Electronic Supplementary Material (ESI) for ChemComm.

The first nucleophilic C–H perfluoroalkylation of aromatic compounds *via* (arene)tricarbonylchromium complexes

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Electronic Supplementary Information

Contents

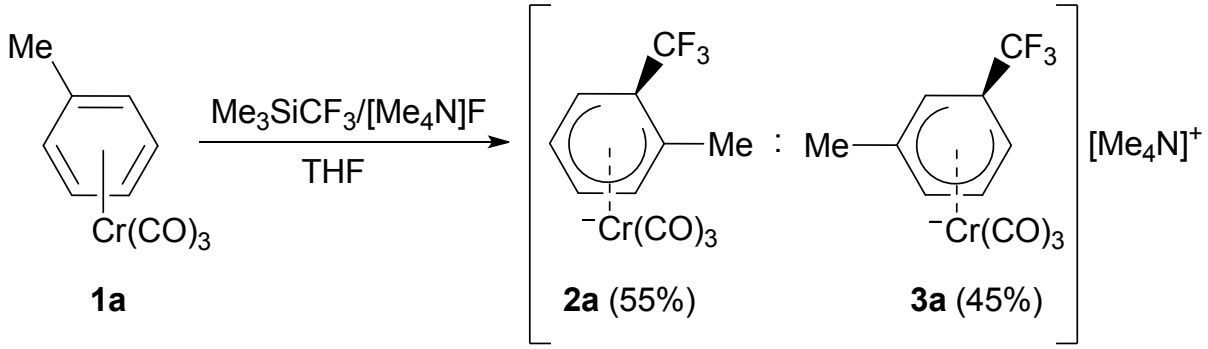
General remarks

All glassware was dried and cooled under vacuum before use. Perfluoroalkylation reactions were carried out in anhydrous solvents under an argon atmosphere using standard Schlenk techniques. Solvents were dried by conventional methods and distilled immediately prior to use. (η^6-Arene)$Cr(CO)_3$ complexes (**1a**–**1h**[1], **1i**[2], **1j**[1]) and $Me_3SiC_2F_5$[3] were synthesized on a multigram scale using literature procedures. Anhydrous $[Me_4N]F$ was prepared using the method reported by Kolomeitsev et al.[4] Other reagents were purchased from commercial suppliers and used without further purification.

All reactions were monitored using ^{19}F NMR spectroscopy. Yields were determined by ^{19}F NMR using fluorobenzene (PhF) as the internal standard (δ = –114 ppm). ^{19}F NMR spectra were recorded on a Bruker AC 200 (188 MHz) spectrometer. Typically, all NMR spectra were recorded at room temperature unless otherwise indicated. ^{19}F NMR spectra for the low-temperature ^{19}F NMR study of (η^6-methylbenzene)$Cr(CO)_3$ trifluoromethylation were recorded using Varian Gemini 2000 (400 MHz) spectrometer**.** ^1H NMR spectra were recorded on a Bruker AMX 300 (300 MHz) spectrometer using TMS as the external standard. Chemical shift (δ) is reported in parts per million (ppm), multiplicities are reported using the following abbreviations: s = singlet, d = doublet, dd = double doublet, m = multiplet. Coupling constants (*J*) are reported in Hz.

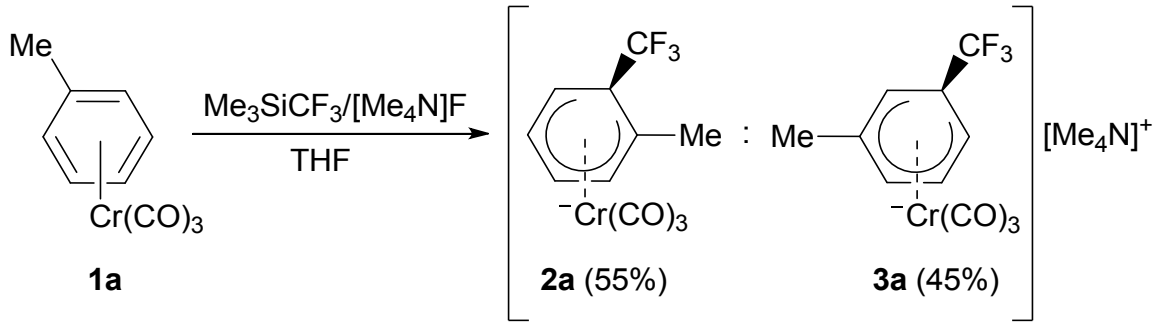
Due to low stability in air and high sensitivity towards oxidation, the novel (η^5-(perfluoroalkyl)cyclohexadienyl)$Cr(CO)_3^-$ adducts **2** and **3** described in the study were characterized according to ^{19}F NMR data as components of the reaction mixtures resulting from Step A of the general procedure.

Low-temperature ^{19}F NMR study for trifluoromethylation of (η^6-methylbenzene)$Cr(CO)_3$



A Schlenk flask (25 mL) equipped with a magnetic stirrer was dried and cooled under vacuum, and filled with argon. The flask was charged with anhydrous THF (5 mL), (η^6-methylbenzene)$Cr(CO)_3$ (**1a**) (228 mg, 1 mmol), sealed with a septum cap, and the mixture was cooled down to –50˚C while stirring under a positive argon pressure. Anhydrous $[Me_4N]F$ (112 mg, 1.2 mmol) and Me_3SiCF_3 (186 mg, 1.3 mmol) were added to the cooled solution in the argon flow. The reaction was kept stirring at –50˚C for 30 min and analyzed by ^{19}F NMR at the same temperature. No signals in the range for Fisher carbene complexes were observed. The silicates $[Me_4N][Me_3Si(CF_3)F]$ and $[Me_4N][Me_3Si(CF_3)_2]$ together with CF_3H were the main products of Me_3SiCF_3 and $[Me_4N]F$ transformations at this temperature. Only traces of the cyclohexadienyl adducts **2a** and **3a** were observed. The reaction mixture was warmed up to room temperature during 1.5 h, and, upon warming, was analyzed by ^{19}F NMR at –35˚C, –20˚C, –10˚C, 0˚C, and at room temperature (Table S1). A notable increase in yield of the desired adducts **2a** and **3a** was observed in the temperature range from –10˚C to 0˚C (Table S1). The total yield of the isomeric adducts **2a** and **3a** was determined by ^{19}F NMR using fluorobenzene as the internal standard (62%, **2a**:**3a** = 1:1). ^{19}F NMR (376 MHz, THF, 0˚C), **2a**: δ –76.77 (d, $^3J_{F–H}$ = 8.7 Hz, CF_3); **3a**: δ –80.91 (d, $^3J_{F–H}$ = 8.7 Hz, CF_3). The reaction mixture was cooled down to –60˚C while stirring under the argon pressure, and iodine (635 mg, 2.5 mmol) dissolved in 5 mL of THF was added in small portions. The reaction mixture was allowed to warm up to room temperature and kept stirring for an extra 4 h. The total yield of the regioisomers **4a** and **4a*** was determined by ^{19}F NMR using fluorobenzene as the internal standard (60%, **4a**:**4a*** = 1:1). ^{19}F NMR (376 MHz, THF), **4a**: δ –61.99 (s, CF_3); **4a***: δ –63.02 (s, CF_3).

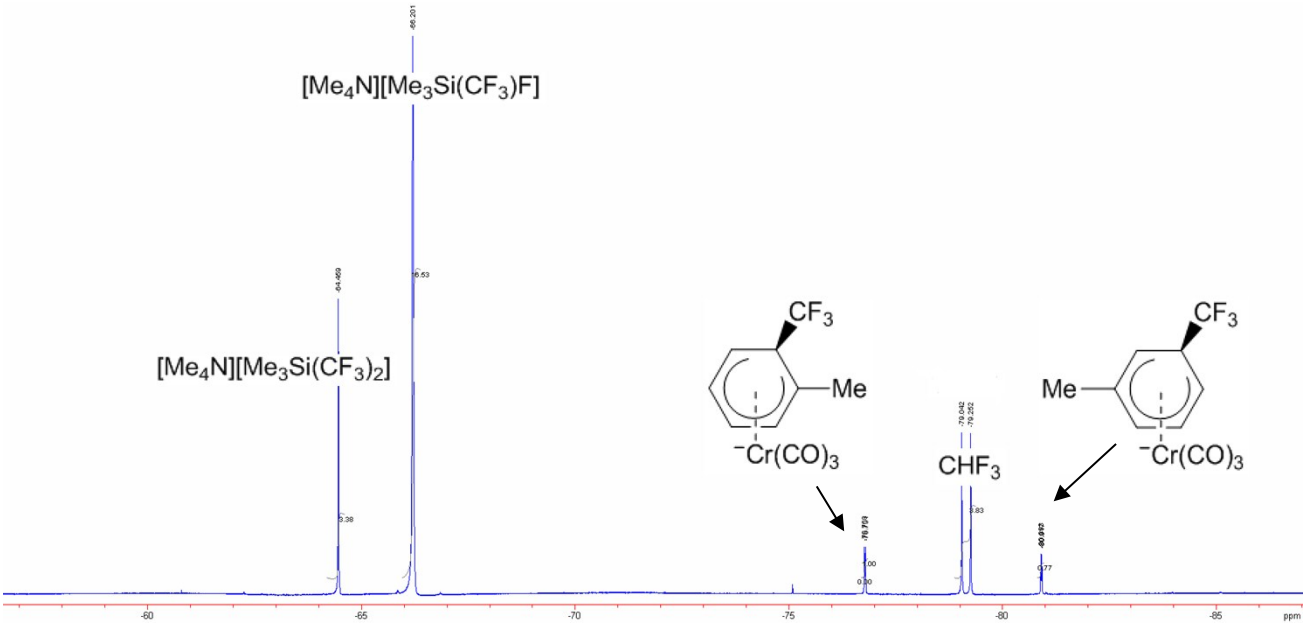
Table S1 Selected optimization experiments for trifluoromethylation of (η^6-methylbenzene)$Cr(CO)_3$ (**1a**).[a]



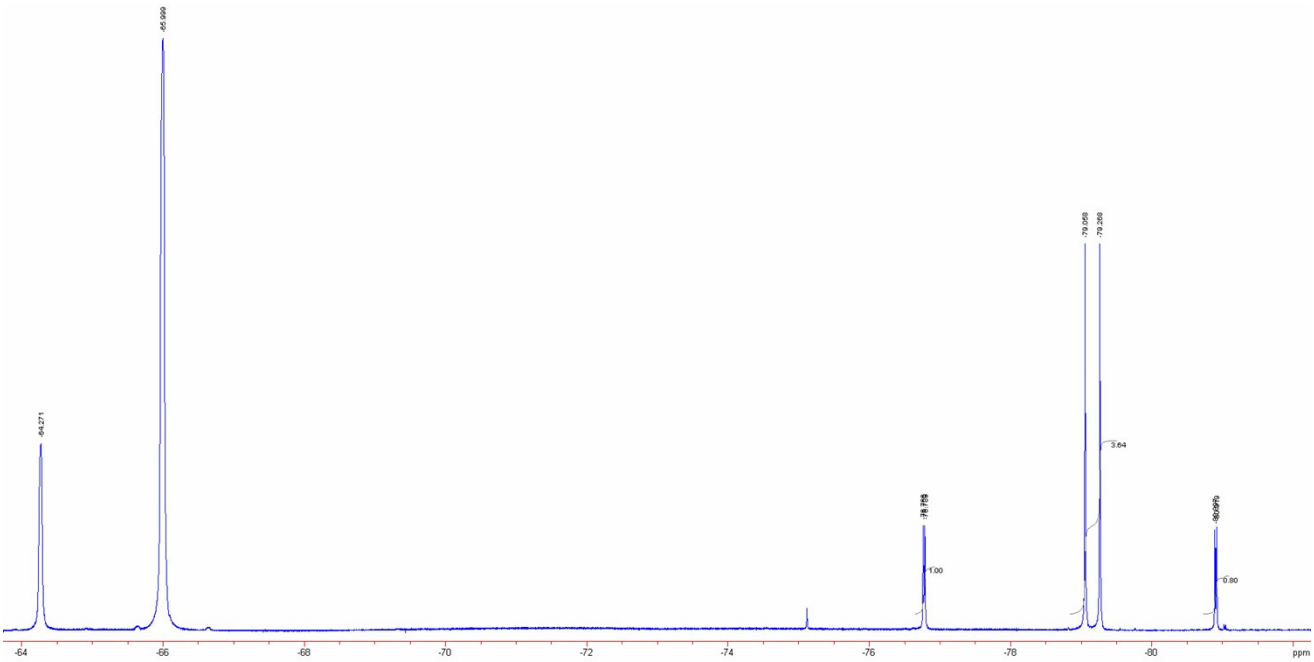
Entry	T (°C)	Yield (%)[b]	Time after addition of $[Me_4N]F$ and Me_3SiCF_3 at –50°C (min)
1	–50	9	30
2	–35	15	45
3	–20	20	60
4	–10	41	75
5	0	62	90
6	20	62	120

[a] Reaction conditions: **1a** (1 mmol), Me_3SiCF_3 (1.3 mmol), $[Me_4N]F$ (1.2 mmol), THF (5 mL). [b] The total yield of the regioisomers **2a** and **3a** determined by ^{19}F NMR spectroscopy using fluorobenzene as the internal standard.

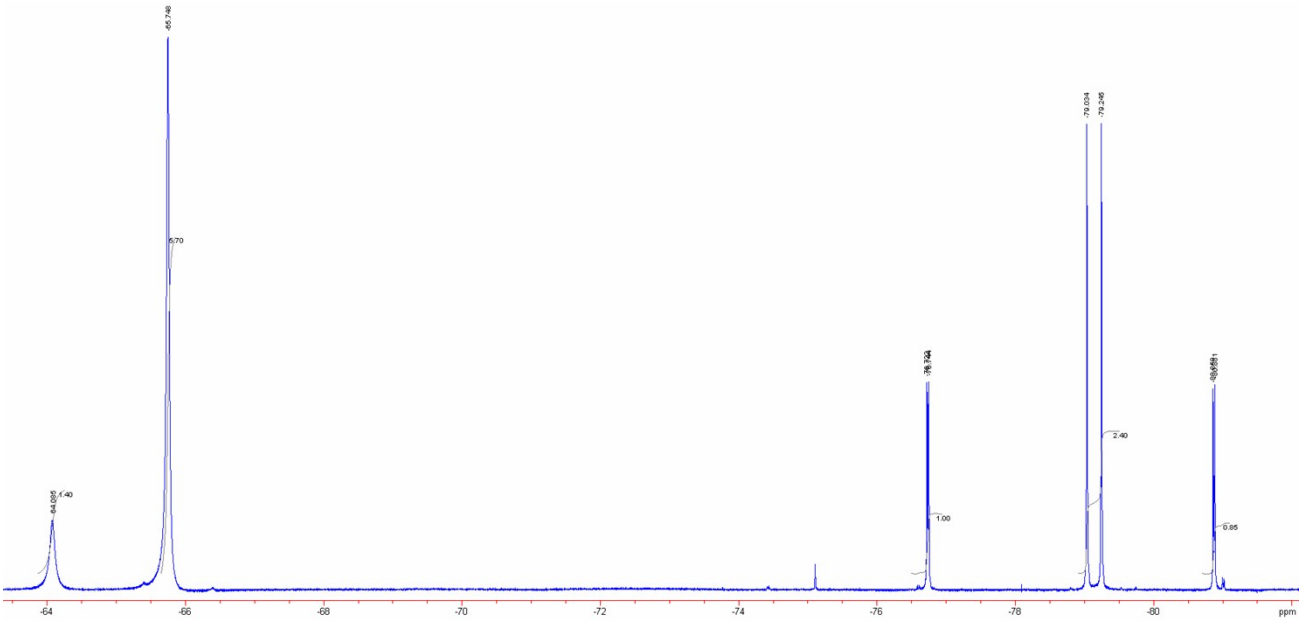
Variable-temperature ^{19}F NMR spectra for trifluoromethylation of (η^6-methylbenzene)$Cr(CO)_3$



