Synthesis of Benzofurans via Ruthenium-Catalyzed Redox-Neutral C-H Functionalization and Reaction with Alkynes under Mild Conditions

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Supporting Information

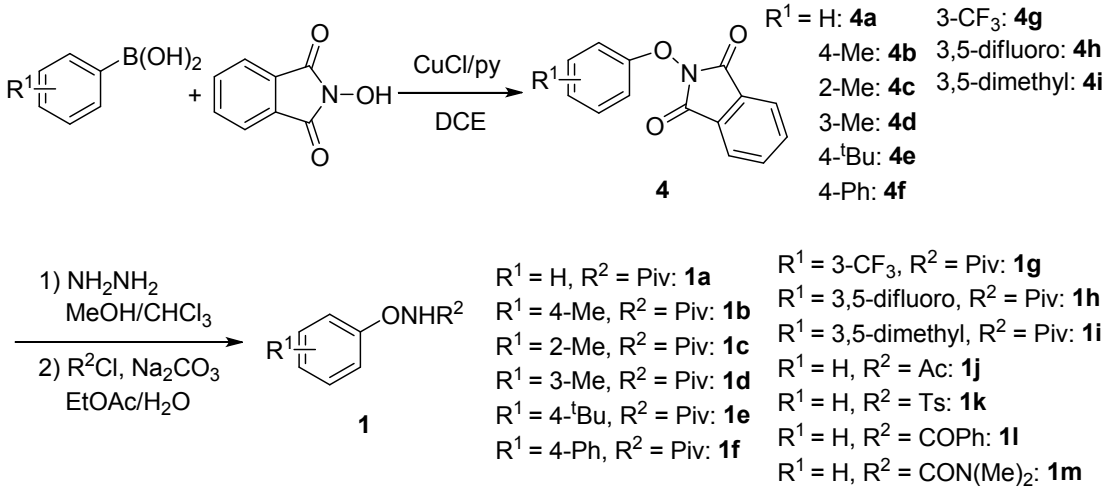
Contents

I. General

NMR spectra were recorded on a Varian Mercury Vx400 spectrometer in solvents as indicated. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. Mass spectra were provided on Agilent 5973 or Agilent 1100 instruments. All melting points were uncorrected. Alkynes were commercially available or synthesized according to known procedure. All other reagents were from commercial sources. No attempts were made to optimize yields for substrate synthesis.

II. Synthesis of substrate 1

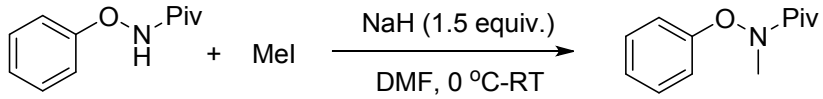
General Procedure for the Synthesis of Substrates 1:



N-aryloxyphthalimides **4** were prepared following a published procedure[1]: In a reaction flask, a mixture of *N*-hydroxyphthalimide (1 eq), arylboronic acid (2 eq), CuCl (1 eq), freshly activated 4-Å molecular sieves (250 mg/mmol) and pyridine (1.1 eq) in 1,2-dichloroethane (0.2 M) were stirred at room temperature. The reaction flask was open to atmosphere. After 48 h, the reaction mixture became green as the reaction proceeded. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the desired *N*-aryloxyphthalimides.

Hydrazine monohydrate (3 eq) was added to the solution of *N*-aryloxyphthalimide **4** (1 eq) in 10% MeOH in $CHCl_3$ (0.1 M). The reaction was allowed to stir at room temperature overnight. The precipitate was filtered off and washed with DCM. The filtrate was concentrated and the resulting oil was passed through a plug of silica gel washing with 30% EtOAc in Petrol ether. The solvent was then removed under reduce pressure to afford the corresponding *N*-aryloxyamine.

N-Aryloxyamine (1 eq) was added to a biphasic mixture of Na_2CO_3 (1.2 eq) in a 2:1 mixture of EtOAc:H_2O (0.6 M). The resulting solution was cooled to 0 °C, followed by dropwise addition of pivaloyl chloride (1 eq). After stirring at 0 °C for 2 h, the reaction was quenched with sat. $NaHCO_3$ and diluted with EtOAc. The organic phase was washed twice with sat. $NaHCO_3$ after which it was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc/PE to give the desired *N*-aryloxypivalamide as colorless crystals.

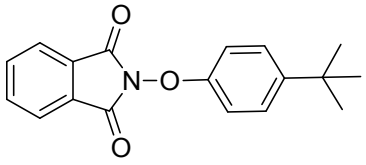


1a **1n**

1a (1 eq) in DMF (0.3 M) was cooled to 0 °C, then NaH (1.5 eq) was added portion wise. After ten minutes, MeI (2.0 eq) was slowly added to the reaction mixture at 0 °C. After stirring at rt overnight, the resulting reaction mixture was quenched with sat. $NaHCO_3$, diluted with EtOAc, washed with water, dried over Na_2SO_4. The purification was performed by flash column chromatography on silica gel to afford the desired *N*-methyl-*N*-phenoxypivalamide (**1n**) in the yield of 58%.

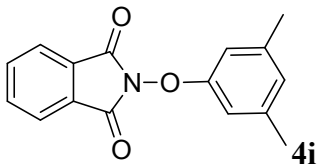
Characterization of Compounds 5 and Substrates 1

4a, 4b, 4c, 4d, 4f, 4g, 4h, 4i,1a, 1j, 1k, 1l are known compounds and all data were in agreement with those reported.[1-3]



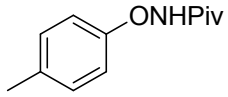
4e

Yield 60%; white solid; m.p. 117-119 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91-7.89 (m, 2H), 7.80-7.78 (m, 2H), 7.34 (d, *J* = 9.2 Hz,2H), 7.11 (d, *J* = 9.2 Hz, 2H), 1.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.1, 156.7, 147.6, 134.9, 128.8, 126.6, 124.0, 114.2, 34.4, 31.5; **IR (neat, cm^{-1}):** ν 2967, 2901, 1788, 1733, 1504, 1077, 704; **MS (m/z, EI):**295, 280, 130, 102, 76; **HRMS** calculated for $C_{18}H_{17}NO_3(M^+)$: 295.1208; Found: 295.1206; $\mathbf{R_f}$ = 0.6 (PE: EtOAc, 3:1).



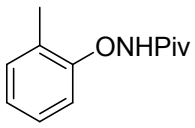
4i

Yield 80%; white solid; m.p. 179-180 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93-7.90 (m, 2H), 7.82-7.80 (m, 2H), 6.77 (s,3H), 2.28 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.1, 159.0, 139.9, 134.9, 129.0, 126.4, 124.1, 111.9, 21.5; **IR (neat, cm^{-1}):** ν 3022, 2917, 1795, 1733, 1590, 1186, 1121, 876, 837, 699; **MS (m/z, ESI):** 268, 163; **HRMS** calculated for $C_{16}H_{14}NO_3$ $(M+H)^+$: 268.0968; Found: 268.0973; $\mathbf{R_f}$ = 0.6 (PE: EtOAc, 3:1).



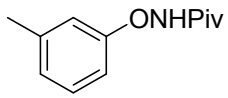
1b

Yield 70% from **4b**; white solid; m.p. 113-114 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.13 (s, 1H), 7.04 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 2.27 (s, 3H), 1.23 (s, 9H); **^{13}C NMR(100MHz, $CDCl_3$):** δ 177.1, 157.7, 132.2, 129.9, 113.3, 38.4, 27.3, 20.6; **IR (neat, cm^{-1}):** ν 3161,2966, 2923, 1658, 1499, 1478, 1189, 827, 816; **MS (m/z, ESI):** 208, 107; **HRMS** calculated for $C_{12}H_{18}NO_2$ $(M+H)^+$: 208.1332; Found: 208.1337; $\mathbf{R_f}$= 0.3 (PE: EtOAc, 5:1).



1c

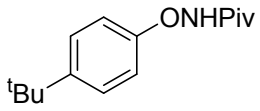
Yield 88% from **4c**; white solid; m.p. 103-104 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.05 (s, 1H), 7.11-7.08 (m, 2H), 6.93-6.90 (m, 2H), 2.27 (s, 3H), 1.24 (s, 9H); **^{13}CNMR (100MHz, $CDCl_3$):** δ 176.9, 157.6, 131.1, 126.9, 124.8, 122.6, 111.6, 38.4, 27.3, 15.9; **IR (neat, cm^{-1}):** ν 3165, 2962, 1658, 1566, 1476, 1132, 771, 685; **MS (m/z, ESI):** 208, 102; **HRMS** calculated for $C_{12}H_{18}NO_2(M+H)^+$: 208.1332; Found: 208.1338; $\mathbf{R_f}$ = 0.5 (PE: EtOAc, 3:1).



1d

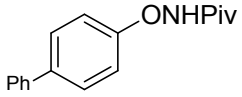
Yield 80% from **4d**; white solid; m.p. 72-74 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.43 (s, 1H), 7.10 (t, *J* = 8 Hz, 1H), 6.80-6.74 (m, 3H), 2.28 (s, 3H), 1.18 (s, 9H); **^{13}CNMR**

(100MHz, $CDCl_3$): δ 177.1, 159.7, 139.4, 129.1, 123.5, 113.9, 110.2, 38.3, 27.2, 21.5; **IR (neat, cm^{-1}):** ν 3165, 2962, 2928, 1658, 1586, 1241, 1207, 1133, 942, 771; **MS (m/z, ESI):** 208, 107; **HRMS** calculated for $C_{12}H_{18}NO_2$ $(M+H)^+$: 208.1332; Found: 208.1336; $\mathbf{R_f}$ = 0.3 (PE: EtOAc, 5:1).



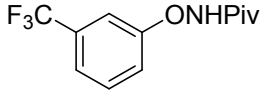
1e

Yield 70% from **4e**; white solid; m.p. 132-134 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.37 (s, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 1.28 (s, 9H), 1.18 (s, 9H); **^{13}C NMR (100MHz, $CDCl_3$):** δ 177.1, 157.5, 145.5, 126.2, 112.8, 38.3, 34.2, 31.6, 27.2; **IR (neat, cm^{-1}):** ν 3139, 2963, 2905, 1664, 1502, 1478, 1164, 930, 835; **MS (m/z, ESI):** 250, 194; **HRMS** calculated for $C_{15}H_{24}NO_2$ $(M+H)^+$: 250.1802; Found: 250.1799; $\mathbf{R_f}$ = 0.5 (PE: EtOAc, 3:1).



1f

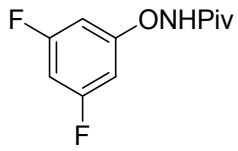
Yield 92% from **4f**; white solid; m.p. 129-132 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.42 (s, 1H), 7.48-7.42 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 1.22 (s, 9H); **^{13}C NMR (100MHz, $CDCl_3$):** δ 177.4, 159.3, 140.6, 136.0, 128.8, 128.2, 127.0, 126.9, 113.6, 38.4, 27.3; **IR (neat, cm^{-1}):** ν 3152, 2959, 1647, 1480, 1191, 1161, 830, 757, 693; **MS (m/z, ESI):** 270, 169, 141; **HRMS** calculated for $C_{17}H_{20}NO_2$ $(M+H)^+$: 270.1489; Found: 270.1492; $\mathbf{R_f}$ = 0.6 (PE: EtOAc, 3:1).



1g

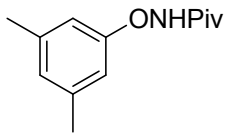
Yield 55% from **4g**; white solid; m.p. 75-78 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.98 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 1.14 (s, 9H); **^{13}C NMR (100MHz, $CDCl_3$):** δ 177.7, 159.8, 132.0, 131.6, 130.0, 125.2, 122.5, 119.5 (d, *J* = 3.7 Hz), 116.6, 110.2 (d, *J* = 3.7 Hz), 38.4, 27.0; **^{19}F**

NMR (376 MHz, $CDCl_3$): -62.9; **IR (neat, cm^{-1}):** ν 3159, 3056, 2966, 1657, 1447, 1328, 1170, 1108, 869, 815; **MS (m/z, ESI):** 262; **HRMS** calculated for $C_{12}H_{14}F_3NO_2$ $(M+H)^+$: 262.1049; Found:262.1044; **R_f** = 0.5 (PE: EtOAc, 3:1).



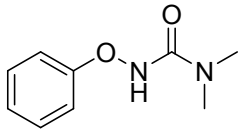
1h

Yield 62% from **4h**; white solid; m.p. 107-109 °C; **^{1}H NMR (400 MHz, DMSO-d_6):** δ 11.83 (br, s, 1H), 6.90-6.85 (m, 1H), 6.76-6.72 (m, 2H), 1.19 (s, 9H); **^{13}C NMR(100MHz,DMSO-d_6):** δ 175.6, 164.2 (d, *J* = 15.5 Hz), 162.2, 162.1, 161.9, 161.7, 97.9, 97.7, 97.4, 97.1, 37.6, 26.9; **^{19}F NMR (376 MHz,DMSO-d_6):** -108.6; **IR (neat, cm^{-1}):** ν 3227, 2976, 2966, 2873, 1666, 1615, 1466, 1112, 993, 830; **MS (m/z, ESI):**230, 130; **HRMS** calculated for $C_{11}H_{14}F_2NO_2$ $(M+H)^+$: 230.0979; Found: 230.0987; **R_f** = 0.7 (PE: EtOAc, 5:1).



1i

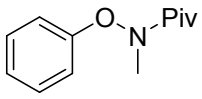
Yield 64% from **4i**; white solid; m.p. 115-116 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.56 (br s, 1H), 6.60 (s, 1H), 6.57 (s, 2H), 2.22 (s, 6H), 1.16 (s, 9H); **^{13}C NMR (100MHz,$CDCl_3$):** δ 177.0, 159.7, 139.0, 124.3, 110.9, 38.2, 27.1, 21.4; **IR (neat, cm^{-1}):** ν 3199, 2987, 2917, 1660, 1592, 1508, 1128, 835, 682; **MS (m/z, ESI):** 222, 121; **HRMS** calculated for $C_{13}H_{20}NO_2$ $(M+H)^+$: 222.1489; Found: 222.1491; **R_f** = 0.6 (PE: EtOAc, 3:1).



1m

Yield 47% from **4m**; gray crystal; m.p. 114-116 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (s, 1H), 7.28 (t, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 2.92 (s, 6H); **^{13}C NMR (100MHz, $CDCl_3$):** δ 160.2, 159.7, 129.4, 122.3, 113.4, 36.5;

IR (neat, cm^{-1}): ν 3149, 2929, 1665, 1649, 1492, 1477, 1187, 1155, 746, 689; **MS (m/z, ESI):** 181; **HRMS** calculated for $C_9H_{13}N_2O_2$ $(M+H)^+$: 181.0972; Found: 181.0973; **R_f** = 0.3 (PE: EtOAc, 3:1).

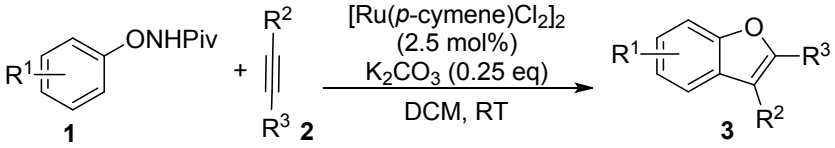


1n

Yield 58% from **1a**; colorless oil；**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 (t, *J* = 8 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8 Hz, 2H), 3.23 (s, 3H), 1.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 181.0, 157.3, 130.0, 123.1, 113.5, 39.8, 36.2, 27.3; **IR (neat, cm^{-1}):** ν 2979, 2965, 2923, 2852, 1644, 1480, 1336, 1153, 1073, 922, 762; **MS (m/z, ESI):** 208, 114; **HRMS** calculated for $C_{12}H_{18}NO_2$ $(M+H)^+$: 208.1332; Found: 208.1323; **R_f** = 0.7(PE: EtOAc, 5:1).

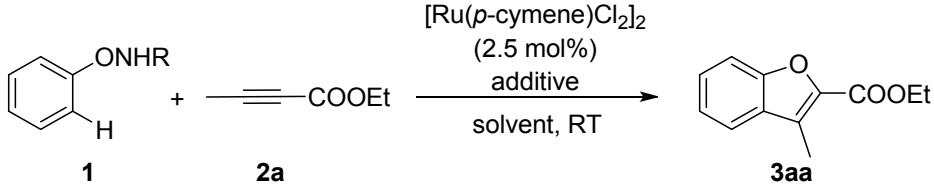
III. Synthesis of Benzofuran

General Procedure



Without any particular precautions to extrude oxygen or moisture, the aryloxypivalamide **1** (1.2eq), the alkyne **2** (1 eq), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol%) and K_2CO_3 (25 mol%) were weighted in a 4 mL vial equipped with a stir bar. DCM (0.4 M) was then added. The reaction was stirred at room temperature and monitored by TLC. Afterwards, it was diluted with EtOAc and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents).

Table S1 Optimization Studies [a]



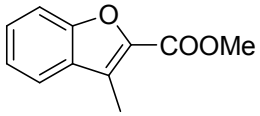
Entry	R	Additive (eq)	Solvent	Yield (%)[b]
1[c,d]	Bz	CsOAc (0.25)	DCM	<5
2[c,d]	$CONMe_2$	CsOAc (0.25)	DCM	NR

3	Piv	NaOAc (0.25)	DCM	86
4	Piv	Na_2CO_3 (0.25)	DCM	78
5	Piv	K_3PO_4 (0.25)	DCM	93
6	Piv	KO^tBu (0.25)	DCM	6
7	Piv	KOAc (0.25)	DCM	84
8	Piv	K_2CO_3 (0.25)	DMF	NR
9	Piv	K_2CO_3 (0.25), HOPiv (2)	DCM	16
10	Piv	K_2CO_3 (0.25), $PivNH_2$(2)	DCM	95
11	Piv	K_2CO_3 (0.25), PhOH (2)	DCM	25

[a] Reaction conditions: **1** (0.12 mmol), **2a** (0.1 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %), and additives in solvent (0.4 M) at room temperature for 12h under air. [b] ^1H NMR yield. [c] Reaction was monitored by TLC, 24-48h. [d] Phenol was detected.

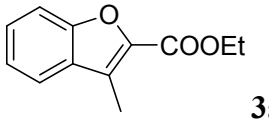
Characterization of products 3

3aa, **3ab**, **3ag**, **3ah**, **3ai**, **3aj**, **3al**, **3an**, **3ga** are known compounds and all data were in agreement with those reported.[3a,4]



3aa[3a]

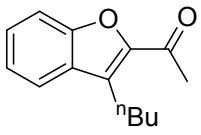
Yield 99%; white solid; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.32-7.28 (m, 1H), 3.98 (s, 3H), 2.59 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.0, 154.4, 140.7, 129.0, 127.9, 126.0, 123.2, 121.2, 112.2, 52.1, 9.4; **IR (neat, cm^{-1}):** ν 2924, 1710, 1439, 1366, 747; **MS (m/z, ESI)**: 280, 248, 221, 189, 159; **Rf:** 0.5 in PE.



3ab[4]

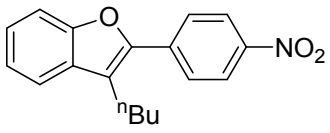
Yield 96%; white solid; **^1H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.6, 154.4, 141.0, 129.2, 127.8, 125.7, 123.2, 121.1, 112.3, 61.2, 14.5, 9.5; **IR (neat, cm^{-1}):** ν 2984, 1708, 1400, 1294, 1143, 745; **MS (m/z, ESI)**: 204, 176, 159, 131, 103, 77; **Rf:**

0.5 in PE.



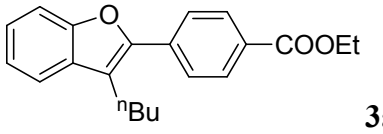
3ac

Yield 93%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 8 Hz, 1H), 7.52-7.44 (m, 2H), 7.29 (t, *J* = 8 Hz, 1H), 3.10 (t, *J* = 7.6 Hz, 2H), 2.62 (s, 3H), 1.70-1.63 (m, 2H), 1.46-1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.3, 154.1, 148.0, 129.2, 129.0, 128.1, 123.3, 121.9, 112.3, 31.9, 28.0, 23.9, 22.9, 14.1; **IR (neat, cm^{-1}):** ν 2957, 2928, 2859, 1679, 1568, 1287, 1262, 1134, 745, 649; **MS (m/z, EI):** 216, 201, 187, 174, 159, 131; **HRMS** calculated for $C_{14}H_{16}O_2$ $(M)^+$: 216.1150; Found: 216.1148; **R_f** = 0.8 (PE: EtOAc, 15:1).



3ad

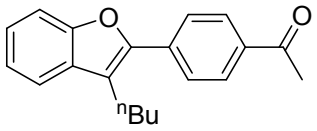
Yield 99%; yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 2.95 (t, *J* = 8 Hz, 2H), 1.77-1.70 (m, 2H), 1.54-1.44 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.3, 147.9, 146,7, 137.5, 130.3, 126.7, 125.9, 124.1, 123.0, 120.7, 120.3, 111.4, 31.9, 24.3, 23.0, 14.0; **IR (neat, cm^{-1}):** ν 2960, 2918, 2853, 1593, 1515, 1334, 1311, 1106, 852, 742; **MS (m/z, EI):** 295, 252, 206, 176, 152; **HRMS** calculated for $C_{18}H_{17}NO_3$ (M^+): 295.1208; Found: 295.1207; **R_f** = 0.3 in PE.



3ae

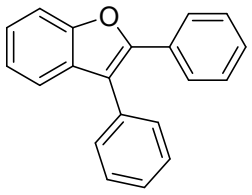
Yield 61%; colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8 Hz, 1H), 7.33 (t, *J* = 8 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 8 Hz, 2H),

1.79-1.71 (m, 2H), 1.53-1.45 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.5, 154.2, 149.4, 135.7, 130.6, 130.0, 129.5, 126.4, 125.1, 122.7, 120.0, 118.8, 111.3, 61.2, 32.0, 24.3, 23.1, 14.5, 14.1; **IR (neat, cm^{-1}):** ν 2957, 2926, 2857, 1717, 1609, 1454, 1272, 1108, 744; **MS (m/z, EI):** 322, 279, 251, 206, 178, 152; **HRMS** calculated for $C_{21}H_{22}O_3$ (M^+): 322.1569; Found: 322.1567; **R_f** = 0.5 (PE: EtOAc, 30:1)



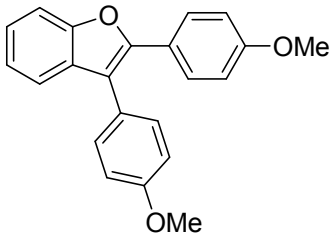
3af

Yield 43%; colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8 Hz, 1H), 7.33 (t, *J* = 8 Hz, 1H), 7.26 (t, *J* = 8 Hz, 1H), 2.96 (t, *J* = 8 Hz, 2H), 2.65 (s, 3H), 1.79-1.71 (m, 2H), 1.54-1.44 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.6, 154.2, 149.2, 136.0, 135.9, 130.6, 128.9, 126.5, 125.2, 122.7, 120.1, 119.2, 111.3, 32.0, 26.8, 24.3, 23.1, 14.1; **IR (neat, cm^{-1}):** ν 2957, 2927, 2858, 1682, 1601, 1356, 1260, 838, 745; **MS (m/z, EI):** 292, 277, 249, 207, 178; **HRMS** calculated for $C_{20}H_{20}O_2$ (M^+): 292.1463; Found: 292.1466; **R_f** = 0.5 (PE: EtOAc, 15:1).



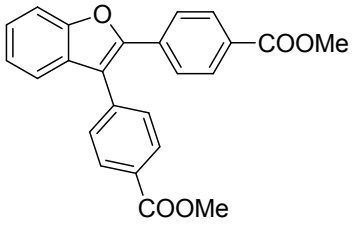
3ag[3a]

Yield 57%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.56-7.38 (m, 7H), 7.32-7.20 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.1, 150.6, 132.9, 130.8, 130.4, 129.9, 129.1, 128.6, 128.5, 127.8, 127.2, 124.8, 123.0, 120.2, 117.6, 111.2; **IR (neat, cm^{-1}):** ν 3062, 1602, 1498, 748, 694; **MS (m/z, EI)**: 270, 255, 239, 165, 134; **Rf:** 0.7 in PE.



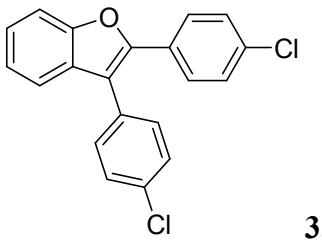
3ah[3a]

Yield 54%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.28 (dt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ159.7, 159.1, 153.9, 150.6, 131.0, 130.7, 128.5, 125.3, 124.3, 123.6, 122.9, 119.8, 115.7, 114.5, 114.0, 111.0, 55.39, 55.38; **IR (neat, cm^{-1}):** ν 2963, 2923, 2851, 1726, 1606, 1500, 1451, 1247, 1024; **MS (m/z, EI)**: 330, 315, 255, 243, 215, 165; **Rf:** 0.5 in PE.



3ai[3a]

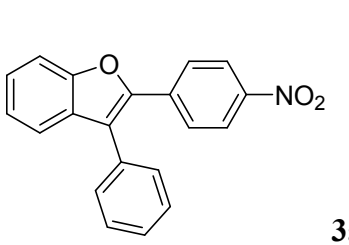
Yield 59%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 3H), 7.48 (d, *J* = 8.0 Hz, 1H),7.38 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.27 (dt, *J* = 7.6, 0.8 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.9, 166.7, 154.4, 149.9, 137.5, 134.5, 130.5, 129.9, 129.82, 129.78, 129.6, 126.9, 125.8, 123.6, 120.2, 118.6, 111.5, 52.4, 52.3 (one signal missing due to overlap); **IR (neat, cm^{-1}):** ν 2923, 2852, 1716, 1607, 1451, 1432, 1412, 1286, 1118, 1066; **MS (m/z, EI)**: 386, 355, 268, 239, 162, 119; **Rf:** 0.5 in PE.



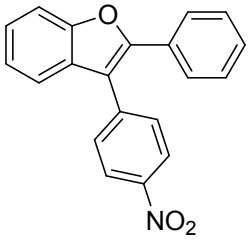
3aj[3a]

Yield 71%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58-7.53 (m, 3H), 7.46-7.39

(m, 5H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.1, 149.7, 134.6, 133.9, 131.1, 129.8, 129.5, 129.0, 128.3, 125.3, 123.4, 120.0, 116.9, 111.4 (two signals missing due to overlap); **IR (neat, cm^{-1}):** ν 3060, 1582, 1497, 834, 751; **MS (m/z, EI)**: 338, 302, 268, 239, 134; **Rf:** 0.7 in PE.

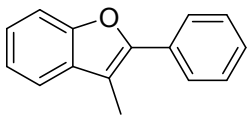


3ak



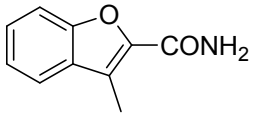
3ak'

Yield 89%; **3ak** and **3ak'** were inseparable yellow solid, **3ak**:**3ak'** = 10:1; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 8.4 Hz, 0.2H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 0.2H), 7.60-7.49 (m, 7.7H), 7.44-7.38 (m, 1.2H), 7.31-7.27 (m, 1.2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.4, 147.9, 147.0, 136.8, 132.0, 130.6, 130.0, 129.7, 129.5, 129.3, 128.9, 128.6, 127.5, 127.1, 126.2, 125.4, 124.4, 123.9, 123.6, 121.4, 120.8, 111.5; **IR (neat, cm^{-1}):** ν 3060, 2956, 2919, 2849, 1593, 1509, 1338, 854, 743, 697; **MS (m/z, EI):** 315, 268, 239, 189, 134, 119; **HRMS** calculated for $C_{20}H_{13}NO_3$ (M^+): 315.0895; Found: 315.0899; **R_f** = 0.6 (PE: EtOAc, 15:1).



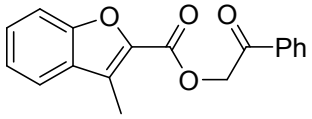
3al[3a]

Yield 36%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):**δ 7.80 (d, *J*= 8.3 Hz, 2H), 7.53-7.45 (m, 4H),7.35 (t, *J*= 7.4 Hz, 1H), 7.31-7.22 (m,2H), 2.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.9, 150.8, 131.6, 131.3, 128.8, 128.0, 126.8, 124.4, 122.5, 119.4, 111.4, 111.1, 9.6; **IR (neat, cm^{-1}):** ν 3059, 2924, 1457, 1362, 743, 693; **MS (m/z, EI)**: 208, 178, 152, 131; **Rf:** 0.7 in PE.



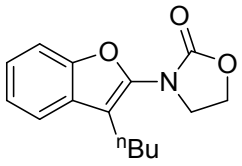
3am

Yield 60%; white solid; m.p. 131-133^{o}C;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.47-7.41 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.57 (br s, 1H), 6.27 (br s, 1H), 2.64 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.5, 153.5, 142.4, 129.8, 127.4, 123.6, 123.2, 121.2, 111.7, 9.1; **IR (neat, cm^{-1}):** ν 3401, 3349, 3168, 2922, 2852, 1693, 1659, 1622, 1607, 1412, 1375, 1163, 1125, 742; **MS (m/z, EI):**175, 159, 131, 102, 77; **HRMS** calculated for $C_{10}H_9NO_2$ (M^+): 175.0633; Found: 175.0629; **R_f =** 0.4 (PE: EtOAc, 2:1).



3an[3a]

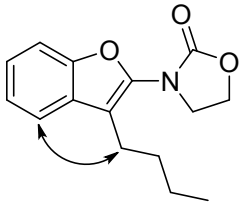
Yield 82%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):**δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.67-7.45 (m, 6H),7.32 (t, *J* = 7.5 Hz, 1H), 5.65 (s, 2H), 2.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.7, 159.8, 154.8, 140.2, 134.2, 134.1, 129.1, 129.0, 128.2, 128.0, 127.4, 123.4, 121.4, 112.4, 66.5, 9.6; **IR (neat, cm^{-1}):** ν 3058, 2939, 1724, 1697, 1448, 743, 687; **MS (m/z, EI)**: 294, 175, 159, 105, 77; **Rf =** 0.6 (EtOAc: PE, 1:4).

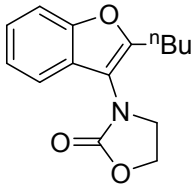


3ao

Yield 39%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.30-7.20 (m, 2H), 4.56 (t, *J* = 8 Hz, 2H), 4.05 (t, *J* = 8 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.70-1.62 (m, 2H), 1.43-1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.7, 152.0, 141.7, 129.0, 124.8, 122.7, 120.1, 113.7, 111.2, 63.0, 46.6, 31.1, 23.1, 22.9, 14.0; **IR (neat, cm^{-1}):** ν 2956, 2926, 2858, 1762, 1646, 1454, 1210, 1102, 1038, 1013, 745; **MS (m/z, EI):** 259, 216, 172, 157, 103, 77; **R_f =** 0.6 (PE: EtOAc, 5:1).

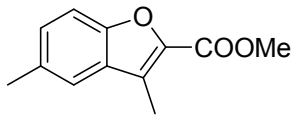
NOESY (400 MHz, $CDCl_3$). The copy of NOESY spectra is shown in page 52.





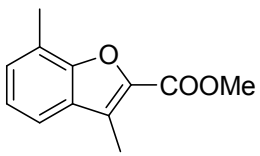
3ao'

Yield 25%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44-7.40 (m, 2H), 7.26-7.23 (m, 2H), 4.59 (t, *J* = 8 Hz, 2H), 3.99 (t, *J* = 8 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.78-1.71 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.9, 155.6, 153.4, 125.2, 124.2, 123.1, 118.2, 114.3, 111.7, 62.7, 47.5, 29.6, 26.3, 22.6, 13.9; **IR (neat, cm^{-1}):** ν 2959, 2926, 2859, 1751, 1454, 1424, 1236, 1117, 1101, 1036, 800, 745; **MS (m/z, EI):** 259, 216, 172, 157, 103, 77; **HRMS** calculated for $C_{15}H_{17}NO_3$ (M^+): 259.1208; Found: 259.1212; **R_f** = 0.4 (PE: EtOAc, 5:1).



3ba

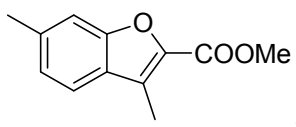
Yield 91%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42-7.39 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 3H), 2.56 (s, 3H), 2.46 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.1, 153.0, 140.8, 132.9, 129.5, 129.1, 125.9, 120.8, 111.8, 52.1, 21.5, 9.5; **IR (neat, cm^{-1}):** ν 3024, 1713, 1588, 1436, 1292, 1146, 1089, 800, 771; **MS (m/z, EI):** 204, 189, 173, 144, 115, 91; **HRMS** calculated for $C_{12}H_{12}O_3$ (M^+): 204.0786; Found: 204.0787; **R_f** = 0.7(PE: EtOAc, 15:1).



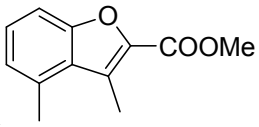
3ca

Yield 96%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 8.0 Hz, 1H),

7.24-7.17 (m, 2H), 3.97 (s, 3H), 2.57 (s, 3H), 2.56 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.2, 153.6, 140.6, 128.6, 126.3, 123.3, 122.6, 118.5, 52.0, 15.2, 9.6 (one signal missing due to overlap); **IR (neat, cm^{-1}):** ν 3029, 1713, 1597, 1438, 1291, 1148, 1085, 1057, 781, 745; **MS (m/z, EI):** 204, 189, 173, 145, 115, 91; **HRMS** calculated for $C_{12}H_{12}O_3(M^+)$: 204.0786; Found: 204.0783; **R_f** = 0.7 (PE: EtOAc, 15:1).

