Supporting Information

Methylations with Methanol via Bioinspired Catalytic C–O Bond Cleavage

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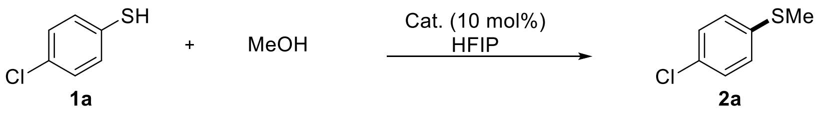
1 General information

Unless otherwise stated, all chemicals used in this manuscript were purchased from Energy chemical company, Bide Pharmatech Ltd, Inno-Chem Ltd, Adamas Company, Sigma Aldrich and Alfa Aesar Company. Other commercially available compounds were used as provided without further purification. HFIP used in the reactions were dried from anhydrous Mg_2SO_4 and distilled in N_2 prior to use. Other solvents are used after processing in accordance with conventional methods. Unless otherwise noted, all reactions were performed under N_2 atmosphere. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm). Visualization was accomplished by irradiation with *p*-methoxybenzaldehyde, ultraviolet lamp (254 nm), alkaline potassium permanganate solution, iodine cylinder and phosphomolybdic acid solution. Flash column chromatography was performed over silica gel (200-300 mesh). The nuclear magnetic resonance data in this paper is measured by Bruker AVANCE III-400 or Bruker AscendTM 600MHZ nuclear magnetic resonance instrument at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.16 for ^{13}C-NMR). Proton spectrum description analysis is as follows: chemical shift (ppm), multiplet analysis (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), unidentified coupling the methods are all analyzed by multiple peak processing, and the carbon spectrum is described in ppm. Coupling constants (*J*) were reported in Hertz (Hz). High resolution mass spectra (HR-MS) were determined on Bruker SolariX 7.0T FT-MS (ESI source). Mass spectra (GC-MS) were determined on Agilent 7890A/5975C (EI source)

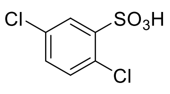
2 Optimization of reaction conditions for Methylation/*d*$_3$-methylation with MeOH/MeOH-*d*$_3$

Table S1. Acid screening



Entry	Addictive	Cat.	Solvent	T (°C)	t (h)	**2a**
1	-	cat.**1**	HFIP	150	24	27
2	-	cat.**2**	HFIP	150	24	40
3	-	cat.**3**	HFIP	150	24	27
4	-	cat.**4**	HFIP	150	24	35
5	-	cat.**5**	HFIP	150	24	37
6	-	cat.**6**	HFIP	150	24	0
7	-	cat.**7**	HFIP	150	24	0
8	-	cat.**8**	HFIP	150	24	8
9	-	cat.**9**	HFIP	150	24	13
10	-	cat.**10**	HFIP	150	24	36
11	-	cat.**11**	HFIP	150	24	15
12	-	cat.**12**	HFIP	150	24	0
13	-	cat.**13**	HFIP	150	24	9
14	-	cat.**14**	HFIP	150	24	13
15	-	cat.**15**	HFIP	150	24	32

Unless mentioned otherwise, reactions were performed with **1a** (1.0 equiv.), MeOH (2.0 equiv.), HFIP (0.4 M), **Cat.** (10 mol%) at 150 ^{o}C for 24 hours. ^{a}Yields were determined by analyzing ^{1}H NMR of the reaction mixture with an internal standard.



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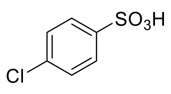

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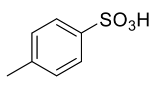

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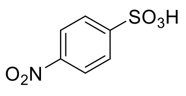

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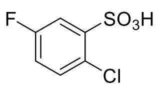

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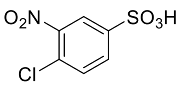

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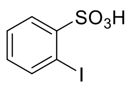

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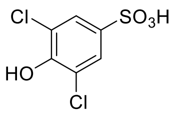

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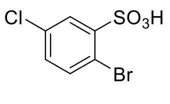

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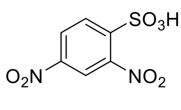

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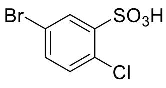

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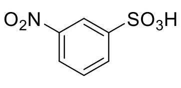

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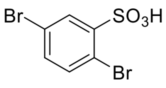

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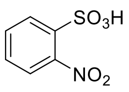

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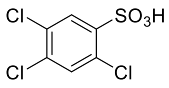

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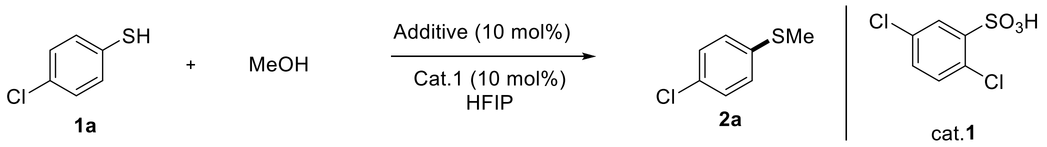
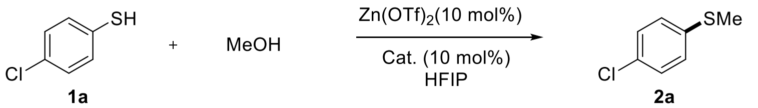
Table S2. Addictive screening



Entry	Addictive	Cat.	Solvent	T (°C)	t (h)	**2a**
1	$ZnCl_2$	cat.**1**	HFIP	150	24	80
2	$ZnBr_2$	cat.**1**	HFIP	150	24	88
3	ZnF_2	cat.**1**	HFIP	150	24	0
4	$Zn(OTf)_2$	cat.**1**	HFIP	150	24	98(90)[b]
5	$ZnSO_4$	cat.**1**	HFIP	150	24	78
6	$Zn(OAc)_2$	cat.**1**	HFIP	150	24	0
7	$Zn(BF_4)_2$	cat.**1**	HFIP	150	24	34
8	$Zn(CN)_2$	cat.**1**	HFIP	150	24	0
9	$Zn(BO_4)_2$	cat.**1**	HFIP	150	24	48
10	$Zn_3(PO_4)_2$	cat.**1**	HFIP	150	24	54
11	$Ba(OTf)_3$	cat.**1**	HFIP	150	24	43
12	$Mg(OTf)_2$	cat.**1**	HFIP	150	24	50
13	$Cu(OTf)_2$	cat.**1**	HFIP	150	24	28
14	$Ni(OTf)_2$	cat.**1**	HFIP	150	24	47

Unless mentioned otherwise, reactions were performed with **1** (1.0 equiv.), MeOH (2.0 equiv.), HFIP (0.4 M), **Cat.1** (10 mol%), Additive (10 mol%) at 150 °C for 24 hours. [a] Yields were determined by analyzing ^{1}H NMR of the reaction mixture with an internal standard. [b] Isolated yield.

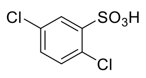
Table S3. Acid screening + $Zn(OTf)_2$



1a **2a**

Entry	Addictive	Cat.	Solvent	T (°C)	t (h)	2a
1	$Zn(OTf)_2$	cat.**1**	HFIP	150	24	98(90)[*b*]
2	$Zn(OTf)_2$	cat.**2**	HFIP	150	24	43
3	$Zn(OTf)_2$	cat.**3**	HFIP	150	24	39
4	$Zn(OTf)_2$	cat.**4**	HFIP	150	24	0
5	$Zn(OTf)_2$	cat.**5**	HFIP	150	24	33
6	$Zn(OTf)_2$	cat.**6**	HFIP	150	24	48
7	$Zn(OTf)_2$	cat.**7**	HFIP	150	24	30
8	$Zn(OTf)_2$	cat.**8**	HFIP	150	24	66
9	$Zn(OTf)_2$	cat.**9**	HFIP	150	24	50
10	$Zn(OTf)_2$	cat.**10**	HFIP	150	24	55
11	$Zn(OTf)_2$	cat.**11**	HFIP	150	24	0
12	$Zn(OTf)_2$	cat.**12**	HFIP	150	24	0
13	$Zn(OTf)_2$	cat.**13**	HFIP	150	24	88
14	$Zn(OTf)_2$	cat.**14**	HFIP	150	24	92
15	$Zn(OTf)_2$	cat.**15**	HFIP	150	24	97
16	$Zn(OTf)_2$	cat.**16**	HFIP	150	24	97
17	$Zn(OTf)_2$	cat.**17**	HFIP	150	24	57

Unless mentioned otherwise, reactions were performed with **1a** (1.0 equiv.), MeOH (2.0 equiv.), HFIP (0.4 M), **Cat.** (10 mol%), $Zn(OTf)_2$ (10 mol%) at 150 ^oC for 24 hours. [a] Yields were determined by analyzing ^1H NMR of the reaction mixture with an internal standard. [b] Isolated yield.



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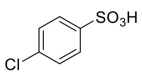

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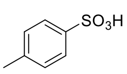

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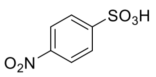

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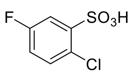

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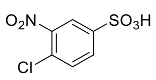

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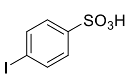

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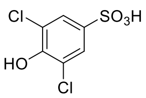

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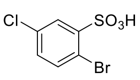

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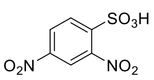

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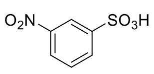

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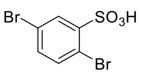

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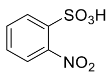

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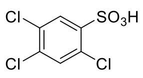

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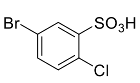

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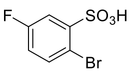

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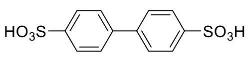

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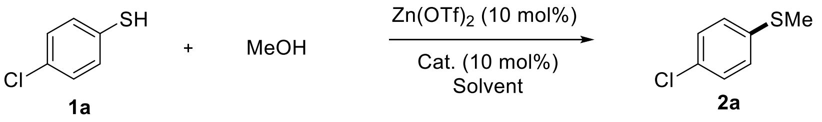
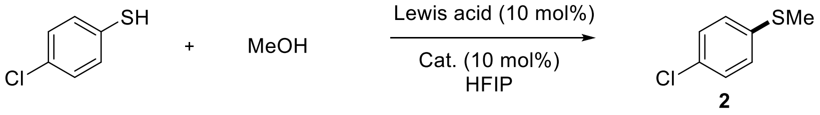
Table S4. Solvent screening



Entry	Addictive	Cat.	Solvent	T (°C)	t (h)	2a
1	$Zn(OTf)_2$	cat.**1**	HFIP	150	24	98(90)[b]
2	$Zn(OTf)_2$	cat.**1**	DCE	150	24	29
3	$Zn(OTf)_2$	cat.**1**	toluene	150	24	0
4	$Zn(OTf)_2$	cat.1	dioxane	150	24	11
5	$Zn(OTf)_2$	cat.**1**	hexane	150	24	27
6	$Zn(OTf)_2$	cat.**1**	cyclohexan	150	24	31
7	$Zn(OTf)_2$	cat.**1**	DMSO	150	24	0
8	$Zn(OTf)_2$	cat.**1**	CH_3CN	150	24	27
9	$Zn(OTf)_2$	cat.**1**	THF	150	24	39
10	$Zn(OTf)_2$	cat.**1**	DCM	150	24	0
11	$Zn(OTf)_2$	cat.**1**	$CDCl_3$	150	24	38
12	$Zn(OTf)_2$	cat.**1**	hexane	150	24	98[c]
13	$Zn(OTf)_2$	cat.**1**	hexane	150	24	79[d]
14	$Zn(OTf)_2$	cat.**1**	hexane	150	24	85[e]

Unless mentioned otherwise, reactions were performed with **1a** (1.0 equiv.), MeOH (2.0 equiv.), HFIP (0.4 M), **Cat.1** (10 mol%), $Zn(OTf)_2$ (10 mol%) at 150 °C for 24 hours. [a] Yields were determined by analyzing ^1H NMR of the reaction mixture with an internal standard. [b] Isolated yield. [c] MeOH (5.0 equiv.) was used. [d] MeOH (3.0 equiv.) was used. [e] MeOH (4.0 equiv.) was used.

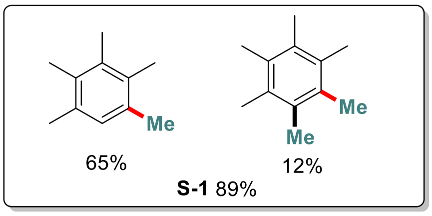
Table S5. Other screening



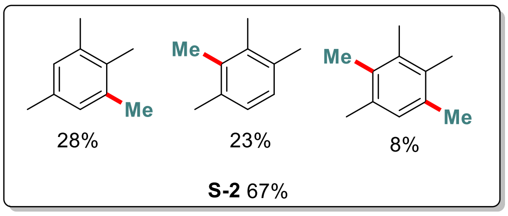
Entry	Addictive	Cat.	Solvent	T (°C)	t (h)	2
1	$Zn(OTf)_2$	-	HFIP	150	24	31
2	-	cat.**1**	HFIP	150	24	27
3	$Zn(OTf)_2$	cat.**1**	HFIP	100	24	0
4	$Zn(OTf)_2$	cat.**1**	HFIP	120	24	35
5	$Zn(OTf)_2$	cat.**1**	HFIP	130	24	44
6	$Zn(OTf)_2$	cat.**1**	HFIP	140	24	86
7	$Zn(OTf)_2$	cat.**1**	HFIP	150	2	19
8	$Zn(OTf)_2$	cat.**9**	HFIP	150	4	24
9	$Zn(OTf)_2$	cat.**10**	HFIP	150	6	30
10	$Zn(OTf)_2$	cat.**11**	HFIP	150	8	31
11	$Zn(OTf)_2$	cat.**12**	HFIP	150	10	81
12	$Zn(OTf)_2$	cat.**13**	HFIP	150	12	84
13	$Zn(OTf)_2$ (5 mol%)	cat.**1** (10 mo%)	HFIP	150	24	88
14	$Zn(OTf)_2$ (5 mol%)	cat.**1** (5 mo%)	HFIP	150	24	90
15	$Zn(OTf)_2$ (10 mol%)	cat.**1** (5 mo%)	HFIP	150	24	95
16	$Zn(OTf)_2$ (10 mol%)	cat.**1** (10 mo%)	HFIP	150	24	98(90)[b]

Unless mentioned otherwise, reactions were performed with **1a** (1.0 equiv.), MeOH (2.0 equiv.), HFIP (0.4 M), **Cat.1** (10 mol%), $Zn(OTf)_2$ (10 mol%) at 150 °C for 24 hours. [a] Yields were determined by analyzing ^1H NMR of the reaction mixture with an internal standard. [b] Isolated yield.

3 Additional substrate scope



S-1 89%

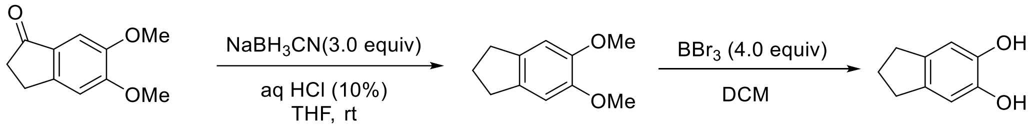


S-2 67%

4 Syntheses of starting materials and spectroscopic data

All substrates were prepared following the literature procedures or the procedures provided in this manuscript. ^{1}H NMR, ^{13}C NMR, ^{19}F-NMR, and HRMS were provided for all compounds not previously reported, for cases where HRMS were not obtained after several tries, GC-MS was provided. Only ^{1}H NMR (and ^{13}C NMR or ^{19}F-NMR) were provided for known compounds to show excellent agreement with reported data.

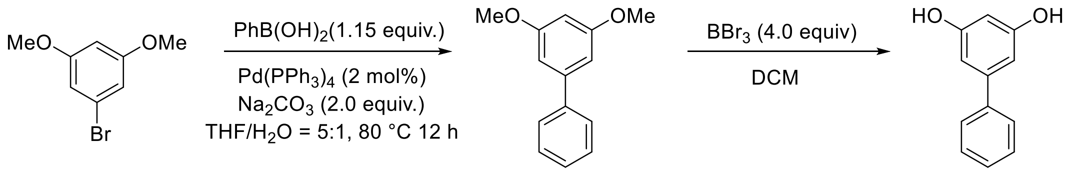
4.1 Procedure for synthesis 3e[1-2]



5,6-Dimethoxy-2,3-dihydro-1H-indene: To a solution of commercially available 5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (1.92 g, 10.0 mmol, 1.0 equiv) in THF (20 mL) at room temperature was added $NaBH_3CN$ (1.86 g, 30.0 mmol, 3.0 equiv). 10% aq HCl (20 mL) was then slowly added to the mixture. After stirring for 5 h, the resulting mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography with (PE/EtOAc = 50:1) afforded (1.7 g, 96%) of 5,6-dimethoxy-2,3-dihydro-1H-indene as a white solid. The procedure and spectroscopic data were according to the literature report.

To a solution of 5,6-Dimethoxy-2,3-dihydro-1H-indene (1.78 mg, 10 mmol) in CH_2Cl_2 (60 mL) was added BBr_3 (40 mmol, 4 equiv.) at 0 °C, and the mixture was allowed to stir at room temperature for 2 h. Water was added dropwise to quench the reaction, and the mixture was extracted with CH_2Cl_2. The organic phase was dried by Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography (PE/EtOAc = 4:1) to yield 2,3-dihydro-1H-indene-5,6-diol (**3e**) as a white solid (1.2 g, 80%). The procedure and spectroscopic data were according to the literature report.

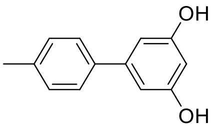
4.2 Procedure for synthesis resorcinol derivatives 3n[3-4]



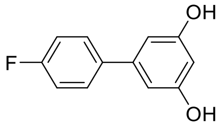
3n

A suspension of 1-bromo-3,5-dimethoxybenzene (2.17 g, 10 mmol), phenylboronic acid (1.4 g, 11.5 mmol), $Pd(PPh_3)_4$ (0.231 g, 0.2 mmol) and Na_2CO_3 (2.12 g, 20 mmol) in THF/water (5/1, 60 mL) was stirred for 12 h under reflux condition. After cooling, the reaction mixture was filtrated through Celite, quenched with sat. NH_4Cl aq., and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under a vacuum. The crude product was purified by silica column chromatography (PE/EtOAc = 50:1) to afford 3,5-dimethoxy-1,1′-biphenyl in 70% yield (1.49 g). BBr_3 (1.0 M in CH_2Cl_2, 40 mL, 40 mmol) was added to a solution of 3,5-dimethoxy-1,1′-biphenyl (2.14 g, 10 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The mixture was stirred for 12 h at room temperature. After cooling to 0 °C, the reaction was quenched with sat. $NaHCO_3$ aq. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under a vacuum. The crude product was purified by silica column chromatography (PE/EtOAc = 2:1) to afford **3n** in 90% yield (1.67 g, white solid). The procedure and spectroscopic data were according to the literature report.

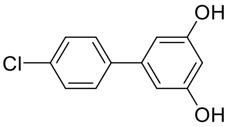
Compounds **3o**, **3p**, **3q**, and **3r** were prepared following the procedure for **3n**.



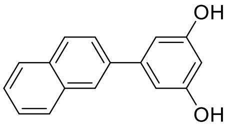
3,5-Dihydroxy-4′-methyl-1,1′-biphenyl (3o)[4] (1.06 g, 53% yield), (2 steps from 1-bromo-3,5-dimethoxybenzene). White solid after isolation by silica-gel column chromatography (PE/EtOAc = 2:1). The spectroscopic data were according to the literature report.



4′-Fluoro-[1,1′-biphenyl]-3,5-diol (3p)[5] (898 mg, 44% yield), (2 steps from 1-bromo-3,5-dimethoxybenzene). White solid after isolation by silica-gel column chromatography (PE/EtOAc = 1:1). The spectroscopic data were according to the literature report.



4′-Choloro-[1,1′-biphenyl]-3,5-diol (3q)[6] (1.01 g, 46% yield), (2 steps from 1-bromo-3,5-dimethoxybenzene). White solid after isolation by silica-gel column chromatography (PE/EtOAc = 1:1). The spectroscopic data were according to the literature report.



5-(Naphthalen-2-yl)benzene-1,3-diol (3r)[3] (898 mg, 38% yield), (2 steps from 1-bromo-3,5-dimethoxybenzene). White solid after isolation by silica-gel column chromatography (PE/EtOAc = 1:1). The spectroscopic data were according to the literature report.

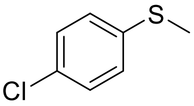
5 General procedure for the Alkylation and Characterization of Alkylation Products.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS were provided for all compounds not previously reported, for cases where HRMS were not obtained after several tries, GC-MS were provided. Only ^{1}H NMR (and ^{13}C NMR or ^{19}F NMR) were provided for known compounds to show excellent agreement with reported data.

General procedure A: To a 10 mL Schlenk tube was charged with **Cat.1** (10 mol%), $Zn(OTf)_2$ (10 mol%), **1** or **3** (1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of an argon atmosphere, HFIP (0.4 M) and MeOH (2.0 equiv.) were added and the reaction mixture was stirred at 150 °C for 24 h. The reaction was then quenched by adding K_2CO_3 (20 mol%), filtration, and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography on silica gel to give the products.

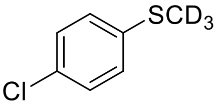
General procedure B: In a nitrogen-filled glove box, to a 10 mL Schlenk tube was charged with **Cat.1** (10 mol%), $Zn(OTf)_2$ (10 mol%), **1** or **3** (1.0 equiv.), Hexane (0.4 M), MeOH (5.0 equiv.) and an oven-dried stirring bar. The tube was sealed and removed from the glove box. After degassing, the reaction mixture was stirred at 150 °C for 24 h. The reaction was then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure, and the residue was purified using flash column chromatography on silica gel to give the products.

General procedure C: To a 10 mL Schlenk tube was charged with **Cat.1** (10 mol%), $Zn(OTf)_2$ (10 mol%), **1** (5 equiv), HFIP (0.4 M), MeOH (8μL, 1.0 equiv.) and an oven-dried stirring bar under air. The reaction mixture was stirred at 150 °C for 48 h. The reaction was then quenched by adding K_2CO_3 (20 mol%), and dodecane or CH_2Br_2 as an internal standard was added, take sample 1-2 drops to check yield by GC or ^{1}H NMR.



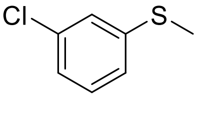
2a: (4-chlorophenyl)(methyl)sulfane.[7]

2a was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration, and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure, and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2a** (28.5 mg, 90%) as a colorless oil **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.22 – 7.18 (m, 2H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 131.0, 129.0, 128.1, 16.2. The spectroscopic data were according to the literature report.



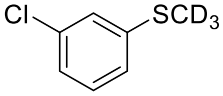
2a-*d*$_3$: (4-chlorophenyl)(methyl-*d*$_3$)sulfane[8].

2a-*d*$_3$ was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2a-*d*$_3$** (31 mg, 97%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.21 – 7.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 131.0, 129.0, 128.0. The spectroscopic data were according to the literature report.



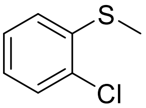
2b: (3-chlorophenyl)(methyl)sulfane[7].

2b was synthesized according to the **General procedure A** With **1b** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2b** (30.5 mg, 96%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.34 (dt, *J* = 8.1, 1.4 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 132.0, 129.5, 127.3, 125.7, 125.6, 15.3. The spectroscopic data were according to the literature report.



2b-*d*₃: (3-chlorophenyl)(methyl-d_3)sulfane[9].

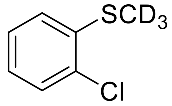
2b-*d*₃ was synthesized according to the **General procedure A** With **1b** (0.2 mmol**,** 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2b-*d*₃** (30.1 mg, 94%) as a colorless oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.15 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.08 (td, *J* = 7.8, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 132.0, 129.5, 127.3, 125.7, 125.6. The spectroscopic data were according to the literature report.



2c: (2-chlorophenyl)(methyl)sulfane[7]

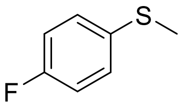
2c was synthesized according to the **General procedure A** With **1c** (0.2 mmol**,** 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2c** (29.8 mg, 93%) as a colorless oil. **^{1}H NMR**

(600 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 2H), 7.13 – 7.09 (m, 2H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 134.9, 129.9, 126.0, 125.2, 124.6, 15.7. The spectroscopic data were according to the literature report.



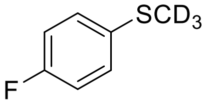
2c-*d*$_3$: (2-chlorophenyl)(methyl-*d*$_3$)sulfane[9].

2c-*d*$_3$ was synthesized according to the **General procedure A** With **1c** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2c-*d*$_3$** (29.1 mg, 91%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 1H), 7.12 – 7.08 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 134.9, 129.9, 126.0, 125.1, 124.6. The spectroscopic data were according to the literature report.



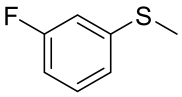
2d: (4-fluorophenyl)(methyl)sulfane[10]

2d was synthesized according to the **General procedure A** With **1d** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2d** (25.6 mg, 90%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.24 (m, 2H), 7.01 – 6.98 (m, 1H), 2.47 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245 Hz), 133.5 (d, *J* = 3 Hz), 129.5 (d, *J* = 7 Hz), 116.1 (d, *J* = 22 Hz), 17.3. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.3 The spectroscopic data were according to the literature report.



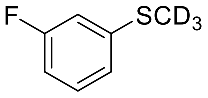
2d-*d*$_3$: (4-fluorophenyl)(methyl-*d*$_3$)sulfane

2d-*d*$_3$ was synthesized according to the **General procedure A** With **1d** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2d-*d*$_3$** (26.8 mg, 91%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.04 – 7.01 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245 Hz), 133.4 (d, *J* = 2 Hz), 129.5 (d, *J* = 7 Hz), 116.2 (d, *J* = 22 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.4. **HRMS** m/z (ESI): calcd. for $C_7H_4D_3FS$ $[M+H]^+$: 146.0514, found: 146.0512.



2e: (3-fluorophenyl)(methyl)sulfane[11]

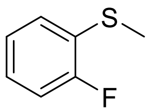
2e was synthesized according to the **General procedure A** With **1e** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2e** (21.6 mg, 76%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.9 (d, *J* = 9.7 Hz, 1H), 6.8 (t, *J* = 8.3 Hz, 1H), 2.48 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4 (d, *J* = 247 Hz), 141.21 (d, *J* = 7 Hz), 130.2 (d, *J* = 9 Hz), 121.9 (d, *J* = 3 Hz), 113.2 (d, *J* = 24 Hz), 111.9 (d, *J* = 21 Hz), 15.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -112.6. The spectroscopic data were according to the literature report.



2e-*d*$_3$: (3-fluorophenyl)(methyl-*d*$_3$)sulfane

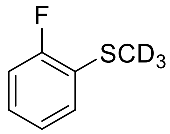
2e-*d*$_3$ was synthesized according to the **General procedure A** With **1e** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD

(16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2e-*d*₃** (24.4 mg, 83%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.04 – 7.02 (m, 1H), 6.98 – 6.94 (m, 1H), 6.86 – 6.81 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4 (d, J = 166 Hz), 141.2 (d, J = 5 Hz), 130.2 (d, J = 6 Hz), 122.0 (d, J = 2 Hz), 113.2 (d, J = 16 Hz), 112.0 (d, J = 14 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -112.6. **HRMS** m/z (ESI): calcd. for $C_7H_4D_3FS$ $[M+H]^+$: 146.0514, found: 146.0510.



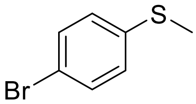
2f: (2-fluorophenyl)(methyl)sulfane[11]

2f was synthesized according to the **General procedure A** With **1f** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2f** (25.3 mg, 89%). as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.19 – 7.01 (m, 3H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, J = 250 Hz), 128.7 (d, J = 3 Hz), 127.0 (d, J = 7 Hz), 125.6 (d, J = 17 Hz), 124.6 (d, J = 3 Hz), 115.4 (d, J = 21 Hz), 15.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.4. The spectroscopic data were according to the literature report.



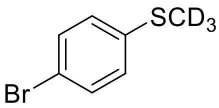
2f-*d*₃: (2-fluorophenyl)(methyl-*d*₃)sulfane

2f-*d*₃ was synthesized according to the **General procedure A** With **1f** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2f-*d*$_3$** (21.2 mg, 72%). as a colorless oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.29 – 7.25 (m, 1H), 7.19 – 7.01 (m, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.4 (d, *J* = 163 Hz), 128.9(d, *J* = 2 Hz), 127.1(d, *J* = 5 Hz), 125.6(d, *J* = 11 Hz), 124.6 (d, *J* = 2 Hz), 115.5(d, *J* = 14 Hz). **^{19}F NMR** (565 MHz, CDCl$_3$) δ -111.4. **HRMS** m/z (ESI): calcd. for $C_7H_4D_3FS$ [M+H]$^+$: 146.0514, found: 146.0514.



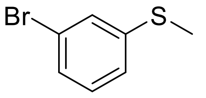
2g: (4-bromophenyl)(methyl)sulfane[11]

2g was synthesized according to the **General procedure A** With **1g** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2g** (34.5 mg, 85%) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 137.9, 131.9, 128.3, 118.8, 16.1. The spectroscopic data were according to the literature report.



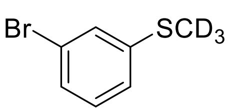
2g-*d*$_3$: (4-bromophenyl)(methyl-*d*$_3$)sulfane[9]

2g-*d*$_3$ was synthesized according to the **General procedure A** With **1g** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2g-*d*$_3$** (32.8 mg, 80%) as a colorless oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 137.8, 131.9, 128.3, 118.7. The spectroscopic data were according to the literature report.



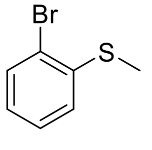
2h: (3-bromophenyl)(methyl)sulfane[11]

2h was synthesized according to the **General procedure A** With **1h** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2h** (37.8 mg, 93%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.27 – 7.24 (m, 1H), 7.18 – 7.13 (m, 2H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 130.2, 128.9, 128.1, 125.2, 123.1, 15.8. The spectroscopic data were according to the literature report.



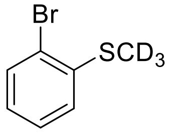
2h-*d*$_3$: (3-bromophenyl)(methyl-*d*$_3$)sulfane

2h-*d*$_3$ was synthesized according to the **General procedure A** With **1h** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2h-*d*$_3$** (34 mg, 83%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.35 (m, 1H), 7.25 – 7.24 (m, 1H), 7.18 – 7.11 (m, 2H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 130.2, 128.8, 128.0, 125.1, 123.0. **HRMS** m/z (ESI): calcd. for $C_7H_4D_3BrS$ [M+H]$^+$: 205.9713, found: 205.9710



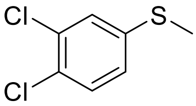
2i: (2-bromophenyl)(methyl)sulfane[12]

2i was synthesized according to the **General procedure A** With **1i** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2i** (36.5 mg, 90%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 132.8, 127.9, 125.8, 125.5, 121.9, 15.9. The spectroscopic data were according to the literature report.



2i-*d*$_3$: (2-bromophenyl)(methyl-*d*$_3$)sulfane[13]

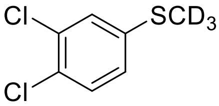
2i-*d*$_3$ was synthesized according to the **General procedure A** With **1i** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2i-*d*$_3$** (40 mg, 98%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.30 (td, *J* = 7.9, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.01 (td, *J* = 7.8, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 132.8, 127.9, 125.8, 125.6, 122.0. The spectroscopic data were according to the literature report.



2j: (3,4-dichlorophenyl)(methyl)sulfane[14]

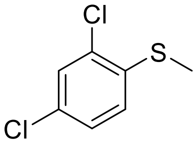
2j was synthesized according to the **General procedure A** With **1j** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2j** (38 mg, 98%) as a white solid. **^{1}H NMR** (600 MHz,

$CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 139.1, 133.0, 130.5, 129.0, 127.8, 125.9, 16.0. The spectroscopic data were according to the literature report.



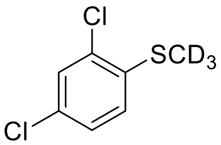
2j-*d*₃:(3,4-dichlorophenyl)(methyl-*d*$_3$)sulfane

2j-*d*₃ was synthesized according to the **General procedure A** With **1j** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2j-*d*₃** (36.1 mg, 92%) as a white solid. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.05 (dd, *J* = 8.5, 2.2 Hz, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 139.0, 133.1, 130.5, 129.0, 127.8, 125.9. **HRMS** m/z (ESI): calcd. for $C_7H_3D_3Cl_2S$ $[M+H]^+$: 195.9828, found: 195.9820.



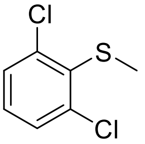
2k: (2,4-dichlorophenyl)(methyl)sulfane

2k was synthesized according to the **General procedure A** With **1k** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2k** (33.5 mg, 87%) as a white solid. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) 136.6, 132.6, 130.8, 129.3, 127.5, 126.6, 15.5. **HRMS** m/z (ESI): calcd. for $C_7H_6Cl_2S$ $[M+H]^+$: 192.9640, found: 192.9644.



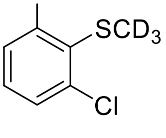
2k-*d*$_3$:(2,4-dichlorophenyl)(methyl-*d*$_3$)sulfane

2k-*d*$_3$ was synthesized according to the **General procedure A** With **1k** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2k-*d*$_3$** (38.4 mg, 98%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.2 Hz, 1H), 7.22 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6, 132.6, 130.8, 129.3, 127.5, 126.6. **HRMS** m/z (ESI): calcd. for $C_{14}H_{12}NO_5$ $[M-H]^-$: 274.0721, found: 274.0722 **HRMS** m/z (ESI): calcd. for $C_7H_3D_3Cl_2S$ $[M+H]^+$: 195.9828, found: 195.9825.



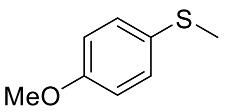
2l: (2,6-dichlorophenyl)(methyl)sulfane

2l was synthesized according to the **General procedure A** With **1l** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2l** (34.7 mg, 90%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 134.7, 129.8, 128.7, 18.4. **HRMS** m/z (ESI): calcd. for $C_7H_6Cl_2S$ $[M+H]^+$: 192.9640, found: 192.9647.



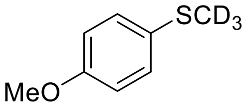
2l-*d*$_3$:(2,6-dichlorophenyl)(methyl-*d*$_3$)sulfane

2l-*d*$_3$ was synthesized according to the **General procedure A** With **1l** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 50:1) on silica gel to give the desired products **2l-*d*$_3$** (38.4 mg, 98%) as a colorless oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.15 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 141.1, 134.6, 129.8, 128.7. **HRMS** m/z (ESI): calcd. for $C_7H_3D_3Cl_2S$ $[M+H]^+$: 195.9828, found: 195.9823.



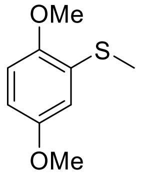
2m: (4-methoxyphenyl)(methyl)sulfane[15]

2m was synthesized according to the **General procedure B** With **1m** (0.2 mmol, 28 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 µL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2m** (24.6 mg, 80%) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 158.3, 130.3, 128.9, 114.7, 55.5, 18.2. The spectroscopic data were according to the literature report.



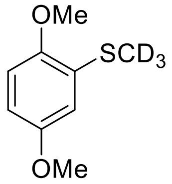
2m-*d*$_3$: (4-methoxyphenyl)(methyl *d*$_3$)sulfane[16]

2m-*d*$_3$ was synthesized according to the **General procedure B** With **1m** (0.2 mmol, 28 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OH (40 µL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2m-*d*$_3$** (20.4 mg, 65%) as a colorless oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 158.3, 130.3, 128.8, 114.8, 55.5. The spectroscopic data were according to the literature report.



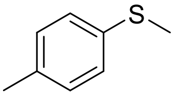
2n: (2,5-dimethoxyphenyl)(methyl)sulfane[17]

2n was synthesized according to the **General procedure B** With **1n** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2n** (22.8 mg, 62%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.76 – 6.74 (m, 2H), 6.65 – 6.63 (m, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 150.7, 128.5, 113.1, 111.1, 109.5, 56.5, 55.8, 14.8. The spectroscopic data were according to the literature report.



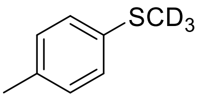
2n-*d*$_3$: (2,5-dimethoxyphenyl)(methyl-*d*$_3$)sulfane

2n-*d*$_3$ was synthesized according to the **General procedure B** With **1n** (0.2 mmol, 34 mg)**, Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2n-*d*$_3$** (22.5 mg, 60%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.76 – 6.73 (m, 2H), 6.65-6.63 (m, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 2.42 (s, 1.92 H, 36% D). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 150.8, 128.5, 113.2, 111.1, 109.5, 56.5, 55.9, 14.8. **HRMS** m/z (ESI): calcd. for $C_9H_9D_3O_2S$ $[M+H]^+$: 188.0819, found: 188.0816.



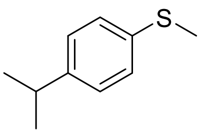
2o: methyl(*p*-tolyl)sulfane[18]

2o was synthesized according to the **General procedure A** With **1o** (0.2 mmol, 25 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2o** (26.5 mg, 96%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.1, 134.8, 129.7, 127.4, 21.0, 16.6. The spectroscopic data were according to the literature report.



2o-*d*₃: (methyl-d_3)(*p*-tolyl)sulfane[19]

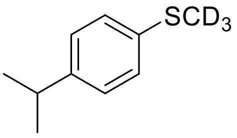
2o-*d*₃ was synthesized according to the **General procedure A** With **1o** (0.2 mmol, 25 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2o-*d*₃** (27.6 mg, 98%) as a Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.2, 134.8, 129.7, 127.4, 21.1. The spectroscopic data were according to the literature report.



2p: (4-isopropylphenyl)(methyl)sulfane[20]

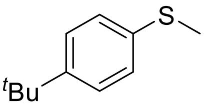
2p was synthesized according to the **General procedure A** With **1p** (0.2 mmol, 31 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2p** (30.5 mg, 92%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.88 (p, *J* = 6.8 Hz, 1H), 2.48 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 146.3, 135.2, 127.4, 127.1, 33.8, 24.1, 16.5. The spectroscopic data were according to the literature report.



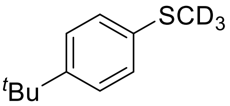
2p-*d*$_3$: (4-isopropylphenyl)(methyl-*d*$_3$)sulfane

2p-*d*$_3$ was synthesized according to the **General procedure A** With **1p** (0.2 mmol**,** 31 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2p-*d*$_3$** (30.5 mg, 90%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 2.87 (p, *J* = 6.8 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 135.1, 127.4, 127.1, 33.8, 24.1. **HRMS** m/z (ESI): calcd. for $C_{10}H_{11}D_3S$ $[M+H]^+$: 170.1077, found: 170.1072.



2q: (4-(tert-butyl)phenyl)(methyl)sulfane[21]

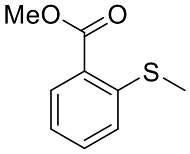
2q was synthesized according to the **General procedure A** With **1q** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2q** (33.2 mg, 92%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.24 – 7.21 (m, 2H), 2.48 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 135.0, 127.1, 126.0, 34.5, 31.4, 16.4. The spectroscopic data were according to the literature report.



2q-*d*$_3$: (4-(tert-butyl)phenyl)(methyl-*d*$_3$)sulfane[16]

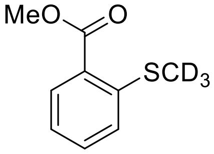
2q-*d*$_3$ was synthesized according to the **General procedure A** With **1q** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%),

CD_3OD (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2q-*d*₃** (35.6 mg, 97%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.23 – 7.21 (m, 2H), 1.31 (s, 9H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 134.9, 127.0, 126.0, 34.5, 31.4. The spectroscopic data were according to the literature report.



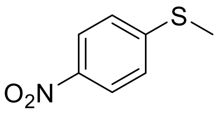
2r: methyl 2-(methylthio)benzoate[22]

2r was synthesized according to the **General procedure A** With **1r** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2r** (30.2 mg, 83%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (td, *J* = 7.8, 1.5 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.17 – 7.13 (m, 1H), 3.92 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 143.4, 132.6, 131.5, 126.9, 124.5, 123.6, 52.2, 15.7. The spectroscopic data were according to the literature report.



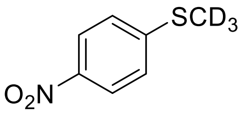
2r-*d*₃: methyl 2-((methyl-*d*₃) thio)benzoate[23]

2r-*d*₃: was synthesized according to the **General procedure A** With **1r** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2r-*d*₃** (25.9 mg, 70%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.99 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 1.44H, 52%D), 2.46 (s, 0.7H, 77%D). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 143.4, 132.6, 131.5, 127.0, 124.5, 123.6, 52.2, 15.7. The spectroscopic data were according to the literature report.



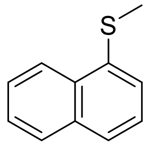
2s: methyl(4-nitrophenyl)sulfane[7]

2s was synthesized according to the **General procedure A** With **1s** (0.2 mmol, 32 mg), **Cat.1** (5.5 mg, 10 mol%), ZnI_2 (6.4 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2s** (28.7 mg, 74%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 144.9, 125.2, 124.1, 15.0. The spectroscopic data were according to the literature report.



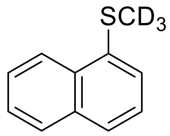
2s-*d*$_3$: (methyl-d_3) (4-nitrophenyl)sulfane[24]

2s-*d*$_3$: was synthesized according to the **General procedure A** With **1s** (0.2 mmol, 32 mg)**,** **Cat.1** (5.5 mg, 10 mol%), ZnI_2 (6.4 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2s-*d*$_3$** (31.5 mg, 80%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 144.9, 125.2, 124.1. The spectroscopic data were according to the literature report.



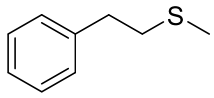
2t: methyl(naphthalen-1-yl)sulfane[21]

2t was synthesized according to the **General procedure A** With **1t** (0.2 mmol, 32 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2t** (30.4 mg, 87%). as a colorless oil. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 3H), 7.60 – 7.62 (m, 1H), 7.49 – 7.37 (m, 3H), 2.59 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 136.2, 134.0, 131.5, 128.3, 127.9, 127.0, 126.7, 125.8, 125.4, 123.6, 16.0. The spectroscopic data were according to the literature report.



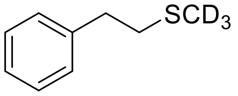
2t-*d*$_3$: (methyl- d_3)(naphthalen-1-yl)sulfane[16]

2t-*d*$_3$: was synthesized according to the **General procedure A** With **1t** (0.2 mmol, 32 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2t-*d*$_3$** (34.8 mg, 98%) as a colorless oil. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 3H), 7.60 – 7.62 (m, 1H), 7.46 – 7.37 (m, 3H), ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 136.2, 134.1, 131.4, 128.3, 127.9, 127.0, 126.7, 125.9, 125.4, 123.5 The spectroscopic data were according to the literature report.



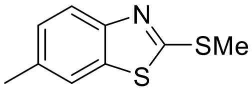
2u: methyl(phenethyl)sulfane[25]

2u was synthesized according to the **General procedure A** With **1u** (0.2 mmol, 28 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2u** (25.6 mg, 84%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.23 – 7.21 (m, 3H), 2.92 – 2.88 (m, 2H), 2.78 – 2.75 (m, 2H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.7, 128.6, 128.6, 126.5, 36.1, 36.0, 15.9. The spectroscopic data were according to the literature report.



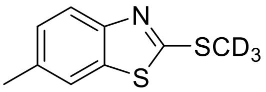
2u-*d*$_3$: (methyl- d_3)(phenethyl)sulfane[16]

2u-*d*$_3$ was synthesized according to the **General procedure A** With **1u** (0.2 mmol, 28 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2u-*d*$_3$** (22.1 mg, 71%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 2H), 7.22 – 7.21 (m, 3H), 2.91 – 2.89 (m, 2H), 2.77 – 2.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.7, 128.6, 128.6, 126.5, 36.1, 35.8. The spectroscopic data were according to the literature report.



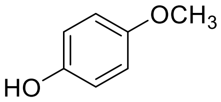
2v: 6-methyl-2-(methylthio)benzo[d]thiazole

2v was synthesized according to the **General procedure A** With **1v** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10: 1) on silica gel to give the desired products **2v** (20.3 mg, 52%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.55 (s, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 2.78 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 151.4, 135.3, 134.4, 127.7, 121.0, 121.0, 21.5, 16.2. **HRMS** m/z (ESI): calcd. for $C_9H_9NS_2$ $[M+H]^+$: 196.0249, found: 196.0249.



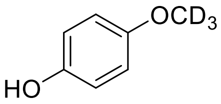
2v-*d*$_3$: 6-methyl-2-((methyl-*d*$_3$)thio)benzo[d]thiazole

2v-*d*$_3$ was synthesized according to the **General procedure A** With **1v** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OD (16 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10: 1) on silica gel to give the desired products **2v-*d*$_3$** (19.9 mg, 50%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.55 (s, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 151.6, 135.4, 134.3, 127.6, 121.0, 121.0, 21.5. **HRMS** m/z (ESI): calcd. for $C_9H_6D_3NS_2$ $[M+H]^+$: 199.0437, found: 199.0433.



2w: 4-methoxyphenol[26]

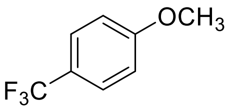
2w was synthesized according to the **General procedure B** With **1w** (2 mmol, 220 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CH_3OH (400 µL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM=5:1) on silica gel to give the desired products **2w** (156 mg, 63%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.80 – 6.77 (m, 4H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.7, 149.6, 116.2, 115.1, 56.0. The spectroscopic data were according to the literature report.



2w-*d*$_3$: 4-(methoxy-*d*$_3$)phenol

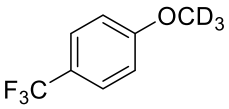
2w-*d*$_3$ was synthesized according to the **General procedure B** With **1w** (2 mmol**,** 220 mg)**, Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CD_3OH (400 µL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at

150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM=5:1) on silica gel to give the desired products **2w-d_3** (153 mg, 60%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 – 6.75 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8, 149.6, 116.2, 115.0. **HRMS** m/z (ESI): calcd. for $C_7H_5D_3O_2$ [M-H]$^-$: 126.0640, found: 126.0643



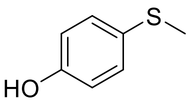
2x: 1-methoxy-4-(trifluoromethyl)benzene[27]

2x was synthesized according to the **General procedure A** With **1x** (0.2 mmol, 32.4 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 5:1) on silica gel to give the desired products **2x** (22 mg, 62%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H). The spectroscopic data were according to the literature report.



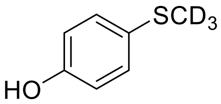
2x-d_3: 1-(methoxy-d_3)-4-(trifluoromethyl)benzene

2x-d_3 was synthesized according to the **General procedure A** With **1x** (0.2 mmol, 32.4 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CD_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 5:1) on silica gel to give the desired products **2x-d_3** (23.3 mg, 65%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 160.0, 132.1, 122.8, 115.4. **HRMS** m/z (ESI): calcd. for $C_{14}H_{12}NO_5$ [M+H]$^+$: 180.0710, found: 180.0711.



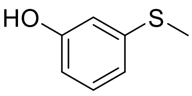
2y: 4-(methylthio)phenol[26]

2y was synthesized according to the **General procedure B** With **1y** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CH_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2y** (236 mg, 84%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 130.6, 129.1, 116.2, 18.2. The spectroscopic data were according to the literature report.



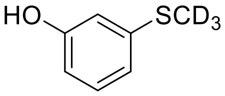
2y-*d*$_3$: 4-((methyl-d_3)thio)phenol

2y-*d*$_3$ was synthesized according to the **General procedure B** With **1y** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CD_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2y-*d*$_3$** (258 mg, 90%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 130.5, 129.0, 116.2. **HRMS** m/z (ESI): calcd. for $C_7H_5D_3OS$ $[M-H]^-$: 142.0411, found: 142.0415



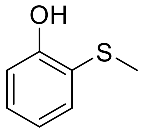
2z: 3-(methylthio)phenol[28]

2z was synthesized according to the **General procedure B** With **1z** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CH_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2z** (230 mg, 82%) as a colorless oil. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 2.0 Hz, 1H), 6.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.46 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.3, 130.0, 119.0, 113.3, 112.2, 15.7. The spectroscopic data were according to the literature report.



2z-*d*₃: 3-((methyl-d_3)thio)phenol

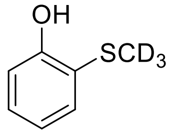
2z-*d*₃ was synthesized according to the **General procedure B** With **1z** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CD_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2z-*d*₃** (255 mg, 89%) as a colorless oil. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 6.7 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.74 (s, 1H), 6.61 (d, *J* = 7.6 Hz, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.2, 130.0, 119.0, 113.3, 112.2. **HRMS** m/z (ESI): calcd. for $C_7H_5D_3OS$ $[M-H]^-$: 142.0411, found: 142.0413



2aa: 2-(methylthio)phenol[29]

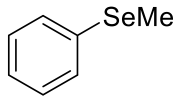
2aa was synthesized according to the **General procedure B** With **1aa** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CH_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2aa** (249 mg, 89%) as a colorless oil. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.9 (t, *J* = 7.5 Hz, 1H), 2.34 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ

156.5, 135.0, 130.9, 121.1, 115.0, 20.0. The spectroscopic data were according to the literature report.



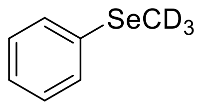
2aa-*d*$_3$: 2-((methyl-*d*$_3$)thio)phenol

2aa-*d*$_3$ was synthesized according to the **General procedure B** With **1aa** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), CD_3OH (400 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 5:1) on silica gel to give the desired products **2aa-*d*$_3$** (249 mg, 87%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.228 – 7.24 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.72 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 134.7, 130.7, 121.0, 114.9. **HRMS** m/z (ESI): calcd. for $C_7H_5D_3OS$ $[M-H]^-$: 142.0411, found: 142.0411.



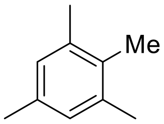
2bb: methyl(phenyl)selane

2bb was synthesized according to the **General procedure A** With **1bb** (0.2 mmol, 252 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), and CH_2Br_2 as an internal standard Subsequently, take sample 1-2 drops to check yield by NMR (NMR yield by 92%).



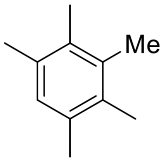
2bb-*d*$_3$: (methyl-*d*$_3$)(phenyl)selane

2bb-*d*$_3$ was synthesized according to the **General procedure B** With **1bb** (0.2 mmol, 252 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), CD_3OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), and CH_2Br_2 as an internal standard Subsequently, take sample 1-2 drops to check yield by NMR (NMR yield by 87%).



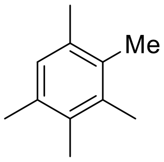
2cc: 1,2,3,5-tetramethylbenzene

2cc was synthesized according to the **General procedure C** With **1cc** (1 mmol, 120.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH_3OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K_2CO_3 (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 87%).



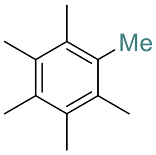
2dd: 1,2,3,4,5-pentamethylbenzene

2dd was synthesized according to the **General procedure C** With **1dd** (1 mmol, 134.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH_3OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K_2CO_3 (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 98%).



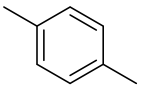
2ee: 1,2,3,4,5-pentamethylbenzene

2ee was synthesized according to the **General procedure C** With **1ee** (1 mmol, 134.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH_3OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K_2CO_3 (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 98%).



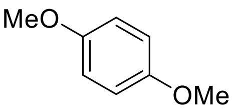
2ff: 1,2,3,4,5,6-hexamethylbenzene

2ff was synthesized according to the **General procedure C** With **1ff** (1 mmol, 148.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH_3OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K_2CO_3 (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 98%).



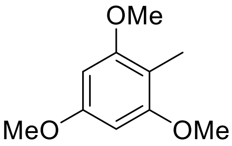
2gg: 1,2,4-trimethylbenzene

2gg was synthesized according to the **General procedure C** With **1gg** (1 mmol, 106.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH$_3$OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K$_2$CO$_3$ (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 30%).



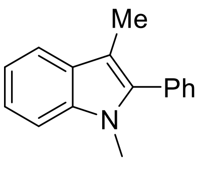
2hh: 1,4-dimethoxy-2-methylbenzene

2hh was synthesized according to the **General procedure C** With **1hh** (1 mmol, 138.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH$_3$OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K$_2$CO$_3$ (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 30%).



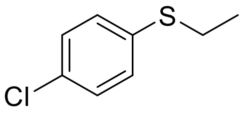
2ii: 1,4-dimethoxy-2-methylbenzene

2ii was synthesized according to the **General procedure C** With **1ii** (1 mmol, 168.2 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH$_3$OH (8 μL, 1.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 48 h then quenched by adding K$_2$CO$_3$ (20 mol%), and dodecane as an internal standard Subsequently, take sample 1-2 drops to check yield by GC (GC yield by 82%).



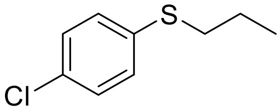
2jj: 1,3-dimethyl-2-phenyl-1H-indole[30]

2jj was synthesized according to the **General procedure A** With **1jj** (0.2 mmol, 41.5 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), CH$_3$OH (16 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **2aa** (35.5 mg, 80%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.43 – 7.40 (m, 3H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 3.62 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 138.3, 132.8, 129.3, 128.5, 127.9, 127.8, 121.6, 120.4, 119.8, 109.6, 101.6, 31.1 The spectroscopic data were according to the literature report.



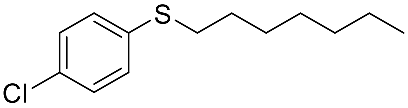
2kk: (4-chlorophenyl)(ethyl)sulfane[31]

2kk was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), alcohol (24 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2kk** (33.2 mg, 96%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 2.93 (q, *J* = 7.4 Hz, 2H), 1.30 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.3, 131.9, 130.5, 129.1, 28.0, 14.4. The spectroscopic data were according to the literature report.



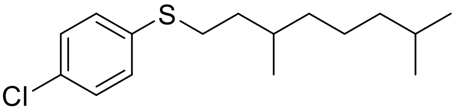
2ll: (4-chlorophenyl)(propyl)sulfane[32]

2ll was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), alcohol (30 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2ll** (36.2 mg, 97%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.65 (q, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.6, 131.8, 130.4, 129.1, 36.0, 22.5, 13.5. The spectroscopic data were according to the literature report.



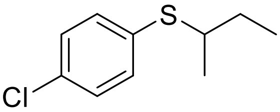
2mm: (4-chlorophenyl)(heptyl)sulfane

2mm was synthesized according to the **general procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), alcohol (57 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2mm** (47.1 mg, 97%) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.24 (s, 4H), 2.88 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.42 – 1.38 (m, 2H), 1.30 – 1.26 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 135.7, 131.7, 130.3, 129.1, 34.0, 31.8, 29.2, 29.0, 28.9, 22.7, 14.2. **HRMS** m/z (ESI): calcd. for C$_{13}$H$_{19}$ClS [M+H]$^+$: 243.0969, found: 243.0967.



2nn: (4-chlorophenyl)(3,7-dimethyloctyl)sulfane

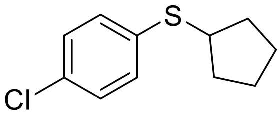
2nn: was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), alcohol (76 µL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2nn** (45 mg, 79%) as a white solid. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.24 (s, 4H), 2.96 – 2.84 (m, 2H), 1.65 – 1.61 (m, 1H), 1.52 – 1.42 (m, 2H), 1.31 – 1.19 (m, 4H), 1.15 – 1.12 (m, 3H), 0.9 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 135.7, 131.7, 130.3, 129.1, 39.3, 37.0, 36.3, 32.3, 31.9, 28.1, 24.8, 22.8, 22.7, 19.5. **HRMS** m/z (ESI): calcd. for C$_{16}$H$_{26}$ClS[M+H]$^+$: 285.1438, found: 285.1435.



2oo: *sec*-butyl(4-chlorophenyl)sulfane

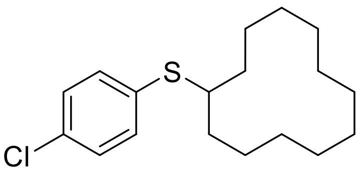
2oo was synthesized according to the **General procedure A**

With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), alcohol (37 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2oo** (36.1 mg, 90%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.31 (m, 2H), 7.26 – 7.25 (m, 2H), 3.12 (p, *J* = 6.5 Hz, 1H), 1.66 – 1.50 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.2, 133.4, 132.8, 129.0, 45.4, 29.5, 20.6, 11.6. **HRMS** m/z (ESI): calcd. for $C_{10}H_{14}ClS[M+H]^+$: 201.0499, found: 201.0497.



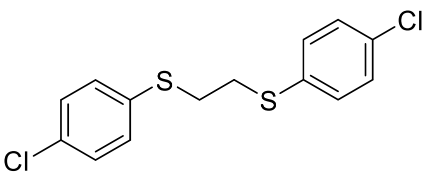
2pp: (4-chlorophenyl)(cyclopentyl)sulfane[33]

2pp was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), alcohol (37 μL, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2pp** (37 mg, 87%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 3.60 – 3.55 (p, *J* = 7.4, 6.8 Hz, 1H), 2.17 – 2.04 (m, 2H), 1.84 – 1.76 (m, 2H), 1.68 – 1.60 (m, 2H), 1.33 – 1.28 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 132.1, 131.5, 129.0, 46.4, 33.6, 24.9.



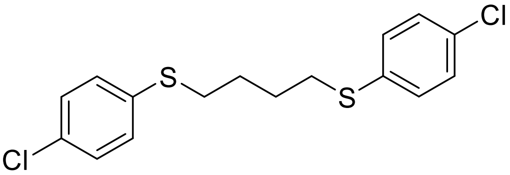
2qq: (4-chlorophenyl)(cyclododecyl)sulfane[34]

2qq was synthesized according to the **General procedure A** With **1a** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), alcohol (74 mg, 2.0 equiv.) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2qq** (47.3 mg, 76%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 3.26 – 3.19 (m, 1H), 1.76 – 1.66 (m, 2H), 1.60 – 1.49 (m, 4H), 1.47 – 1.31 (m, 16H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.7, 132.8, 132.6, 129.1, 45.4, 30.0, 24.3, 24.0, 23.5, 23.5, 22.3.



2rr: 1,2-bis((4-chlorophenyl)thio)ethane[35]

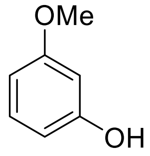
2rr was synthesized according to the **General procedure A** With **1a** (0.6 mmol, 87 mg), **Cat.1** (11 mg, 10 mol%), $Zn(OTf)_2$ (14.4 mg, 10 mol%), alcohol (12 µL, 0.2 mmol) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2rr** (49 mg, 77%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 8H), 3.03 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.6, 133.0, 131.7, 129.4, 33.8.



2ss: 1,2-bis((4-chlorophenyl)thio)ethane

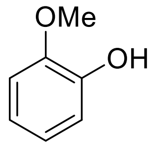
2ss was synthesized according to the **General procedure A** With **1a** (0.6 mmol, 87 mg), **Cat.1** (11 mg, 10 mol%), $Zn(OTf)_2$ (14.4 mg, 10 mol%), alcohol (18 µL, 0.2 mmol) and HFIP (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **2ss** (55.4 mg, 81%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 8H), 2.92 (s, 4H), 1.78 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.0, 132.1, 130.8, 129.2, 33.6, 28.0. **HRMS**

m/z (ESI): calcd. for $C_{10}H_{14}ClS[M+H]^+$: 343.0143, found: 343.0140.



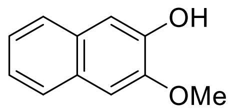
4b: 3-methoxyphenol[29]

4b was synthesized according to the **General procedure B** With **3b** (0.2 mmol, 22 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4b** (21 mg, 85%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.2 Hz, 1H), 6.56 – 6.54 (m, 1H), 6.51 – 6.47 (m, 2H), 3.80 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.8, 156.8, 130.3, 108.1, 106.6, 101.7, 55.4. The spectroscopic data were according to the literature report.



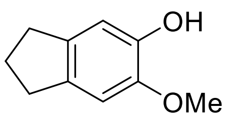
4c: 2-methoxyphenol[36]

4c was synthesized according to the **General procedure B** With **3c** (0.2 mmol, 22 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4c** (20 mg, 80%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.03 – 7.01 (m, 1H), 6.95 – 6.92 (m, 3H), 5.85 (s, 1H), 3.92 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.7, 145.7, 121.5, 120.2, 114.7, 110.9, 55.9. The spectroscopic data were according to the literature report.



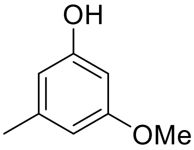
4d: 3-methoxynaphthalen-2-ol[37]

4d was synthesized according to the **General procedure B** With **3d** (0.2 mmol, 32 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4d** (24.7 mg, 71%). as a yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (td, *J* = 8.2, 6.8, 4.8 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.26 (m, 1H), 7.13 (s, 1H), 4.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 145.8, 129.8, 129.1, 126.6, 126.5, 124.4, 124.0, 109.5, 105.8, 56.0. The spectroscopic data were according to the literature report.



4e: 6-methoxy-2,3-dihydro-1H-inden-5-ol[38]

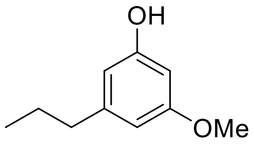
4e was synthesized according to the **General procedure B** With **3e** (0.2 mmol, 30 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4e** (15.5 mg, 47%) (61% yield by nmr) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.75 (s, 1H), 3.86 (s, 3H), 2.83 (q, *J* = 7.6 Hz, 4H), 2.05 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 145.8, 129.8, 129.1, 126.6, 126.5, 124.4, 124.0, 109.5, 105.8, 56.0. The spectroscopic data were according to the literature report.



4f: 3-methoxy-5-methylphenol[39]

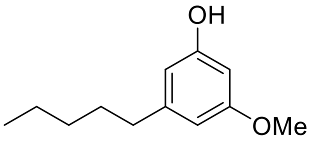
4f was synthesized according to the **General procedure B** With **3f** (0.2 mmol**,** 25 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4f** (21 mg, 76%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.32 (s, 1H), 6.26 (s, 1H), 6.23 (s, 1H), 3.76

(s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 156.7, 140.7, 108.7, 107.5, 98.7, 55.4, 21.7. The spectroscopic data were according to the literature report.



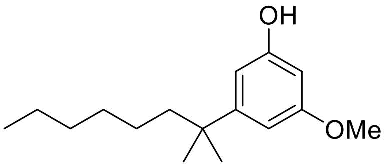
4g: 3-methoxy-5-propylphenol

4g was synthesized according to the **General procedure B** With **3g** (0.2 mmol, 31 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4g** (28.3 mg, 85%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 6.29 (s, 1H), 6.26 (t, *J* = 2.2 Hz, 1H), 3.79 (s, 3H), 2.52 (t, *J* = 7.3 Hz, 2H), 1.68 – 1.59 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 156.6, 145.7, 108.1, 107.0, 98.8, 55.4, 38.3, 24.4, 14.0. **HRMS** m/z (ESI): calcd. for $C_{10}H_4O_2$ $[M-H]^-$: 165.0921, found: 165.0925



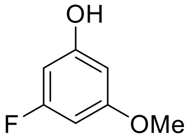
4h: 3-methoxy-5-pentylphenol[40]

4h was synthesized according to the **General procedure B** With **3h** (0.2 mmol, 36 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4h** (32.2 mg, 83%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 6.26 (s, 1H), 6.23 (t, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 2.51 (t, *J* = 6.7 Hz, 2H), 1.32 – 1.25 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 156.6, 145.9, 108.0, 106.9, 98.8, 55.4, 36.2, 31.6, 31.0, 22.7, 14.2. The spectroscopic data were according to the literature report.



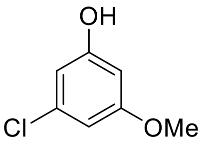
4i: 3-methoxy-5-(2-methyloctan-2-yl)phenol[41]

4i was synthesized according to the **General procedure B** With **3i** (0.2 mmol, 47.3 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4i** (41 mg, 82%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.47 (s, 1H), 6.40 (s, 1H), 6.24 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 1.55 – 1.52 (m, 2H), 1.23 (s, 6H), 1.21 – 1.17 (m, 6H), 1.01 – 1.01 (m, 2H), 0.84 (t, *J* = 7.1 Hz, 3H) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 156.4, 153.2, 105.8, 105.3, 98.0, 55.3, 44.6, 38.0, 31.9, 30.2, 29.0, 24.8, 22.8, 14.2. The spectroscopic data were according to the literature report.



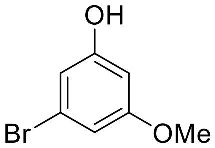
4j: 5-fluorobenzene-1,3-diol[42]

4j was synthesized according to the **General procedure B** With **3j** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4j** (10 mg, 36%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.22 (dt, *J* = 10.7, 2.2 Hz, 1H), 6.19 – 6.17 (m, 2H), 3.76 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.1(d, *J* = 242 Hz), 161.8(d, *J* = 15.1 Hz), 157.6 (d, *J* = 13.6 Hz), 97.7(d, *J* = 3 Hz), 96.1(d, *J* = 25.7 Hz), 94.6(d, *J* = 25.7 Hz), 55.7. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.0 The spectroscopic data were according to the literature report.



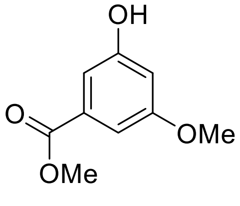
4k: 3-chloro-5-methoxyphenol[42]

4k was synthesized according to the **General procedure B** With **3k** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4k** (26.6 mg, 84%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 6.46 (s, 1H), 6.29 (t, *J* = 2.1 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 157.2, 135.4, 108.7, 107.2, 100.5, 55.7. The spectroscopic data were according to the literature report.



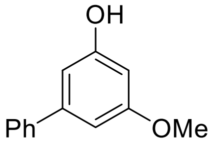
4l: 3-bromo-5-methoxyphenol[43]

4l was synthesized according to the **General procedure B** With **3l** (0.2 mmol, 38 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give the desired products **4l** (38.6 mg, 95%) as a yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.65 (s, 1H), 6.61 (s, 1H), 6.33 (t, *J* = 2.1 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 157.3, 123.1, 111.6, 110.1, 101.0, 55.7. The spectroscopic data were according to the literature report.



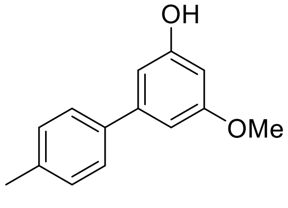
4m: methyl 3-hydroxy-5-methoxybenzoate[43]

4m was synthesized according to the **general procedure B** With **3m** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 5:1) on silica gel to give the desired products **4m** (18.2 mg, 50%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.14 (m, 2H), 6.62 (t, *J* = 2.3 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.1, 161.0, 156.9, 132.2, 109.4, 107.2, 106.8, 55.7, 52.5. The spectroscopic data were according to the literature report.



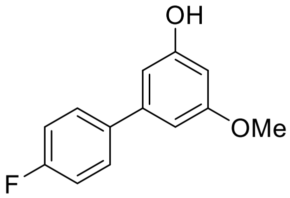
4n: 5-methoxy-[1,1'-biphenyl]-3-ol[44]

4n was synthesized according to the **General procedure B** With **3n** (0.2 mmol, 37 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4n** (25.2 mg, 63%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.73 (m, 1H), 6.67 – 6.66 (m, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3, 157.1, 143.9, 140.9, 128.9, 127.8, 127.2, 107.0, 105.8, 100.5, 55.6. The spectroscopic data were according to the literature report.



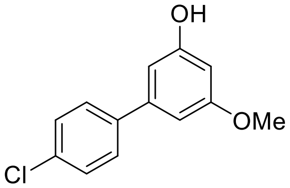
4o: 5-methoxy-4'-methyl-[1,1'-biphenyl]-3-ol

4o was synthesized according to the **General procedure B** With **3o** (0.2 mmol, 40 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4o** (30 mg, 70%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.71 – 6.70 (m, 1H), 6.65 – 6.64 (m, 1H), 6.39 (t, *J* = 2.2 Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3, 157.0, 143.8, 138.0, 137.6, 129.6, 127.1, 106.8, 105.6, 100.2, 55.6, 21.3. **HRMS** m/z (ESI): calcd. for $C_{14}H_{14}O_2$ $[M-H]^-$: 213.0921, found: 213.0924



4p: 4'-fluoro-5-methoxy-[1,1'-biphenyl]-3-ol

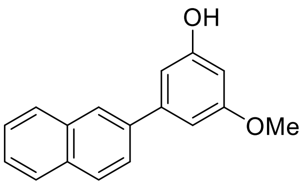
4p was synthesized according to the **General procedure B** With **3p** (0.2 mmol, 41 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4p** (33.6 mg, 77%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 6.67 – 6.65 (m, 1H), 6.61 – 6.60 (m, 1H), 6.41 (t, *J* = 2.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0(d, *J* = 247.5 Hz), 161.4(d, *J* = 428.2 Hz), 142.9, 137.0 (d, *J* = 3.03 Hz),128.8 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 21.2 Hz), 106.9, 105.8, 100.4, 55.6. **HRMS** m/z (ESI): calcd. for $C_{13}H_{11}FO_2$ $[M-H]^-$: 217.0670, found: 217.0677



4q: 4'-chloro-5-methoxy-[1,1'-biphenyl]-3-ol

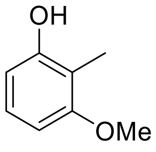
4q was synthesized according to the **General procedure B** With **3q** (0.2 mmol, 45 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4q** (22.1 mg, 47%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.66 – 6.67 (m, 1H), 6.61 – 6.62 (m, 1H), 6.41

(t, *J* = 2.2 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 157.2, 142.6, 139.4, 133.8, 129.0, 128.5, 106.8, 105.8, 100.7, 55.6. **HRMS** m/z (ESI): calcd. for $C_{13}H_{11}ClO_2$ $[M-H]^-$: 233.0375, found: 233.0375



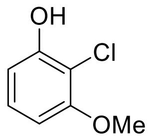
4r: 3-methoxy-5-(naphthalen-2-yl)phenol

4r was synthesized according to the **General procedure B** With **3r** (0.2 mmol, 48 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (16 μL, 2.0 equiv.) and Hexane (0.5 mL, 0.4M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4r** (41 mg, 82%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.90 – 7.86 (m, 3H), 7.71 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 6.86 – 6.85 (m, 1H), 6.80 – 6.79 (m, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 157.1, 143.8, 138.2, 133.7, 132.9, 128.5, 128.4, 127.8, 126.5, 126.2, 126.0, 125.6, 107.3, 106.1, 100.6, 55.6. **HRMS** m/z (ESI): calcd. for $C_{17}H_{14}O_2$ $[M-H]^-$: 249.0921, found: 249.0920



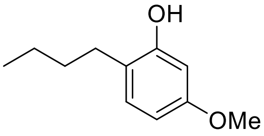
4s: 3-methoxy-2-methylphenol[45]

4s was synthesized according to the **General procedure B** With **3s** (0.2 mmol, 25 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4s** (12.7 mg, 46%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.2 Hz, 1H), 6.47 (dd, *J* = 13.4, 8.2 Hz, 2H), 3.82 (s, 3H), 2.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 154.6, 126.6, 112.2, 108.2, 103.2, 55.8, 8.1. The spectroscopic data were according to the literature report.



4t: 2-chloro-3-methoxyphenol

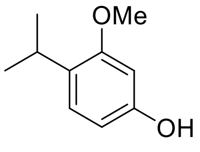
4t was synthesized according to the **General procedure B** With **3t** (0.2 mmol, 29 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4t** (14 mg, 44%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.3 Hz, 1H), 6.68 (d, *J* = 9.3 Hz, 1H), 6.52 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 152.7, 127.8, 108.7, 103.9, 56.5. **HRMS** m/z (ESI): calcd. for $C_7H_7ClO_2$ [M-H]$^-$: 157.0062, found: 257.0067



4u:4u' = 1.7:1

4u: 2-butyl-5-methoxyphenol

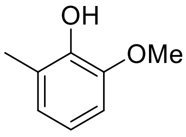
4u was synthesized according to the **General procedure B** With **3u** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4u** (32.1 mg, 89%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.3 Hz, 1H), 6.44 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.39 – 6.37 (m, 1H), 3.78 (s, 1H), 3.76 (s, 3H), 2.53 (q, *J* = 7.0, 6.5 Hz, 3H), 1.60 – 1.47 (m, 3H), 1.42 – 1.23 (m, 3H), 0.95 – 0.88 (t, *J* = 7.2 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 158.5, 154.8, 154.3, 130.6, 130.2, 123.7, 120.9, 106.5, 106.0, 101.8, 98.9, 55.4, 55.4, 32.4, 32.3, 29.3, 29.1, 22.7, 22.7, 14.2, 14.1. **HRMS** m/z (ESI): calcd. for $C_{11}H_{16}O_2$ [M-H]$^-$: 179.1078, found:179.1077



4v:4v' = 1.5:1

4v: 2-isopropyl-5-methoxyphenol[46]

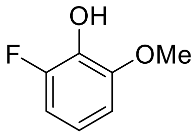
4v was synthesized according to the **General procedure B** With **3v** (0.2 mmol, 30.4 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4v** (27.2 mg, 82%) as a yellow oli. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.11 (d, *J* = 8.4 Hz, 1H), 6.51 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 3.78 (s, 0.59H), 3.77 (s, 3H), 3.25 – 3.12 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 1H) **^{13}C NMR** (151 MHz, CDCl$_3$) δ 158.4, 157.9, 154.6, 153.7, 127.2, 127.2, 127.0, 126.6, 106.8, 106.0, 101.9, 99.1, 58.8, 55.4, 26.6, 26.3, 23.0, 22.9. The spectroscopic data were according to the literature report.



4w:4w' =3:1

4w: 2-methoxy-6-methylphenol

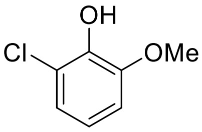
4w was synthesized according to the **General procedure B** With **3w** (0.2 mmol, 25 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4w** (18 mg, 65%) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 6.76 – 6.71 (m, 3H), 3.88 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 146.4, 143.9, 124.1, 123.3, 119.3, 108.4, 56.1, 15.5. **HRMS** m/z (ESI): calcd. for $C_8H_{10}O_2$ [M-H]$^-$: 137.0608, found: 137.0607



4x:4x' =3:1

4x: 2-fluoro-6-methoxyphenol[47, 48]

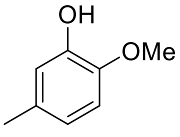
4x was synthesized according to the **General procedure B** With **3x** (0.2 mmol, 26 mg), **Cat.1** (16.5 mg, 10 mol%), Zn(OTf)$_2$ (21.6 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4x** (15 mg, 49%), (67% yield by nmr) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 6.80 – 6.72 (m, 2.42H), 6.68 – 6.61 (m, 1.45H), 4.0 (s, 1H), 3.91 (s, 3H). The spectroscopic data were according to the literature report.



4y:4y' =6.7:1

4y: 2-chloro-6-methoxyphenol[48]

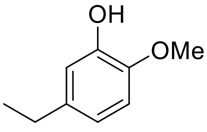
4y was synthesized according to the **General procedure B** With **3y** (0.2 mmol, 29 mg), **Cat.1** (16.5 mg, 10 mol%), Zn(OTf)$_2$ (21.6 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4y** (20 mg, 63%) as a colorless oil. **^{1}H NMR** (600 MHz, CDCl$_3$) δ 6.98 (dd, J = 7.3, 2.4 Hz, 1H), 6.84 – 6.80 (m, 2H), 3.96 (s, 0.45H), 3.93 (s, 3H). The spectroscopic data were according to the literature report.



4z:4z' =1.2:1

4z: 2-methoxy-5-methylphenol[49]

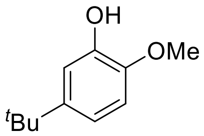
4z was synthesized according to the **General procedure B** With **3z** (0.2 mmol, 25 mg), **Cat.1** (5.5 mg, 10 mol%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K$_2$CO$_3$ (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4z** (20.5 mg, 74%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (d, *J* = 7.8 Hz, 0.81H), 6.76 – 6.72 (m, 2H), 6.68 – 6.63 (m, 2.67H), 3.87 (s, 2.45H), 3.86 (s, 3H), 2.29 (s, 2.49H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 145.5, 144.6, 143.5, 131.3, 129.8, 121.6, 120.4, 115.5, 114.2, 111.8, 110.8, 56.2, 56.0, 21.2, 20.9. The spectroscopic data were according to the literature report.



4aa:4aa' =1.3:1

4aa: 5-ethyl-2-methoxyphenol[50]

4aa was synthesized according to the **General procedure B** With **3aa** (0.2 mmol, 28 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4aa** (20.4 mg, 67%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89– 6.84 (m, 1.15H), 6.81 – 6.77 (m, 1.65H), 6.72 – 6.67 (m, 2.58H), 3.89 (s, 3H), 3.87 (s, 2.58H), 2.63 – 2.54 (m, 3.71H), 1.25 – 1.20 (m, 5.54H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.5, 145.5, 144.7, 143.6, 137.8, 136.4, 120.4, 119.1, 114.3, 110.8, 110.6, 56.1, 56.0, 28.7, 28.4, 16.1, 15.9. The spectroscopic data were according to the literature report.

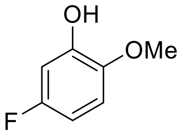


4bb:4bb' =1.4:1

4bb: 5-(tert-butyl)-2-methoxyphenol[51]

4bb was synthesized according to the **General procedure B** With **3bb** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products

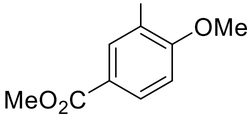
4bb (17 mg, 47%) as a colorless oil. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.00 – 6.99 (m, 0.95H), 6.90 – 6.84 (m, 3.02H), 6.80 – 6.78 (m 1H), 3.9 (s, 2.15H), 3.87 (s, 3H), 1.31 (s, 6.42H), 1.29 (s, 9H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 146.1, 145.2, 144.9, 144.4, 143.5, 143.4, 118.0, 116.6, 113.9, 112.3, 110.3, 108.4, 56.1, 56.0, 34.6, 34.4, 31.7, 31.6. The spectroscopic data were according to the literature report.



4cc:4cc' =2.4:1

4cc: 5-fluoro-2-methoxyphenol[42,52]

4cc was synthesized according to the **General procedure B** With **3cc** (0.2 mmol, 26 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **4cc** (14 mg, 50%), (63% yield by nmr) as a colorless oil. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.85 – 6.82 (m, 0.45H), 6.78 – 6.74 (m, 1.04H), 6.70 – 6.66 (m, 0.97H), 6.64 – 6.51 (m, 1.93H), 3.88 (s, 1.34H), 3.87 (s, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 158.5 (d, J = 237.1 Hz), 157.6 (d, J = 237.1 Hz), 147.0 (d, J = 10.6 Hz), 146.6 (d, J = 12.1 Hz), 143.1(d, J = 3 Hz), 141.8(d, J = 3 Hz), 114.4 (d, J = 9.1 Hz), 111.0 (d, J = 9.1 Hz), 107.0 (d, J =22.7 Hz), 105.8 (d, J = 22.7 Hz), 103.0 (d, J = 27.2 Hz), 99.5 (d, J = 27.2 Hz), 56.6, 56.2. ^{19}**F NMR** (565 MHz, $CDCl_3$) δ -121.3, -121.9. The procedure and spectroscopic data were according to the literature report.



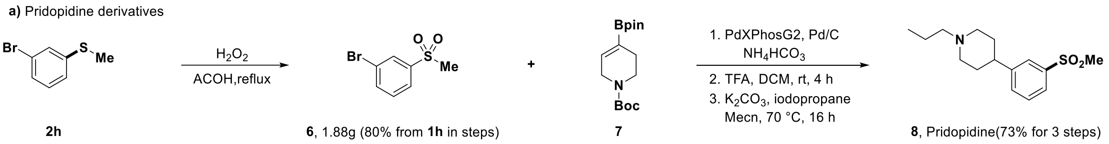
4dd:4dd' =1:1.7

4dd: methyl 3-hydroxy-4-methoxybenzoate[53,54]

4dd was synthesized according to the **General procedure B** With **3dd** (0.2 mmol, 34 mg), **Cat.1** (5.5 mg, 10 mol%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), MeOH (40 μL, 5.0 equiv.) and Hexane (0.5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EtOAc = 5:1) on silica gel to give the desired products **4dd** (22.6 mg, 62%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 1.16H), 6.94 – 6.86 (m, 0.61H), 3.94 (s, 1.71H), 3.88 (s, 1H), 3.87 (s, 0.63H). The procedure and spectroscopic data were according to the literature report.

6 Synthetic applications and spectroscopic data

6.1 Pridopidine derivatives



(3-bromophenyl)(methyl)sulfane(2h): To a 100 mL Schlenk tube was charged with **Cat.1** (276mg 10 mol%), $Zn(OTf)_2$ (360mg 10 mol%), **1h** (10 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.4 M) and CH_3OH (810 μL, 2.0 equiv.) was added and the reaction mixture was stirred at 150 °C for 24 h. The reaction was then quenched by adding K_2CO_3 (20 mol%), filtration and then washing the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was without purified for next step.

1-bromo-3-(methylsulfonyl)benzene (6)[55,56]: Crude product (**2h**) was placed in 100 mL Schlenk tube, acetic acid (5 mL) was added, to the stirred reaction mixture H_2O_2 aq (5 mL, 30% v/v) was added dropwise, and reaction mixture was heated to 100 °C (oil bath). After 3 h reaction mixture was poured onto water/ice (100 mL), solid Na_2CO_3 was added to pH = 7, mixture was extracted with ethyl acetate (3 × 20 mL), combined organic phases dried over anhydrous $MgSO_4$. The mixture was filtered, evaporated, and The crude product was purified by silica column chromatography to afford **6** in 80% yield over 2 steps (1.88 g, white solid) The procedure and spectroscopic data were according to the literature report.

Pridopidine (8)

Steps1: tert-butyl 4-(3-(methylsulfonyl)phenyl)piperidine-1-carboxylate (8-S1)[57]

To an oven dried 10 mL Schlenk tube was added boronic ester (155mg, 0.5 mmol, 1 equiv.), $PdXPhosG_2$ (4 mg, 0.005 mmol, 0.01 equiv.), 10% Pd/C (64 mg, 0.08 mmol, 0.12 equiv.), K_3PO_4 (318 mg, 0.15 mmol, 3 equiv.) and **6** (118mg, 0.5 mmol, 1 equiv.). The tube was capped and purged, then 1,4-dioxane (1.6 mL) and water (400 μL) were added. The reaction mixture was stirred at 80 °C for 4 h, followed by the addition of NH_4HCO_2 in MeOH (1.25 M) (316 mg NH_4HCO_2 in 4 mL MeOH). After this, the reaction was stirred for 16 h at room temperature, and the reaction mixture was diluted with ethyl acetate, filtered through Celite and rinsed through with further ethyl acetate. The solvent was removed in vacuo and the crude product was purified by silica column chromatography to afford **8-S1** in 90% yield (152 mg, yellow oil). The procedure and spectroscopic data were according to the literature report.

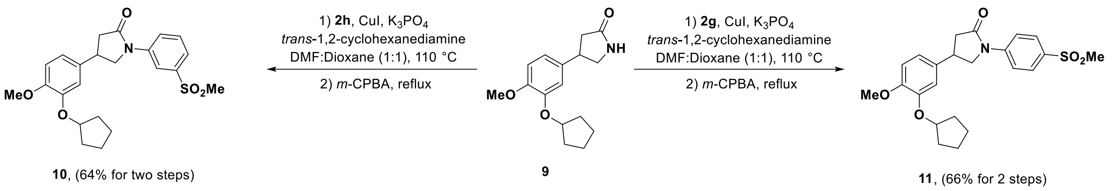
Steps2: 4-(3-(methylsulfonyl)phenyl)piperidine TFA-salt (8-S2)

In a 10 mL Schlenk tube tert-butyl 4-(3- (methylsulfonyl)phenyl)piperidine-1-carboxylate (**8-S1**) (0.168 mmol, 1.0 equiv) were dissolved in 1 mL DCM/TFA (9:1). The mixture was stirred for 1 h. Afterwards the solvent was removed under reduced pressure, the residue was dissolved in fluorobenzene and the solvent was again removed under reduced pressure. The crude product (**8-S2**) was without purified for next step.

Steps3: 4-(3-(Methylsulfonyl)phenyl)-1-propylpiperidine / Pridopidine (8)[58]

Crude 4-(3-(methylsulfonyl)phenyl)piperidine TFA-salt was dissolved in 1 mL acetonitrile and 70 mg K_2CO_3 (0.5 mmol, 3.0 equiv) and 34 mg 1-iodopropane (0.2 mmol, 1.2 equiv) were added. The reaction mixture was stirred at rt overnight. The mixture was quenched by the addition of water and then extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was purified by silica column chromatography to afford **8** in 81% yield over 2 steps (38.3 mg, yellow oil). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 3.08 – 3.06 (m, 2H), 3.04 (s, 3H), 2.61 (td, *J* = 11.5, 5.4 Hz, 1H), 2.34 (dt, *J* = 8.6, 4.1 Hz, 2H), 2.04 (dt, *J* = 11.8, 6.0 Hz, 2H), 1.87 – 1,78 (m, 4H), 1.57 – 1.51 (m, 2H), 0.92 (td, *J* = 7.5, 2.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 140.7, 132.2, 129.5, 125.9, 125.1, 61.1, 54.2, 44.6, 42.7, 33.4, 20.3, 12.1. The procedure and spectroscopic data were according to the literature report.

6.2 HIV virus inhibitor analogs



4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(3-(methylsulfonyl)phenyl)pyrrolidin-2-one(10)

Steps1: 4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(3-(methylthio)phenyl) pyrrolidin-2-one (10-S1)

A mixture of 4-(3-cyclopentyloxy-4-methoxy-phenyl)-pyrrolidin-2-one (276 mg, 1 mmol), (3-bromophenyl)(methyl)sulfane(**2h**) (283mg, 1.4 mmol), K_3PO_4 (318 mg, 1.5 mmol), DMF (3.0 mL), dioxane (3.0 mL) and 1,2-*trans*-cyclohexanediamine (25 μL) was stirred under N_2 for 5 min before CuI (35 mg) was added. The reaction mixture was heated at 110 °C for 20 h under N_2 with stirring, then cooled down to rt The mixture was diluted with EtOAc, washed with saturated NH_4Cl (3x10 mL) and dried over Na_2SO_4 The crude product was purified by silica column chromatography to afford **10-S1** in 75% yield (298.1 mg, yellow oil).

Steps2: 4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(3-(methylsulfonyl)phenyl)pyrrolidin-2-one(10)[59]

10-S1 (398 mg, 1 mmol) in CH_2Cl_2 was cooled by an ice water bath, *m*-CPBA (379 mg, 2.2 mmol) was added and the reaction mixture was stirred for 3 h at rt. The reaction was quenched with 10% $Na_2S_2O_3$ and the mixture was extracted with EtOAc. The organic layer was washed with sat. $NaHCO_3$ and dried over Na_2SO_4. The crude product was purified by silica column chromatography to afford **10** in 85% yield (365 mg, yellow solid). The procedure and spectroscopic data were according to the literature report.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 8.04 (t, *J* = 2.0 Hz, 1H), 7.71 (ddd, *J* = 7.8, 1.8, 1.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.82 – 6.79 (m, 2H), 4.78 (tt, *J* = 6.0, 3.4 Hz, 1H), 4.22 (dd, *J* = 9.4, 8.0 Hz, 1H), 3.90 – 3.88 (m, 1H), 3.84 (s, 3H), 3.67 (p, *J* = 8.3 Hz, 1H), 3.07 (s, 3H), 3.02 (dd, *J* = 17.1, 8.7 Hz, 1H), 2.82 (dd, *J* = 17.1, 9.0 Hz, 1H), 1.94 – 1.81 (m, 6H), 1.64 – 1.59 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.6, 149.5, 148.1, 141.2, 140.2, 133.4, 133.3, 130.1, 124.8, 124.8, 122.8, 122.8, 118.8, 117.7, 113.8, 112.4, 80.7, 56.2, 55.7, 44.4, 40.3, 36.7, 32.9, 32.9, 24.1. The procedure and spectroscopic data were according to the literature report.

4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(4-(methylsulfonyl)phenyl)pyrrolidin-2-one (11)

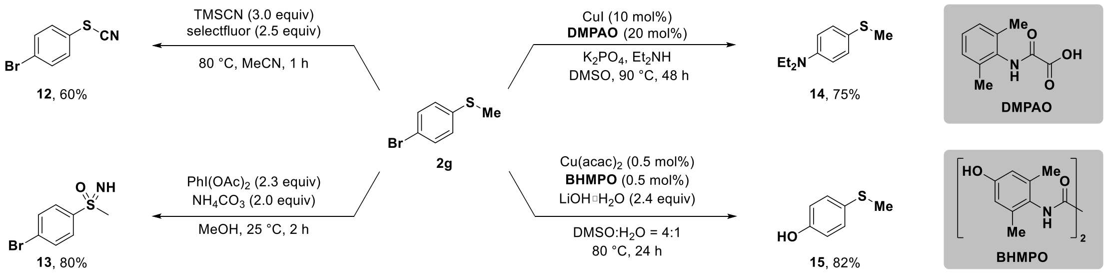
Steps1: 4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(4-(methylthio)phenyl)pyrrolidin-2-one (11-S1)

A mixture of 4-(3-cyclopentyloxy-4-methoxy-phenyl)-pyrrolidin-2-one (276 mg, 1 mmol), (4-bromophenyl)(methyl)sulfane (**2g**) (283mg, 1.4 mmol), K_3PO_4 (318 mg, 1.5 mmol), DMF (3.0 mL), dioxane (3.0 mL) and 1,2-*trans*-cyclohexanediamine (25 μL) was stirred under N_2 for 5 min before CuI (35 mg) was added. The reaction mixture was heated at 110 °C for 20 h under N_2 with stirring, then cooled down to rt. The mixture was diluted with EtOAc, washed with saturated NH_4Cl (3x10 mL) and dried over Na_2SO_4 The crude product was purified by silica column chromatography to afford **11-S1** in 80% yield (318 mg, yellow oil).

Steps2: 4-(3-(cyclopentyloxy)-4-methoxyphenyl)-1-(4-(methylsulfonyl)phenyl)pyrrolidin-2-one (11)[59]

11-S1 (398 mg, 1 mmol) in CH_2Cl_2 was cooled by an ice water bath, *m*-CPBA (379 mg, 2.2 mmol) was added and the reaction mixture was stirred for 3 h at rt. The reaction was quenched with 10% $Na_2S_2O_3$ and the mixture was extracted with EtOAc. The organic layer was washed with sat. $NaHCO_3$ and dried over Na_2SO_4 The crude product was purified by silica column chromatography to afford **11** in 83% yield (356 mg, yellow solid). The procedure and spectroscopic data were according to the literature report. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.87 – 7.85 (m, 2H), 6.86 – 6.78 (m, 3H), 4.77 (tt, *J* = 5.7, 3.4 Hz, 1H), 4.21 (dd, *J* = 9.5, 8.0 Hz, 1H), 3.89 – 3.87 (m, 1H), 3.84 (s, 3H), 3.67 (p, *J* = 8.4 Hz, 1H), 3.07 – 3.00 (m, 4H), 2.83 (dd, *J* = 17.2, 9.1 Hz, 1H), 1.95 – 1.80 (m, 6H), 1.65 – 1.56 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 149.7, 148.2, 143.9, 135.6, 133.3, 128.6, 119.5, 118.9, 113.9, 112.5, 80.8, 56.3, 55.7, 44.8, 40.6, 36.8, 33.0, 32.9, 24.1. The procedure and spectroscopic data were according to the literature report.

