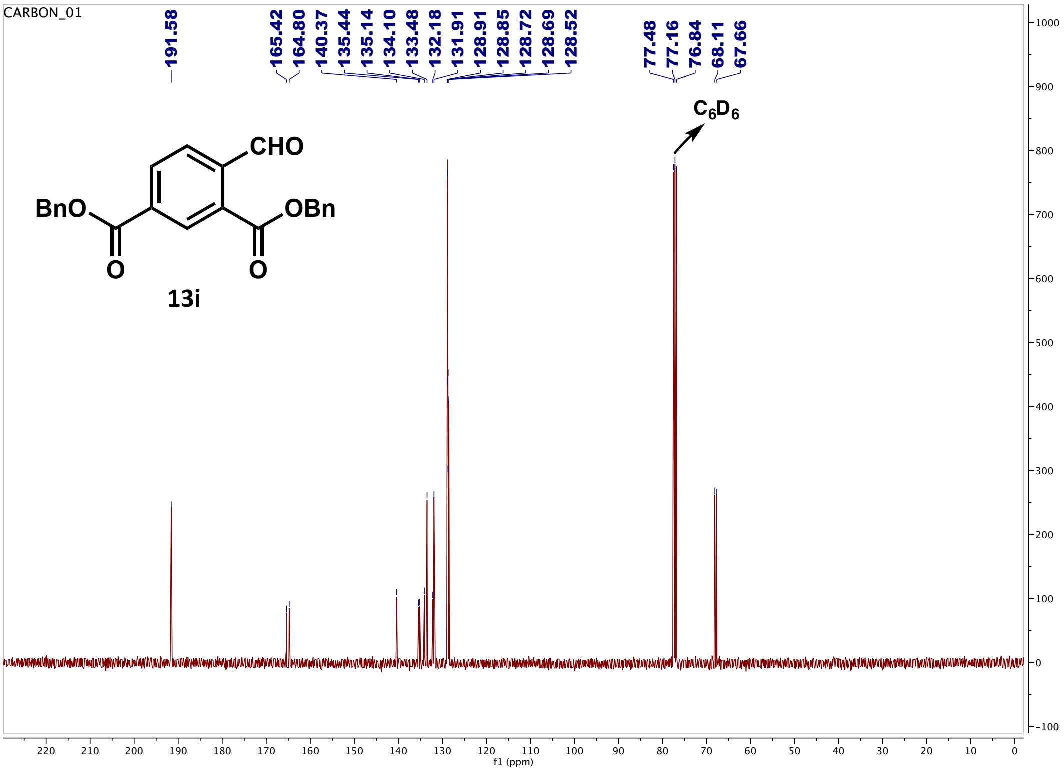

13i

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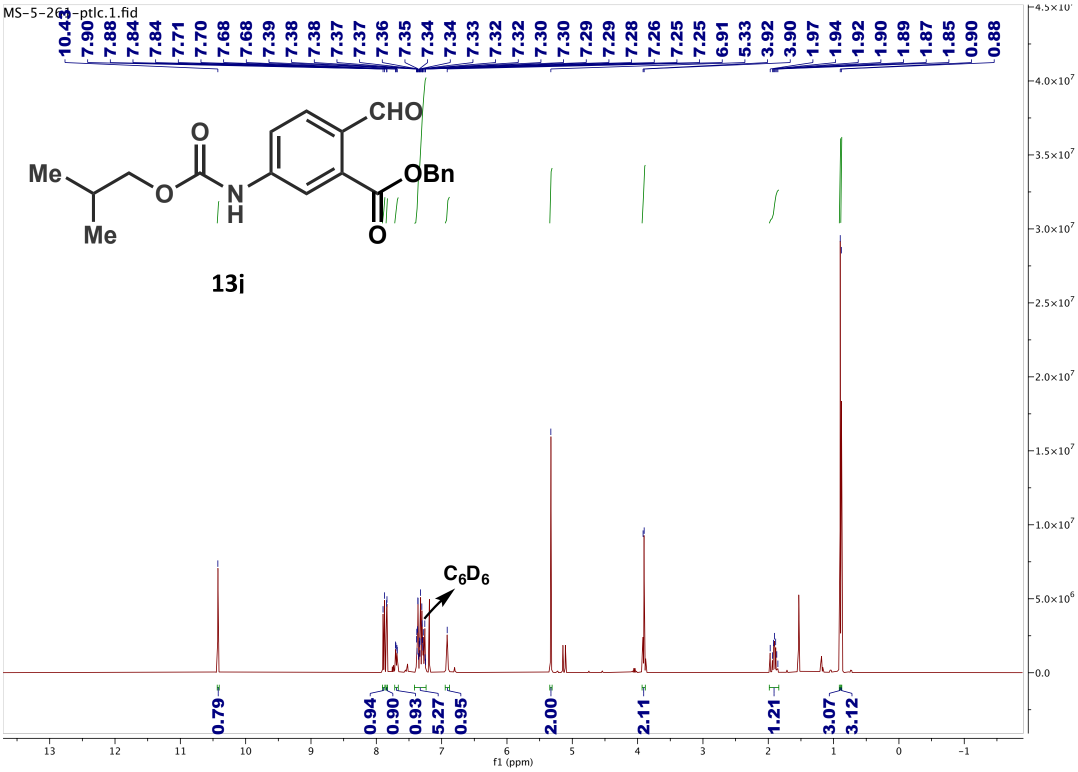

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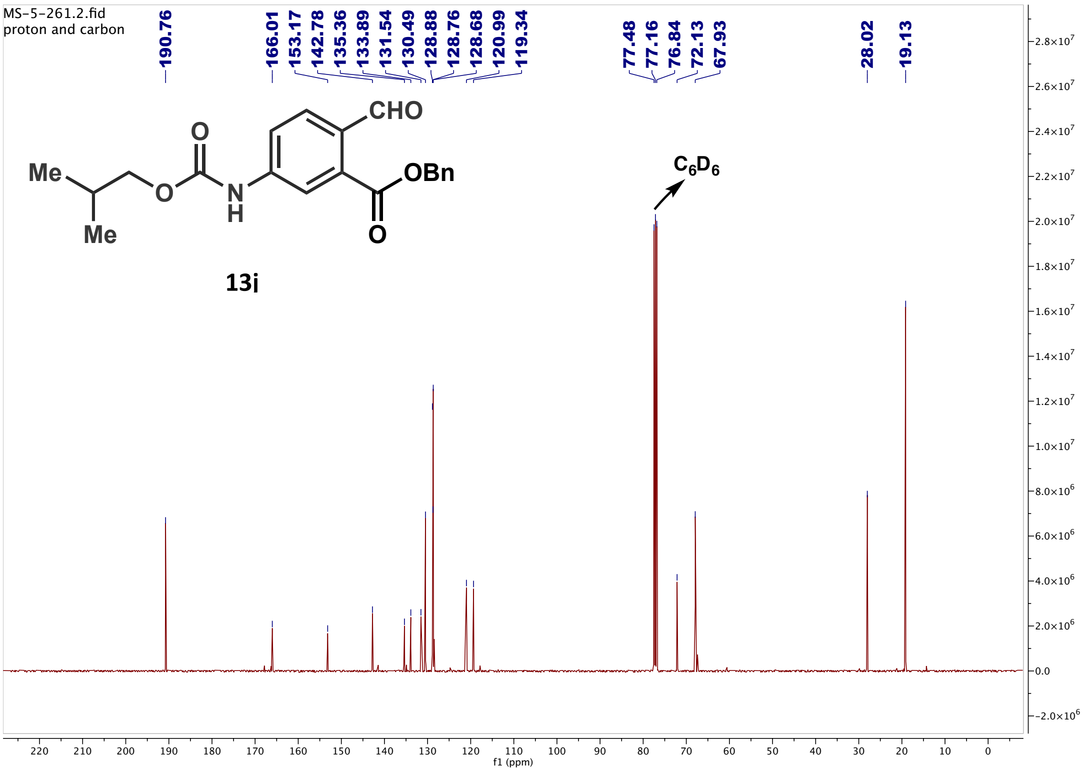

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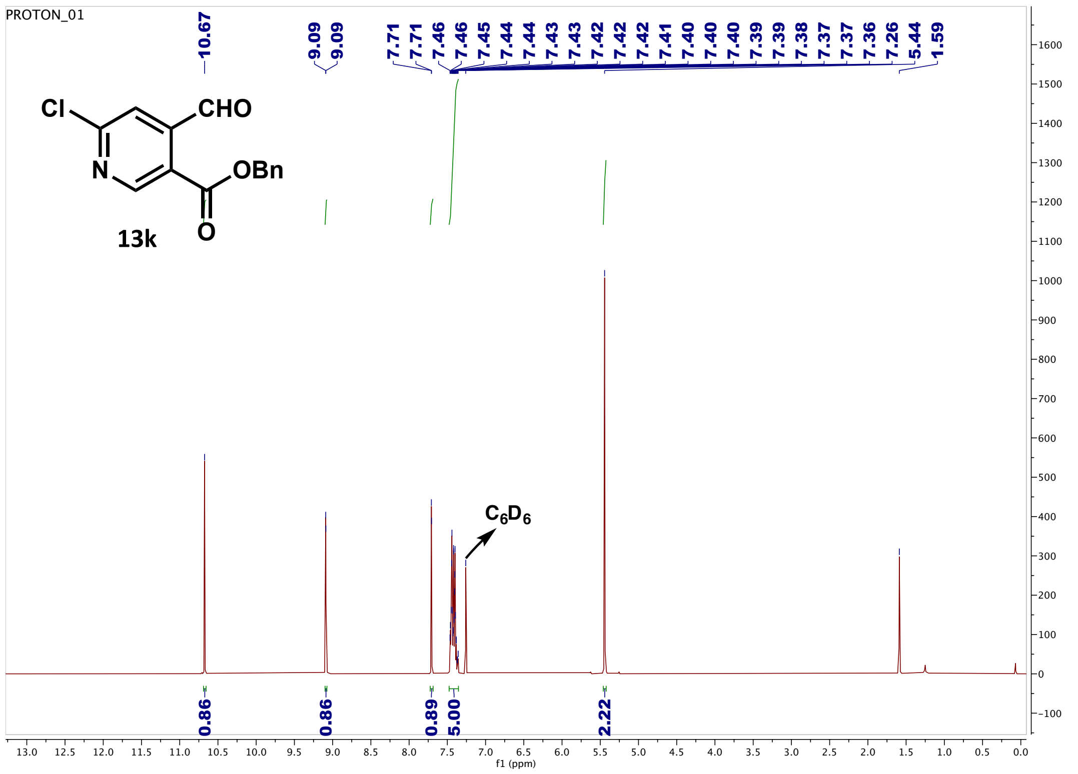

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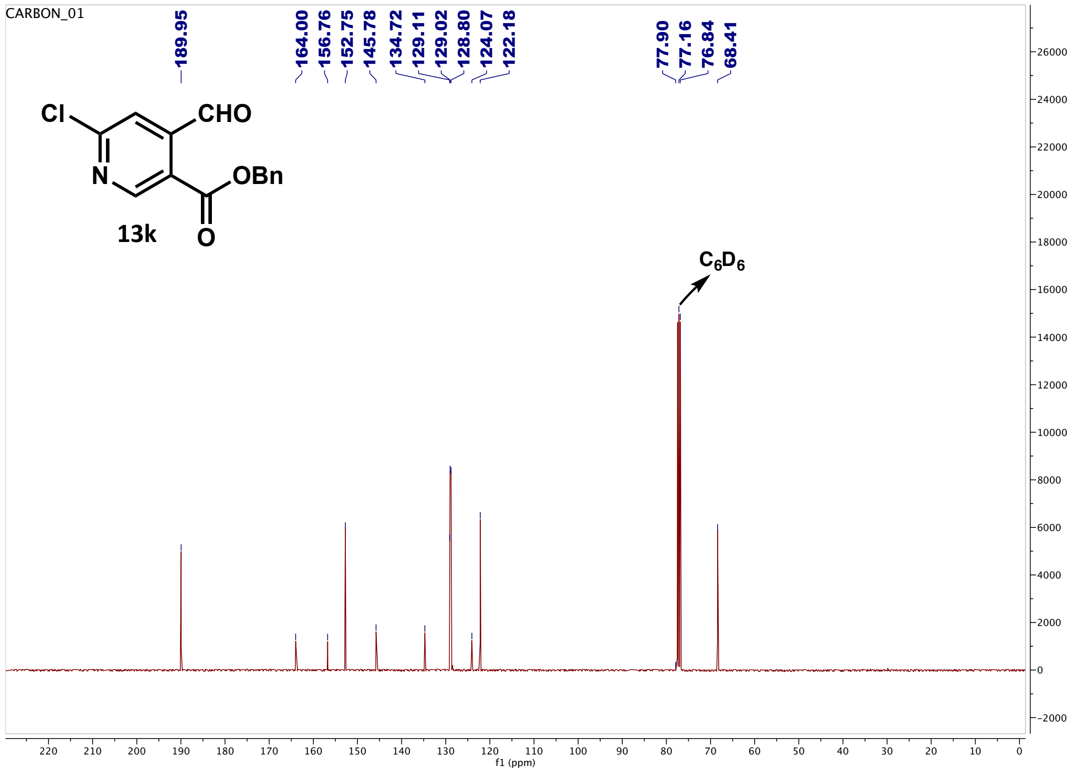

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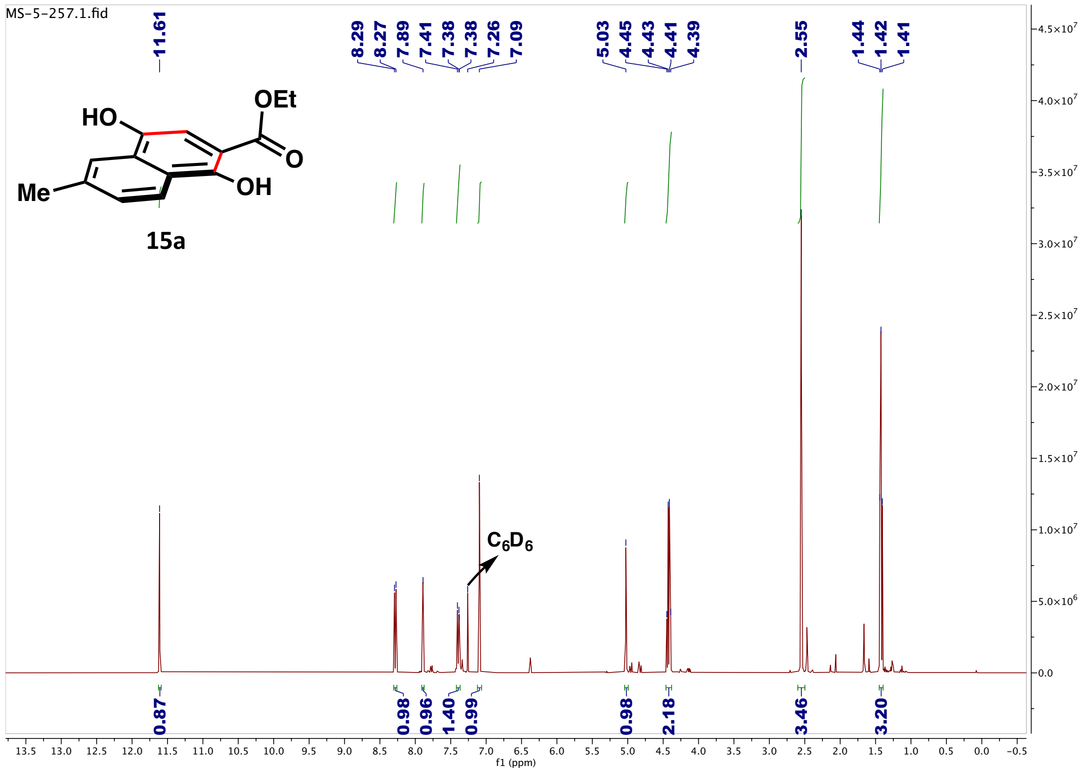

