Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Photoredox radical C–H oxygenation of aromatics with aroyloxylutidinium salts

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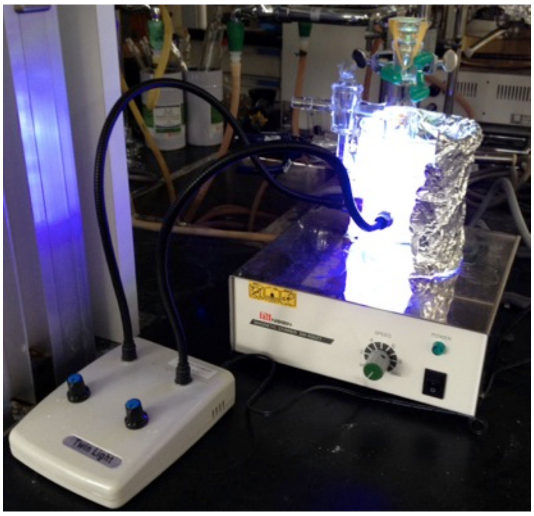
Contents

Materials and methods

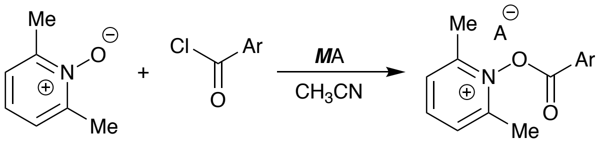
$[Ru(bpy)_3](PF_6)_2$,[1a] *fac*-$[Ir(ppy)_3]$,[1b] and $[Ir(ppy)_2(dtbbpy)](PF_6)$[1c] were prepared according to the reported procedures. Arenes **2a, 2b, 2c, 2d, 2e, 2f, 2h, 2i, 2j** and, **2o** were purchased from TCI, **2n** purchased from Wako and **2k, 2l** and **2m** were purchased from Kanto. 4-Trimethylsilylanisole **2g** was prepared according to the reported literature procedure.[2] Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. CH_2Cl_2 was purified through columns containing alumina and alumina-Cu catalyst and stored under nitrogen. Thin-layer chromatography was performed on silica gel TLC plates (60 F_{254}, Merck). Column chromatography was performed using Aldrich silica gel 60 Å. Visible light irradiation was performed with Relyon LED lamps (3 W x 2: $\lambda = 425$ nm ± 15 nm). ^1H NMR spectra were acquired on a Bruker AVANCE-400 spectrometers (400 MHz) and a Bruker AVANCE-HD500 (500 MHz) NMR Chemical shifts were referenced to residual protio impurities in the deuterated solvents. Electrochemical measurements were recorded on a Hokutodenkou HZ-5000 analyzer (observed in 0.002 M CH_3CN; $[NBu_4](PF_6) = 0.1$ M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple). Recycled GPC was performed with a JAI LC-9201R/U. Emission spectra were recorded at room temperature by SHIMADZU RF-5300PC. HRMS (ESI-TOF Mass) spectra were obtained with a Bruker microTOF II spectrometer. Elemental analysis was carried out by a MICRO CORDER JM10 at Technical Department of Tokyo Institute of Technology.

Reaction apparatus

Visible light irradiation was performed with a Relyon LED lamp (3W x 2; $\lambda_{max} = 425$ nm ± 15 nm) .



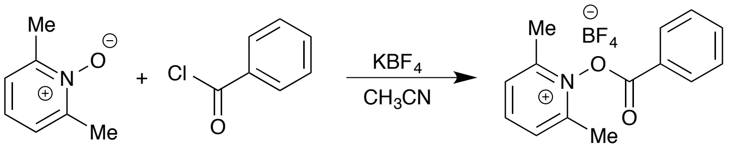
General procedure for the synthesis of aroyloxy-2,6-lutidinium salts



1•A

Under N$_2$, to a mixture of 2,6-lutidine *N*-oxide (1.0 eq.), *M*A (1-1.2 eq.) and dry CH$_3$CN, carboxylic acid chloride (1.0-1.2 eq.) was added. The reaction mixture was stirred for the reaction time at rt. The volatiles were removed under the reduced pressure and the residue was extract with CH$_2$Cl$_2$ and filtered. The filtrate was concentrated *in vacuo*. The residue was washed with Et$_2$O and obtained as a white solid.

1-Benzoyloxy-2,6-lutidinium tetrafluoroborate (1a•BF$_4$)

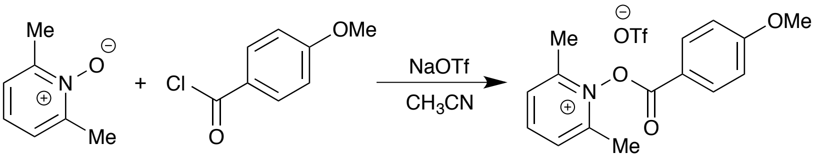


1a•BF$_4$

The reaction of 2,6-lutidine *N*-oxide (237 mg, 1.93 mmol), potassium tetrafluoroborate (254 mg, 2.02 mmol) and benzoyl chloride (324 mg, 2.31 mmol) following the general procedure afforded **1a**•BF$_4$ (547 mg, 90%, reaction time = 5 h) as a white solid.

^{1}H NMR (400 MHZ, CD$_3$CN, rt) δ 8.43 (t, ^3J = 8.0 Hz, 1H; $\mathrm{C_5N}\mathit{H}\mathrm{H_2}$), 8.29 (dd, ^3J = 8.4 Hz, q, ^4J = 1.2 Hz, 2H; $\mathrm{C_5NH}\mathit{H}_2$), 7.95–7.92 (m, 3H; $\mathrm{C_6}\mathit{H}_3\mathrm{H_2}$), 7.73–7.71 (m, 2H), 2.72 (s, 6H; $\mathrm{C}\mathit{H}_3$ x 2). **^{13}C NMR** (125 MHz, CD$_3$CN, rt) δ 162.4, 155.0, 147.1, 137.9, 132.0, 130.7, 129.3, 123.8, 18.4. **HRMS** (ESI-TOF) calculated for $[C_{14}H_{14}NO_2]^+$ requires 228.1019, found 228.1019.

1-(4-Methoxybenzoyloxy)-2.6-lutidinium trifluoromethanesulfonate (1b•OTf)

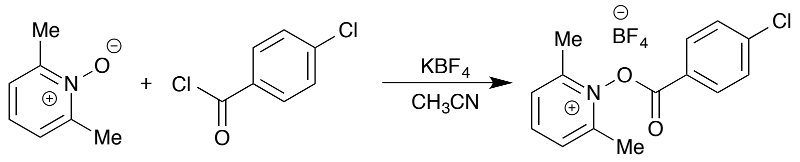


1b•OTf

The reaction of 2,6-lutidine *N*-oxide (248 mg, 2.01 mmol), sodium trifluoromethanesulfonate (429 mg, 2.49 mmol) and 4-methoxybenzoyl chloride (345 mg, 2.02 mmol) following the general procedure afforded **1b**•OTf (686 mg, 84%, reaction time = 2 h) as a white solid.

^{1}H NMR (400 MHz, CD$_3$CN) δ 8.41 (m 1H; $\mathrm{C_5N}\mathit{H}\mathrm{H_2}$), 8.24 (d, ^3J = 8.8 Hz, 2H; $\mathrm{C_6}\mathit{H}_2\mathrm{H_2}$), 7.93 (d, ^3J = 7.6 Hz, 2H; $\mathrm{C_5NH}\mathit{H}_2$), 7.20 (d, ^3J = 9.2 Hz, 2H; $\mathrm{C_6H_2}\mathit{H}_2$), 3.96 (s, 3H; $\mathrm{OC}\mathit{H}_3$), 2.70 (s, 6H; $\mathrm{C}\mathit{H}_3$ x 2). **^{13}C NMR** (125 MHz, CD$_3$CN, rt) δ 166.6, 160.9, 154.1, 145.9, 133.6, 128.2, 121.2 (q, ^2J = 319 Hz; $\mathit{C}\mathrm{F_3SO_3}$), 115.2, 114.3, 55.9, 17.5. **HRMS** (ESI-TOF): calculated for $[C_{15}H_{16}NO_3]^+$ requires 258.1125, found 258.1125.

1-(4-Chlorobenzoyloxy)-2,6-lutidinium tetrafluoroborate (1c•BF_4)

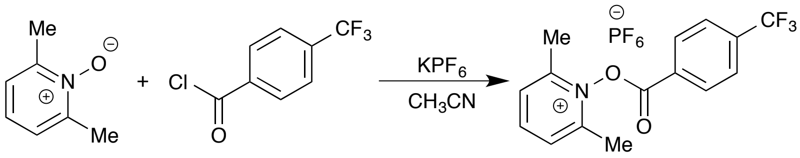


1c•BF4

The reaction of 2,6-lutidine *N*-oxide (238 mg, 1.93 mmol), potassium tetrafluoroborate (254 mg, 2.02 mmol) and 4-chlorobenzoyl chloride (367 mg, 2.01 mmol) following the general procedure afforded **1c**•BF_4 (570 mg, 85%, reaction time = 16 h) as a white solid.

^{1}H NMR (400 MHZ, CD_3CN, rt) δ 8.43 (t, ^3J = 8.0 Hz, 1H; C_5NHH_2), 8.26 (d, ^3J = 8.4 Hz, 2H; $C_6H_2H_2$), 7.94 (d, ^3J = 8.0 Hz, 2H; C_5NHH_2), 7.74 (d, ^3J = 8.8 Hz, 2H; $C_6H_2H_2$), 2.71 (s, 6H; CH_3 x 2). **^{13}C NMR** (125 MHz, CD_3CN, rt) δ 161.7, 155.0, 147.2, 144.0, 133.7, 130.9, 129.2, 122.6, 18.4. **HRMS** (ESI-TOF) calculated for $[C_{14}H_{13}ClNO_2]^+$ requires 262.0629, found 262.0626.

1-(4-Trifluoromethylbenzoyloxy)-2,6-lutidinium hexafluorophosphate (1d•PF_6)

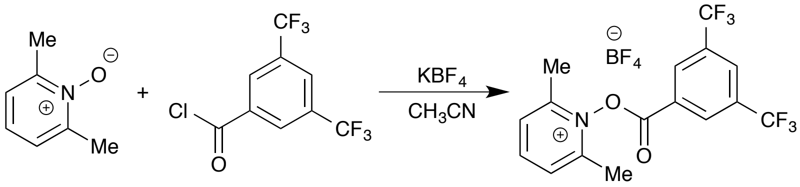


1d•PF6

The reaction of 2,6-lutidine *N*-oxide (236 mg, 1.91 mmol), potassium hexafluorophosphate (446 mg, mmol) and 4-trifluoromethylbenzoyl chloride (381 mg, 2.14 mmol) following the general procedure afforded **1d**•PF_6 (817 mg, 97%, reaction time = 5 h) as a white solid.

^{1}H NMR (400 MHZ, CD_3CN, rt) δ 8.47–8.43 (m, 3H; C_5NHH_2+$C_6H_2H_2$), 8.04 (d, ^3J = 8.8 Hz, 2H; $C_6H_2H_2$), 7.96 (d, ^3J = 8.0 Hz, 2H; C_5NHH_2), 2.73 (s, 6H; CH_3 x 2). **^{13}C NMR** (125 MHz, CD_3CN, rt) δ 161.5, 155.0, 147.3, 137.7 (q, $^2J_{CF}$ = 32.6 Hz), 132.9, 129.4, 127.7, 127.5 (q, $^3J_{CF}$ = 3.9 Hz), 124.4 (q, $^1J_{CF}$ = 271 Hz), 18.5. **^{19}F NMR** (376 MHz, CD_3CN, rt) δ –64.2, –73.0 (d, $^1J_{FP}$ = 706 Hz; PF_6). **HRMS** (ESI-TOF) calculated for $[C_{15}H_{13}F_3NO_2]^+$ requires 296.0893, found 296.0893.

1-(3,5-Bis(trifluoromethyl)benzoyloxy)-2,6-lutidinium tetrafluoroborate (1e•BF_4)

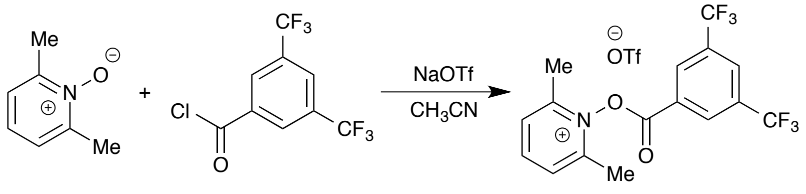


1e•BF4

The reaction of 2,6-lutidine *N*-oxide (241 mg, 1.95 mmol), potassium tetrafluoroborate (251 mg, 2.00 mmol) and 3,5-bis(trifluoromethyl)benzoyl chloride (594 mg, 2.15 mmol) following the general procedure afforded **1e**•BF_4 (248 mg, 28%, reaction time = 13 h) as a white solid after washed with as small amount of $CHCl_3$.

^{1}H NMR (400 MHZ, CD_3CN, rt) δ 8.79 (s, 2H; $C_6H_2H(CF_3)_2$), 8.54 (s, 1H; $C_6H_2H(CF_3)_2$), 8.47 (t, ^3J = 8.0 Hz, 1H; C_5NHH_2), 7.97 (d, ^3J = 8.0 Hz, 2H; C_5NHH_2), 2.74 (s, 6H; CH_3 x 2). **^{13}C NMR** (125 MHz, CD_3CN, rt) δ 160.5, 154.9, 147.6, 133.4 (q, $^2J_{CF}$ = 34.4 Hz), 132.7 (q, $^3J_{CF}$ = 3.5 Hz), 131.1 (apparent q, $^3J_{CF}$ = 3.1 Hz), 129.5, 126.7, 123.7 (q, $^1J_{CF}$= 271 Hz), 18.4. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –64.3, –154.3. **HRMS** (ESI-TOF) calculated for $[C_{16}H_{12}F_6NO_2]^+$ requires 364.0767, found 364.0763.

1-(3,5-Bis(trifluoromethyl)benzoyloxy)-2,6-lutidinium trifluoromethanesulfonate (1e•OTf**)**



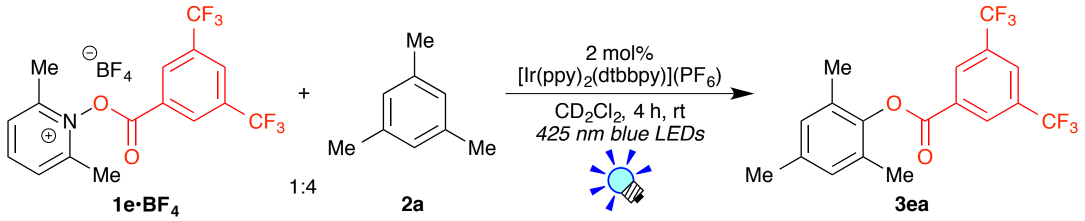
1e•OTf

The reaction of 2,6-lutidine *N*-oxide (249 mg, 2.02 mmol), sodium trifluoromethanesulfonate (691 mg, 2.50 mmol) and 3,5-bis(trifluoromethyl)benzoyl chloride (427 mg, 2.48 mmol) following the general procedure afforded **1e**•OTf (944 mg, 91%, reaction time = 3 h) as a white solid.

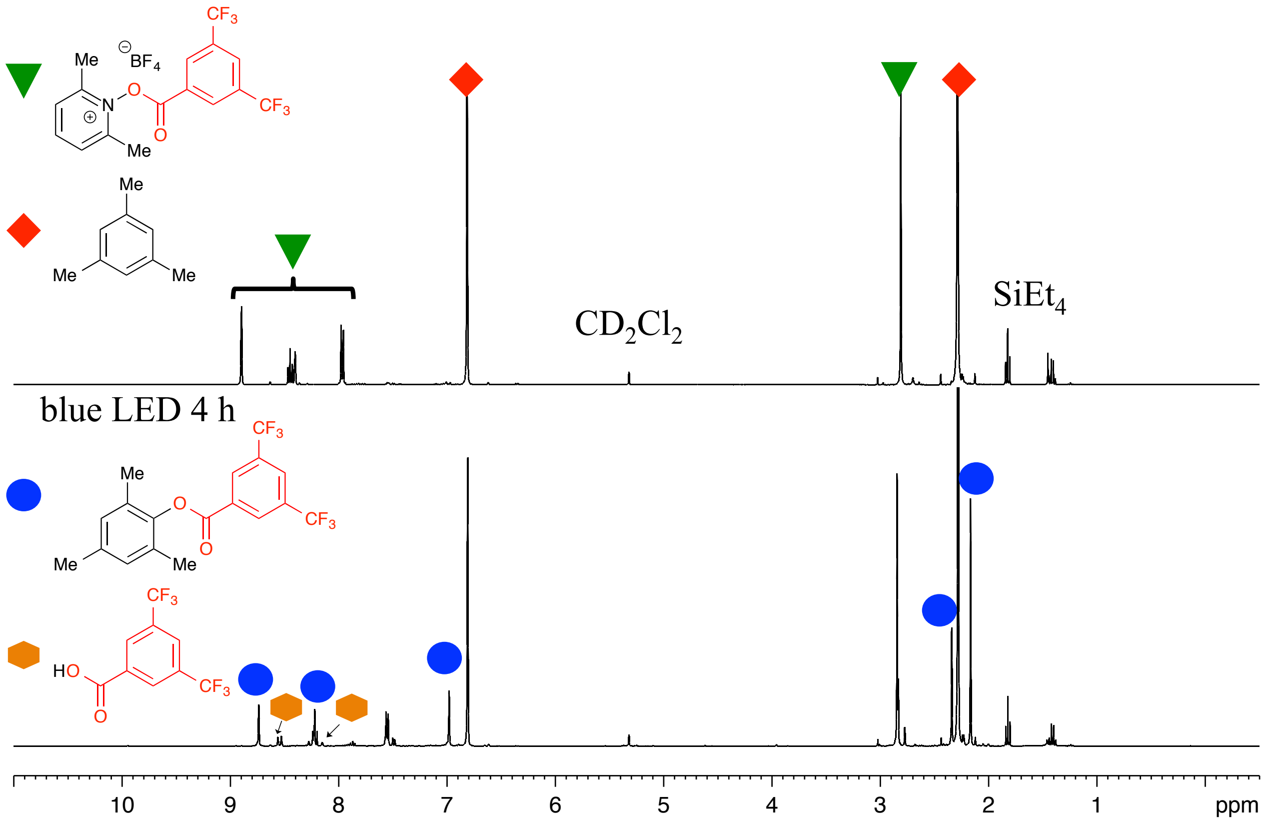
^{1}H NMR (400 MHZ, CD_3CN, rt) δ 8.79 (s, 2H; $C_6H_2H(CF_3)_2$), 8.54 (s, 1H; $C_6H_2H(CF_3)_2$), 8.47 (t, ^3J = 8.0 Hz, 1H; C_5NHH_2), 7.98 (d, ^3J = 8.0 Hz, 2H; C_5NHH_2), 2.75 (s, 6H; CH_3 x 2). **^{13}C NMR** (125 MHz, CD_3CN, rt) δ 160.5, 155.0, 147.6, 133.4 (q, $^2J_{CF}$ = 34.4 Hz), 132.7 (q, $^3J_{CF}$ = 3.1 Hz), 131.1 (apparent q, $^3J_{CF}$ = 3.1 Hz), 129.5, 126.7, 123.7 (q, $^1J_{CF}$ = 271 Hz), 121.9 (q, $^1J_{CF}$ = 366 Hz; CF_3SO_3), 18.5. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –64.4, –79.8. **HRMS** (ESI-TOF) calculated for $[C_{16}H_{12}F_6NO_2]^+$ requires 364.0767, found 364.0763. **EA**: calculated for $C_{17}H_{12}F_9O_5S$: C, 39.78; H, 2.36; N, 2.73, found: C, 39.59; H, 2.34; N, 2.83.

Typical NMR experimental procedure

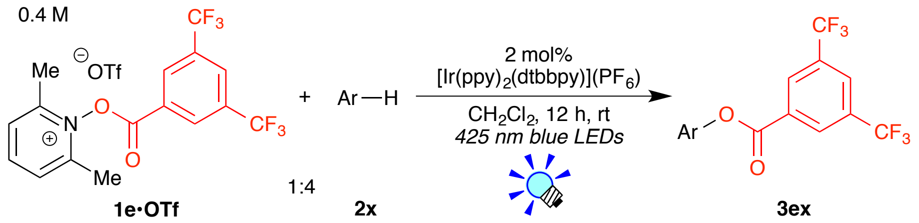
*Photocatalytic aroyloxylation of mesitylene (**2a**)*



Under N_2, to a CD_2Cl_2 (0.50 mL) solution of mesitylene (**2a**) (0.20 mmol) in an NMR tube, **1e**•BF_4 (50.0 μmol), *fac*-[Ir(ppy)$_3$] (1.00 μmol) and tetraethylsilane (a standard dissolved CD_3CN in a capillary tube) were added. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of 2-3 cm from the blue LED lamp: *hν* = 425 ± 15 nm).

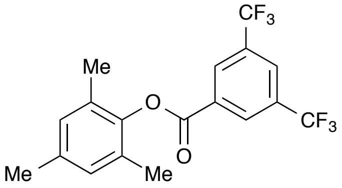


General procedure for the photocatalytic aroyloxylation of arenes with 1e•OTf



Under N_2, to a dry and degassed CH_2Cl_2 (1.0 mL) solution of arene (**2x**) (1.60 mmol) in a 20 mL-Schlenk tube, **1e**•OTf (0.40 mmol) and $[Ir(ppy)_2(dtbbpy)](PF_6)$ or *fac*-$[Ir(ppy)_3]$ (8.0 µmol) were added. The tube was placed at a distance of 2-3 cm from blue LED lamp (hν = 425 ± 15 nm). The resulting mixture was stirred at room temperature (water bath) under visible light irradiation. Then, the reaction mixture was concentrated *in vacuo* to remove volatile compounds. The residue was purified by flash column chromatography on silica gel to give **3ex**. Then the reaction was followed by ^{1}H NMR spectroscopy.

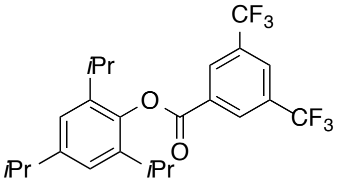
Mesityl 3,5-bis(trifluoromethyl)benzoate (3ea)



The reaction of **1e**•OTf (206 mg, 0.40 mmol), mesitylene (**2a**) (193 mg, 1.60 mmol), and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (7.2 mg, 7.9 µmol) following the general procedures afforded **3ea** (141 mg, 93% yield, reaction time = 6 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.68 (s, 2H; $C_6H_2H(CF_3)_2$), 8.16 (s, 1H; $C_6H_2H(CF_3)_2$), 6.94 (s, 2H; $C_6H_2(CH_3)_3$), 2.31 (s, 3H; $C_6H_2(CH_3)(CH_3)_2$), 2.15 (s, 6H; $C_6H_2(CH_3)(CH_3)_2$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 162.1, 145.7, 136.2, 132.7 (q, $^2J_{CF}$ = 33.8 Hz), 131.7, 130.3 (overlapped) (q, ^3J = 3.1 Hz), 129.7, 127.1 (apparent quin, $^3J_{CF}$ = 3.5 Hz), 123.0 (q, $^1J_{CF}$ = 272 Hz), 21.0, 16.4. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **EA**: calculated for $C_{18}H_{14}F_6O_2$: C, 57.45; H, 3.75, found: C, 57.36; H, 3.79.

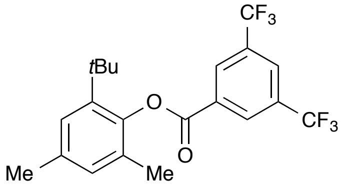
2,4,6-Triisopropylphenyl 3,5-bis(trifluoromethyl)benzoate (3eb)



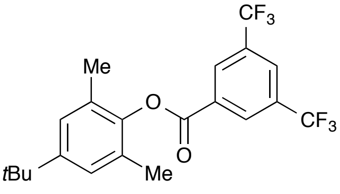
The reaction of **1e**•OTf (206 mg, 0.399 mmol), 1,3,5-triisopropylbenzen (**2b**) (328 mg, 1.61 mmol), and *fac*-$[Ir(ppy)_3]$ (13.1 mg, 20.0 µmol) following the general procedures afforded **3eb** (131 mg, 71% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.67 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.17 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.06 (s, 2H; $C_6\mathit{H}_2(CH_3)_3$), 2.93 (apparent seq, ^{3}J= 6.8 Hz, 1H; $(CH_3)_2C\mathit{H}$), 2.88 (apparent seq, ^{3}J = 6.8 Hz, 2H; $(CH_3)_2C\mathit{H}$), 1.28 (d, ^{3}J = 6.8 Hz, 6H; $(C\mathit{H}_3)_2CH$)), 1.21 (d, ^{3}J = 6.8 Hz, 12H; $(C\mathit{H}_3)_2CH$)). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 163.0, 147.5, 143.4, 139.8, 132.8 (q, ^{3}J = 34.0 Hz), 131.9, 130.3 (q, $^{3}J_{CF}$ = 3.1 Hz)), 127.1 (apparent quin, $^{3}J_{CF}$ = 3.6 Hz), 123.0 (q, $^{1}J_{CF}$ = 271 Hz), 122.3, 34.3, 28.0, 24.3, 24.0, 22.9. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{24}H_{26}F_6O_2+Na]^+$ requires 483.1729, found 483.1732.

2-(*tert*-Butyl)-4,6-dimethylphenyl 3,5-bis(trifluoromethyl)benzoate (3ec•A) and 4-(*tert*-Butyl)-2,6-dimethylphenyl 3,5-bis(trifluoromethyl)benzoate (3ec•B)



3ec·A

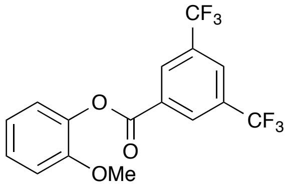


3ec·B

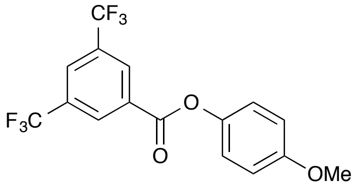
The reaction of **1e**•OTf (205 mg, 0.400 mmol), 5-*tert*-butyl-*m*-xylene (**2c**) (260 mg, 1.60 mmol), and *fac*-[Ir(ppy)$_3$] (13.2 mg, 20.2 μmol) following the general procedures afforded **3ec** (a 1:1 mixture of **3ec•A** and **3ec•B**) (137 mg, 82% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 100:1). Regioisomeric ratio (1:1) was determined by ^{1}H NMR analysis of the crude product before chromatography.

^{1}H NMR (a mixture of **3ec•A** and **3ec•B**) (400 MHz, $CDCl_3$, rt) **3ec•A**: δ 8.68 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.16 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.11 (s, 1H; $C_6\mathit{H}H$), 6.98 (s, 1H; $C_6H\mathit{H}$), 2.34 (s, 3H; $C_6H_2(C\mathit{H}_3)(CH_3)$), 2.09 (s, 3H; $C_6H_2(CH_3)(C\mathit{H}_3)$), 1.34 or 1.33 (s, 9H; $(C\mathit{H}_3)_3$). **3ec•B**: δ 8.68 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.16 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.13 (s, 2H; $C_6\mathit{H}_2$), 2.18 (s, 6H; $C_6H_2(C\mathit{H}_3)_2$), 1.34 or 1.33 (s, 9H; $(C\mathit{H}_3)_3$). **^{13}C NMR** (a mixture of **3ec•A** and **3ec•B**) (125 MHz, $CDCl_3$, rt) δ 162.4, 162.1, 149.4, 145.8, 145.7, 141.1, 135.9, 132.8 (q, $^{2}J_{CF}$ = 33.9 Hz), 132.7 (q, $^{2}J_{CF}$ = 34.1 Hz), 132.1, 131.8, 130.8, 130.3 (apparent brs) (overlapped), 130.2, 129.2, 127.1 (apparent quin, $^{3}J_{CF}$ = 3.3 Hz)) (overlapped), 126.3, 126.1, 123.0 (q, $^{1}J_{CF}$ = 271 Hz) (overlapped), 34.7, 34.5, 31.6, 30.8, 21.3, 17.0, 16.8. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9, –63.9. **HRMS** (ESI-TOF): calculated for $[C_{21}H_{20}F_6O_2+Na]^+$ requires 441.1260, found 441.1261.

2-Methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (*o*-3ed) and 4-methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (*p*-3ed)



***o*-3ed**



***p*-3ed**

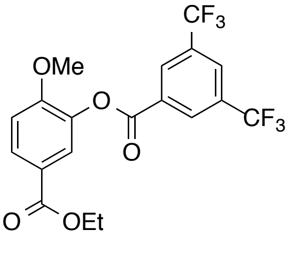
The reaction of **1e**•OTf (205 mg, 0.40 mmol), anisole (**2d**) (173 mg, 1.60 mmol), and *fac*-[Ir(ppy)$_3$] (13.0 mg, 20.0 μmol) following the general procedures afforded **3ed** (a 3:1 mixture of ***o*-3ed** and ***p*-3ed**) (114 mg, 78% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1). Regioisomeric ratio (3:1) was determined by ^{1}H NMR analysis of the crude product before chromatography.

***o*-3ed**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.66 (s, 2H; $C_6H_2H(CF_3)_2$), 8.14 (s, 1H; $C_6H_2H(CF_3)_2$), 7.30 (m, 1H; C_6HHHH), 7.17 (m, 1H; C$_6$H*H*HH), 7.05 (m, 1H; C$_6$HH*H*H), 7.03 (m, 1H; C$_6$HHH*H*), 3.835 (s, 3H; OCH_3). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 162.3, 151.1, 139.5, 132.5 (q, $^2J_{CF}$ = 34.0 Hz), 131.9, 130.5 (q, $^3J_{CF}$ = 3.1 Hz), 127.7, 126.9. (apparent quin, $^3J_{CF}$ = 3.8 Hz), 122.7, 123.0 (q, $^1J_{CF}$ = 271 Hz), 121.0, 112.7, 56.0. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –63.90.