6.3 Derivatization of 2g



1-bromo-4-thiocyanatobenzene (12)[60]

To a reaction tube were sequentially added (4-bromophenyl)(methyl)sulfide **2g** (0.2 mmol), TMSCN (74 μL, 0.6 mmol, 3 equiv), Selectfluor reagent (177 mg, 0.5 mmol, 2.5 equiv). The tube was evacuated and backfilled with nitrogen for three times. Then, 1 mL of dry acetonitrile was added via a syringe, and the resulting solution was stirred at 80°C (oil bath). When the reaction was completed (monitored by TLC), the solvent was removed by distillation under reduced pressure. The crude product was purified by silica column chromatography to afford **12** in 60% yield (25.7 mg, white solid). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 – 7.57 (m, 2H), 7.41 – 7.40 (m, 2H). The procedure and spectroscopic data were according to the literature report.

(4-bromophenyl)(imino)(methyl)-l6-sulfanone (13)[61]

Under an ambient atmosphere, to a stirred solution of (4-bromophenyl)(methyl)sulfide (**2g**) (203 mg, 1.00 mmol, 1.00 equiv) in MeOH (10.0 mL, 0.10 M) was added $(NH_4)_2CO_3$ (192 mg, 2.00 mmol, 2.00 equiv.). Subsequently, $PhI(OAc)_2$ (741 mg, 2.30 mmol, 2.30 equiv.) was added, then the reaction mixture was stirred at 25 °C for 2 h. The solvent was removed under reduced pressure, The crude product was purified by silica column chromatography to afford **13** in 80% yield (187 mg, colorless solid) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 3.10 (s, 3H), 2.05 (s, 1H). The procedure and spectroscopic data were according to the literature report.

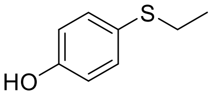
***N,N*-diethyl-4-(methylthio)aniline (14)**[62]

An oven-dried Schlenk tube was charged with CuI (19 mg, 0.1 mmol), DMPAO (38 mg, 0.2 mmol), (4-bromophenyl)(methyl)sulfide (**2g**) (1 mmol), K_3PO_4 (2 mmol). The tube was evacuated and backfilled with argon, and then amine (1.5 mmol) and DMSO (1 mL) was added. The reaction mixture was stirred at 90°C for 48 h. After aryl halide was consumed, water was added and the mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by chromatography to give the desired product. The crude product was purified by silica column chromatography to afford **14** in 75% yield (146 mg, colorless solid) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.6 Hz, 2H), 6.61 (d, *J* = 6.6 Hz, 2H), 3.32 (q, *J* = 5.4 Hz, 4H), 2.40 (s, 3H), 1.14 (t, *J* = 5.4 Hz, 6H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 132.2, 121.8, 112.4, 44.5, 19.7, 12.6 The procedure and spectroscopic data were according to the literature report.

4-(methylthio)phenol (15)[42]

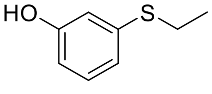
The (4-bromophenyl)(methyl)sulfide (**2g**) (4.0 mmol), $Cu(acac)_2$ (0.02 mmol, 5.3 mg), $LiOH{\cdot}H_2O$ (8.4 mmol, 352 mg) and BHMPO (0.02 mmol, 6.6 mg) were placed into a Schlenk tube (25 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon three times, then DMSO (3.2 mL) and degassed water (0.8 mL) were added under a positive argon pressure (Note: for liquid substrates, they were added after the tube was backfilled with argon). The reaction mixture was heated at 80 °C for 24 h under vigorous stirring. The cooled solution was acidified with 2 N HCl, then diluted with ethyl acetate and washed with brine. The organic phase was dried over Na_2SO_4 and and evaporated. The crude product was purified by silica column chromatography to afford **15** in 82% yield (460 mg, colorless oil). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 130.6, 129.1, 116.2, 18.2. The spectroscopic data were according to the literature report.

6.4 Ethylation with ethanol



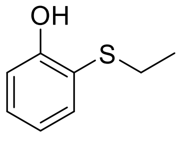
2y': 4-(ethylthio)phenol[63]

2y' was synthesized according to the **General procedure B** With **1y** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), EtOH (584 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then wash the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 3:1) on silica gel to give the desired products **2y'** (281 mg, 91%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 2.84 (q, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 133.5, 126.9, 116.1, 30.0, 14.8. The spectroscopic data were according to the literature report.



2z': 3-(ethylthio)phenol[64]

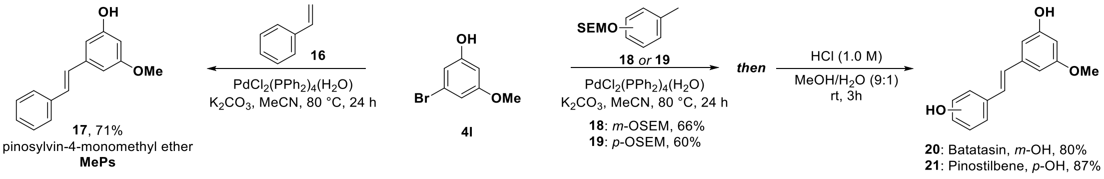
2z' was synthesized according to the **General procedure B** With **1z** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), EtOH (584 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then wash the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/DCM = 3:1) on silica gel to give the desired products **2z'** (256 mg, 82%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.81 – 6.80 (m, 1H), 6.63 (dd, *J* = 8.1, 2.1 Hz, 1H), 2.92 (q, *J* = 7.3 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 138.5, 130.0, 121.1, 115.4, 113.0, 27.4, 14.4. The spectroscopic data were according to the literature report.



2aa': 2-(ethylthio)phenol[65]

2aa' was synthesized according to the **General procedure B** With **1aa** (2 mmol, 252 mg), **Cat.1** (55 mg, 10 mol%), $Zn(OTf)_2$ (72 mg, 10 mol%), EtOH (584 μL, 5.0 equiv.) and Hexane (5 mL, 0.4 M). The reaction was stirred at 150 °C for 24 h then quenched by adding K_2CO_3 (20 mol%), filtration and then wash the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography on silica gel to give the desired products **2aa'** (271mg, 88%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 2.73 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2, 136.2, 131.2, 120.8, 118.8, 114.8, 30.9, 15.0. The spectroscopic data were according to the literature report.

6.5 Synthetic applications of monomethylation of benzene diols



$PdCl_2(PPh_2)_4(H_2O)$

A soln of Ph_2PCl (0.375 mL, 2.025 mmol) in THF (2.5 mL) was added dropwise with stirring to a Schlenk flask containing a soln of $[PdCl_2(PhCN)_2]$ (0.38 g, 1.0 mmol) in THF (5 mL) at rt. When the complete formation of the dichlorophosphane complex had been confirmed by ^{31}P NMR spectroscopy (δ = 87 ppm), H_2O (0.25 mL) was added to the mixture and it was stirred at r.t. After 48 h, ^{31}P NMR analysis of an aliquot exclusively showed one signal at (δ = 78.4 ppm). The solvent was removed under vacuum to give the complex 1 (0.5 g, 92%) as a yellow crystalline powder; ^{31}P NMR (121.4 MHz, $CDCl_3$): 78.4. The spectroscopic data were according to the literature report.

Pinosylvin-4-monomethyl ether (17)[66]

3-bromo-5-methoxyphenol (**4l**) (1 mmol), styrene (1.0 mmol), K_2CO_3 (2 mmol), and $PdCl_2(PPh_2)_4(H_2O)$ (1 mol%) in MeCN (3 mL) was heated at 110 °C (oil bath) equipped with a condenser system for 12 h. When the reaction was complete, the mixture was cooled to rt., diluted with EtOAc (15 mL), washed with brine dried (Na_2SO_4), and concentrated under vacuum. The residue was purified using flash column chromatography on silica gel to give the desired products **17** (161mg, 71%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.08 – 6.99 (m, 2H), 6.64 (d, *J* = 26.7 Hz, 2H), 6.36 (s, 1H), 3.82 (s, 3H). The spectroscopic data were according to the literature report.

General method for prepare 18 and 19

N, N-Diisopropylethylamine (16.65 mmol, 1.5 equiv) and 2- (trimethylsilyl)ethoxymethyl chloride (SEMCl) (13.32 mmol, 1.2 equiv) were added sequentially to a solution of compound Hydroxystyrene (11.1 mmol, 1.0 equiv) in anhydrous dichloromethane (30 mL) at room temperature. After stirring at room temperature for 16 hours, saturated sodium bicarbonate (50 mL) was added to quench the reaction. The layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified using flash column chromatographyon silica gel to give the desired products.

(E)-3-(3-hydroxystyryl)-5-methoxyphenol / Thunalbene (20)[67]

(E)-3-methoxy-5-(3-((2-(trimethylsilyl)ethoxy)methoxy)styryl)phenol (20-S1)

3-bromo-5-methoxyphenol (**4l**) (1 mmol), styrene **18** (1.0 mmol), K_2CO_3 (2 mmol), and $PdCl_2(PPh_2)_4(H_2O)$ (1 mol%) in MeCN (3 mL) was heated at 80 °C (oil bath) equipped with a condenser system for 12 h. When the reaction was complete, the mixture was cooled to r.t, diluted with EtOAc (15 mL), washed with brine dried (Na_2SO_4), and concentrated under vacuum. The residue was purified using flash column chromatography on silica gel to give the desired products **20-S1** (246mg, 66%).

To a solution of HCl (1 mL) in MeOH (9 mL) was added to the **20-S1** (1.0 mmol) at room temperature, When the reaction was complete, diluted with EtOAc (15 mL), washed with $NaHCO_3$, and concentrated under vacuum. The residue was purified using flash column chromatography on silica gel to give the desired products **20** (194mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 6.9 Hz, 3H), 6.75 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.63 (s, 1H), 6.63 – 6.59 (m, 1H), 6.34 (d, *J* = 2.2 Hz, 1H), 5.0 (s, 2H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3, 157.0, 156.0, 139.7, 139.0, 130.0, 129.1, 128.9, 119.7, 115.0, 113.2, 106.1, 105.2, 101.2, 55.5. The spectroscopic data were according to the literature report.

(E)-3-(4-hydroxystyryl)-5-methoxyphenol / Pinostilbene (21)[68]

(E)-3-methoxy-5-(4-((2-(trimethylsilyl)ethoxy)methoxy)styryl)phenol (21-S1)

3-bromo-5-methoxyphenol (**4l**) (1 mmol), styrene **19** (1.0 mmol), K_2CO_3 (2 mmol), and $PdCl_2(PPh_2)_4(H_2O)$ (1 mol%) in MeCN (3 mL) was heated at 80 °C (oil bath) equipped with a condenser system for 12 h. When the reaction was complete, the mixture was cooled to rt., diluted with EtOAc (15 mL), washed with brine dried (Na_2SO_4), and concentrated under vacuum. The residue was purified using flash column chromatography (PE/EtOAc = 10:1) on silica gel to give the desired products **21-S1** (224mg, 60%).

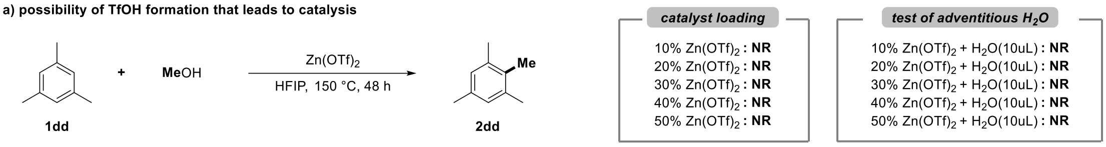
To a solution of HCl (1 mL) in MeOH (1 mL) was added to the **21-S1** (1.0 mmol) at room temperature, When the reaction was complete, diluted with EtOAc (15 mL), washed with $NaHCO_3$, and concentrated under vacuum. The residue was purified using flash column chromatography on silica gel to give the desired products **20**

(211mg, 87%). **^{1}H NMR** (600 MHz, CD_3OD) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.63 – 6.52 (m, 2H), 6.33 – 6.22 (m, 1H), 3.79 (s, 3H). **^{13}C NMR** (151 MHz, CD_3OD) δ 161.1, 158.3, 157.0, 139.9, 129.0, 128.3, 127.5, 125.5, 115.1, 105.3, 103.0, 100.0, 54.3, 48.0, 47.9, 47.8, 47.6, 47.5, 47.3, 47.2. The spectroscopic data were according to the literature report.

7 Mechanistic experiments

7.1 Possibility of TfOH formation that leads to catalysis

a) possibility of TfOH formation that leads to catalysis



catalyst loading

10% $Zn(OTf)_2$: **NR**
20% $Zn(OTf)_2$: **NR**
30% $Zn(OTf)_2$: **NR**
40% $Zn(OTf)_2$: **NR**
50% $Zn(OTf)_2$: **NR**

test of adventitious H_2O

10% $Zn(OTf)_2$ + H_2O(10uL) : **NR**
20% $Zn(OTf)_2$ + H_2O(10uL) : **NR**
30% $Zn(OTf)_2$ + H_2O(10uL) : **NR**
40% $Zn(OTf)_2$ + H_2O(10uL) : **NR**
50% $Zn(OTf)_2$ + H_2O(10uL) : **NR**

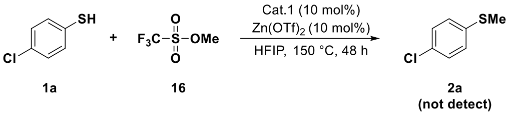
Catalyst loading:

To a 10 mL Schlenk tube was charged with $Zn(OTf)_2$ (from 10 mol% to 50%), Mesitylene **(1dd)** (1 mmol, 5.0 equiv.) HFIP (0.5 mL, 0.4 M), MeOH (8μL, 1.0 equiv.) and an oven-dried stirring bar. the reaction mixture was stirred at 150 °C for 48 h, The reaction was then quenched by adding K_2CO_3 (10 mol%), dodecane as an internal standard was added and take sample 1-2 drops to check yield by GC.

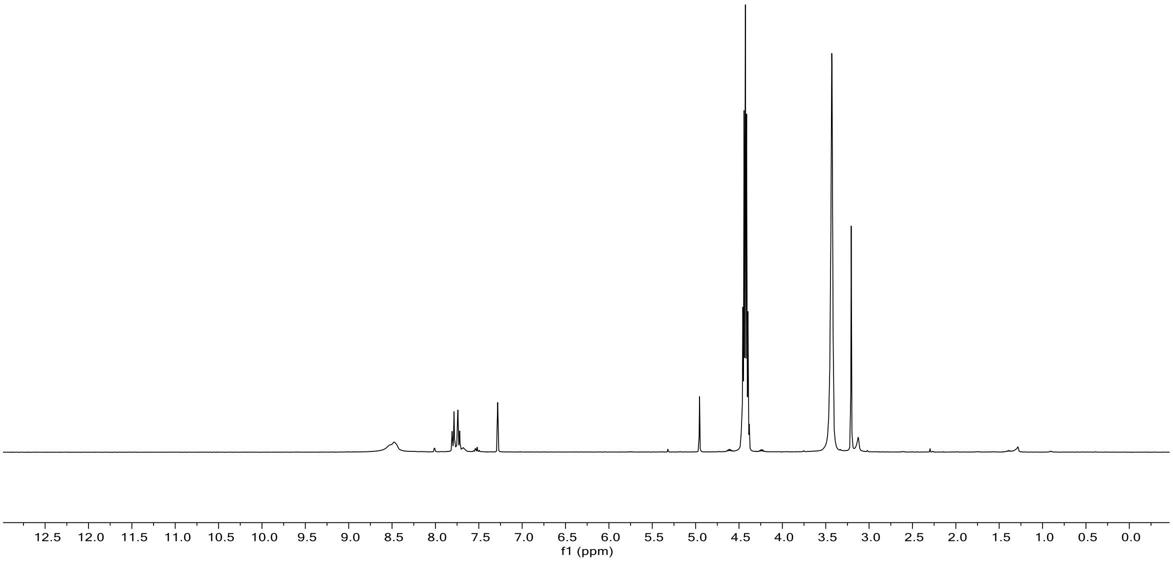
Test of adventitious H_2O

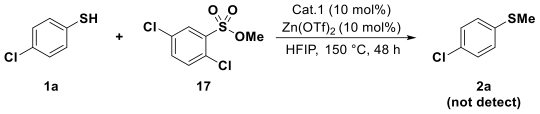
To a 10 mL Schlenk tube was charged with $Zn(OTf)_2$ (from 10 mol% to 50%), Mesitylene **(1dd)** (1 mmol, 5.0 equiv.) HFIP (0.5 mL, 0.4 M), MeOH (8μL, 1.0 equiv.), H_2O (10μL) and an oven-dried stirring bar. the reaction mixture was stirred at 150 °C for 48h, The reaction was then quenched by adding K_2CO_3 (10 mol%), dodecane as an internal standard was added and take sample 1-2 drops to check yield by GC.

7.2 Possibility of methyl sulfonates as a key intermediate

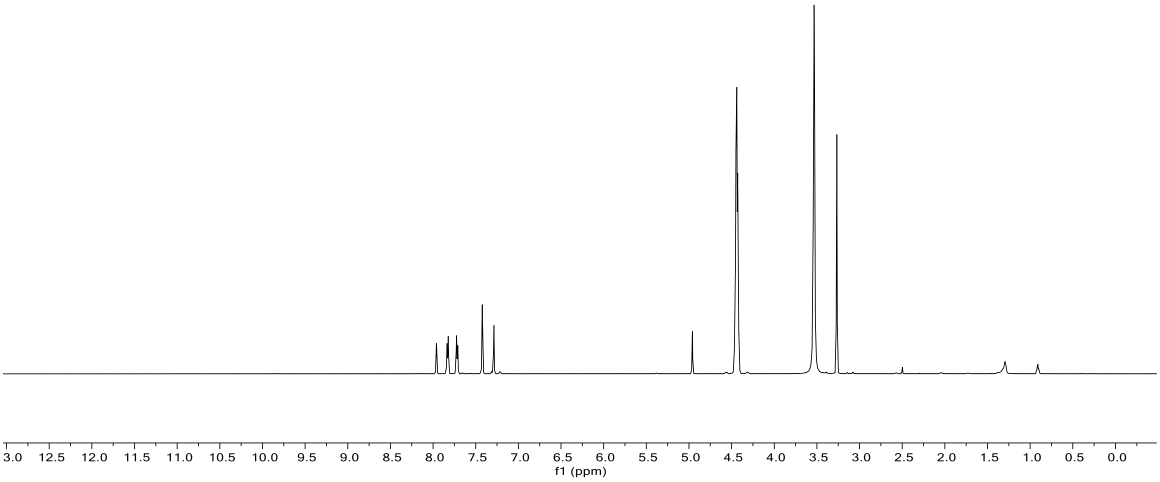


To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), Zn(OTf)$_2$ (7.2 mg, 10 mol%), 4-Chlorothiophenol **(1a)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), Methyl trifluoromethanesulfonate (**16**) (45 μL, 2.0 equiv.) was added and the reaction mixture was stirred at 150 °C, The reaction was then quenched by adding K$_2$CO$_3$ (20 mol%), CH$_2$Br$_2$ (7 μL) was added as an internal standard, The composition of mixture was analyzed by ^{1}H NMR.





To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), $Zn(OTf)_2$ (7.2 mg, 10 mol%), 4-Chlorothiophenol **(1a)** (0.2 mmol, 1.0 equiv.) methyl 2,5-dichlorobenzenesulfonate (**17**) (90 mg, 2.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), was added and the reaction mixture was stirred at 150 °C, The reaction was then quenched by adding K_2CO_3 (20 mol%), CH_2Br_2 (7 µL) was added as an internal standard, The composition of mixture was analyzed by ^1H NMR.

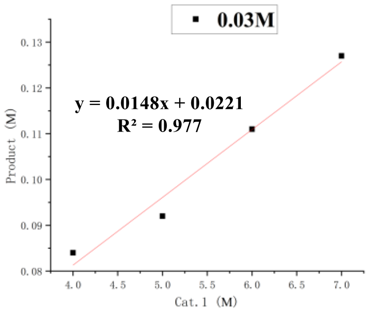


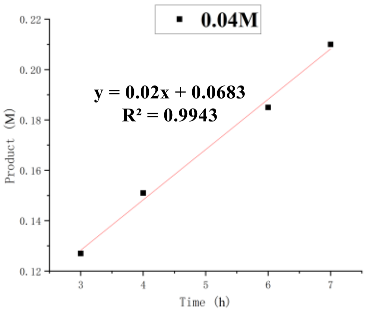
7.3 Kinetic Studies in HFIP

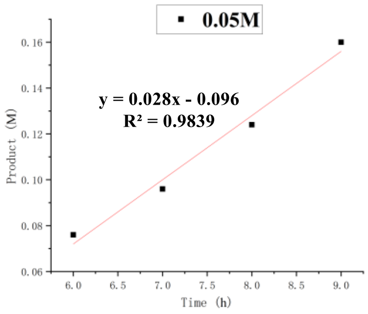
A: Kinetic Order in Cat.1 in HFIP

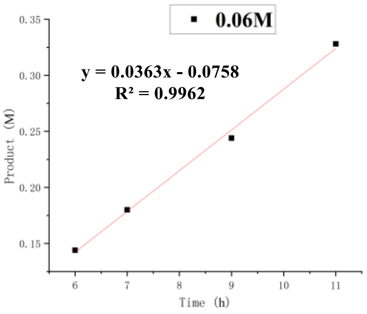
The order in **Cat.1** was determined according to the following procedure:

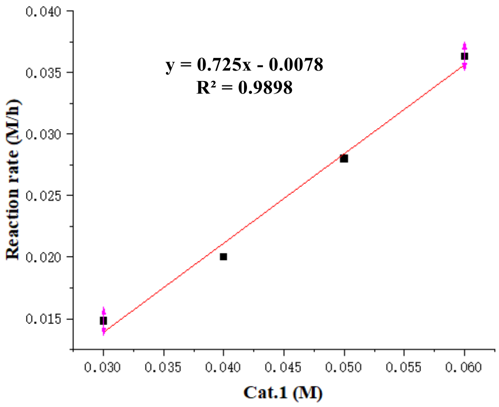
To a 10 mL Schlenk tube was charged with **Cat.1** (from 0.03M to 0.06M), Zn(OTf)$_2$ (7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.







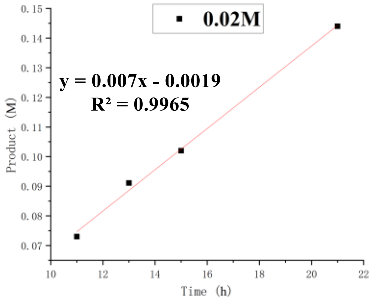


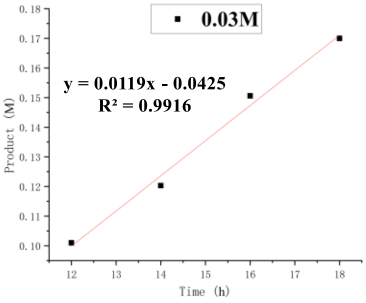


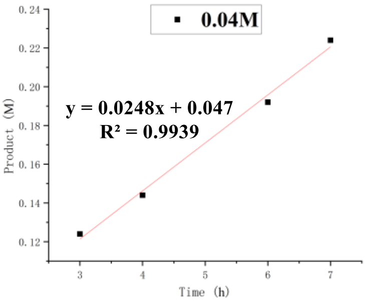
B: Kinetic Order in Zn(OTf)$_2$ in HFIP

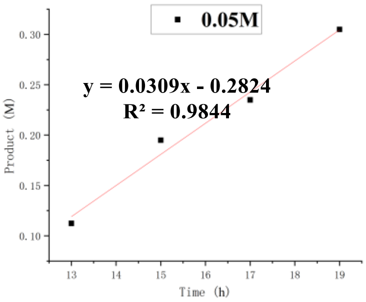
The order in **Zn(OTf)$_2$** was determined according to the following procedure:

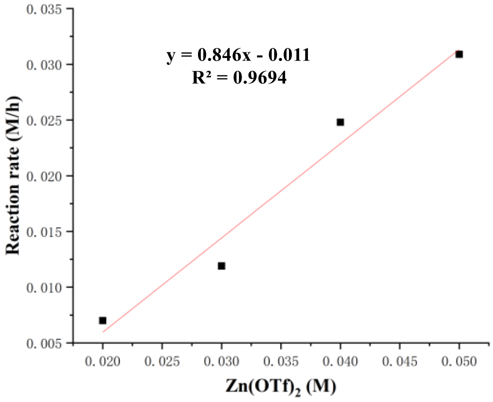
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), Zn(OTf)$_2$ (from 0,02M to 0,05M), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.







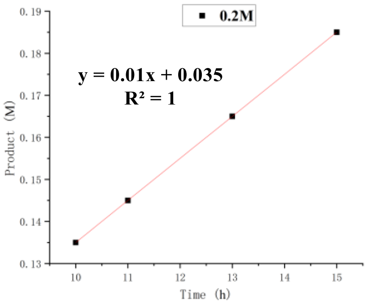


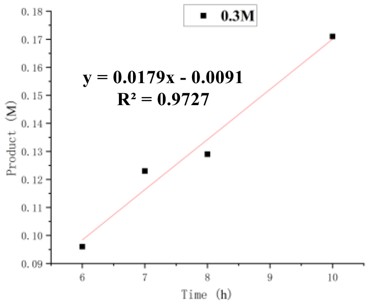


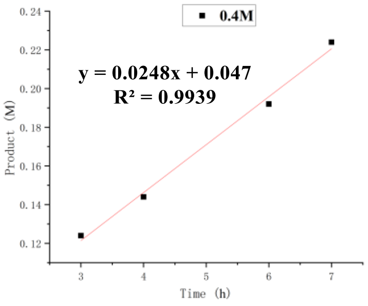
C: Kinetic Order in *p*-Toluenethiol (1o) in HFIP

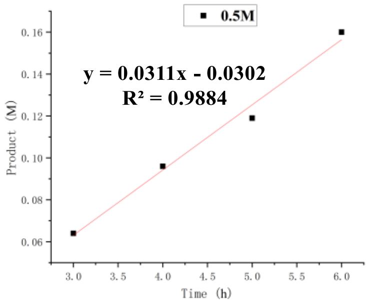
The order in ***p*-Toluenethiol (1o)** was determined according to the following procedure:

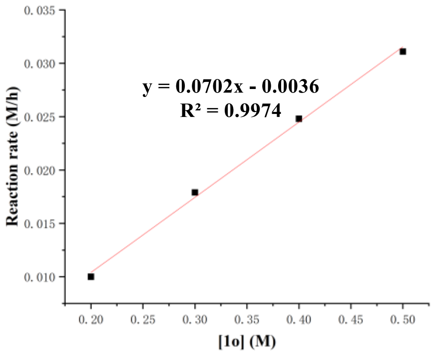
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), $Zn(OTf)_2$(7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (from 0.2M to 0.5M) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.







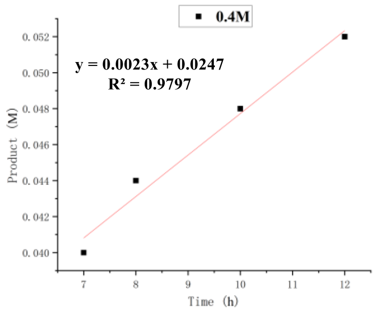


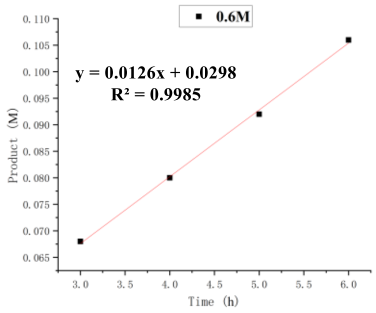


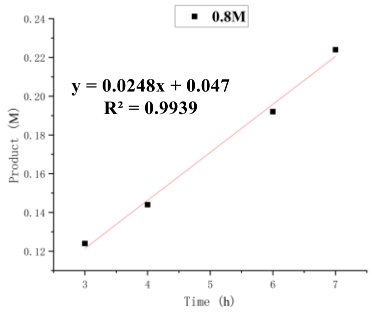
D: Kinetic Order in MeOH in HFIP

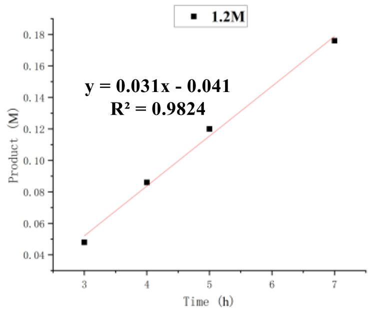
The order in **MeOH** was determined according to the following procedure:

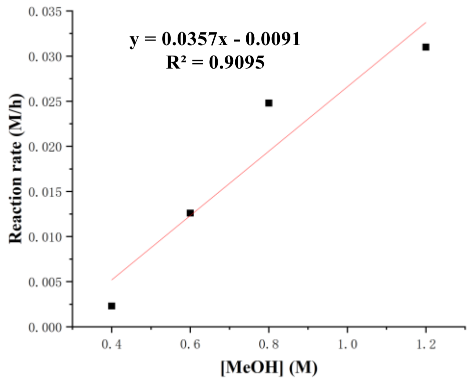
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), Zn(OTf)$_2$(7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (from 0.4M to 1.2M) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.











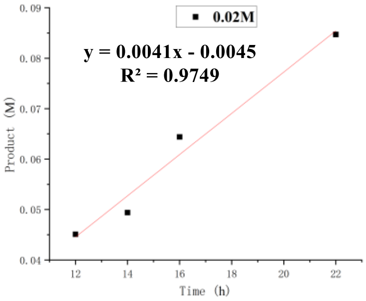
7.4 Kinetic Studies in Hexane

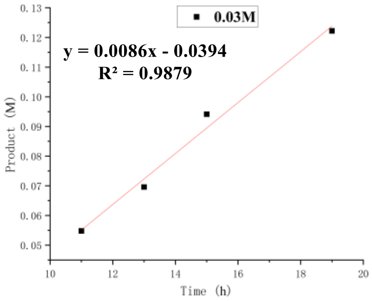
A: Kinetic Order in Cat.1 in Hexane

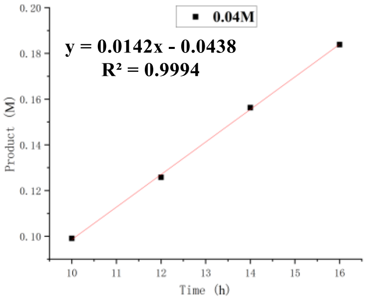
The order in **Cat.1** was determined according to the following procedure:

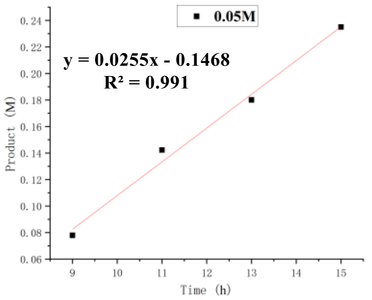
To a 10 mL Schlenk tube was charged with **Cat.1** (from 0.02M to 0.05M), $Zn(OTf)_2$ (7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–

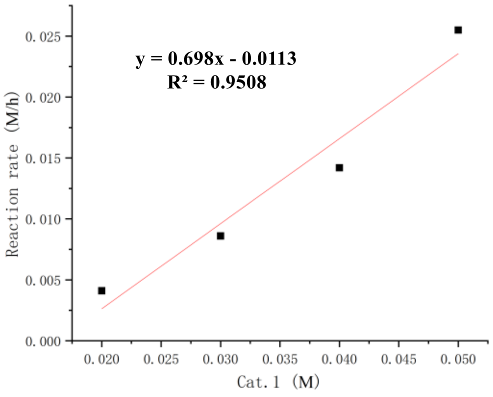
depressurization using dry argon. After that, under the protection of argon atmosphere, Hexane (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.









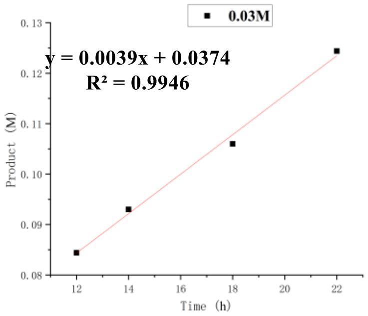


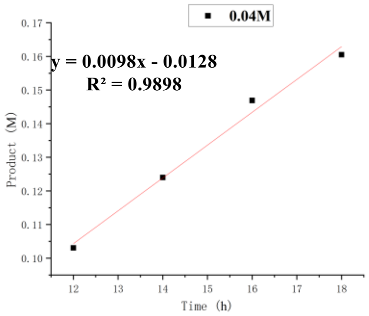
B: Kinetic Order in $Zn(OTf)_2$ in Hexane

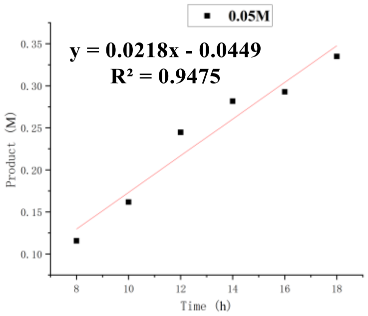
The order in **$Zn(OTf)_2$** was determined according to the following procedure:

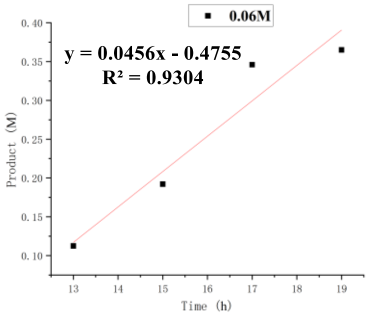
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), $Zn(OTf)_2$ (from 0.03M to 0.06M), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar.

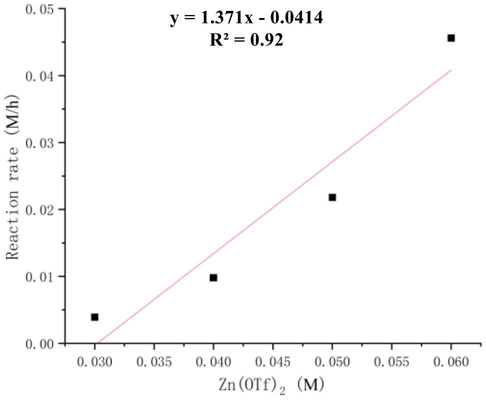
The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, Hexane (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.







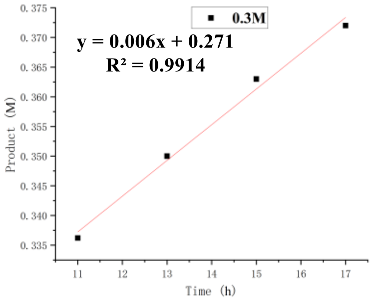


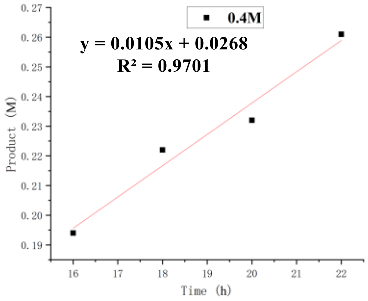


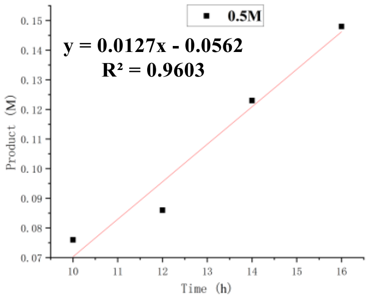
C: Kinetic Order in *p*-Toluenethiol (1o) in Hexane

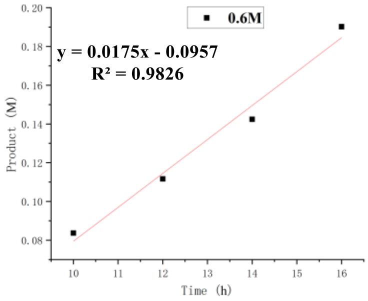
The order in ***p*-Toluenethiol (1o)** was determined according to the following procedure:

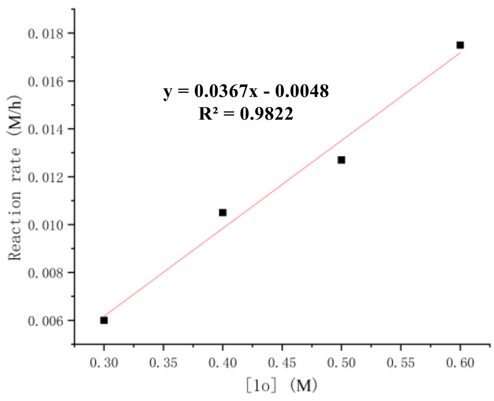
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), Zn(OTf)$_2$(7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (from 0.3M to 0.6M) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (16μL, 2.0 equiv.) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.







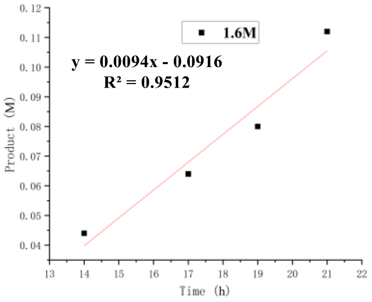


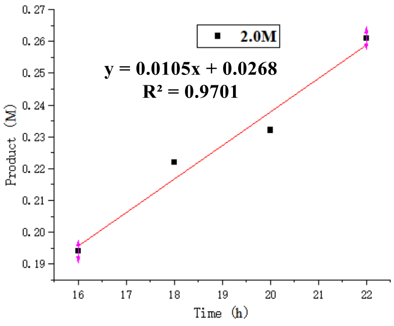


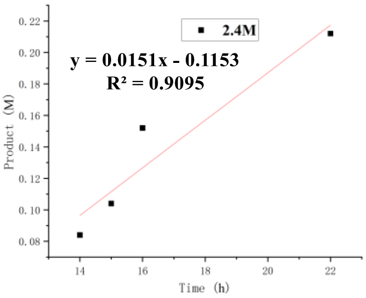
D: Kinetic Order in MeOH in Hexane

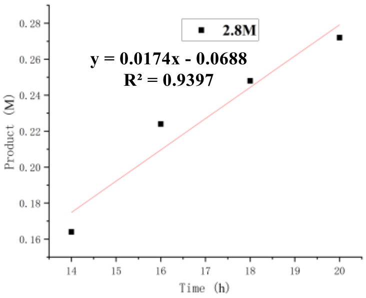
The order in **MeOH** was determined according to the following procedure:

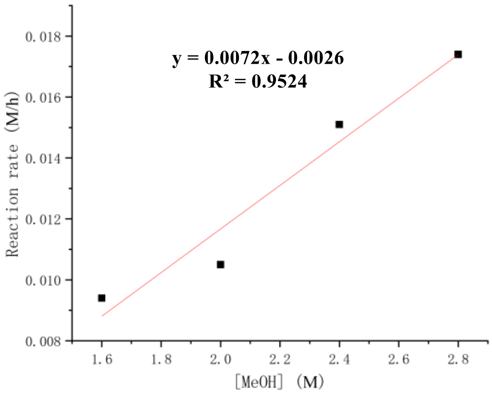
To a 10 mL Schlenk tube was charged with **Cat.1** (5.5 mg 10%), Zn(OTf)$_2$(7.2 mg, 10 mol%), *p*-Toluenethiol **(1o)** (0.2 mmol, 1.0 equiv.) and an oven-dried stirring bar. The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, HFIP (0.5 mL, 0.4 M), MeOH (from 1.6 M to 2.8 M) and dodecane as an internal standard was added and the reaction mixture was stirred at 150 °C, Subsequently, appropriate time to take sample 1-2 drops to check yield by GC.



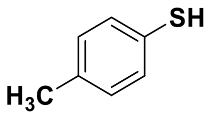




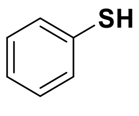



y = 0.0072x - 0.0026
R² = 0.9524
Reaction rate (M/h)
0.008
0.010
0.012
0.014
0.016
0.018
1.6
1.8
2.0
2.2
2.4
2.6
2.8
[MeOH] (M)

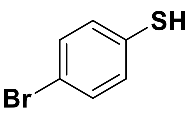
7.5 Hammett plot



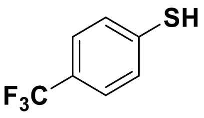
1o



1tt



1g



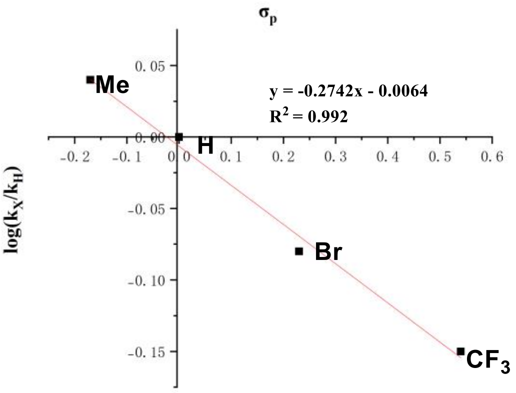
1uu

To a 10 mL Schlenk tube was charged with **Cat.1** (11 mg, 20 mol%), $Zn(OTf)_2$ (14.4 mg, 10 mol%), The Schlenck tube was subjected to three cycles of pressurization–depressurization using dry argon. After that, under the protection of argon atmosphere, mixture two different *p*-substituted substrates **1** (**1o** and **1tt**; **1g** and **1tt**; **1u** and **1tt**, 0.2 mmol each, 1.0 equiv), HFIP (1 mL), MeOH (32 μL 2.0 equiv.) and CH_2Br_2 (7 μL) was added as an internal standard and then the reaction mixture was stirred at 150 °C. The aliquot (approximately 50 μL) of the reaction mixture was taken at the indicated time intervals, and immediately added with CD_3Cl to filter with a filter head. The composition of mixture was analyzed by ^1H NMR to determine the reduced molar amount of **1**. The k_X / k_H data was calculated based on the reduced molar amount of **1** and the results were summarized as follows equation.

$$\frac{K_X}{K_H} = \frac{\frac{C_{X0}-C_{Xt}}{t}}{\frac{C_{H0}-C_{Ht}}{t}} = \frac{\frac{n_{X0}-n_{Xt}}{V}}{\frac{n_{H0}-n_{Ht}}{V}} = \frac{n_{X0}-n_{Xt}}{n_{H0}-n_{Ht}}$$

Entry	k_X/k_H	*p*-substituted X	σ_p[a]	$\log(k_X/k_H)$
1	1.1	CH_3	-0.17	0.04
2	1	H	0	0
3	0.827	Br	0.23	-0.08
4	0.7	CF_3	0.54	-0.15

[a] Data from: Hansch, C.; Leo, A.; Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev*. **1991**, *91*, 165–195.



Hammett plots of $\log(k_X/k_H)$ vs σ_p

7.6 DFT calculations

Section 1. Computational Details

All DFT calculations were using the Gaussian16 quantum chemistry package[69]. Structures were optimized at the B3LYP[70,71] theoretical levels in conjunction with the D3 dispersion correction,[72–73] Stuttgart-Dresden ECP (SDD) basis set[74] was used for Zn and 6-31G(d, p) basis set for other atoms. Frequency calculations were carried out at the same level of theory to obtain free energy corrections at 423.15 K[75–76] and to confirm the nature of the optimized geometries as minima (no imaginary frequency) or transition states (TS, one imaginary frequency). The single-point calculations of the optimized geometries were performed with B3LYP functional, SDD basis set for Zn and 6-311+G(2d,2p) basis set for other atoms. Solvent effects were considered in the single-point calculations with SMD continuum solvation model[77] in MeOH.

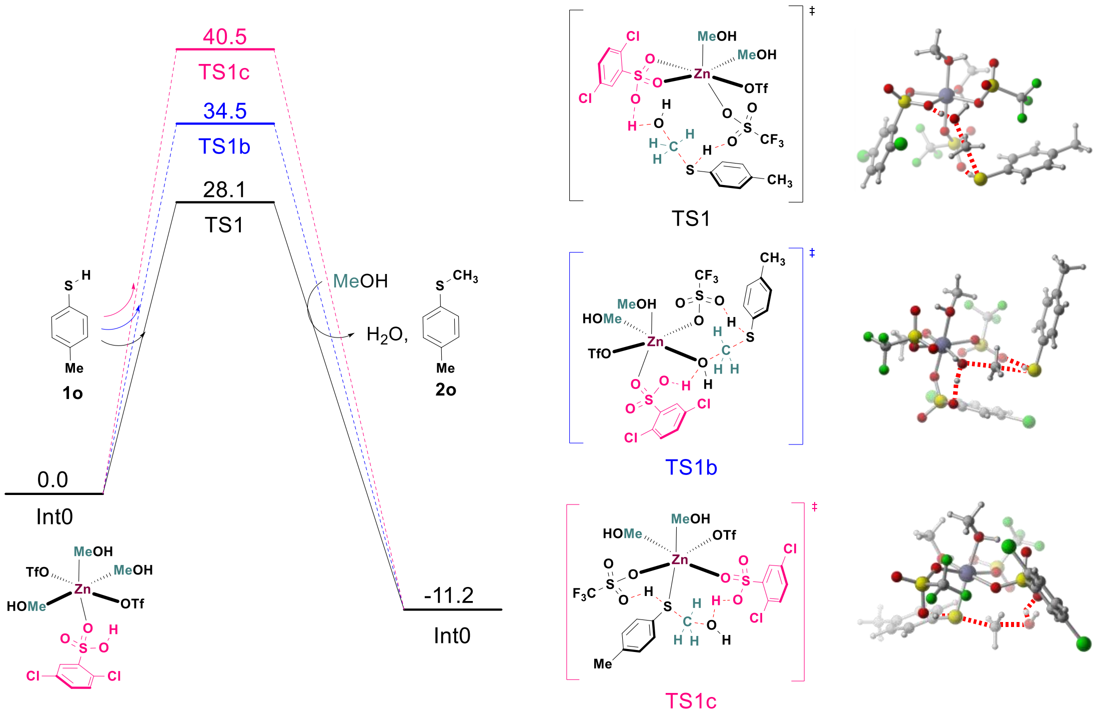


Fig. S1. Gibbs free energy profile (kcal/mol) for reaction profile of benzenethiol S-methylation (alternative pathways).

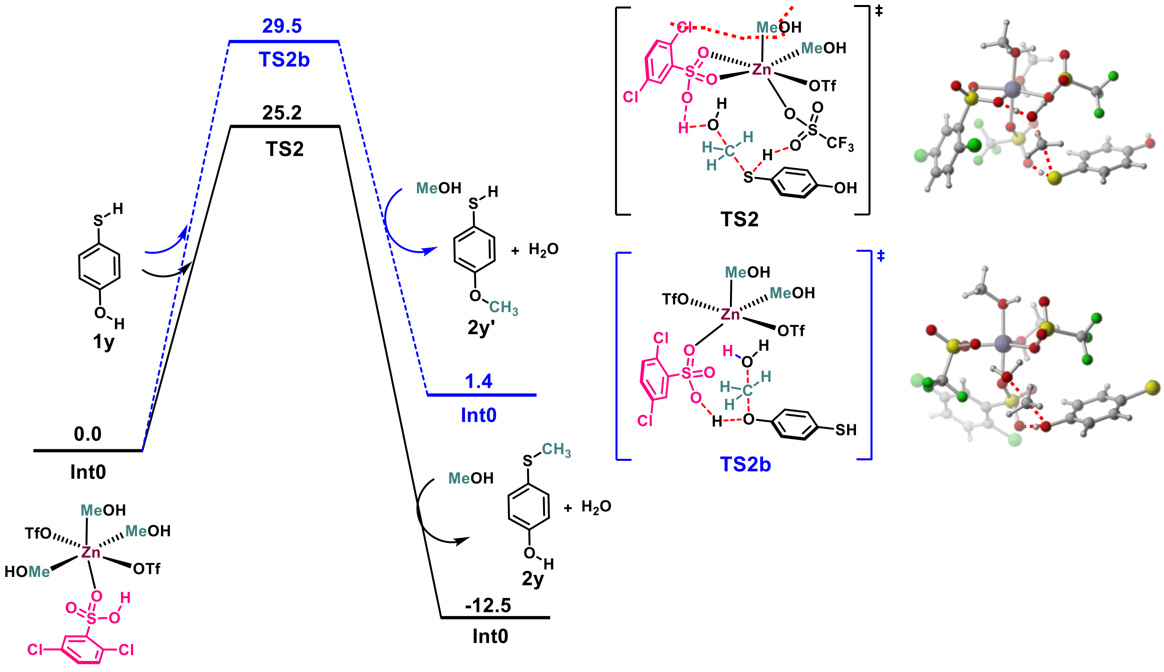
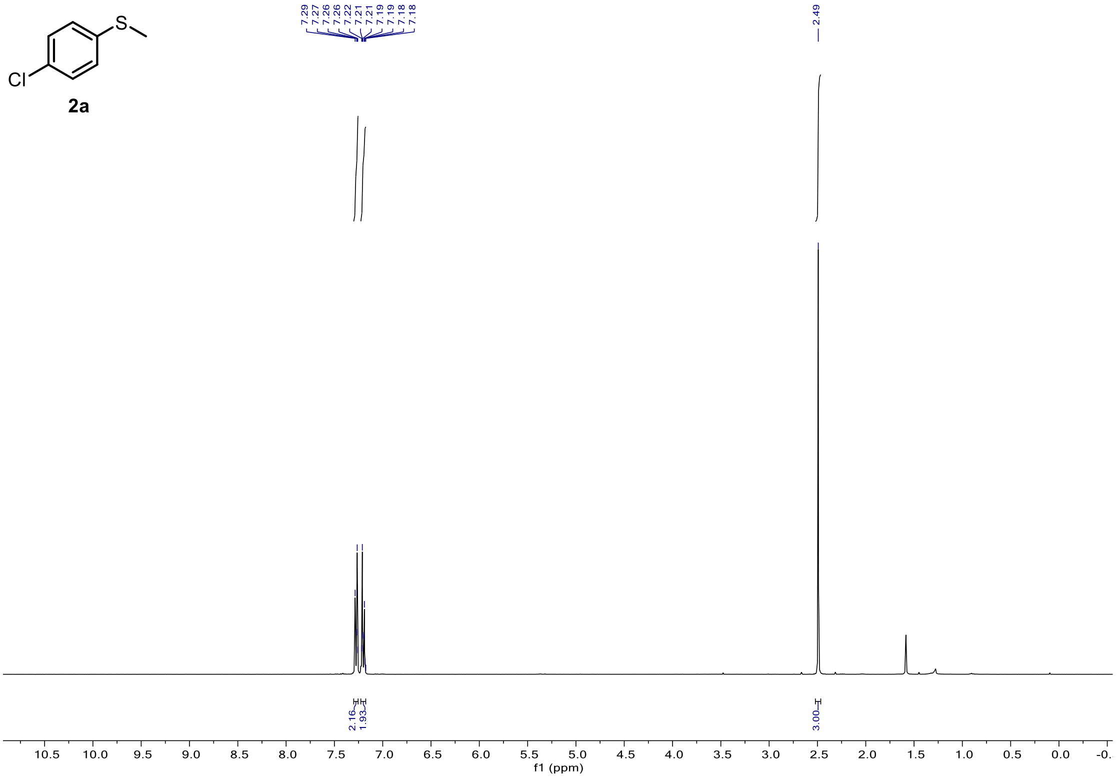
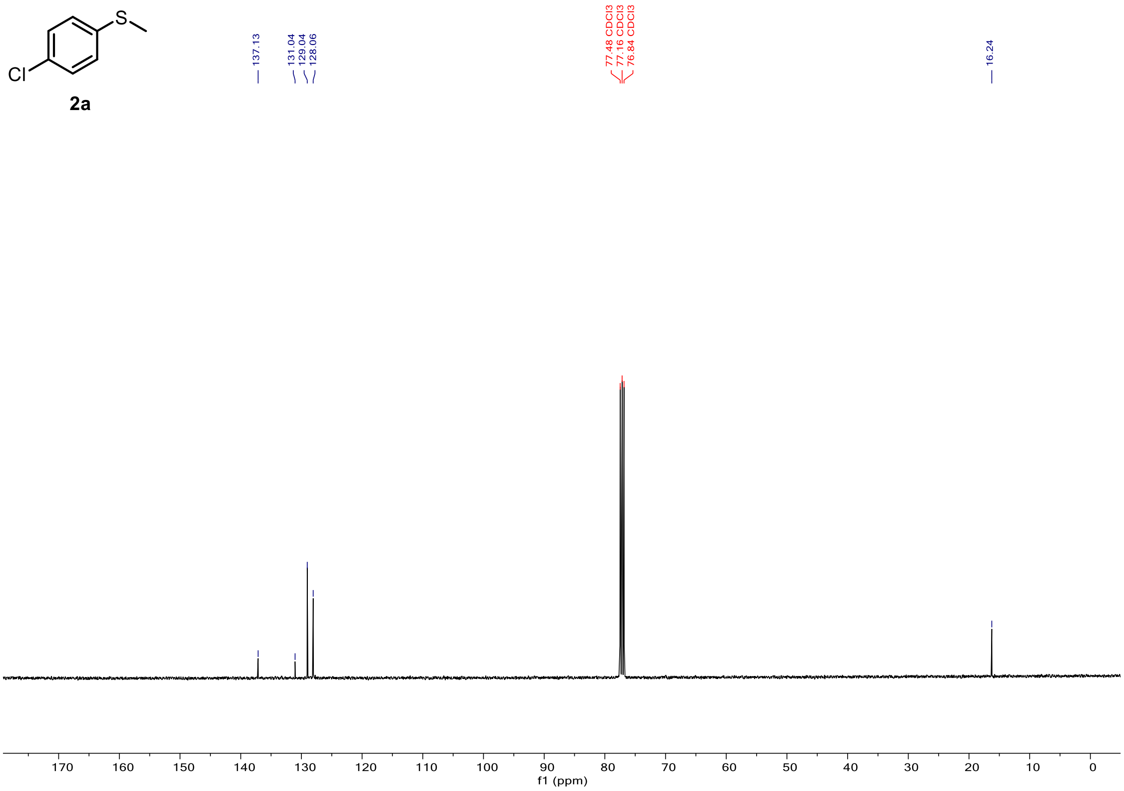
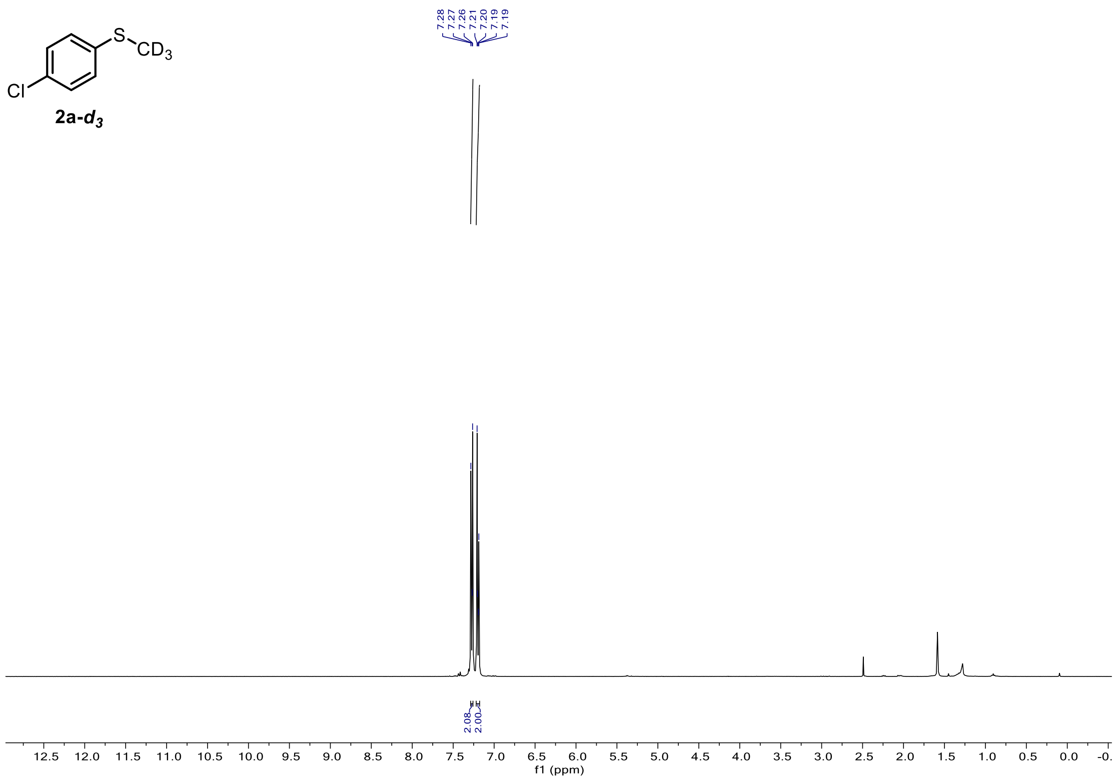


Fig. S2. Gibbs free energy profile (kcal/mol) for reaction profile of selective S-methylation over O-methylation

8 NMR spectroscopic data


2a


2a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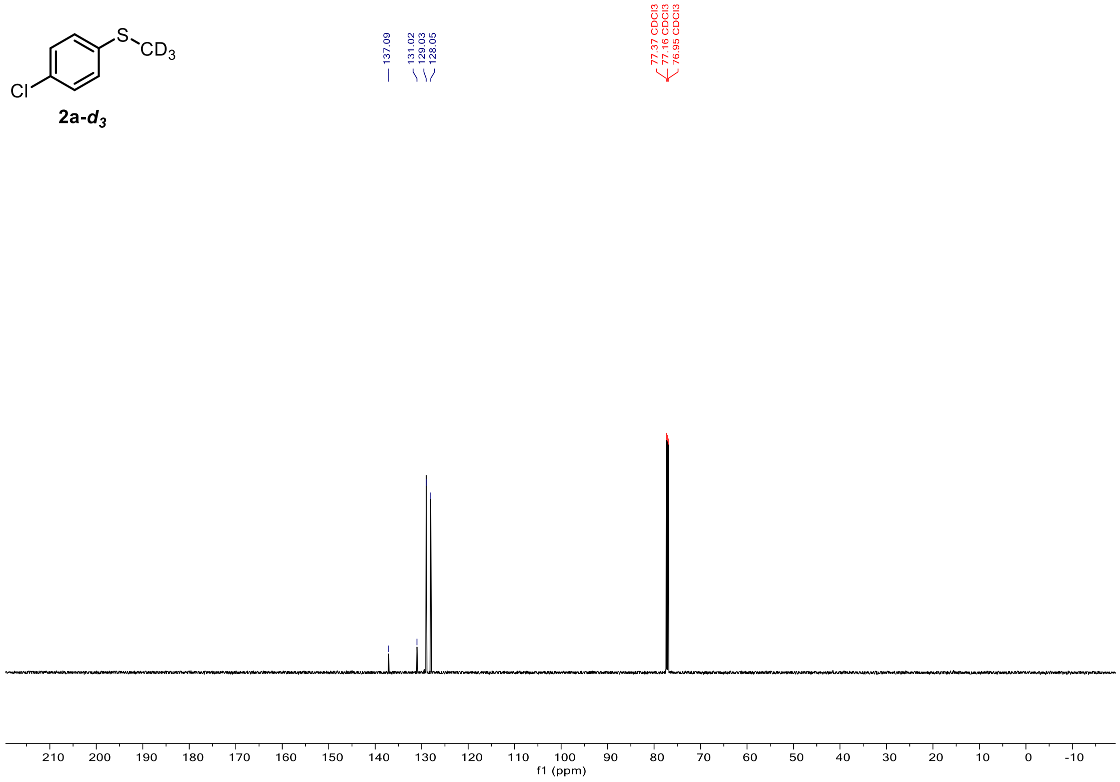
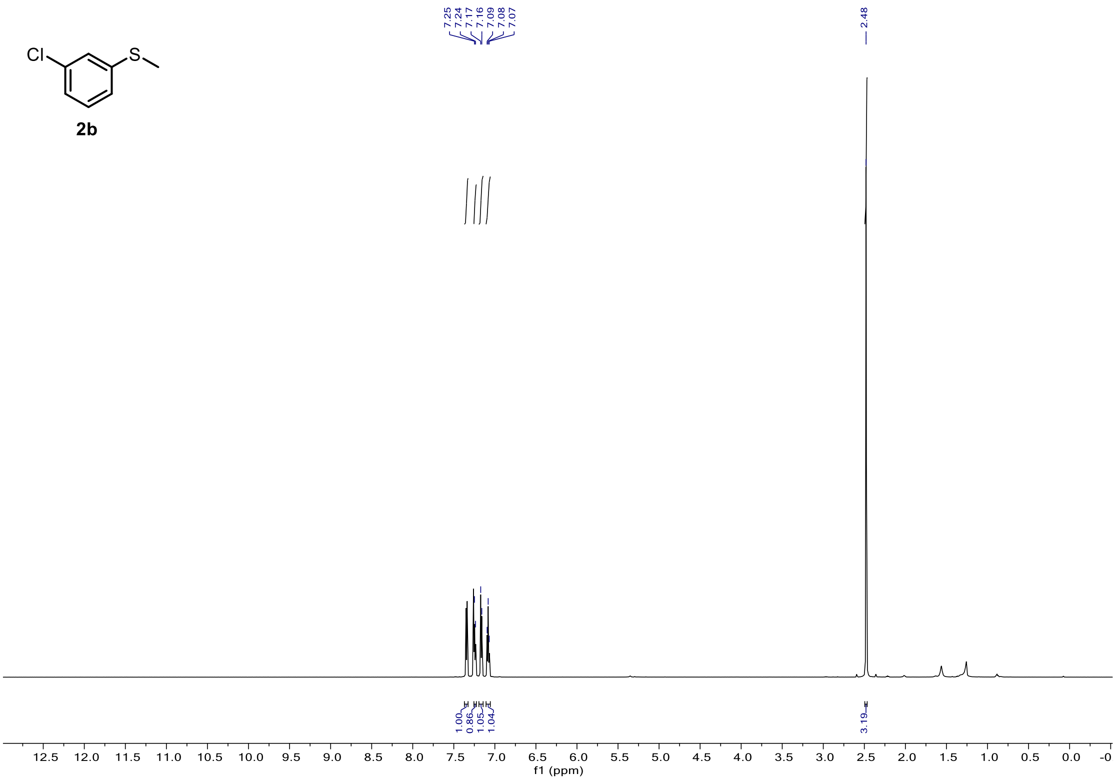
CD3
Cl
2a-d_3
7.28
7.27
7.26
7.21
7.20
7.19
2.08
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


S
CD3
Cl
2a-d_3
137.09
131.02
129.03
128.05
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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S
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7.24
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7.16
7.09
7.08
7.07
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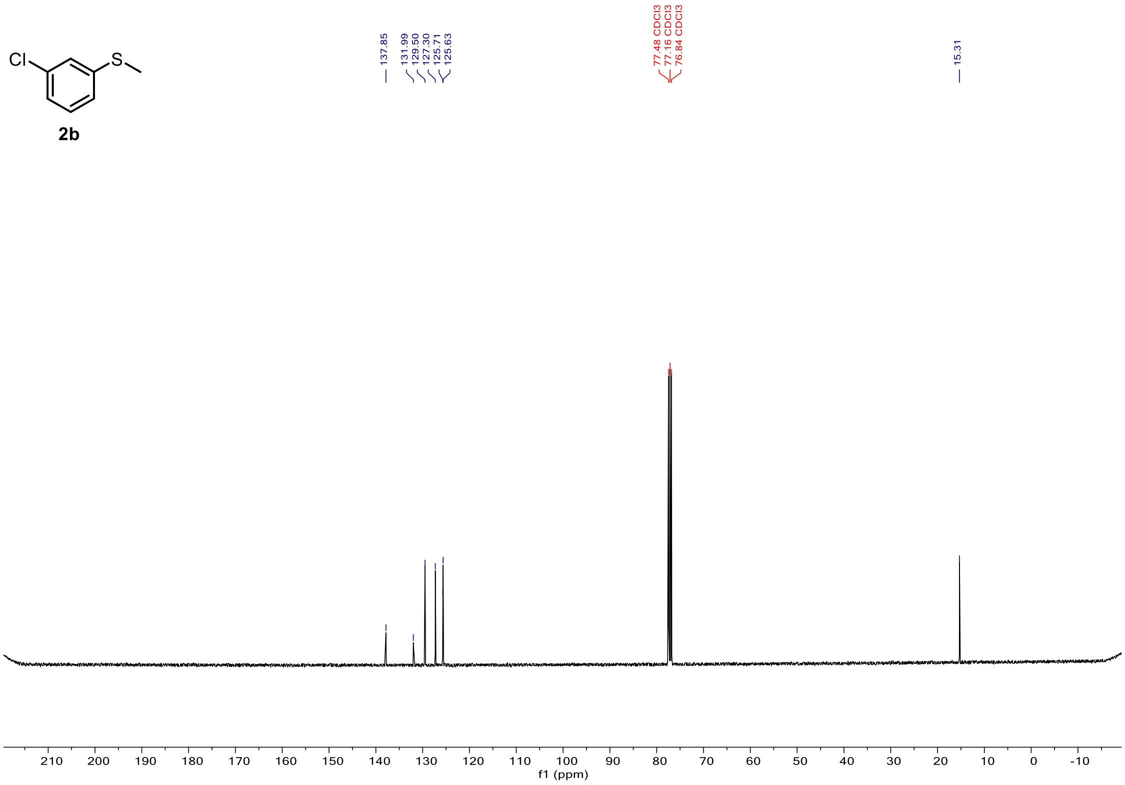
1.00
0.86
1.05
1.04
3.19
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

2b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S
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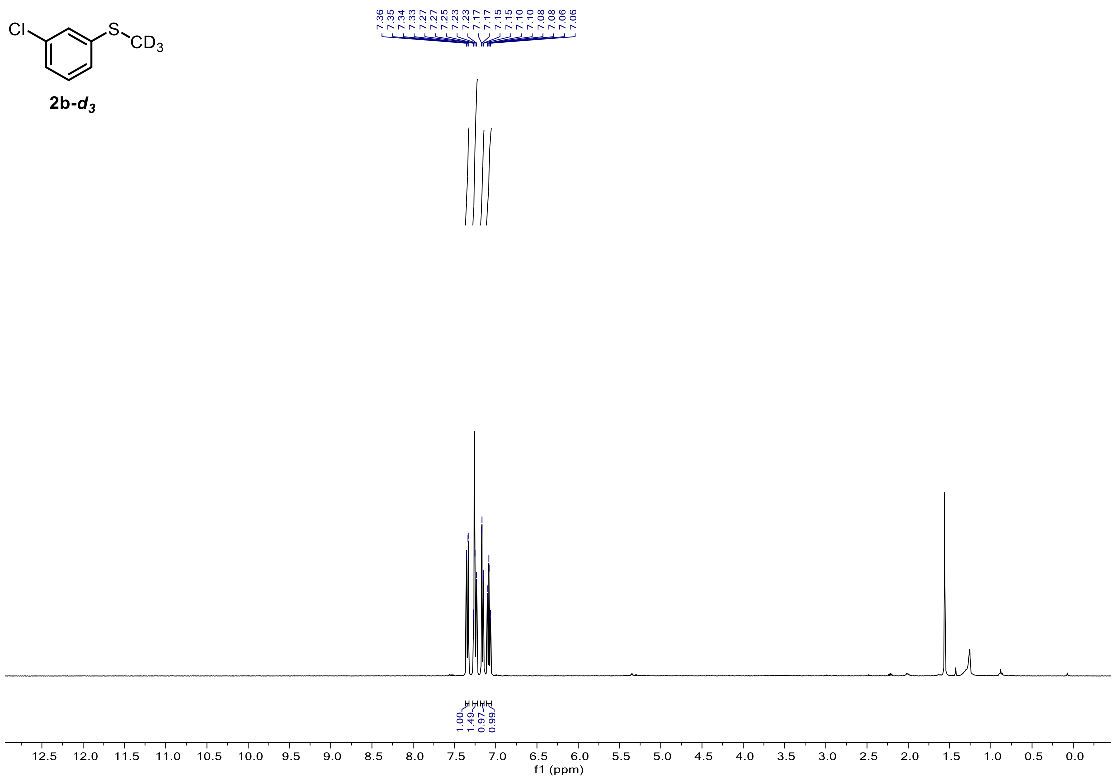
131.99
129.50
127.30
125.71
125.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2b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S
CD3
2b-d3
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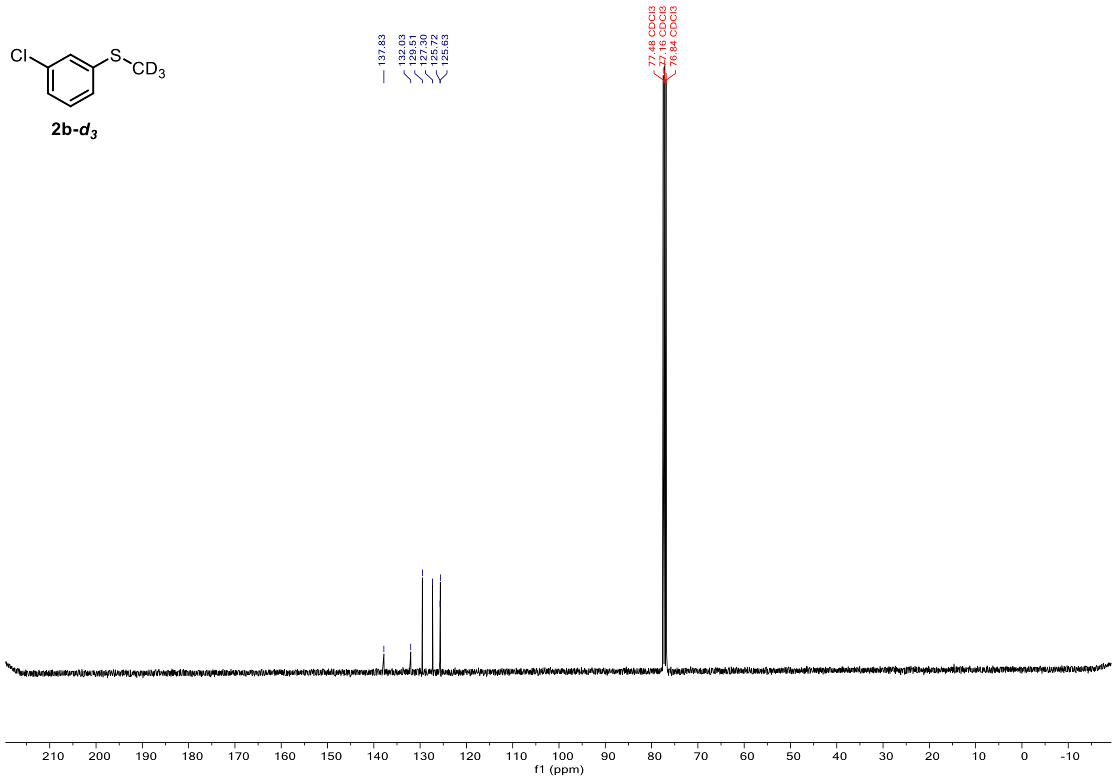
7.35
7.34
7.33
7.27
7.25
7.23
7.23
7.17
7.17
7.15
7.15
7.10
7.10
7.08
7.08
7.06
7.06
1.00
1.49
0.97
0.99
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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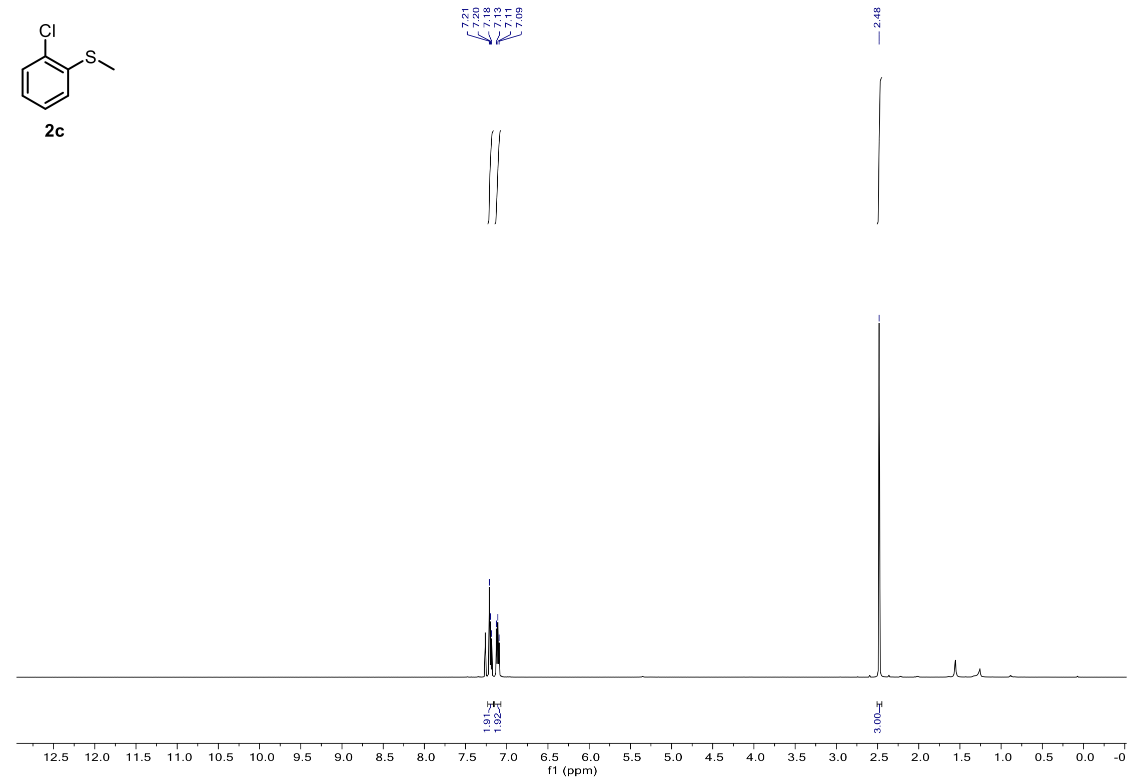
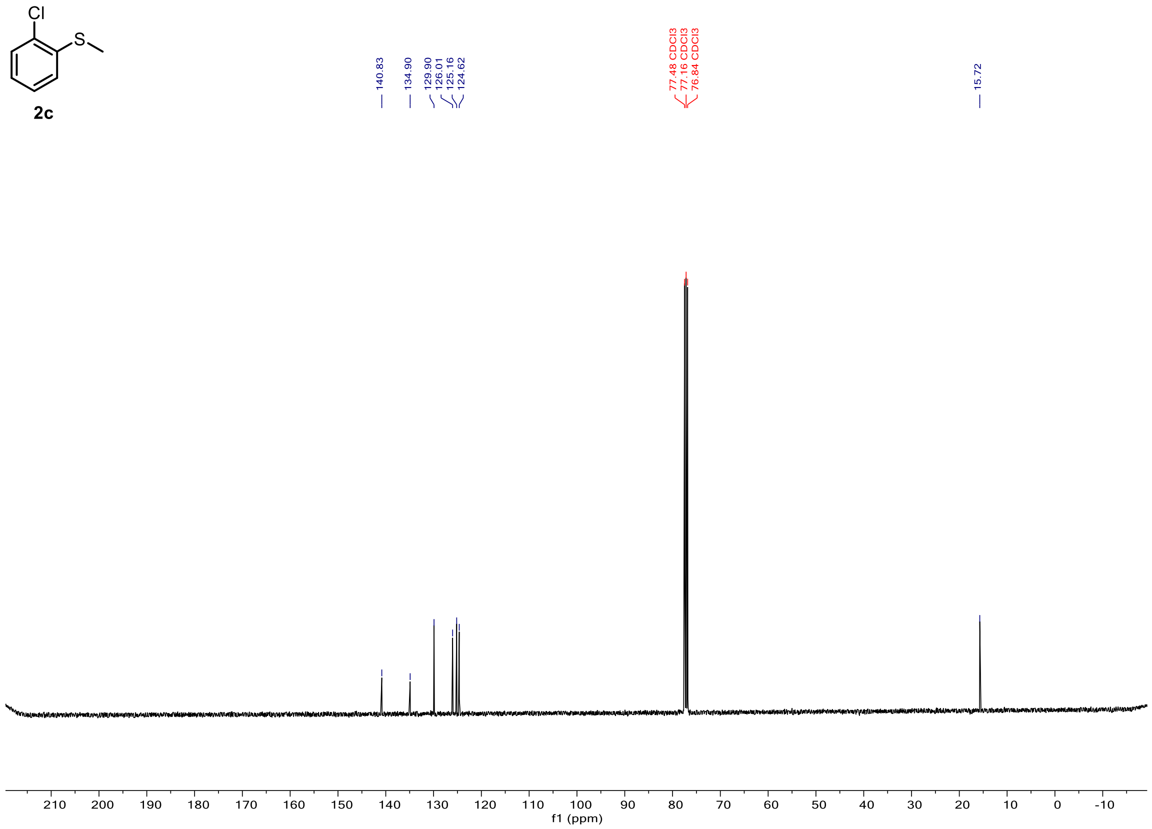
S
CD3
2b-d3
137.83
132.03
129.51
127.30
125.72
125.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



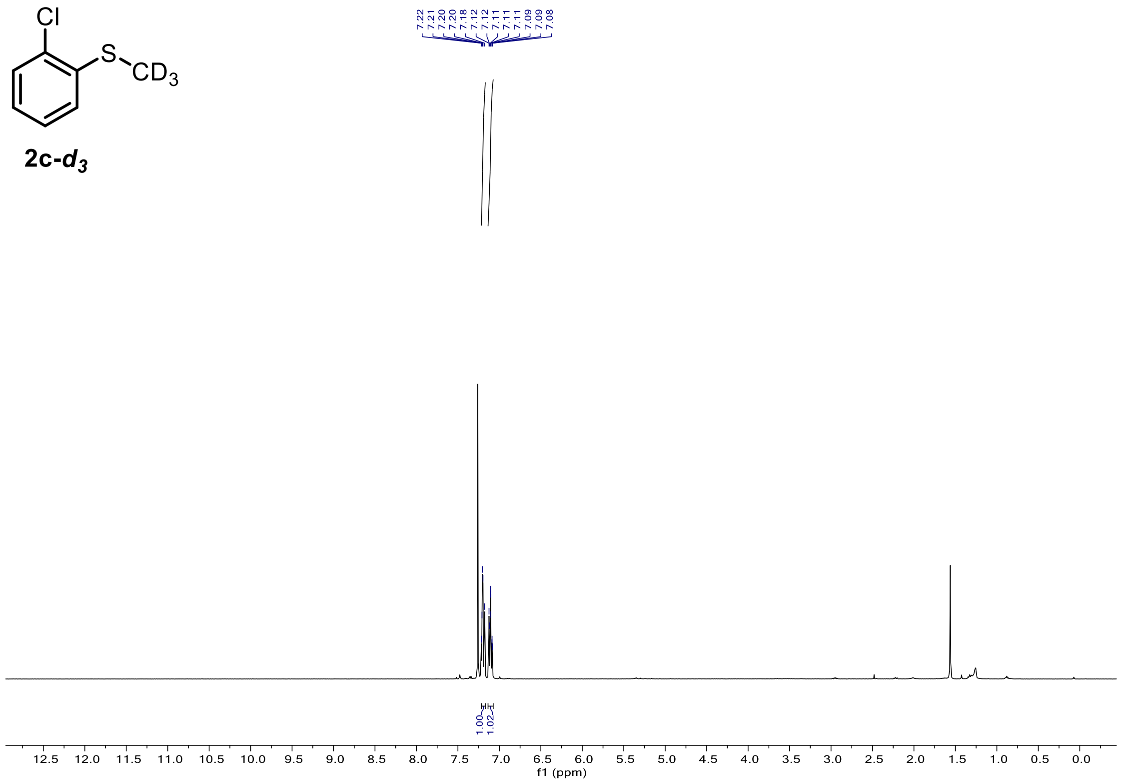
2c

Cl
S
7.21
7.20
7.18
7.13
7.11
7.09
2.48
1.91
1.92
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)



2c

Cl
S
140.83
134.90
129.90
126.01
125.16
124.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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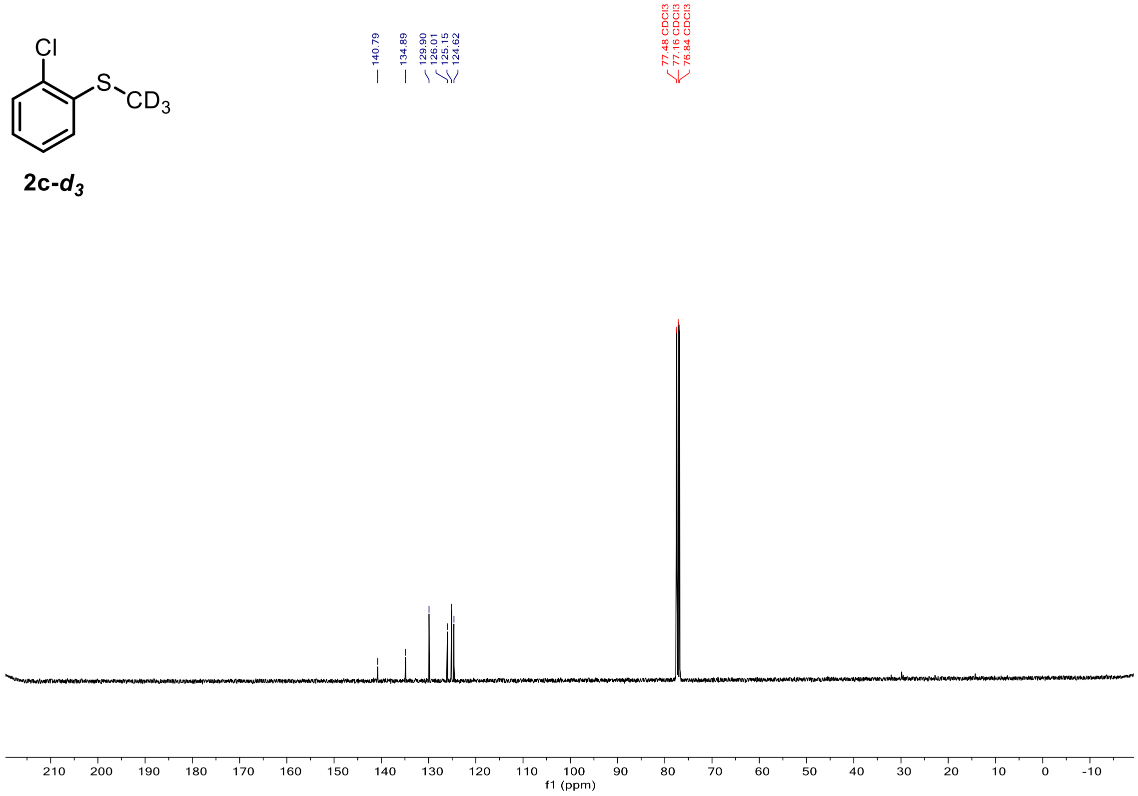
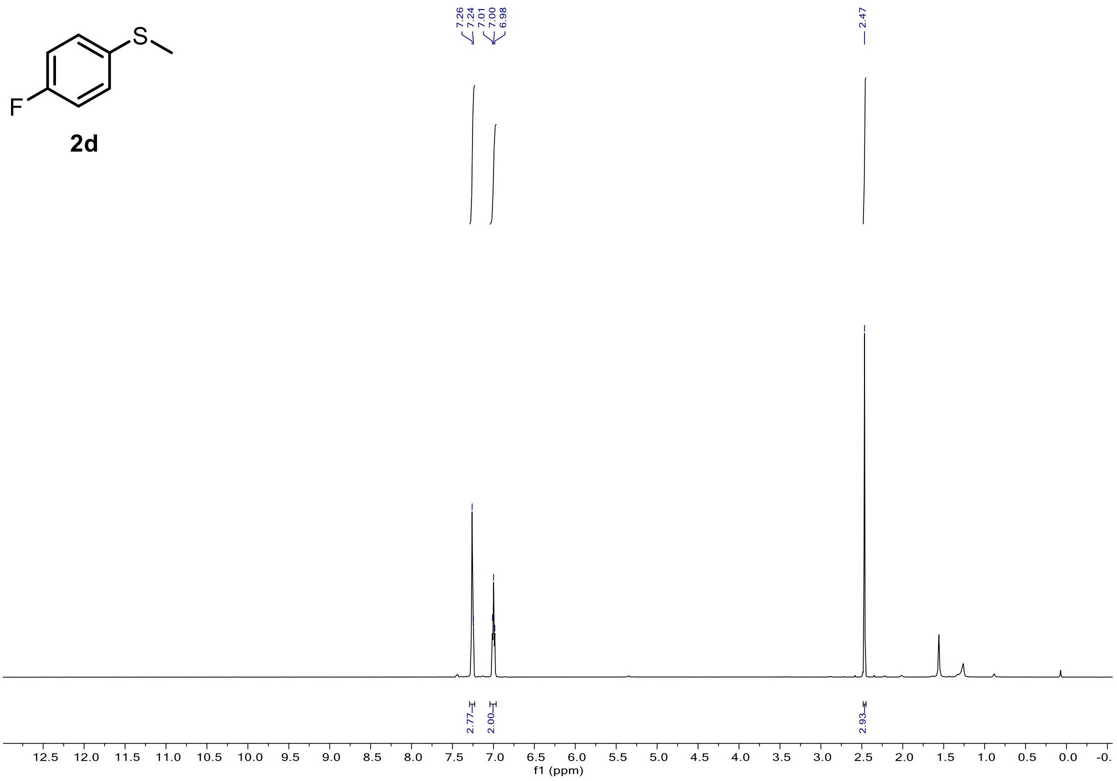
S
CD3
7.22
7.21
7.20
7.20
7.18
7.12
7.12
7.11
7.11
7.11
7.09
7.09
7.08
1.00
1.02
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

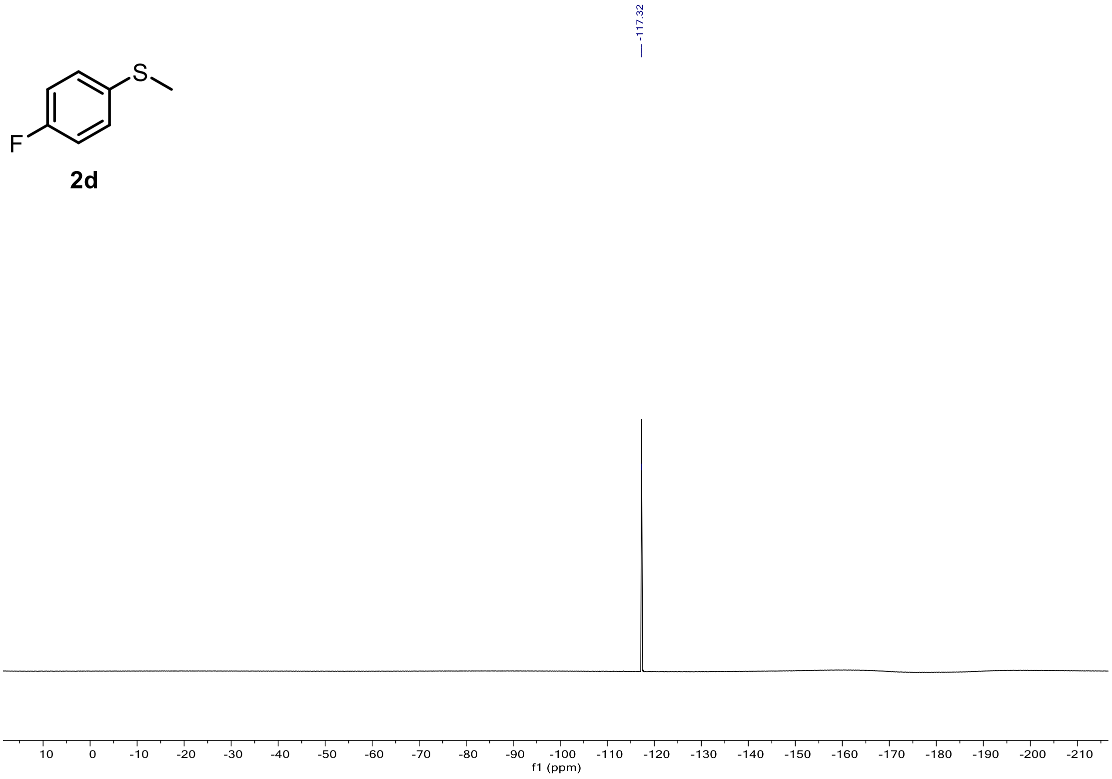
2c-*d*$_3$


Cl
S
CD3
140.79
134.89
129.90
126.01
125.15
124.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

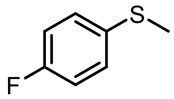
2c-*d*$_3$


S
F
7.26
7.24
7.01
7.00
6.98
2.47
2.77
2.00
2.93
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