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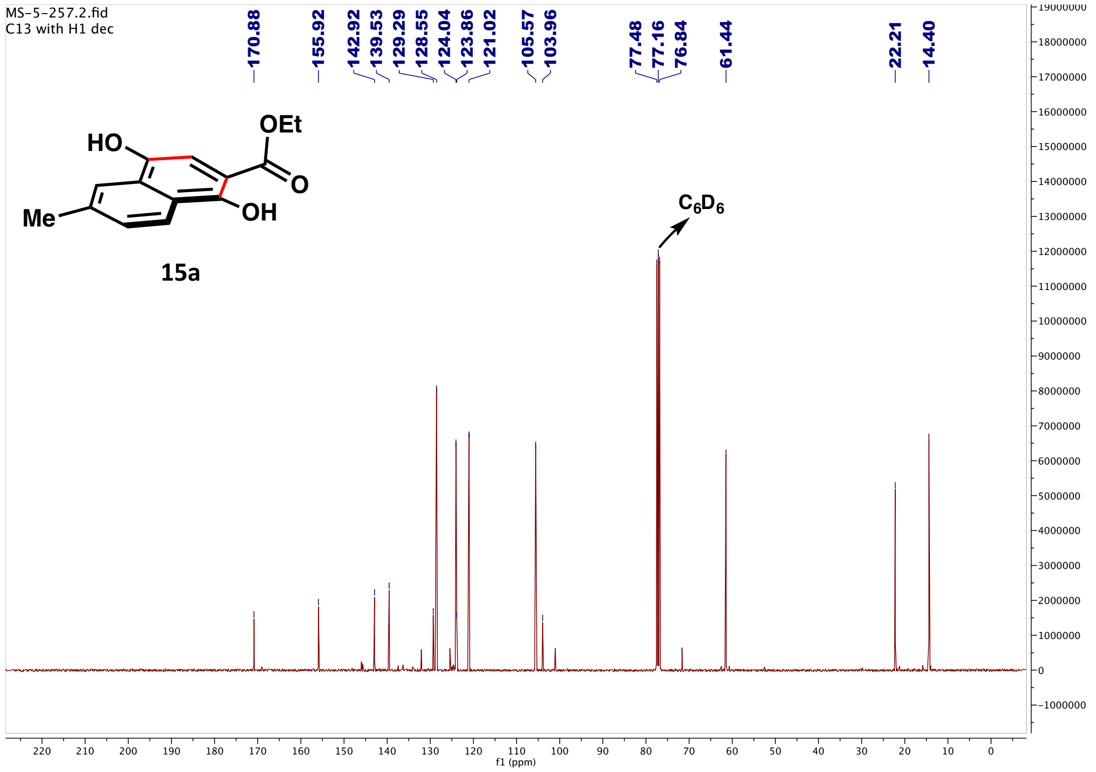

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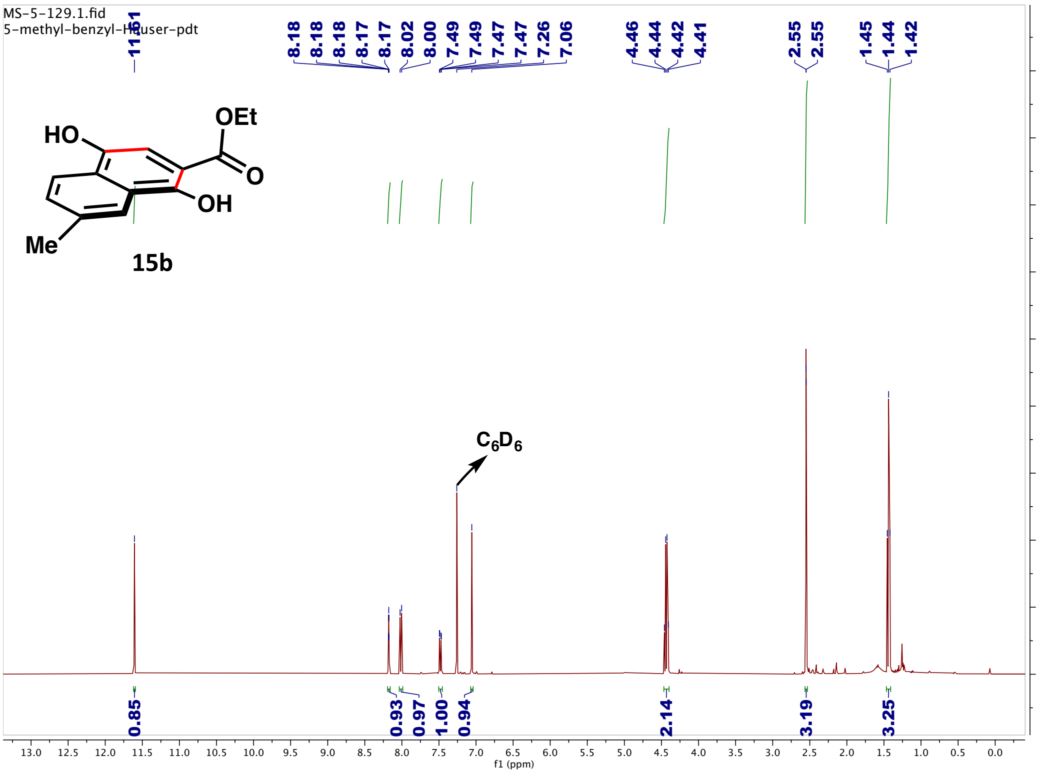

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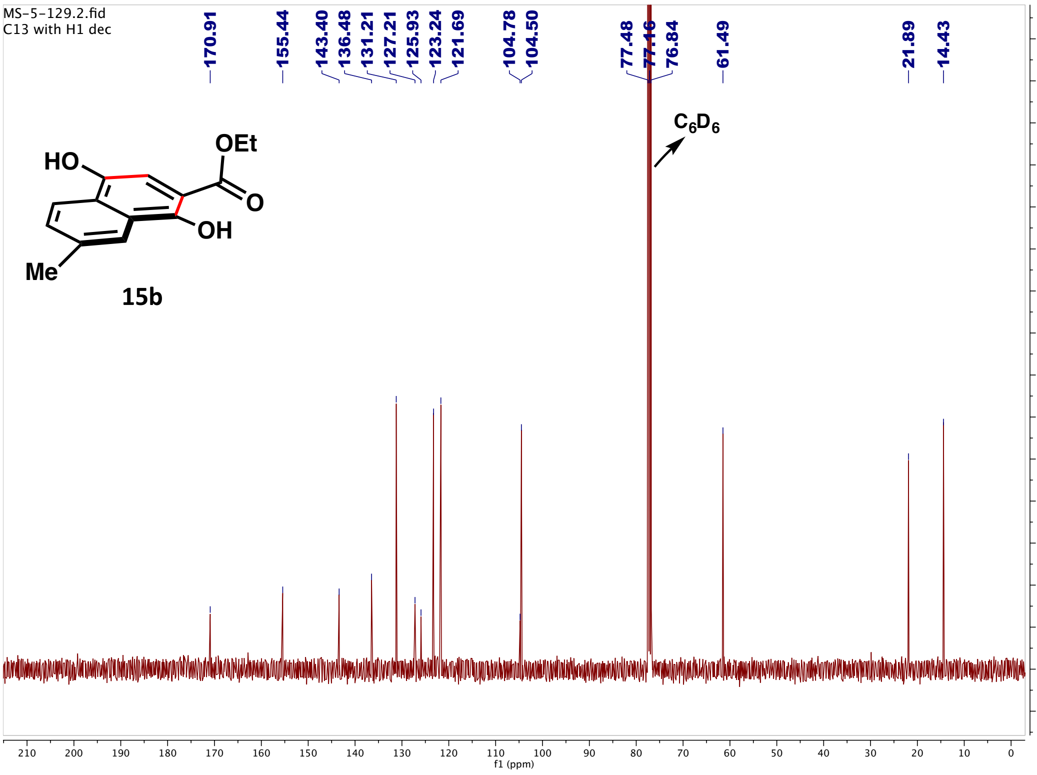

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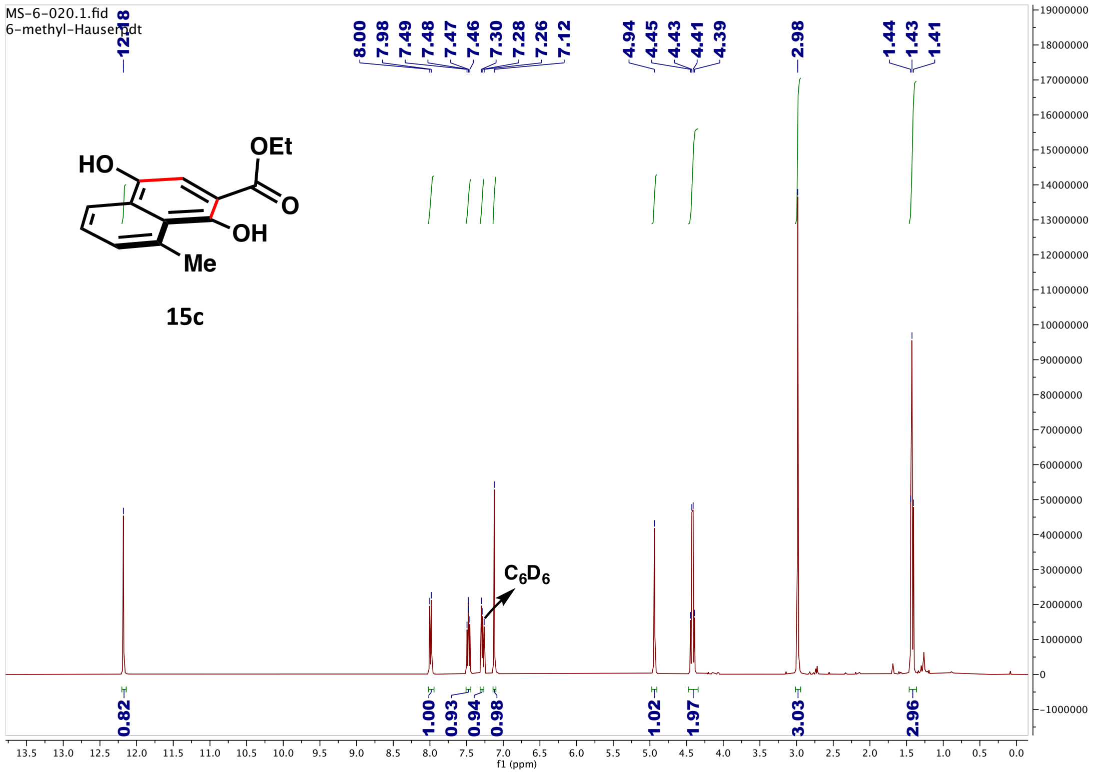

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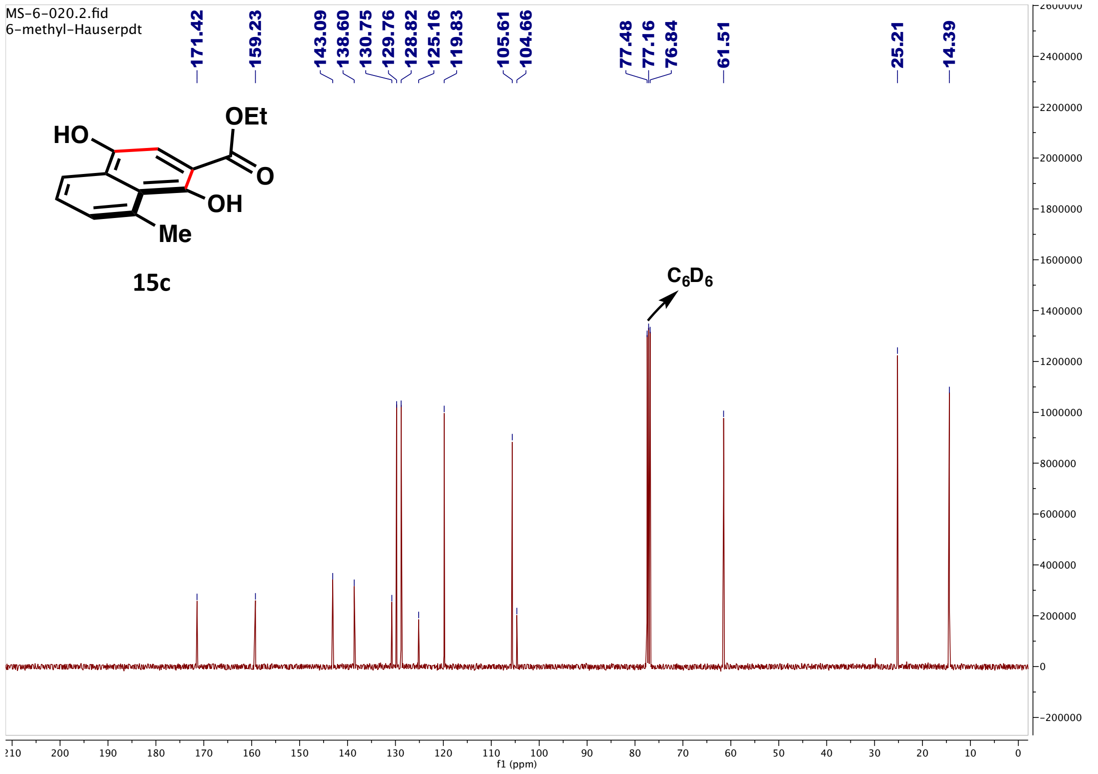

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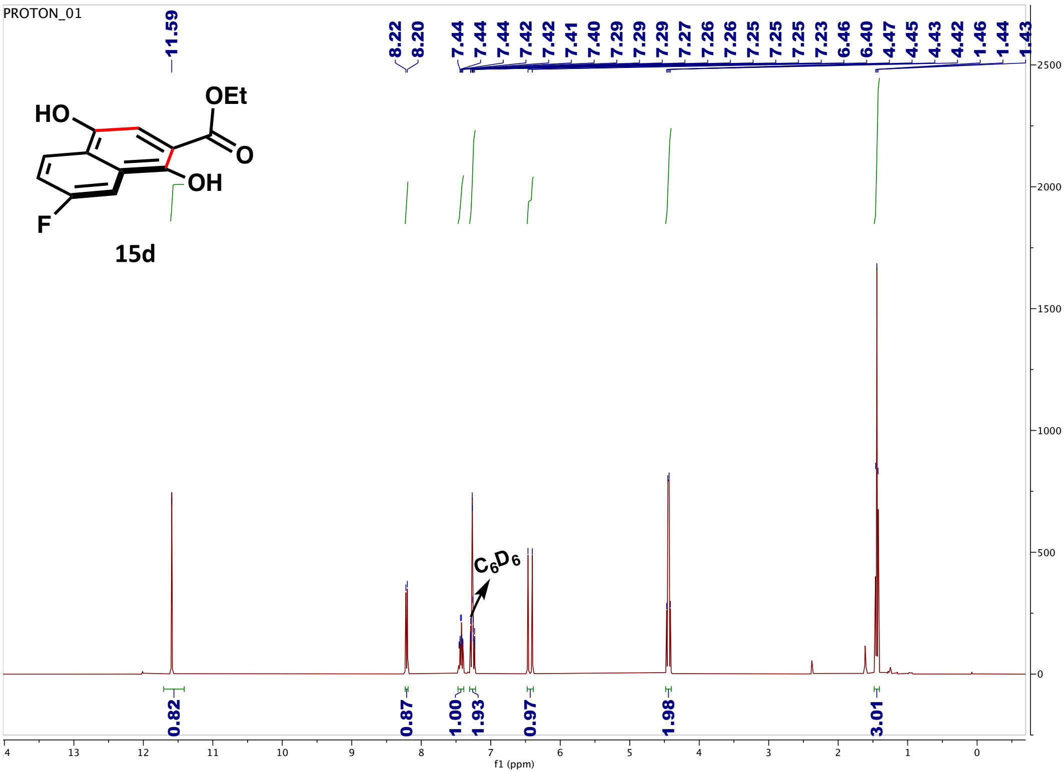