***p*-3ed**: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.64 (s, 2H; $C_6H_2H(CF_3)_2$), 8.14 (s, 1H; $C_6H_2H(CF_3)_2$), 7.18-7.13 (2H; $C_6H_2H_2$) (overlaped), 6.97 (d, ^3J = 6.8 Hz, 2H; $C_6H_2H_2$), 3.843 (s, 3H; OCH_3). **^{13}C NMR** (500 MHz, CDCl$_3$, rt) δ 163.1, 157.9, 143.9, 132.6 (q, $^2J_{CF}$ = 34.0 Hz), 132.1, 130.4 (q, $^3J_{CF}$ = 3.3 Hz), 127.0 (apparent quin, $^3J_{CF}$ = 3.5 Hz), 123.0 (q, $^1J_{CF}$ = 271 Hz), 122.3, 114.8, 55.8. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –64.91.

HRMS (ESI-TOF): calculated for $[C_{16}H_{10}F_6O_3+Na]^+$ requires 387.0426, found 387.0424.

Ethyl 3-(3,5-bis(trifluoromethyl)benzoyloxy)-4-methoxybenzoate (3ee)

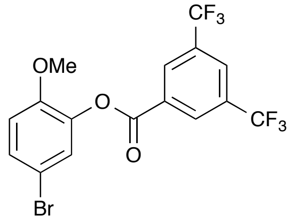


The reaction of **1e**•OTf (206 mg, 0.401 mmol), ethyl *p*-anisate (**2e**) (288 mg, 1.60 mmol), and [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (7.4 mg, 8.1 μmol) following the general procedures afforded **3ee** (129 mg, 74% yield, reaction time = 12 h) as a colorless oil after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1-20:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.65 (s, 2H; $C_6H_2H(CF_3)_2$), 8.15 (s, 1H; $C_6H_2H(CF_3)_2$), 8.03 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H; C$_6$*H*HH), 7.87 (d, ^4J = 2.0 Hz, 1H; C$_6$H*H*H), 7.06 (d, ^3J = 8.4 Hz, 1H; C$_6$HH*H*), 4.37 (q, ^3J =

7.2 Hz, 2H; CH_3CH_2COO), 3.89 (s, 3H; CH_3O), 1.38 (t, ^3J = 7.2 Hz, 3H; CH_3CH_2COO). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 165.6, 162.1, 154.9, 139.0, 132.6 (q, $^2J_{CF}$ = 34.1 Hz), 131.5, 130.5 (q, $^3J_{CF}$ = 3.0 Hz), 129.9, 127.2 (apparent quin, $^3J_{CF}$ = 3.6 Hz), 124.3, 123.6, 123.0 (q, $^1J_{CF}$ = 271 Hz), 111.9, 61.2, 56.3, 14.5. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{19}H_{14}F_6O_5+Na]^+$ requires 459.0638, found 459.0639.

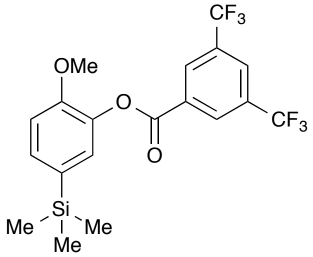
5-Bromo-2-methoxyphenyl 3,5-bis(trifluoromethyl)benzoate (3ef)



The reaction of **1e**•OTf (206 mg, 0.401 mmol), 4-bromoanisole (**2f**) (301 mg, 1.61 mmol), and *fac*-[Ir(ppy)$_3$] (12.8 mg, 19.5 μmol) following the general procedures afforded **3ef** (97.2 mg, 55% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 100:1) and GPC ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63, (s, 2H; $C_6H_2H(CF_3)_2$), 8.15 (s, 1H; $C_6H_2H(CF_3)_2$), 7.41 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H; C_6HHH), 7.34 (d, ^4J = 2.4 Hz, 1H; C_6HHH), 6.92 (d, ^3J = 8.8 Hz, 1H; C_6HHH), 3.82 (s, 3H; OCH_3). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 161.9, 150.6, 139.9, 132.6 (q, $^2J_{CF}$ = 34.1 Hz), 131.4, 130.5 (q, $^3J_{CF}$ = 3.4 Hz), 130.5, 127.2 (apparent quin, $^3J_{CF}$ = 3.5 Hz), 126.0, 122.9 (q, $^1J_{CF}$ = 272 Hz), 114.0, 112.3, 56.2. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **EA**: calculated for $C_{16}H_9BrF_6O_3$: C, 43.37; H, 2.05, found: C, 43.29; H, 2.02.

2-Methoxy-5-trimethylsilylphenyl 3,5-bis(trifluoromethyl)benzoate (3eg)

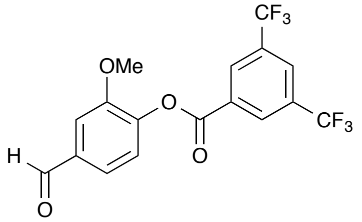


The reaction of **1e**•OTf (206 mg, 0.401 mmol), 4-trimethylsilylanisole (**2g**) (289 mg, 1.60 mmol), and *fac*-[Ir(ppy)$_3$] (13.1 mg, 20.0 μmol) following the general procedures afforded **3eg** (90.2 mg, 52% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1) and GPC ($CHCl_3$).

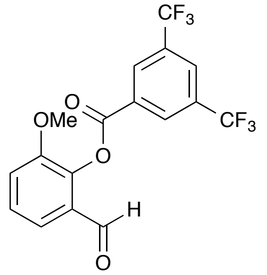
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67, (s, 2H; $C_6H_2H(CF_3)_2$), 8.14 (s, 1H; $C_6H_2H(CF_3)_2$), 7.42 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H; C_6HHH), 7.27 (d, ^4J = 1.6 Hz, 1H; C_6HHH), 7.04 (d, ^3J = 8.0 Hz, 1H; C_6HHH), 3.83 (s, 1H;

$OC\mathit{H}_3$), 0.27 (s, 9H; $Si(C\mathit{H}_3)_3$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 162.3, 151.6, 139.2, 133.0, 132.8, 132.5 (q, $^2J_{CF}$ = 33.9 Hz), 131.9, 130.5 (q, $^3J_{CF}$ = 3.1 Hz), 127.2, 126.9 (apparent quin, $^3J_{CF}$ = 3.8 Hz), 123.0 (q, $^1J_{CF}$ = 271 Hz), 112.4, 55.9, -0.89. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **EA**: calculated for $C_{19}H_{18}F_6O_3Si$: C, 52.29; H, 4.16, found: C, 52.12; H, 3.95.

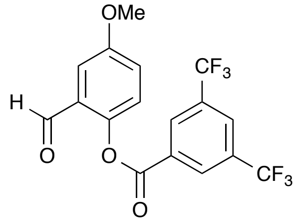
4-Formyl-2-methoxy 3,5-bis(trifluoromethyl)benzoate (3eh•6),
6-Formyl-2-methoxy 3,5-bis(trifluoromethyl)benzoate (3eh•2) and
2-Formyl-4-methoxy 3,5-bis(trifluoromethyl)benzoate (3eh•4)



3eh•6



3eh•2



3eh•4

The reaction of **1e**•OTf (205 mg, 0.400 mmol), *m*-anisaldehyde (**2h**) (218 mg, 1.60 mmol), and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (7.5 mg, 8.2 μmol) following the general procedures afforded **3eh** (a mixture of **3eh•6**, **3eh•2**, and **3eh•4**) (92 mg, 58% yield, reaction time = 12 h) as pale yellow solids respectively after purification with flash column chromatography on silica gel (hexane:EtOAc = 10:1) and GPC ($CHCl_3$). Regioisomer ratio (**3eh•6**:**3eh•2**:**3eh•4**=45:37:18) was determined by ^{1}H NMR analysis of the crude product before chromatography.

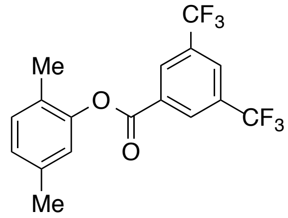
3eh•6: ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 10.0 (s, 1H; $C\mathit{H}O$), 8.66 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.16 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.55-7.58 (m, 2H; $C_6\mathit{HH}H$), 7.37 (d, ^3J = 7.6 Hz, 1H; $C_6HH\mathit{H}$), 3.91 (s, 3H; $OC\mathit{H}_3$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 191.1, 161.7, 152.0, 144.5, 135.9, 132.7 (q, $^2J_{CF}$ = 34.0 Hz), 131.2, 130.6 (q, $^3J_{CF}$ = 3.3 Hz), 127.3 (apparent quin, $^3J_{CF}$ = 3.5 Hz), 124.9, 123.4, 122.9 (q, $^1J_{CF}$ = 271 Hz), 111.2, 56.3. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{17}H_{10}F_6O_4+Na]^+$ requires 415.0375, found 415.0376.

3eh•2 ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 10.1 (s, 1H; $C\mathit{H}O$), 8.61 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.10 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.45 (dd,^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H; $C_6\mathit{H}HH$), 7.38 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1H; $C_6H\mathit{H}H$), 7.23 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 1H; $C_6HH\mathit{H}$)) 3.81 (s, 3H; $OC\mathit{H}_3$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 188.7, 162.1, 151.9, 140.3, 132.7 (q, $^2J_{CF}$ = 34.0 Hz), 131.2, 130.7 (q, $^3J_{CF}$ = 3.6 Hz), 129.3, 127.7, 127.3 (seq, $^3J_{CF}$ = 3.4 Hz), 123.0 (apparent quin, $^1J_{CF}$ = 271 Hz), 122.7, 118.1, 56.5. **^{19}F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{17}H_{10}F_6O_4+Na]^+$ requires 415.0375, found 415.0379.

3eh•4 ^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 10.1 (s, 1H; $C\mathit{H}O$), 8.66 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.12 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.42 (apparent br. t, 1H; $C_6\mathit{H}HH$), 7.23 (apparent br. d, 1H; $C_6H\mathit{H}H$), 7.23 (br. s, 1H; $C_6HH\mathit{H}$), 3.94 (s, 3H; $OC\mathit{H}_3$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 188.4, 163.1, 158.3, 144.4, 132.7 (q, $^2J_{CF}$ =

34.0 Hz), 131.4, 130.5 (q, $^3J_{CF}$ = 3.4 Hz), 128.5, 127.4 (seq, $^3J_{CF}$ = 3.5 Hz), 124.5, 122.9 (apparent quin, $^1J_{CF}$ = 271 Hz), 121.9, 115.4, 56.1. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{17}H_{10}F_6O_4+Na]^+$ requires 415.0375, found 415.0379.

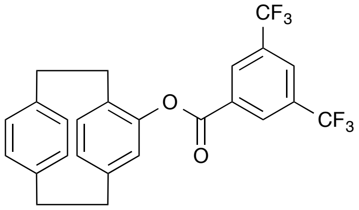
2,5-Dimethylphenyl 3,5-bis(trifluoromethyl)benzoate (3ei)



The reaction of **1e**•OTf (206 mg, 0.401 mmol), *p*-xylene (**2i**) (170 mg, 1.60 mmol), and [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (7.3 mg, 8.0 μmol) following the general procedures afforded **3ei** (108 mg, 74% yield, reaction time = 12 h) as a colorless oil after purification with flash column chromatography on silica gel (hexane:EtOAc = 100:1).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 8.66 (s, 2H; C$_6$*H*$_2$H(CF$_3$)$_2$), 8.15 (s, 1H; C$_6$H$_2$*H*(CF$_3$)$_2$), 7.19 (d, ^3J = 8.0 Hz, 1H; C$_6$*H*HH), 7.04 (d, ^3J = 8.0 Hz, 1H; C$_6$H*H*H), 6.96 (s, 1H; C$_6$HH*H*), 2.36 (s, 3H; C$_6$H$_3$(C*H*$_3$)(CH$_3$)), 2.19 (s, 3H; C$_6$H$_3$(CH$_3$)(C*H*$_3$)). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 162.5, 149.0, 137.5, 132.7 (q, $^2J_{CF}$ = 34.1 Hz), 131.9, 131.3, 130.3 (q, $^3J_{CF}$ = 3.1 Hz), 127.7, 127.1 (apparent quin, $^3J_{CF}$ = 3.5 Hz), 126.8, 123.0 (q, $^1J_{CF}$ = 271 Hz), 122.2, 21.1, 15.9. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{17}H_{12}F_6O_2+Na]^+$ requires 385.0634, found 385.0635.

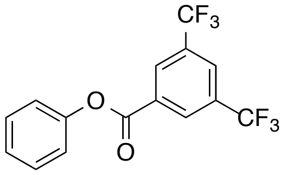
4-(3,5-bis(trifluoromethyl)benzoyloxy)[2,2]paracyclophane (3ej)



The reaction of **1e**•OTf (205 mg, 0.400 mmol), [2,2]paracyclophane (**2j**) (100 mg, 0.481 mmol), and [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (7.2 mg, 7.9 μmol) in CH$_2$Cl$_2$ (4.0 mL) following the general procedures afforded **3ej** (48.1 mg, 26% yield, reaction time = 12 h) as a colorless oil after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1) and GPC (CHCl$_3$).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 8.72 (s, 2H; C$_6$*H*$_2$H(CF$_3$)$_2$), 8.20 (s, 1H; C$_6$H$_2$*H*(CF$_3$)$_2$), 6.94 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H; C$_6$*H*HHO), 6.62–6.58 (m, 2H; C$_6$*H*$_2$H$_2$), 6.55 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H; C$_6$H*H*HO), 6.49 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H; C$_6$H$_2$*H*$_2$), 6.20 (s, 1H; C$_6$H*H*HO), 3.21–3.00 (m, 7H; (C*H*$_2$) x 3, C*H*H), 2.79 (m, 1H; CH*H*). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 161.9, 148.7, 142.3, 139.5, 139.4, 135.8, 133.7, 133.4, 132.8 (q, $^2J_{CF}$ = 34.1 Hz), 132.4, 132.3, 131.1, 131.0, 130.1 (q, $^3J_{CF}$ = 3.4 Hz), 129.4, 127.8, 127.1 (apparent quin, $^3J_{CF}$ = 3.8 Hz), 123.0 (q, $^1J_{CF}$ = 272 Hz), 35.4, 35.0, 34.7, 31.9. ^{19}**F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{25}H_{18}F_6O_2+Na]^+$ requires 487.1103, found 487.1102.

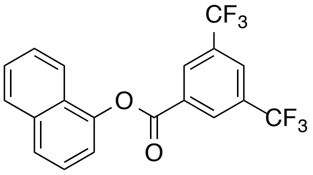
Phenyl 3,5-bis(trifluoromethyl)benzoate (3ek)



The reaction of **1e**•OTf (206 mg, 0.401 mmol), benzene (**2k**) (125 mg, 1.60 mmol), and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (7.3 mg, 8.0 μmol) following the general procedures afforded **3ek** (69.8 mg, 52% yield, reaction time = 12 h) as a colorless oil after purification with flash column chromatography on silica gel (hexane:EtOAc = 100:1).

^{1}**H NMR** (400 MHz, $CDCl_3$, rt) δ 8.65 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 8.15 (s, 1H; $C_6H_2\mathit{H}(CF_3)_2$), 7.47 (t, ^3J = 8.0 Hz, 2H; $C_6\mathit{H}_2H_2H$), 7.33 (t, ^3J = 8.0 Hz, 1H; $C_6H_2H_2\mathit{H}$, 1H), 7.254 (d, ^3J = 7.6 Hz, 2H; $C_6H_2\mathit{H}_2H$). ^{13}**C NMR** (125 MHz, $CDCl_3$, rt) δ 162.7, 150.5, 132.6 (q, $^2J_{CF}$ = 34.3 Hz), 132.0, 130.4 (q, $^3J_{CF}$ = 3.3 Hz), 129.9, 127.1 (apparent quin, $^3J_{CF}$ = 3.6 Hz), 126.7, 123.0 (q, $^1J_{CF}$ = 271 Hz), 121.5. ^{19}**F NMR** (376 MHz, $CDCl_3$, rt) δ –63.9. **HRMS** (ESI-TOF): calculated for $[C_{14}H_{18}O_4+Na]^+$ requires 261.1097, found 261.1105.

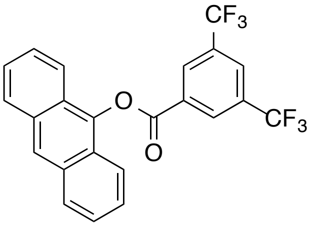
Naphthalen-1-yl 3,5-bis(trifluoromethyl)benzoate (3el)



The reaction of **1e**•OTf (206.6 mg, 0.402 mmol), naphthalene (**2l**) (206.3 mg, 1.61 mmol), and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (7.3 mg, 8.0 μmol) following the general procedures afforded **3el** (137.6 mg, 89% yield, reaction time = 12 h) as a pale beige solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 50:1).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.21 (s, 2H; $C_6\mathit{H}_2H(CF_3)_2$), 7.95 (m, 1H $C_6H_2\mathit{H}(CF_3)_2$), 7.86–7.84 (m, 2H; naphthyl-*H*), 7.57–7.53 (m, 3H; naphthyl-*H*), 7.39 (m, 1H; naphthyl-*H*). ^{13}**C NMR** (125 MHz, $CDCl_3$, rt) δ 162.8, 146.4, 134.9, 132.8 (q, $^2J_{CF}$ = 34.1 Hz), 131.8, 130.5 (q, $^3J_{CF}$ = 3.5 Hz), 128.4, 127.3 (apparent quin, $^3J_{CF}$ = 4.0 Hz), 127.03, 126.98, 126.9, 126.6, 125.6, 123.0 (q, $^1J_{CF}$ = 271 Hz), 120.9, 118.2. ^{19}**F NMR** (376 MHz, $CDCl_3$, rt) δ –64.2. **HRMS** (ESI-TOF): calculated for $[C_{19}H_{10}F_6O_2+Na]^+$ requires 407. 0477, found 407.0474.

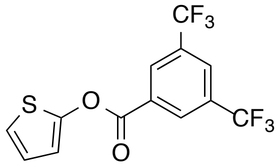
Anthracen-9-yl 3,5-bis(trifluoromethyl)benzoate (3em)



The reaction of **1e**•OTf (204.8 mg, 0.399 mmol), anthracene (**2m**) (142.2 mg, 0.798 mmol), and *fac*-[Ir(ppy)$_3$] (13.3 mg, 20.3 μmol) following the general procedures afforded **3em** (64.9 mg, 37% yield, reaction time = 6 h) as a pale yellow solid after purification with flash column chromatography on silica gel (hexane:EtOAc = 1:0-50:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.90 (s, 2H; $C_6H_2H(CF_3)_2$), 8.45 (s, 1H; anthracenyl-*H*), 8.26 (s, 1H; $C_6H_2H(CF_3)_2$), 8.10–8.07 (m, 2H; anthracenyl-*H*), 7.93–7.90 (m, 2H; anthracenyl-*H*), 7.53–7.50 (m, 4H; anthracenyl-*H*). **^{13}C NMR** (125 MHz, CDCl$_3$, rt), δ 162.9, 141.6, 133.0 (q. $^2J_{CF}$ = 33.9 Hz) 132.0, 131.4, 130.7 (apparent br. d., $^3J_{CF}$ = 3.8 Hz), 128.8, 127.6 (apparent br. quin, $^3J_{CF}$ = 3.6 Hz), 126.9, 125.9, 125.7, 123.9, 123 (q, $^1J_{CF}$ = 271 Hz), 121.0. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –64.2. **HRMS** (ESI-TOF): calculated for $[C_{23}H_{12}F_6O_2+Na]^+$ requires 457.0634, found 457.0632.

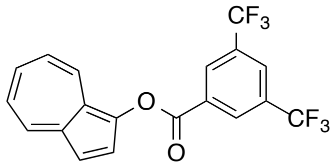
Thiopen-2-yl 3,5-bis(trifluoromethyl)benzoate (3en)



The reaction of **1e**•OTf (205 mg, 0.400 mmol), thiophene (**2n**) (134 mg, 1.60 mmol), and [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (7.3 mg, 8.0 μmol) following the general procedures afforded **3en** (61.7 mg, 45% yield, reaction time = 12 h) as a white solid after purification with flash column chromatography on silica gel (hexane).

^{1}H NMR (400 MHz, acetone-*d*$_6$) δ 8.74 (s, 2H; $C_6H_2H(CF_3)_2$), 8.45 (s, 1H; $C_6H_2H(CF_3)_2$), 7.18 (dd, ^3J = 5.6 Hz, ^4J = 1.6 Hz, 1H; thiophenyl-*H*), 7.04 (dd, ^3J = 3.6 Hz, ^4J = 1.6 Hz, 1H; thiophenyl-*H*), 6.97 (dd, ^3J = 5.6 Hz, ^3J = 4.0 Hz, 1H; thiophenyl-*H*). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 161.0, 151.5, 132.8 (q, $^2J_{CF}$ = 33.3 Hz), 130.9, 130.4, 127.4 (apparent br. d, $^3J_{CF}$ = 3.1 Hz), 123.8, 122.9 (apparent quin, $^3J_{CF}$ = 271 Hz), 119.0, 114.5. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –64.3. **EA**: calculated for $C_{13}H_6F_6O_2S$: C, 45.89; H, 1.78, found: C, 45.82; H, 1.80.

Azulen-1-yl 3,5-bis(trifluoromethyl)benzoate (3eo)



The reaction of **1e**•OTf (246.4 mg, 0.480 mmol), azulene (**2o**) (51.2 mg, 0.399 mmol), and *fac*-[Ir(ppy)$_3$] (13.0 mg, 19.9 μmol) following the general procedures afforded **3eo** (34.2 mg, 22% yield, reaction time = 24 h) as a dark green solid after purification with flash column chromatography on silica gel (hexane).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (s, 2H; $C_6H_2H(CF_3)_2$), 8.33 (d, ^3J = 9.2 Hz, 1H; C_7H_4H), 8.28 (d, ^3J = 9.6 Hz, 1H; C_7H_4H), 8.18 (s, 1H; $C_6H_2H(CF_3)_2$), 7.95 (d, ^3J = 4.4 Hz, 1H; C_5HH), 7.65 (dd, ^3J = 9.6 Hz, ^3J = 9.6 Hz, 1H; C_7H_4H), 7.35 (d, ^3J = 4.4 Hz, 1H; C_5HH), 7.17 (dd, ^3J = 9.6 Hz, ^3J = 9.2 Hz, 2H; C_7H_4H). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 162.6, 139.1, 138.8, 137.1, 136.9, 132.7 (q, $^2J_{CF}$ = 34.0 Hz), 132.3, 132.1, 130.4 (q, $^3J_{CF}$ = 3.1 Hz), 127.7, 127.0 (apparent quin, $^2J_{CF}$ = 3.8 Hz), 126.5, 123.4, 123.0 (q, $^1J_{CF}$ = 271 Hz), 122.6, 114.3. **^{19}F NMR** (376 MHz, CDCl$_3$, rt) δ –64.2. **HRMS** (ESI-TOF): calculated for $[C_{14}H_{18}O_4+Na]^+$ requires 261.1097, found 261.1105.

Cyclic voltammograms

Electrochemical measurements were recorded on a Hokutodenkou HZ-5000 analyzer (observed in 0.002 M CH_3CN; $[(NBu_4)PF_6]$ = 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple).

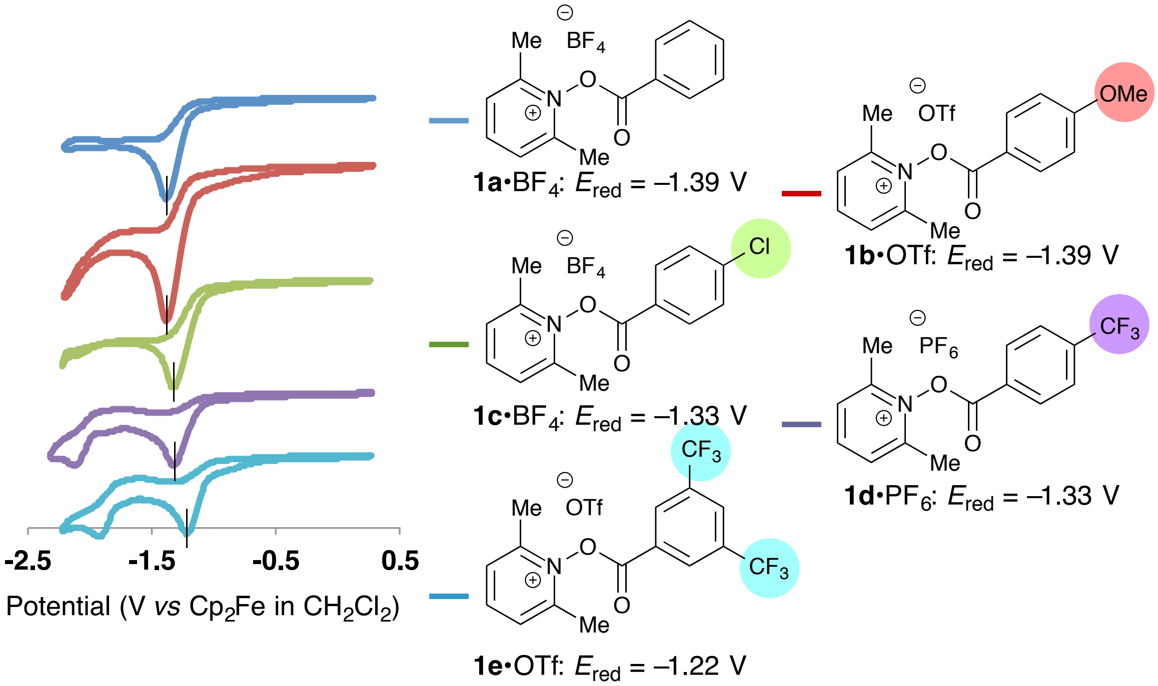


Figure S1. CV traces for **1a**•BF_4, **1b**•OTf, **1c**•BF_4, **1d**•PF_6 and **1e**•OTf

Luminescence quenching experiments

A solution of *fac*-[Ir(ppy)$_3$] was prepared as to show the absorbance 0.1 at the excitation wavelength (363 nm) and degassed by three freeze-pump-thaw cycles in a 1 cm quartz cell equipped with a sphere moiety for freeze. The solution of quencher was added to the solution of the Ir catalyst before measurement of emission intensities at 506 nm.

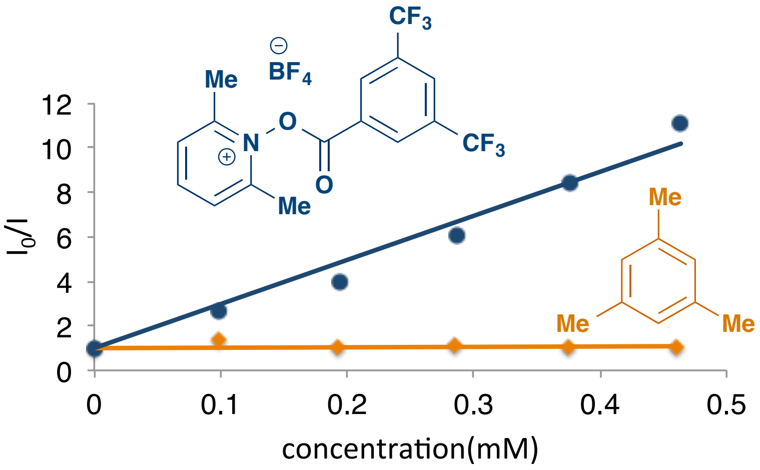


Figure S2. Stern-Volmer plots for **1e**•BF$_4$ and **2a**

Experiment for kinetic isotope effect

Under N_2, to benzene (**2k**) (62.8 mg, 0.80 mmol) and benzene-d_6 (**2k**-d_6) (67.6 mg, 0.80 mmol) dissolved in a dry and dehydrated CH_2Cl_2 (1.0 mL) in a 20 mL-Schlenk tube, **1e**•OTf (205.1 mg, 0.40 mmol) and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (7.3 mg, 0.020 mmol) were added. The tube was placed at a distance of 2-3 cm from blue LED lamps (hν = 425 ± 15 nm). The resulting mixture was stirred at room temperature (water bath) under visible light irradiation. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (Hexane:EtOAc=50:1) to give a mixture of **3ek** and **3ek**-d_5 (**3ek**/**3ek**-d_5 = 0.91, 55% yield). The KIE was determined by the ^{1}H NMR spectra (Figure S3 and **3ek**, *vide infra*) .

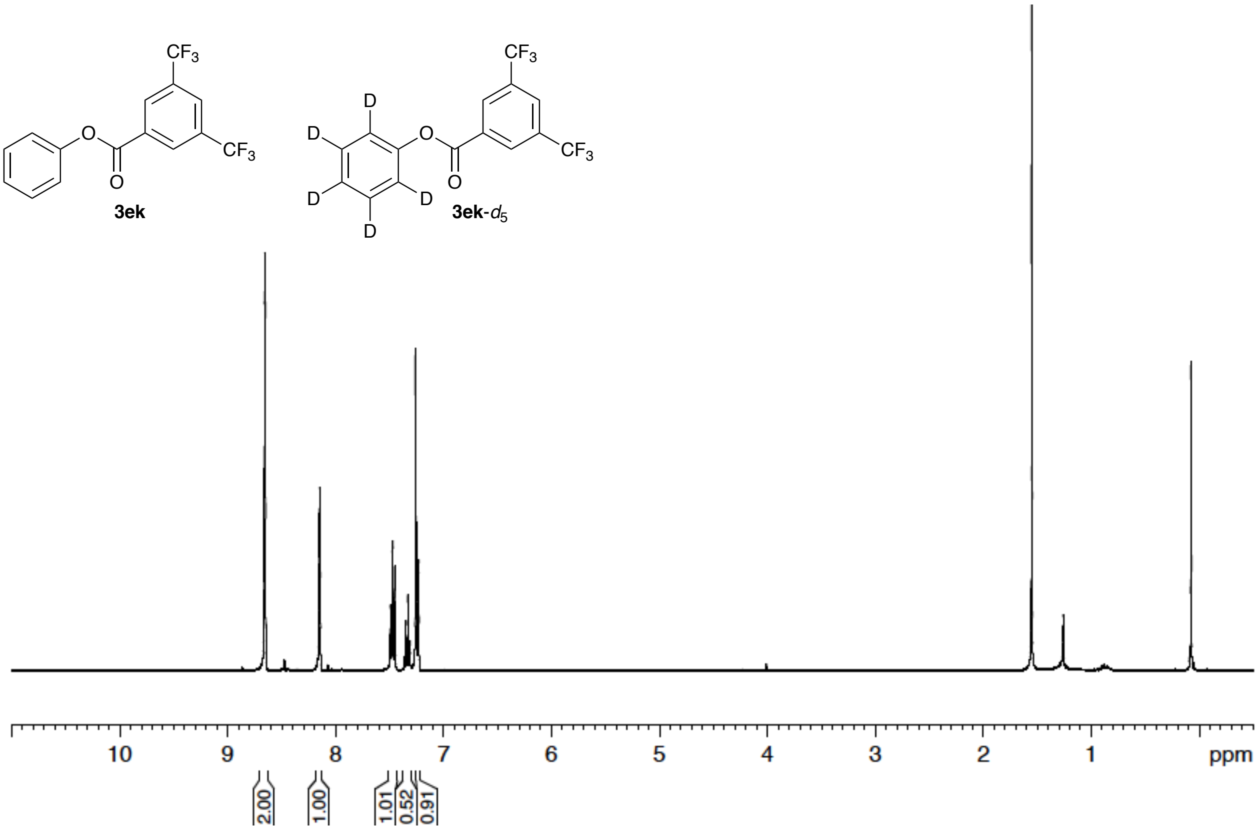


Figure S3 Reaction of a mixture of C_6H_6 and C_6D_6

Time profile for photocatalytic aroyloxylation of 1e•BF$_4$ with 2a

The photocatalytic aroyloxylation of **1e**•BF$_4$ with **2a** using *fac*-[Ir(ppy)$_3$] was performed with/without light irradiation. The time profile is shown in Figure S4. As a result, continuous irradiation of visible light is essential for efficient reaction.

