Electronic Supplementary Material (ESI) for ChemComm.

Redox-active Alkylsulfones as a Precursor for Alkyl Radicals Under Photoredox Catalysis

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Supporting Information

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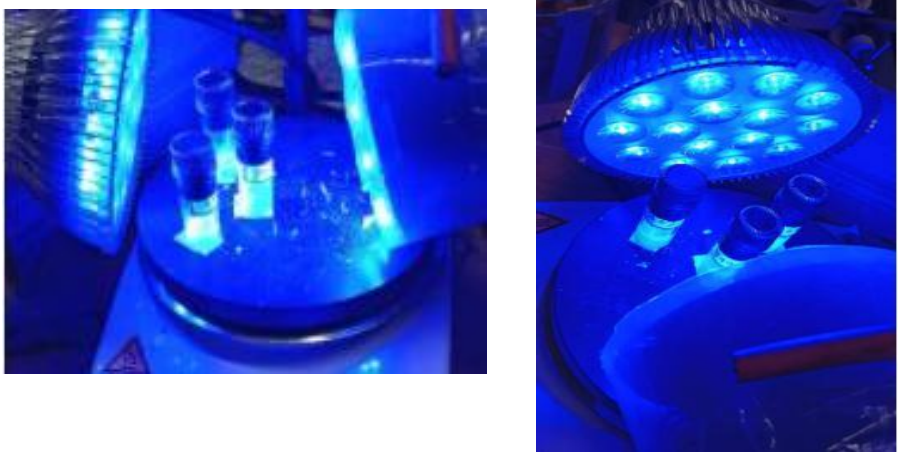
1. General Information:

All reactions were performed in flame-dried glassware under an argon atmosphere unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled before use. $CDCl_3$ was stored over 4Å molecular sieves. Chemicals used in this project were purchased from Sigma-Aldrich, TCI, Alfa-Aesar and Sisco Research Laboratories (SRL) and used without further purification. All the liquid chemicals were distilled freshly prior to use. Blue leds GRPAR38-24W were purchased from ABI. Analytical thin-layer chromatography (TLC) was performed on using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by UV radiation, basic aqueous potassium permangante (KMnO4), *p*-anisaldehyde stains as developing agents.

Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from Merck using the indicated solvents. Organic solutions were concentrated under reduced pressure on Heidolph rotary evaporator. NMR spectra were acquired on a JEOL JNM ECS-400, instrument running at 400 MHz for ^{1}H, 101 MHz ^{13}C and 376 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for **^{1}H NMR**, $CDCl_3$, 77.16 ppm for **^{13}C NMR**). Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), coupling constants (Hz), and integration. All fluorescence data were recorded using Perkin Elmer LS55 fluorescence spectrophotometer instrument.

Figure S1: *Photochemical reaction set up.*

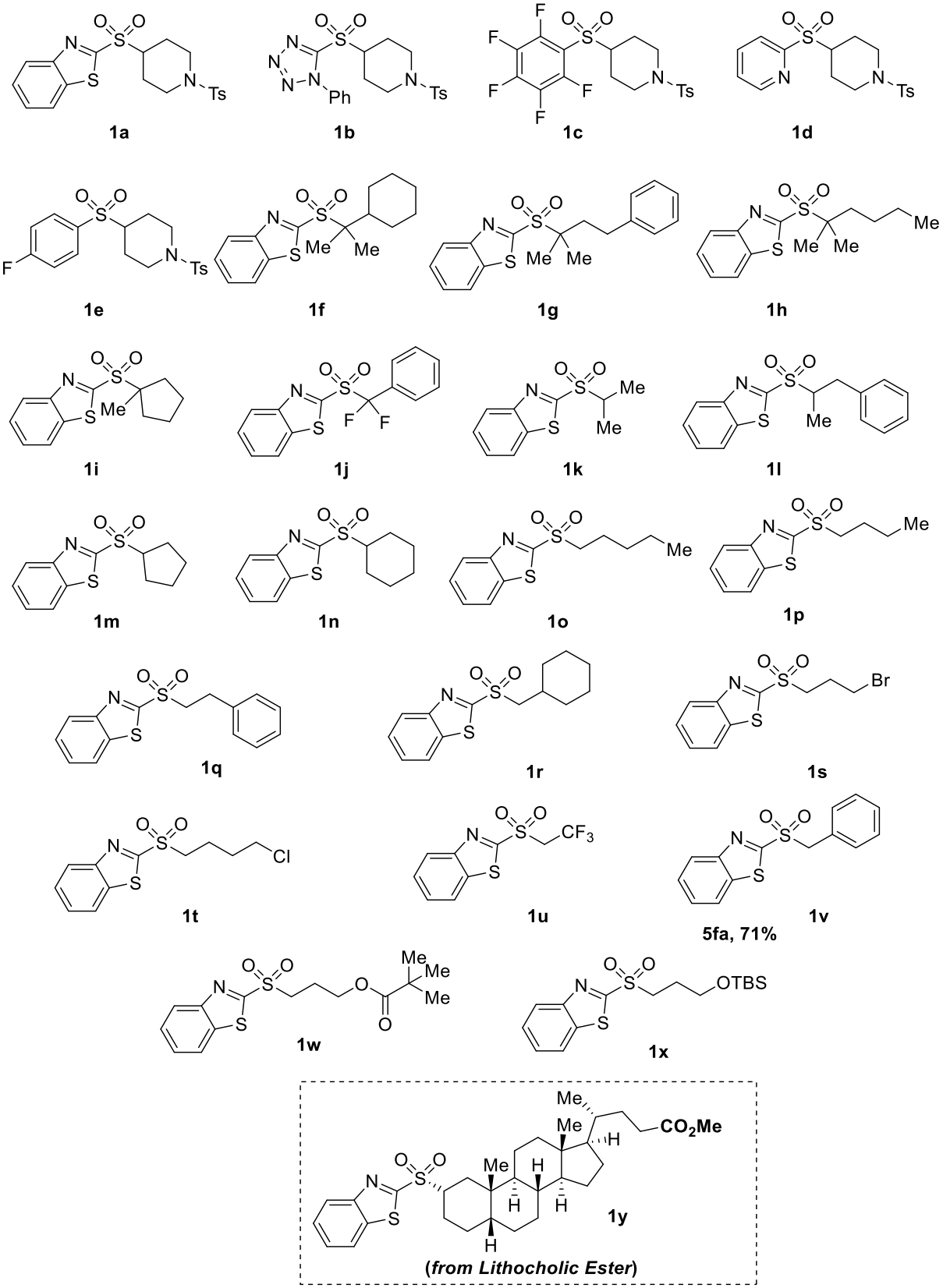


2. List of starting substrates prepared:

2.1 List of sulfone compounds prepared:[S1-S2]

The lists of substrates prepared according to **GP-1**–**GP-4** are given bellow.

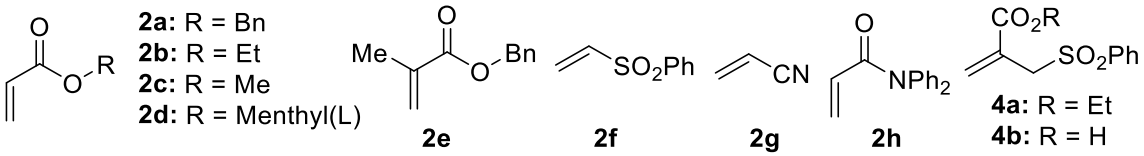
List of successful sulfones



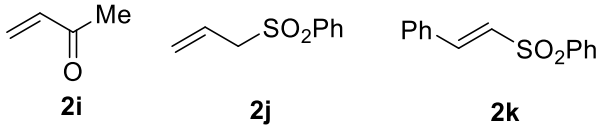
2.2 List of acceptors prepared:

All acceptors were prepared according to the previous literatures.[S2-S3]

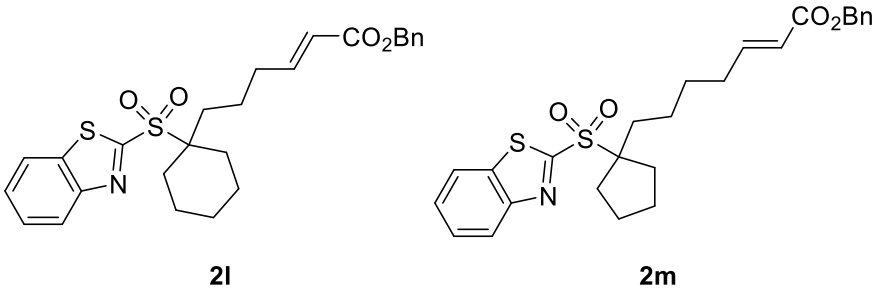
List of successful acceptors



List of Unsuccessful acceptors

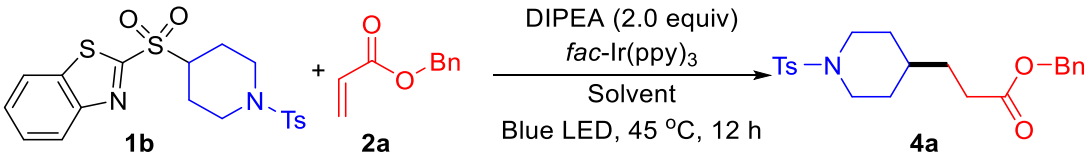


Starting substrates for intramolecular reaction



3.1 Optimization Table:

Table S1: *Evaluation of solvents*[a]

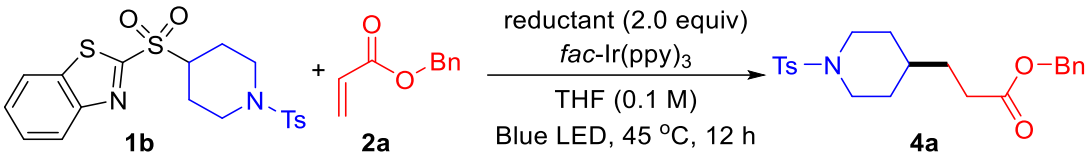


Entry	Solvent (0.1 M)	Yield (%)[b]
1	MeCN	n.r
2	**THF**	**59%**
3	DMA	35%
4	1,4-dioxane	n.r.
5	Et_2O	n.r.
6	DCM	n.r.
7	DMSO	54%
8	DMF	n.r.
9	DCE	49%

10	NMP	32%
11	DMPU	30%
12	MeOH	n.r.
13	HFIP	n.r.

[a]Reactions were carried out in 0.1 mmol scale. [b]Yields reported are the isolated yield.

Table S2: *Evaluation of reductant*[a]



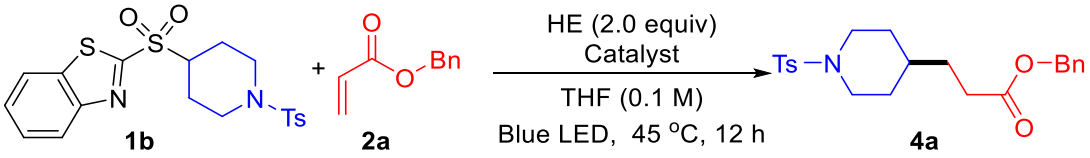
1b **2a** **4a**

1 equiv. **2.5 equiv.**

Entry	Reductant	Yield (%)[b]
1	DIPEA	59%
2	Diisobutylamine	trace
3	Diisopropylamine	trace
4	Piperidine	n.r.
5	Pyrrolidine	35%
6	TEA	20%
7	**Hantzsch ester**	**70%**
8	Hz.ester/TMP	35%
9	NMP	n.r.

[a]Reactions were carried out in 0.1 mmol scale. [b]Yields reported are the isolated yield.

Table S3: *Evaluation of Catalyst*[a]



1b **2a** **4a**

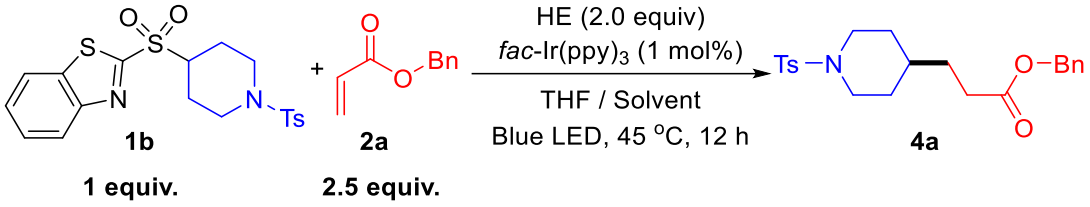
1 equiv. **2.5 equiv.**

Entry	Catalyst	Yield (%)[b]
1	***fac*-Ir(ppy)$_3$**	**70%**
2	4-CzIPN	n.r.
3	Eosin Y[c]	n.r.

4	Acridinium	n.r.
5	$Ru(bpy)_3(PF_6)_2$	trace
6	$[Ir(dtbbpy)(ppy)_2]PF_6$	50%
7	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	32%

[a]Reactions were carried out in 0.1 mmol scale. [b]Yields reported are the isolated yield. [c] Green light as a light source

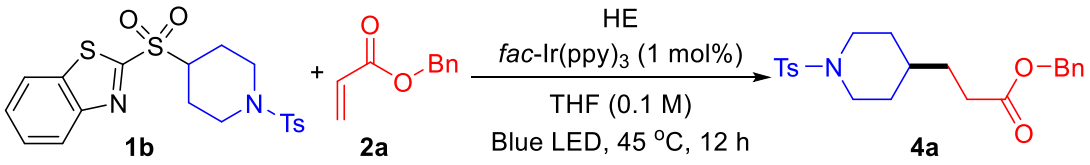
Table S4: *Evaluation of solvents mixture with best reductant HE*[a]



Entry	Solvent (0.1 M)	Yield (%)[b]
1	**THF**	**70%**
2	NMP	30%
3	PhMe	65%
4	DMPU	45%
5	DMA	45%
6	DCE	54%
7	DMSO	40%

[a]Reactions were carried out in 0.1 mmol scale. [b]Yields reported are the isolated yield.

Table S5: *Evaluation of equivalency*[a]



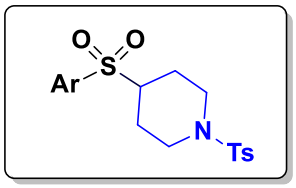
Entry	1a	2a	HE	Yield (%)[b]
1	1	2.5	2	70%
2	**1**	**3**	**2**	**75%**
3	1	1	2	40%
4	2	1	2	44%
5	1	3	2.5	70%

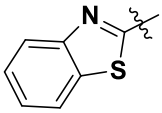
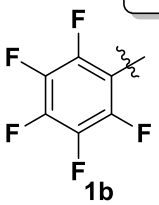
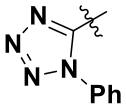
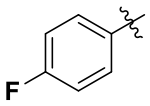
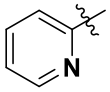
[a]Reactions were carried out in 0.1 mmol scale. [b]Yields reported are the isolated yield.

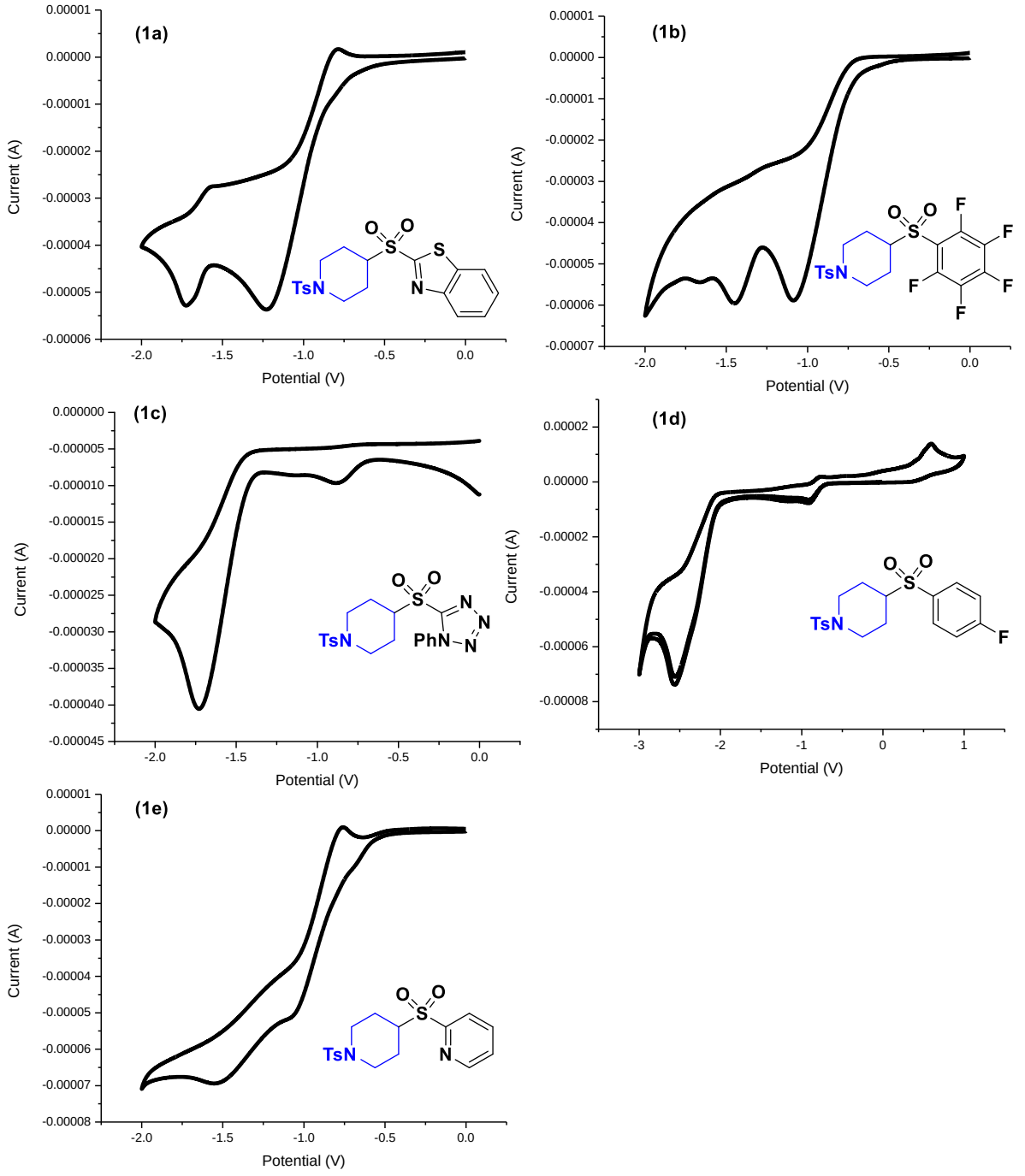
3.2 Cyclic voltammetry:

Cyclic voltammograms of (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, (e) **1e**, in THF with a 0.1 M n-Bu_4NPF_6 as a supporting electrolyte. Working electrode: Pt wire; Counter electrode: Pt wire; Reference electrode: Ag/AgCl; Scan rate: 0.05 V/s Ferrocene/ferrocenium ion redox couple was used as an external reference.

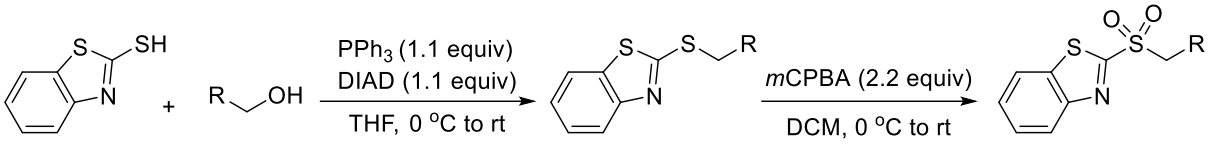
Table S6: *Reduction potential*



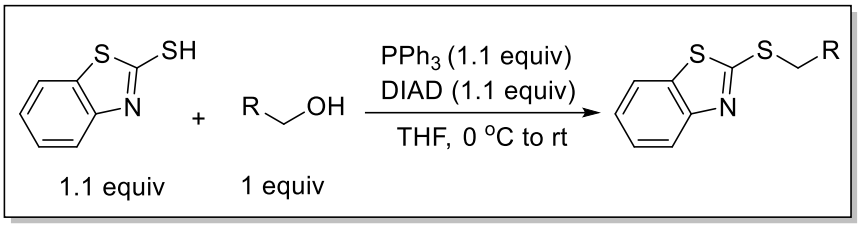
Ar:					
	1a	**1b**	**1c**	**1d**	**1e**
E(V) : (V vs Fc/Fc^+)	**-1.715**	**-1.441**	**-1.762**	**-2.549**	**-1.515**



4. General Procedures:

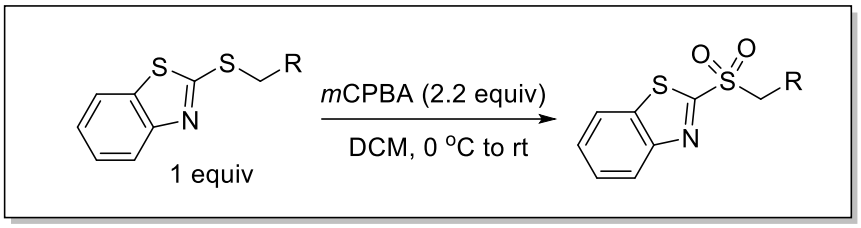


4.1 General Procedure 1: Mitsunobu reaction of thiol with alkyl alcohols (GP-1)



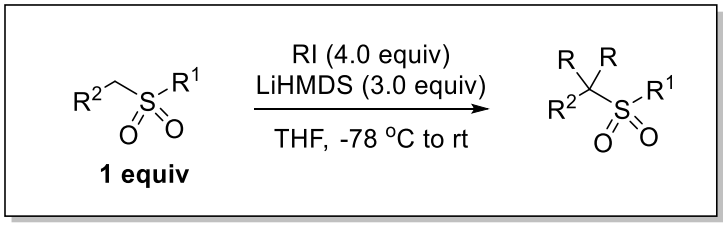
According to previous literature,[S1] a round bottom flask was charged with alcohol (1.0 equiv.), triphenyl phosphine (1.1 equiv.) and thiol (1.1 equiv.). The flask was evacuated and backfilled or continuously purged with argon. Anhydrous THF (0.2 M) was added, and the mixture was cooled to 0 °C in an ice/water bath. DIAD (neat, 1.1 equiv.) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stir overnight. The mixture was concentrated and purified by column chromatography to afford pure thioether.

4.2 General Procedure 2: Oxidation with *m*CPBA (GP-2)



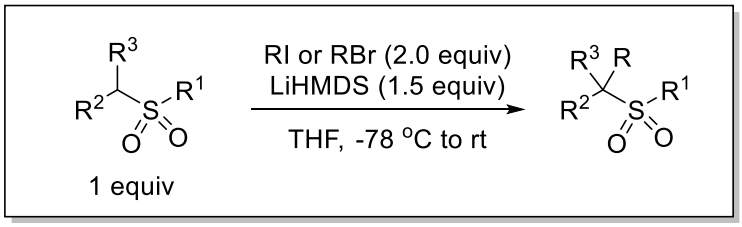
According to previous literature,[S1] to a solution of thioether (1.0 equiv.) in CH_2Cl_2 (0.2 M) at 0 °C in an ice / water bath was added mCPBA (2.2 equiv.) portionwise, and the mixture was stirred until complete conversion to the sulfone was observed by TLC (the mixture was allowed to warm to room temperature). Saturated aq. $NaHCO_3$ solution and saturated aq. $Na_2S_2O_3$ solution were added slowly, and the mixture was stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2, and the organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting crude material was purified by recrystallization (typically from CH_2Cl_2 / MeOH) or column chromatography (silica) to afford pure sulfone.

4.3 General Procedure 3: Preparation of tertiary sulfones from primary sulfones (GP-3).



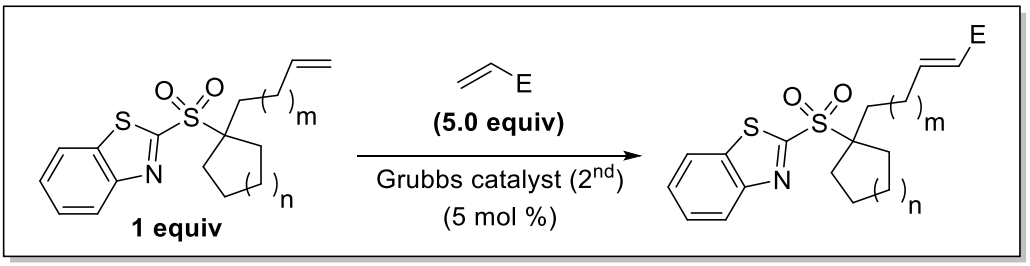
According to previous literature,[S1-S2] A two-neck Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added primary sulfone (1 equiv) and dry THF (5 mL per mmol of sulfone). A solution of LiHMDS (1.3 M in THF, 3 equiv) was added drop wise to the reaction mixture at -78 °C under argon. After stirring for 30 min, alkyl iodide (4 equiv) was added, the mixture was stirred at rt for 16 h. Sat. NH_4Cl aq was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with EtOAc (3 times), and the combined organic layer was washed with sat. $NaHCO_3$ aq and brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography to afford the corresponding tertiary sulfone.

4.4 General Procedure 4: Preparation of tertiary sulfones from secondary sulfones (GP-4).



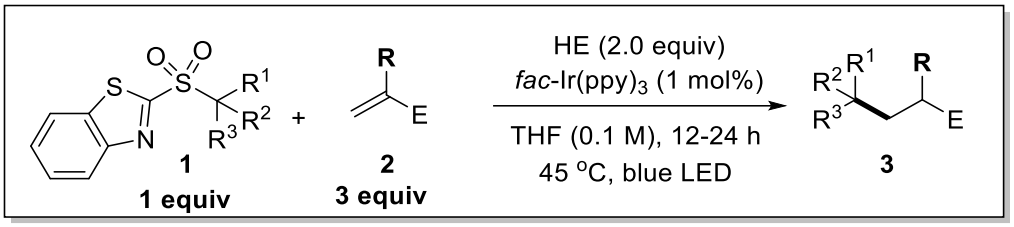
According to previous literature,[S2] A two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added primary sulfone (1 equiv) and dry THF (5 mL per mmol of sulfone). A solution of LiHMDS (1.3 M in THF, 1.5 equiv) was added drop wise to the reaction mixture at -78 °C under argon. After stirring for 30 min, alkyl bromide or iodide (2 equiv) was added, the mixture was stirred at rt for 16 h. Sat. NH_4Cl aq was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with EtOAc (3 times), and the combined organic layer was washed with sat. $NaHCO_3$ aq and brine. The organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography to afford the corresponding tertiary sulfone.

4.5 General Procedure 5: Preparation of compound **2l** and **2m** for Intramolecular Giese reaction (GP-5).



According to previous literature,[S2] A 20-mL two-neck flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added sulfone (1.0 equiv), DCM (7.5 mL per mmol), olefin (5 equiv), and Grubbs catalyst 2nd generation (5 mol %) under a stream of argon. This mixture was heated at 40 ºC for 12 h. After cooling to room temperature, the mixture was passed through a pad of silica gel with copious washings with EtOAc (~10 mL). The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography to afford the corresponding sulfone.

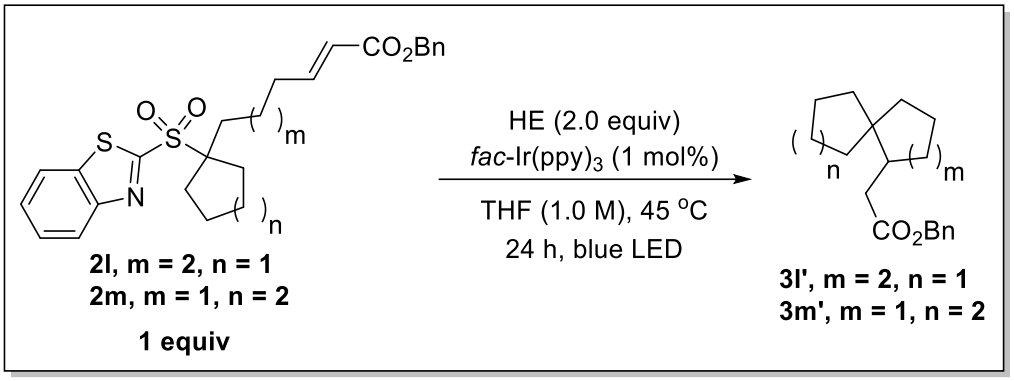
4.6 General Procedure 6: Photocatalytic Desulfonative Cross-Coupling Reaction (GP-6).



Sulfone benzothiazole **1** (0.2 mmol, 1.0 equiv), {*fac*-Ir(ppy)$_3$} (0.002 mmol, 1 mol%), diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **(HE)** (0.4 mmol, 2.0 equiv) and acceptor **2** (0.6 mmol, 3.0 equiv) was charged in an oven-dried 5 mL glass vial under argon atmosphere

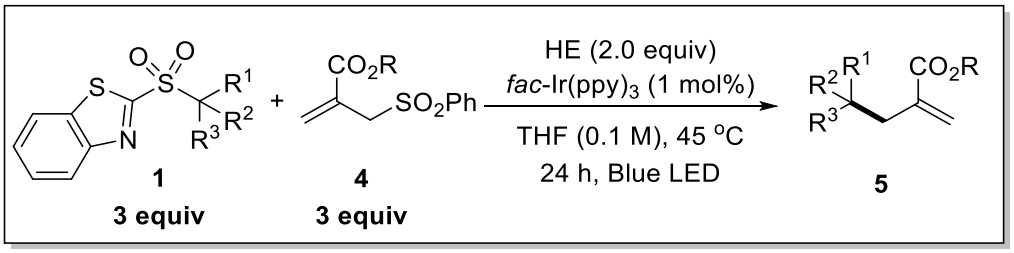
in glove box. The reaction mixture was dissolved in 0.1 M dry THF and the vial was sealed with a Teflon cap and wrapped with parafilm in glove box. The resulting mixture was stirred under the irradiation of 2x24W Blue LEDs for 12-24 h at 45 °C (oil bath temperature). Upon completion the mixture was transferred to a round bottom flask and the glass vial was washed with CH_2Cl_2 (2 × 2 mL). The crude mixture was concentrated and purified via flash column chromatography or purified by pTLC to afford the corresponding Coupling product.

4.7 General Procedure 7: Intramolecular Giese reaction of tertiary sulfone (GP-7).



Sulfone benzothiazole **2l, 2m** (0.1 mmol, 1.0 equiv), {*fac*-Ir(ppy)$_3$} (0.001 mmol, 1 mol%), diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **(HE)** (0.2 mmol, 2.0 equiv) was charged in an oven-dried 5 mL glass vial under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry THF and the vial was sealed with a Teflon cap and wrapped with parafilm in glove box. The resulting mixture was stirred under the irradiation of 2x24W Blue LEDs for 24 h at 45 °C (oil bath temperature). Upon completion the mixture was transferred to a round bottom flask and the glass vial was washed with CH_2Cl_2 (2 × 2 mL). The crude mixture was concentrated and purified via flash column chromatography or purified by pTLC to afford the corresponding Coupling product.

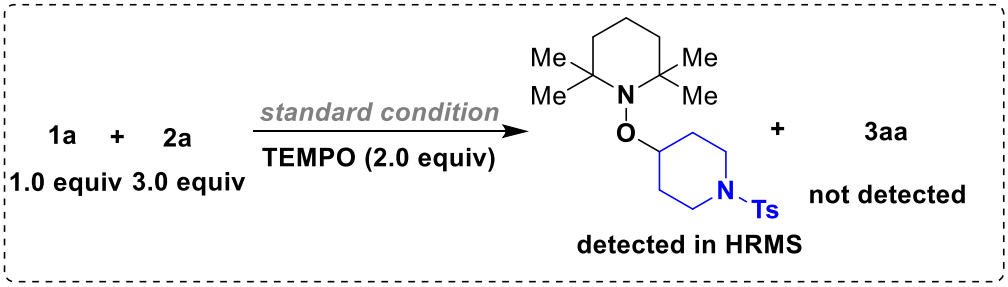
4.8 General Procedure 8: Photocatalytic Desulfonative Coupling with allyl sulfone (GP-8).



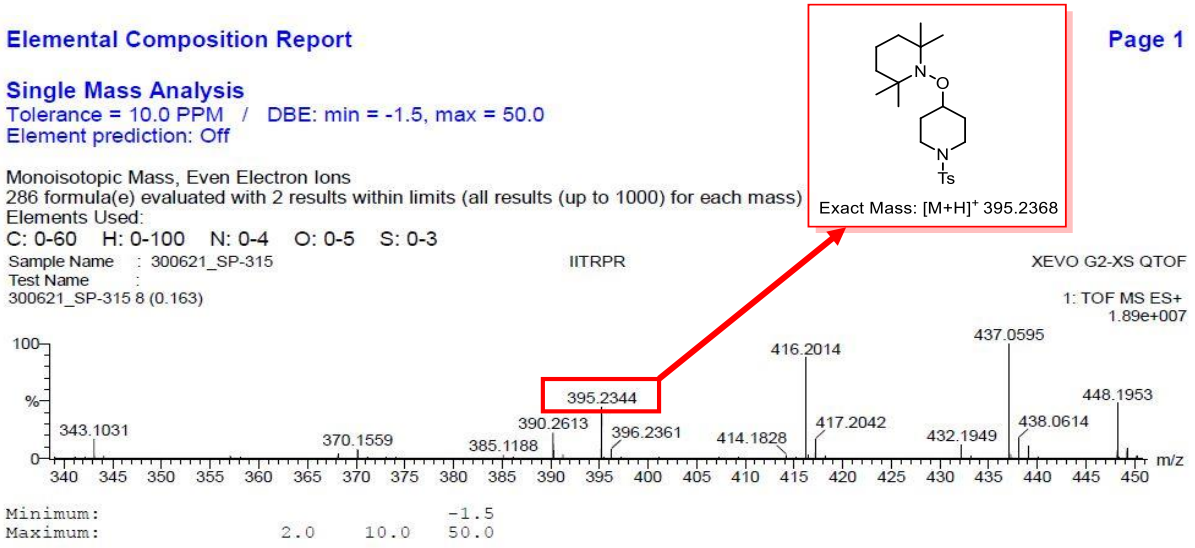
Sulfone benzothiazole (0.2 mmol, 1.0 eq.), {*fac*-Ir(ppy)$_3$} (0.002 mmol, 1 mol%), diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HE) (0.4 mmol, 2.0 eq.) and acceptor (0.6 mmol, 3.0 eq.) was charged in an oven-dried 5 mL glass vial under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry THF and the vial was sealed with a Teflon cap and wrapped with parafilm in glove box. The resulting mixture was stirred under the irradiation of 2x24W Blue LEDs for 24 h at 45 °C (oil bath temperature). Upon completion the mixture was transferred to a round bottom flask and the glass vial was washed with CH_2Cl_2 (2 × 2 mL). The crude mixture was concentrated and purified via flash column chromatography or purified by pTLC to afford the corresponding Coupling product.

5. Mechanistic study and proposal

5.1 Using TEMPO as radical scavenger

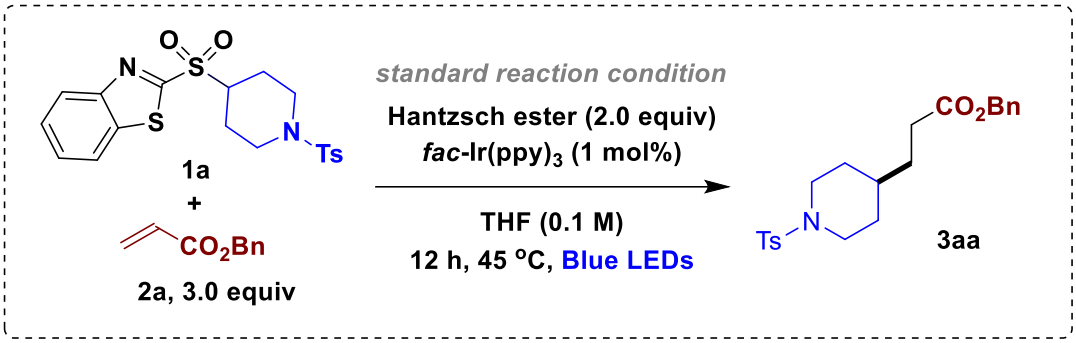


To an oven-dried 5 mL glass vial was charged with **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), **TEMPO** (63.0 mg, 0.4 mmol, 2.0 equiv) **HE** (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box.The reaction mixture was dissolved in 0.1 M dry THF and the vial was sealed with a Teflon cap and wrapped with parafilm in glove box. The resulting mixture was stirred under the irradiation of 2x24W Blue LEDs for 12 h at 45 ^{o}C (oil bath temperature). The corresponding coupling product **3aa** was not observed based on ^{1}H NMR analysis, and the corresponding product of radical trapping, 2,2,6,6-tetramethyl-1-((1-tosylpiperidin-4-yl)oxy)piperidine was observed by mass spectrometry (HRMS)



5.2 Fluorescence quenching experiments (Stern-Volmer study)

Emission intensities were recorded using a Perkin Elmer LS55 fluorescence spectrophotometer. In a typical experiment, a 0.5 mM solution of {*fac*-Ir(ppy)$_3$} (PC) in THF was added to the appropriate amount of quencher in a PTEF capped 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at λ = 450 nm (absorption maximum of the photocatalyst) and the emission intensity was collected at 546 nm (emission maximum).[S5]



Sulfone (1a) as a Quencher

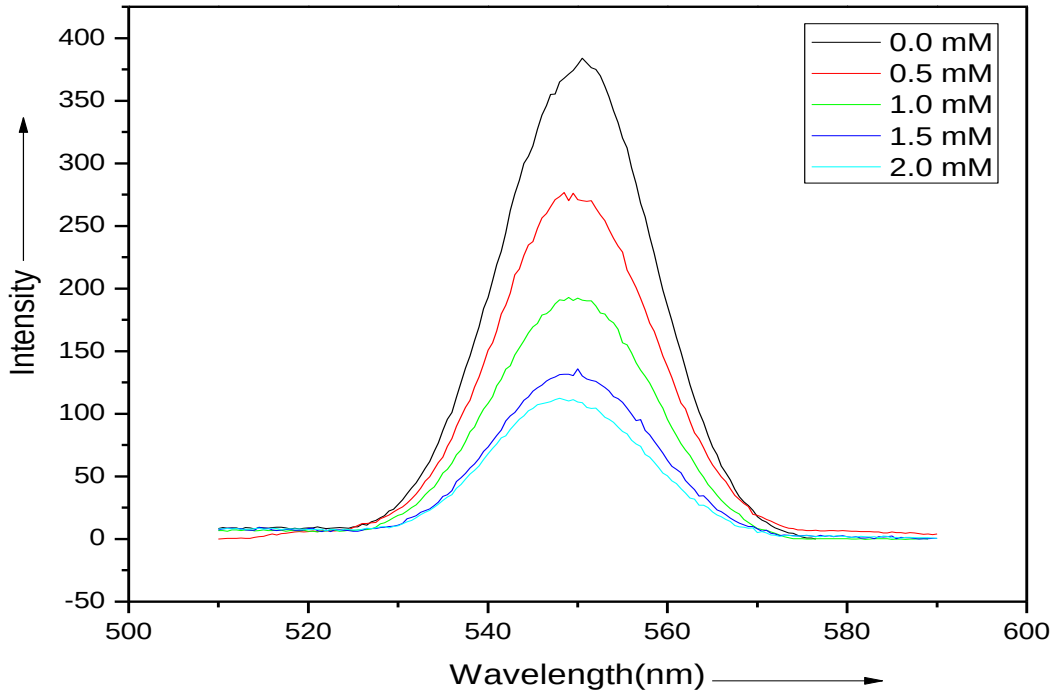


Figure S2a: Fluorescence quenching of PC with **1a**

Stern Volmer plot

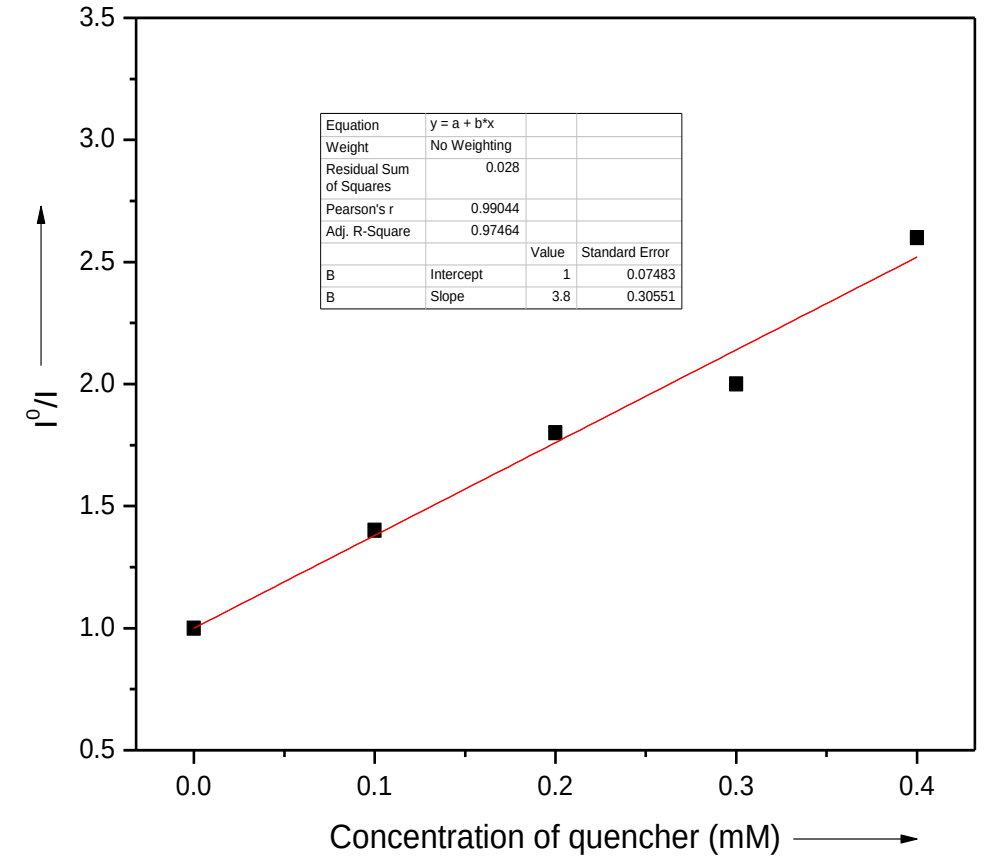


Figure S2b: Stern-Volmer plot of PC with **1a**

Hantzsch ester (HE) as a Quencher

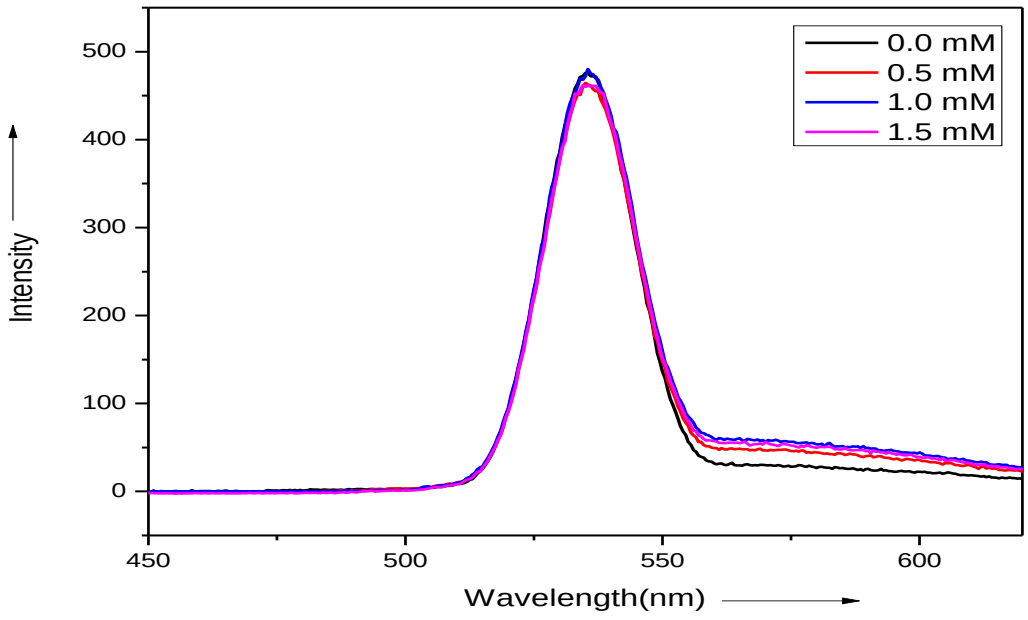


Figure S2c: Fluorescence quenching of PC with **HE**

Stern Volmer plot

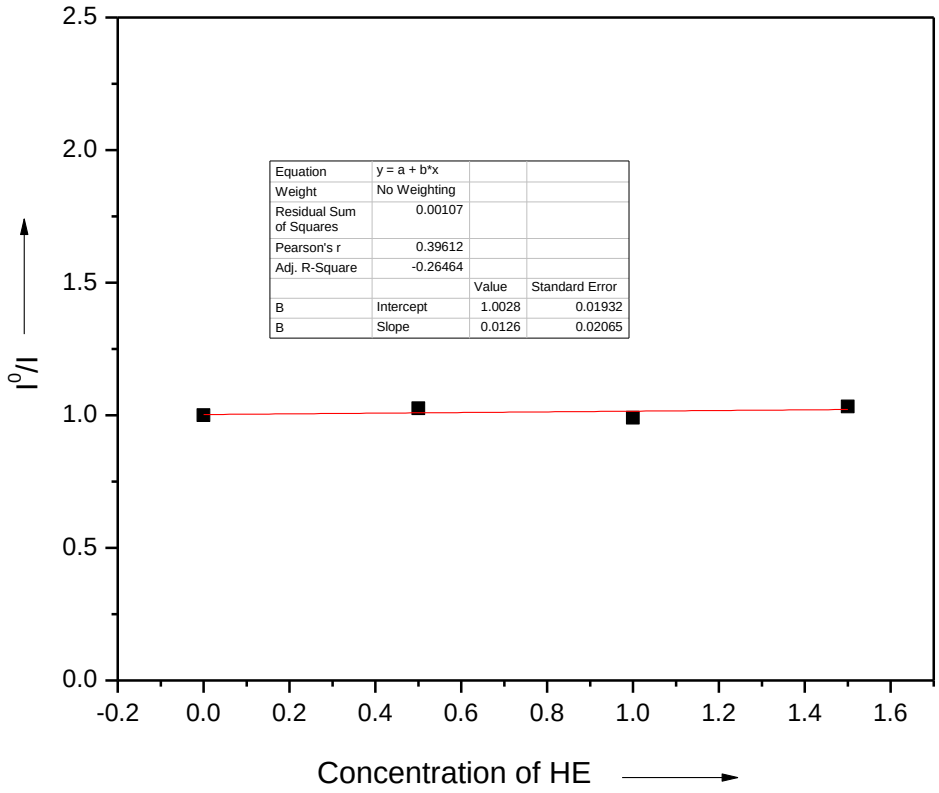


Figure S2d: Stern-Volmer plot of PC with **HE**

6.0 References:

S1. R. R. Merchant, J. T. Edwards, T. Qin, M. M. Kruszyk, C. Bi, G. Che, D. H. Bao, W. Qiao, L. Sun, M. R. Collins, O. O. Fadeyi, G. M. Gallego, J. J. Mousseau, P. Nuhant and P. S. Baran, *Science*, 2018, **360**, 75.

S2. M. Nambo, Y. Tahara, J. C.-H. Yim, D. Yokogawa and C. M. Crudden, *Chem. Sci.*, 2021, **12**, 4866.

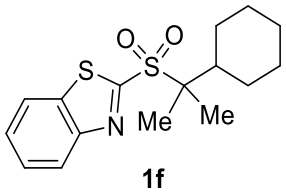
S3. M. M. Zhang and F. Liu, *Org. Chem. Front.*, 2018, **5**, 3443.

S4. S. T.-C. Eey and M. J. Lear, *Org. Lett.*, 2010, **12**, 5510.

S5. J. L. Jeffrey, F. R. Petronijevic´ and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2015, **137**, 8404.

7.0 Experimental Details for the Synthesized Starting Materials Sulfones

7.1. 2-((2-cyclohexylpropan-2-yl)sulfonyl)benzo[d]thiazole (1f)



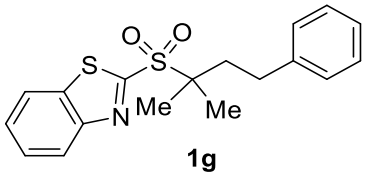
1f

$C_{16}H_{21}NO_2S_2$

M. W. 323.1014 g/mol

Following General Procedure **GP1**, **GP2**, **GP3**, to afford the title compound **1f**, white solid. **HRMS (ESI):** m/z $[M+H]^+$ Calculated for $[C_{16}H_{22}NO_2S_2]^+$: 324.1092; Found:. 324.1102. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26–8.24 (m, 1H), 8.02–7.99 (m, 1H), 7.65–7.56 (m, 2H), 2.10–2.06 (m, 2H), 2.03–1.97 (m, 1H), 1.83–1.78 (m, 2H), 1.47 (s, 6H), 1.30–1.12 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 153.2, 137.4, 128.0, 127.6, 125.8, 122.2, 69.5, 42.3, 28.4, 26.8, 26.2, 20.1.

7.2. 2-((2-methyl-4-phenylbutan-2-yl)sulfonyl)benzo[d]thiazole (1g)



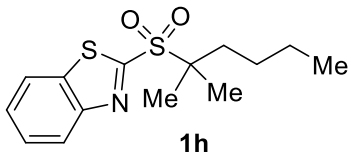
1g

$C_{18}H_{19}NO_2S_2$

M. W. 345.0857 g/mol

Following General Procedure **GP1**, **GP2**, **GP3**, to afford the title compound **1g**, white solid. **HRMS (ESI):** m/z $[M+H]^+$ Calculated for $[C_{18}H_{20}NO_2S_2]^+$: 346.0935; Found:. 346.0945. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27–8.25 (m, 1H), 8.03–8.00 (m, 1H), 7.66–7.58 (m, 2H), 7.30–7.26 (m, 2H), 7.22–7.18 (m, 3H), 2.79–2.75 (m, 2H), 2.22–2.17 (m, 2H), 1.60 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.1, 153.3, 141.0, 137.4, 128.7, 128.5, 128.1, 127.7, 126.4, 125.8, 122.3, 65.3, 37.4, 30.4, 21.2.

7.3. 2-((2-methylhexan-2-yl)sulfonyl)benzo[d]thiazole (1h)



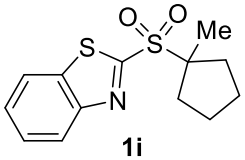
1h

$C_{14}H_{19}NO_2S_2$

M. W. 297.0857 g/mol

Following General Procedure **GP1**, **GP2**, **GP3**, to afford the title compound **1h**, white solid. **HRMS (ESI):** m/z $[M+H]^+$ Calculated for $[C_{14}H_{20}NO_2S_2]^+$: 298.0935; Found:. 298.0934. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26– 8.24 (m, 1H), 8.02–8.00 (m, 1H), 7.65–7.56 (m, 2H), 1.90–1.86 (m, 2H), 1.49 (s, 6H), 1.39–1.29 (m, 4H), 0.90–0.88 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.2, 153.2, 137.4, 128.0, 127.6, 125.8, 122.2, 65.5, 34.7, 25.9, 23.2, 20.8, 14.1.

7.4. 2-((1-methylcyclopentyl)sulfonyl)benzo[d]thiazole (1i)

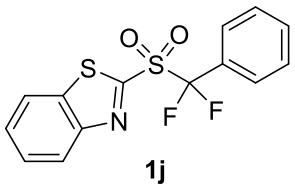


1i

$C_{13}H_{15}NO_2S_2$
M. W. 281.0544 g/mol

Following General Procedure **GP1**, **GP2**, **GP4**, to afford the title compound **1i**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{13}H_{16}NO_2S_2]^+$: 282.0622; Found:. 282.0628.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.23 (m, 1H), 8.02–8.00 (m, 1H), 7.65–7.57 (m, 2H), 2.71–2.64 (m, 2H), 1.88–1.80 (m, 2H), 1.79–1.72 (m, 2H), 1.70–1.63 (m, 2H), 1.56 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 153.2, 137.3, 128.0, 127.6, 125.7, 122.2, 70.7, 35.3, 25.9, 23.8.

7.5. 2-((difluoro(phenyl)methyl)sulfonyl)benzo[d]thiazole (1j)

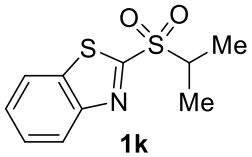


1j

$C_{14}H_9F_2NO_2S_2$
M. W. 325.0043 g/mol

Following General Procedure **GP1**, **GP2**, **GP3**, to afford the title compound **1j**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{10}F_2NO_2S_2]^+$: 326.0121; Found:. 326.0135.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38–8.36 (m, 1H), 8.07–8.05 (m, 1H), 7.77–7.75 (m, 2H), 7.72–7.63 (m, 3H), 7.57–7.53 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 153.1, 138.39, 133.12, 129.0, 128.9, 128.2, 128.1 (d, J = 2.4 Hz), 128.1, 126.4, 122.6 (t, J = 259.2Hz), 122.3.**^{19}F NMR (376 MHz, $CDCl_3$)** δ -99.65.

7.6. 2-(isopropylsulfonyl)benzo[d]thiazole (1k)

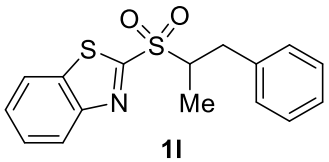


1k

$C_{10}H_{11}NO_2S_2$
M. W. 241.0231 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1k**, white solid.
HRMS (ESI): *m/z* $[M+H]^+$ Calculated for $[C_{10}H_{12}NO_2S_2]^+$: 242.0309; found 242.0301.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.22 (m, 1H), 8.03–8.01 (m, 1H), 7.66–7.58 (m, 2H), 3.78–3.71 (m, 1H), 1.47 (d, *J* = 6.9 Hz, 6H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 153.0, 137.0, 128.1, 127.7, 125.6, 122.4, 55.5, 15.5.

7.7. 2-((1-phenylpropan-2-yl)sulfonyl)benzo[d]thiazole (1l)

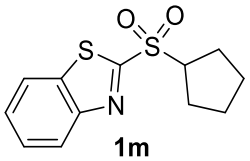


1l

$C_{16}H_{15}NO_2S_2$
M. W. 317.0544 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1l**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{16}NO_2S_2]^+$: 318.0622; Found:. 318.0560.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.23 (m, 1H), 8.03–8.01 (m, 1H), 7.69–7.56 (m, 2H), 7.32–7.19 (m, 3H), 7.17–7.13 (m, 2H), 3.90–3.84 (m, 1H), 3.56–3.52 (m, 1H), 2.80–2.74 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.0, 153.0, 137.0, 136.4, 129.3, 128.9, 128.2, 127.8, 127.2, 125.6, 122.4, 61.2, 35.2, 12.5.

7.8. 2-(cyclopentylsulfonyl)benzo[d]thiazole (1m)

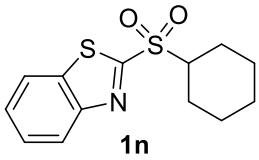


1m

$C_{12}H_{13}NO_2S_2$
M. W. 267.0388 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1m**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{12}H_{14}NO_2S_2]^+$: 268.0466; Found:. 268.0455.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.20 (m, 1H), 8.02–8.00 (m, 1H), 7.65–7.57 (m, 2H), 4.04–4.00 (m, 1H), 2.30–2.21 (m, 2H), 2.09–1.97 (m, 2H), 1.88–1.76 (m, 2H), 1.74–1.61 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 153.0, 136.9, 128.0, 127.7, 125.6, 122.4, 63.4, 27.2, 26.1.

7.9. 2-(cyclohexylsulfonyl)benzo[d]thiazole (1n)

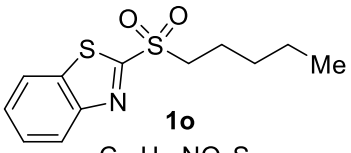


1n

$C_{13}H_{15}NO_2S_2$
M. W. 281.0544 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1n**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{13}H_{16}NO_2S_2]^+$: 282.0622; Found:. 282.0616.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.23 (m, 1H), 8.03–8.01 (m, 1H), 7.67–7.57 (m, 2H), 3.51–3.44 (m, 1H), 2.21–2.16 (m, 2H), 1.95–1.88 (m, 2H), 1.73–1.68 (m, 1H), 1.66–1.62 (m, 1H), 1.36–1.16 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 153.1, 137.1, 128.0, 127.7, 125.7, 122.4, 63.2, 25.2, 25.1, 25.1.

7.10. 2-(pentylsulfonyl)benzo[d]thiazole (1o)



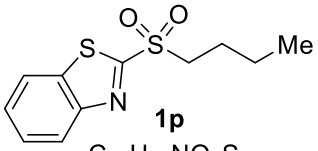
1o

$C_{12}H_{15}NO_2S_2$

M. W. 269.0544 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1o**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{12}H_{16}NO_2S_2]^+$: 270.0622; Found:. 270.0628.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.20 (m, 1H), 8.02–8.00 (m, 1H), 7.66–7.57 (m, 2H), 3.52–3.48 (m, 2H), 1.91–1.83 (m, 2H), 1.45–1.27 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H**). ^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 152.8, 136.9, 128.1, 127.8, 125.6, 122.5, 54.8, 30.4, 22.1, 22.0, 13.8.

7.11. 2-(butylsulfonyl)benzo[d]thiazole (1p)



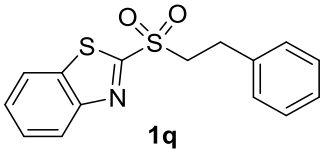
1p

$C_{11}H_{13}NO_2S_2$

M. W. 255.0388 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1p**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_{14}NO_2S_2]^+$: 256.0466; Found:. 256.0471.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 8.03–8.01 (m, 1H), 7.66–7.57 (m, 2H), 3.53–3.49 (m, 2H), 1.90–1.82 (m, 2H), 1.52–1.43 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 152.9, 136.9, 128.1, 127.8, 125.6, 122.5, 54.6, 24.3, 21.7, 13.6.

7.12. 2-(phenethylsulfonyl)benzo[d]thiazole (1q)



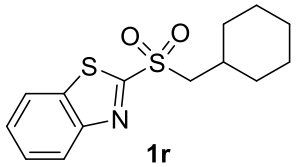
1q

$C_{15}H_{13}NO_2S_2$

M. W. 303.0388 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1q**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{15}H_{14}NO_2S_2]^+$: 304.0466; Found:. 304.0472.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.22 (m, 1H), 8.05–8.03 (m, 1H), 7.69–7.61 (m, 2H), 7.30–7.26 (m, 2H), 7.23–7.19 (m, 3H), 3.85–3.81 (m, 2H), 3.26–3.21 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.7, 152.8, 137.0, 136.9, 128.9, 128.5, 128.2, 127.8, 127.2, 125.6, 122.5, 56.0, 28.5.

7.13. 2-((cyclohexylmethyl)sulfonyl)benzo[d]thiazole (1r)

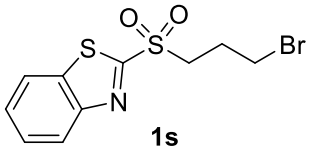


1r

$C_{14}H_{17}NO_2S_2$
M. W. 295.0701 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1r**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{18}NO_2S_2]^+$: 296.0779; Found:. 296.0781.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.16 (m, 1H), 7.99–7.96 (m, 1H), 7.62–7.53 (m, 2H), 3.41–3.40 (m, 2H), 2.18–2.07 (m, 1H), 1.92–1.88 (m, 2H), 1.69–1.56 (m, 3H), 1.31–1.20 (m, 2H), 1.17–1.05 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.7, 152.6, 136.6, 128.0, 127.6, 125.3, 122.4, 60.9, 32.9, 32.6, 25.6, 25.6.

7.14. 2-((3-bromopropyl)sulfonyl)benzo[d]thiazole (1s)

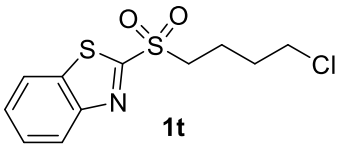


1s

$C_{10}H_{10}BrNO_2S_2$
M. W. 318.9336 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1s**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{10}H_{11}BrNO_2S_2]^+$: 319.9415; Found:. 319.9429.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 8.04–8.01 (m, 1H), 7.76–7.59 (m, 2H), 3.72–3.68 (m, 2H), 3.55–3.52 (m, 2H), 2.51–2.44 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 152.7, 136.8, 128.3, 127.9, 125.6, 122.5, 53.4, 30.6, 25.7.

7.15. 2-((4-chlorobutyl)sulfonyl)benzo[d]thiazole (1t)

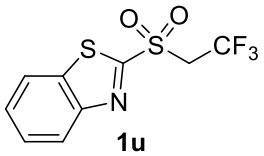


1t

$C_{11}H_{12}ClNO_2S_2$
M. W. 288.9998 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1t**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{11}H_{13}ClNO_2S_2]^+$: 290.0076; Found:. 290.0084.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 8.04–8.01 (m, 1H), 7.67–7.58 (m, 2H), 3.58–3.54 (m, 4H), 2.21–2.05 (m, 2H), 2.00–1.93 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.6, 152.8, 136.9, 128.3, 127.9, 125.6, 122.5, 53.9, 43.8, 30.9, 20.1.

7.16. 2-((2,2,2-trifluoroethyl)sulfonyl)benzo[d]thiazole (1u)



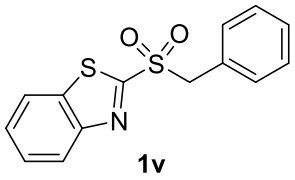
1u

$C_9H_6F_3NO_2S_2$

M. W. 280.9792 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1u**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_9H_7F_3NO_2S_2]^+$: 281.9870; Found:. 281.9878.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 8.04–8.01 (m, 1H), 7.68–7.60 (m, 2H), 4.47–4.41 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.3, 152.4, 137.0, 128.7, 128.1, 125.7, 122.5, 121.0 (q, J = 278.4 Hz), 56.3 (q, *J* = 32.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.6.

7.17. 2-(benzylsulfonyl)benzo[d]thiazole (1v)



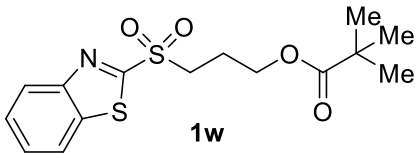
1v

$C_{14}H_{11}NO_2S_2$

M. W. 289.0231 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1v**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{12}NO_2S_2]^+$: 290.0309; Found:. 290.0315.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.24 (m, 1H), 7.93–7.91 (m, 1H), 7.66–7.54 (m, 2H), 7.33–7.24 (m, 5H), 4.75 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 152.6, 137.1, 131.2, 129.3, 129.0, 128.1, 127.8, 126.4, 125.5, 122.4, 61.1.

7.18. 3-(benzo[d]thiazol-2-ylsulfonyl)propyl pivalate (1w)



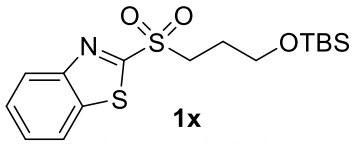
1w

$C_{15}H_{19}NO_4S_2$

M. W. 341.0755 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1v**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{15}H_{20}NO_4S_2]^+$: 342.0834; Found:. 342.0834.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.20 (m, 1H), 8.07–7.99 (m, 1H), 7.67–759 (m, 2H), 4.17 (t, J = 6.1 Hz, 2H), 3.63–3.59 (m, 2H), 2.27–2.20 (m, 2H), 1.17 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.3, 165.5, 152.8, 136.9, 128.3, 127.9, 125.6, 122.5, 61.8, 51.8, 38.9, 27.26, 22.5.

7.19. 2-((3-((tert-butyldimethylsilyl)oxy)propyl)sulfonyl)benzo[d]thiazole (1x)



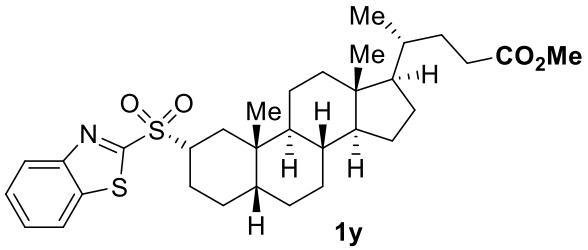
1x

$C_{16}H_{25}NO_3S_2Si$

M. W. 371.1045 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1v**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{26}NO_3S_2Si]^+$: 372.1123; Found:. 372.1123.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 8.03–8.01 (m, 1H), 7.66–7.58 (m, 2H), 3.71 (t, J = 5.8 Hz, 2H), 3.65–3.61 (m, 2H), 2.11–2.04 (m, 2H), 0.85 (s, 9H), 0.01 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.9, 152.9, 136.9, 128.2, 127.8, 125.7, 122.5, 60.7, 52.1, 26.0, 25.9, 18.3, -5.3.

7.20. methyl (R)-4-((2R,5R,8R,9S,10S,13R,14S,17R)-2-(benzo[d]thiazol-2-ylsulfonyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (1y)



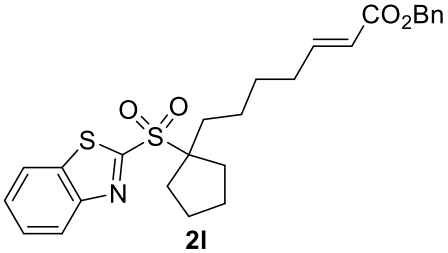
1y

$C_{32}H_{45}NO_4S_2$

M. W. 571.2790 g/mol

Following General Procedure **GP1**, **GP2**, to afford the title compound **1v**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{32}H_{46}NO_4S_2]^+$: 572.2868; Found:. 572.2869.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.19 (m, 1H), 8.02–8.00 (m, 1H), 7.65–7.56 (m, 2H), 3.93–3.89 (m, 1H), 3.65 (s, 3H), 2.38–2.30 (m, 1H), 2.26–2.14 (m, 3H), 2.05–2.00 (m, 1H), 1.98–1.87 (m, 3H), 1.86–1.74 (m, 4H), 1.71–1.67 (m, 1H), 1.63–1.53 (m, 2H), 1.43–1.36 (m, 3H), 1.33–1.23 (m, 7H), 1.10–1.02 (m, 3H), 1.00 (s, 3H), 0.89 (d, J = 6.4 Hz, 3H), 0.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.9, 166.5, 153.1, 137.1, 128.0, 127.7, 125.6, 122.4, 59.6, 56.7, 56.1, 51.6, 42.8, 40.5, 40.2, 37.3, 35.6, 35.5, 34.6, 31.6, 31.2, 31.1, 28.3, 26.5, 25.9, 24.6, 24.3, 23.6, 21.1, 19.3, 18.4, 12.2.

7.21. benzyl (E)-7-(1-(benzo[d]thiazol-2-ylsulfonyl)cyclopentyl)hept-2-enoate (2l)



2l

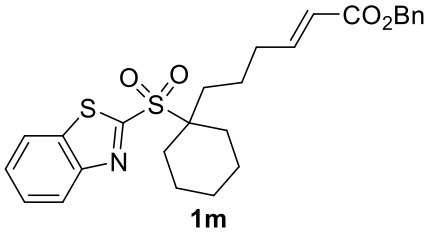
$C_{26}H_{29}NO_4S_2$

M. W. 483.1538 g/mol

Following General Procedure **GP1**, **GP2**, **GP4**, **GP5** to afford the title compound **1l**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{26}H_{30}NO_4S_2]^+$: 484.1616; Found:. 484.1626.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.72–7.52 (m, 2H), 7.44–7.27 (m, 5H), 6.96 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.83 (dd, *J* = 15.9, 1.8 Hz, 1H), 5.16 (s, 2H), 2.70–2.60 (m, 2H), 2.20 (qd, *J* = 7.1, 1.7 Hz, 2H), 1.89 (dd, *J* = 11.5, 4.3 Hz, 2H), 1.84–1.72 (m, 4H), 1.66 (dt, *J* = 10.4, 4.0 Hz, 2H), 1.46 (h, *J* = 6.2 Hz, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 165.0, 153.2, 149.4, 137.3, 136.2, 128.7, 128.3, 128.3, 128.0, 127.6, 125.8, 122.2, 121.4, 74.4, 66.2, 35.7, 32.9, 32.0, 28.5, 26.8, 23.8.

7.22. benzyl (E)-7-(1-(benzo[d]thiazol-2-ylsulfonyl)cyclohexyl)hept-2-enoate (2m)



1m

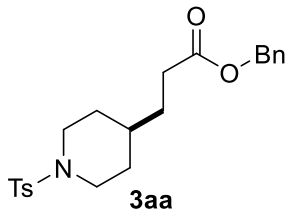
$C_{26}H_{29}NO_4S_2$

M. W. 483.1538 g/mol

Following General Procedure **GP1**, **GP2**, **GP4**, **GP5** to afford the title compound **1l**, white solid.
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{26}H_{30}NO_4S_2]^+$: 484.1616; Found:. 484.1627.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.24 (m, 1H), 8.00–7.98 (m, 1H), 7.63–7.55 (m, 2H), 7.38–7.30 (m, 5H), 7.00 (dt, J = 15.9, 6.9 Hz, 1H), 5.88 (dt, J = 15.9, 1.7 Hz, 1H), 5.17 (s, 2H), 2.23 (qd, J = 7.2, 1.7 Hz, 2H), 2.01–1.98 (m, 4H), 1.95–1.91 (m, 2H), 1.84–1.71 (m, 4H), 1.67–1.62 (m, 1H), 1.39–1.31 (m, 2H), 1.22–1.14 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 164.4, 153.3, 149.0, 137.4, 136.2, 128.7, 128.3, 128.3, 128.0, 127.6, 125.9, 122.3, 121.8, 68.5, 66.2, 32.7, 29.6, 28.7, 24.7, 22.1, 21.5.

8.0 Experimental Details for the Substrate Scope

8.1. benzyl 3-(1-tosylpiperidin-4-yl)propanoate (3aa)



3aa

$C_{22}H_{27}NO_4S$

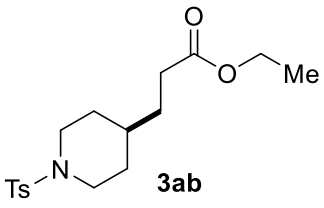
M. W. 401.1661 g/mol

Following General Procedure **GP6** for the title compound **3aa**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by column chromatography on silica gel or pTLC (Hexane / EtOAc = 5:1).to afford **3aa** as colourless oil (60.0 mg, 75%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{22}H_{28}NO_4S]^+$: 402.1739; Found:. 402.1738.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.35–7.27 (m, 7H), 5.06 (s, 2H), 3.75–3.70 (m, 2H), 2.42 (s, 3H), 2.33–2.29 (m, 2H), 2.17–2.10 (m, 2H), 1.70–1.64 (m, 2H), 1.58–1.52 (m, 2H), 1.32–1.21 (m, 2H), 1.17–1.07 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 143.6, 136.0, 133.2, 129.7, 128.7, 128.4, 128.4, 127.9, 66.4, 46.4, 34.6, 31.5, 31.2, 31.0, 21.7.

For 1 mmol scale reaction require **1a** (436.0 mg, 1.0 mmol, 1.0 equiv), **2a** (486.0 mg, 3.0 mmol, 3.0 equiv), HE (505.0 mg, 2.0 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (6.5 mg, 0.01 mmol,

1 mol%), in THF for 12 h at 45 °C. Purification was carried out by column chromatography on silica gel (Hexane / EtOAc = 5:1).to afford **3aa** as colourless oil (241.0 mg, 60%).

8.2. ethyl 3-(1-tosylpiperidin-4-yl)propanoate (3ab)



3ab

$C_{17}H_{25}NO_4S$

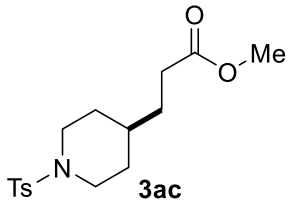
M. W. 339.1504 g/mol

Following General Procedure **GP6** for the title compound **3ab**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2b** (60.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 5:1).to afford **3ab** as colourless oil (37.0 mg, 54%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{26}NO_4S]^+$: 340.1583; Found:. 340.1590.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.09 (q, *J* = 7.3 Hz, 2H), 3.78–3.73 (m, 2H), 2.43 (s, 3H), 2.28–2.25 (m, 2H), 2.23–2.17 (m, 2H), 1.73–1.69 (m, 2H), 1.58–1.52 (m, 3H), 1.35–1.28 (m, 2H), 1.24–1.21 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 143.5, 133.1, 129.7, 127.8, 60.5, 46.4, 34.6, 31.5, 31.2, 31.0, 21.6, 14.3.

8.3. methyl 3-(1-tosylpiperidin-4-yl)propanoate(3ac)



3ac

$C_{16}H_{23}NO_4S$

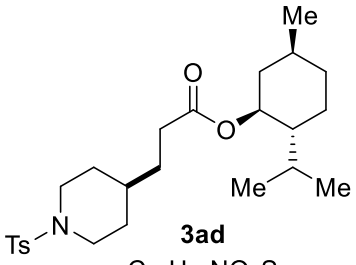
M. W. 325.1348 g/mol

Following General Procedure **GP6** for the title compound **3ab**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2c** (51.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 5:1).to afford **3ab** as colourless oil (33.0 mg, 51%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{24}NO_4S]^+$: 326.1426; Found:. 326.1436.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.78–3.73 (m, 2H), 3.63 (s, 3H), 2.43 (s, 3H), 2.28 (t, *J* = 7.7 Hz, 2H), 2.23–2.16 (m, 2H), 1.74–1.69 (m, 2H), 1.58–1.52 (m, 2H), 1.34–1.24 (m, 2H), 1.22–1.17 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0, 143.6, 133.1, 129.7, 127.9, 51.8, 46.4, 34.6, 31.3, 31.2, 31.0, 21.7.

8.4. (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 3-(1-tosylpiperidin-4-yl)propanoate (3ad)



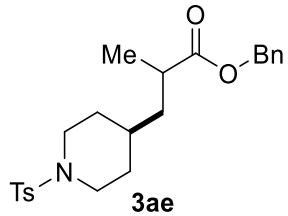
3ad

$C_{25}H_{39}NO_4S$

M. W. 449.2600 g/mol

Following General Procedure **GP6** for the title compound **3ab**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2d** (126.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 5:1).to afford **3ab** as colourless oil (44.0 mg, 49%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{25}H_{40}NO_4S]^+$: 450.2678; Found:. 450.2684.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.31–7.29 (m, 2H), 4.65–4.58 (m, 1H), 3.76–3.72 (m, 2H), 2.41 (s, 3H), 2.26–2.22 (m, 2H), 2.16 (tt, *J* = 11.8, 2.9 Hz, 2H), 1.93–1.88 (m, 1H), 1.81–1.74 (m, 2H), 1.72–1.71 (m, 1H), 1.65–1.61 (m, 2H), 1.53 (q, *J* = 7.3 Hz, 2H), 1.47–1.39 (m, 1H), 1.35–1.23 (m, 4H), 1.18–1.11 (m, 1H), 1.05–0.94 (m, 2H), 0.87–0.85 (m, 3H), 0.84–0.83 (m, 3H), 0.69–0.66 (m, 3H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.2, 143.6, 133.1, 129.7, 127.9, 74.3, 47.1, 46.5, 41.0, 34.7, 34.3, 32.0, 31.5, 31.3, 31.2, 26.3, 23.4, 22.1, 21.7, 20.9, 16.3.

8.5. benzyl 2-methyl-3-(1-tosylpiperidin-4-yl)propanoate (3ae)



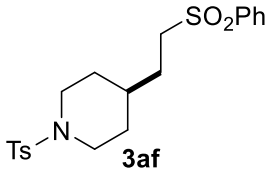
3ae

$C_{23}H_{29}NO_4S$

M. W. 415.1817 g/mol

Following General Procedure **GP6** for the title compound **3ab**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2e** (105.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 5:1).to afford **3ab** as colourless oil (47.0 mg, 56%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{23}H_{30}NO_4S]^+$: 416.1896; Found:. 416.1906.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.34–7.32 (m, 2H), 7.30–7.22 (m, 5H), 5.11 (d, *J* = 12.3 Hz, 1H), 5.02 (d, *J* = 12.2 Hz, 1H), 3.73–3.67 (m, 2H), 2.56–2.49 (m, 1H), 2.45 (s, 3H), 2.09–2.00 (m, 2H), 1.75–1.69 (m, 1H), 1.66–1.60 (m, 2H), 1.29–1.25(m, 1H), 1.24–1.19 (m, 2H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07–1.00 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.4, 143.5, 136.2, 133.2, 129.7, 128.6, 128.4, 128.3, 127.9, 66.2, 46.4(2C), 40.4, 36.9, 33.1, 31.7, 31.2, 21.7, 17.8.

8.6. 4-(2-(phenylsulfonyl)ethyl)-1-tosylpiperidine (3af)



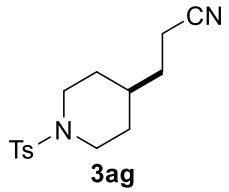
3af

$C_{20}H_{25}NO_4S_2$

M. W. 407.1225 g/mol

Following General Procedure **GP6** for the title compound **3af**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2f** (105.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 5:3).to afford **3af** as colourless oil (49.0 mg, 60%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{20}H_{26}NO_4S_2]^+$: 408.1303; Found:. 408.1311.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89–7.86 (m, 2H), 7.68–7.64 (m, 1H), 7.62–7.54 (m, 4H), 7.32–7.29 (m, 2H), 3.76–3.71 (m, 2H), 3.05–3.01 (m, 2H), 2.42 (s, 3H), 2.21–2.15 (m, 2H), 1.69–1.64 (m, 4H), 1.32–1.21 (m, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.7, 139.1, 134.0, 133.0, 129.8, 129.5, 128.1, 127.8, 53.8, 46.2, 34.1, 31.1, 28.6, 21.7.

8.7. 3-(1-tosylpiperidin-4-yl)propanenitrile (3ag)



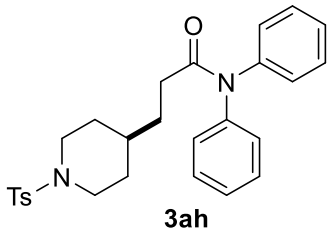
3ag

$C_{15}H_{20}N_2O_2S$

M. W. 292.1245 g/mol

Following General Procedure **GP6** for the title compound **3ag**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2g** (105.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 10:3).to afford **3ag** as white solid (34.0 mg, 58%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{15}H_{21}N_2O_2S]^+$: 293.1324; Found:. 293.1334.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65–7.62 (m, 2H), 7.34–7.32 (m, 2H), 3.83–3.78 (m, 2H), 2.44 (s, 3H), 2.35 (t, J = 7.1 Hz, 2H), 2.26–2.19 (m, 2H), 1.76–1.73 (m, 2H), 1.61–1.58 (m, 2H), 1.39–1.30 (m, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.8, 132.9, 129.8, 127.8, 119.4, 46.3, 34.1, 31.2, 30.9, 21.7, 14.7.

8.8. N,N-diphenyl-3-(1-tosylpiperidin-4-yl)propanamide (3ah)



3ah

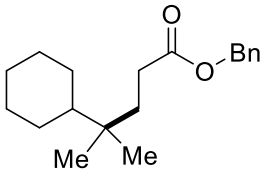
$C_{27}H_{30}N_2O_3S$

M. W. 462.1977 g/mol

Following General Procedure **GP6** for the title compound **3ah**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **2h** (105.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-

$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 10:3).to afford **3ah** as white solid (60.0 mg, 65%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{27}H_{31}N_2O_3S]^+$: 463.2055; Found:. 463.2068.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.51–7.25 (m, 7H), 7.22–7.20 (m, 5H), 3.69–3.67 (m, 2H), 2.41 (s, 3H), 2.22–2.18 (m, 2H), 2.15–2.08 (m, 2H), 1.59–1.57 (m, 3H), 1.21–1.18 (m, 3H), 0.87–0.83 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.9, 143.5, 142.8, 133.1, 130.0, 129.7, 129.0, 127.8, 126.4, 46.4, 34.6, 32.4, 31.6, 31.2, 21.6.

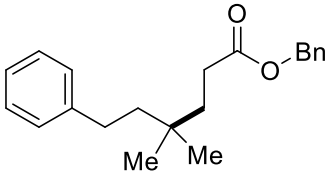
8.9. benzyl 4-cyclohexyl-4-methylpentanoate (3fa)



3fa
$C_{19}H_{28}O_2$
M. W. 288.2089 g/mol

Following General Procedure **GP6** for the title compound **3fa**, by using **1f** (65.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3fa** as colourless oil (37.0 mg, 65%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{29}O_2]^+$: 289.2168; Found:. 289.2181.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.11 (s, 2H), 2.31–2.27 (m, 2H), 1.78–1.73 (m, 2H), 1.70–1.65 (m, 2H), 1.61–1.59 (m, 3H), 1.19–1.09 (m, 3H), 1.03–0.93 (m, 3H), 0.80 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.6, 136.2, 128.7, 128.4, 128.3, 66.3, 46.0, 35.1, 34.7, 29.5, 27.3, 27.2, 26.8, 24.6.

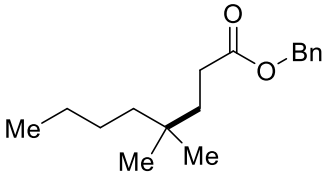
8.10. benzyl 4,4-dimethyl-6-phenylhexanoate (3ga)



3ga
$C_{21}H_{26}O_2$
M. W. 310.1933 g/mol

Following General Procedure **GP6** for the title compound **3ga**, by using **1g** (70.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ga** as colourless oil (32.0 mg, 52%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{21}H_{27}O_2]^+$: 311.2011; Found:. 311.2024.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 5H), 7.19–7.15 (m, 2H), 7.09–7.05 (m, 3H), 5.02 (s, 2H), 2.47–2.43 (m, 2H), 2.28–2.24 (m, 2H), 1.58–1.54 (m, 2H), 1.42–1.37 (m, 2H), 0.84 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.3, 143.2, 136.1, 128.7, 128.5, 128.4(2C), 128.4, 125.8, 66.4, 44.2, 36.4, 32.8, 30.7, 29.7, 26.8.

8.11. benzyl 4,4-dimethyloctanoate (3ha)



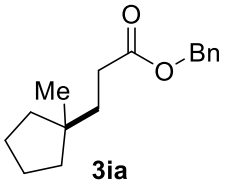
3ha

$C_{17}H_{26}O_2$

M. W. 262.1933 g/mol

Following General Procedure **GP6** for the title compound **3ha**, by using **1h** (60.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ha** as colourless oil (33.0 mg, 62%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{27}O_2]^+$: 263.2011; Found:. 263.2011.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 5H), 5.11 (s, 2H), 2.32–2.28 (m, 2H), 1.58–1.54 (m, 2H), 1.27–1.23 (m, 2H), 1.21–1.13 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.84 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.5, 136.2, 128.7, 128.4, 128.3, 66.3, 41.6, 36.6, 32.5, 29.8, 27.0, 26.3, 23.7, 14.3.

8.12. benzyl 3-(1-methylcyclopentyl)propanoate (3ia)



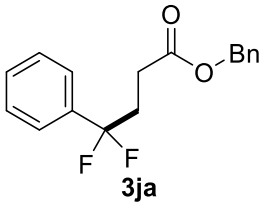
3ia

$C_{16}H_{22}O_2$

M. W. 246.1620 g/mol

Following General Procedure **GP6** for the title compound **3ia**, by using **1i** (56.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ia** as colourless oil (33.0 mg, 68%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{23}O_2]^+$: 247.1698; Found:. 247.1711.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.30 (m, 5H), 5.11 (s, 2H), 2.38–2.33 (m, 2H), 1.69–1.65 (m, 2H), 1.63–1.58 (m, 4H), 1.39–1.29 (m, 4H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.5, 136.2, 128.7, 128.4, 128.3, 66.3, 41.8, 39.3, 37.1, 31.0, 25.7, 24.5.

8.13. benzyl 4,4-difluoro-4-phenylbutanoate (3ja)



3ja

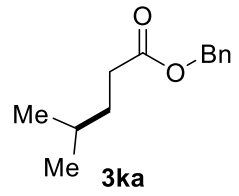
$C_{17}H_{16}F_2O_2$

M. W. 290.1118 g/mol

Following General Procedure **GP6** for the title compound **3ja**, by using **1j** (65.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-

$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ja** as colourless oil (26.0 mg, 45%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}F_2O_2]^+$: 291.1197; Found:. 291.1190.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.44–7.39 (m, 3H), 7.37–7.31 (m, 5H), 5.10 (s, 2H), 2.60–2.46 (m, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, δ 136.7 (t, J = 26.3 Hz), 135.7, 130.0, 128.7, 128.6, 128.5, 128.4, 125.0 (t, J = 6.2 Hz), 122.3 (t, J = 242.5 Hz), 66.7, 34.4 (t, J = 28.4 Hz), 27.9 (t, J = 4.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -96.9 (d, *J* = 32.3 Hz).

8.14. benzyl 4-methylpentanoate (3ka)

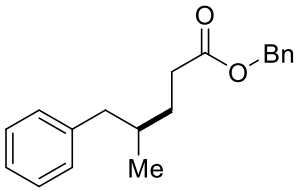


3ka

$C_{13}H_{18}O_2$
M. W. 206.1307 g/mol

Following General Procedure **GP6** for the title compound **3ka**, by using **1k** (48.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ka** as colourless oil (25.0 mg, 61%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{13}H_{19}O_2]^+$: 207.1385; Found:. 207.1383.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 5.10 (s, 2H), 2.37–2.33 (m, 2H), 1.56–1.53 (m, 3H), 0.88 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.1, 136.3, 129.9, 128.7, 128.3, 66.3, 33.9, 32.6, 27.8, 22.4.

8.15. benzyl (R)-4-methyl-5-phenylpentanoate (3la)

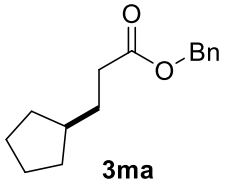


3la

$C_{19}H_{22}O_2$
M. W. 282.1620 g/mol

Following General Procedure **GP6** for the title compound **3la**, by using **1l** (64.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3la** as colourless oil (32.0 mg, 57%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{23}O_2]^+$: 283.1698; Found:. 283.1681.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 7.28–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.13–7.11 (m, 2H), 5.11 (s, 2H), 2.66–2.62 (m, 1H), 2.45–2.36 (m, 3H), 1.80–1.71 (m, 2H), 1.55–1.48 (m, 1H), 0.86 (d, *J* = 6.4 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.8, 141.0, 136.2, 129.3, 128.7, 128.5, 128.4, 128.3, 125.9, 66.3, 43.5, 34.7, 32.3, 31.7, 19.1.

8.16. benzyl 3-cyclopentylpropanoate (3ma)



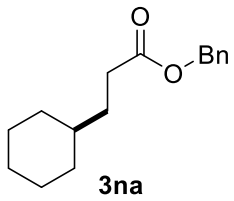
3ma

$C_{15}H_{20}O_2$

M. W. 232.1463 g/mol

Following General Procedure **GP6** for the title compound **3ma**, by using **1m** (54.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ma** as colourless oil (26.0 mg, 56%).
HRMS (ESI): m/z [M+H]$^+$ Calculated for $[C_{15}H_{21}O_2]^+$: 233.1542; Found:. 233.1558.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 5H), 5.11 (s, 2H), 2.39–2.35 (m, 2H), 1.79–1.71 (m, 3H), 1.69–1.64 (m, 2H), 1.62–1.58 (m, 3H), 1.53–1.48 (m, 2H), 1.10–1.06 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0, 136.2, 128.7, 128.3, 128.3, 66.2, 39.8, 33.8, 32.5, 31.2, 25.2.

8.17. benzyl 3-cyclohexylpropanoate (3na)



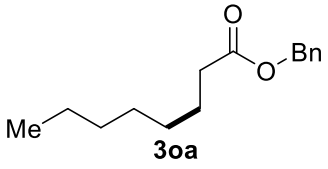
3na

$C_{16}H_{22}O_2$

M. W. 246.1620 g/mol

Following General Procedure **GP6** for the title compound **3na**, by using **1n** (56.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3na** as colourless oil (30.0 mg, 60%).
HRMS (ESI): m/z [M-H]$^+$ Calculated for $[C_{16}H_{21}O_2]^+$: 245.1542; Found:. 245.1534.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.11 (s, 2H), 2.38–2.34 (m, 2H), 1.70–1.65 (m, 4H), 1.54–1.51 (m, 2H), 1.19–1.13 (m, 4H), 0.89–0.83 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.2, 136.2, 128.7, 128.3, 128.3, 66.2, 37.3, 33.1, 32.5, 32.1, 26.6, 26.3.

8.18. benzyl octanoate (3oa)



3oa

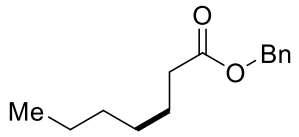
$C_{15}H_{22}O_2$

M. W. 234.1620 g/mol

Following General Procedure **GP6** for the title compound **3oa**, by using **1o** (54.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3oa** as colourless oil (24.0 mg, 50%).
HRMS (ESI): m/z [M+H]$^+$ Calculated for $[C_{15}H_{23}O_2]^+$: 235.1698; Found: 235.1698.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 5H), 5.11 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.66–1.60 (m, 3H), 1.33–1.27 (m, 7H), 0.89–0.86 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 136.3, 128.7, 128.3 (2C), 66.2, 34.5, 31.6, 28.9, 25.1, 22.6, 14.2.

8.19. benzyl heptanoate (3pa)



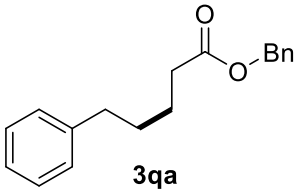
3pa

$C_{14}H_{20}O_2$

M. W. 220.1463 g/mol

Following General Procedure **GP6** for the title compound **3pa**, by using **1p** (51.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3pa** as colourless oil (23.0 mg, 52%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{21}O_2]^+$: 221.1542; Found:. 221.1538.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.11 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.66–1.62 (m, 2H), 1.33–1.27 (m, 6H), 0.90–0.86 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 136.3, 128.7, 128.3(2C), 66.2, 34.5, 31.6, 28.9, 25.1, 22.6, 14.2.

8.20. benzyl 5-phenylpentanoate (3qa)



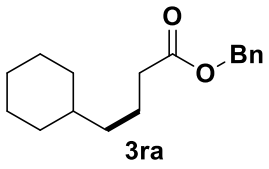
3qa

$C_{18}H_{20}O_2$

M. W. 268.1463 g/mol

Following General Procedure **GP6** for the title compound **3qa**, by using **1q** (61.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-$Ir(ppy)_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3qa** as colourless oil (20.0 mg, 65%).
HRMS (ESI): m/z $[M-H]^+$ Calculated for $[C_{18}H_{19}O_2]^+$: 267.1385; Found:. 267.1391.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 7.29–7.27 (m, 1H), 7.26–7.24 (m, 1H), 7.20–7.14 (m, 3H), 5.11 (s, 2H), 2.62 (t, J = 7.3 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.72–1.62 (m, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 142.3, 136.2, 130.1, 128.7, 128.5, 128.5, 128.3, 125.9, 66.3, 35.7, 34.3, 31.0, 24.7.

8.21. benzyl 4-cyclohexylbutanoate (3ra)



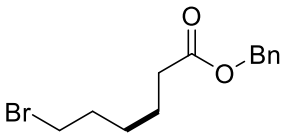
3ra

$C_{17}H_{24}O_2$

M. W. 260.1776 g/mol

Following General Procedure **GP6** for the title compound **3ra**, by using **1r** (59.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ra** as colourless oil (20.0 mg, 38%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{25}O_2]^+$: 261.1855; Found:. 261.1849.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.11 (s, 2H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.70–1.62 (m, 7H), 1.23–1.13 (m, 6H), 0.90–0.81 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9, 136.3, 128.7, 128.3, 128.3, 66.2, 37.5, 37.0, 34.8, 33.4, 26.8, 26.5, 22.5.

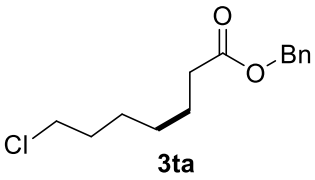
8.22. benzyl 6-bromohexanoate (3sa)



3sa
$C_{13}H_{17}BrO_2$
M. W. 284.0412 g/mol

Following General Procedure **GP6** for the title compound **3sa**, by using **1s** (64.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3sa** as colourless oil (27.0 mg, 48%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{13}H_{18}BrO_2]^+$: 285.0490; Found:. 285.0484.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32(m, 5H), 5.12 (s, 2H), 3.39 (t, J = 6.8 Hz, 2H), 2.38 (t, J = 7.5 Hz, 2H), 1.90–1.83 (m, 2H), 1.72–1.64 (m, 2H), 1.51–1.45 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 136.1, 128.7, 128.5, 128.4, 66.4, 34.2, 33.6, 32.5, 27.8, 24.2.

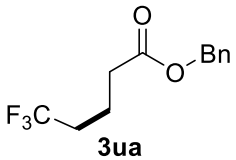
8.23. benzyl 8-chlorooctanoate (3ta)



3ta
$C_{14}H_{19}ClO_2$
M. W. 254.1074 g/mol

Following General Procedure **GP6** for the title compound **3ta**, by using **1t** (61.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ta** as colourless oil (24.0 mg, 45%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{20}ClO_2]^+$: 255.1152; Found:. 255.1163.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 5H), 5.10 (s, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.78–1.71 (m, 2H), 1.69–1.61 (m, 2H), 1.47–1.39 (m, 2H), 1.36–1.30 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 136.2, 128.7, 128.4 (2C), 66.3, 45.1, 34.3, 32.5, 28.5, 26.6, 24.9.

8.24. benzyl 5,5,5-trifluoropentanoate (3ua)



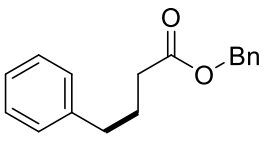
3ua

$C_{12}H_{13}F_3O_2$

M. W. 246.0868 g/mol

Following General Procedure **GP6** for the title compound **3ua**, by using **1u** (56.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3ua** as colourless oil (21.0 mg, 41%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{12}H_{14}F_3O_2]^+$: 247.0946; Found:. 247.0953.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.32 (m, 5H), 5.13 (s, 2H), 2.46 (t, J = 7.3 Hz, 2H), 2.19–2.09 (m, 2H), 1.95–1.88 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.4, 135.9, 128.8, 128.5, 128.5, 128.4, 66.6, 33.2, 32.9, 17.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -66.29.

8.25. benzyl 4-phenylbutanoate (3va)



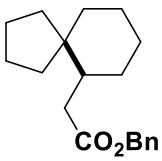
3va

$C_{17}H_{18}O_2$

M. W. 254.1307 g/mol

Following General Procedure **GP6** for the title compound **3va**, by using **1v** (61.0 mg, 0.2 mmol, 1.0 equiv), **2a** (97.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3va** as colourless oil (27.0 mg, 53%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{19}O_2]^+$: 255.1385; Found:. 255.1393.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 5H), 7.30–7.26 (m, 3H), 7.21–7.14 (m, 2H), 5.11 (s, 2H), 2.66–2.63 (m, 2H), 2.38 (t, J = 7.5 Hz, 2H), 2.02–1.94 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.4, 141.4, 136.1, 128.7, 128.6, 128.5, 128.3 (2C), 126.1, 66.3, 35.2, 33.7, 26.6.

8.26. benzyl 2-(spiro[4.5]decan-6-yl)acetate(3l')



3l'

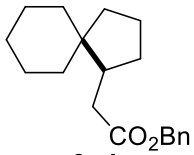
$C_{19}H_{26}O_2$

M. W. 286.1933 g/mol

Following General Procedure **GP7** for the title compound **3l'**, by using **2l** (48.3 mg, 0.1 mmol, 1.0 equiv), HE (51.0 mg, 0.2 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (0.7 mg, 0.001 mmol, 1 mol%), in THF for 24 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3l'** as colourless oil (15.0 mg, 54%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{27}O_2]^+$: 287.2011; Found:. 287.2010.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5H), 5.10 (s, 2H), 2.46 (dd, J = 15.0, 3.3 Hz, 1H), 2.14 (dd, J = 15.0, 10.6 Hz, 1H), 1.84 (tt, J = 10.5, 3.3 Hz, 1H), 1.62–1.58 (m, 1H), 1.54–1.49 (m, 4H), 1.46–1.39 (m, 3H), 1.38–1.21 (m, 7H), 1.18–1.10 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.2, 136.3, 128.7, 128.3, 128.3, 66.2, 45.5, 42.2, 38.6, 36.2, 32.9, 29.5, 25.9, 25.5, 25.3, 24.6, 23.2.

8.27. benzyl 2-(spiro[4.5]decan-1-yl)acetate (3m')



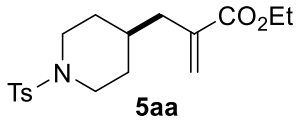
3m'

$C_{19}H_{26}O_2$

M. W. 286.1933 g/mol

Following General Procedure **GP7** for the title compound **3m'**, by using **2m** (48.3 mg, 0.1 mmol, 1.0 equiv), HE (51.0 mg, 0.2 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (0.7 mg, 0.001 mmol, 1 mol%), in THF for 24 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **3m'** as colourless oil (17.0 mg, 60%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{27}O_2]^+$: 287.2011; Found:. 287.2010.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 5H), 5.10 (s, 2H), 2.44 (dd, J = 14.6, 3.6 Hz, 1H), 2.11 (dd, J = 14.7, 10.6 Hz, 1H), 1.90–1.82 (m, 2H), 1.74–1.67 (m, 1H), 1.60–1.48 (m, 6H), 1.36–1.26 (m, 6H), 1.14–1.07 (m, 1H), 1.00 (td, J = 12.6, 3.9 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.2, 136.2, 128.6, 128.3, 128.3, 66.2, 46.6, 44.3, 37.4, 35.3, 34.9, 30.4, 30.2, 26.6, 24.0, 22.7, 21.5.

8.28. ethyl 2-((1-tosylpiperidin-4-yl)methyl)acrylate (5aa)



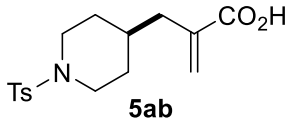
5aa

$C_{18}H_{25}NO_4S$

M. W. 351.1504 g/mol

Following General Procedure **GP6** for the title compound **5aa**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 7:3).to afford **5aa** as colourless oil (42.0 mg, 60%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{18}H_{26}NO_4S]^+$: 352.1583; Found:. 352.1587.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.31–7.29 (m, 2H), 6.15 (d, *J* = 1.7 Hz, 1H), 5.47 (d, *J* = 1.4 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.77–3.72 (m, 2H), 2.42 (s, 3H), 2.21–2.19 (m, 3H), 2.18–2.14 (m, 2H), 1.72–1.67 (m, 2H), 1.44–1.34 (m, 1H), 1.32–1.29 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 143.5, 138.3, 133.1, 129.7, 127.8, 126.7, 60.8, 46.5, 38.9, 34.2, 31.3, 21.6, 14.3.

8.29. 2-((1-tosylpiperidin-4-yl)methyl)acrylic acid (5ab)



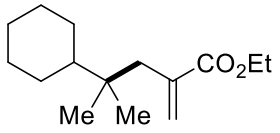
5ab

$C_{16}H_{21}NO_4S$

M. W. 323.1191 g/mol

Following General Procedure **GP6** for the title compound **5ab**, by using **1a** (87.0 mg, 0.2 mmol, 1.0 equiv), **4b** (135.6 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 3:7).to afford **5ab** as white solid (42.0 mg, 65%).
HRMS (ESI): m/z [M+H]$^+$ Calculated for [$C_{16}H_{22}NO_4S$]$^+$: 324.1270; Found:. 324.1277.
^{1}H NMR (400 MHz, CDCl$_3$) δ 10.53 (s, broad, 1H)7.63–7.61 (m, 2H), 7.32–7.30 (m, 2H), 6.29 (d, J = 1.4 Hz, 1H), 5.61 (d, J = 1.3 Hz, 1H), 3.77–3.75 (m, 2H), 2.43 (s, 3H), 2.21–2.20 (m, 2H), 2.18–2.15 (m, 1H) 1.72–1.69 (m, 3H), 1.43–1.40 (m, 1H), 1.33–1.29 (m, 2H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.6, 143.6, 137.2, 133.1, 129.7, 129.3, 127.9, 46.5, 38.7, 34.1, 31.3, 21.7.

8.30. ethyl 4-cyclohexyl-4-methyl-2-methylenepentanoate (5fa)



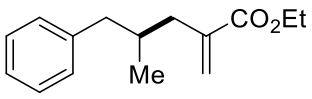
5fa

$C_{15}H_{26}O_2$

M. W. 238.1933 g/mol

Following General Procedure **GP6** for the title compound **5fa**, by using **1f** (65.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5fa** as colourless oil (34.0 mg, 71%).
HRMS (ESI): m/z [M+H]$^+$ Calculated for [$C_{15}H_{27}O_2$]$^+$: 239.2011; Found:. 239.2034.
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.15 (d, *J* = 1.8 Hz, 1H), 5.41 (d, *J* = 1.7 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 2H), 2.31 (s, 2H), 1.80–1.74 (m, 4H), 1.67–1.60 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21–1.13 (m, 2H), 1.10–1.05 (m, 1H), 1.01–0.94 (m, 2H), 0.75 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 168.7, 139.5, 126.9, 60.8, 47.3, 40.3, 36.4, 27.5, 27.3, 26.9, 24.1, 14.3.

8.31. ethyl 4-methyl-2-methylene-5-phenylpentanoate (5la)



5la

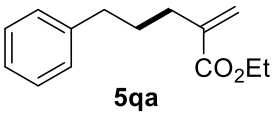
$C_{15}H_{20}O_2$

M. W. 232.1463 g/mol

Following General Procedure **GP6** for the title compound **5la**, by using **1l** (64.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5la** as colourless oil (32.0 mg, 69%).
HRMS (ESI): m/z [M+H]$^+$ Calculated for [$C_{15}H_{21}O_2$]$^+$: 233.1542; Found:. 233.1559.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.20–7.14 (m, 3H), 6.19 (d, *J* = 1.7 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 4.23–4.15 (m, 2H), 2.71–2.66 (m, 1H), 2.45–2.35 (m, 2H), 2.13–2.08 (m, 1H), 2.04–1.95 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.5, 141.1, 139.8, 129.3, 128.2, 126.0, 125.9, 60.7, 43.5, 39.5, 34.1, 19.1, 14.3.

8.32. ethyl 2-methylene-5-phenylpentanoate (5qa)



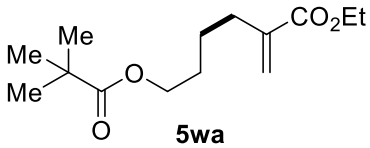
5qa

$C_{14}H_{18}O_2$

M. W. 218.1307 g/mol

Following General Procedure **GP6** for the title compound **5qa**, by using **1q** (61.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5qa** as colourless oil (26.0 mg, 60%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{19}O_2]^+$: 219.1385; Found:. 219.1377.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.20–7.16 (m, 3H), 6.15 (d, J = 1.5 Hz, 1H), 5.53–5.52 (m, 1H), 4.20 (q, J = 6.9 Hz, 2H), 2.67–2.63 (m, 2H), 2.37–2.33 (m, 2H), 1.85–1.77 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.4, 142.3, 140.8, 128.6, 128.5, 125.9, 124.7, 60.8, 35.6, 31.6, 30.2, 14.4.

8.33. ethyl 2-methylene-6-(pivaloyloxy)hexanoate (5wa)



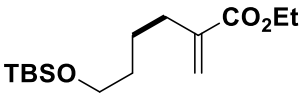
5wa

$C_{14}H_{24}O_4$

M. W. 256.1675 g/mol

Following General Procedure **GP6** for the title compound **5wa**, by using **1w** (68.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 °C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5wa** as colourless oil (31.0 mg, 60%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{14}H_{25}O_4]^+$: 257.1753; Found:. 257.1753.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (d, J = 1.5 Hz, 1H), 5.52 (q, J = 1.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 6.4 Hz, 2H), 2.34 (t, J = 7.7 Hz, 2H), 1.68–1.62 (m, 2H), 1.57–1.52 (m, 2H), 1.30 (t, J = 7.3 Hz, 3H), 1.19 (s, 9H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.8, 167.3, 140.6, 124.7, 64.2, 60.8, 38.9, 31.6, 28.1, 27.4, 26.6, 14.6.

8.34. ethyl 6-((tert-butyldimethylsilyl)oxy)-2-methylenehexanoate (5xa)



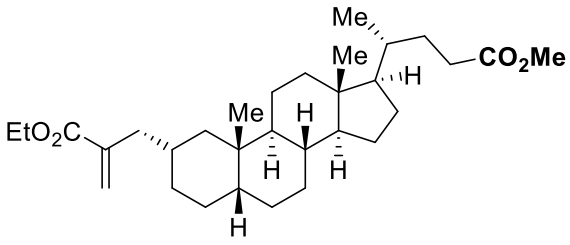
5xa

$C_{15}H_{30}O_3Si$

M. W. 286.4870 g/mol

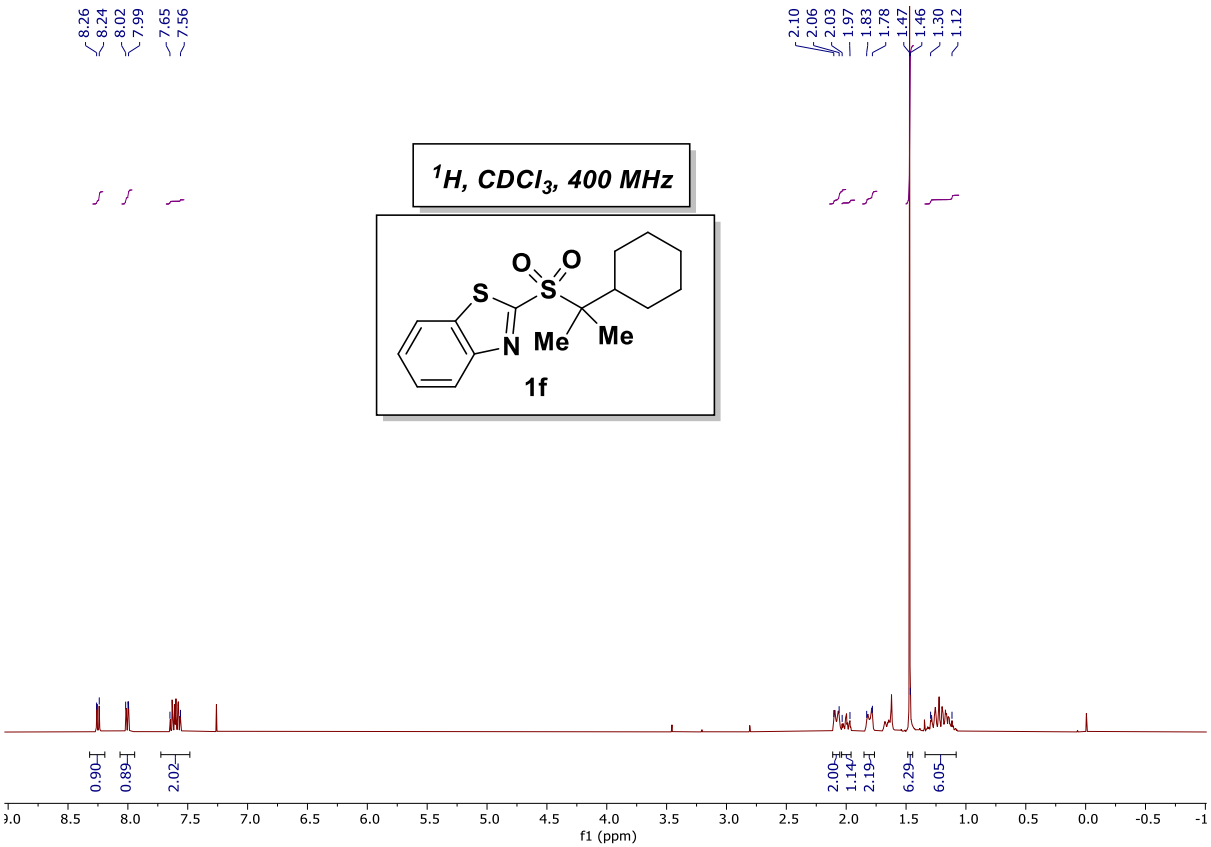
Following General Procedure **GP6** for the title compound **5xa**, by using **1x** (74.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5xa** as colourless oil (33.0 mg, 58%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{15}H_{31}O_3Si]^+$: 287.2042; Found:. 287.2046.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, J = 1.5 Hz, 1H), 5.52 (q, J = 1.6 Hz, 1H), 4.20 (q, J = 7.0 Hz, 2H), 3.62 (t, J = 5.9 Hz, 2H), 2.31 (t, J = 6.4 Hz, 2H), 1.54–1.51 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.4, 141.0, 124.4, 63.1, 60.6, 32.4, 31.6, 26.0, 24.7, 18.4, 14.3, -5.2.

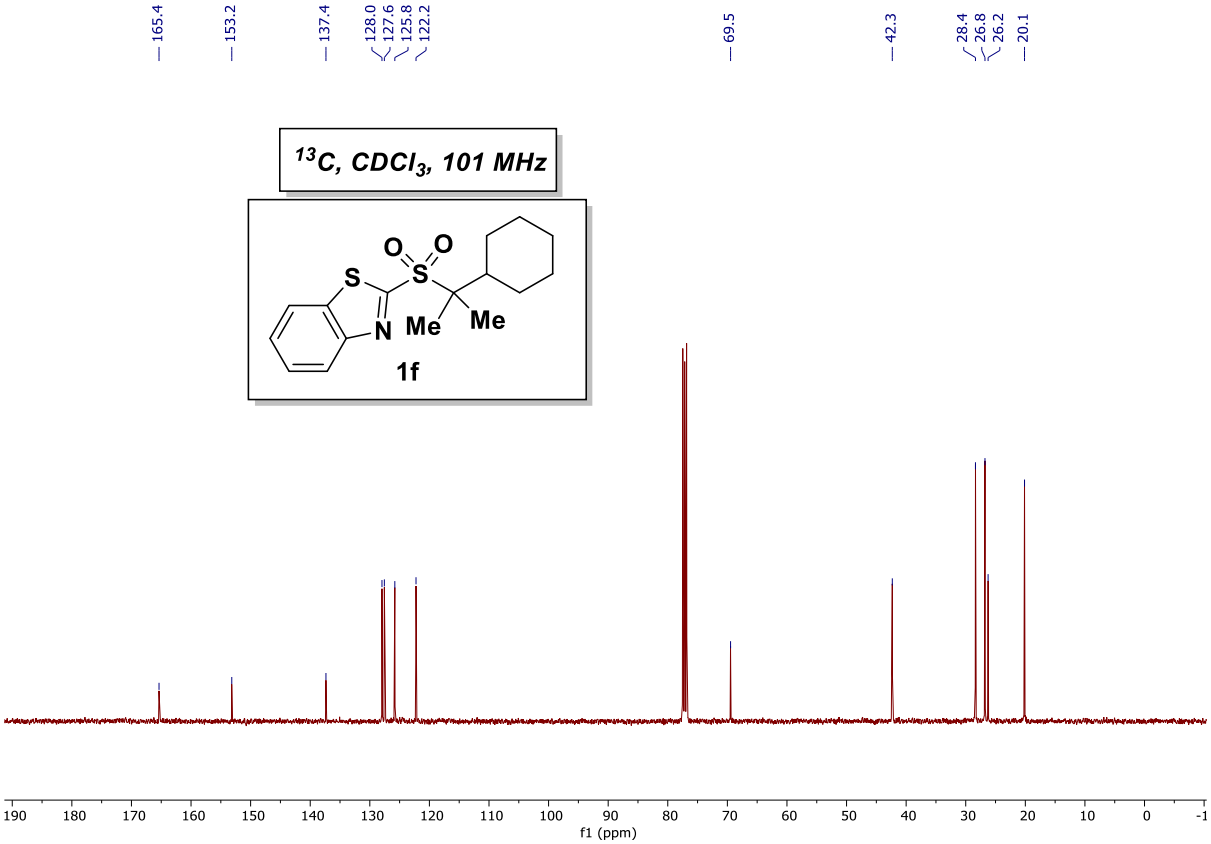
8.35. methyl (R)-4-((2S,5S,8R,9S,10S,13R,14S,17R)-2-(2-(ethoxycarbonyl)allyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (5ya)

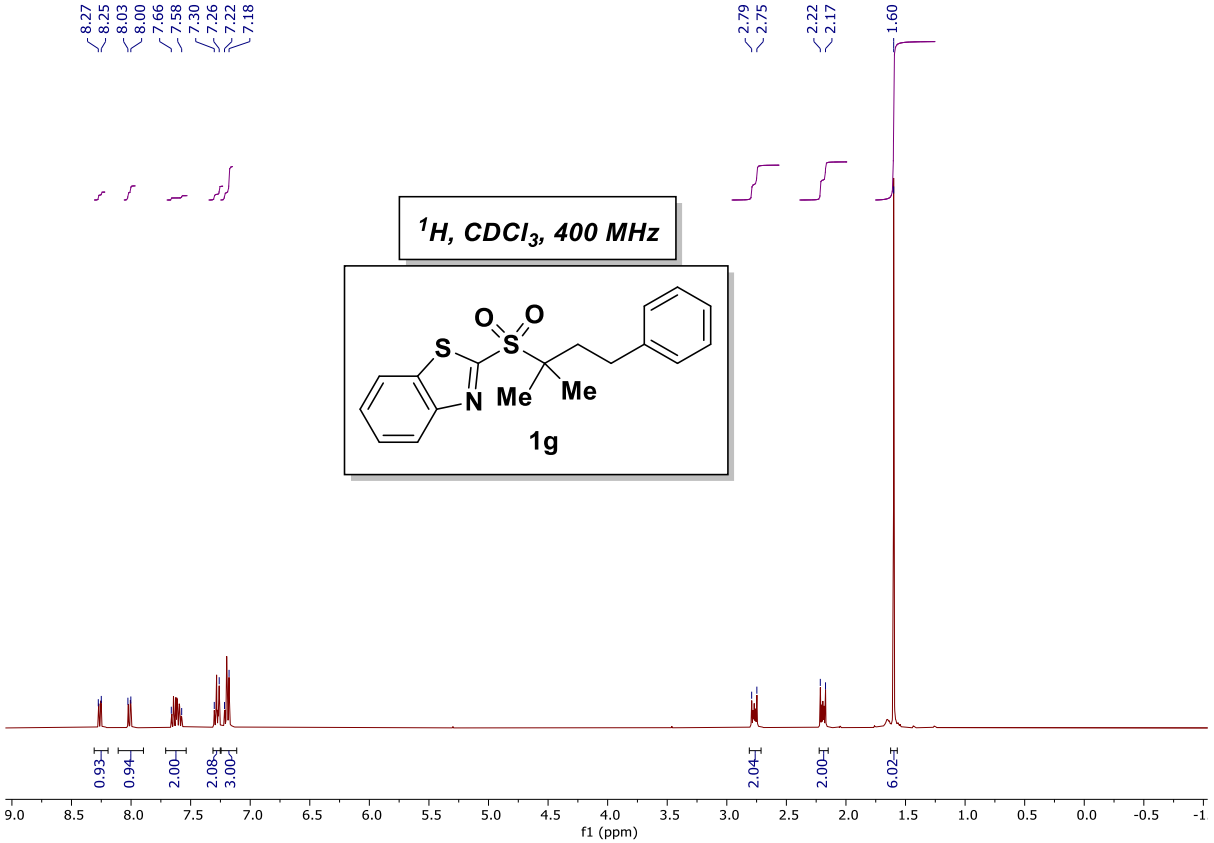


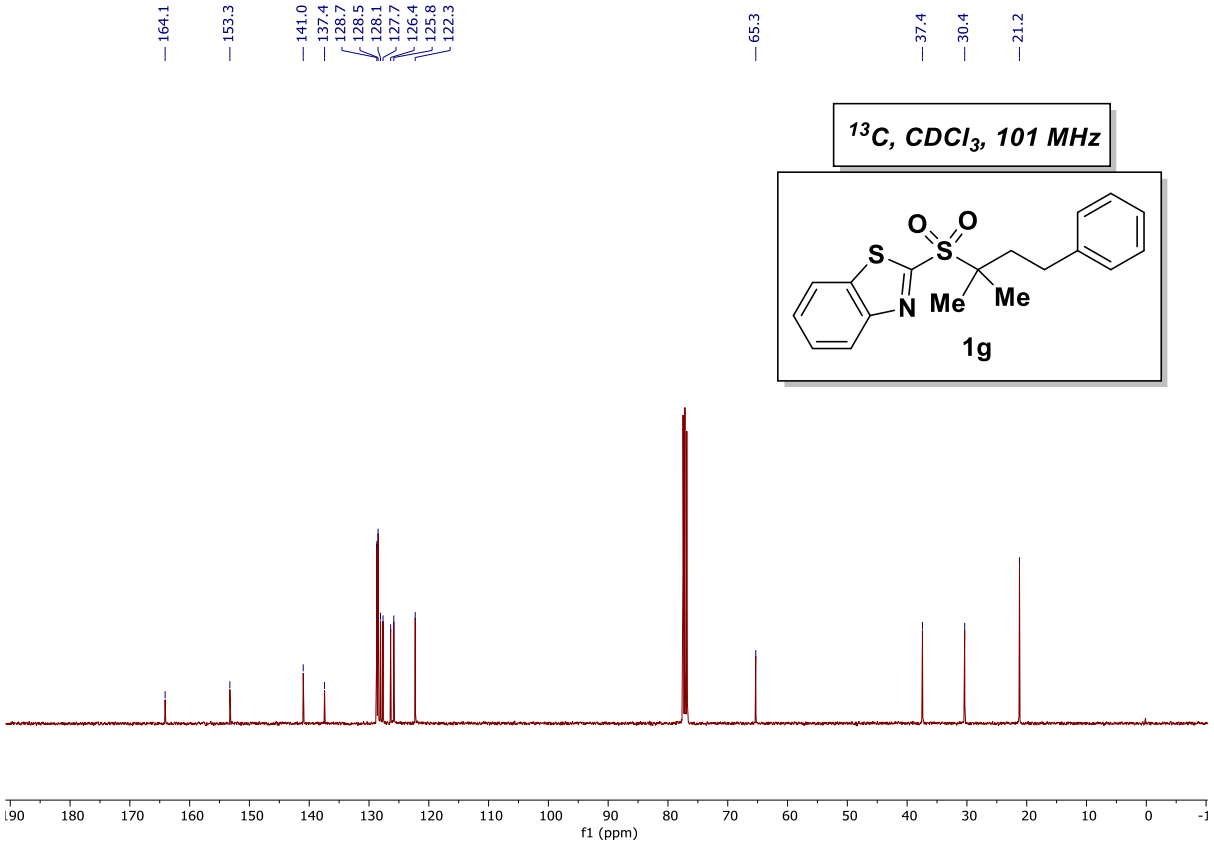
5ya
$C_{31}H_{50}O_4$
M. W. 486.3709 g/mol

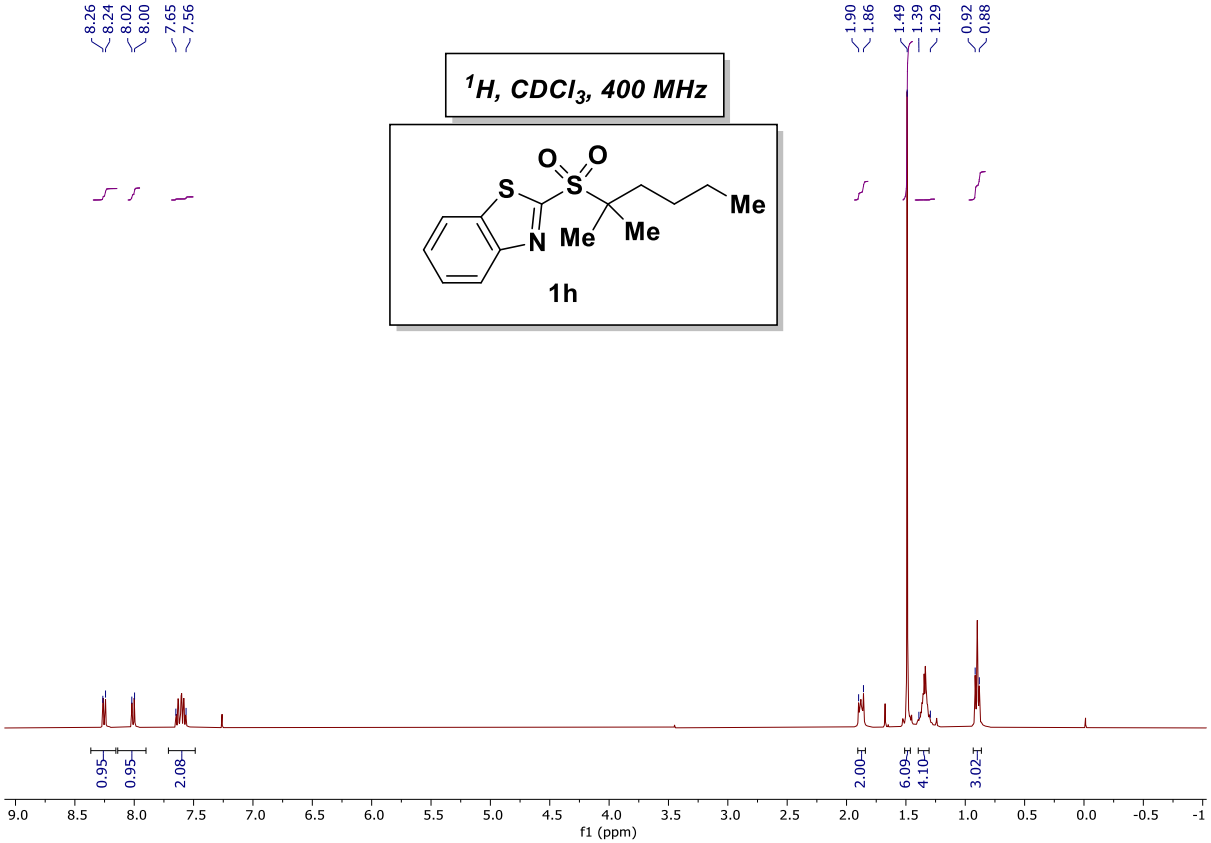
Following General Procedure **GP6** for the title compound **5ya**, by using **1y** (114.0 mg, 0.2 mmol, 1.0 equiv), **4a** (152.0 mg, 0.6 mmol, 3.0 equiv), HE (101.0 mg, 0.4 mmol, 2.0 equiv) and [*fac*-Ir(ppy)$_3$] (1.3 mg, 0.002 mmol, 1 mol%), in THF for 12 h at 45 ^{o}C. Purification was carried out by PTLC (Hexane/EtOAc = 40:1).to afford **5ya** as colourless oil (63.0 mg, 65%).
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{31}H_{51}O_4]^+$: 487.3787; Found:. 487.3788.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (dd, J = 5.2, 1.8 Hz, 1H), 5.46 (s, 1H), 4.19 (q, J = 7.0 Hz, 2H), 3.66 (s, 3H), 2.40–2.37 (m, 2H), 2.36–2.31 (m, 1H), 2.23–2.18 (m, 1H), 2.00–1.92 (m, 3H), 1.86–1.75 (m, 3H), 1.53–1.45 (m, 4H), 1.42–1.33 (m, 7H), 1.29 (t, J = 7.1 Hz, 3H), 1.17–1.01 (m, 10H), 0.93 (s, 3H), 0.90 (d, J = 6.4 Hz, 3H), 0.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.9, 167.7, 140.5, 125.4, 60.6, 56.7, 56.0, 51.6, 42.8, 40.3, 40.1, 37.4, 35.8, 35.5, 35.5, 34.3, 32.4, 31.1, 31.1, 30.0, 29.8, 28.3, 27.3, 26.4, 24.3, 24.3, 24.1, 21.0, 18.4, 14.3, 12.1.

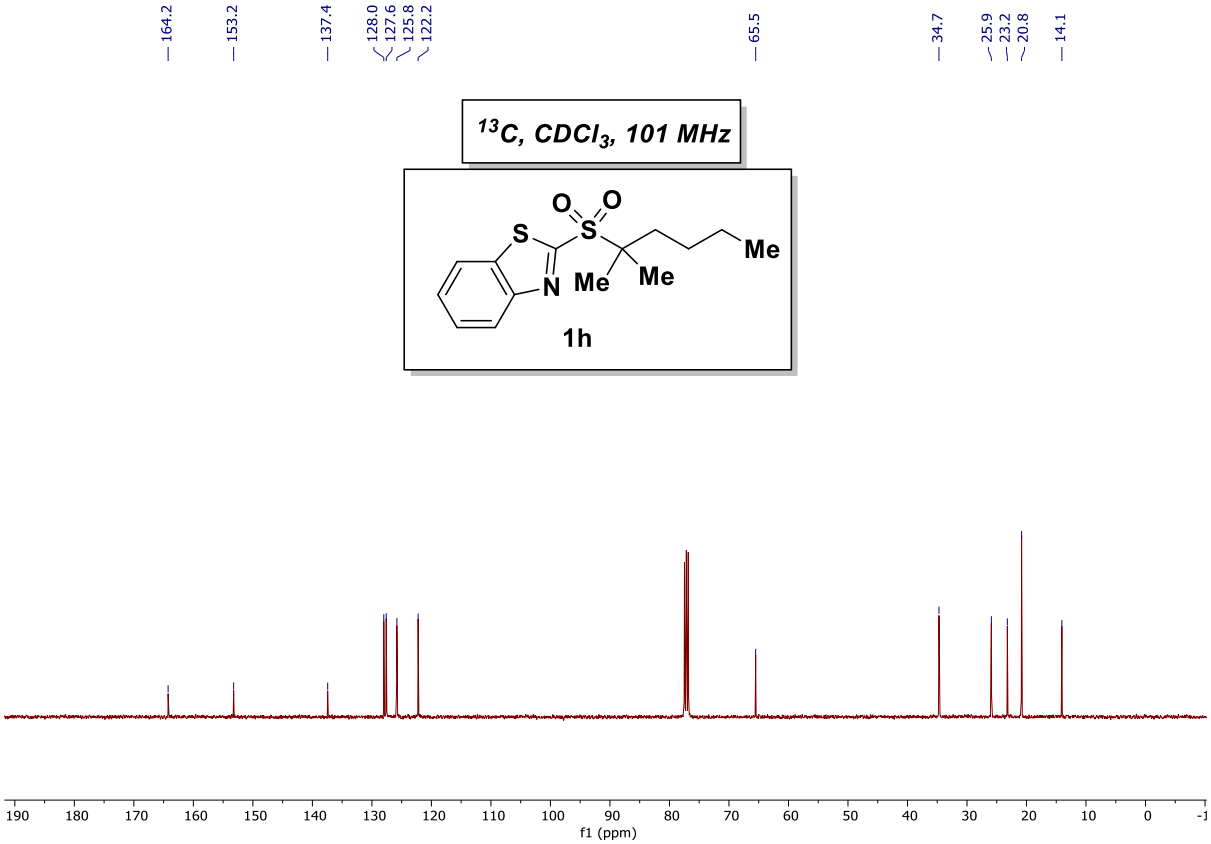

8.26
8.24
8.02
7.99
7.65
7.56
2.10
2.06
2.03
1.97
1.83
1.78
1.47
1.46
1.30
1.12
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
N
Me
Me
1f
0.90
0.89
2.02
2.00
1.14
2.19
6.29
6.05
f1 (ppm)

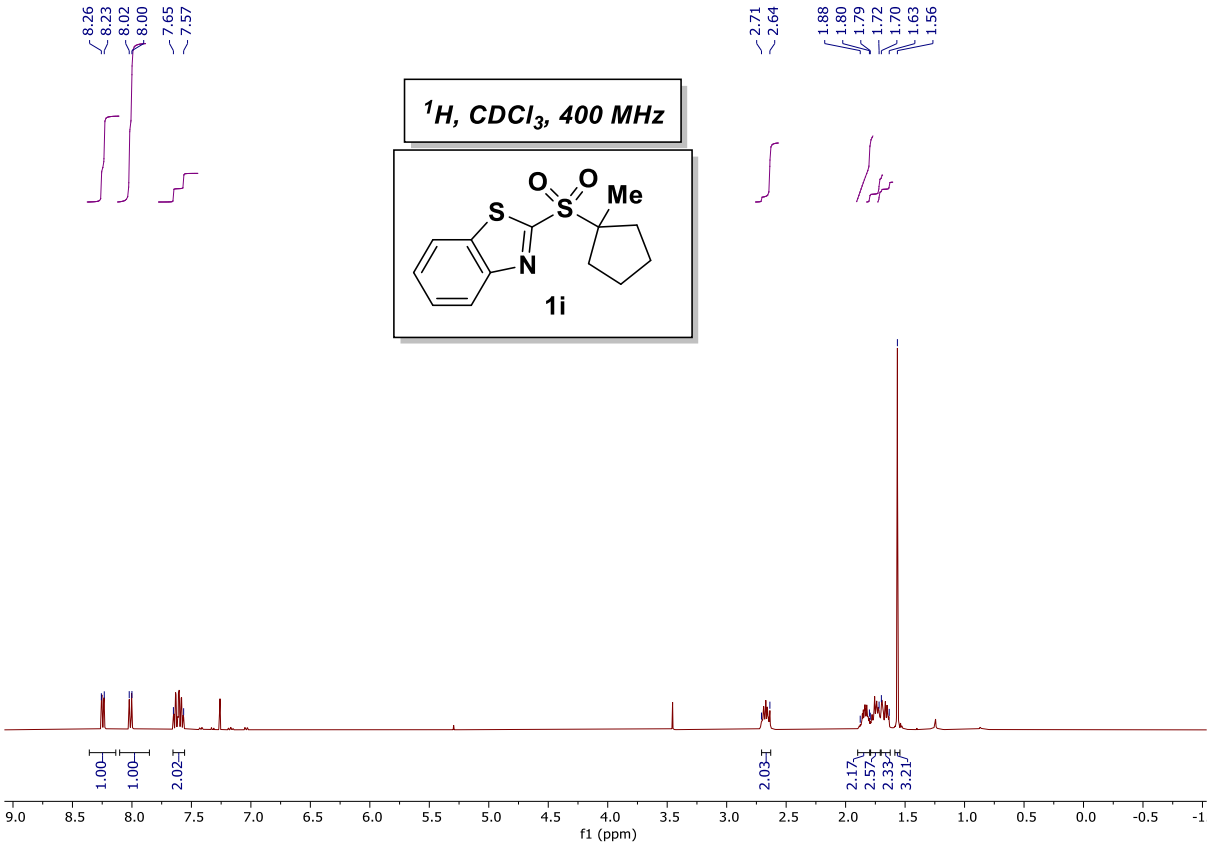

165.4
153.2
137.4
128.0
127.6
125.8
122.2
69.5
42.3
28.4
26.8
26.2
20.1
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
N
Me
Me
1f
f1 (ppm)

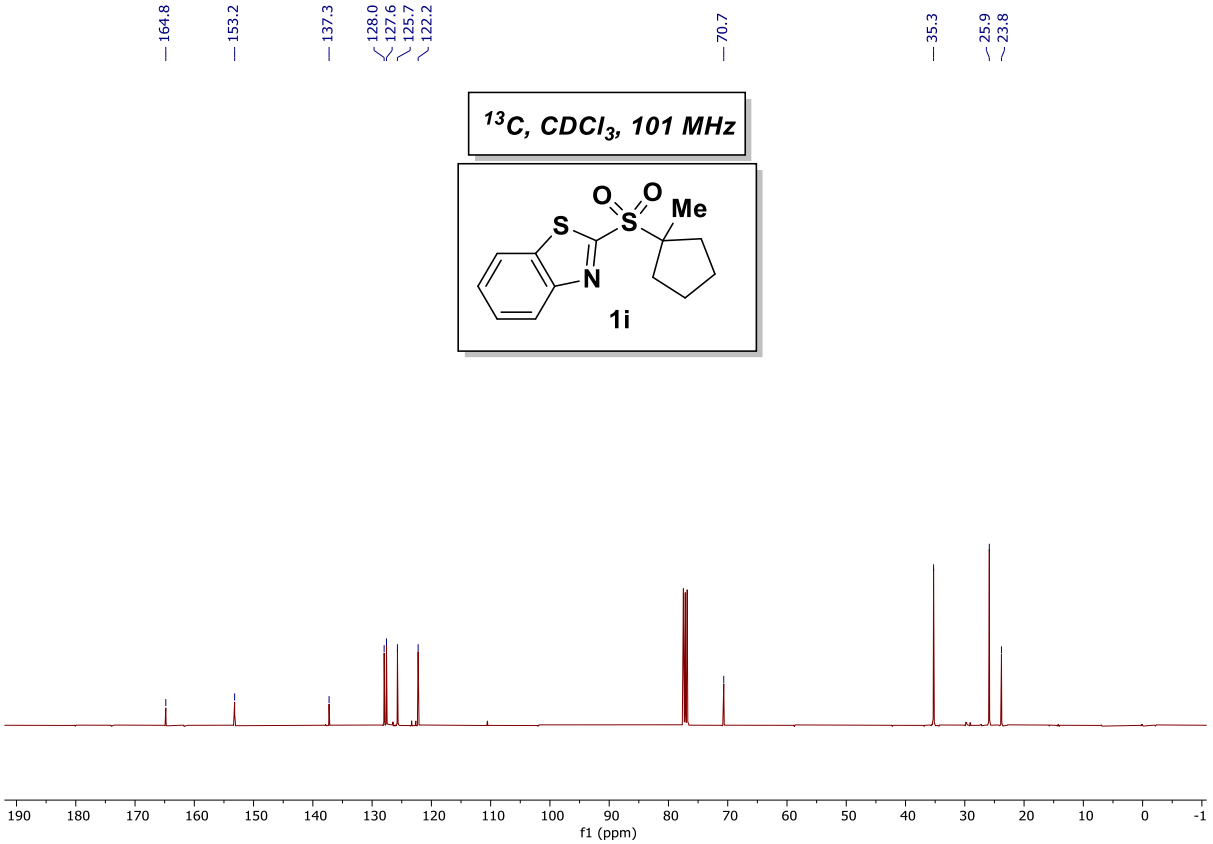

8.27
8.25
8.03
8.00
7.66
7.58
7.30
7.26
7.22
7.18
2.79
2.75
2.22
2.17
1.60
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
N
Me
Me
1g
0.93
0.94
2.00
2.08
3.00
2.04
2.00
6.02
f1 (ppm)

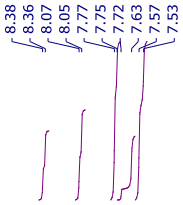

164.1
153.3
141.0
137.4
128.7
128.5
128.1
127.7
126.4
125.8
122.3
65.3
37.4
30.4
21.2
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
N
Me
Me
1g
f1 (ppm)


8.26
8.24
8.02
8.00
7.65
7.56
1.90
1.86
1.49
1.39
1.29
0.92
0.88
^{1}H, $CDCl_3$, 400 MHz
Me
Me
Me
1h
0.95
0.95
2.08
2.00
6.09
4.10
3.02
f1 (ppm)

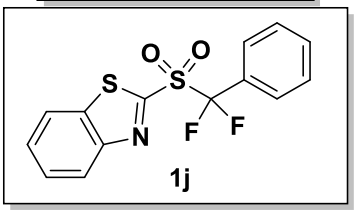

164.2
153.2
137.4
128.0
127.6
125.8
122.2
65.5
34.7
25.9
23.2
20.8
14.1
^{13}C, $CDCl_3$, 101 MHz
Me
Me
Me
1h
f1 (ppm)


8.26
8.23
8.02
8.00
7.65
7.57
2.71
2.64
1.88
1.80
1.79
1.72
1.70
1.63
1.56
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
Me
N
1i
1.00
1.00
2.02
2.03
2.17
2.57
2.33
3.21
f1 (ppm)

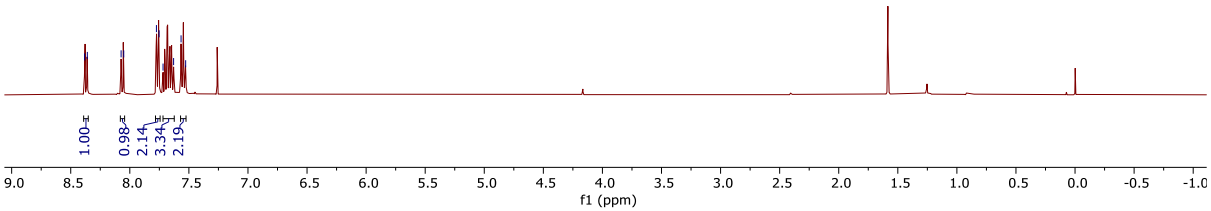

164.8
153.2
137.3
128.0
127.6
125.7
122.2
70.7
35.3
25.9
23.8
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
Me
N
1i
f1 (ppm)

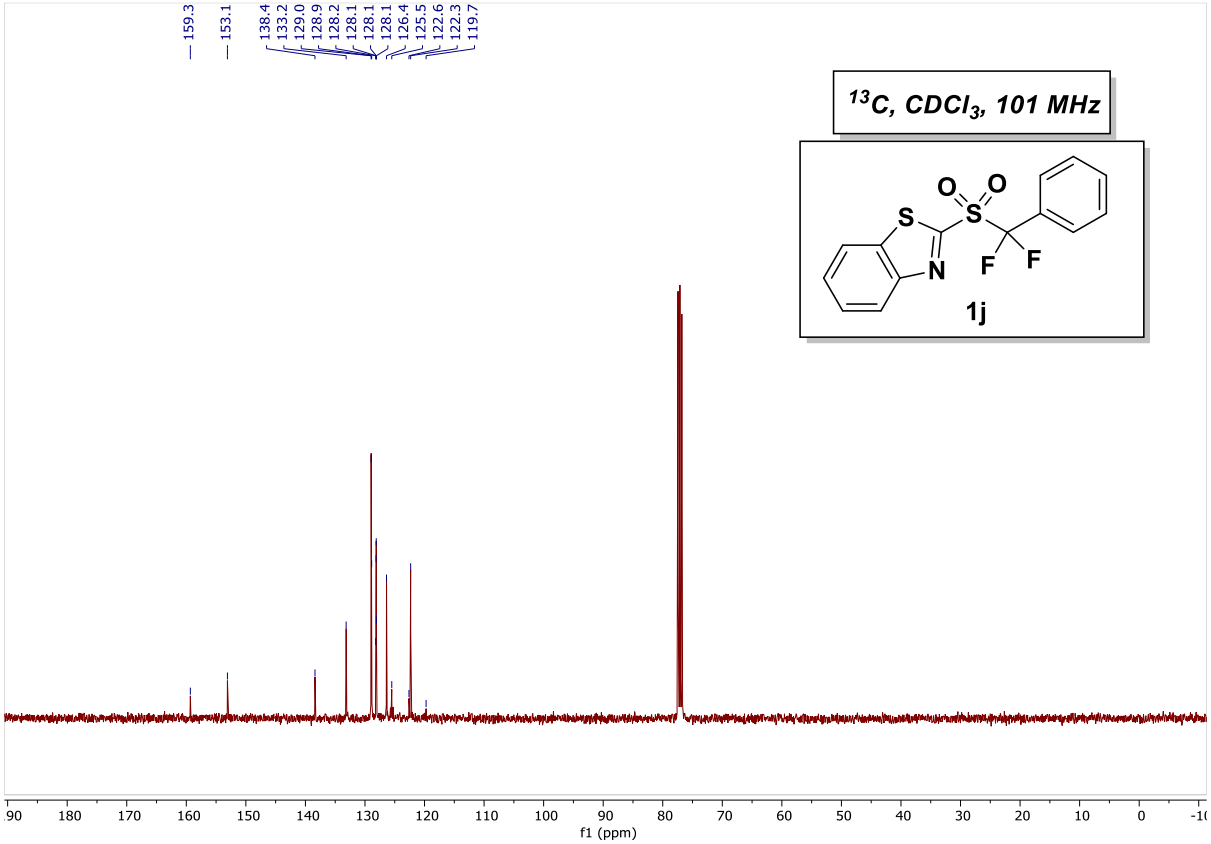


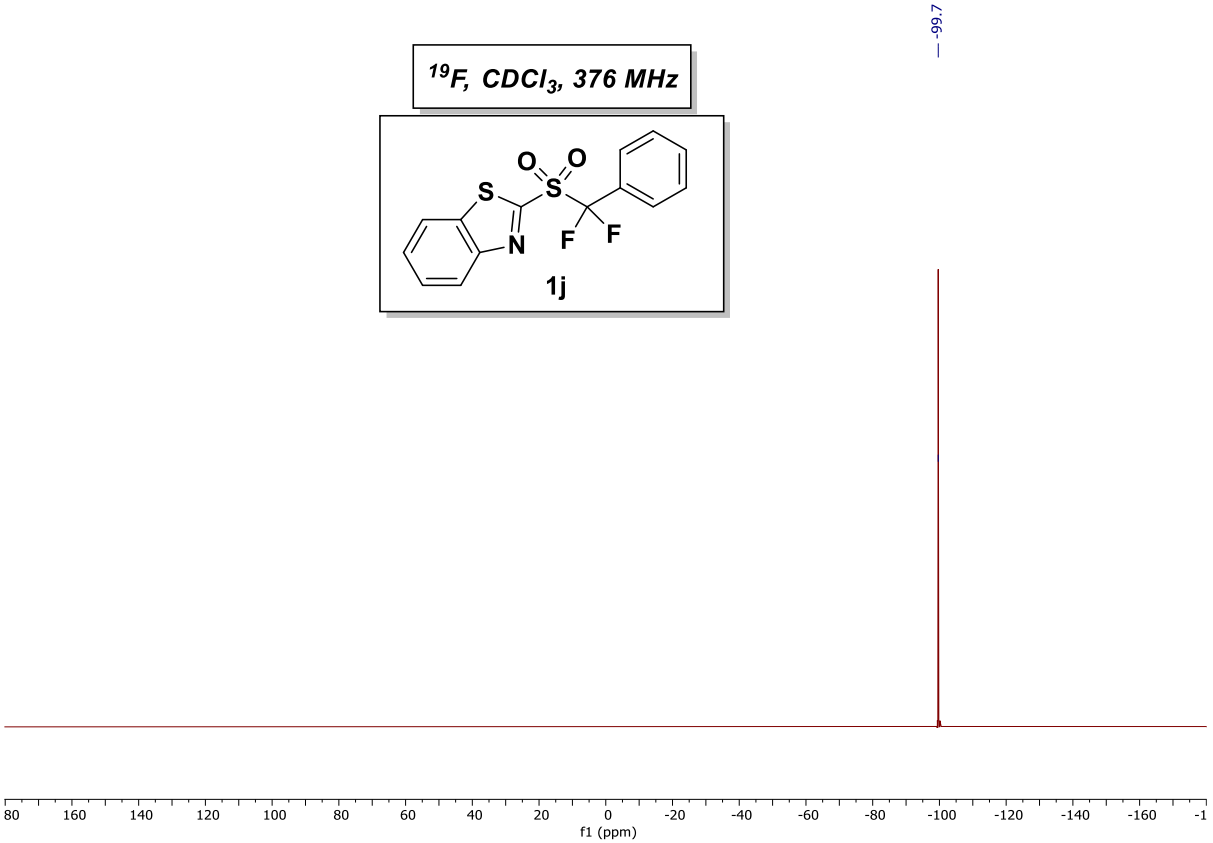
^{1}H, $CDCl_3$, 400 MHz

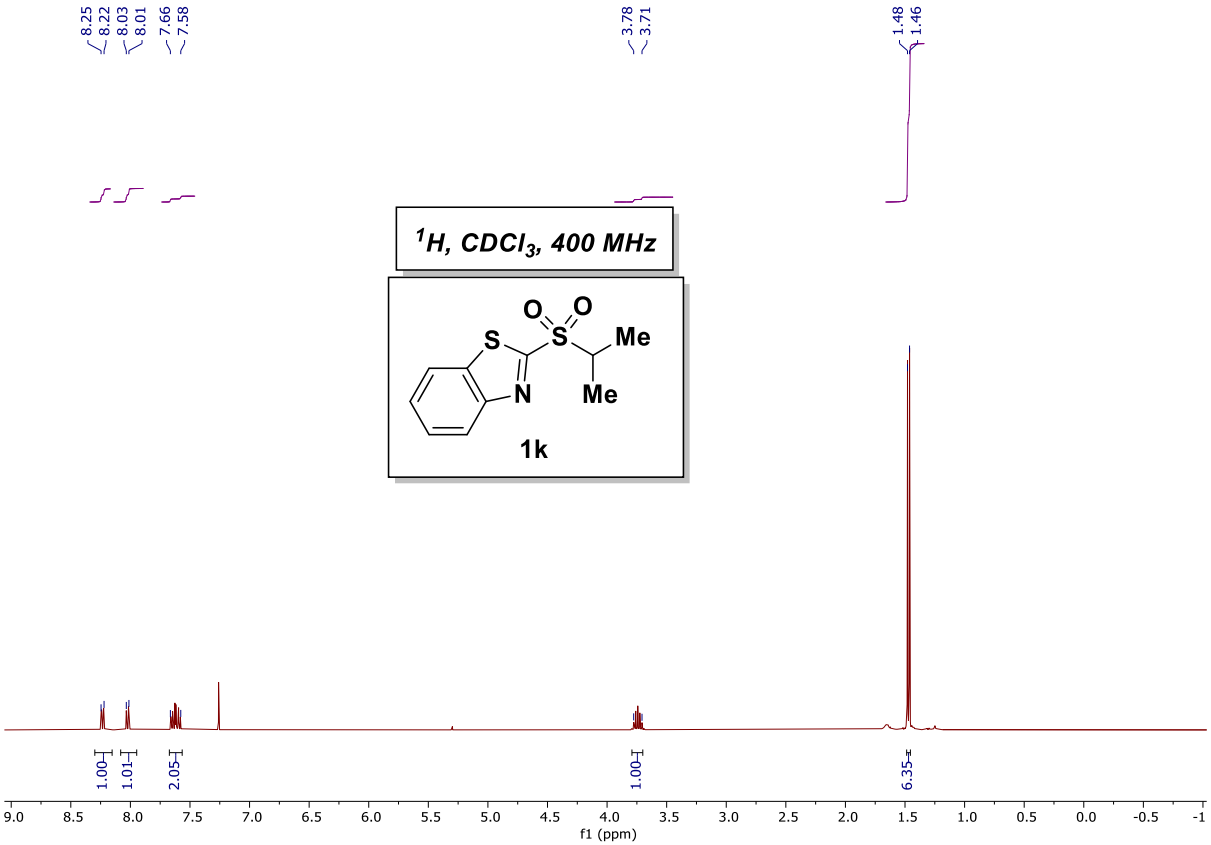


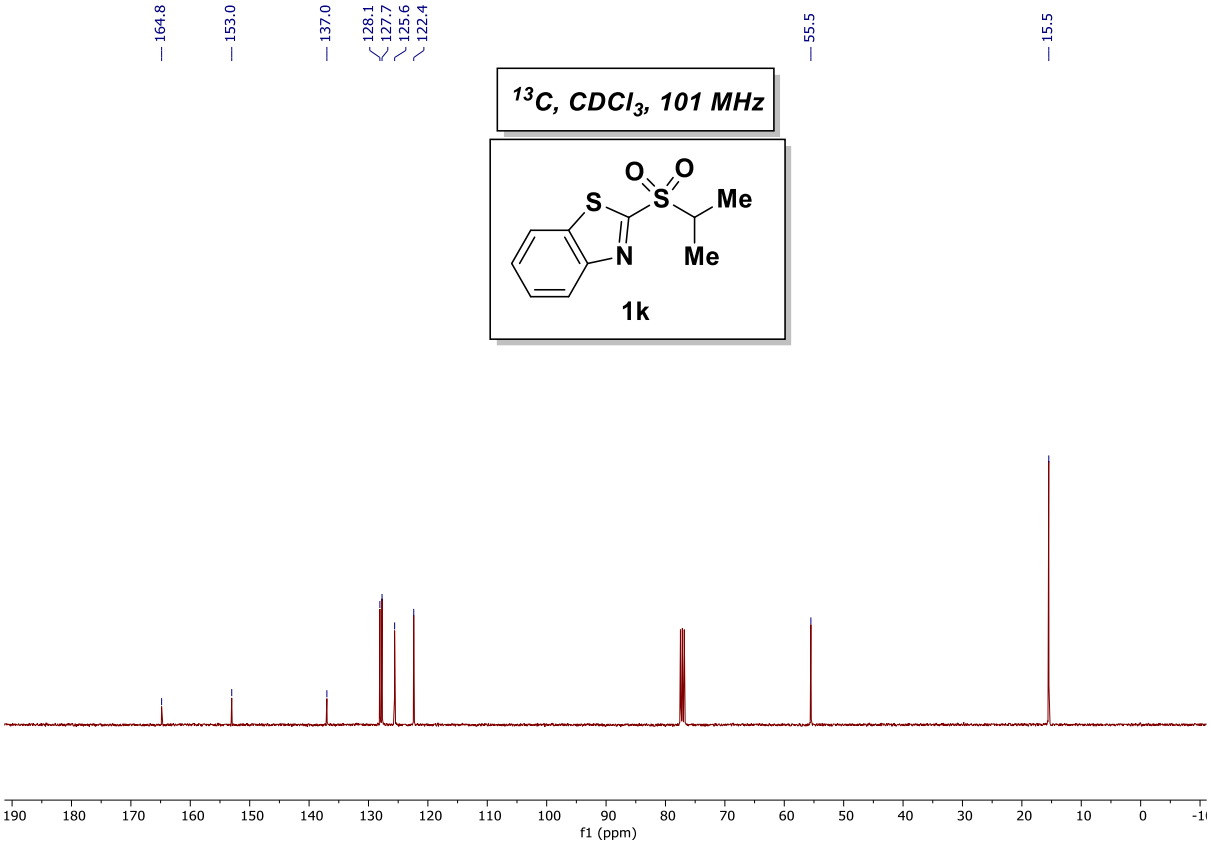
1j

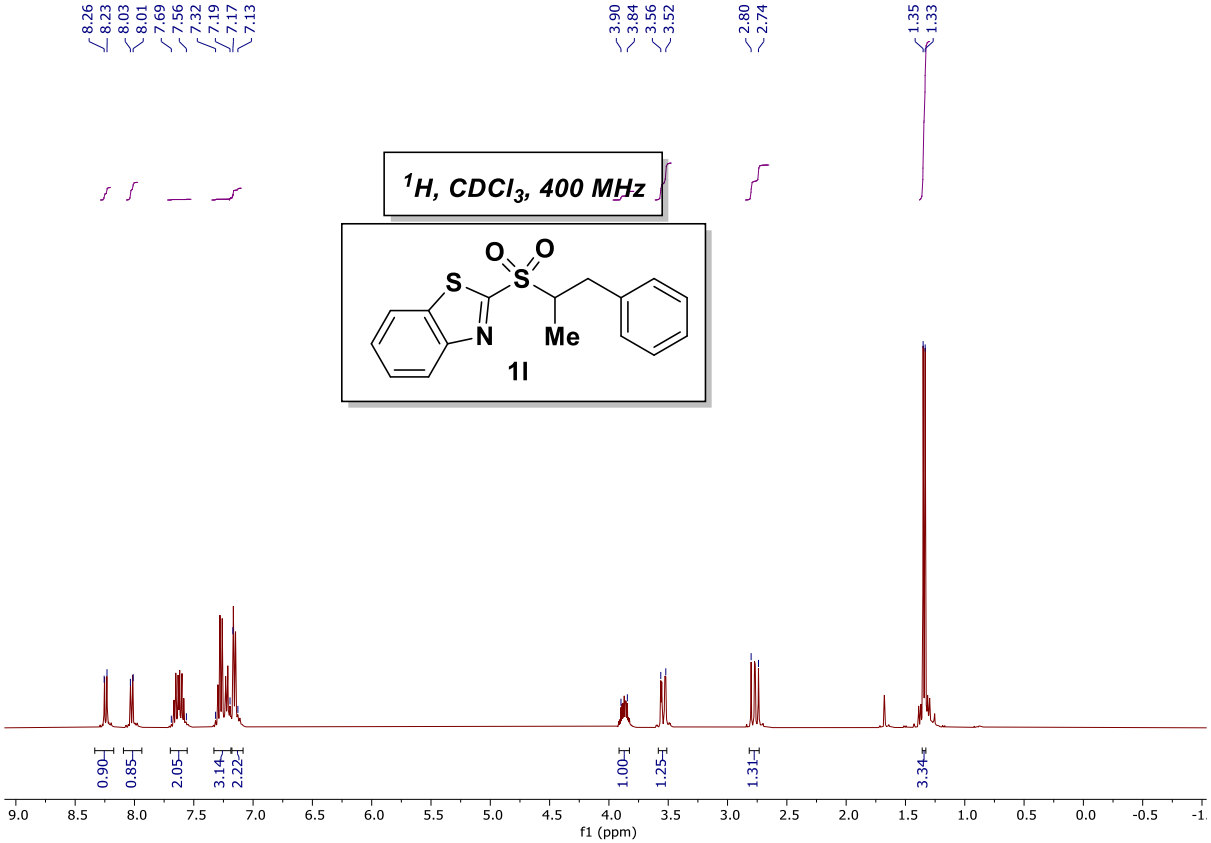


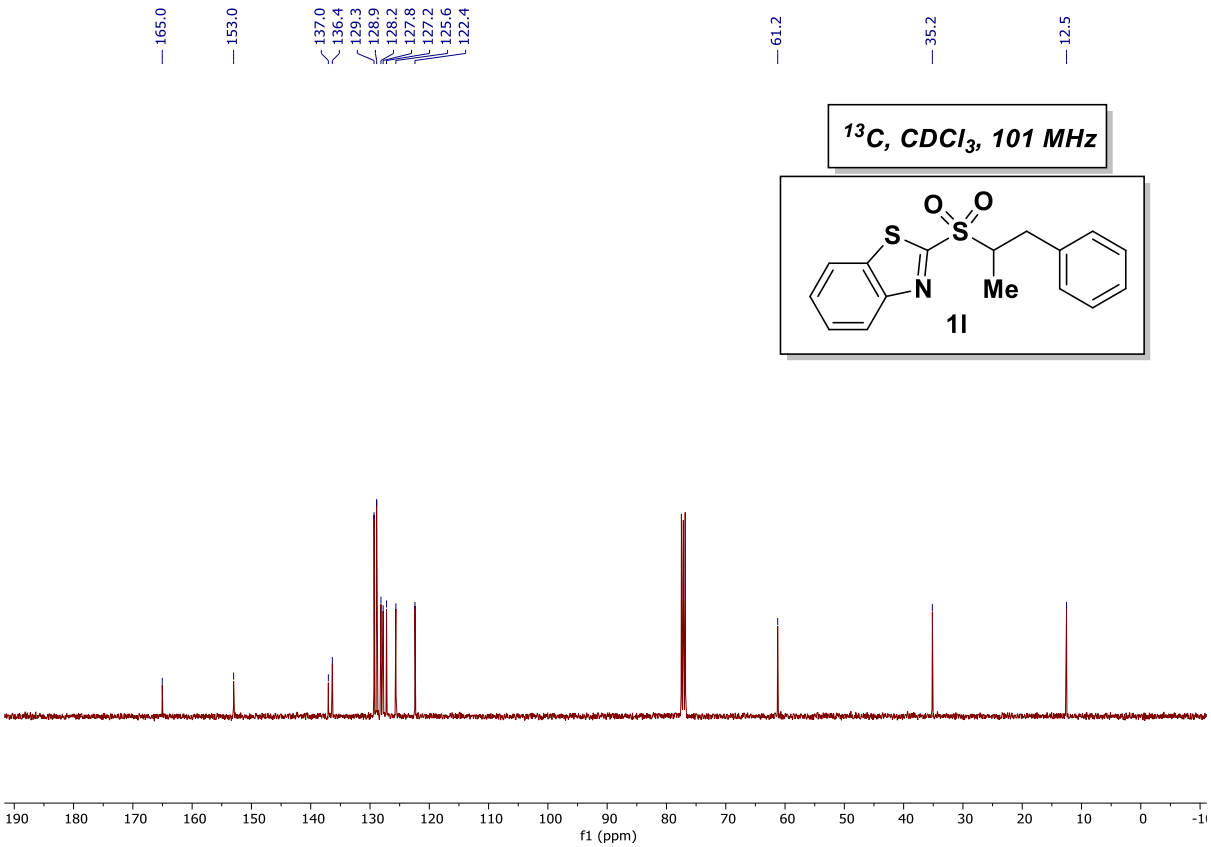


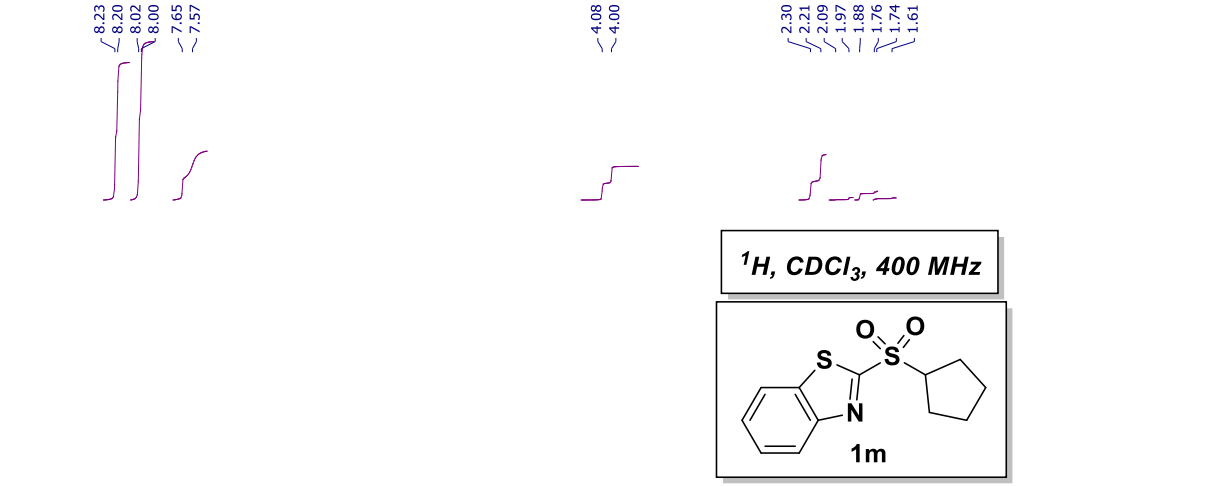

^{19}F, $CDCl_3$, 376 MHz
O
O
S
S
N
F
F
1j
-99.7
80
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-1
f1 (ppm)

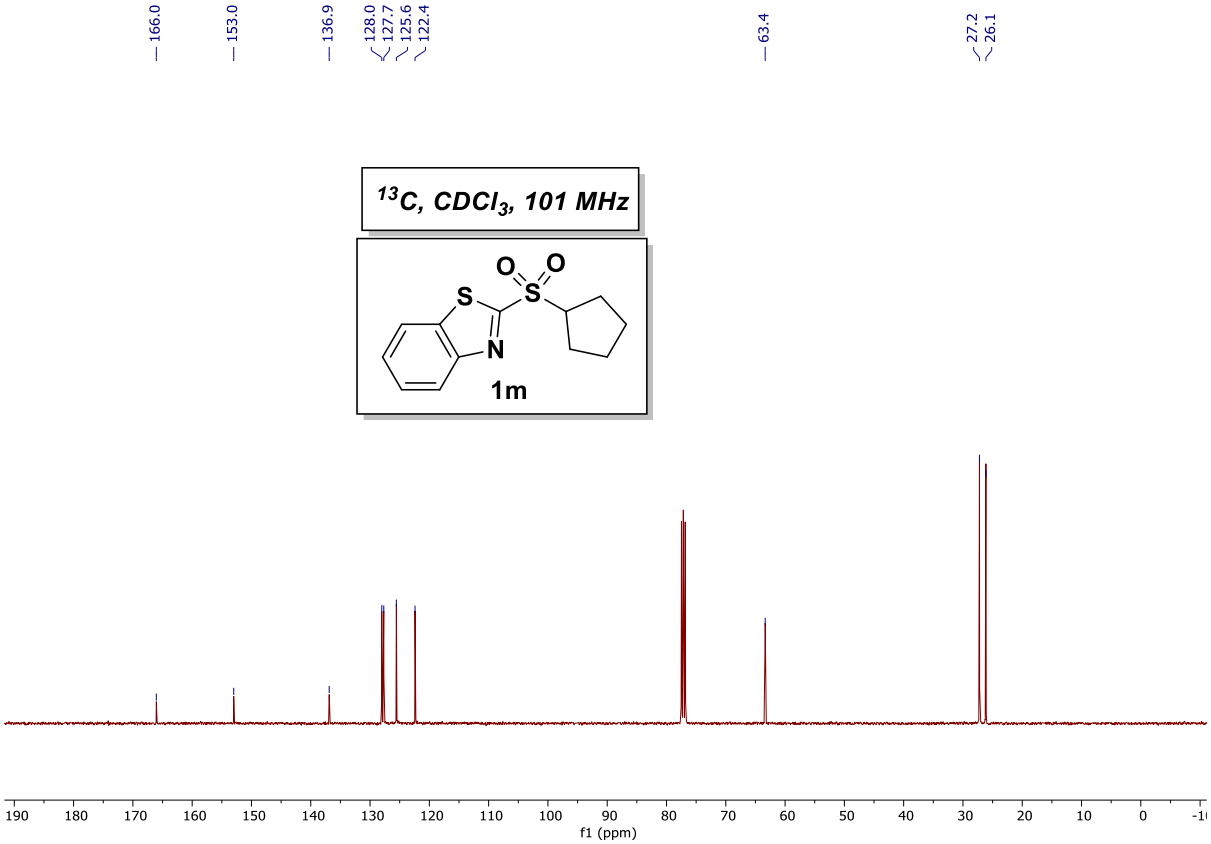

8.25
8.22
8.03
8.01
7.66
7.58
3.78
3.71
1.48
1.46
1H, CDCl3, 400 MHz
O
O
S
S
Me
N
Me
1k
1.00
1.01
2.05
1.00
6.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

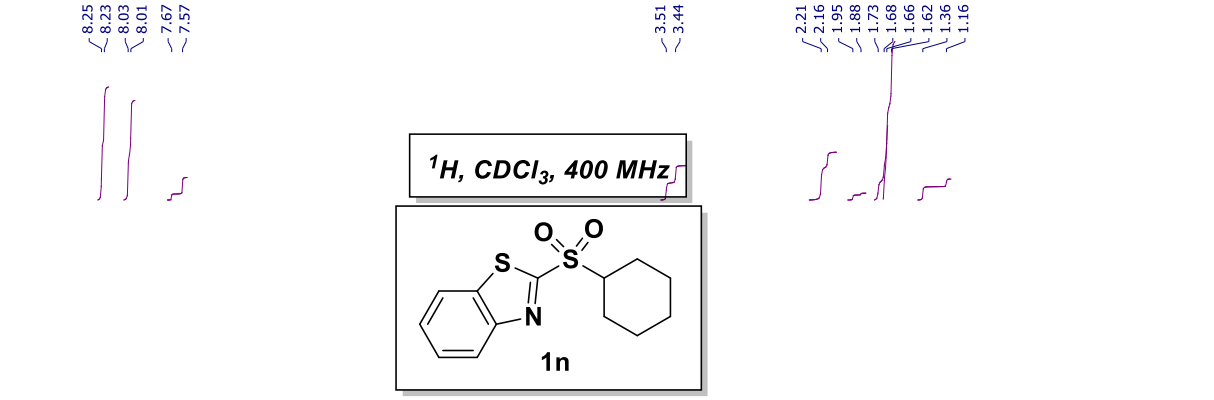

164.8
153.0
137.0
128.1
127.7
125.6
122.4
55.5
15.5
13C, CDCl3, 101 MHz
O
O
S
S
Me
N
Me
1k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

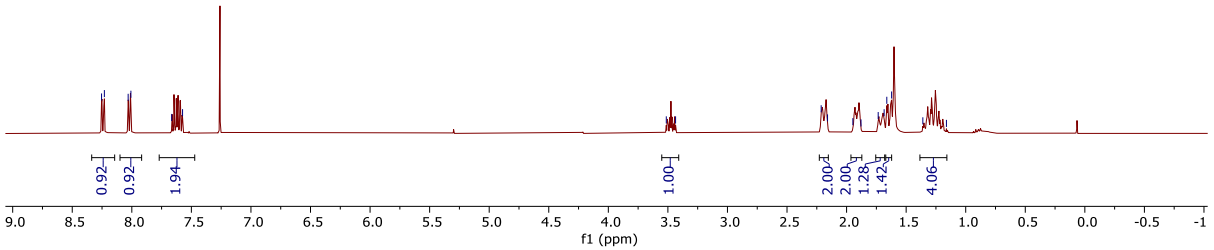

8.26
8.23
8.03
8.01
7.69
7.56
7.32
7.19
7.17
7.13
3.90
3.84
3.56
3.52
2.80
2.74
1.35
1.33
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
N
Me
1l
0.90
0.85
2.05
3.14
2.22
1.00
1.25
1.31
3.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

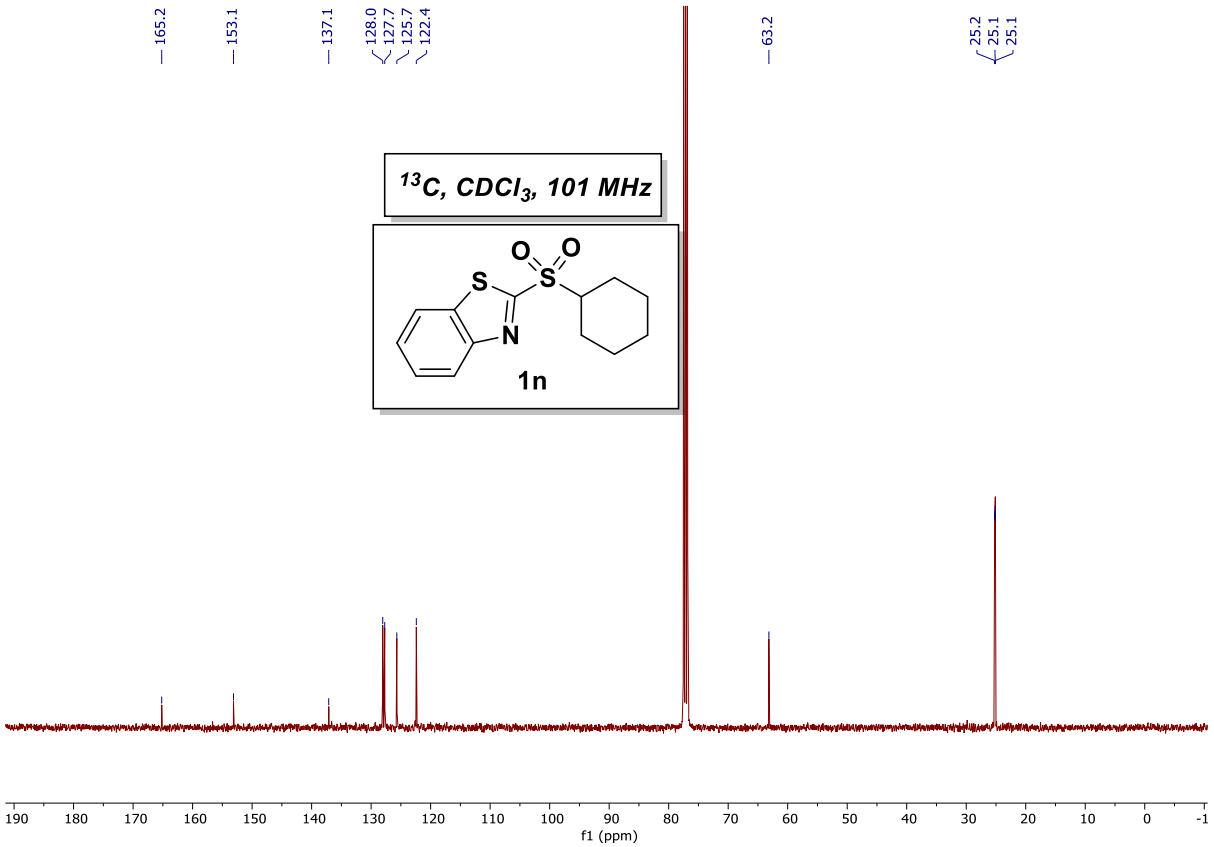

165.0
153.0
137.0
136.4
129.3
128.9
128.2
127.8
127.2
125.6
122.4
61.2
35.2
12.5
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
N
Me
1l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

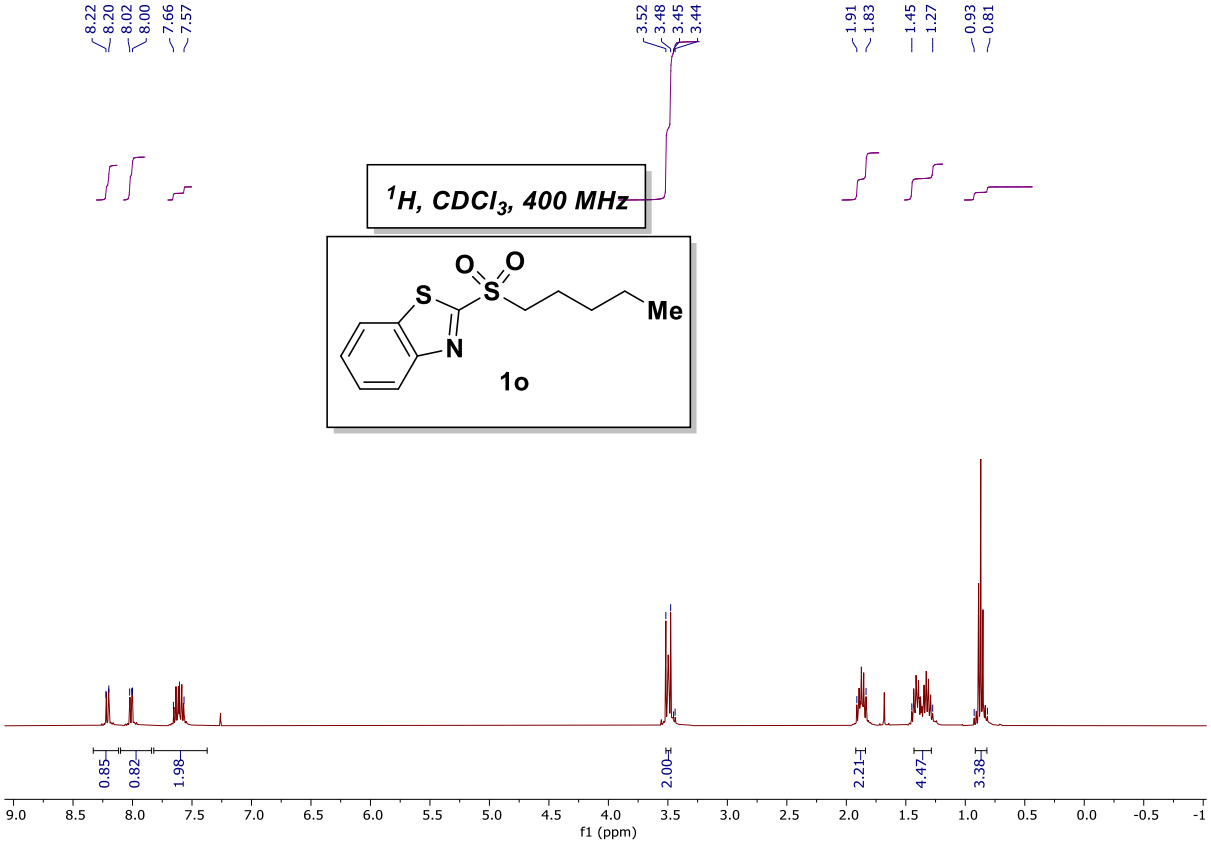

8.23
8.20
8.02
8.00
7.65
7.57
4.08
4.00
2.30
2.21
2.09
1.97
1.88
1.76
1.74
1.61
1H, CDCl3, 400 MHz
O
O
S
S
N
1m
1.00
0.98
2.00
1.00
2.23
2.27
2.17
2.48
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

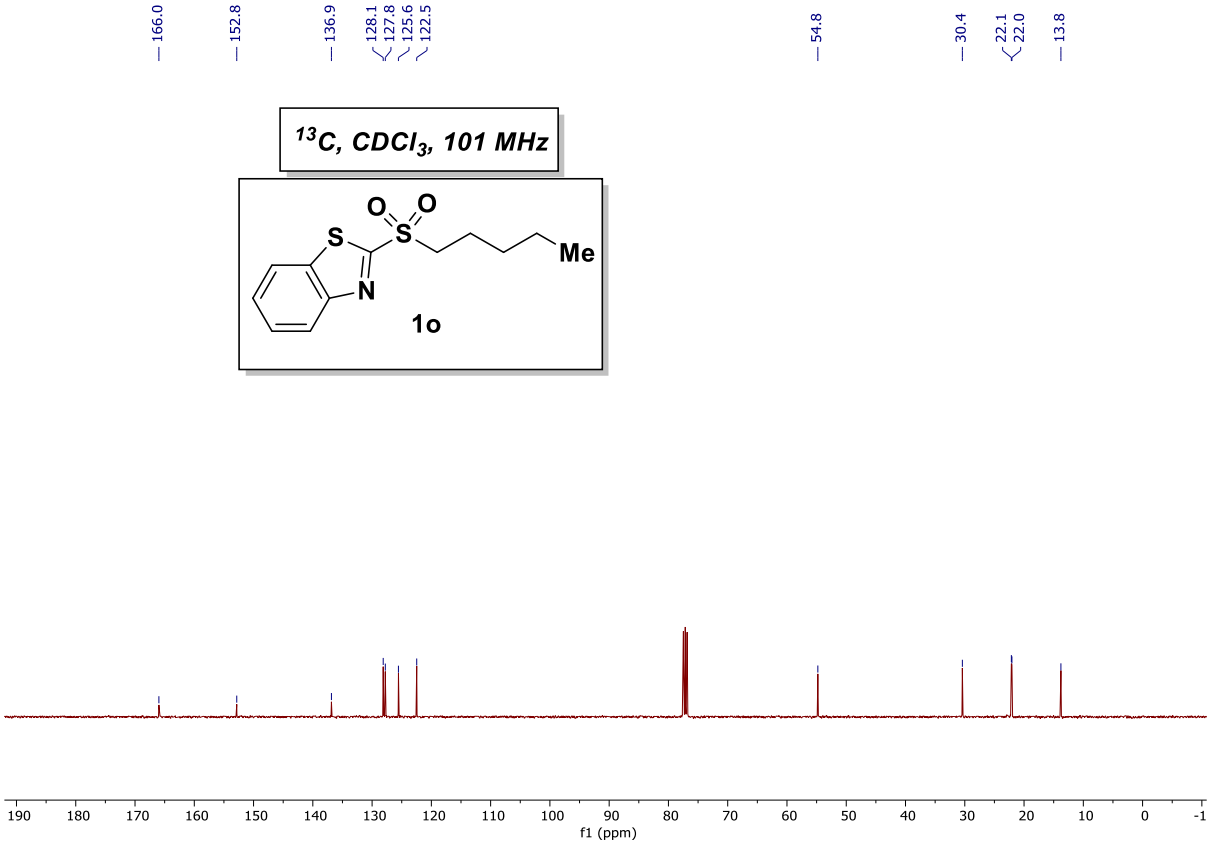

166.0
153.0
136.9
128.0
127.7
125.6
122.4
63.4
27.2
26.1
13C, CDCl3, 101 MHz
O
O
S
S
N
1m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

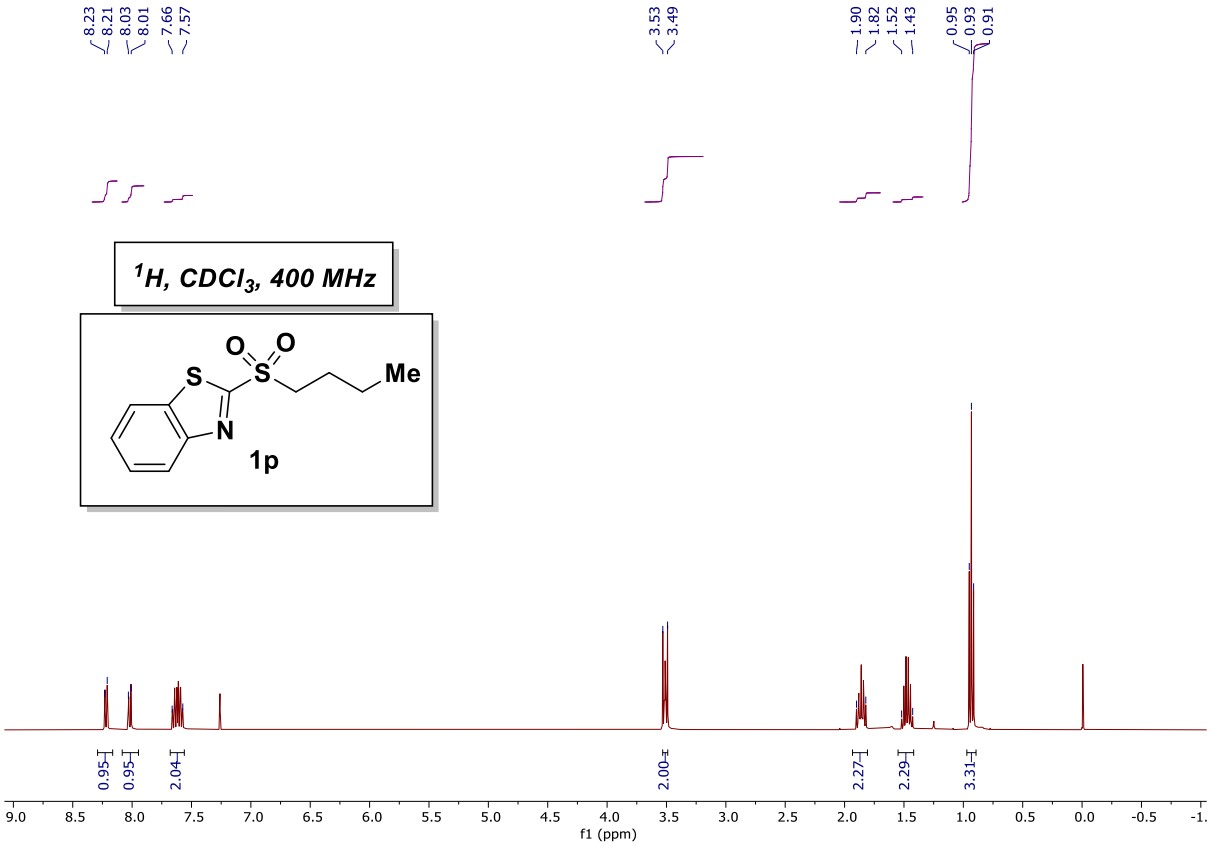

8.25
8.23
8.03
8.01
7.67
7.57
3.51
3.44
2.21
2.16
1.95
1.88
1.73
1.68
1.66
1.62
1.36
1.16
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
N
1n

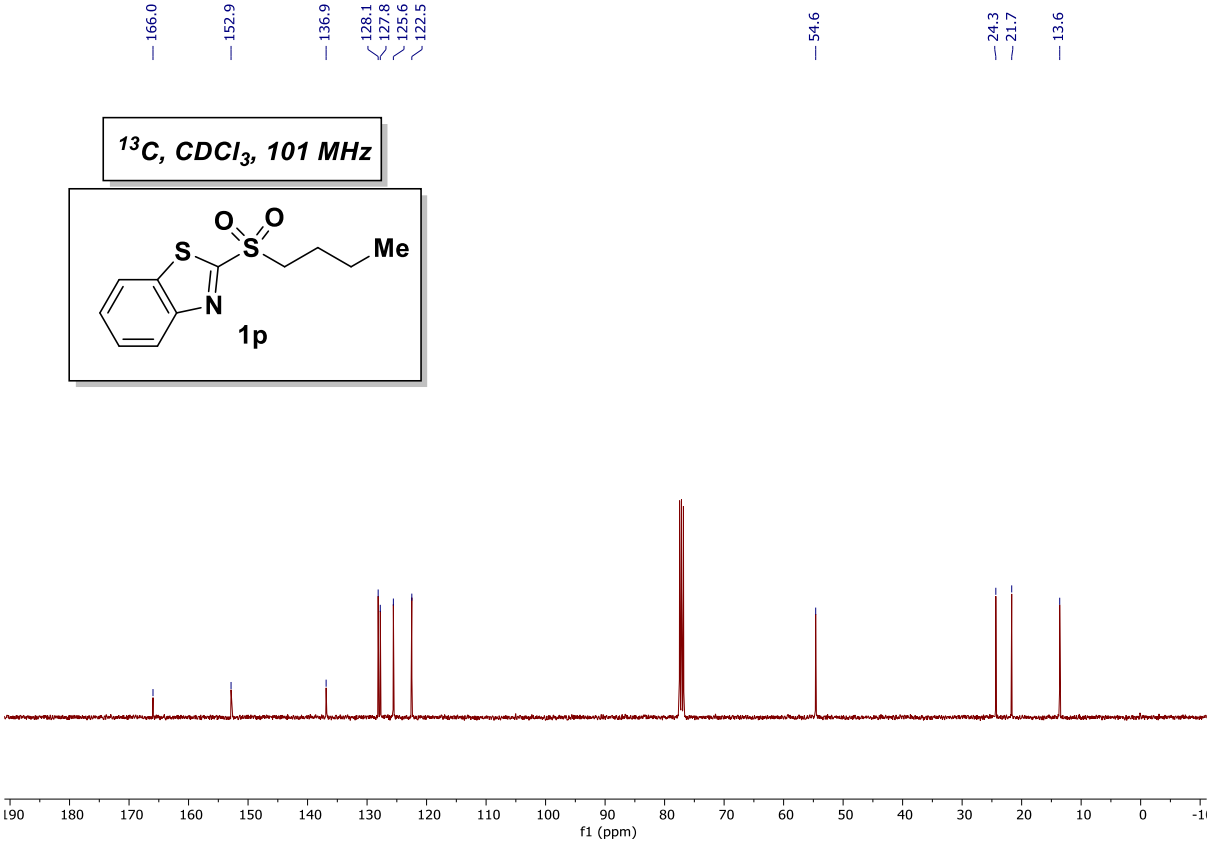

0.92
0.92
1.94
1.00
2.00
2.00
1.28
1.42
4.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


165.2
153.1
137.1
128.0
127.7
125.7
122.4
63.2
25.2
25.1
25.1
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
N
1n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

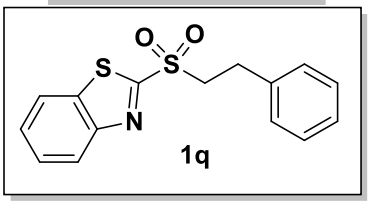

8.22
8.20
8.02
8.00
7.66
7.57
3.52
3.48
3.45
3.44
1.91
1.83
1.45
1.27
0.93
0.81
^{1}H, $CDCl_3$, 400 MHz
Me
1o
0.85
0.82
1.98
2.00
2.21
4.47
3.38
f1 (ppm)

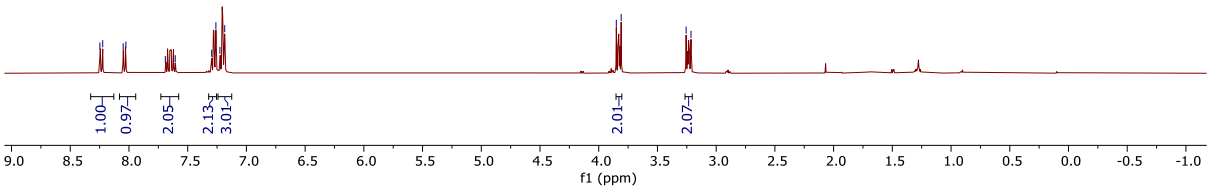

166.0
152.8
136.9
128.1
127.8
125.6
122.5
54.8
30.4
22.1
22.0
13.8
^{13}C, $CDCl_3$, 101 MHz
Me
1o
f1 (ppm)


8.23
8.21
8.03
8.01
7.66
7.57
3.53
3.49
1.90
1.82
1.52
1.43
0.95
0.93
0.91
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
Me
N
1p
0.95
0.95
2.04
2.00
2.27
2.29
3.31
f1 (ppm)

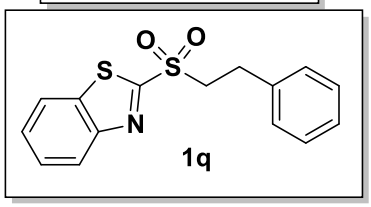

166.0
152.9
136.9
128.1
127.8
125.6
122.5
54.6
24.3
21.7
13.6
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
Me
N
1p
f1 (ppm)

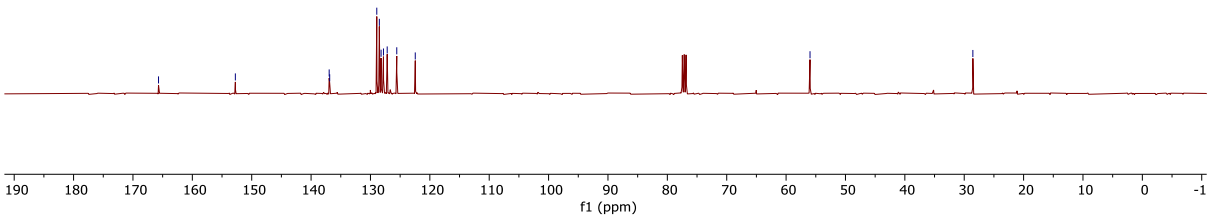
^{1}H, $CDCl_3$, 400 MHz

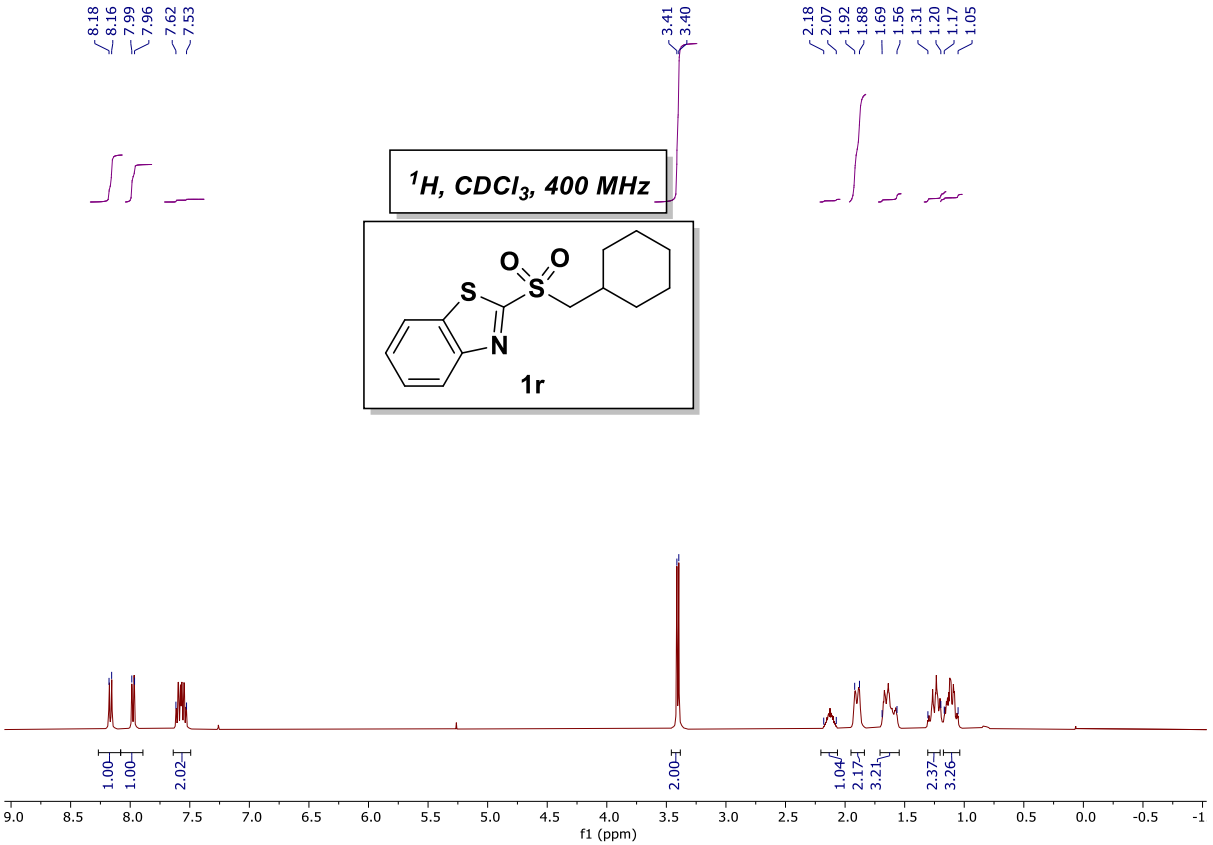


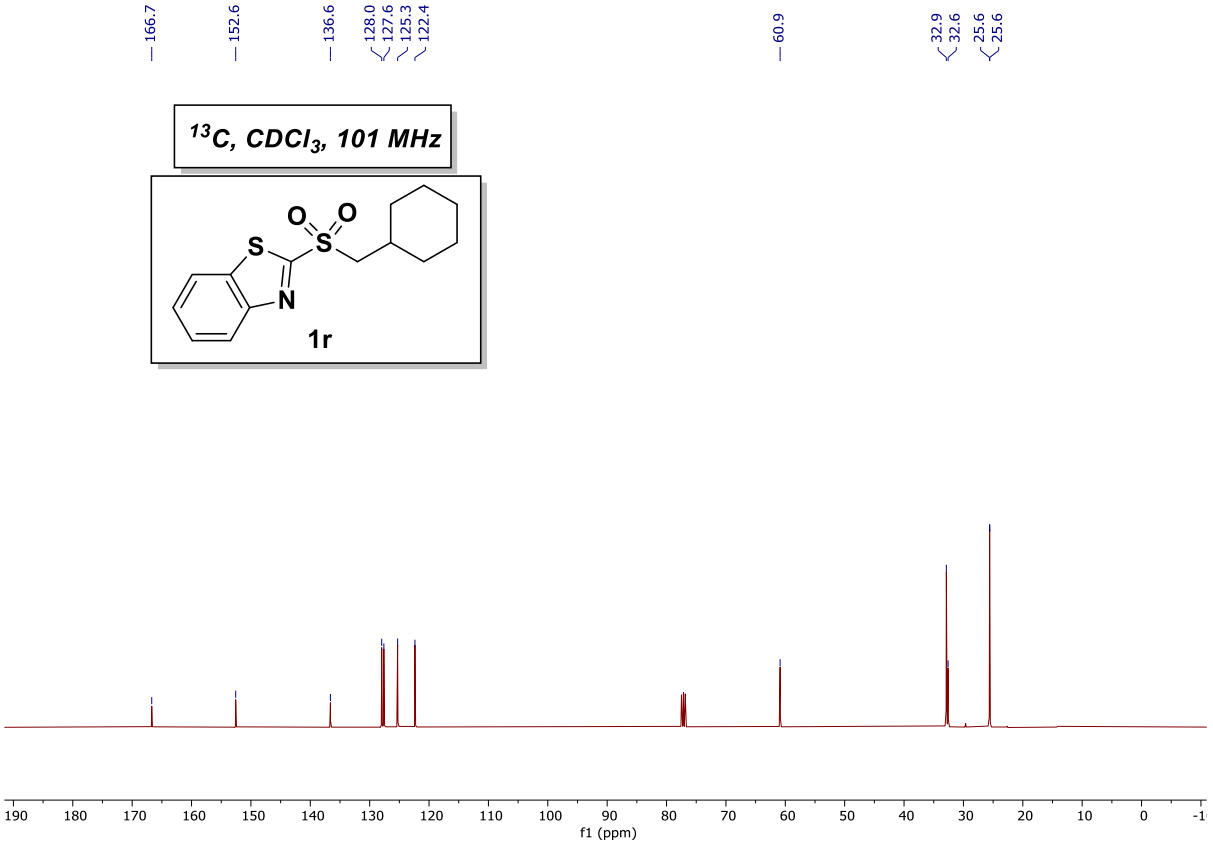


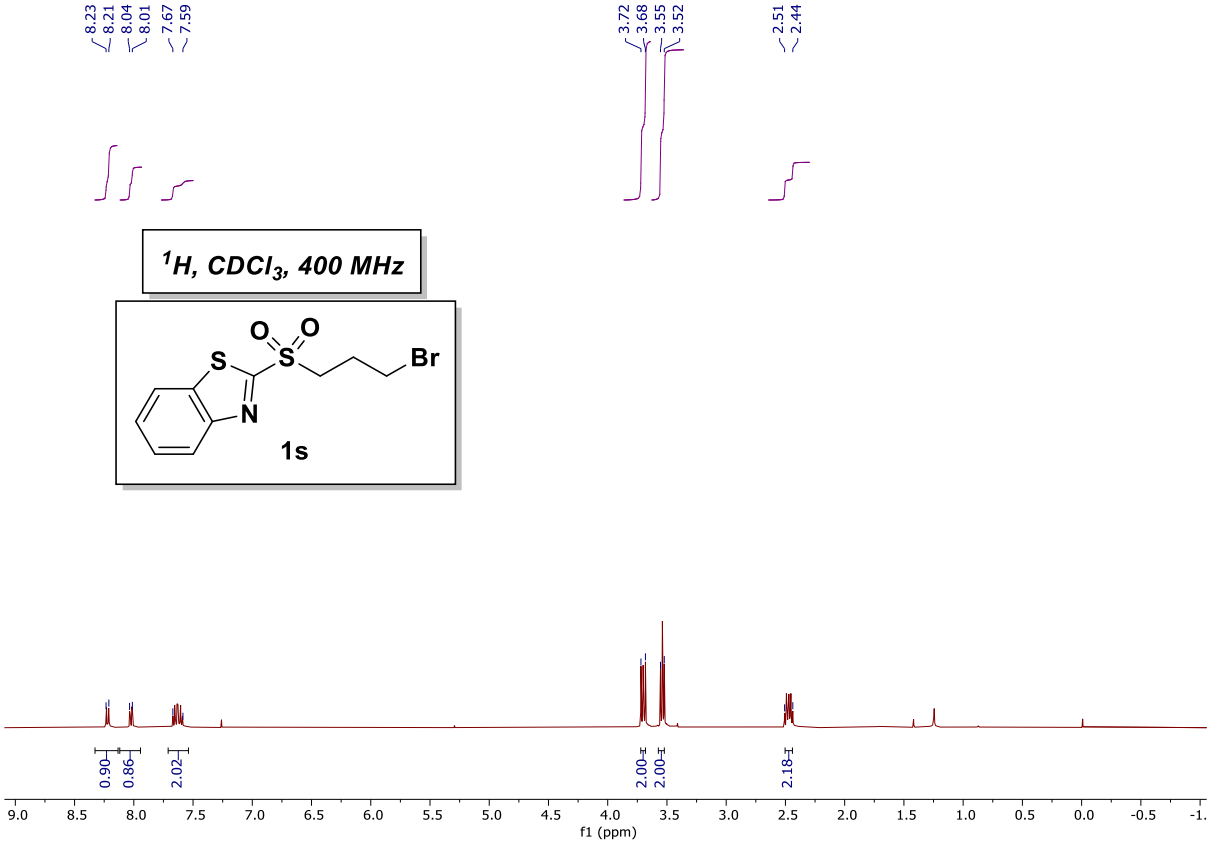
^{13}C, $CDCl_3$, 101 MHz

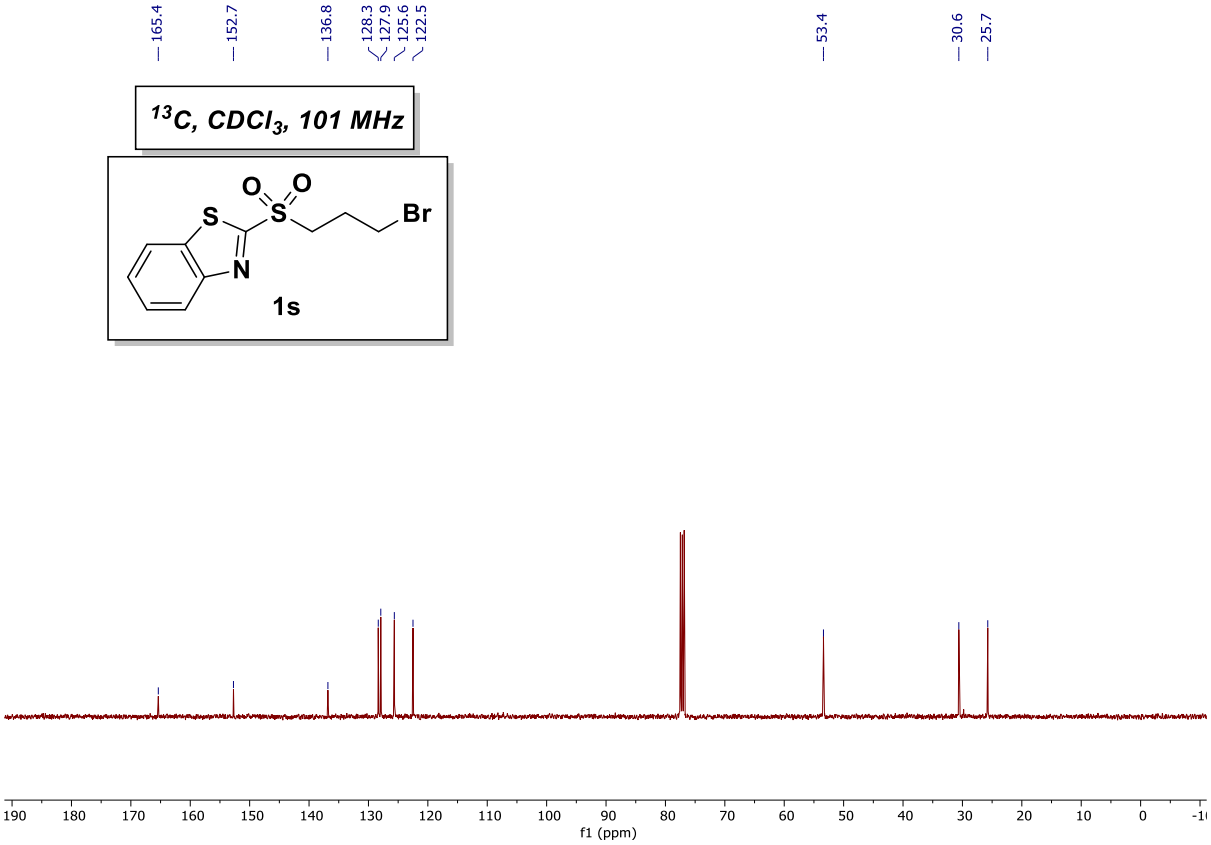


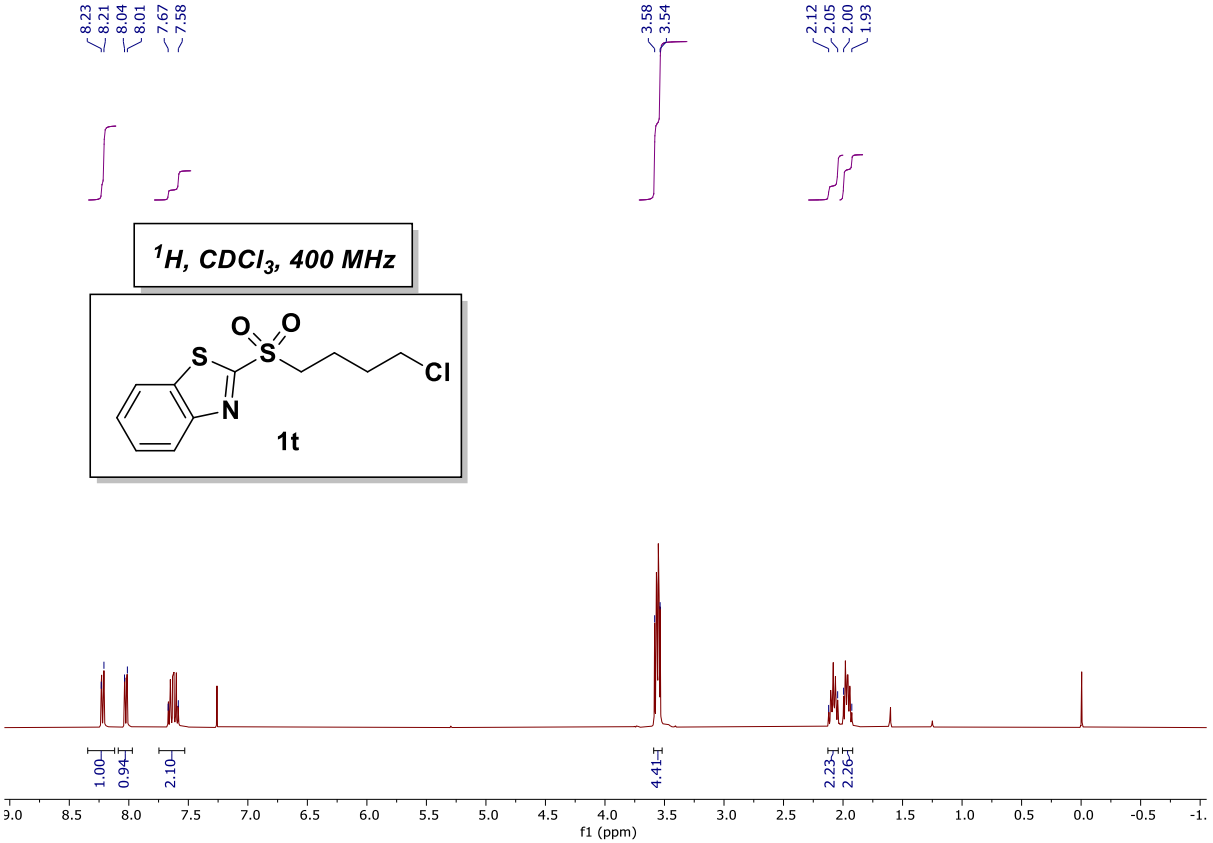


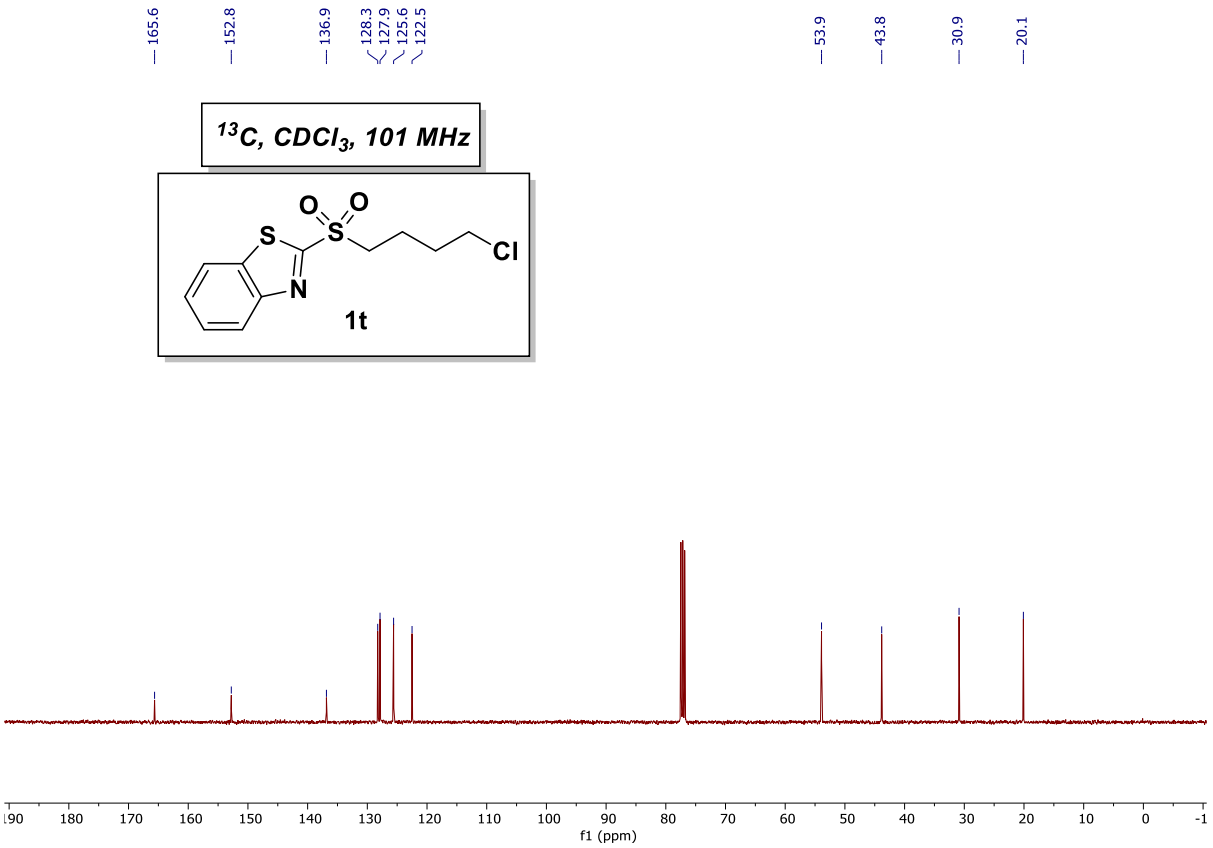

8.18
8.16
7.99
7.96
7.62
7.53
3.41
3.40
2.18
2.07
1.92
1.88
1.69
1.56
1.31
1.20
1.17
1.05
1H, CDCl3, 400 MHz
O
O
S
S
N
1r
1.00
1.00
2.02
2.00
1.04
2.17
3.21
2.37
3.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

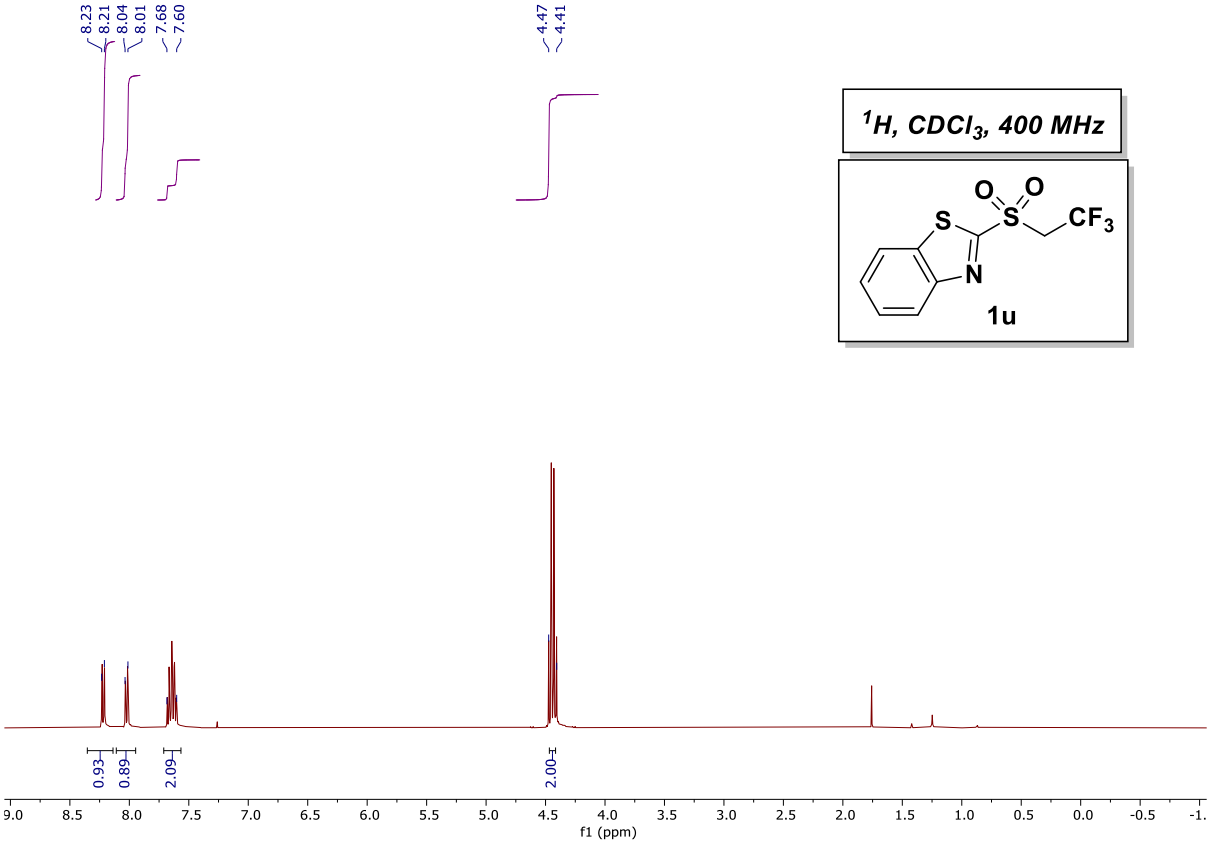

166.7
152.6
136.6
128.0
127.6
125.3
122.4
60.9
32.9
32.6
25.6
25.6
13C, CDCl3, 101 MHz
O
O
S
S
N
1r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


8.23
8.21
8.04
8.01
7.67
7.59
3.72
3.68
3.55
3.52
2.51
2.44
^{1}H, $CDCl_3$, 400 MHz
O
O
S
S
Br
N
1s
0.90
0.86
2.02
2.00
2.00
2.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


165.4
152.7
136.8
128.3
127.9
125.6
122.5
53.4
30.6
25.7
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
Br
N
1s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

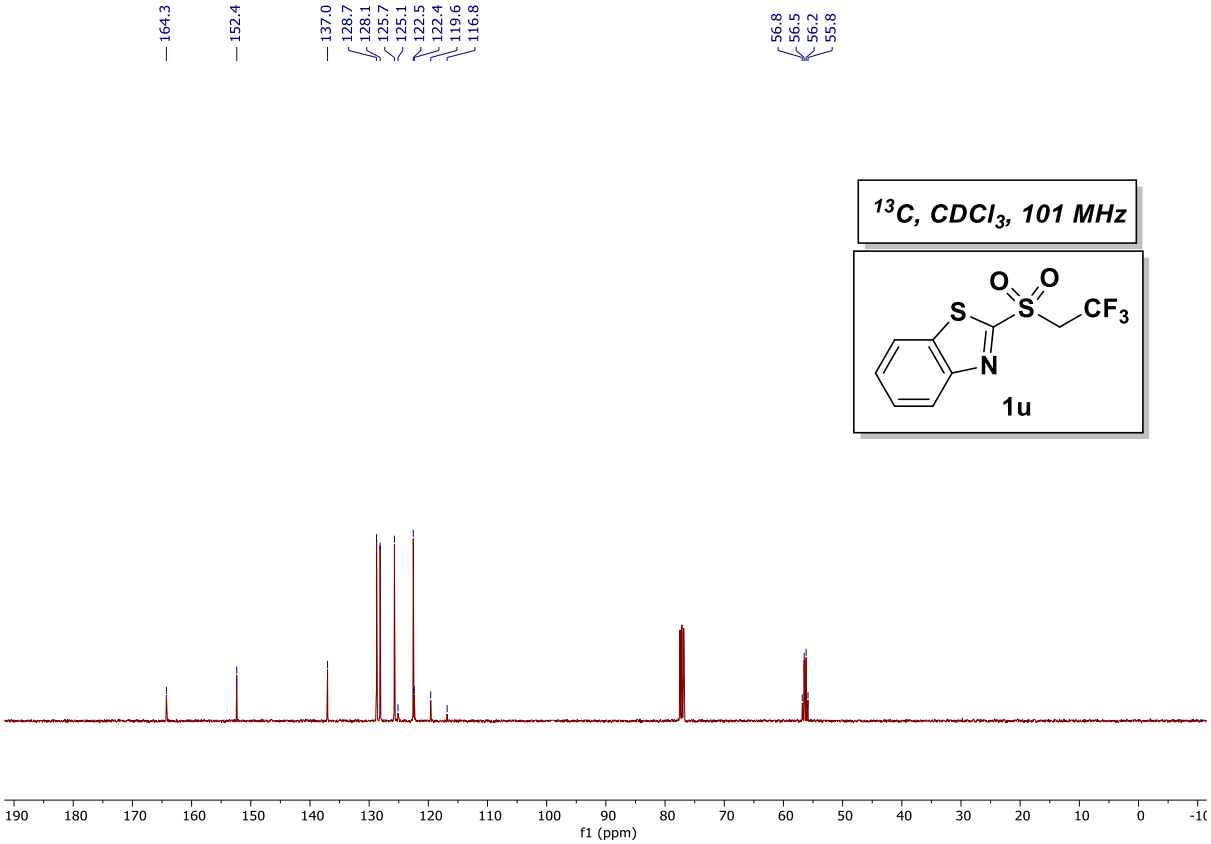

8.23
8.21
8.04
8.01
7.67
7.58
3.58
3.54
2.12
2.05
2.00
1.93
^1H, $CDCl_3$, 400 MHz
O
O
S
S
Cl
N
1t
1.00
0.94
2.10
4.41
2.23
2.26
f1 (ppm)


165.6
152.8
136.9
128.3
127.9
125.6
122.5
53.9
43.8
30.9
20.1
^{13}C, $CDCl_3$, 101 MHz
O
O
S
S
Cl
N
1t
f1 (ppm)



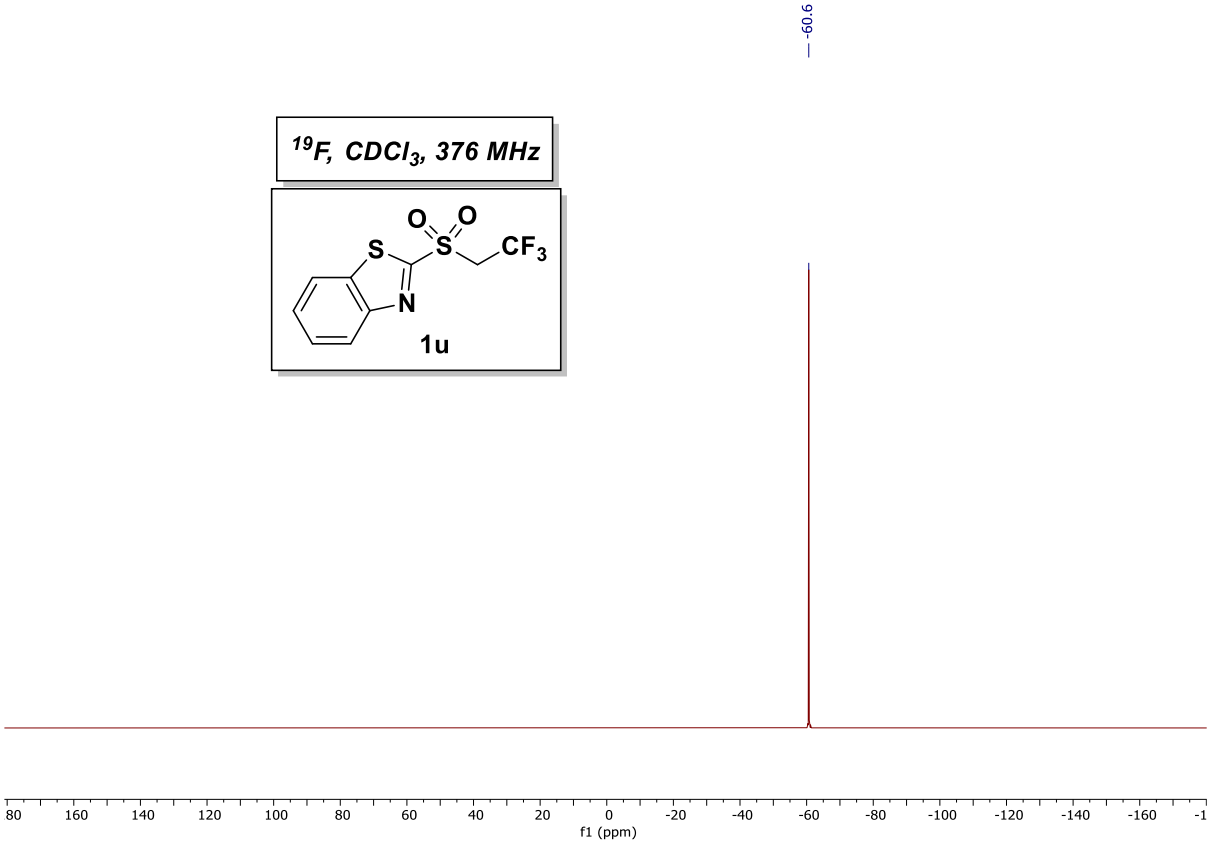
^{1}H, $CDCl_3$, 400 MHz

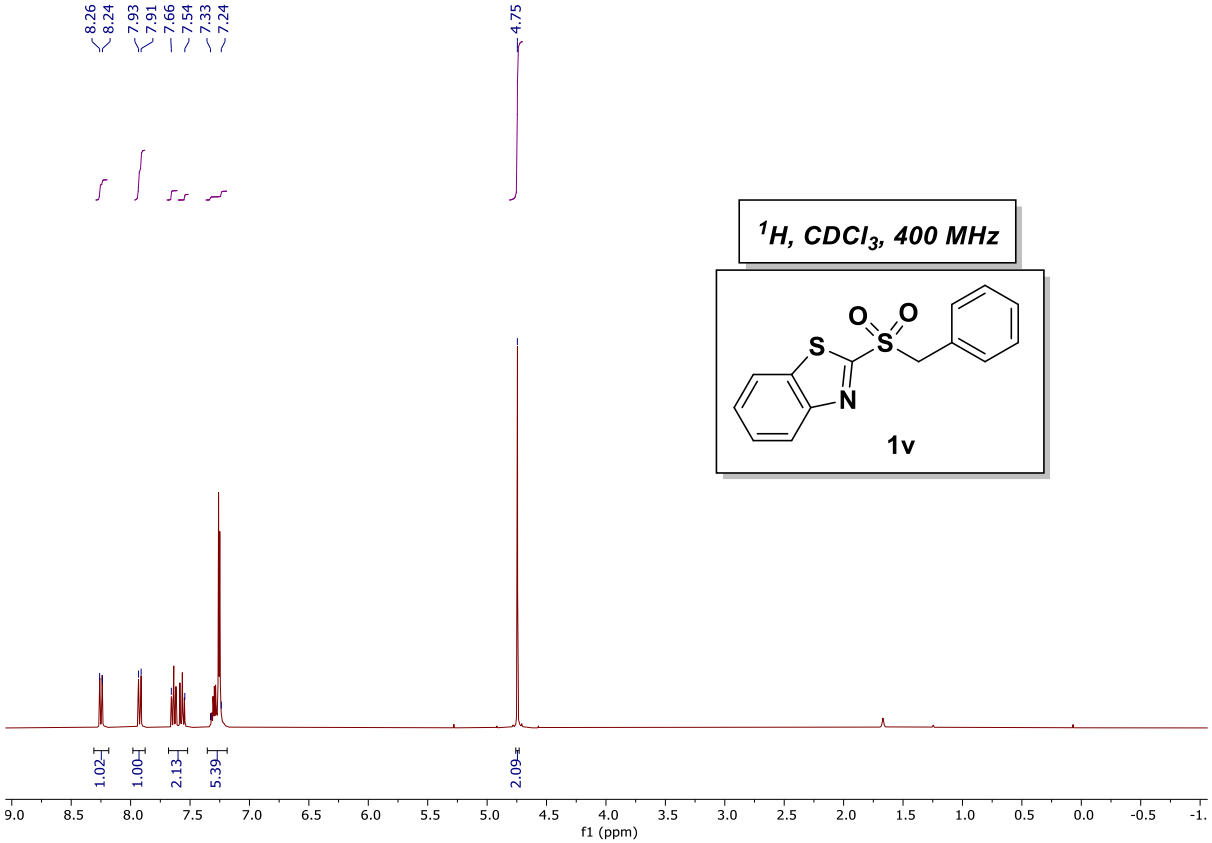
1u



^{13}C, $CDCl_3$, 101 MHz

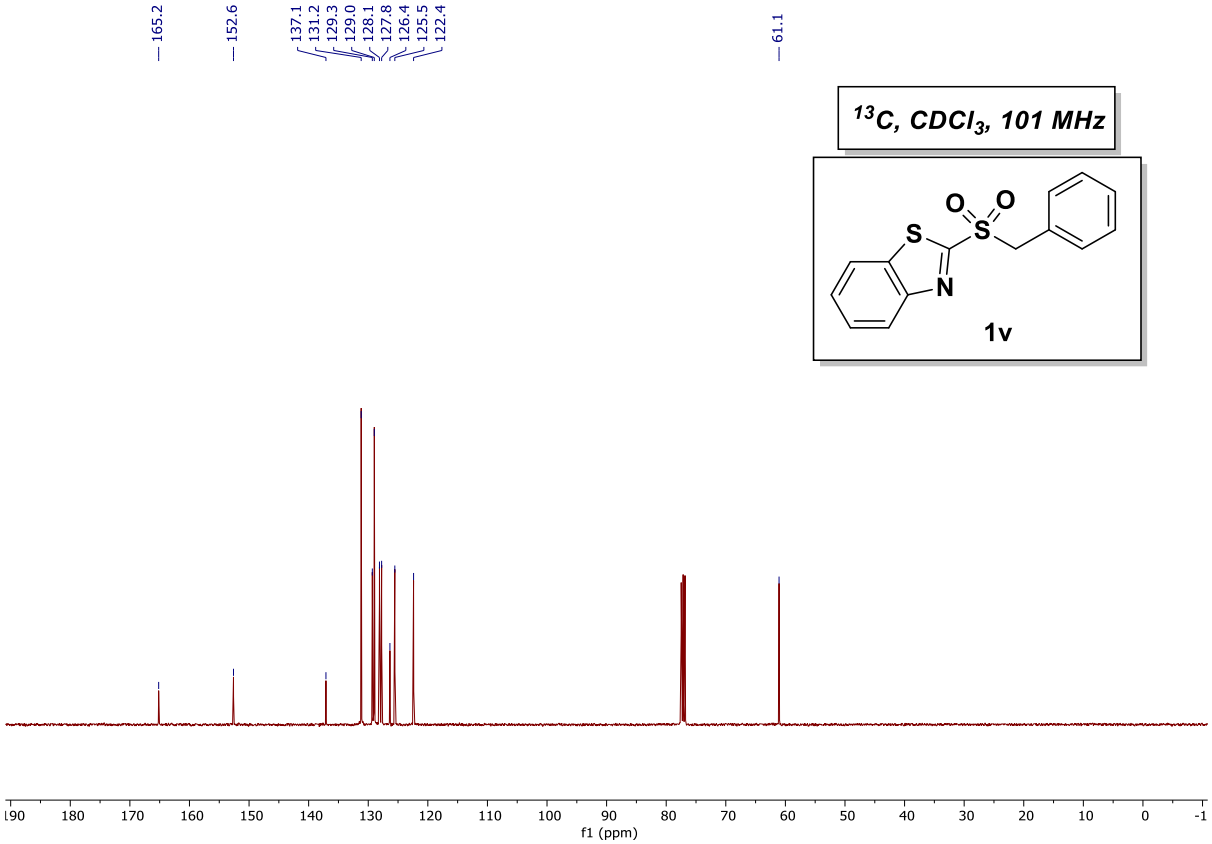
1u


-60.6
^{19}F, $CDCl_3$, 376 MHz
O
O
S
S
CF_3
N
1u
80
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-1
f1 (ppm)



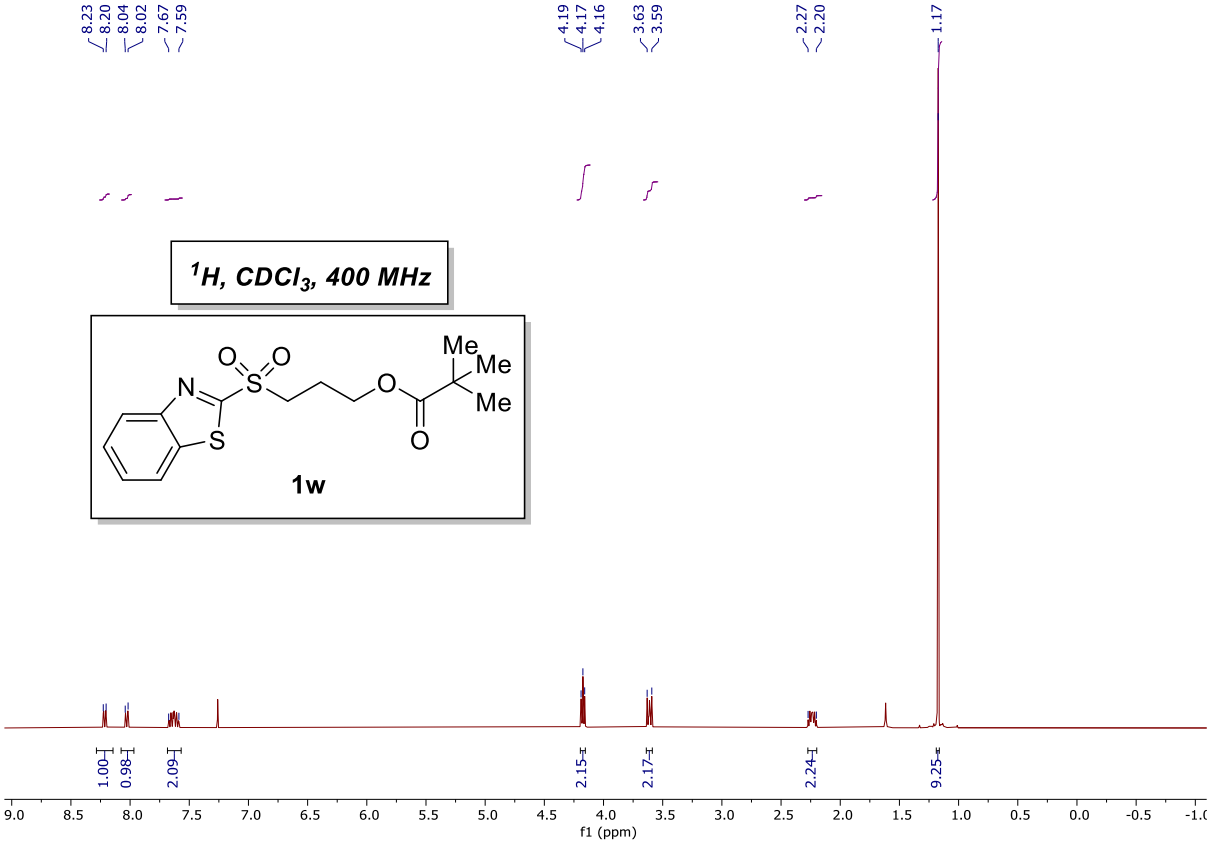
^{1}H, $CDCl_3$, 400 MHz

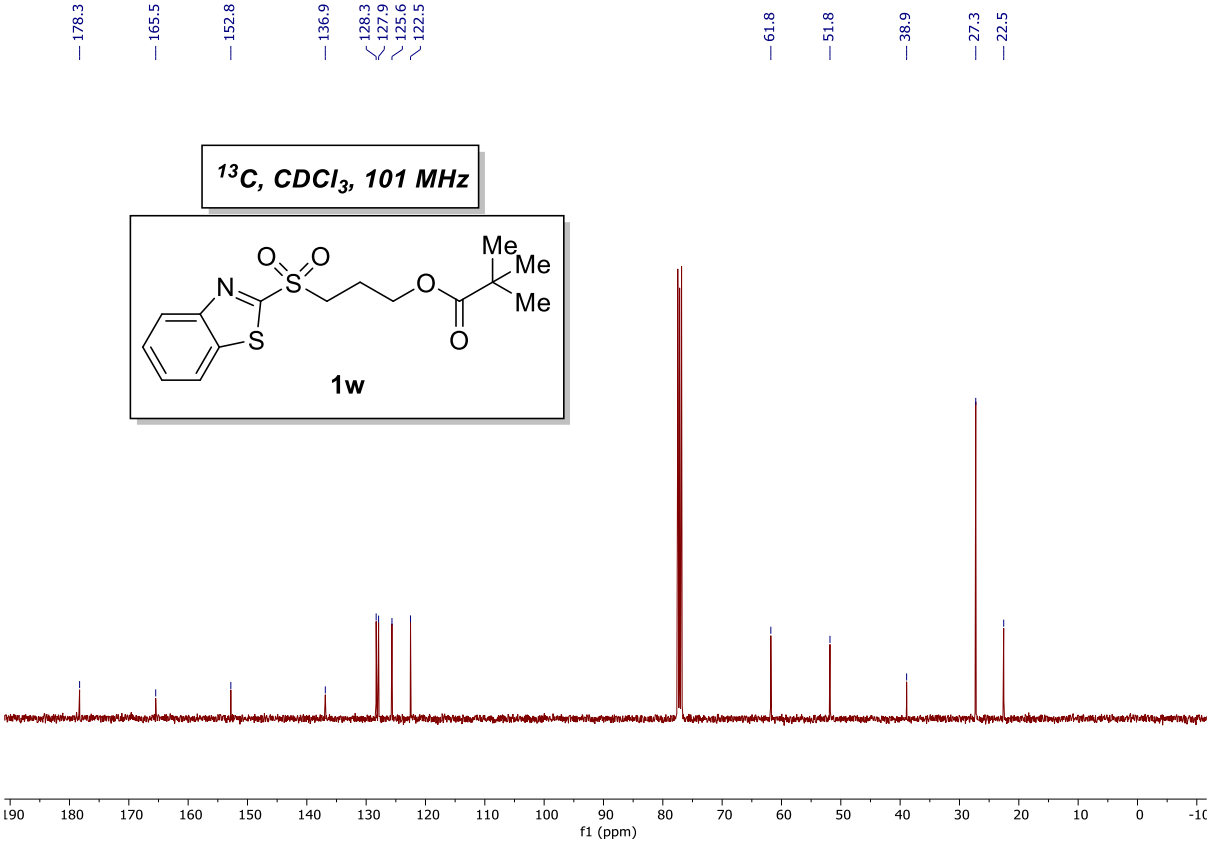
1v

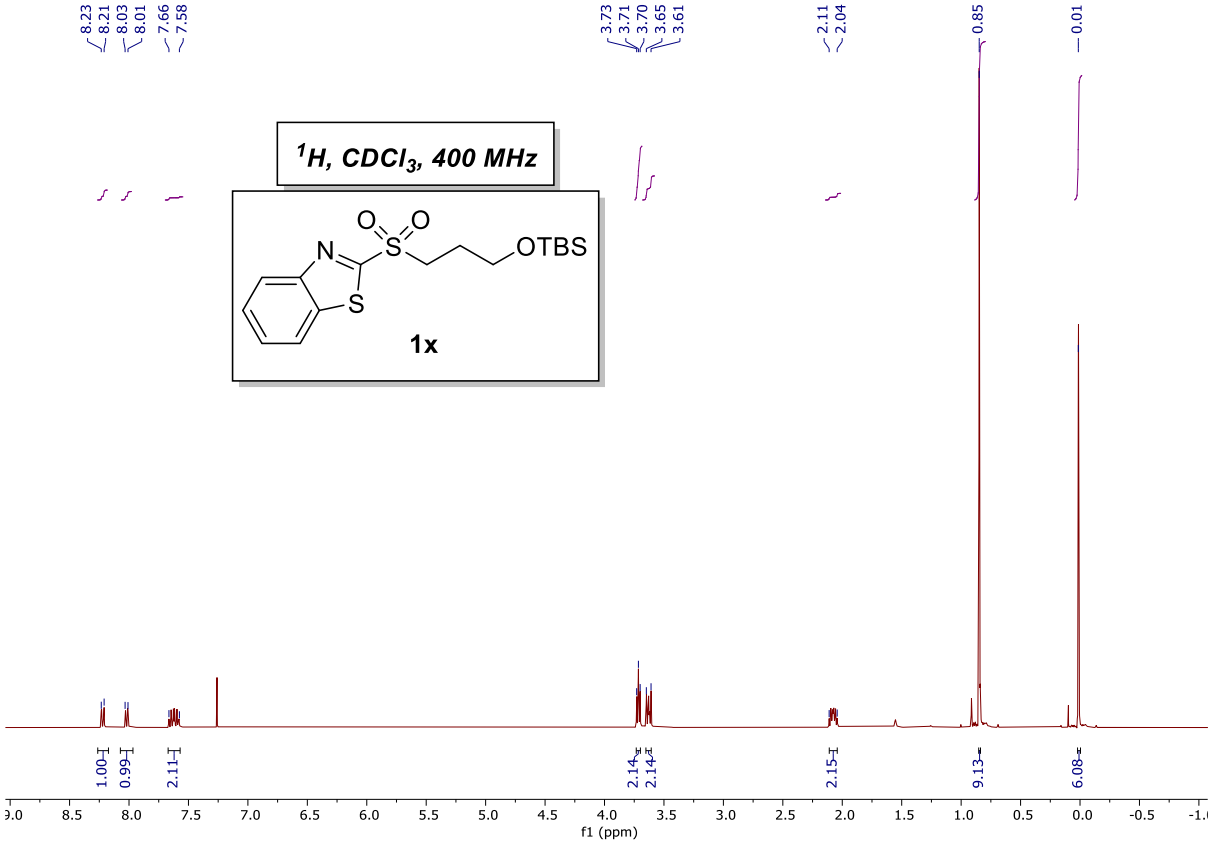


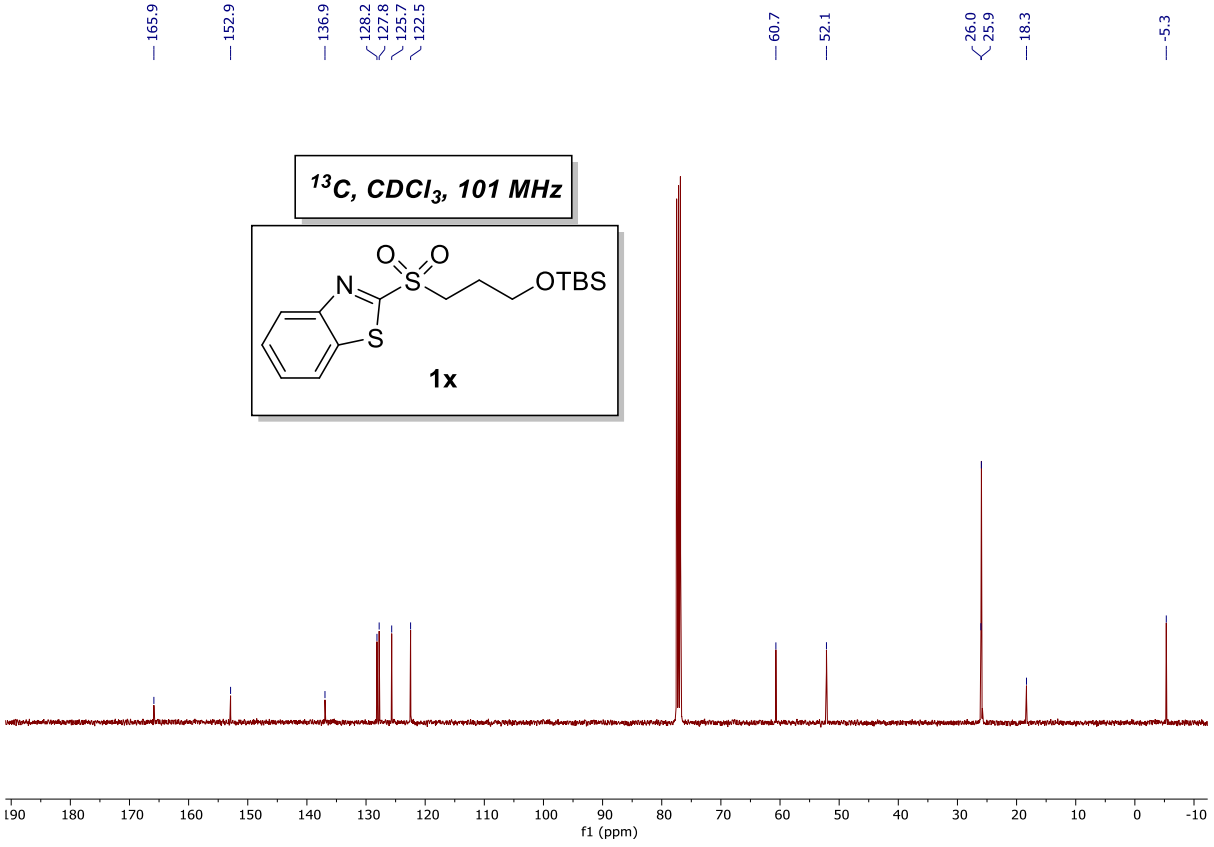
^{13}C, $CDCl_3$, 101 MHz

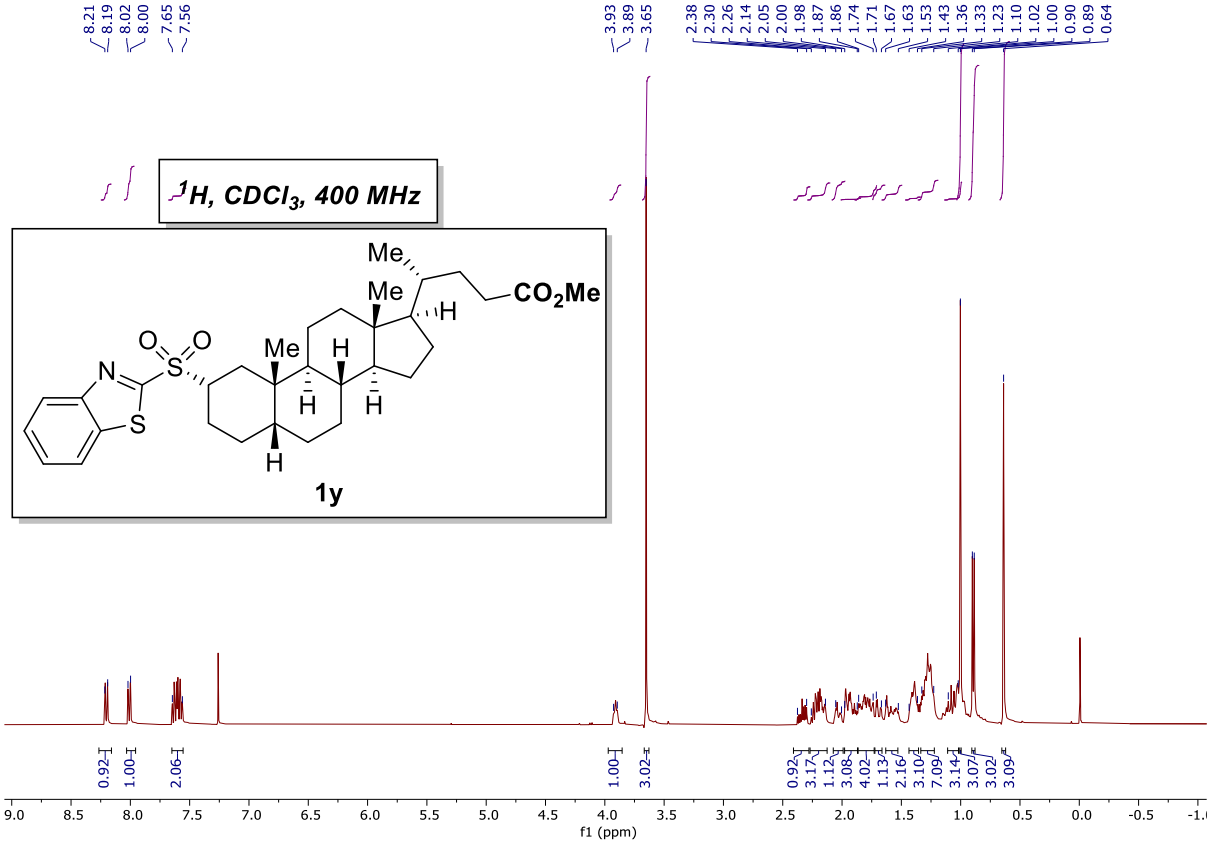
1v

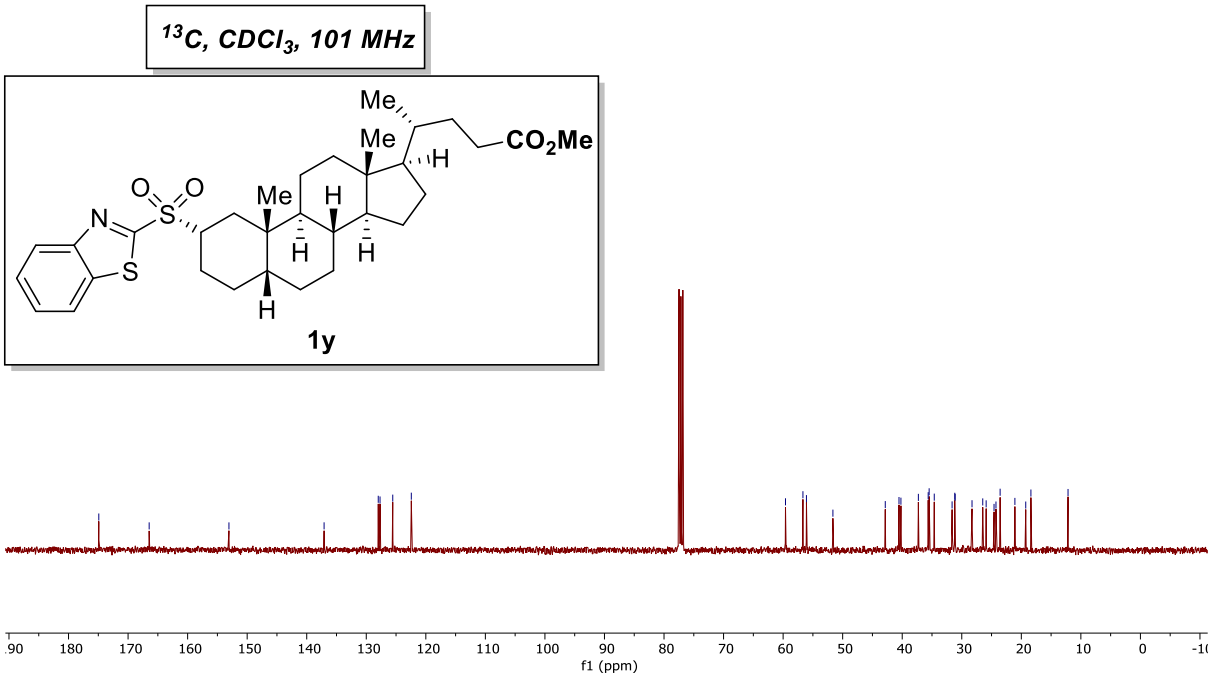

8.23
8.20
8.04
8.02
7.67
7.59
4.19
4.17
4.16
3.63
3.59
2.27
2.20
1.17
1H, CDCl3, 400 MHz
Me
Me
Me
O
O
N
S
O
S
O
1w
1.00
0.98
2.09
2.15
2.17
2.24
9.25
f1 (ppm)

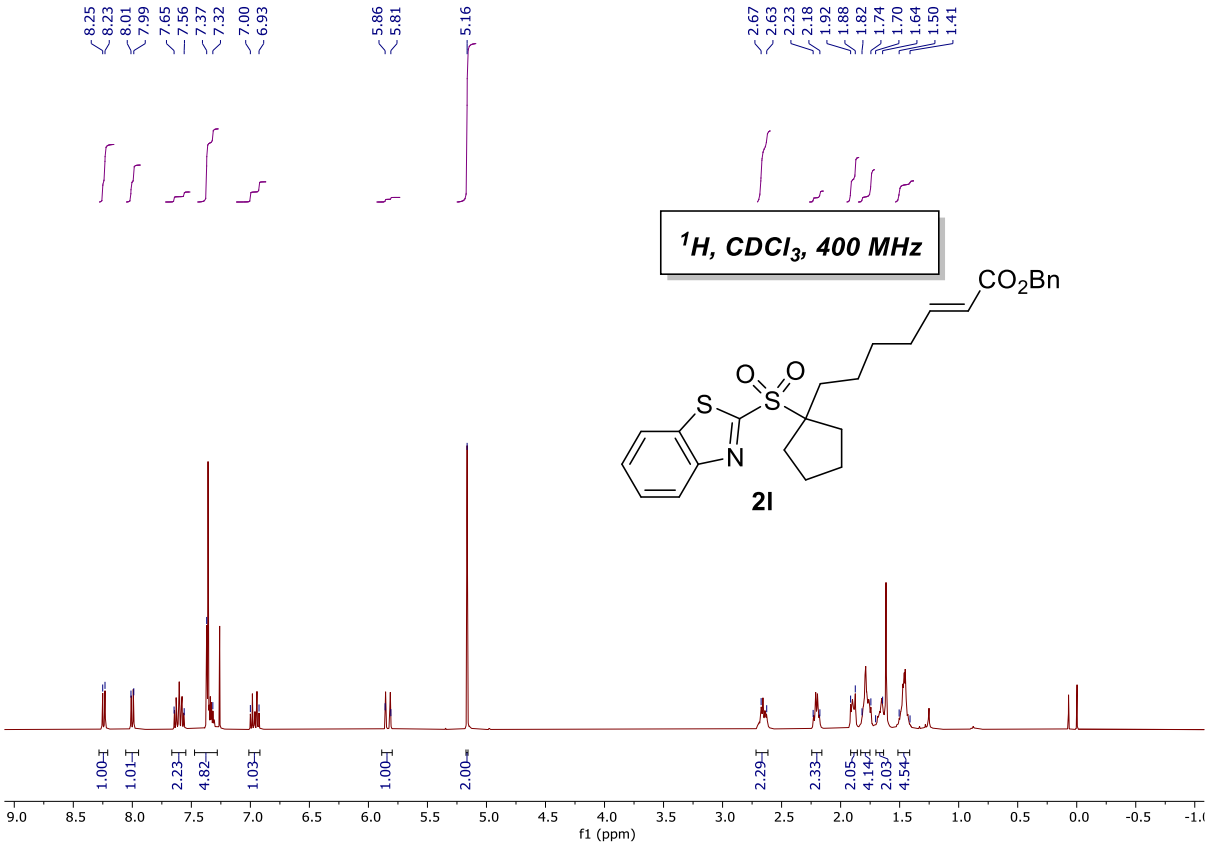

178.3
165.5
152.8
136.9
128.3
127.9
125.6
122.5
61.8
51.8
38.9
27.3
22.5
13C, CDCl3, 101 MHz
Me
Me
Me
O
O
N
S
O
S
O
1w
f1 (ppm)

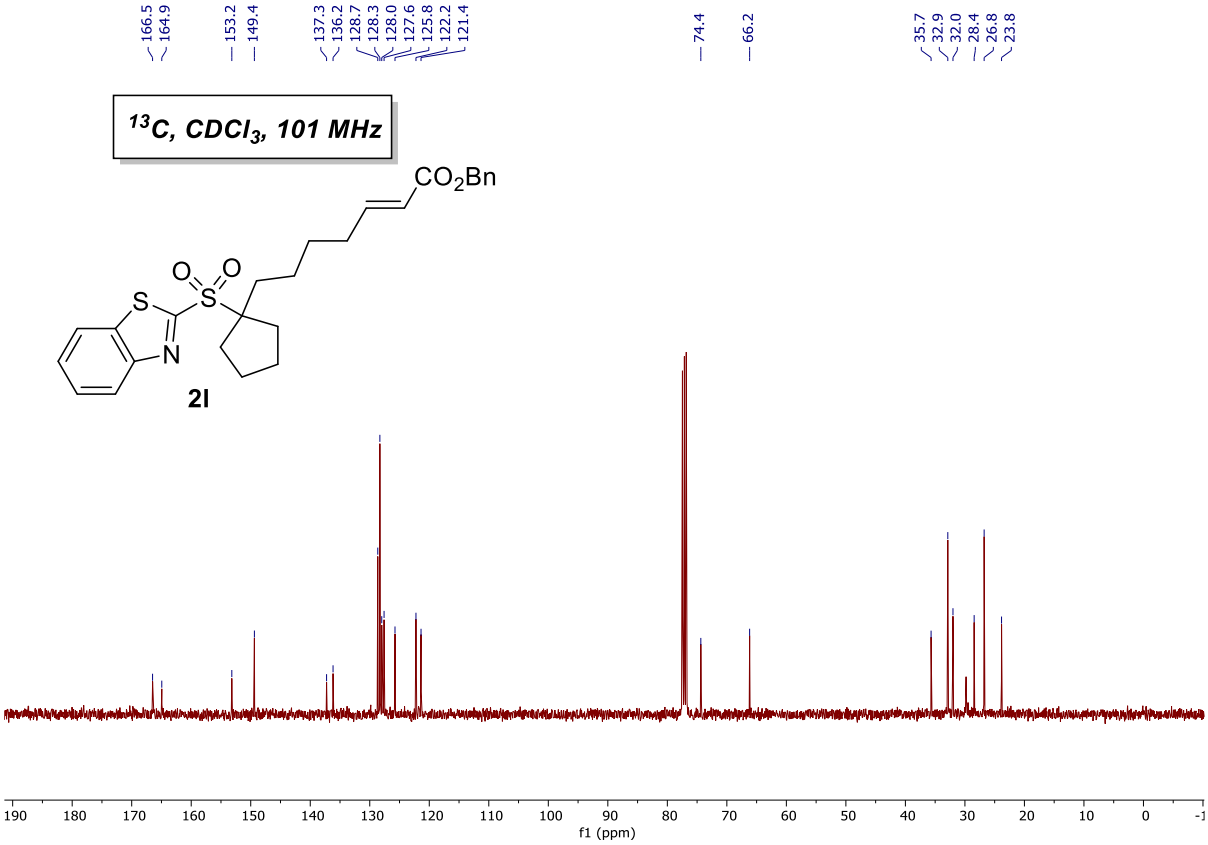

8.23
8.21
8.03
8.01
7.66
7.58
3.73
3.71
3.70
3.65
3.61
2.11
2.04
0.85
0.01
^1H, $CDCl_3$, 400 MHz
O
O
N
S
OTBS
S
1x
1.00
0.99
2.11
2.14
2.14
2.15
9.13
6.08
f1 (ppm)

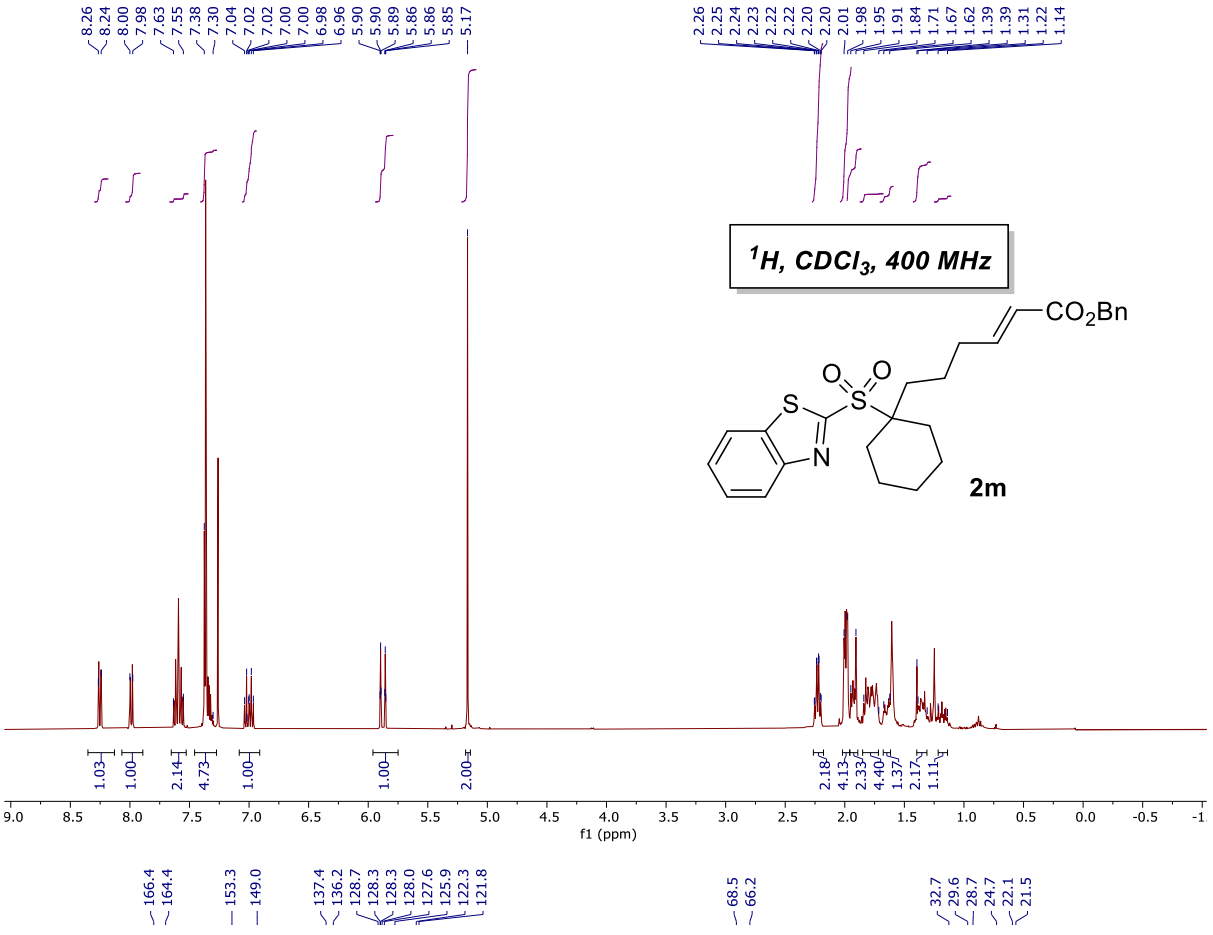

165.9
152.9
136.9
128.2
127.8
125.7
122.5
60.7
52.1
26.0
25.9
18.3
-5.3
^{13}C, $CDCl_3$, 101 MHz
O
O
N
S
OTBS
S
1x
f1 (ppm)

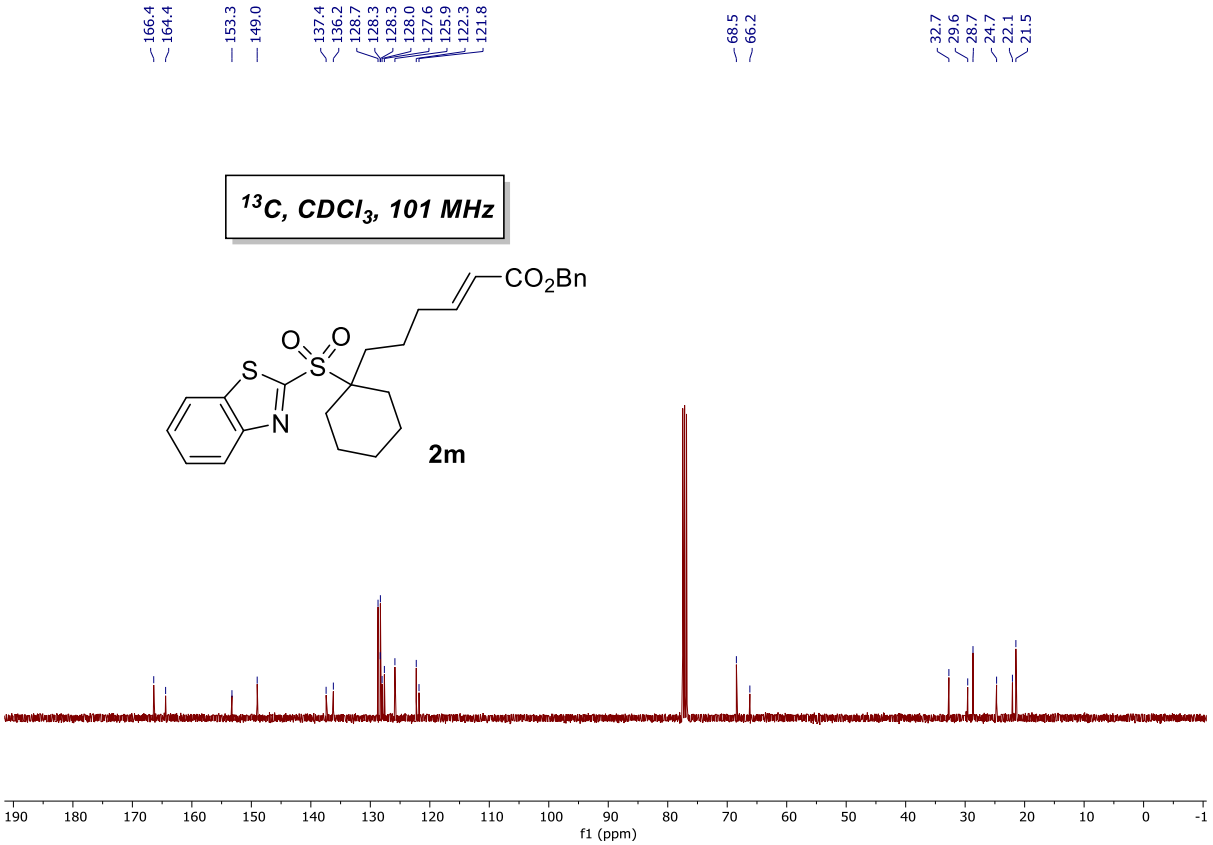

^{1}H, CDCl$_3$, 400 MHz
Me
Me
CO$_2$Me
H
O
O
S
N
S
Me
H
H
H
H
1y
f1 (ppm)

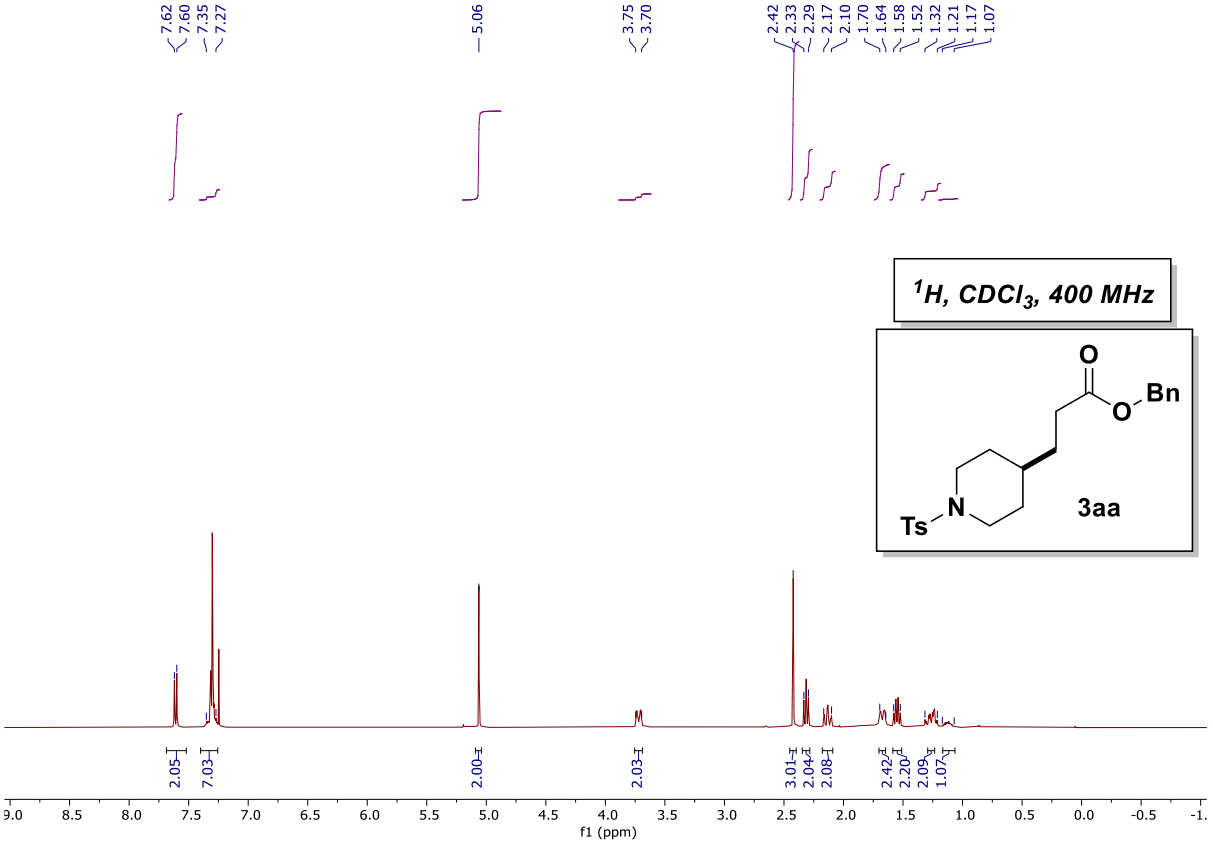

^{13}C, CDCl$_3$, 101 MHz
Me
Me
CO$_2$Me
H
O
O
S
N
S
Me
H
H
H
H
1y
f1 (ppm)


8.25
8.23
8.01
7.99
7.65
7.56
7.37
7.32
7.00
6.93
5.86
5.81
5.16
2.67
2.63
2.23
2.18
1.92
1.88
1.82
1.74
1.70
1.64
1.50
1.41
1H, CDCl3, 400 MHz
CO2Bn
O
O
S
S
N
2l
1.00
1.01
2.23
4.82
1.03
1.00
2.00
2.29
2.33
2.05
4.14
2.03
4.54
f1 (ppm)

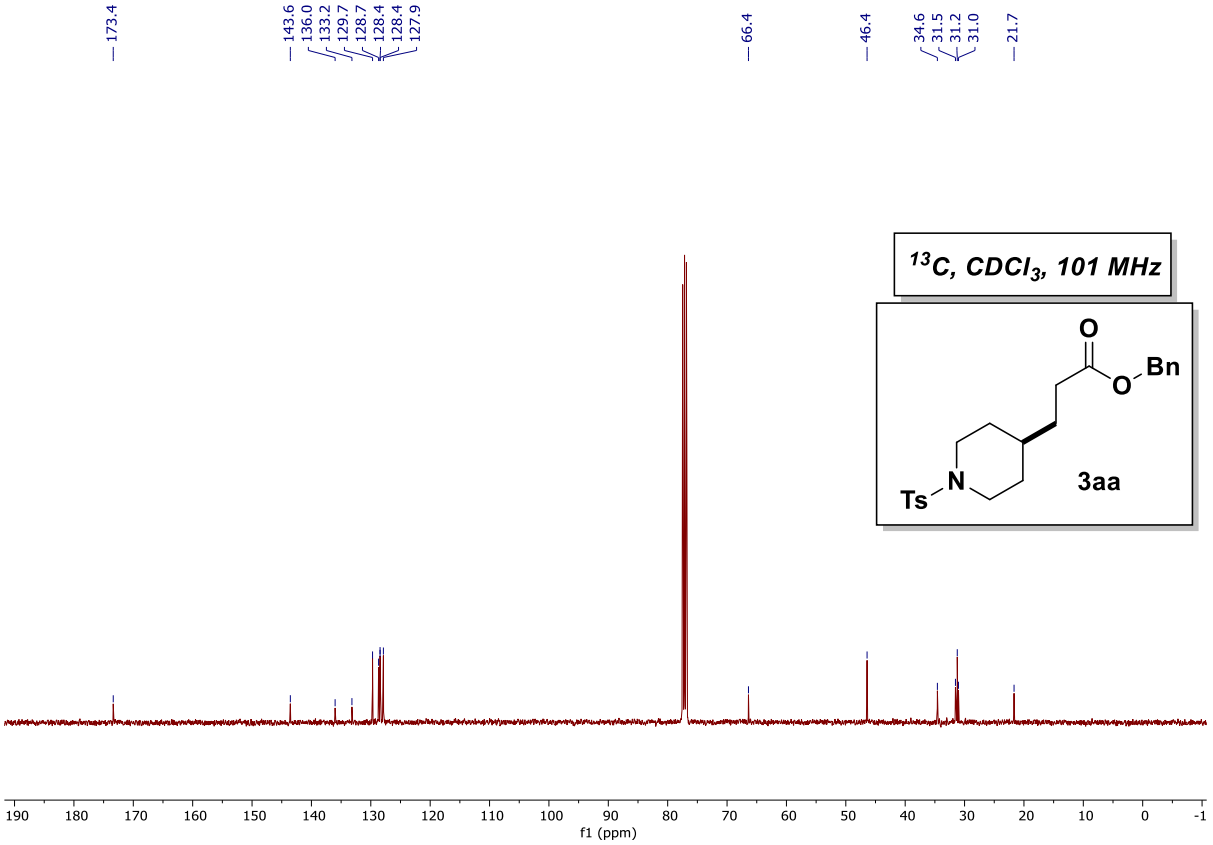

166.5
164.9
153.2
149.4
137.3
136.2
128.7
128.3
128.0
127.6
125.8
122.2
121.4
74.4
66.2
35.7
32.9
32.0
28.4
26.8
23.8
13C, CDCl3, 101 MHz
CO2Bn
O
O
S
S
N
2l
f1 (ppm)


8.26
8.24
8.00
7.98
7.63
7.55
7.38
7.30
7.04
7.02
7.02
7.00
7.00
6.98
6.96
5.90
5.90
5.89
5.86
5.85
5.17
2.26
2.25
2.24
2.23
2.22
2.22
2.20
2.20
2.01
1.98
1.95
1.91
1.84
1.71
1.67
1.62
1.39
1.39
1.31
1.22
1.14
1H, CDCl3, 400 MHz
CO2Bn
O
O
S
S
N
2m
1.03
1.00
2.14
4.73
1.00
1.00
2.00
2.18
4.13
2.33
4.40
1.37
2.17
1.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

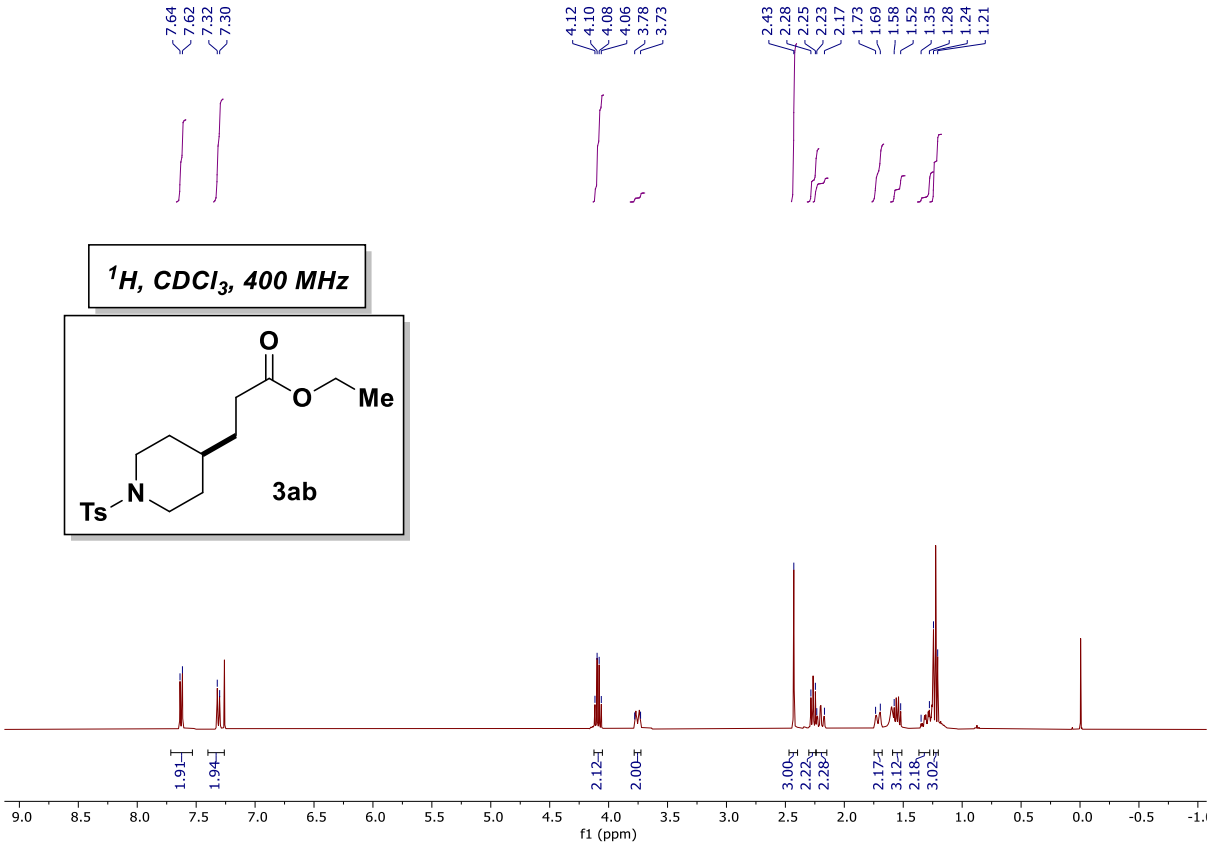

166.4
164.4
153.3
149.0
137.4
136.2
128.7
128.3
128.3
128.0
127.6
125.9
122.3
121.8
68.5
66.2
32.7
29.6
28.7
24.7
22.1
21.5
13C, CDCl3, 101 MHz
CO2Bn
O
O
S
S
N
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

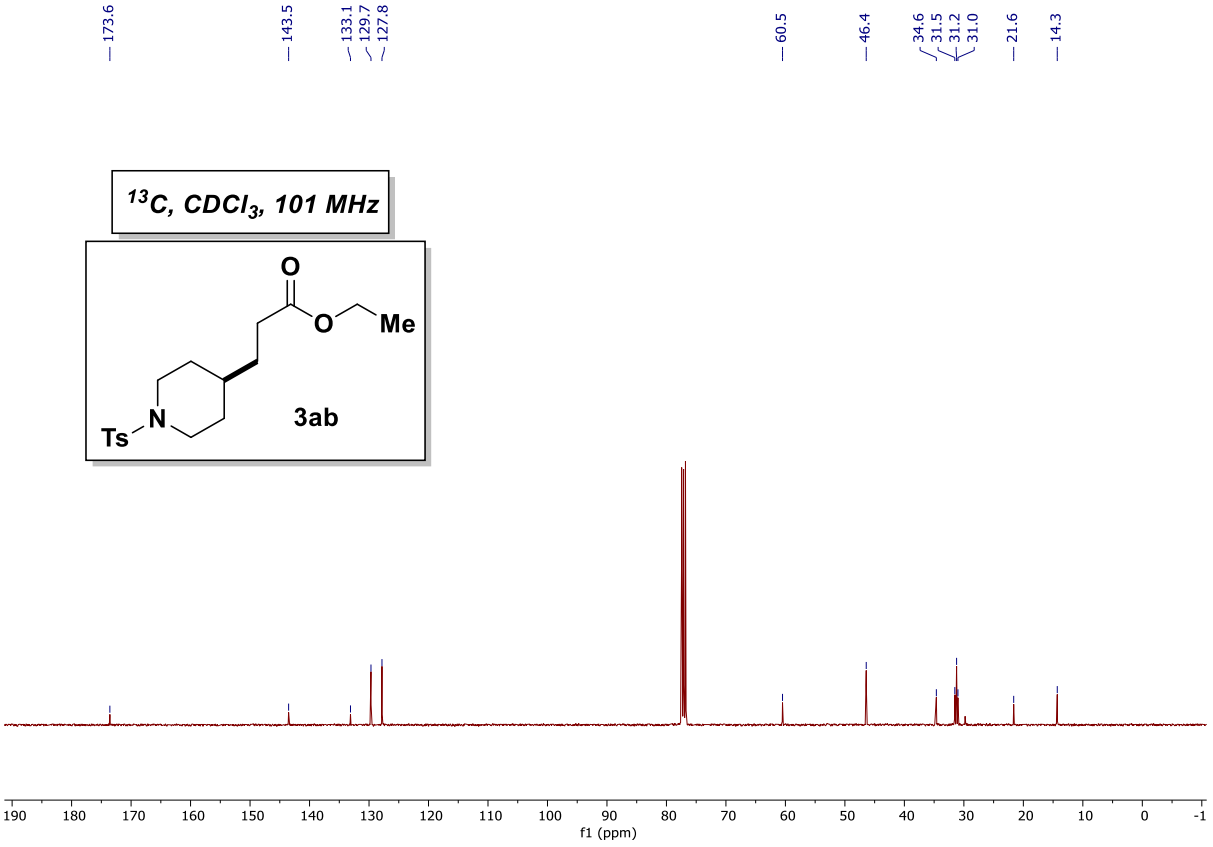


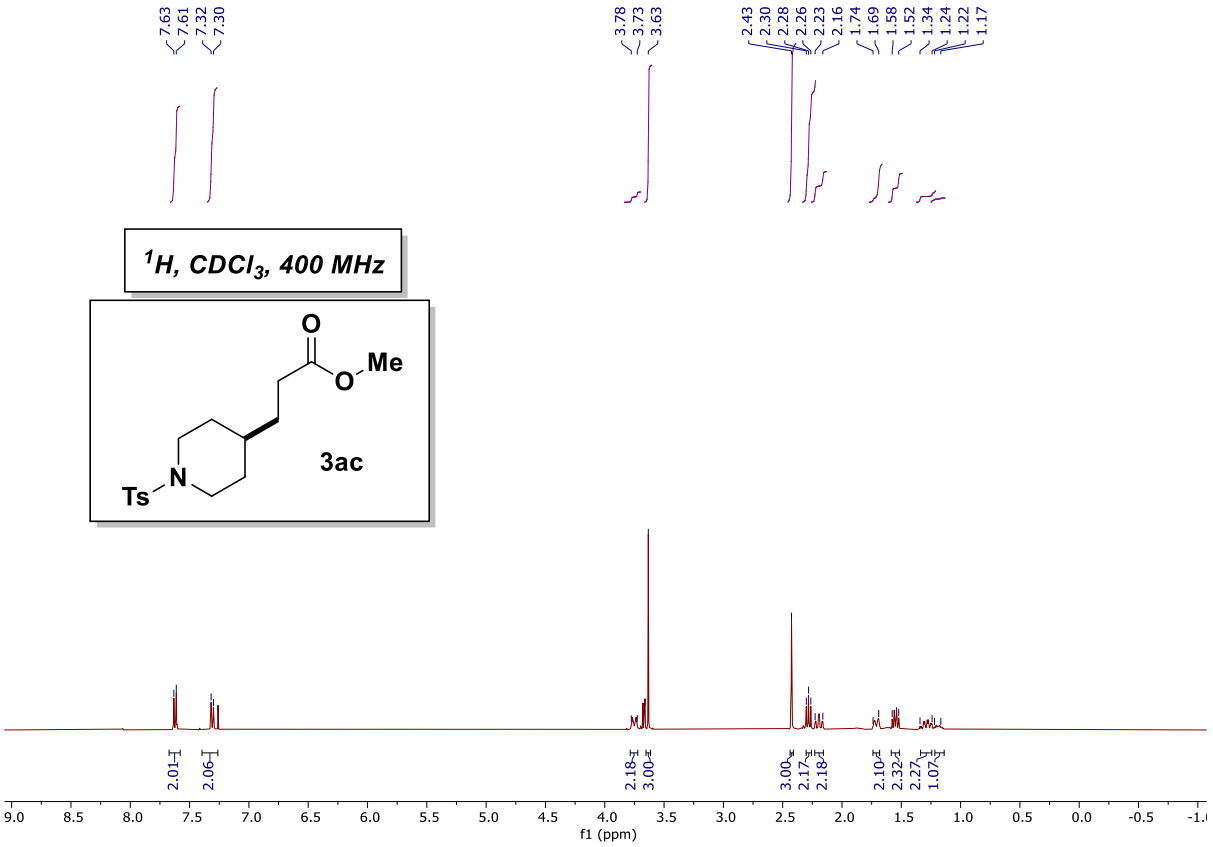
^{1}H, $CDCl_3$, 400 MHz

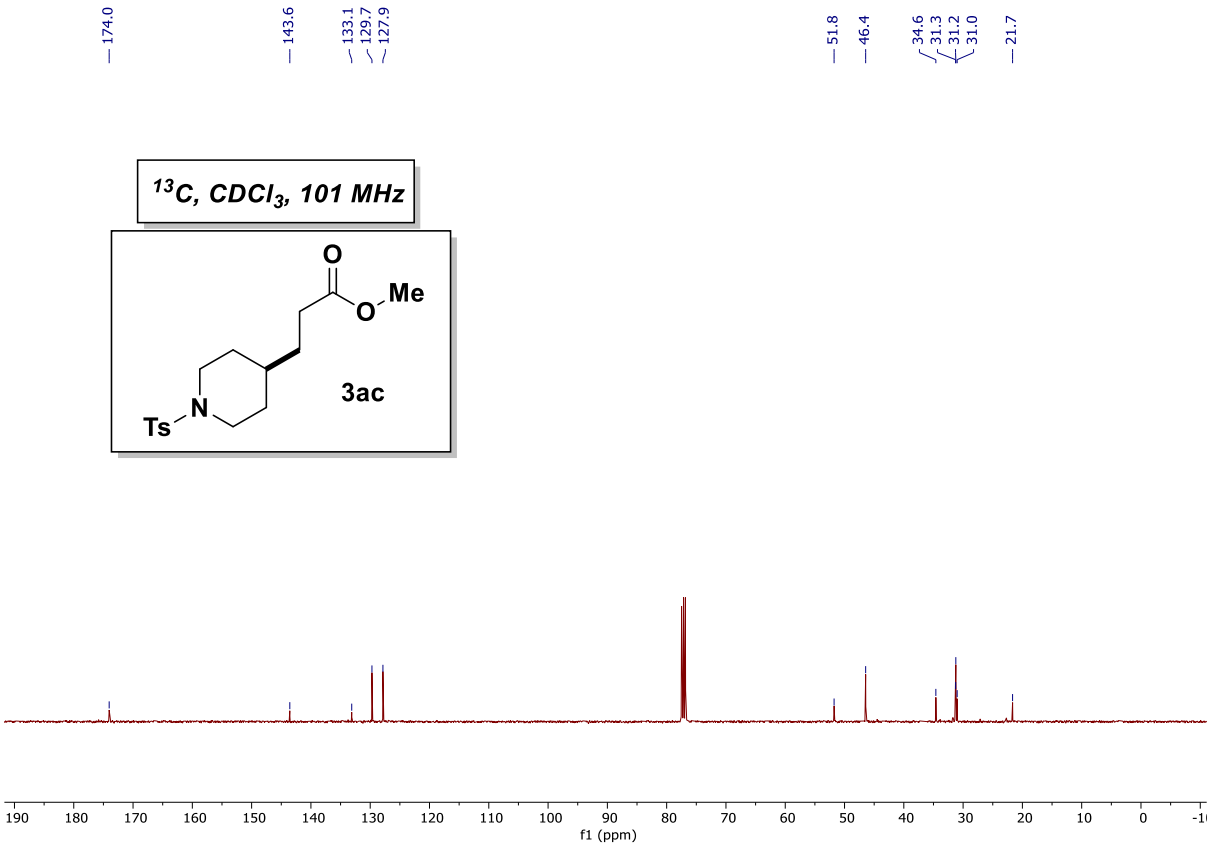


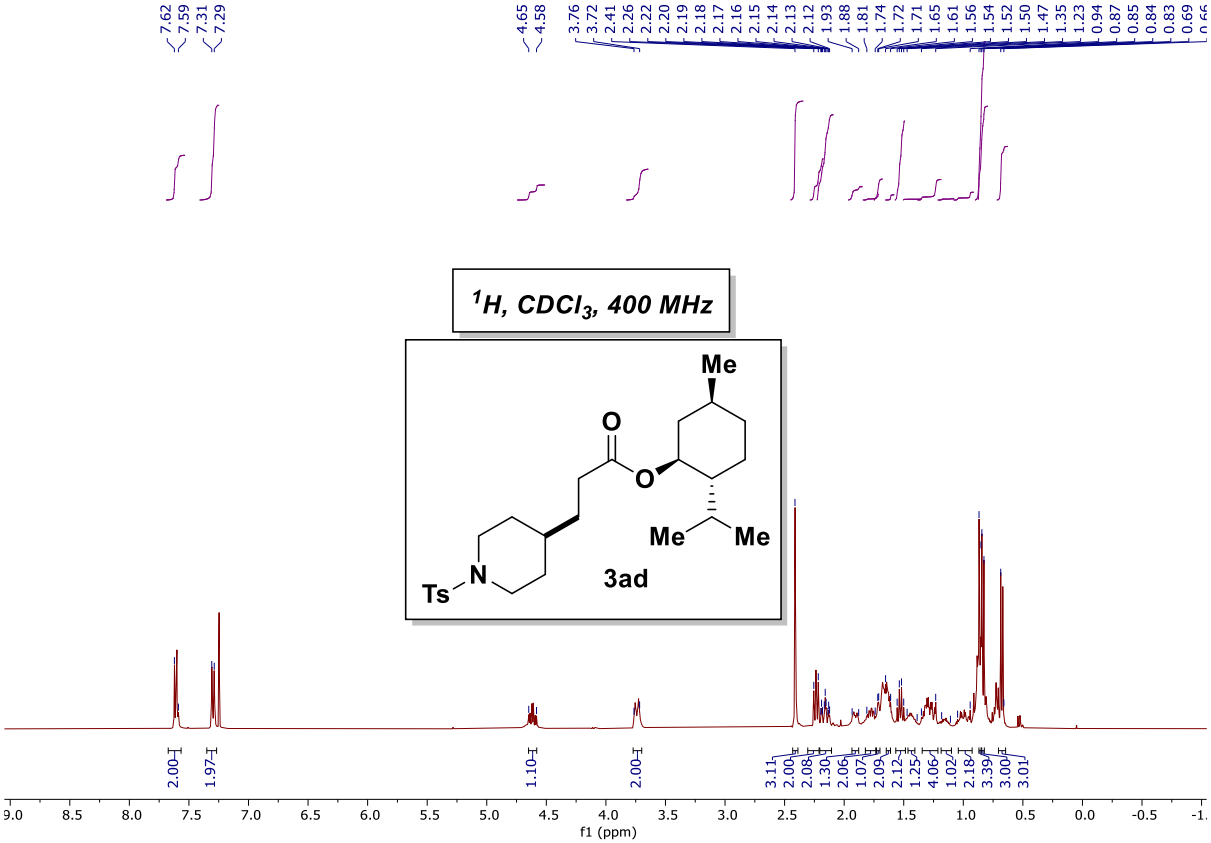
^{13}C, $CDCl_3$, 101 MHz

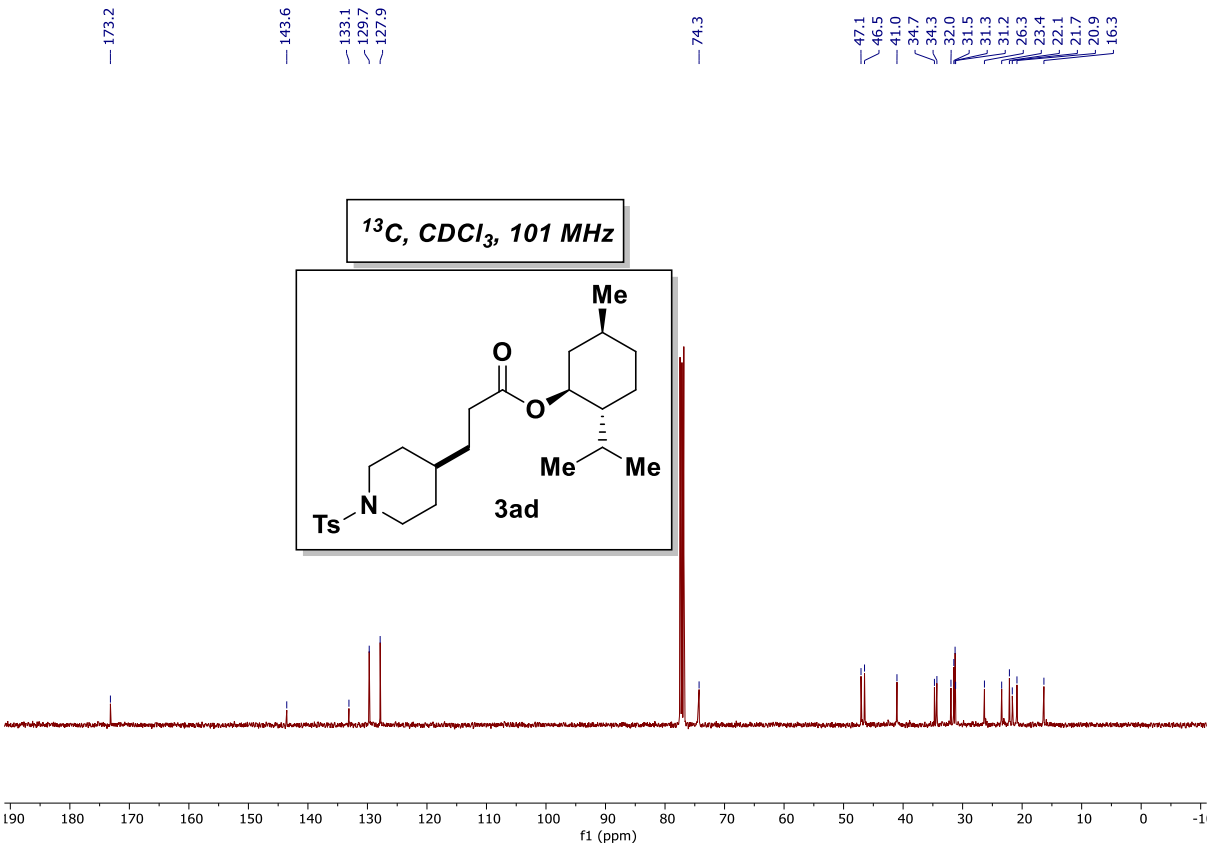

7.64
7.62
7.32
7.30
4.12
4.10
4.08
4.06
3.78
3.73
2.43
2.28
2.25
2.23
2.17
1.73
1.69
1.58
1.52
1.35
1.28
1.24
1.21
^{1}H, $CDCl_3$, 400 MHz
O
O
Me
N
Ts
3ab
1.91
1.94
2.12
2.00
3.00
2.22
2.28
2.17
3.12
2.18
3.02
f1 (ppm)

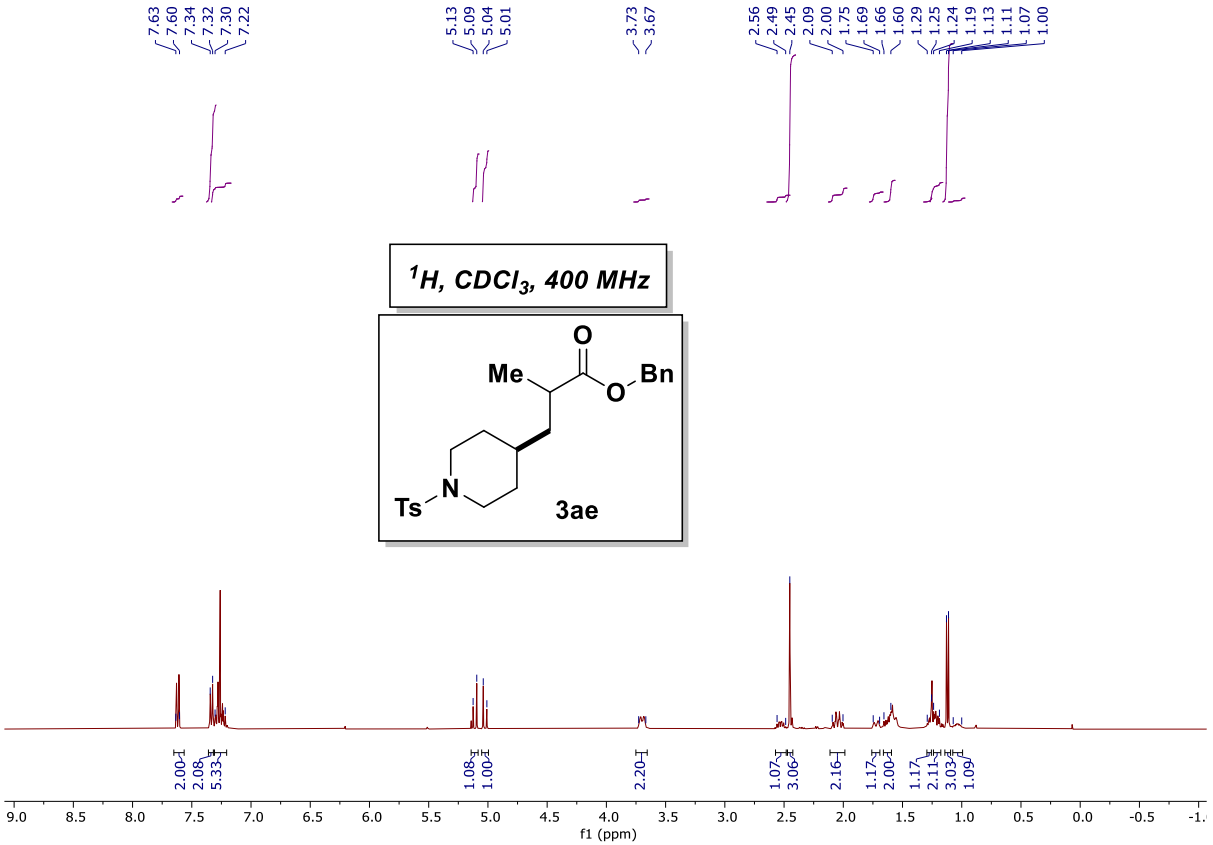

173.6
143.5
133.1
129.7
127.8
60.5
46.4
34.6
31.5
31.2
31.0
21.6
14.3
^{13}C, $CDCl_3$, 101 MHz
O
O
Me
N
Ts
3ab
f1 (ppm)


7.63
7.61
7.32
7.30
3.78
3.73
3.63
2.43
2.30
2.28
2.26
2.23
2.16
1.74
1.69
1.58
1.52
1.34
1.24
1.22
1.17
^{1}H, $CDCl_3$, 400 MHz
O
Me
O
N
Ts
3ac
2.01
2.06
2.18
3.00
3.00
2.17
2.18
2.10
2.32
2.27
1.07
f1 (ppm)


174.0
143.6
133.1
129.7
127.9
51.8
46.4
34.6
31.3
31.2
31.0
21.7
^{13}C, $CDCl_3$, 101 MHz
O
Me
O
N
Ts
3ac
f1 (ppm)


7.62
7.59
7.31
7.29
4.65
4.58
3.76
3.72
2.41
2.26
2.22
2.20
2.19
2.18
2.17
2.16
2.15
2.14
2.13
2.12
1.93
1.88
1.81
1.74
1.72
1.71
1.65
1.61
1.56
1.54
1.52
1.50
1.47
1.35
1.23
0.94
0.87
0.85
0.84
0.83
0.69
^{1}H, CDCl$_3$, 400 MHz
Me
O
O
Me
Me
N
Ts
3ad
2.00
1.97
1.10
2.00
3.11
2.00
2.08
1.30
2.06
1.07
2.09
2.12
1.25
4.06
1.02
2.18
3.39
3.00
3.01
f1 (ppm)


173.2
143.6
133.1
129.7
127.9
74.3
47.1
46.5
41.0
34.7
34.3
32.0
31.5
31.3
31.2
26.3
23.4
22.1
21.7
20.9
16.3
^{13}C, CDCl$_3$, 101 MHz
Me
O
O
Me
Me
N
Ts
3ad
f1 (ppm)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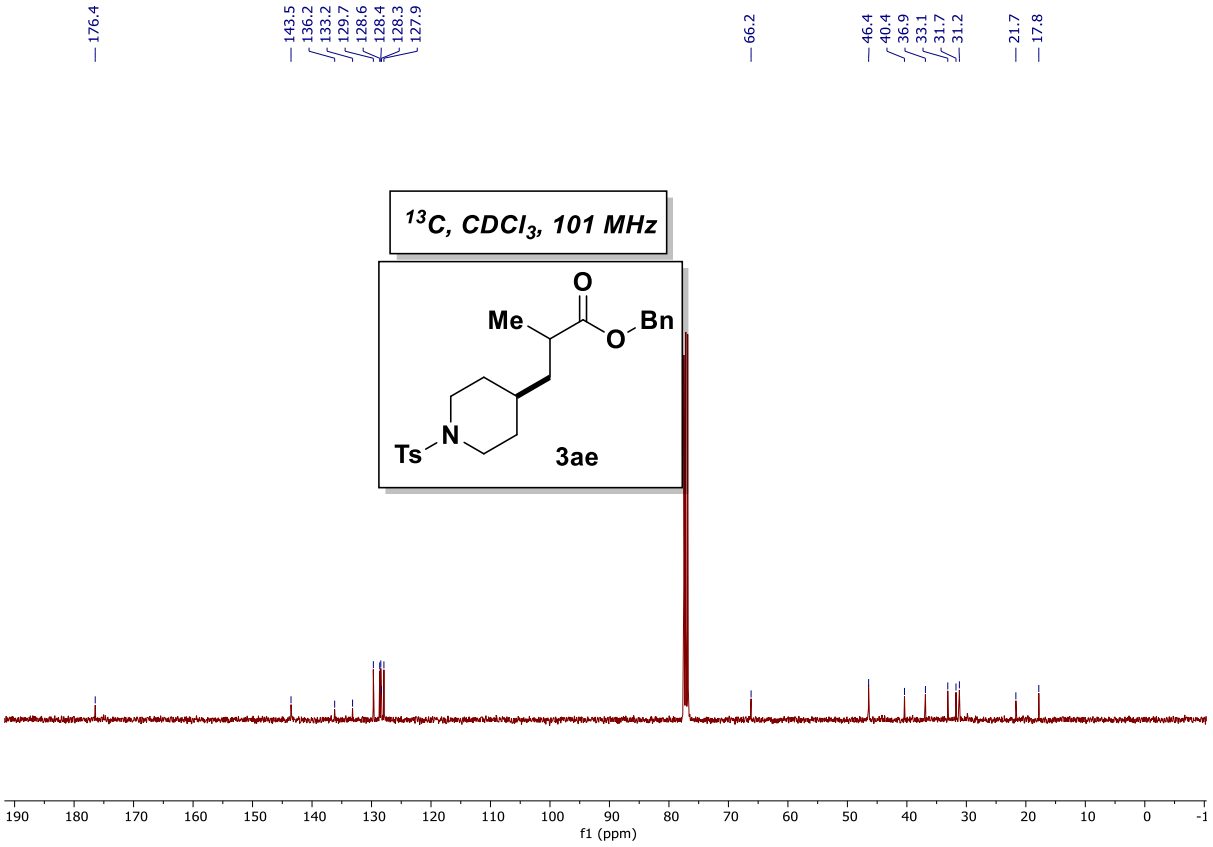
7.60
7.34
7.32
7.30
7.22
5.13
5.09
5.04
5.01
3.73
3.67
2.56
2.49
2.45
2.09
2.00
1.75
1.69
1.66
1.60
1.29
1.25
1.24
1.19
1.13
1.11
1.07
1.00
^{1}H, $CDCl_3$, 400 MHz
Me
O
Bn
Ts
N
3ae
2.00
2.08
5.33
1.08
1.00
2.20
1.07
3.06
2.16
1.17
2.00
1.17
2.11
3.03
1.09
f1 (ppm)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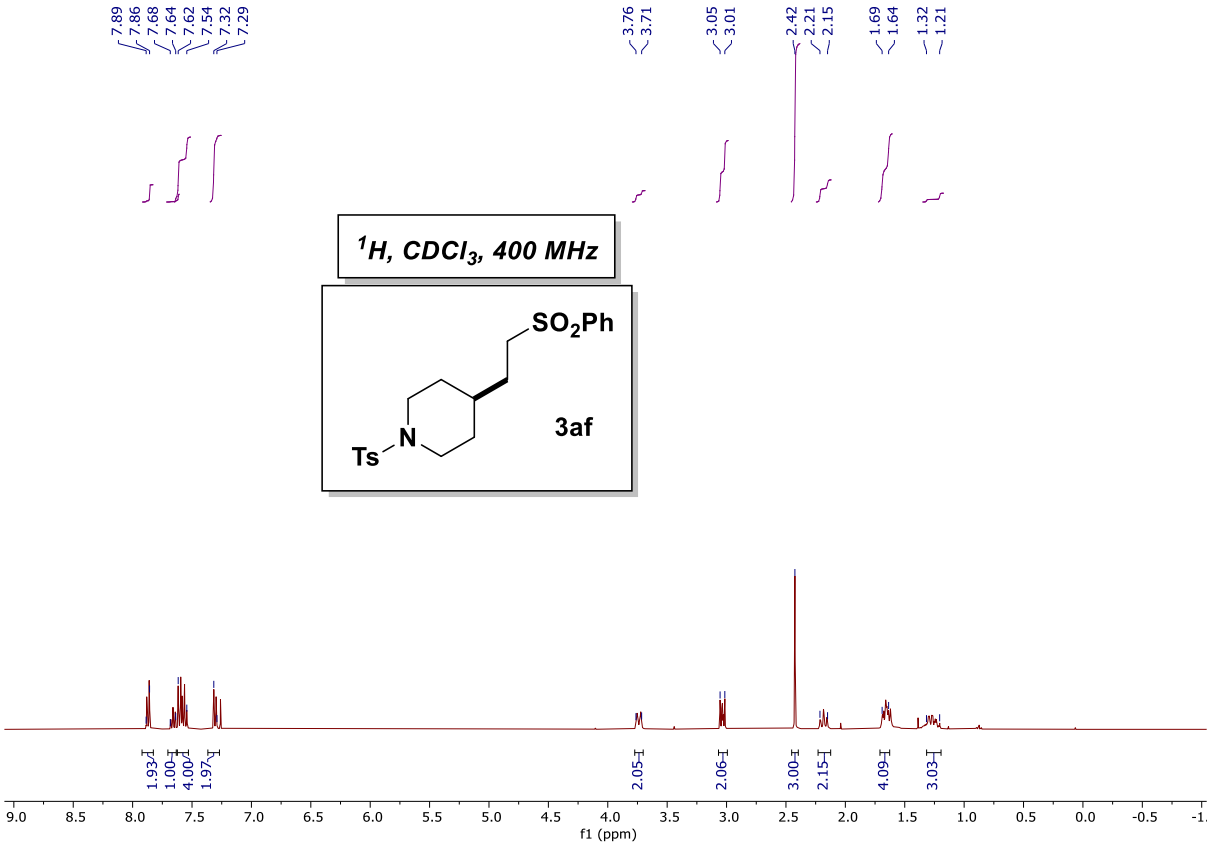
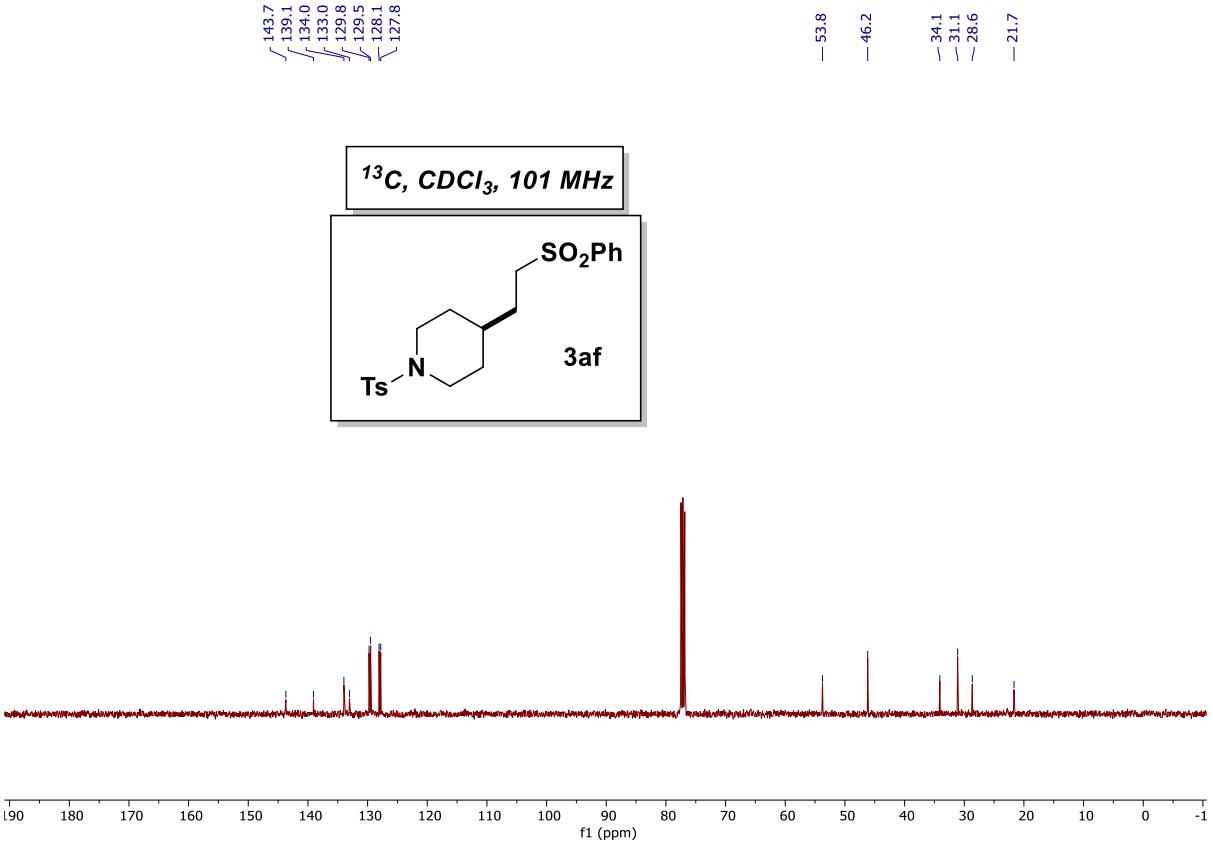
143.5
136.2
133.2
129.7
128.6
128.4
128.3
127.9
66.2
46.4
40.4
36.9
33.1
31.7
31.2
21.7
17.8
^{13}C, $CDCl_3$, 101 MHz
Me
O
Bn
Ts
N
3ae
f1 (ppm)


7.89
7.86
7.68
7.64
7.62
7.54
7.32
7.29
3.76
3.71
3.05
3.01
2.42
2.21
2.15
1.69
1.64
1.32
1.21
1H, CDCl3, 400 MHz
SO2Ph
Ts
N
3af
1.93
1.00
4.00
1.97
2.05
2.06
3.00
2.15
4.09
3.03
f1 (ppm)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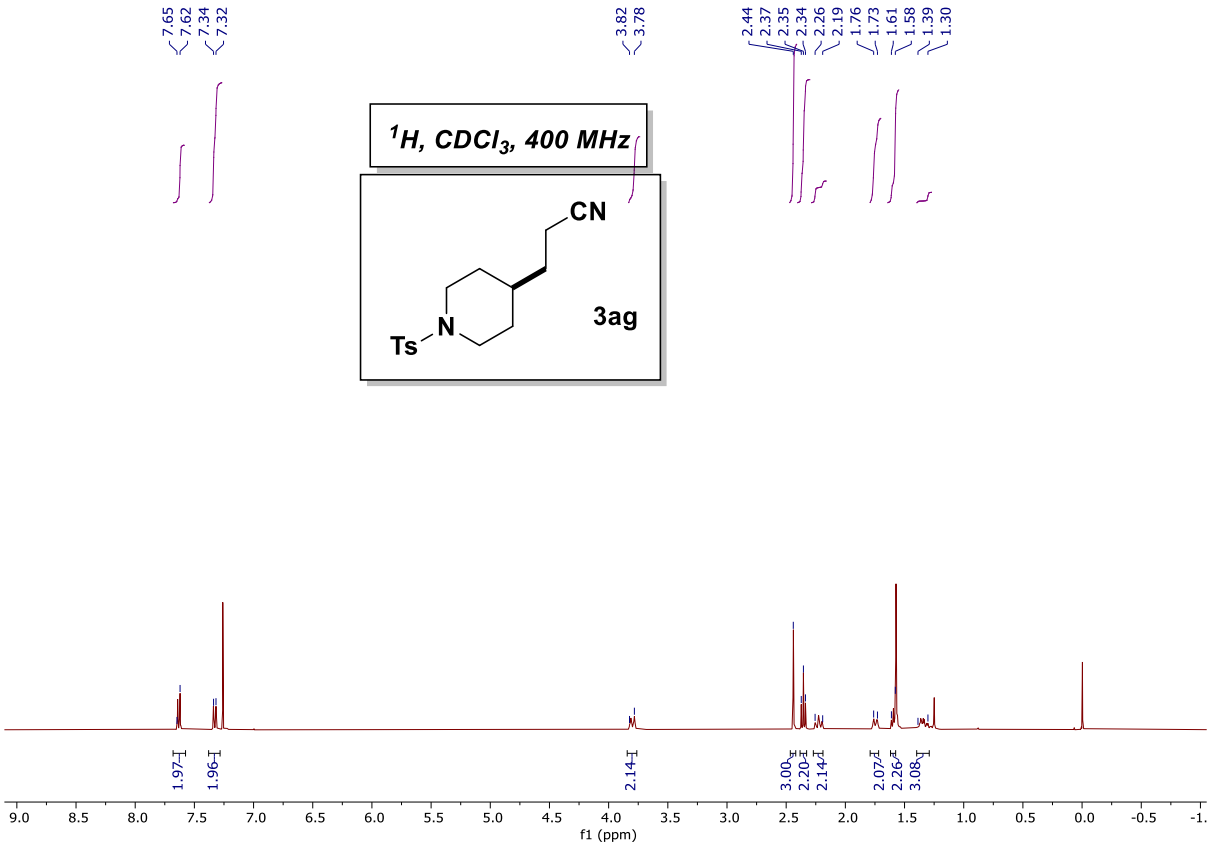
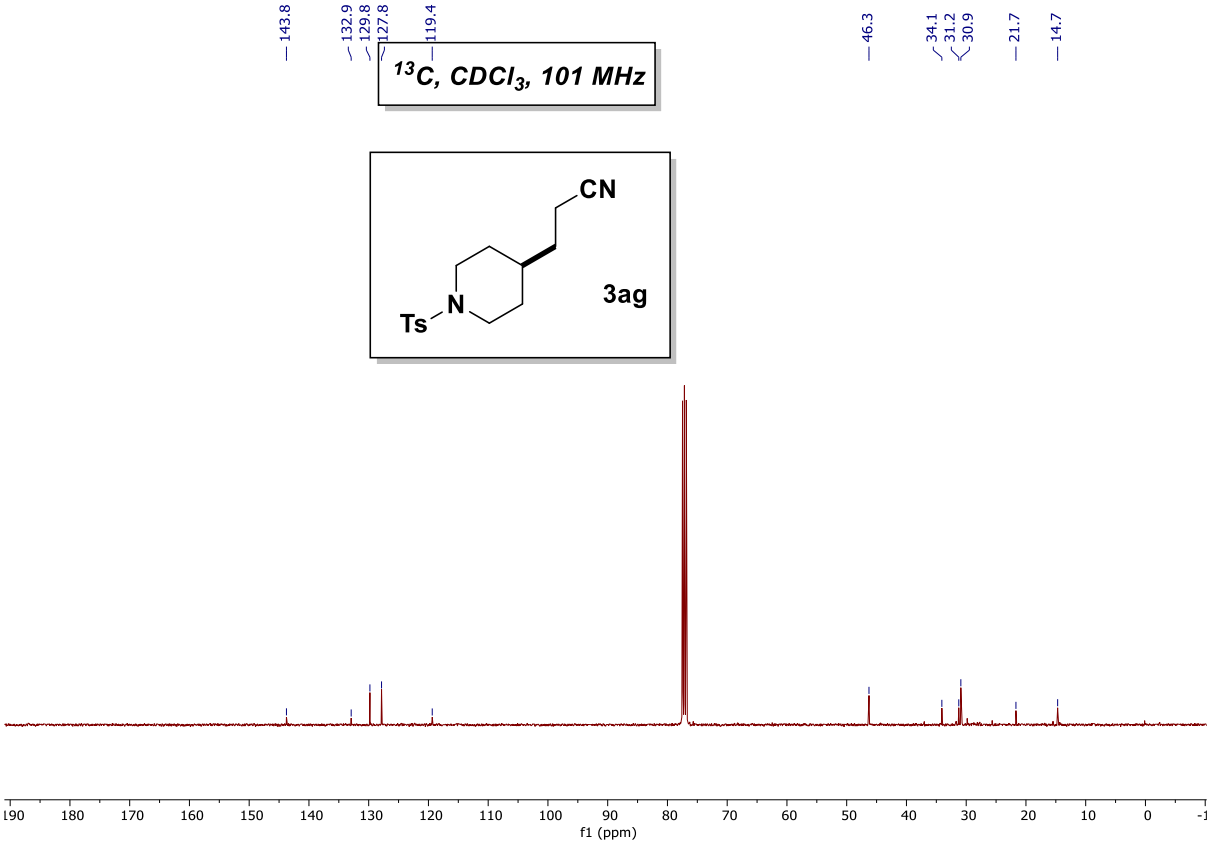
139.1
134.0
133.0
129.8
129.5
128.1
127.8
53.8
46.2
34.1
31.1
28.6
21.7
13C, CDCl3, 101 MHz
SO2Ph
Ts
N
3af
f1 (ppm)


7.65
7.62
7.34
7.32
3.82
3.78
2.44
2.37
2.35
2.34
2.26
2.19
1.76
1.73
1.61
1.58
1.39
1.30
^{1}H, $CDCl_3$, 400 MHz
CN
N
Ts
3ag
1.97
1.96
2.14
3.00
2.20
2.14
2.07
2.26
3.08
f1 (ppm)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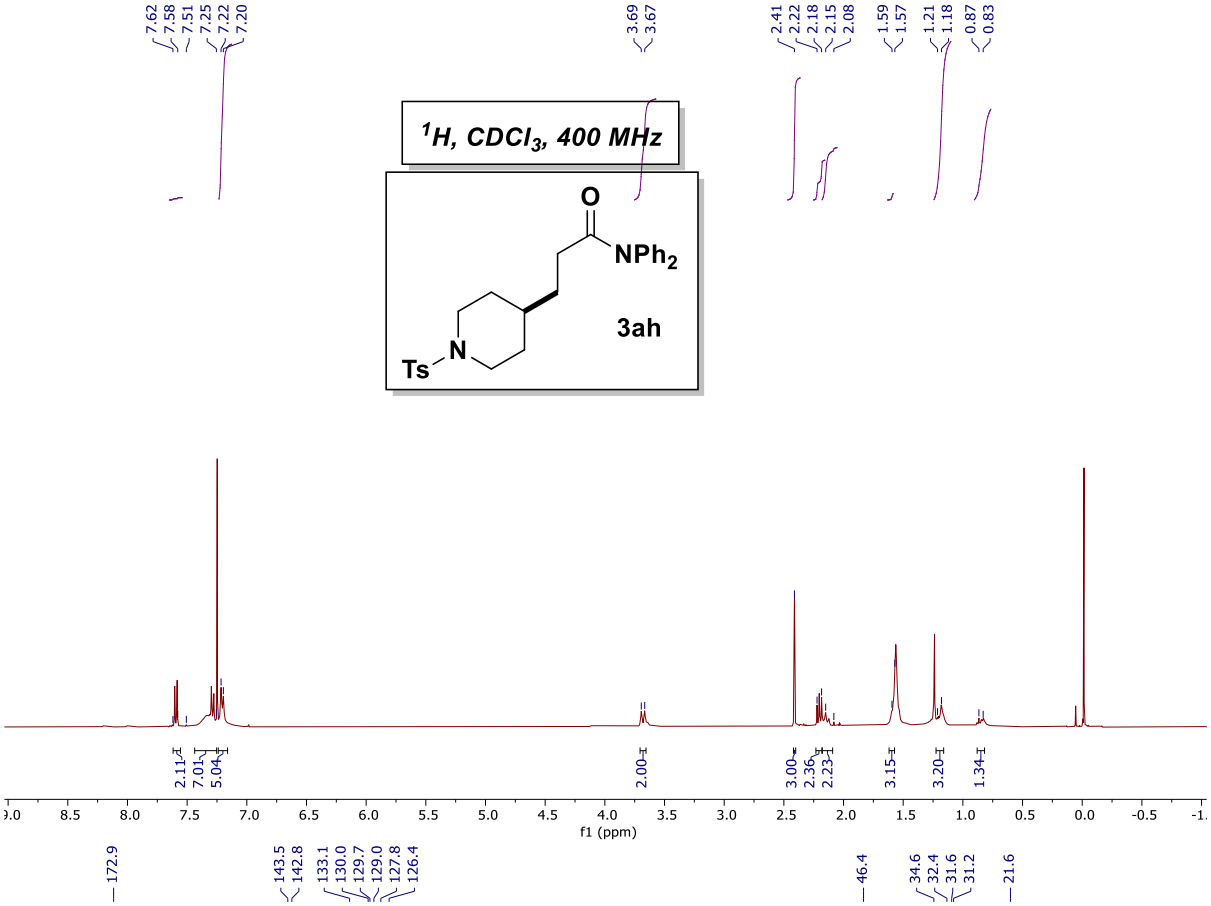
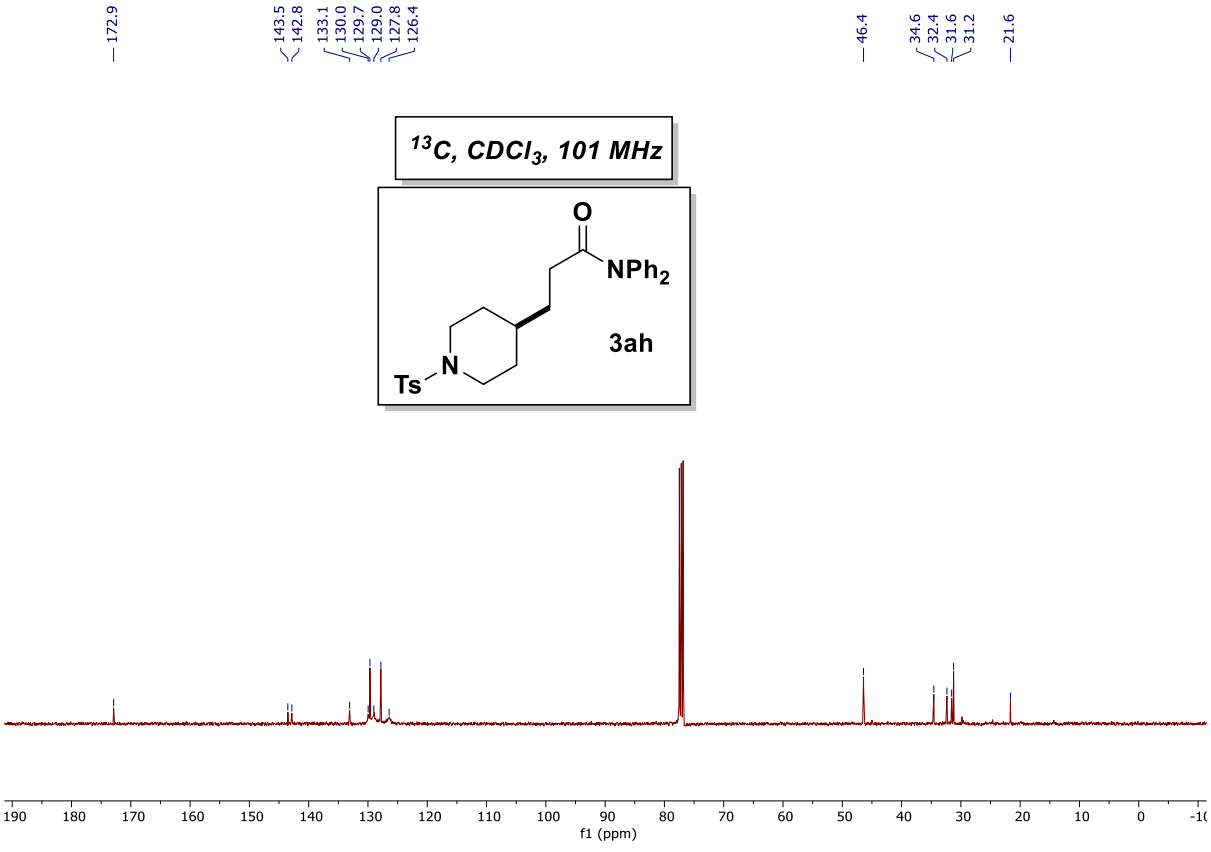
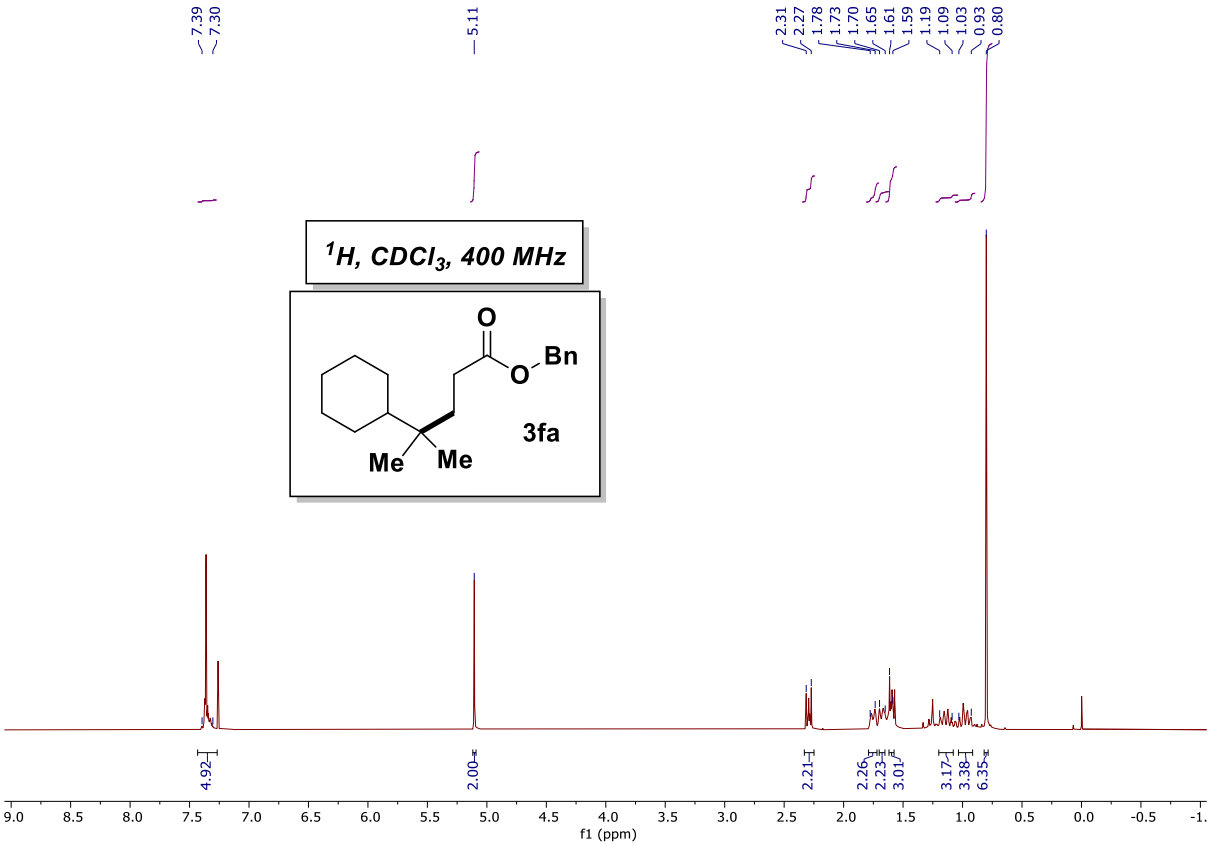
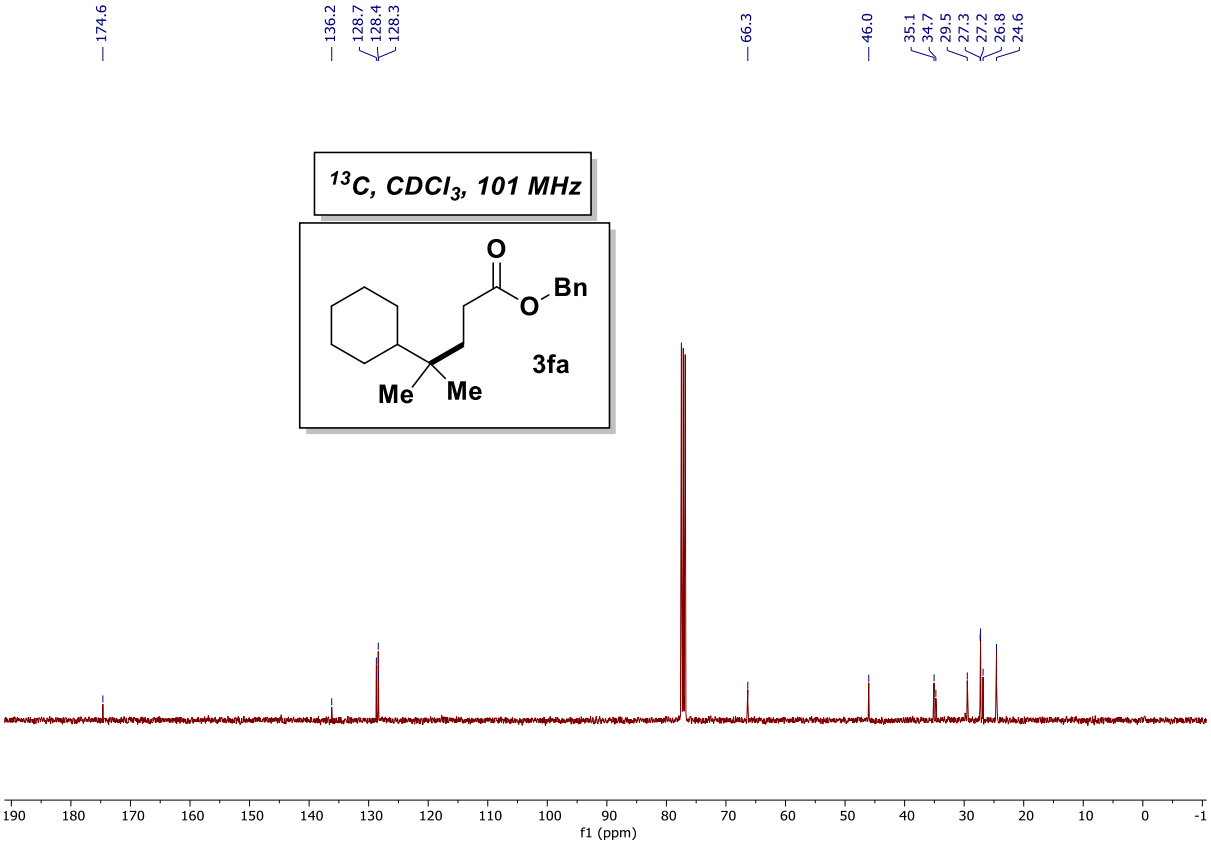
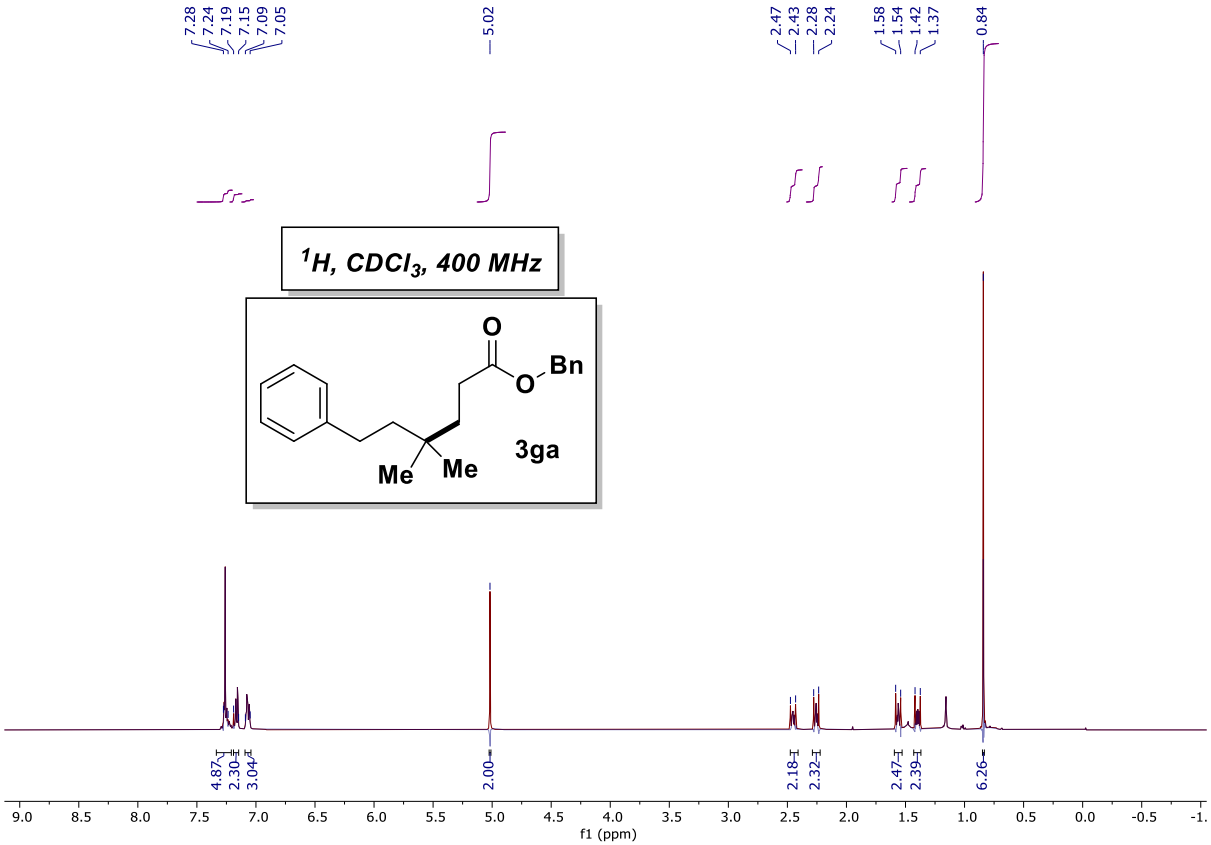
132.9
129.8
127.8
119.4
46.3
34.1
31.2
30.9
21.7
14.7
^{13}C, $CDCl_3$, 101 MHz
CN
N
Ts
3ag
f1 (ppm)

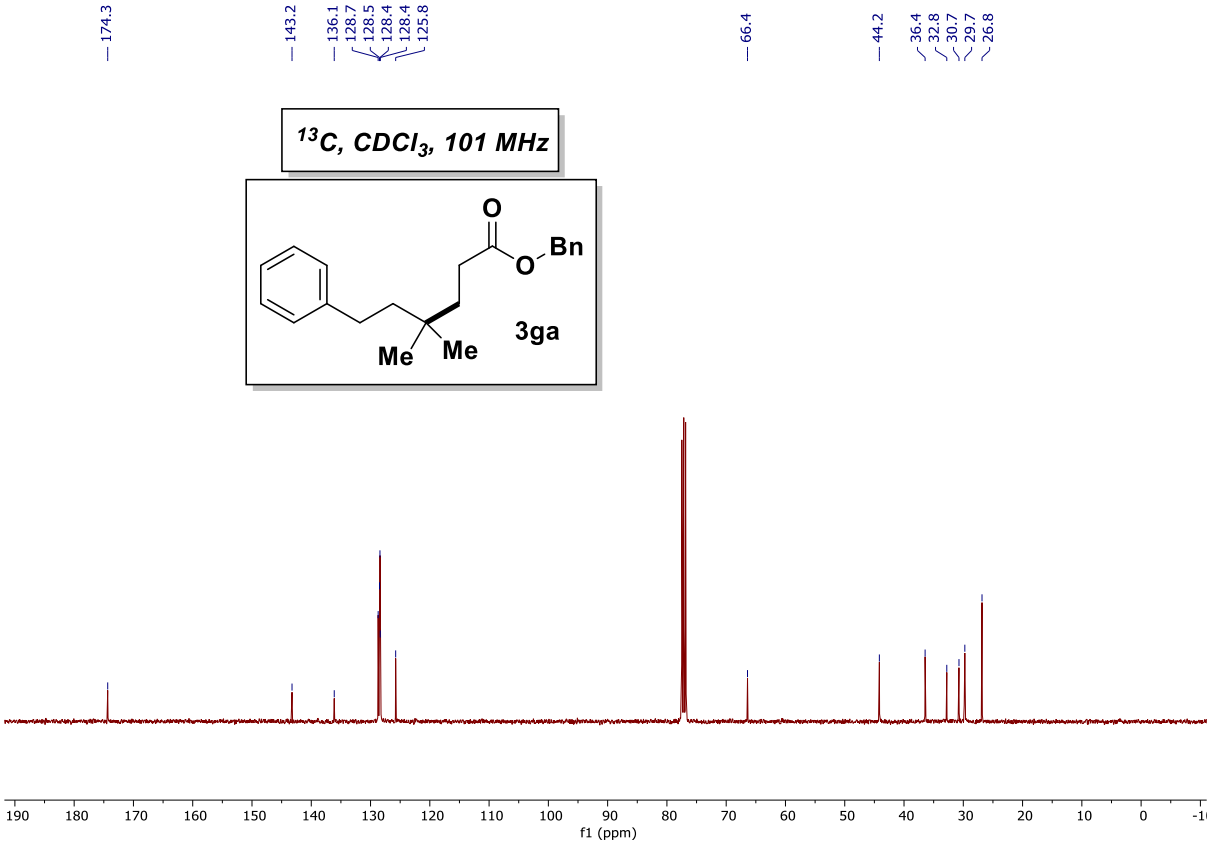

7.62
7.58
7.51
7.25
7.22
7.20
3.69
3.67
2.41
2.22
2.18
2.15
2.08
1.59
1.57
1.21
1.18
0.87
0.83
^{1}H, $CDCl_3$, 400 MHz
O
NPh2
3ah
N
Ts
2.11
7.01
5.04
2.00
3.00
2.36
2.23
3.15
3.20
1.34
f1 (ppm)


172.9
143.5
142.8
133.1
130.0
129.7
129.0
127.8
126.4
46.4
34.6
32.4
31.6
31.2
21.6
^{13}C, $CDCl_3$, 101 MHz
O
NPh2
3ah
N
Ts
f1 (ppm)


7.39
7.30
5.11
2.31
2.27
1.78
1.73
1.70
1.65
1.61
1.59
1.19
1.09
1.03
0.93
0.80
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Me
Me
3fa
4.92
2.00
2.21
2.26
2.23
3.01
3.17
3.38
6.35
f1 (ppm)


174.6
136.2
128.7
128.4
128.3
66.3
46.0
35.1
34.7
29.5
27.3
27.2
26.8
24.6
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Me
Me
3fa
f1 (ppm)


7.28
7.24
7.19
7.15
7.09
7.05
5.02
2.47
2.43
2.28
2.24
1.58
1.54
1.42
1.37
0.84
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Me
Me
3ga
4.87
2.30
3.04
2.00
2.18
2.32
2.47
2.39
6.26
f1 (ppm)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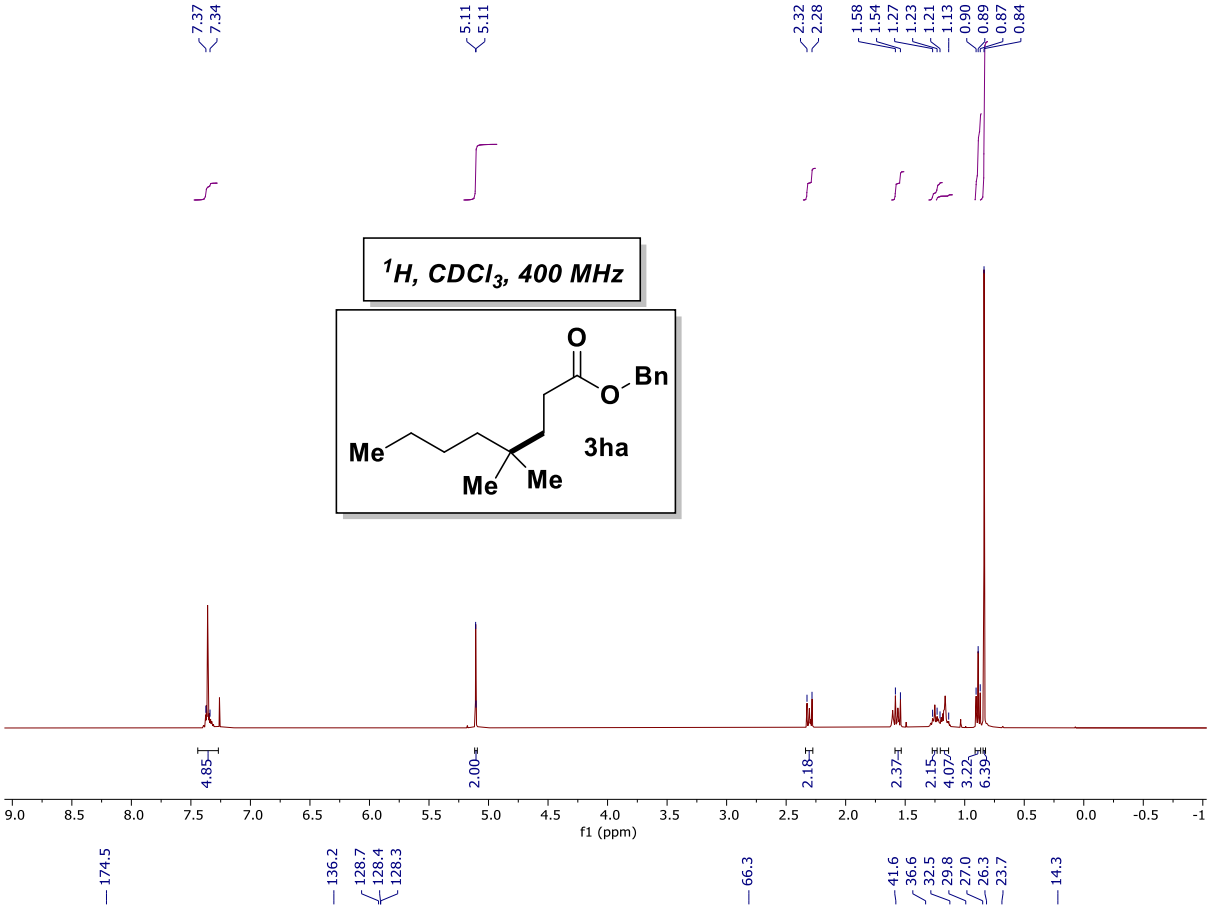
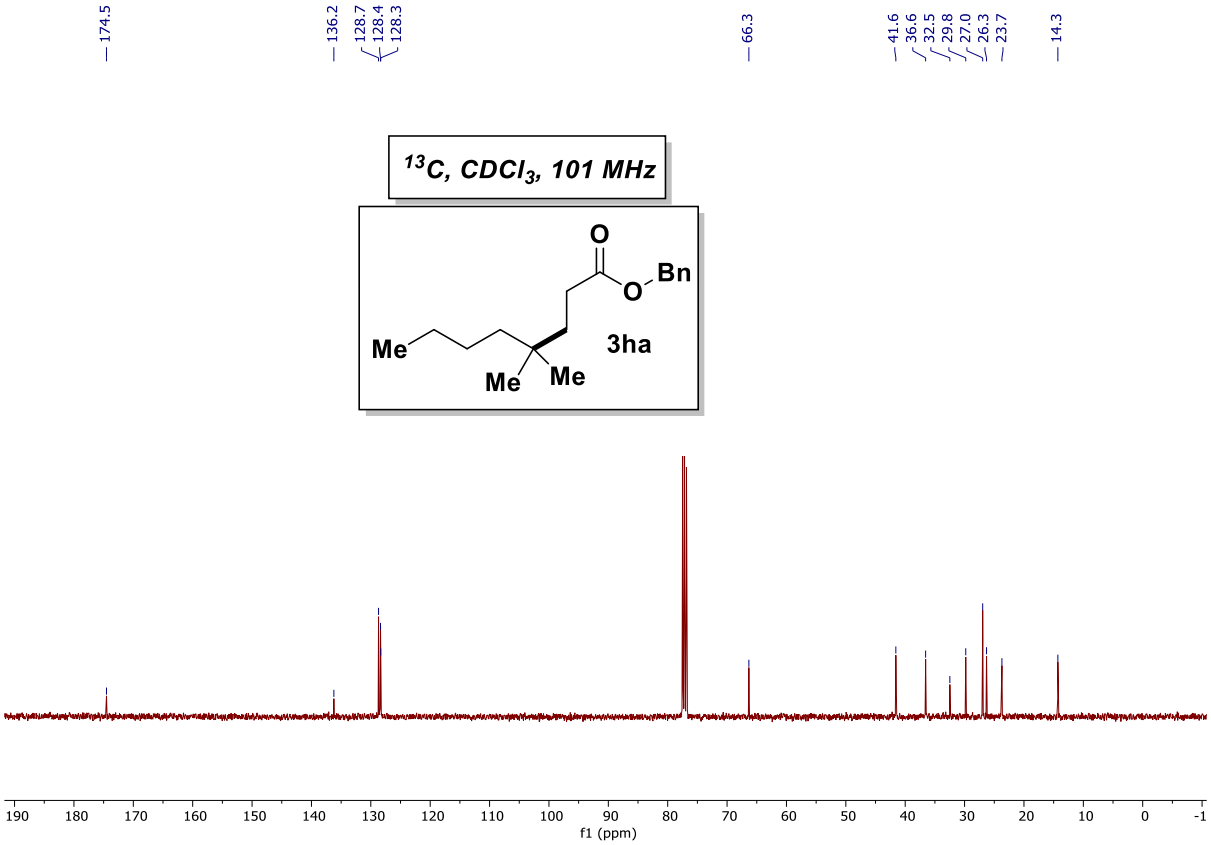
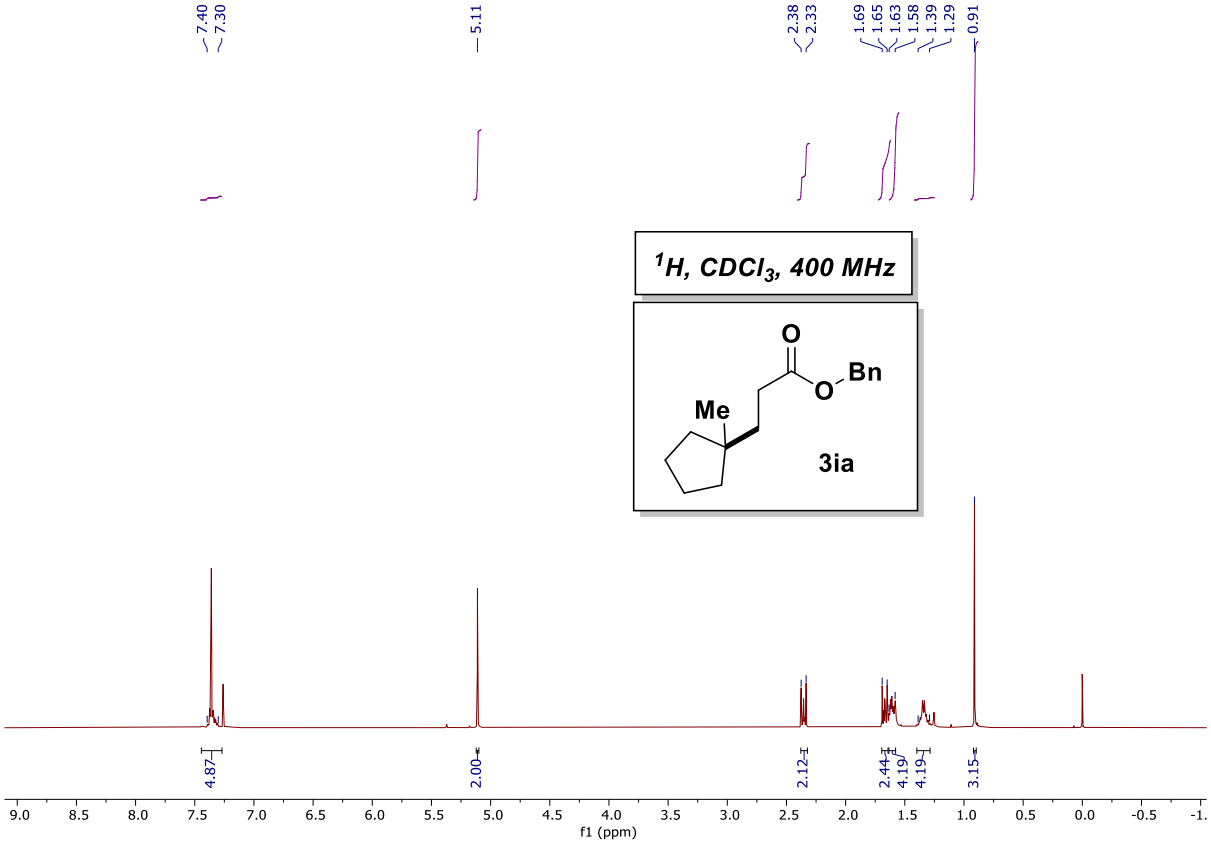
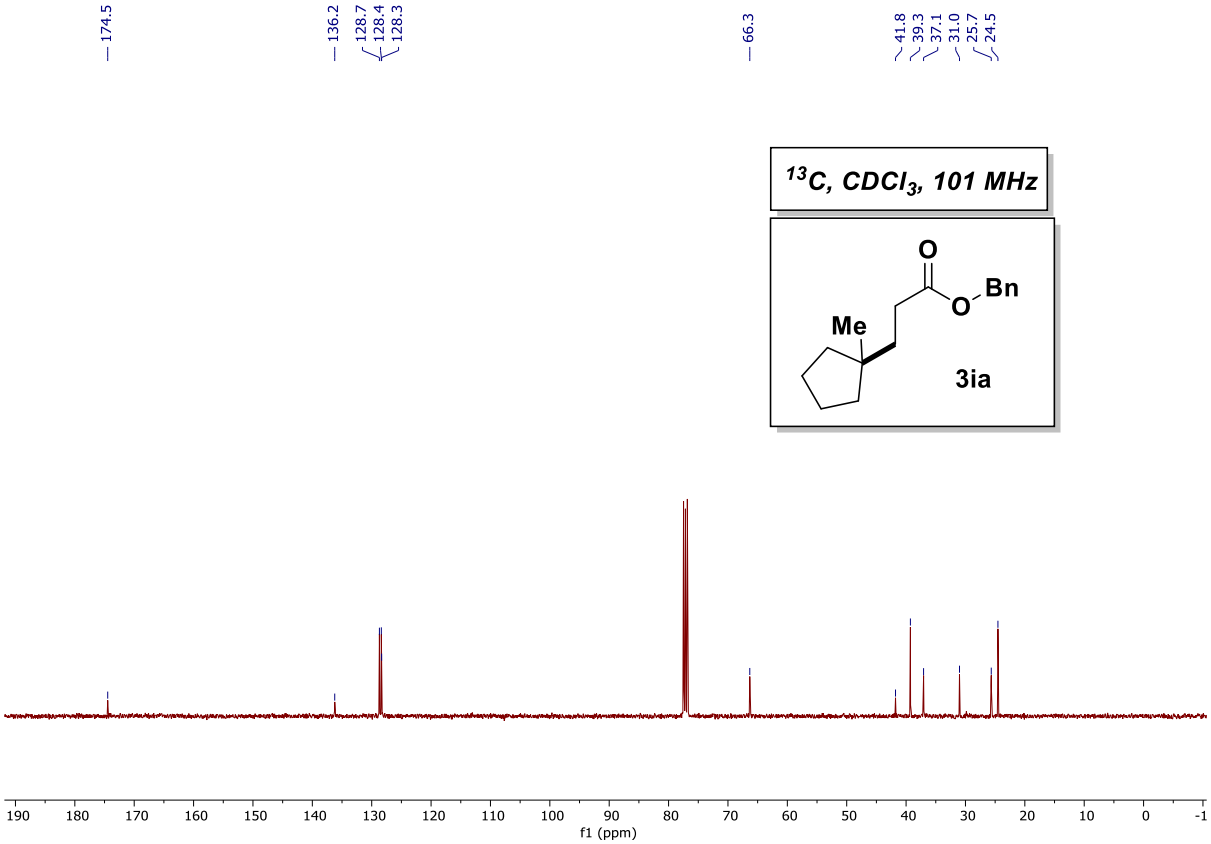
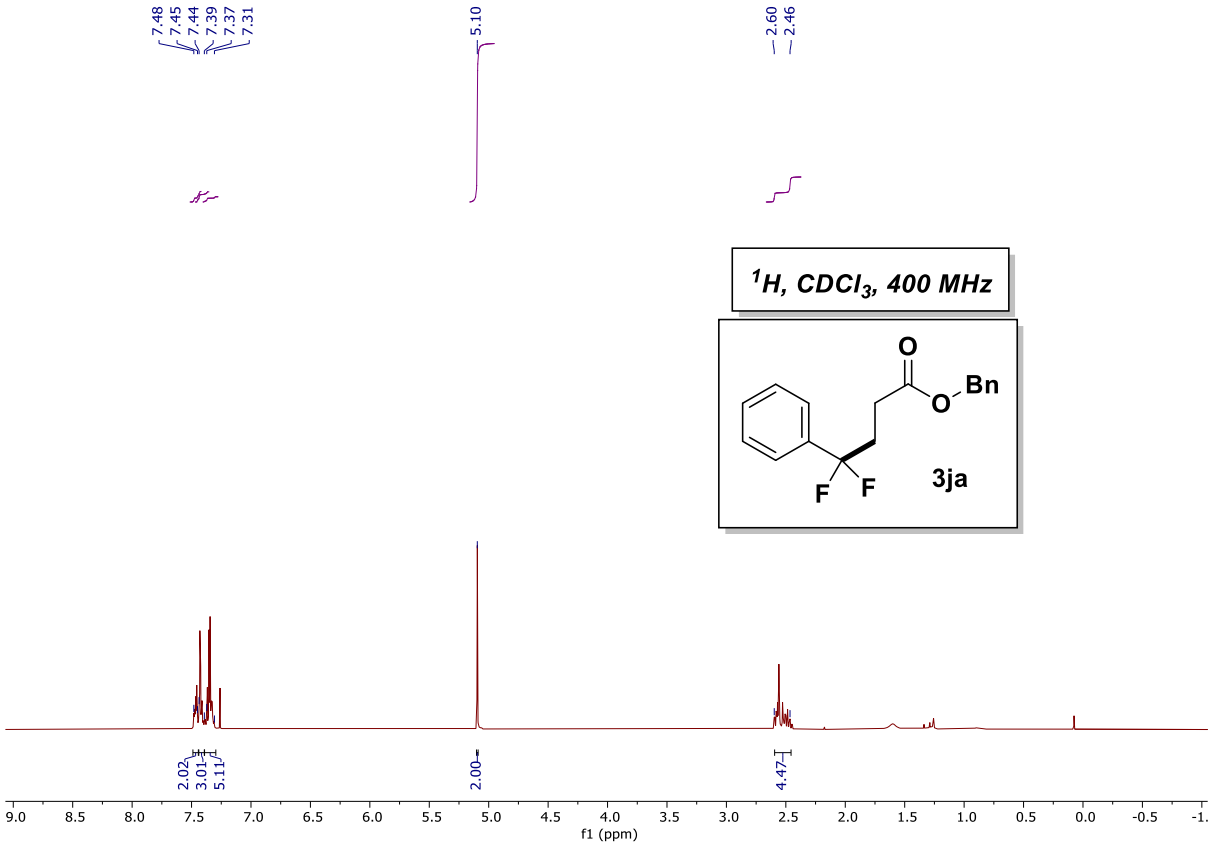
143.2
136.1
128.7
128.5
128.4
128.4
125.8
66.4
44.2
36.4
32.8
30.7
29.7
26.8
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Me
Me
3ga
f1 (ppm)

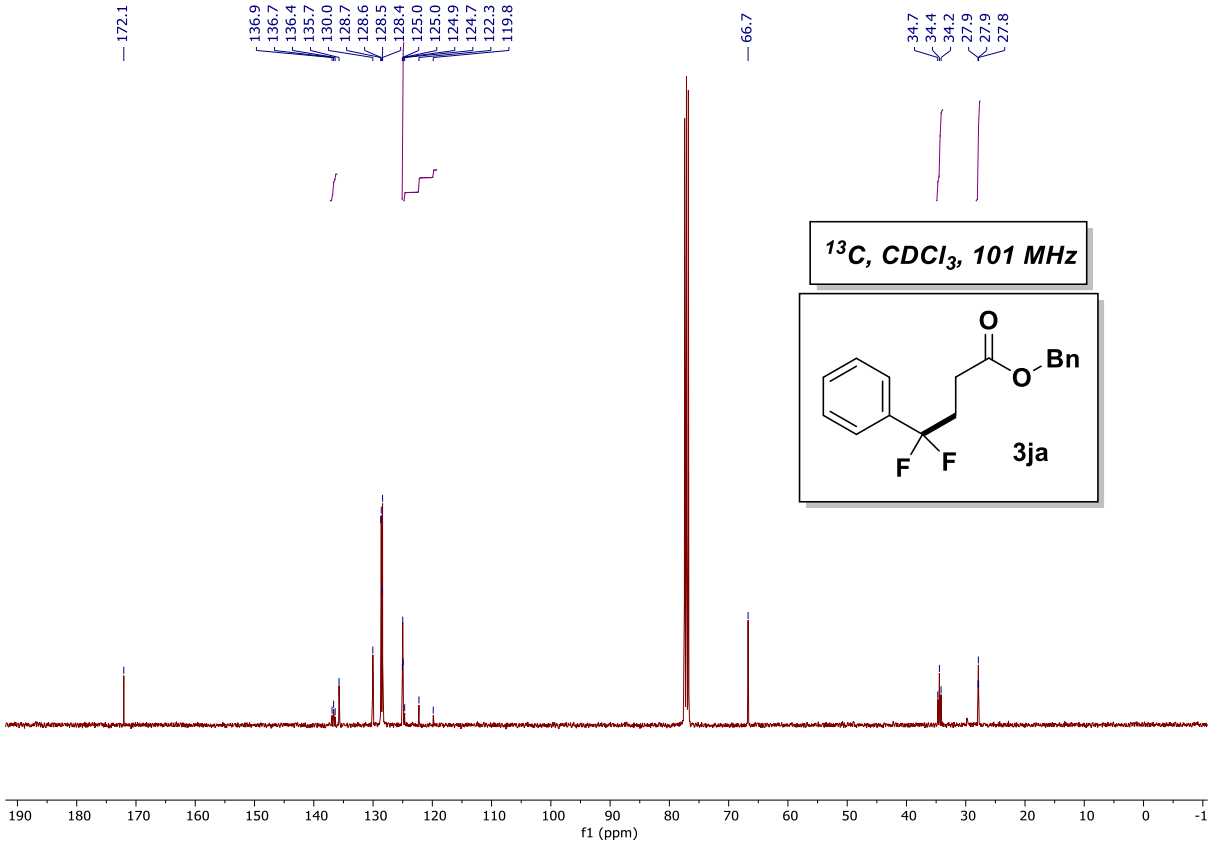

7.37
7.34
5.11
5.11
2.32
2.28
1.58
1.54
1.27
1.23
1.21
1.13
0.90
0.89
0.87
0.84
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Me
Me
Me
3ha
4.85
2.00
2.18
2.37
2.15
4.07
3.22
6.39
f1 (ppm)

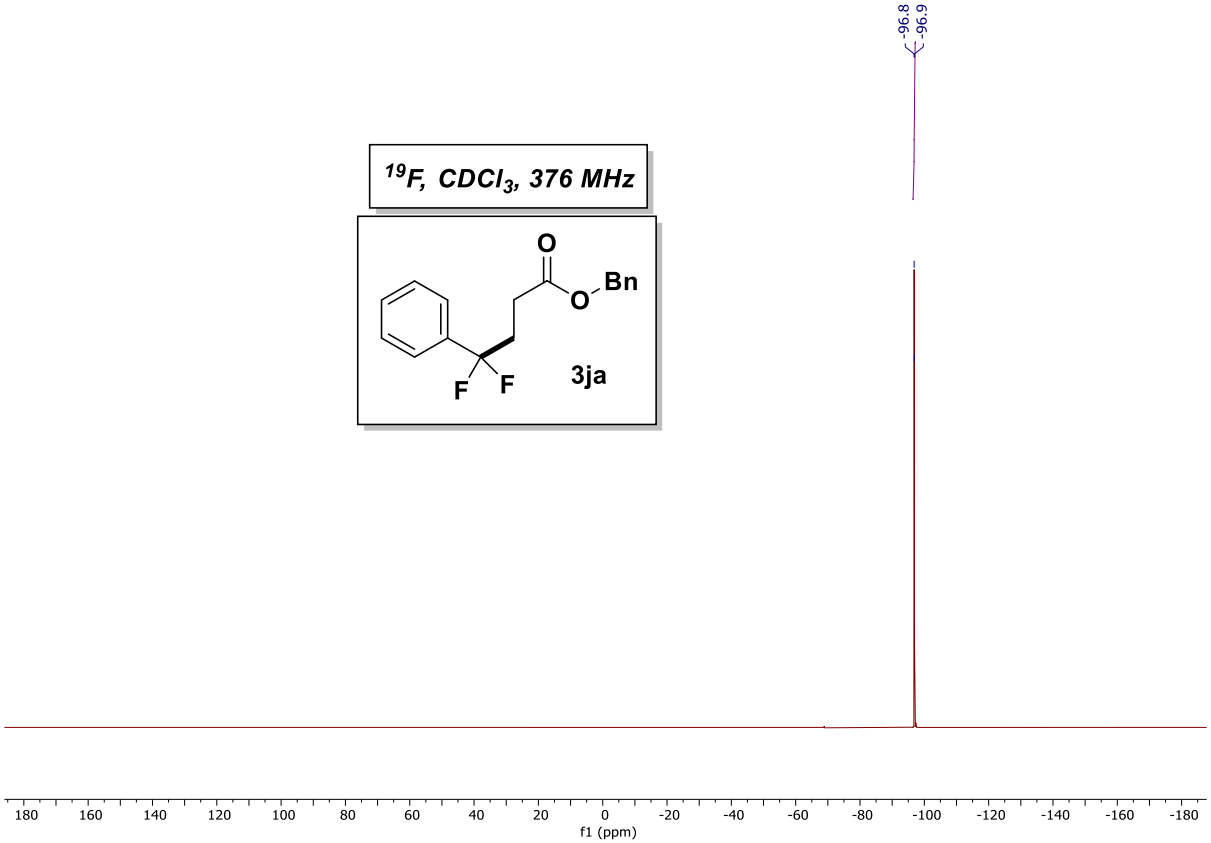

174.5
136.2
128.7
128.4
128.3
66.3
41.6
36.6
32.5
29.8
27.0
26.3
23.7
14.3
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Me
Me
Me
3ha
f1 (ppm)

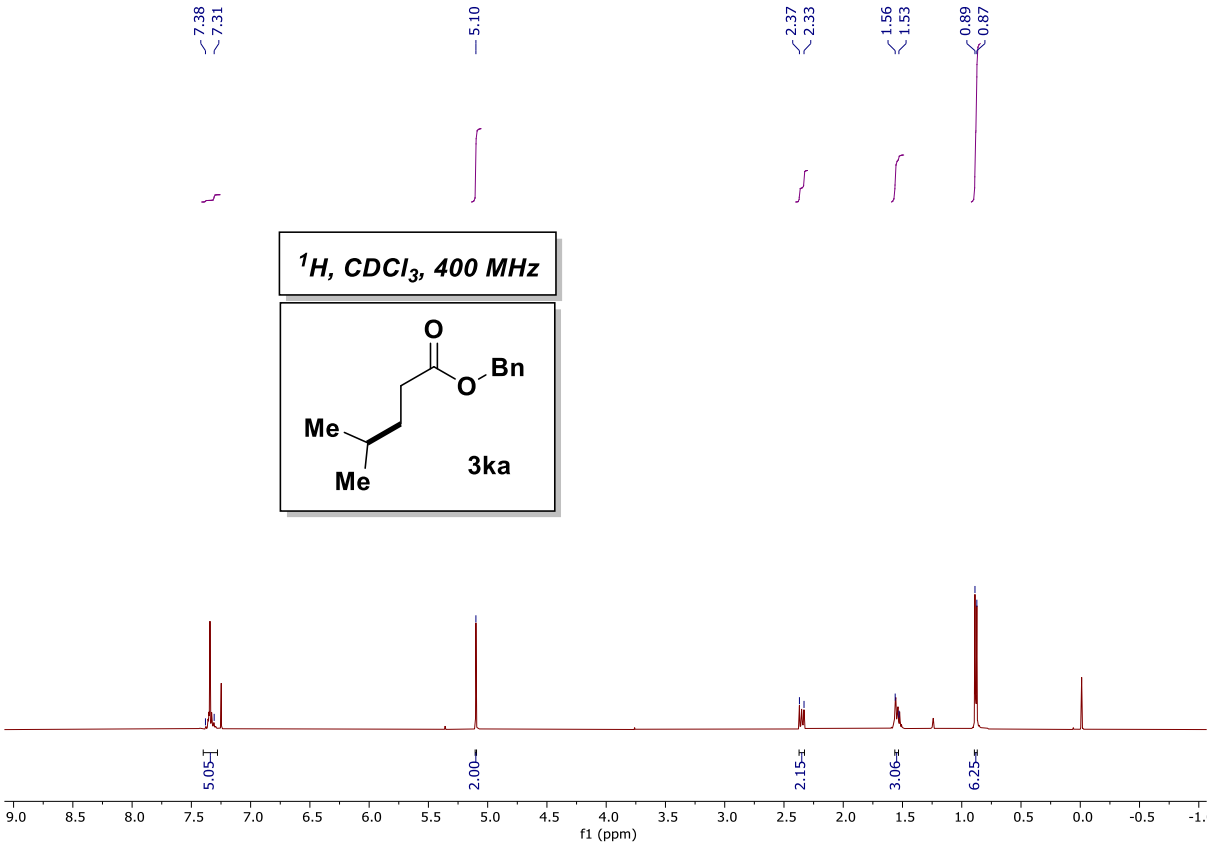

7.40
7.30
5.11
2.38
2.33
1.69
1.65
1.63
1.58
1.39
1.29
0.91
^{1}H, $CDCl_3$, 400 MHz
O
Bn
O
Me
3ia
4.87
2.00
2.12
2.44
4.19
4.19
3.15
f1 (ppm)

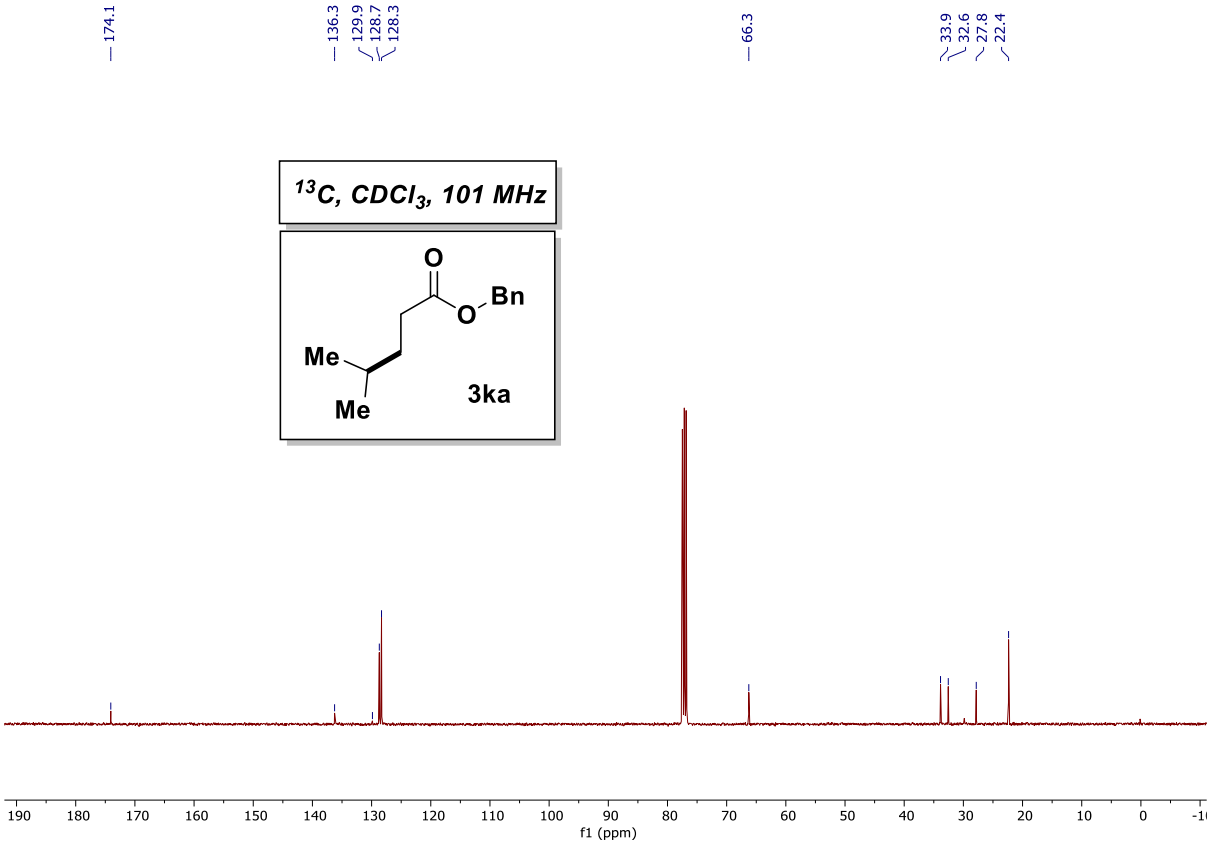

174.5
136.2
128.7
128.4
128.3
66.3
41.8
39.3
37.1
31.0
25.7
24.5
^{13}C, $CDCl_3$, 101 MHz
O
Bn
O
Me
3ia
f1 (ppm)

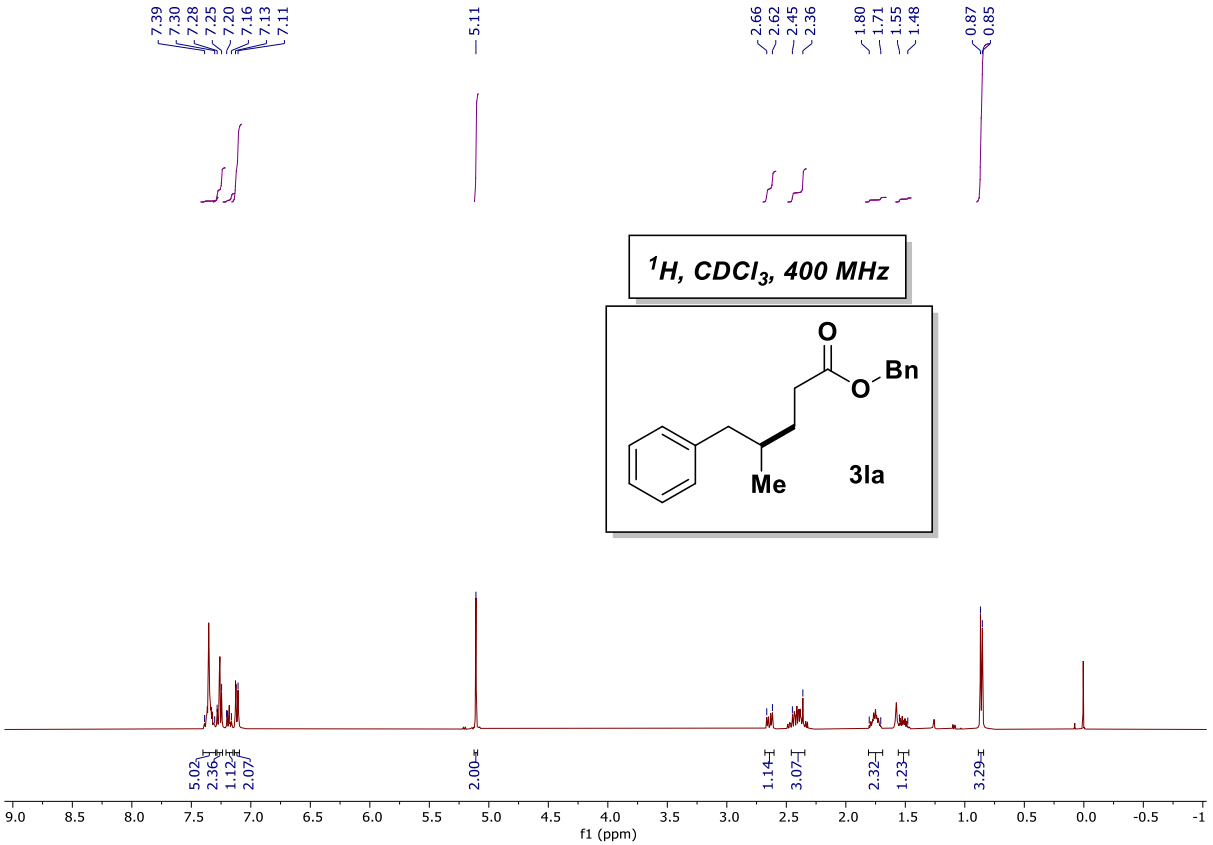

7.48
7.45
7.44
7.39
7.37
7.31
5.10
2.60
2.46
^{1}H, $CDCl_3$, 400 MHz
O
Bn
O
F
F
3ja
2.02
3.01
5.11
2.00
4.47
f1 (ppm)


172.1
136.9
136.7
136.4
135.7
130.0
128.7
128.6
128.5
128.4
125.0
124.9
124.7
122.3
119.8
66.7
34.7
34.4
34.2
27.9
27.9
27.8
^{13}C, $CDCl_3$, 101 MHz
O
Bn
O
F
F
3ja
f1 (ppm)

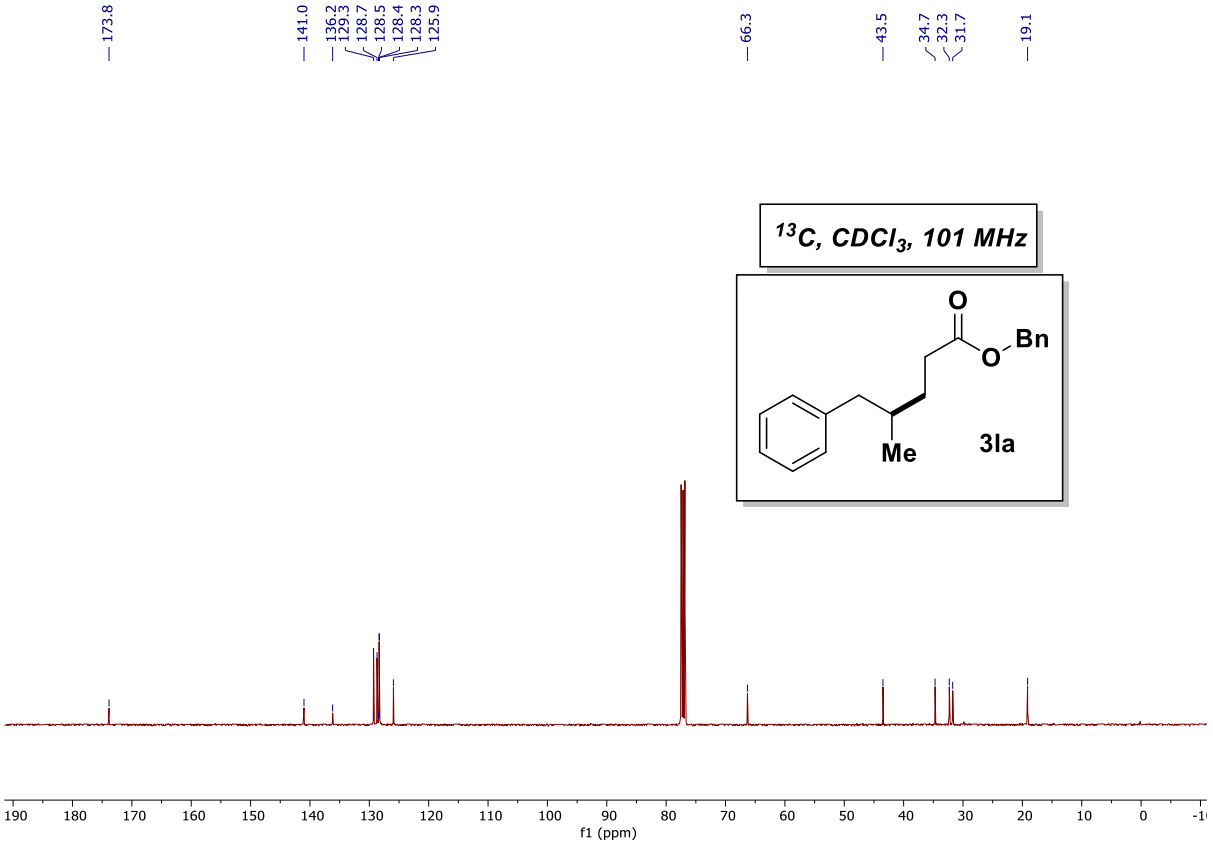

-96.8
-96.9
^{19}F, $CDCl_3$, 376 MHz
O
O
Bn
F
F
3ja
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)


7.38
7.31
5.10
2.37
2.33
1.56
1.53
0.89
0.87
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Me
Me
3ka
5.05
2.00
2.15
3.06
6.25
f1 (ppm)

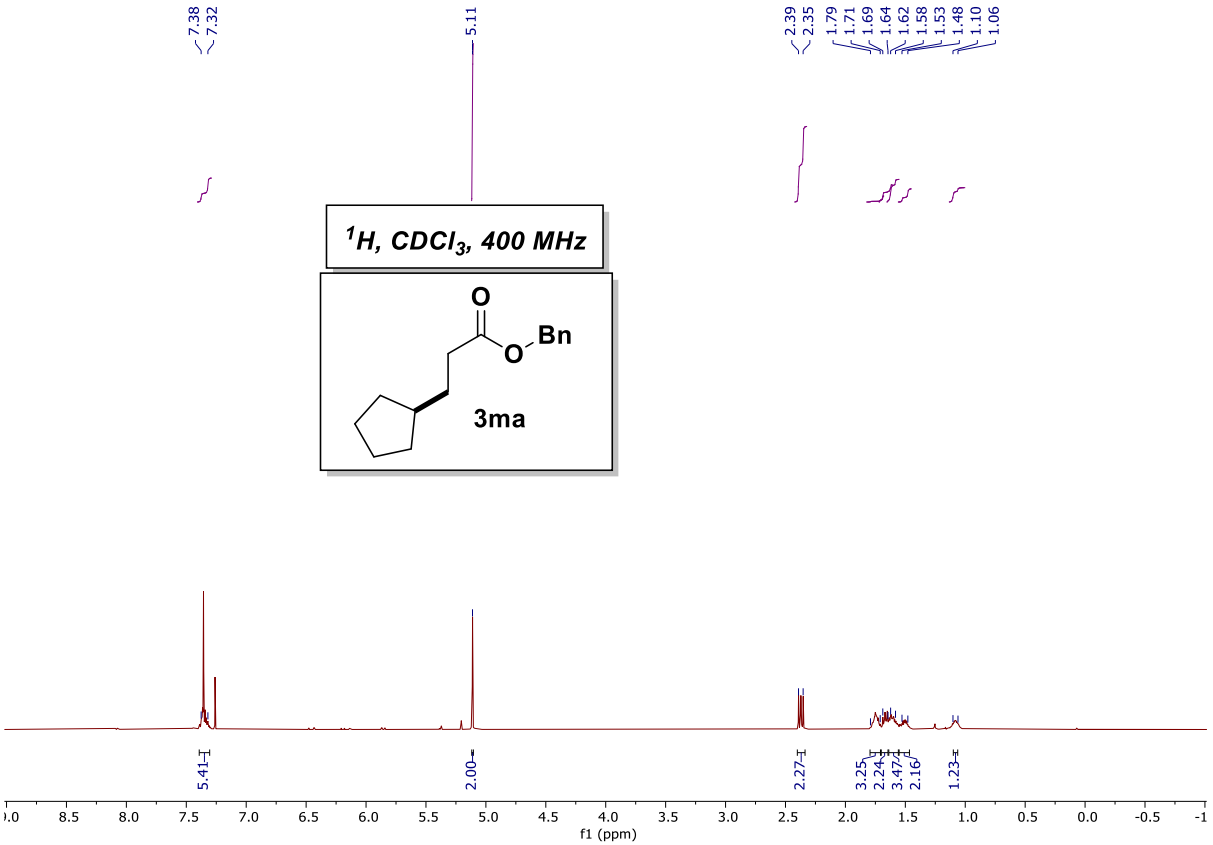

174.1
136.3
129.9
128.7
128.3
66.3
33.9
32.6
27.8
22.4
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Me
Me
3ka
f1 (ppm)