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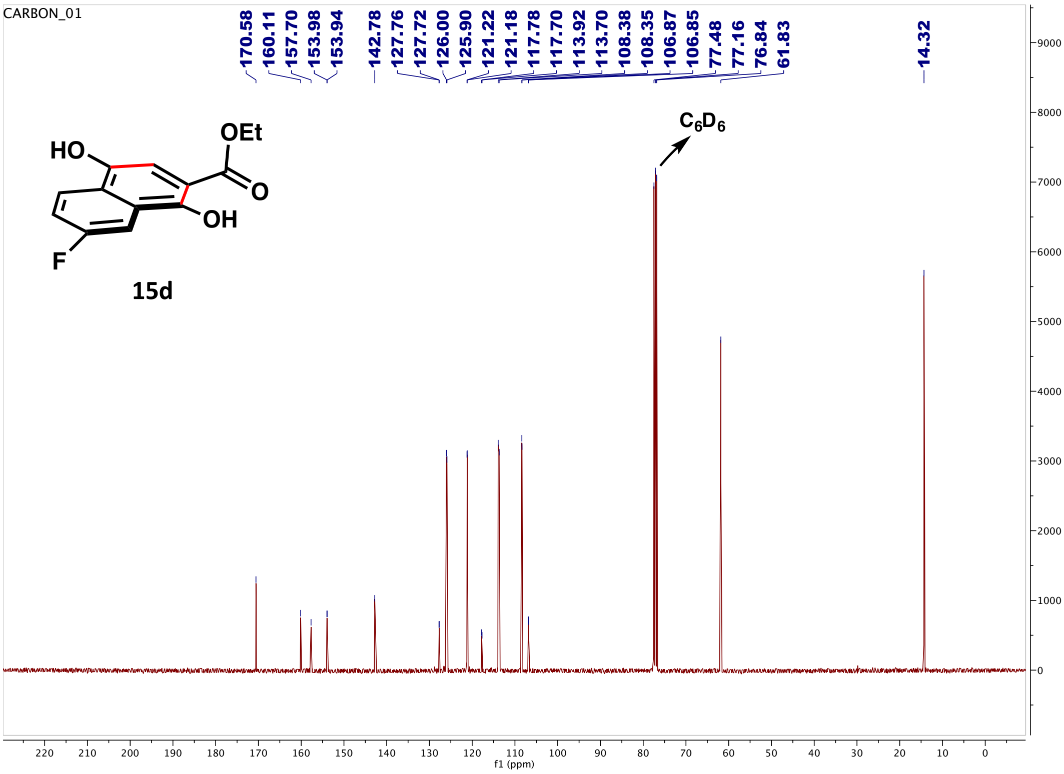

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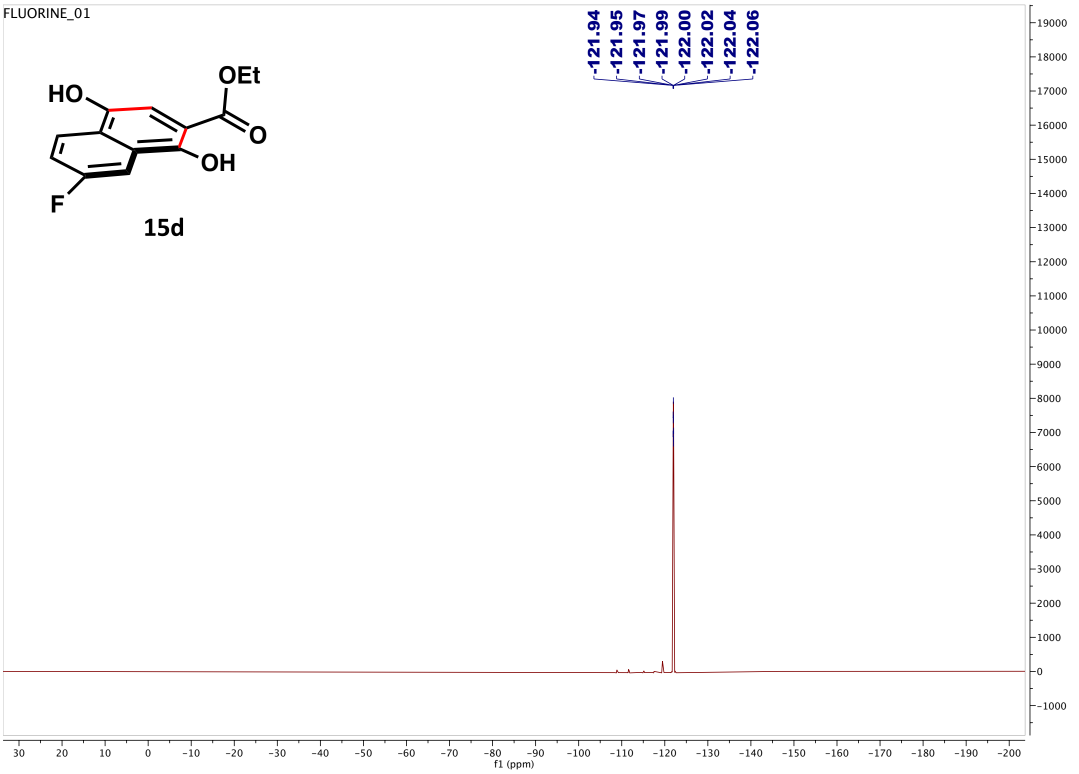

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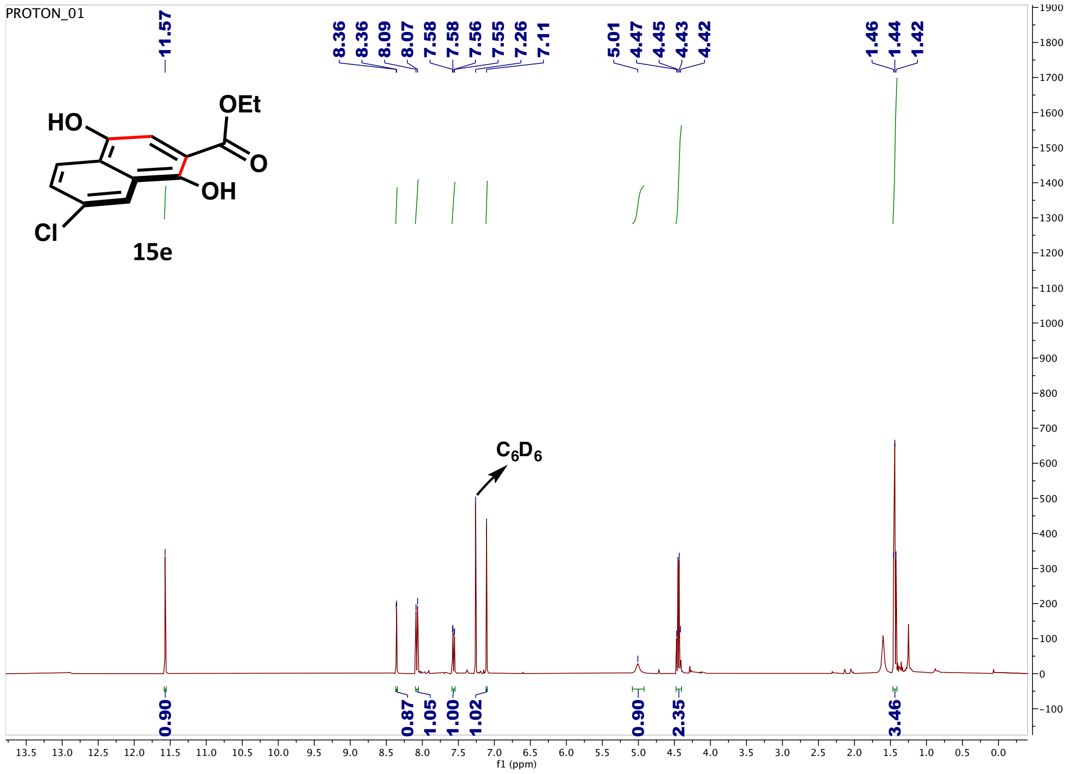

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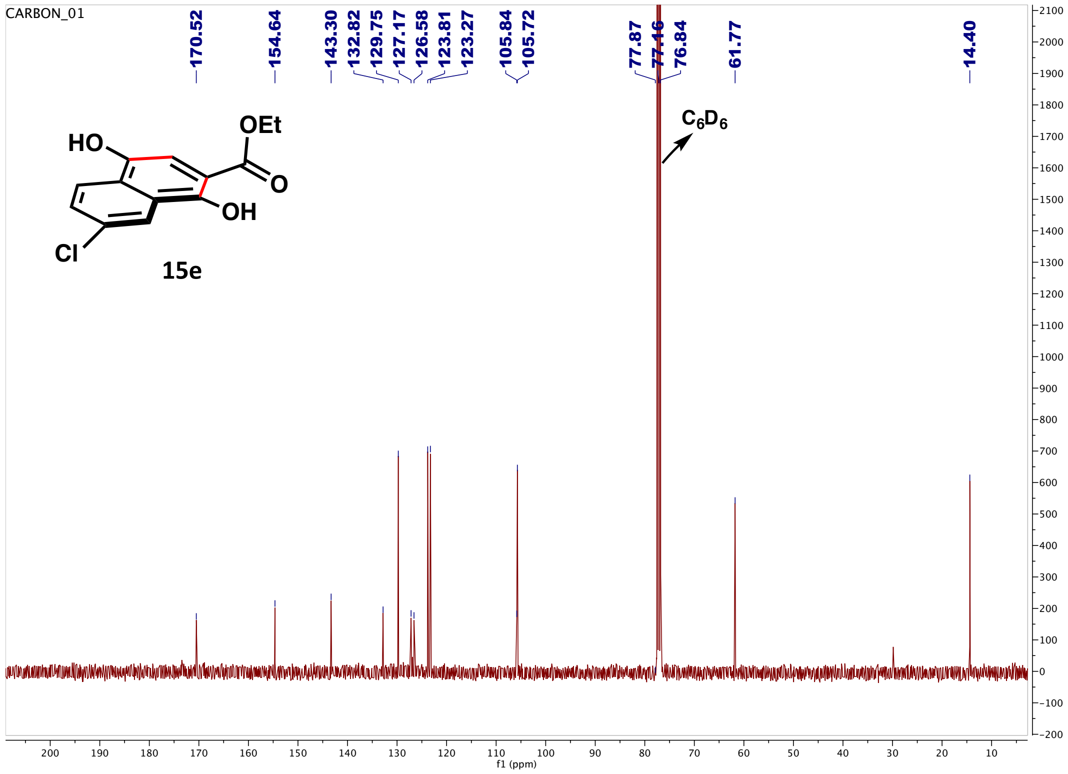

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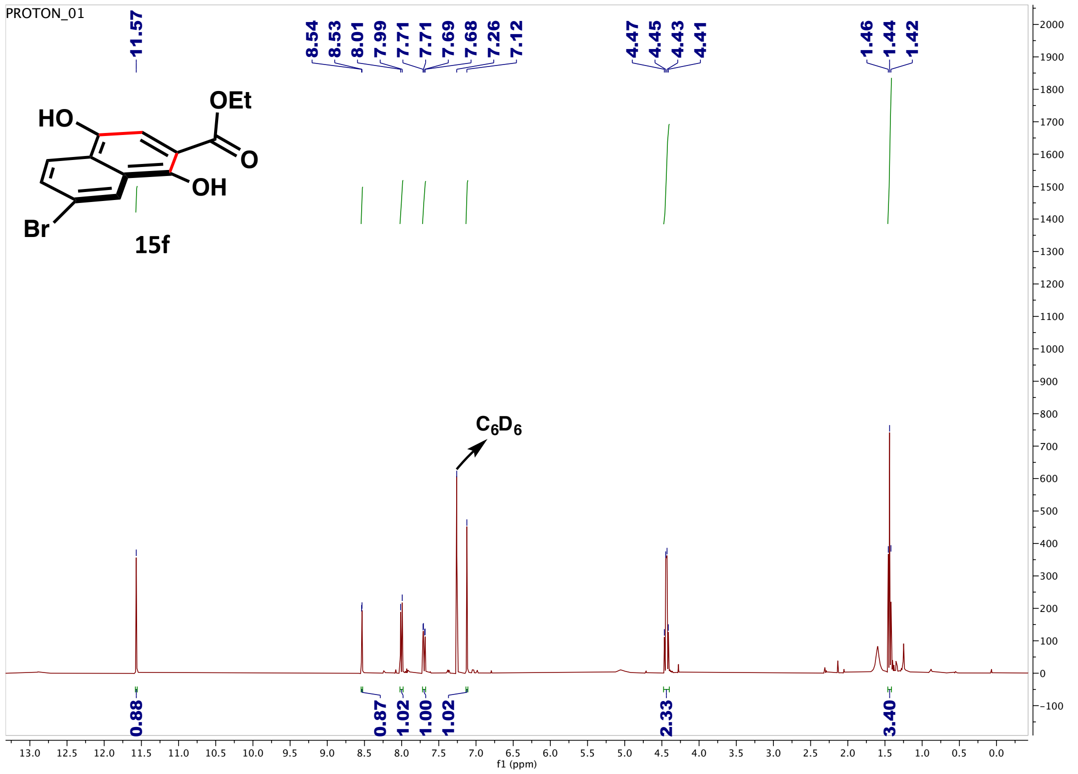

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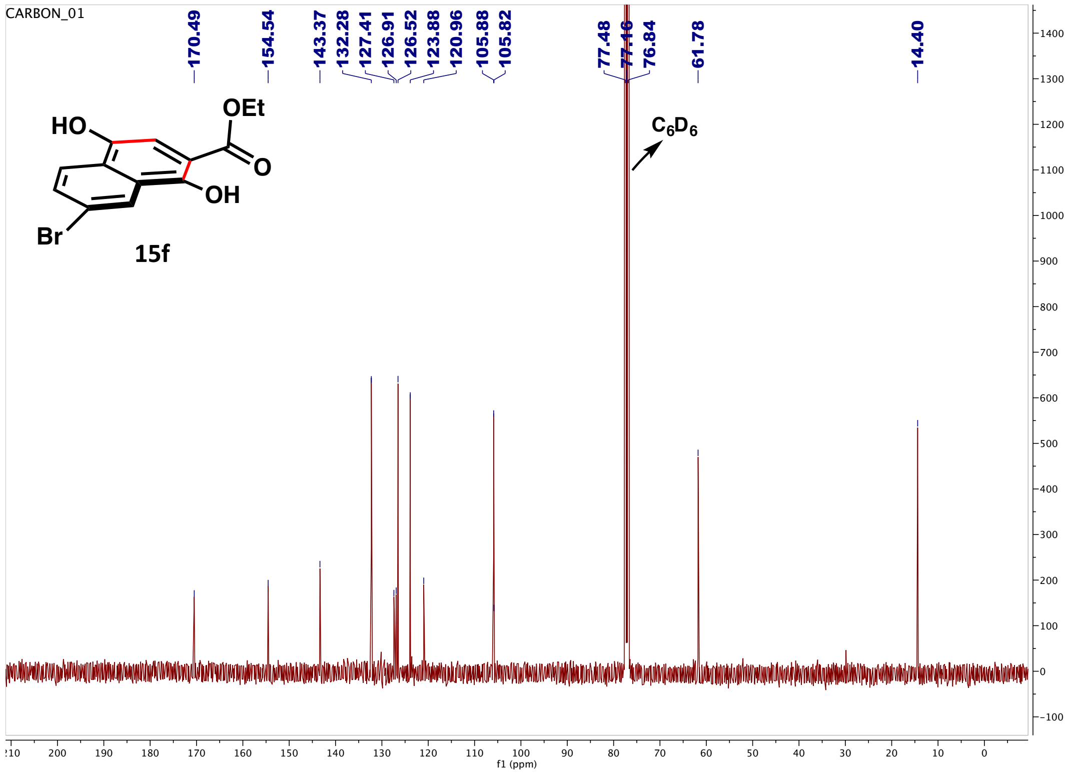