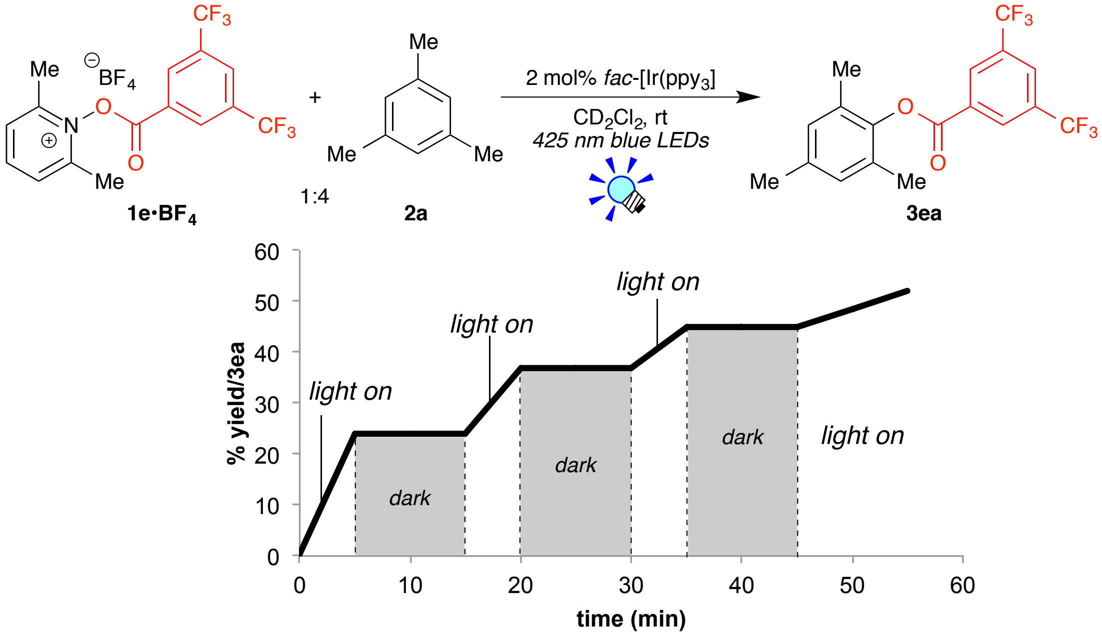


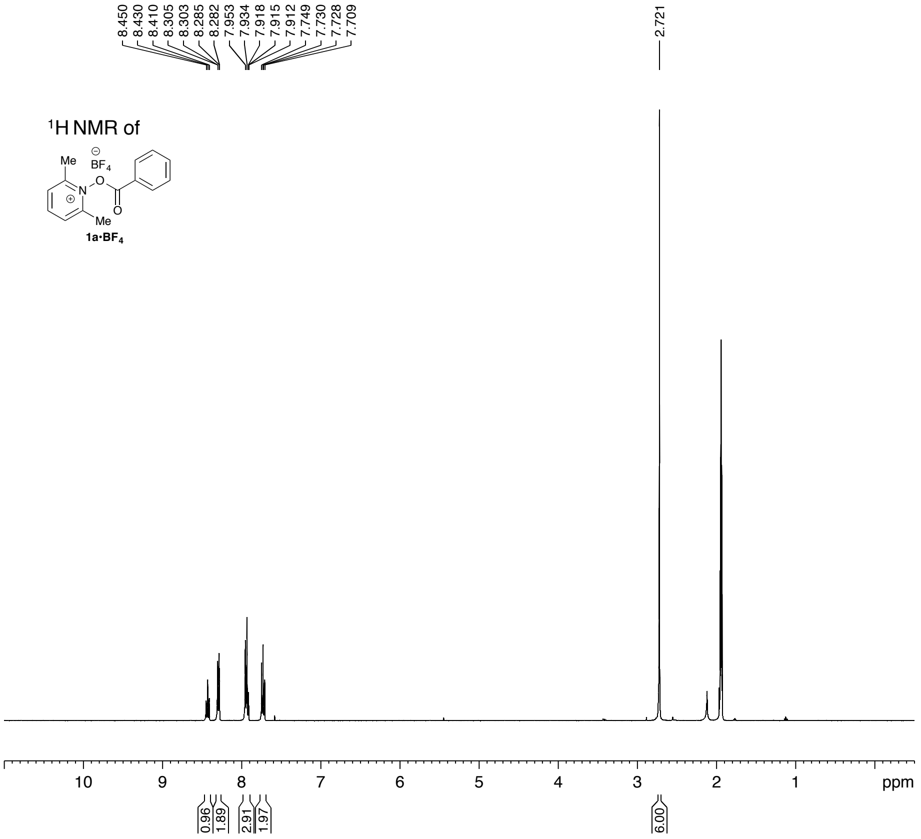
Figure S4. Reaction profile with intermittent irradiation

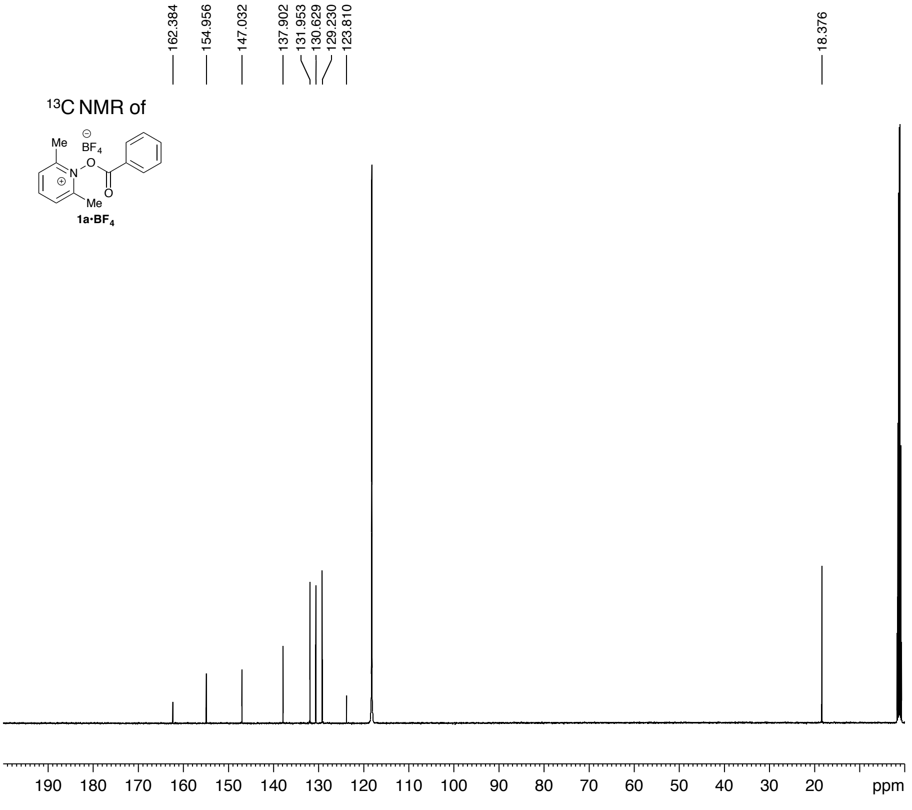
References

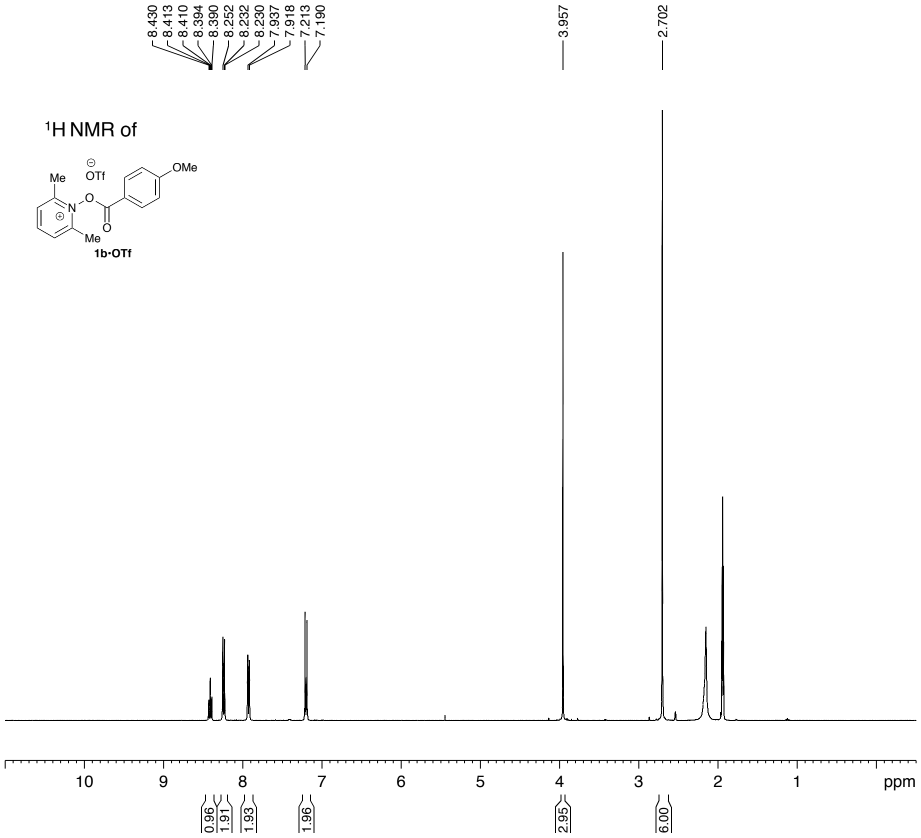
1 (a) H. B. Ross, M. Boldaji, D. P. Rilema, C. B. Blanton and R. P. White, *Inorg, Chem.* 1989, **28**, 1013-1021; (b) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* 2003, **125***,* 7377-7387; (c) J. D. Slinker, Alon. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard and G. G. Malliaras. *J. Am. Chem. Soc.* 2004, **126**, 2763-2767.