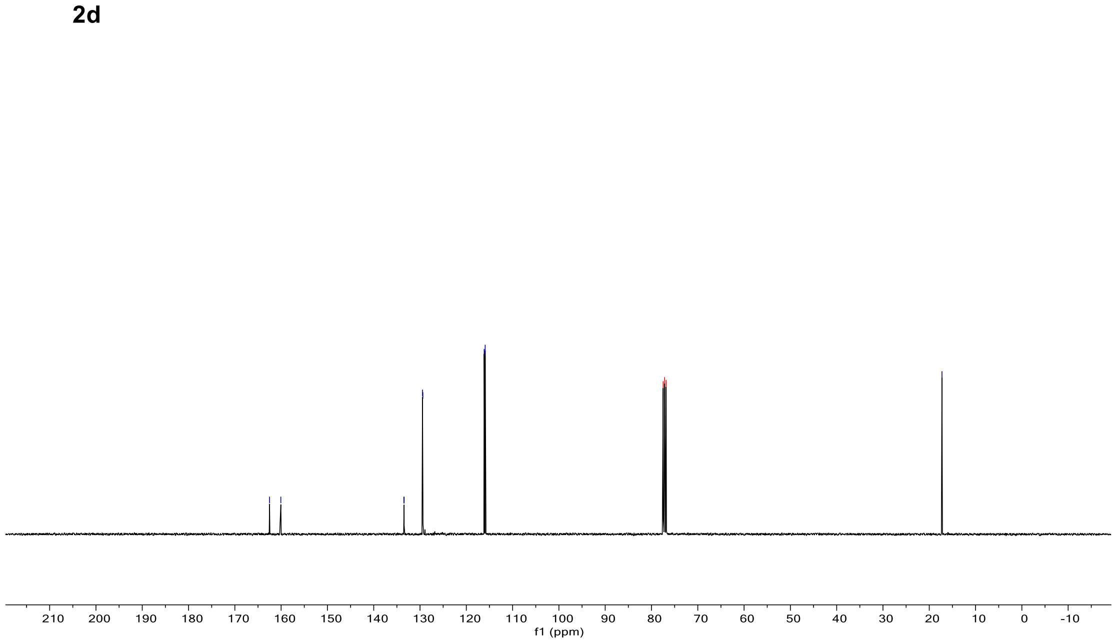
2d


S
F
-117.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

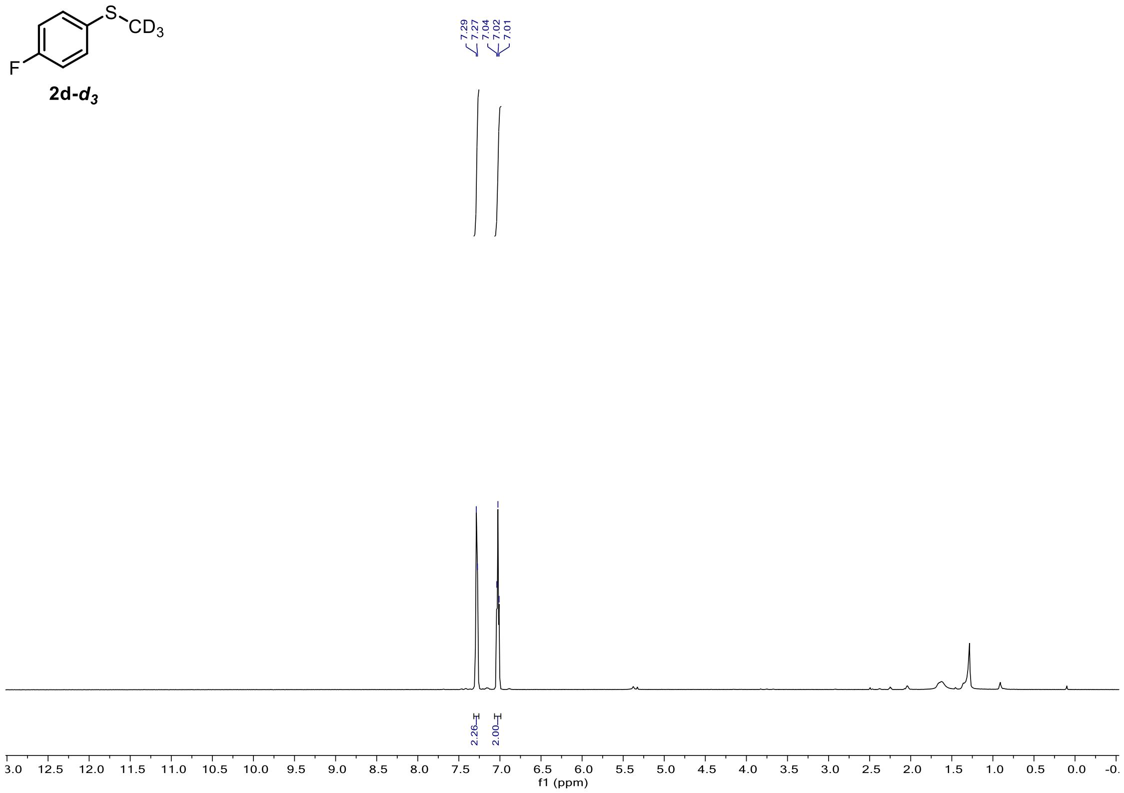
2d



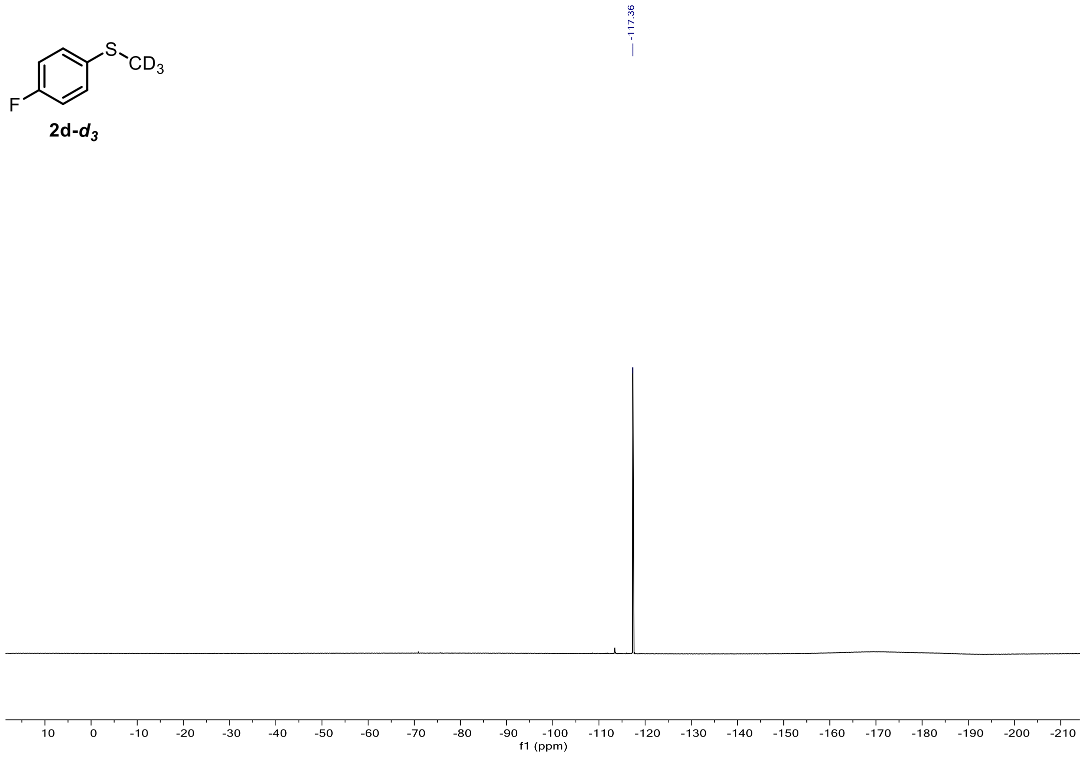
2d



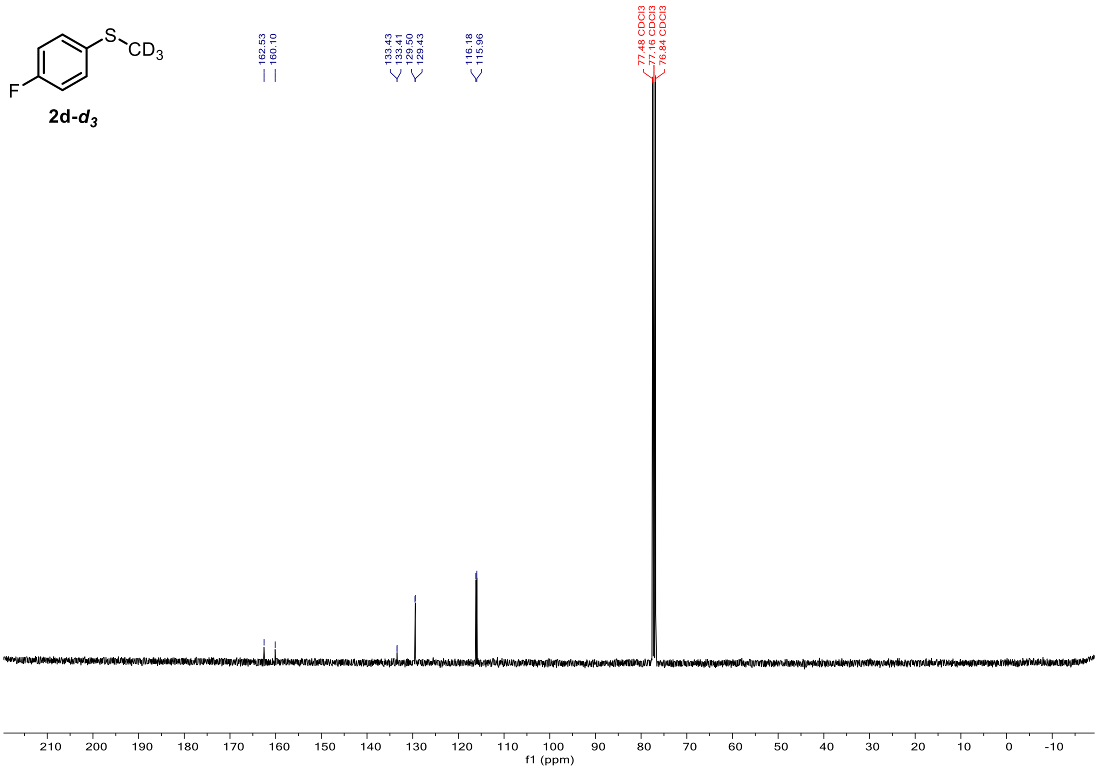
162.50
160.07
133.47
133.44
129.46
129.38
116.14
115.92
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
17.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

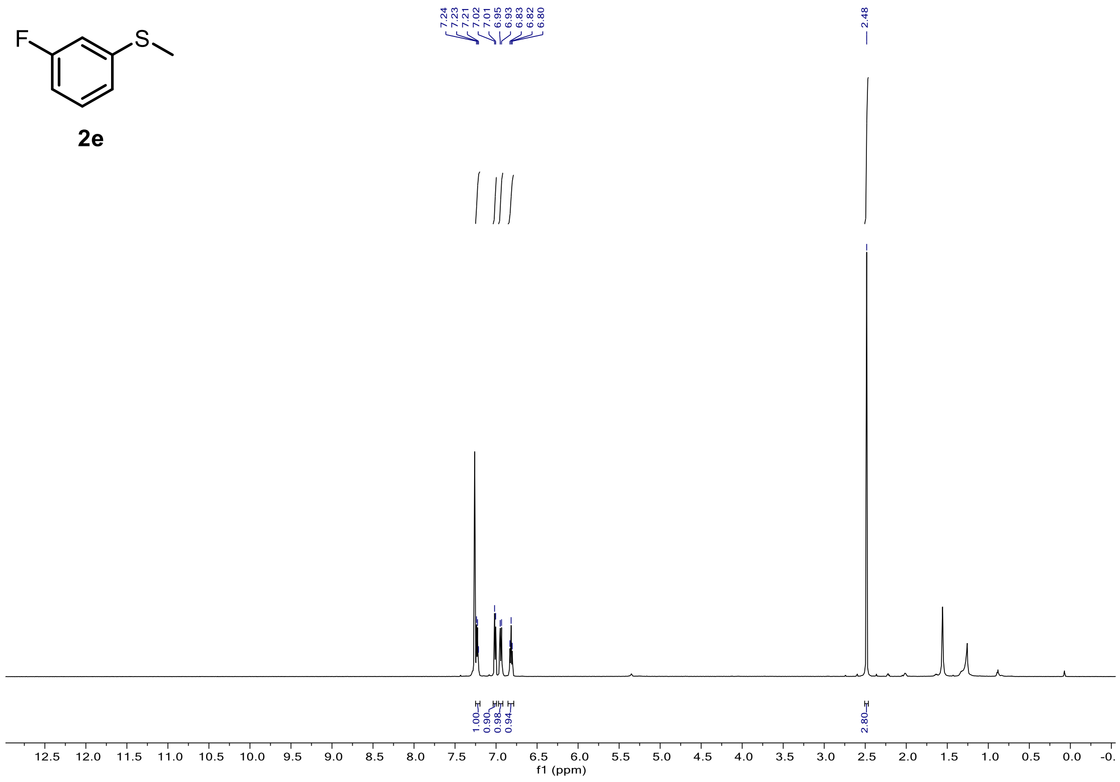

2d-d_3

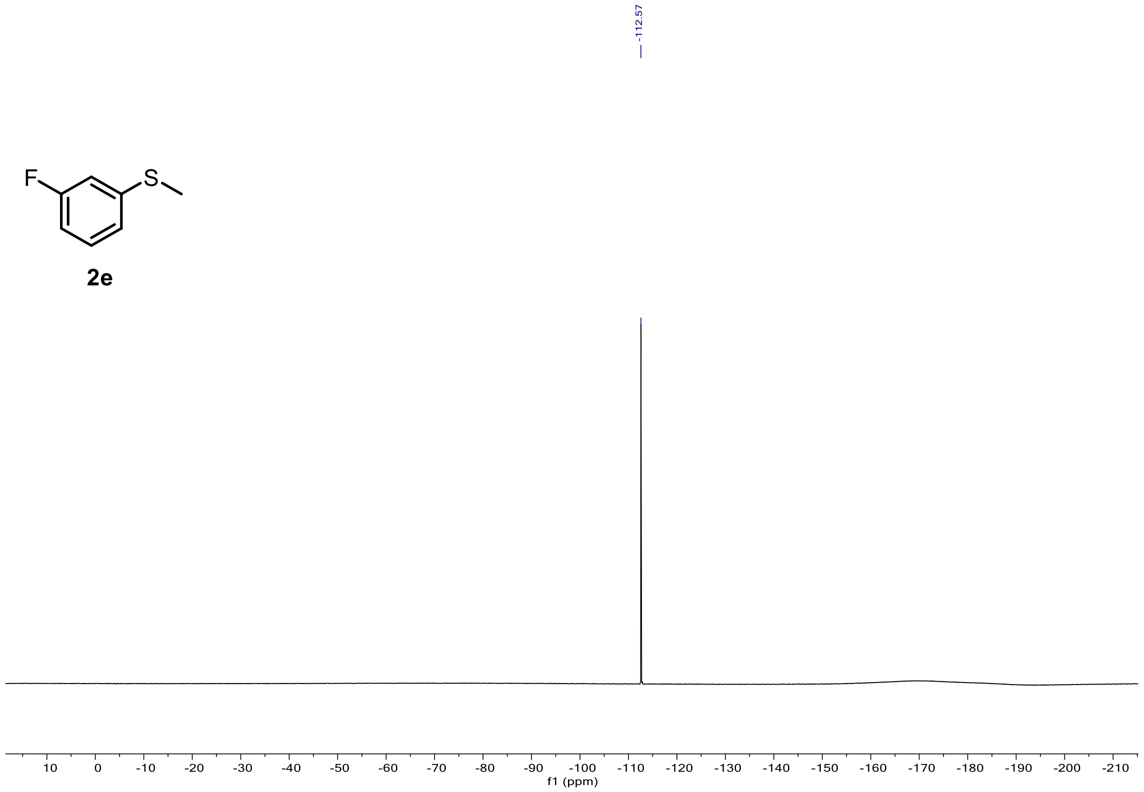
S
CD3
F
7.29
7.27
7.04
7.02
7.01
2.26
2.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


2d-d_3

S
CD3
F
-117.36
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


S
CD3
F
2d-d3
162.53
160.10
133.43
133.41
129.50
129.43
116.18
115.96
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
S
2e
7.24
7.23
7.21
7.02
7.01
6.95
6.93
6.83
6.82
6.80
2.48
1.00
0.90
0.98
0.94
2.80
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)


-112.57
F
S
2e
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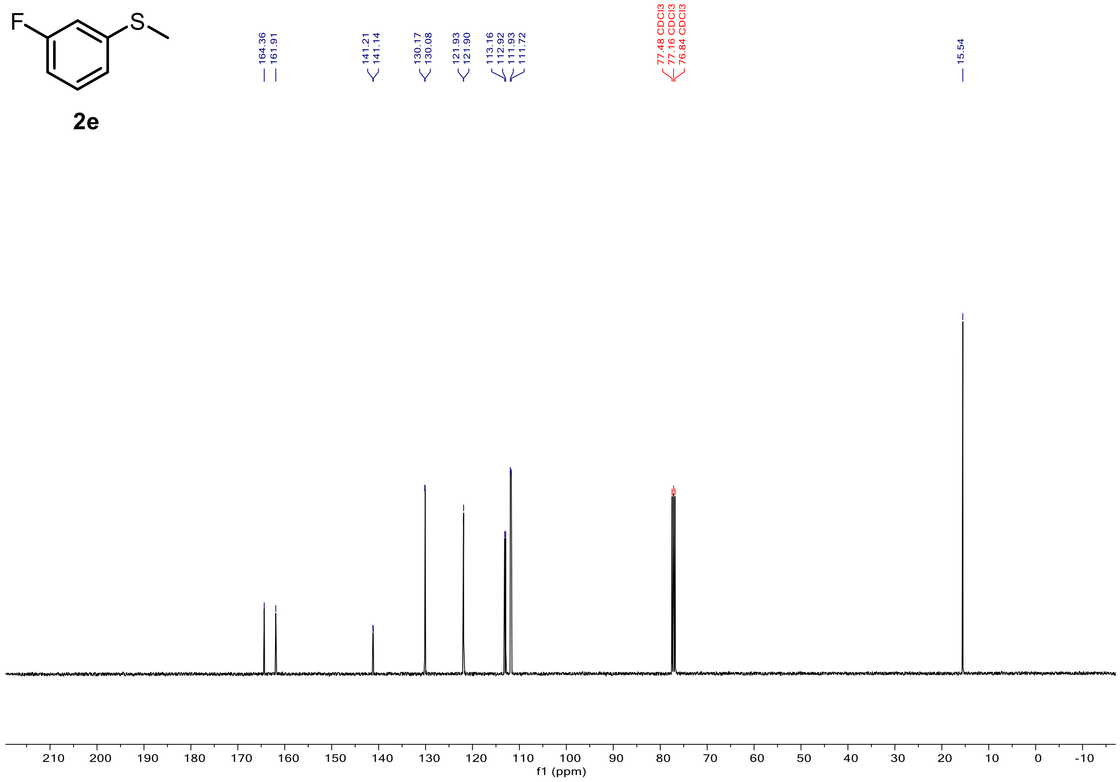
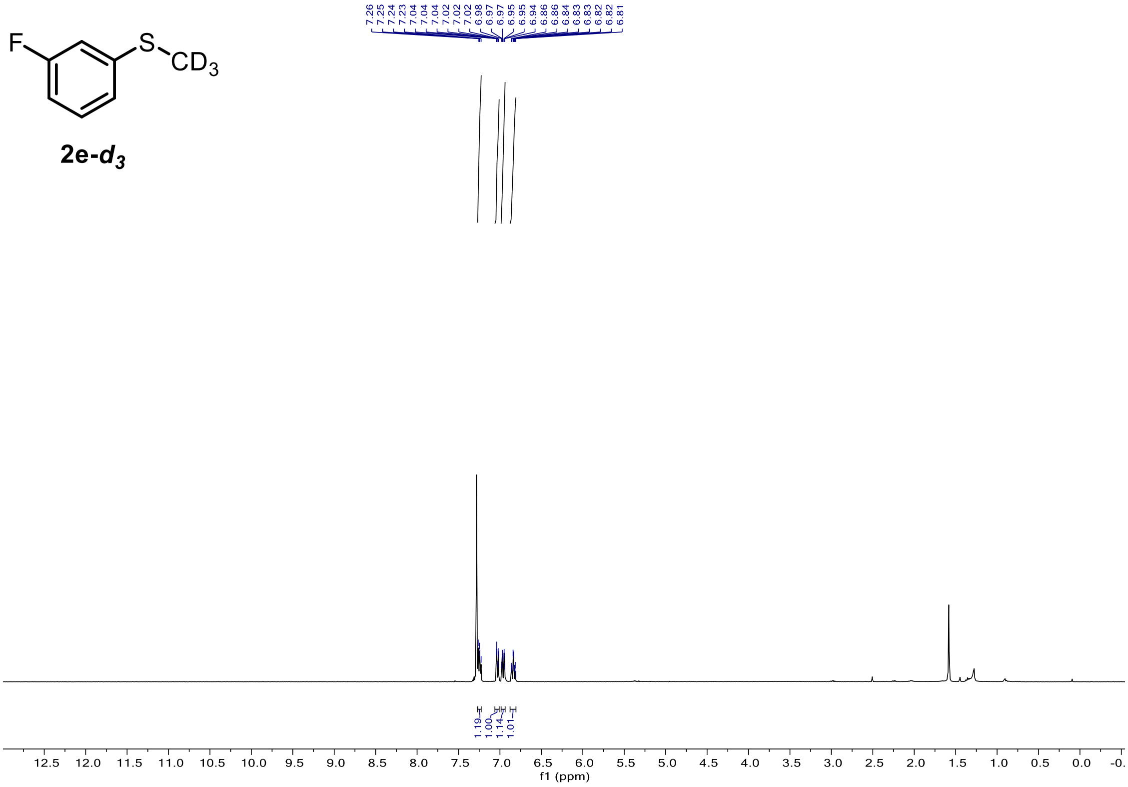
f1 (ppm)



2e

F
S
164.36
161.91
141.21
141.14
130.17
130.08
121.93
121.90
113.16
112.92
111.93
111.72
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2e-d_3

7.26
7.25
7.24
7.23
7.04
7.04
7.04
7.02
7.02
7.02
6.98
6.97
6.97
6.95
6.95
6.94
6.86
6.86
6.84
6.83
6.83
6.82
6.82
6.81
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1.14
1.01
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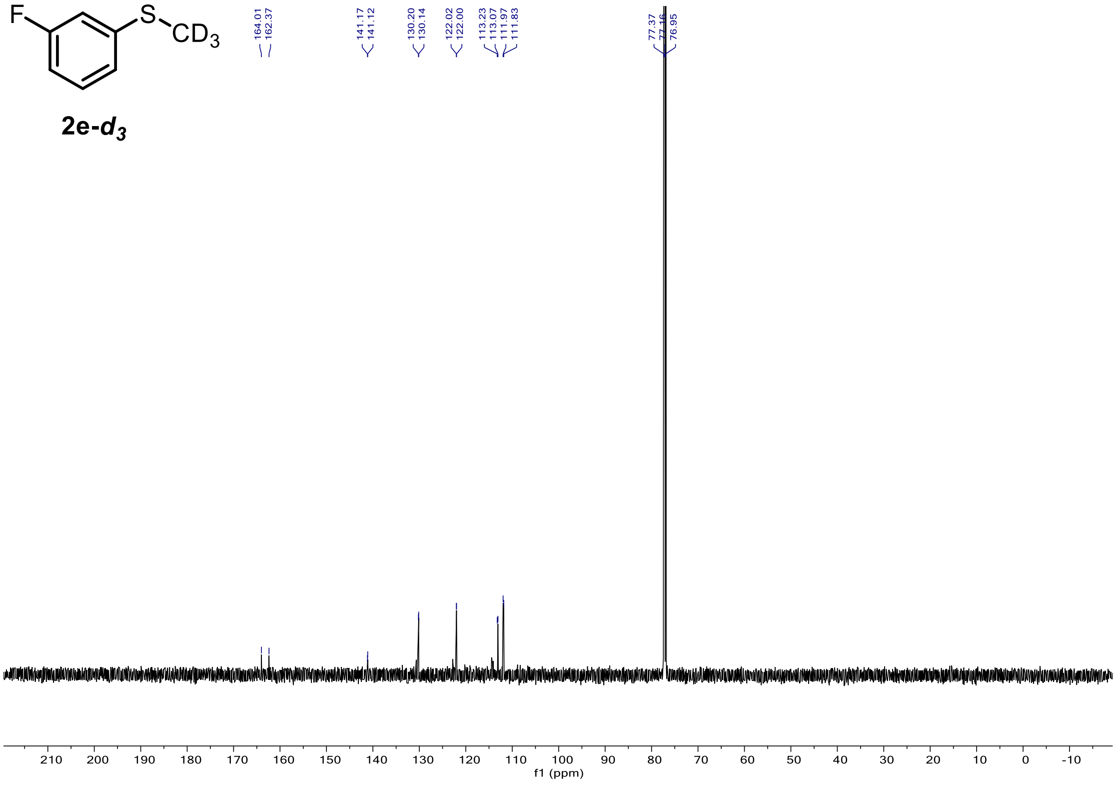
f1 (ppm)
F
S
CD3



2e-d_3

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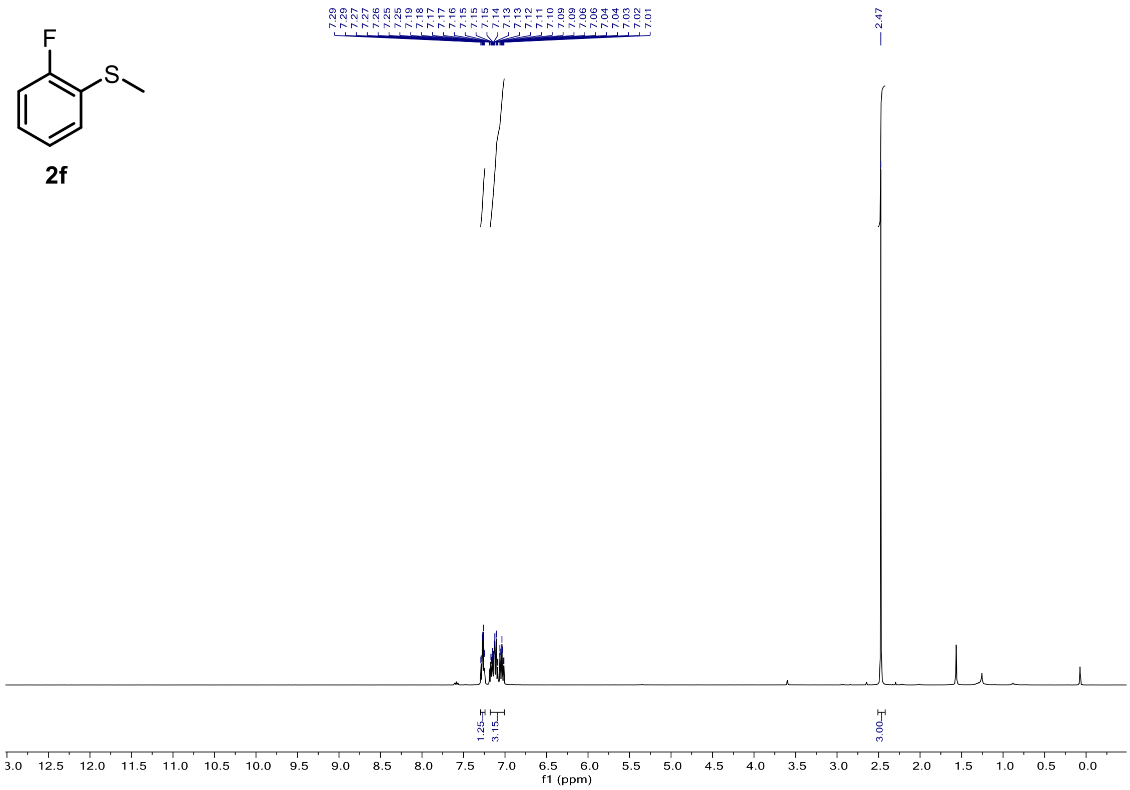
162.37
141.17
141.12
130.20
130.14
122.02
122.00
113.23
113.07
111.97
111.83
77.37
77.16
76.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
F
S
CD3


2f

F
S
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7.27
7.27
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7.25
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7.19
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7.16
7.15
7.15
7.15
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7.13
7.12
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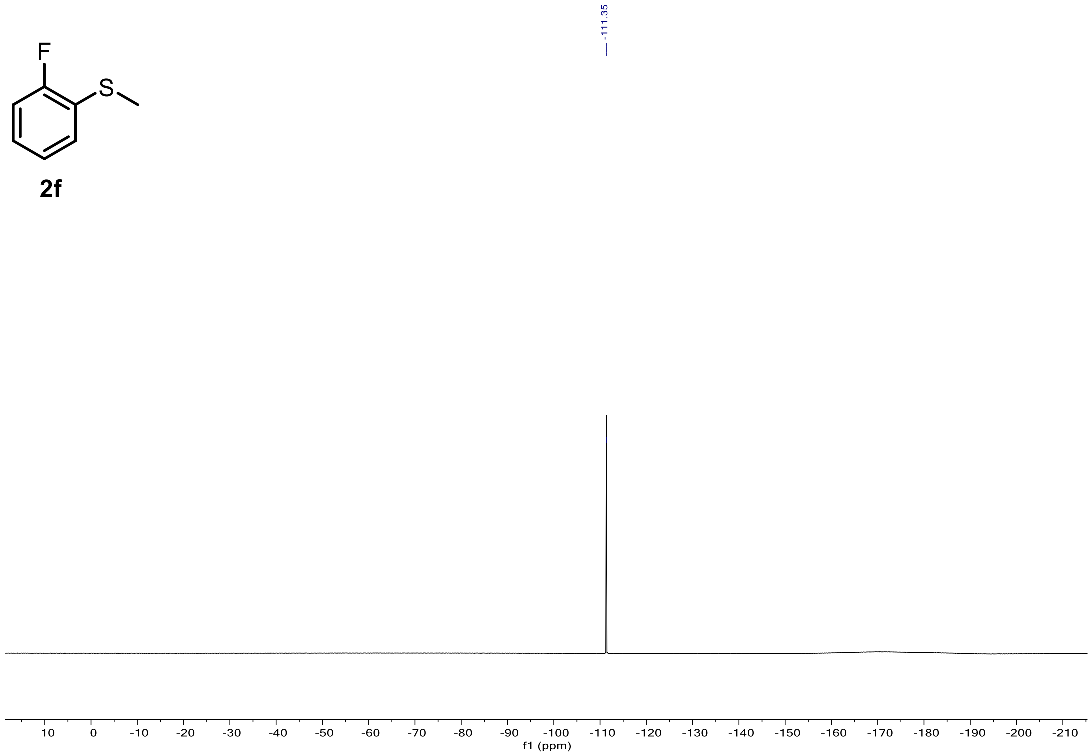
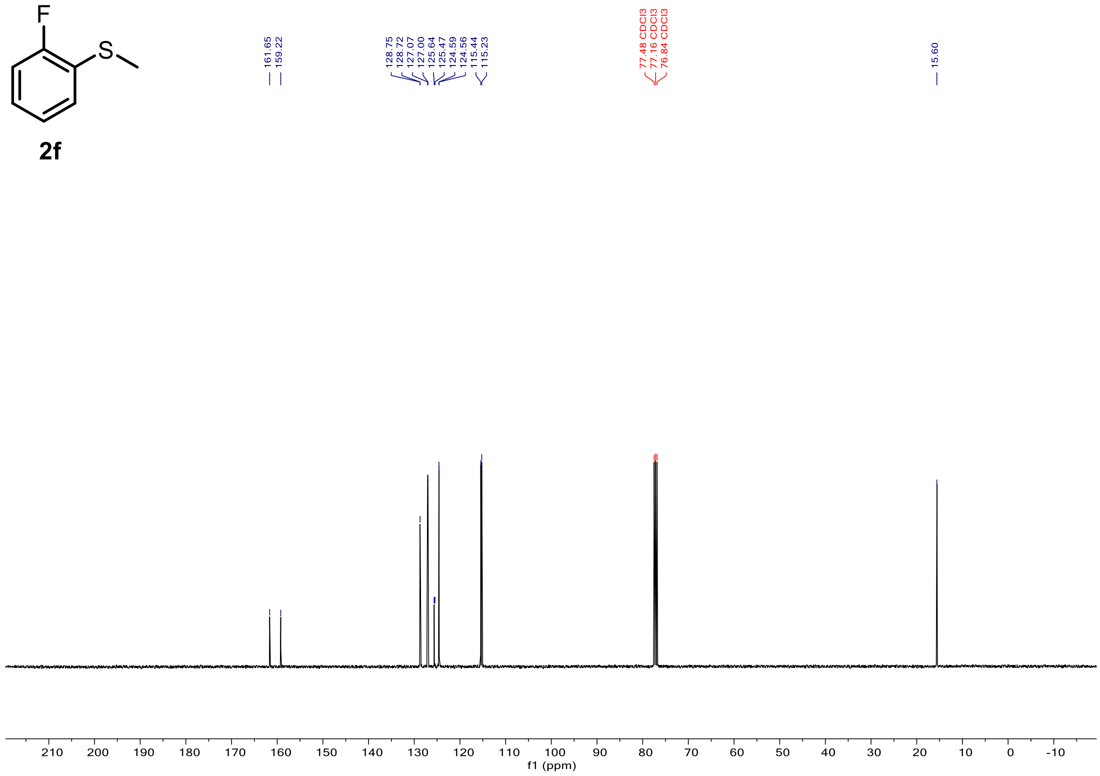
7.10
7.09
7.09
7.06
7.06
7.04
7.04
7.03
7.02
7.01
2.47
1.25
3.15
3.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

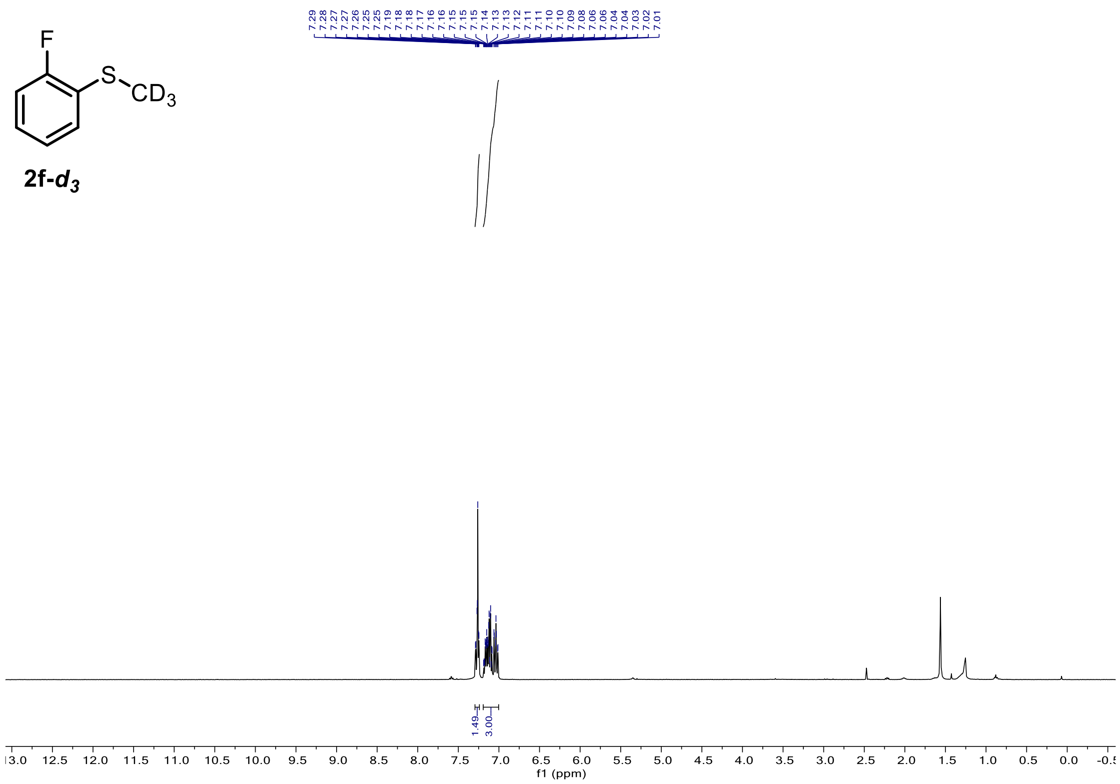

2f

F
S
-111.35
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



2f

161.65
159.22
128.75
128.72
127.07
127.00
125.64
125.47
124.59
124.56
115.44
115.23
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.60
F
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


F
S
CD3
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7.25
7.25
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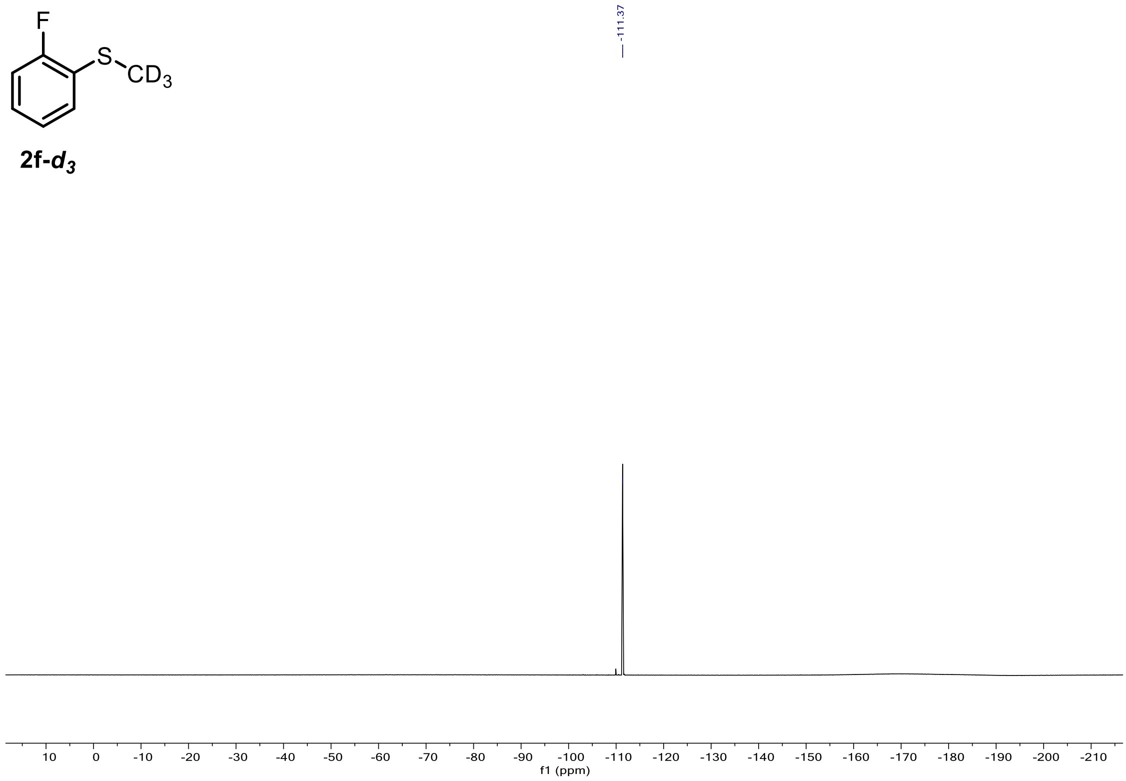
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.15
7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
7.06
7.06
7.04
7.04
7.03
7.02
7.01
1.49
3.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

2f-*d*$_3$


F
S
CD3
-111.37
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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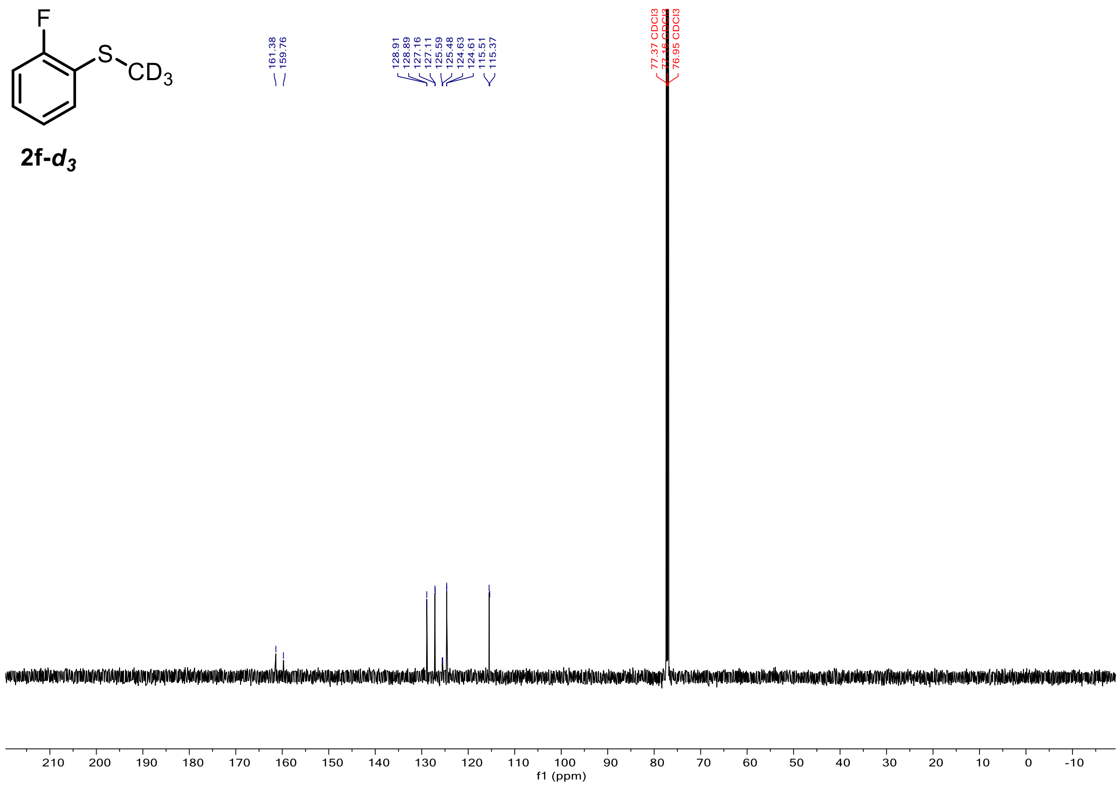
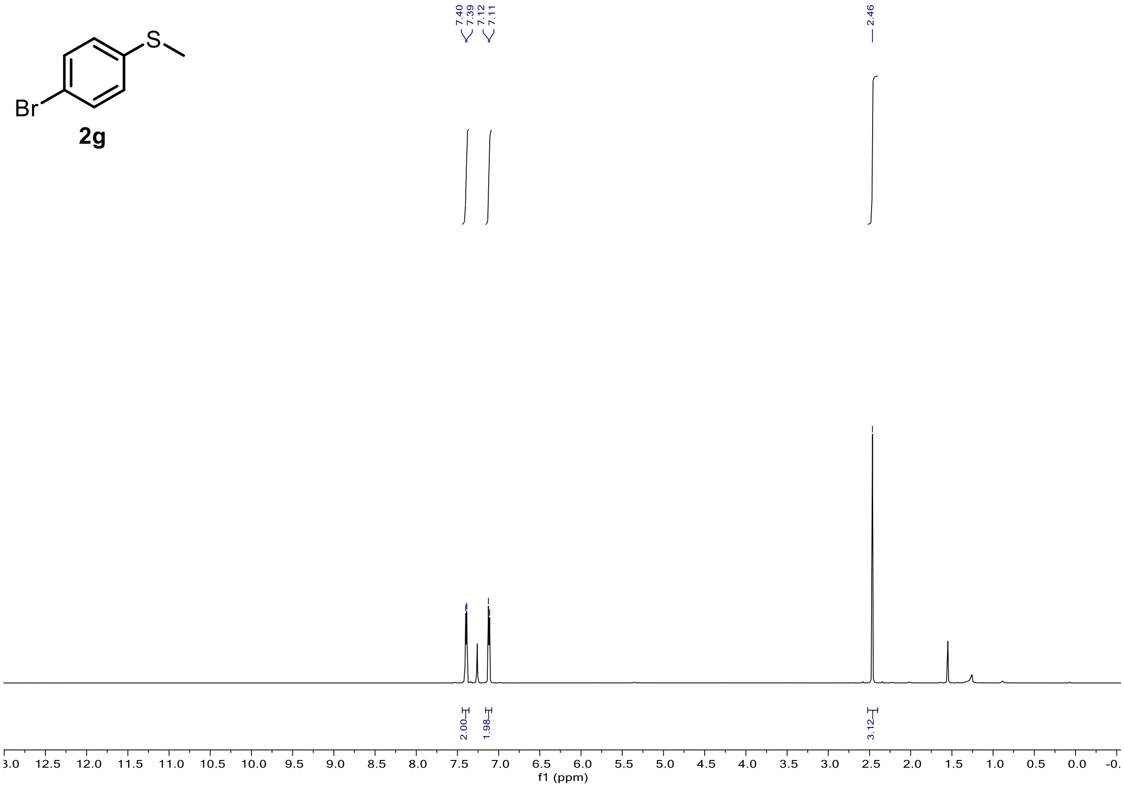
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

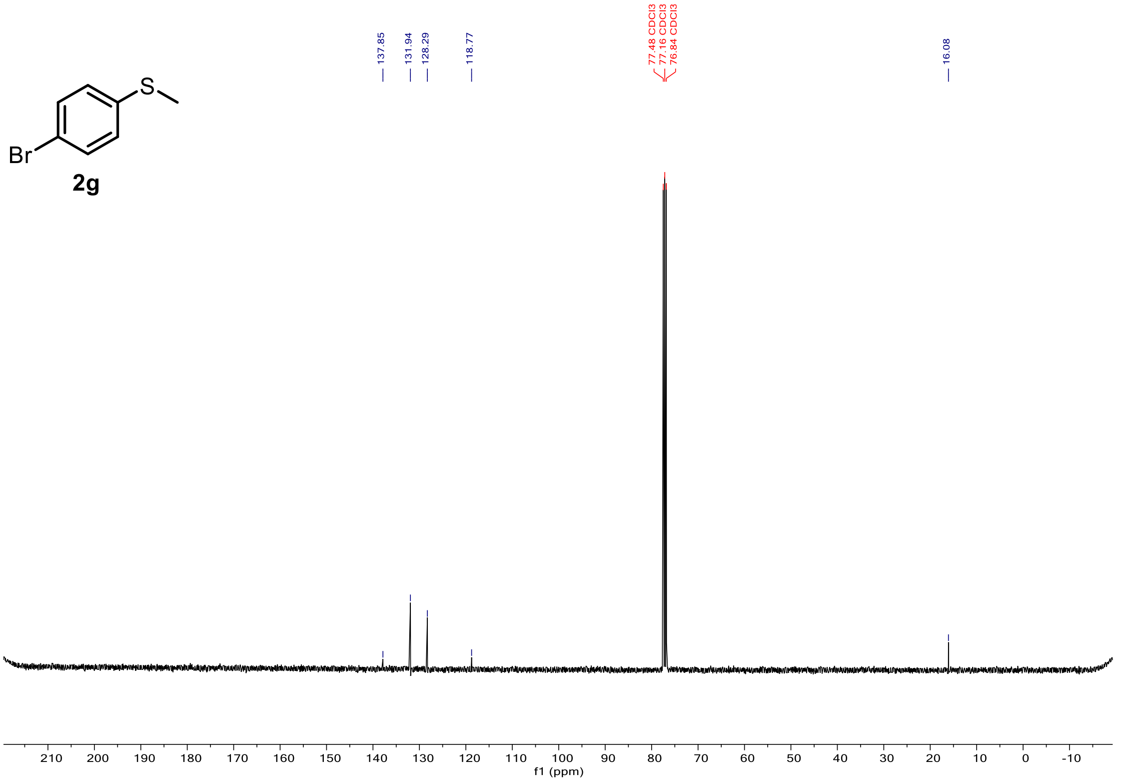
2f-*d*$_3$

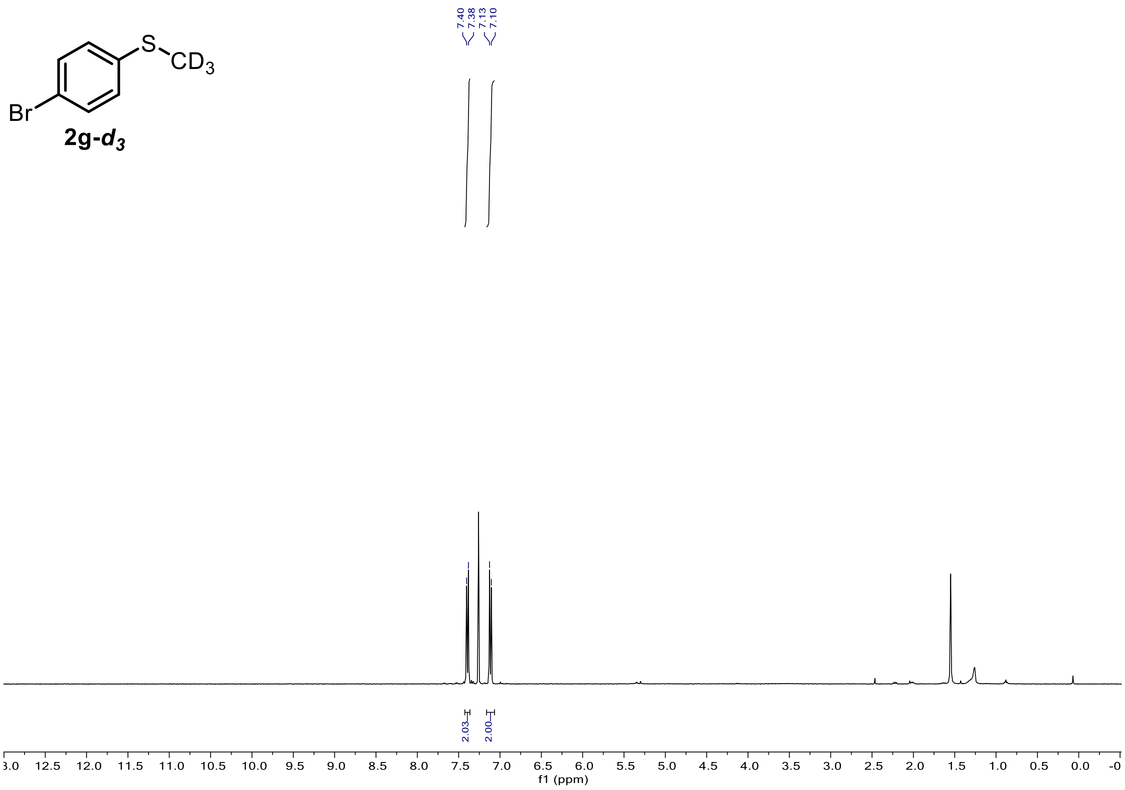

F
S
CD3

2f-d_3

161.38
159.76
128.91
128.89
127.16
127.11
125.59
125.48
124.63
124.61
115.51
115.37
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

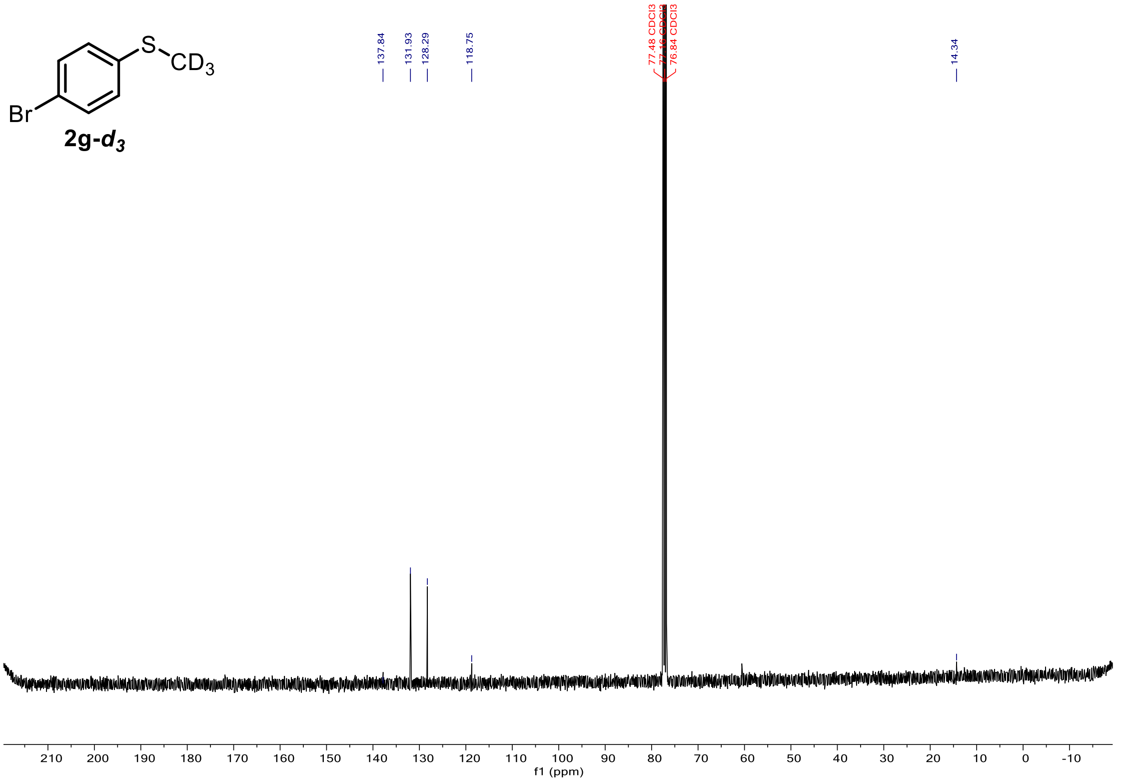

Br
S
2g
7.40
7.39
7.12
7.11
2.46
2.00
1.98
3.12
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


Br
S
2g
137.85
131.94
128.29
118.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
16.08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



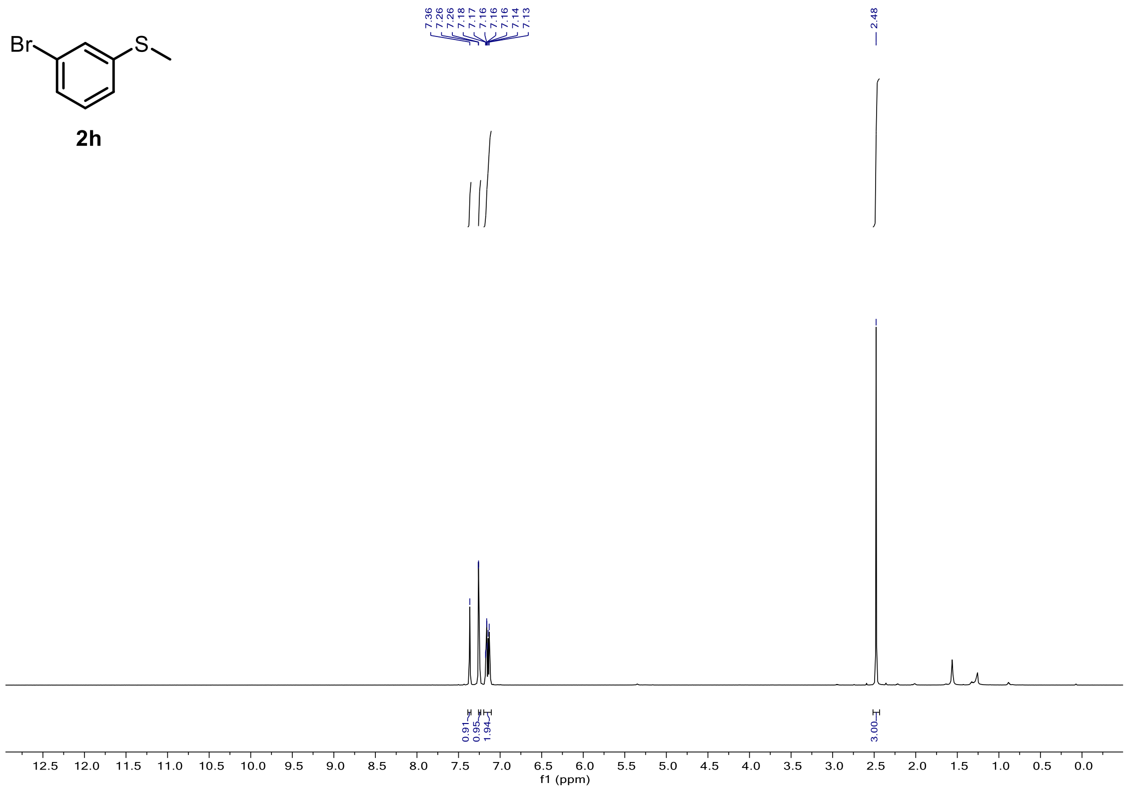
2g-d_3

S
CD3
Br
7.40
7.38
7.13
7.10
2.03
2.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

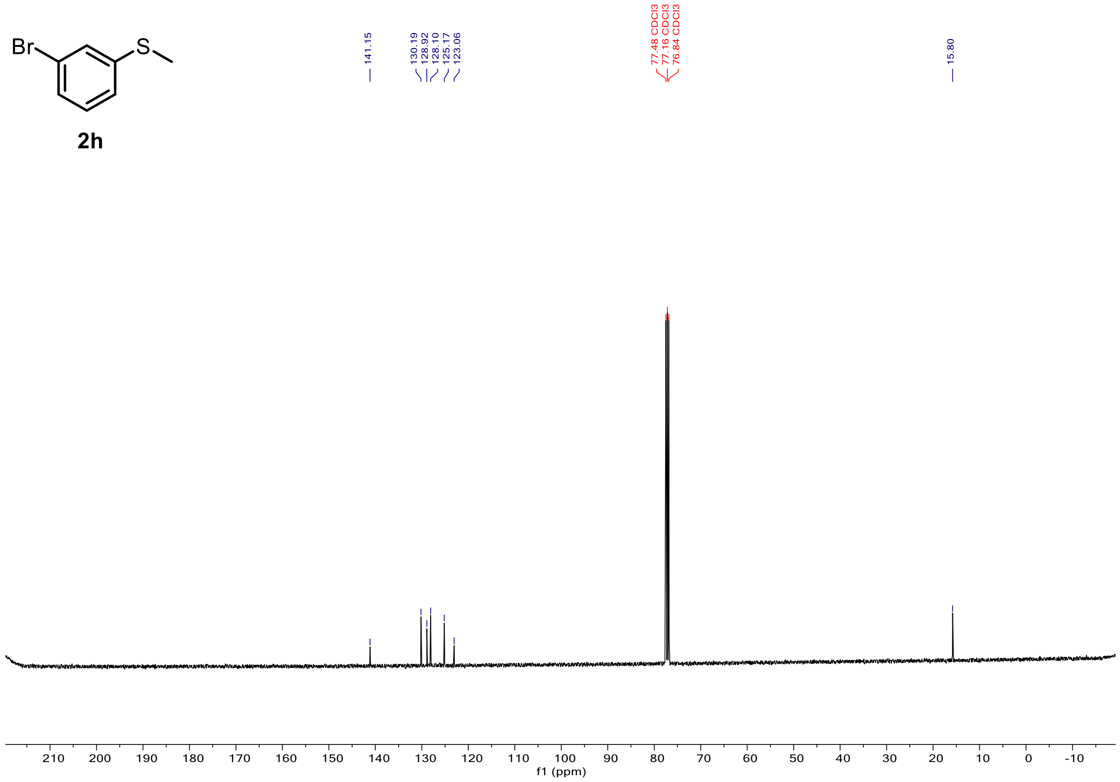


2g-d_3

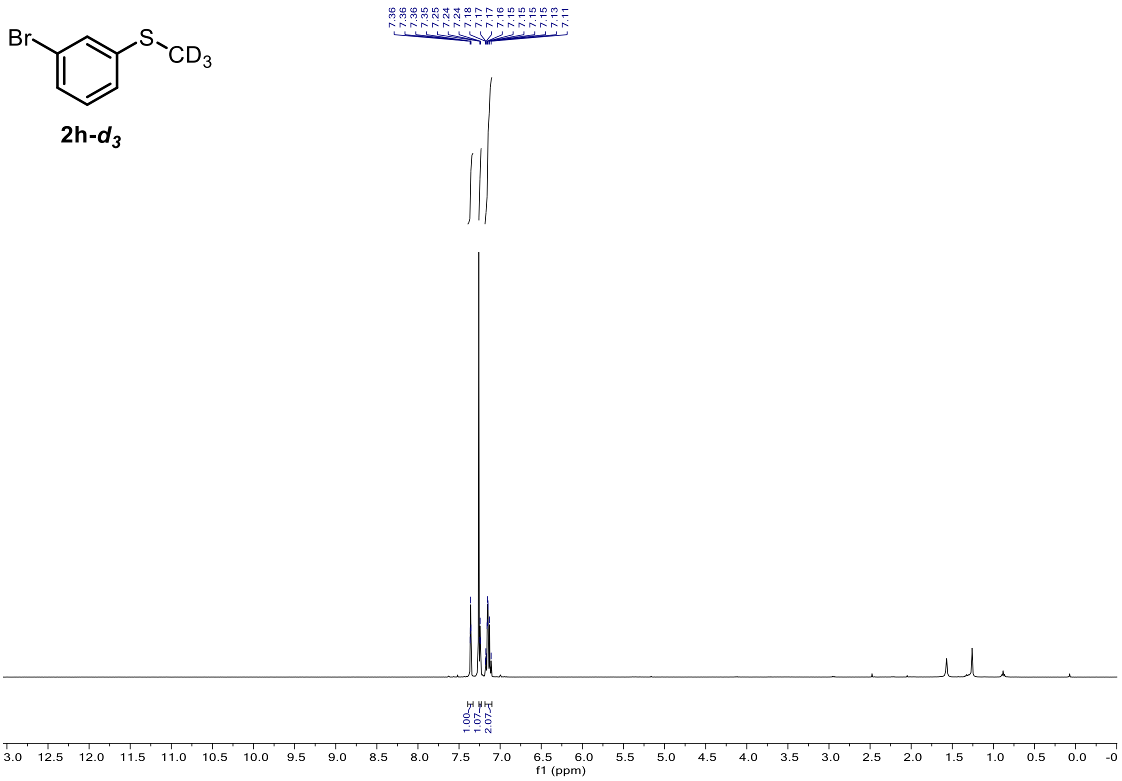
S
CD3
Br
137.84
131.93
128.29
118.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
14.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

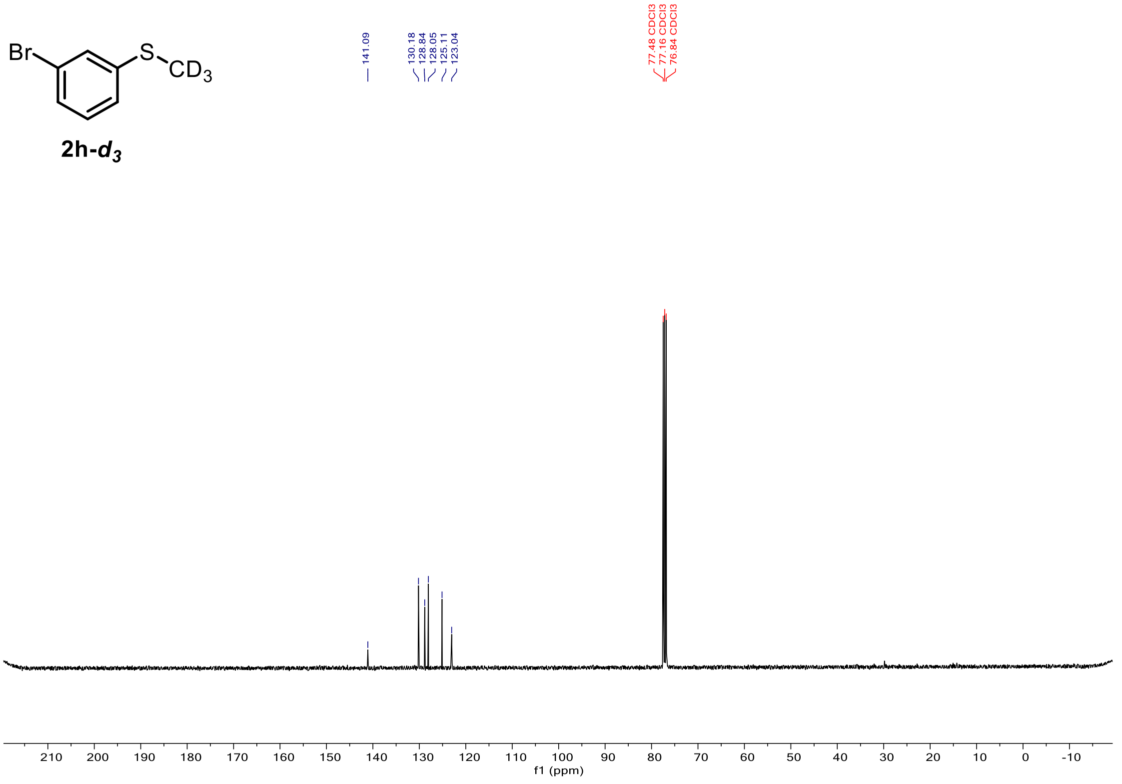

Br
S
7.36
7.26
7.26
7.18
7.17
7.16
7.16
7.16
7.14
7.13
2.48
0.91
0.95
1.94
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

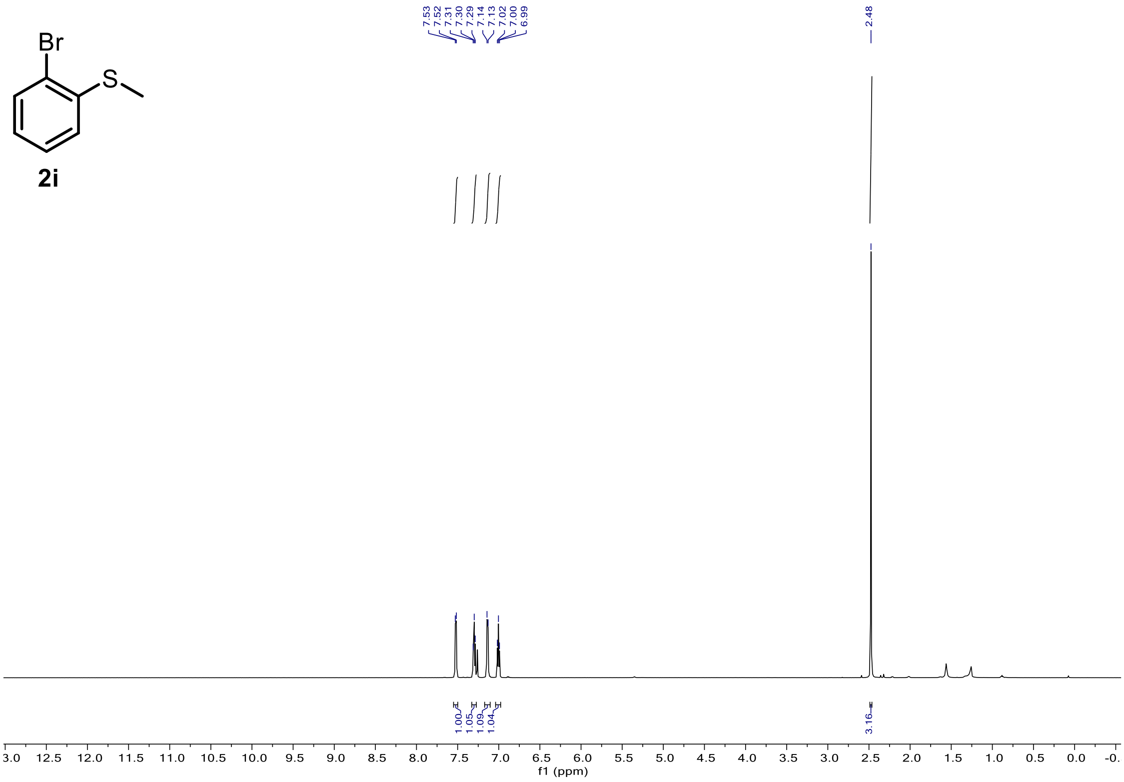
2h


Br
S
141.15
130.19
128.92
128.10
125.17
123.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2h

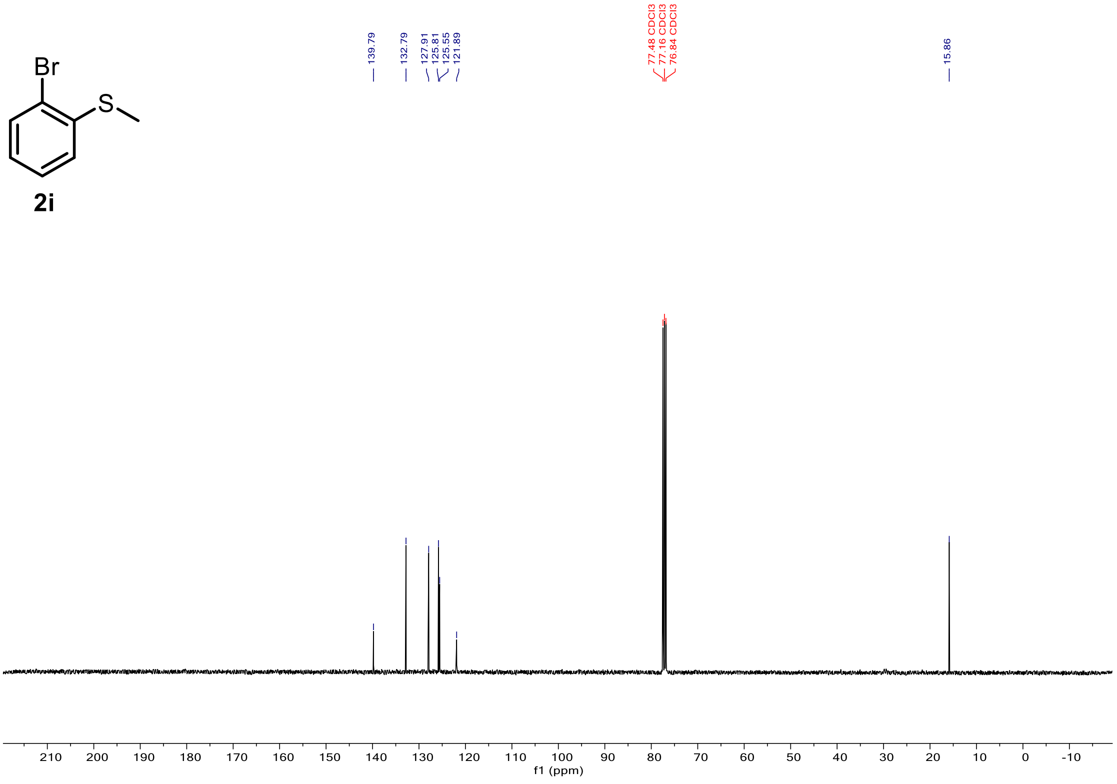

2h-*d*$_3$
Br
S
CD3
7.36
7.36
7.36
7.35
7.25
7.24
7.24
7.18
7.17
7.17
7.16
7.15
7.15
7.15
7.15
7.13
7.11
1.00
1.07
2.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


2h-*d*$_3$
Br
S
CD3
141.09
130.18
128.84
128.05
125.11
123.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



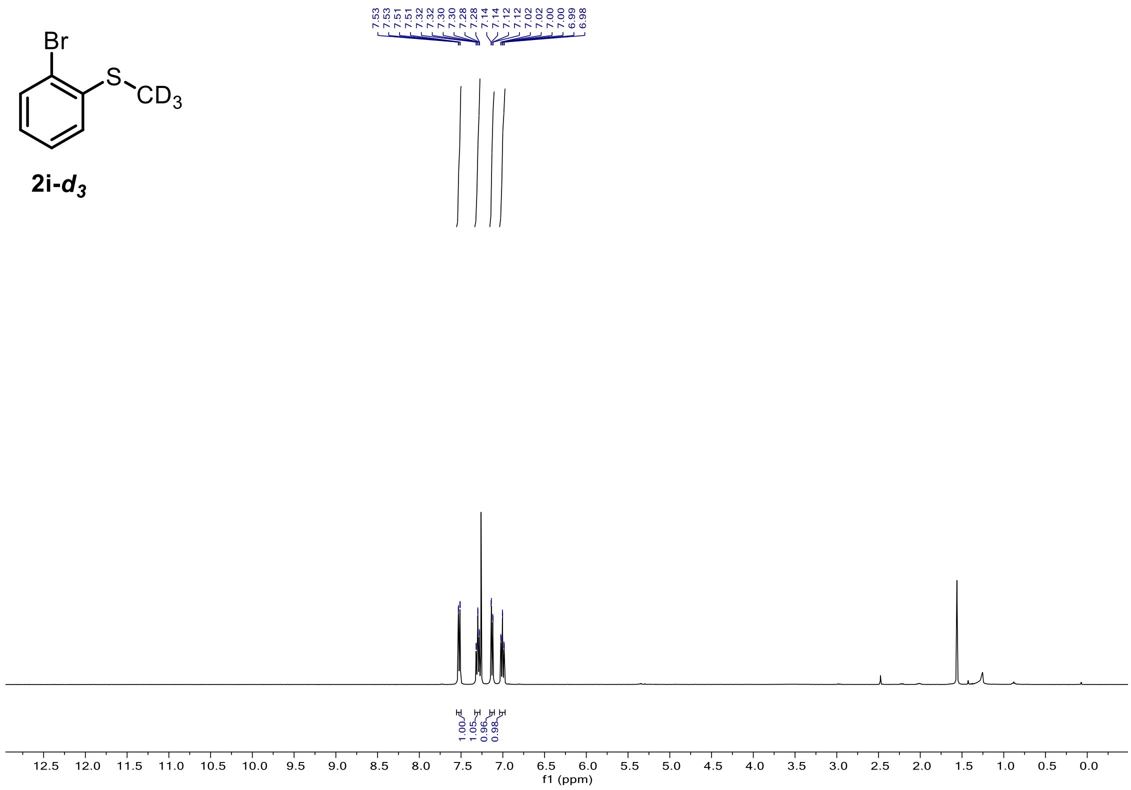
2i

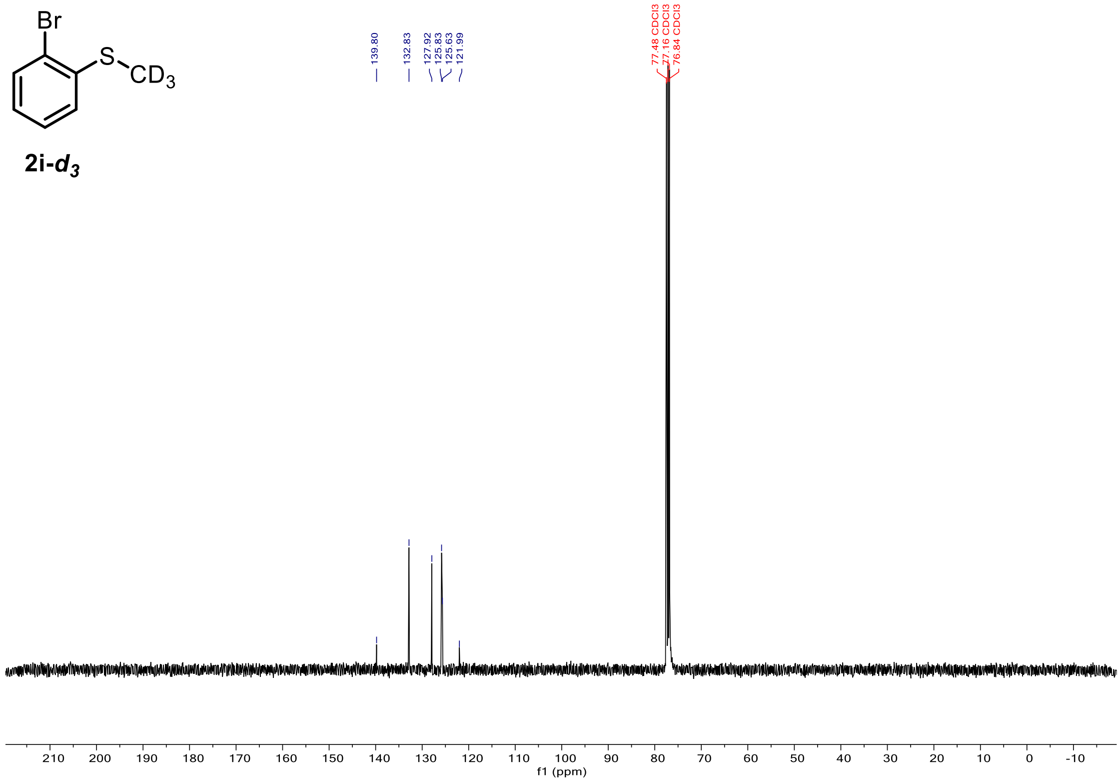
Br
S
7.53
7.52
7.31
7.30
7.29
7.14
7.13
7.02
7.00
6.99
2.48
1.00
1.05
1.09
1.04
3.16
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

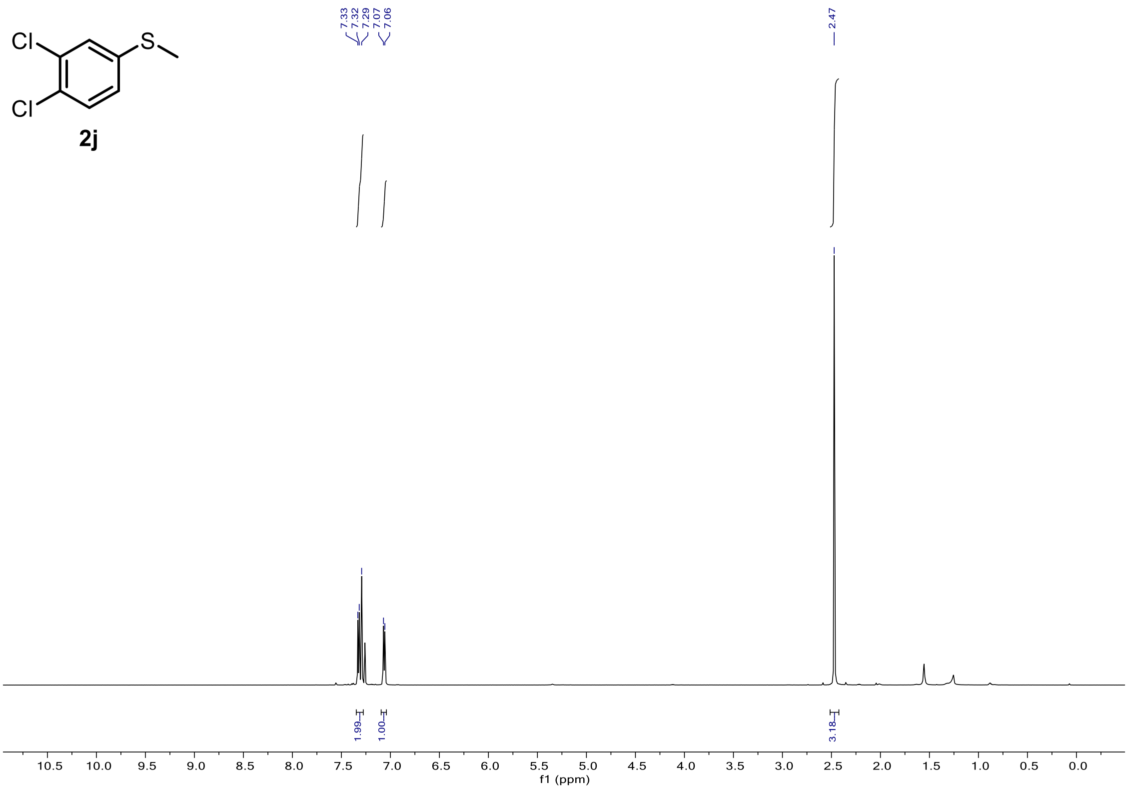


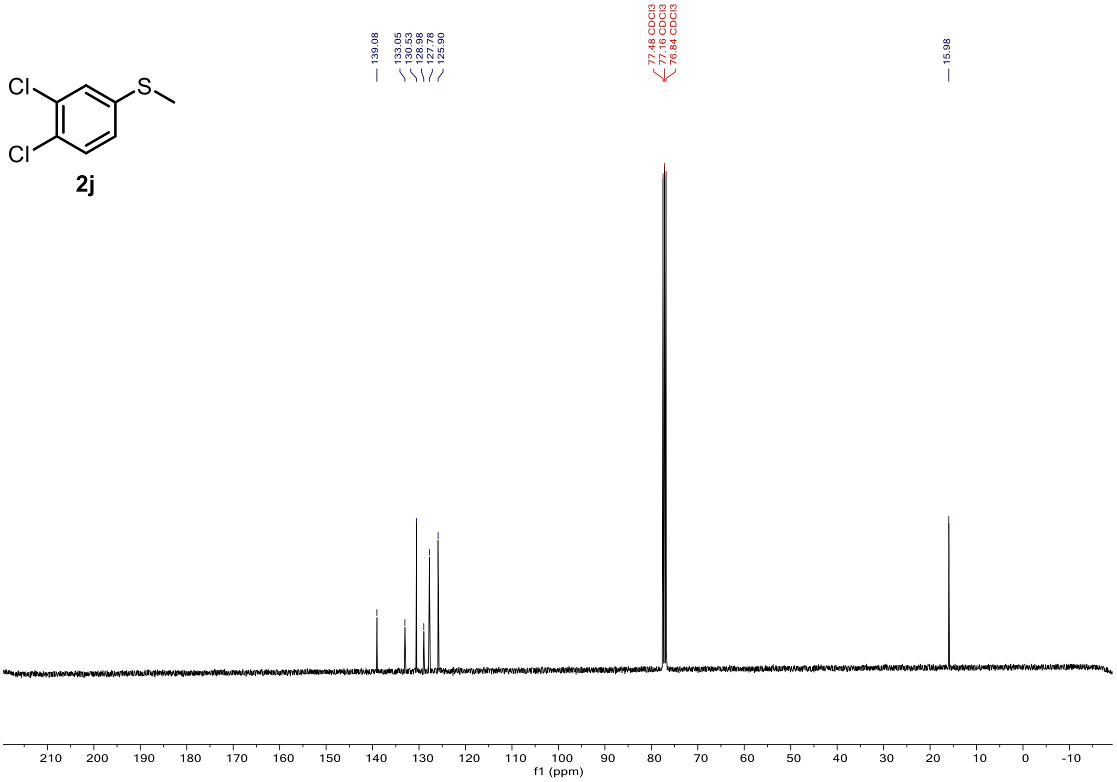
2i

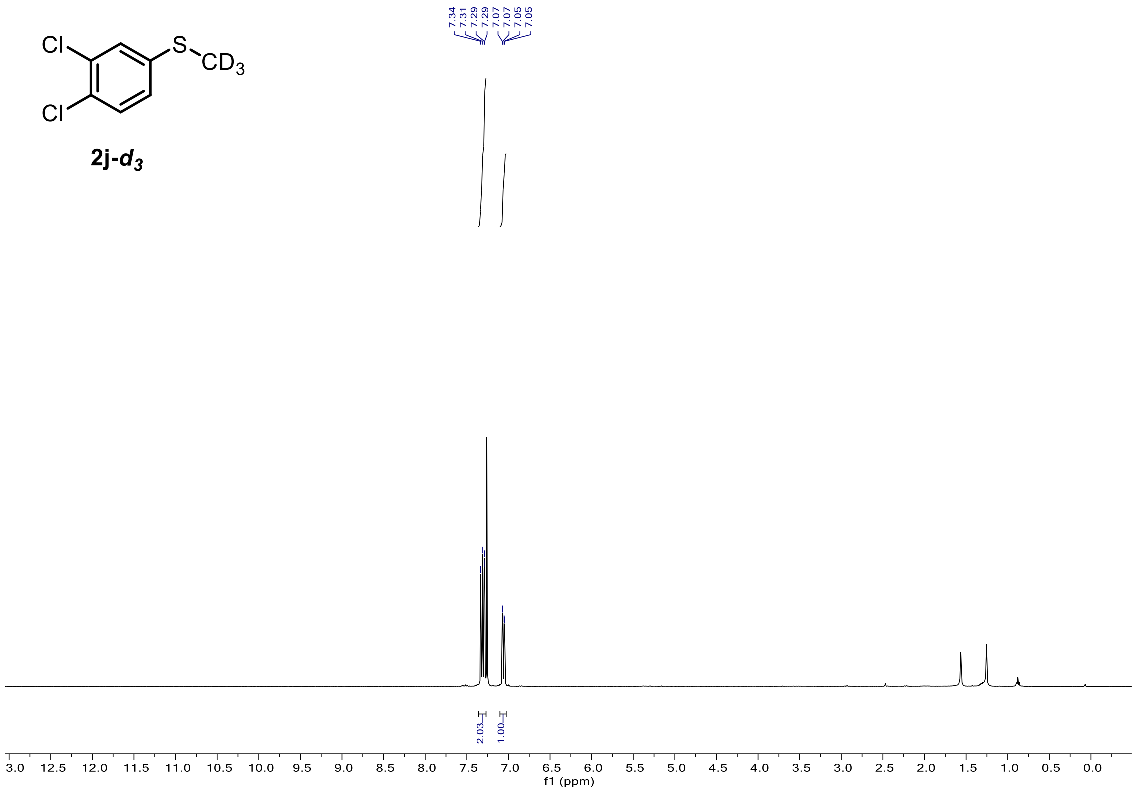
Br
S
139.79
132.79
127.91
125.81
125.55
121.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2i-d_3
Br
S
CD_3
7.53
7.53
7.51
7.51
7.32
7.32
7.30
7.30
7.28
7.28
7.14
7.14
7.12
7.12
7.02
7.02
7.00
7.00
6.99
6.98
1.00
1.05
0.96
0.98
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

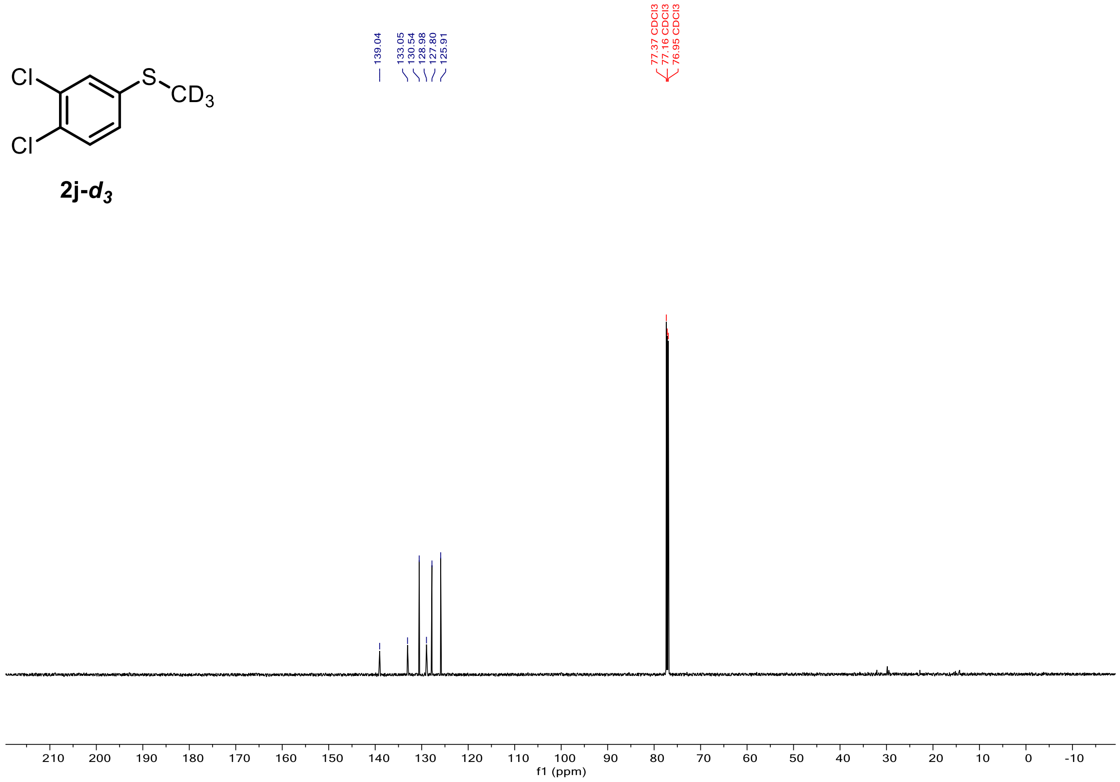

2i-d_3
Br
S
CD_3
139.80
132.83
127.92
125.83
125.63
121.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
Cl
S
2j
7.33
7.32
7.29
7.07
7.06
2.47
1.99
1.00
3.18
10.5
10.0
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
f1 (ppm)

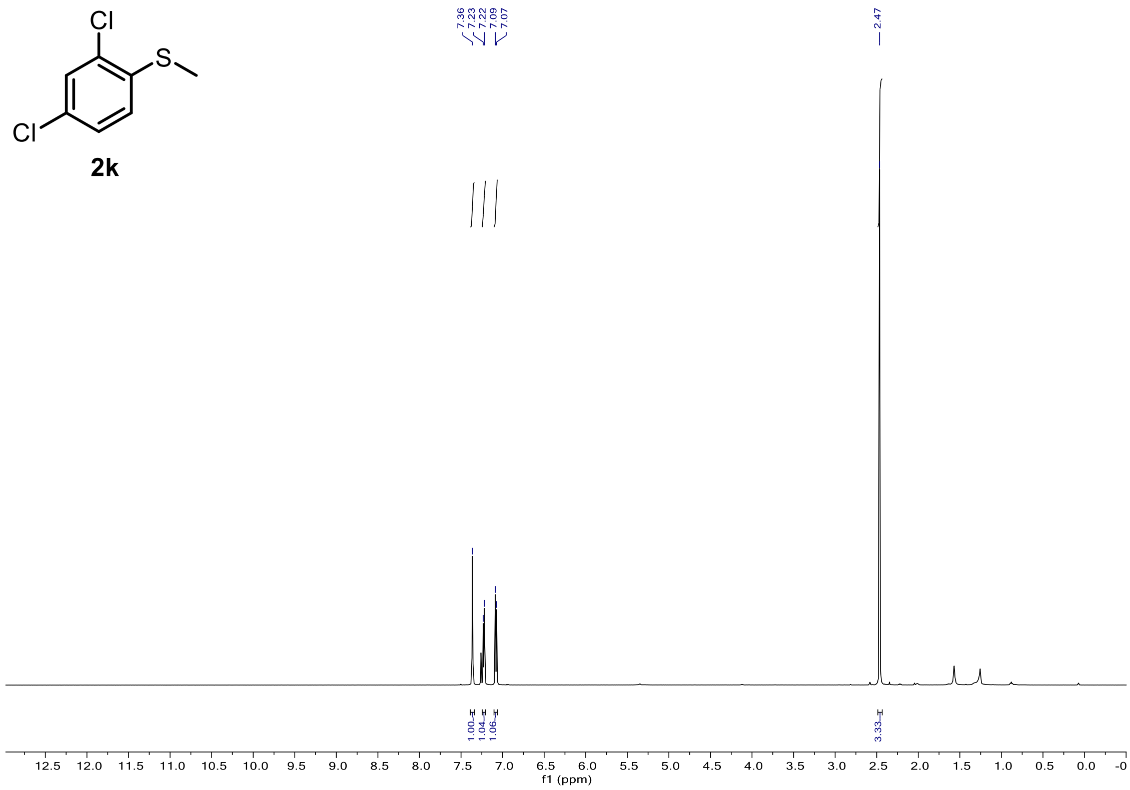

Cl
Cl
S
2j
139.08
133.05
130.53
128.98
127.78
125.90
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

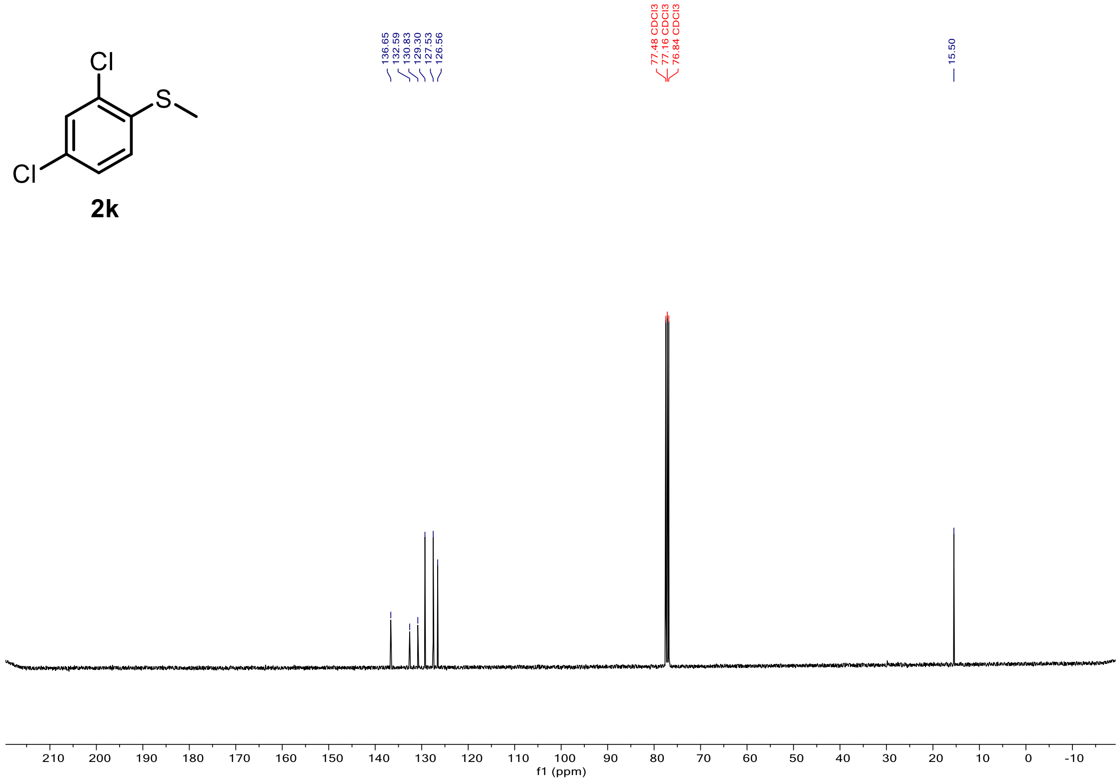

2j-*d*$_3$

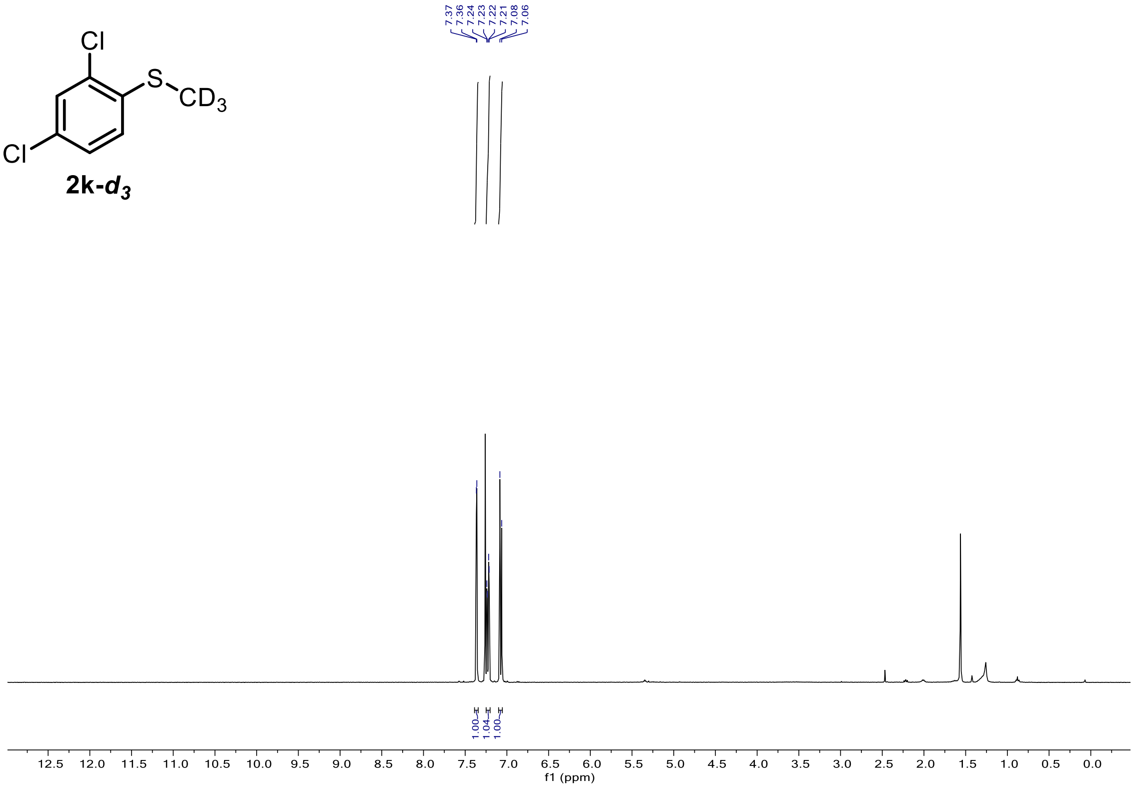
Cl
Cl
S
CD3
7.34
7.31
7.29
7.29
7.07
7.07
7.05
7.05
2.03
1.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2j-*d*$_3$