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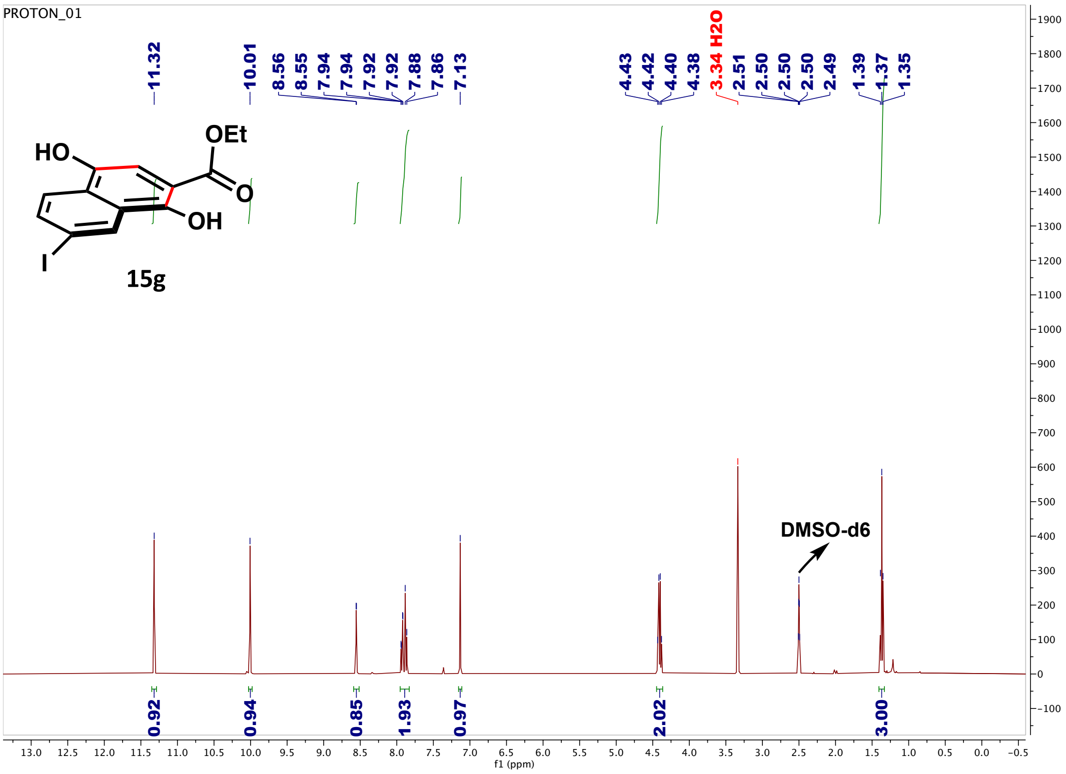

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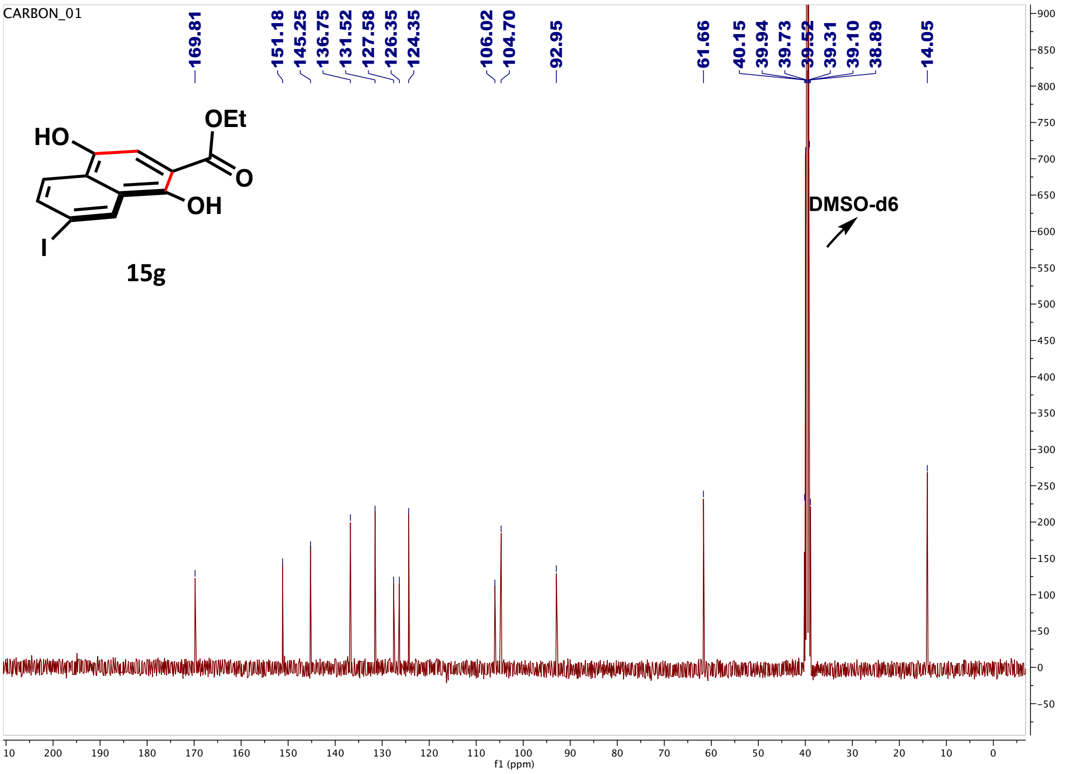

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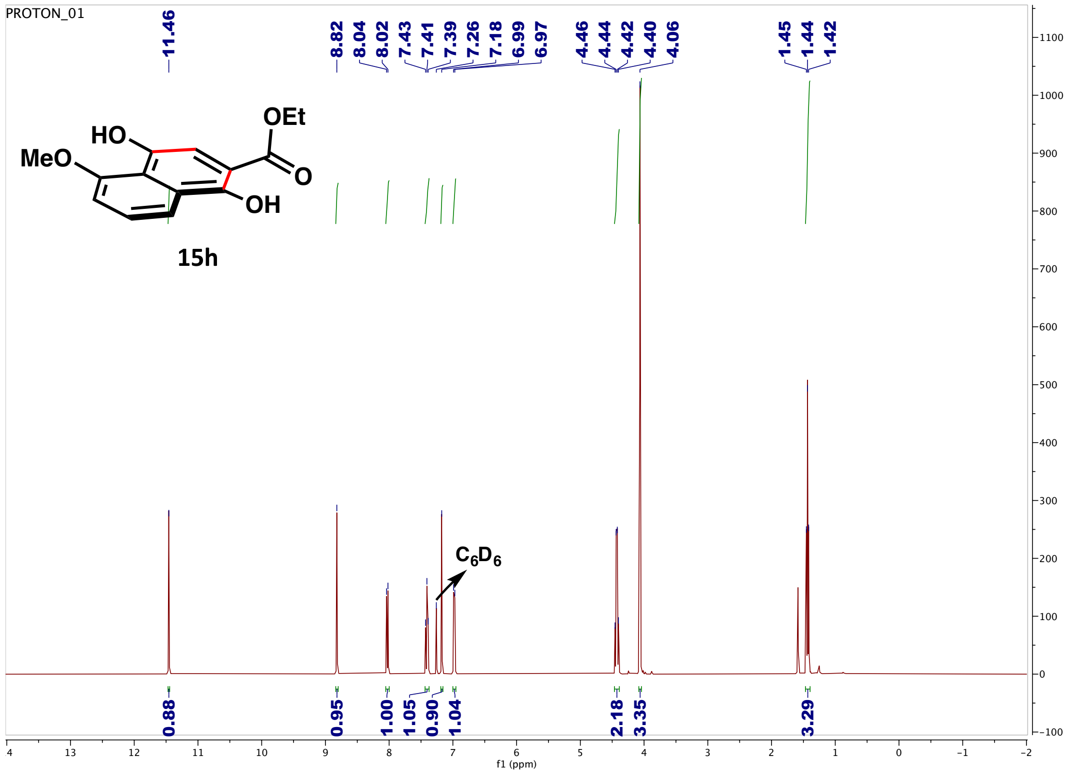

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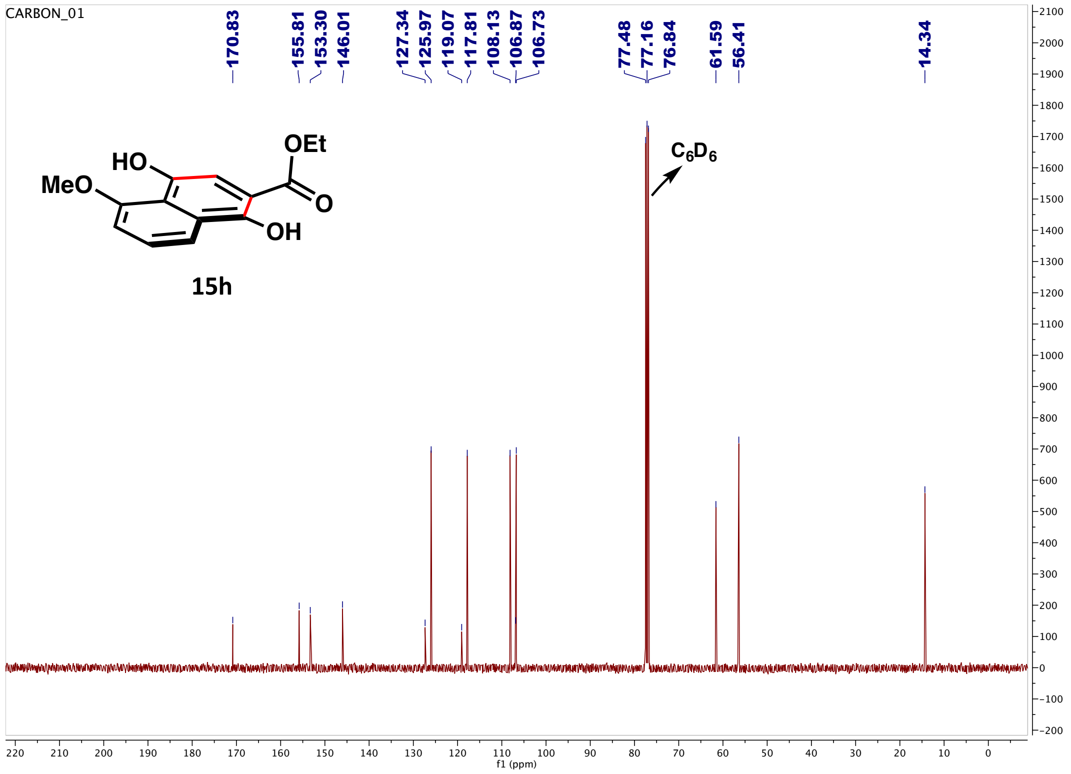

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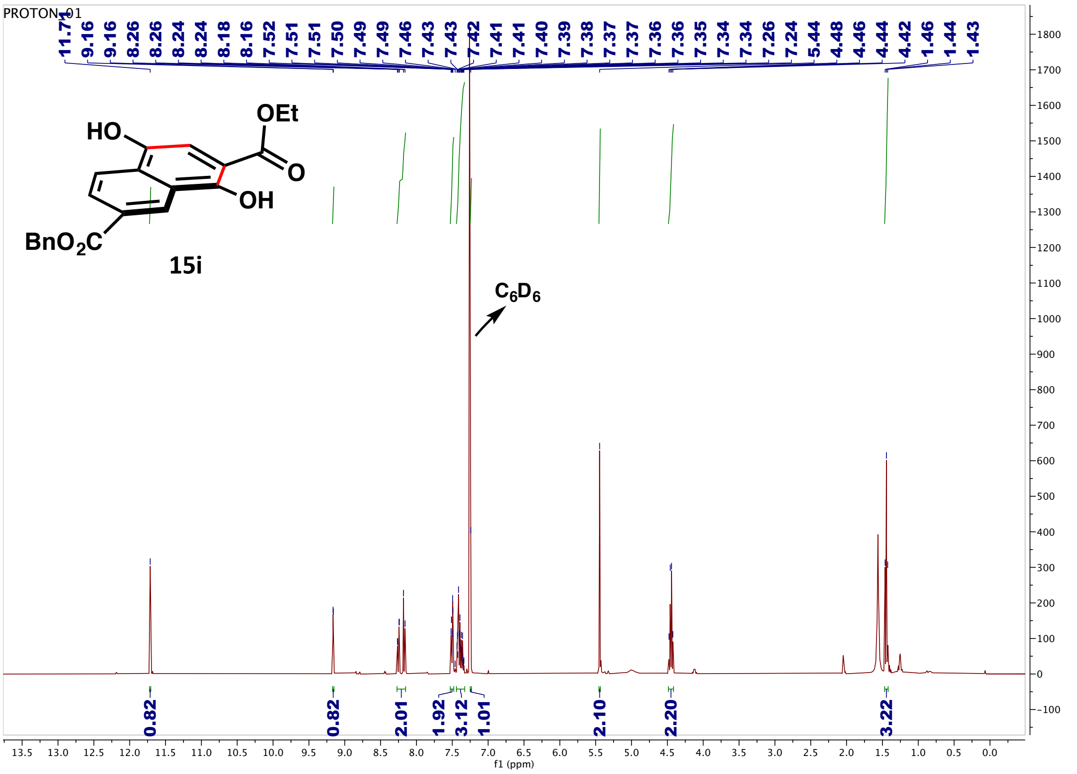

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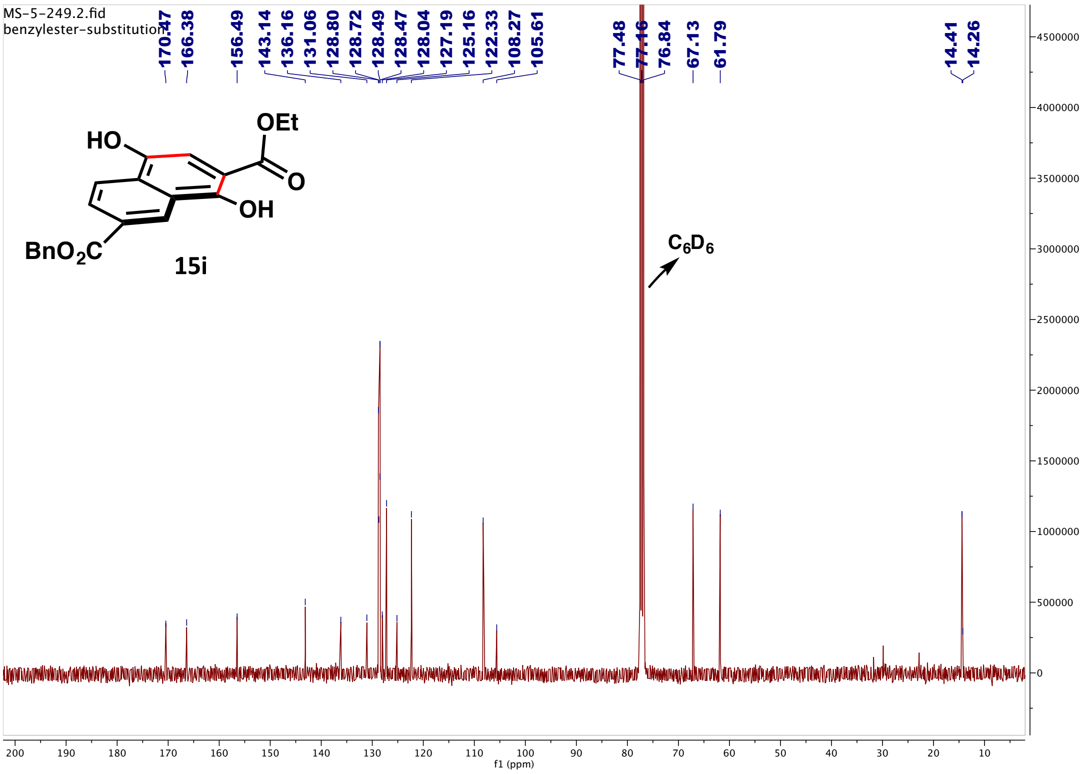

