Nickel-Catalyzed Carboxylation of Aryl and Heteroaryl Fluorosulfates Using Carbon Dioxide

(Supporting Information)

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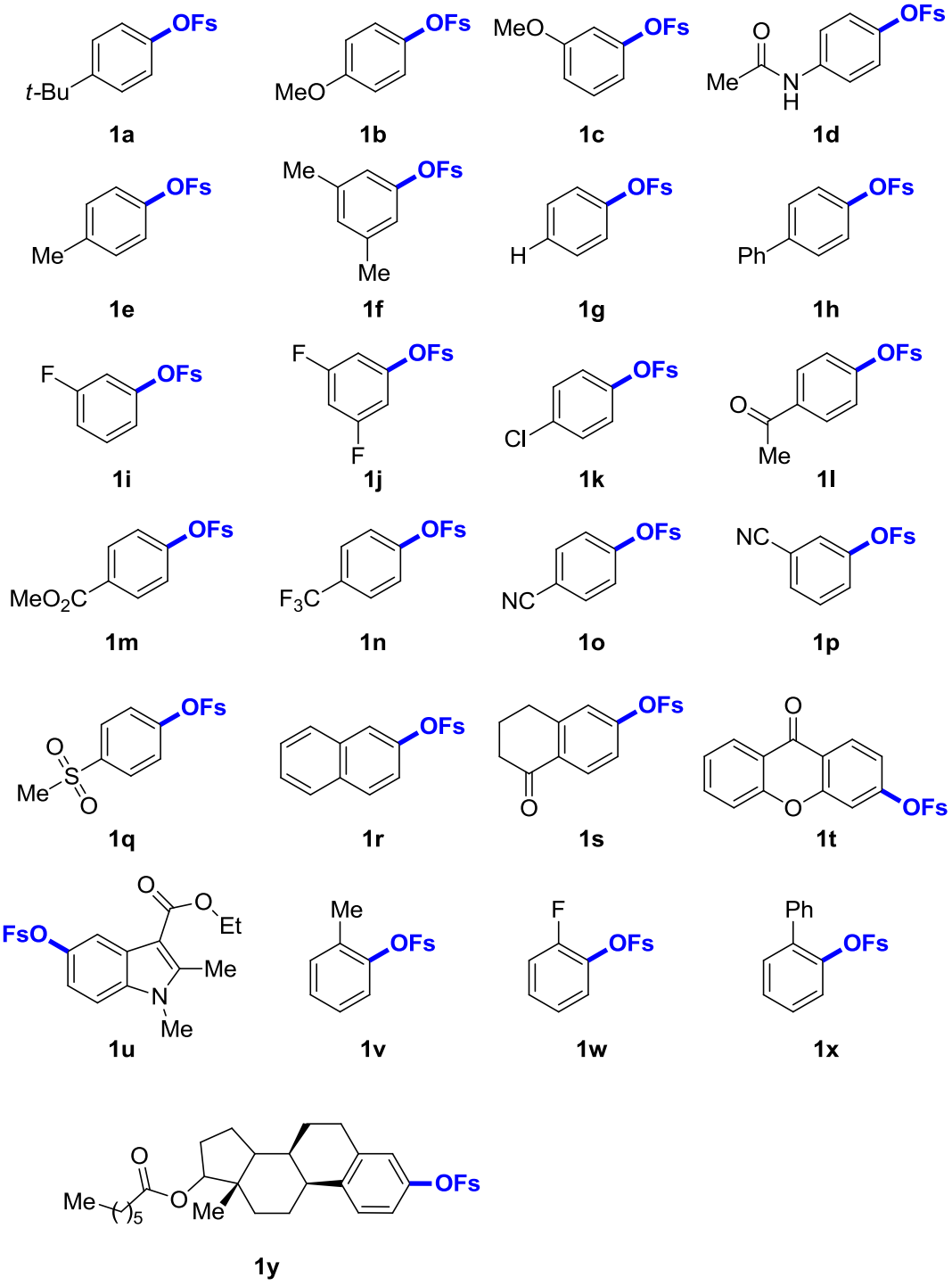
1. General Information

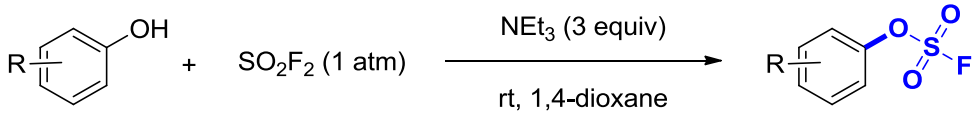
All commercial reagents were purchased from TCI, Sigma-Aldrich, Adamas-beta, Bide Pharmatech Ltd. of the highest purity grade. They were used without further purification unless specified. Solvents and commercially available reagents were used without purification. Column chromatography was performed using either 100-200 Mesh or 300-400 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber. ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (400 MHz and 100 MHz, respectively). The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution mass spectra were recorded at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry. Analytical and spectral data of all those known compounds are exactly matching with the reported values.

2. The Synthesis of Aryl Fluorosulfates

2.1 Scope of aryl fluorosulfates



2.3 General Procedure I for the Synthesis of Aryl Fluorosulfates

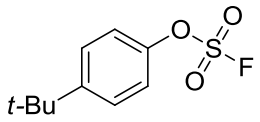


1

All the aryl fluorosulfates were synthesized according to literature[1]. To a 100 mL round bottom flask with a stir bar was added the corresponding phenol (1.0 equiv), NEt_3 (3 equiv) and 1,4-dioxane (50 mL). The flask was capped with a rubber septum.

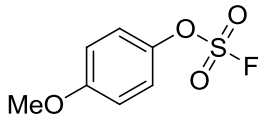
Then SO_2F_2 gas was introduced into the stirring reaction mixture by slow bubbling through a SO_2F_2 balloon at the room temperature. The resulting solution was stirred at room temperature for 24 h. The reaction mixture was then purged with N_2 for 30 min to remove most of the residual SO_2F_2, and water was added. The mixture was acidified with concentrated HCl, and the product was extracted into dichloromethane. The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The products were purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

3. Characterization of Aryl Fluorosulfates



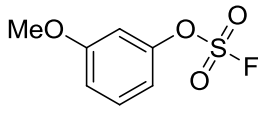
1a

1a was obtained as a colorless oil starting from 4-(tert-butyl)phenol (3.0 g, 20 mmol) according to the General Procedure I in 93% yield (4.31 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.29 – 7.22 (m, 2H), 1.34 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.12. ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.92, 147.85, 127.30, 120.24, 34.75, 31.26. **HRMS** (ESI-TOF) m/z Calcd for $C_{10}H_{14}FO_3S$ $[M+H]^+$ 233.0642, found 233.0644.



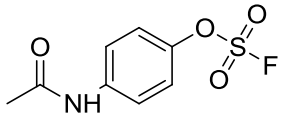
1b

1b was obtained as a colorless oil starting from 4-methoxyphenol (2.48 g, 20 mmol) according to the General Procedure I in 93% yield (3.85 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H). Spectral data matched those previously reported.[1]



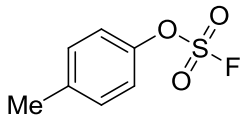
1c

1c was obtained as a colorless oil starting from methyl 3-methoxyphenol (2.48 g, 20 mmol) according to the General Procedure I in 89% yield (4.18 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.3 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.87 (d, *J* = 2.1 Hz, 1H), 3.83 (s, 3H). Spectral data matched those previously reported.[1]



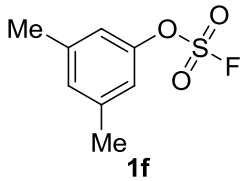
1d

1d was obtained as a white solid starting from methyl *N*-(4-hydroxyphenyl)acetamide (3.02 g, 20 mmol) according to the General Procedure I in 76% yield (3.55 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.0 Hz, 2H), 7.39 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 2.20 (s, 3H).Spectral data matched those previously reported.[4]



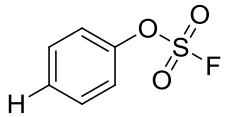
1e

1e was obtained as a colorless oil starting from *p*-cresol (2.16 g, 20 mmol) according to the General Procedure I in 95% yield (3.69 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (q, *J* = 8.6 Hz, 4H), 2.39 (s, 3H). Spectral data matched those previously reported.[1]



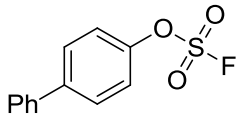
1f

1f was obtained as a colorless oil starting from methyl 3,5-methylphenol (2.44 g, 20 mmol) according to the General Procedure I in 87% yield (3.56 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H).^{19}F NMR (376 MHz, $CDCl_3$) δ 39.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.89, 138.05, 131.84, 129.28, 127.11, 121.21, 20.81, 15.53. **HRMS** (ESI-TOF) m/z Calcd for $C_8H_{10}FO_3S$ $[M+H]^+$ 205.0329, found 205.0331.



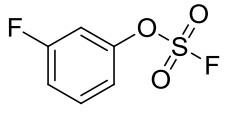
1g

1g was obtained as a colorless oil starting from phenol (1.88 g, 20 mmol) according to the General Procedure I in 75% yield (2.69 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H). Spectral data matched those previously reported.[1]



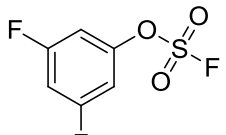
1h

1h was obtained as a white solid starting from [1,1'-biphenyl]-4-ol (3.4 g, 20 mmol) according to the General Procedure I in 93% yield (4.74 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 3H). Spectral data matched those previously reported.[1]



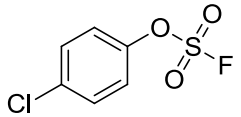
1i

1i was obtained as a colorless oil starting from methyl 3-fluorophenol (2.24 g, 20 mmol) according to the General Procedure I in 84% yield (3.27 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 8.3, 6.3 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.15 – 7.08 (m, 1H). Spectral data matched those previously reported.[1]



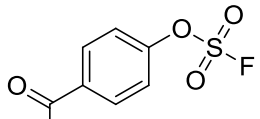
1j

1j was obtained as a colorless oil starting from methyl 3,5-difluorophenol (2.6 g, 20 mmol) according to the General Procedure I in 67% yield (2.85 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 16.9, 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.52, -105.10, -105.12, -105.12, -105.14. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.38, 164.24, 161.86, 161.72, 150.22, 150.08, 149.94, 105.83, 105.75, 105.63, 105.54, 105.06, 104.81, 104.56. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_4F_3O_3S$ $[M+H]^+$ 212.9828, found 212.983.



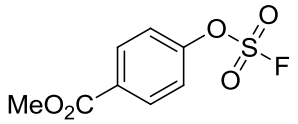
1k

1k was obtained as a colorless oil starting from 4-chlorophenol (2.56 g, 20 mmol) according to the General Procedure I in 86% yield (3.61 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 15.4, 9.0 Hz, 2H), 7.28 (t, *J* = 9.2 Hz, 2H). Spectral data matched those previously reported.[1]



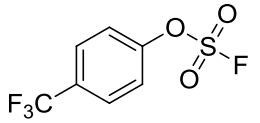
1l

1l was obtained as a white solid starting from 1-(4-hydroxyphenyl)ethanone (2.72 g, 20 mmol) according to the General Procedure I in 85% yield (3.75 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 15.4, 9.0 Hz, 2H), 7.28 (t, *J* = 9.2 Hz, 2H). Spectral data matched those previously reported.[2]



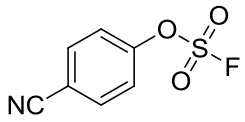
1m

1m was obtained as a colorless oil starting from methyl 4-hydroxybenzoate (3.04 g, 20 mmol) according to the General Procedure I in 89% yield (4.18 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H). Spectral data matched those previously reported.[1]



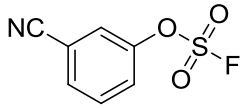
1n

1n was obtained as a colorless oil starting from 4-hydroxybenzonitrile (3.24 g, 20 mmol) according to the General Procedure I in 83% yield (4.03 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H). Spectral data matched those previously reported.[1]



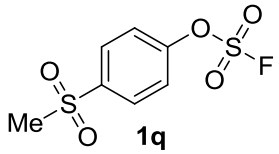
1o

1o was obtained as a white solid starting from 4-hydroxybenzonitrile (2.38 g, 20 mmol) according to the General Procedure I in 91% yield (3.67 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H). Spectral data matched those previously reported.[1]



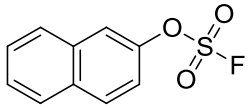
1p

1p was obtained as a colorless oil starting from methyl 3-hydroxybenzonitrile (2.38 g, 20 mmol) according to the General Procedure I in 92% yield (3.73 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.9 Hz, 1H), 7.65 (dd, *J* = 14.2, 6.7 Hz, 3H).Spectral data matched those previously reported.[1]



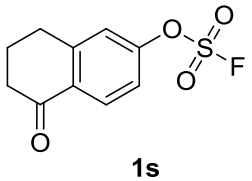
1q

1q was obtained as a white solid starting from methyl 4-(methylsulfonyl)phenol (3.44 g, 20 mmol) according to the General Procedure I in 85% yield (4.31 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 3.10 (s, 3H). Spectral data matched those previously reported.[3]



1r

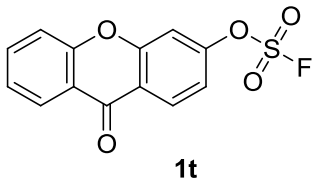
1r was obtained as a colorless oil starting from naphthalen-2-ol (2.88 g, 20 mmol) according to the General Procedure I in 81% yield (3.66 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.82 (s, 1H), 7.63 – 7.55 (m, 2H), 7.44 (dd, *J* = 9.0, 2.2 Hz, 1H). Spectral data matched those previously reported.[1]



1s

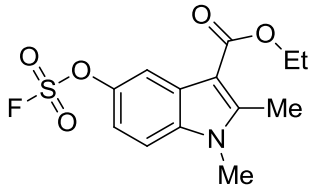
1s was obtained as a colorless oil starting from methyl 6-hydroxy-3,4-dihydronaphthalen-1(2H)-one (3.24 g, 20 mmol) according to the General Procedure I in 87% yield (3.56 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 3.02 (t, *J* = 5.6 Hz, 2H), 2.73 – 2.61 (m, 2H), 2.24 – 2.10 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.42. ^{13}C NMR (101 MHz, $cdcl_3$) δ 196.18, 147.73, 136.65, 134.90, 127.77, 127.56, 125.70,

38.36, 23.19, 22.04. **HRMS** (ESI-TOF) m/z Calcd for $C_{10}H_{10}FO_4S$ $[M+H]^+$ 245.0278, found 245.028.



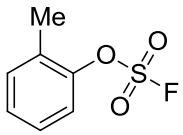
1t

1t was obtained as a white solid starting from methyl 3-hydroxy-9H-xanthen-9-one (4.24 g, 20 mmol) according to the General Procedure I in 50% yield (2.93 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.8 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.38. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.80, 156.56, 156.18, 153.26, 135.51, 129.70, 126.84, 124.79, 121.73, 121.62, 117.98, 116.70, 110.90. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_7FO_5S$ $[M+H]^+$ 295.0071, found 295.0073.



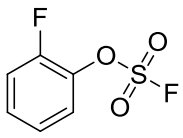
1u

1u was obtained as a colorless oil starting from methyl 3-hydroxy-9H-xanthen-9-one (4.66 g, 20 mmol) according to the General Procedure I in 57% yield (3.59 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 4.40 (dd, *J* = 14.1, 7.0 Hz, 2H), 3.70 (s, 3H), 2.77 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 36.56. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.26, 147.52, 145.61, 135.33, 127.06, 114.53, 113.63, 110.14, 104.73, 59.77, 29.93, 14.49, 12.01. **HRMS** (ESI-TOF) m/z Calcd for $C_{13}H_{18}FN_2O_5S$ $[M+NH_4]^+$ 333.0915, found 333.091.



1v

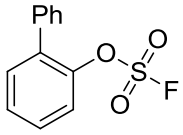
1v was obtained as a colorless oil starting from *o*-cresol (2.16 g, 20 mmol) according to the General Procedure I in 52% yield (1.97 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 2.36 (s, 3H). Spectral data matched those previously reported.[1]



1w

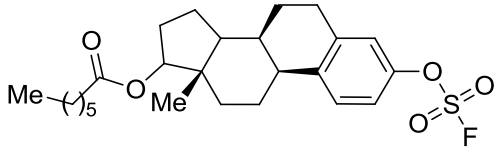
1w was obtained as a colorless oil starting from 2-fluorophenol (2.24 g, 20 mmol) according to the General Procedure I in 71% yield (2.77 g). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.47 – 7.35 (m, 2H), 7.33 – 7.20 (m, 2H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 7.31 – 7.22 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.03 (d, *J* = 10.3 Hz), -127.81 – -128.09 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.83, 152.30, 130.12, 130.05, 125.16, 125.11, 123.23, 117.99, 117.82. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_5F_2O_3S$ $[M+H]^+$ 194.9922, found 194.9923.



1x

1x was obtained as a white solid starting from [1,1'-biphenyl]-2-ol (2.16 g, 20 mmol) according to the General Procedure I in 62% yield (3.12 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 9H). Spectral data matched those previously reported.[1]

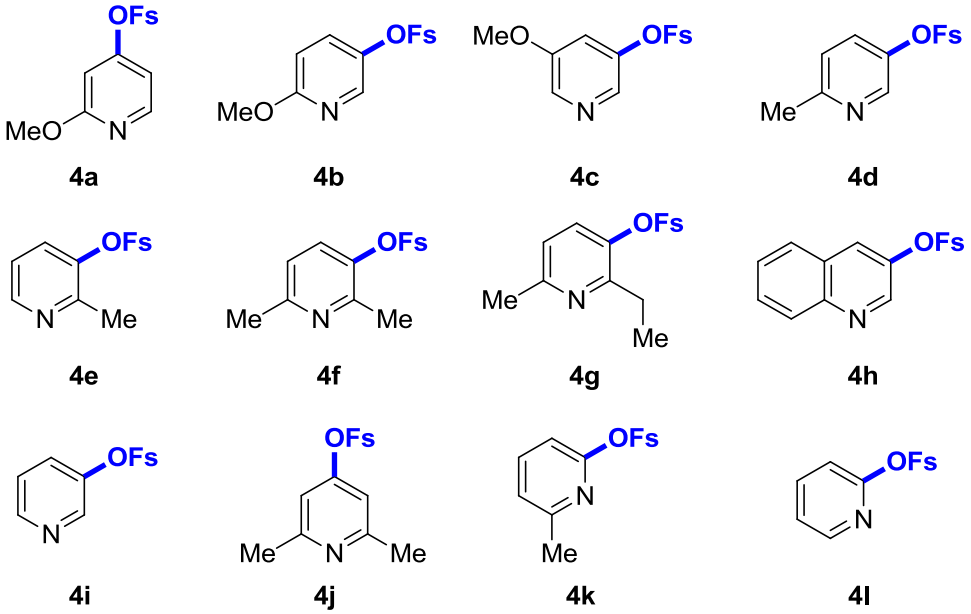


1y

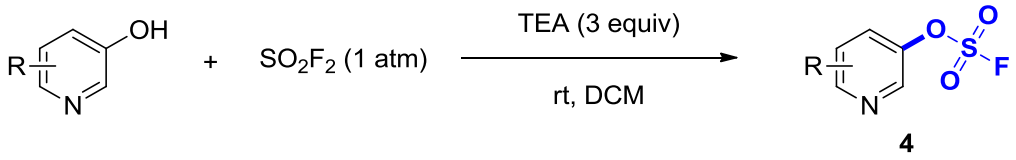
1y was obtained as a colorless oil starting from oestradiol 17-heptanoate (3.84 g, 10 mmol) according to the General Procedure I in 86% yield (4.0 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.03 (s, 1H), 4.71 (t, *J* = 8.5 Hz, 1H), 2.90 (dd, *J* = 8.5, 4.0 Hz, 2H), 2.34 – 2.16 (m, 5H), 1.96 – 1.86 (m, 2H), 1.81 – 1.70 (m, 1H), 1.63 (dt, *J* = 11.2, 5.6 Hz, 2H), 1.59 – 1.22 (m, 13H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.28. ^{13}C NMR (101 MHz, $cdcl_3$) δ 173.93, 147.98, 141.02, 139.58, 127.33, 120.61, 117.63, 82.18, 49.77, 43.93, 42.85, 37.94, 36.78, 34.58, 31.47, 29.49, 28.82, 27.54, 26.74, 25.98, 25.08, 23.24, 22.52, 14.05, 12.04. **HRMS** (ESI-TOF) m/z Calcd for $C_{25}H_{39}FNO_5S$ $[M+NH_4]^+$ 484.2527, found 484.2527.

4. The Synthesis of Pyridinyl Fluorosulfates

4.1 Scope of Pyridinyl Fluorosulfates

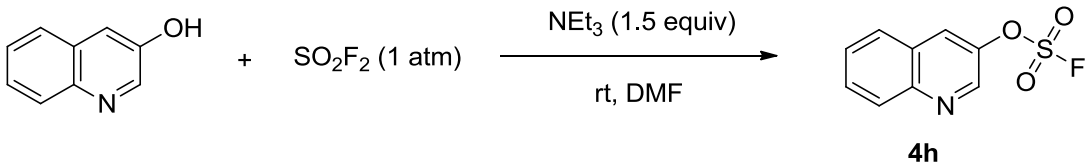


4.2 General Procedure II for the Synthesis of Pyridinyl Fluorosulfates



All the aryl fluorosulfates were synthesized according to literature[2]. A three-neck round-bottom flask equipped with a thermometer was charged with the corresponding pyridinol, TEA (3.03 g, 1.5 equiv, 30 mmol), DCM (50 mL). The flask was capped with a rubber septum. Then SO_2F_2 gas was introduced into the stirring reaction mixture by slow bubbling through a SO_2F_2 balloon at the room temperature. The reaction mixture was vigorously stirred at room temperature for 24 h, monitoring by TLC. After completion, the solvent was removed by rotary evaporation. The residue was dissolved in EtOAc, washed with saturated sodium bicarbonate and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

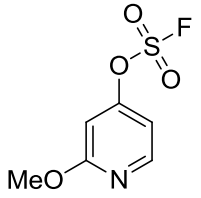
4.3 Synthesis of 4h



A three-neck round-bottom flask equipped with a thermometer was charged with the quinolin-3-ol (2.9 g, 20 mmol), TEA (3.03 g, 1.5 equiv, 30 mmol), DMF (20 mL). The flask was capped with a rubber septum. Then SO_2F_2 gas was introduced into the stirring reaction mixture by slow bubbling through a SO_2F_2 balloon at the room

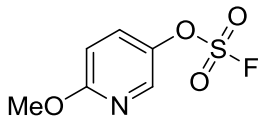
temperature. The reaction mixture was vigorously stirred at room temperature for 24 hours, monitoring by TLC. After completion, the mixture was extracted with DCM (50 mL x 3), and washed with saturated sodium bicarbonate and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent to give the product as a white solid in 62% yield (2.77 g).

5. Characterization of Pyridinyl Fluorosulfates



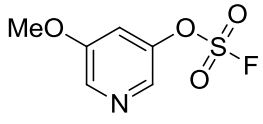
4a

4a was obtained as a colorless oil starting from 6-methoxypyridin-3-ol (2.5 g, 20 mmol) according to the General Procedure II in 57% yield (2.35 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.7 Hz, 1H), 6.88 (d, *J* = 5.5 Hz, 1H), 6.71 (s, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 40.12. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.91, 157.79, 149.43, 108.92, 102.83, 77.34, 77.02, 76.70, 54.34. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_7FNO_4S$ $[M+H]^+$ 208.0074, found 208.0077.



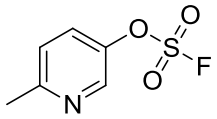
4b

4b was obtained as a white solid starting from 6-methoxypyridin-3-ol (2.5 g, 20 mmol) according to the General Procedure II in 73% yield (3.02 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 36.75. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.32, 141.94, 139.35, 131.59, 112.32, 54.20. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_7FNO_4S$ $[M+H]^+$ 208.0074, found 208.0077.



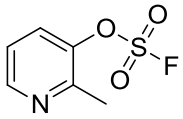
4c

4c was obtained as a white solid starting from 5-methoxypyridin-3-ol (2.5 g, 20 mmol) according to the General Procedure II in 78% yield (3.23 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.29 (s, 1H), 7.19 (s, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.45. ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.45, 147.09, 138.15, 133.98, 113.33, 56.20. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_7FNO_4S$ $[M+H]^+$ 208.0074, found 208.0072.



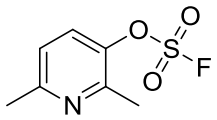
4d

4d was obtained as a colorless oil starting from 6-methylpyridin-3-ol (2.18 g, 20 mmol) according to the General Procedure II in 85% yield (3.24 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.59 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 2.62 (s, 3H). Spectral data matched those previously reported.[5]



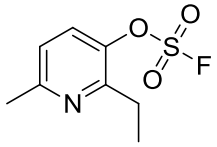
4e

4e was obtained as a colorless oil starting from 2-methylpyridin-3-ol (2.18 g, 20 mmol) according to the General Procedure II in 76% yield (3.14 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.1, 4.9 Hz, 1H), 2.65 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.86. ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.59, 149.12, 145.78, 128.75, 122.64, 19.37. **HRMS** (ESI-TOF) m/z Calcd for $C_6H_7FNO_3S$ $[M+H]^+$ 192.0125, found 192.0123.



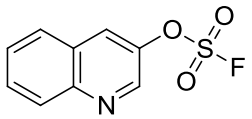
4f

4f was obtained as a colorless oil starting from 2,6-dimethylpyridin-3-ol (2.46 g, 20 mmol) according to the General Procedure II in 67% yield (2.74 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 2.55 (d, *J* = 6.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.29. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.43, 150.34, 143.91, 128.85, 122.14, 23.98, 19.22. **HRMS** (ESI-TOF) m/z Calcd for $C_7H_9FNO_3S$ $[M+H]^+$ 206.0282, found 206.0279.



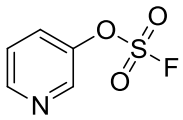
4g

4g was obtained as a colorless oil starting from 2-ethyl-6-methylpyridin-3-ol (2.74 g, 20 mmol) according to the General Procedure II in 71% yield (3.10 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 2.85 (q, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.44. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54, 154.81, 143.48, 128.67, 122.02, 25.57, 24.05. **HRMS** (ESI-TOF) m/z Calcd for $C_8H_{11}FNO_3S$ $[M+H]^+$ 220.0438, found 220.0436.



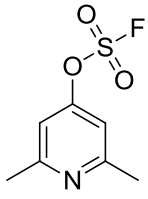
4h

4h was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.18 (d, *J* = 13.8 Hz, 2H), 7.94 – 7.77 (m, 2H), 7.67 (t, *J* = 7.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.45. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.30, 143.47, 143.37, 130.86, 129.68, 128.45, 128.01, 127.51, 126.58. **HRMS** (ESI-TOF) m/z Calcd for $C_9H_7FNO_3S$ $[M+H]^+$ 228.0125, found 228.0123.



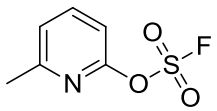
4i

4i was obtained as a colorless oil starting from pyridin-3-ol (1.9 g, 20 mmol) according to the General Procedure II in 80% yield (2.82 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.62 (m, 2H), 7.74 – 7.65 (m, 1H), 7.45 (dd, *J* = 8.5, 4.8 Hz, 1H). Spectral data matched those previously reported.[5]



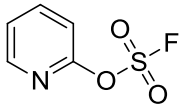
4j

4j was obtained as a colorless oil starting from 2,6-dimethylpyridin-3-ol (2.46 g, 20 mmol) according to the General Procedure II in 53% yield (2.17 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.56 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 40.05. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.38, 157.00, 111.81, 24.60. **HRMS** (ESI-TOF) m/z Calcd for $C_7H_9FNO_3S$ $[M+H]^+$ 206.0282, found 206.028.



4k

4k was obtained as a colorless oil starting from 6-methylpyridin-2-ol (2.18 g, 20 mmol) according to the General Procedure II in 89% yield (3.39 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 6.0 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.56 (s, 3H). Spectral data matched those previously reported.[5]



4l

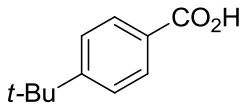
4l was obtained as a colorless oil starting from pyridin-2-ol (1.9 g, 20 mmol) according to the General Procedure II in 84% yield (2.97 g). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.39 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.91 (td, *J* = 8.1, 1.9 Hz, 1H), 7.40 (dd, *J* = 7.3, 4.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H). Spectral data matched those previously reported.[5]

6. General Procedure for the Carboxylation of Aryl Fluorosulfates

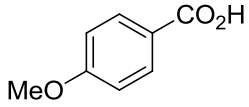
General Procedure III: All operations were carried out under standard Schlenk and glovebox techniques. In a N_2-filled glovebox, to a 50 mL Schlenk tube with a stir bar was added the $Ni(PPh_3)_2Cl_2$ (16.3 mg, 0.025 mmol, 0.05 equiv), Neocuproine (10.4 mg, 0.05 mmol, 0.1 equiv), and Mn powder (82.3 mg, 1.5 mmol, 3 equiv). Then the Schlenk tube was stirred and evacuated under the vacuum pump for 30 minutes. Then CO_2 gas was introduced into the stirring reaction mixture for three times. After that DMF (0.5 mL) was injected into the tube under the CO_2 atmosphere. Then the reaction mixture was stirred for 10 minutes and the mixture was gradually turned into dark blue. Then aryl fluorosulfates (0.5 mmol) and another DMF (0.5 mL) were introduced into the Schlenk tube under the CO_2 atmosphere. Then the resulting solution was stirred at room temperature for 20 h. After completion of the reaction, the reaction mixture was quenched with 6 M HCl and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The products were purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

7. Characterization Data for the Carboxylative Products of Aryl Fluorosulfates



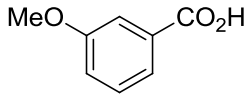
2a

2a was obtained as a white solid starting from **1a** (116 mg, 0.5 mmol) according to the General Procedure III in 96% yield (85.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.63 (brs, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.43, 157.57, 130.10, 126.50, 125.46, 35.18, 31.08. Spectral data matched those previously reported.[6]



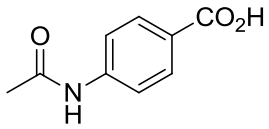
2b

2b was obtained as a white solid starting from **1b** (103 mg, 0.5 mmol) according to the General Procedure III in 94% yield (71.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.03, 162.84, 131.37, 122.97, 113.81, 55.44. Spectral data matched those previously reported.[6]



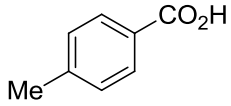
2c

2c was obtained as a white solid starting from **1c** (103 mg, 0.5 mmol) according to the General Procedure III in 89% yield (67.5 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.48 (s, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.17, 159.24, 132.20, 129.73, 121.58, 118.91, 113.91, 55.25. Spectral data matched those previously reported.[6]



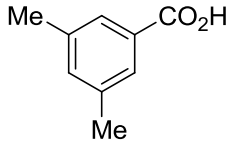
2d

2d was obtained as a white solid starting from **1d** (117 mg, 0.5 mmol) according to the General Procedure III in 83% yield (74.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.75 (brs, 1H), 10.29 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.93, 167.02, 143.40, 130.45, 124.91, 118.20, 24.23. Spectral data matched those previously reported.[8]



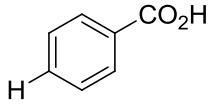
2e

2e was obtained as a white solid starting from **1e** (95 mg, 0.5 mmol) according to the General Procedure III in 96% yield (65.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.57, 144.65, 130.24, 129.19, 126.57, 21.76. Spectral data matched those previously reported.[6]



2f

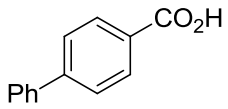
2f was obtained as a white solid starting from **1f** (102 mg, 0.5 mmol) according to the General Procedure III in 92% yield (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.72 (s, 1H), 7.88 (s, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.78, 138.23, 135.39, 133.75, 131.98, 131.84, 128.03, 21.67, 20.75. Spectral data matched those previously reported.[11]



2g

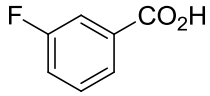
2g was obtained as a white solid starting from **1g** (88 mg, 0.5 mmol) according to the General Procedure III in 95% yield (58.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.76

(brs, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.64, 133.86, 130.23, 129.31, 128.50. Spectral data matched those previously reported.[6]



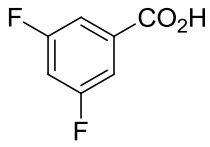
2h

2h was obtained as a white solid starting from **1h** (126 mg, 0.5 mmol) according to the General Procedure III in 97% yield (95.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.18, 144.33, 139.04, 130.00, 129.62, 129.12, 128.33, 127.00, 126.85. Spectral data matched those previously reported.[6]



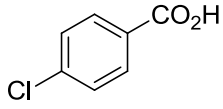
2i

2i was obtained as a white solid starting from **1i** (97 mg, 0.5 mmol) according to the General Procedure III in 87% yield (60.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.47 (dd, *J* = 13.4, 7.6 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.00, -112.02, -112.04, -112.06. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.20, 163.75, 161.29, 130.21, 130.14, 125.97, 125.94, 121.10, 120.89, 117.16, 116.93. Spectral data matched those previously reported.[9]



2j

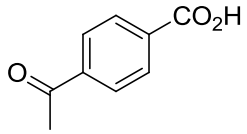
2j was obtained as a white solid starting from **1j** (106 mg, 0.5 mmol) according to the General Procedure III in 87% yield (68.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 7.62 (d, *J* = 4.7 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.03, -108.05, -108.07. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.21, 164.06, 163.94, 161.57, 161.45, 132.37, 132.27, 132.18, 113.37, 113.29, 113.17, 113.10, 109.68, 109.43, 109.18. Spectral data matched those previously reported.[10]



2k

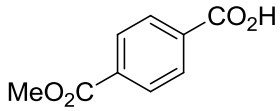
2k was obtained as a white solid starting from **1k** (105 mg, 0.5 mmol) according to the General Procedure III in 83% yield (64.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.23 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.48, 137.81, 131.16, 129.63, 128.80. Spectral data matched those

previously reported.[6]



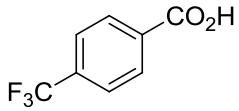
2l

2l was obtained as a white solid starting from **1l** (109 mg, 0.5 mmol) according to the General Procedure III in 87% yield (71.2 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.34 (s, 1H), 8.09 (s, 4H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.74, 166.67, 139.83, 134.51, 129.57, 128.35, 27.04. Spectral data matched those previously reported.[6]



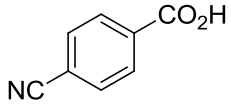
2m

2m was obtained as a white solid starting from **1m** (117 mg, 0.5 mmol) according to the General Procedure III in 93% yield (83.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.43 (s, 1H), 8.09 (s, 4H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.57, 165.61, 134.83, 133.14, 129.60, 129.36, 52.49. Spectral data matched those previously reported.[6]



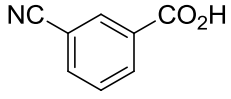
2n

2n was obtained as a white solid starting from **1n** (112 mg, 0.5 mmol) according to the General Procedure III in 91% yield (86.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.52 (s, 1H), 8.16 (d, *J* = 5.8 Hz, 2H), 7.88 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.80 (s), 135.18 (s), 133.10 (q, *J* = 31.6 Hz), 131.27 – 130.22 (m), 126.08 (s), 125.73 (s), 123.02 (s). Spectral data matched those previously reported.[6]



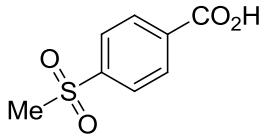
2o

2o was obtained as a white solid starting from **1o** (101 mg, 0.5 mmol) according to the General Procedure III in 97% yield (71.2 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.62 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.97, 134.78, 132.69, 129.96, 118.20, 115.05. Spectral data matched those previously reported.[6]



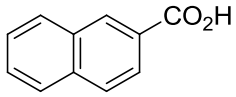
2p

2p was obtained as a white solid starting from **1p** (100.5 mg, 0.5 mmol) according to the General Procedure III in 89% yield (65.4 mg). ^{1}H NMR (400 MHz, DMSO) δ 8.31 – 8.26 (m, 1H), 8.26 – 8.21 (m, 1H), 8.12 – 8.06 (m, 1H), 7.73 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 166.31, 136.80, 134.34, 133.35, 132.70, 130.64, 118.67, 112.50. Spectral data matched those previously reported.[9]



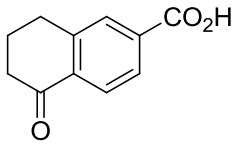
2q

2q was obtained as a white solid starting from **1q** (127 mg, 0.5 mmol) according to the General Procedure III in 81% yield (80.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, *J* = 7.7 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.40, 144.39, 135.43, 130.44, 127.53. Spectral data matched those previously reported.[7]



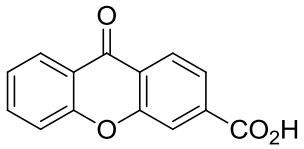
2r

2r was obtained as a white solid starting from **1r** (113 mg, 0.5 mmol) according to the General Procedure III in 91% yield (78.4 mg). ^{1}H NMR (400 MHz, DMSO) δ 13.12 (s, 1H), 8.63 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 5.3 Hz, 3H), 7.65 (dd, *J* = 13.3, 7.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 167.98, 135.46, 132.68, 131.06, 129.82, 128.87, 128.71, 128.19, 127.35, 125.69. Spectral data matched those previously reported.[6]



2s

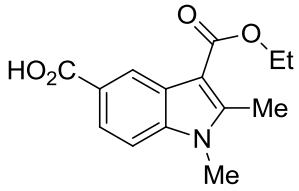
2s was obtained as a white solid starting from **1s** (122 mg, 0.5 mmol) according to the General Procedure III in 86% yield (81.5 mg). ^{1}H NMR (400 MHz, DMSO) δ 13.31 (s, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 3.33 (t, *J* = 5.6 Hz, 2H), 2.73 (t, *J* = 6.1 Hz, 2H), 2.20 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 197.68, 168.85, 145.39, 135.27, 133.76, 132.04, 130.43, 126.80, 38.61, 27.73, 22.80. Spectral data matched those previously reported.[12]



2t

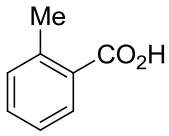
2t was obtained as a white solid starting from **1t** (147 mg, 0.5 mmol) according to the General Procedure III in 90% yield (107.7 mg). ^{1}H NMR (400 MHz, DMSO) δ 11.00

(s, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.88 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 175.30, 164.56, 158.08, 156.08, 135.33, 128.54, 126.39, 124.65, 121.74, 118.41, 114.68, 114.53, 102.68. Spectral data matched those previously reported.[14]



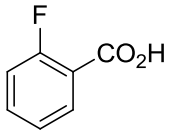
2u

2u was obtained as a white solid starting from **1u** (158 mg, 0.5 mmol) according to the General Procedure III in 84% yield (109 mg). ^{1}H NMR (400 MHz, DMSO) δ 12.63 (s, 1H), 8.67 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 4.33 (dd, *J* = 13.0, 6.5 Hz, 2H), 3.74 (s, 3H), 2.73 (s, 3H), 1.38 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.73, 165.18, 147.85, 139.17, 126.01, 124.19, 123.47, 110.39, 104.05, 59.68, 30.46, 15.01, 12.28. **HRMS** (ESI-TOF) m/z Calcd for $C_{14}H_{16}NO_4[M+H]^+$ 262.1074, found 262.1074.