2 L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Chem. Eur. J.* 2012, **18**, 2931-2937.

^{1}H, ^{13}C, ^{19}F NMR and 2D NMR spectra



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2.702
^{1}H NMR of
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OMe
Me
N
O
O
Me
1b•OTf
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9
8
7
6
5
4
3
2
1
ppm
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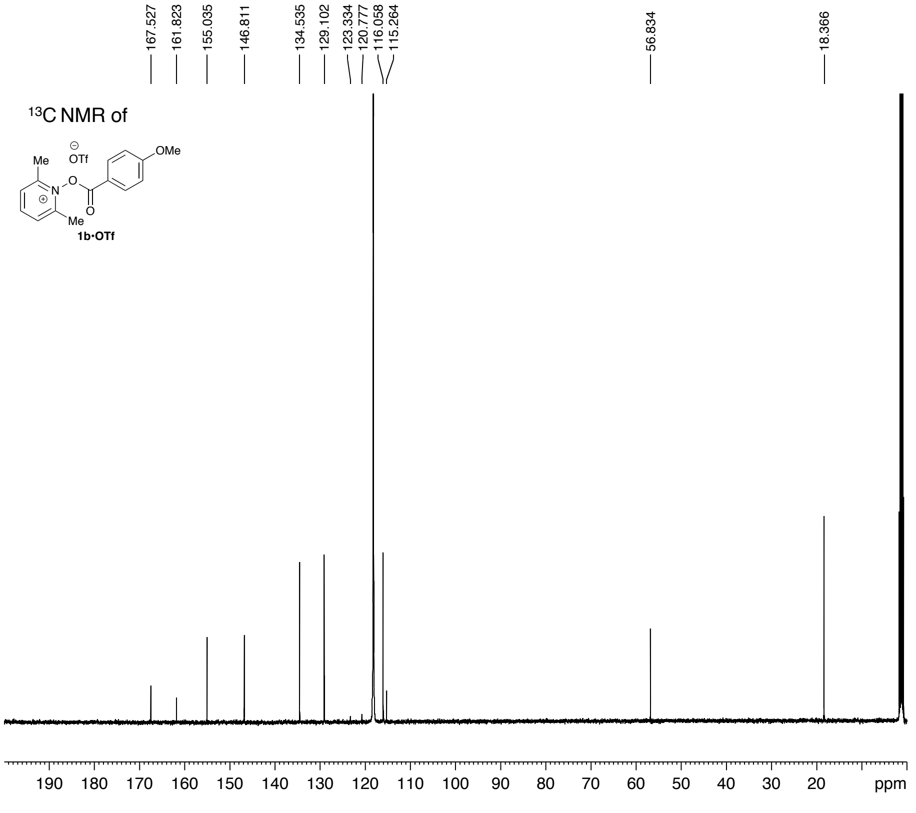
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^{13}C NMR of
OTf
OMe
Me
N
O
O
Me
1b•OTf
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180
170
160
150
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130
120
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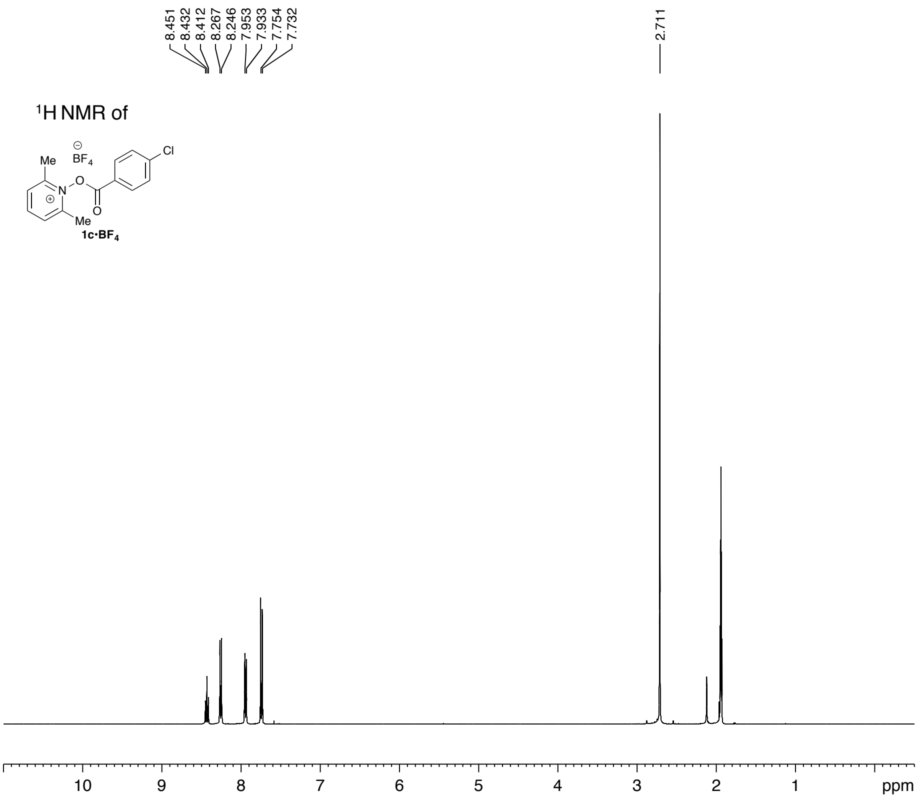
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O
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Me
1c·BF$_4$
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9
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7
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4
3
2
1
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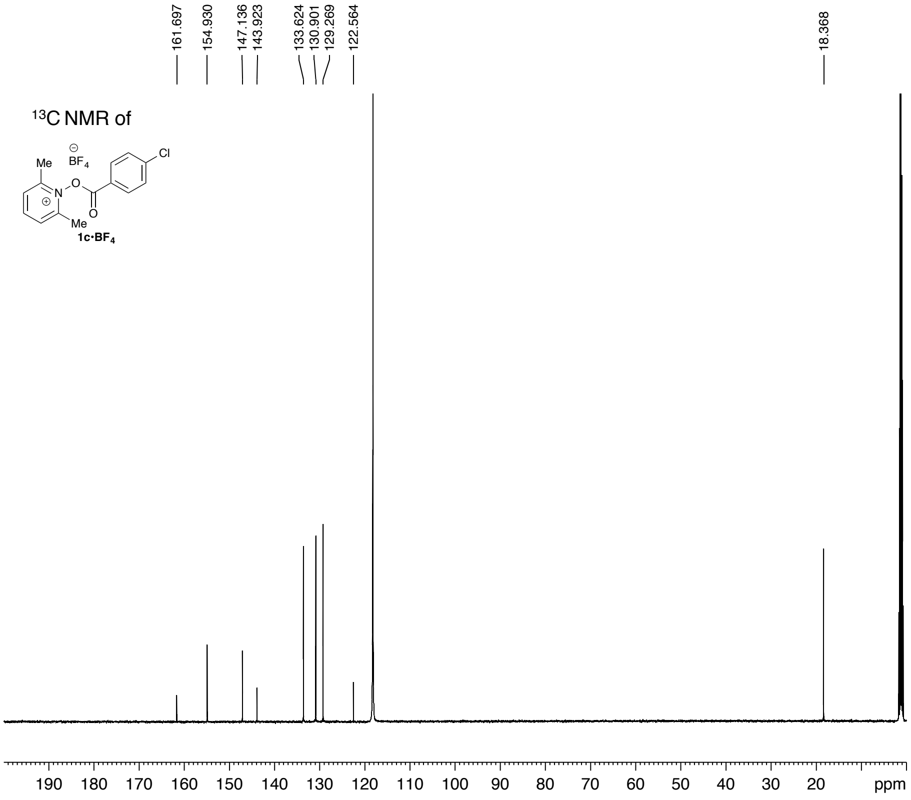
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Cl
N
O
O
Me
1c·BF$_4$
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160
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120
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100
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70
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40
30
20
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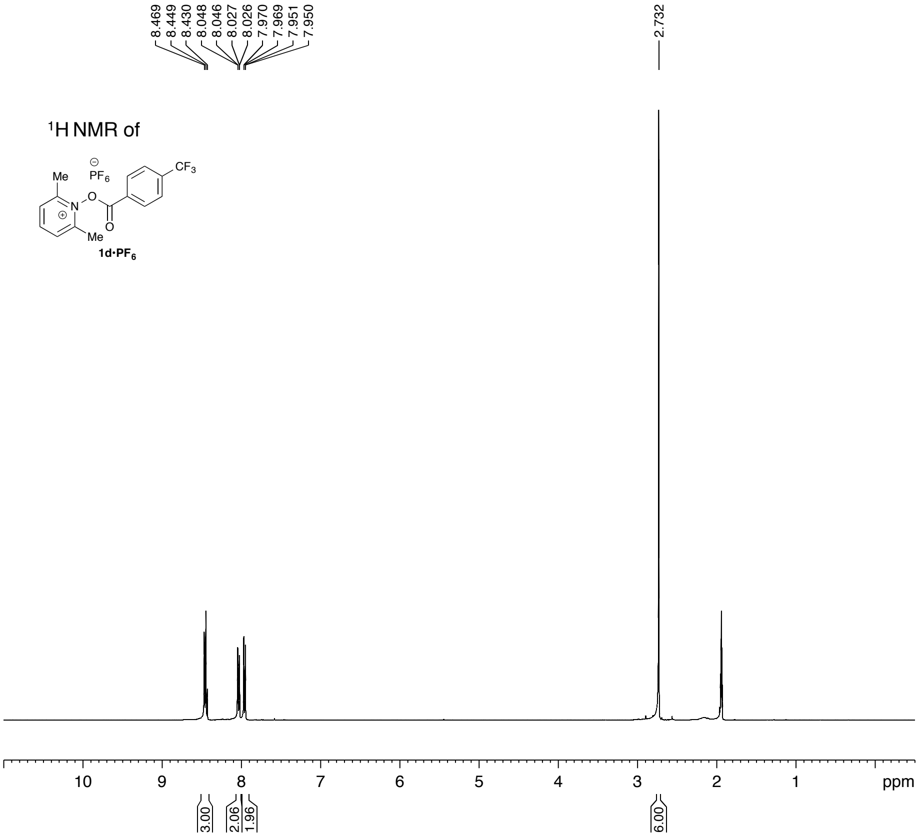
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PF_6
CF_3
N
O
O
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1d·PF6
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8
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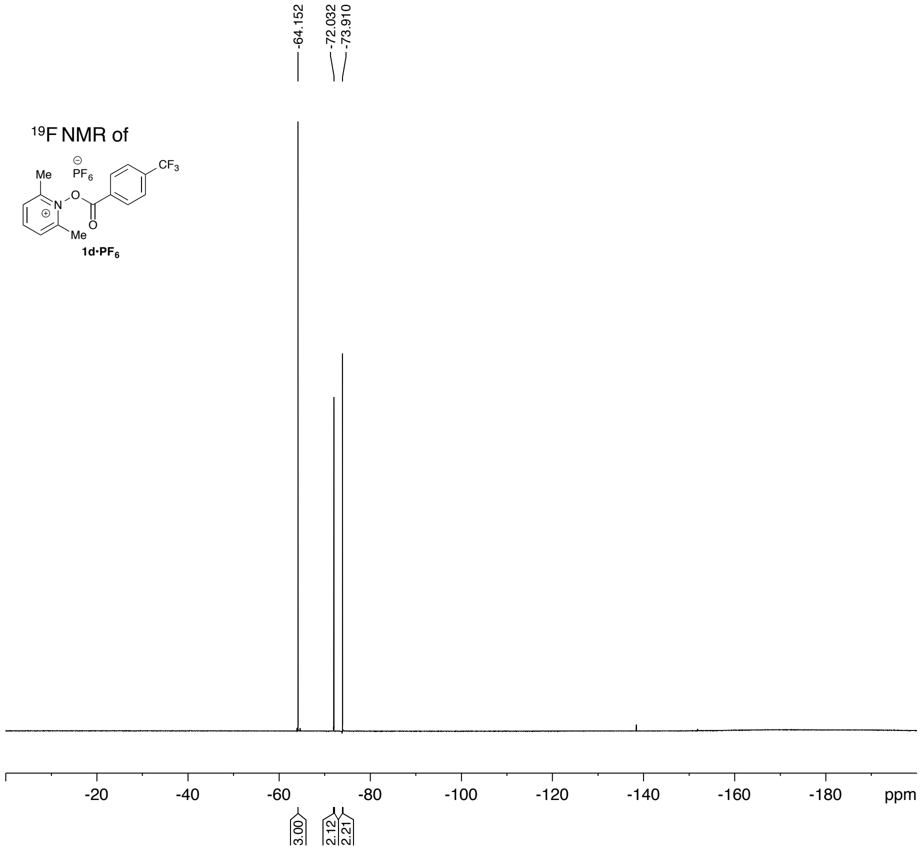
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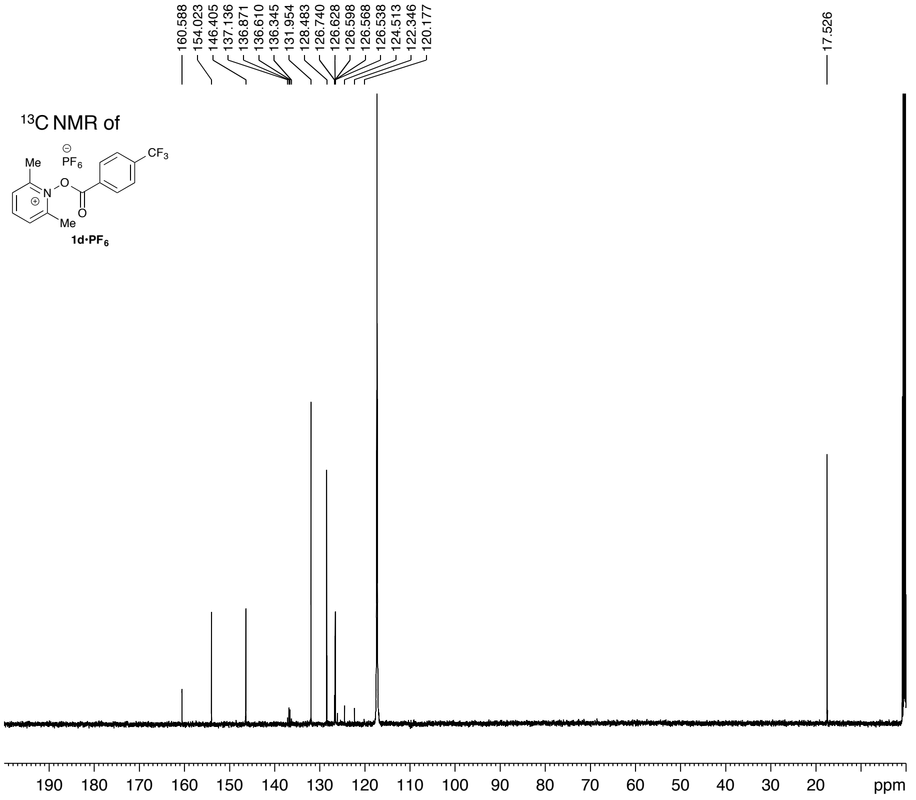
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PF$_6$
CF$_3$
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O
O
Me
1d·PF$_6$
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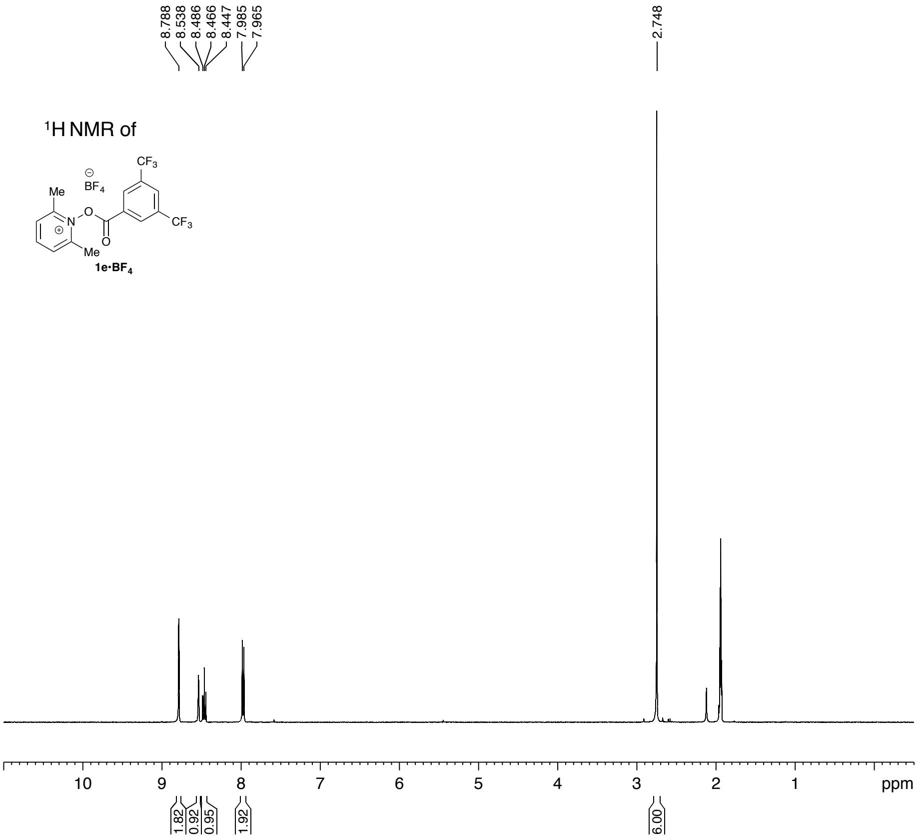
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BF$_4$
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O
O
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Me
1e·BF$_4$
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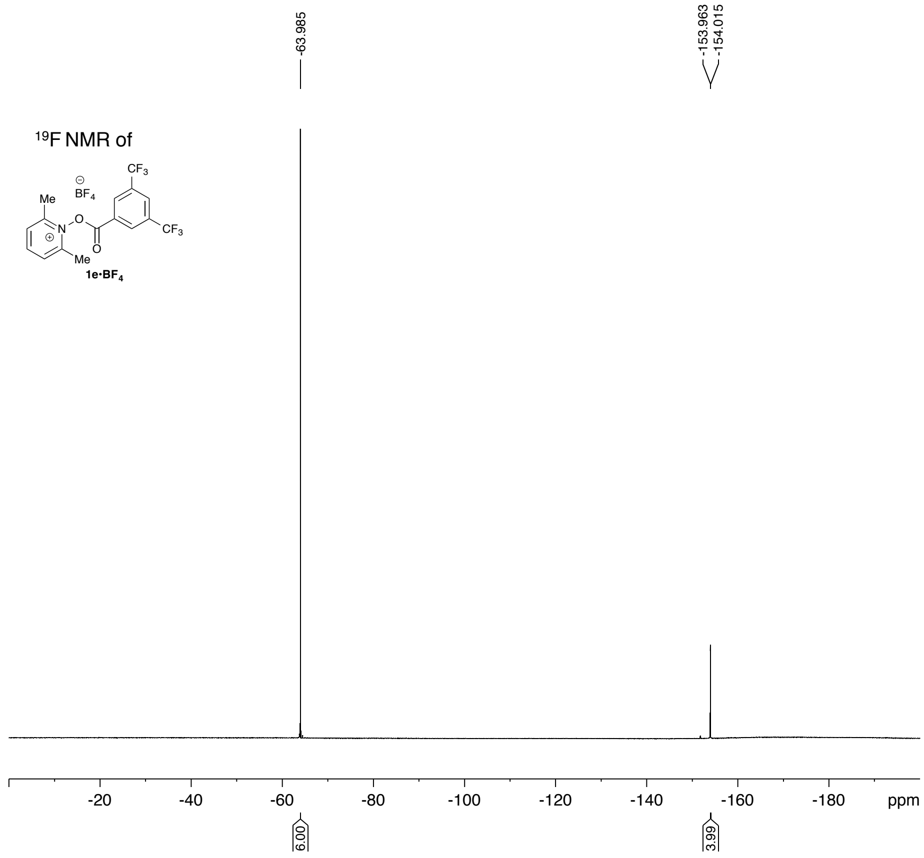
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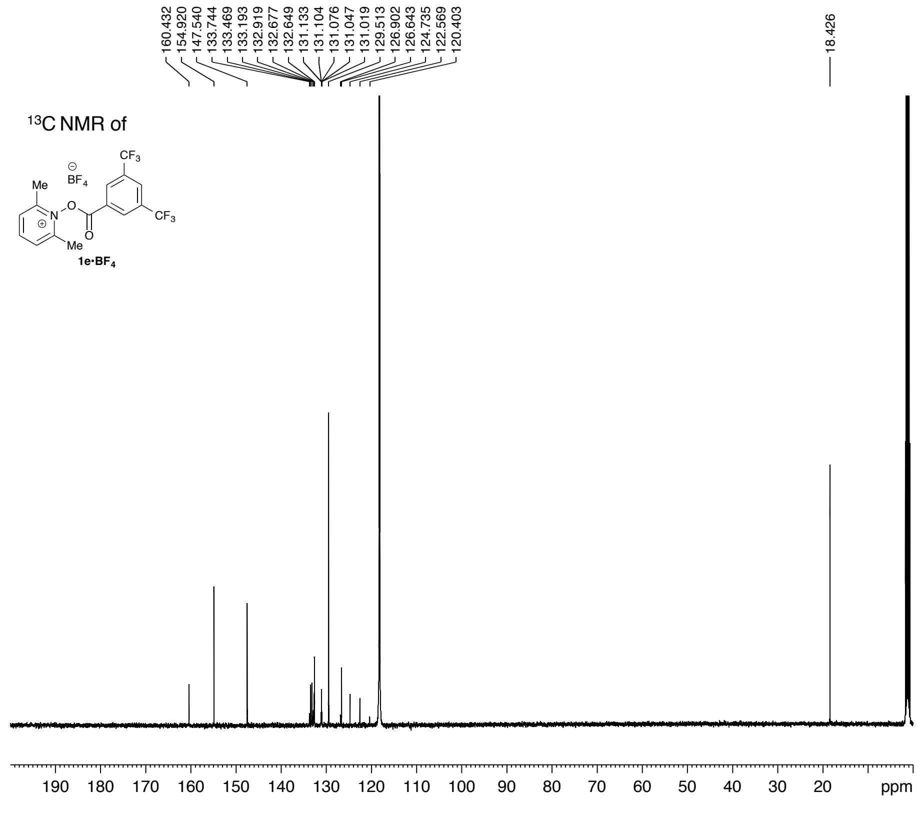
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BF4
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O
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Me
1e·BF4
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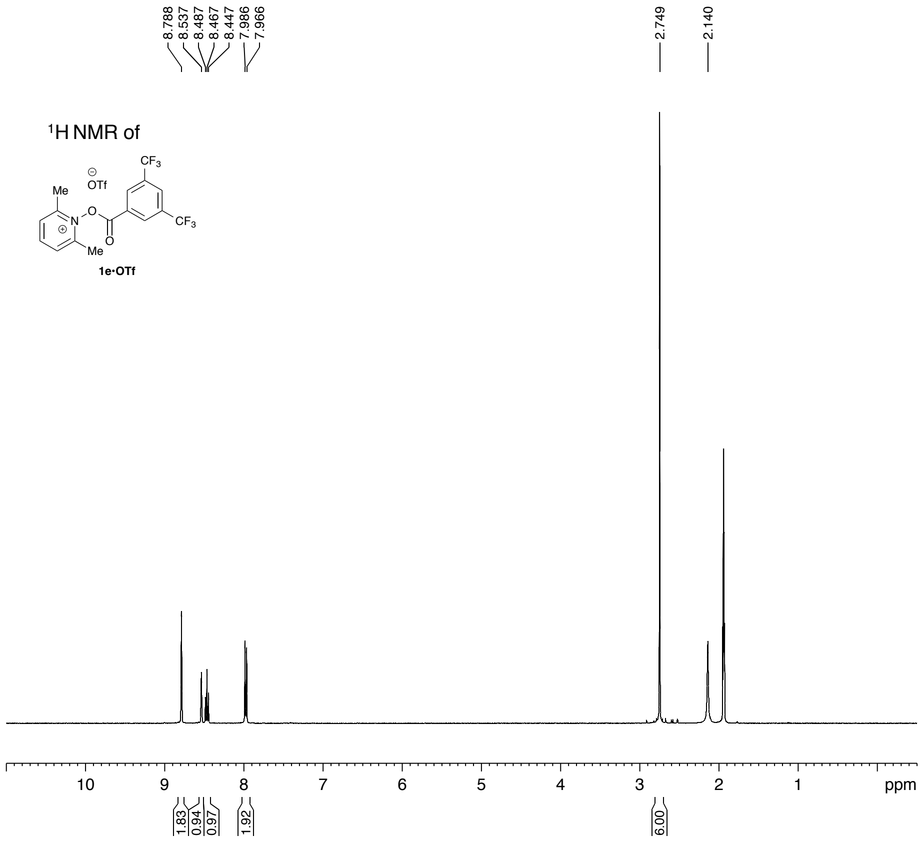
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OTf
Me
N
O
O
CF3
Me
1e·OTf
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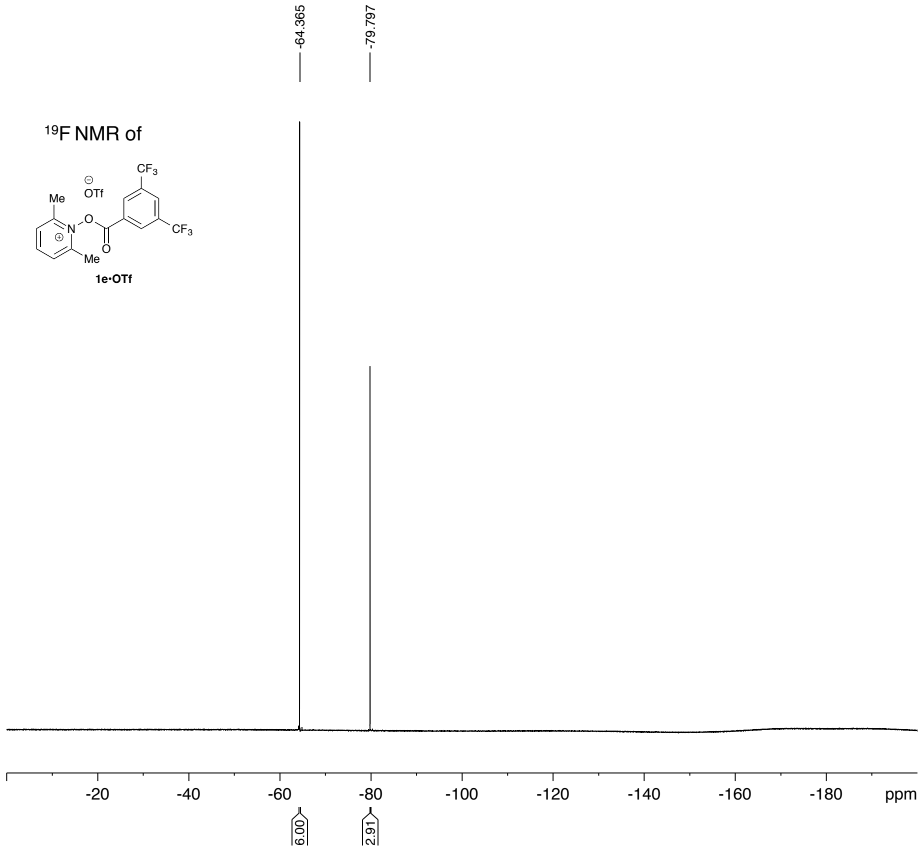
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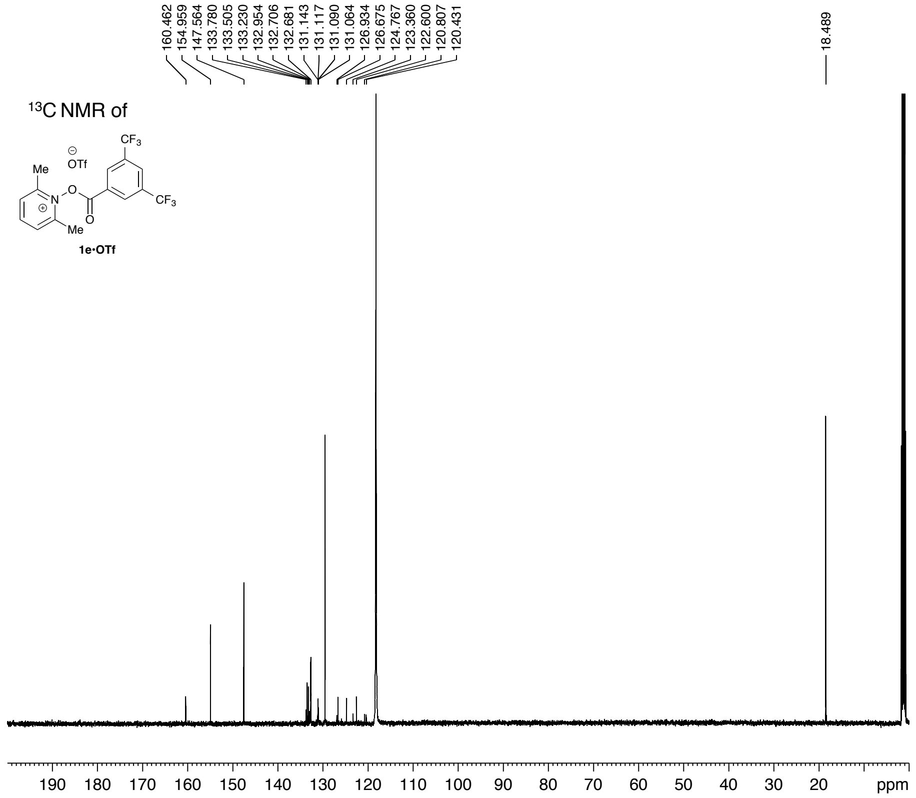
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13C NMR of
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OTf
Me
N
O
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CF3
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1e•OTf
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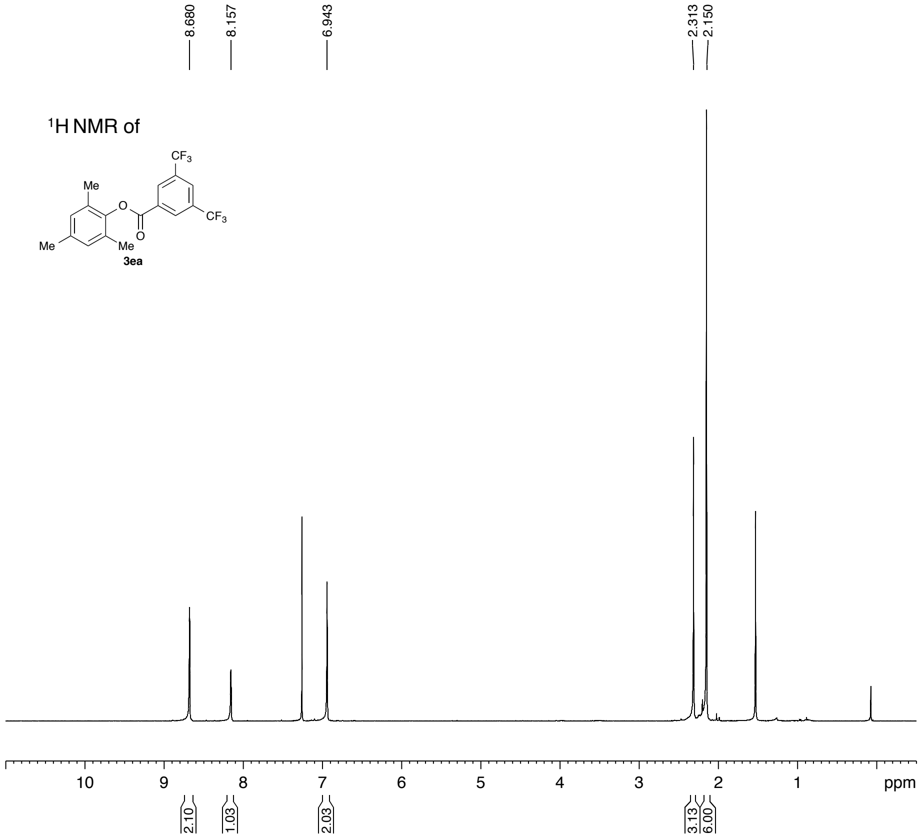
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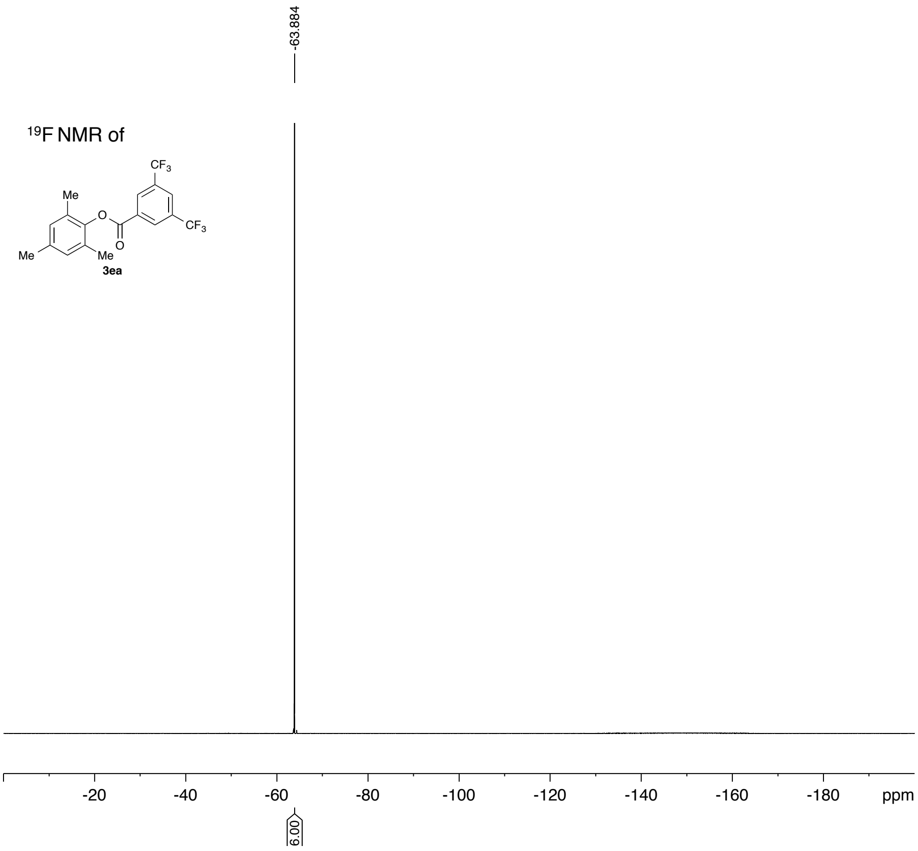
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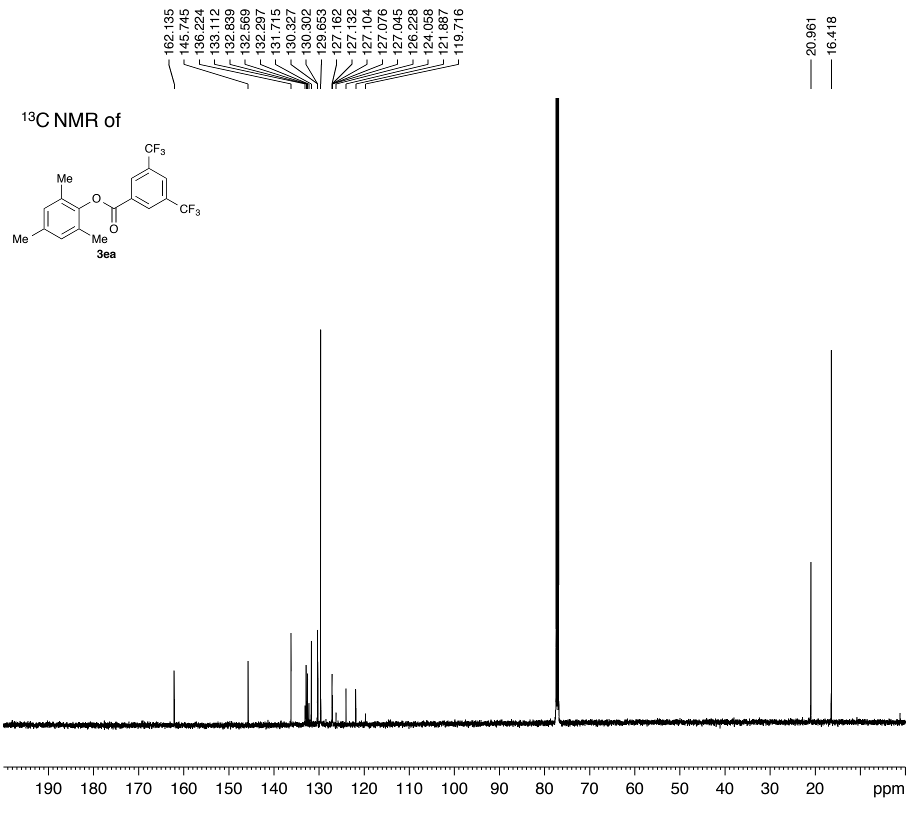
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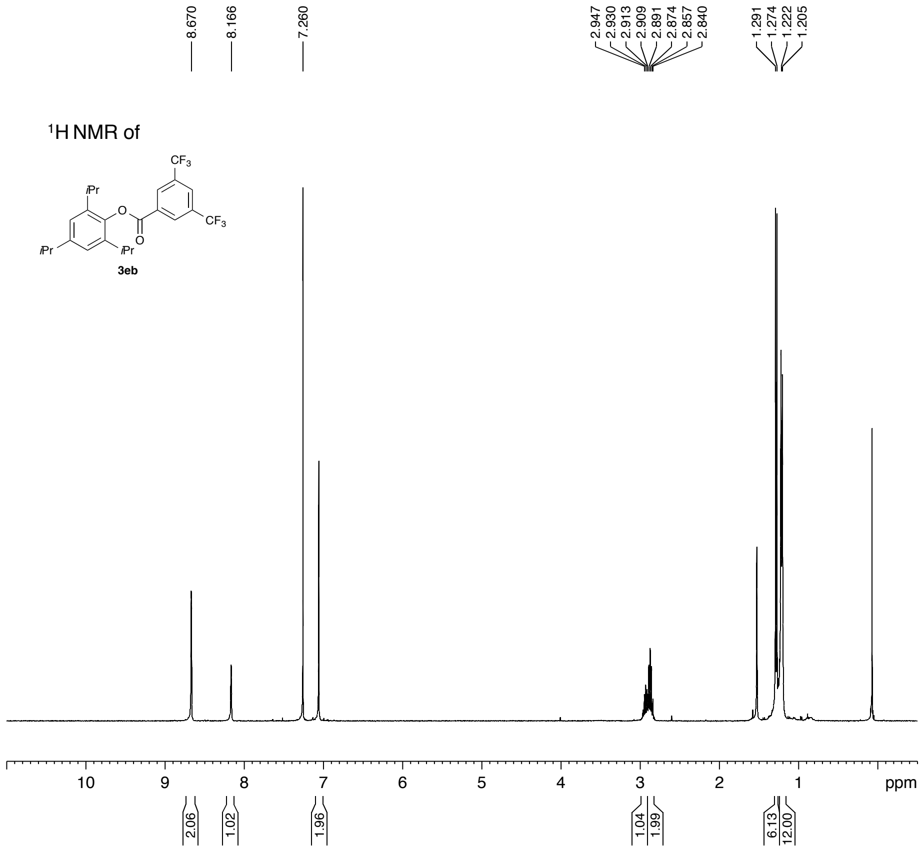
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*i*Pr
3eb
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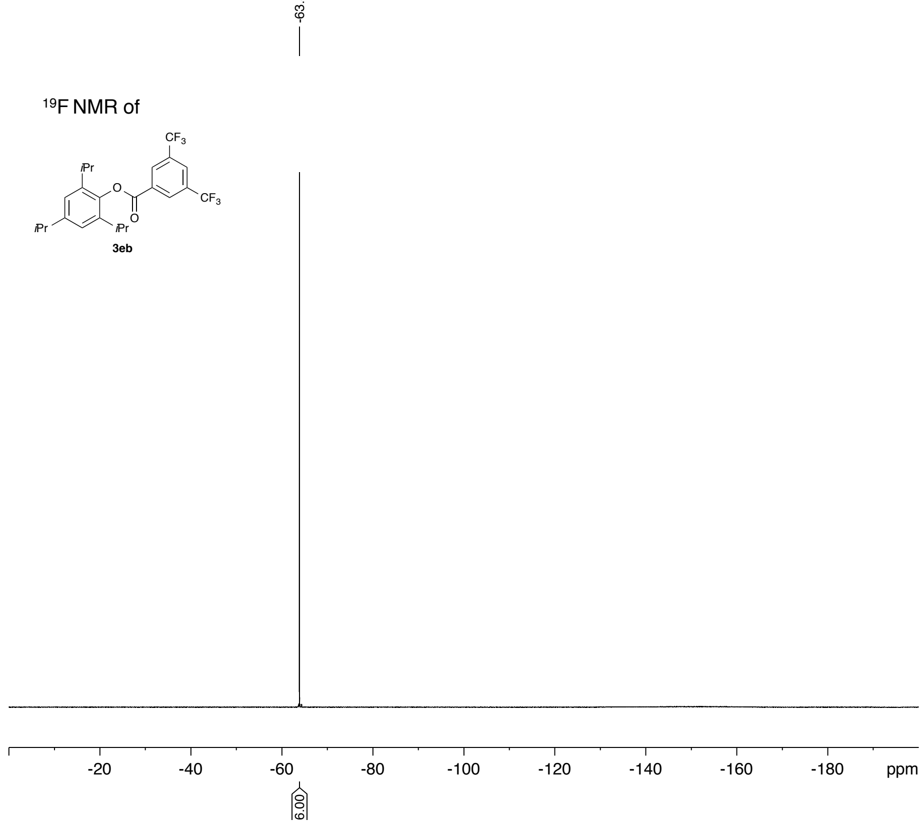
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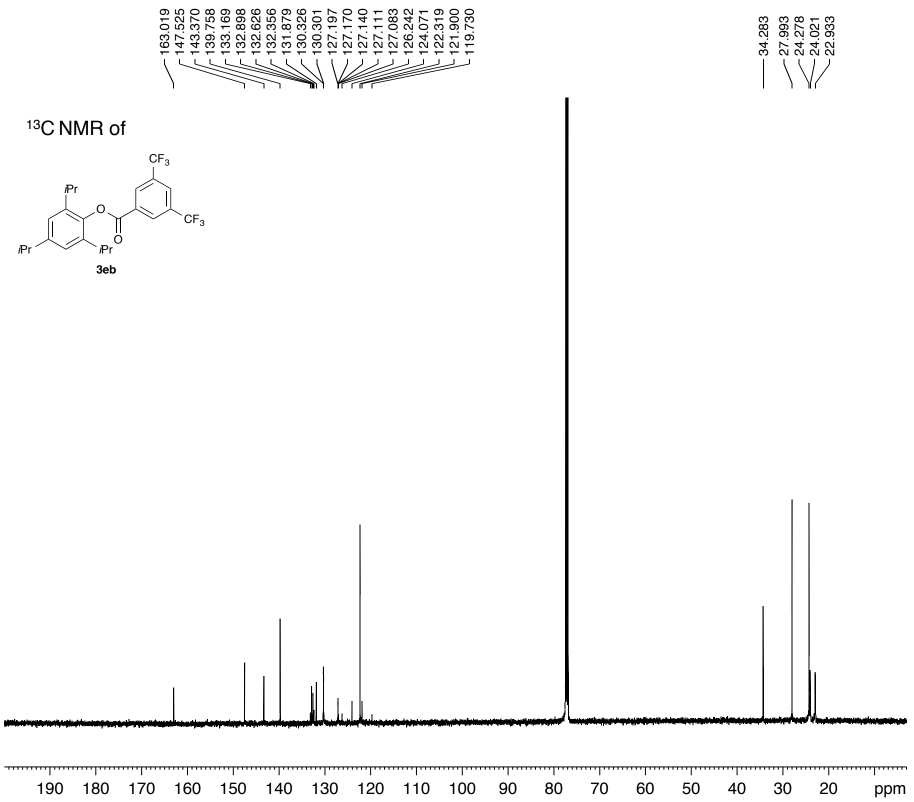
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CF$_3$
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*i*Pr
O
O
3eb
190
180
170
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50
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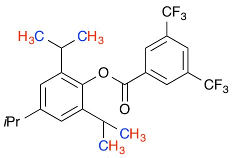
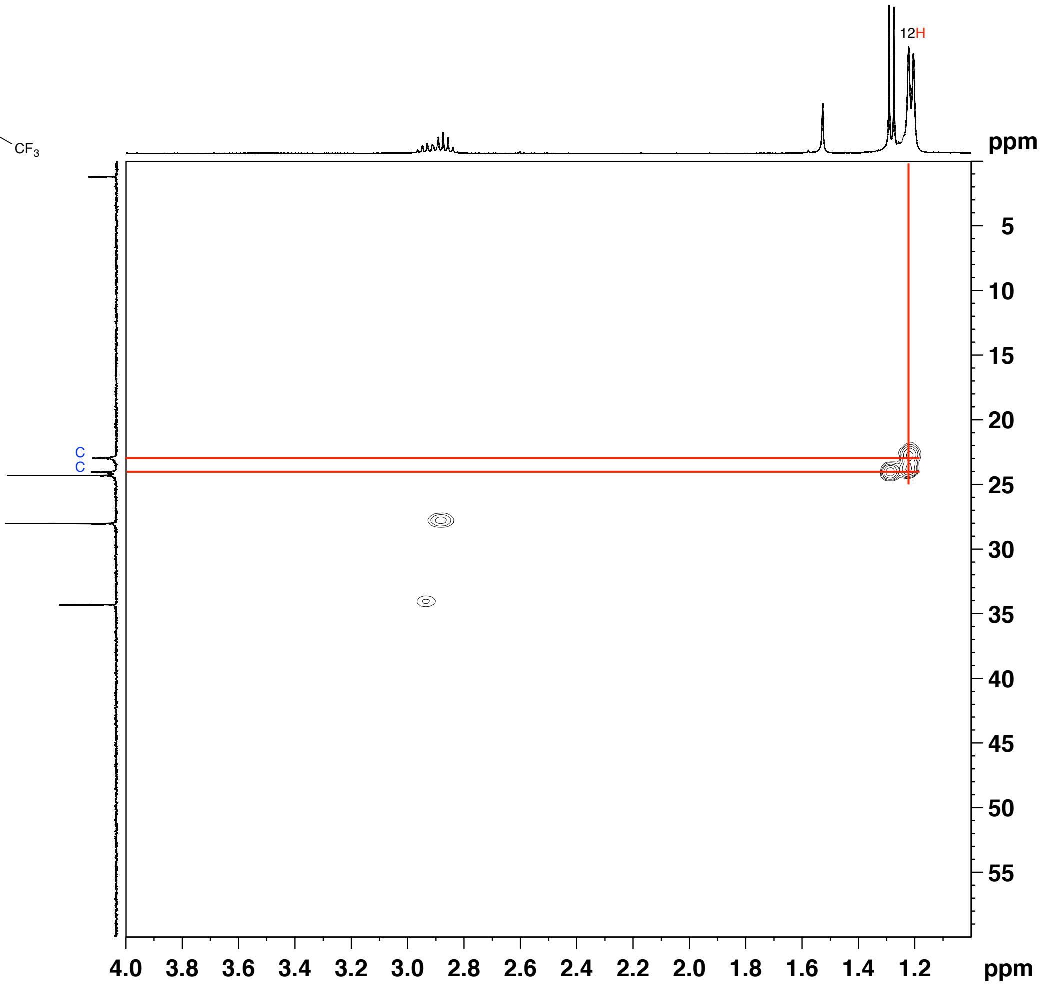
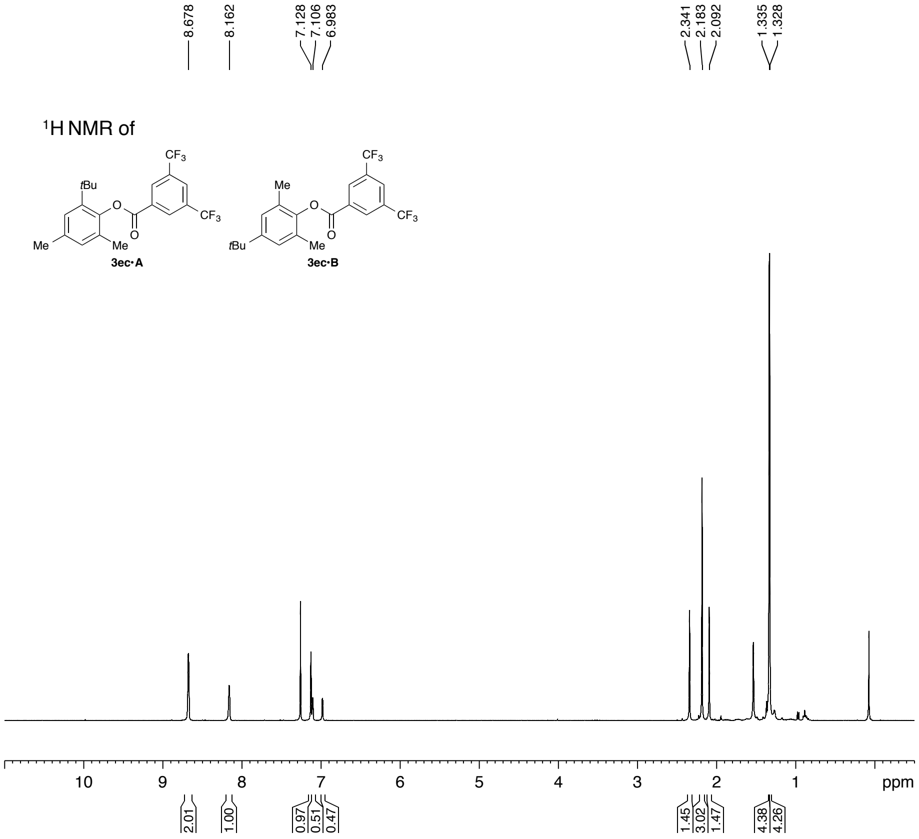
ppm