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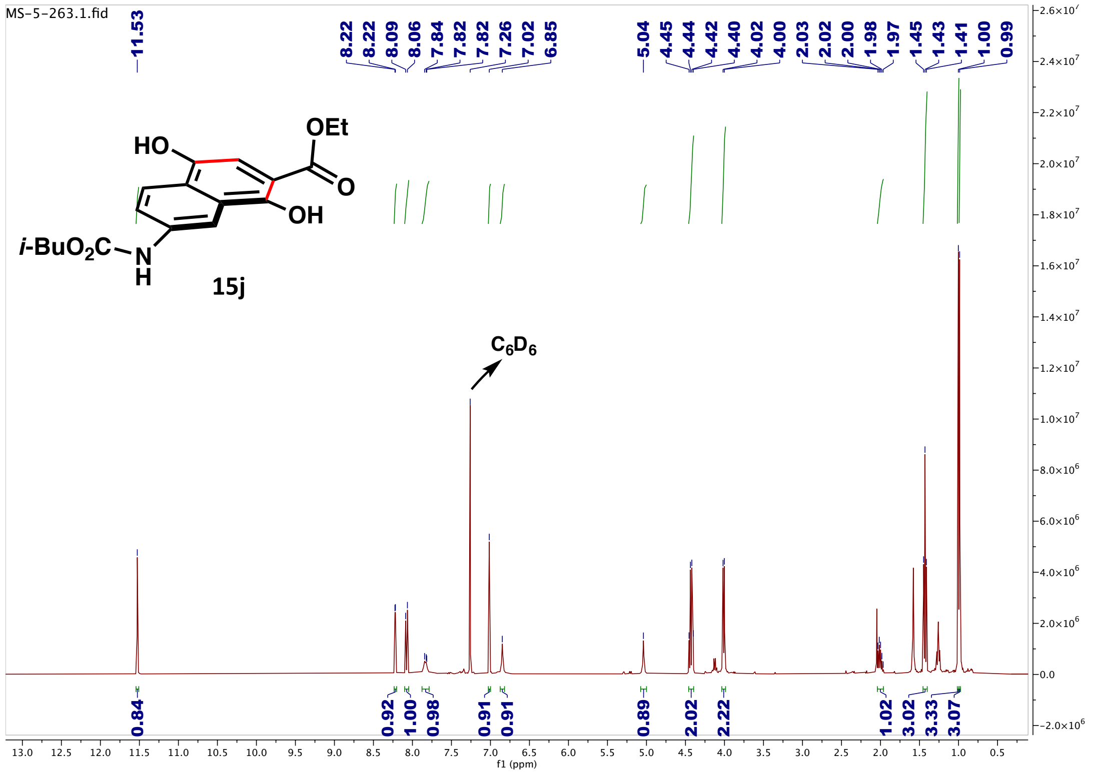

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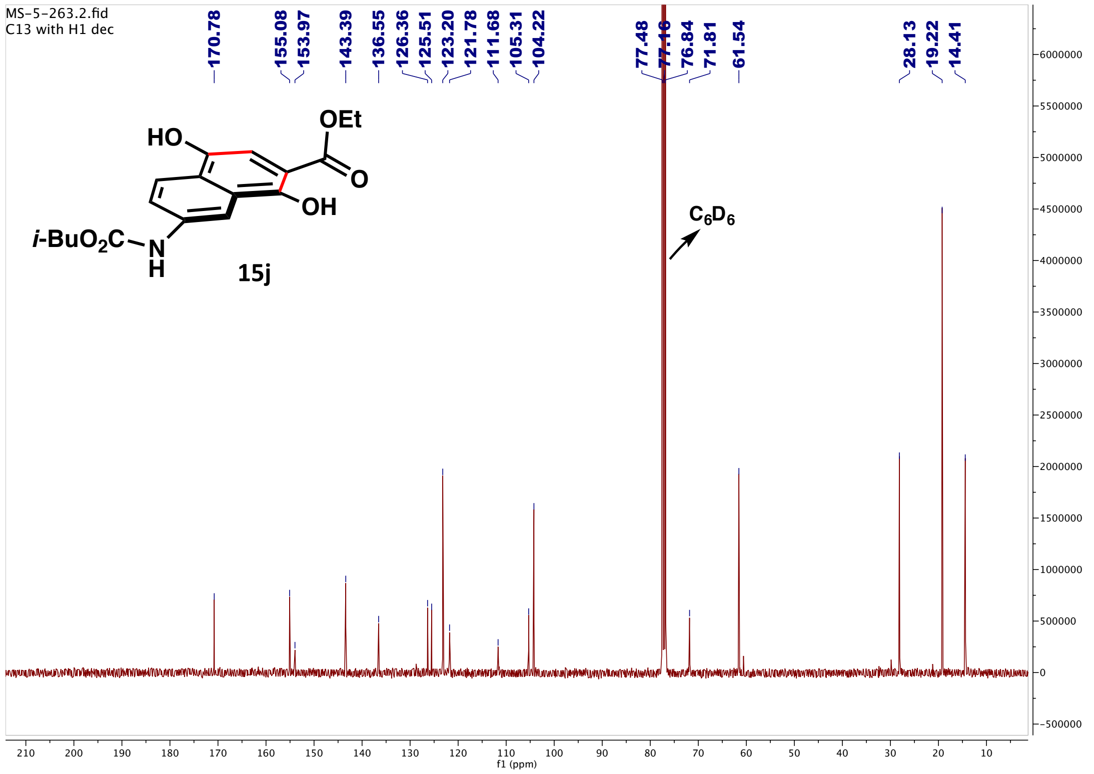

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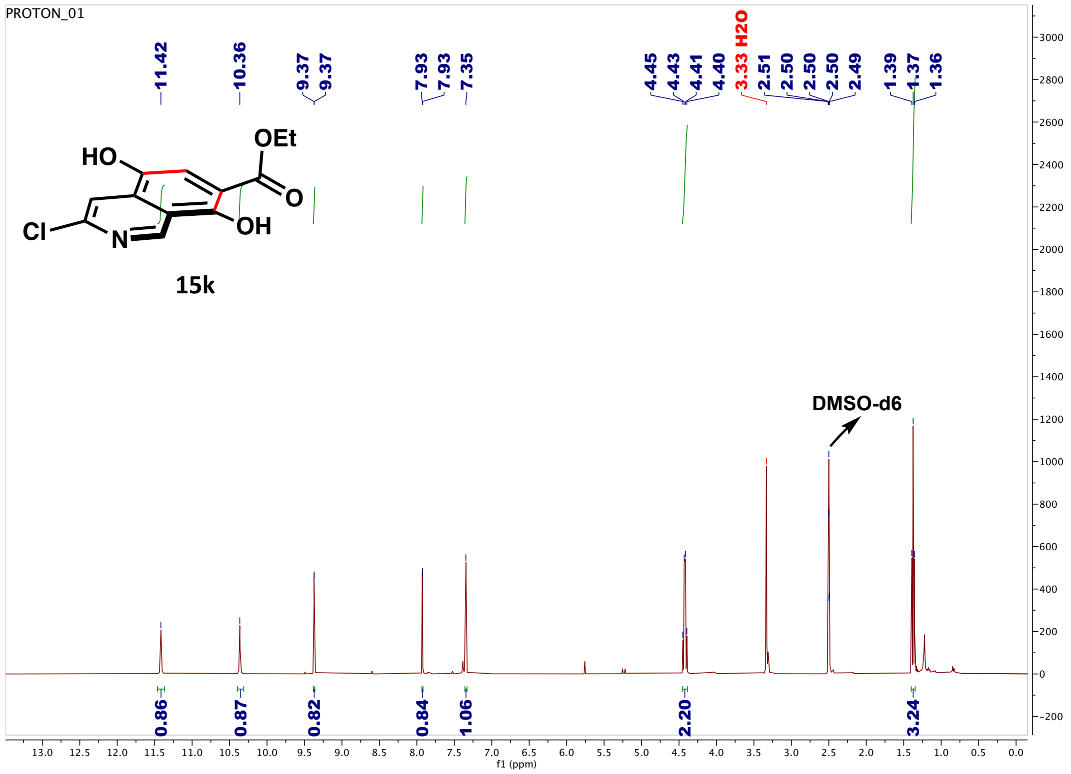

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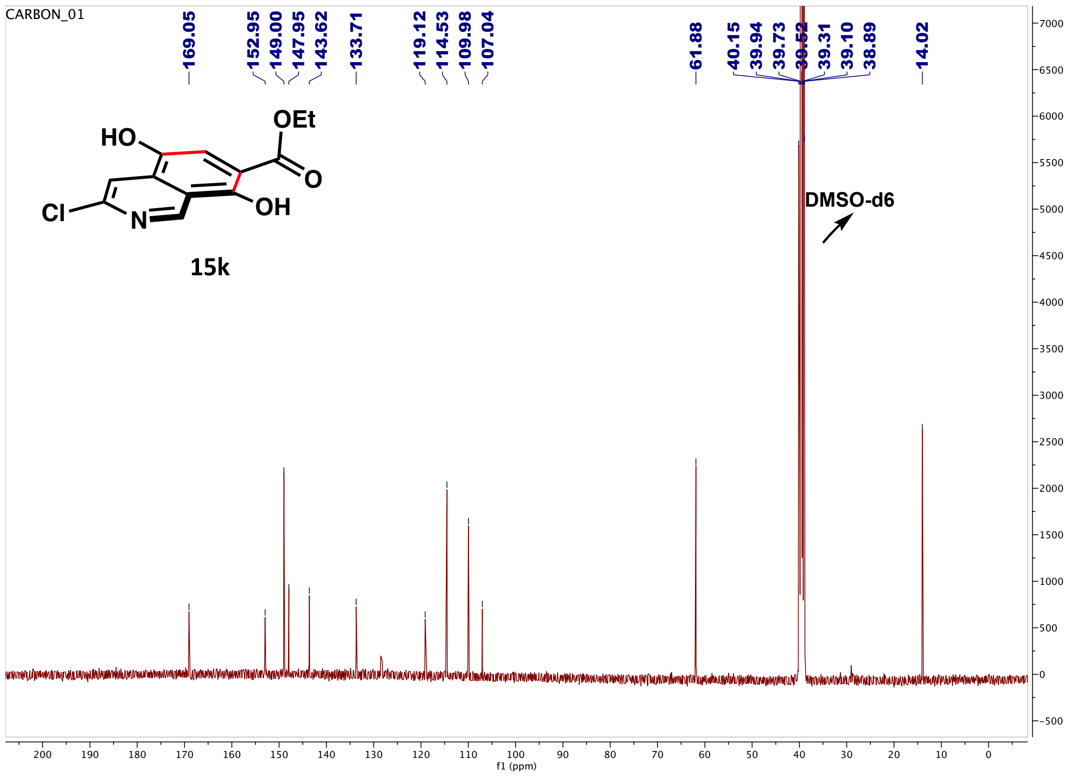

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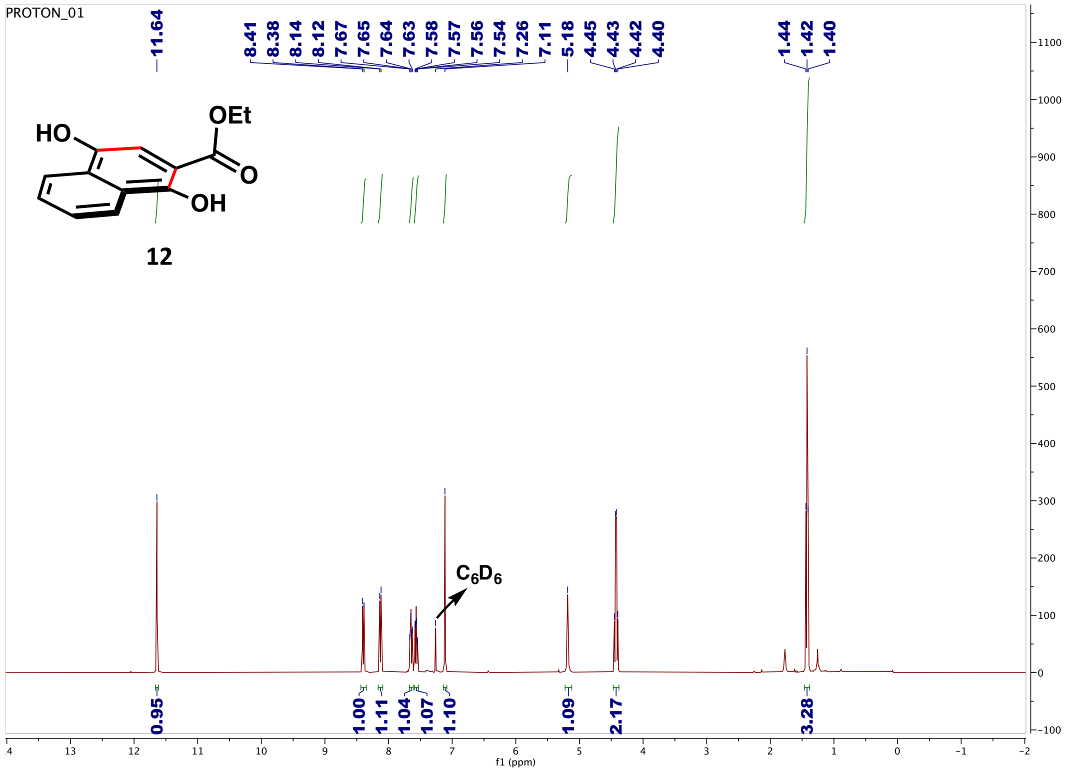

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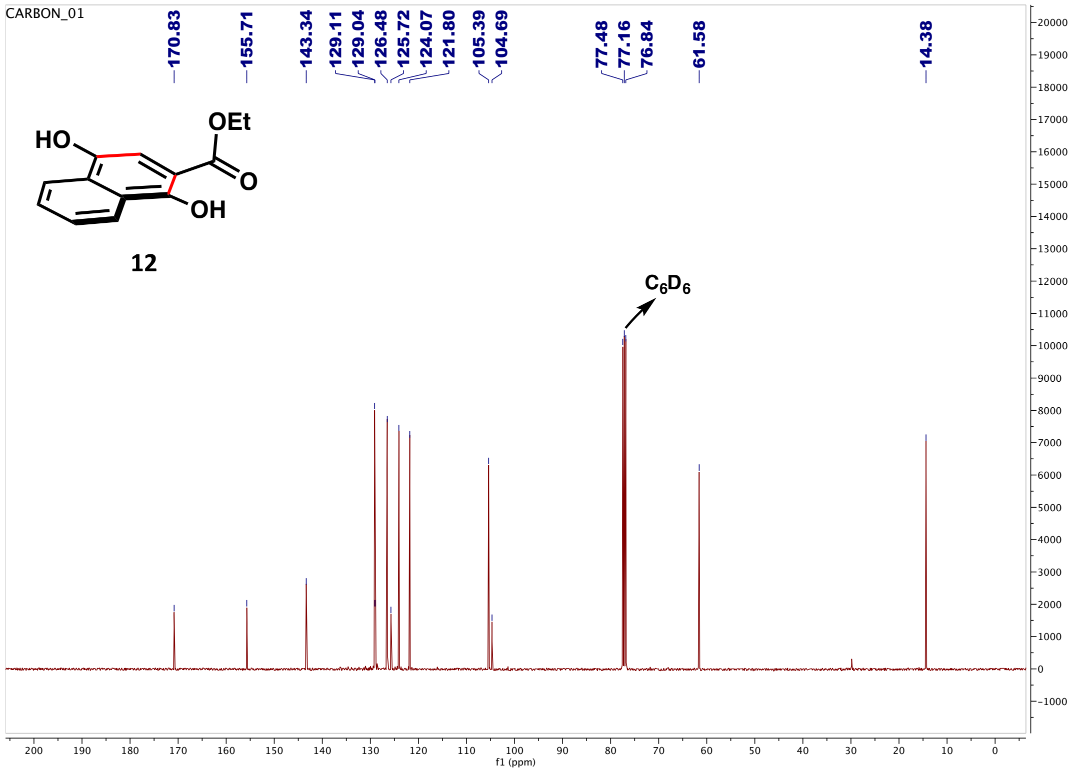

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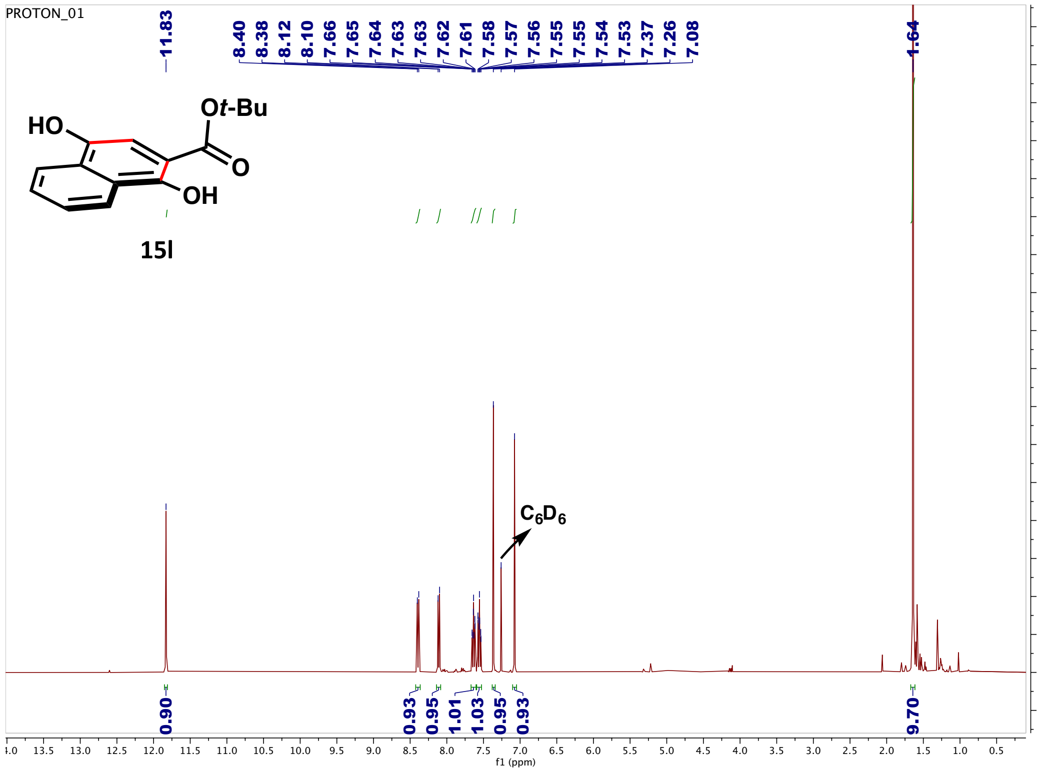

