Supporting Information

Transition-Metal-Free Tunable Regioselective [3+2] Cycloaddition of Diaryliodonium salts with 1, 3-Dicarbonyl and Its Derivatives

Yixi Yang[a#], Shaoqing Wang[a#], Lin Wang[a], Na Dang[a], Tao Qin*[a], Heye Zhou[a], Bin Liu*[a,b]

[a] College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, Hubei 443002, PR China China
[b] Hubei Three Gorges Laboratory, Yichang 443007
E-mail: qintao@ctgu.edu.cn; liubin1@ctgu.edu.cn

Table of Contents

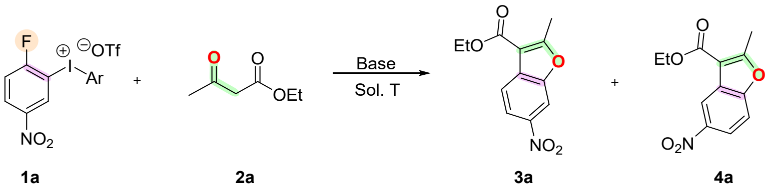
1. General Information

All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^{1}H, ^{13}C spectra were recorded with, Bruker 400 MHz (Avance-400) and JNM-ECZL 600 MHz instrument. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$) and 2.50 ppm (DMSO-d_6). All ^{13}C NMR spectra are decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$) and 39.52 ppm (DMSO-d_6). High-resolution mass spectra HRMS (ESI-TOF) were recorded on Brucker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 × 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light.

Materials. Reaction solvents THF and toluene were distilled over sodium and stored under nitrogen atmosphere. While DCM, Dioxane and CH_3CN was distilled over CaH_2 and stored under nitrogen atmosphere. All diaryliodonium salts **1** in the article were known and prepared according to the previously reported procedures.[1] All other commercial reagents and solvents were purchased from Energy-Chemical Ltd, and used as received unless otherwise noted.

2. Detailed Optimization Studies

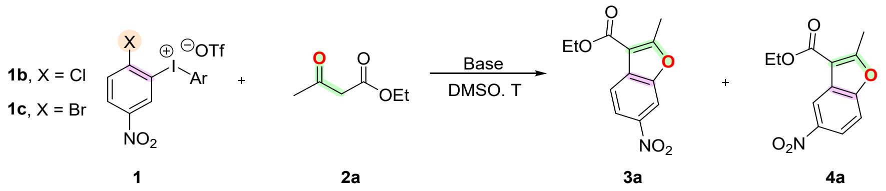
Table S1. Screening of reaction conditions for synthesis of 3a.[a]



Entry	2a	Base	Sol.	3a (%)[b]	4a (%)[b]	Ratio 3a/4a
1	1.5 eq.	Cs_2CO_3 (2.0 eq.)	CH_3CN	32	17	2:1
2	1.5 eq.	Cs_2CO_3 (2.0 eq.)	THF	35	8	4:1
3	1.5 eq.	Cs_2CO_3 (2.0 eq.)	Dioxane	21	14	3:2
4	1.5 eq.	Cs_2CO_3 (2.0 eq.)	Toluene	16	4	4:1
5	1.5 eq.	Cs_2CO_3 (2.0 eq.)	DCM	18	2	9:1
6	1.5 eq.	Cs_2CO_3 (2.0 eq.)	DMF	49	7	7:1
7	1.5 eq.	Cs_2CO_3 (2.0 eq.)	DMSO	65	7	9:1
8	1.5 eq.	K_2CO_3 (2.0 eq.)	DMSO	68	6	11:1
9	1.5 eq.	Na_2CO_3 (2.0 eq.)	DMSO	45	3	15:1
10	1.5 eq.	$KHCO_3$ (2.0 eq.)	DMSO	63	4	16:1
11	1.5 eq.	Et_3N (2.0 eq.)	DMSO	10	trace	--
12	1.5 eq.	DMAP (2.0 eq.)	DMSO	trace	trace	--
13	1.5 eq.	NaOH (2.0 eq.)	DMSO	60	6	10:1
14	1.5 eq.	$KHCO_3$ (3.0 eq.)	DMSO	74	5	15:1
15	2.0 eq.	$KHCO_3$ (3.0 eq.)	DMSO	82	4	20:1

[a] Reaction conditions: **1a** (0.1 mmol), **2** (x mmol), base (y equiv), solvent (0.1 M), rt, 12 h. [b] ^{1}H NMR yields using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Screening of reaction conditions for synthesis of 4a.[a]

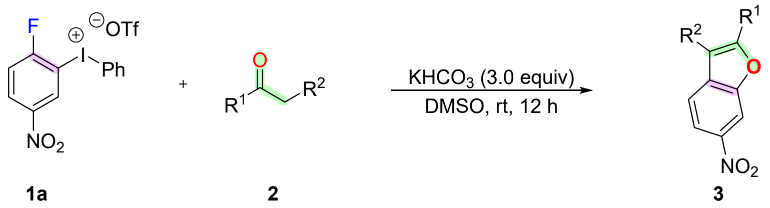


Entry	1	Base	T	3a (%)[b]	4a (%)[b]	Ratio 3a/4a
1	**1b**	$KHCO_3$ (3.0 eq.)	rt	9	18	1:2
2	**1c**	$KHCO_3$ (3.0 eq.)	rt	6	30	1:5
3	**1c**	Cs_2CO_3 (2.0 eq.)	rt	7	42	1:6
4	**1c**	K_2CO_3 (3.0 eq.)	rt	9	36	1:4
5	**1c**	Na_2CO_3 (3.0 eq.)	rt	7	35	1:4
6	**1c**	$NaHCO_3$ (3.0	rt	8	22	1:3
7	**1c**	DBU (3.0 eq.)	rt	4	16	1:4
8	**1c**	^{t}BuOK (3.0 eq.)	rt	trace	32	--
9	**1c**	NaH (3.0 eq.)	rt	2	35	1:17
10	**1c**	NaH (3.0 eq.)	40	2	36	1：18
11	**1c**	NaH (3.0 eq.)	60	2	41	1：20
12	**1c**	NaH (3.0 eq.)	80	2	43	1：22
13	**1c**	NaH (3.0 eq.)	100	3	60	1:20

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol), base (3 equiv), DMSO (0.1 M), rt, 12 h. [b] ^{1}H NMR yields using 1,3,5-trimethoxybenzene as internal standard.

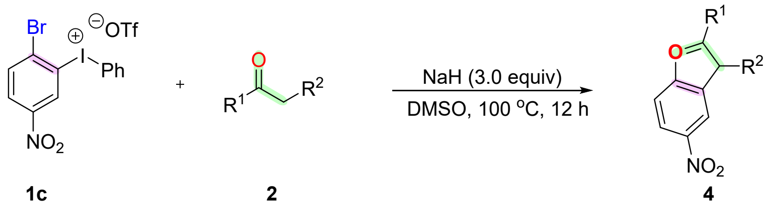
3. Experimental Procedures

a) General procedure for 3



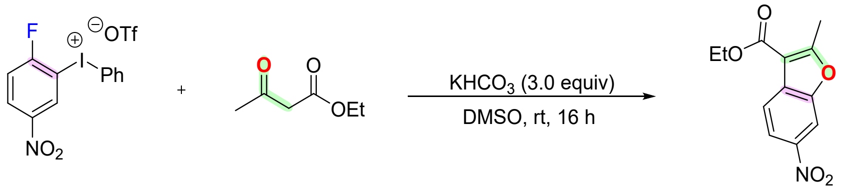
A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with diaryliodonium salt **1a** (49.6 mg, 0.1 mmol, 1.0 equiv), and anhydrous $KHCO_3$ (0.3 mmol, 30 mg, 3.0 equiv.). Then the sealed tube was wrapped with rubber stopper and connected to the vacuum, ultra dry DMSO (1 mL) and ketones derivatives **2** (0.2 mmol, 2.0 equiv) were added under argon atmosphere, then the reaction vessel was allowed to stir at rt for 12 h. Until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with ethyl acetate (3×5 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **3**.

b) General procedure for 4



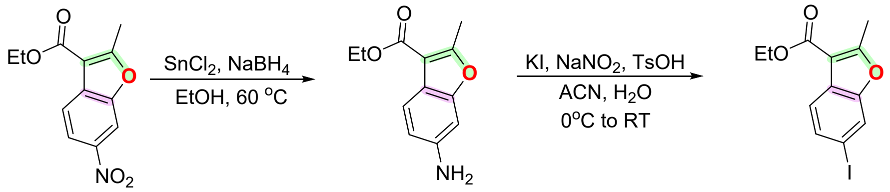
A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with diaryliodonium salt **1c** (55.3 mg, 0.1 mmol, 1.0 equiv), and NaH (0.3 mmol, 3.0 equiv). Then the sealed tube was wrapped with rubber stopper and connected to the vacuum, ultra dry DMSO (1 mL) and ketones derivatives **2** (0.2 mmol, 2.0 equiv) were added under argon atmosphere, then the reaction vessel was allowed to stir at 100 °C for 12 h. Until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with ethyl acetate (3×5 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **4**.

c) A gram scale synthesis and late-stage functionalization



1a, 8 mmol **2a,** 16 mmol **3a,** 79% (1.58 g)

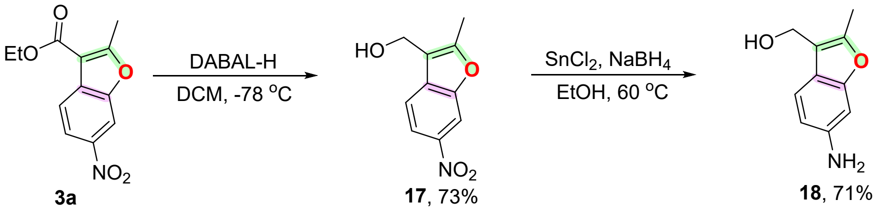
A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with diaryliodonium salt **1a** (3.94 g, 8 mmol, 1.0 equiv), and anhydrous $KHCO_3$ (24 mmol, 2.4 g, 3.0 equiv.). Then the sealed tube was wrapped with rubber stopper and connected to the vacuum, ultra dry DMSO (30 mL) and ketones derivatives **2a** (2.08 g, 16 mmol, 2.0 equiv) were added under argon atmosphere, then the reaction vessel was allowed to stir at rt for 16 h. Until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H_2O, extracted with ethyl acetate (3×80 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **3a** (1.58g, 79%).



3a **15,** 82% **16,** 75%

Added **3a** (249 mg, 1.0 mmol) and $NaBH_4$ (18.9 mg, 0.5 mmol, 0.5 equiv) in 20 mL of ethyl alcohol followed by dropwise addition of 5M $SnCl_2$ solution (5 ml) at 60 °C and the mixture was allowed to stir for 1 h at 60 °C, until the reaction was complete as indicated by TLC. The reaction mixture was quenched with H_2O and adjusted to pH 10.5 with KOH. The solution was extracted with Ethyl ether (3×30 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **15** (179.6 mg, 82%).

Added **15** (43.8 mg, 0.2 mmol, 1.0equiv) and *p*-toluenesulfonic acid monohydrate (114.1 mg, 3.0 equiv) in acetonitrile (3 mL). The reaction was cooled to 0 °C before a solution of $NaNO_2$ (27.6 mg, 2.0 equiv) and KI (58 mg, 2.5 equiv) in water (1 mL) was added drop wise. Upon complete addition of the reagents, the mixture was allowed to reach room temperature where it was stirred for 24 hours. Until the reaction was complete as indicated by TLC. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **16** (49.5 mg, 75%).

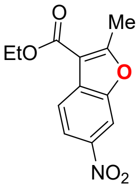


Added **3a** (43.8 mg, 0.5 mmol, 1.0equiv) in 2 mL of CH_2Cl_2 and the mixture was allowed to stir at -78 °C. Next, a solution of diisobutylaluminium hydride (1.25 mL, 1.25 mmol, 2.5 equiv) in toluene (1.0 M) was carefully added using a syringe. The reaction mixture was slowly warmed to room temperature and stirred for 1 hour. The reaction was quenched with saturated aqueous NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **17** (75.6 mg, 73%).

Added **17** (41.4 mg, 0.2 mmol, 1.0equiv) and $NaBH_4$ (3.8 mg, 0.1 mmol, 0.5 equiv) in 4 mL of ethyl alcohol followed by dropwise addition of 5M $SnCl_2$ solution (1 ml, 1.0 mmol, 5.0 equiv) at 60 °C and the mixture was allowed to stir for 1 h at 60 °C, until the reaction was complete as indicated by TLC. The reaction mixture was quenched with H_2O and adjusted to pH 10.5 with KOH. The solution was extracted with ethyl ether (3×10 mL) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product **18** (25.2 mg, 71%).

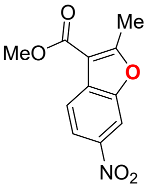
4. Analytical data of New Compounds

Ethyl 2-methyl-6-nitrobenzofuran-3-carboxylate (3a)[2]



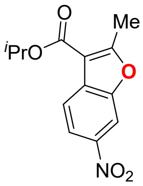
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3a** as white solid (20.4 mg, 82% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.84 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.7, 163.5, 152.3, 145.1, 132.4, 121.9, 119.7, 109.8, 107.4, 61.0, 15.0, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}NO_5$ ([M - H]$^-$), 248.0564, found, 248.0561.

Methyl 2-methyl-6-nitrobenzofuran-3-carboxylate (3b)



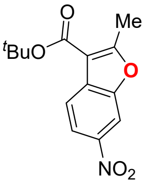
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3b** as white solid (18.6 mg, 79% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 3H), 2.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 163.9, 152.4, 145.2, 132.3, 121.9, 119.7, 109.7, 107.5, 52.0, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8NO_5$ ([M - H]$^-$), 234.0408, found, 234.0408.

Isopropyl 2-methyl-6-nitrobenzofuran-3-carboxylate (3c)



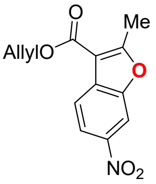
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3c** as white solid (18.7 mg, 71% yield), TLC: $R_f = 0.20$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 5.38 – 5.25 (m, 1H), 2.84 (s, 3H), 1.44 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 163.1, 152.4, 145.1, 132.6, 121.9, 119.6, 110.1, 107.7, 68.7, 22.3, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_5$ ([M - H]$^-$), 262.0721, found, 262.0718.

Tert-butyl 2-methyl-6-nitrobenzofuran-3-carboxylate (3d)



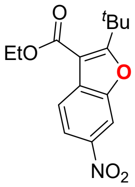
The crude was purified by flash chromatography using Petroleum ether/Ethyl acetate 50:1 to afford **3d** as white solid (17.7 mg, 64% yield), TLC: $R_f = 0.20$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 2.81 (s, 3H), 1.65 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.3, 162.7, 152.3, 145.0, 132.7, 121.9, 119.5, 111.0, 107.3, 82.2, 28.6, 15.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_5$ ($[M - H]^-$), 276.0877, found, 276.0876.

Allyl 2-methyl-6-nitrobenzofuran-3-carboxylate (3e)



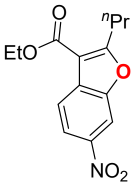
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3e** as white solid (17.5 mg, 71% yield), TLC: R_f = 0.18 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 6.15 – 6.02 (m, 1H), 5.48 – 5.33 (m, 2H), 4.89 (d, *J* = 6.0 Hz, 2H), 2.86 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.0, 163.2, 152.4, 145.2, 132.3, 132.0, 121.9, 119.7, 119.2, 109.6, 107.5, 65.7, 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{10}NO_5$ ($[M - H]^-$), 260.0564, found, 260.0564.

Ethyl 2-(tert-butyl)-6-nitrobenzofuran-3-carboxylate (3f)



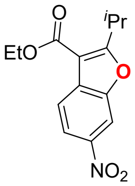
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3f** as white solid (17.5 mg, 43% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 50:1) [UV].**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.57 (s, 9H), 1.48 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.3, 163.3, 151.0, 145.0, 133.7, 122.3, 119.4, 108.9, 107.6, 61.6, 35.9, 28.2, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{16}NO_5$ ($[M - H]^-$), 290.1034, found, 290.1032.

Ethyl 6-nitro-2-propylbenzofuran-3-carboxylate (3g)



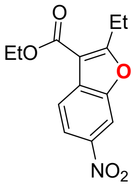
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3g** as white solid (20.0 mg, 72% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 163.5, 152.4, 145.1, 132.5, 122.0, 119.6, 109.5, 107.5, 61.0, 30.5, 21.4, 14.5, 14.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_5$ ($[M - H]^-$), 276.0877, found, 276.0878.

Ethyl 2-isopropyl-6-nitrobenzofuran-3-carboxylate (3h)



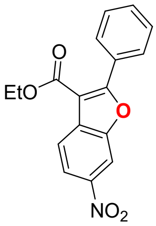
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3h** as white solid (16.6 mg, 60% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.11 – 4.00 (m, 1H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.40 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.5, 163.4, 152.3, 145.1, 132.5, 122.4, 119.6, 107.9, 107.6, 61.0, 28.1, 20.5, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_5$ ([M - H]$^-$), 276.0877, found, 276.0876.

Ethyl 2-ethyl-6-nitrobenzofuran-3-carboxylate (3i)



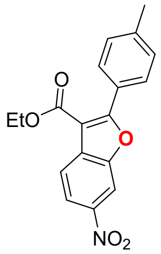
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3i** as white solid (16.1 mg, 61% yield), TLC: R_f = 0.24 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.27 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.4, 163.4, 152.4, 145.4, 132.5, 122.0, 119.6, 108.9, 107.5, 61.0, 22.3, 14.5, 11.9. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_5$ ([M - H]$^-$), 262.0721, found, 262.0718.

Ethyl 6-nitro-2-phenylbenzofuran-3-carboxylate (3j)



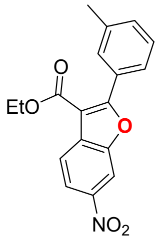
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3j** as white solid (22.4 mg, 72% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.56-7.53 (m, 3H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.4, 163.1, 152.5, 145.6, 133.3, 131.5, 129.9, 128.6, 128.4, 123.0, 119.8, 109.3, 107.7, 61.4, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}NO_5$ ([M + H]$^+$), 312.0866, found, 312.0868.

Ethyl 6-nitro-2-(p-tolyl)benzofuran-3-carboxylate (3k)



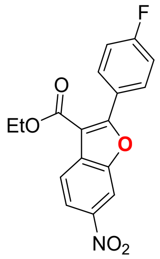
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3k** as white solid (19.8 mg, 61% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 163.2, 152.3, 145.4, 142.2, 133.4, 129.8, 129.2, 125.7, 122.8, 119.7, 108.7, 107.6, 61.3, 21.8, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NO_5$ ($[M + H]^+$), 326.1023, found, 326.1024.

Ethyl 6-nitro-2-(m-tolyl)benzofuran-3-carboxylate (3l)



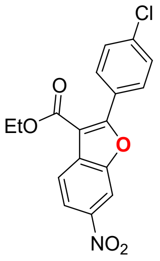
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3l** as white solid (19.5 mg, 60% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.45 – 7.33 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 163.1, 152.4, 145.5, 138.2, 133.4, 132.3, 130.3, 128.5, 128.3, 127.1, 122.9, 119.7, 109.2, 107.7, 61.3, 21.6, 14.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NO_5$ ($[M + H]^+$), 326.1023, found, 326.1029.

Ethyl 2-(4-fluorophenyl)-6-nitrobenzofuran-3-carboxylate (3m)



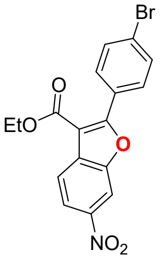
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **3m** as white solid (16.1 mg, 49% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.15 – 8.06 (m, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7 (d, *J*=252.0 Hz), 164.4, 163.1, 152.4, 145.7, 133.2, 132.6 (d, *J* = 9.0 Hz), 124.8 (d, *J*=3.0 Hz), 123.1, 119.8, 115.8 (d, *J*=21.0 Hz), 109.5, 107.7, 61.5, 14.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.15 (s, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}FNO_5$ ([M + H]+), 330.0772, found, 330.0774.

Ethyl 2-(4-chlorophenyl)-6-nitrobenzofuran-3-carboxylate (3n)



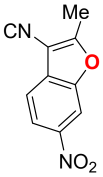
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **3n** as white solid (14.8 mg, 43% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 163.0, 152.4, 145.8, 137.8, 133.1, 131.2, 128.8, 127.0, 123.1, 119.9, 109.7, 107.8, 61.5, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}ClNO_5$ ($[M + H]^+$), 346.0477, found, 346.0476.

Ethyl 2-(4-bromophenyl)-6-nitrobenzofuran-3-carboxylate (3o)



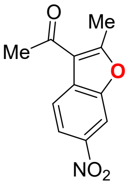
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **3o** as white solid (19.8 mg, 51% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.1, 163.0, 152.5, 145.8, 133.1, 131.8, 131.3, 127.5, 126.4, 123.2, 119.9, 109.8, 107.8, 61.5, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}BrNO_5$ ($[M + H]^+$), 389.9972, found, 289.9974.

2-Methyl-6-nitrobenzofuran-3-carbonitrile (3p)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3p** as light yellow solid (10.5 mg, 52% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 2.76 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.0, 152.6, 146.1, 131.8, 120.3, 119.8, 112.0, 108.2, 92.4, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_5N_2O_3$ ($[M - H]^-$), 201.0306, found, 201.0299.

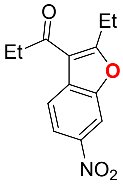
1-(2-Methyl-6-nitrobenzofuran-3-yl)ethan-1-one (3q)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3q** as white solid (17.5 mg, 80% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ

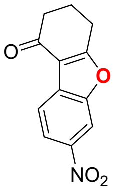
8.32 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 2.86 (s, 3H), 2.66 (s, 3H). ^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 193.2, 167.5, 152.3, 145.2, 132.2, 121.8, 119.8, 118.0, 107.4, 31.2, 16.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8NO_4$ ([M - H]$^-$), 218.0459, found, 218.0454.

1-(2-Ethyl-6-nitrobenzofuran-3-yl)propan-1-one (3r)



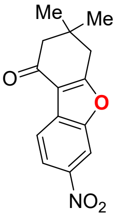
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3r** as white solid (12.6 mg, 51% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 3.25 (q, *J* = 7.8 Hz, 2H), 2.99 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.8 Hz, 3H). ^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 196.4, 172.4, 152.7, 145.0, 132.2, 121.8, 119.7, 116.7, 107.6, 36.6, 23.1, 11.9, 7.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_4$ ([M - H]$^-$), 246.0772, found, 246.0768.

7-Nitro-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (3s)



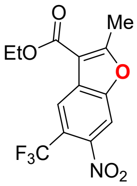
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **3s** as white solid (11.6 mg, 50% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 10:1) [UV]. ^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 1.8 Hz,1H), 8.28 (dd, *J* = 1.8, 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 3.13 (t, *J* = 6.0 Hz, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 2.37 – 2.30 (m, 2H). ^{13}**C NMR** (150 MHz, Chloroform-*d*) δ 194.1, 175.2, 153.5, 145.6, 129.8, 121.9, 120.5, 116.6, 107.8, 37.9, 24.2, 22.3. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}NO_4$ ([M + H]$^+$), 232.0604, found, 232.0604.

3,3-Dimethyl-7-nitro-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (3t)



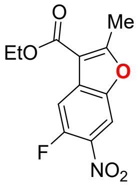
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **3t** as white solid (16.3 mg, 63% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 30:1) [UV]. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 2.99 (s, 2H), 2.53 (s, 2H), 1.23 (s, 6H). ^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 193.6, 174.7, 153.8, 145.5, 129.6, 121.8, 120.4, 115.4, 107.9, 52.3, 38.1, 35.5, 28.8. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_4$ ([M + H]$^+$), 260.0917, found, 260.0918.

Ethyl 2-methyl-6-nitro-5-(trifluoromethyl)benzofuran-3-carboxylate (3u)



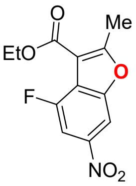
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3u** as white solid (20.9 mg, 66% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.04 (s, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 2.87 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.2, 162.8, 153.1, 145.2, 130.0, 122.6 (d, *J* = 272.0 Hz), 121.9 (q, *J* = 6.0 Hz.), 120.5 (d, *J* = 34.0 Hz), 110.1, 109.3, 61.4, 14.9, 14.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -58.58 (s, 3F). HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_9F_3NO_5$ ([M - H]$^-$), 316.0438, found, 316.0434.

Ethyl 5-fluoro-2-methyl-6-nitrobenzofuran-3-carboxylate (3v)



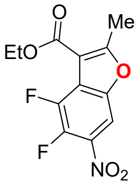
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3v** as white solid (14.7 mg, 55% yield), TLC: R_f = 0.25(Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 6.0 Hz, 1H), 7.82 (d, *J* = 10.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.84 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.1, 163.0, 153.3 (d, *J* = 258.0 Hz), 147.8, 134.3 (d, *J* = 9.0 Hz), 132.6 (d, *J* = 10.5 Hz), 110.2 (d, *J* = 25.5 Hz), 110.0 (d, *J* = 4.5 Hz), 109.0 (d, *J* = 1.5 Hz), 61.2, 15.1, 14.5. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -122.64 (s, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_9FNO_5$ ([M - H]$^-$), 266.0470, found, 266.0467.

Ethyl 4-fluoro-2-methyl-6-nitrobenzofuran-3-carboxylate (3w)



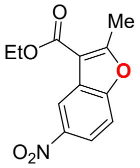
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3w** as white solid (17.9 mg, 67% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.92 (d, *J* = 9.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.82 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 162.8, 155.7, 154.0 (d, *J* = 9.7 Hz), 153.1, 145.1, 120.6 (d, *J* = 19.1 Hz), 107.2 (d, *J* = 27.0 Hz), 104.0, 61.4, 14.9, 14.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -108.02 (s, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_9FNO_5$ ([M - H]$^-$), 266.0470, found, 266.0469.

Ethyl 4,5-difluoro-2-methyl-6-nitrobenzofuran-3-carboxylate (3x)



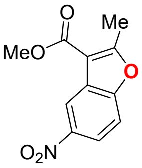
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **3x** as white solid (10.0 mg, 35% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.82 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 162.1, 147.7 (d, *J* = 9.0 Hz), 144.8 (dd, *J* = 93.0, 15.0 Hz), 142.2 (dd, *J* = 92.0, 15.0 Hz), 129.2, 121.0, 109.8, 104.2 (t, *J* = 4.0 Hz), 61.6, 15.0, 14.3. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -132.74 (d, *J* = 18.8 Hz, 1F), -148.41 (d, *J* = 18.8 Hz, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}F_2NO_5$ ($[M + H]^+$), 286.0522, found, 286.0520.

Ethyl 2-methyl-5-nitrobenzofuran-3-carboxylate (4a)[2]



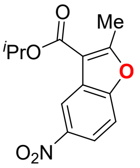
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4a** as white solid (15.1 mg, 60% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 2.83 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 163.5, 156.3, 145.1, 127.1, 120.5, 118.6, 111.4, 110.4, 61.1, 14.7, 14.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}NO_5$ ($[M - H]^-$), 248.0564, found, 248.0562.

Methyl 2-methyl-5-nitrobenzofuran-3-carboxylate (4b)



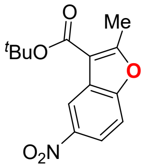
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4b** as white solid (12.9 mg, 53% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 3H), 2.83 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 163.9, 156.4, 145.1, 126.9, 120.5, 118.5, 111.4, 110.0, 52.1, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_8NO_5$ ($[M - H]^-$), 234.0408, found, 234.0410.

Isopropyl 2-methyl-5-nitrobenzofuran-3-carboxylate (4c)



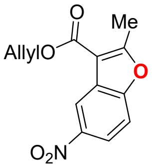
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4c** as white solid (10.5 mg, 41% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 5.36 – 5.28 (m, 1H), 2.82 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.5, 163.0, 156.3, 145.1, 127.2, 120.4, 118.6, 111.3, 110.4, 68.8, 22.2, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_5$ ([M - H]$^-$), 262.0721, found, 262.0720.

Tert-butyl 2-methyl-5-nitrobenzofuran-3-carboxylate (4d)



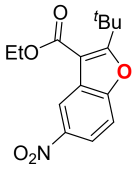
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4d** as white solid (11.6 mg, 39% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 2.80 (s, 3H), 1.67 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.2, 162.7, 156.3, 145.0, 127.3, 120.3, 118.6, 111.3, 111.2, 82.3, 28.5, 14.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_5$ ([M - H]$^-$), 276.0877, found, 276.0877.

Allyl 2-methyl-5-nitrobenzofuran-3-carboxylate (4e)



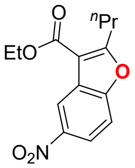
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4e** as white solid (10.7 mg, 42% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 6.18 – 6.02 (m, 1H), 5.53 – 5.36 (m, 2H), 4.94 (d, *J* = 5.6 Hz, 2H)), 2.86 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.0, 163.1, 156.3, 145.2, 132.0, 127.0, 120.5, 119.2, 118.5, 111.4, 109.9, 65.7, 14.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{10}NO_5$ ([M - H]$^-$), 260.0564 found, 260.0562.

Ethyl 2-(tert-butyl)-5-nitrobenzofuran-3-carboxylate (4f)



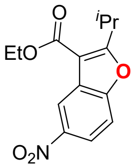
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4f** as white solid (11.6 mg, 40% yield), TLC: R_f = 0.20 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.56 (s, 9H), 1.50 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.2, 163.2, 155.0, 144.9, 128.2, 120.23, 119.0, 111.5, 109.2, 61.3, 35.6, 28.3, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{18}NO_5$ ([M + H]$^+$), 292.1179found, 292.1180

Ethyl 5-nitro-2-propylbenzofuran-3-carboxylate (4g)



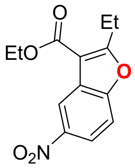
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4g** as white solid (10.8 mg, 39% yield), TLC: $R_f = 0.2$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H), 1.84 (q, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.4, 163.4, 156.4, 145.0, 127.1, 120.4, 118.7, 111.4, 109.8, 61.0, 30.2, 21.4, 14.5, 14.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_5$ ([M - H]$^-$), 276.0877, found, 276.0875.

Ethyl 2-isopropyl-5-nitrobenzofuran-3-carboxylate (4h)



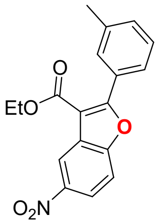
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4h** as white solid (15.2 mg, 55% yield), TLC: $R_f = 0.20$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.86 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 4.12 – 3.98 (m, 1H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.40 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 174.5, 163.4, 156.3, 145.0, 127.1, 122.1, 120.4, 118.8, 111.5, 107.6, 61.0, 27.8, 20.6, 14.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}O_5$ ([M - H]$^-$), 276.0877, found, 276.0876.

Ethyl 2-ethyl-5-nitrobenzofuran-3-carboxylate (4i)



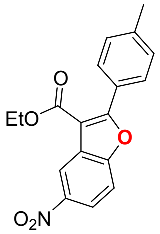
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4i** as white solid (16.1 mg, 61% yield), TLC: $R_f = 0.25$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 3.26 (q, *J* = 7.8 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.8 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.4, 163.4, 156.4, 145.1, 127.1, 120.4, 118.7, 111.5, 109.2, 61.1, 22.0, 14.5, 12.0. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_5$ ([M - H]$^-$), 262.0721, found, 262.0719.

Ethyl 5-nitro-2-(m-tolyl)benzofuran-3-carboxylate (4j)



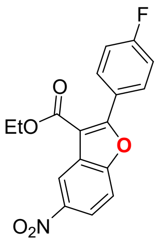
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **4j** as white solid (11.7 mg, 36% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.45 – 7.33 (m, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.9, 163.0, 156.4, 145.2, 138.2, 132.1, 130.2, 128.5, 128.3, 128.1, 127.1, 121.1, 119.6, 111.7, 109.5, 61.4, 21.6, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NO_5$ ([M + H]$^+$), 326.1023 found, 326.1018.

Ethyl 5-nitro-2-(p-tolyl)benzofuran-3-carboxylate (4k)



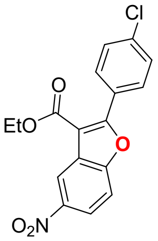
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **4k** as white solid (13.7 mg, 42% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.0, 163.1, 156.3, 141.9, 129.7, 129.4, 129.2, 128.6, 125.7, 121.0, 119.5, 111.6, 109.1, 61.4, 21.8, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NO_5$ ([M + H]$^+$), 326.1023 found, 326.1025.

Ethyl 2-(4-fluorophenyl)-5-nitrobenzofuran-3-carboxylate (4l)



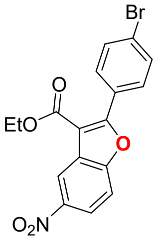
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **4l** as white solid (13.5 mg, 41% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.97 (s, 1H), 8.30 (d, *J* = 9.2 Hz, 1H), 8.15 - 8.11 (m, 2H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.22 (t, *J* = 8.8 Hz, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.6 (d, *J* = 251.0 Hz), 163.0, 162.7, 156.3, 145.3, 132.1 (d, *J* = 9.0 Hz), 127.9, 124.7 (d, *J* = 3.0 Hz), 121.3, 119.7, 115.7 (d, *J* = 21.0 Hz), 111.7, 109.6, 61.5, 14.4. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -107.51 (s, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}FNO_5$ ([M + H]$^+$), 330.0772 found, 330.0769.

Ethyl 2-(4-chlorophenyl)-5-nitrobenzofuran-3-carboxylate (4m)



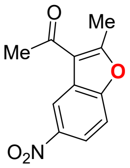
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **4m** as white solid (16.2 mg, 47% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 162.9, 162.4, 156.3, 145.3, 137.6, 131.1, 128.8, 127.9, 127.0, 121.4, 119.7, 111.8, 110.1, 61.6, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}ClNO_5$ ([M + H]$^+$), 346.0477, found, 346.0475

Ethyl 2-(4-bromophenyl)-5-nitrobenzofuran-3-carboxylate (4n)



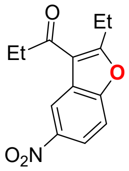
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **4n** as white solid (15.2 mg, 39% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 20:1) [UV]. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 162.9, 162.4, 156.3, 145.3, 131.8, 131.2, 127.9, 127.4, 126.1, 121.4, 119.7, 111.8, 110.1, 61.6, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}BrNO_5$ ([M + H]$^+$), 389.9972, found, 389.9966.

1-(2-Methyl-5-nitrobenzofuran-3-yl)ethan-1-one (4o)



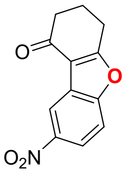
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4o** as white solid (9.9 mg, 45% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.92 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 2.84 (s, 3H), 2.68 (s, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 193.1, 165.5, 156.3, 145.2, 129.0, 127.0, 120.7, 118.3, 111.5, 31.2, 15.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{11}H_{10}NO_4$ ([M + H]$^+$), 220.0604, found, 220.0603.

1-(2-Ethyl-5-nitrobenzofuran-3-yl)propan-1-one (4p)



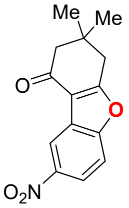
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4p** as white solid (6.9 mg, 28% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 3.24 (q, *J* = 7.6 Hz, 2H), 3.02 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.3, 170.2, 156.4, 145.1, 126.8, 120.5, 118.4, 116.8, 111.6, 36.6, 22.8, 12.0, 7.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{14}NO_4$ ($[M + H]^+$), 248.0917, found, 248.0917.

8-Nitro-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (4q)[3]



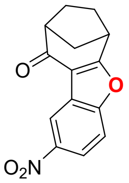
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **4q** as white solid (10.6 mg, 46% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 10:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.4 Hz, 1H), 8.26 (dd, *J* = 2.4, 9.0 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 3.10 (t, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 6.0 Hz, 2H), 2.33 (p, *J* = 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 173.4, 157.3, 145.8, 124.6, 121.1, 118.3, 117.0, 111.7, 37.8, 24.0, 22.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}NO_4$ ($[M + H]^+$), 232.0604, found, 232.0603.

3,3-Dimethyl-8-nitro-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (4r)



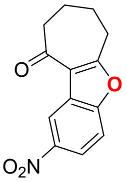
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **4r** as white solid (13.5 mg, 52% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 2.96 (s, 2H), 2.53 (s, 2H), 1.23 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 172.6, 157.7, 145.5, 124.5, 121.0, 118.2, 115.8, 111.8, 52.2, 37.9, 35.5, 28.8 **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{14}NO_4$ ($[M + H]^+$), 260.0917, found, 260.0913.

2-Nitro-6,7,8,9-tetrahydro-10H-6,9-methanocyclohepta[b]benzofuran-10-one (4s)



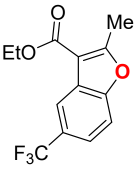
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **4s** as white solid (11.7 mg, 46% yield), TLC: Rf = 0.16 (Petroleum ether : Ethyl acetate = 10:1) [UV]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.85 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 3.64 (t, *J* = 4.8 Hz, 1H), 3.21 – 3.17 (m, 1H), 2.37 – 2.27 (m, 3H), 1.98 – 1.92 (m, 2H), 1.75 – 1.69 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 196.8, 179.4, 157.4, 145.4, 124.8, 120.8, 118.0, 114.0, 111.9, 50.3, 41.3, 37.6, 30.1, 25.5. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{12}NO_4$ ($[M + H]^+$), 258.0761, found, 258.0765.

2-Nitro-6,7,8,9-tetrahydro-10H-cyclohepta[b]benzofuran-10-one (4t)



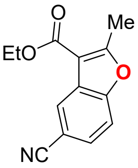
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 20:1 to afford **4t** as white solid (9.8 mg, 40% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 20:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 3.25 (t, *J* = 6.0 Hz, 2H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.18 – 2.10 (m, 2H), 2.07 – 2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 168.7, 156.8, 145.7, 127.8, 121.0, 119.7, 118.5, 111.0, 45.1, 30.4, 24.6, 22.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_4$ ($[M + H]^+$), 246.0761, found, 246.0762.

Ethyl 2-methyl-5-(trifluoromethyl)benzofuran-3-carboxylate (4u)[2]



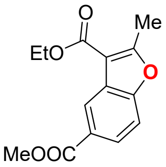
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4u** as white solid (12.3 mg, 42% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.57 – 7.48 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.80 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.4, 164.0, 155.0, 126.6 126.5 (d, *J* = 32.0 Hz), 126.1 (d, *J* = 8.0 Hz), 123.3, 120.7 (dm, *J* = 195.0 Hz), 111.3, 109.5, 60.8, 14.6, 14.5. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -61.01 (s, 3F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{10}F_3O_3$ ($[M - H]^-$), 271.0588, found, 271.0588.

Ethyl 5-cyano-2-methylbenzofuran-3-carboxylate (4v)



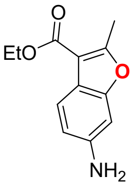
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 30:1 to afford **4v** as white solid (9.2 mg, 36% yield), TLC: R_f = 0.25 (Petroleum ether : Ethyl acetate = 30:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.81 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 163.6, 155.3, 128.3, 127.0, 122.9, 119.5, 115.1, 112.1, 107.9, 61.0, 14.8, 14.6. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{13}H_{12}NO_3$ ($[M + H]^+$), 230.0812, found, 230.0812.

3-Ethyl 5-methyl 2-methylbenzofuran-3,6-dicarboxylate (4w)[2]



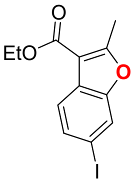
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 50:1 to afford **4w** as white solid (10.5 mg, 38% yield), TLC: $R_f = 0.24$ (Petroleum ether : Ethyl acetate = 50:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 2.79 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 165.0, 164.1, 156.2, 126.5, 126.34, 126.26, 124.3, 110.8, 109.7, 60.7, 52.3, 14.60, 14.56. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{14}H_{15}O_5$ ($[M + H]^+$), 263.0914, found, 263.0911.

Ethyl 6-amino-2-methylbenzofuran-3-carboxylate (15)



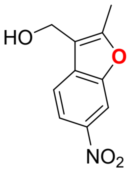
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **15** as brown solid (179.6 mg, 82% yield), TLC: $R_f = 0.20$ (Petroleum ether : Ethyl acetate = 10:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.4 Hz, 1H), 6.73 (s, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 2H), 2.70 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 161.7, 155.1, 144.4, 122.2, 118.2, 112.9, 109.1, 97.2, 60.2, 14.6, 14.4. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{14}NO_3$ ($[M + H]^+$), 220.0968, found, 220.0965.

Ethyl 6-iodo-2-methylbenzofuran-3-carboxylate (16)



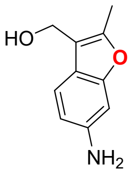
The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 10:1 to afford **16** as brown solid (49.5 mg, 75% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 10:1) [UV]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.75 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.2, 164.0, 154.1, 133.0, 126.2, 123.4, 120.2, 109.3, 87.8, 60.6, 14.54, 14.51. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{12}H_{10}IO_3$ ($[M - H]^-$), 328.9680, found, 328.9669.

(2-Methyl-6-nitrobenzofuran-3-yl)methanol (17)



The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 4:1 to afford **17** as colorless solid (75.6 mg, 73% yield), TLC: $R_f = 0.26$ (Petroleum ether : Ethyl acetate = 4:1) [UV]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 4.81 (d, *J* = 4.0 Hz, 2H), 2.54 (s, 3H), 1.73 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.9, 152.8, 144.7, 134.8, 119.2, 118.7, 115.2, 107.3, 55.3, 12.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_8NO_4$ ([M - H]$^-$), 206.0459, found, 206.0452.

(6-Amino-2-methylbenzofuran-3-yl)methanol (18)

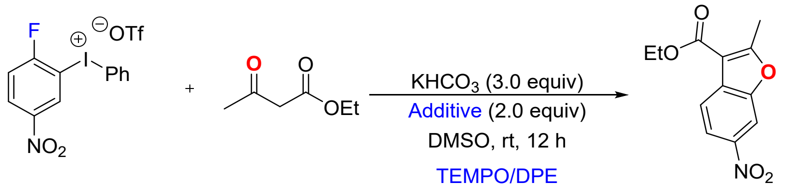


The crude was purified by flash chromatography using Petroleum ether/ Ethyl acetate 2:1 to afford **18** as brown solid (25.2 mg, 71% yield), TLC: R_f = 0.26 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 5.01 (s, 2H), 4.81 (t, *J* = 5.2 Hz, 1H), 4.45 (d, *J* = 5.2 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 154.9, 147.8, 145.9, 119.., 118.5, 114.9, 110.7, 95.3, 53.6, 11.7. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{10}H_{12}NO_2$ ([M + H]$^+$), 178.0863, found, 178.0860.

4. Mechanistic investigation

4.1 Trapping experiment

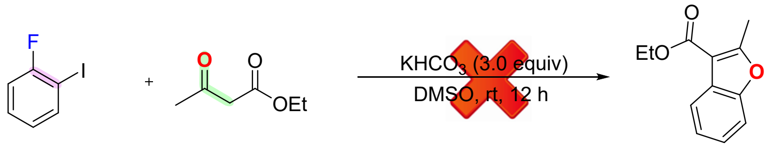
In order to explore whether the transformation proceeds *via* the radical pathway, a series of reactions were carried out in the presence of the trapping reagents TEMPO and DPE. Under the standard conditions, two equivalents of radical scavengers (TEMPO, DPE) were added to the reaction. The standard product **3a** was obtained in yields of 76% and 78%. No significant decrease of yield was observed. Hence, it can be inferred that the reaction does not proceed *via* a radical pathway.



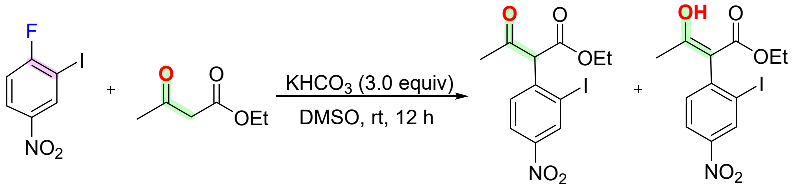
1a **2a** **3a,** 76%/78%

4.2 Controlled experiments

To clarify the sequence of two consecutive nucleophilic substitutions during the cycloaddition reaction of the diaryliodonium salt, several controlled experiments were performed. When fluoroaromatic **1d** was subjected to the reaction conditions, no cycloaddition product **5** or any other substituted products were observed. In contrast, compound **1e**, containing a para-positioned nitro group—a strong electron-withdrawing group—underwent a reaction with **2a**, resulting in the formation of *C*-arylated products **6** and **7**. This observation suggests that electron-withdrawing groups can facilitate the initial nucleophilic substitution. These experimental results are aligning with findings from previous studies [1], [4-6].



1d **2a** **5,** n.d.