^{1}H-^{13}C HSQC of



3eb

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Me
O
Me
3ec•A
CF3
Me
O
CF3
tBu
O
Me
3ec•B
10
9
8
7
6
5
4
3
2
1
ppm
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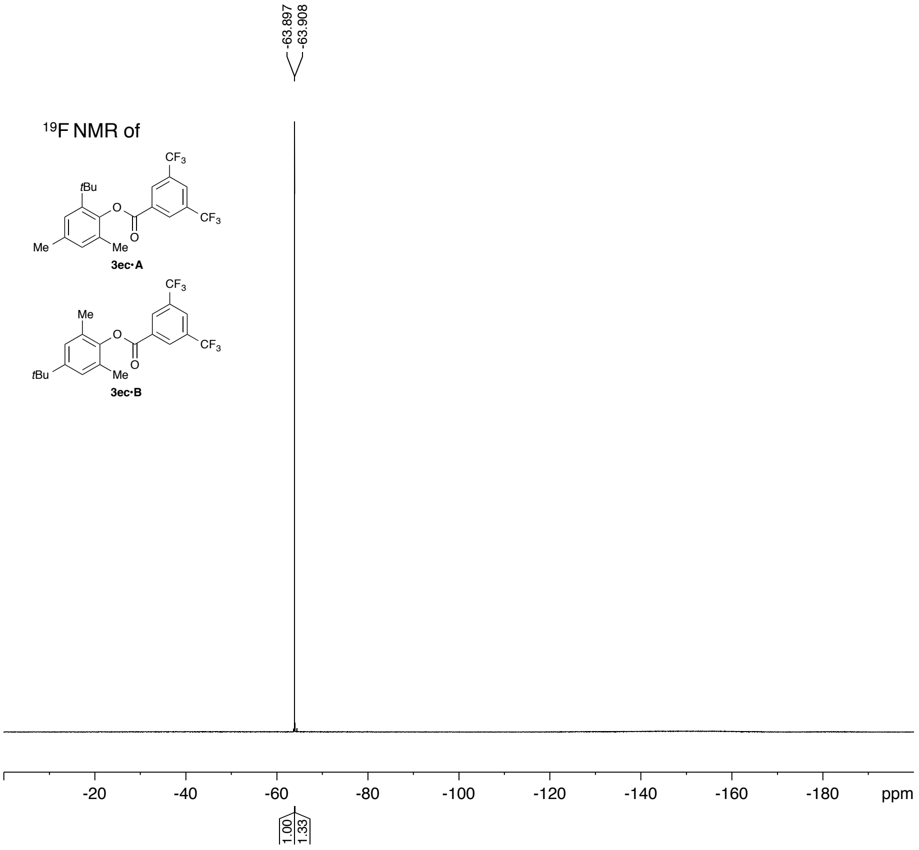
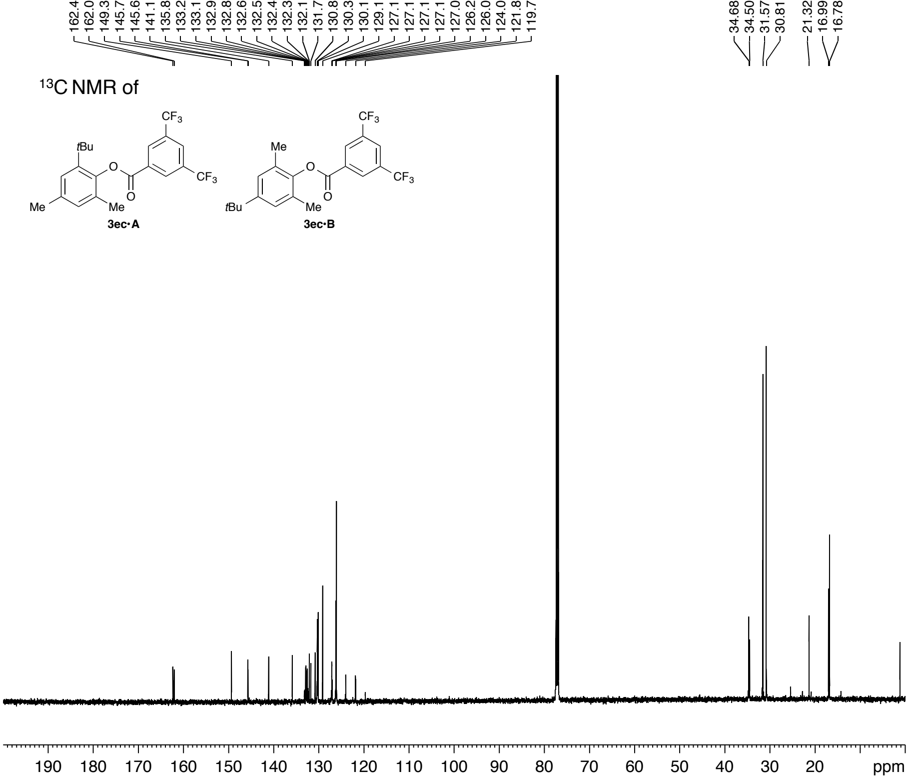
1.00
0.97
0.51
0.47
1.45
3.02
1.47
4.38
4.26


-63.897
-63.908
19F NMR of
CF3
tBu
O
CF3
Me
O
Me
3ec•A
CF3
Me
O
CF3
tBu
O
Me
3ec•B
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
1.00
1.33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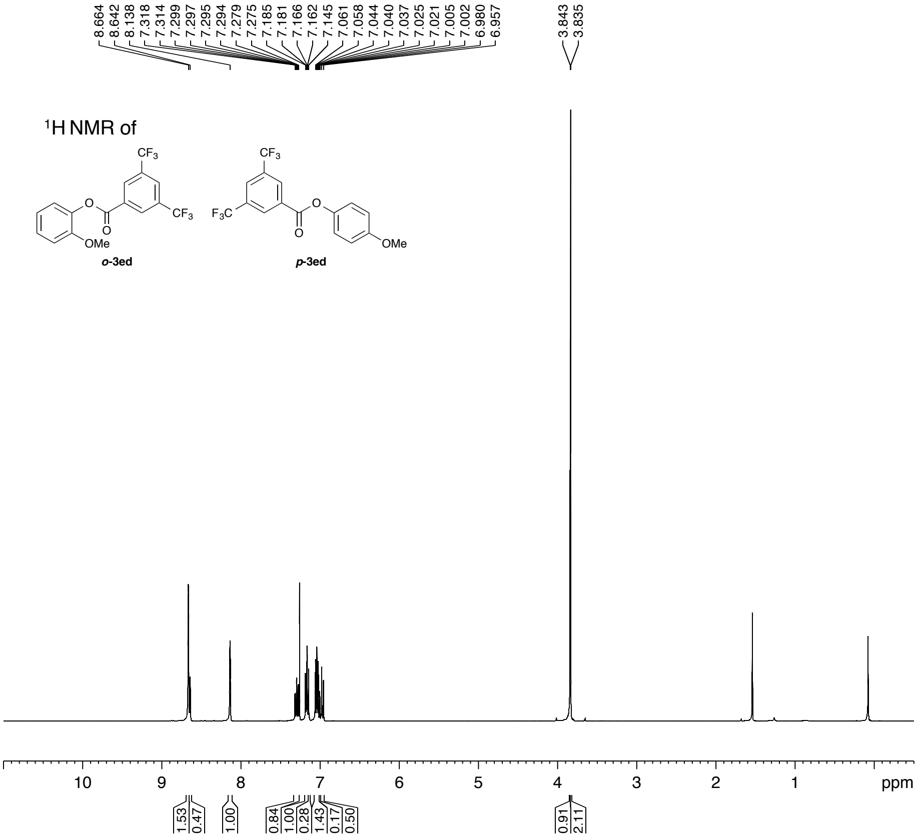
162.083
149.390
145.756
145.692
141.134
135.895
133.229
133.118
132.957
132.849
132.686
132.576
132.414
132.305
132.114
131.775
130.847
130.334
130.168
129.175
127.182
127.153
127.128
127.100
127.075
126.251
126.090
124.063
121.894
119.723
34.688
34.500
31.576
30.814
21.327
16.997
16.780
^{13}C NMR of
CF3
tBu
O
Me
Me
O
CF3
3ec·A
CF3
Me
O
tBu
Me
O
CF3
3ec·B
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.642
8.138
7.318
7.314
7.299
7.297
7.295
7.294
7.279
7.275
7.185
7.181
7.166
7.162
7.145
7.061
7.058
7.044
7.040
7.037
7.025
7.021
7.005
7.002
6.980
6.957
3.843
3.835
^{1}H NMR of
CF3
O
O
CF3
OMe
o-3ed
CF3
F3C
O
O
OMe
p-3ed
10
9
8
7
6
5
4
3
2
1
ppm
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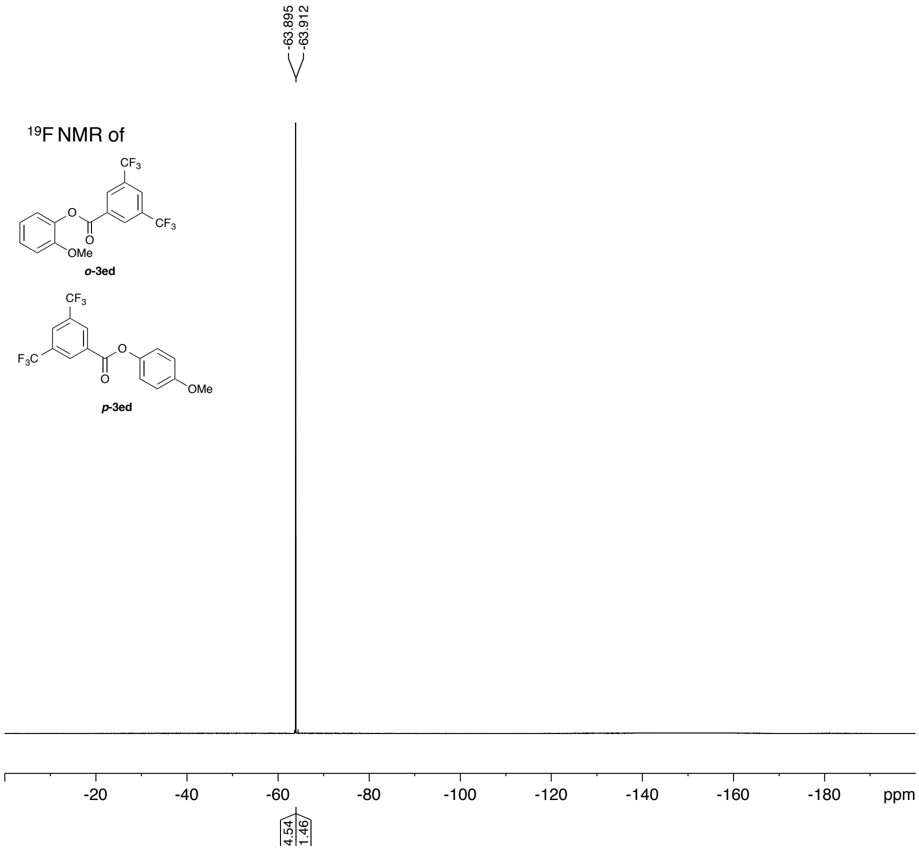
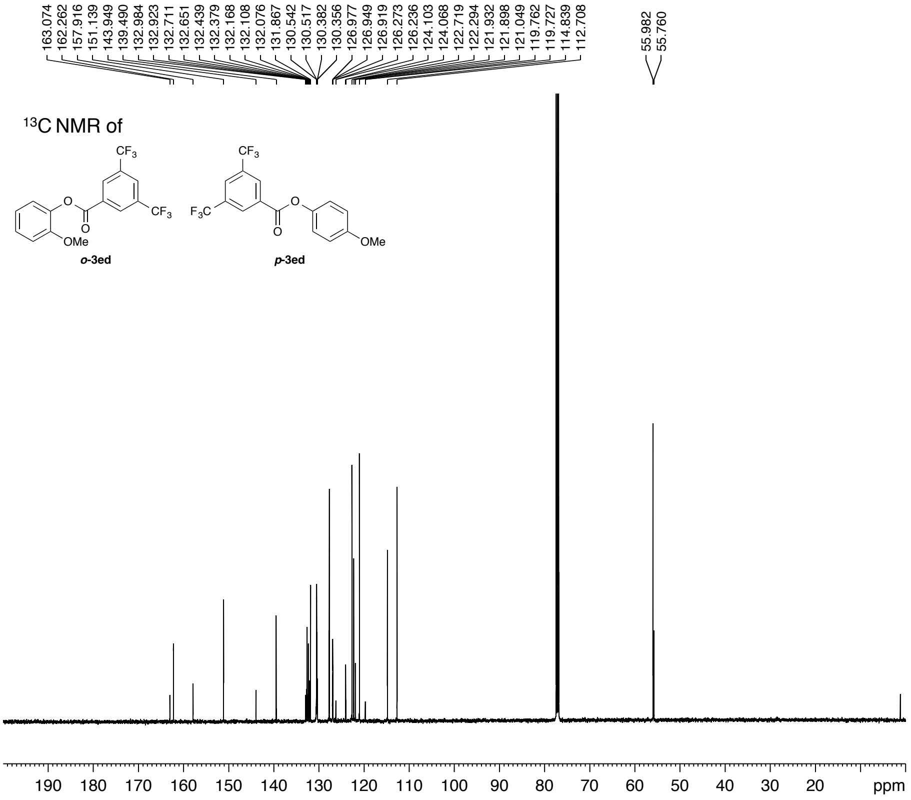
0.47
1.00
0.84
1.00
0.28
1.43
0.17
0.50
0.91
2.11


-63.895
-63.912
19F NMR of
CF3
O
O
OMe
CF3
o-3ed
CF3
F3C
O
O
OMe
p-3ed
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
4.54
1.46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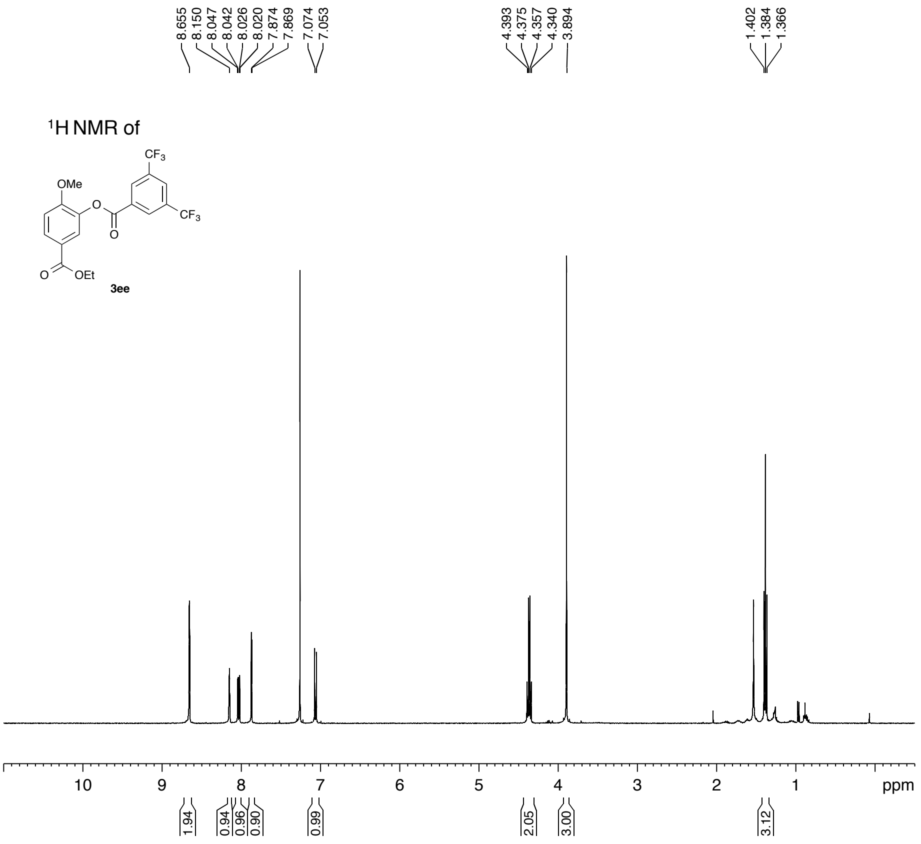
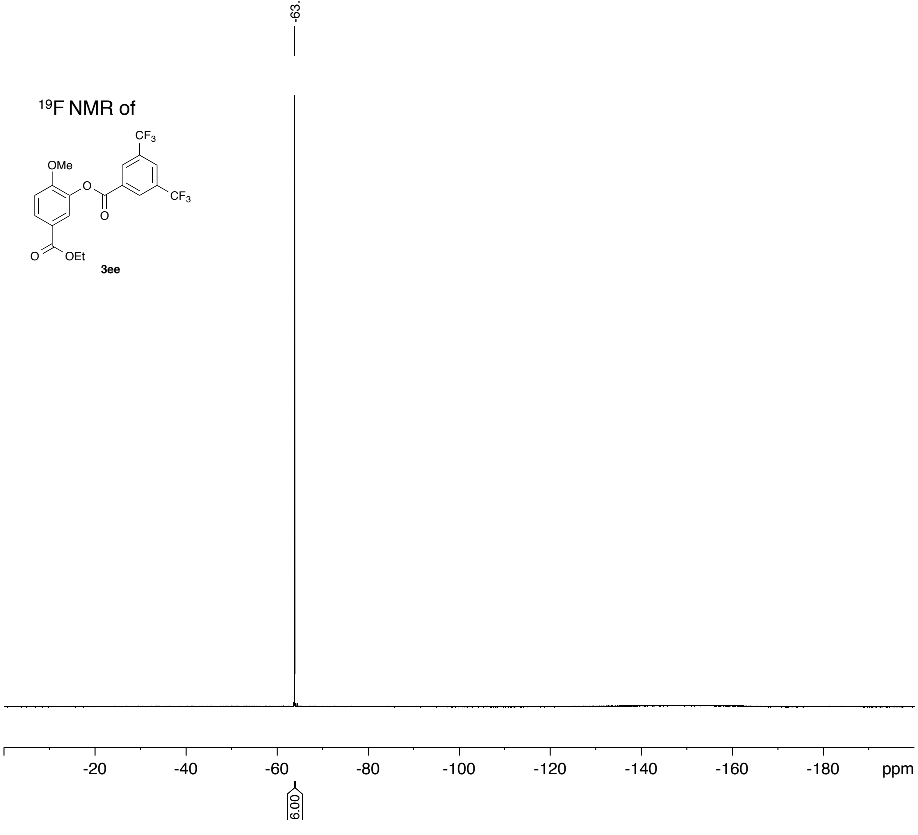
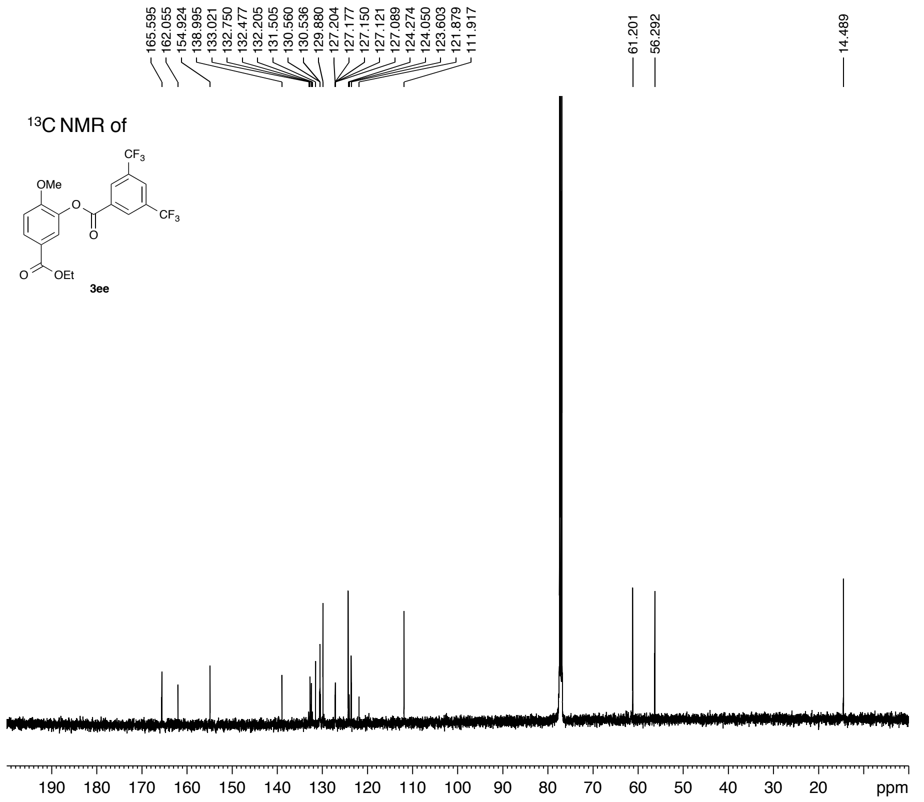
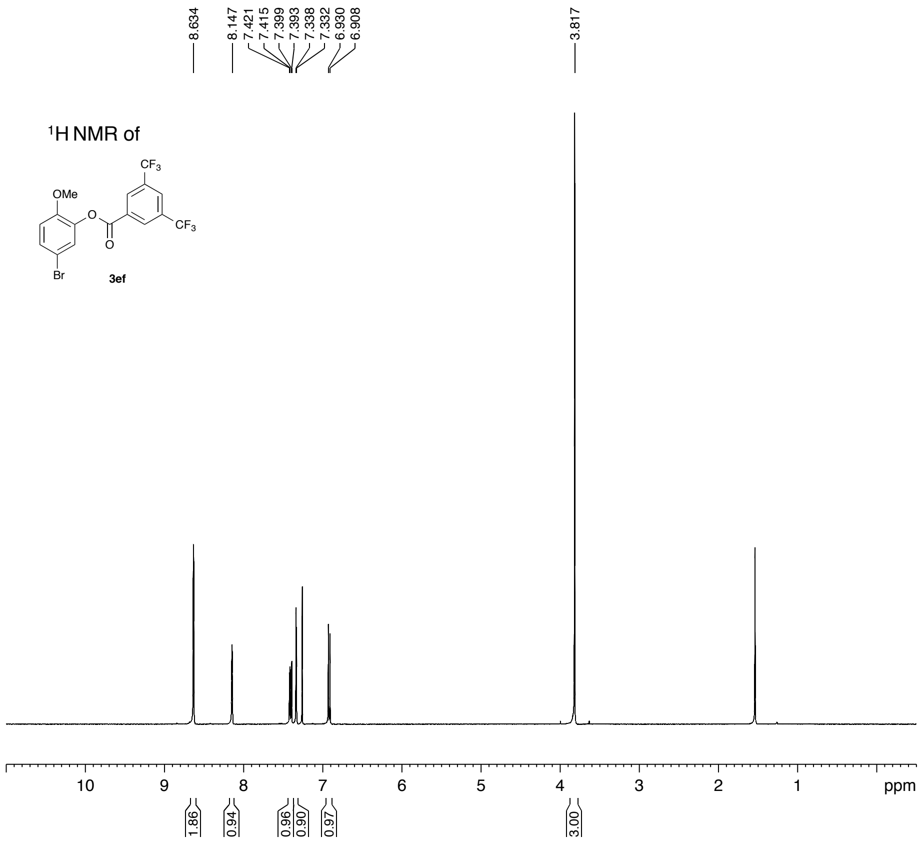
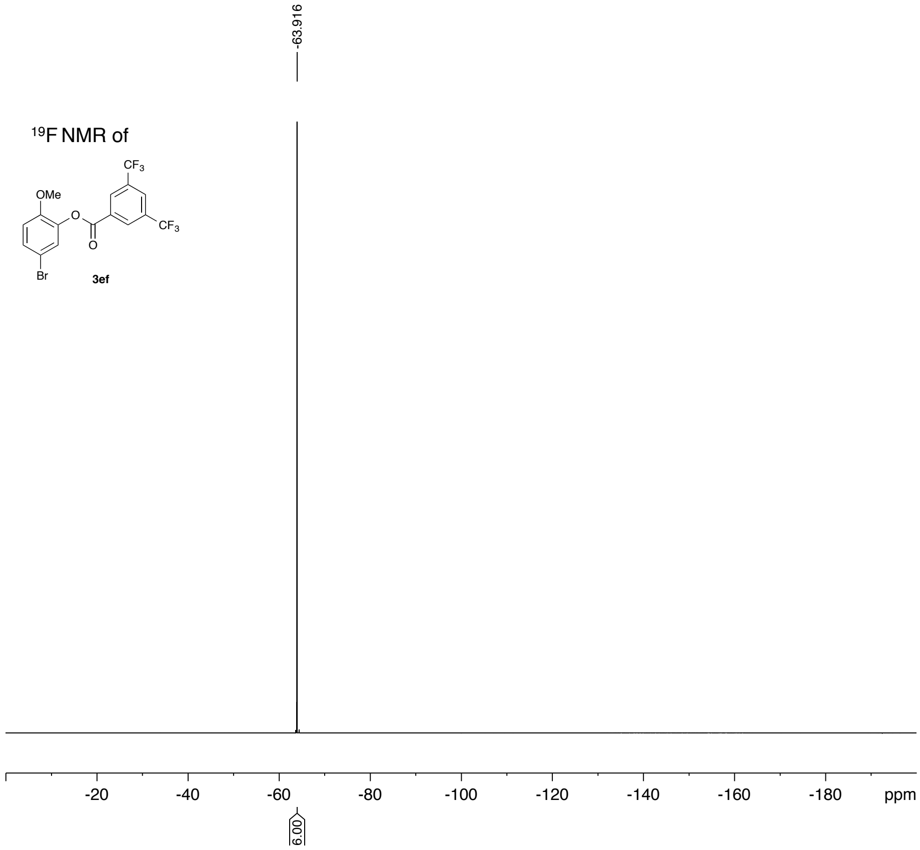
162.262
157.916
151.139
143.949
139.490
132.984
132.923
132.711
132.651
132.439
132.379
132.168
132.108
132.076
131.867
130.542
130.517
130.382
130.356
126.977
126.949
126.919
126.273
126.236
124.103
124.068
122.719
122.294
121.932
121.898
121.049
119.762
119.727
114.839
112.708
55.982
55.760
13C NMR of
CF3
O
O
OMe
CF3
o-3ed
CF3
F3C
O
O
OMe
p-3ed
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

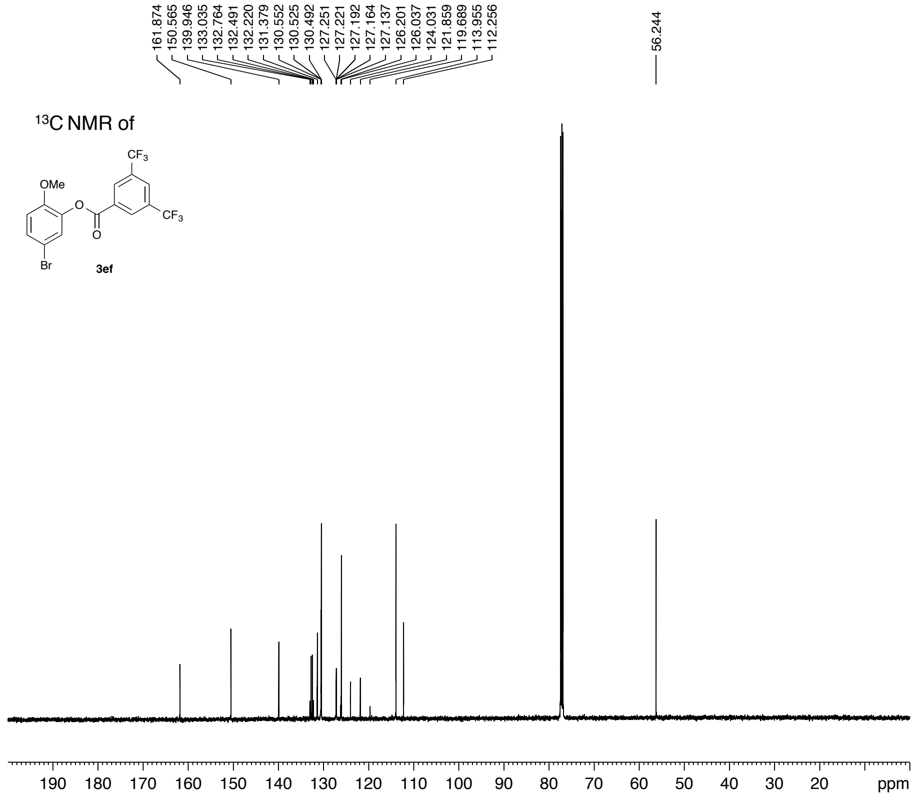

8.655
8.150
8.047
8.042
8.026
8.020
7.874
7.869
7.074
7.053
4.393
4.375
4.357
4.340
3.894
1.402
1.384
1.366
^{1}H NMR of
CF3
OMe
O
O
CF3
O
OEt
3ee
10
9
8
7
6
5
4
3
2
1
ppm
1.94
0.94
0.96
0.90
0.99
2.05
3.00
3.12