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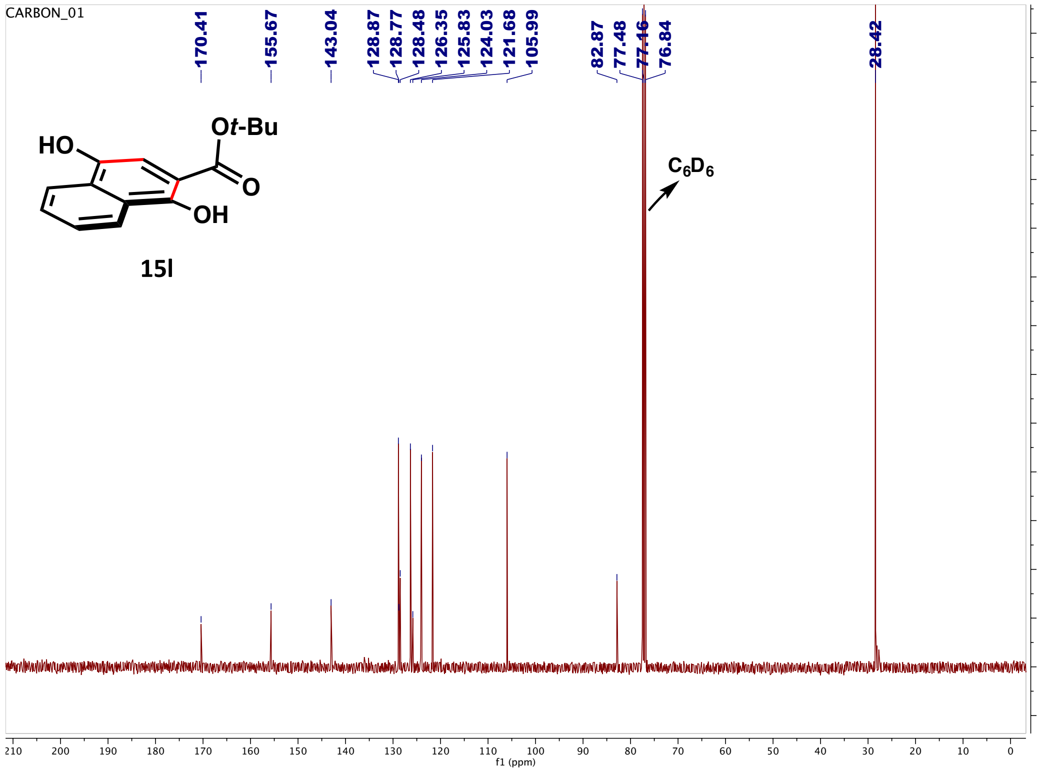

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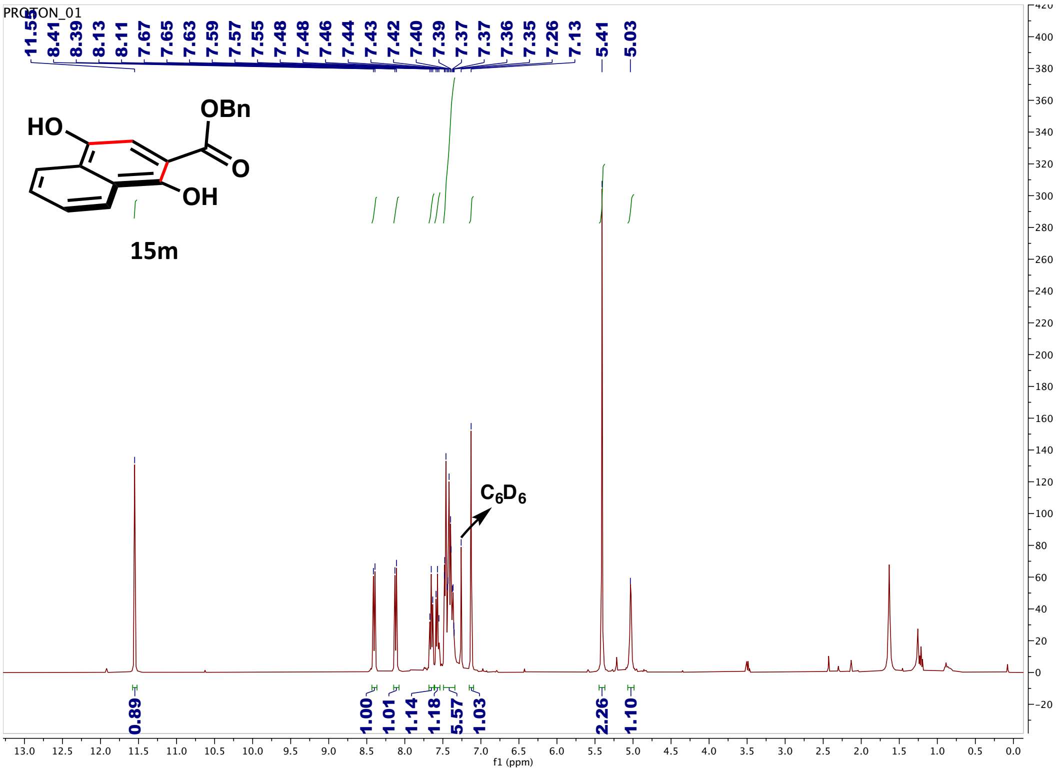

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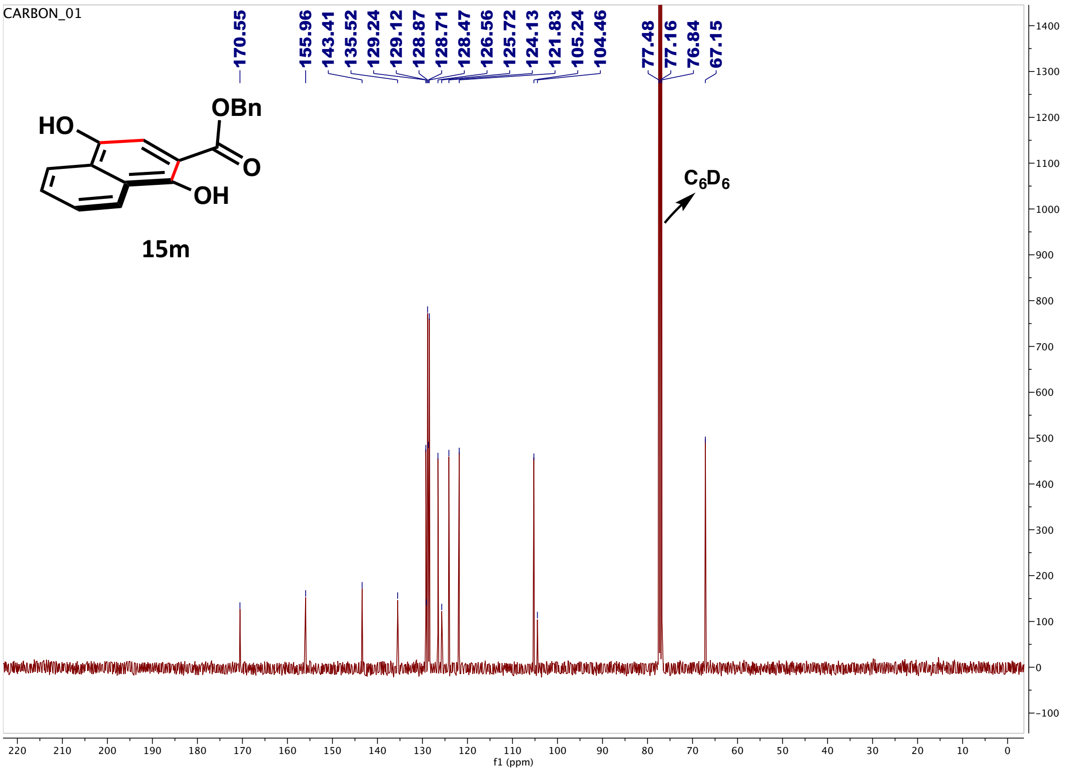

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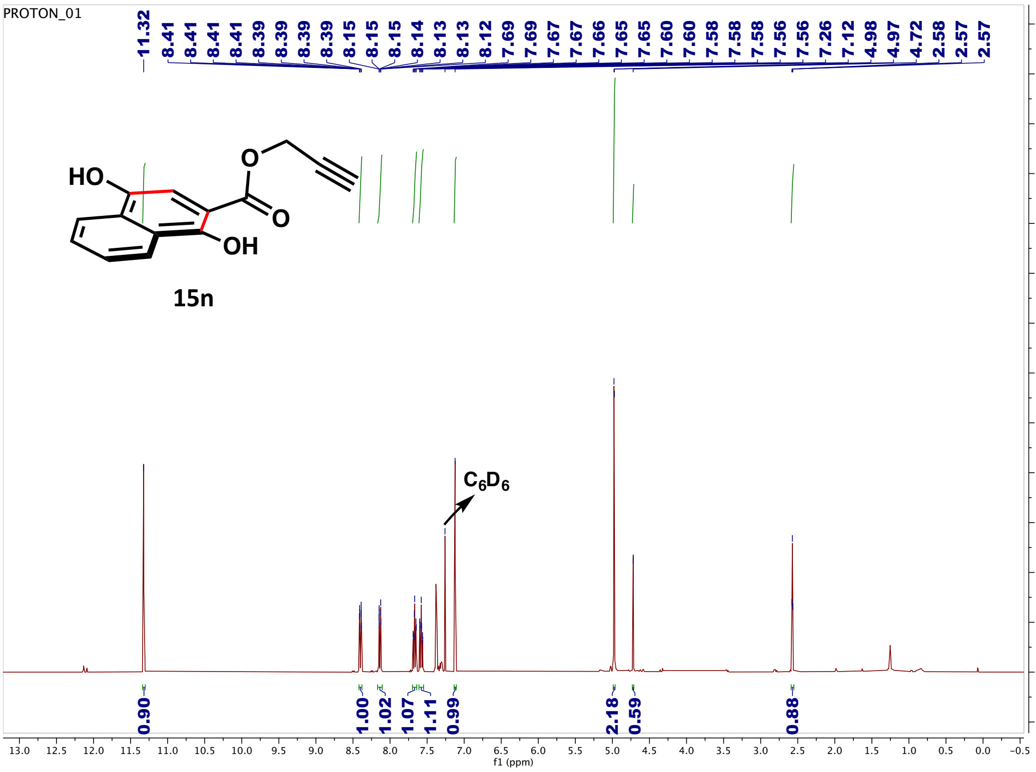

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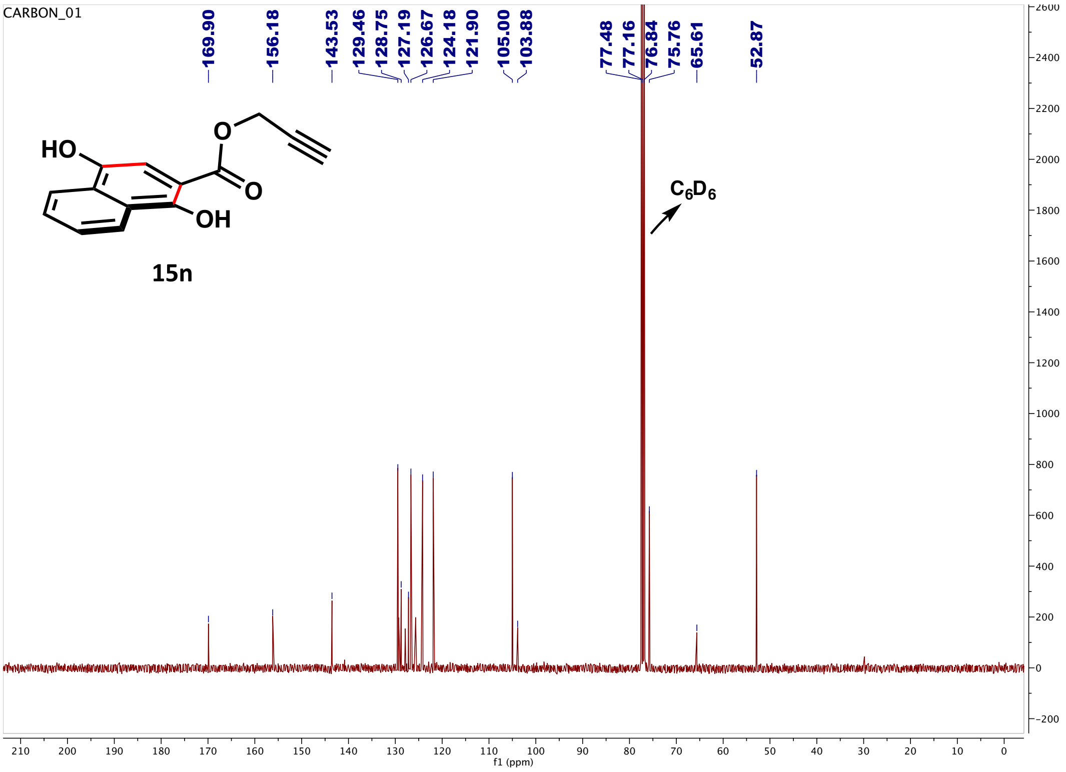

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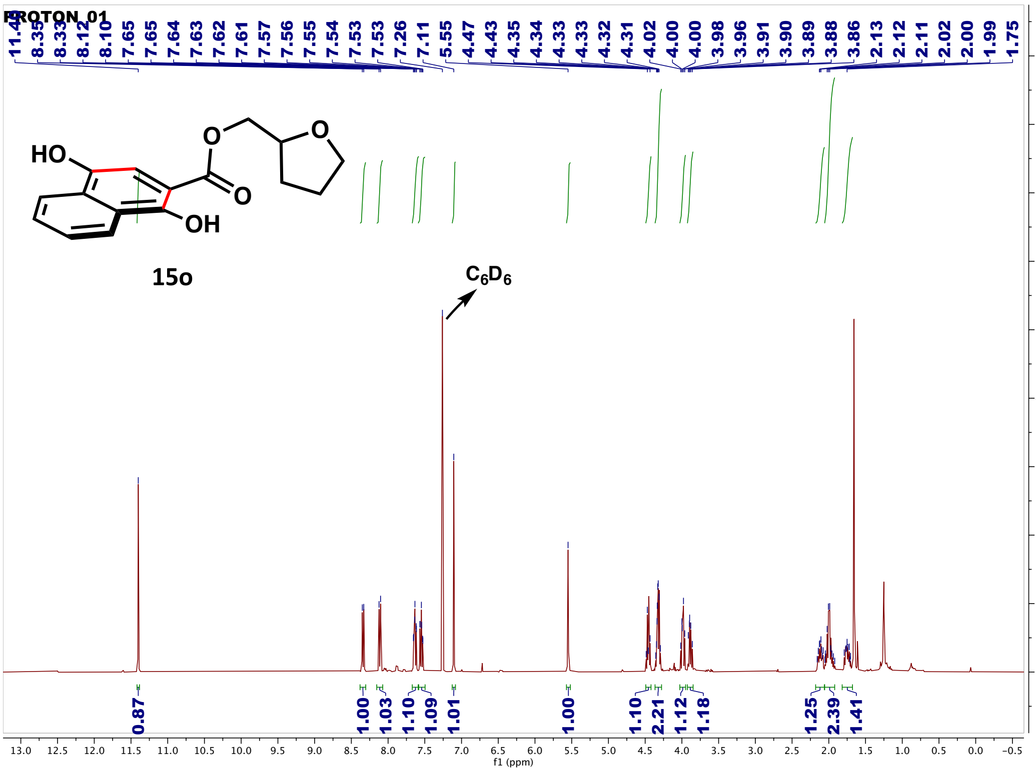