Cl
Cl
S
CD3
139.04
133.05
130.54
128.98
127.80
125.91
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

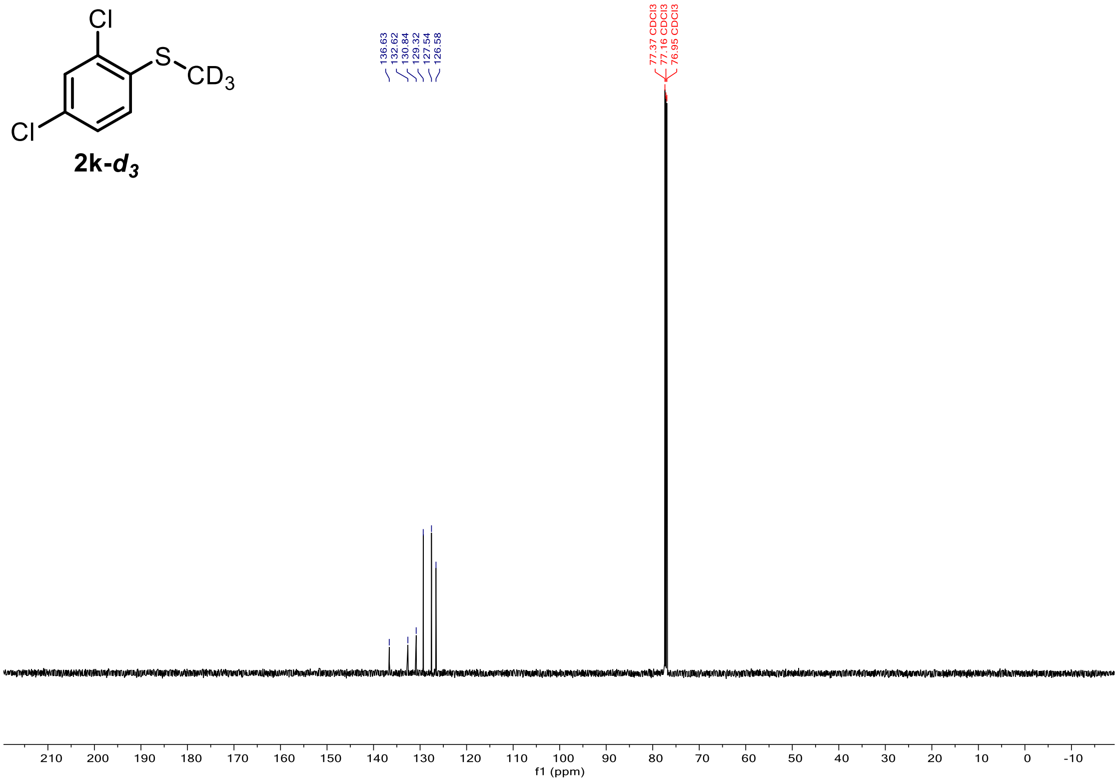

Cl
S
Cl
2k
7.36
7.23
7.22
7.09
7.07
2.47
1.00
1.04
1.06
3.33
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


Cl
S
Cl
2k
136.65
132.59
130.83
129.30
127.53
126.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



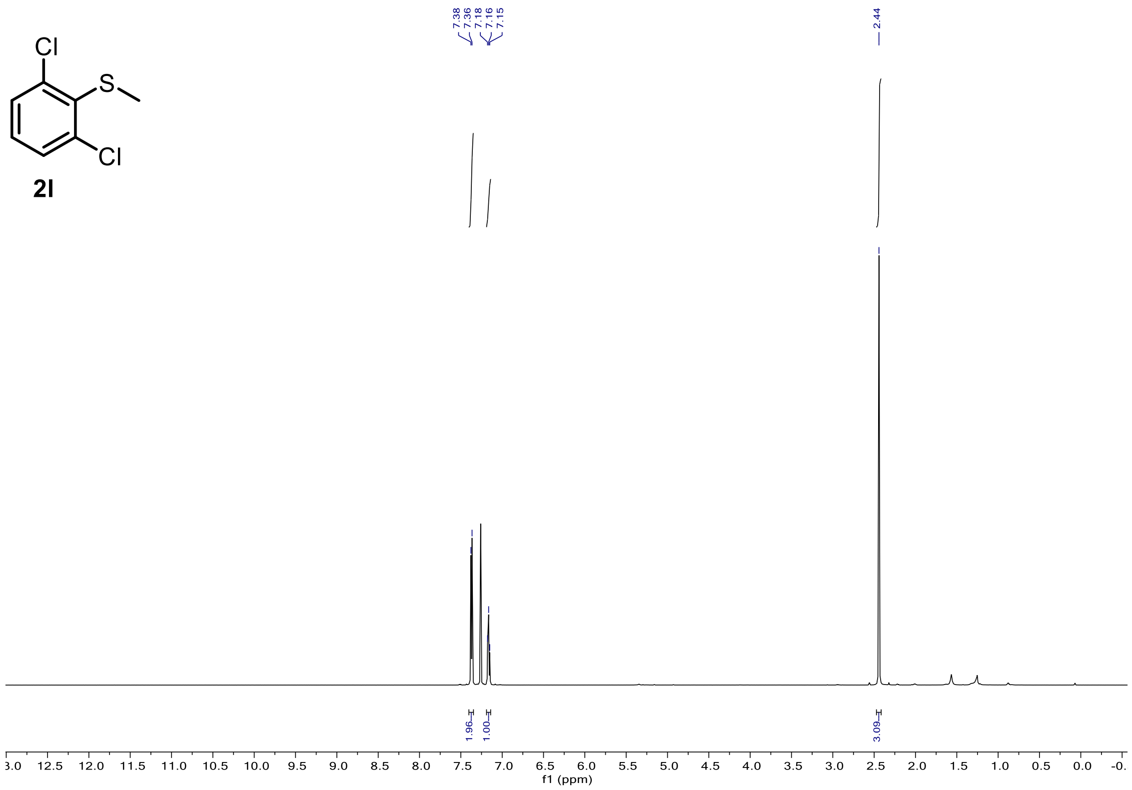
2k-*d*$_3$

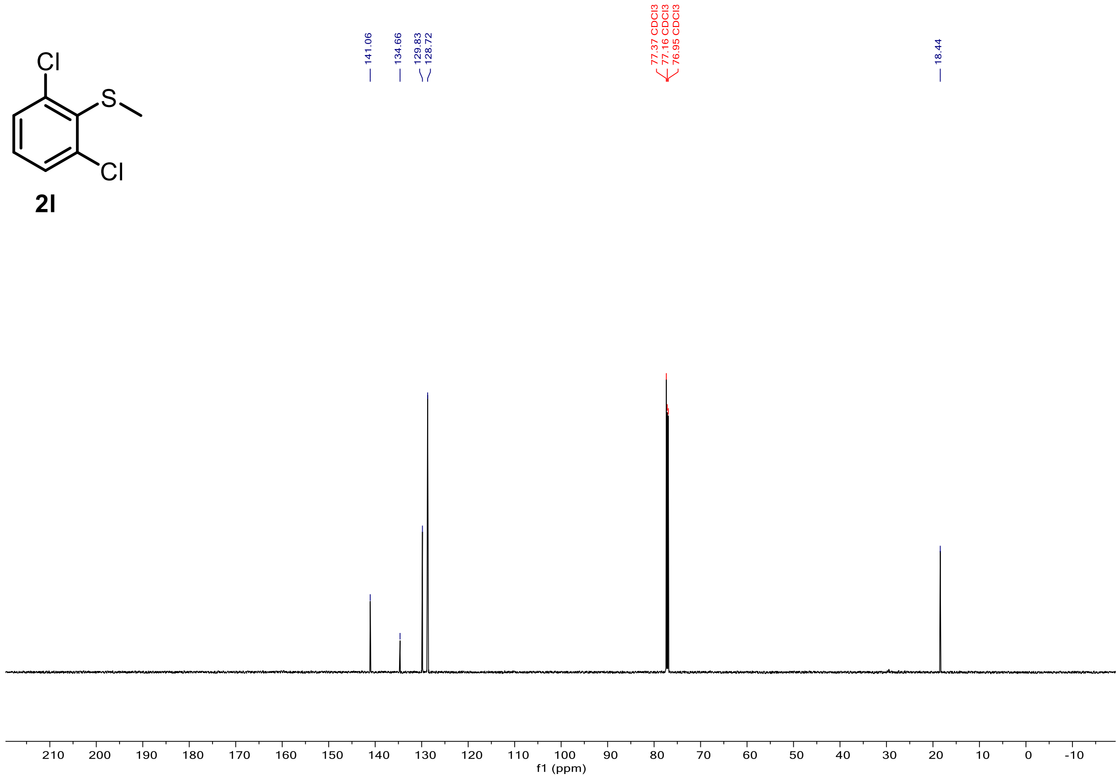
Cl
S
CD3
Cl
7.37
7.36
7.24
7.23
7.22
7.21
7.08
7.06
1.00
1.04
1.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

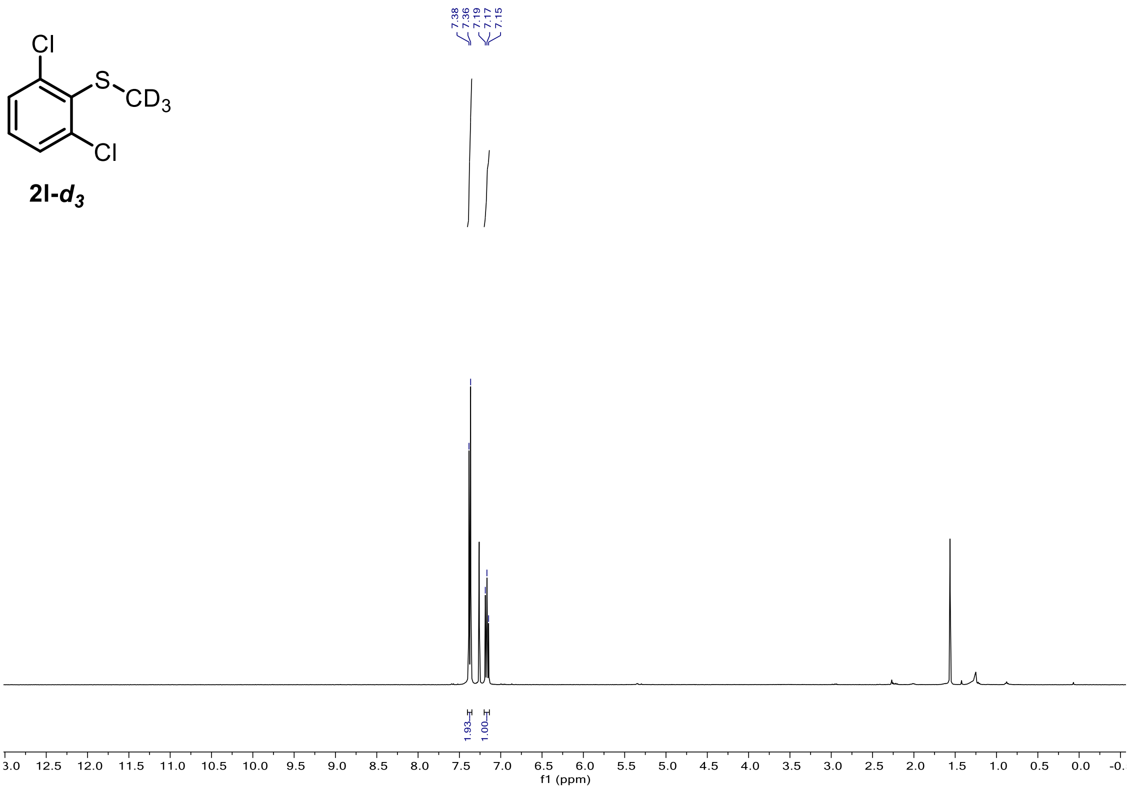


2k-*d*$_3$

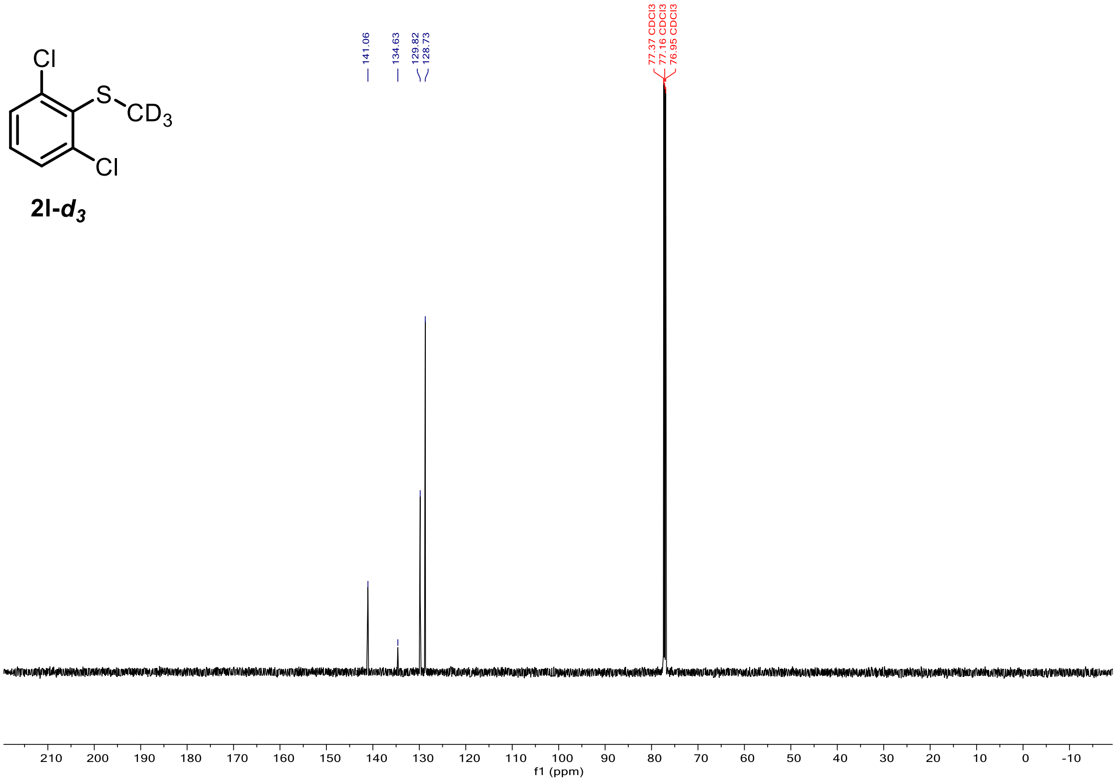
Cl
S
CD3
Cl
136.63
132.62
130.84
129.32
127.54
126.58
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
S
Cl
2l
7.38
7.36
7.18
7.16
7.15
2.44
1.96
1.00
3.09
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)

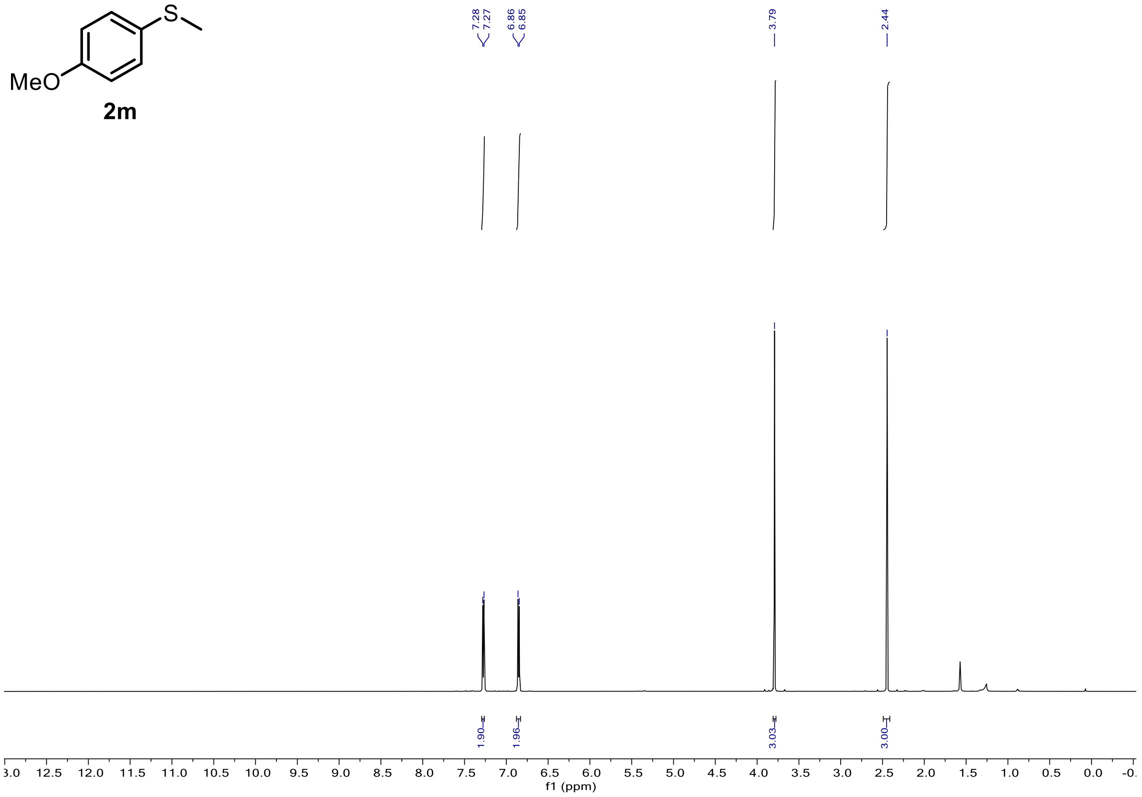

Cl
S
Cl
2l
141.06
134.66
129.83
128.72
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
18.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

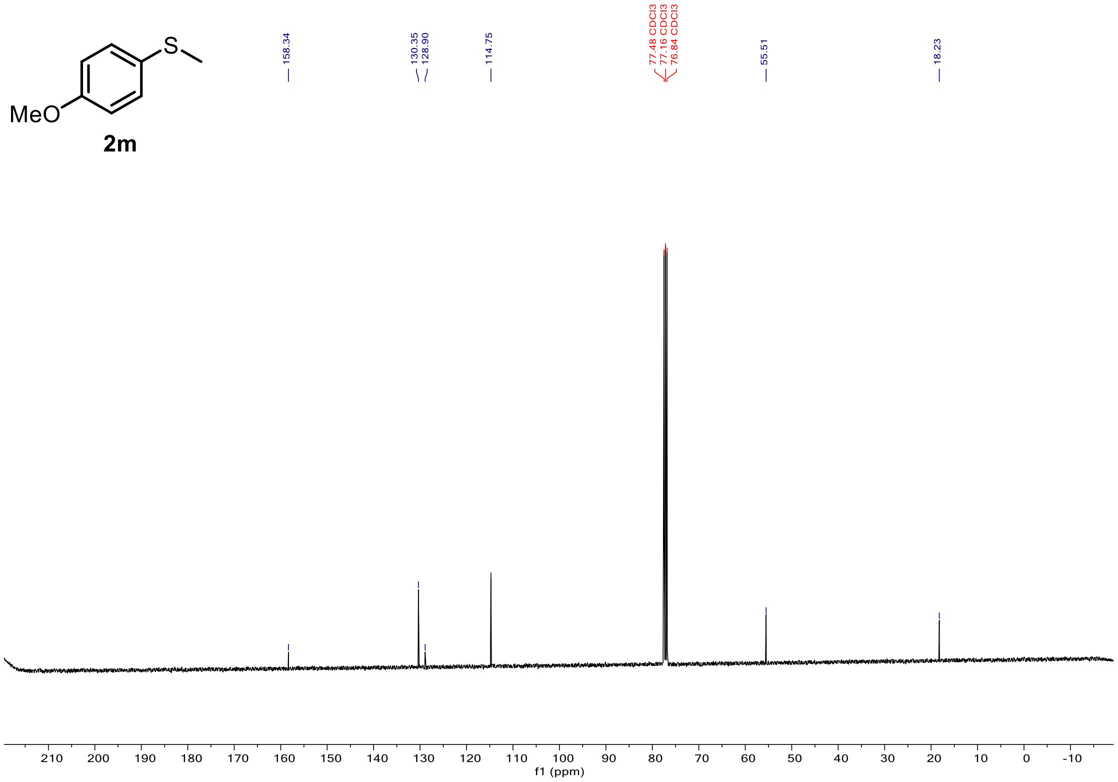

Cl
S
CD3
Cl
7.38
7.36
7.19
7.17
7.15
1.93
1.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

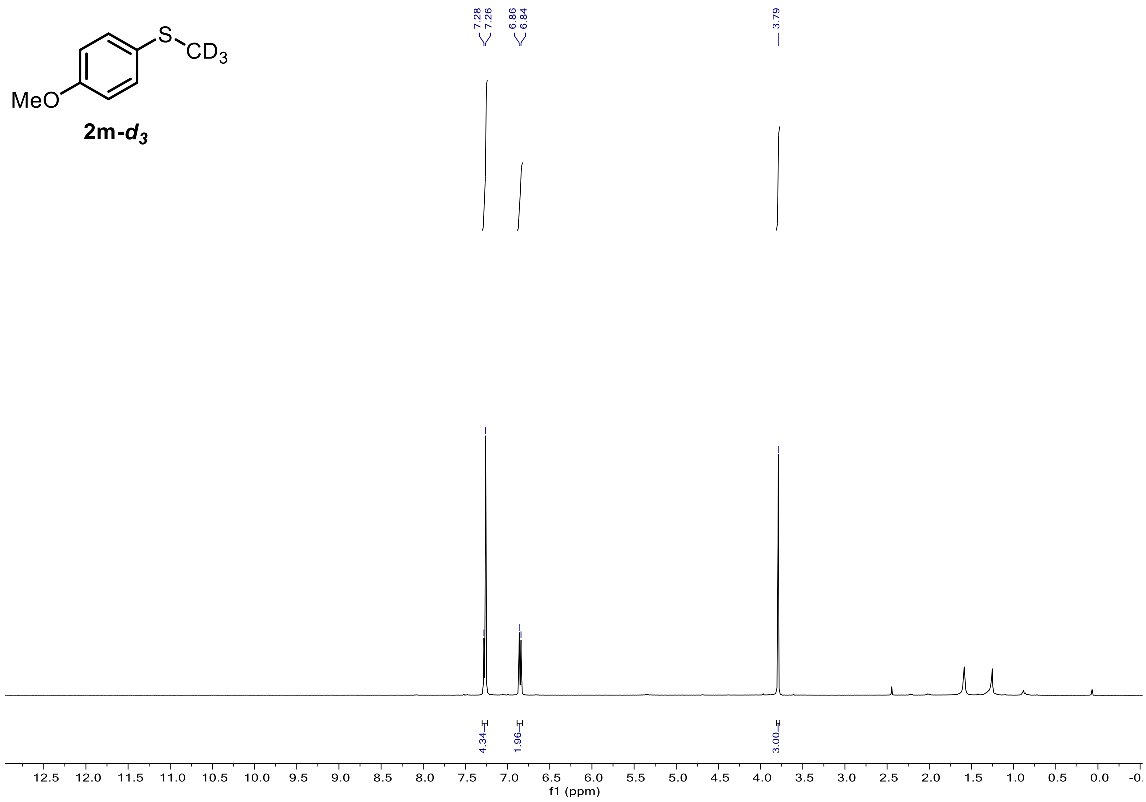
2l-d_3

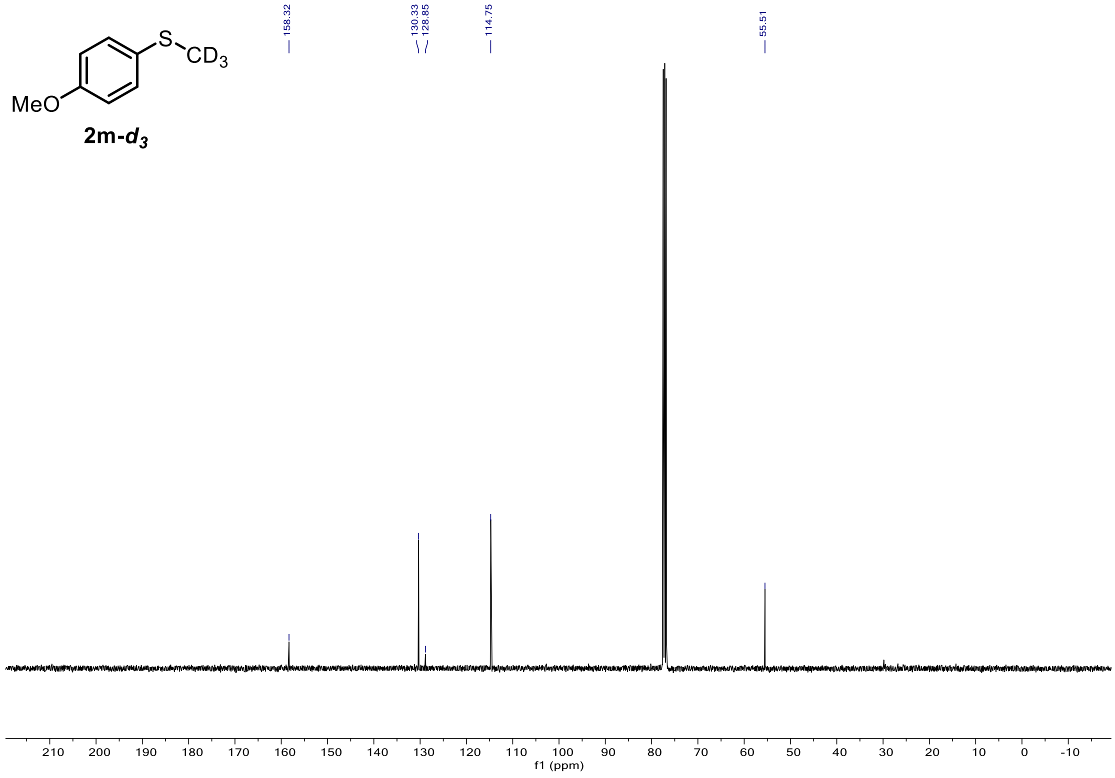

Cl
S
CD3
Cl
141.06
134.63
129.82
128.73
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

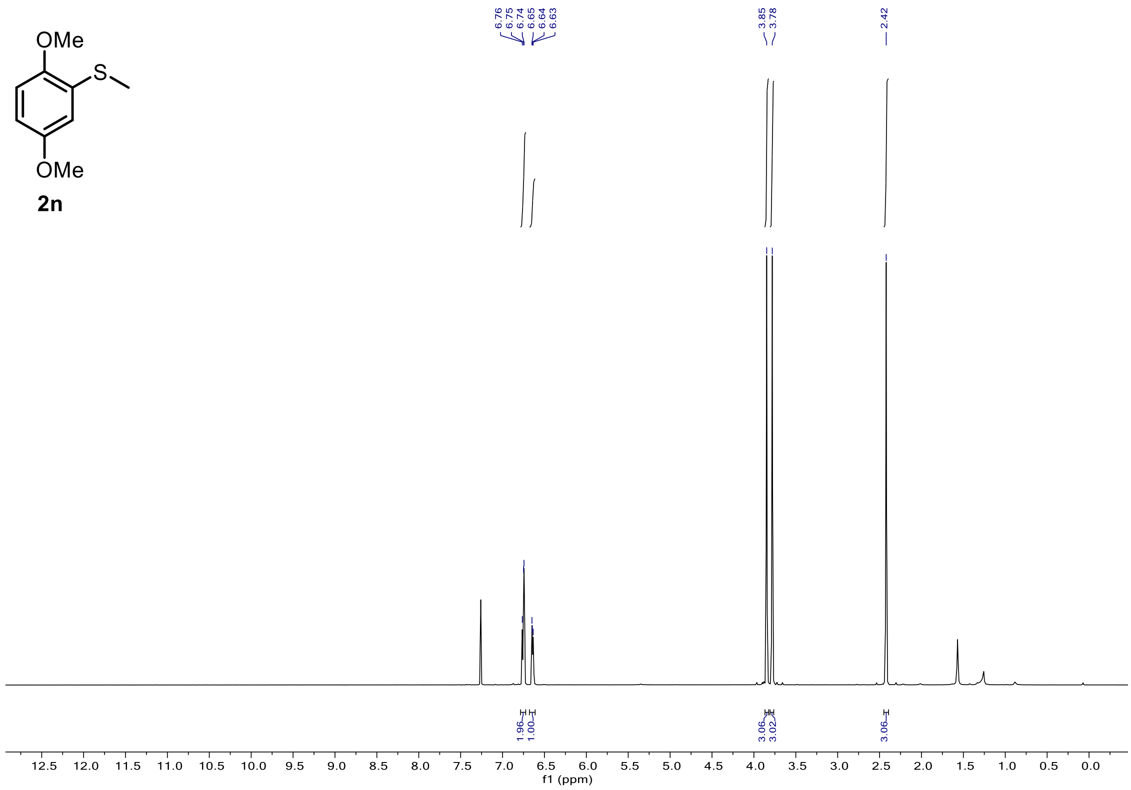
2l-d_3

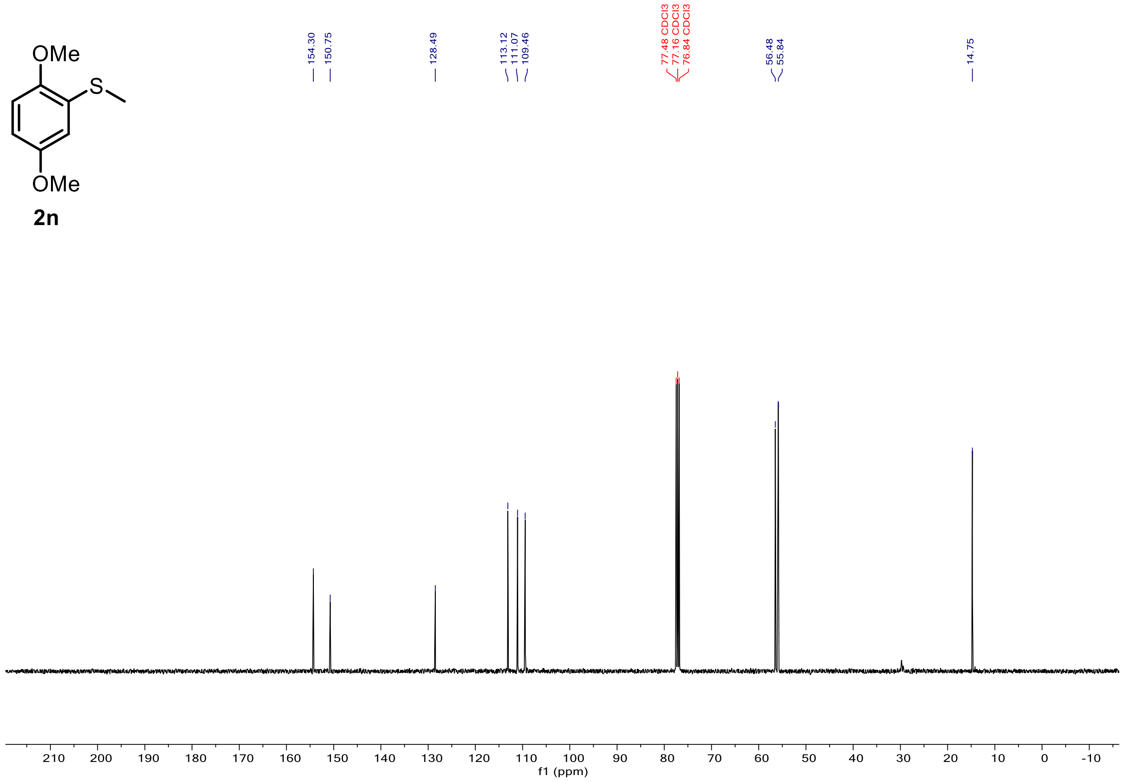

MeO
S
2m
7.28
7.27
6.86
6.85
3.79
2.44
1.90
1.96
3.03
3.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

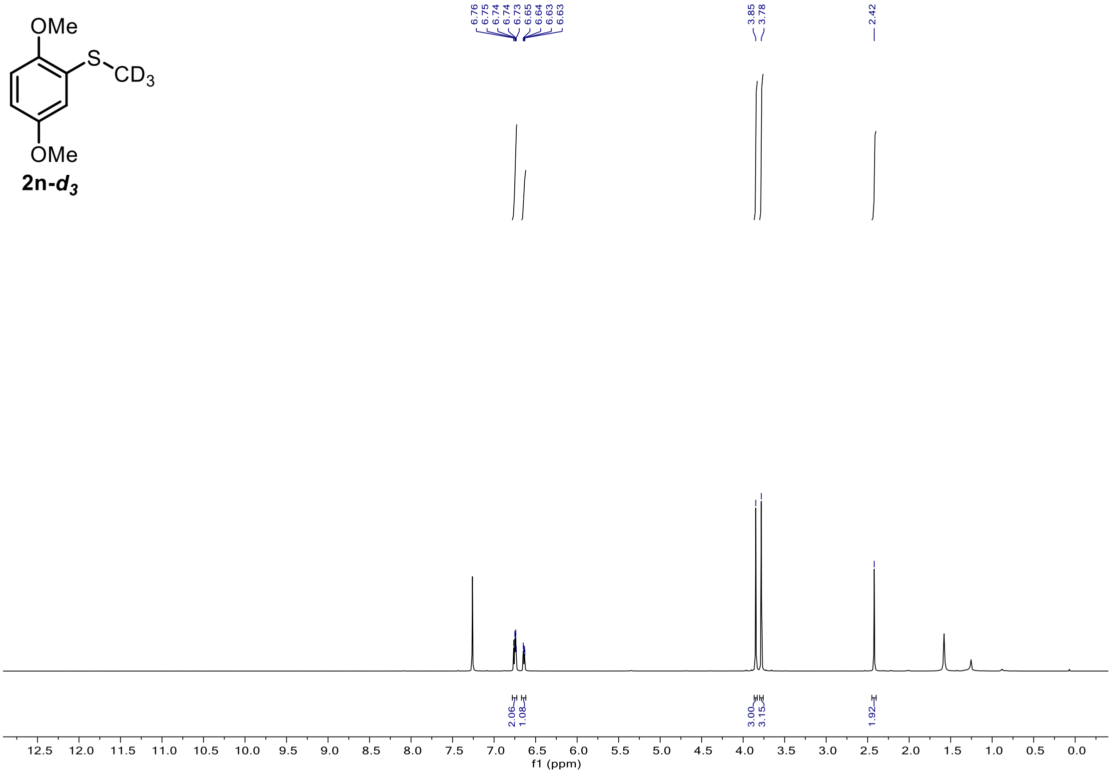

MeO
S
2m
158.34
130.35
128.90
114.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.51
18.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
S
CD3
2m-d3
7.28
7.26
6.86
6.84
3.79
4.34
1.96
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

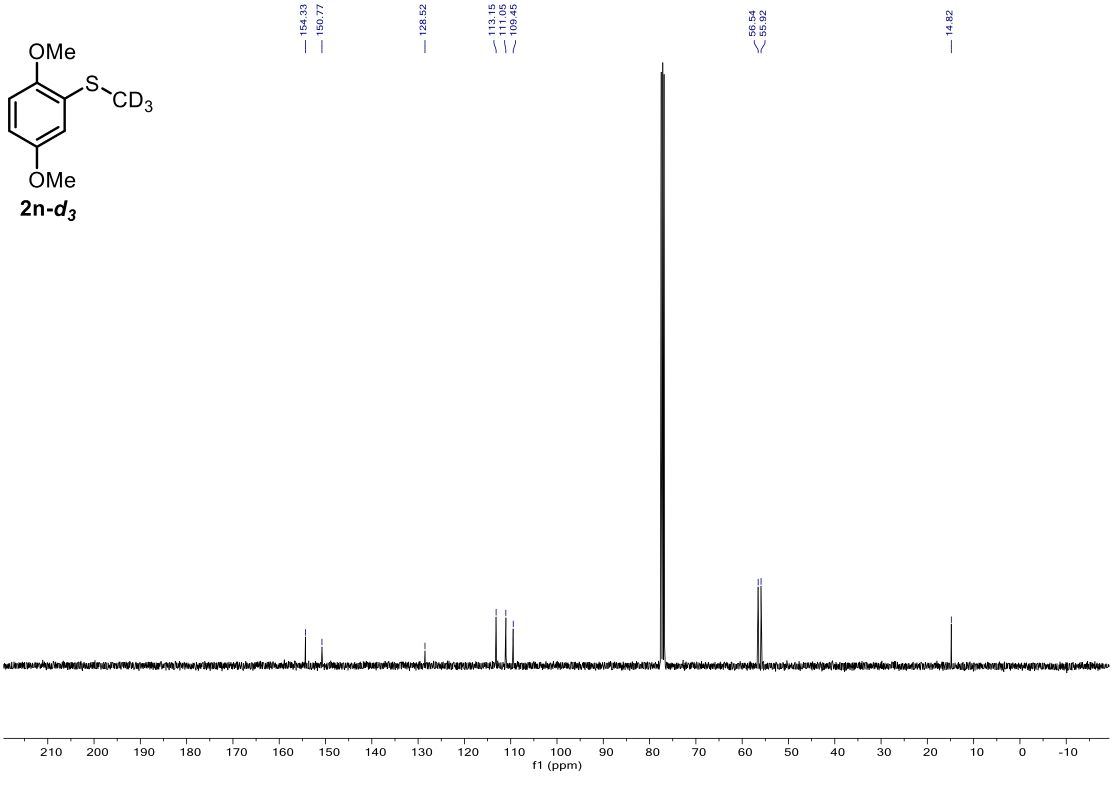

MeO
S
CD3
2m-d3
158.32
130.33
128.85
114.75
55.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
S
OMe
2n
6.76
6.75
6.74
6.65
6.64
6.63
3.85
3.78
2.42
1.96
1.00
3.06
3.02
3.06
12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

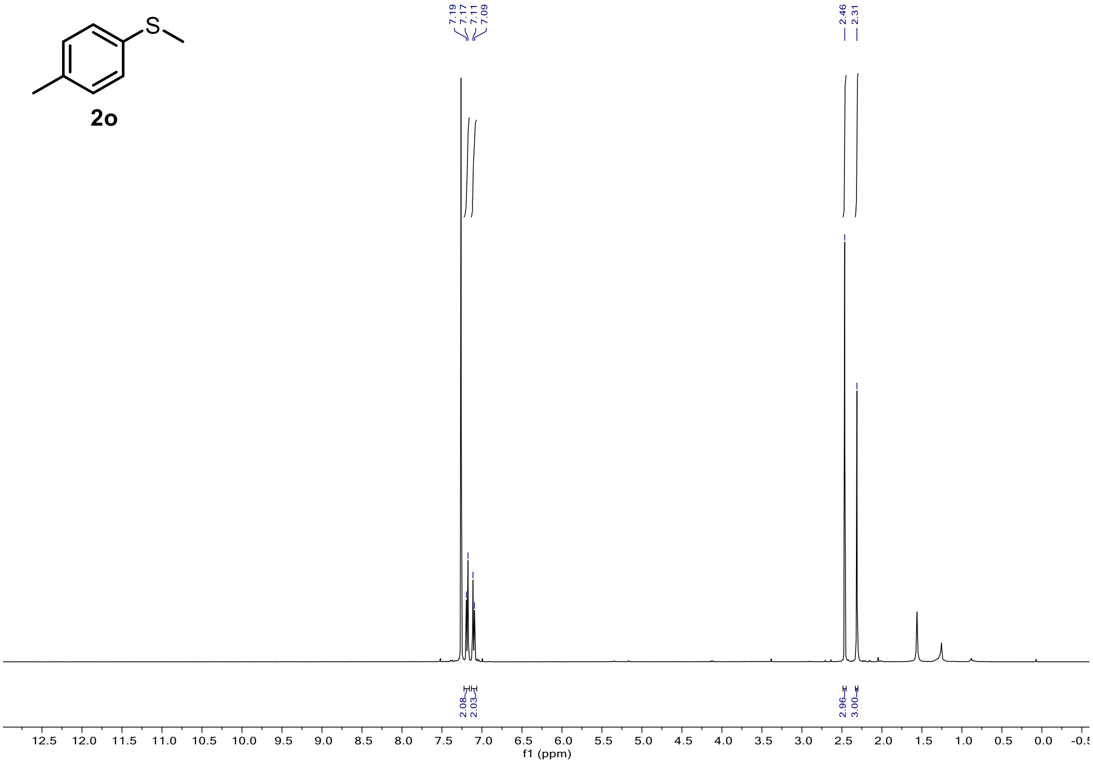

OMe
S
OMe
2n
154.30
150.75
128.49
113.12
111.07
109.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.48
55.84
14.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

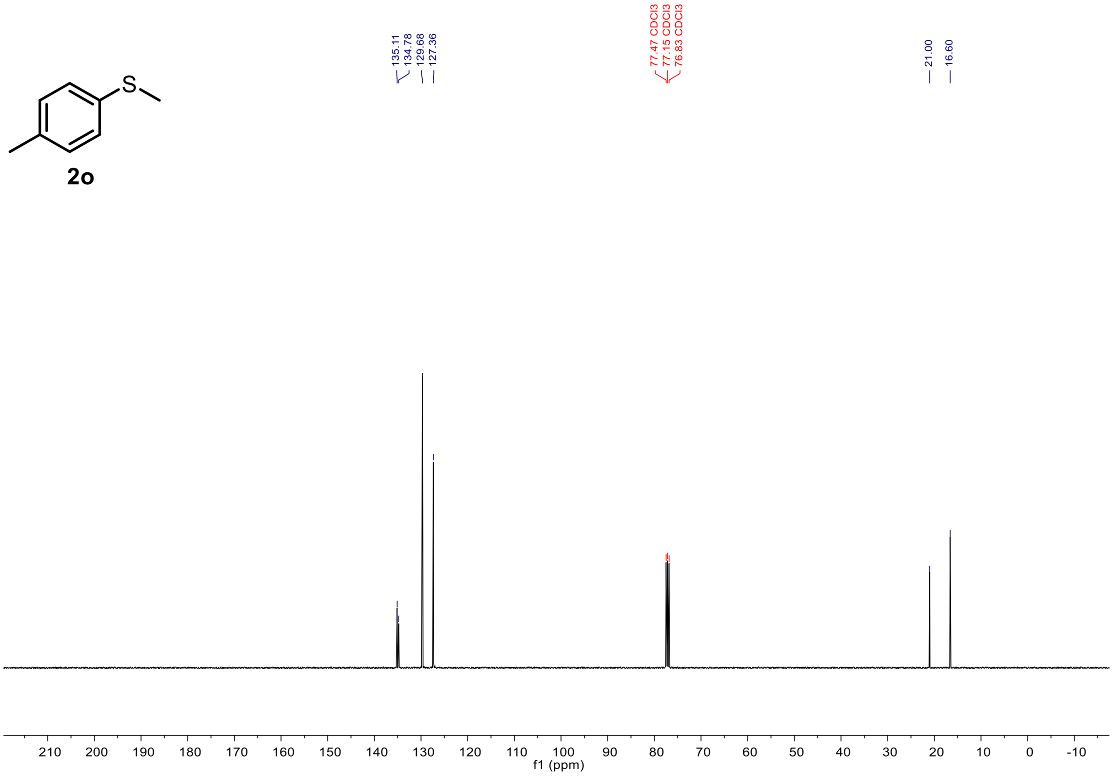

OMe
S
CD3
OMe
6.76
6.75
6.74
6.74
6.73
6.65
6.64
6.63
6.63
3.85
3.78
2.42
2.06
1.08
3.00
3.15
1.92
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

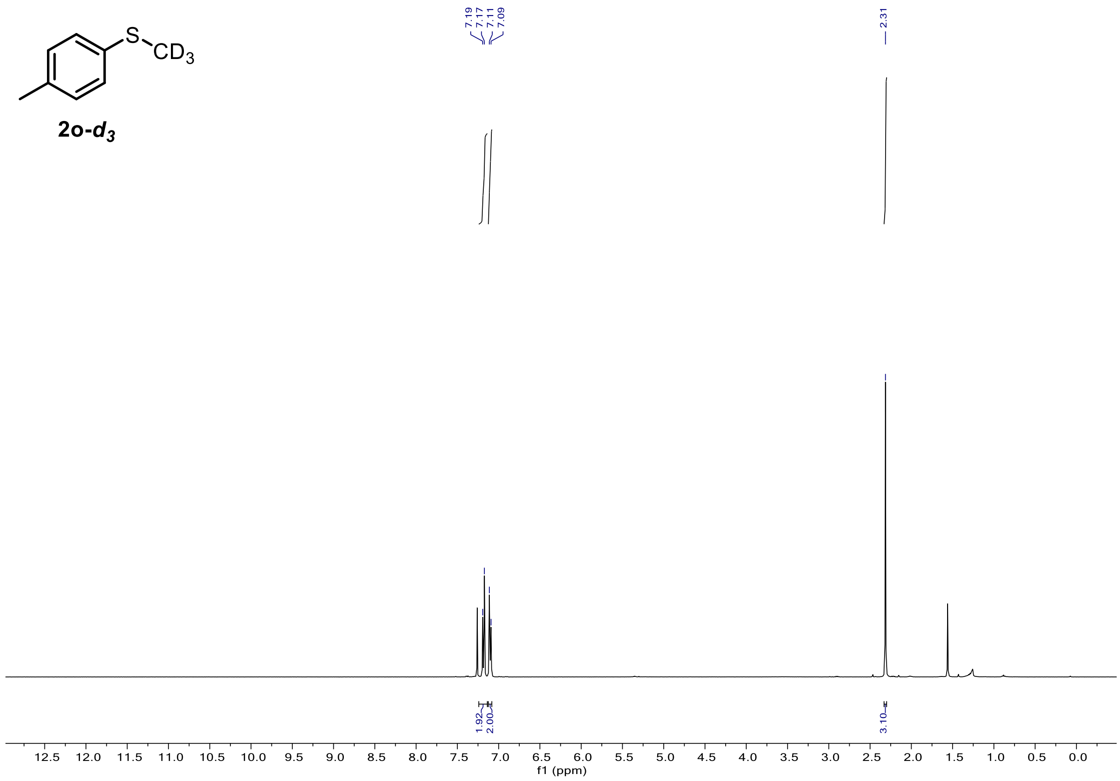
2n-*d*$_3$


OMe
S
CD3
OMe
154.33
150.77
128.52
113.15
111.05
109.45
56.54
55.92
14.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2n-*d*$_3$

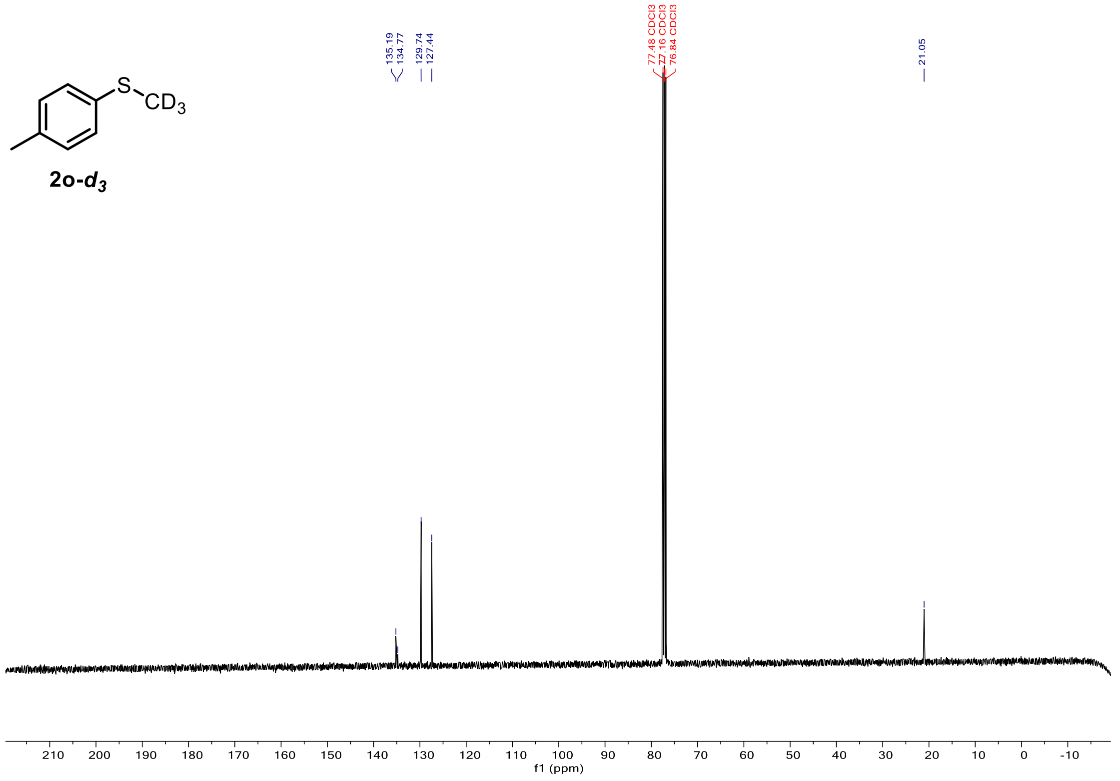

2o
7.19
7.17
7.11
7.09
2.46
2.31
2.08
2.03
2.96
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2o
135.11
134.78
129.68
127.36
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
21.00
16.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



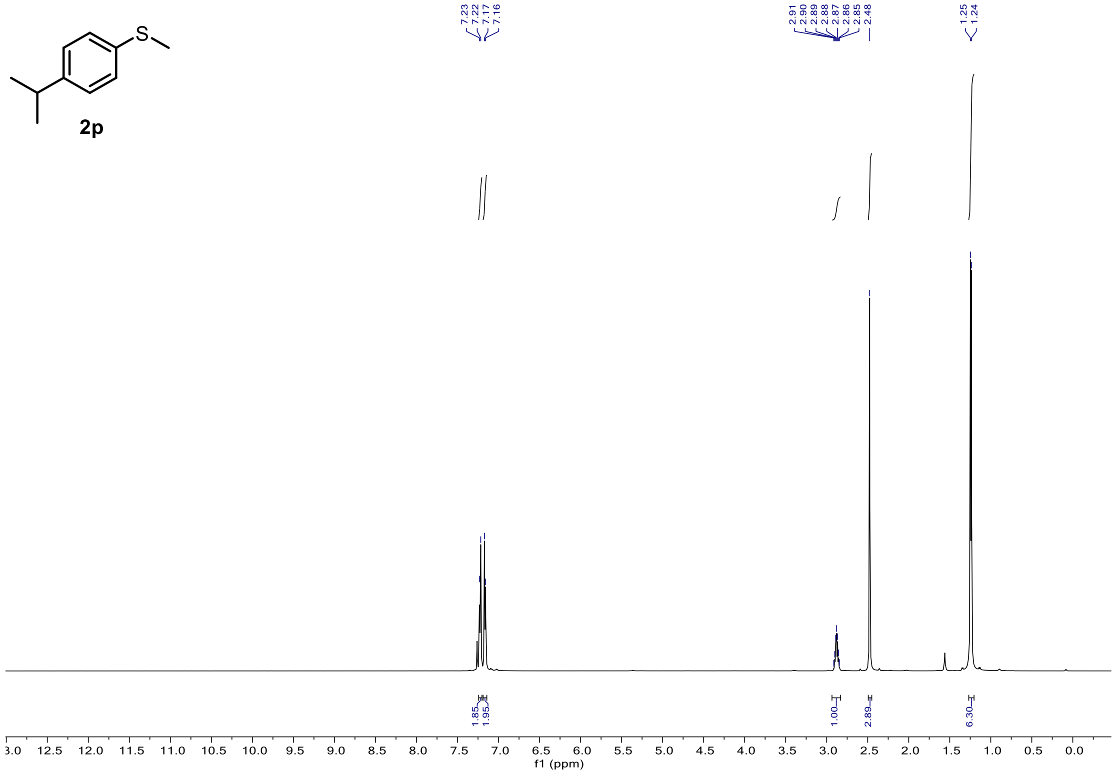
2o-*d*$_3$

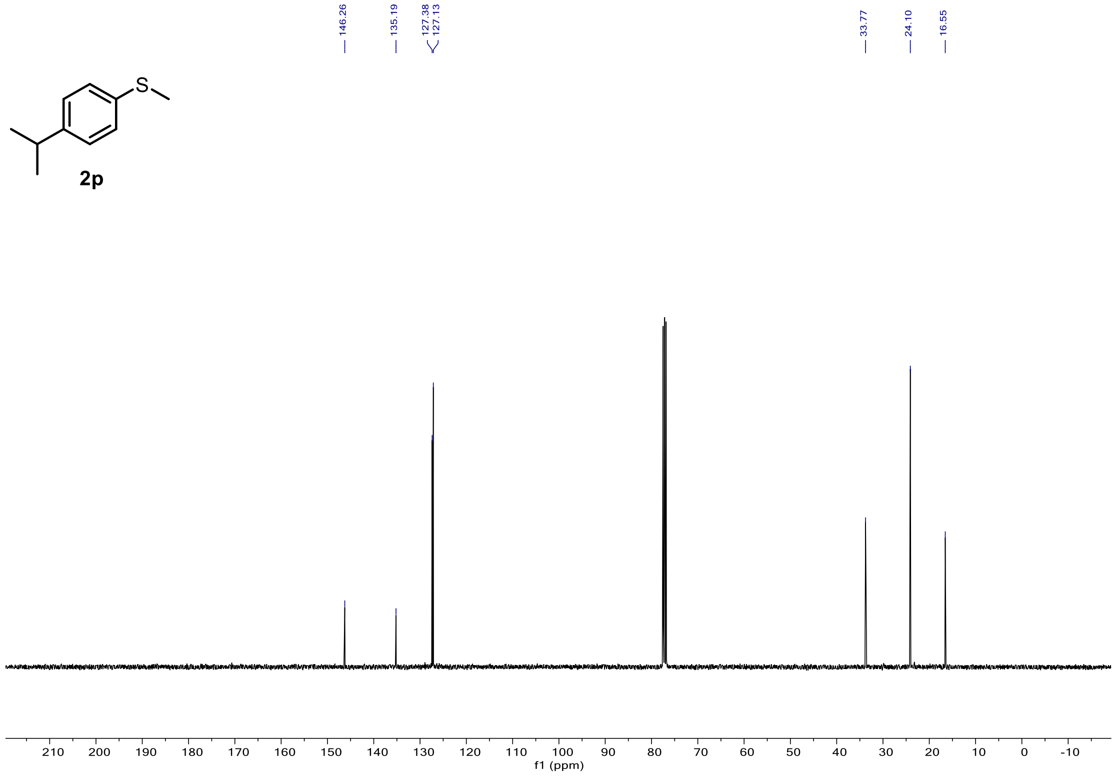
S
CD3
7.19
7.17
7.11
7.09
2.31
1.92
2.00
3.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

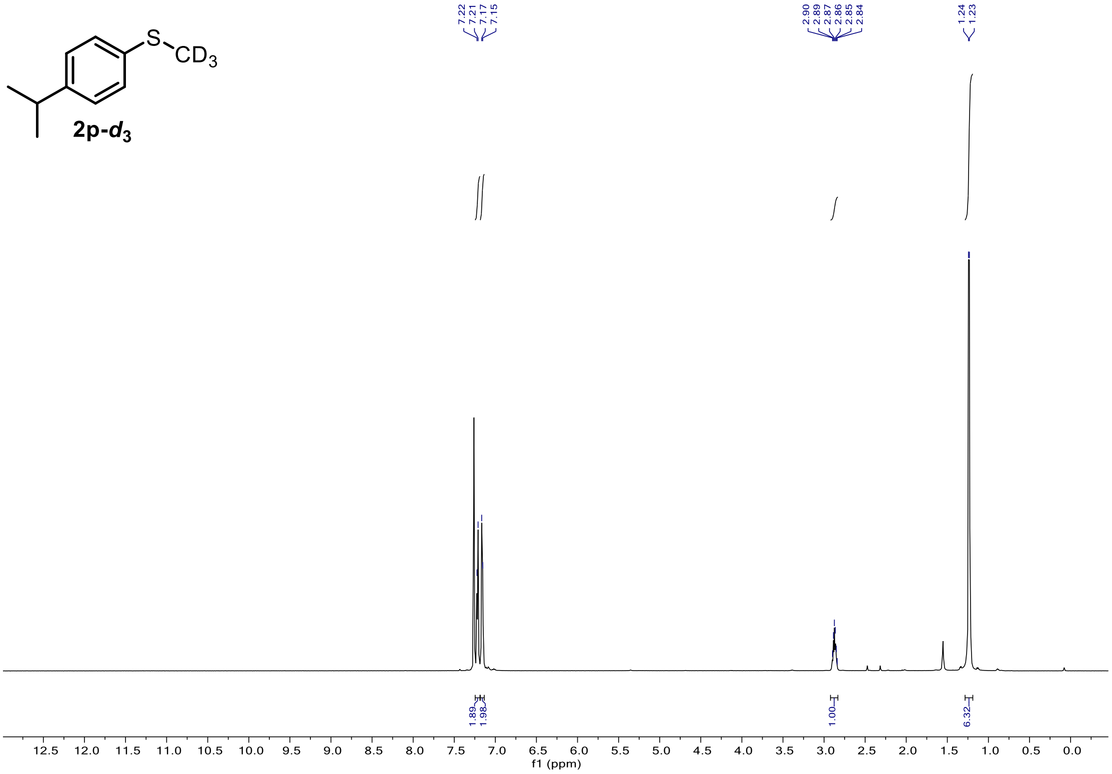


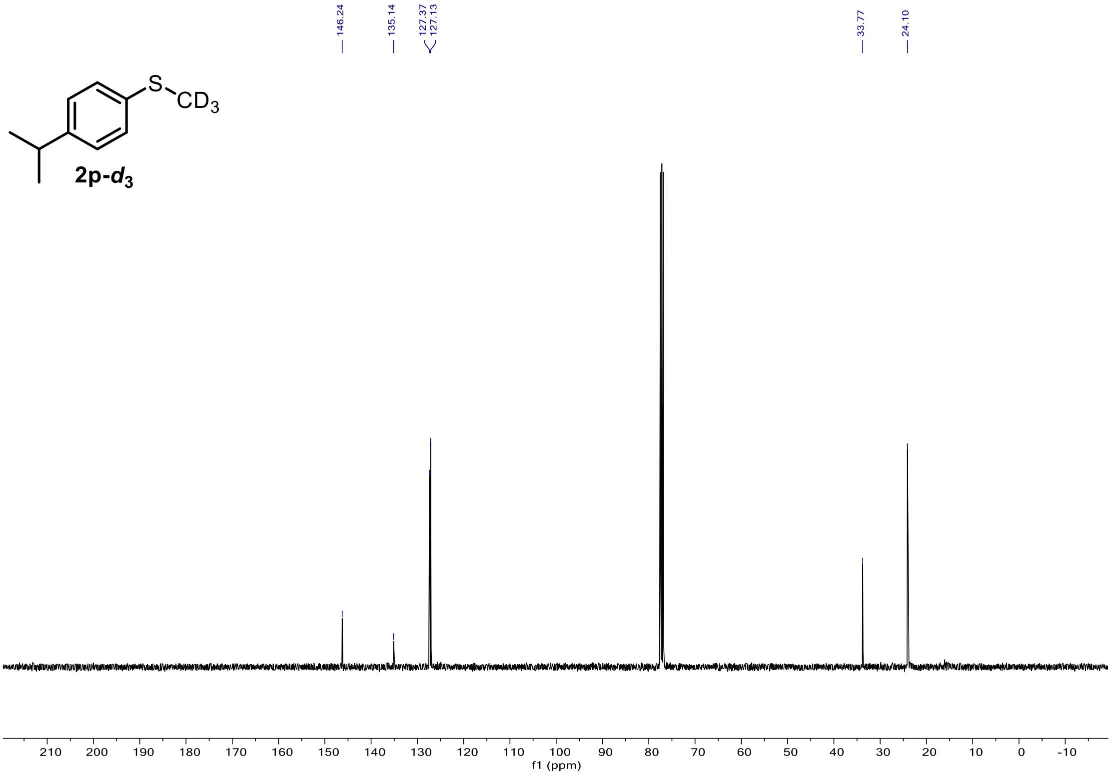
2o-*d*$_3$

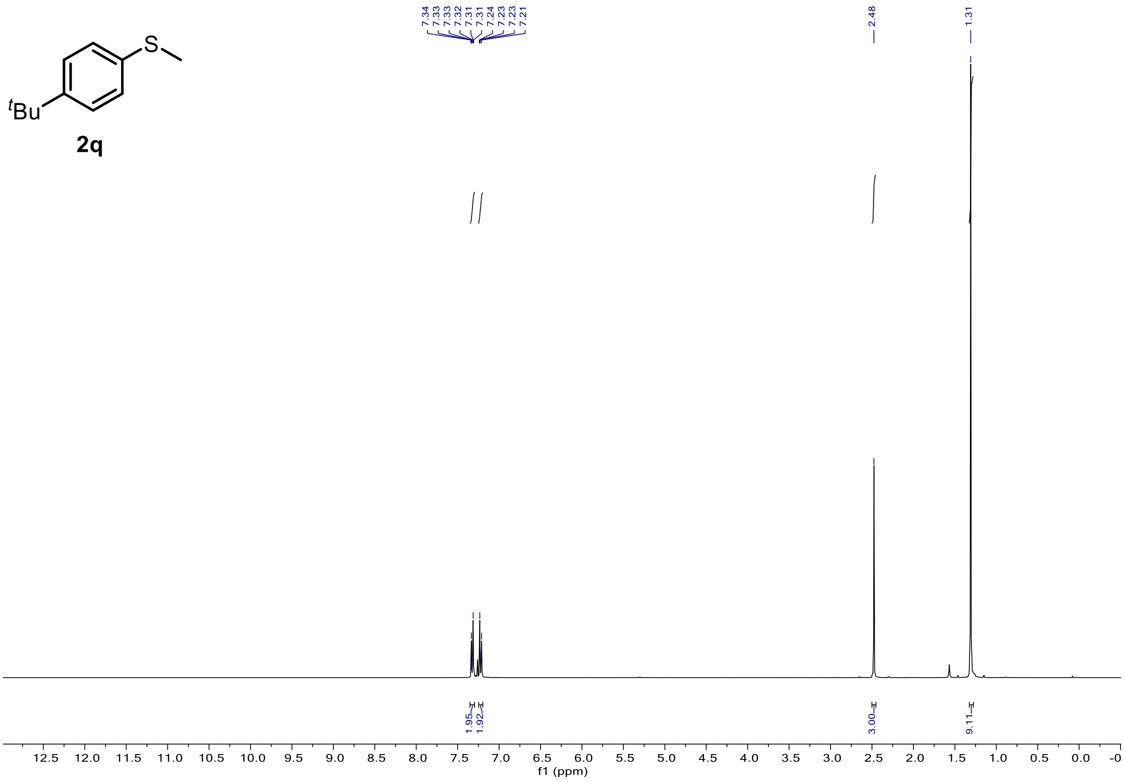
S
CD3
135.19
134.77
129.74
127.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


S
2p
7.23
7.22
7.17
7.16
2.91
2.90
2.89
2.88
2.87
2.86
2.85
2.48
1.25
1.24
1.85
1.95
1.00
2.89
6.30
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)


146.26
135.19
127.38
127.13
33.77
24.10
16.55
S
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

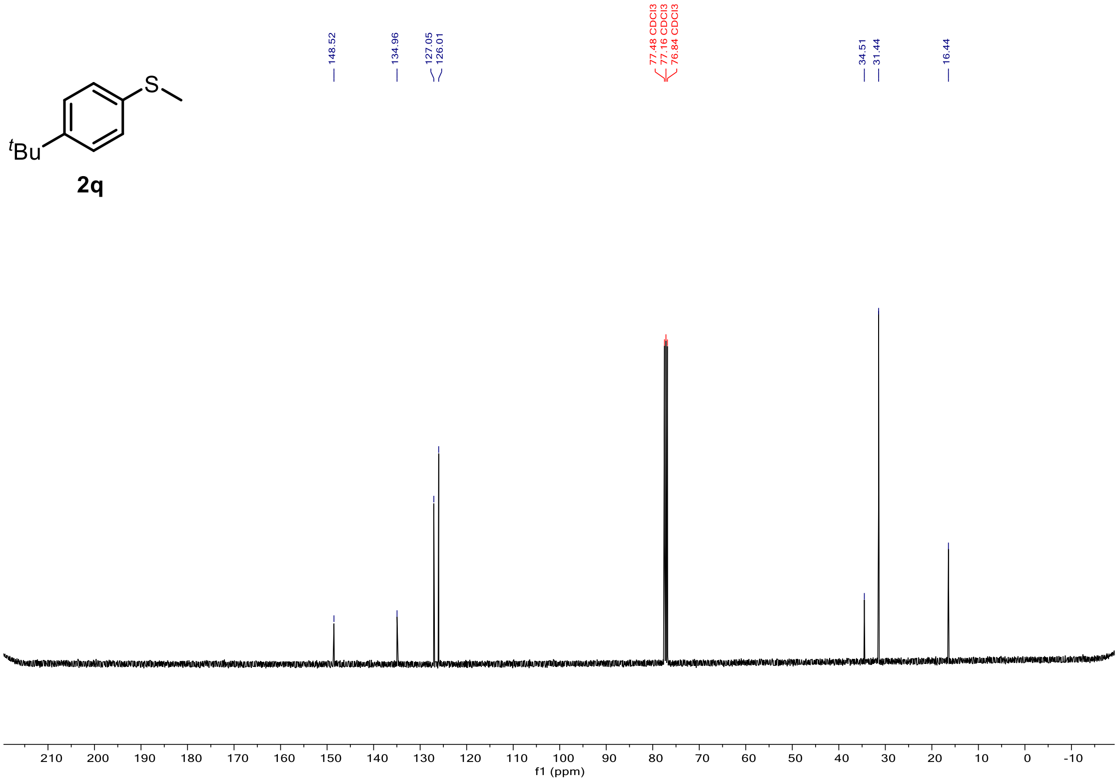

S
CD3
2p-d3
7.22
7.21
7.17
7.15
2.90
2.89
2.87
2.86
2.85
2.84
1.24
1.23
1.89
1.98
1.00
6.32
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


S
CD3
2p-d3
146.24
135.14
127.37
127.13
33.77
24.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



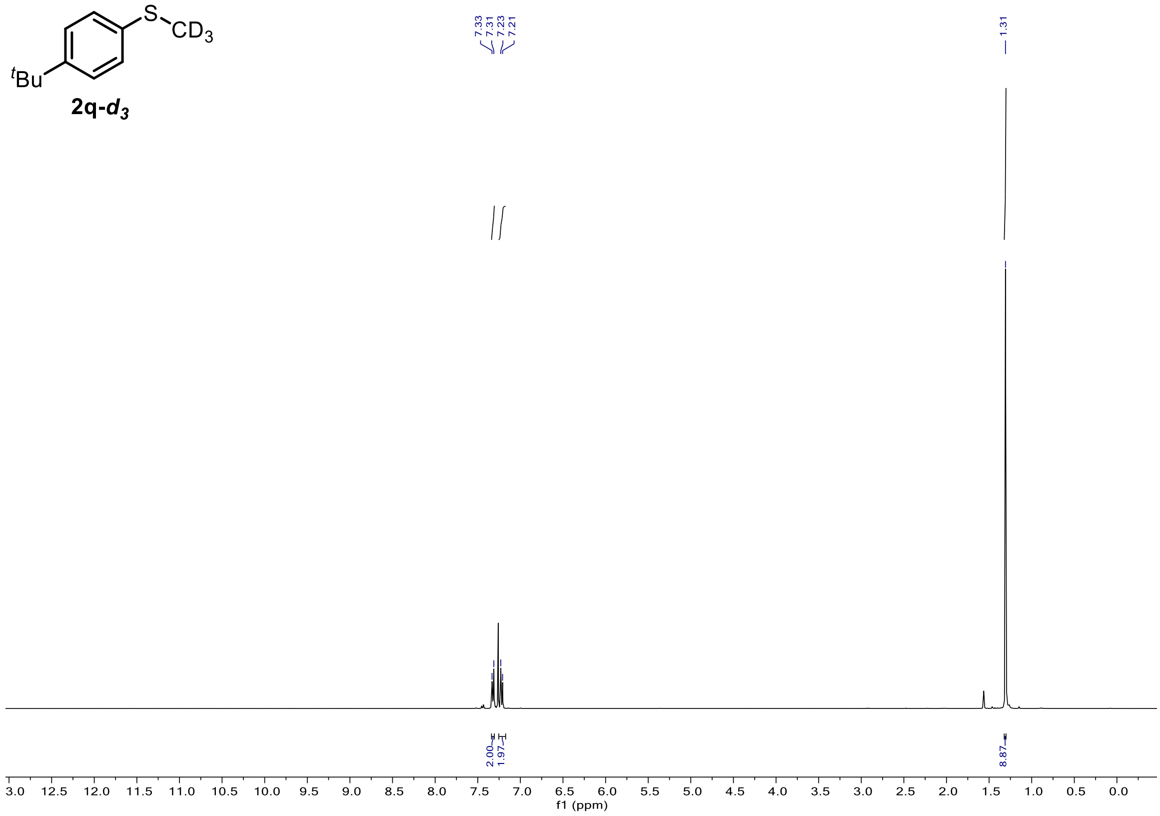
2q

tBu
S
7.34
7.33
7.33
7.32
7.31
7.31
7.24
7.23
7.23
7.21
2.48
1.31
1.95
1.92
3.00
9.11
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

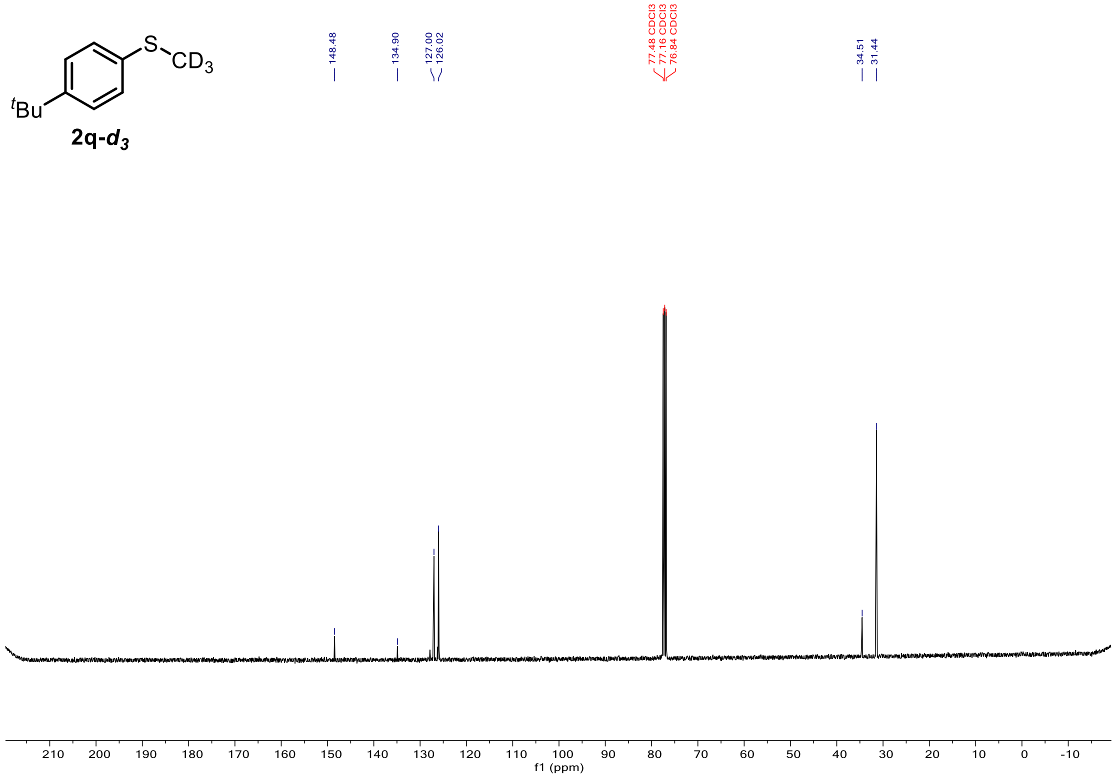


2q

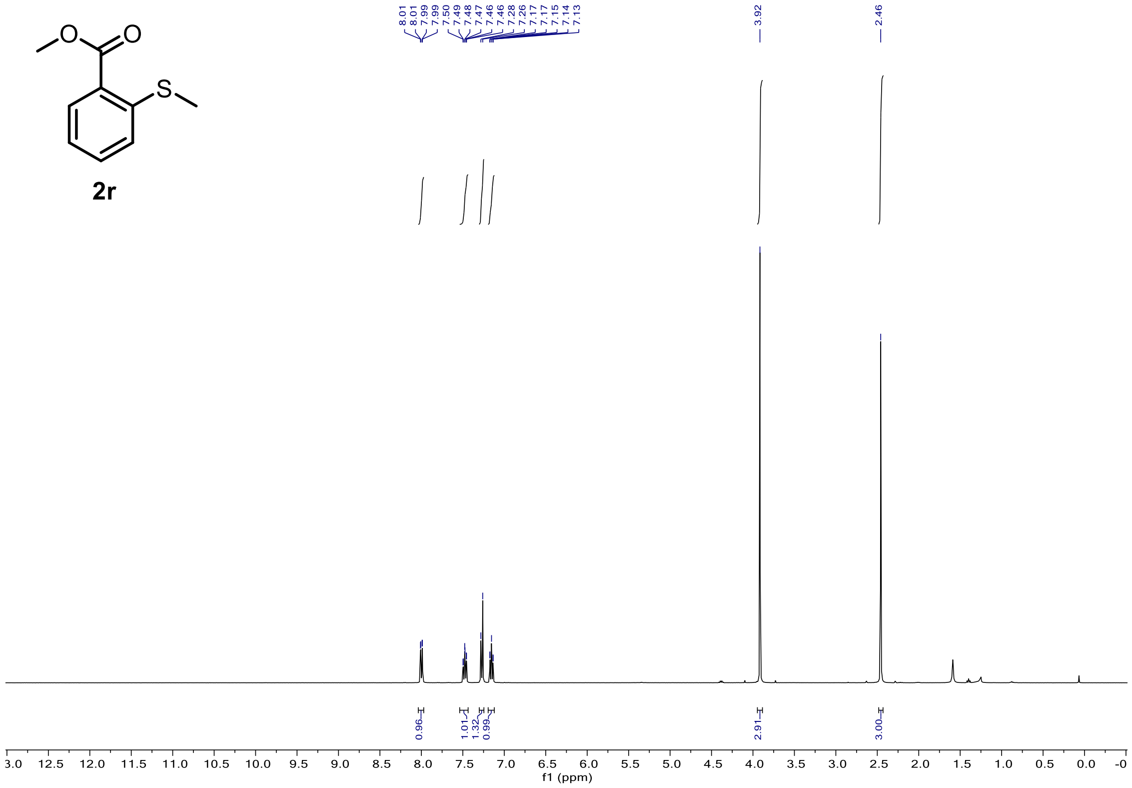
tBu
S
148.52
134.96
127.05
126.01
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
34.51
31.44
16.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

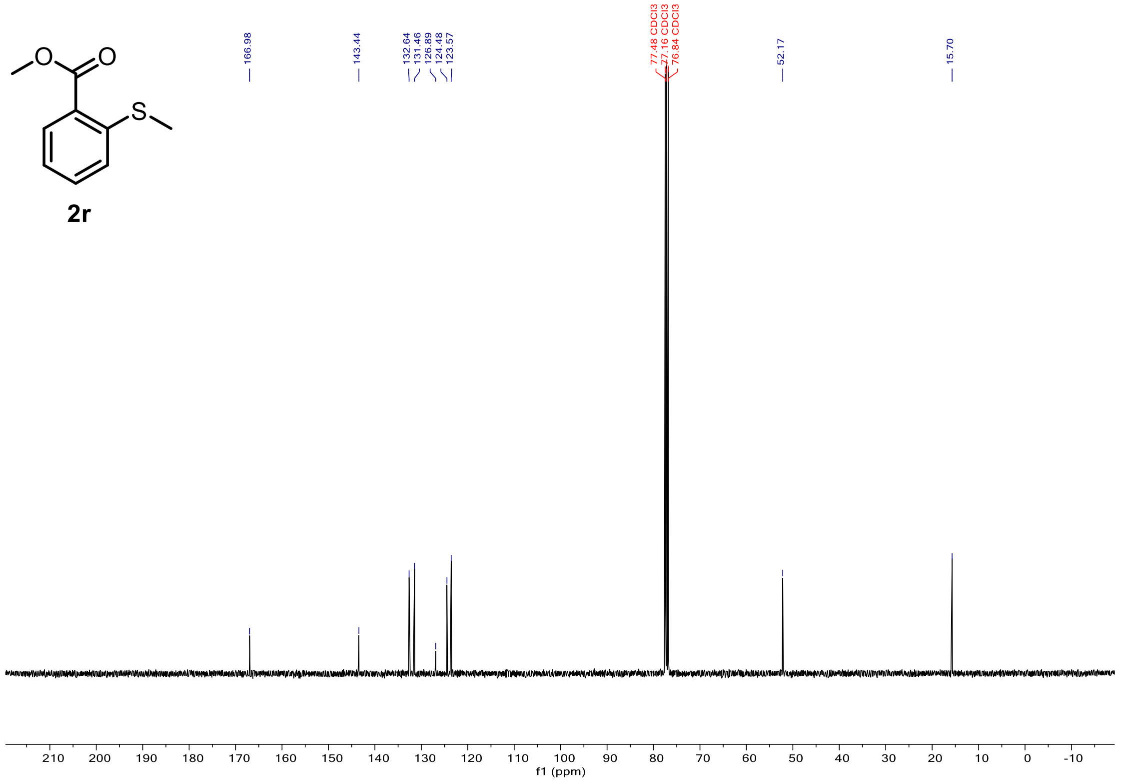

S
CD3
tBu
7.33
7.31
7.23
7.21
1.31
2.00
1.97
8.87
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2q-*d*₃


S
CD3
tBu
148.48
134.90
127.00
126.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
34.51
31.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

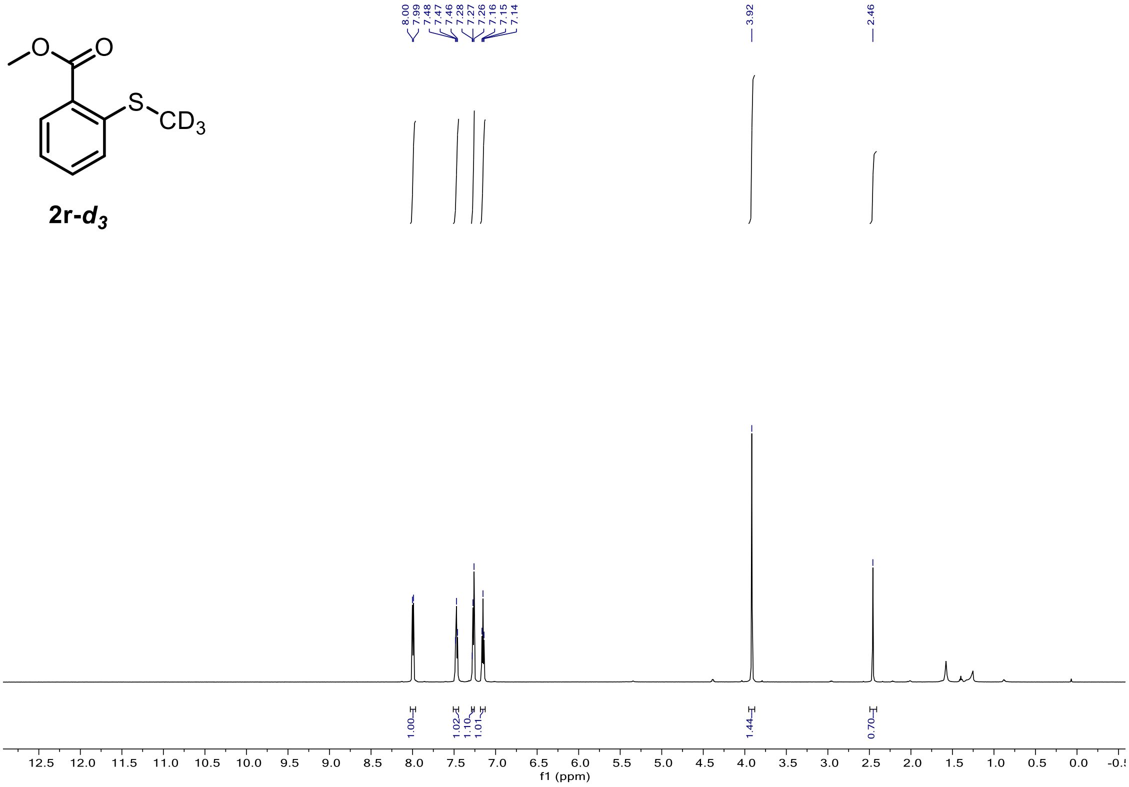
2q-*d*₃


2r
8.01
8.01
7.99
7.99
7.50
7.49
7.48
7.47
7.46
7.46
7.28
7.26
7.17
7.17
7.15
7.14
7.13
3.92
2.46
0.96
1.01
1.32
0.99
2.91
3.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)
O
O
S


2r
166.98
143.44
132.64
131.46
126.89
124.48
123.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
52.17
15.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
O
S

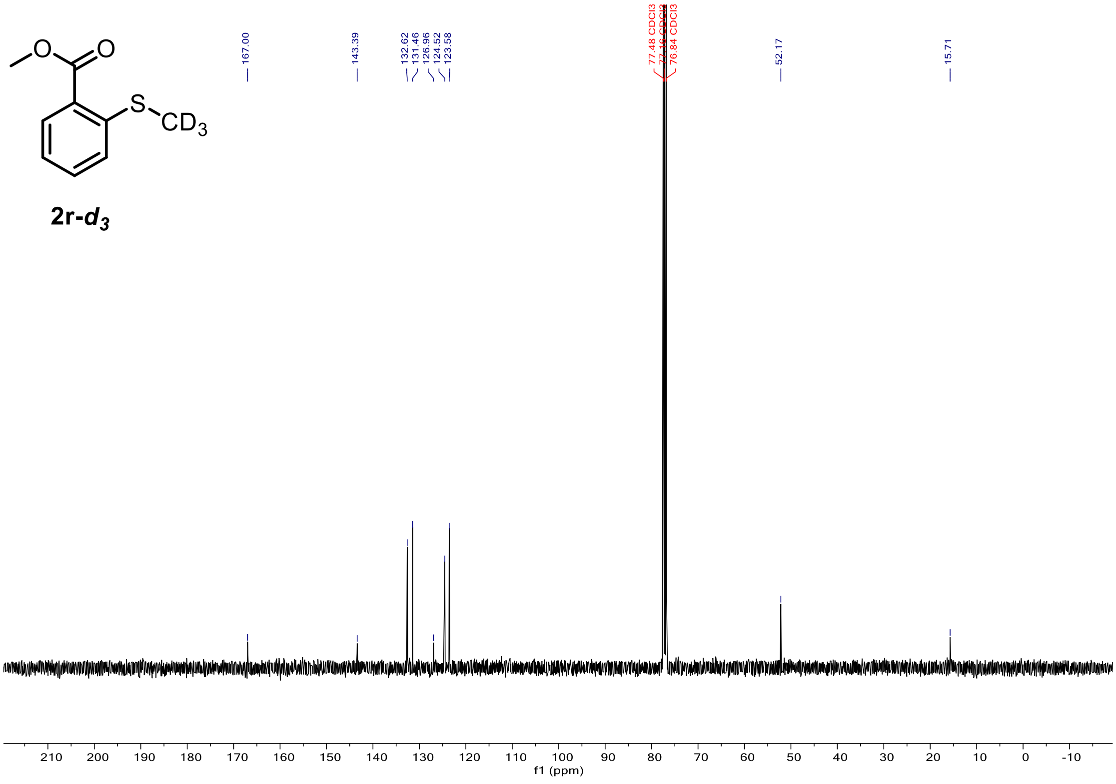
O
O
S
CD3

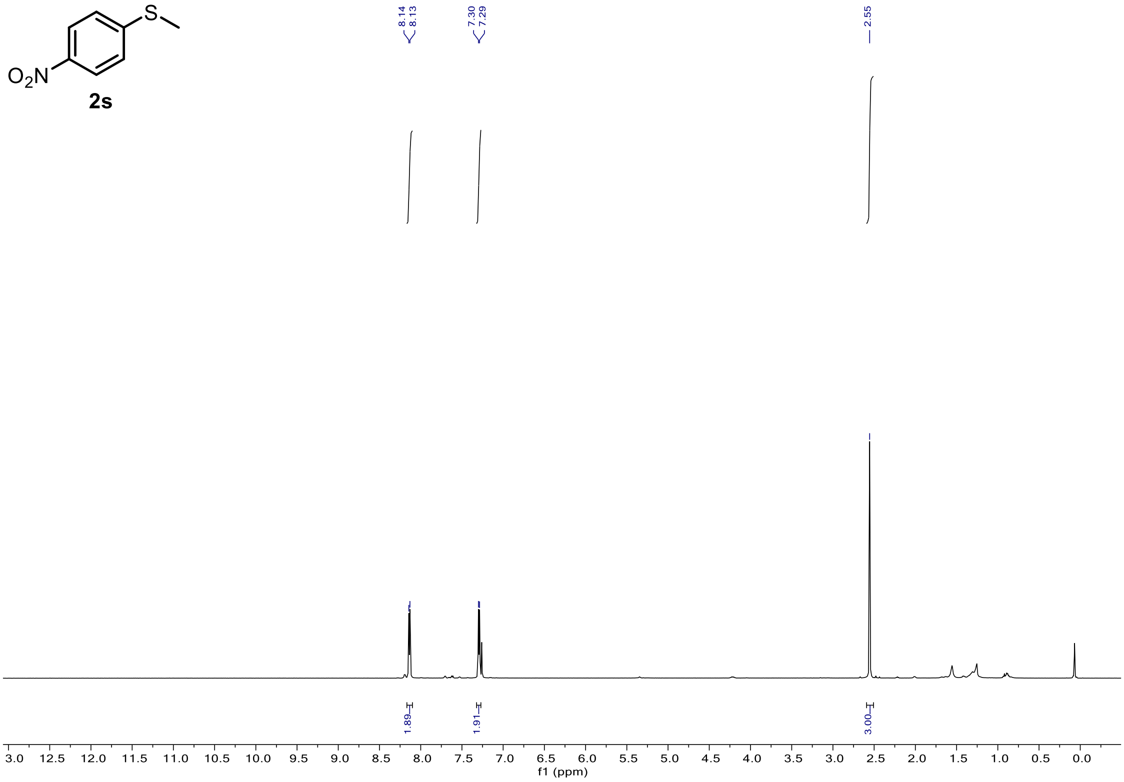
2r-*d*$_3$


8.00
7.99
7.48
7.47
7.46
7.28
7.27
7.26
7.16
7.15
7.14
3.92
2.46
1.00
1.02
1.10
1.01
1.44
0.70
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)

O
O
S
CD3

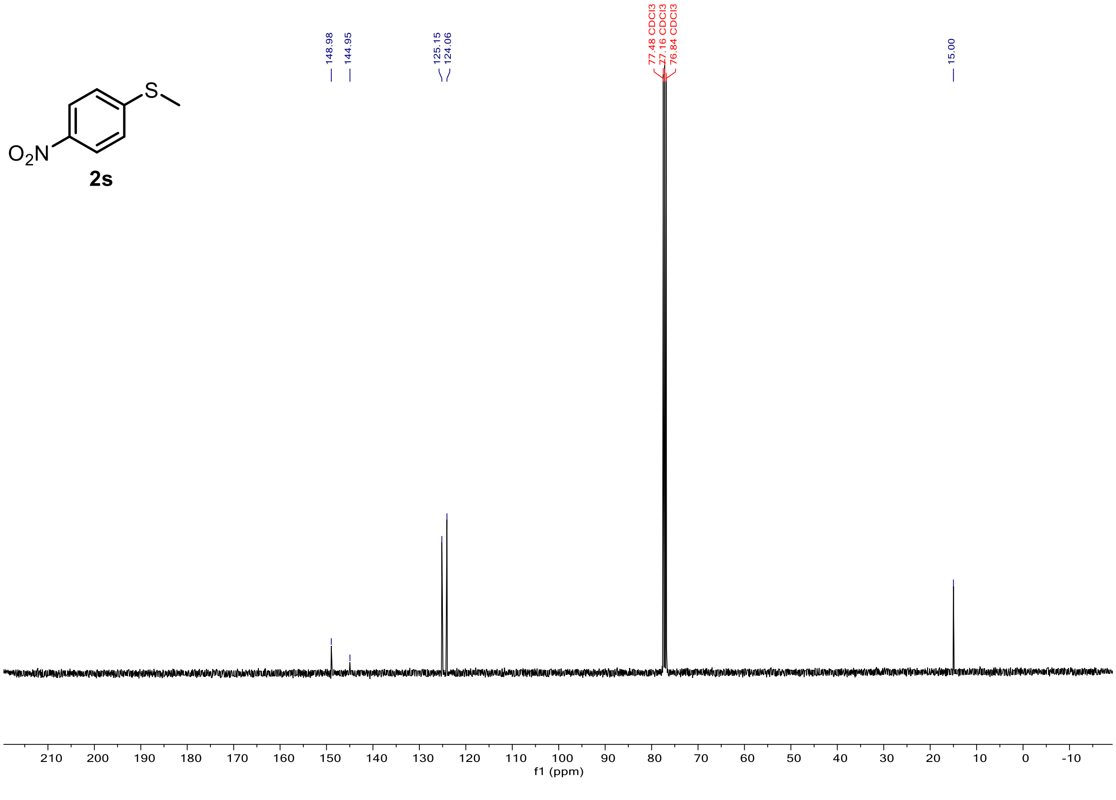
2r-*d*$_3$


167.00
143.39
132.62
131.46
126.96
124.52
123.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
52.17
15.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



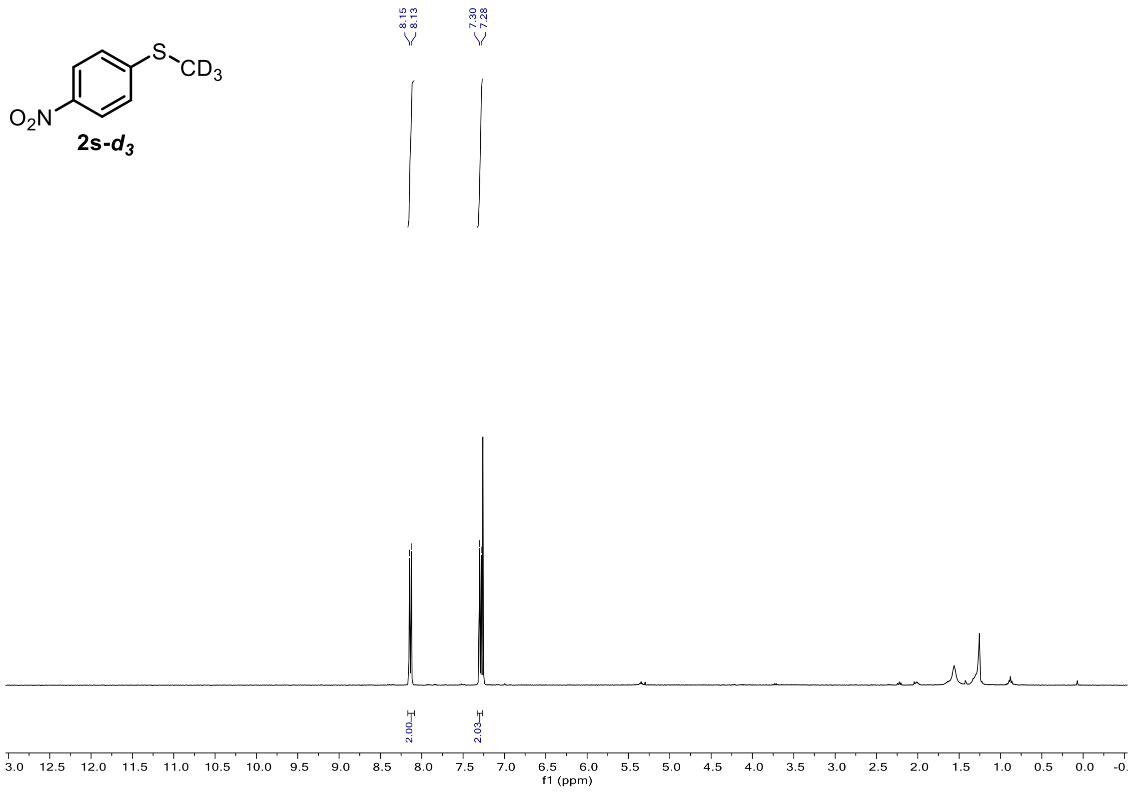
2s

O2N
S
8.14
8.13
7.30
7.29
2.55
1.89
1.91
3.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)



