Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Photoelectro-Catalyzed Undirected C–H Trifluoromethylation of Arenes: Catalyst Evaluation and Scope

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General Remarks

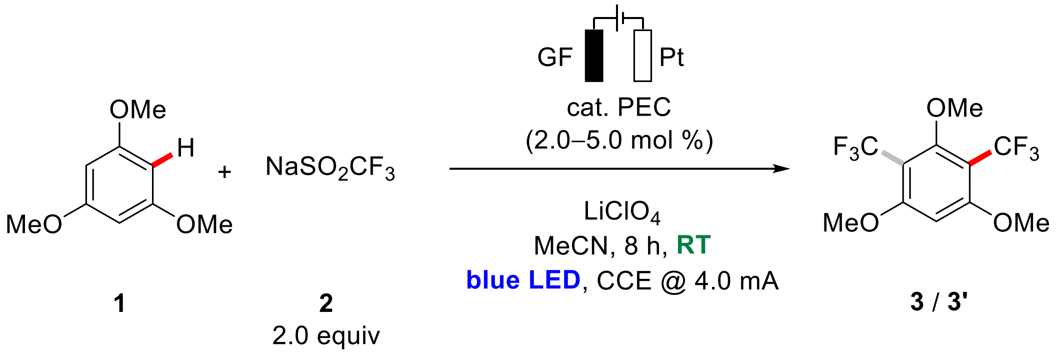
Catalytic reactions were performed under an inert atmosphere of N_2 using pre-dried glassware and standard Schlenk techniques. Substrates, $NaSO_2CF_3$, $Zn(SO_2CF_3)_2$ and solvents were obtained from commercial sources and were used without further purification. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and graphite felt electrodes (10 mm × 15 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat or a Metrohm MULTI AUTOLAB M204 potentiostat in two-electrode constant current mode. Yields refer to isolated compounds estimated to be >95% pure as determined by ^{1}H-NMR and GC. TLC was performed on Merck TLC Silica Gel 60 F_{254} with detection under UV light at 254 nm. Chromatographic separations were carried out on Merck Geduran SI-60 (0.040–0.063 mm, 230–400 mesh ASTM). Recycling preparative HPLC system from Japan Analytical Industries (*LC-92XX II Series, UV and RI Detector*) connected to JAIGEL 2HH series column with HPLC grade chloroform were employed for purification. IR spectra were recorded on a Bruker FT-IR alpha-P device. ESI-MS was recorded on Bruker Daltonik *micrOTOF* and *maXis*. The ratios of mass to charge (*m/z*) are reported and the intensity relative to the base peak (I = 100) is given in parentheses. Melting points (m.p.) were measured on Stuart® melting point apparatus SMP3, values are uncorrected. Nuclear magnetic resonance (NMR) spectroscopy was performed at 300 or 400 MHz (^{1}H-NMR), 75 or 100 MHz (^{13}C-NMR, APT), and 282 or 377 MHz (^{19}F-NMR) on Bruker *Avance III HD 300, Avance III 300, Avance III 400, Avance III HD 400, Avance Neo 400* instruments. Chemical shifts (δ) are provided in ppm and spectra referred to non-deuterated solvent signal.

General Procedure for the Photoelectrochemical C–H Trifluoromethylation

The photoelectrocatalysis was carried out in an undivided cell with a GF anode (10 mm × 15 mm × 6 mm) and a Pt cathode (10 mm × 15 mm × 0.25 mm). Unless in case of volatile substrates, the (hetero-)arene (0.25 mmol, 1.0 equiv), $NaSO_2CF_3$ (**2**, 78 mg, 0.50 mmol, 2.0 equiv), $LiClO_4$ (42 mg, 0.40 mmol) and the photocatalyst (2.0 or 5.0 mol %) were placed into a 10 mL Schlenkflask and closed with a stopper with integrated electrode holders. The vial was evacuated and purged with N_2 three times, before volatile compounds were added and the components were dissolved in CH_3CN (4.0 mL) under N_2. The photoelectrocatalysis was performed at ambient temperature with a constant current of 4.0 mA maintained for 8–16 h under visible light irradiation (2 × Kessil A360N or 2× Kessil A160WE). After completion of the reaction time, the resulting mixture was transferred into a round bottom flask. The vial was rinsed carefully and the GF anode was washed with CH_2Cl_2 (3 × 10 mL) in an ultrasonic bath. Evaporation of the solvent and subsequent column chromatography on silica gel afforded the corresponding products.

Screening of Various Photoelectrocatalysts

Table S1: Comparison of different photoelectrocatalysts in the trifluoromethylation of arene **1**.



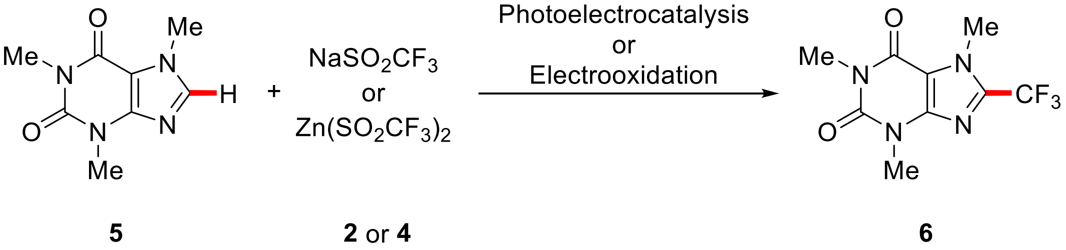
Entry	Photoelectrocatalyst	Conversion[a]	Ratio (**3**:**3'**)
1	[Mes-Acr]ClO_4	95% (88%)	4.9:1
2	TAC	89% (87%)	6.4:1
3	DDQ	93%	1.7:1
4	DCA	96%	5.0:1
5	DCN	90%	4.3:1
6	TBAI	95%	2.2:1
7	TBABr	97%	1.5:1
8	TBACl	95%	1.4:1
9	$CeCl_3\cdot 7H_2O$	90%	3.5:1
10	$CeCl_3\cdot 7H_2O$[b]	93%	2.6:1
11	$[Ru(bpy)_3](PF_6)_2$[c]	91%	3.3:1
12	$[Ni(bpy)_3]Br_2$[c]	89%	5.2:1
13	$[Fe(bpy)_3](PF_6)_2$[c]	87%	3.8:1
14	$(n\text{-}Bu_4N)_4[W_{10}O_{32}]$[c]	85%	5.5:1
15	---	9%	---
16	[Mes-Acr]ClO_4[d]	7%	---
17	[Mes-Acr]ClO_4[e]	4%	---
18	TBABr[d]	39%	12.0:1
19	[Mes-Acr-ClO_4][f]	63%	20:1

[a] Reaction conditions: Undivided cell, GF anode (10 mm × 15 mm × 6 mm), Pt cathode (10 mm × 15 mm × 0.25 mm), constant current electrolysis at 4.0 mA. **1** (0.25 mmol), **2** (0.50 mmol), catalyst (5.0 mol %), $LiClO_4$ (0.1 M), MeCN (4.0 mL), 30–35 °C, 8 h, under N_2, blue LEDs (450 nm); conversions were determined by ^{1}H-NMR using dimethyl terephthalate as internal standard. Yield in parenthesis refer to isolated yields. [b] 390 nm wavelength. [c] Photocatalyst (2.0 mol %). [d] In the dark under otherwise identical reaction conditions using aluminium foil to cover the vial. [e] In the absence of current. [f] $Zn(SO_2CF_3)_2$ (**4**, 0.25 mmol).

Comparison to Electrooxidative Trifluoromethylation

Following the general procedure or the procedure for the electrooxidative trifluoromethylation described in the literature[1], control experiments were conducted to compare the efficacy of the procedures for the different sulfinate sources $NaSO_2CF_3$ (**2**) or $Zn(SO_2CF_3)_2$ (**4**) by using caffeine (**5**, 0.25 mmol) as arene substrate. After 8 h, the conversion was determined by ^{19}F-NMR using 1-fluorononane as internal standard.

Table S2: Influence of the irradiation with blue LED light on the trifluoromethylation of caffeine (**5**).



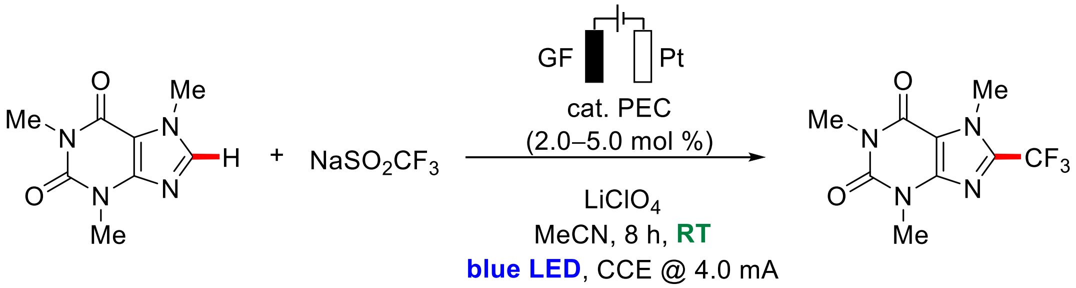
Entry	Sulfinate	Conditions	Yield (6)
1	$Zn(SO_2CF_3)_2$ (**4**)	Electrooxidation, Undivided Cell[a]	(26%)
2	$Zn(SO_2CF_3)_2$ (**4**)	Electrooxidation, Divided Cell[a]	(64%)
3	$Zn(SO_2CF_3)_2$ (**4**)	Photoelectrocatalysis[b]	(80%)
4	$NaSO_2CF_3$ (**2**)	Electrooxidation, Undivided Cell[a]	(21%)
5	$NaSO_2CF_3$ (**2**)	Electrooxidation, Divided Cell[a]	(33%)
6	$NaSO_2CF_3$ (**2**)	Photoelectrocatalysis[b]	70% (81%)

Reaction conditions: [a] Divided cell or undivided cell, GF anode (10 mm × 15 mm × 6 mm), GF cathode (10 mm × 15 mm × 6 mm), constant current electrolysis at 4.0 mA. **5** (0.25 mmol), **2** (0.5 mmol) or **4** (0.35 mmol), *n*-Bu_4NClO_4 (0.15 M), DMSO (5.0 mL), 8 h. [b] Undivided cell, GF anode (10 mm × 15 mm × 6 mm), Pt cathode (10 mm × 15 mm × 0.25 mm), constant current electrolysis at 4.0 mA. **5** (0.25 mmol), **2** (0.5 mmol) or **4** (0.35 mmol), [Mes-Acr]ClO_4 (5.0 mol %), $LiClO_4$ (0.1 M), MeCN (4.0 mL), 30–35 °C, 8 h, under N_2, blue LEDs (450 nm). Yields refer to the isolated product, conversions were determined by ^{19}F-NMR using 1-fluorononane as internal standard.

Kinetic Studies

Following the general procedure, caffeine (**5**, 58.2 mg, 0.3 mmol, 1.0 equiv), CF_3SO_2Na (**2**, 93.6 mg, 0.60 mmol, 2.0 equiv), $LiClO_4$ (42 mg, 0.40 mmol) and the photocatalyst (2.0 or 5.0 mol %) were placed into a 10 mL Schlenkflask and closed with a stopper with integrated electrode holders. After evacuation and purging with N_2 three times, 1-fluorononane (43.8 mg, 0.3 mmol) was added as internal standard followed by CH_3CN (4.0 mL). Equipped with a N_2-ballon, the photoelectrocatalysis was performed at ambient temperature with a constant current of 4.0 mA maintained for 8 h under visible light irradiation (2 × Kessil A360N or 2 × Kessil A160WE). During the course of the reaction, an aliquot of 100 μL was removed via syringe after 2 h, 4 h and 8 h. The sample was diluted with MeCN-d_3, filtered through a short plug of silica gel and analyzed by crude $^{19}F\{^1H\}$-NMR.

Table S3: Comparison of different photoelectrocatalysts in the trifluoromethylation of caffeine (**5**).

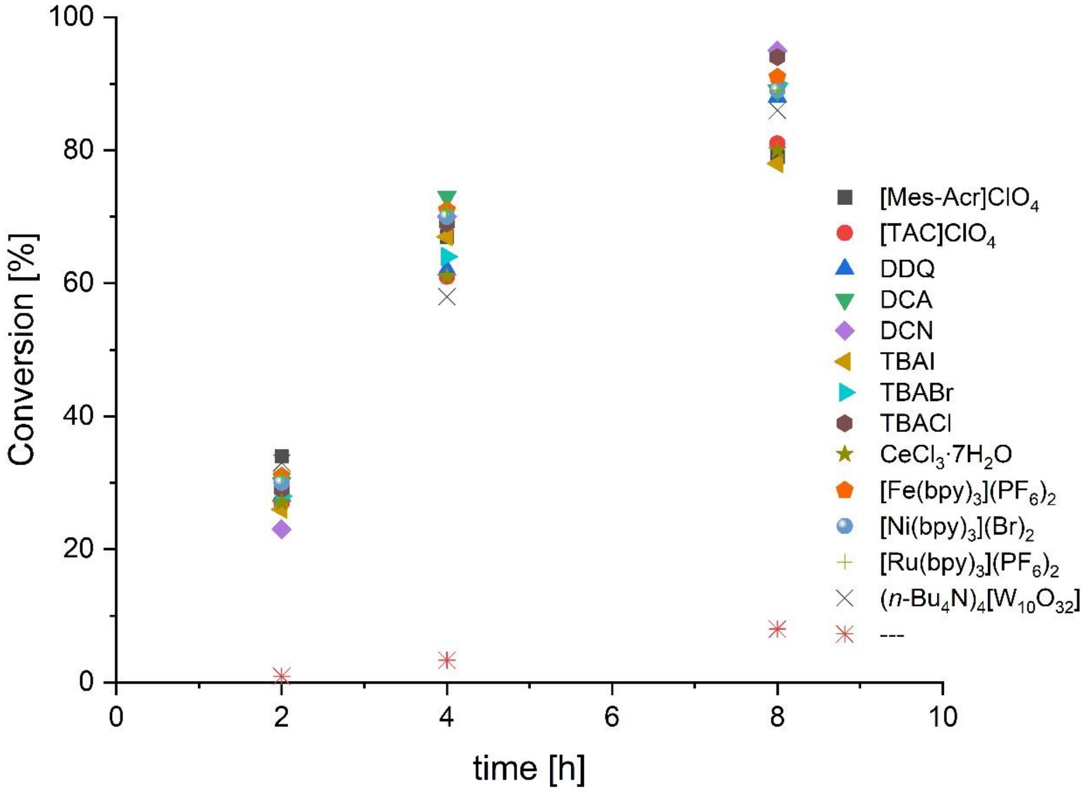


5 **2** **6**

Entry	Photoelectroatalyst[a]	**6** (%) 2 h	**6** (%) 4 h	**6** (%) 8 h
1	[Mes-Acr]ClO_4	34%	67%	79%
2	[TAC]ClO_4	27%	61%	81%
3	DDQ	28%	62%	88%
4	DCA	30%	73%	83%
5	DCN	23%	70%	94%
6	TBAI	26%	63%	83%
7	TBABr	28%	68%	90%

8	TBACl	29%	73%	94%
9	$CeCl_3·7H_2O$	27%	61%	79%
10	$CeCl_3·7H_2O$[b]	31%	71%	93%
11	$[Fe(bpy)_3](PF_6)_2$[c]	31%	71%	89%
12	$[Ni(bpy)_3]Br_2$[c]	30%	70%	89%
13	$[Ru(bpy)_3](PF_6)_2$[c]	33%	65%	86%
14	$(n\text{-}Bu_4N)_4[W_{10}O_{32}]$[c]	34%	67%	79%
15	---	1%	3%	8%

[a] Reaction conditions: Undivided cell, GF anode (10 mm × 15 mm × 6 mm), Pt cathode (10 mm × 15 mm × 0.25 mm), constant current electrolysis at 4.0 mA. **5** (0.25 mmol), **2** (0.50 mmol), photoelectrocatalyst (5.0 mol %), $LiClO_4$ (0.1 m), MeCN (4.0 mL), 30–35 °C, 8 h, under N_2, blue LEDs (450 nm); conversions were determined by ^{19}F-NMR using 1-fluorononane as internal standard. [b] 390 nm wavelength. [c] Photocatalyst (2.0 mol %).



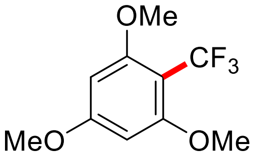
Characterization Data

1,3,5-Trimethoxy-2-(trifluoromethyl)benzene (1)

1,3,5-Trimethoxy-2,4-bis(trifluoromethyl)benzene (1)

The general procedure was followed using 1,3,5-trimethoxybenzene (**1**, 0.25 mmol, 42.0 mg). After electrolysis at 4 mA under blue light irradiation for 8 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **3** and **3’** as white solids. When [Mes-Acr]ClO_4 was used as photocatalyst, the mono-functionalized product **3** was obtained in 72% (42.3 mg) and the difunctionalized product **3’** in 16% (12.1 mg), while the use of [TAC]ClO_4 gave **3** in 78% (46.0 mg) and **3’** in 9% (6.8 mg).

1,3,5-Trimethoxy-2-(trifluoromethyl)benzene (3)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.14 (s, 2H), 3.83 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.7 (C_q), 160.5 (q, $^{3}J_{C–F}$ = 1.4 Hz, C_q), 124.3 (q, $^{1}J_{C–F}$ = 273.3 Hz, C_q), 100.5 (q, $^{2}J_{C–F}$ = 30.2 Hz, C_q), 91.4 (CH), 56.4 (CH_3), 55.5 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 54.2 (s).

m.p.: 63–64 °C.

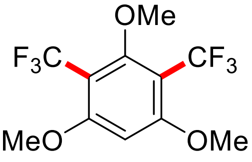
IR (ATR): $\tilde{\nu}$ = 1589, 1459, 1417, 1278, 1232, 1207, 1161, 1092, 1024, 814 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 259 (100) $[M+Na]^+$, 237 (90) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{10}H_{12}F_3O_3^+$ $[M+H]^+$ 237.0733, found 237.0735.

The spectral data is in accordance with those reported in the literature.[2]

1,3,5-Trimethoxy-2,4-bis(trifluoromethyl)benzene (3’)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.35 (s, 1H), 3.96 (s, 6H), 3.82 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.5 (C_q), 160.7 (C_q), 123.6 (q, $^{1}J_{C–F}$ = 273.9 Hz, C_q), 106.3 (q, $^{2}J_{C–F}$ = 30.2 Hz, C_q), 92.7 (CH), 64.9 (CH_3), 56.5 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 55.5 (s).

m.p.: 98–100 °C.

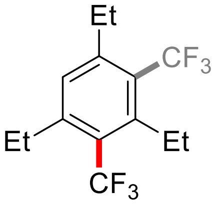
IR (ATR): $\tilde{\nu}$ = 1604, 1577, 1311, 1257, 1218, 1105, 1059, 731 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 327 (100) $[M+Na]^+$, 305 (10) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{11}H_{11}F_6O_3^+$ $[M+H]^+$ 305.0607, found 305.0609.

The spectral data is in accordance with those reported in the literature.[3]

1,3,5-Triethyl-2-(trifluoromethyl)benzene (9)



The general procedure was followed using 1,3,5-triethylbenzene (0.25 mmol, 40.6 mg). After electrolysis at 4 mA under blue light irradiation for 8 h, purification by column chromatography (*n*-pentane) yielded **9** as a colourless oil. When [Mes-Acr]ClO_4 was used as photocatalyst, the product **9** was obtained in 63% (36.8 mg), while the use of [TAC]ClO_4 gave 57% (32.7 mg). In both cases, the product was obtained as a mixture with a minor amount of the di-functionalized product in a ratio of 3.6:1. The ratio was determined based on the ^{1}H-NMR of the isolated product.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.97 (s, 2H), 2.90–2.77 (m, 4H), 2.63 (q, J = 7.6 Hz, 2H), 1.24 (td, J = 7.7, 3.4 Hz, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.4 (C_q), 144.1 (q, $^3J_{C-F}$ = 2.0 Hz, C_q), 128.7 (CH), 126.3 (q, $^1J_{C-F}$ = 276.3 Hz, C_q), 123.8 (q, $^2J_{C-F}$ = 28.3 Hz, C_q), 28.6 (CH_2), 28.1 (CH_2), 16.7 (CH_3), 15.3 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 52.4 (s).

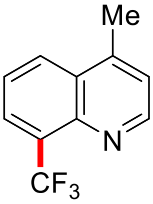
IR (ATR): $\tilde{\nu}$ = 2968, 1609, 1575, 1459, 1294, 1199, 1144, 1105, 1062, 1038 cm^{-1}.

MS (EI) *m*/*z* (relative intensity): 230 (10) $[M]^+$, 215 (100) $[M–CH_3]^+$.

HR-MS (EI): *m*/*z* calcd for $C_{13}H_{17}F_3^+$ $[M]^+$ 230.1277, found 230.1279.

The spectral data is in accordance with those reported in the literature.[2]

4-Methyl-8-(trifluoromethyl)quinoline (10)



The general procedure was followed using 4-methylquinoline (0.25 mmol, 37.1 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 10:1) yielded **10** as a colourless oil. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 52% (27.9 mg), while the use of [TAC]ClO_4 gave 60% (31.6 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.92 (*d*, J = 4.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.3 Hz, 1H), 7.66–7.55 (m, 1H), 7.33 (d, J = 4.4 Hz, 1H), 2.73 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 151.0 (CH), 144.7 (q, $^3J_{C–F}$ = 3.4 Hz, C$_q$), 144.7 (C$_q$), 128.9 (C$_q$), 128.5 (CH), 128.1 (q, $^2J_{C–F}$ = 30.0 Hz, C$_q$), 127.7 (q, $^3J_{C–F}$ = 5.9 Hz, CH), 124.4 (q, $^1J_{C–F}$ = 275.4 Hz, C$_q$), 125.0 (CH), 122.8 (CH), 19.1 (CH$_3$).

^{19}F-NMR (377 MHz, CDCl$_3$): δ = – 60.0 (s).

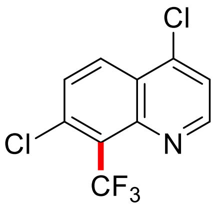
IR (ATR): $\tilde{\nu}$ = 1600, 1315, 1294, 1120, 1092, 1079, 1047, 838, 762, 713 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 234 (12) [M+Na]$^+$, 212 (100) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{11}H_9NF_3^+$ [M+H]$^+$ 212.0682, found 212.0684.

The spectral data is in accordance with those reported in the literature.[2]

4,7-Dichloro-8-(trifluoromethyl)quinoline (11)



The general procedure was followed using 4,7-dichloroquinoline (0.25 mmol, 49.5 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 20:1) and purification by recycling preparative HPLC yielded **11** as a white solid. When [Mes-Acr]ClO$_4$ was used as photocatalyst, the product was obtained in 31% (20.7 mg), while the use of [TAC]ClO$_4$ gave 35% (23.3 mg).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 8.93 (d, J = 4.7 Hz, 1H), 8.30 (d, J = 9.1 Hz, 1H), 7.69 (d, J = 9.1 Hz, 1H), 7.59 (d, J = 4.7 Hz, 1H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 151.1 (CH), 147.5 (C$_q$), 142.9 (C$_q$), 136.6 (q, $^3J_{C–F}$ = 4.8 Hz, C$_q$), 131.1 (CH), 128.6 (CH), 125.6 (C$_q$), 125.5 (q, $^2J_{C–F,}$ = 32.2 Hz, C$_q$), 123.4 (q, $^1J_{C–F,}$ = 275.2 Hz, C$_q$) 122.2 (CH).

^{19}F-NMR (377 MHz, CDCl$_3$): δ = – 53.0 (s).

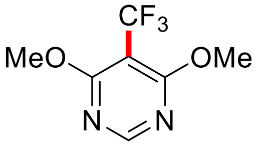
m.p.: 113–116 °C.

IR (ATR): $\tilde{\nu}$ = 1586, 1561, 1485, 1405, 1263, 1204, 1151, 1129, 895, 788 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 268 (75), [M(^{37}Cl)+H]$^+$, 266 (100) [M(^{35}Cl)+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{10}H_5NF_3{}^{35}Cl_2^+$ [M+H]$^+$ 265.9946, found 265.9947.

4,6-Dimethoxy-5-(trifluoromethyl)pyrimidine (12)



The general procedure was followed using 4,6-dimethoxy pyrimidine (0.25 mmol, 35.0 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 30:1 to 20:1) yielded **12** as a white solid. When [Mes-Acr]ClO$_4$ was used as photocatalyst, the product was obtained in 68% (35.4 mg), while the use of [TAC]ClO$_4$ gave 61% (31.7 mg).

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.46 (s, 1H), 4.03 (s, 6H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 168.1 (C$_q$), 159.1 (CH), 123.0 (q, $^1J_{C\text{–}F}$ = 273.0 Hz, C$_q$), 95.6 (q, $^2J_{C\text{–}F}$ = 33.7 Hz, C$_q$), 55.1 (CH$_3$).

^{19}F-NMR (377 MHz, CDCl$_3$): δ = – 57.0 (s).

m.p.: 94–96 °C.

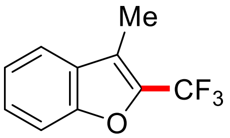
IR (ATR): $\tilde{\nu}$ = 1573, 1475, 1414, 1324, 1247, 1107, 1035, 733, 703 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 231 (50) [M+Na]$^+$, 209 (100) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_7H_8F_3N_2O_2N^+$ [M+H]$^+$ 209.0538, found 209.0541.

The spectral data is in accordance with those reported in the literature.[2]

3-Methyl-2-(trifluoromethyl)benzofuran (13)



The general procedure was followed using 3-methylbenzofurane (0.25 mmol, 33.0 mg). After electrolysis at 4 mA under blue light irradiation for 8 h, purification by column chromatography (*n*-hexane) yielded **13** as a colourless oil. When [Mes-Acr]ClO$_4$ was used as photocatalyst, the product was obtained in 71% (35.5 mg), while the use of [TAC]ClO$_4$ gave 72% (36.0 mg).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.61 (dd, J = 7.7, 1.2 Hz, 1H), 7.52 (dd, J = 8.3, 0.9 Hz, 1H), 7.47–7.40 (m, 1H), 7.33 (dd, J = 7.5, 1.1 Hz, 1H), 2.42 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 154.2 (C$_q$), 138.6 (q, $^2J_{C\text{–}F}$ = 39.7 Hz, C$_q$), 128.5 (C$_q$), 127.1 (CH), 123.5 (CH), 120.8 (CH), 120.4 (q, $^1J_{C\text{–}F}$ = 269.4 Hz, C$_q$), 118.4 (q, $^3J_{C\text{–}F}$ = 2.6 Hz, C$_q$), 112.0 (CH), 7.8 (q, $^4J_{C\text{–}F}$ = 1.8 Hz, CH$_3$).