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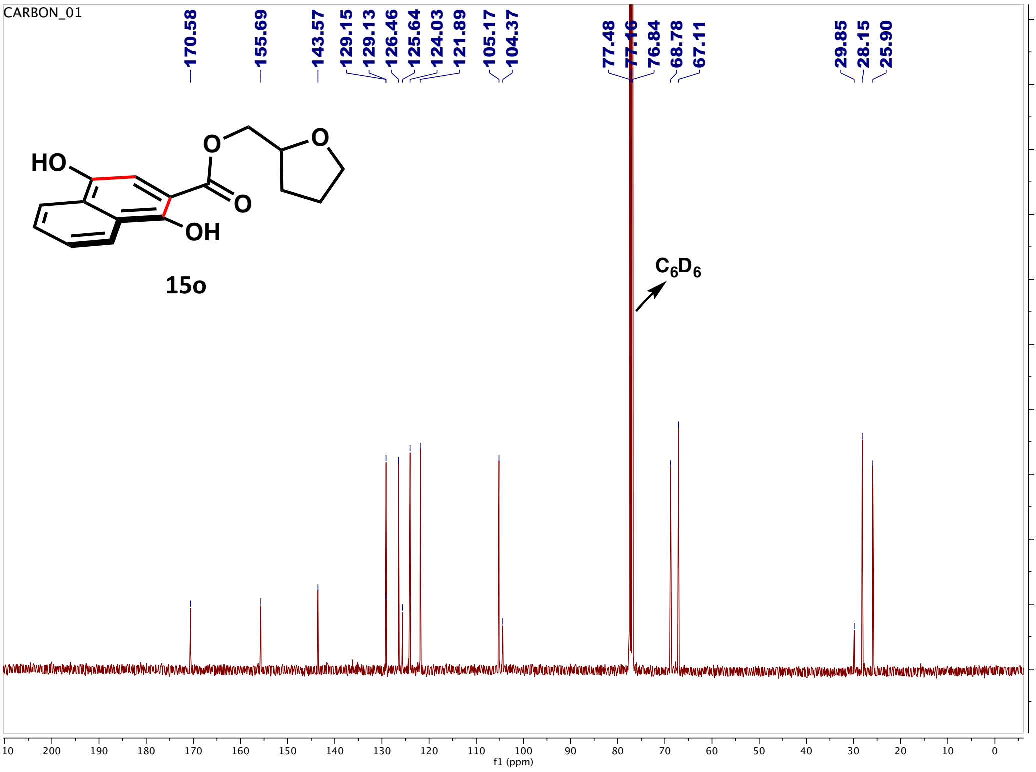

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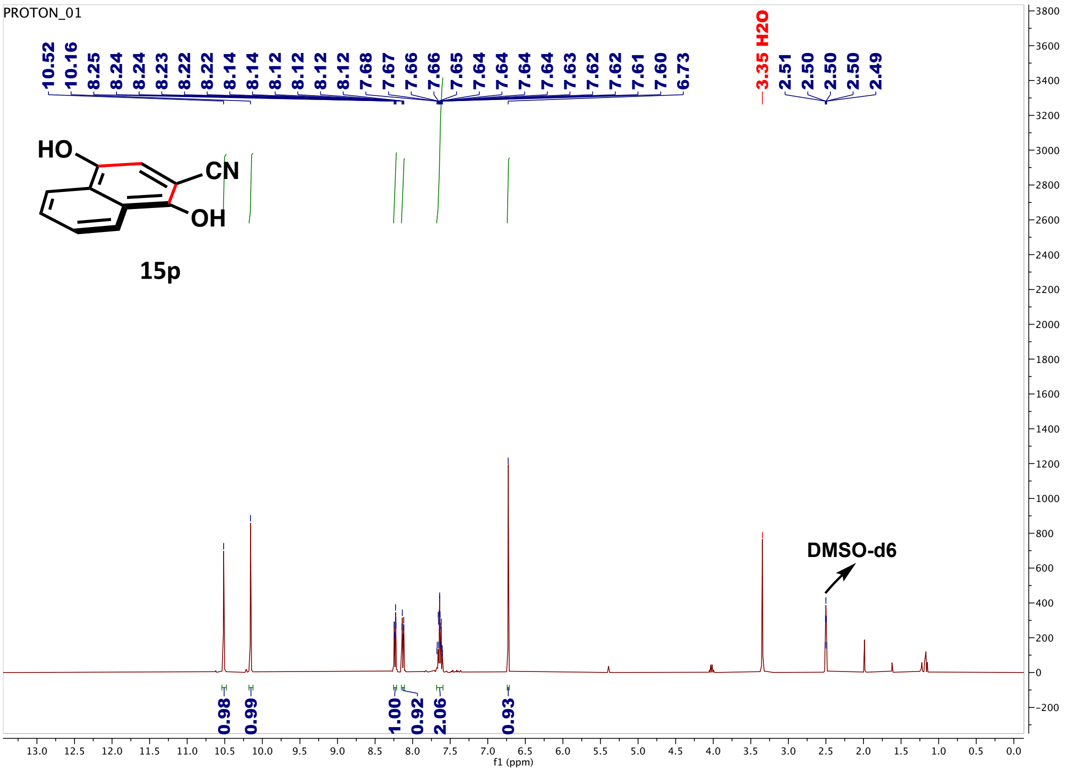

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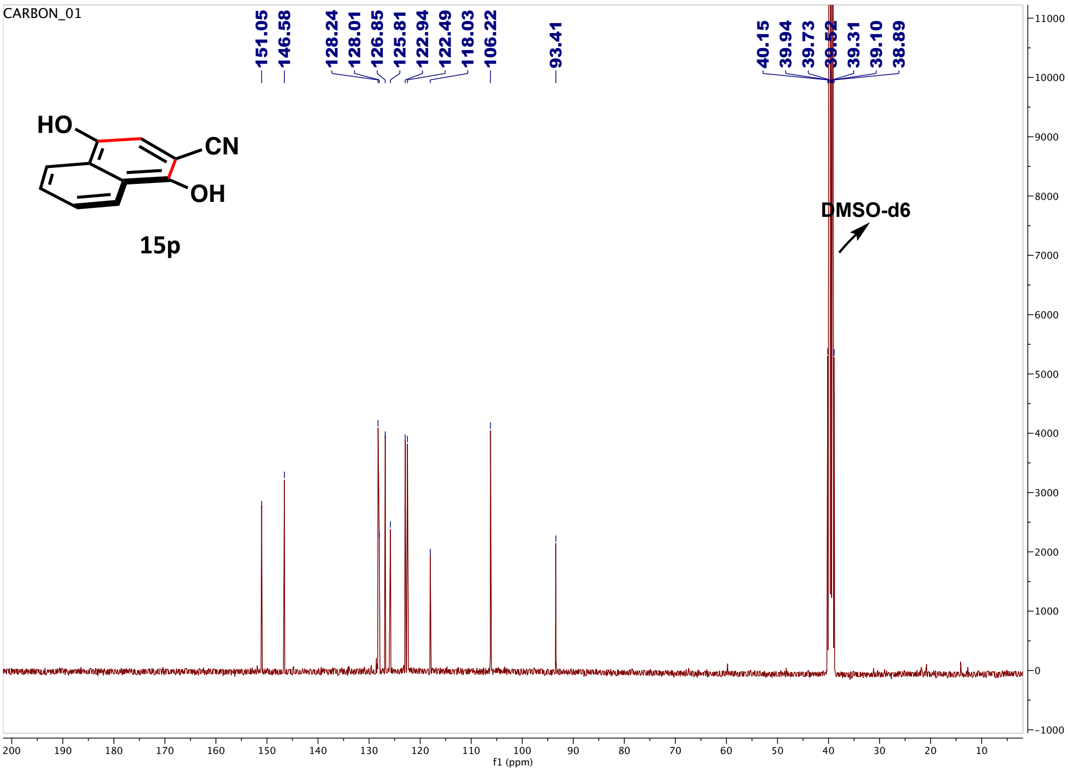

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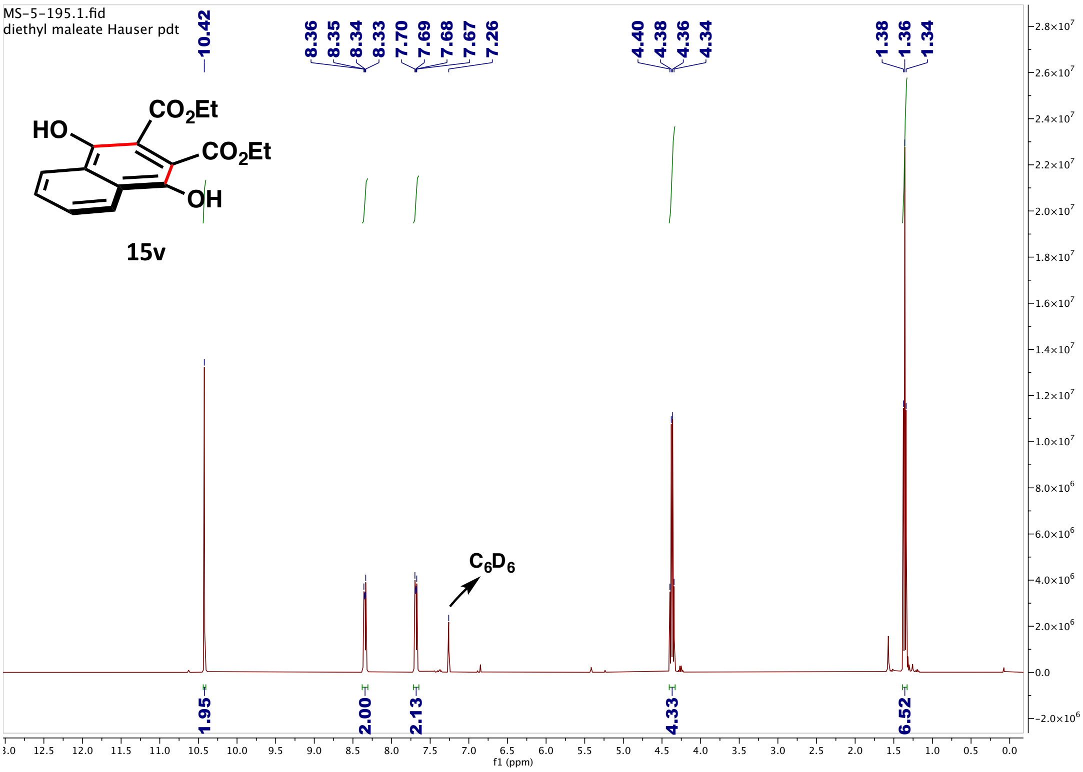

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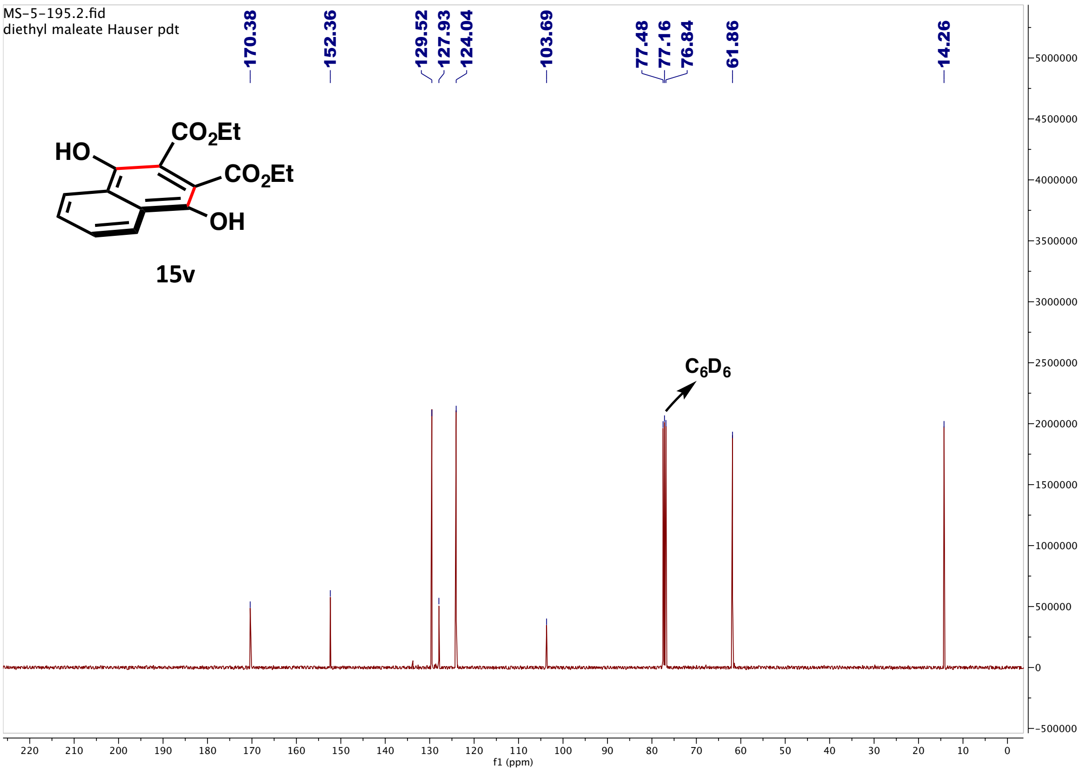

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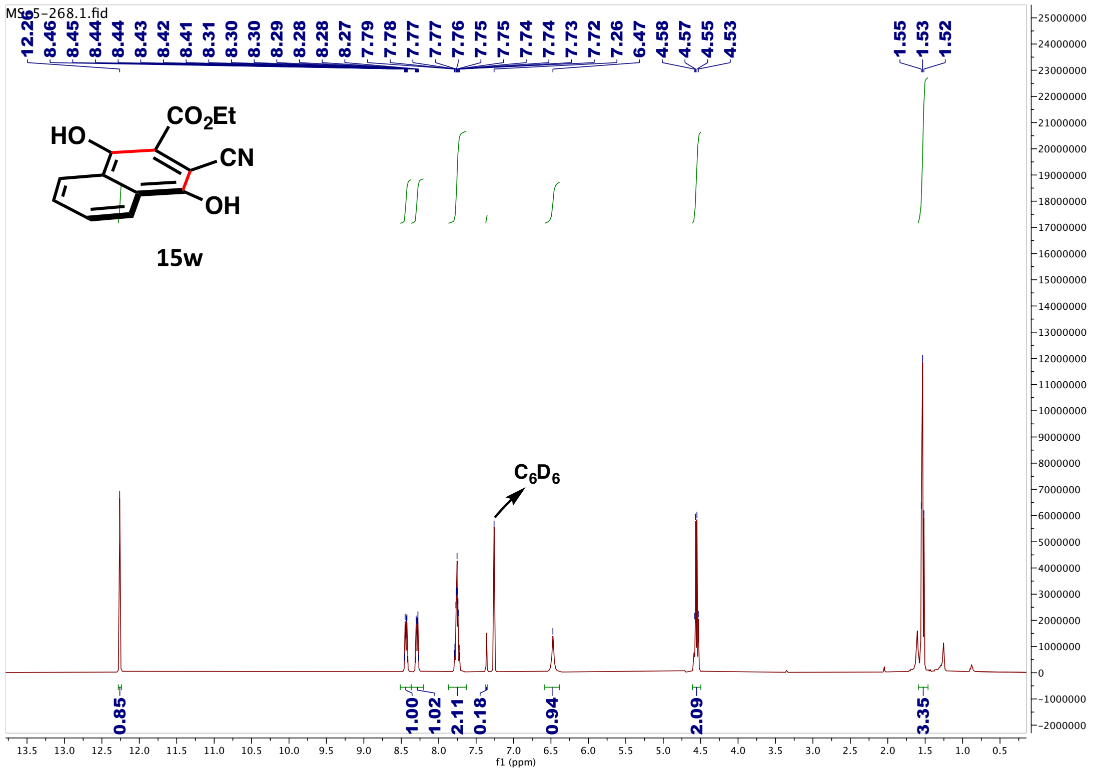

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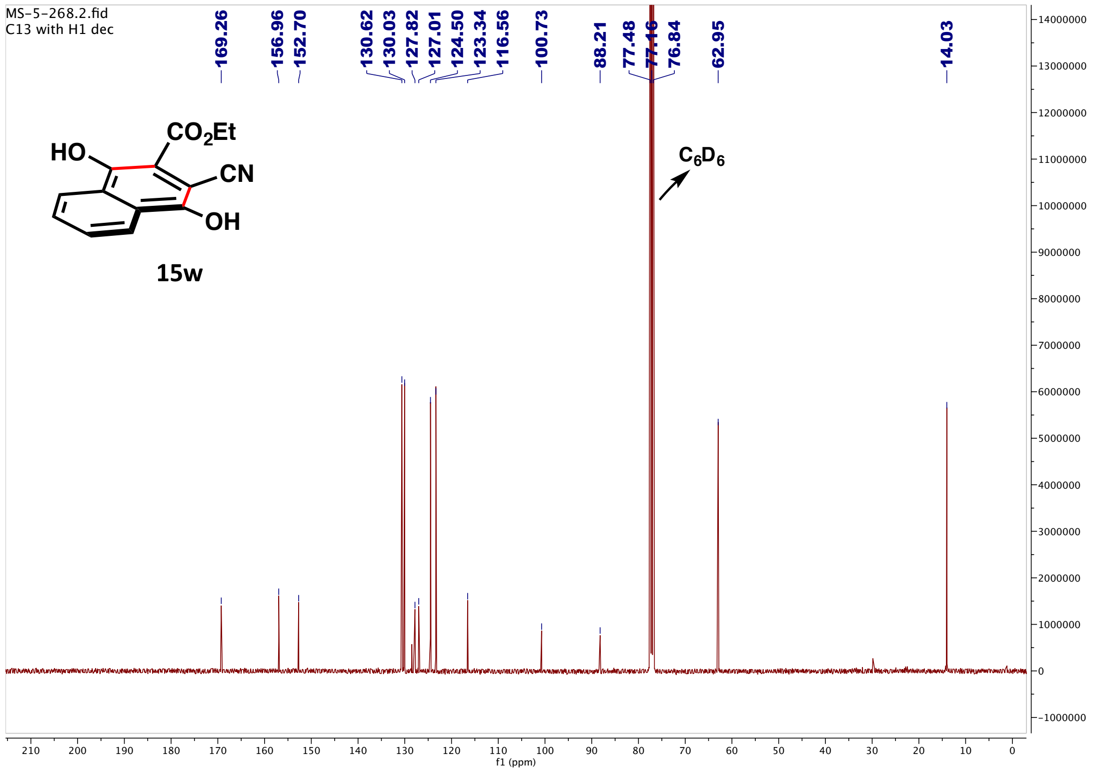

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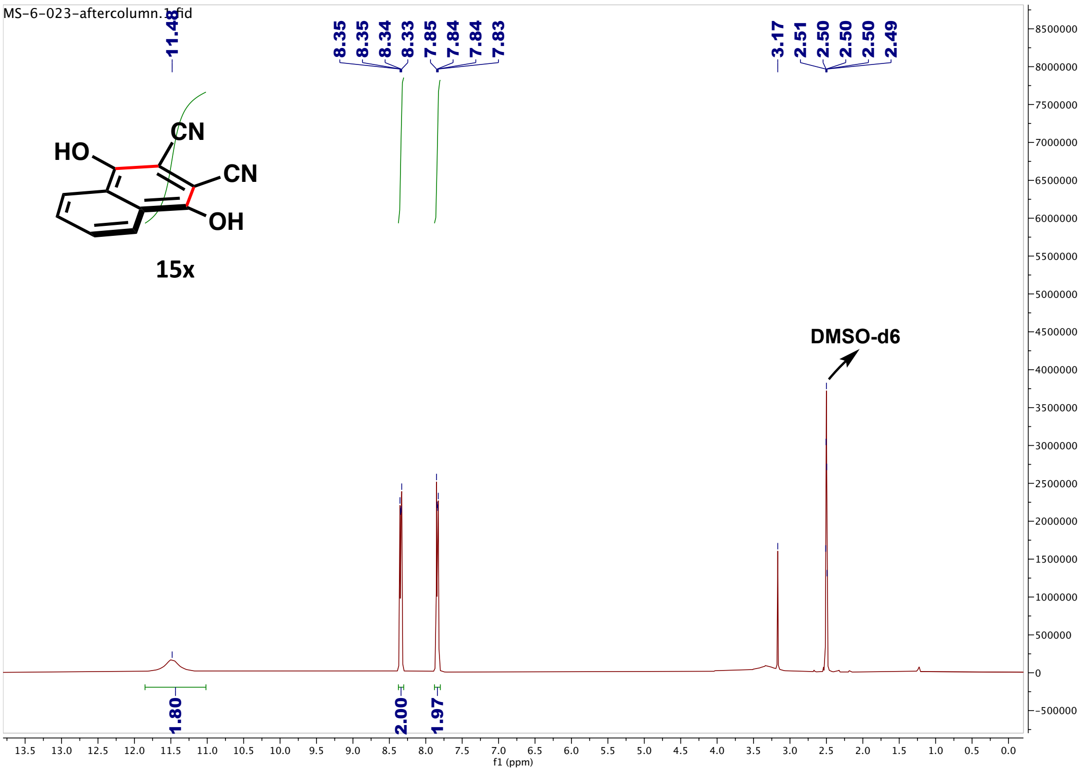

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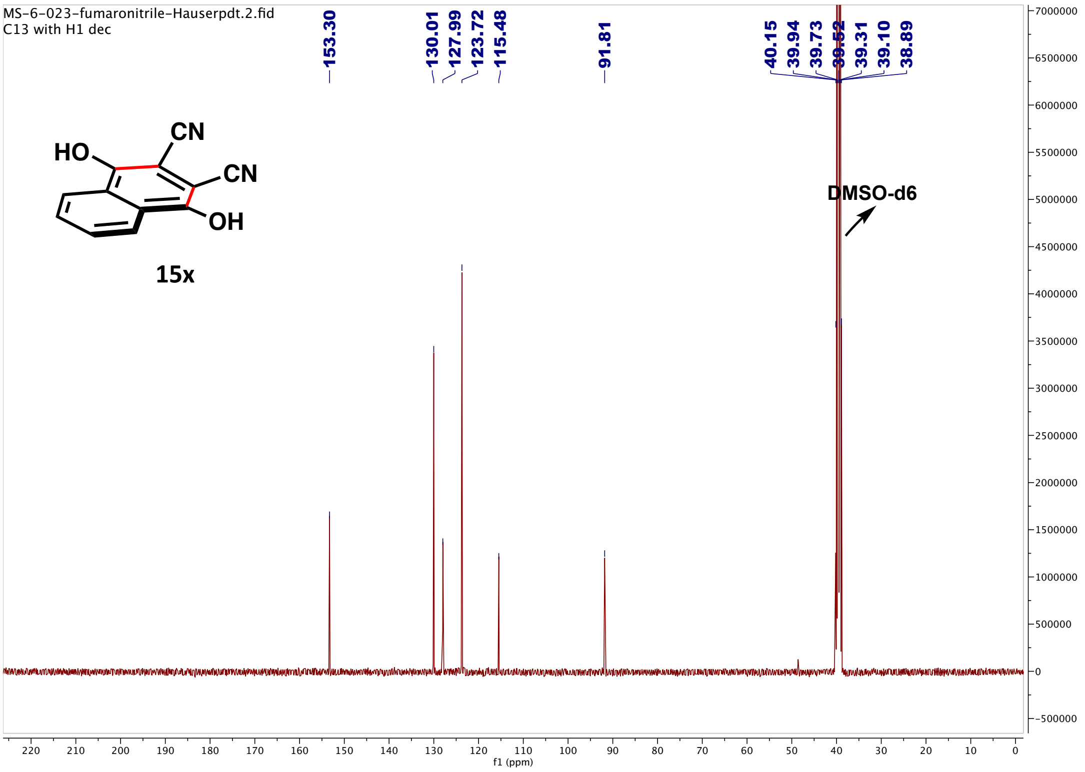

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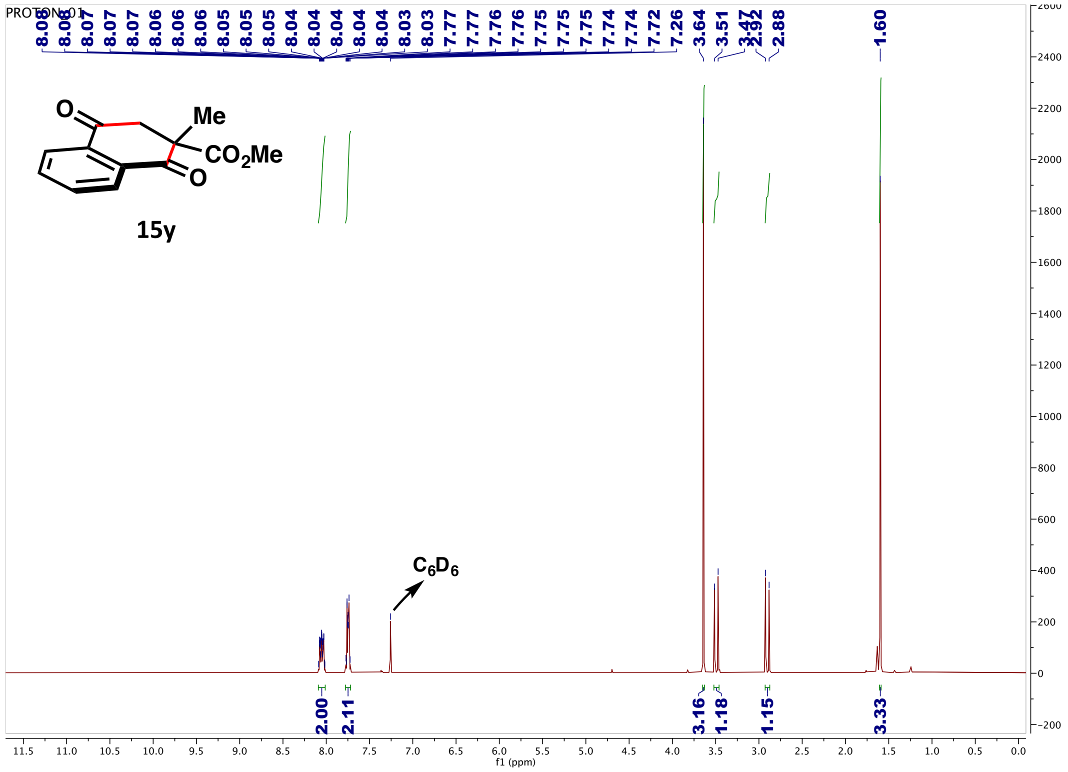

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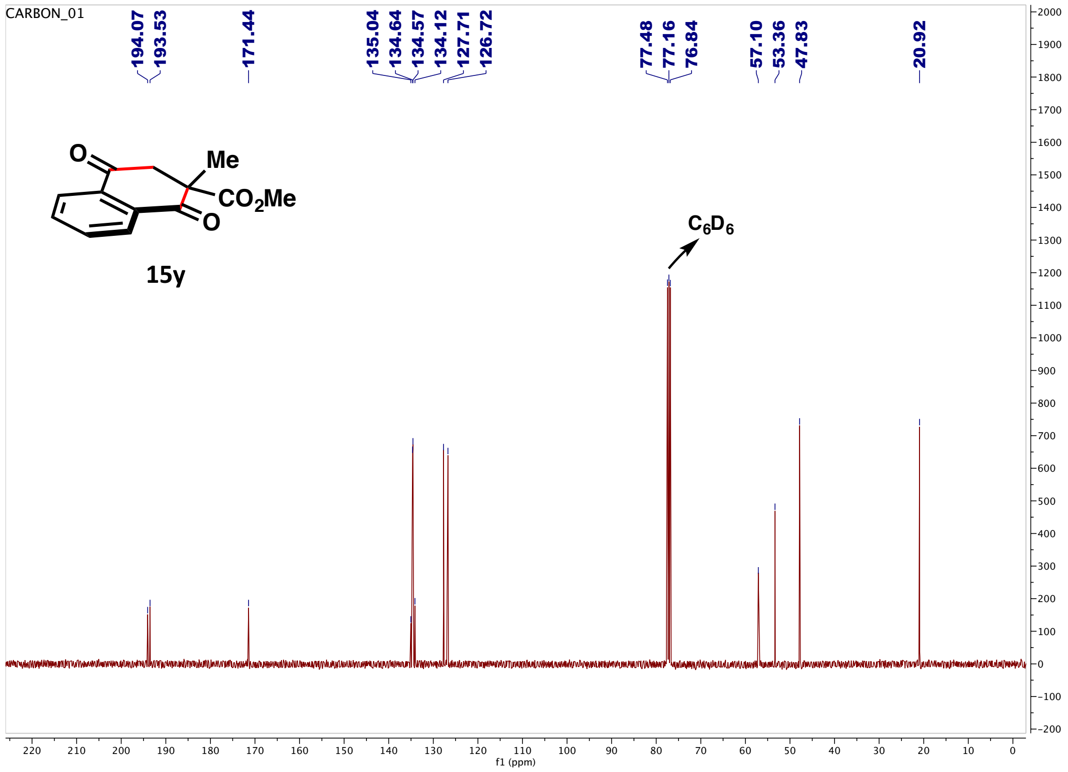

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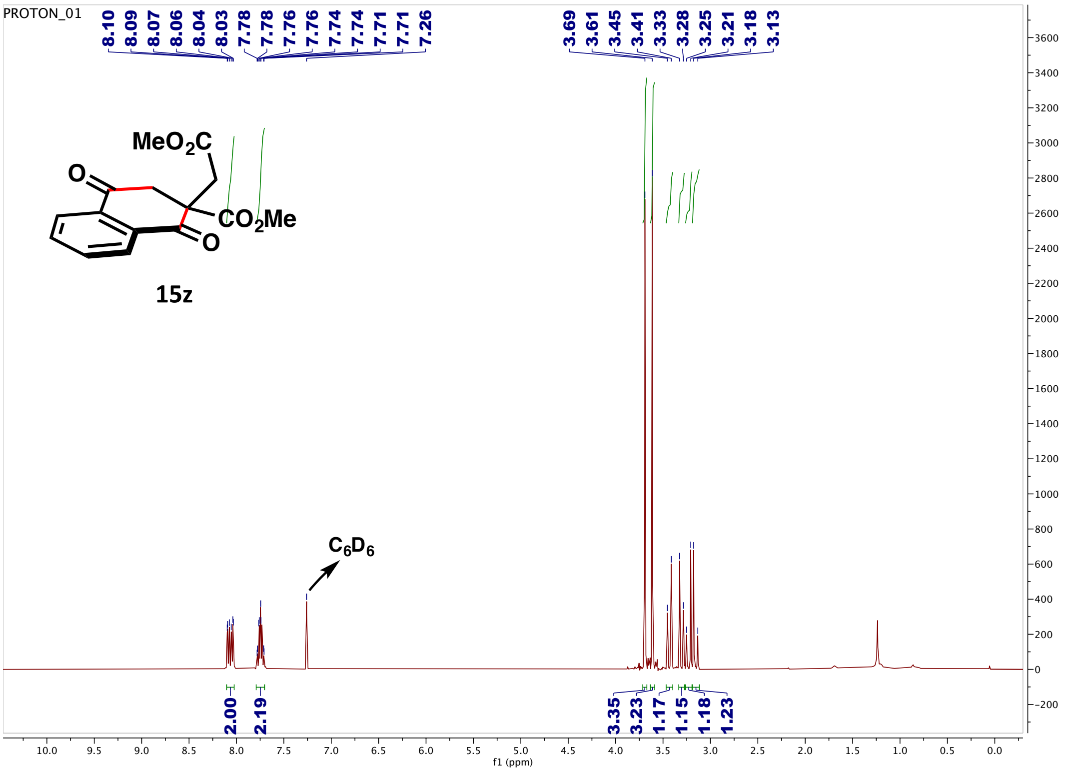

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