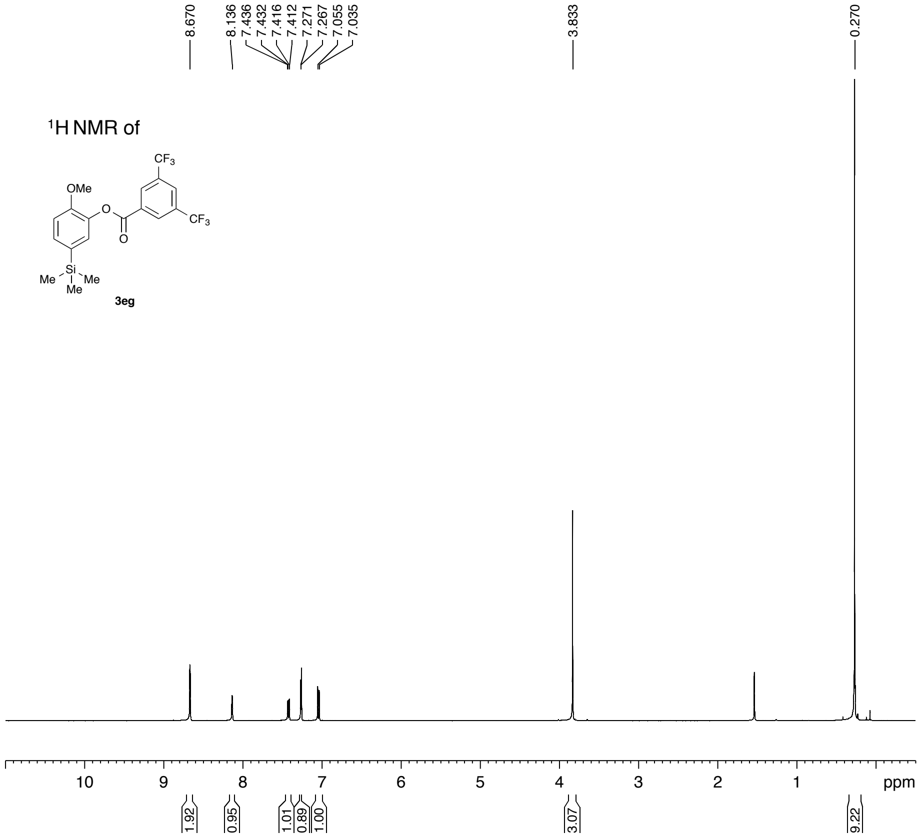

-63.900
^{19}F NMR of
CF3
OMe
O
O
CF3
O
OEt
3ee
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00

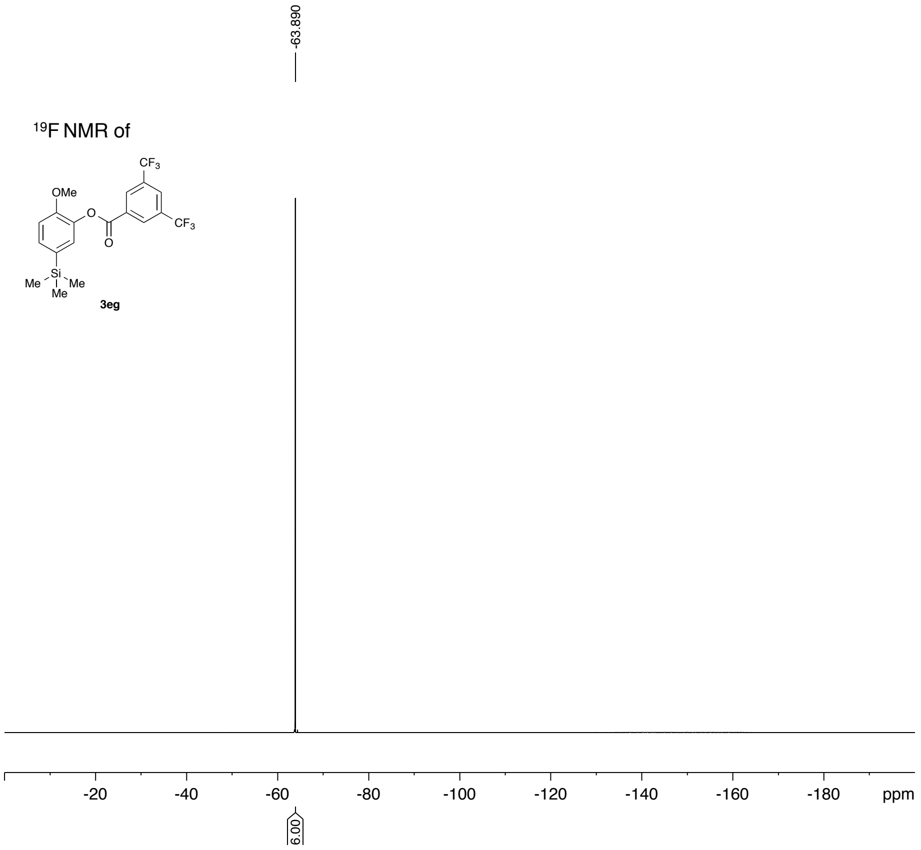

165.595
162.055
154.924
138.995
133.021
132.750
132.477
132.205
131.505
130.560
130.536
129.880
127.204
127.177
127.150
127.121
127.089
124.274
124.050
123.603
121.879
111.917
61.201
56.292
14.489
^{13}C NMR of
CF$_3$
OMe
O
CF$_3$
O
O
OEt
3ee
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

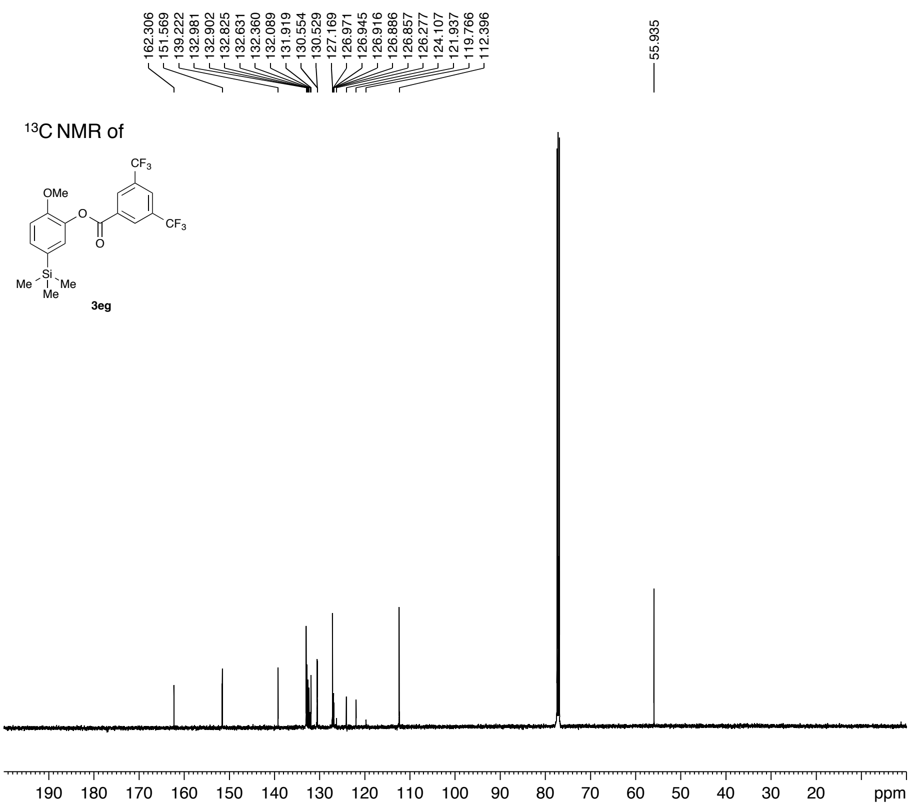

8.634
8.147
7.421
7.415
7.399
7.393
7.338
7.332
6.930
6.908
3.817
^{1}H NMR of
CF$_3$
OMe
O
CF$_3$
O
Br
3ef
10
9
8
7
6
5
4
3
2
1
ppm
1.86
0.94
0.96
0.90
0.97
3.00

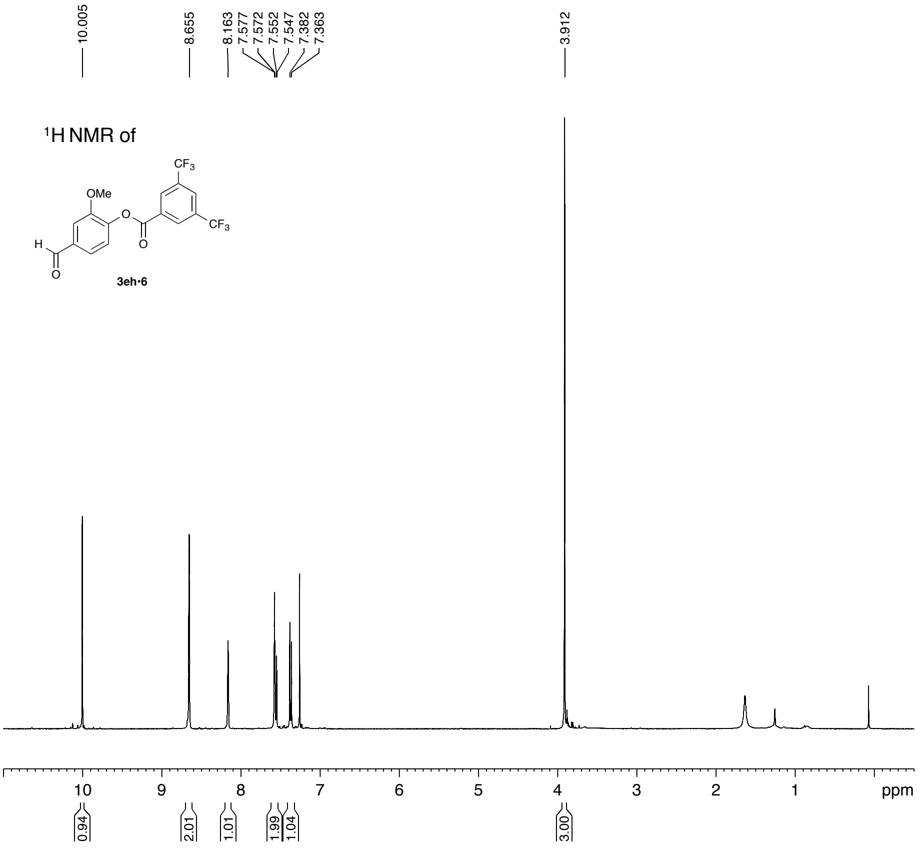

-63.916
19F NMR of
CF3
OMe
O
O
CF3
Br
3ef
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00

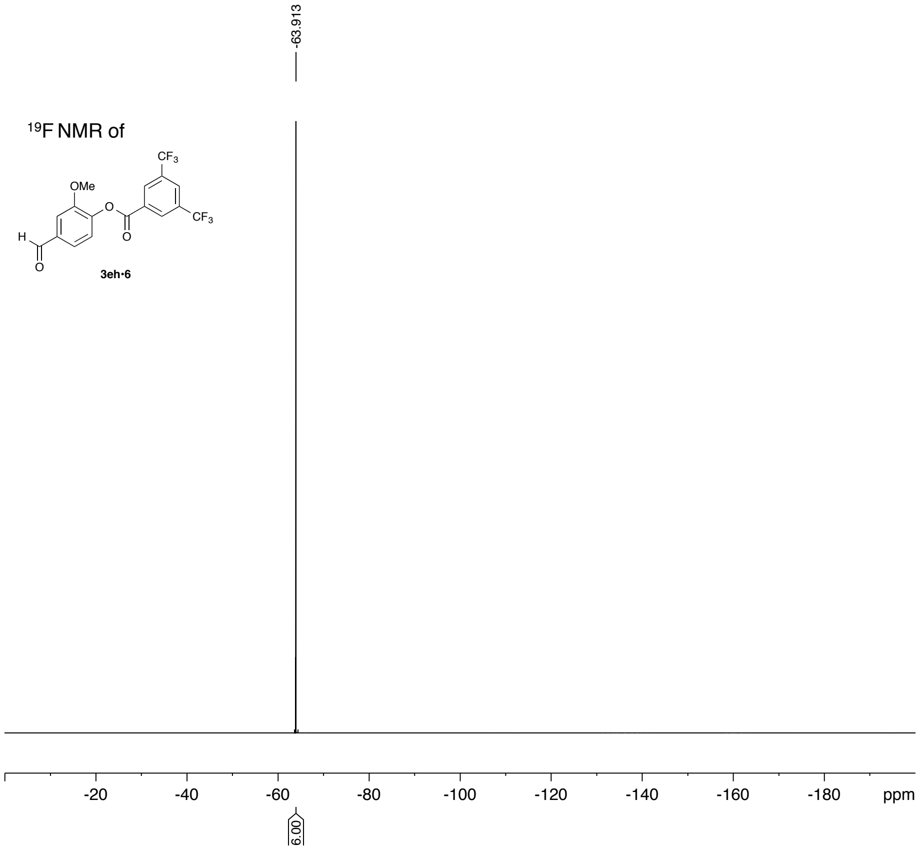

161.874
150.565
139.946
133.035
132.764
132.491
132.220
131.379
130.552
130.525
130.492
127.251
127.221
127.192
127.164
127.137
126.201
126.037
124.031
121.859
119.689
113.955
112.256
56.244
13C NMR of
CF3
OMe
O
O
CF3
Br
3ef
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.670
8.136
7.436
7.432
7.416
7.412
7.271
7.267
7.055
7.035
3.833
0.270
1H NMR of
CF3
OMe
O
O
CF3
Si
Me
Me
Me
3eg
10
9
8
7
6
5
4
3
2
1
ppm
1.92
0.95
1.01
0.89
1.00
3.07
9.22


-63.890
19F NMR of
CF3
OMe
O
O
CF3
Si
Me
Me
Me
3eg
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00


162.306
151.569
139.222
132.981
132.902
132.825
132.631
132.360
132.089
131.919
130.554
130.529
127.169
126.971
126.945
126.916
126.886
126.857
126.277
124.107
121.937
119.766
112.396
55.935
^{13}C NMR of
CF3
OMe
O
O
CF3
Me
Si
Me
Me
3eg
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


10.005
8.655
8.163
7.577
7.572
7.552
7.547
7.382
7.363
3.912
^{1}H NMR of
CF3
OMe
O
CF3
H
O
O
3eh-6
10
9
8
7
6
5
4
3
2
1
ppm
0.94
2.01
1.01
1.99
1.04
3.00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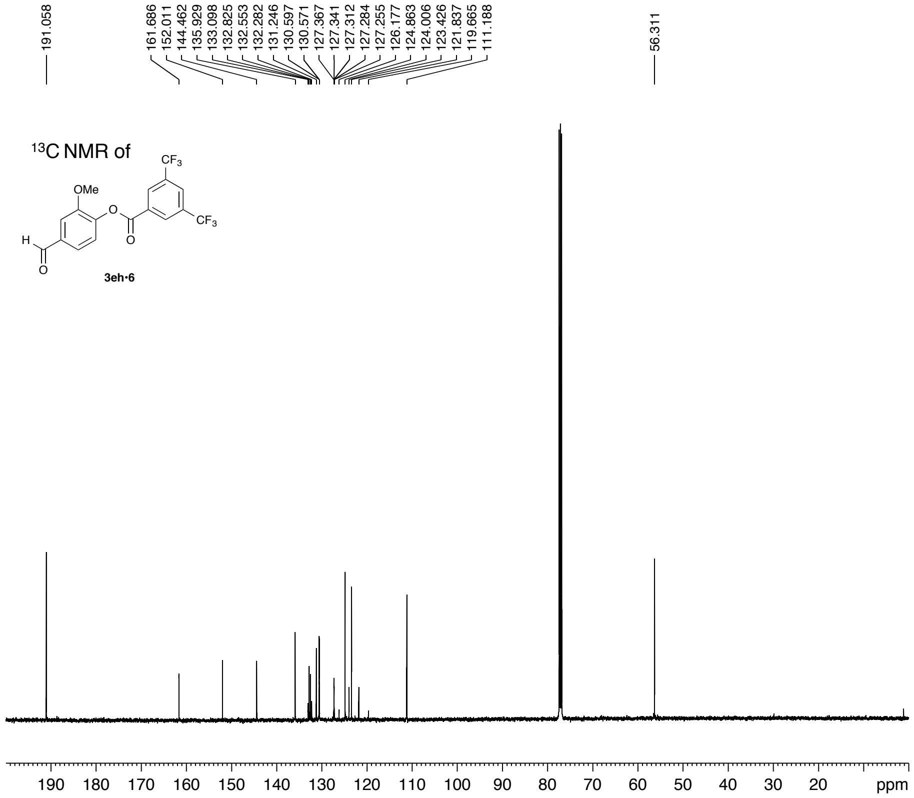
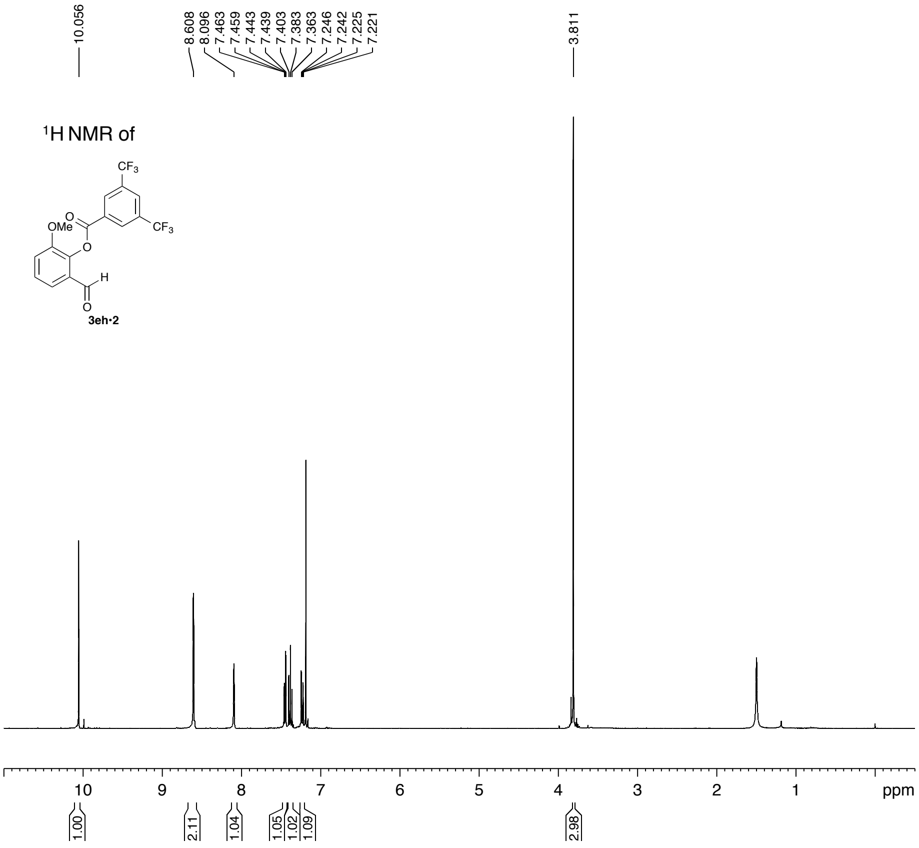
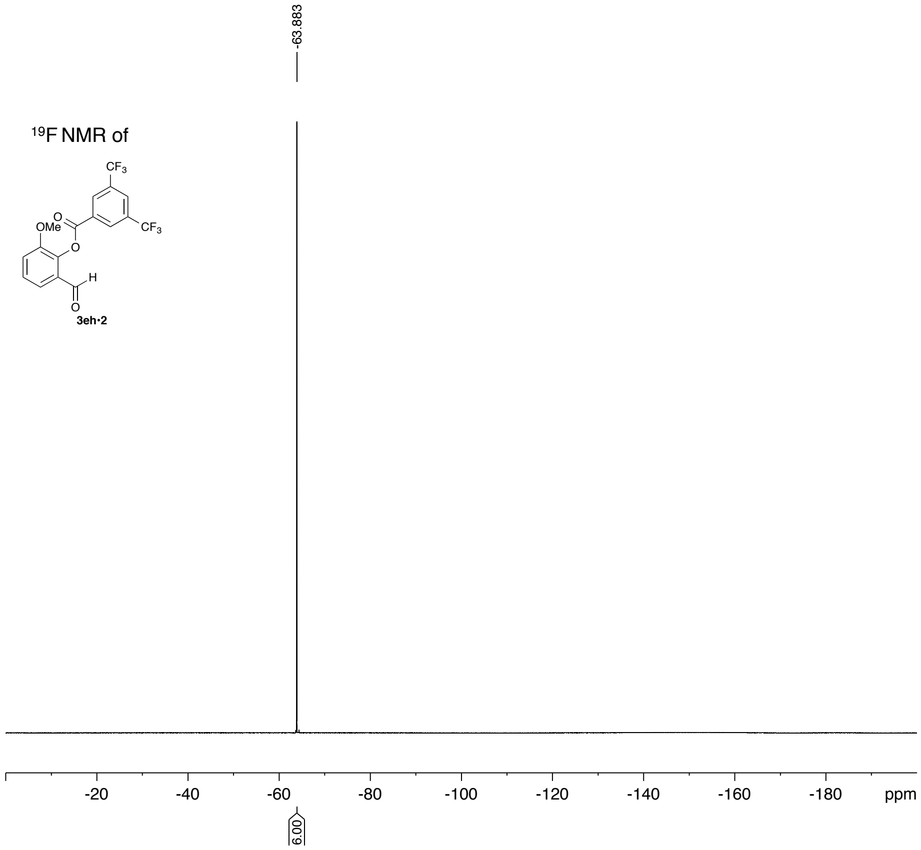
19F NMR of
CF3
OMe
O
CF3
H
O
O
3eh·6
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00


191.058
161.686
152.011
144.462
135.929
133.098
132.825
132.553
132.282
131.246
130.597
130.571
127.367
127.341
127.312
127.284
127.255
126.177
124.863
124.006
123.426
121.837
119.665
111.188
56.311
13C NMR of
CF3
OMe
O
CF3
H
O
O
3eh·6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


10.056
8.608
8.096
7.463
7.459
7.443
7.439
7.403
7.383
7.363
7.246
7.242
7.225
7.221
3.811
^{1}H NMR of
CF$_3$
CF$_3$
OMe
O
O
H
O
3eh·2
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.11
1.04
1.05
1.02
1.09
2.98


-63.883
^{19}F NMR of
CF$_3$
CF$_3$
OMe
O
O
H
O
3eh·2
-20
-40
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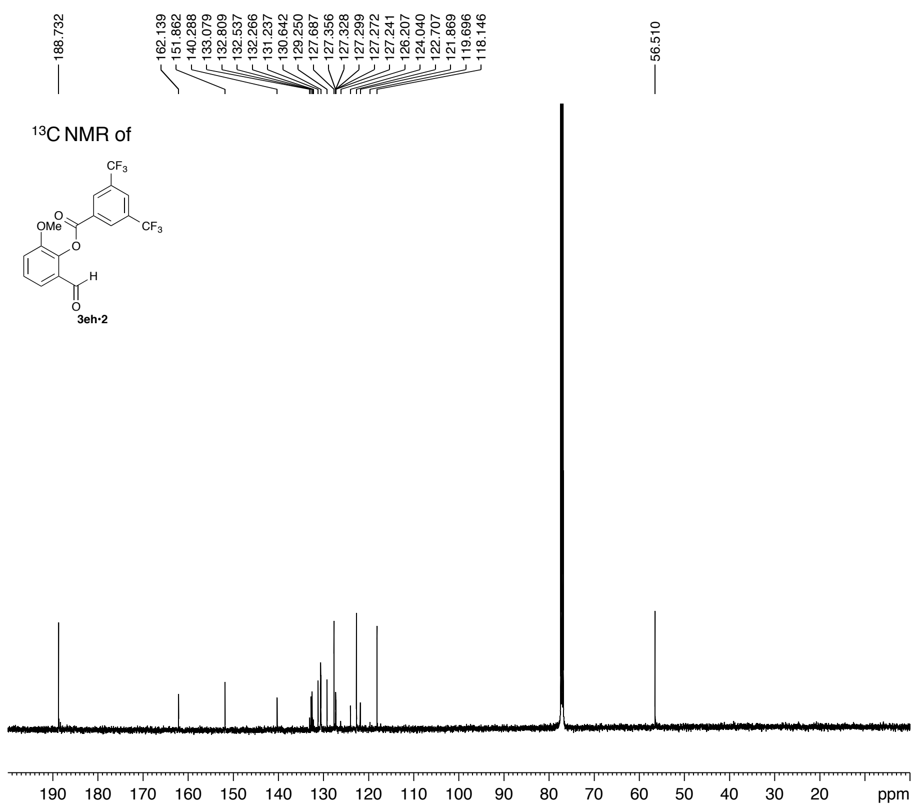
-80
-100
-120
-140
-160
-180
ppm
6.00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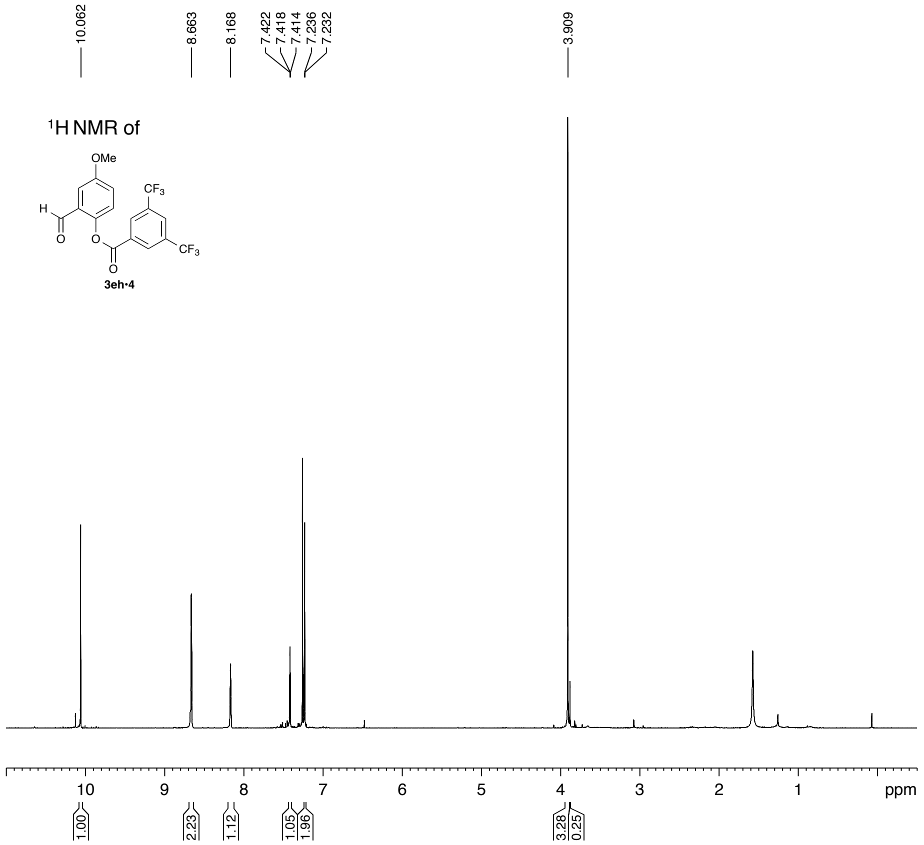
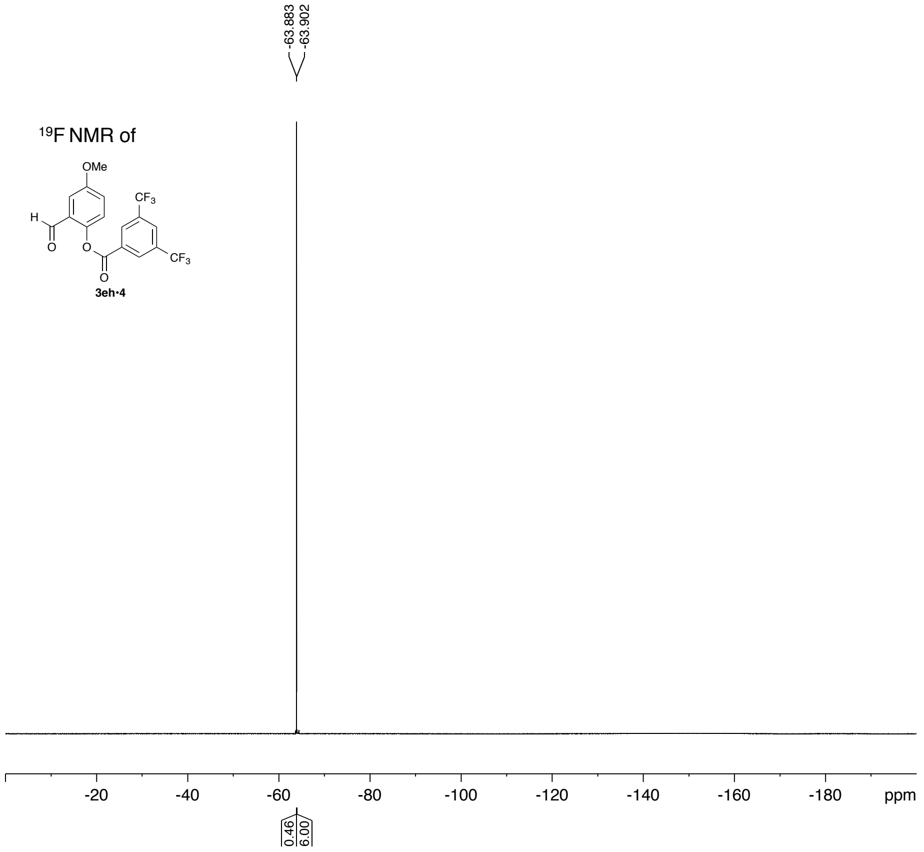
151.862
140.288
133.079
132.809
132.537
132.266
131.237
130.642
129.250
127.687
127.356
127.328
127.299
127.272
127.241
126.207
124.040
122.707
121.869
119.696
118.146
56.510
^{13}C NMR of
CF3
O
OMe
O
CF3
H
O
3eh·2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


10.062
8.663
8.168
7.422
7.418
7.414
7.236
7.232
3.909
^{1}H NMR of
OMe
CF3
H
O
O
CF3
O
3eh·4
10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.23
1.12
1.05
1.96
3.28
0.25