^{19}F-NMR (282 MHz, CDCl$_3$): δ = – 62.0 (s).

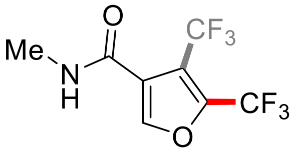
IR (ATR): $\tilde{\nu}$ = 1635, 1395, 1383, 1301, 1367, 1179, 1111, 1082, 1038, 743 cm^{-1}.

MS (EI) *m*/*z* (relative intensity): 200 (100) [M]$^+$.

HR-MS (EI): *m*/*z* calcd for $C_{10}H_7F_3O$ [M]$^+$ 200.0444, found 200.0448.

The spectral data is in accordance with those reported in the literature.[2]

N-Methyl-5-(trifluoromethyl)furan-3-carboxamide (14)



The general procedure was followed using *N*-methylfuran-3-carboxamide (0.25 mmol, 31.2 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:1 to 1:2) yielded **14** as a pale yellow oil. When [Mes -Acr]ClO_4 was used as photocatalyst, the product was obtained in 69% (33.3 mg), while the use of [TAC]ClO_4 gave 74% (35.7 mg) in both cases as mixture of isomers in a ratio of 3.0:1 as determined based on the ^{1}H-NMR of the isolated product. The reported NMR data corresponds to the main isomer.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 6.70 (s, 1H), 6.35 (s br, 1H), 2.94 (d, J = 4.9 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.6 (C_q), 143.9 (q, $^3J_{C–F}$ = 2.4 Hz, CH), 139.8 (q, $^2J_{C–F}$ = 42.3 Hz, C_q), 123.6 (C_q), 118.9 (q, $^1J_{C–F}$ = 268.7 Hz, C_q), 111.6 (CH), 26.7 (CH_3).

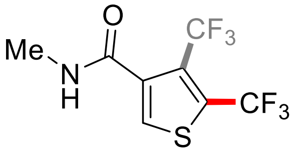
^{19}F-NMR (282 MHz, $CDCl_3$): δ = – 61.2 (s).

IR (ATR): $\tilde{\nu}$ = 1406, 1304, 1266, 1175, 1131, 1105, 935, 894, 734, 702 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 216 (100) $[M+Na]^+$, 194 (12) $[M+H]^+$.

HR-MS (EI): *m*/*z* calcd for $C_7H_6NO_2F_3Na$ $[M+Na]^+$ 216.0243, found 216.0253.

N-Methyl-5-(trifluoromethyl)thiophene-3-carboxamide (15)



The general procedure was followed using *N*-methylthiophen-3-carboxamide (0.25 mmol, 35.2 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 2:1 to 1:1) yielded **15** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 65% (33.8 mg), while the use of [TAC]ClO_4 gave 68% (35.8 mg) in both cases as mixture of isomers in a ratio of 2.7:1 as determined based on the ^{1}H-NMR of the isolated product. The reported NMR data corresponds to the main isomer.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, J = 3.2, 2.3 Hz, 1H), 7.32–7.03 (m, 1H), 6.16 (s br, 1H), 3.19–2.89 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.5 (C_q), 137.6 (C_q), 129.9 (q, $^2J_{C–H}$ = 36.9 Hz, C_q), 129.1 (CH), 127.1 (q, $^3J_{C–H}$ = 5.6 Hz, CH), 122.0 (q, $^1J_{C–H}$ = 269.7 Hz, C_q), 27.0 (CH_3).

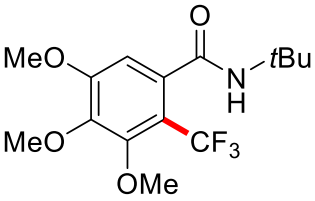
^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 52.8 (s).

IR (ATR): $\tilde{\nu}$ = 1638, 1562, 1523, 1431, 1276, 1159, 1119, 1019, 1007 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 232 (100) $[M+Na]^+$, 210 (9) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_7H_6SNOF_3Na$ $[M+Na]^+$ 232.0014, found 232.0020.

N-(*tert*-Butyl)-3,4,5-trimethoxy-2-(trifluoromethyl)benzamide (16)



The general procedure was followed using *N*-(*tert*-butyl)-3,4,5-trimethoxybenzamide (0.25 mmol, 42.0 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 4:1 to 2:1) yielded **16** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 56% (46.9 mg), while the use of [TAC]ClO_4 gave 53% (44.4 mg). The obtained product shows in the ^{1}H- and ^{13}C-NMR in $CDCl_3$ a splitting of the signals in two sets as a consequence of the limited rotation along the amide bond.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.65 (s, 1H), 5.45 (s br, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H), 1.42 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.4 (C_q), 156.2 (C_q), 153.2 (C_q), 143.4 (C_q), 133.7 (q, $^3J_{C–F}$ = 2.6 Hz, C_q), 123.5 (q, $^1J_{C–F}$ = 273.7 Hz, C_q), 113.6 (q, $^2J_{C–F}$ = 30.5 Hz, C_q), 106.8 (CH), 61.9 (CH_3), 61.0 (CH_3), 56.4 (CH_3), 52.3 (C_q), 28.6 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 55.6 (s).

m.p.: 107–108 °C.

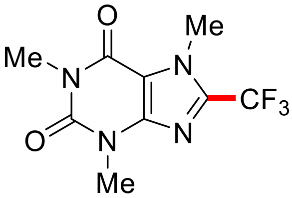
IR (ATR): $\tilde{\nu}$ = 1641, 1580, 1496, 1453, 1403, 1302, 1116, 1009, 930 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 358 (100) $[M+Na]^+$, 336 (5) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{15}H_{20}NO_4F_3Na$ $[M+Na]^+$ 358.1237, found 358.1237.

The spectral data is in accordance with those reported in the literature.[4]

1,3,7-Trimethyl-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (6)



The general procedure was followed using caffeine (0.25 mmol, 48.5 mg). After electrolysis at 4 mA under blue light irradiation for 8 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **6** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 71% (46.5 mg), while the use of [TAC]ClO_4 gave 70% (45.8 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 3H), 3.56 (s, 3H), 3.38 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.5 (C_q), 151.4 (C_q), 146.6 (C_q), 138.9 (q, $^2J_{C–F}$ = 39.9 Hz, C_q), 118.2 (q, $^1J_{C–F}$ = 270.4 Hz, C_q), 109.7 (C_q), 33.3 (q, $^4J_{C–F}$ = 1.9 Hz, CH_3), 30.0 (CH_3), 28.3 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 62.4 (s).

IR (ATR): $\tilde{\nu}$ = 1709, 1665, 1548, 1247, 1202, 1178, 1098, 973, 745 cm^{-1}.

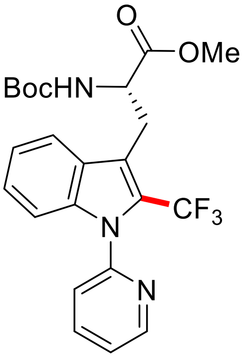
m.p.: 129–130 °C.

MS (ESI) *m*/*z* (relative intensity): 285 (80) [M+Na]$^+$, 263 (100) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_9H_{10}N_4F_3O_2^+$ [M+H]$^+$ 263.0750, found 263.2754.

The spectral data is in accordance with those reported in the literature.[2]

Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(1-(pyridin-2-yl)-2-(trifluoromethyl)-1*H*-indol-3-yl)propanoate (17)



The general procedure was followed using the tryptophan derivative methyl *N*$^{\alpha}$-(*tert*-butoxycarbonyl)-1-(pyridin-2-yl)-L-tryptophanate (0.25 mmol, 98.8 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 4:1) yielded **17** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 49% (56.7 mg), while the use of [TAC]ClO_4 gave 53% (61.3 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.79–8.50 (m, 1H), 7.91 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.51–7.39 (m, 2H), 7.35–7.03 (m, 3H), 5.23 (s, 1H), 4.69 (t, *J* = 7.1 Hz, 1H), 3.66 (s, 3H), 3.48 (d, *J* = 6.6 Hz, 2H), 1.40 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.4 (C_q), 155.1 (C_q), 150.6 (C_q), 149.8 (CH), 138.7 (CH), 138.2 (C_q), 127.1 (C_q), 125.8 (CH), 124.3 (q, $^2J_{C\text{–}F}$ = 34.2 Hz, C_q), 123.7 (CH), 122.4 (CH), 121.9 (q, $^1J_{C\text{–}F}$ = 273.4 Hz, C_q), 121.8 (CH), 120.5 (CH), 115.8 (C_q), 111.4 (CH), 79.9 (C_q), 54.1 (CH), 52.4 (CH_3), 28.4 (CH_3), 27.9 (CH_2).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 53.5 (s).

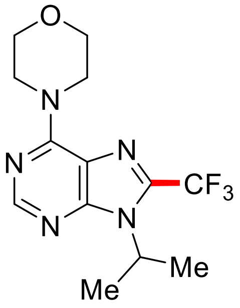
m.p.: 108–109 °C.

IR (ATR): $\tilde{\nu}$ = 1746, 1714, 1590, 1469, 1438, 1367, 1276, 1113, 1059 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 486 (100) [M+Na]$^+$, 464 (100) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{23}H_{24}F_3N_3O_4Na^+$ [M+Na]$^+$ 486.1611, found 486.1617.

4-(9-Isopropyl-8-(trifluoromethyl)-9*H*-purin-6-yl)morpholine (18)



The general procedure was followed using 4-(9-isopropyl-9*H*-purin-6-yl)morpholine (0.25 mmol, 61.8 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 3:1) yielded **18** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 49% (38.6 mg), while the use of [TAC]ClO_4 gave 56% (44.1 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 4.84 (hept, J = 6.9 Hz, 1H), 4.32 (s br, 4H), 3.84 (t, J = 4.6 Hz, 4H), 1.75 (d, J = 6.8 Hz, 6H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.7 (C_q), 153.4 (CH), 152.5 (C_q), 135.9 (q, $^2J_{C\text{–}F}$ = 39.0 Hz, C_q), 119.4 (C_q), 119.1 (q, $^1J_{C\text{–}F}$ = 270.7 Hz, C_q), 67.2 (CH_2), 67.2 (CH_2), 50.6 (CH), 21.1 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 62.1 (s).

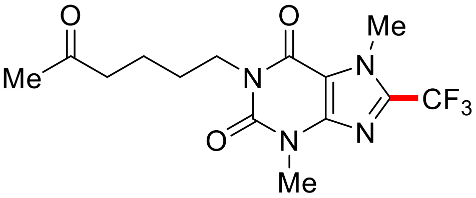
m.p.: 99–101 °C.

IR (ATR): $\tilde{\nu}$ = 1588, 1496, 1441, 1263, 1181, 1163, 1112, 1053, 1009, 930 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 316 (100) $[M+H]^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{13}H_{17}F_3N_5O^+$ $[M+H]^+$ 316.380, found 316.1385.

3,7-Dimethyl-1-(5-oxohexyl)-8-(trifluoromethyl)-3,7-dihydro-1*H*-purine-2,6-dione (19)



The general procedure was followed using Pentoxifylline (0.25 mmol, 69.5 mg). After electrolysis at 4 mA under blue light irradiation for 16 h, purification by column chromatography (*n*-hexane/EtOAc 1:1) yielded **19** as a white solid. When [Mes-Acr]ClO_4 was used as photocatalyst, the product was obtained in 73% (63.1 mg), while the use of [TAC]ClO_4 gave 72% (62.2 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.13 (t, J = 1.6 Hz, 3H), 3.99 (t, J = 8.0 Hz, 2H), 3.56 (s, 3H), 2.49 (t, J = 6.9 Hz, 2H), 2.13 (s, 3H), 1.67–1.56 (m, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 208.7 (C_q), 155.4 (C_q), 151.2 (C_q), 146.7 (C_q), 139.0 (q, $^2J_{C\text{–}F}$ = 40.1 Hz, C_q), 118.3 (q, $^1J_{C\text{–}F}$ = 271.4 Hz, C_q), 109.8 (C_q), 43.2 (CH_2), 41.2 (CH_2), 33.3 (q, $^4J_{C\text{–}F}$ = 2.0 Hz, CH_3), 30.1 (CH_3), 30.0 (CH_3), 27.4 (CH_2), 21.0 (CH_2).

^{19}F-NMR (282 MHz, $CDCl_3$): δ = – 62.4 (s).

m.p.: 70–72 °C.

IR (ATR): $\tilde{\nu}$ = 1705, 1656, 1546, 1468, 1248, 1170, 1128, 1099, 766 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 369 (100) [M+Na]$^+$, 347 (10) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_{14}H_{17}F_3N_4O_3Na^+$ [M+Na]$^+$ 369.1145, found 369.1153.

The spectral data is in accordance with those reported in the literature.[1]

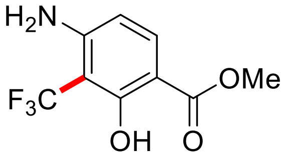
Methyl 4-amino-2-hydroxy-3-(trifluoromethyl)benzoate (21a)

Methyl 4-amino-2-hydroxy-5-(trifluoromethyl)benzoate (21b)

Methyl 4-amino-2-hydroxy-3,5-bis(trifluoromethyl)benzoate (21c)

The general procedure was followed using methyl 4-amino-2-hydroxybenzoate (**20**, 0.50 mmol, 84.3 mg). After electrolysis at 4 mA under blue light irradiation for 8 h, purification by column chromatography (*n*-hexane/EtOAc 9:1) yielded **21a** and **21b** and **21c** as white solids. When [Mes-Acr]ClO_4 was used as photocatalyst, the mono-functionalized product **21a** was obtained in 28% (33.8 mg), **21b** in 11% (12.8 mg) and the difunctionalized **21c** in 3% (4.8 mg), while the use of [TAC]ClO_4 gave **21a** in 50% (58.5 mg), **21b** in 15% (17.9 mg) and **21c** in 9% (14.1 mg).

Methyl 4-amino-2-hydroxy-3-(trifluoromethyl)benzoate (21a)



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 12.05 (s, 1H), 7.67 (d, J = 8.9 Hz, 1H), 6.12 (d, J = 8.9 Hz, 1H), 4.83 (s, 2H), 3.89 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.5 (C_q), 163.5 (q, $^3J_{C–F}$ = 1.6 Hz, C_q), 151.3 (C_q), 133.6 (CH), 125.4 (q, $^1J_{C–F}$ = 273.8 Hz, C_q), 108.4 (CH), 102.4 (C_q), 100.1 (q, $^2J_{C–F}$ = 29.4 Hz, C_q), 52.2 (CH_3).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = – 55.1 (s).

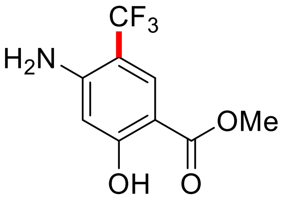
m.p.: 73–75 °C.

IR (ATR): $\tilde{\nu}$ = 1627, 1575, 1505, 1441, 1352, 1272, 1105, 1070, 969, 759 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 258 (100) [M+Na]$^+$, 236 (90) [M+H]$^+$.

HR-MS (ESI): *m*/*z* calcd for $C_9H_9F_3O_3^+$ [M+H]$^+$ 236.0529, found 236.0522.

Methyl 4-amino-2-hydroxy-5-(trifluoromethyl)benzoate (21b)



^{1}H-NMR (400 MHz, CDCl$_3$): δ = 11.05 (s, 1H), 7.96 (s, 1H), 6.20 (s, 1H), 4.56 (s, 2H), 3.91 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 169.9 (C$_q$), 165.1 (C$_q$), 150.6 (q, $^{4}J_{C–F}$ = 1.4 Hz, C$_q$), 130.5 (q, $^{3}J_{C–F}$ = 5.4 Hz, CH), 124.6 (q, $^{1}J_{C–F}$ = 271.1 Hz, C$_q$), 106.5 (q, $^{2}J_{C–F}$ = 31.2 Hz, C$_q$), 103.0 (C$_q$), 102.5 (CH), 52.2 (CH$_3$).

^{9}F-NMR (377 MHz, CDCl$_3$): δ = – 61.6 (s).

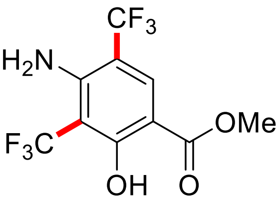
m.p.: 93–95 °C.

IR (ATR): $\tilde{\nu}$ = 1671, 1638, 1331, 1255, 1234, 1211, 1076, 786, 683 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 234 (100) [M–H]$^-$.

HR-MS (ESI): *m*/*z* calcd for $C_9H_7F_3O_3^-$ [M–H]$^-$ 234.0384, found 234.0374.

Methyl 4-amino-2-hydroxy-3,5-bis(trifluoromethyl)benzoate (21c)



^{1}H-NMR (400 MHz, CDCl$_3$): δ = 12.29 (s, 1H), 8.09 (s, 1H), 5.38 (s, 2H), 3.94 (s, 3H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ = 169.9 (C$_q$), 165.1 (C$_q$), 149.0 (C$_q$), 132.7 (q, $^{3}J_{C–F}$ = 5.7 Hz, CH), 124.7 (q, $^{1}J_{C–F}$ = 274.7 Hz, C$_q$), 124.7 (q, $^{1}J_{C–F}$ = 271.5 Hz, C$_q$), 106.8 (q, $^{2}J_{C–F}$ = 30.9 Hz, C$_q$), 101.9 (C$_q$), 101.3 (q, $^{2}J_{C–F}$ = 29.3 Hz, C$_q$), 52.7 (CH$_3$).

^{19}F-NMR (377 MHz, CDCl$_3$): δ = – 55.1 (s), – 62.1 (s).

m.p.: 112–113 °C.

IR (ATR): $\tilde{\nu}$ = 1648, 1591, 1489, 1438, 1232, 1069, 968, 801, 643 cm^{-1}.

MS (ESI) *m*/*z* (relative intensity): 302 (100) [M–H]$^-$.

HR-MS (ESI): *m*/*z* calcd for $C_{10}H_6F_6O_3^-$ [M–H]$^-$ 302.0257, found 302.0260.

References

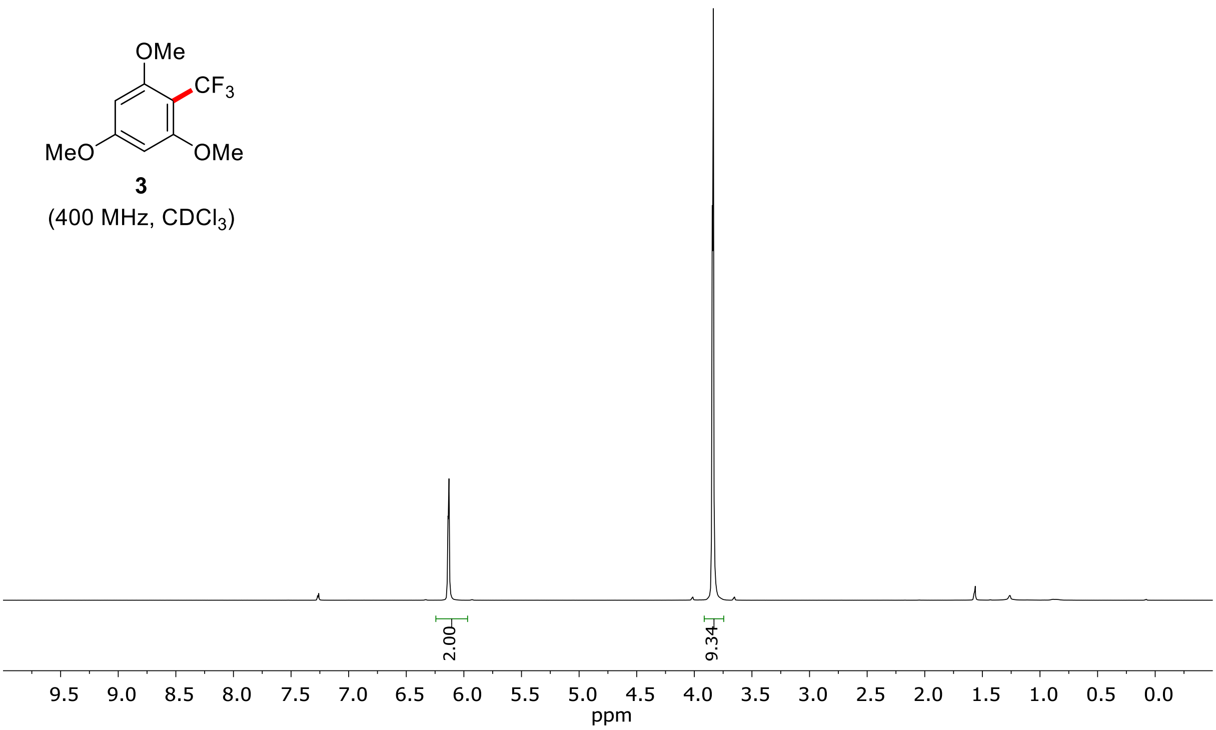
[1] A. G. O'Brien, A. Maruyama, Y. Inokuma, M. Fujita, P. S. Baran, D. G. Blackmond, *Angew. Chem. Int. Ed.* **2014**, *53*, 11868–11871.

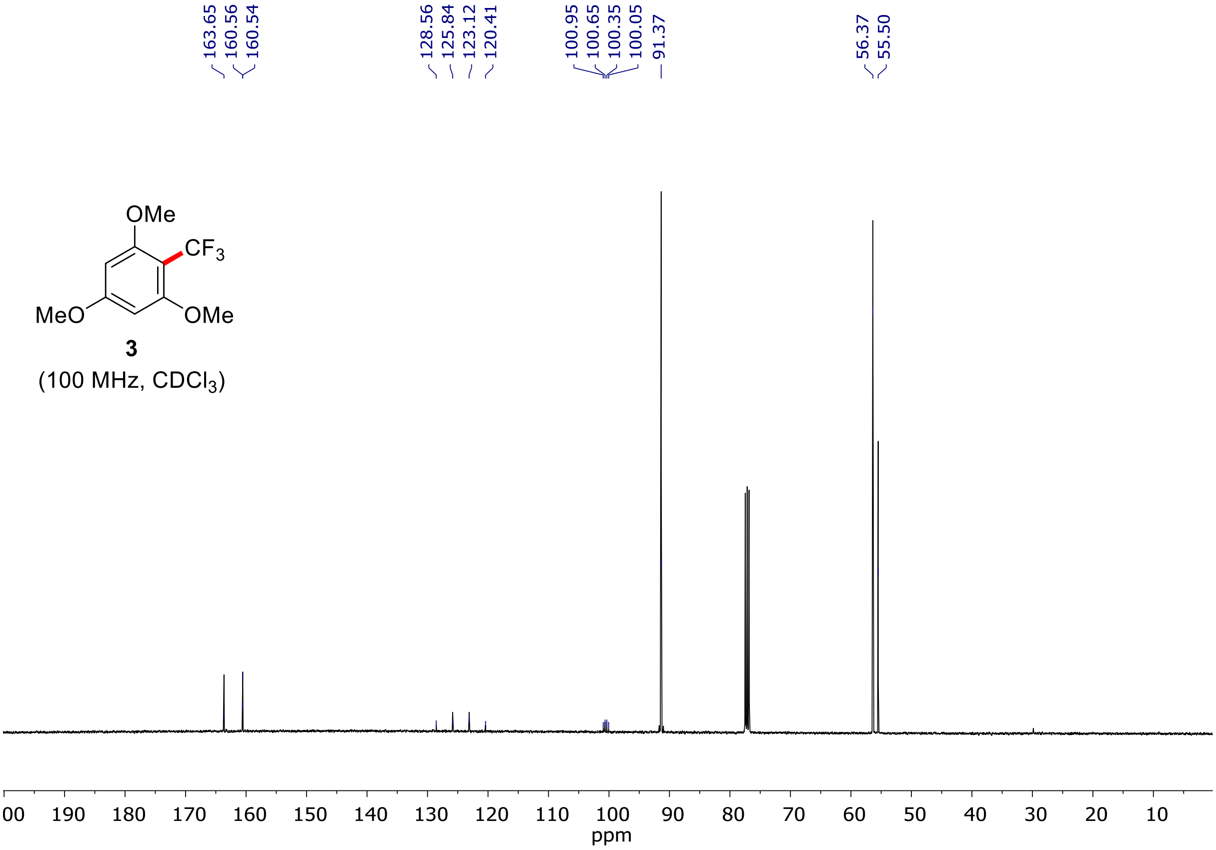
[2] Y. Qiu, A. Scheremetjew, L. H. Finger, L. Ackermann, *Chem. Eur. J.* **2020**, *26*, 3241–3246.

[3] L. Li, X. Mu, W. Liu, Y. Wang, Z. Mi, C.-J. Li, *J. Am. Chem. Soc.* **2016**, *138*, 5809–5812.

[4] X. Lu, R. Kawazu, J. Song, Y. Yoshigoe, T. Torigoe, Y. Kuninobu, *Org. Lett.* **2021**, *23*, 4327–4331.