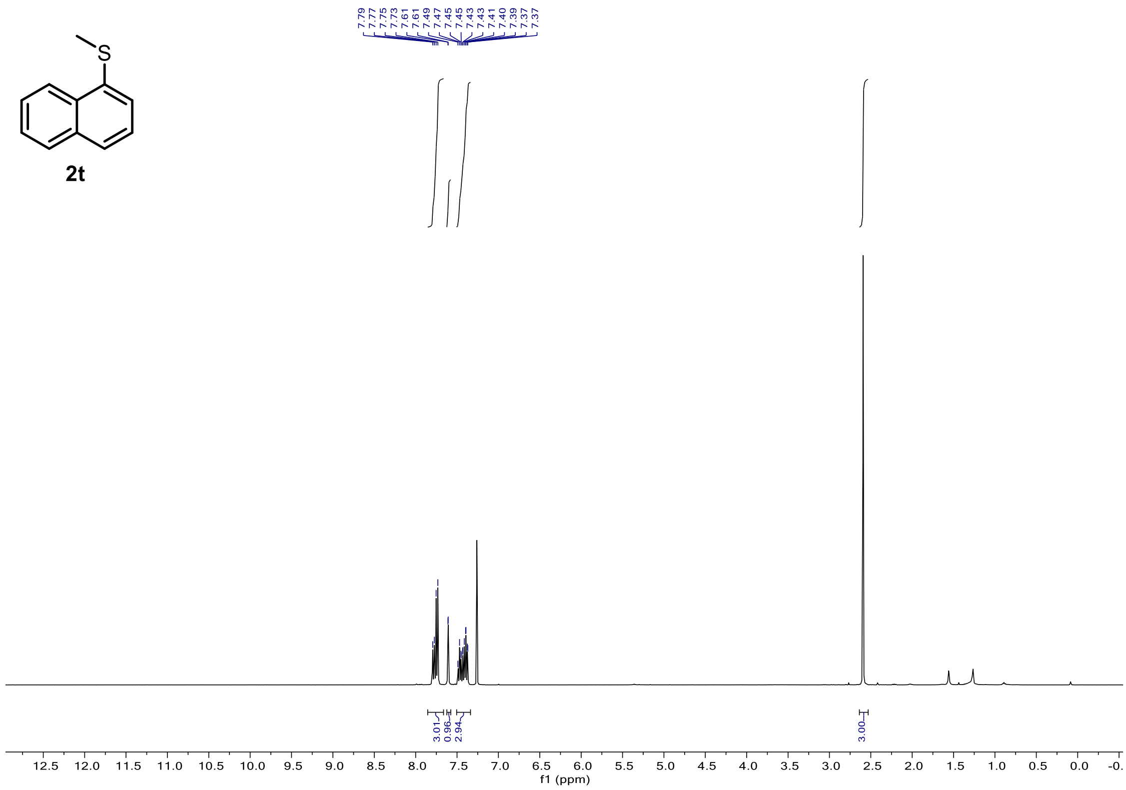
2s

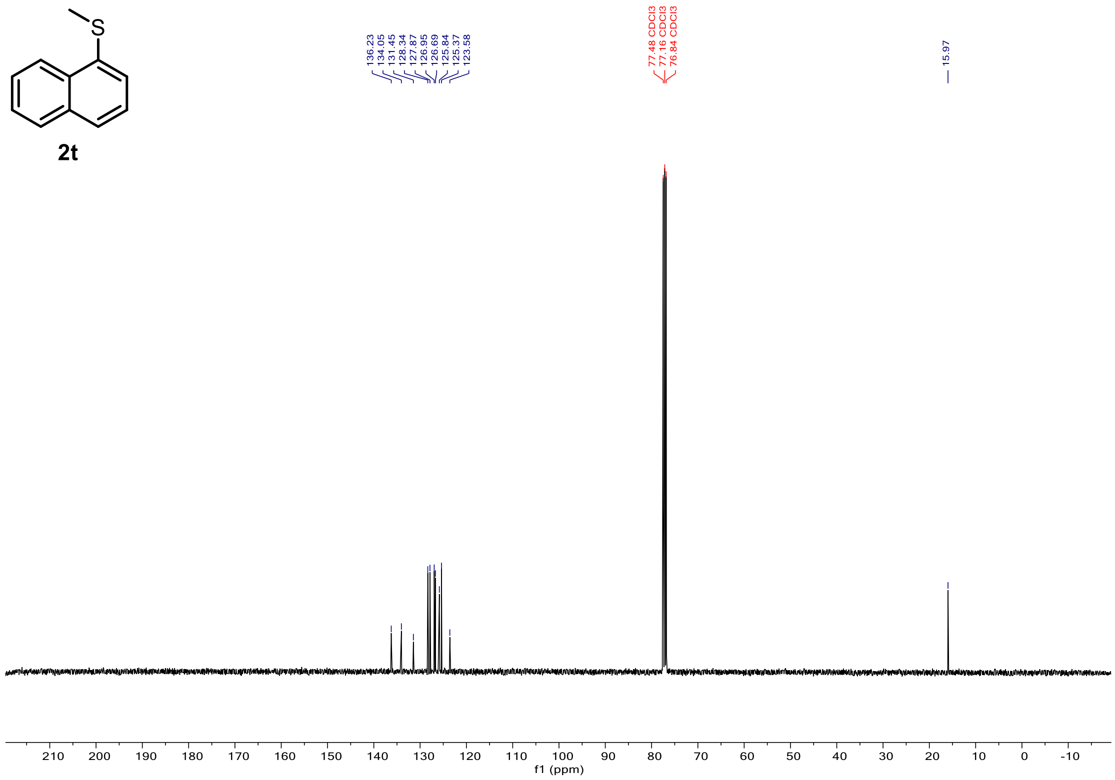
O2N
S
148.98
144.95
125.15
124.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

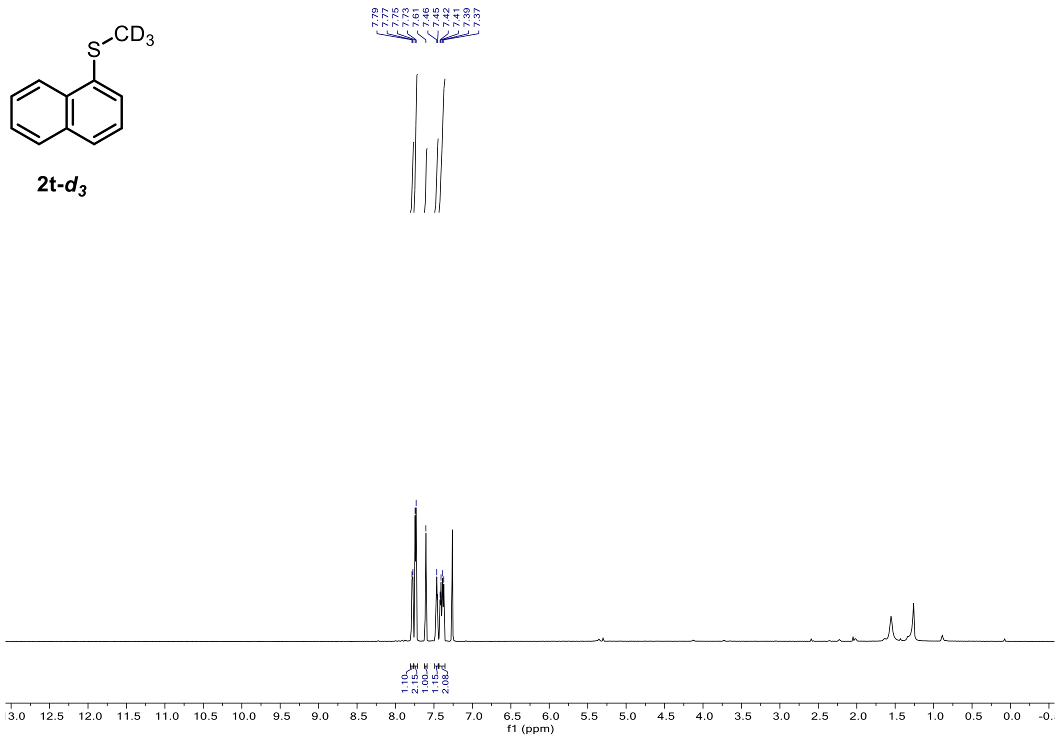


2s-*d*₃

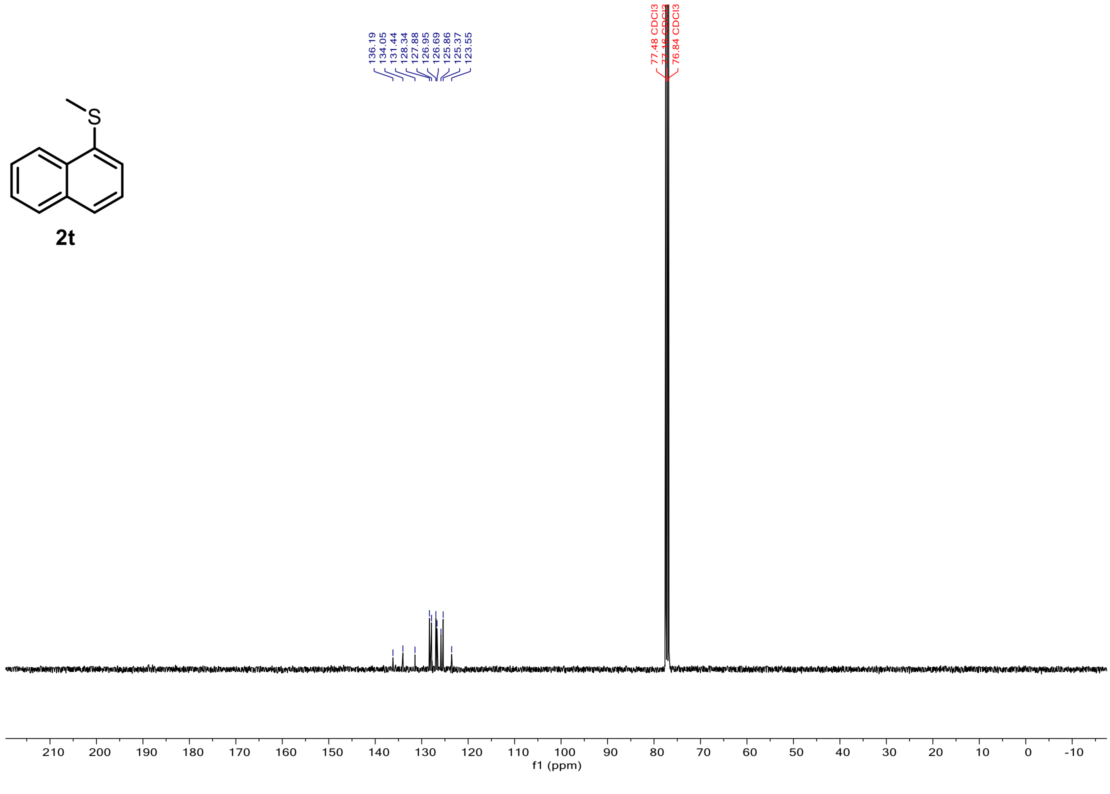
S
CD3
O2N
8.15
8.13
7.30
7.28
2.00
2.03
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


2t
7.79
7.77
7.75
7.73
7.61
7.61
7.49
7.47
7.45
7.45
7.43
7.43
7.41
7.40
7.39
7.37
7.37
3.01
0.96
2.94
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

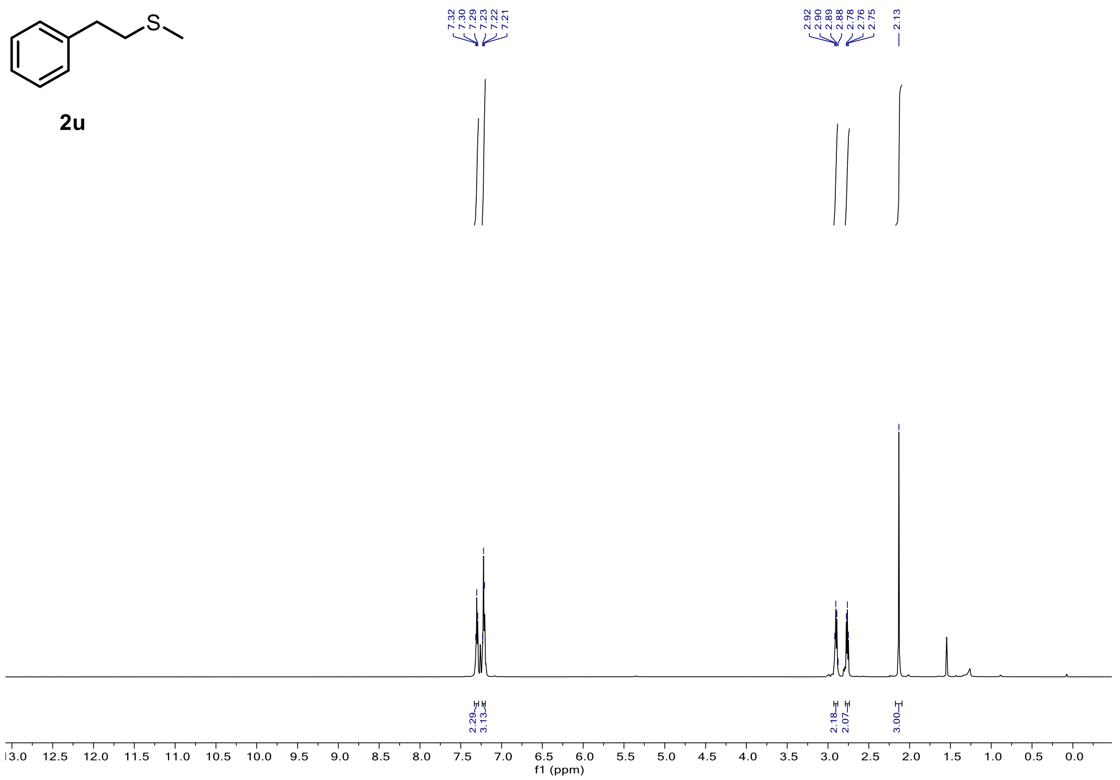

2t
136.23
134.05
131.45
128.34
127.87
126.95
126.69
125.84
125.37
123.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
15.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2t-*d*₃

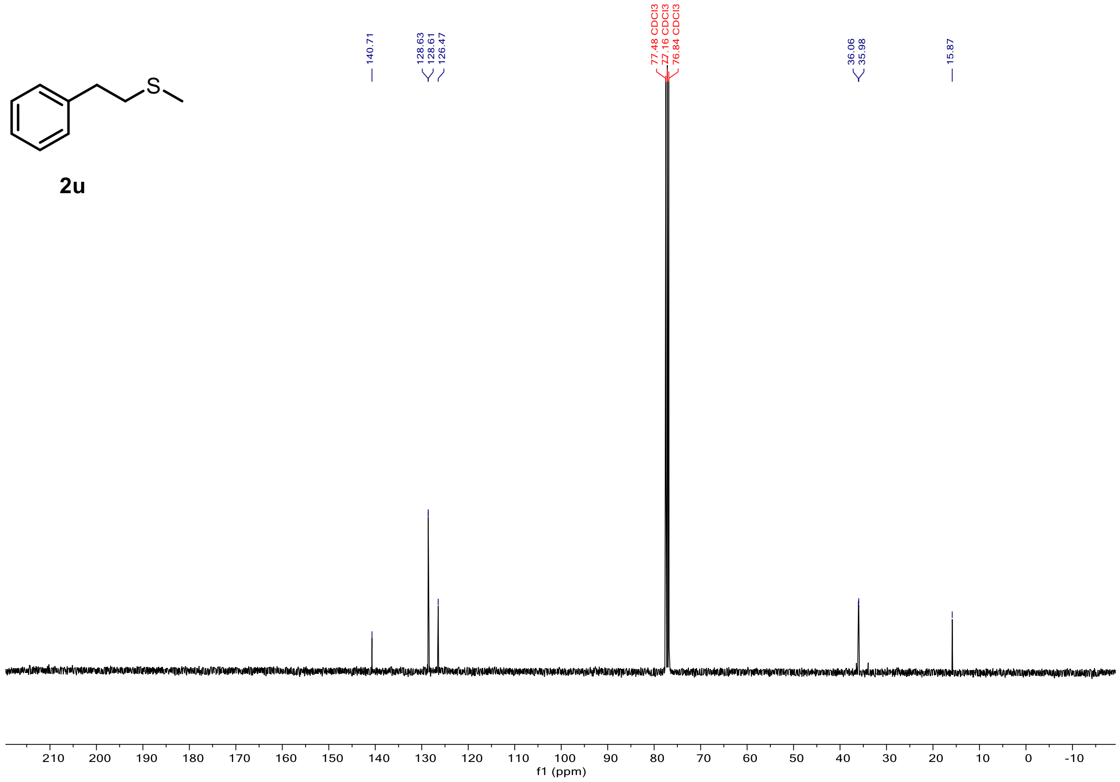
S
CD3
7.79
7.77
7.75
7.73
7.61
7.46
7.45
7.42
7.41
7.39
7.37
1.10
2.15
1.00
1.15
2.08
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


2t

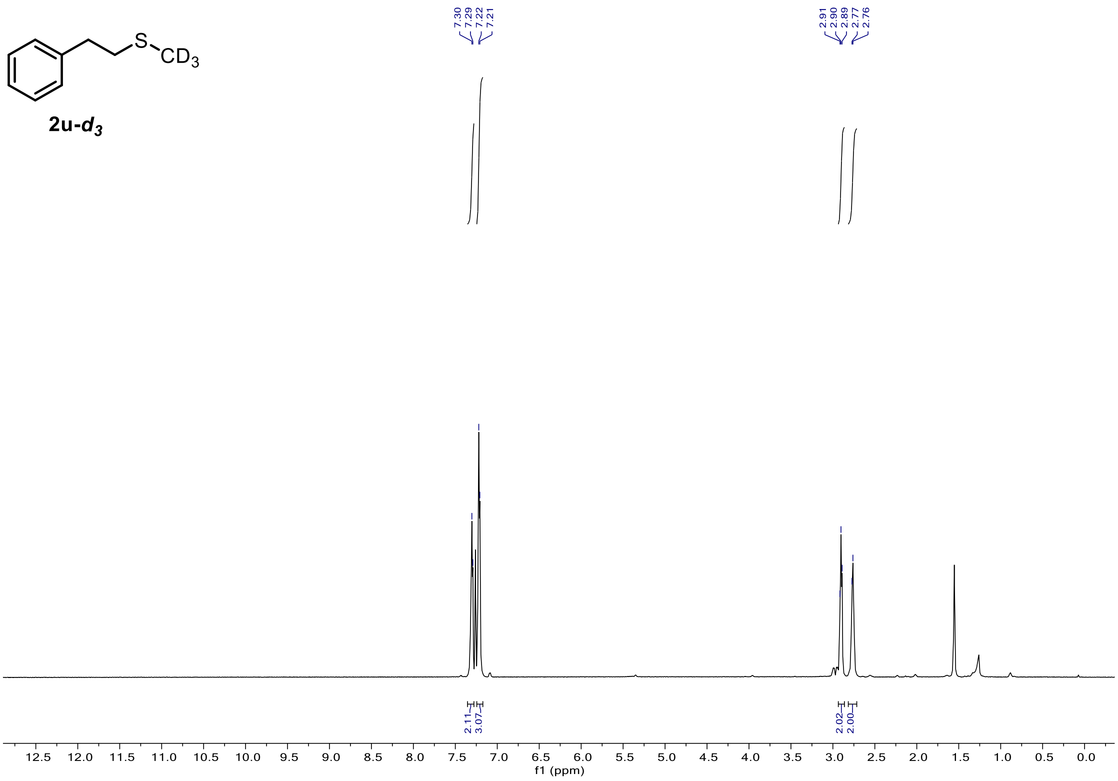
S
136.19
134.05
131.44
128.34
127.88
126.95
126.69
125.86
125.37
123.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2u

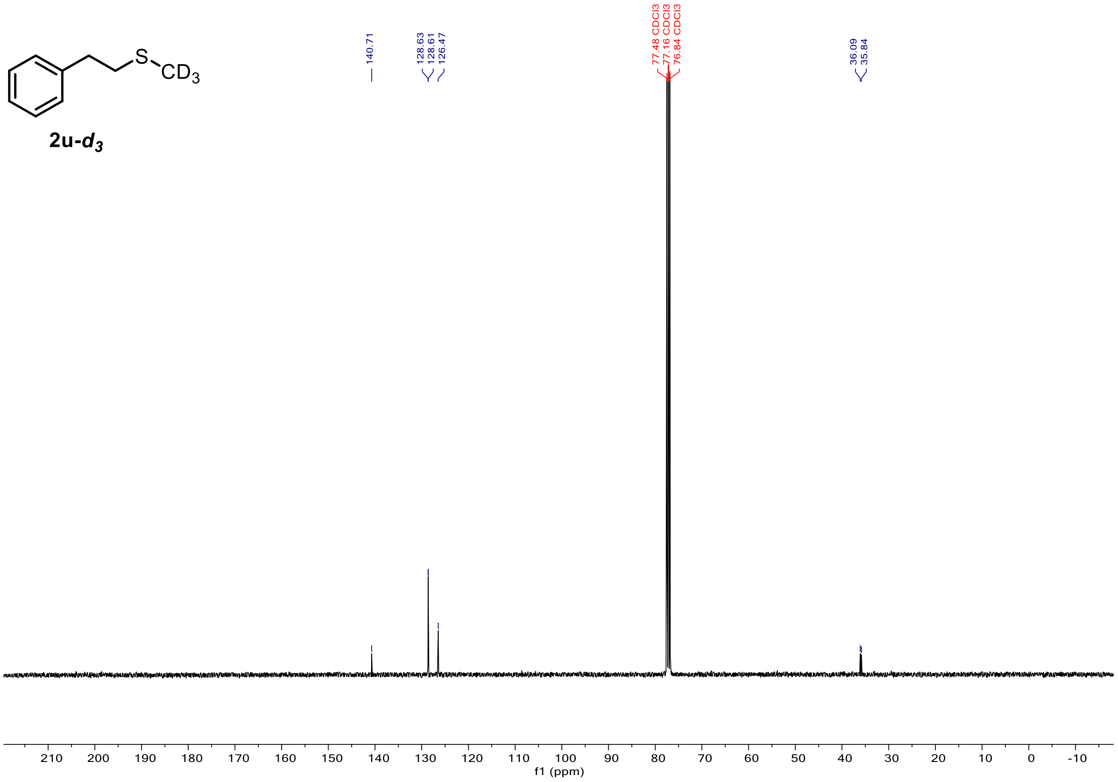
7.32
7.30
7.29
7.23
7.22
7.21
2.92
2.90
2.89
2.88
2.78
2.76
2.75
2.13
2.29
3.13
2.18
2.07
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S


2u

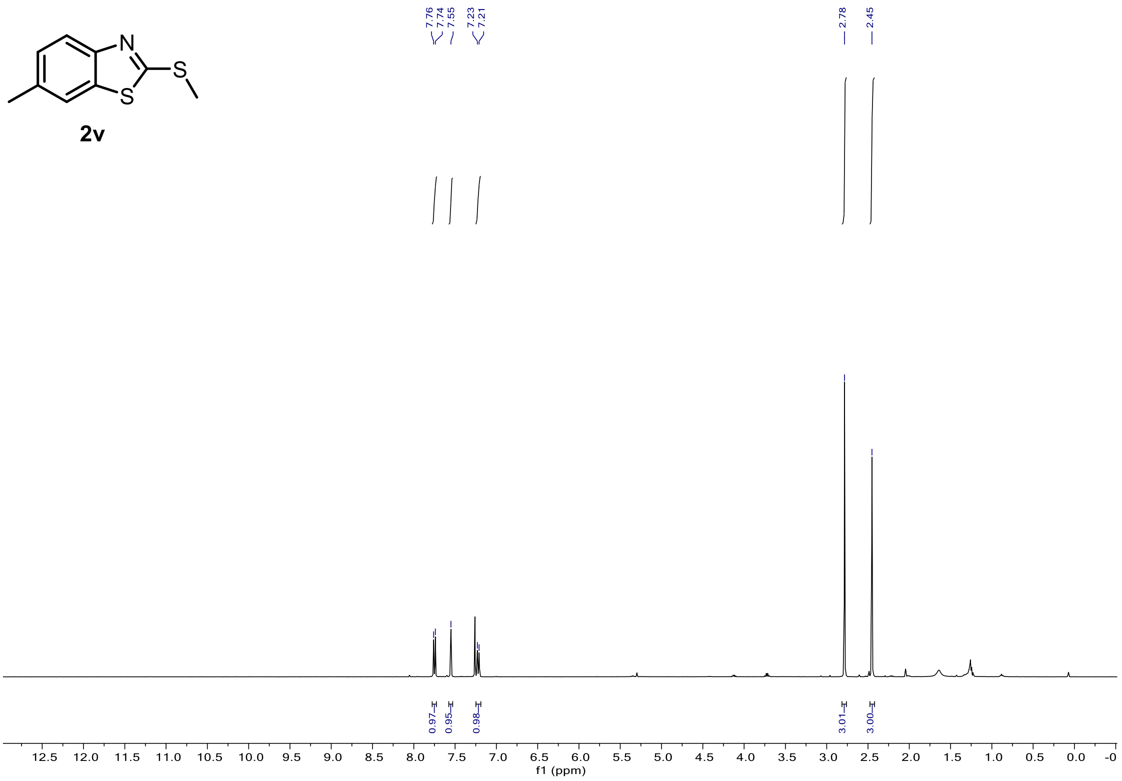
140.71
128.63
128.61
126.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
36.06
35.98
15.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
S

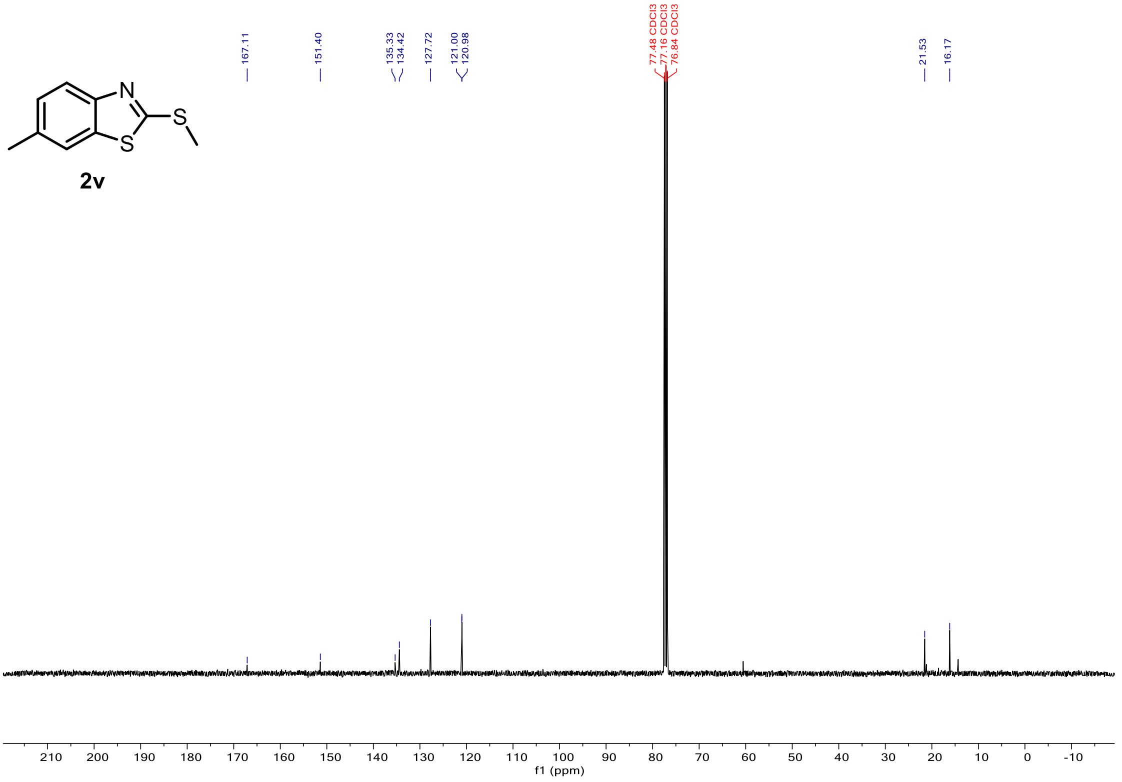

2u-d_3

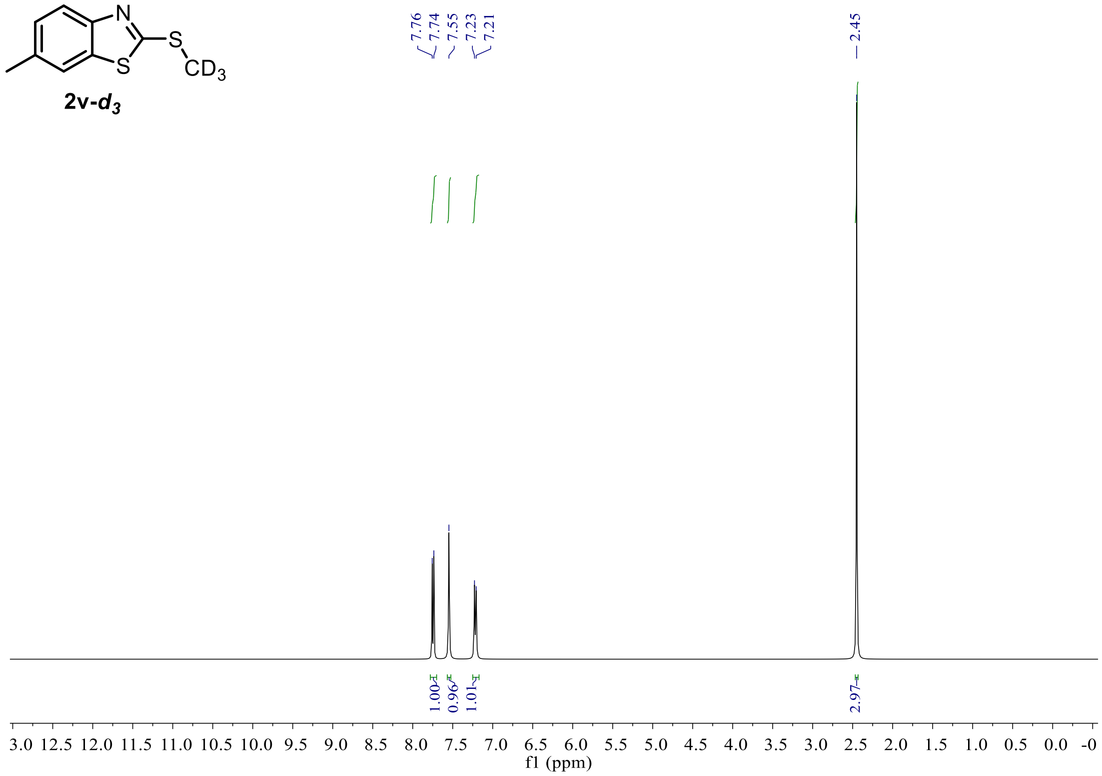
7.30
7.29
7.22
7.21
2.91
2.90
2.89
2.77
2.76
2.11
3.07
2.02
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2u-d_3

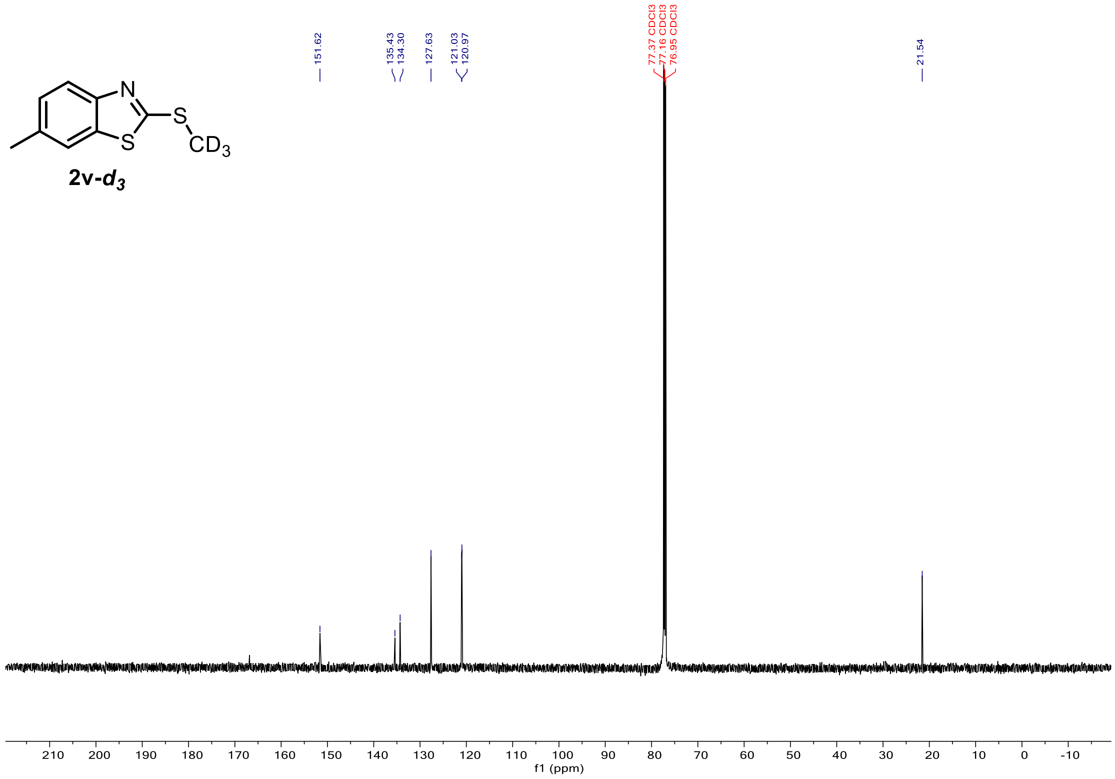
140.71
128.63
128.61
126.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
36.09
35.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
S
S
2v
7.76
7.74
7.55
7.23
7.21
2.78
2.45
0.97
0.95
0.98
3.01
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

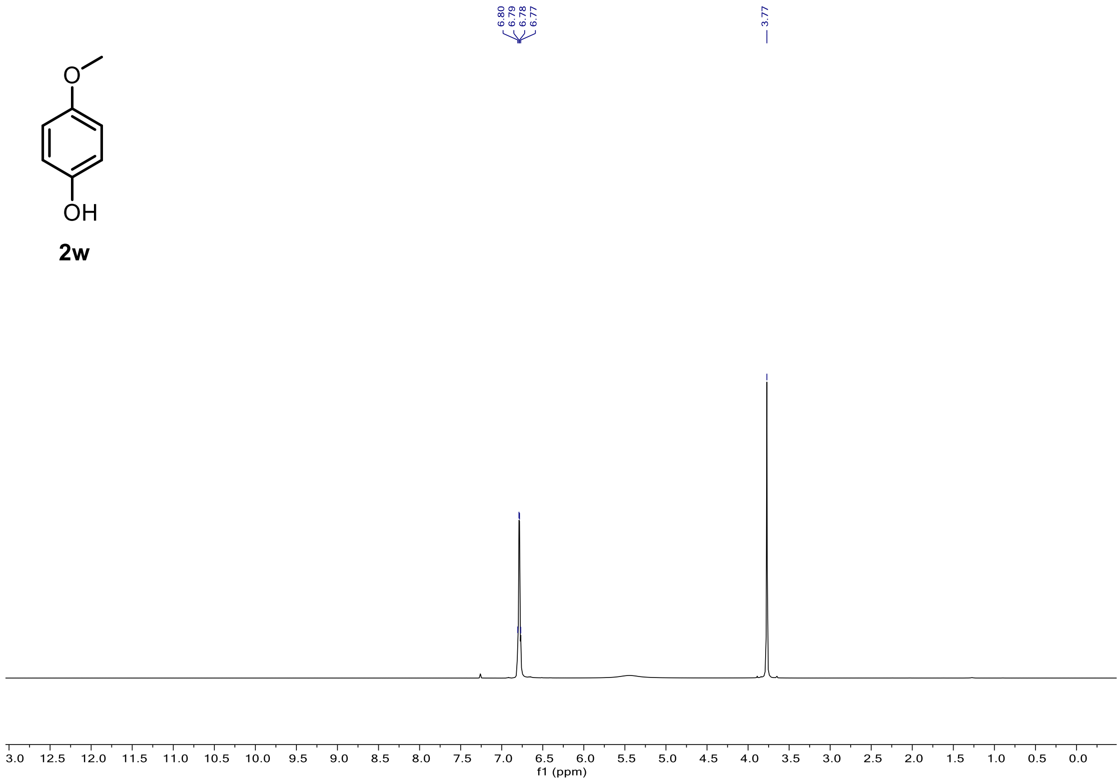

N
S
S
2v
167.11
151.40
135.33
134.42
127.72
121.00
120.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.53
16.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

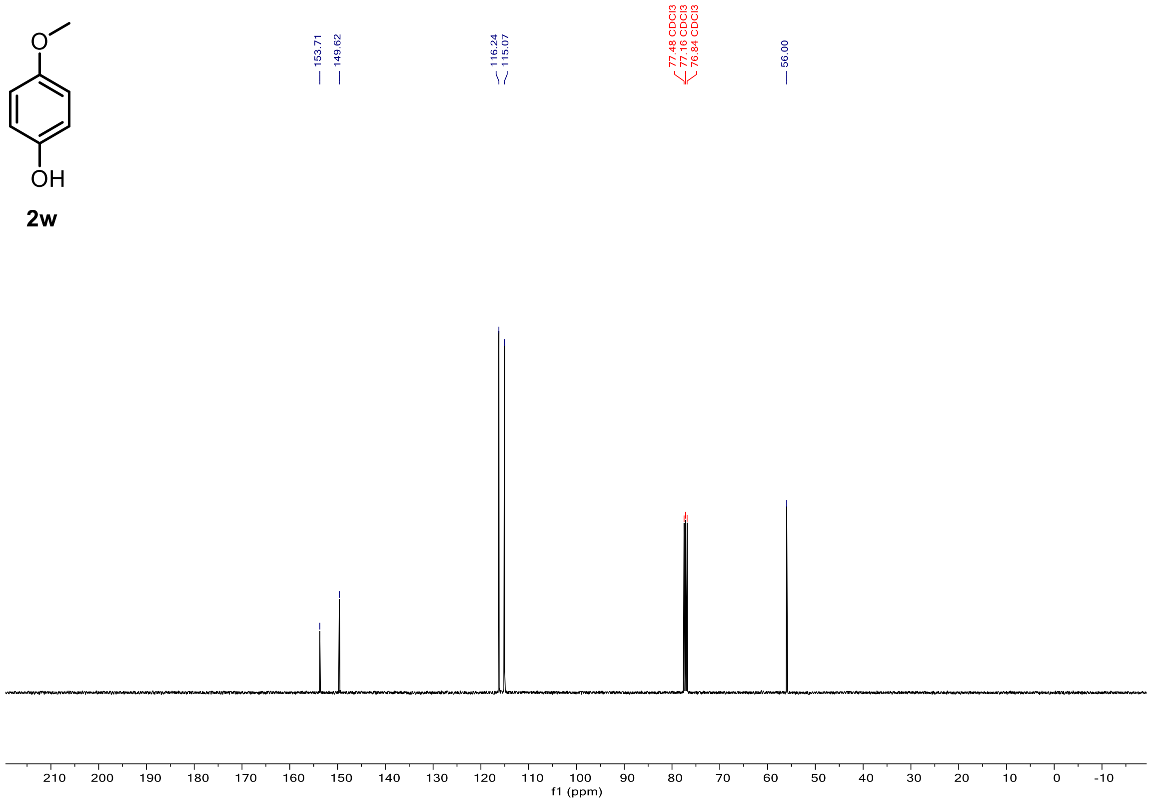

N
S
S
CD3
7.76
7.74
7.55
7.23
7.21
2.45
1.00
0.96
1.01
2.97
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

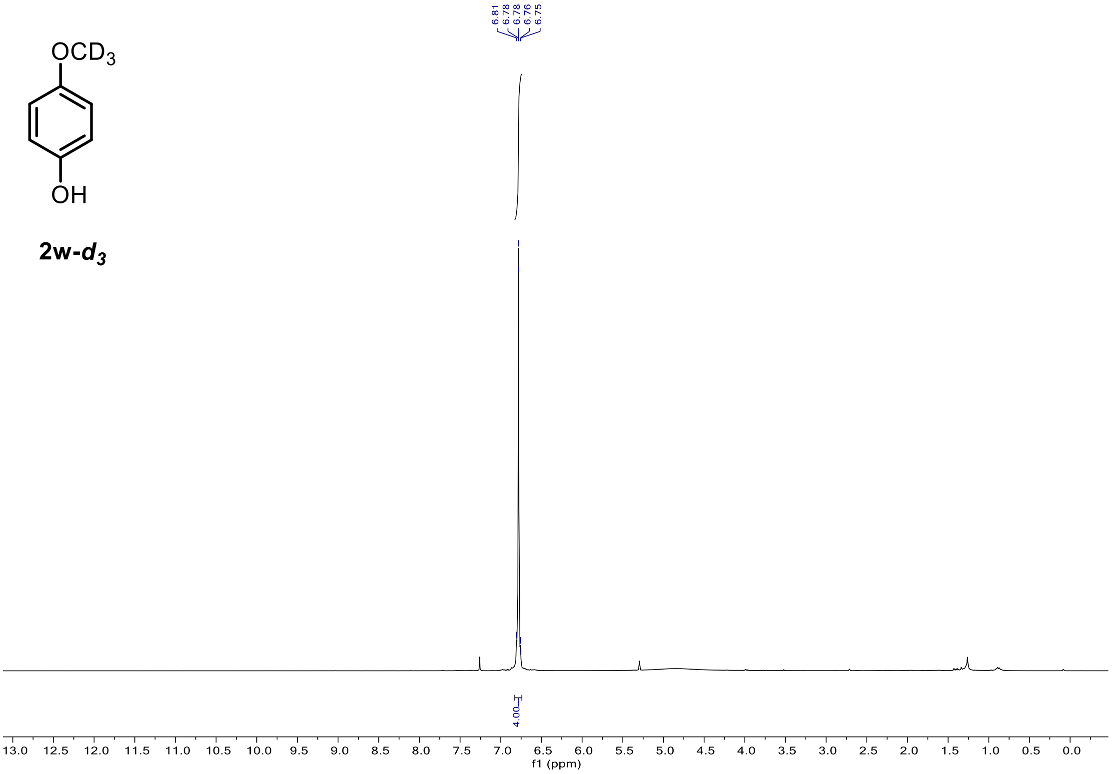
2v-d_3


N
S
S
CD3
151.62
135.43
134.30
127.63
121.03
120.97
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
21.54
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

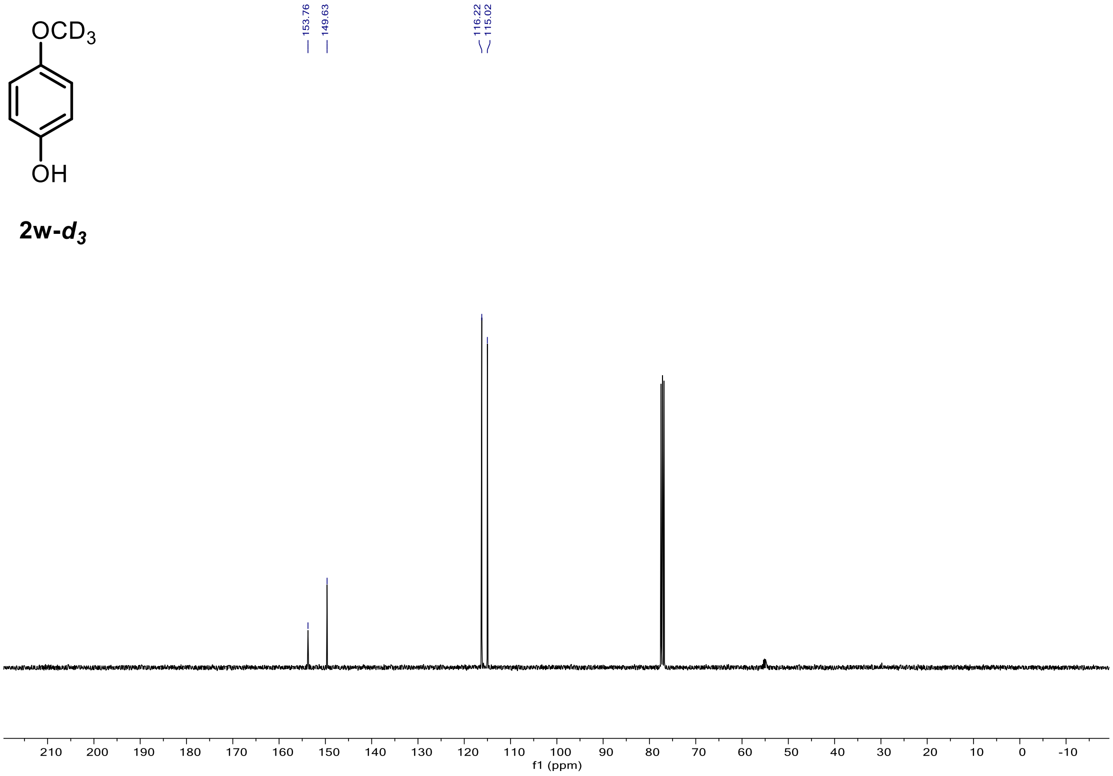
2v-d_3


2w
OH
O
6.80
6.79
6.78
6.77
3.77
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

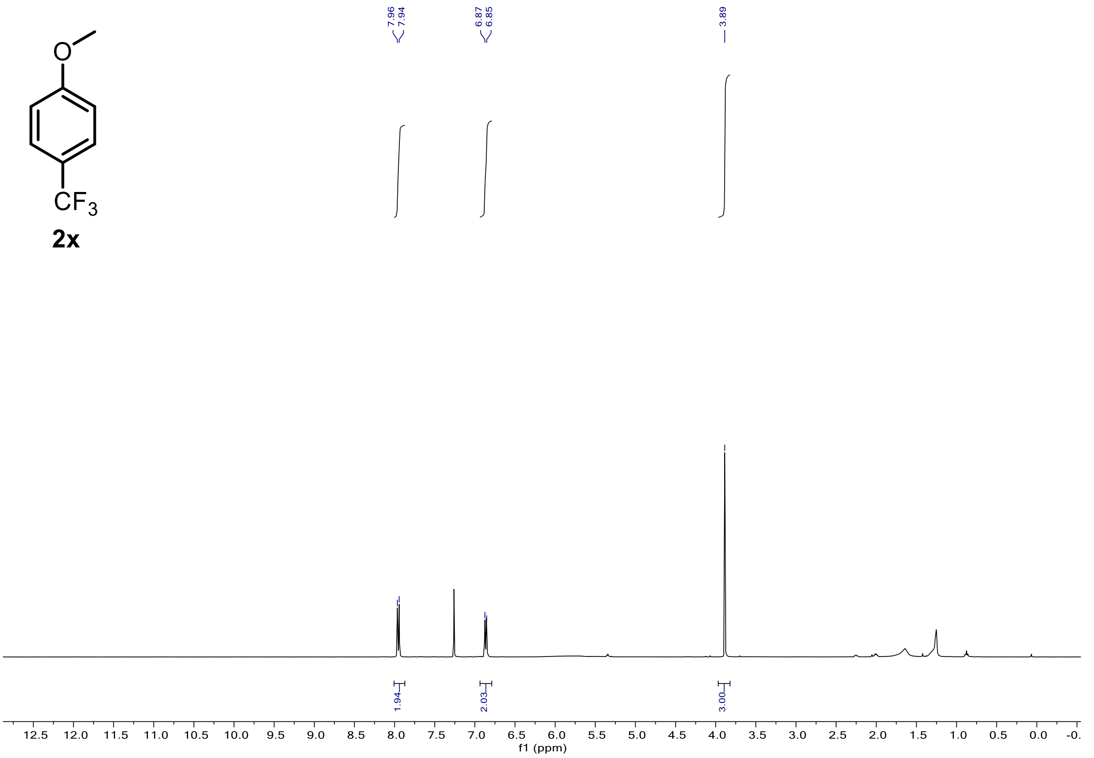

2w
OH
O
153.71
149.62
116.24
115.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OCD3
OH
6.81
6.78
6.78
6.76
6.75
4.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

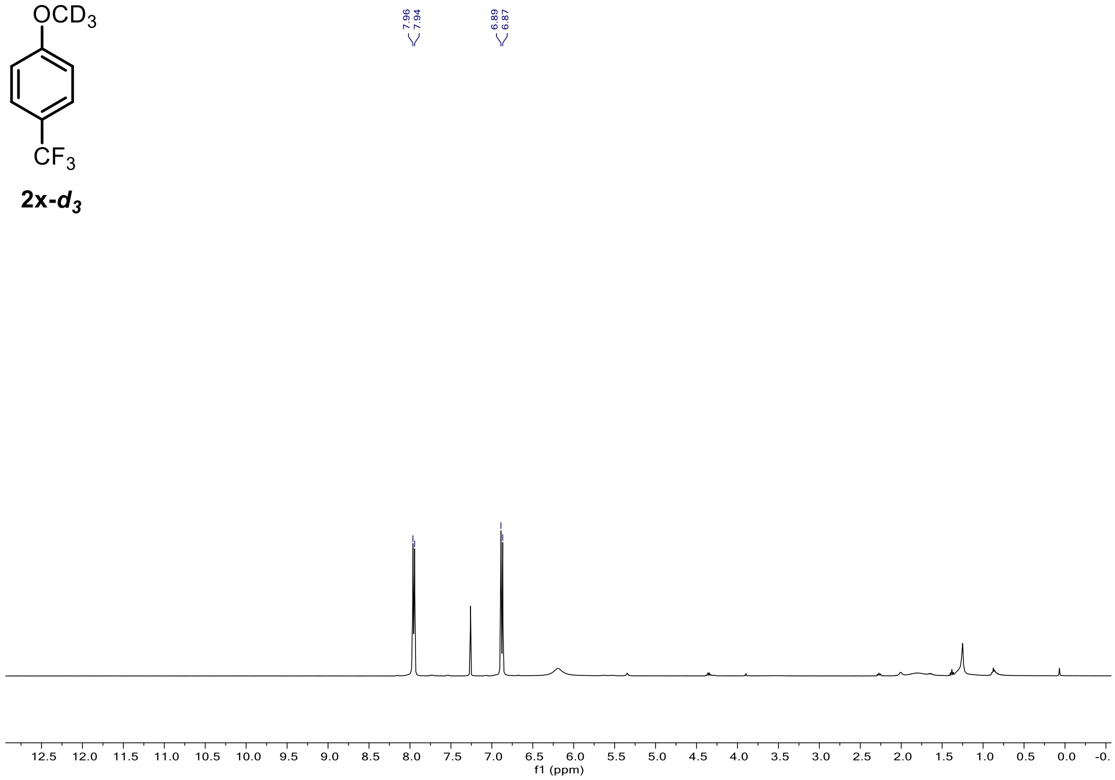
2w-*d*$_3$


OCD3
OH
153.76
149.63
116.22
115.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

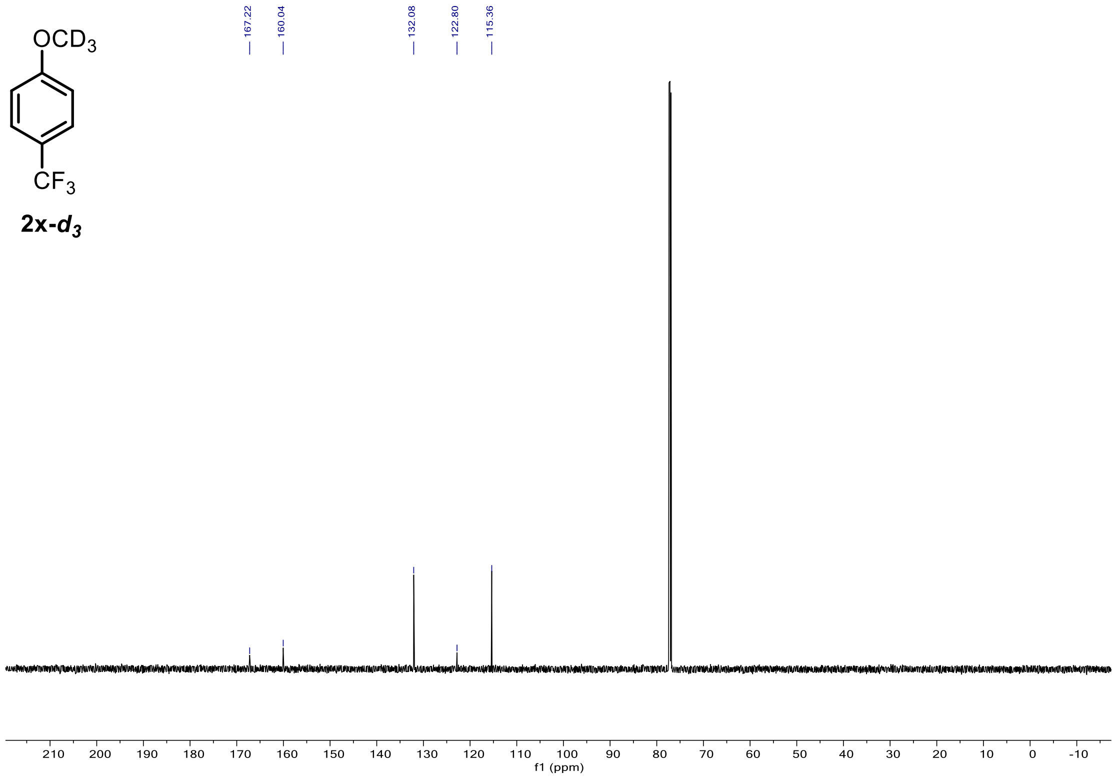
2w-*d*$_3$


O
CF3
7.96
7.94
6.87
6.85
3.89
1.94
2.03
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

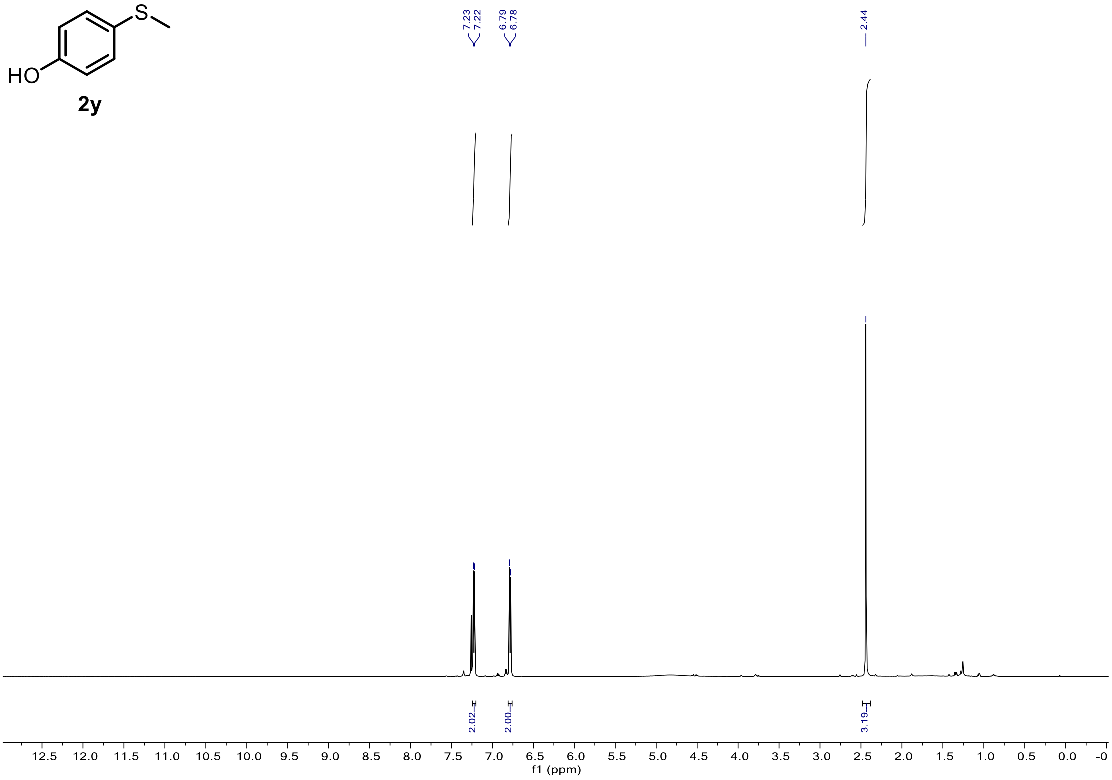
2x

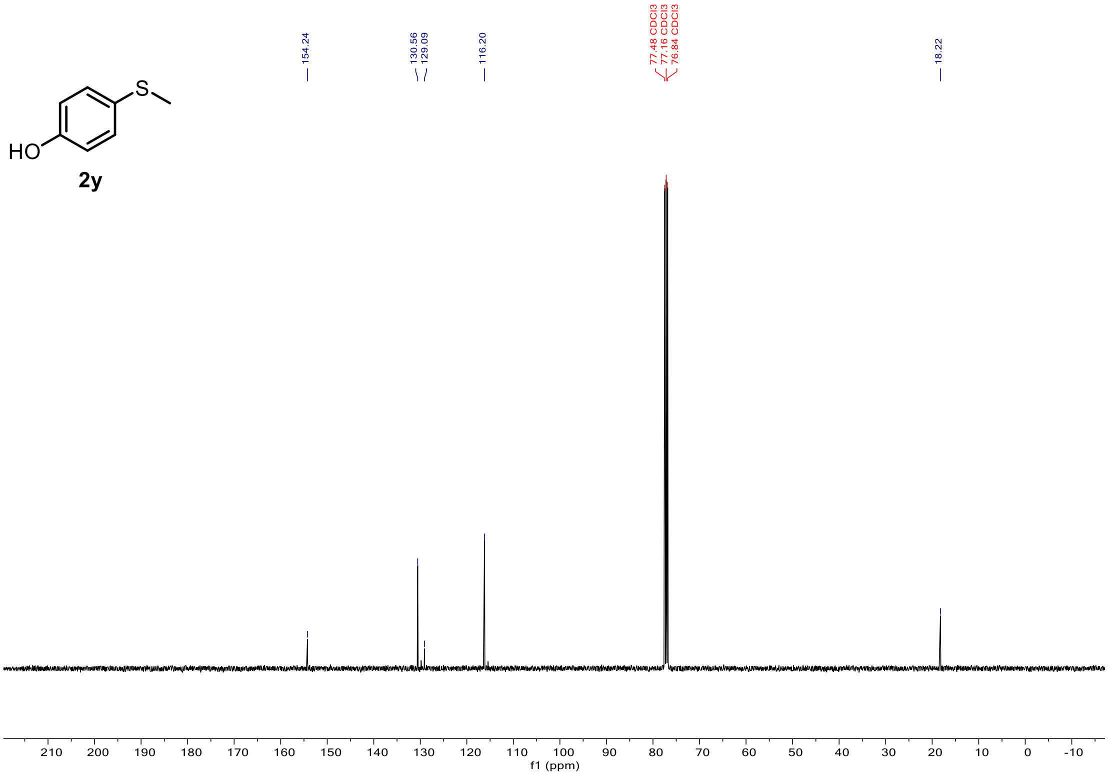

OCD3
CF3
7.96
7.94
6.89
6.87
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

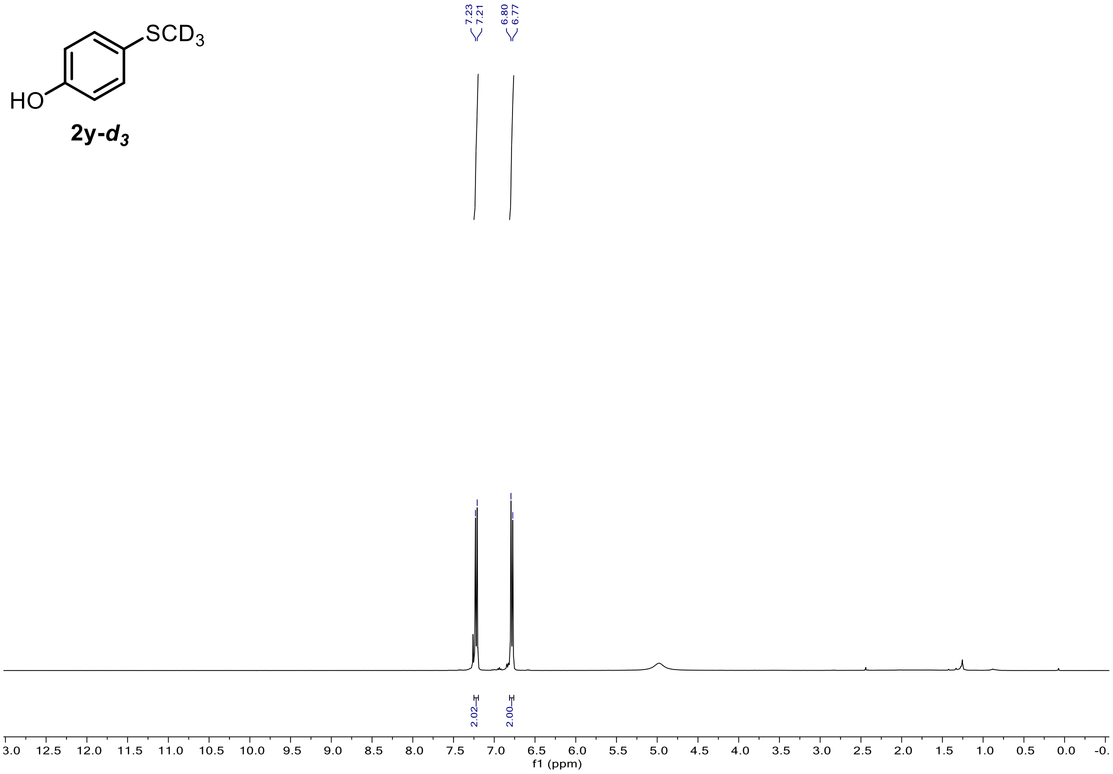
2x-d_3

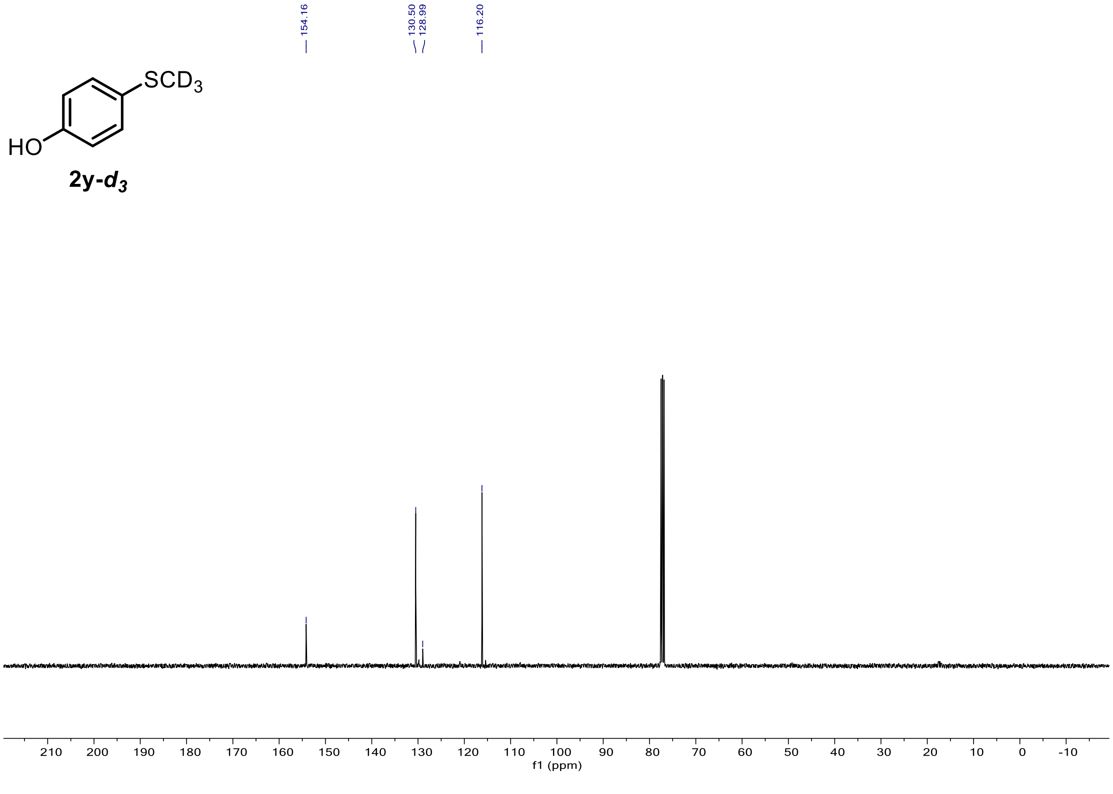

OCD3
CF3
167.22
160.04
132.08
122.80
115.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

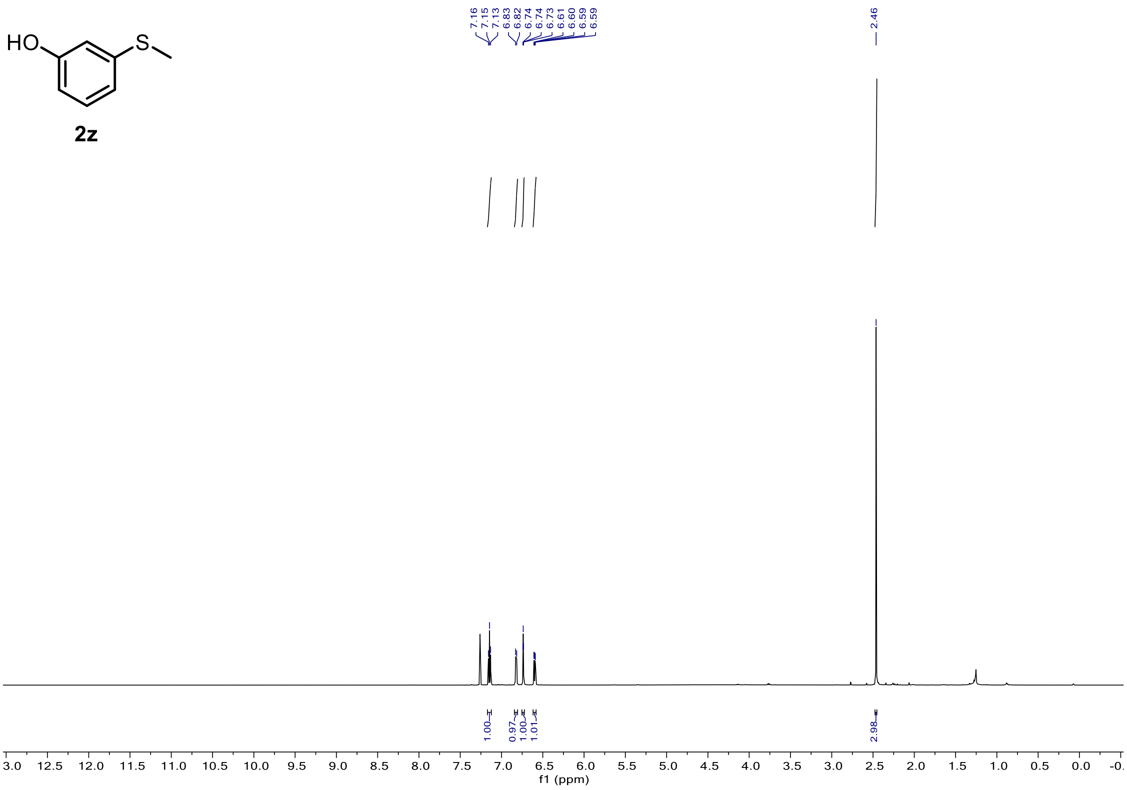
2x-d_3


HO
S
2y
7.23
7.22
6.79
6.78
2.44
2.02
2.00
3.19
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

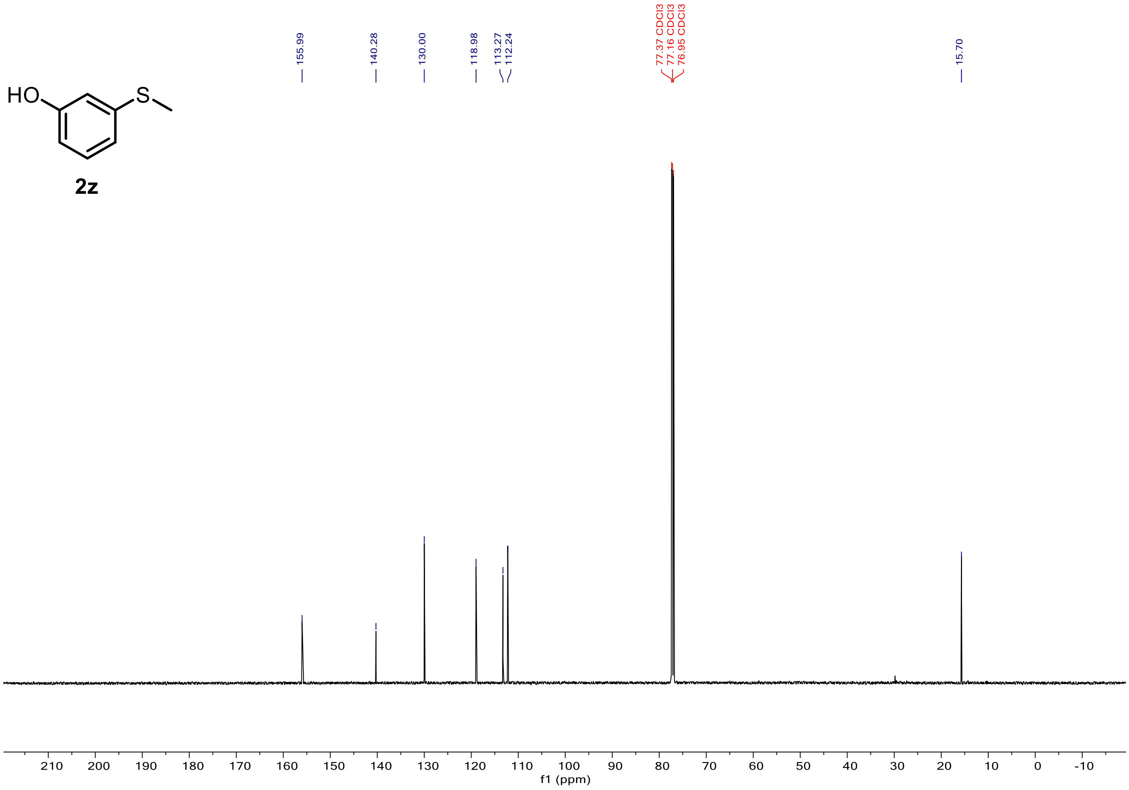

HO
S
2y
154.24
130.56
129.09
116.20
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
18.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SCD3
HO
2y-d3
7.23
7.21
6.80
6.77
2.02
2.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)

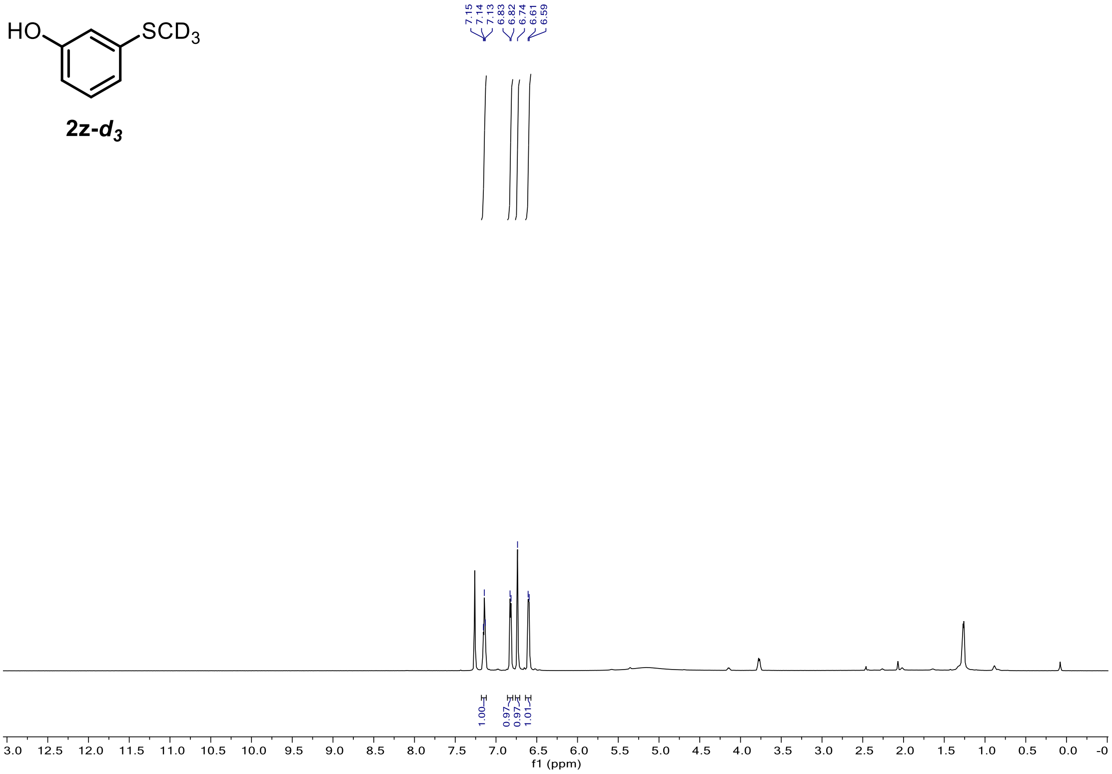

154.16
130.50
128.99
116.20
SCD3
HO
2y-d3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
S
7.16
7.15
7.13
6.83
6.82
6.74
6.74
6.73
6.61
6.60
6.59
6.59
2.46
1.00
0.97
1.00
1.01
2.98
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

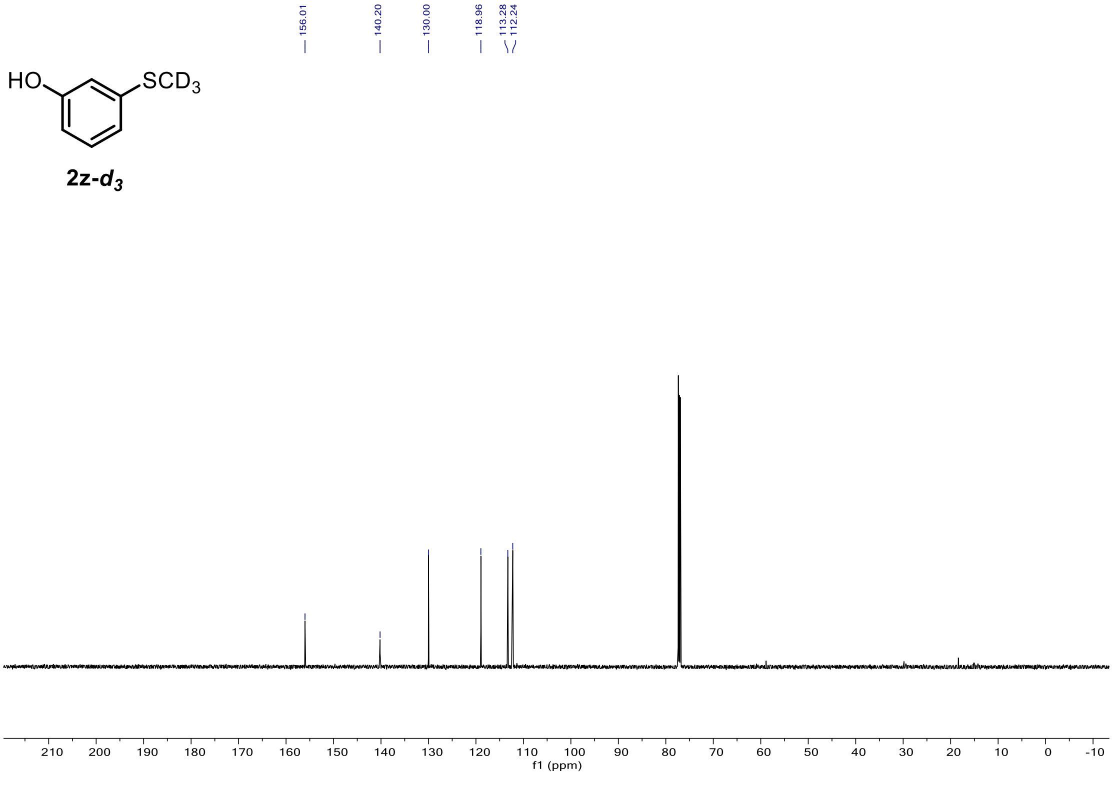
2z


HO
S
155.99
140.28
130.00
118.98
113.27
112.24
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
15.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

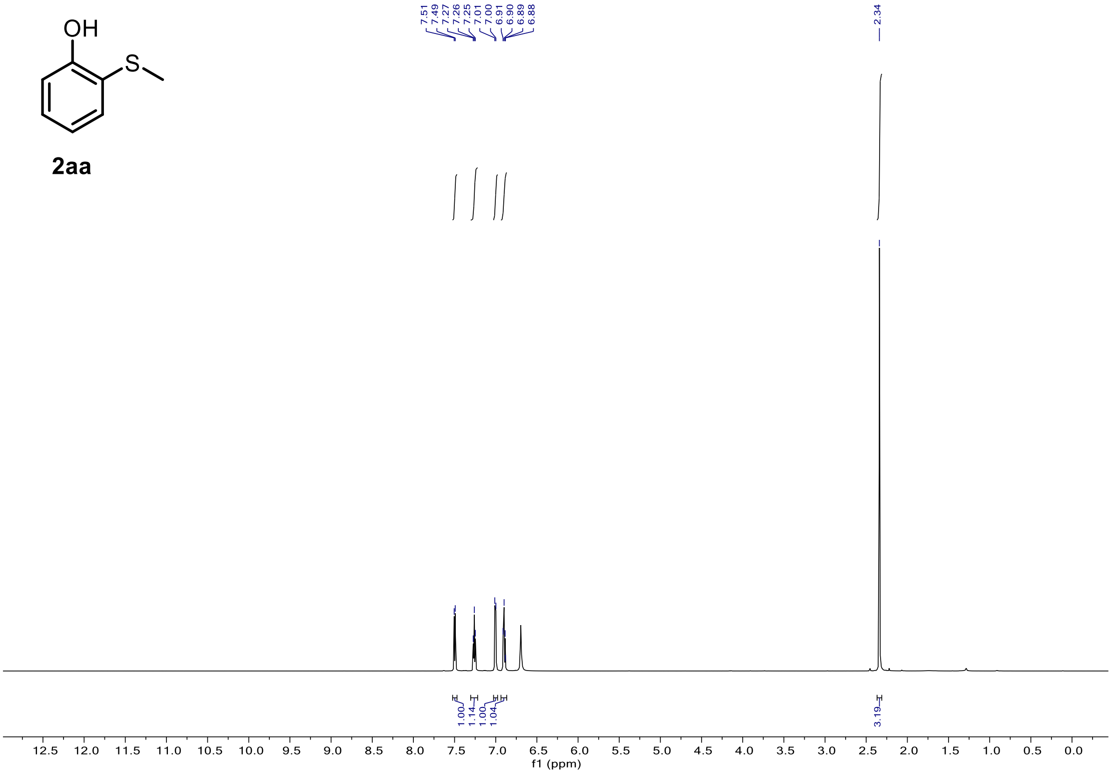
2z

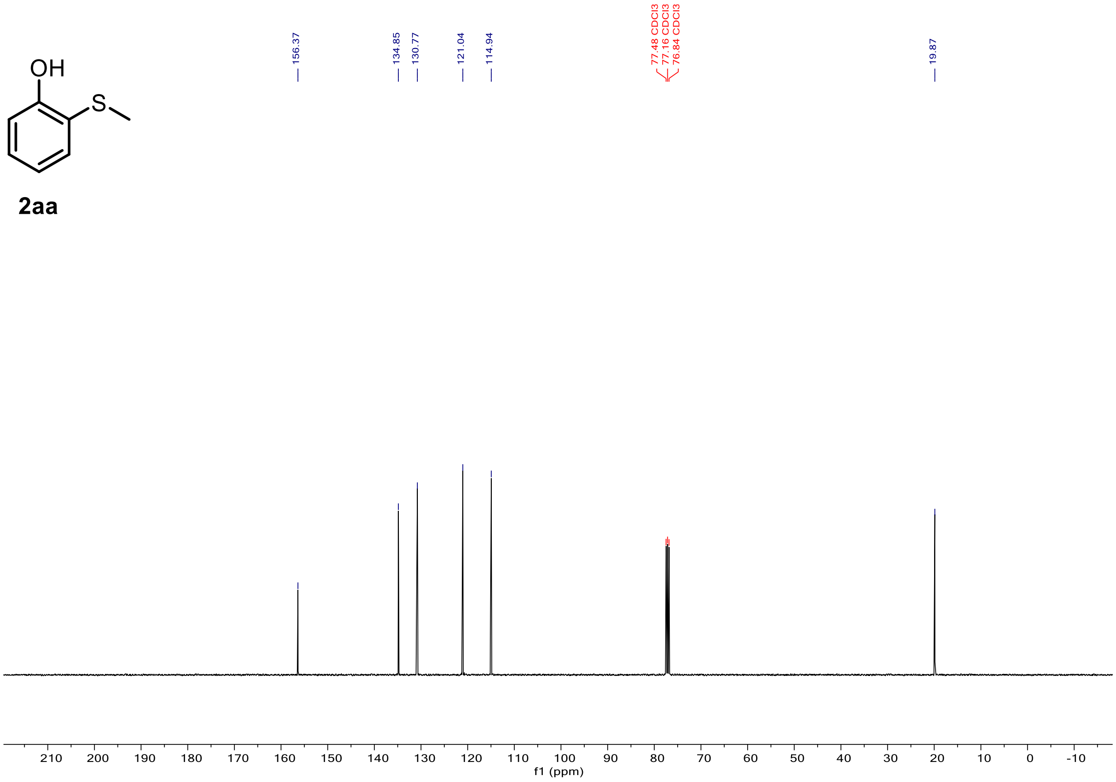

HO
SCD3
7.15
7.14
7.13
6.83
6.82
6.74
6.61
6.59
1.00
0.97
0.97
1.01
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

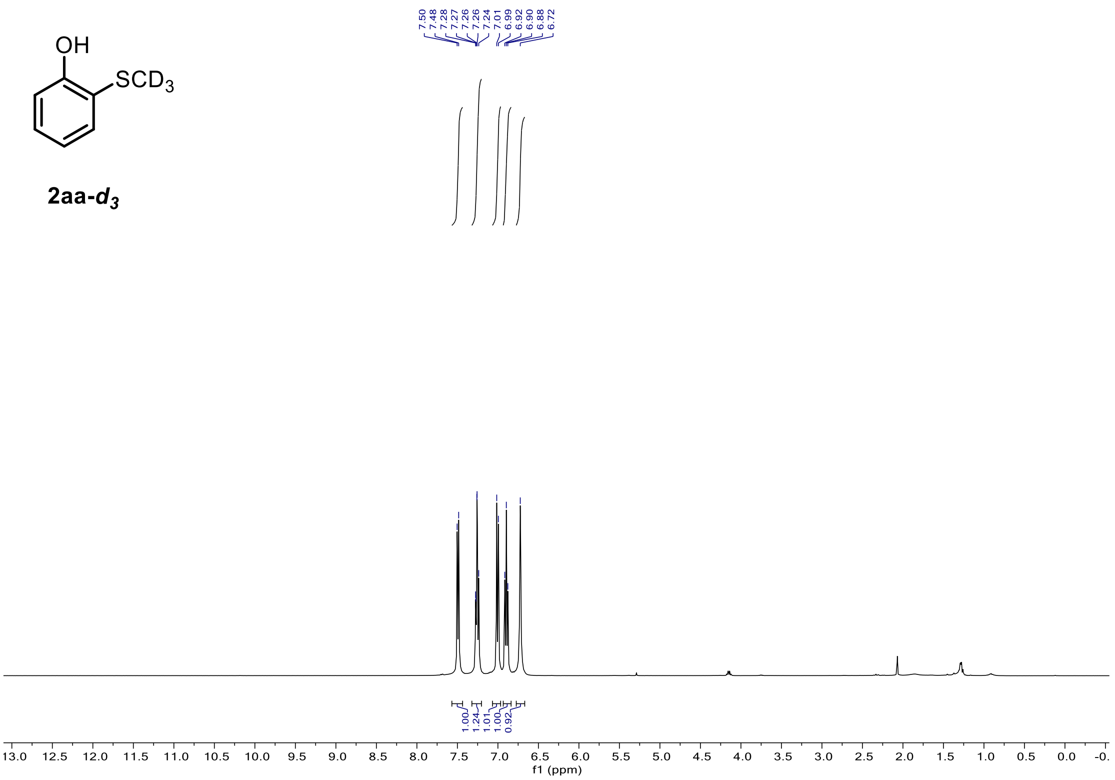
2z-d_3


156.01
140.20
130.00
118.96
113.28
112.24
HO
SCD3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

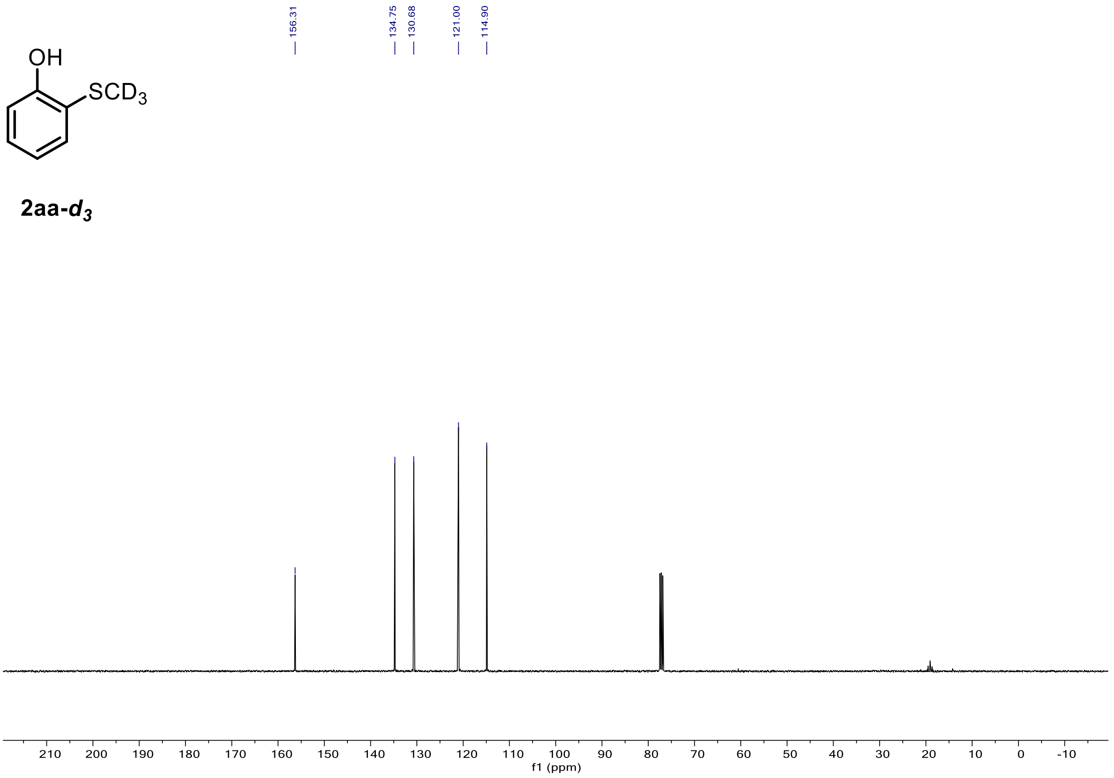
2z-d_3


OH
S
2aa
7.51
7.49
7.27
7.26
7.25
7.01
7.00
6.91
6.90
6.89
6.88
2.34
1.00
1.14
1.00
1.04
3.19
12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

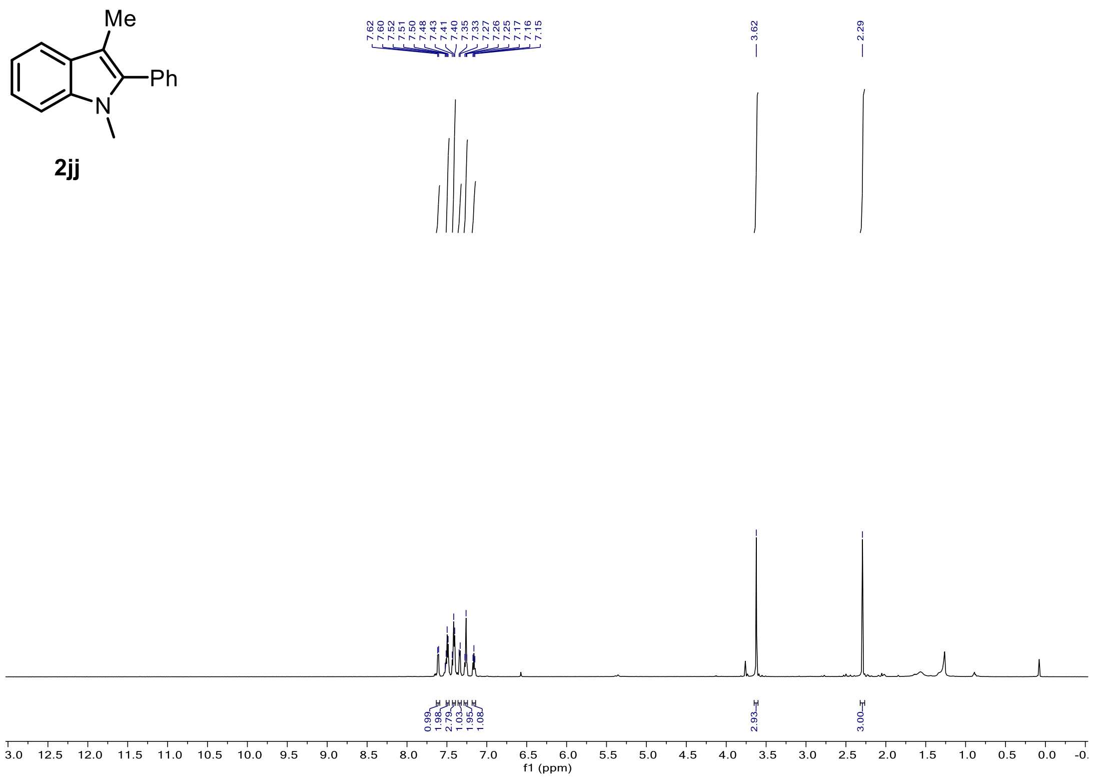

OH
S
2aa
156.37
134.85
130.77
121.04
114.94
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
19.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
SCD3
7.50
7.48
7.28
7.27
7.26
7.26
7.24
7.01
6.99
6.92
6.90
6.88
6.72
1.00
1.24
1.01
1.00
0.92
13.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)