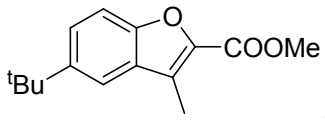


3da



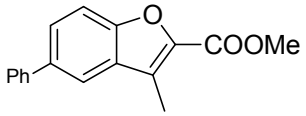
3da'

Yield 99%; **3da** and **3da'** were inseparable colorless liquid, **3da**:**3da'** = 5:1; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1×0.2 = 0.2H),7.31 (s, 1H), 7.28 (s, 1×0.2 = 0.2H), 7.11 (d, J = 8.0 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1×0.2 = 0.2H),3.97 (s, 3+3×0.2 =3.6H), 2.77 (s, 3×0.2 = 0.6H), 2.67 (s, 3×0.2 = 0.6H), 2.56 (s, 3H), 2.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.1, 154.9, 140.3, 138.7, 134.1, 127.8, 126.7, 126.2, 124.9, 124.8, 120.7, 112.2, 110.0, 52.0, 22.1, 19.7, 11.7, 9.5; **IR (neat, cm^{-1}):** ν 3031, 1712, 1621, 1436, 1293, 1137, 1096, 803, 769; **MS (m/z, EI):** 204, 189, 173, 146, 115, 91; **HRMS** calculated for$C_{12}H_{12}O_3$ (M^+): 204.0786; Found: 204.0790; **R_f** = 0.6(PE: EtOAc, 15:1).



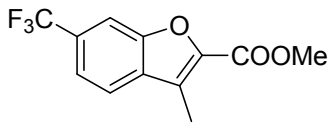
3ea

Yield 65%; yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 3H), 2.60 (s, 3H), 1.39 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.1, 152.8, 146.5, 140.9, 128.7, 126.4, 126.3, 116.9, 111.7, 52.1, 35.0, 31.9, 9.5; **IR (neat, cm^{-1}):** ν2957, 1716, 1600, 1507, 1463, 1438, 1148, 1114, 1018, 809; **MS (m/z, EI):**246, 231, 215, 203, 172, 128, 115, 86; **HRMS** calculated for $C_{15}H_{18}O_3$ (M^+): 246.1256; Found: 246.1257; **R_f** = 0.7 (PE: EtOAc, 15:1).



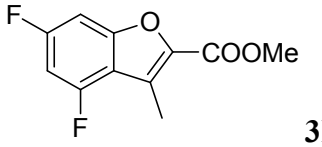
3fa

Yield 88%; white solid; m.p. 88-90 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 1.2 Hz,1H), 7.67-7.56 (m, 4H), 7.45 (t, *J* = 8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 3.98 (s, 3H), 2.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.9, 154.0, 141.3, 141.1, 137.1, 129.6, 128.9, 127.7, 127.5, 127.3, 126.2, 119.5, 112.4, 52.1, 9.5; **IR (neat, cm^{-1}):** ν 2947, 2920, 2849, 1713, 1601, 1585, 1436, 1298, 1142, 1096, 760, 696; **MS (m/z, EI):** 266, 235, 207, 178, 152, 117, 89; **HRMS** calculated for $C_{17}H_{14}O_3$ (M^+): 266.0943; Found: 266.0938; **R_f =** 0.6 (PE: EtOAc, 15:1).



3ja[3a]

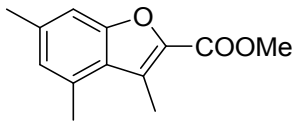
Yield 23%; white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 (s, 1H), 7.73 (d, *J*= 8.3 Hz, 1H),7.55 (d, *J*= 8.3 Hz, 1H), 4.00 (s, 3H), 2.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.5, 153.4, 143.0, 131.9, 130.1, 129.8, 125.5, 125.4, 122.8, 122.3, 121.9, 120.2, 120.1, 110.0, 109.9, 52.4, 9.4; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -61.6; **IR (neat, cm^{-1}):** ν 3075, 2964, 1716, 1673, 1432, 1361, 850, 820; **MS (m/z, EI)**: 258, 243, 227, 199, 151; **Rf:** 0.7 with 10% EtOAc in PE.



3ka

Yield 13%; white solid;m.p. 69-71 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06 (dd, *J*= 8.4, 0.8Hz,1H), 6.76 (td, *J* = 10.0, 2.0 Hz,1H), 3.98 (s, 3H), 2.70 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.0 (d, *J* = 12.1 Hz), 161.5 (d, *J* = 12.1 Hz), 160.2, 158.9 (d, *J* = 15.1 Hz), 156.2 (d, *J* = 15.1 Hz)， 155.4 (dd, *J* = 15.2, 12.1 Hz), 141.4, 124.6, 114.8 (d, *J* = 19.0 Hz), 99.6 (dd, *J* = 27.7, 23.9 Hz), 96.2 (dd,*J* = 26.6,4.6 Hz), 52.2, 10.7; **^{19}F NMR (376 MHz,$CDCl_3$):** δ -108.9, -117.8; **IR (neat, cm^{-1}):** ν 3079, 2961,

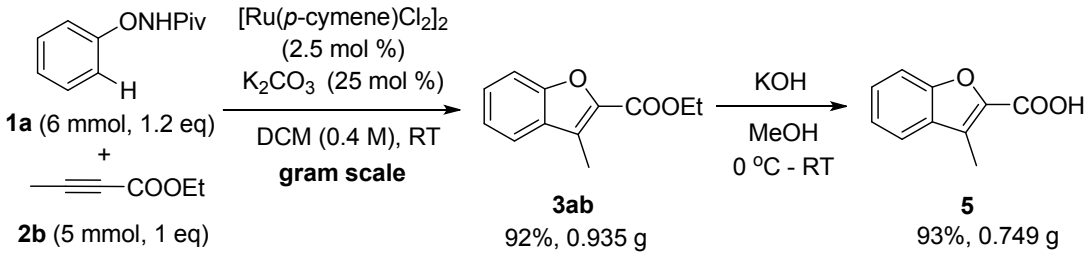
2919, 2850, 1716, 1597, 1439, 1279, 1122, 1059, 853, 835; **MS (m/z, EI):** 226, 211, 195, 167, 138, 127, 119, 99; **HRMS** calculated for $C_{11}H_8F_2O_3$ (M^+): 226.0442; Found: 226.0438; $\mathbf{R_f}$ = 0.6(PE: EtOAc, 15:1).



3la

Yield 83%; white solid; m.p.97-99 ^oC; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.13 (s, 1H), 6.82 (s, 1H), 3.96 (s, 3H), 2.74 (s,3H), 2.62 (s, 3H), 2.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.2, 155.3, 139.9, 138.5, 133.5, 127.4, 126.6, 125.0, 110.0, 52.0, 21.8, 19.6, 11.7; **IR (neat, cm^{-1}):** ν 2955, 2923, 2851, 1703, 1619, 1586, 1431, 1389, 1264, 1148, 844,772; **MS (m/z, EI):** 218, 203, 187, 160, 128, 115, 91; **HRMS** calculated for $C_{13}H_{14}O_3$ (M^+): 218.0943; Found: 218.0941; $\mathbf{R_f}$ = 0.6 (PE: EtOAc, 15:1).

Gram Scale Synthesis of Ethyl 3-methylbenzofuran-2-carboxylate (3ab)



Without any particular precautions to extrude oxygen or moisture, phenoxypivalamide (**1a**) (1.158 g, 6 mmol, 1.2 eq), ethyl 2-butynoate (**2b**) (0.58 ml, 5 mmol, 1 eq), [Ru(*p*-cymene)Cl_2]$_2$ (30.6 mg, 0.05 mmol, 2.5 mol%) and K_2CO_3 (0.1725 g, 1.25 mmol, 0.25 eq) were weighted in a 25 mL vial equipped with a stir bar. DCM (12.5 mL, 0.4M) was then added. The reaction mixture was stirred at room temperature and monitored by TLC. Afterwards, it was diluted with EtOAc and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.

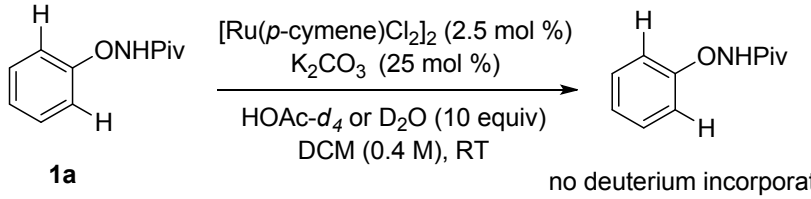
5 was prepared following a published procedure[5]. To an ice-cold, stirred solution of **3ab** (0.935 g, 4.6 mmol, 1 eq) in methanol (5 ml) was slowly added a solution of potassium hydroxide (0.308 g, 5.5 mmol, 2 eq) in methanol (10 ml). The resulting solution was stirred without further cooling until completion. Afterwards, MeOH was evaporated. The residue was dissolved in water and ether and the separated aqueous layer was acidified with 2 M hydrochloric acid. The liberated acid was extracted into

ether (3 x 30 ml); the combined extracts were dried and evaporated. Recrystallization of the residue from ether-petrol gave the acid **5** (0.749 g, 93%) as a colourless solid.

5 is a known compound and all data were in agreement with those reported.[5] m.p. 185-187 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.15 (br s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 2.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):**δ 166.0, 155.0, 140.1, 129.1, 128.7, 128.6, 123.5, 121.5, 112.5, 9.8; **IR (neat, cm^{-1}):** ν 2848, 1671, 1591, 1436, 1300, 918, 741; **MS (m/z, EI):** 176, 131, 102, 77.

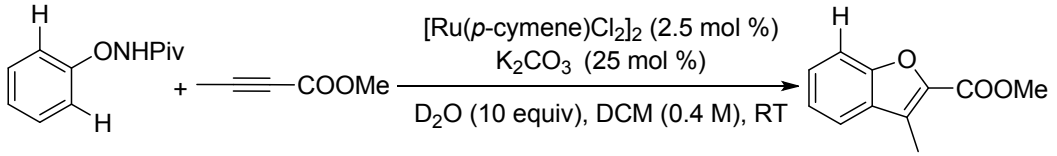
IV Mechanism Studies

Ortho Deuteration Experiments



1a no deuterium incorporation

Without any particular precautions to extrude oxygen or moisture, the phenoxypivalamide (**1a**) (19.3 mg, 0.1mmol, 1.0 eq), [Ru(*p*-cymene)Cl_2]$_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%) and K_2CO_3 (3.5 mg, 0.025 mmol, 25 mol%) were weighted in a 4 mL vial equipped with a stir bar. DCM (0.25 ml, 0.4M), HOAc-d_4 (56 μL, 10 eq) or D_2O (20 μL, 10 eq) was then added, and the mixture was stirred at room temperature for 3 hours. Crude NMR indicated no deuterium incorporation at the *ortho* position of the substrate.

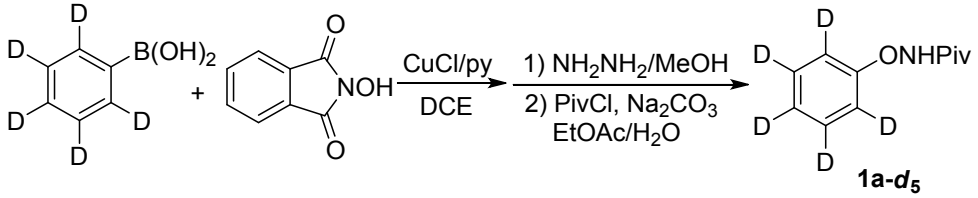


1a **2a** **3aa:** Yield 99%
no deuterium incorporation

Without any particular precautions to extrude oxygen or moisture, the phenoxypivalamide (**1a**) (23.2 mg, 0.12 mmol, 1.2 eq), [Ru(*p*-cymene)Cl_2]$_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%), alkyne **2a** (10.0 μL, 0.1 mmol, 1.0 eq) and K_2CO_3 (3.5 mg, 0.025 mmol, 25 mol%) were weighted in a 4 mL vial equipped with a stir bar. DCM (0.25 ml) and D_2O (20 μL, 10 eq) were then added, and the mixture was stirred at room temperature for 12 hours. Afterwards, it was diluted with EtOAc and transferred to a round bottom flask. Silica gel was added to the flask and voliates were evaporated under reduced pressure. After purification by flash column chromatography, **3a** (19 mg, 99% yield) was isolated and no deuterium incorporation was found.

KIE experiments

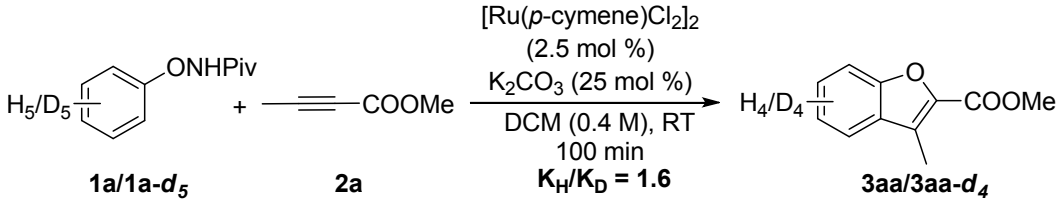
Synthesis of deuterated substrate 1a-*d_5*



(D_5-phenyl)boronic acidwas prepared according to the known procedure.[6]

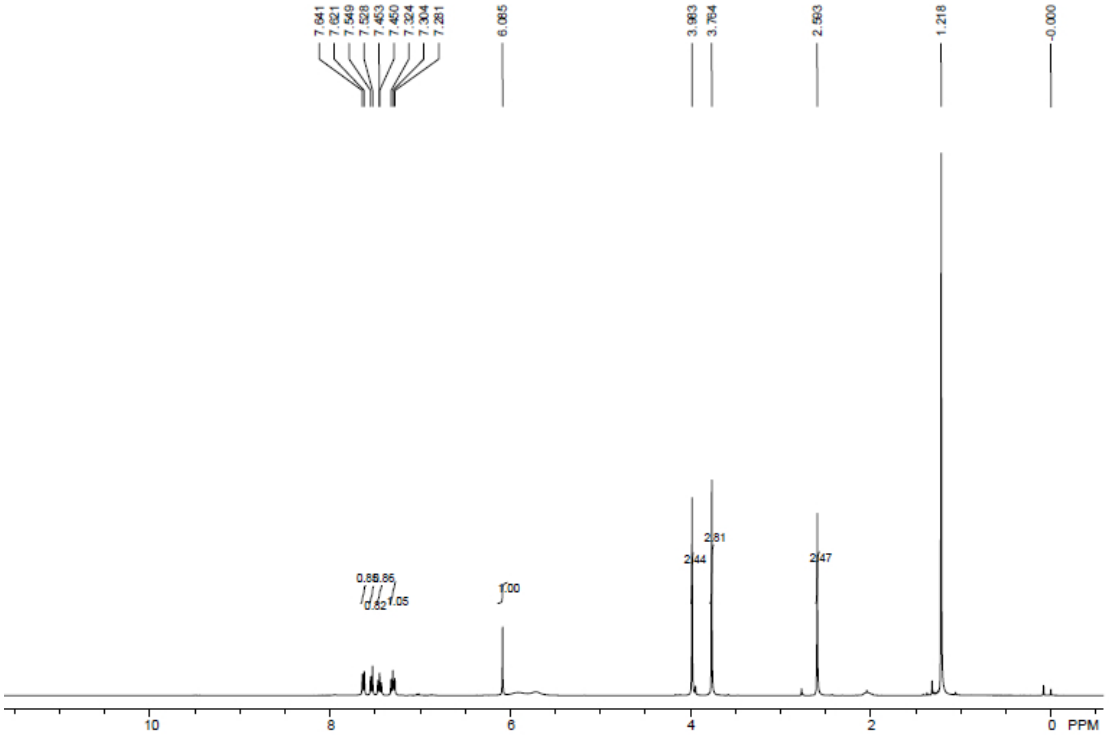
Following the general procedure for the synthesis of substrate, deuterated substrate **1a-*d_5*** was obtained in 63% yield (two steps) from (D_5-phenyl)boronic acid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 1.24 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.3, 159.6, 129.0 (t, *J* = 24.0 Hz), 122.3 (t, *J* = 23.2 Hz), 112.9 (t, *J* = 24.6 Hz), 38.4, 27.3; **IR (neat, cm^{-1}):** ν3136, 2964, 2930, 1658, 1363, 1142, 928, 667; **MS (m/z, ESI):**199; **HRMS** calculated for $C_9H_{11}D_5NO_2$ $(M+H)^+$: 199.1489; Found: 199.1497; **R_f** = 0.5 (PE: EtOAc, 3:1).

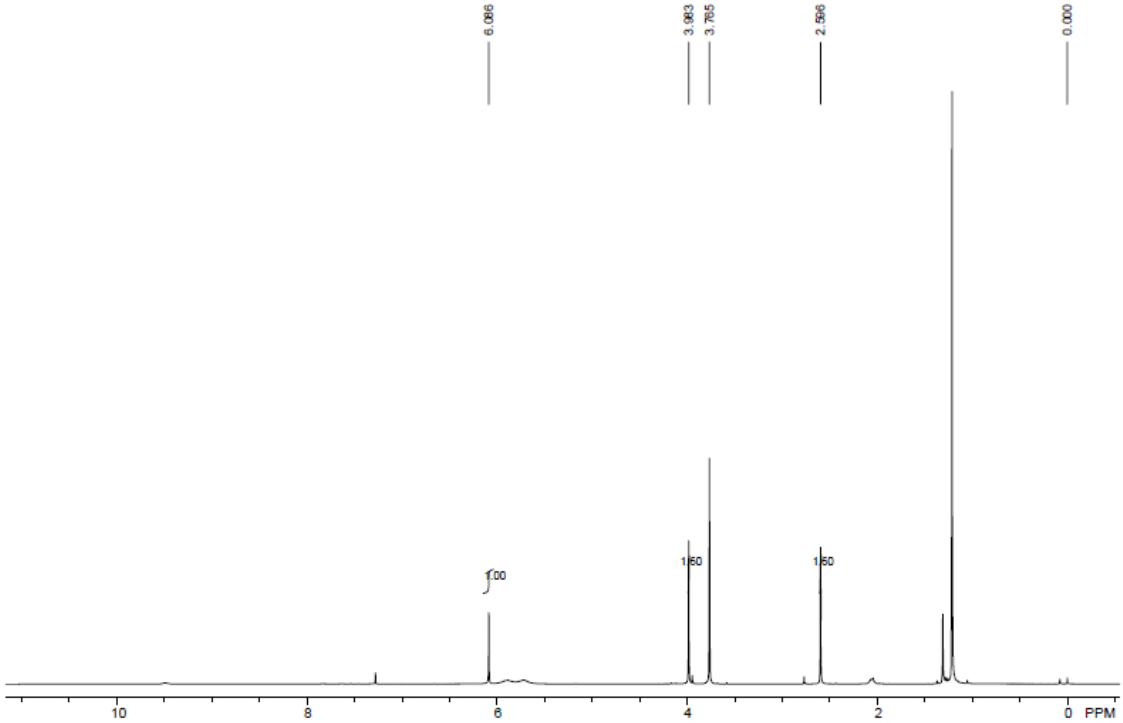


Without any particular precautions to extrude oxygen or moisture, **1a** (23.2 mg, 0.12 mmol, 1.2 eq) or **1a-*d_5*** (23.8 mg, 0.12 mmol, 1.2 eq), [Ru(*p*-cymene)Cl_2]$_2$ (1.5 mg, 0.0025 mmol, 2.5 mol%), K_2CO_3 (3.5 mg, 0.025 mmol, 25 mol%) were mixed with 0.25 mL DCM. After addition of **2a** (10 µl, 0.10 mmol, 1.0 eq.), the mixture was stirred at rt and timing was started. After 100 min, two reaction mixtures were filtered separately through silica column, washed with 10 mL of DCM. The solvent was then removed under reduced pressure and ^{1}H NMR was taken for these two samples separately using trimethoxybenzene (5.6 mg) as the internal standard. **3aa** was obtained in 83% yield and **3aa-*d_5*** was obtained in 52% yield. Thus the KIE was found to be 1.6.

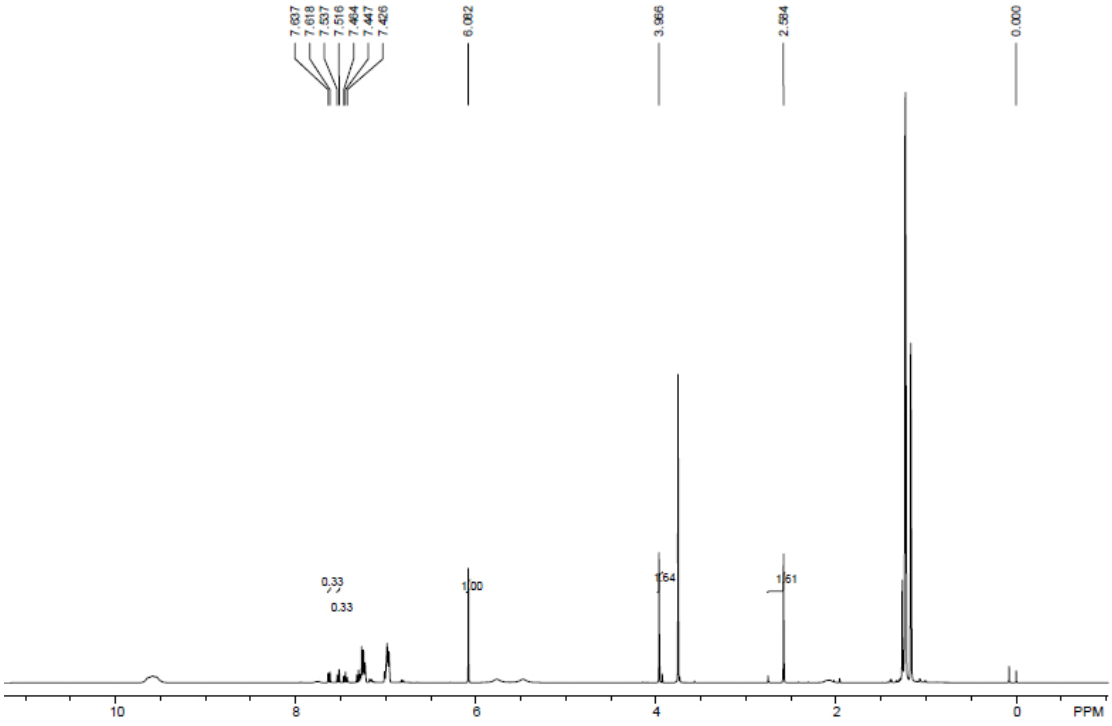
Crude ^{1}H NMR of the reaction of **1a** and **2a** under standard condition for 100 min



Crude ^{1}H NMR of the reaction of **1a**-d_5 and **2a** under standard condition for 100 min



Another intermolecular KIE experiment was performed by treating 1.2 equiv of **1a**, 1.2 equiv of **1a-*d*$_5$**, and 1.0 equiv of **2a** under the standard conditions in one pot for 100 min. The KIE was also determined to be $k_{H/D}$ = 1.6.



V References

[1] (a) H. M. Petrassi, K. B. Sharpless, J. W. Kelly,*Org. Lett.*2001, **3**, 139; (b) N. Takeda, O. Miyata, T. Naito,*Eur. J. Org. Chem.*2007, 1491; (c) D. Tang, Y. Gai, A.Polemeropoulos, Z. Chen, Z. Wang, *Bioorg. Med. Chem. Lett.*2008, **18**, 5078.