NMR Spectra


OMe
CF3
MeO
OMe
3
(400 MHz, CDCl3)
2.00
9.34
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


163.65
160.56
160.54
128.56
125.84
123.12
120.41
100.95
100.65
100.35
100.05
91.37
56.37
55.50
OMe
CF3
MeO
OMe
3
(100 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
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100
90
80
70
60
50
40
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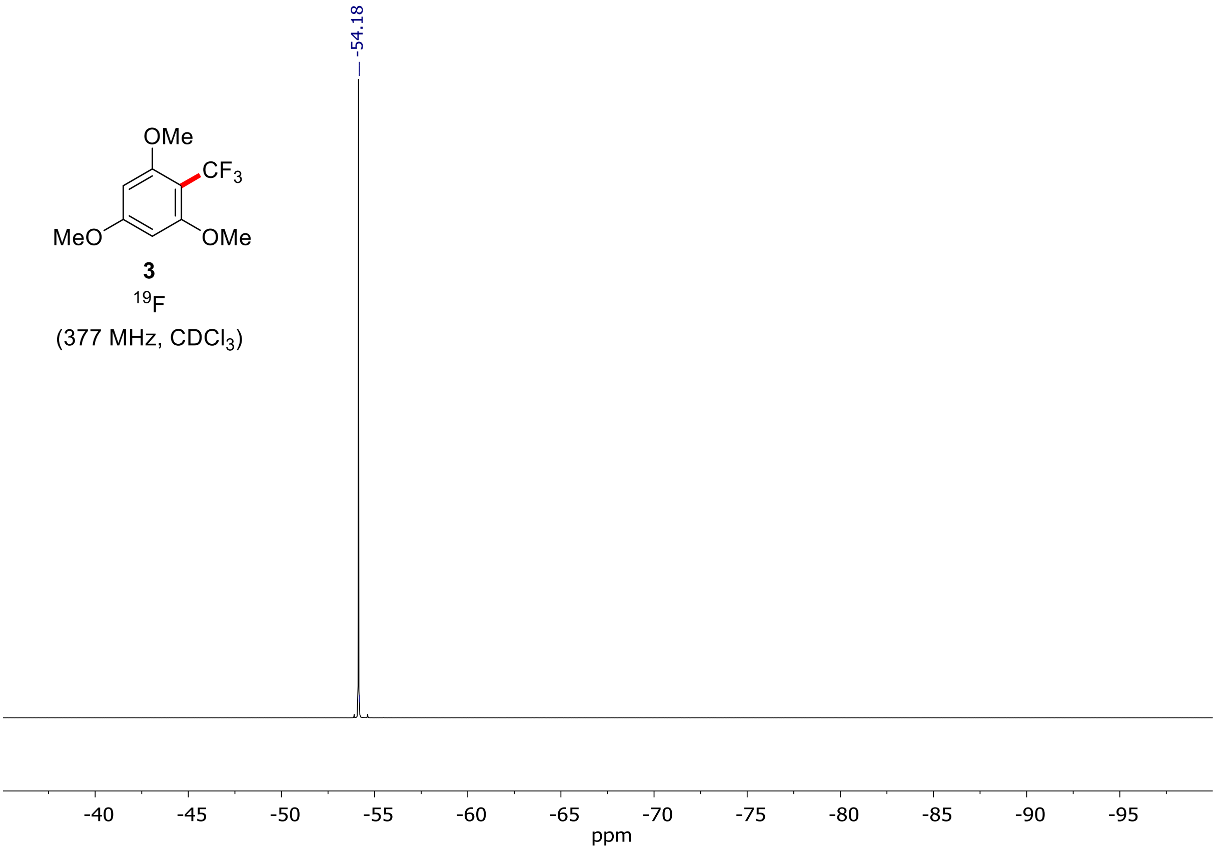
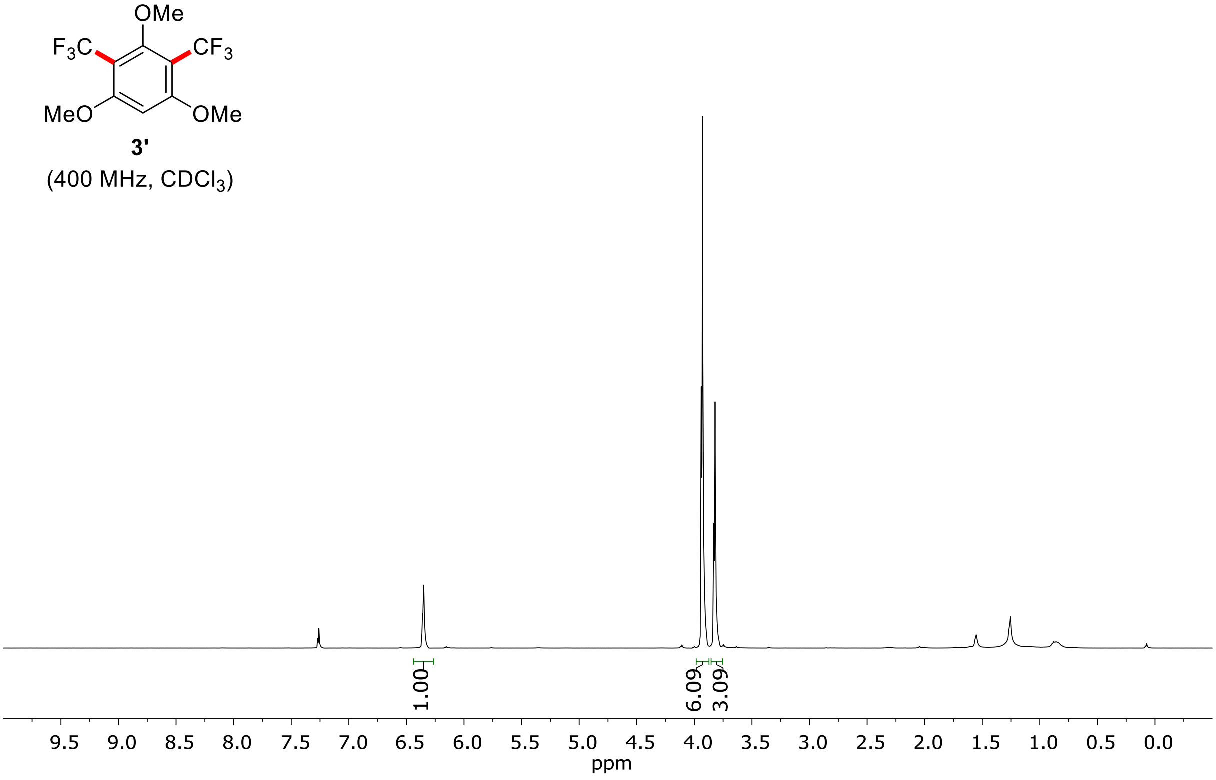
10
ppm



3

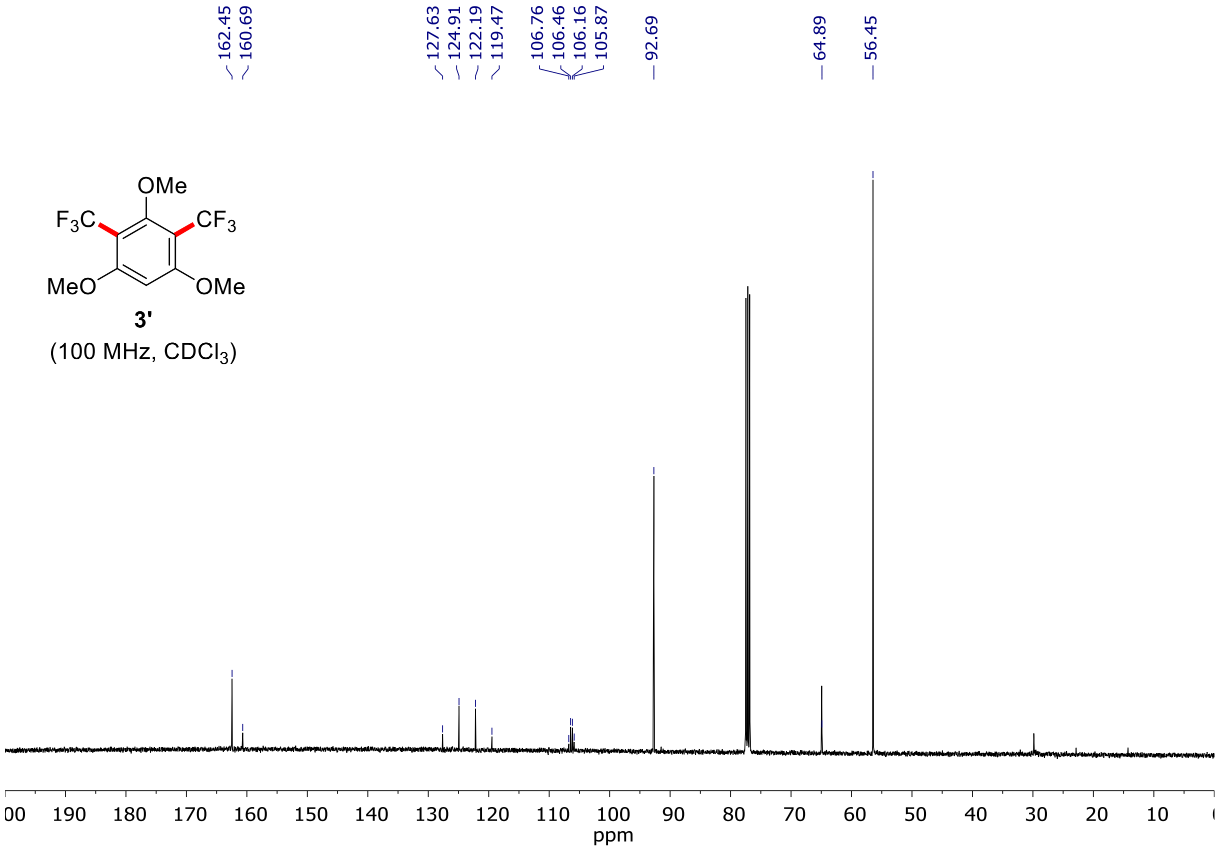
^{19}F

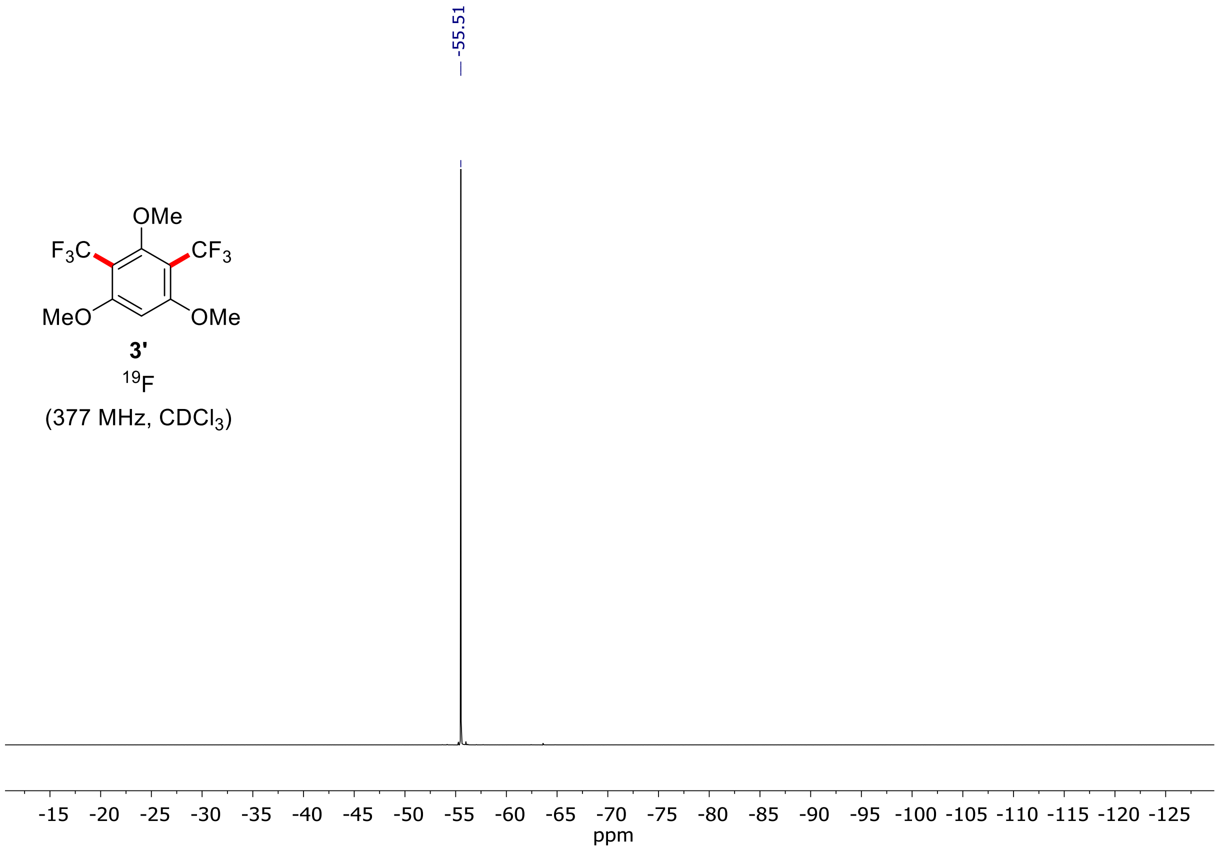
(377 MHz, $CDCl_3$)

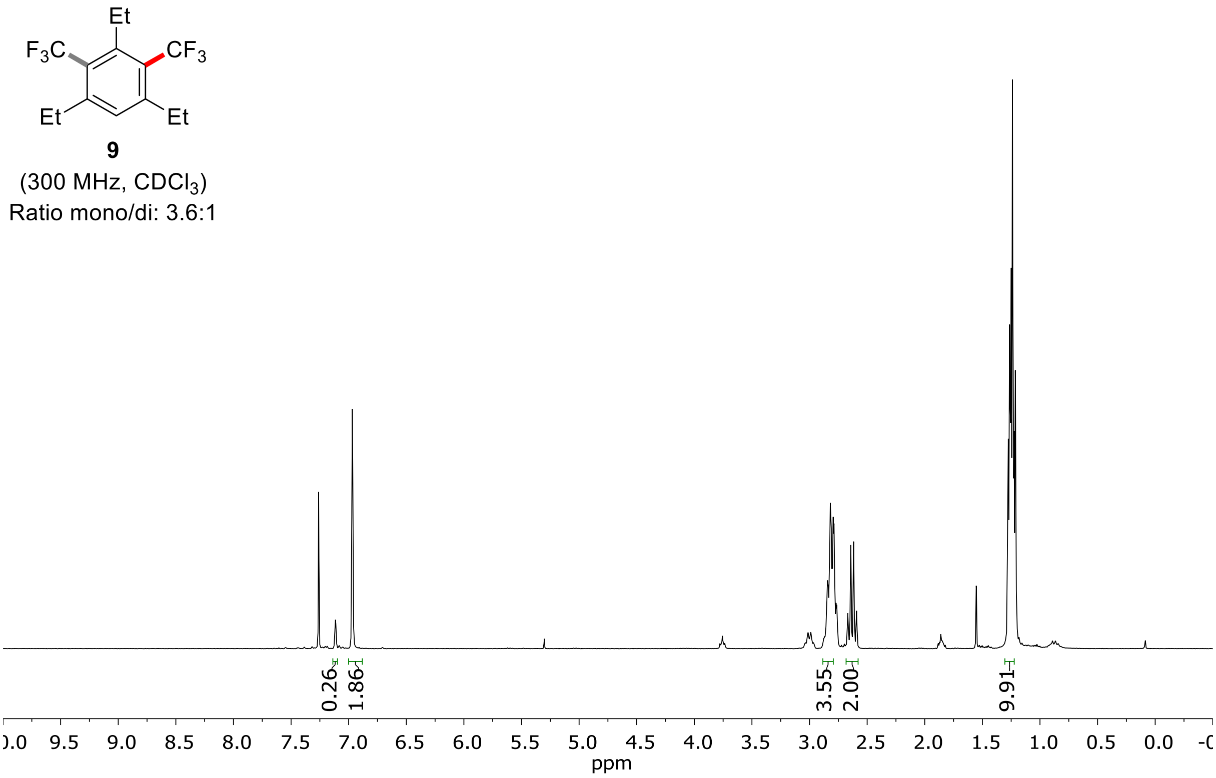


3'

(400 MHz, $CDCl_3$)


162.45
160.69
127.63
124.91
122.19
119.47
106.76
106.46
106.16
105.87
92.69
64.89
56.45
OMe
F3C
CF3
MeO
OMe
3'
(100 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

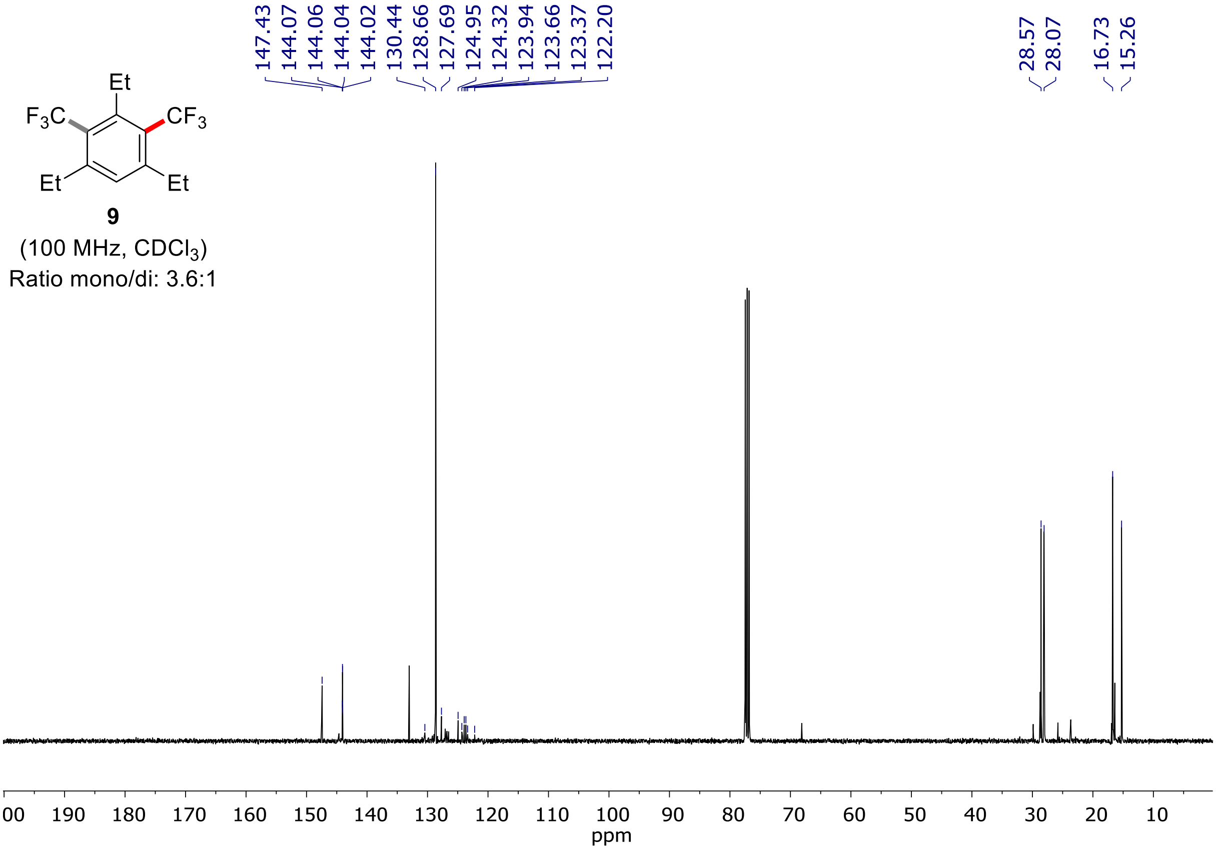

-55.51
OMe
F3C
CF3
MeO
OMe
3'
19F
(377 MHz, CDCl3)
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
ppm



9

(300 MHz, $CDCl_3$)

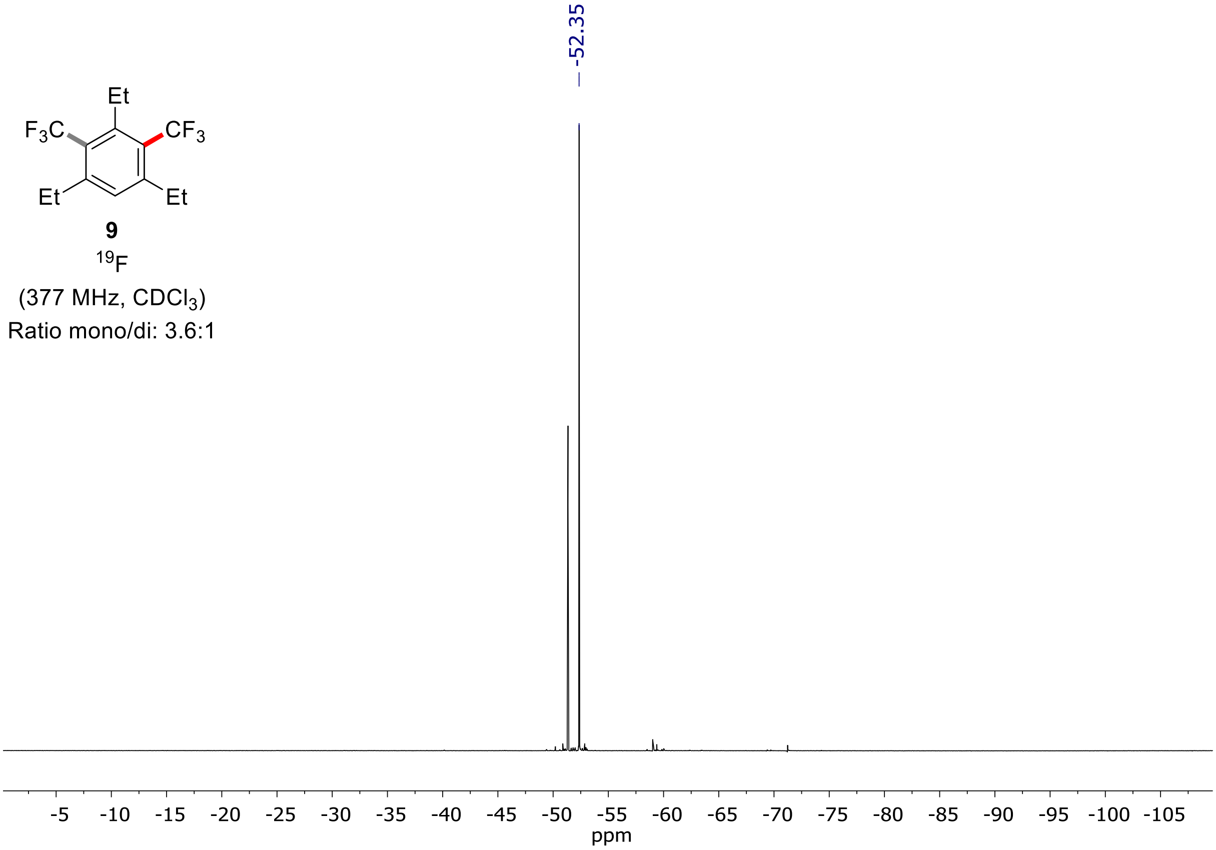
Ratio mono/di: 3.6:1



9

(100 MHz, $CDCl_3$)

Ratio mono/di: 3.6:1

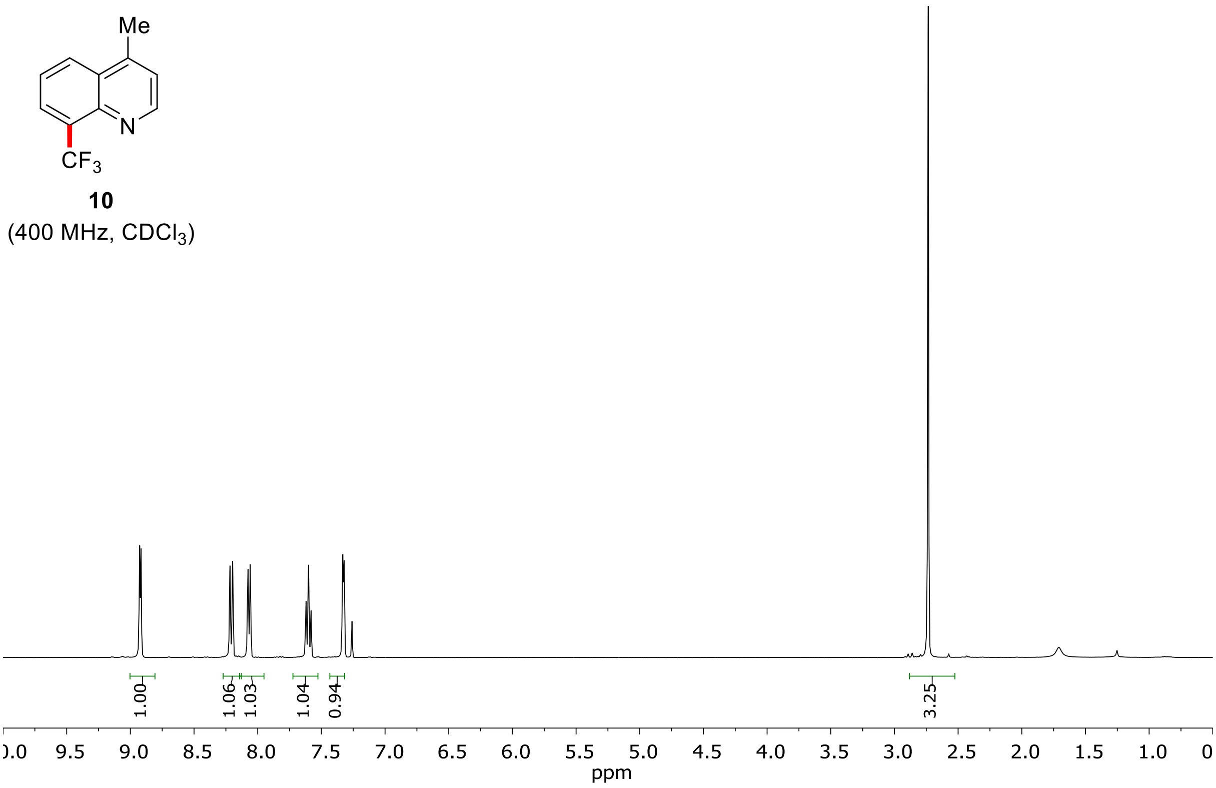


9

^{19}F

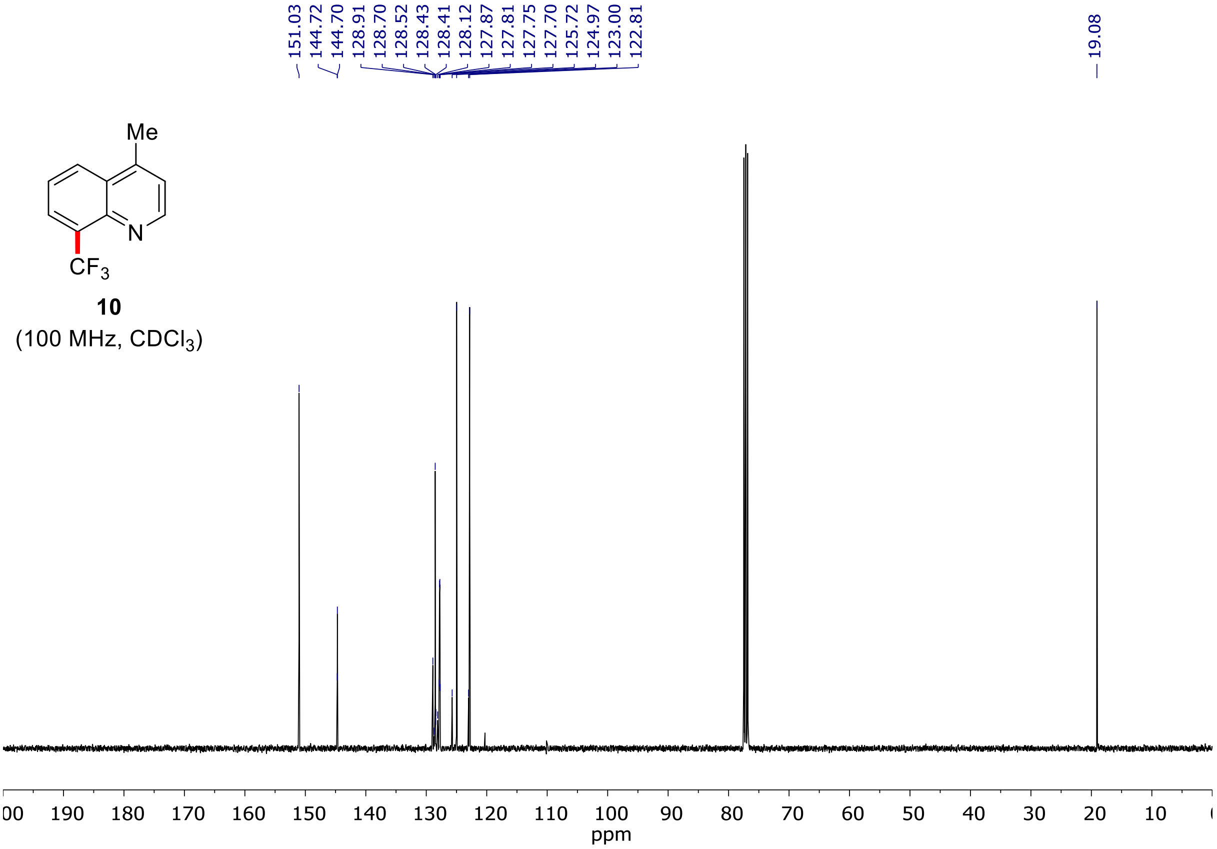
(377 MHz, $CDCl_3$)

Ratio mono/di: 3.6:1



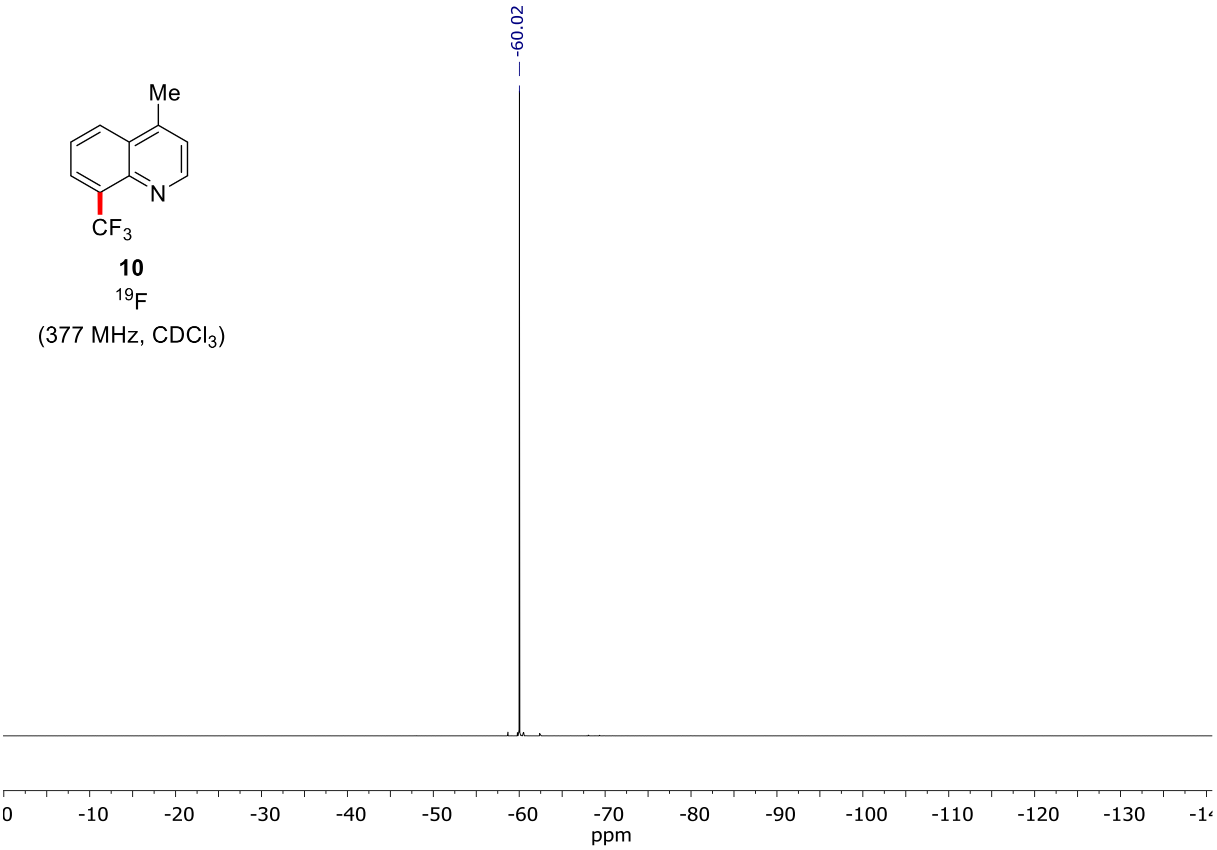
10

(400 MHz, $CDCl_3$)



10

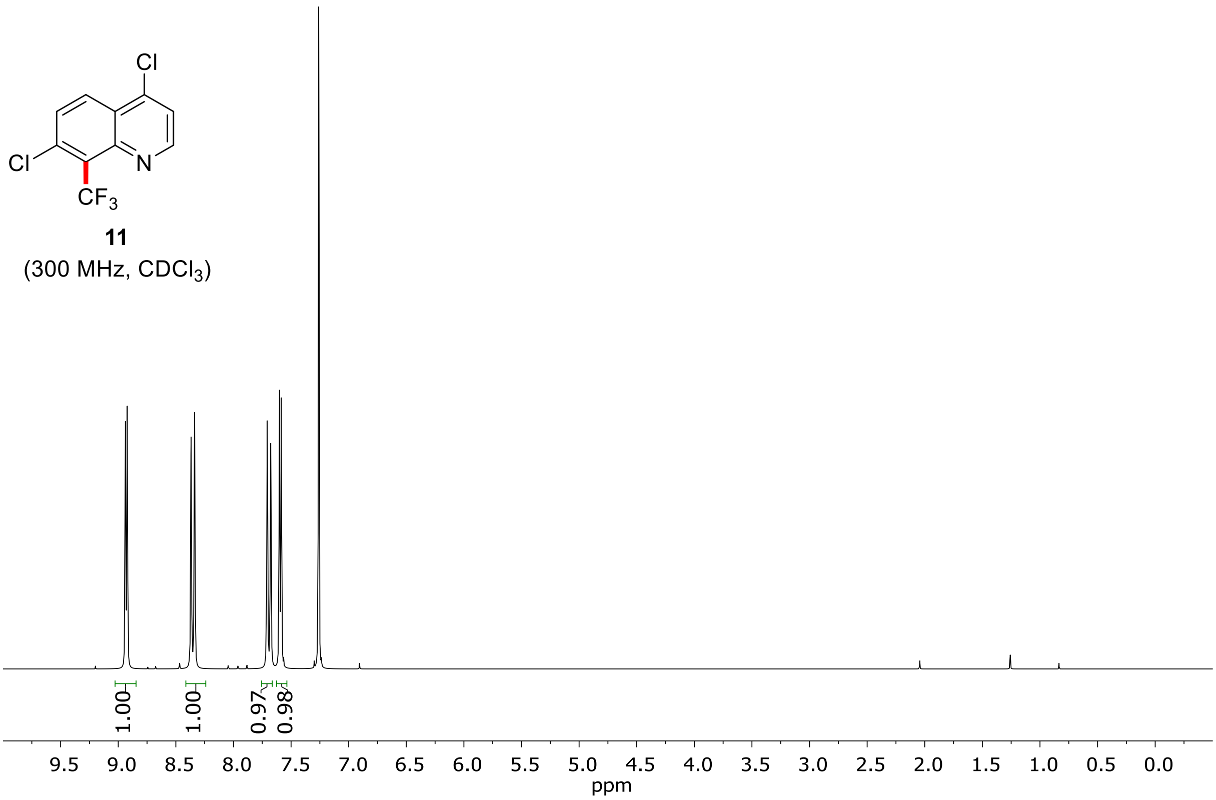
(100 MHz, $CDCl_3$)



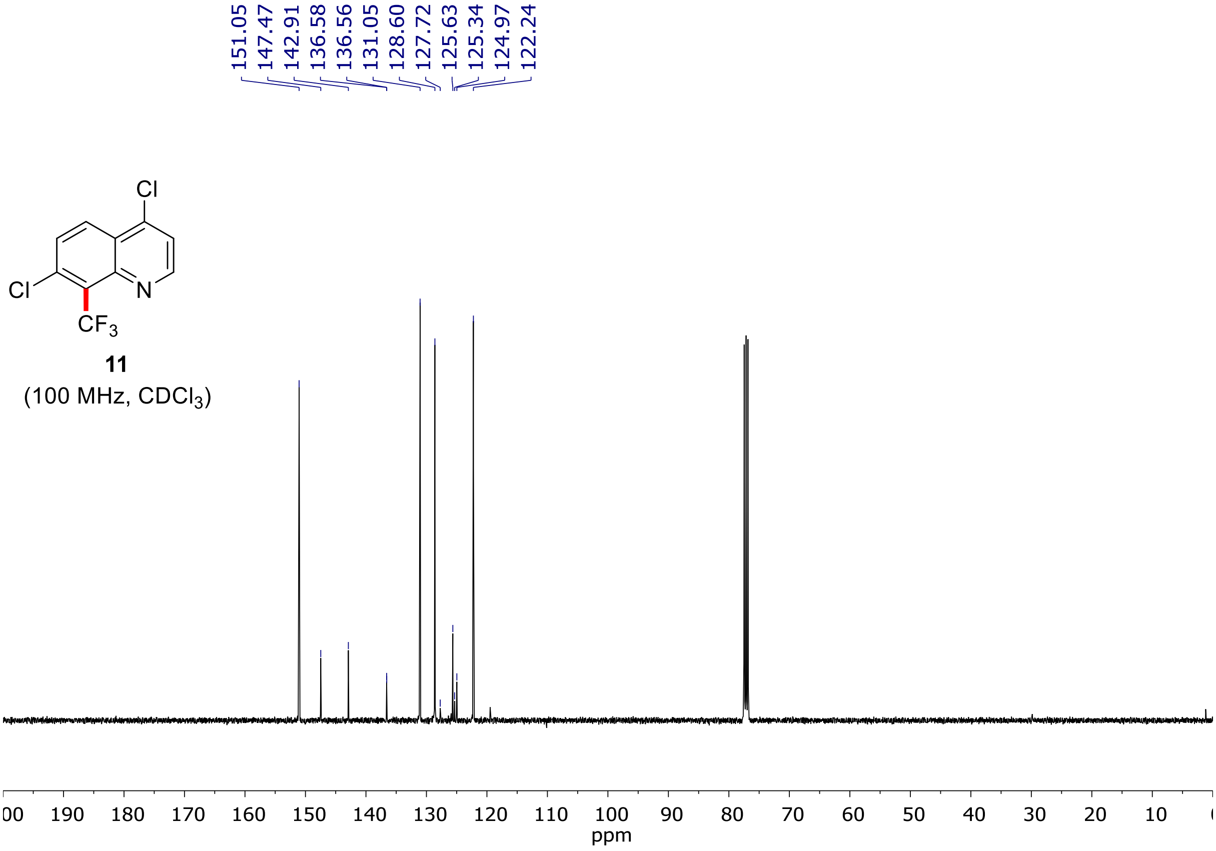
10

^{19}F

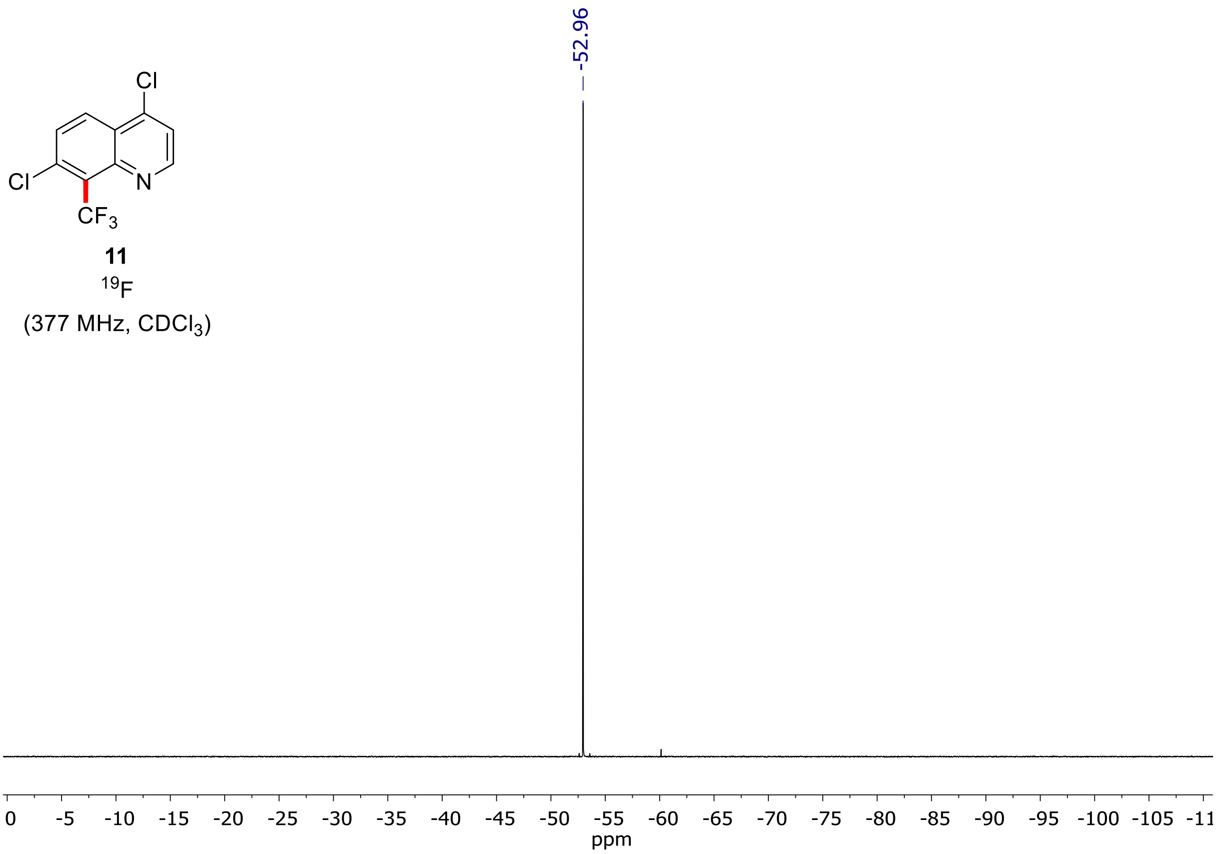
(377 MHz, $CDCl_3$)



11
(300 MHz, $CDCl_3$)



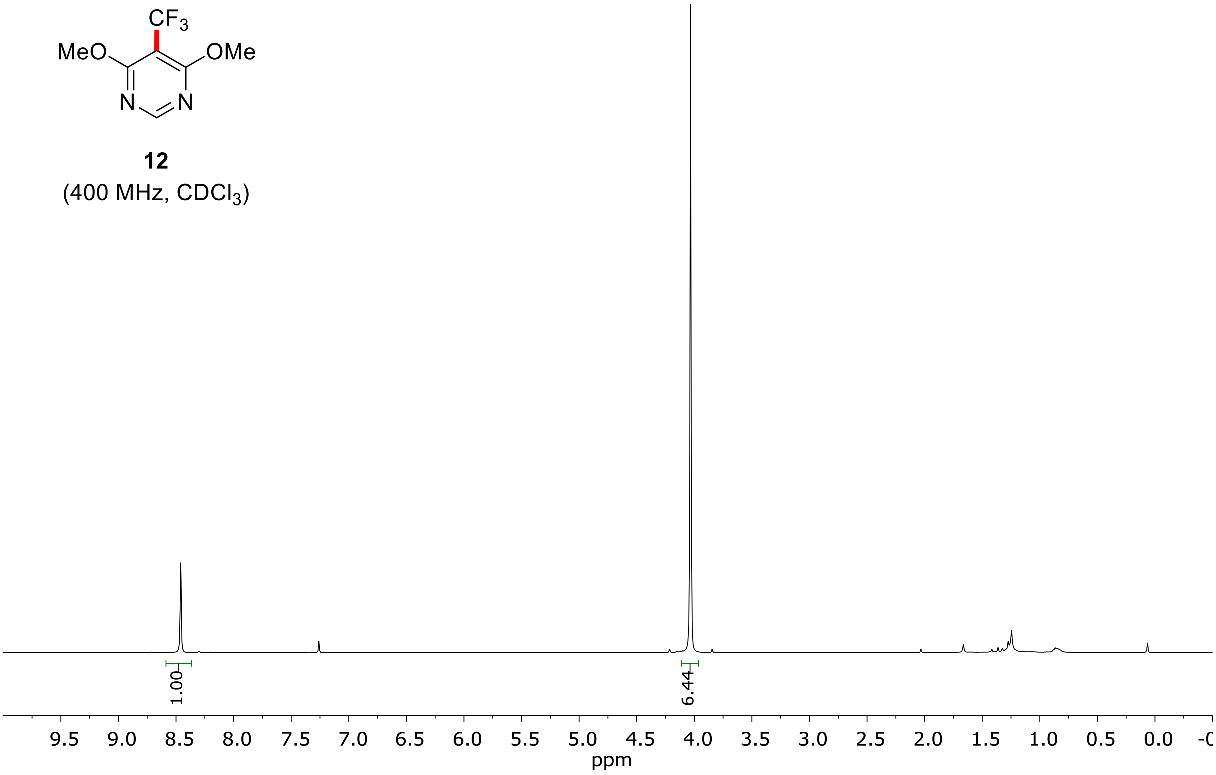
11
(100 MHz, $CDCl_3$)



11

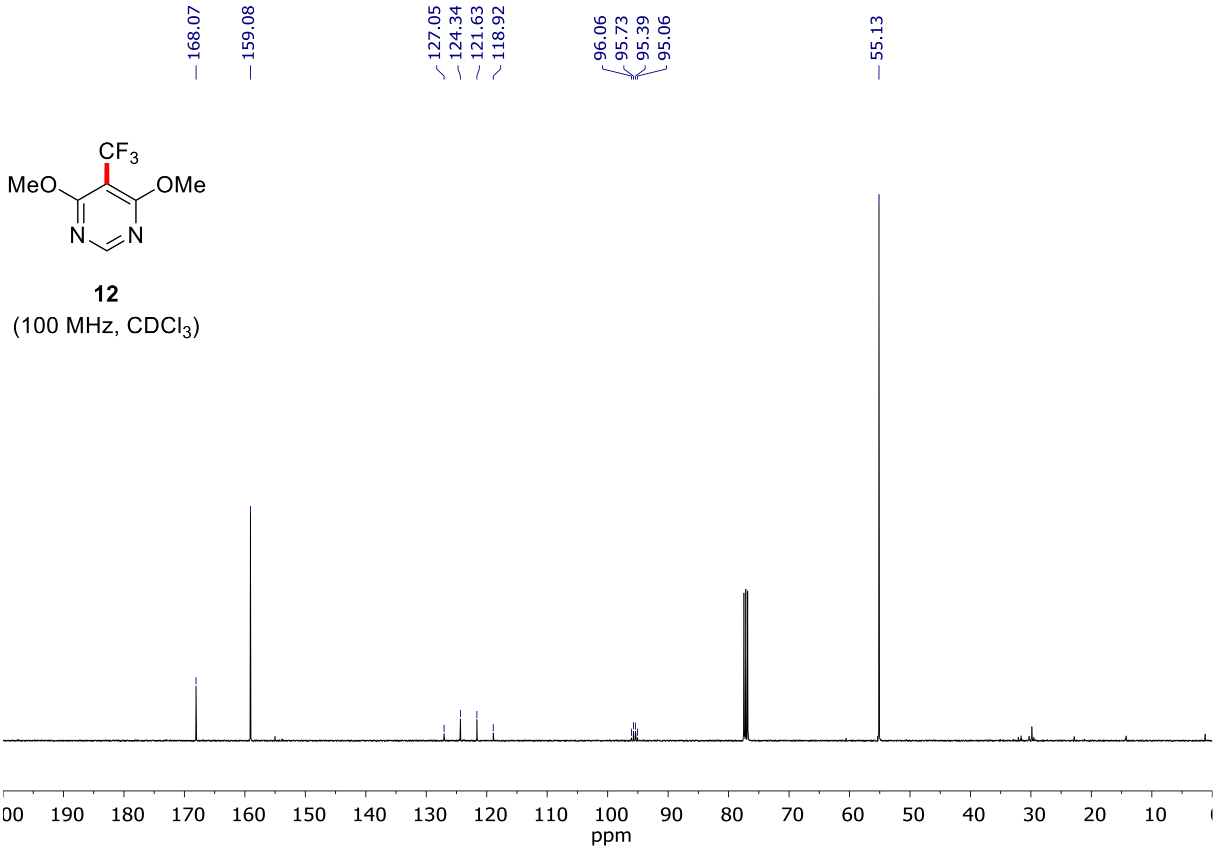
^{19}F

(377 MHz, $CDCl_3$)



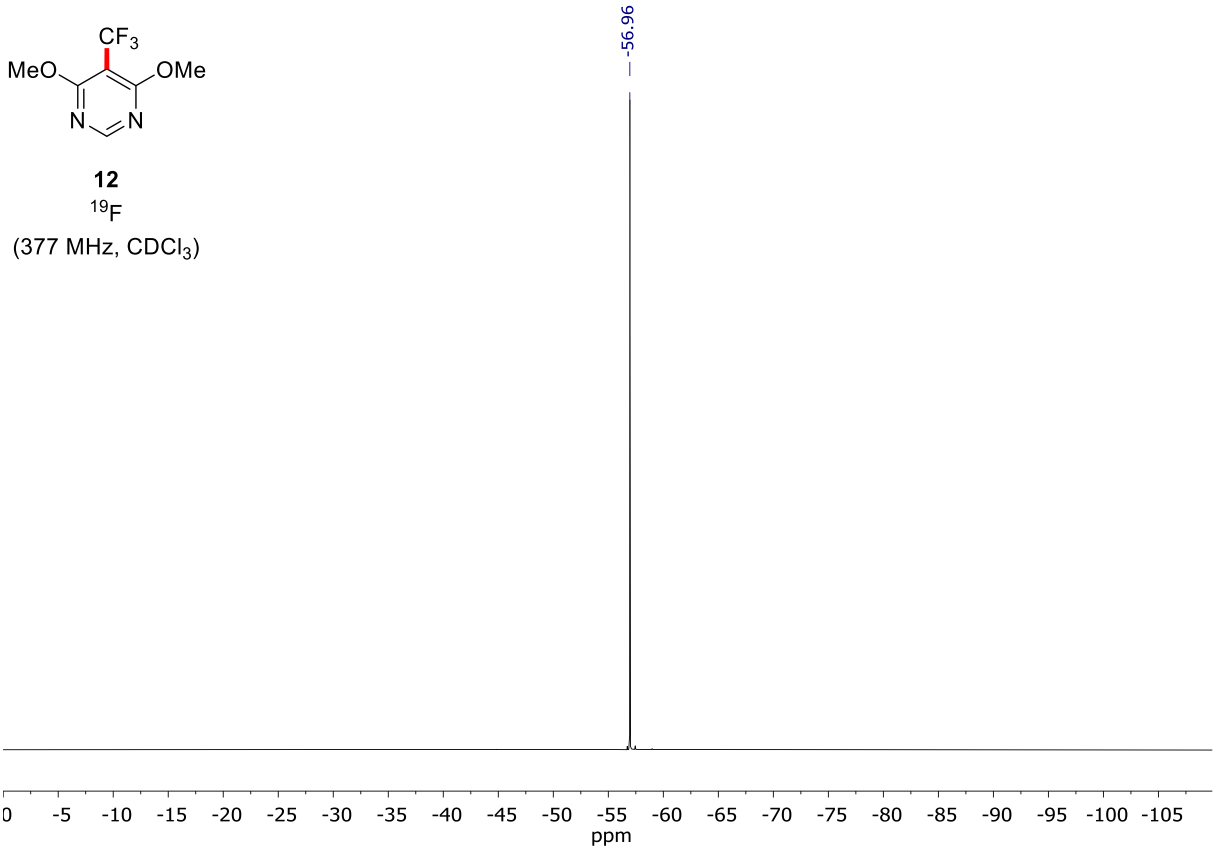
12

(400 MHz, $CDCl_3$)



12

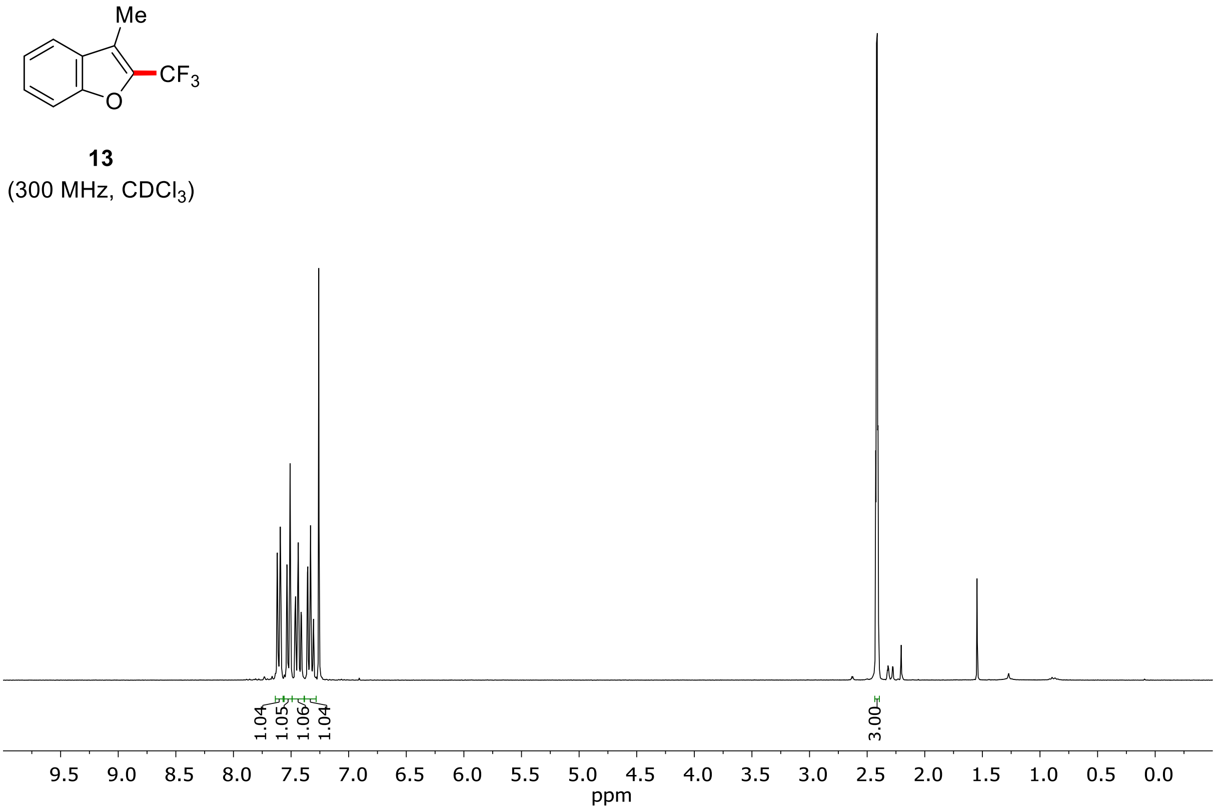
(100 MHz, $CDCl_3$)



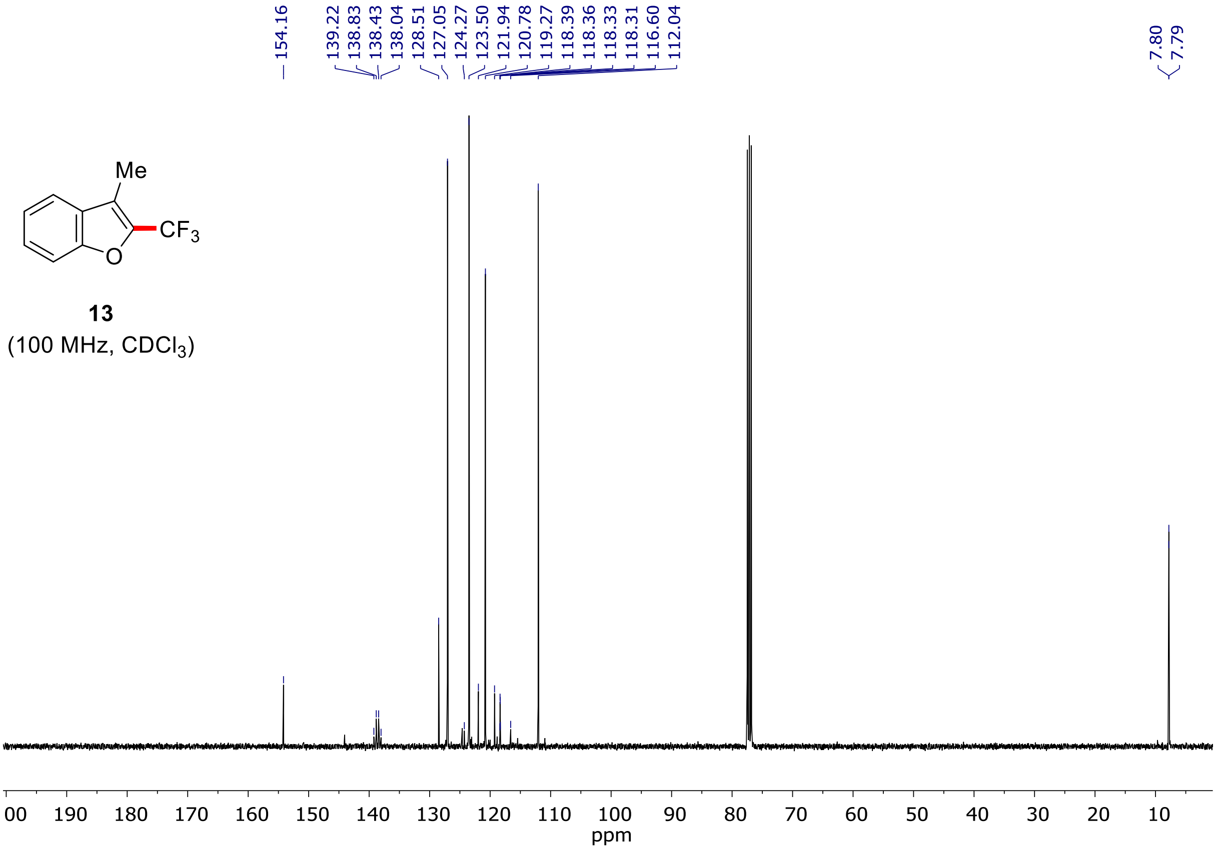
12

^{19}F

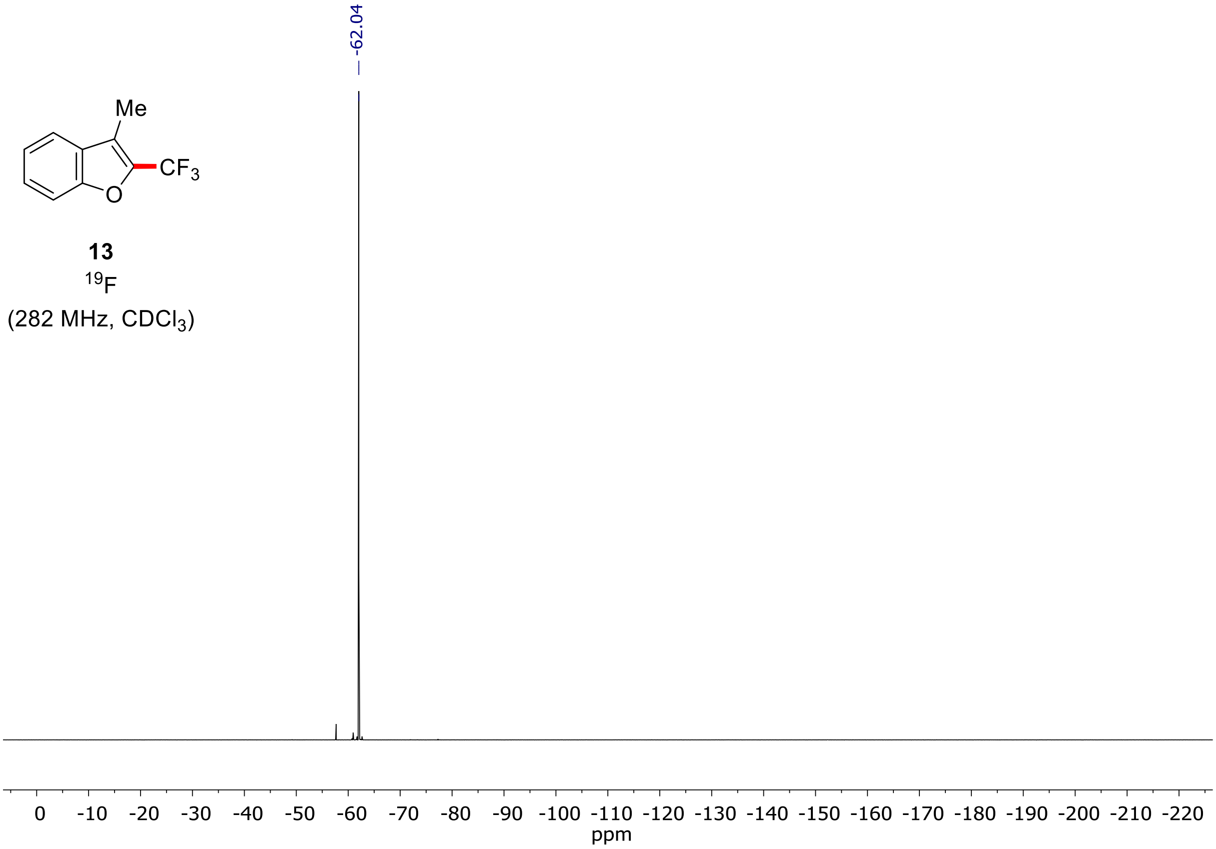
(377 MHz, $CDCl_3$)



13
(300 MHz, $CDCl_3$)



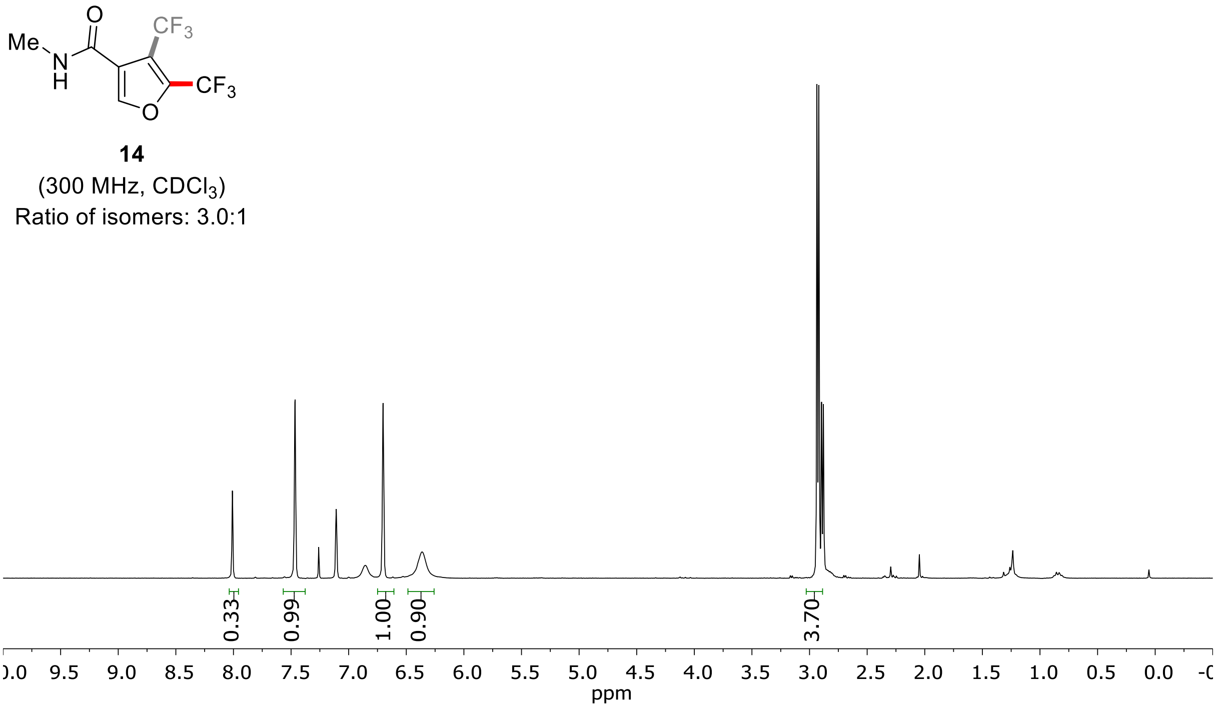
13
(100 MHz, $CDCl_3$)



13

^{19}F

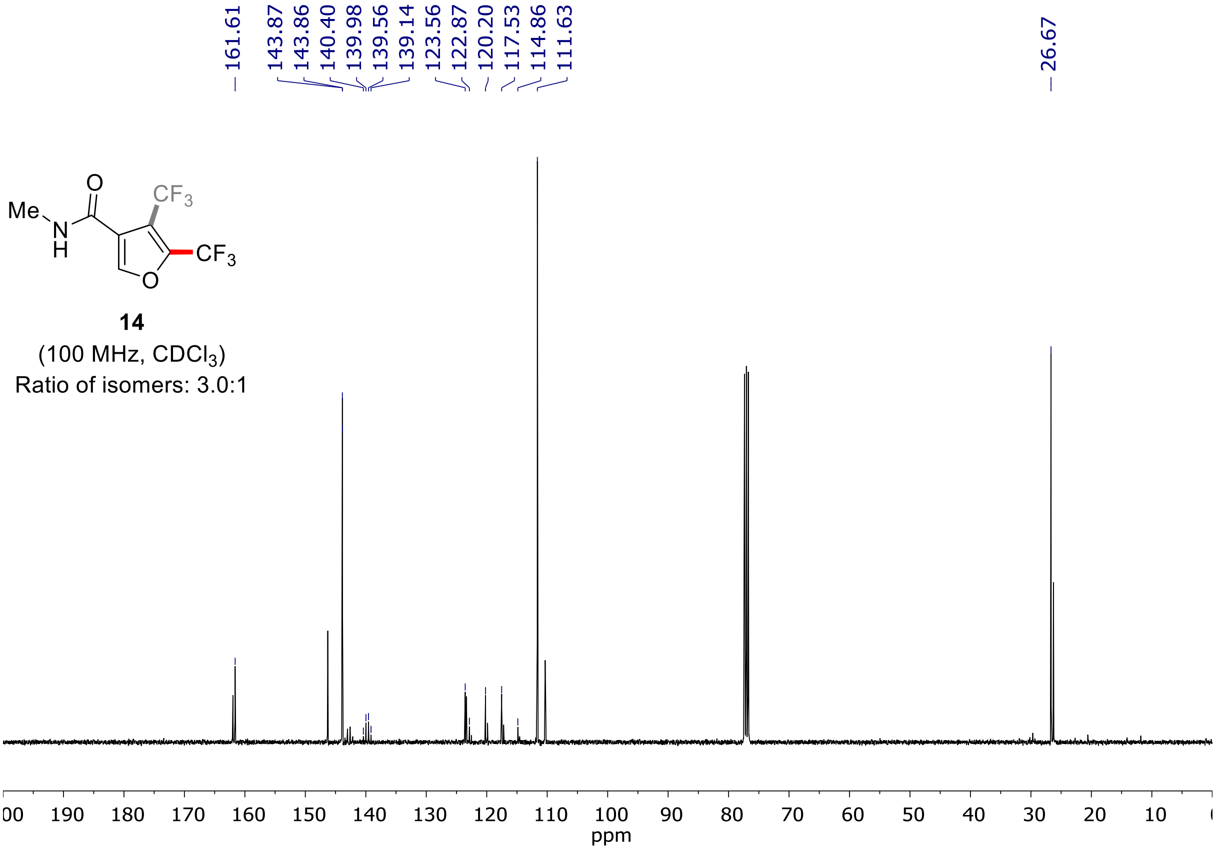
(282 MHz, CDCl$_3$)



14

(300 MHz, CDCl$_3$)

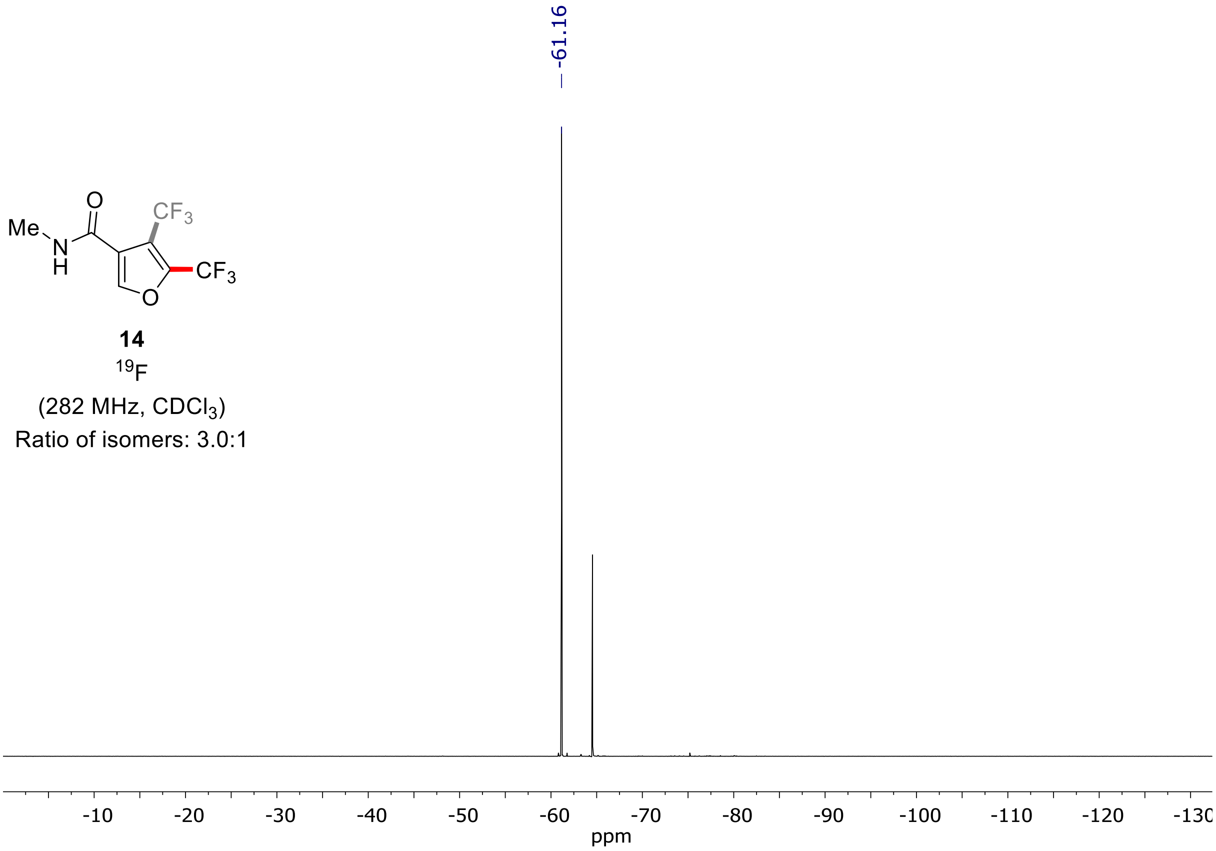
Ratio of isomers: 3.0:1



14

(100 MHz, CDCl$_3$)

Ratio of isomers: 3.0:1

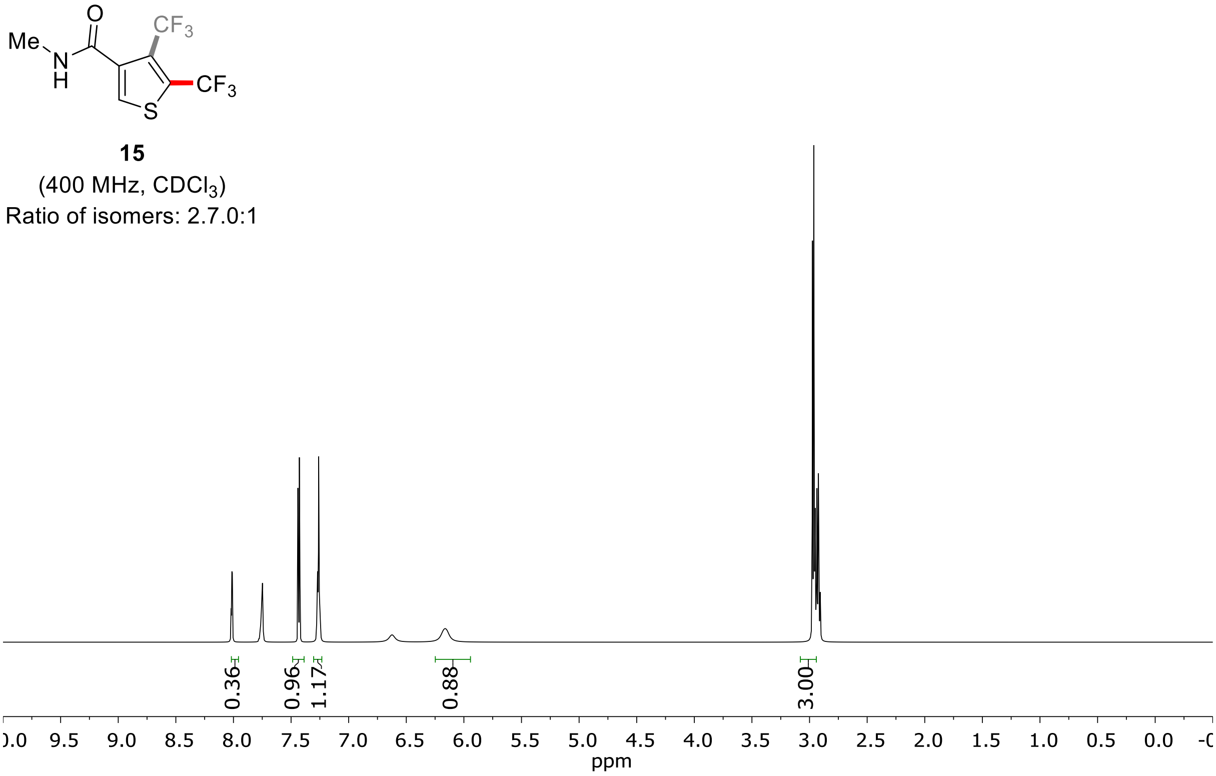


14

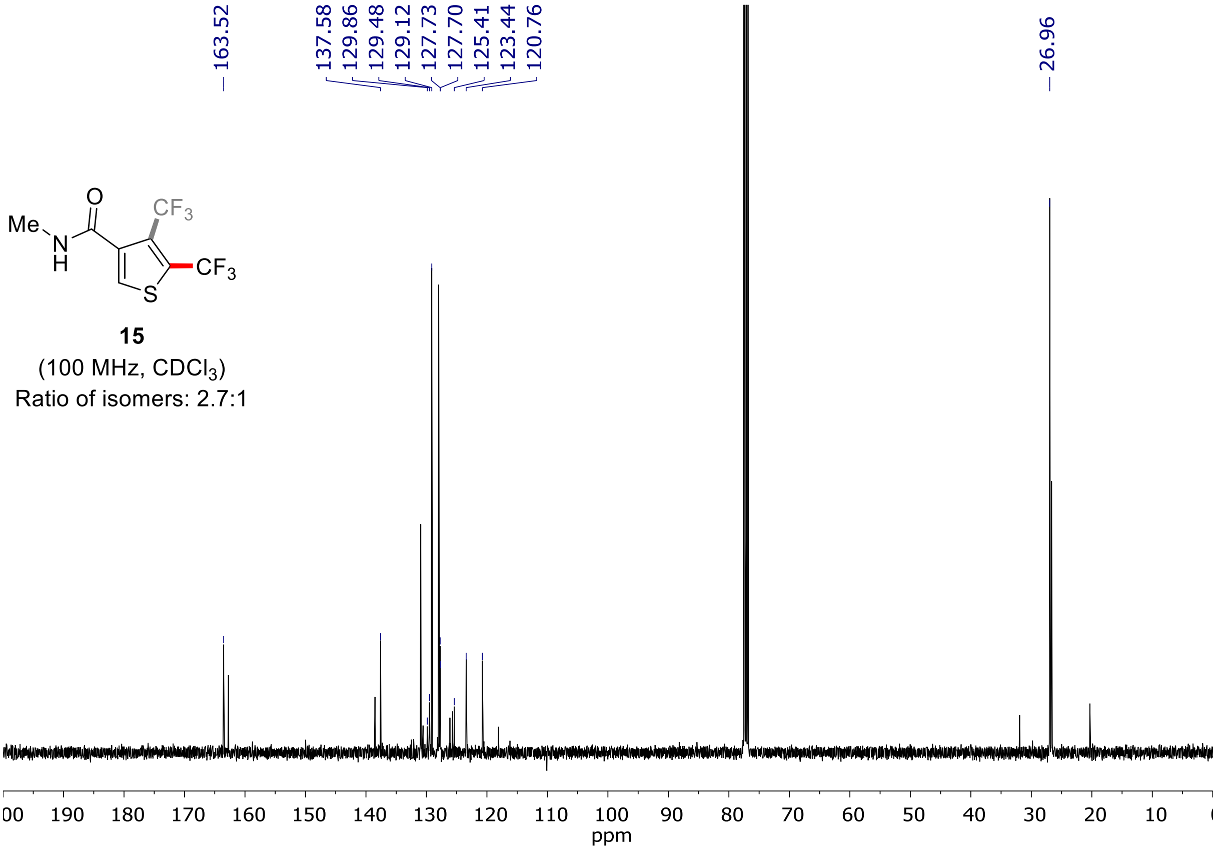
^{19}F

(282 MHz, CDCl$_3$)

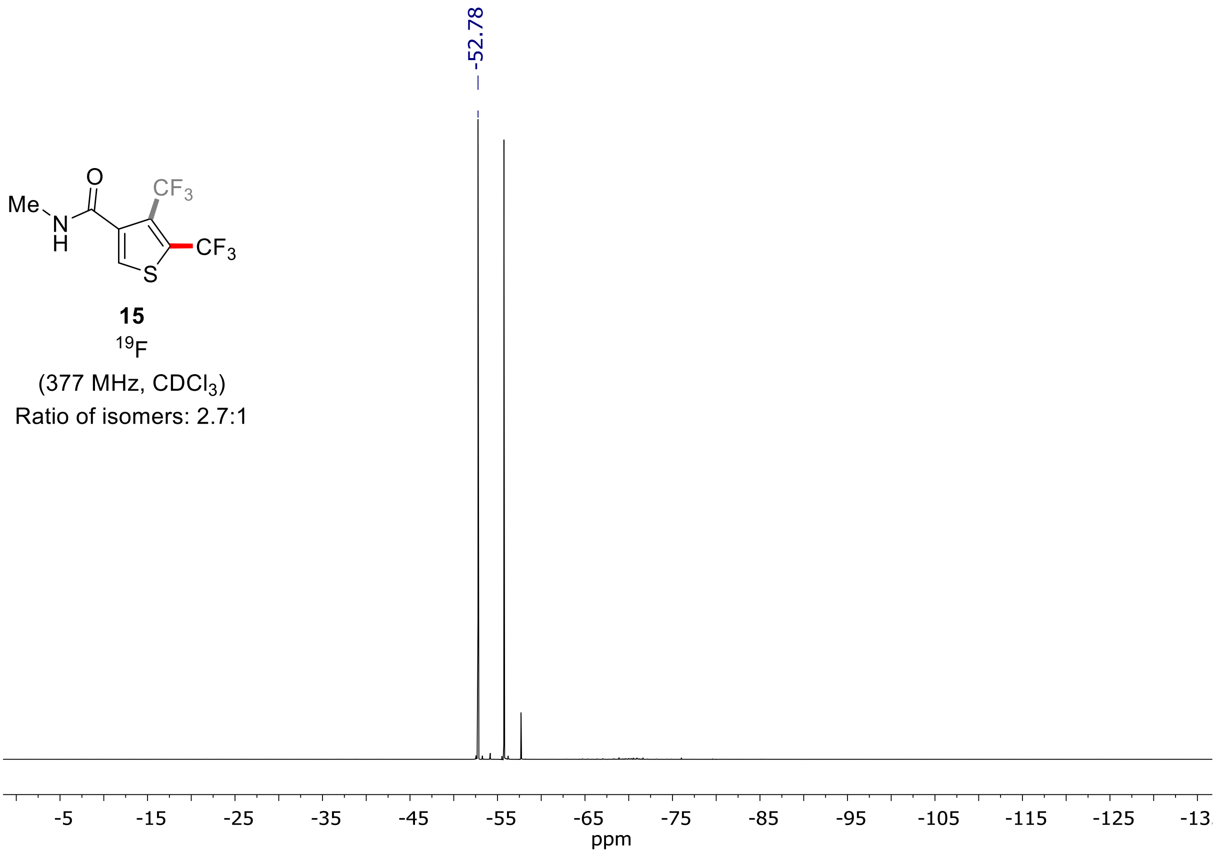
Ratio of isomers: 3.0:1



15
(400 MHz, $CDCl_3$)
Ratio of isomers: 2.7.0:1



15
(100 MHz, $CDCl_3$)
Ratio of isomers: 2.7:1

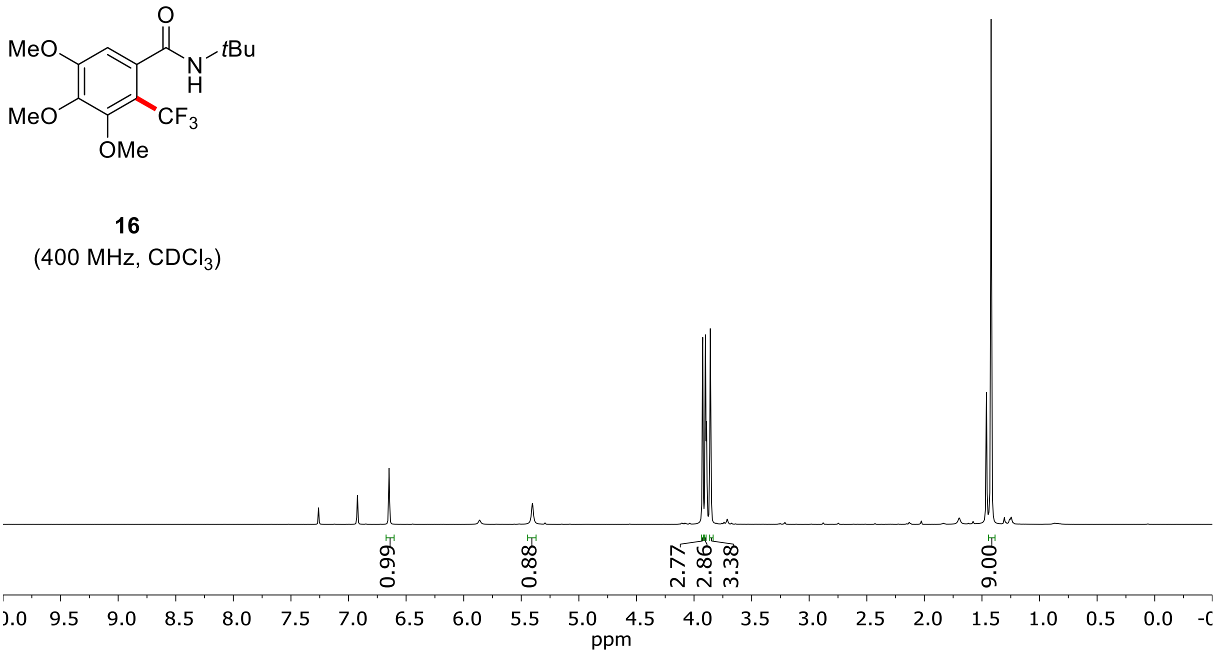


15

^{19}F

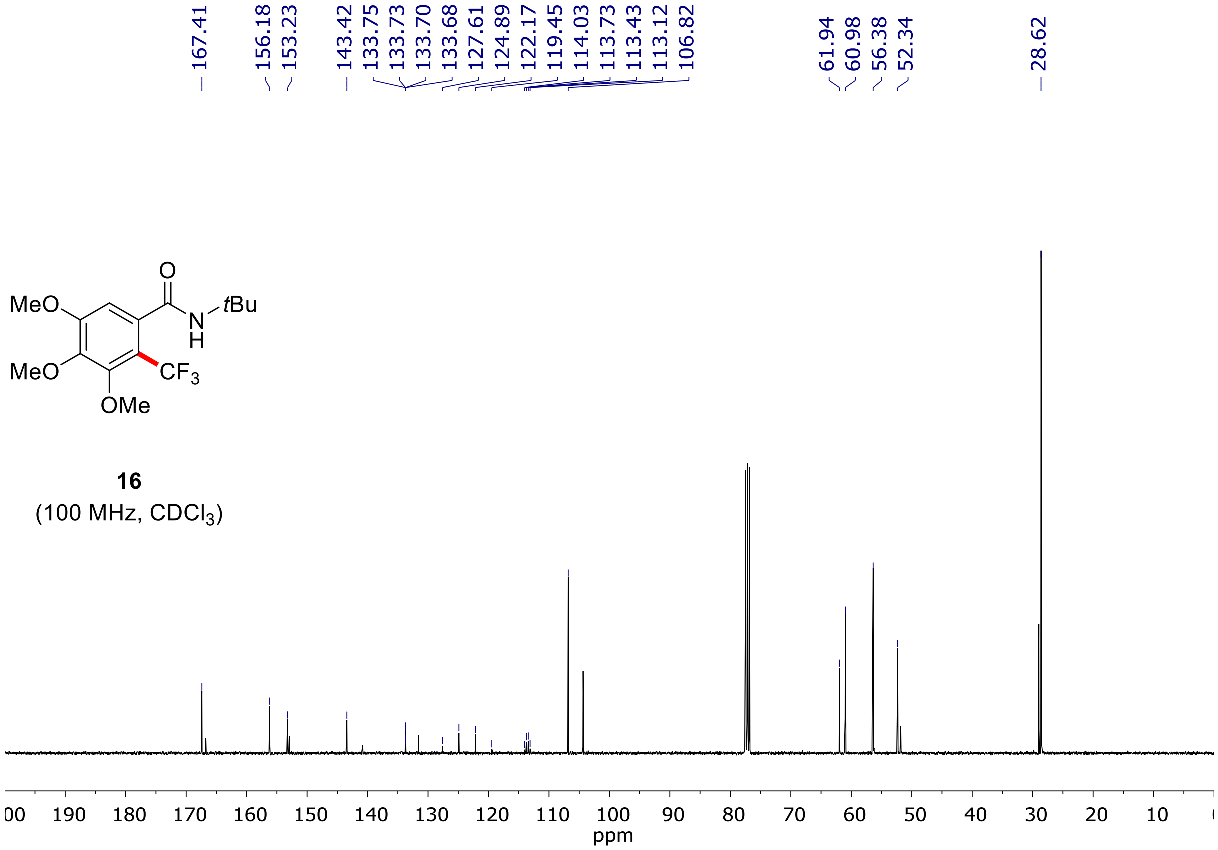
(377 MHz, $CDCl_3$)

Ratio of isomers: 2.7:1

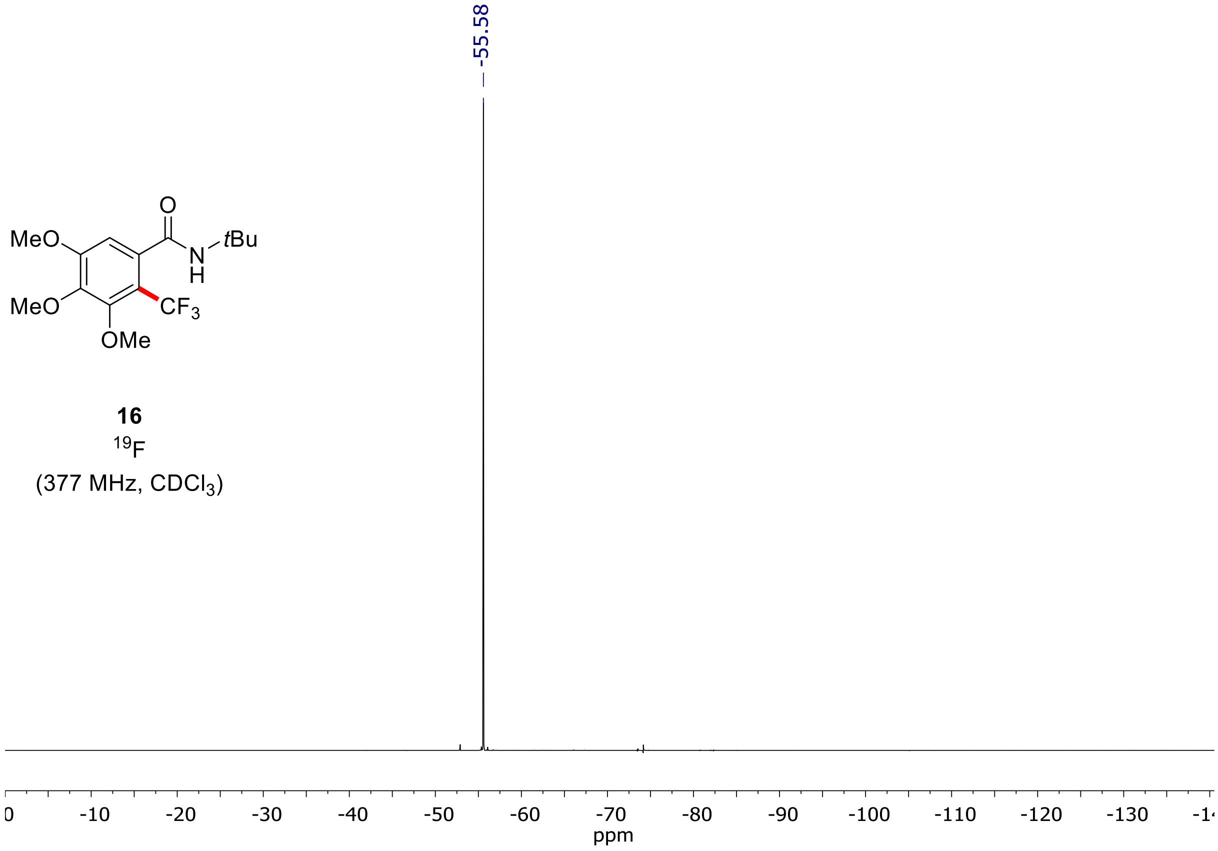


16

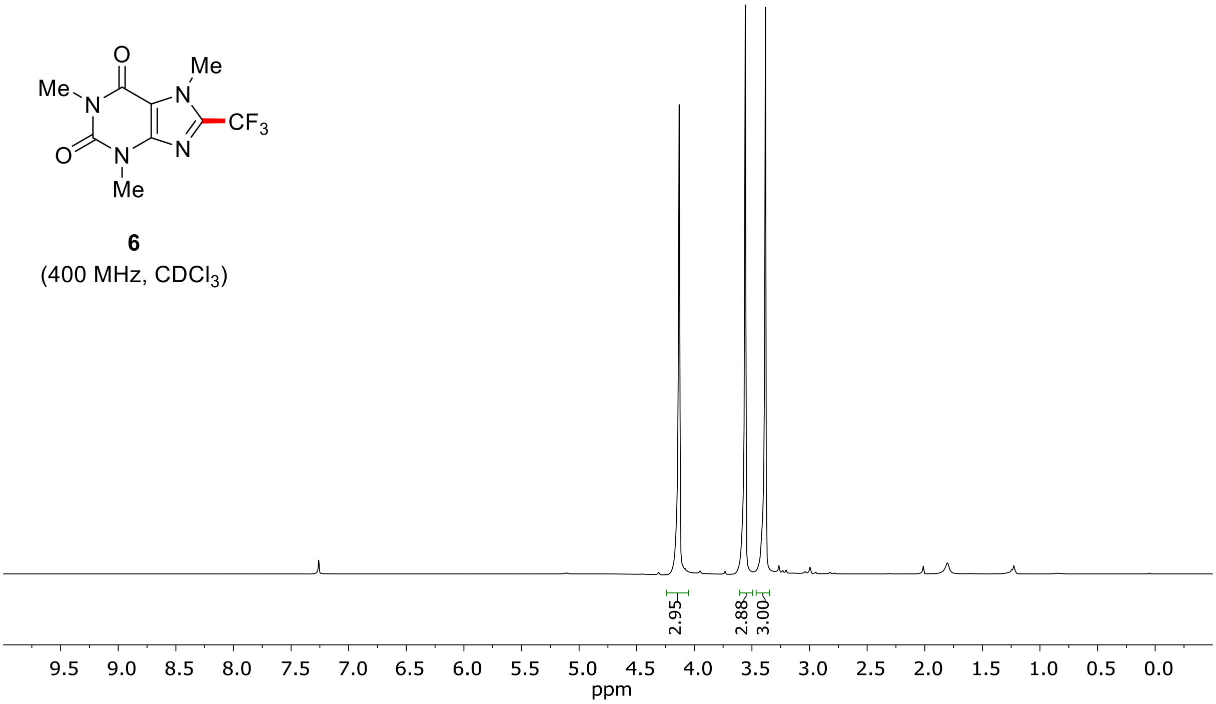
(400 MHz, $CDCl_3$)



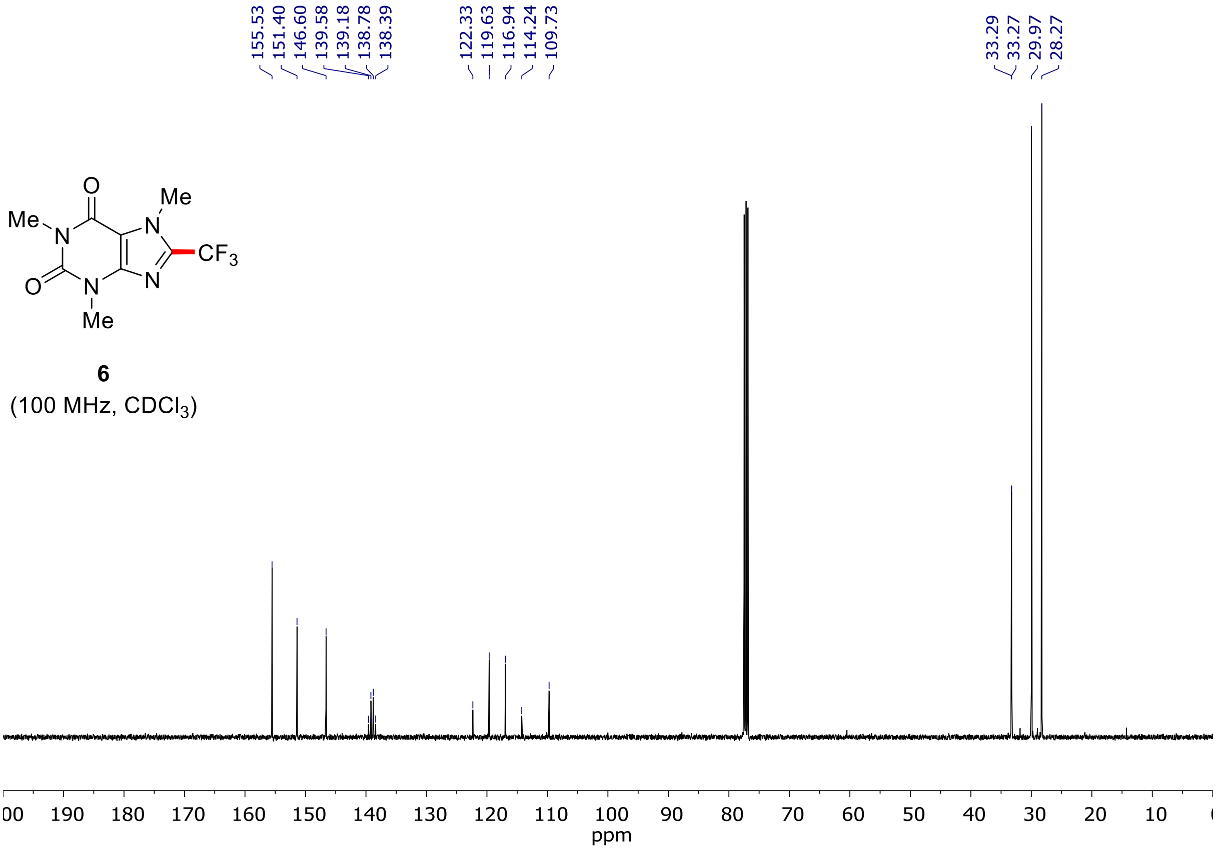
16
(100 MHz, $CDCl_3$)



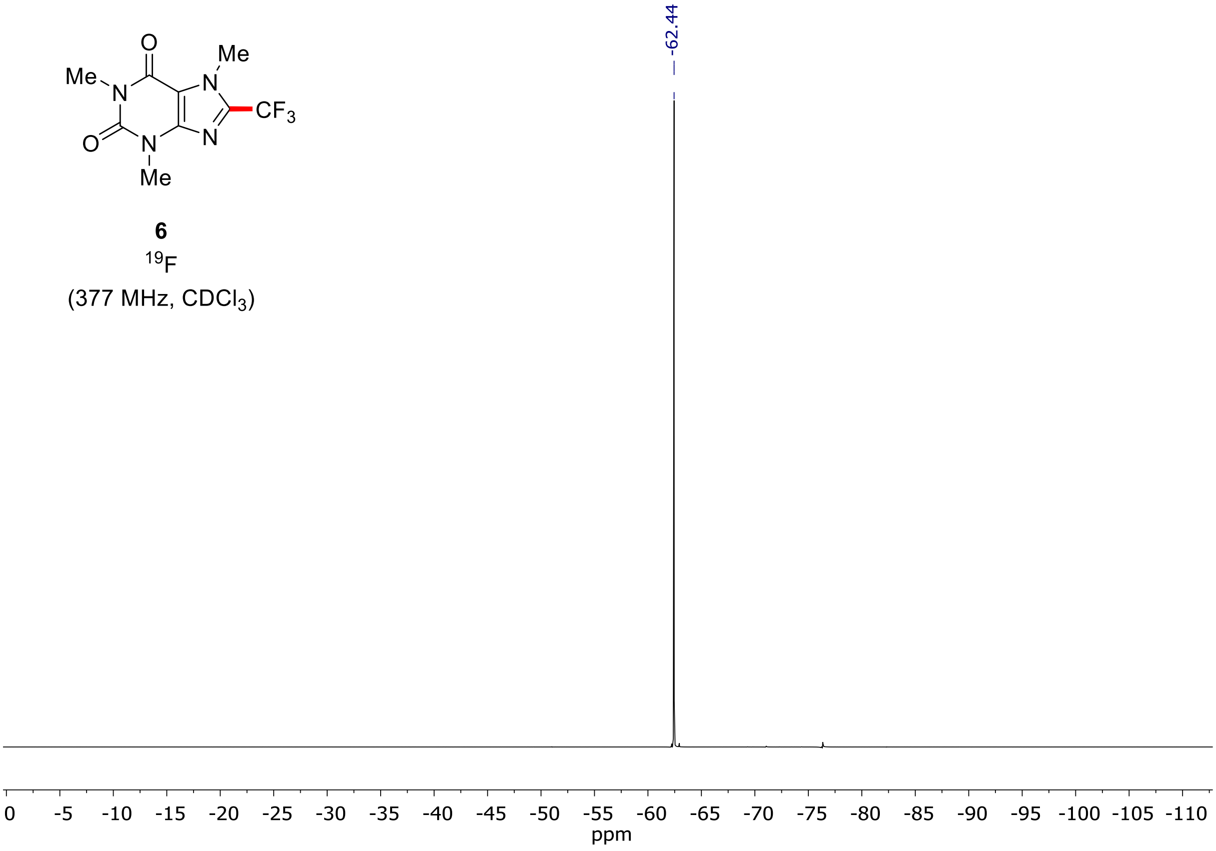
16
^{19}F
(377 MHz, $CDCl_3$)



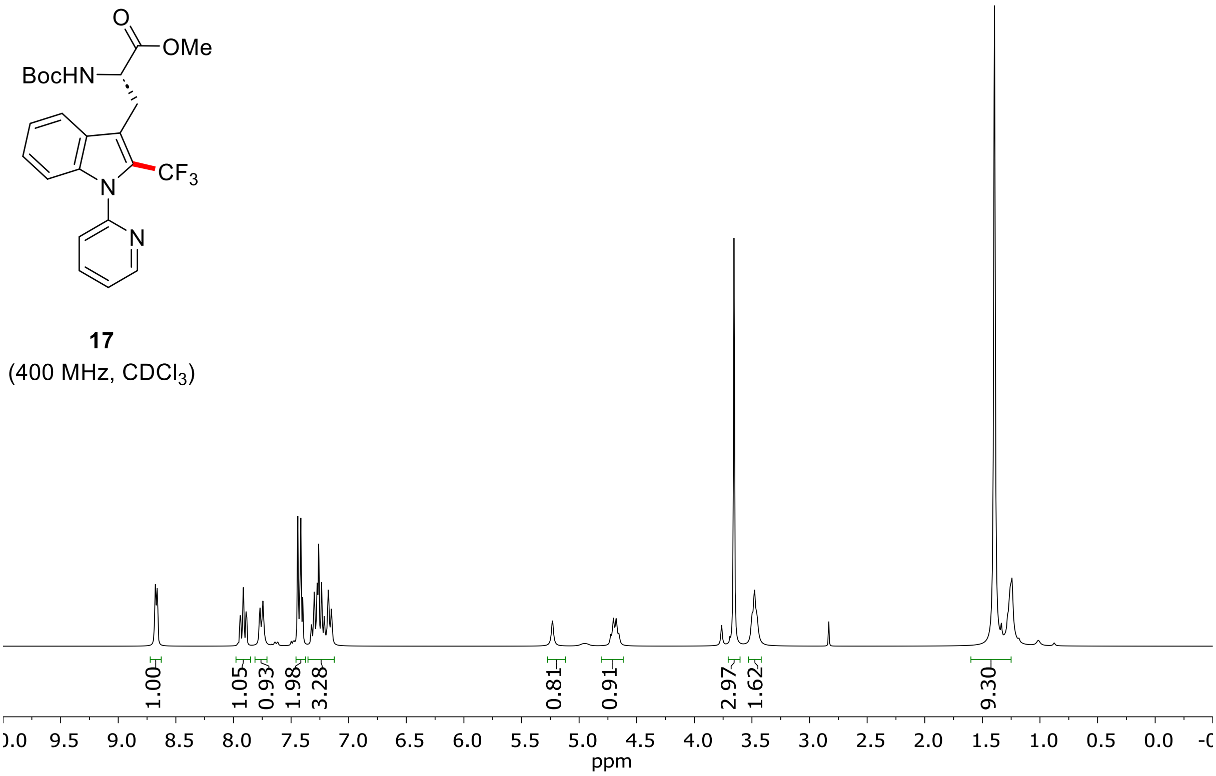
6
(400 MHz, $CDCl_3$)



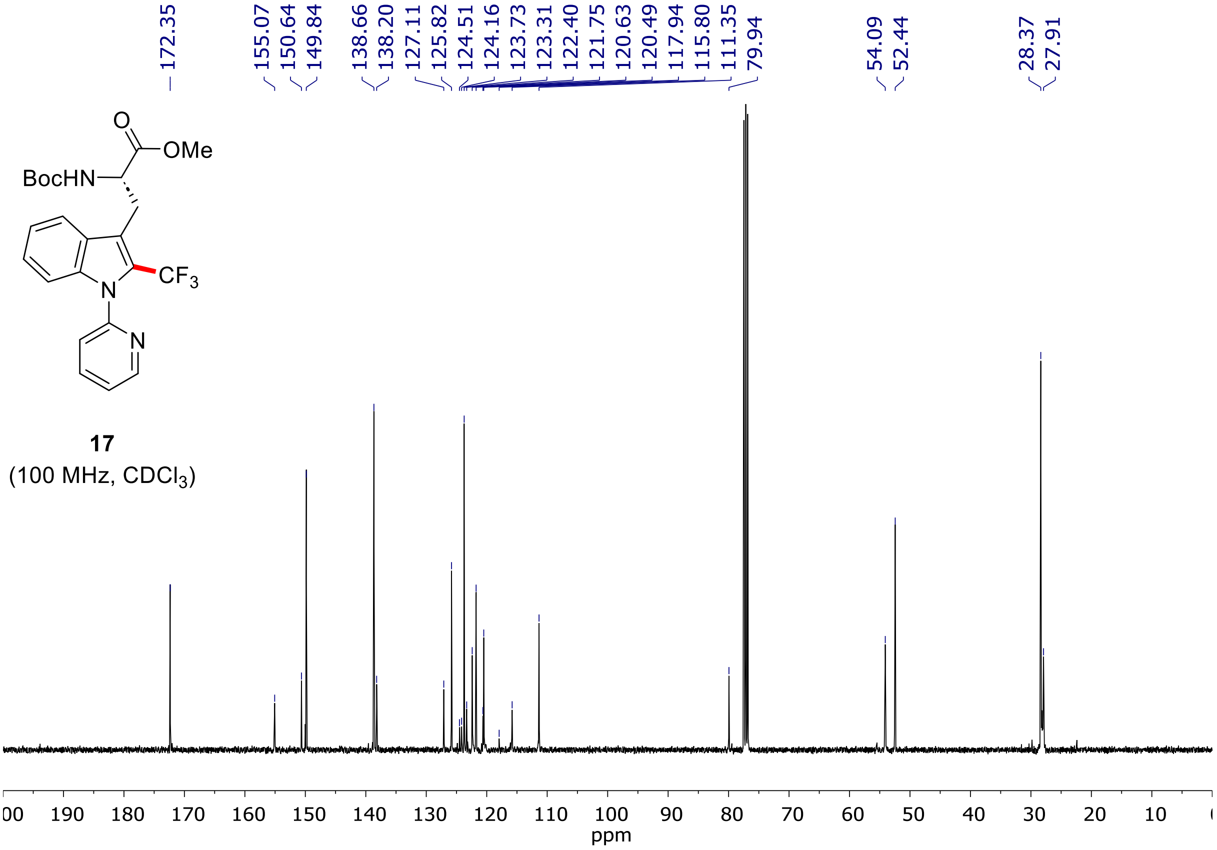
6
(100 MHz, $CDCl_3$)



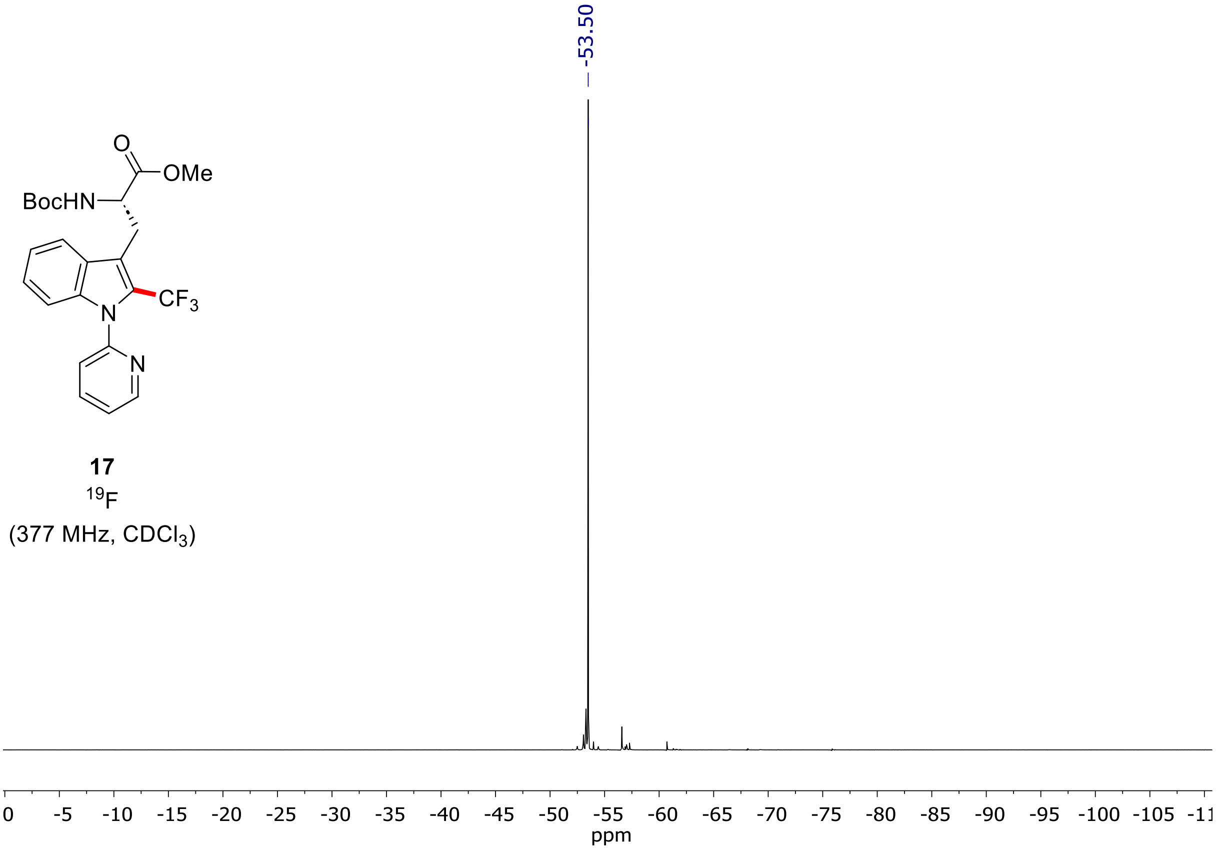
6
^{19}F
(377 MHz, $CDCl_3$)



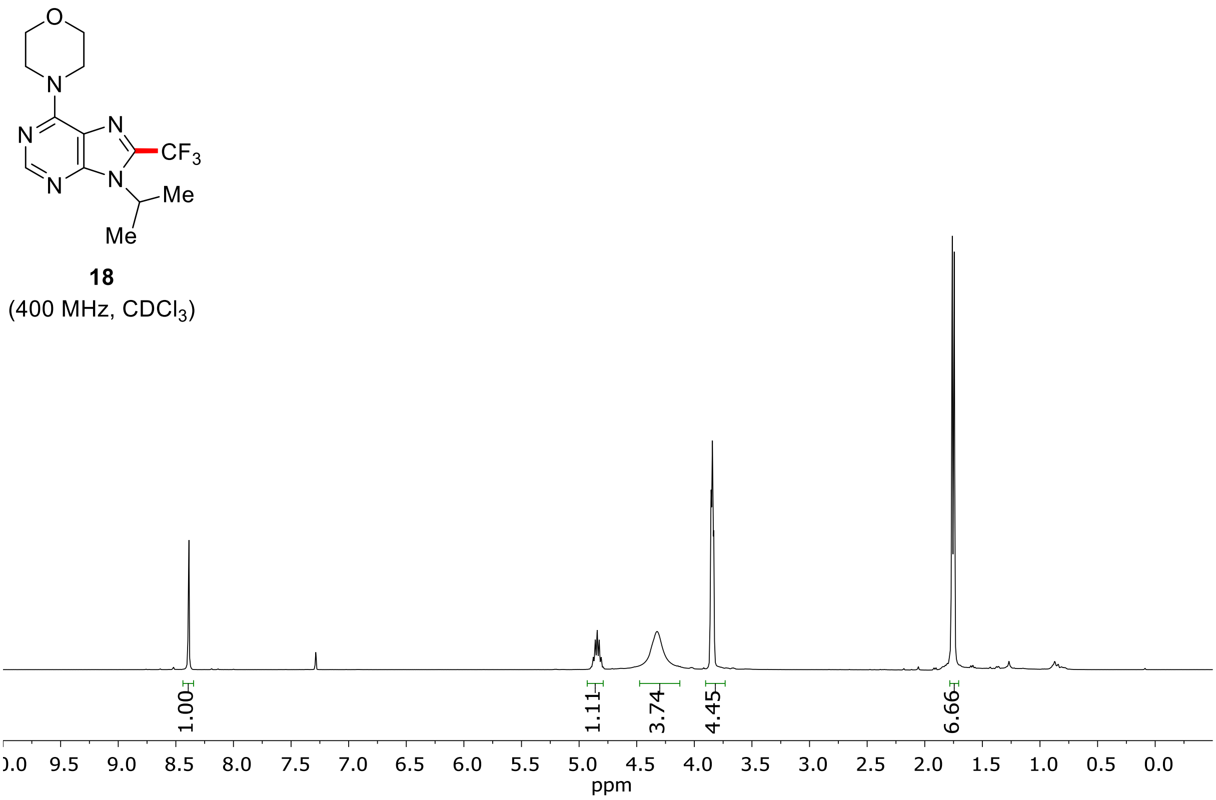
17
(400 MHz, $CDCl_3$)



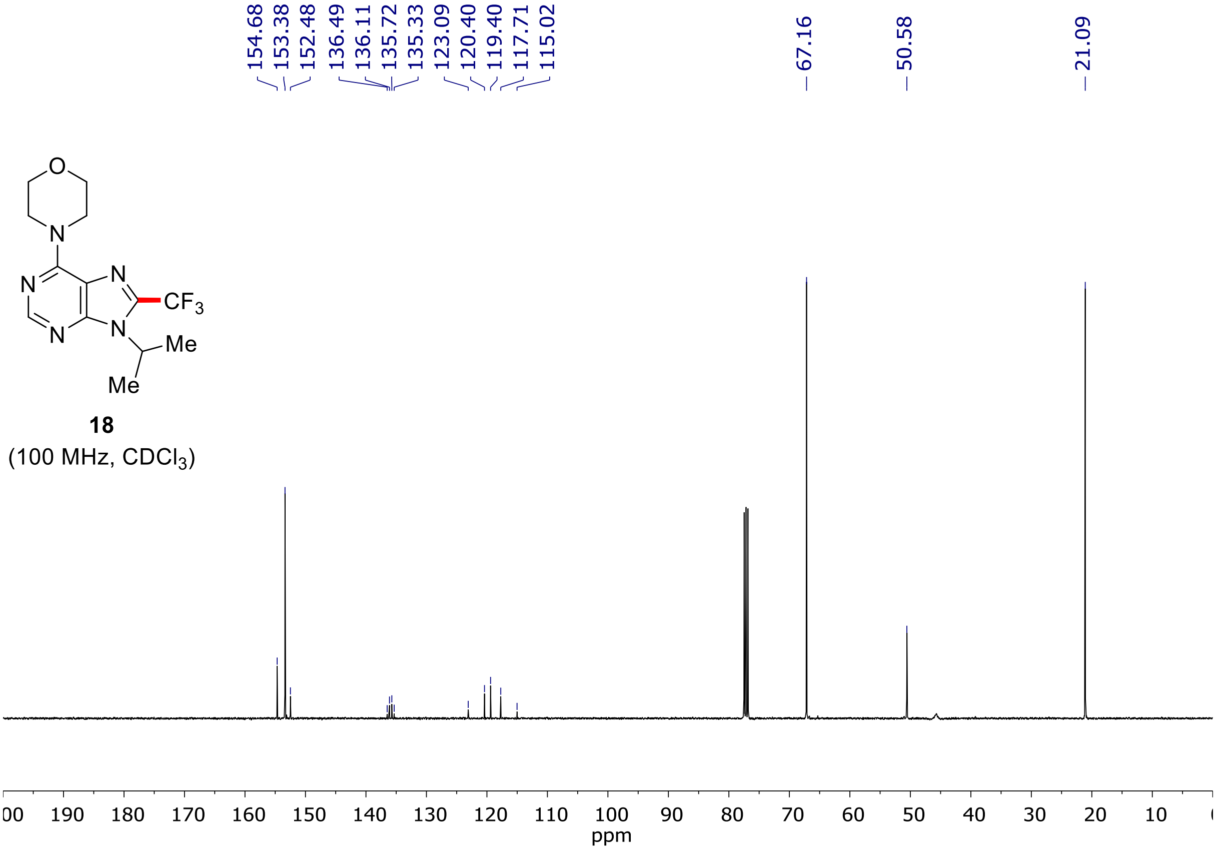
17
(100 MHz, $CDCl_3$)



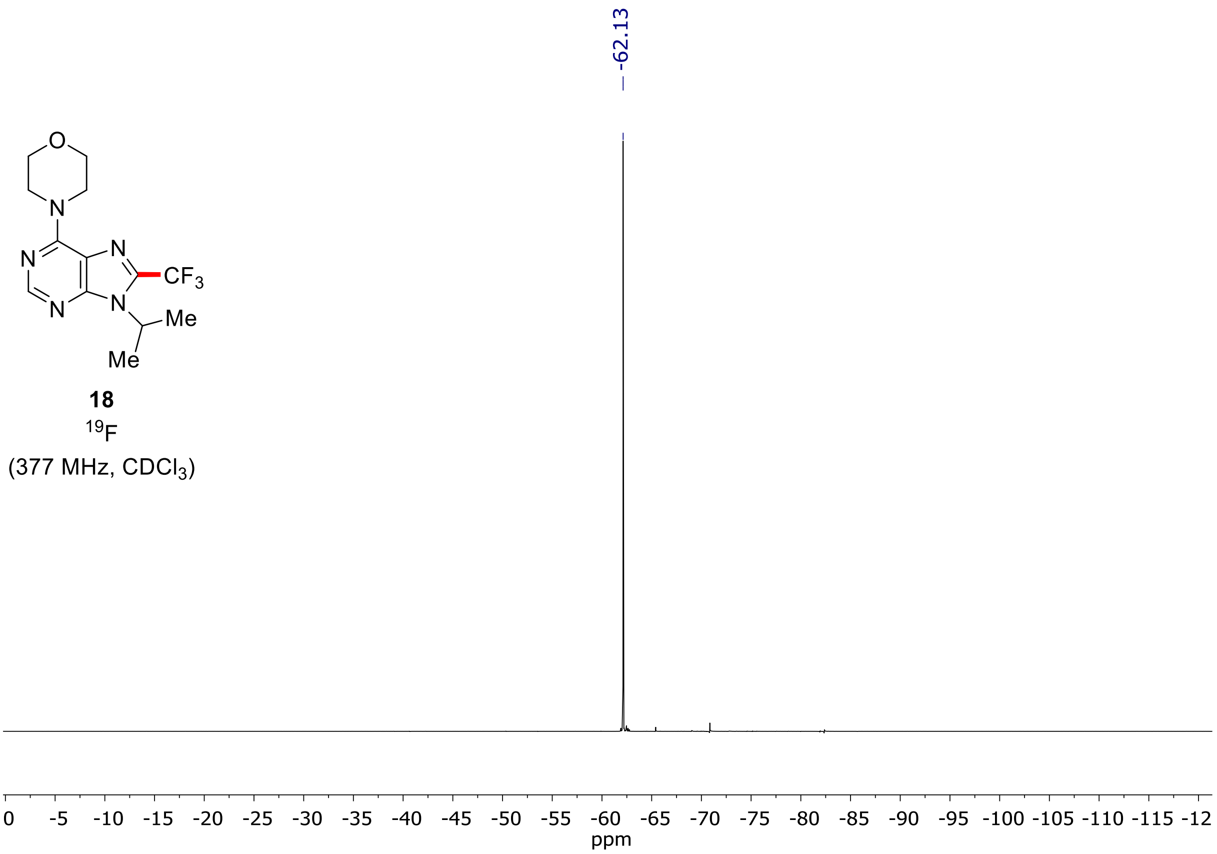
17
^{19}F
(377 MHz, $CDCl_3$)



18
(400 MHz, $CDCl_3$)



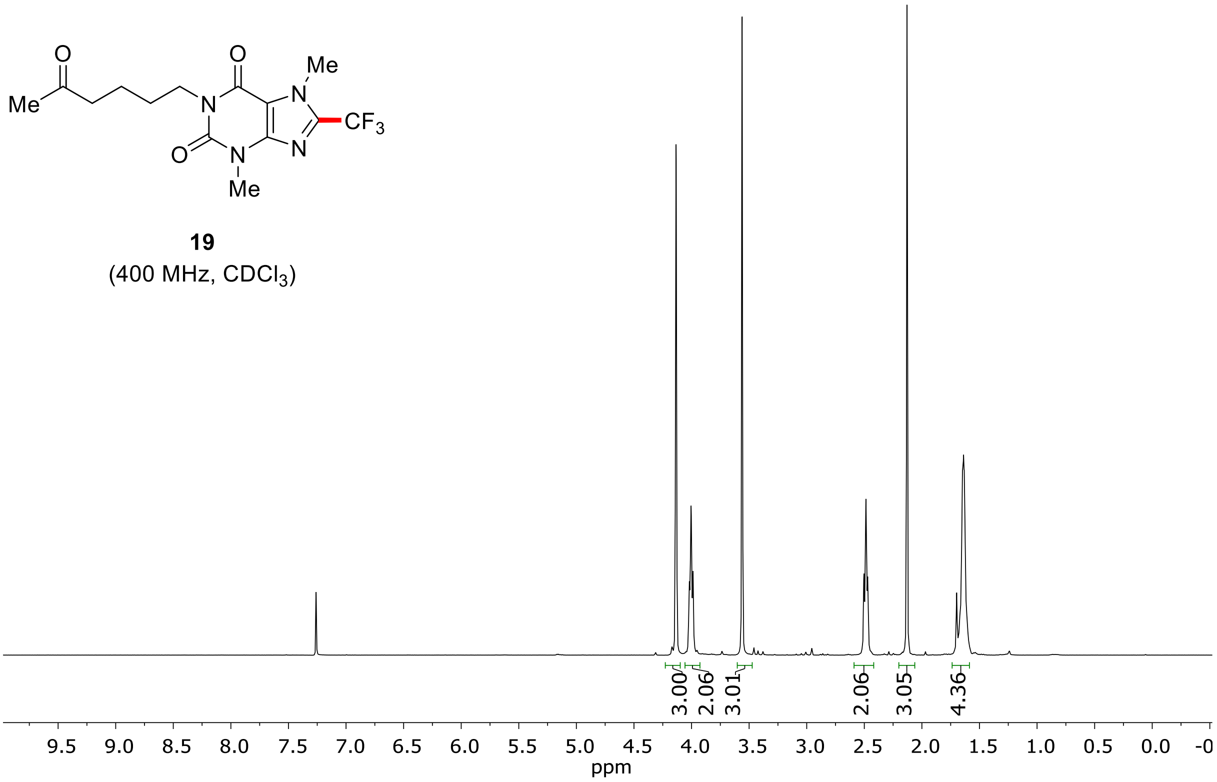
18
(100 MHz, $CDCl_3$)



18

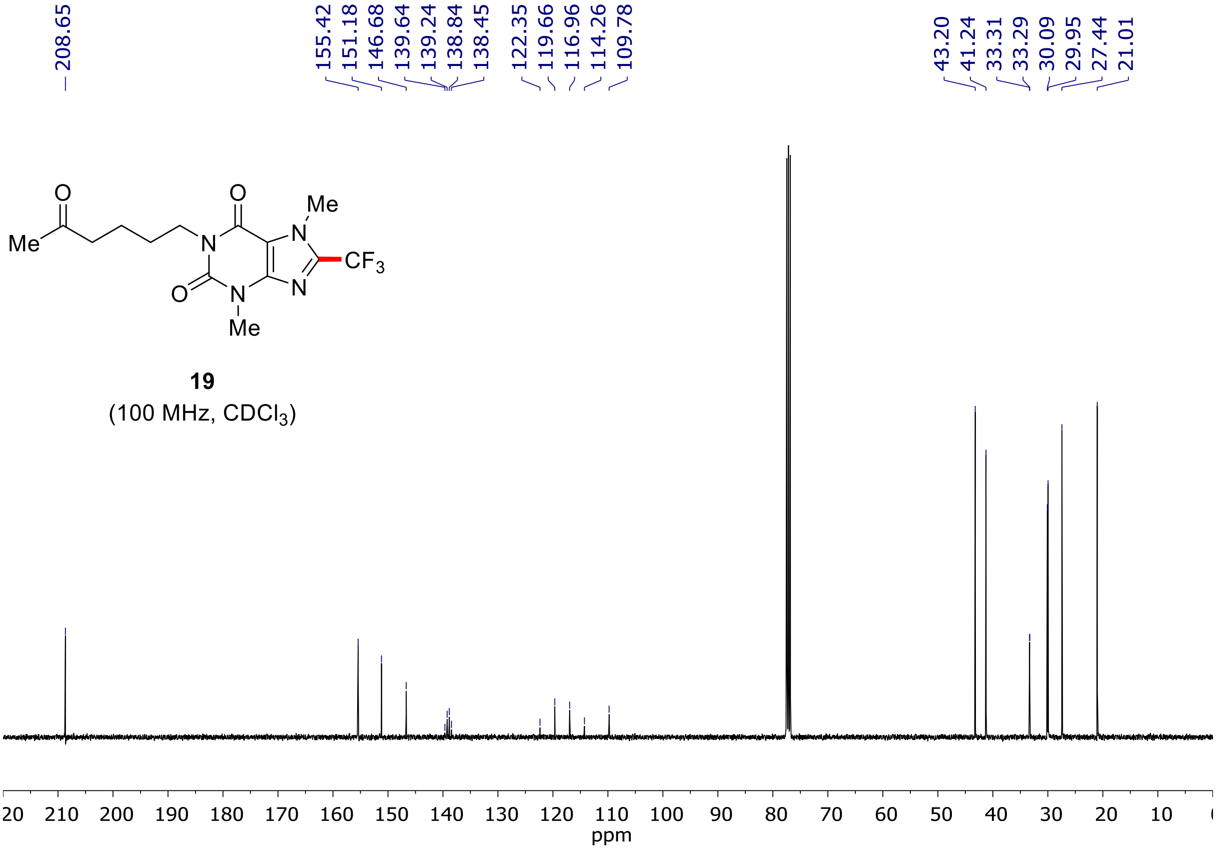
^{19}F

(377 MHz, $CDCl_3$)



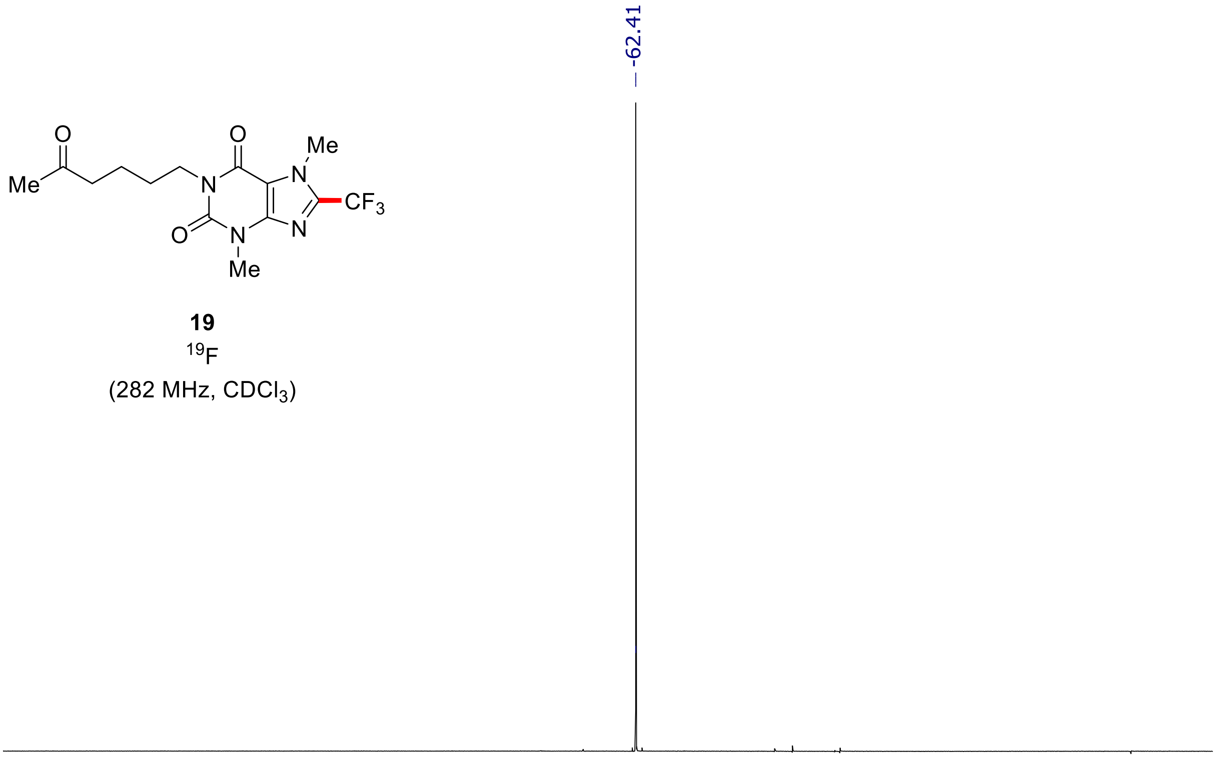
19

(400 MHz, $CDCl_3$)



19

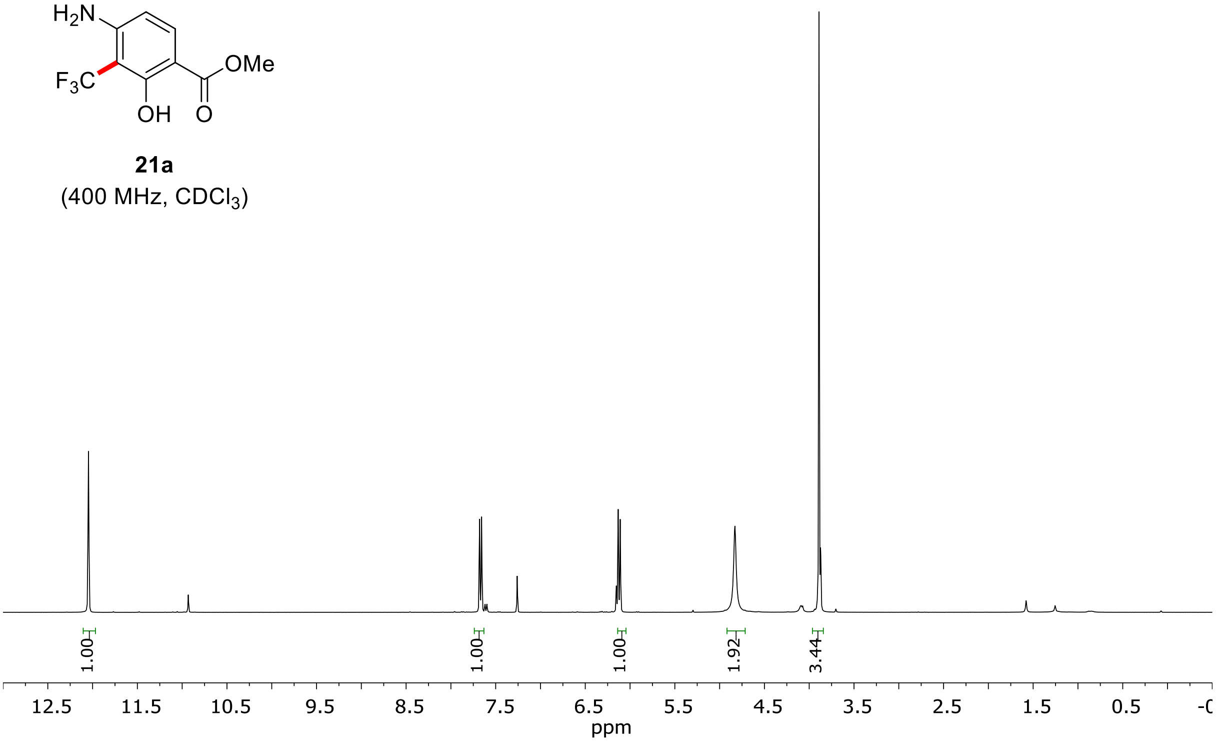
(100 MHz, $CDCl_3$)



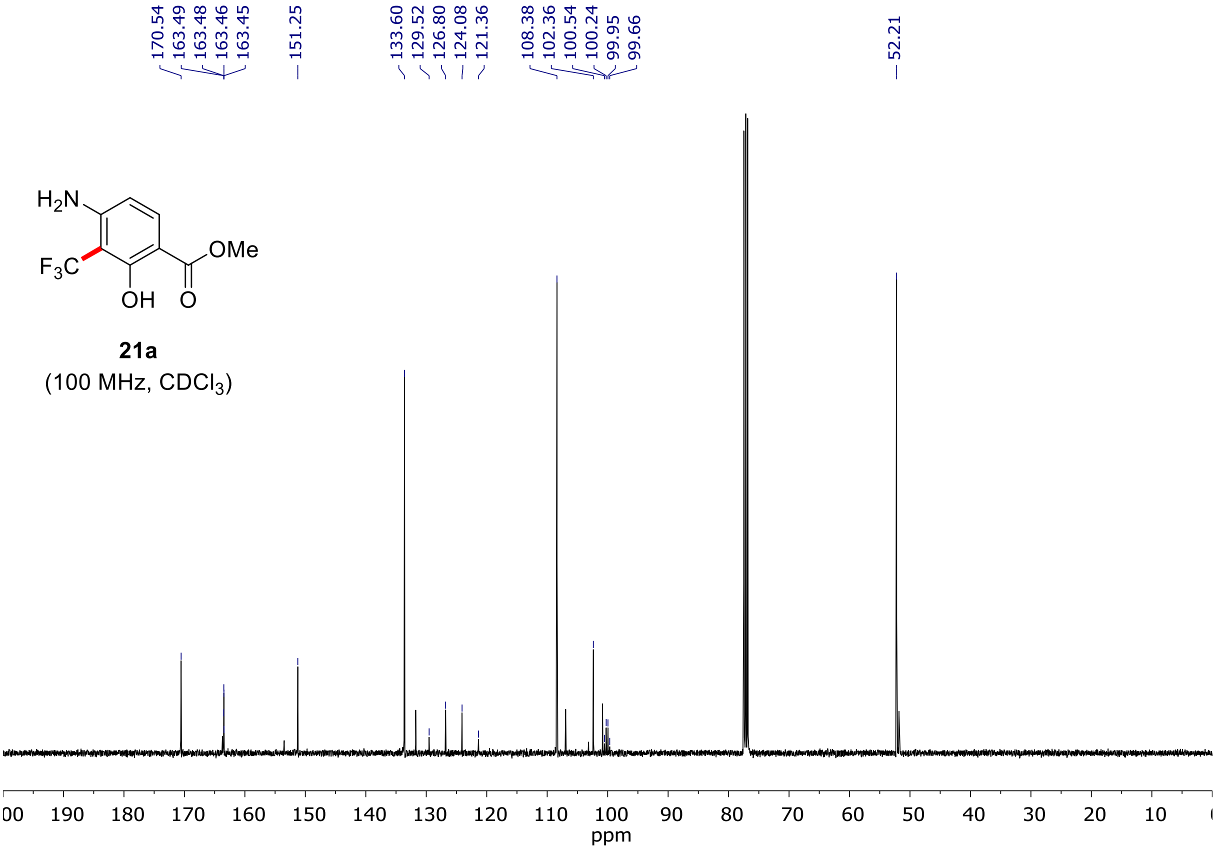
19

^{19}F

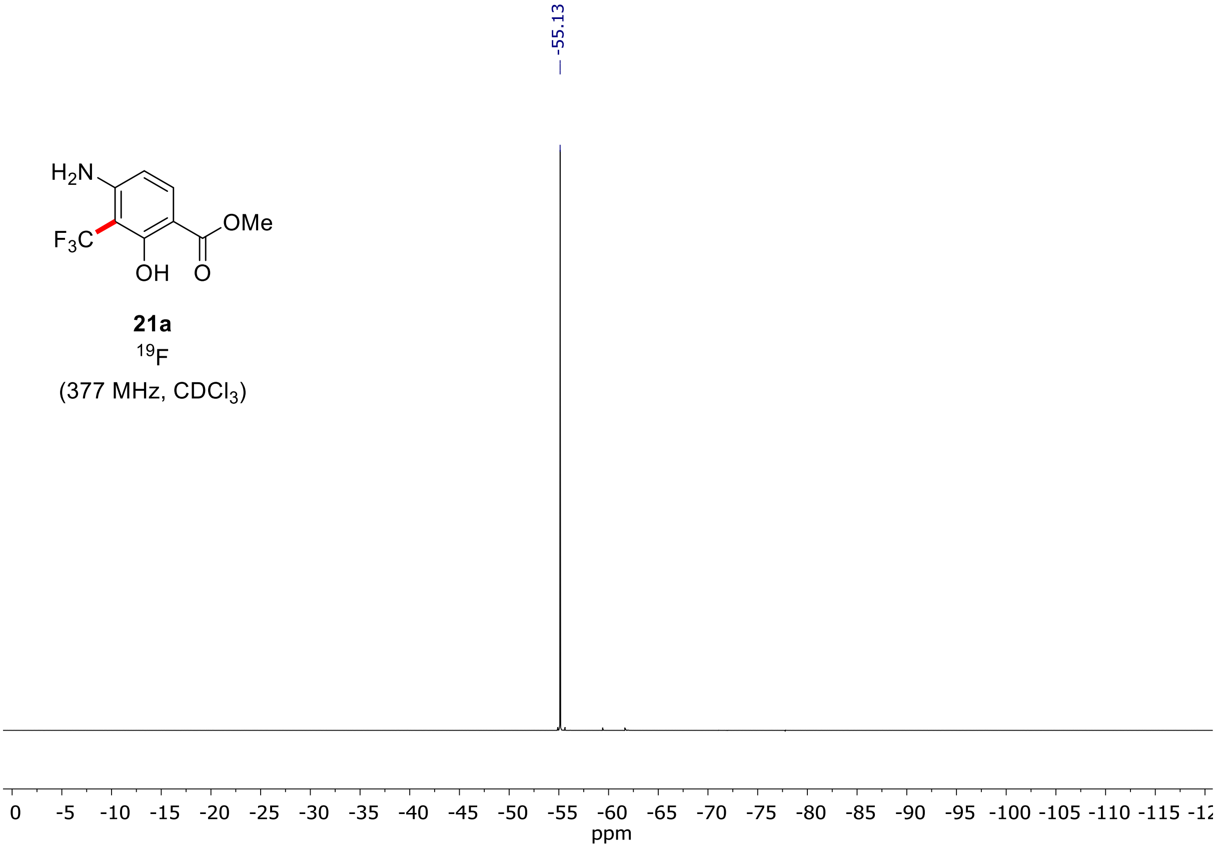
(282 MHz, $CDCl_3$)



21a
(400 MHz, $CDCl_3$)

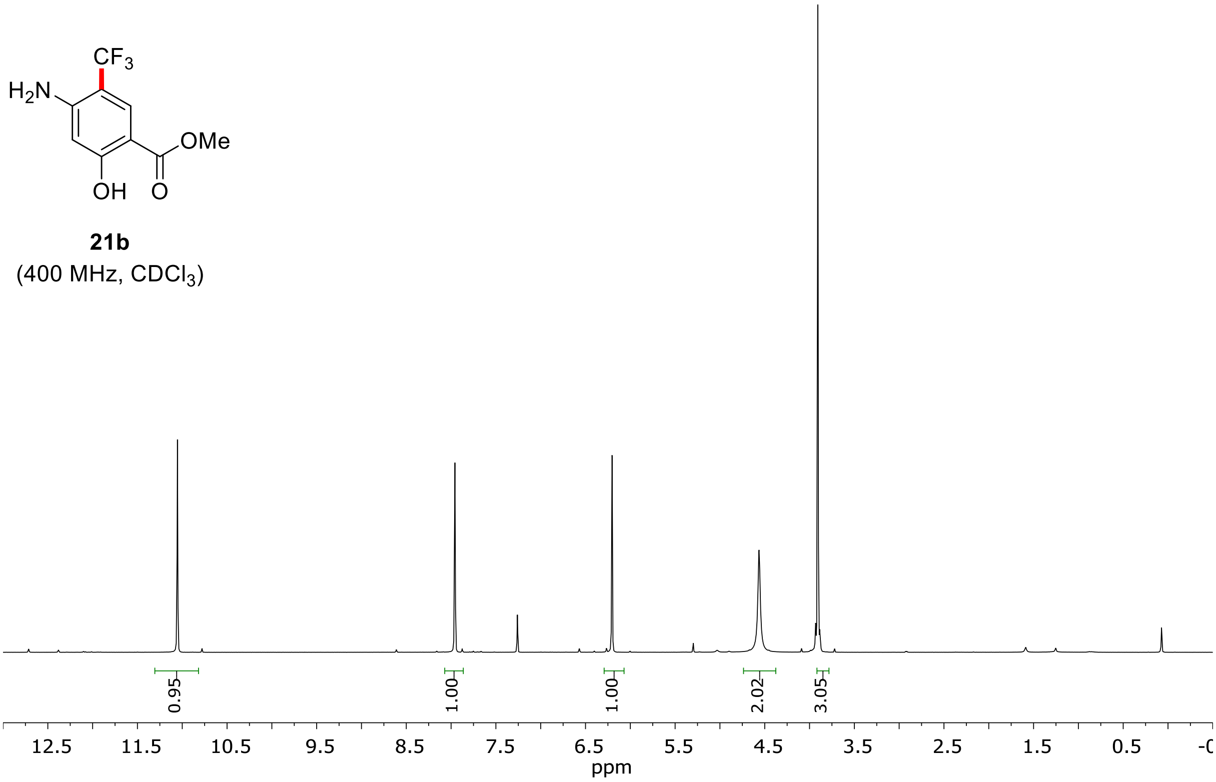


21a
(100 MHz, $CDCl_3$)

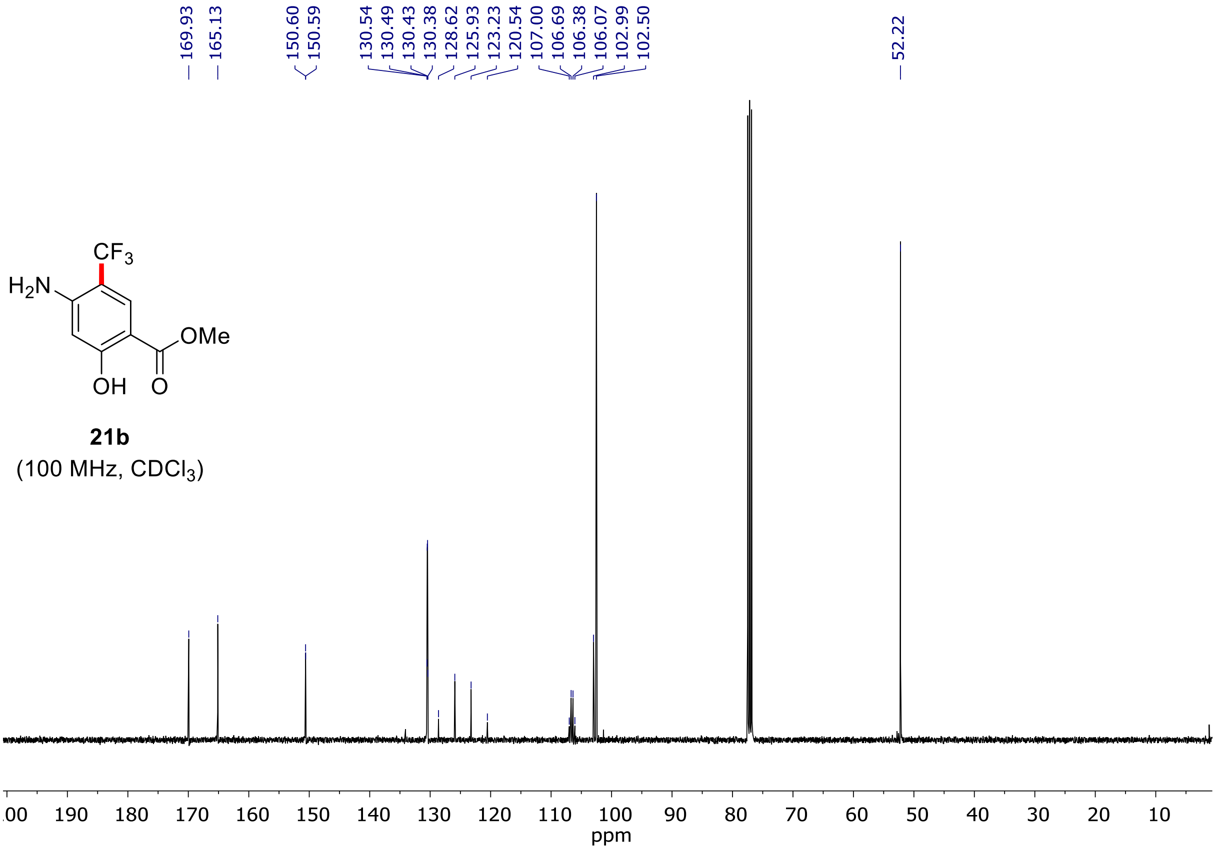

21a

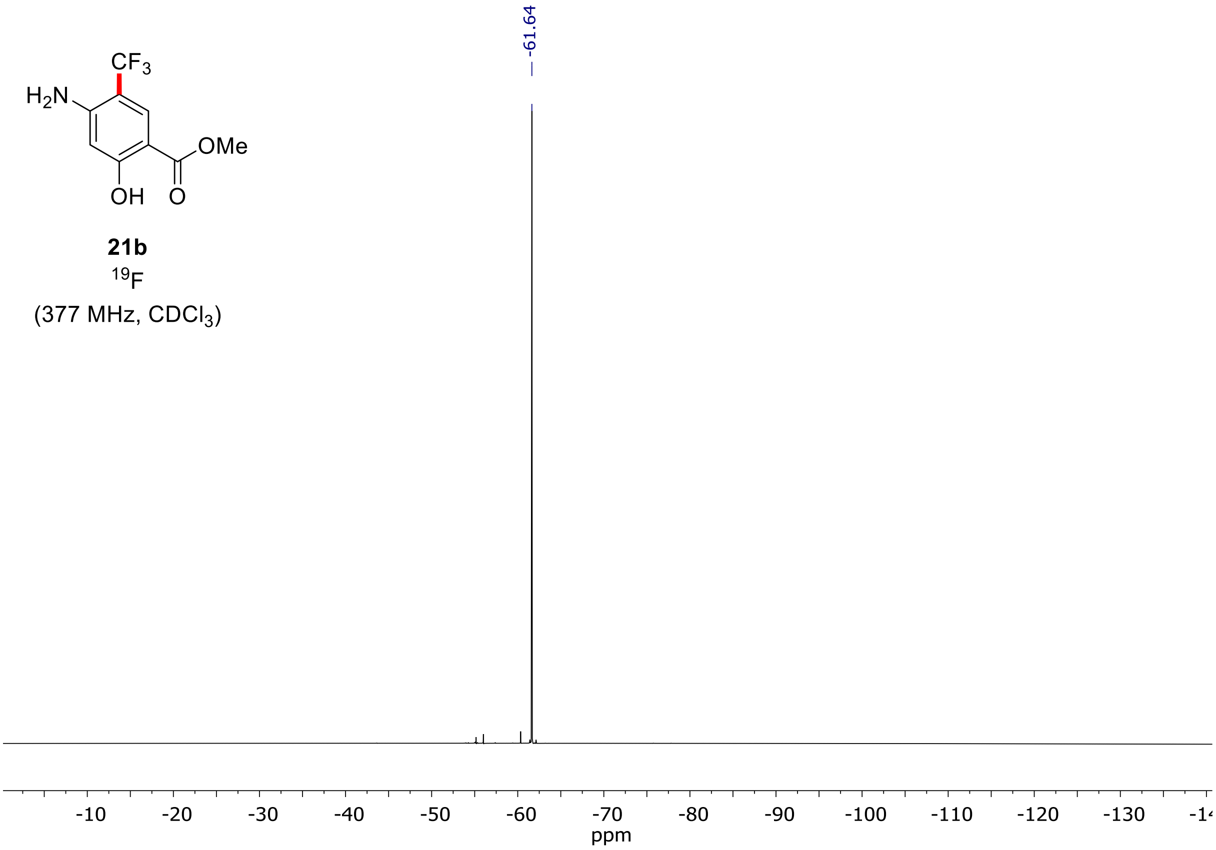
^{19}F

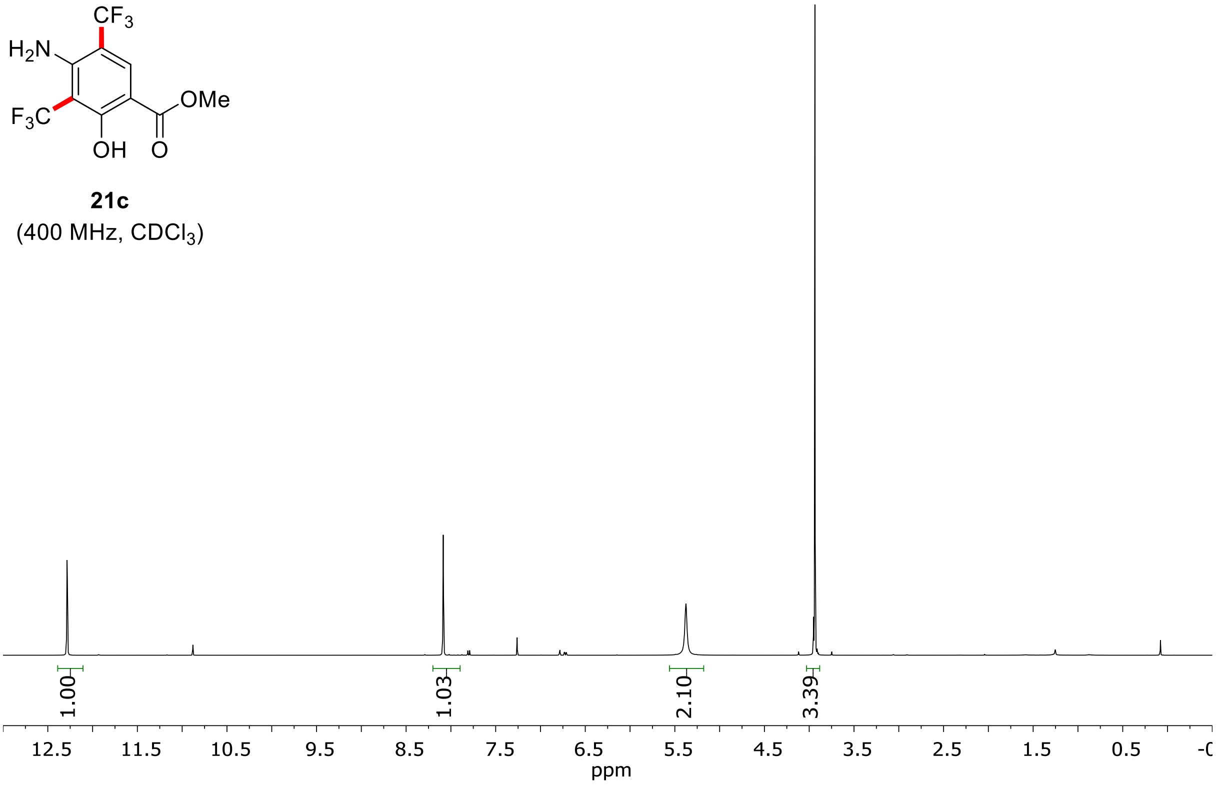
(377 MHz, CDCl$_3$)


21b

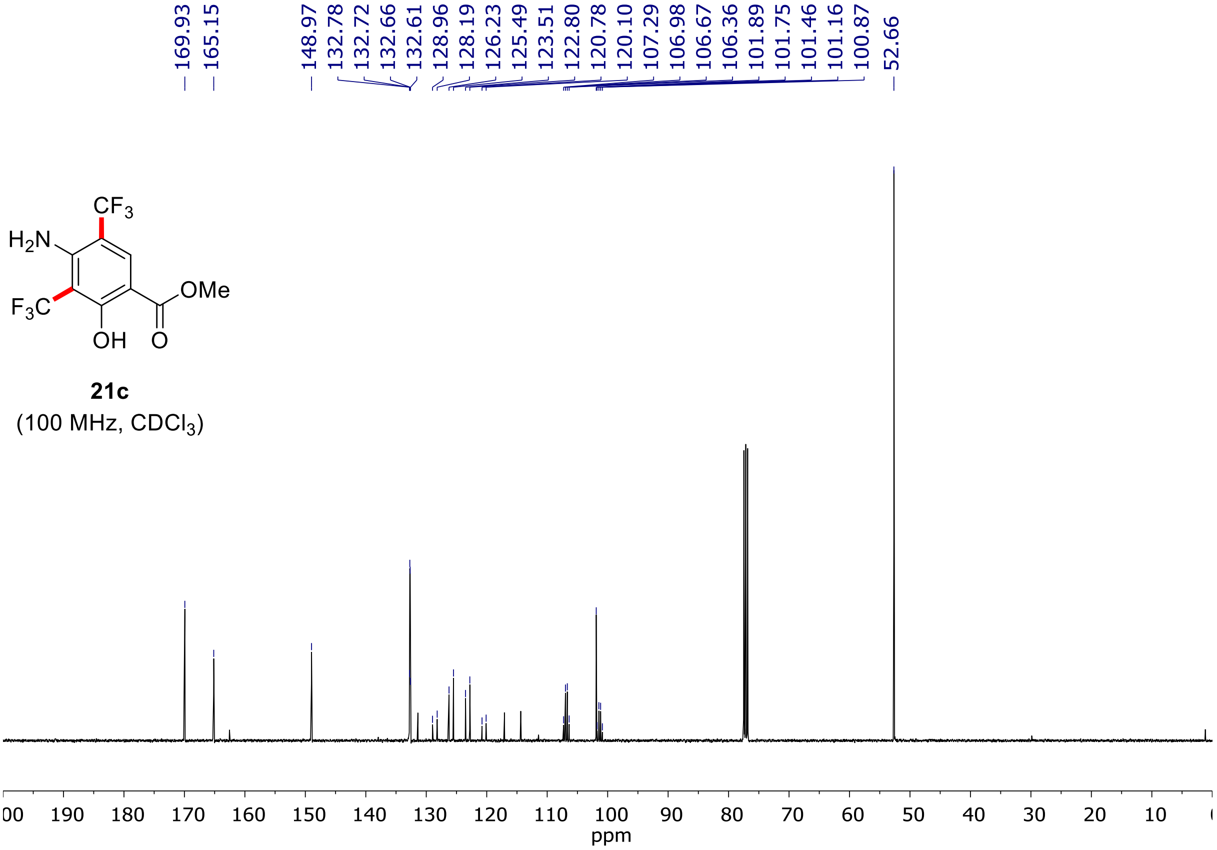
(400 MHz, CDCl$_3$)


169.93
165.13
150.60
150.59
130.54
130.49
130.43
130.38
128.62
125.93
123.23
120.54
107.00
106.69
106.38
106.07
102.99
102.50
52.22
CF3
H2N
OMe
OH
O
21b
(100 MHz, CDCl3)
.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

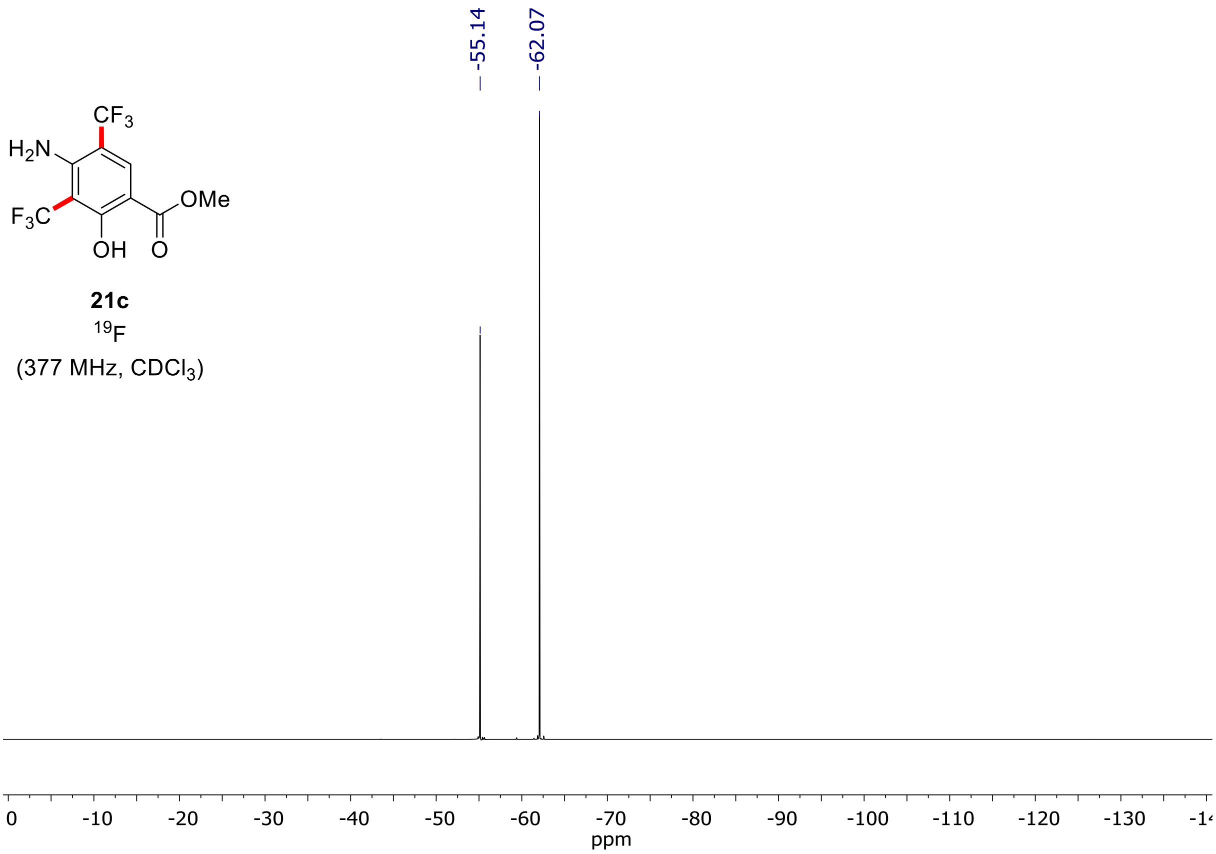

-61.64
CF3
H2N
OMe
OH
O
21b
19F
(377 MHz, CDCl3)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-1
ppm



CF3
H2N
F3C
OMe
OH
O
21c
(400 MHz, CDCl3)
1.00
1.03
2.10
3.39
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm



169.93
165.15
148.97
132.78
132.72
132.66
132.61
128.96
128.19
126.23
125.49
123.51
122.80
120.78
120.10
107.29
106.98
106.67
106.36
101.89
101.75
101.46
101.16
100.87
52.66
CF3
H2N
F3C
OMe
OH
O
21c
(100 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-55.14
-62.07
CF3
H2N
OMe
F3C
OH
O
21c
19F
(377 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
ppm