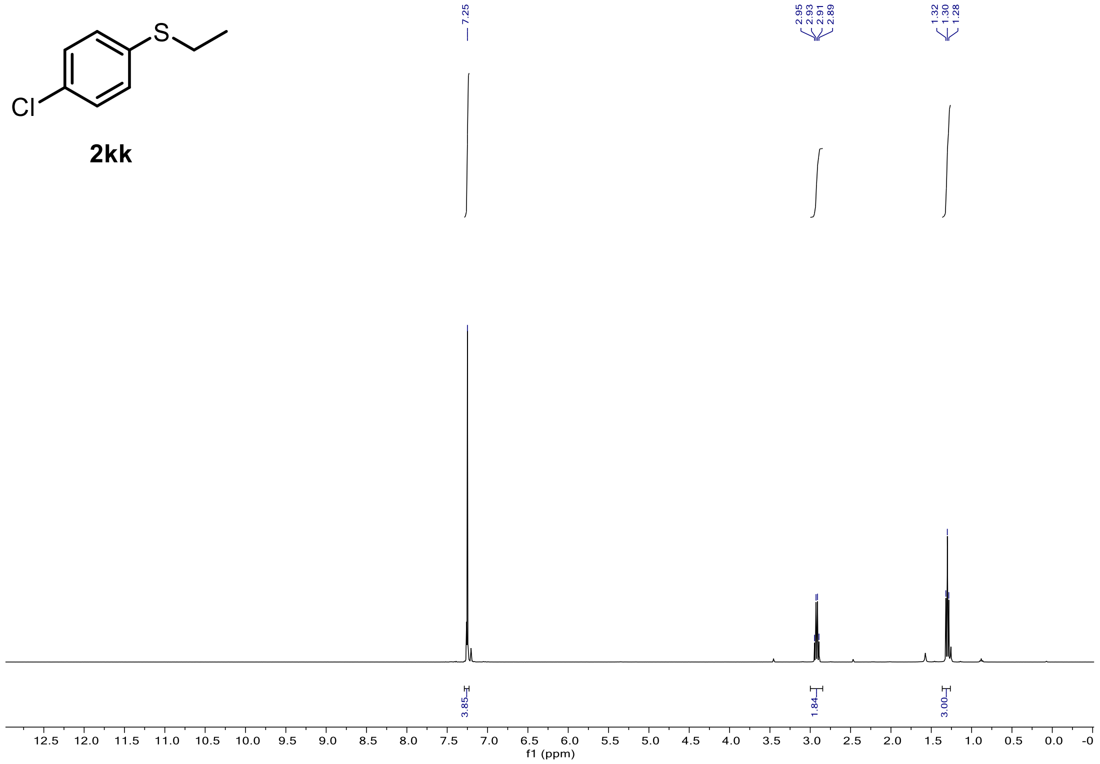
2aa-d_3


OH
SCD3
156.31
134.75
130.68
121.00
114.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2aa-d_3

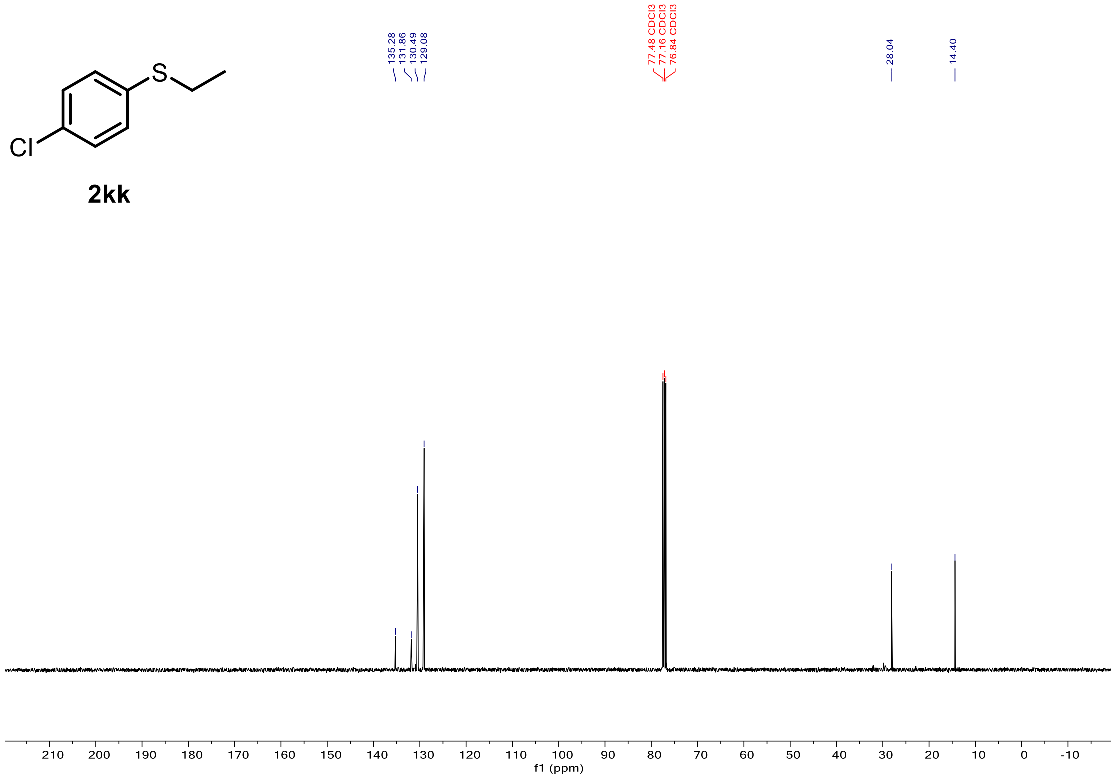

Me
Ph
N
7.62
7.60
7.52
7.51
7.50
7.48
7.43
7.41
7.40
7.35
7.33
7.27
7.26
7.25
7.17
7.16
7.15
3.62
2.29
0.99
1.98
2.79
1.03
1.95
1.08
2.93
3.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

2jj



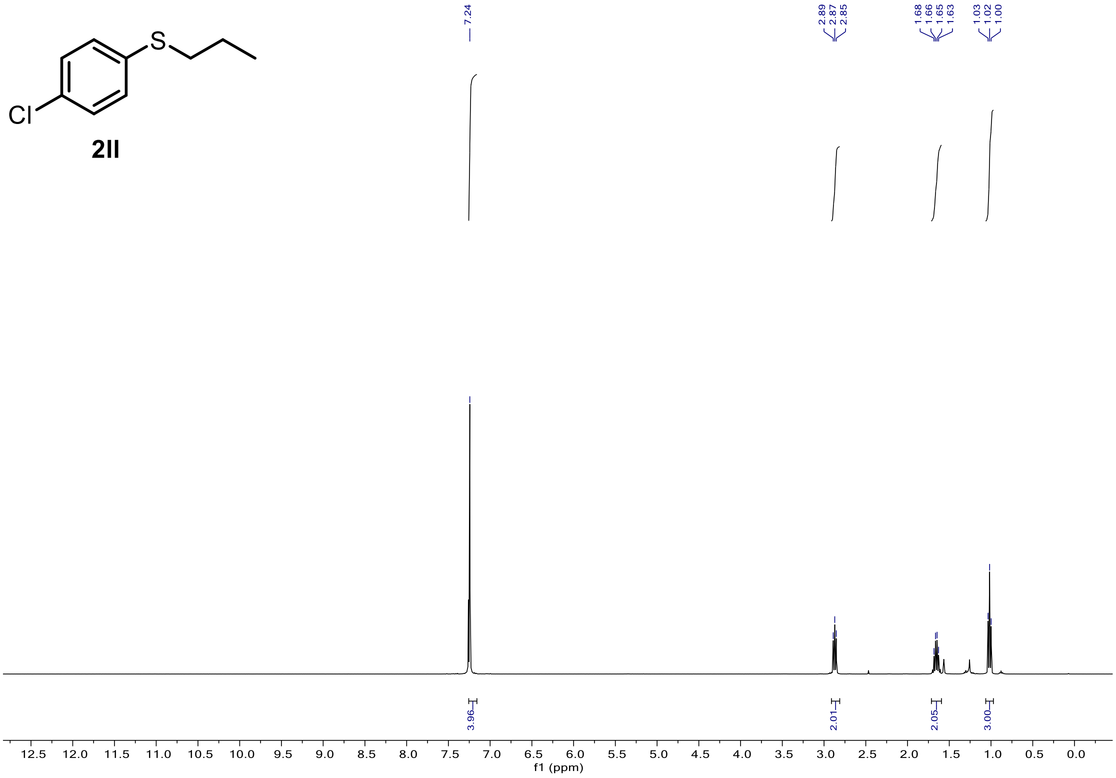
2kk

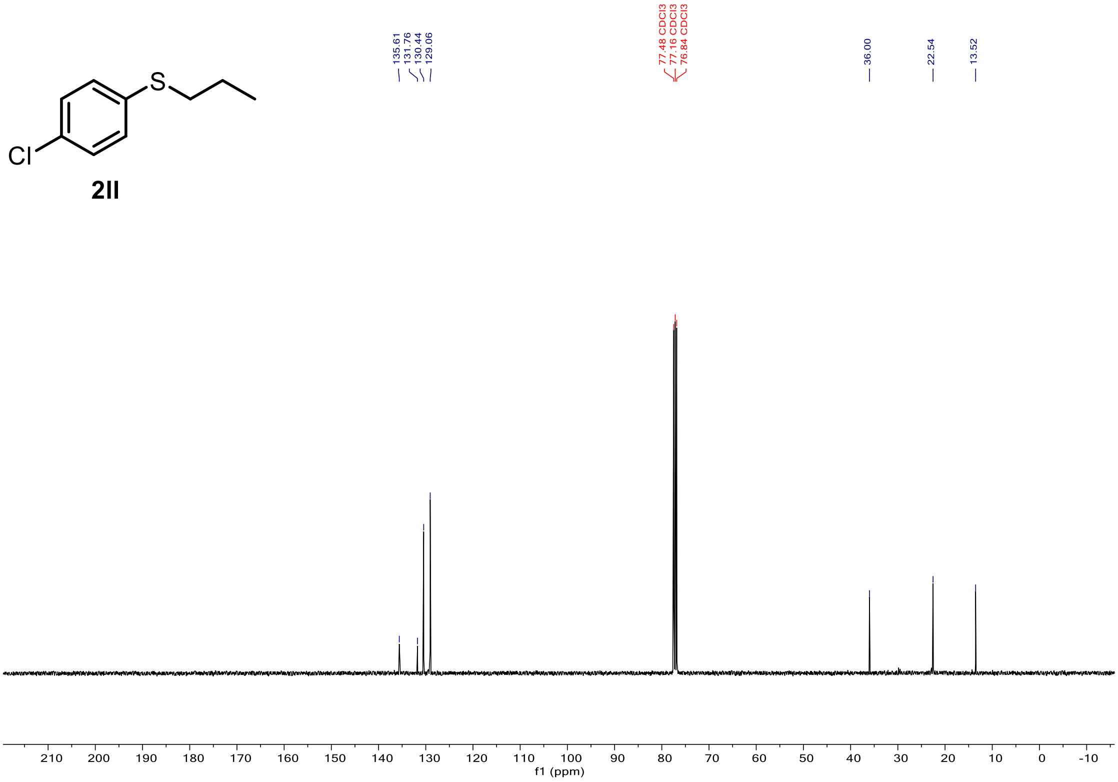
7.25
2.95
2.93
2.91
2.89
1.32
1.30
1.28
3.85
1.84
3.00
Cl
S
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



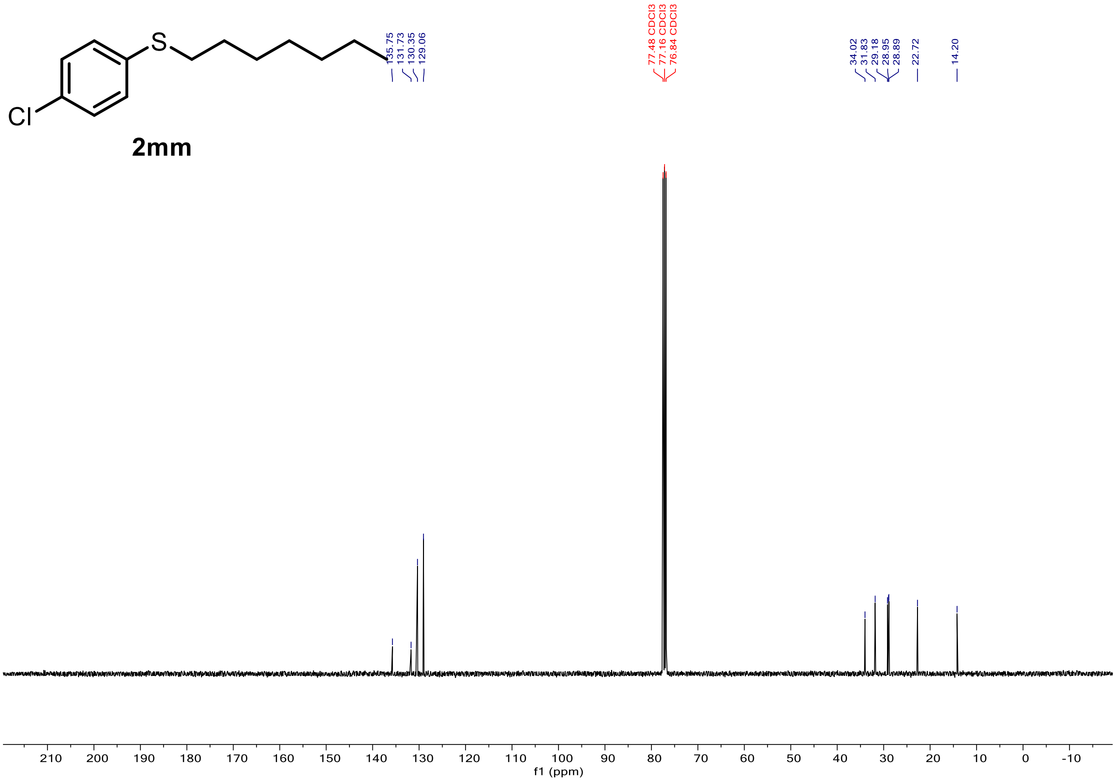
2kk

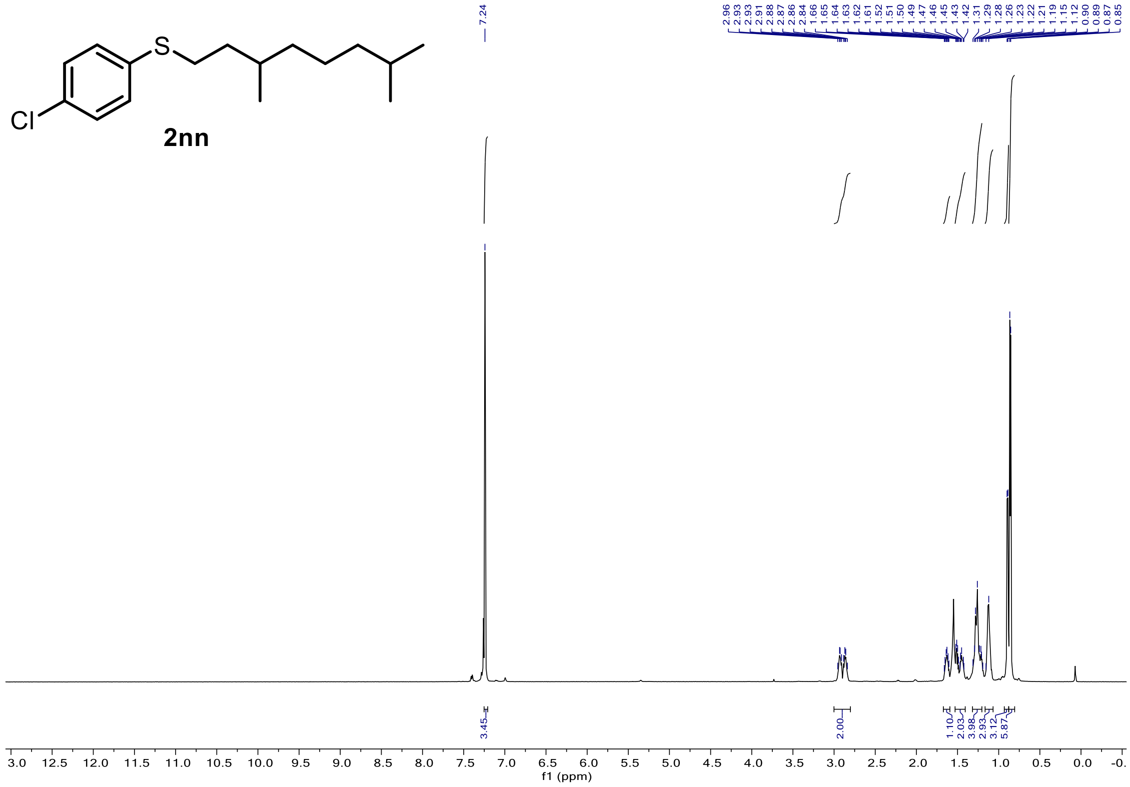
135.28
131.86
130.49
129.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
28.04
14.40
Cl
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2ll
7.24
2.89
2.87
2.85
1.68
1.66
1.65
1.63
1.03
1.02
1.00
3.96
2.01
2.05
3.00
12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

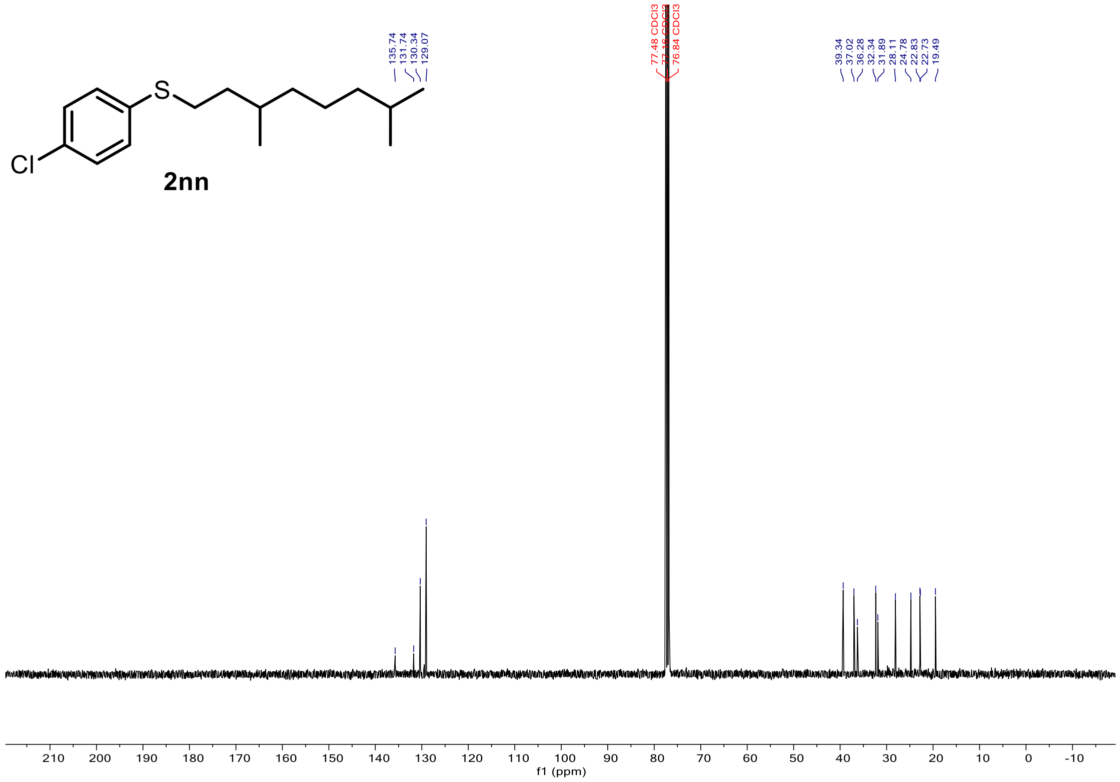

2ll
135.61
131.76
130.44
129.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
36.00
22.54
13.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
S
2mm
7.24
2.90
2.88
2.87
1.65
1.64
1.63
1.61
1.60
1.42
1.40
1.39
1.38
1.30
1.29
1.27
1.26
0.89
0.88
0.87
4.03
2.00
2.06
2.16
6.13
3.17
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

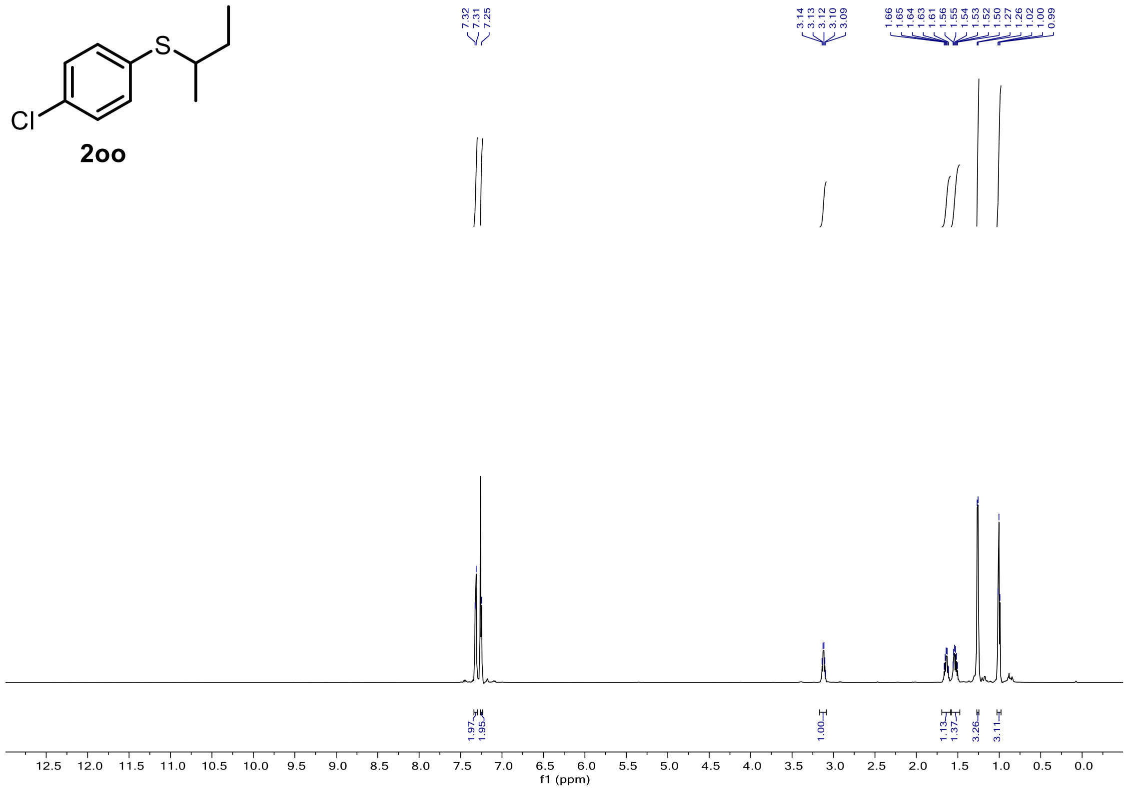

Cl
S
2mm
135.75
131.73
130.35
129.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
34.02
31.83
29.18
28.95
28.89
22.72
14.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

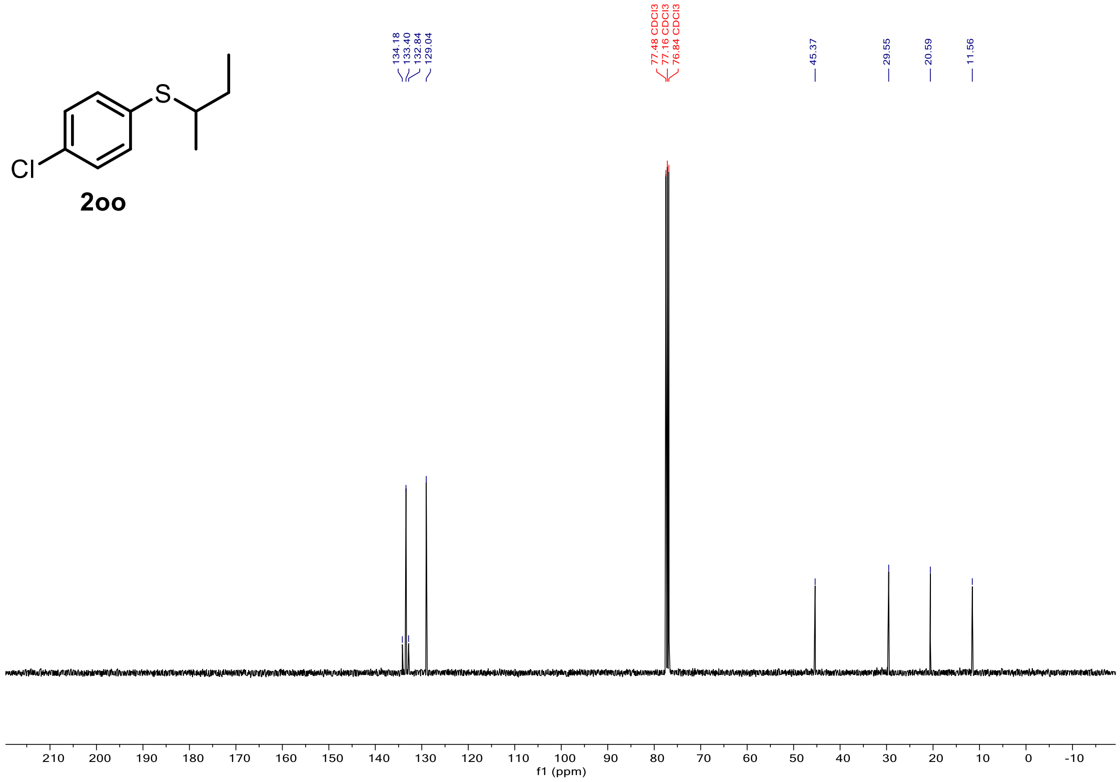

2nn

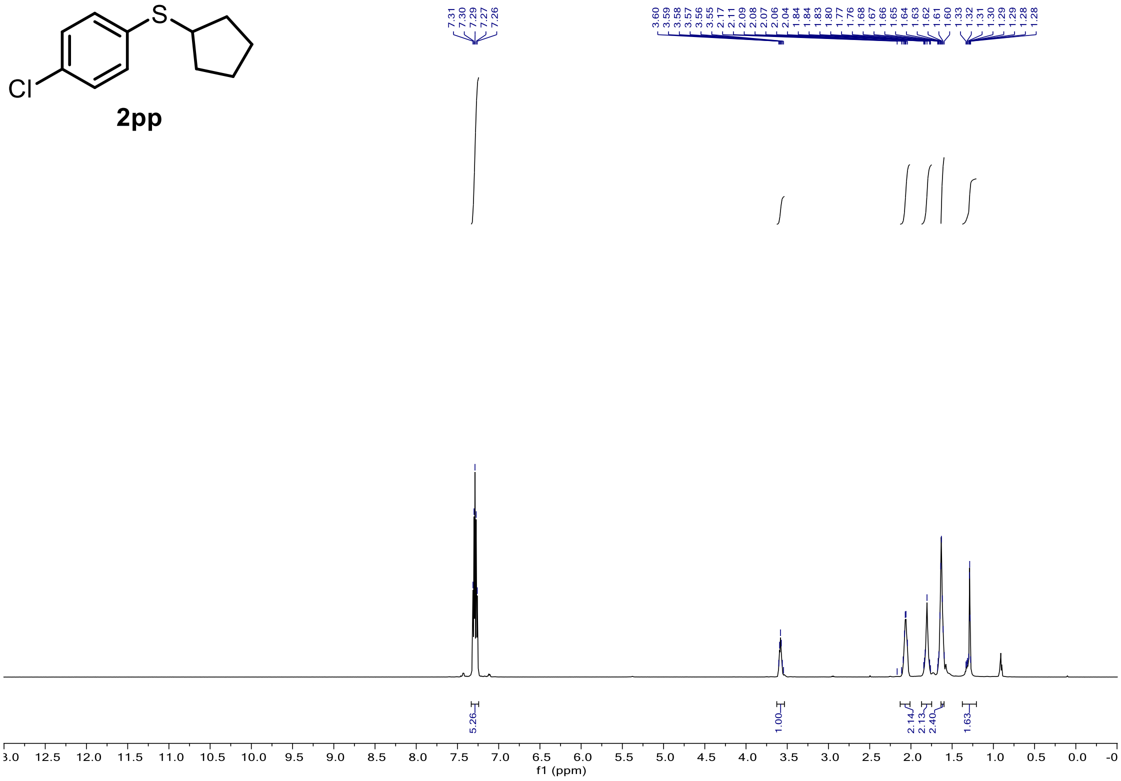
Cl
S
7.24
2.96
2.93
2.93
2.91
2.88
2.87
2.86
2.84
1.66
1.65
1.64
1.63
1.62
1.61
1.52
1.51
1.50
1.49
1.47
1.46
1.45
1.43
1.42
1.31
1.29
1.28
1.26
1.23
1.22
1.21
1.19
1.15
1.12
0.90
0.89
0.87
0.85
3.45
2.00
1.10
2.03
3.98
2.93
3.12
5.87
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

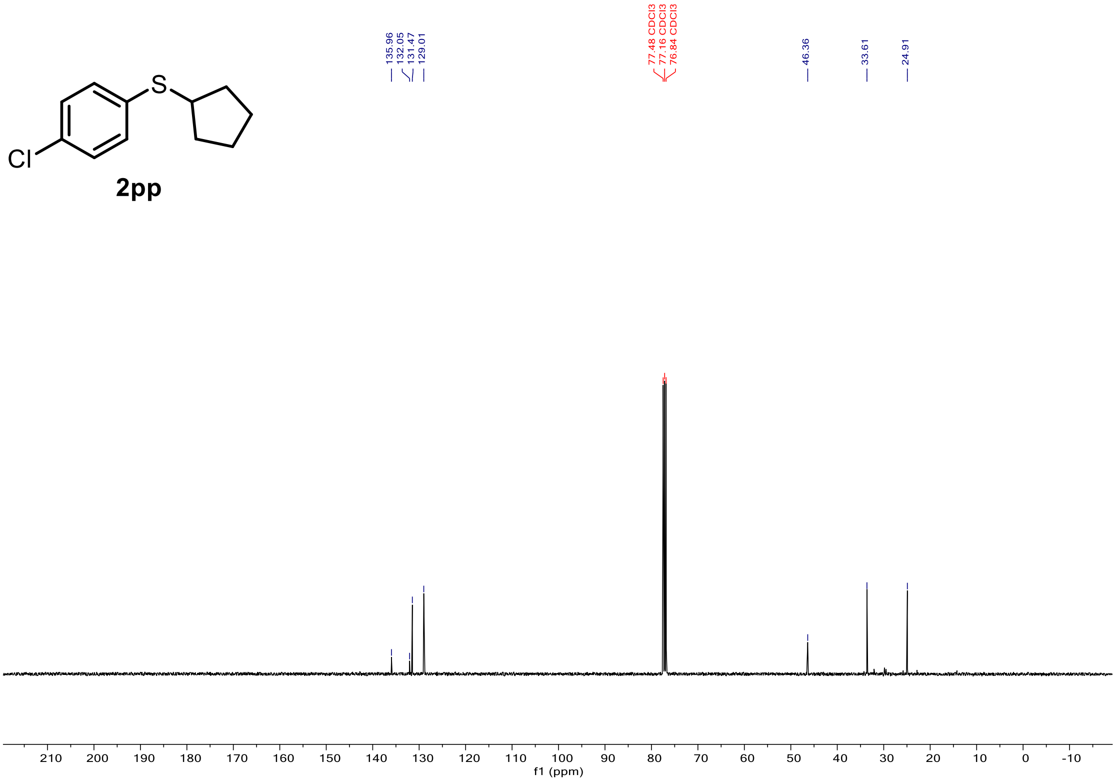

2nn

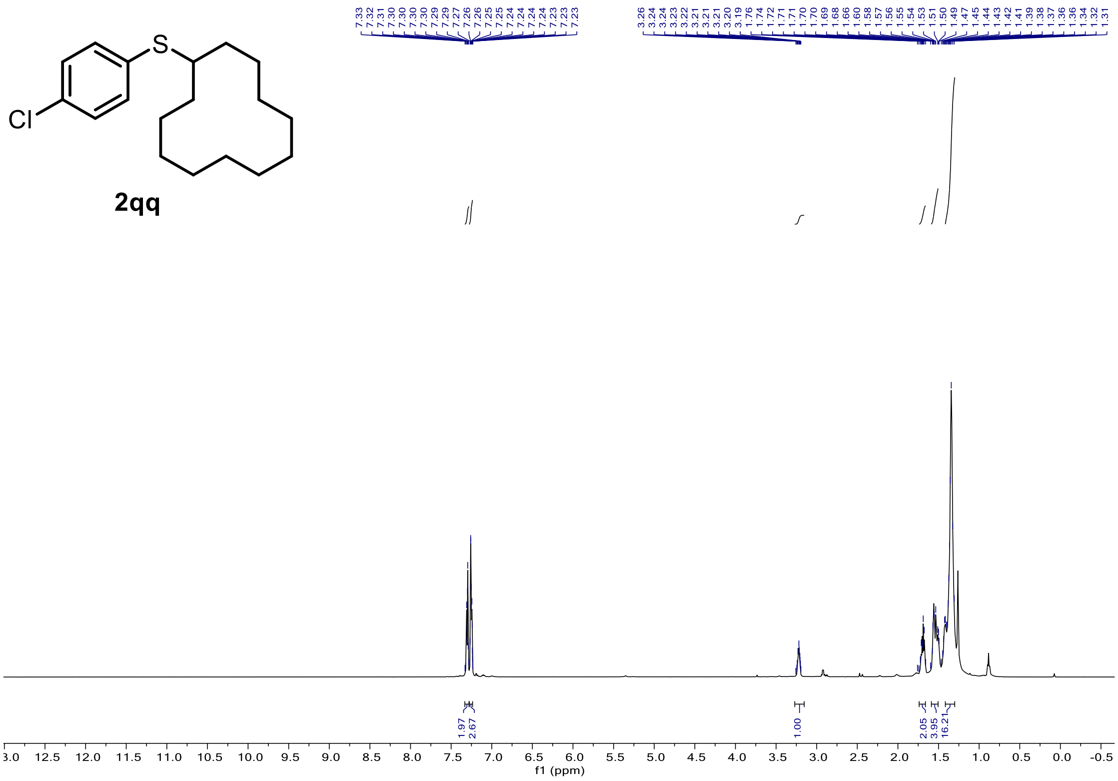
Cl
S
135.74
131.74
130.34
129.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.34
37.02
36.28
32.34
31.89
28.11
24.78
22.83
22.73
19.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


S
Cl
2oo
7.32
7.31
7.25
3.14
3.13
3.12
3.10
3.09
1.66
1.65
1.64
1.63
1.61
1.56
1.55
1.54
1.53
1.52
1.50
1.27
1.26
1.02
1.00
0.99
1.97
1.95
1.00
1.13
1.37
3.26
3.11
12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

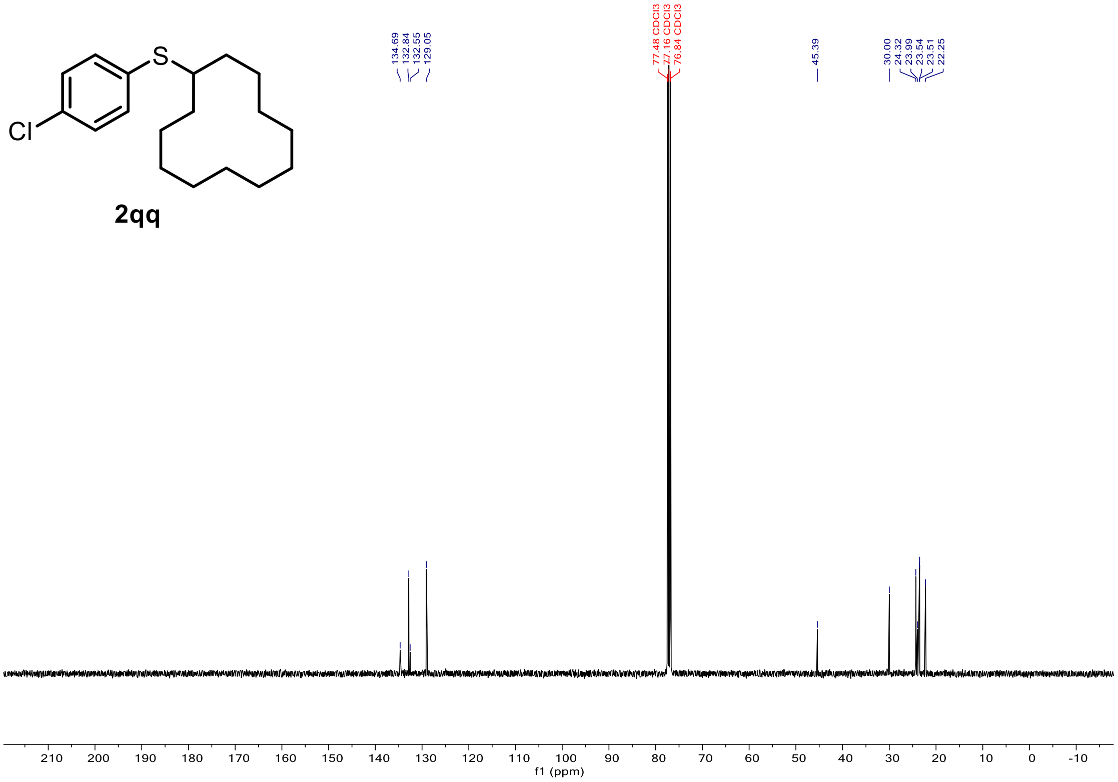

S
Cl
2oo
134.18
133.40
132.84
129.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.37
29.55
20.59
11.56
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2pp
7.31
7.30
7.29
7.27
7.26
3.60
3.59
3.58
3.57
3.56
3.55
2.17
2.11
2.09
2.08
2.07
2.06
2.04
1.84
1.84
1.83
1.80
1.77
1.76
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.33
1.32
1.31
1.30
1.29
1.29
1.28
1.28
5.26
1.00
2.14
2.13
2.40
1.63
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

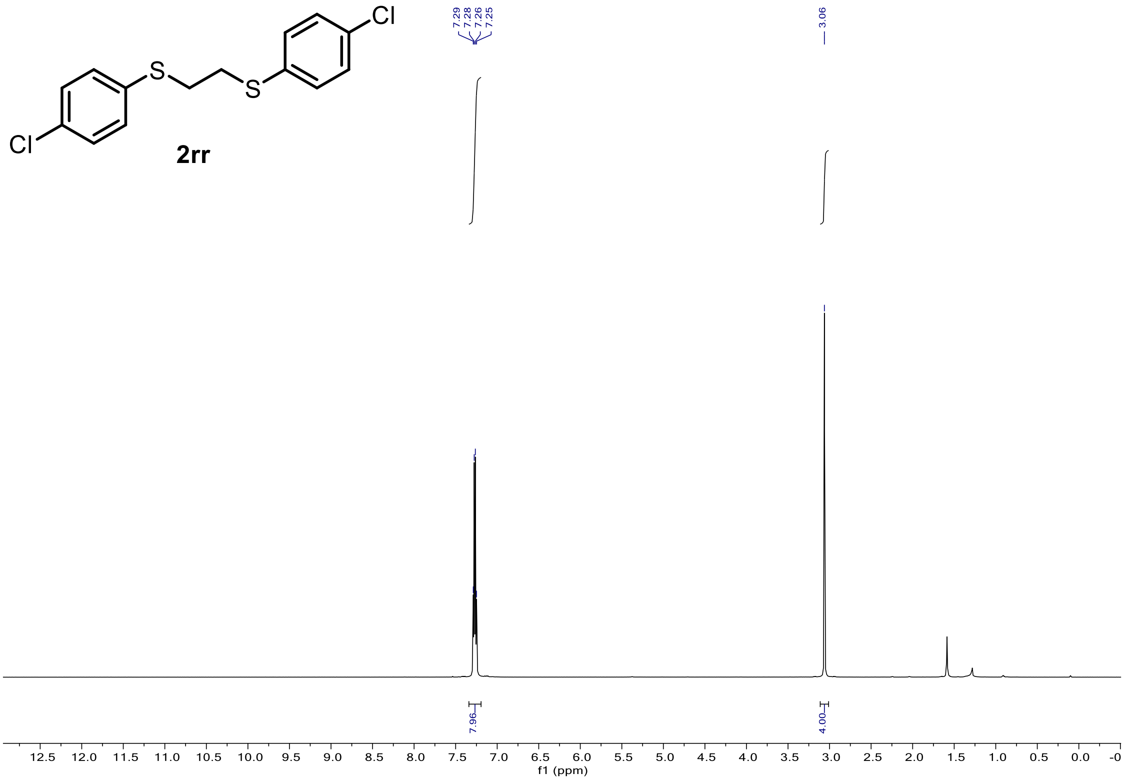

2pp
135.96
132.05
131.47
129.01
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
46.36
33.61
24.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
S
7.33 7.32 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.23
3.26 3.24 3.24 3.23 3.22 3.21 3.21 3.21 3.20 3.19 1.76 1.74 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.66 1.60 1.58 1.57 1.56 1.55 1.54 1.53 1.51 1.50 1.49 1.47 1.45 1.44 1.43 1.42 1.41 1.39 1.38 1.37 1.36 1.36 1.34 1.32 1.31
1.97
2.67
1.00
2.05
3.95
16.21
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0.5
f1 (ppm)

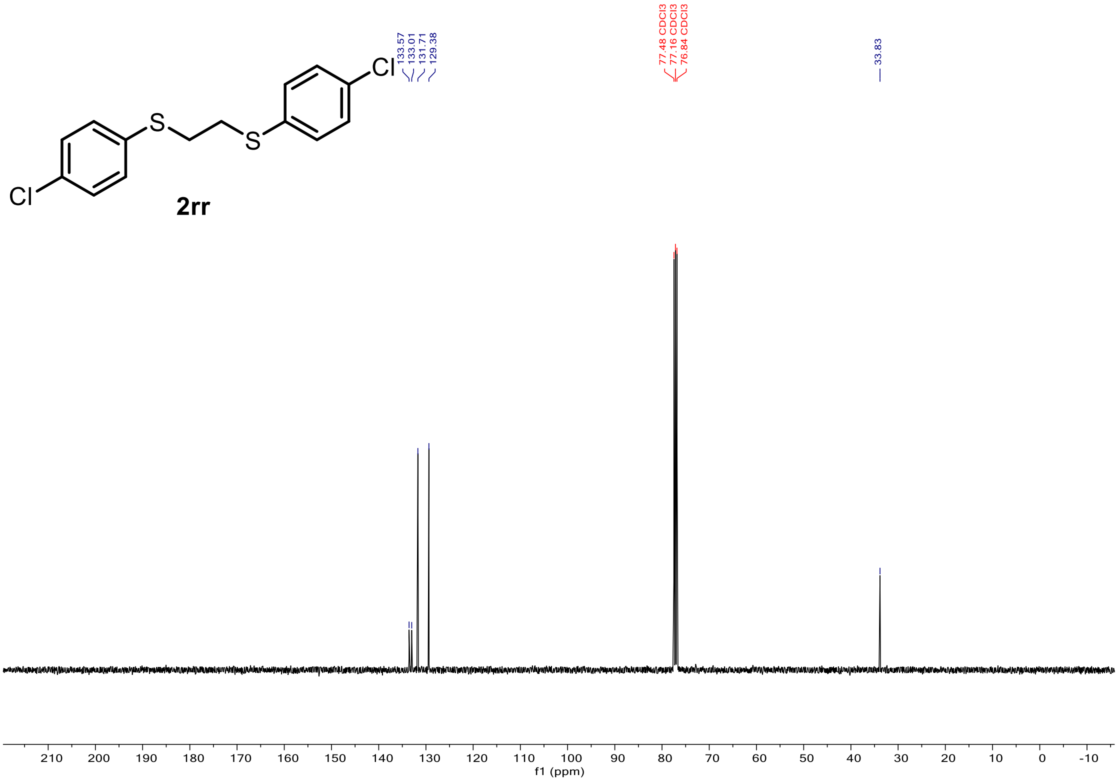
2qq


Cl
S
134.69
132.84
132.55
129.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.39
30.00
24.32
23.99
23.54
23.51
22.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

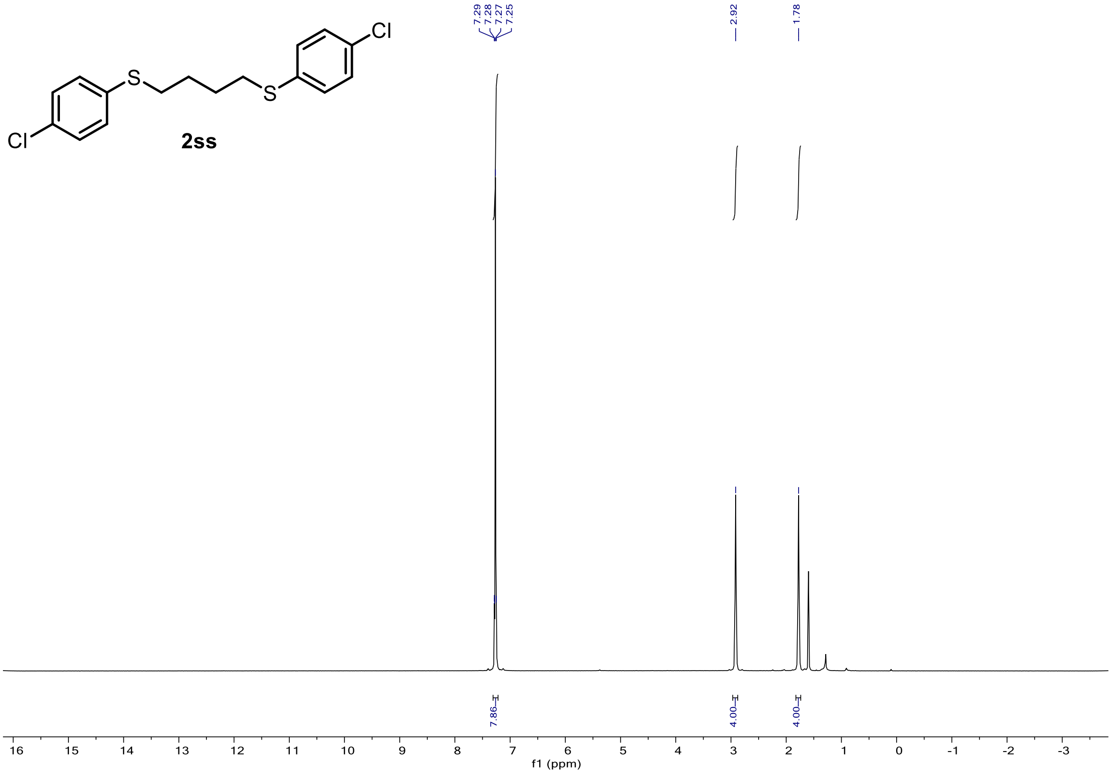
2qq


2rr

Cl
S
S
Cl
7.29
7.28
7.26
7.25
3.06
7.96
4.00
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

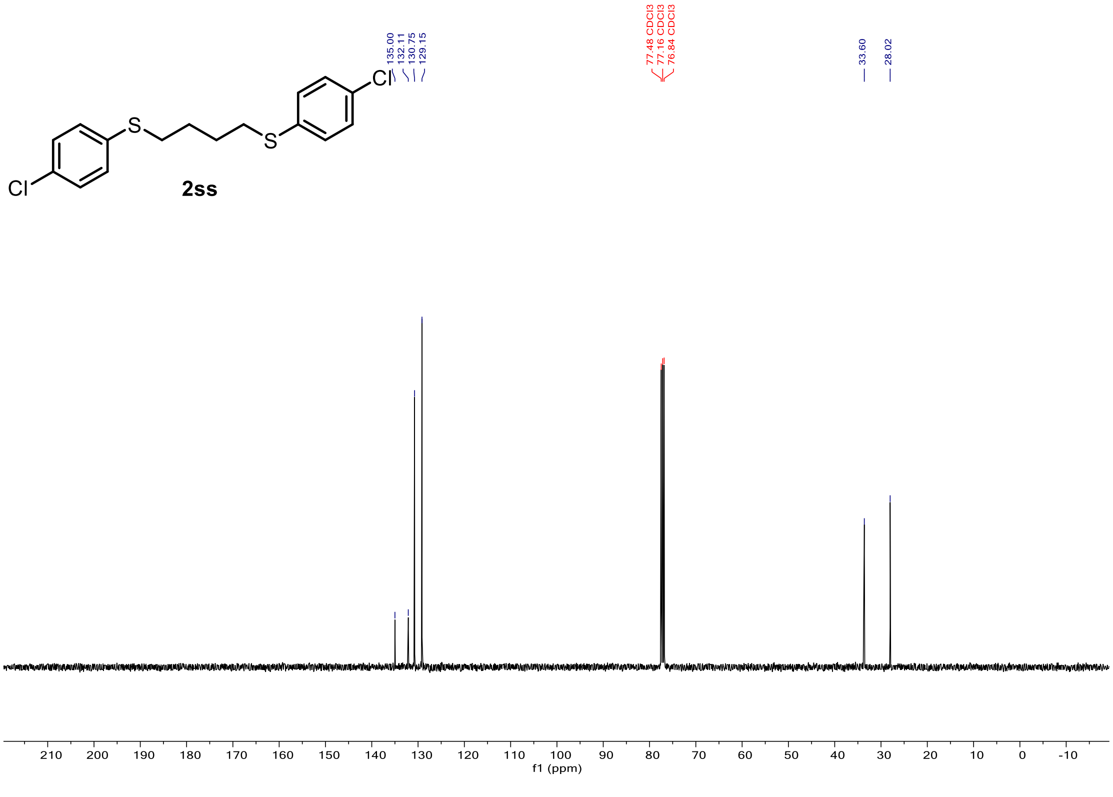

2rr

Cl
S
S
Cl
133.57
133.01
131.71
129.38
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
33.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



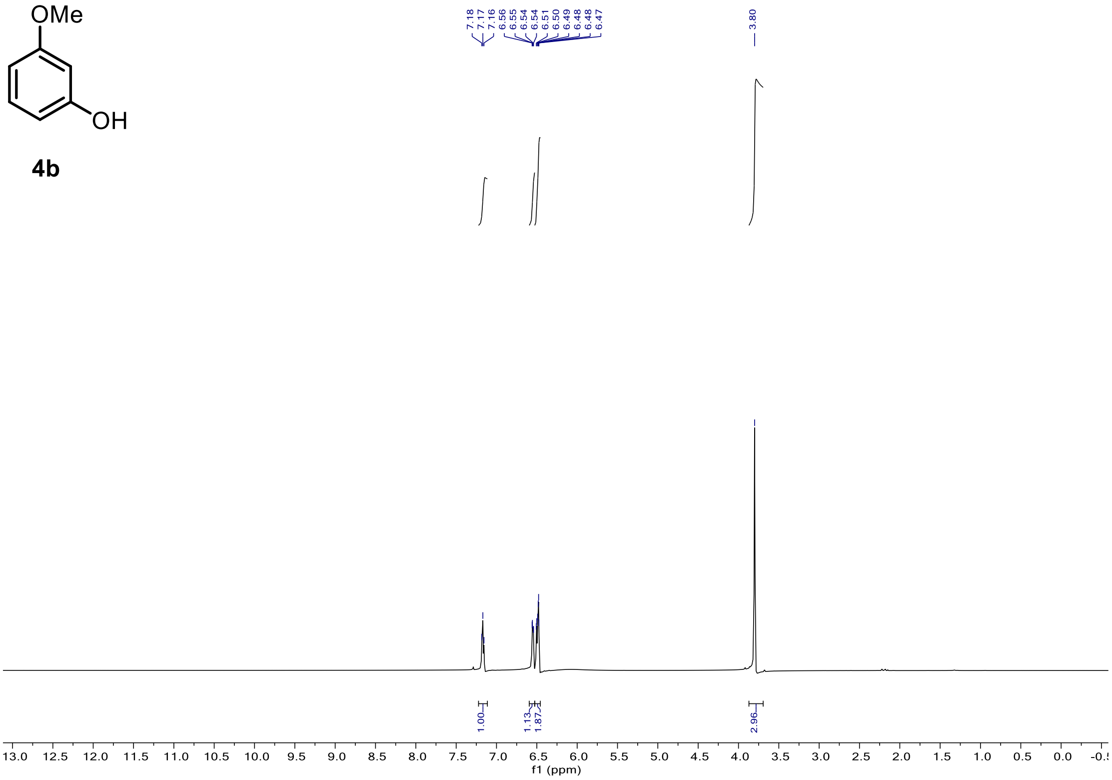
2ss

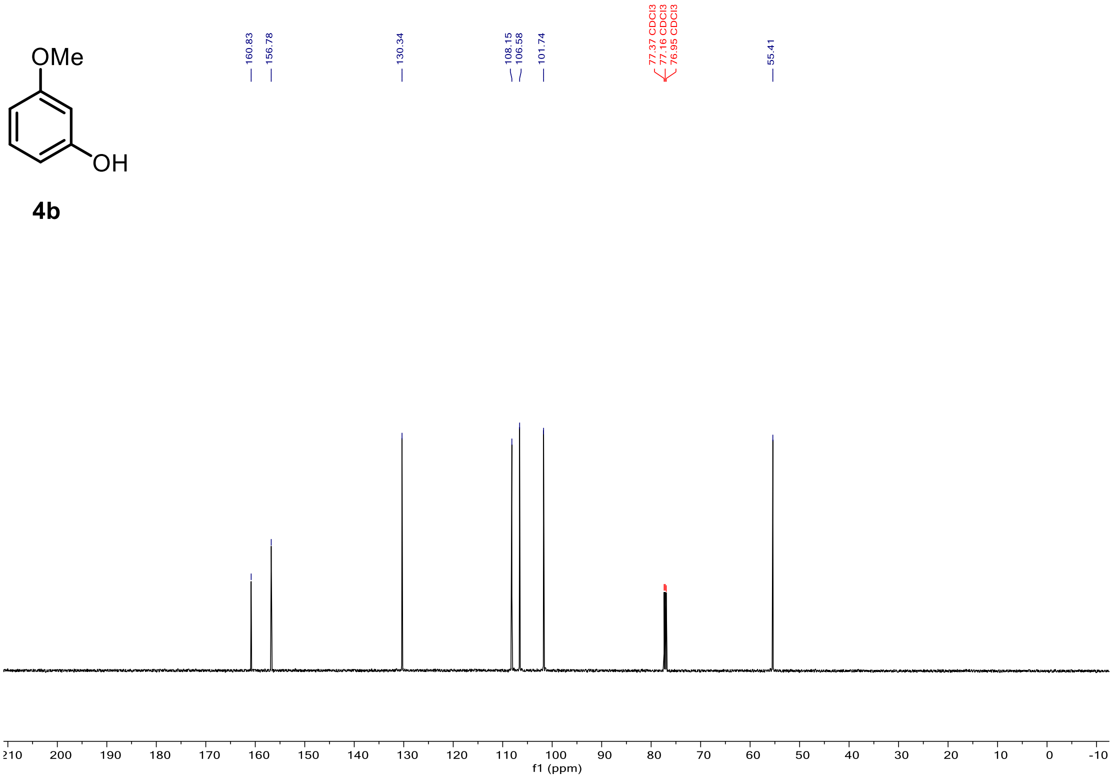
Cl
S
S
Cl
7.29
7.28
7.27
7.25
2.92
1.78
7.86
4.00
4.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

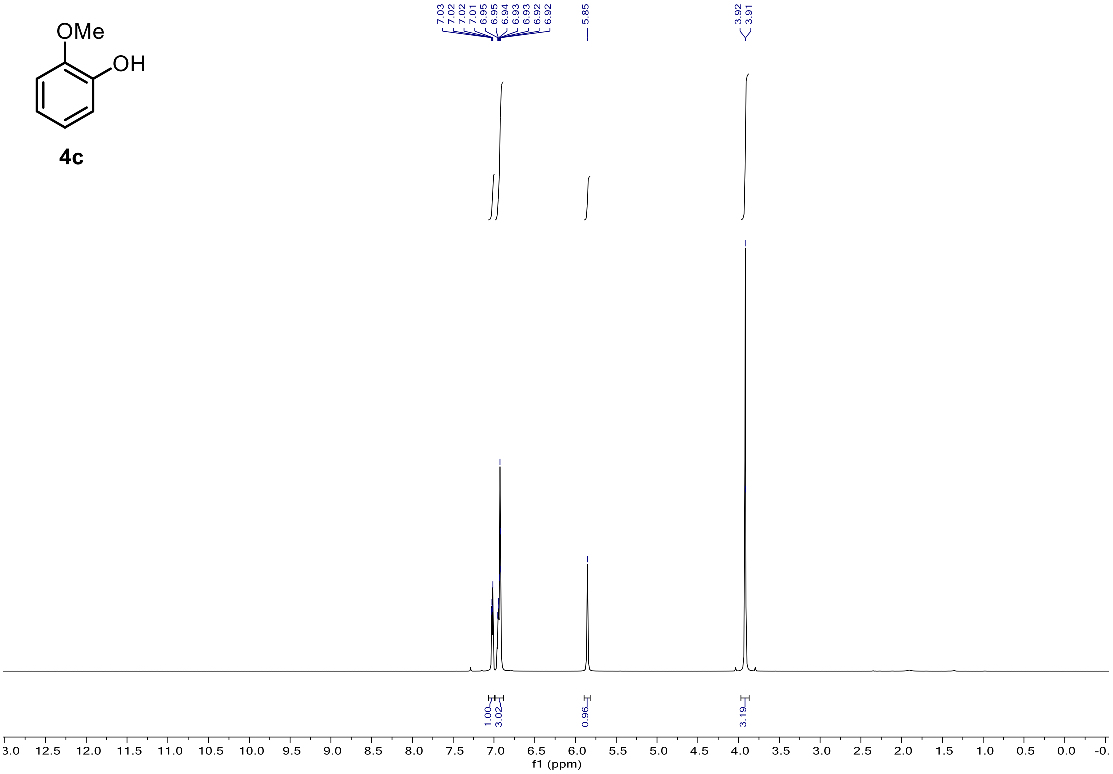


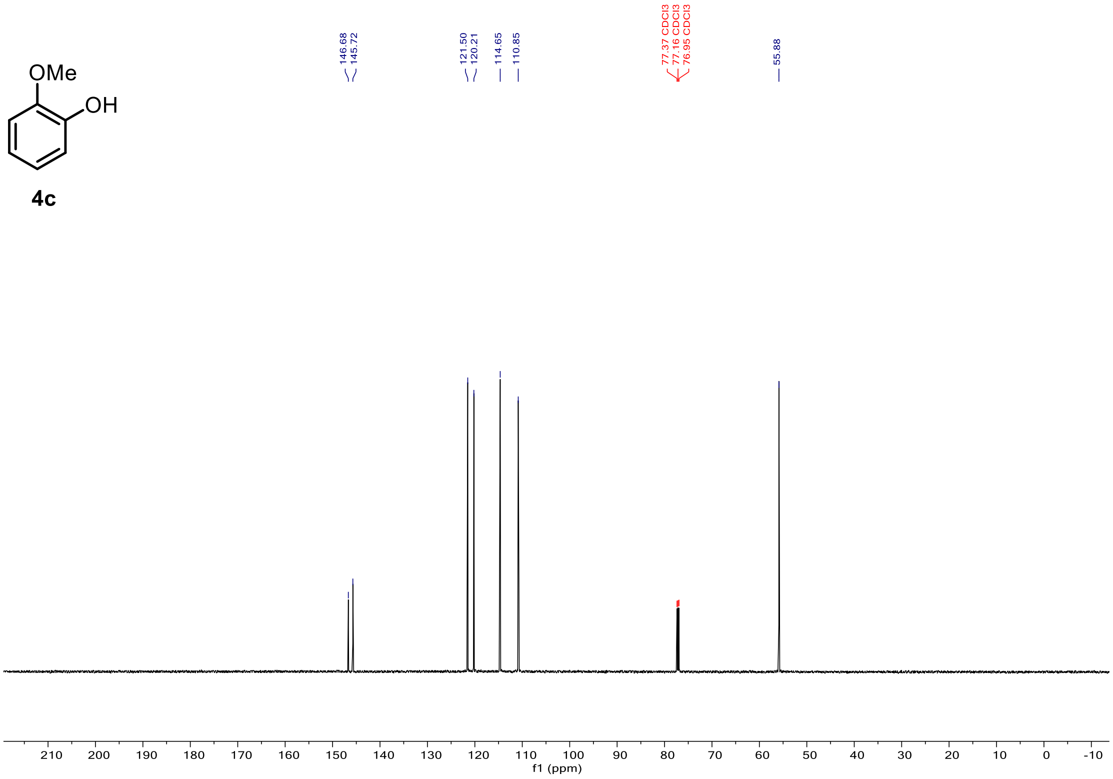
2ss

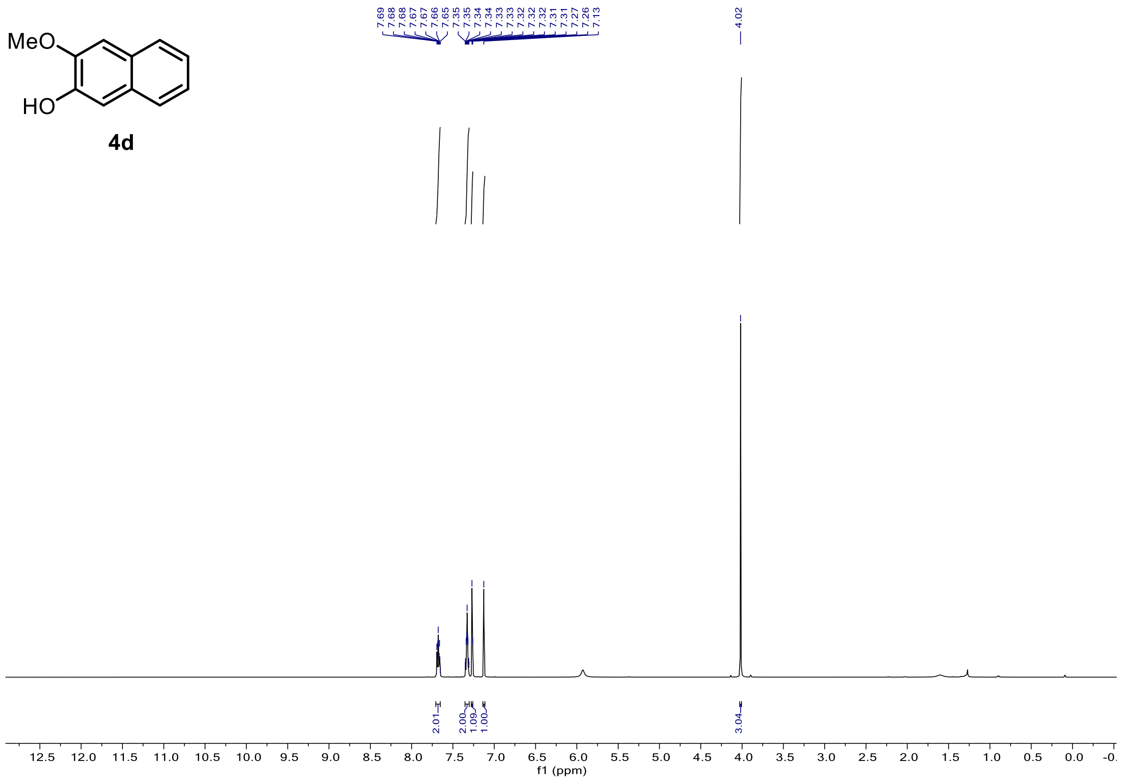
Cl
S
S
Cl
135.00
132.11
130.75
129.15
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
33.60
28.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

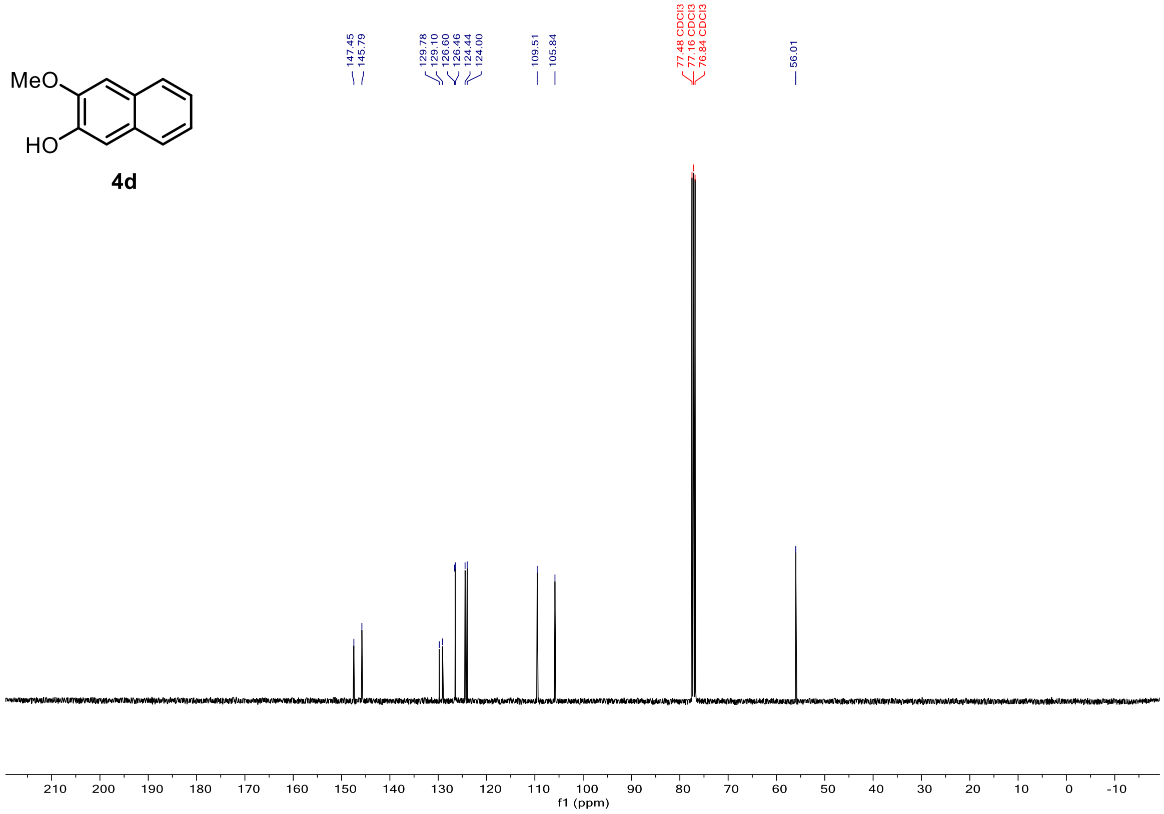

OMe
OH
4b
7.18
7.17
7.16
6.56
6.55
6.54
6.54
6.51
6.50
6.49
6.48
6.48
6.47
3.80
1.00
1.13
1.87
2.96
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

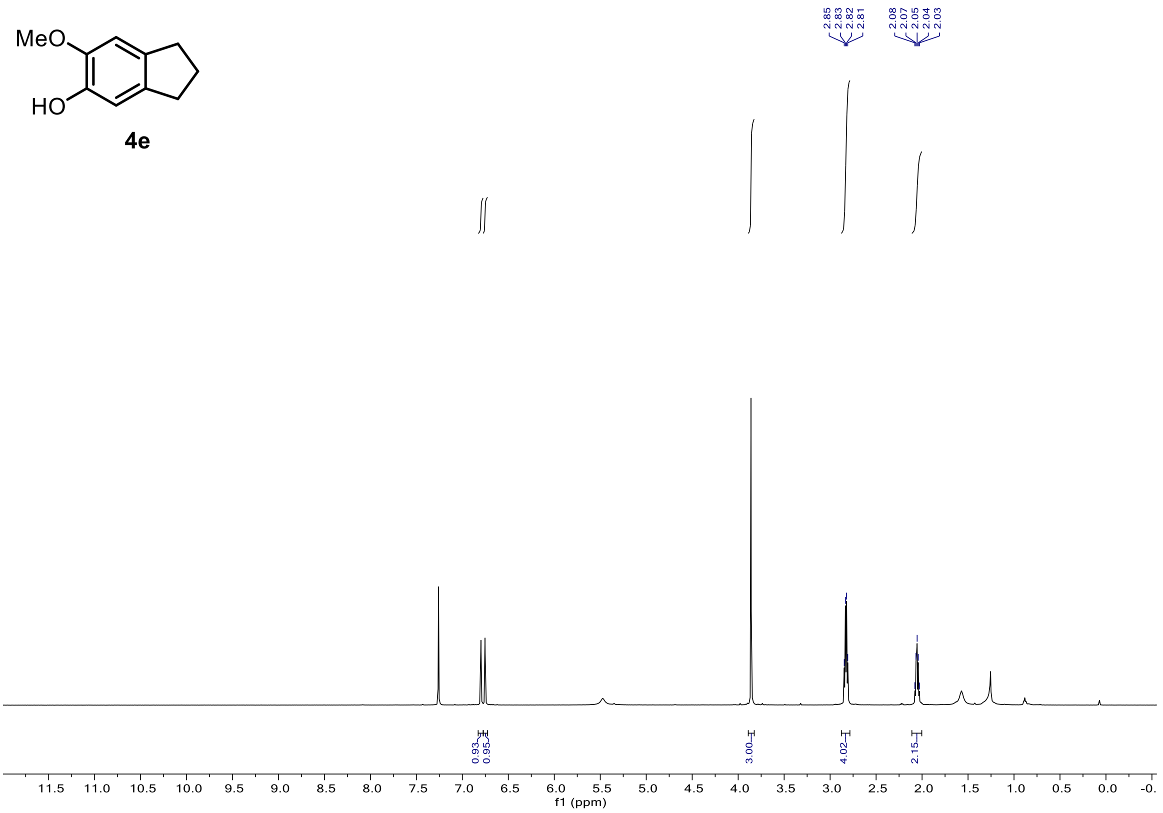

OMe
OH
4b
160.83
156.78
130.34
108.15
106.58
101.74
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
OH
4c
7.03
7.02
7.02
7.01
6.95
6.95
6.94
6.93
6.93
6.92
6.92
5.85
3.92
3.91
1.00
3.02
0.96
3.19
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)


OMe
OH
4c
146.68
145.72
121.50
120.21
114.65
110.85
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

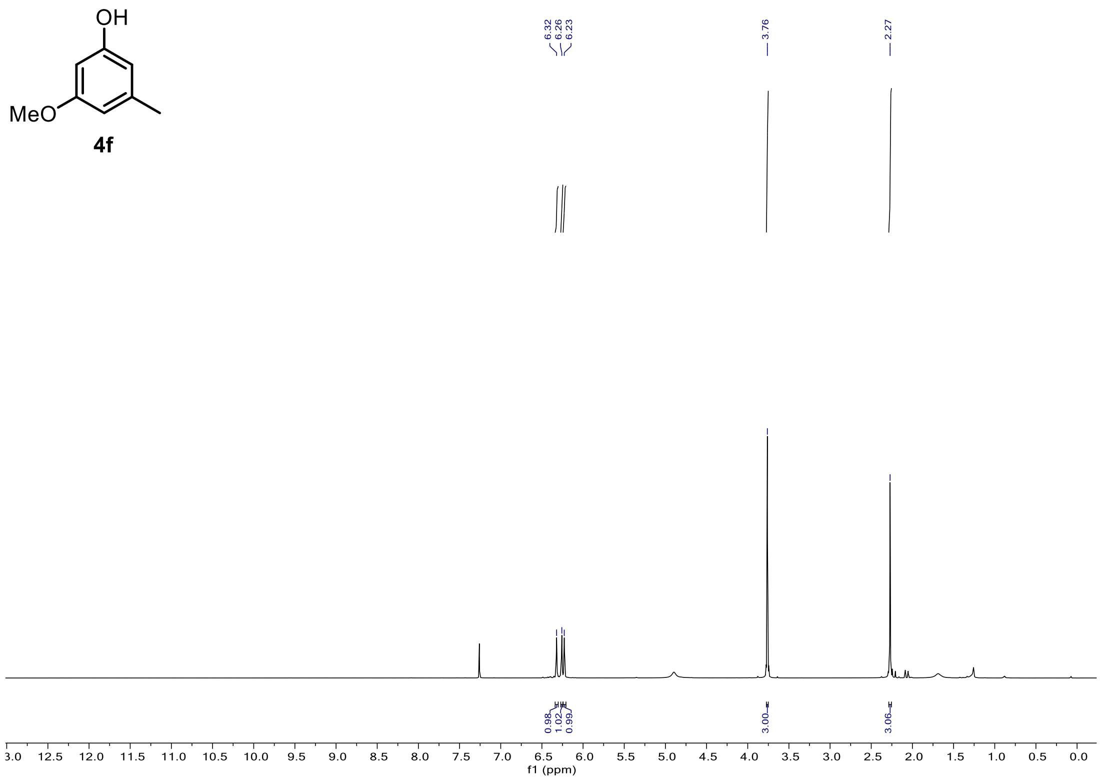

MeO
HO
4d
7.69
7.68
7.68
7.67
7.67
7.66
7.65
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.27
7.26
7.13
4.02
2.01
2.00
1.09
1.00
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


MeO
HO
4d
147.45
145.79
129.78
129.10
126.60
126.46
124.44
124.00
109.51
105.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



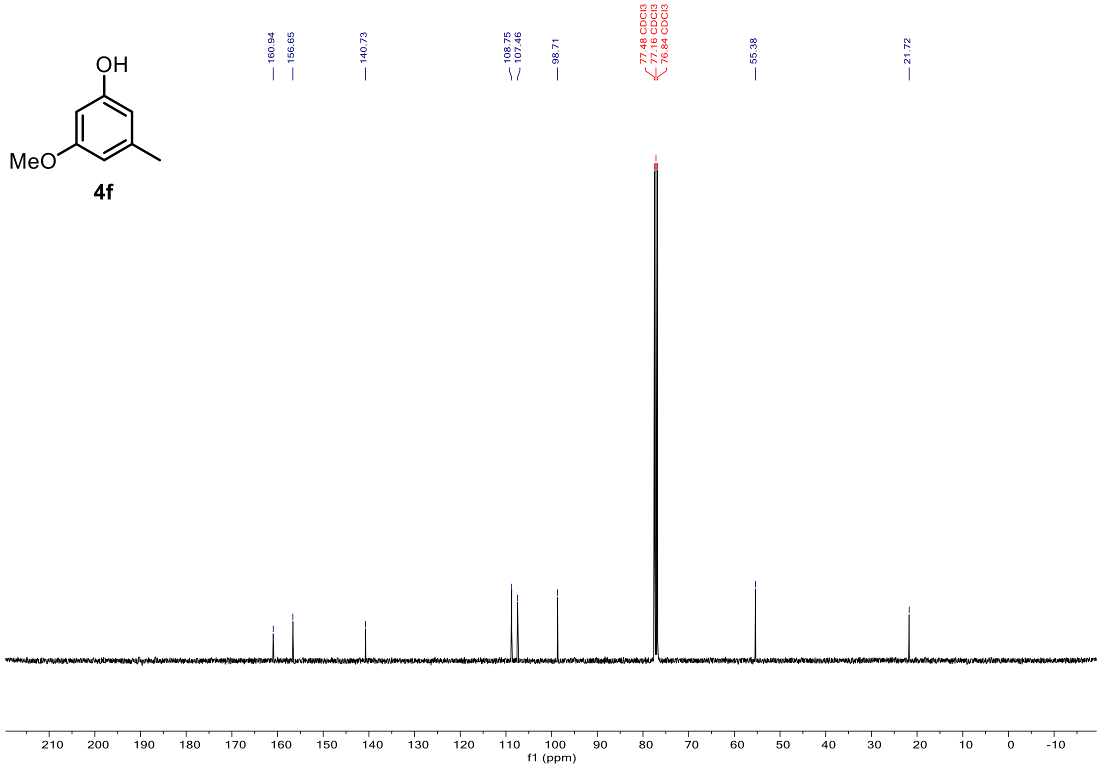
4e

MeO
HO
2.85
2.83
2.82
2.81
2.08
2.07
2.05
2.04
2.03
0.93
0.95
3.00
4.02
2.15
11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)



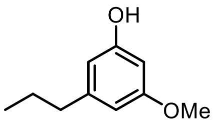
4f

OH
MeO
6.32
6.26
6.23
3.76
2.27
0.98
1.02
0.99
3.00
3.06
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

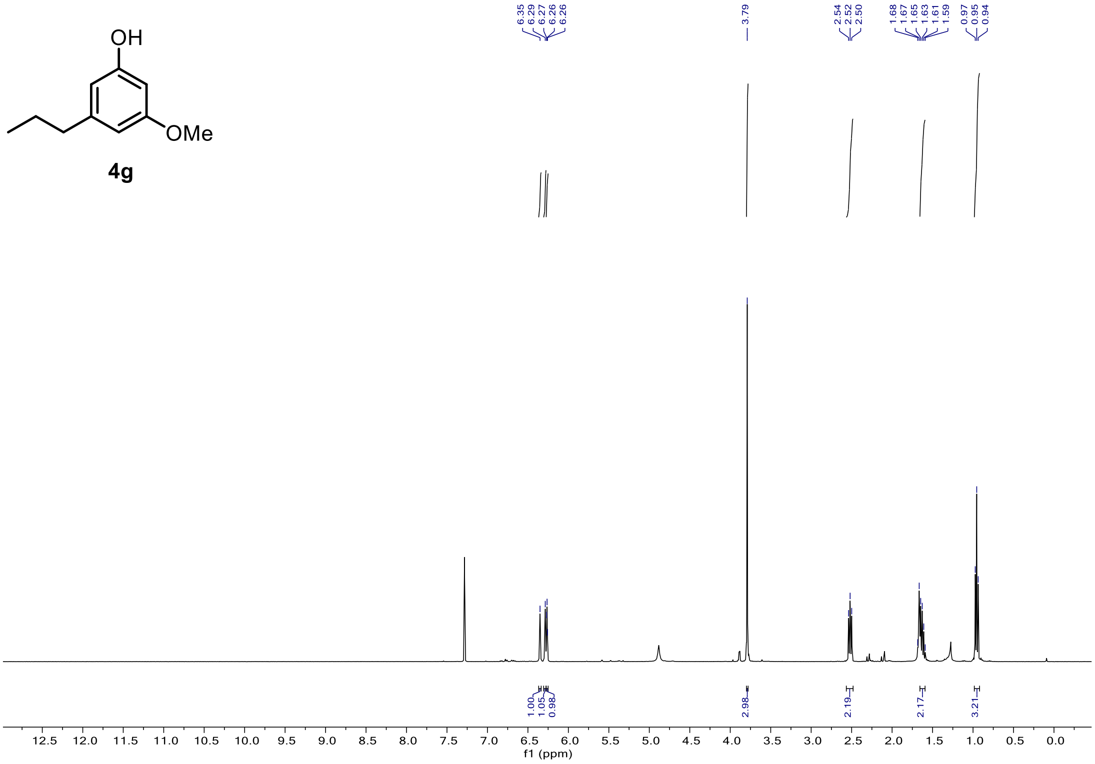


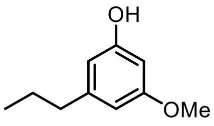
4f

OH
MeO
160.94
156.65
140.73
108.75
107.46
98.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.38
21.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

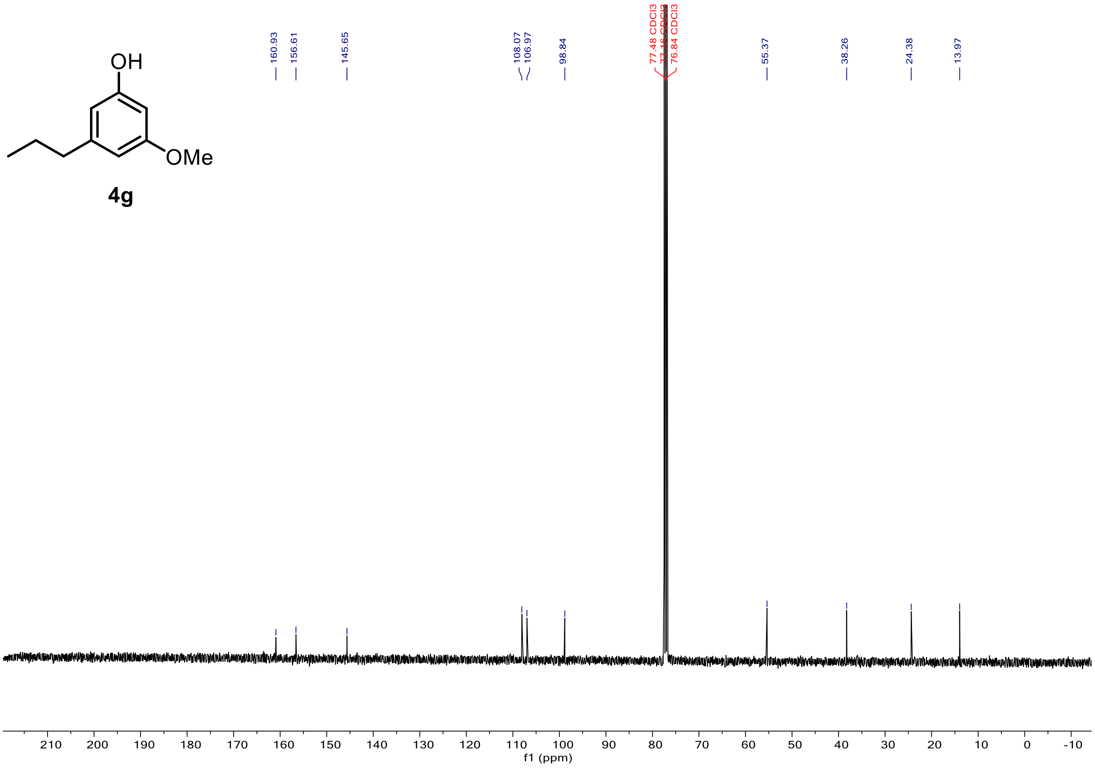

OH
OMe

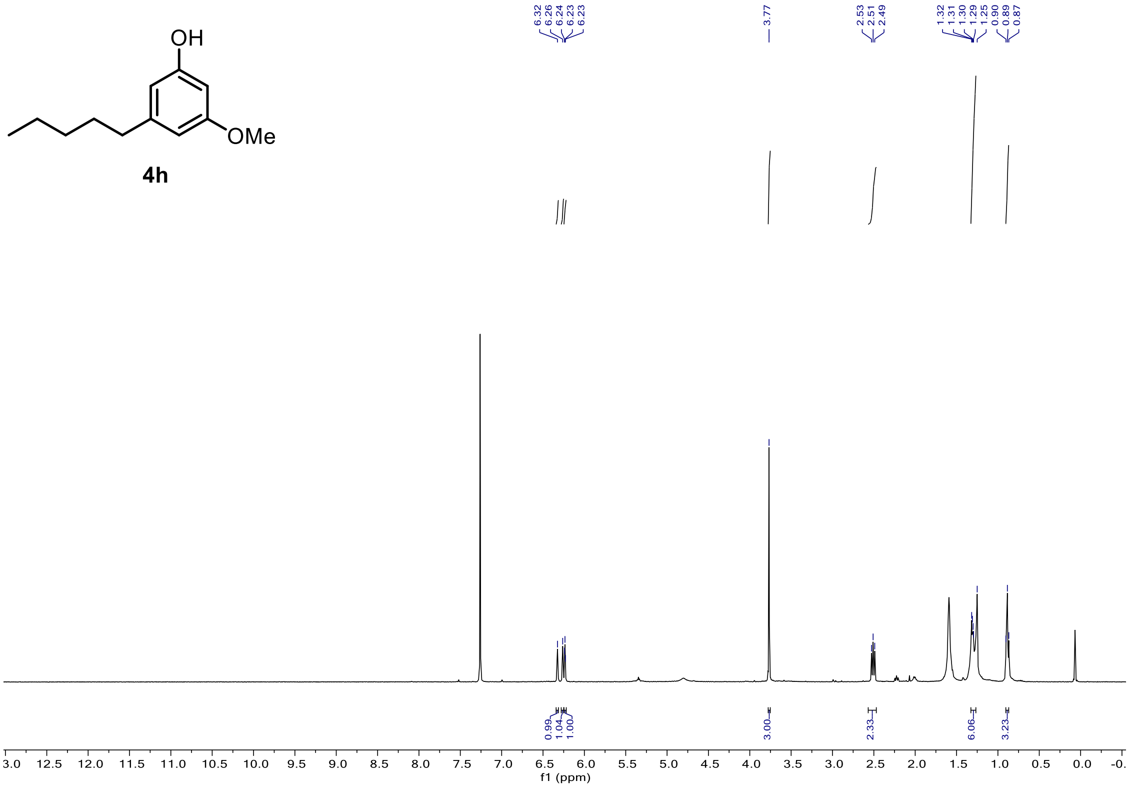
4g

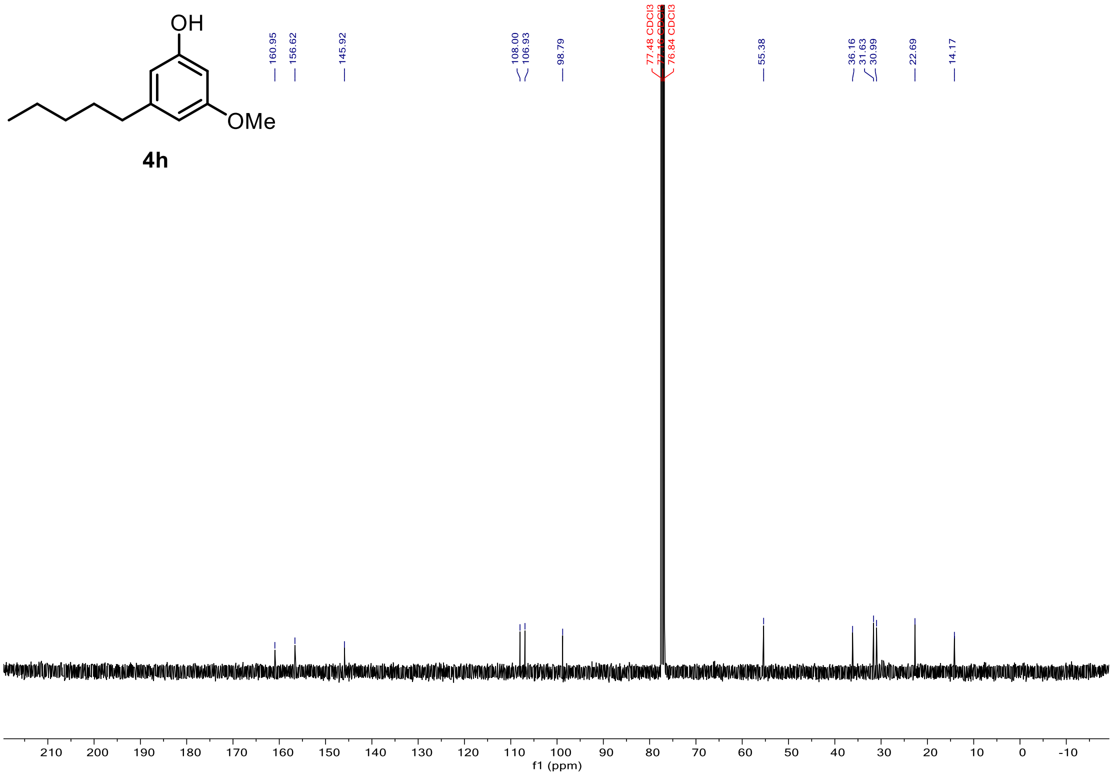

6.35
6.29
6.27
6.26
6.26
3.79
2.54
2.52
2.50
1.68
1.67
1.65
1.63
1.61
1.59
0.97
0.95
0.94
1.00
1.05
0.98
2.98
2.19
2.17
3.21
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

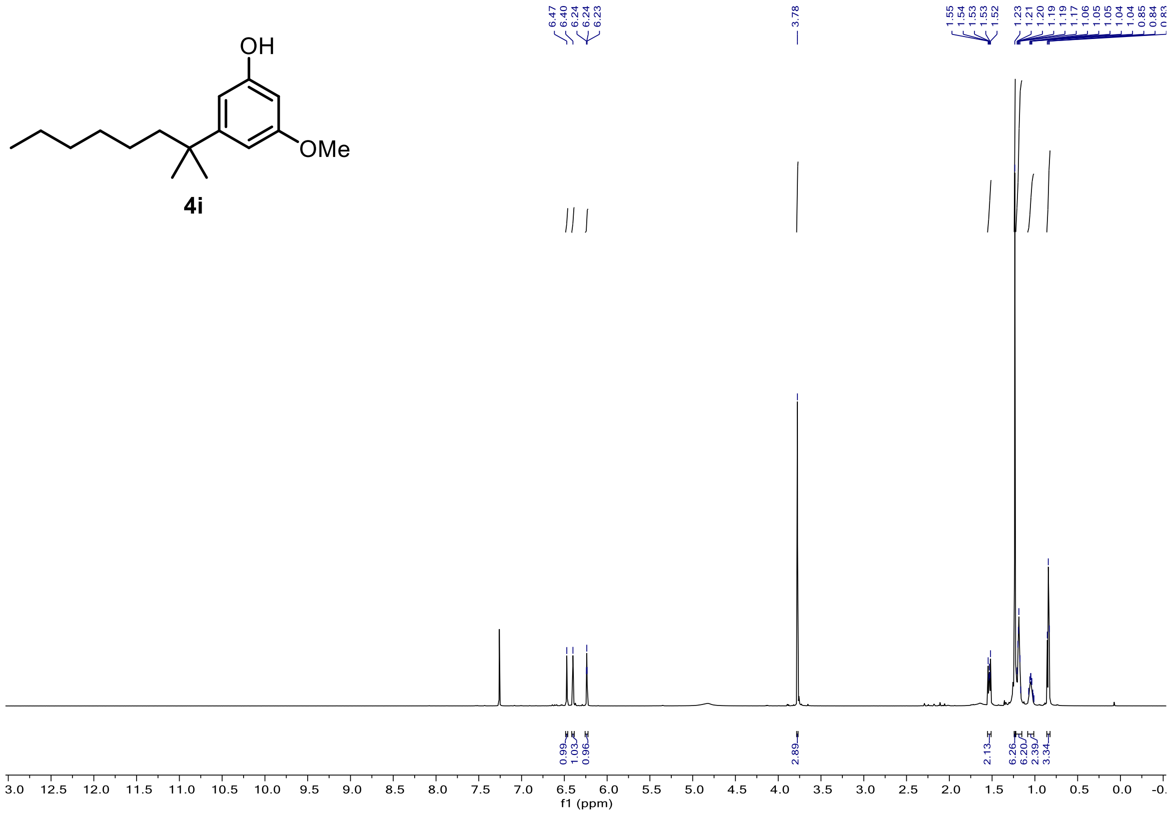

OH
OMe

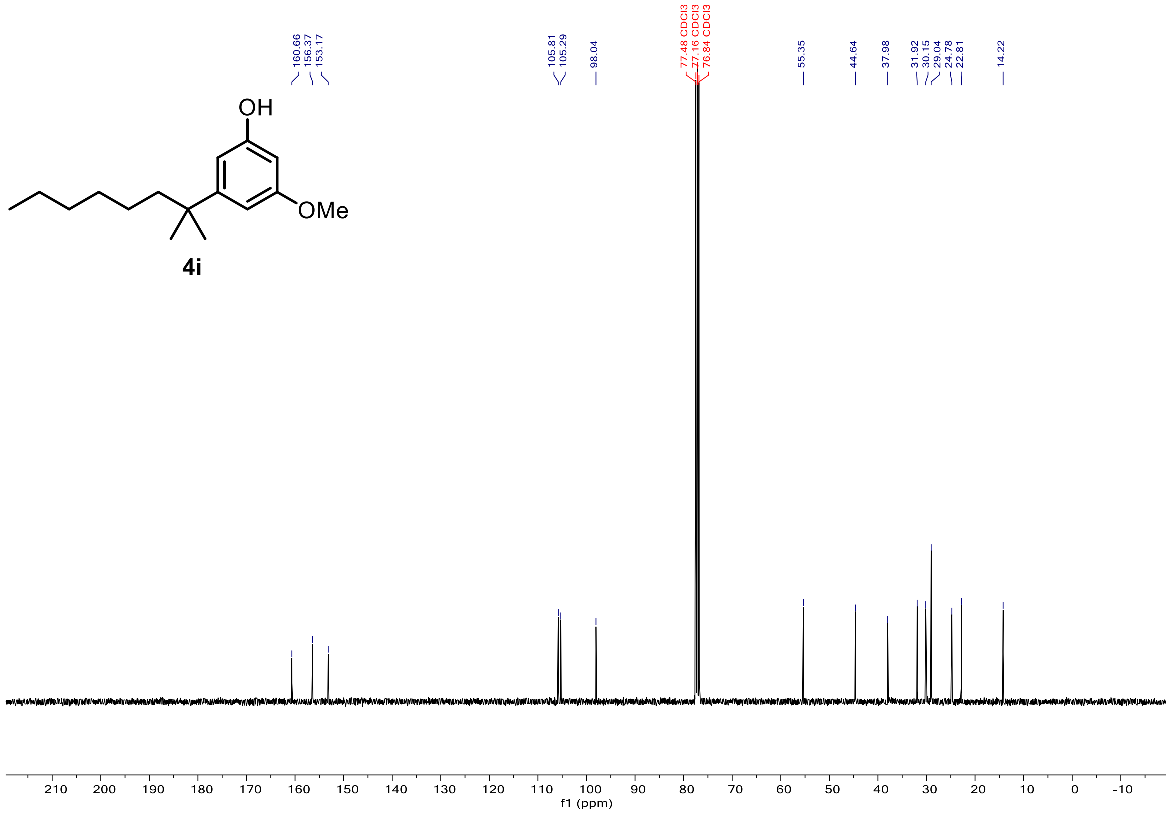
4g

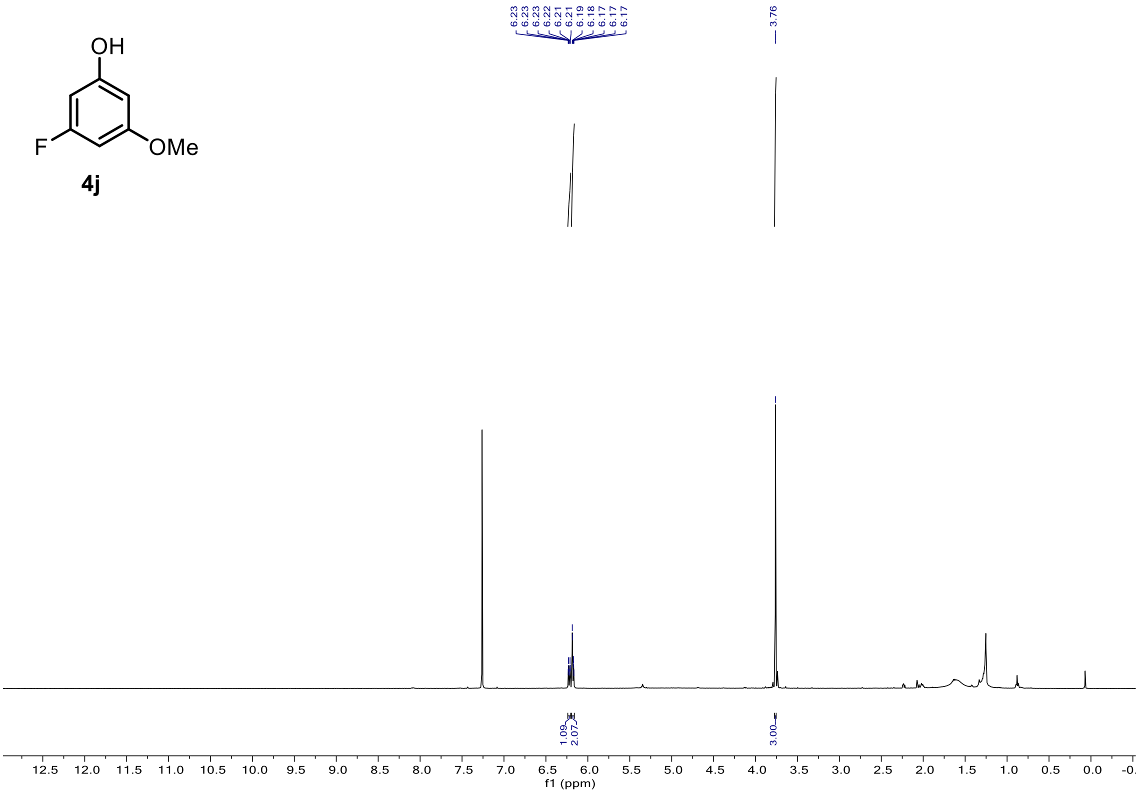

160.93
156.61
145.65
108.07
106.97
98.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.37
38.26
24.38
13.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

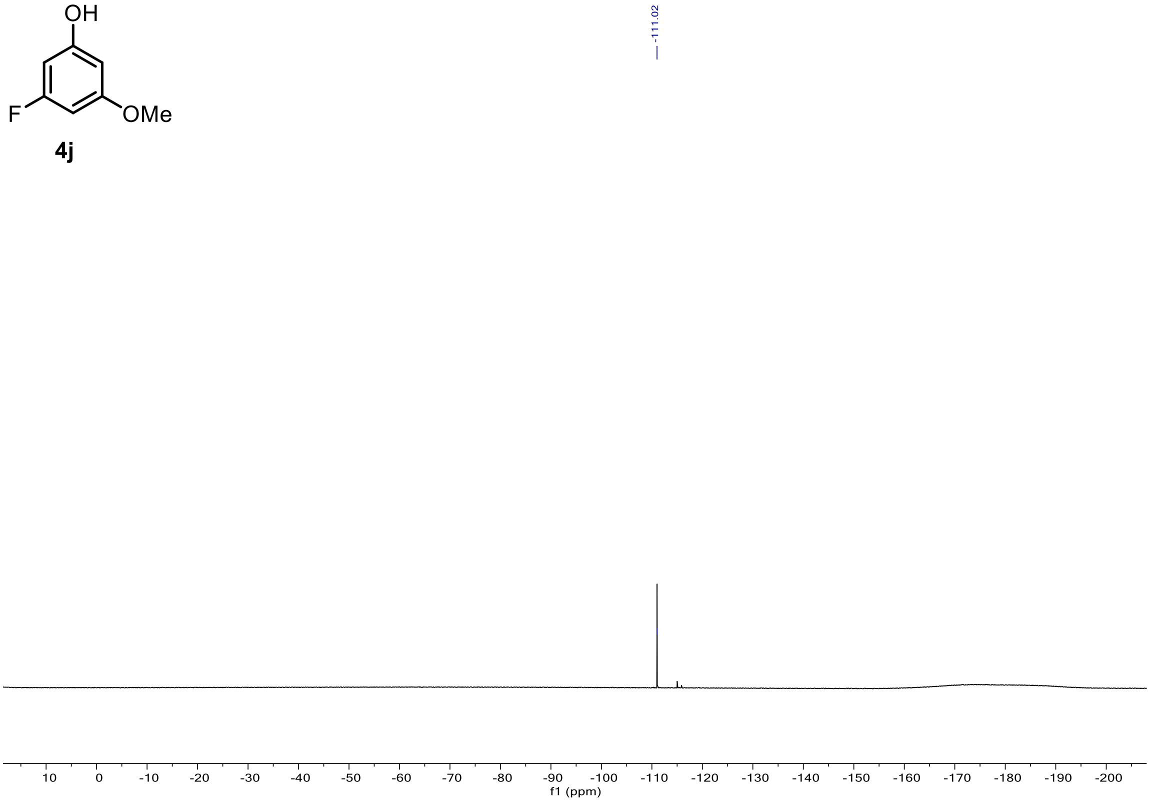

OH
OMe
4h
6.32
6.26
6.24
6.23
6.23
3.77
2.53
2.51
2.49
1.32
1.31
1.30
1.29
1.25
0.90
0.89
0.87
0.99
1.04
1.00
3.00
2.33
6.06
3.23
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

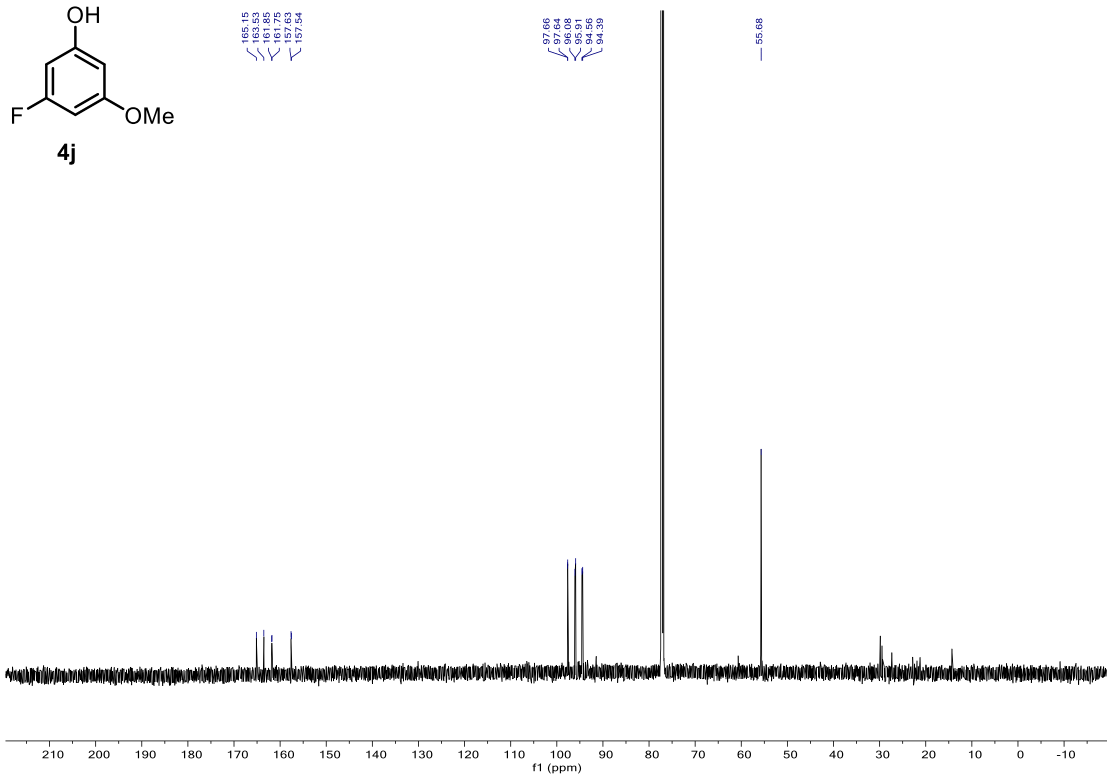

OH
OMe
4h
160.95
156.62
145.92
108.00
106.93
98.79
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.38
36.16
31.63
30.99
22.69
14.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


6.47
6.40
6.24
6.24
6.23
3.78
1.55
1.54
1.53
1.53
1.52
1.23
1.21
1.20
1.19
1.17
1.06
1.05
1.05
1.04
1.04
0.85
0.84
OH
OMe
4i
0.99
1.03
0.96
2.89
2.13
6.26
6.20
2.39
3.34
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)


160.66
156.37
153.17
105.81
105.29
98.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.35
44.64
37.98
31.92
30.15
29.04
24.78
22.81
14.22
OH
OMe
4i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

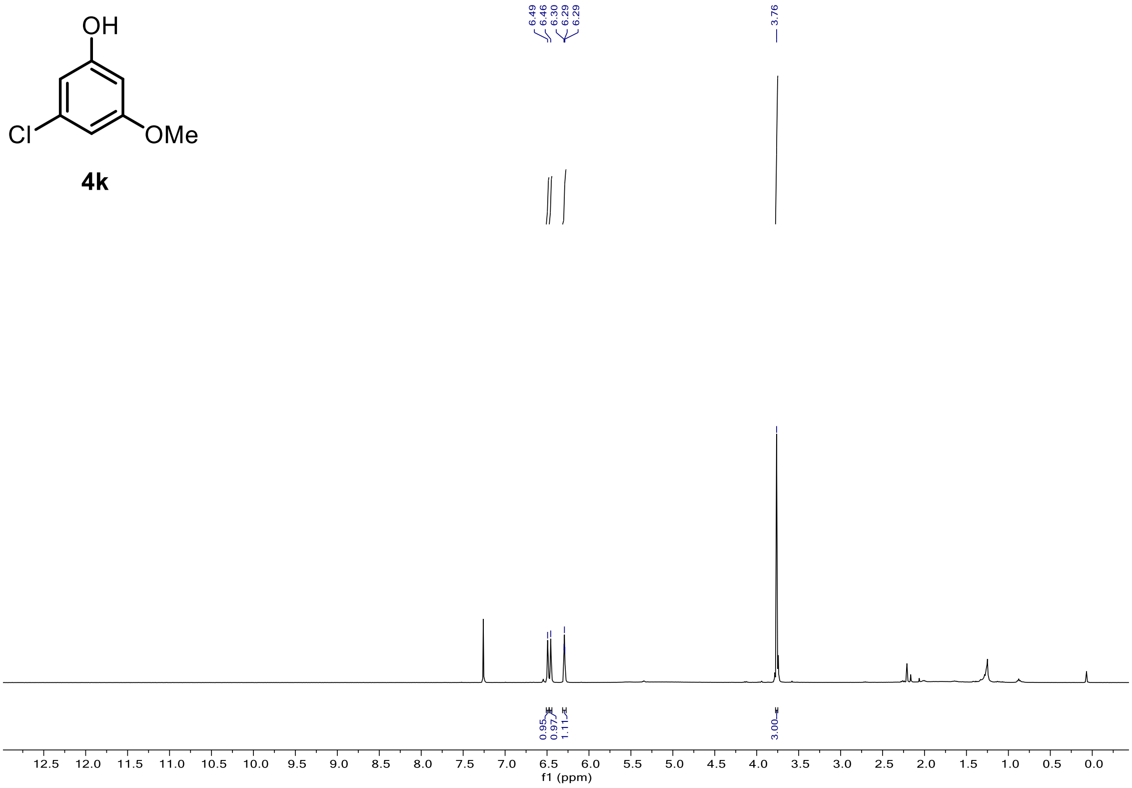

OH
F
OMe
4j
6.23
6.23
6.23
6.22
6.21
6.21
6.19
6.18
6.17
6.17
6.17
3.76
1.09
2.07
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

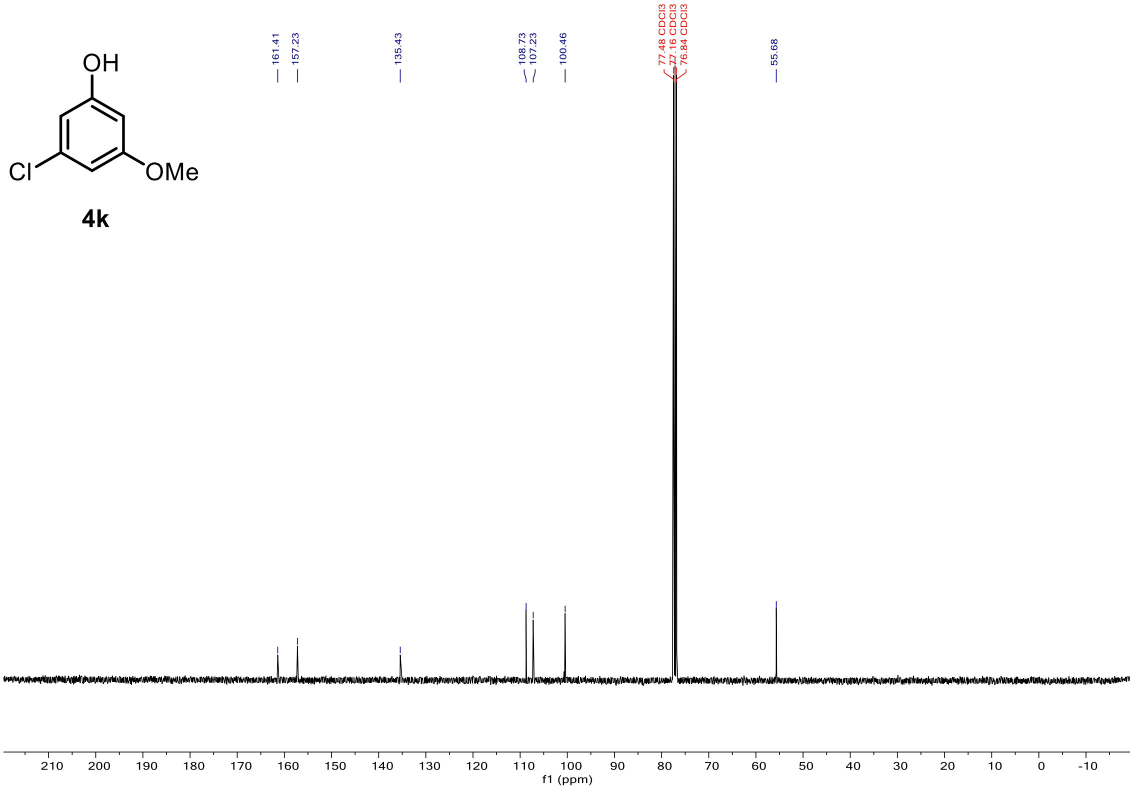

OH
F
OMe
4j
-111.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

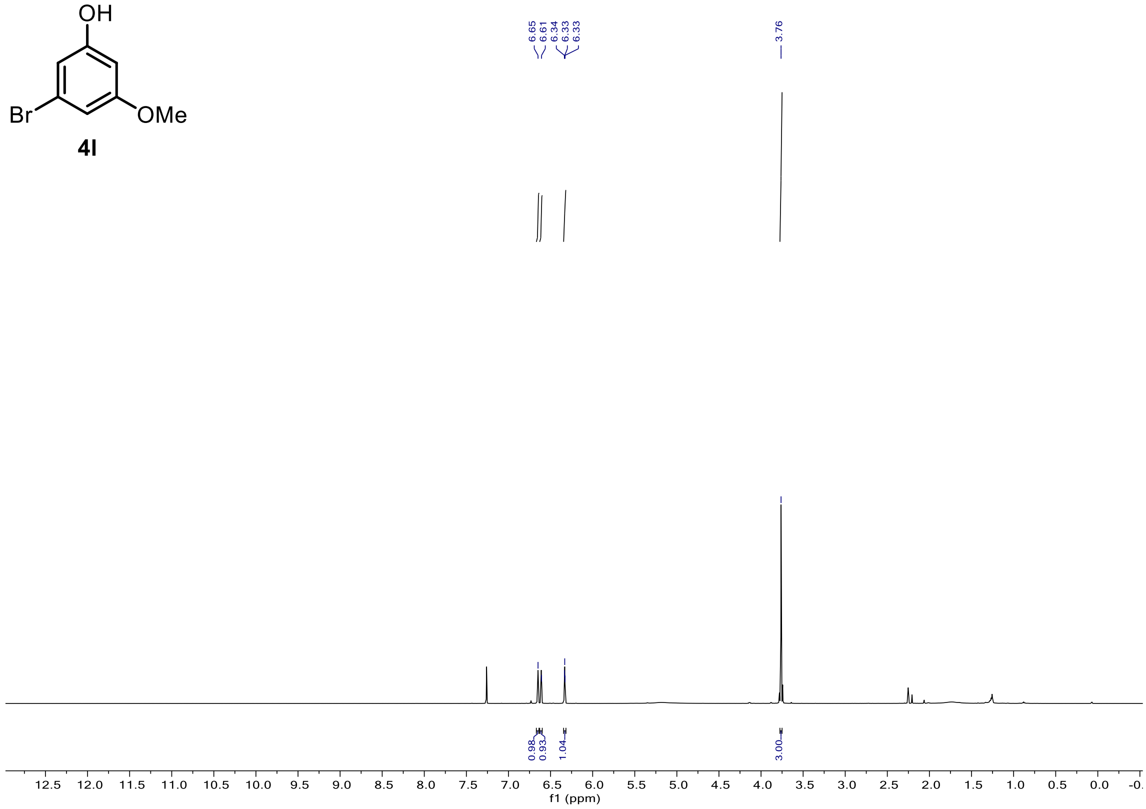


4j

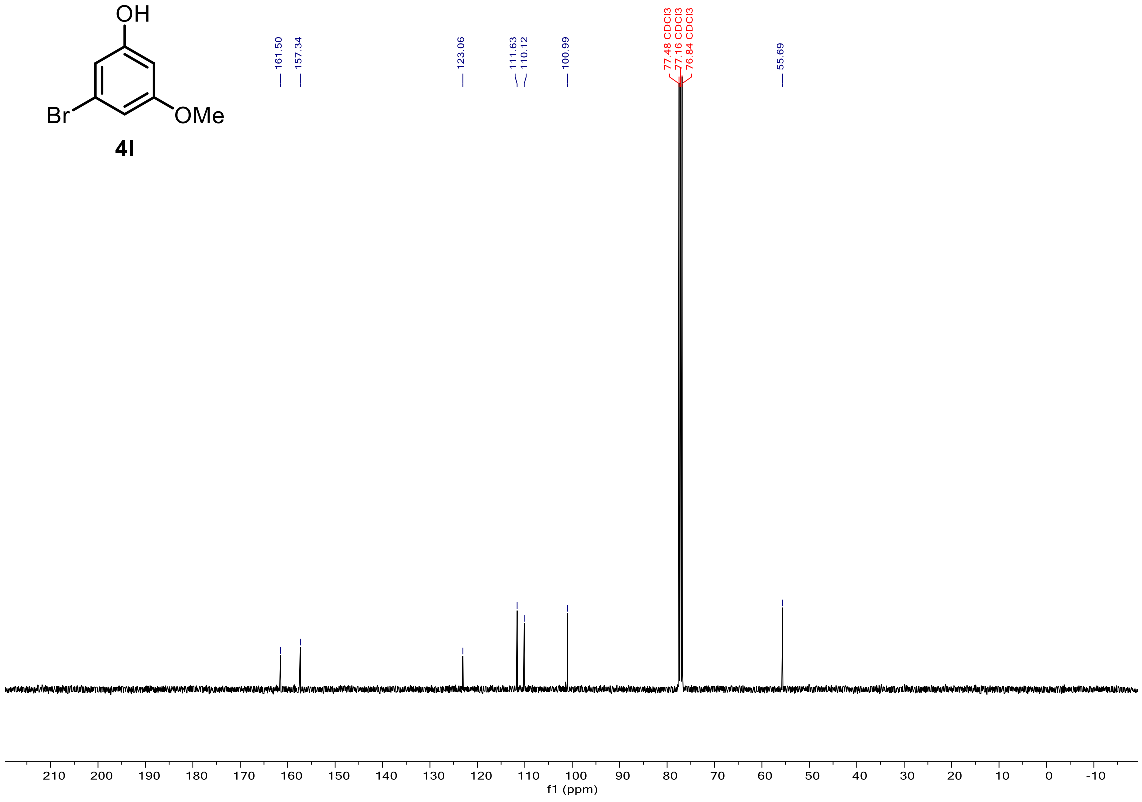
OH
F
OMe
165.15
163.53
161.85
161.75
157.63
157.54
97.66
97.64
96.08
95.91
94.56
94.39
55.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
Cl
OMe
4k
6.49
6.46
6.30
6.29
6.29
3.76
0.95
0.97
1.11
3.00
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

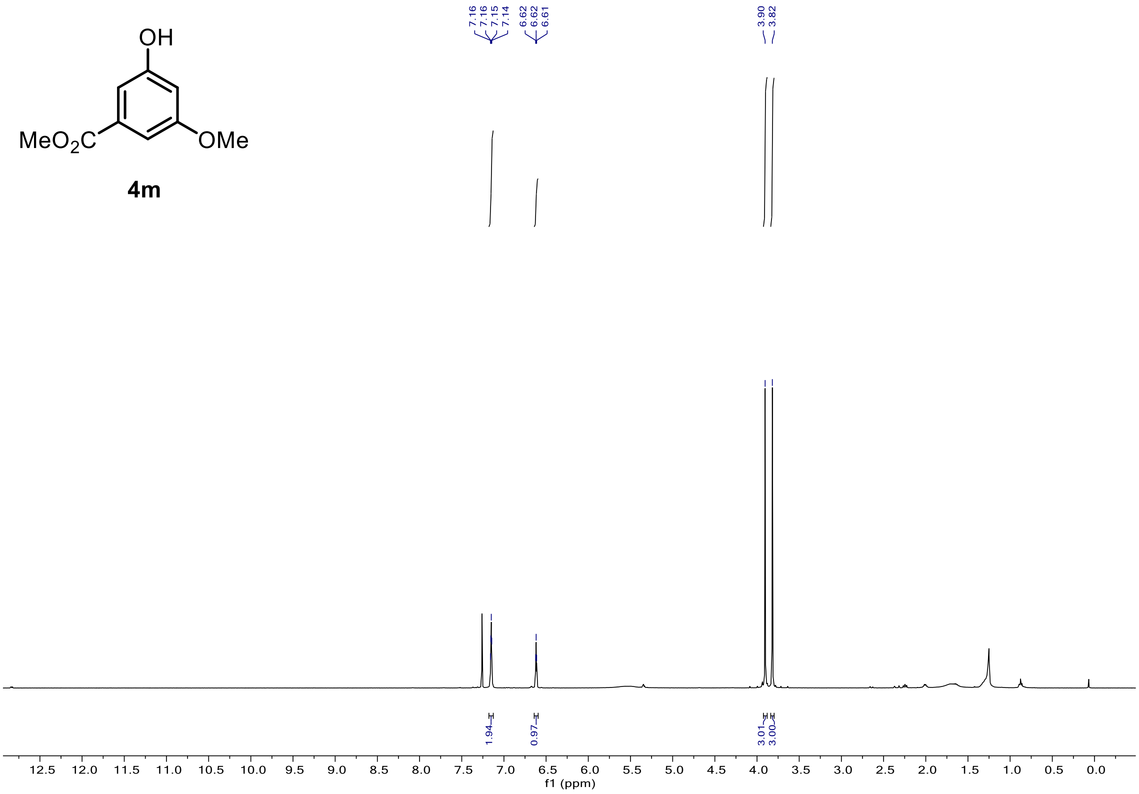

OH
Cl
OMe
4k
161.41
157.23
135.43
108.73
107.23
100.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

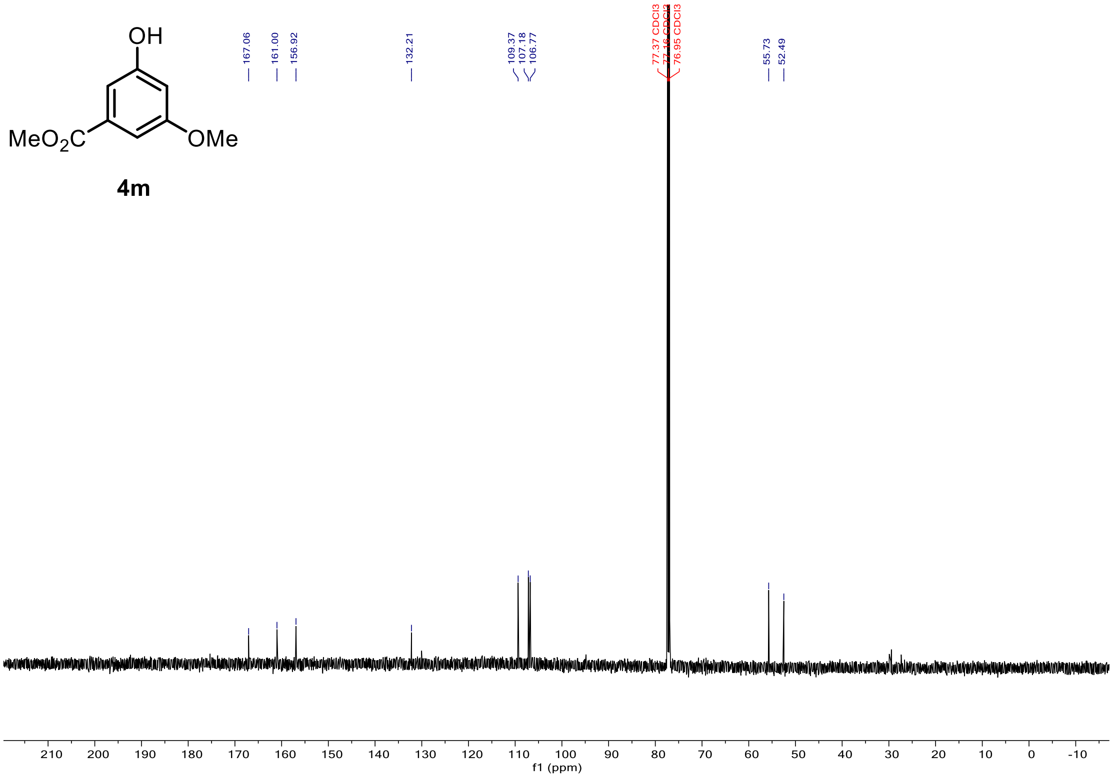

4l

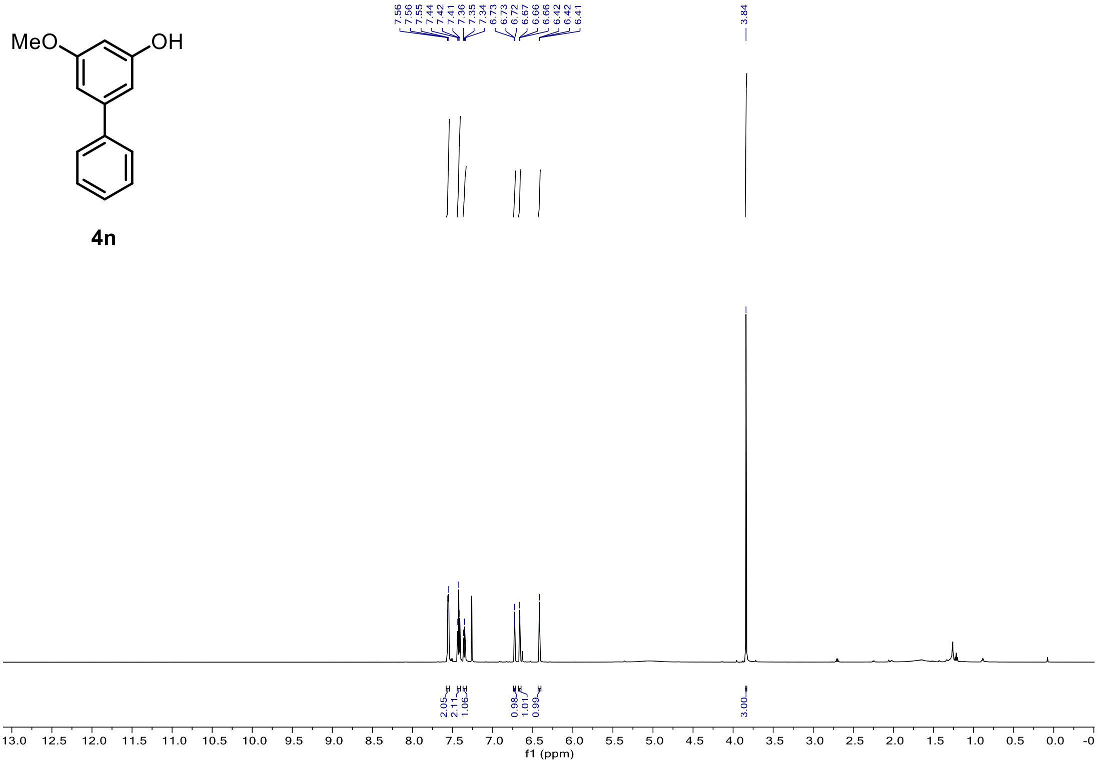
OH
Br
OMe
6.65
6.61
6.34
6.33
6.33
3.76
0.98
0.93
1.04
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

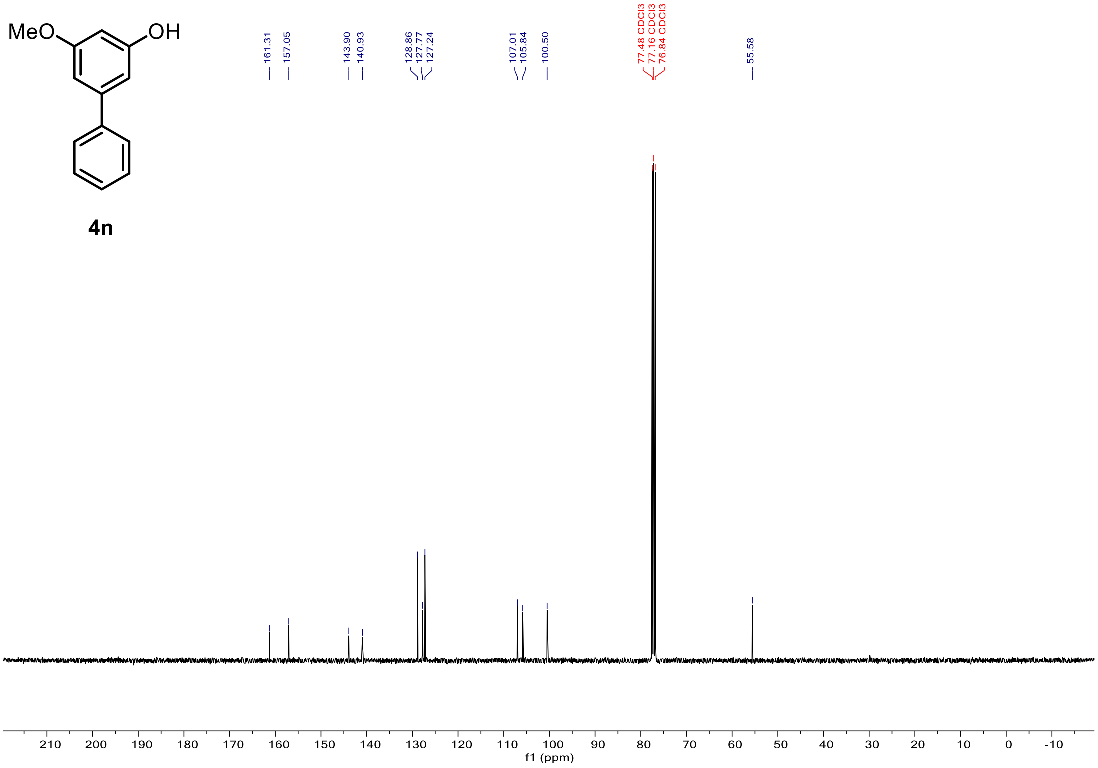

4l

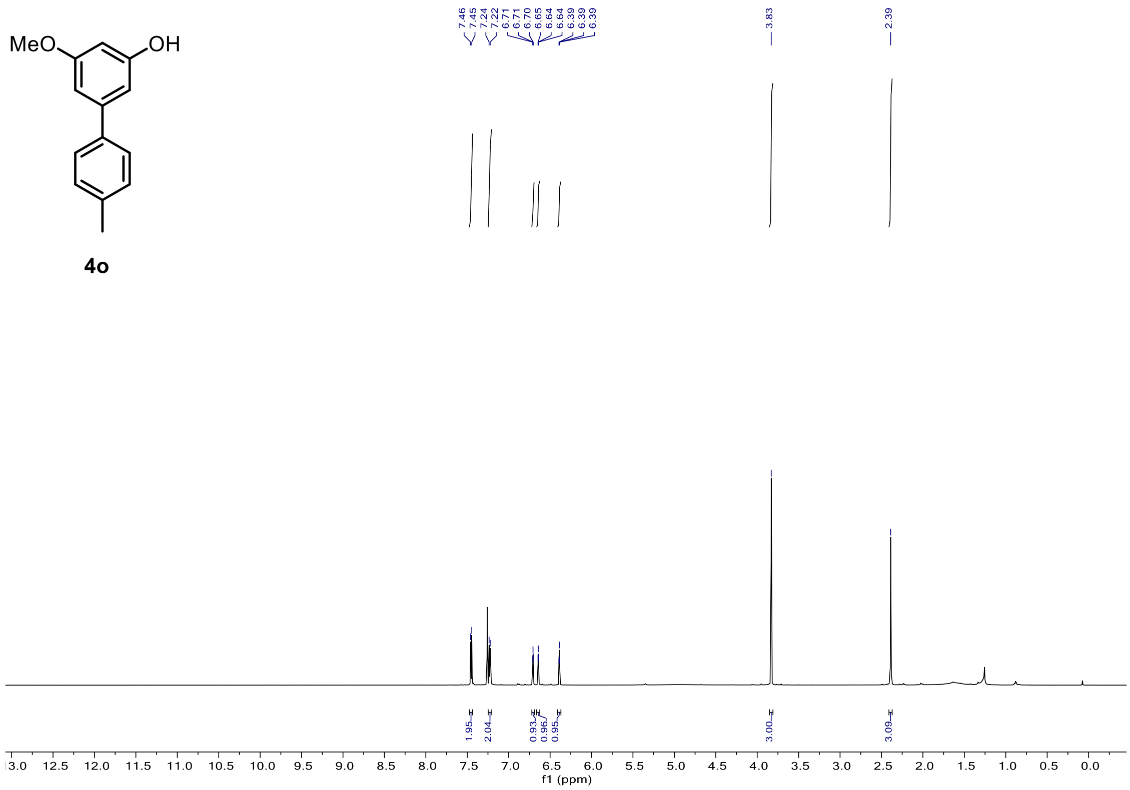
OH
Br
OMe
161.50
157.34
123.06
111.63
110.12
100.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

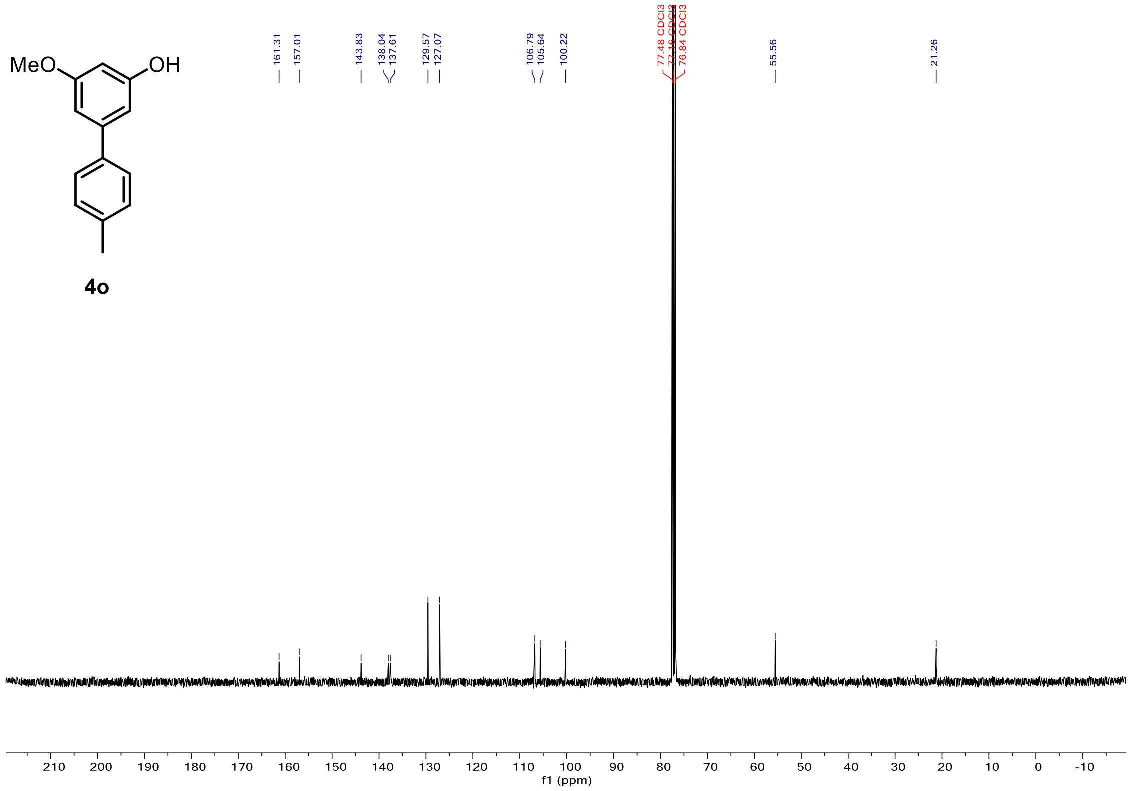

OH
MeO$_2$C
OMe
4m
7.16
7.16
7.15
7.14
6.62
6.62
6.61
3.90
3.82
1.94
0.97
3.01
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

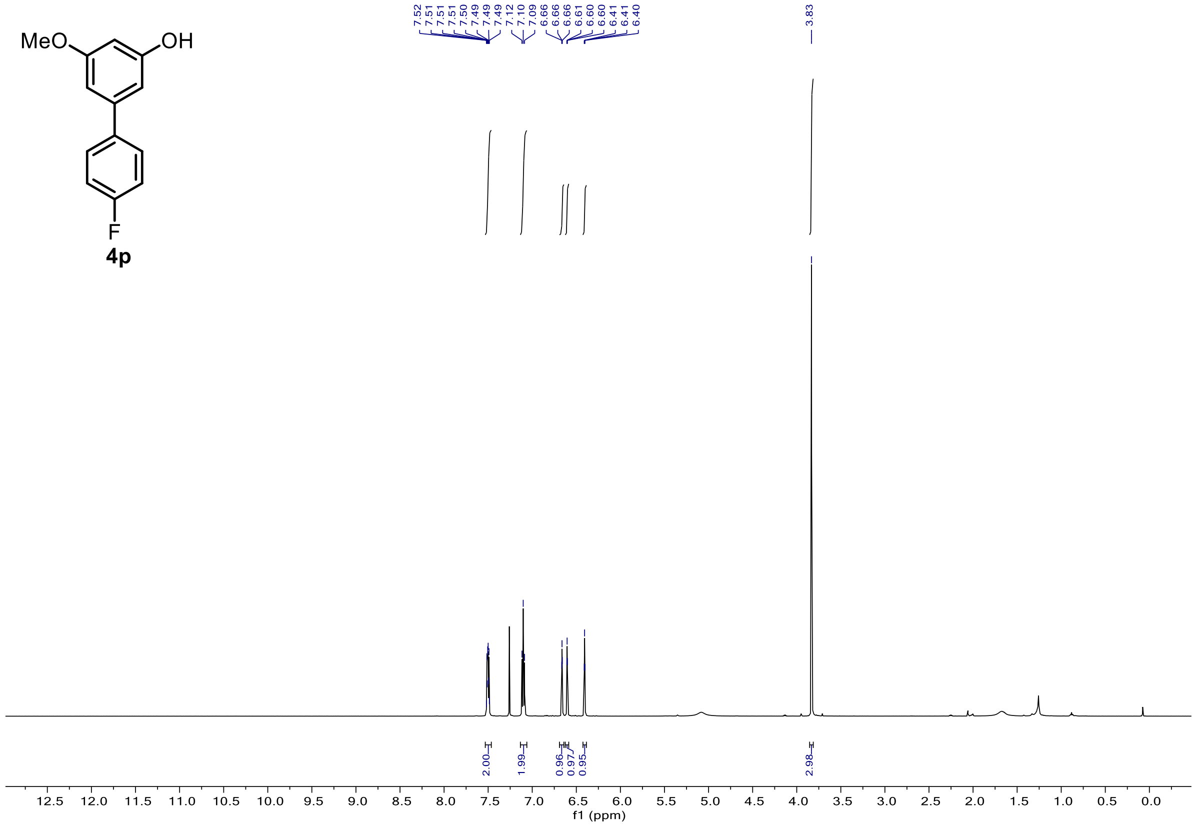

OH
MeO$_2$C
OMe
4m
167.06
161.00
156.92
132.21
109.37
107.18
106.77
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.73
52.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
OH
4n
7.56
7.56
7.55
7.44
7.42
7.41
7.36
7.35
7.34
6.73
6.73
6.72
6.67
6.66
6.66
6.42
6.42
6.41
3.84
2.05
2.11
1.06
0.98
1.01
0.99
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

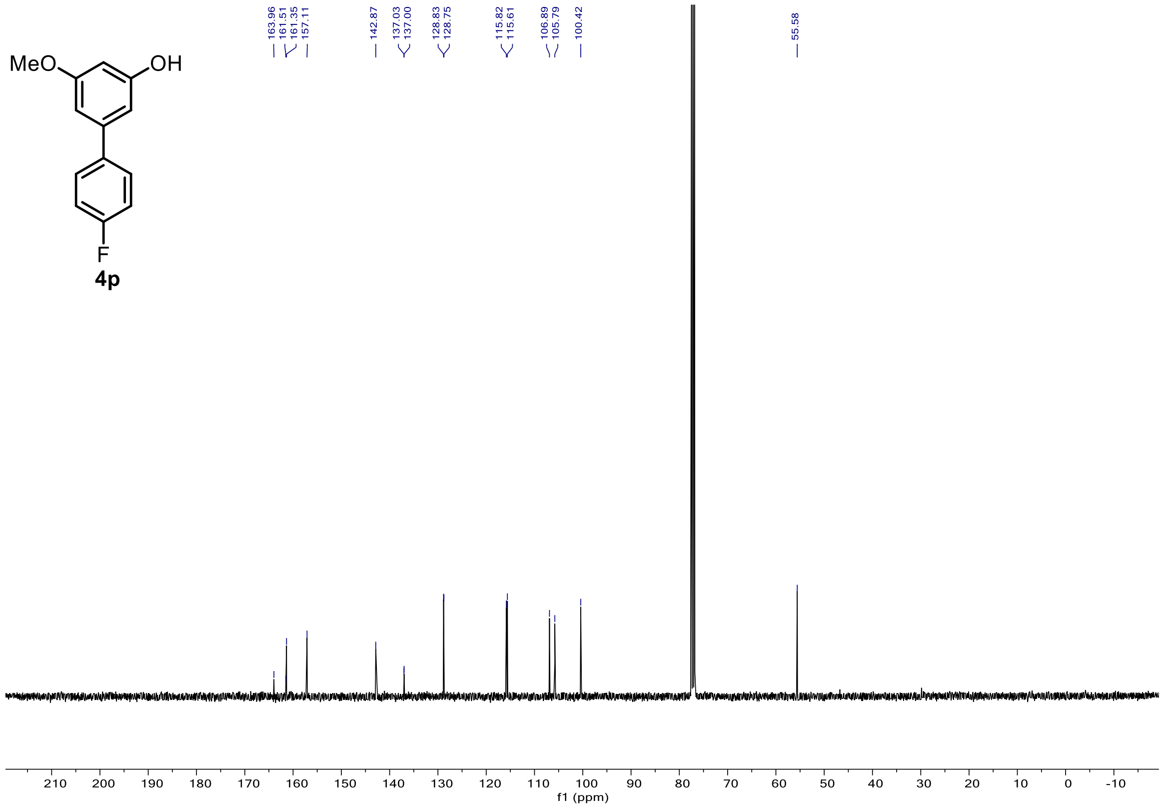

MeO
OH
4n
161.31
157.05
143.90
140.93
128.86
127.77
127.24
107.01
105.84
100.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
OH
4o
7.46
7.45
7.24
7.22
6.71
6.71
6.70
6.65
6.64
6.64
6.39
6.39
6.39
3.83
2.39
1.95
2.04
0.93
0.96
0.95
3.00
3.09
13.0
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

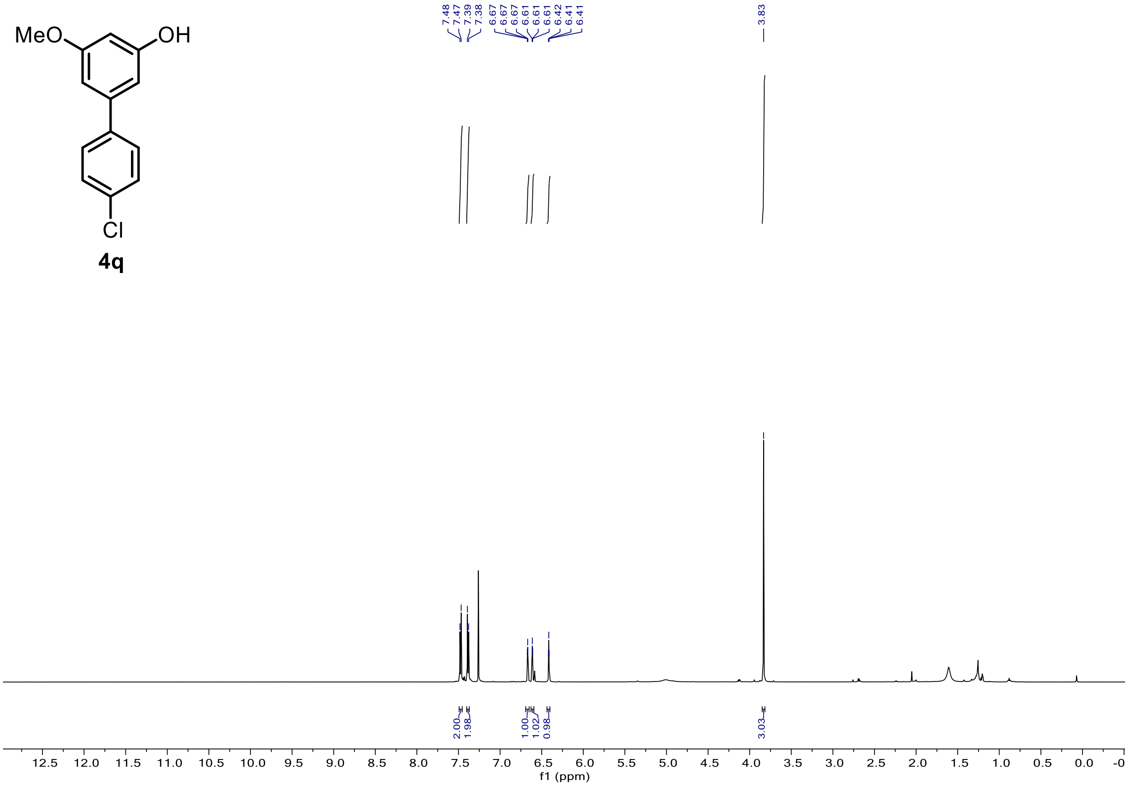

MeO
OH
4o
161.31
157.01
143.83
138.04
137.61
129.57
127.07
106.79
105.64
100.22
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.56
21.26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
OH
F
7.52
7.51
7.51
7.50
7.49
7.49
7.49
7.12
7.10
7.09
6.66
6.66
6.66
6.61
6.60
6.60
6.41
6.41
6.40
3.83
2.00
1.99
0.96
0.97
0.95
2.98
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

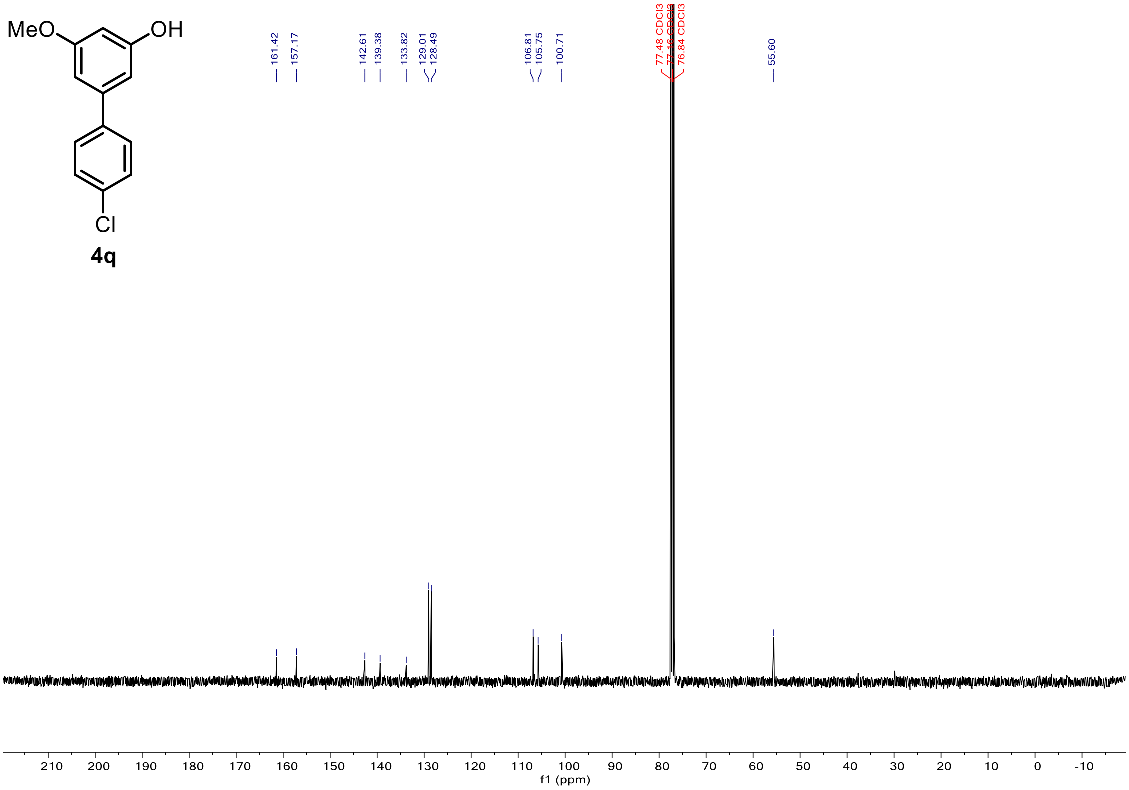
4p


MeO
OH
F
163.96
161.51
161.35
157.11
142.87
137.03
137.00
128.83
128.75
115.82
115.61
106.89
105.79
100.42
55.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

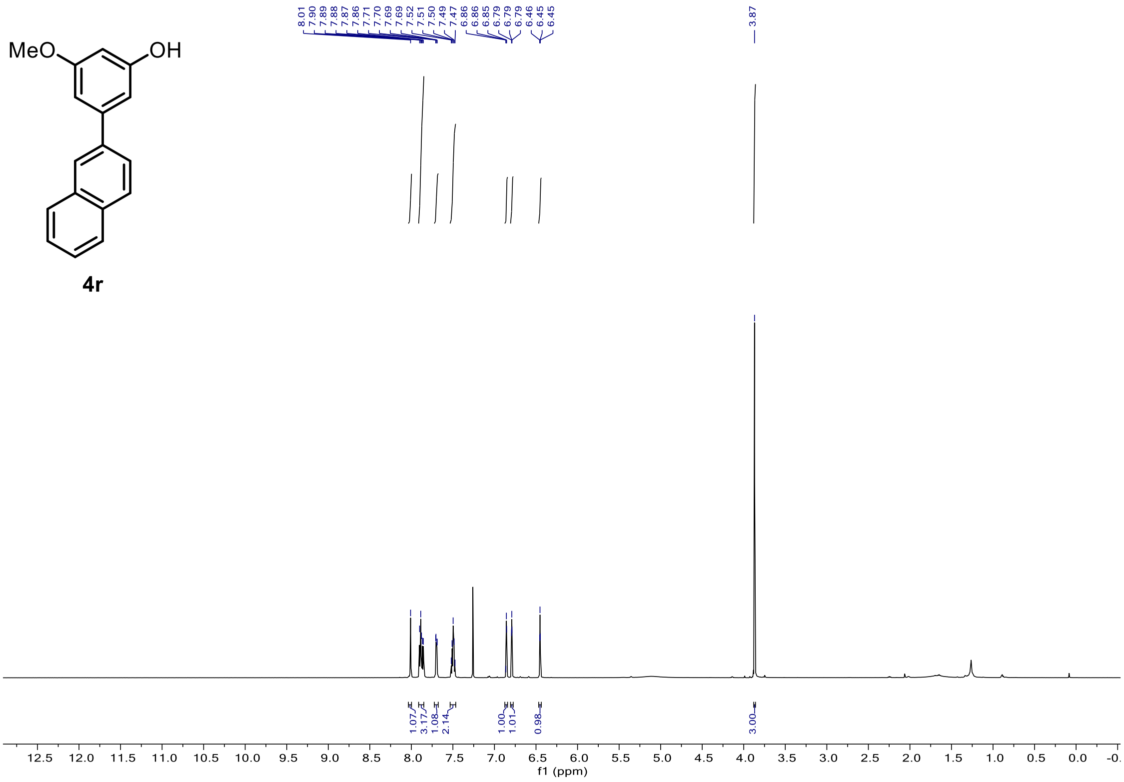
4p

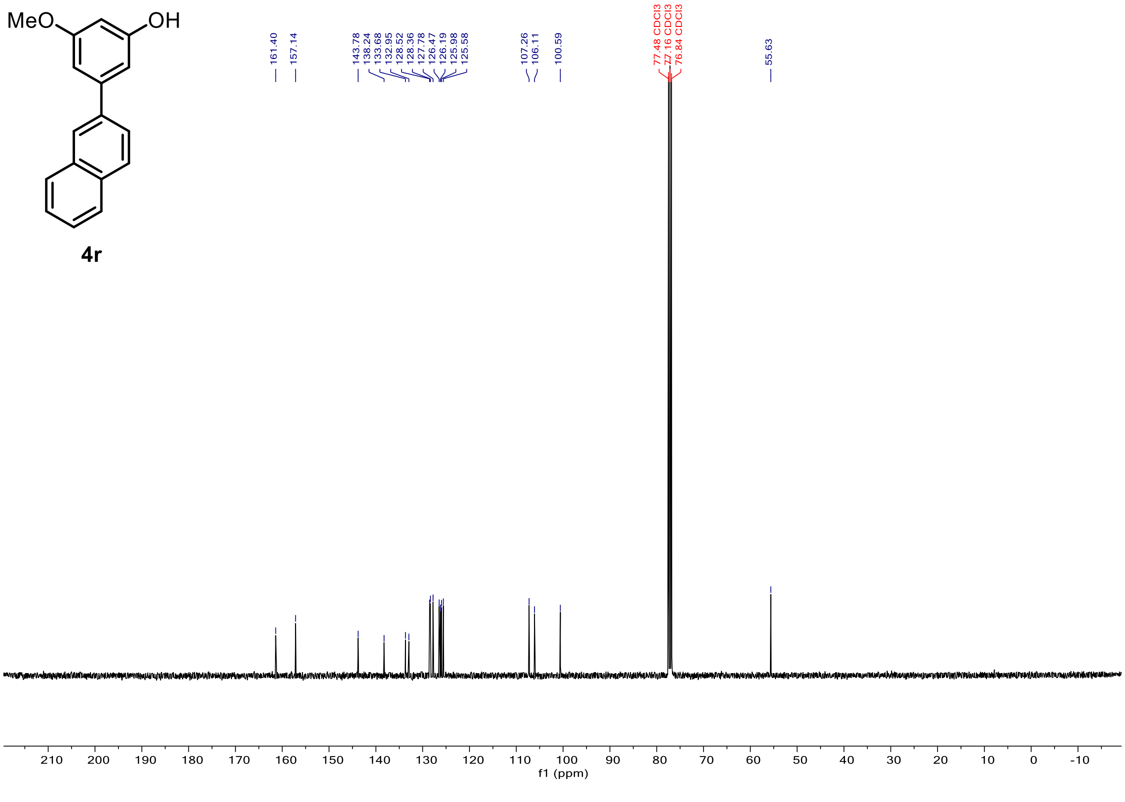

MeO
OH
Cl
7.48
7.47
7.39
7.38
6.67
6.67
6.67
6.61
6.61
6.61
6.42
6.41
6.41
3.83
2.00
1.98
1.00
1.02
0.98
3.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

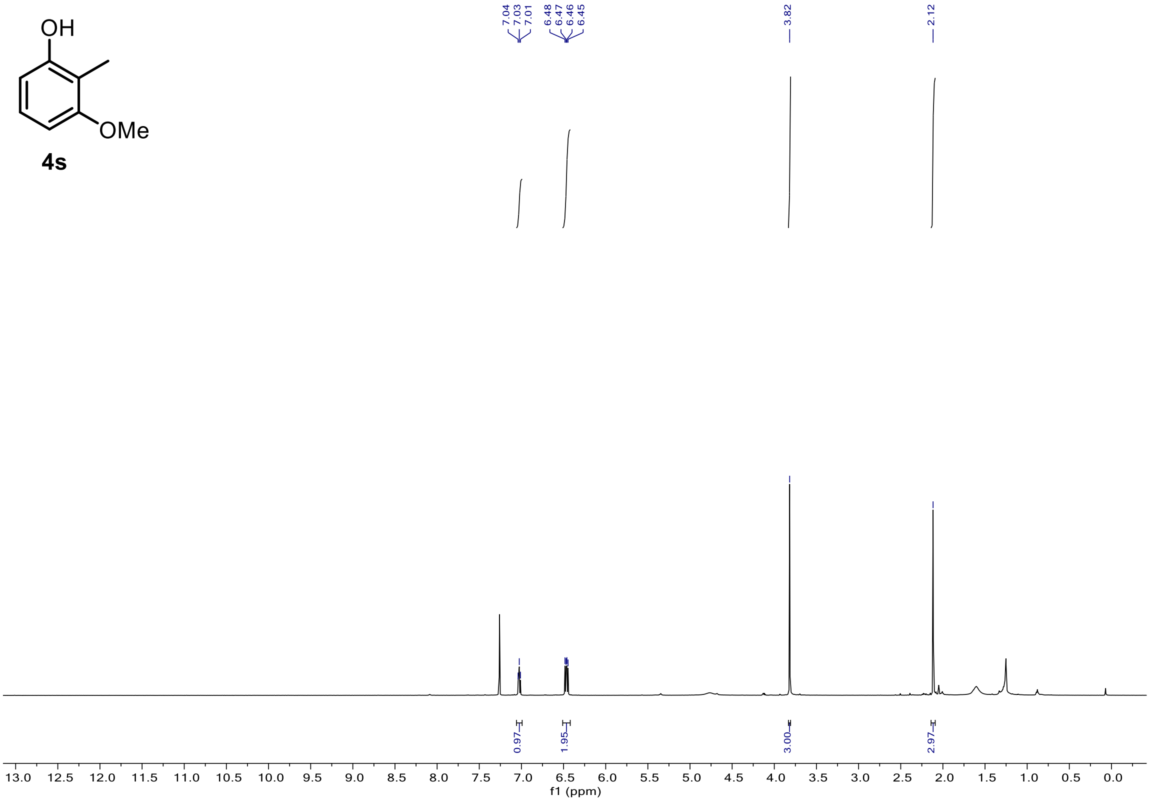
4q

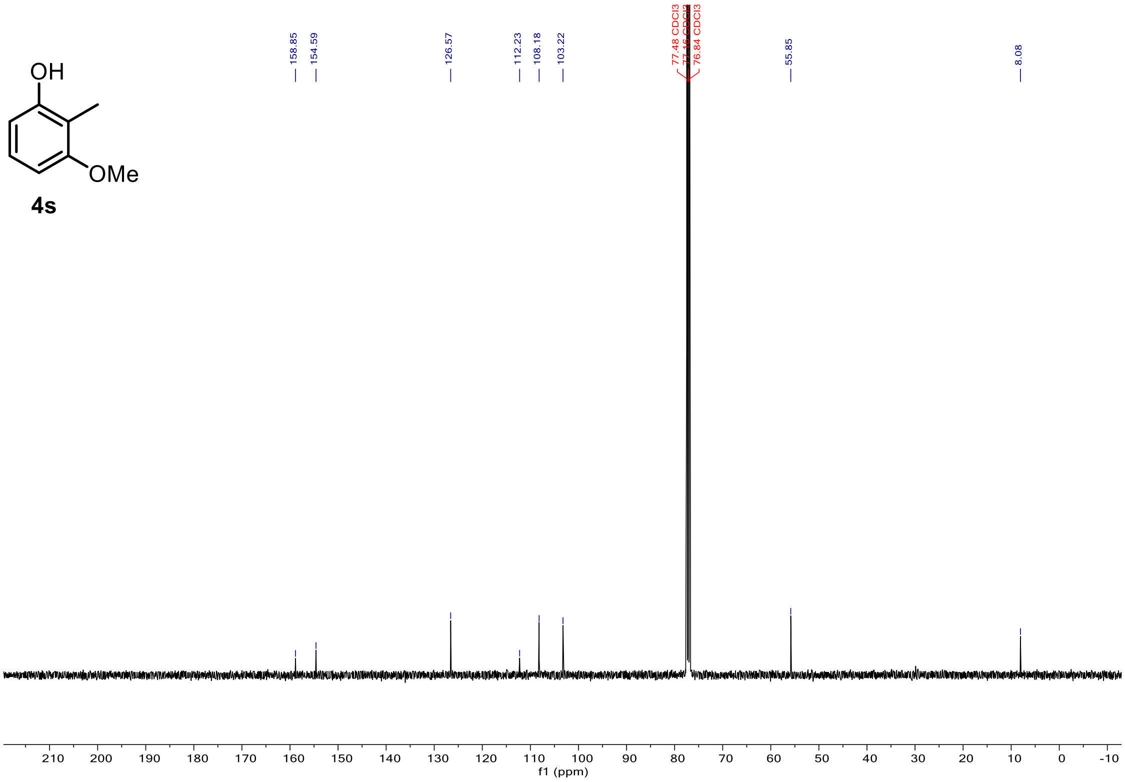

MeO
OH
Cl
161.42
157.17
142.61
139.38
133.82
129.01
128.49
106.81
105.75
100.71
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

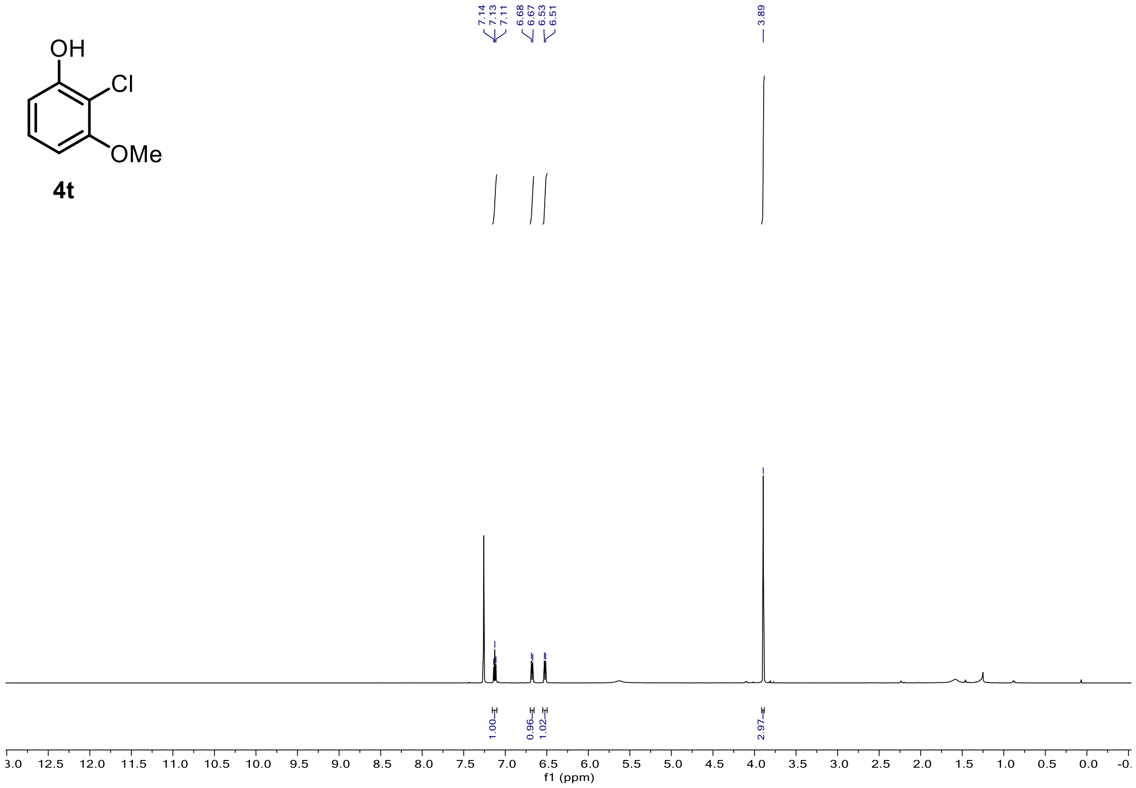
4q

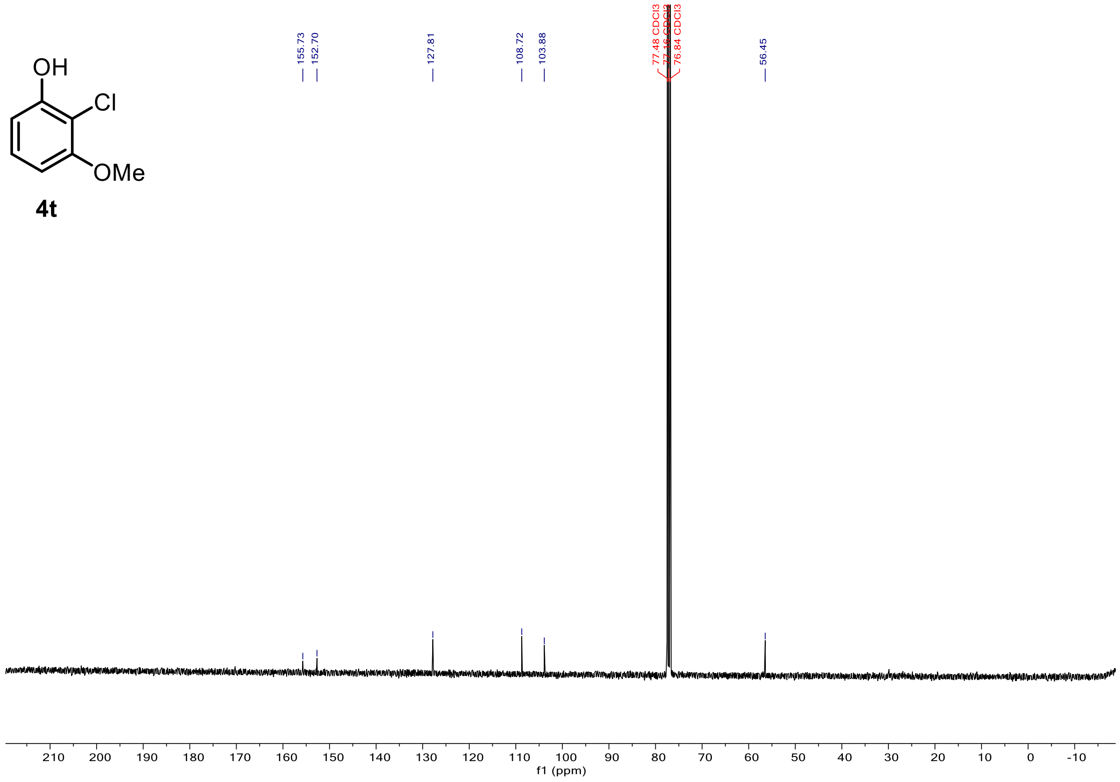

4r
MeO
OH
8.01
7.90
7.89
7.88
7.87
7.86
7.71
7.70
7.69
7.69
7.52
7.51
7.50
7.49
7.47
6.86
6.86
6.85
6.79
6.79
6.79
6.46
6.45
6.45
3.87
1.07
3.17
1.08
2.14
1.00
1.01
0.98
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

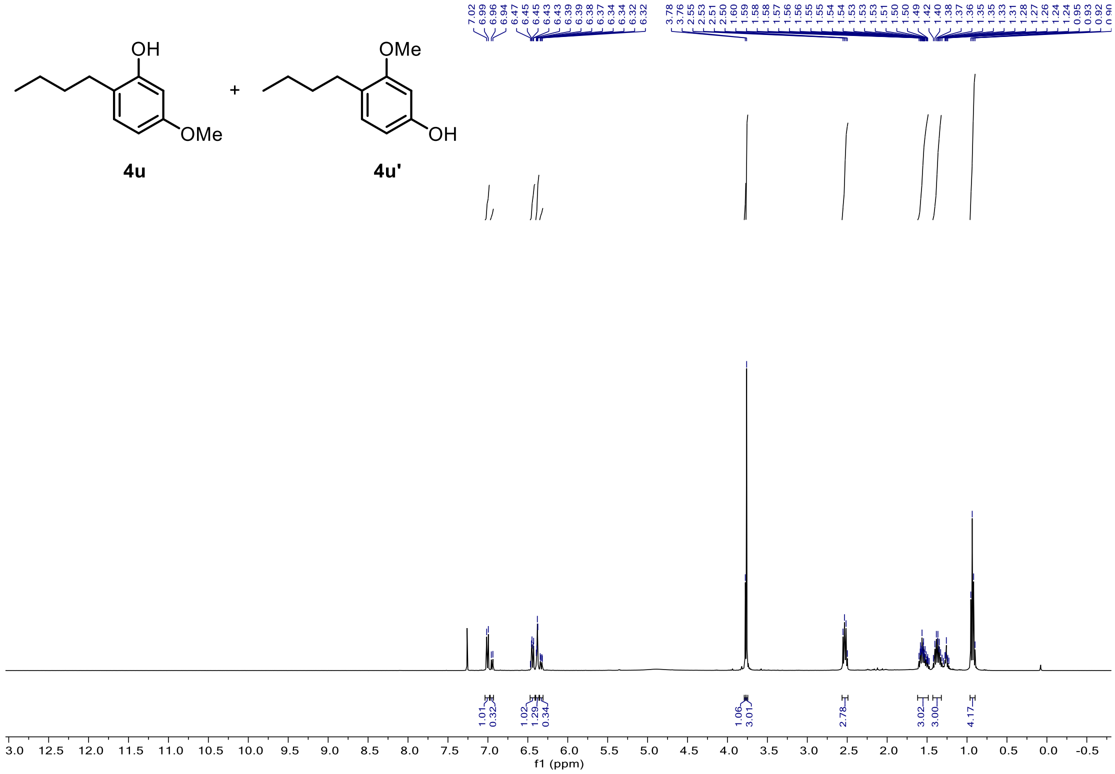

4r
MeO
OH
161.40
157.14
143.78
138.24
133.68
132.95
128.52
128.36
127.78
126.47
126.19
125.98
125.58
107.26
106.11
100.59
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

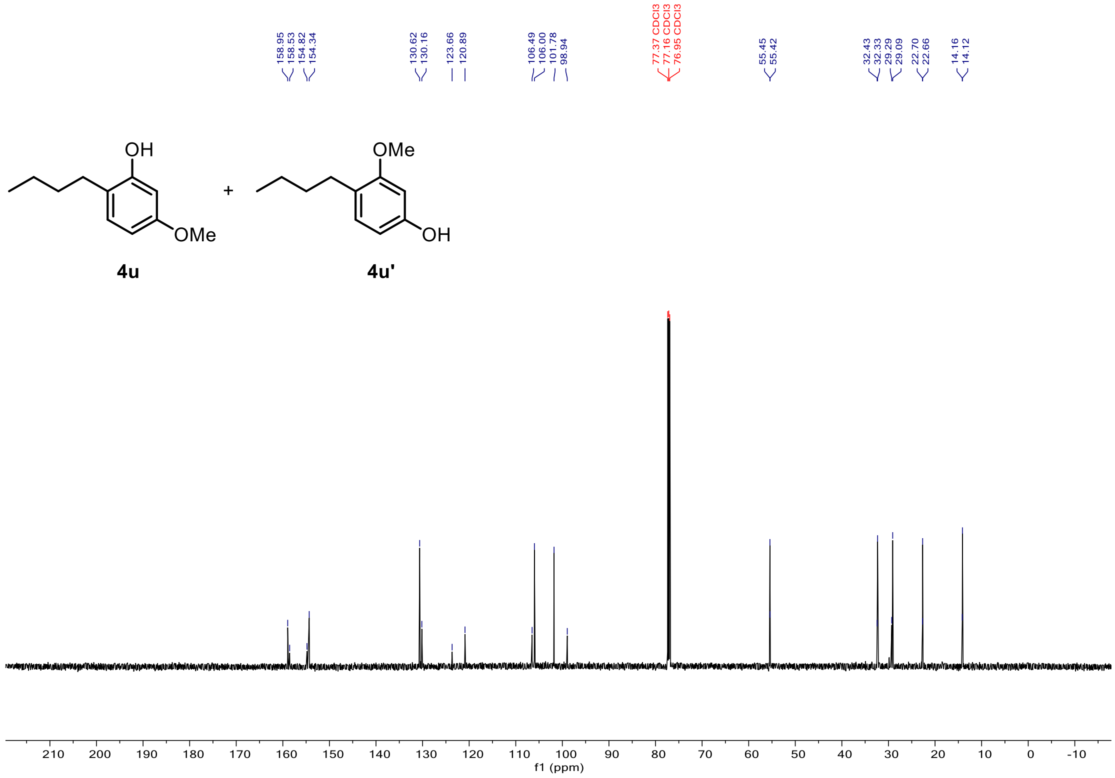

OH
OMe
4s
7.04
7.03
7.01
6.48
6.47
6.46
6.45
3.82
2.12
0.97
1.95
3.00
2.97
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

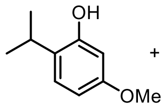

OH
OMe
4s
158.85
154.59
126.57
112.23
108.18
103.22
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.85
8.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
Cl
OMe
4t
7.14
7.13
7.11
6.68
6.67
6.53
6.51
3.89
1.00
0.96
1.02
2.97
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)


OH
Cl
OMe
4t
155.73
152.70
127.81
108.72
103.88
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

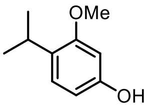

OH
OMe
+
OMe
OH
4u
4u'
7.02
6.99
6.96
6.94
6.47
6.45
6.45
6.43
6.43
6.39
6.39
6.38
6.37
6.34
6.34
6.32
6.32
3.78
3.76
2.55
2.53
2.51
2.50
1.60
1.59
1.58
1.58
1.57
1.56
1.56
1.55
1.55
1.54
1.54
1.53
1.53
1.53
1.51
1.50
1.50
1.49
1.42
1.40
1.38
1.37
1.36
1.35
1.35
1.33
1.31
1.28
1.27
1.26
1.24
1.24
0.95
0.93
0.92
0.90
1.01
0.32
1.02
1.29
0.34
1.06
3.01
2.78
3.02
3.00
4.17
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.5
f1 (ppm)


158.95
158.53
154.82
154.34
130.62
130.16
123.66
120.89
106.49
106.00
101.78
98.94
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.45
55.42
32.43
32.33
29.29
29.09
22.70
22.66
14.16
14.12
OH
OMe
+
OMe
OH
4u
4u'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

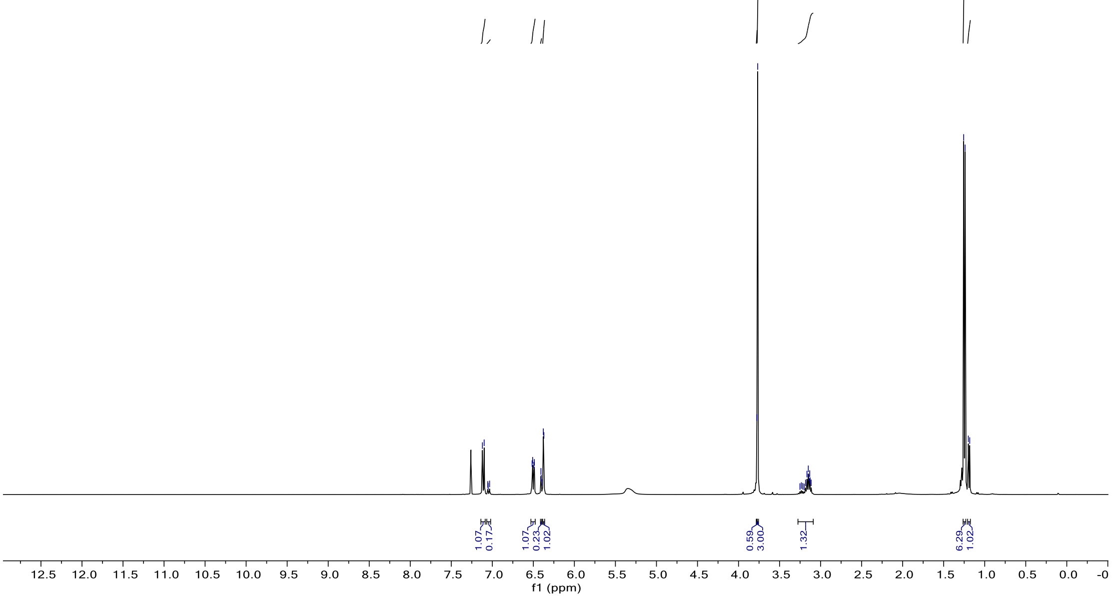


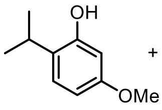
4v

+



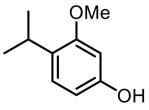
4v'


7.12
7.10
7.06
7.05
7.03
6.52
6.51
6.49
6.49
6.41
6.40
6.39
6.38
6.37
3.78
3.77
3.25
3.23
3.22
3.20
3.18
3.17
3.15
3.14
3.13
3.13
3.12
1.26
1.24
1.20
1.18
1.07
0.17
1.07
0.23
1.02
0.59
3.00
1.32
6.29
1.02
12.5
12.0
11.5
11.0
10.5
10.0
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
-0
f1 (ppm)

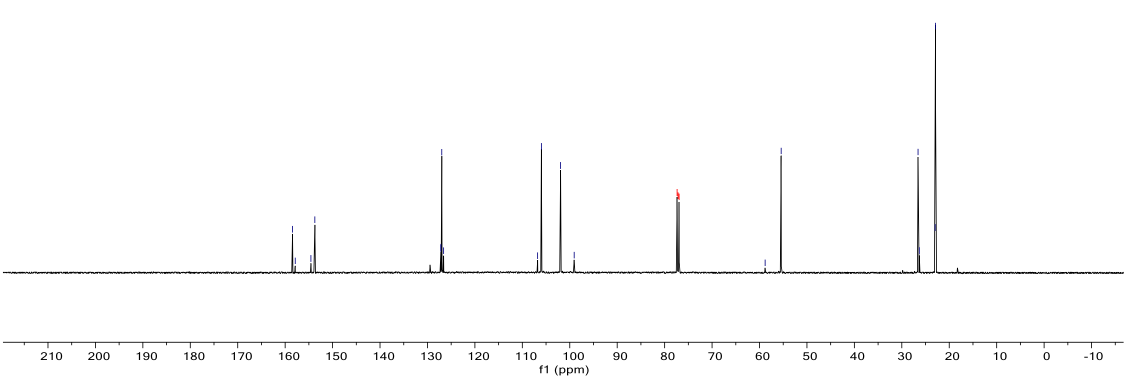


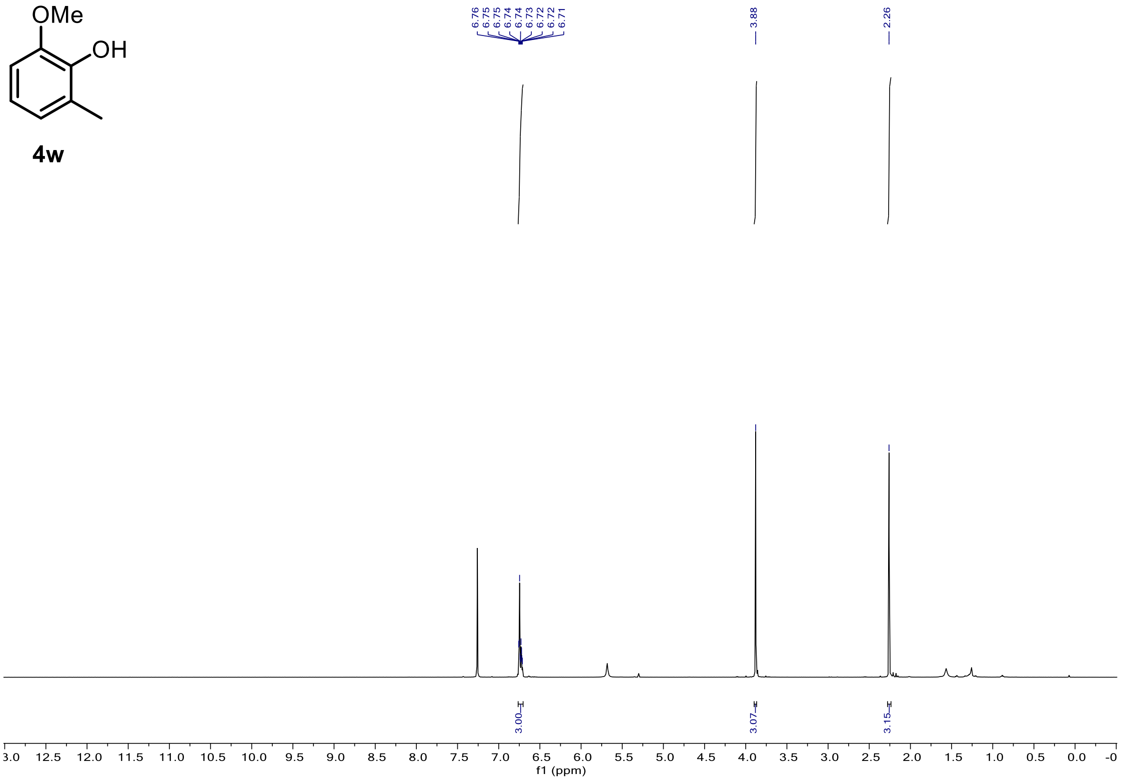
4v

+

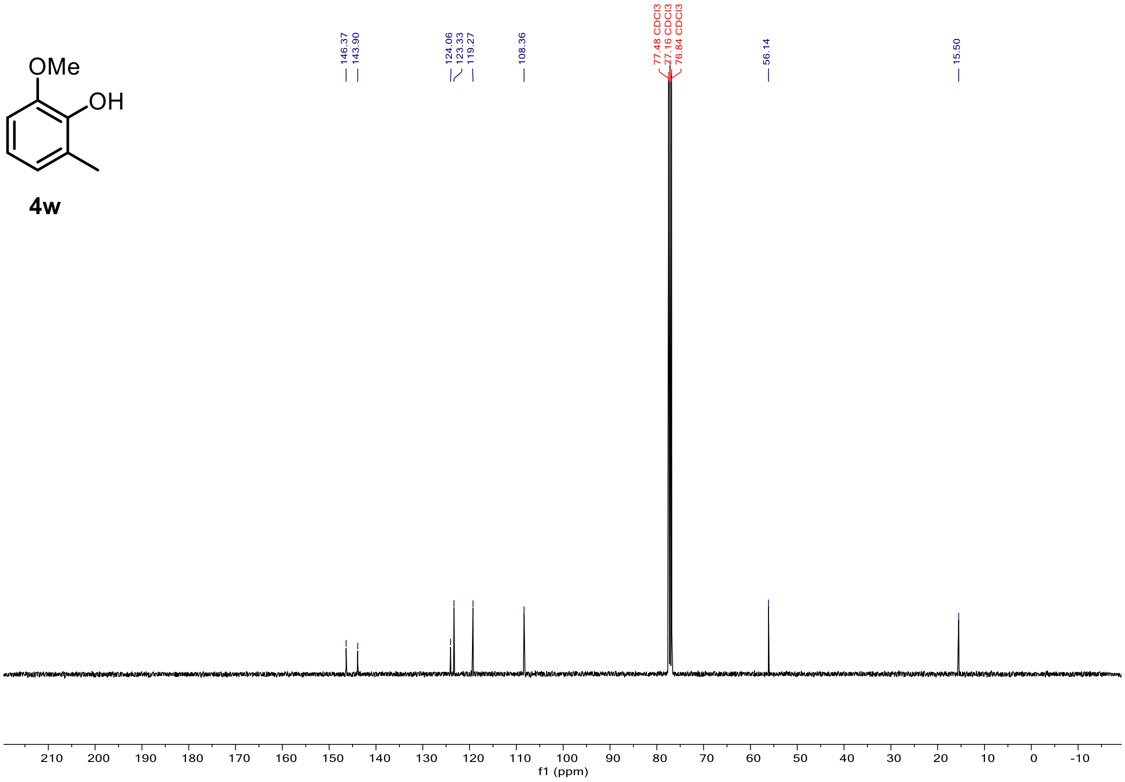


4v'

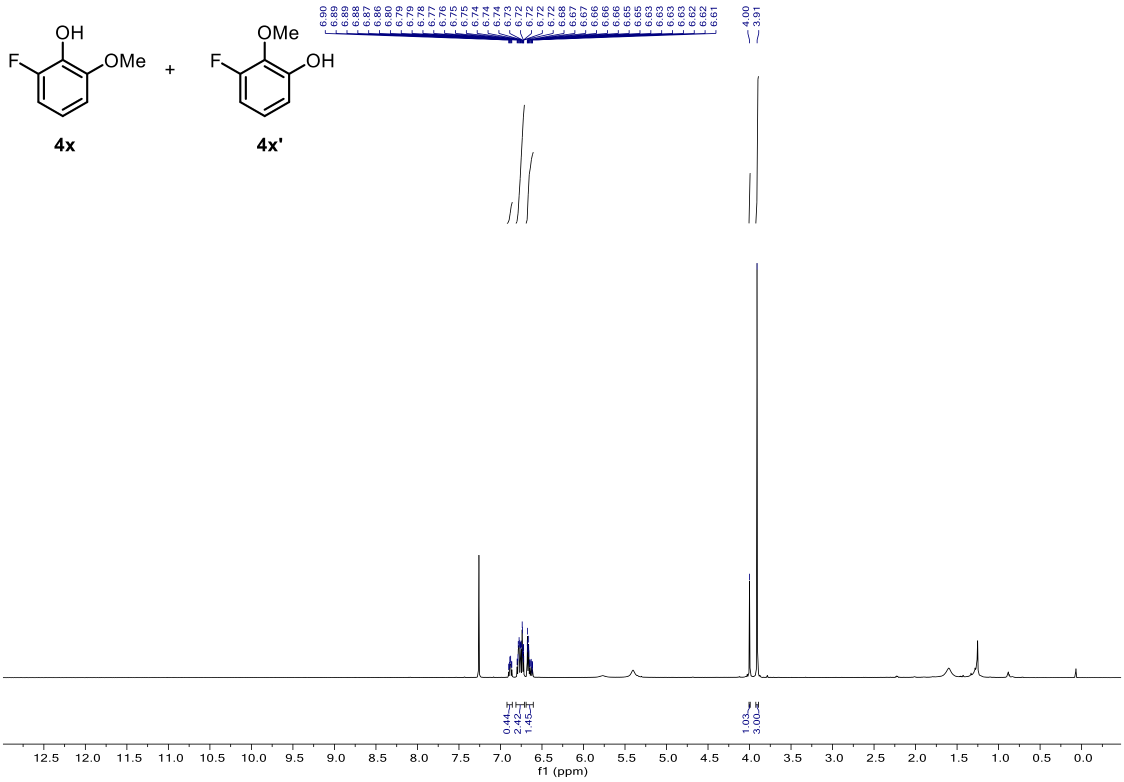

158.44
157.87
154.57
153.74
127.19
127.17
126.98
126.59
106.78
105.98
101.93
99.07
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
58.81
55.43
26.58
26.31
22.97
22.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OMe
OH
6.76
6.75
6.75
6.74
6.74
6.73
6.72
6.72
6.71
3.88
2.26
3.00
3.07
3.15
3.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

4w


OMe
OH
146.37
143.90
124.06
123.33
119.27
108.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.14
15.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4w

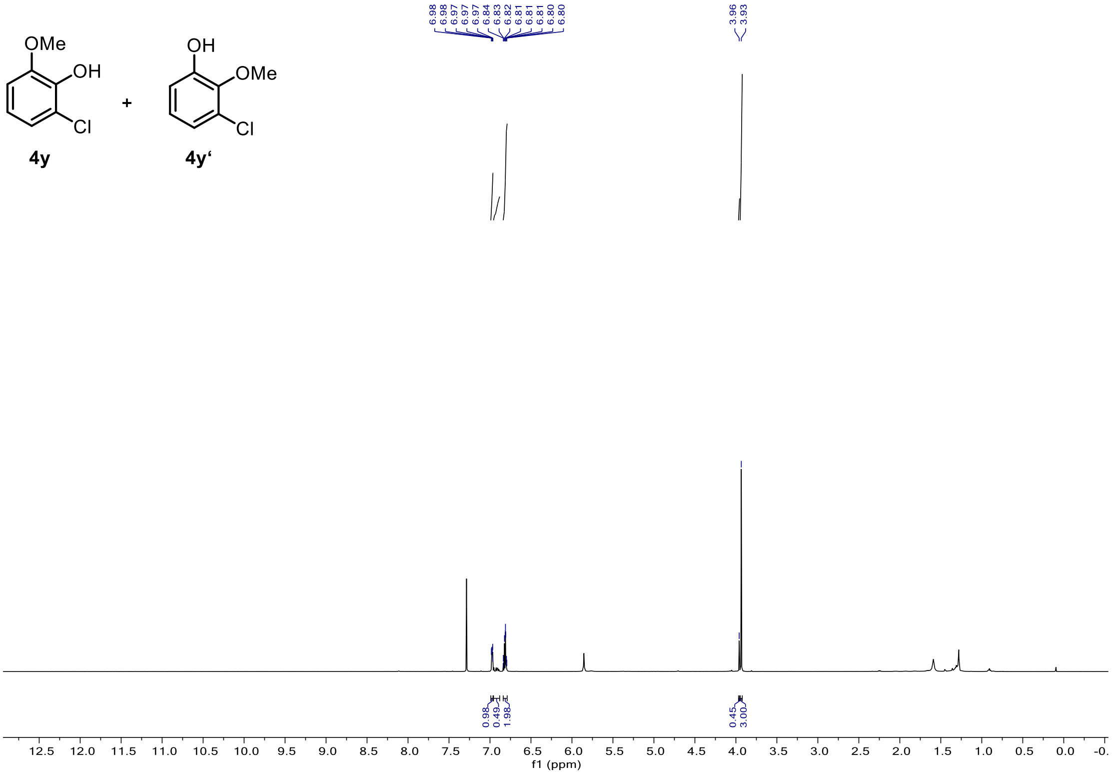


4x

+

4x'

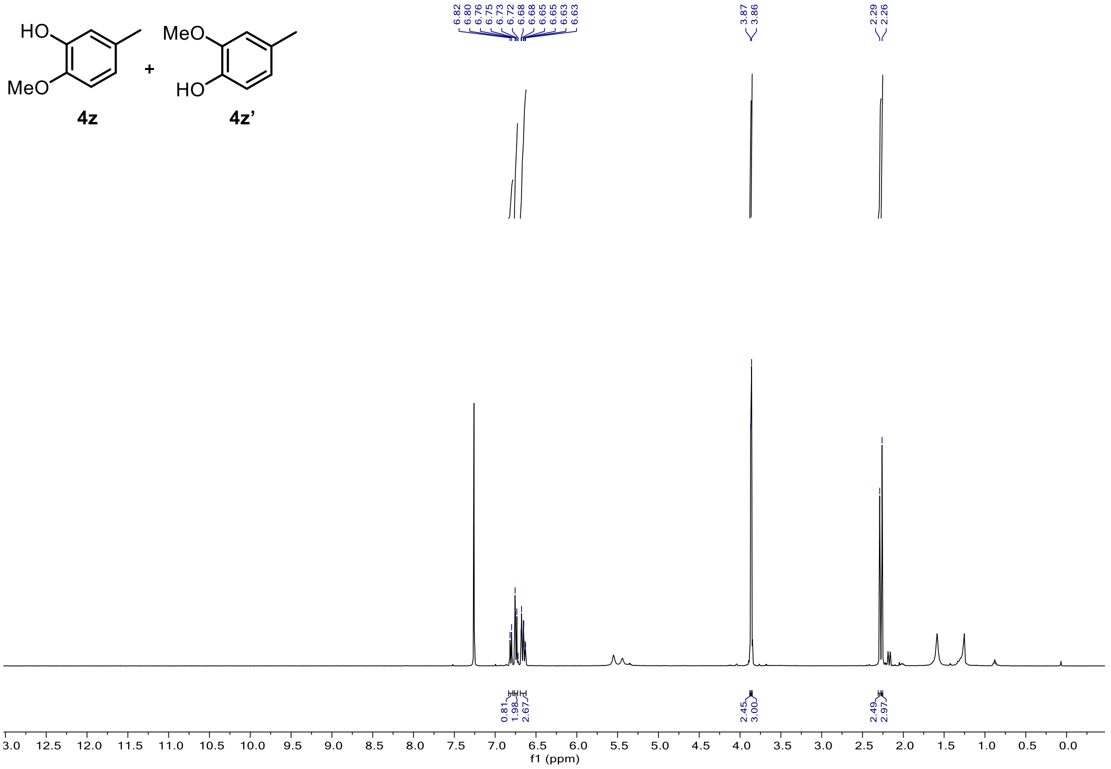
6.90
6.89
6.89
6.88
6.87
6.86
6.80
6.79
6.79
6.79
6.78
6.77
6.76
6.75
6.75
6.74
6.74
6.74
6.73
6.72
6.72
6.72
6.72
6.68
6.67
6.67
6.66
6.66
6.66
6.65
6.65
6.63
6.63
6.63
6.63
6.62
6.62
6.61
4.00
3.91
0.44
2.42
1.45
1.03
3.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

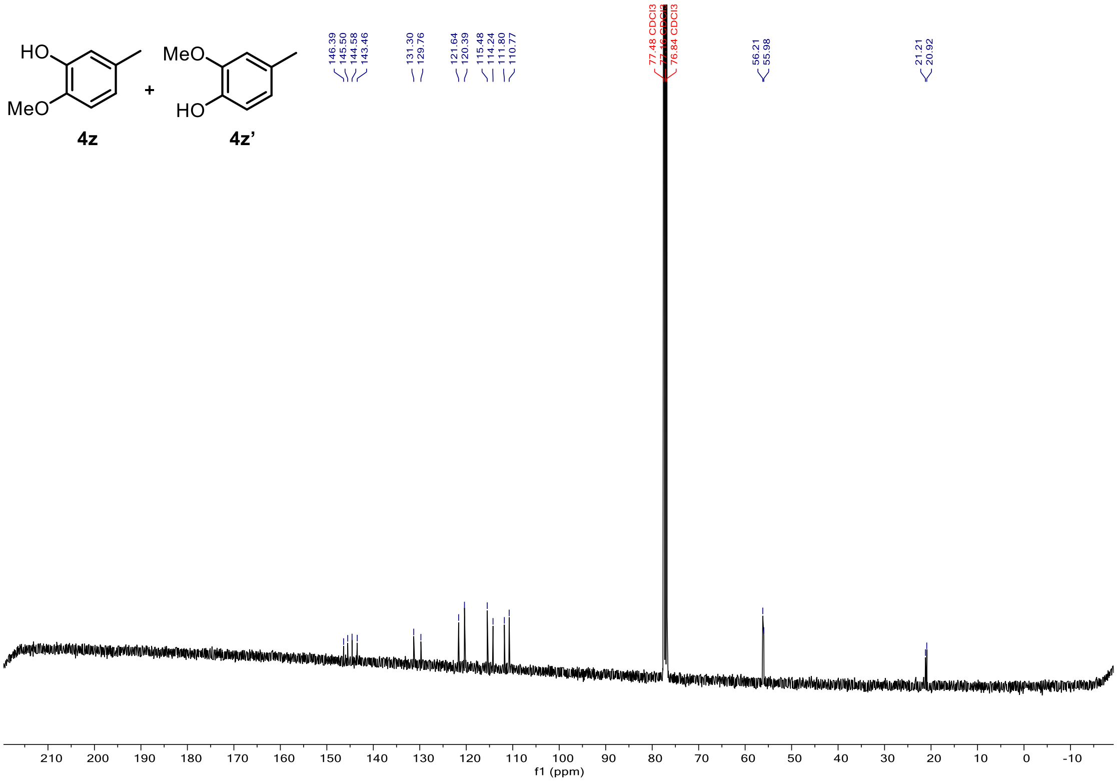


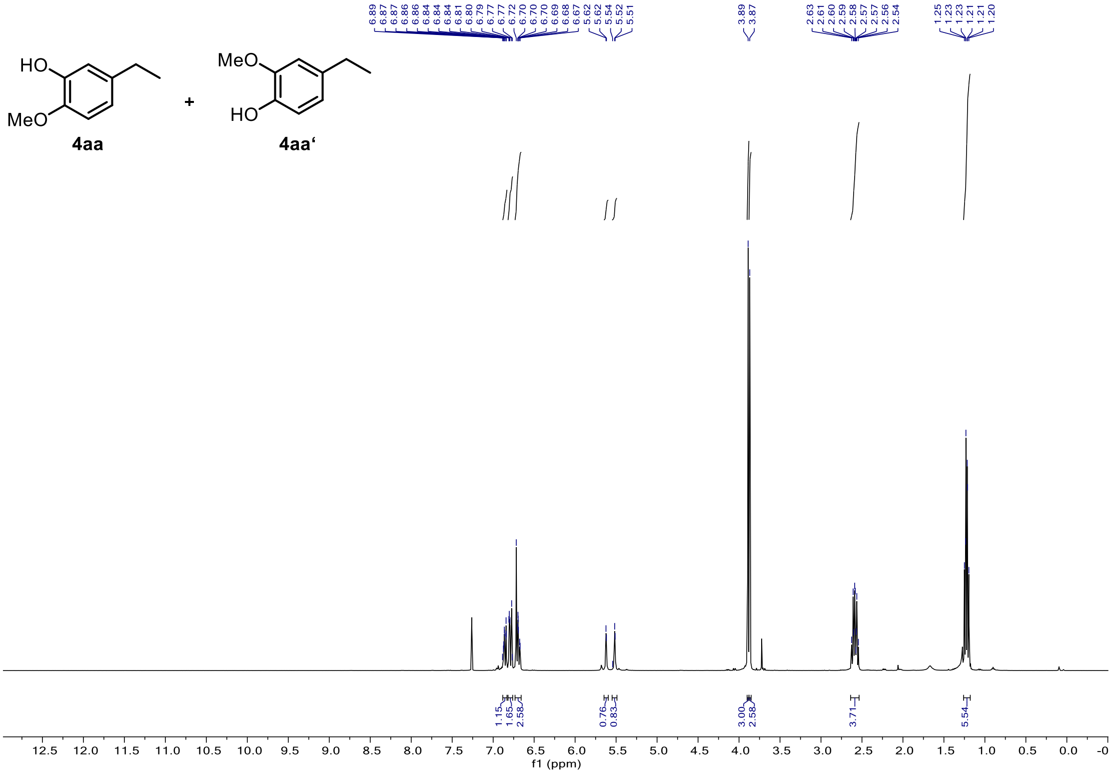
4y

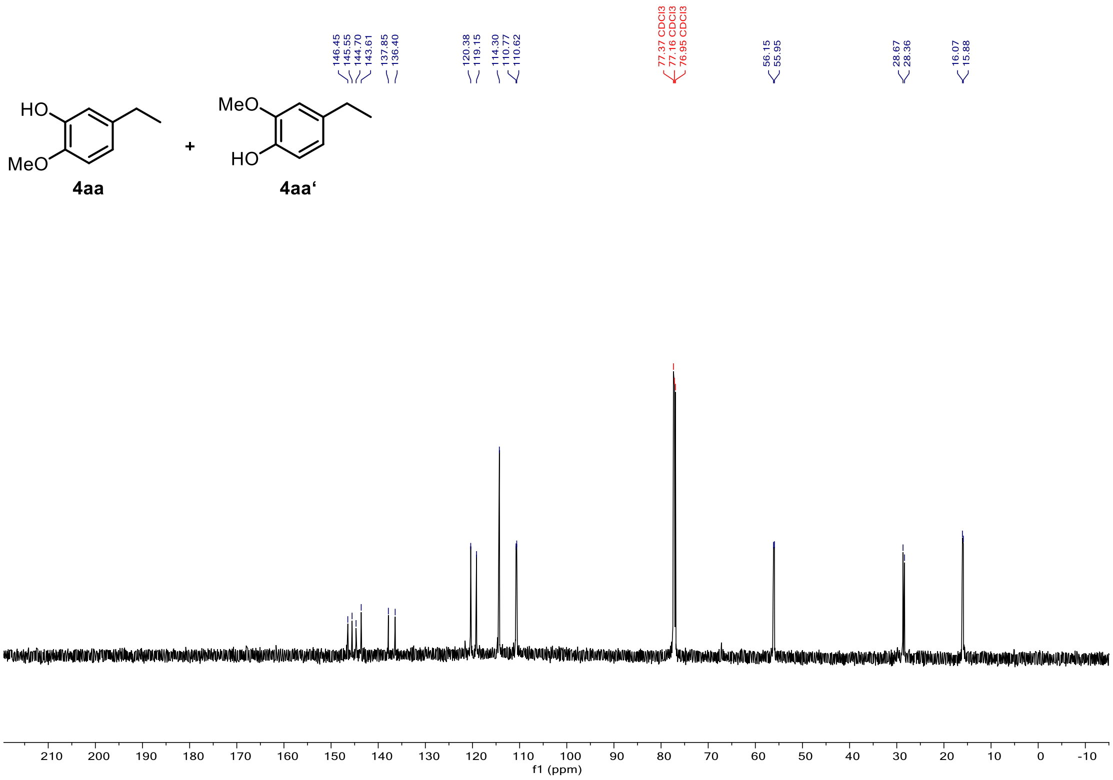
+

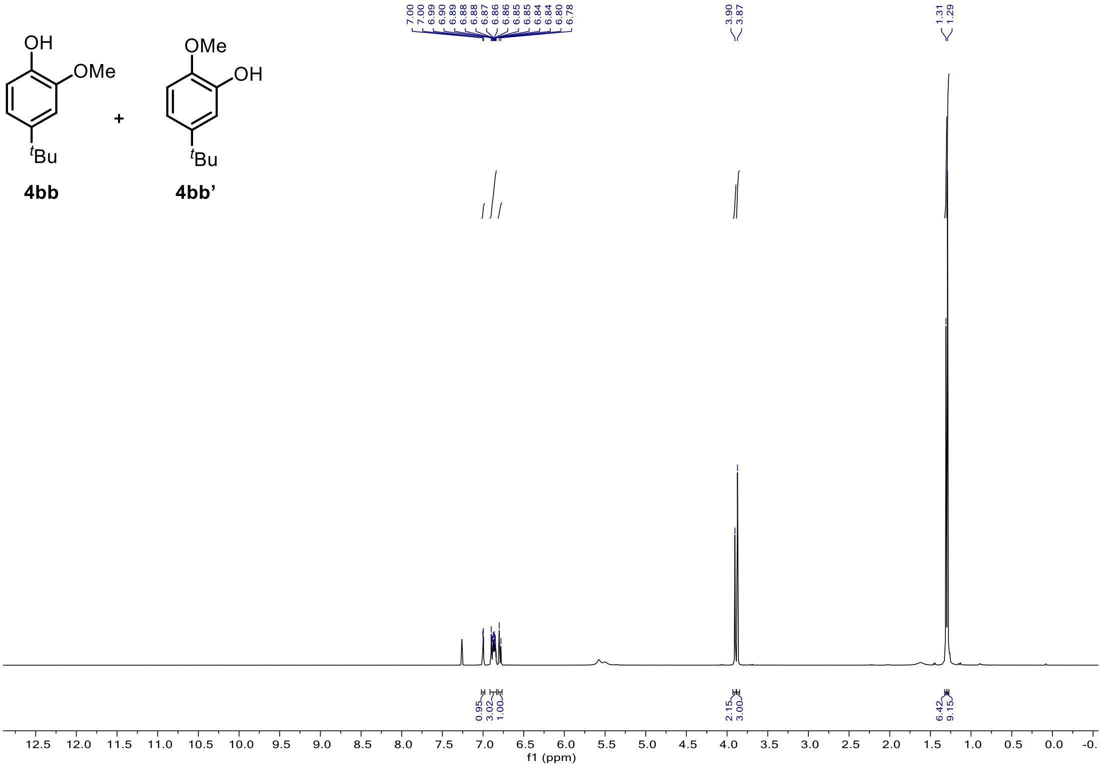
4y'
6.98
6.98
6.97
6.97
6.97
6.84
6.83
6.82
6.81
6.81
6.81
6.80
6.80
3.96
3.93
0.98
0.49
1.98
0.45
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

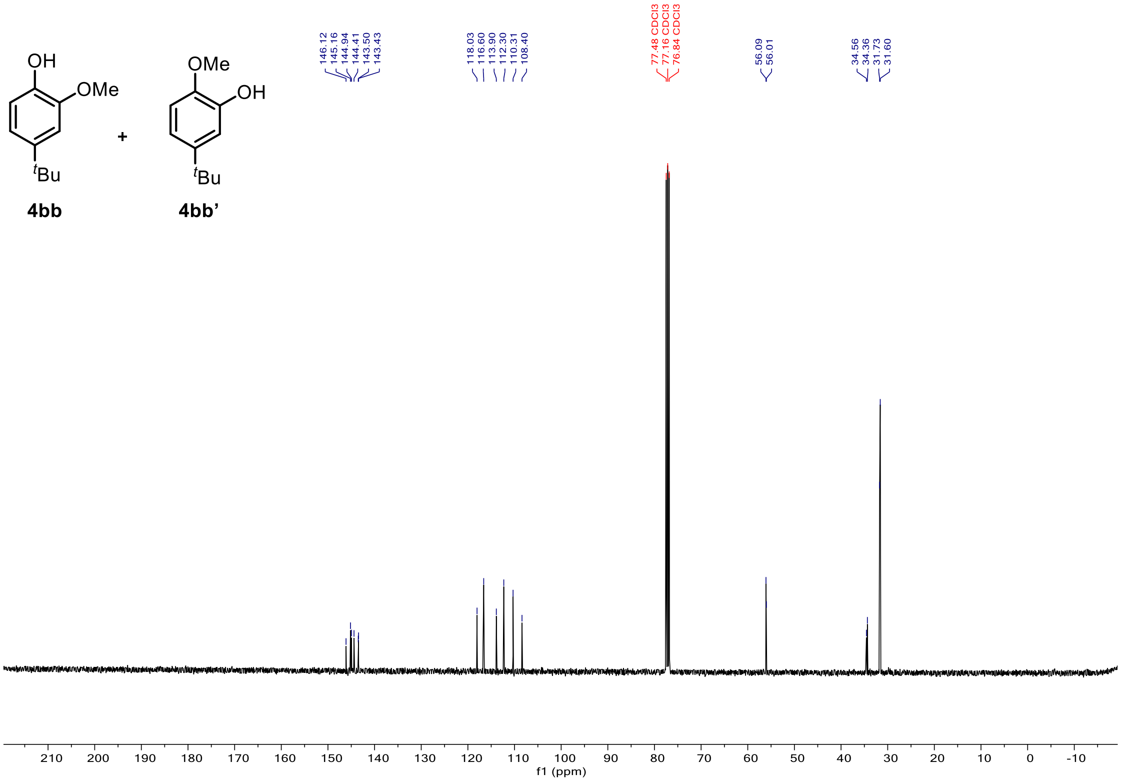

HO
MeO
4z
+
MeO
HO
4z'
6.82
6.80
6.76
6.75
6.73
6.72
6.68
6.68
6.65
6.65
6.63
6.63
3.87
3.86
2.29
2.26
0.81
1.98
2.67
2.45
3.00
2.49
2.97
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

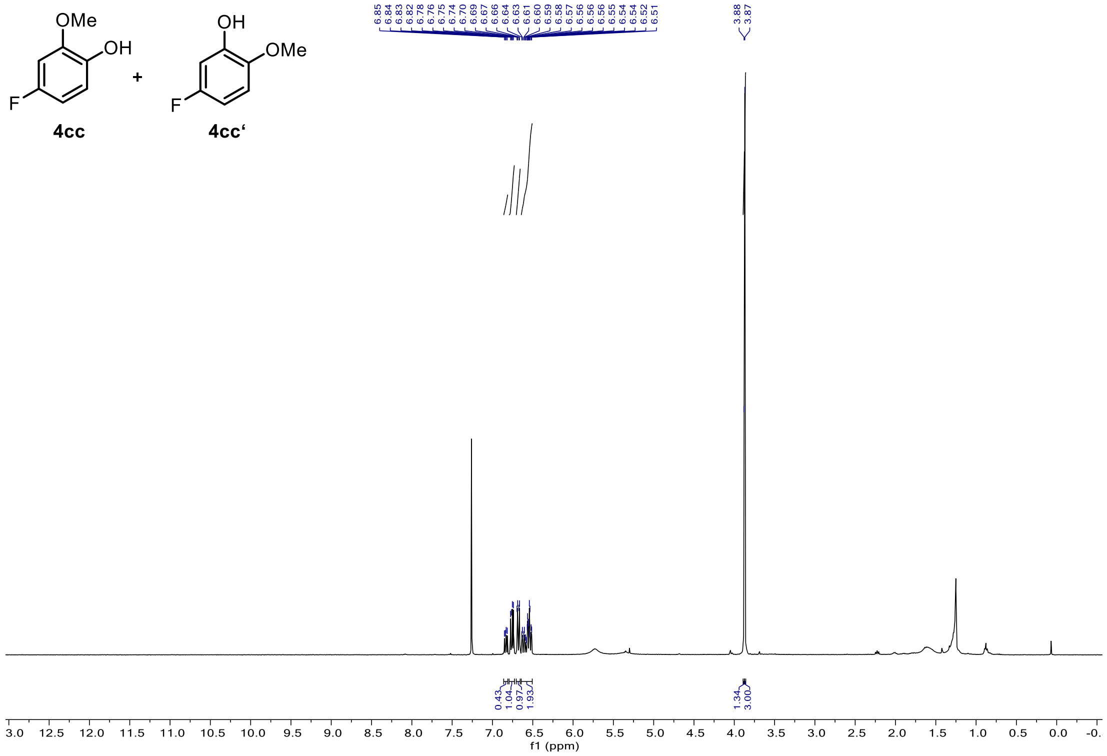

HO
MeO
4z
+
MeO
HO
4z'
146.39
145.50
144.58
143.46
131.30
129.76
121.64
120.39
115.48
114.24
111.80
110.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.21
55.98
21.21
20.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

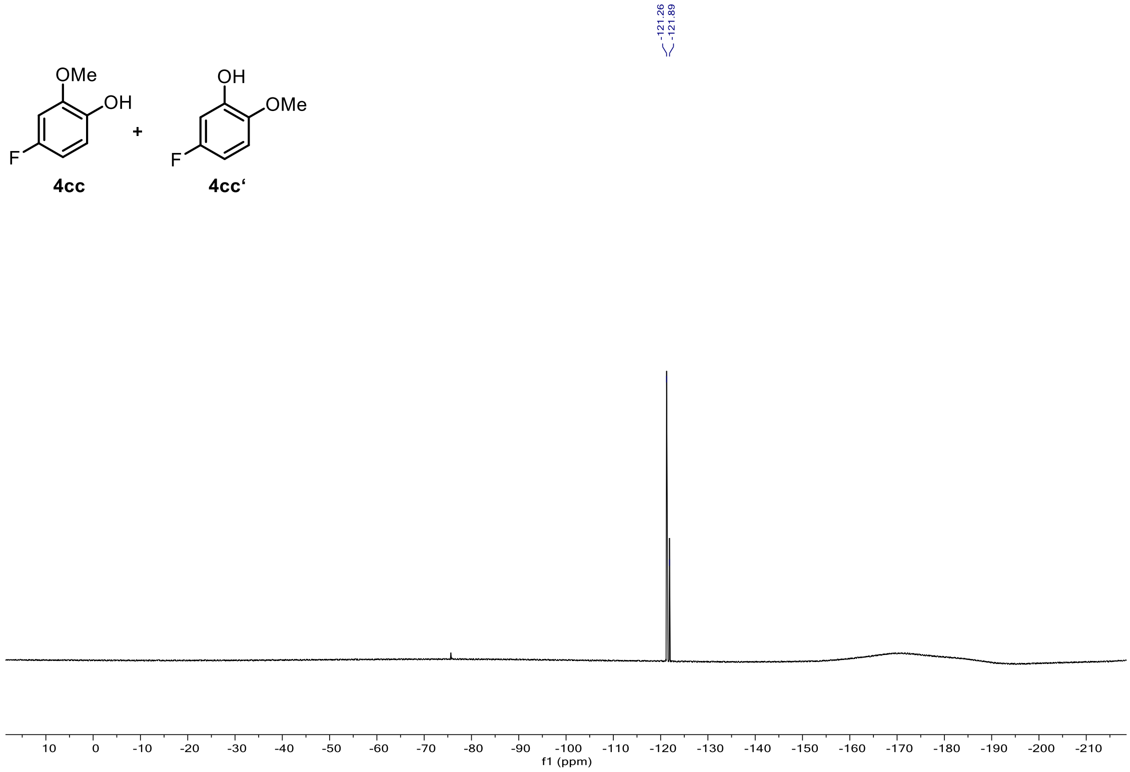

6.89 6.87 6.87 6.86 6.86 6.84 6.84 6.81 6.80 6.79 6.77 6.77 6.72 6.70 6.70 6.70 6.69 6.68 6.67 5.62 5.62 5.54 5.52 5.51
3.89 3.87
2.63 2.61 2.60 2.59 2.58 2.57 2.57 2.56 2.54
1.25 1.23 1.23 1.21 1.21 1.20
HO
MeO
4aa
+
MeO
HO
4aa'
1.15
1.65
2.58
0.76
0.83
3.00
2.58
3.71
5.54
12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

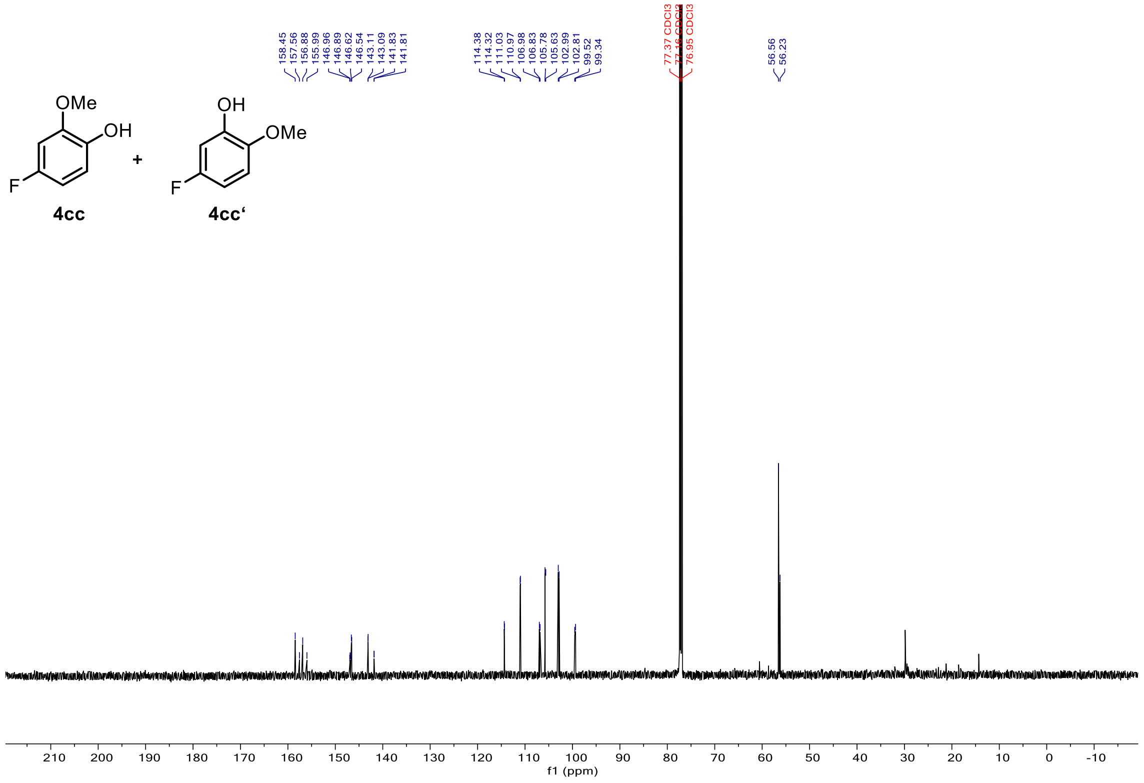

146.45 145.55 144.70 143.61 137.85 136.40
120.38 119.15 114.30 110.77 110.62
77.37 CDCl3 77.16 CDCl3 76.95 CDCl3
56.15 55.95
28.67 28.36
16.07 15.88
HO
MeO
4aa
+
MeO
HO
4aa'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

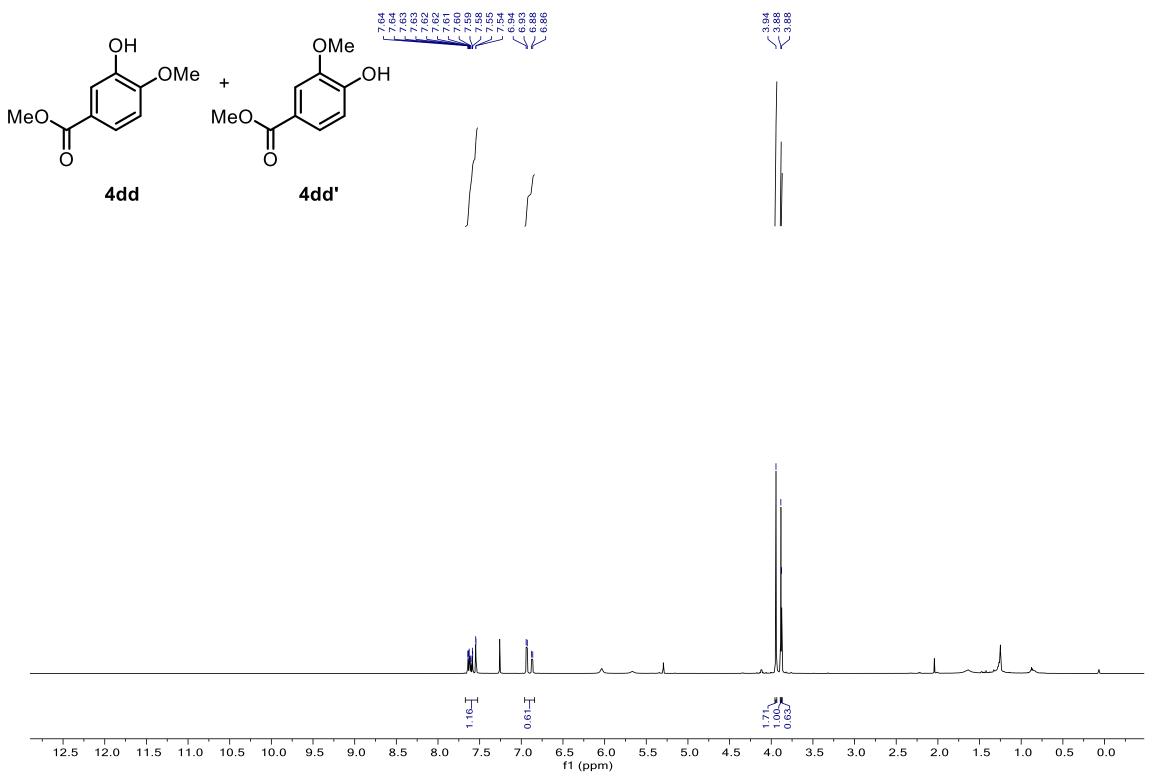

OH
OMe
tBu
+
OMe
OH
tBu
4bb
4bb'
7.00
7.00
6.99
6.90
6.89
6.88
6.88
6.87
6.86
6.86
6.85
6.85
6.84
6.84
6.80
6.78
3.90
3.87
1.31
1.29
0.95
3.02
1.00
2.15
3.00
6.42
9.15
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


OH
OMe
tBu
+
OMe
OH
tBu
4bb
4bb'
146.12
145.16
144.94
144.41
143.50
143.43
118.03
116.60
113.90
112.30
110.31
108.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.09
56.01
34.56
34.36
31.73
31.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

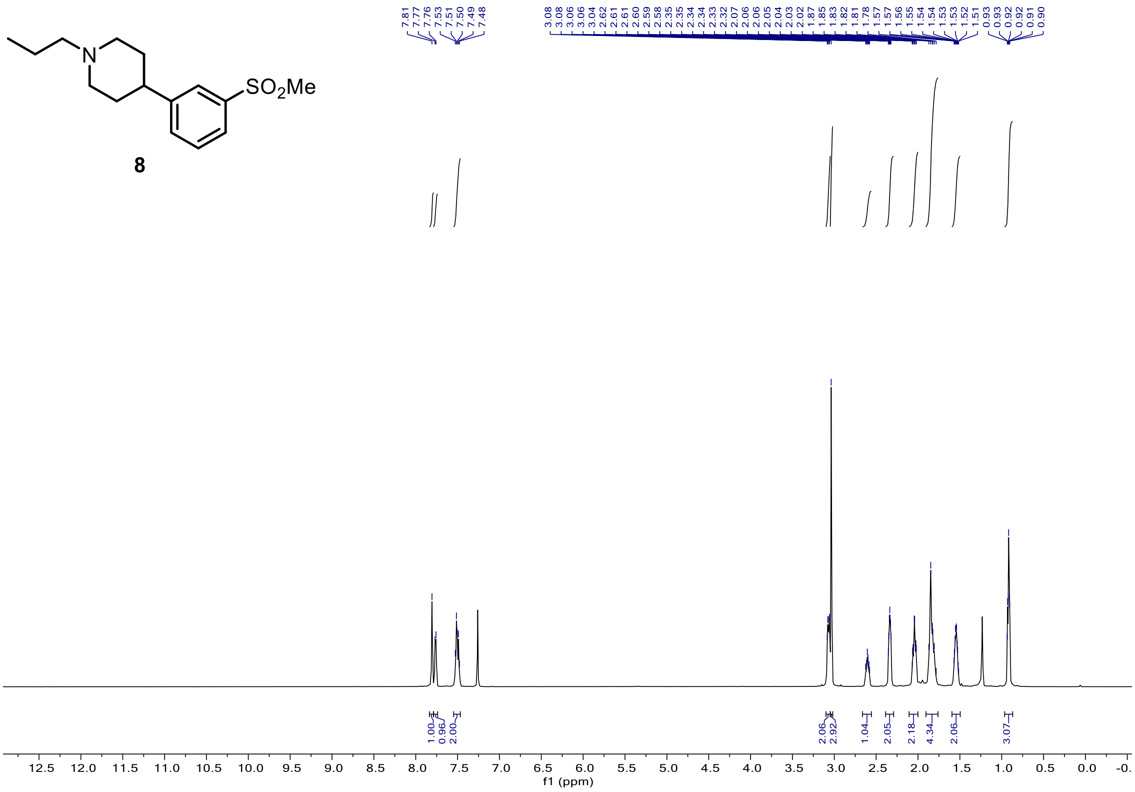

OMe
OH
F
4cc
+
OH
OMe
F
4cc'
6.85
6.84
6.83
6.82
6.78
6.76
6.75
6.74
6.70
6.69
6.67
6.66
6.64
6.63
6.61
6.60
6.59
6.58
6.57
6.56
6.56
6.56
6.55
6.54
6.54
6.52
6.51
3.88
3.87
0.43
1.04
0.97
1.93
1.34
3.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


-121.26
-121.89
OMe
OH
F
4cc
+
OH
OMe
F
4cc'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

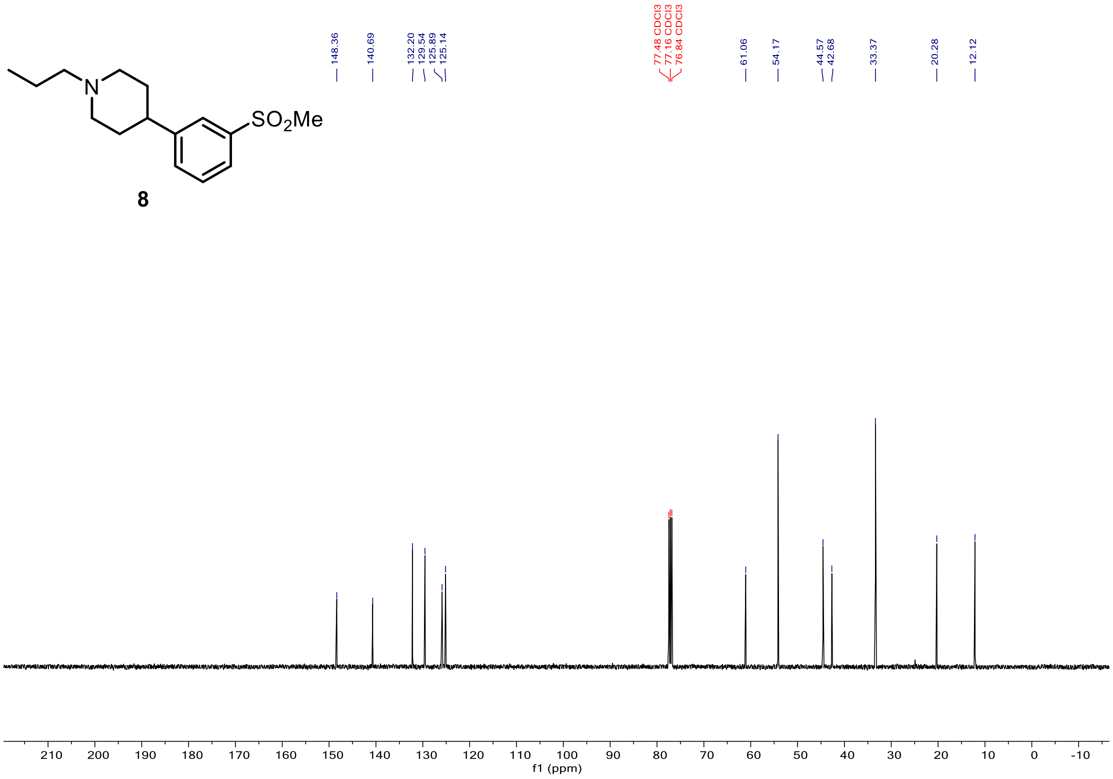

158.45
157.56
156.88
155.99
146.96
146.89
146.62
146.54
143.11
143.09
141.83
141.81
114.38
114.32
111.03
110.97
106.98
106.83
105.78
105.63
102.99
102.81
99.52
99.34
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
56.56
56.23
OMe
OH
F
4cc
+
OH
OMe
F
4cc'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


4dd + 4dd'

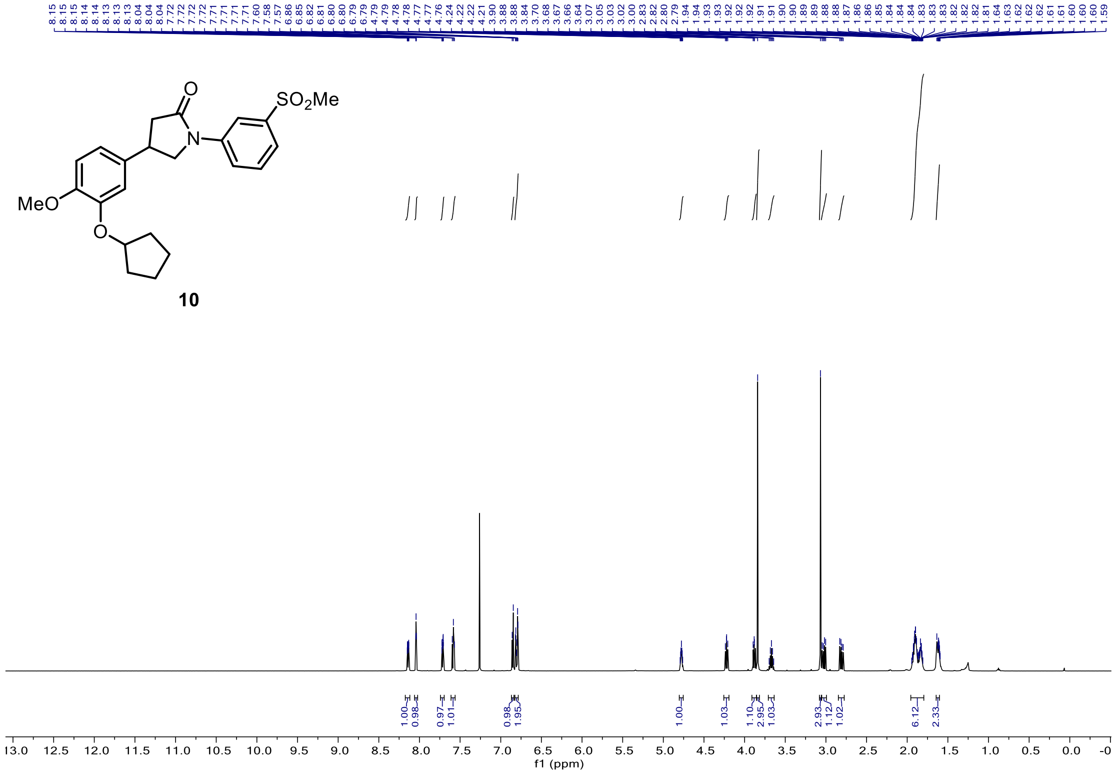
OH
OMe
MeO
O
+
OMe
OH
MeO
O
7.64
7.64
7.63
7.63
7.62
7.61
7.60
7.59
7.58
7.55
7.54
6.94
6.93
6.88
6.86
3.94
3.88
3.88
1.16
0.61
1.71
1.00
0.63
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

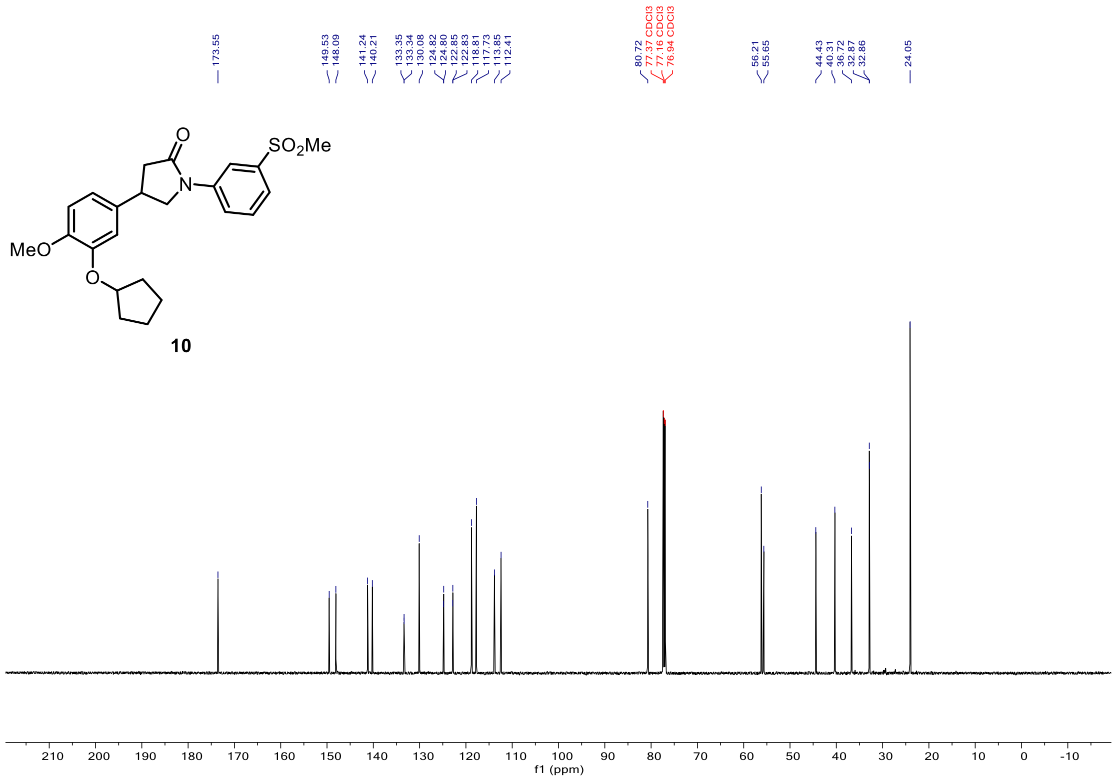

SO2Me
N
7.81
7.77
7.76
7.53
7.51
7.50
7.49
7.48
3.08
3.08
3.06
3.06
3.04
2.62
2.61
2.60
2.59
2.58
2.35
2.35
2.34
2.34
2.33
2.32
2.07
2.06
2.06
2.05
2.04
2.03
2.02
1.87
1.85
1.83
1.82
1.81
1.78
1.57
1.57
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.51
0.93
0.93
0.92
0.92
0.91
0.90
1.00
0.96
2.00
2.06
2.92
1.04
2.05
2.18
4.34
2.06
3.07
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

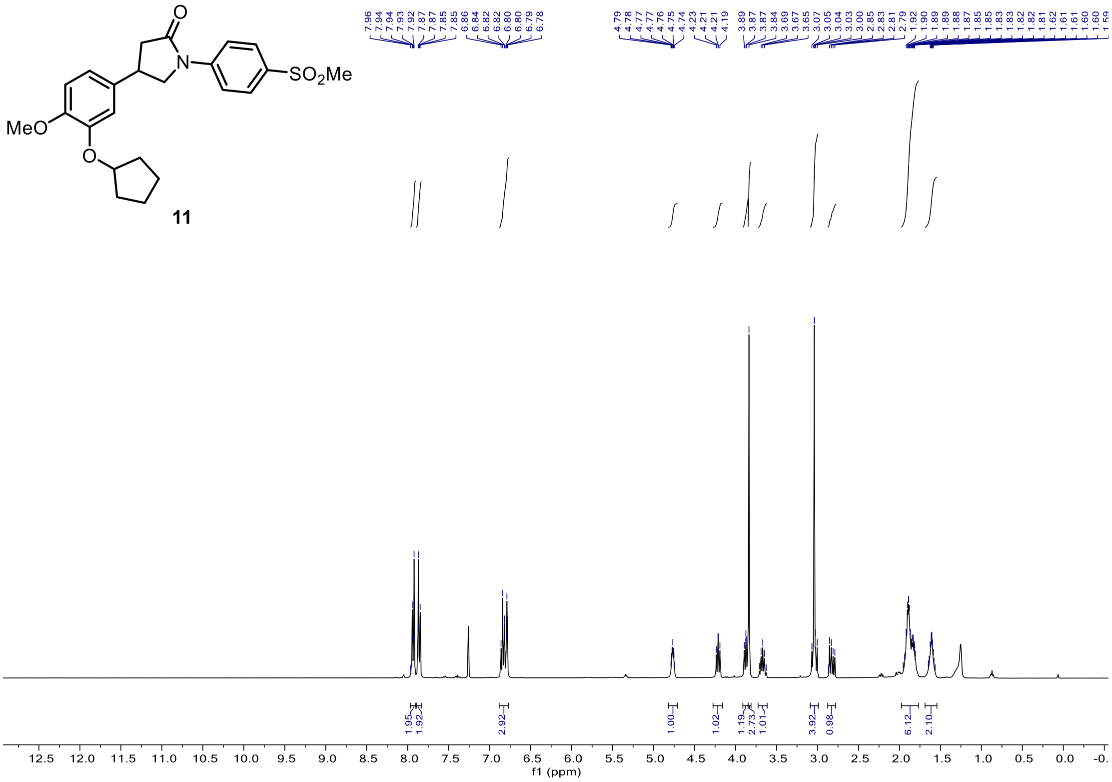
8

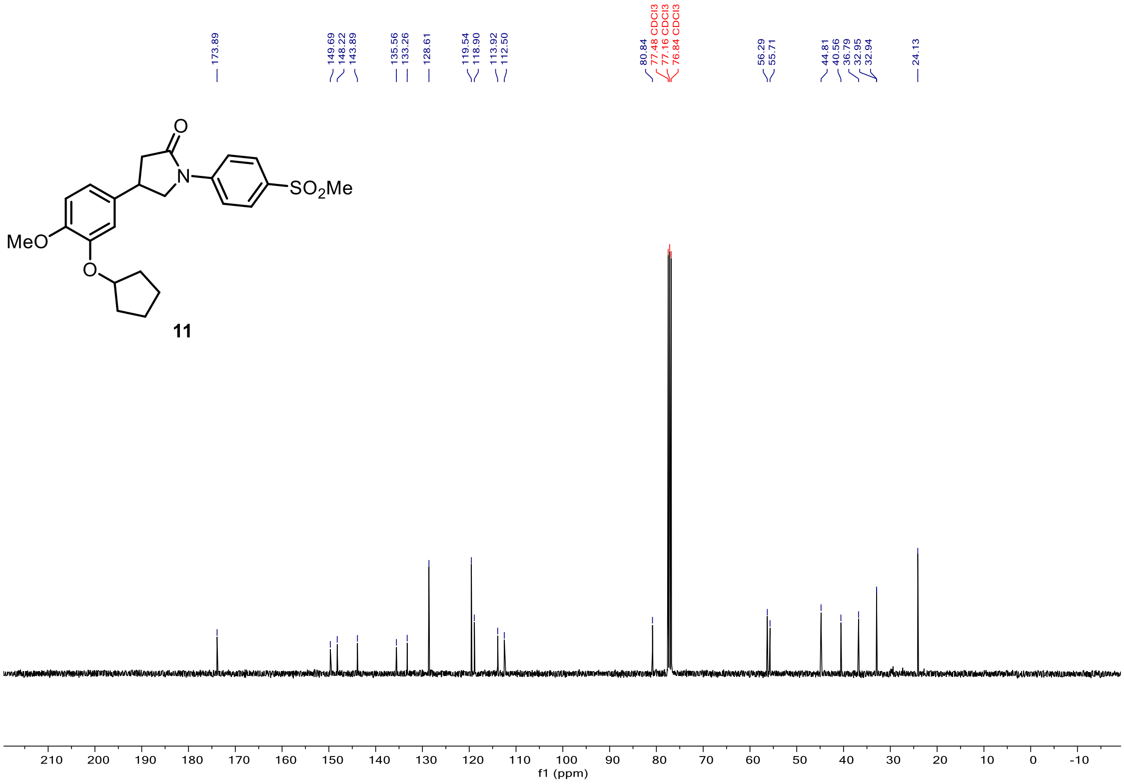

SO2Me
N
148.36
140.69
132.20
129.54
125.89
125.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.06
54.17
44.57
42.68
33.37
20.28
12.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

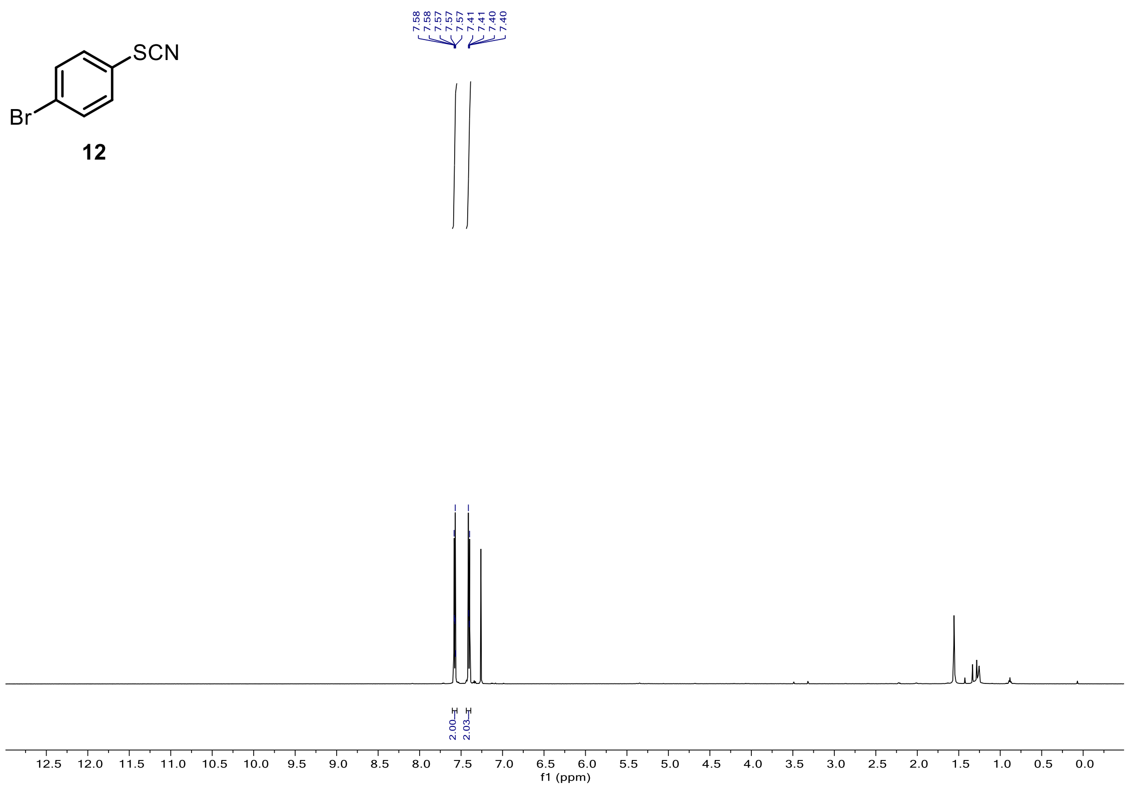
8

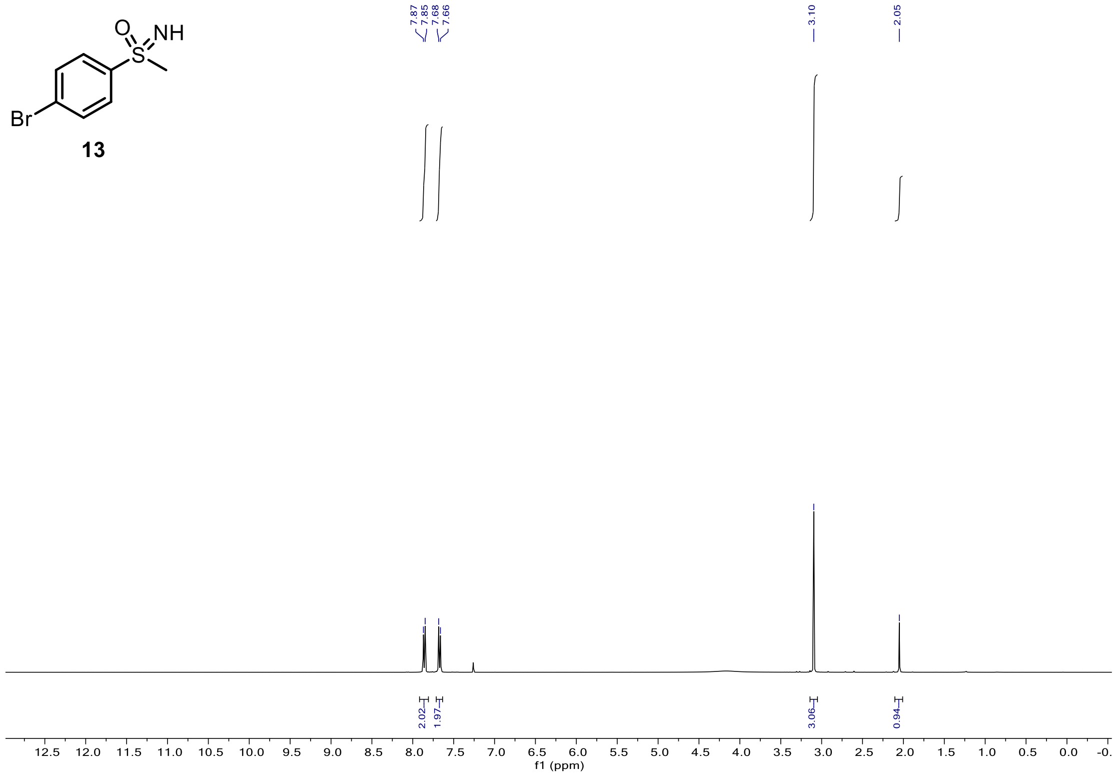

8.15
8.15
8.15
8.14
8.13
8.13
8.13
8.04
8.04
8.04
7.72
7.72
7.72
7.71
7.71
7.71
7.60
7.58
7.57
6.86
6.85
6.82
6.81
6.80
6.80
6.79
6.79
4.79
4.79
4.78
4.78
4.77
4.77
4.76
4.24
4.22
4.22
4.21
3.90
3.88
3.88
3.84
3.70
3.68
3.67
3.66
3.64
3.07
3.05
3.03
3.02
3.00
2.83
2.82
2.80
2.79
1.94
1.94
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.88
1.87
1.86
1.86
1.85
1.84
1.84
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
O
SO2Me
N
MeO
O
10
1.00
0.98
0.97
1.01
0.98
1.95
1.00
1.03
1.10
2.95
1.03
2.93
1.12
1.02
6.12
2.33
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 -0
f1 (ppm)

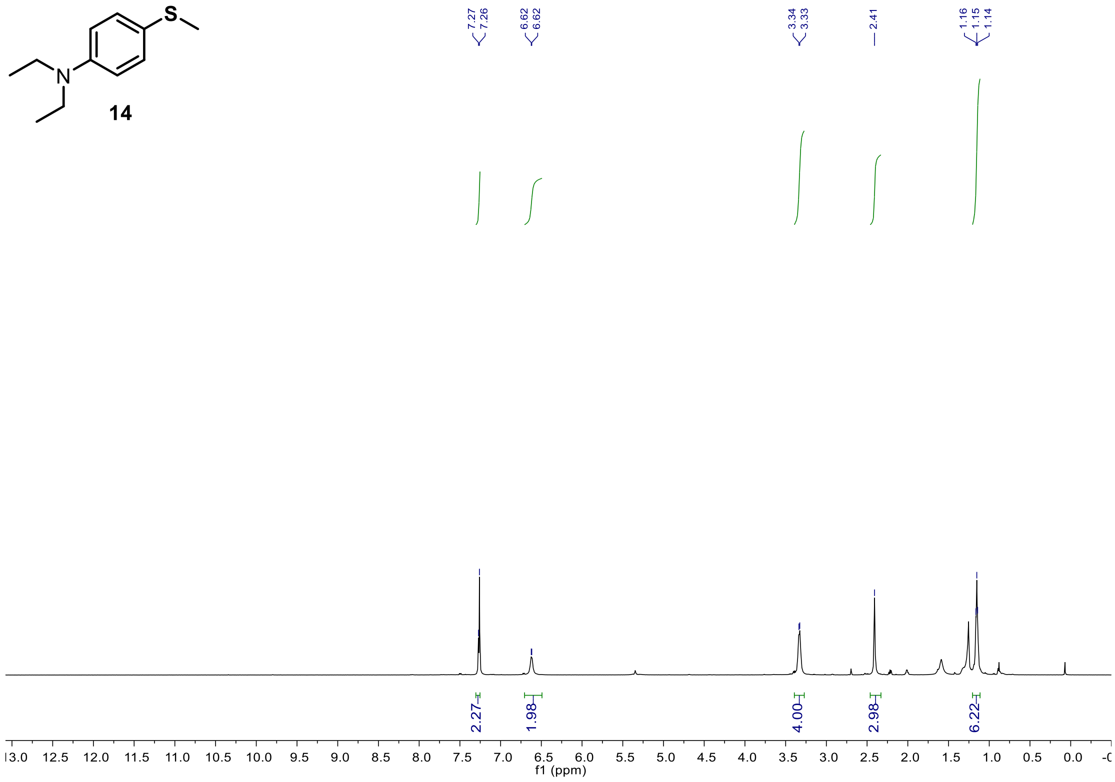

173.55
149.53
148.09
141.24
140.21
133.35
133.34
130.08
124.82
124.80
122.85
122.83
118.81
117.73
113.85
112.41
80.72
77.37 CDCl3
77.16 CDCl3
76.94 CDCl3
56.21
55.65
44.43
40.31
36.72
32.87
32.86
24.05
O
SO2Me
N
MeO
O
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
O
N
SO$_2$Me
11
7.96 7.94 7.94 7.93 7.92 7.87 7.87 7.85 7.85 6.86 6.84 6.82 6.82 6.80 6.80 6.79 6.78
4.79 4.78 4.77 4.76 4.75 4.74 4.23 4.21 4.21 4.19 3.89 3.87 3.87 3.84 3.69 3.67 3.65 3.07 3.05 3.04 3.03 3.00 2.85 2.83 2.81 2.79 1.92 1.90 1.89 1.89 1.88 1.87 1.85 1.83 1.83 1.82 1.82 1.81 1.62 1.61 1.61 1.60 1.59
1.95
1.92
2.92
1.00
1.02
1.19
2.73
1.01
3.92
0.98
6.12
2.10
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.
f1 (ppm)

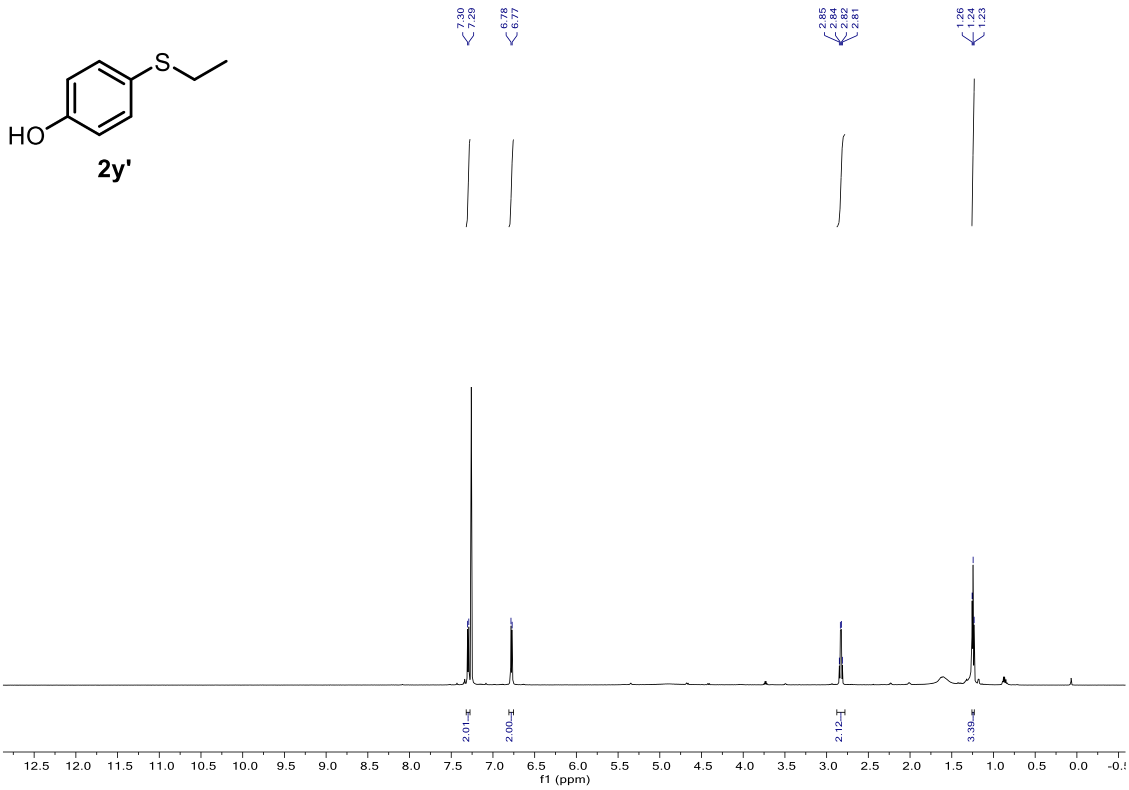

173.89
149.69 148.22 143.89
135.56 133.26
128.61
119.54 118.90
113.92 112.50
80.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.29 55.71
44.81 40.56 36.79 32.95 32.94
24.13
MeO
O
N
SO$_2$Me
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

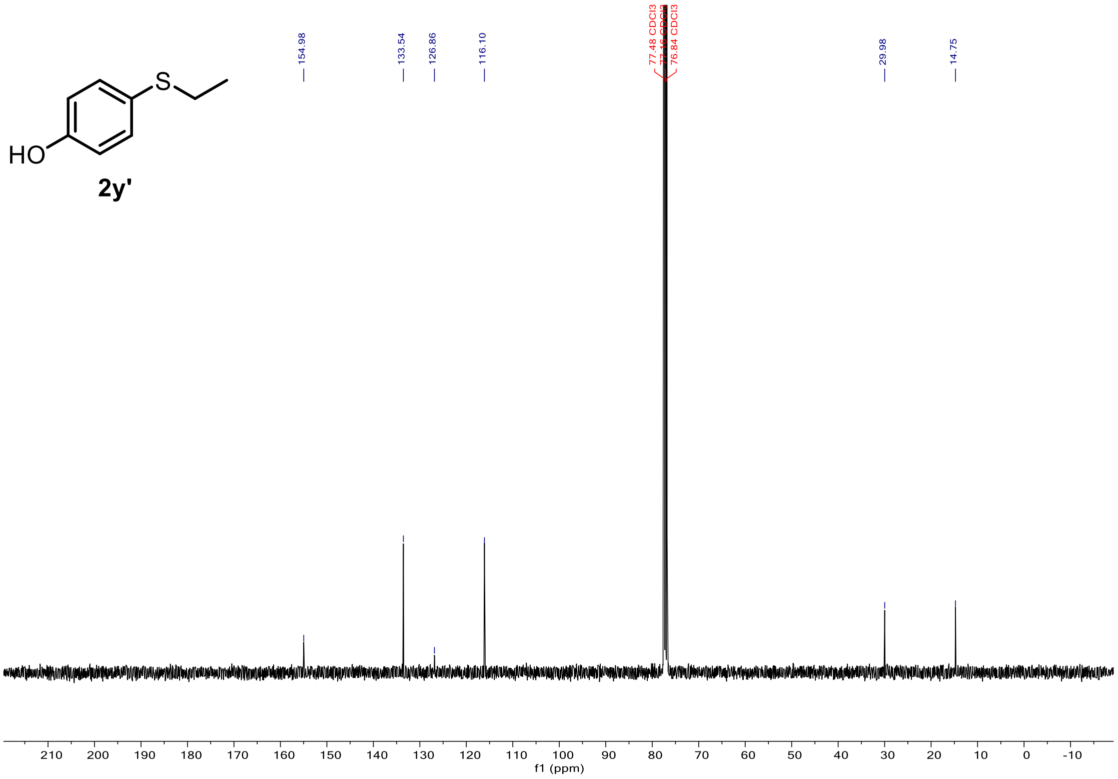

12
SCN
Br
7.58
7.58
7.57
7.57
7.57
7.41
7.41
7.40
7.40
2.00
2.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

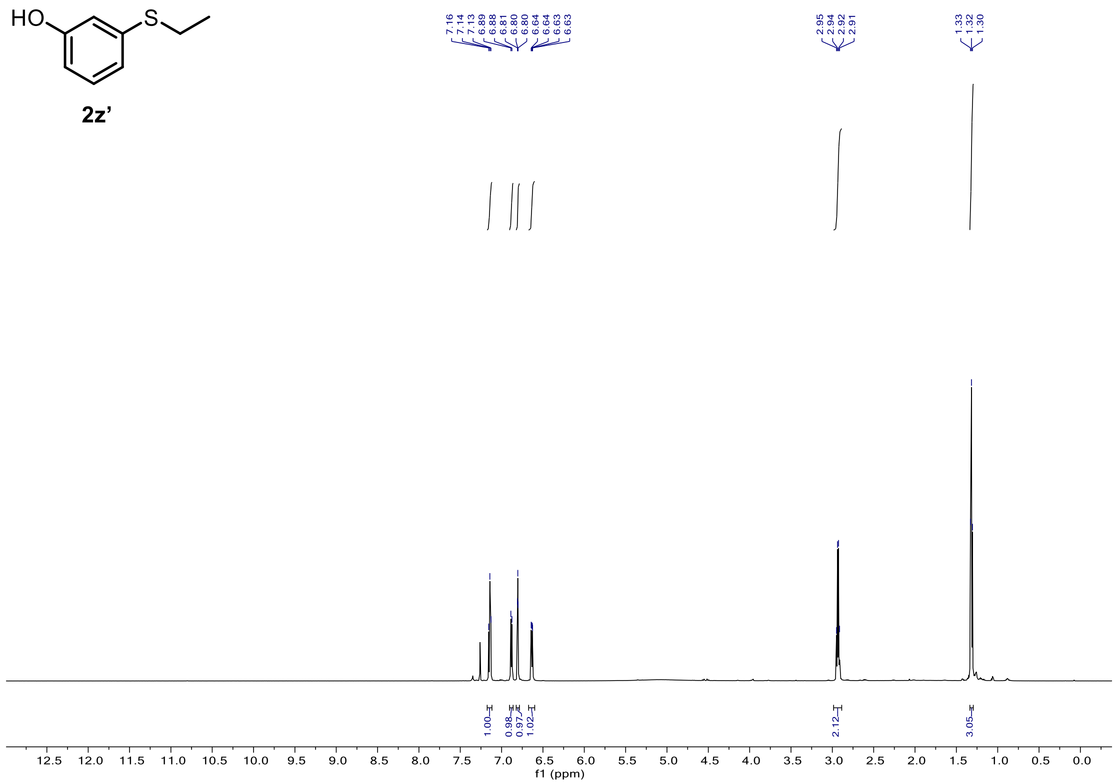

13
O
NH
S
Br
7.87
7.85
7.68
7.66
3.10
2.05
2.02
1.97
3.06
0.94
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


14

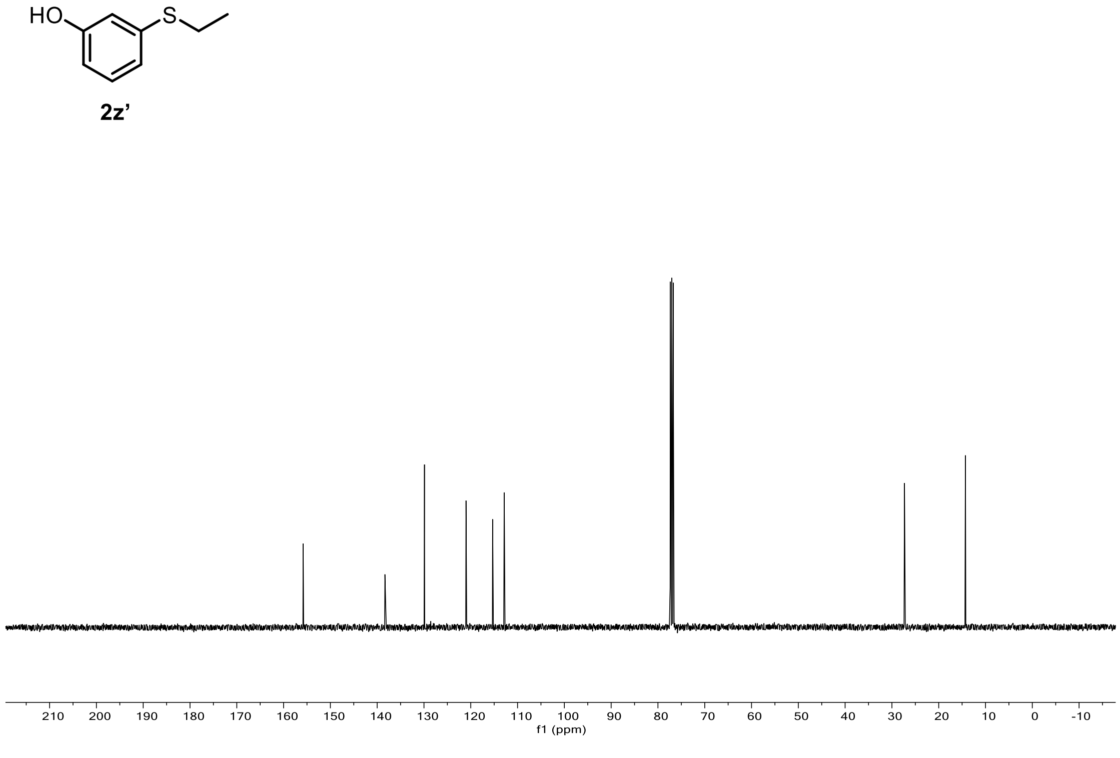
7.27
7.26
6.62
6.62
3.34
3.33
2.41
1.16
1.15
1.14
2.27
1.98
4.00
2.98
6.22
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S
N


2y'
HO
S
7.30
7.29
6.78
6.77
2.85
2.84
2.82
2.81
1.26
1.24
1.23
2.01
2.00
2.12
3.39
12.5 12.0 11.5 11.0 10.5 10.0 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 -0.5
f1 (ppm)

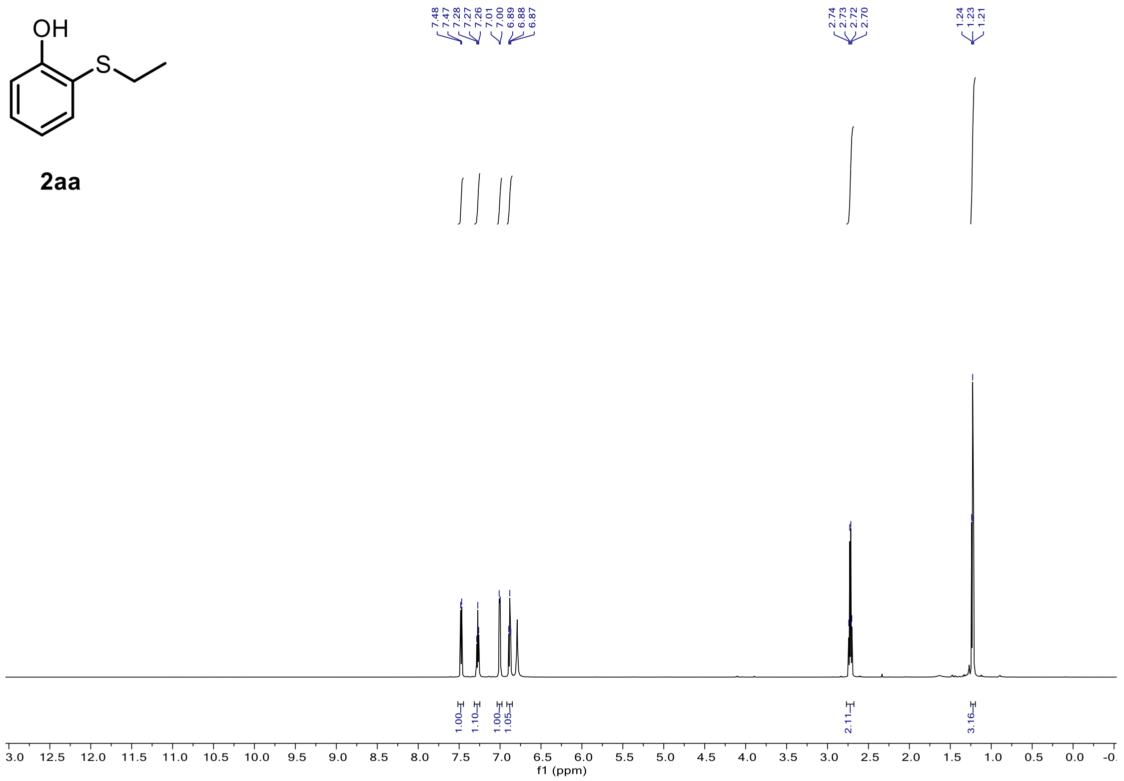

2y'
HO
S
154.98
133.54
126.86
116.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
29.98
14.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2z’

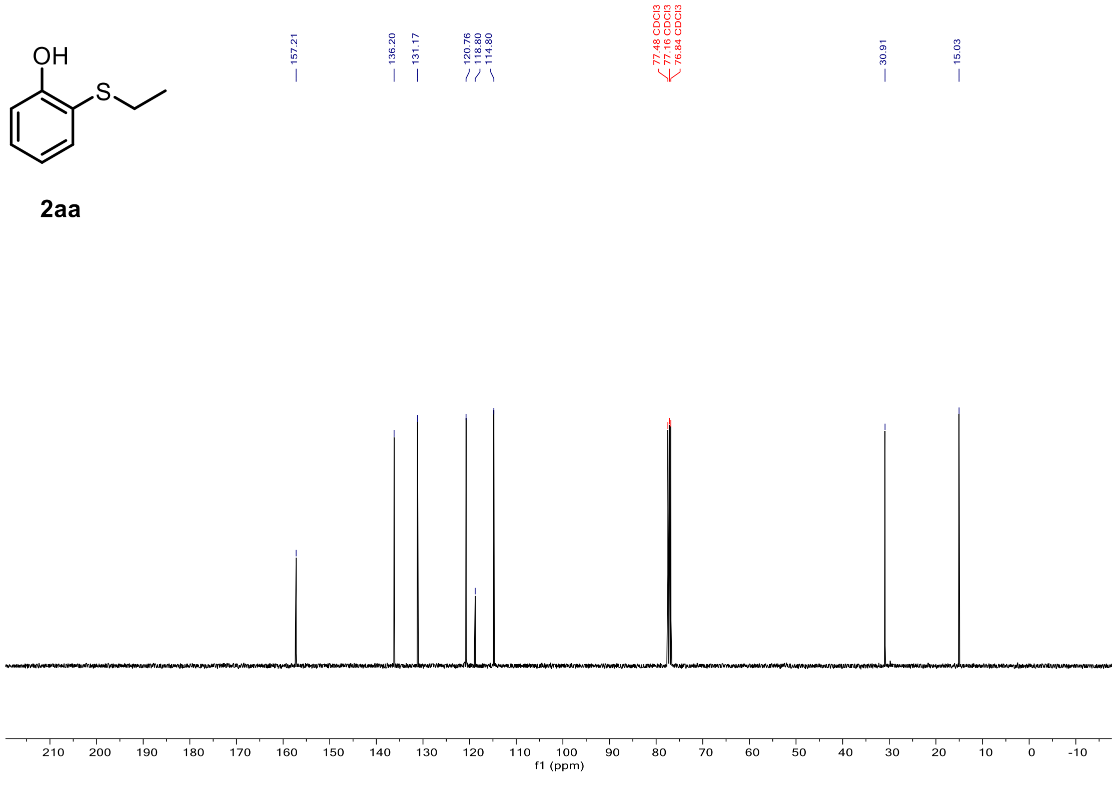
HO
S
7.16
7.14
7.13
6.89
6.88
6.81
6.80
6.80
6.64
6.64
6.63
6.63
2.95
2.94
2.92
2.91
1.33
1.32
1.30
1.00
0.98
0.97
1.02
2.12
3.05
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2z’

HO
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
S
7.48
7.47
7.28
7.27
7.26
7.01
7.00
6.89
6.88
6.87
2.74
2.73
2.72
2.70
1.24
1.23
1.21
1.00
1.10
1.00
1.05
2.11
3.16
3.0
12.5
12.0
11.5
11.0
10.5
10.0
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
-0.
f1 (ppm)

2aa


OH
S
157.21
136.20
131.17
120.76
118.80
114.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
30.91
15.03
210
200
190
180
170
160
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30
20
10
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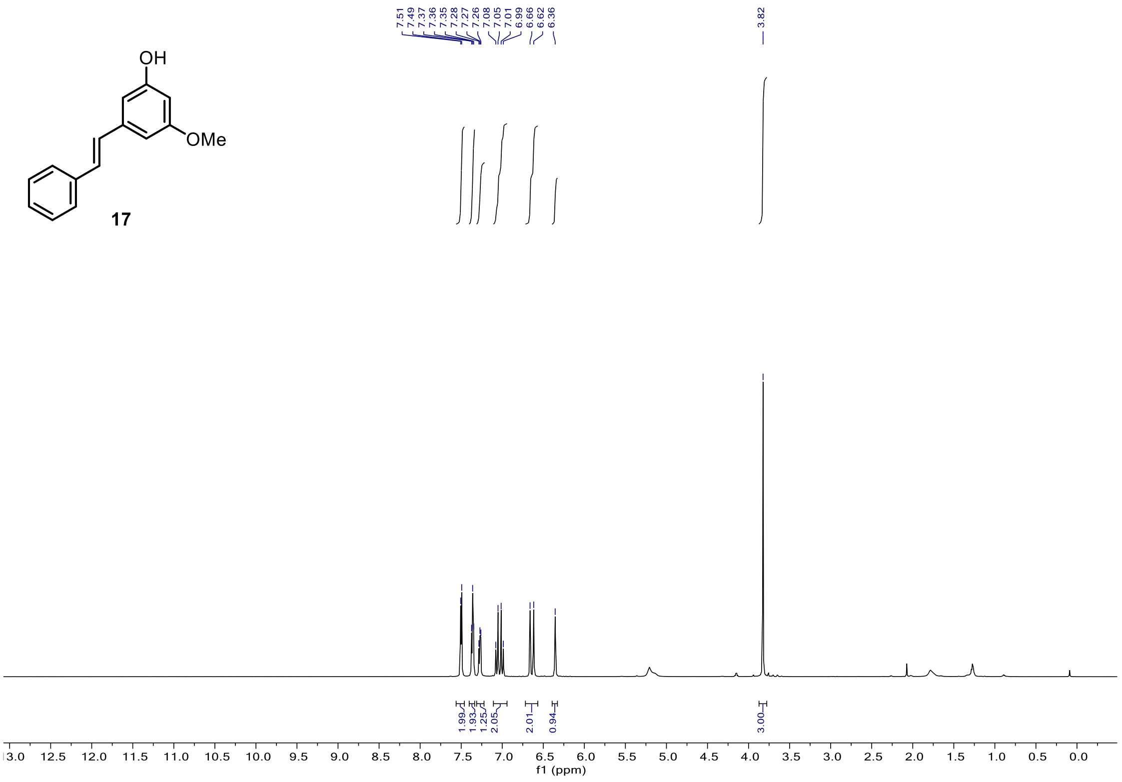
-10
f1 (ppm)

2aa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6.99
6.66
6.62
6.36
3.82
1.99
1.93
1.25
2.05
2.01
0.94
3.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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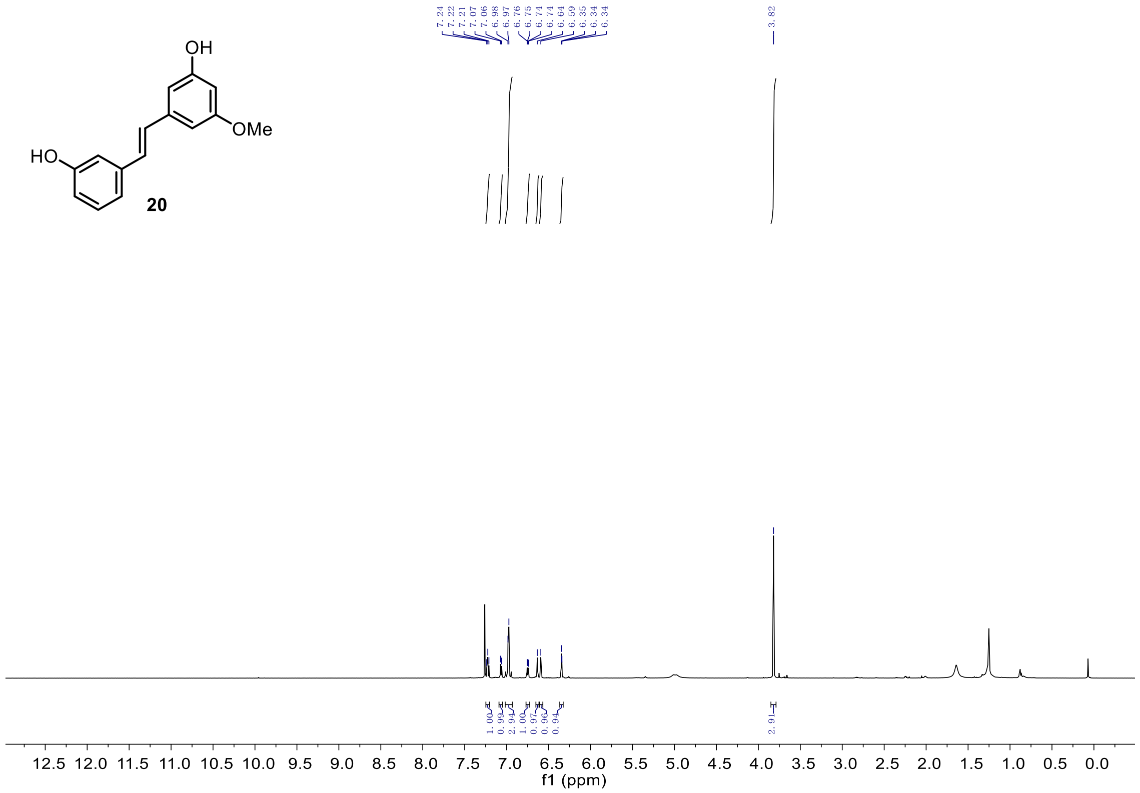
f1 (ppm)

17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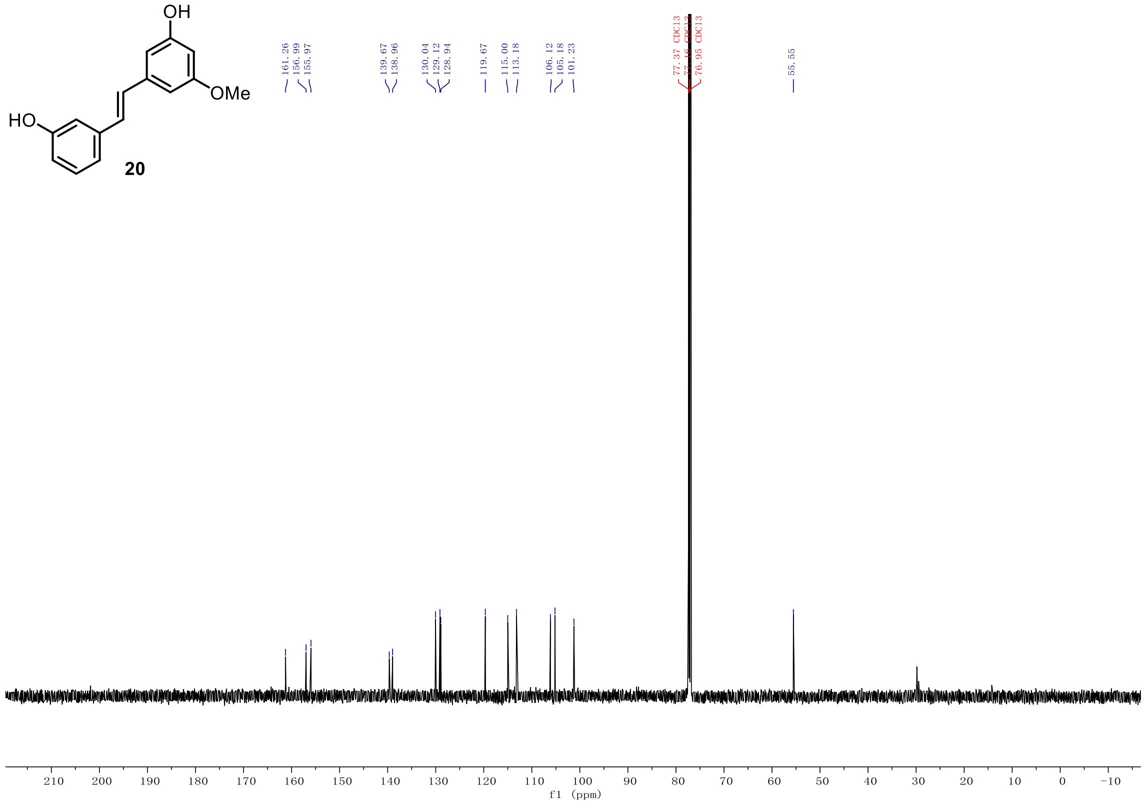
6.74
6.64
6.59
6.35
6.34
6.34
3.82
1.00
0.99
2.94
1.00
0.97
0.96
0.94
2.91
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.00
113.18
106.12
105.18
101.23
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.55
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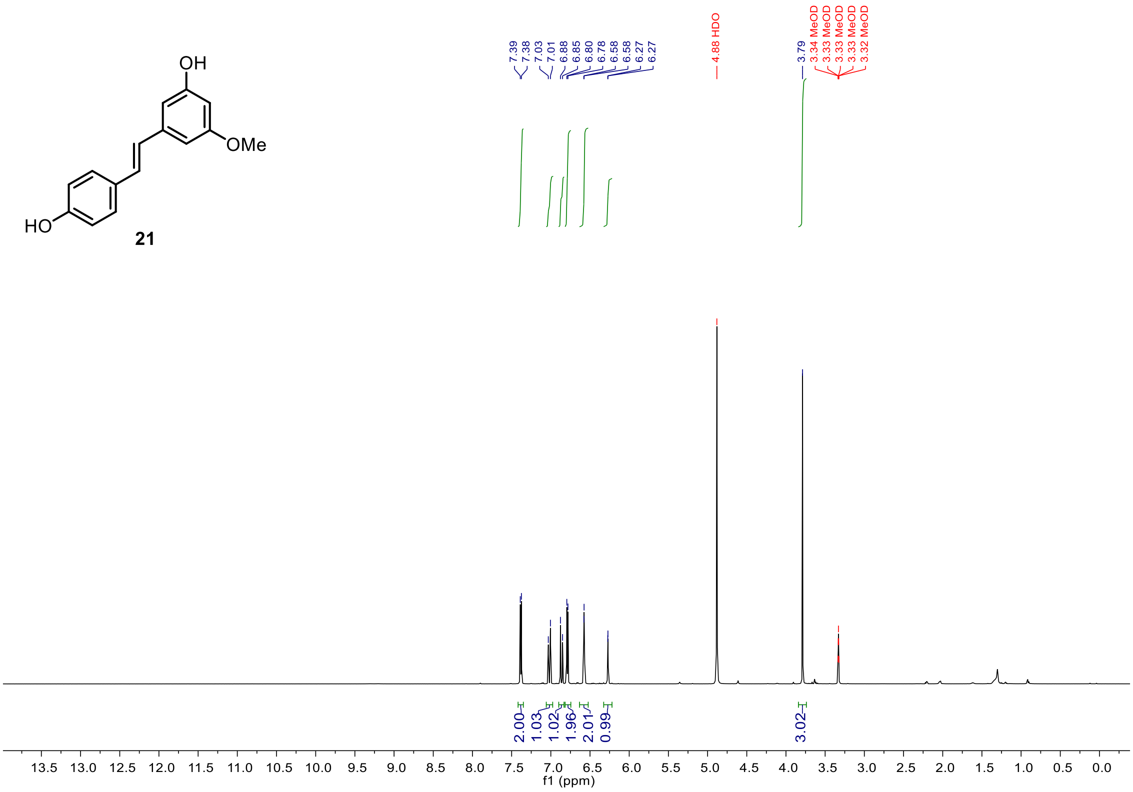
f1 (ppm)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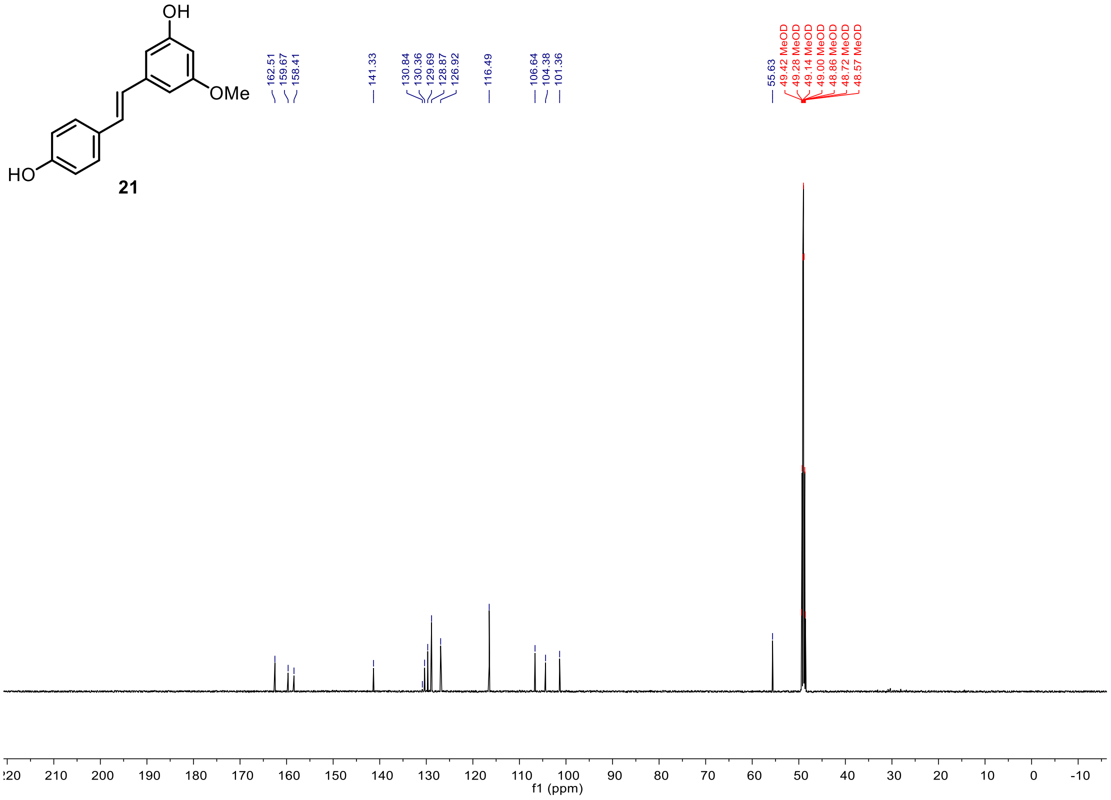
6.27
6.27
4.88 HDO
3.79
3.34 MeOD
3.33 MeOD
3.33 MeOD
3.33 MeOD
3.32 MeOD
2.00
1.03
1.02
1.96
2.01
0.99
3.02
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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104.38
101.36
55.63
49.42 MeOD
49.28 MeOD
49.14 MeOD
49.00 MeOD
48.86 MeOD
48.72 MeOD
48.57 MeOD
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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