1e **2a** **6,** 21% **7,** 33%

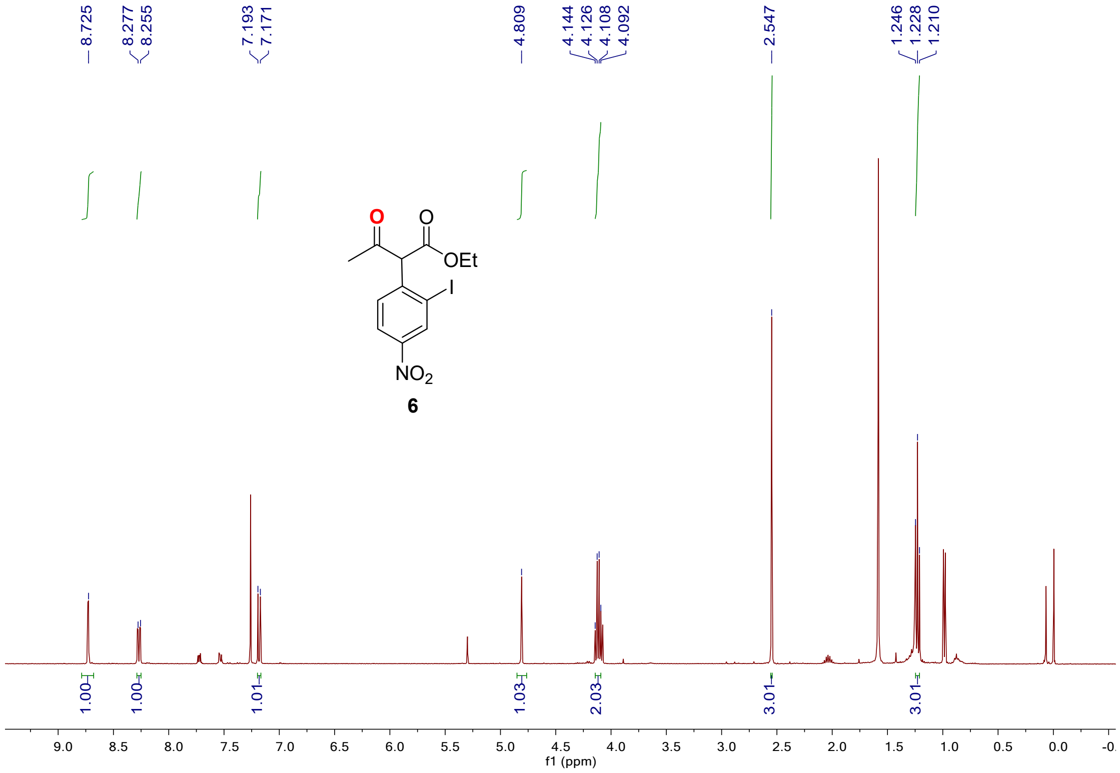


Fig. S1 ^{1}H NMR data of **6**

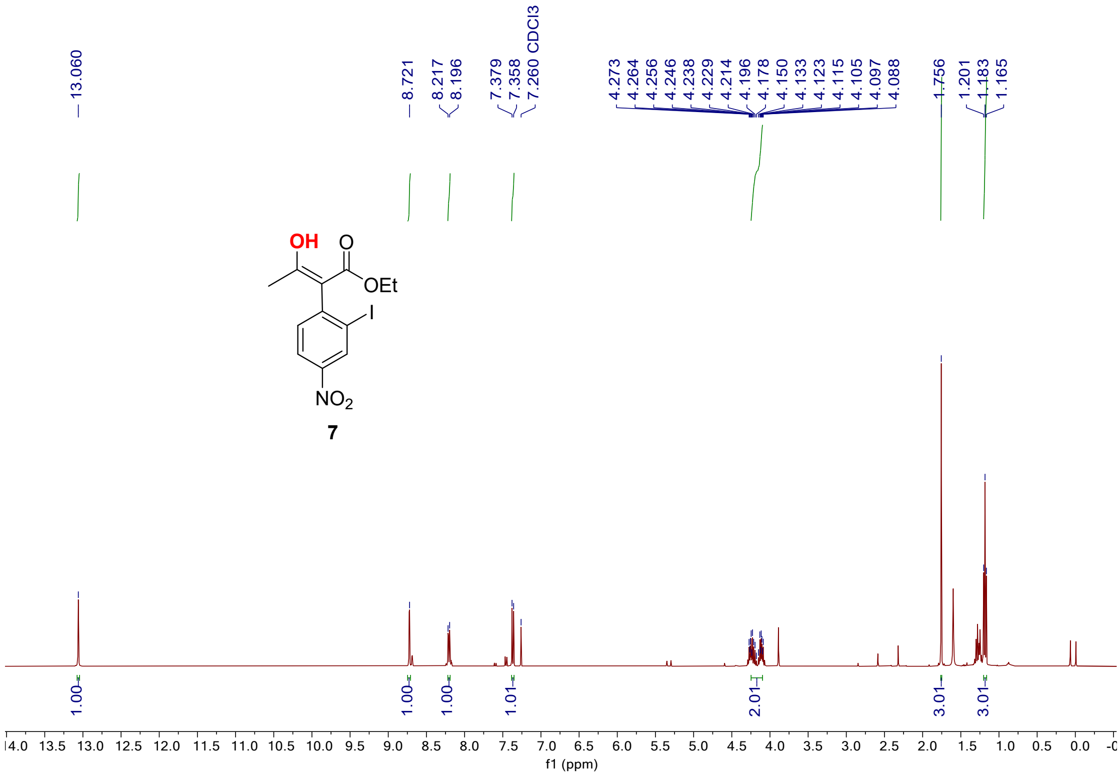
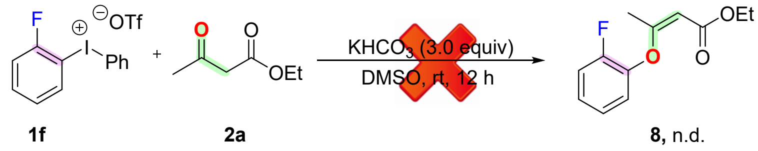
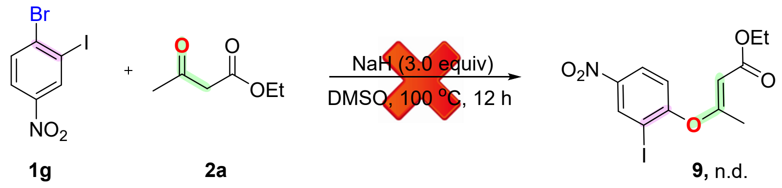


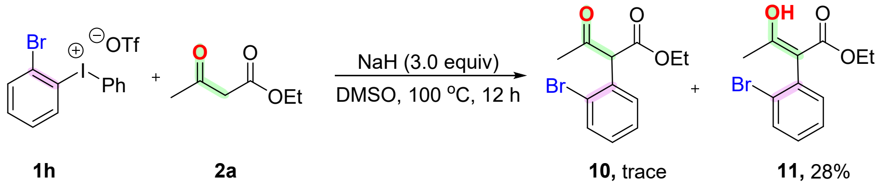
Fig. S2 ^{1}H NMR data of **7**

Further, in order to prove whether the *O*-arylation reaction of diaryliodonium salt with ethyl acetoacetate is the first step of cyclization reaction. Diaryliodonium salt **1f**, lacking the nitro substitution, was used, no *O*-arylation product **8** and other useful products were detected under standard conditions. This indicates that *O*-arylation is unlikely to be the first step in the cyclization process.



Meanwhile, control experiments analogous to those with fluoroaryl derivatives were conducted using 1-bromo-2-iodo-4-nitrobenzene (**1g**) and (2-bromophenyl)(phenyl)iodonium trifluoromethanesulfonate (**1h**). Interestingly, when 1-bromo-2-iodo-4-nitrobenzene (**1g**) was used, no *O*-arylation product (**9**) was detected under standard conditions.[11] In contrast, when diaryliodonium salt **1h** was employed, *C*-arylated products **10** and **11** were observed. These findings suggest that the initial step in the formation of the cyclized product **4** involves an enolate attack on the carbon atom bonded to the iodine atom of the iodonium salt.





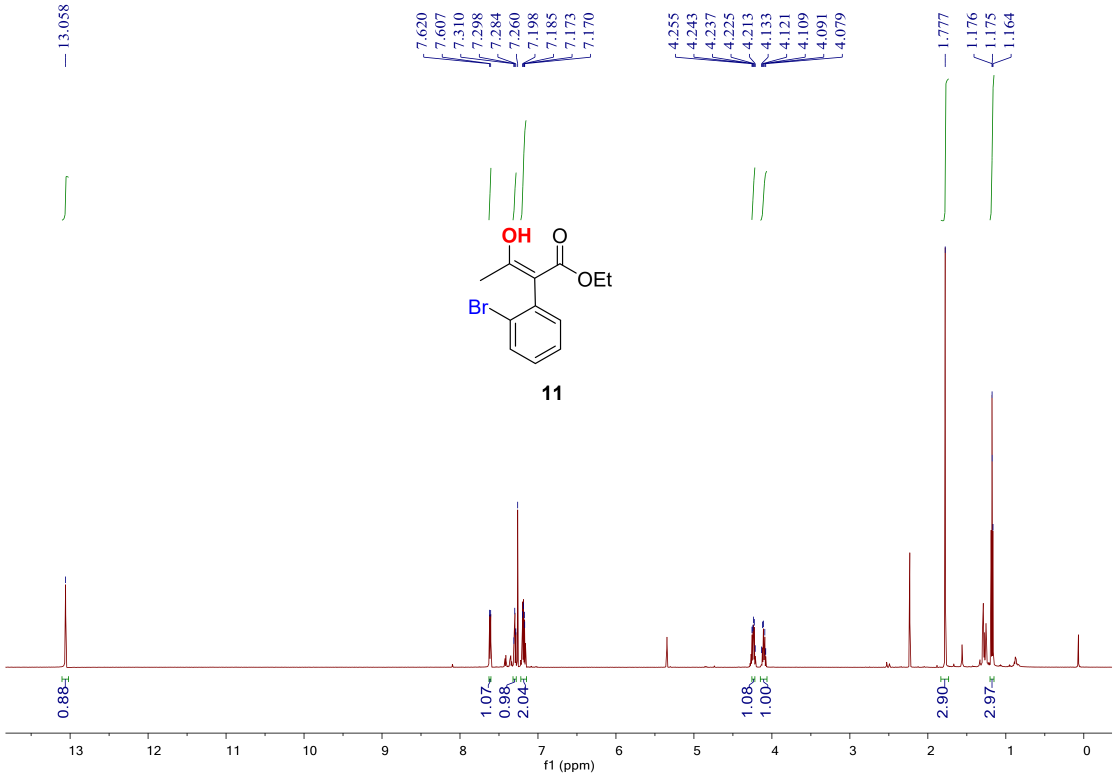
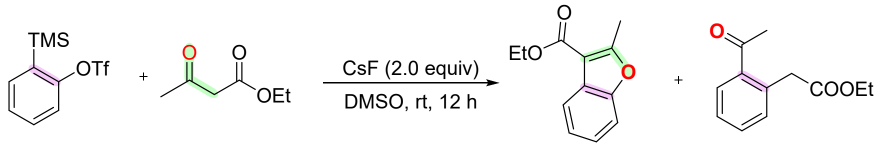


Fig. S3 ^{1}H NMR data of **11**

Finally, in order to verify whether aryne intermediate is involved in the cyclization reaction, we directly utilized the aryne generated from 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **12** in the presence of CsF to conduct a cycloaddition reaction with ethyl acetoacetate **2a**. It is worth noting that acyl-alkylated product **14** was finally obtained in good yield [7], and no cycloaddition products were detected. These findings suggest that the aryne intermediate may not be involved in the reaction process.



12 **2a** **13,** n.d. **14,** 57%

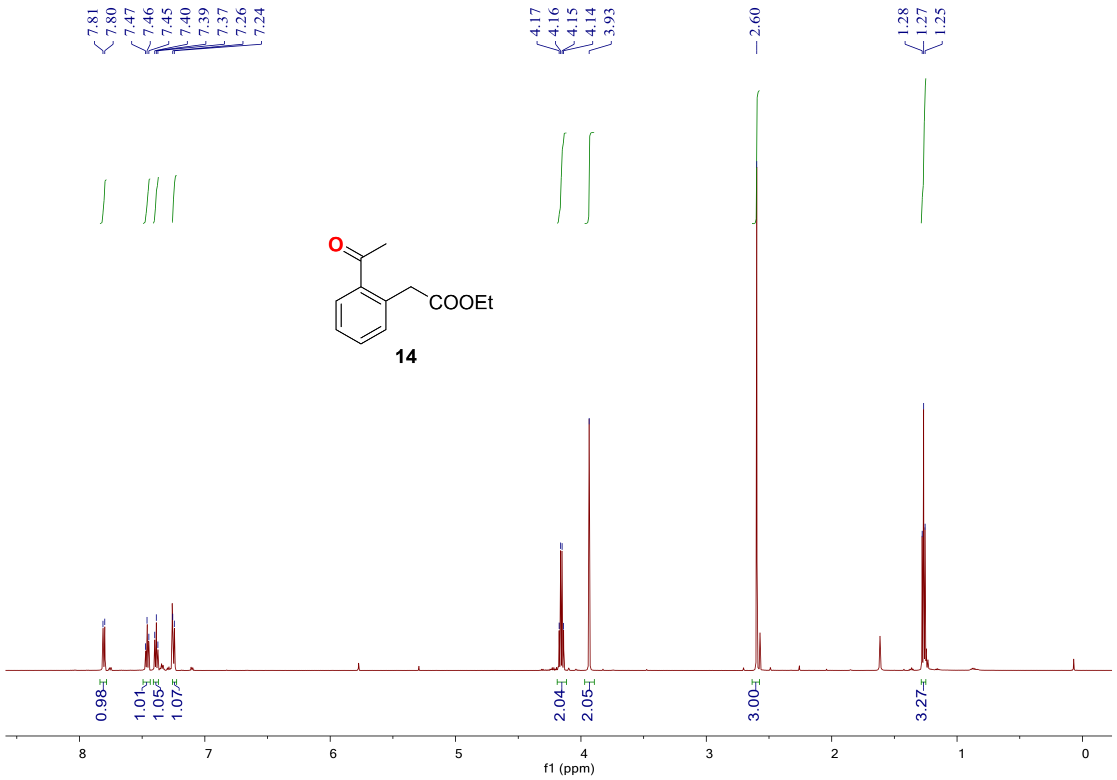


Fig. S4 ^{1}H NMR data of **14**

Overall, these control experiments indicate the importance of electron-withdrawing groups in the iodized salt, which play a crucial role in promoting the reaction. The observed difference in regionselectivity resulting from the use of diaryliodonium salts substituted with various halogens may be attributed to the leaving ability of the halogen atom and the electrophilicity of the C-X bond.

5. References

[1] E. Linde, D. Bulfield, G. Kervefors, N. Purkait, B. Olofsson, *Chem.* 2022, **8**, 850.

[2] B. Lu, B. Wang, Y. Zhang, D. Ma, *J. Org. Chem.* 2007, **72**, 5337.

[3] X. Li, Y. Shen, G. Zhang, X. Zheng, Q. Zhao, Z. Song, *Org. Lett.* 2022, **24**, 5281.

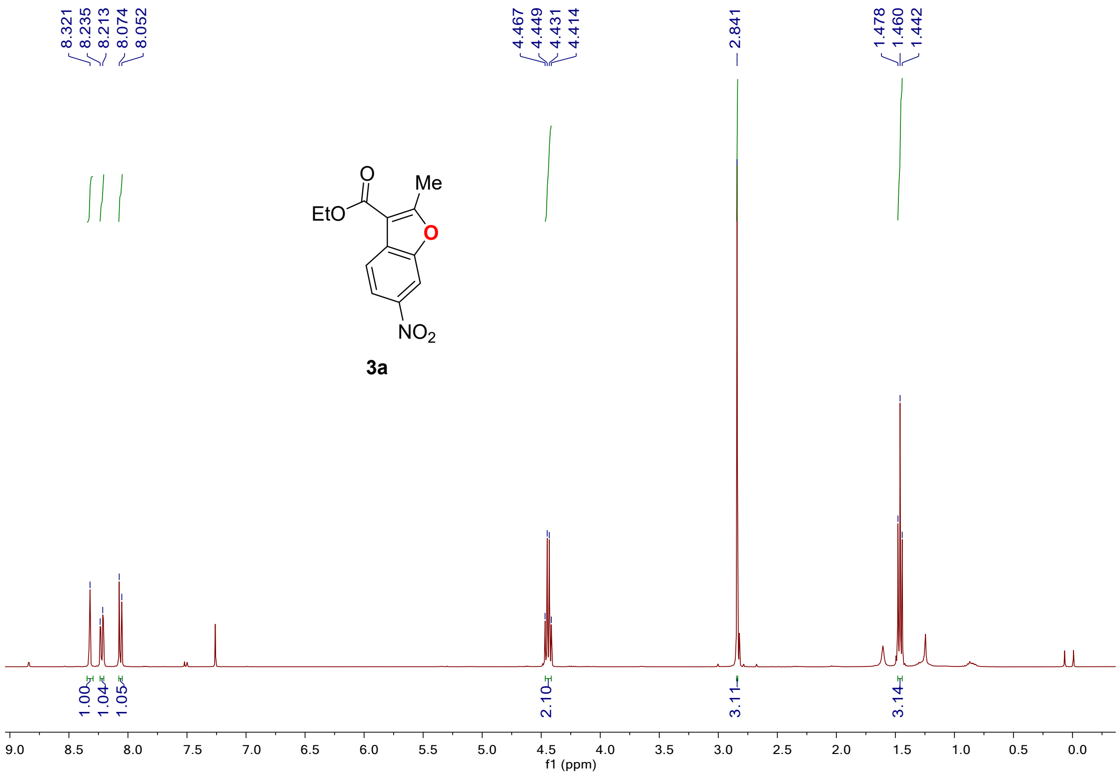
[4] S. Mondal, E. M. Di Tommaso, B. Olofsson, *Angew. Chem. Int. Ed.* 2023, **62***,* e202216296.

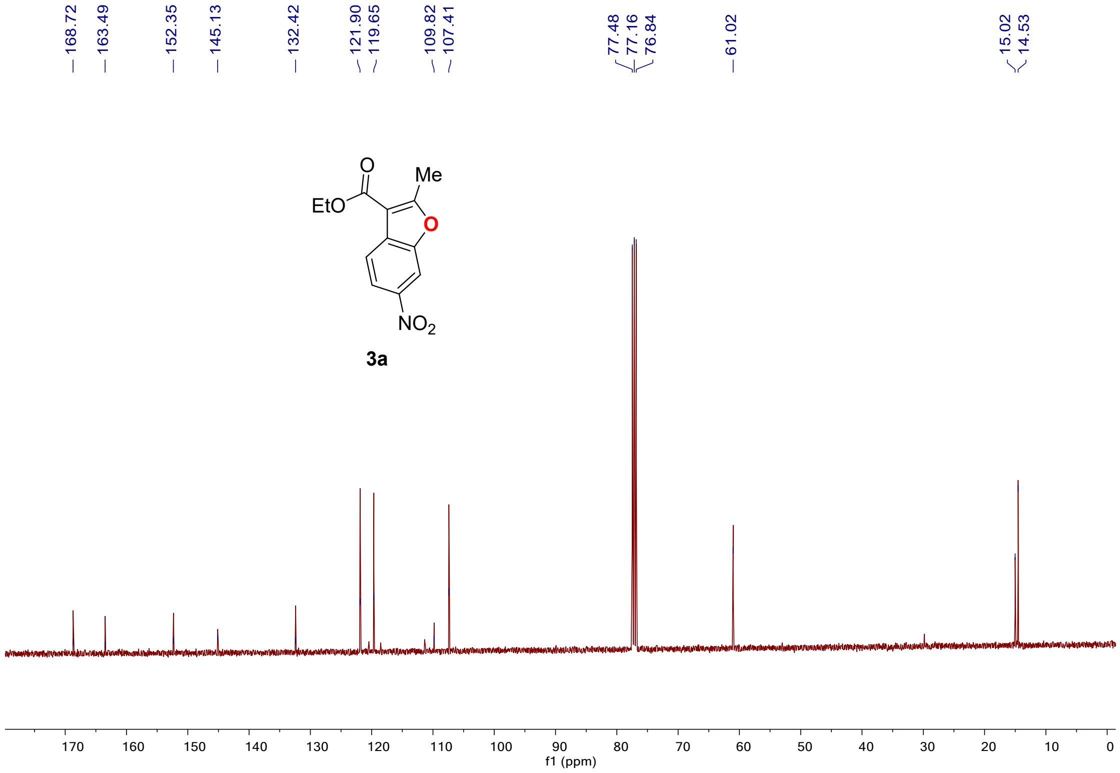
[5] E. Linde, B. Olofsson, *Angew. Chem. Int., Ed.* 2023, **62**, e202310921.

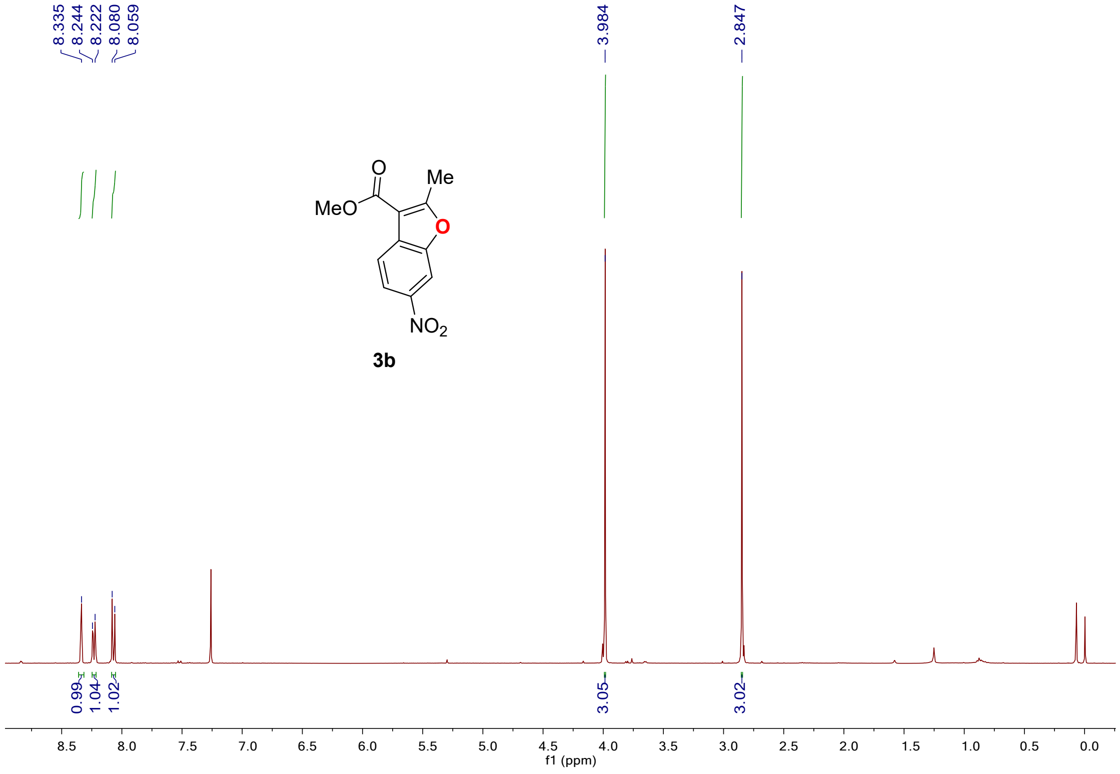
[6] S. Mondal, B. Gunschera, B. Olofsson, *JACS Au.* 2024, **4**, 2832.

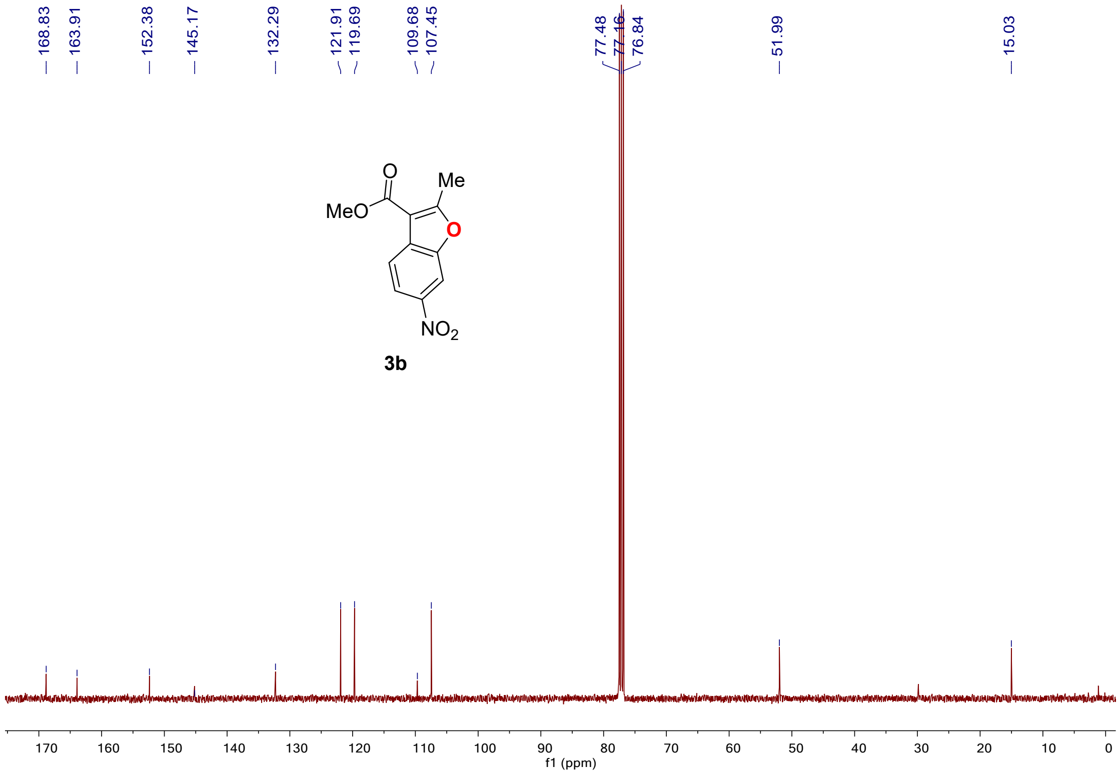
[7] S. Kovacs, A. I. Csincsi, T. Z. Nagy, S. Boros, G. Tim´ ari and Z. Novak, *Org. Lett.* 2012, **14**, 2022.

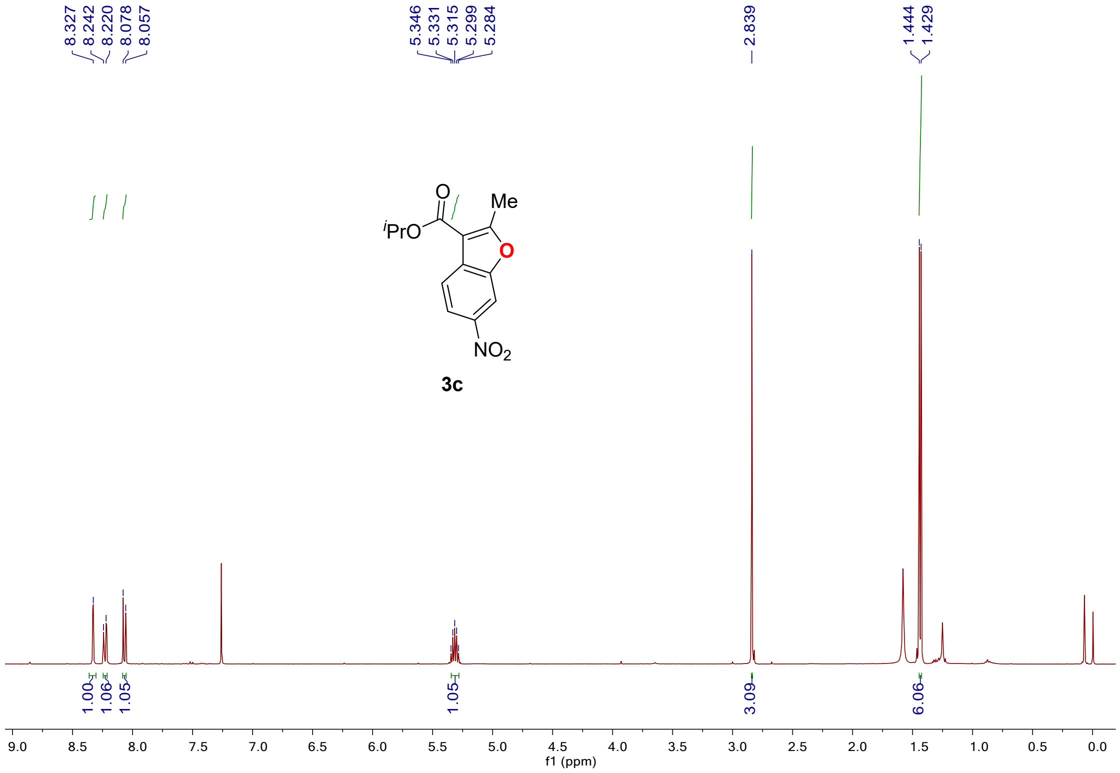
6. ^{1}H, ^{13}C, ^{19}F Spectra of New Compounds

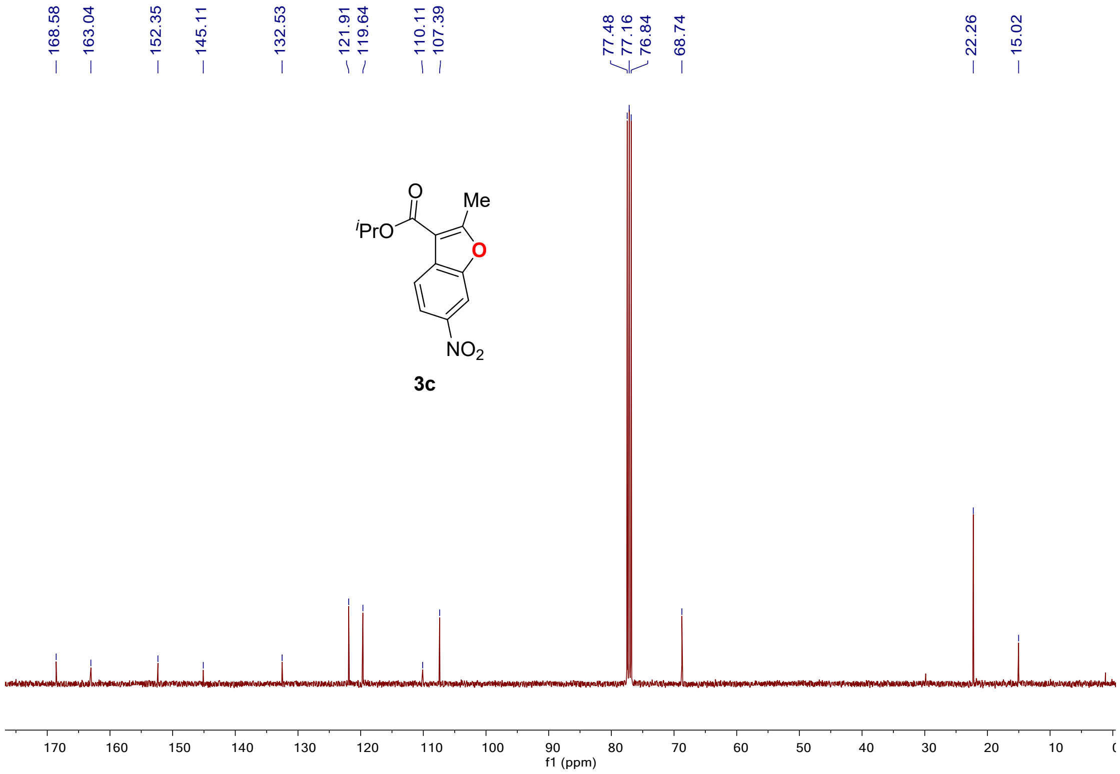


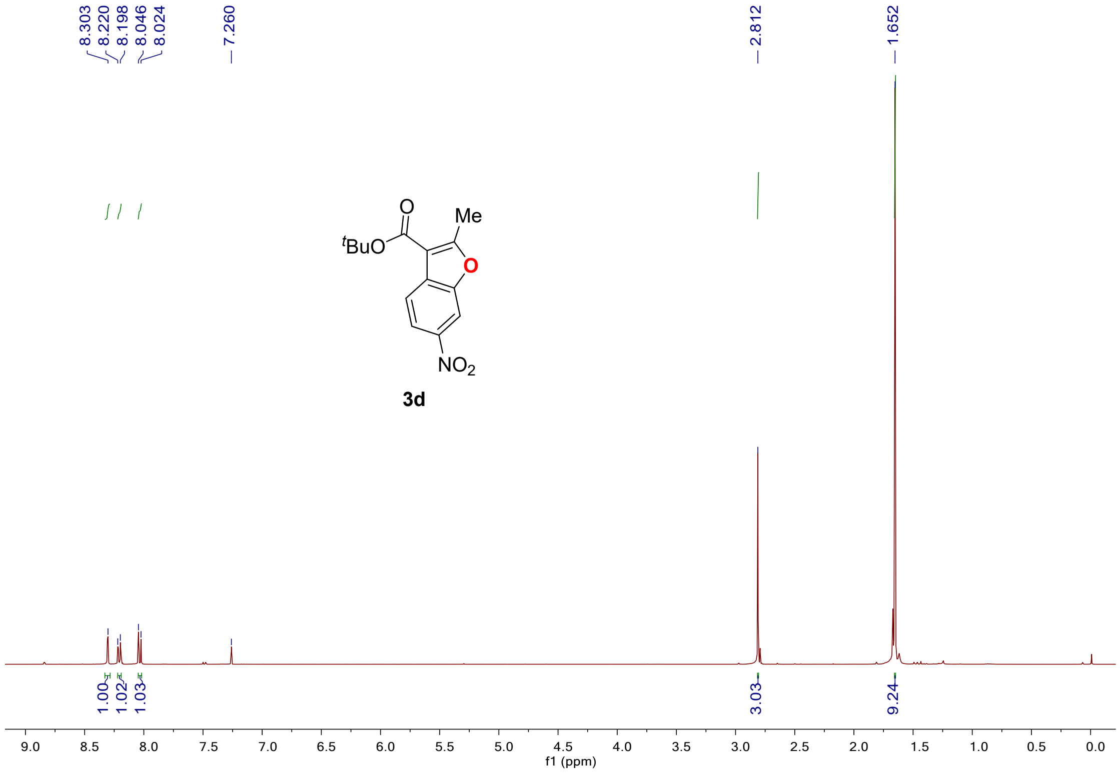


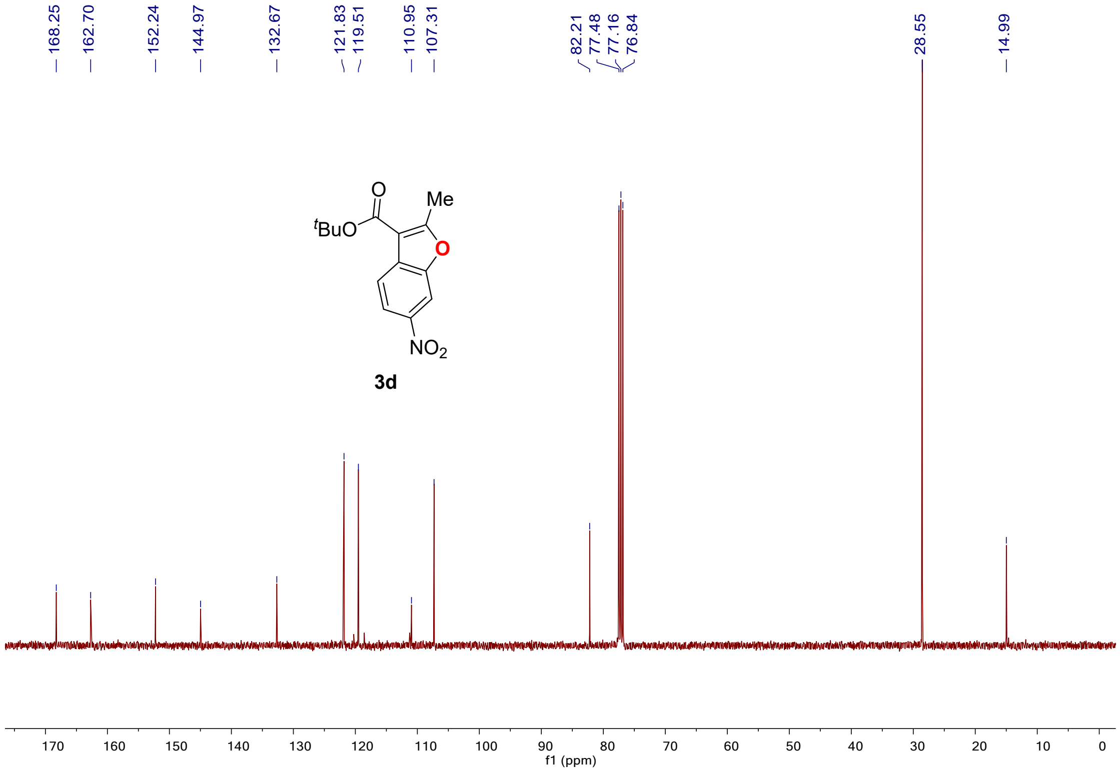

8.335
8.244
8.222
8.080
8.059
3.984
2.847
MeO
O
Me
O
NO2
3b
0.99
1.04
1.02
3.05
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

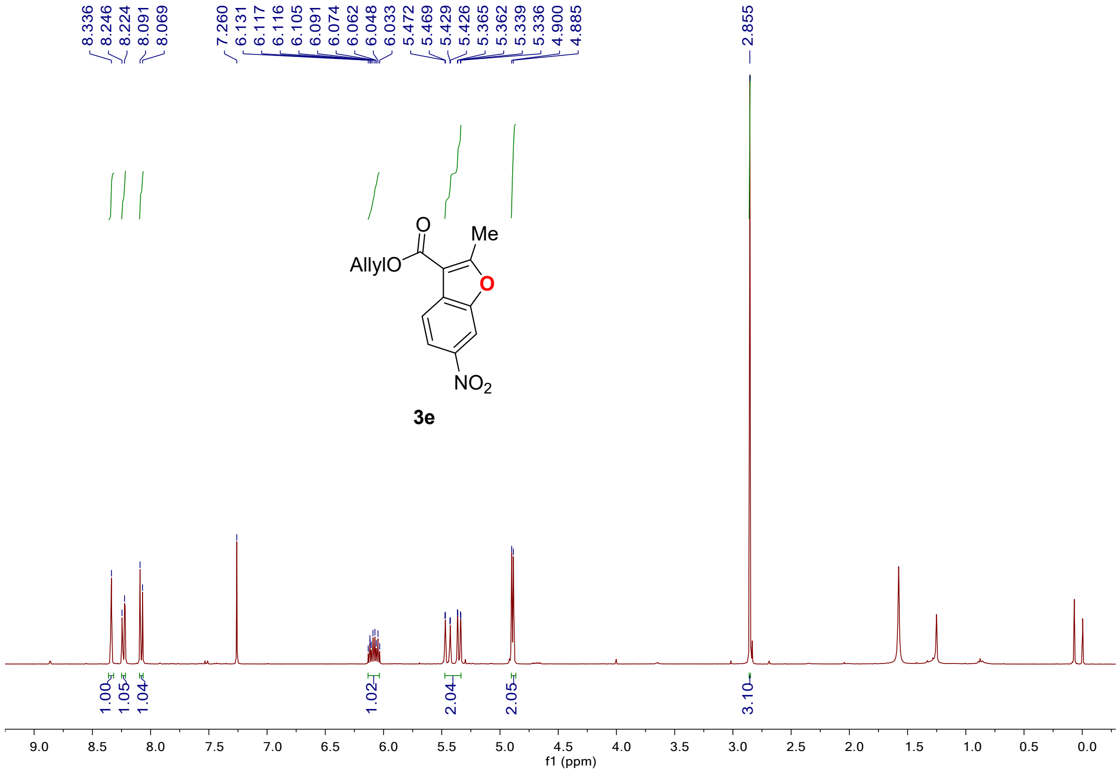

168.83
163.91
152.38
145.17
132.29
121.91
119.69
109.68
107.45
77.48
77.16
76.84
51.99
15.03
MeO
O
Me
O
NO2
3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.327
8.242
8.220
8.078
8.057
5.346
5.331
5.315
5.299
5.284
2.839
1.444
1.429
O
Me
iPrO
O
NO2
3c
1.00
1.06
1.05
1.05
3.09
6.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

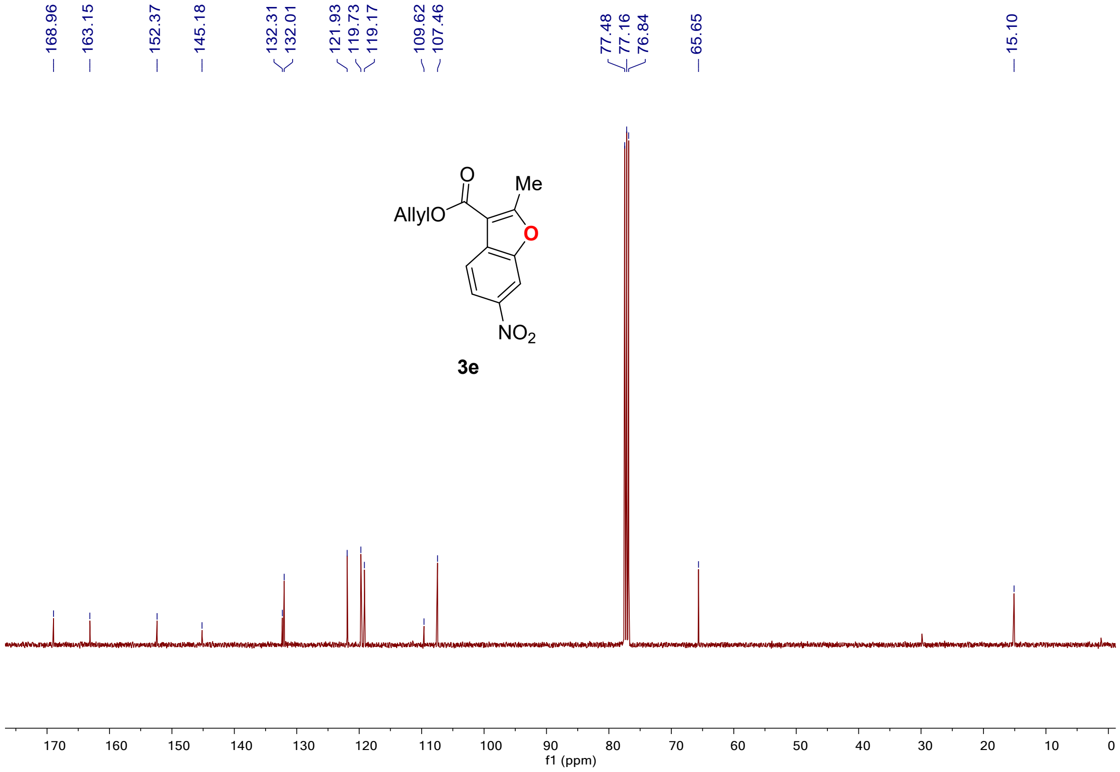

168.58
163.04
152.35
145.11
132.53
121.91
119.64
110.11
107.39
77.48
77.16
76.84
68.74
22.26
15.02
O
Me
iPrO
O
NO2
3c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.303
8.220
8.198
8.046
8.024
7.260
2.812
1.652
tBuO
O
Me
O
NO2
3d
1.00
1.02
1.03
3.03
9.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

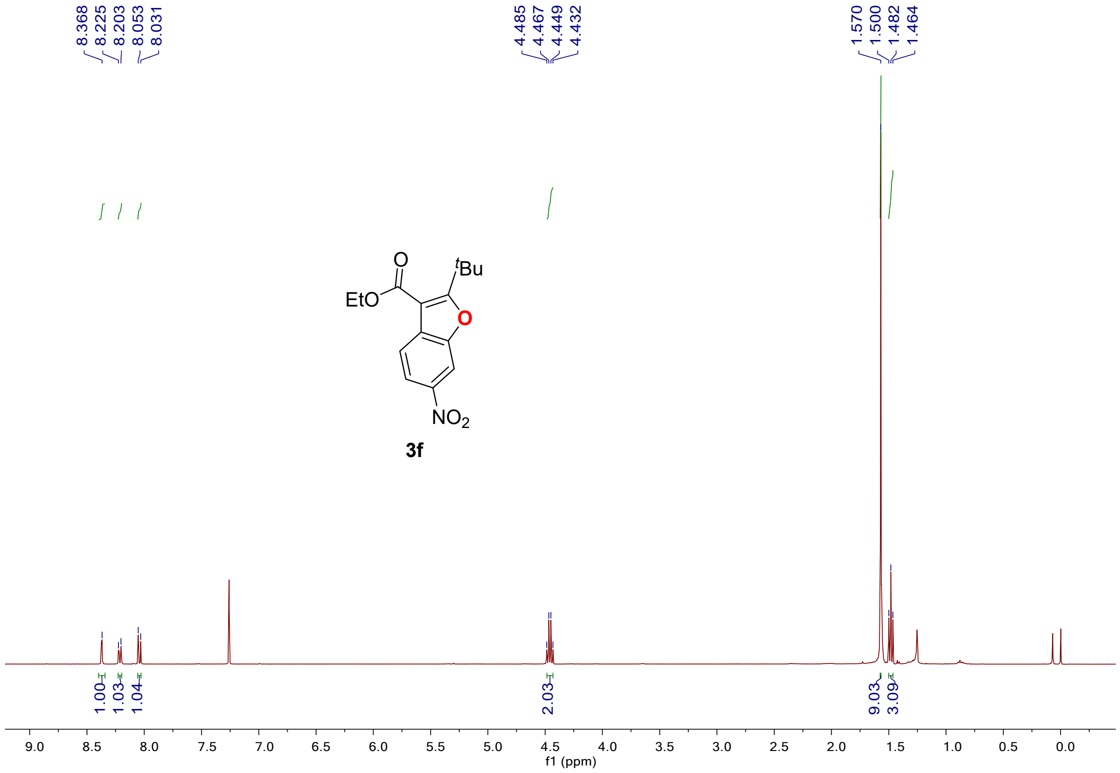

168.25
162.70
152.24
144.97
132.67
121.83
119.51
110.95
107.31
82.21
77.48
77.16
76.84
28.55
14.99
tBuO
O
Me
O
NO2
3d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

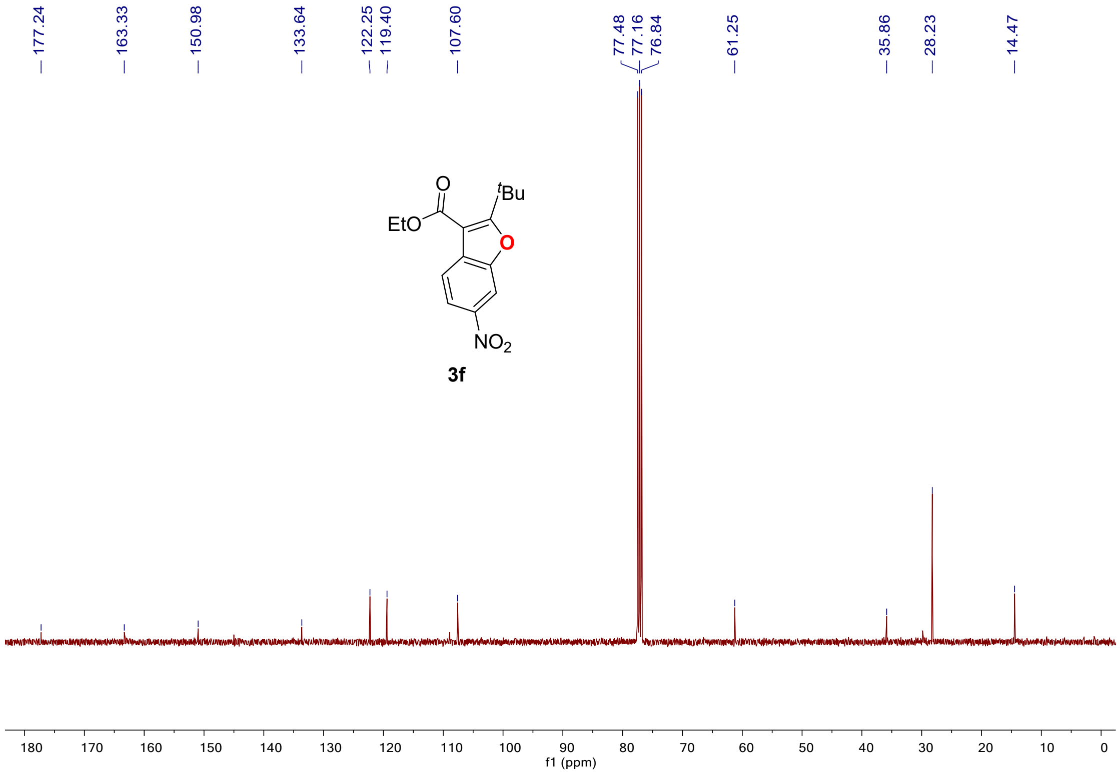

8.336
8.246
8.224
8.091
8.069
7.260
6.131
6.117
6.116
6.105
6.091
6.074
6.062
6.048
6.033
5.472
5.469
5.429
5.426
5.365
5.362
5.339
5.336
4.900
4.885
2.855
AllylO
O
Me
O
NO2
1.00
1.05
1.04
1.02
2.04
2.05
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