-63.883
-63.902
19F NMR of
OMe
CF3
H
O
O
CF3
O
3eh•4
-20
-40
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-80
-100
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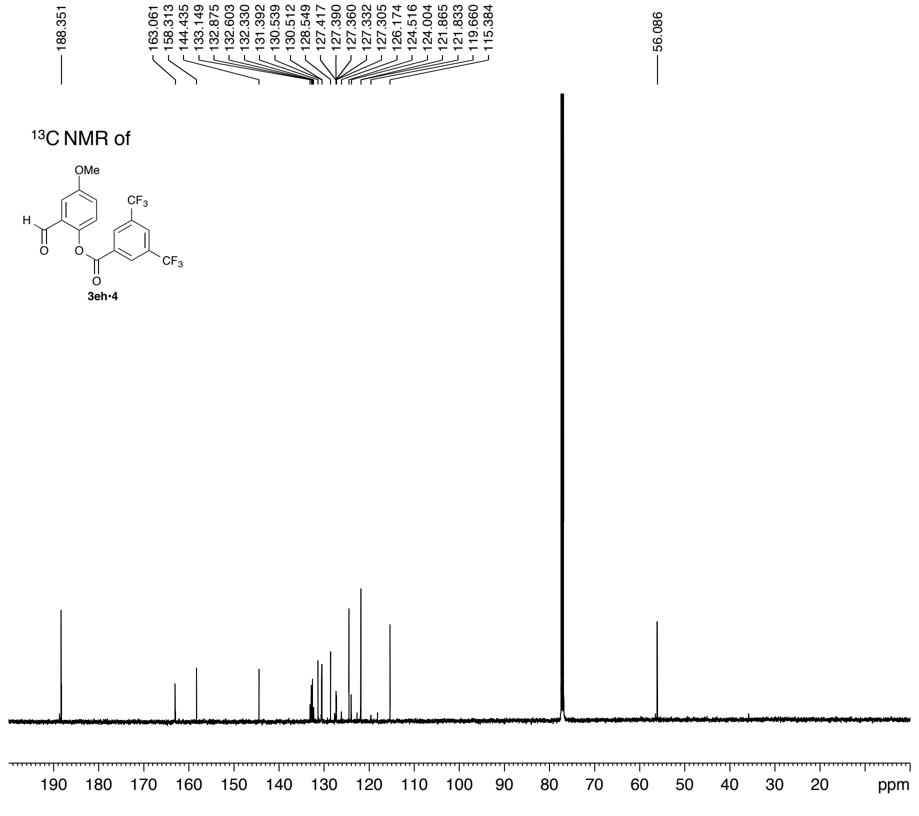
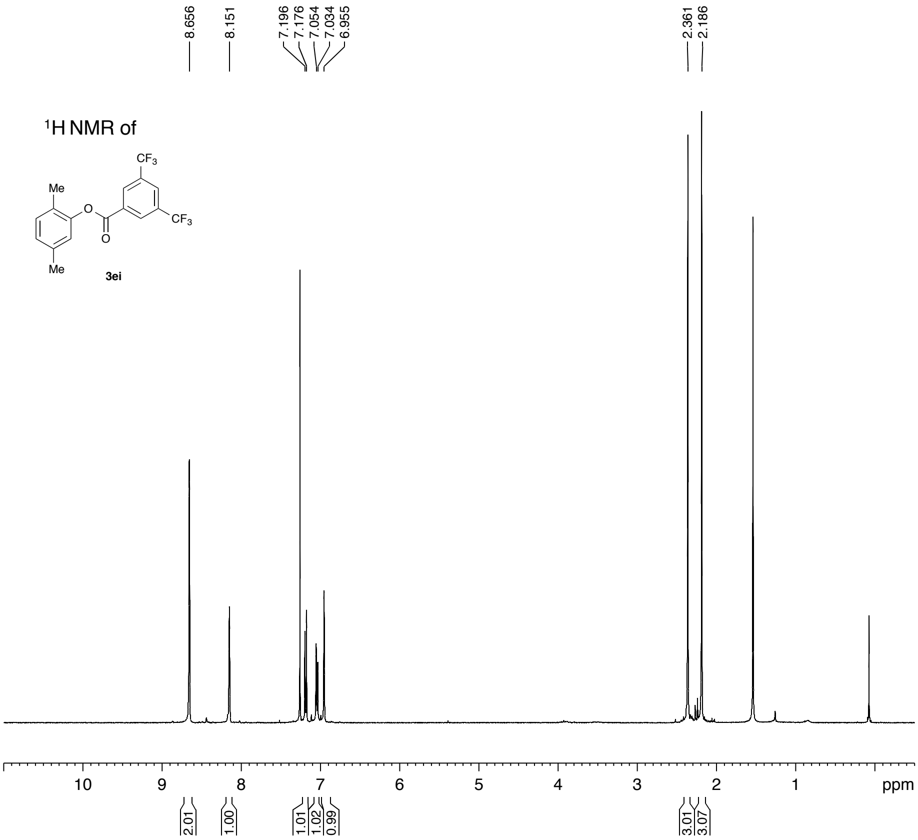
-160
-180
ppm
0.46
6.00


188.351
163.061
158.313
144.435
133.149
132.875
132.603
132.330
131.392
130.539
130.512
128.549
127.417
127.390
127.360
127.332
127.305
126.174
124.516
124.004
121.865
121.833
119.660
115.384
56.086
13C NMR of
OMe
CF3
H
O
O
CF3
O
3eh•4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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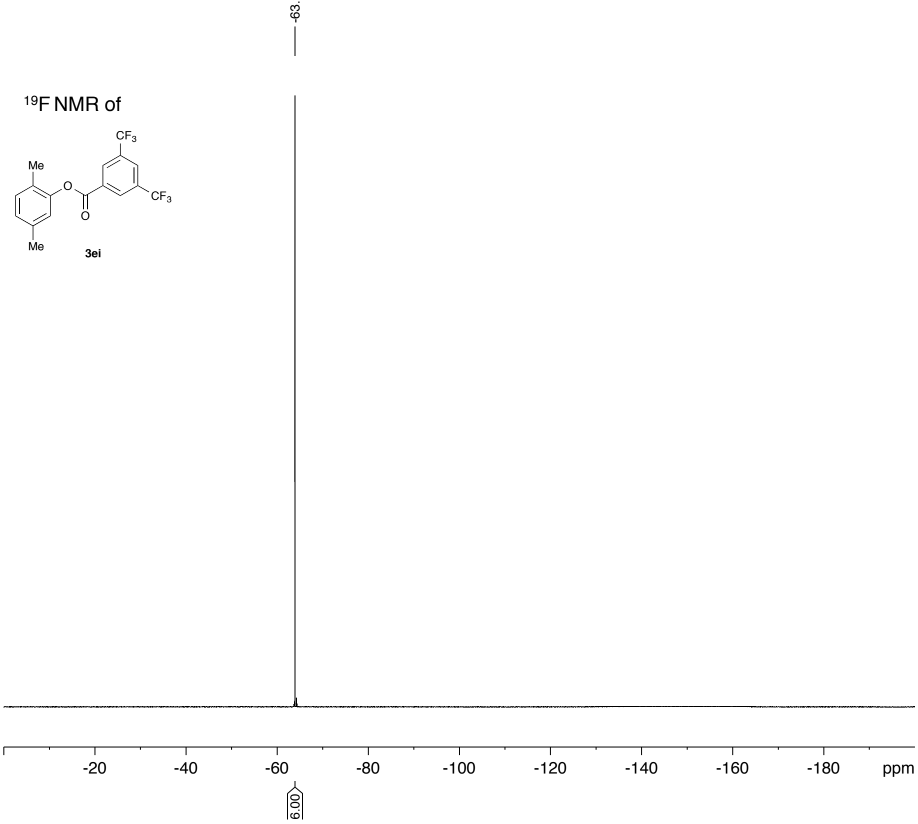
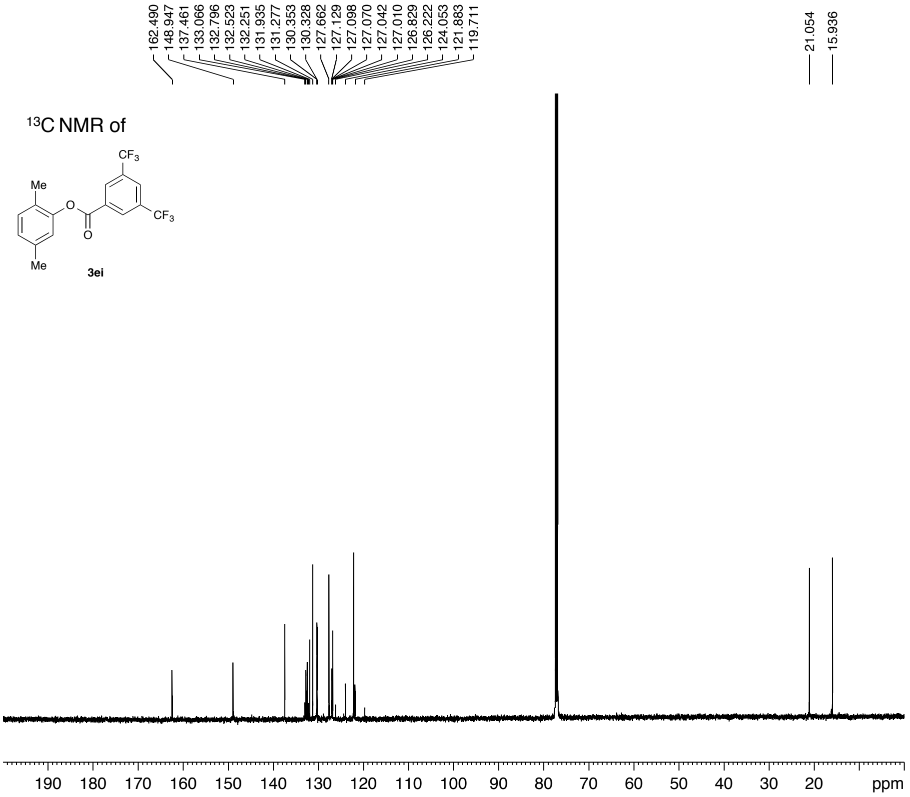
8.151
7.196
7.176
7.054
7.034
6.955
2.361
2.186
¹H NMR of
CF3
Me
O
CF3
O
Me
3ei
10
9
8
7
6
5
4
3
2
1
ppm
2.01
1.00
1.01
1.02
0.99
3.01
3.07


-63.908
¹⁹F NMR of
CF3
Me
O
CF3
O
Me
3ei
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00



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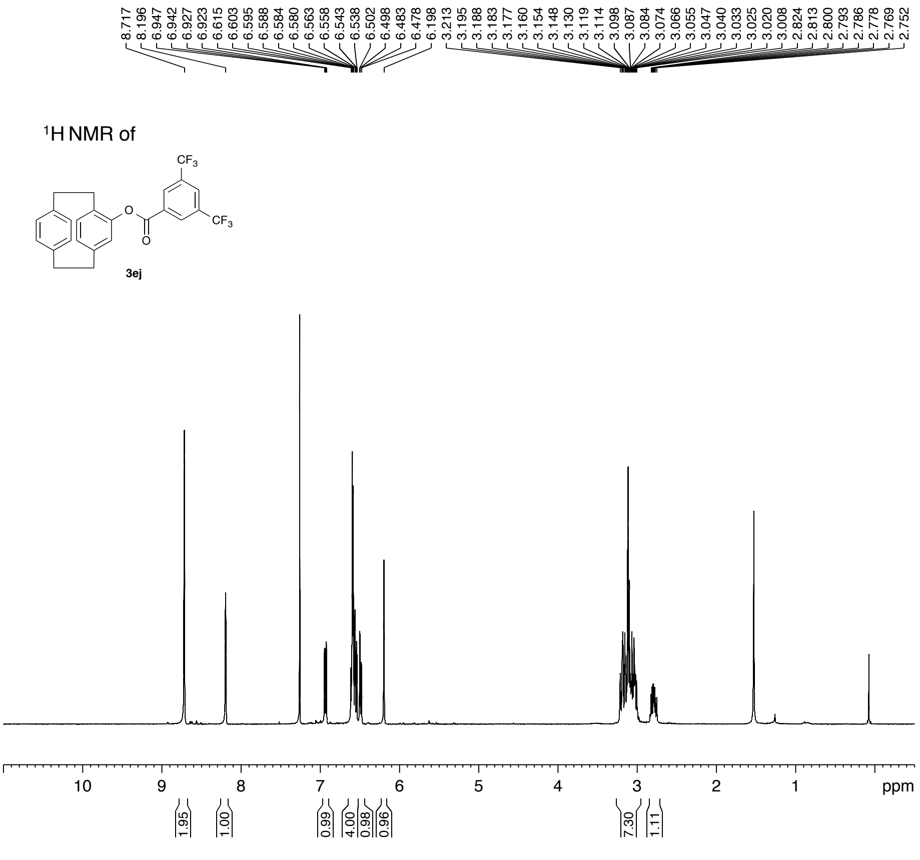
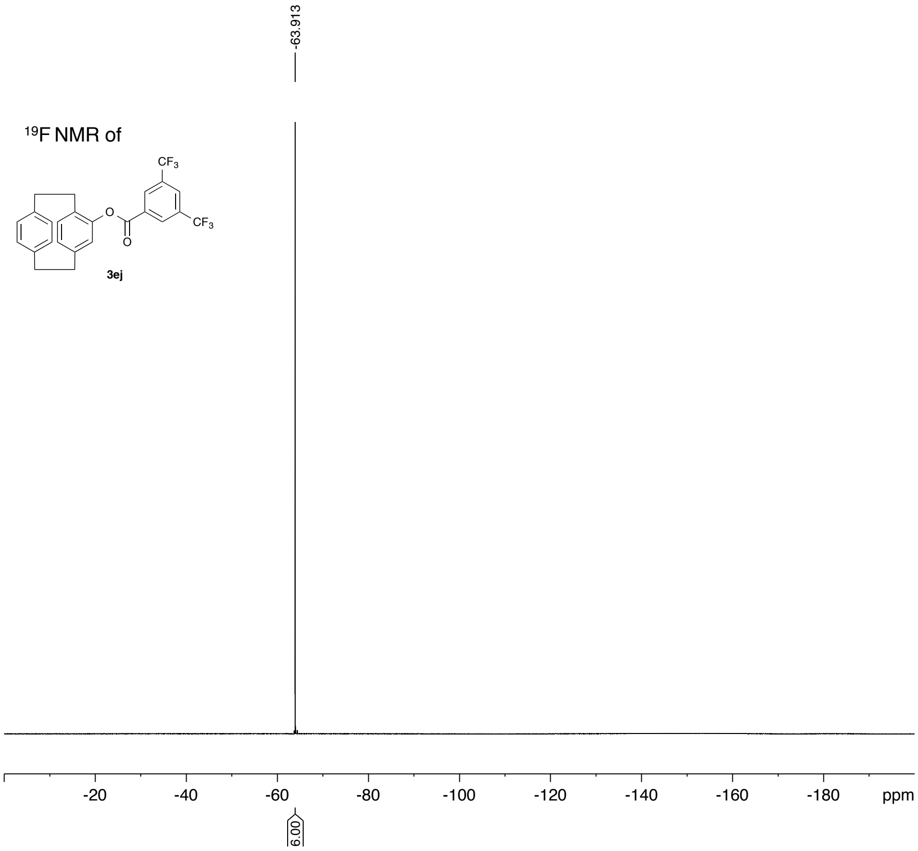
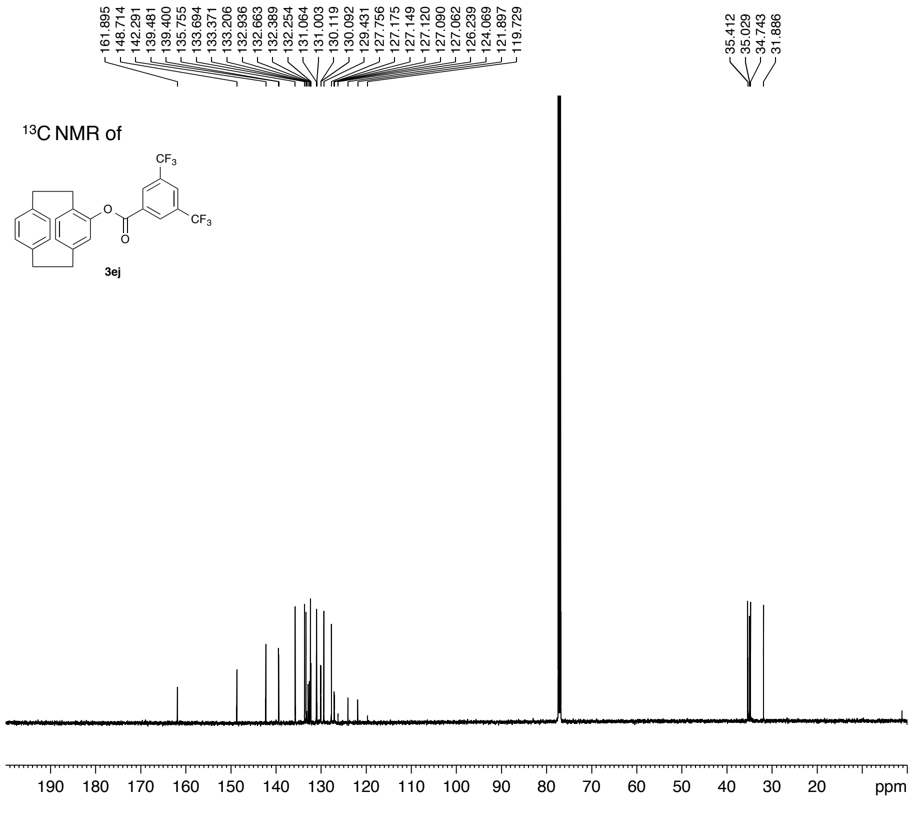
148.947
137.461
133.066
132.796
132.523
132.251
131.935
131.277
130.353
130.328
127.662
127.129
127.098
127.070
127.042
127.010
126.829
126.222
124.053
121.883
119.711
21.054
15.936
^{13}C NMR of
CF$_3$
Me
O
CF$_3$
O
Me
3ei
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



8.717
8.196
6.947
6.942
6.927
6.923
6.615
6.603
6.595
6.588
6.584
6.580
6.563
6.558
6.543
6.538
6.502
6.498
6.483
6.478
6.198
3.213
3.195
3.188
3.183
3.177
3.160
3.154
3.148
3.130
3.119
3.114
3.098
3.087
3.084
3.074
3.066
3.055
3.047
3.040
3.033
3.025
3.020
3.008
2.824
2.813
2.800
2.793
2.786
2.778
2.769
2.752
^{1}H NMR of
CF$_3$
O
CF$_3$
O
3ej
10
9
8
7
6
5
4
3
2
1
ppm
1.95
1.00
0.99
4.00
0.98
0.96
7.30
1.11


-63.913
19F NMR of
CF3
O
CF3
O
3ej
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00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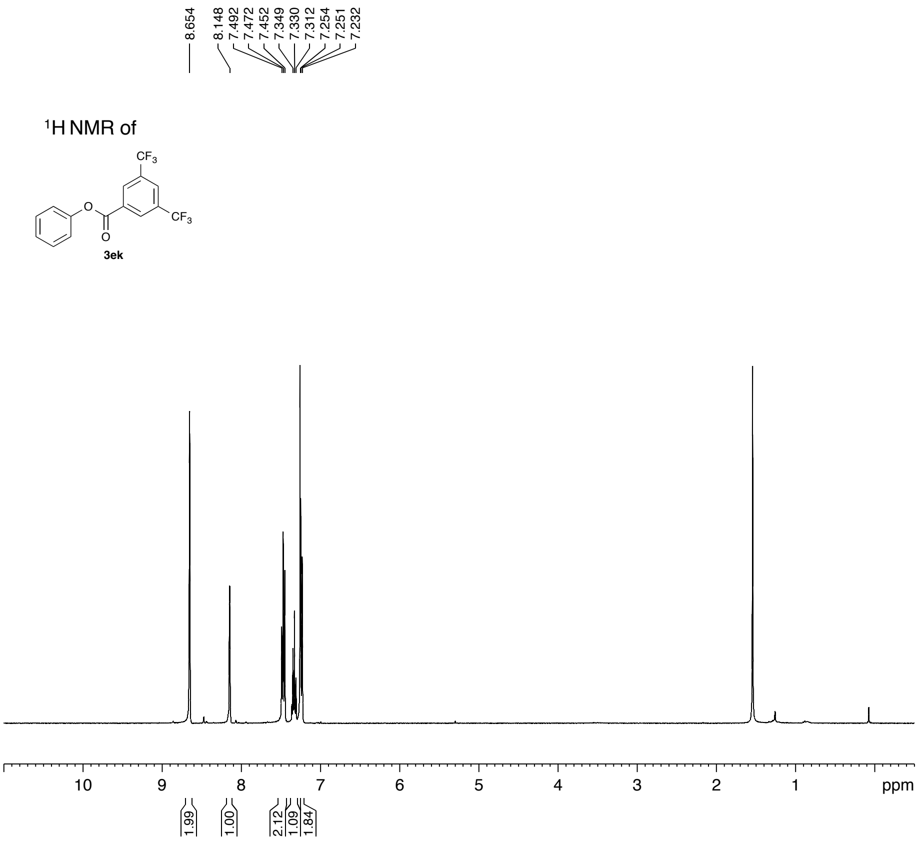
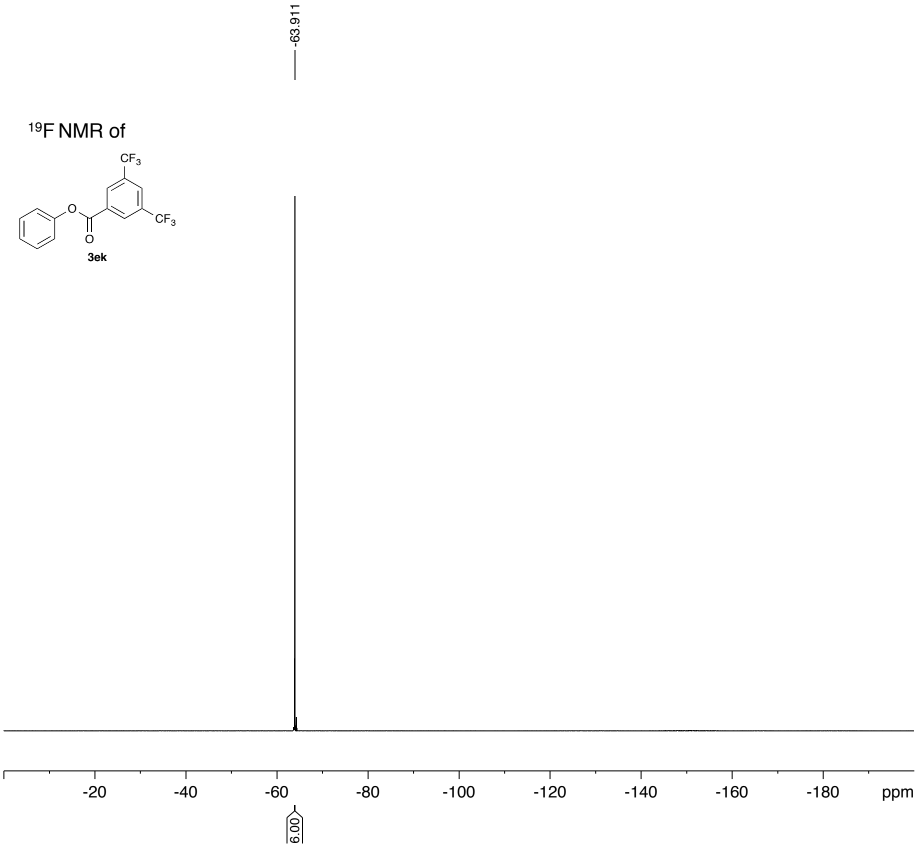
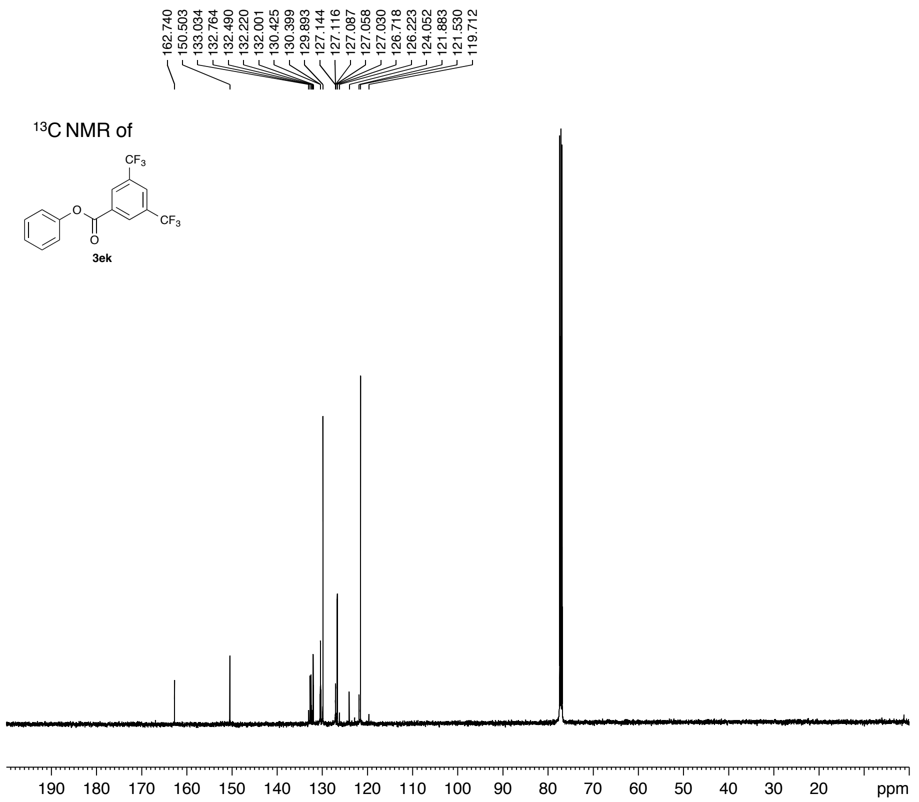
148.714
142.291
139.481
139.400
135.755
133.694
133.371
133.206
132.936
132.663
132.389
132.254
131.064
131.003
130.119
130.092
129.431
127.756
127.175
127.149
127.120
127.090
127.062
126.239
124.069
121.897
119.729
35.412
35.029
34.743
31.886
13C NMR of
CF3
O
CF3
O
3ej
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