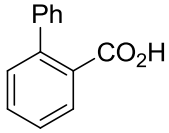
2v

2v was obtained as a white solid starting from **1v** (95 mg, 0.5 mmol) according to the General Procedure III in 92% yield (62.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.87, 141.74, 133.33, 132.28, 131.94, 128.61, 126.21, 22.52. Spectral data matched those previously reported.[11]



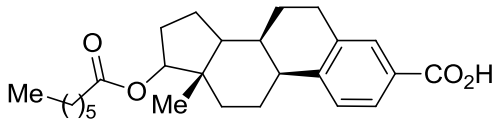
2w

2w was obtained as a white solid starting from **1w** (97 mg, 0.5 mmol) according to the General Procedure III in 87% yield (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 12.7, 7.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.15 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.05 – -108.26 (m). ^{13}C NMR (101 MHz, $cdcl_3$) δ 169.88, 163.94, 161.33, 135.71, 135.62, 132.77, 124.14, 124.10, 117.56, 117.47, 117.29, 117.07. Spectral data matched those previously reported.[9]



2x

2x was obtained as a white solid starting from **1x** (95 mg, 0.5 mmol) according to the General Procedure III in 87% yield (86.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.30 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.86, 143.37, 140.98, 132.14, 131.23, 130.72, 129.28, 128.46, 128.09, 127.37, 127.20. Spectral data matched those previously reported.[13]

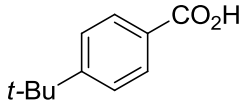


2y

2y was obtained as a white solid starting from **1y** (233.3 mg, 0.5 mmol) according to the General Procedure III in 89% yield (365.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ12.25 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 4.72 (t, *J* = 8.4 Hz, 1H), 2.93 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.40 – 2.17 (m, 5H), 1.93 (dd, *J* = 15.8, 7.2 Hz, 2H), 1.83 – 1.72 (m, 1H), 1.69 – 1.23 (m, 16H), 0.89 (t, *J* = 6.5 Hz, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.37, 172.71, 147.03, 137.36, 131.11, 127.70, 126.88, 125.92, 82.62, 50.27, 44.93, 43.20, 38.30, 37.20, 34.95, 31.81, 29.65, 29.16, 27.89, 27.26, 26.17, 25.43, 23.62, 22.85, 14.39, 12.41. **HRMS** (ESI-TOF) m/z Calcd for $C_{26}H_{37}O_4$ $[M+H]^+$ 413.2686, found 413.2684.

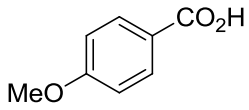
8. General Procedure for the Direct Carboxylation of Aryl Phenols

General Procedure IV: To a solution of oxime aryl phenols (0.5 mmol, 1.0 equiv) in DMF (1 mL), NaH (20 mg, 0.5 mmol, 1.0 equiv) was added. After stirring for 30 min at room temperature, the solution was transferred to a N_2-filled glovebox. Then the solution was added the $Ni(PPh_3)_2Cl_2$ (16.3 mg, 0.025 mmol, 0.05 equiv), Neocuproine (10.4 mg, 0.05 mmol, 0.1 equiv), and Mn powder (82.3 mg, 1.5 mmol, 3 equiv) at the same time. Then the Schlenk tube was transferred out immediately. The solution turned into dark blue. Then the resulting solution was changed into CO_2 atmosphere using standard Schlenk techniques and stirred at room temperature for 20 h. After completion of the reaction, the reaction mixture was quenched with 6 M HCl and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The products were purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.



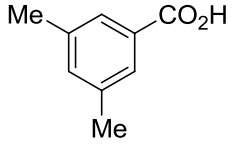
2a

2a was obtained as a white solid starting from 4-(*tert*-butyl)phenol (116 mg, 0.5 mmol) according to the General Procedure IV in 76% yield (67.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.63 (brs, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 1.34 (s, 9H). Spectral data matched those previously reported.[6]



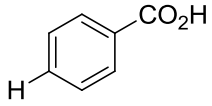
2b

2b was obtained as a white solid starting from 4-methoxyphenol (103 mg, 0.5 mmol) according to the General Procedure IV in 79% yield (60 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H). Spectral data matched those previously reported.[6]



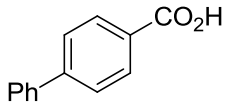
2f

2f was obtained as a white solid starting from 3,5-dimethylphenol (102 mg, 0.5 mmol) according to the General Procedure IV in 77% yield (57.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.72 (s, 1H), 7.88 (s, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 2.35 (s, 3H). Spectral data matched those previously reported.[11]



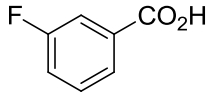
2g

2g was obtained as a white solid starting from phenol (88 mg, 0.5 mmol) according to the General Procedure IV in 77% yield (46.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.76 (brs, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H). Spectral data matched those previously reported.[6]



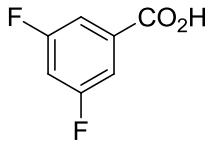
2h

2h was obtained as a white solid starting from [1,1'-biphenyl]-4-ol (126 mg, 0.5 mmol) according to the General Procedure IV in 73% yield (72.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H). Spectral data matched those previously reported.[6]



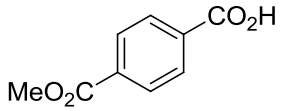
2i

2i was obtained as a white solid starting from 3-fluorophenol (97 mg, 0.5 mmol) according to the General Procedure IV in 73% yield (51.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.47 (dd, *J* = 13.4, 7.6 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H). Spectral data matched those previously reported.[9]



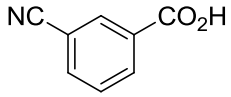
2j

2j was obtained as a white solid starting from 3,5-difluorophenol (106 mg, 0.5 mmol) according to the General Procedure IV in 76% yield (59.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 7.62 (d, *J* = 4.7 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H). Spectral data matched those previously reported.[10]



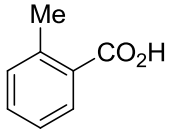
2m

2m was obtained as a white solid starting from methyl 4-hydroxybenzoate (117 mg, 0.5 mmol) according to the General Procedure IV in 69% yield (62 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.43 (s, 1H), 8.09 (s, 4H), 3.92 (s, 3H). Spectral data matched those previously reported.[6]



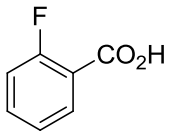
2p

2p was obtained as a white solid starting from 3-hydroxybenzonitrile (100.5 mg, 0.5 mmol) according to the General Procedure IV in 62% yield (45.5 mg). ^{1}H NMR (400 MHz, DMSO) δ 8.31 – 8.26 (m, 1H), 8.26 – 8.21 (m, 1H), 8.12 – 8.06 (m, 1H), 7.73 (t, *J* = 7.8 Hz, 1H). Spectral data matched those previously reported.[9]



2v

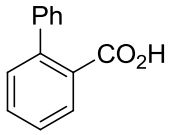
2v was obtained as a white solid starting from *o*-cresol (95 mg, 0.5 mmol) according to the General Procedure IV in 69% yield (46.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 2.68 (s, 3H). Spectral data matched those previously reported.[11]



2w

2w was obtained as a white solid starting from 2-fluorophenol (97 mg, 0.5 mmol) according to the General Procedure IV in 72% yield (54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 12.7, 7.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.15 (m, 1H). Spectral data matched those previously

reported.[9]



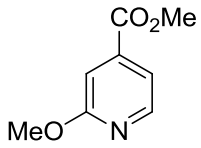
2x

2x was obtained as a white solid starting from [1,1'-biphenyl]-2-ol (95 mg, 0.5 mmol) according to the General Procedure IV in 60% yield (59 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.30 (m, 7H). Spectral data matched those previously reported.[13]

9. General Procedure for the Carboxylation of Pyridinyl Fluorosulfates

General Procedure V: All operations were carried out under standard Schlenk and glovebox techniques. In a N_2-filled glovebox, to a 50 mL Schlenk tube with a stir bar was added the $Ni(PPh_3)_2Cl_2$ (16.3 mg, 0.025 mmol, 0.05 equiv), Neocuproine (10.4 mg, 0.05 mmol, 0.1 equiv), and Mn powder (82.3 mg, 1.5 mmol, 3 equiv). Then the Schlenk tube was stirred and evacuated under the vacuum pump for 30 minutes. Then CO_2 gas was introduced into the stirring reaction mixture for three times. After that DMF (0.5 mL) was injected into the tube under the CO_2 atmosphere. Then the reaction mixture was stirred for 10 minutes and the mixture was gradually turned into dark blue. Then pyridinyl fluorosulfates (0.5 mmol) and another DMF (0.5 mL) were introduced into the Schlenk tube under the CO_2 atmosphere. Then the resulting solution was stirred at room temperature for 20 h. After completion of the reaction, the reaction mixture was quenched with 6 M NaOH. The solution was filtered. The filtrate was neutralized with 6 M HCl to PH = 2. Then the solution was evaporated to dryness and MeOH (15 mL) was added. Then excess CH_2N_2 in ether was slowly dropped into the solution until the solution turn into light yellow. Caution: CH_2N_2 was poisonous. Then the solution was evaporated and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The products were purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent.

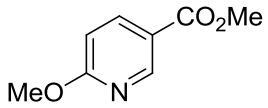
10. Characterization Data for the Carboxylative Products of Pyridinyl Fluorosulfates



5a

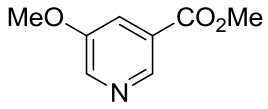
5a was obtained as a colorless oil starting from **4a** (104 mg, 0.5 mmol) according to

the General Procedure V in 67% yield (55.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.1 Hz, 1H), 7.38 (d, *J* = 4.9 Hz, 1H), 7.29 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.49, 164.76, 147.65, 140.01, 115.65, 111.18, 77.32, 77.00, 76.68, 53.79, 52.59. Spectral data matched those previously reported.[21]



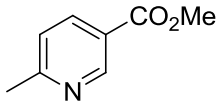
5b

5b was obtained as a colorless oil starting from **4b** (104 mg, 0.5 mmol) according to the General Procedure V in 79% yield (66.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.15 – 8.07 (m, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.76, 165.87, 149.97, 139.43, 119.56, 110.60, 53.95, 51.97. Spectral data matched those previously reported.[18]



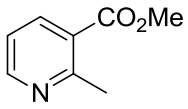
5c

5c was obtained as a colorless oil starting from **4c** (104 mg, 0.5 mmol) according to the General Procedure V in 83% yield (69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.43 (s, 1H), 7.72 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 155.42, 142.90, 142.41, 126.36, 119.88, 55.70, 52.47. Spectral data matched those previously reported.[17]



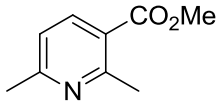
5d

5d was obtained as a colorless oil starting from **4d** (96 mg, 0.5 mmol) according to the General Procedure V in 72% yield (54.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.88, 163.05, 150.36, 137.27, 123.27, 122.89, 52.19, 24.65. Spectral data matched those previously reported.[19]



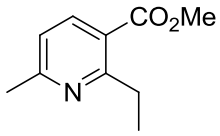
5e

5e was obtained as a colorless oil starting from **4e** (96 mg, 0.5 mmol) according to the General Procedure V in 71% yield (53.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 3.6 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.90 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.92, 159.84, 151.77, 138.40, 125.29, 120.85, 52.26, 24.77. Spectral data matched those previously reported.[15]



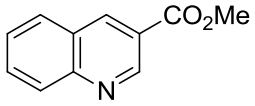
5f

5f was obtained as a colorless oil starting from **4f** (103 mg, 0.5 mmol) according to the General Procedure V in 82% yield (67.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 2.70 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 161.19, 159.38, 138.73, 122.19, 120.40, 51.96, 24.64, 24.50. Spectral data matched those previously reported.[15]



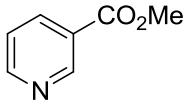
5g

5g was obtained as a colorless oil starting from **4g** (118 mg, 0.5 mmol) according to the General Procedure V in 85% yield (75.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.09 (q, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06, 164.37, 161.38, 138.87, 121.84, 120.37, 52.08, 30.42, 24.68, 14.38. **HRMS** (ESI-TOF) m/z Calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1019, found 180.1020.



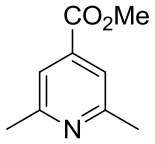
5h

5h was obtained as a white solid starting from **4h** (114 mg, 0.5 mmol) according to the General Procedure V in 74% yield (69.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.75 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.72, 149.88, 149.68, 138.67, 131.78, 129.35, 129.03, 127.36, 126.69, 122.83, 52.41. Spectral data matched those previously reported.[19]



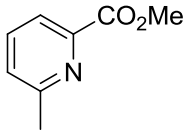
5i

5i was obtained as a colorless oil starting from **4i** (88.6 mg, 0.5 mmol) according to the General Procedure V in 63% yield (43 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 1.0 Hz, 1H), 8.71 (d, *J* = 4.7 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.67, 153.36, 150.82, 136.99, 125.92, 123.26, 52.39. Spectral data matched those previously reported.[16]



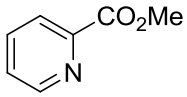
5j

5j was obtained as a colorless oil starting from **4j** (103 mg, 0.5 mmol) according to the General Procedure V in 61% yield (50.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 3.92 (s, 3H), 2.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.11, 158.81, 137.80, 119.43, 52.51, 24.45. Spectral data matched those previously reported.[20]



5k

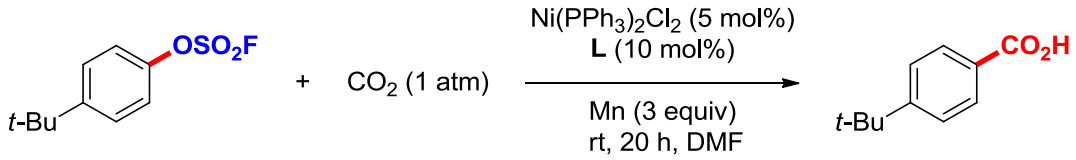
5k was obtained as a colorless oil starting from **4k** (96 mg, 0.5 mmol) according to the General Procedure V in 53% yield (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 4.0 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.74, 158.77, 147.23, 136.98, 126.71, 122.24, 52.70, 24.48. Spectral data matched those previously reported.[20]



5l

5l was obtained as a colorless oil starting from **4l** (89 mg, 0.5 mmol) according to the General Procedure V in 46% yield (29.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 3.7 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.54 – 7.34 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.62, 149.74, 147.81, 137.01, 126.93, 125.08, 52.84. Spectral data matched those previously reported.[16]

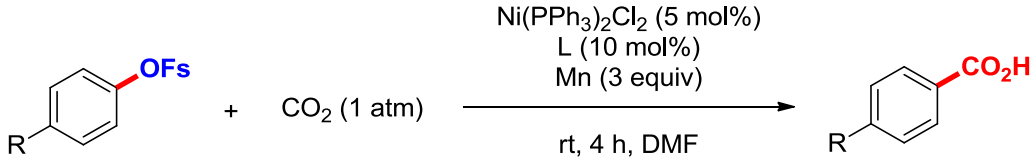
11.1 mmol Scale Synthesis



The operation was carried out under standard Schlenk and glovebox techniques. In a N_2-filled glovebox, to a 100 mL Schlenk tube with a stir bar was added the $Ni(PPh_3)_2Cl_2$ (32.6 mg, 0.05 mmol, 0.05 equiv), Neocuproine (20.8 mg, 0.1 mmol, 0.1 equiv), and Mn powder (164 mg, 3 mmol, 3 equiv). Then the Schlenk tube was stirred and evacuated under the vacuum pump for 30 minutes. Then CO_2 gas was introduced into the stirring reaction mixture for three times. After that DMF (1 mL) was injected into the tube under the CO_2 atmosphere. Then the reaction mixture was stirred for 10 minutes and the mixture was gradually turned into dark blue. Then aryl fluorosulfates

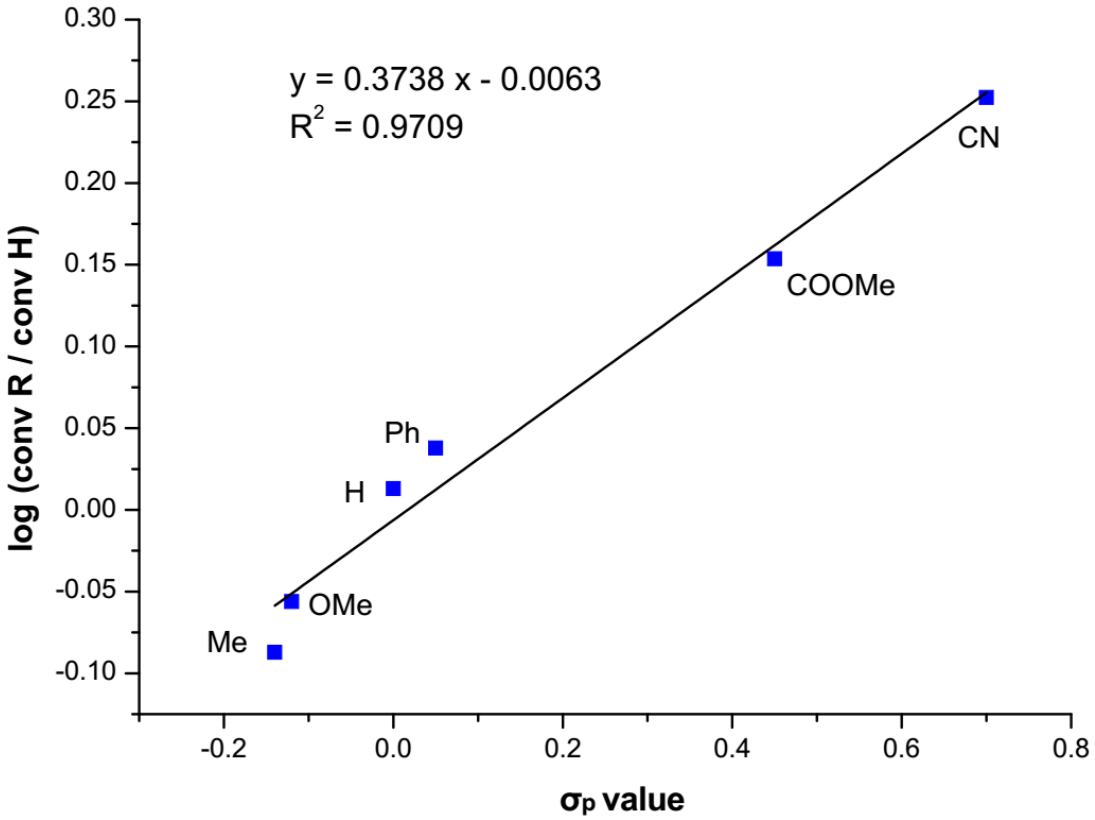
1a (232 mg, 1 mmol) and another DMF (1 mL) were introduced into the Schlenk tube under the CO_2 atmosphere. Then the resulting solution was stirred at room temperature for 20 h. After completion of the reaction, the reaction mixture was quenched with 6 M HCl and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The products were purified by column chromatography on silica gel using hexanes/ethyl acetate as the eluent to afford **2a** as a white solid in 93% yield (165.5 mg).

12.Hammett plot Analysis



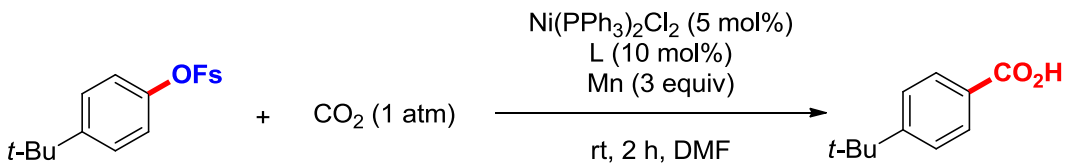
All operations were carried out under standard Schlenk and glovebox techniques. In a N_2-filled glovebox, to a 50 mL Schlenk tube with a stir bar was added the $Ni(PPh_3)_2Cl_2$ (16.3 mg, 0.025 mmol, 0.05 equiv), Neocuproine (10.4 mg, 0.05 mmol, 0.1 equiv), and Mn powder (82.3 mg, 1.5 mmol, 3 equiv). Then the Schlenk tube was stirred and evacuated under the vacuum pump for 30 minutes. Then CO_2 gas was introduced into the stirring reaction mixture for three times. After that DMF (0.5 mL) was injected into the tube under the CO_2 atmosphere. Then the reaction mixture was stirred for 10 minutes and the mixture was gradually turned into dark blue. Then aryl fluorosulfates (0.5 mol) and another DMF (0.5 mL) were introduced into the Schlenk tube under the CO_2 atmosphere. Then the resulting solution was stirred at room temperature for 4 h. After completion of the reaction, the reaction mixture was quenched with 6 M HCl and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The conversions were determined by ^1H NMR with CH_2Br_2 as an internal standard.

entry	Substituent	Conv	σ_{para}	log(conv.R/conv.H)
1	Me	13.5	-0.14	-0.087
2	OMe	14.5	-0.12	-0.056
3	H	17	0	0.013
4	Ph	18	0.05	0.038
5	COOMe	23.5	0.45	0.154
6	CN	29.5	0.70	0.252

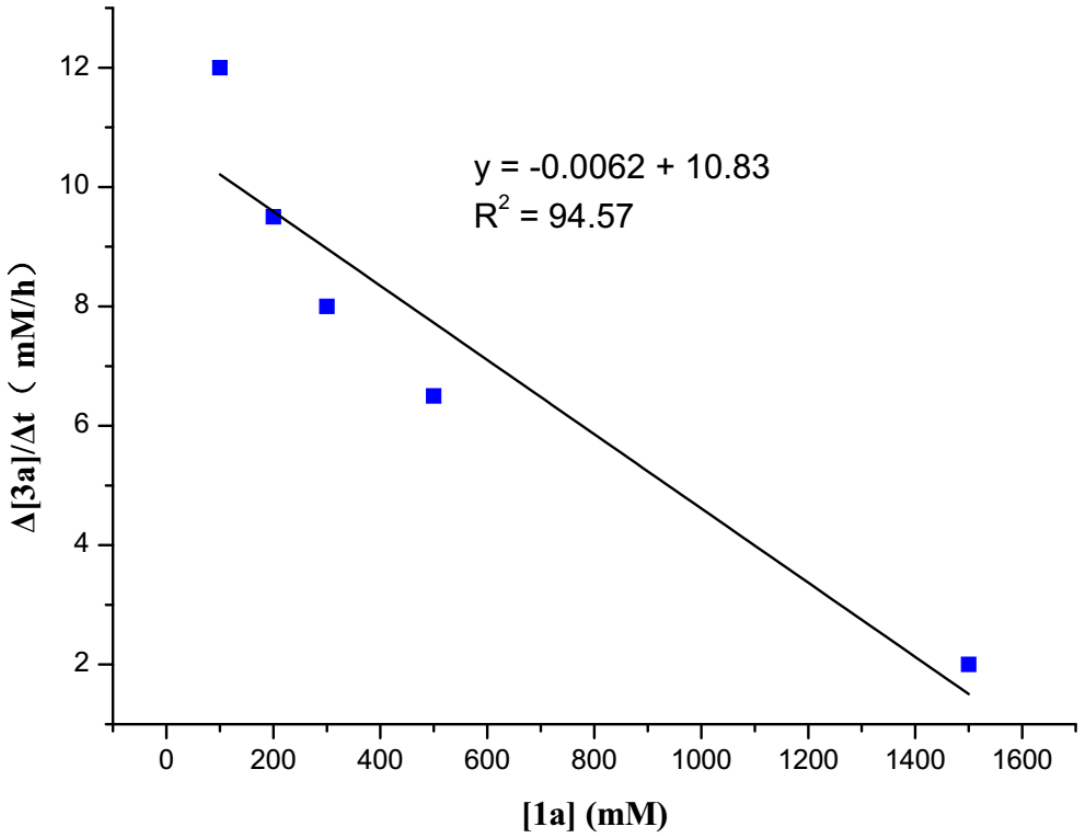


13.General Procedure for Kinetic Experiments

Kinetics experiments were run up to about 3–30% conversion. All operations were carried out under standard Schlenk and glovebox techniques. In a N_2-filled glovebox, to a 50 mL Schlenk tube with a stir bar was added the $Ni(PPh_3)_2Cl_2$ (16.3 mg, 0.025 mmol, 0.05 equiv), Neocuproine (10.4 mg, 0.05 mmol, 0.1 equiv), and Mn powder (82.3 mg, 1.5 mmol, 3 equiv). Then the Schlenk tube was stirred and evacuated under the vacuum pump for 30 minutes. Then CO_2 gas was introduced into the stirring reaction mixture for three times. After that DMF (0.5 mL) was injected into the tube under the CO_2 atmosphere. Then the reaction mixture was stirred for 10 minutes and the mixture was gradually turned into dark blue. Then aryl fluorosulfates (0.5 mmol) and another DMF (0.5 mL) were introduced into the Schlenk tube under the CO_2 atmosphere. Then the resulting solution was stirred at room temperature for 2 h. After completion of the reaction, the reaction mixture was quenched with 6 M HCl and extracted with EtOAc (30 mL x 5). The organic layer was collected, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The conversions were determined by ^1H NMR with CH_2Br_2 as an internal standard.



entry	1a (mmol)	[1a] (mM)	Conv 2a (%)	Initial rate [mM/h]
1	0.1	100	24	12
2	0.2	200	19	9.5
3	0.3	300	15	7.5
4	0.5	500	13	6.5
5	1.5	1500	4	2



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2. Hanley, P. S.; Ober, M. S.; Krasovskiy, A. L.; Whiteker, G. T.; Kruper, W. J. *ACS Catal.***2015**, *5*, 5041.
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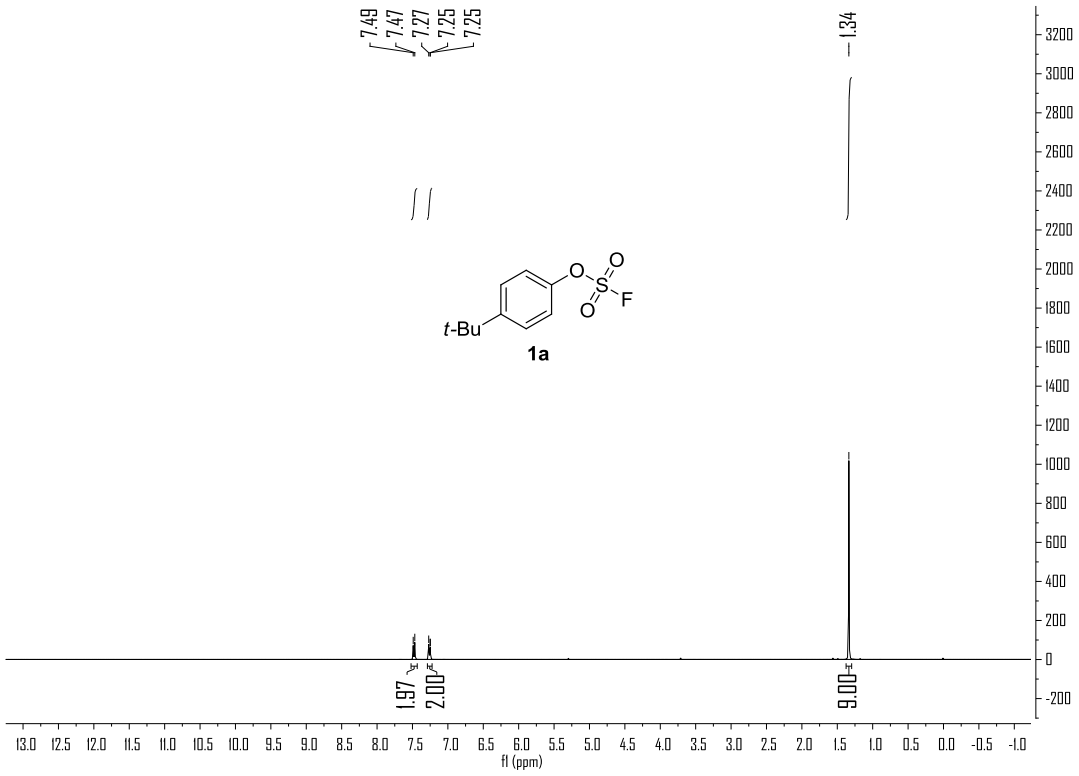
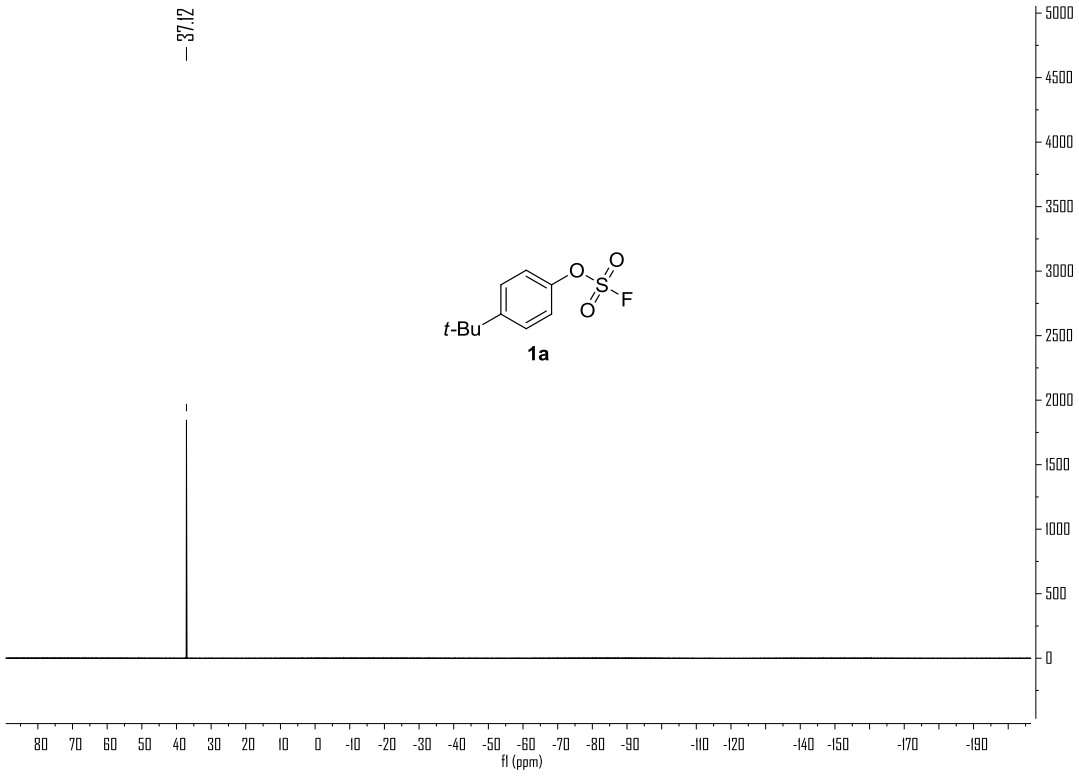
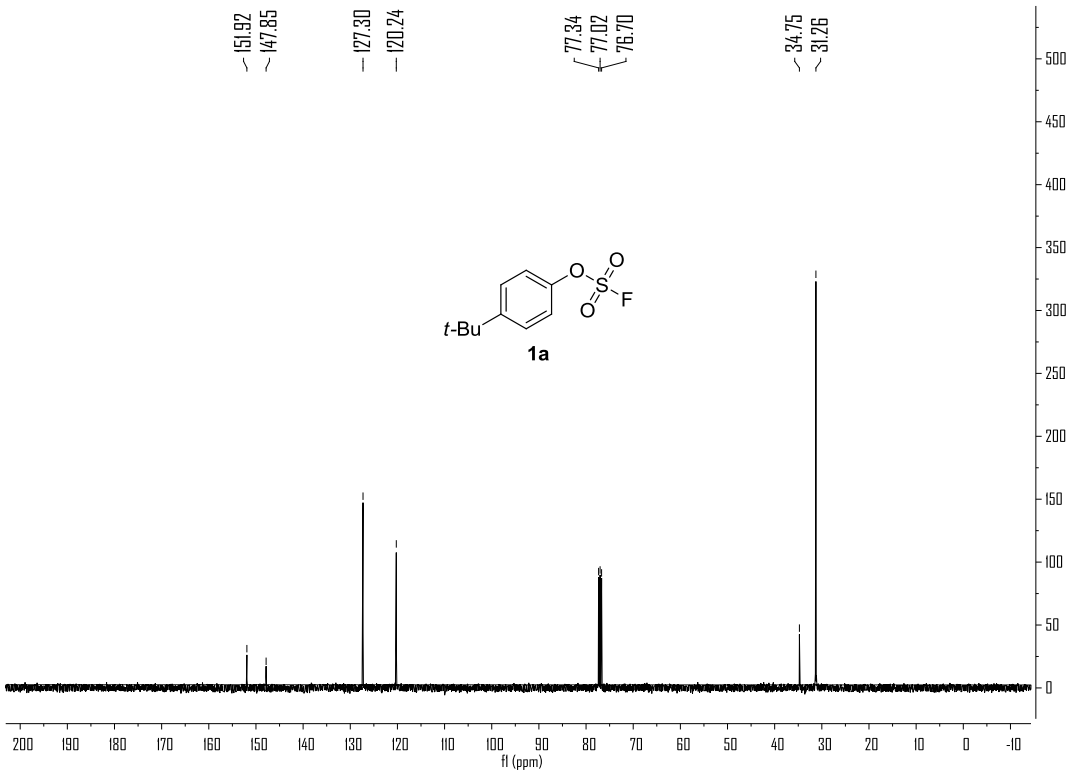
15.Copies of NMR Spectrum



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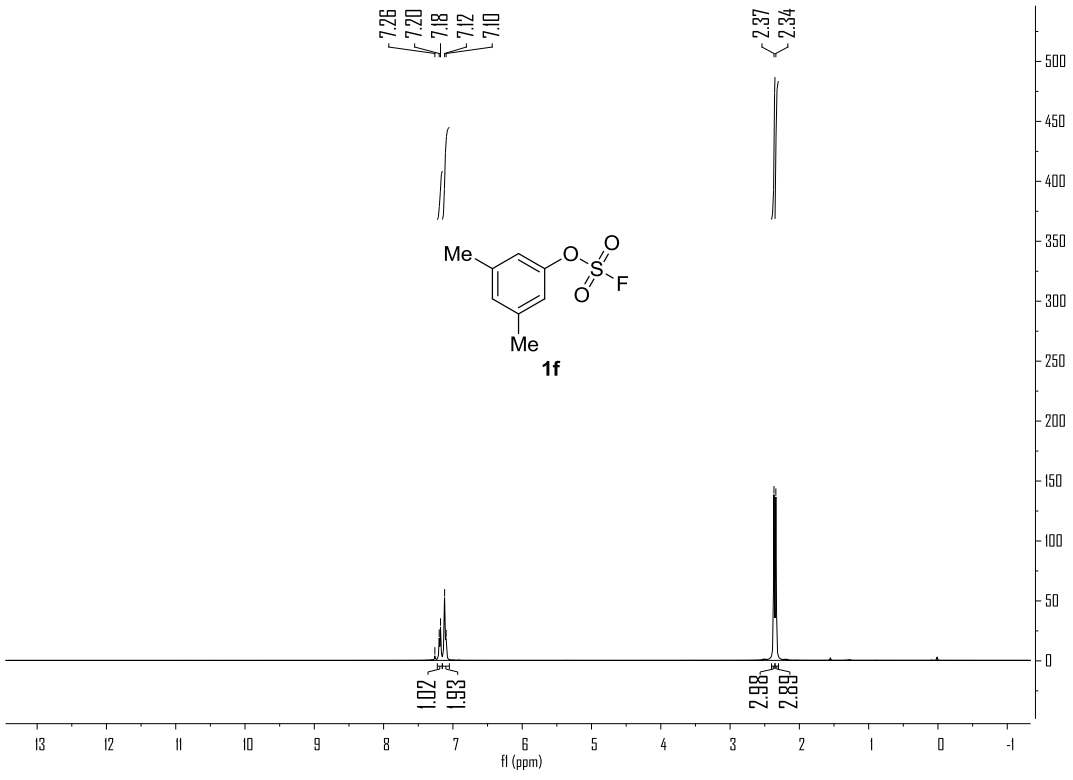
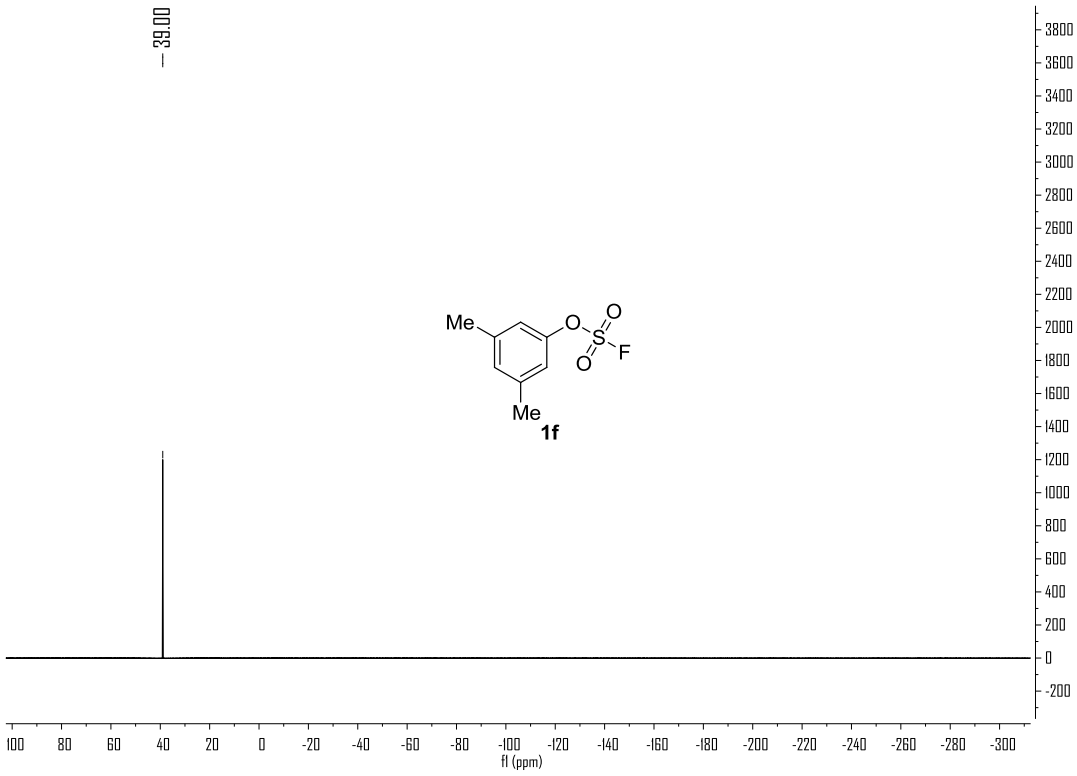
147.85
127.30
120.24
77.34
77.02
76.70
34.75
31.26
t-Bu
O
S
O
O
F
1a
f1 (ppm)