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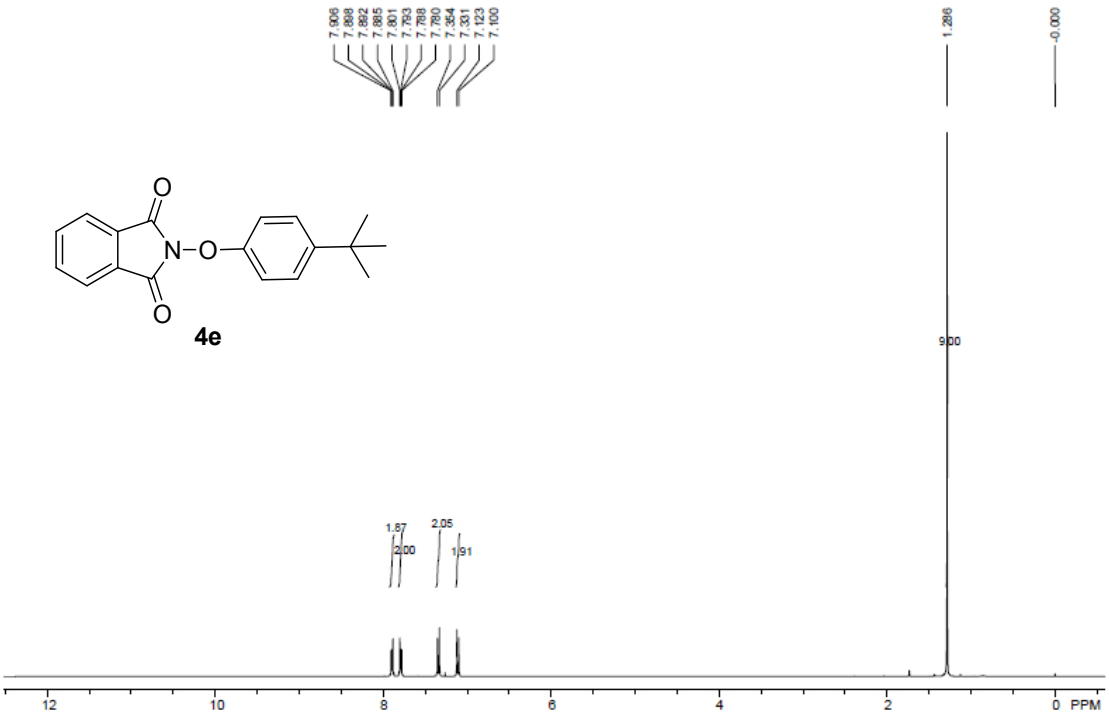
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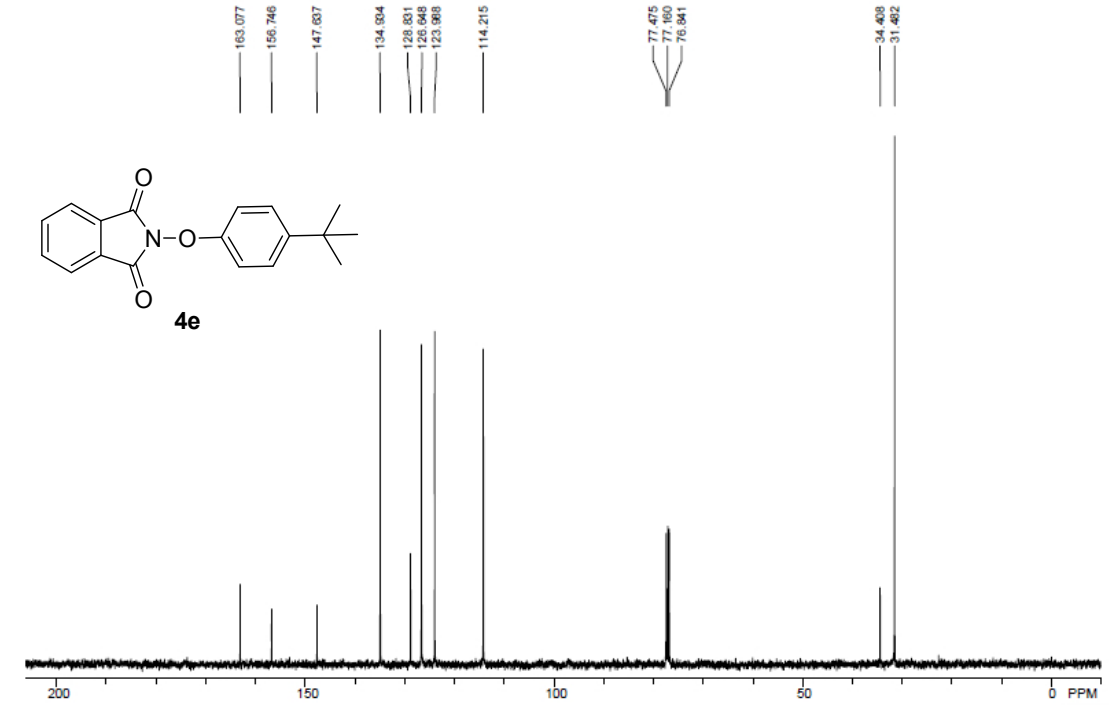
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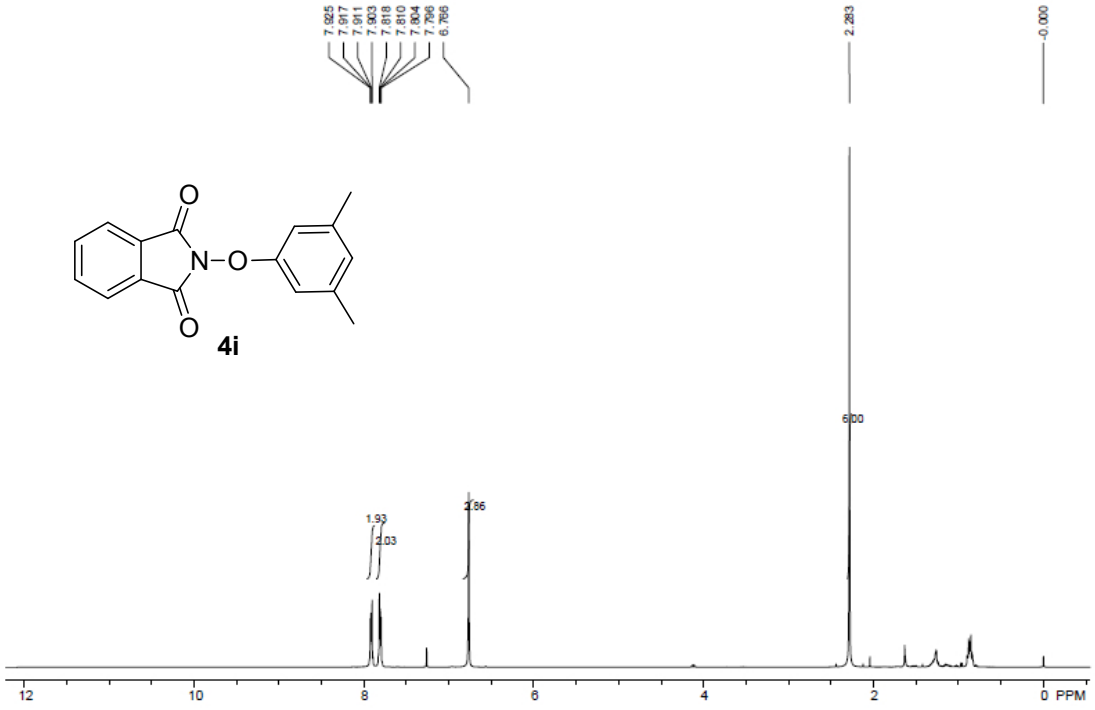
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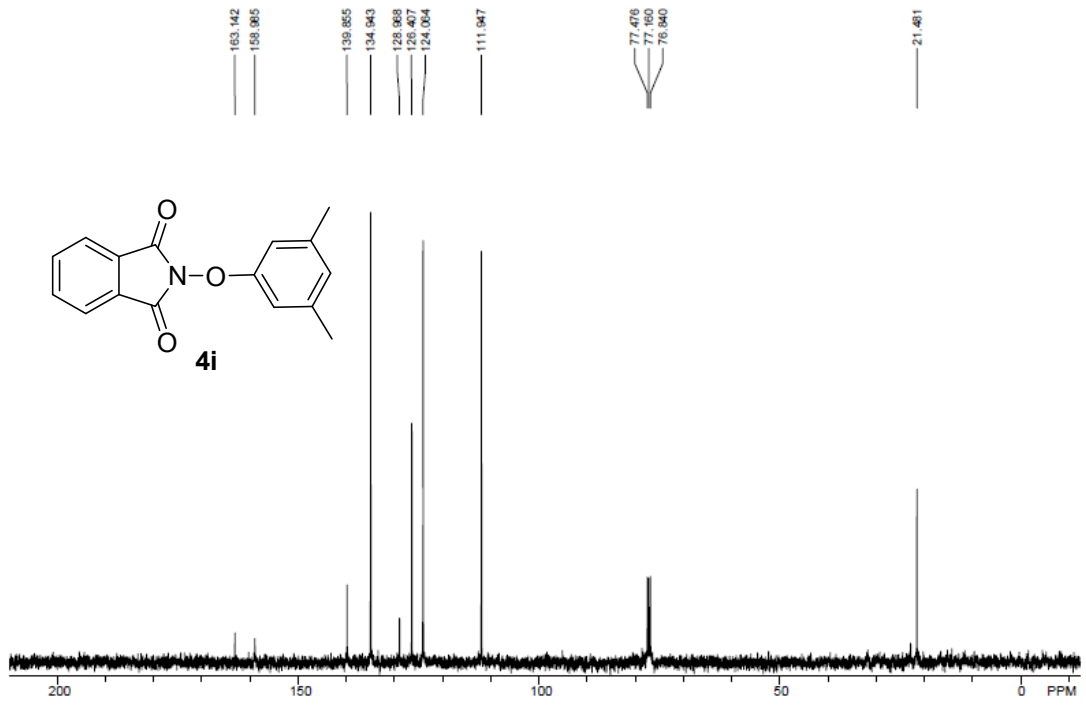
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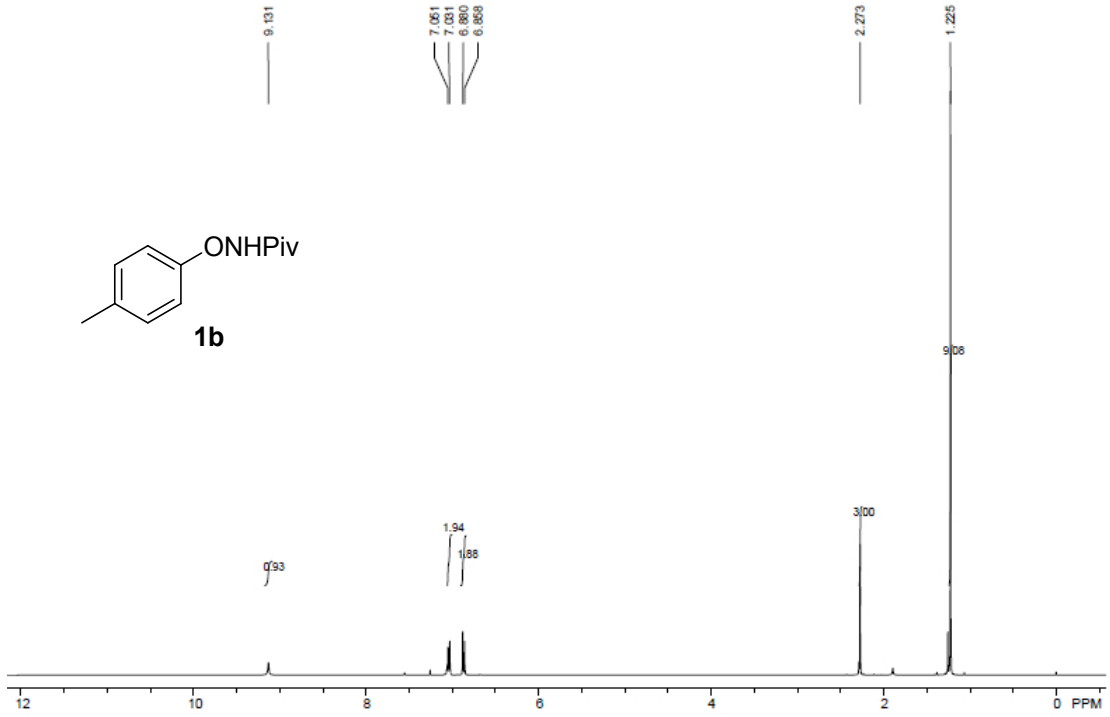
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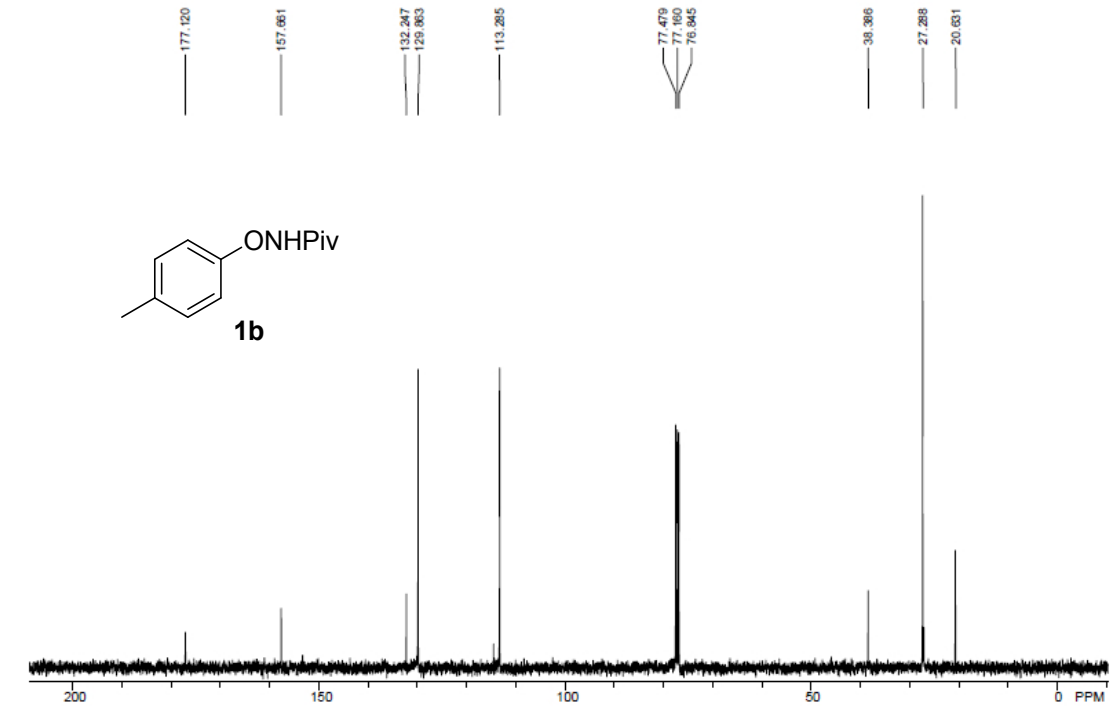
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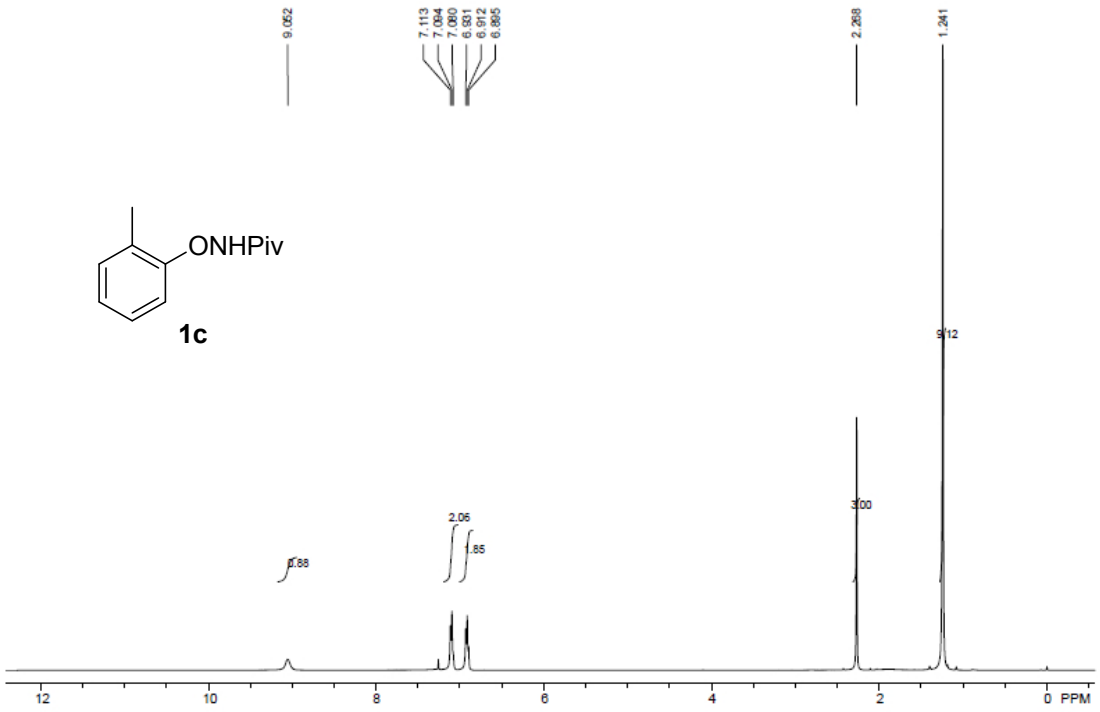
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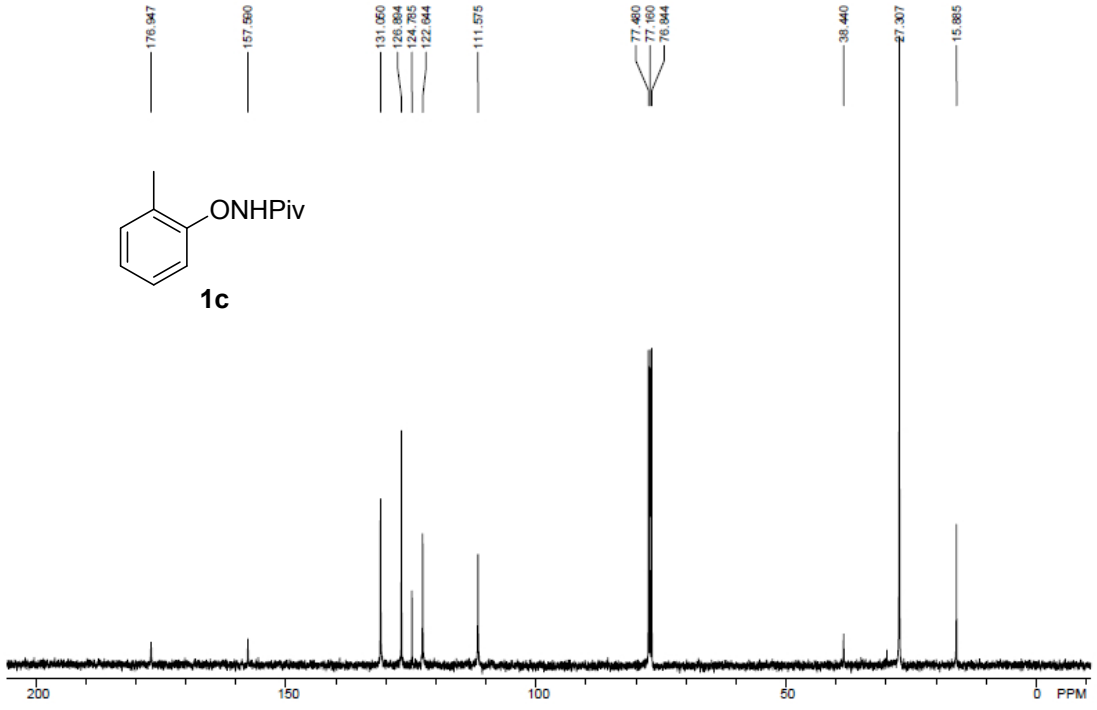
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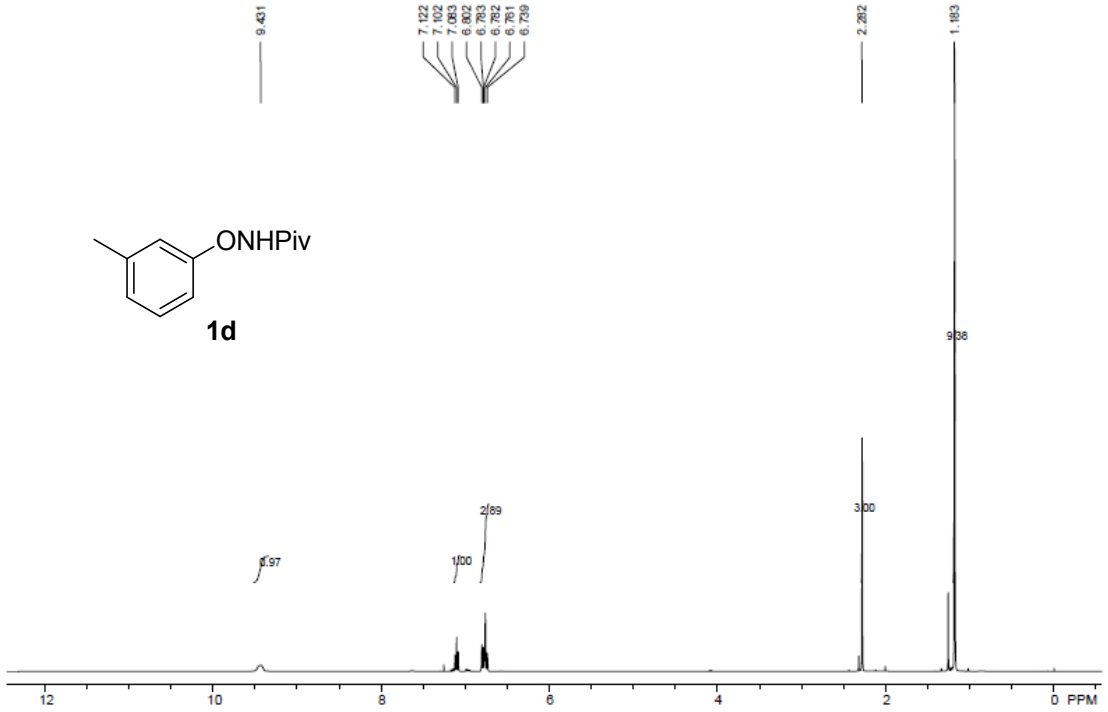
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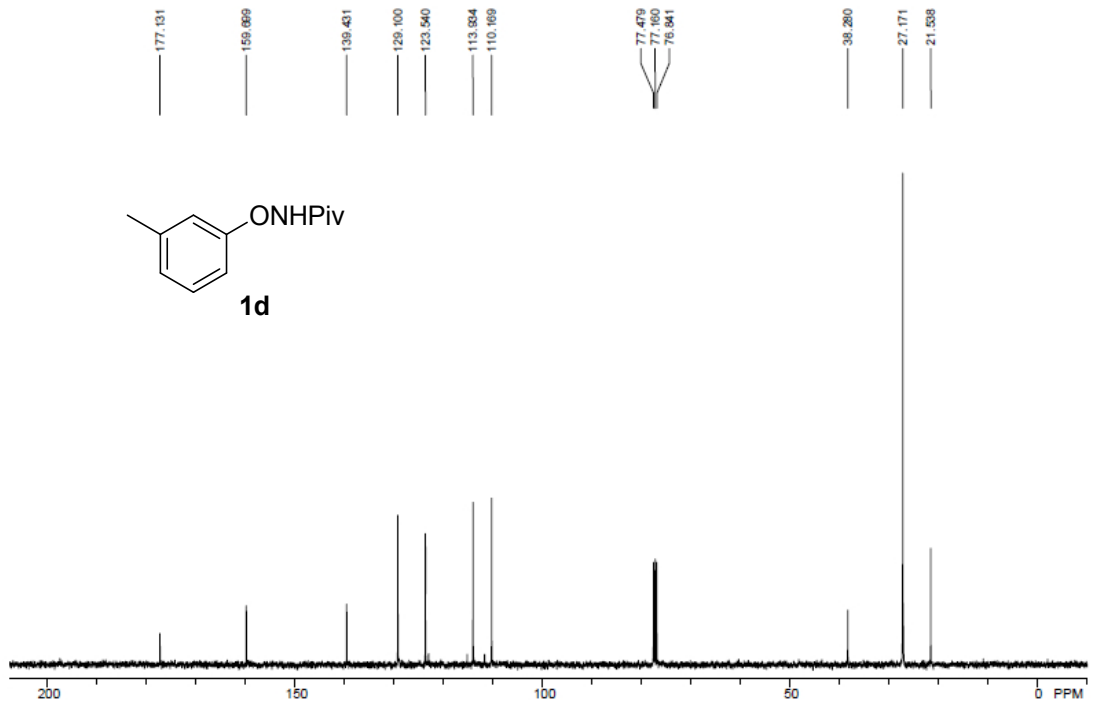
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76.841
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27.171
21.538
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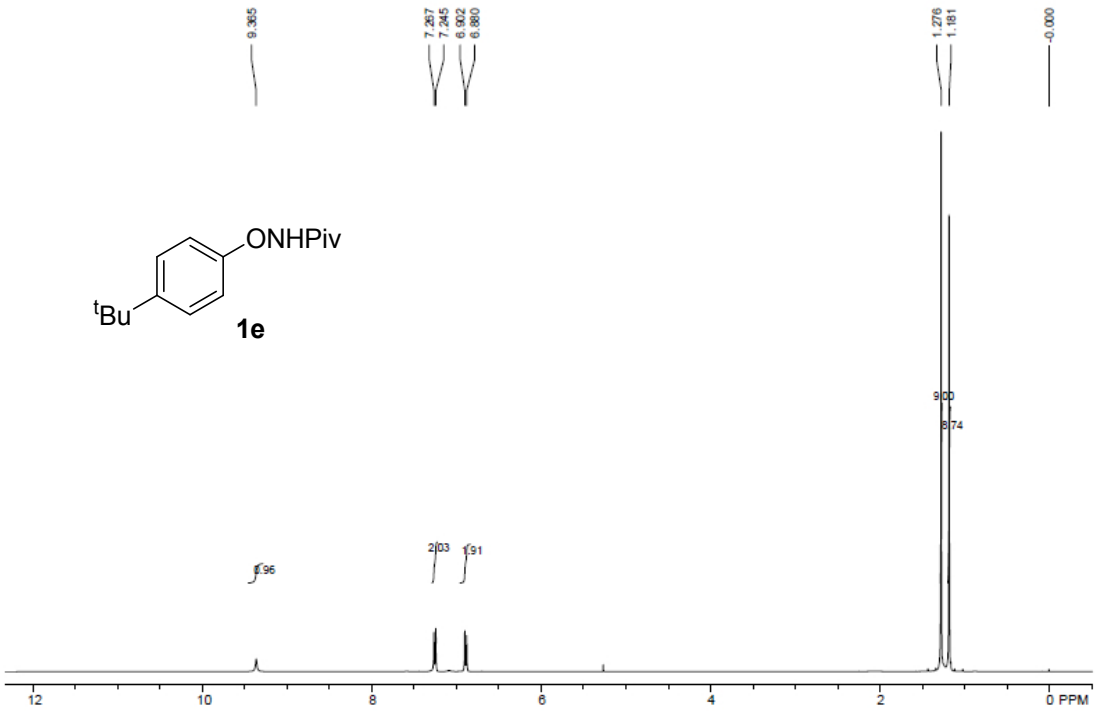
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1.181
-0.000
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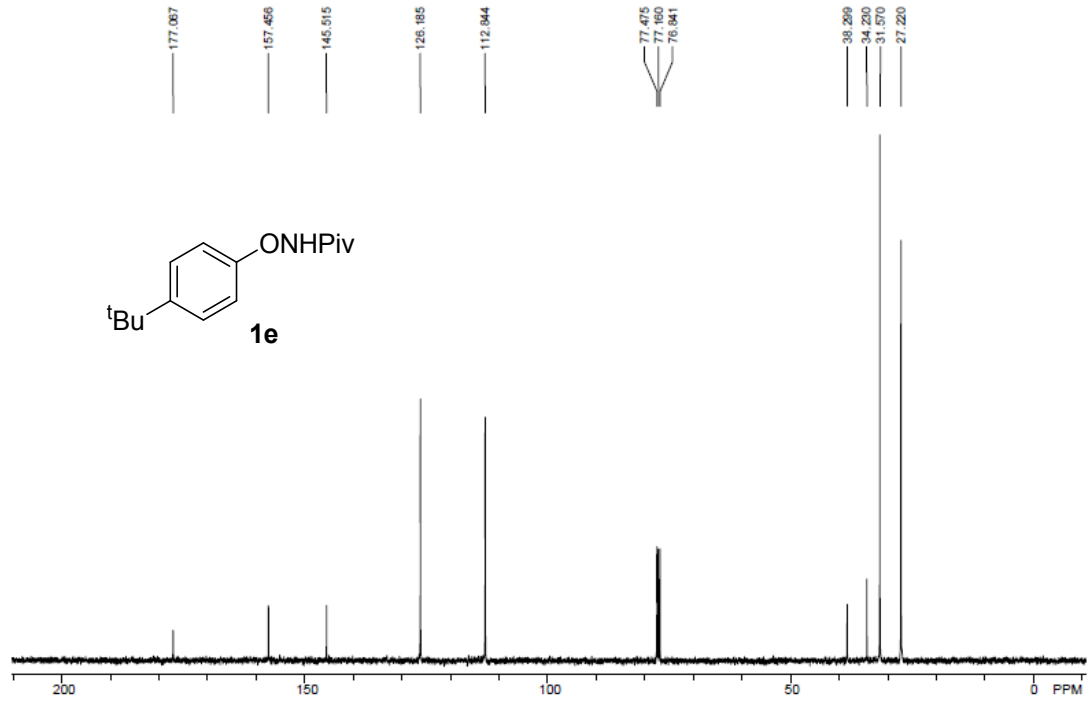
0 PPM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76.841
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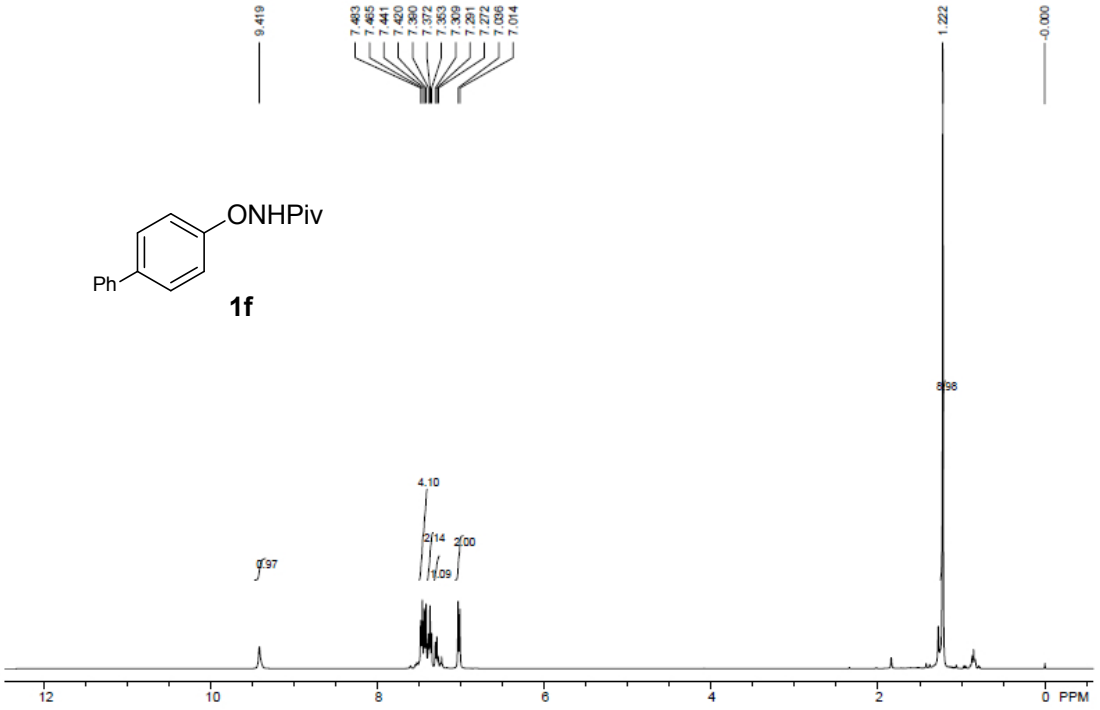
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7.380
7.372
7.353
7.309
7.291
7.272
7.036
7.014
1.222
-0.000
ONHPiv
Ph
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12
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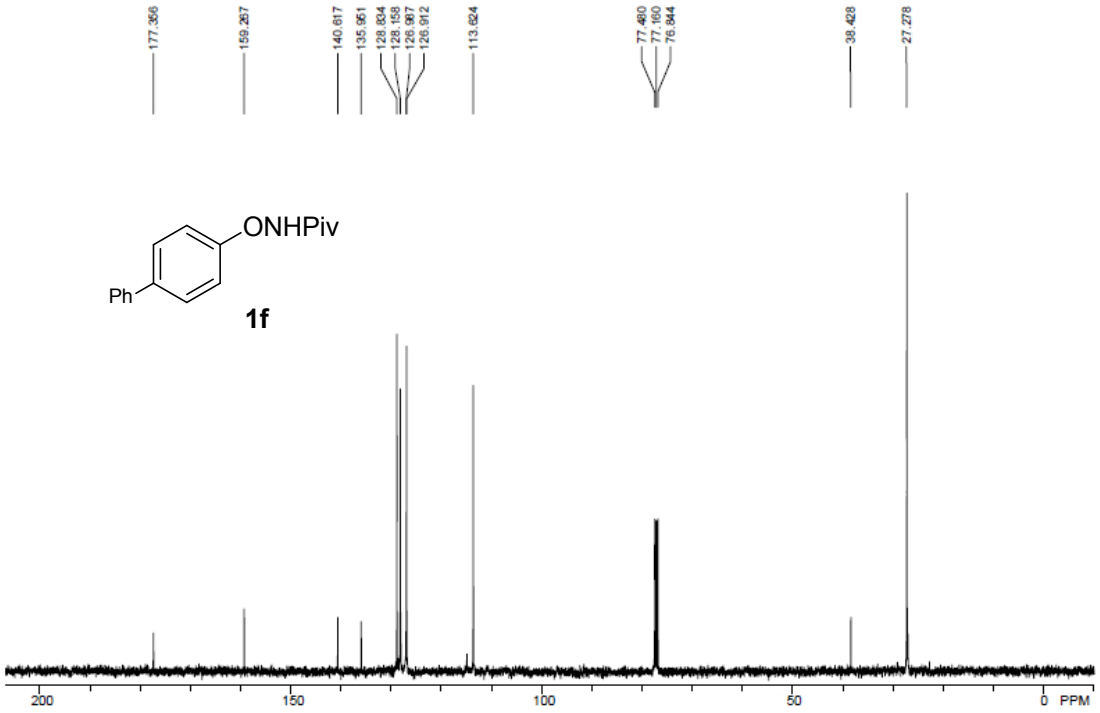
0 PPM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126.987
126.912
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Ph
1f
200
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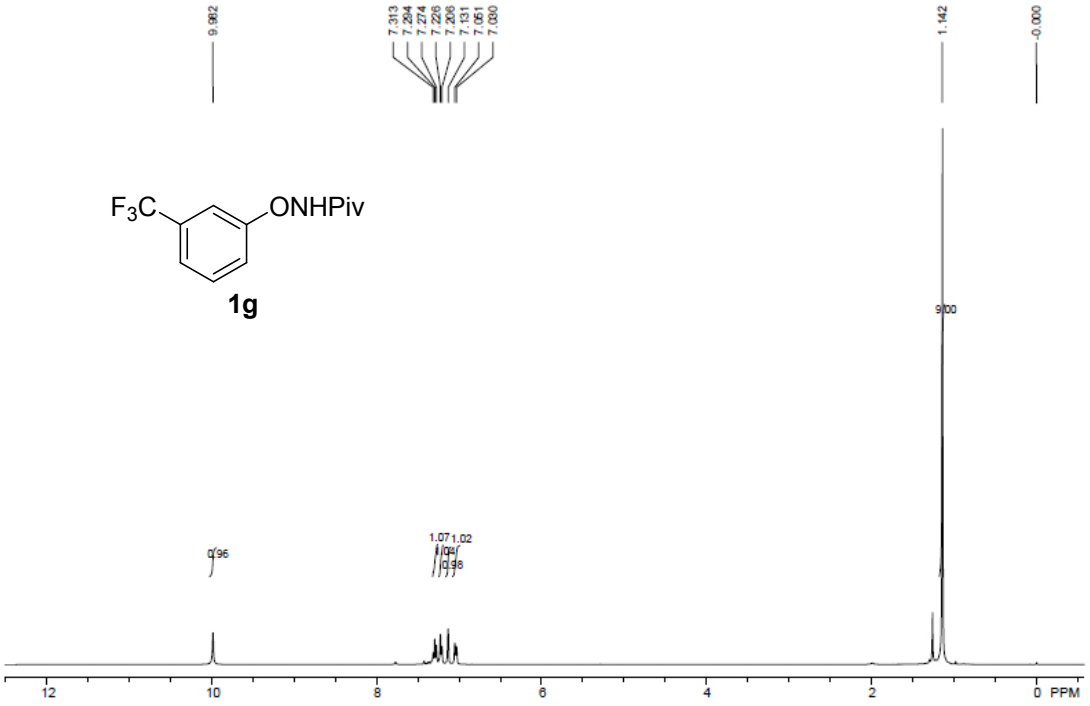
100
50
0 PPM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7.226
7.206
7.151
7.061
7.030
1.142
0.000
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12
10
8
6
4
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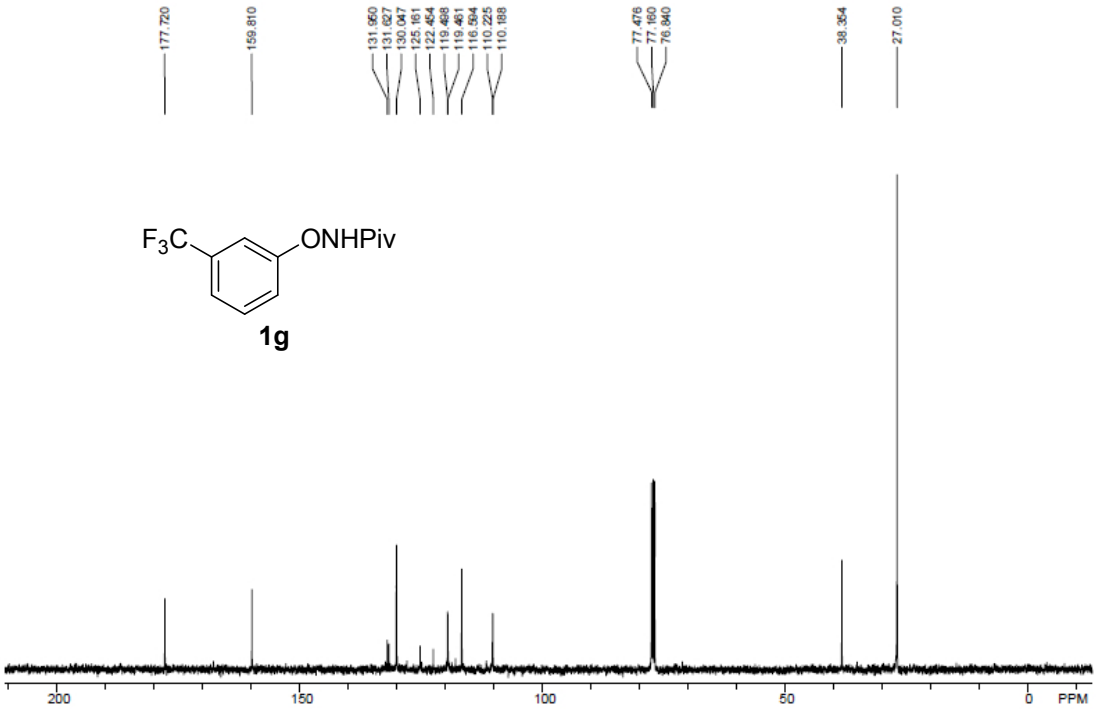
0 PPM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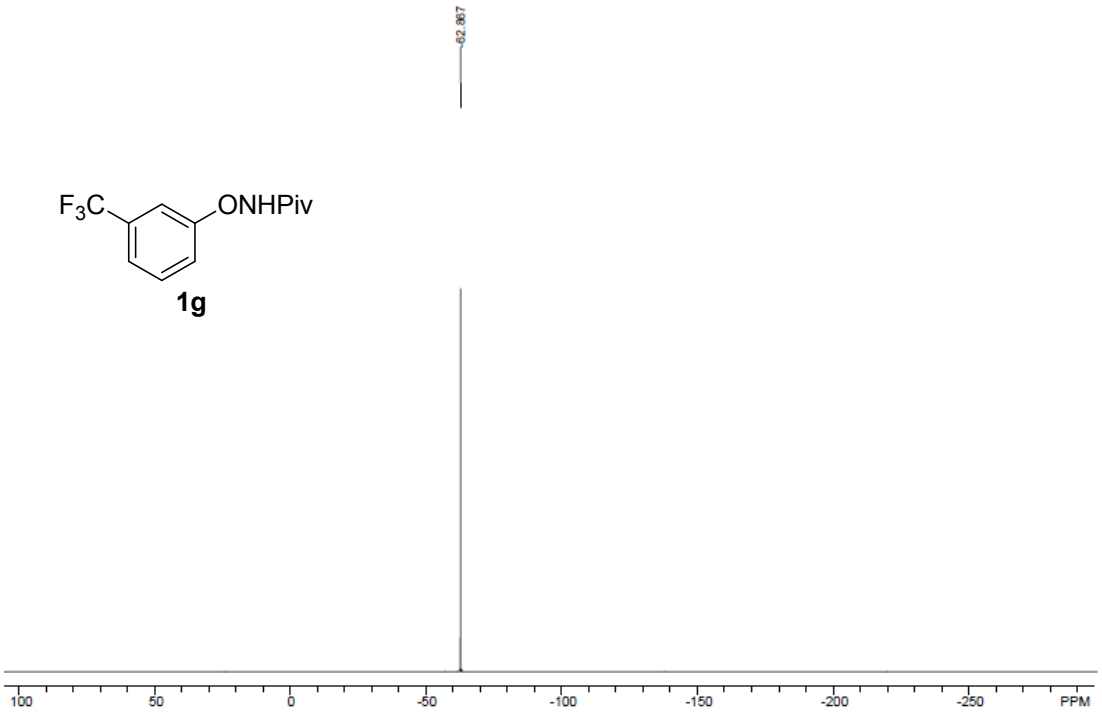
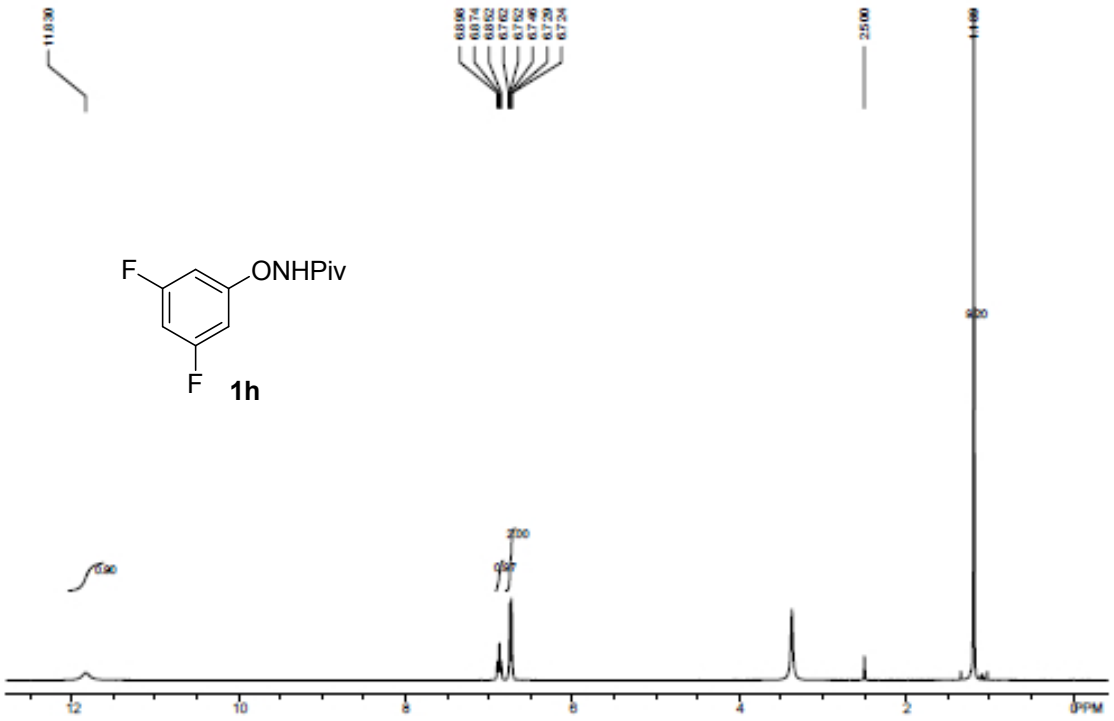
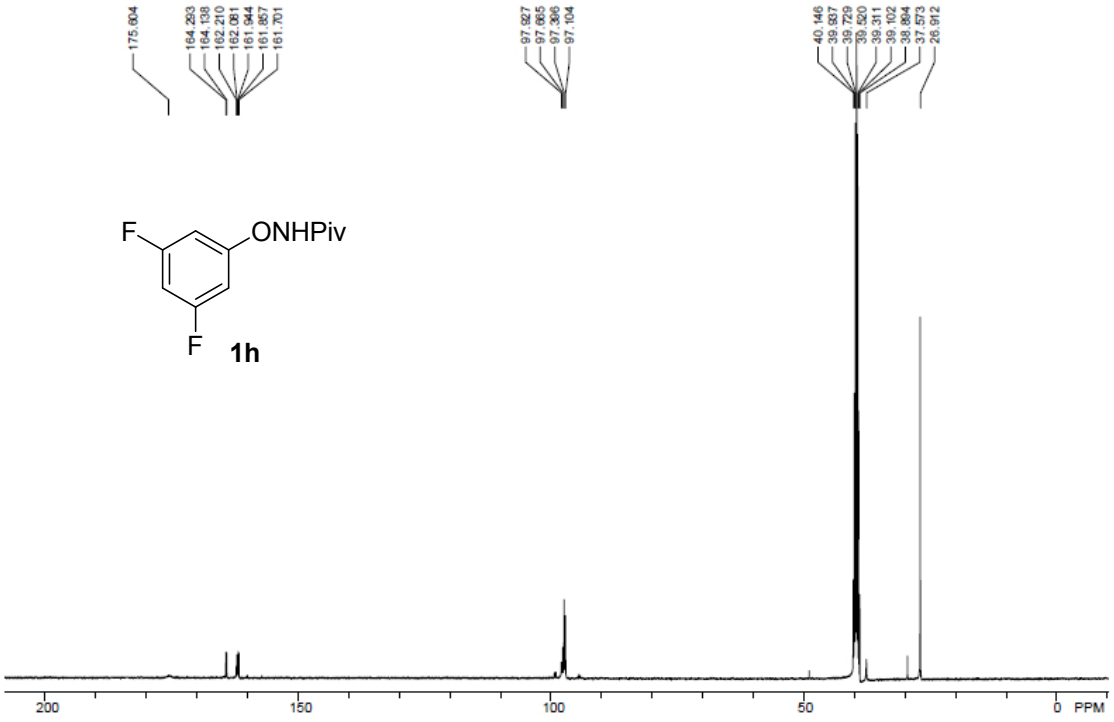
131.627
130.047
125.161
122.454
119.498
119.461
116.594
110.225
110.188
77.476
77.160
76.840
38.364
27.010
F3C
ONHPiv
1g
200
150
100
50
0 PPM

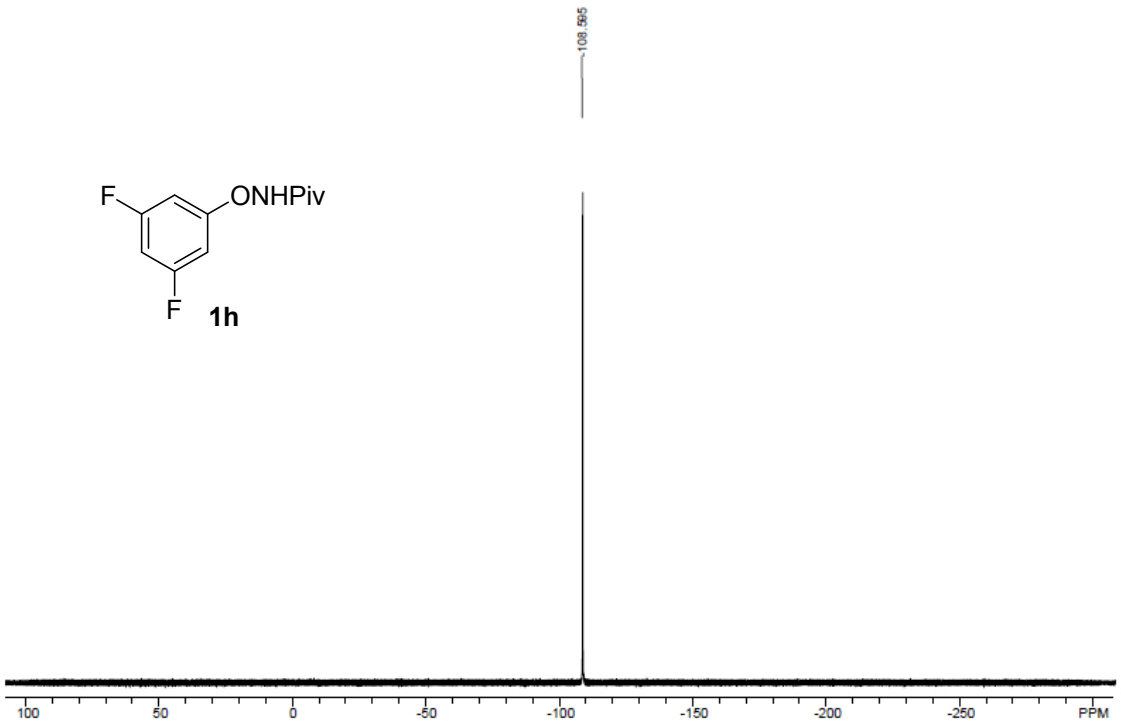
^{19}F Spectra of **1g**

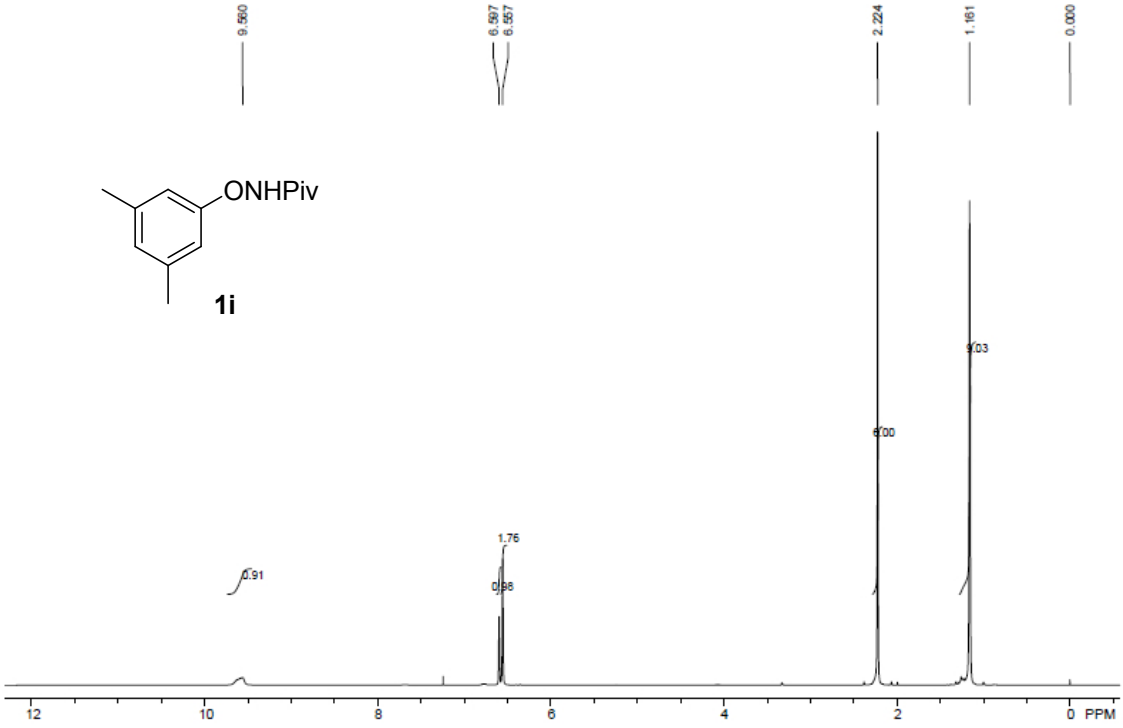



F
ONHPiv
F
1h
12
10
8
6
4
2
0 PPM


F
ONHPiv
F
1h
200
150
100
50
0 PPM

^{19}F Spectra of **1h**

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6.597
6.557
2.224
1.161
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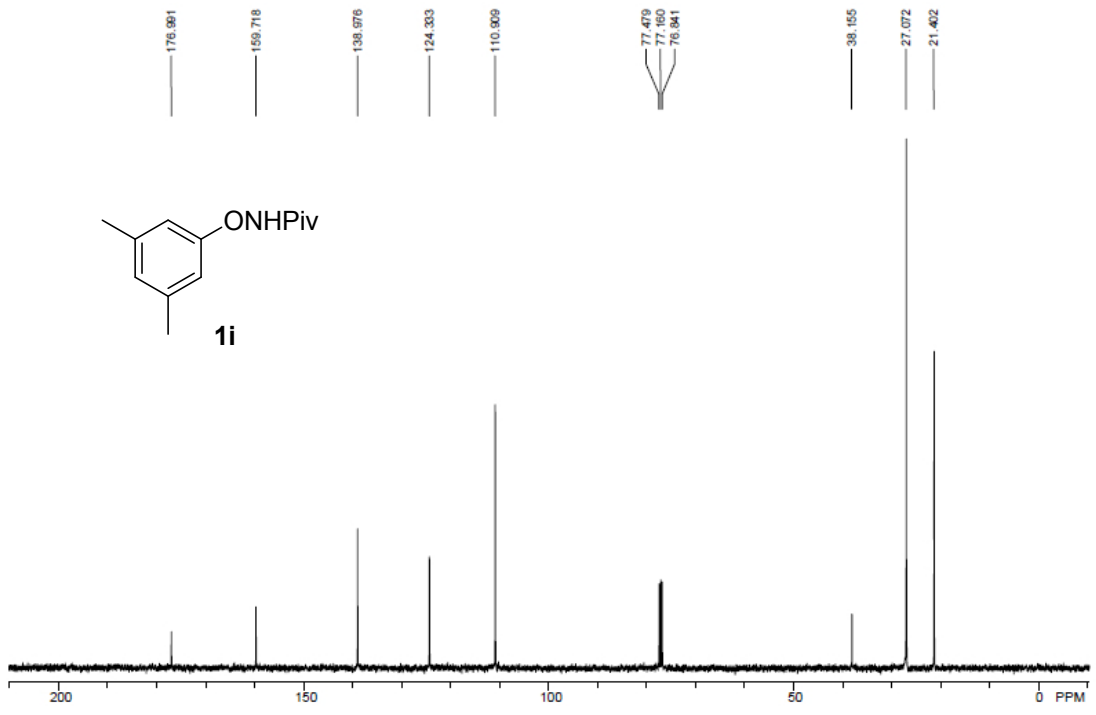
ONHPiv
1i
9.03
6.00
1.76
0.91
0.98
12
10
8
6
4
2
0 PPM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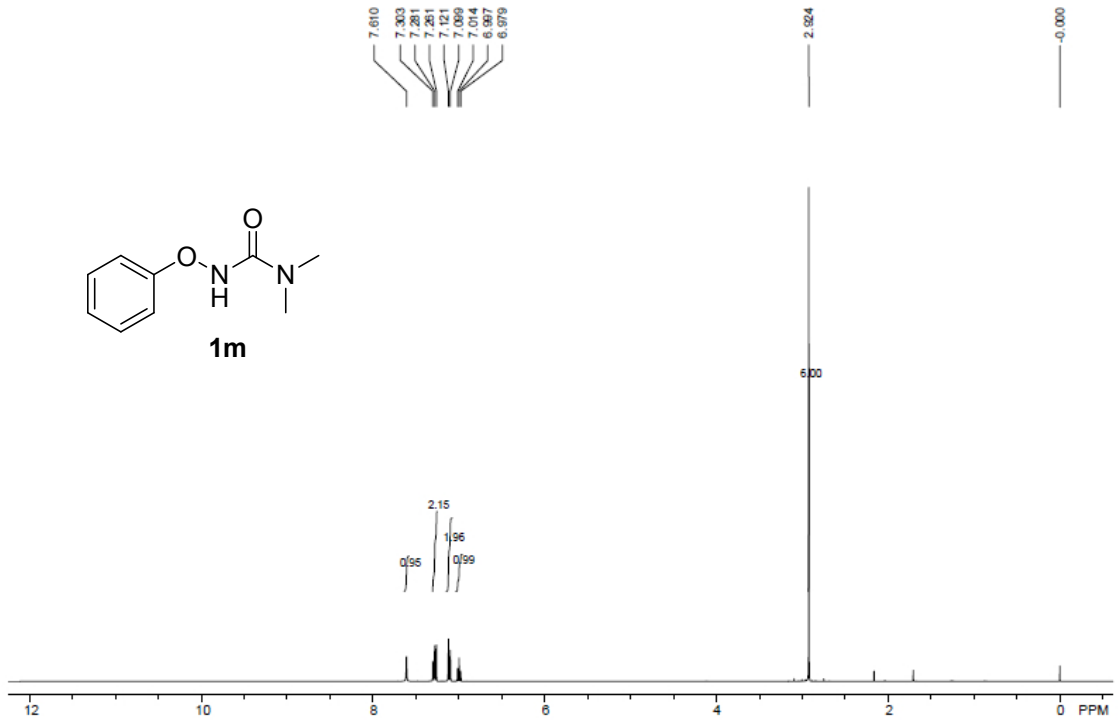
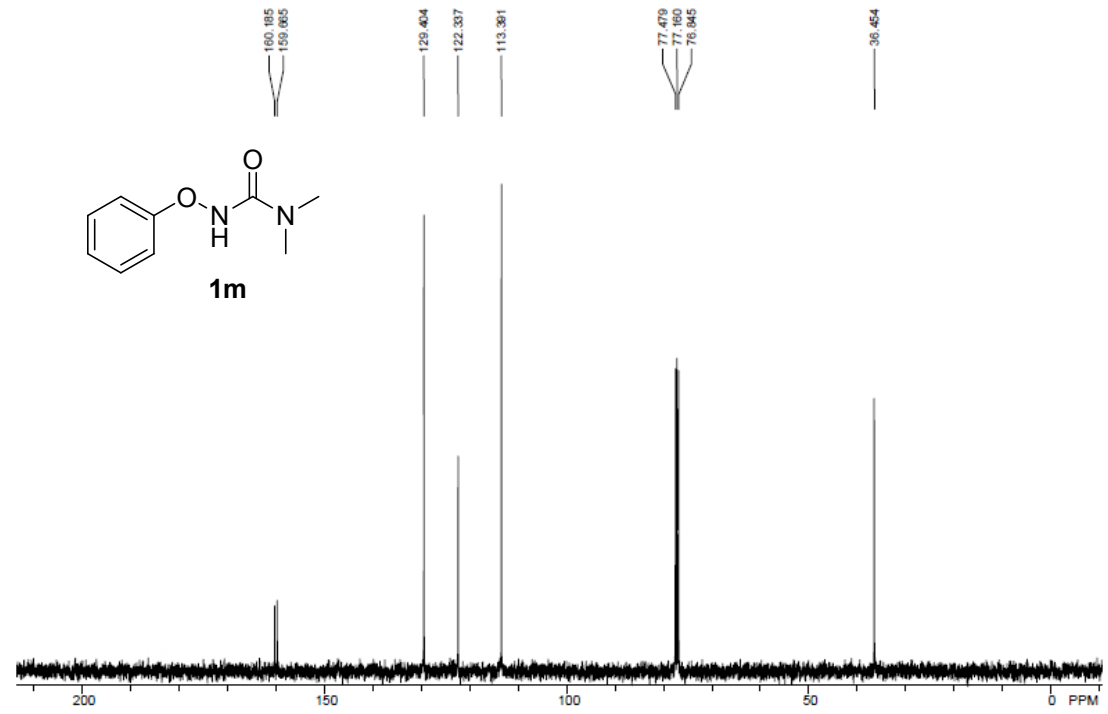
159.718
138.976
124.333
110.909
77.479
77.160
76.841
38.155
27.072
21.402
ONHPiv
1i
200
150
100
50
0 PPM


7.610
7.303
7.281
7.261
7.121
7.069
7.014
6.997
6.979
2.924
-0.000
6.00
2.15
1.96
0.95
0.99
12
10
8
6
4
2
0 PPM

1m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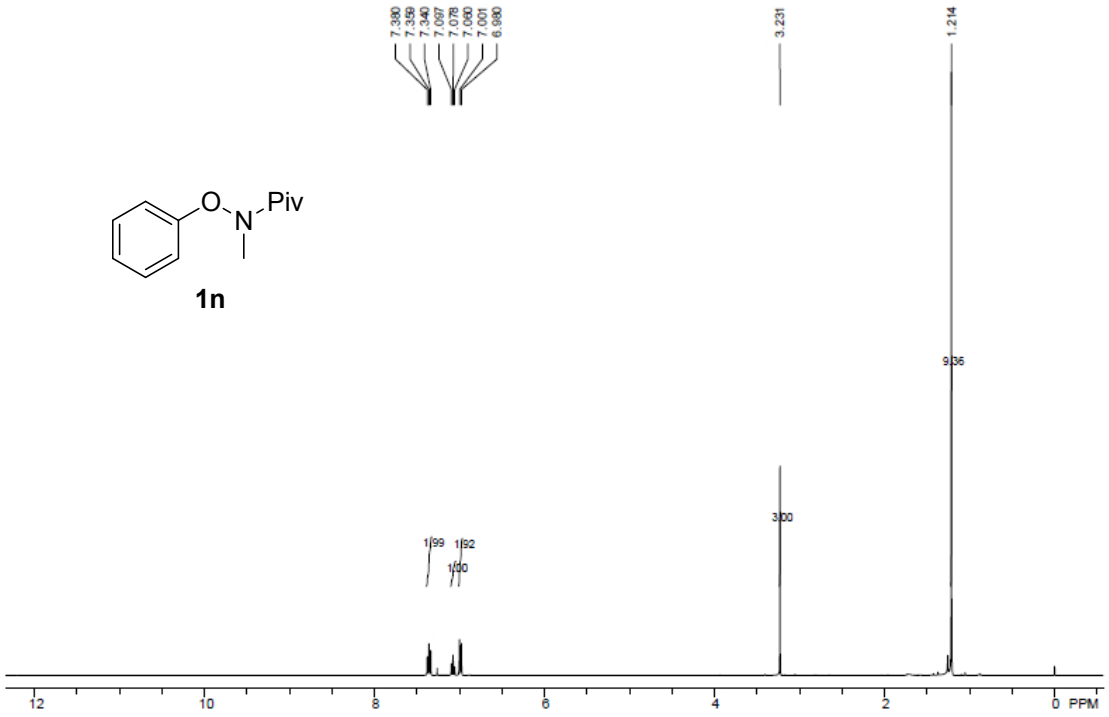
159.665
129.404
122.337
113.361
77.479
77.160
76.845
36.454
200
150
100
50
0 PPM

1m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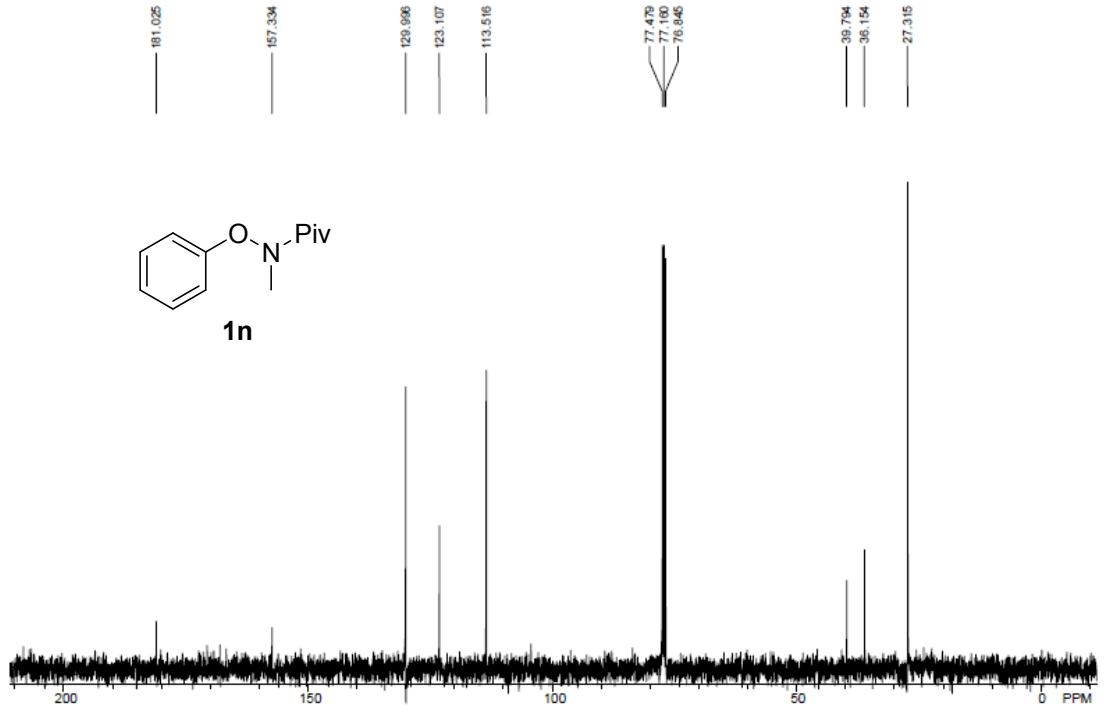
7.359
7.340
7.097
7.078
7.060
7.001
6.990
3.231
1.214
9.36
3.00
1.99
1.92
1.00
O
N
Piv
1n
12
10
8
6
4
2
0 PPM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157.334
129.996
123.107
113.516
77.479
77.160
76.845
39.794
36.154
27.315
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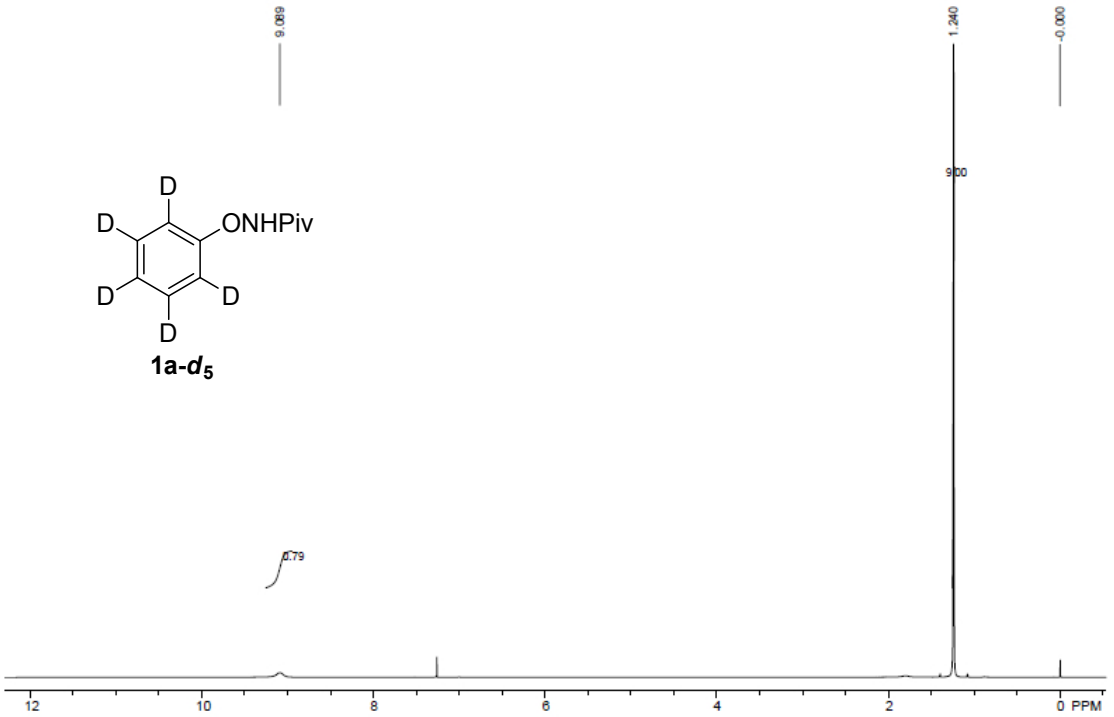
N
Piv
1n
200
150
100
50
0 PPM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1.240
-0.000
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D
ONHPiv
D
D
D
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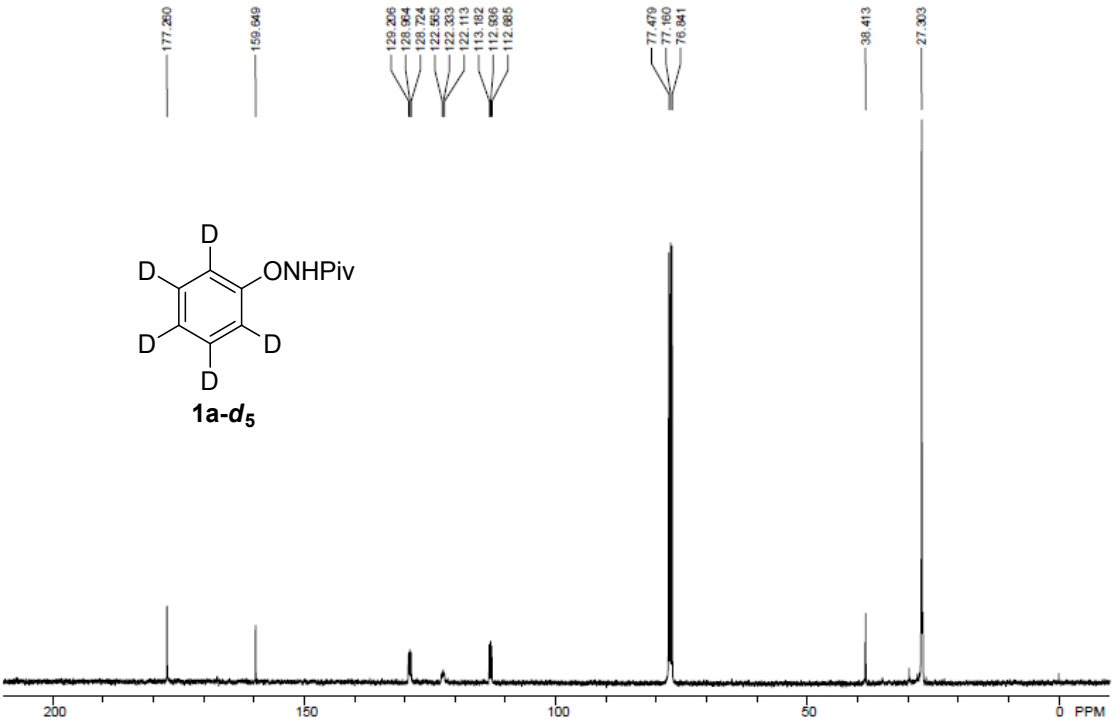
10
8
6
4
2
0 PPM

1a-d_5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128.964
128.724
122.565
122.333
122.113
113.182
112.896
112.685
77.479
77.160
76.841
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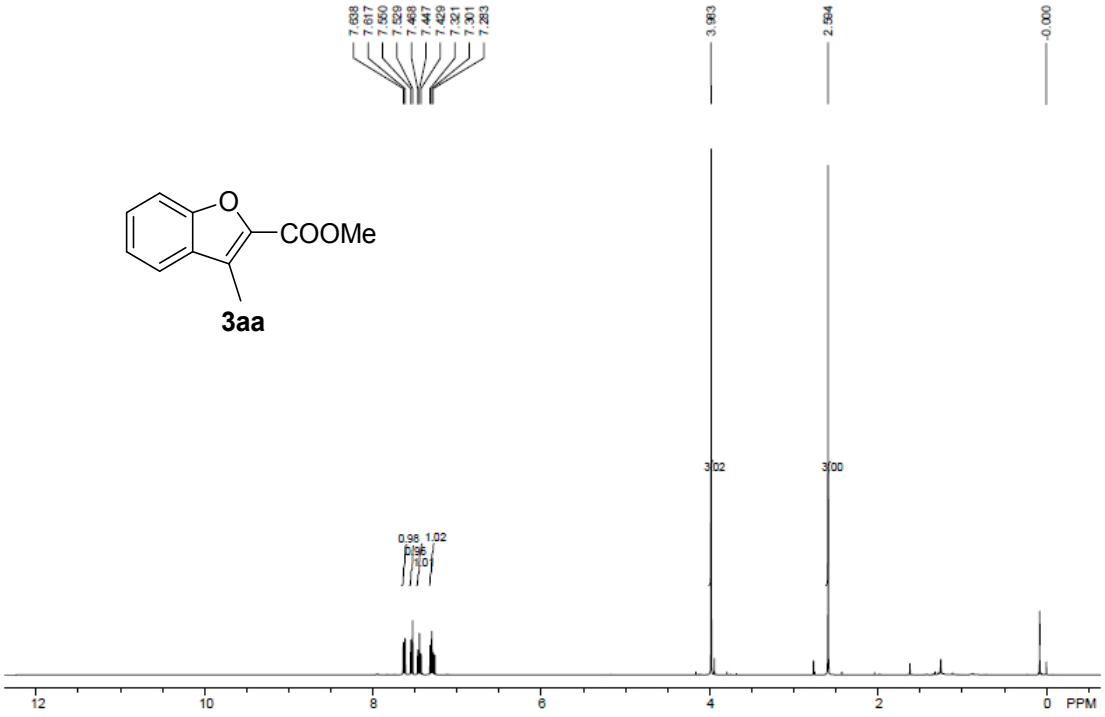
D
D
ONHPiv
D
D
D
200
150
100
50
0 PPM

1a-d_5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7.468
7.447
7.429
7.321
7.301
7.283
3.983
2.594
-0.000
O
COOMe
3aa
3.02
3.00
0.98
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0.96
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2
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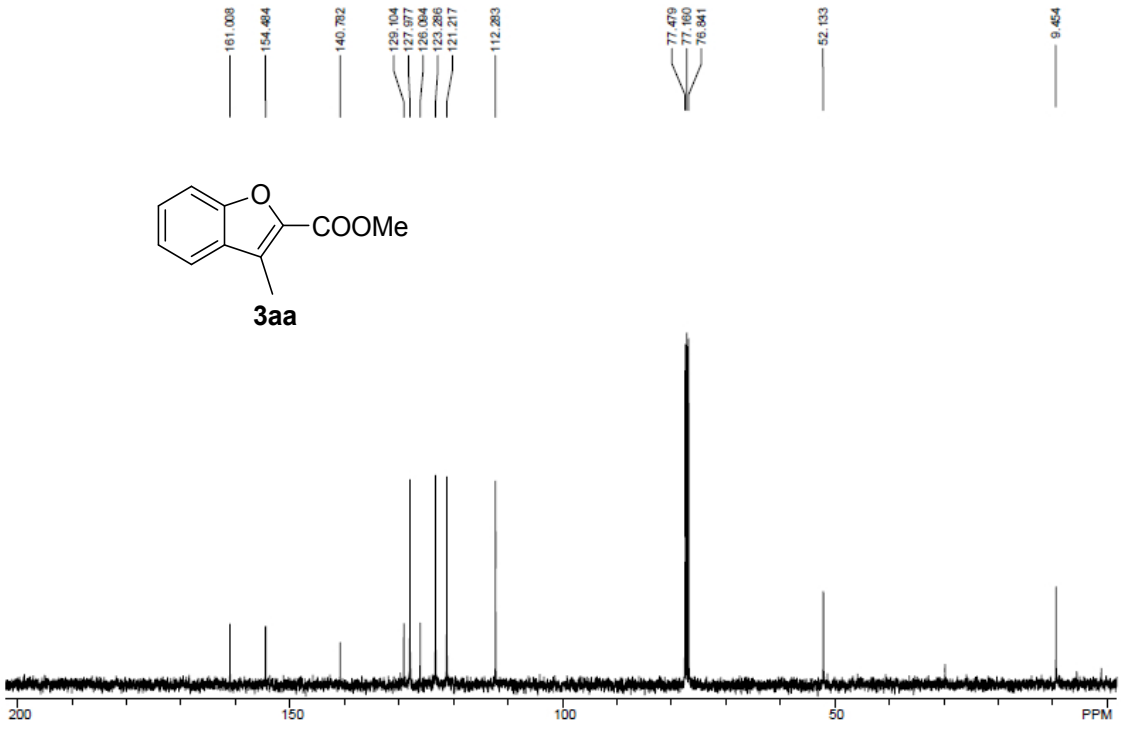
PPM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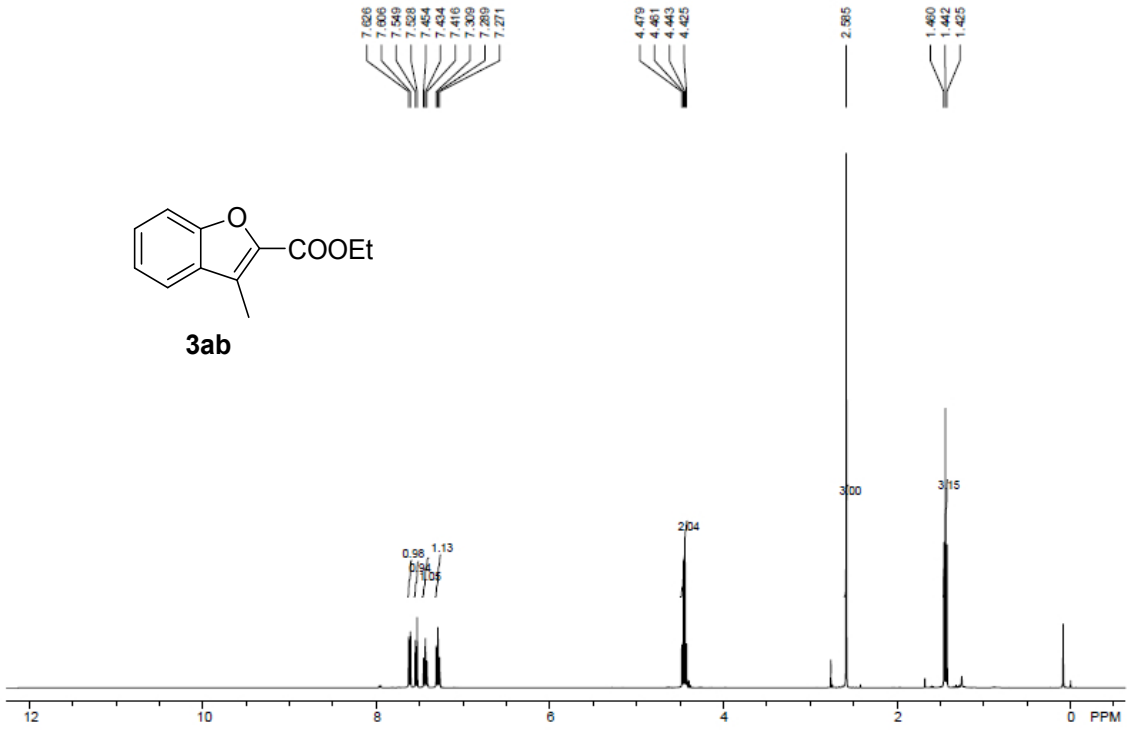
140.782
129.104
127.977
126.094
123.286
121.217
112.283
77.479
77.160
76.841
52.133
9.454
O
COOMe
3aa
200
150
100
50
PPM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7.528
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7.434
7.416
7.309
7.289
7.271
4.479
4.461
4.443
4.425
2.595
1.460
1.442
1.425
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3.00
3.15
12
10
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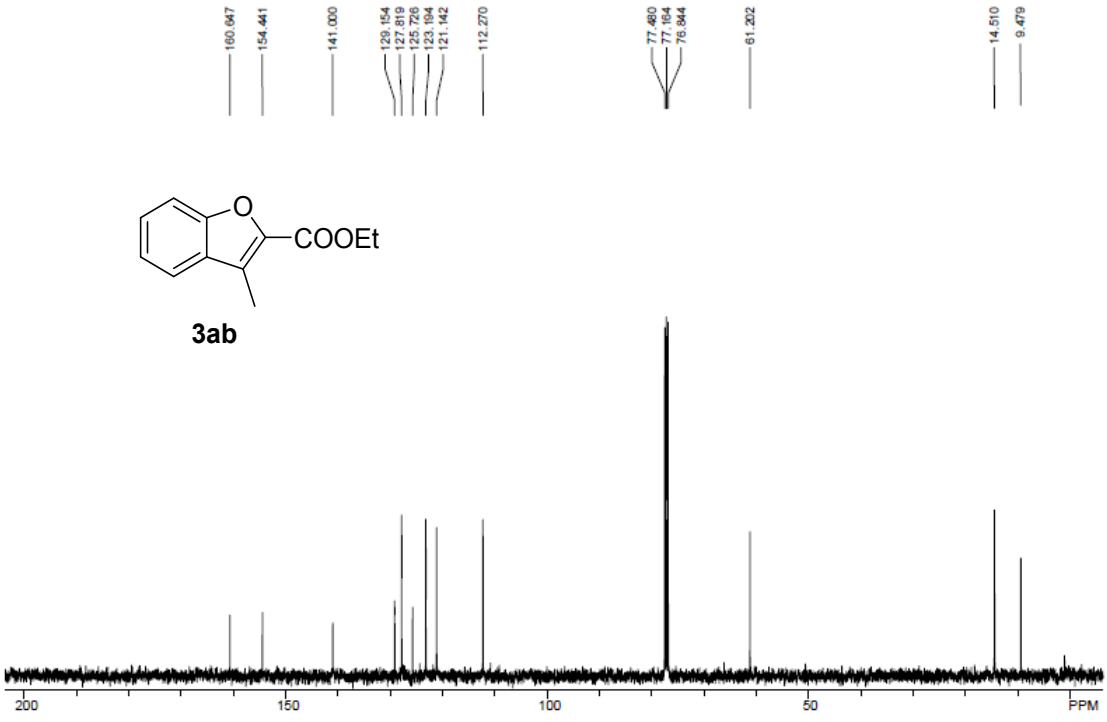
6
4
2
0
PPM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123.194
121.142
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61.202
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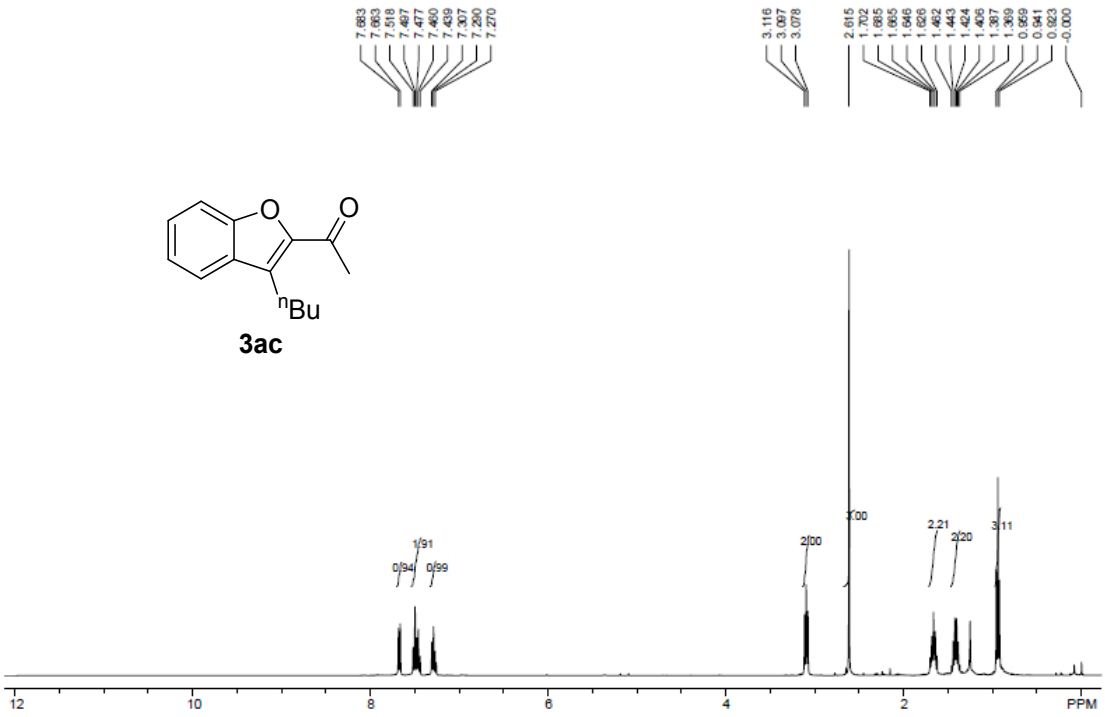
COOEt
3ab
200
150
100
50
PPM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7.460
7.439
7.307
7.290
7.270
3.116
3.097
3.078
2.615
1.702
1.685
1.665
1.646
1.626
1.462
1.443
1.424
1.406
1.387
1.369
0.959
0.941
0.923
-0.000
O
O
nBu
3ac
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0.99
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2.00
3.00
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2.20
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12
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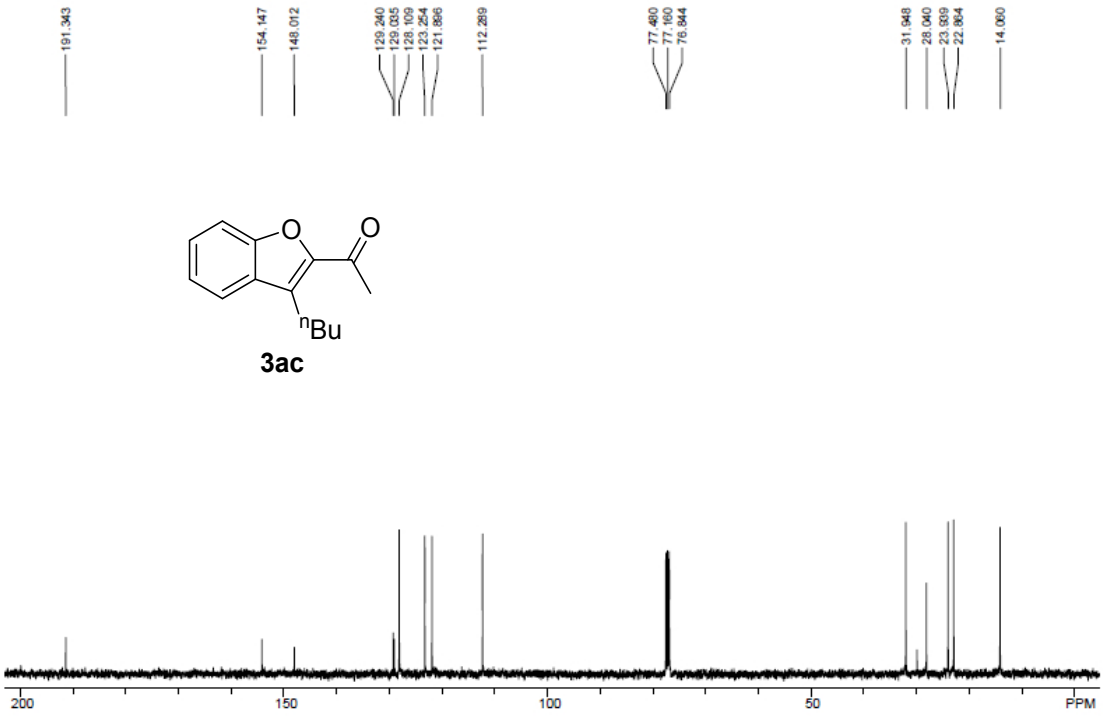
6
4
2
PPM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128.109
123.254
121.896
112.289
77.480
77.160
76.844
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23.939
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nBu
3ac
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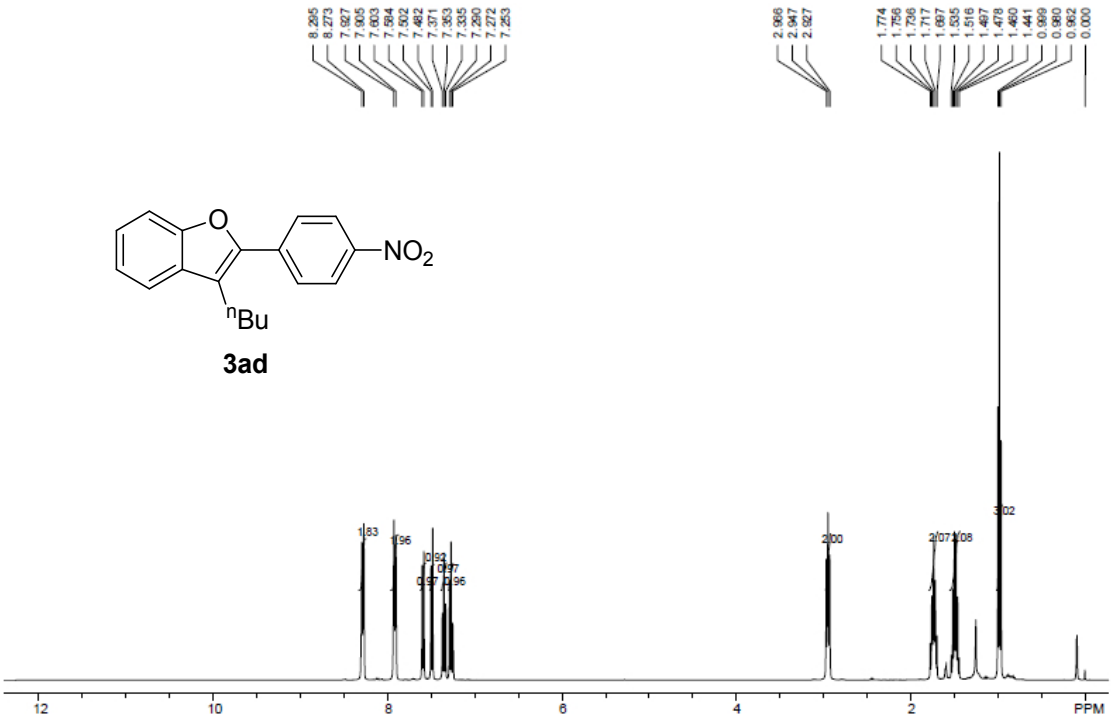
50
PPM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7.353
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7.290
7.272
7.253
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2.927
1.774
1.756
1.736
1.717
1.697
1.535
1.516
1.497
1.478
1.460
1.441
0.999
0.980
0.962
0.000
O
NO2
nBu
3ad
1.83
1.96
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2.07
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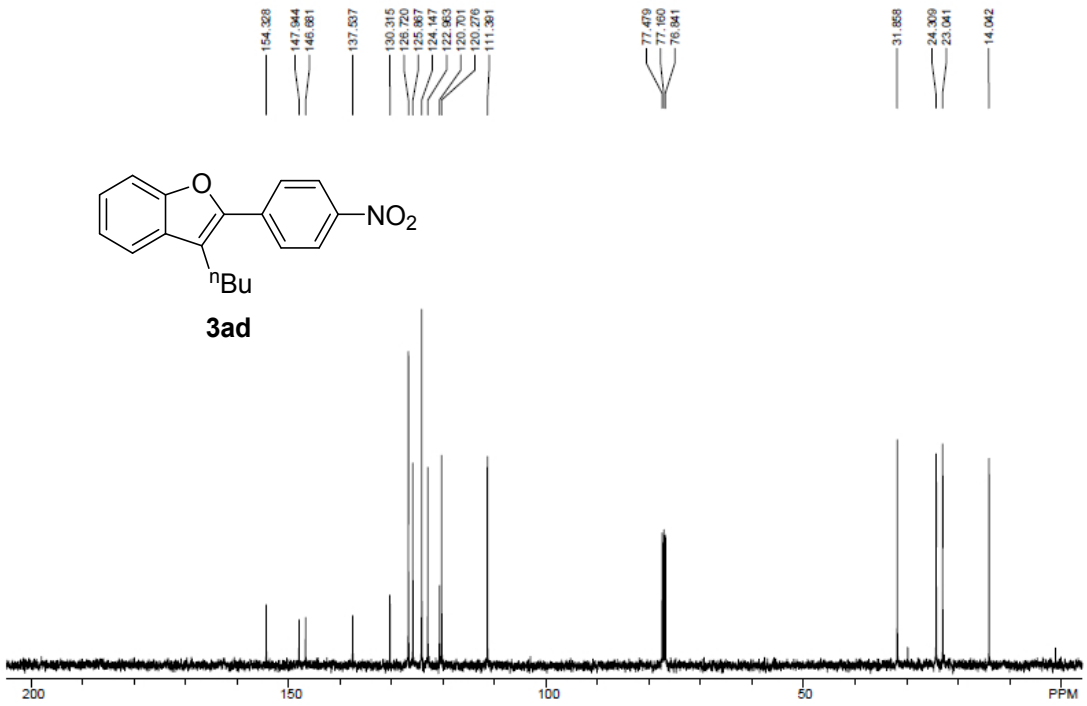
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120.276
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77.479
77.160
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14.042
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NO2
nBu
3ad
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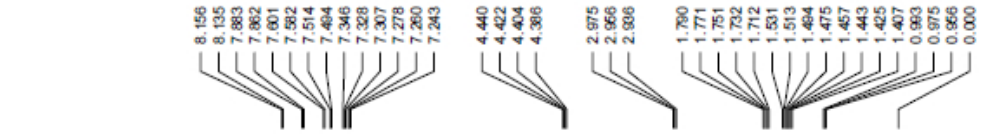
150
100
50
PPM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7.260
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4.404
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1.771
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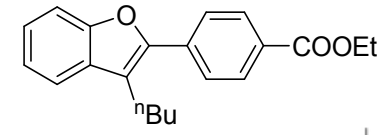
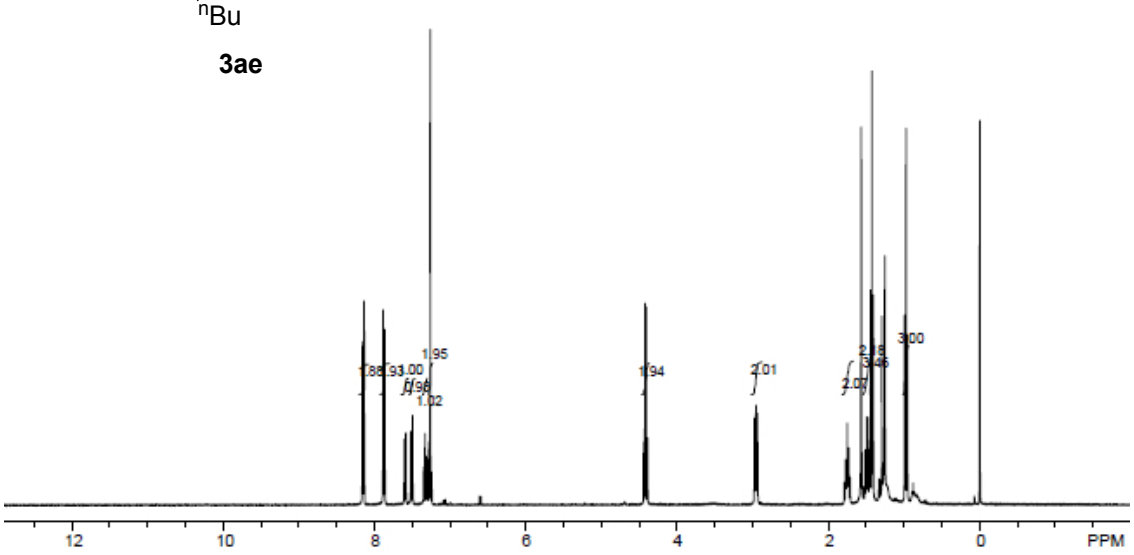

O
COOEt
nBu

3ae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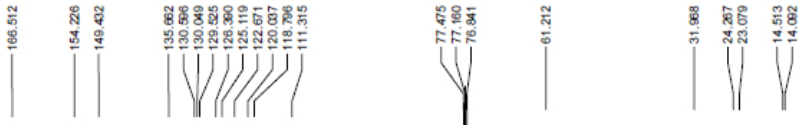
2.07
3.00
12
10
8
6
4
2
0
PPM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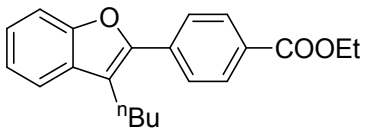
76.841
61.212
31.968
24.267
23.079
14.513
14.092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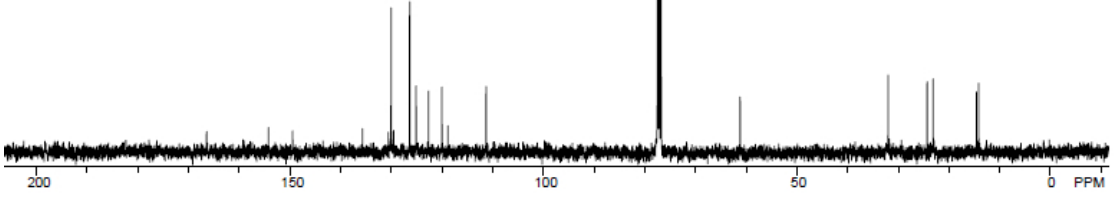
COOEt
nBu

3ae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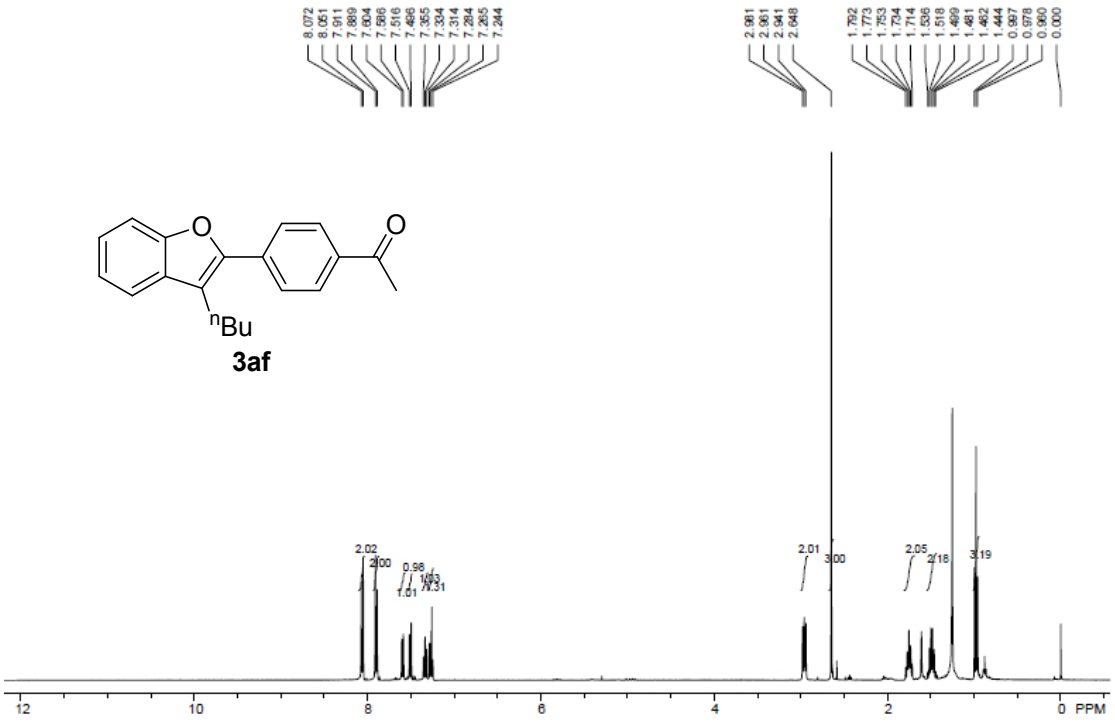
PPM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7.496
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7.265
7.244
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2.961
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2.648
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1.773
1.753
1.734
1.714
1.536
1.518
1.469
1.461
1.462
1.444
0.997
0.978
0.960
0.000
O
O
nBu
3af
2.02
2.00
0.98
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2.01
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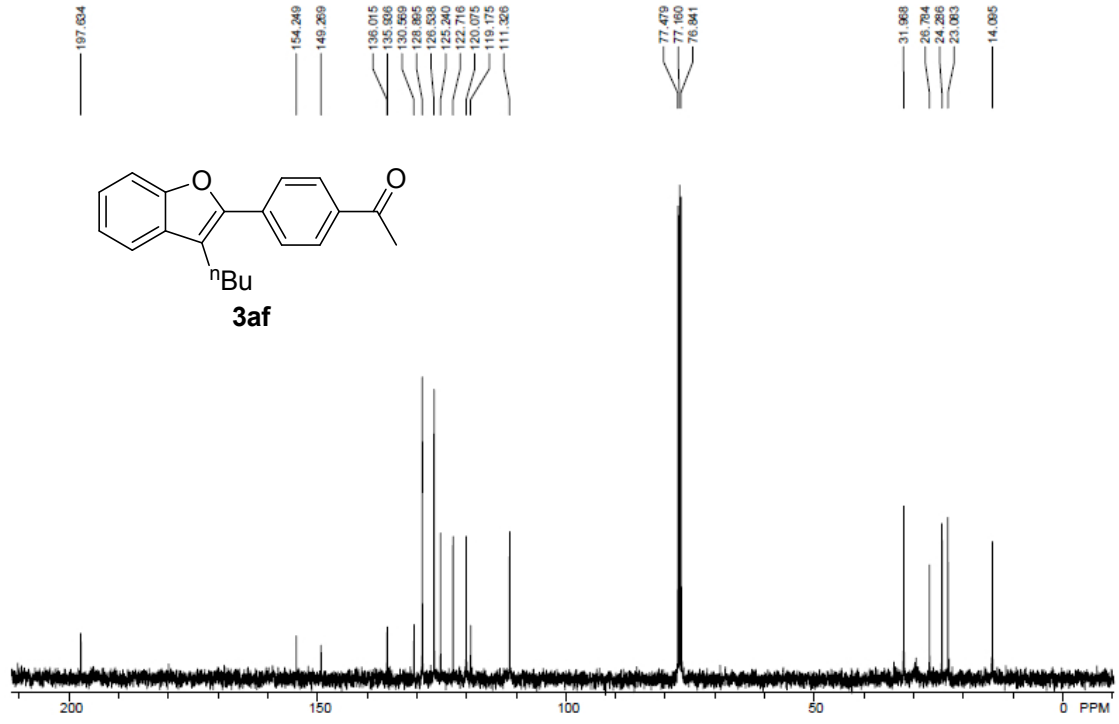
0 PPM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128.895
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122.716
120.075
119.175
111.326
77.479
77.160
76.841
31.968
26.784
24.285
23.063
14.065
O
O
nBu
3af
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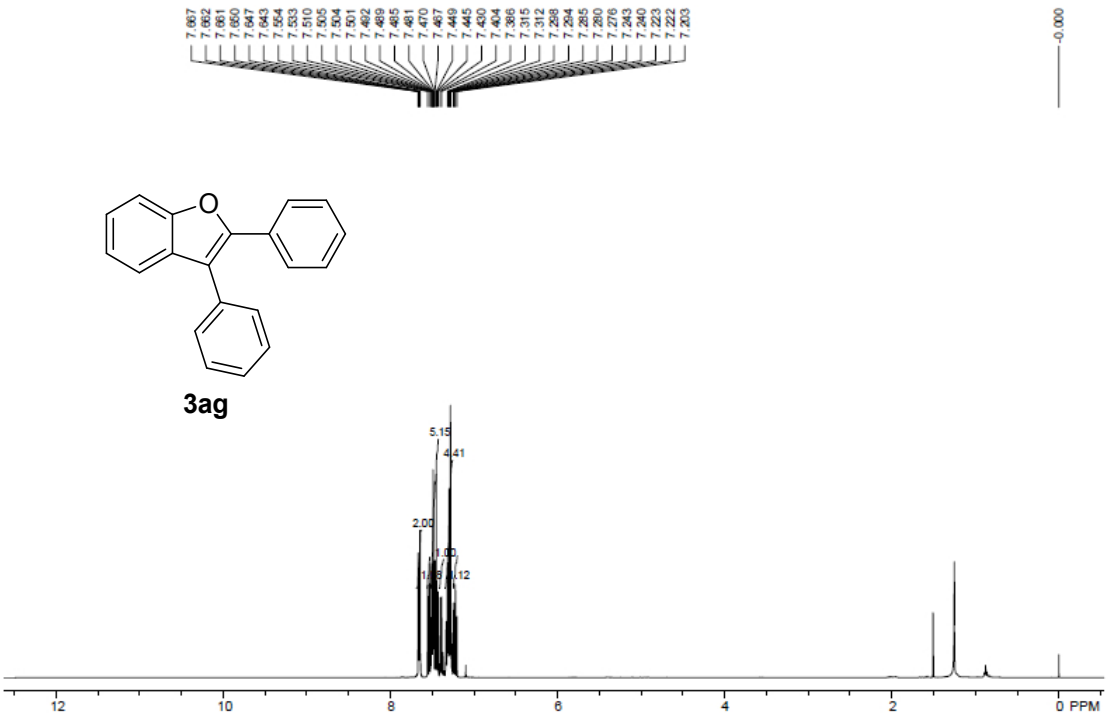
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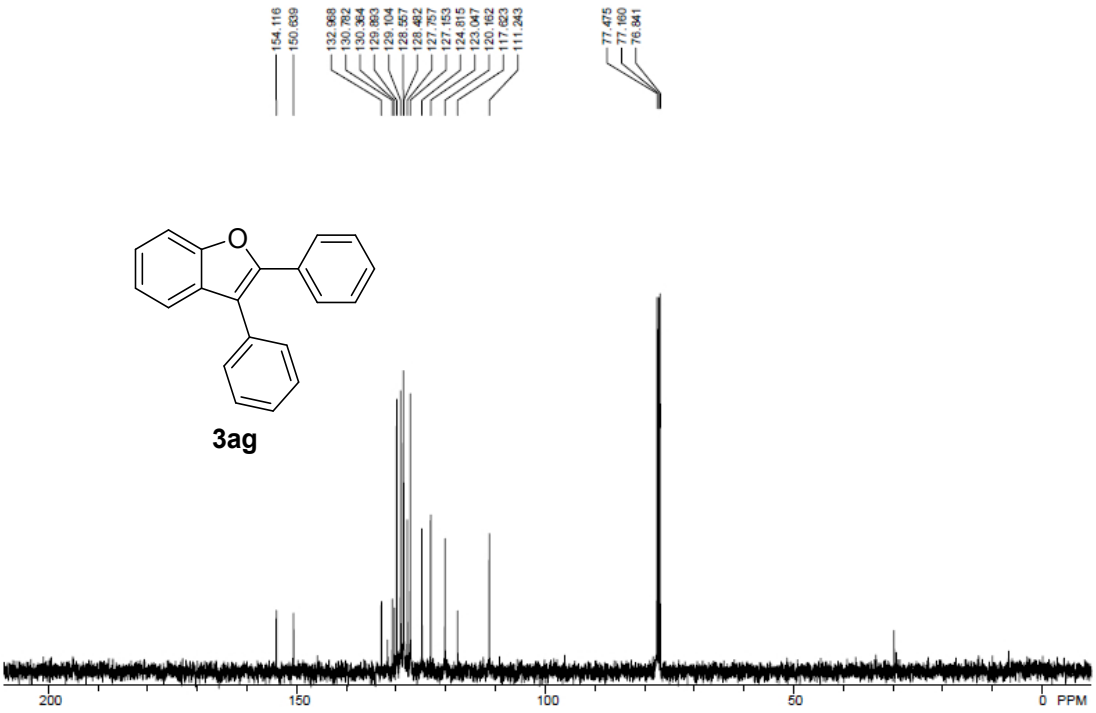
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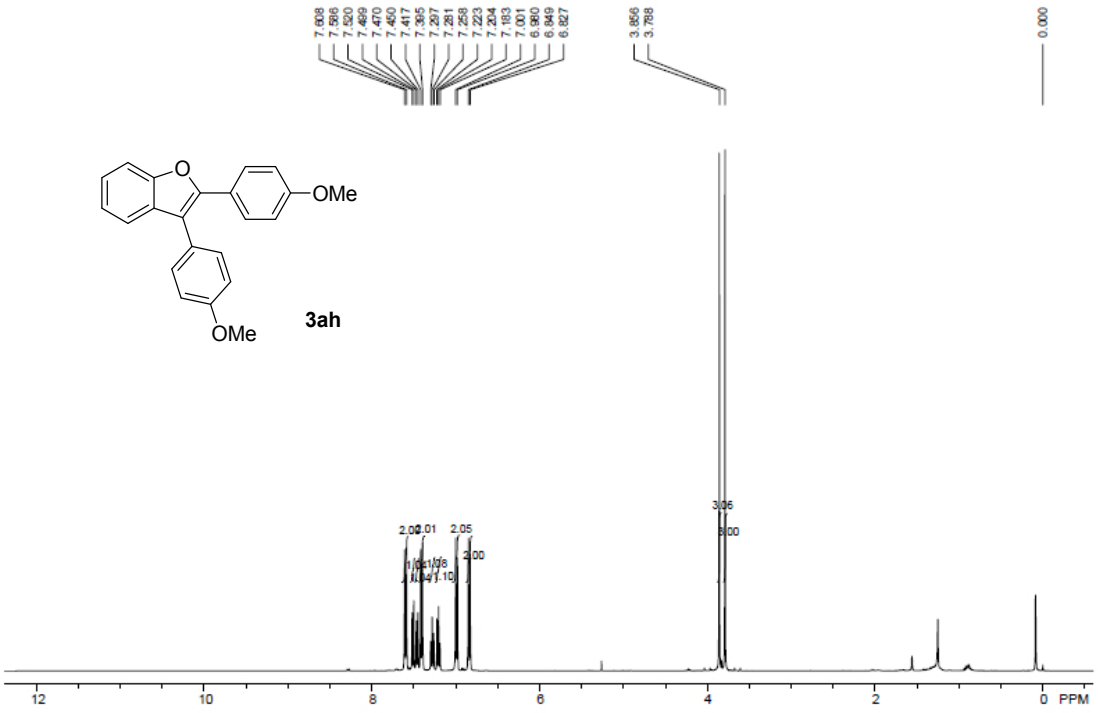
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OMe
OMe
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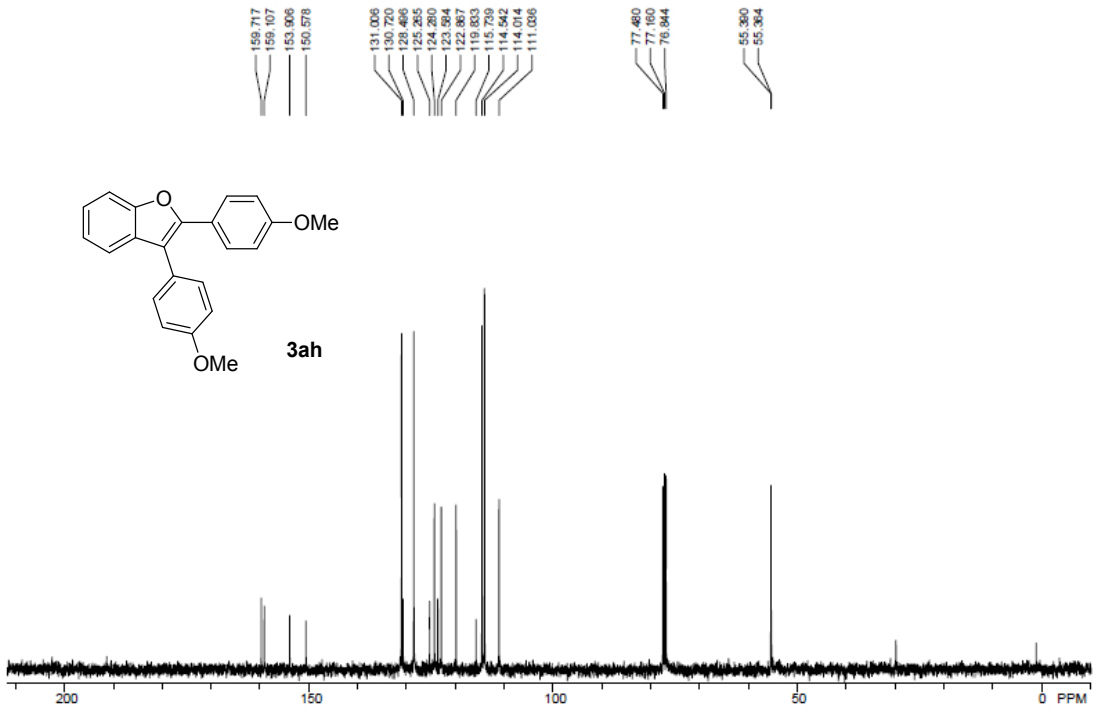
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OMe
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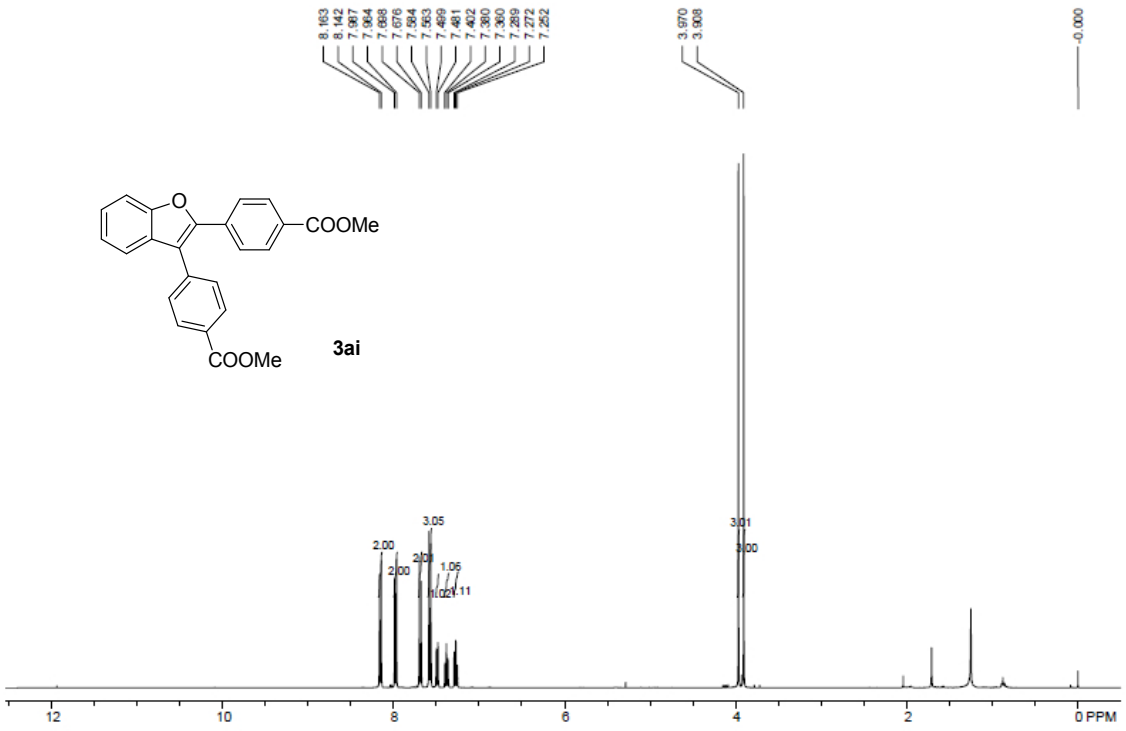
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-0.000
O
COOMe
COOMe
3ai
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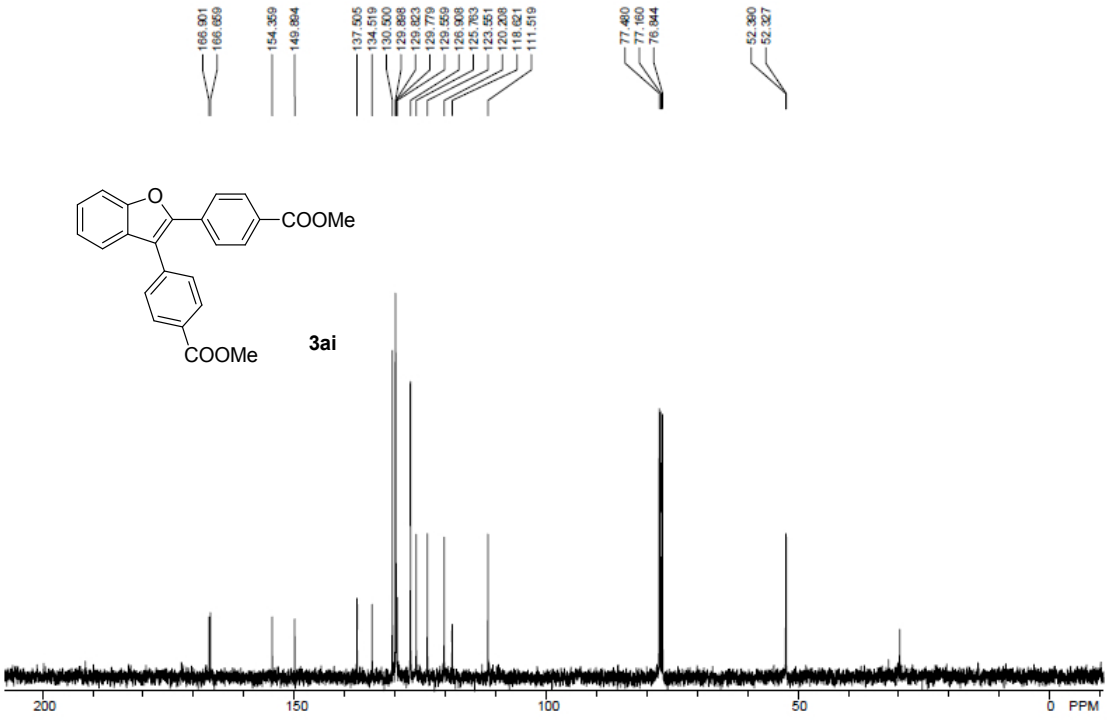
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COOMe
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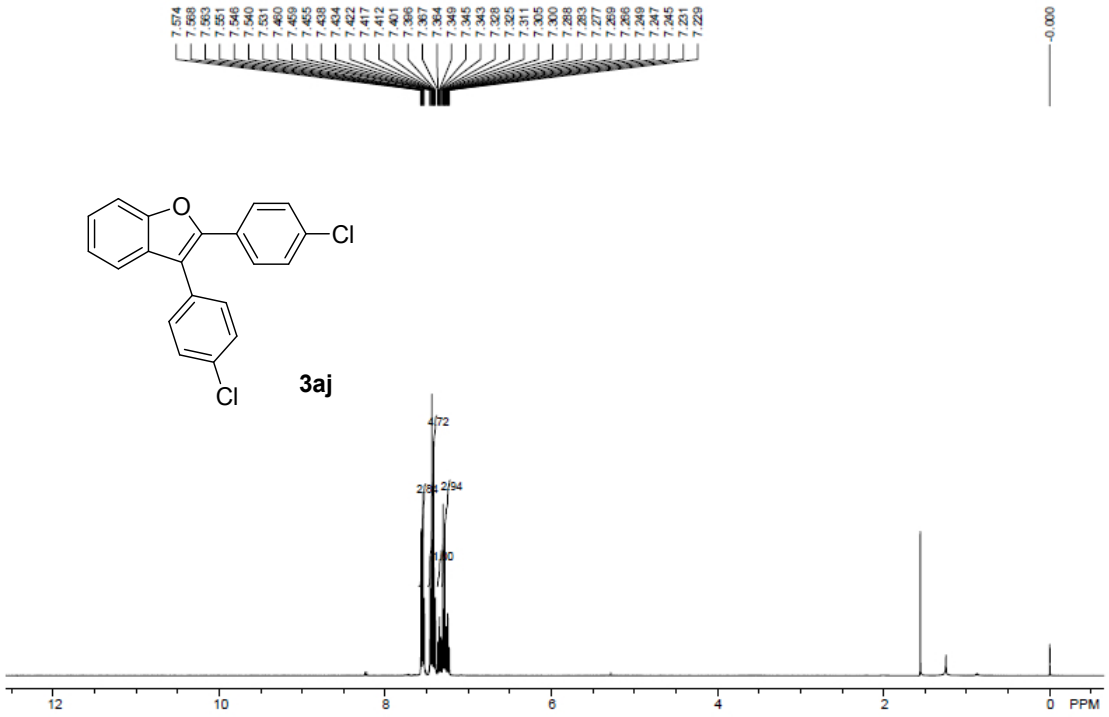
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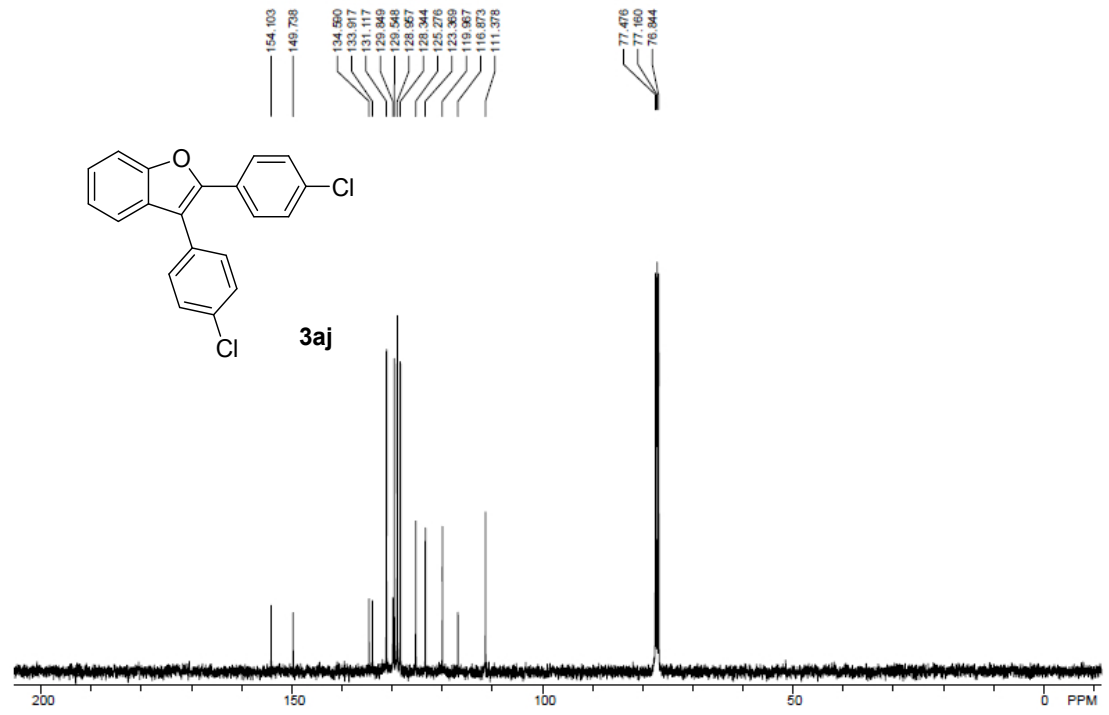
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Cl
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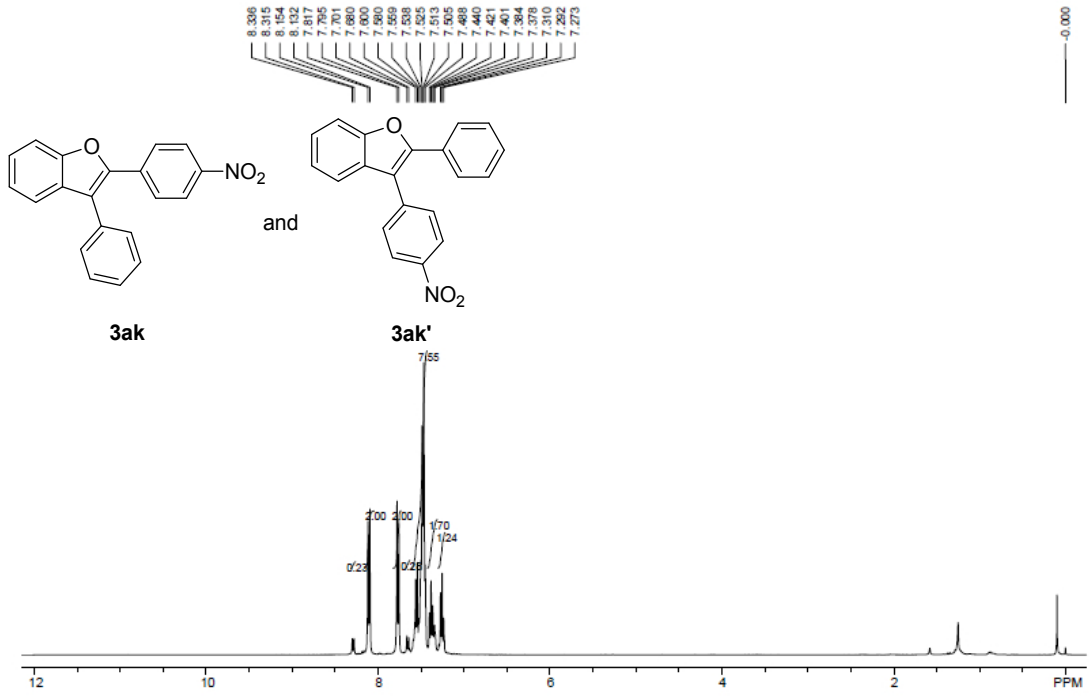
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7.488
7.440
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7.378
7.310
7.292
7.273
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O
NO2
and
O
NO2
3ak
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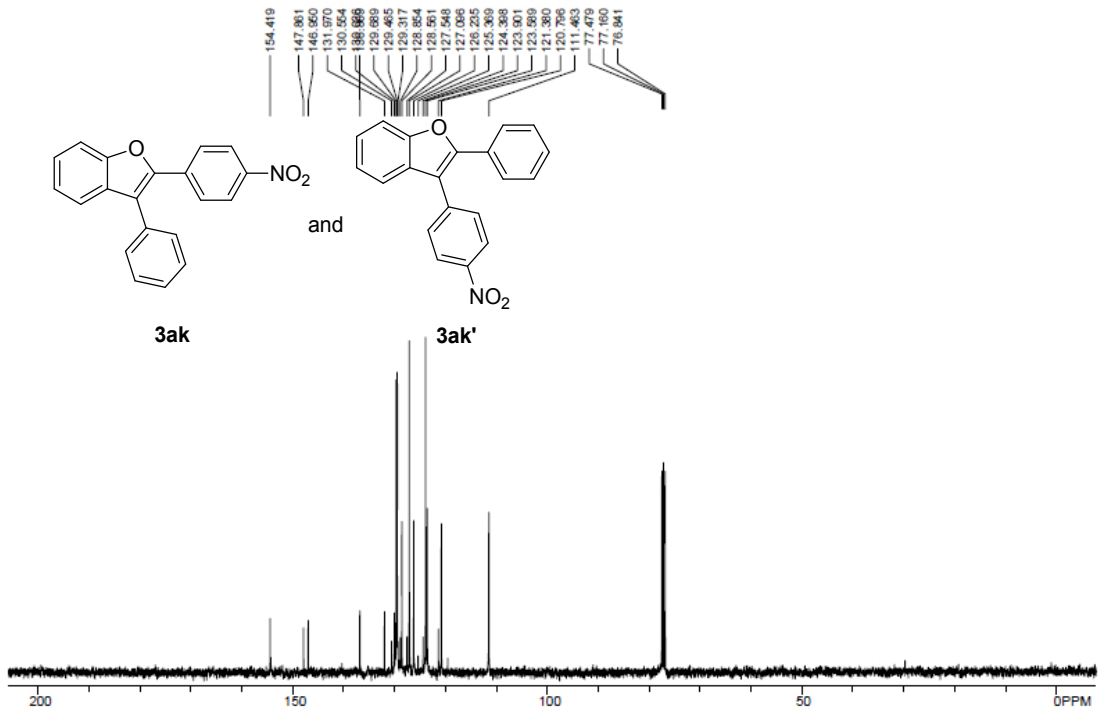
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123.589
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120.766
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and
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NO2
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3ak'
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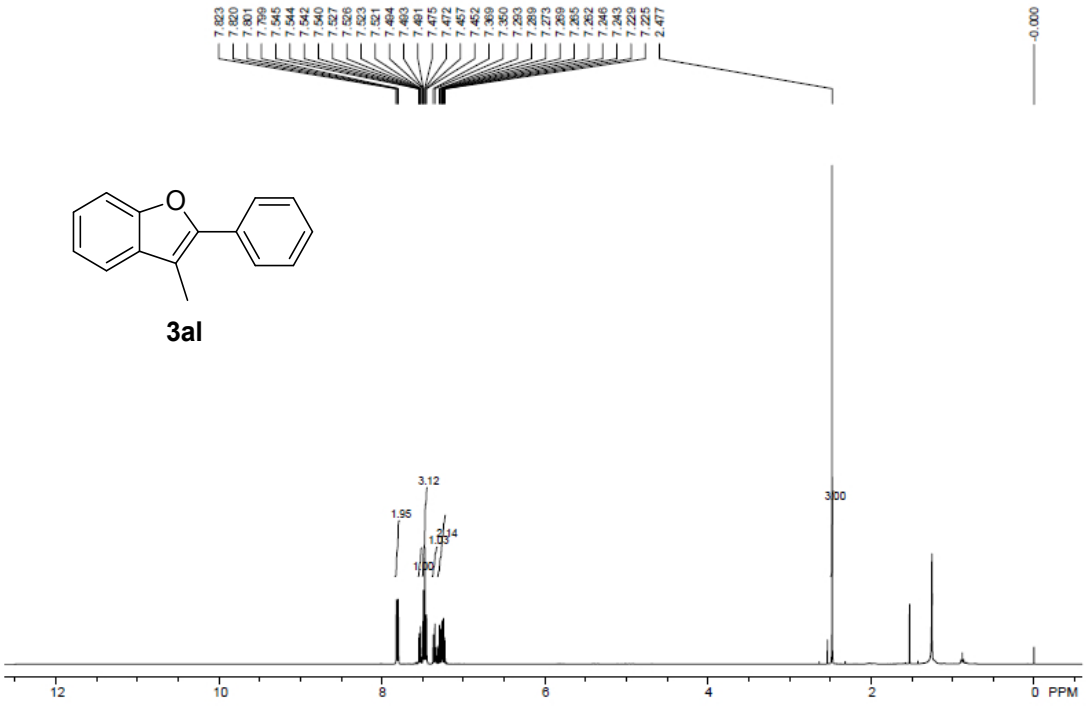
50
0PPM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7.462
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7.273
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7.265
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7.246
7.243
7.229
7.225
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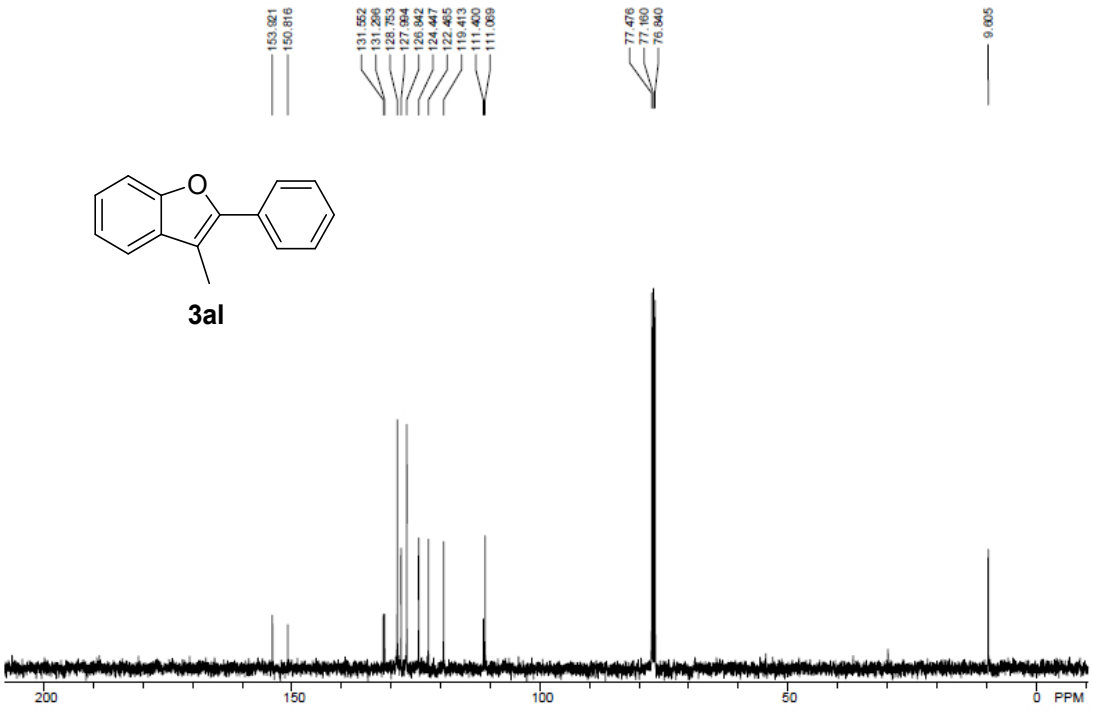
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50
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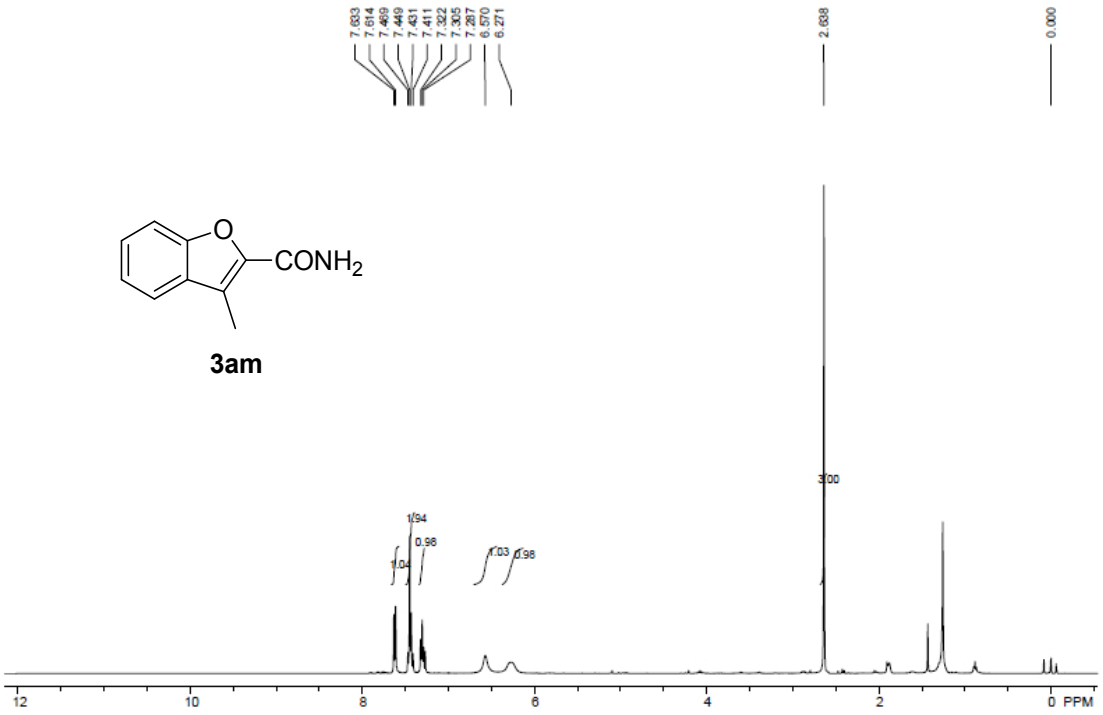
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1.03
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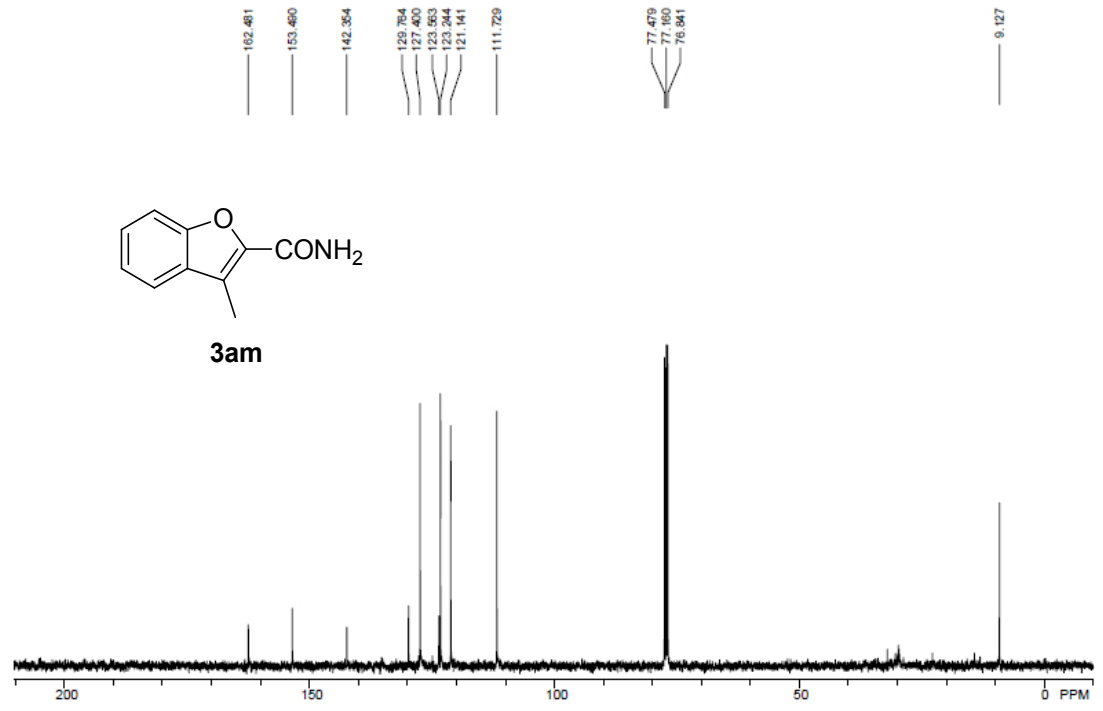
0 PPM

3am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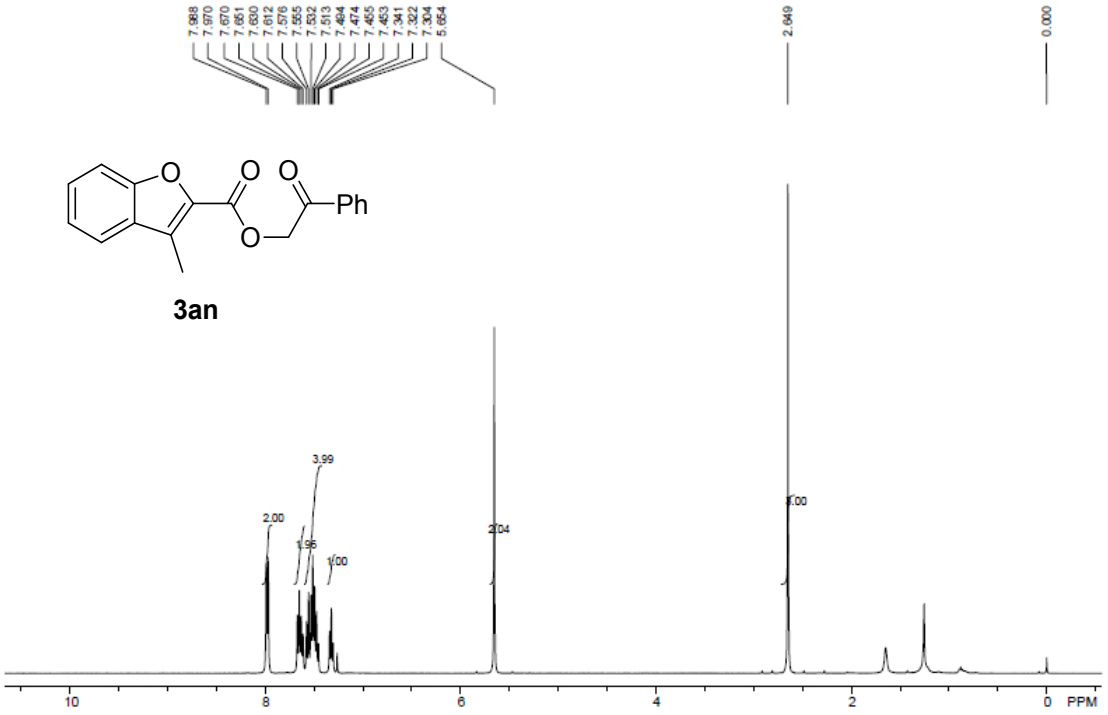
50
0 PPM

3am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7.341
7.322
7.304
5.654
2.649
0.000
O
O
O
O
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1.00
2.04
3.00
10
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4
2
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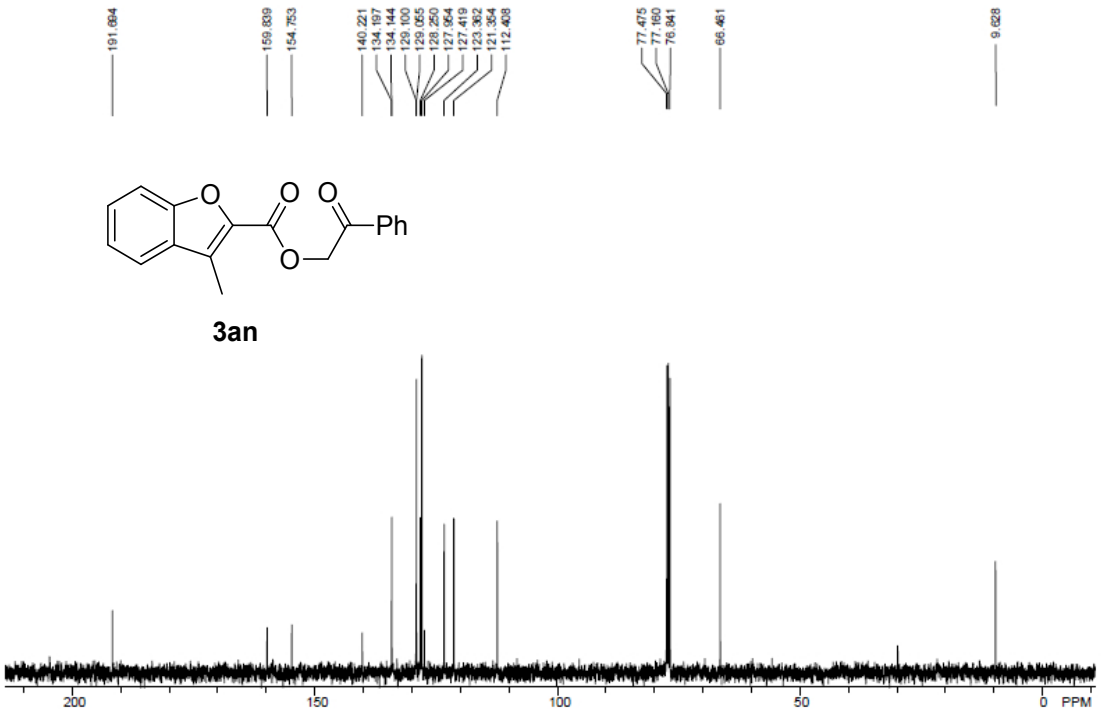
PPM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112.408
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Ph
3an
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100
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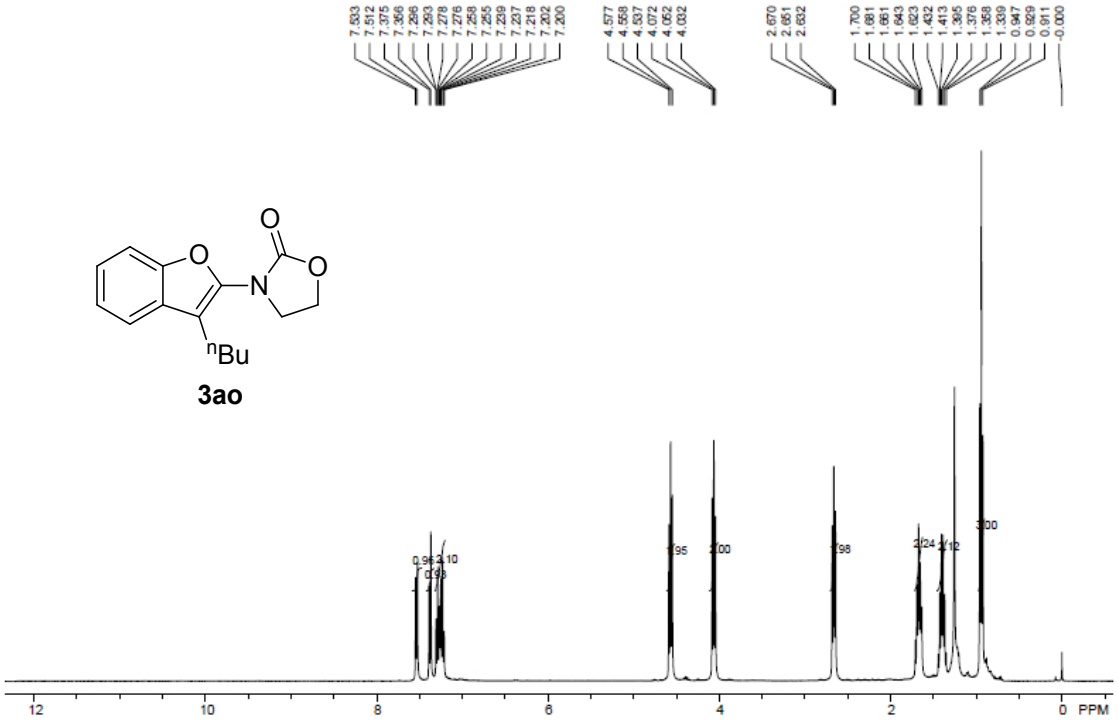
PPM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0.911
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8
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4
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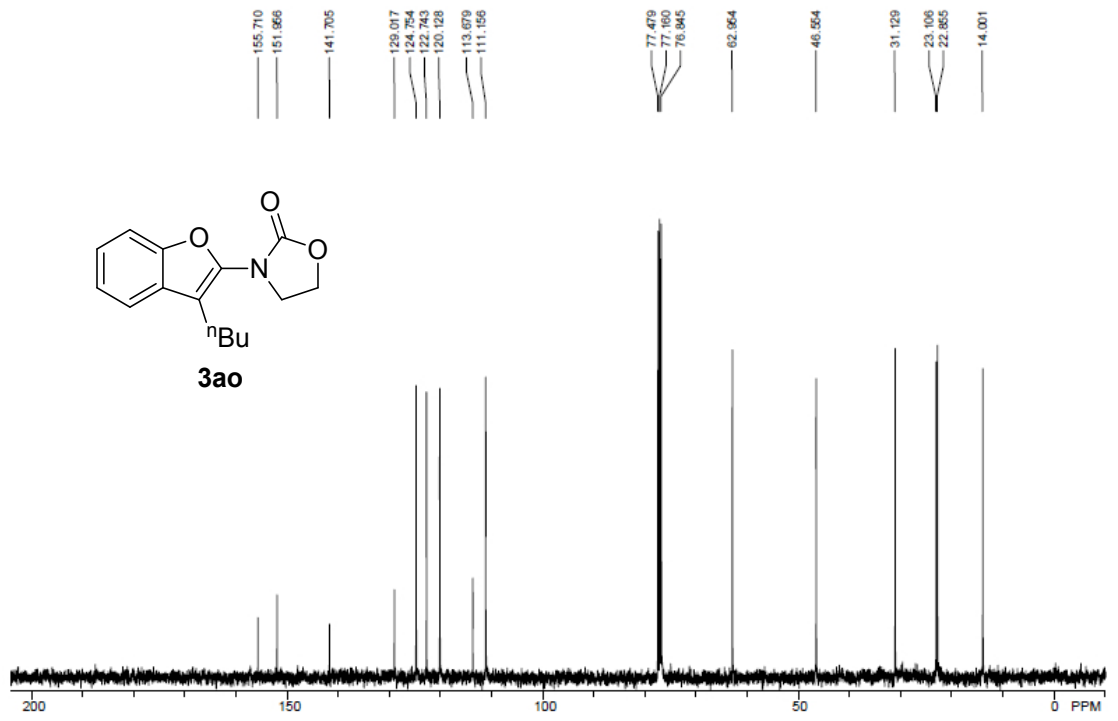
N
O
nBu

3ao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100
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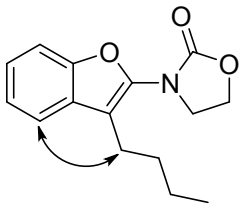
N
O
nBu

3ao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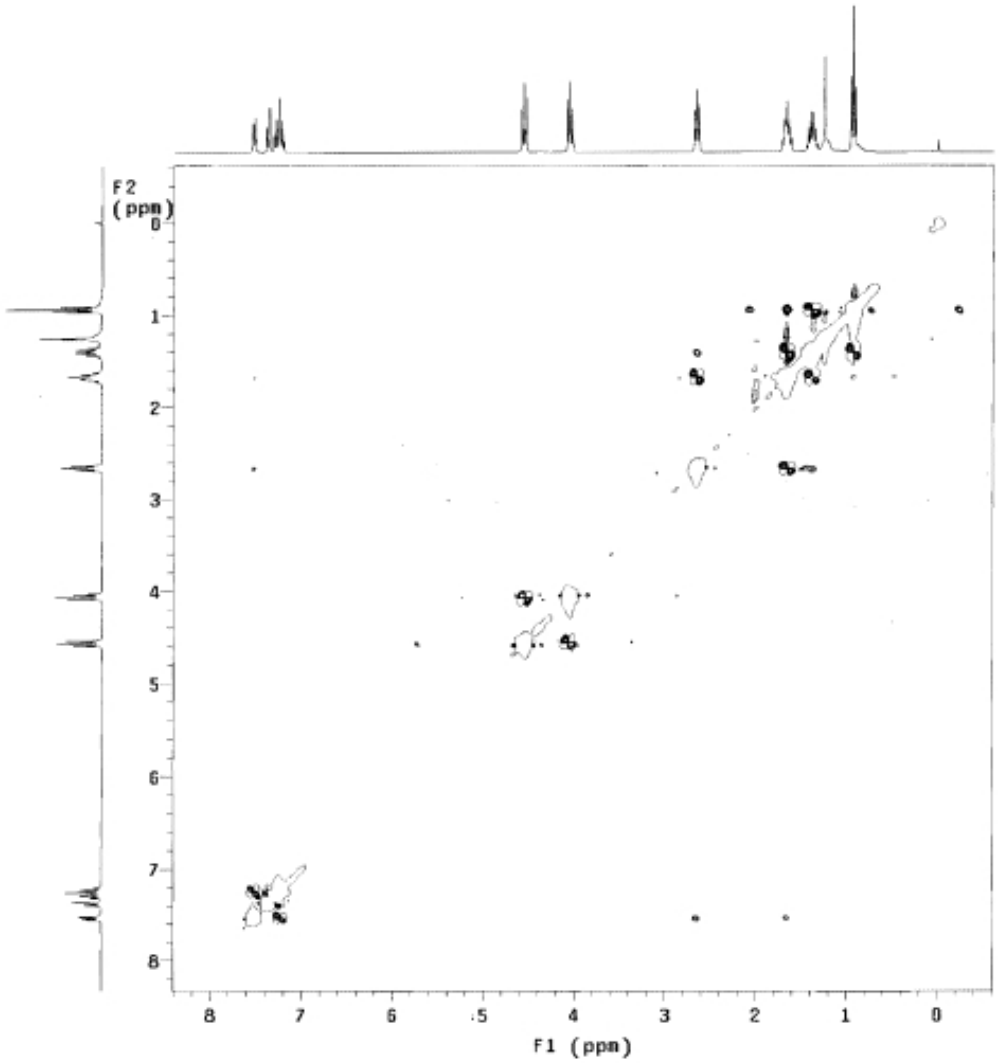
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(ppm)
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4
3
2
1
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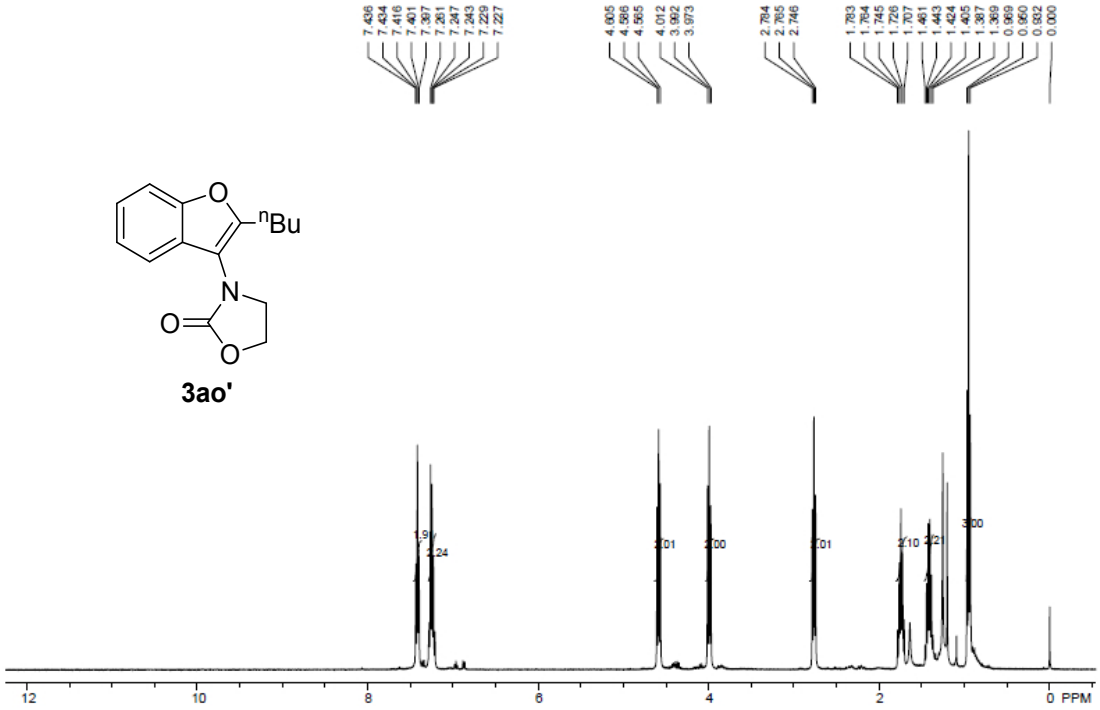
F1 (ppm)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7.243
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7.227
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4.565
4.012
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1.764
1.745
1.726
1.707
1.461
1.443
1.424
1.405
1.387
1.369
0.969
0.950
0.932
0.000
O
nBu
N
O
O
3ao'
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2.00
2.01
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4
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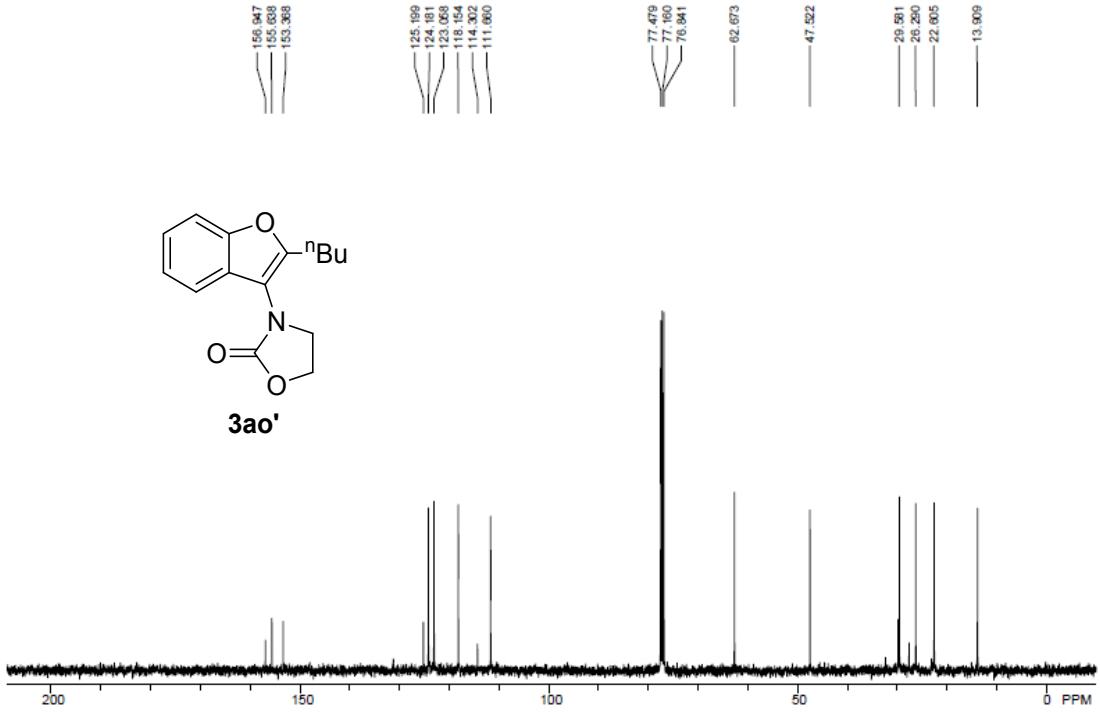
0 PPM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76.841
62.673
47.522
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22.605
13.909
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nBu
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O
3ao'
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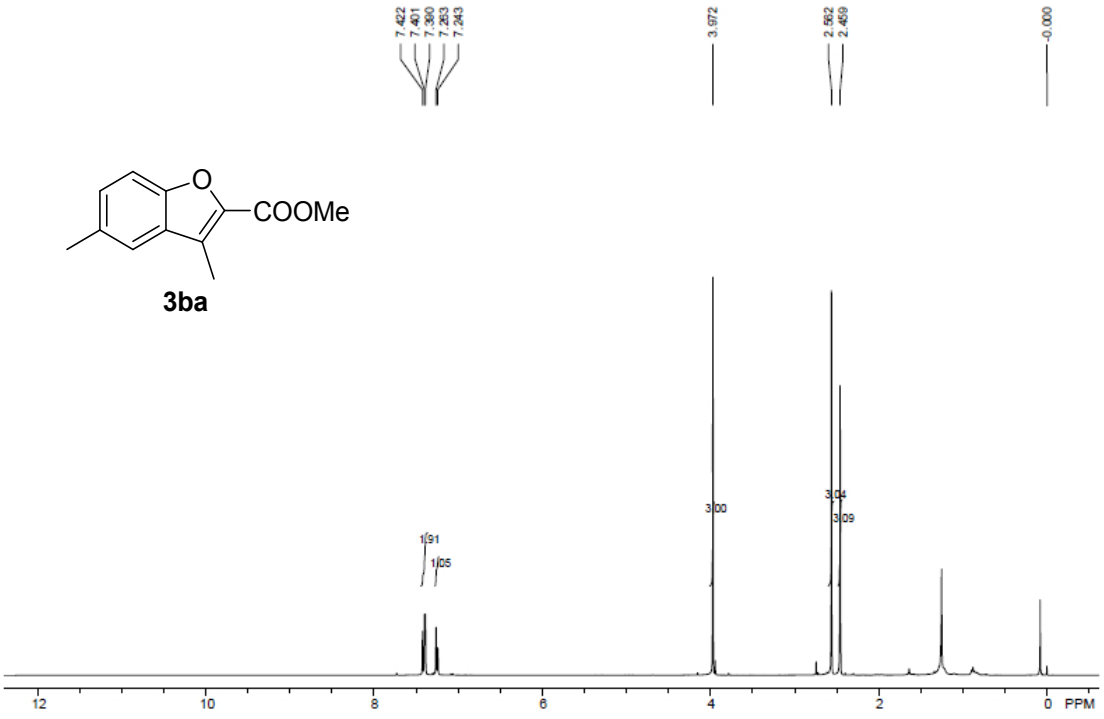
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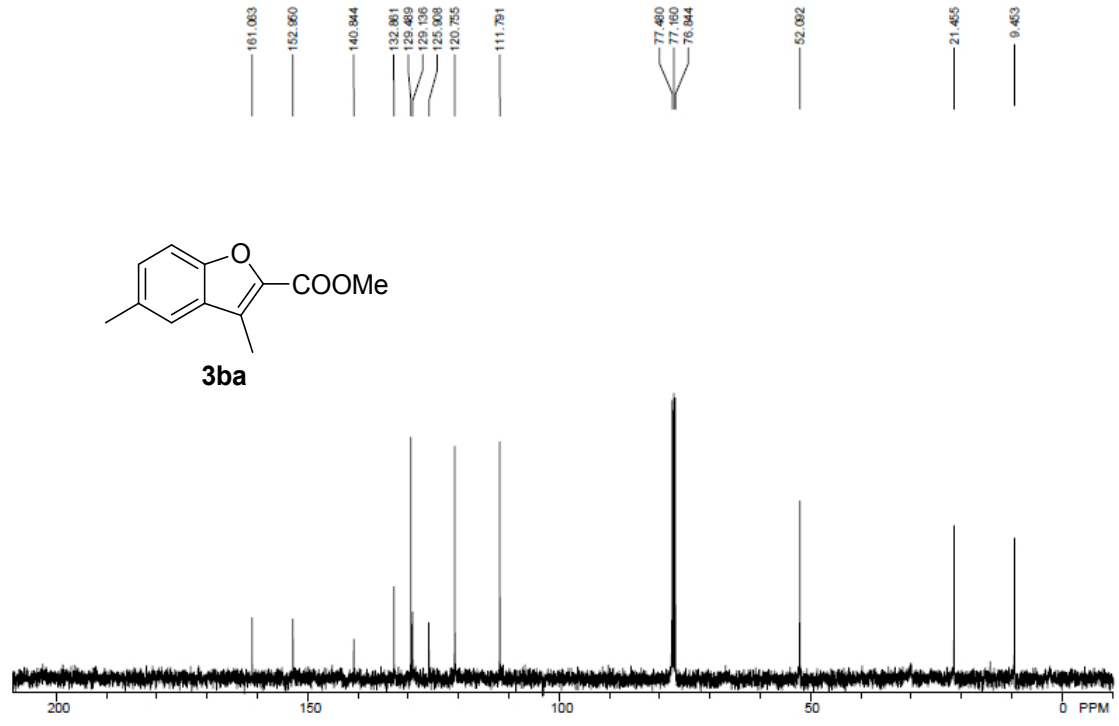
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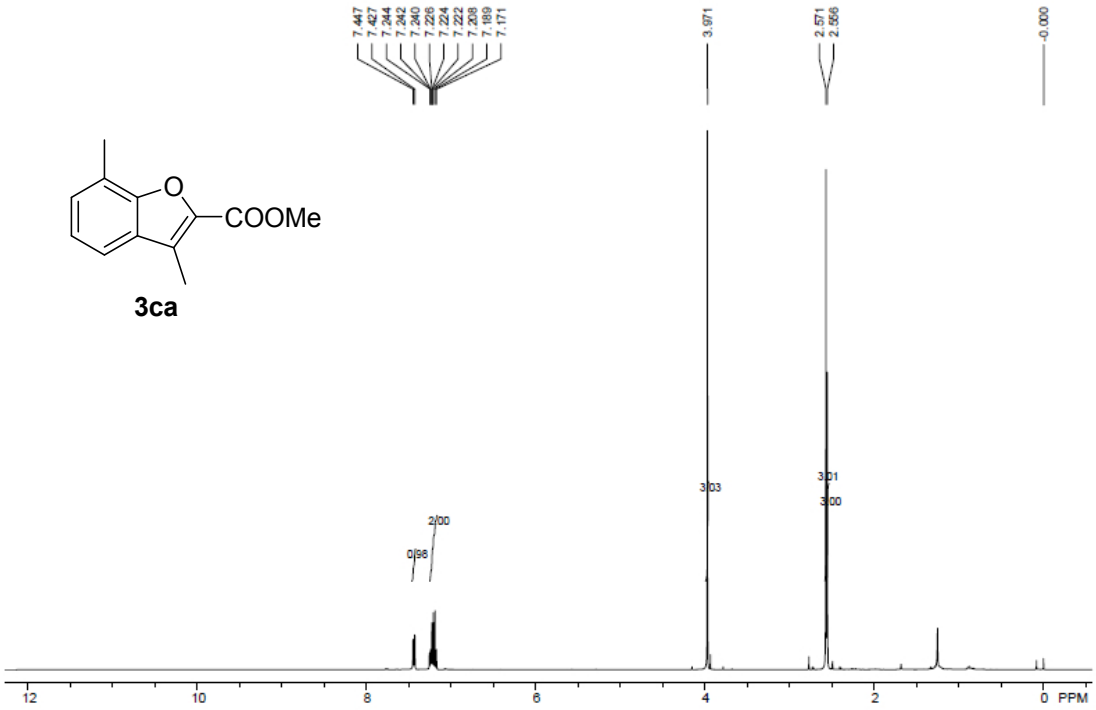
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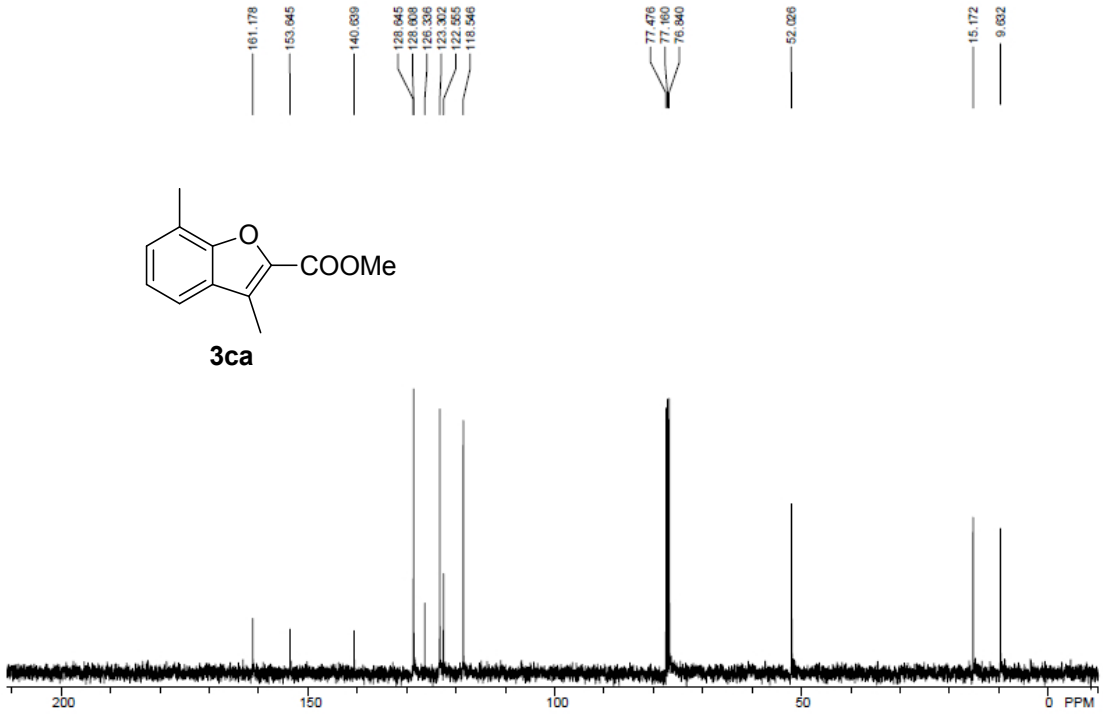
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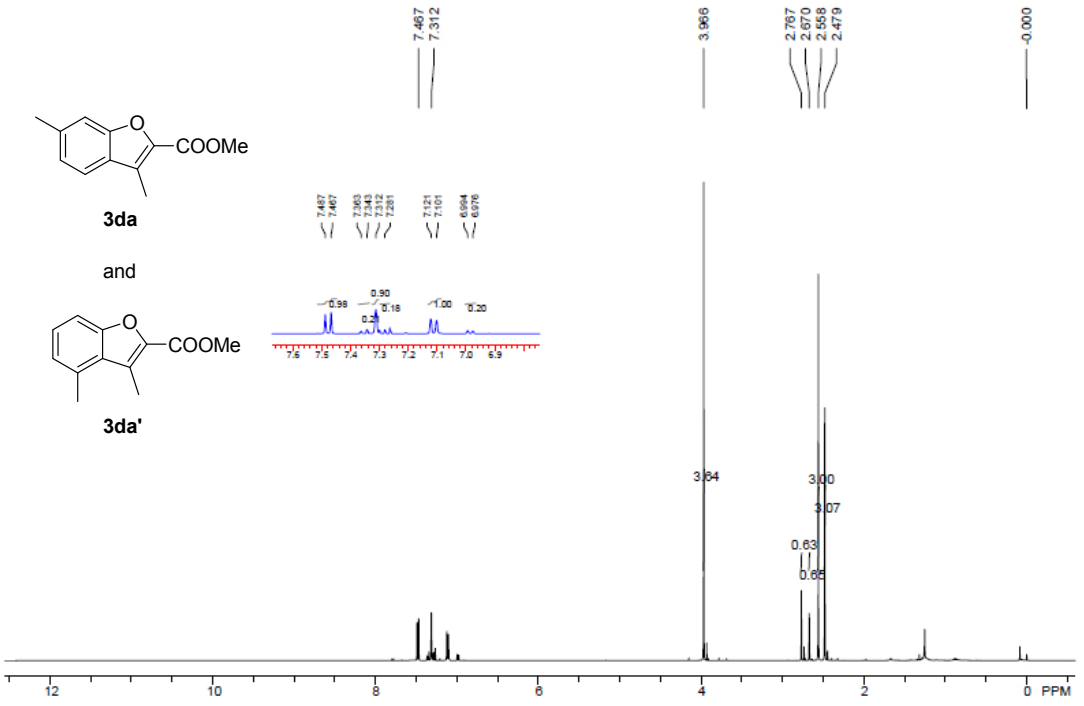
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3da
and
COOMe
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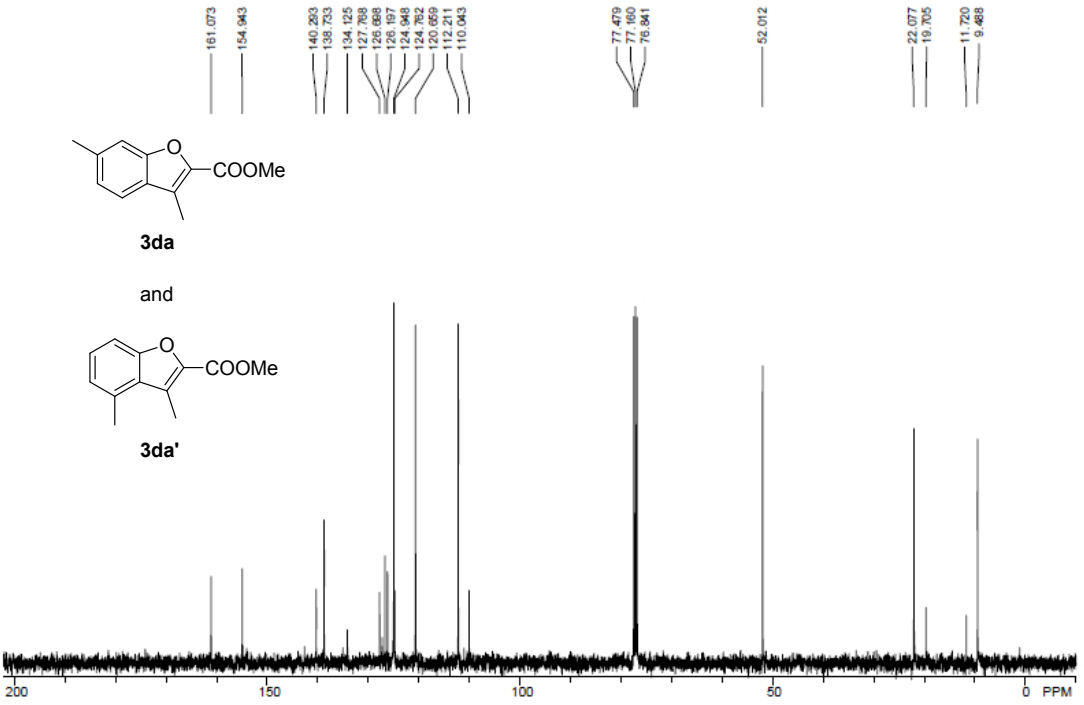
0 PPM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76.841
52.012
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COOMe
3da
and
COOMe
3da'
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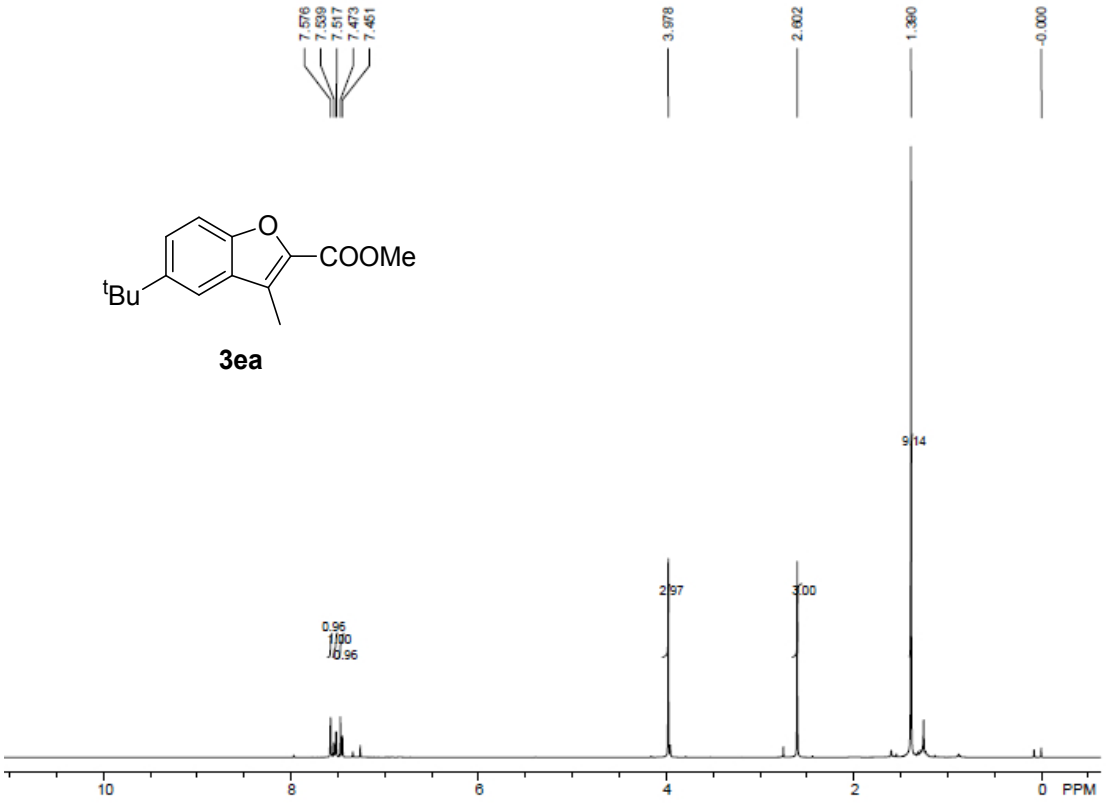
150
100
50
0 PPM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COOMe
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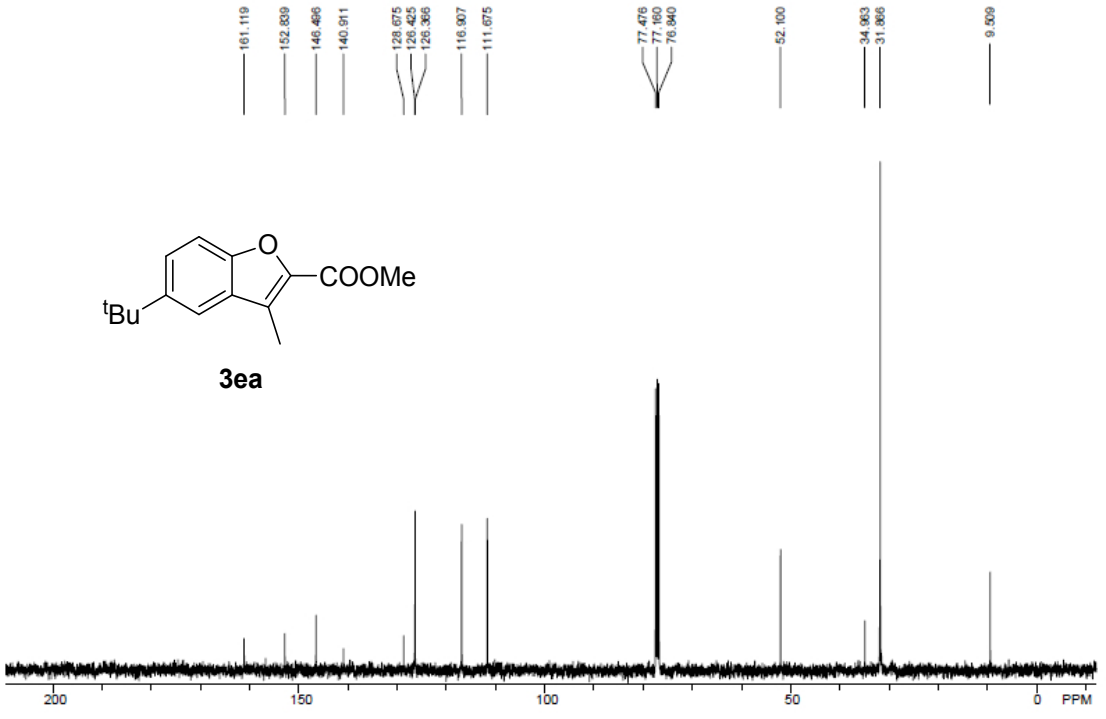
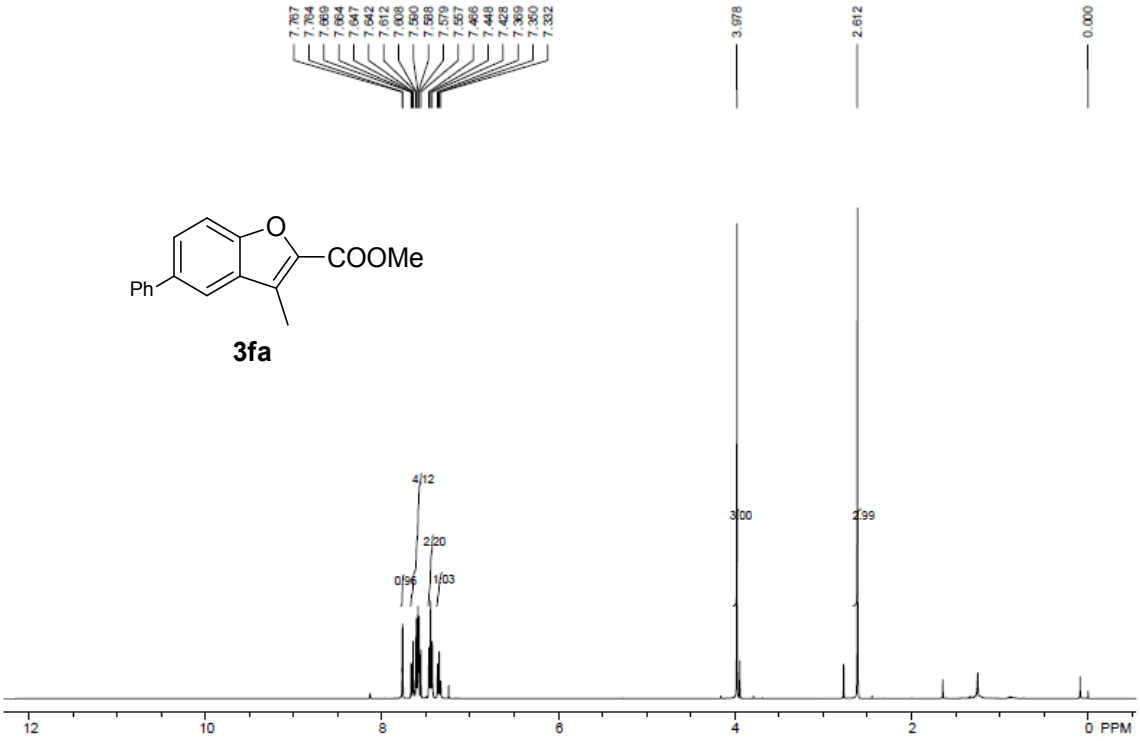
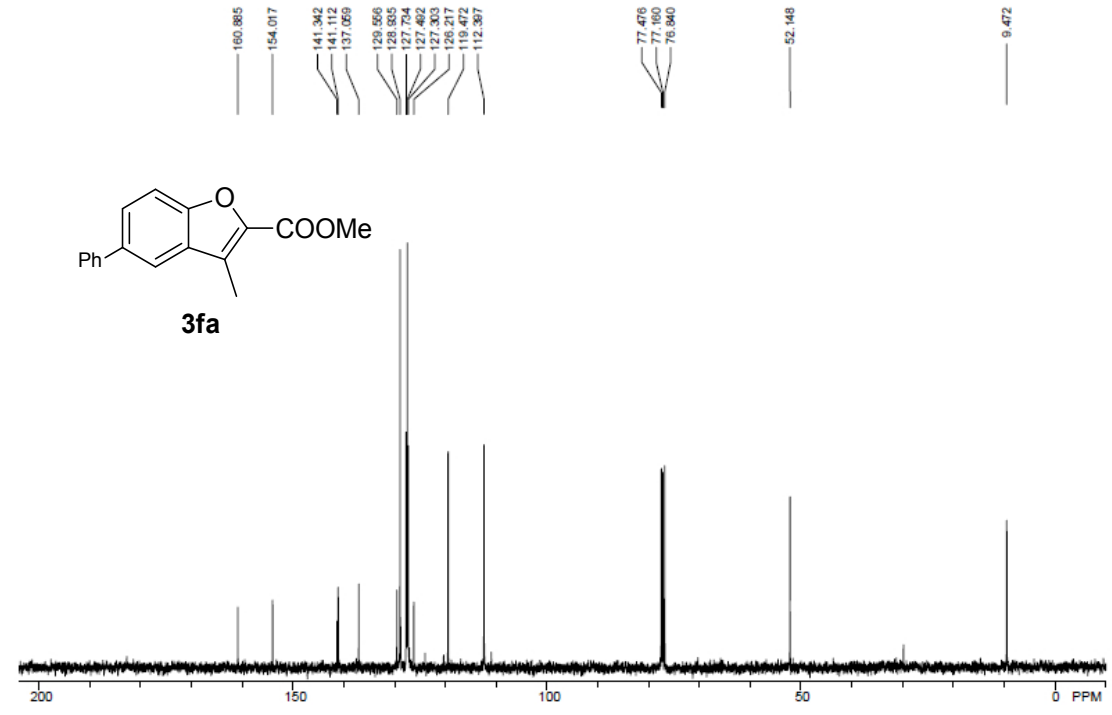
PPM


161.119
152.839
146.496
140.911
128.675
126.425
126.366
116.907
111.675
77.476
77.160
76.840
52.100
34.963
31.866
9.509
O
COOMe
tBu
3ea
200
150
100
50
0
PPM


7.767
7.764
7.669
7.664
7.647
7.642
7.612
7.608
7.590
7.588
7.579
7.557
7.466
7.448
7.428
7.369
7.360
7.332
3.978
2.612
0.000
O
COOMe
Ph
3fa
4.12
3.00
2.99
2.20
0.96
1.03
12
10
8
6
4
2
0 PPM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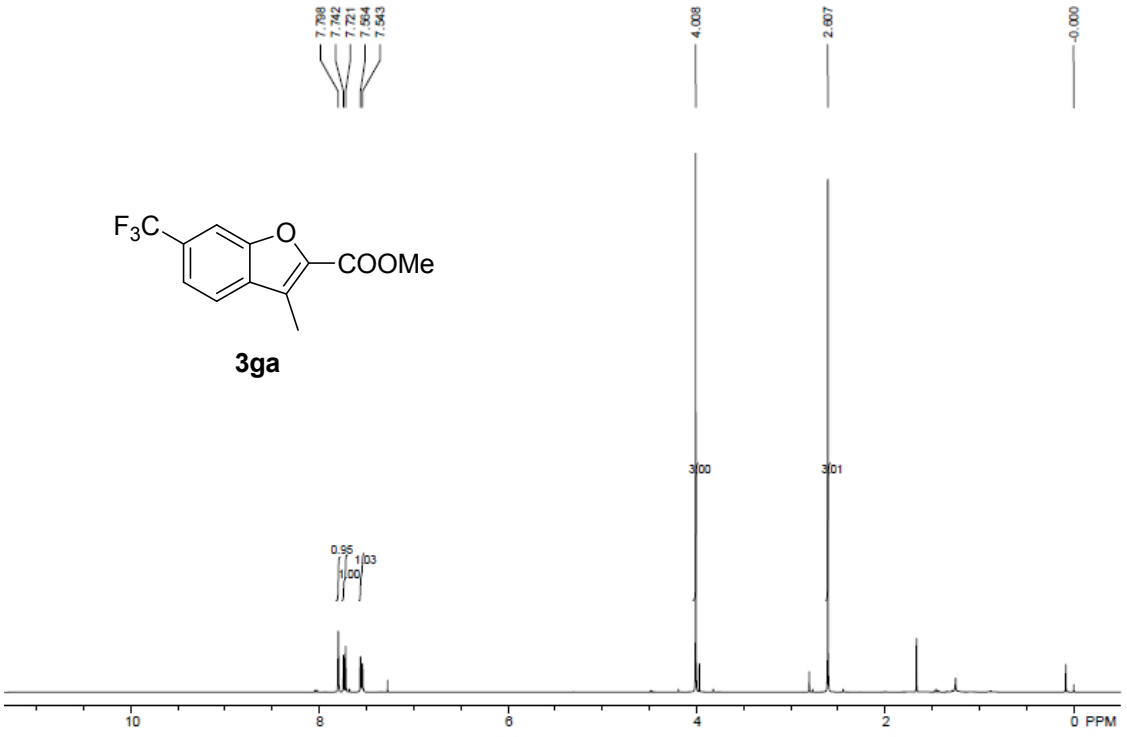
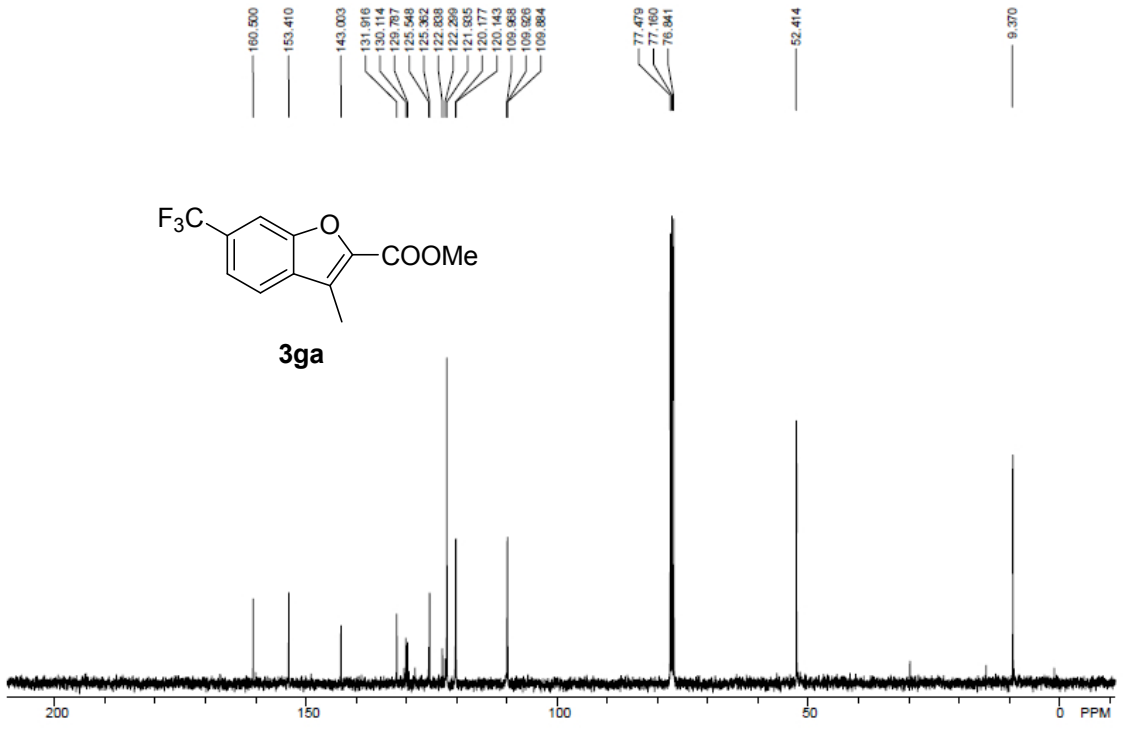
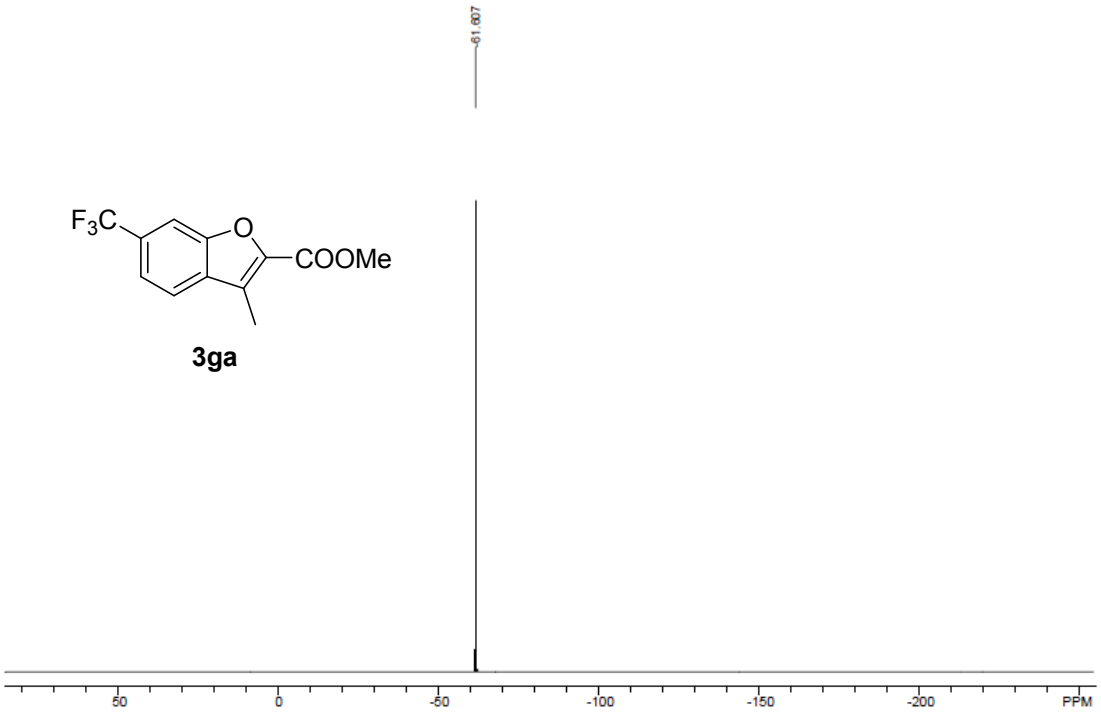
154.017
141.342
141.112
137.059
129.556
128.935
127.734
127.462
127.303
126.217
119.472
112.397
77.476
77.160
76.840
52.148
9.472
O
COOMe
Ph
3fa
200
150
100
50
0 PPM

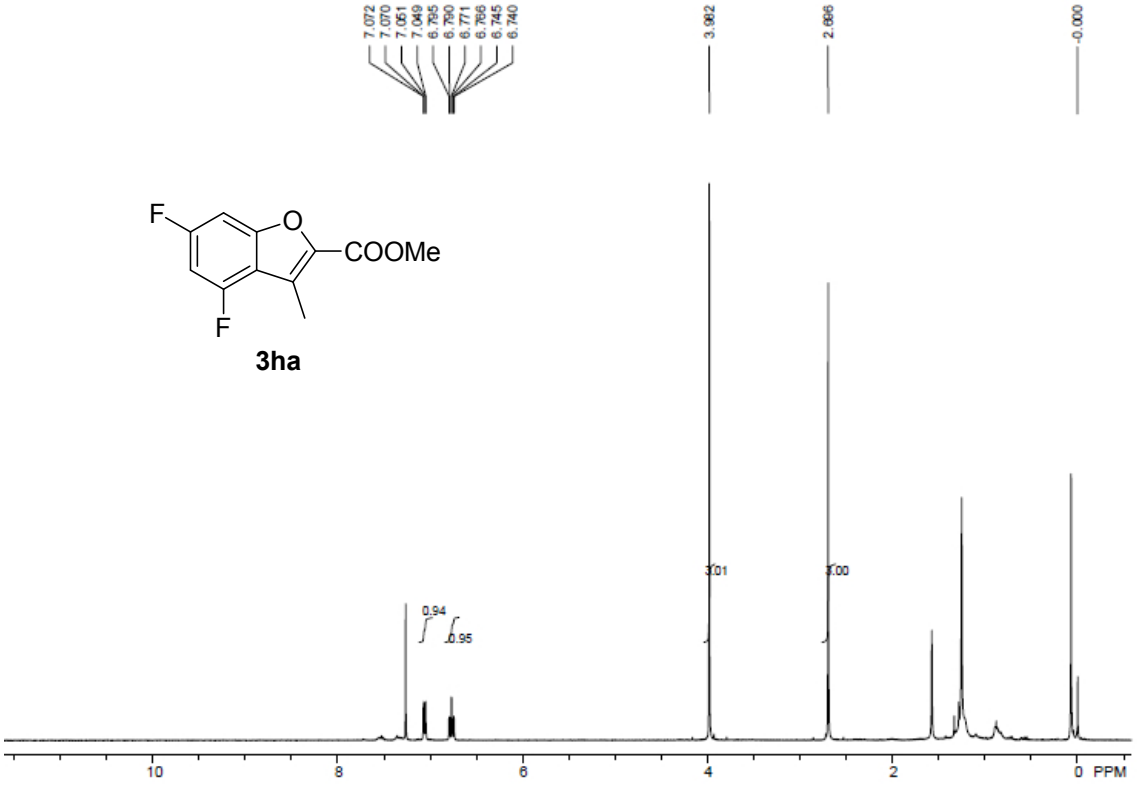

7.798
7.742
7.721
7.564
7.543
4.008
2.607
-0.000
F3C
O
COOMe
3ga
3.00
3.01
0.95
1.03
1.00
10
8
6
4
2
0 PPM

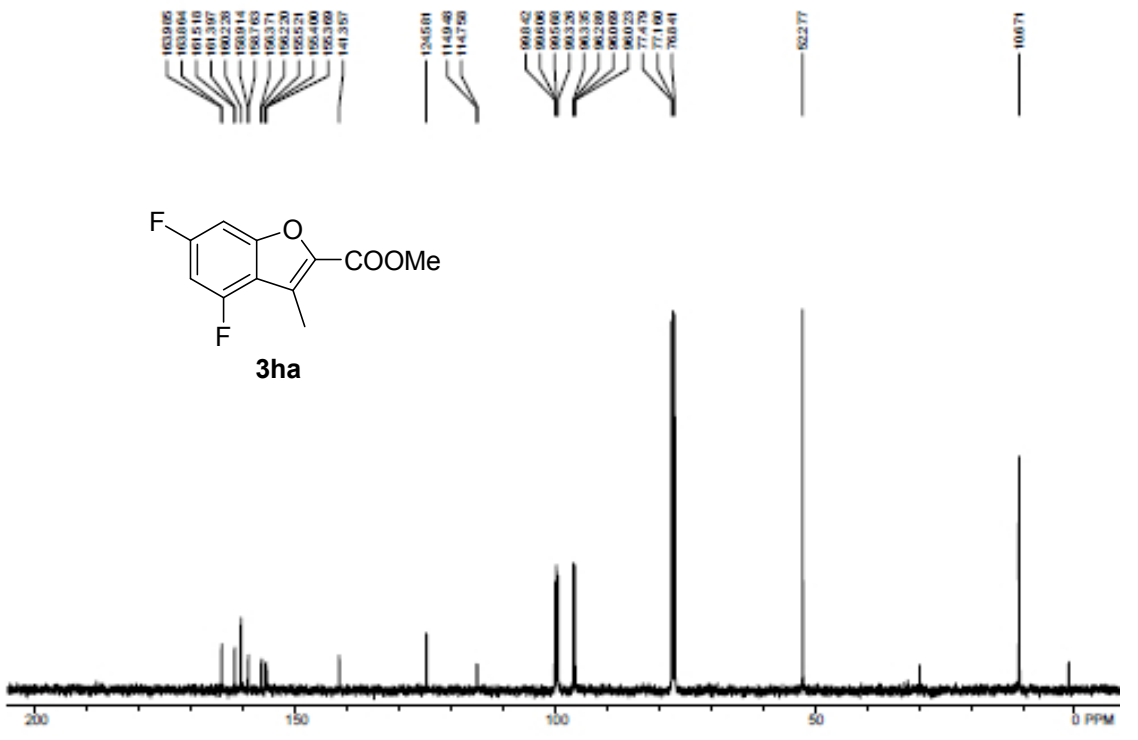

160.500
153.410
143.003
131.916
130.114
129.767
125.548
125.362
122.838
122.269
121.935
120.177
120.143
109.968
109.926
109.884
77.479
77.160
76.841
52.414
9.370
F3C
O
COOMe
3ga
200
150
100
50
0 PPM

^{19}F Spectra of **3ga**



3ga


7.072
7.070
7.051
7.049
6.795
6.790
6.771
6.766
6.745
6.740
3.982
2.866
-0.000
F
O
COOMe
F
3ha
0.94
0.95
3.01
3.00
10
8
6
4
2
0 PPM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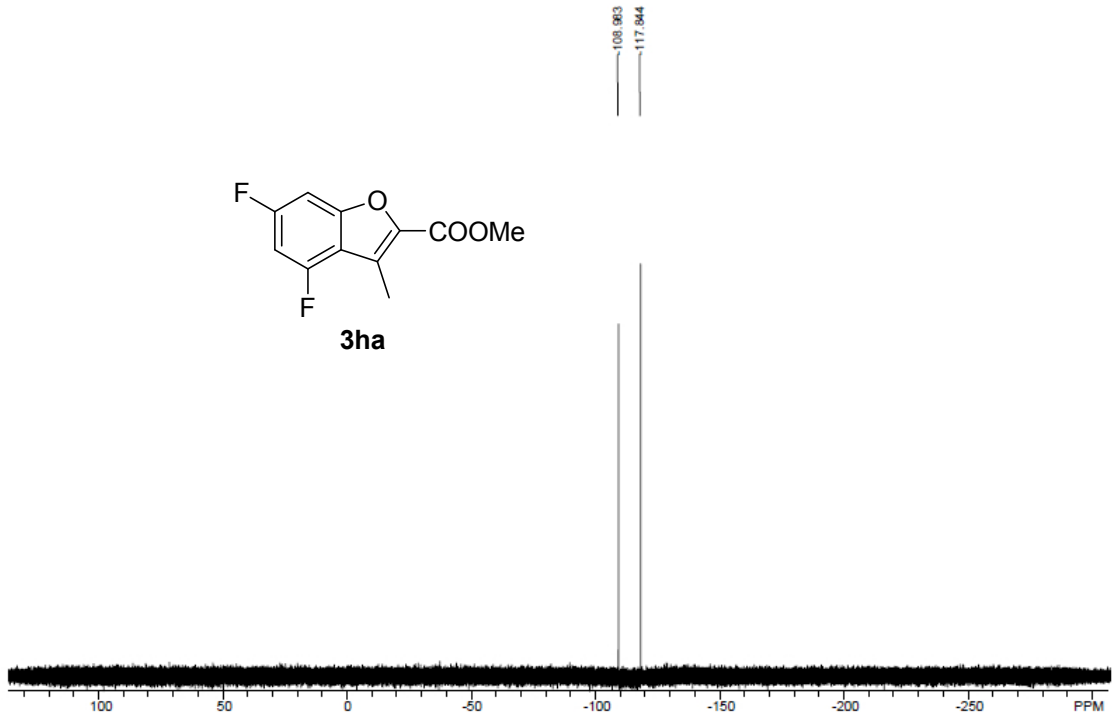
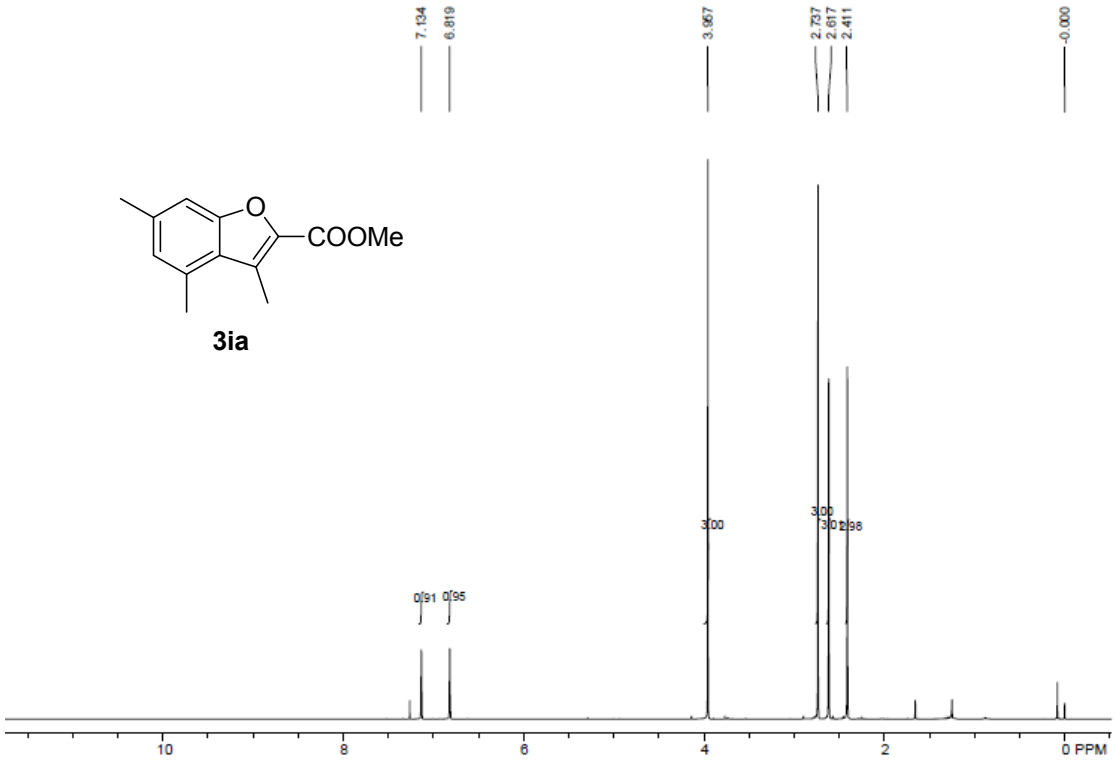
163.864
161.516
161.397
160.238
160.014
158.763
158.371
156.230
155.521
155.400
155.369
141.357
124.561
114.948
114.758
99.842
99.606
99.568
99.328
99.335
99.289
99.069
99.023
77.479
77.160
76.841
52.277
10.671
F
O
COOMe
F
3ha
200
150
100
50
0 PPM

^{19}F Spectra of **3ha**



3ha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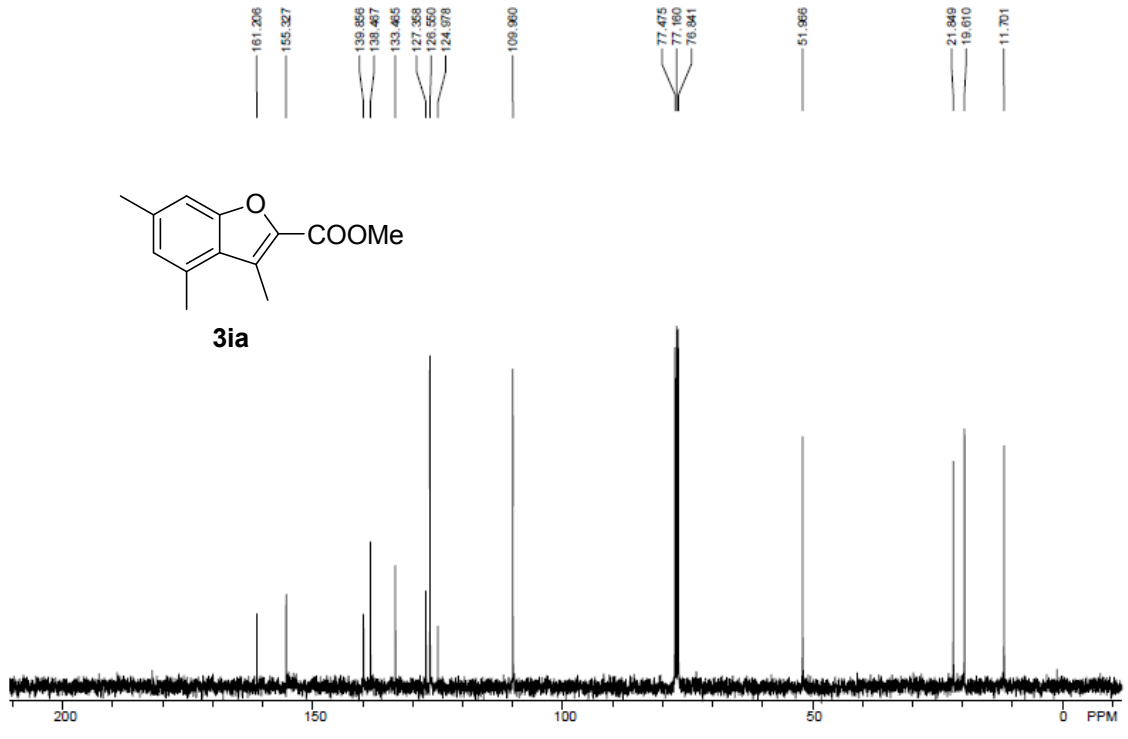
6.819
3.967
2.737
2.617
2.411
-0.000
O
COOMe
3ia
3.00
3.00
3.01
2.98
0.91
0.95
10
8
6
4
2
0 PPM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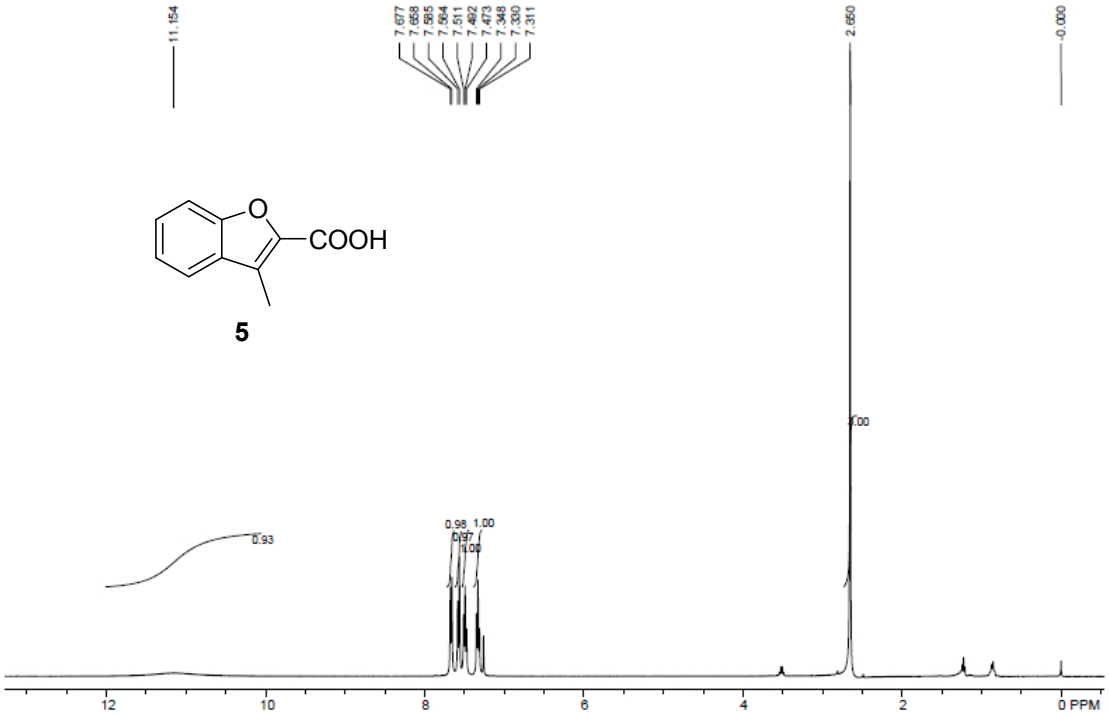
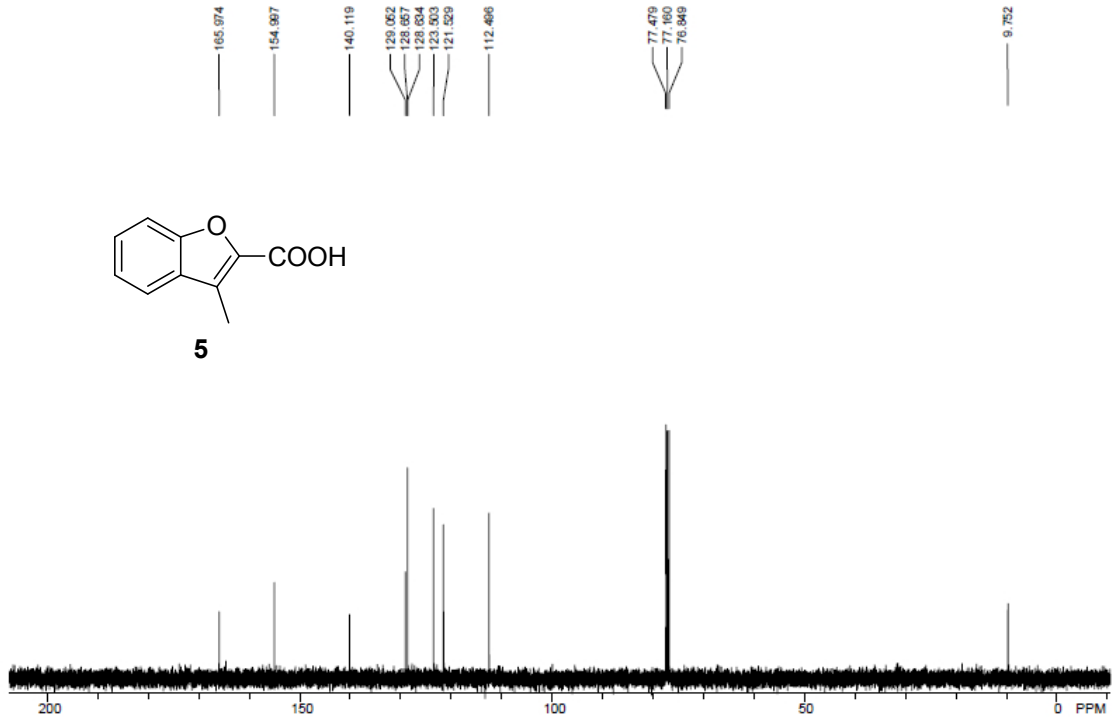
155.327
139.856
138.467
133.465
127.358
126.550
124.978
109.960
77.475
77.160
76.841
51.966
21.849
19.610
11.701
O
COOMe
3ia
200
150
100
50
0 PPM


11.154
7.677
7.658
7.585
7.564
7.511
7.492
7.473
7.348
7.330
7.311
2.650
-0.000
O
COOH
5
2.00
0.93
0.98
1.00
0.97
1.00
12
10
8
6
4
2
0 PPM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154.997
140.119
129.062
128.657
128.634
123.503
121.529
112.496
77.479
77.160
76.849
9.752
O
COOH
5
200
150
100
50
0 PPM