Supporting Information

Monitoring Electrophilic Intermediates in Reactions of Thiols in Aqueous Solution Directly With ^{19}F NMR

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Table of Contents

Experimental Section

Measurement of pKa values for **1** and **6**

The pKa values for both the thiol (**1**) and sulfenic acid (**6**) were obtained in both H_2O (Figure S1) and the 3:1 mixture of D_2O and THF in which the reactions were carried out (Figure S2). Measurements were made in accordance with a previously reported procedure.[1] Briefly, 3.0 mL solutions of **1** and **6** (1 mM) were prepared in each medium and the pH was measured with a standard aqueous electrode. 5 µL of a 20 mM aqueous solution of NaOH was added and the pH was measured again. This was repeated for 15 readings. pKa measurements were carried out in triplicate for each compound.

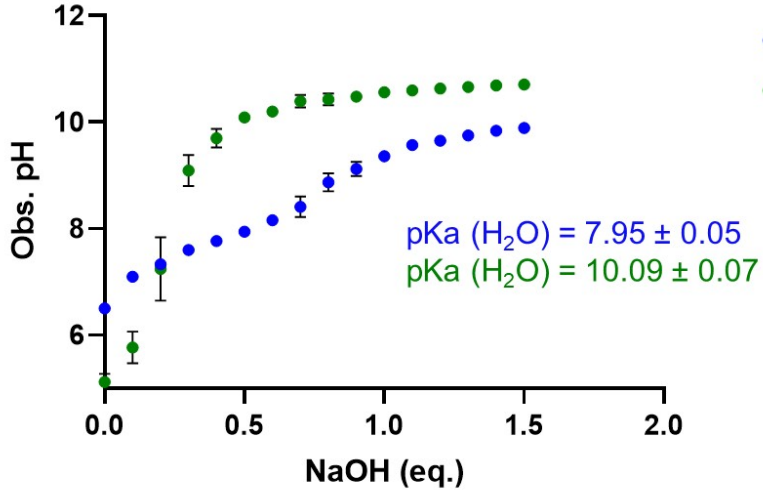


Figure S1. Titration of a 1 mM solution of **1** (•) and **6** (•) at 24°C in H_2O with 20 mM NaOH.

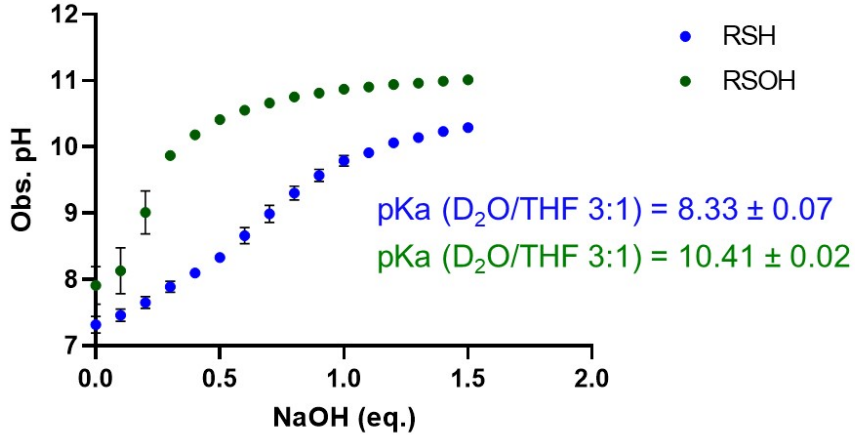


Figure S2. Titration of a 1 mM solution of **1** (•) and **6** (•) at 24°C in D_2O/THF (3:1) with 20 mM NaOH.

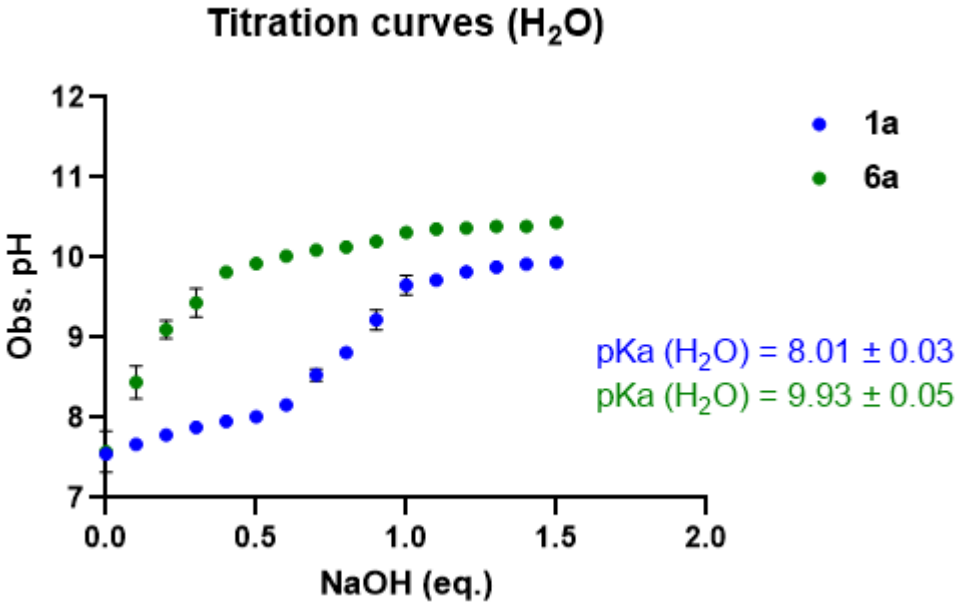


Figure S3. Titration of a 1 mM solution of isomerically pure **1a** (•) and **6a** (•) at 24°C in H_2O with 20 mM NaOH.

Observed rate constants for the reactions of **1a**, **6a**, **7a**, **1b**, **6b**, and **7b** with H_2O_2

The rate constants for the reactions of each of the thiolate, sulfenate and sulfinate with H_2O_2 that are given in Figure 2A of the manuscript (and the associated text on page 2), were derived from the average values of observed rate constants obtained from fitting the reaction progress data shown for both isomers in Figure 2C. The observed rate constants for the individual isomers obtained from these fits are given in Table S1.

Table S1. Observed rate constants for the reaction of each isomer of **1**, **6** and **7** with H_2O_2 in pD 7.8 D_2O/THF (3:1).

Compound	**1a**	**6a**	**7a**	**1b**	**6b**	**7b**
k_{obs} ($M^{-1}s^{-1}$)	9.40 ± 0.13 × 10^{-2}	1.43 ± 0.14 × 10^{-2}	1.27 ± 0.18 × 10^{-3}	9.15 ± 0.22 × 10^{-2}	1.34 ± 0.26 × 10^{-2}	1.43 ± 0.31 × 10^{-3}

Mass balance changes during the reaction of **1** with thermally generated $^1O_2$

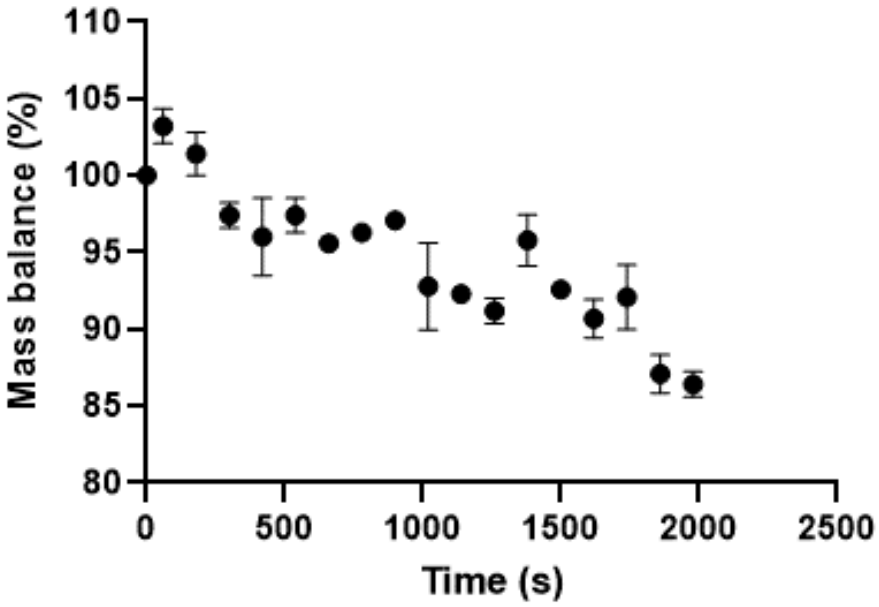


Figure S4. The mass balance of fluorinated triptycenes relative to the internal standard (trifluoroethanol) in the experiment in Figure 4A of the manuscript. The downward trend is observed likely due to formation of paramagnetic species in the reaction of thiols with $^1O_2$.

Photosensitized Oxidation of Thiol **9** in CD_3OD/H_2O (15:1)

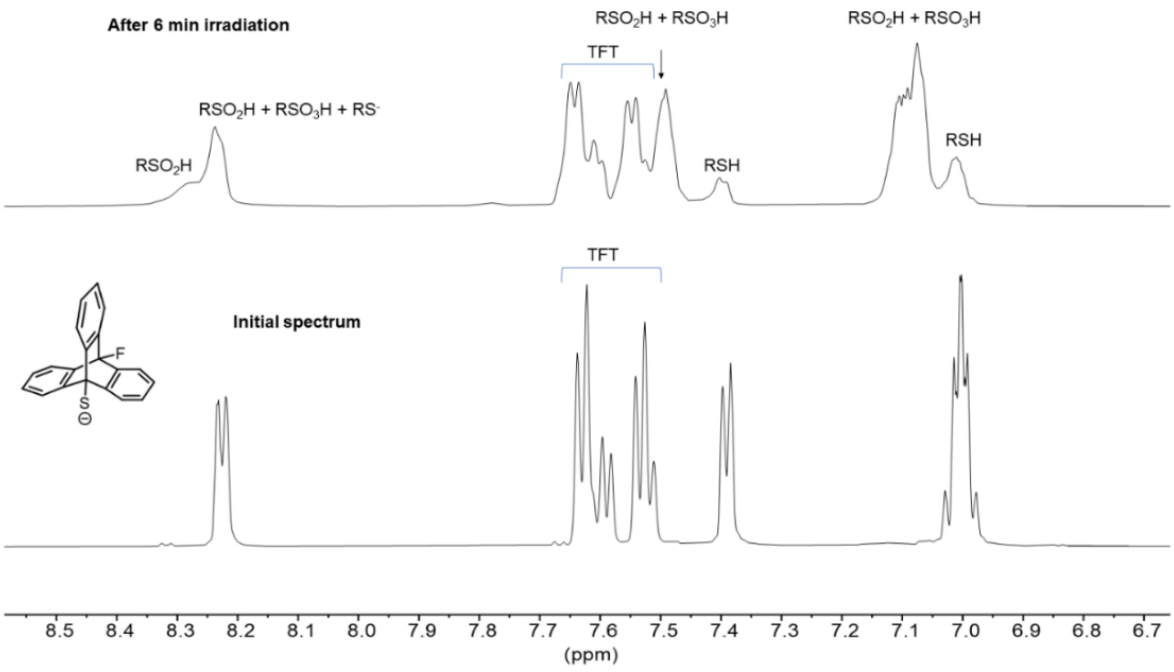


Figure S5. Representative ^1H NMR spectra of **9** (20 mM) in the presence of 200 μM of Rose Bengal in 12:1 CD_3OD/H_2O containing 60 mM NaOH (corresponding to the experiment in Figure 4B of the manuscript). Peaks corresponding to thiolate **9**, sulfinate **11** and sulfonate **12** are annotated.

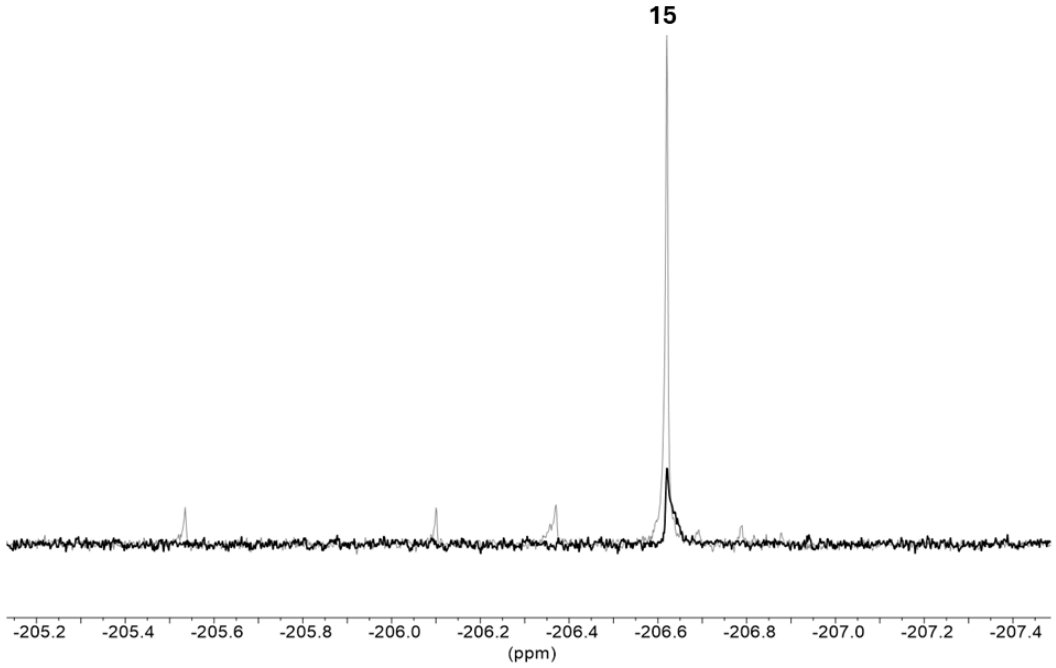
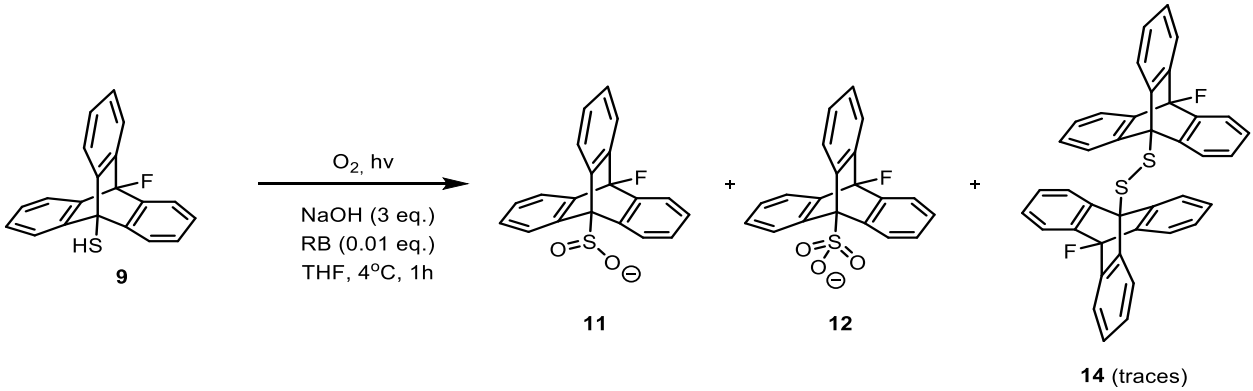


Figure S6. Representative ^{19}F NMR (C_6D_6, 283 MHz) spectrum of an authentic sample of **15** (in black) stacked over the crude ^{19}F NMR spectrum of the photo-oxygenation of **9** suspended in C_6D_6 (in gray). The reaction was continued until **9** was completely consumed. **11** and **12** were not detected as they are insoluble in C_6D_6.

Photosensitized Oxidation of Thiol **9** in THF



Thiol **9** (4.8 mg, 0.016 mmol) was dissolved in THF (10 mL). To this suspension was added 50 µL of a 1M solution of NaOH in water (3 eq.). Rose Bengal (*ca.* 0.01 eq.) was added, and the reaction mixture was cooled to 4°C. Trifluorotoluene (10 mM) was used as an internal standard for NMR quantification. Oxygen was bubbled continuously through the solution, after which the reaction vessel was irradiated with a 400W HPS lamp. After 1h, the reaction was concentrated *in vacuo*. Analysis of the mixture by ^{19}F

NMR in CD_3OD in the observation of sulfonate **11** as the major product (34%), with **15** being undetectable. Initial progress of the reaction is shown in Fig. S5. Attempts to isolate/characterize the unknown downfield of **12** were unsuccessful. The unknown was not observed when the reaction was performed in the absence of THF in CD_3OD (Fig. 3B of the manuscript).

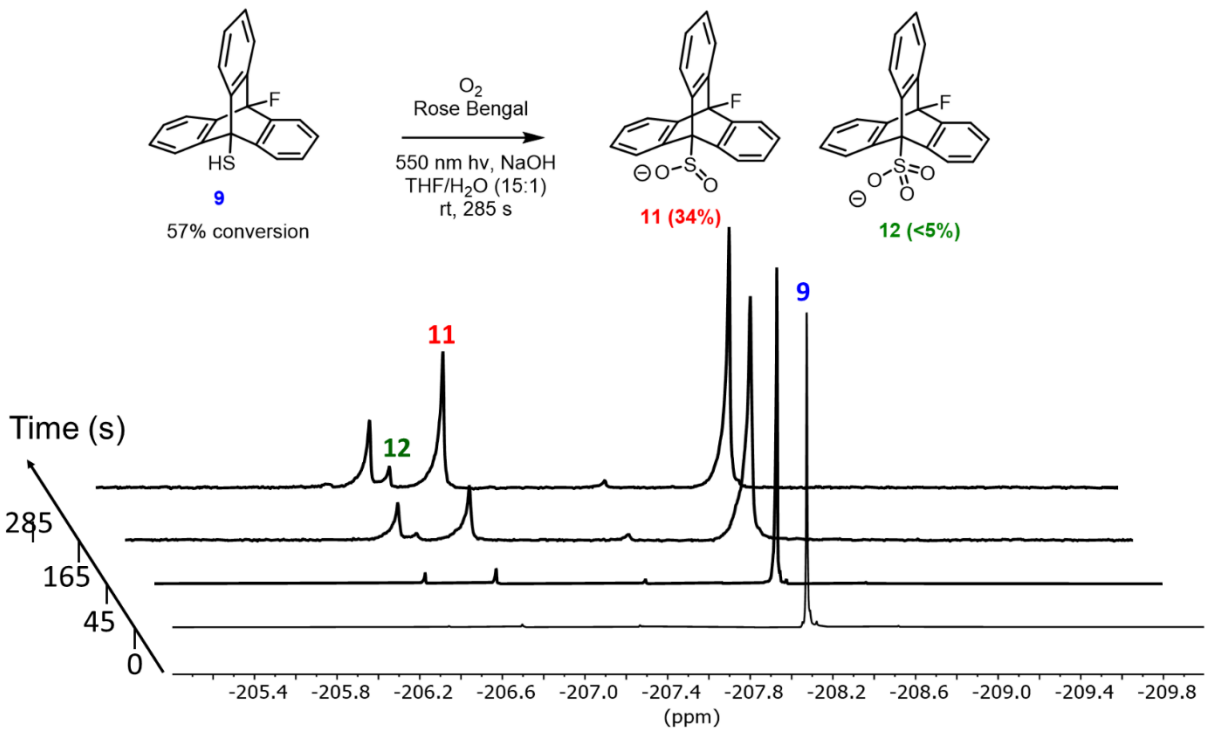
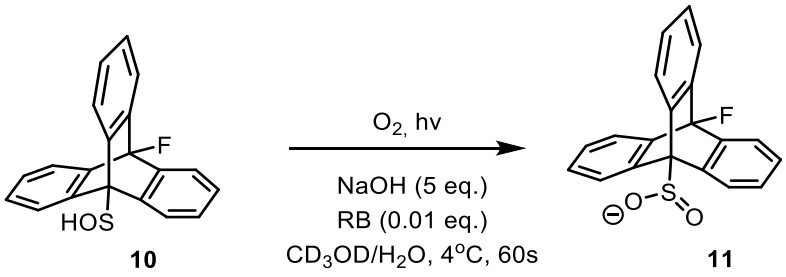


Figure S7. Representative ^{19}F NMR monitoring of the reaction of **9** (20 mM) in the presence of 200 μM of Rose Bengal in 15:1 THF/H_2O containing 60 mM NaOH. The known peaks of **9**, **11** and **12** are annotated.

Photosensitized Oxidation of Sulfenic Acid **10**



In an NMR tube, to a 5.3 mM solution of **10** in CD_3OD (690 µL) was added sodium hydroxide as a 1M solution in water (20 µL, 0.06 mmol, 8.5 eq.). 2 µL of a 1.5 mM aqueous solution of Rose Bengal (*ca.* 0.01 eq.) was added and the reaction mixture was cooled to *ca.* 4°C. Trifluorotoluene (10 mM) was used as an internal standard for NMR quantification. Oxygen was bubbled through the solution after which an initial NMR spectrum was acquired, which showed the formation of **11**. This is likely a result of Rose Bengal excitation by ambient light, as autoxidation of **10** is unlikely to occur on this timescale. The reaction vessel was subsequently irradiated with a 400W HPS lamp for 60s, upon which 85% of **10** was converted to **11** (Figure S8).

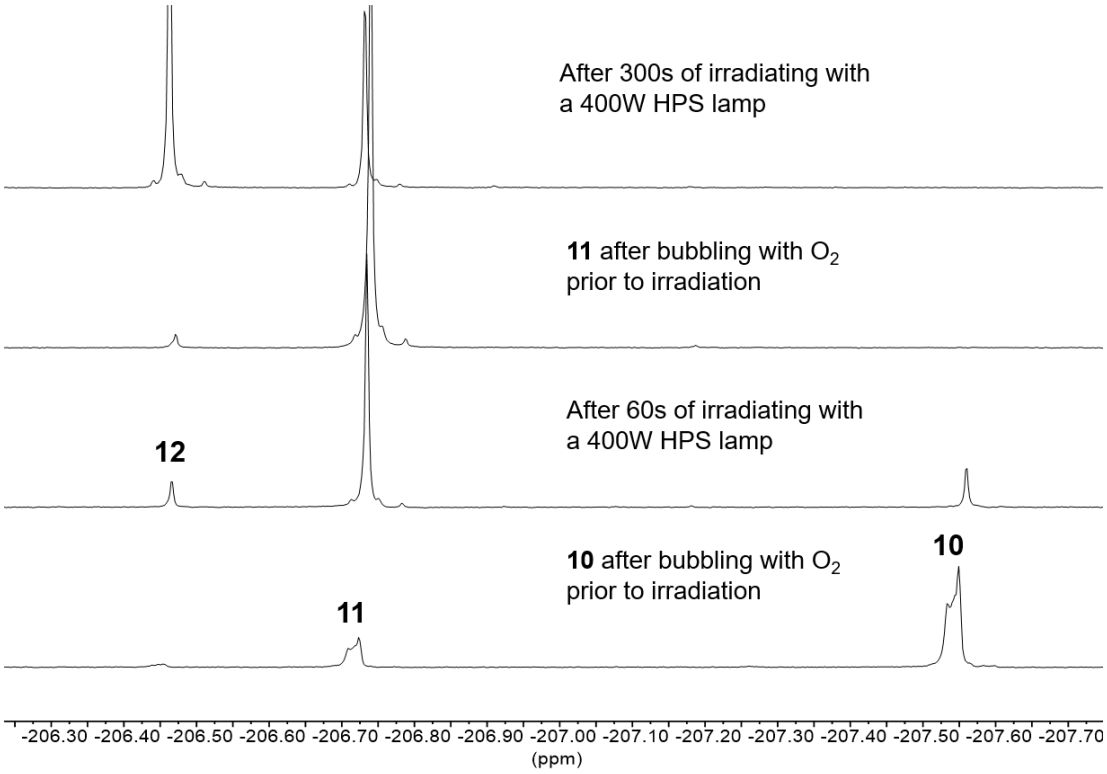


Figure S8. Representative ^{19}F NMR spectra of **10** (5 mM) in the presence of 50 μM Rose Bengal in aqueous THF in the presence of 5 eq. of NaOH. Initial time point before irradiating the NMR tube with a 400W HPS lamp is shown below. The spectrum above was acquired after irradiating for 60s. Proposed mechanism is shown below. Subsequent oxidation of **11** is also shown.

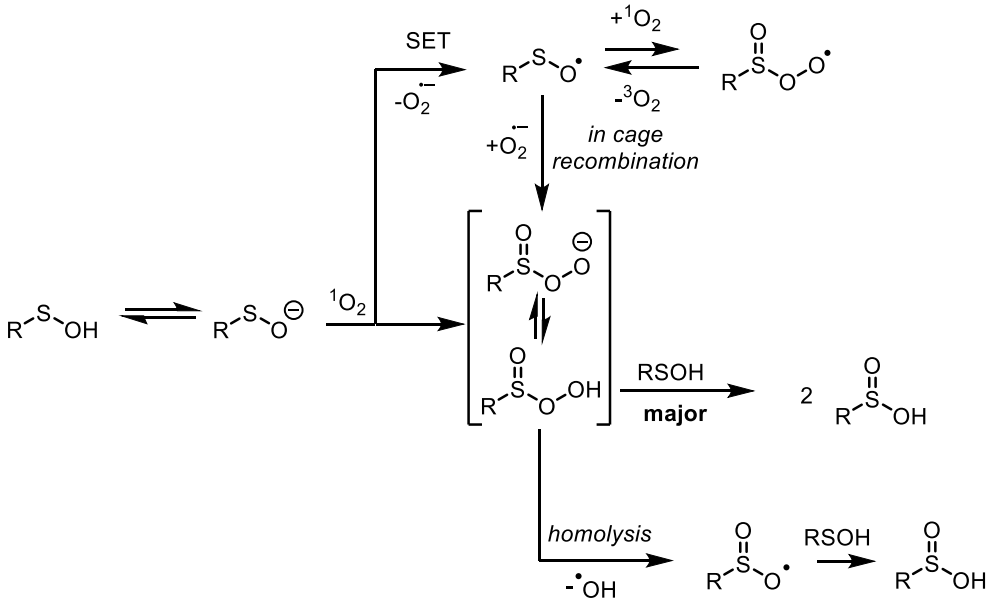


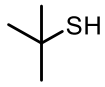
Figure S9. Proposed mechanism among other possibilities for the reaction of RSOH with $^1O_2$. SET = single electron transfer. The observation of sulfinate as the major product strongly supports the formation of a sulfonyl hydroperoxide that then reacts with an additional equivalent of RSOH resulting in the formation of two equivalents of RSO_2H. We propose that homolysis is less likely to occur since in-cage recombination

would result in a higher yield of RSO_3H relative to RSO_2H during initial time points, which was not observed (*vide supra*).

Computational Section

Gas-phase Cartesian coordinates and energetics of stationary points

Tert-butanethiol



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Sum of electronic and zero-point Energies	-555.840294	-555.843627
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Sum of electronic and thermal Enthalpies	-555.832080	-555.835383
Sum of electronic and thermal Free Energies	-555.870425	-555.873799

0 1

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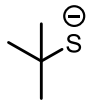
C	-0.84246900	-0.72909800	-1.26247200
H	-0.49491100	-0.22331400	-2.16556900
H	-0.48815000	-1.76255100	-1.28875400
H	-1.93756700	-0.74838700	-1.27940300
C	-0.83170100	1.45525200	0.00000100
H	-1.92520400	1.48149200	0.00000300
H	-0.48098200	1.98859500	0.88704500
H	-0.48098600	1.98859400	-0.88704700
C	-0.84246300	-0.72909600	1.26247700
H	-0.48814300	-1.76254900	1.28876000
H	-0.49490000	-0.22331000	2.16557200
H	-1.93756000	-0.74838500	1.27941400
S	1.51490600	0.08144900	-0.00000400
H	1.74704400	-1.24300300	-0.00000300

Tert-butanethiolate



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Sum of electronic and thermal Free Energies	-555.310802	-555.407462

-1 1

C	0.29823400	0.00003100	0.00004700
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H	0.48264500	-0.97114300	-1.94626800
H	0.47743100	0.79577700	-2.02466100
H	1.92316300	-0.06004000	-1.45791100
C	0.82330100	-1.21898500	0.77707800
H	1.92149500	-1.23099200	0.78763500
H	0.47542000	-1.20185300	1.81329900
H	0.47955900	-2.15139100	0.32133300
C	0.82151600	1.28263200	0.66806500
H	0.47678200	2.17124100	0.13263600
H	0.47306300	1.35533800	1.70166600
H	1.91969900	1.29681300	0.67804100
S	-1.57732400	-0.00063500	-0.00095100

Tert-butanethiyl radical

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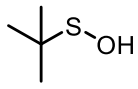
Sum of electronic and thermal Energies	-555.194947	-555.197787
Sum of electronic and thermal Enthalpies	-555.194003	-555.196843
Sum of electronic and thermal Free Energies	-555.232290	-555.235152

0 2

C	0.31152200	0.00000000	-0.00659600
C	0.85997700	-1.26527300	-0.68380800
H	0.47871300	-2.16632500	-0.20017000
H	0.57910500	-1.30217500	-1.73912600
H	1.95436400	-1.27531200	-0.62673700
C	0.66638200	0.00000000	1.49506700
H	1.75702800	0.00000000	1.59943500
H	0.27760600	0.88727000	1.99960400
H	0.27760600	-0.88727000	1.99960400
C	0.85997800	1.26527200	-0.68380900
H	0.57910600	1.30217400	-1.73912600
H	0.47871500	2.16632500	-0.20017100
H	1.95436500	1.27531100	-0.62673700
S	-1.53273500	0.00000000	-0.07448100

Tert-butanesulfenic acid



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Sum of electronic and thermal Free Energies	-631.000321	-631.006078

0 1

C	-0.66261500	0.08275000	0.00100600
C	-0.76343500	1.01531600	-1.21123400
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H	-0.67544500	0.45909400	-2.14716900
H	-1.72967800	1.52999700	-1.20536400
C	-0.79955700	0.86777200	1.31039300
H	-1.73854200	1.43090500	1.31266900
H	-0.79738700	0.19767300	2.17293300
H	0.02323600	1.57699600	1.42163600
C	-1.69845100	-1.04820700	-0.08349400
H	-1.60138200	-1.61577100	-1.01273200
H	-1.60978600	-1.73976300	0.75875600
H	-2.70319100	-0.61671900	-0.05726200
S	0.96477900	-0.81141000	-0.01736600
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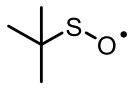
H	2.30423800	0.73787400	-0.78599200

Tert-butanesulfinyl radical



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Sum of electronic and thermal Free Energies	-630.393921	-630.399013

0 2

C	0.64524600	0.06018200	0.00000000
C	0.78650200	0.91550200	1.26431200
H	0.00388800	1.67602100	1.30041100
H	0.71571400	0.30651800	2.16927500
H	1.75837700	1.41965800	1.26791500

C	0.78651700	0.91546800	-1.26433400
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H	0.00391600	1.67600100	-1.30044800
C	1.60560900	-1.13351100	0.00002200
H	1.47055300	-1.75999600	0.88635200
H	1.47054800	-1.76003400	-0.88628100
H	2.63995300	-0.77670300	0.00001100
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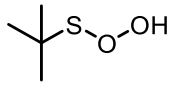
O	-2.04023200	0.48241200	0.00000000

Tert-butanesulfenyl hydroperoxide



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0 1

C	-0.97905000	0.15645100	0.01209000
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H	-0.58341100	1.30978500	-1.79643100
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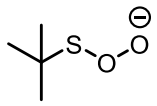
C	-1.18164600	0.39012500	1.51229400
H	-2.01261400	1.08544800	1.66792100
H	-1.41189200	-0.54299500	2.03109500
H	-0.28696900	0.82464400	1.96240300
C	-2.16686300	-0.60176000	-0.60261100
H	-2.01294800	-0.80242800	-1.66636400
H	-2.35151500	-1.54975200	-0.09095300
H	-3.06655400	0.01258700	-0.50670900

S	0.44346100	-1.01286700	-0.24790400
O	1.69578500	-0.29351300	0.58493300
O	2.45354000	0.68090600	-0.25277900
H	3.19504300	0.12167900	-0.53177500

Tert-butanesulfenyl peroxide



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Sum of electronic and thermal Free Energies	-705.483555	-705.586200

-1 1

C	-0.93192700	0.14967800	0.01622000
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H	-0.64964900	1.32486000	-1.79474200
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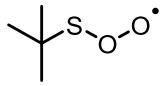
H	-1.85467600	1.12416400	1.72535400
H	-1.34345700	-0.54609300	2.03924700
H	-0.13451700	0.74356800	1.94128400
C	-2.17221600	-0.54284700	-0.56134000
H	-2.04900100	-0.75886200	-1.62678600
H	-2.38988600	-1.48076600	-0.04278800
H	-3.04366800	0.11190200	-0.45406500
S	0.47821600	-1.03493300	-0.27435000
O	1.75883000	-0.31289600	0.51817500
O	2.46018800	0.71957600	-0.28249700

Tert-butanethiyl peroxyl radical



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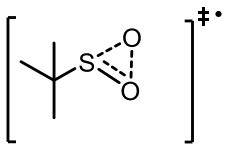
Sum of electronic and thermal Enthalpies	-705.371358	-705.374815
Sum of electronic and thermal Free Energies	-705.417033	-705.420713

0 2

C	-0.93053200	0.15845200	0.00396700
C	-0.66636400	1.37212200	-0.89415600
H	0.23105400	1.91019900	-0.58445000
H	-0.53986000	1.07363900	-1.93635900
H	-1.51255400	2.06477800	-0.83061200
C	-1.10905600	0.57310600	1.46913400
H	-1.94032200	1.28130400	1.55224700
H	-1.32631200	-0.29065100	2.10034700
H	-0.21118700	1.06061000	1.85292300
C	-2.14821900	-0.63932200	-0.49556000
H	-2.02625900	-0.95781100	-1.53395900
H	-2.33637700	-1.52099300	0.12216300
H	-3.03402600	0.00121200	-0.44452500
S	0.45402300	-1.07001400	-0.14607900
O	1.79470100	-0.07539000	0.53729500
O	2.52486100	0.53936400	-0.34489700

Thiyl peroxyl radical rearrangement TS



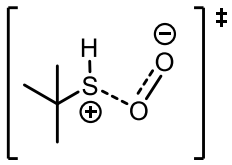
Imaginary frequency: -817.40 (CBS-QB3)

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-705.356334	-705.364402
Sum of electronic and thermal Energies	-705.347260	-705.499673
Sum of electronic and thermal Enthalpies	-705.346316	-705.498729
Sum of electronic and thermal Free Energies	-705.390553	-705.543082

0 2

C	-0.89080900	0.07211900	0.06977400
C	-0.69203700	0.41779200	1.54313300
H	-0.45180100	-0.46694600	2.13479400
H	0.11674600	1.13824900	1.66285200
H	-1.61840100	0.85226700	1.93115200
C	-1.91728200	-1.05412500	-0.13133100
H	-2.90368900	-0.70589900	0.19019800
H	-1.99878600	-1.34923700	-1.18170300
H	-1.66189200	-1.93958900	0.45476000
C	-1.25866500	1.30786600	-0.76489500
H	-0.52954800	2.10426600	-0.61505100
H	-1.30437200	1.07811600	-1.83365500
H	-2.24689700	1.66830500	-0.46233600
S	0.72293800	-0.57802000	-0.62854400
O	1.73693600	-0.65311400	0.53923800
O	1.96111300	0.95397300	-0.10478700

$^1O_2$-TS1



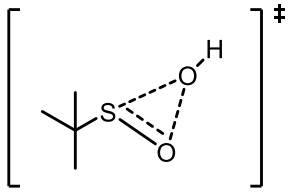
Imaginary frequency: -452.40 (CBS-QB3), -355.62 (PCM CBS-QB3)

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-705.935340	-705.955002
Sum of electronic and thermal Energies	-705.926138	-705.945512
Sum of electronic and thermal Enthalpies	-705.925194	-705.944568
Sum of electronic and thermal Free Energies	-705.968559	-705.989111

0 1 0 1 0 1

C(Fragment=1)	-0.99558500	0.48201500	1.52725700
H(Fragment=1)	-1.22198100	-0.41069200	2.11512900
H(Fragment=1)	-0.03934900	0.88832600	1.85720700
H(Fragment=1)	-1.77461300	1.22343500	1.72510400
C(Fragment=1)	-0.97905500	0.18103100	0.02920700
C(Fragment=1)	-2.25324300	-0.52819900	-0.44050800
H(Fragment=1)	-2.20633200	-0.78825400	-1.50005700
H(Fragment=1)	-2.45347200	-1.43328700	0.13706500
H(Fragment=1)	-3.09759200	0.15362400	-0.29942100
C(Fragment=1)	-0.67084900	1.43215800	-0.80532300
H(Fragment=1)	0.31004600	1.83691300	-0.55045400
H(Fragment=1)	-0.69075600	1.21173900	-1.87530100
H(Fragment=1)	-1.43668000	2.18455300	-0.59966000
S(Fragment=1)	0.44169800	-0.99683600	-0.34249700
H(Fragment=1)	0.16094400	-1.91216400	0.60812000
O(Fragment=2)	1.84249800	-0.23620300	0.51980500
O(Fragment=2)	2.50437800	0.68534800	-0.27000200

RSOOH rearrangement TS



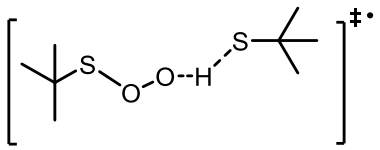
Imaginary frequency: -426.33 (CBS-QB3), -415.92 (PCM CBS-QB3)

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-706.007064	-706.009723
Sum of electronic and thermal Energies	-705.997461	-705.999870
Sum of electronic and thermal Enthalpies	-705.996517	-705.998926
Sum of electronic and thermal Free Energies	-706.041165	-706.044230

0 1

C	-0.93160300	0.15117300	0.06630700
C	-0.64471100	0.56796600	1.50598500
H	-0.55949000	-0.29732600	2.16612600
H	0.29011800	1.12678600	1.55185700
H	-1.46425900	1.19797200	1.86552900
C	-2.14855200	-0.78172000	-0.05251000
H	-3.05373900	-0.23190100	0.22391200
H	-2.28633700	-1.14603600	-1.07532000
H	-2.05960800	-1.64520300	0.61046300
C	-1.07547100	1.36814700	-0.86223600
H	-0.19790800	2.00875300	-0.77764100
H	-1.18434900	1.06985300	-1.90950800
H	-1.97104300	1.93322000	-0.58383900
S	0.53326700	-0.82502000	-0.57356800
O	1.53915800	-0.91987700	0.52371500
O	2.19428100	0.89681800	-0.14114600
H	2.88885800	1.53527600	0.09968500

Thiyl peroxyl HAT from thiol TS



Imaginary frequency: -1590.45 (CBS-QB3), -1695.82 (PCM CBS-QB3)

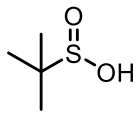
	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-1261.210326	-1261.215305
Sum of electronic and thermal Energies	-1261.192416	-1261.197395
Sum of electronic and thermal Enthalpies	-1261.191471	-1261.196450
Sum of electronic and thermal Free Energies	-1261.259545	-1261.264524

0 2

O	0.98820400	-0.98358100	0.81453400
O	0.01076900	-0.00560800	0.74436800
S	-2.29702500	-1.16400900	-0.26088200
H	-1.07684300	-0.61467300	0.47252200
C	-3.41063800	0.32251200	-0.05757700
C	-3.51577600	0.69584900	1.42650700
H	-2.54218500	0.97300900	1.83712200
H	-4.18839400	1.55195400	1.54438300
H	-3.91217000	-0.13459500	2.01438200
C	-2.84727000	1.49064200	-0.88011600
H	-2.77675200	1.23023200	-1.93803000
H	-3.50976300	2.35721400	-0.78157600
H	-1.85456500	1.78212400	-0.53048400
C	-4.78025500	-0.10955200	-0.60694700
H	-5.47926100	0.72811600	-0.51824900
H	-4.71790100	-0.39011500	-1.66083000
H	-5.18979700	-0.95240900	-0.04521900
S	2.07900600	-0.98586700	-0.51308900
C	3.28462100	0.36289700	-0.06095800
C	2.61269500	1.73852000	-0.11297700
H	1.81691400	1.82073900	0.62878300
H	3.35880700	2.51051600	0.10155300
H	2.18727300	1.93528100	-1.09894100

C	3.87805100	0.07859600	1.32206900
H	4.38662000	-0.88722000	1.34500600
H	4.60511500	0.85777700	1.57118500
H	3.10341100	0.08163000	2.09120600
C	4.34743800	0.22659700	-1.16555200
H	3.92383000	0.38937500	-2.15997500
H	5.11556200	0.98787200	-1.00272600
H	4.83343400	-0.75165900	-1.14449300

Tert-butanesulfinic acid



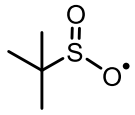
	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-706.119032	-706.129097
Sum of electronic and thermal Energies	-706.109594	-706.119613
Sum of electronic and thermal Enthalpies	-706.108649	-706.118669
Sum of electronic and thermal Free Energies	-706.152246	-706.162389

0 1

C	-0.84682000	0.03011800	0.03875600
C	-1.39941900	1.28434500	-0.64356100
H	-0.90528700	2.18558800	-0.27995900
H	-1.27758900	1.23469800	-1.72965200
H	-2.46959100	1.36724700	-0.43340700
C	-0.89122900	0.11271200	1.56459400
H	-1.93339000	0.10130300	1.89633700
H	-0.37937400	-0.74232200	2.01101700
H	-0.42337900	1.02886000	1.92679300
C	-1.54601900	-1.23601400	-0.47598600
H	-1.46484800	-1.32794000	-1.56303900
H	-1.12629400	-2.13417900	-0.01939800
H	-2.60831500	-1.18642900	-0.22273500

S	0.93515100	-0.16877700	-0.50972500
O	1.48098700	-1.31844000	0.25514100
O	1.45610200	1.25192300	0.23549900
H	2.22986800	1.55877900	-0.25830100

Tert-butanesulfonyl radical

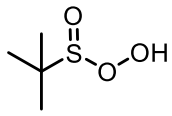


	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-705.500452	-705.508889
Sum of electronic and thermal Energies	-705.491383	-705.499673
Sum of electronic and thermal Enthalpies	-705.490439	-705.498729
Sum of electronic and thermal Free Energies	-705.534391	-705.543082

0 2

C	-0.88766100	-0.00000100	0.02506800
C	-1.44107100	1.27236200	-0.60618600
H	-0.95956700	2.16114700	-0.19732000
H	-1.31043300	1.27364400	-1.69113100
H	-2.51428700	1.33387400	-0.39800700
C	-0.98454600	0.00003300	1.55053300
H	-2.04220000	0.00000900	1.83515700
H	-0.51386900	-0.88745300	1.97641200
H	-0.51391900	0.88756700	1.97636700
C	-1.44105700	-1.27239800	-0.60612900
H	-1.31037400	-1.27374700	-1.69106900
H	-0.95957900	-2.16116300	-0.19719100
H	-2.51428400	-1.33388100	-0.39799500
S	1.02117500	0.00000000	-0.35884600
O	1.55161000	-1.27339800	0.14666300
O	1.55160500	1.27340200	0.14666100

Tert-butanesulfonyl hydroperoxide

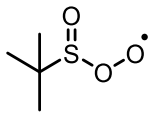


	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-781.168662	-781.177385
Sum of electronic and thermal Energies	-781.157907	-781.166576
Sum of electronic and thermal Enthalpies	-781.156963	-781.165632
Sum of electronic and thermal Free Energies	-781.204061	-781.212819

0 1

C	-0.84682000	0.03011800	0.03875600
C	-1.39941900	1.28434500	-0.64356100
H	-0.90528700	2.18558800	-0.27995900
H	-1.27758900	1.23469800	-1.72965200
H	-2.46959100	1.36724700	-0.43340700
C	-0.89122900	0.11271200	1.56459400
H	-1.93339000	0.10130300	1.89633700
H	-0.37937400	-0.74232200	2.01101700
H	-0.42337900	1.02886000	1.92679300
C	-1.54601900	-1.23601400	-0.47598600
H	-1.46484800	-1.32794000	-1.56303900
H	-1.12629400	-2.13417900	-0.01939800
H	-2.60831500	-1.18642900	-0.22273500
S	0.93515100	-0.16877700	-0.50972500
O	1.48098700	-1.31844000	0.25514100
O	1.45610200	1.25192300	0.23549900
H	2.22986800	1.55877900	-0.25830100

Tert-butane sulfonyl methyl peroxide

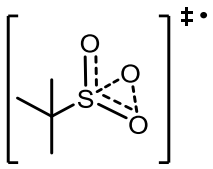


	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-820.386367	
Sum of electronic and thermal Energies	-820.374247	
Sum of electronic and thermal Enthalpies	-820.373302	
Sum of electronic and thermal Free Energies	-820.423936	

0 2

C	0.96789000	-0.39419000	0.04173100
C	0.63755400	-1.79397200	-0.48276500
H	-0.23890500	-2.21802300	0.00744700
H	0.45966900	-1.79172300	-1.56200500
H	1.48712600	-2.45587500	-0.28972100
C	1.08583300	-0.33087800	1.56480400
H	1.97929600	-0.87752100	1.88133200
H	1.17827100	0.70330400	1.90168100
H	0.21810500	-0.77848800	2.05115600
C	2.21972200	0.17861200	-0.64378800
H	2.12202900	0.18326600	-1.73350000
H	2.42458300	1.19690300	-0.30855800
H	3.08139900	-0.44604000	-0.39062200
O	-2.51762100	-0.87949600	-0.23153700
O	-1.77660000	-0.14231500	0.51987200
S	-0.40674400	0.76871200	-0.50805100
O	-0.16448800	2.05023200	0.17313000

<u>*Tert*-butane sulfonyl peroxyl rearrangement TS</u>



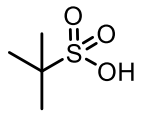
	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-780.470809	-780.468142
Sum of electronic and thermal Energies	-780.460180	-780.457472
Sum of electronic and thermal Enthalpies	-780.459236	-780.456527
Sum of electronic and thermal Free Energies	-780.507103	-780.504444

Imaginary frequency: -636.78 (CBS-QB3), -453.25 (PCM CBS-QB3)

0 2

C	0.96789000	-0.39419000	0.04173100
C	0.63755400	-1.79397200	-0.48276500
H	-0.23890500	-2.21802300	0.00744700
H	0.45966900	-1.79172300	-1.56200500
H	1.48712600	-2.45587500	-0.28972100
C	1.08583300	-0.33087800	1.56480400
H	1.97929600	-0.87752100	1.88133200
H	1.17827100	0.70330400	1.90168100
H	0.21810500	-0.77848800	2.05115600
C	2.21972200	0.17861200	-0.64378800
H	2.12202900	0.18326600	-1.73350000
H	2.42458300	1.19690300	-0.30855800
H	3.08139900	-0.44604000	-0.39062200
O	-2.51762100	-0.87949600	-0.23153700
O	-1.77660000	-0.14231500	0.51987200
S	-0.40674400	0.76871200	-0.50805100
O	-0.16448800	2.05023200	0.17313000

Tert-butanesulfonic acid



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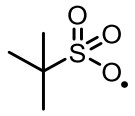
	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-781.287942	-781.299667
Sum of electronic and thermal Energies	-781.277962	-781.289730
Sum of electronic and thermal Enthalpies	-781.277017	-781.288786
Sum of electronic and thermal Free Energies	-781.321987	-781.333640

0 1

C	0.99040100	0.03742300	-0.00632400
C	1.35656400	1.39437600	0.60615500
H	0.95688000	2.21885900	0.01331900
H	0.98517900	1.48006600	1.62828800
H	2.44561400	1.49047900	0.62686500
C	1.41991500	-0.06325800	-1.47533900
H	2.50915600	0.01981300	-1.52957700
H	1.12375600	-1.01930400	-1.90783100
H	0.98447600	0.73913700	-2.07278500
C	1.55925800	-1.12320100	0.82673900
H	1.22042300	-1.07075500	1.86286900
H	1.26571000	-2.08836600	0.41133200
H	2.65063800	-1.06066200	0.81692200
S	-0.83821700	-0.16226800	0.07100900
O	-1.20948400	-1.35868900	-0.63186000
O	-1.30530000	0.09335700	1.41537800
O	-1.34359300	1.10445400	-0.83943800
H	-1.82015900	1.70202000	-0.24557300

Tert-butane oxysulfonyl radical



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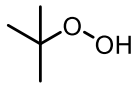
	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-780.619763	
Sum of electronic and thermal Energies	-780.609624	
Sum of electronic and thermal Enthalpies	-780.608680	
Sum of electronic and thermal Free Energies	-780.654961	

0 2

C	0.97378900	0.00002800	-0.00004600
C	1.42946700	1.16164900	-0.89473900
H	1.07380900	1.03791500	-1.91897300
H	1.07237800	2.12012000	-0.51443000
H	2.52232100	1.18484800	-0.91159500
C	1.42926100	-1.35572000	-0.55871400
H	2.52209700	-1.38225900	-0.56957500
H	1.07281800	-2.18093000	0.06003600
H	1.07291200	-1.50518100	-1.57925200
C	1.42935500	0.19399700	1.45335400
H	1.07327000	1.14261500	1.85855300
H	1.07269300	-0.61493100	2.09309800
H	2.52220500	0.19749900	1.48183500
S	-0.85928300	0.00006100	0.00005700
O	-1.32595200	-1.10752700	0.85209400
O	-1.32613900	1.29174600	0.53296900
O	-1.32631000	-0.18426900	-1.38503100

t*ert*-butyl hydroperoxide



	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-308.290544	-308.296595
Sum of electronic and thermal Energies	-308.282489	-308.288581
Sum of electronic and thermal Enthalpies	-308.281545	-308.287637
Sum of electronic and thermal Free Energies	-308.321510	-308.327519

0 1

C	-0.39096500	-0.00048200	0.03696200
C	-0.31734100	1.16330400	1.02926500
H	0.56860600	1.07396200	1.66009700
H	-0.27565200	2.11679900	0.49564000
H	-1.19647400	1.17232400	1.67867100
C	-0.40706700	-1.35577400	0.74760800
H	-1.27416600	-1.43228600	1.40937000
H	-0.45450400	-2.16495100	0.01542400
H	0.49708900	-1.48325700	1.34393000
C	-1.58187100	0.14932400	-0.91311200
H	-1.53888100	1.10534200	-1.43959400
H	-1.58301200	-0.65391400	-1.65264400
H	-2.51597800	0.10449900	-0.34824000
O	1.97295900	-0.10251000	-0.15111600
H	2.35103100	0.77962800	-0.26250800
O	0.72771800	0.05796200	-0.88694500

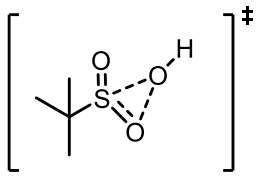
t*ert*-butyl alkoxyl radical

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-232.567582	-232.571848
Sum of electronic and thermal Energies	-232.560949	-232.565229
Sum of electronic and thermal Enthalpies	-232.560004	-232.564284
Sum of electronic and thermal Free Energies	-232.597235	-232.601477

0 2

C	0.00000500	-0.02692900	0.08045500
C	-1.27713000	-0.79264900	-0.31484700
H	-1.30450200	-1.75954800	0.19372000
H	-2.16163400	-0.22556700	-0.01834900
H	-1.31455800	-0.97229500	-1.39300400
C	1.27733500	-0.79232800	-0.31483500
H	1.31482100	-0.97196700	-1.39299300
H	2.16169400	-0.22502200	-0.01833000
H	1.30494600	-1.75921900	0.19373300
C	-0.00017300	1.38896500	-0.57814100
H	-0.88898800	1.94647000	-0.28079400
H	0.88849300	1.94670000	-0.28077900
H	-0.00014700	1.26160400	-1.66352400
O	-0.00004300	0.26206200	1.42806600

RS(O)OOH rearrangement TS



Imaginary frequency: -480.01 (CBS-QB3), -435.13 (PCM CBS-QB3)

	CBS-QB3	PCM CBS-QB3
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Sum of electronic and thermal Energies	-781.130554	-781.129472
Sum of electronic and thermal Enthalpies	-781.129609	-781.128528
Sum of electronic and thermal Free Energies	-781.175934	-781.176206

0 1

C	1.08157000	0.16168500	0.02061400
C	1.07633900	1.45020100	-0.78840800
H	1.01399300	1.25795200	-1.86131600
H	0.24796500	2.08898100	-0.48630000
H	2.02462900	1.96319500	-0.59264200
C	2.10906300	-0.86223900	-0.46654900
H	3.10770500	-0.45549700	-0.28269500
H	2.02765400	-1.80737900	0.07443600
H	2.01727400	-1.05704000	-1.53677500
C	1.14333700	0.37969500	1.53110200
H	0.41747500	1.13407700	1.82678900
H	0.94135900	-0.54166900	2.07866000
H	2.16105800	0.70423600	1.77667400
S	-0.64097600	-0.67452400	-0.33976900
O	-1.54236500	0.13234000	-1.13693600
O	-1.61081100	1.39168400	0.62532700
H	-2.45694400	1.18502500	1.04576600
O	-1.06037500	-1.58096700	0.71325400

Singlet oxygen

O=O

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-150.118992	-150.119835
Sum of electronic and thermal Energies	-150.116628	-150.117472
Sum of electronic and thermal Enthalpies	-150.115684	-150.116528
Sum of electronic and thermal Free Energies	-150.137921	-150.138764

0 1

O	0.00000000	0.00000000	0.60329800
O	0.00000000	0.00000000	-0.60329800

Triplet oxygen

$^{\bullet}O-O^{\bullet}$

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-150.164558	-150.164646
Sum of electronic and thermal Energies	-150.162195	-150.162283
Sum of electronic and thermal Enthalpies	-150.161250	-150.161339
Sum of electronic and thermal Free Energies	-150.184523	-150.184611

0 3

O	0.00000000	0.00000000	0.60259800
O	0.00000000	0.00000000	-0.60259800

Superoxide

$O_2^{\bullet-}$

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-150.181199	-150.295826
Sum of electronic and thermal Energies	-150.178820	-150.293448
Sum of electronic and thermal Enthalpies	-150.177876	-150.292504
Sum of electronic and thermal Free Energies	-150.201000	-150.315622

-1 2

O	0.00000000	0.00000000	0.67407800
O	0.00000000	0.00000000	-0.67407800

Hydroperoxyl radical

$HO-O^{\bullet}$

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-150.741092	
Sum of electronic and thermal Energies	-150.738232	
Sum of electronic and thermal Enthalpies	-150.737287	
Sum of electronic and thermal Free Energies	-150.763268	

0 2

O	0.05528600	-0.60965600	0.00000000
H	-0.88457100	-0.87073400	0.00000000
O	0.05528600	0.71849800	0.00000000

Hydroxyl radical

$^{\bullet}OH$

	CBS-QB3	PCM CBS-QB3
Sum of electronic and zero-point Energies	-75.649713	-75.654400
Sum of electronic and thermal Energies	-75.647353	-75.652040
Sum of electronic and thermal Enthalpies	-75.646408	-75.651096

Sum of electronic and thermal Free Energies	-75.666640	-75.671329

0 2

O	0.00000000	0.00000000	0.10835600
H	0.00000000	0.00000000	-0.86685200

NMR spectra

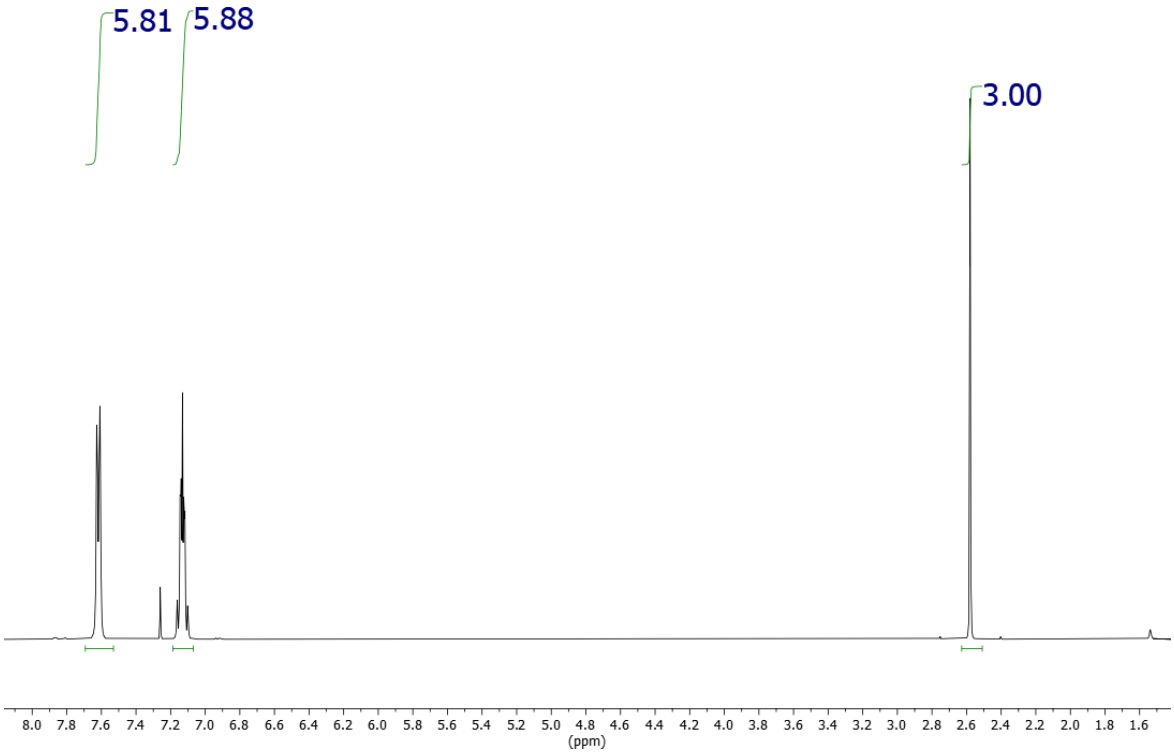

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

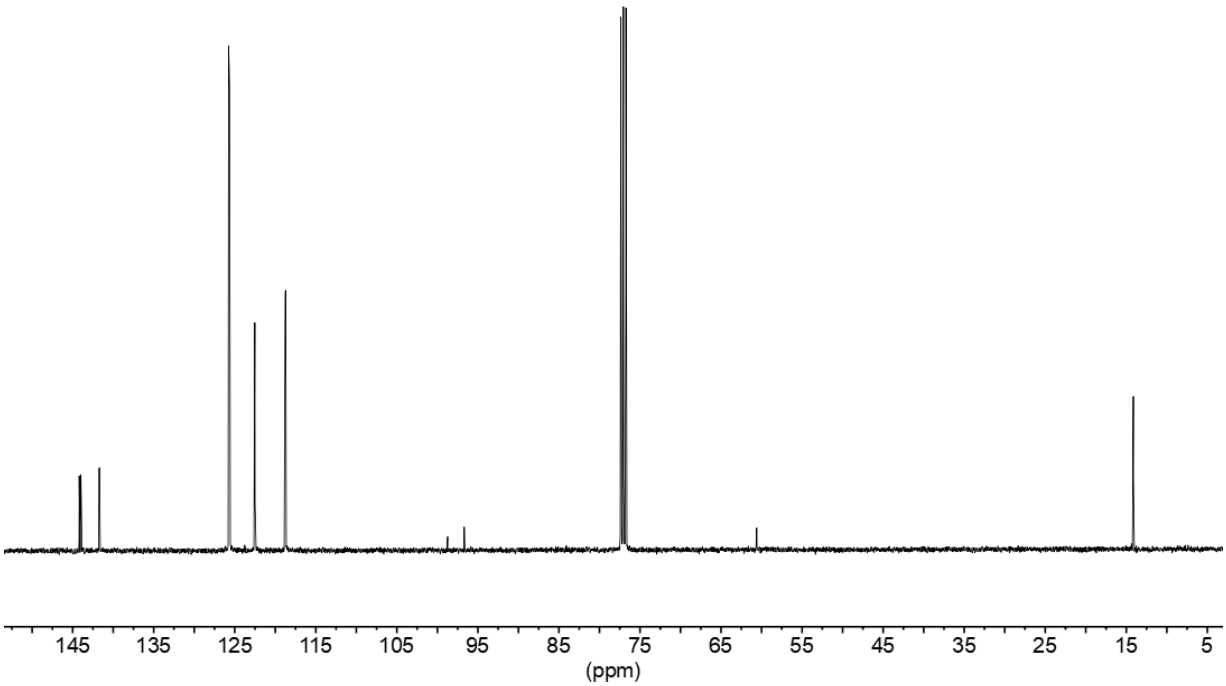

Figure S11. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3**.

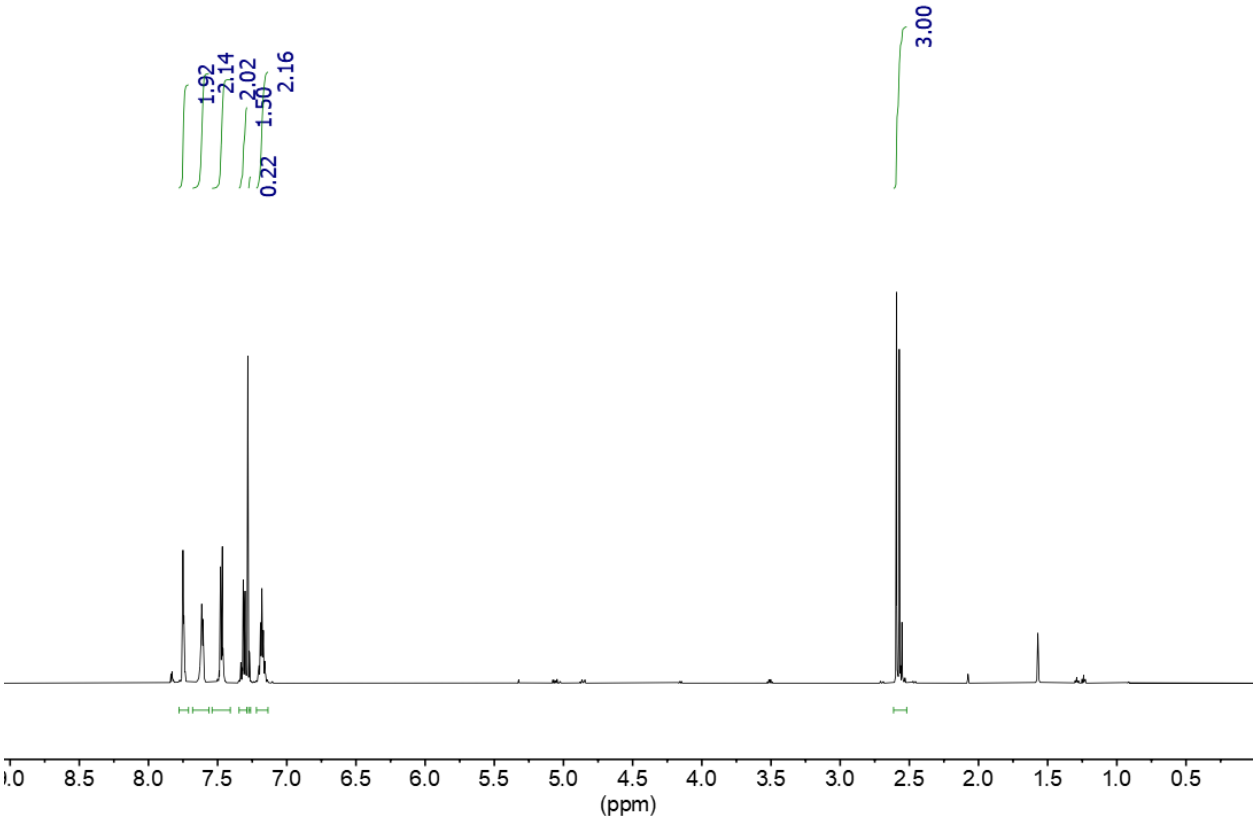

Figure S12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4a** + **4b**.

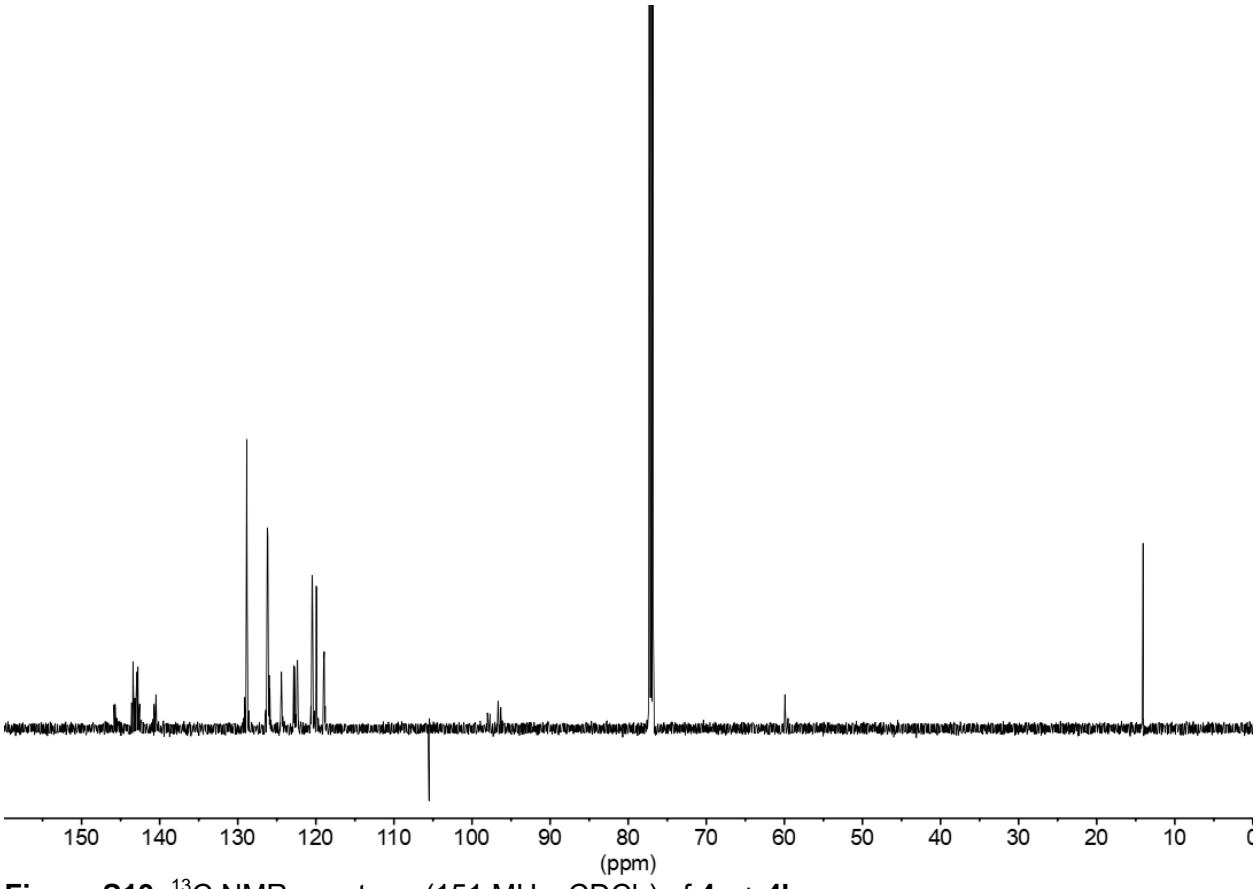

Figure S13. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4a** + **4b**.

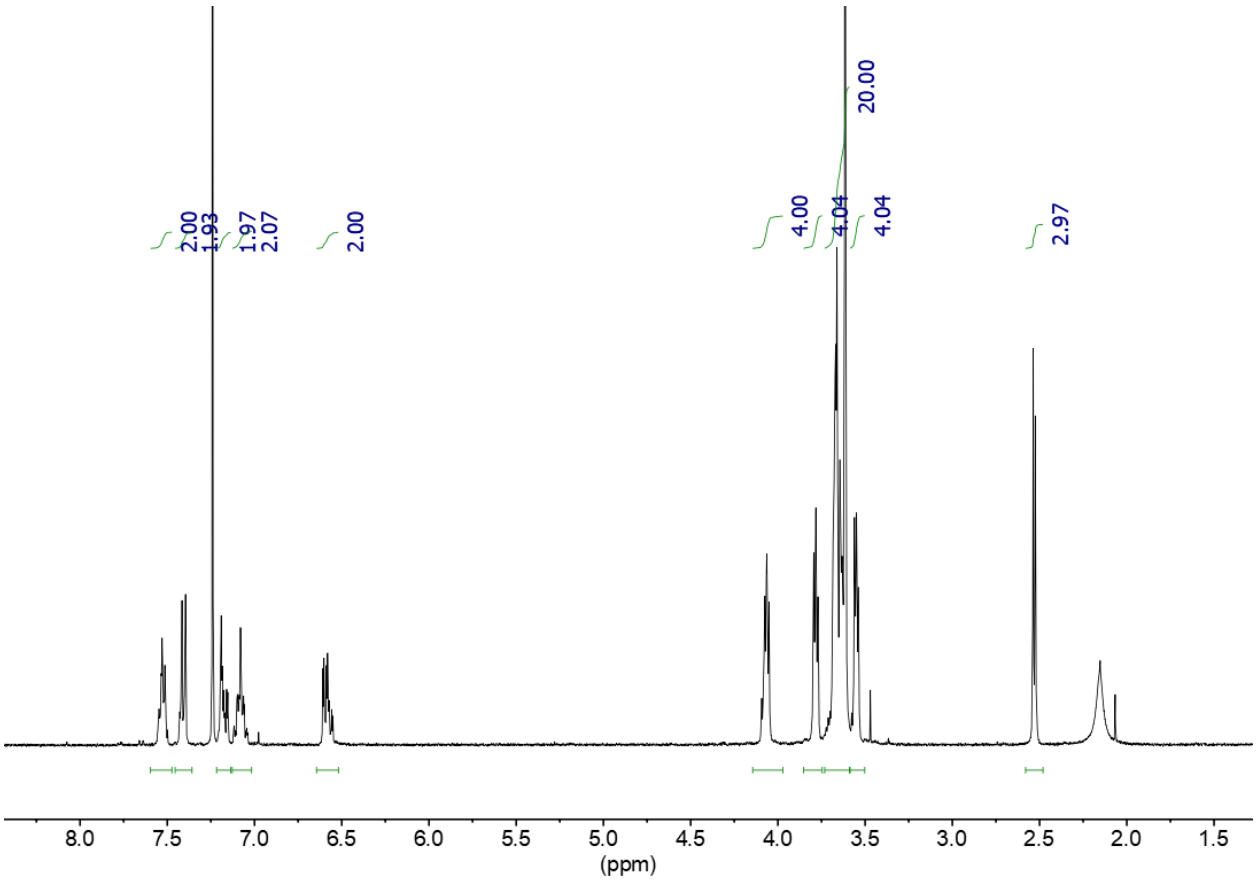

Figure S14. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5a** + **5b**.

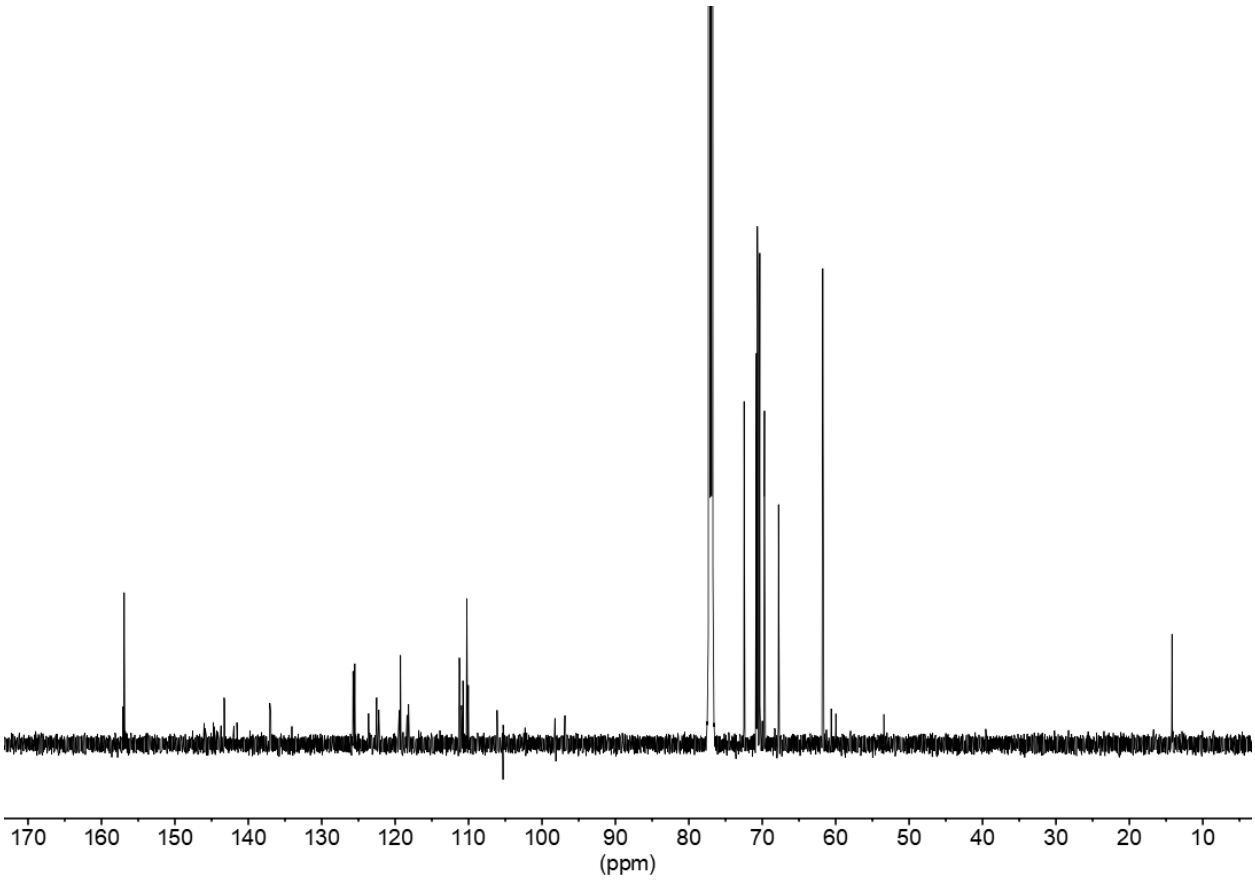

Figure S15. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5a** + **5b**.

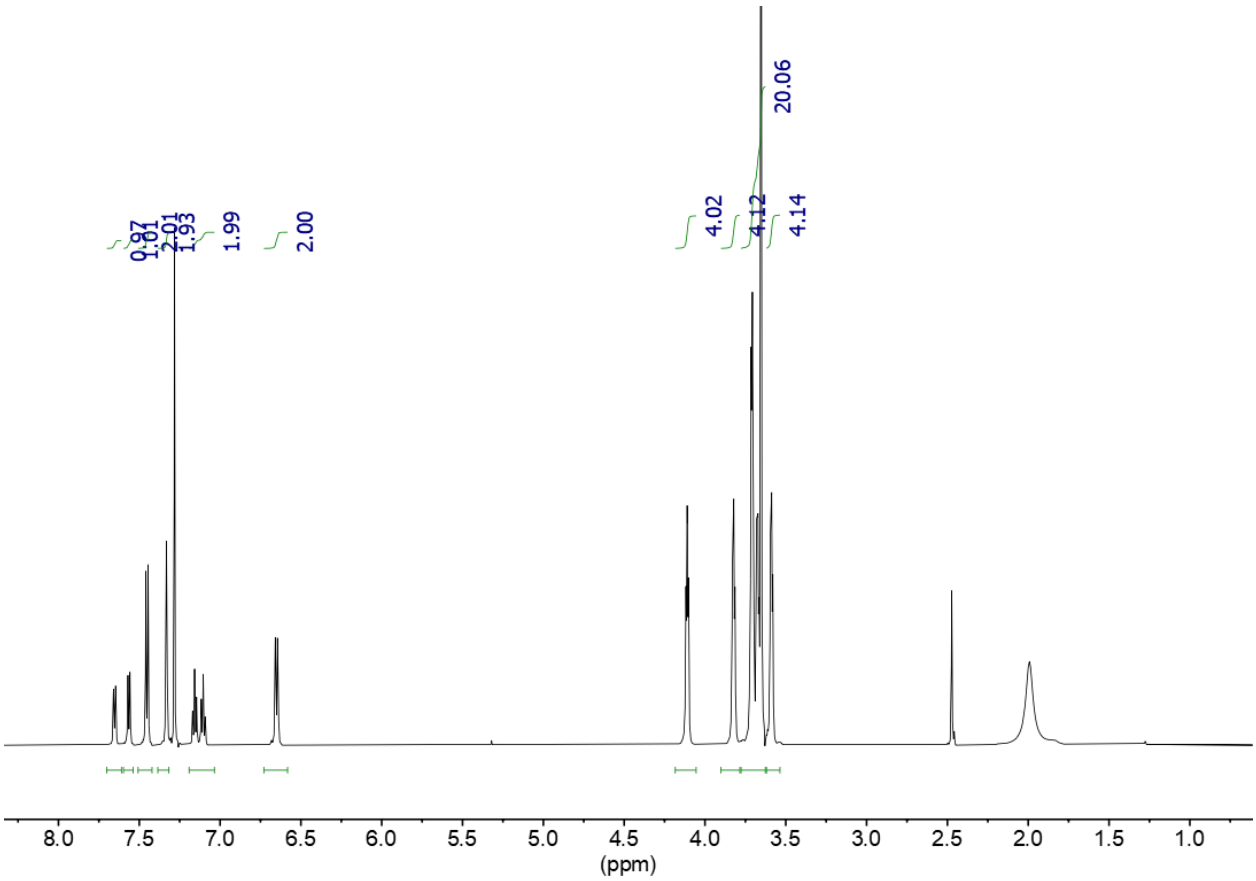

Figure S16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1a**.

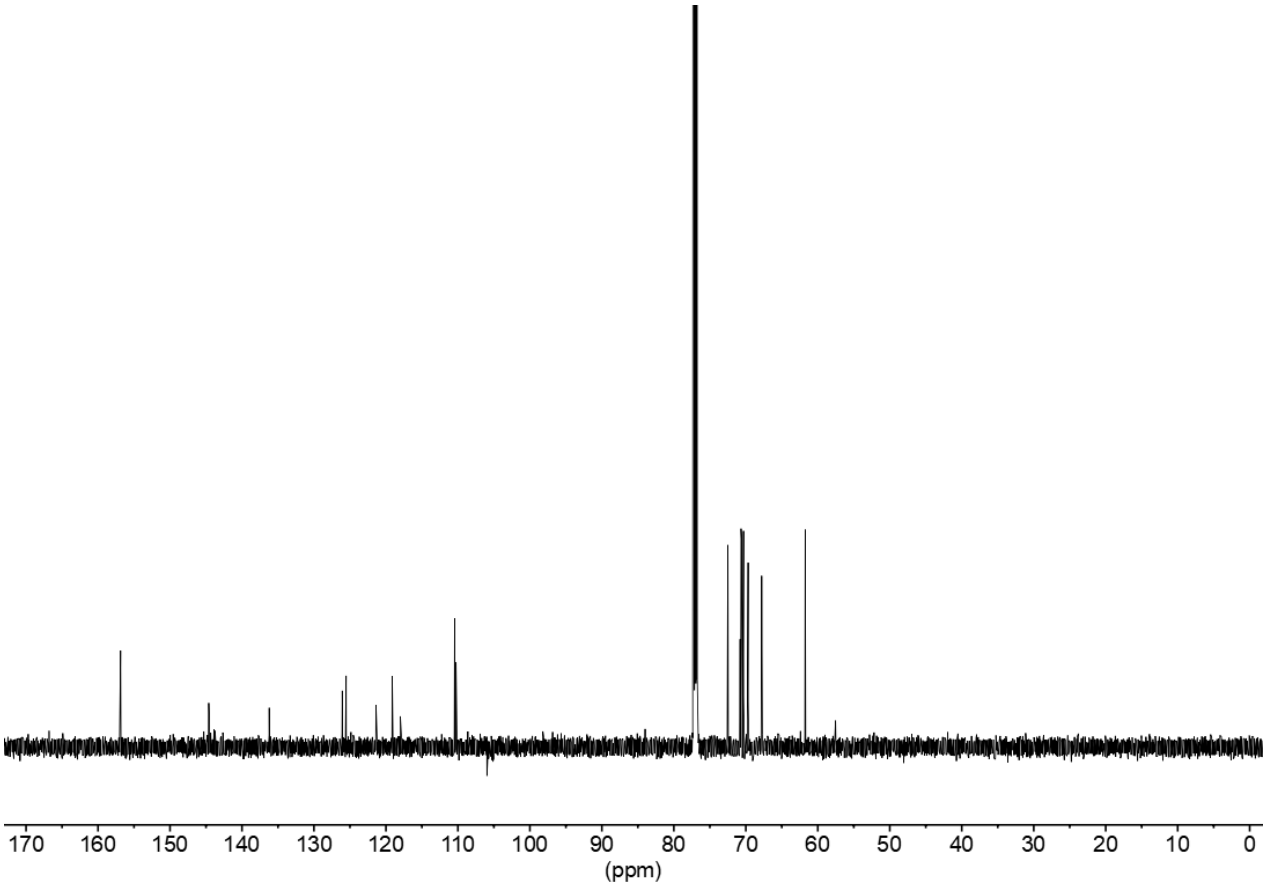

Figure S17. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1a**.

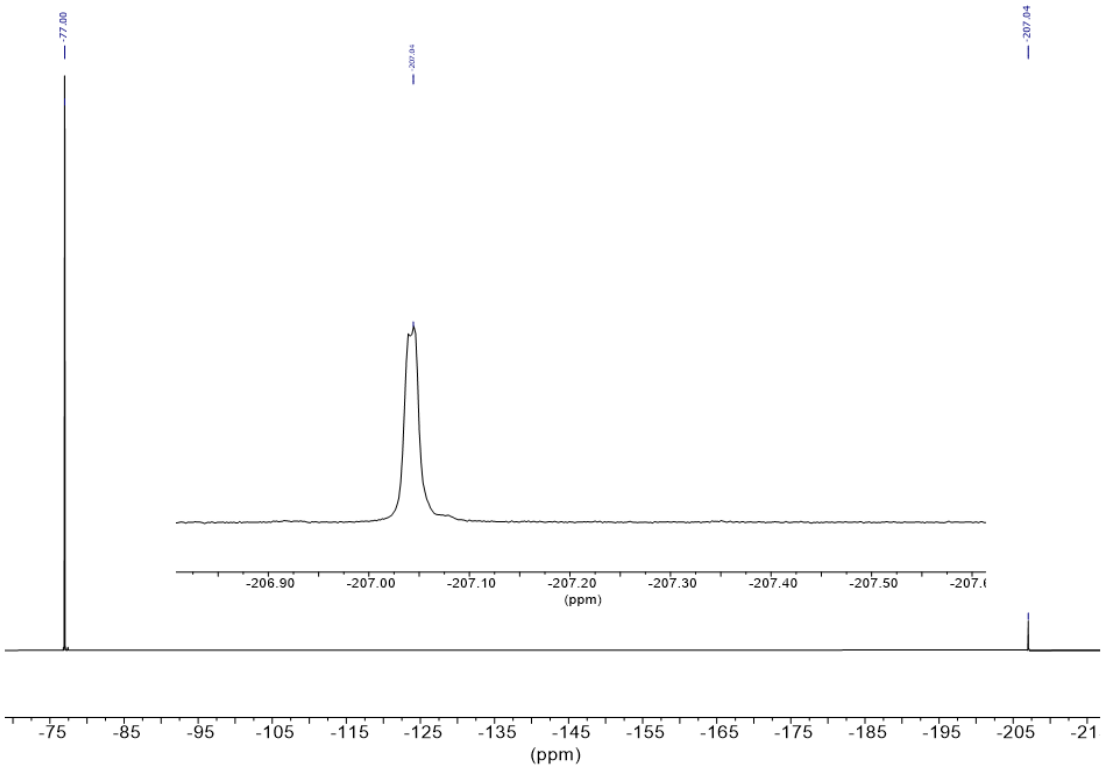

Figure S18. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **1a**.

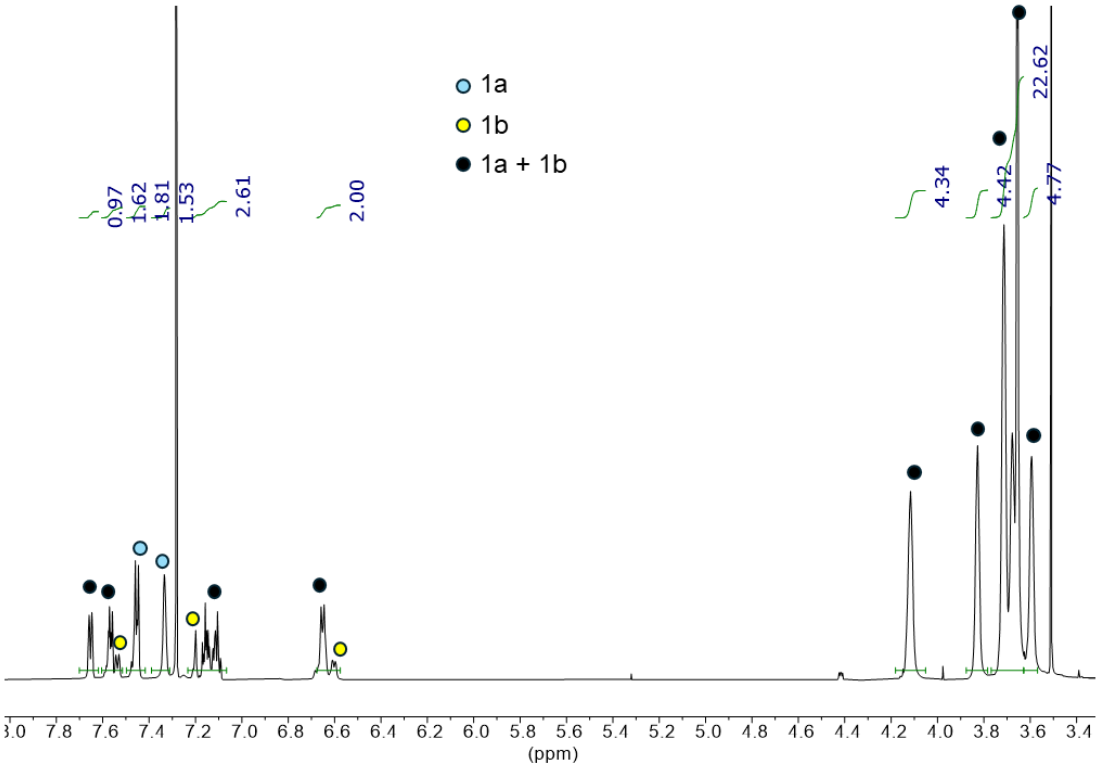

Figure S19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1a** + **1b**.

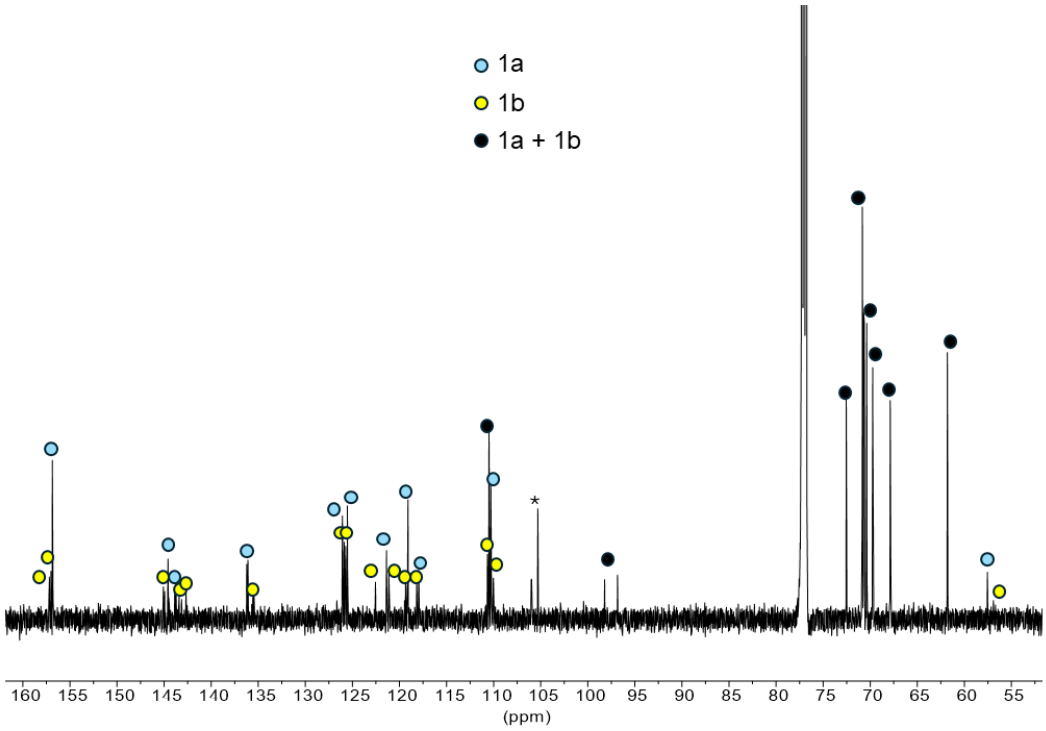

Figure S20. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1a** + **1b**. * = CH_3OH.

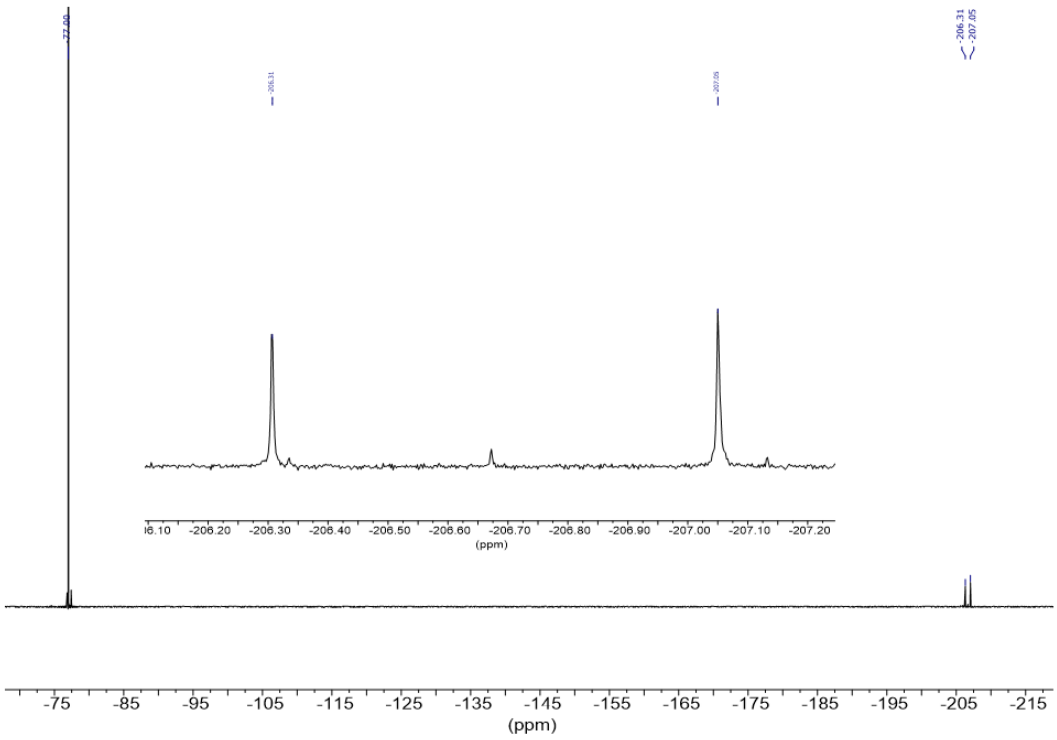

Figure S21. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **1a** + **1b**.

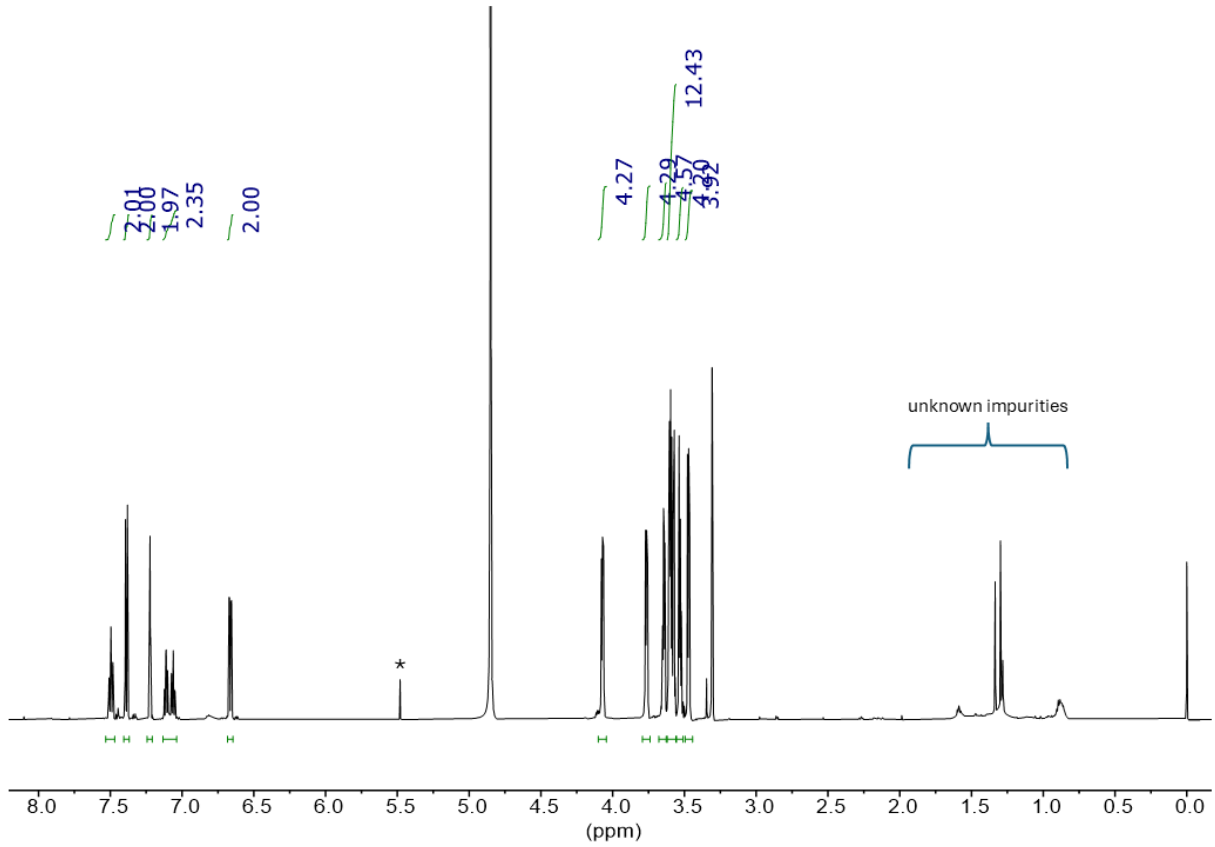

Figure S22. ^{1}H NMR spectrum (600 MHz, CD_3OD) of **6a**. * = CH_2Cl_2.

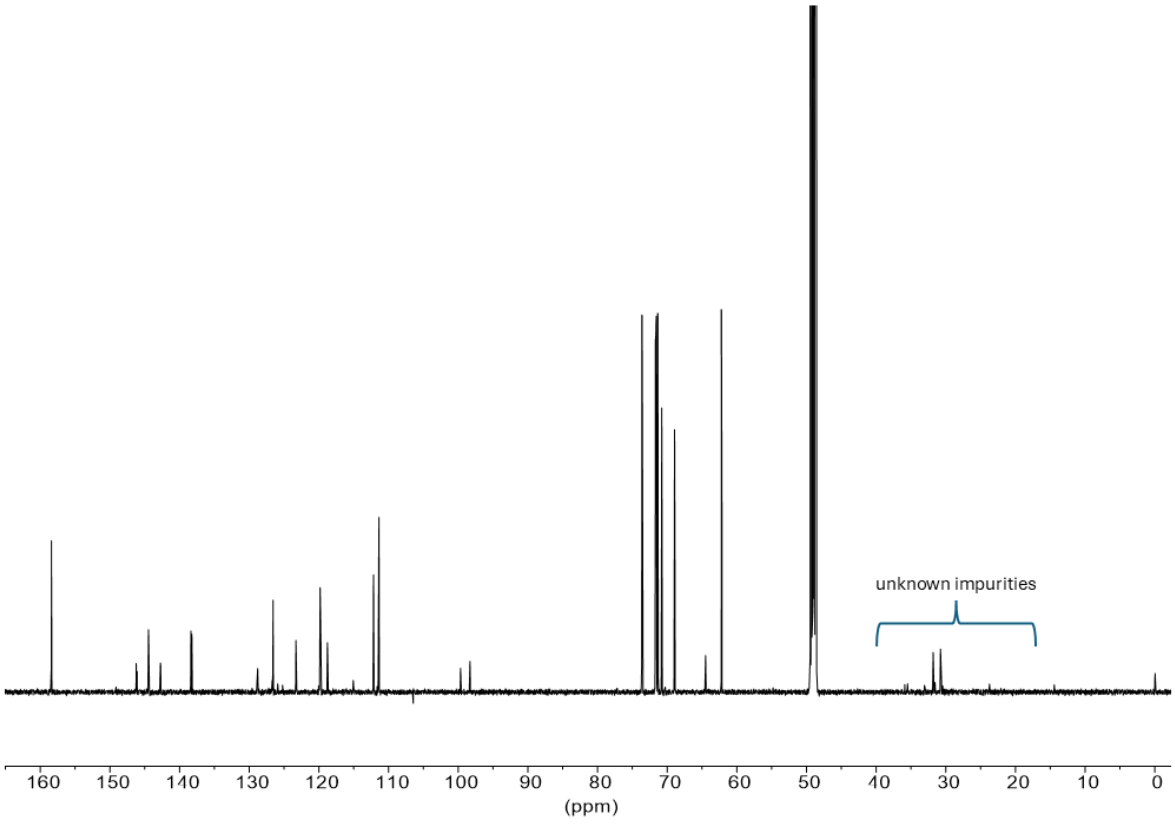

Figure S23. ^{13}C NMR spectrum (151 MHz, CD_3OD) of **6a**.

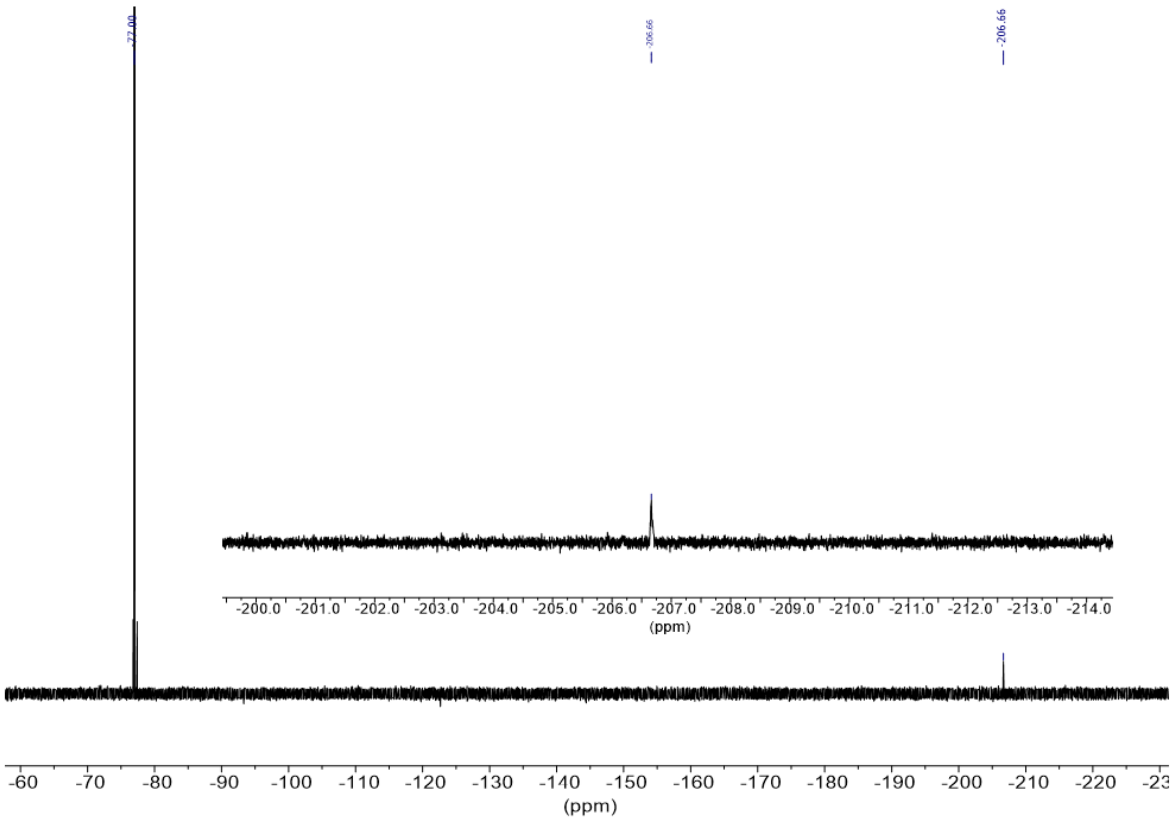

Figure S24. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **6a**.

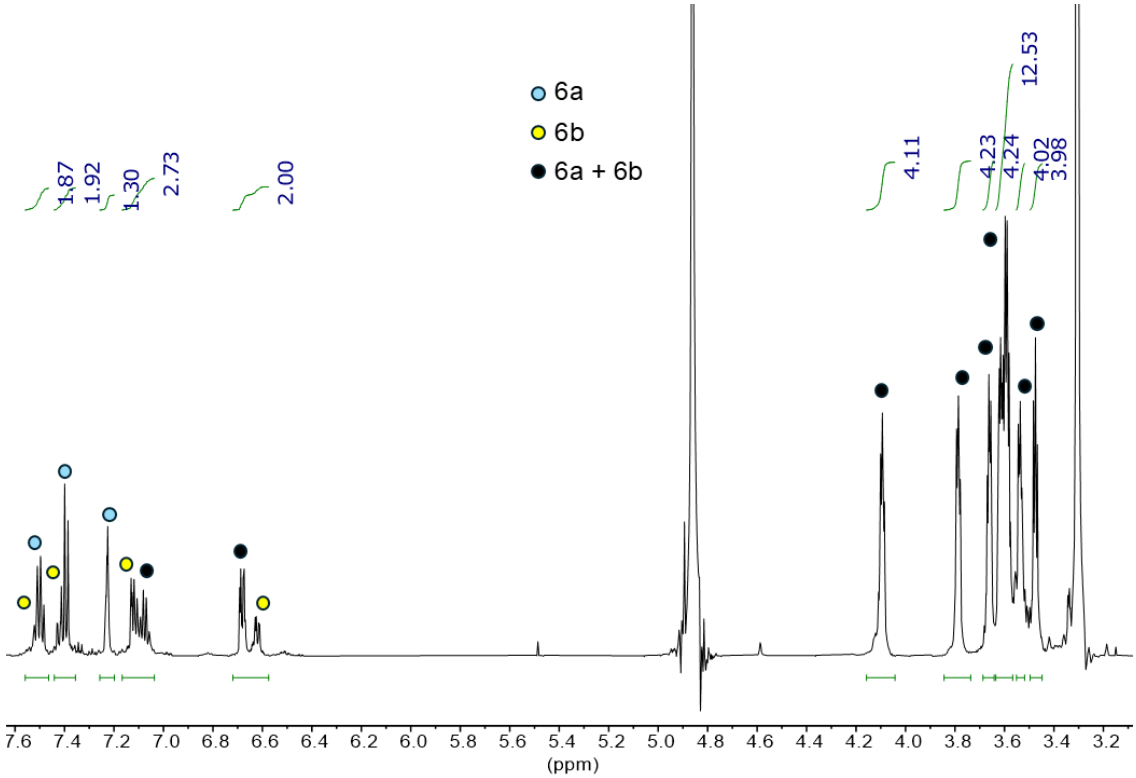

Figure S25. ^{1}H NMR spectrum (600 MHz, CD_3OD) of **6a** + **6b**.

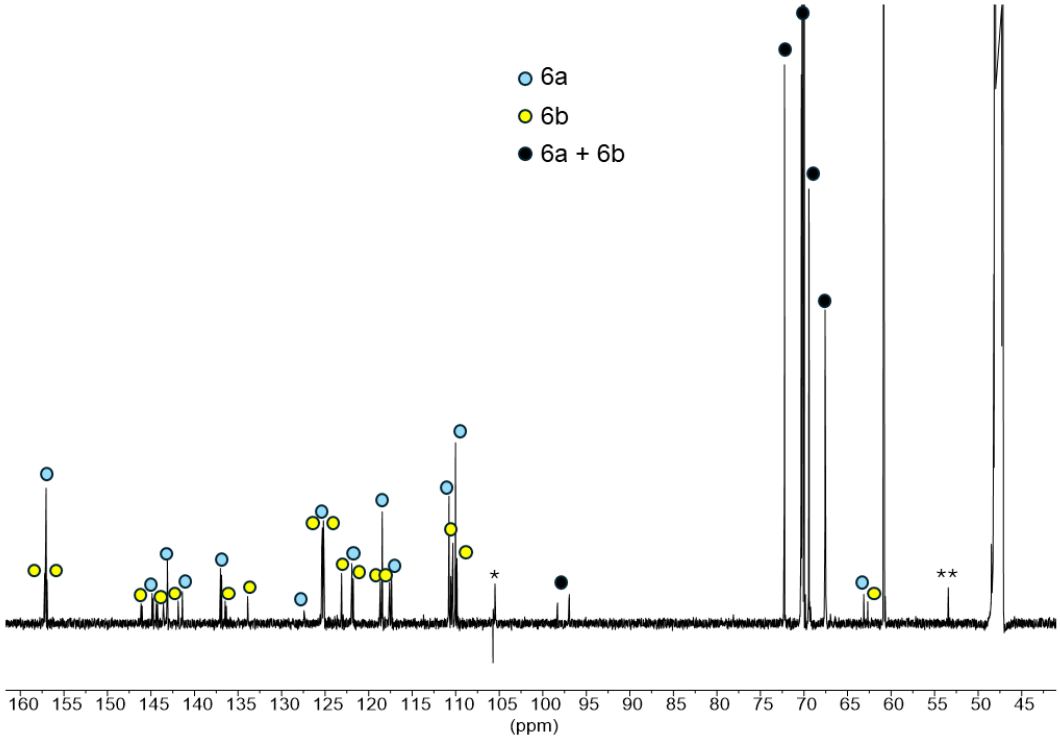

Figure S26. ^{13}C NMR spectrum (151 MHz, CD_3OD) of **6a** + **6b**. * = artefact, ** = CH_2Cl_2.

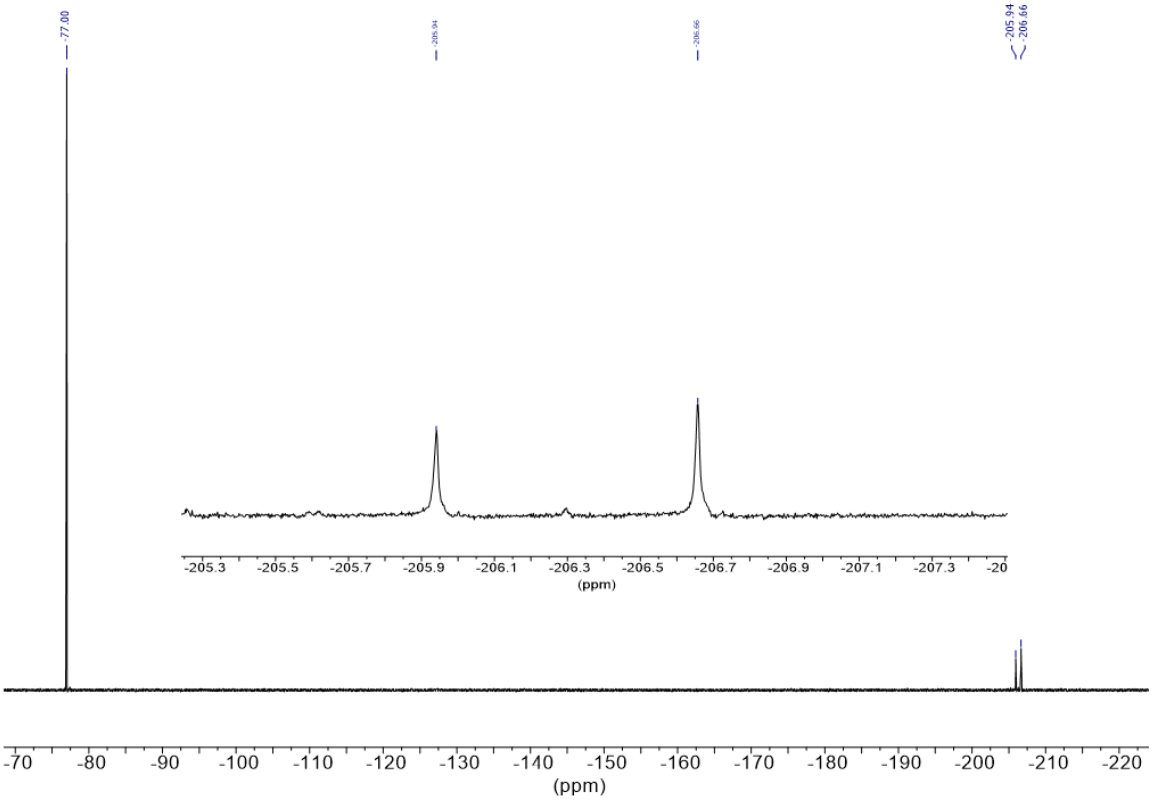

Figure S27. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **6a** + **6b**.

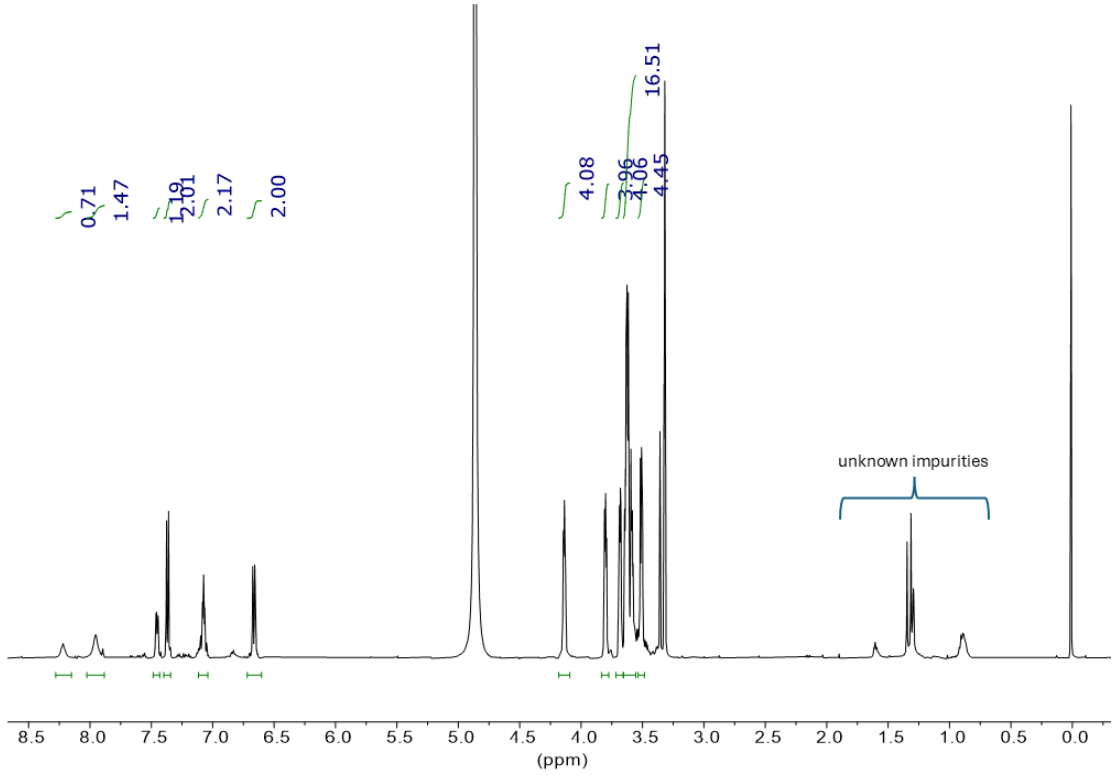

Figure S28. ^{1}H NMR spectrum (500 MHz, CD_3OD) of **7a**.

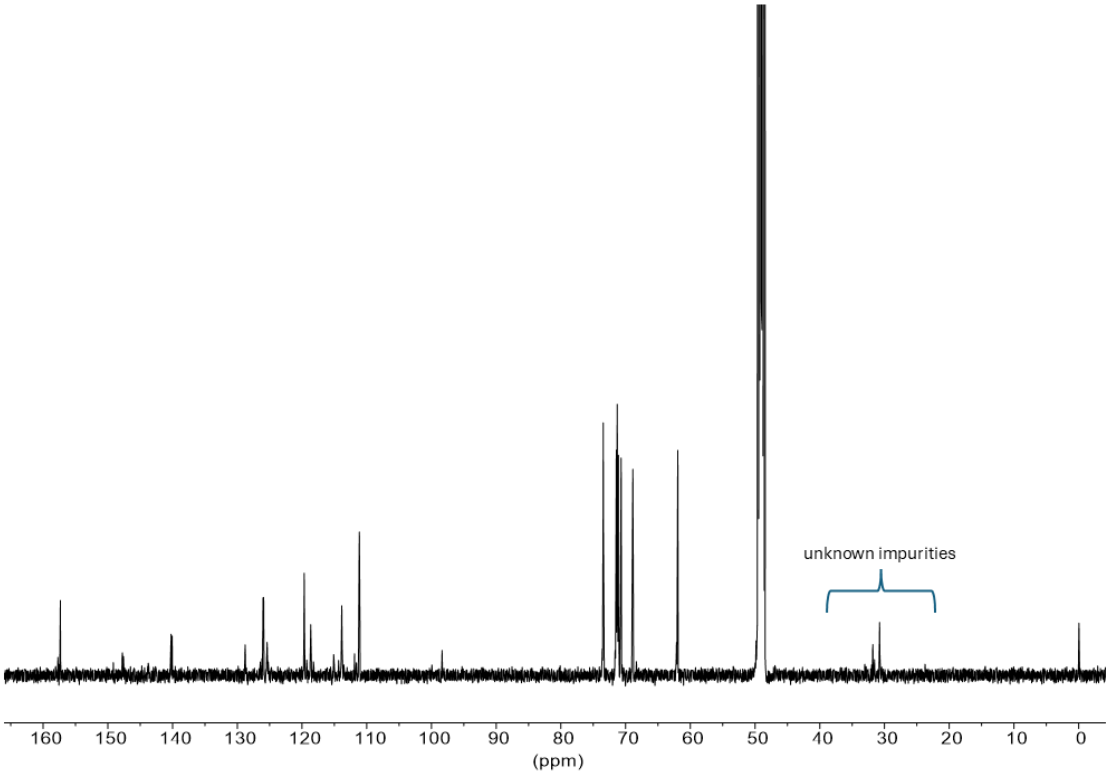

Figure S29. ^{13}C NMR spectrum (126 MHz, CD_3OD) of **7a**.

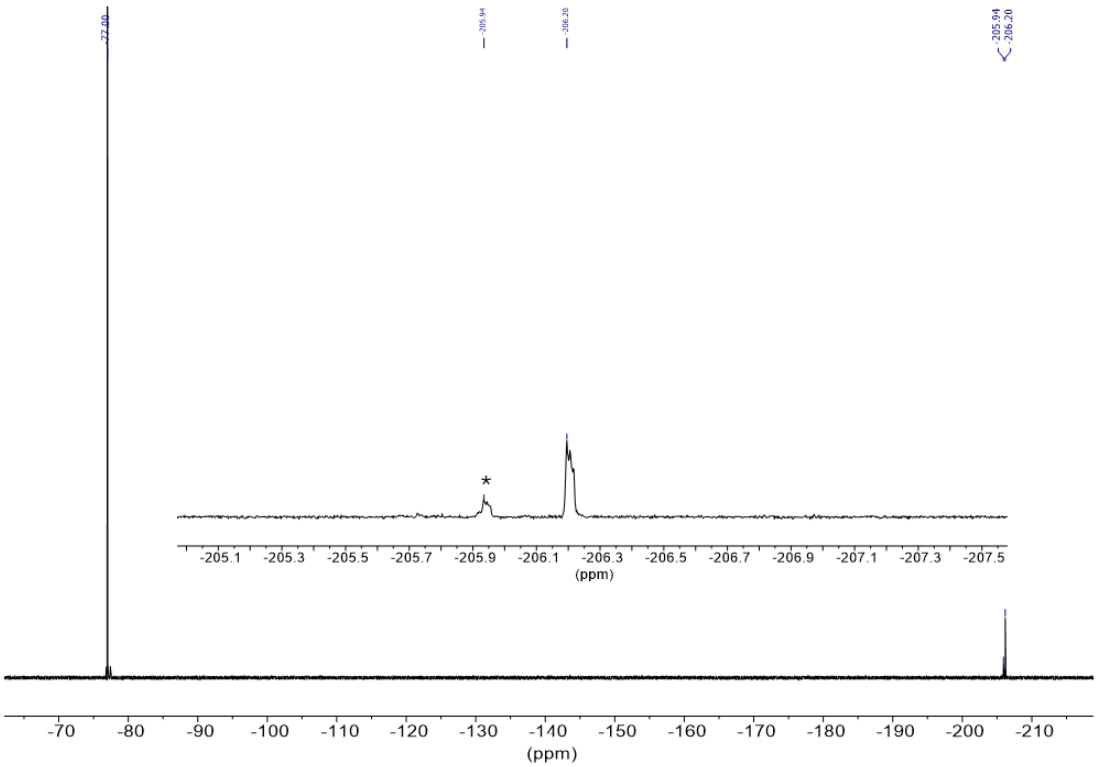

Figure S30. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **7a**. * = **8a** formed as a result of autoxidation of **7a** under ambient conditions.

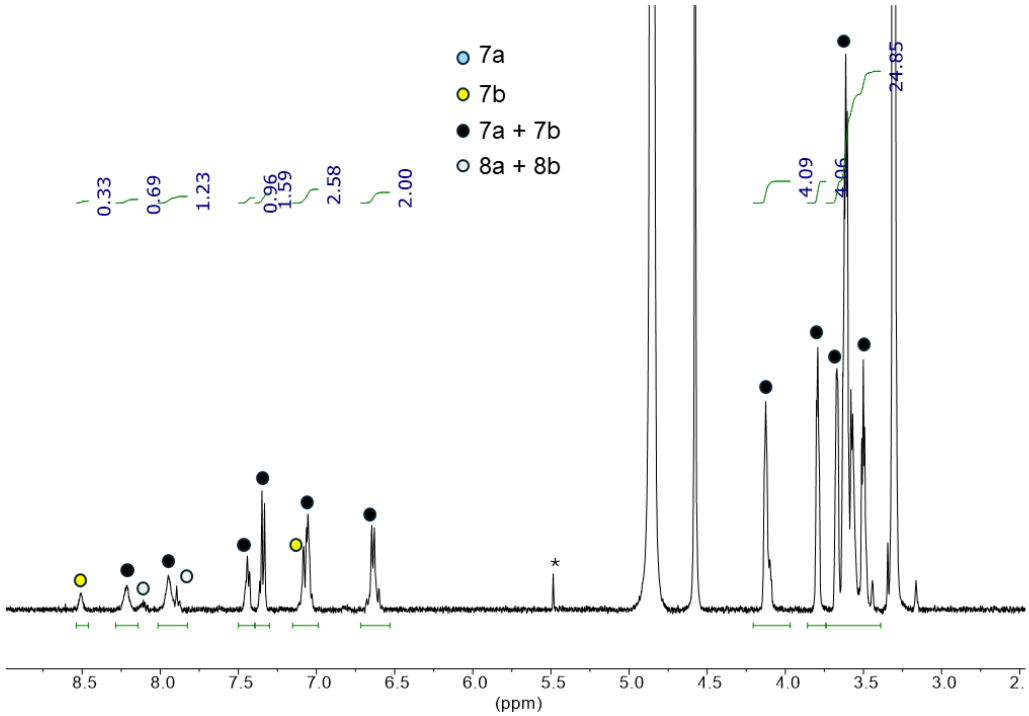

Figure S31. ^1H NMR spectrum (600 MHz, CD_3OD) of **7a** + **7b**. * = CH_2Cl_2. **8a** and **8b** are formed as a result of autoxidation of **7a/b** under ambient conditions.

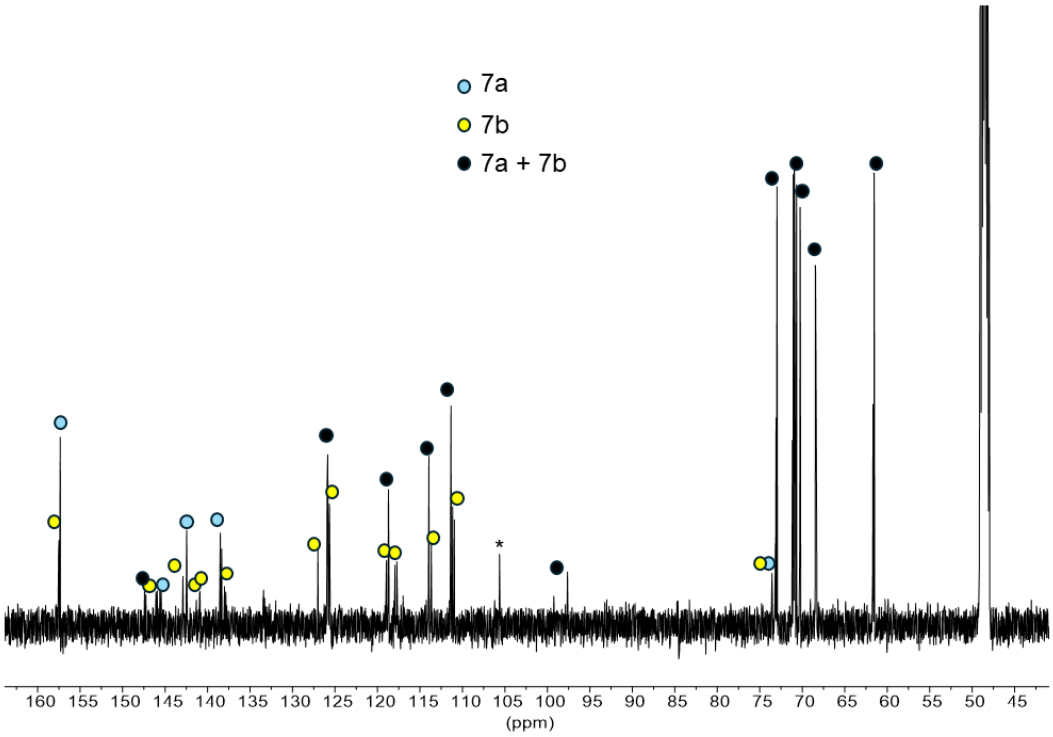

Figure S32. ^{13}C NMR spectrum (151 MHz, CD_3OD) of **7a** + **7b**. * = artefact.

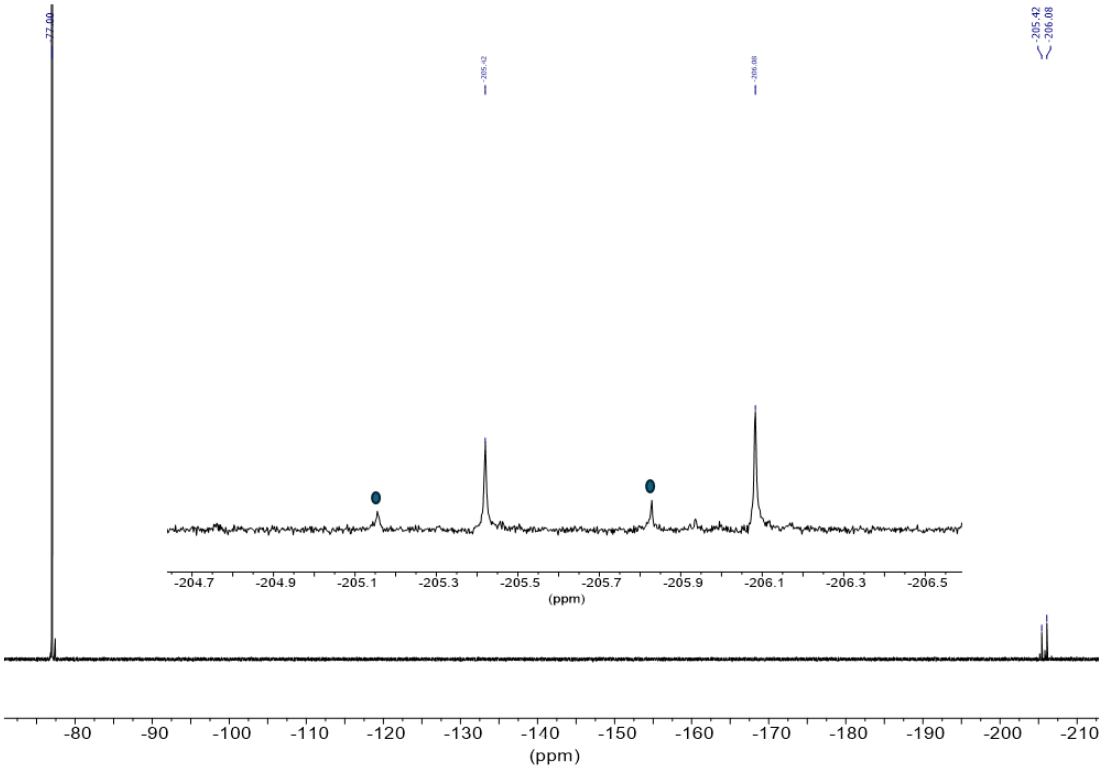

Figure S33. ^{19}F NMR spectrum (471 MHz, D_2O) of **7a** + **7b**. ● = peaks corresponding to **8a** and **8b**.

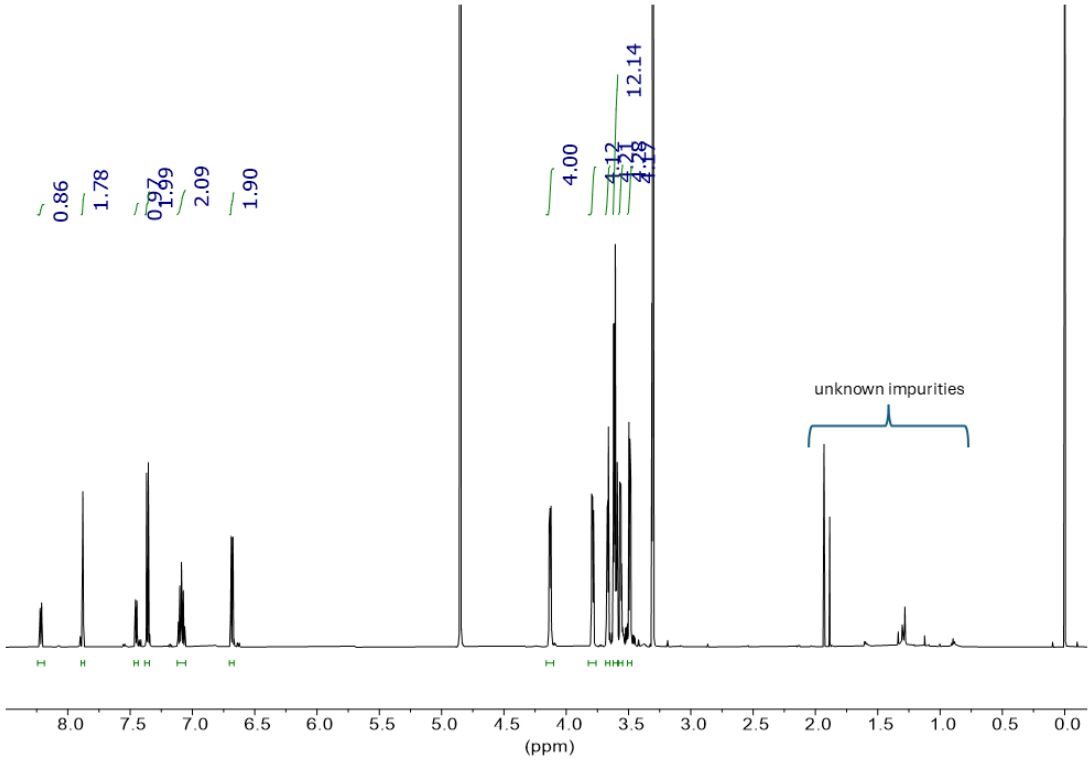

Figure S34. ^{1}H NMR spectrum (600 MHz, CD_3OD) of **8a**.

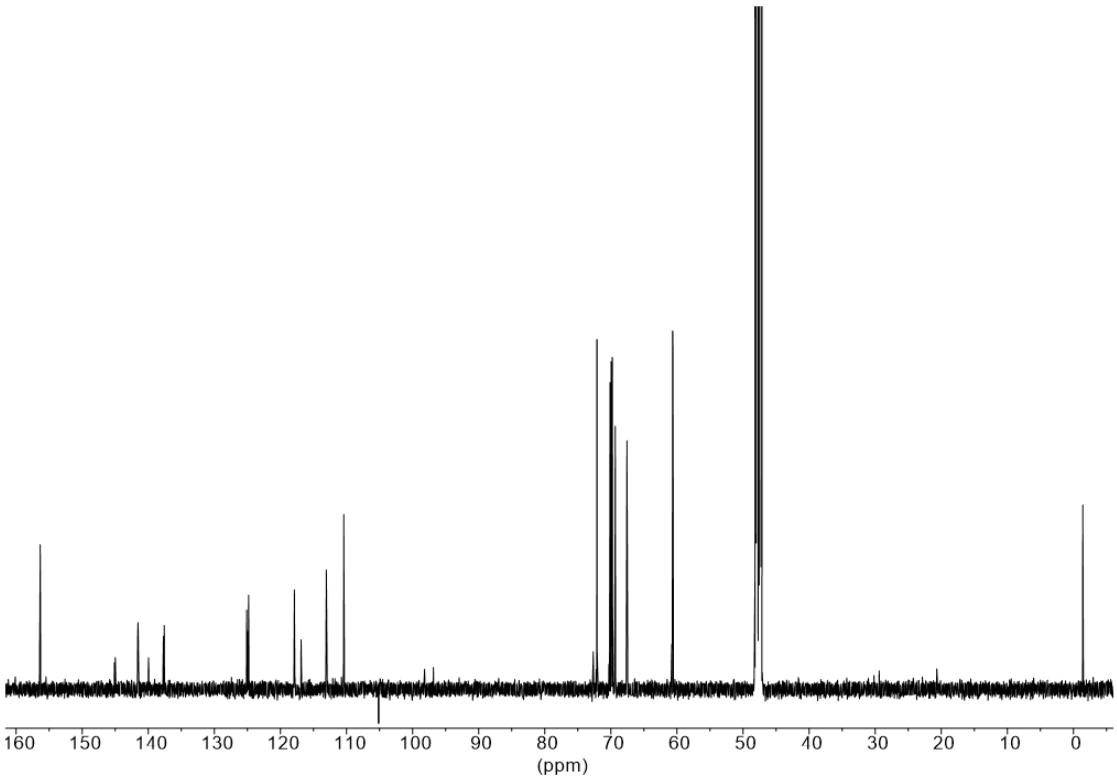

Figure S35. ^{13}C NMR spectrum (151 MHz, CD_3OD) of **8a**.

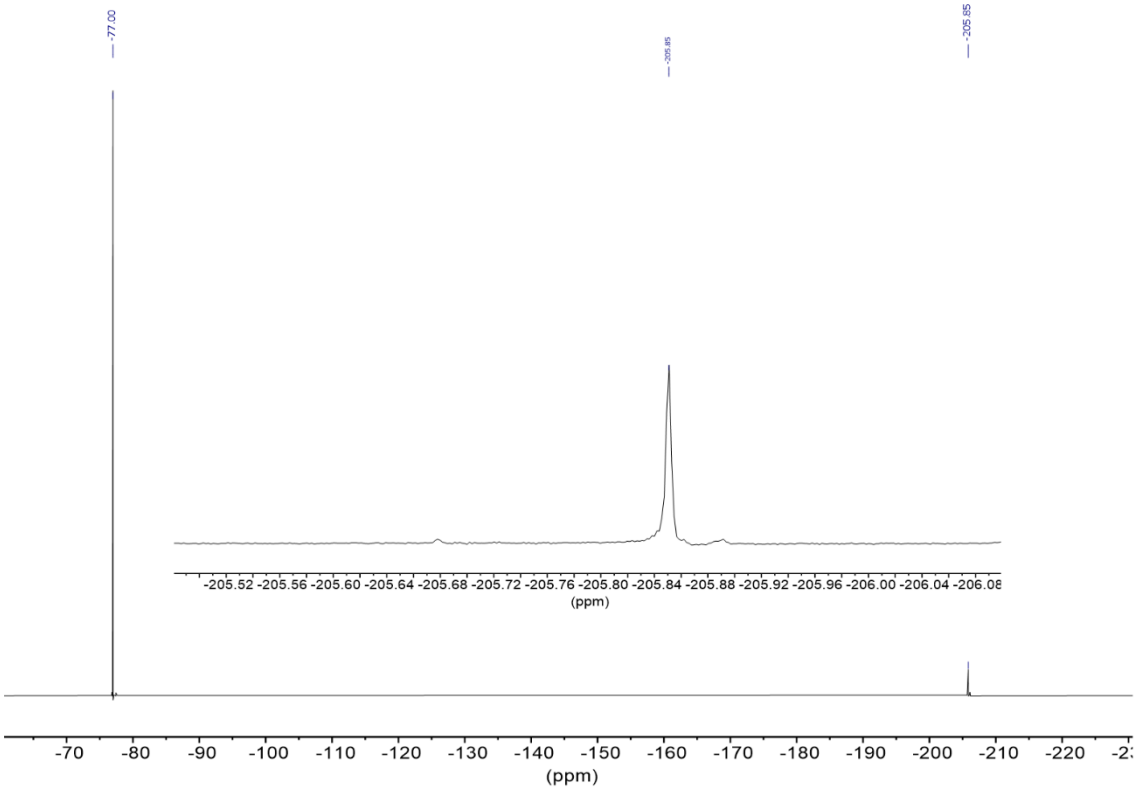

Figure S36. ^{19}F NMR spectrum (471 MHz, D_2O) of **8a**.

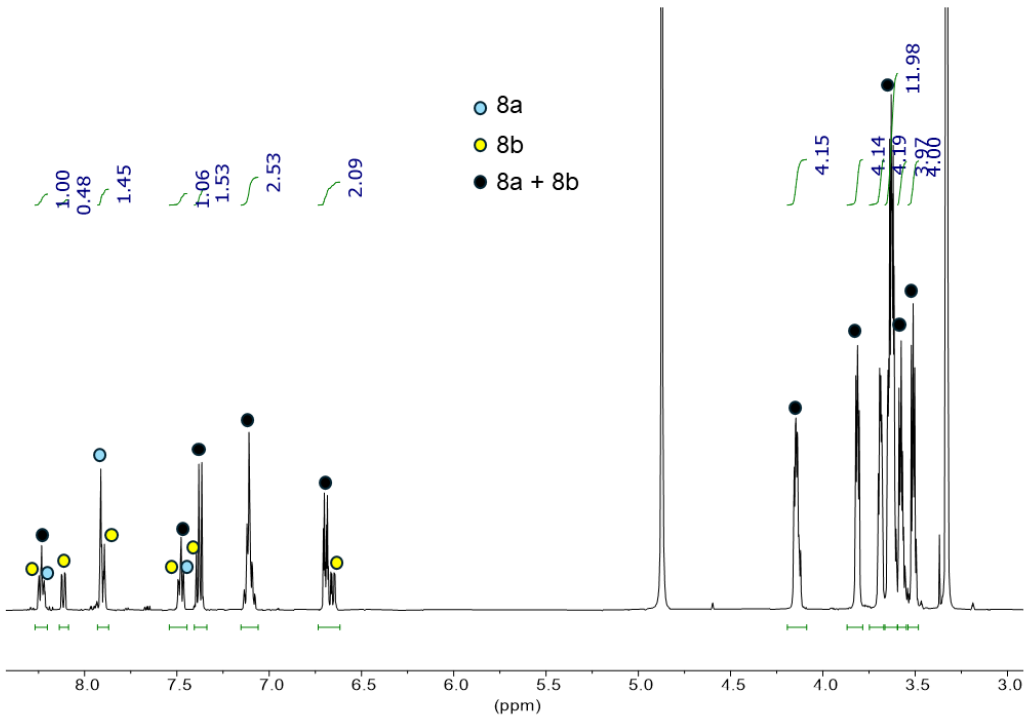

Figure S37. ^{1}H NMR spectrum (600 MHz, CD_3OD) of **8a** + **8b**.

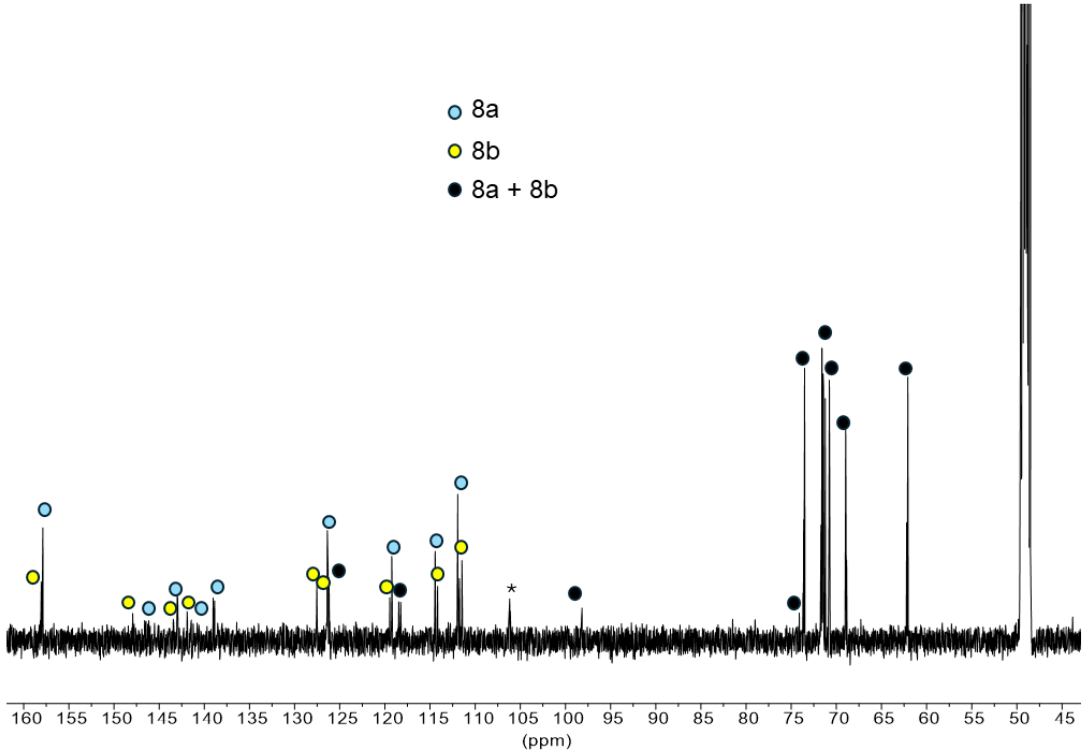

Figure S38. ^{13}C NMR spectrum (126 MHz, CD_3OD) of **8a** + **8b**. * = unknown impurity.

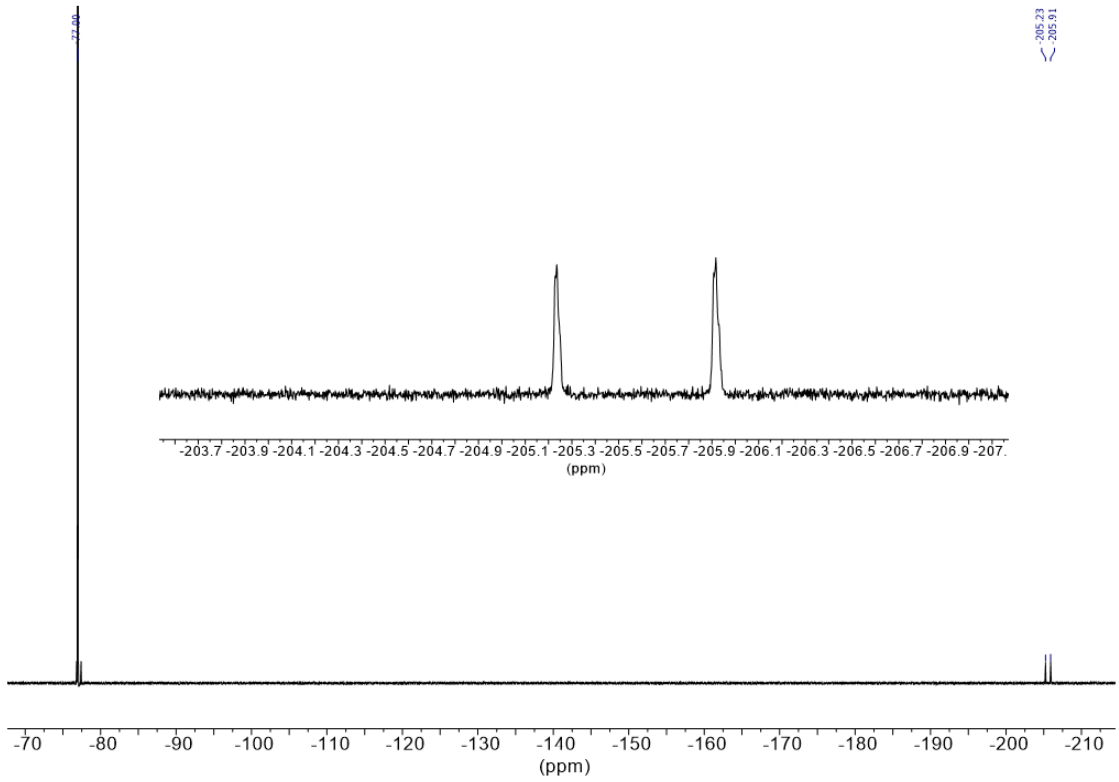

Figure S39. ^{19}F NMR spectrum (471 MHz, D_2O) of **8a** + **8b**.

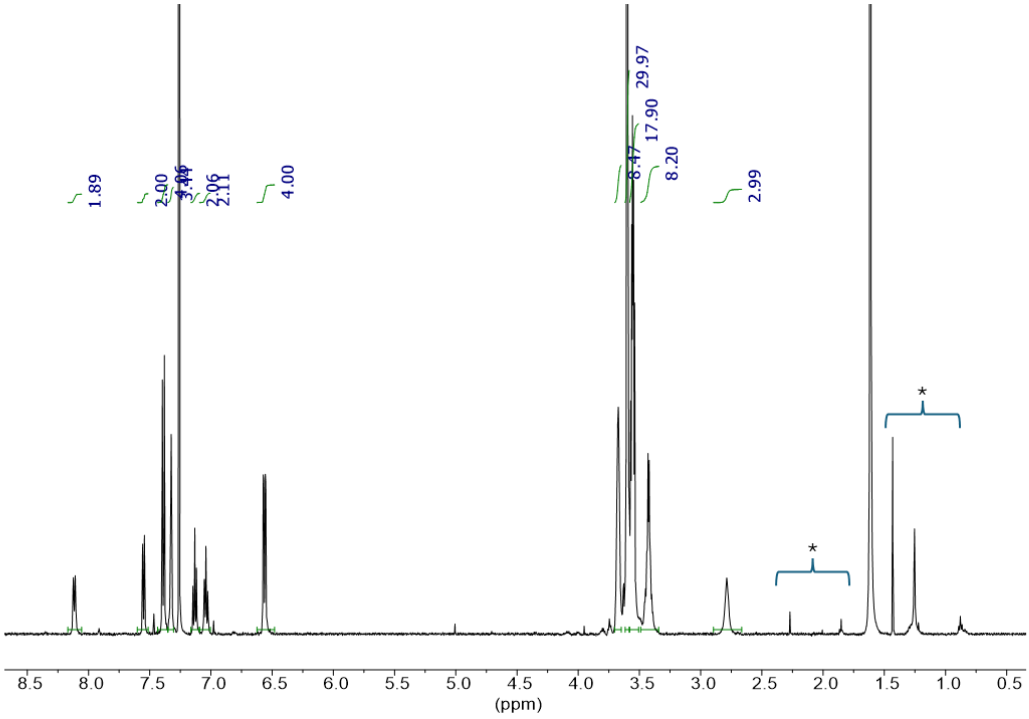

Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **13a**. * = unknown impurities.

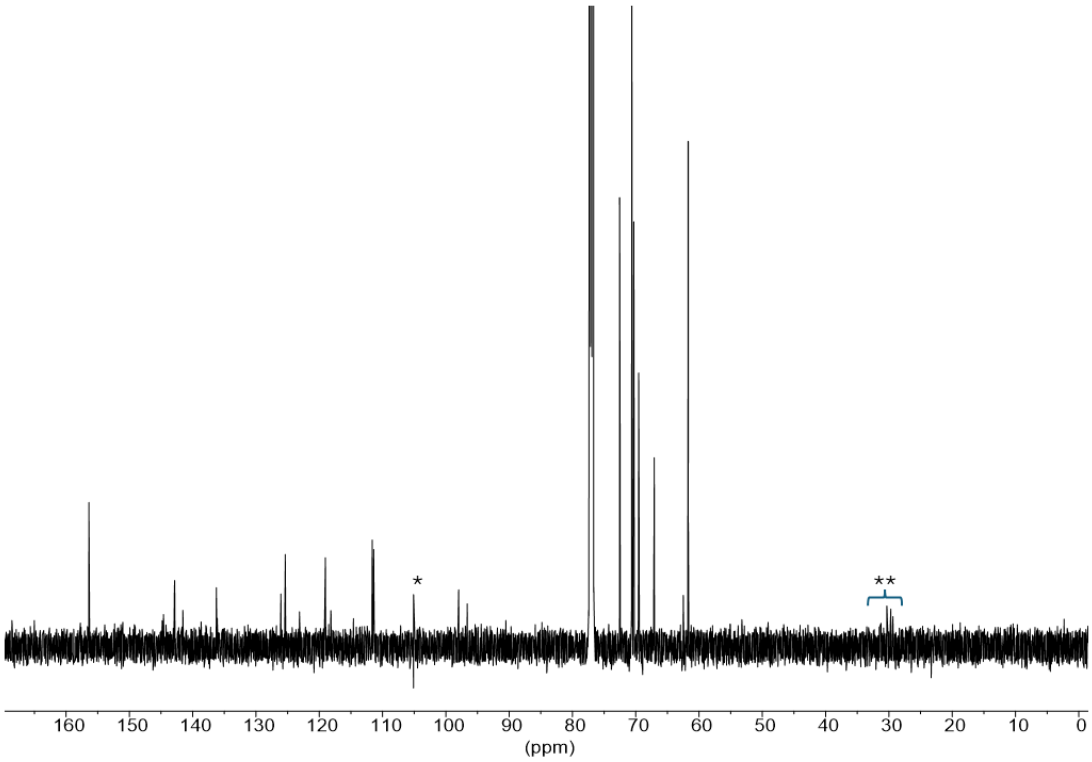

Figure S41. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) **13a**. * = artefact, ** = unknown impurities.

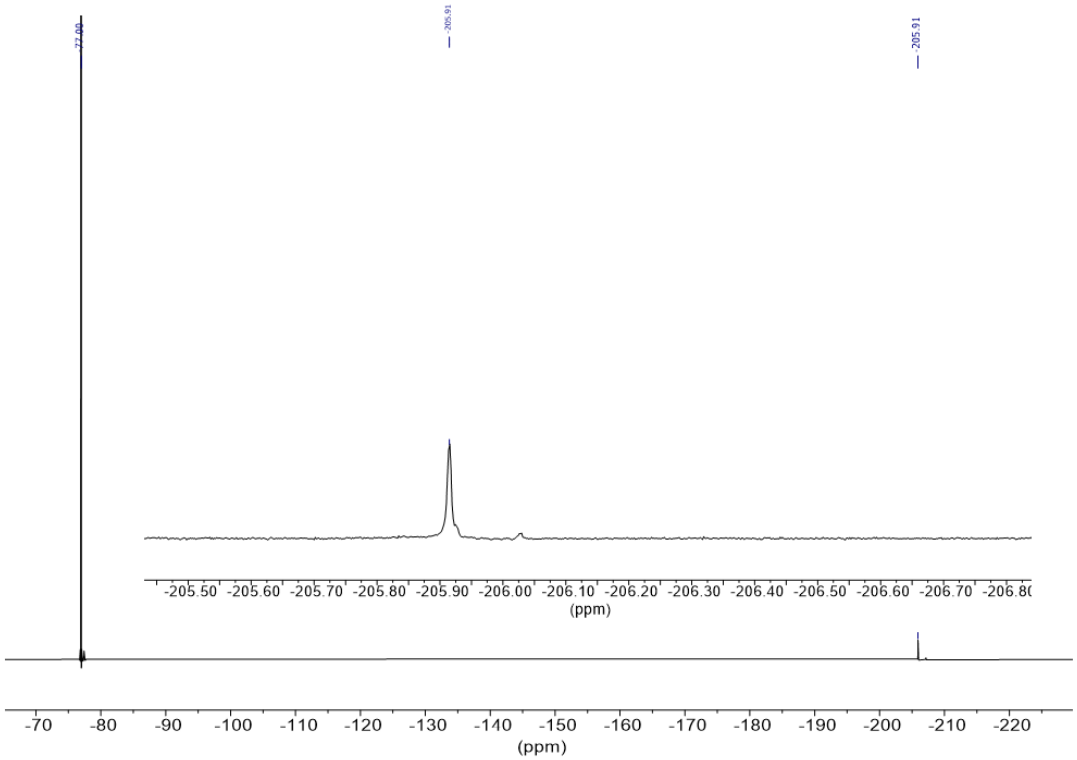

Figure S42. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **13a**.

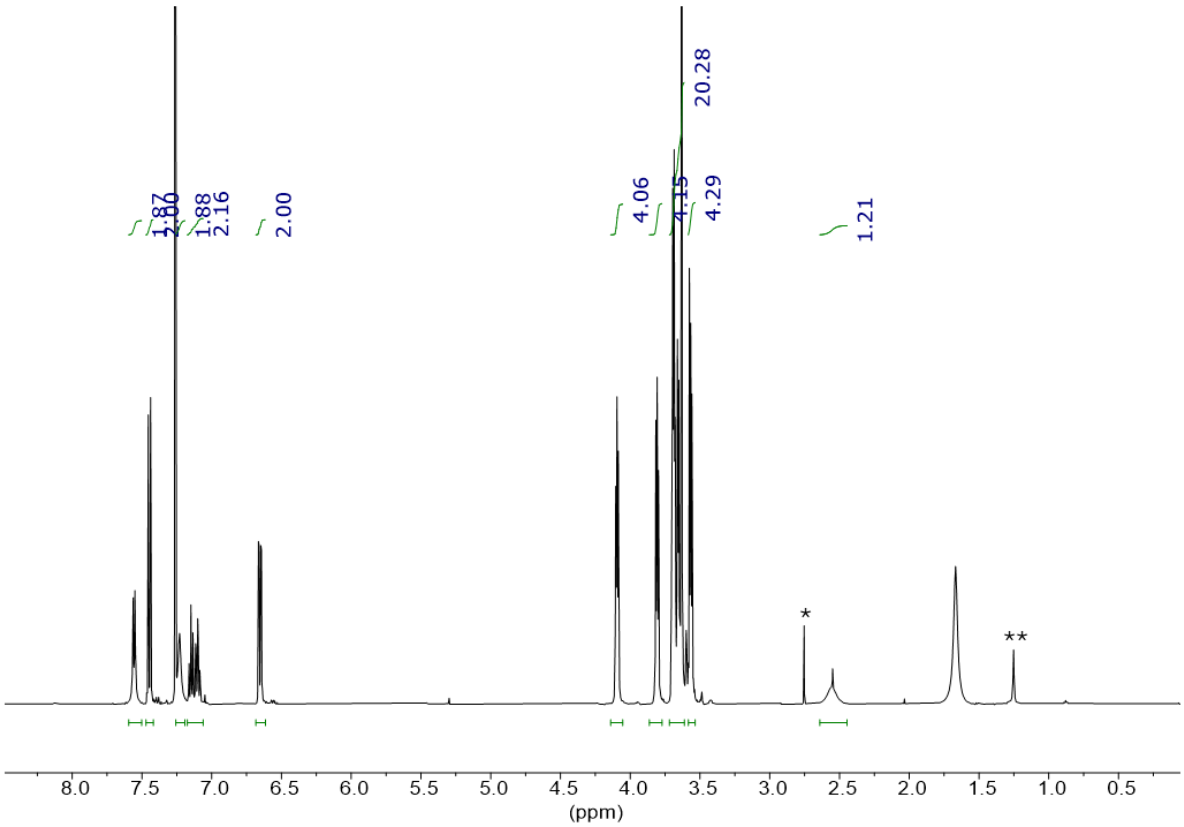

Figure S43. ^1H NMR spectrum (500 MHz, $CDCl_3$) of **14a**. * = N-hydroxysuccinimide, ** = unknown impurity.

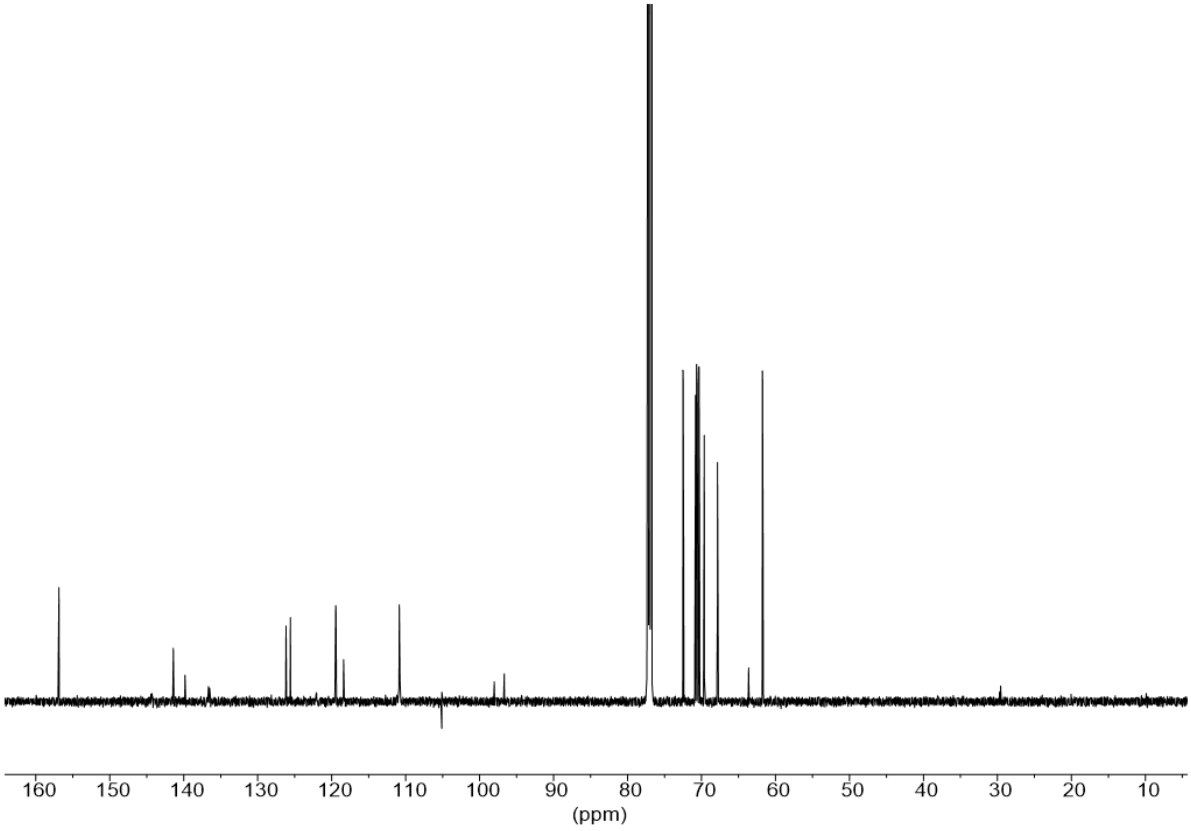

Figure S44. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **14a**.

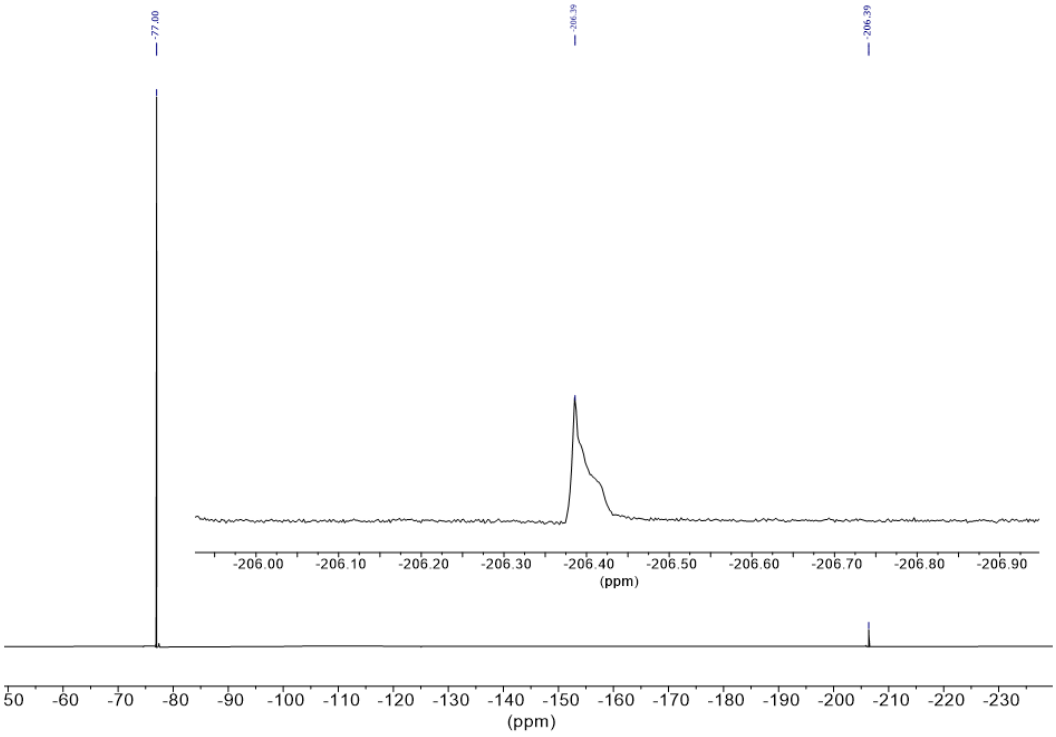

Figure S45. ^{19}F NMR spectrum (471 MHz, D_2O/THF) of **14a**.

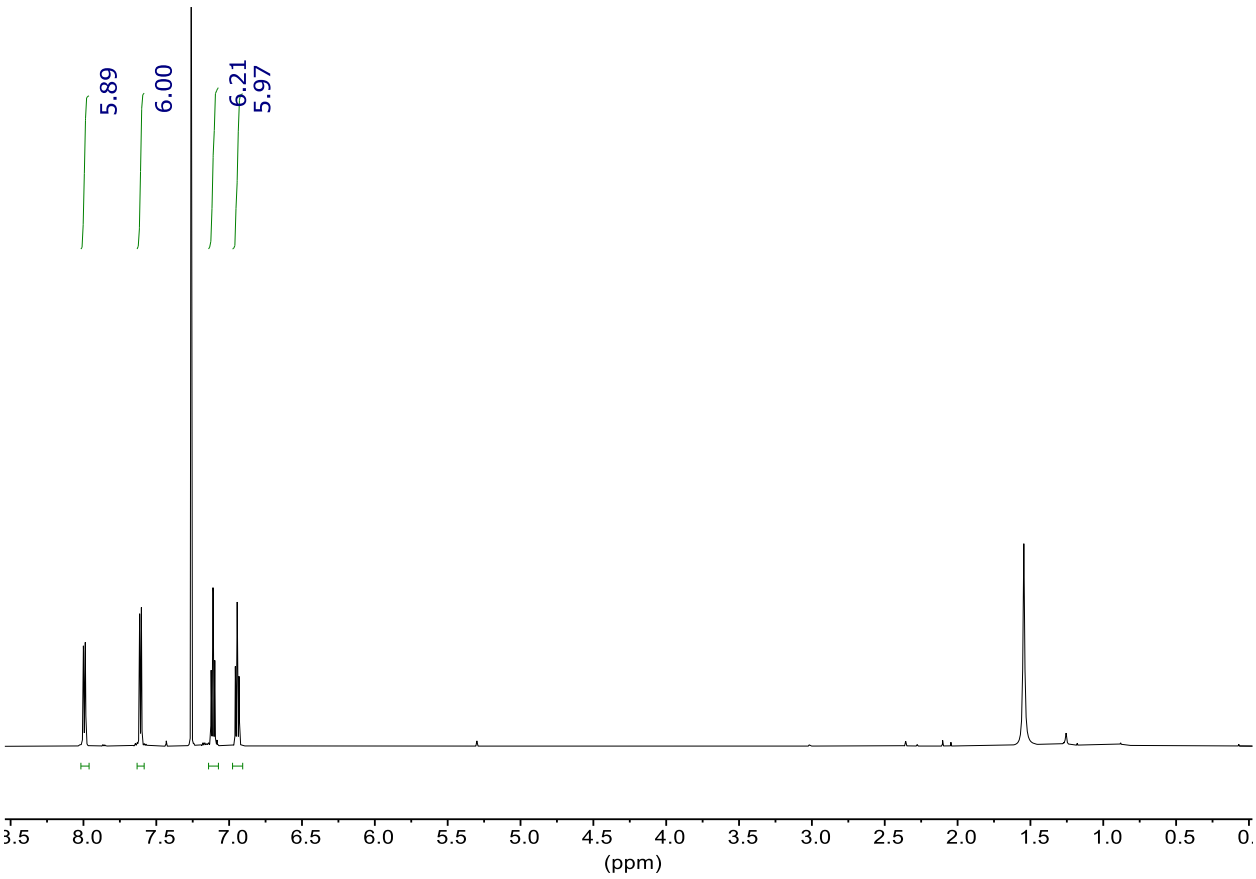

Figure S46. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **15**.

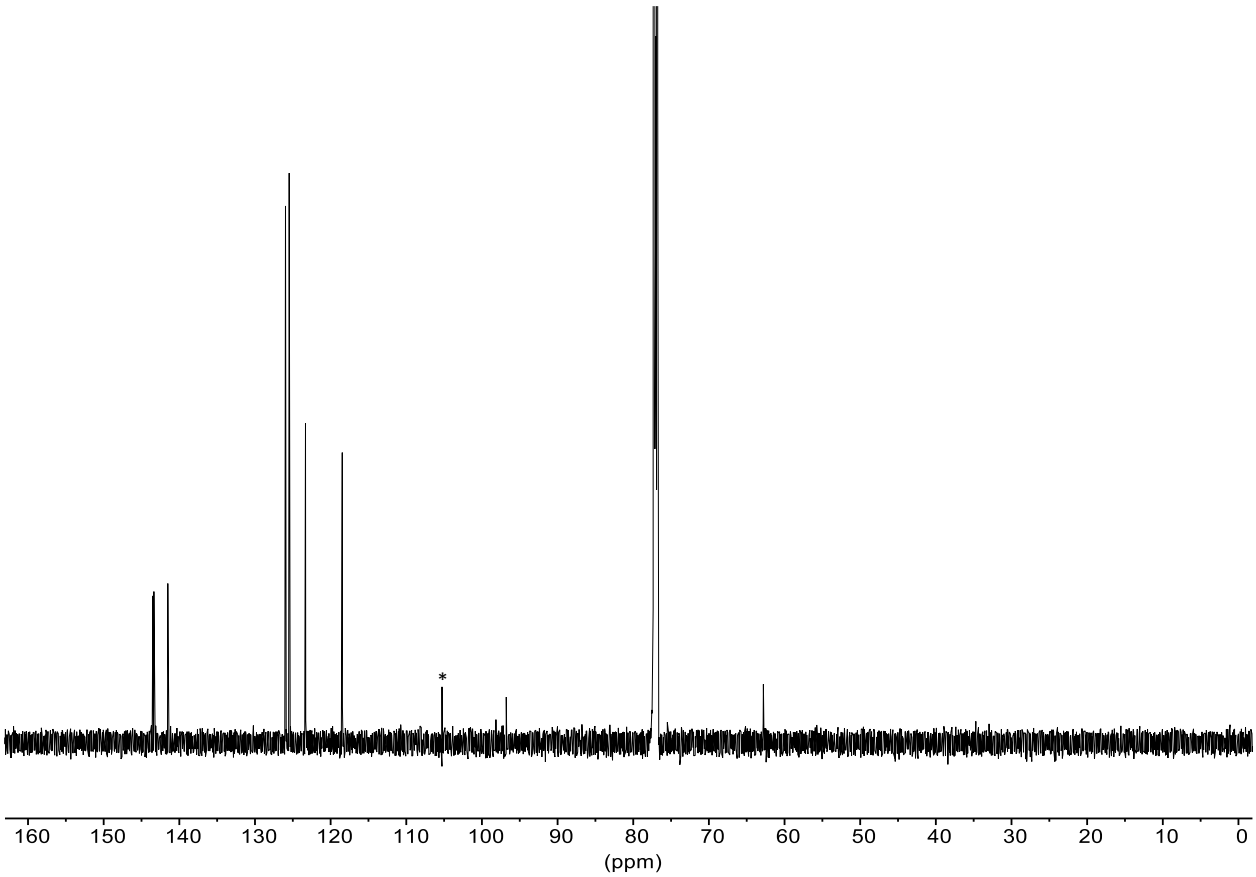

Figure S47. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **15**. * = artefact.

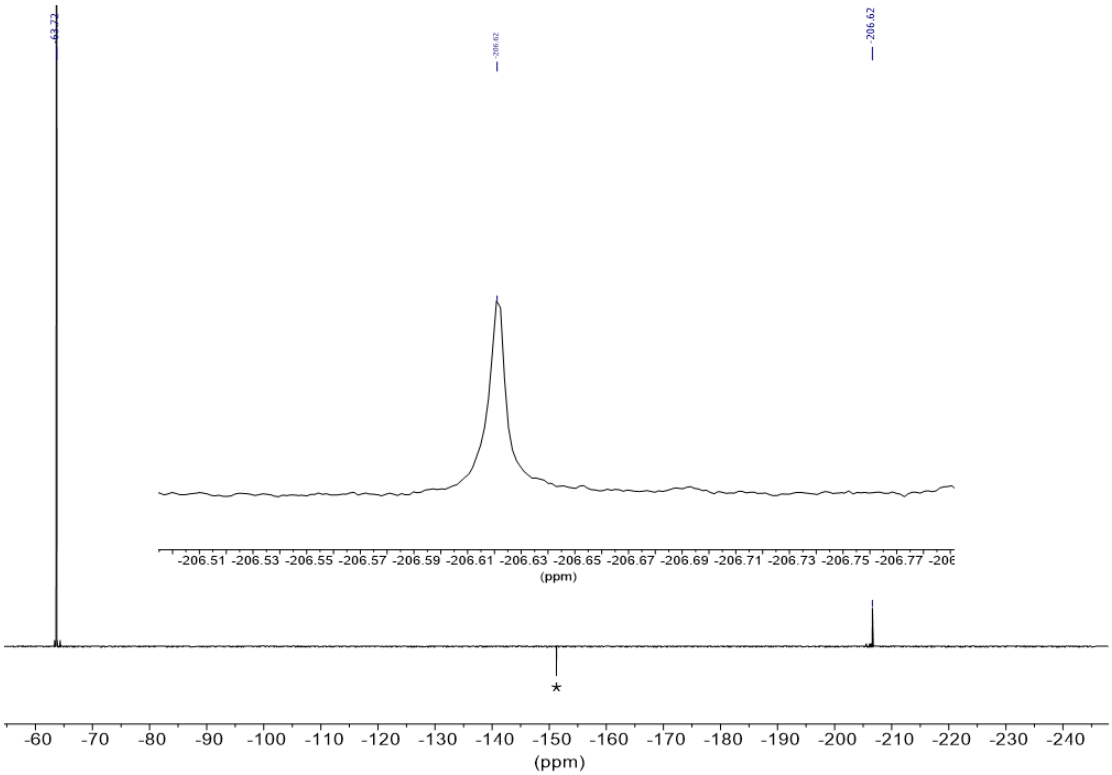

Figure S48. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **15**. * = artefact peak at -151 ppm.

References

1. J.-P. R. Chauvin and D. A. Pratt, *Angewandte Chemie International Edition*, 2017, **56**, 6255–6259.