7.26
7.20
7.18
7.12
7.10
2.37
2.34
Me
Me
1a
1.02
1.93
2.98
2.89
f1 (ppm)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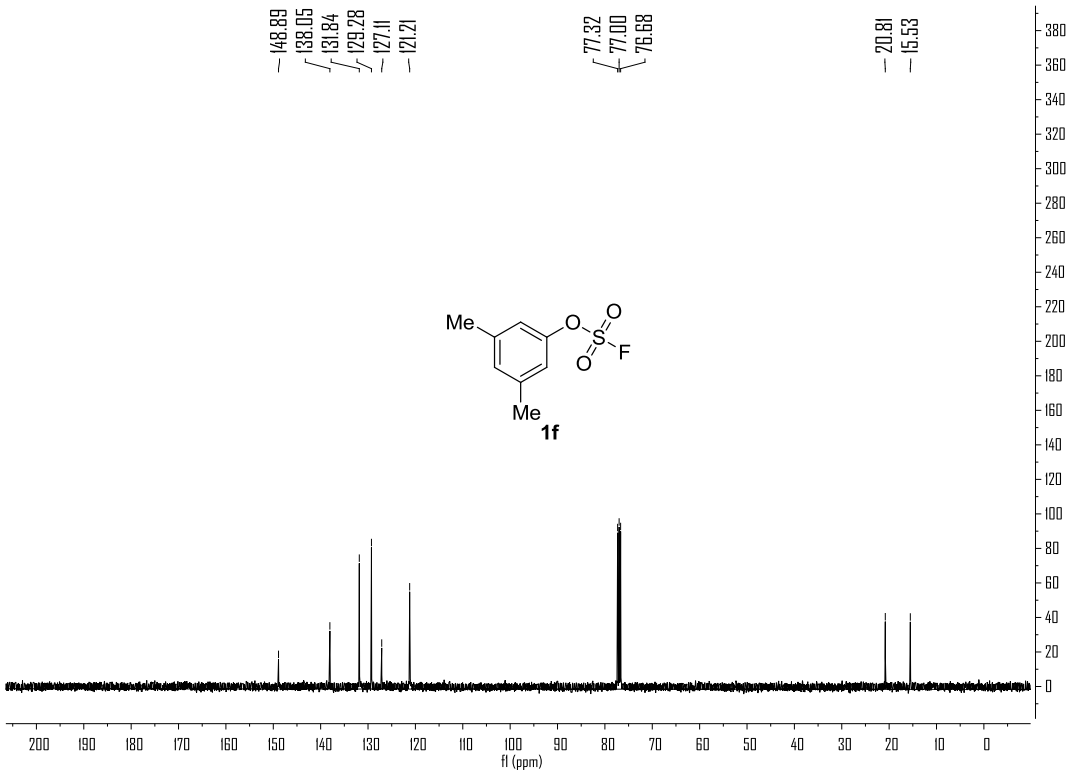
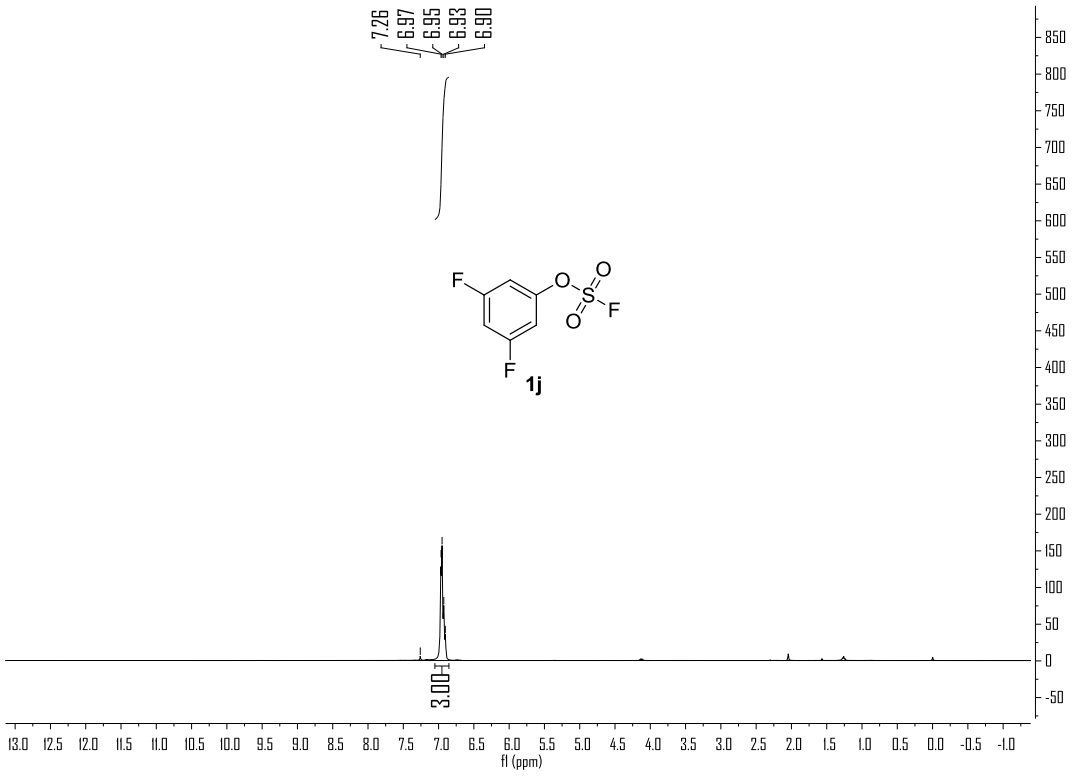
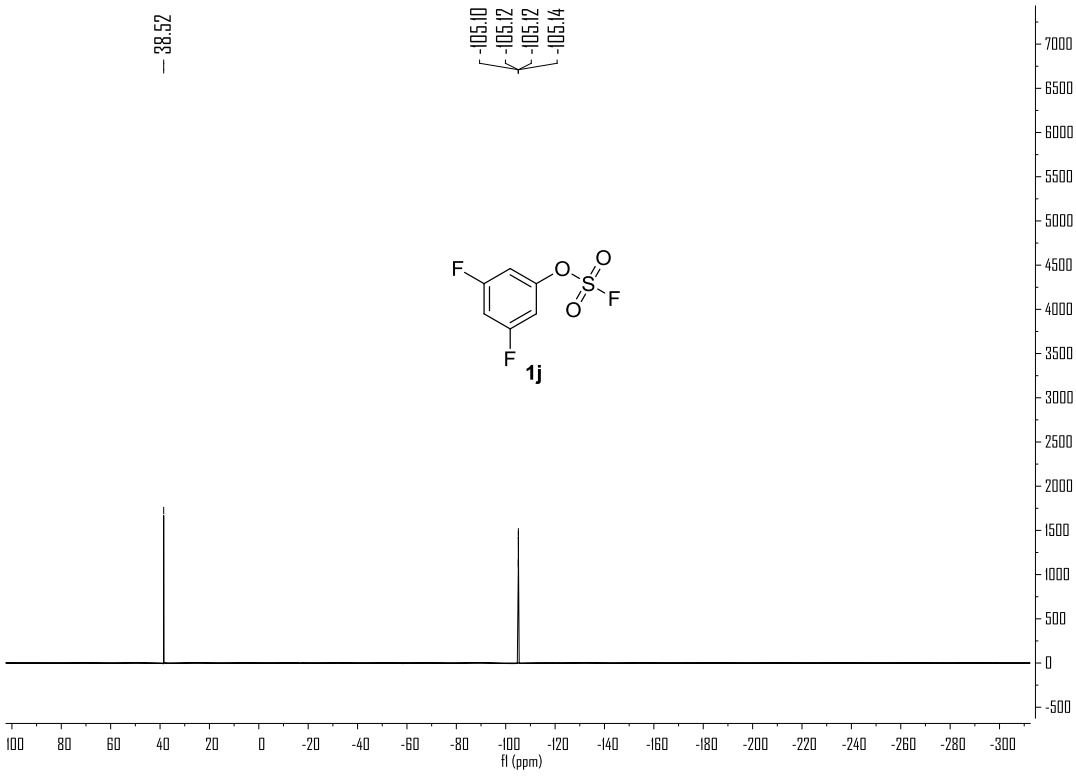
Me
O
S
O
O
F
Me
1f
f1 (ppm)


148.89
138.05
131.84
129.28
127.11
121.21
77.32
77.00
76.68
20.81
15.53
Me
O
S
O
O
F
Me
1f
f1 (ppm)


7.26
6.97
6.95
6.93
6.90
F
O
S
O
O
F
F
1j
3.00
f1 (ppm)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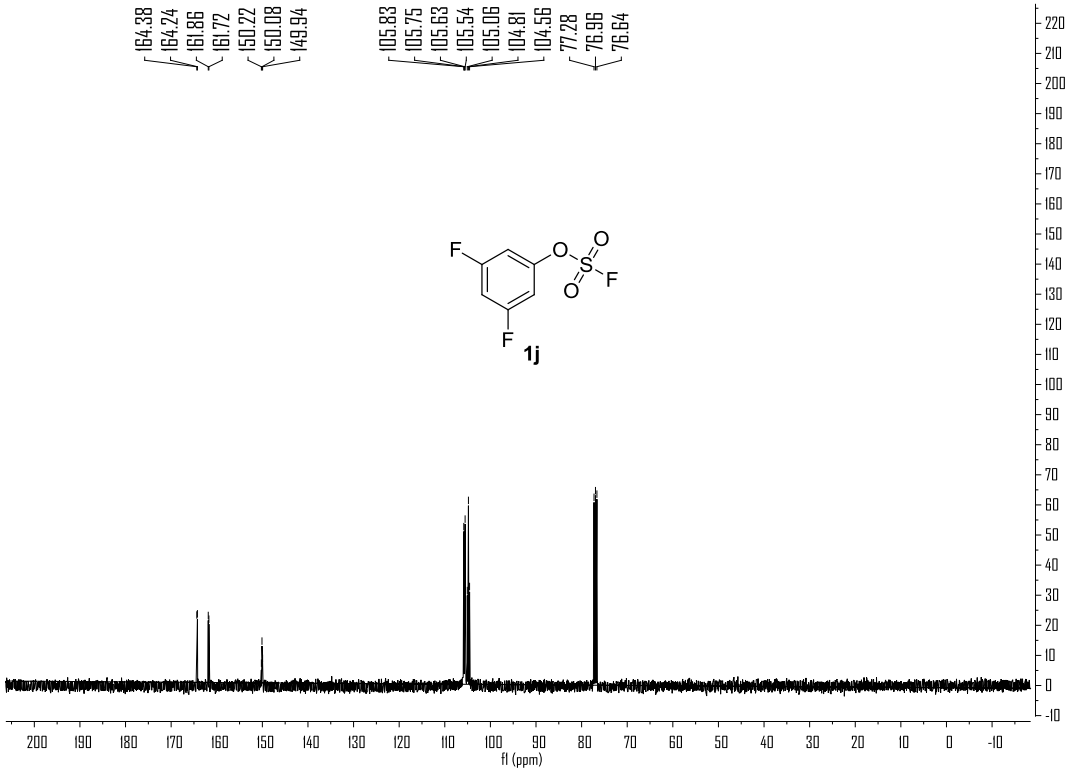
-105.14
F
O
S
O
O
F
F
1j
f1 (ppm)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161.86
161.72
150.22
150.08
149.94
105.83
105.75
105.63
105.54
105.06
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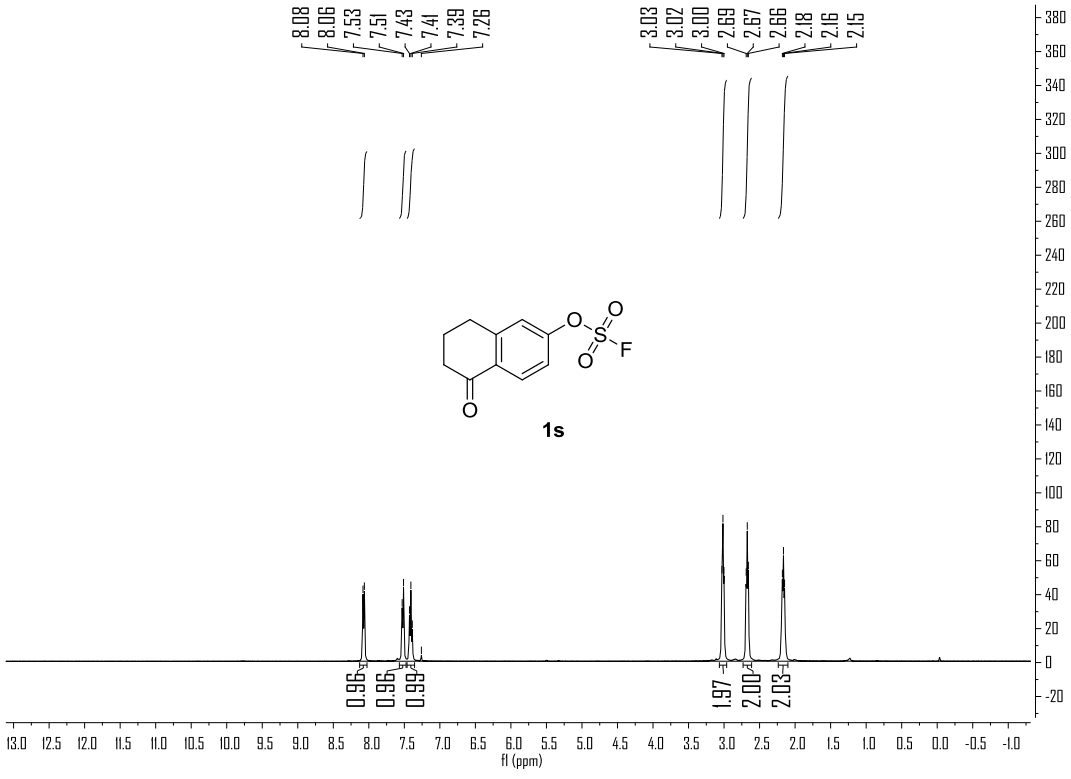
104.56
77.28
76.96
76.64
F
O
S
O
O
F
F
1j
f1 (ppm)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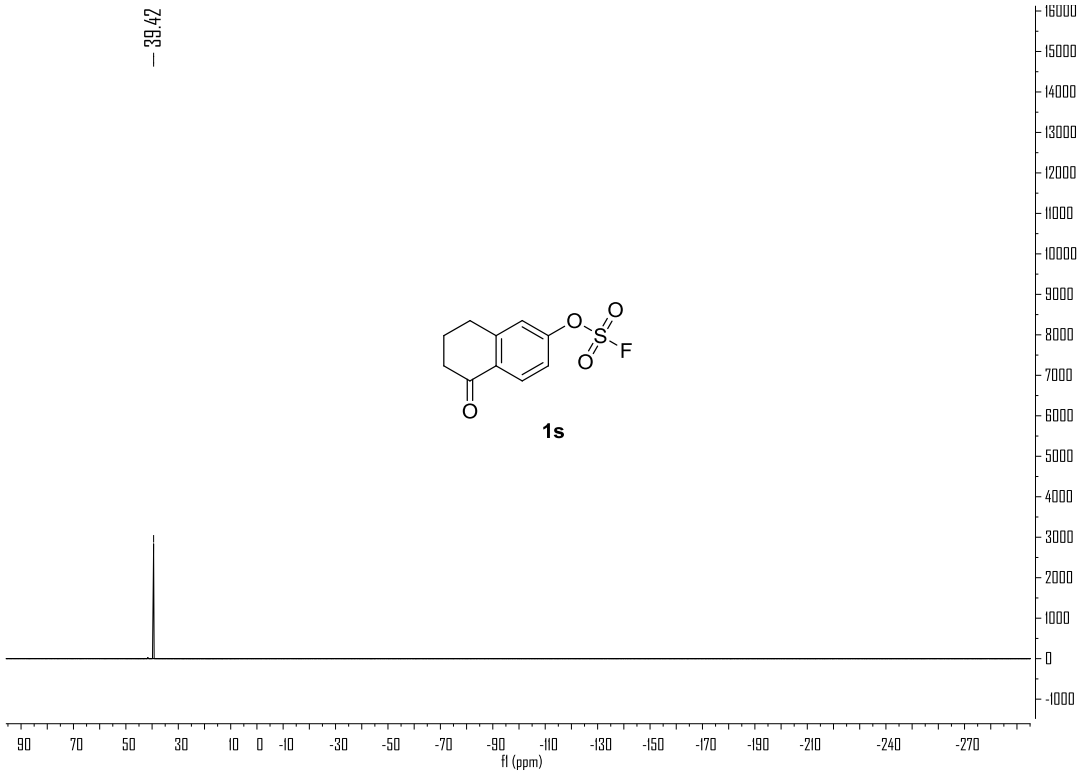
8.06
7.53
7.51
7.43
7.41
7.39
7.26
3.03
3.02
3.00
2.69
2.67
2.66
2.18
2.16
2.15
O
S
O
O
F
O
1s
0.96
0.96
0.99
1.97
2.00
2.03
f1 (ppm)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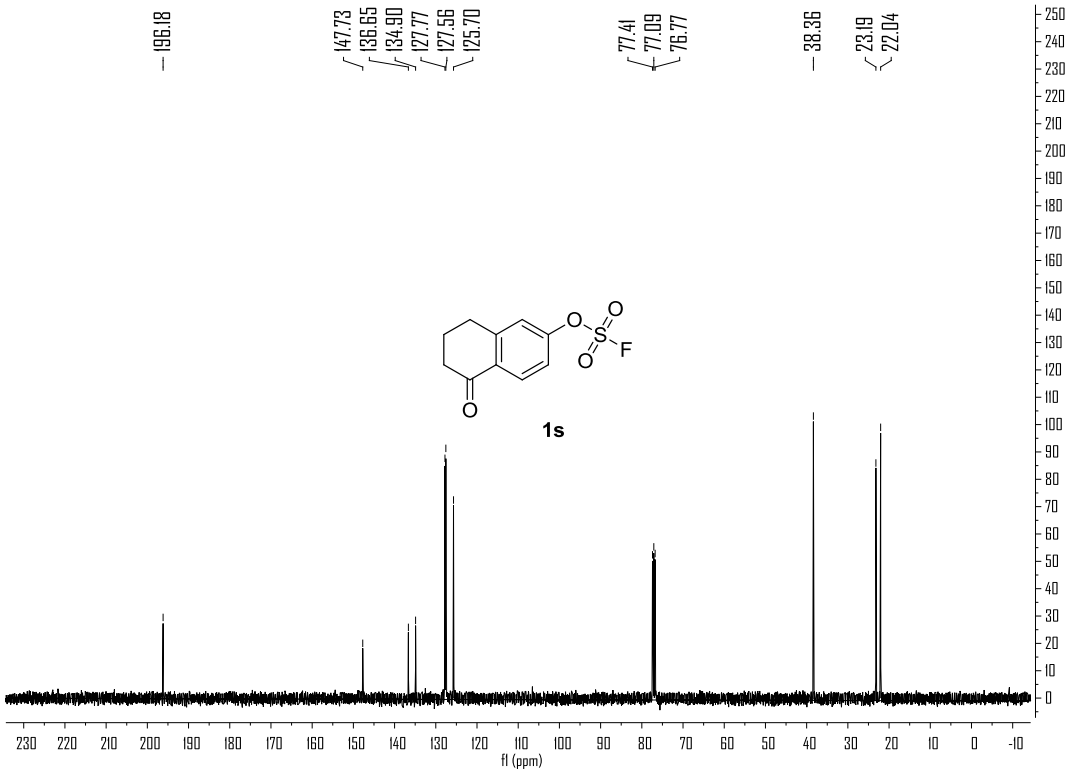
f1 (ppm)


196.18
147.73
136.65
134.90
127.77
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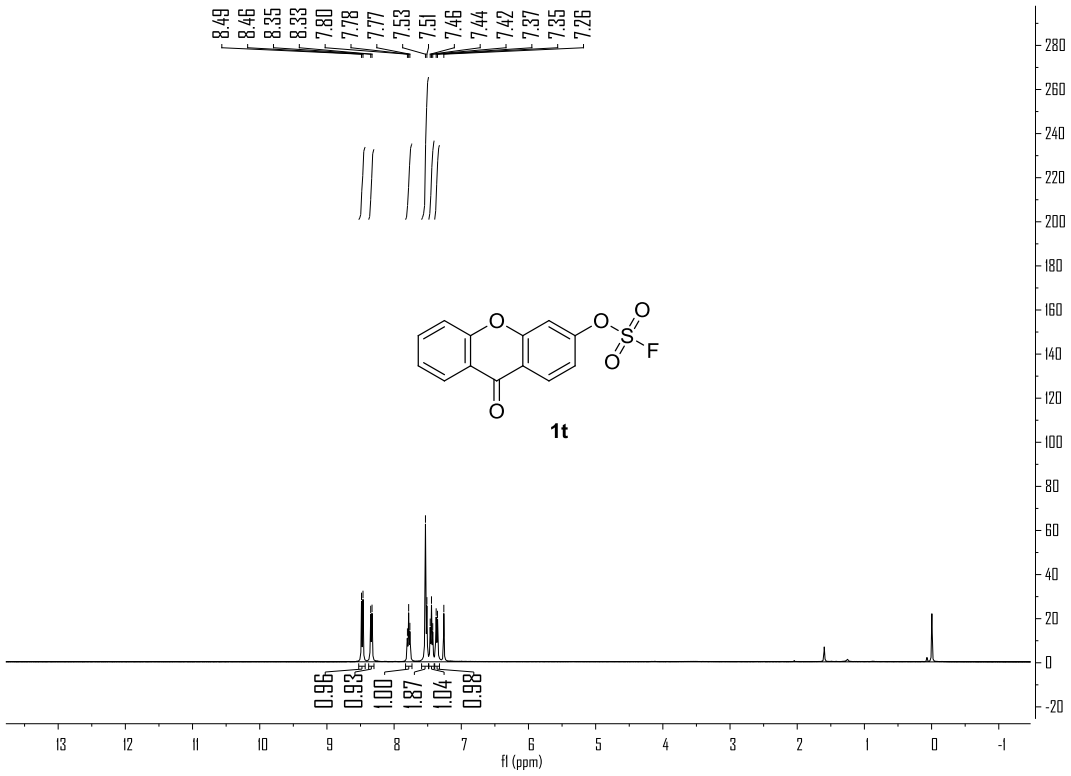
125.70
77.41
77.09
76.77
38.36
23.19
22.04
1s
f1 (ppm)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7.77
7.53
7.51
7.46
7.44
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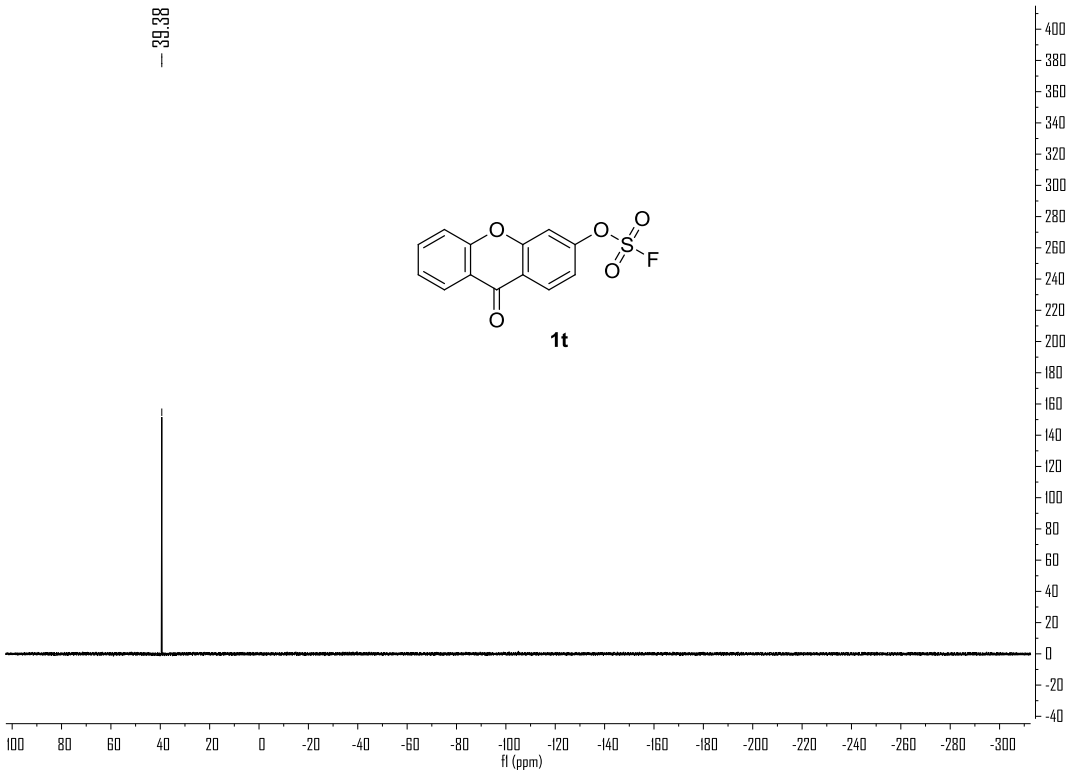
7.26
1t
0.96
0.93
1.00
1.87
1.04
0.98
f1 (ppm)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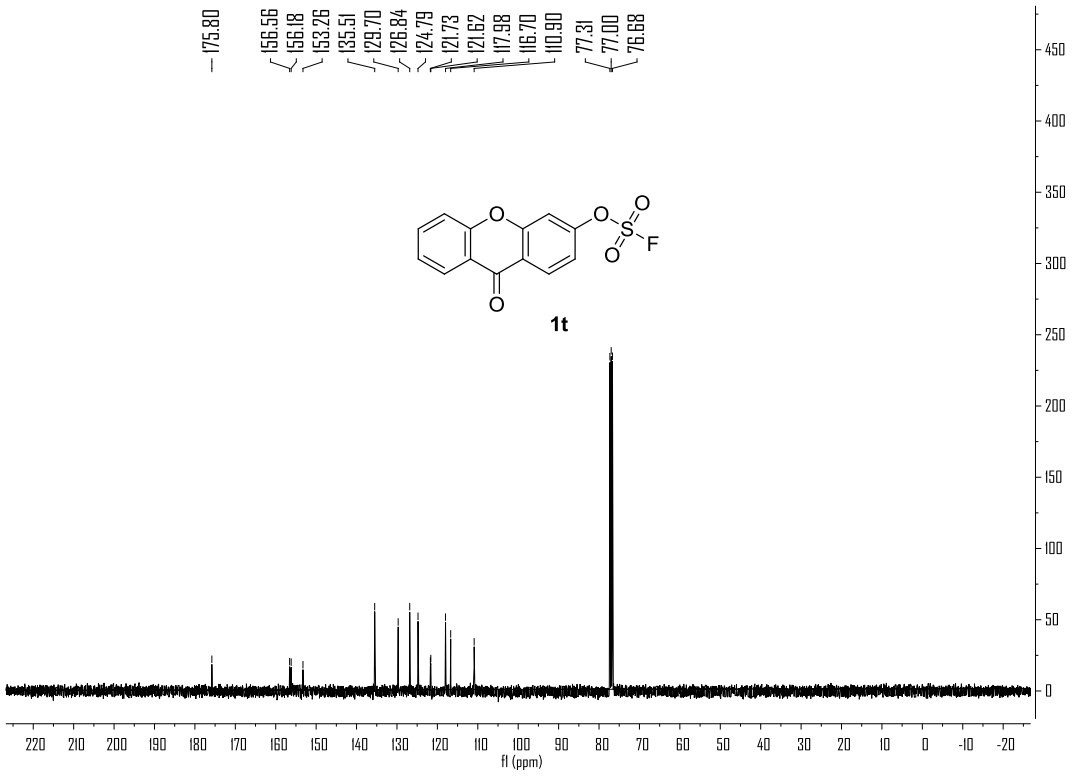
f1 (ppm)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156.56
156.18
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129.70
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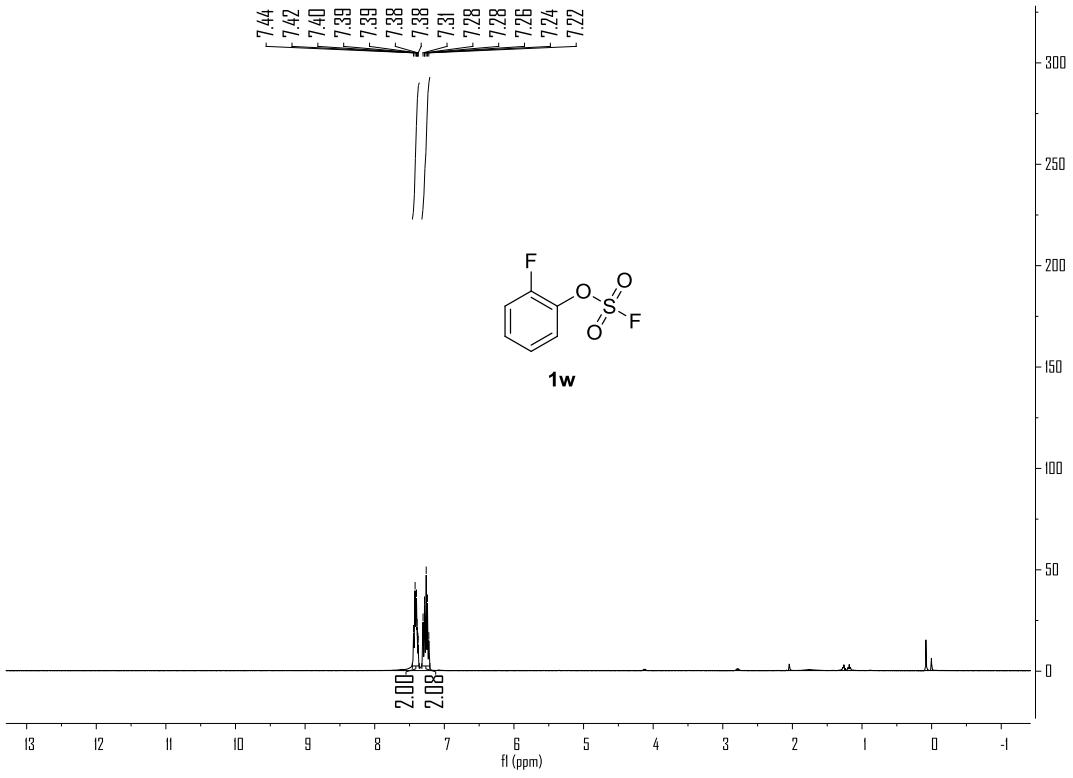
77.31
77.00
76.68
1t
f1 (ppm)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7.42
7.40
7.39
7.39
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7.28
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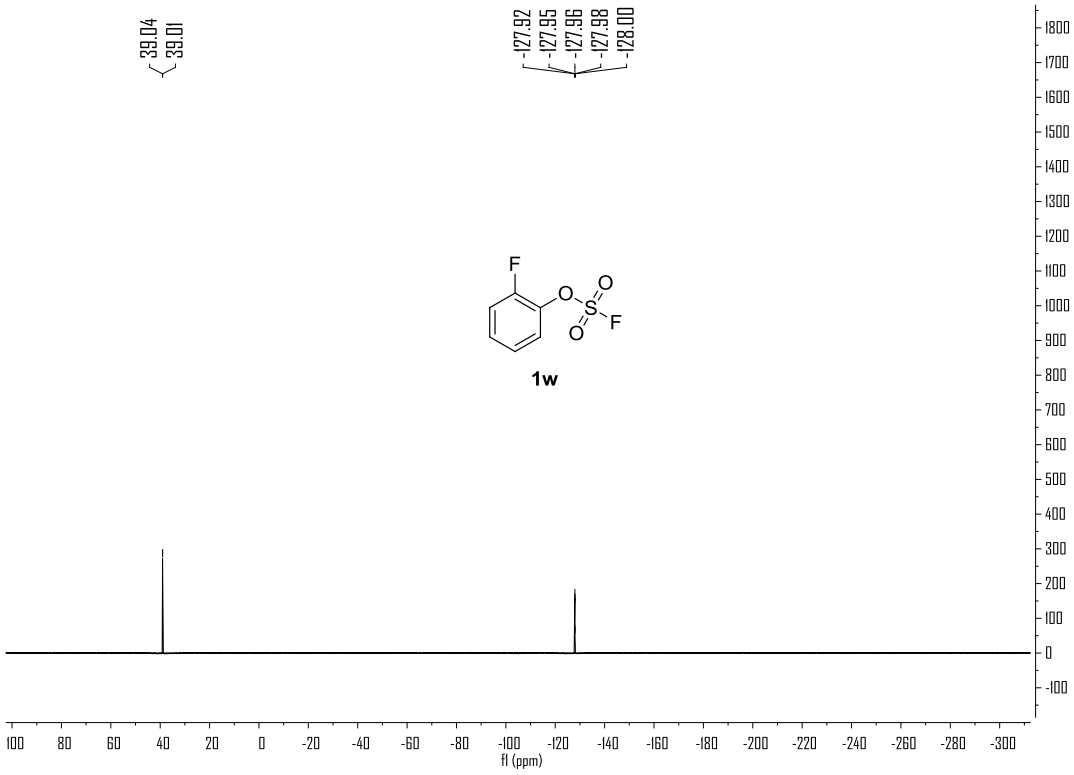
7.24
7.22
2.00
2.08
1w
f1 (ppm)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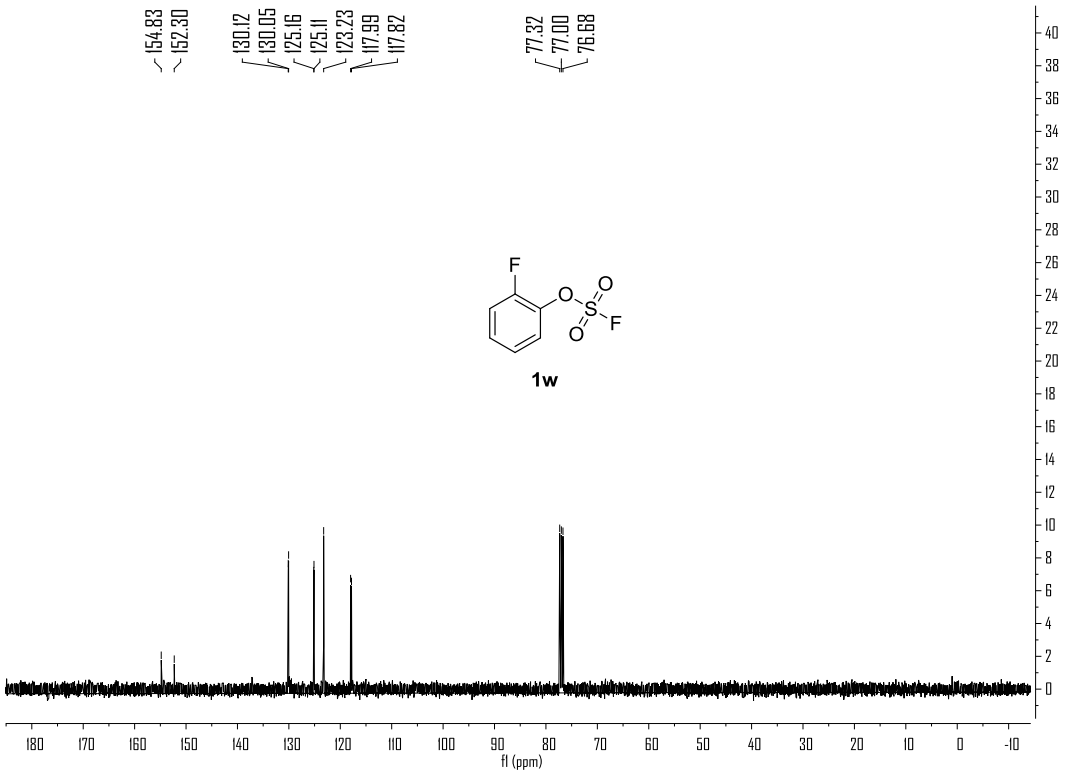
F
O
S
O
O
F
1w
f1 (ppm)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152.30
130.12
130.05
125.16
125.11
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117.82
77.32
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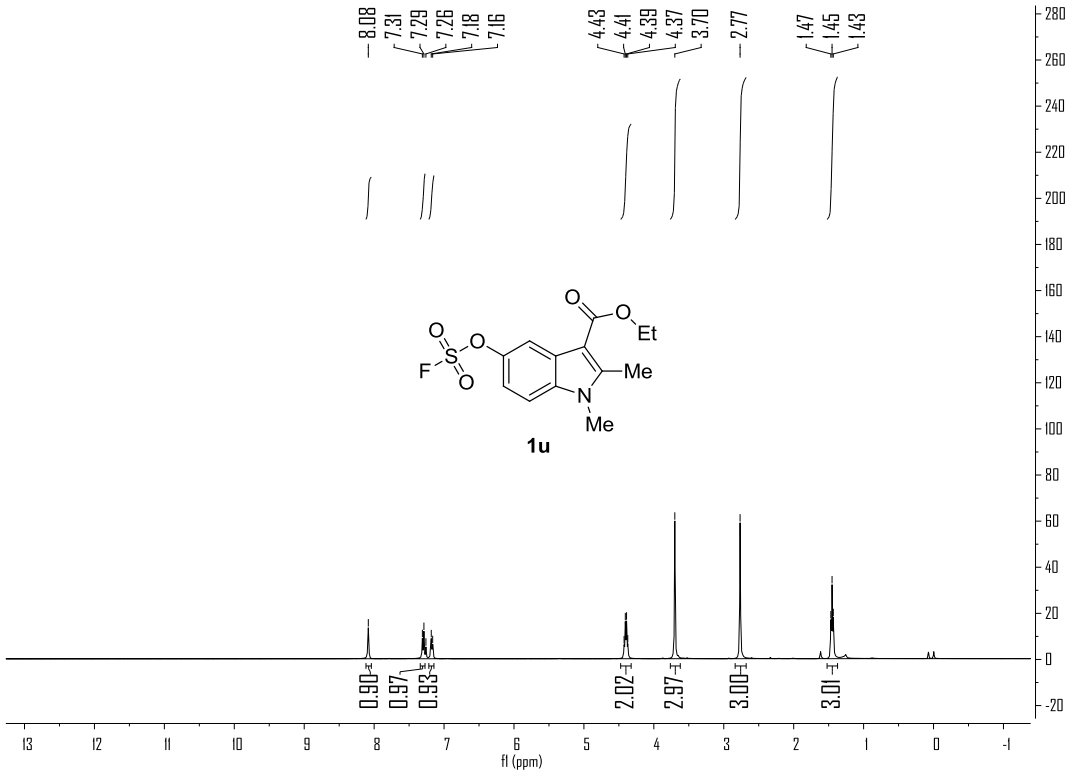
76.68
F
O
S
O
O
F
1w
f1 (ppm)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7.31
7.29
7.26
7.18
7.16
4.43
4.41
4.39
4.37
3.70
2.77
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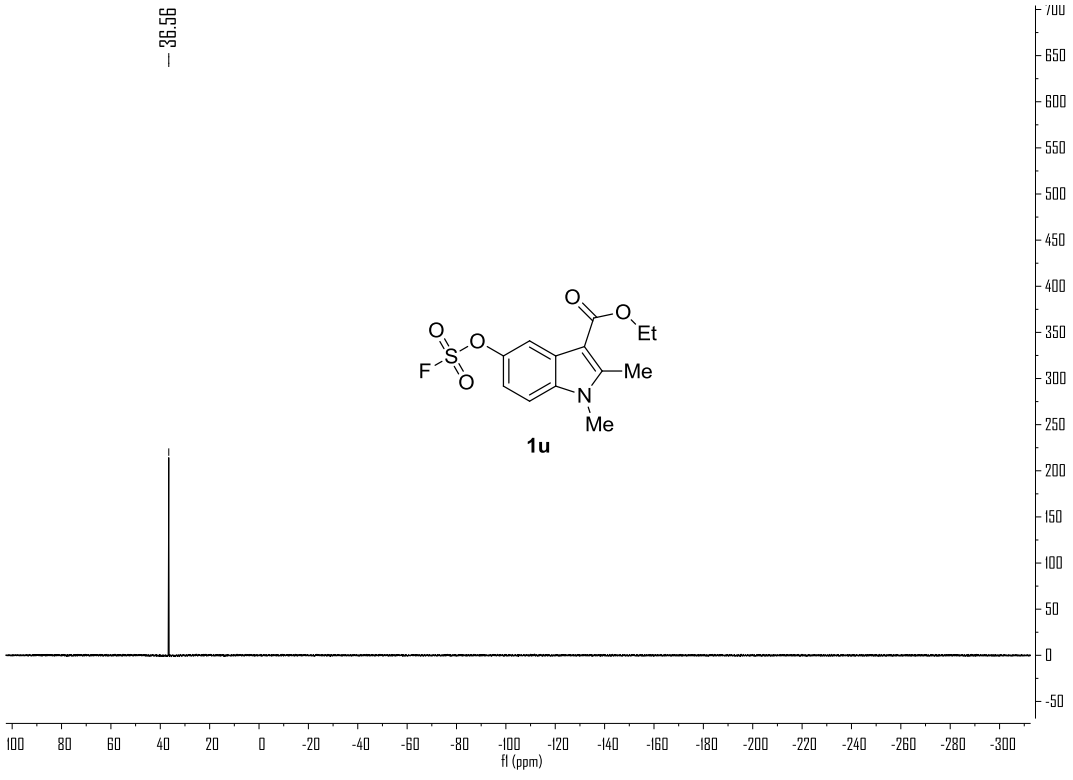
1.45
1.43
0.90
0.97
0.93
2.02
2.97
3.00
3.01
f1 (ppm)