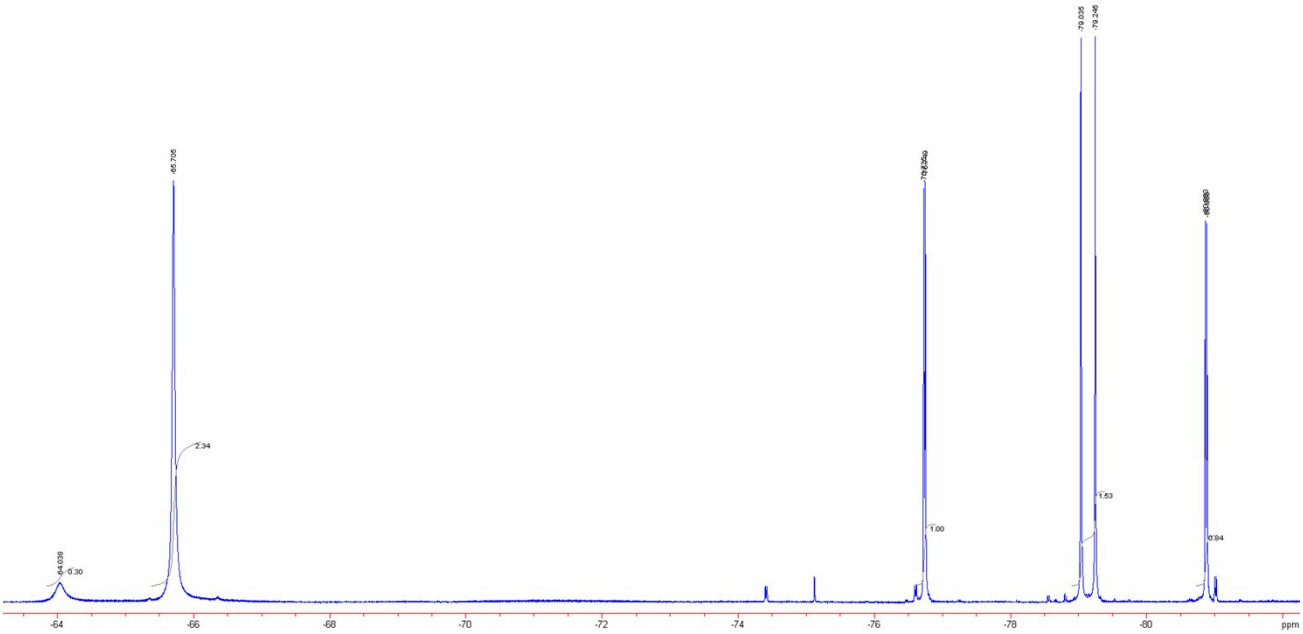
^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 1)



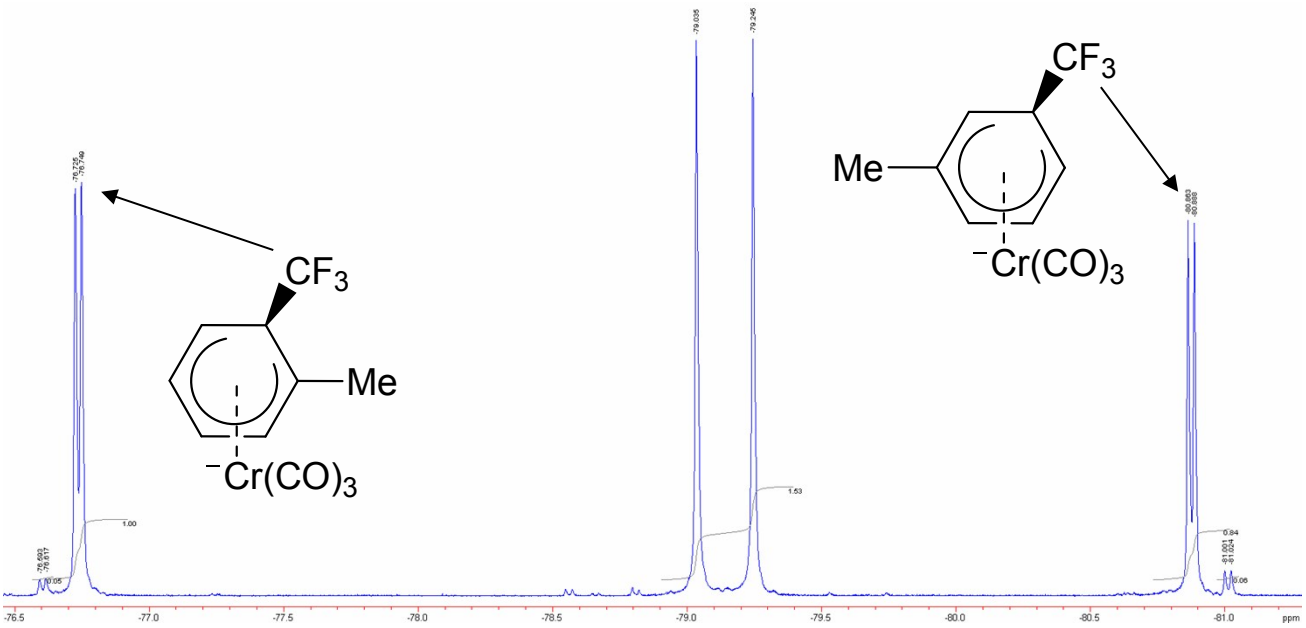
^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 2)



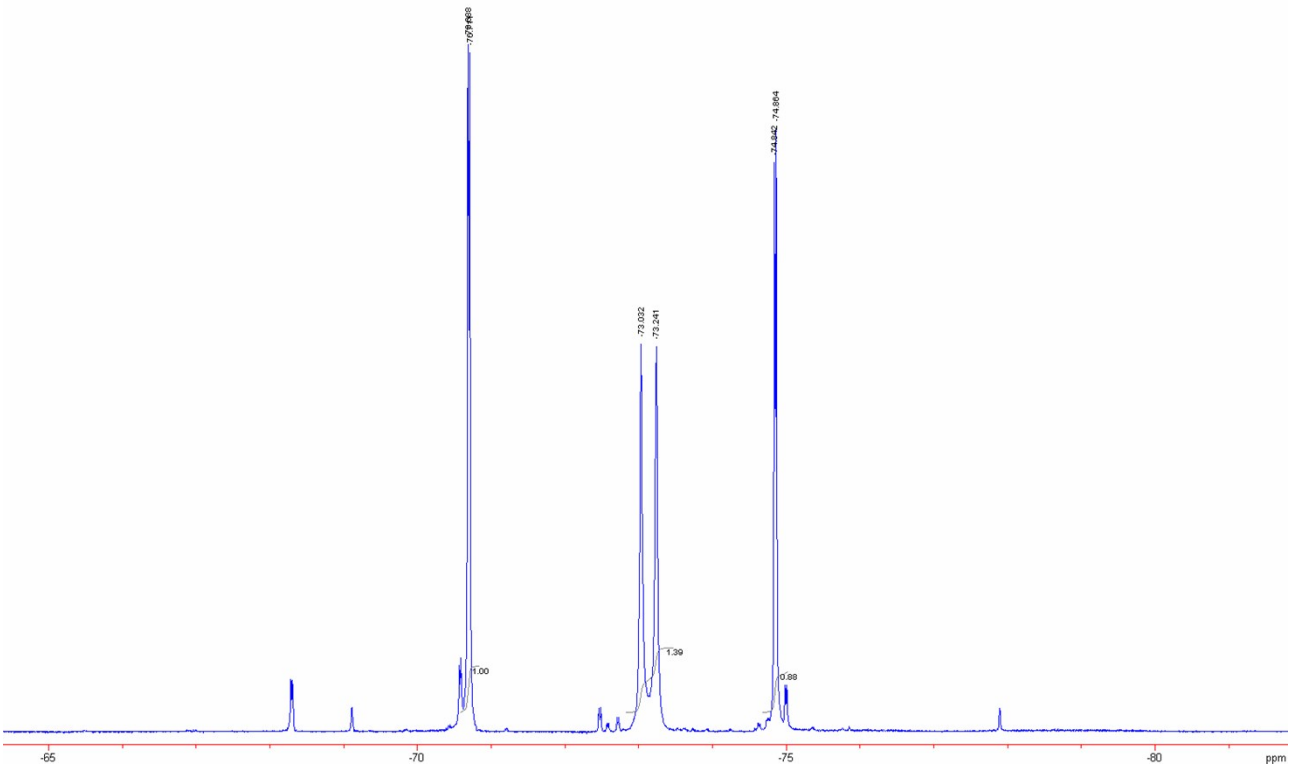
^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 3)



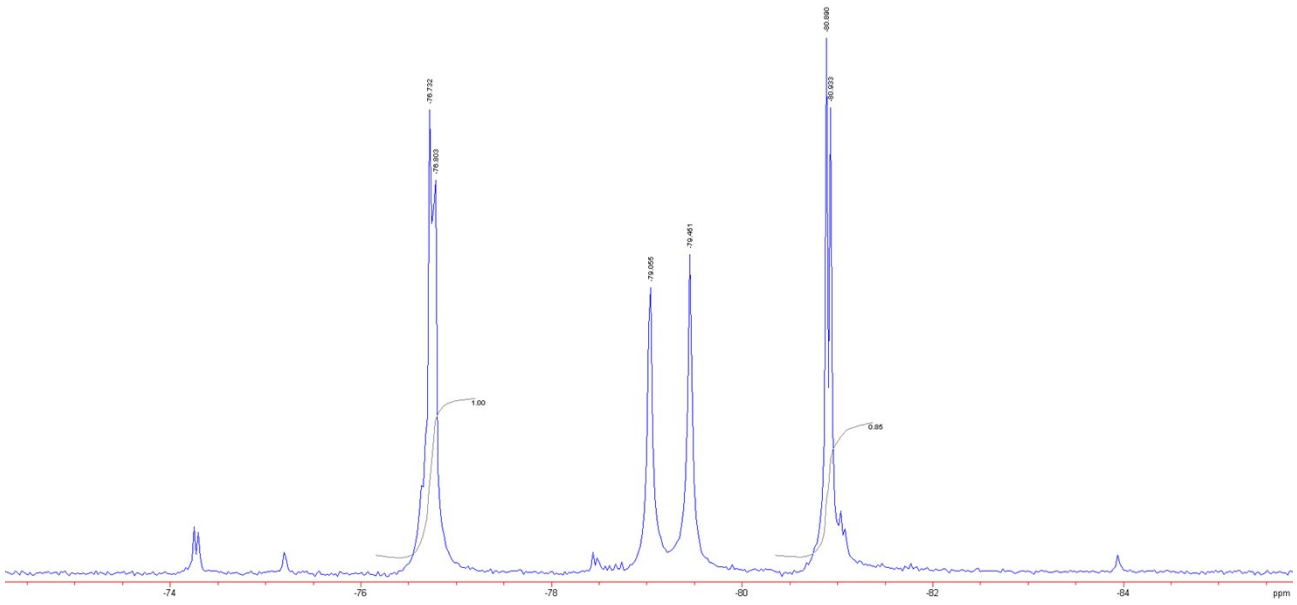
^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 4)



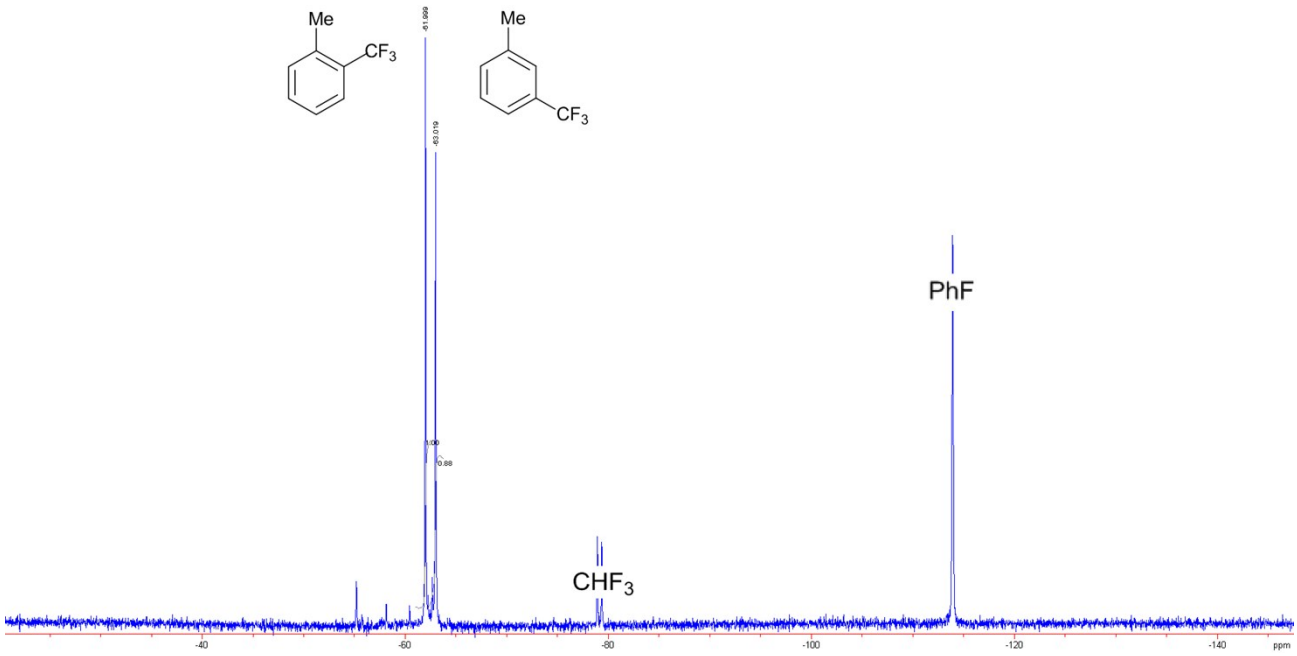
^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 4), close-up



^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 5)



^{19}F NMR spectrum of the reaction mixture containing the adduct s **2a** and **3a** (Table S1, Entry 6)



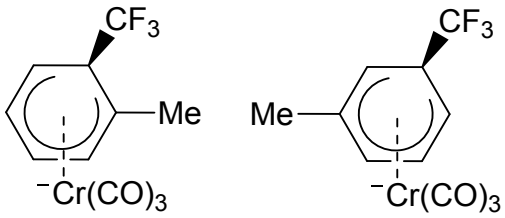
^{19}F NMR spectrum of the reaction mixture containing benzotrifluorides **4a** and **4a*** after oxidation with iodine (THF)

General procedure for perfluoroalkylation of aromatic compounds *via* (η^6-arene)$Cr(CO)_3$ complexes

Step A: Perfluoroalkylation

A Schlenk flask (25 mL) equipped with a magnetic stirrer was dried and cooled under vacuum, and filled with argon. The flask was charged with an (η^6-arene)$Cr(CO)_3$ complex (1 mmol), anhydrous $[Me_4N]F$ (186 mg, 2 mmol), and DME (5 mL) as the solvent unless otherwise specified. The flask was sealed with a septum cap, and the mixture was cooled down to –10˚C while stirring under a positive argon pressure. Unless otherwise indicated, Me_3SiCF_3 (312 mg, 2.2 mmol) was being added via syringe in small portions within 45 min, and the reaction mixture was kept stirring at the same temperature for an extra 1 h. Yields of (η^5-(perfluoroalkyl)cyclohexadienyl)-$Cr(CO)_3$ adducts **2** and **3** were determined by ^{19}F NMR using fluorobenzene as the internal standard.