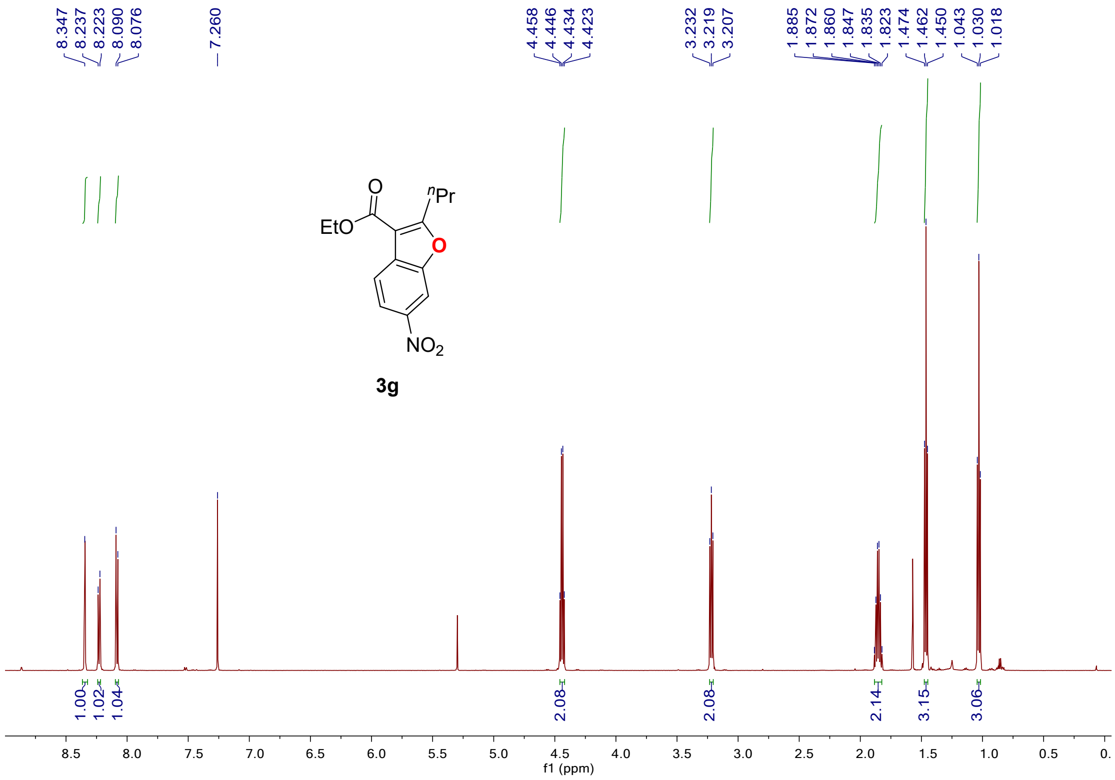
3e

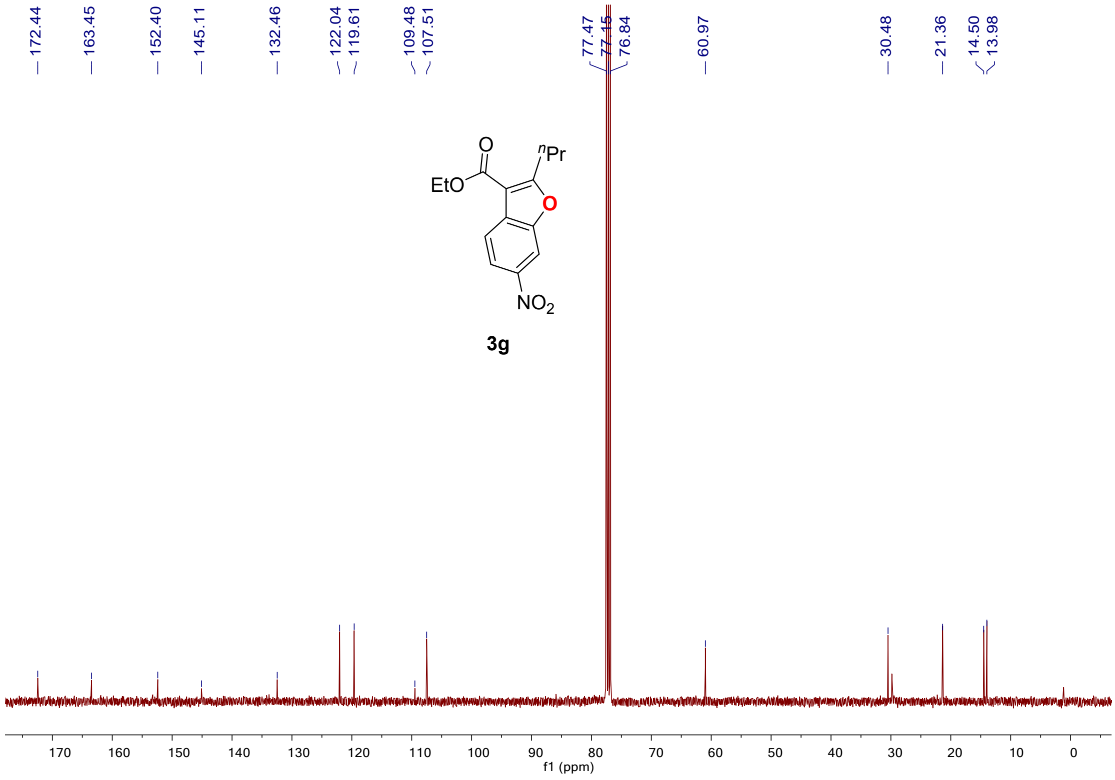

168.96
163.15
152.37
145.18
132.31
132.01
121.93
119.73
119.17
109.62
107.46
77.48
77.16
76.84
65.65
15.10
AllylO
O
Me
O
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

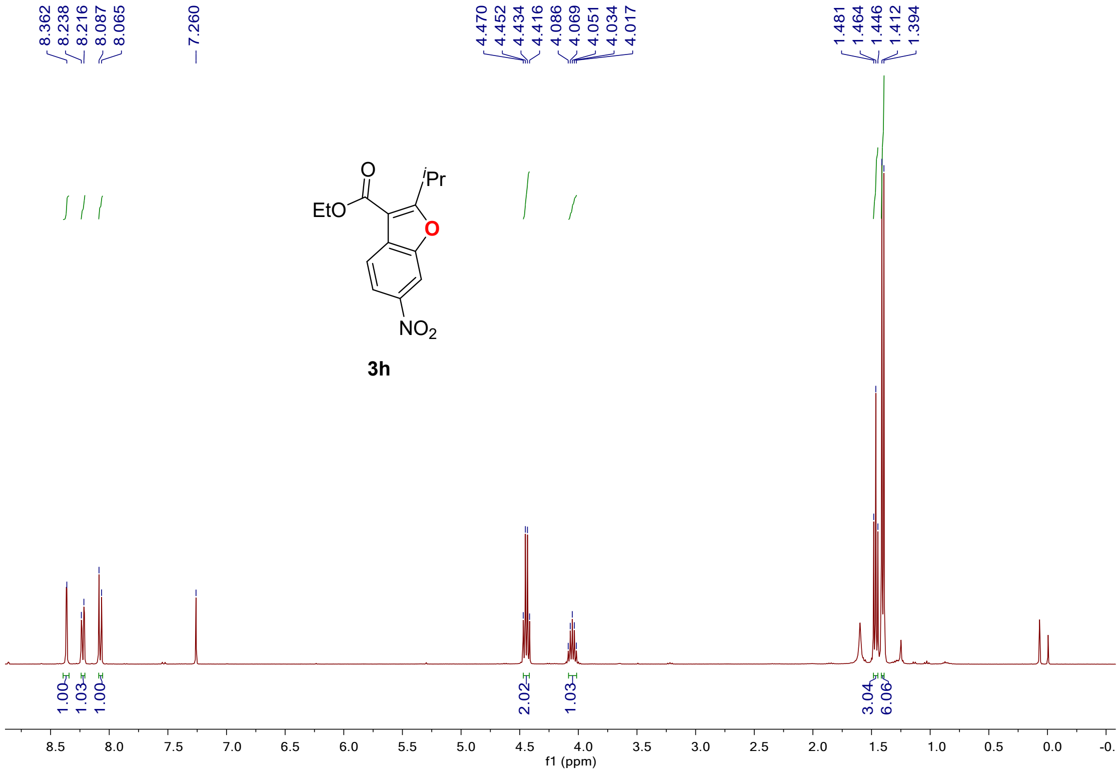
3e


8.368
8.225
8.203
8.053
8.031
4.485
4.467
4.449
4.432
1.570
1.500
1.482
1.464
O
EtO
tBu
O
NO2
3f
1.00
1.03
1.04
2.03
9.03
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

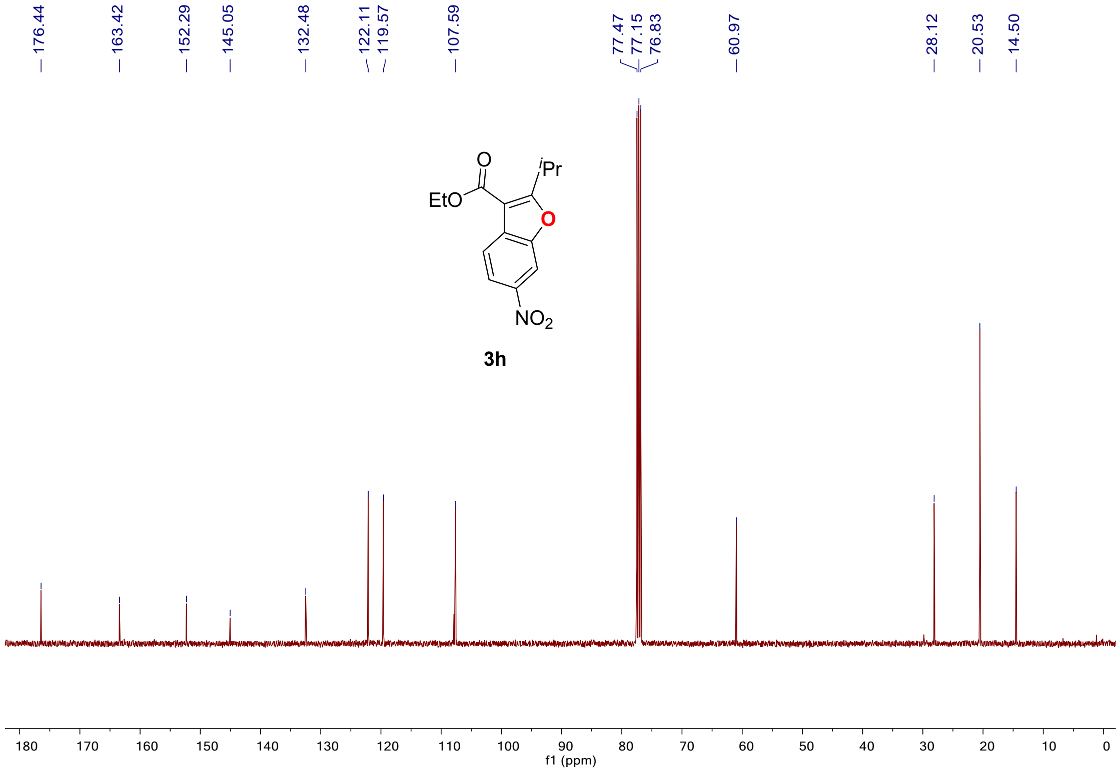

177.24
163.33
150.98
133.64
122.25
119.40
107.60
77.48
77.16
76.84
61.25
35.86
28.23
14.47
O
EtO
tBu
O
NO2
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.347
8.237
8.223
8.090
8.076
7.260
4.458
4.446
4.434
4.423
3.232
3.219
3.207
1.885
1.872
1.860
1.847
1.835
1.823
1.474
1.462
1.450
1.043
1.030
1.018
EtO
O
nPr
O
NO2
3g
1.00
1.02
1.04
2.08
2.08
2.14
3.15
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

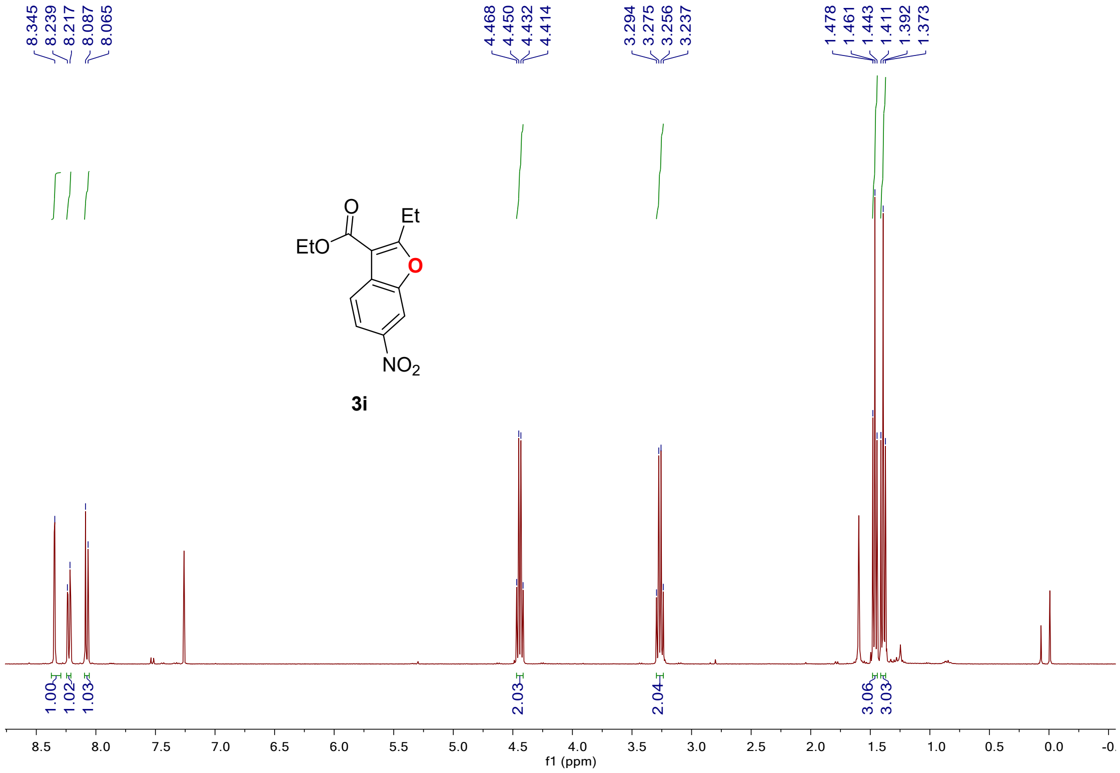

172.44
163.45
152.40
145.11
132.46
122.04
119.61
109.48
107.51
77.47
77.15
76.84
60.97
30.48
21.36
14.50
13.98
EtO
O
nPr
O
NO2
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

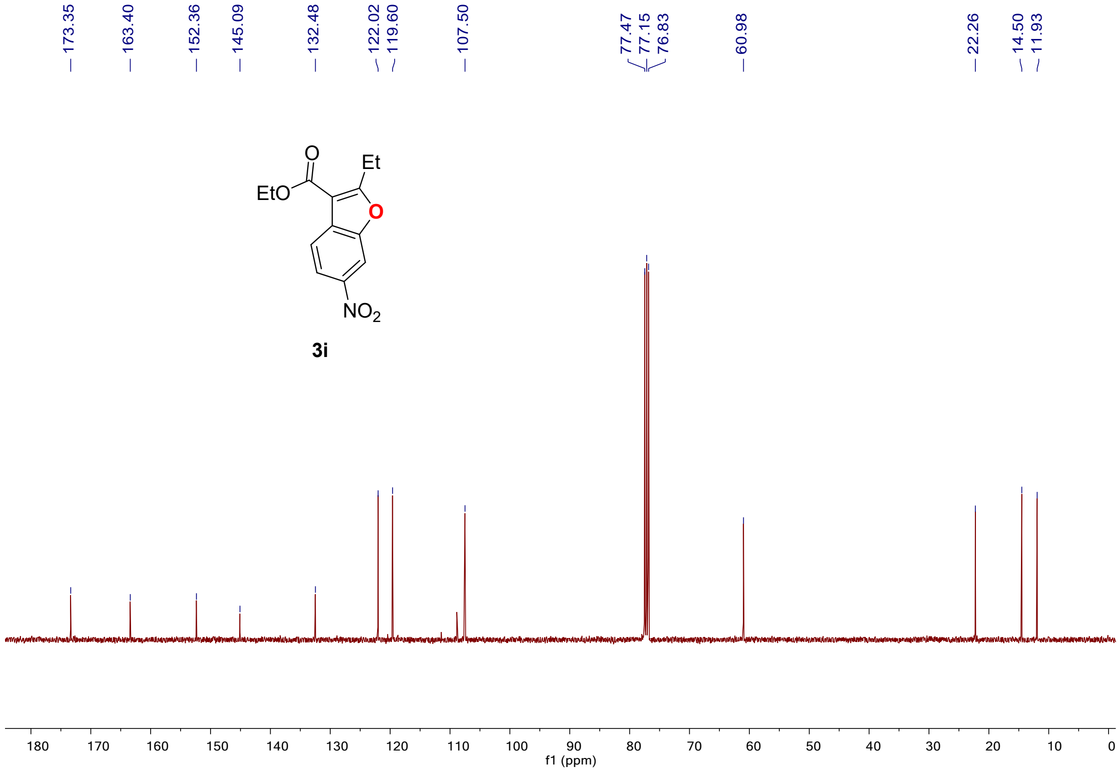

8.362
8.238
8.216
8.087
8.065
7.260
4.470
4.452
4.434
4.416
4.086
4.069
4.051
4.034
4.017
1.481
1.464
1.446
1.412
1.394
EtO
O
iPr
O
NO2
1.00
1.03
1.00
2.02
1.03
3.04
6.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

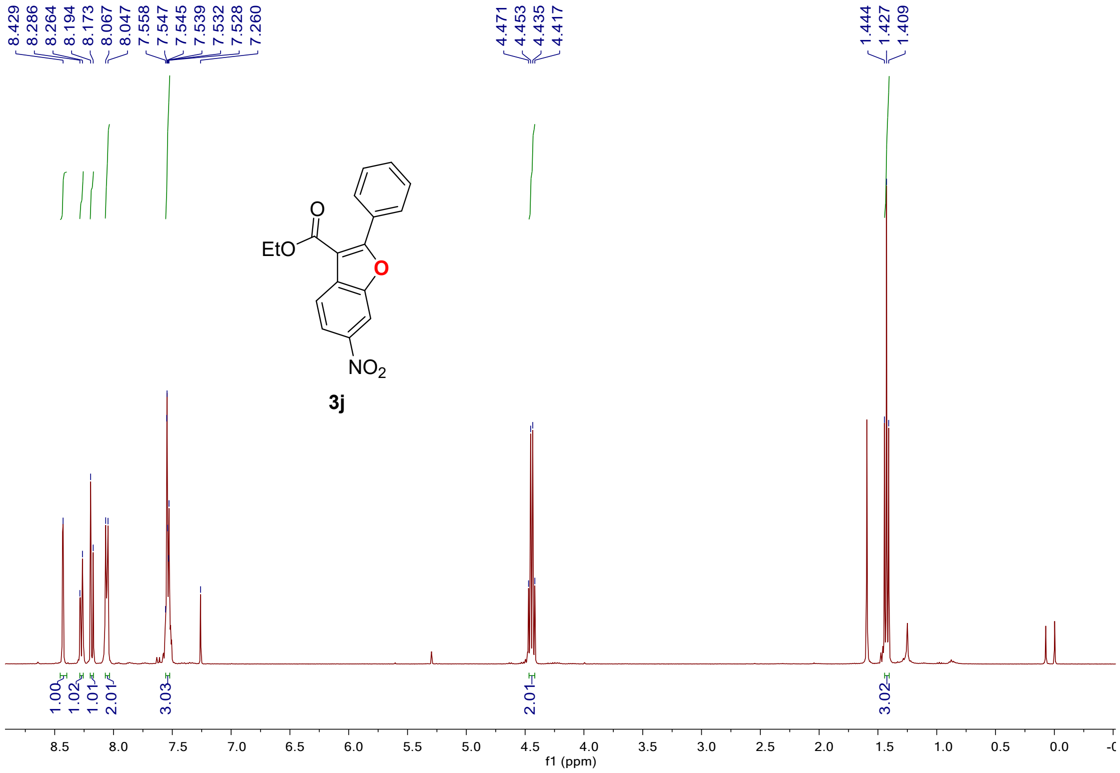
3h

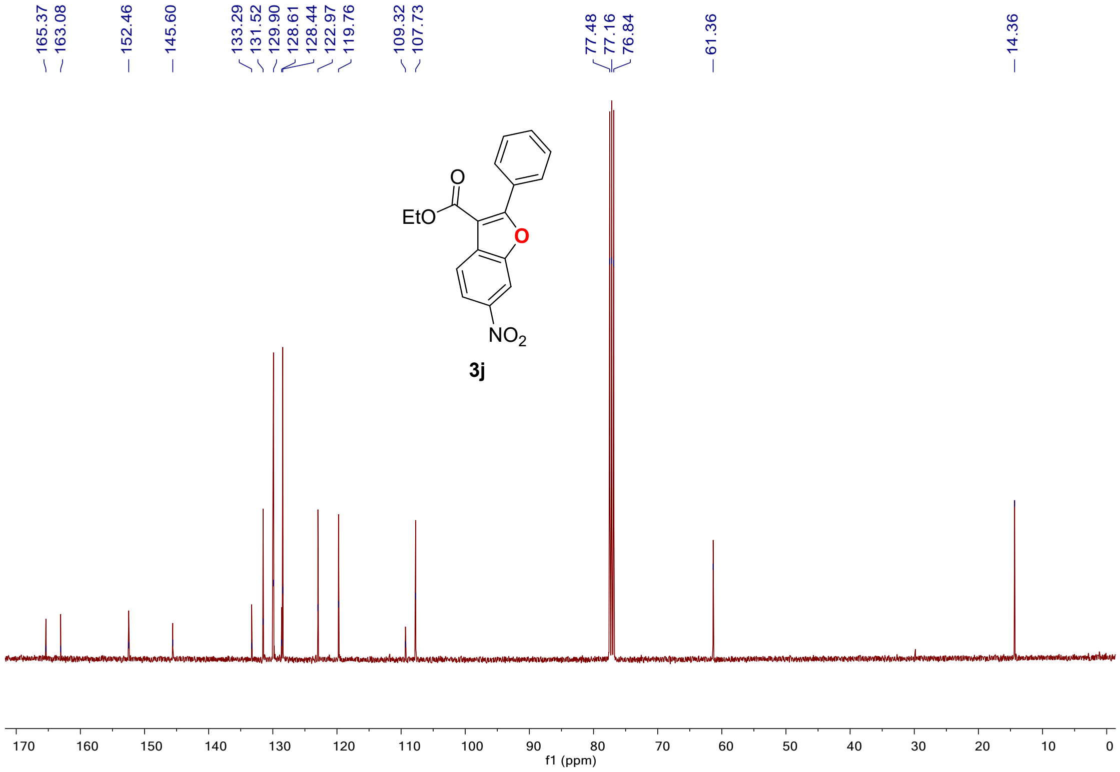

176.44
163.42
152.29
145.05
132.48
122.11
119.57
107.59
77.47
77.15
76.83
60.97
28.12
20.53
14.50
EtO
O
iPr
O
NO2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

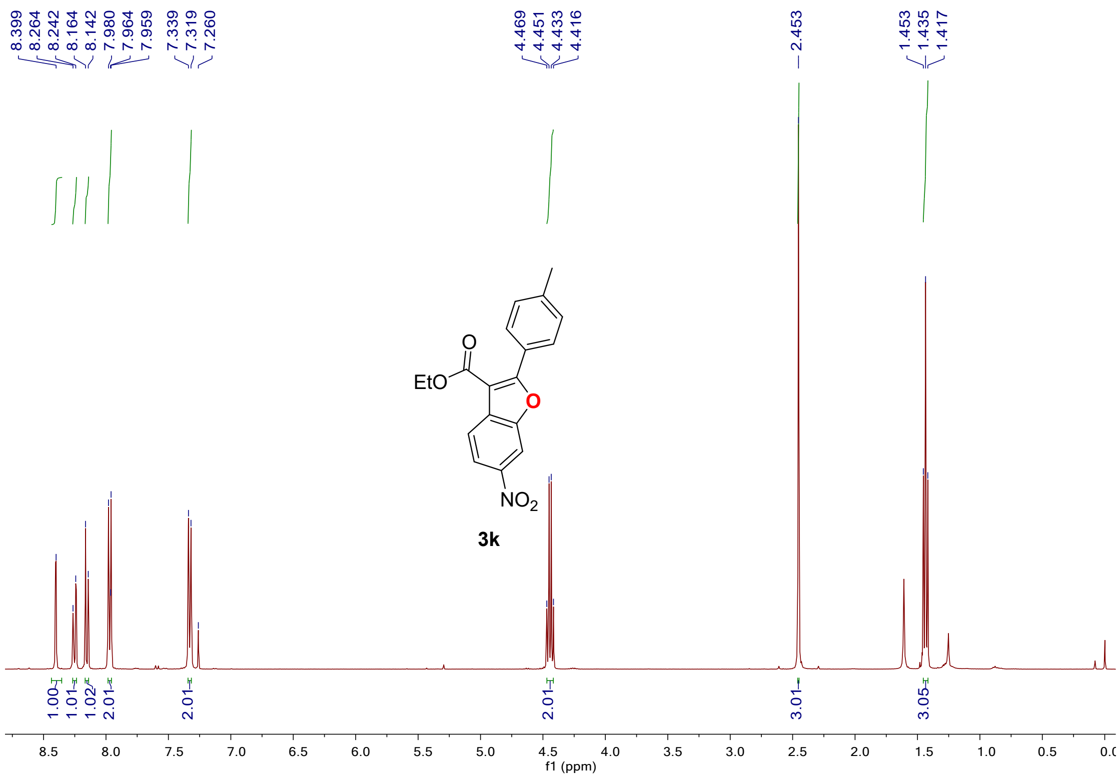
3h


8.345
8.239
8.217
8.087
8.065
4.468
4.450
4.432
4.414
3.294
3.275
3.256
3.237
1.478
1.461
1.443
1.411
1.392
1.373
O
Et
EtO
O
NO2
3i
1.00
1.02
1.03
2.03
2.04
3.06
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

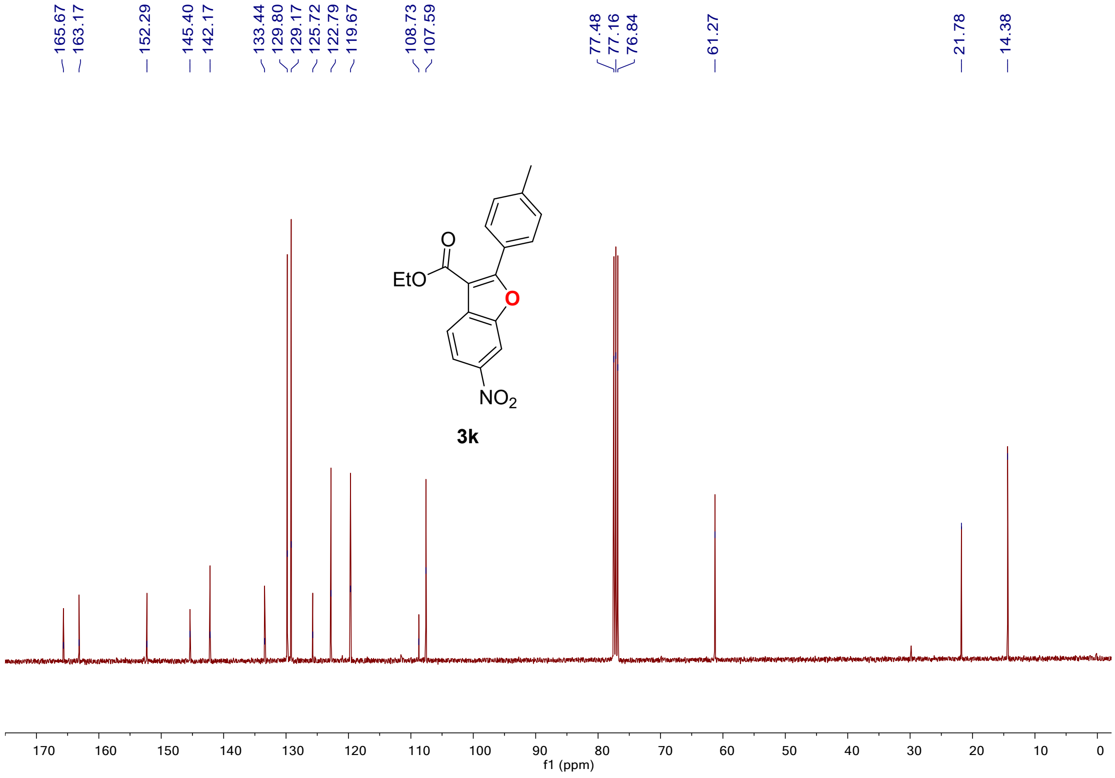

173.35
163.40
152.36
145.09
132.48
122.02
119.60
107.50
77.47
77.15
76.83
60.98
22.26
14.50
11.93
O
Et
EtO
O
NO2
3i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.429
8.286
8.264
8.194
8.173
8.067
8.047
7.558
7.547
7.545
7.539
7.532
7.528
7.260
4.471
4.453
4.435
4.417
1.444
1.427
1.409
O
EtO
O
NO2
3j
1.00
1.02
1.01
2.01
3.03
2.01
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

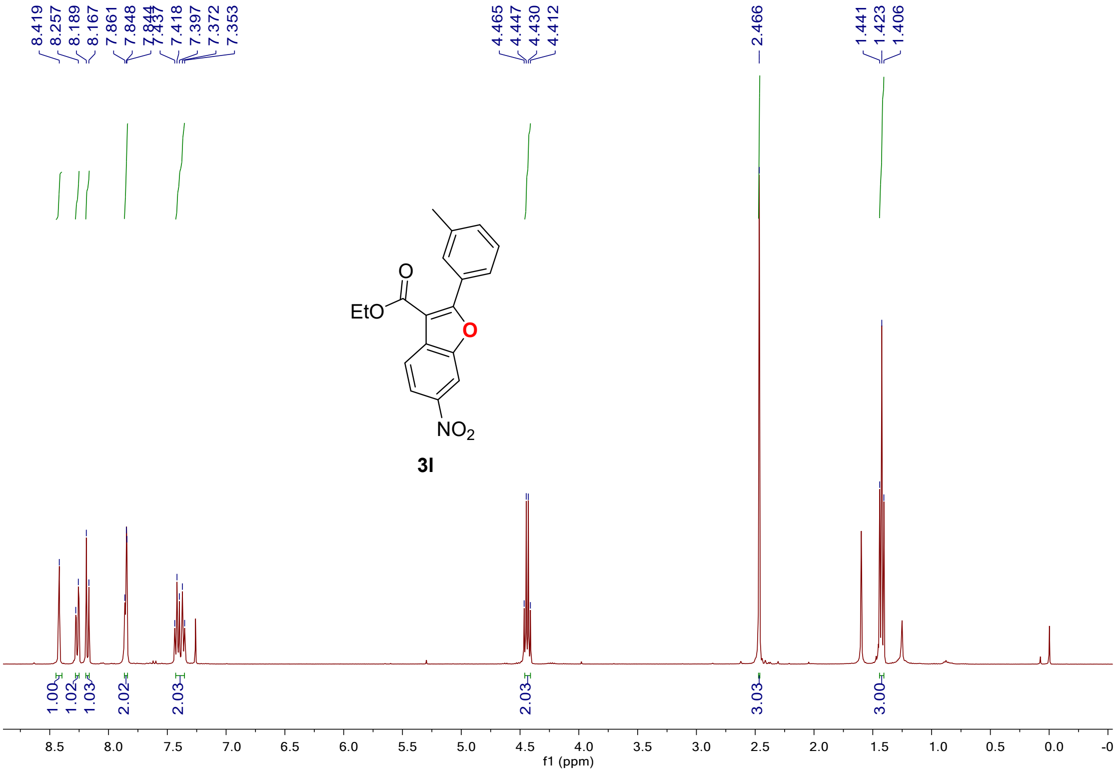

165.37
163.08
152.46
145.60
133.29
131.52
129.90
128.61
128.44
122.97
119.76
109.32
107.73
77.48
77.16
76.84
61.36
14.36
O
EtO
O
NO2
3j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.399
8.264
8.242
8.164
8.142
7.980
7.964
7.959
7.339
7.319
7.260
4.469
4.451
4.433
4.416
2.453
1.453
1.435
1.417
EtO
O
O
NO2
1.00
1.01
1.02
2.01
2.01
2.01
3.01
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

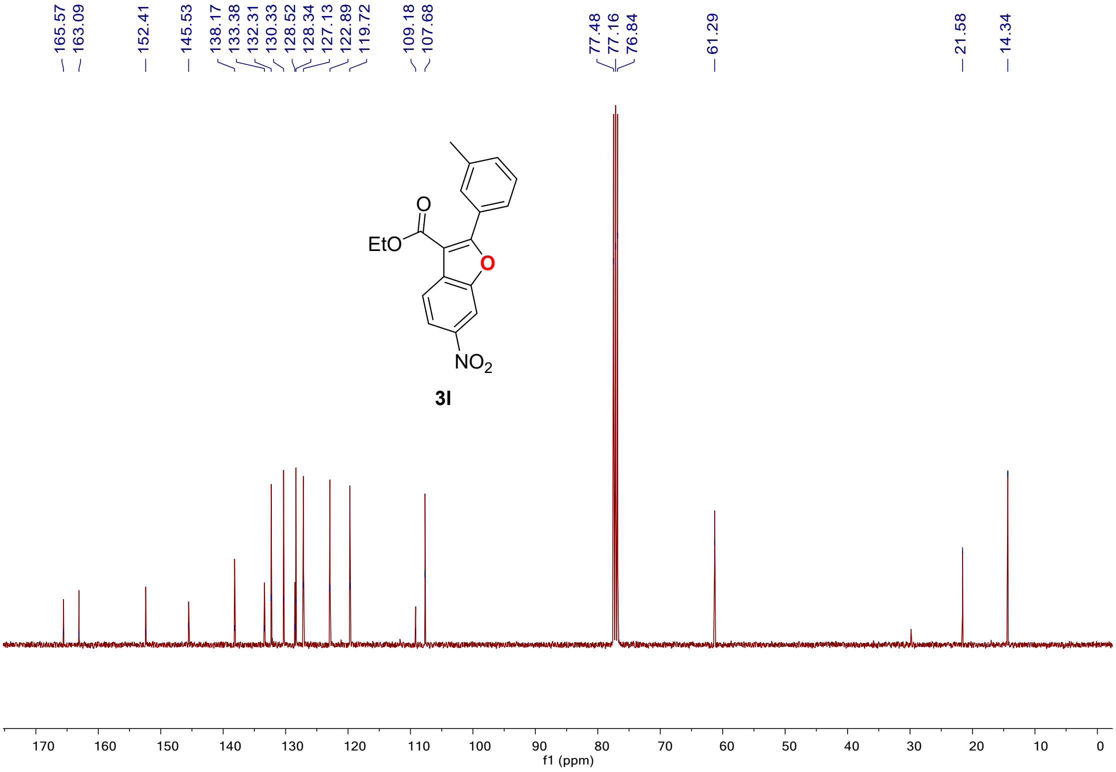
3k


165.67
163.17
152.29
145.40
142.17
133.44
129.80
129.17
125.72
122.79
119.67
108.73
107.59
77.48
77.16
76.84
61.27
21.78
14.38
EtO
O
O
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

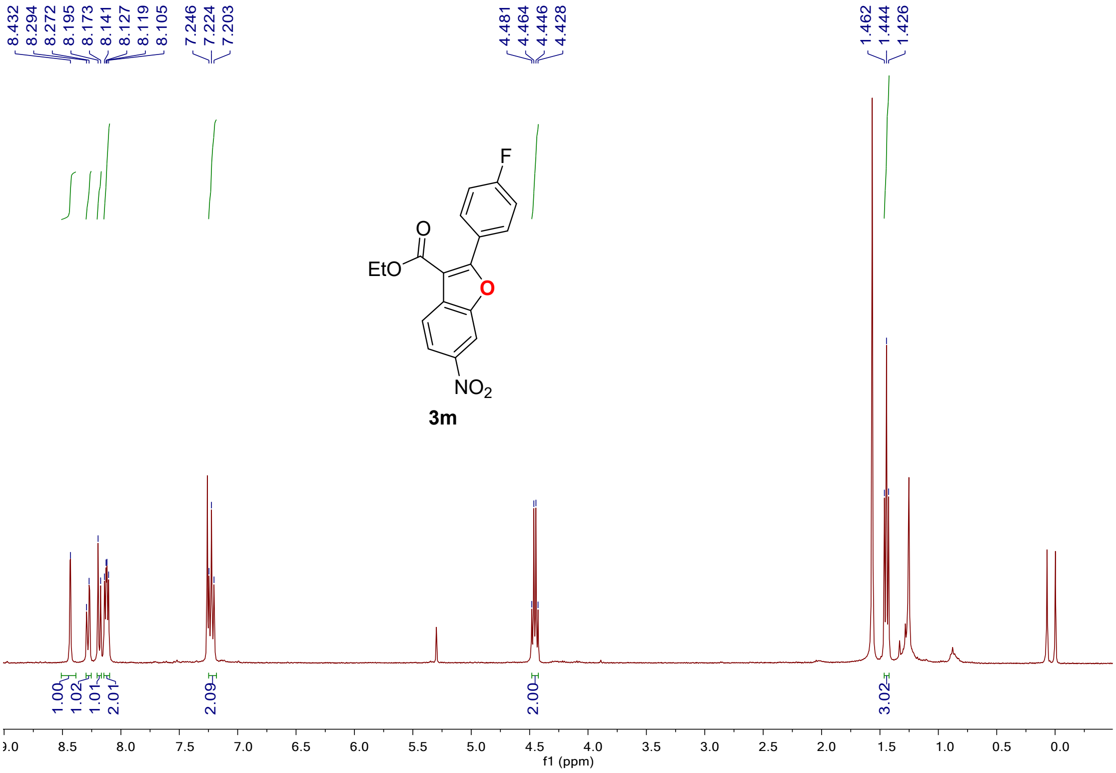
3k

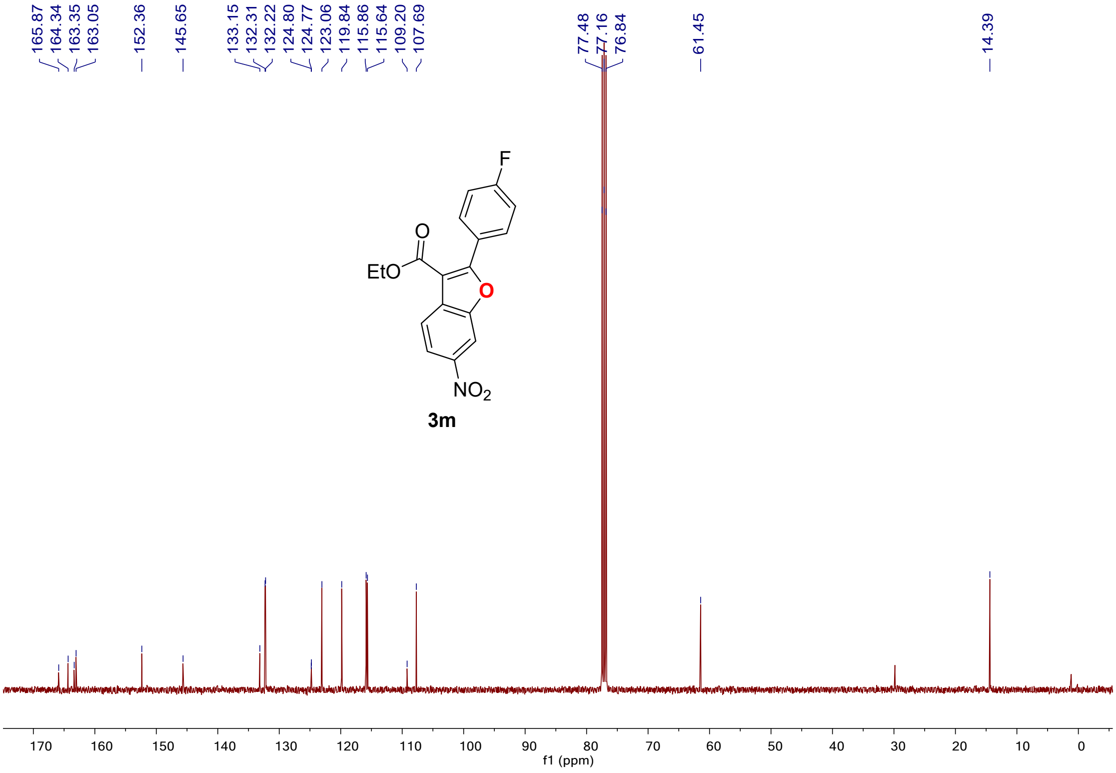

8.419
8.257
8.189
8.167
7.861
7.848
7.844
7.437
7.418
7.397
7.372
7.353
4.465
4.447
4.430
4.412
2.466
1.441
1.423
1.406
EtO
O
O
NO2
1.00
1.02
1.03
2.02
2.03
2.03
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

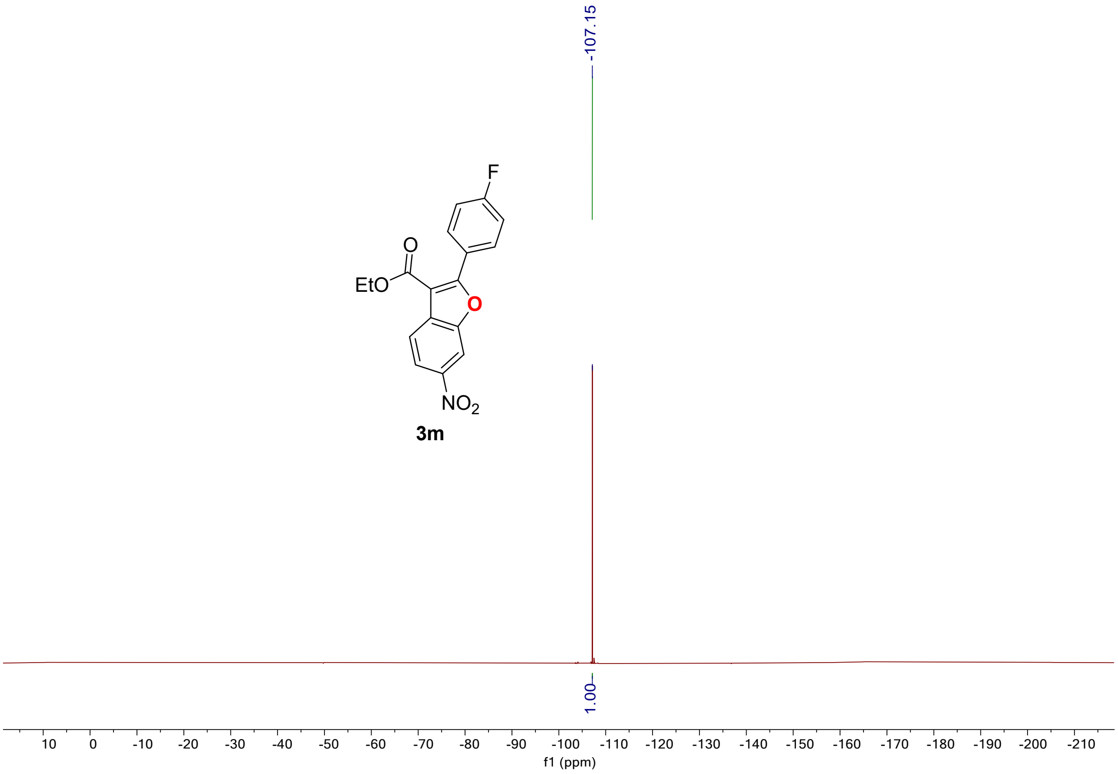
3l


165.57
163.09
152.41
145.53
138.17
133.38
132.31
130.33
128.52
128.34
127.13
122.89
119.72
109.18
107.68
77.48
77.16
76.84
61.29
21.58
14.34
EtO
O
O
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

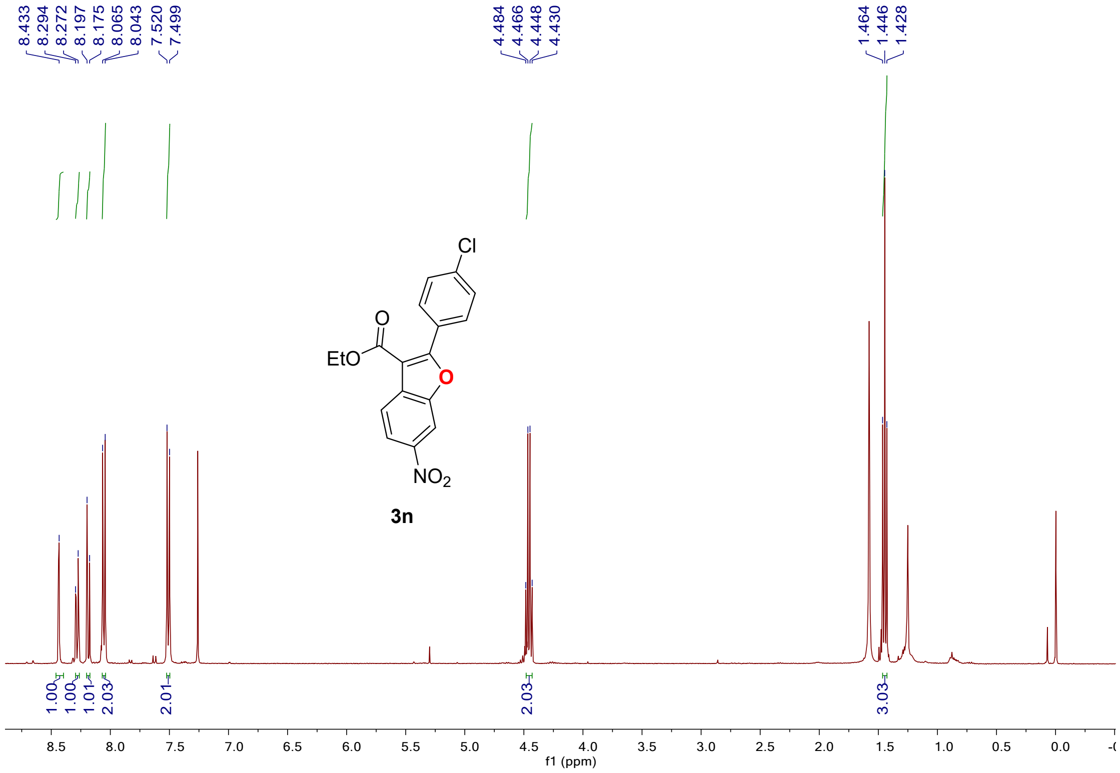
3l


8.432
8.294
8.272
8.195
8.173
8.141
8.127
8.119
8.105
7.246
7.224
7.203
4.481
4.464
4.446
4.428
1.462
1.444
1.426
F
O
EtO
O
NO2
3m
1.00
1.02
1.01
2.01
2.09
2.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