1u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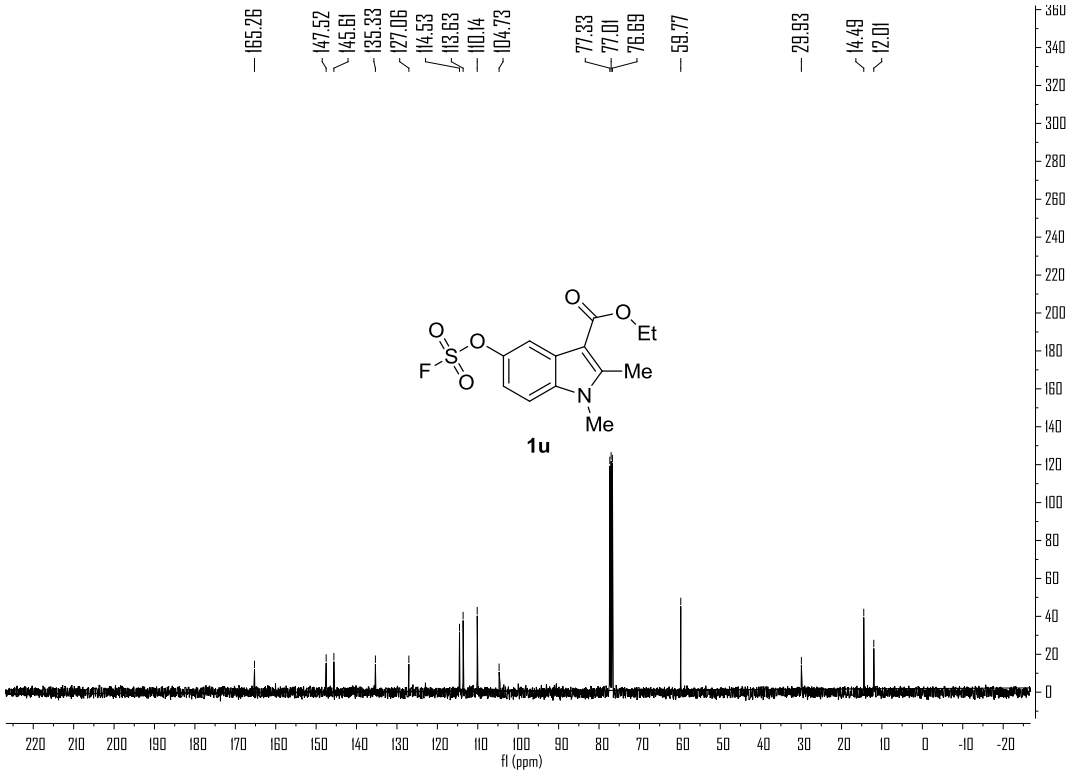
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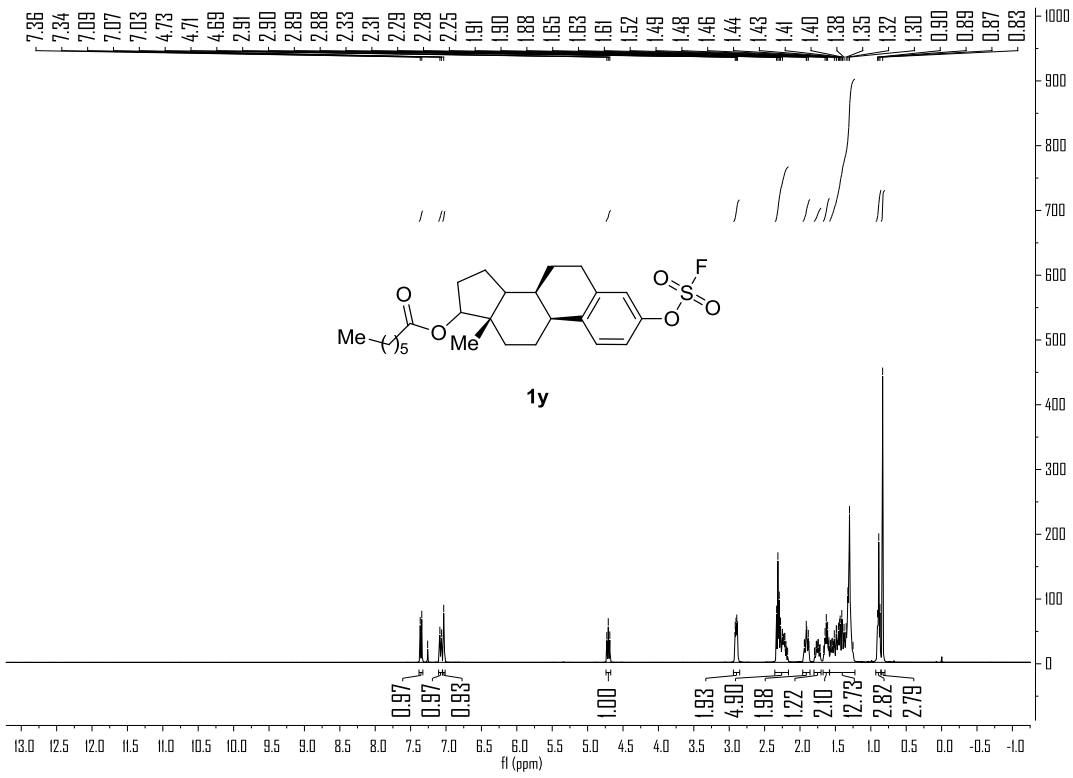
12.01
1u
f1 (ppm)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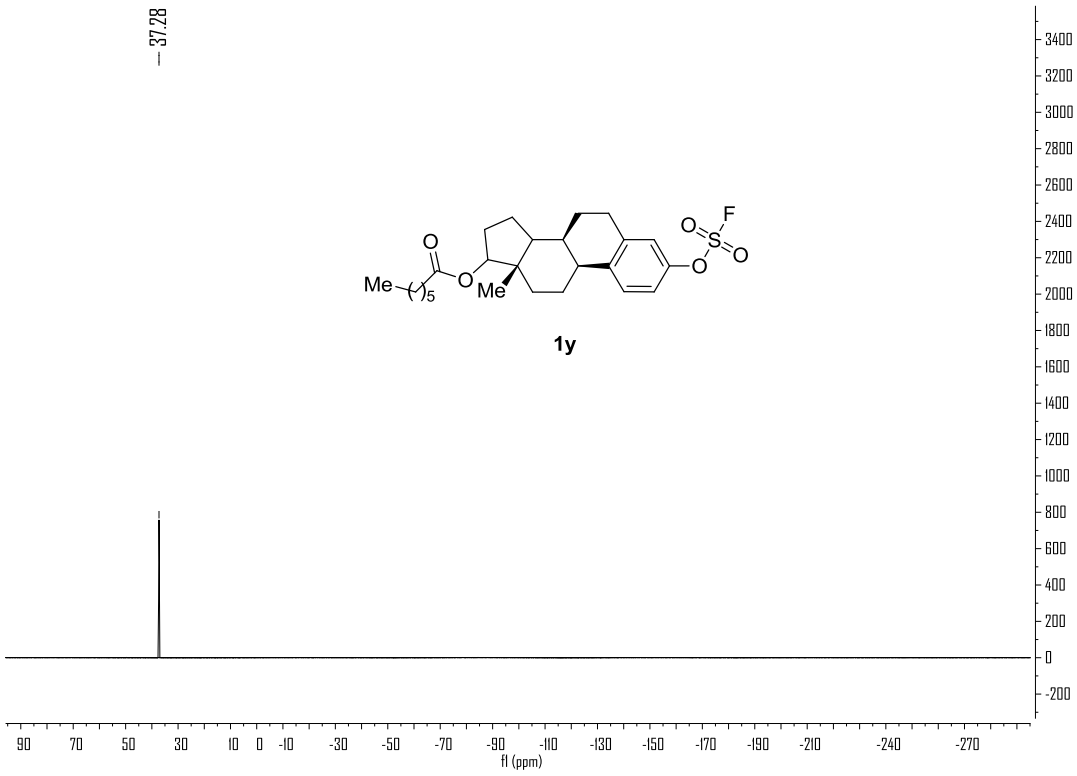
4.71
4.69
2.91
2.90
2.89
2.88
2.33
2.31
2.29
2.28
2.25
1.91
1.90
1.88
1.65
1.63
1.61
1.52
1.49
1.48
1.46
1.44
1.43
1.41
1.40
1.38
1.35
1.32
1.30
0.90
0.89
0.87
0.83
0.97
0.97
0.93
1.00
1.93
4.90
1.98
1.22
2.10
12.73
2.82
2.79
1y
f1 (ppm)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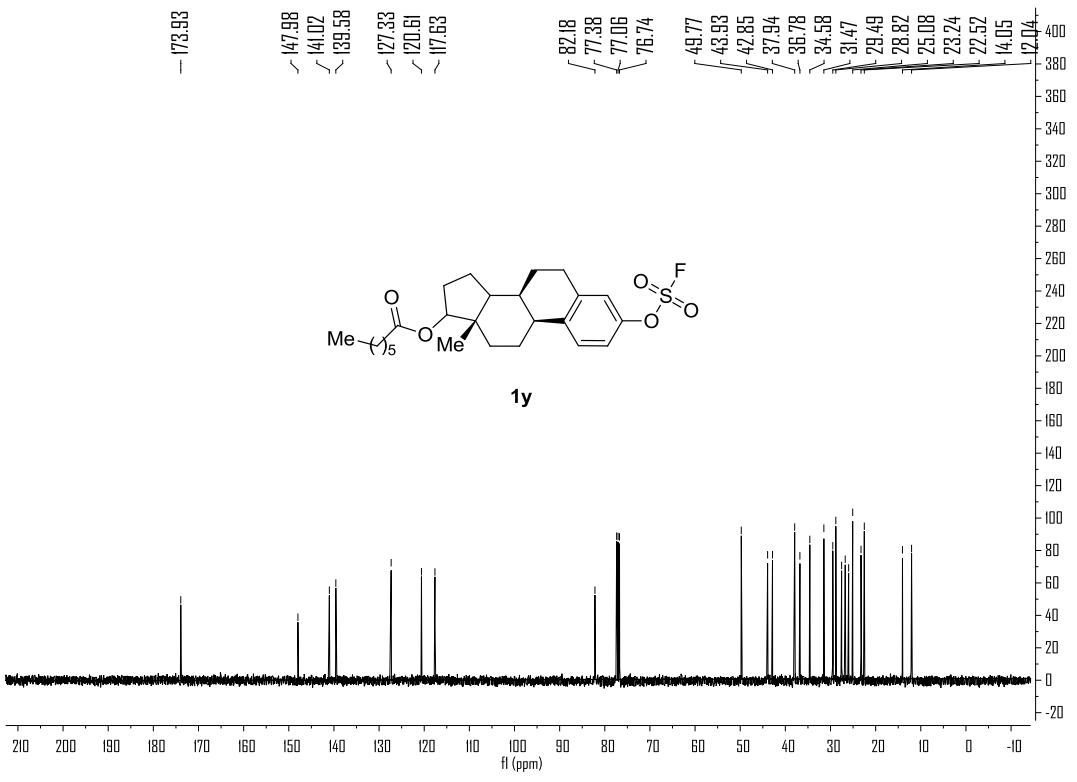
fl (ppm)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77.38
77.06
76.74
49.77
43.93
42.85
37.94
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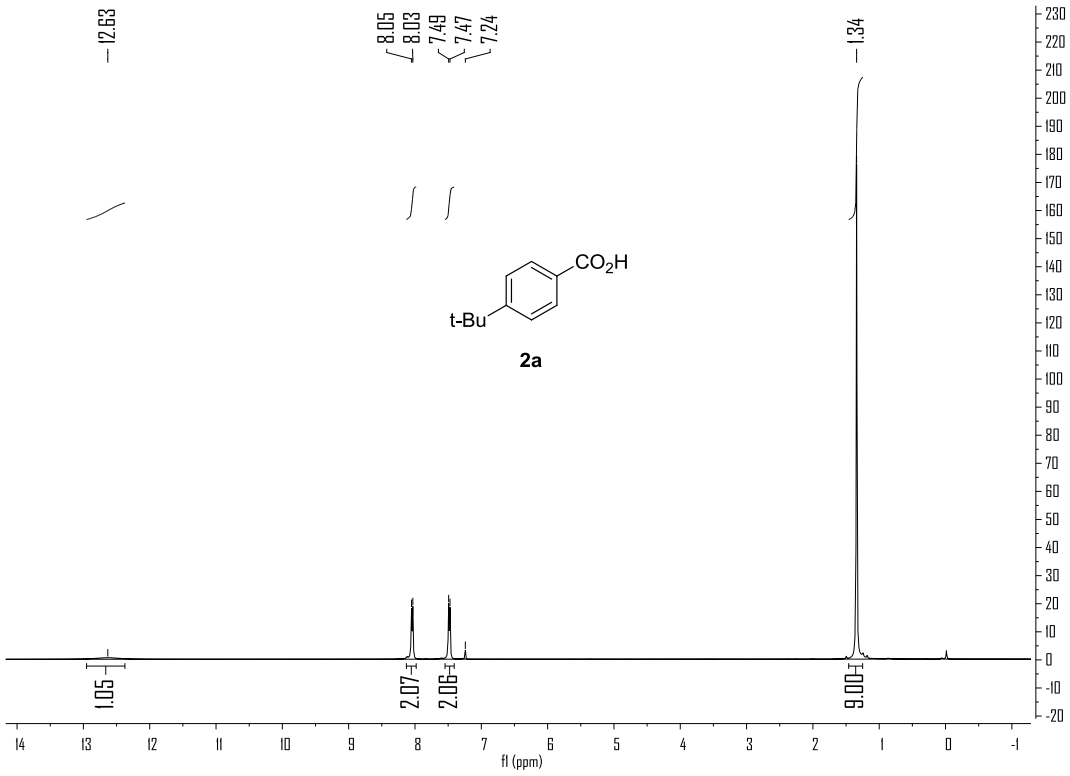
31.47
29.49
28.82
25.08
23.24
22.52
14.05
12.04
1y
fl (ppm)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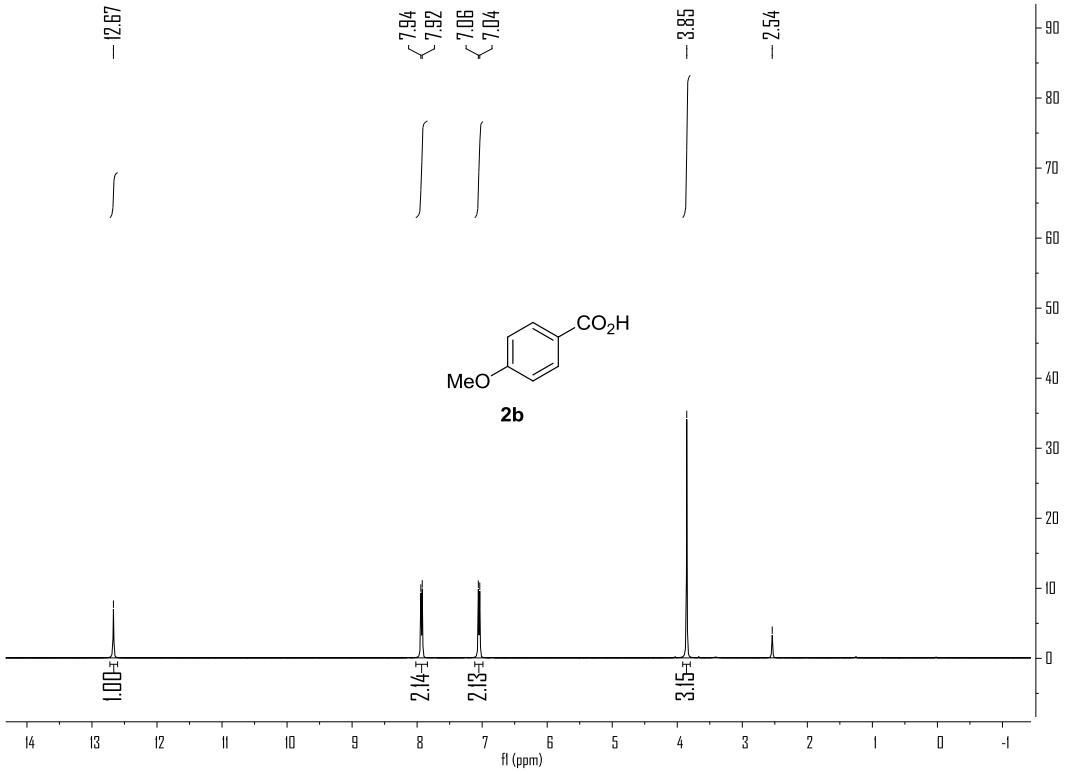
8.03
7.49
7.47
7.24
1.34
CO2H
t-Bu
2a
1.05
2.07
2.06
9.00
f1 (ppm)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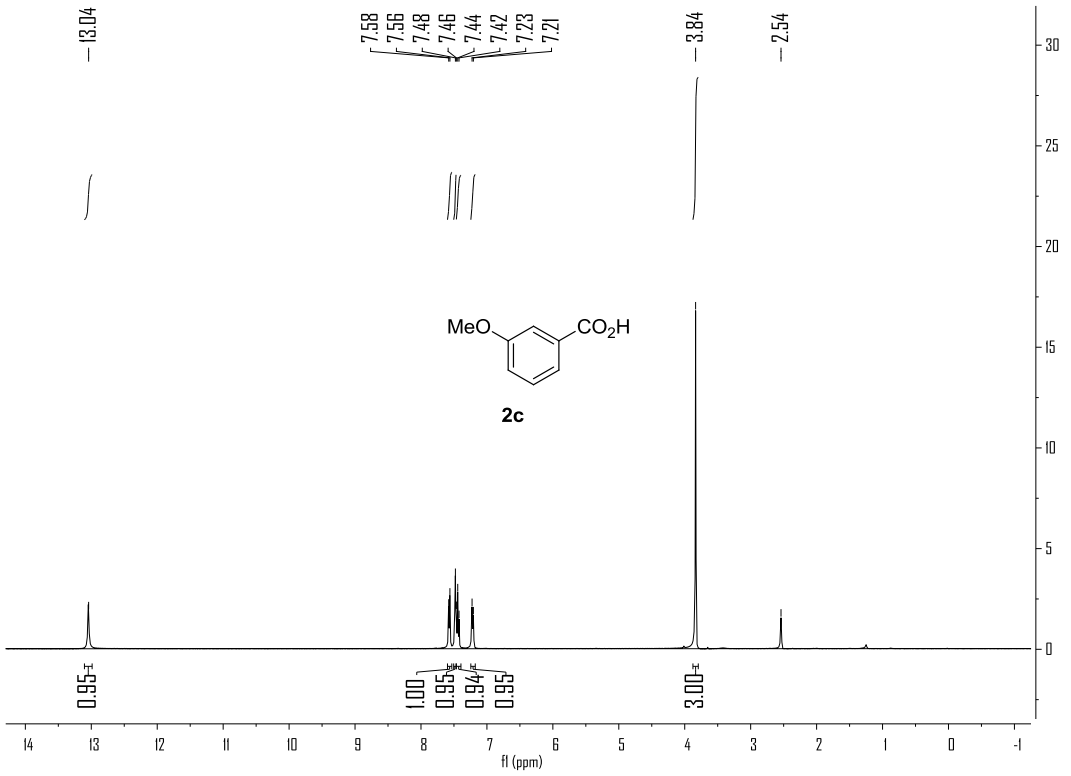
f1 (ppm)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7.56
7.48
7.46
7.44
7.42
7.23
7.21
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MeO
CO2H
2c
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0.95
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0.95
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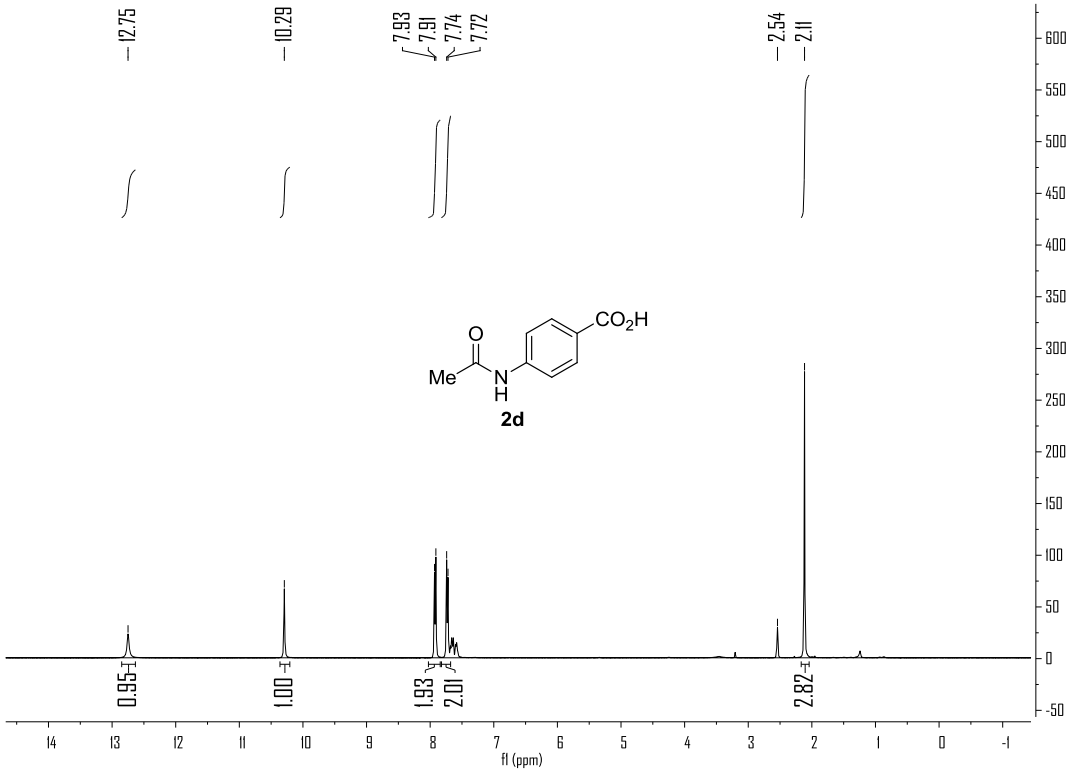
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7.72
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O
Me
N
H
2d
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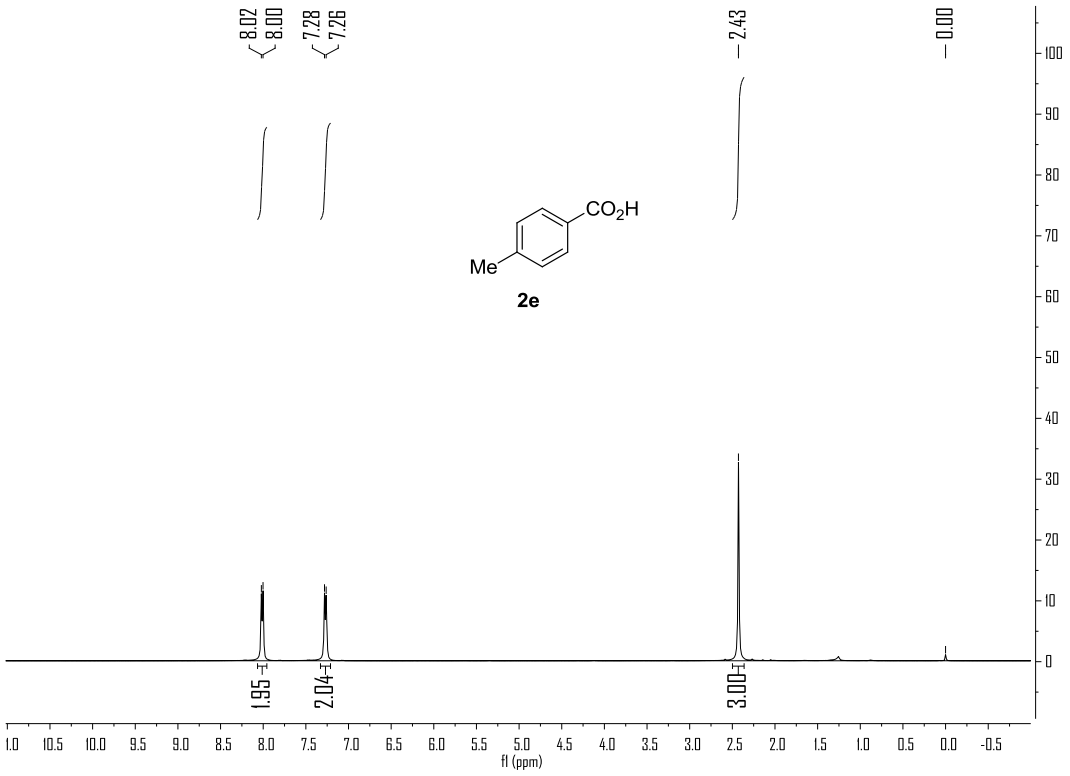
1.00
1.93
2.01
2.82
f1 (ppm)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CO2H
Me
2e
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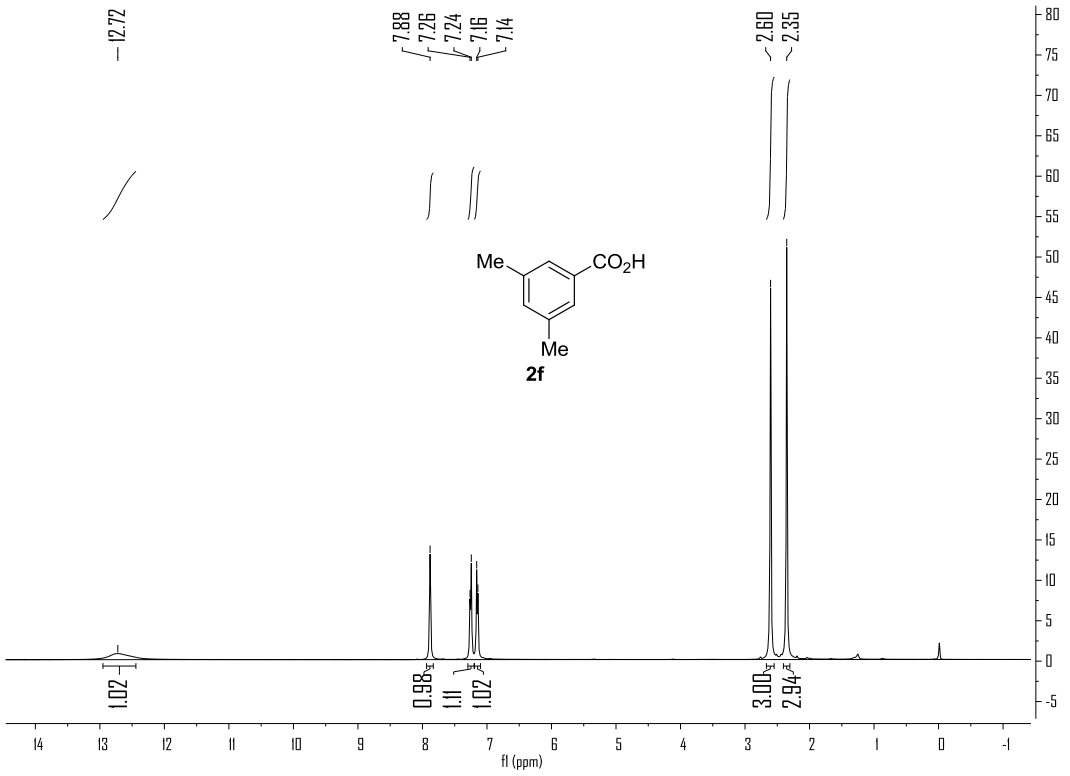
2.04
3.00
f1 (ppm)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7.16
7.14
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CO2H
Me
2f
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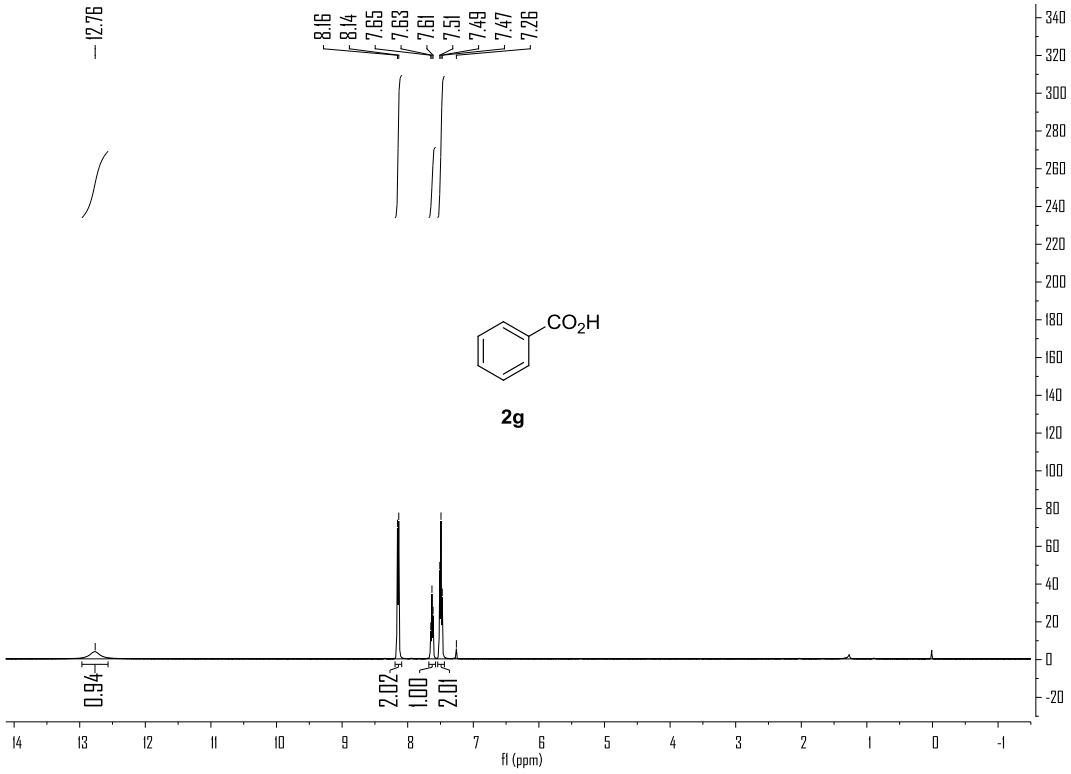
1.11
1.02
3.00
2.94
f1 (ppm)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7.63
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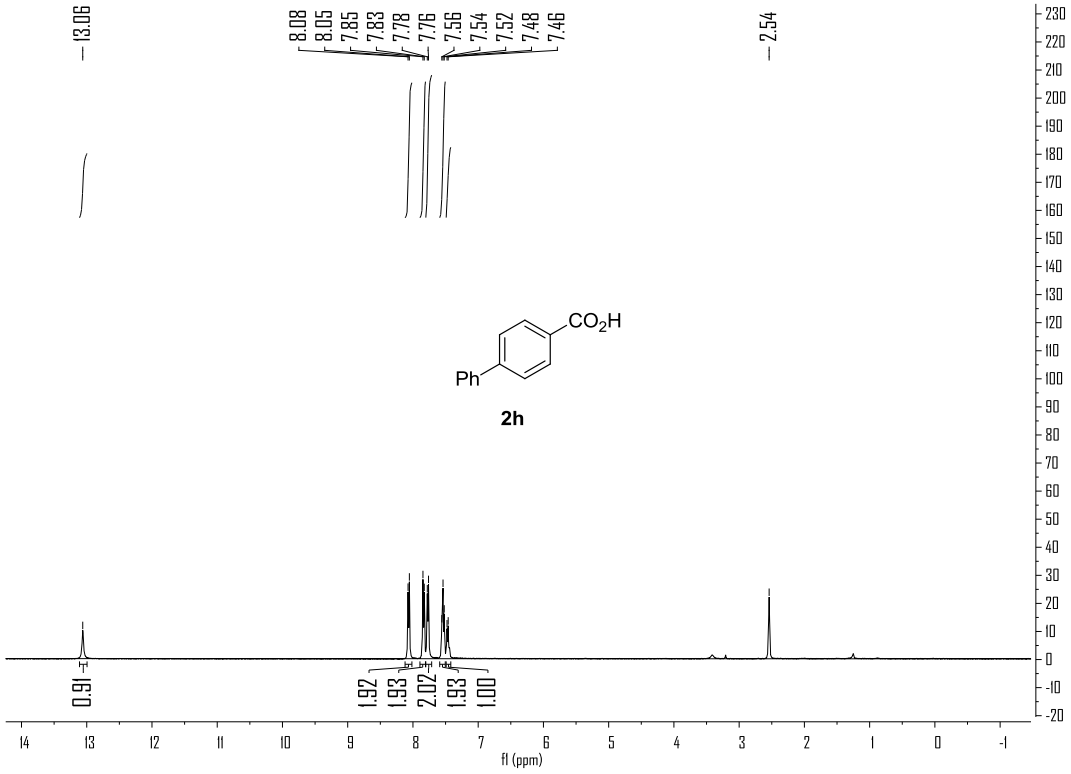
7.47
7.26
CO2H
0.94
2.02
1.00
2.01
f1 (ppm)

2g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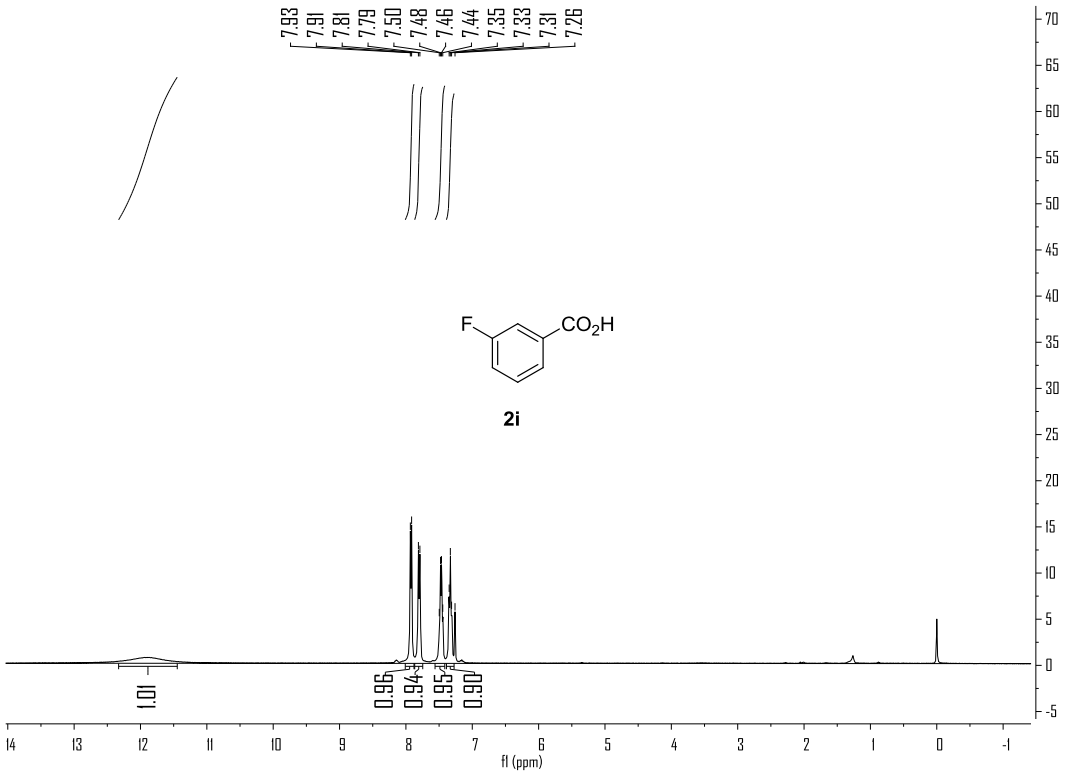
8.05
7.85
7.83
7.78
7.76
7.56
7.54
7.52
7.48
7.46
2.54
CO2H
Ph
0.91
1.92
1.93
2.02
1.93
1.00
f1 (ppm)