^{1}H NMR of

3ek

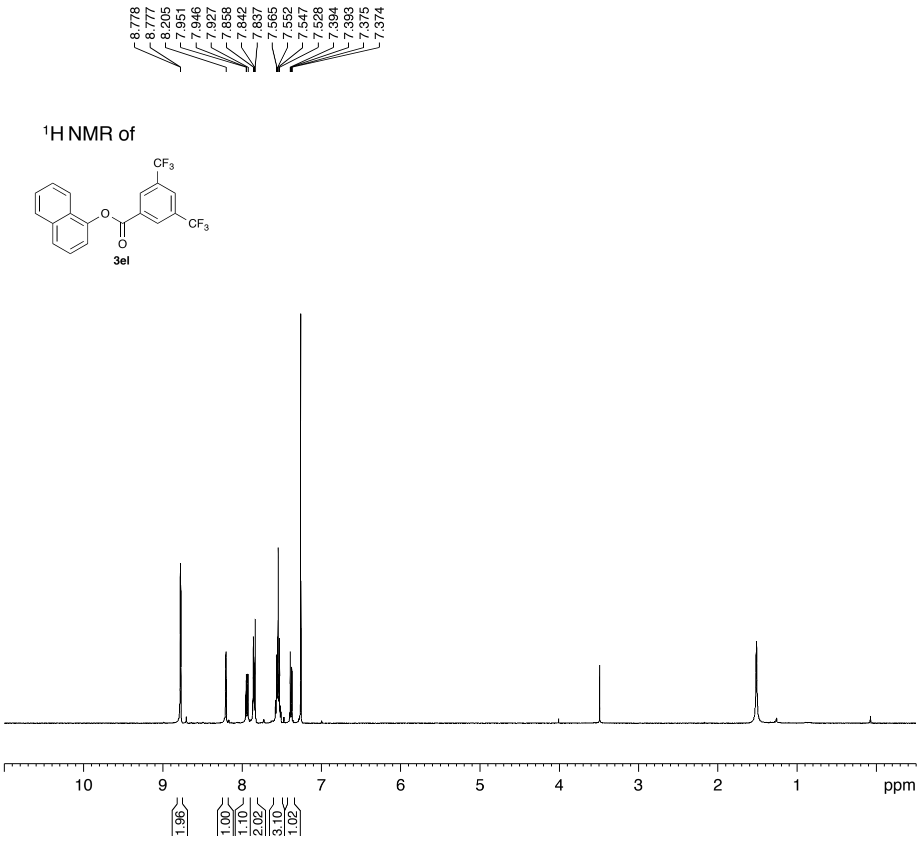

^{19}F NMR of

3ek



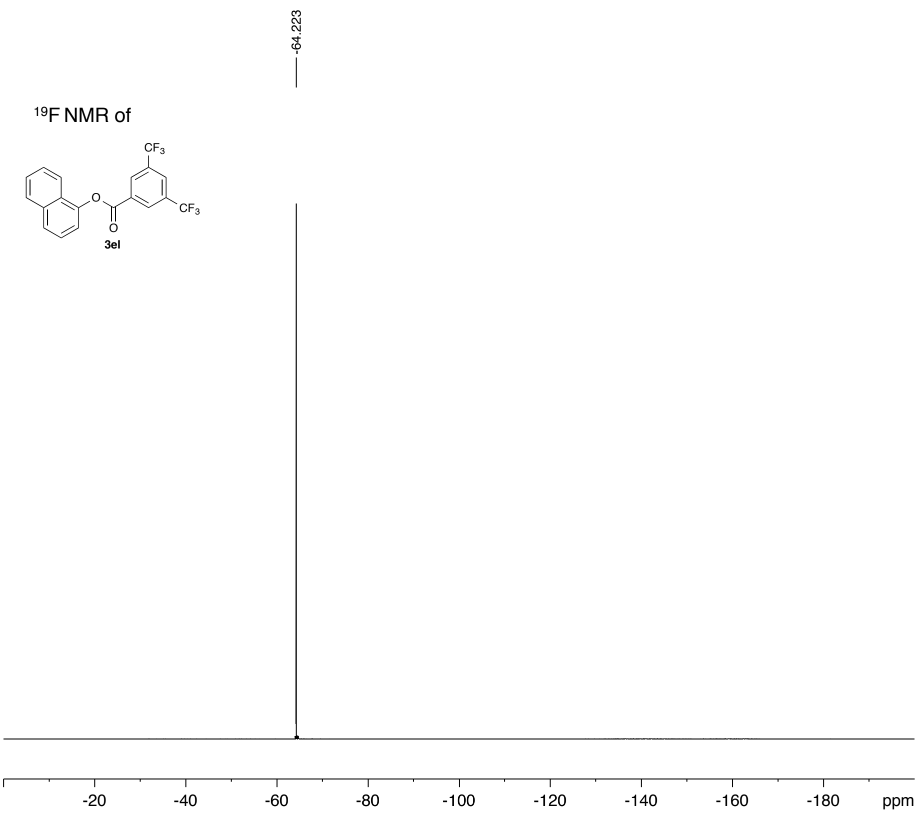
^{13}C NMR of

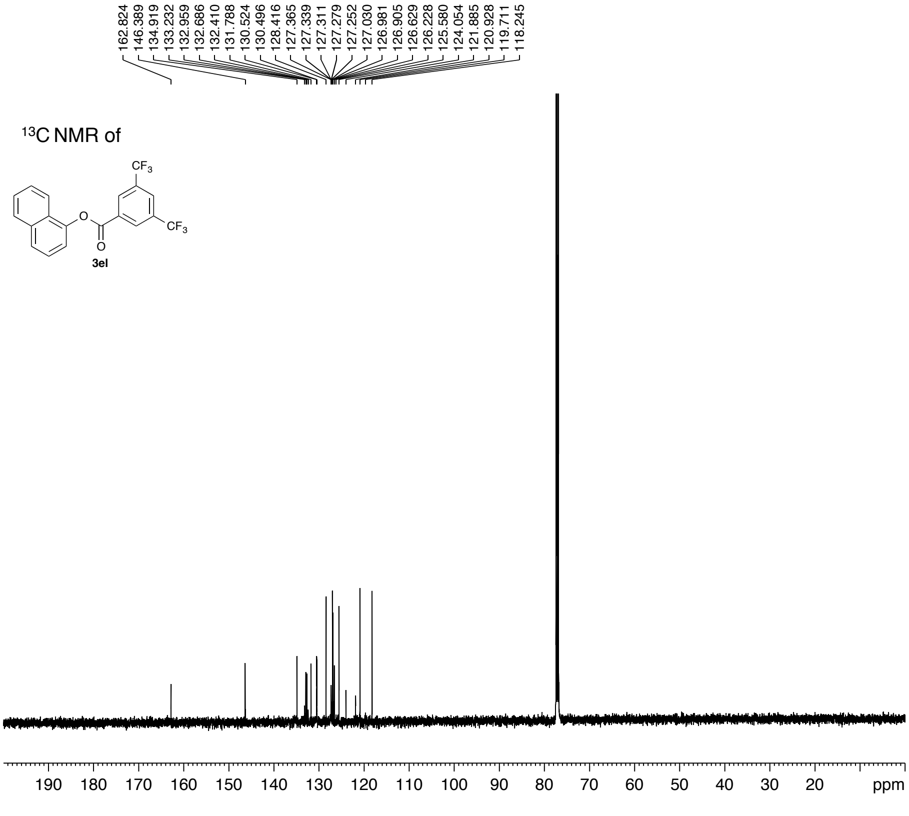
3ek

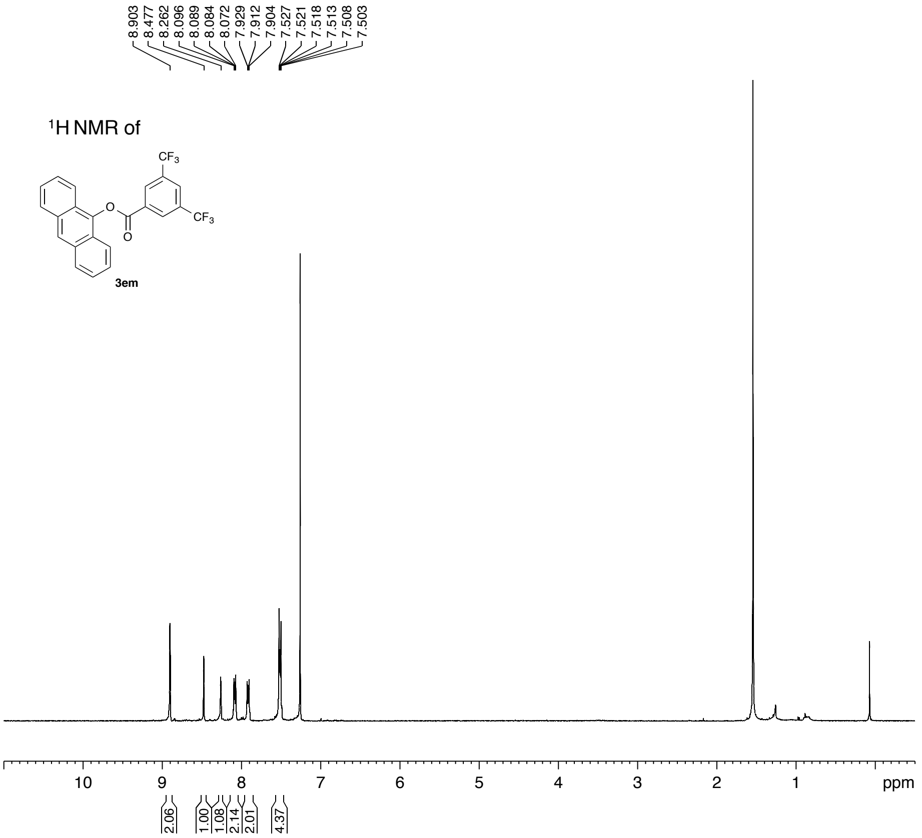


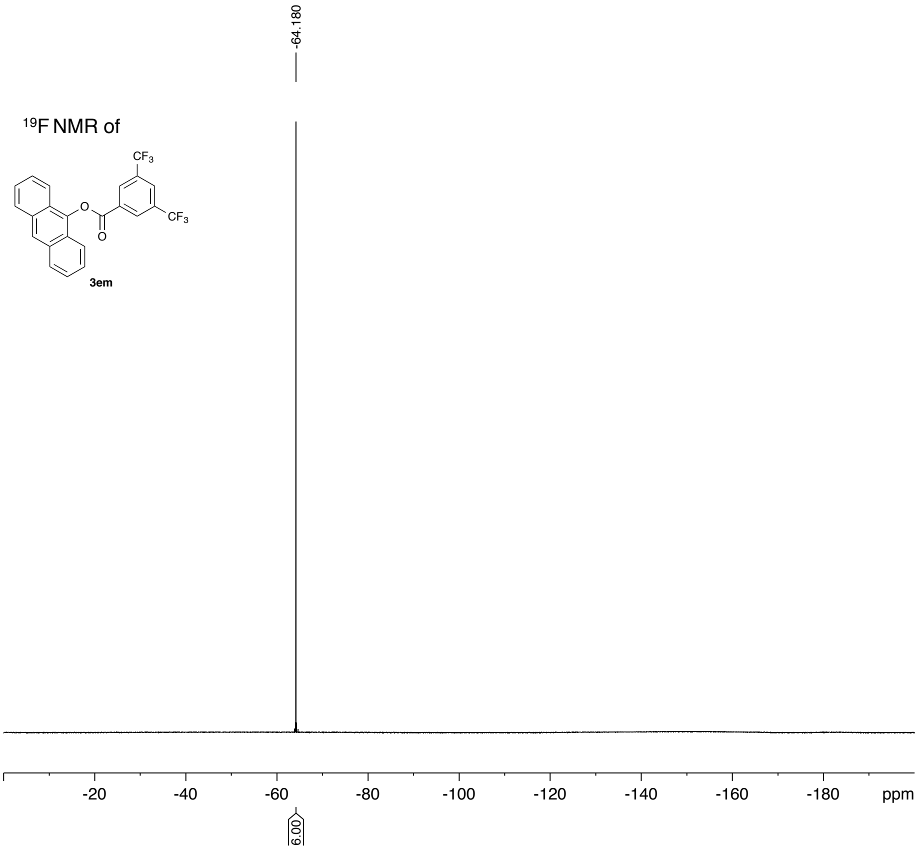
^{1}H NMR of

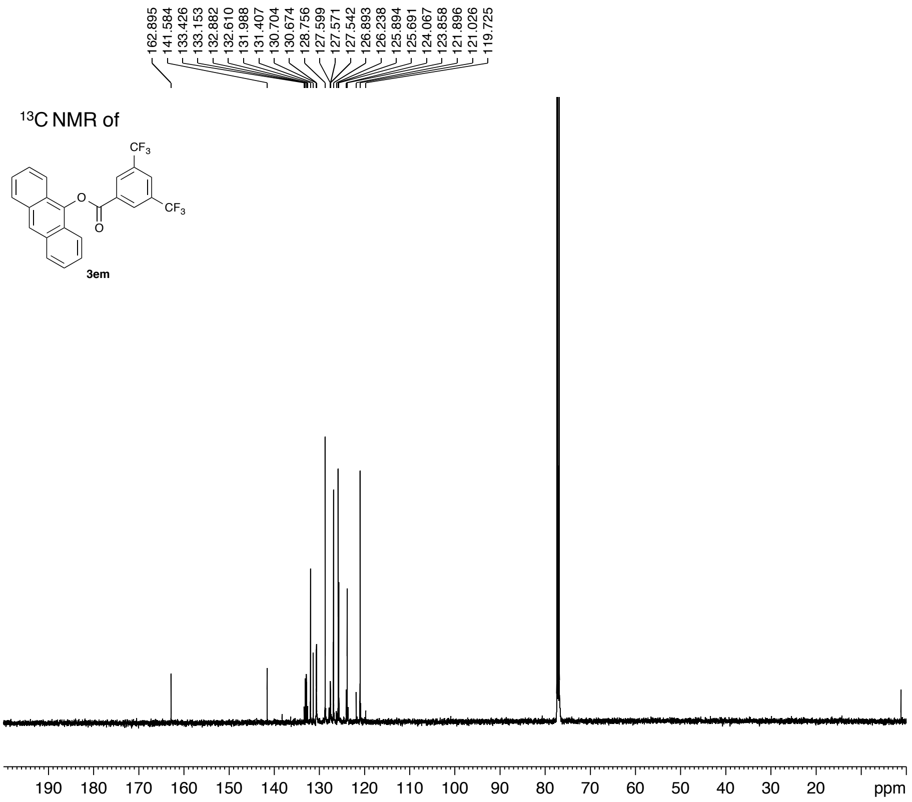
3el

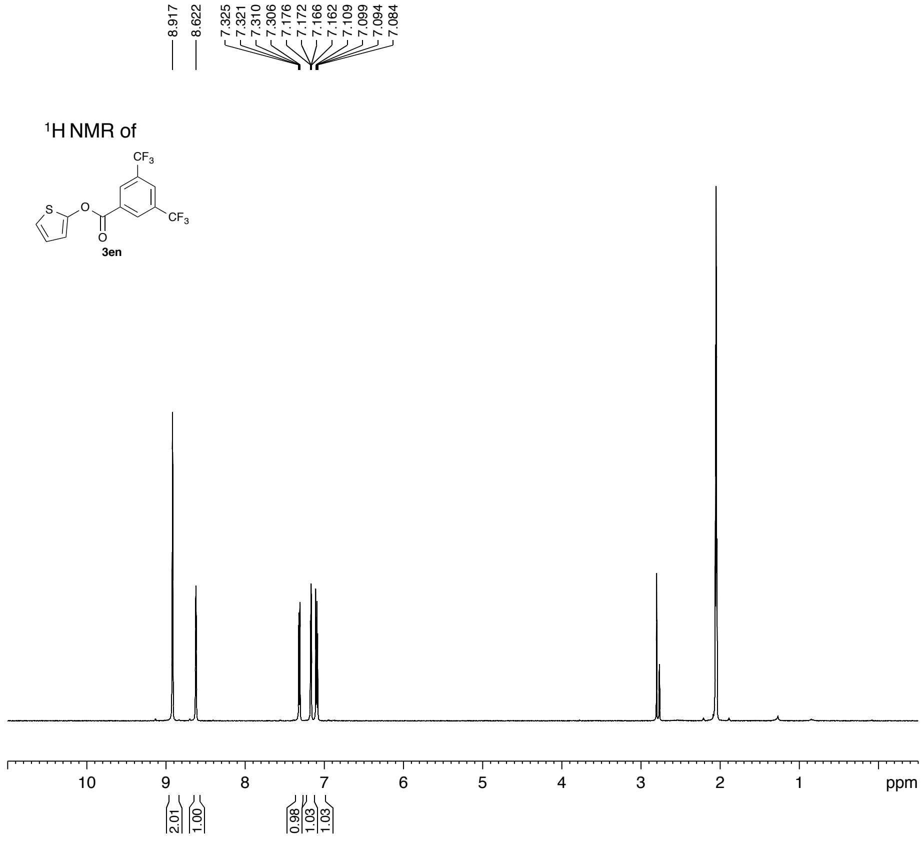

-64.223
^{19}F NMR of
CF$_3$
O
O
CF$_3$
3el
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

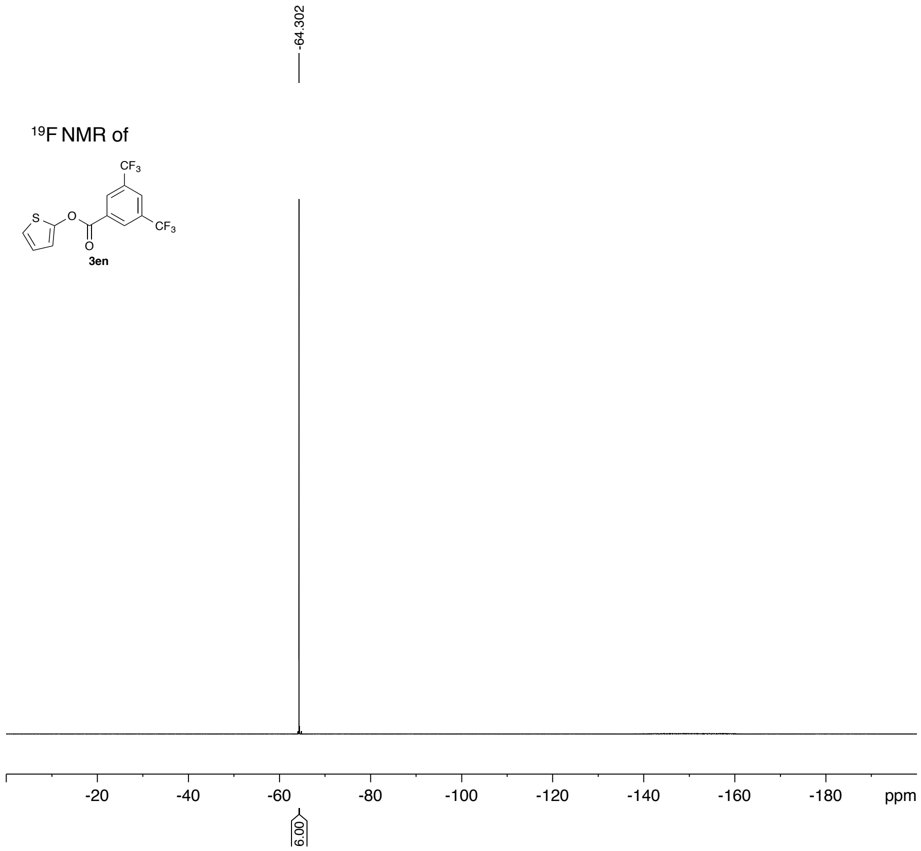

162.824
146.389
134.919
133.232
132.959
132.686
132.410
131.788
130.524
130.496
128.416
127.365
127.339
127.311
127.279
127.252
127.030
126.981
126.905
126.629
126.228
125.580
124.054
121.885
120.928
119.711
118.245
^{13}C NMR of
CF$_3$
O
O
CF$_3$
3el
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

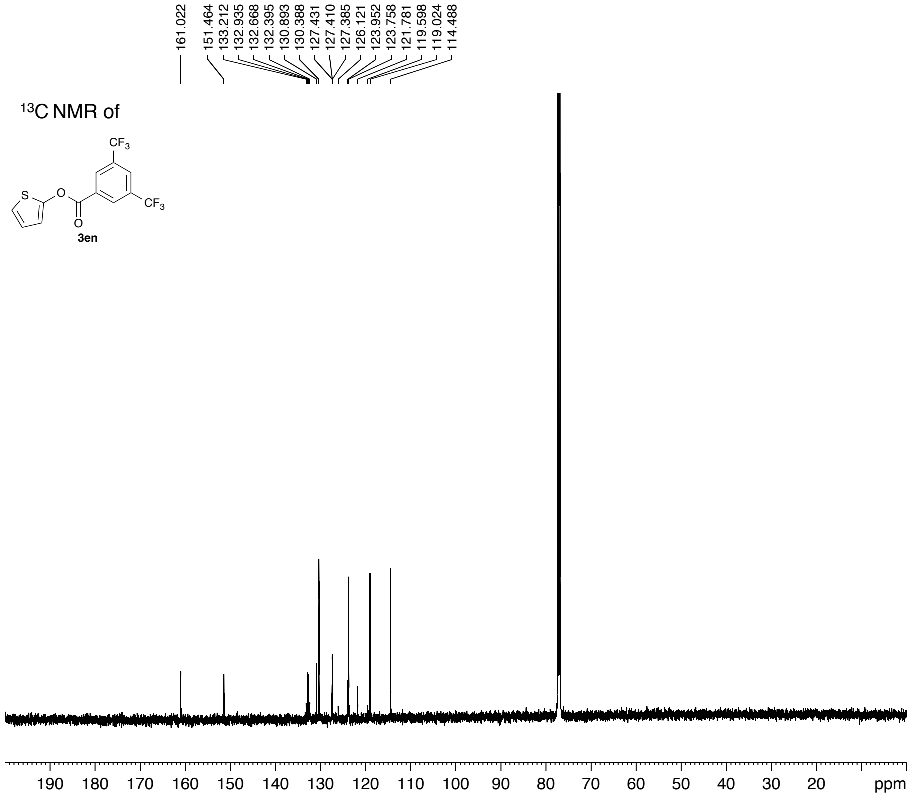

8.903
8.477
8.262
8.096
8.089
8.084
8.072
7.929
7.912
7.904
7.527
7.521
7.518
7.513
7.508
7.503
¹H NMR of
CF₃
O
O
CF₃
3em
10
9
8
7
6
5
4
3
2
1
ppm
2.06
1.00
1.08
2.14
2.01
4.37


-64.180
¹⁹F NMR of
CF₃
O
O
CF₃
3em
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00

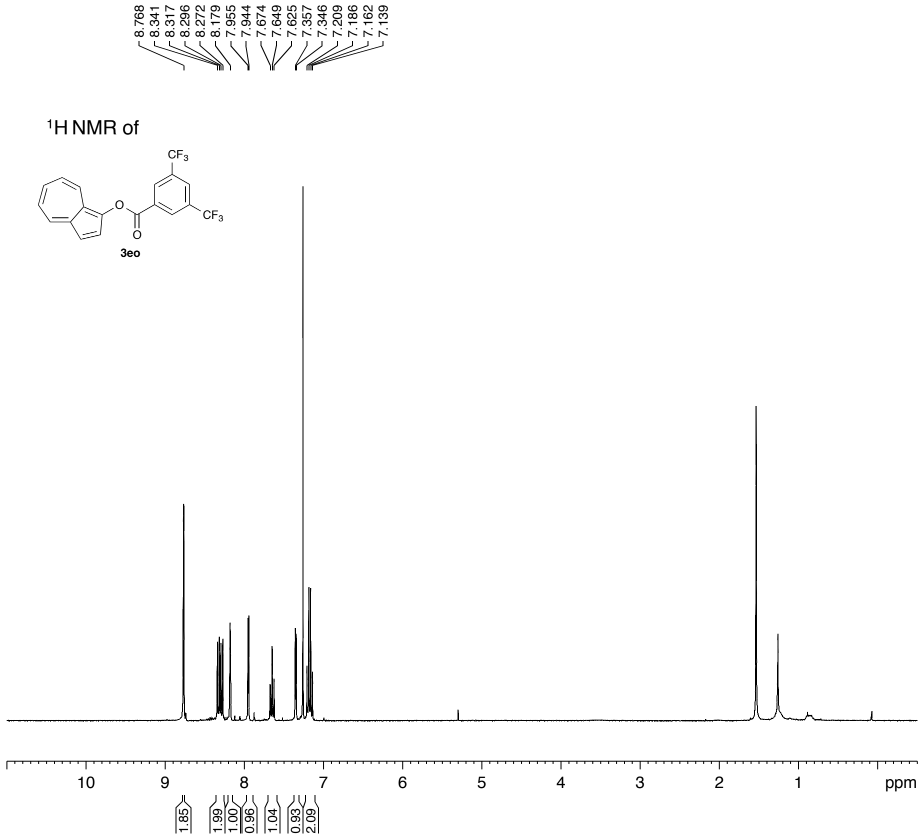

162.895
141.584
133.426
133.153
132.882
132.610
131.988
131.407
130.704
130.674
128.756
127.599
127.571
127.542
126.893
126.238
125.894
125.691
124.067
123.858
121.896
121.026
119.725
^{13}C NMR of
CF$_3$
O
O
CF$_3$
3em
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.917
8.622
7.325
7.321
7.310
7.306
7.176
7.172
7.166
7.162
7.109
7.099
7.094
7.084
^{1}H NMR of
CF$_3$
S
O
O
CF$_3$
3en
10 9 8 7 6 5 4 3 2 1 ppm
2.01
1.00
0.98
1.03
1.03

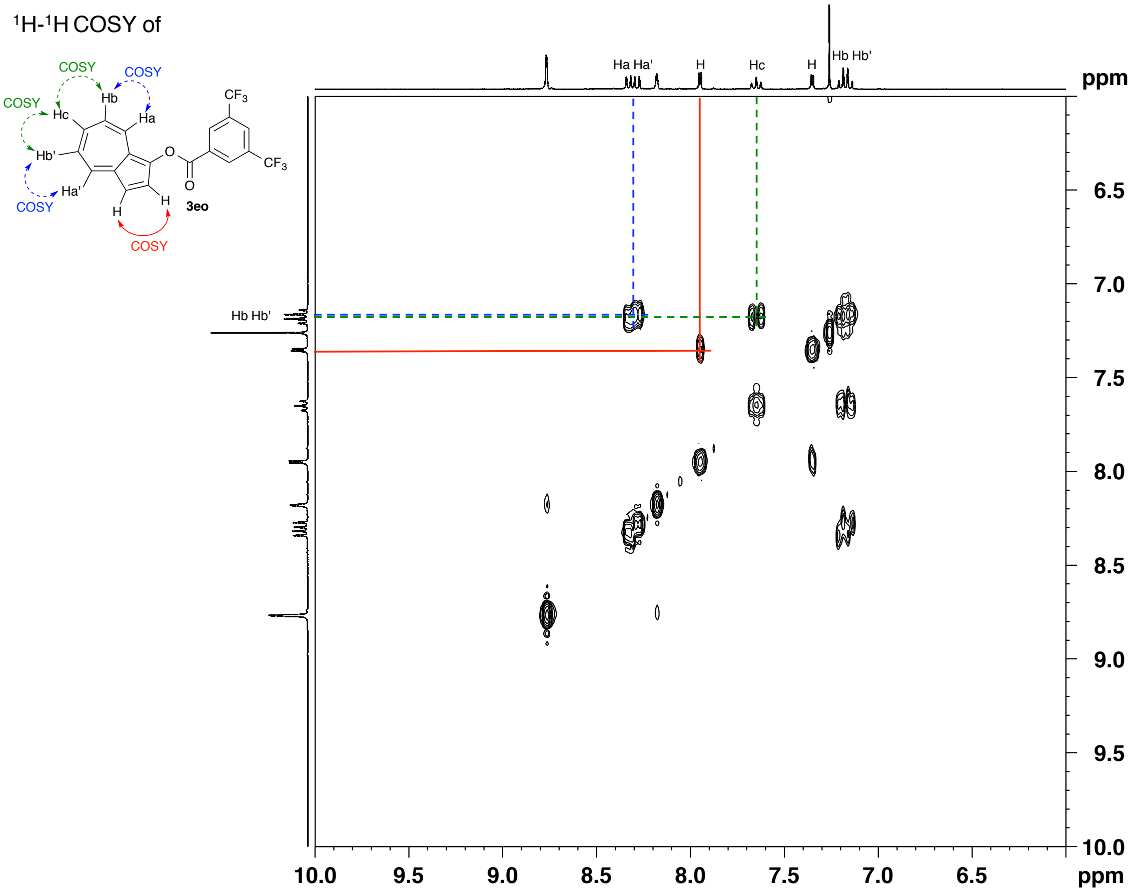

-64.302
^{19}F NMR of
CF$_3$
S
O
O
CF$_3$
3en
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00

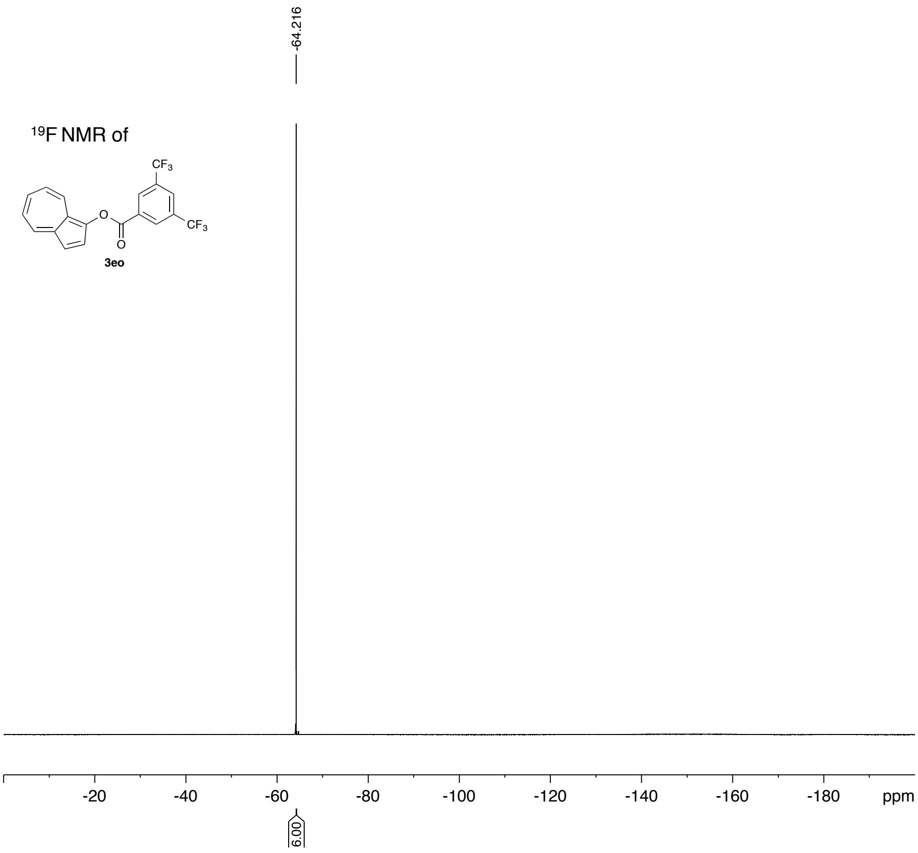

161.022
151.464
133.212
132.935
132.668
132.395
130.893
130.388
127.431
127.410
127.385
126.121
123.952
123.758
121.781
119.598
119.024
114.488
^{13}C NMR of
CF$_3$
S
O
O
CF$_3$
3en
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

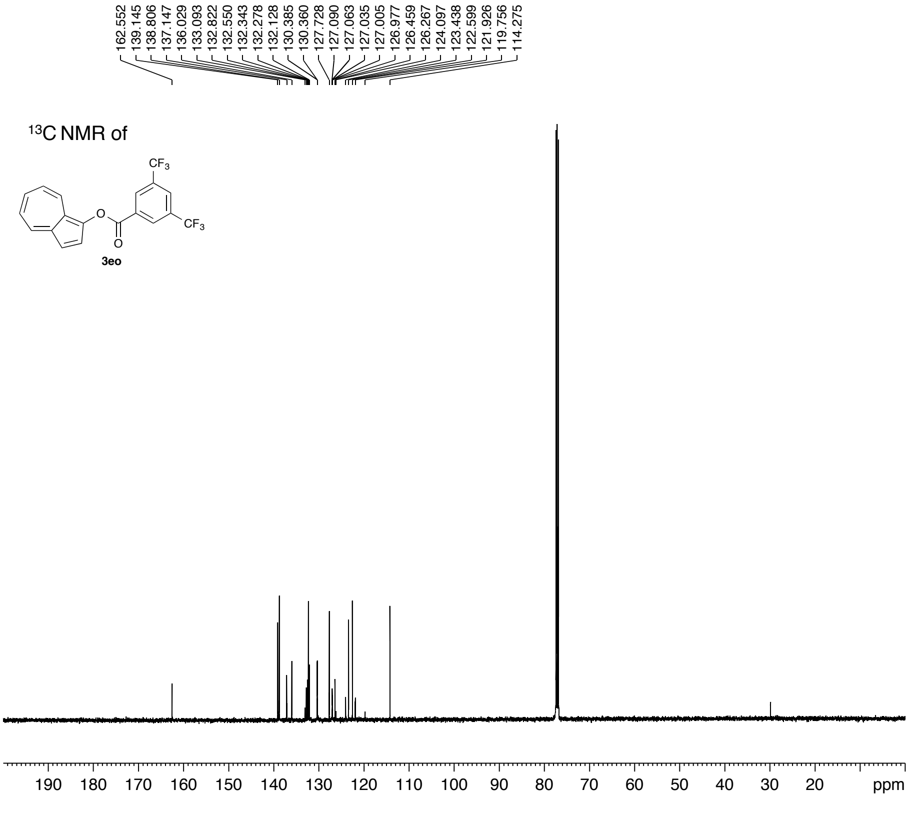
^{1}H NMR of



^{1}H-^{1}H COSY of




-64.216
19F NMR of
CF3
O
O
CF3
3eo
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
6.00


162.552
139.145
138.806
137.147
136.029
133.093
132.822
132.550
132.343
132.278
132.128
130.385
130.360
127.728
127.090
127.063
127.035
127.005
126.977
126.459
126.267
124.097
123.438
122.599
121.926
119.756
114.275
13C NMR of
CF3
O
O
CF3
3eo
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm