Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

C(sp^3)–H Ritter amination by excitation of *in situ* generated Iodine (III) - BF_3 complexes

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1 General information

Starting materials and reagents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar, Acros or Fluka) and were used without further purification. Solvents were used as p.a. grade. Reactions were monitored by analytic thin layer chromatography (TLC) using Fluka silica gel or NH2-Modified Silica Plates with a fluorescent indicator. Visualization of the developed TLC chromatogram was performed using 254 nm UV light source. Organic solutions were concentrated using Büchi rotary evaporator. Flash column chromatography was performed either by hand in filled Pasteour pipettes or on a Biotage® IsoleraTM Spektra. The columns were filled either with Silica gel (60-200 µm) or basic alumina (50-200 µm).

NMR spectroscopy

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F) NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant J, number of protons), relative to the solvent residual peaks as the internal standard. Coupling constants J are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet.

Gas chromatography

GC measurements were performed on a GC 7890 from Agilent Technologies system coupled to a FID. The system was equipped with a capillary column (HP-5ms UI, length 30 m, diam. 0.25 mm, film 0.25 µm) and worked with H_2 as carrier gas. GC program: The initial temperature of the GC was set to 40 °C and kept for 1.5 minutes. Subsequently, the oven temperature was increased at a rate of 25 °C/min. until reaching 280 °C, which was maintained for 3 min. Then, temperature was further increased (42 °C/min) until reaching 300 °C and final temperature was hold for 5 minutes. Injector temperature was set to 280 °C and temperature of the detecting unit to 310 °C. A split ratio of 30:1 (split flow 42 mL/min) was applied, and the column flow was set to 1.4 mL/min. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04.

Mass spectrometry

High resolution mass spectrometry (HRMS) was performed at the Central Analytical Laboratory of the University of Regensburg. Mass spectra were measured on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or Agilent Q-TOF 6540 UHD instrumenta and a Waters Acquity UPLC system equipped with Waters PDA, sample manager, sample organiser, column oven and Waters Xevo QTOF mass spectrometer.

UV-Vis

Absorption spectra were measured on an Agilent Cary 100 UV/Vis spectrometer in a 10 mm × 10 mm quartz cuvette at 25.0 °C under air atmosphere.

1.1 Photochemical setups

Photochemical reactions were performed in sealed reaction vials, placed approximately 2 cm above a 400 nm LED array and stirred under irradiation (**Figure S1**). The reaction temperature was controlled by a thermostated (25 °C) metal cooling block. The reactor setup is a custom-made device (University of Regensburg workshop) and is not a commercially available product.

A) regular 400 nm setup (optical power 100-120 mW/ LED spot)

B) Higher power 400 nm setup (optical power 600-800 mW/ LED spot)

Figure S1: Photochemical setups used in this work from different perspectives.

1.2 General experimental procedures

General procedure for preparative scale reactions

The reactions were set in 2 parallel vials, each containing 0.2 mmol of the substrate. A C(sp^3)–H precursor (0.2 mmol, 1 eq.), 4-tertbutylbenzoic acid (17.8 mg, 0.1 mmol, 0.5 eq.) and Selectfluor (142 mg, 0.40 mmol, 2 eq.) were weighed into a crimp reaction vial. Then, 2 ml of a stock solution containing iodobenzene (6.7 µl, 0.06 mmol, 0.3 eq.) and H_2O (3.6 µl, 0.2 mmol, 1 eq.) in dry MeCN were added. A stirring bar was added, and the vial was capped. The reaction mixture was degassed by 4 nitrogen-vacuum cycles. Afterwards BF_3 (200 µl of 16% BF_3 in MeCN, 0.4 mmol, 2 eq.) was added, and the vial was placed in a thermostated cooling block (25 °C) and irradiated through the plane bottom side of the vial by a 400 nm

LED for 16 hours (see **Figure S1**). After the completion, the two reaction batches were combined, and the solvent was removed *in vacuo*. The solid residue was dissolved in 2 ml H_2O and 4 ml EtOAc and transferred into a separatory funnel containing 2 ml of brine. The aqueous layer was washed two times with 5 ml of EtOAc. Combined organic phases were concentrated *in vacuo* to ca 0.5 ml solvent volume. The sample was filtered through a small basic alumina column (packed in a Pasteur pipette). The column was then washed with approximately 5 ml of EtOAc. In that way, we remove remaining hypervalent iodine species, 4-tertbutylbenzoic acid and polymeric side products. The obtained eluent always contained only the product and some remaining substrate. The solvent was removed in vacuo and the product mixture was redissolved in a minimal amount of DCM and applied on silica gel column (packed in a Pasteur pipette). The column was first washed with DCM (5 ml) to elute the remaining substrate, and then with EtOAc (5 ml) to elute the product. Removal of the solvent afforded analytical pure samples of the products. In some cases, we were able to skip the second (silica gel) column. The decision was based on the TLC of the eluent after the first column.

General procedure for screening and optimization studies:

Selectfluor (typically 71 mg, 0.2 mmol, 2 eq.) was weighed into a crimp reaction vial together with any other solid materials (different ligands, Lewis acids/bases, PIDA, PIFA, …). Then, 1 ml of a stock solution containing, 4-fluorotoluene (11.0 µl, 0.1 mmol, 1 eq.), iodobenzene (3.3 µl, 0.03 mmol, 0.3 eq.) and H_2O (1.8 µl, 0.1 mmol, 1 eq.) in dry MeCN were added. A stirring bar was added, and the vial was capped. The reaction mixture was degassed by 4 nitrogen-vacuum cycles. Afterwards, BF_3 (100 µl of 16% BF_3 in MeCN, 0.2 mmol, 2 eq.) or any other liquids (Lewis acids) were added, and the vial was placed in a thermostated cooling block (25 °C) and irradiated through the plane bottom side of the vial by a 400 nm LED for 16 hours (see **Figure S1**). After the completion, the analysis was done following the typical procedure for 19F NMR yield determination (*vide infra*).

Note: The reaction is a bit sensitive (**Table S3**) to the amount of water in the reaction mixture. Stock solutions containing 4-fluorotoluene, H_2O and PhI were always used in order to have all the entries within the series (optimization table) comparable.

Procedure for NMR yield determination

The screening and optimization reactions were all performed on a 0.1 mmol scale following the above-described general procedure. After the reaction completion, internal standard trifluorotoluene (12.3 µl, 0.1 mmol) was added into the vial. The reaction vial was well shaken before we took out 0.4 ml of the reaction mixture and transferred it into a 2 ml conical bottom Eppendorf vial. Then 0.4 ml $CDCl_3$ was added to precipitate the remaining Selectfluor and quench the reaction. The vials were centrifuged, and the clean solution was submitted for ^{19}F NMR analysis.

2 UV-Vis of hypervalent iodine (III)-BF_3 complex of 1i

The absorption increases upon addition of BF_3 to the hypervalent iodine reagent **1i** due to the formation of the complex **1i-BF_3**.[1]

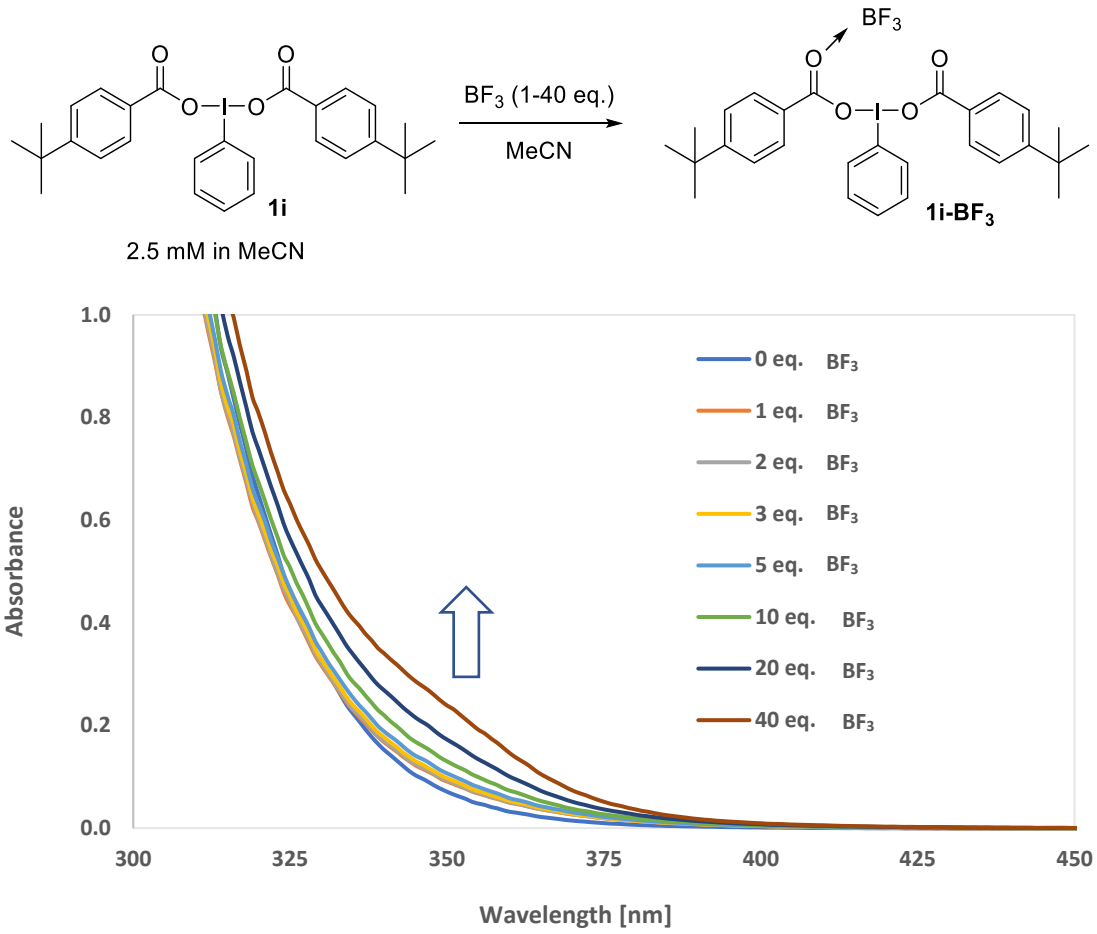


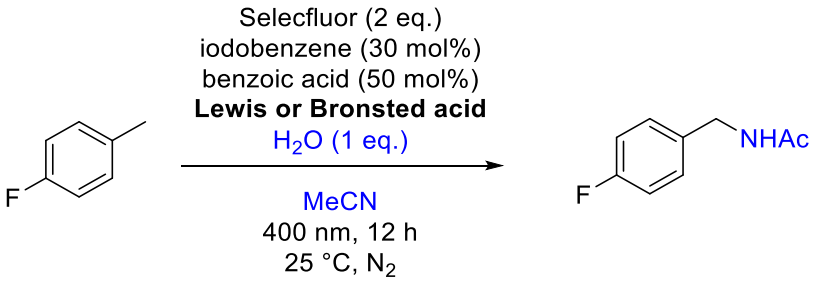
Figure S2: Spectral changes upon addition of BF_3 to **1i**.

3 Optimization tables

3.1 Screening of different Lewis acids

Different acids have been screened for the C-H Ritter type amination. Most of the tested acids are ineffective supporting our previously disclosed findings about necessity of complexation of the hypervalent iodine reagent with BF_3.[2]

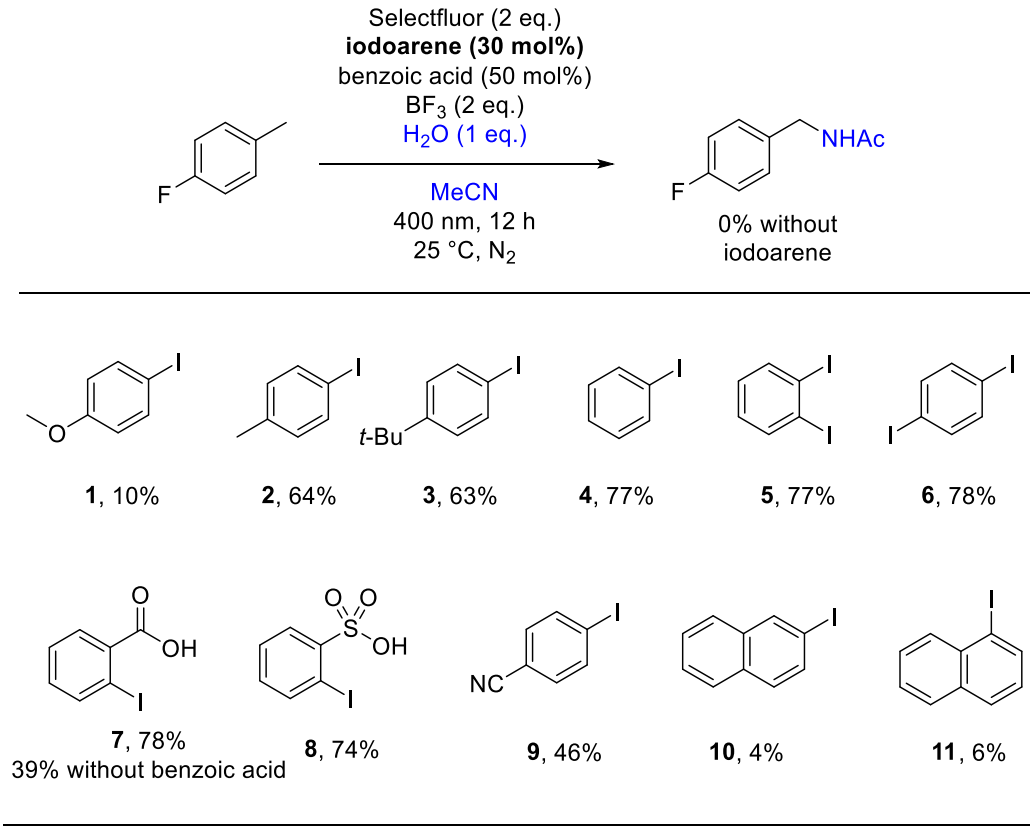
Table S1: Screening of different Lewis acids.



Entry	Acid/base	Yields [%]
A	-	14
B	Cs_2CO_3 (2 eq.)	0
C	TFA (2 eq.)	15
D	H_2SO_4 (2 eq.)	48
E	$HClO_4$ (70%, 2 eq.)	36
F	HFIP (2 eq.)	13
G	**BF_3 (16% in MeCN, 2 eq.)**	77
H	$BF_3 \times 2H_2O$ (2 eq.)	21
I	$B(OH)_3$ (2 eq.)	18
J	HBF_4 (32% in water, 2 eq.)	26
K	$LiBF_4$ (2 eq.)	13
L	$Zn(OTf)_2$ (0.5 eq.)	20
M	$Sc(OTf)_3$ (0.5 eq.)	28

0.1 mmol substrate, 30 mol% of the PhI, 50 mol% benzoic acid, 2 eq. Selectfluor, 2 eq. or 0.5 eq. of the indicated Lewis acid, 1 eq. H_2O, 1 ml MeCN (0.1 M) under N_2 atmosphere, 25 °C, 12 h. Yields were determined by ^{19}F NMR using trifluorotoluene as internal standard.

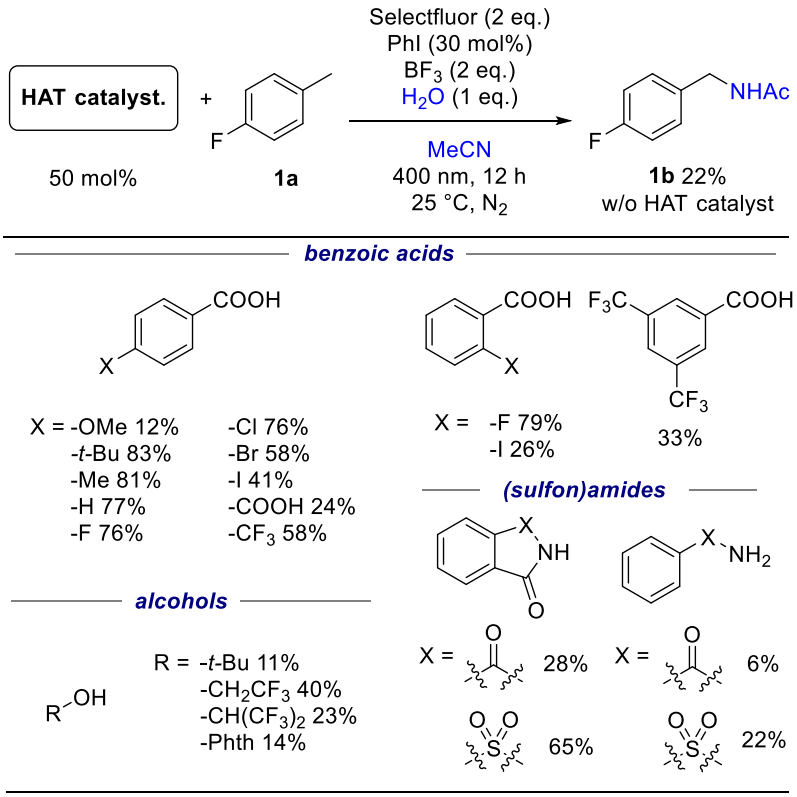
3.2 Screening of different iodoarenes



Scheme S1: Screening of different iodoarenes, precursors of the *in situ* formed hypervalent iodine (III) reagent. [a] 0.1 mmol substrate, 30 mol% of the indicated ArI, 50 mol% benzoic acid, 2 eq. Selectfluor, 2 eq. $BF_3 \times MeCN$, 1 eq. H_2O, 1 ml MeCN (0.1 M) under N_2 atmosphere, 25 °C, 12 h. Yields were determined by ^{19}F NMR using trifluorotoluene as internal standard.

Iodoarenes **10** and **11** underwent decomposition after the addition of BF_3 even without light irradiation.

3.3 Screening of different HAT catalysts



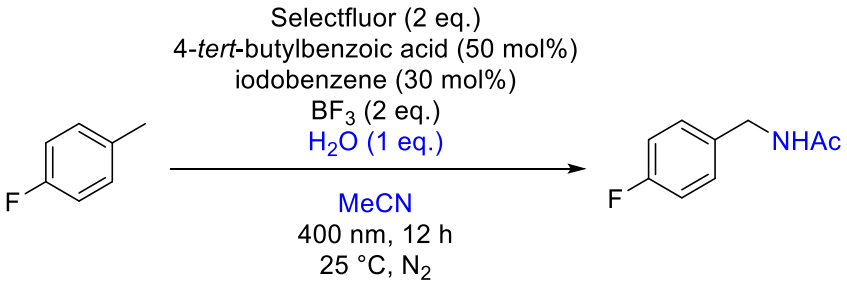
Scheme 2: Optimization of the ligand of the hypervalent iodine (III) reagent for hydrogen abstraction. [a] 0.1 mmol substrate, 30 mol% PhI, 50 mol% of the indicated HAT reagent, 2 eq. Selectfluor, 2 eq. BF_3 × MeCN, 1 eq. H_2O, 1 ml MeCN (0.1 M) under N_2 atmosphere, 25 °C, 12 h. Yields were determined by ^{19}F NMR using trifluorotoluene as internal standard.

Table S2: Correlation of substituent electronic properties of the benzoic acid with the reaction yield.

Substituent	Hammet constant σ_p[3]	Reaction yield	Note
-OMe	-0.27	12%	Decomposition
-*t*-Bu	-0.20	83%	
-Me	-0.17	81%	
-H	0.00	77%	
-F	0.06	76%	
-I	0.18 or 0.88 for -I(OAc)$_2$	41%	4-Iodobenzoic gets oxidized under the reaction conditions.
-Cl	0.22	76%	
-Br	0.23	58%	
-COOH	0.45	24%	Solubility issue. The iodine (III) reagent is not dissolved even after addition of BF_3.
-CF_3	0.54	58%	

3.4 Optimization of catalysts loadings and reagent quantities

Table S3:Effect of catalysts loadings and reagent quantities.

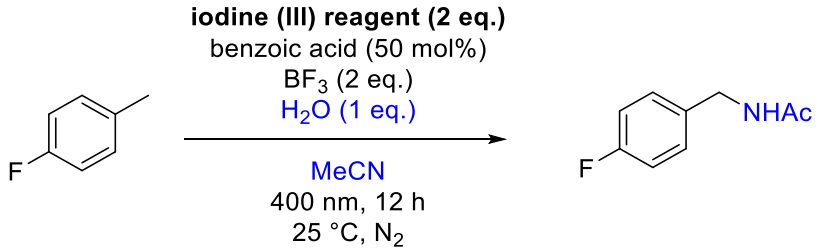


Entry	Selectfluor [eq.]	*4-tert*-butylbenzoic acid [mol%]	PhI [mol%]	BF_3 [eq.]	H_2O [eq.]	λ [nm]	Yield [%]
A	1	50	30	2	1	400	57
B	1.3	50	30	2	1	400	69
C	1.5	50	30	2	1	400	77
D	**2**	**50**	**30**	**2**	**1**	**400**	**83**
E	2	30	30	2	1	400	71
F	2	10	30	2	1	400	32
G	2	50	20	2	1	400	77
H	2	50	10	2	1	400	74
I	2	50	30	1	1	400	35
J	2	50	30	3	1	400	80
K	2	50	30	2	5	400	21
L	2	50	30	2	1	455	79
M	2	50	30	2	1	525	21

[a] All the entries are deviations of the entry D: 0.1 mmol substrate, 30 mol% PhI, 50 mol% of the 4-*tert*-butylbenzoic acid, 2 eq. Selectfluor, 2 eq. BF_3 × MeCN, 1 eq. H_2O, 1 ml MeCN (0.1 M) under N_2 atmosphere, 25 °C, 12 h. Yields were determined by ^{19}F NMR using trifluorotoluene as internal standard.

3.5 Control experiments with different iodine (III) sources and additives

Table S4: Control experiments with preformed iodine (III) reagent.



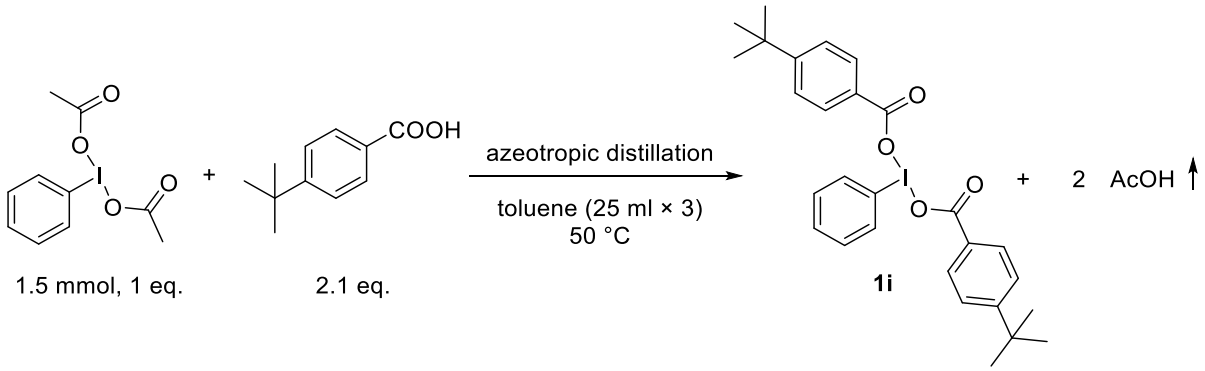
Entry	Iodine (III) reagent	BF_3	Additive	Yield [
A	$PhI(OAc)_2$ (2 eq.)	Yes	-	19
B	$PhI(OAc)_2$ (2 eq.)	-	-	3
C	$PhI(OC(O)CF_3)_2$ (2 eq.)	Yes	-	8
D	$PhI(OC(O)CF_3)_2$ (2 eq.)	-	-	7
E	Selectfluor (2 eq.) + PhI (0.3 eq.)	Yes	-	77
F	Selectfluor (2 eq.) + PhI (0.3 eq.)	Yes	AcOH (4 eq.)	73
G	Selectfluor (2 eq.) + PhI (0.3 eq.)	Yes	TFA (4 eq.)	77

The approach by *in situ* generation of aryl iodine (III) reagent gives higher yield than the use of commercially available aryliodine (III) reagents. A possible reason could be competitive decarboxylation of (trifluroo)acetate ligands in the reaction conditions. This parasitic reaction leads to unproductive consumption of the hypervalent iodine (III) reagent.

4 Synthesis and characterization of starting materials, intermediates and products

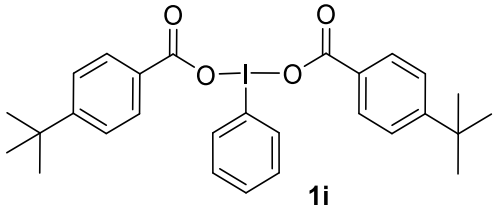
4.1 Synthesis and characterization data of substrates and intermediates

Synthesis of hypervalent iodine reagent **1i**



The reagent was prepared following adapted literature procedure.[4] Phenyliodine (III) diacetate (PIDA, 482 mg, 1.50 mmol, 1.0 eq.) and 4-*tert*-butylbenzoic acid (547 mg, 3.08 mmol, 2.1 eq.) were dissolved in toluene (25 mL) and the toluene was removed with a rotary evaporator (50 °C) over 10 minutes. After its removal, toluene (25 mL) was added again and removed with the rotary evaporator. This process was repeated three times in total. After drying *in vacuo*, the remaining solid material was dissolved in $CDCl_3$ and submitted for ^{1}H- and ^{13}C-NMR measurements. The reagent was used in the mechanistic experiments without any additional purification.

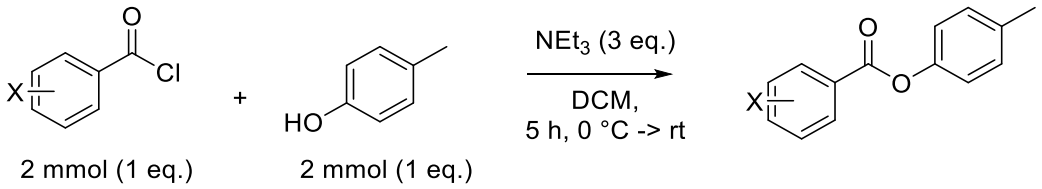
Iodobenzene bis(4-tert-butylbenzoate) (1i)



1i

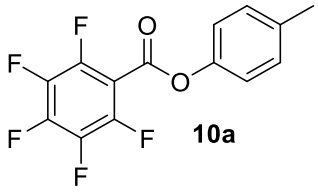
Yield	Quant, White powder
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 4H), 1.32 (s, 18H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 156.1, 134.8, 131.6, 130.9, 130.0, 127.5, 125.2, 122.6, 35.1, 31.2.

Synthesis of **10a** and **11a**



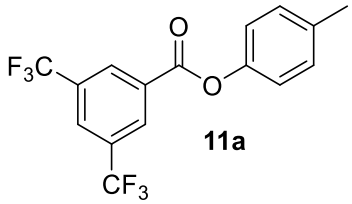
p-Cresol (2 mmol, 216 µl) and triethylamine (6 mmol, 835 µl) were dissolved in DCM (3 ml) in a 10 ml reaction vial and cooled down to 0 °C. Substituted benzoyl chloride (2 mmol) was dissolved in DCM (3 ml) in another vial and slowly added (ca. 5 min) to the reaction mixture in the first vial. After addition, the ice bath was removed, and the reaction mixture was stirred for 5 h at rt. After the reaction completion, the reaction mixture was transferred into a separatory funnel, diluted with DCM (20 ml), and quenched with HCl (10 ml; 0.1 M). The organic layer was washed again with a base NaOH (10 ml; 0.1 M) to remove any remaining benzoyl chloride or substrate, and then once again with HCl (10 ml; 0.1 M). The organic fraction was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The products were analyzed by NMR spectroscopy and used without any additional purification.

p-tolyl 2,3,4,5,6-pentafluorobenzoate (10a)



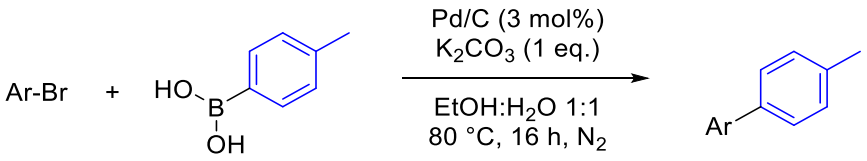
Yield	77%, White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) (except for C_6F_5) δ 157.7, 147.9, 136.6, 130.2, 120.9, 20.9.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -137.8 – -137.9 (m), -148.0 (tt, *J* = 20.9, 4.8 Hz), -160.4 – -160.6 (m).
HR-MS (EI)	$(M)^{+\cdot}$: calc. 302.0361, found 302.0355

p-tolyl 3,5-bis(trifluoromethyl)benzoate (11a)



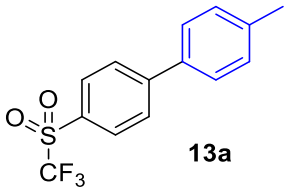
Yield	72%, colourless oil
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 2H), 8.14 (s, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.06 (m, 2H), 2.40 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 148.2, 136.3, 132.6 (q, *J* = 34.0 Hz), 132.0, 130.3 (bs), 126.9 (p, *J* = 3.8 Hz), 122.8 (q, *J* = 273.0 Hz), 121.0, 20.9.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 348.0579, found 348.0574

Synthesis of **13a** and **15a**



The Suzuki cross-coupling reactions[5] were performed by dissolving the 4-Methylphenylboronic acid (204 mg, 1.50 mmol, 1.5 eq.) and sodium bicarbonate (138 mg, 1.00 mmol, 1.0 eq.) as a base in a mixture of ethanol and water (1:1, 8 mL) inside a 10 mL crimp vial. To each vial, an aryl bromide and Pd/C as catalyst (31.8 mg corresponding to 0.03 mmol, 0.03 eq. of pure Pd) was added before it was closed, degassed and set under N_2 atmosphere. The reaction mixtures were stirred overnight at elevated temperature (16 h, 80 °C). After the completion, most of the ethanol was removed *in vacuo*, and the products were isolated by extraction (ethyl acetate/brine 1:1, 15 mL each). The product-containing organic phases were dried over sodium sulfate and after filtration, a spoon-full of flush silica gel (60M, Ø 0.04 – 0.036 mm) was added to prepare a dry load for a column chromatography. The dry load was transferred onto a silica gel column and the products were eluted with ethyl acetate as eluent (a single fraction collected). Products were analyzed by NMR spectroscopy.

4-methyl-4'-((trifluoromethyl)sulfonyl)-1,1'-biphenyl (13a)

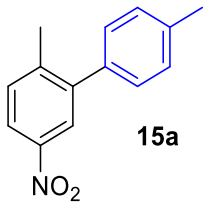


13a

Yield	48%, white solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 139.7, 135.5, 131.3, 130.0, 129.1, 128.1, 127.4, 119.9 (q, *J* = 325.8 Hz), 21.3.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -78.9.

A similar compound **14a** is commercially available.

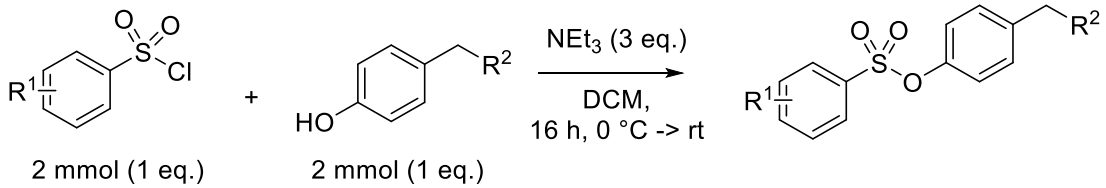
2,4'-dimethyl-5-nitro-1,1'-biphenyl (15a)



15a

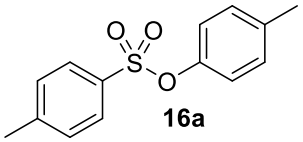
Yield	94%, orange oil
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.44 – 7.36 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.18 (m, 2H), 2.43 (s, 3H), 2.37 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.6, 143.1, 137.7, 136.7, 131.1, 129.2, 128.8, 124.7, 121.9, 21.2, 20.9.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 227.0941, found 227.0945

Synthesis of **16a, 17a** and **23a**



The corresponding phenol (2 mmol) and triethylamine (6 mmol, 835 µl) were dissolved in DCM (3 ml) in a 10 ml reaction vial and cooled down to 0 °C. Sulfonyl chloride (2 mmol) was dissolved in DCM (3 ml) in another vial and slowly added (ca. 5 min) to the reaction mixture in the first vial. After addition, the ice bath was removed, and the reaction mixture was stirred overnight (16 h) at rt. After the reaction completion, the reaction mixture was transferred into a separatory funnel, diluted with DCM (20 ml), and quenched with HCl (10 ml; 0.1 M). The organic layer was washed again with a base NaOH (10 ml; 0.1 M) to remove any remaining substrate, and then once again with HCl (10 ml; 0.1 M). The organic fraction was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The products were analyzed by NMR spectroscopy and used without any additional purification.

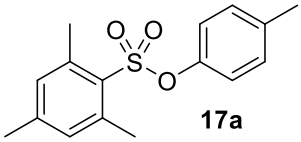
p-tolyl 4-methylbenzenesulfonate (16a)



16a

Yield	87%, White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.61 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.88 – 6.80 (m, 2H), 2.44 (s, 3H), 2.30 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.2, 137.0, 132.6, 130.1, 129.7, 128.6, 122.1, 21.7, 20.9.
HR-MS (ESI)	$(M+H)^+$: calc. 263.0736, found 263.0736

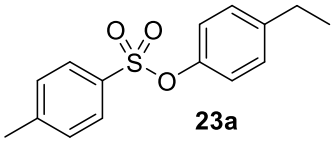
p-tolyl 2,4,6-trimethylbenzenesulfonate (17a)



17a

Yield	78%, White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.2 Hz, 2H), 6.96 (s, 2H), 6.86 – 6.81 (m, 2H), 2.55 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 143.7, 140.5, 136.8, 131.7, 130.7, 130.1, 122.0, 22.8, 21.1, 20.9.
HR-MS (ESI)	$(M+H)^+$: calc. 291.1049, found 291.1051

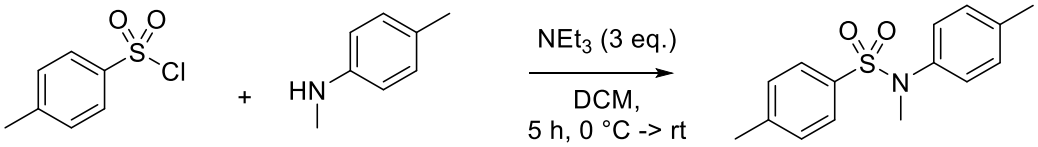
4-ethylphenyl 4-methylbenzenesulfonate (23a)



23a

Yield	83%, colorless oil
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.04 (m, 2H), 6.94 – 6.81 (m, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.2, 143.2, 132.6, 129.7, 128.9, 128.6, 122.1, 28.3, 21.7, 15.4.
HR-MS (ESI)	$(M+H)^+$: calc. 277.0893 , found 277.0896

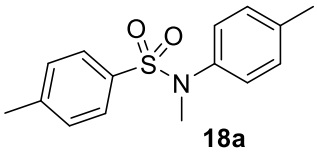
Synthesis of **18a**



2 mmol (1 eq.) 2 mmol (1 eq.) **18a**

N,4-dimethylaniline (2 mmol, 242 mg) and triethylamine (6 mmol, 835 µl) were dissolved in DCM (3 ml) in a 10 ml reaction vial and cooled down to 0 °C. Tosyl chloride (2 mmol, 380 mg) was dissolved in DCM (3 ml) in another vial and slowly added (ca. 5 min) to the reaction mixture in the first vial. After addition, the ice bath was removed, and the reaction mixture was stirred for 5 h at rt. After the reaction completion, the reaction mixture was transferred into a separatory funnel, diluted with DCM (20 ml), and quenched with HCl (10 ml; 0.1 M). The organic layer was washed again with a base NaOH (10 ml; 0.1 M) to remove any remaining tosyl chloride, and then once again with HCl (10 ml; 0.1 M). The organic fraction was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The products were analyzed by NMR spectroscopy and used without any additional purification.

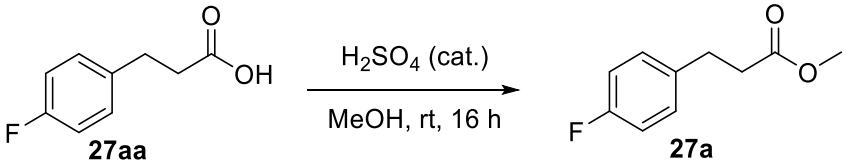
N,4-dimethyl-N-(p-tolyl)benzenesulfonamide (18a)



18a

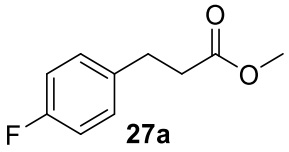
Yield	85%, slightly brownish oil
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.93 (m, 2H), 3.13 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.0, 137.3, 133.7, 129.5, 129.3, 128.0, 126.6, 38.2, 21.6, 21.1.
HR-MS (ESI)	$(M+H)^+$: calc. 276.1053, found 276.1052

Synthesis of **27a**



The carboxylic acid **27aa** (1.68 g, 10.00 mmol, 1.0 eq.) was dissolved in methanol (50 mL) inside a 250 mL round-bottom flask and five drops of conc. H_2SO_4 were added as an acid catalyst. The reaction mixture was stirred overnight (~16 h, r.t.) and after the completion of the reaction, the methanol was removed by a rotary evaporator. The remaining oil was dissolved in ethyl acetate (20 mL) and washed twice with saturated brine (20 mL each). The organic phase was dried over Na_2SO_4 and after filtrating the drying agent off, the ethyl acetate was removed *in vacuo to obtain* a pure product **27a**.

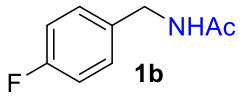
N-(4-(trifluoromethoxy)benzyl)acetamide (27a)



Yield	81%, colourless oil
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 3.66 (s, 3H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 161.5 (d, *J* = 244.0 Hz), 136.2 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.2 Hz), 51.7, 35.8, 30.1.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 182.0738, found 182.0741

4.2 Characterization of the products of photochemical reactions

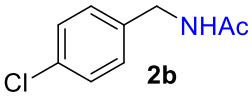
N-(4-fluorobenzyl)acetamide (1b)[6]



1b

Yield	81% (54 mg, 0.32 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.13 (m, 2H), 7.07 – 6.89 (m, 2H), 6.33 (s, 1H), 4.32 (d, *J* = 5.8 Hz, 2H), 1.96 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 162.1 (d, *J* = 245.5 Hz), 134.2 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.5 Hz), 42.9, 23.1.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7.

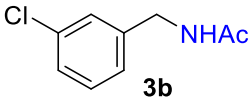
N-(4-chlorobenzyl)acetamide (2b)[6]



2b

Yield	78% (57 mg, 0.31 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.37 (s, 1H), 4.31 (d, *J* = 5.9 Hz, 2H), 1.96 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 136.9, 133.2, 129.1, 128.8, 42.9, 23.1.

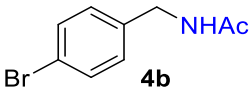
N-(3-chlorobenzyl)acetamide (3b)[7]



3b

Yield	43% (31 mg, 0.17 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 3H), 7.17 – 7.10 (m, 1H), 6.19 (s, 1H), 4.36 (d, *J* = 5.9 Hz, 2H), 2.00 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 140.4, 134.5, 130.0, 127.8, 127.6, 125.9, 43.1, 23.2.

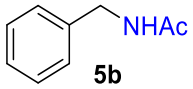
N-(4-bromobenzyl)acetamide (4b)[6]



4b

Yield	73% (67 mg, 0.29 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.26 (s, 1H), 4.31 (d, *J* = 5.9 Hz, 2H), 1.97 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 137.4, 131.7, 129.5, 121.3, 43.0, 23.2.

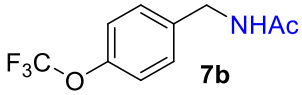
N-benzylacetamide (5b)[6]



5b

Yield	50% (30 mg, 0.20 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 5H), 6.04 (s, 1H), 4.39 (d, *J* = 5.7 Hz, 2H), 1.99 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 138.3, 128.7, 127.9, 127.5, 43.7, 23.2.

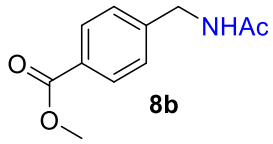
N-(4-(trifluoromethoxy)benzyl)acetamide (7b)[2]



7b

Yield	50% (47 mg, 0.20 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 4.39 (d, *J* = 5.9 Hz, 2H), 1.99 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 148.5 (d, *J* = 1.8 Hz), 137.2, 129.2, 121.7 (q, *J* = 258.6 Hz), 121.2, 42.9, 23.2.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4.

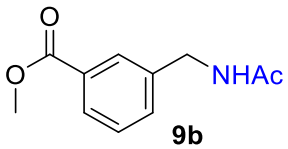
methyl 4-(acetamidomethyl)benzoate (8b)



8b

Yield	29% (24 mg, 0.12 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.12 (s, 1H), 4.45 (d, *J* = 5.9 Hz, 2H), 3.89 (s, 3H), 2.03 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.17, 166.9, 143.6, 123.0, 129.3, 127.5, 52.2, 43.3, 23.2.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 207.0890, found 207.0891

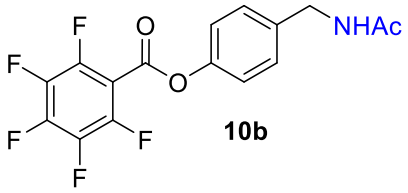
methyl 3-(acetamidomethyl)benzoate (9b)



9b

Yield	40% (33 mg, 0.16 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 2H), 7.49 – 7.42 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.88 (s, 3H), 2.01 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 166.9, 138.8, 132.4, 130.5, 128.8, 128.7, 52.2, 43.3, 23.2.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 207.0890, found 207.0887

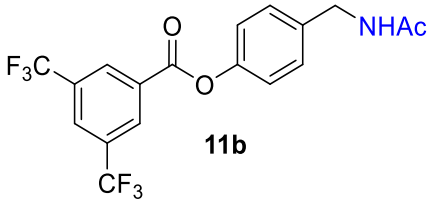
4-(acetamidomethyl)phenyl 2,3,4,5,6-pentafluorobenzoate (10b)



10b

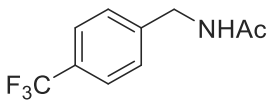
Yield	61% (88 mg, 0.24 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.37 (s, 1H), 4.40 (d, *J* = 5.7 Hz, 2H), 2.00 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$): (except for C_6F_5) δ 170.4, 157.6, 149.2, 137.1, 129.2, 121.5, 43.0, 23.1.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -137.6 – -137.8 (m), -147.5 (tt, *J* = 21.3, 5.4 Hz), -160.2 – -160.4 (m).
HR-MS (ESI)	$(M+H)^+$: calc. 360.0654 , found 360.0656

4-(acetamidomethyl)phenyl 3,5-bis(trifluoromethyl)benzoate (11b)



11b

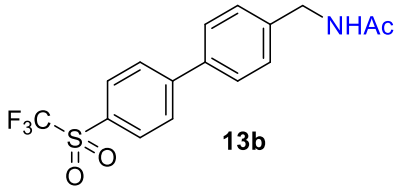
Yield	57% (92 mg, 0.23 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 2H), 8.13 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.12 (m, 2H), 6.45 (s, 1H), 4.42 (d, *J* = 5.8 Hz, 2H), 2.01 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 162.7, 149.6, 136.9, 132.5 (q, *J* = 34.2 Hz), 131.7, 130.3 (d, *J* = 3.1 Hz), 129.2, 127.0 (p, *J* = 3.6 Hz), 122.8 (q, *J* = 272.9 Hz), 121.6, 43.0, 23.1.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5.
HR-MS (ESI)	$(M+H)^+$: calc. 406.0872 , found 406.0876



12b

12b was not obtained according to ^{1}H NMR. SM remained unreacted.

N-((4'-((trifluoromethyl)sulfonyl)-[1,1'-biphenyl]-4-yl)methyl)acetamide (13b)

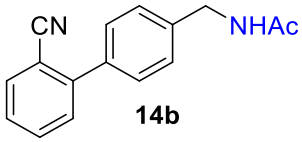


13b

Yield	48% (35 mg, 0.1 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.92 – 7.72 (m, 2H), 7.65 – 7.53 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.06 (s, 1H), 4.49 (d, *J* = 5.9 Hz, 2H), 2.05 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 139.9, 137.5, 131.4, 128.6, 128.3, 127.8, 119.9 (q, *J* = 325.8 Hz), 43.2, 23.3.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -78.9.
HR-MS (ESI)	$(M+H)^+$: calc. 358.0719 , found 358.0723

Experiment was performed on a 0.2 mmol scale (only one reaction vial).

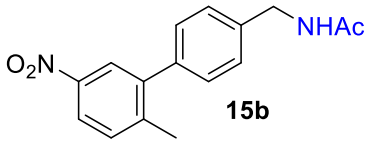
N-((2'-cyano-[1,1'-biphenyl]-4-yl)methyl)acetamide (14b)



14b

Yield	81% (81 mg, 0.32 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.62 (td, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.39 – 7.33 (m, 2H), 6.47 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 1.99 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 145.1, 139.1, 137.3, 133.7, 133.0, 130.1, 129.0, 128.2, 127.7, 118.8, 111.1, 43.3, 23.1.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 250.1101, found 250.1098

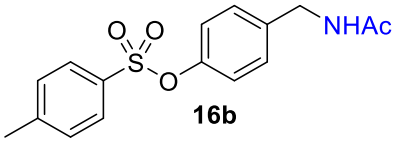
N-((2'-methyl-5'-nitro-[1,1'-biphenyl]-4-yl)methyl)acetamide (15b)



15b

Yield	37% (42 mg, 0.15 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.97 (m, 2H), 7.45 – 7.33 (m, 3H), 7.28 – 7.21 (m, 2H), 6.14 (s, 1H), 4.48 (d, *J* = 5.9 Hz, 2H), 2.33 (s, 3H), 2.05 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 146.2, 143.6, 142.7, 138.8, 138.2, 131.2, 129.3, 127.9, 124.6, 122.2, 43.4, 23.3, 20.8.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 284.1155, found 284.1157

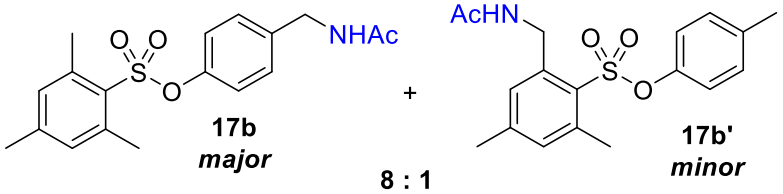
4-(acetamidomethyl)phenyl 4-methylbenzenesulfonate (16b)[2]



16b

Yield	37% (47 mg, 0.15 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.92 (s, 1H), 4.37 (d, *J* = 5.9 Hz, 2H), 2.45 (s, 3H), 2.00 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 148.8, 145.5, 137.5, 132.4, 129.9, 129.0, 128.5, 122.6, 42.9, 23.3, 21.8.

4-(acetamidomethyl)phenyl 2,4,6-trimethylbenzenesulfonate (17b - major)

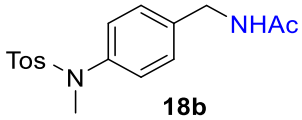


17b ***major*** **8 : 1** **17b'** ***minor***

Yield	38% (51 mg, 0.15 mmol), slightly brownish oil
^{1}H NMR (major)	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.96 (s, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.15 (s, 1H), 4.34 (d, *J* = 5.9 Hz, 2H), 2.53 (s, 6H), 2.37 – 2.26 (m, 4H), 1.98 (s, 3H).
^{13}C NMR (major)	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 148.7, 144.0, 140.4, 137.3, 131.9, 128.9, 122.4, 42.9, 23.1, 22.7, 21.1.
HR-MS (ESI)	$(M+H)^+$: calc. 348.1264 , found 348.1267 (major), 348.1265 (minor) (the isomers separate well in LC-QTOF instrument)

See chapter 4.3 for more detailed information about the identification of the minor isomer.

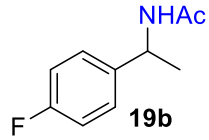
N-(4-((N,4-dimethylphenyl)sulfonamido)benzyl)acetamide (18b)



18b

Yield	59% (78 mg, 0.23 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.33 (s, 1H), 4.36 (d, *J* = 5.8 Hz, 2H), 3.09 (s, 3H), 2.39 (s, 3H), 1.98 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 143.8, 140.8, 137.7, 133.5, 129.5, 128.2, 127.9, 126.8, 43.0, 38.1, 23.2, 21.6.
HR-MS (ESI)	$(M+H)^+$: calc. 333.1267 , found 333.1268

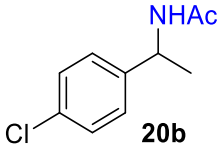
N-(1-(4-fluorophenyl)ethyl)acetamide (19b)[8]



19b

Yield	72% (52 mg, 0.29 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.19 (s, 1H), 5.07 (p, *J* = 7.1 Hz, 1H), 1.97 (s, 3H), 1.45 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.0 (d, *J* = 245.6 Hz), 139.0 (d, *J* = 3.2 Hz), 127.8 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.4 Hz), 48.3, 23.2, 21.8.
^{19}F NMR	^{19}F NMR (377 MHz, $CDCl_3$) δ -115.9.

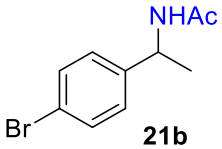
N-(1-(4-chlorophenyl)ethyl)acetamide (20b)[8]



20b

Yield	77% (61 mg, 0.31 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 6.26 (d, *J* = 7.7 Hz, 1H), 5.04 (p, *J* = 7.1 Hz, 1H), 1.95 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 142.0, 132.9, 128.7, 127.6, 48.2, 23.3, 21.8.

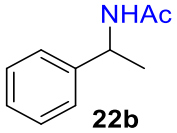
N-(1-(4-bromophenyl)ethyl)acetamide (21b)[8]



21b

Yield	57% (55 mg, 0.23 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.22 – 7.14 (m, 2H), 5.75 (s, 1H), 5.07 (p, *J* = 7.1 Hz, 1H), 1.98 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.3, 131.8, 128.0, 121.2, 48.3, 23.4, 21.7.

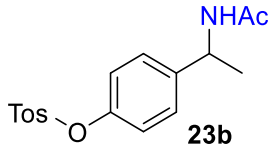
N-(1-phenylethyl)acetamide (22b)[2]



22b

Yield	58% (38 mg, 023 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 5.94 (s, 1H), 5.11 (p, *J* = 7.0 Hz, 1H), 1.96 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.2, 128.7, 127.4, 126.2, 48.8, 23.4, 21.8.

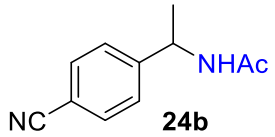
4-(1-acetamidoethyl)phenyl 4-methylbenzenesulfonate (23b)



23b

Yield	87% (116 mg, 0.35 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.89 (dd, *J* = 8.6, 2.0 Hz, 2H), 6.21 (s, 1H), 5.04 (p, *J* = 7.1 Hz, 1H), 2.43 (s, 3H), 1.93 (d, *J* = 2.8 Hz, 3H), 1.40 (dd, *J* = 6.9, 2.2 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 148.6, 145.5, 142.4, 132.4, 129.9, 128.4, 127.5, 122.4, 48.1, 23.2, 21.8, 21.7.
HR-MS (ESI)	$(M+H)^+$: calc. 334.1108, found 334.1106

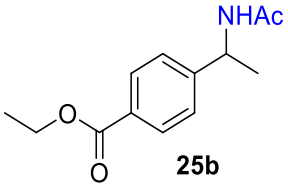
N-(1-(4-cyanophenyl)ethyl)acetamide (24b)[9]



24b

Yield	60% (45 mg, 0.24 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 5.91 (s, 1H), 5.11 (p, *J* = 7.1 Hz, 1H), 2.00 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 148.9, 132.5, 126.9, 118.8, 111.1, 48.7, 23.3, 21.8.

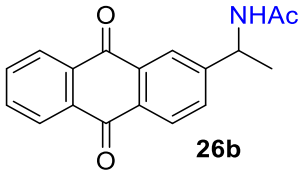
ethyl 4-(1-acetamidoethyl)benzoate (25b)



25b

Yield	69% (65 mg, 0.28 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.47 (d, *J* = 7.5 Hz, 1H), 5.10 (p, *J* = 7.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.96 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 4H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 166.4, 148.6, 129.9, 129.4, 126.1, 70.0, 48.7, 23.2, 21.8, 14.3.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 235.1203, found 235.1202

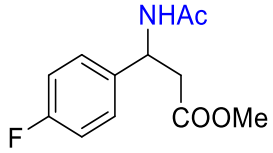
N-(1-(9,10-dioxo-9,10-dihydroanthracen-2-yl)ethyl)acetamide (26b)



26b

Yield	62% (73 mg, 0.25 mmol), lightly yellowish solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.27 (m, 2H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 1.6 Hz, 1H), 7.87 – 7.75 (m, 2H), 7.73 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.06 (d, *J* = 6.6 Hz, 1H), 5.23 (p, *J* = 7.1 Hz, 1H), 2.06 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 183.2, 182.8, 169.6, 150.4, 134.2, 134.1, 133.8, 133.5, 132.6, 132.4, 127.9, 127.3, 124.1, 49.0, 23.4, 22.1.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 293.1046, found 293.1041

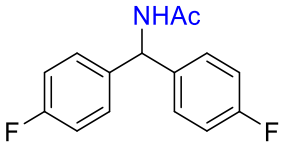
methyl 3-acetamido-3-(4-fluorophenyl)propanoate (27b)



27b

Yield	64% (61 mg, 0.26 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 2H), 7.01 – 6.87 (m, 3H), 5.43 – 5.29 (m, 1H), 3.58 (s, 3H), 2.86 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.76 (dd, *J* = 15.7, 6.2 Hz, 1H), 1.95 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 169.5, 162.1 (d, *J* = 246.0 Hz), 136.5 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.5 Hz), 51.9, 49.1, 39.9, 23.2.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4.
HR-MS (EI)	$(M)^{+\cdot}$: calc. 239.0952, found 239.0947

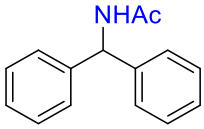
N-(bis(4-fluorophenyl)methyl)acetamide (28b)[8]



28b

Yield	91% (95 mg, 0.36 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 7.03 – 6.93 (m, 4H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 1.96 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.1 (d, *J* = 246.5 Hz), 137.2 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.5 Hz), 55.7, 23.1.
^{19}F NMR	^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3.

N-benzhydrylacetamide (29b)[6]



29b

Yield	62% (56 mg, 0.25 mmol), White solid
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 10H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 8.1 Hz, 1H), 1.98 (s, 3H).
^{13}C NMR	^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 141.6, 128.7, 127.6, 127.5, 57.1, 23.2.

4.3 Characterization of the minor isomer in reaction mixture 17b

The isomers cannot be separated on a silica TLC plate. The identification of the structure of the minor isomer was done by the ^{1}H NMR (**Figure S3** and **Figure S4**). The ortho isomer **17b'** shows 3 different benzylic signals, while isomer **17b''** is more symmetric and should show only 2 different benzylic protons. The ratio of integrals of the aliphatic NMR signals (1:1:1:1) additionally supports the structure of **17b'** as a minor isomer in the product mixture.

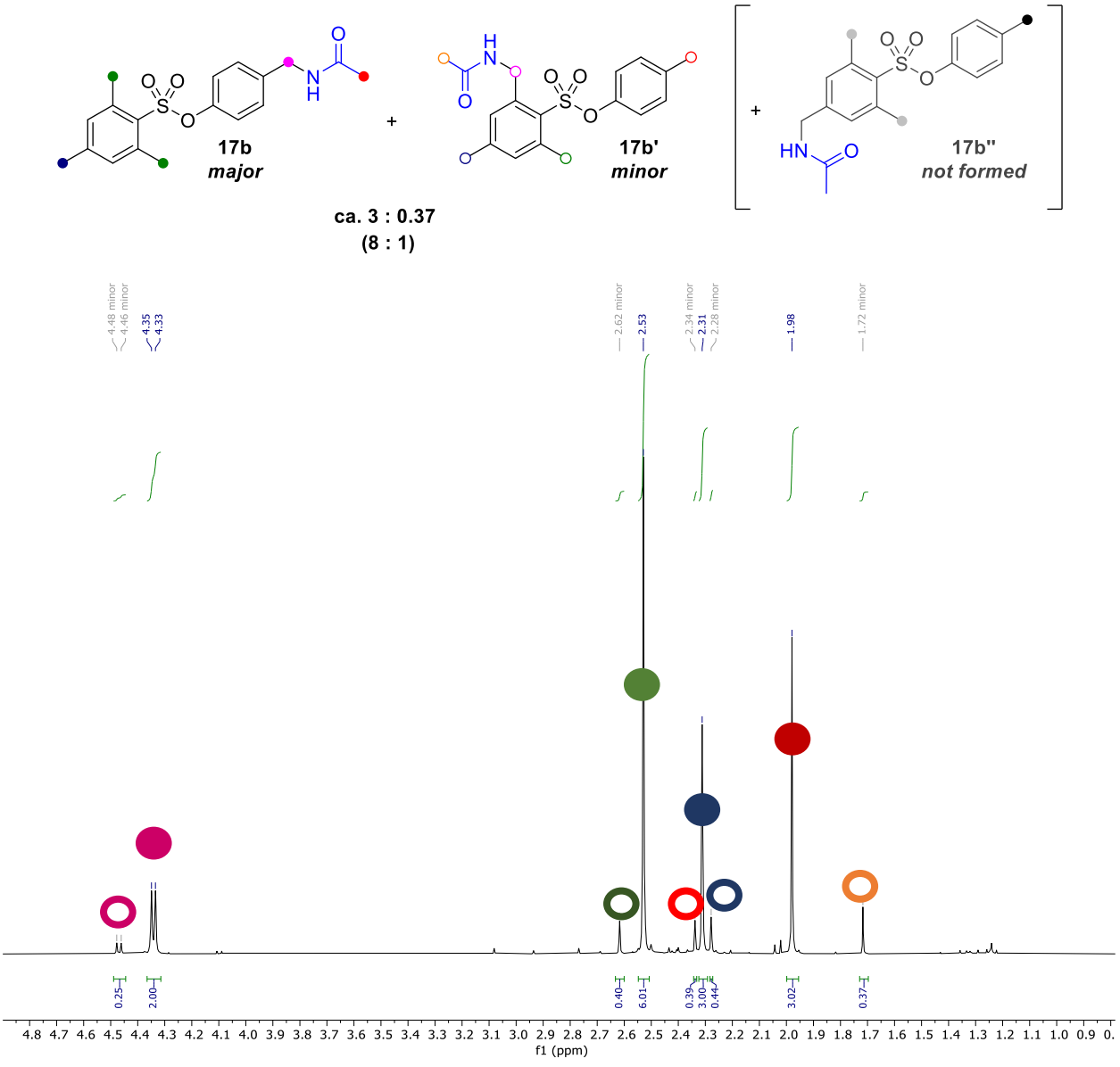


Figure S3: Identification of the minor isomer in the product mixture **17b** – aliphatic region.

The assignments of the signals were done with the help of the ChemDraw NMR predictor. The only signal which is significantly different from the predicted value is signal of acetyl group of **17b'** at 1.72 ppm. The reason for the shift could be the proximity of magnetic field inducing π-systems.

The aromatic region of the ^{1}H NMR (**Figure S4**) shows quite complex pattern of signals which would fit better to the structure **17b'** than the symmetric molecule **17b''**.

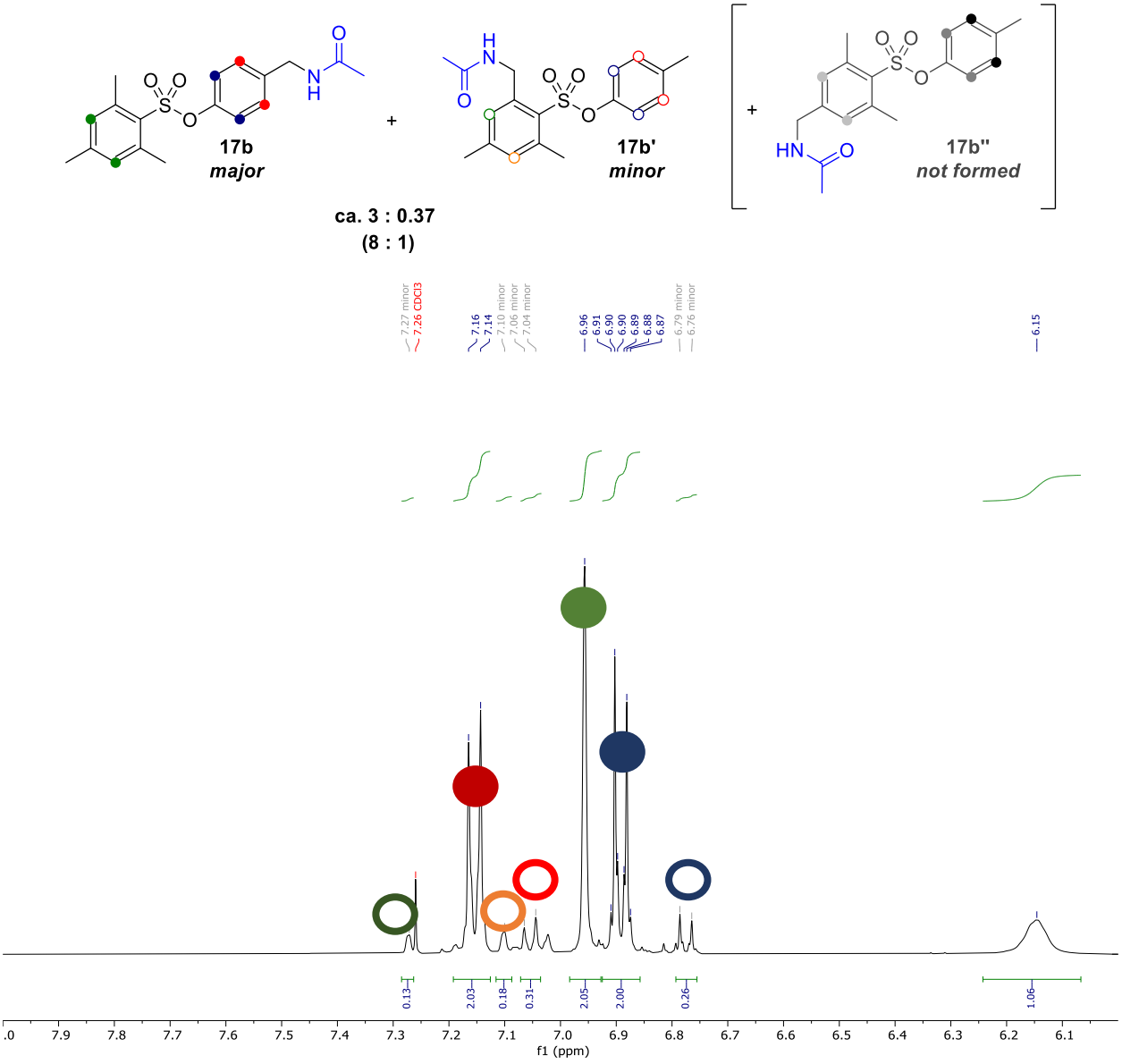


Figure S4: Identification of the minor isomer in the product mixture **17b** – aromatic region.

5 Copies of NMR spectra

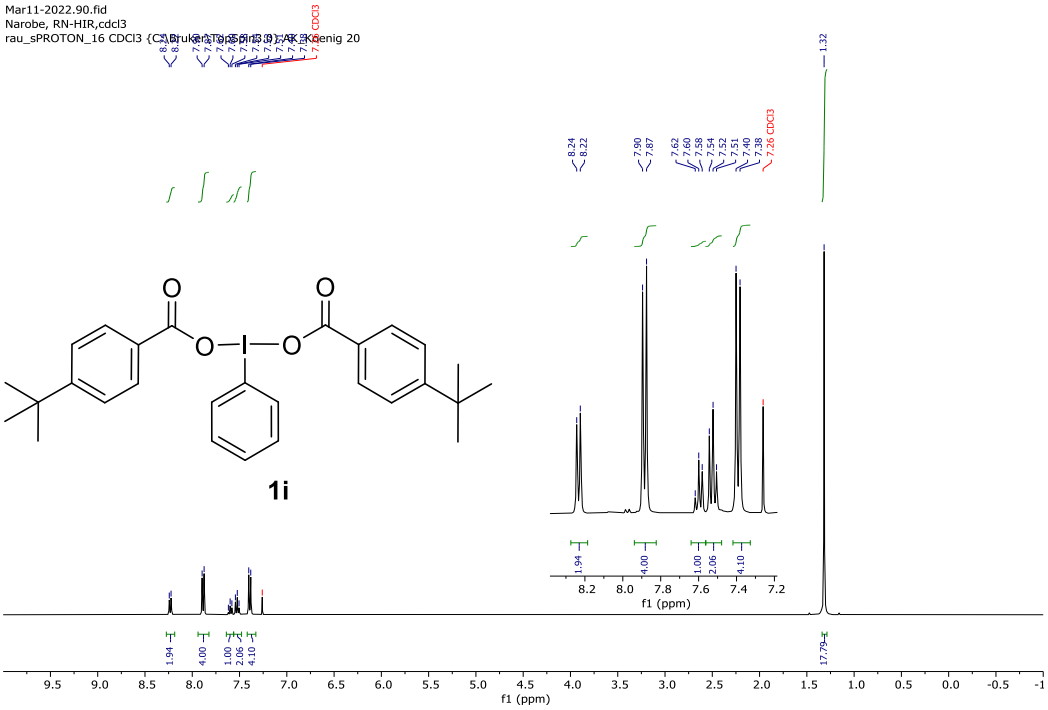


Figure S5: ^{1}H NMR spectrum of compound **1i** (400 MHz in $CDCl_3$).

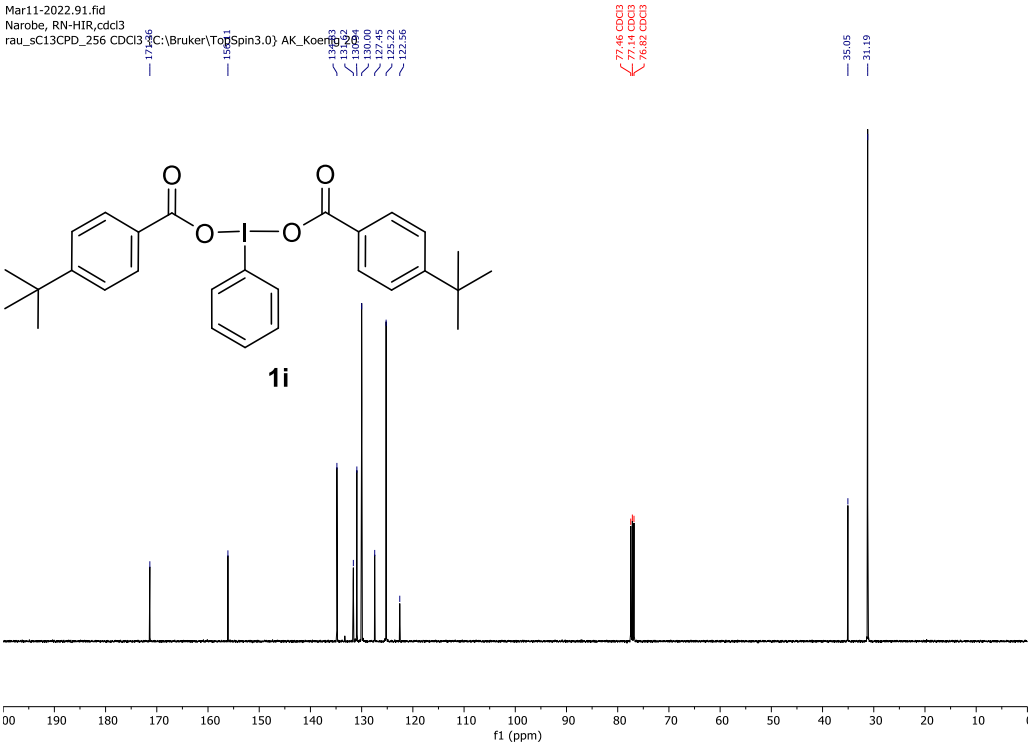


Figure S6: ^{13}C NMR spectrum of compound **1i** (101 MHz in $CDCl_3$).

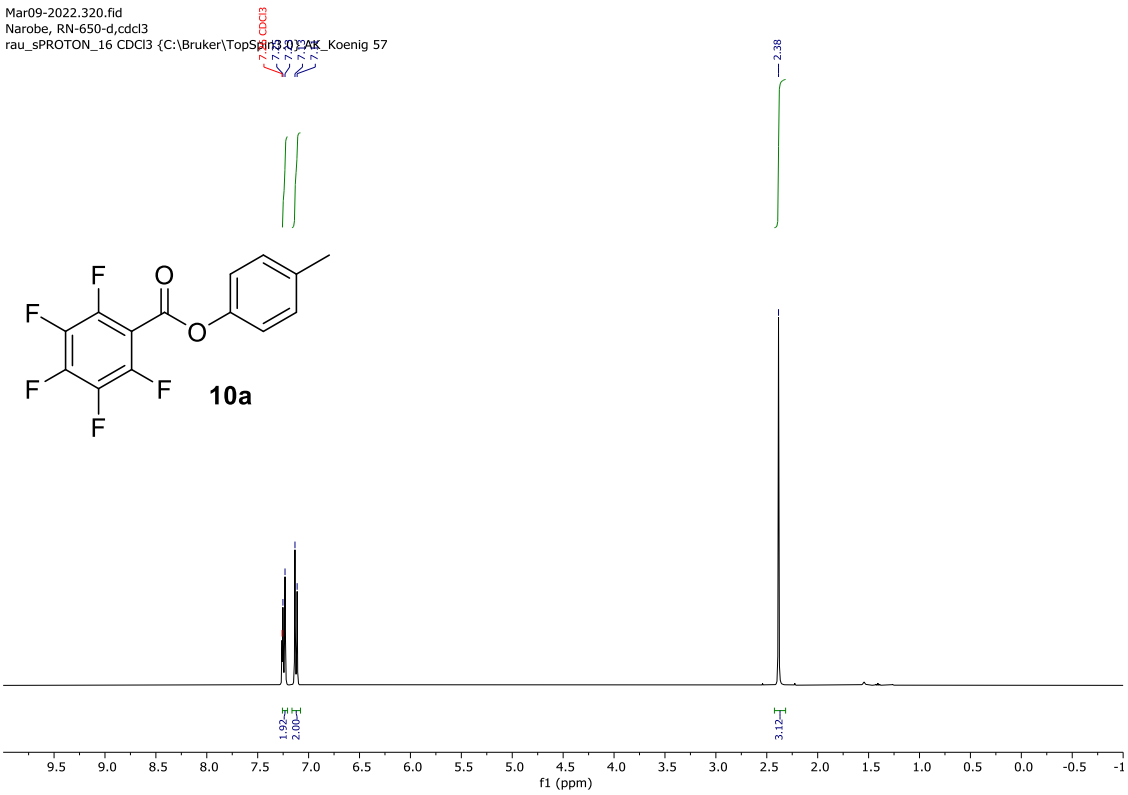


Figure S7: ^{1}H NMR spectrum of compound **10a** (400 MHz in $CDCl_3$).

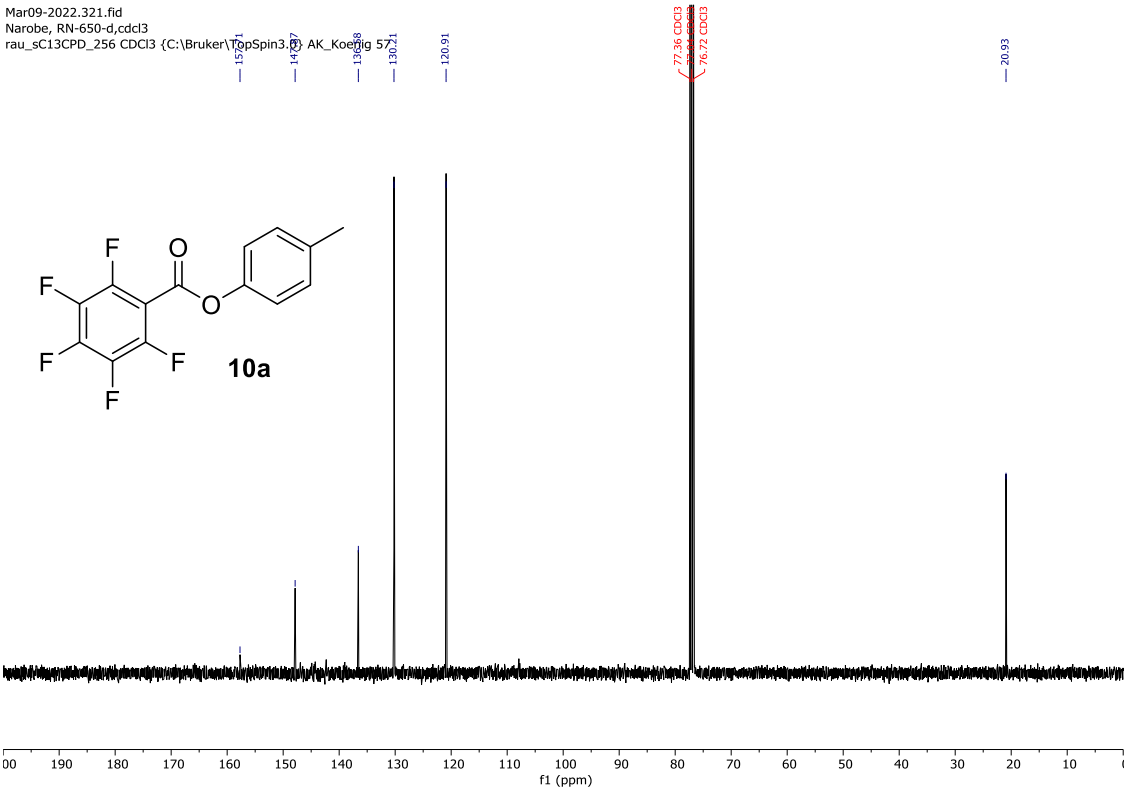


Figure S8: ^{13}C NMR spectrum of compound **10a** (101 MHz in $CDCl_3$).

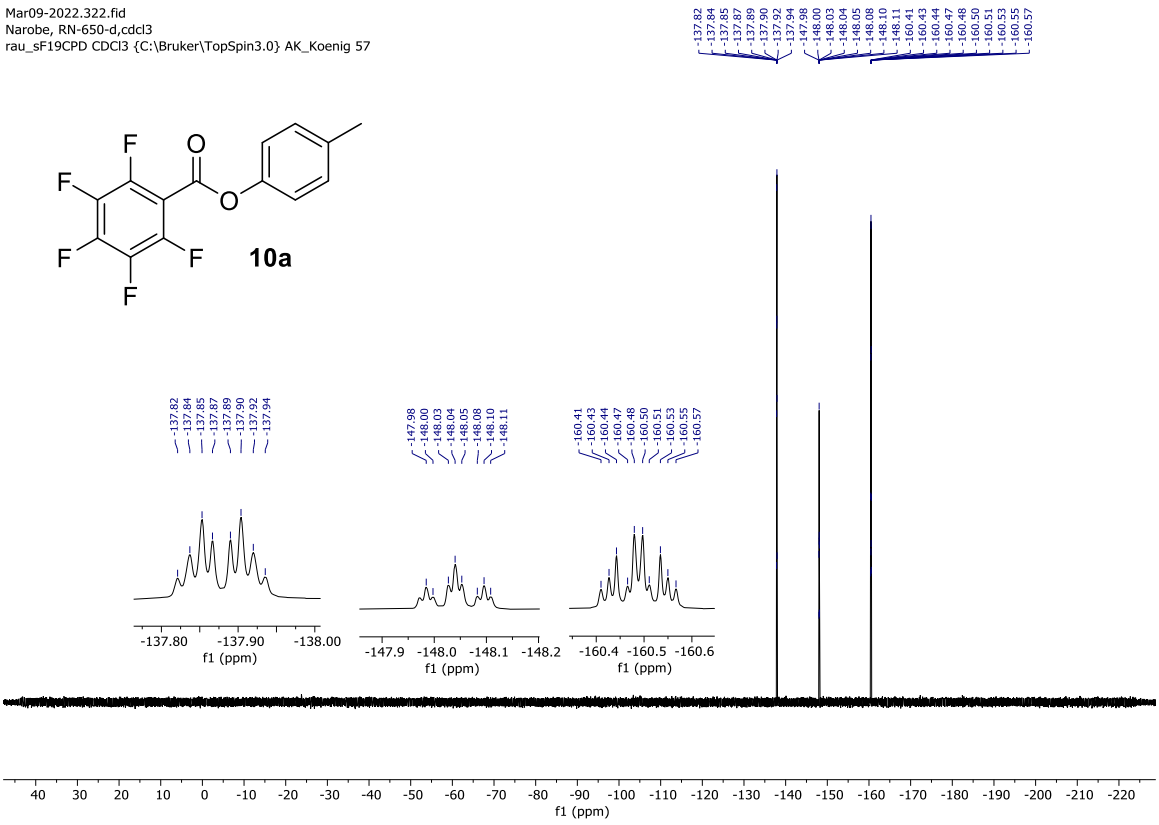


Figure S9: ^{19}F NMR spectrum of compound **10a** (377 MHz in $CDCl_3$).

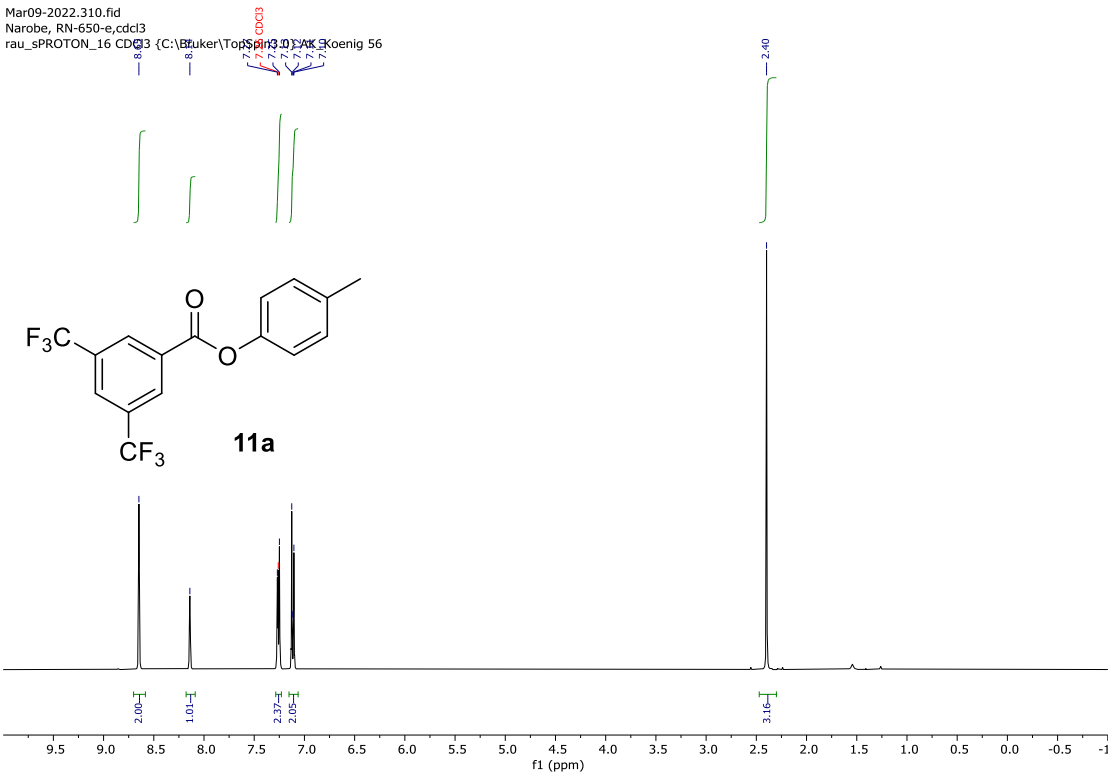


Figure S10: ^{1}H NMR spectrum of compound **11a** (400 MHz in $CDCl_3$).

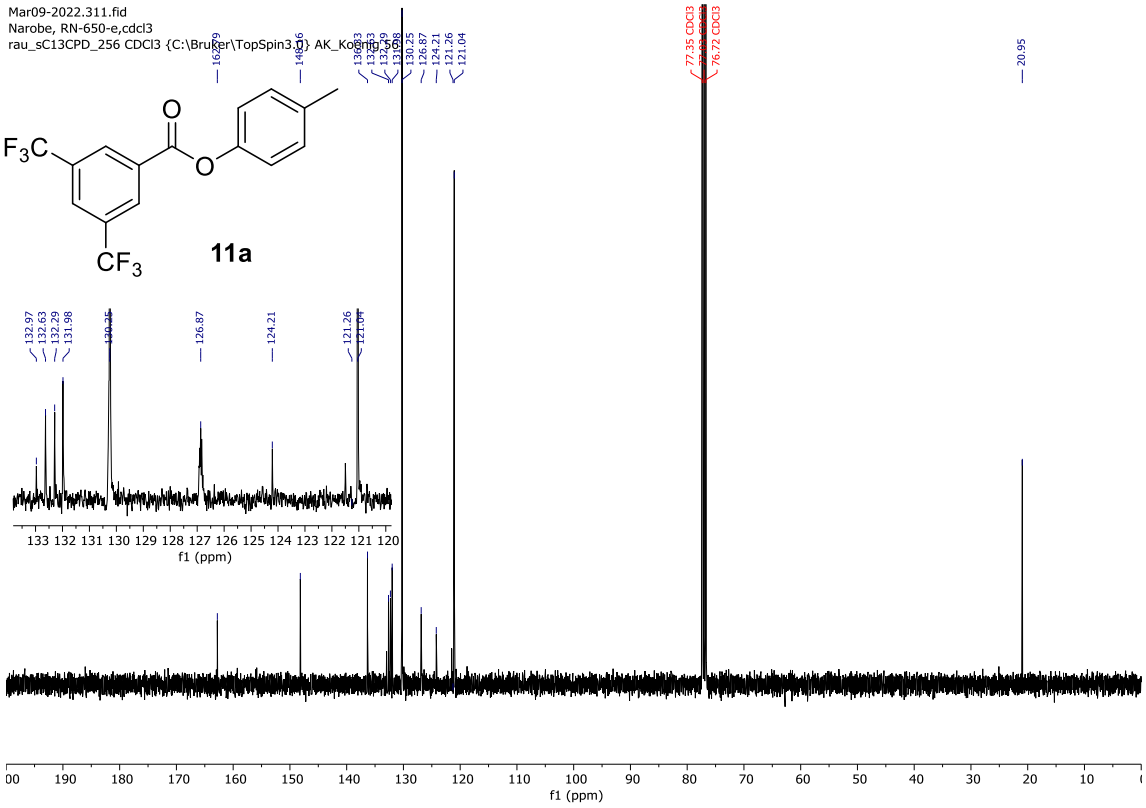


Figure S11: ^{13}C NMR spectrum of compound **11a** (101 MHz in $CDCl_3$).

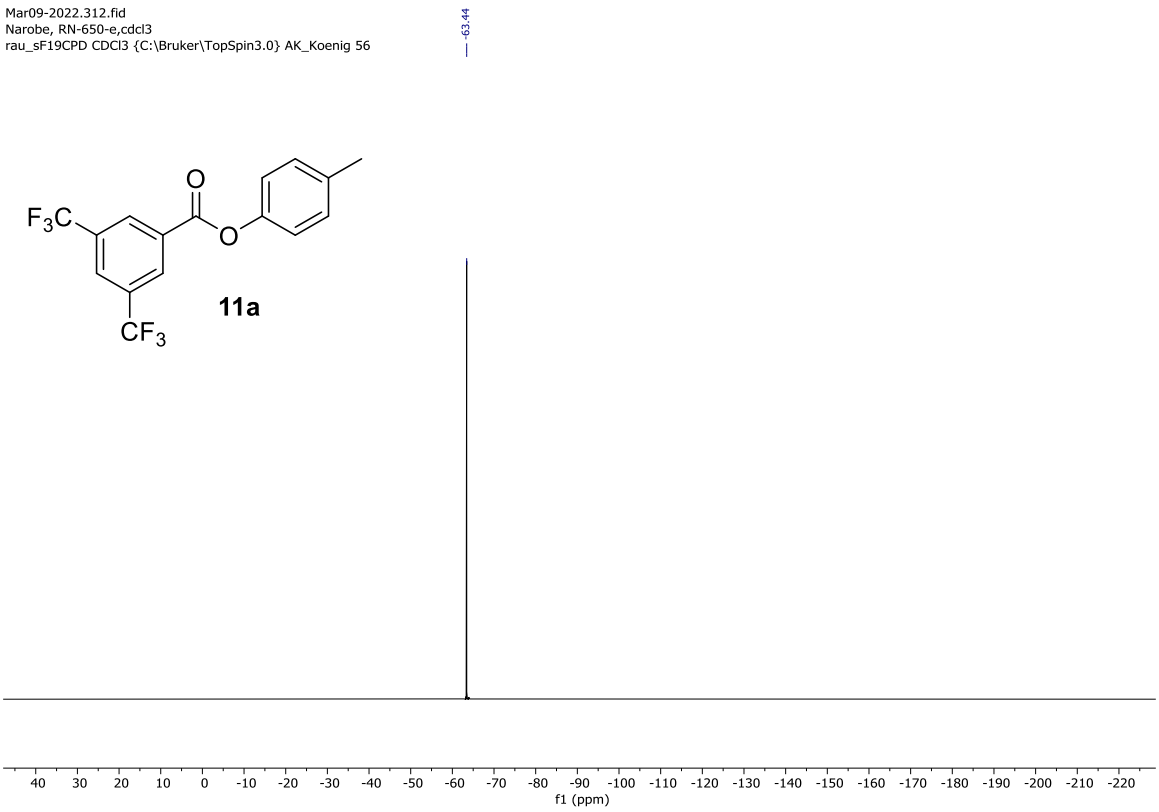


Figure S12: ^{19}F NMR spectrum of compound **11a** (377 MHz in $CDCl_3$).

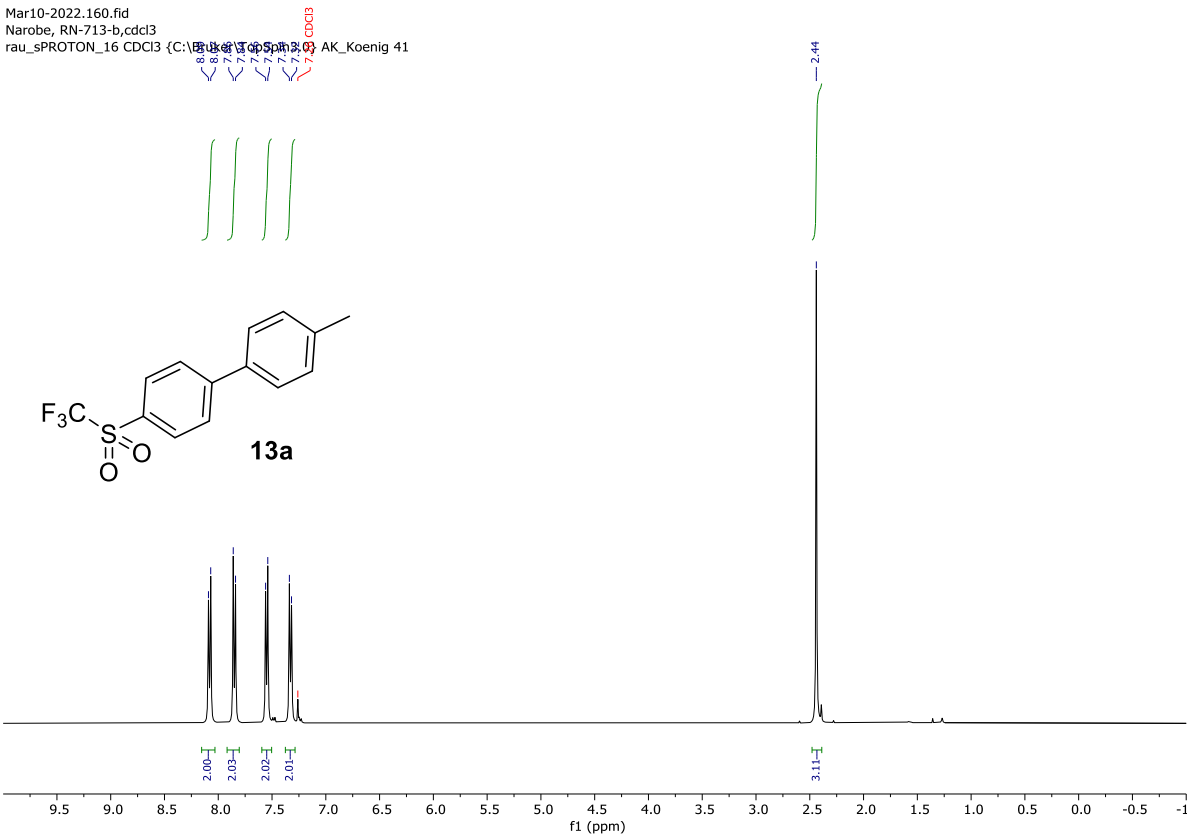


Figure S13: ^{1}H NMR spectrum of compound **13a** (400 MHz in $CDCl_3$).

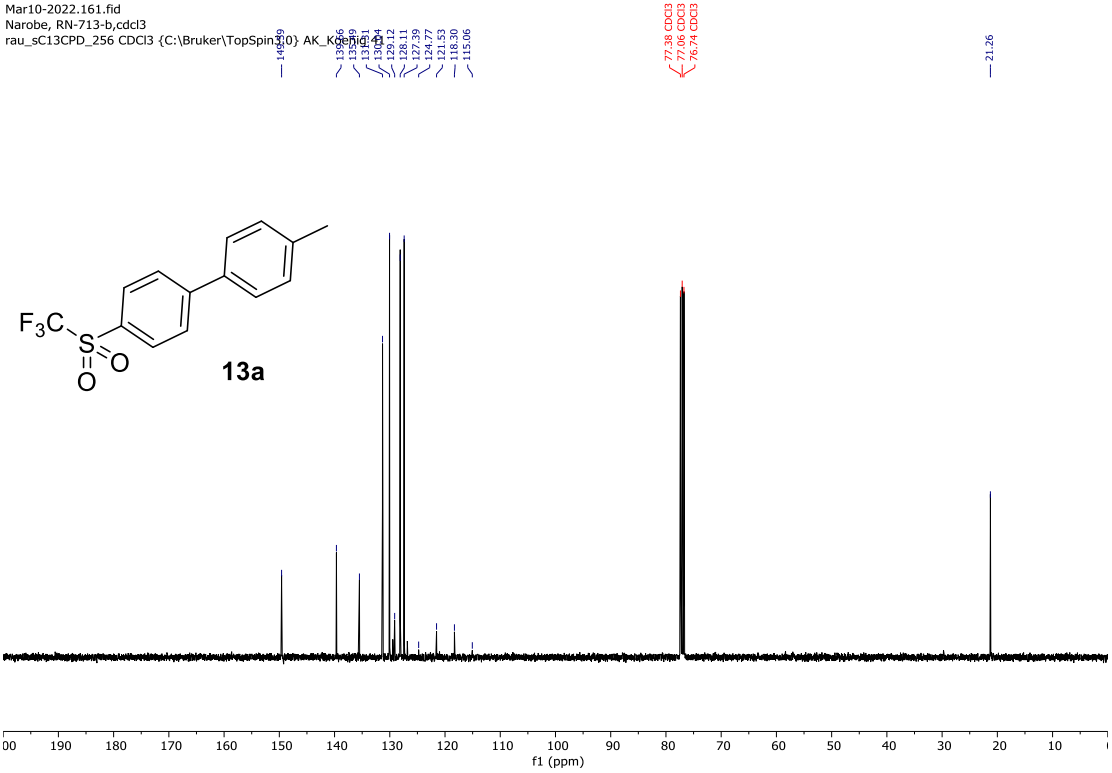


Figure S14: ^{13}C NMR spectrum of compound **13a** (101 MHz in $CDCl_3$).

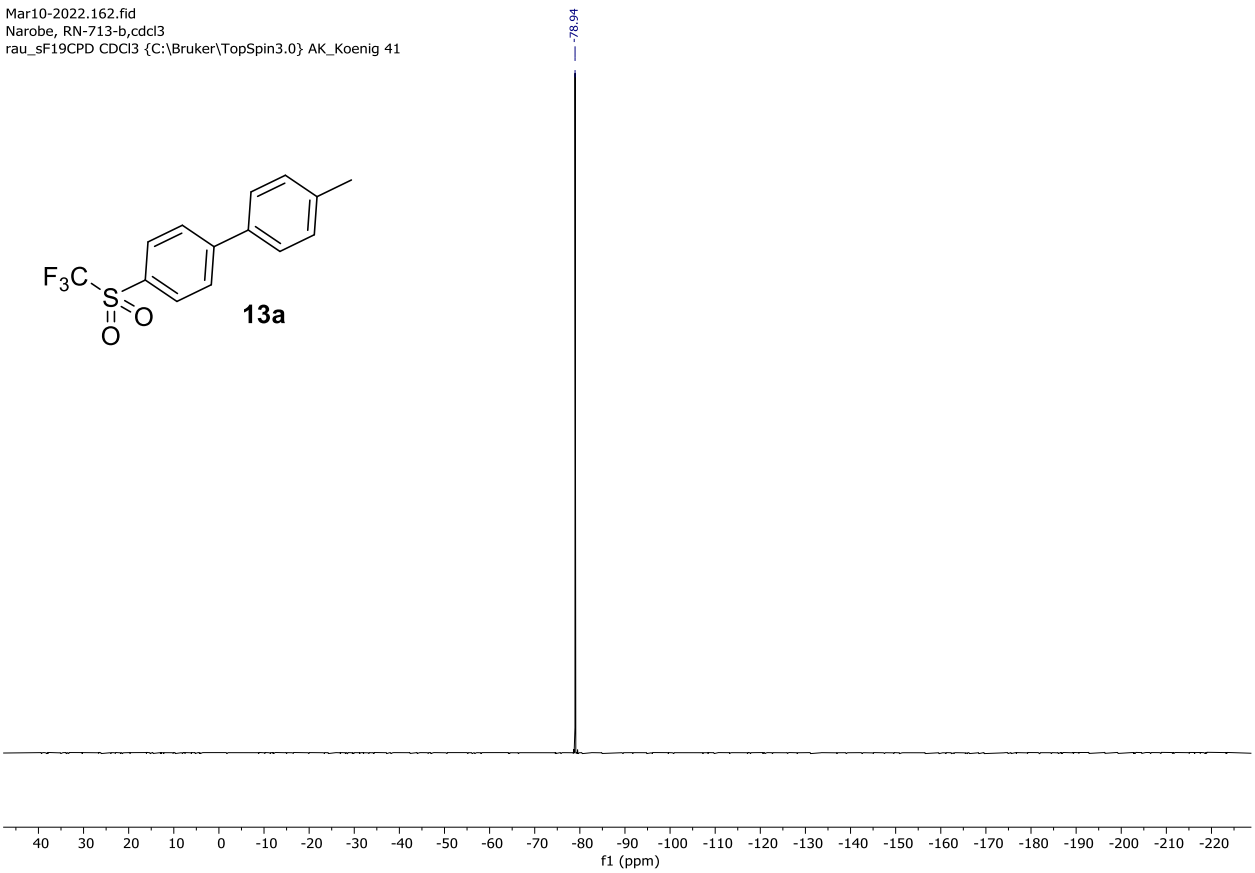


Figure S15: ^{19}F NMR spectrum of compound **13a** (377 MHz in $CDCl_3$).

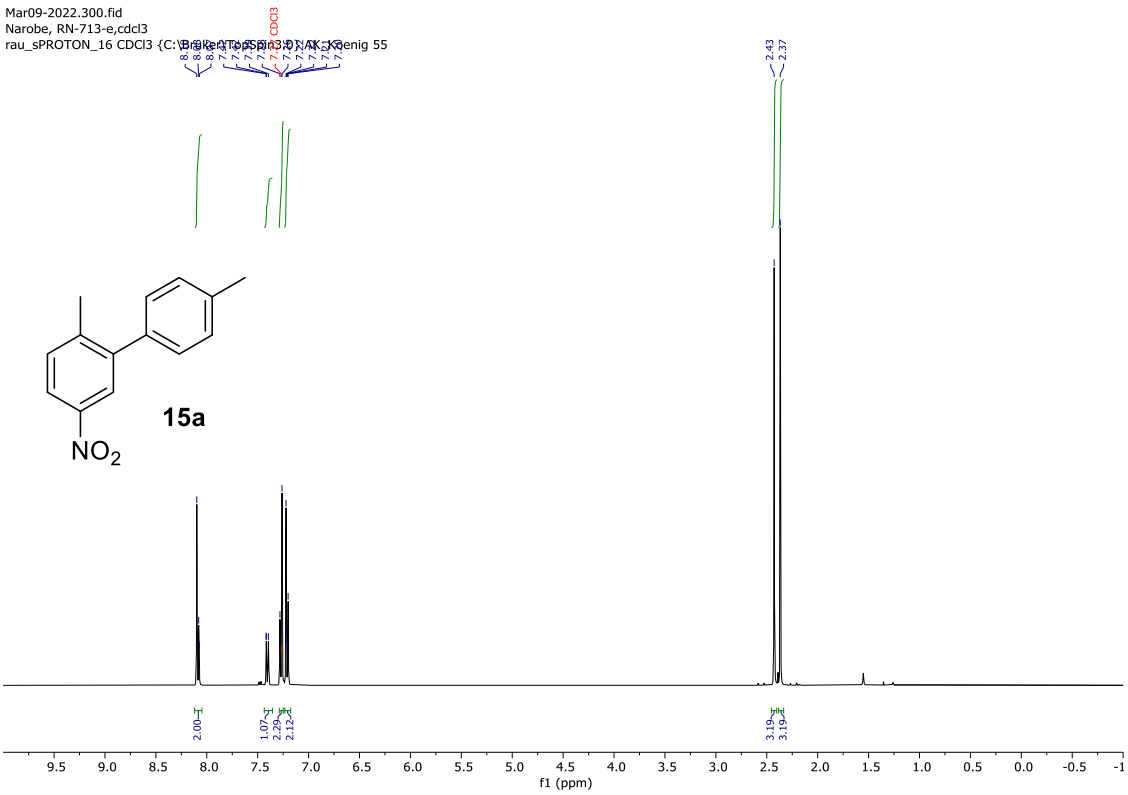


Figure S16: ^{1}H NMR spectrum of compound **15a** (400 MHz in $CDCl_3$).

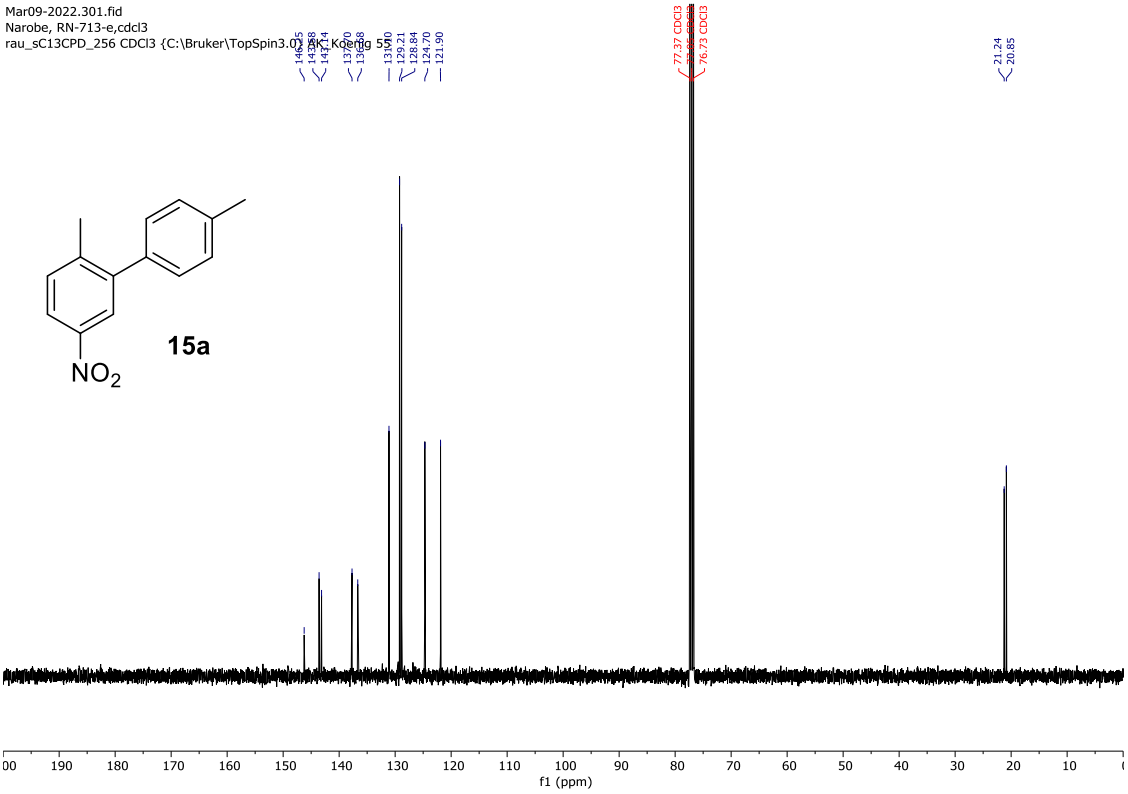


Figure S17: ^{13}C NMR spectrum of compound **15a** (101 MHz in $CDCl_3$).

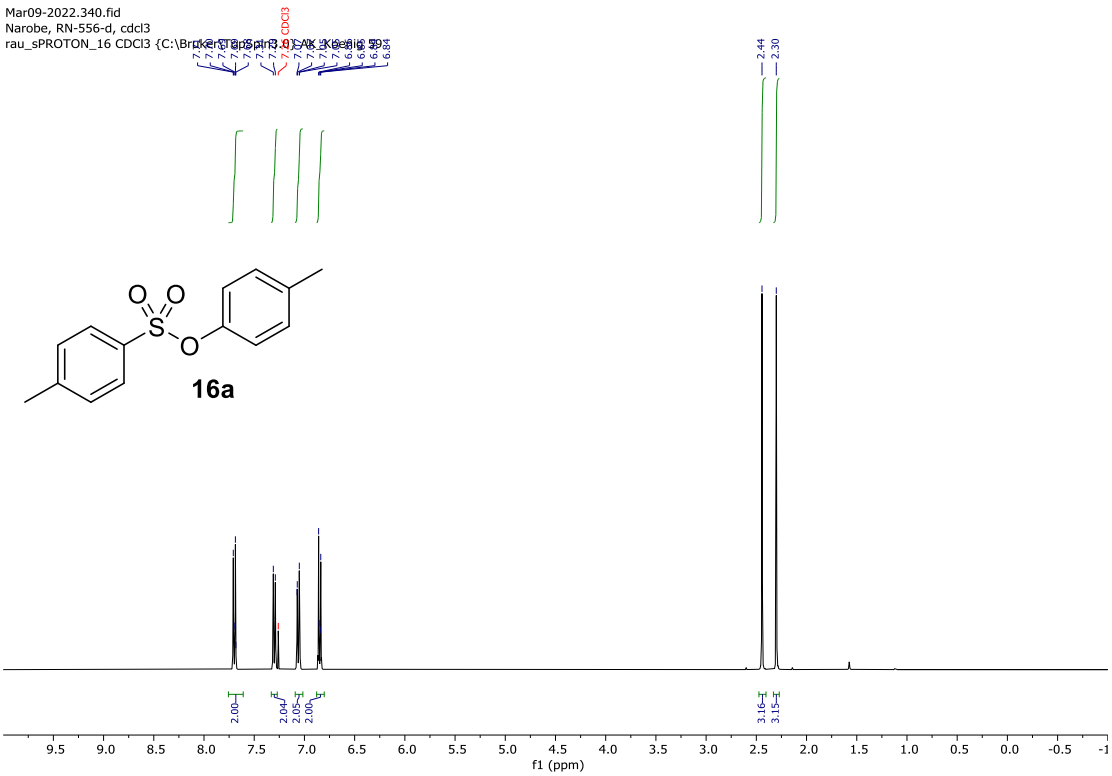


Figure S18: ^{1}H NMR spectrum of compound **16a** (400 MHz in $CDCl_3$).

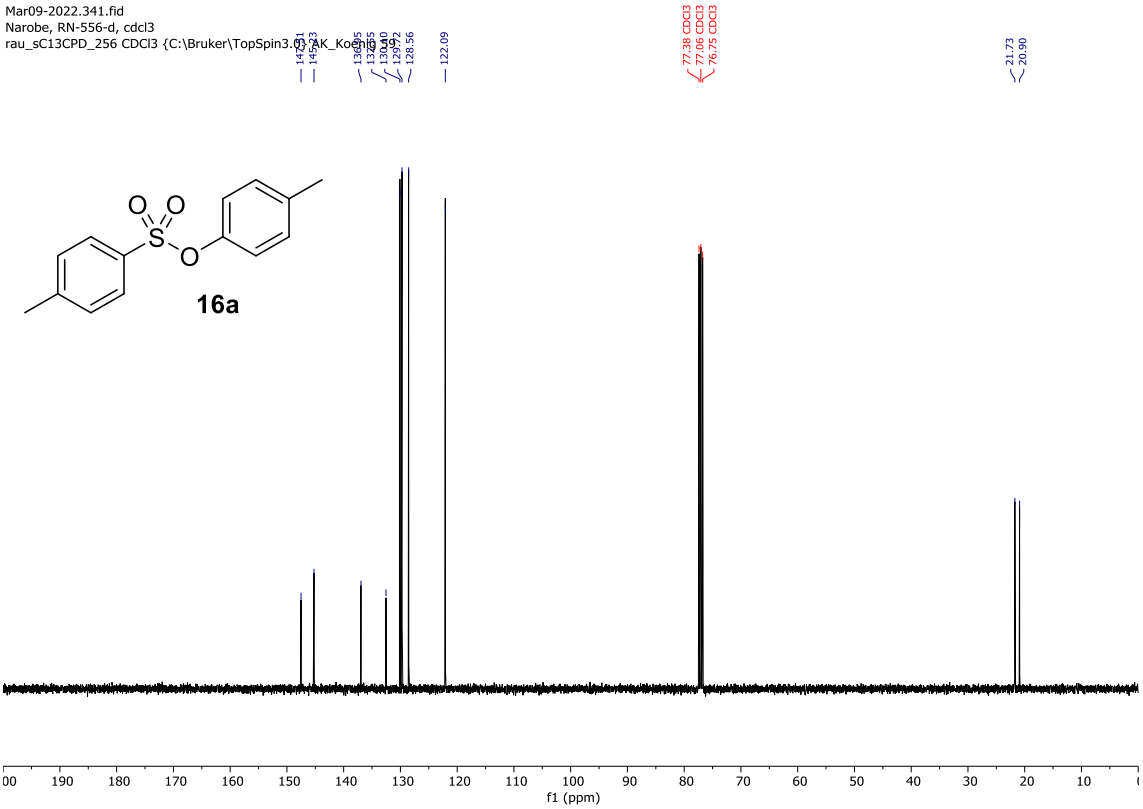


Figure S19: ^{13}C NMR spectrum of compound **16a** (101 MHz in $CDCl_3$).

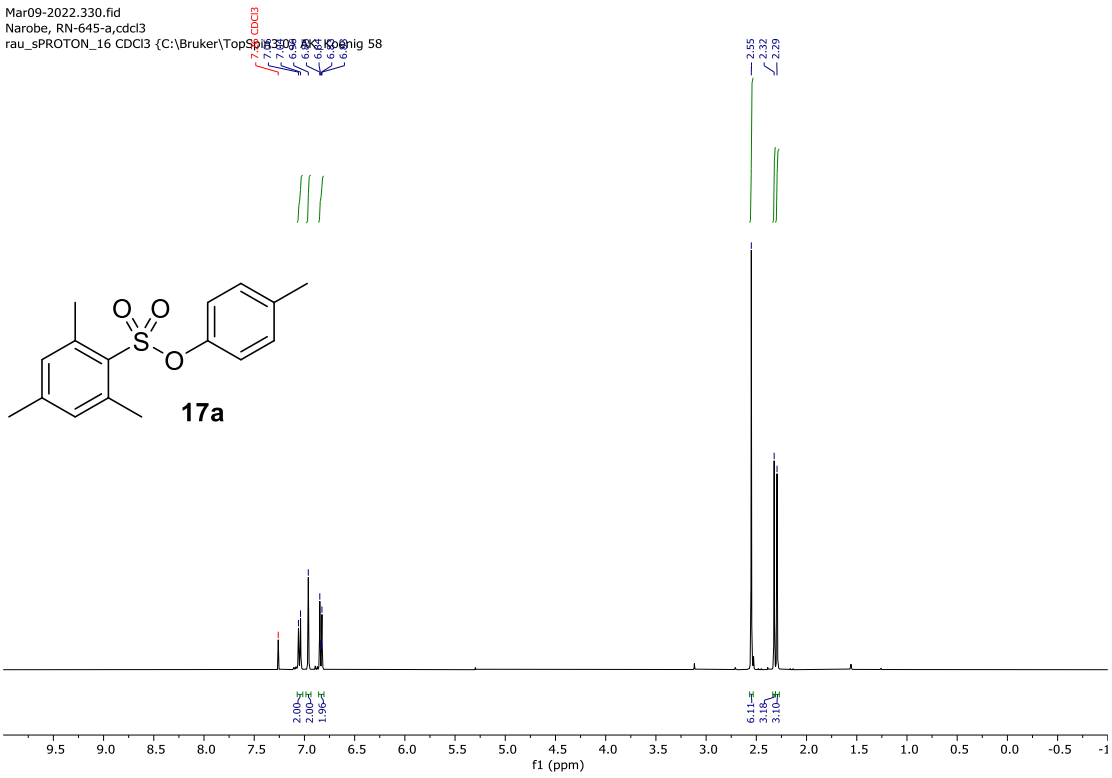


Figure S20: ^{1}H NMR spectrum of compound **17a** (400 MHz in $CDCl_3$).

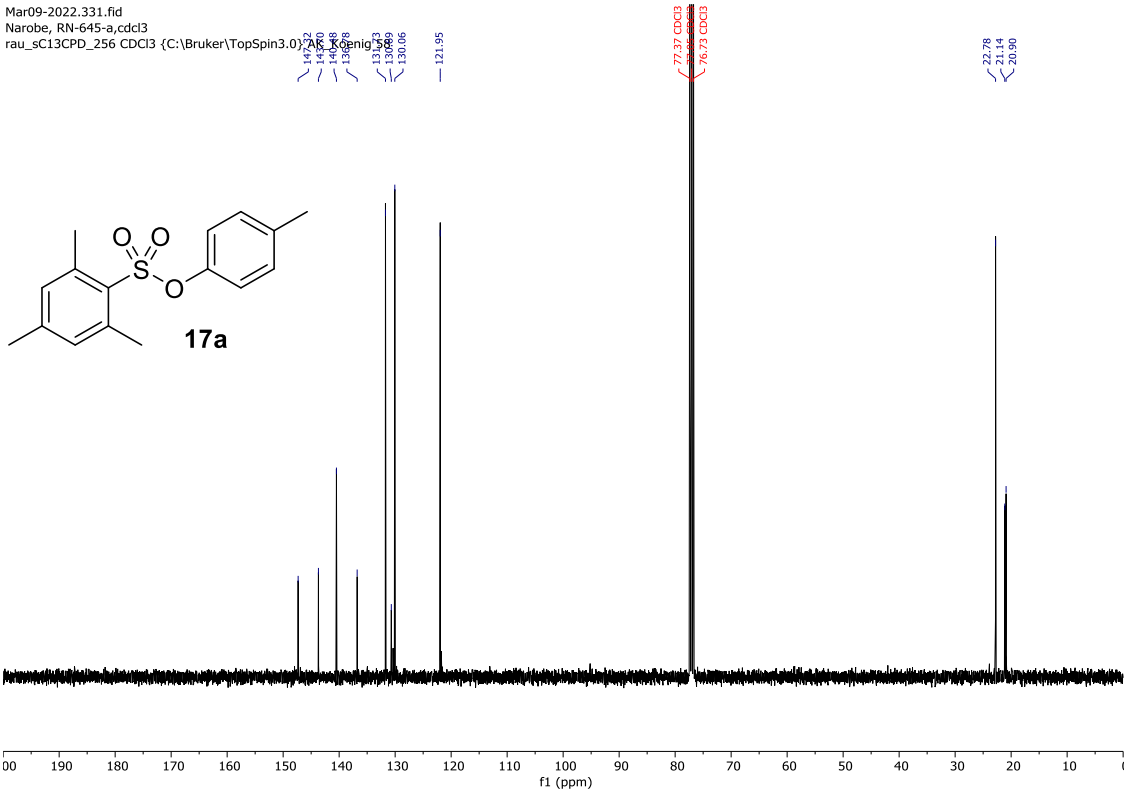


Figure S21: ^{13}C NMR spectrum of compound **17a** (101 MHz in $CDCl_3$).

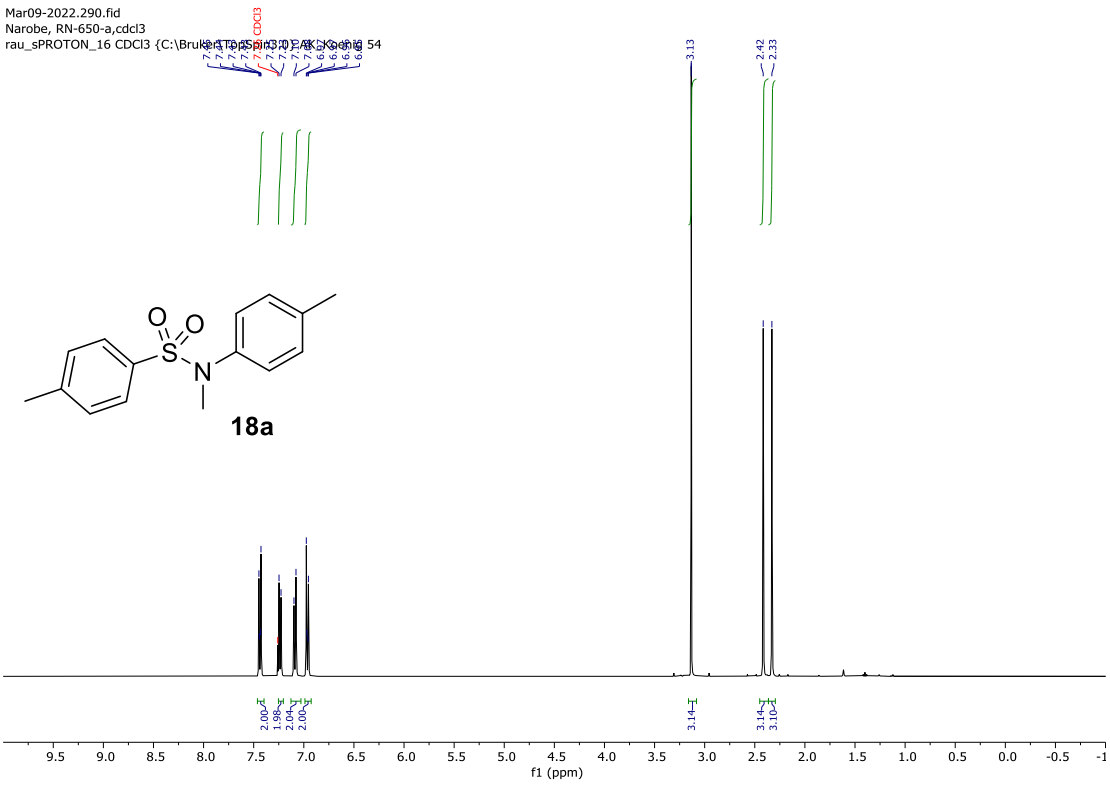


Figure S22: ^{1}H NMR spectrum of compound **18a** (400 MHz in $CDCl_3$).

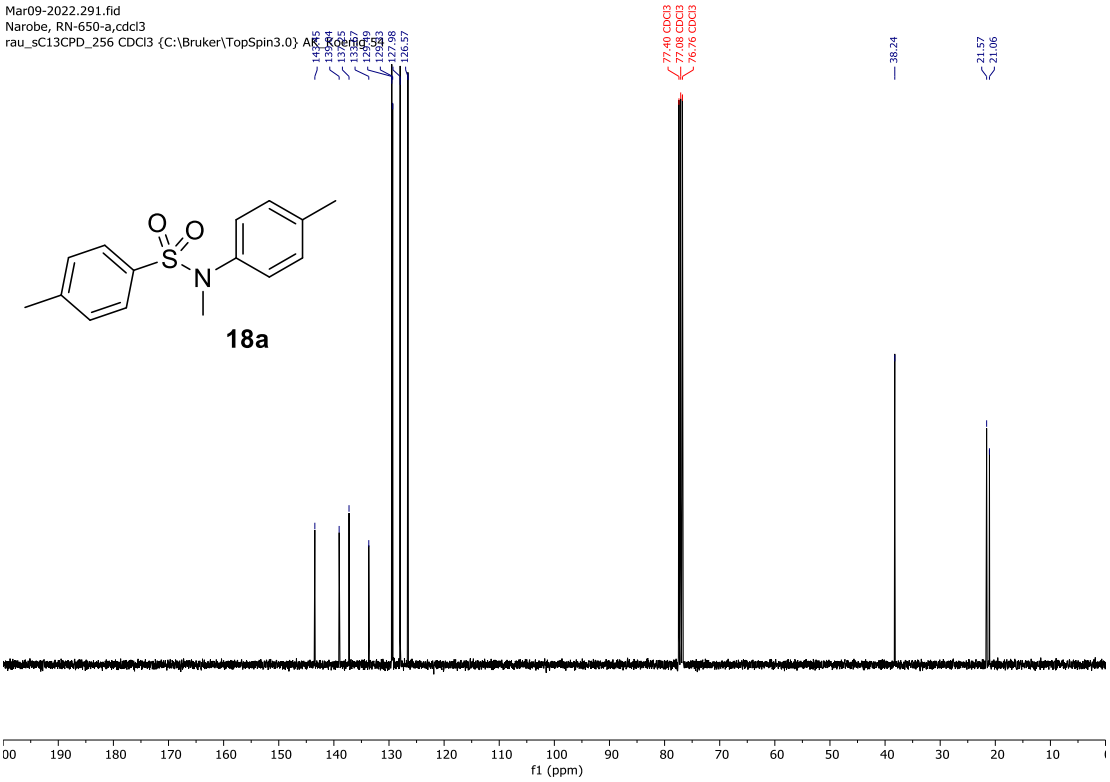


Figure S23: ^{13}C NMR spectrum of compound **18a** (101 MHz in $CDCl_3$).

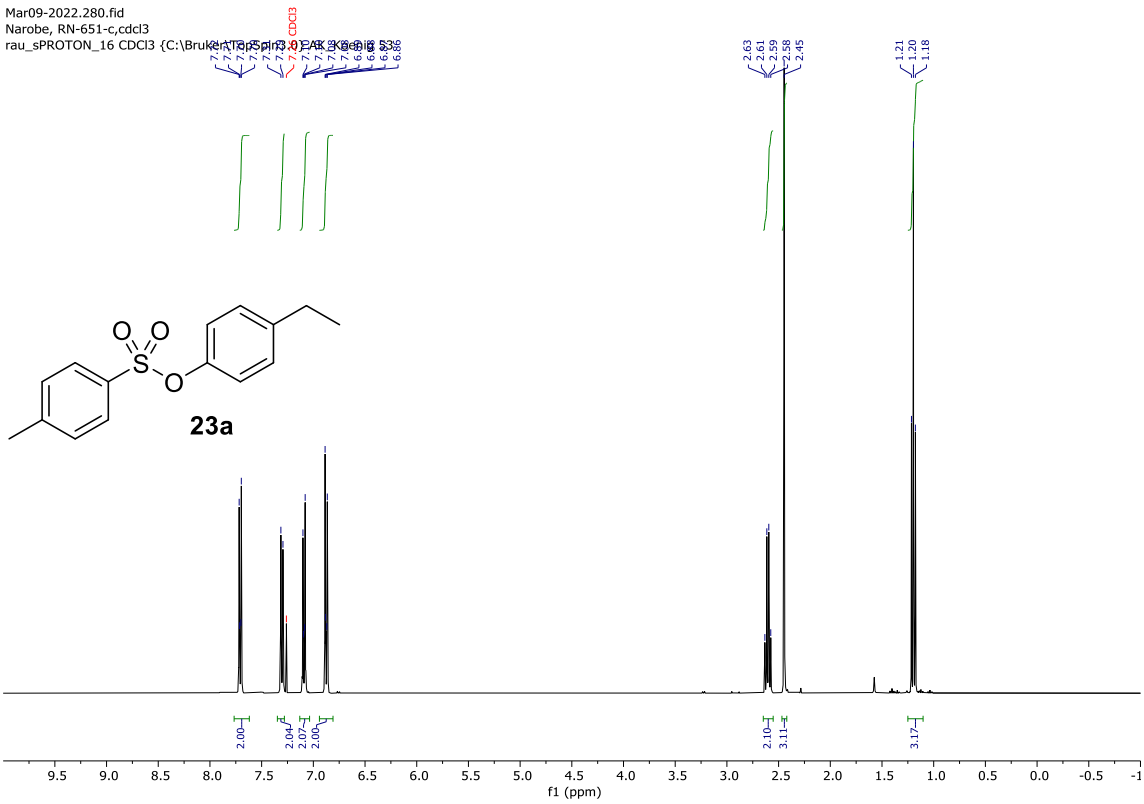


Figure S24: ^{1}H NMR spectrum of compound **23a** (400 MHz in $CDCl_3$).

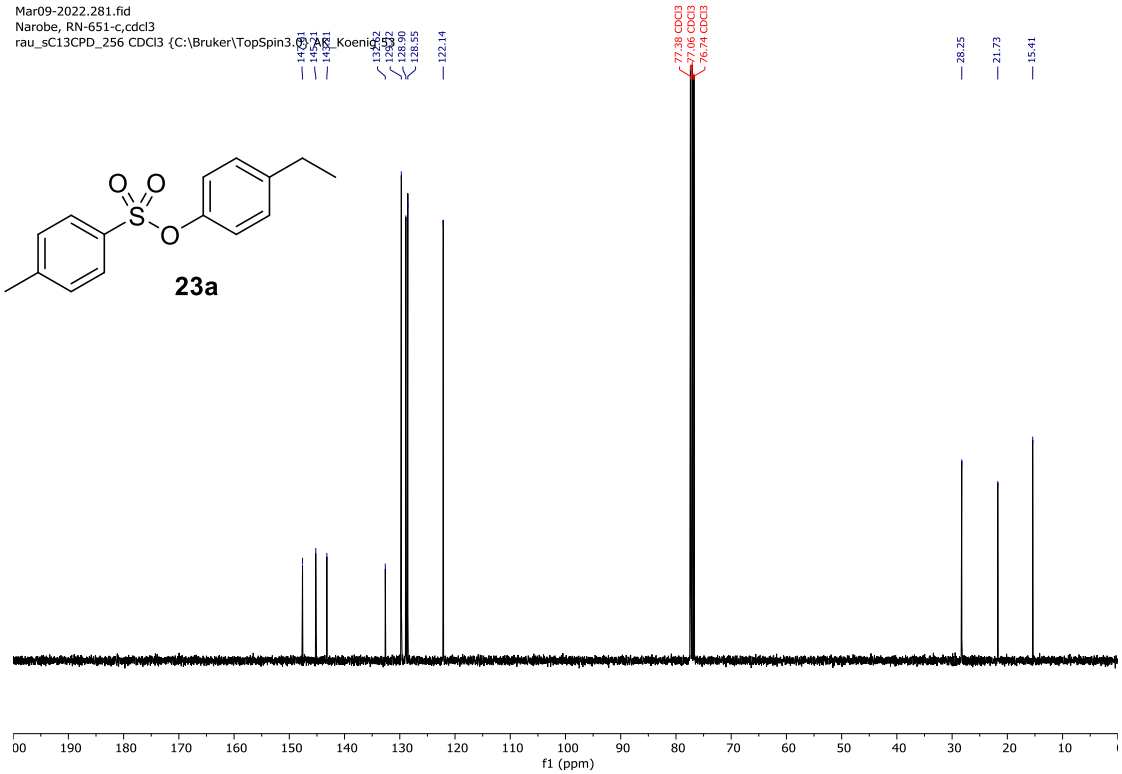


Figure S25: ^{13}C NMR spectrum of compound **23a** (101 MHz in $CDCl_3$).

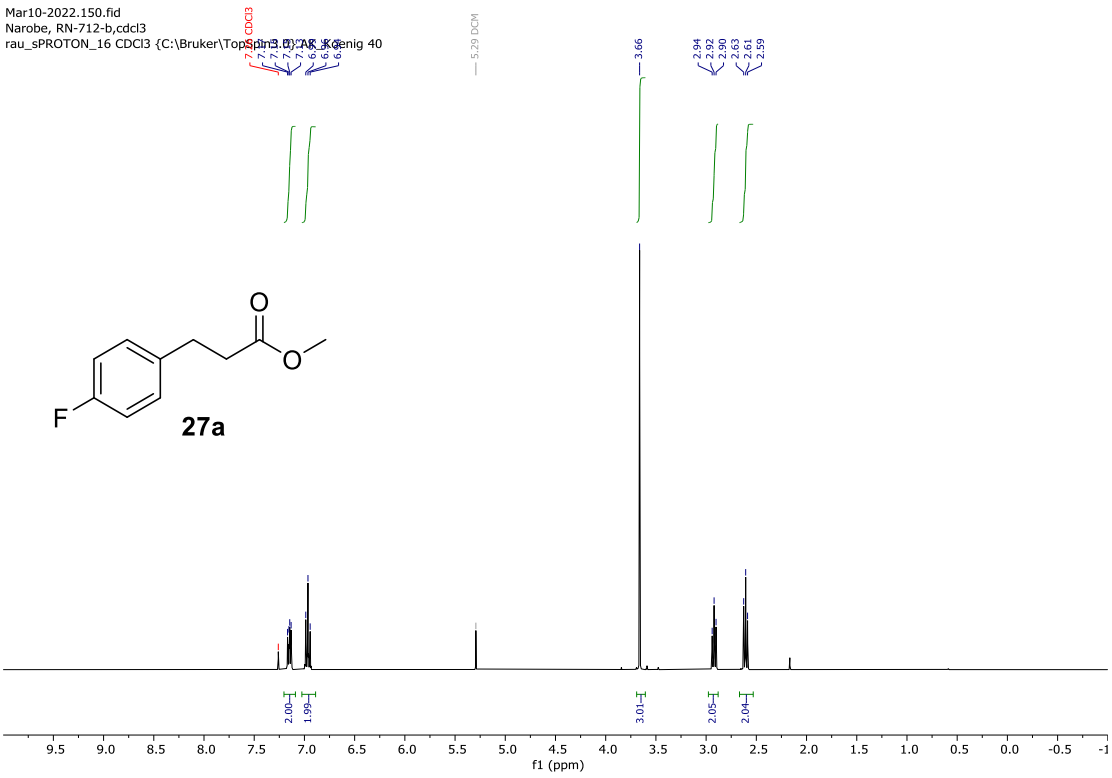


Figure S26: ^{1}H NMR spectrum of compound **27a** (400 MHz in $CDCl_3$).

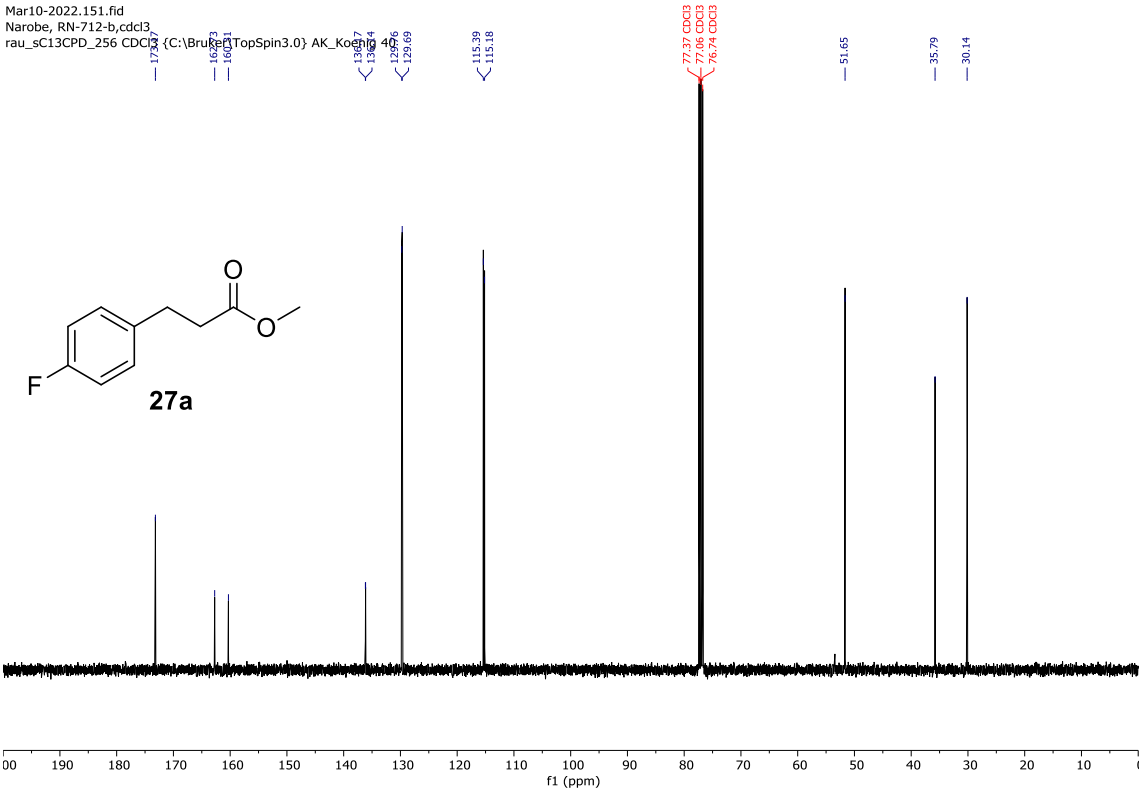


Figure S27: ^{13}C NMR spectrum of compound **27a** (101 MHz in $CDCl_3$).

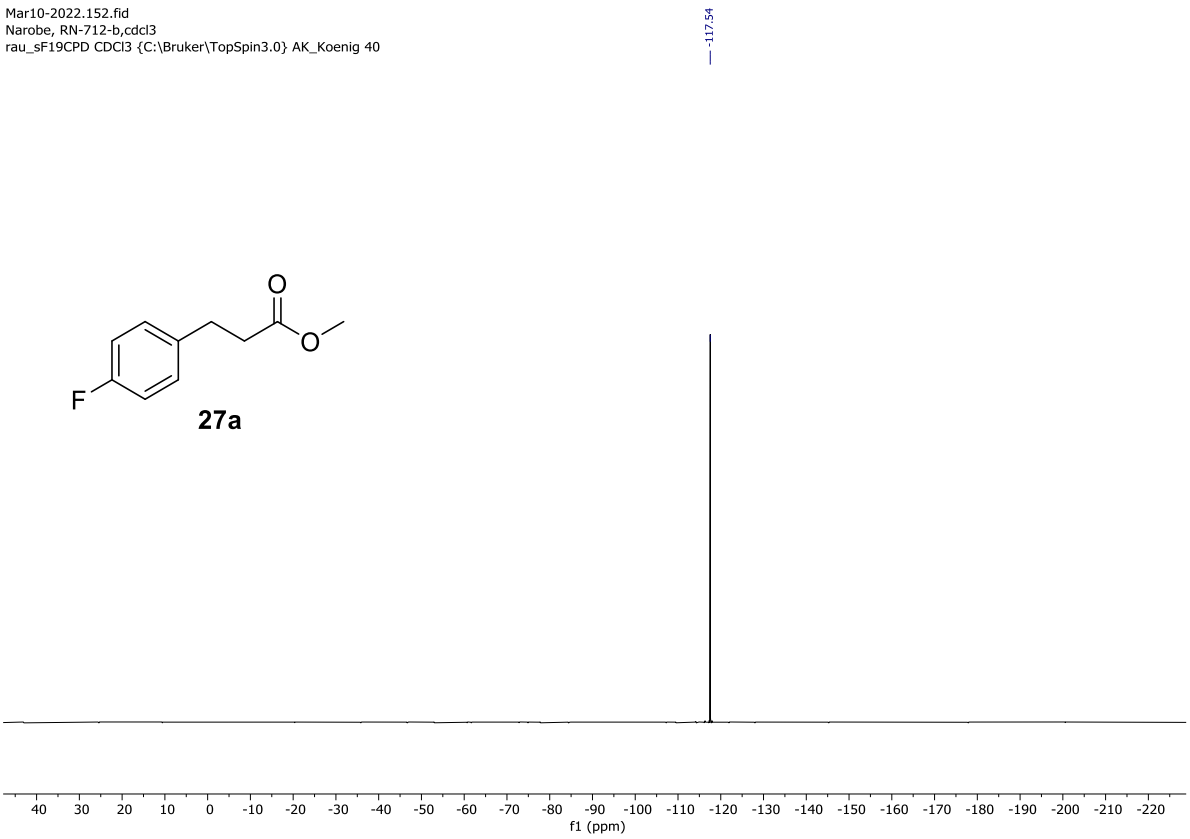


Figure S28: ^{19}F NMR spectrum of compound **27a** (377 MHz in $CDCl_3$).

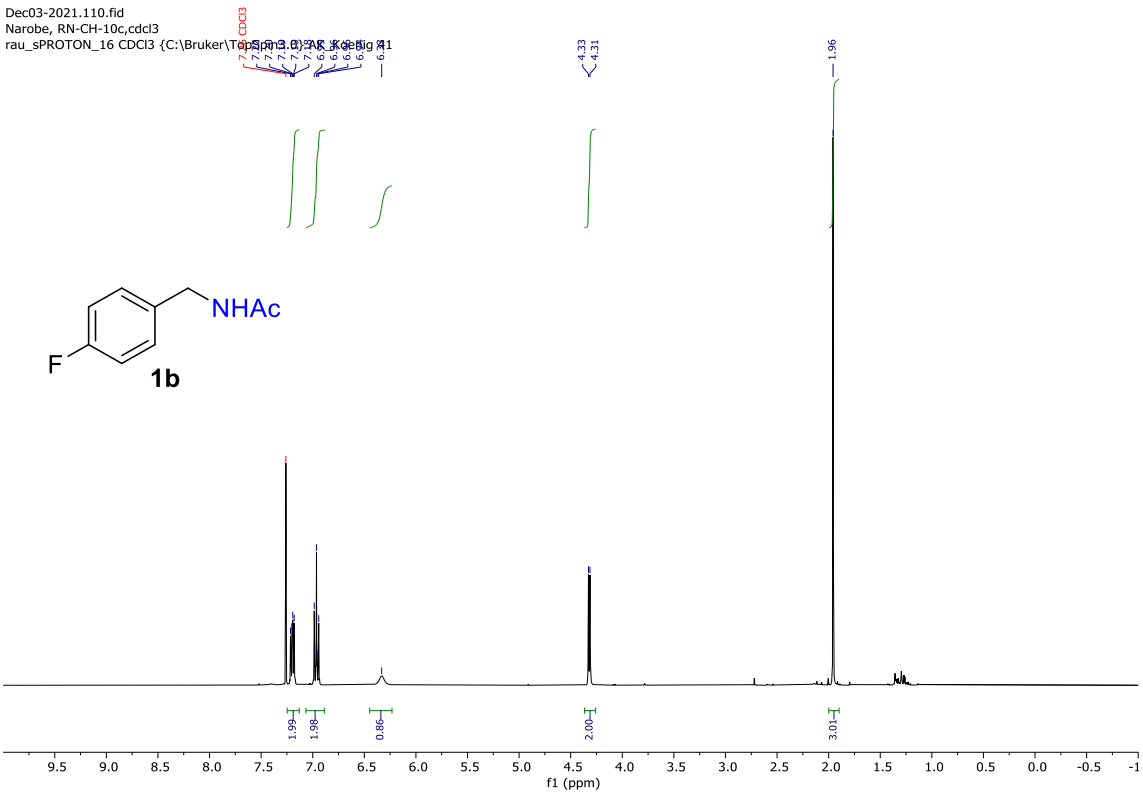


Figure S29: ^{1}H NMR spectrum of compound **1b** (400 MHz in $CDCl_3$).

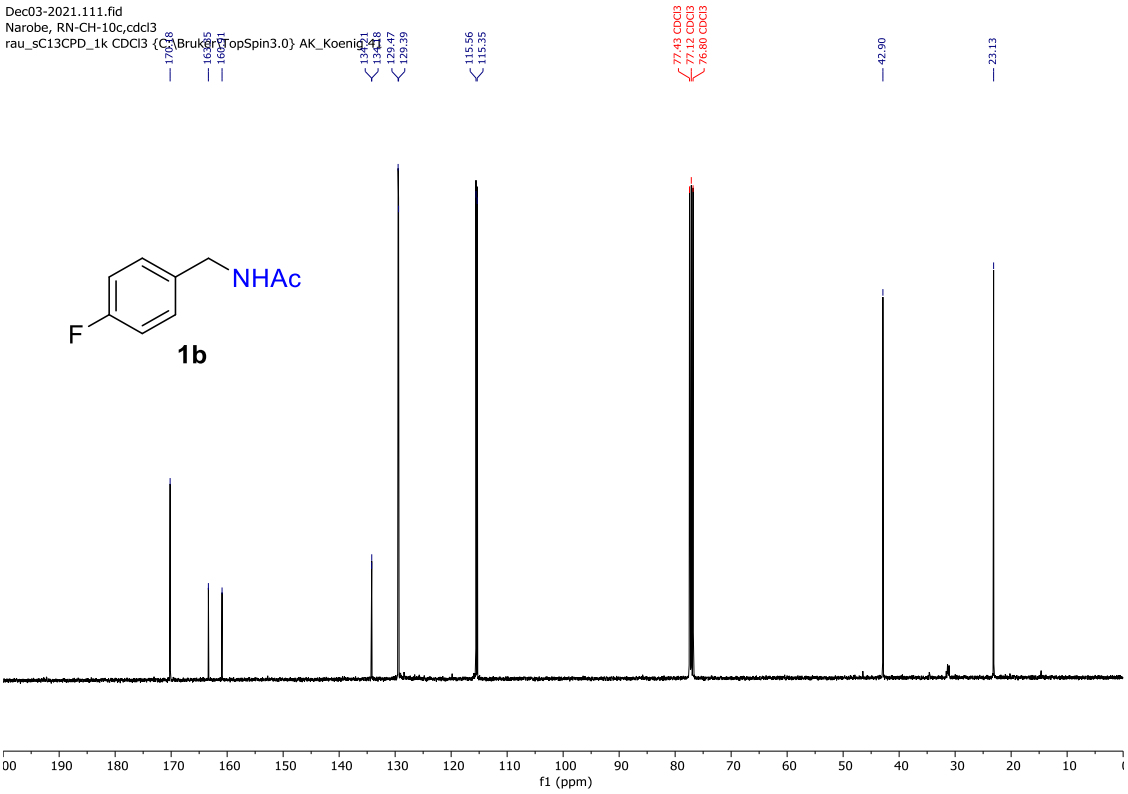


Figure S30: ^{13}C NMR spectrum of compound **1b** (101 MHz in $CDCl_3$).

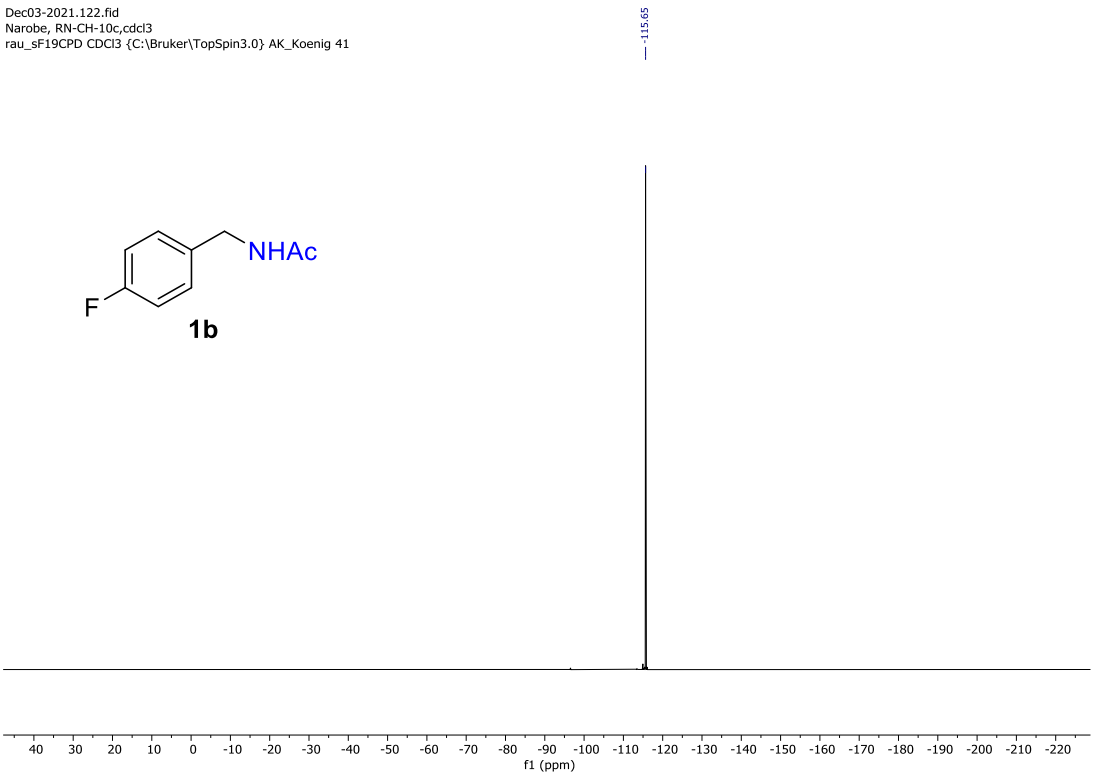


Figure S31: ^{19}F NMR spectrum of compound **1b** (377 MHz in $CDCl_3$).

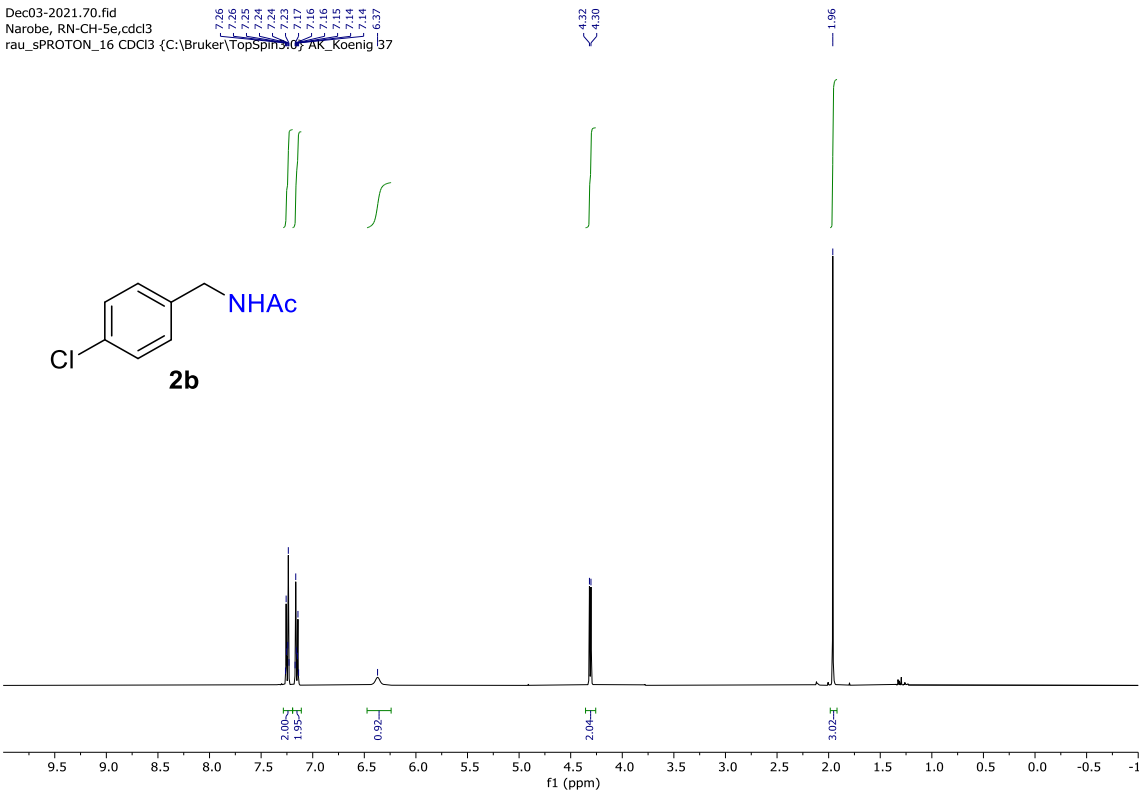


Figure S32: ^{1}H NMR spectrum of compound **2b** (400 MHz in $CDCl_3$).

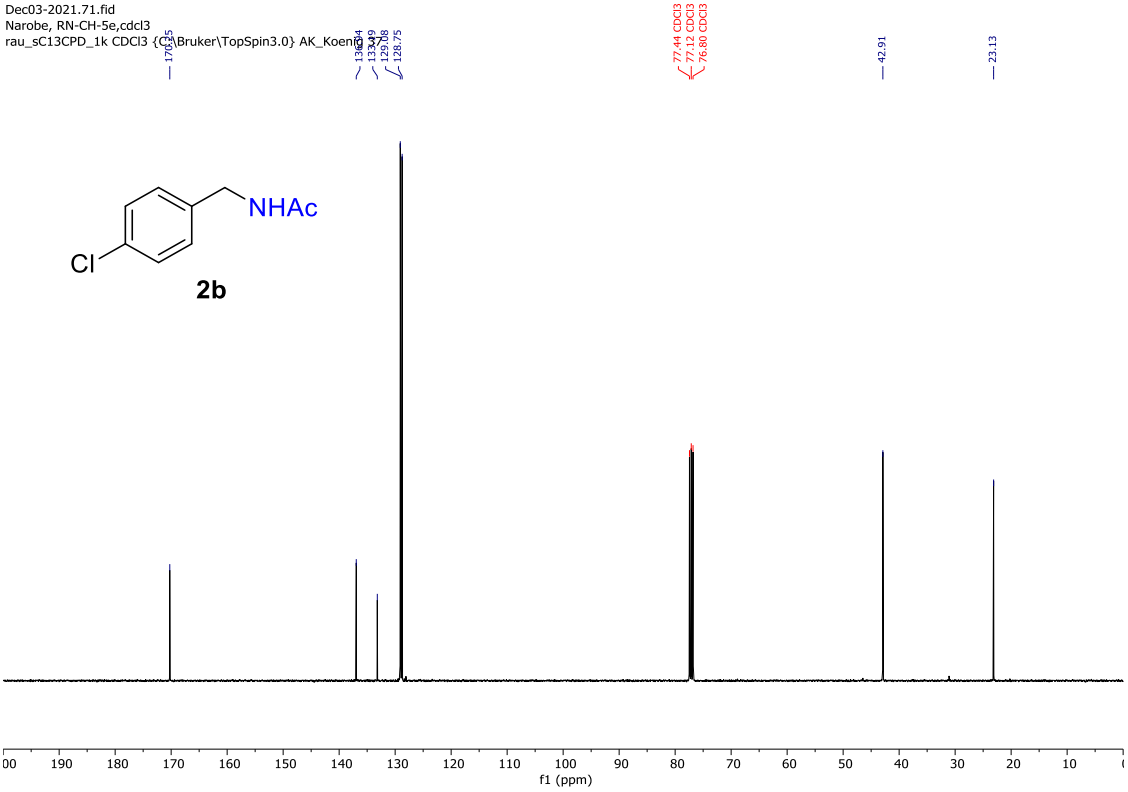


Figure S33: ^{13}C NMR spectrum of compound **2b** (101 MHz in $CDCl_3$).

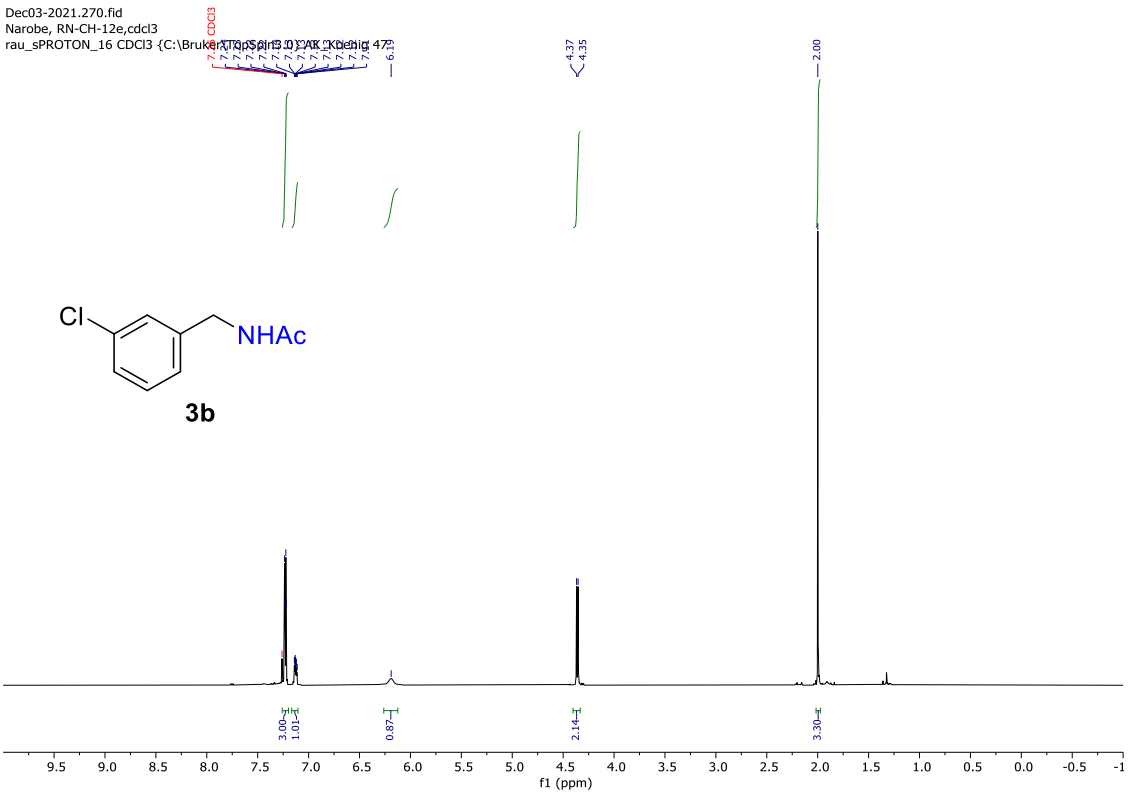


Figure S34: ^{1}H NMR spectrum of compound **3b** (400 MHz in $CDCl_3$).

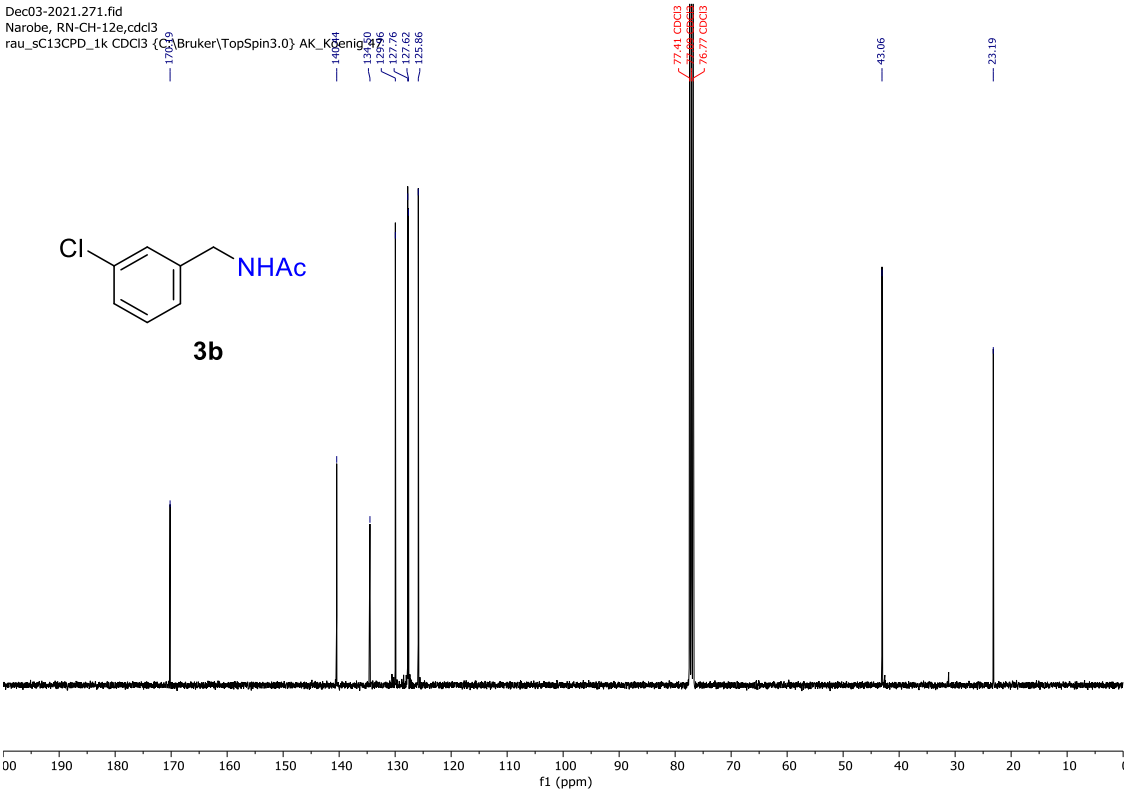


Figure S35: ^{13}C NMR spectrum of compound **3b** (101 MHz in $CDCl_3$).

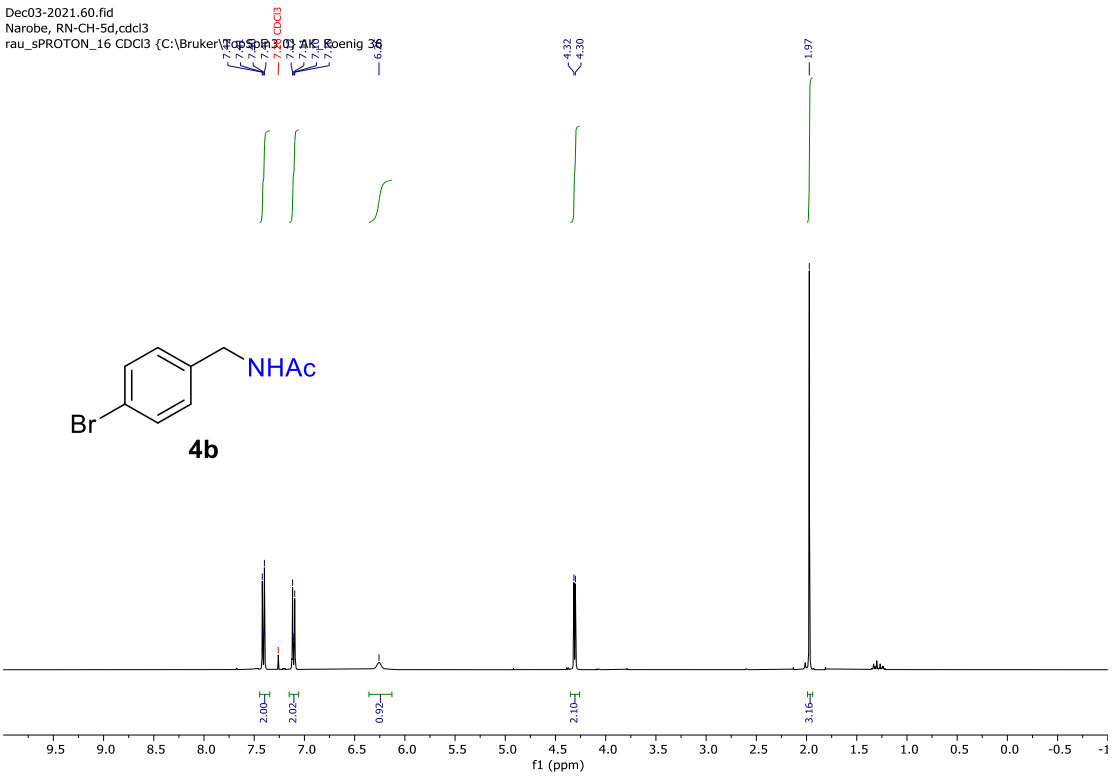


Figure S36: ^{1}H NMR spectrum of compound **4b** (400 MHz in $CDCl_3$).

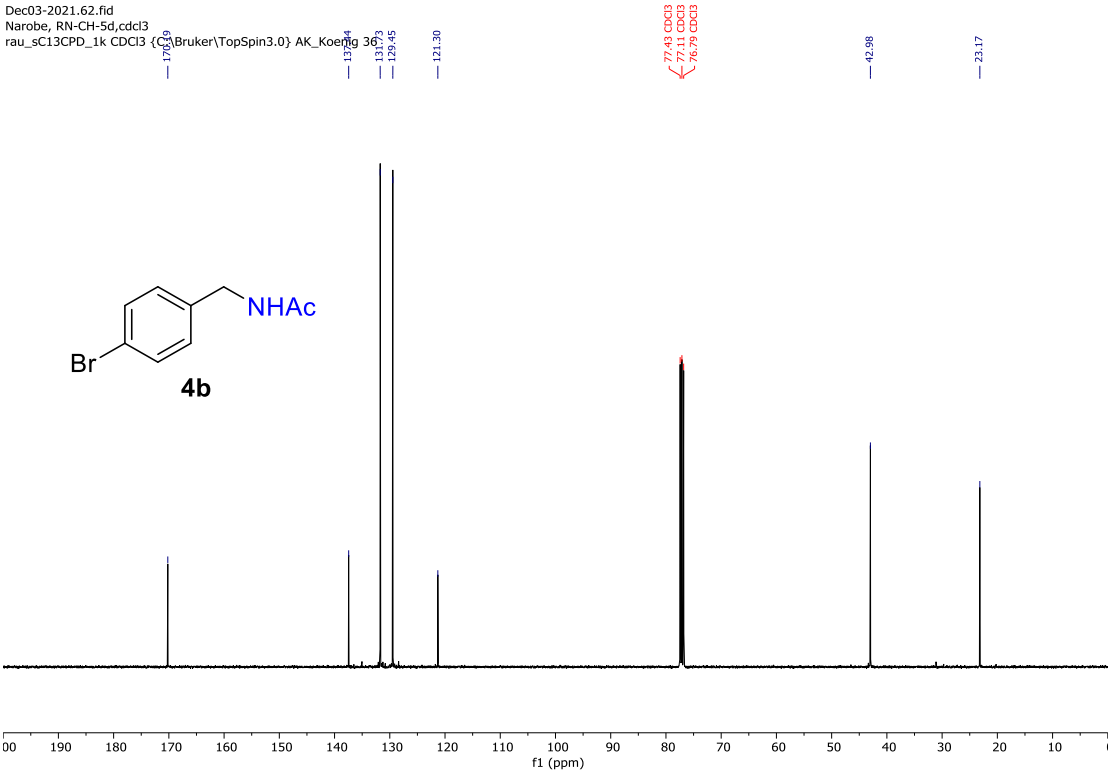


Figure S37: ^{13}C NMR spectrum of compound **4b** (101 MHz in $CDCl_3$).

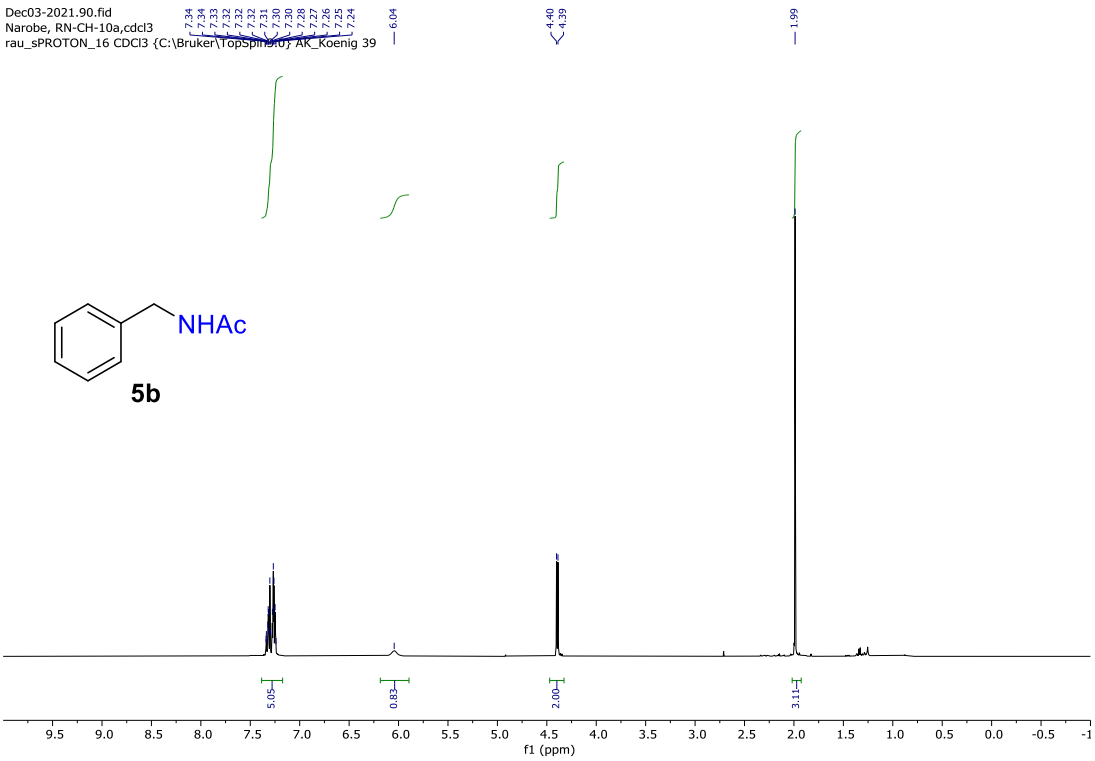


Figure S38: ^{1}H NMR spectrum of compound **5b** (400 MHz in $CDCl_3$).

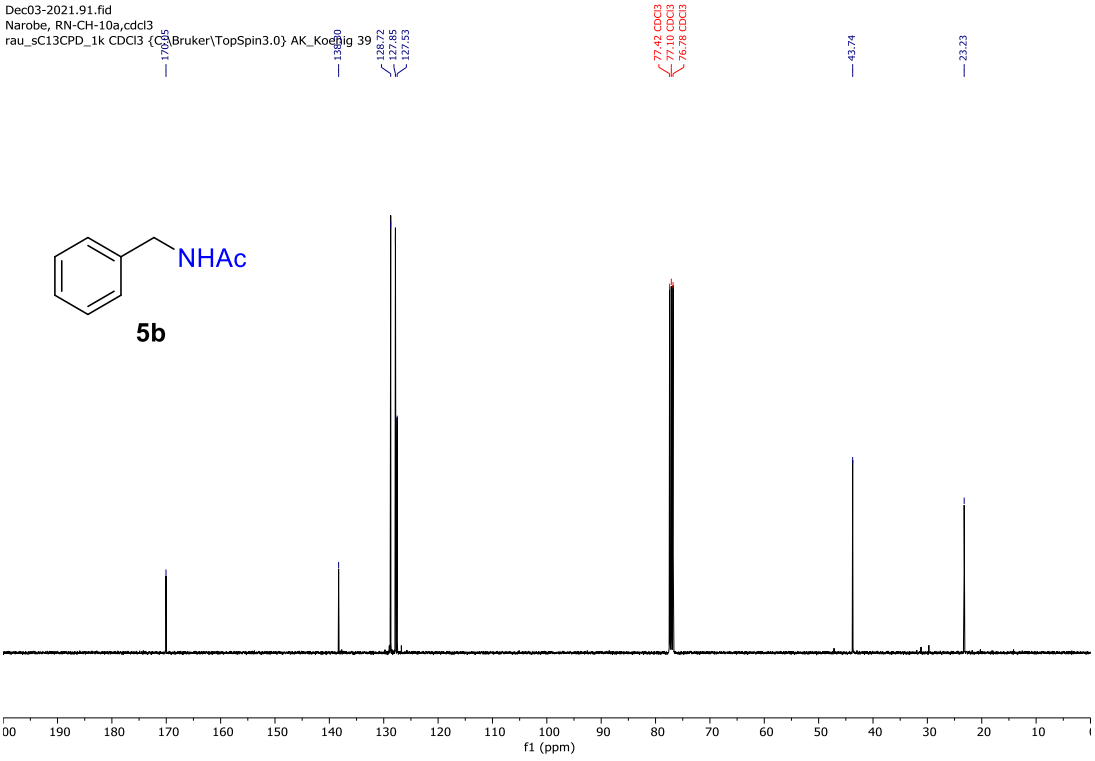


Figure S39: ^{13}C NMR spectrum of compound **5b** (101 MHz in $CDCl_3$).

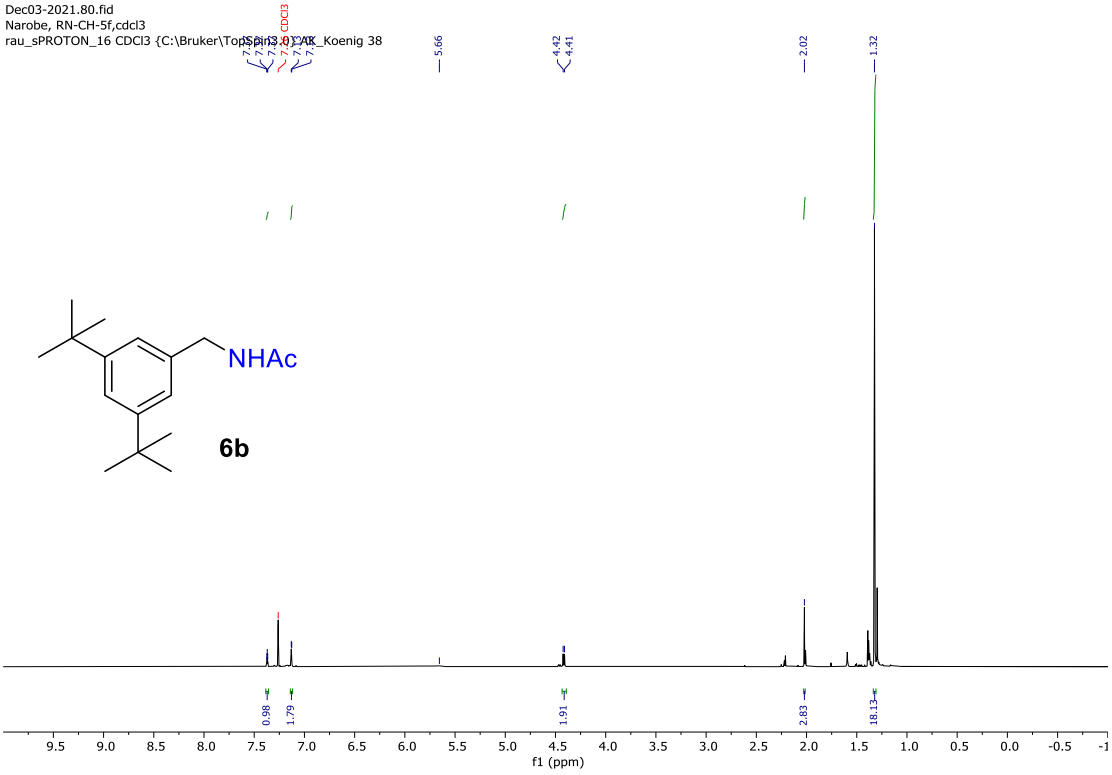


Figure S40: ^{1}H NMR spectrum of compound **6b** (400 MHz in $CDCl_3$).

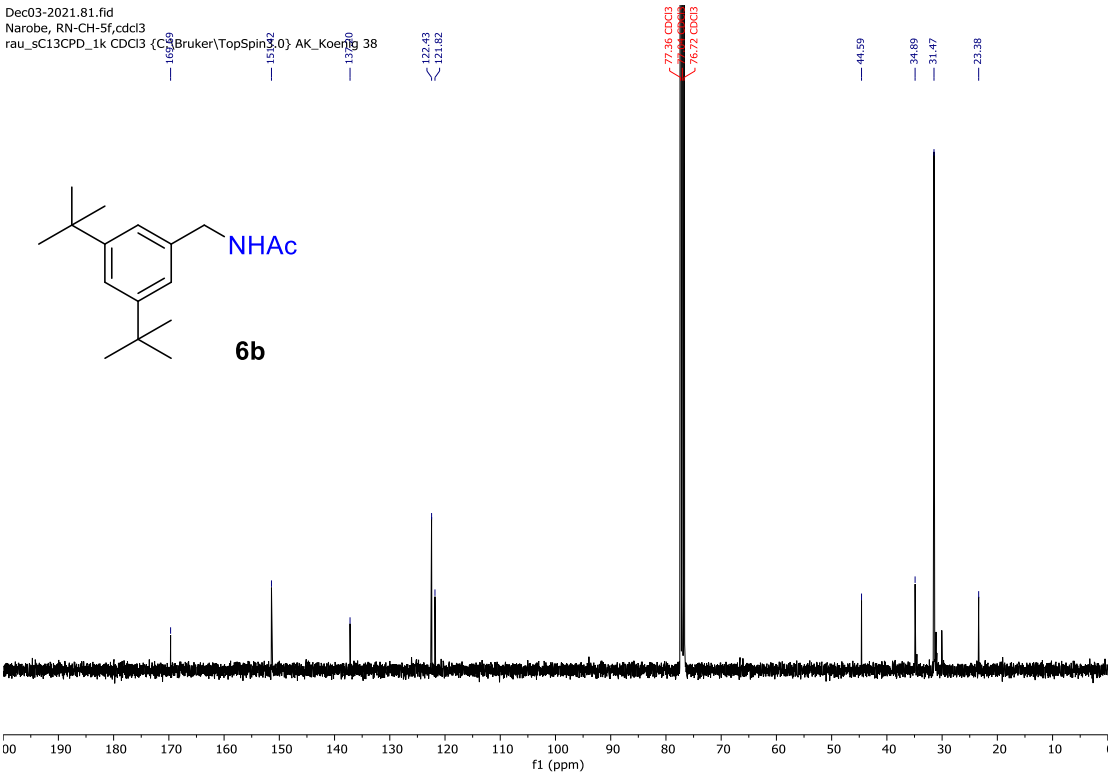


Figure S41: ^{13}C NMR spectrum of compound **6b** (101 MHz in $CDCl_3$).

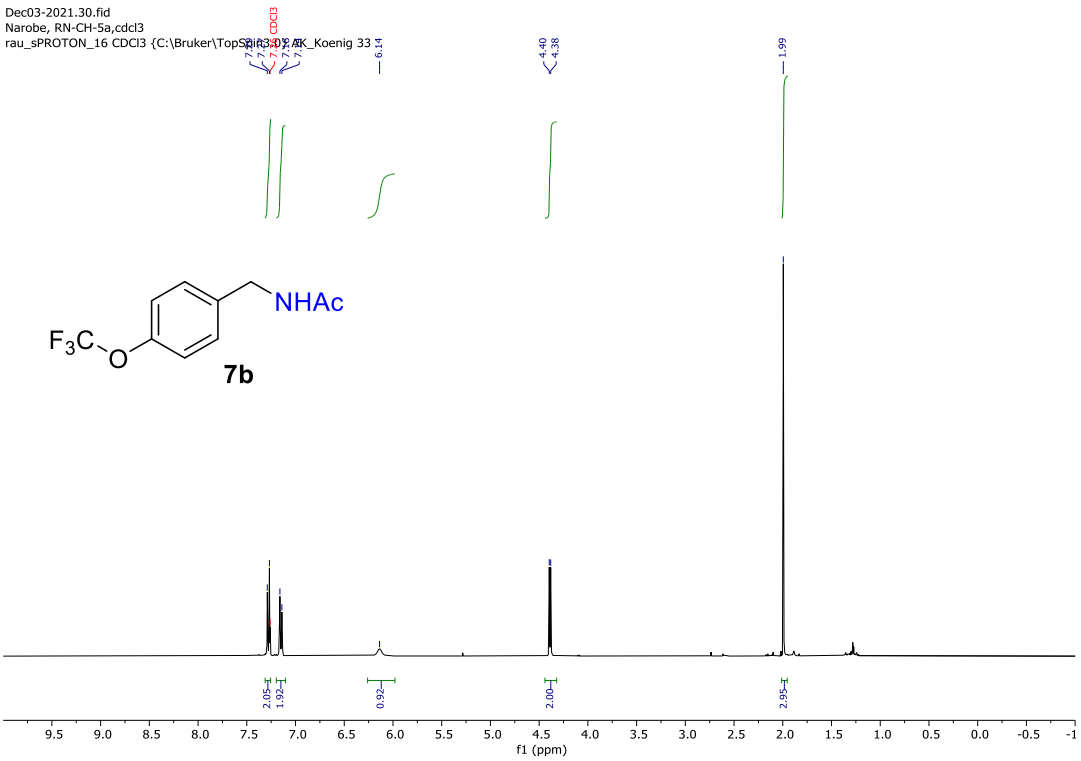


Figure S42: ^{1}H NMR spectrum of compound **7b** (400 MHz in $CDCl_3$).

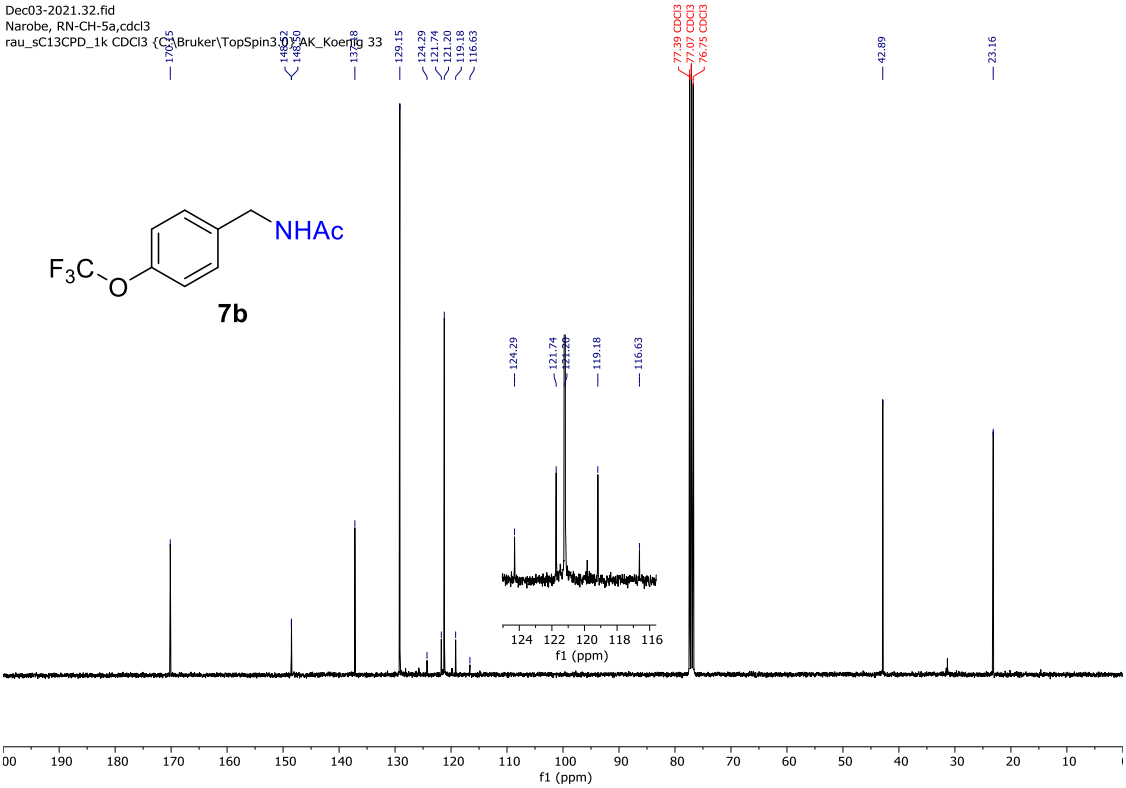


Figure S43: ^{13}C NMR spectrum of compound **7b** (101 MHz in $CDCl_3$).

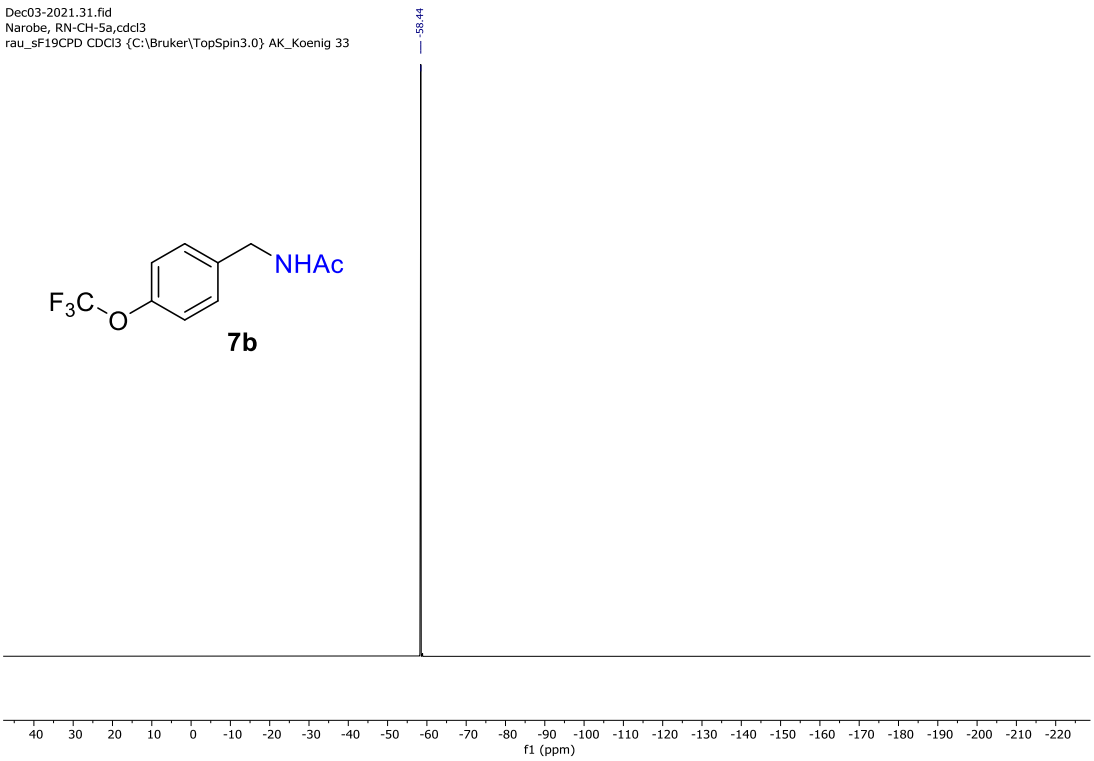


Figure S44: ^{19}F NMR spectrum of compound **7b** (377 MHz in $CDCl_3$).

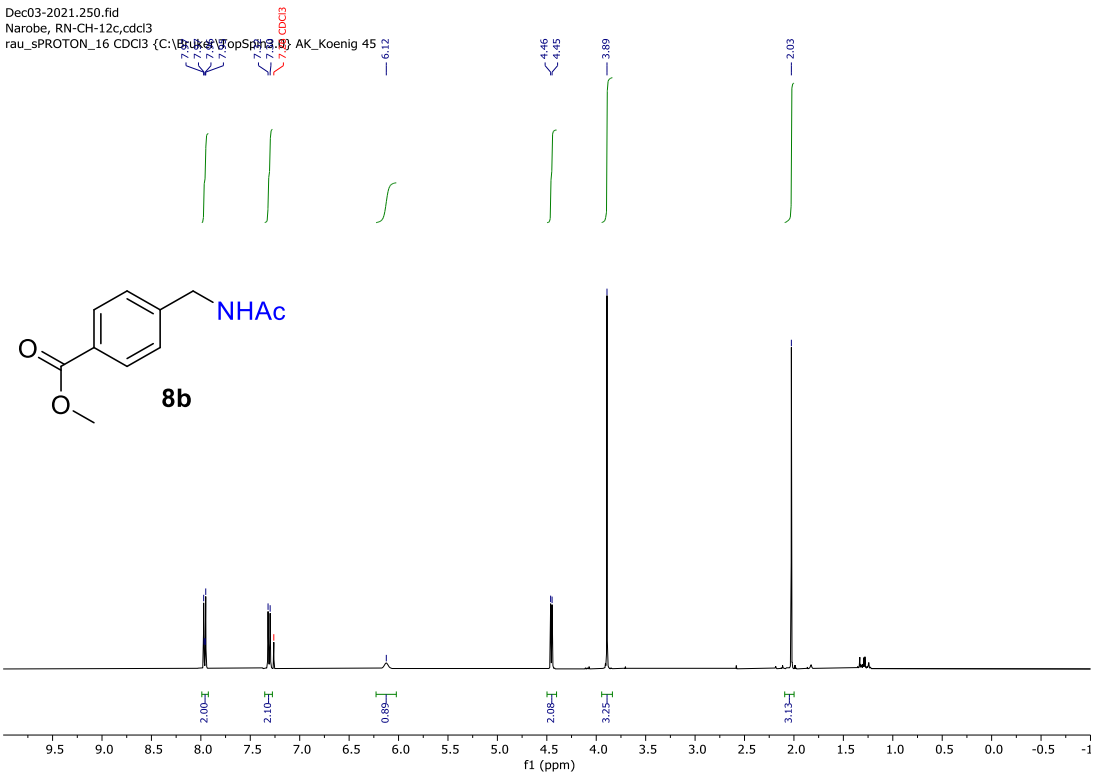


Figure S45: ^{1}H NMR spectrum of compound **8b** (400 MHz in $CDCl_3$).

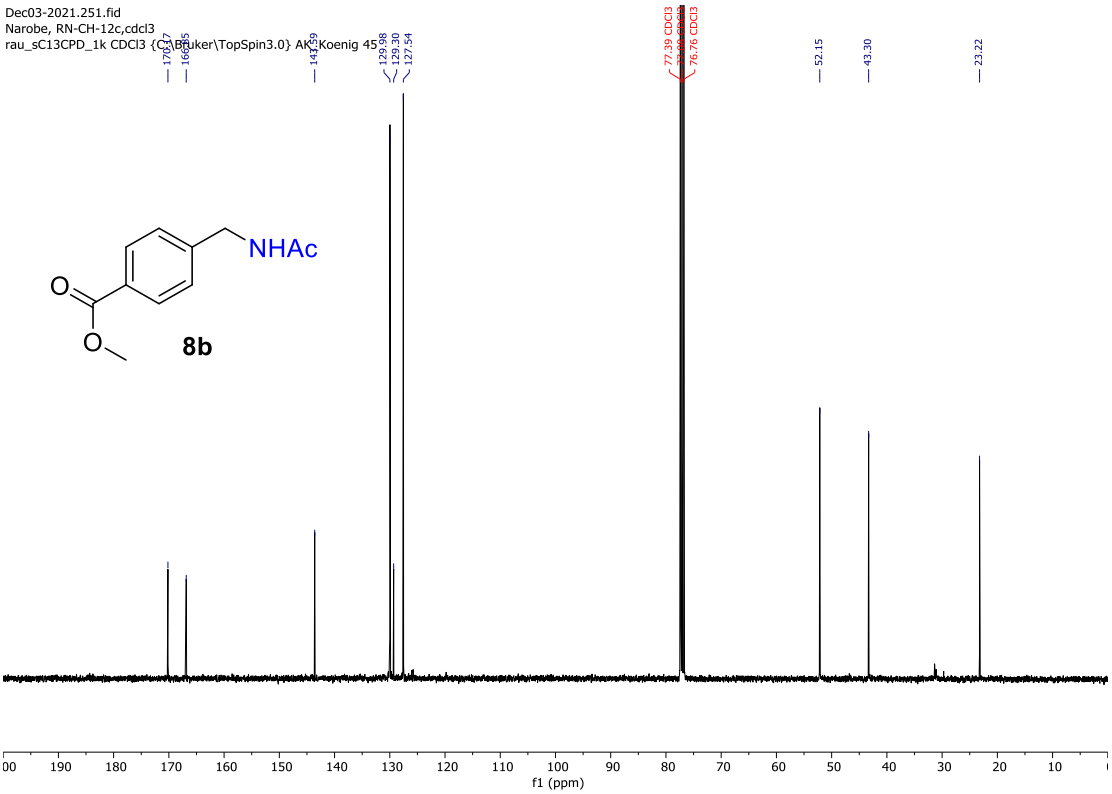


Figure S46: ^{13}C NMR spectrum of compound **8b** (101 MHz in $CDCl_3$).

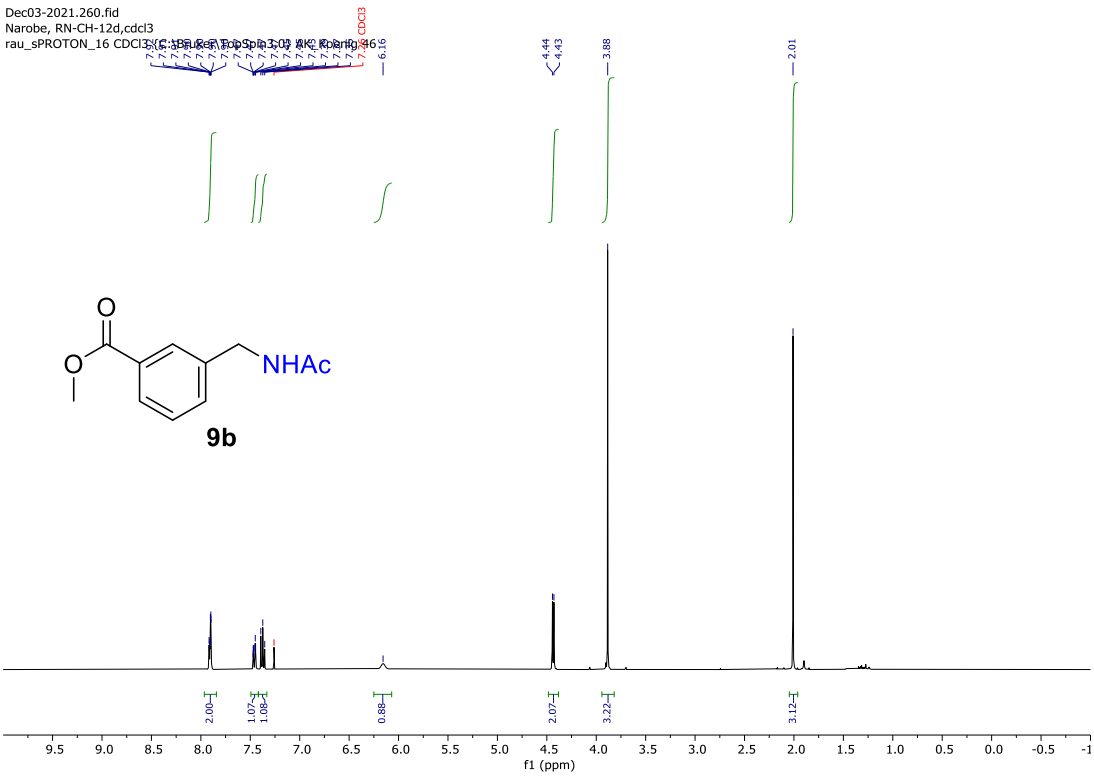


Figure S47: ^{1}H NMR spectrum of compound **9b** (400 MHz in $CDCl_3$).

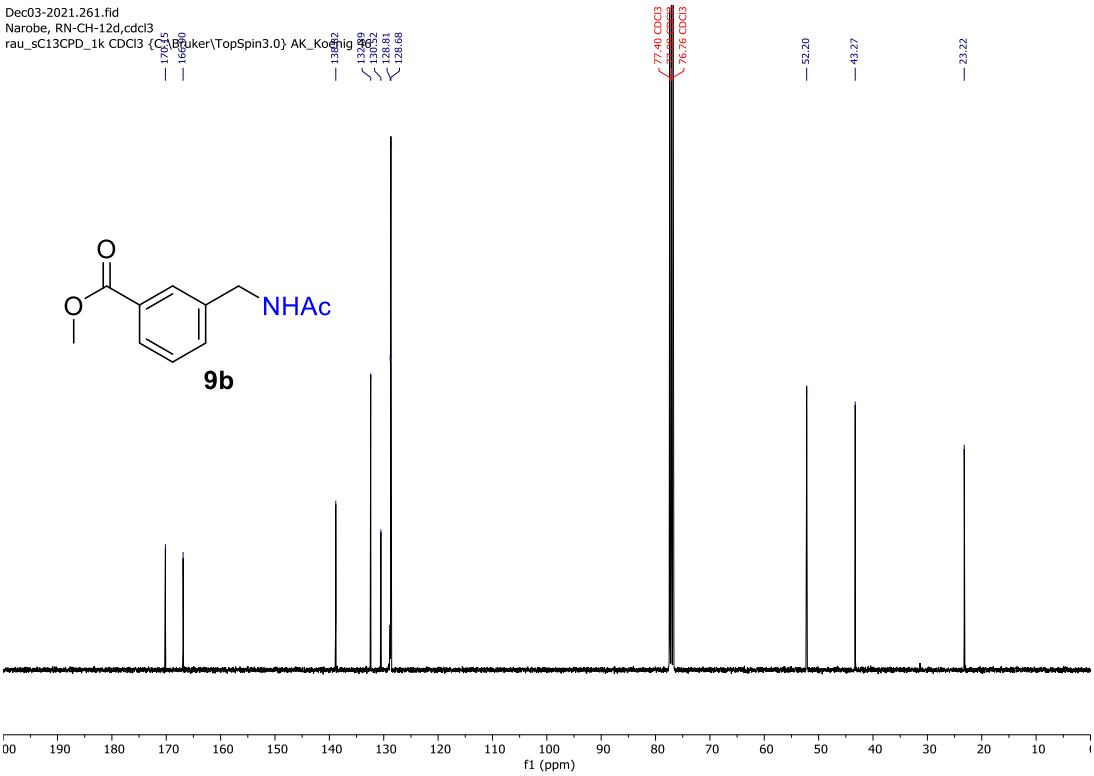


Figure S48: ^{13}C NMR spectrum of compound **9b** (101 MHz in $CDCl_3$).

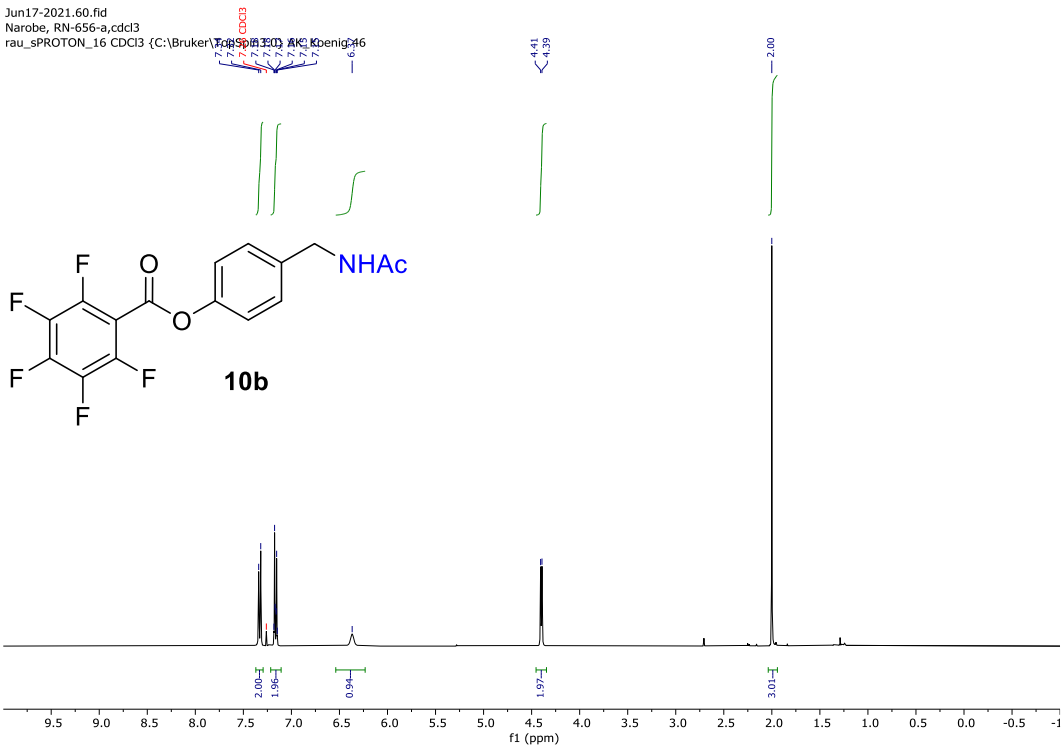


Figure S49: ^{1}H NMR spectrum of compound **10b** (400 MHz in $CDCl_3$).

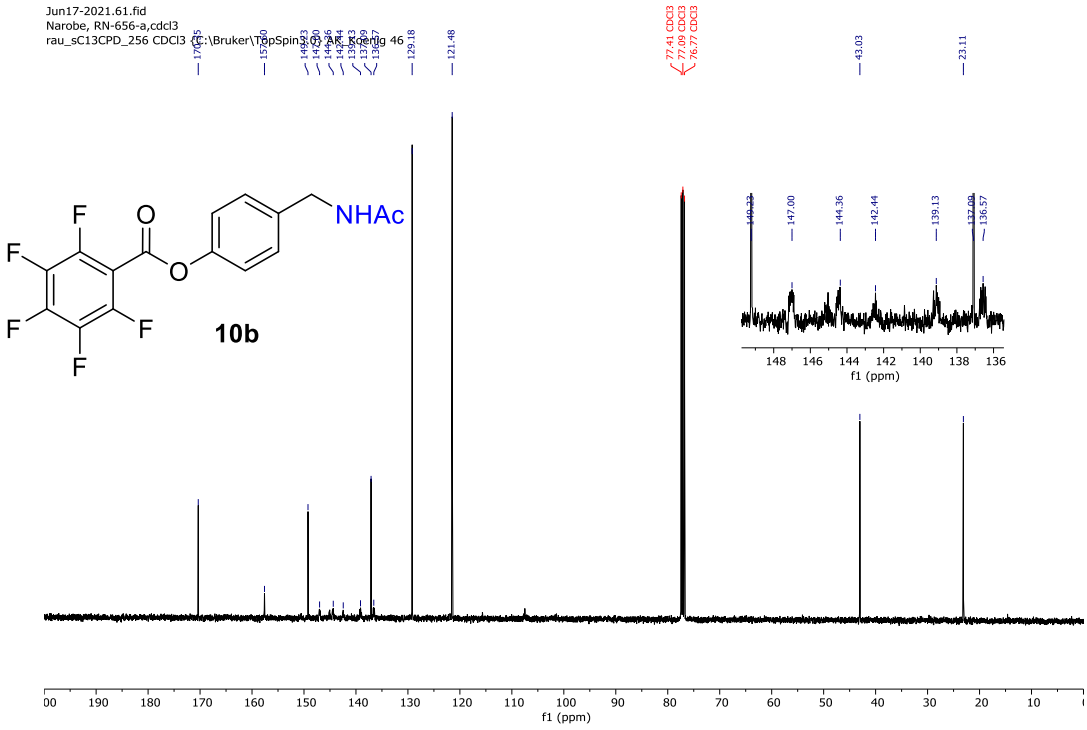


Figure S50: ^{13}C NMR spectrum of compound **10b** (101 MHz in $CDCl_3$).

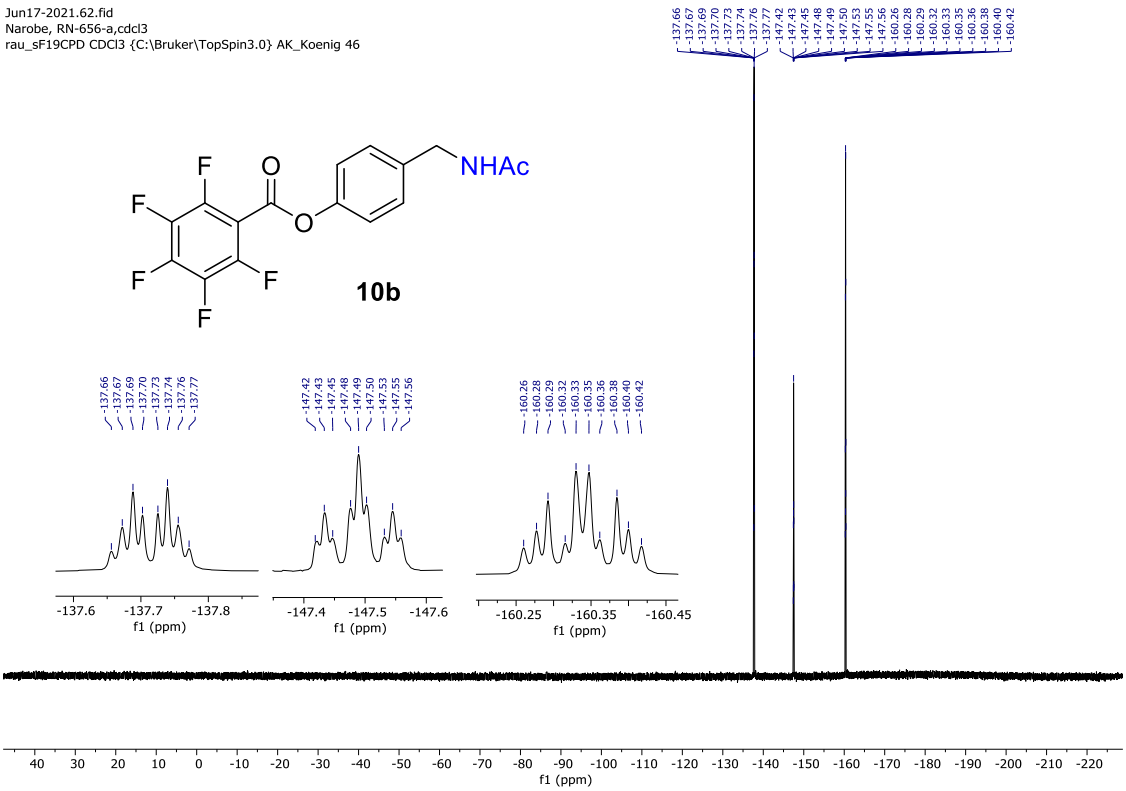


Figure S51: ^{19}F NMR spectrum of compound **10b** (377 MHz in $CDCl_3$).

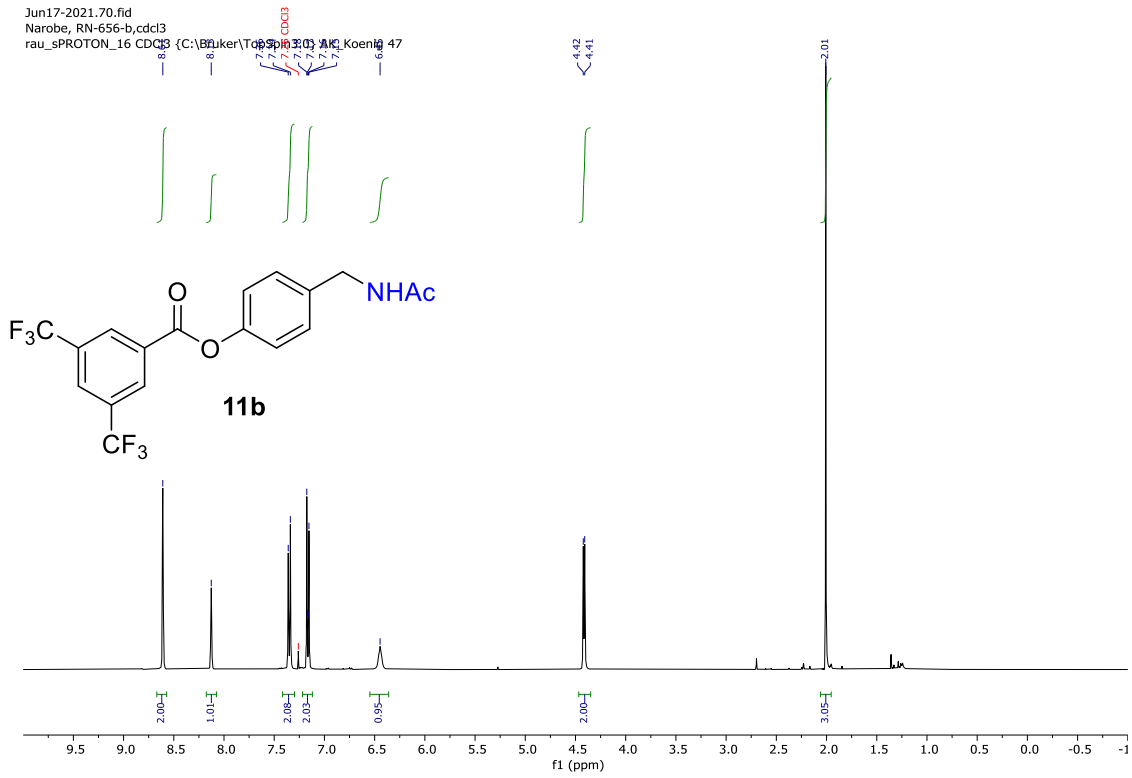


Figure S52: ^{1}H NMR spectrum of compound **11b** (400 MHz in $CDCl_3$).

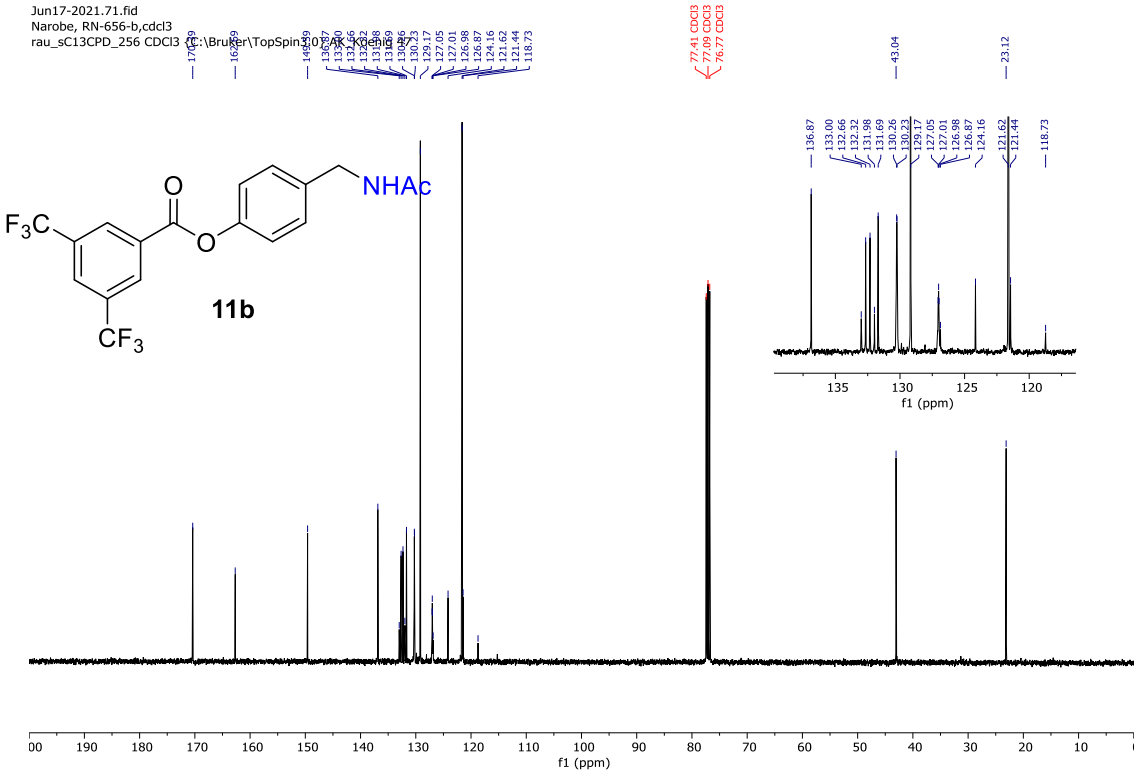


Figure S53: ^{13}C NMR spectrum of compound **11b** (101 MHz in $CDCl_3$).

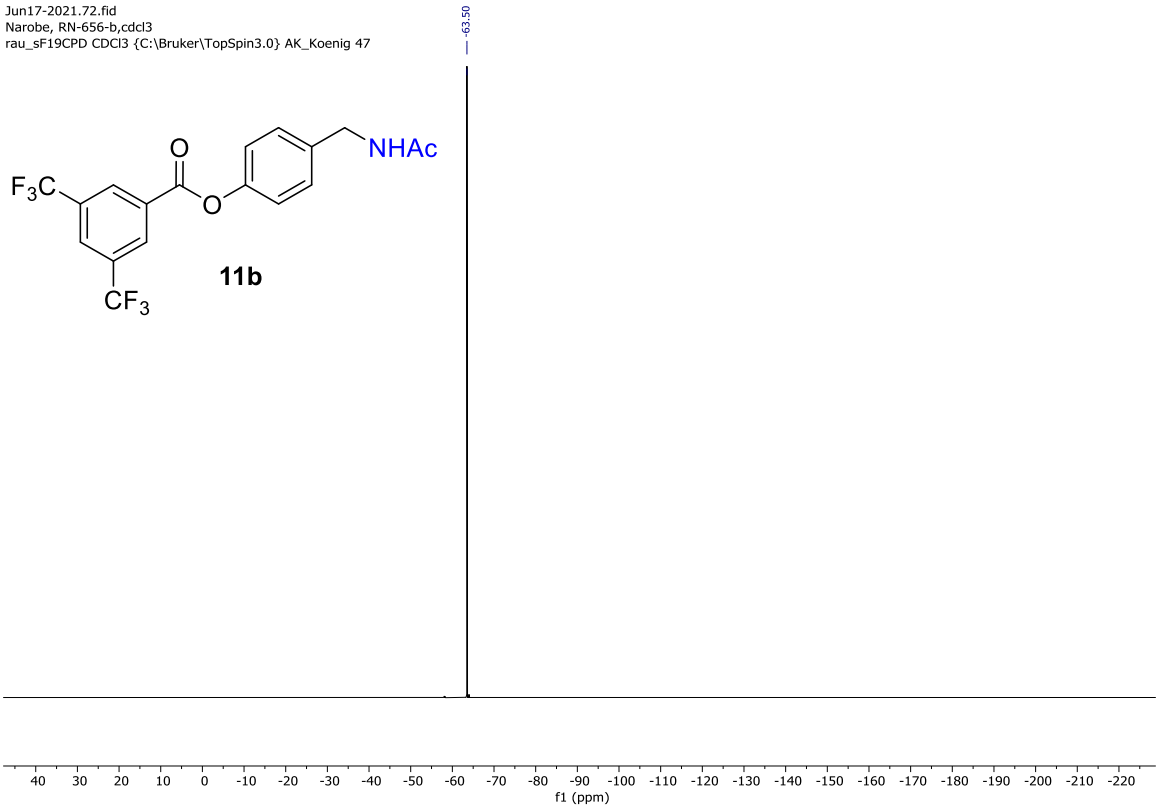


Figure S54: ^{19}F NMR spectrum of compound **11b** (377 MHz in $CDCl_3$).

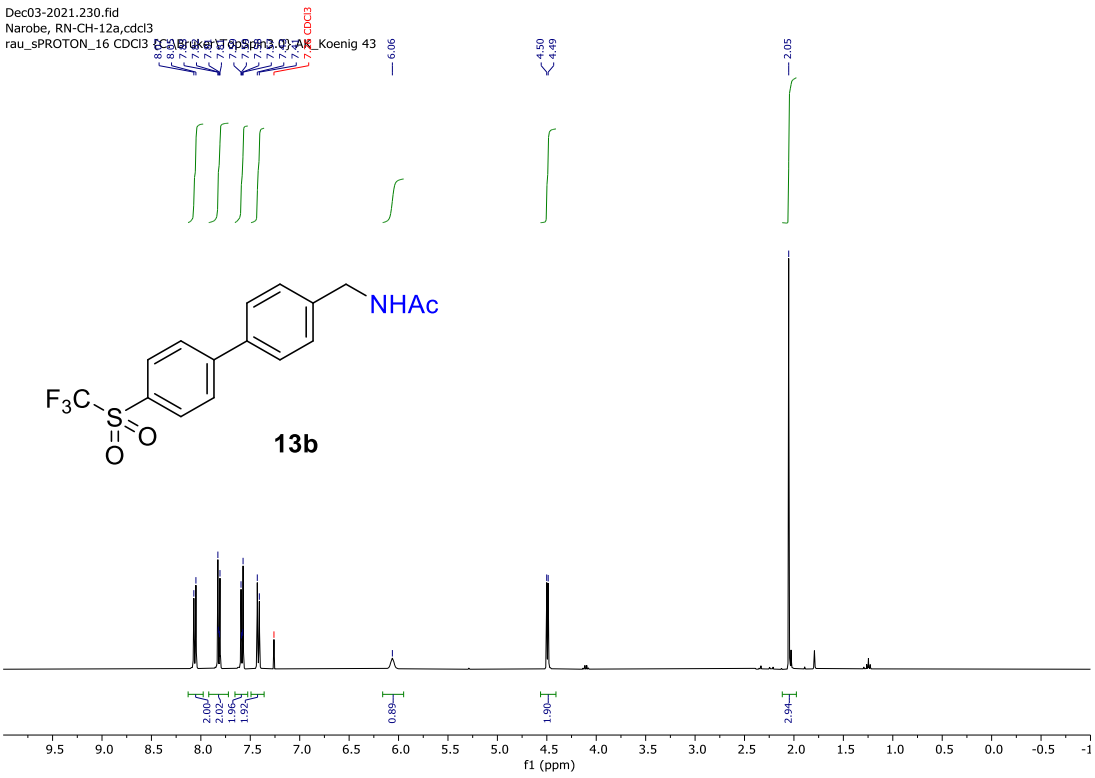


Figure S55: ^{1}H NMR spectrum of compound **13b** (400 MHz in $CDCl_3$).

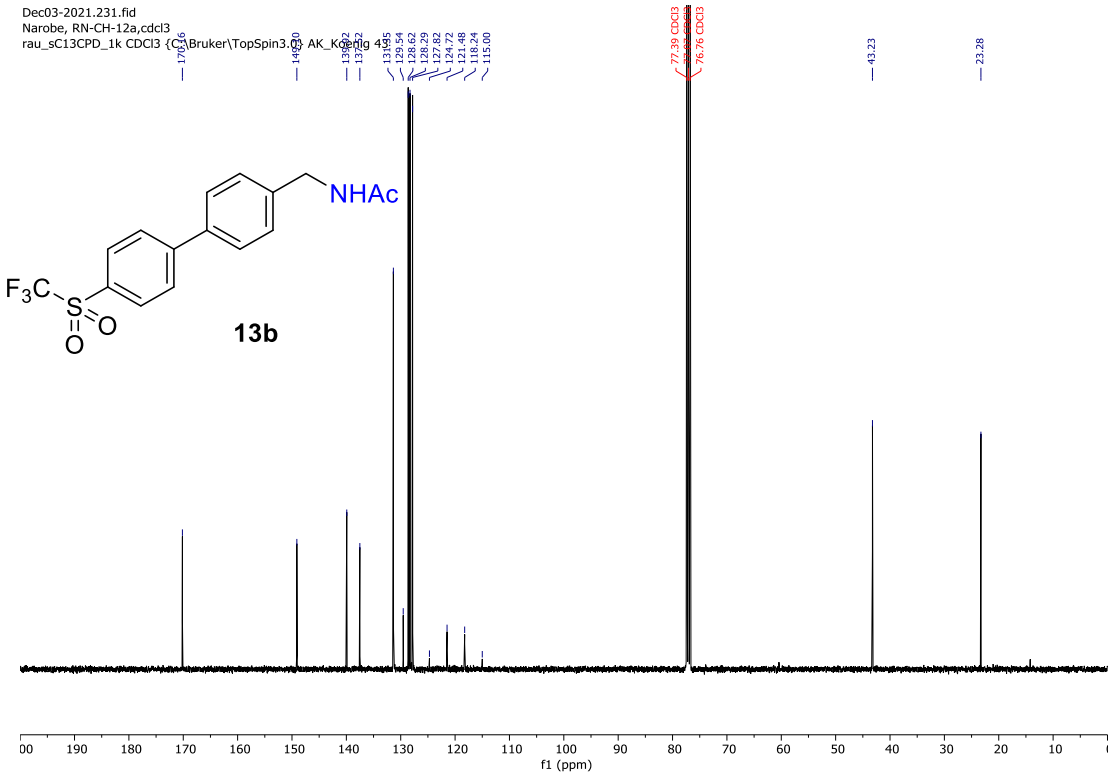


Figure S56: ^{13}C NMR spectrum of compound **13b** (101 MHz in $CDCl_3$).

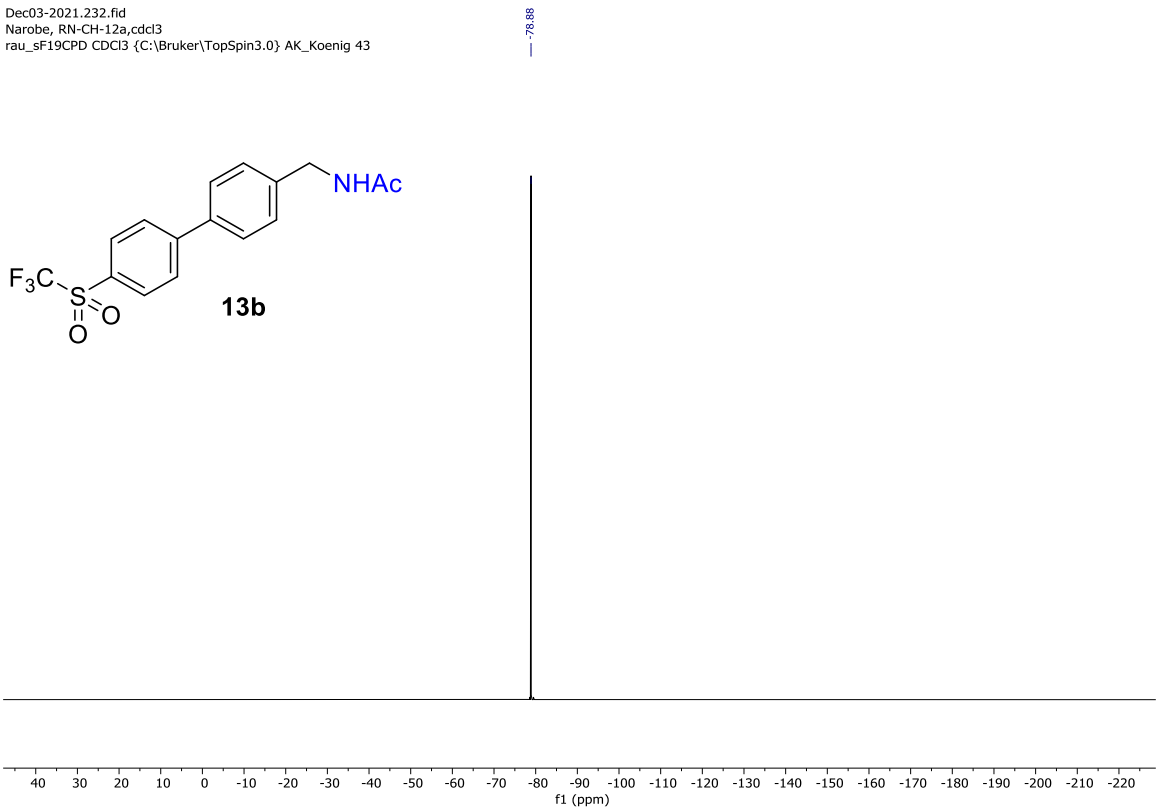


Figure S57: ^{19}F NMR spectrum of compound **13b** (377 MHz in $CDCl_3$).

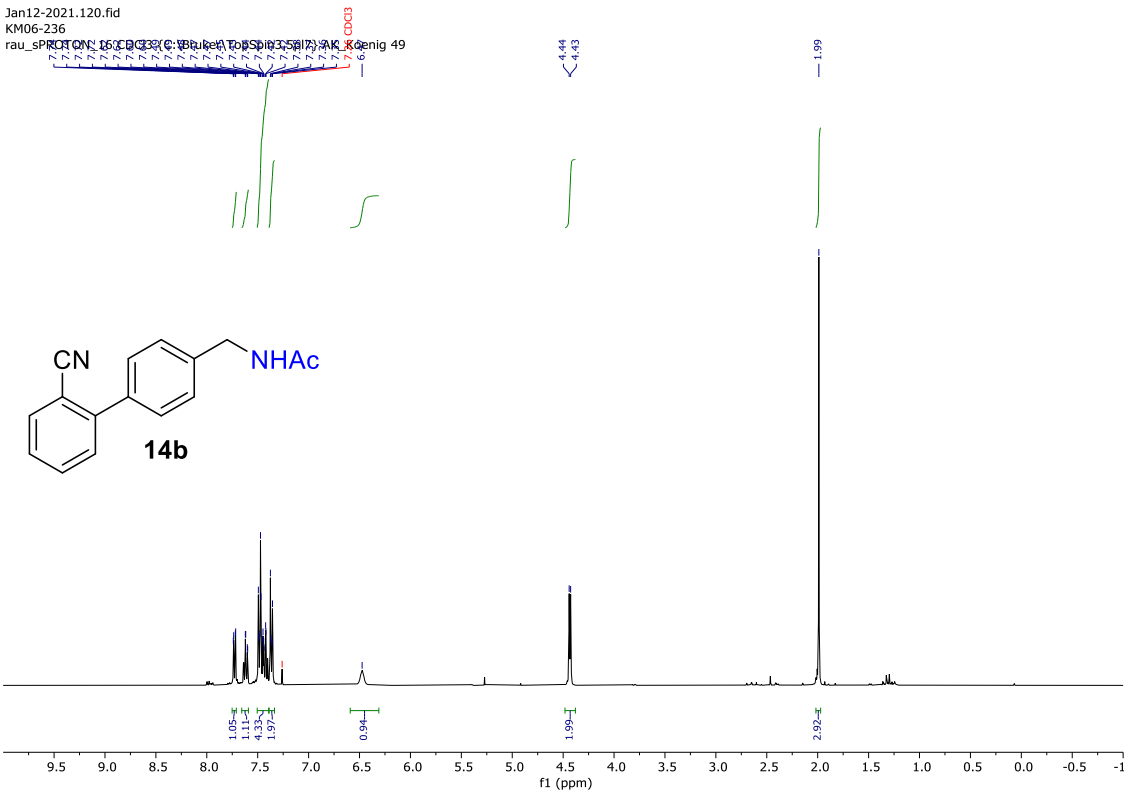


Figure S58: ^{1}H NMR spectrum of compound **14b** (400 MHz in $CDCl_3$).

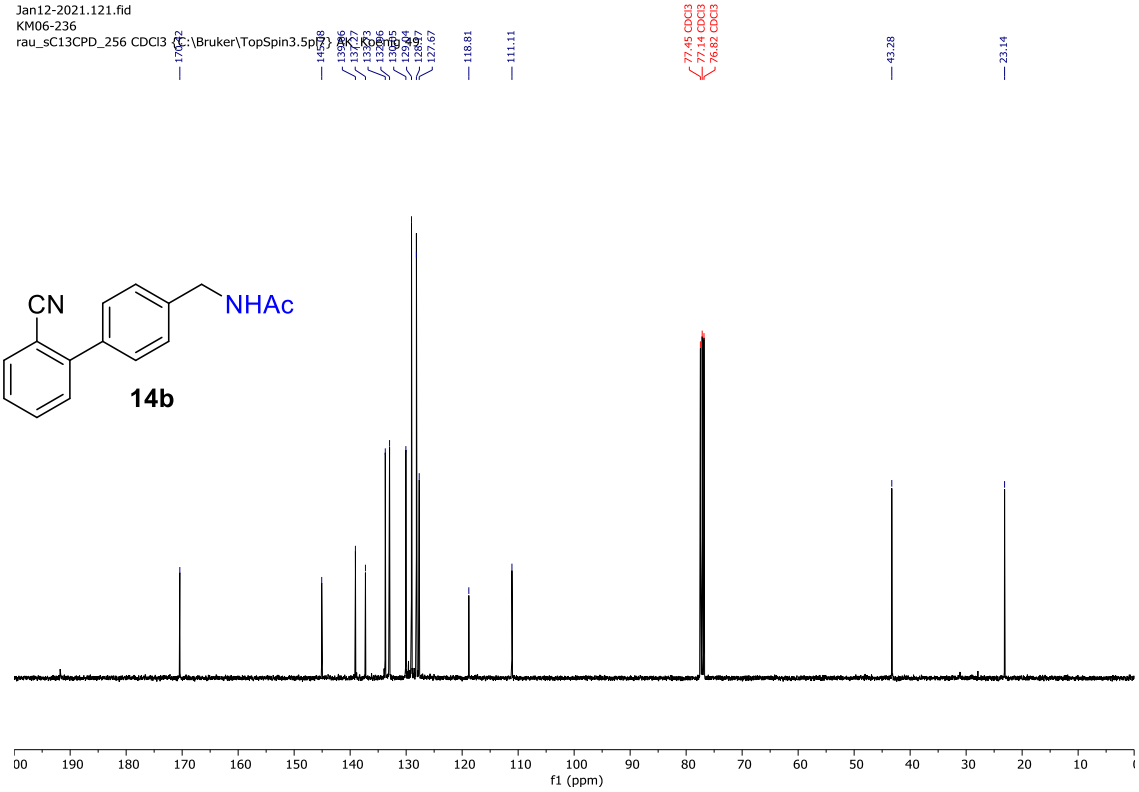


Figure S59: ^{13}C NMR spectrum of compound **14b** (101 MHz in $CDCl_3$).

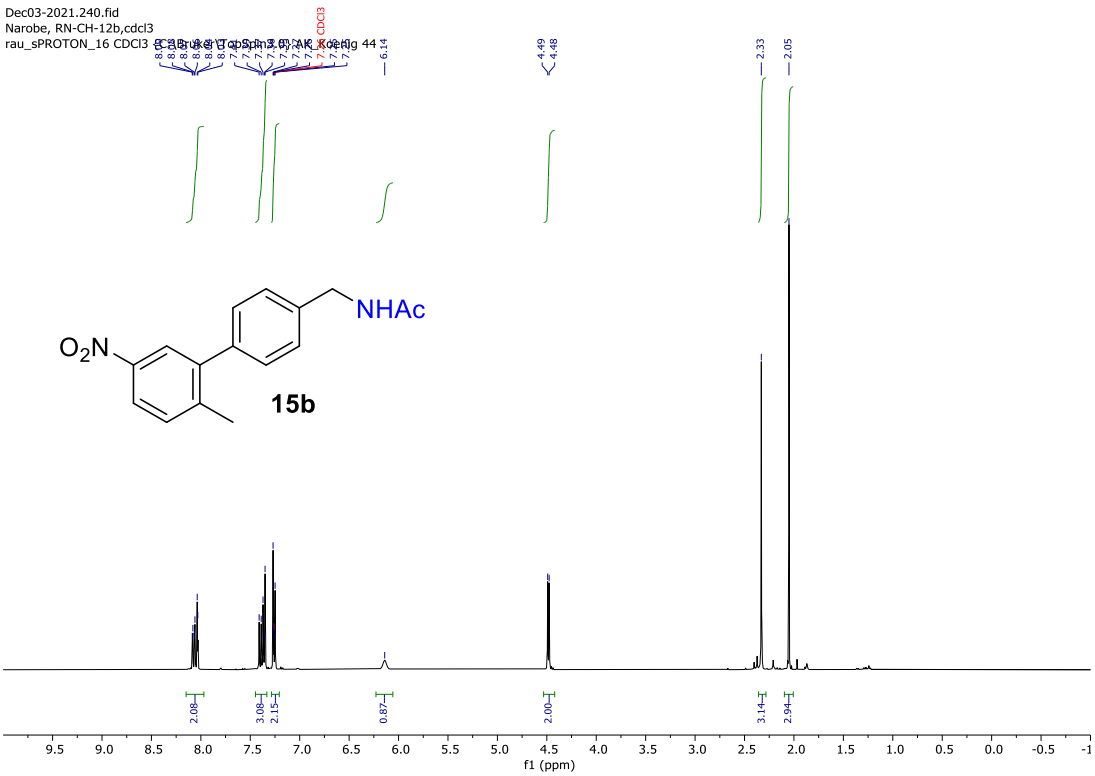


Figure S60: ^{1}H NMR spectrum of compound **15b** (400 MHz in $CDCl_3$).

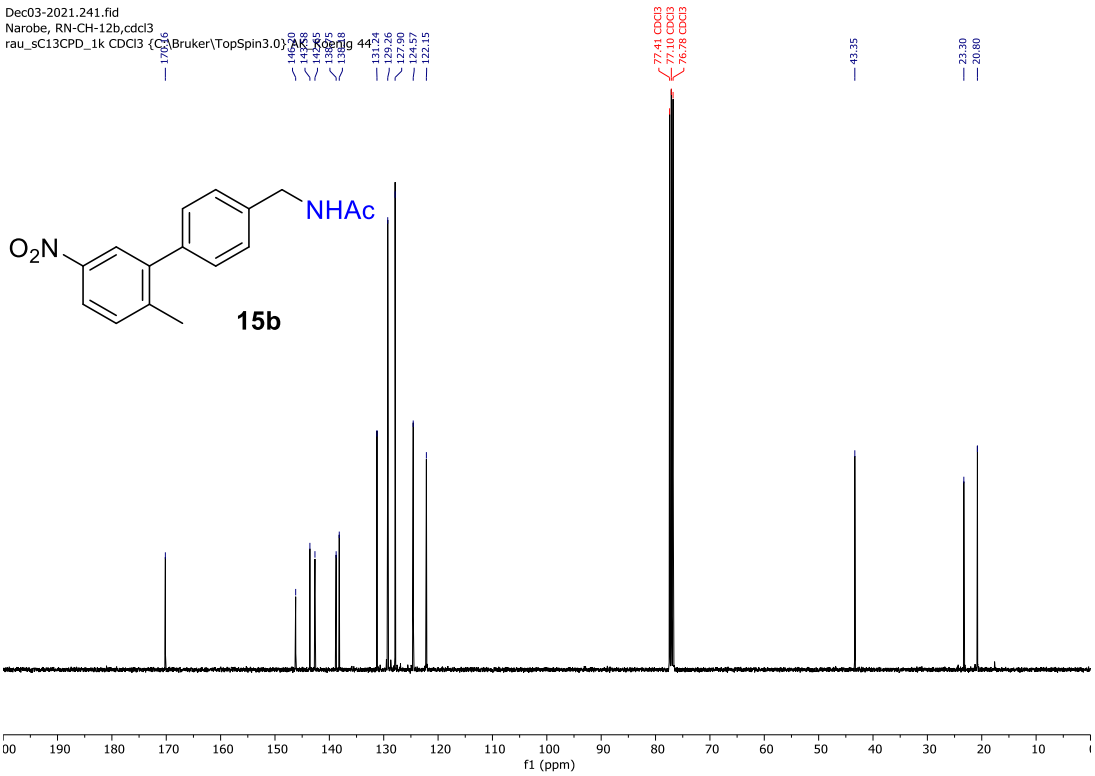


Figure S61: ^{13}C NMR spectrum of compound **15b** (101 MHz in $CDCl_3$).

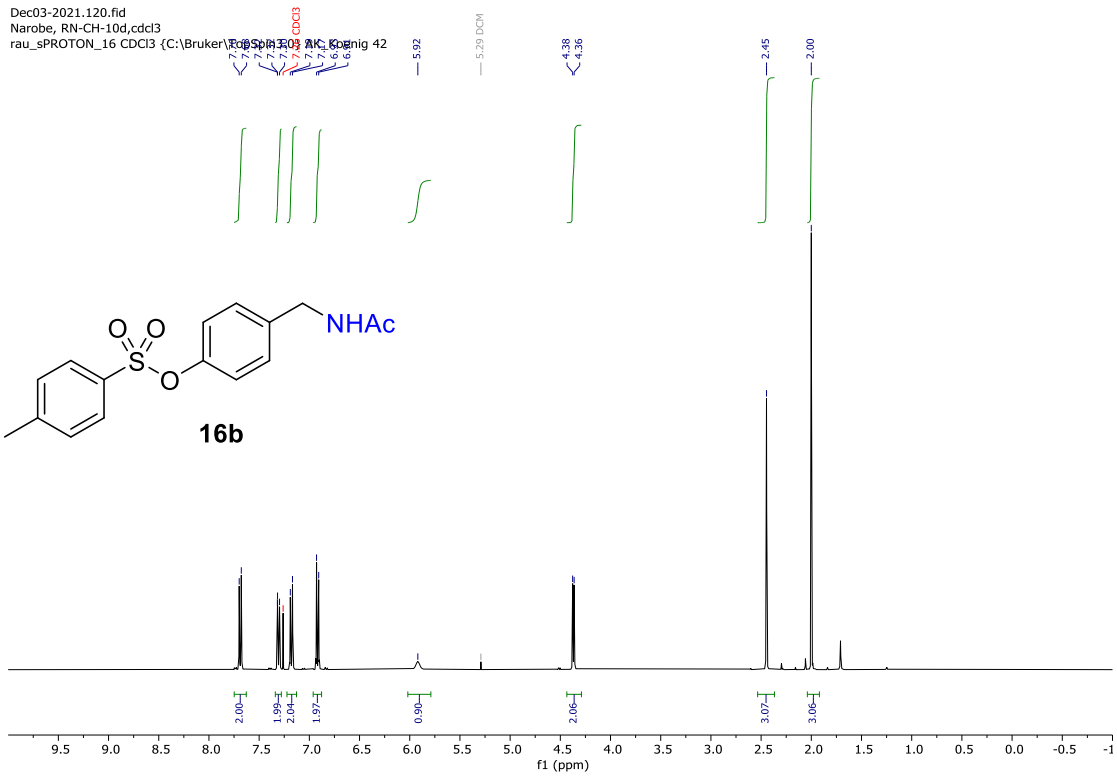


Figure S62: ^{1}H NMR spectrum of compound **16b** (400 MHz in $CDCl_3$).

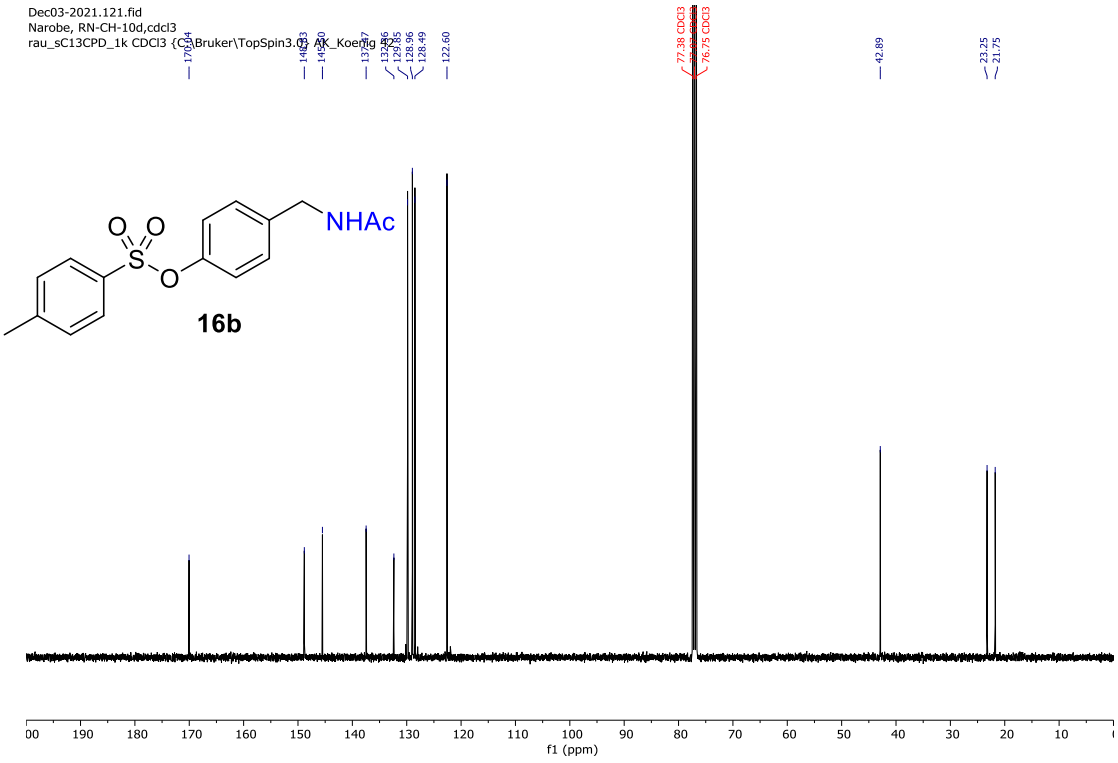


Figure S63: ^{13}C NMR spectrum of compound **16b** (101 MHz in $CDCl_3$).

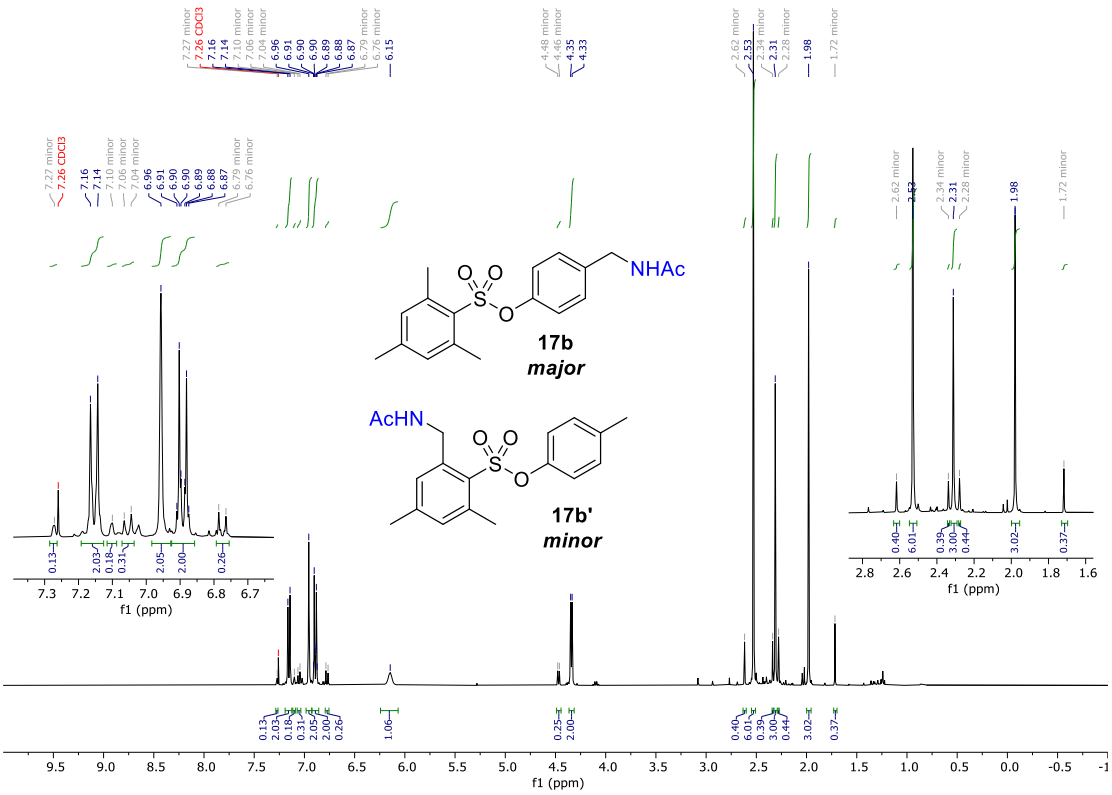


Figure S64: ^{1}H NMR spectrum of compound **17b** (400 MHz in $CDCl_3$).

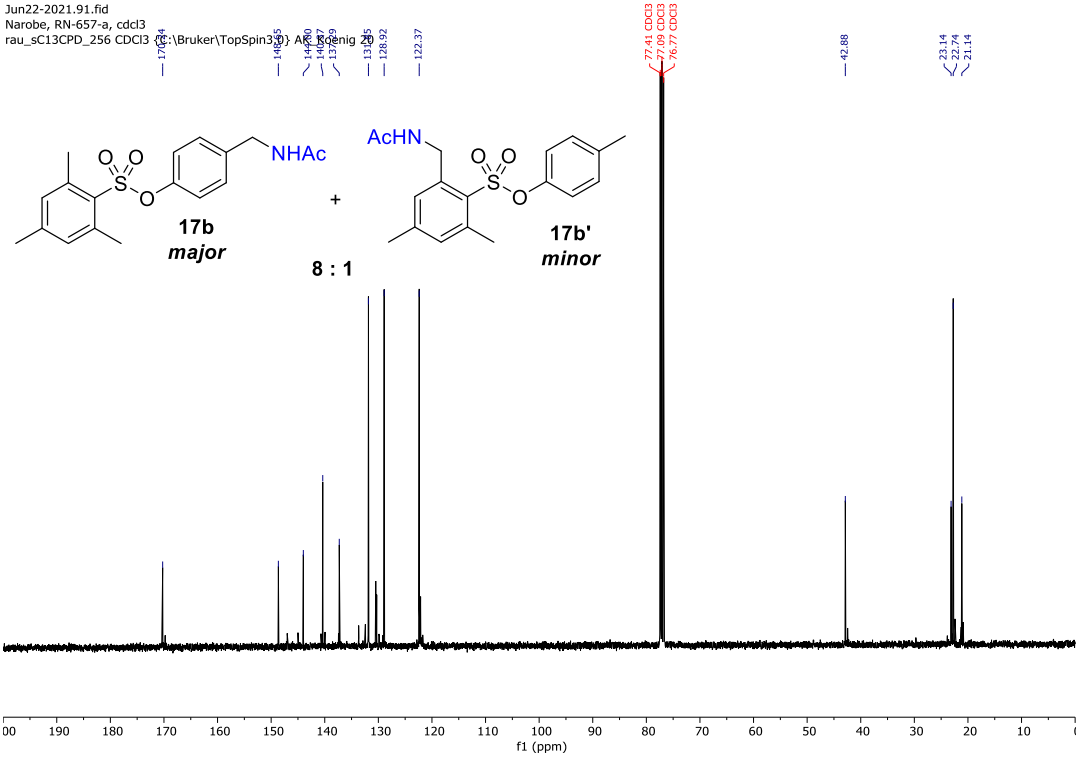


Figure S65: ^{13}C NMR spectrum of compound **17b** (101 MHz in $CDCl_3$).

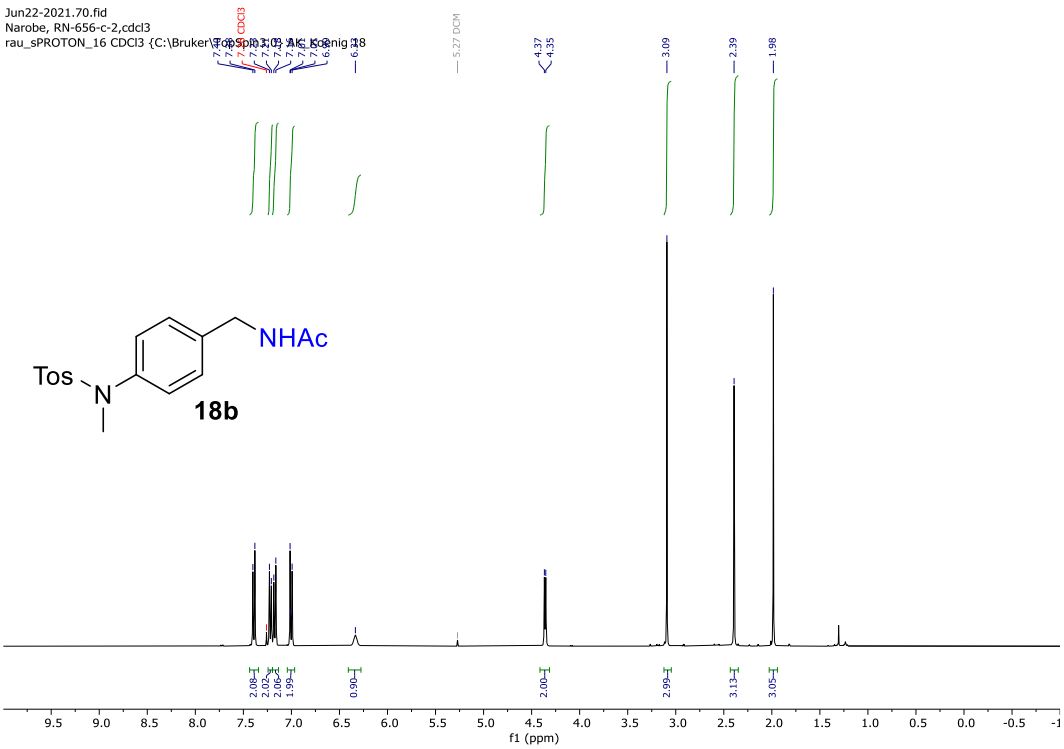


Figure S66: ^{1}H NMR spectrum of compound **18b** (400 MHz in $CDCl_3$).

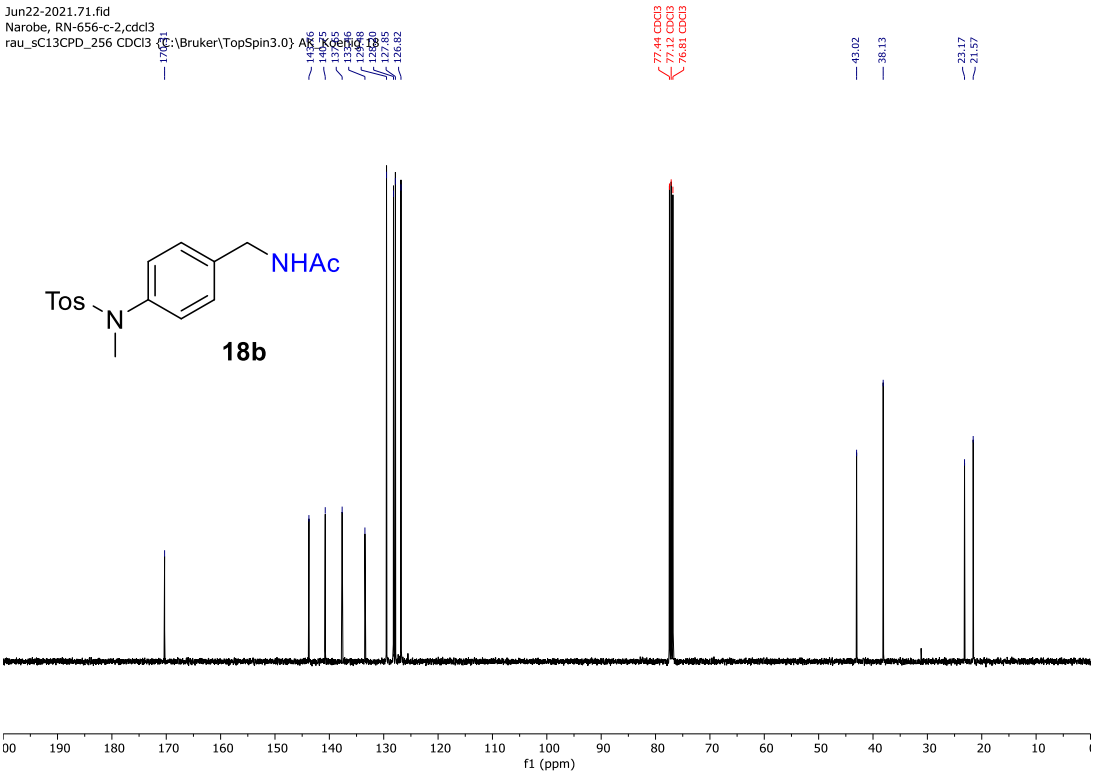


Figure S67: ^{13}C NMR spectrum of compound **18b** (101 MHz in $CDCl_3$).

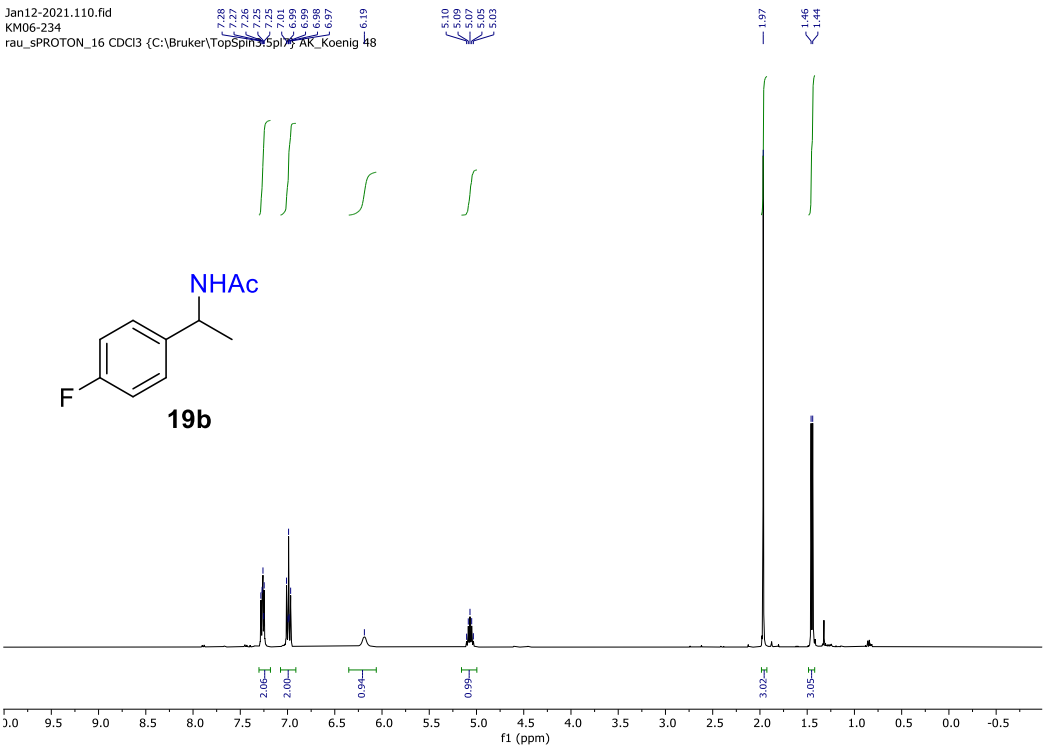


Figure S68: ^{1}H NMR spectrum of compound **19b** (400 MHz in $CDCl_3$).

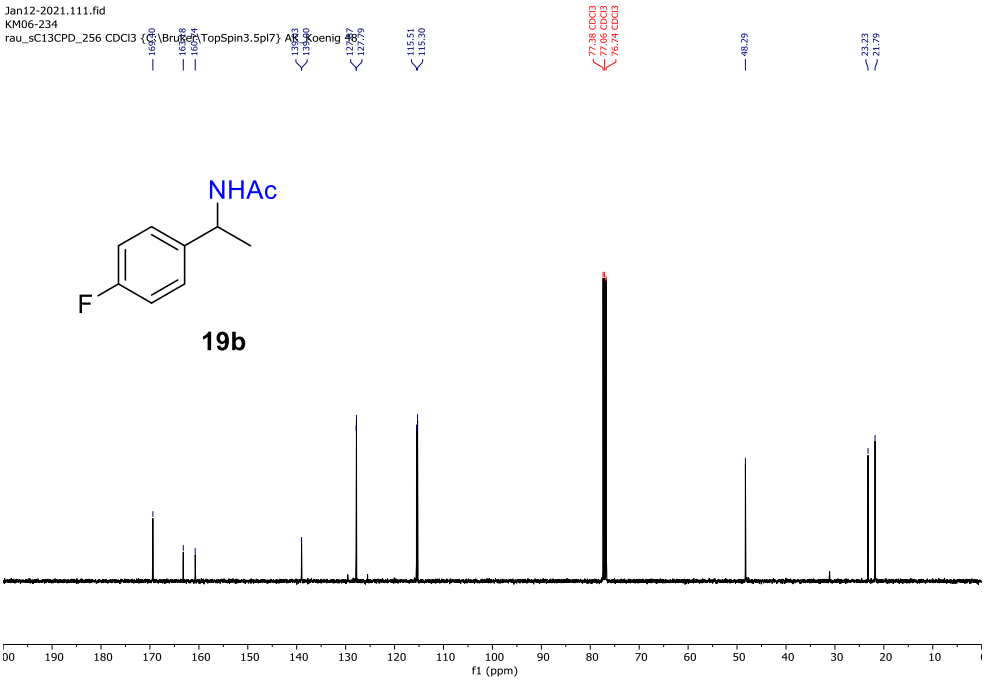


Figure S69: ^{13}C NMR spectrum of compound **19b** (101 MHz in $CDCl_3$).

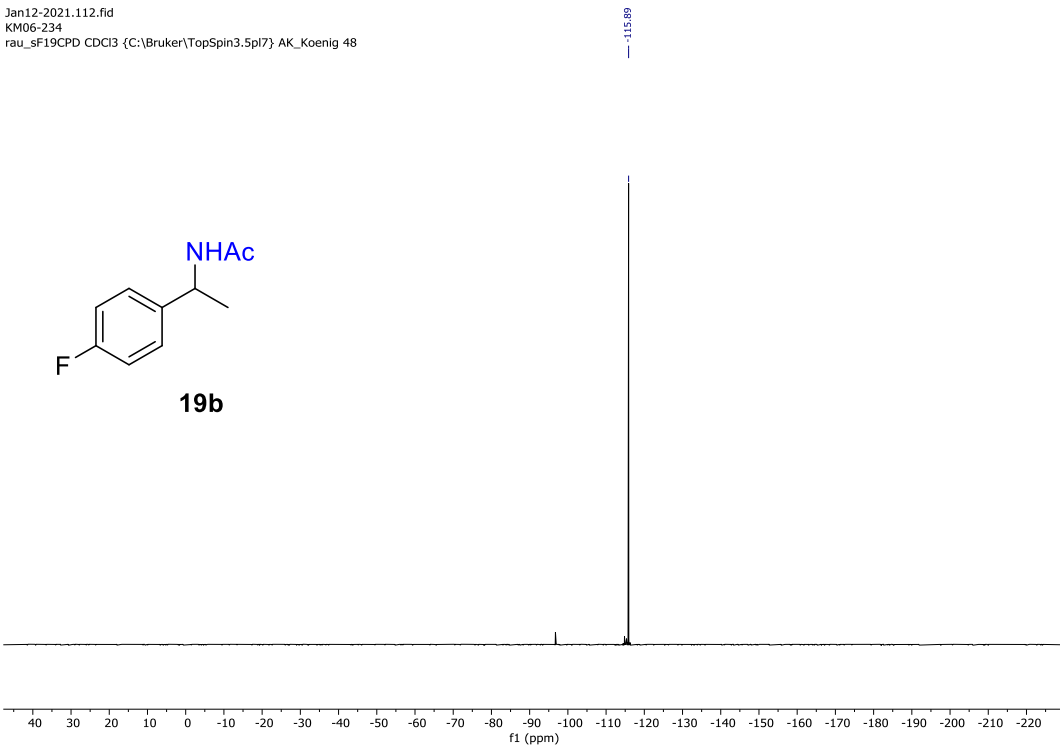


Figure S70: ^{19}F NMR spectrum of compound **19b** (377 MHz in $CDCl_3$).

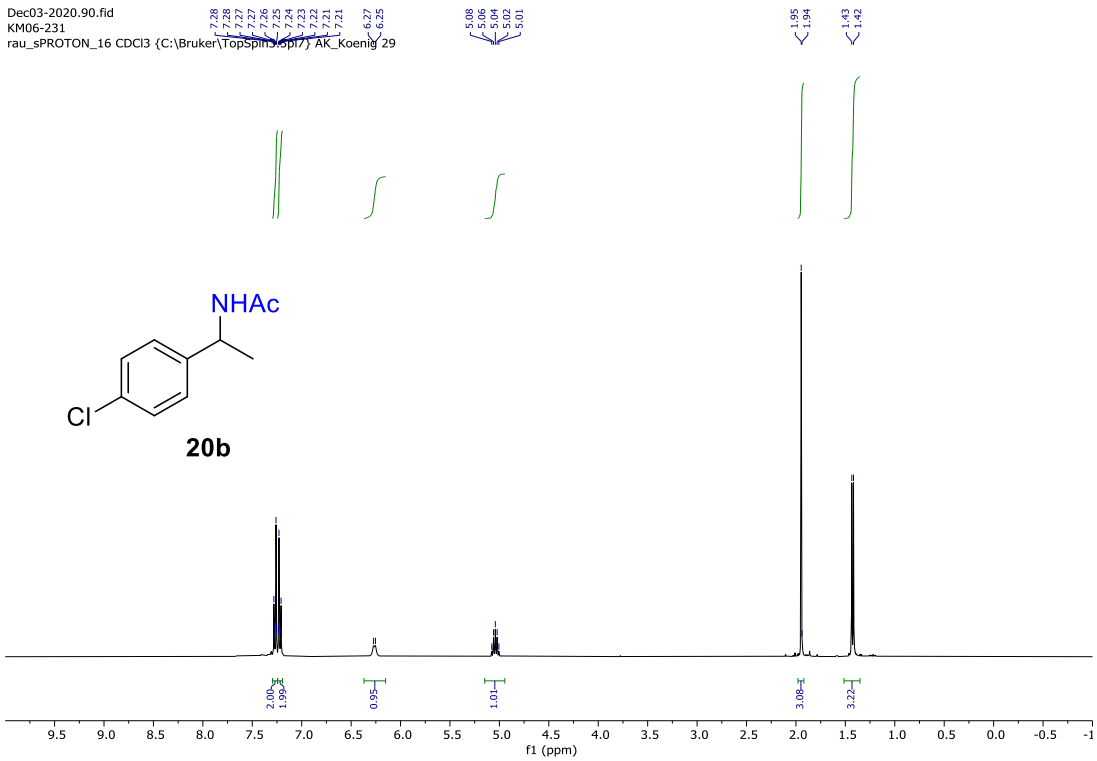


Figure S71: ^{1}H NMR spectrum of compound **20b** (400 MHz in $CDCl_3$).

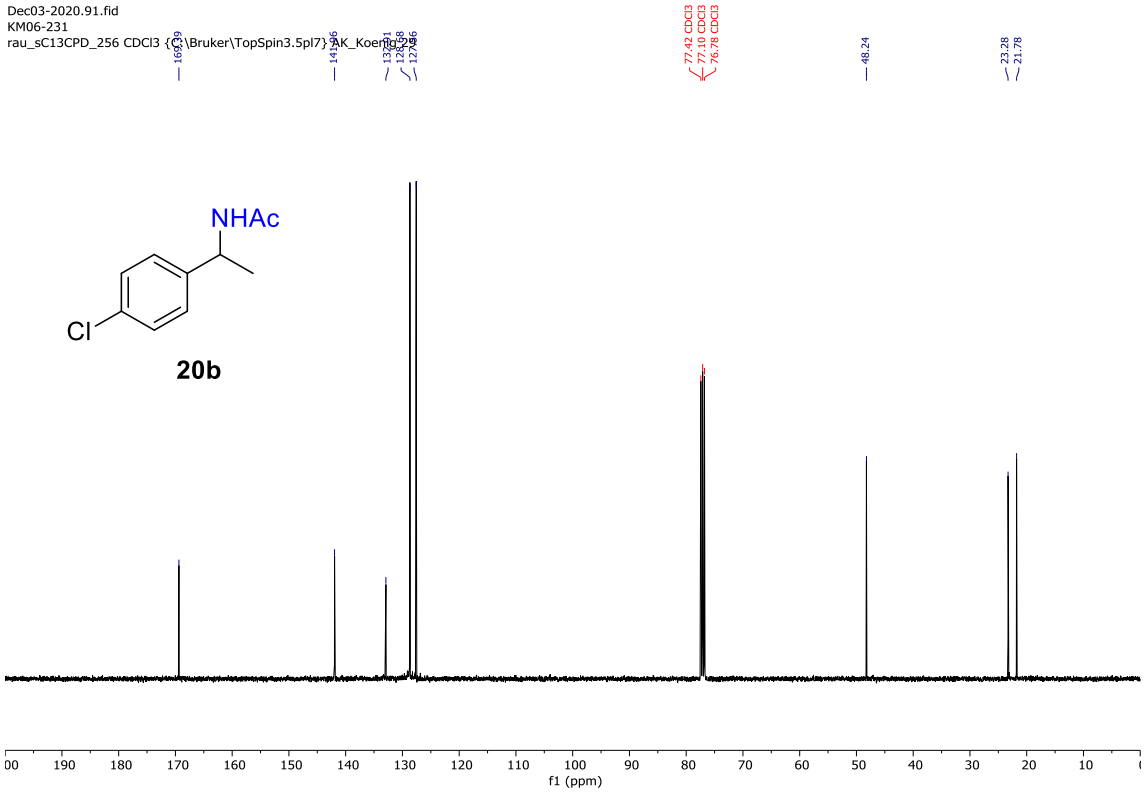


Figure S72: ^{13}C NMR spectrum of compound **20b** (101 MHz in $CDCl_3$).

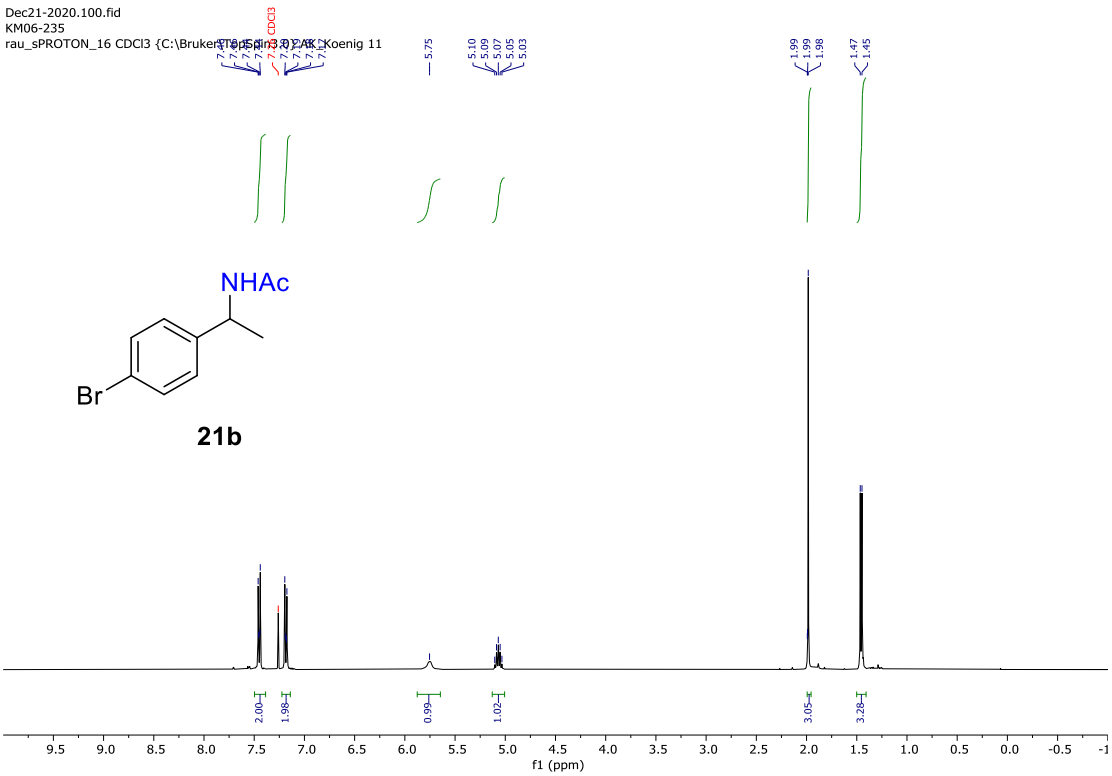


Figure S73: ^{1}H NMR spectrum of compound **21b** (400 MHz in $CDCl_3$).

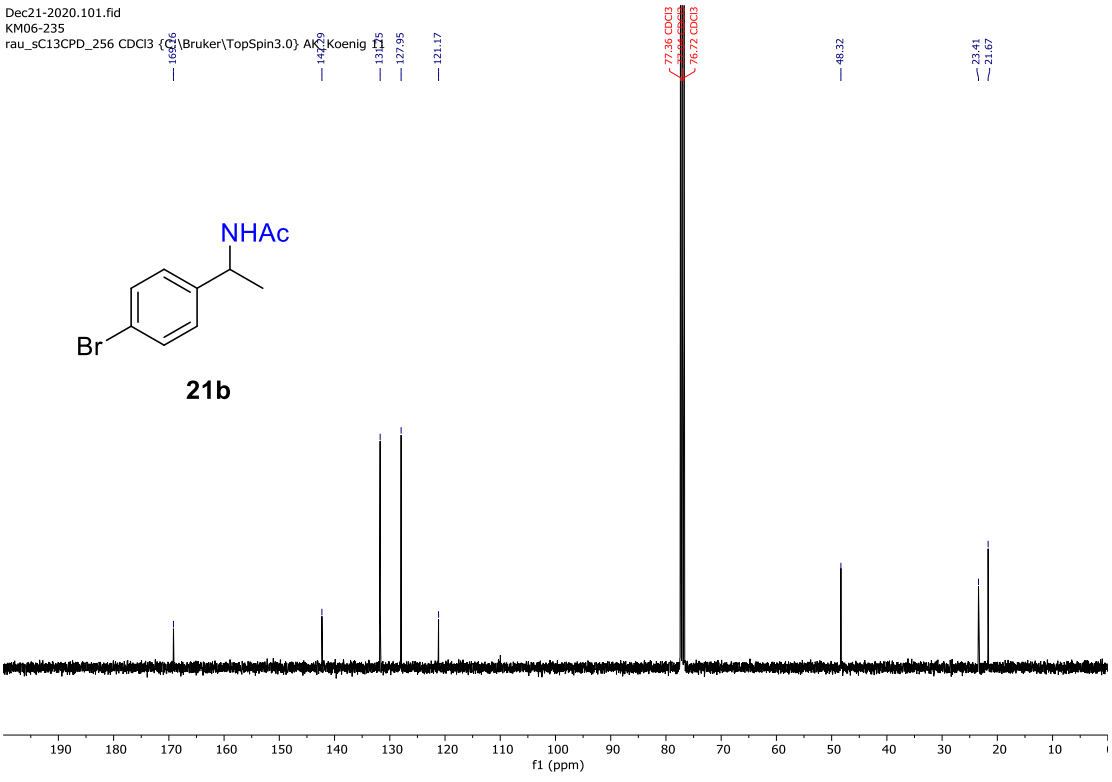


Figure S74: ^{13}C NMR spectrum of compound **21b** (101 MHz in $CDCl_3$).

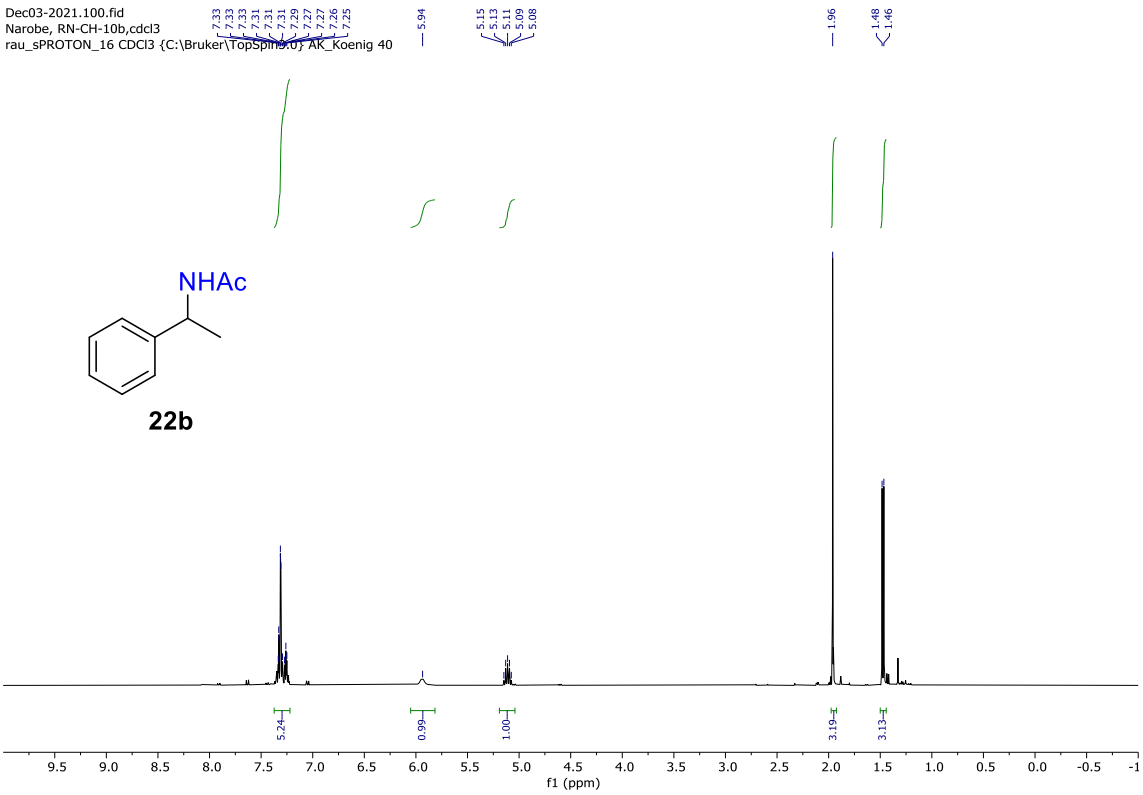


Figure S75: ^{1}H NMR spectrum of compound **22b** (400 MHz in $CDCl_3$).

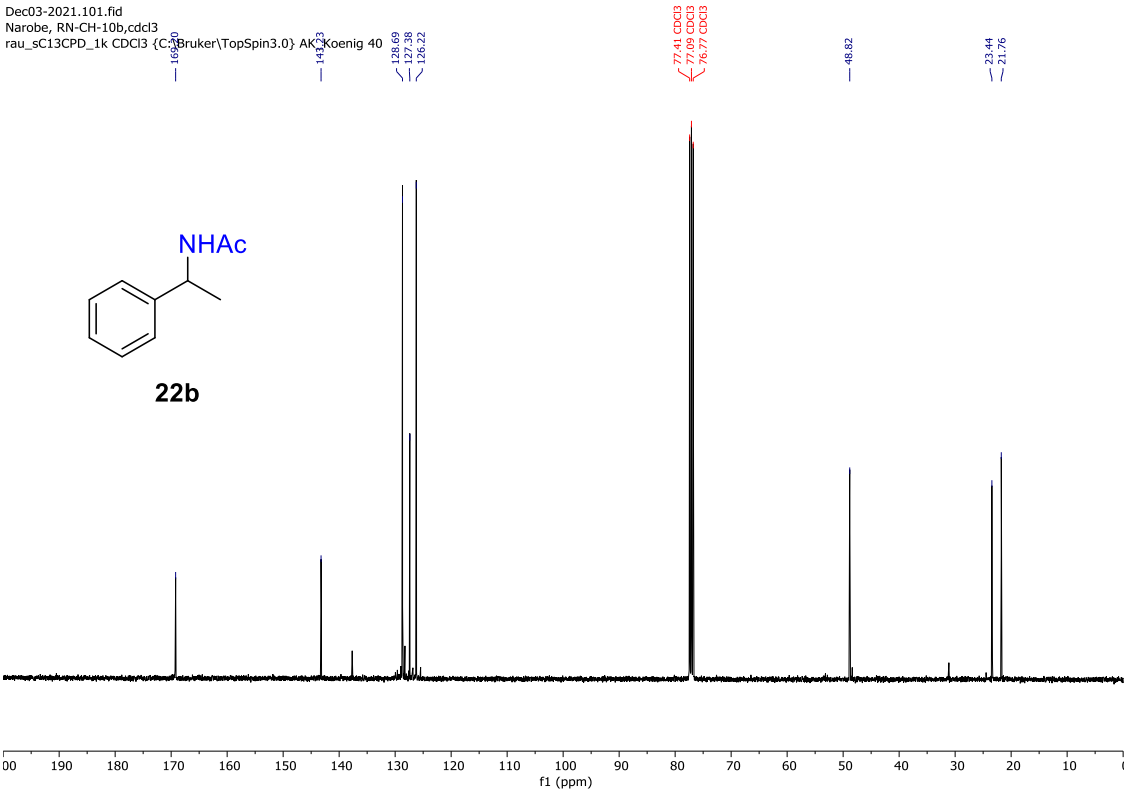


Figure S76: ^{13}C NMR spectrum of compound **22b** (101 MHz in $CDCl_3$).

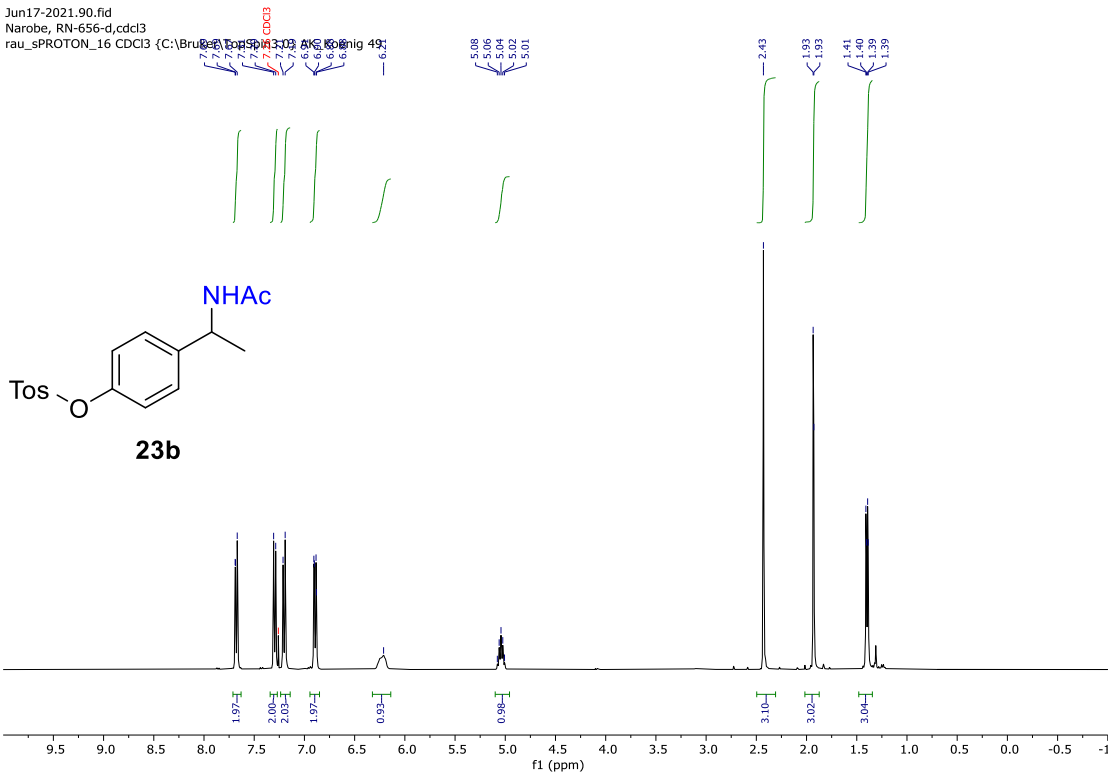


Figure S77: ^{1}H NMR spectrum of compound **23b** (400 MHz in $CDCl_3$).

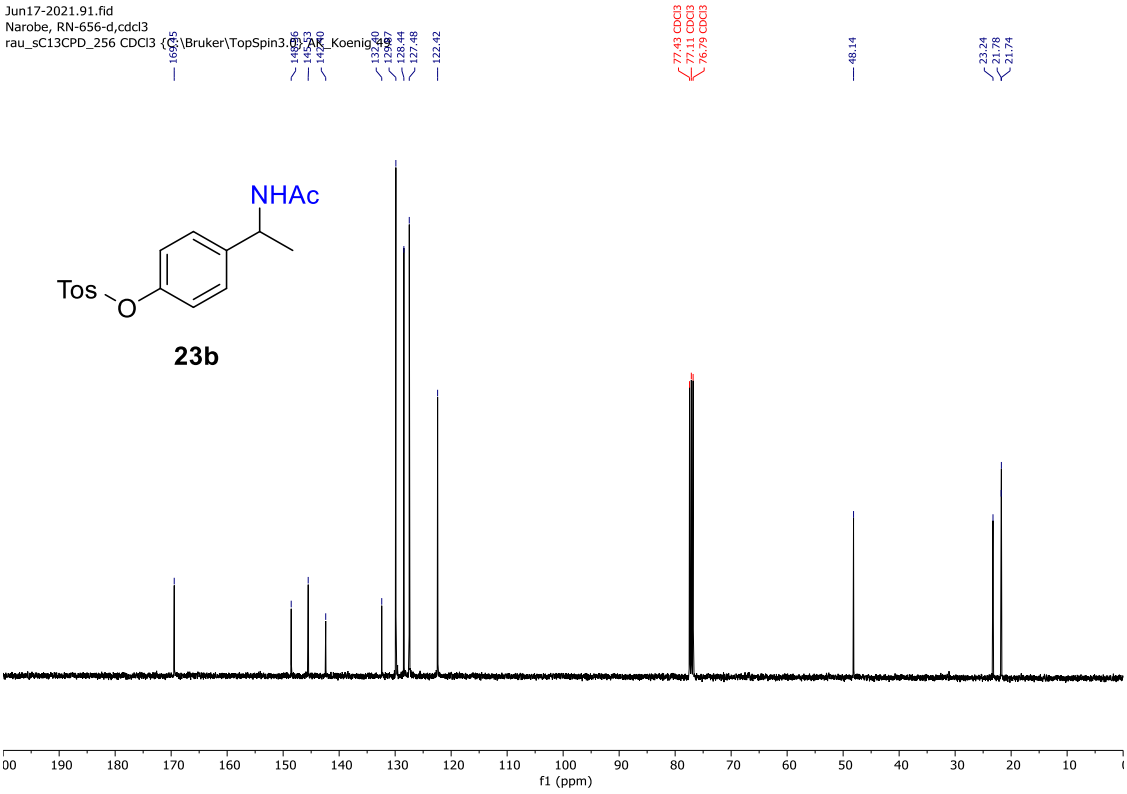


Figure S78: ^{13}C NMR spectrum of compound **23b** (101 MHz in $CDCl_3$).

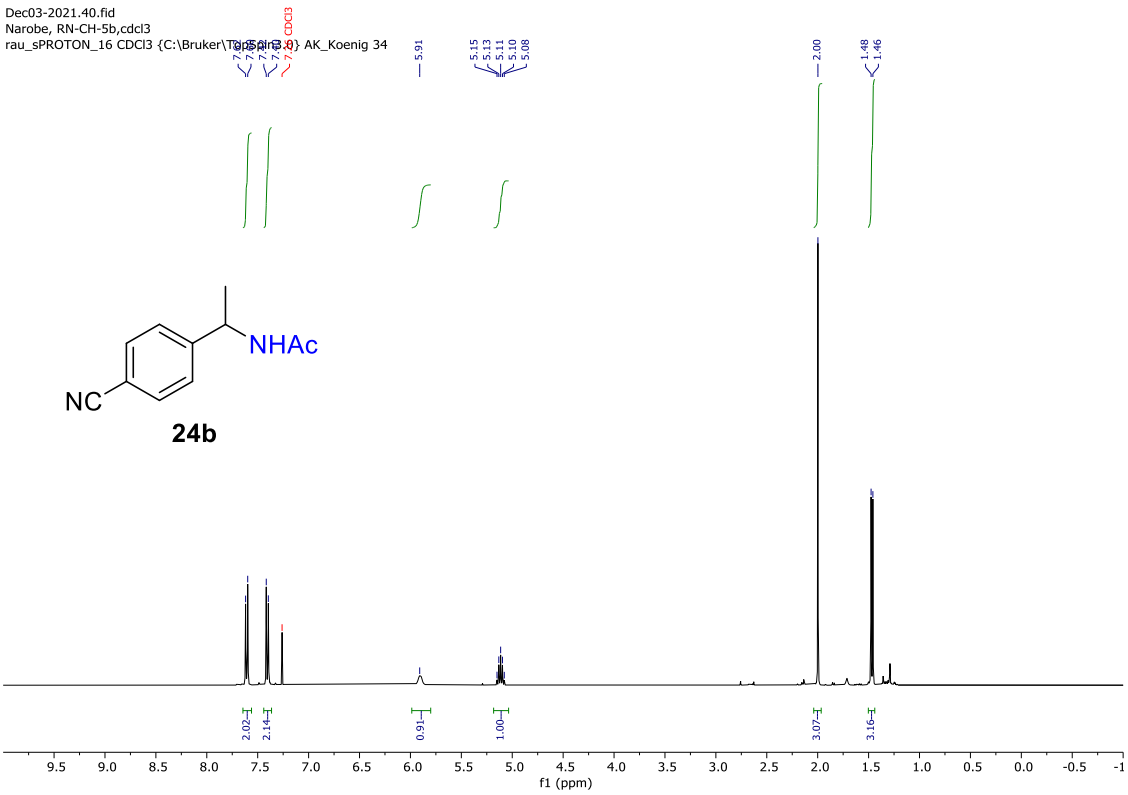


Figure S79: ^{1}H NMR spectrum of compound **24b** (400 MHz in $CDCl_3$).

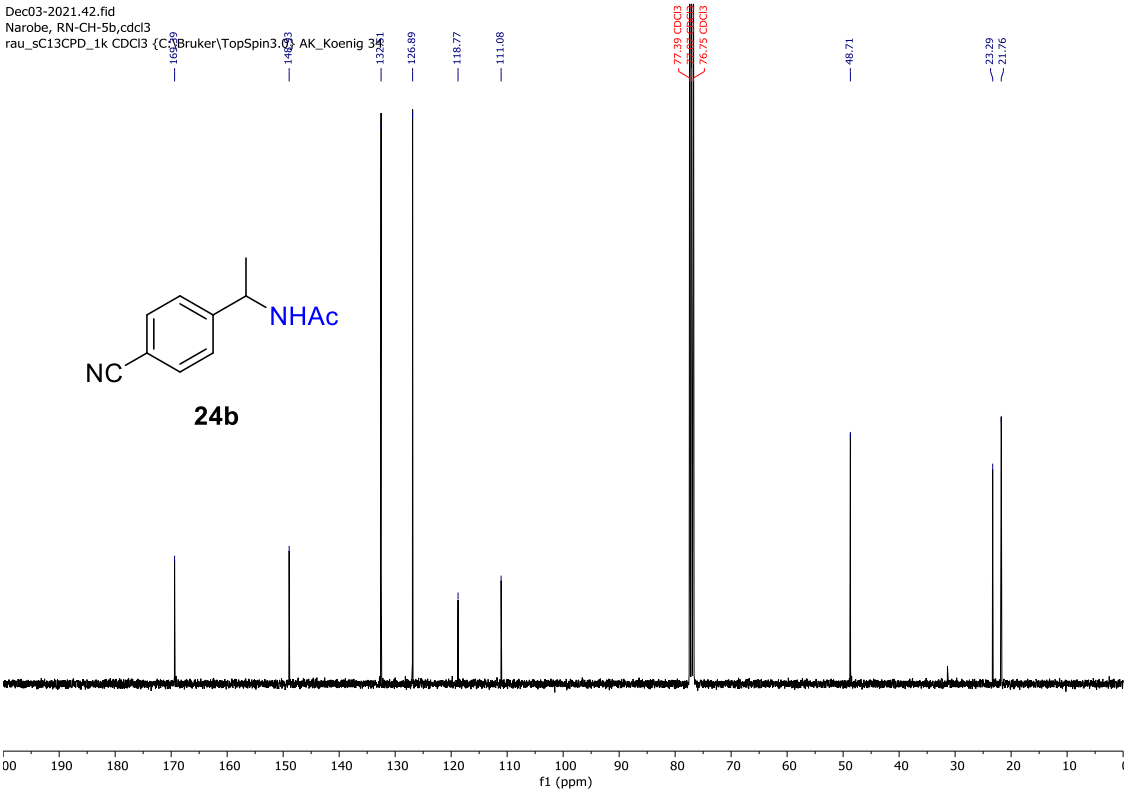


Figure S80: ^{13}C NMR spectrum of compound **24b** (101 MHz in $CDCl_3$).

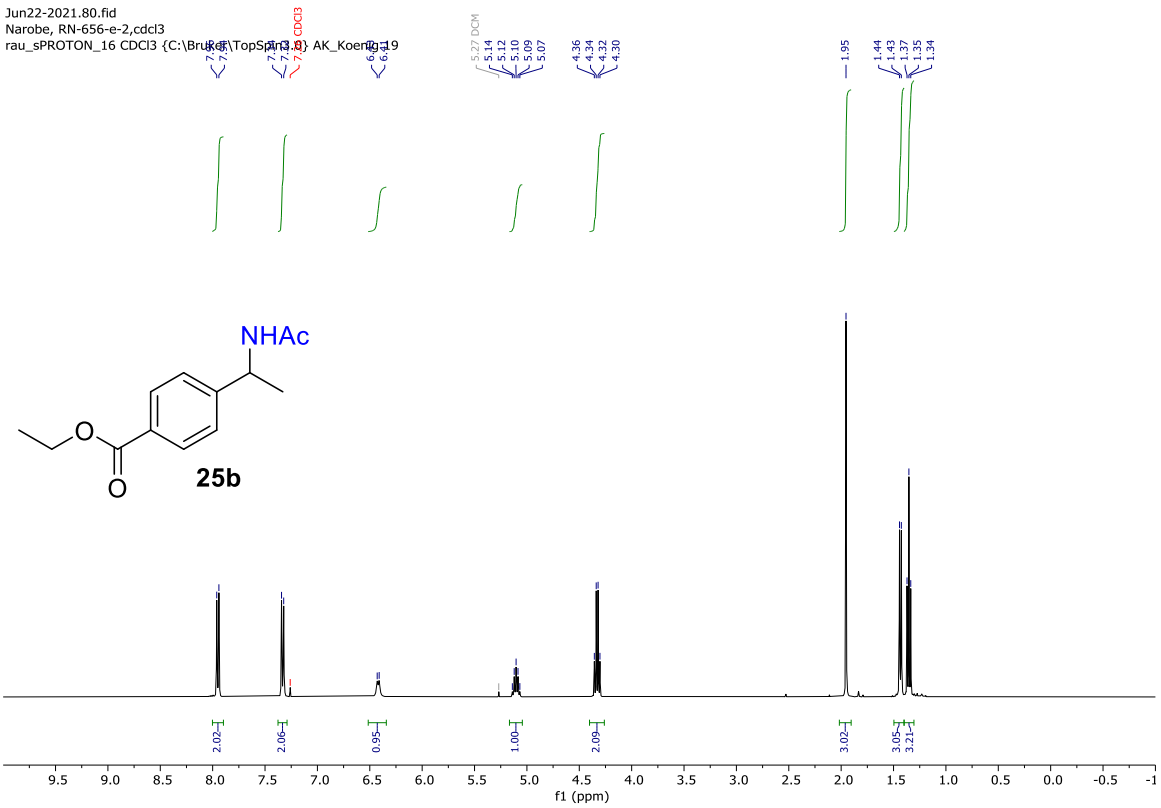


Figure S81: ^{1}H NMR spectrum of compound **25b** (400 MHz in $CDCl_3$).

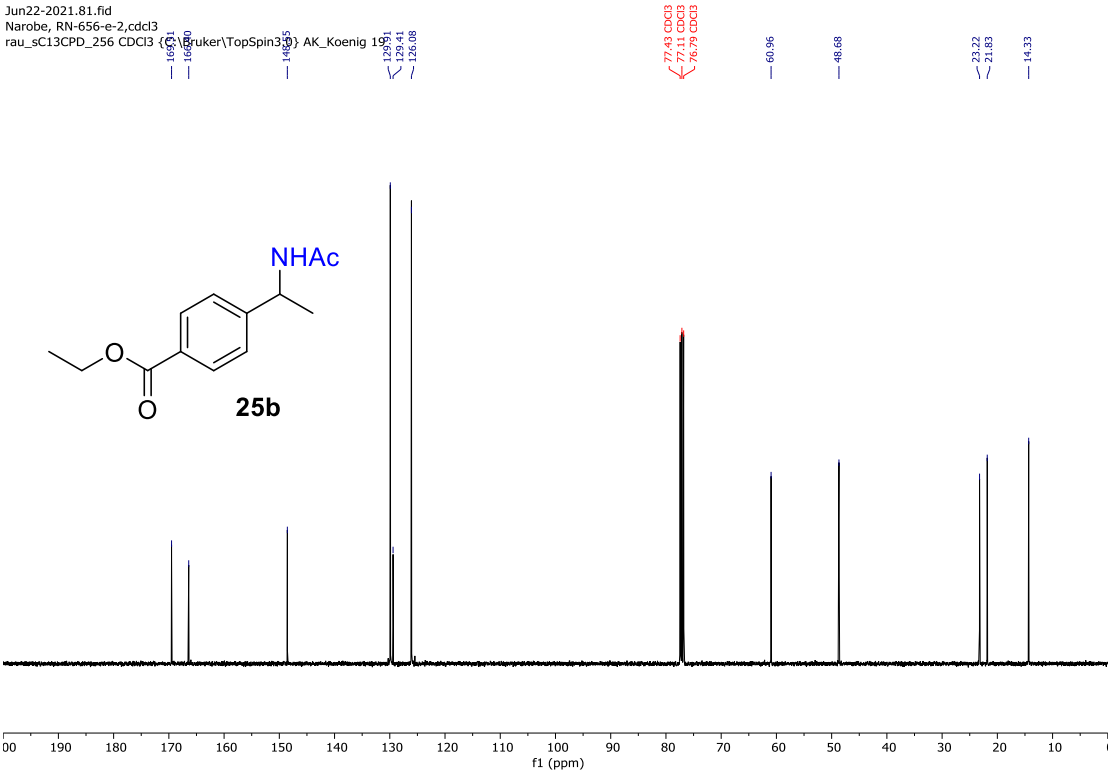


Figure S82: ^{13}C NMR spectrum of compound **25b** (101 MHz in $CDCl_3$).

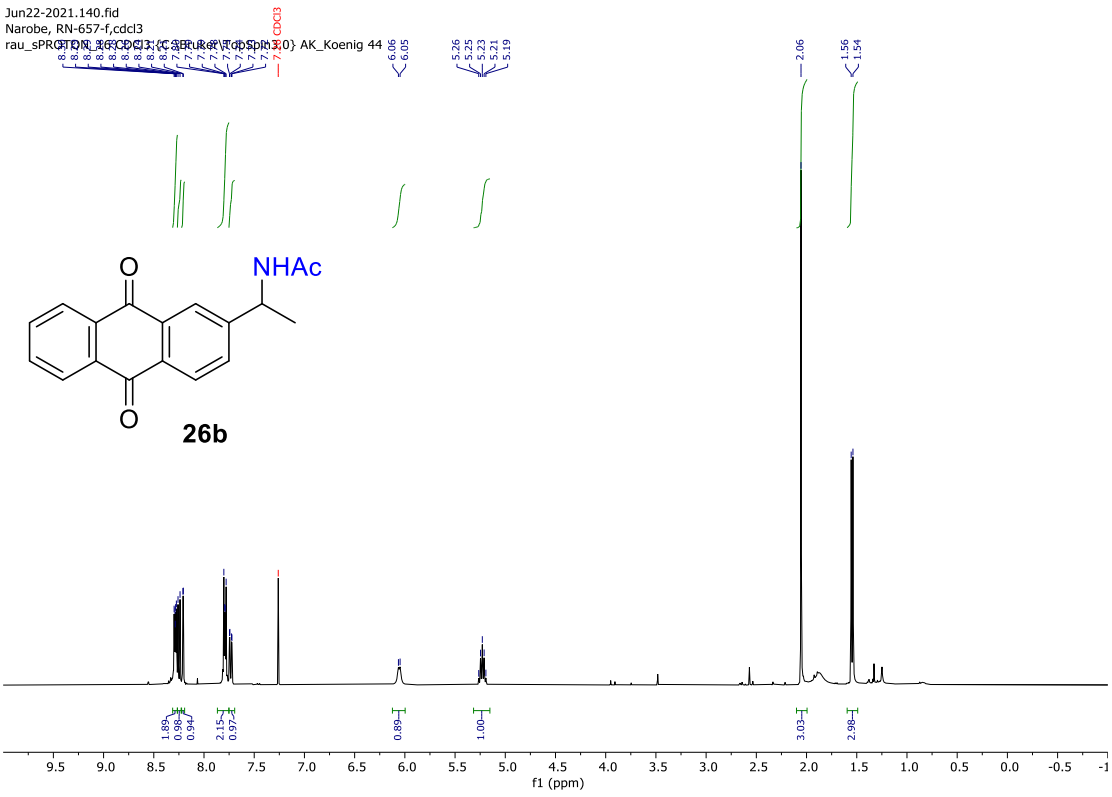


Figure S83: ^{1}H NMR spectrum of compound **26b** (400 MHz in $CDCl_3$).

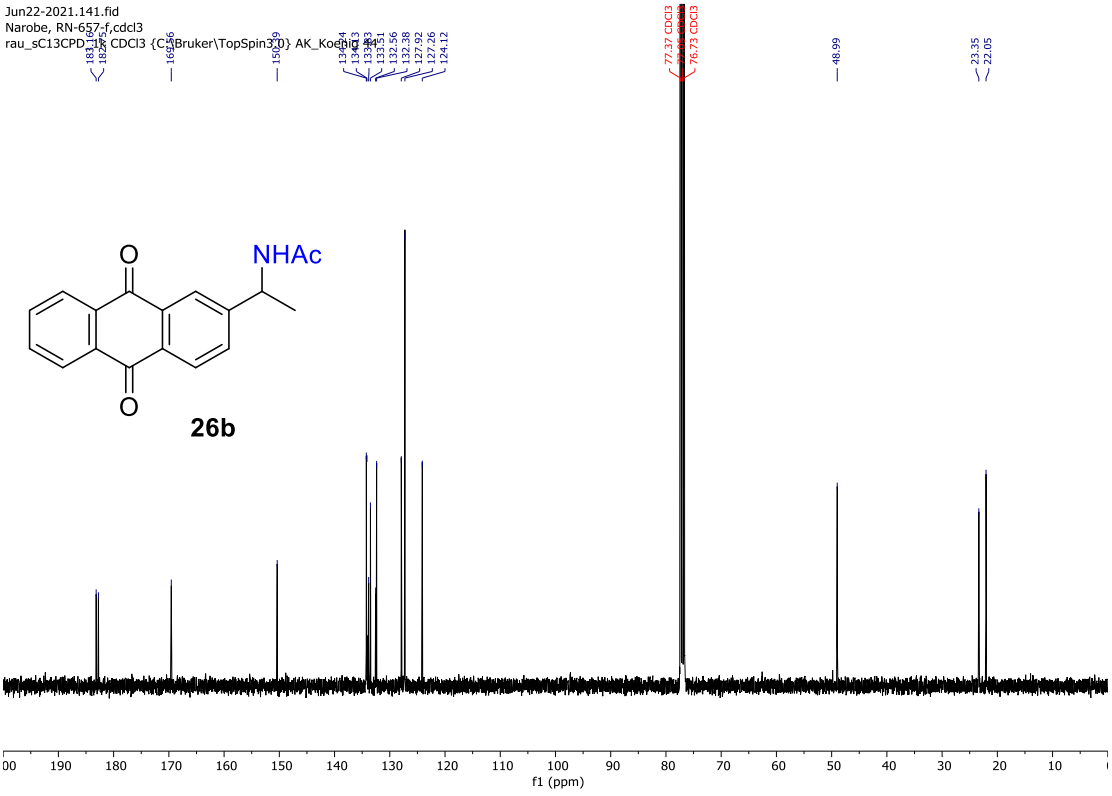


Figure S84: ^{13}C NMR spectrum of compound **26b** (101 MHz in $CDCl_3$).

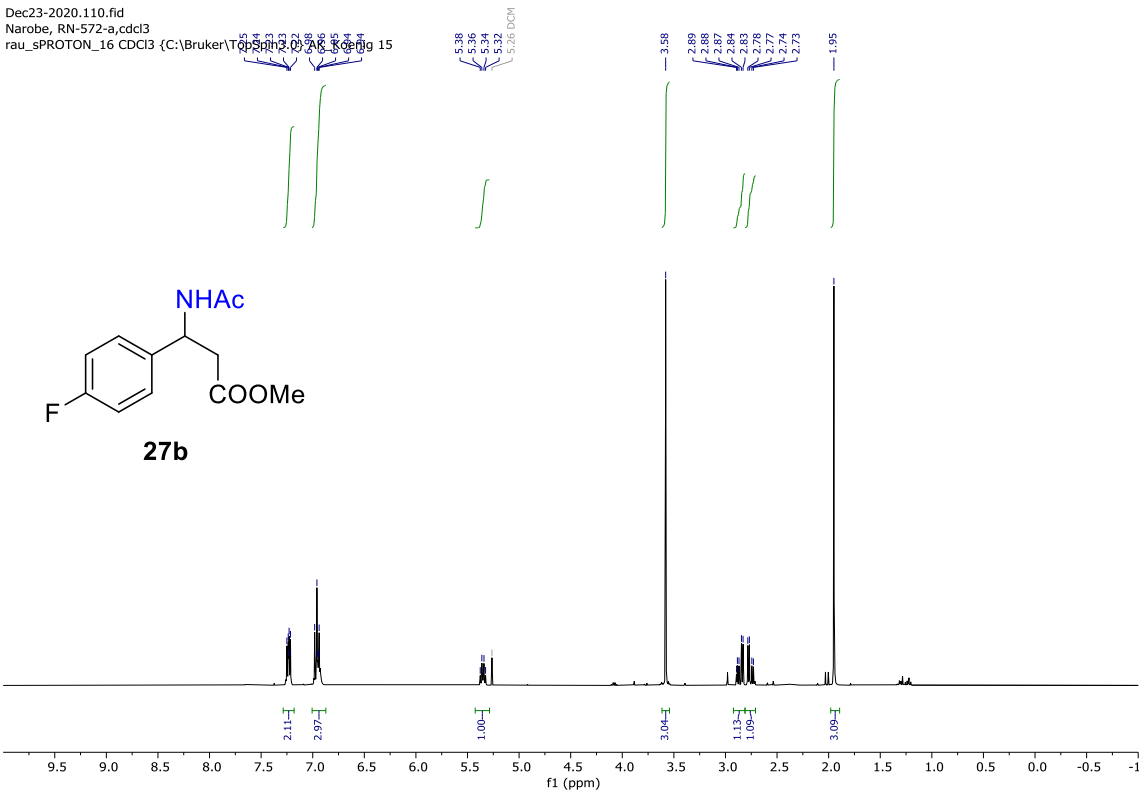


Figure S85: ^{1}H NMR spectrum of compound **27b** (400 MHz in $CDCl_3$).

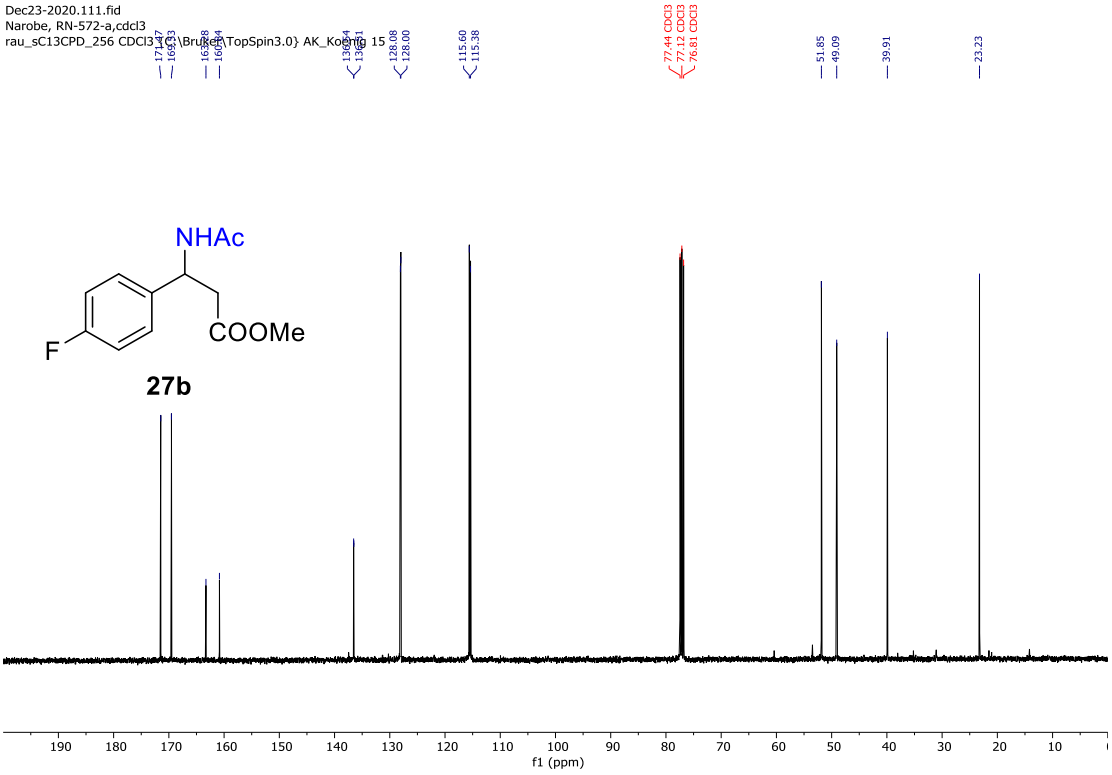


Figure S86: ^{13}C NMR spectrum of compound **27b** (101 MHz in $CDCl_3$).

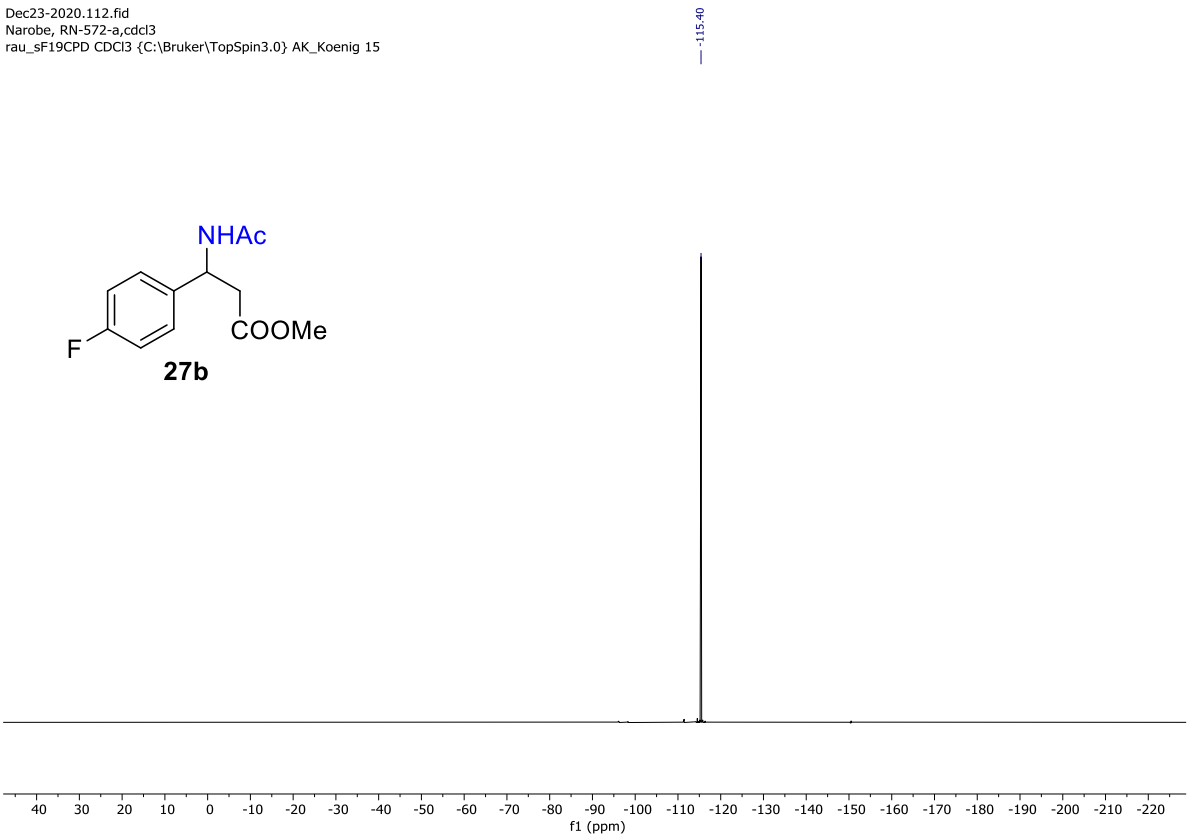


Figure S87: ^{19}F NMR spectrum of compound **27b** (377 MHz in $CDCl_3$).

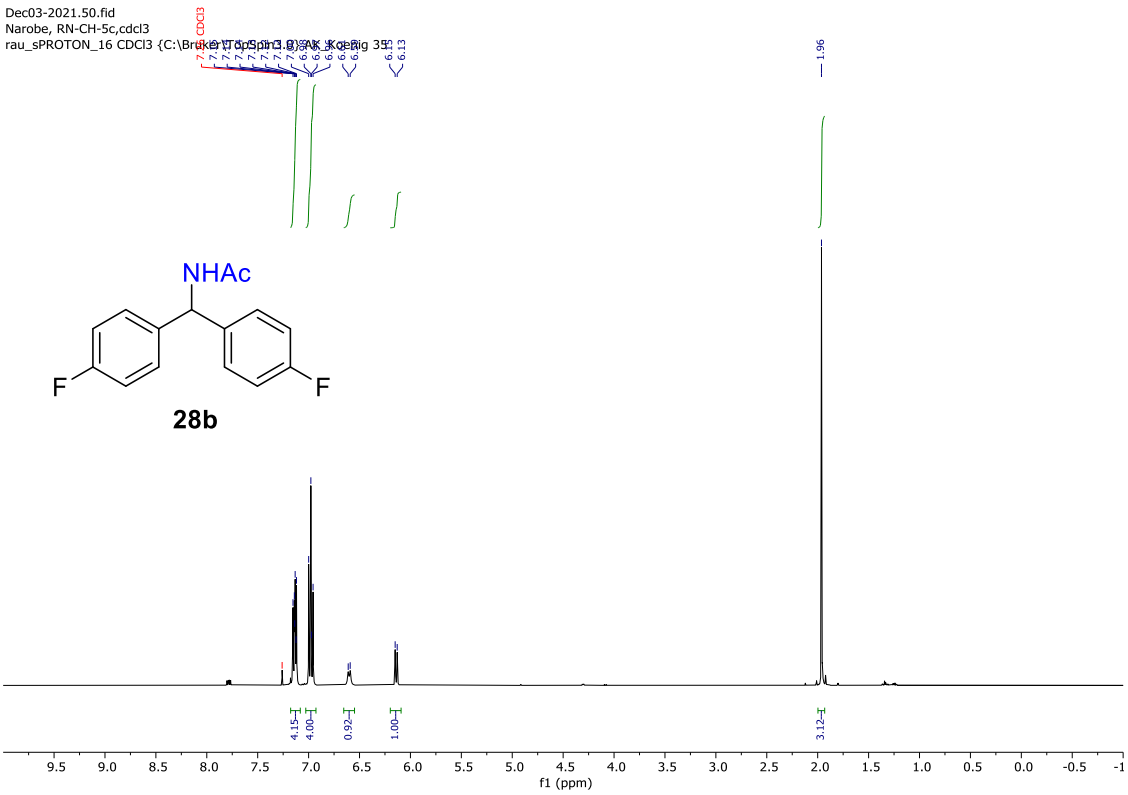


Figure S88: ^{1}H NMR spectrum of compound **28b** (400 MHz in $CDCl_3$).

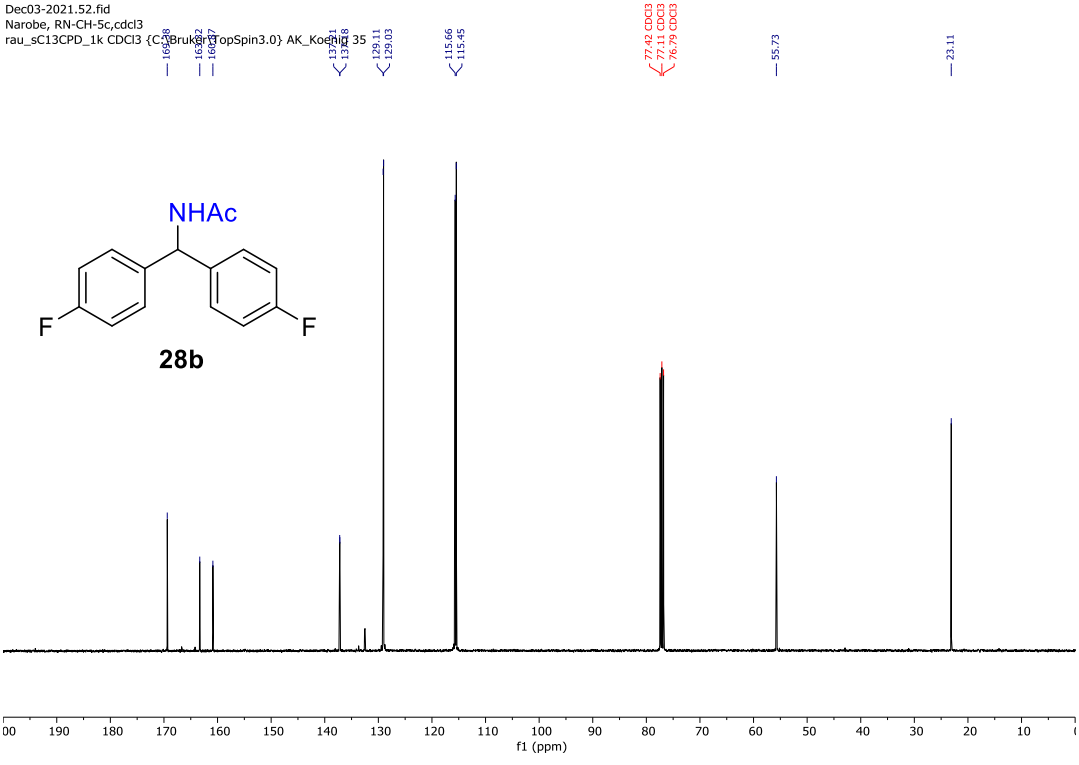


Figure S89: ^{13}C NMR spectrum of compound **28b** (101 MHz in $CDCl_3$).

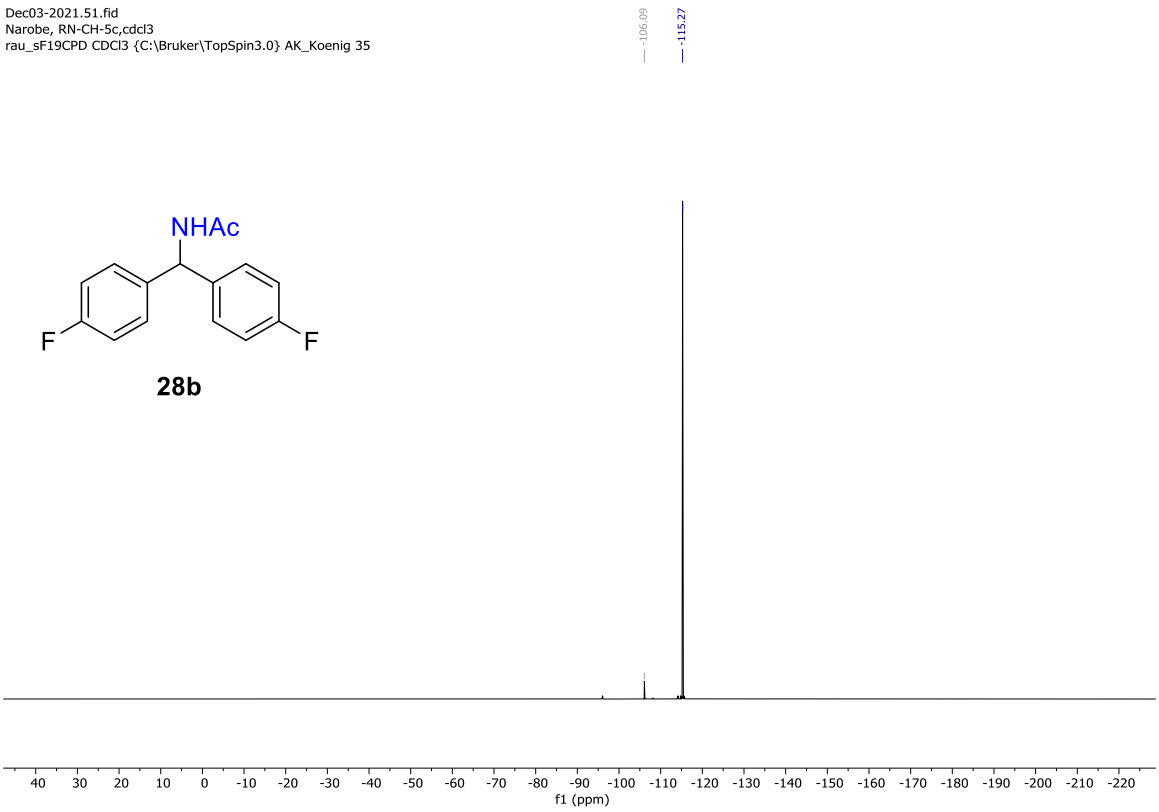


Figure S90: ^{19}F NMR spectrum of compound **28b** (377 MHz in $CDCl_3$).

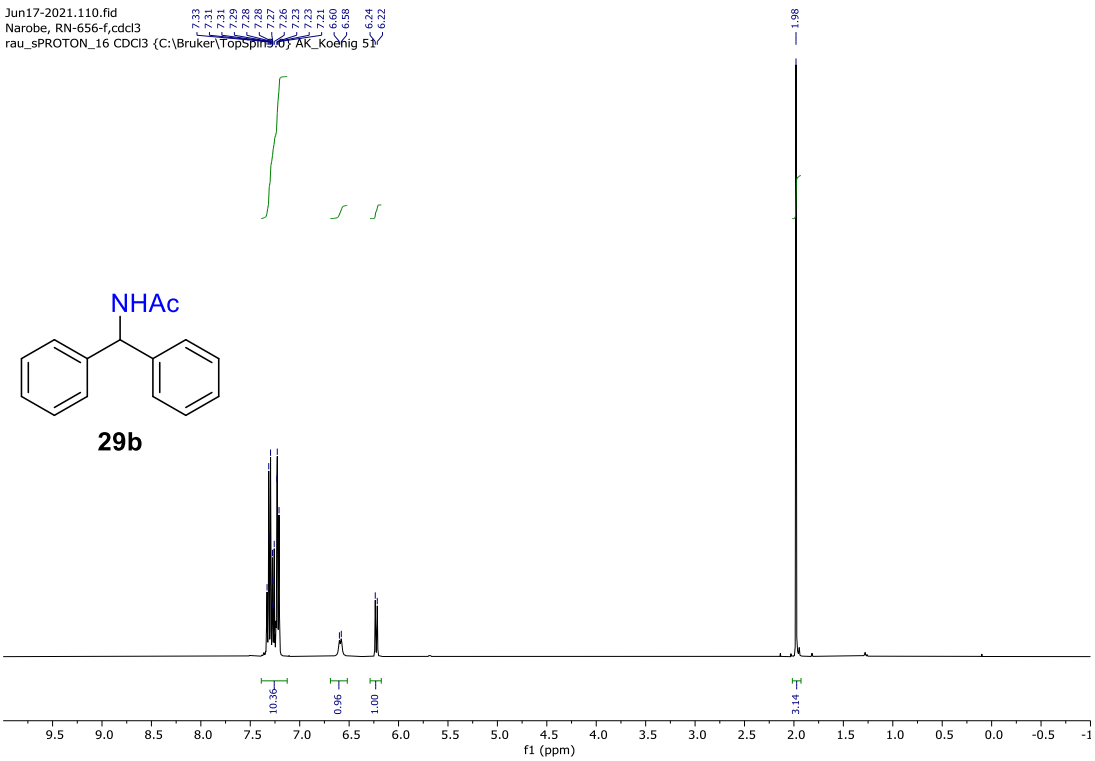


Figure S91: ^{1}H NMR spectrum of compound **29b** (400 MHz in $CDCl_3$).

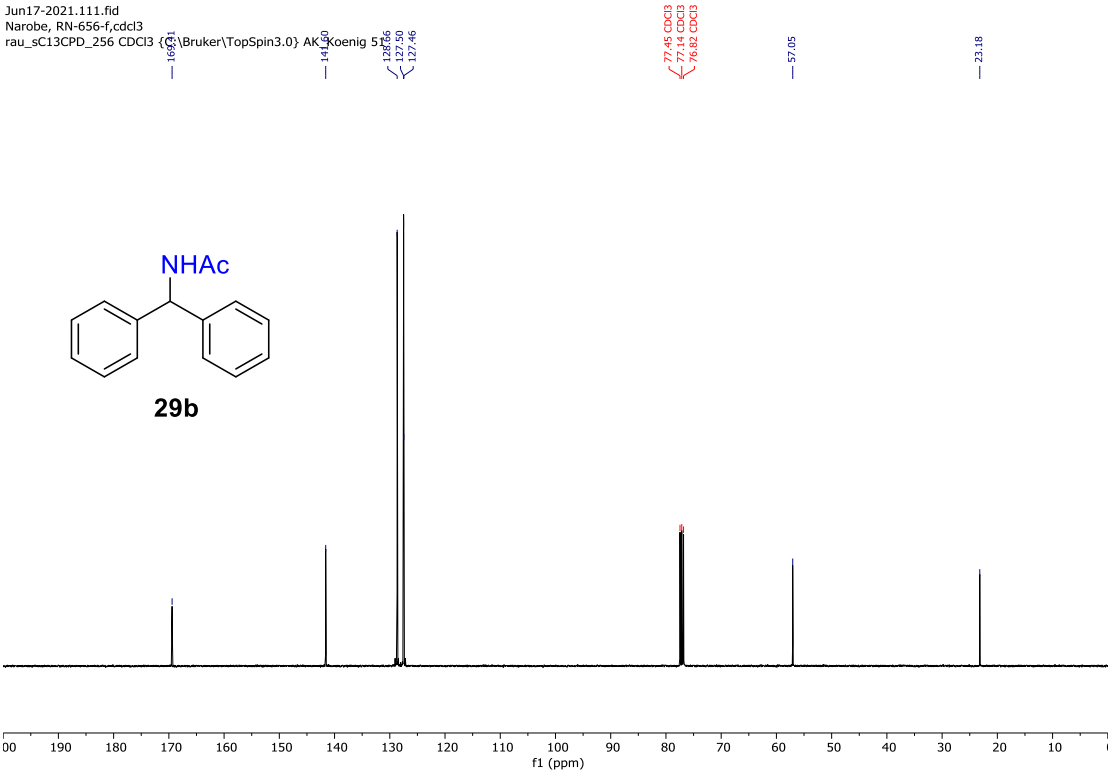


Figure S92: ^{13}C NMR spectrum of compound **29b** (101 MHz in $CDCl_3$).

6 Literature

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