(η^5-1-Methyl-2-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2a) and (η^5-1-methyl-2-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3a)



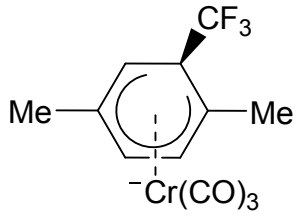
Prepared following Step A of the general procedure using (η^6-methylbenzene)$Cr(CO)_3$ (**1a**) (228 mg, 1 mmol). The total yield of the isomeric adducts **2a** and **3a** was determined by ^{19}F NMR using fluorobenzene as the internal standard (92%, **2a**:**3a** = 1:1). ^{19}F NMR (188 MHz, DME), **2a**: δ –76.25 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3); **3a**: δ –80.41 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

The cyclohexadienyl adducts **2a** and **3a** were also prepared in THF as the solvent. A Schlenk flask (25 mL) equipped with a magnetic stirrer was dried and cooled under vacuum, and filled with argon. The flask was charged with (η^6-methylbenzene)$Cr(CO)_3$ (**1a**) (228 mg, 1 mmol), THF (5 mL), and sealed with a septum cap. The mixture was cooled down to –10˚C while stirring under a positive argon pressure, and anhydrous $[Me_4N]F$ (112

mg, 1.2 mmol) was added in the argon flow to the cooled solution. Me_3SiCF_3 (186 mg, 1.3 mmol) was being added via syringe in small portions within 45 min, and the reaction mixture was kept stirring at the same temperature for an extra 1 h. The total yield of the isomeric adducts **2a** and **3a** was determined by ^{19}F NMR using fluorobenzene as the internal standard (69%, **2a**:**3a** = 1:1). ^{19}F NMR (188 MHz, THF), **2a**: δ –76.80 (d, $^3J_{F-H}$ = 8.7 Hz, CF_3); **3a**: δ –80.94 (d, $^3J_{F-H}$ = 8.7 Hz, CF_3).

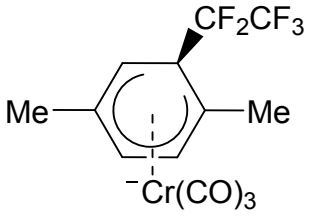
Following step A of the general procedure and using diethyl ether or acetonitrile as the solvent did not yield the desired adducts **2a** and **3a**.

(η^5-1,4-Dimethyl-2-(trifluoromethyl)cyclohexadienyl)Cr(CO)$_3^-$ (2b)



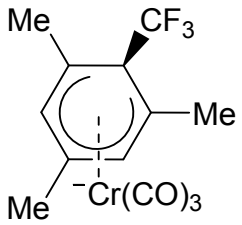
Prepared following Step A of the general procedure using (η^6-1,4-dimethylbenzene)$Cr(CO)_3$ (**1b**) (242 mg, 1mmol). The yield of **2b** was determined by ^{19}F NMR using fluorobenzene as the internal standard (93%). ^{19}F NMR (188 MHz, DME): δ –76.91 (d, $^3J_{F-H}$ = 8.1 Hz, CF_3).

(η^5-1,4-Dimethyl-2-(pentafluoroethyl)cyclohexadienyl)Cr(CO)$_3^-$ (1S)



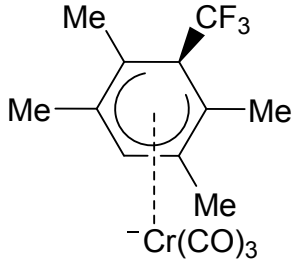
Prepared following Step A of the general procedure using (η^6-1,4-dimethylbenzene)$Cr(CO)_3$ (**1b**) (242 mg, 1mmol), $[Me_4N]F$ (116 mg, 1.25 mmol), and $Me_3SiC_2F_5$ (250 mg, 1.3 mmol). The yield of **1S** was determined by ^{19}F NMR using fluorobenzene as the internal standard (92%). ^{19}F NMR (188 MHz, DME): δ –123.80 (AB system, $^2J_{AB}$ = 266.8 Hz, $^3J_{F-H}$ = 20.2 Hz, 1F, C$\underline{F_2}$CF$_3$), δ –117.93 (AB system, $^2J_{AB}$ = 266.8 Hz, 1F, C$\underline{F_2}$CF$_3$), δ –80.53 (s, CF$_2$C$\underline{F_3}$).

(η^5-1,3,5-Trimethyl-2-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2c)



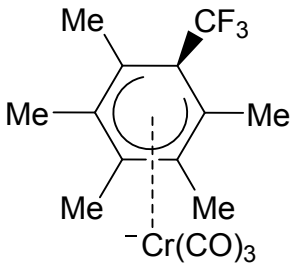
Prepared following Step A of the general procedure using (η^6-1,3,5-trimethylbenzene)$Cr(CO)_3$ (**1c**) (256 mg, 1mmol). The yield of **2c** was determined by ^{19}F NMR using fluorobenzene as the internal standard (54%). ^{19}F NMR (188 MHz, DME): δ –73.19 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

(η^5-1,2,4,5-Tetramethyl-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2d)



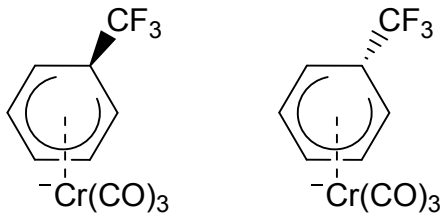
A Schlenk flask (50 mL) equipped with a magnetic stirrer was dried and cooled under vacuum, and filled with argon. The flask was charged with (η^6-1,2,4,5-tetramethylbenzene)$Cr(CO)_3$ (**1d**) (1.35 g, 5 mmol), anhydrous $[Me_4N]F$ (0.92 g, 10 mmol), DME (25 mL), and sealed with a septum cap. The mixture was cooled down to –10˚C while stirring under a positive argon pressure, Me_3SiCF_3 (1.62 g, 11.39 mmol) was being added via syringe in small portions within 1 h, and the reaction was kept stirring at the same temperature for an extra 1.5 h. The yield of **2d** was determined by ^{19}F NMR using fluorobenzene as the internal standard (89%). ^{19}F NMR (188 MHz, DME): δ –72.84 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

(η^5-1,2,3,4,5-Pentamethyl-6-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2e)



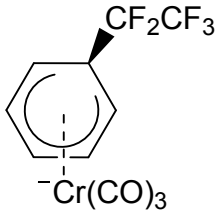
Prepared following Step A of the general procedure using (η^6-1,2,3,4,5-pentamethylbenzene)$Cr(CO)_3$ (**1e**) (284 mg, 1mmol). The yield of **2e** was determined by ^{19}F NMR using fluorobenzene as the internal standard (12%). ^{19}F NMR (188 MHz, DME): δ –74.20 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

(η^5-(Trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2f)



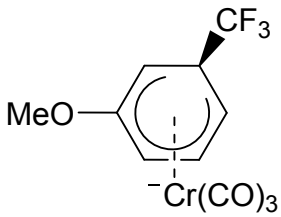
Prepared following Step A of the general procedure using (η^6-benzene)$Cr(CO)_3$ (**1f**) (214 mg, 1mmol). The total yield of the *exo*- and *endo*-adducts **2f** was determined by ^{19}F NMR using fluorobenzene as the internal standard (95%, *exo:endo* = 10:1). ^{19}F NMR (188 MHz, DME): δ –80.34 (d, $^3J_{F–H}$ = 8.1 Hz, *exo*-CF_3), δ –77.87 (d, $^3J_{F–H}$ = 8.1 Hz, *endo*-CF_3).

(η^5-(Pentafluoroethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2S)



Prepared following Step A of the general procedure using (η^6-benzene)$Cr(CO)_3$ (**1f**) (214 mg, 1mmol), $[Me_4N]F$ (116 mg, 1.25 mmol), and $Me_3SiC_2F_5$ (250 mg, 1.3 mmol). The yield of **2S** was determined by ^{19}F NMR using fluorobenzene as the internal standard (93%). ^{19}F NMR (188 MHz, DME): δ –126.41 (s, C$\underline{F_2}$$CF_3$), δ –81.74 (s, $CF_2C\underline{F_3}$).

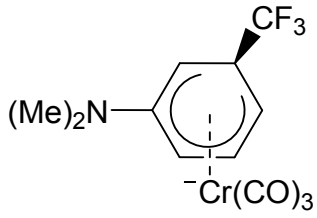
(η^5-1-Methoxy-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3g)



Prepared following Step A of the general procedure using (η^6-1-methoxybenzene)$Cr(CO)_3$ (**1g**) (244 mg, 1mmol). The yield of **3g** was determined by ^{19}F NMR using fluorobenzene as the internal standard (87%). ^{19}F NMR (188 MHz, DME):, δ –80.27 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

The cyclohexadienyl adduct **3g** was also prepared following Step A of the general procedure using (η^6-1-methoxybenzene)$Cr(CO)_3$ (**1g**) (244 mg, 1mmol) and DMF (5 mL) as the solvent. The yield of **3g** was determined by ^{19}F NMR using fluorobenzene as the internal standard (68%). ^{19}F NMR (188 MHz, DMF):, δ –80.26 (d, $^3J_{F–H}$ = 8.7 Hz, CF_3).

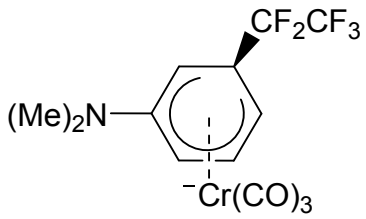
(η^5-*N,N*-Dimethyl-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3h)



A Schlenk flask (25 mL) equipped with a magnetic stirrer was dried and cooled under vacuum, and filled with argon. The flask was charged with (η^6- *N,N*-dimethylaniline)$Cr(CO)_3$ (**1h**) (0.77 g, 3 mmol), anhydrous $[Me_4N]F$ (0.55 g, 6 mmol), DME (10 mL), and sealed with a septum cap. The mixture was cooled down to –10˚C while stirring under a positive argon pressure, Me_3SiCF_3 (0.94 g, 6.6 mmol) was being added via syringe in small portions within 1 h, and the reaction was kept stirring at the same temperature for an extra 1 h. The yield of **3h** was determined by ^{19}F NMR using fluorobenzene as the internal standard (93%). ^{19}F NMR (188 MHz, DME): δ –80.49 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

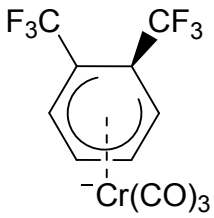
The cyclohexadienyl adduct **3h** was also prepared following Step A of the general procedure using (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$ (**1h**) (257 mg, 1mmol) and DMF (5 mL) as a solvent. The yield of **3h** was determined by ^{19}F NMR using fluorobenzene as the internal standard (70%). ^{19}F NMR (188 MHz, DME): δ –76.77 (d, $^3J_{F–H}$ = 8.7 Hz, CF_3).

(η^5-*N,N*-Dimethyl-3-(pentafluoroethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3S)



Prepared following Step A of the general procedure using (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$ (257 mg, 1mmol), $[Me_4N]F$ (116 mg, 1.25 mmol), and $Me_3SiC_2F_5$ (**1h**) (250 mg, 1.3 mmol). The yield of **3S** was determined by ^{19}F NMR using fluorobenzene as the internal standard (54%). ^{19}F NMR (188 MHz, DME): δ –125.88 (AB system, $^2J_{AB}$ = 262.8 Hz, $^3J_{F–H}$ = 16.2 Hz, 1F, C$\underline{F_2}$CF$_3$), δ –128.88 (AB system, $^2J_{AB}$ = 262.8 Hz, 1F, C$\underline{F_2}$CF$_3$), δ –81.48 (s, CF$_2$C$\underline{F_3}$).

(η^5-1,2-Bis(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2i)

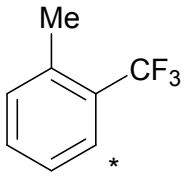


Prepared following Step A of the general procedure using (η^6-(trifluoromethyl)benzene)$Cr(CO)_3$ (**1i**) (282 mg, 1mmol). The yield of **2i** was determined by ^{19}F NMR using fluorobenzene as the internal standard (53%).^{19}F NMR (188 MHz, DME): –77.25 (d, $^3J_{F–H}$ = 8.1 Hz, CF_3).

Step B: Oxidative decomplexation

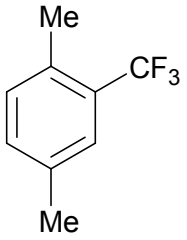
The oxidative decomplexation was performed with one of the following oxidants: iodine (635 mg, 2.5 mmol) dissolved in 5 mL of DME, 1,4-benzoquinone (432 mg, 4 mmol) dissolved in 5 mL of DME, or ceric ammonium nitrate (5.5 mmol). The reaction mixture resulting from the Step A was cooled down to –60˚C while stirring and the oxidant was added in small portions. The refluxed reaction mixture was allowed to warm up to room temperature and kept stirring for an extra 4 h. The yield of a perfluoroalkyl arene was determined by ^{19}F NMR using fluorobenzene as the internal standard added to the reaction mixture.

1-Methyl-2-(trifluoromethyl)benzene and 1-methyl-3-(trifluoromethyl)benzene (4a and 4a*)



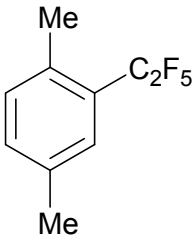
Prepared following Step B of the general procedure using iodine as the oxidant added to the reaction mixture containing the adducts **2a** and **3a**. The total yield of the regioisomers **4a** and **4a*** was determined by ^{19}F NMR using fluorobenzene as the internal standard (63%, **4a**:**4a*** = 1:1). ^{19}F NMR (188 MHz, DME), **4a**: δ –61.35 (s, CF_3); **4a***: δ –62.30 (s, CF_3).

1,4-Dimethyl-2-(trifluoromethyl)benzene (4b)



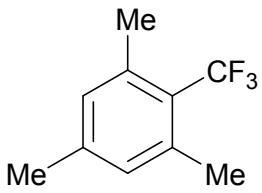
Prepared following Step B of the general procedure using iodine as the oxidant added to the reaction mixture containing the adduct **2b**. The yield of **4b** was determined by ^{19}F NMR using fluorobenzene as the internal standard (85%). ^{19}F NMR (188 MHz, DME): δ –62.00 (s, CF_3).

1,4-Dimethyl-2-(pentafluoroethyl)benzene (5b)



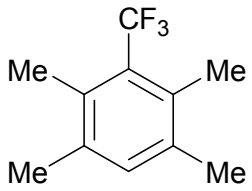
Prepared following Step B of the general procedure using iodine as the oxidant added to the reaction mixture containing the adduct **1S**. The yield of **5b** was determined by ^{19}F NMR using fluorobenzene as the internal standard (95%). ^{19}F NMR (188 MHz, DME): δ –110.35 (s, $C\underline{F_2}CF_3$), δ –84.80 (s, $CF_2C\underline{F_3}$).

1,3,5-Trimethyl-2-(trifluoromethyl)benzene (4c)



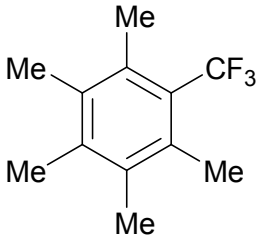
Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant added to the reaction mixture containing the adduct **2c**. The yield of **4c** was determined by ^{19}F NMR using fluorobenzene as the internal standard (42%). ^{19}F NMR (188 MHz, DME): δ –53.63 (s, CF_3).

1,2,4,5-Tetramethyl-3-(trifluoromethyl)benzene (4d)



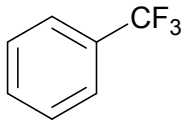
Prepared following Step B of the general procedure using ceric ammonium nitrate (15 g, 5.5 mmol) as the oxidant added to the reaction mixture containing the adduct **2d**. The yield of **4d** was determined by ^{19}F NMR using fluorobenzene as the internal standard (80%). ^{19}F NMR (188 MHz, DME): δ –51.39 (s, CF_3). The reaction mixture was evaporated under reduced pressure, and the product was extracted with hexane (3 x 20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was sublimed from the crude under reduced pressure to afford **4d** as a white solid (0.55 g, 54%), mp. 35–36˚C (lit.[5] mp. 35–37˚C). ^{19}F NMR (188 MHz, $CDCl_3$): δ –51.94 (s, CF_3). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 6H), δ 2.32 (s, 6H), δ 7.08 (s, 1H).

1,2,3,4,5-Pentamethyl-6-(trifluoromethyl)benzene (4e)



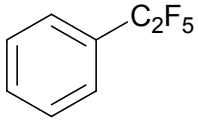
Prepared following Step B of the general procedure using iodine as the oxidant added to the reaction mixture containing the adduct **2e**. The yield of **4e** was determined by ^{19}F NMR using fluorobenzene as the internal standard (9%). ^{19}F NMR (188 MHz, DME): δ –51.39 (s, CF_3).

(Trifluoromethyl)benzene (4f)



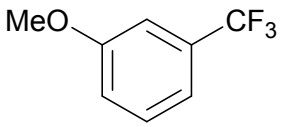
Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant added to the reaction mixture containing the adduct **2f**. The yield of **4f** was determined by ^{19}F NMR using fluorobenzene as the internal standard (9%). ^{19}F NMR (188 MHz, DME): δ –62.83 (s, CF_3).

(Pentafluoroethyl)benzene (5f)



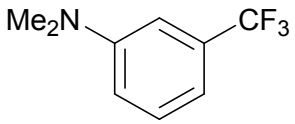
Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant added to the reaction mixture containing the adduct **2S**. The yield of **5f** was determined by ^{19}F NMR using fluorobenzene as the internal standard (86%). ^{19}F NMR (188 MHz, DME): δ –115.32 (s, $C\underline{F_2}CF_3$), δ –85.64 (s, $CF_2C\underline{F_3}$).

1-Methoxy-3-(trifluoromethyl)benzene (4g)



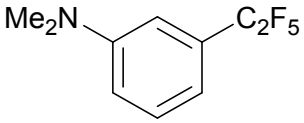
Prepared following Step B of the general procedure using iodine as the oxidant added to the reaction mixture containing the adduct **2g** prepared in DME. The yield of **4g** was determined by ^{19}F NMR using fluorobenzene as the internal standard (57%). ^{19}F NMR (188 MHz, DMF): δ –62.77 (s, CF_3).

***N,N*-Dimethyl-3-(trifluoromethyl)aniline (4h)**



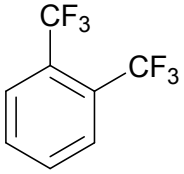
Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant. 1,4-Benzoquinone (1.3 g, 12 mmol) was added to the reaction mixture containing the adduct **2h** prepared in DME. The yield of **4h** was determined by ^{19}F NMR using fluorobenzene as the internal standard (88%). ^{19}F NMR (188 MHz, DME): δ –62.19 (s, CF_3). The reaction mixture was evaporated under reduced pressure, and the product was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was distilled from the crude under reduced pressure to afford **4d** as a pale yellow oil (0.42 g, 75%). ^{19}F NMR (188 MHz, $CDCl_3$): δ –62.2 (s, CF_3). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.99 (s, 6H), δ 6.91 (m, 2H), δ 7.39 (m, 2H).

***N,N*-Dimethyl-3-(pentafluoroethyl)aniline (5h)**



Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant added to the reaction mixture containing the adduct **3S**. The yield of **5h** was determined by ^{19}F NMR using fluorobenzene as the internal standard (77%). ^{19}F NMR (188 MHz, DME): δ –114.84 (s, $C\underline{F_2}CF_3$), δ –85.15 (s, $CF_2C\underline{F_3}$).

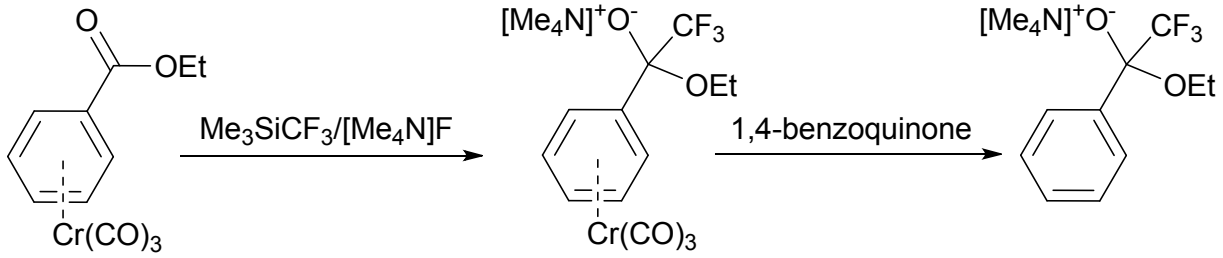
1,2-Bis(trifluoromethyl)benzene (4b)



Prepared following Step B of the general procedure using 1,4-benzoquinone as the oxidant added to the reaction mixture containing the adduct **2i**. The yield of **4i** was determined by ^{19}F NMR using fluorobenzene as the internal standard (43%). ^{19}F NMR (188 MHz, DME): δ –59.40 (s, CF_3). The product was distilled from the reaction mixture under reduced pressure into a liquid nitrogen-cooled trap. The crude product was redistilled to afford **4b** as

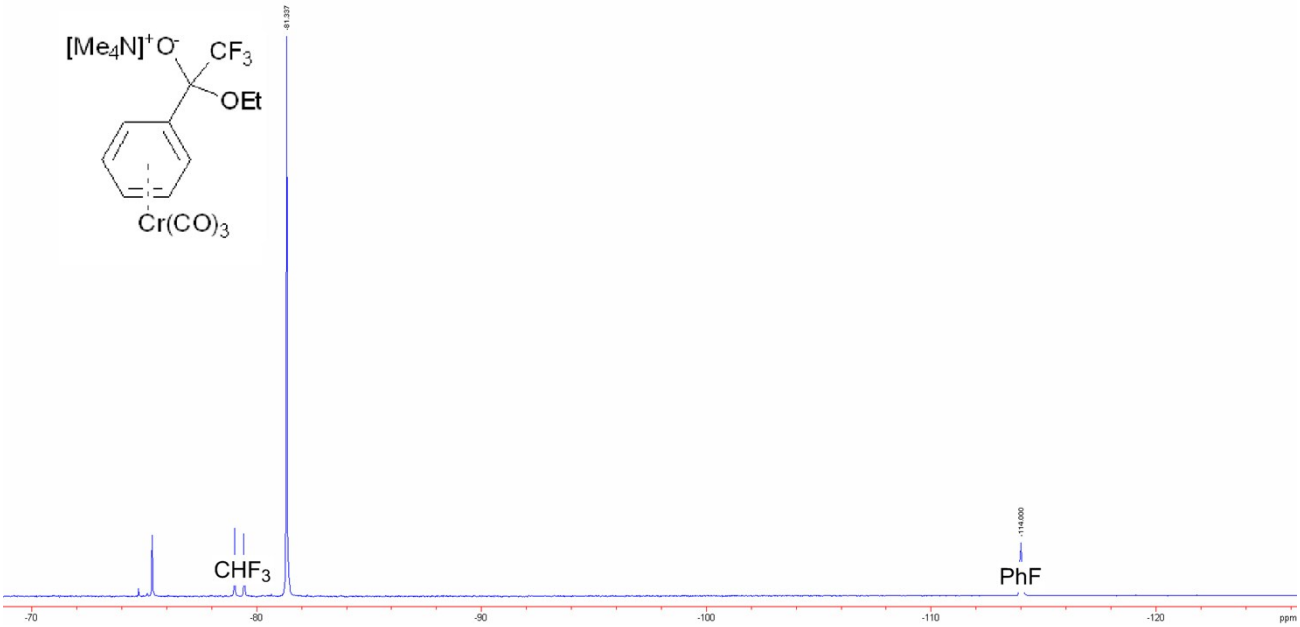
a colorless oil (19 mg, 9%). ^{19}F NMR (188 MHz, $CDCl_3$): δ –58.66 (s, CF_3). ^1H NMR (300 MHz, $CDCl_3$): δ 8.89 (m, 4H).

Trifluoromethylation of (η^6-ethylbenzoate)$Cr(CO)_3$ on the ester carbonyl site

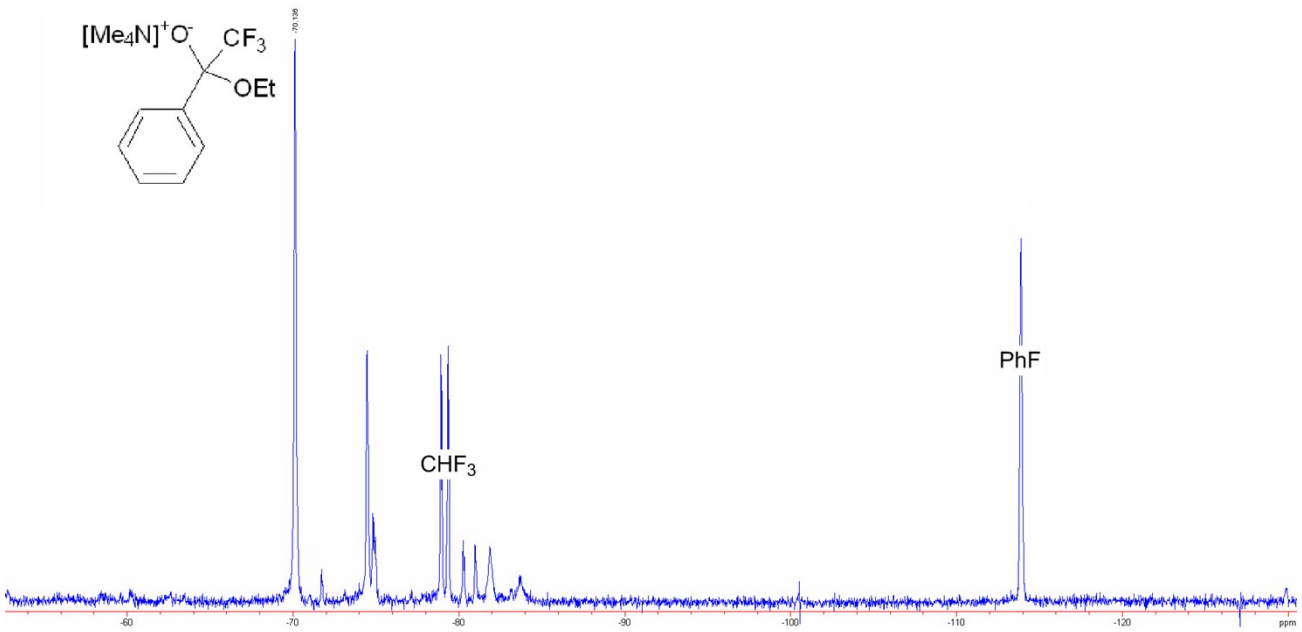


1j **4S** **5S**

The reaction was conducted following Step A of the general procedure using (η^6-ethylbenzoate)$Cr(CO)_3$ (**1j**) (272 mg, 1mmol). The yield of the intermediate **4S** was determined by ^{19}F NMR using fluorobenzene as the internal standard (89%). ^{19}F NMR (188 MHz, DME): –81.33 (s, CF_3). Oxidative decomplexation was performed with 1,4-benzoquinone following Step B of the general procedure, and no signals for the corresponding benzofluorides were observed by ^{19}F NMR. The yield of the product **5S** was determined by ^{19}F NMR using fluorobenzene as the internal standard (63%). ^{19}F NMR (188 MHz, DME): –70.13 (s, CF_3).



^{19}F NMR monitoring of the trifluoromethylation of (η^6-ethylbenzoate)$Cr(CO)_3$ (**1j**) at the ester carbonyl group (before adding 1,4-benzoquinone)



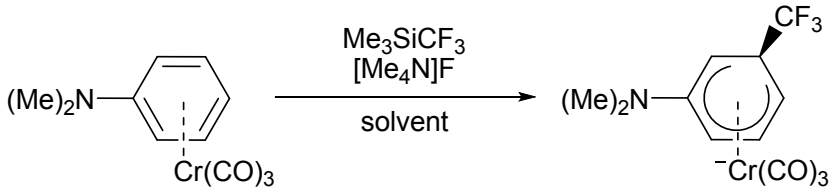
^{19}F NMR monitoring of the trifluoromethylation of (η^6-ethylbenzoate)Cr(CO)$_3$ (**1j**) at the ester carbonyl group (after addition of 1,4-benzoquinone)

Optimization experiments

Trifluoromethylation of (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$

Trifluoromethylation reactions were carried out in anhydrous solvents under an argon atmosphere using standard Schlenk techniques. Experimental details of the trifluoromethylation optimization using (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$ (**1h**) as a model substrate are presented in Table S2.

TableS2 Trifluoromethylation of (η^6-*N,N*-dimethylaniline)$Cr(CO)_3$ (**1h**)



1h **3h**

Entry	Solvent (mL)	1h (mg/mmol/ equiv)	Me_3SiCF_3 (mg/mmol/ equiv)	Me_4NF (mg/mmol/ equiv)	T (°C)	Yield[a] (%)
1	DMF (9)	170/0.66/1	200/1.40/2.13	78/0.83/1.27	–18±2	35[b]
2	DMF (8)	178/0.69/1	130/0.91/1.32	77/0.83/1.2	–18±2	53[c]
3	DMF (6)	180/0.7/1	185/1.3/1.86	100/1.07/1.53	–50→–10	66[d]
4	DMF (5)	257/1/1	312/2.2/2.2	160/1.71/2	–20→0	70[e]
5	DMF (5)	220/0.85/1	280/1.97/2.3	160/1.71/2	–50→–10	65[d]
6	DMF (5)	190/0.73/1	120/0.84/1.1	70/0.75/1	–50→–10	25[d]
7	DME (12)	770/2.99/1	560/3.94/1.32	335/3.6/1.2	–8±3	50[f]
8	DME (5)	180/0.7/1	218/1.53/2.19	130/1.39/2	–8±3	85[g]
9	DME (5)	220/0.85/1	200/1.42/1.65	120/1.28/1.5	–8±3	45[g]
10	DME (5)	257/1/1	312/2.2/2.2	160/1.71/2	–8±3	95[g]
11	MeCN (8)	237/0.92/1	210/1.47/1.6	98/1.05/1.14	–10	–[h]
12	$(Et)_2O$ (8)	223/0.86/1	160/1.47/1.13	95/1.05/1.18	–5	–[h]

[a] Yields determined by ^{19}F NMR (fluorobenzene as the internal standard) in 1 h after addition of Me_3SiCF_3

[b] Me_3SiCF_3 was being added in small portions within 15 min

[c] Me_3SiCF_3 in DMF (1 mL) was being added in small portions within 45 min

[d] **1h** dissolved in DMF (2 mL) was added to Me_3SiCF_3 and Me_4NF in DMF

[e] Me_3SiCF_3 dissolved in DMF (2 mL) was being added in small portions within 45 min

[f] Me_3SiCF_3 was being added in small portions within 30 min

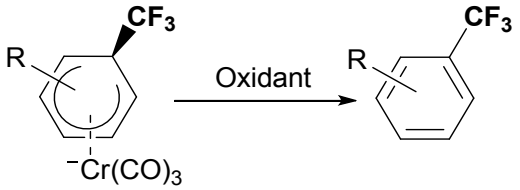
[g] Me_3SiCF_3 was being added in small portions within 45 min

[h] Me_3SiCF_3 was being added in small portions within 10 min

Oxidation of (η^5-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ adducts

The adducts resulting from Step A of the general procedure and prepared from 1 mmol of the starting substrates **1a**–**1i** were subjected to oxidation with iodine, 1,4-benzoquinone, ceric ammonium nitrate or air. The oxidation was conducted according to Step B of the general procedure unless otherwise indicated. Experimental details of the oxidation optimization are presented in Table S3.

Table S3 Oxidation of the trifluoromethylated (η^5-cyclohexadienyl)$Cr(CO)_3^-$ adducts



2, 3 **4**

Adduct (1 mmol)	Oxidant (mmol)	Product	Yield[c], %
2a and **3a**	iodine (2.5)	**4a** and **4a***	63
2a and **3a**	1,4-benzoquinone (4)	**4a** and **4a***	41
2a and **3a**	CAN (5.5)	**4a** and **4a***	< 30
2b	iodine (2.5)	**3b**	85
2c	iodine (2.5)	**3c**	30
2c	1,4-benzoquinone (4)	**3c**	42
2d	1,4-benzoquinone (4)	**3d**	71
2d	CAN (5.5)	**3d**	80
2d	air[a]	**3d**	35
2e	1,4-benzoquinone (4)	**3e**	9
2f	iodine (2.5)	**3f**	73
2f	1,4-benzoquinone (4)	**3f**	79
2f	CAN (5.5)	**3f**	< 30
3g	iodine (2.5)	**4g**	25
3g	1,4-benzoquinone (4)	**4g**	57
3h	iodine (2.5)	**4h**	59
3h	1,4-benzoquinone (4)	**4h**	88
3h	CAN (5.5)	**4h**	< 30
2i	iodine[b] (2.5)	**3i**	< 30
2i	CAN (5.5)	**3i**	< 30

[a] Reaction mixture resulting from Step A of the general procedure was degassed from argon, filled with air and refluxed for 30 min at room temperature

[b] Dissolved in 10 mL of DME and added according to Step B of the general procedure

[c] Yields determined by ^{19}F NMR (fluorobenzene as the internal standard) in 4 h after the reaction mixture was warmed up to room temperature

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3. R. Krischnamurti, D. R. Bellew., G. K. S. Prakash, *J. Org. Chem.* **1991**, *56*, 984–989.

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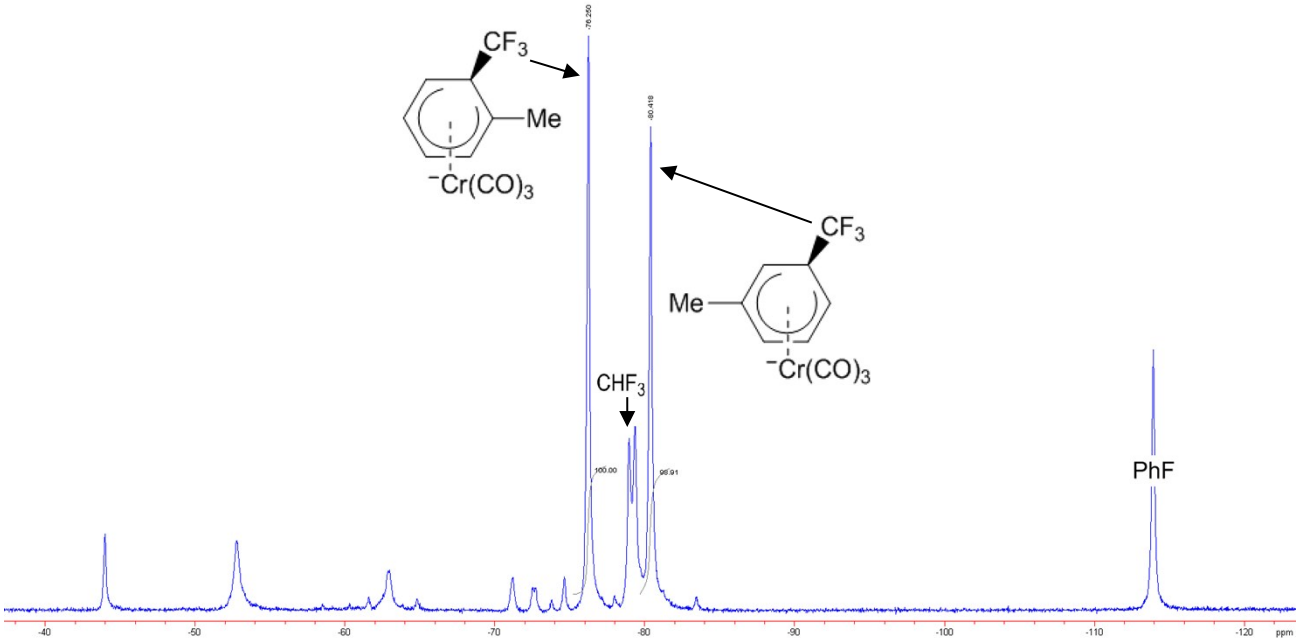
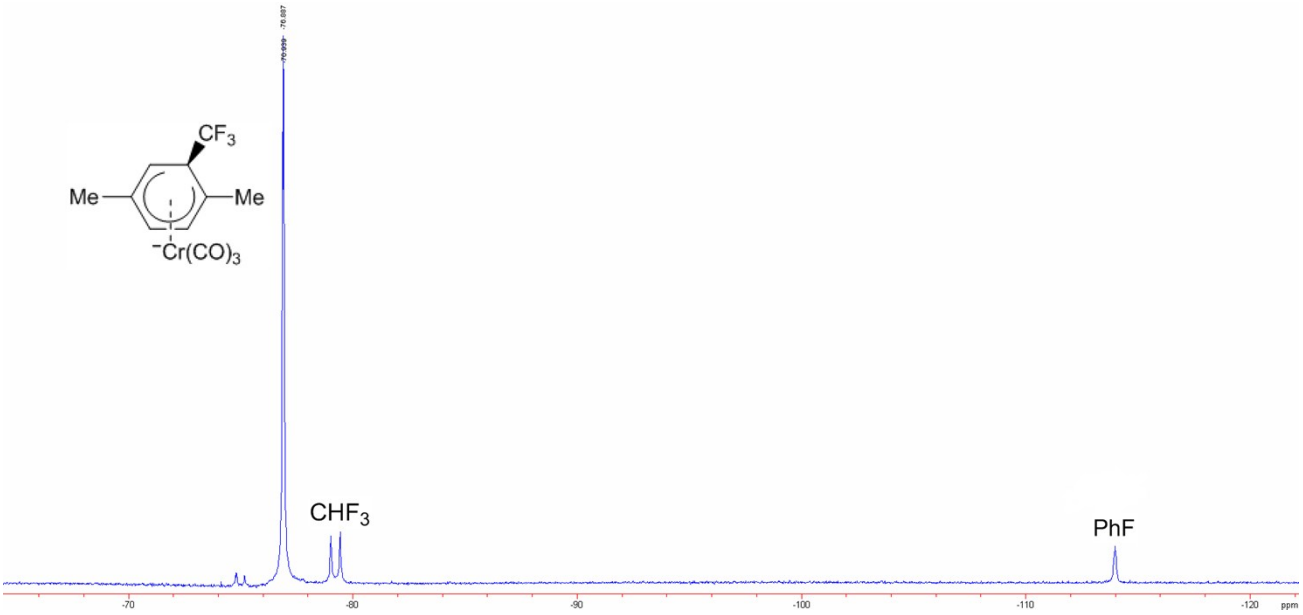
^{19}F NMR spectra of the reaction mixtures containing (η^5-(perfluoroalkyl)cyclohexadienyl)Cr(CO)$_3^-$ adducts

(η^5-1-Methyl-2-(trifluoromethyl)cyclohexadienyl)Cr(CO)$_3^-$ (2a) and (η^5-1-methyl-2-(trifluoromethyl)cyclohexadienyl)Cr(CO)$_3^-$ (3a)



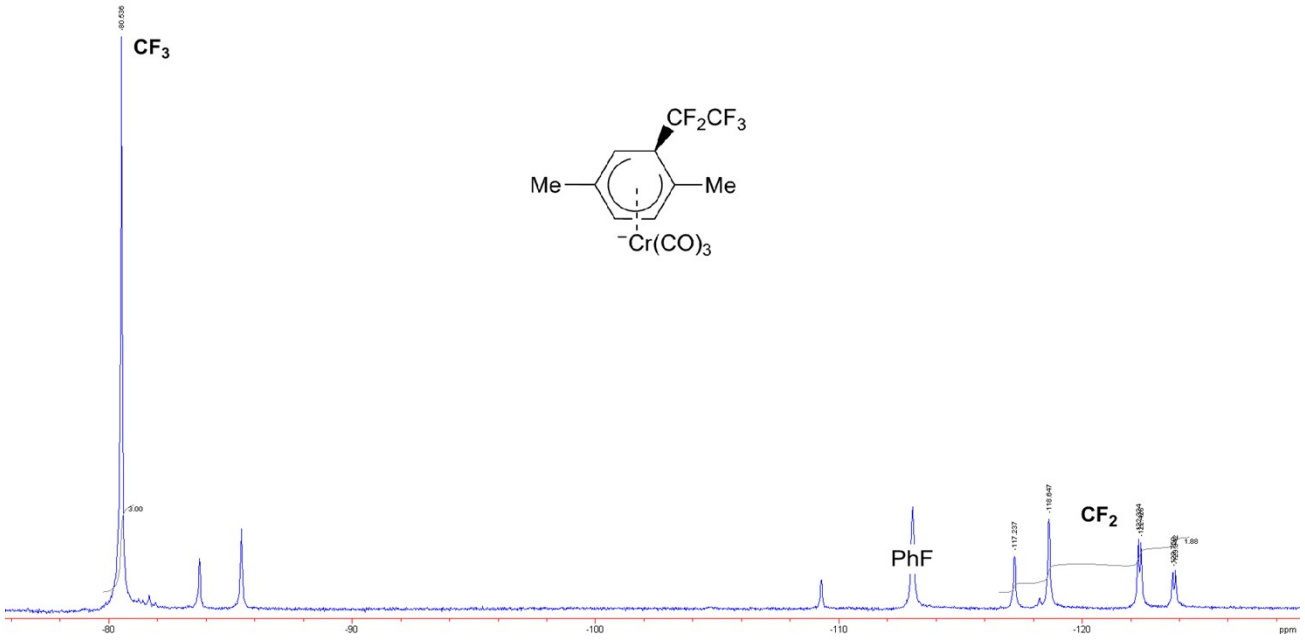
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-1,4-Dimethyl-2-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2b)

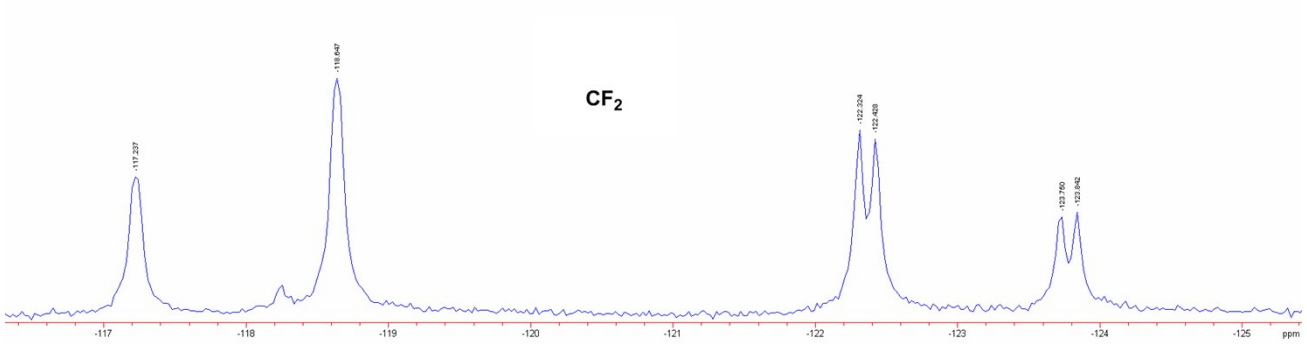


^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-1,4-Dimethyl-2-(pentafluoroethyl)cyclohexadienyl)$Cr(CO)_3^-$ (1S)

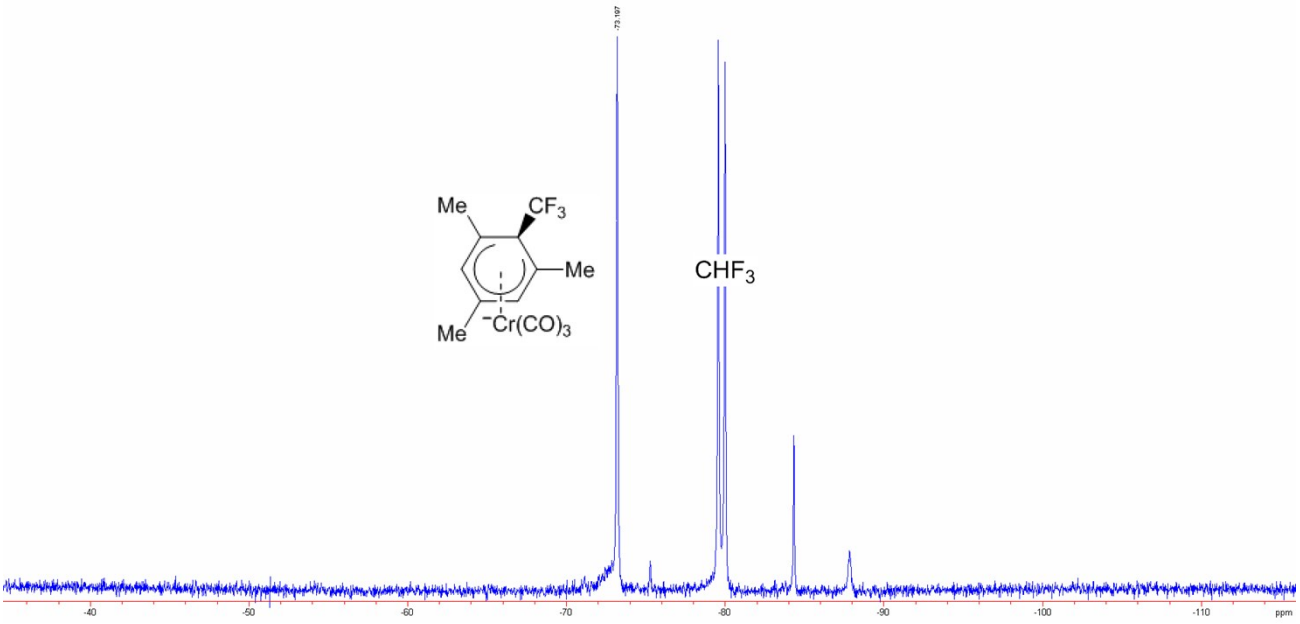


^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure



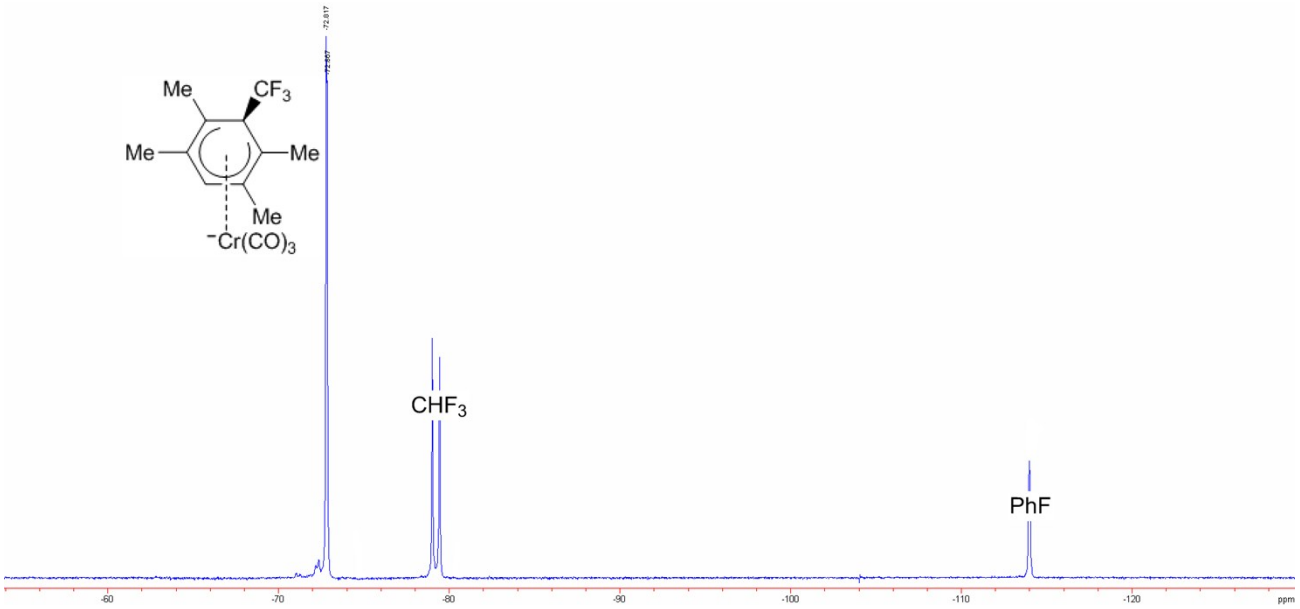
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure (close-up)

(η^5-1,3,5-Trimethyl-2-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2c)



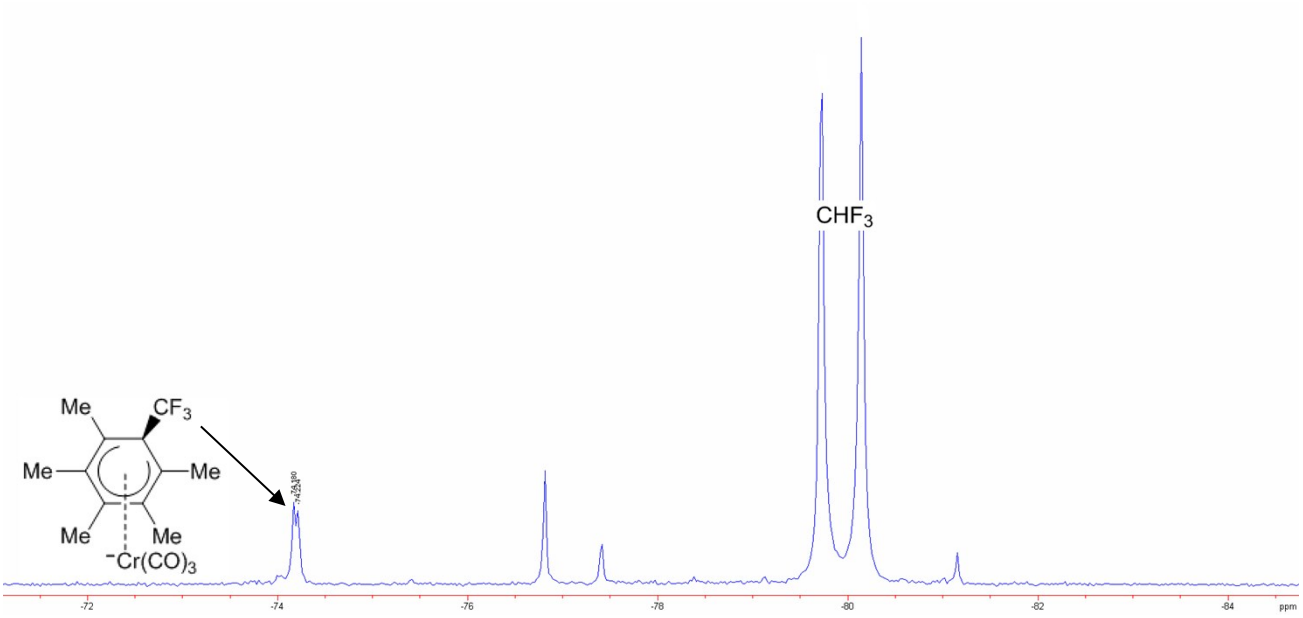
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-1,2,4,5-Tetramethyl-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2d)



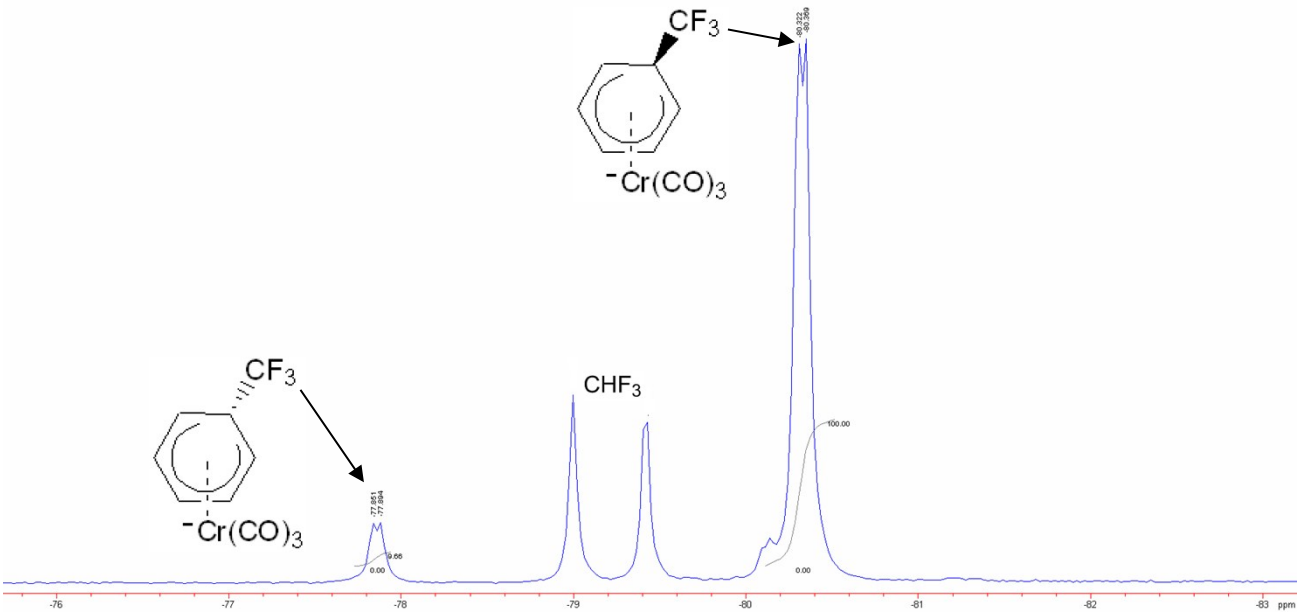
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-1,2,3,4,5-Pentamethyl-6-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2e)



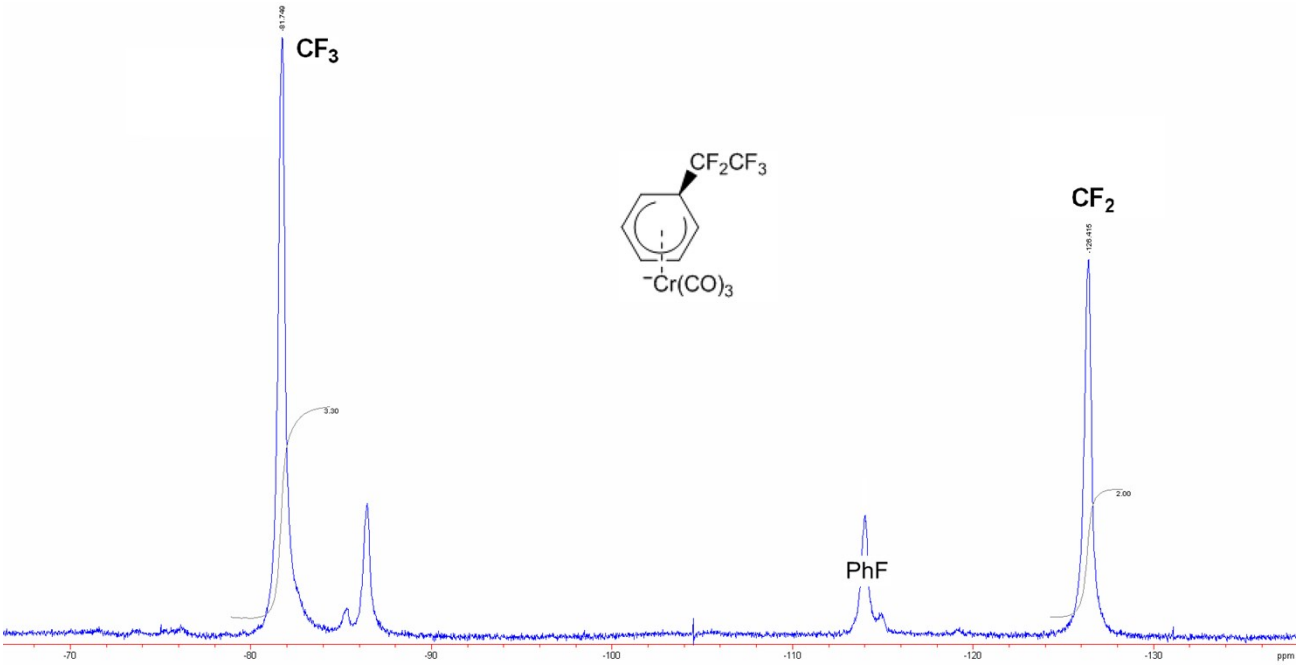
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-(Trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$(2f)



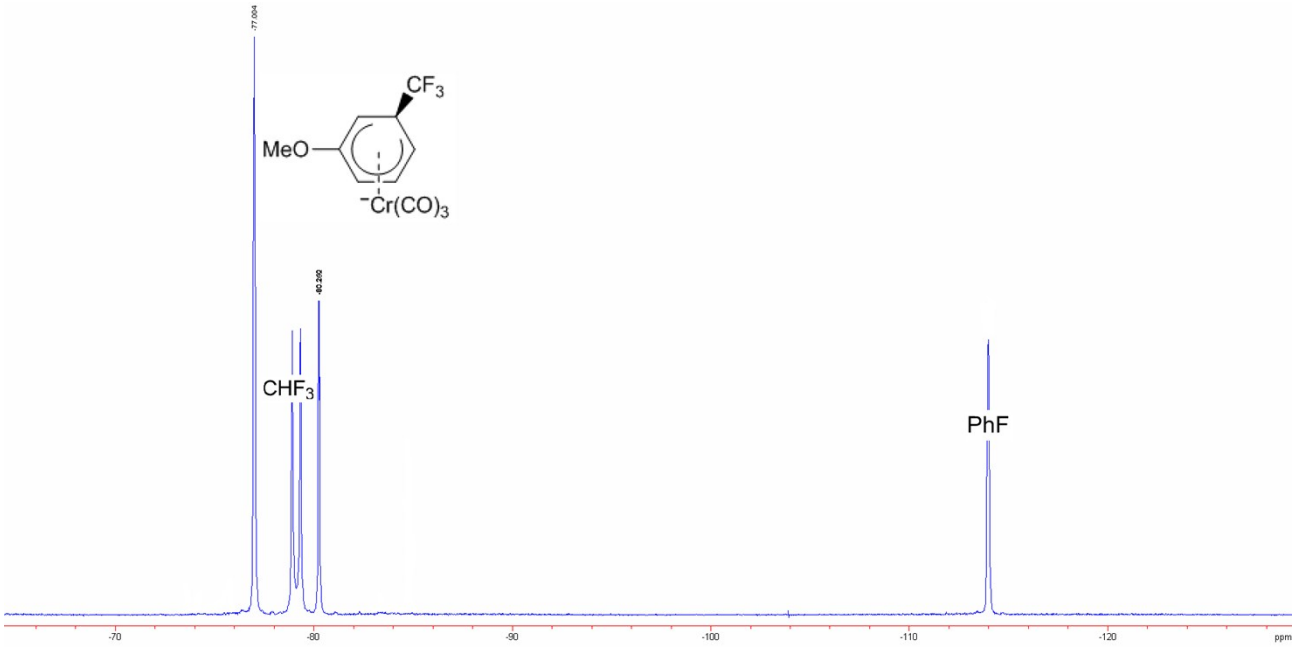
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-(Pentafluoroethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2S)



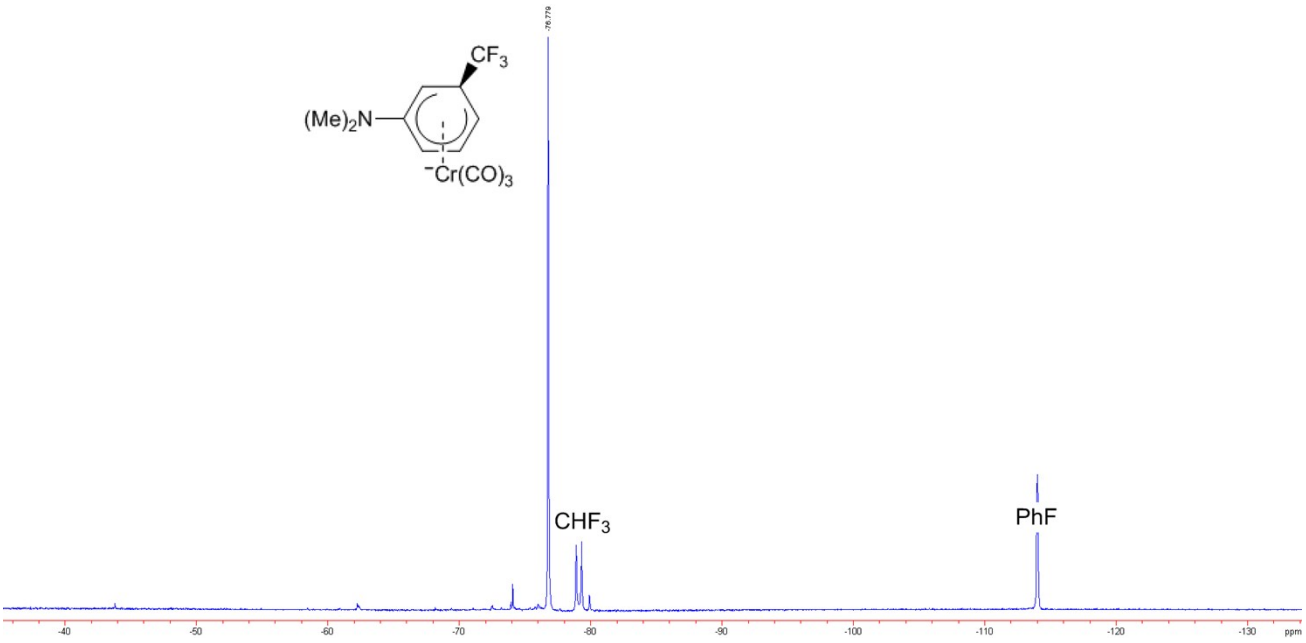
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-1-Methoxy-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3g)



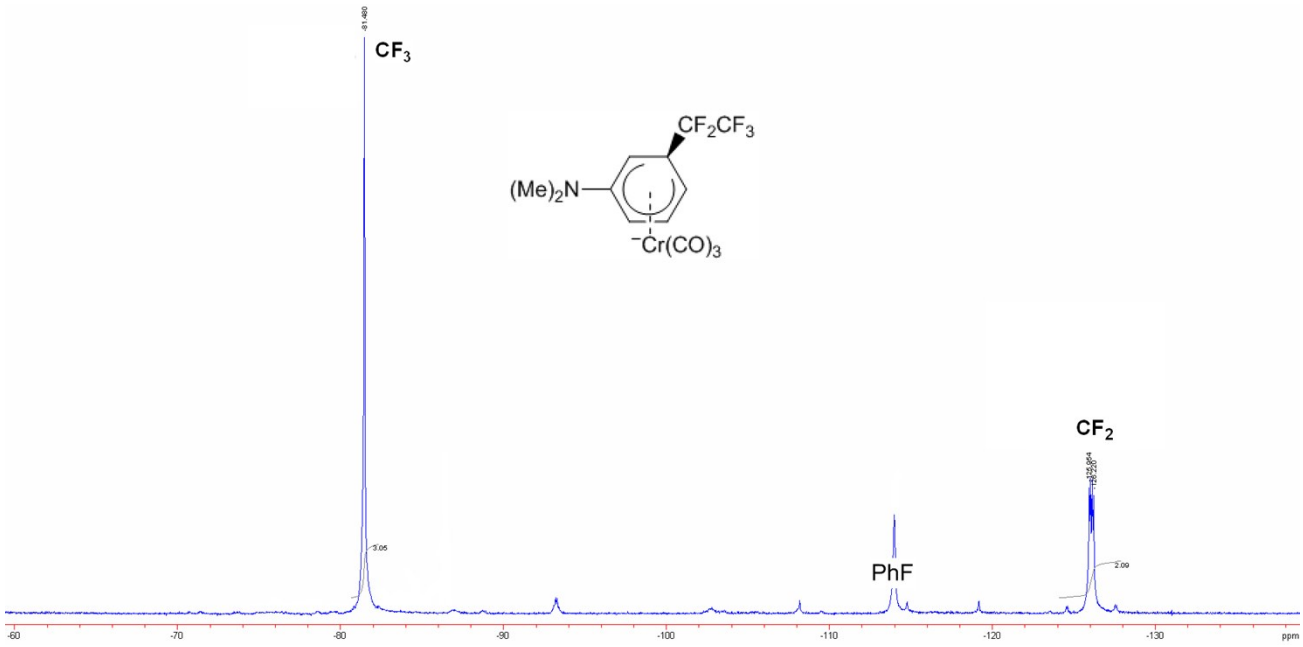
^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-*N,N*-Dimethyl-3-(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (3h)

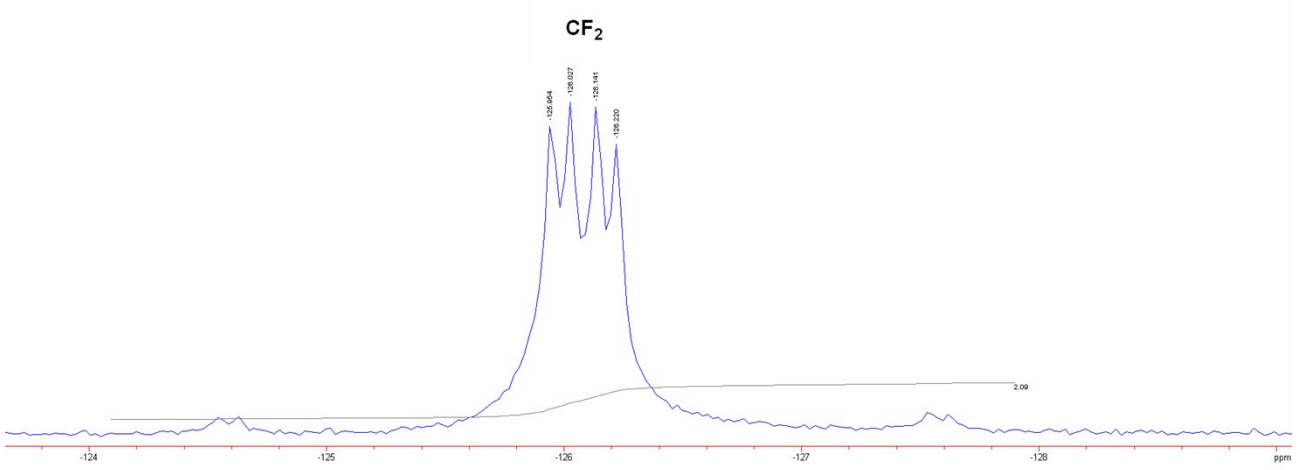


^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure

(η^5-*N,N*-Dimethyl-3-(pentafluoroethyl)cyclohexadienyl)$Cr(CO)_3^-$(3S)

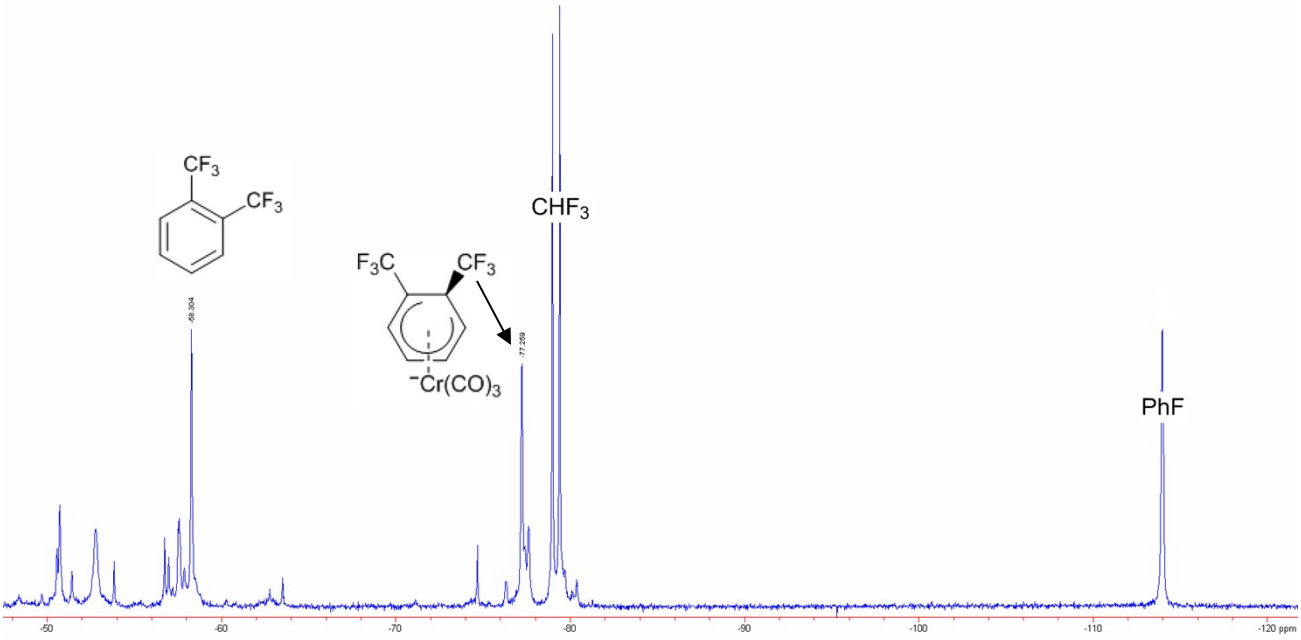


^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure



^{19}F NMR spectrum of the reaction mixture resulting from Step A of the general procedure (close-up)

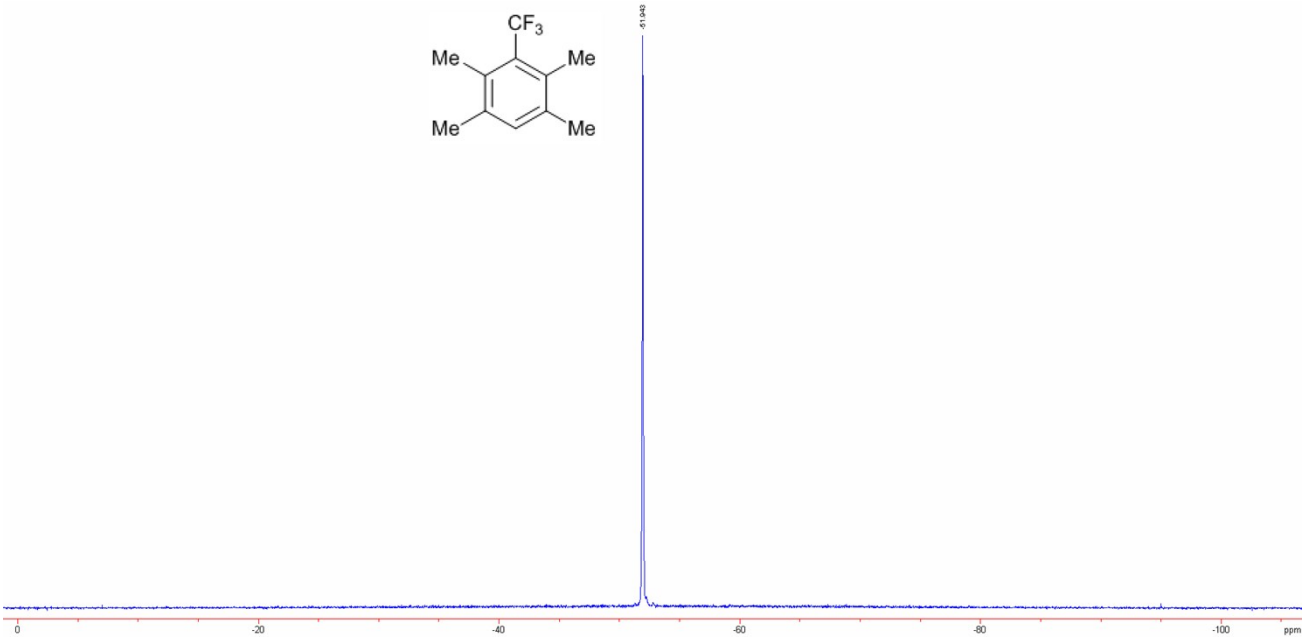
(η^5-1,2-Bis(trifluoromethyl)cyclohexadienyl)$Cr(CO)_3^-$ (2i)



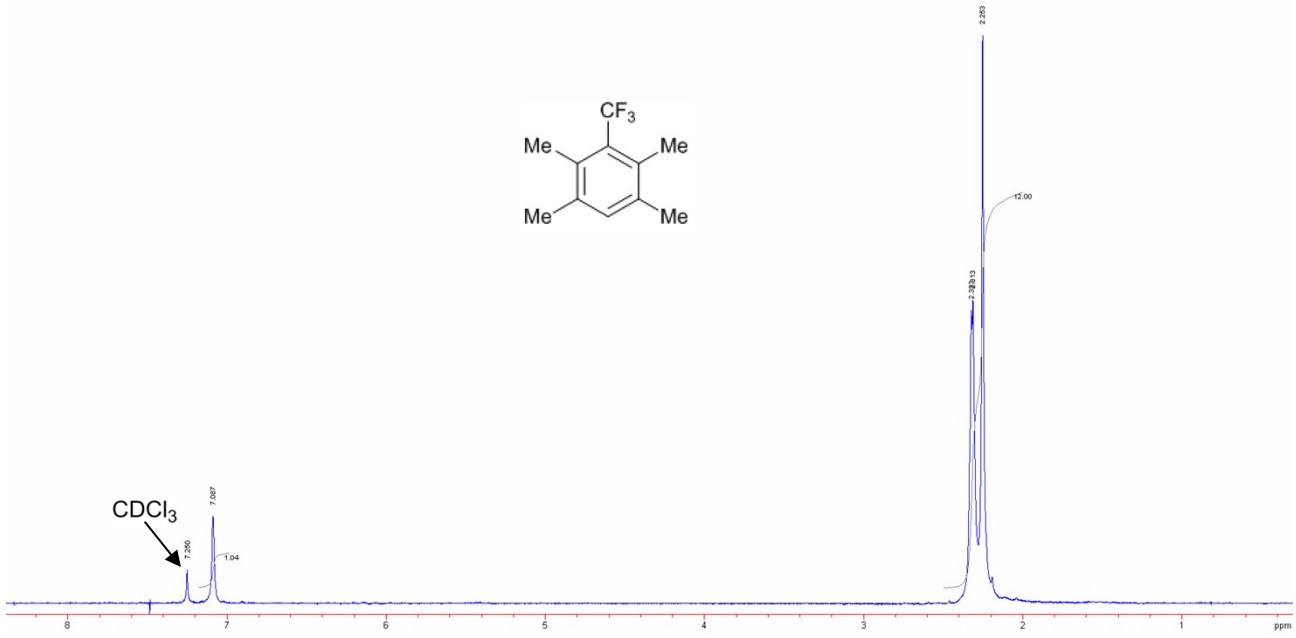
^{19}F NMR spectrum of the reaction mixture conrainresulting from Step A of the general procedure

NMR spectra of isolated compounds

1,2,4,5-Tetramethyl-3-(trifluoromethyl)benzene (4d)

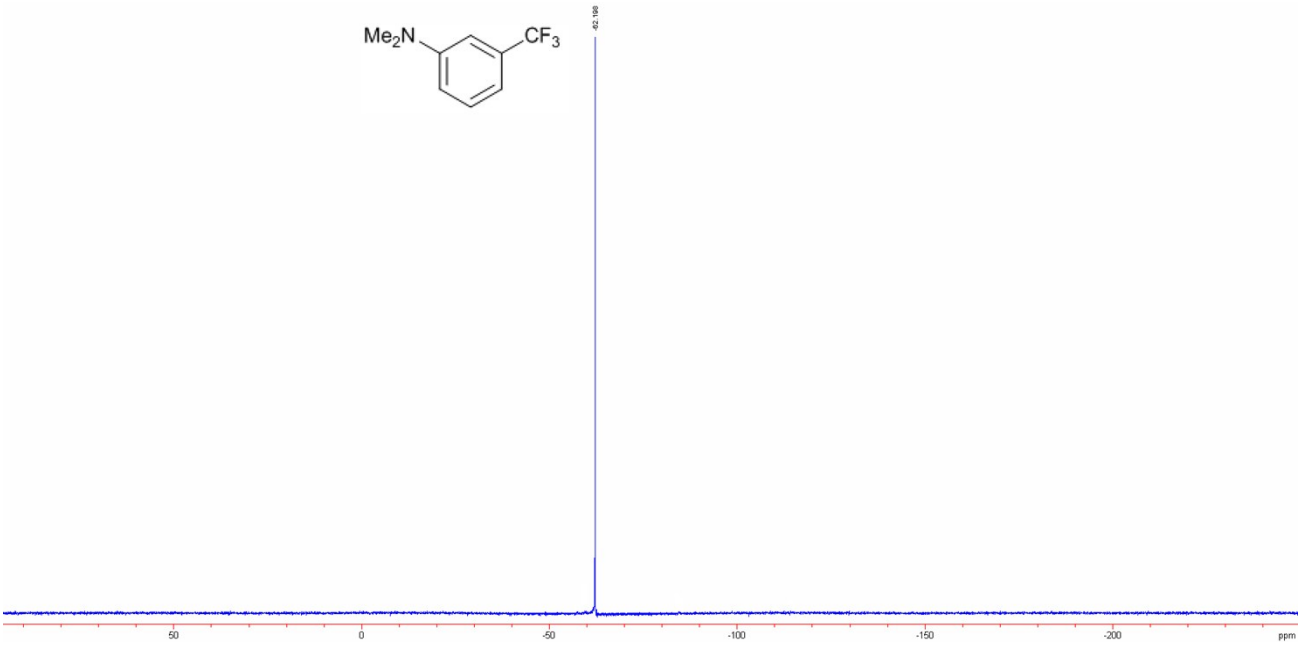


^{19}F NMR spectrum of 1,2,4,5-tetramethyl-3-(trifluoromethyl)benzene (**4d**)