2h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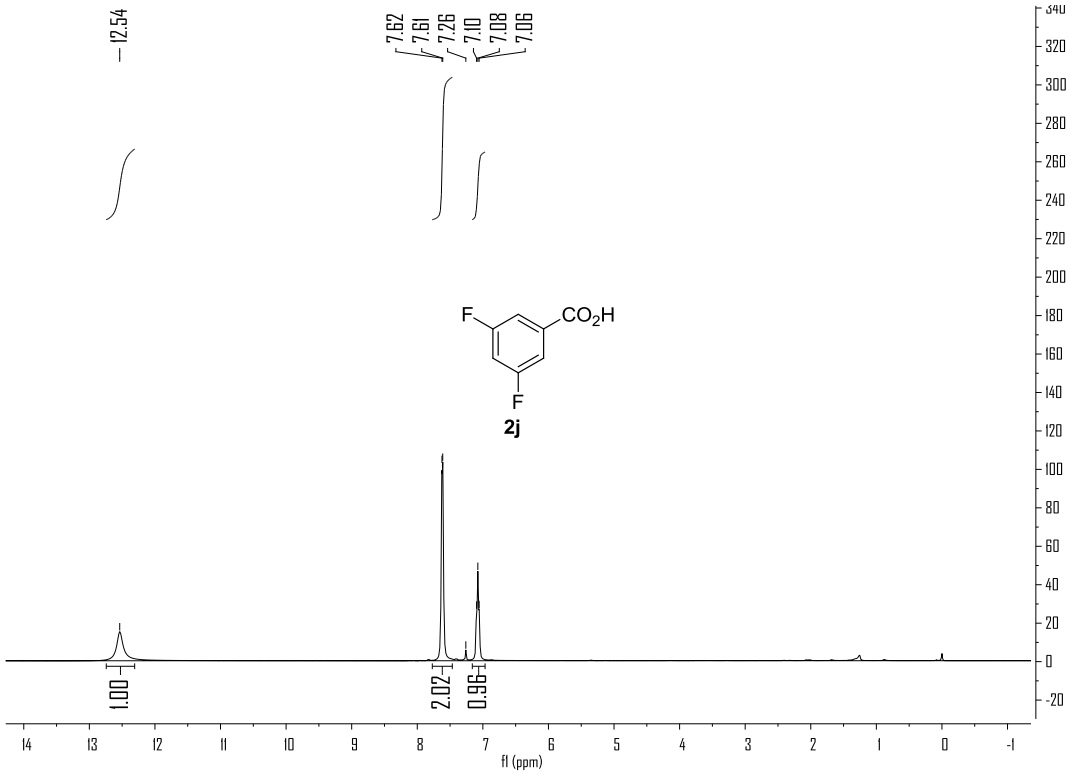
7.81
7.79
7.50
7.48
7.46
7.44
7.35
7.33
7.31
7.26
F
CO2H
2i
1.01
0.96
0.94
0.95
0.90
f1 (ppm)


12.54
7.62
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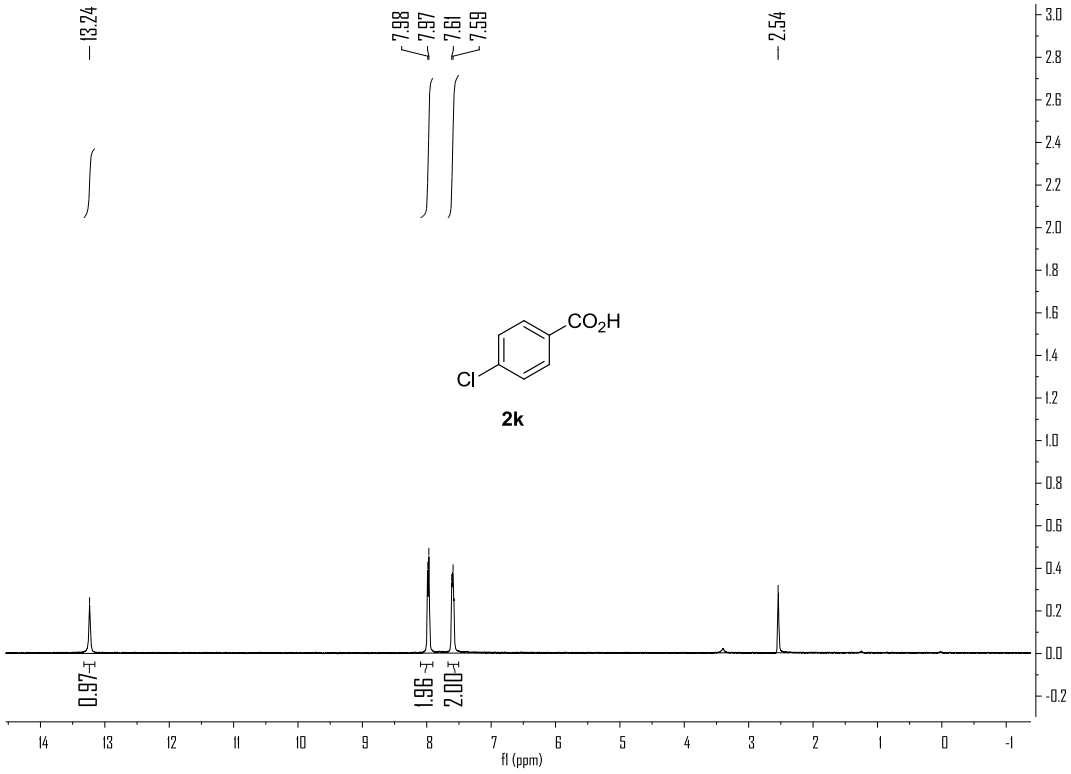
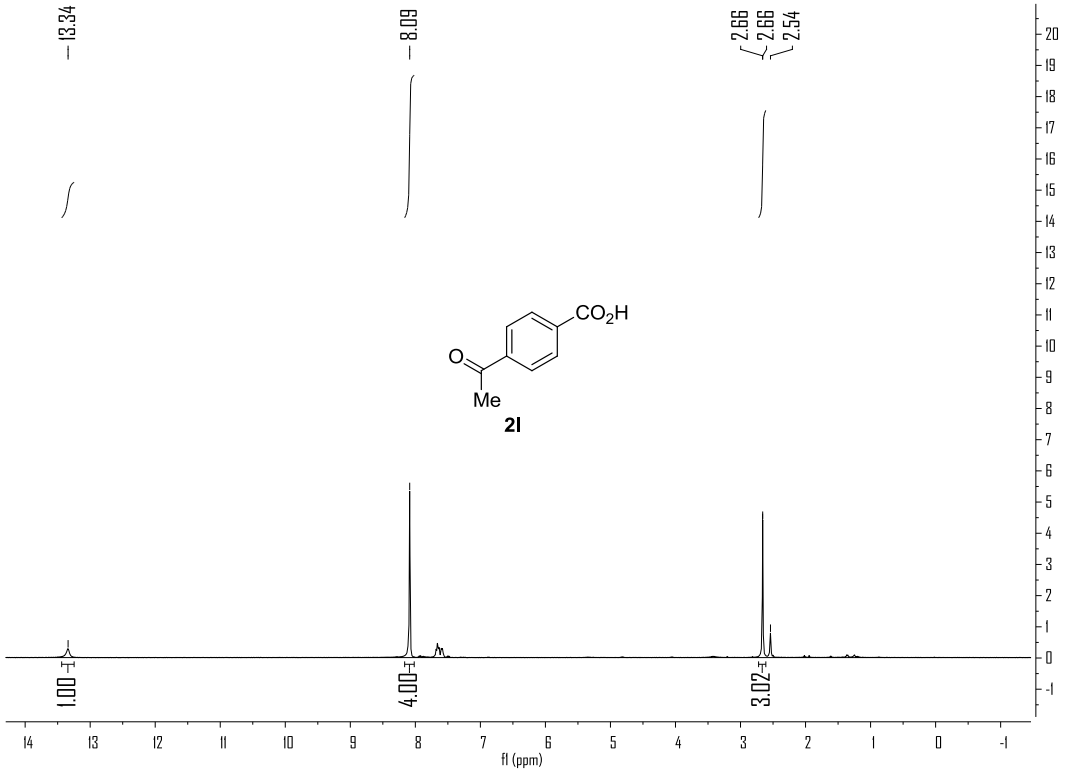
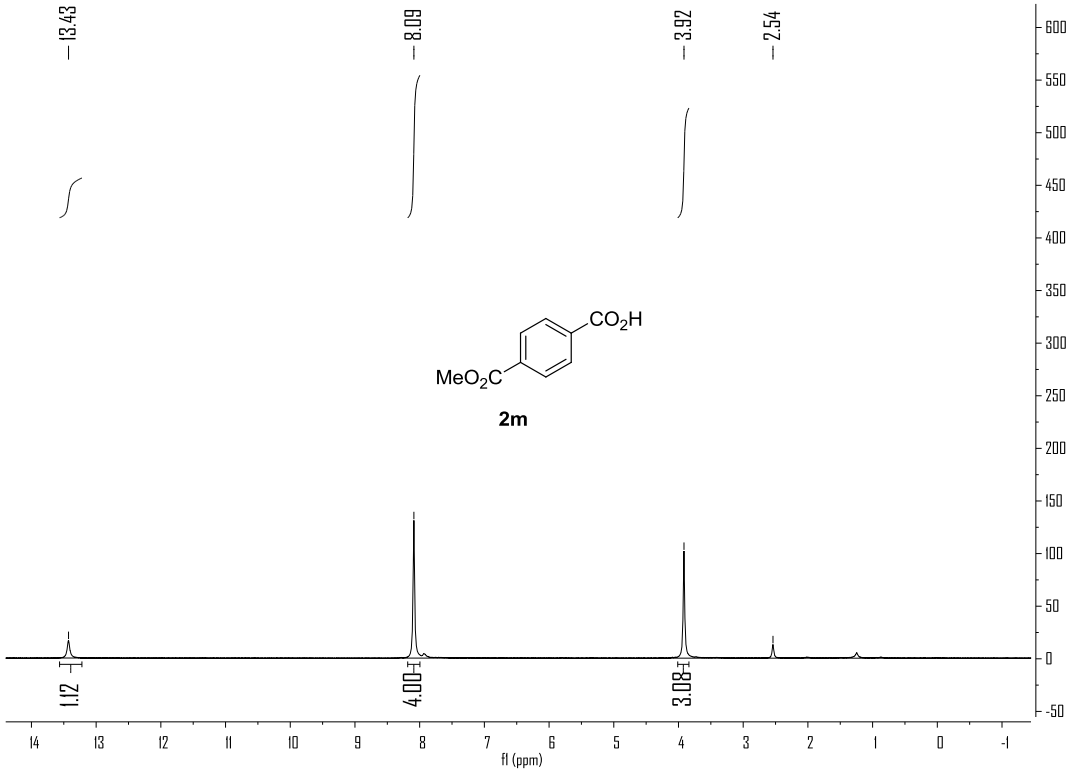
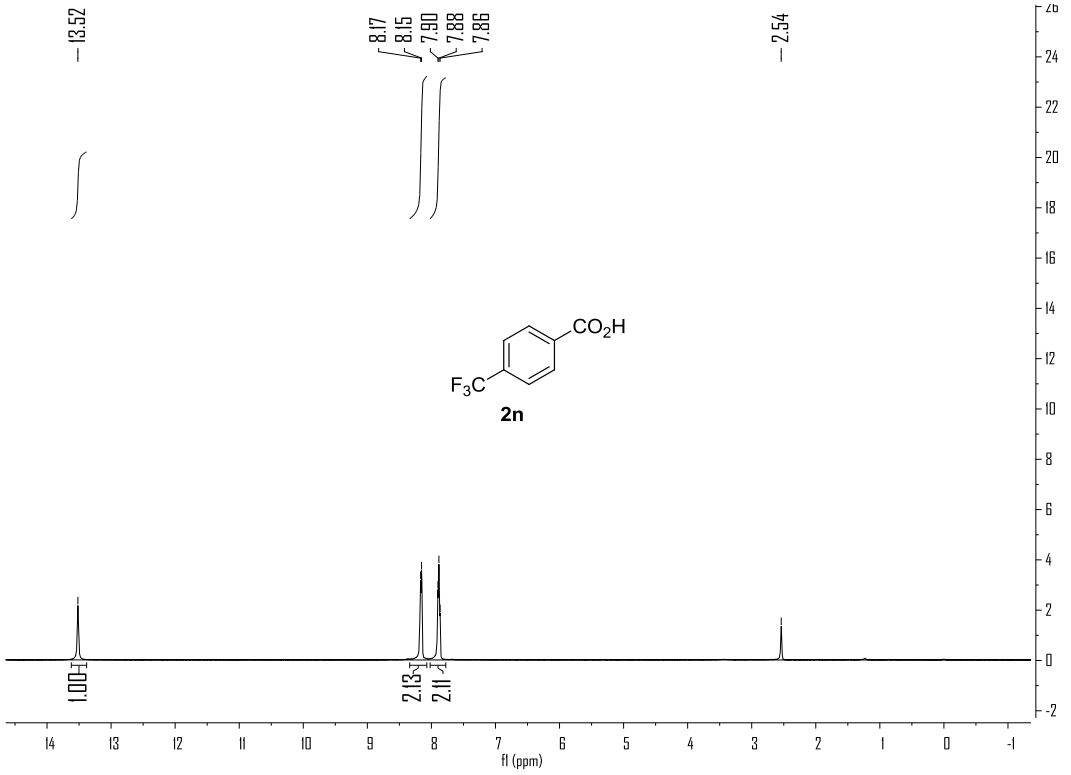
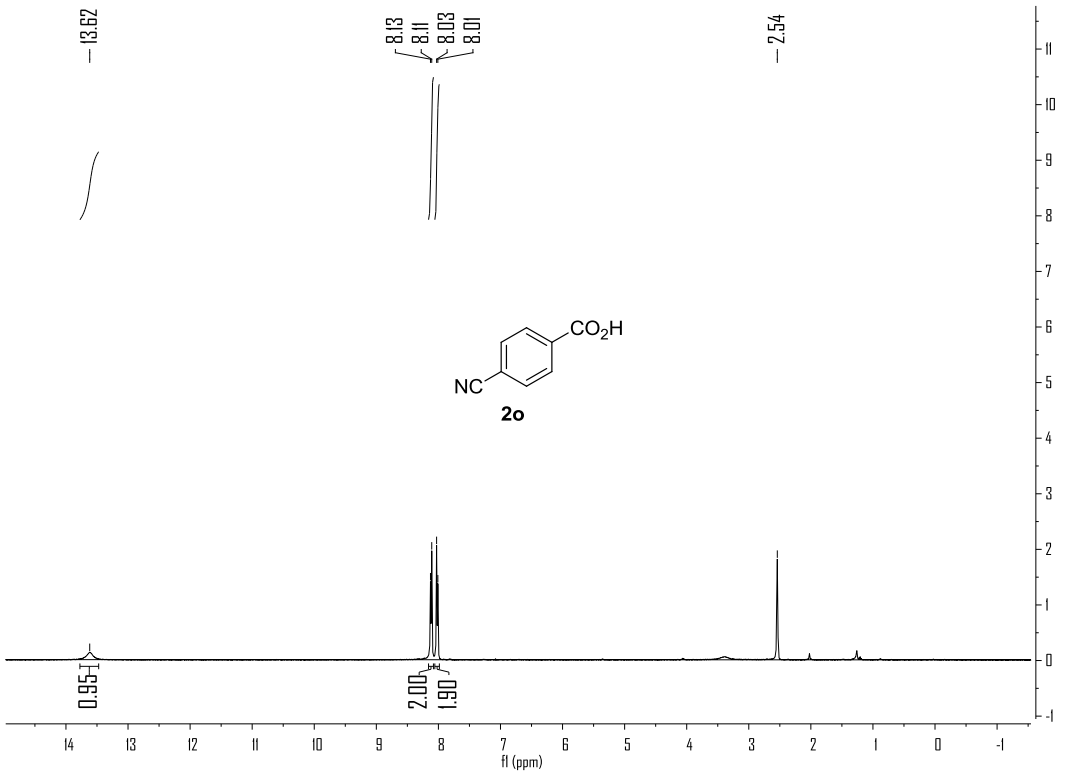
7.26
7.10
7.08
7.06
F
CO2H
F
2j
1.00
2.02
0.96
f1 (ppm)

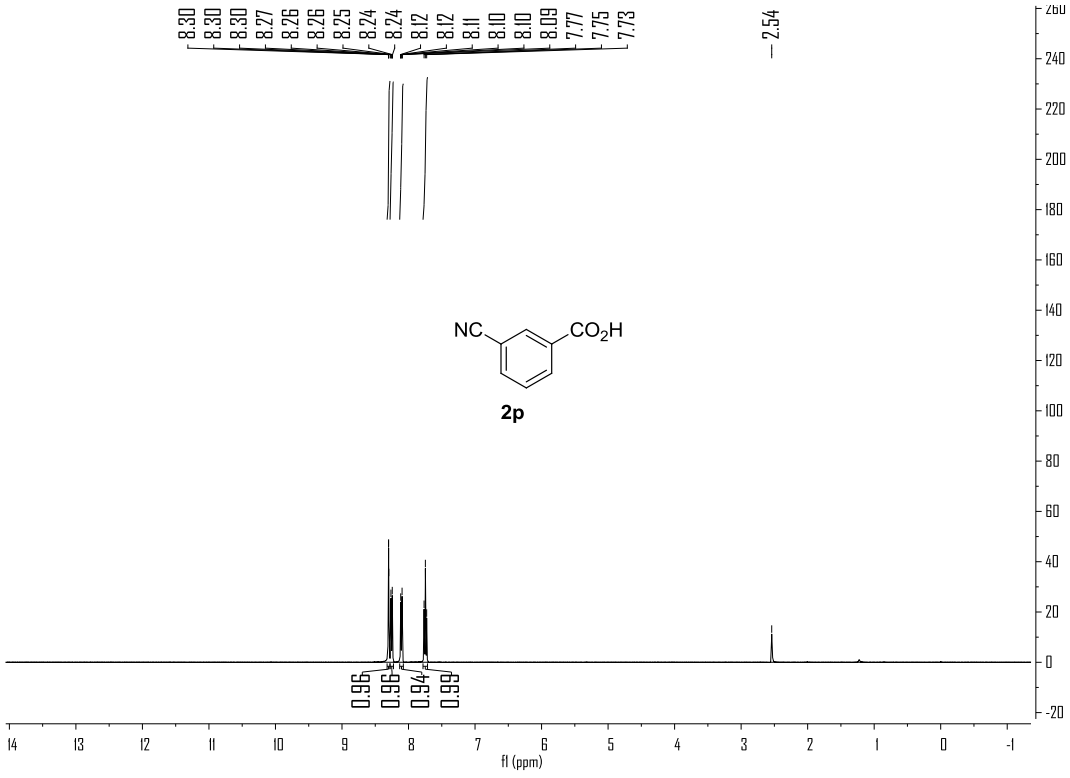

13.24
7.98
7.97
7.61
7.59
2.54
CO2H
Cl
2k
0.97
1.96
2.00
f1 (ppm)

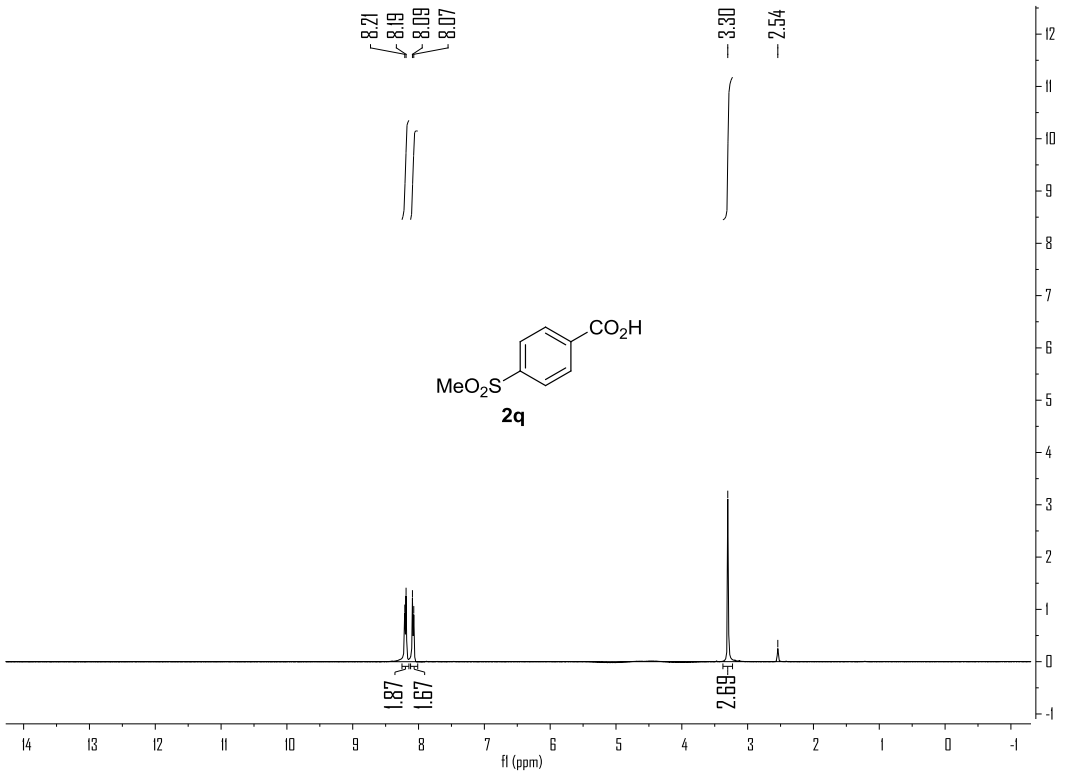

13.34
8.09
2.66
2.66
2.54
CO2H
O
Me
2l
1.00
4.00
3.02
f1 (ppm)

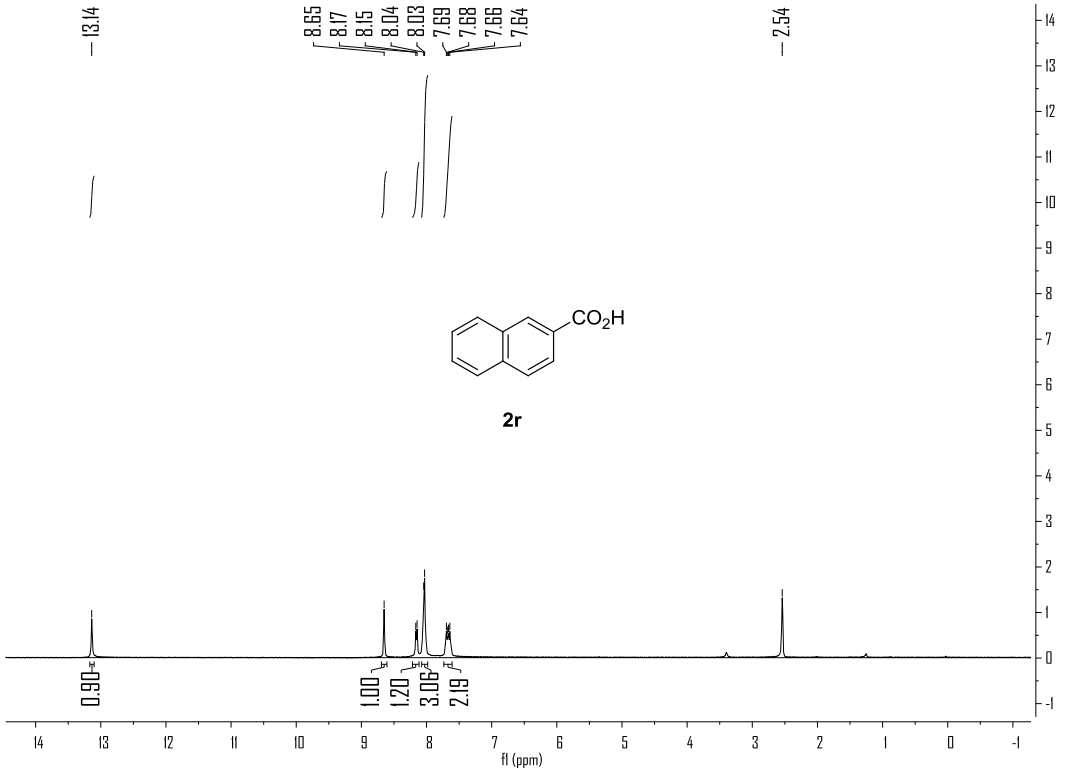

13.43
8.09
3.92
2.54
CO2H
MeO2C
2m
1.12
4.00
3.08
f1 (ppm)

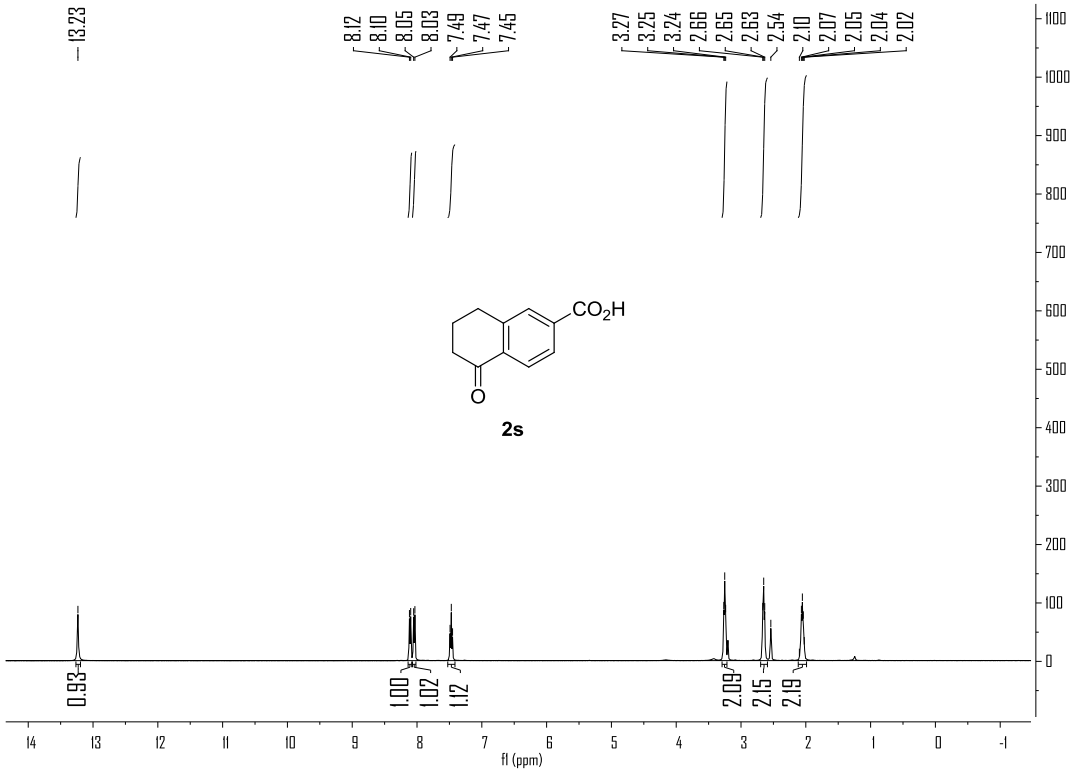

13.52
8.17
8.15
7.90
7.88
7.86
2.54
CO2H
F3C
2n
1.00
2.13
2.11
f1 (ppm)


13.62
8.13
8.11
8.03
8.01
2.54
CO2H
NC
2o
0.95
2.00
1.90
f1 (ppm)

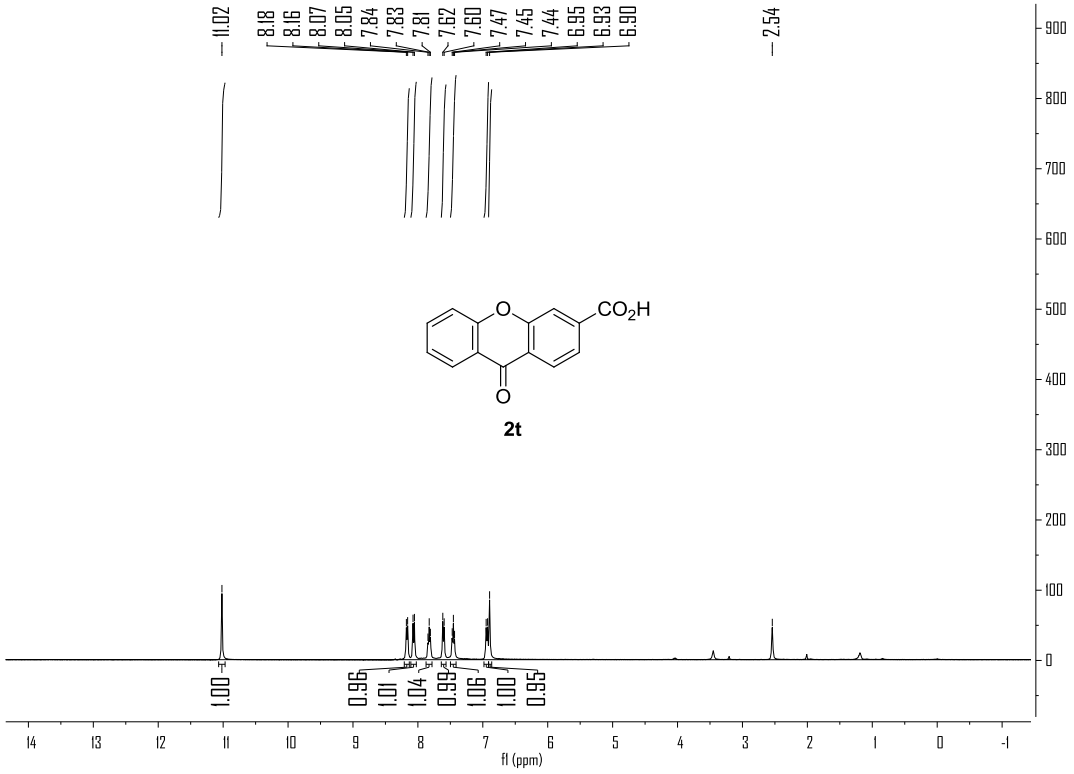

8.30
8.30
8.30
8.27
8.26
8.26
8.25
8.24
8.24
8.12
8.12
8.11
8.10
8.10
8.09
7.77
7.75
7.73
2.54
NC
CO2H
2p
0.96
0.96
0.94
0.99
f1 (ppm)


8.21
8.19
8.09
8.07
3.30
2.54
CO2H
MeO2S
2q
1.87
1.67
2.69
f1 (ppm)

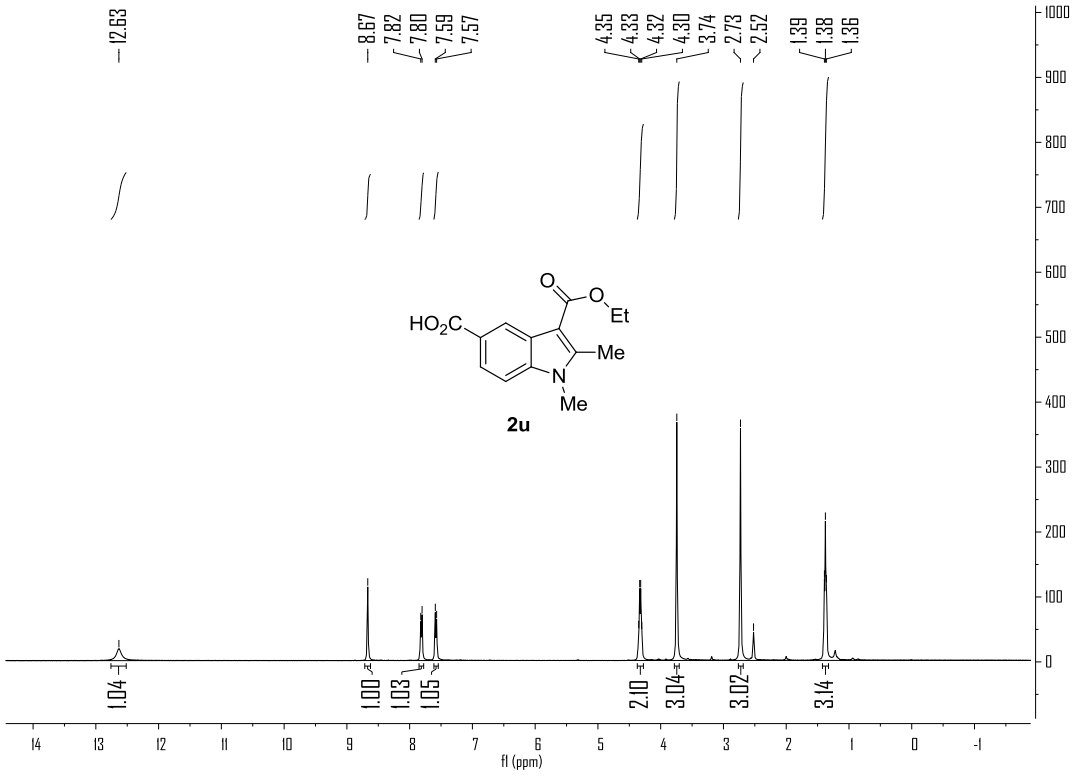

13.14
8.65
8.17
8.15
8.04
8.03
7.69
7.68
7.66
7.64
2.54
CO2H
2r
0.90
1.00
1.20
3.06
2.19
f1 (ppm)

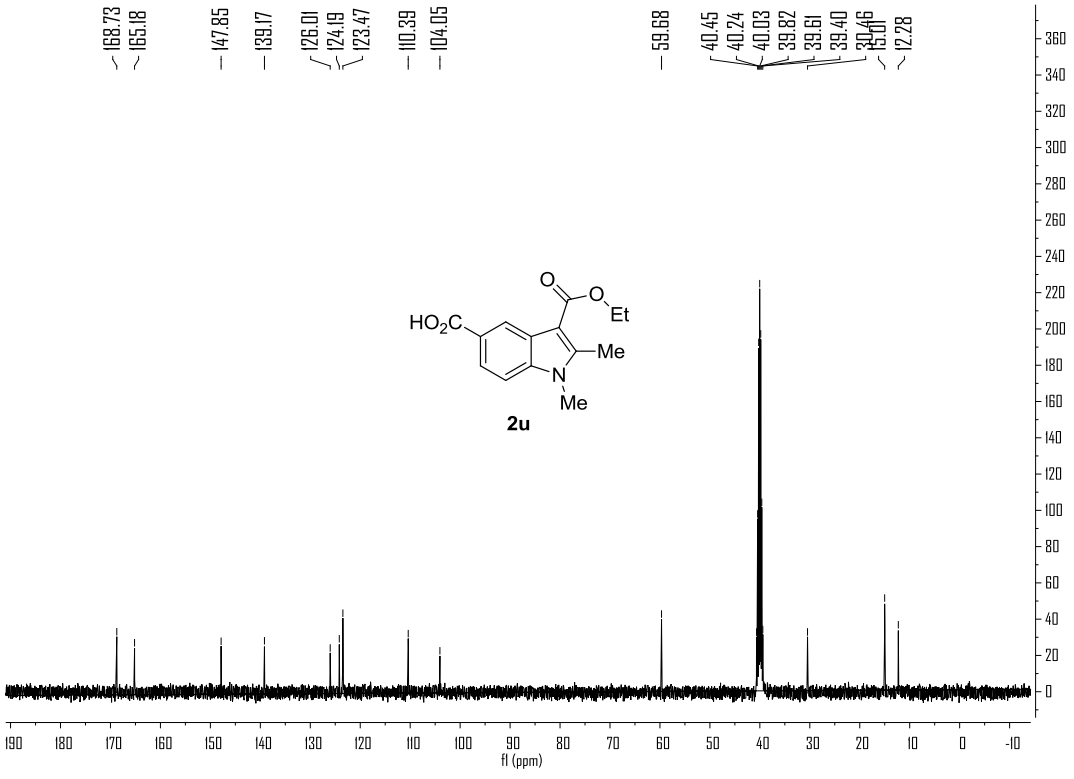

13.23
8.12
8.10
8.05
8.03
7.49
7.47
7.45
3.27
3.25
3.24
2.66
2.65
2.63
2.54
2.10
2.07
2.05
2.04
2.02
CO2H
O
0.93
1.00
1.02
1.12
2.09
2.15
2.19
f1 (ppm)

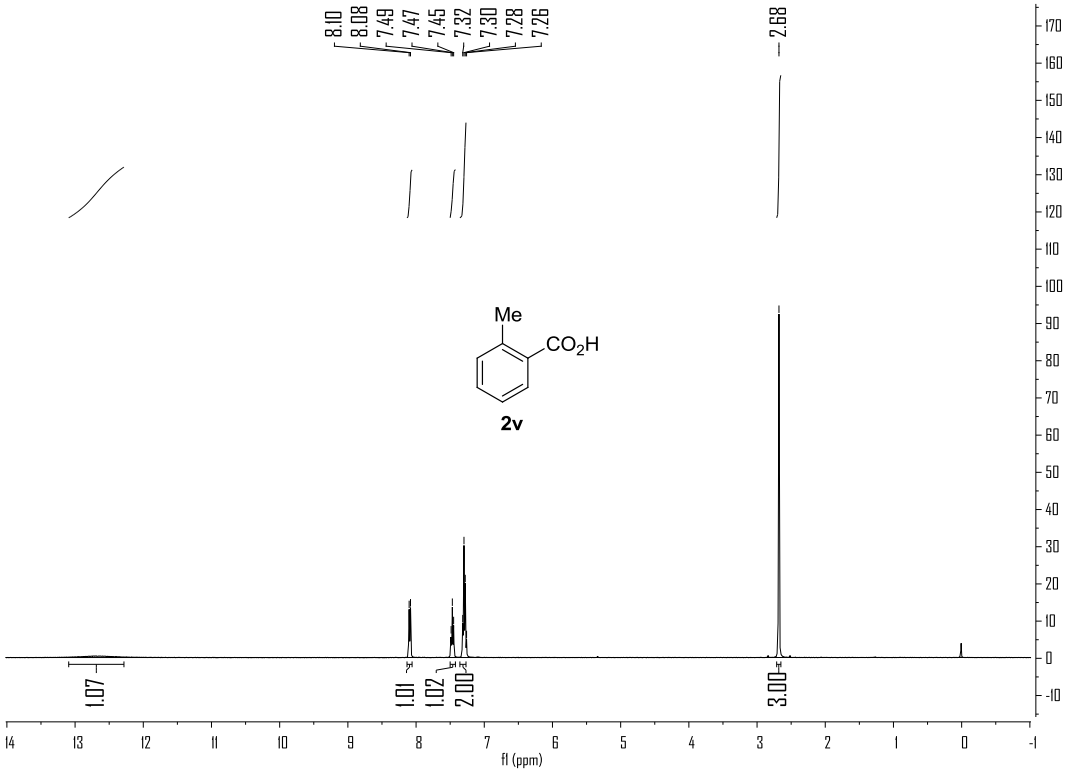
2s

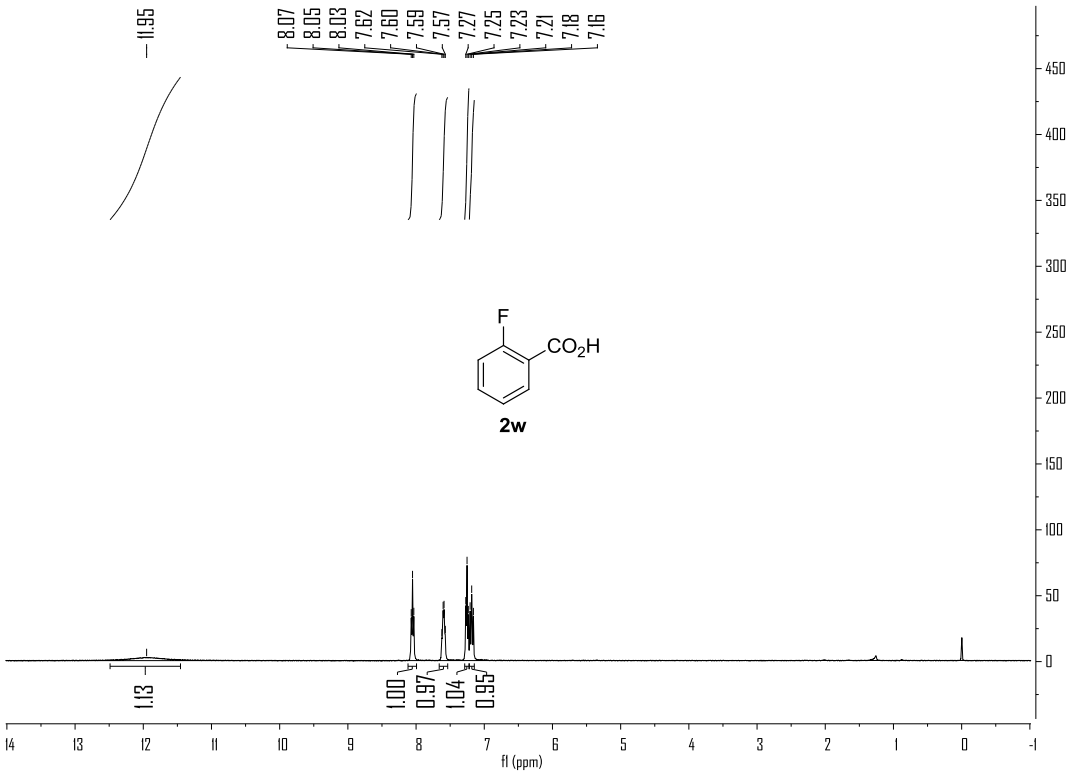

11.02
8.18
8.16
8.07
8.05
7.84
7.83
7.81
7.62
7.60
7.47
7.45
7.44
6.95
6.93
6.90
2.54
O
CO2H
O
1.00
0.96
1.01
1.04
0.99
1.06
1.00
0.95
f1 (ppm)

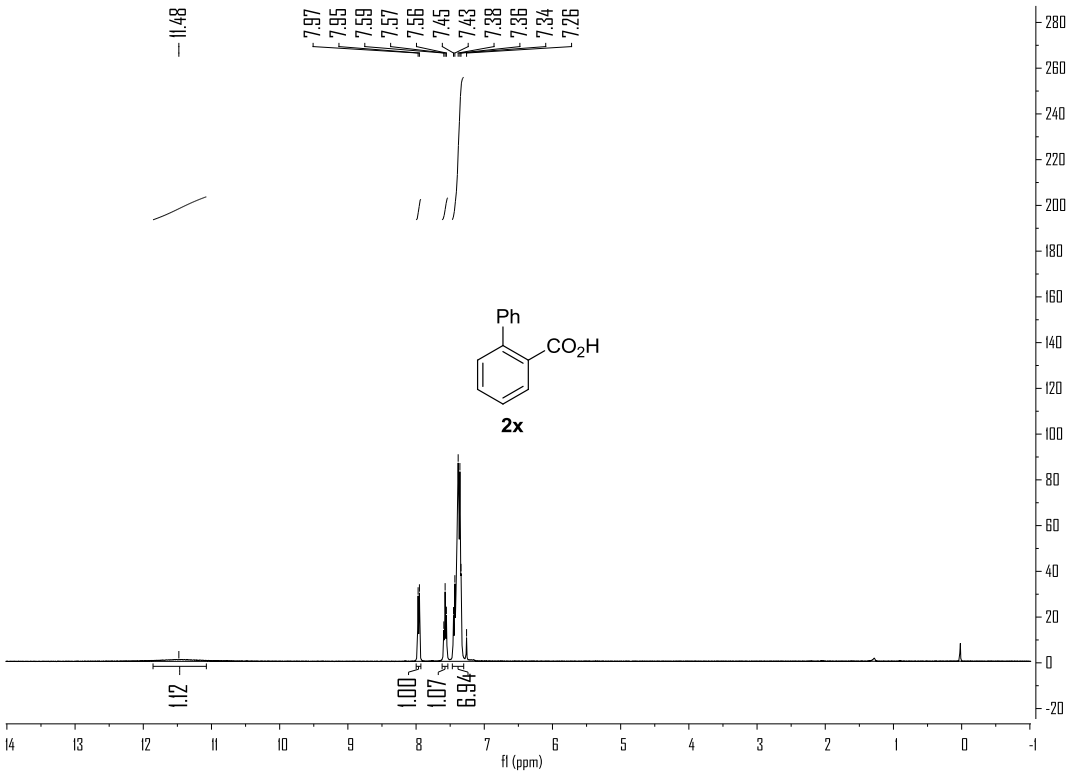
2t

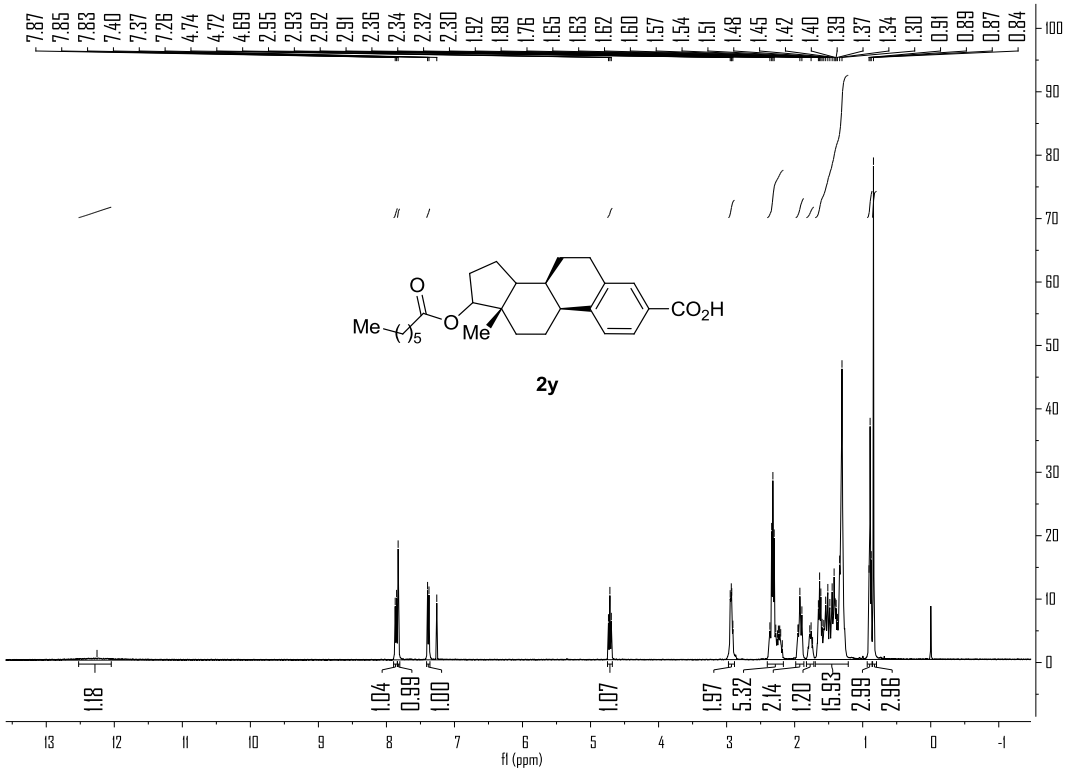

12.63
8.67
7.82
7.80
7.59
7.57
4.35
4.33
4.32
4.30
3.74
2.73
2.52
1.39
1.38
1.36
HO2C
O
O
Et
Me
N
Me
2u
1.04
1.00
1.03
1.05
2.10
3.04
3.02
3.14
f1 (ppm)

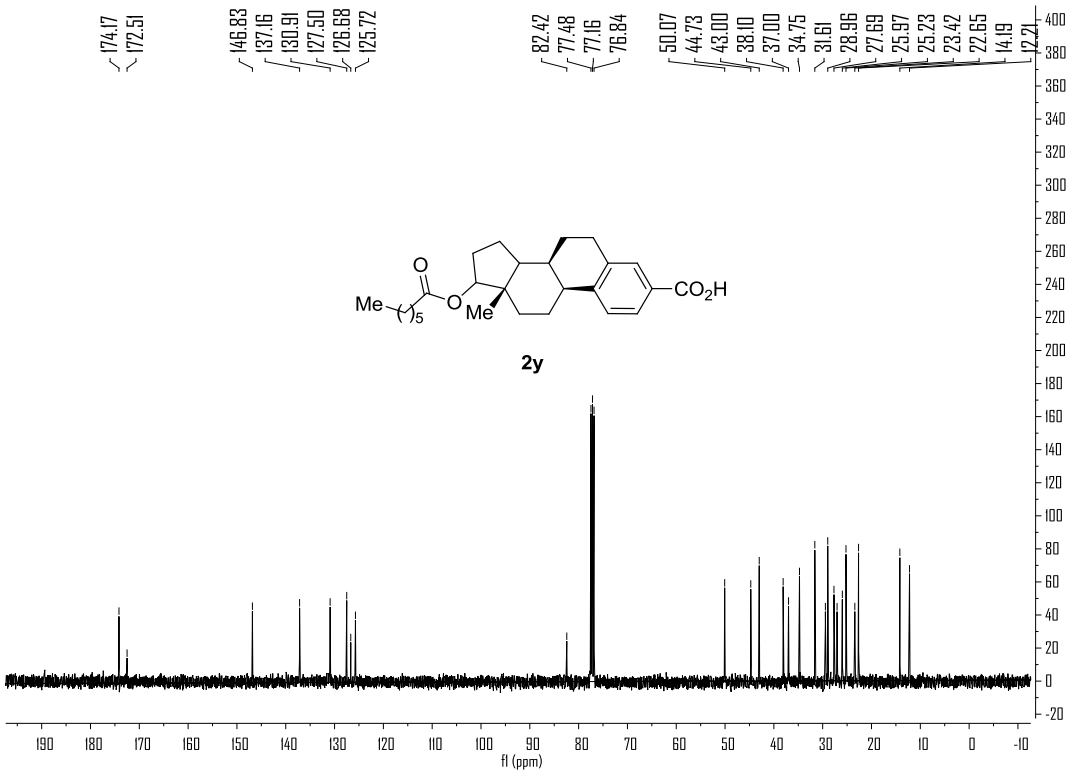

168.73
165.18
147.85
139.17
126.01
124.19
123.47
110.39
104.05
59.68
40.45
40.24
40.03
39.82
39.61
39.40
30.46
15.01
12.28
HO2C
O
O
Et
Me
N
Me
2u
f1 (ppm)


8.10
8.08
7.49
7.47
7.45
7.32
7.30
7.28
7.26
2.68
Me
CO2H
2v
1.07
1.01
1.02
2.00
3.00
f1 (ppm)


11.95
8.07
8.05
8.03
7.62
7.60
7.59
7.57
7.27
7.25
7.23
7.21
7.18
7.16
F
CO2H
2w
1.13
1.00
0.97
1.04
0.95
f1 (ppm)

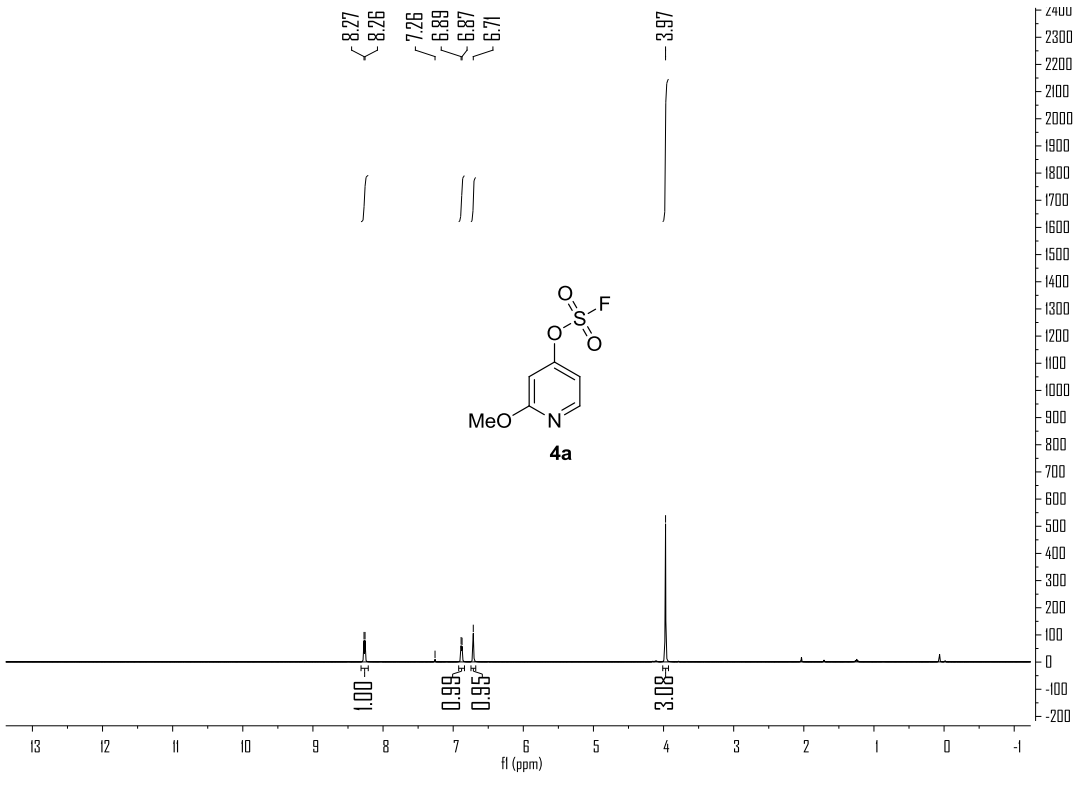

11.48
7.97
7.95
7.59
7.57
7.56
7.45
7.43
7.38
7.36
7.34
7.26
Ph
CO2H
2x
1.12
1.00
1.07
6.94
f1 (ppm)


7.87
7.85
7.83
7.40
7.37
7.26
4.74
4.72
4.69
2.95
2.93
2.92
2.91
2.36
2.34
2.32
2.30
1.92
1.89
1.76
1.65
1.63
1.62
1.60
1.57
1.54
1.51
1.48
1.45
1.42
1.40
1.39
1.37
1.34
1.30
0.91
0.89
0.87
0.84
O
O
Me
5
Me
CO2H
2y
1.18
1.04
0.99
1.00
1.07
1.97
5.32
2.14
1.20
15.93
2.99
2.96
f1 (ppm)


174.17
172.51
146.83
137.16
130.91
127.50
126.68
125.72
82.42
77.48
77.16
76.84
50.07
44.73
43.00
38.10
37.00
34.75
31.61
28.96
27.69
25.97
25.23
23.42
22.65
14.19
14.21
f1 (ppm)

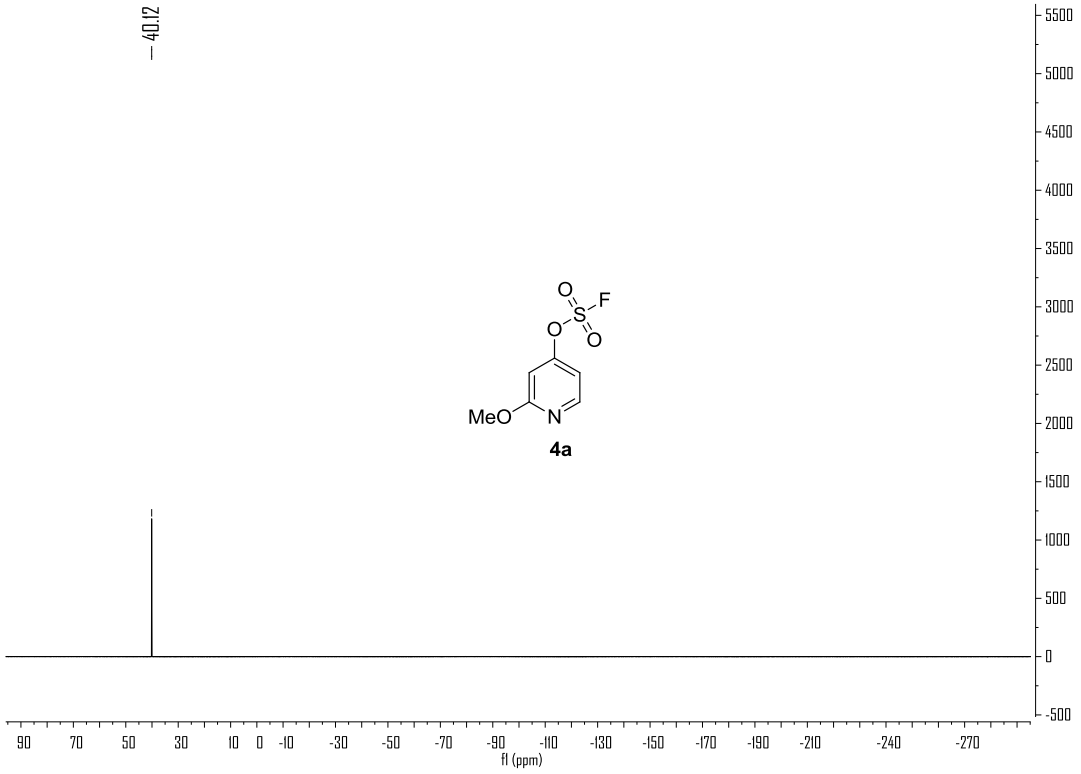
O
O
Me
5
O
Me
CO2H

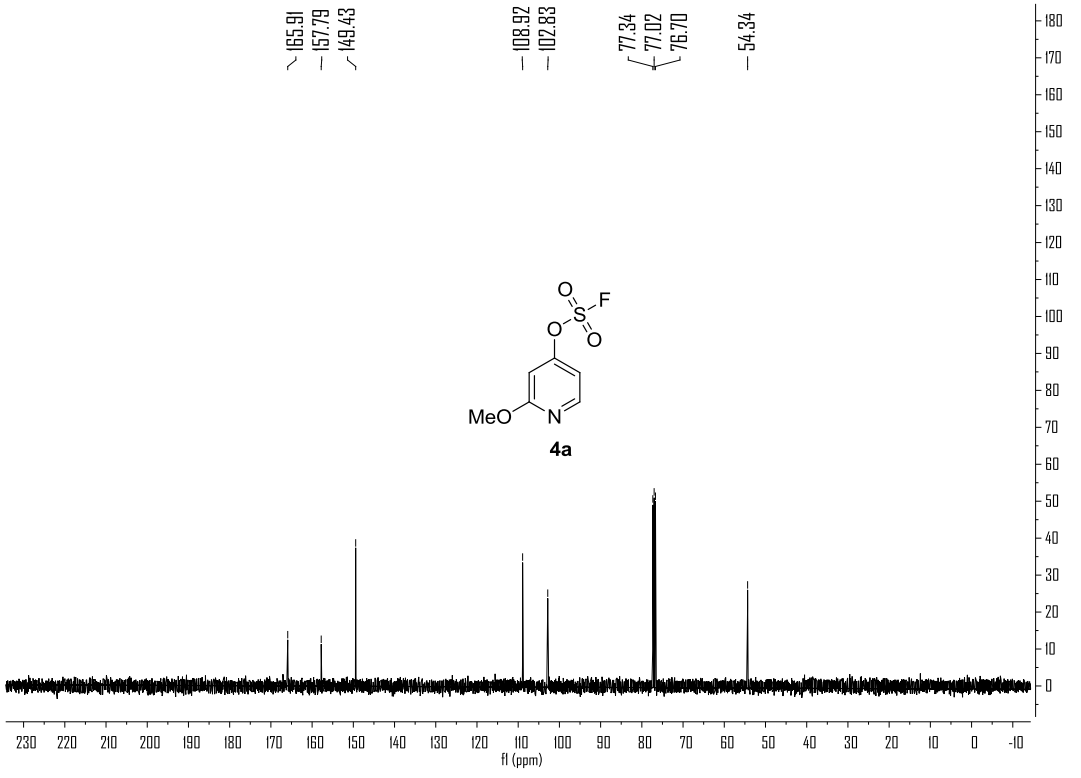
2y

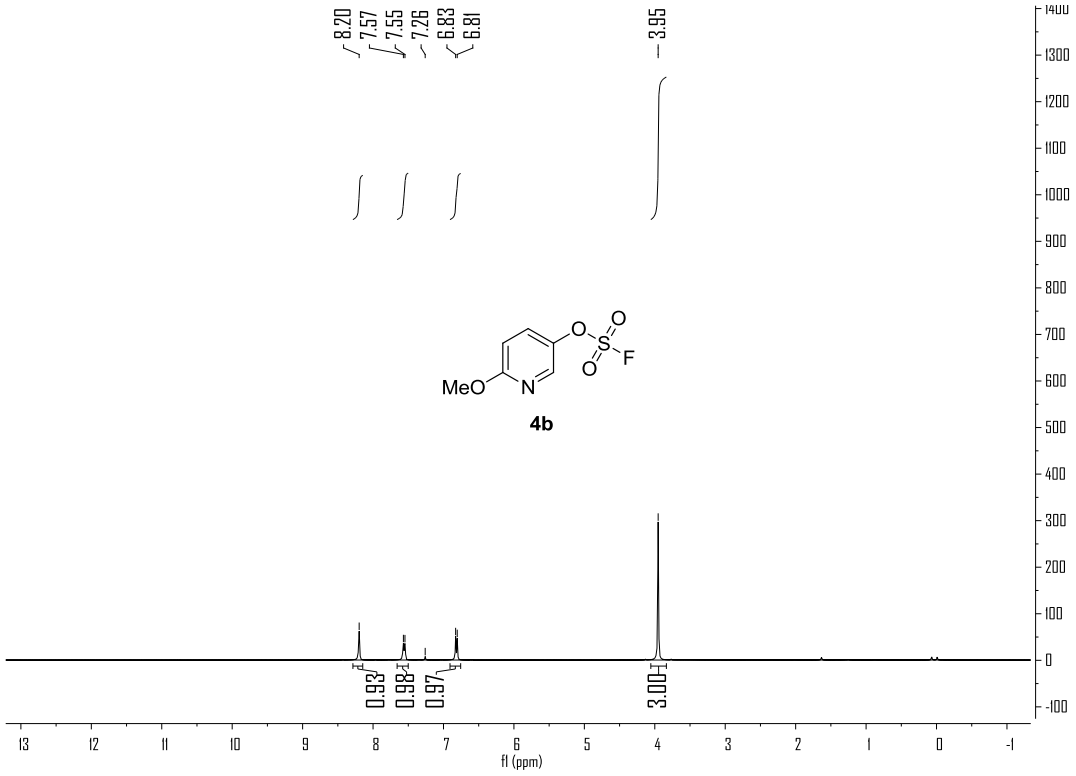

8.27
8.26
7.26
6.89
6.87
6.71
3.97
1.00
0.99
0.95
3.08
f1 (ppm)

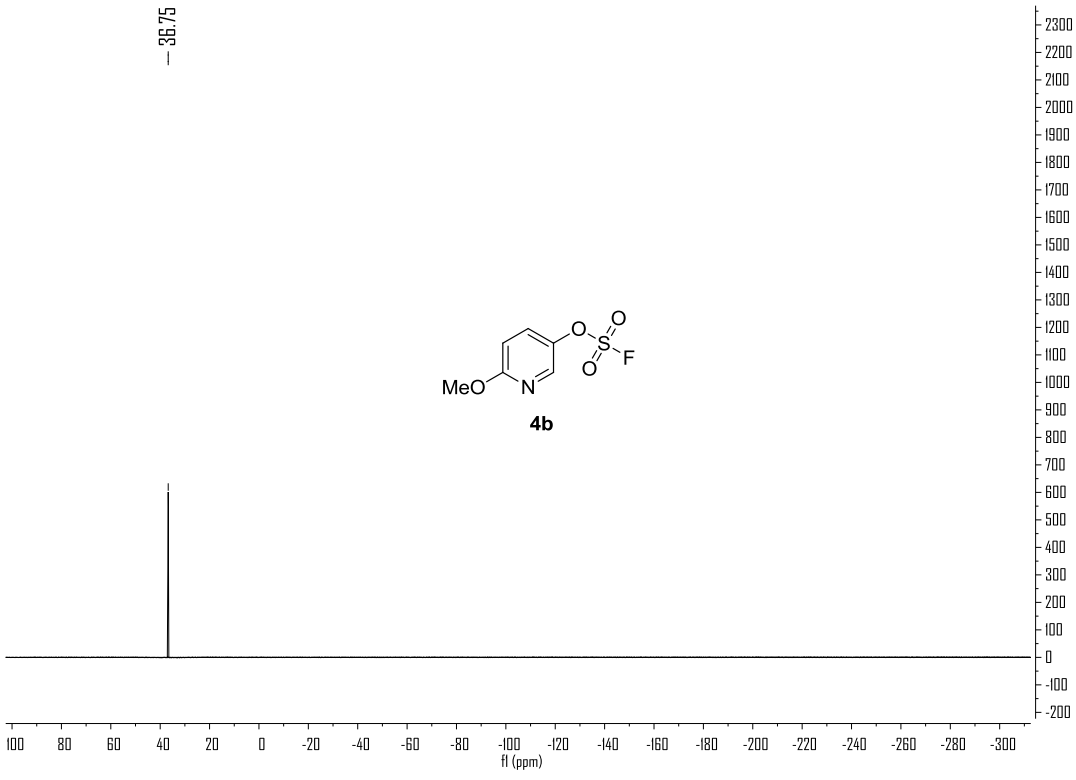
O
S
F
O
O
MeO
N

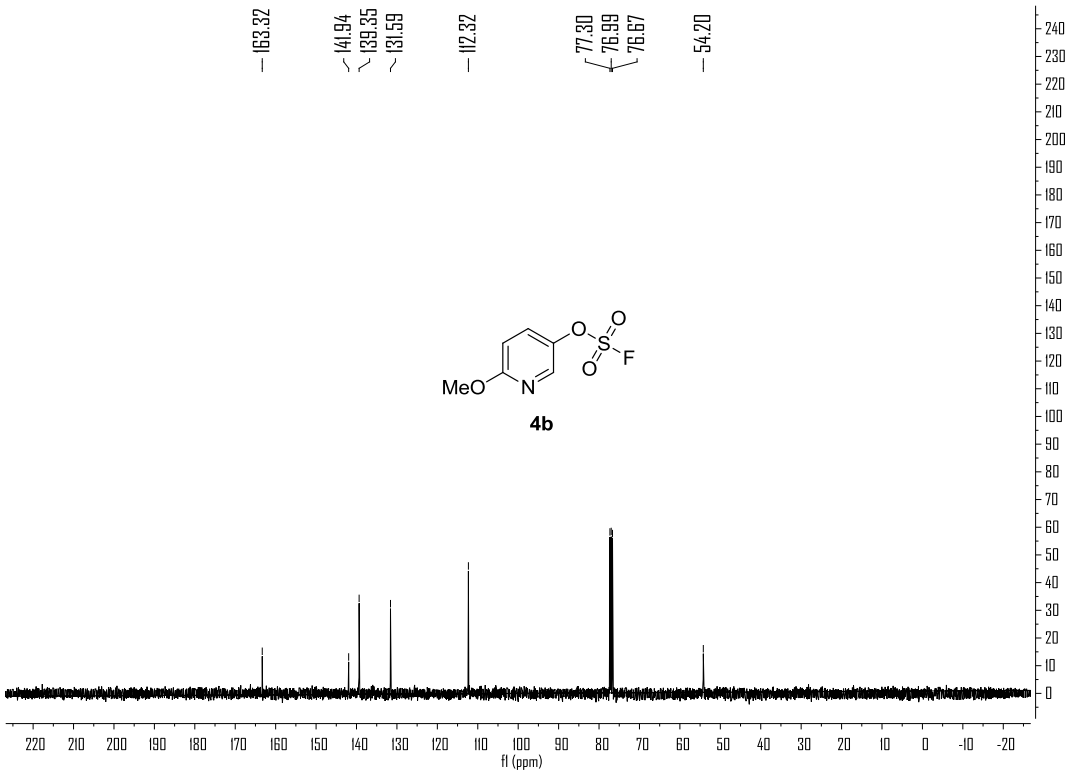
4a

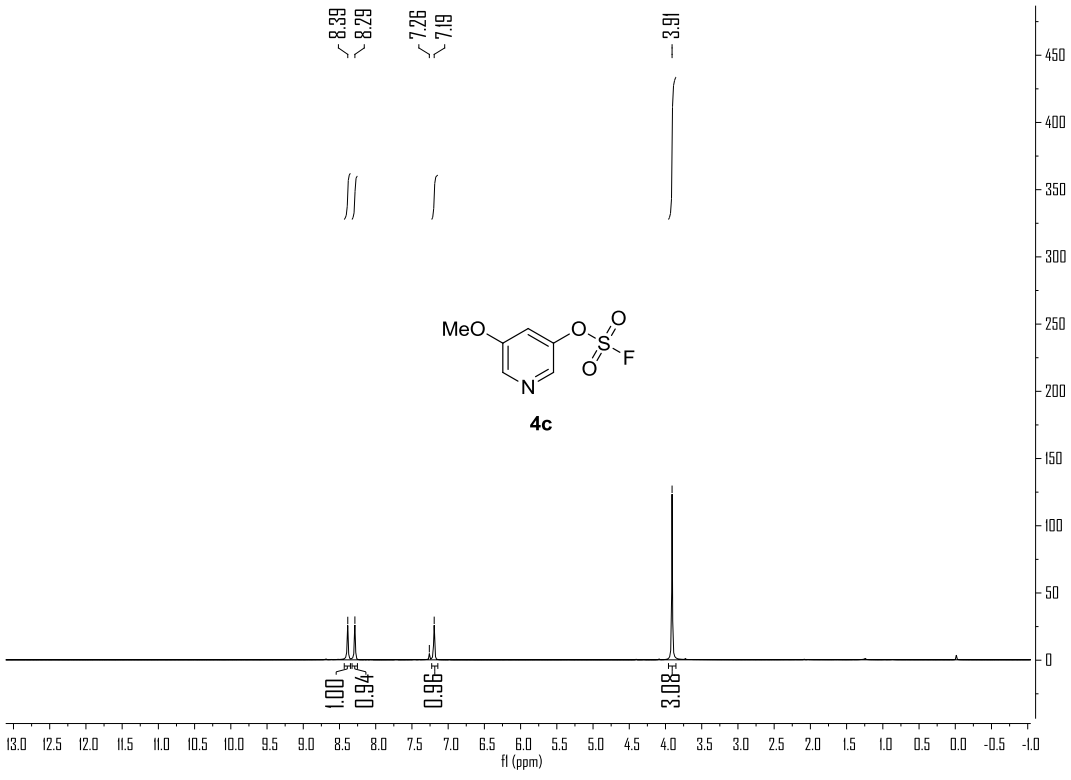

40.12
MeO
N
4a
f1 (ppm)

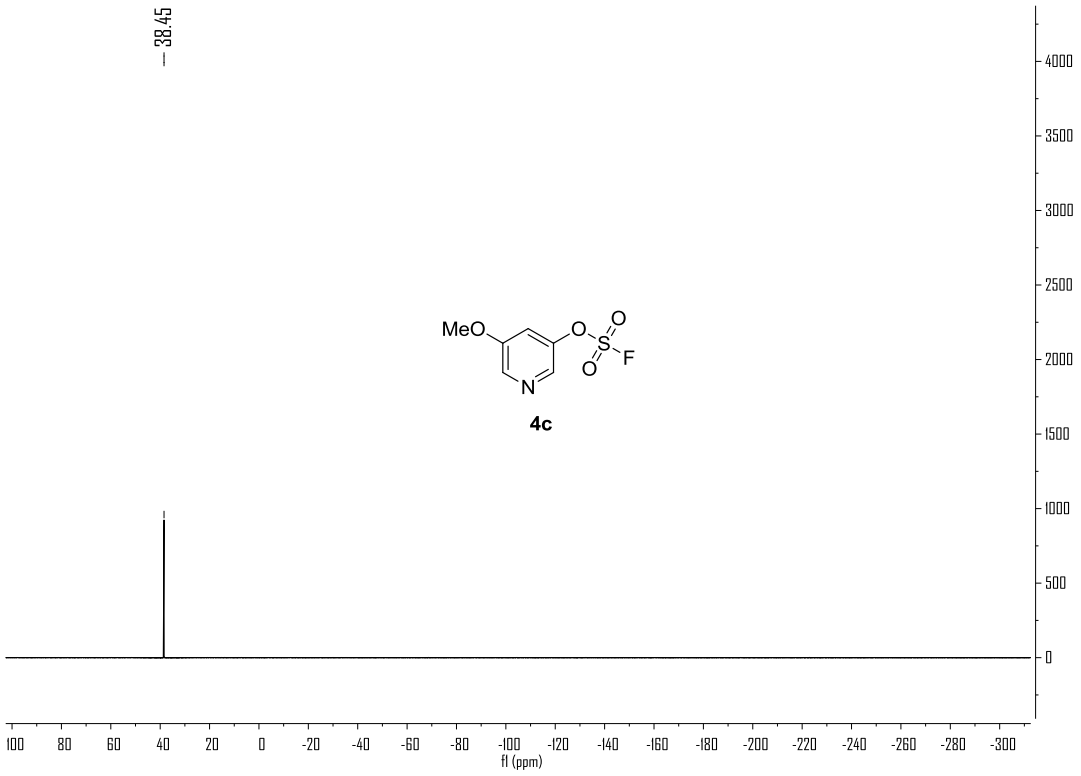

165.91
157.79
149.43
108.92
102.83
77.34
77.02
76.70
54.34
MeO
N
4a
f1 (ppm)

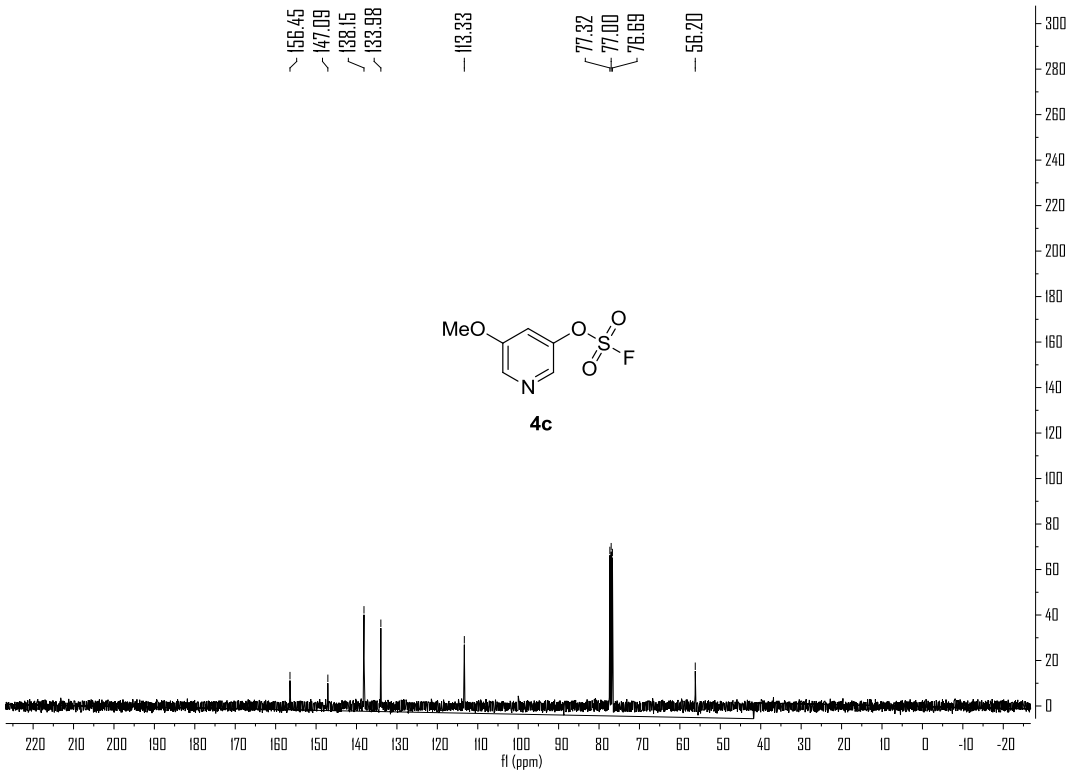

8.20
7.57
7.55
7.26
6.83
6.81
3.95
MeO
N
O
S
F
4b
0.93
0.98
0.97
3.00
f1 (ppm)

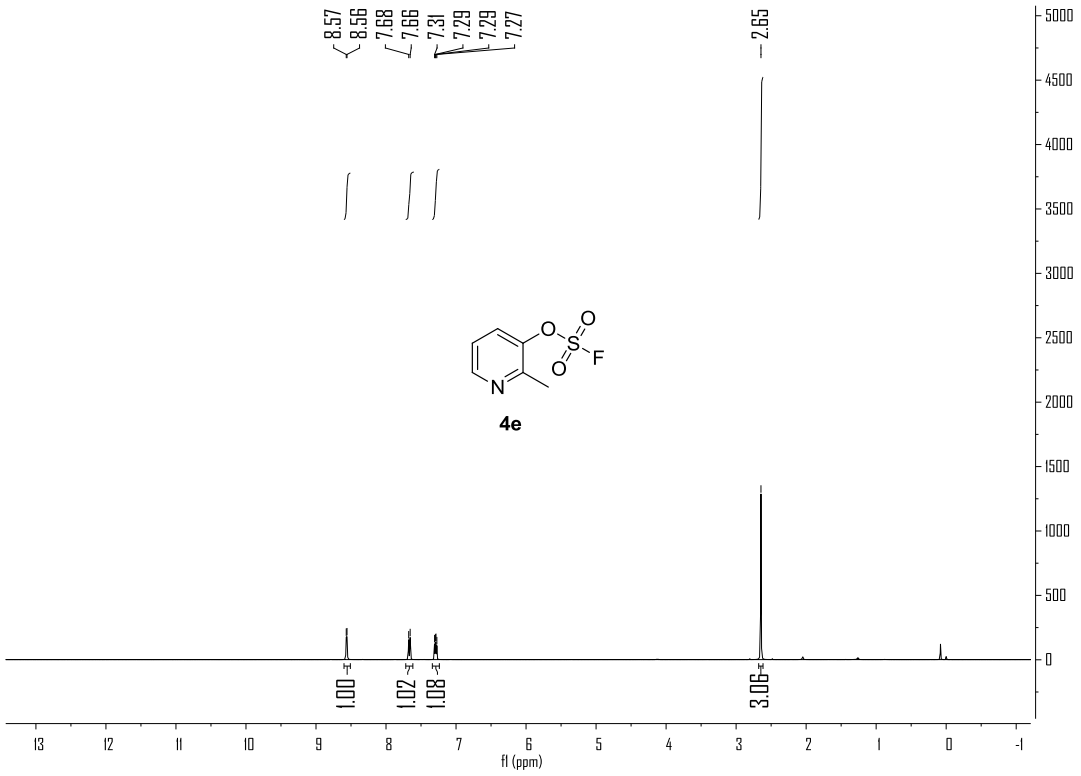

36.75
MeO
N
O
S
F
4b
f1 (ppm)

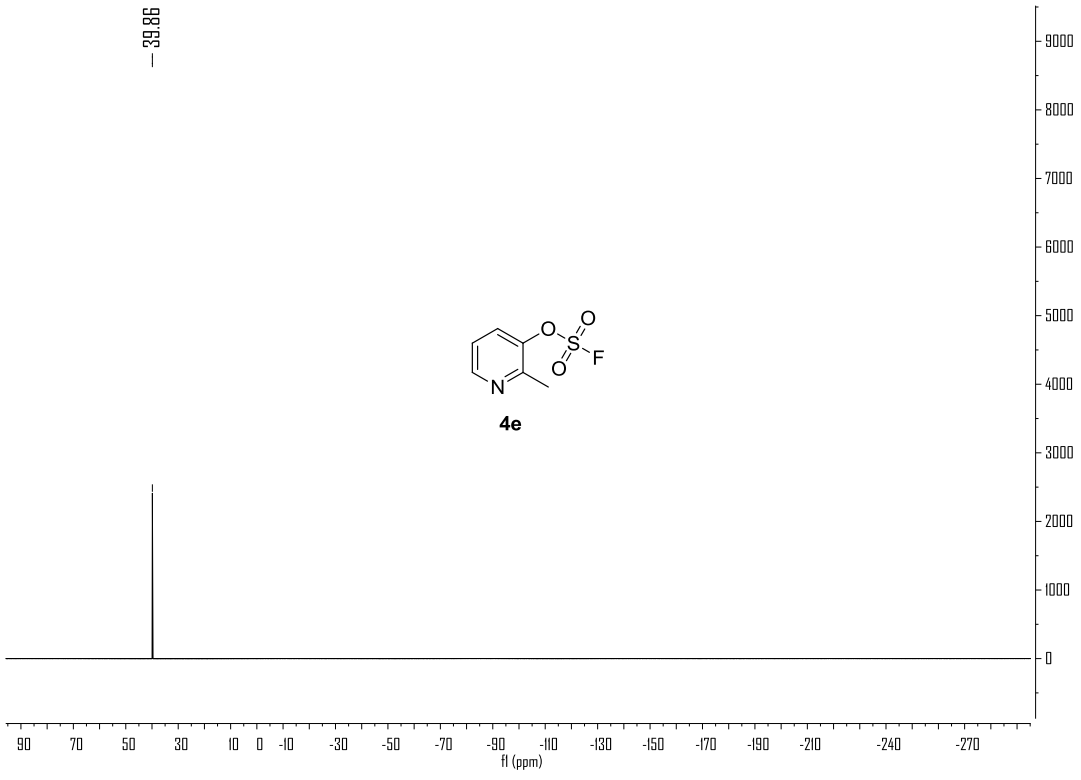

163.32
141.94
139.35
131.59
112.32
77.30
76.99
76.67
54.20
MeO
N
O
S
F
4b
f1 (ppm)

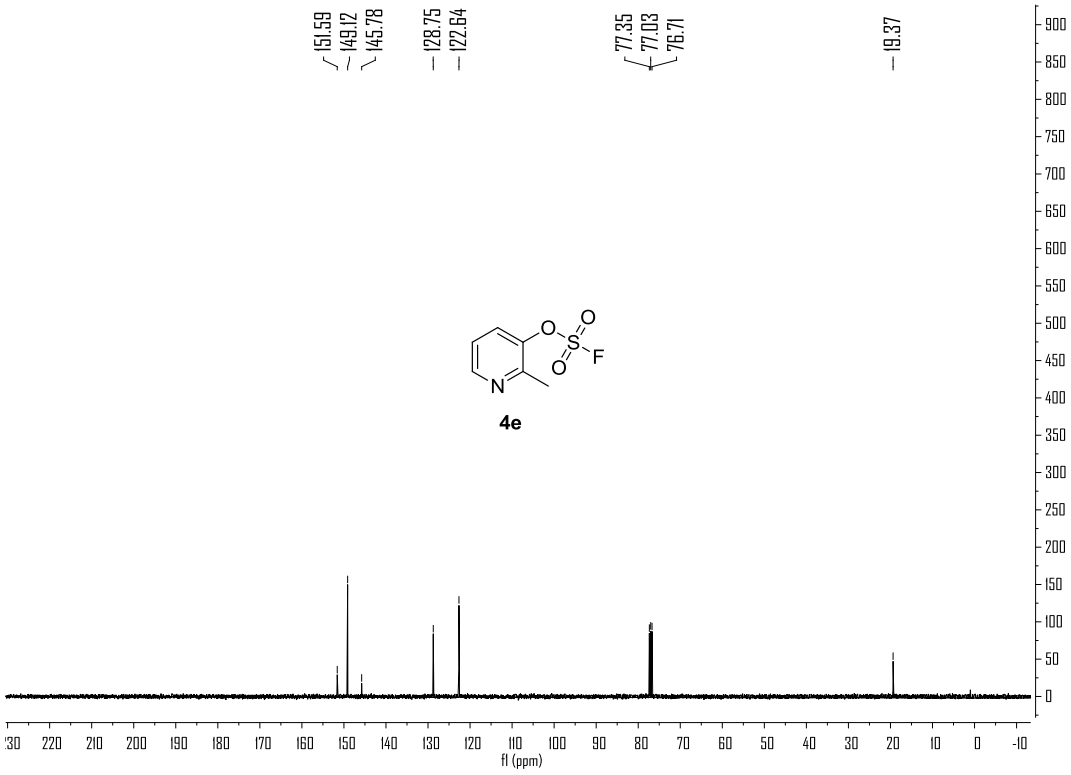

8.39
8.29
7.26
7.19
3.91
MeO
N
O
S
F
4c
1.00
0.94
0.96
3.08
f1 (ppm)

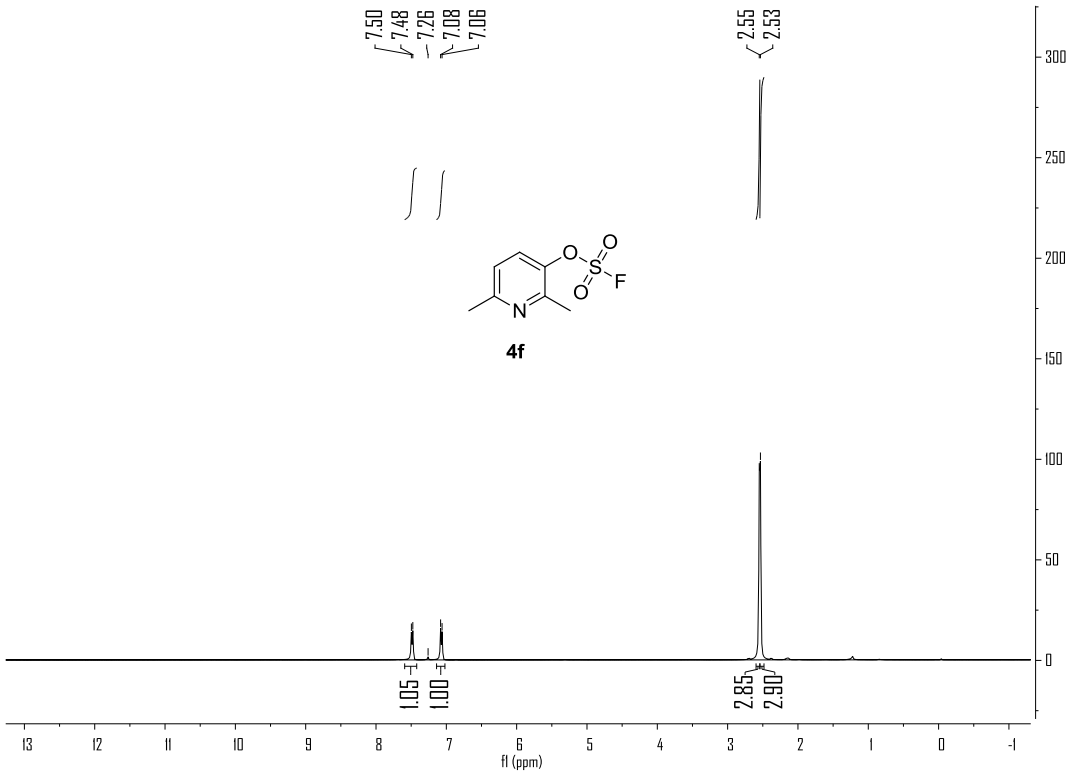

38.45
MeO
O
S
O
O
F
N
4c
4000
3500
3000
2500
2000
1500
1000
500
0
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

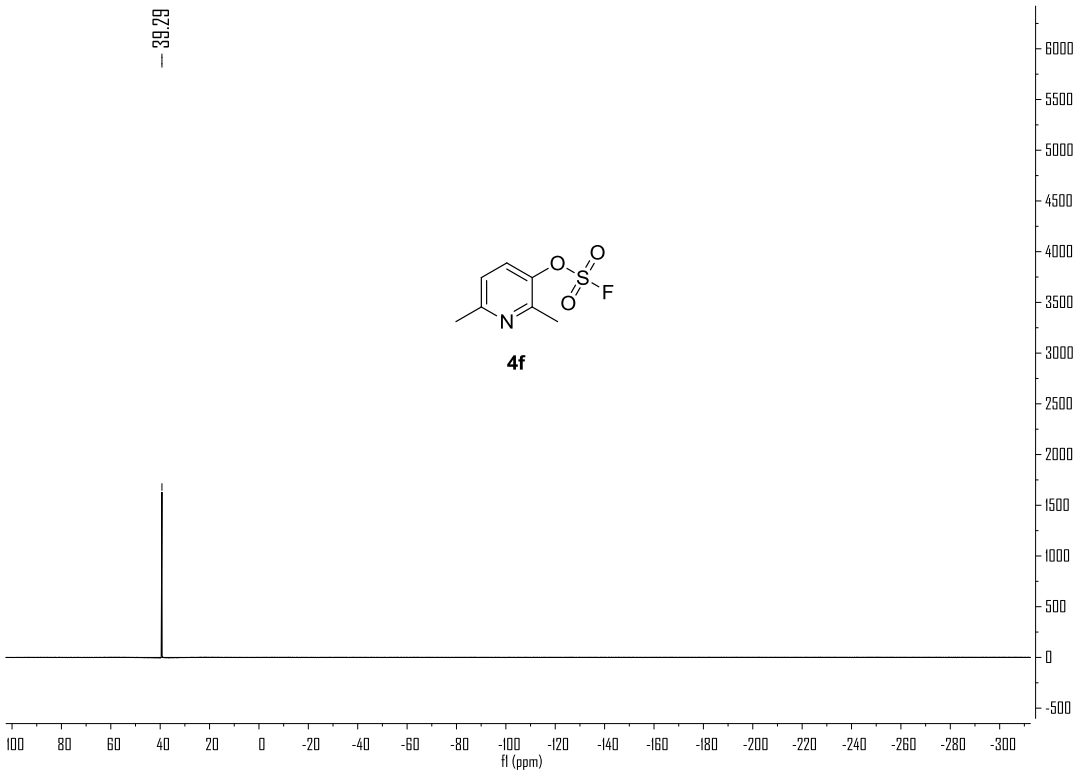

156.45
147.09
138.15
133.98
113.33
77.32
77.00
76.69
56.20
MeO
O
S
O
O
F
N
4c
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

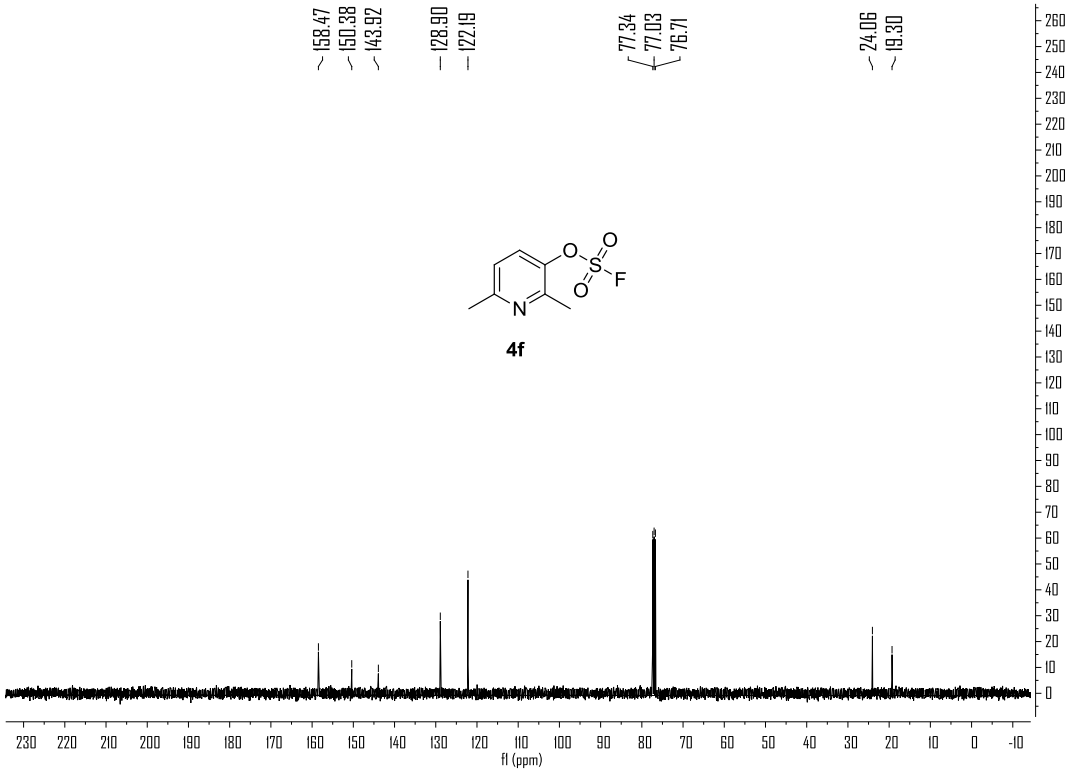

8.57
8.56
7.68
7.66
7.31
7.29
7.29
7.27
2.65
4e
1.00
1.02
1.08
3.06
f1 (ppm)

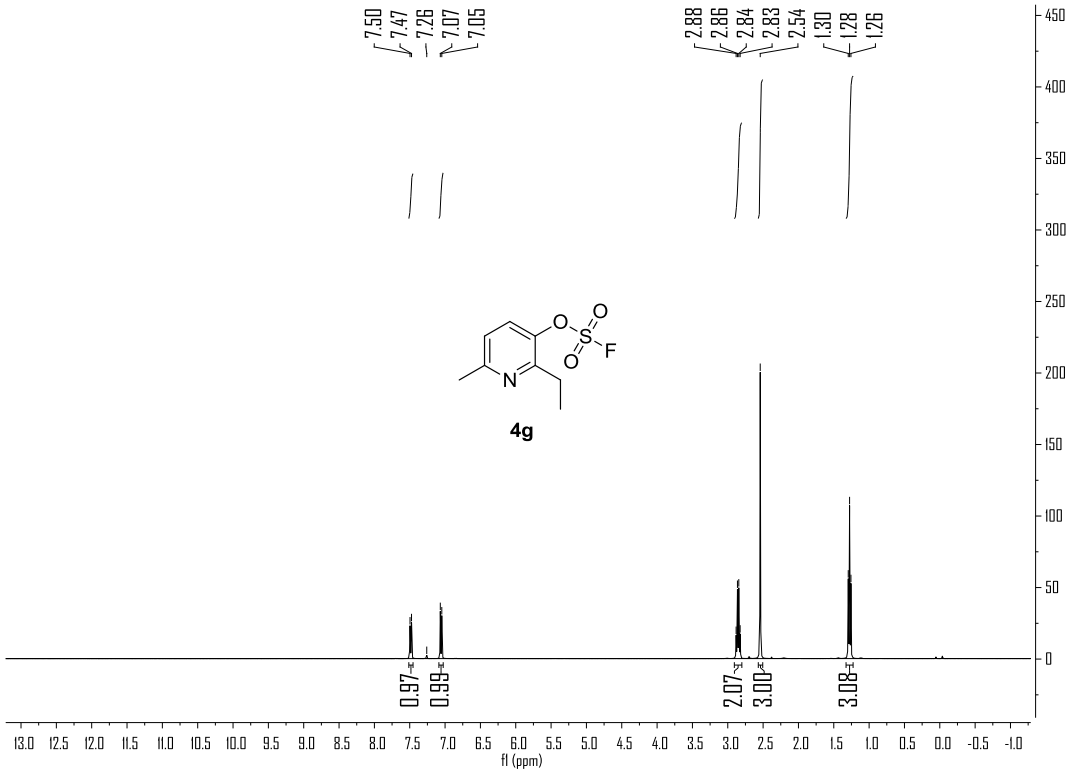

39.86
4e
f1 (ppm)


151.59
149.12
145.78
128.75
122.64
77.35
77.03
76.71
19.37
4e
fl (ppm)

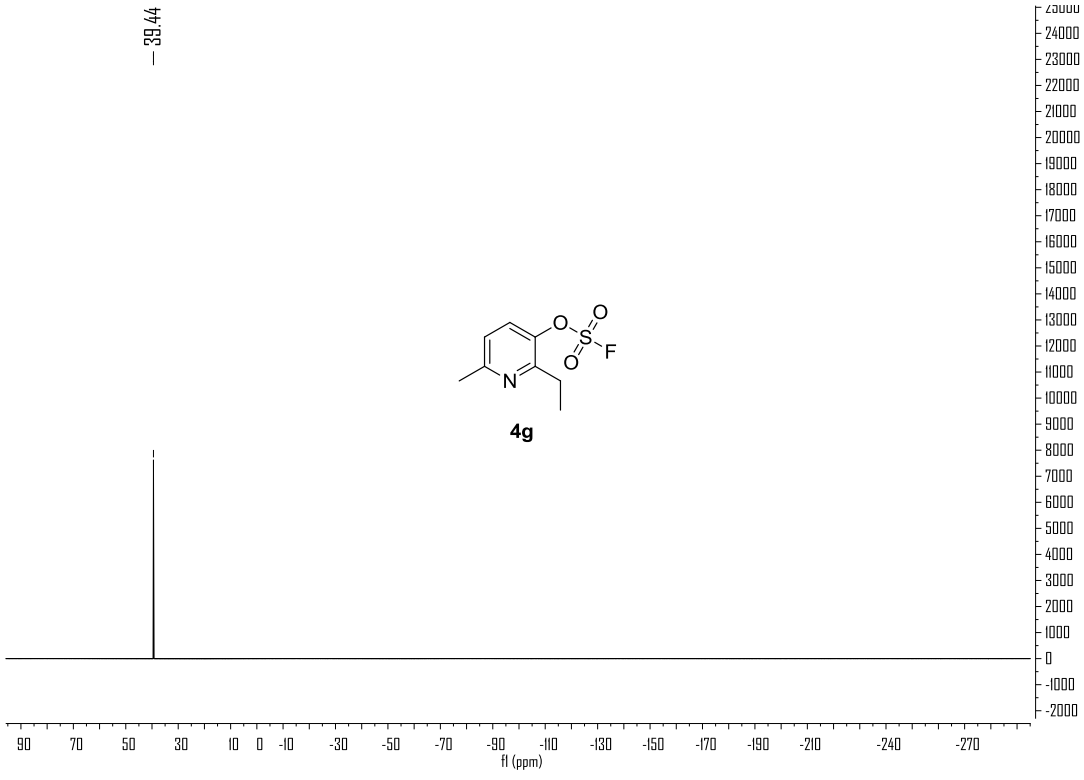

7.50
7.48
7.26
7.08
7.06
2.55
2.53
4f
1.05
1.00
2.85
2.90
fl (ppm)


39.29
4f
f1 (ppm)

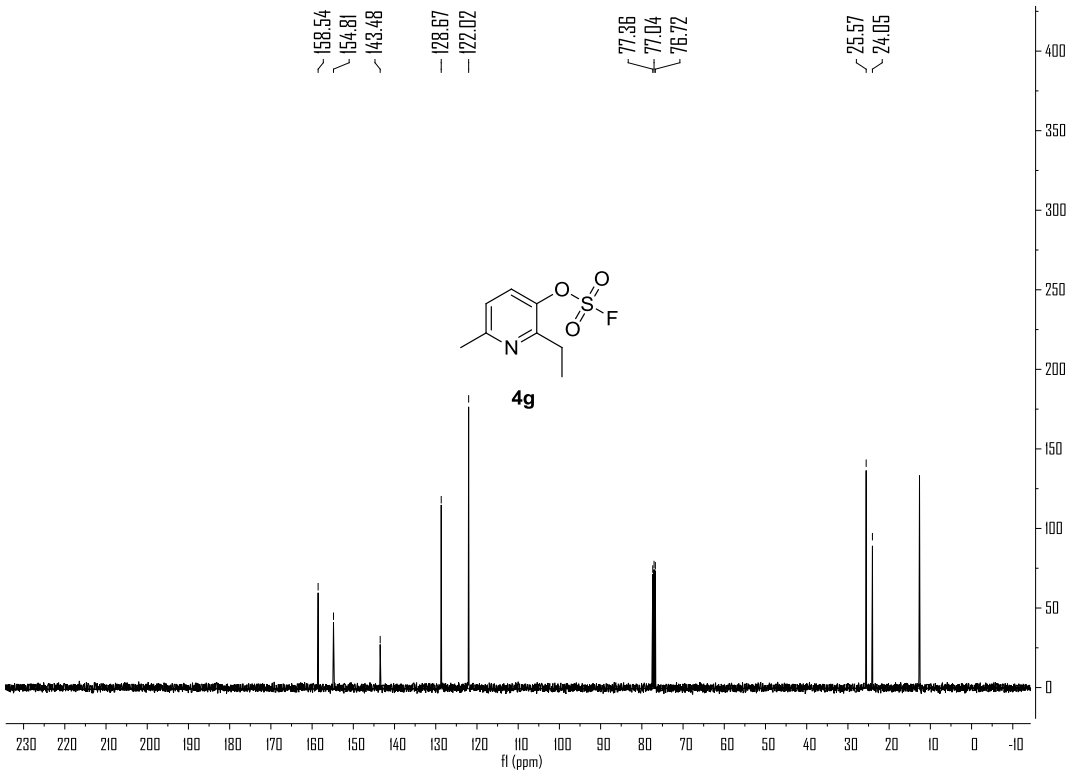

158.47
150.38
143.92
128.90
122.19
77.34
77.03
76.71
24.06
19.30
4f
f1 (ppm)

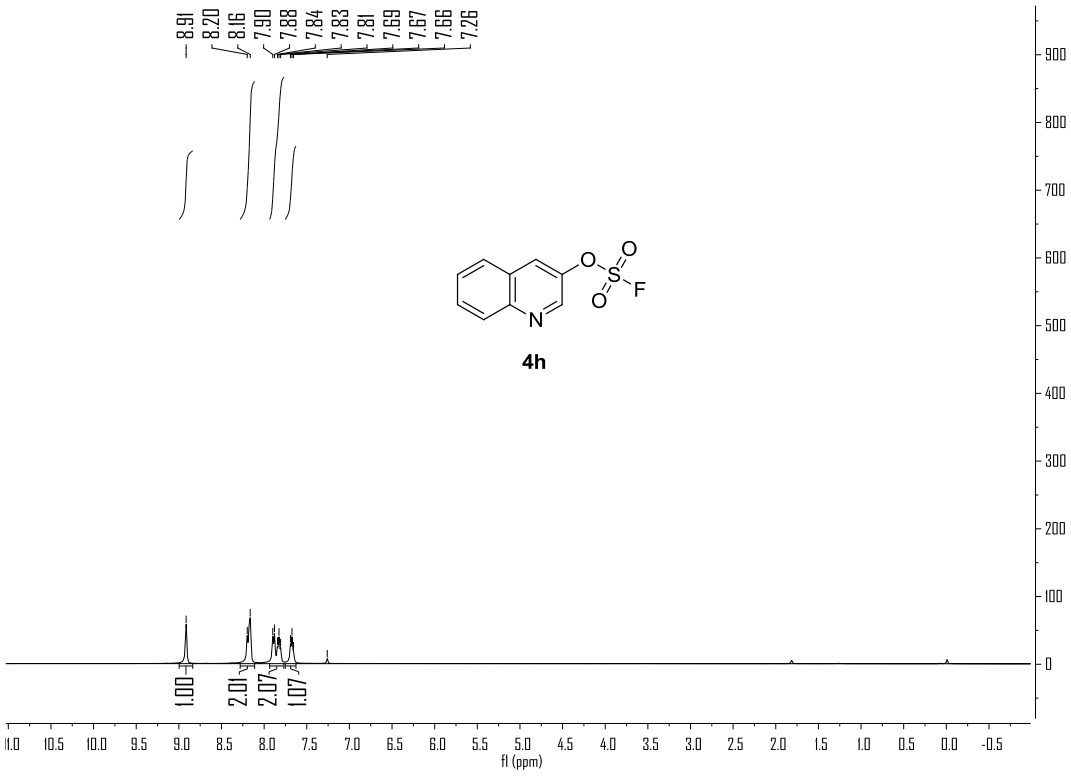

7.50
7.47
7.26
7.07
7.05
2.88
2.86
2.84
2.83
2.54
1.30
1.28
1.26
0.97
0.99
2.07
3.00
3.08
f1 (ppm)

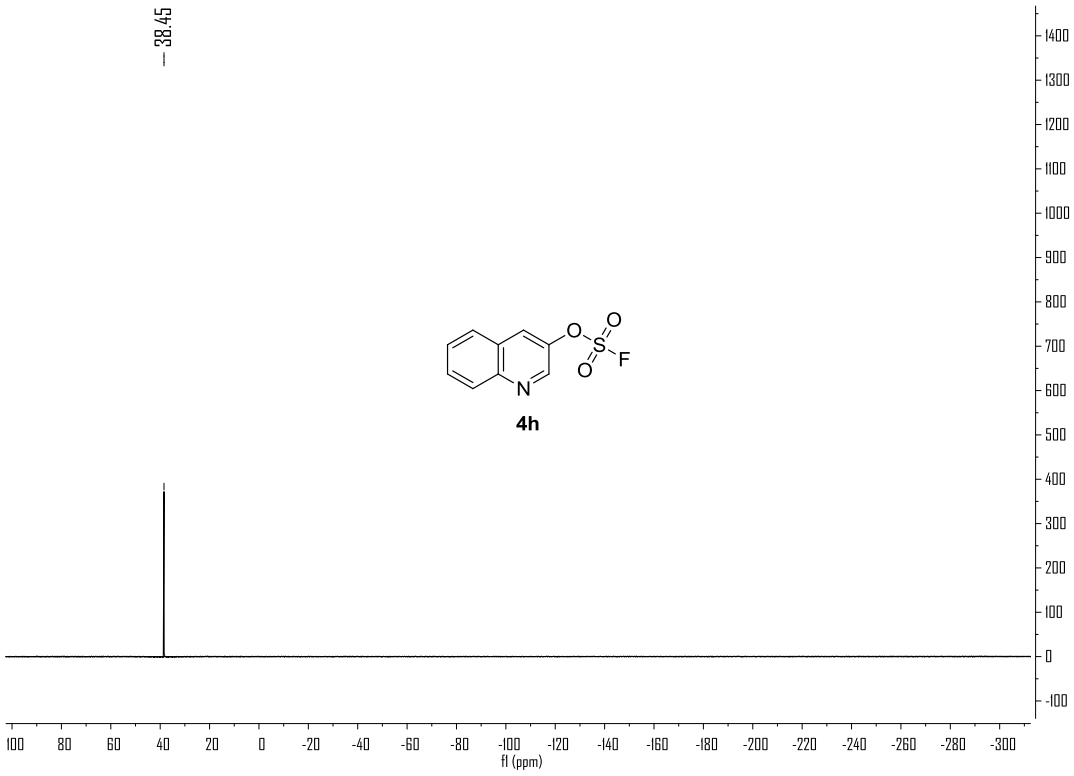
4g

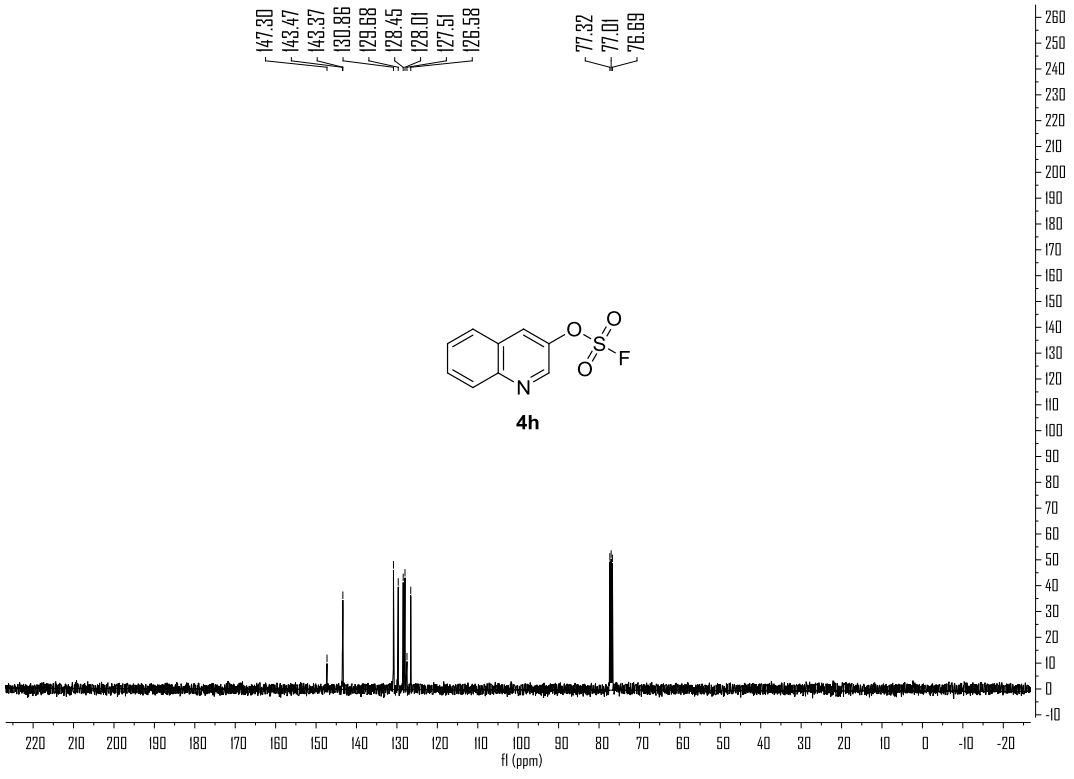

39.44
f1 (ppm)

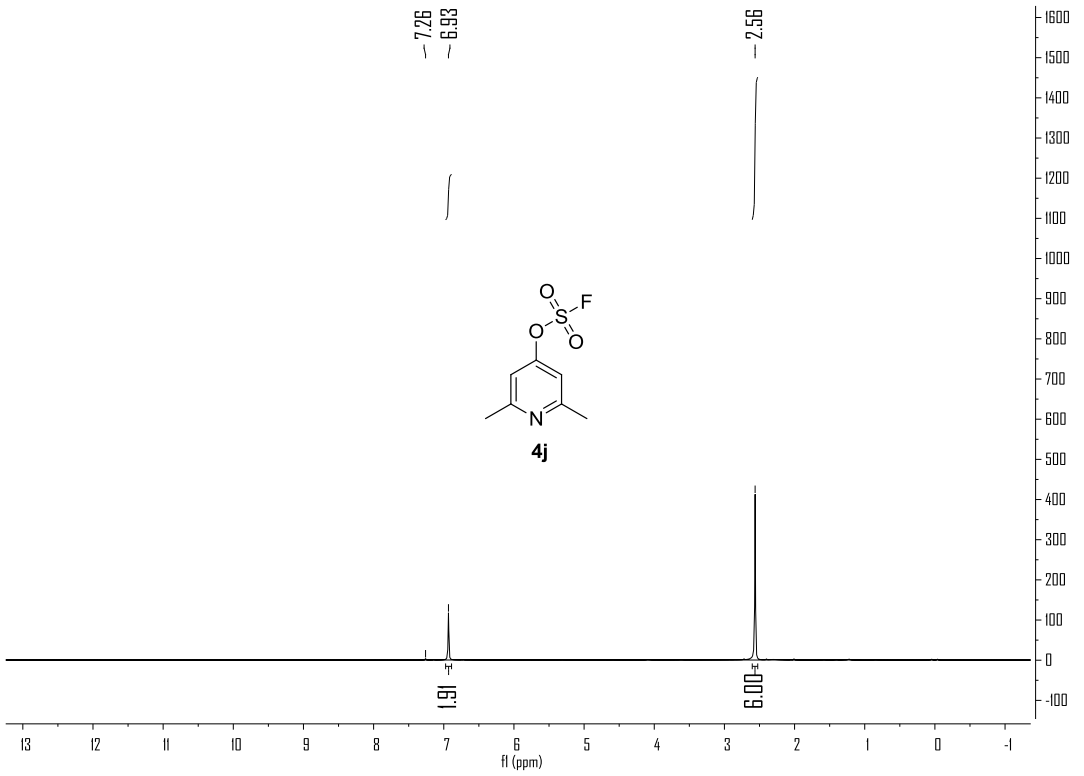
4g

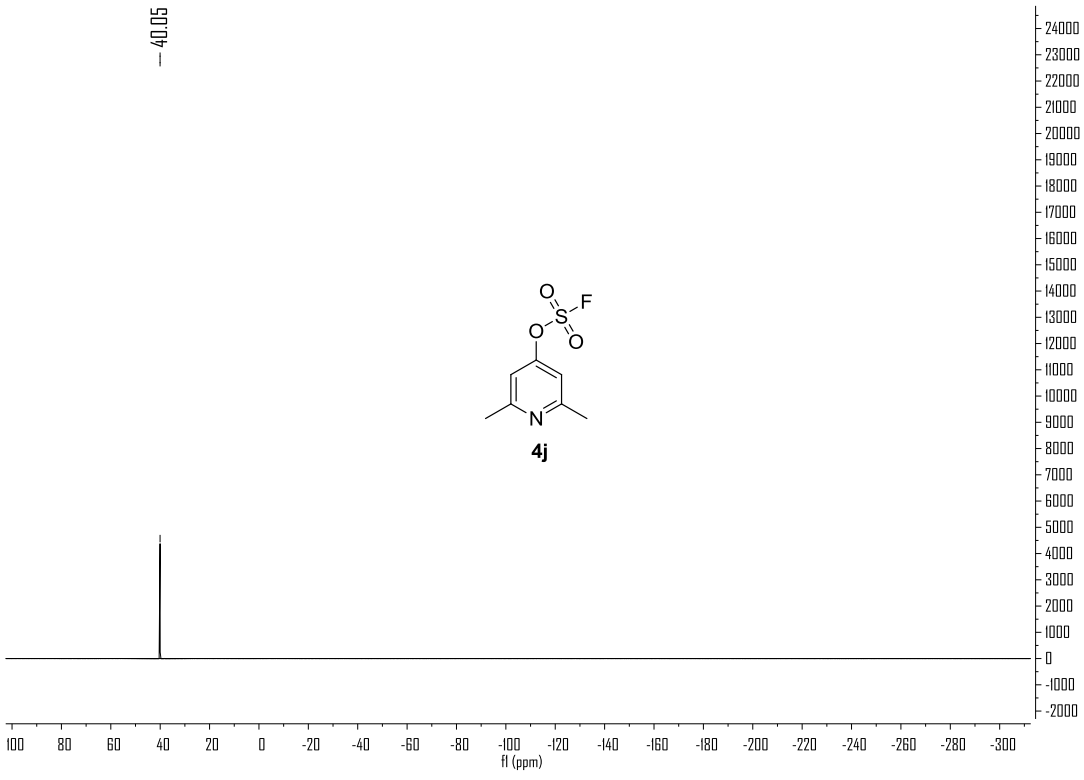

158.54
154.81
143.48
128.67
122.02
77.36
77.04
76.72
25.57
24.05
4g
f1 (ppm)

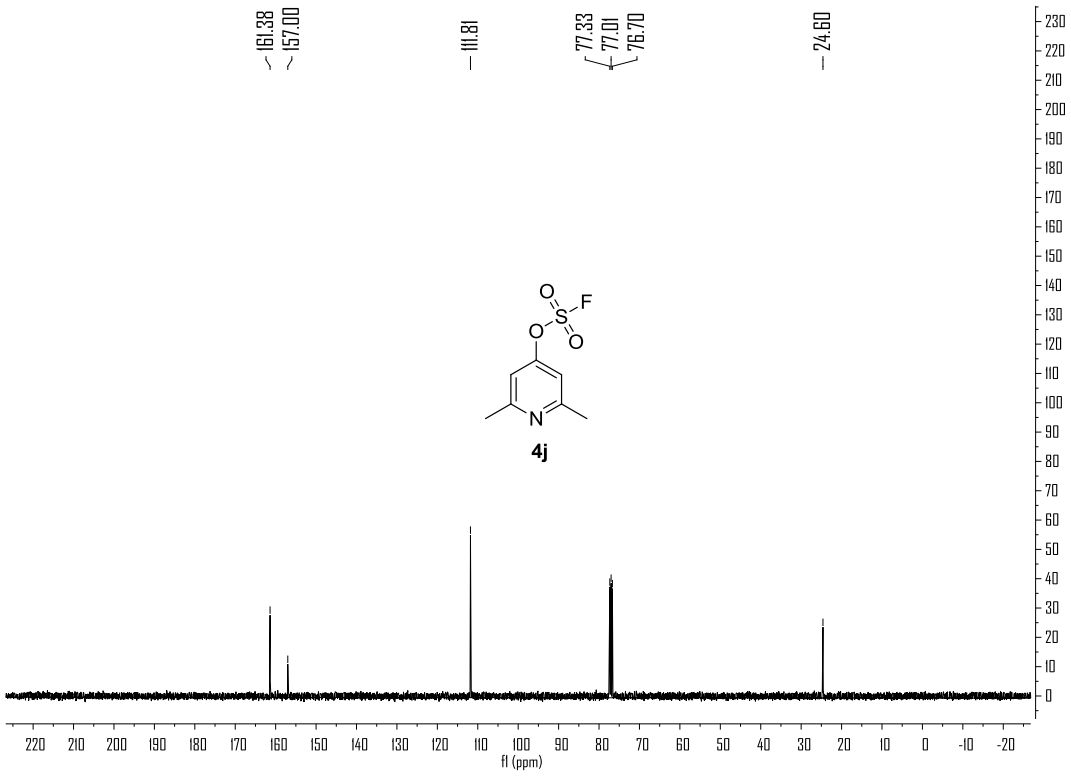

8.91
8.20
8.16
7.90
7.88
7.84
7.83
7.81
7.69
7.67
7.66
7.26
1.00
2.01
2.07
1.07
4h
f1 (ppm)

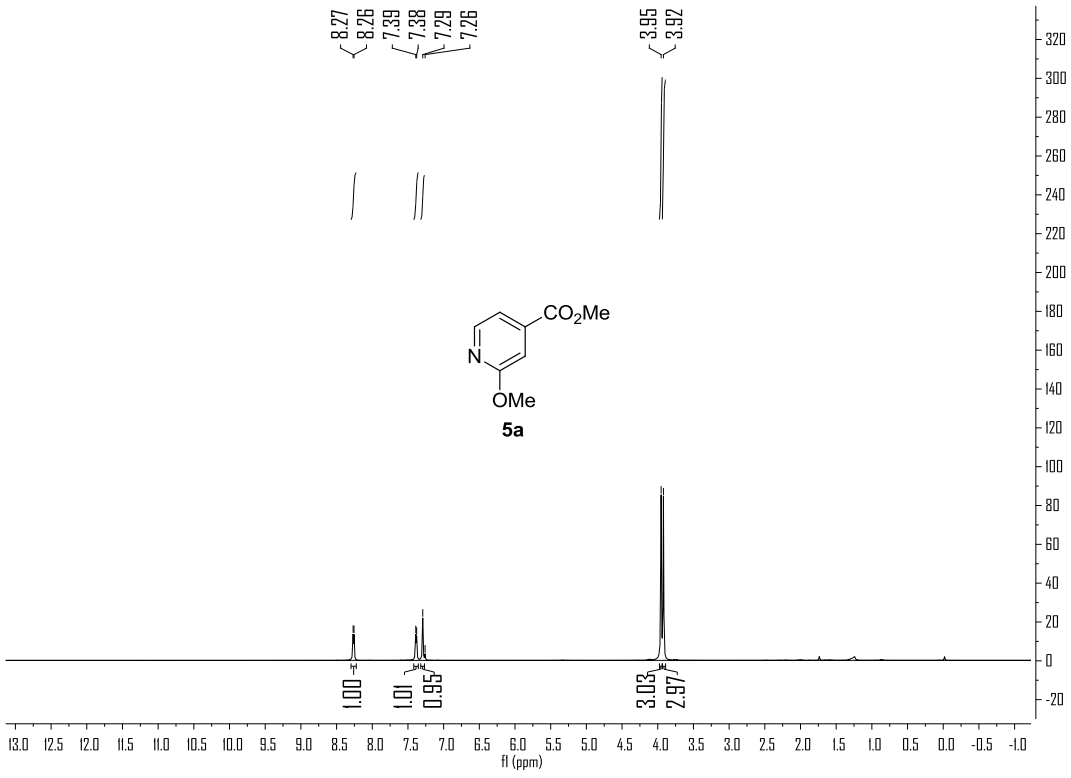

38.45
4h
f1 (ppm)

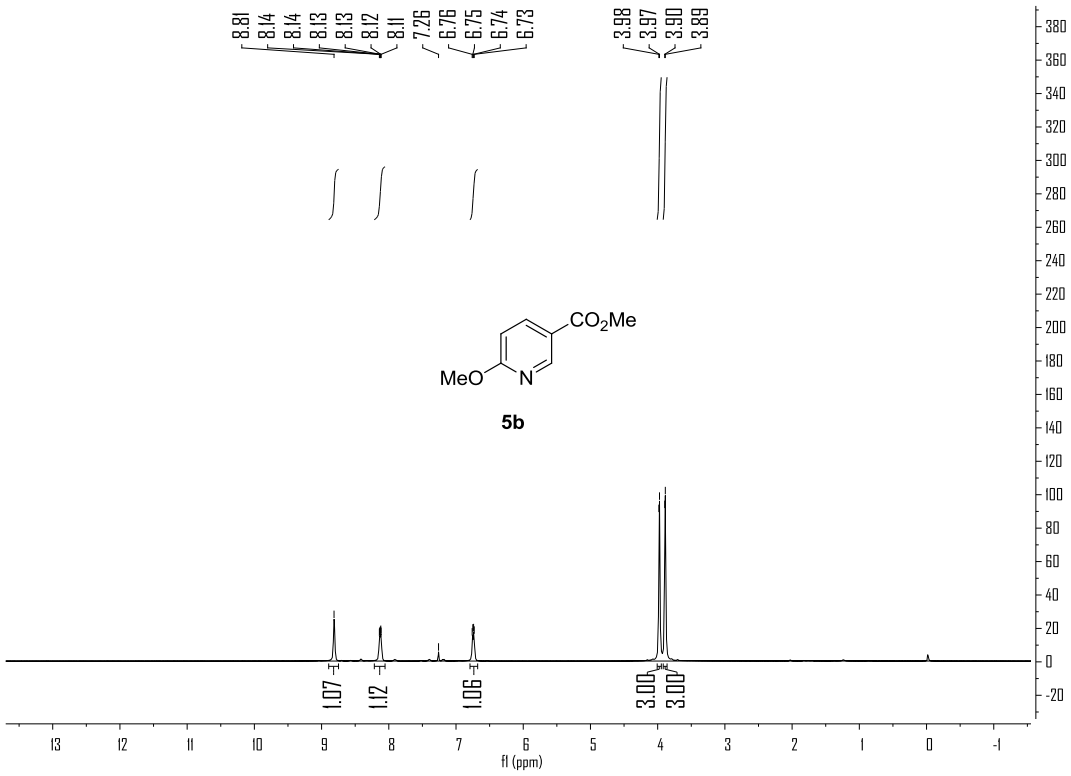

147.30
143.47
143.37
130.86
129.68
128.45
128.01
127.51
126.58
77.32
77.01
76.69
4h
f1 (ppm)


7.26
6.93
2.56
4j
1.91
6.00
f1 (ppm)

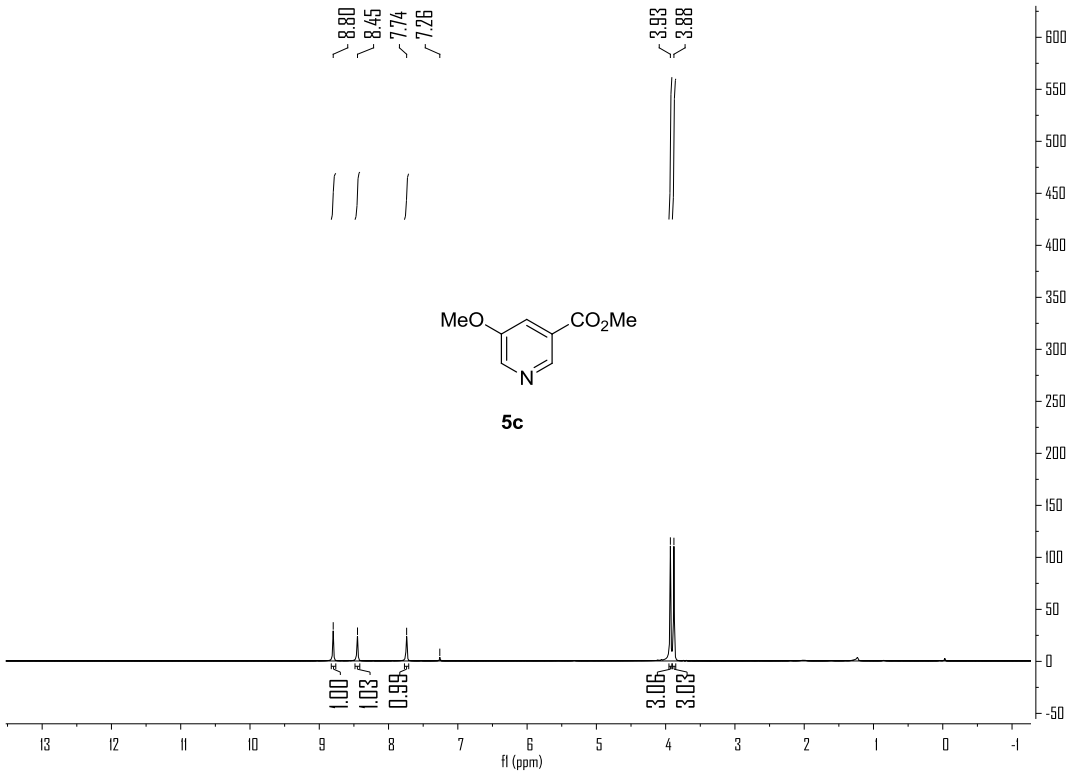

40.05
4j
f1 (ppm)


161.38
157.00
111.81
77.33
77.01
76.70
24.60
O
S
F
O
O
N
4j
f1 (ppm)

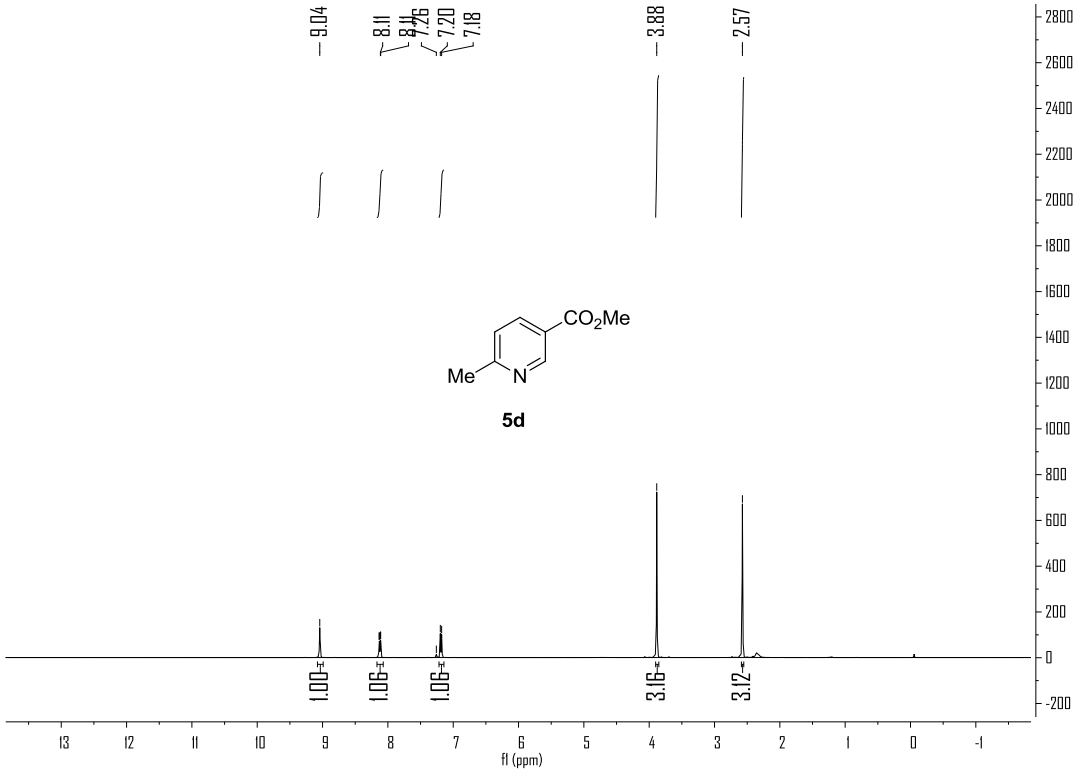

8.27
8.26
7.39
7.38
7.29
7.26
3.95
3.92
CO2Me
N
OMe
5a
1.00
1.01
0.95
3.03
2.97
f1 (ppm)


8.81
8.14
8.14
8.13
8.13
8.12
8.11
7.26
6.76
6.75
6.74
6.73
3.98
3.97
3.90
3.89
CO2Me
MeO
N
1.07
1.12
1.06
3.00
3.00
f1 (ppm)

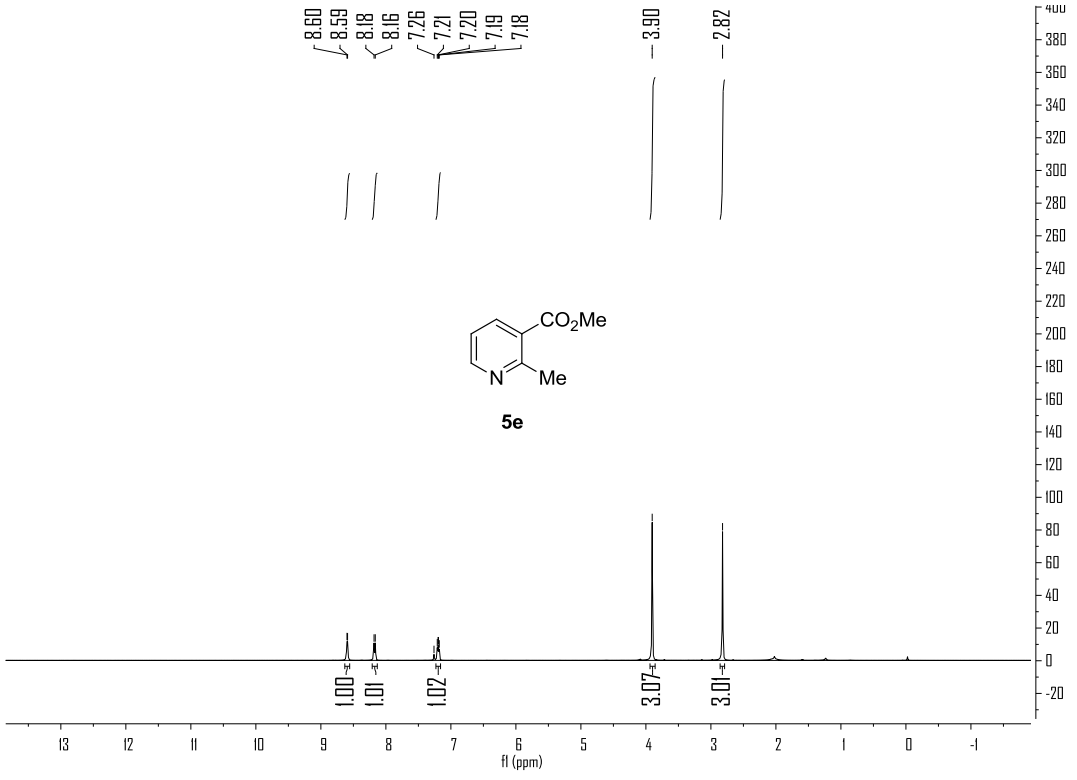
5b


8.80
8.45
7.74
7.26
3.93
3.88
MeO
CO2Me
N
1.00
1.03
0.99
3.06
3.03
f1 (ppm)

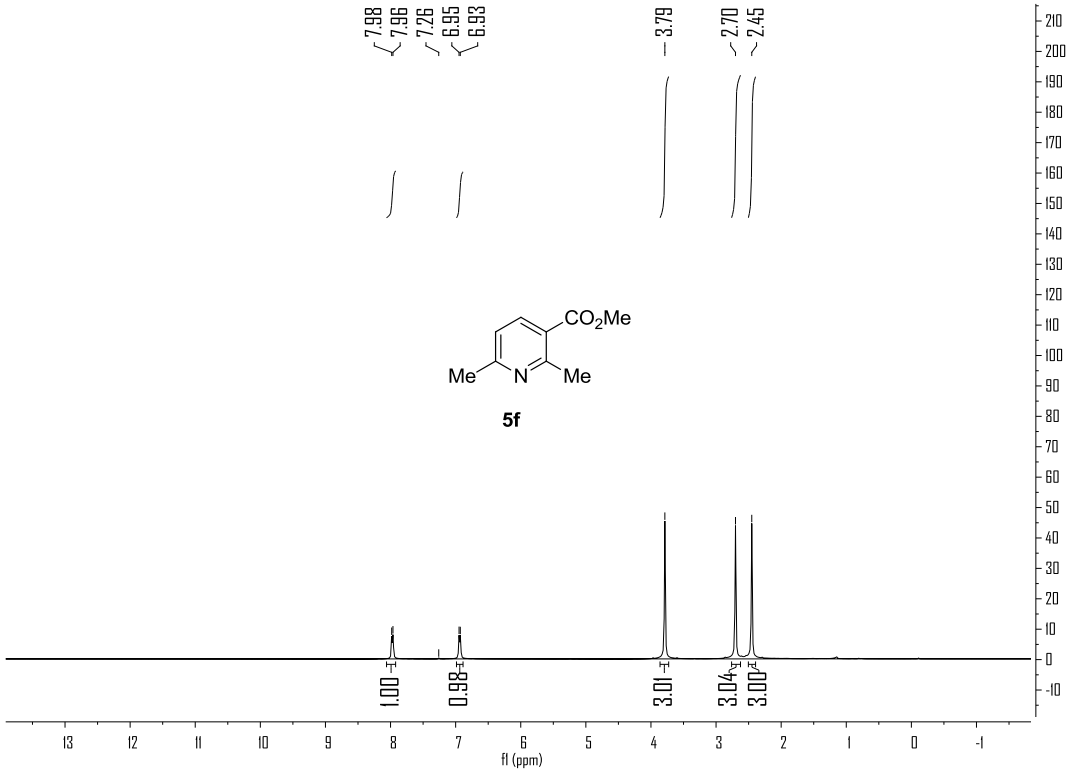
5c


9.04
8.11
7.26
7.20
7.18
3.88
2.57
CO2Me
Me
N
1.00
1.06
1.06
3.16
3.12
f1 (ppm)

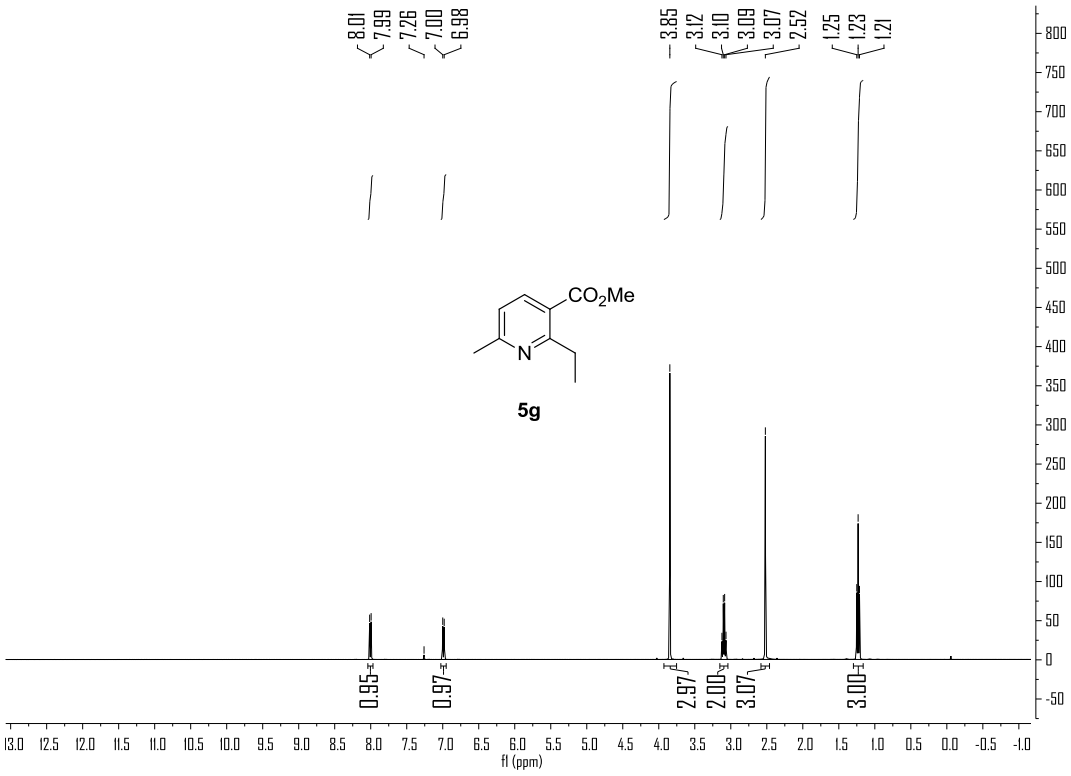
5d


8.60
8.59
8.18
8.16
7.26
7.21
7.20
7.19
7.18
3.90
2.82
CO2Me
N
Me
1.00
1.01
1.02
3.07
3.01
f1 (ppm)

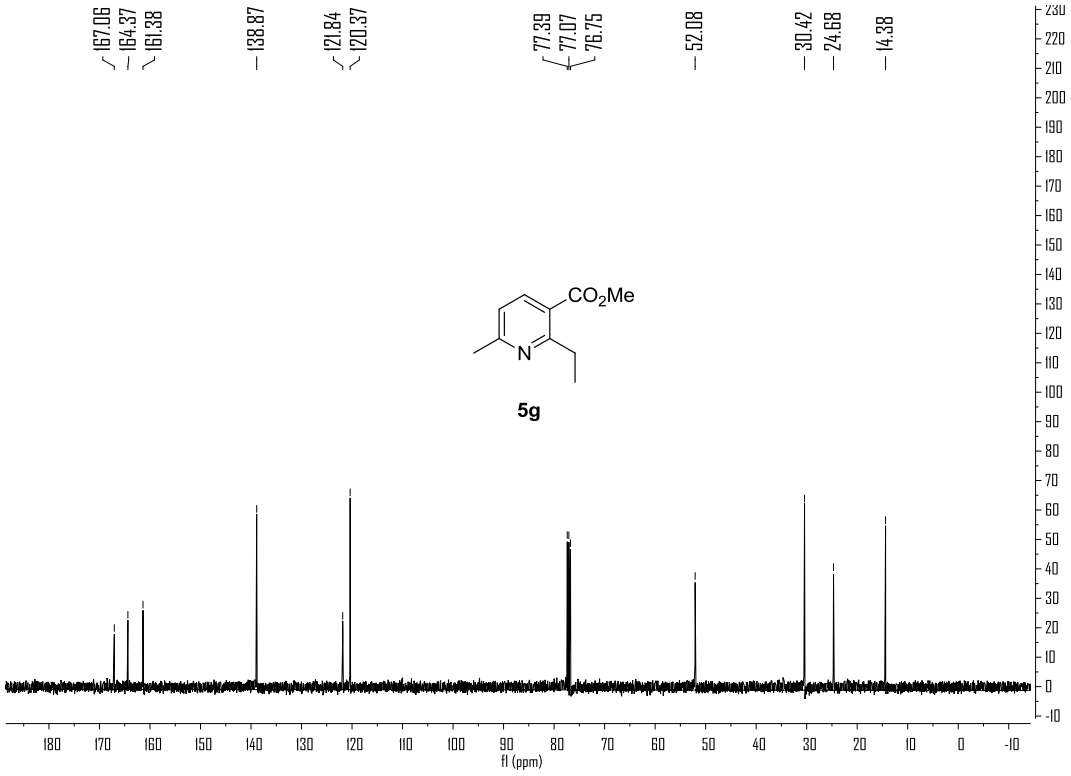
5e

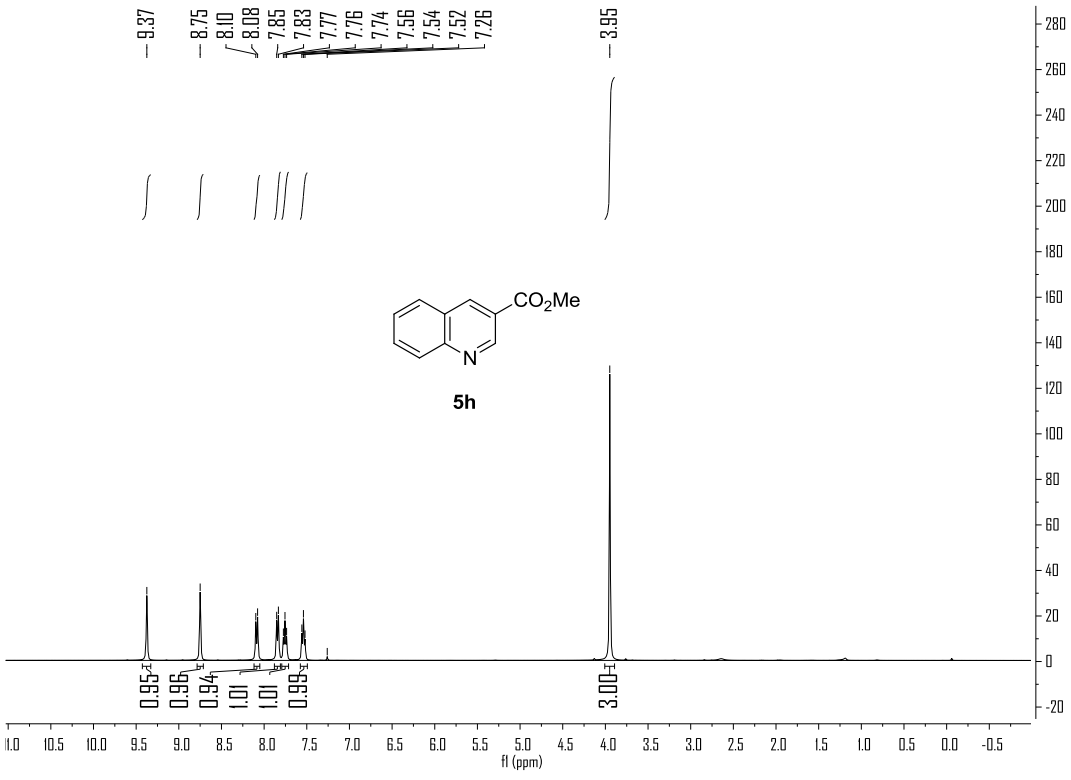

7.98
7.96
7.26
6.95
6.93
3.79
2.70
2.45
CO2Me
Me
N
Me
1.00
0.98
3.01
3.04
3.00
f1 (ppm)

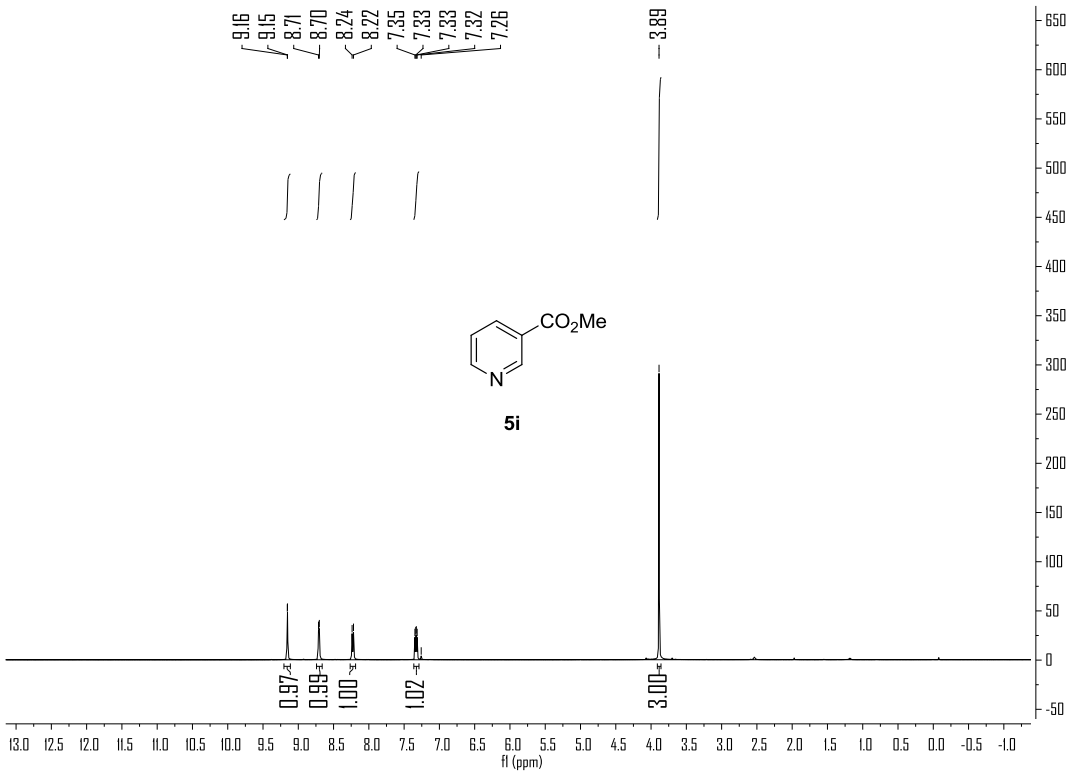
5f

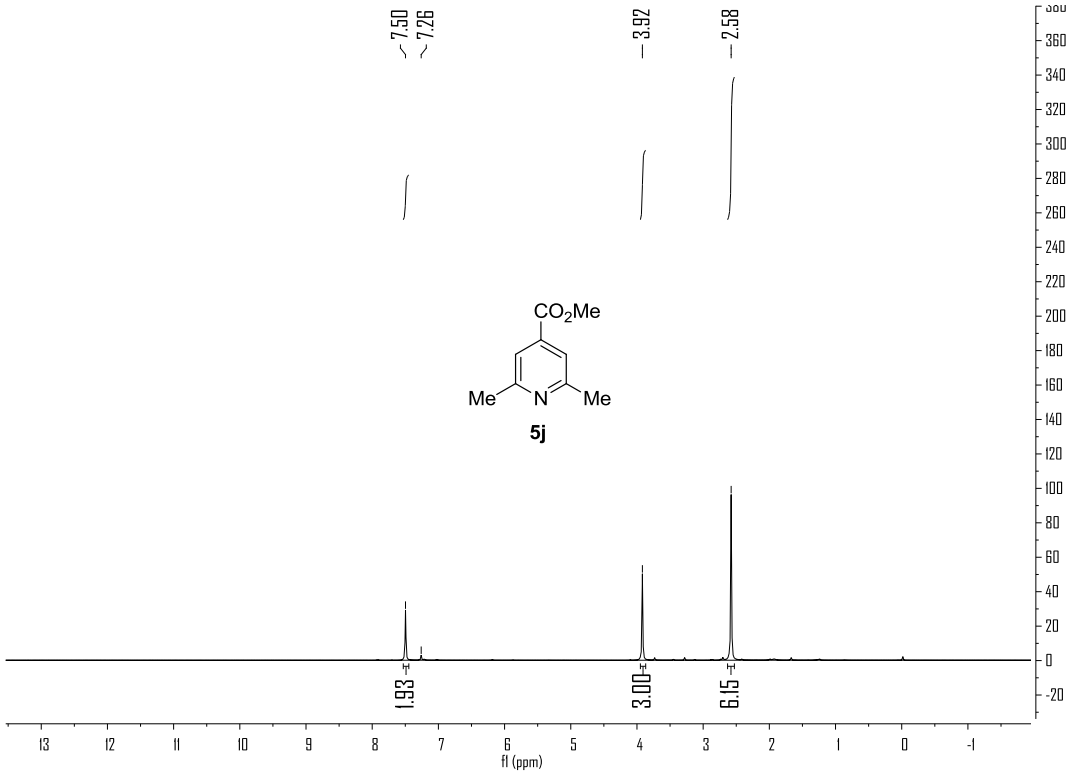

8.01
7.99
7.26
7.00
6.98
3.85
3.12
3.10
3.09
3.07
2.52
1.25
1.23
1.21
CO2Me
N
0.95
0.97
2.97
2.00
3.07
3.00
f1 (ppm)

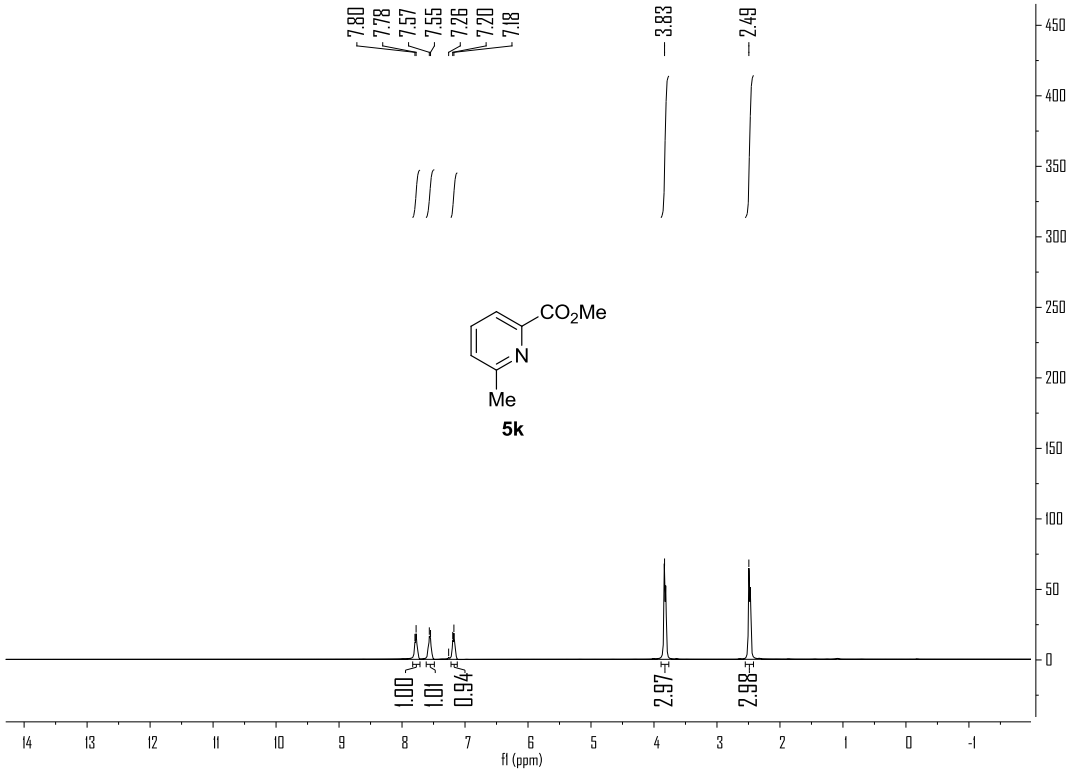
5g

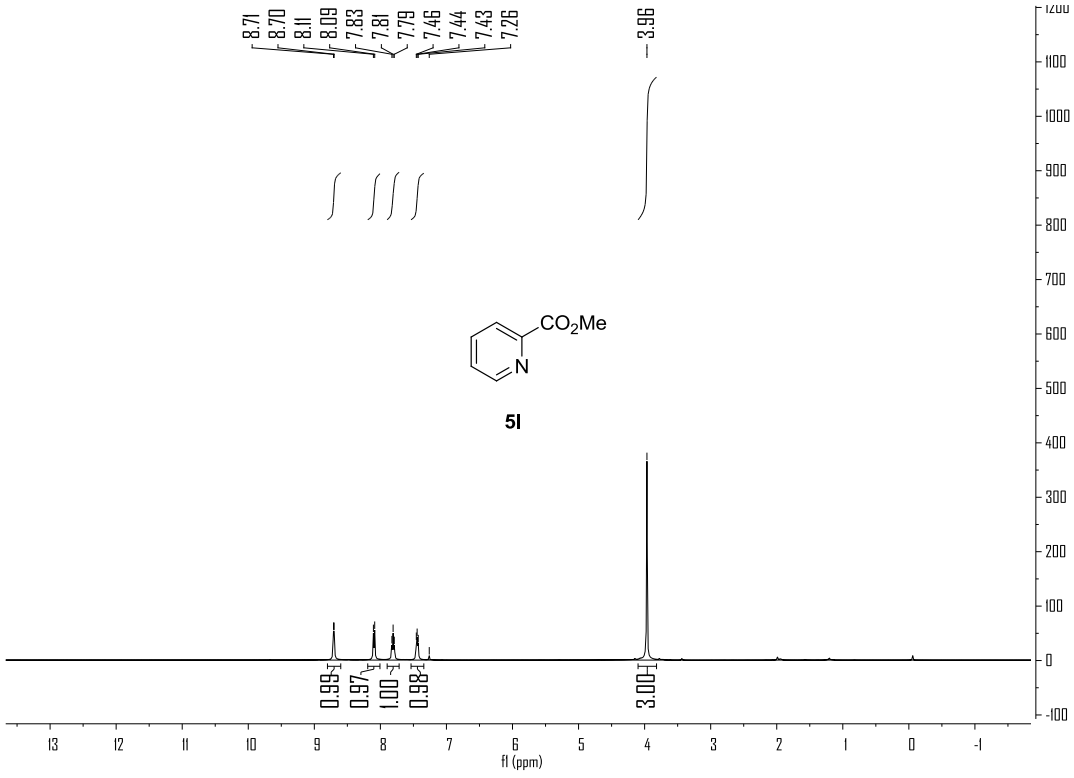

167.06
164.37
161.38
138.87
121.84
120.37
77.39
77.07
76.75
52.08
30.42
24.68
14.38
CO2Me
N
5g
f1 (ppm)


9.37
8.75
8.10
8.08
7.85
7.83
7.77
7.76
7.74
7.56
7.54
7.52
7.26
3.95
CO2Me
N
5h
0.95
0.96
0.94
1.01
1.01
0.99
3.00
f1 (ppm)


9.16
9.15
8.71
8.70
8.24
8.22
7.35
7.33
7.33
7.32
7.26
3.89
CO2Me
N
5i
0.97
0.99
1.00
1.02
3.00
f1 (ppm)


7.50
7.26
3.92
2.58
CO2Me
Me
N
Me
5j
1.93
3.00
6.15
f1 (ppm)


7.80
7.78
7.57
7.55
7.26
7.20
7.18
3.83
2.49
CO2Me
N
Me
5k
1.00
1.01
0.94
2.97
2.98
f1 (ppm)


8.71
8.70
8.11
8.09
7.83
7.81
7.79
7.46
7.44
7.43
7.26
3.96
CO2Me
N
5l
0.99
0.97
1.00
0.98
3.00
f1 (ppm)