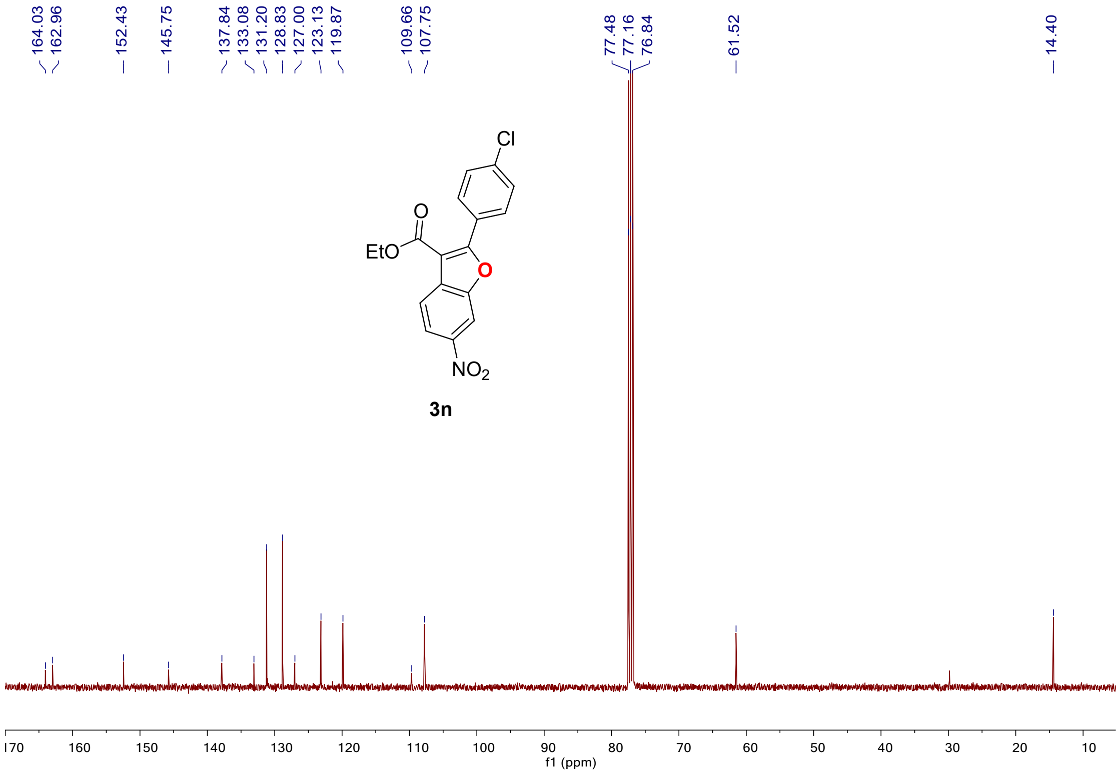

165.87
164.34
163.35
163.05
152.36
145.65
133.15
132.31
132.22
124.80
124.77
123.06
119.84
115.86
115.64
109.20
107.69
77.48
77.16
76.84
61.45
14.39
F
O
EtO
O
NO2
3m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-107.15
F
O
EtO
O
NO2
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

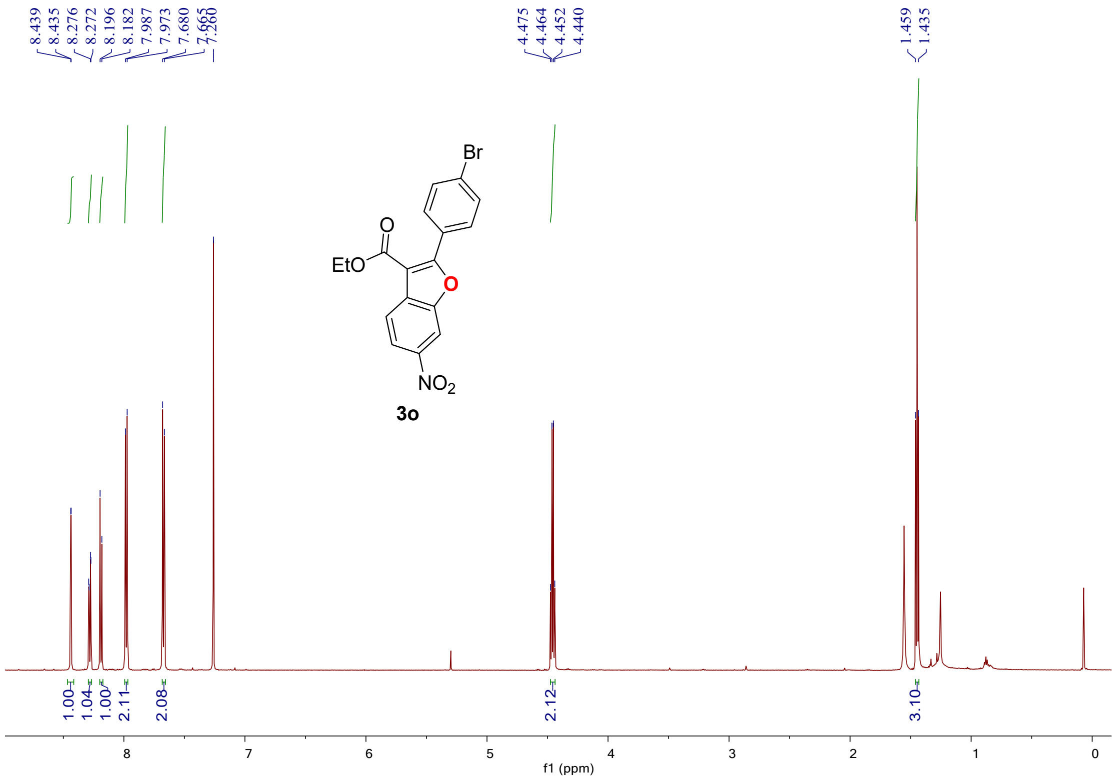
3m

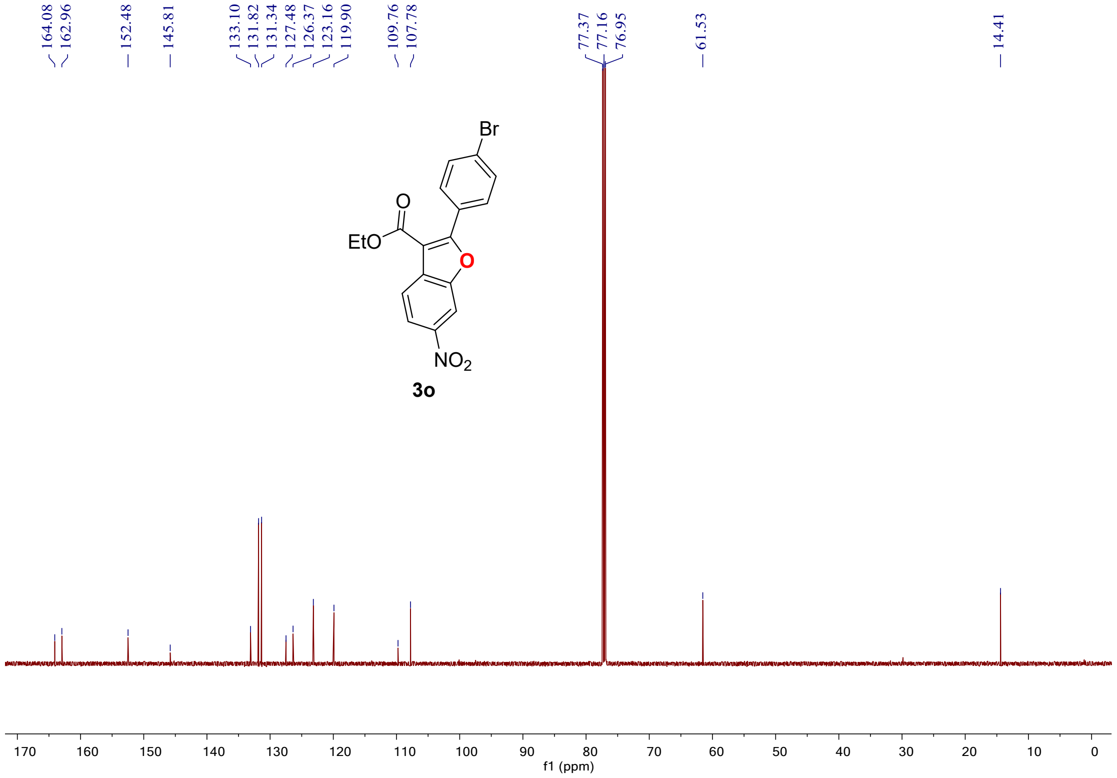

8.433
8.294
8.272
8.197
8.175
8.065
8.043
7.520
7.499
4.484
4.466
4.448
4.430
1.464
1.446
1.428
Cl
O
EtO
O
NO2
1.00
1.00
1.01
2.03
2.01
2.03
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

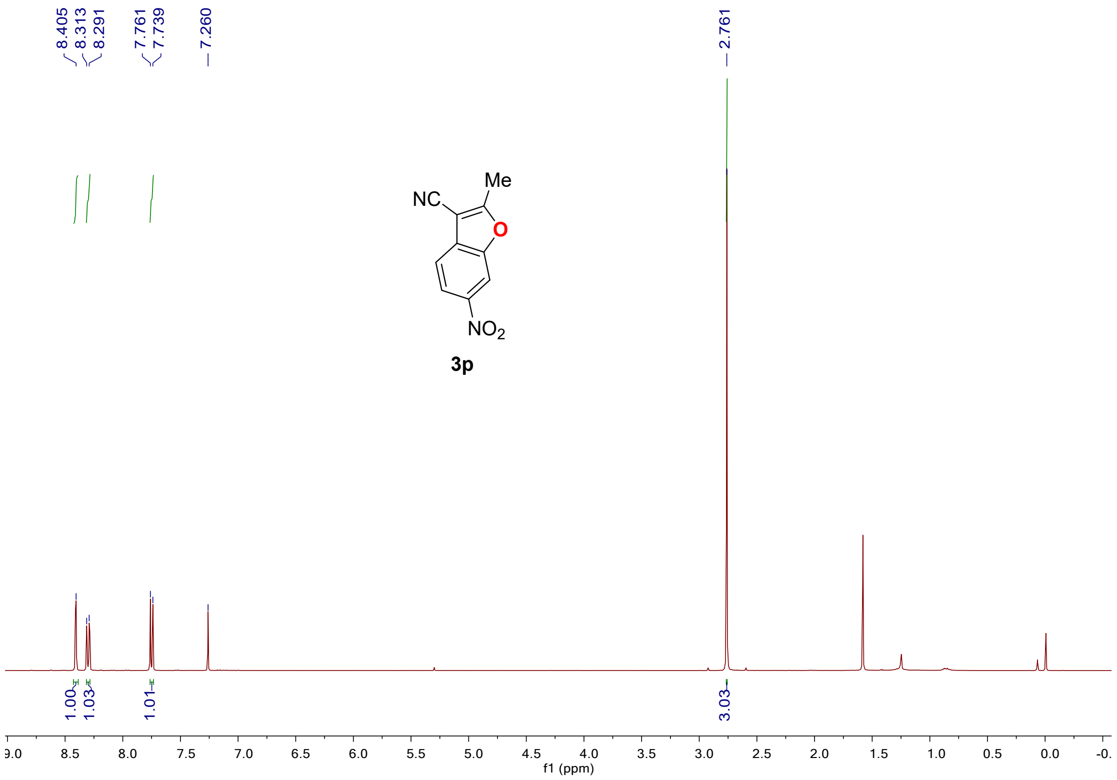
3n

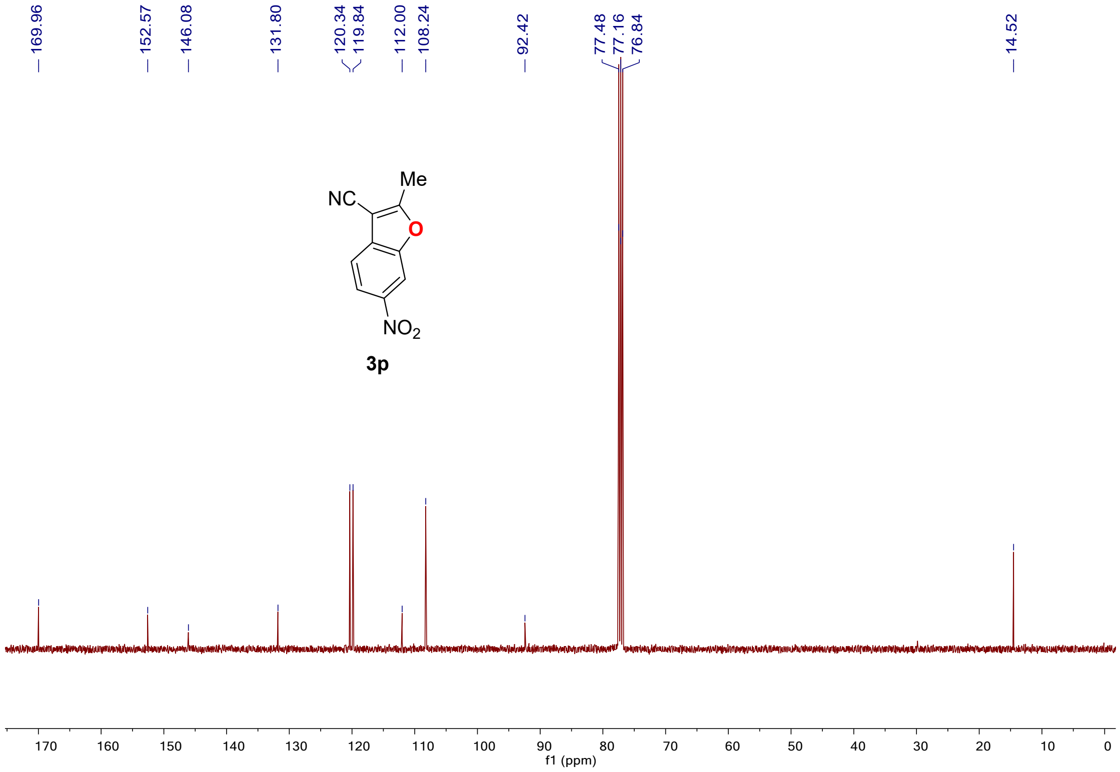

164.03
162.96
152.43
145.75
137.84
133.08
131.20
128.83
127.00
123.13
119.87
109.66
107.75
77.48
77.16
76.84
61.52
14.40
Cl
O
EtO
O
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

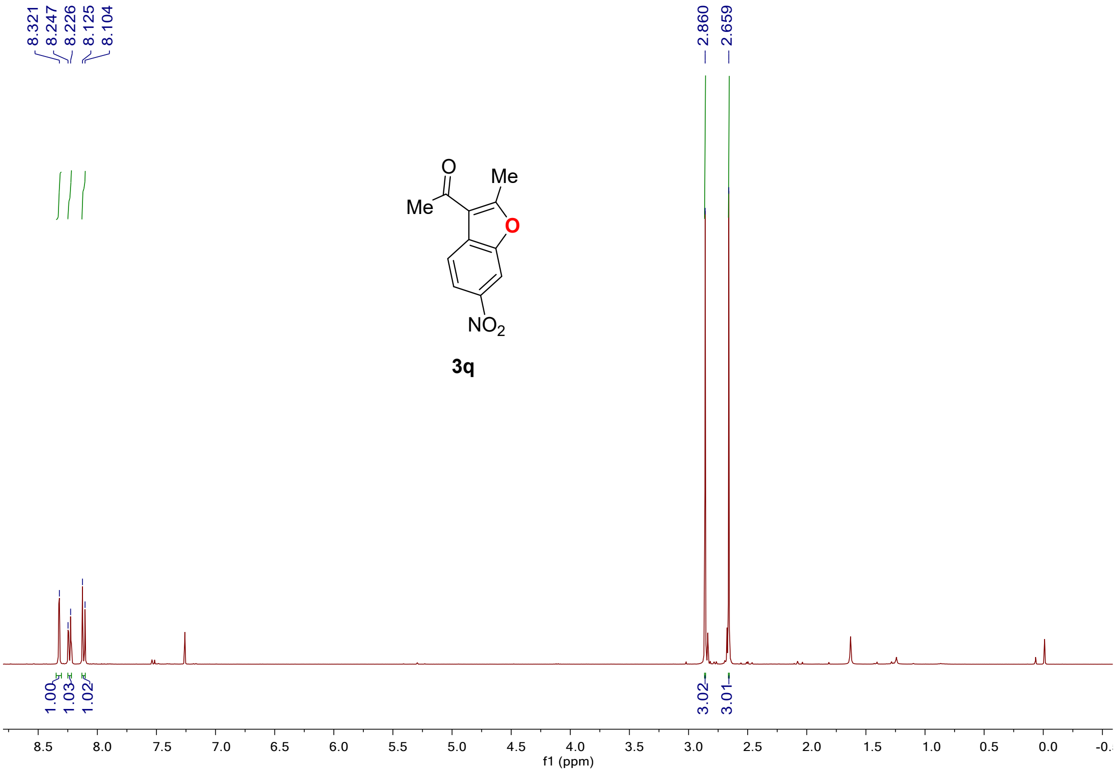
3n

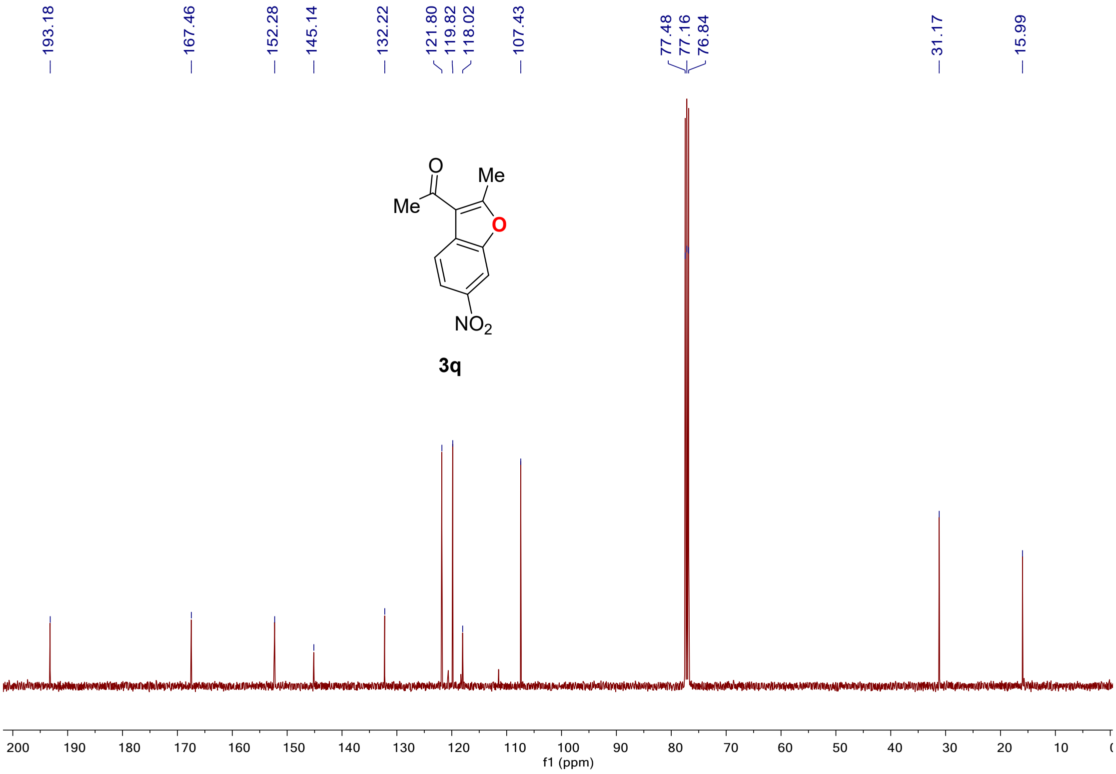

8.439
8.435
8.276
8.272
8.196
8.182
7.987
7.973
7.680
7.665
7.260
4.475
4.464
4.452
4.440
1.459
1.435
Br
O
EtO
O
NO2
3o
1.00
1.04
1.00
2.11
2.08
2.12
3.10
8
7
6
5
4
3
2
1
0
f1 (ppm)

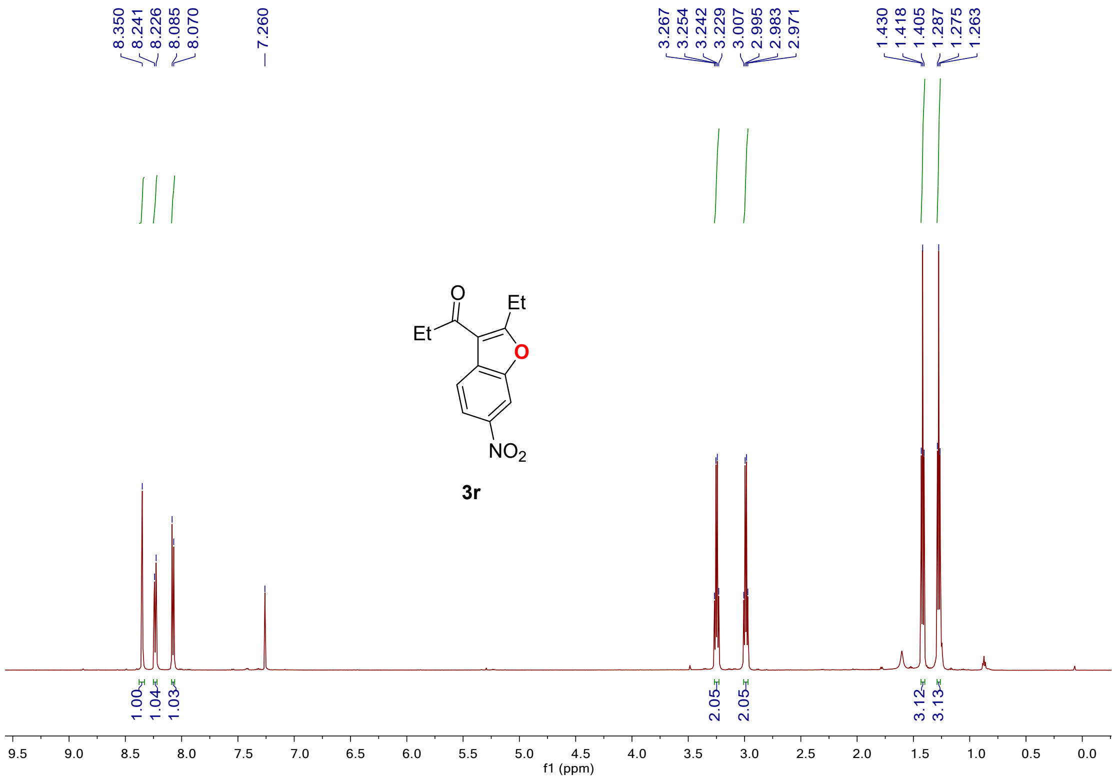

164.08
162.96
152.48
145.81
133.10
131.82
131.34
127.48
126.37
123.16
119.90
109.76
107.78
77.37
77.16
76.95
61.53
14.41
Br
O
EtO
O
NO2
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

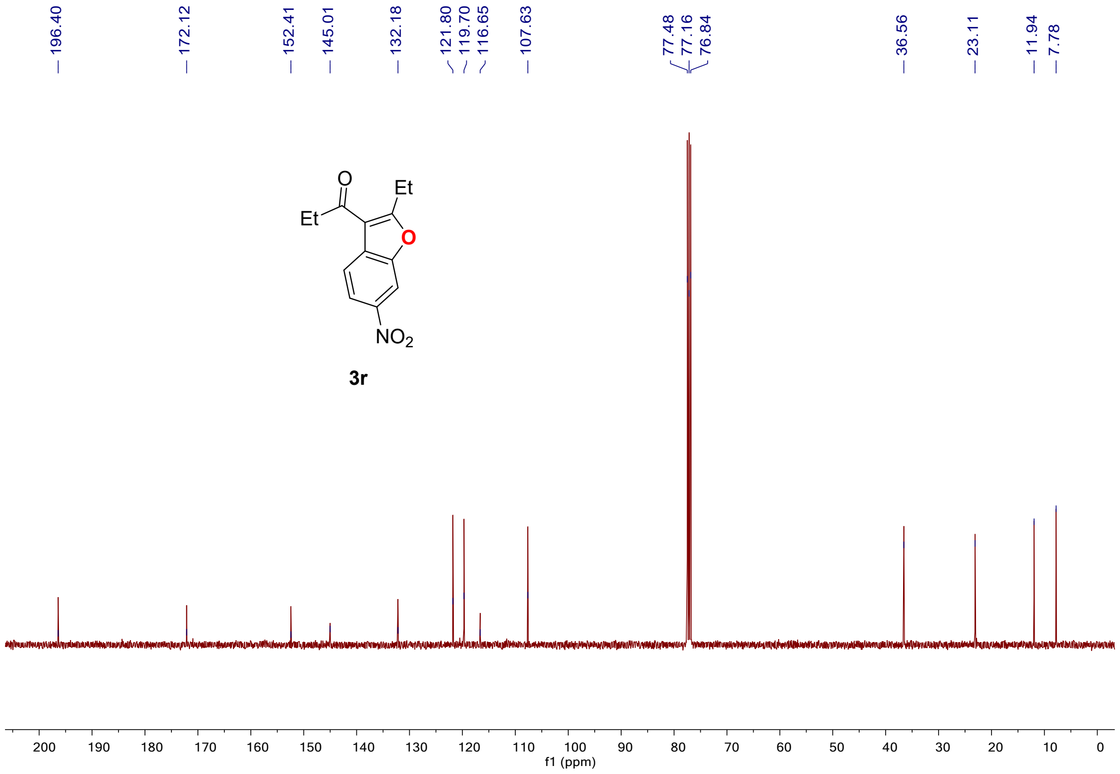

8.405
8.313
8.291
7.761
7.739
7.260
2.761
NC
Me
O
NO2
3p
1.00
1.03
1.01
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

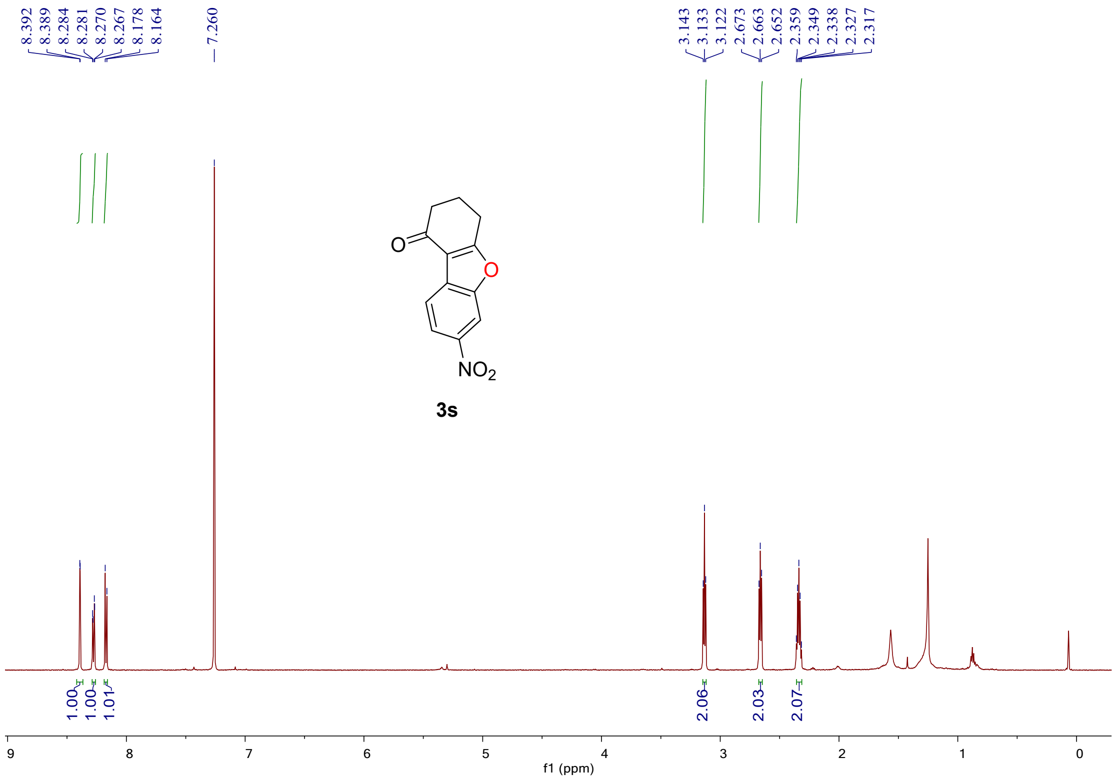

169.96
152.57
146.08
131.80
120.34
119.84
112.00
108.24
92.42
77.48
77.16
76.84
14.52
NC
Me
O
NO2
3p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

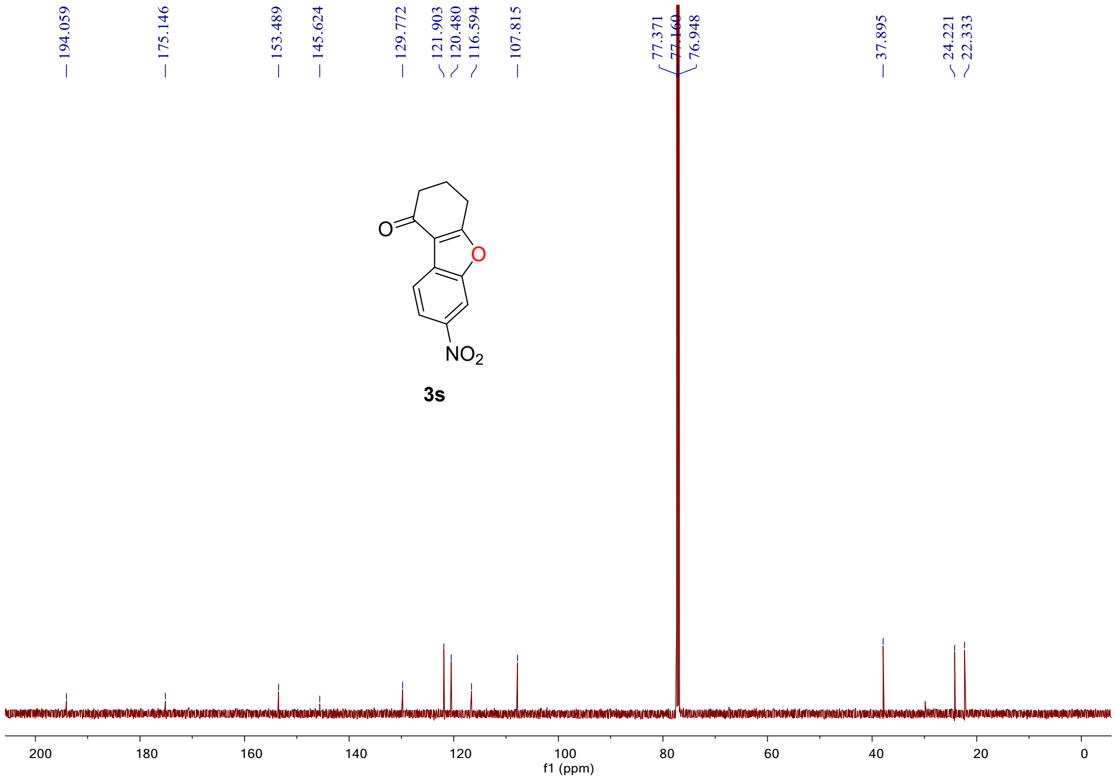

8.321
8.247
8.226
8.125
8.104
2.860
2.659
O
Me
Me
O
NO$_2$
3q
1.00
1.03
1.02
3.02
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

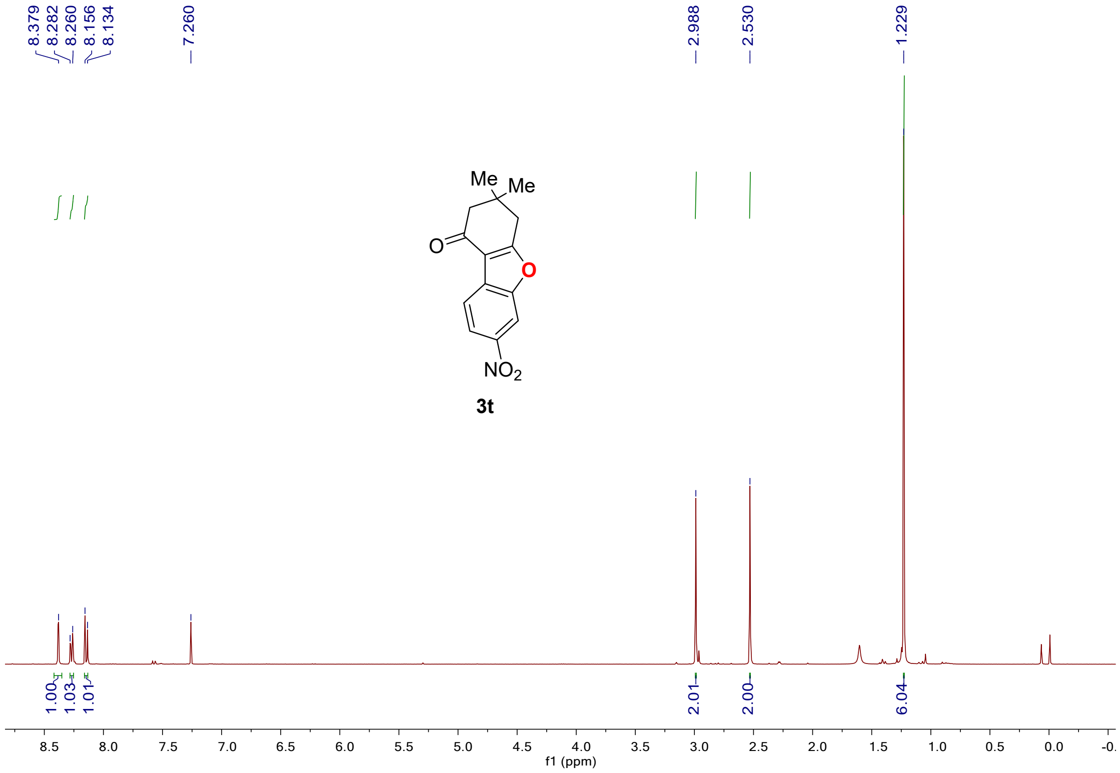

193.18
167.46
152.28
145.14
132.22
121.80
119.82
118.02
107.43
77.48
77.16
76.84
31.17
15.99
O
Me
Me
O
NO$_2$
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

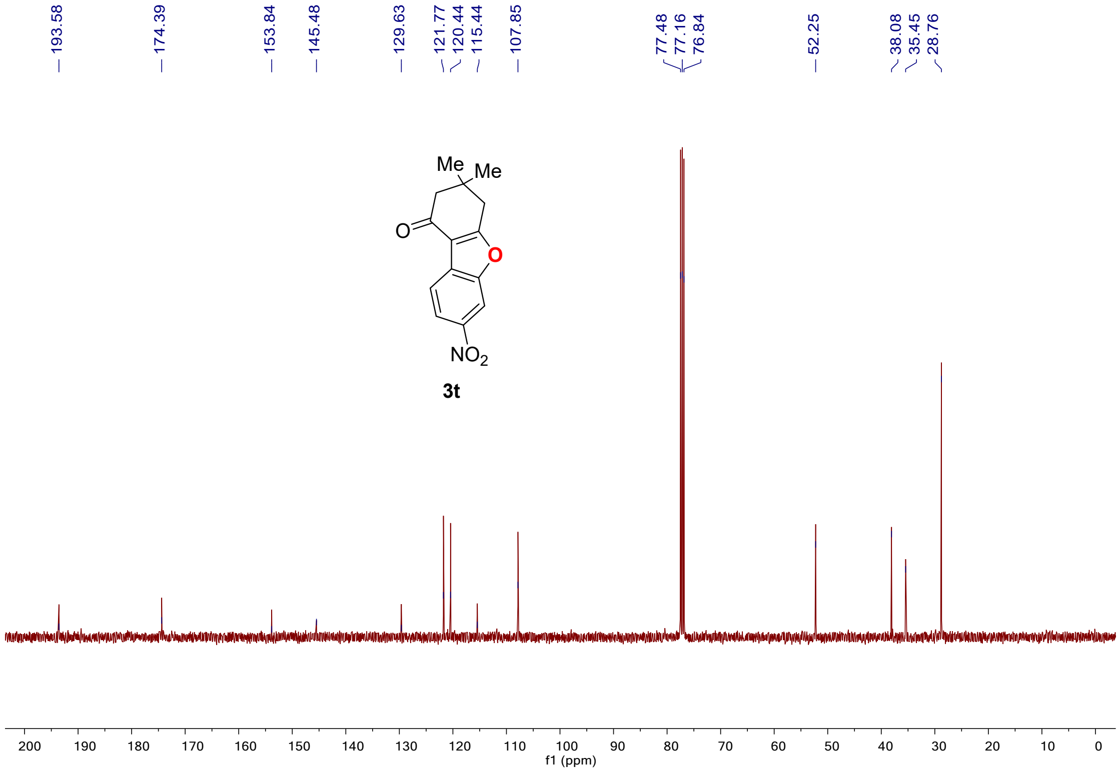

8.350
8.241
8.226
8.085
8.070
7.260
3.267
3.254
3.242
3.229
3.007
2.995
2.983
2.971
1.430
1.418
1.405
1.287
1.275
1.263
O
Et
Et
O
NO$_2$
3r
1.00
1.04
1.03
2.05
2.05
3.12
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

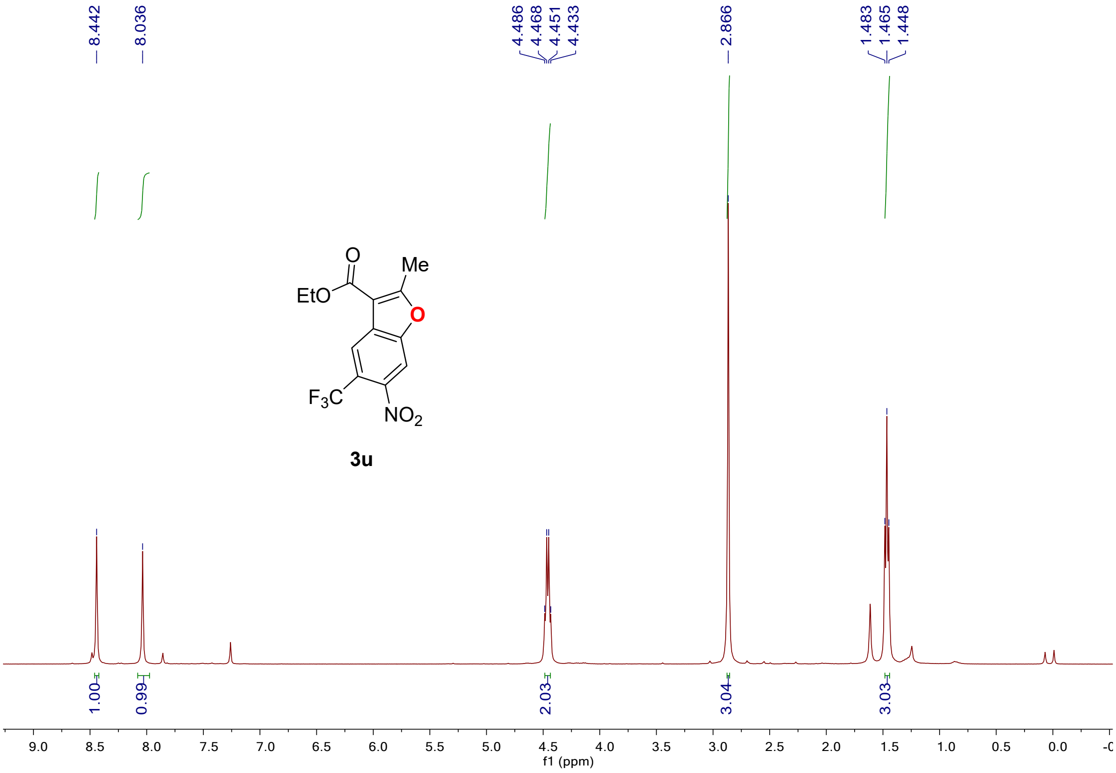

196.40
172.12
152.41
145.01
132.18
121.80
119.70
116.65
107.63
77.48
77.16
76.84
36.56
23.11
11.94
7.78
O
Et
Et
O
NO$_2$
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.392
8.389
8.284
8.281
8.270
8.267
8.178
8.164
7.260
3.143
3.133
3.122
2.673
2.663
2.652
2.359
2.349
2.338
2.327
2.317
O
O
NO2
3s
1.00
1.00
1.01
2.06
2.03
2.07
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


194.059
175.146
153.489
145.624
129.772
121.903
120.480
116.594
107.815
77.371
77.160
76.948
37.895
24.221
22.333
O
O
NO2
3s
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

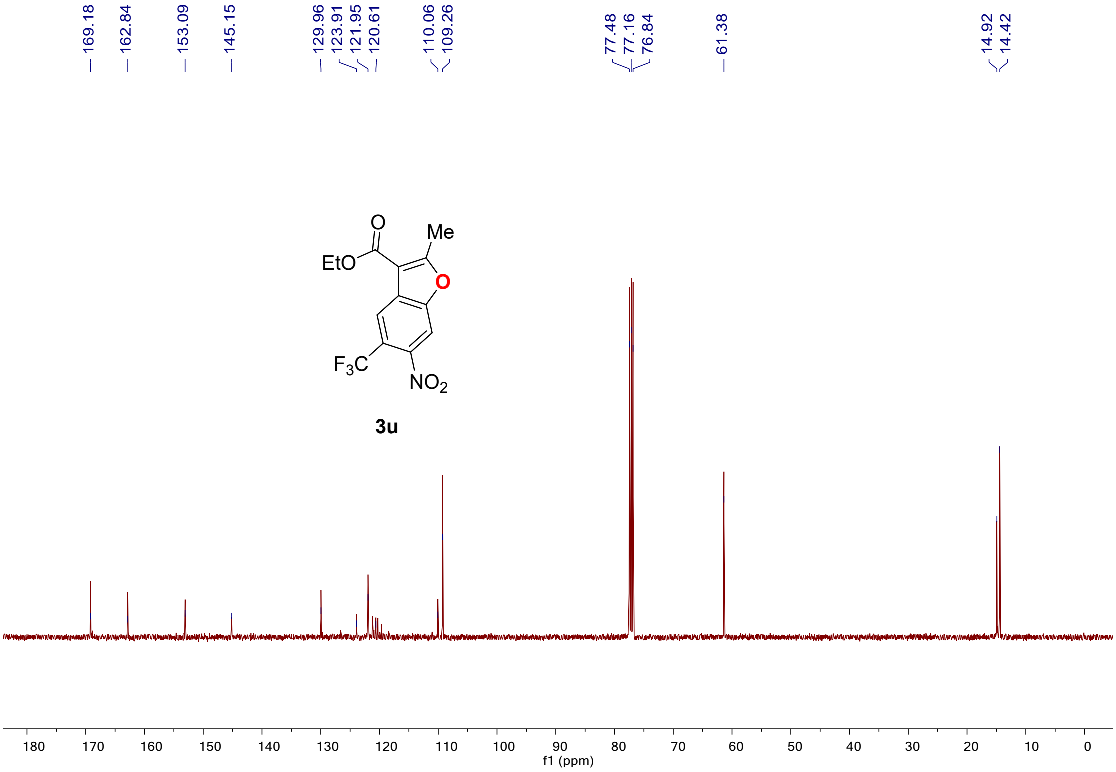

8.379
8.282
8.260
8.156
8.134
7.260
2.988
2.530
1.229
Me
Me
O
O
NO2
3t
1.00
1.03
1.01
2.01
2.00
6.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


193.58
174.39
153.84
145.48
129.63
121.77
120.44
115.44
107.85
77.48
77.16
76.84
52.25
38.08
35.45
28.76
Me
Me
O
O
NO2
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



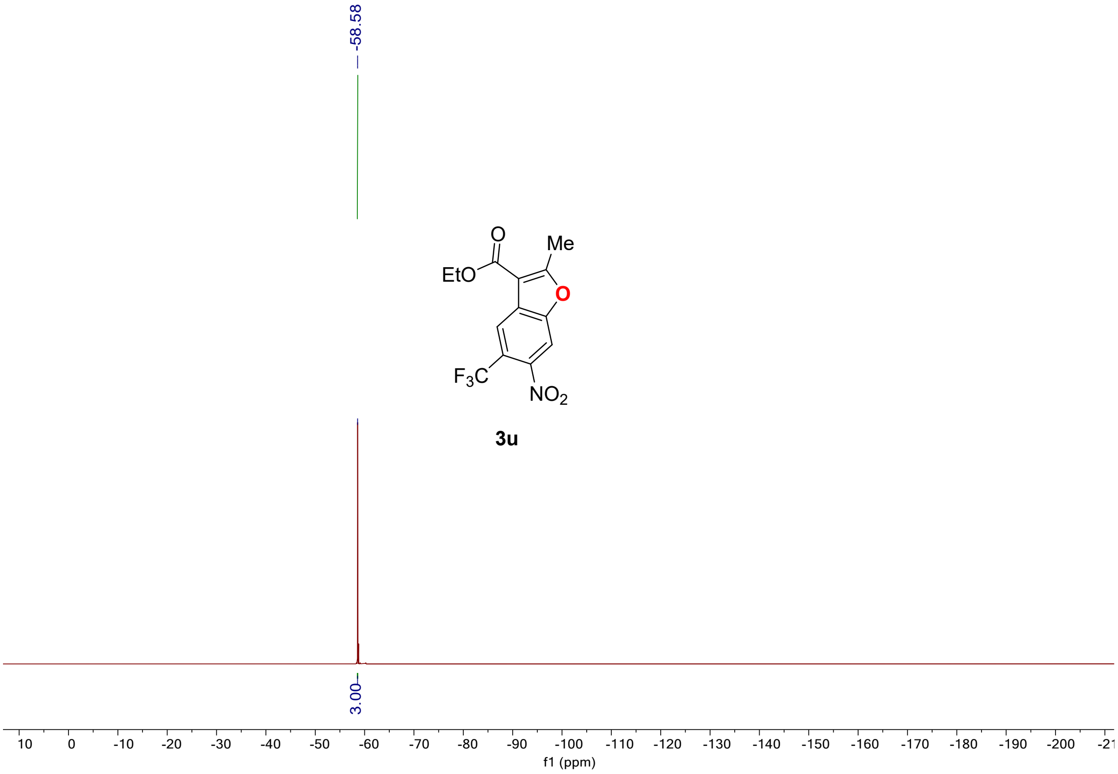
3u

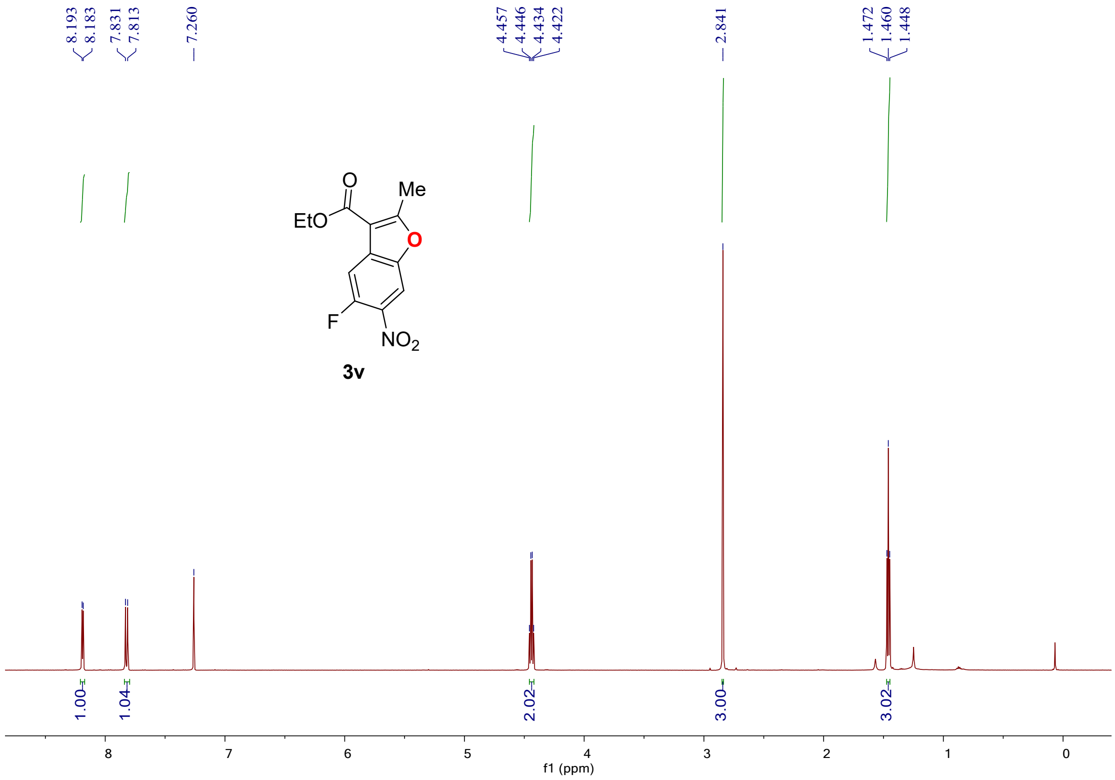
8.442
8.036
4.486
4.468
4.451
4.433
2.866
1.483
1.465
1.448
EtO
O
Me
O
F3C
NO2
1.00
0.99
2.03
3.04
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

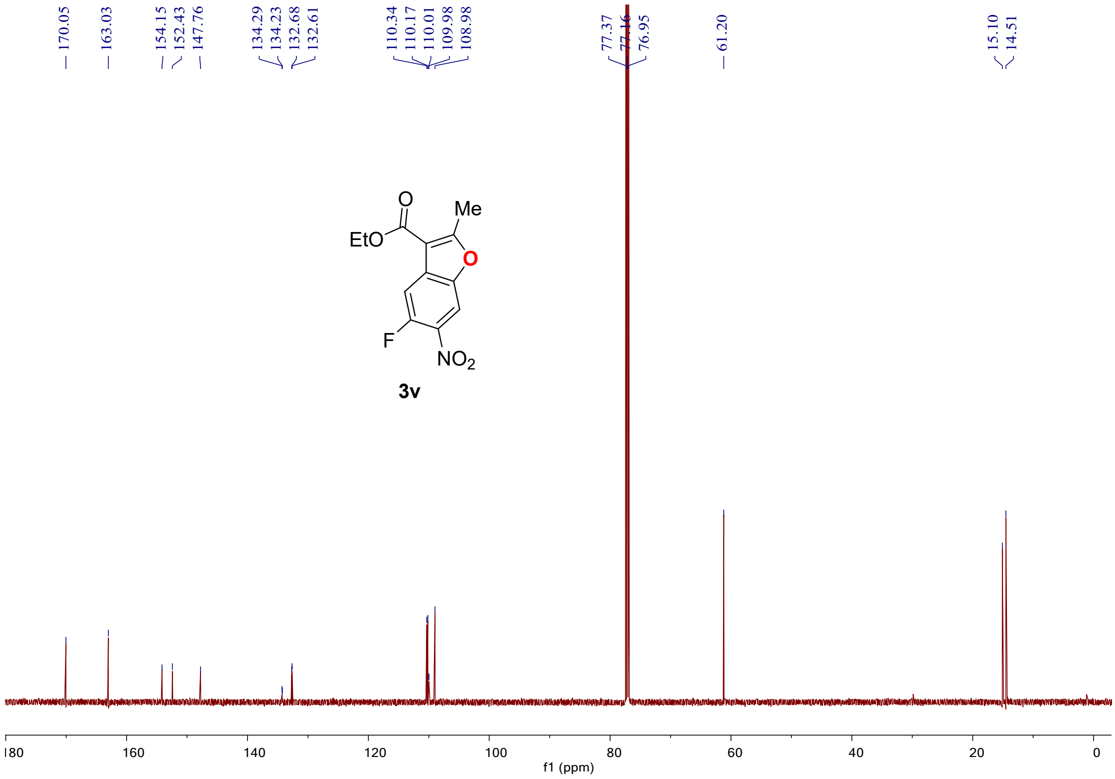


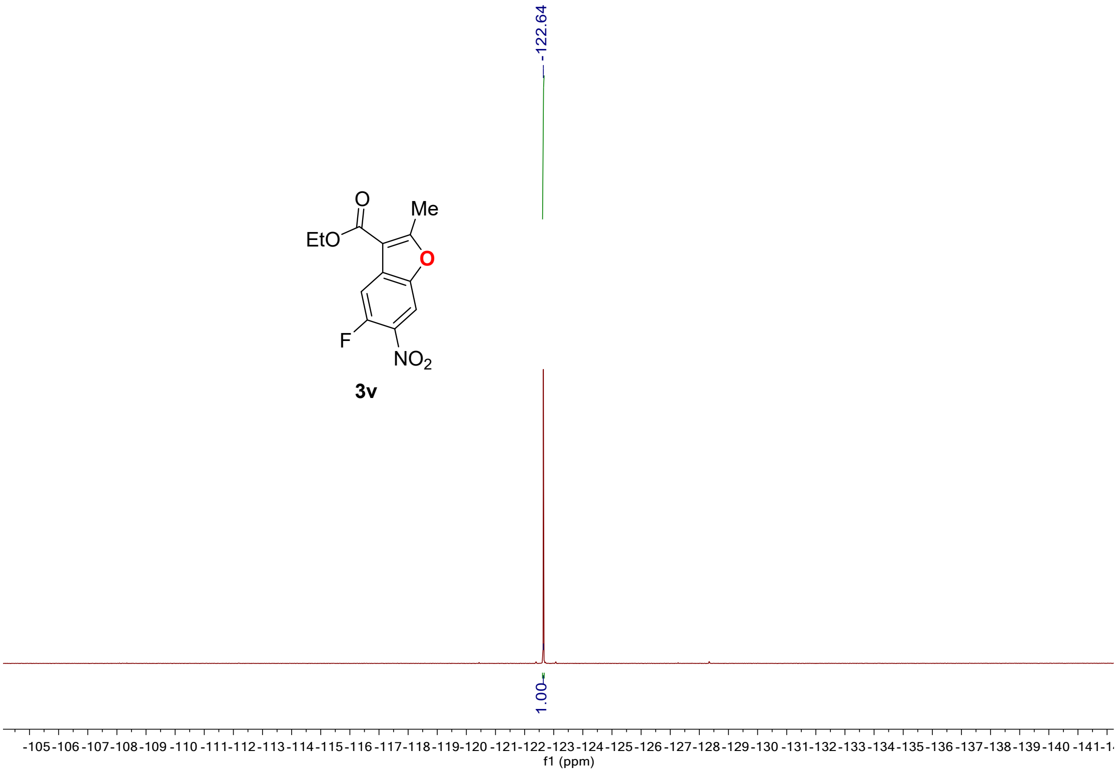
3u

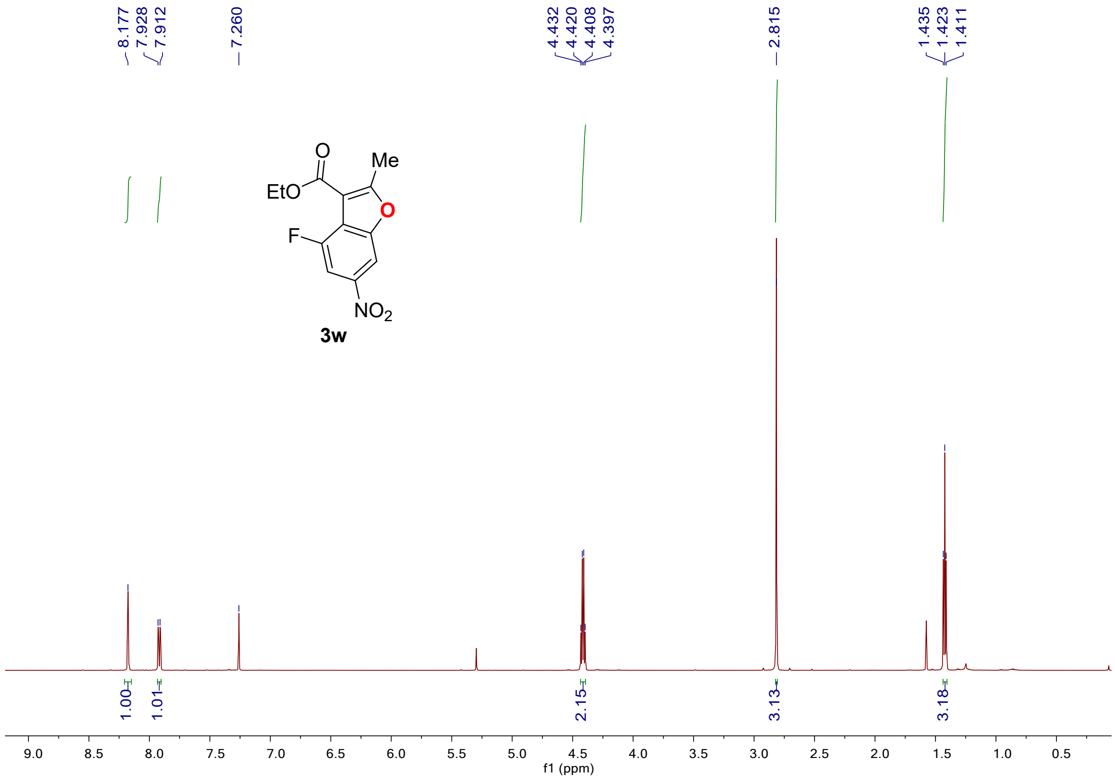
169.18
162.84
153.09
145.15
129.96
123.91
121.95
120.61
110.06
109.26
77.48
77.16
76.84
61.38
14.92
14.42
EtO
O
Me
O
F3C
NO2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

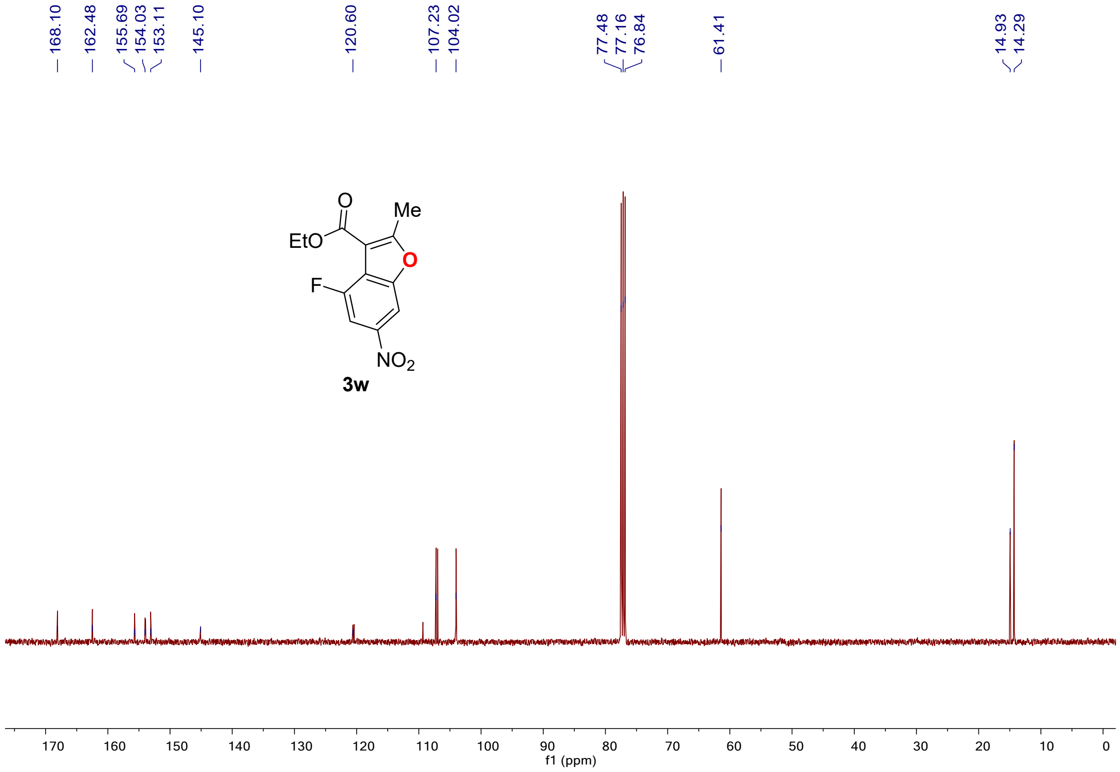

-58.58
EtO
O
Me
O
F3C
NO2
3u
3.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

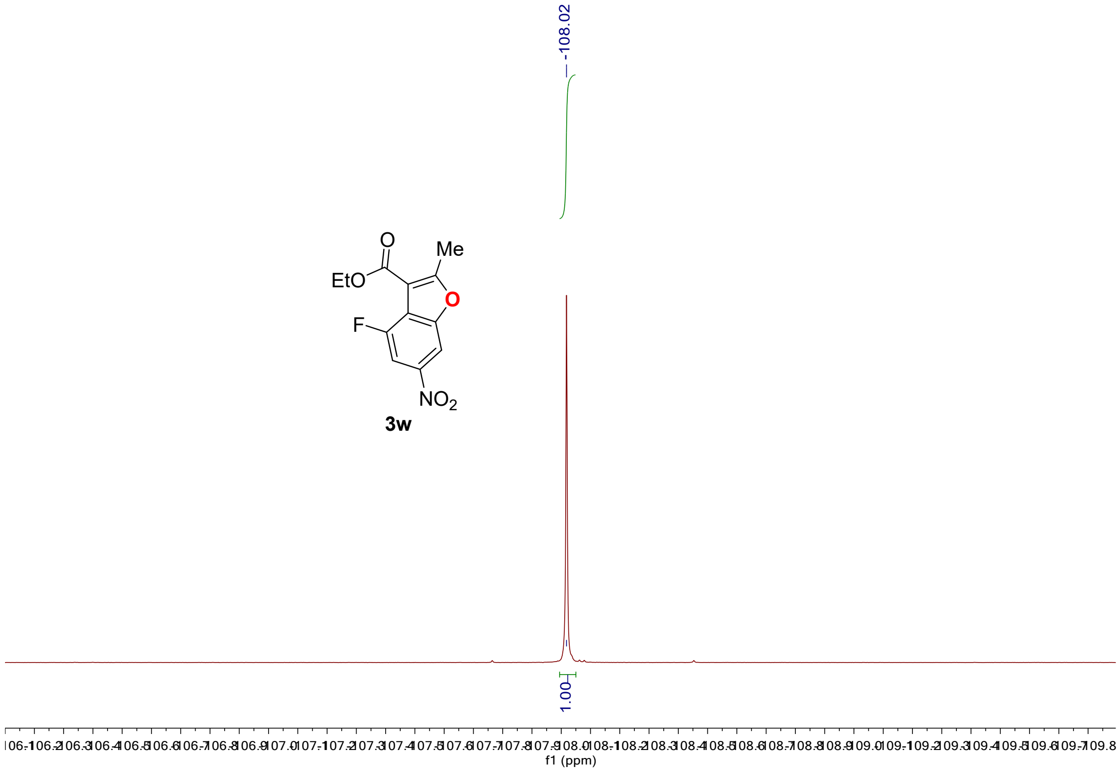

8.193
8.183
7.831
7.813
7.260
4.457
4.446
4.434
4.422
2.841
1.472
1.460
1.448
EtO
O
Me
O
F
NO2
3v
1.00
1.04
2.02
3.00
3.02
8
7
6
5
4
3
2
1
0
f1 (ppm)

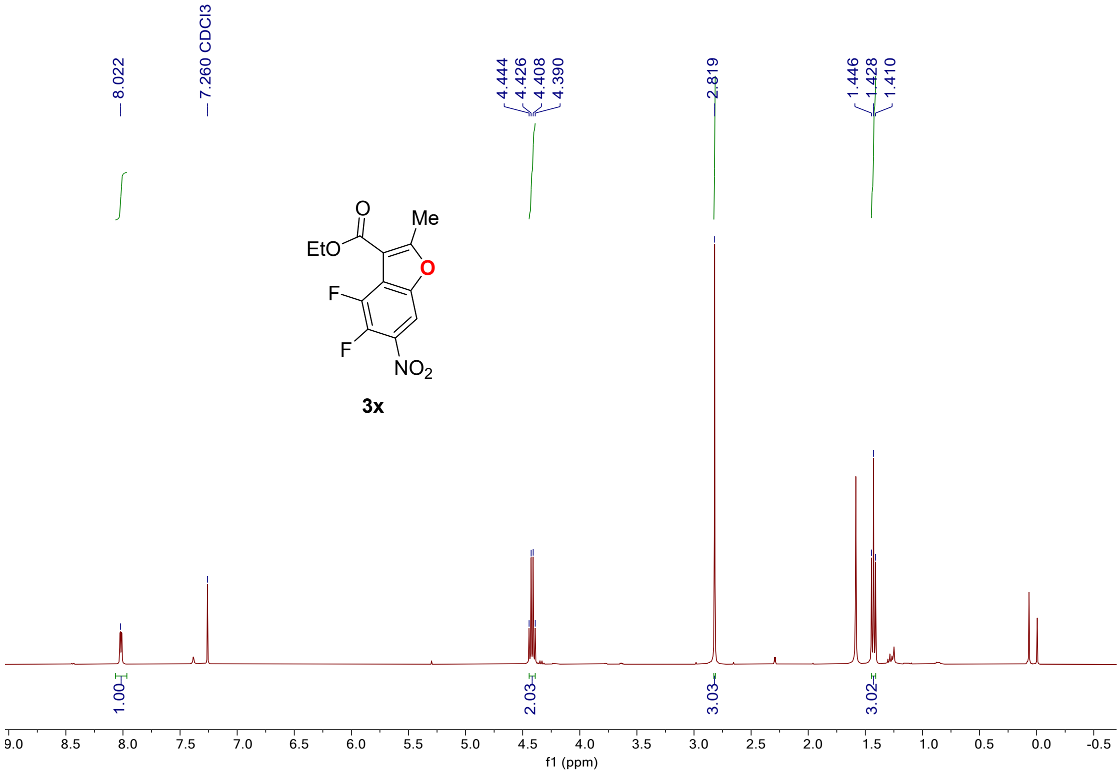

170.05
163.03
154.15
152.43
147.76
134.29
134.23
132.68
132.61
110.34
110.17
110.01
109.98
108.98
77.37
77.16
76.95
61.20
15.10
14.51
EtO
O
Me
O
F
NO2
3v
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

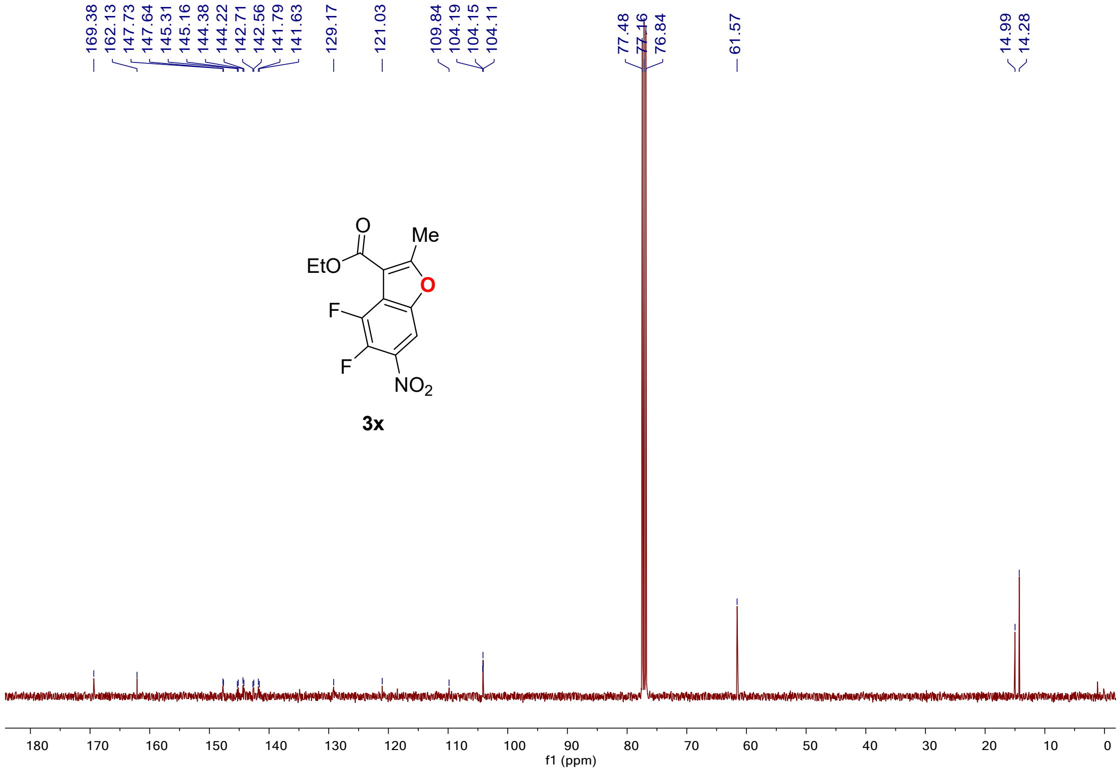

-122.64
Me
O
EtO
O
F
NO2
3v
1.00
-105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129 -130 -131 -132 -133 -134 -135 -136 -137 -138 -139 -140 -141
f1 (ppm)

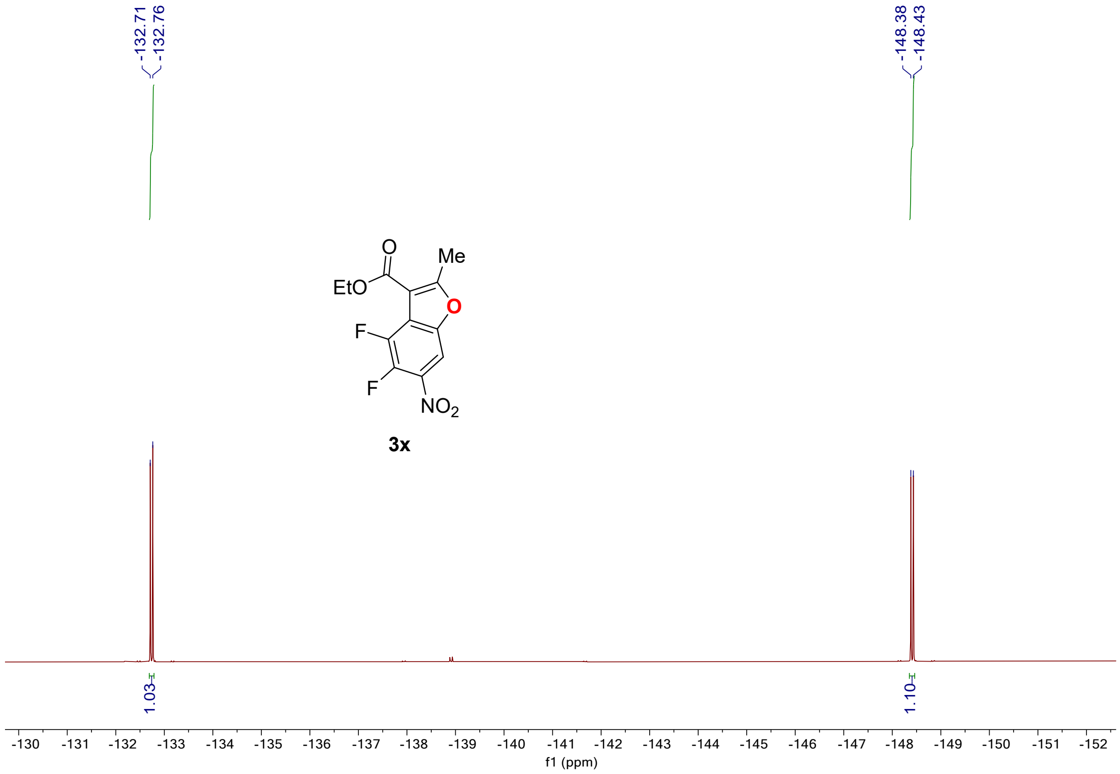

8.177
7.928
7.912
7.260
4.432
4.420
4.408
4.397
2.815
1.435
1.423
1.411
EtO
O
Me
O
F
NO2
3w
1.00
1.01
2.15
3.13
3.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

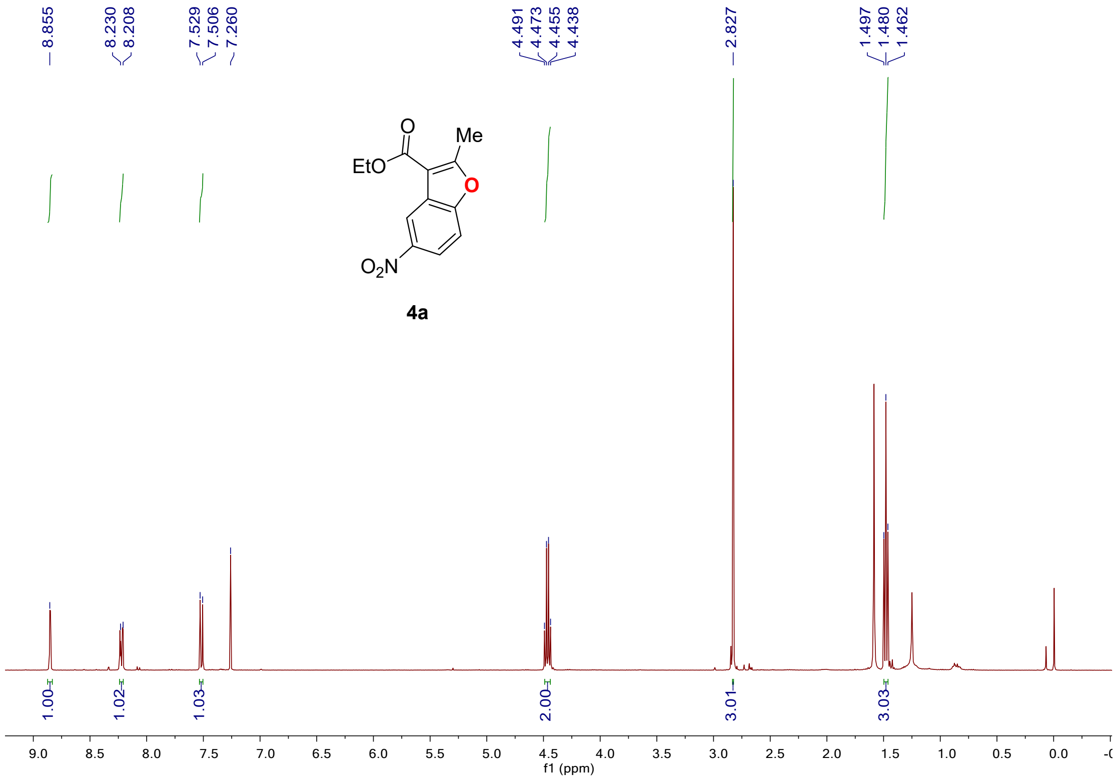

168.10
162.48
155.69
154.03
153.11
145.10
120.60
107.23
104.02
77.48
77.16
76.84
61.41
14.93
14.29
EtO
O
Me
O
F
NO2
3w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

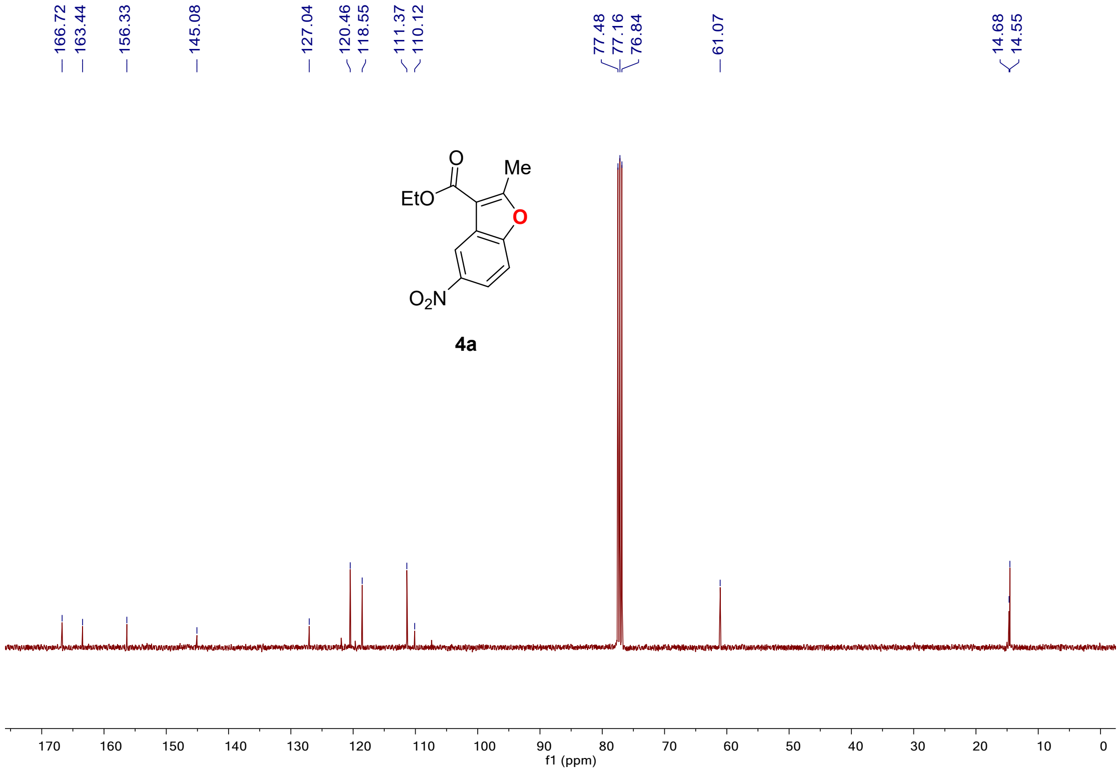

-108.02
EtO
O
Me
O
F
NO2
3w
1.00
106.1
-106.2
-106.3
-106.4
-106.5
-106.6
-106.7
-106.8
-106.9
-107.0
-107.1
-107.2
-107.3
-107.4
-107.5
-107.6
-107.7
-107.8
-107.9
-108.0
-108.1
-108.2
-108.3
-108.4
-108.5
-108.6
-108.7
-108.8
-108.9
-109.0
-109.1
-109.2
-109.3
-109.4
-109.5
-109.6
-109.7
-109.8
f1 (ppm)

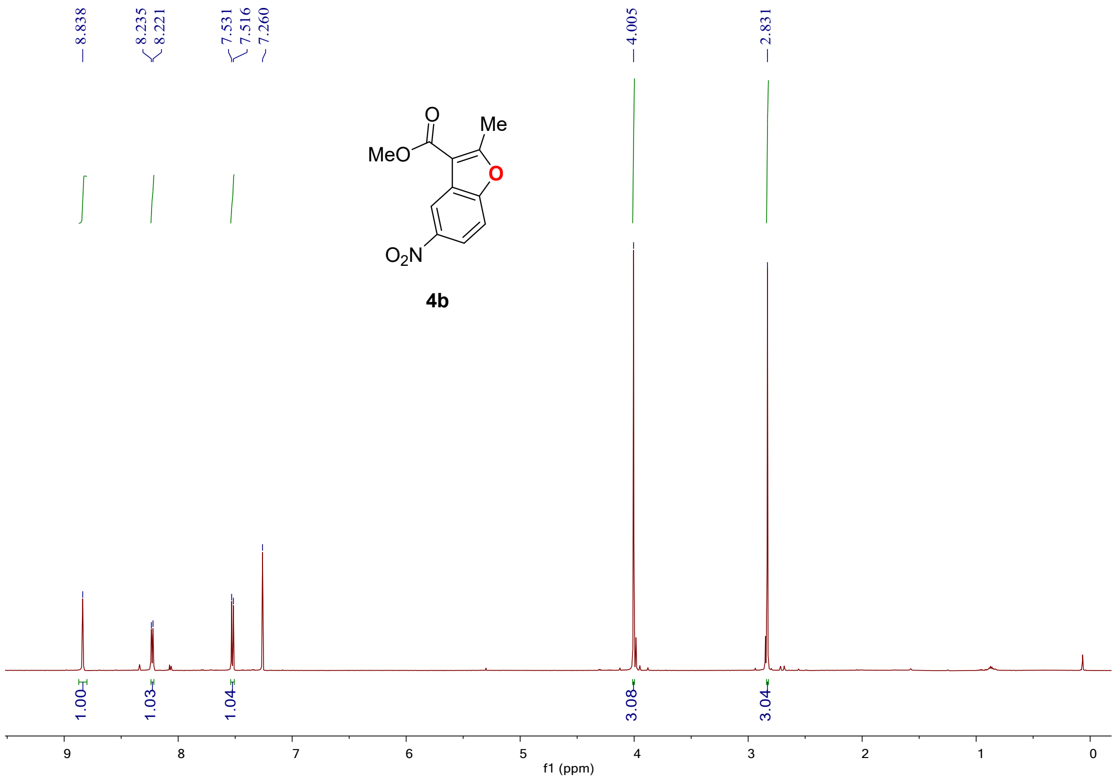

8.022
7.260 CDCl3
4.444
4.426
4.408
4.390
2.819
1.446
1.428
1.410
O
Me
EtO
O
F
F
NO2
3x
1.00
2.03
3.03
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

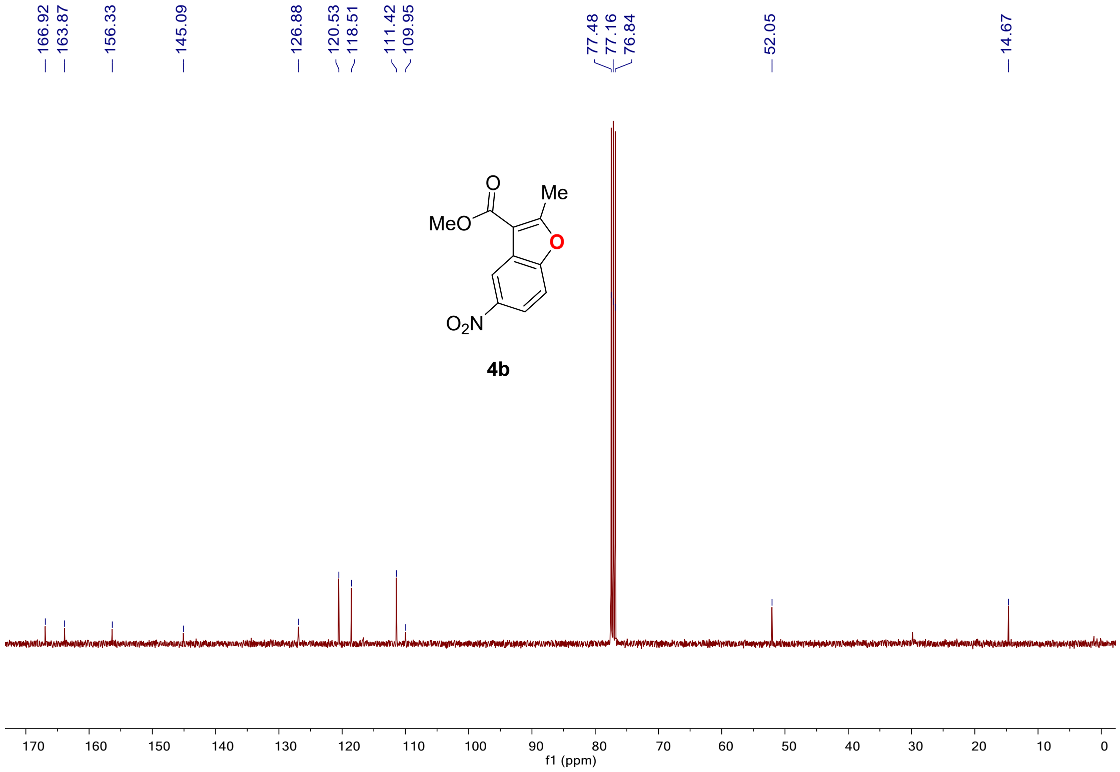

169.38
162.13
147.73
147.64
145.31
145.16
144.38
144.22
142.71
142.56
141.79
141.63
129.17
121.03
109.84
104.19
104.15
104.11
77.48
77.16
76.84
61.57
14.99
14.28
O
Me
EtO
O
F
F
NO2
3x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

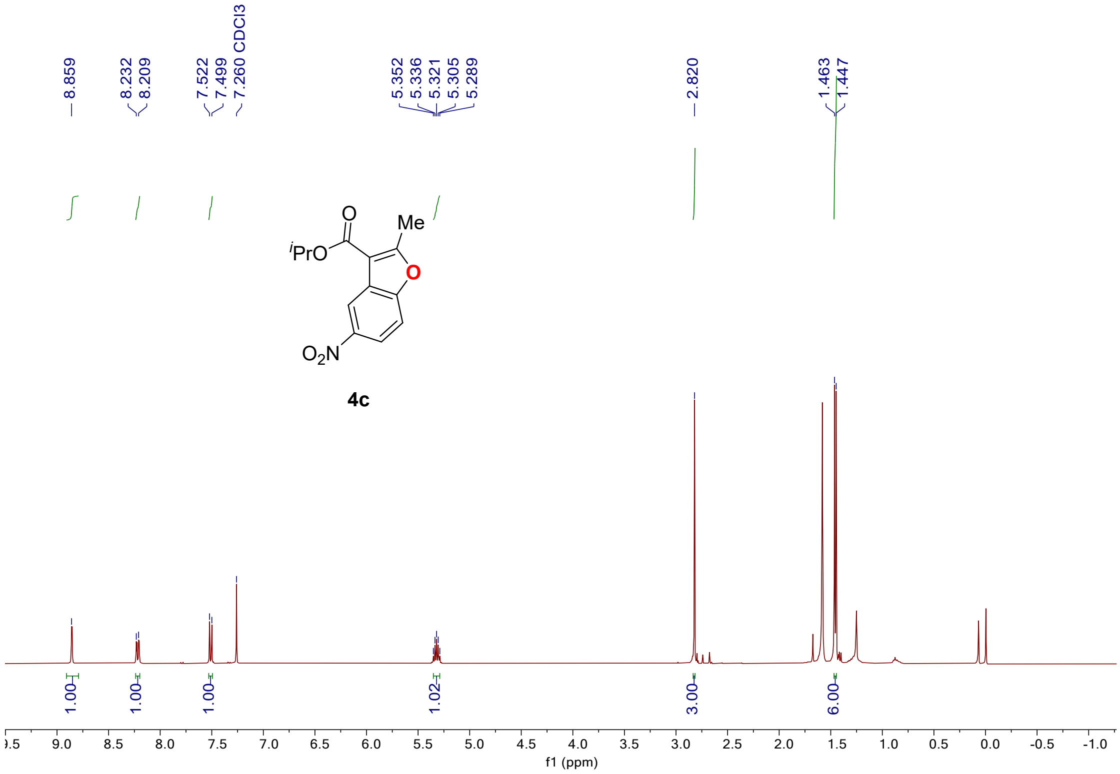

-132.71
-132.76
-148.38
-148.43
EtO
O
Me
O
F
F
NO2
3x
1.03
1.10
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139
-140
-141
-142
-143
-144
-145
-146
-147
-148
-149
-150
-151
-152
f1 (ppm)


8.855
8.230
8.208
7.529
7.506
7.260
4.491
4.473
4.455
4.438
2.827
1.497
1.480
1.462
EtO
O
Me
O
O_2N
4a
1.00
1.02
1.03
2.00
3.01
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

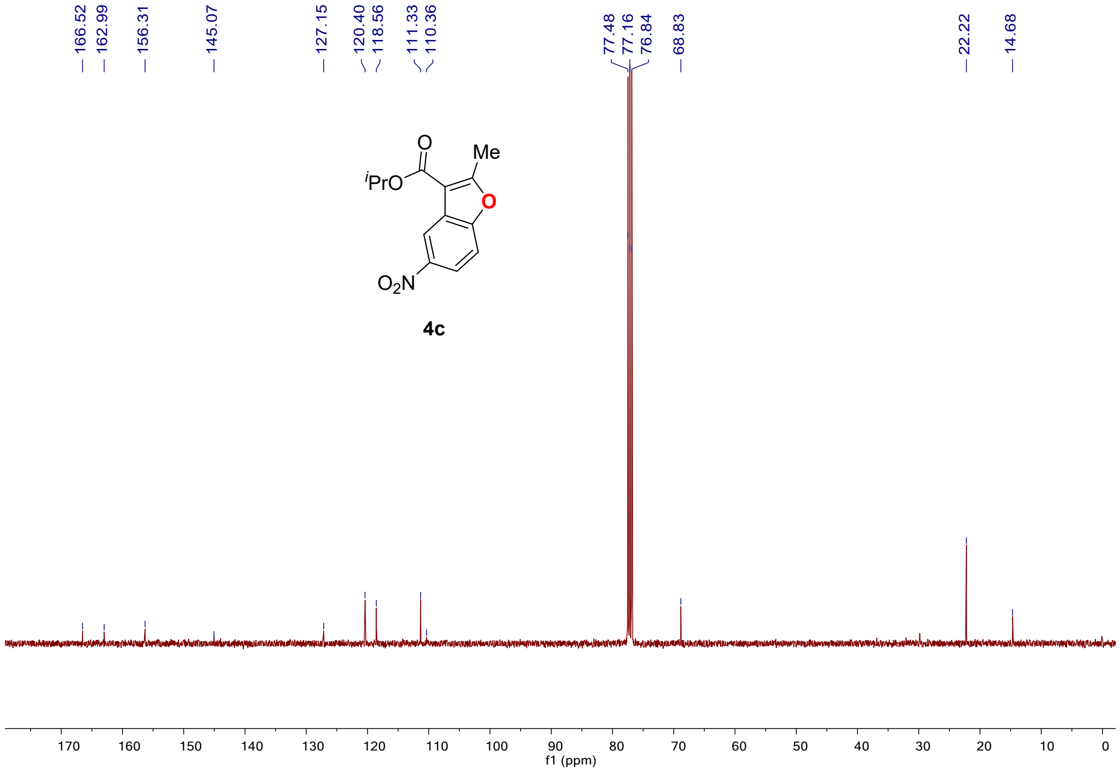

166.72
163.44
156.33
145.08
127.04
120.46
118.55
111.37
110.12
77.48
77.16
76.84
61.07
14.68
14.55
EtO
O
Me
O
O_2N
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.838
8.235
8.221
7.531
7.516
7.260
4.005
2.831
MeO
O
Me
O
O2N
4b
1.00
1.03
1.04
3.08
3.04
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

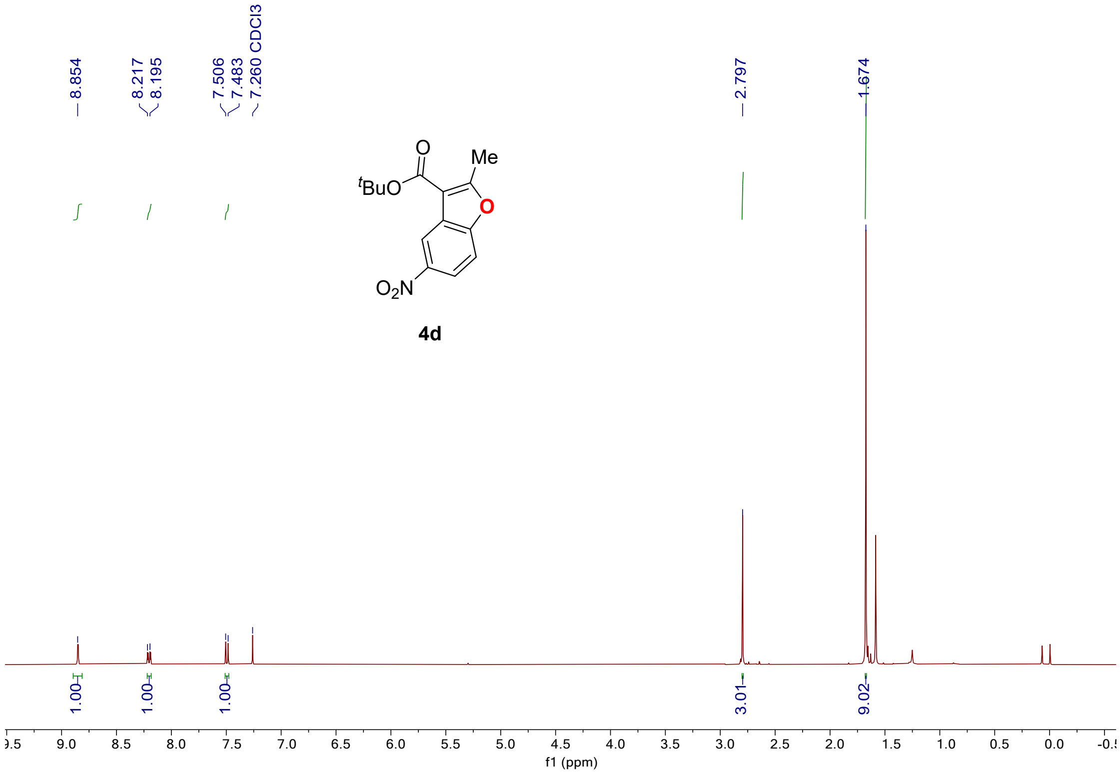

166.92
163.87
156.33
145.09
126.88
120.53
118.51
111.42
109.95
77.48
77.16
76.84
52.05
14.67
MeO
O
Me
O
O2N
4b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.859
8.232
8.209
7.522
7.499
7.260 CDCl3
5.352
5.336
5.321
5.305
5.289
2.820
1.463
1.447
1.00
1.00
1.00
1.02
3.00
6.00
O
Me
^{i}PrO
O
O_2N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

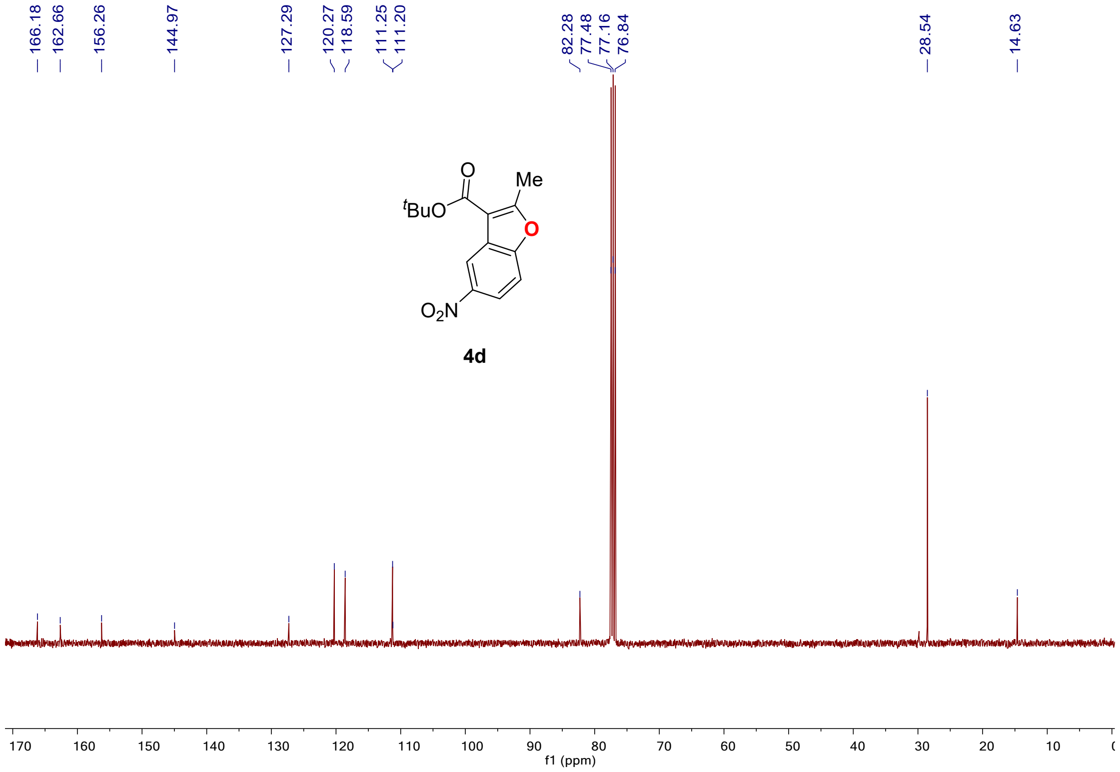
4c


166.52
162.99
156.31
145.07
127.15
120.40
118.56
111.33
110.36
77.48
77.16
76.84
68.83
22.22
14.68
O
Me
^{i}PrO
O
O_2N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

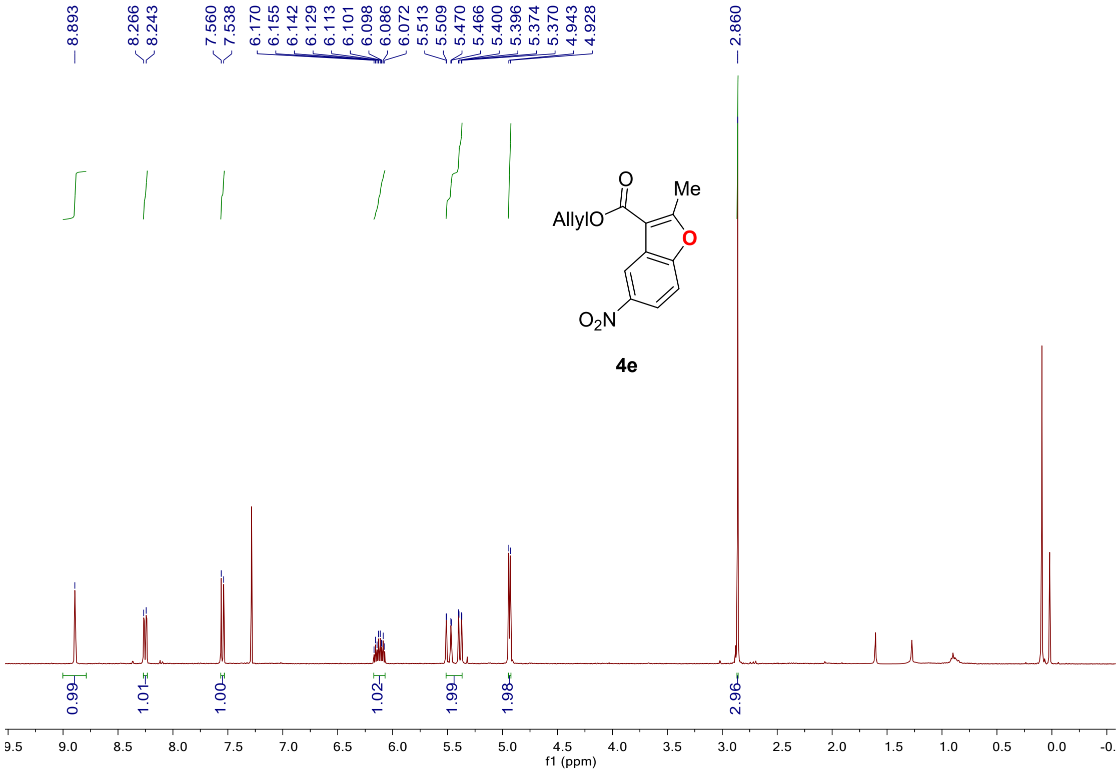
4c

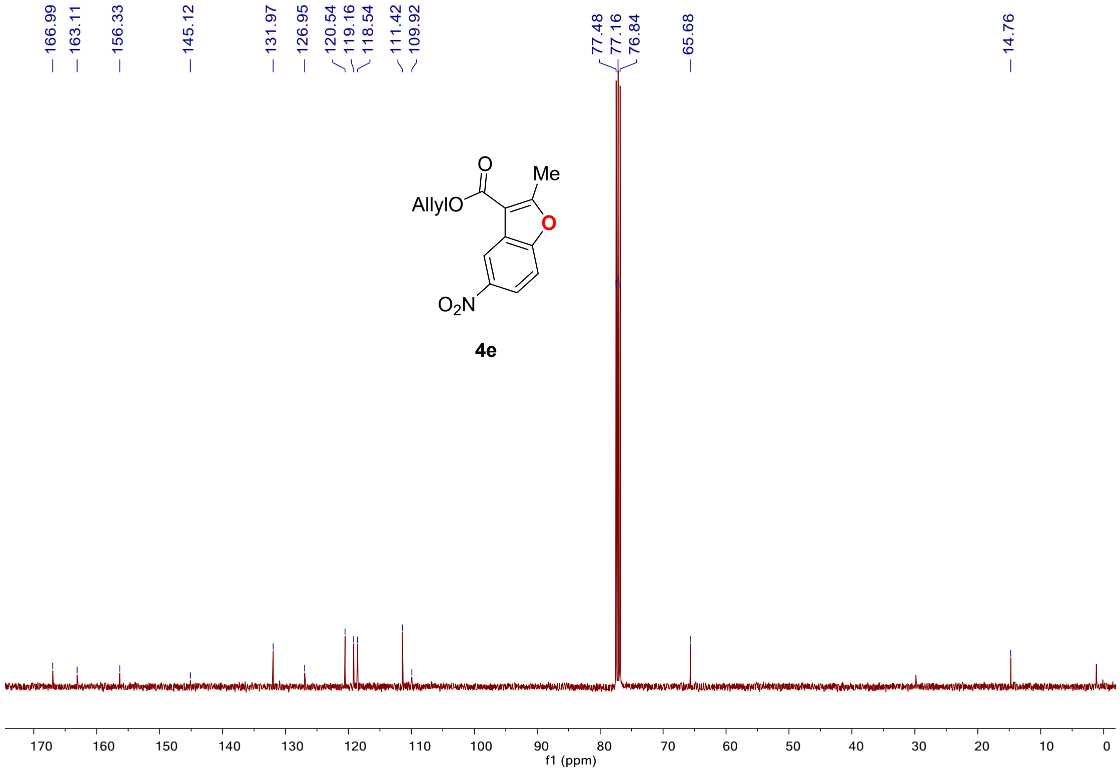


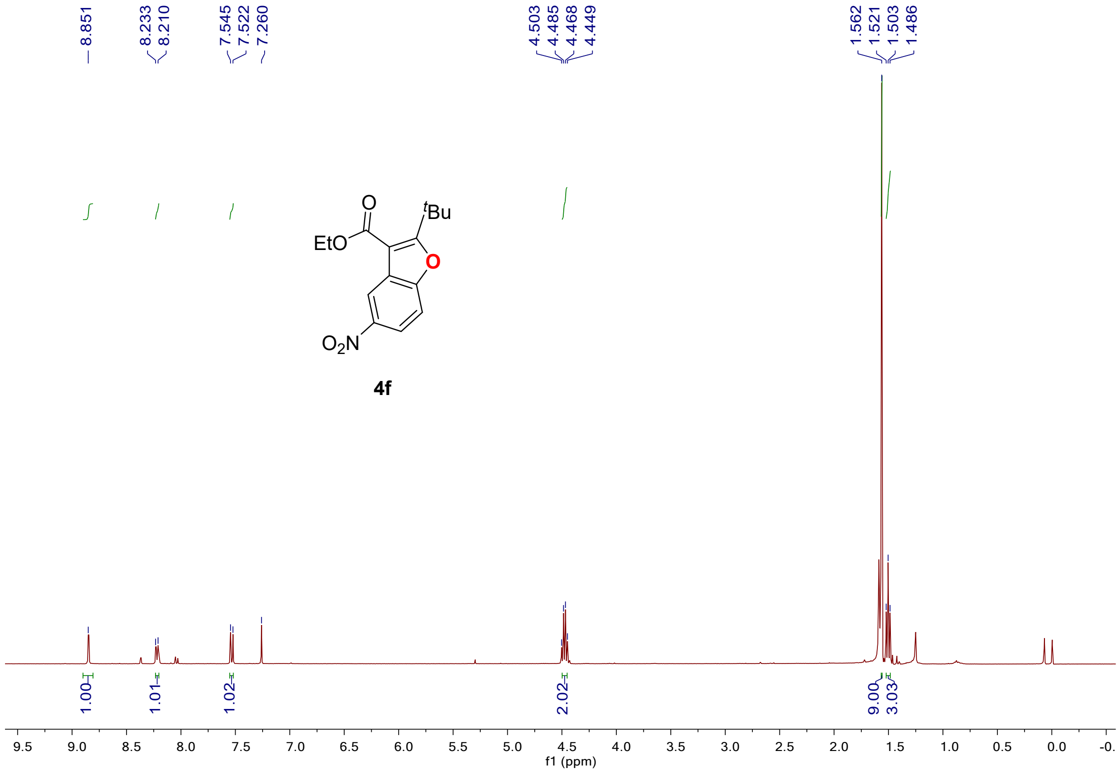
8.854
8.217
8.195
7.506
7.483
7.260 CDCl3
2.797
1.674
1.00
1.00
1.00
3.01
9.02
Me
O
^{t}BuO
O_2N
4d
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

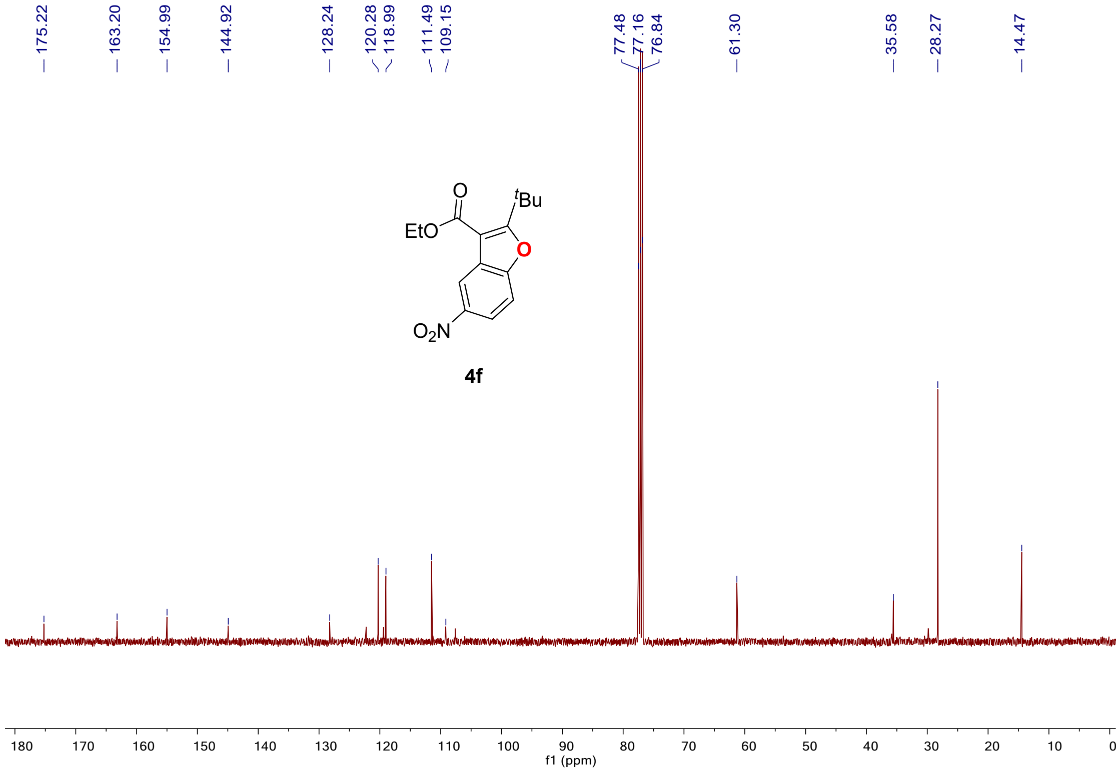


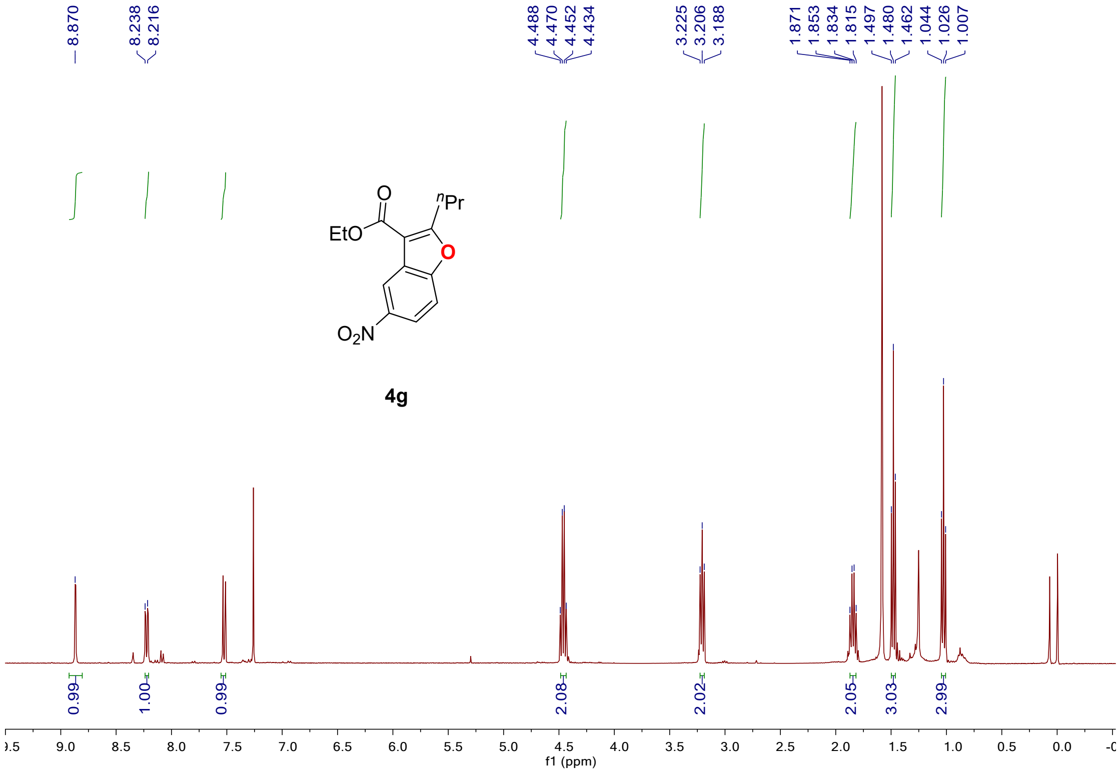
166.18
162.66
156.26
144.97
127.29
120.27
118.59
111.25
111.20
82.28
77.48
77.16
76.84
28.54
14.63
Me
O
^{t}BuO
O_2N
4d
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

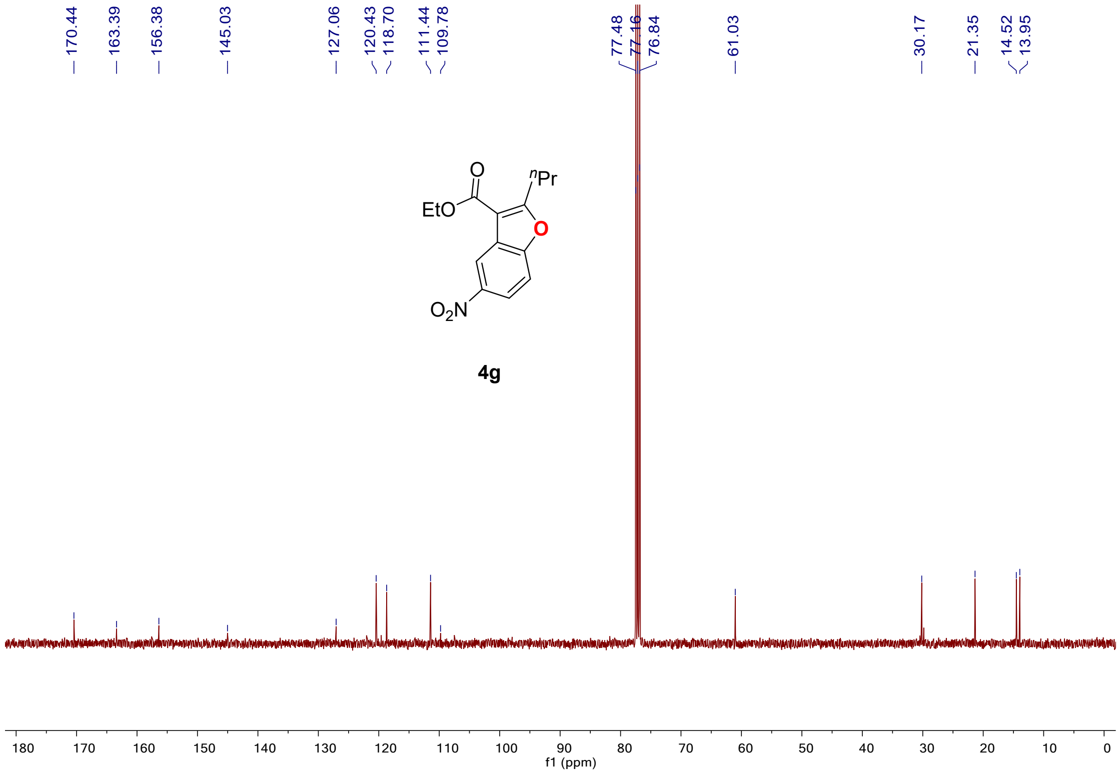

8.893
8.266
8.243
7.560
7.538
6.170
6.155
6.142
6.129
6.113
6.101
6.098
6.086
6.072
5.513
5.509
5.470
5.466
5.400
5.396
5.374
5.370
4.943
4.928
2.860
AllylO
O
Me
O
O_2N
4e
0.99
1.01
1.00
1.02
1.99
1.98
2.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

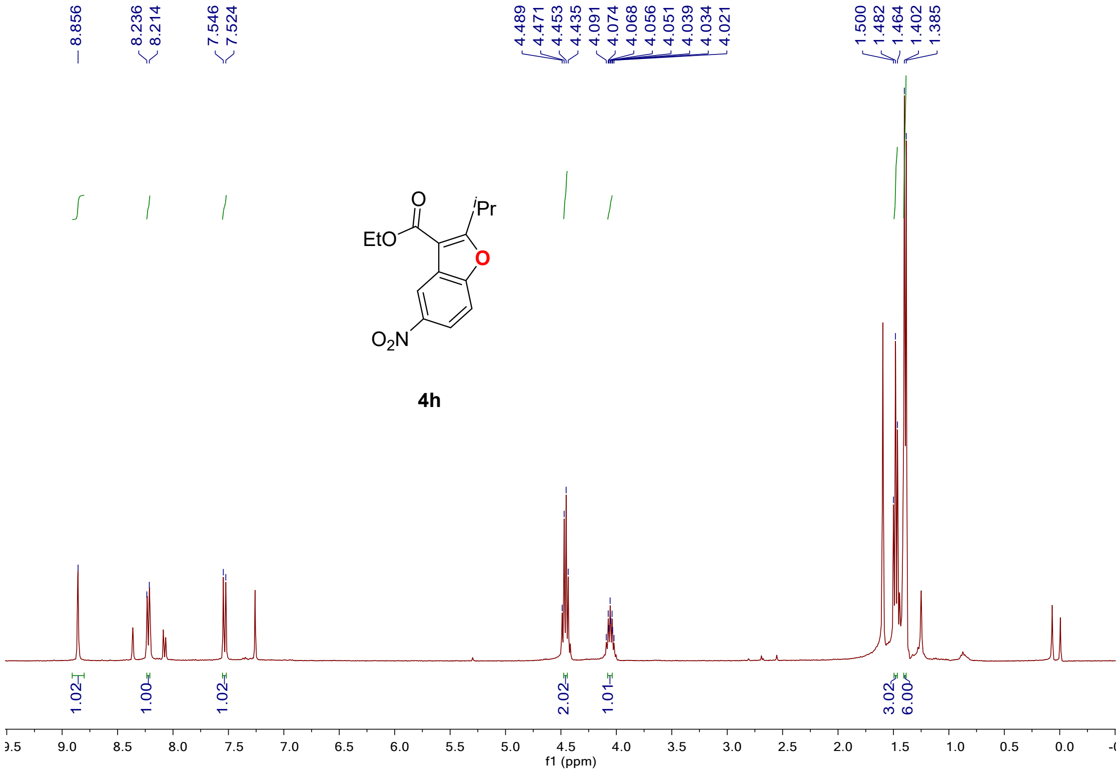

166.99
163.11
156.33
145.12
131.97
126.95
120.54
119.16
118.54
111.42
109.92
77.48
77.16
76.84
65.68
14.76
AllylO
O
Me
O
O_2N
4e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

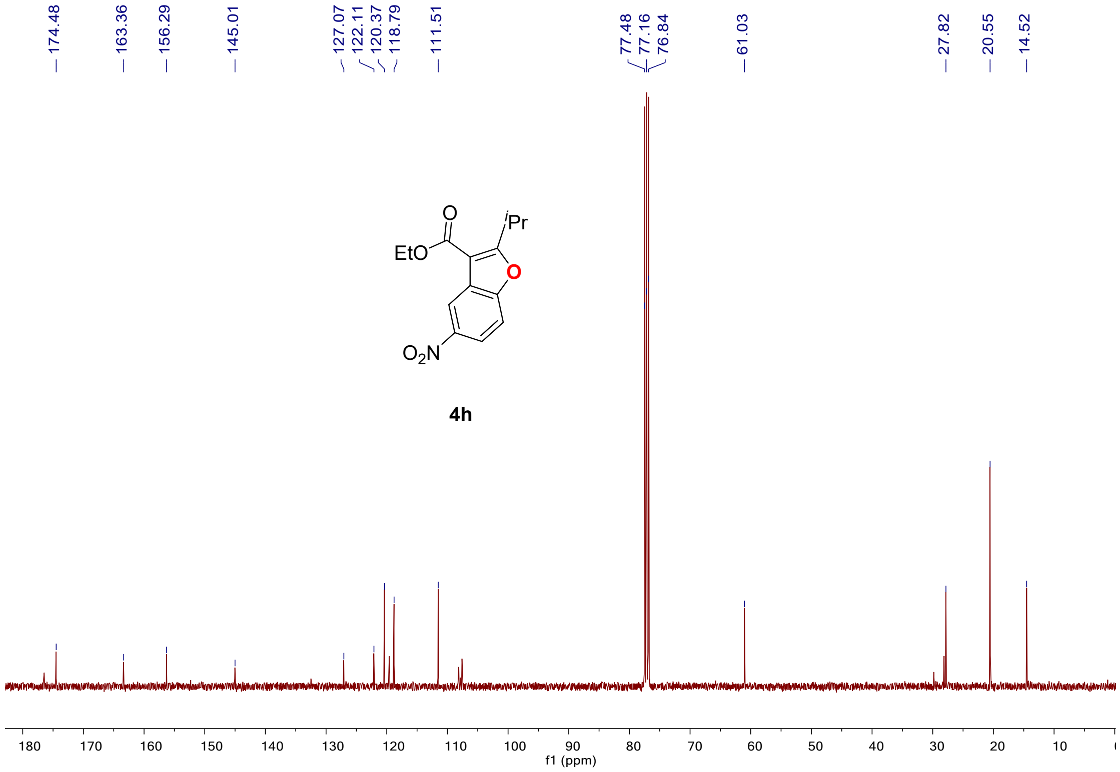

8.851
8.233
8.210
7.545
7.522
7.260
4.503
4.485
4.468
4.449
1.562
1.521
1.503
1.486
1.00
1.01
1.02
2.02
9.00
3.03
EtO
O
^{t}Bu
O
O$_2$N
4f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

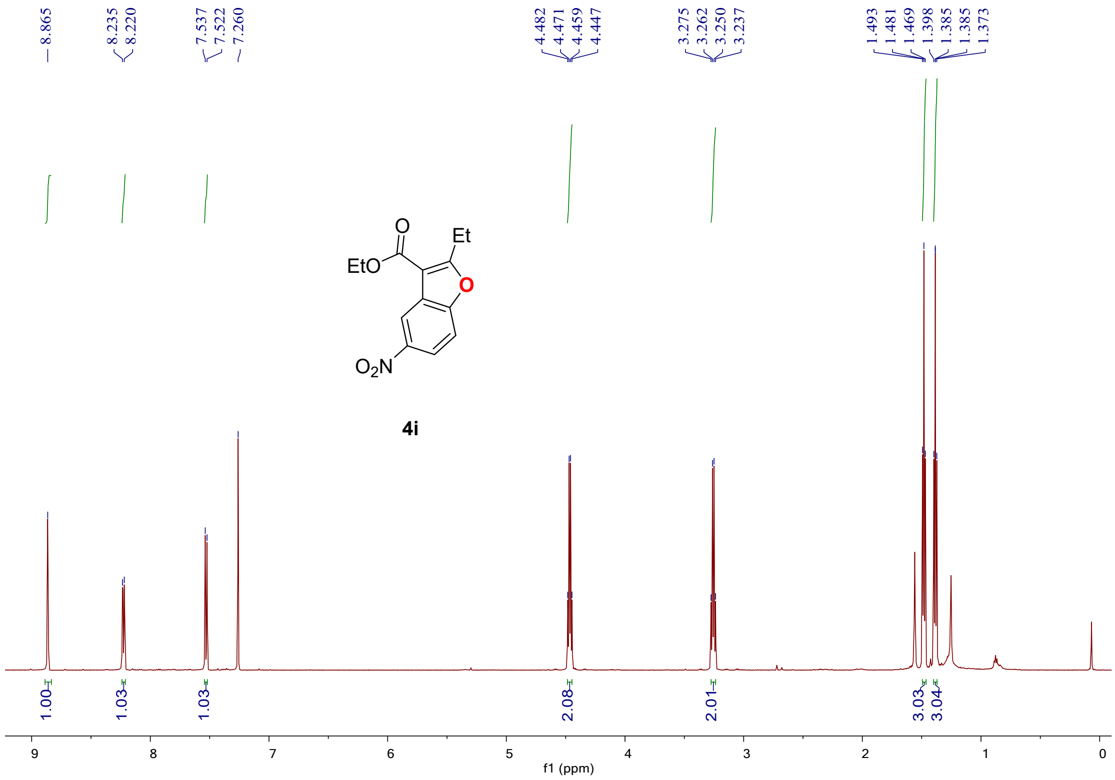

175.22
163.20
154.99
144.92
128.24
120.28
118.99
111.49
109.15
77.48
77.16
76.84
61.30
35.58
28.27
14.47
EtO
O
^{t}Bu
O
O$_2$N
4f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

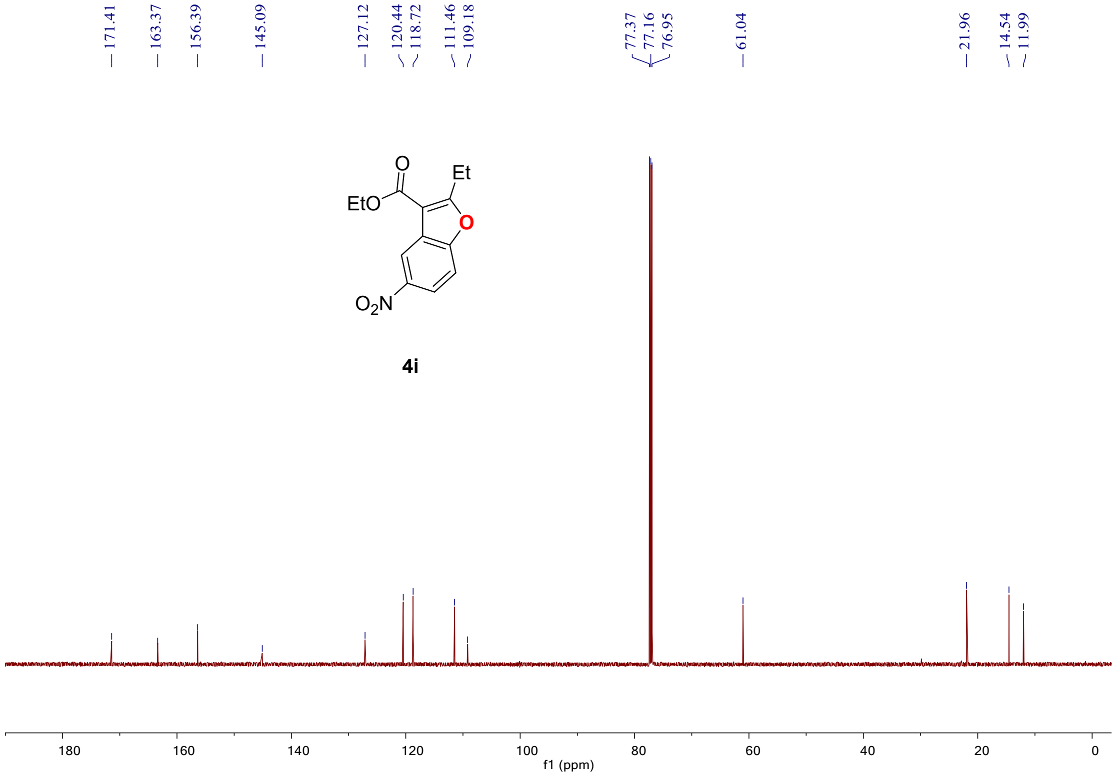

8.870
8.238
8.216
4.488
4.470
4.452
4.434
3.225
3.206
3.188
1.871
1.853
1.834
1.815
1.497
1.480
1.462
1.044
1.026
1.007
EtO
O
ⁿPr
O
O₂N
4g
0.99
1.00
0.99
2.08
2.02
2.05
3.03
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

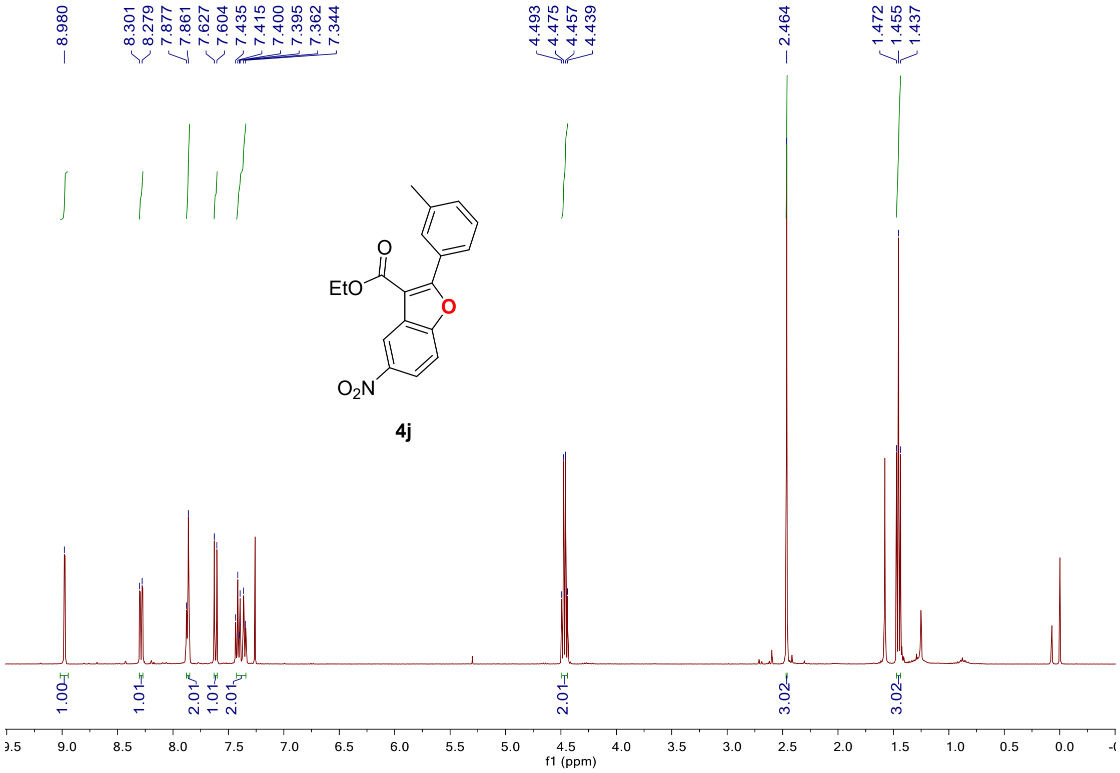

170.44
163.39
156.38
145.03
127.06
120.43
118.70
111.44
109.78
77.48
77.16
76.84
61.03
30.17
21.35
14.52
13.95
EtO
O
ⁿPr
O
O₂N
4g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

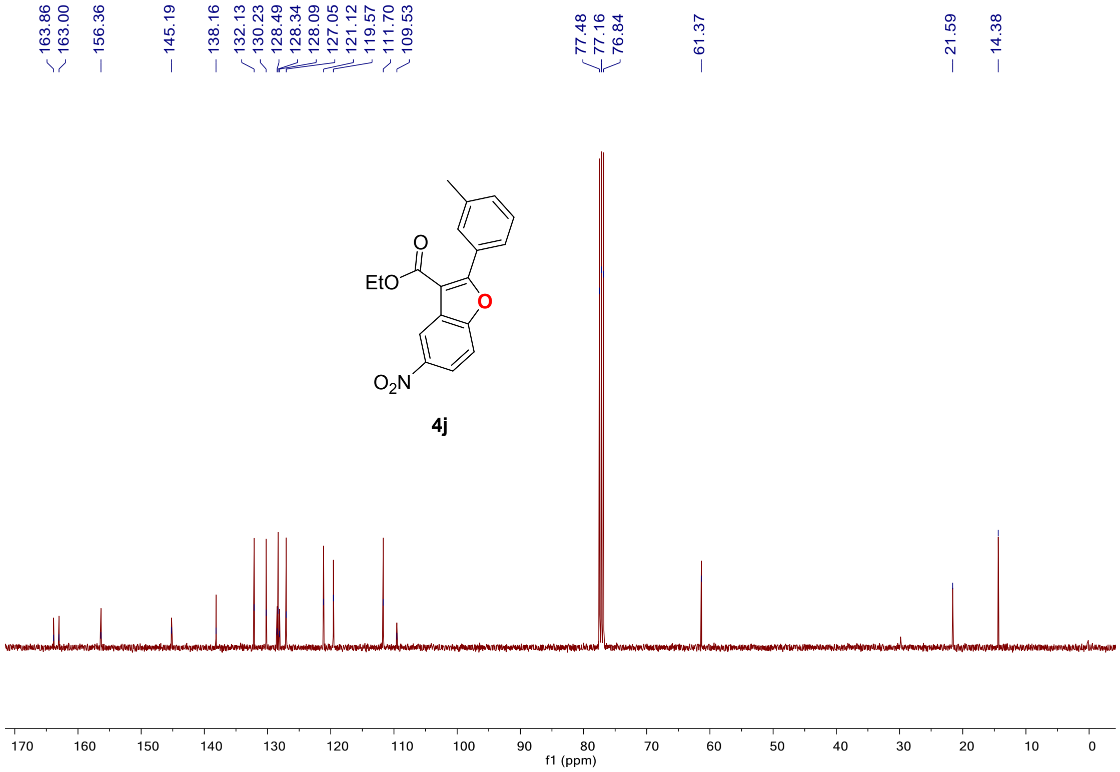

8.856
8.236
8.214
7.546
7.524
4.489
4.471
4.453
4.435
4.091
4.074
4.068
4.056
4.051
4.039
4.034
4.021
1.500
1.482
1.464
1.402
1.385
EtO
O
iPr
O
O2N
4h
1.02
1.00
1.02
2.02
1.01
3.02
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

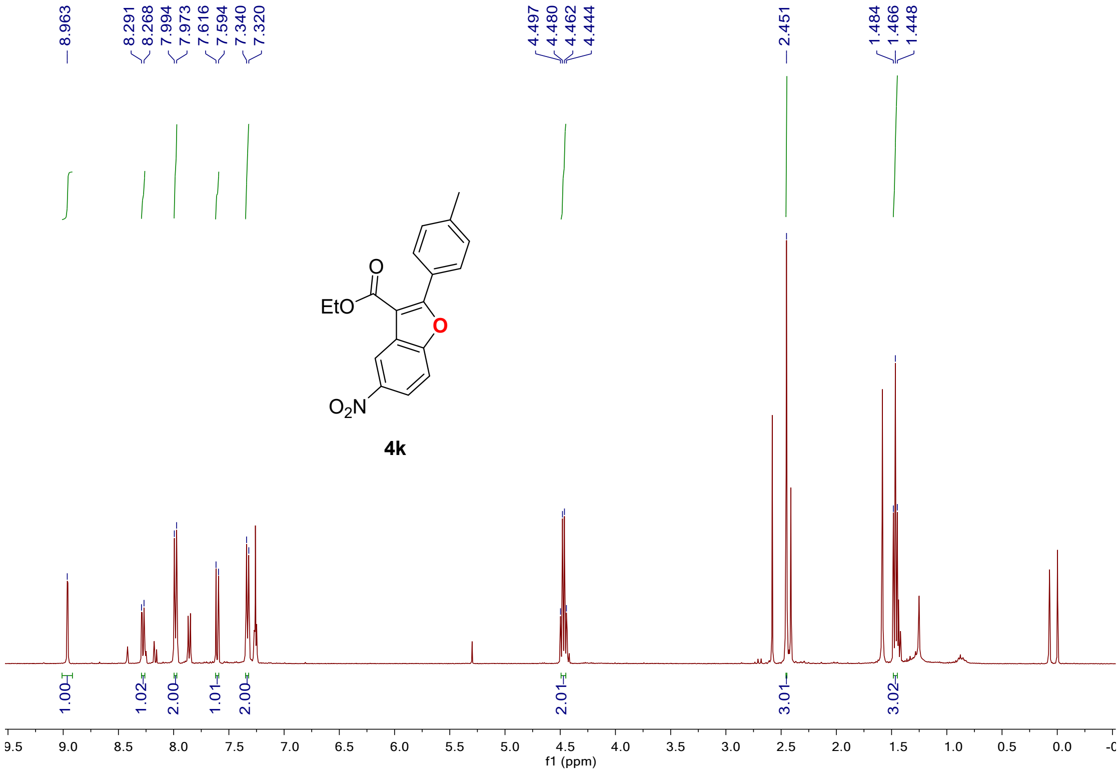

174.48
163.36
156.29
145.01
127.07
122.11
120.37
118.79
111.51
77.48
77.16
76.84
61.03
27.82
20.55
14.52
EtO
O
iPr
O
O2N
4h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.865
8.235
8.220
7.537
7.522
7.260
4.482
4.471
4.459
4.447
3.275
3.262
3.250
3.237
1.493
1.481
1.469
1.398
1.385
1.385
1.373
EtO
O
Et
O
O_2N
4i
1.00
1.03
1.03
2.08
2.01
3.03
3.04
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

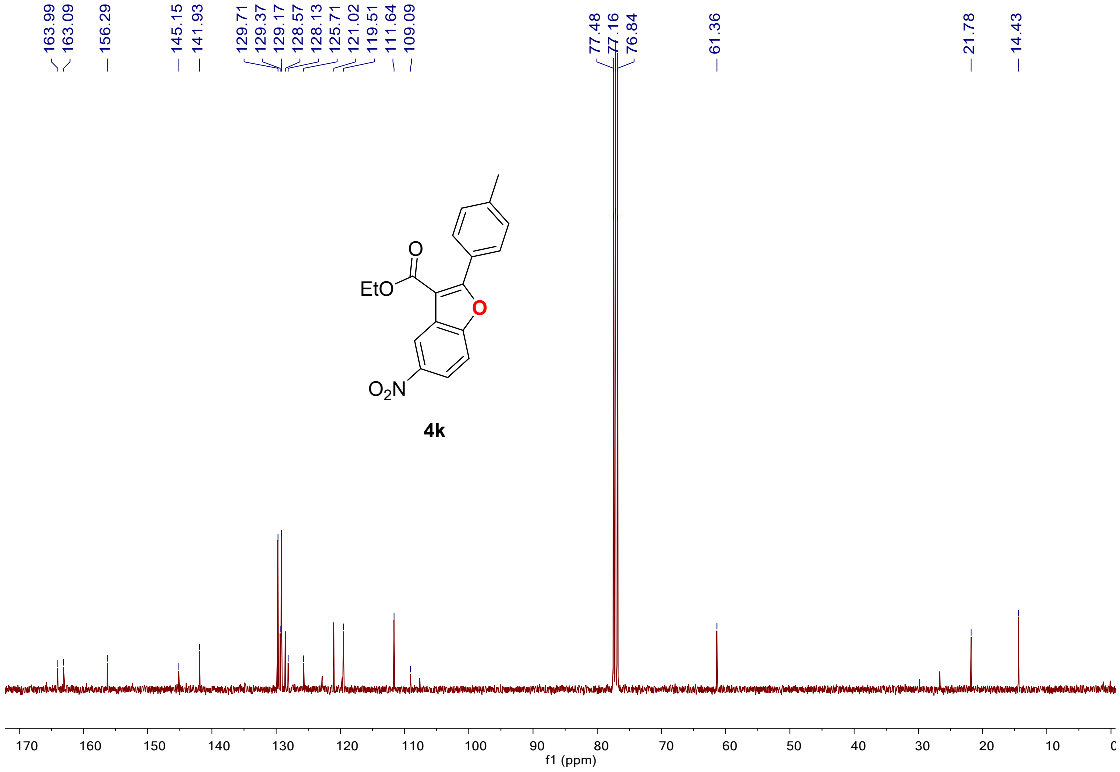

171.41
163.37
156.39
145.09
127.12
120.44
118.72
111.46
109.18
77.37
77.16
76.95
61.04
21.96
14.54
11.99
EtO
O
Et
O
O_2N
4i
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.980
8.301
8.279
7.877
7.861
7.627
7.604
7.435
7.415
7.400
7.395
7.362
7.344
4.493
4.475
4.457
4.439
2.464
1.472
1.455
1.437
EtO
O
O
O_2N
4j
1.00
1.01
2.01
1.01
2.01
2.01
3.02
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

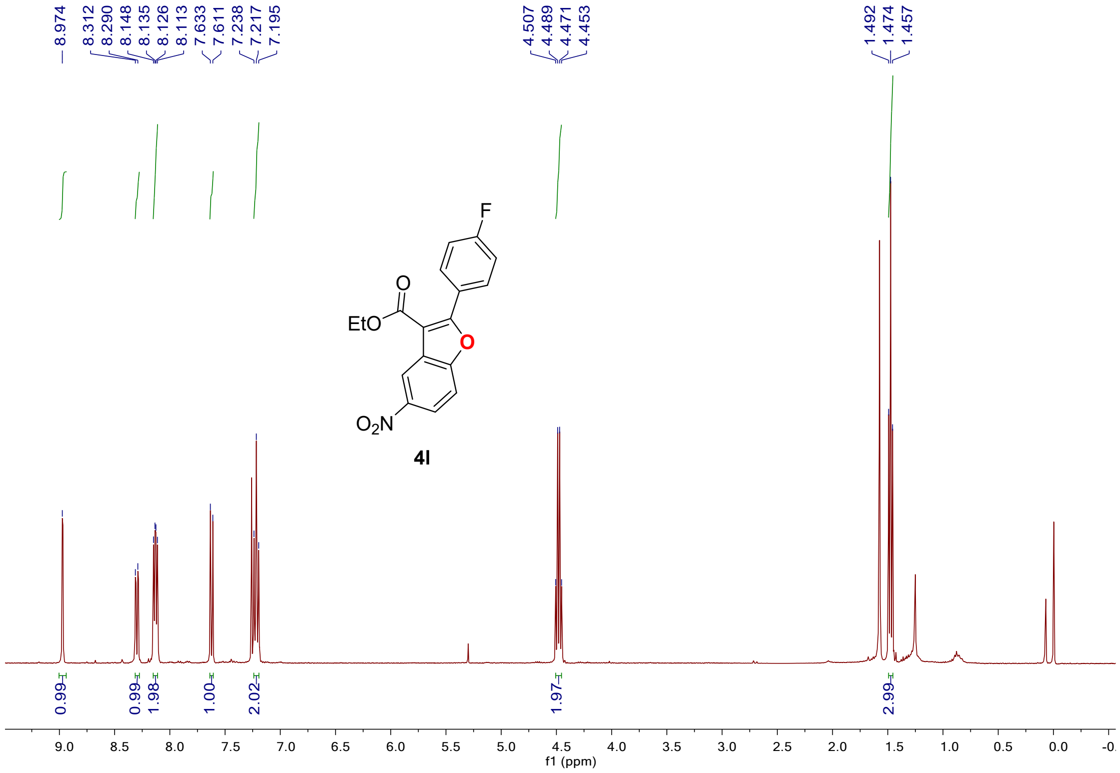

163.86
163.00
156.36
145.19
138.16
132.13
130.23
128.49
128.34
128.09
127.05
121.12
119.57
111.70
109.53
77.48
77.16
76.84
61.37
21.59
14.38
EtO
O
O
O_2N
4j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

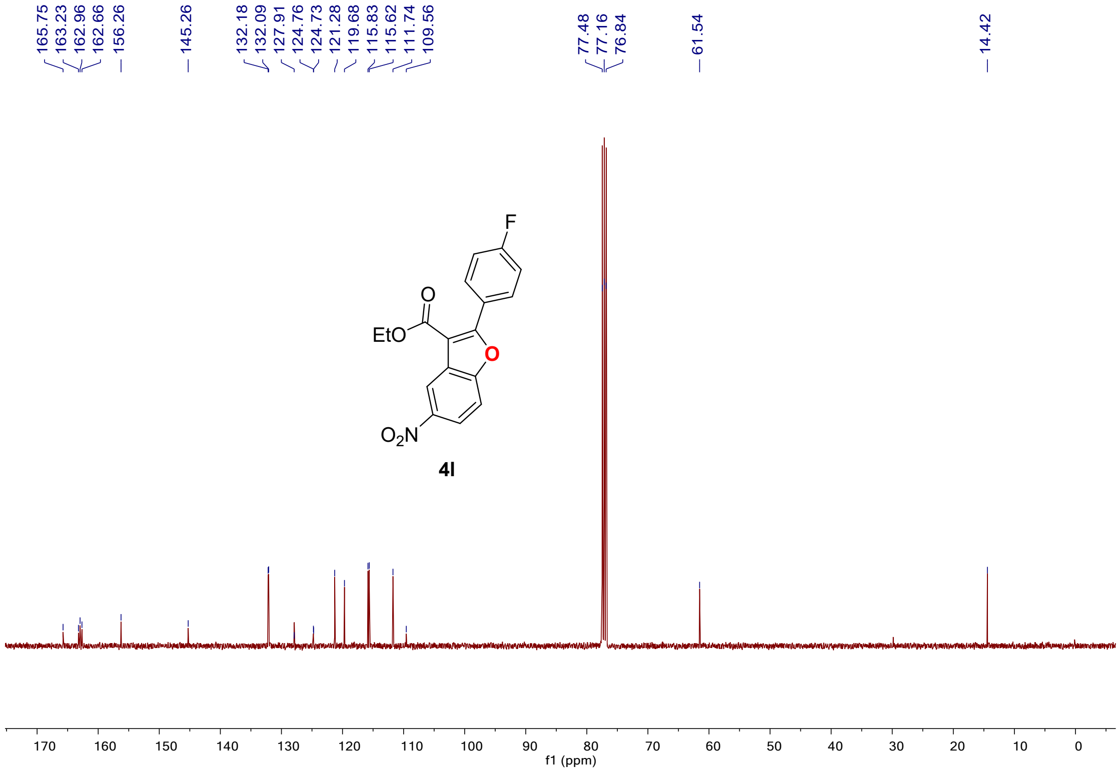

8.963
8.291
8.268
7.994
7.973
7.616
7.594
7.340
7.320
4.497
4.480
4.462
4.444
2.451
1.484
1.466
1.448
EtO
O
O
O$_2$N
1.00
1.02
2.00
1.01
2.00
2.01
3.01
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

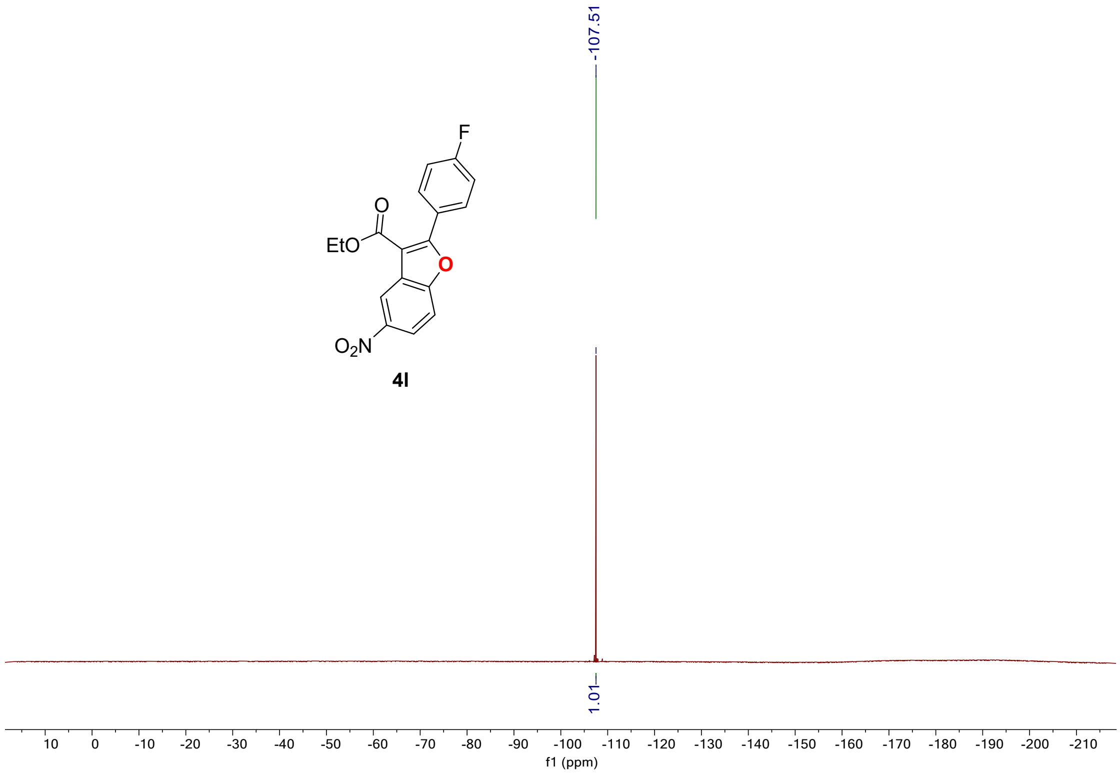
4k

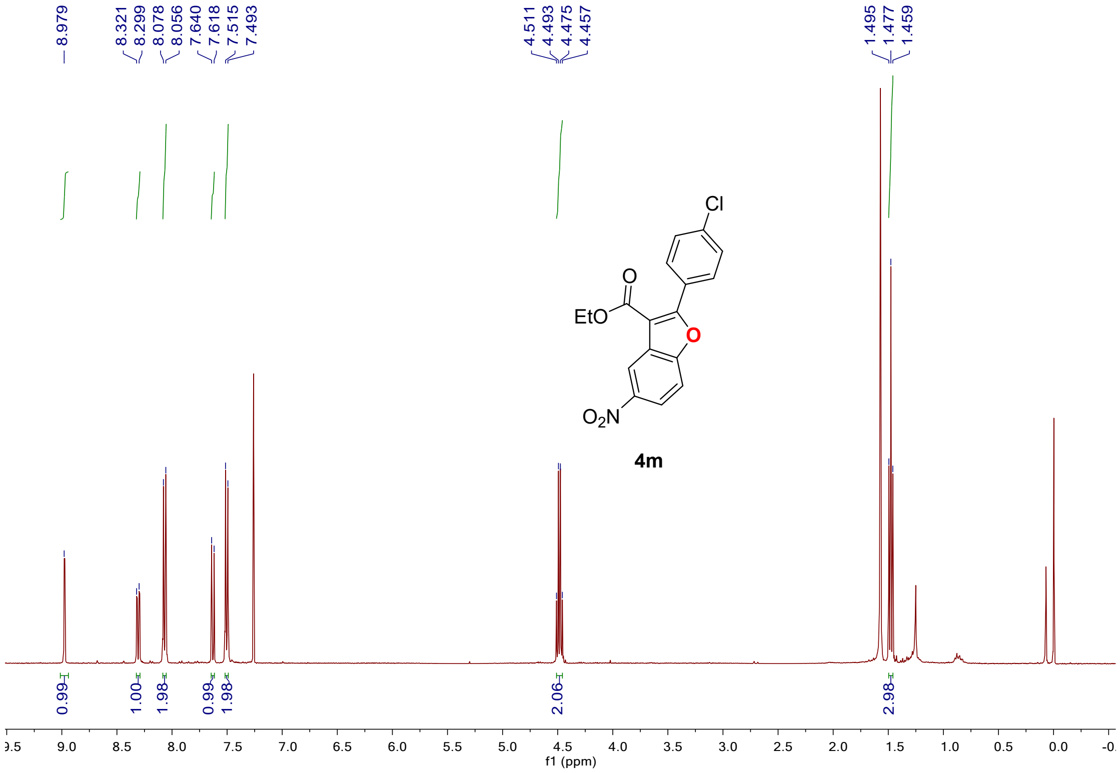

163.99
163.09
156.29
145.15
141.93
129.71
129.37
129.17
128.57
128.13
125.71
121.02
119.51
111.64
109.09
77.48
77.16
76.84
61.36
21.78
14.43
EtO
O
O
O$_2$N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

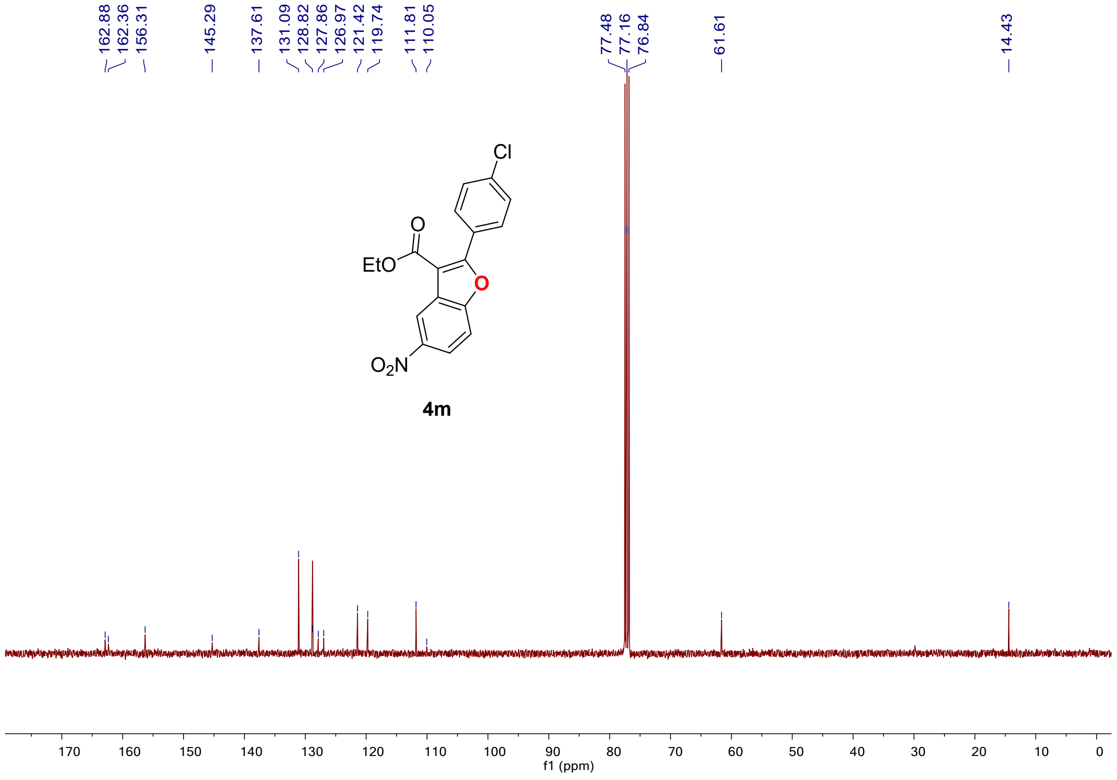
4k

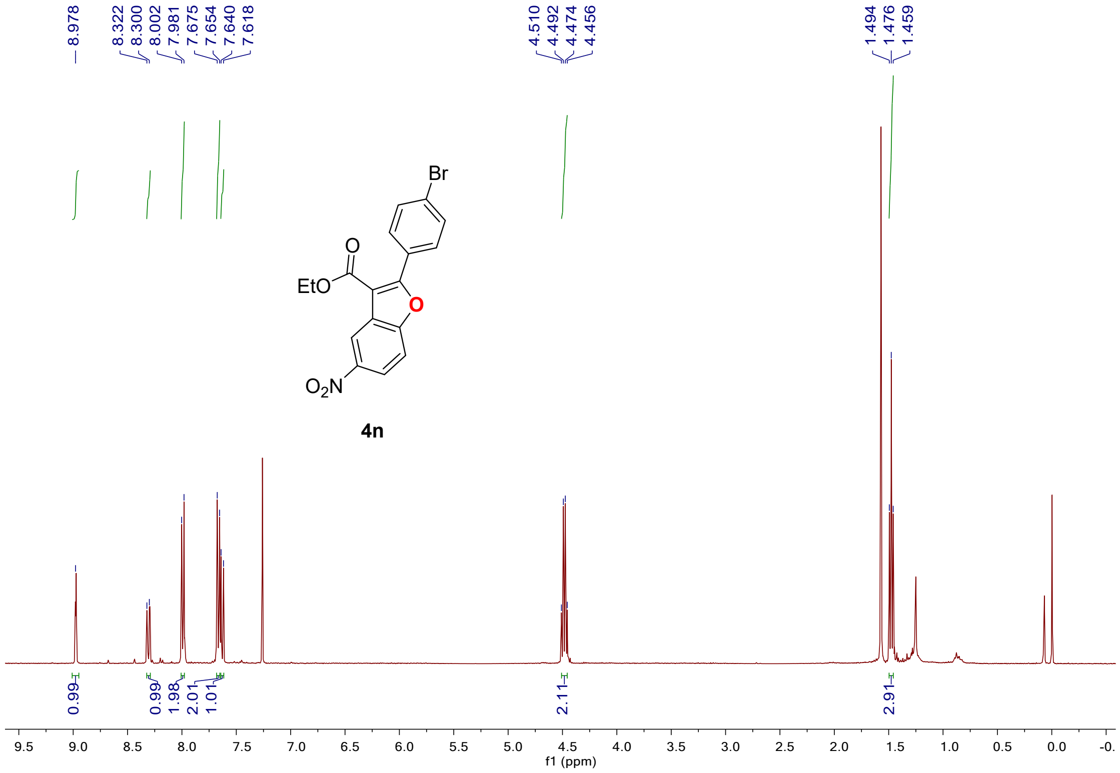

8.974
8.312
8.290
8.148
8.135
8.126
8.113
7.633
7.611
7.238
7.217
7.195
4.507
4.489
4.471
4.453
1.492
1.474
1.457
EtO
O
F
O
O_2N
4l
0.99
0.99
1.98
1.00
2.02
1.97
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

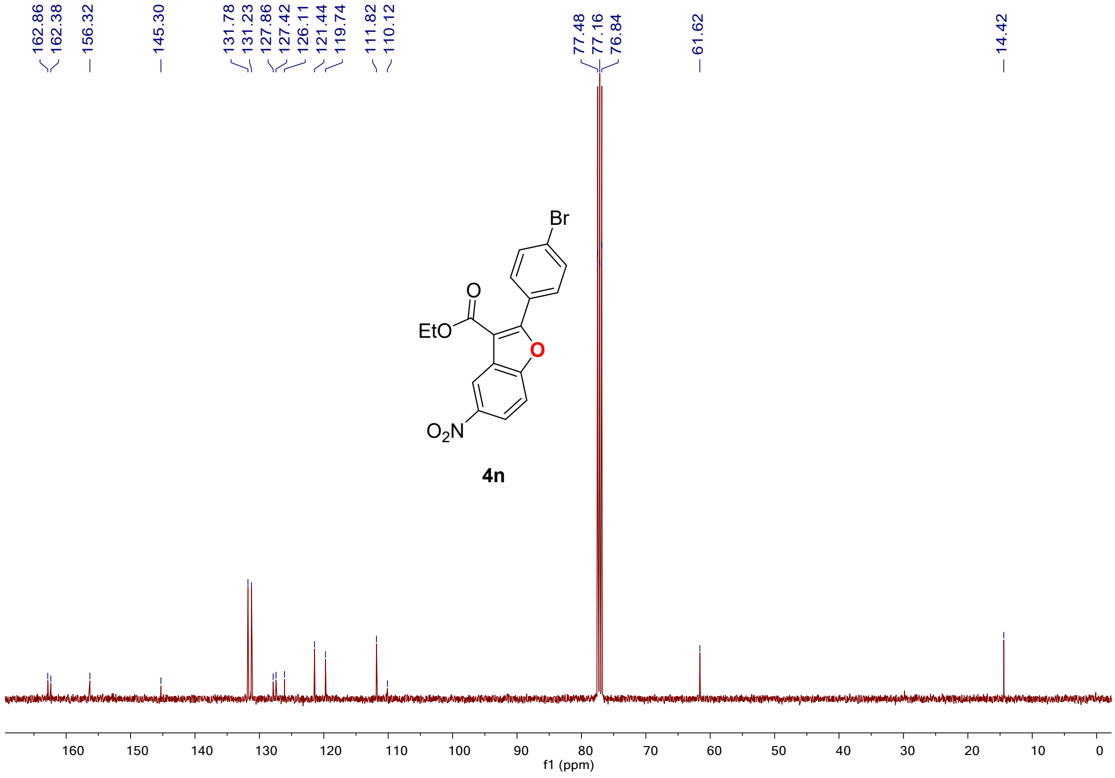

165.75
163.23
162.96
162.66
156.26
145.26
132.18
132.09
127.91
124.76
124.73
121.28
119.68
115.83
115.62
111.74
109.56
77.48
77.16
76.84
61.54
14.42
EtO
O
F
O
O_2N
4l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

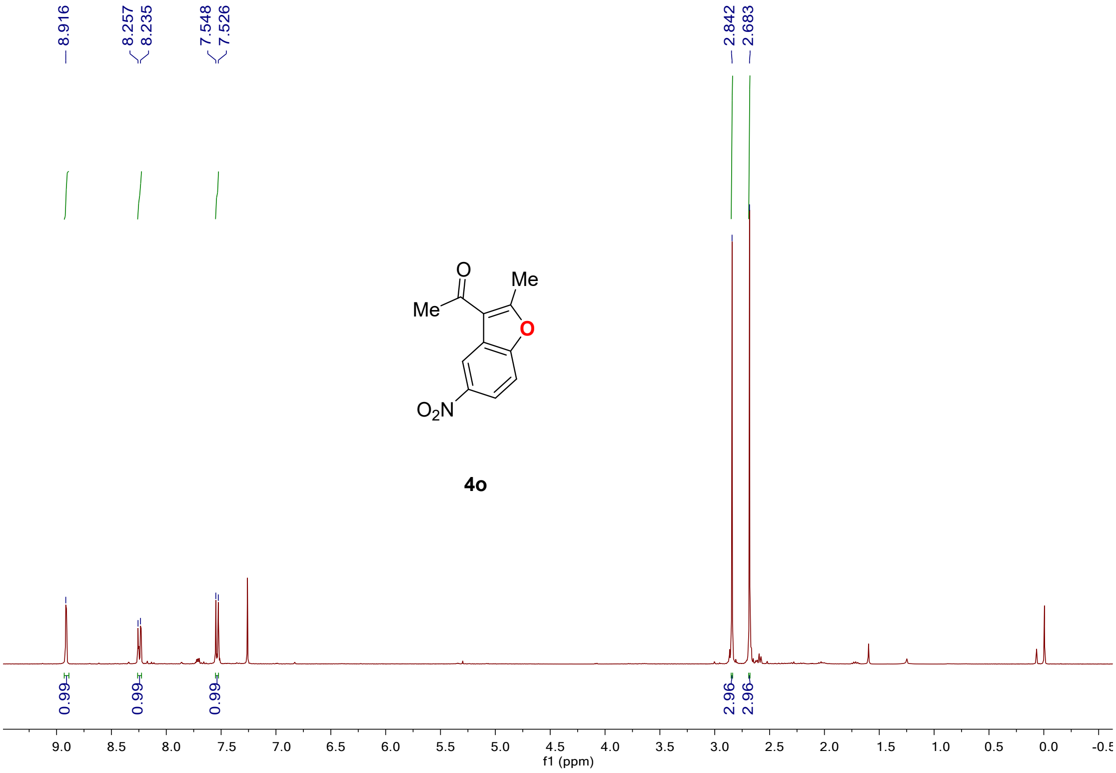

-107.51
F
O
EtO
O
O_2N
4l
1.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.979
8.321
8.299
8.078
8.056
7.640
7.618
7.515
7.493
4.511
4.493
4.475
4.457
1.495
1.477
1.459
Cl
O
EtO
O
O_2N
4m
0.99
1.00
1.98
0.99
1.98
2.06
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

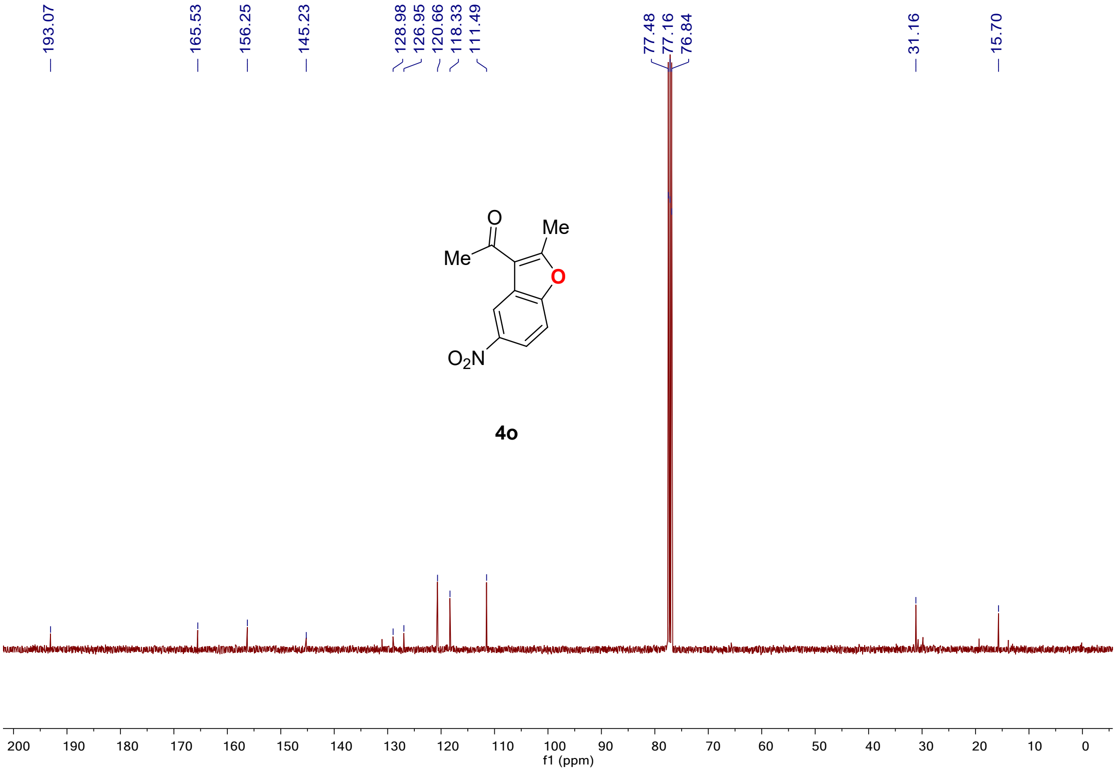

162.88
162.36
156.31
145.29
137.61
131.09
128.82
127.86
126.97
121.42
119.74
111.81
110.05
77.48
77.16
76.84
61.61
14.43
Cl
O
EtO
O
O_2N
4m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.978
8.322
8.300
8.002
7.981
7.675
7.654
7.640
7.618
4.510
4.492
4.474
4.456
1.494
1.476
1.459
Br
O
EtO
O
O_2N
4n
0.99
0.99
1.98
2.01
1.01
2.11
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

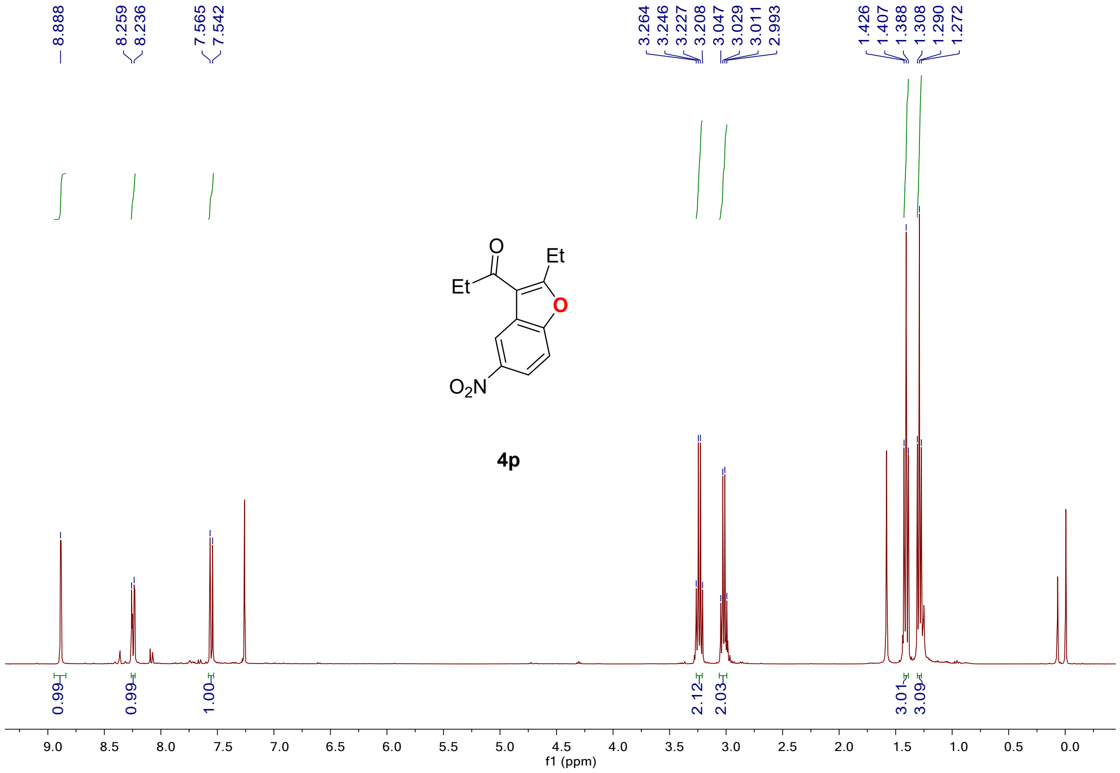

162.86
162.38
156.32
145.30
131.78
131.23
127.86
127.42
126.11
121.44
119.74
111.82
110.12
77.48
77.16
76.84
61.62
14.42
Br
O
EtO
O
O_2N
4n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

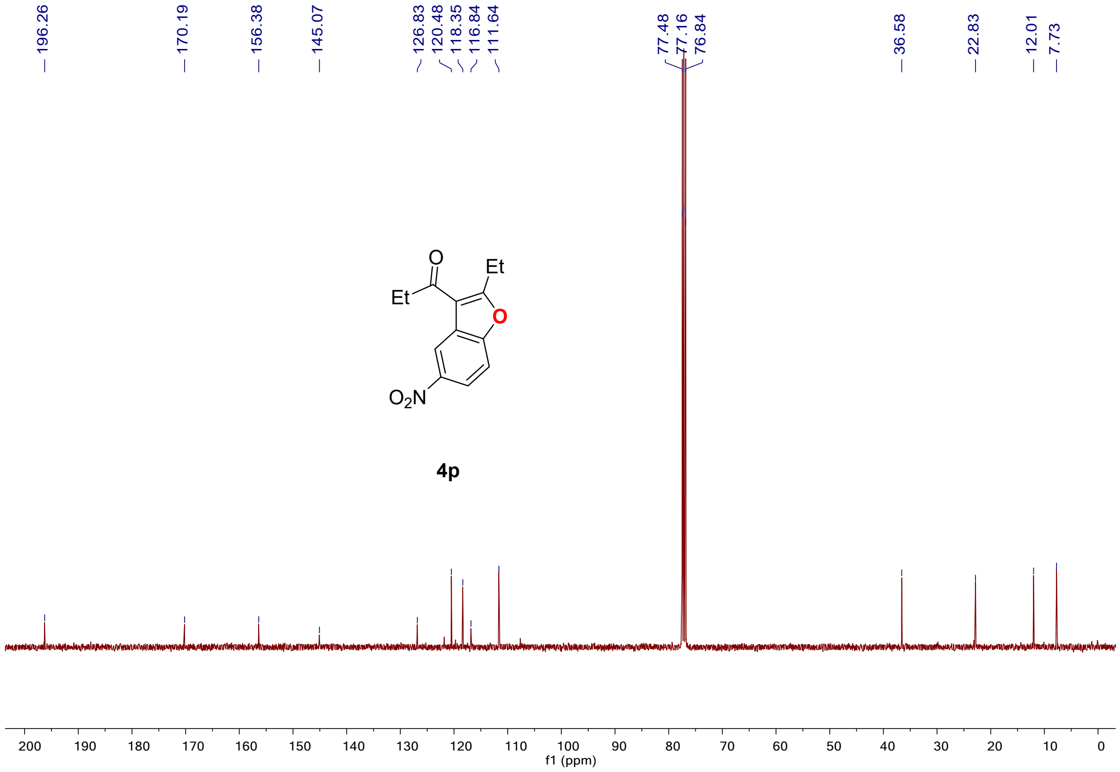

8.916
8.257
8.235
7.548
7.526
2.842
2.683
0.99
0.99
0.99
2.96
2.96
Me
O
Me
O
O_2N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

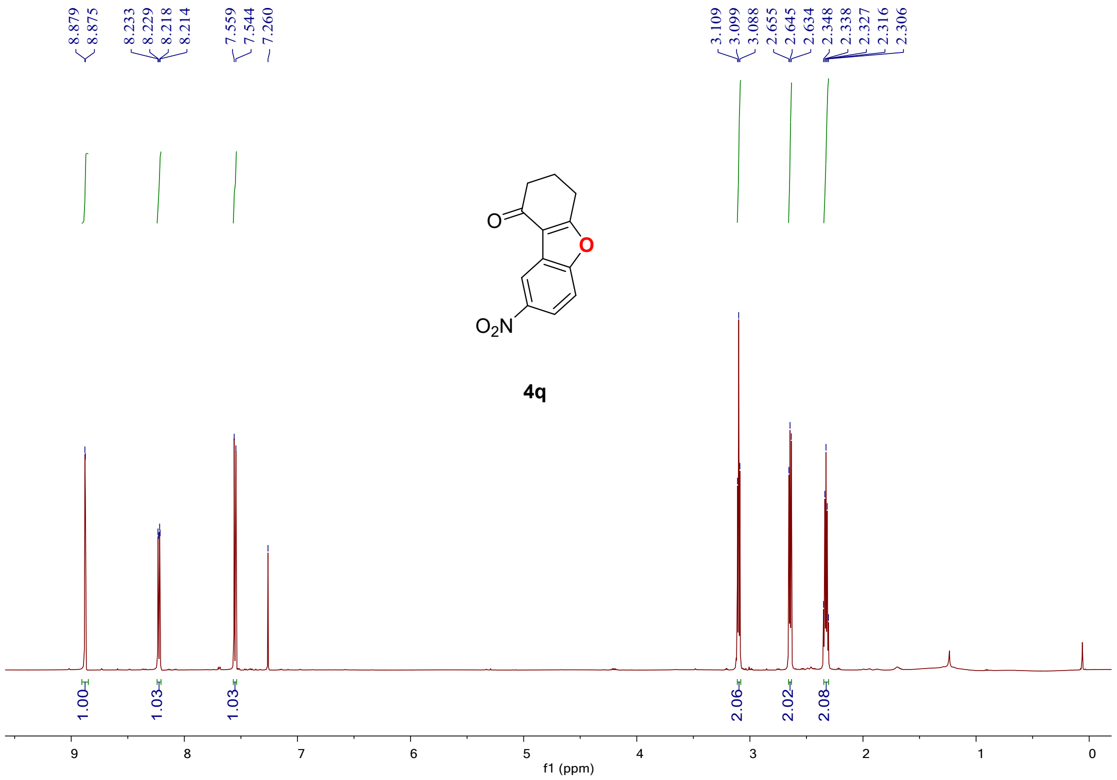
4o

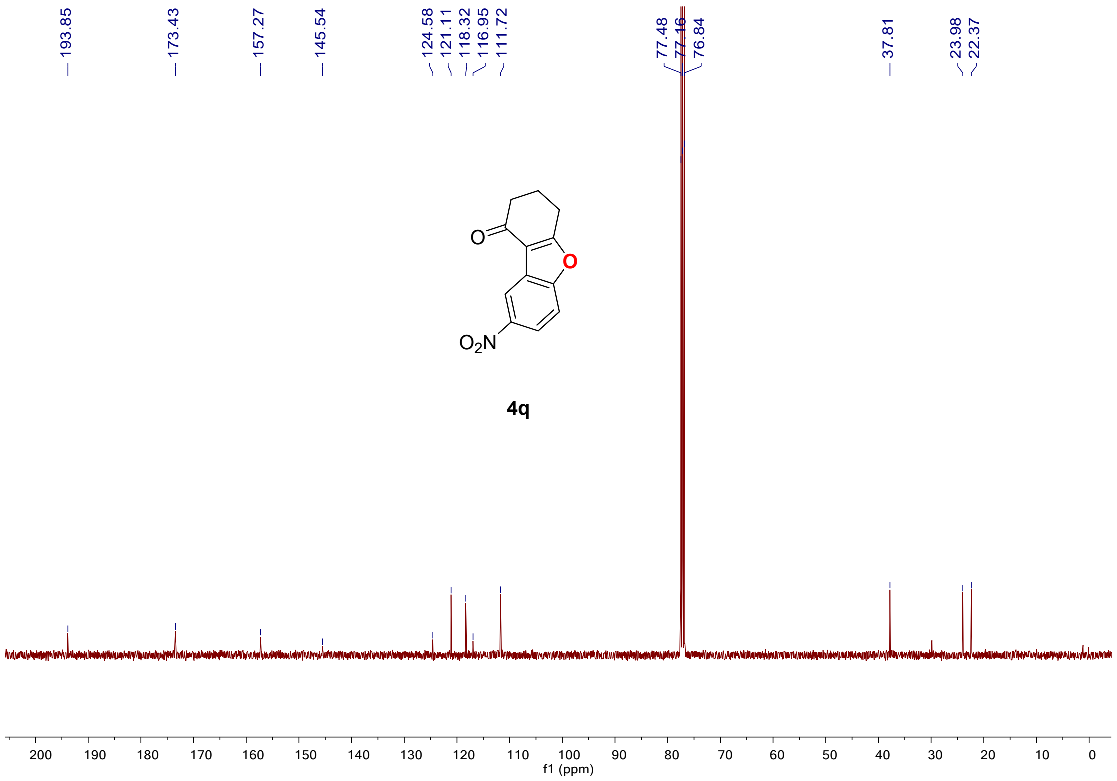

193.07
165.53
156.25
145.23
128.98
126.95
120.66
118.33
111.49
77.48
77.16
76.84
31.16
15.70
Me
O
Me
O
O_2N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

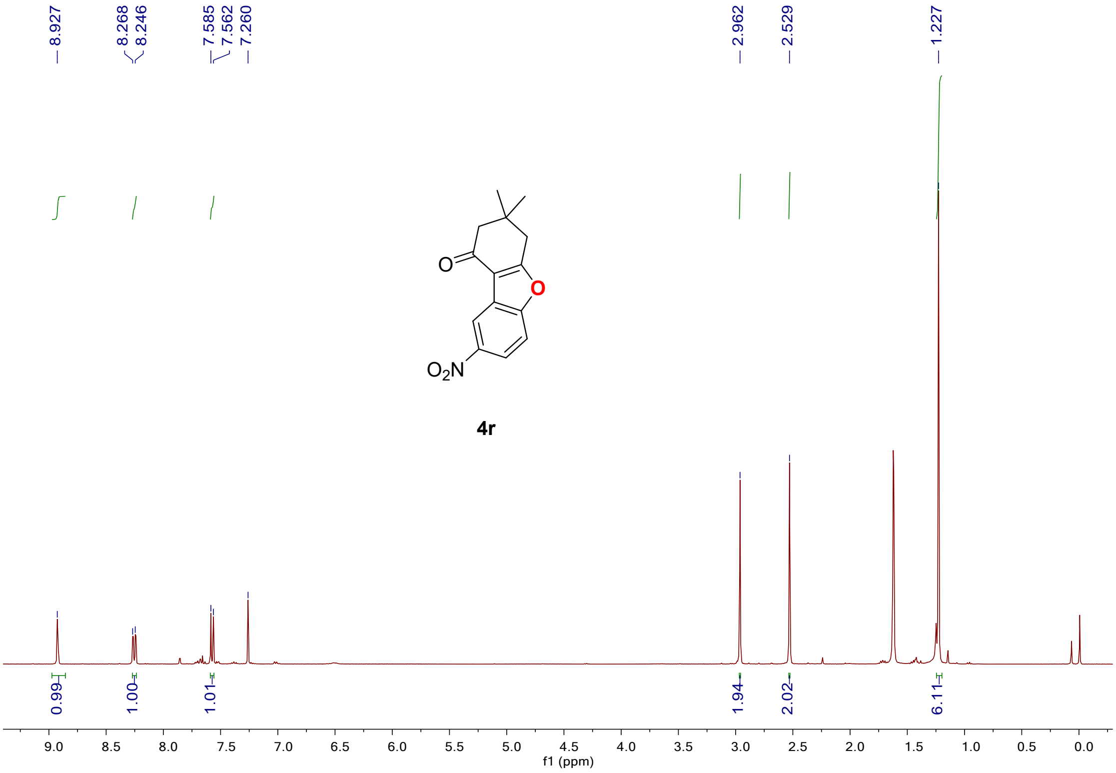
4o

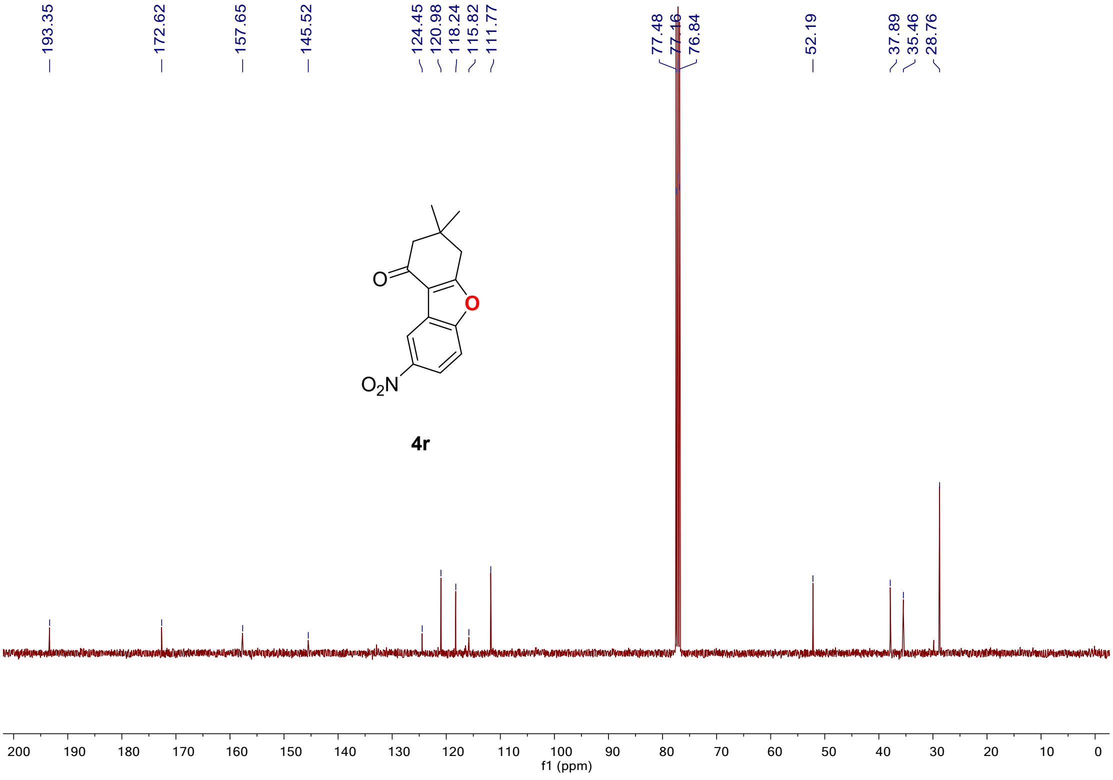

8.888
8.259
8.236
7.565
7.542
3.264
3.246
3.227
3.208
3.047
3.029
3.011
2.993
1.426
1.407
1.388
1.308
1.290
1.272
O
Et
Et
O
O2N
4p
0.99
0.99
1.00
2.12
2.03
3.01
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

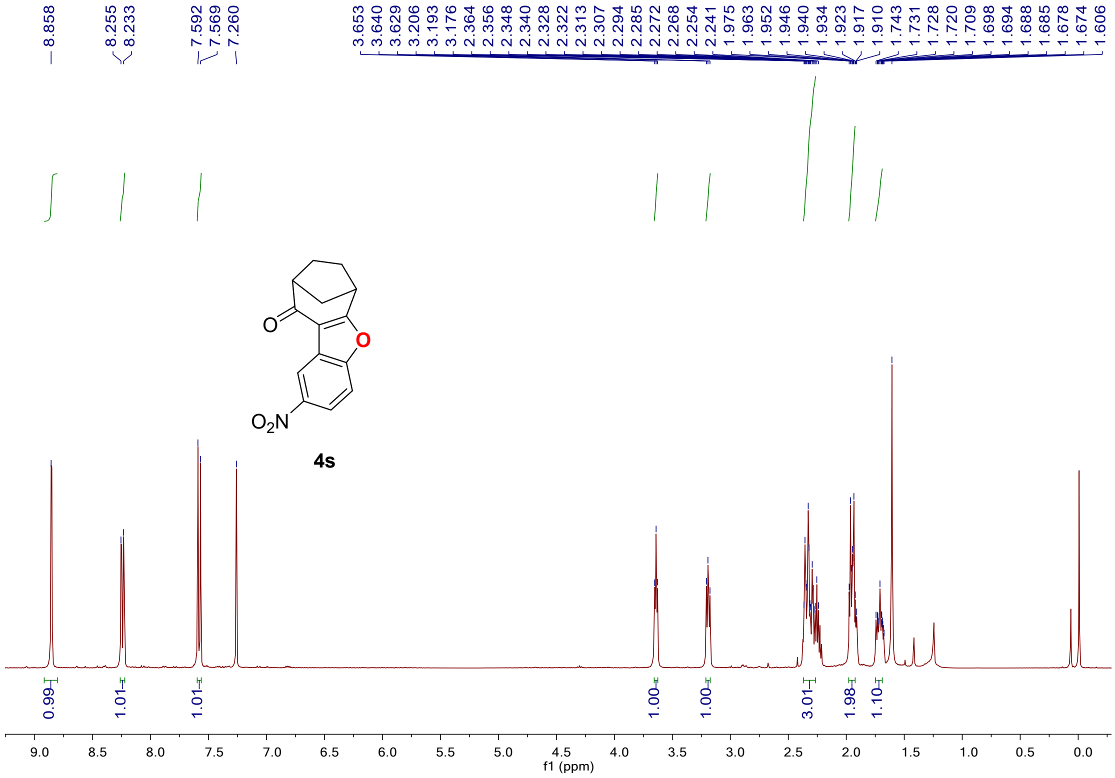

196.26
170.19
156.38
145.07
126.83
120.48
118.35
116.84
111.64
77.48
77.16
76.84
36.58
22.83
12.01
7.73
O
Et
Et
O
O2N
4p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

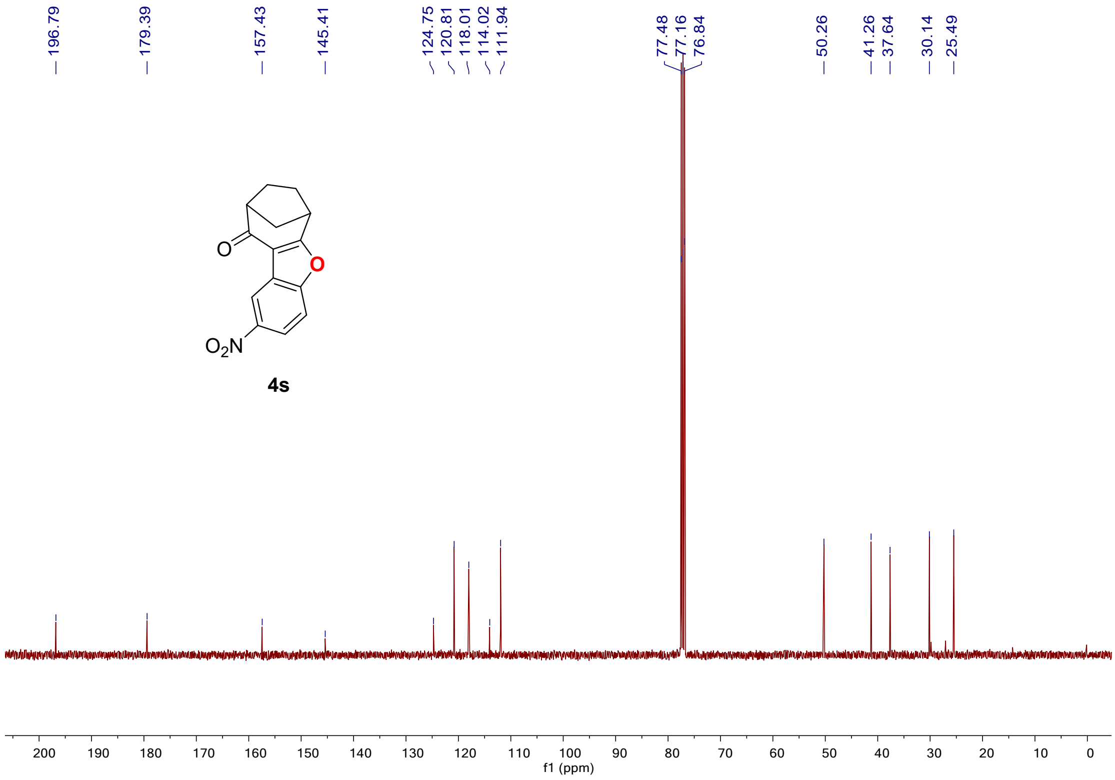

8.879
8.875
8.233
8.229
8.218
8.214
7.559
7.544
7.260
3.109
3.099
3.088
2.655
2.645
2.634
2.348
2.338
2.327
2.316
2.306
O
O
O_2N
4q
1.00
1.03
1.03
2.06
2.02
2.08
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

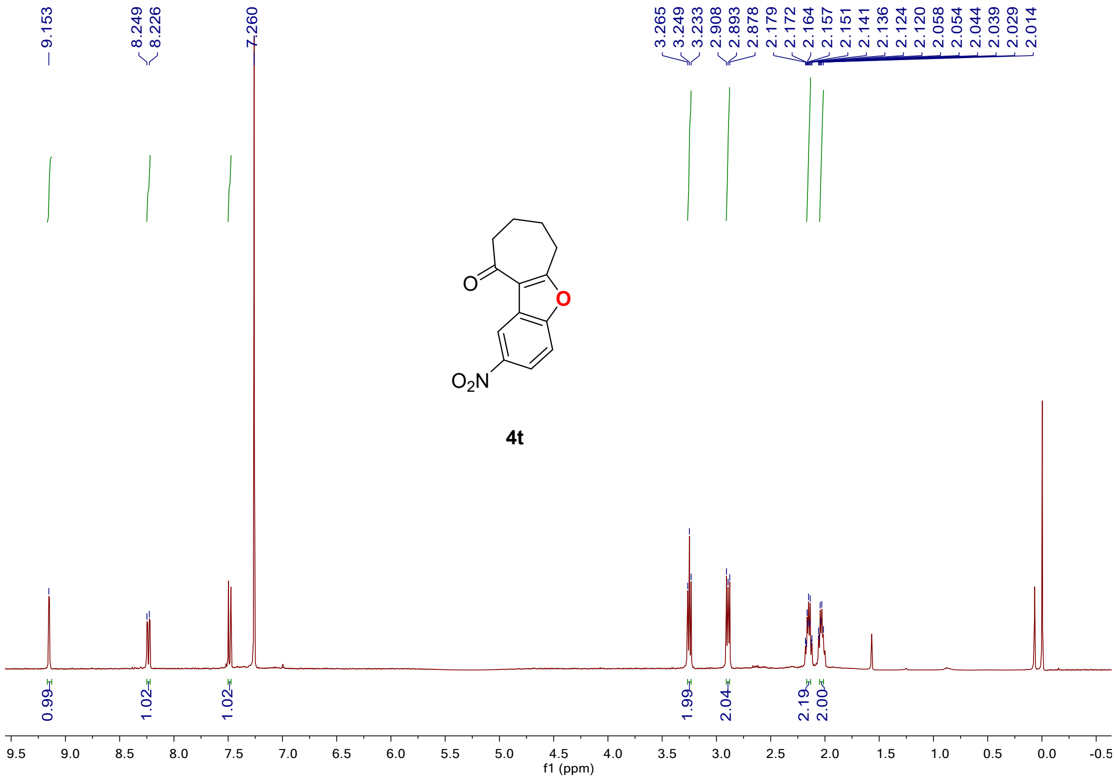

193.85
173.43
157.27
145.54
124.58
121.11
118.32
116.95
111.72
77.48
77.16
76.84
37.81
23.98
22.37
O
O
O_2N
4q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

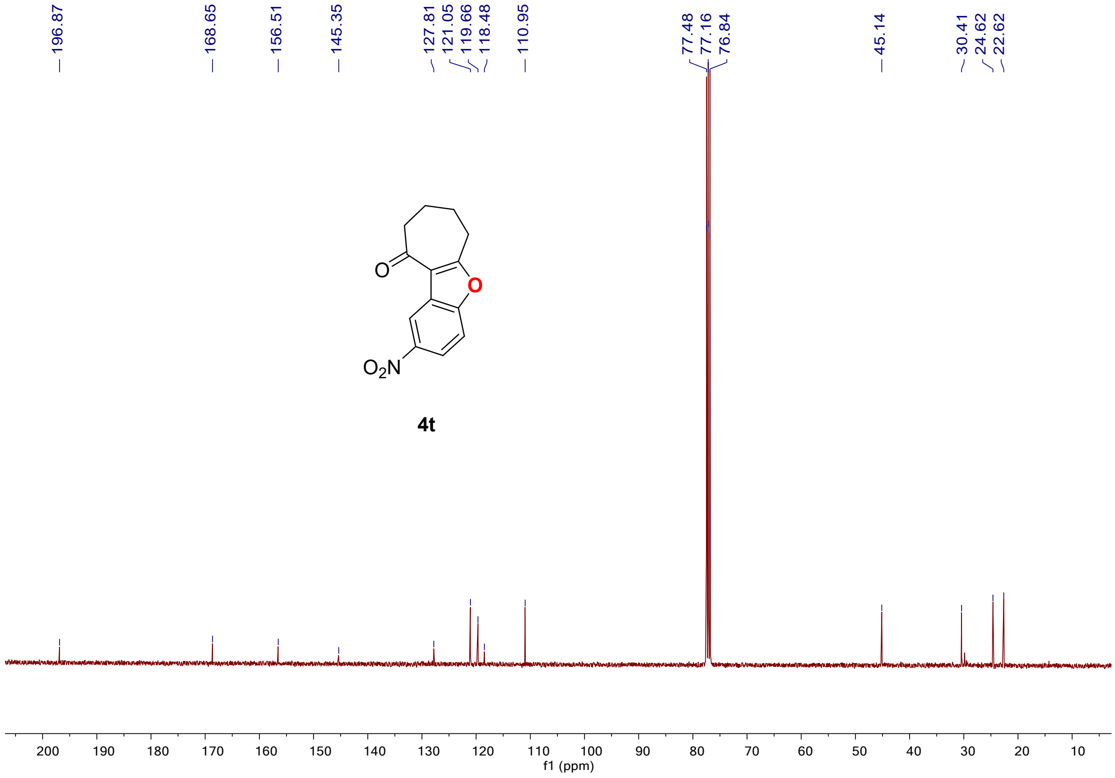

8.927
8.268
8.246
7.585
7.562
7.260
2.962
2.529
1.227
O
O
O2N
4r
0.99
1.00
1.01
1.94
2.02
6.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

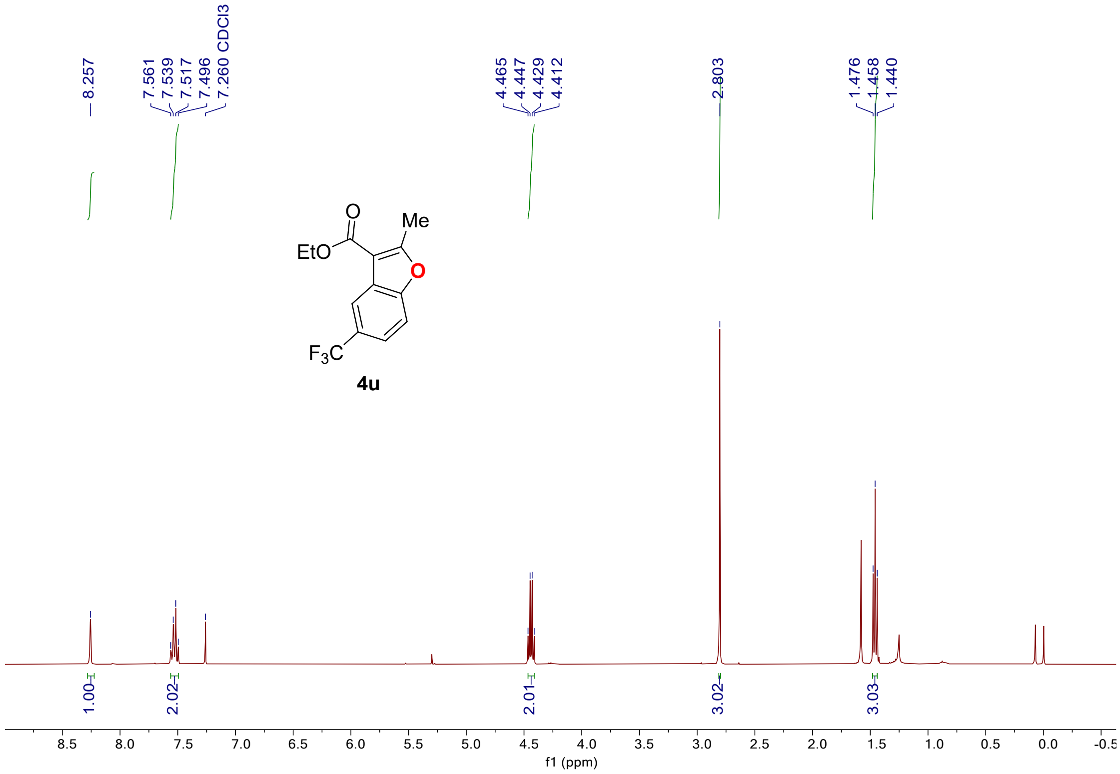

193.35
172.62
157.65
145.52
124.45
120.98
118.24
115.82
111.77
77.48
77.16
76.84
52.19
37.89
35.46
28.76
O
O
O2N
4r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

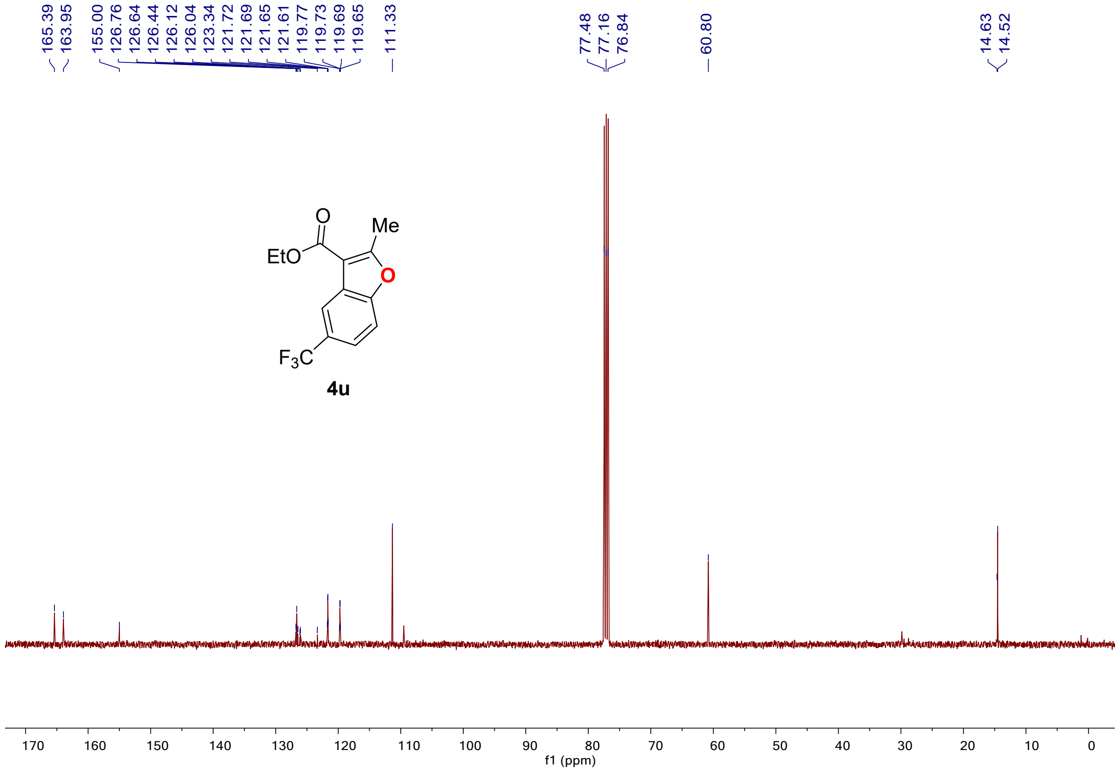

8.858
8.255
8.233
7.592
7.569
7.260
3.653
3.640
3.629
3.206
3.193
3.176
2.364
2.356
2.348
2.340
2.328
2.322
2.313
2.307
2.294
2.285
2.272
2.268
2.254
2.241
1.975
1.963
1.952
1.946
1.940
1.934
1.923
1.917
1.910
1.743
1.731
1.728
1.720
1.709
1.698
1.694
1.688
1.685
1.678
1.674
1.606
O
O
O_2N
4s
0.99
1.01
1.01
1.00
1.00
3.01
1.98
1.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

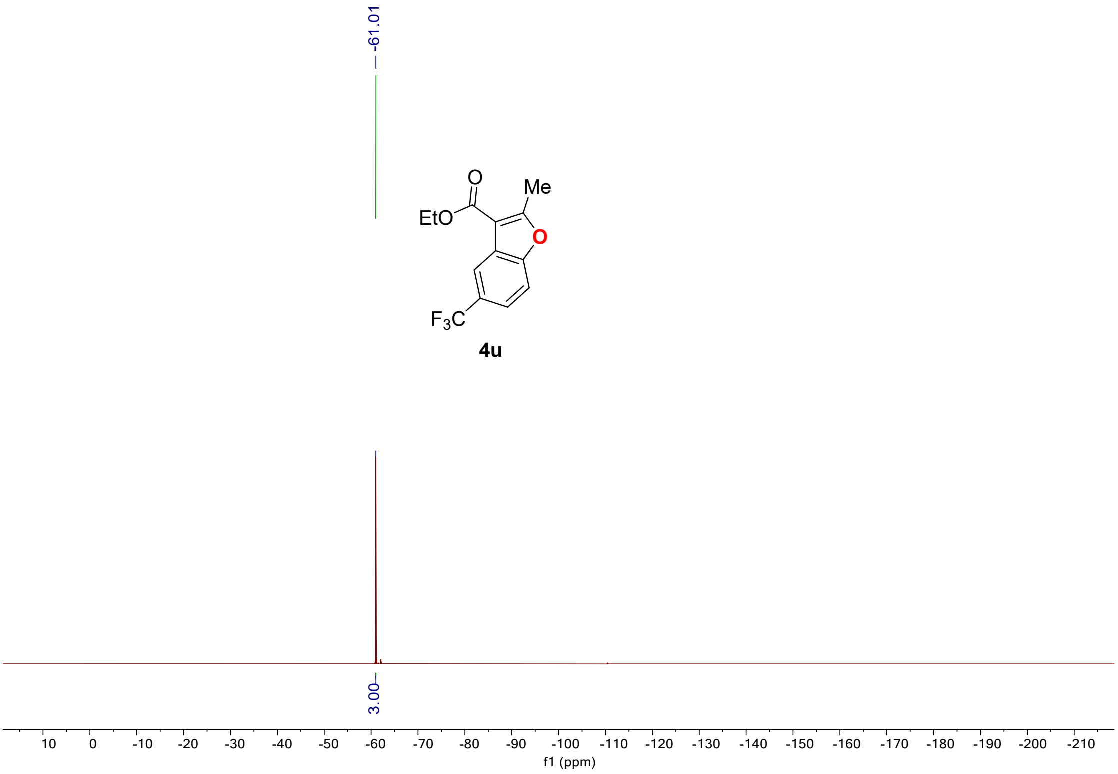

196.79
179.39
157.43
145.41
124.75
120.81
118.01
114.02
111.94
77.48
77.16
76.84
50.26
41.26
37.64
30.14
25.49
O
O
O_2N
4s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.153
8.249
8.226
7.260
3.265
3.249
3.233
2.908
2.893
2.878
2.179
2.172
2.164
2.157
2.151
2.141
2.136
2.124
2.120
2.058
2.054
2.044
2.039
2.029
2.014
O
O
O_2N
4t
0.99
1.02
1.02
1.99
2.04
2.19
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

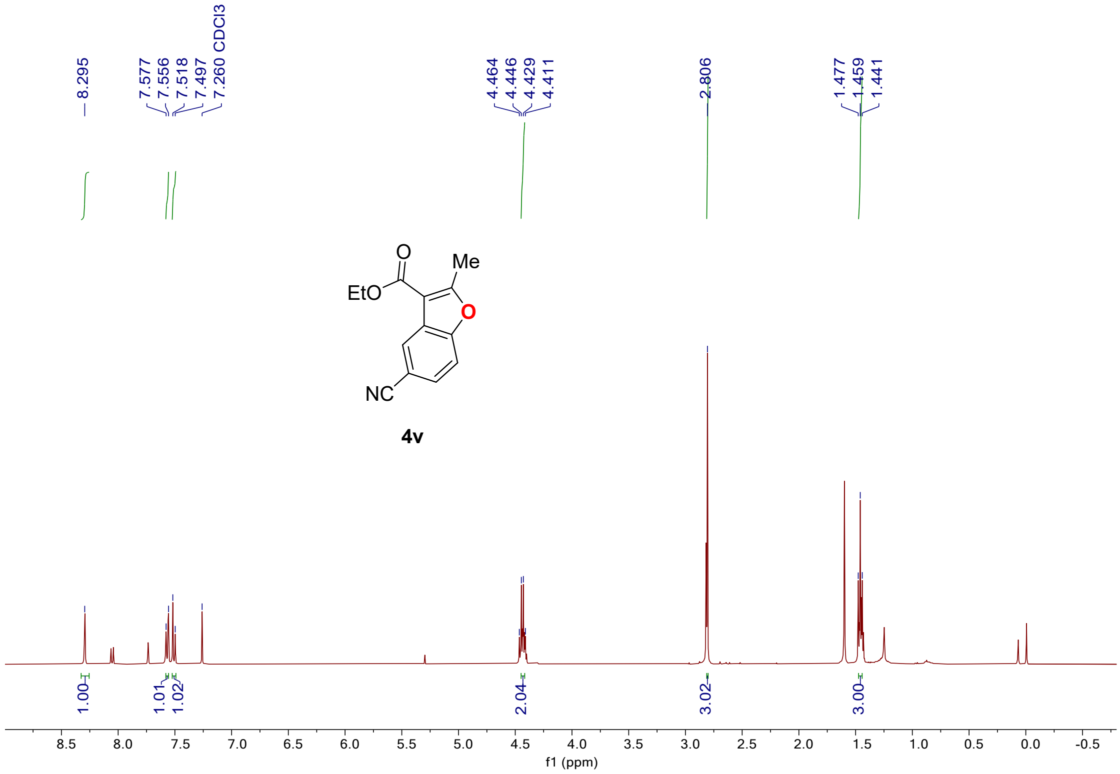

196.87
168.65
156.51
145.35
127.81
121.05
119.66
118.48
110.95
77.48
77.16
76.84
45.14
30.41
24.62
22.62
O
O
O_2N
4t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.257
7.561
7.539
7.517
7.496
7.260 CDCl3
4.465
4.447
4.429
4.412
2.803
1.476
1.458
1.440
EtO
O
Me
O
F3C
4u
1.00
2.02
2.01
3.02
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

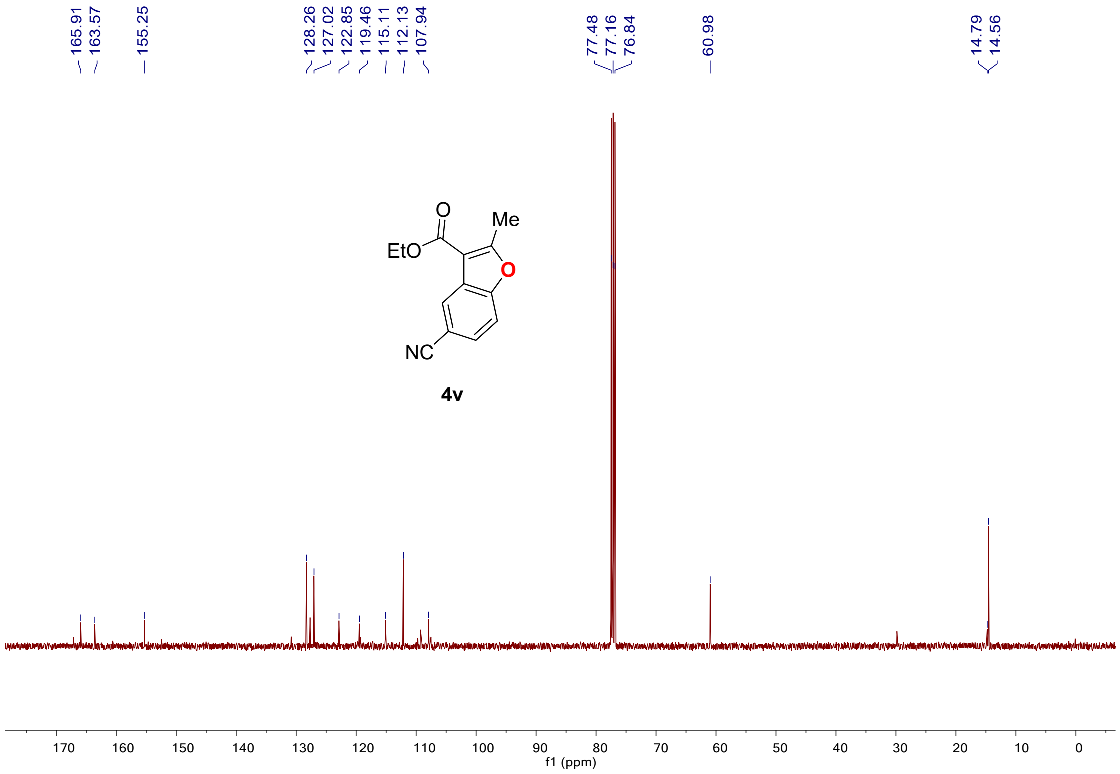

165.39
163.95
155.00
126.76
126.64
126.44
126.12
126.04
123.34
121.72
121.69
121.65
121.61
119.77
119.73
119.69
119.65
111.33
77.48
77.16
76.84
60.80
14.63
14.52
EtO
O
Me
O
F3C
4u
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

-61.01
O
Me
EtO
O
F3C
3.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

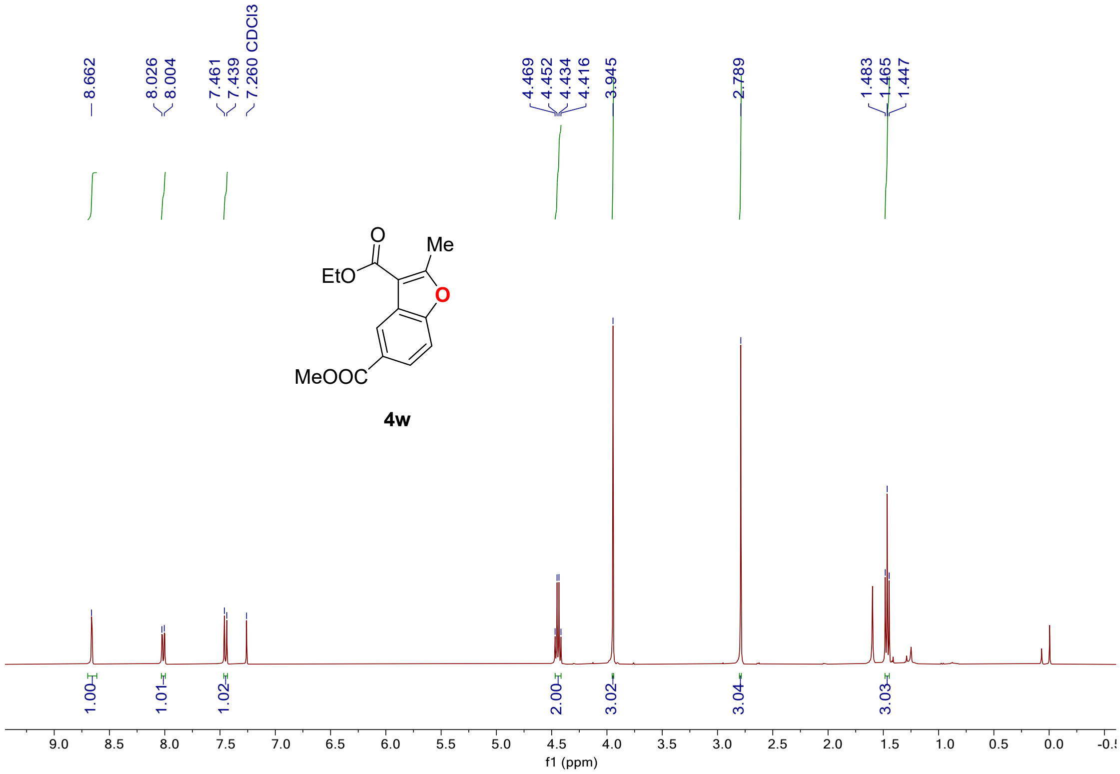
4u

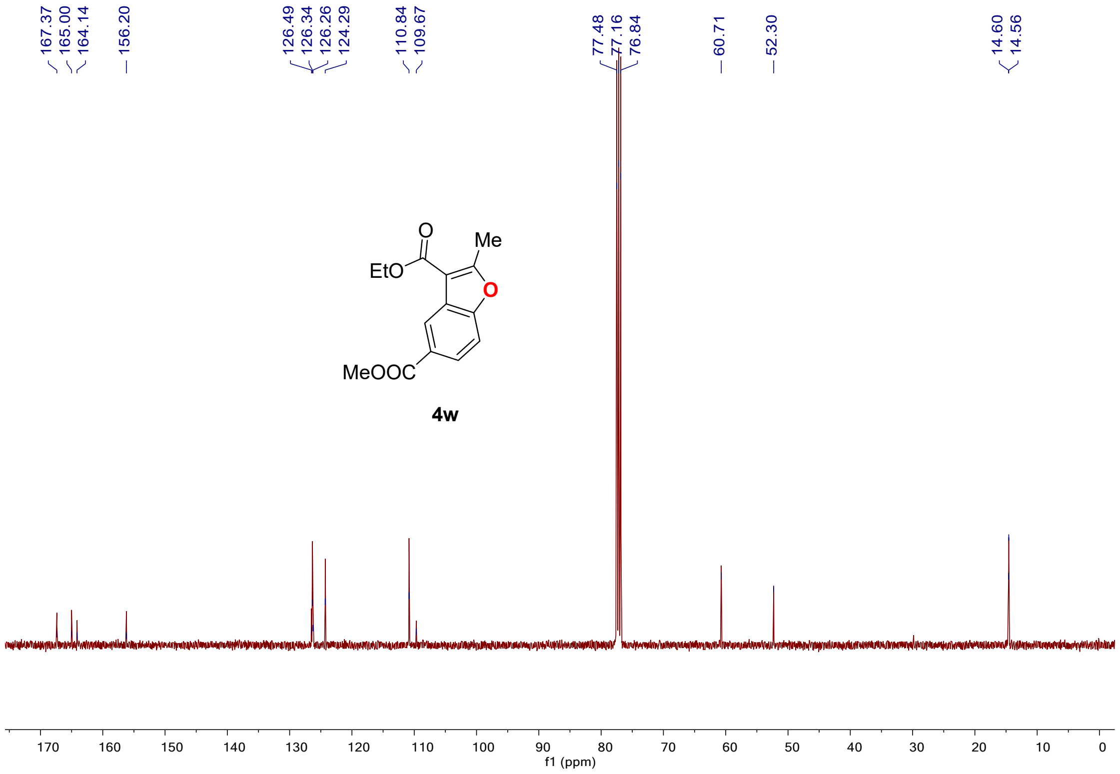

8.295
7.577
7.556
7.518
7.497
7.260 CDCl3
4.464
4.446
4.429
4.411
2.806
1.477
1.459
1.441
EtO
O
Me
O
NC
1.00
1.01
1.02
2.04
3.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

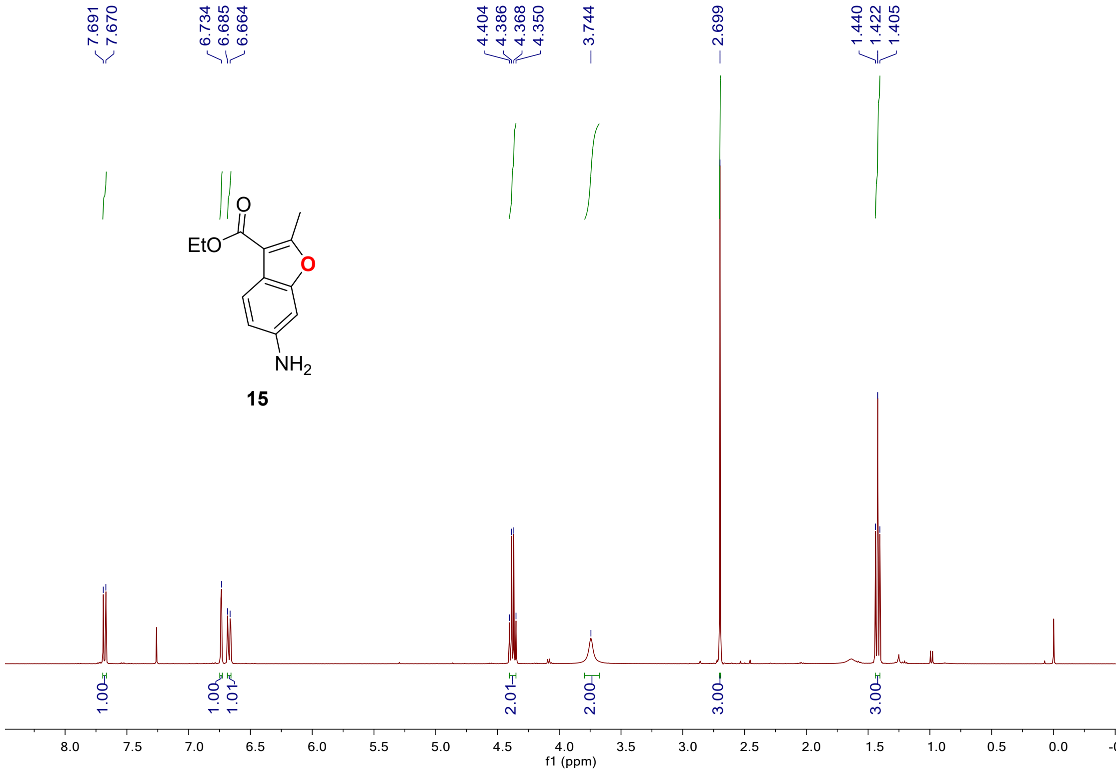
4v

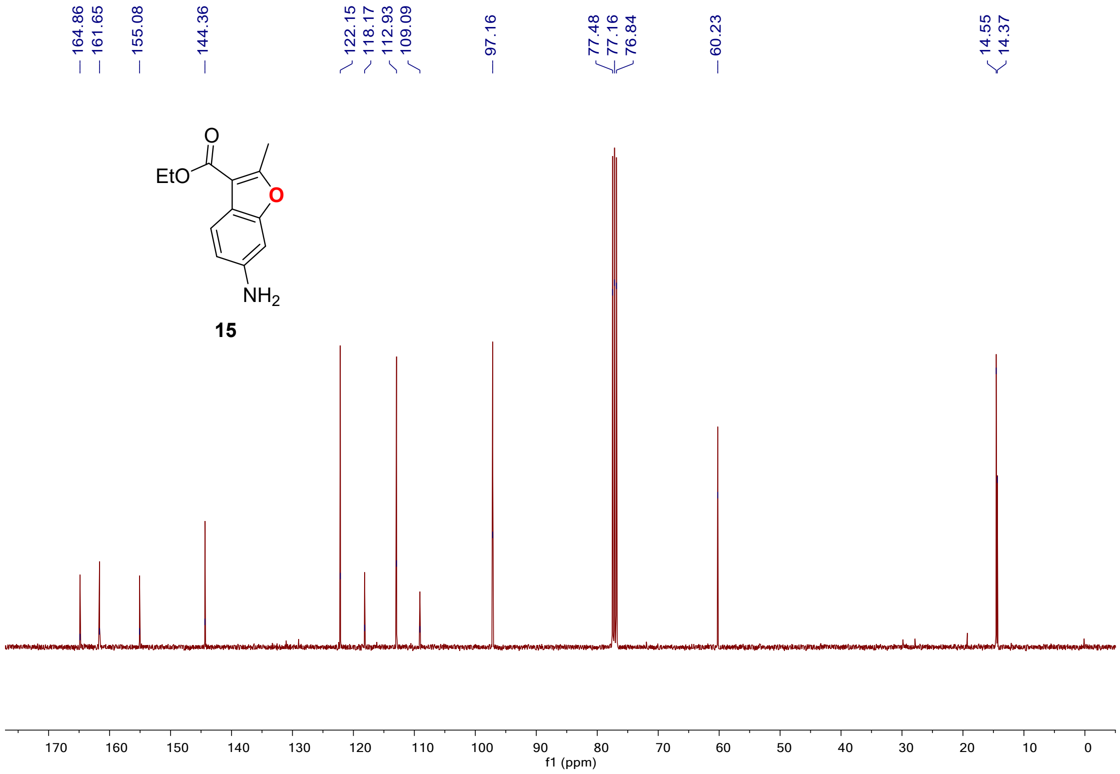

165.91
163.57
155.25
128.26
127.02
122.85
119.46
115.11
112.13
107.94
77.48
77.16
76.84
60.98
14.79
14.56
EtO
O
Me
O
NC
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

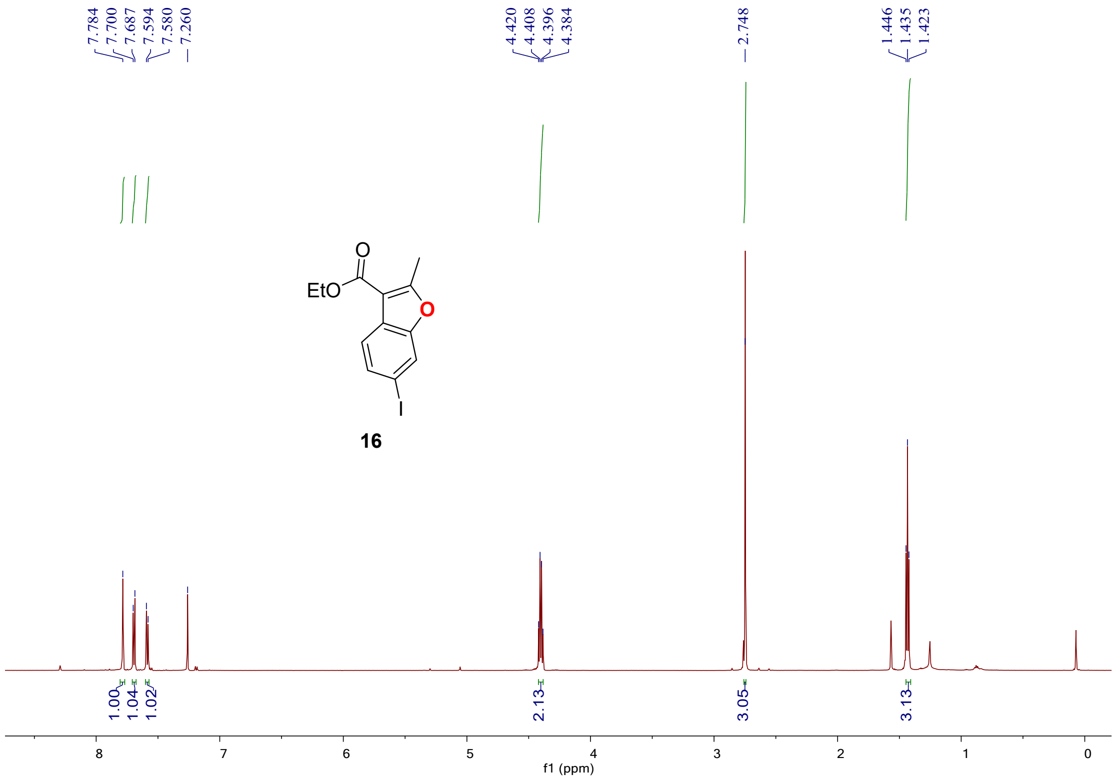
4v


8.662
8.026
8.004
7.461
7.439
7.260 CDCl3
4.469
4.452
4.434
4.416
3.945
2.789
1.483
1.465
1.447
EtO
O
Me
O
MeOOC
4w
1.00
1.01
1.02
2.00
3.02
3.04
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


167.37
165.00
164.14
156.20
126.49
126.34
126.26
124.29
110.84
109.67
77.48
77.16
76.84
60.71
52.30
14.60
14.56
EtO
O
Me
O
MeOOC
4w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

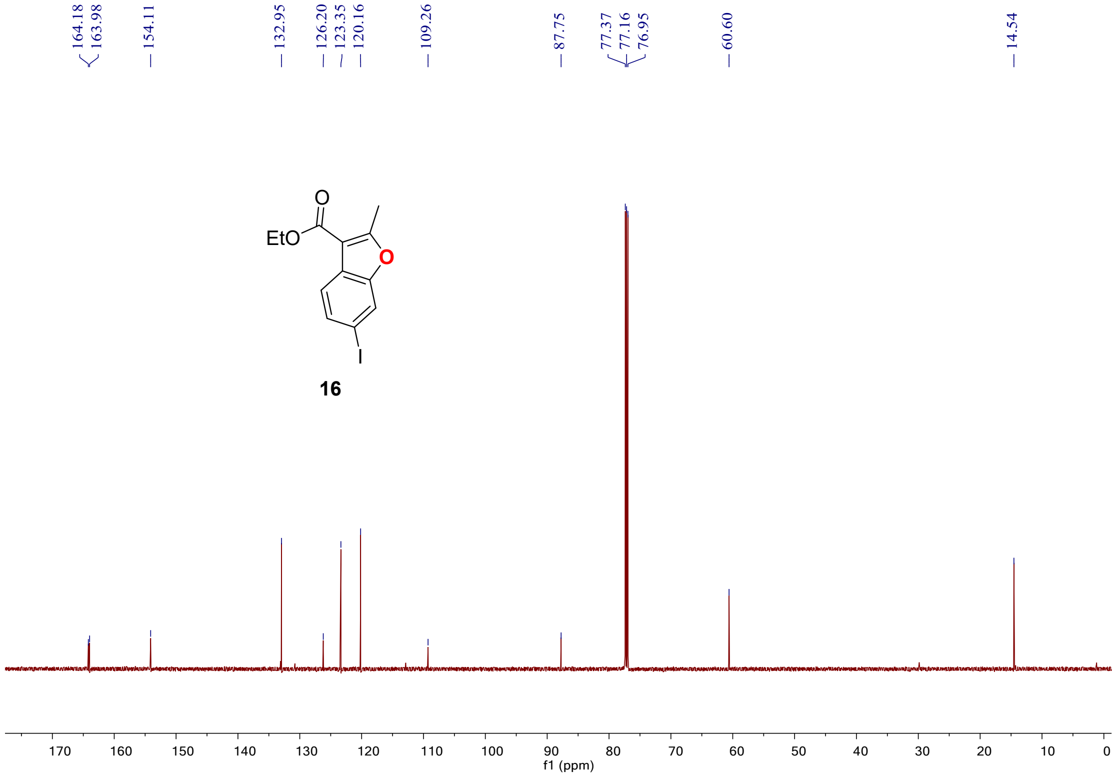

7.691
7.670
6.734
6.685
6.664
4.404
4.386
4.368
4.350
3.744
2.699
1.440
1.422
1.405
EtO
O
O
NH2
15
1.00
1.00
1.01
2.01
2.00
3.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.86
161.65
155.08
144.36
122.15
118.17
112.93
109.09
97.16
77.48
77.16
76.84
60.23
14.55
14.37
EtO
O
O
NH2
15
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



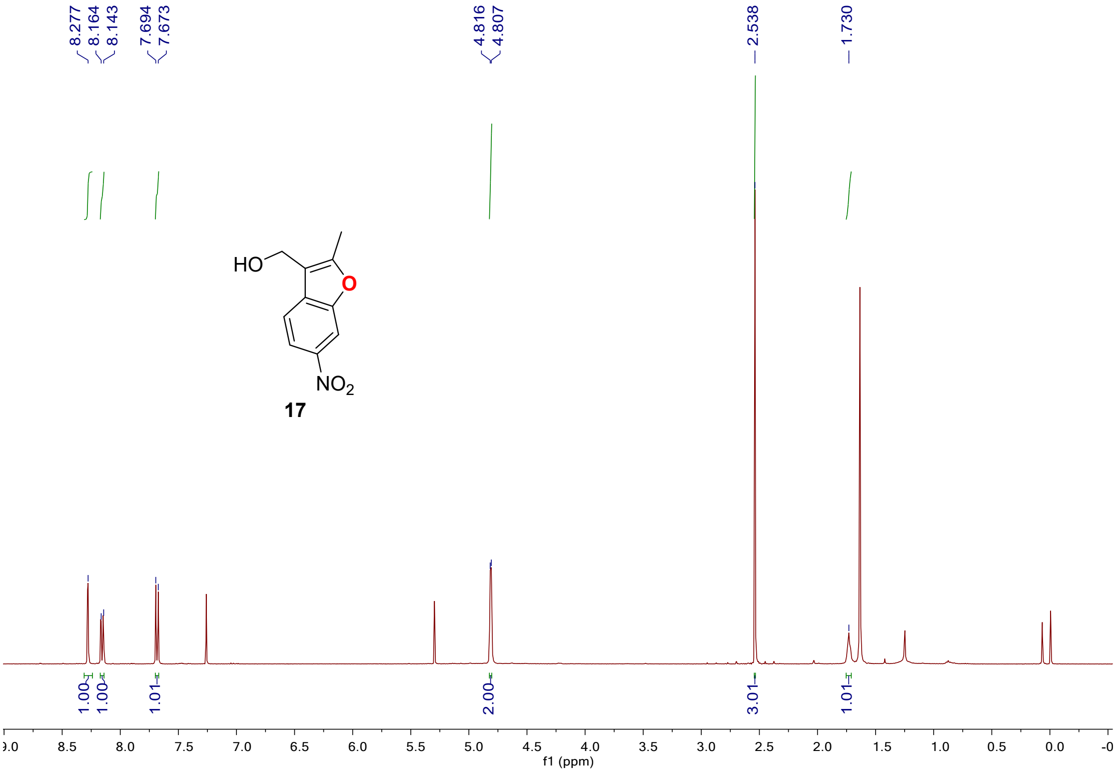
16

7.784
7.700
7.687
7.594
7.580
7.260
4.420
4.408
4.396
4.384
2.748
1.446
1.435
1.423
EtO
O
1.00
1.04
1.02
2.13
3.05
3.13
8
7
6
5
4
3
2
1
0
f1 (ppm)

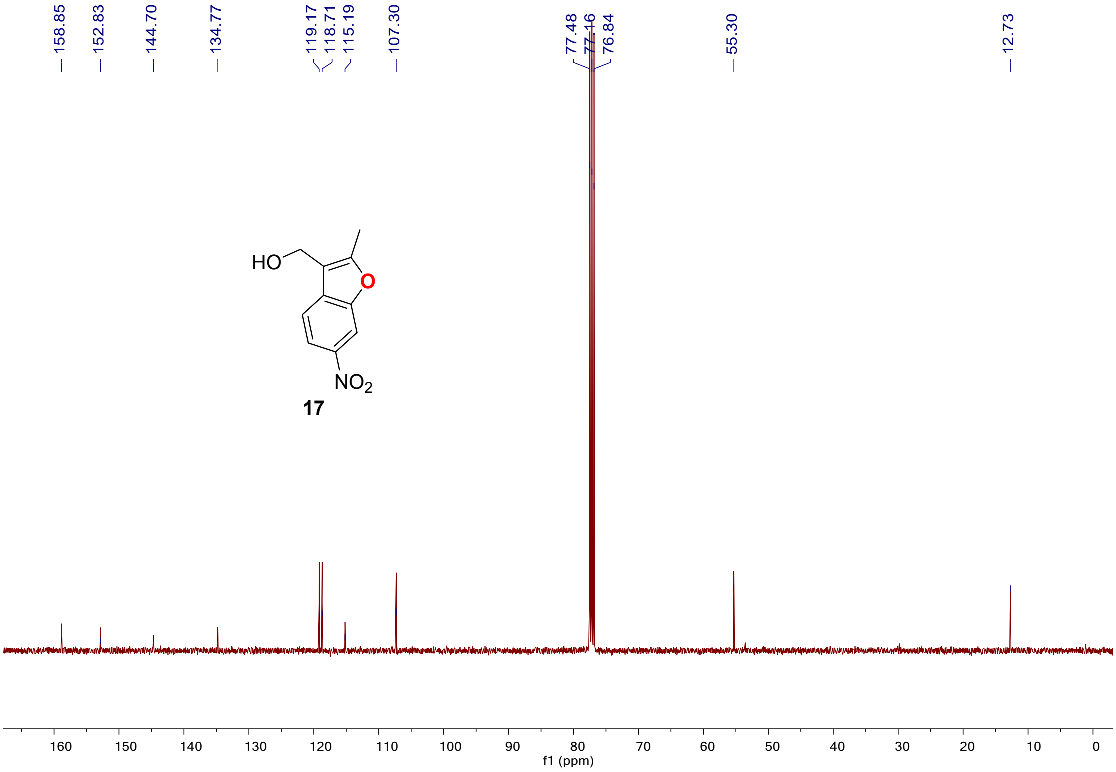


16

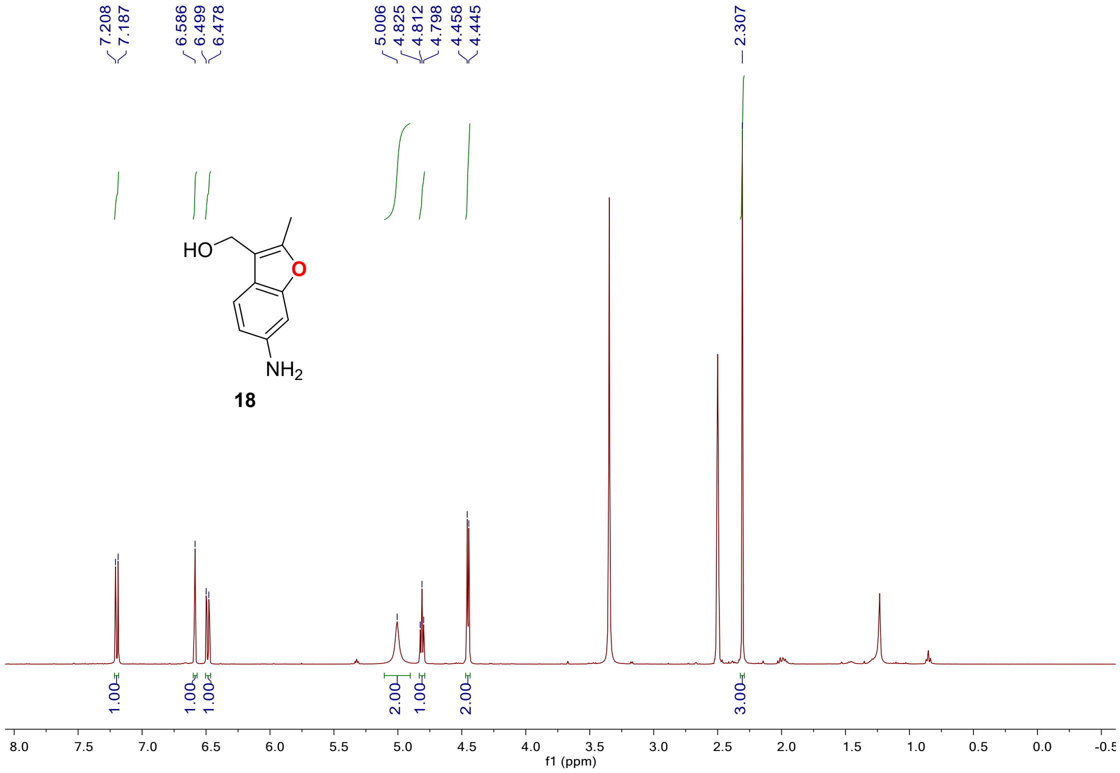
164.18
163.98
154.11
132.95
126.20
123.35
120.16
109.26
87.75
77.37
77.16
76.95
60.60
14.54
EtO
O
I
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

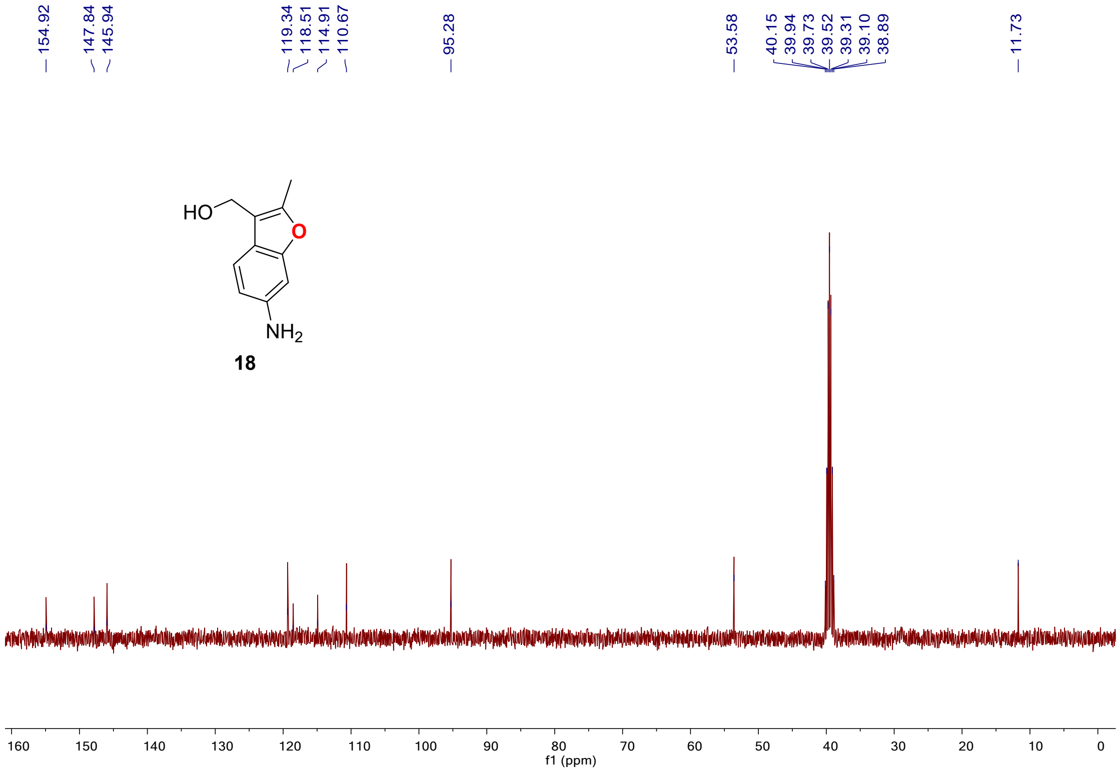

17

8.277
8.164
8.143
7.694
7.673
4.816
4.807
2.538
1.730
HO
O
NO2
1.00
1.00
1.01
2.00
3.01
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


17

158.85
152.83
144.70
134.77
119.17
118.71
115.19
107.30
77.48
77.16
76.84
55.30
12.73
HO
O
NO2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.208
7.187
6.586
6.499
6.478
5.006
4.825
4.812
4.798
4.458
4.445
2.307
HO
O
NH2
18
1.00
1.00
1.00
2.00
1.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


154.92
147.84
145.94
119.34
118.51
114.91
110.67
95.28
53.58
40.15
39.94
39.73
39.52
39.31
39.10
38.89
11.73
HO
O
NH2
18
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)