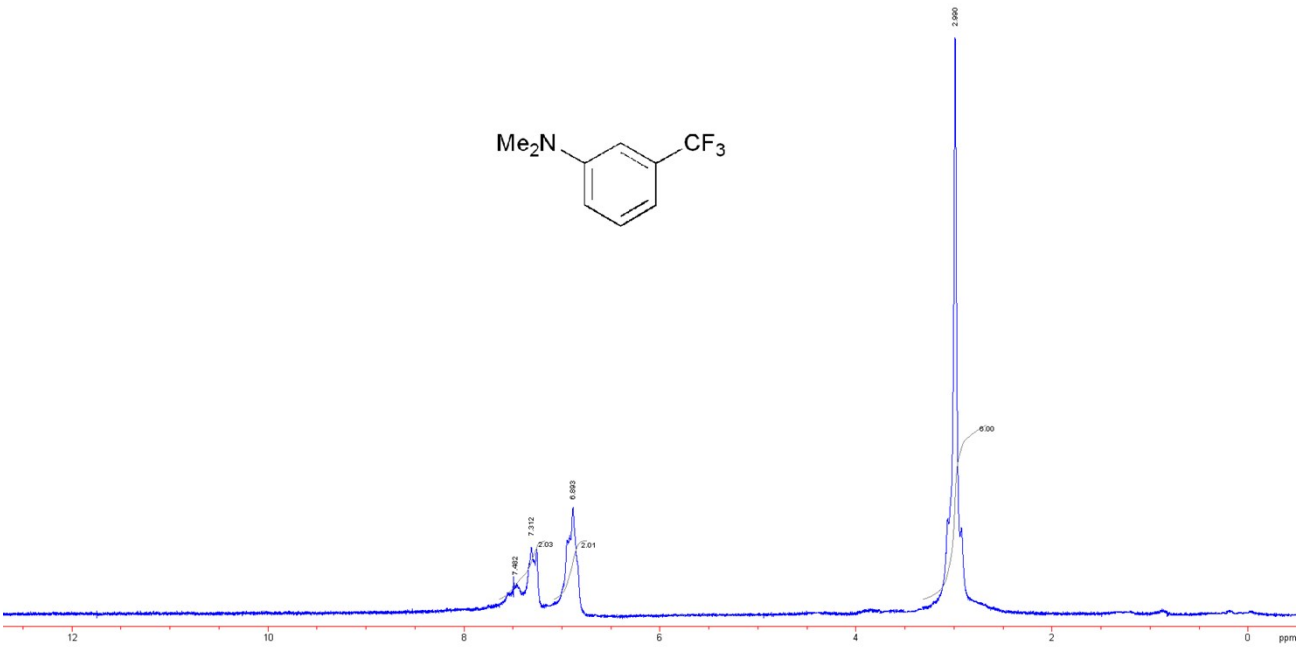


^{1}H NMR spectrum of 1,2,4,5-tetramethyl-3-(trifluoromethyl)benzene (**4d**)

***N,N*-Dimethyl-3-(trifluoromethyl)aniline (4h)**



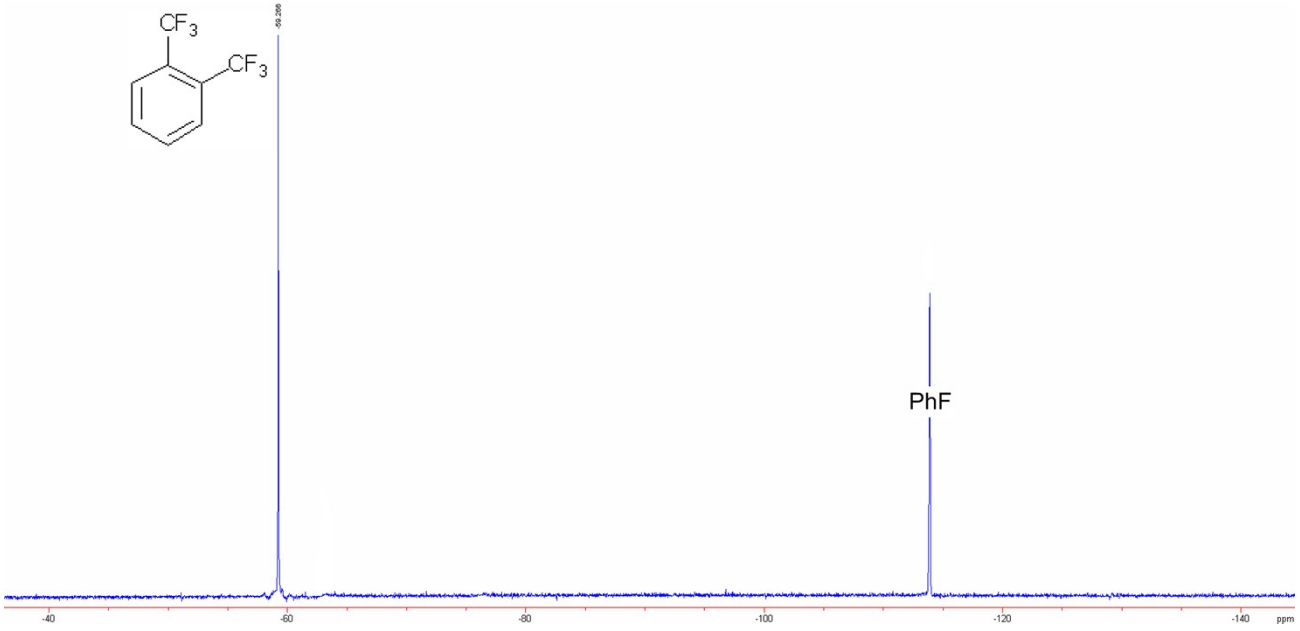
^{19}F NMR spectrum of *N,N*-dimethyl-3-(trifluoromethyl)aniline (**4h**)



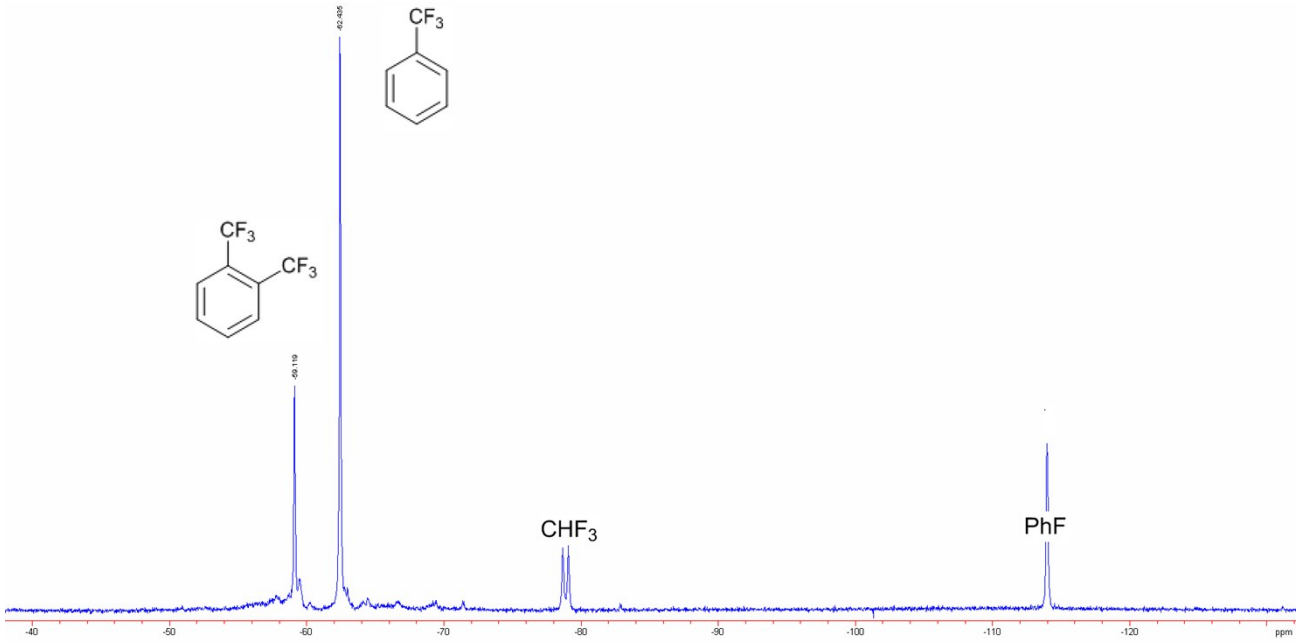
^{1}H NMR spectrum of *N,N*-dimethyl-3-(trifluoromethyl)aniline (**4h**)

1,2-Bis(trifluoromethyl)benzene (4b)

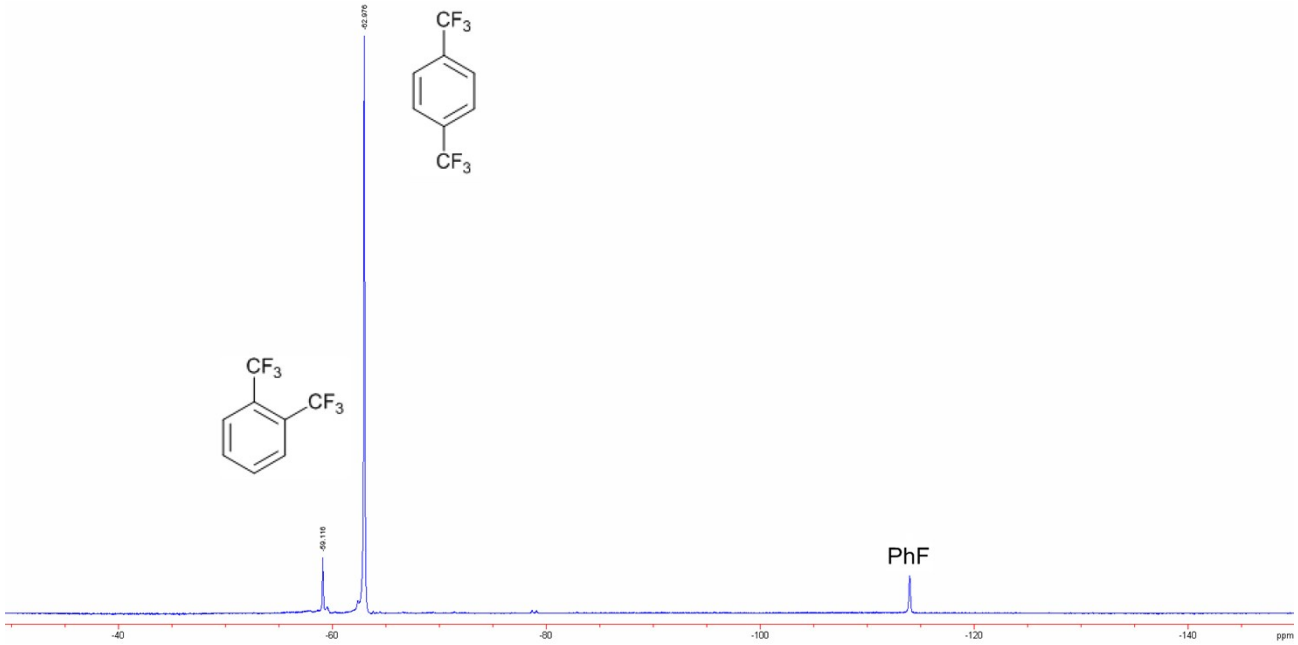
Due to high volatility of 1,2-bis(trifluoromethyl)benzene (**4b**), the product **4b** was distilled directly from the reaction mixture under reduced pressure and condensed into a liquid nitrogen-cooled trap. Along with the product, the distillate also contained some amount of the solvent (DME) and fluorobenzene used as the internal standard after Step A of the general procedure (^{19}F NMR spectrum 1). Trifluoromethylbenzene was added to a sample of the distillate as the internal standard in order to discard the possibility of the trifluoromethylation failure (^{19}F NMR spectrum 2). 1,4-Bis(trifluoromethyl)benzene was then added to the same sample in order to discard the possibility of *para*-trifluoromethylation of the cyclohexadienyl adduct **2i** (^{19}F NMR spectrum 3). The crude product was redistilled to afford **4b** as a colorless oil (^{19}F NMR spectrum 4).



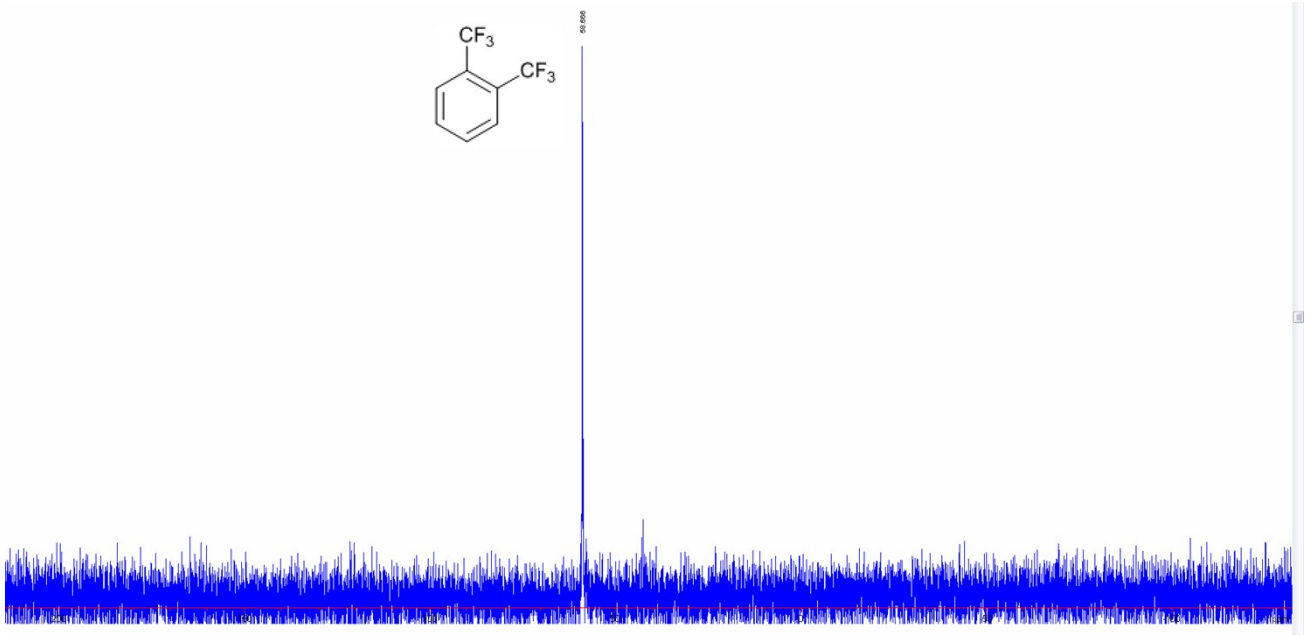
^{19}F NMR spectrum 1



^{19}F NMR spectrum 2



^{19}F NMR spectrum 3



^{19}F NMR spectrum 4