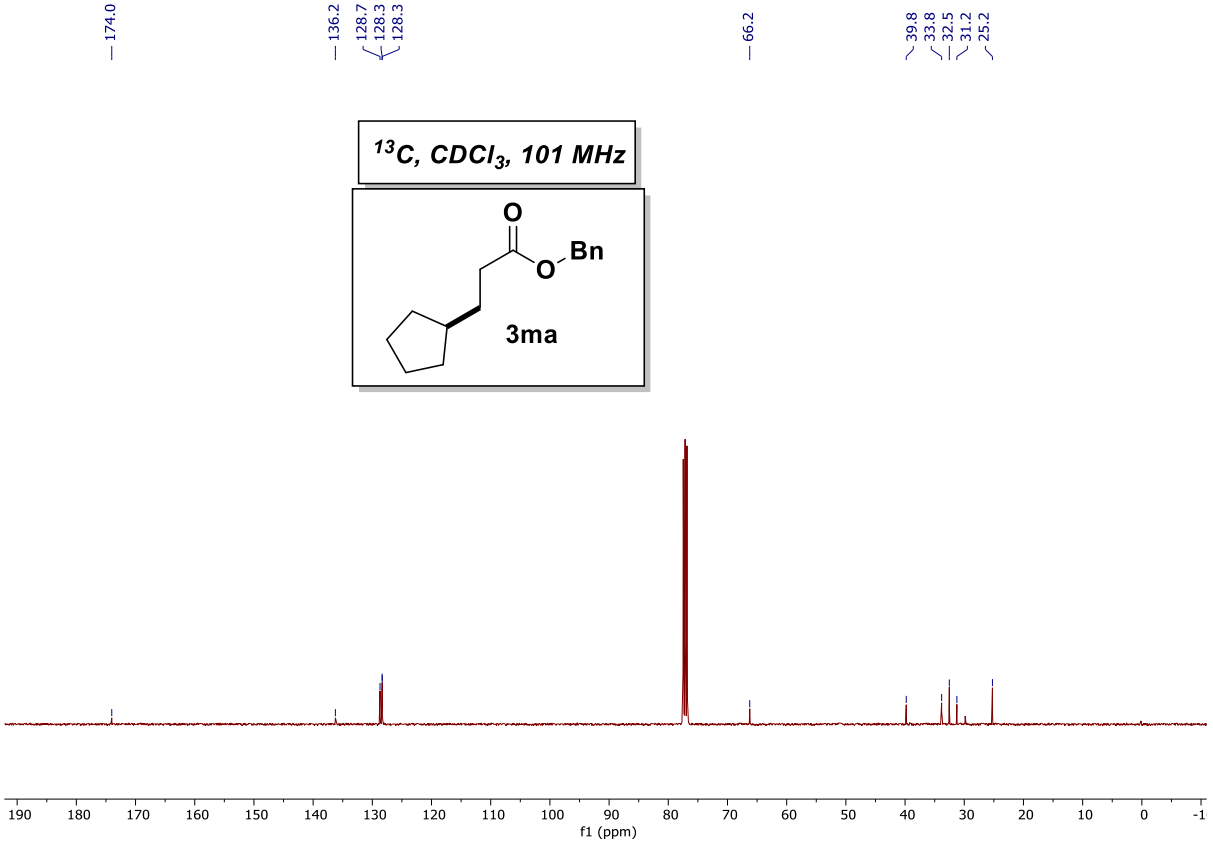


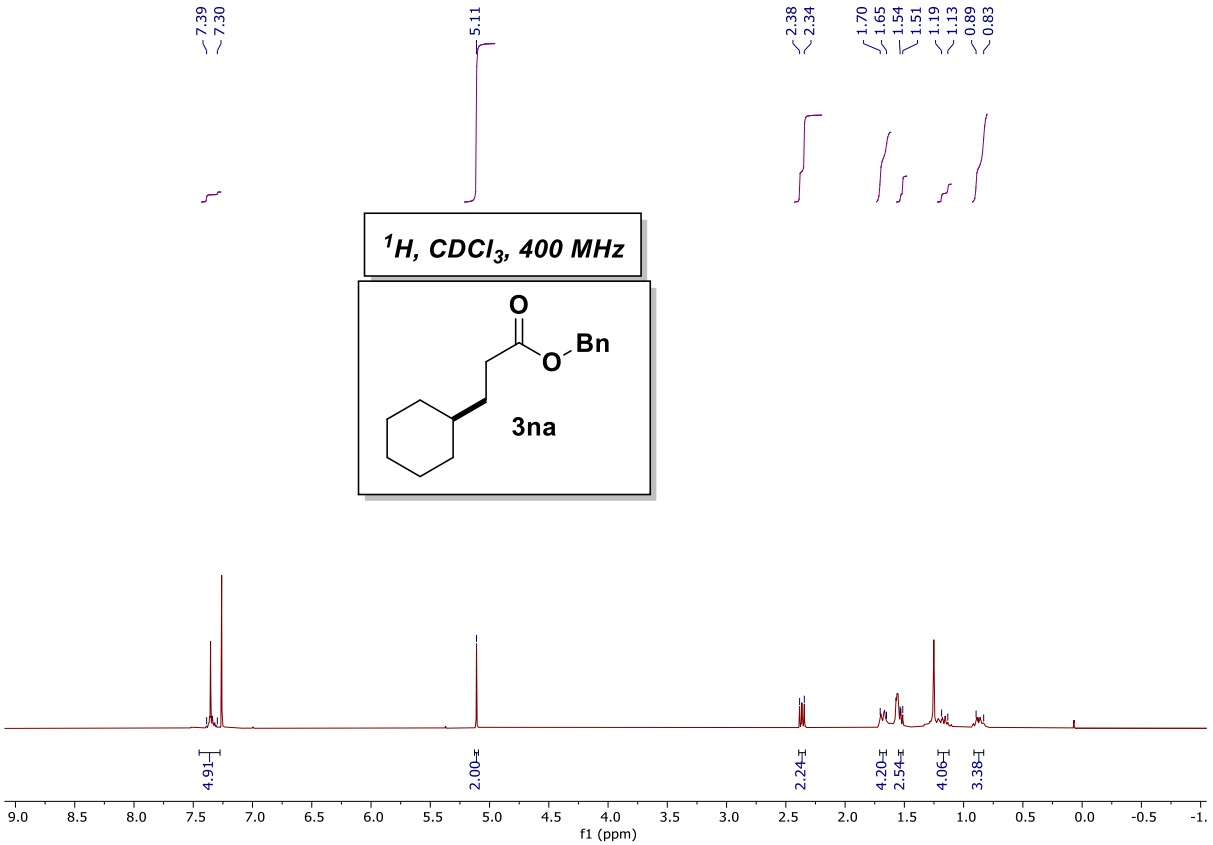
^{1}H, $CDCl_3$, 400 MHz

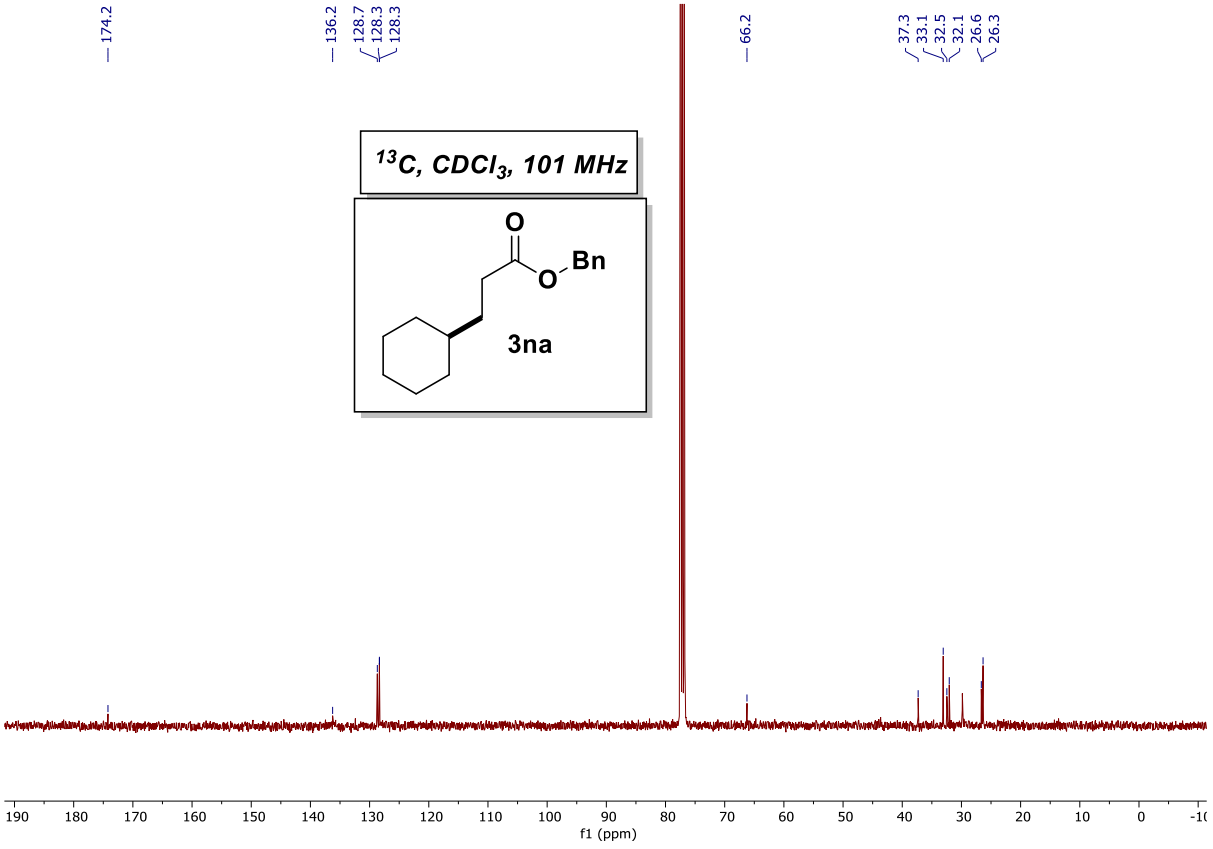


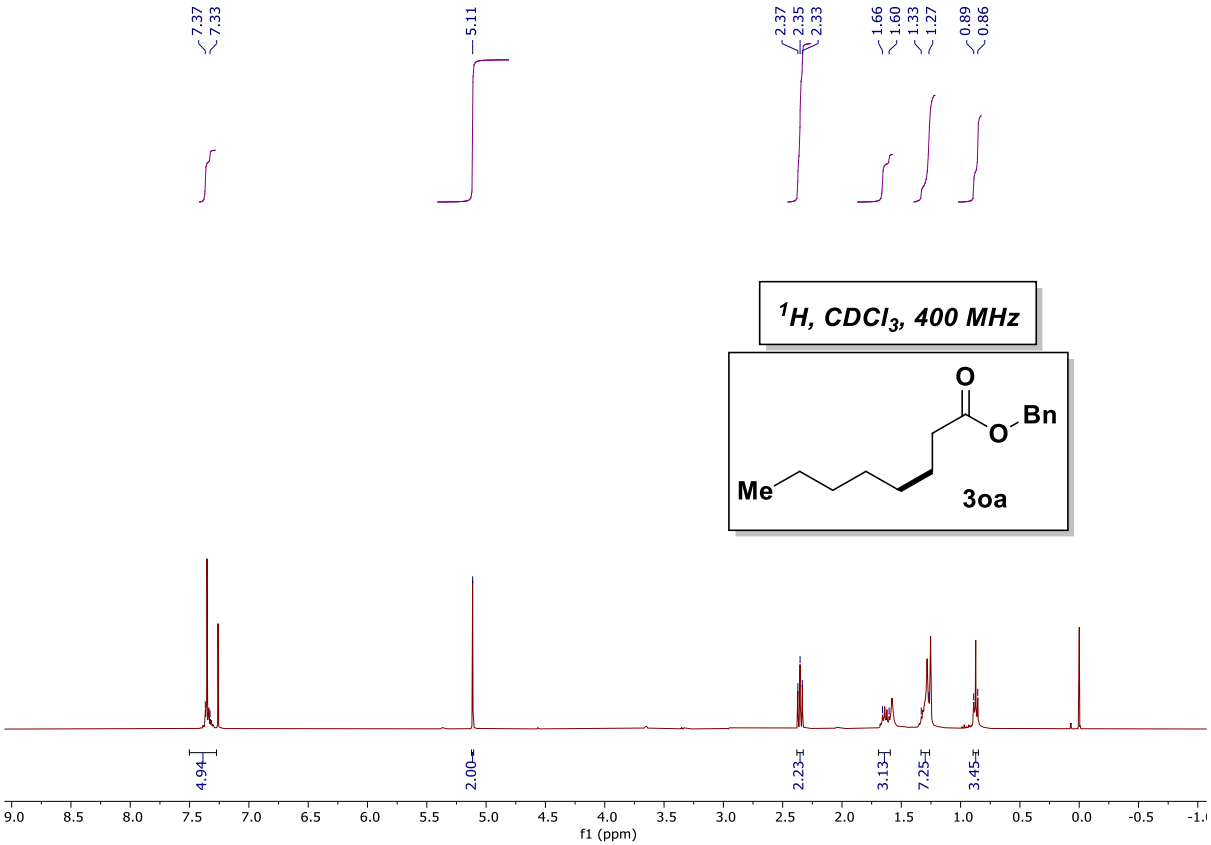
^{13}C, $CDCl_3$, 101 MHz

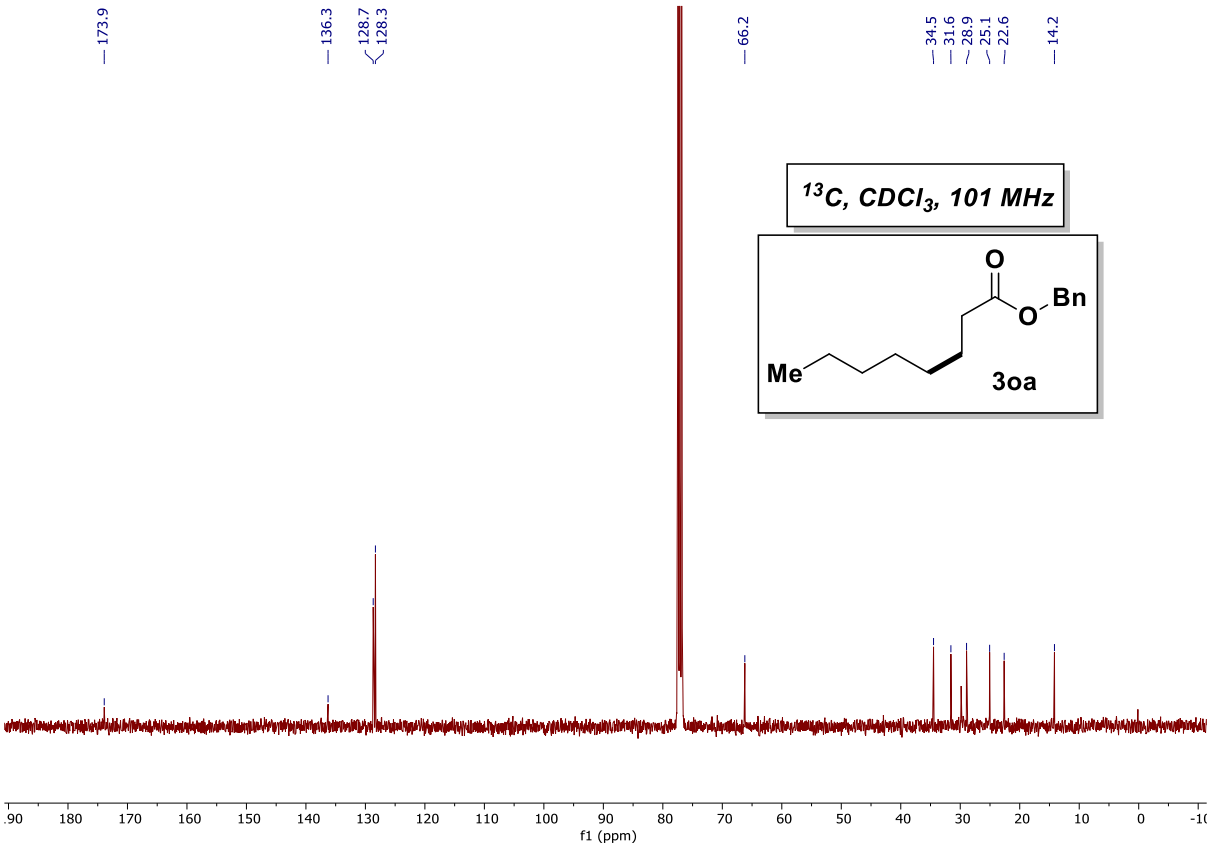

7.38
7.32
5.11
2.39
2.35
1.79
1.71
1.69
1.64
1.62
1.58
1.53
1.48
1.10
1.06
^{1}H, CDCl$_3$, 400 MHz
O
O
Bn
3ma
5.41
2.00
2.27
3.25
2.24
3.47
2.16
1.23
f1 (ppm)

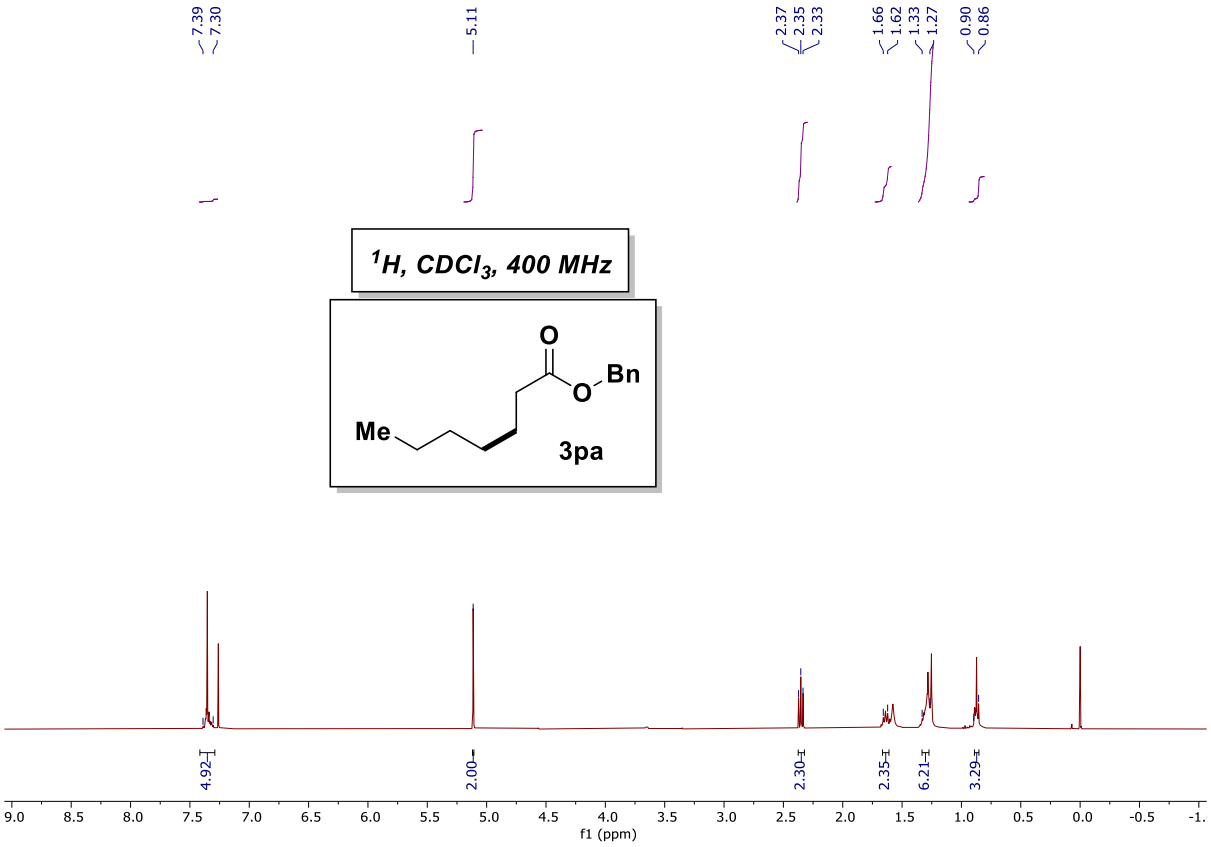

174.0
136.2
128.7
128.3
128.3
66.2
39.8
33.8
32.5
31.2
25.2
^{13}C, CDCl$_3$, 101 MHz
O
O
Bn
3ma
f1 (ppm)

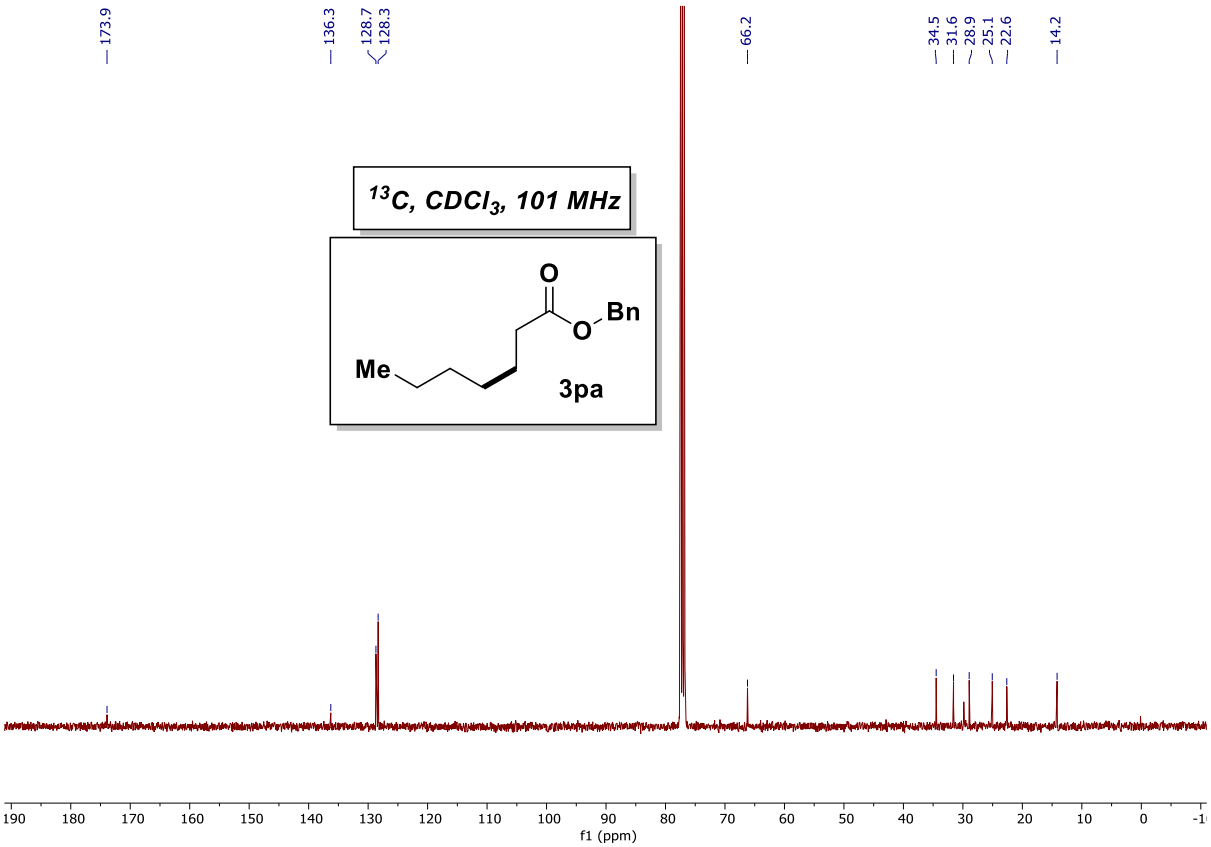

7.39
7.30
5.11
2.38
2.34
1.70
1.65
1.54
1.51
1.19
1.13
0.89
0.83
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
3na
4.91
2.00
2.24
4.20
2.54
4.06
3.38
f1 (ppm)

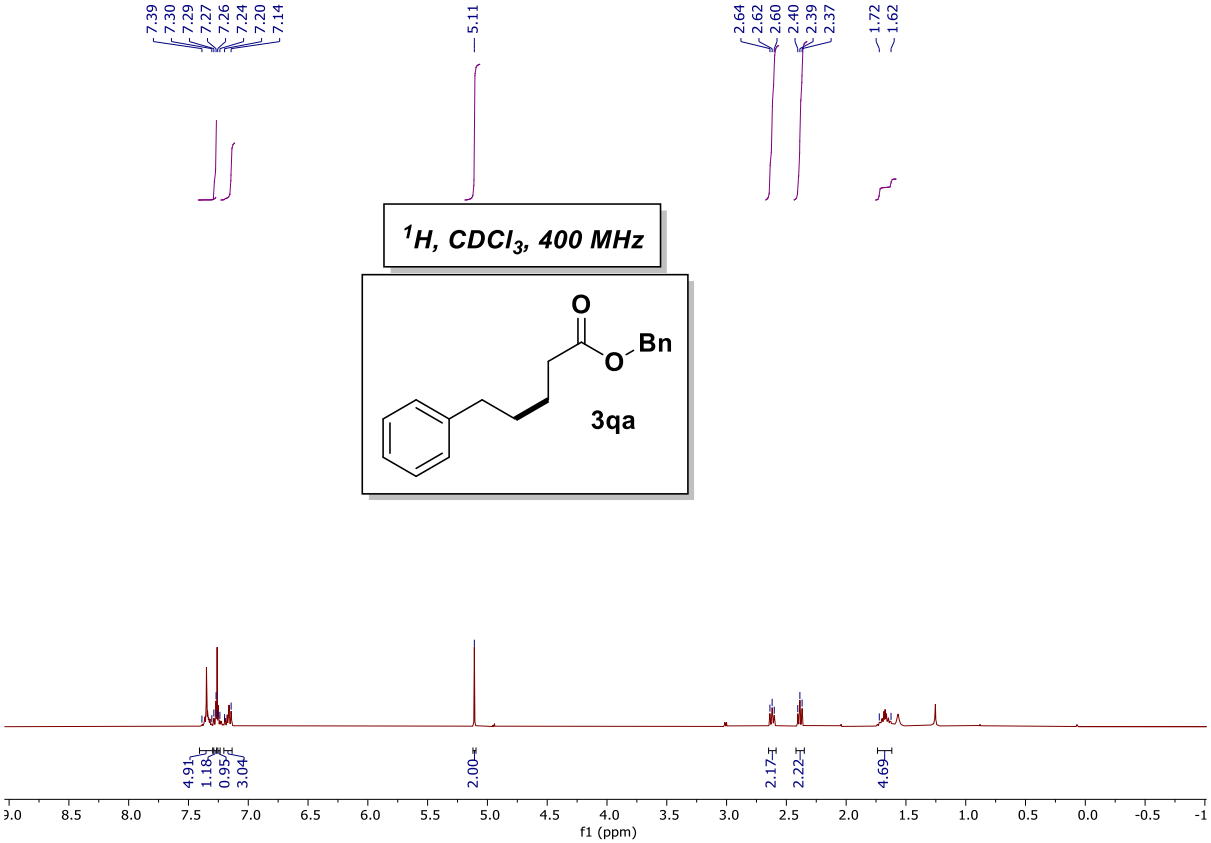

174.2
136.2
128.7
128.3
128.3
66.2
37.3
33.1
32.5
32.1
26.6
26.3
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
3na
f1 (ppm)

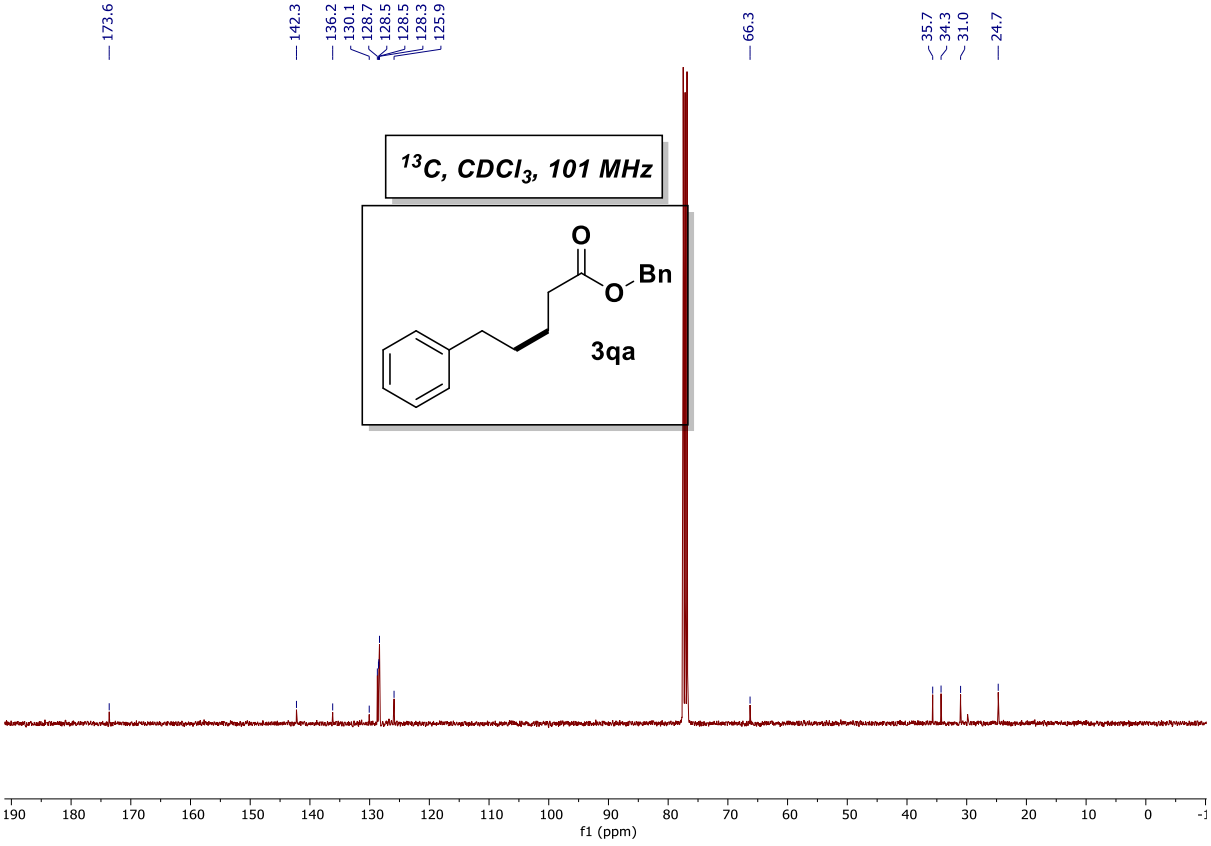

7.37
7.33
5.11
2.37
2.35
2.33
1.66
1.60
1.33
1.27
0.89
0.86
^{1}H, $CDCl_3$, 400 MHz
O
Bn
O
Me
3oa
4.94
2.00
2.23
3.13
7.25
3.45
f1 (ppm)

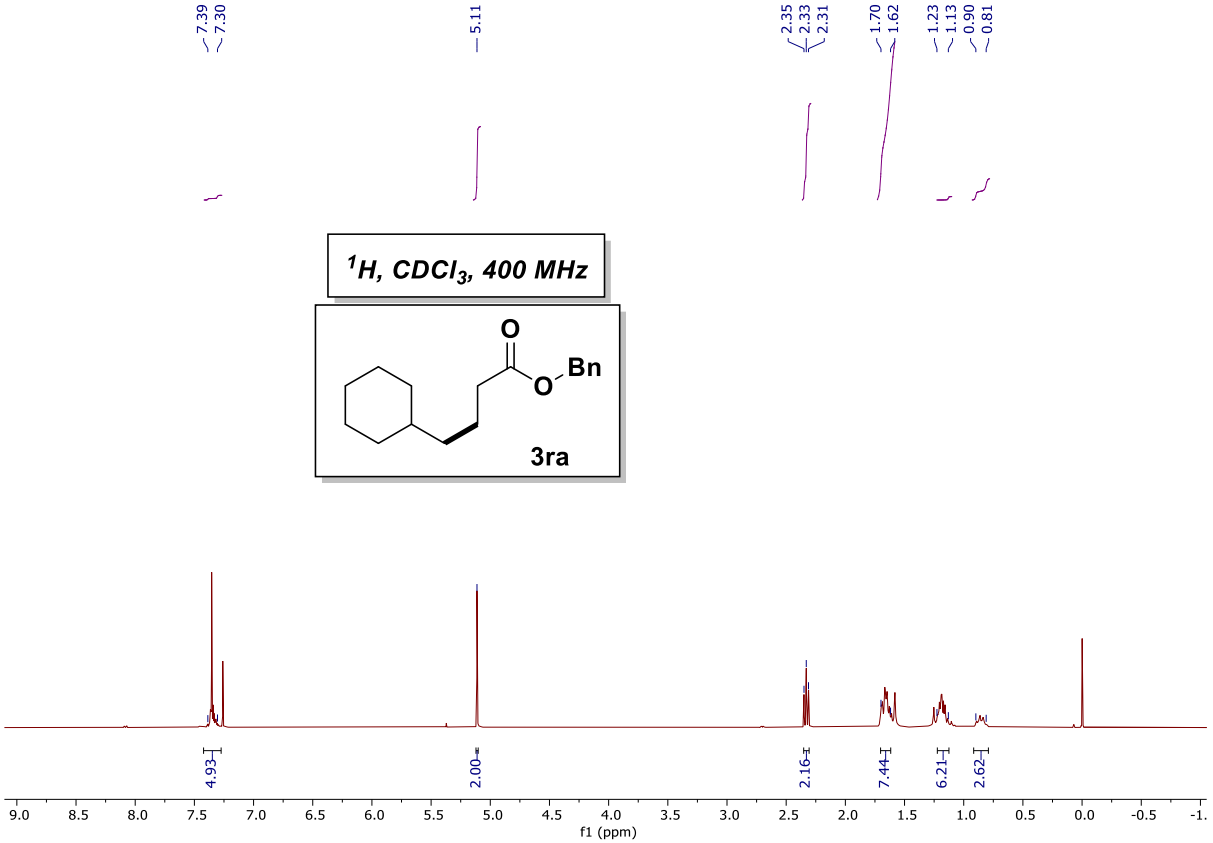

173.9
136.3
128.7
128.3
66.2
34.5
31.6
28.9
25.1
22.6
14.2
^{13}C, $CDCl_3$, 101 MHz
O
Bn
O
Me
3oa
f1 (ppm)

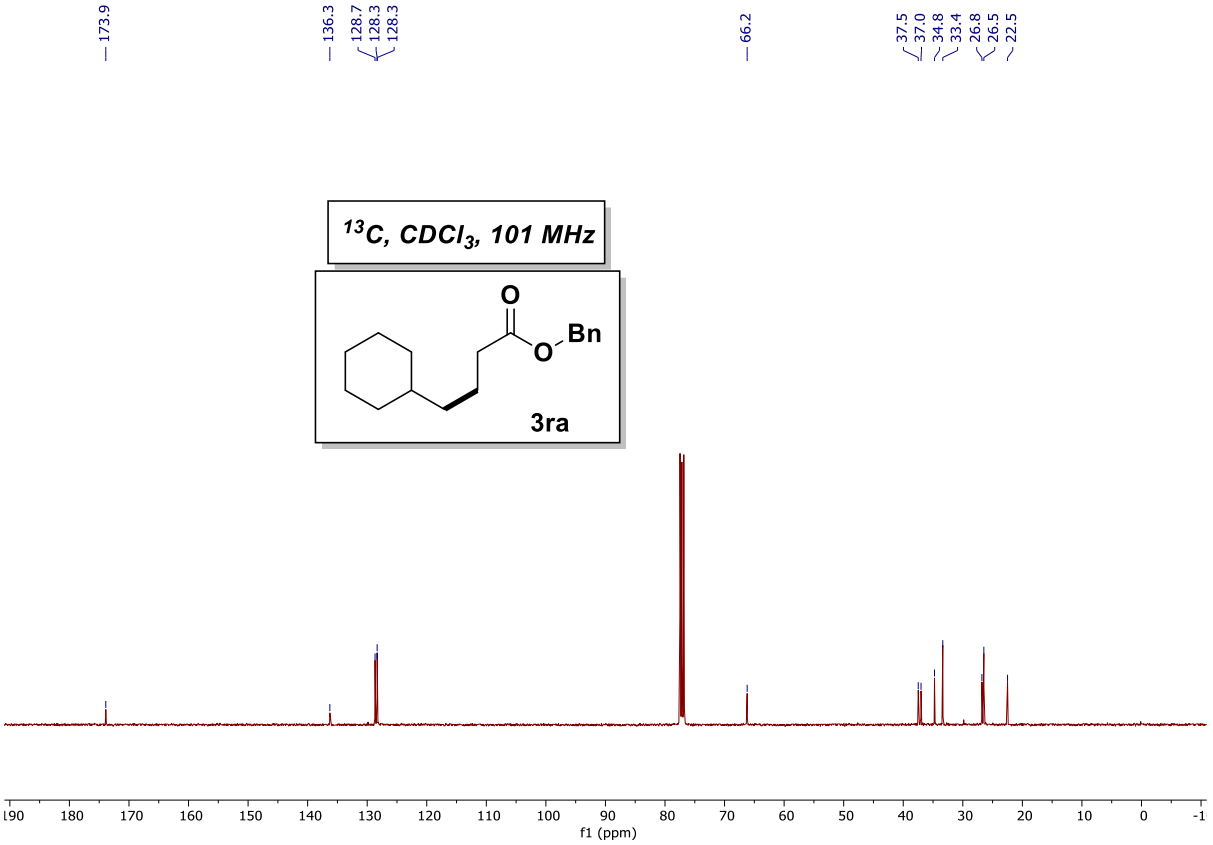

7.39
7.30
5.11
2.37
2.35
2.33
1.66
1.62
1.33
1.27
0.90
0.86
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Me
3pa
4.92
2.00
2.30
2.35
6.21
3.29
f1 (ppm)

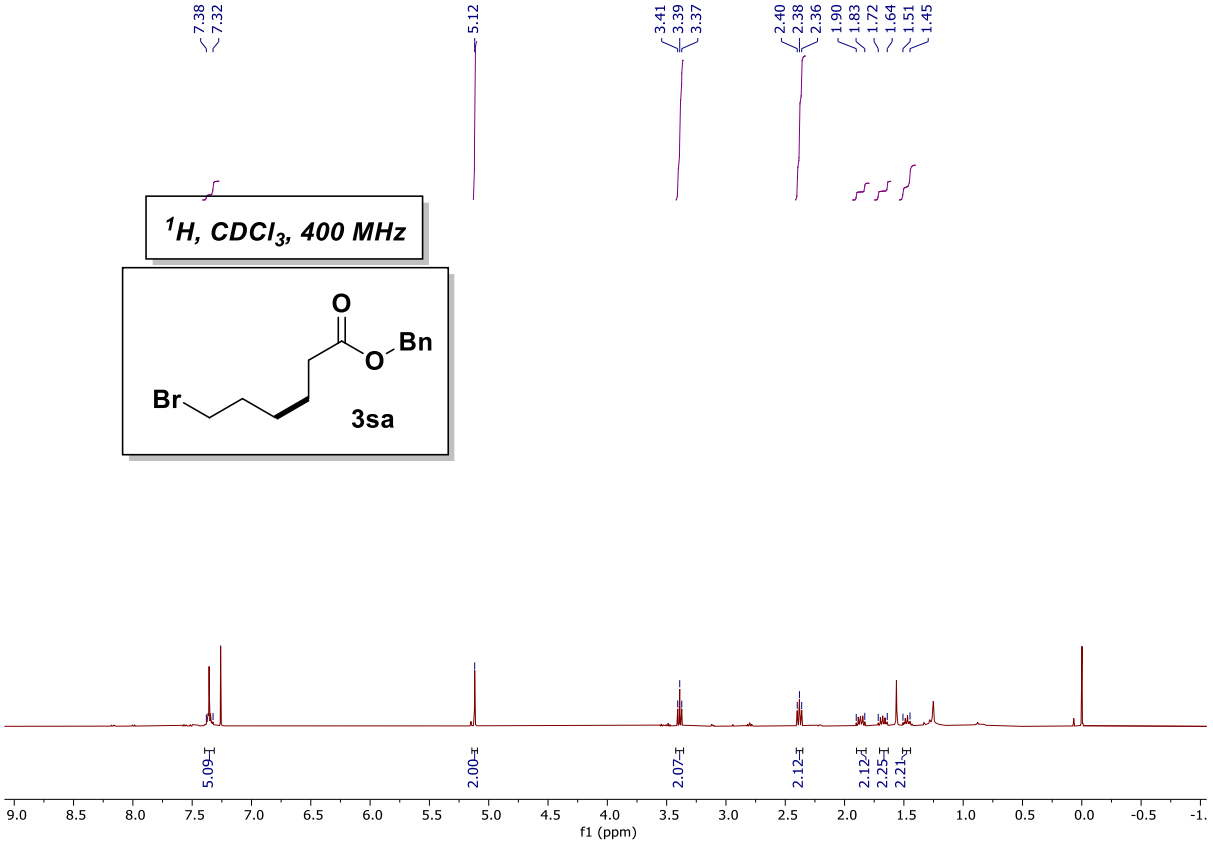

173.9
136.3
128.7
128.3
66.2
34.5
31.6
28.9
25.1
22.6
14.2
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Me
3pa
f1 (ppm)

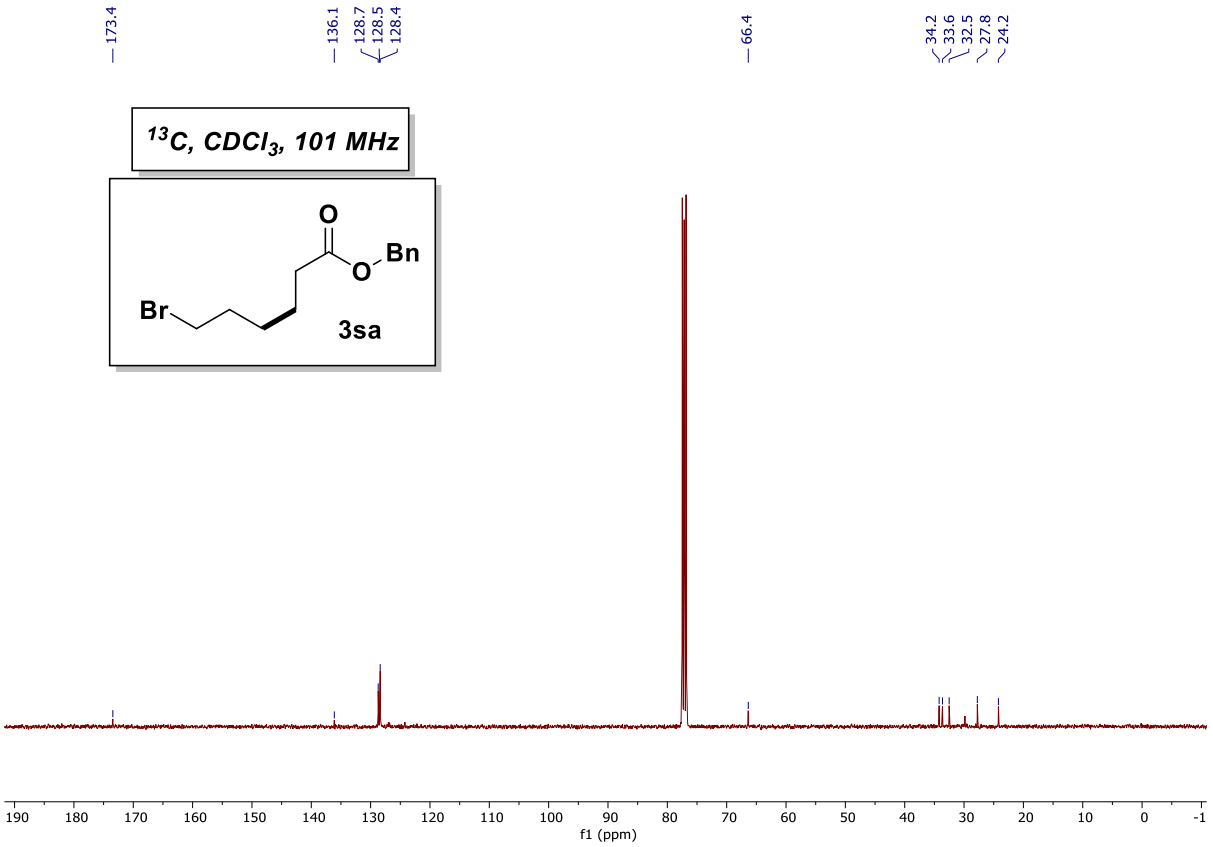

7.39
7.30
7.29
7.27
7.26
7.24
7.20
7.14
5.11
2.64
2.62
2.60
2.40
2.39
2.37
1.72
1.62
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
3qa
4.91
1.18
0.95
3.04
2.00
2.17
2.22
4.69
f1 (ppm)

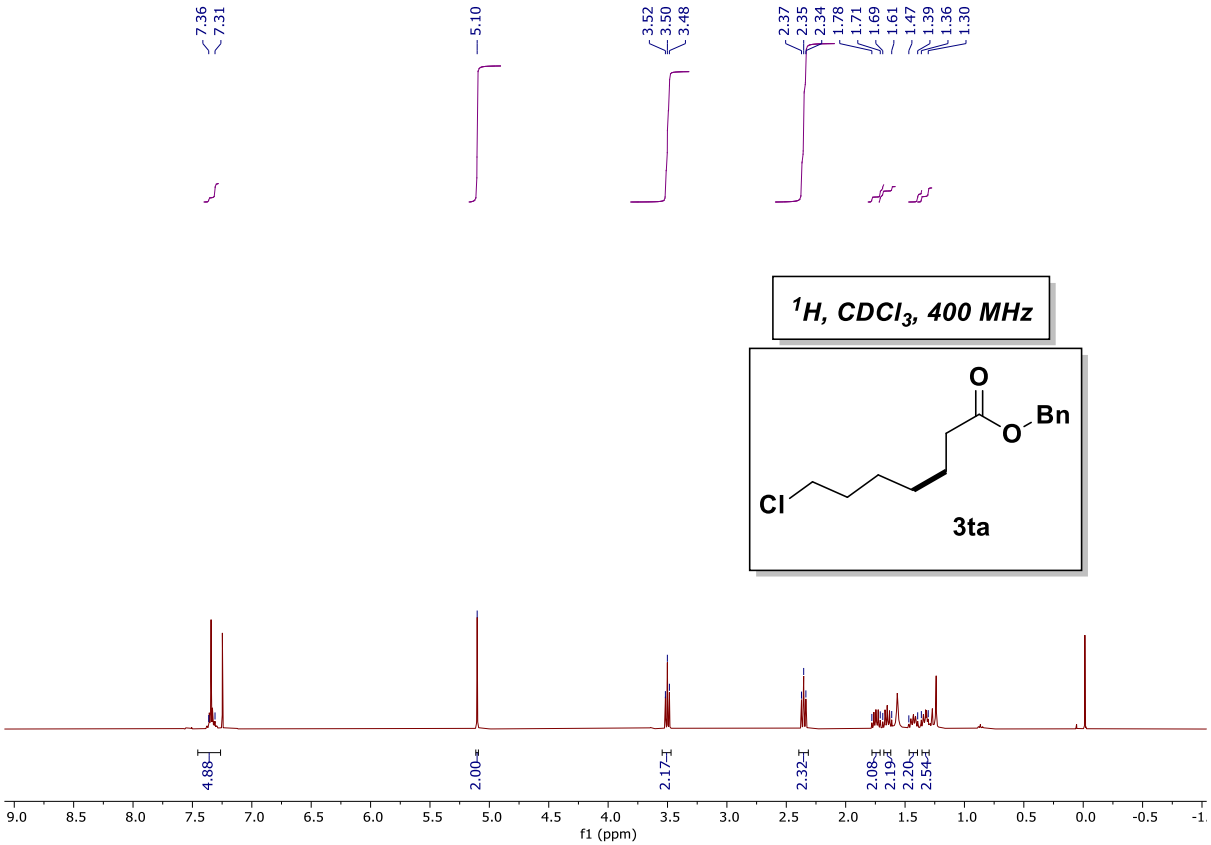

173.6
142.3
136.2
130.1
128.7
128.5
128.5
128.3
125.9
66.3
35.7
34.3
31.0
24.7
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
3qa
f1 (ppm)

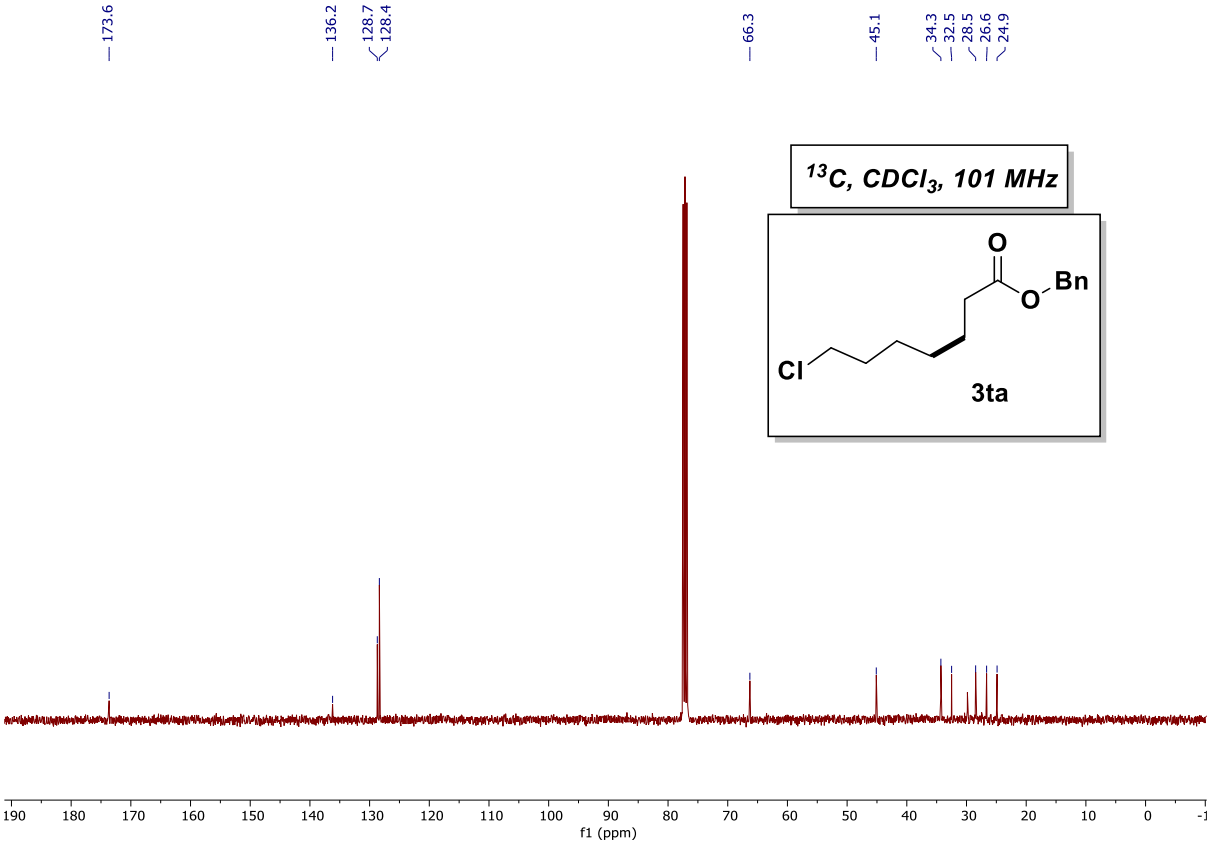

7.39
7.30
5.11
2.35
2.33
2.31
1.70
1.62
1.23
1.13
0.90
0.81
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
3ra
4.93
2.00
2.16
7.44
6.21
2.62
f1 (ppm)

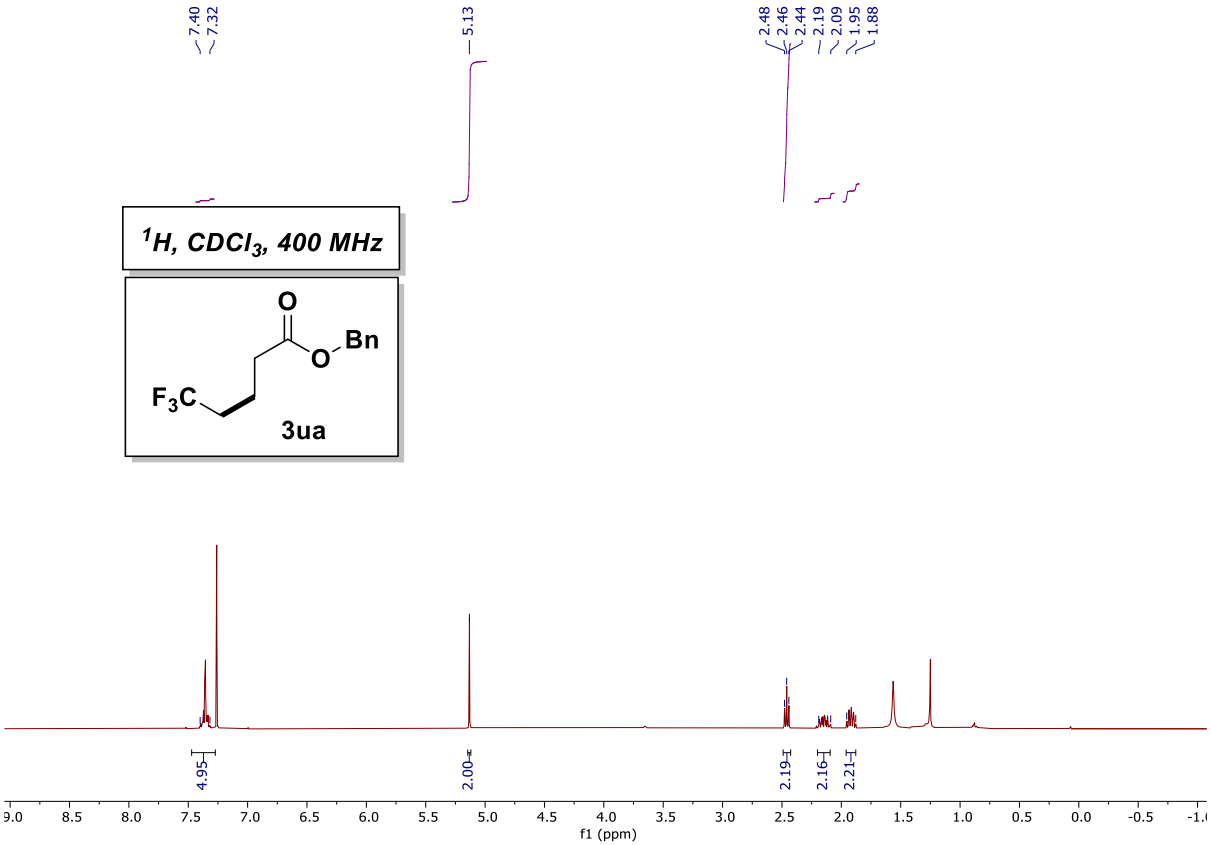

173.9
136.3
128.7
128.3
128.3
66.2
37.5
37.0
34.8
33.4
26.8
26.5
22.5
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
3ra
f1 (ppm)

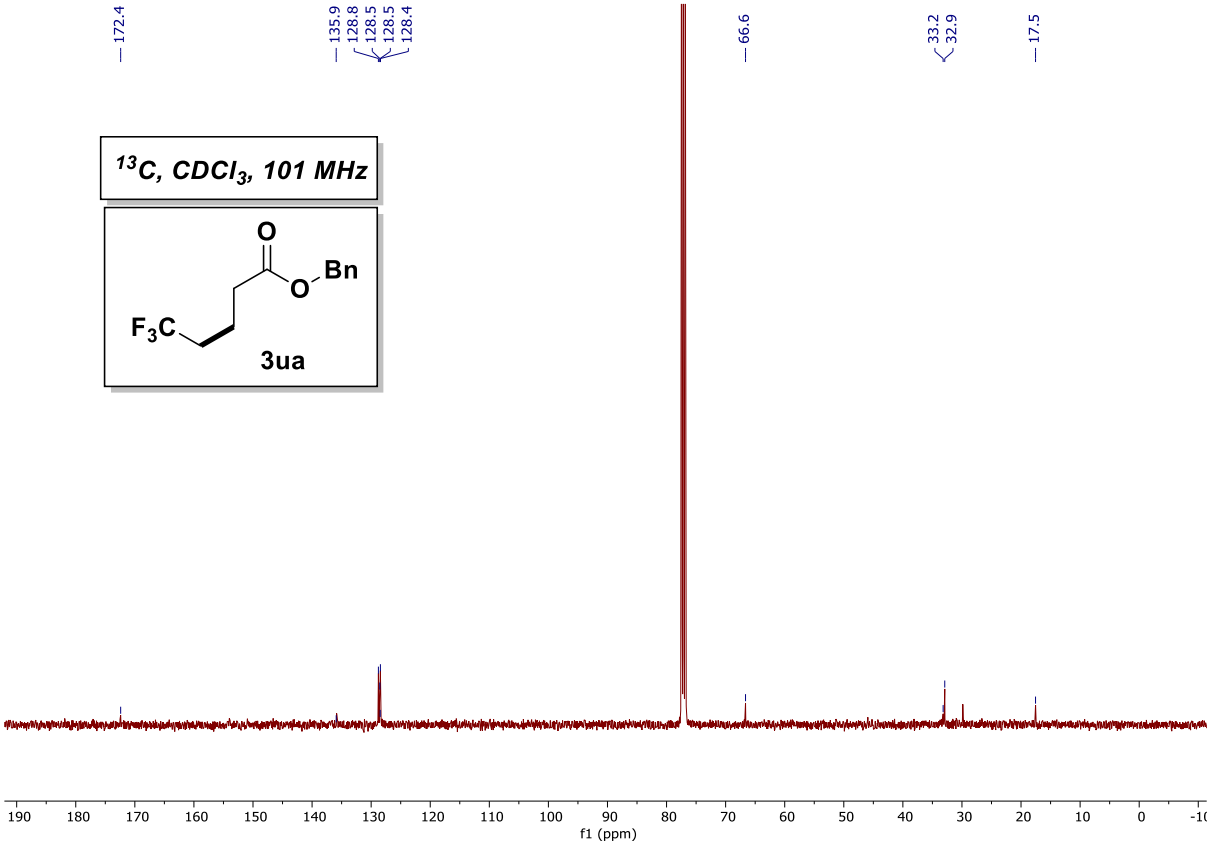

7.38
7.32
5.12
3.41
3.39
3.37
2.40
2.38
2.36
1.90
1.83
1.72
1.64
1.51
1.45
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Br
3sa
5.09
2.00
2.07
2.12
2.12
2.25
2.21
f1 (ppm)

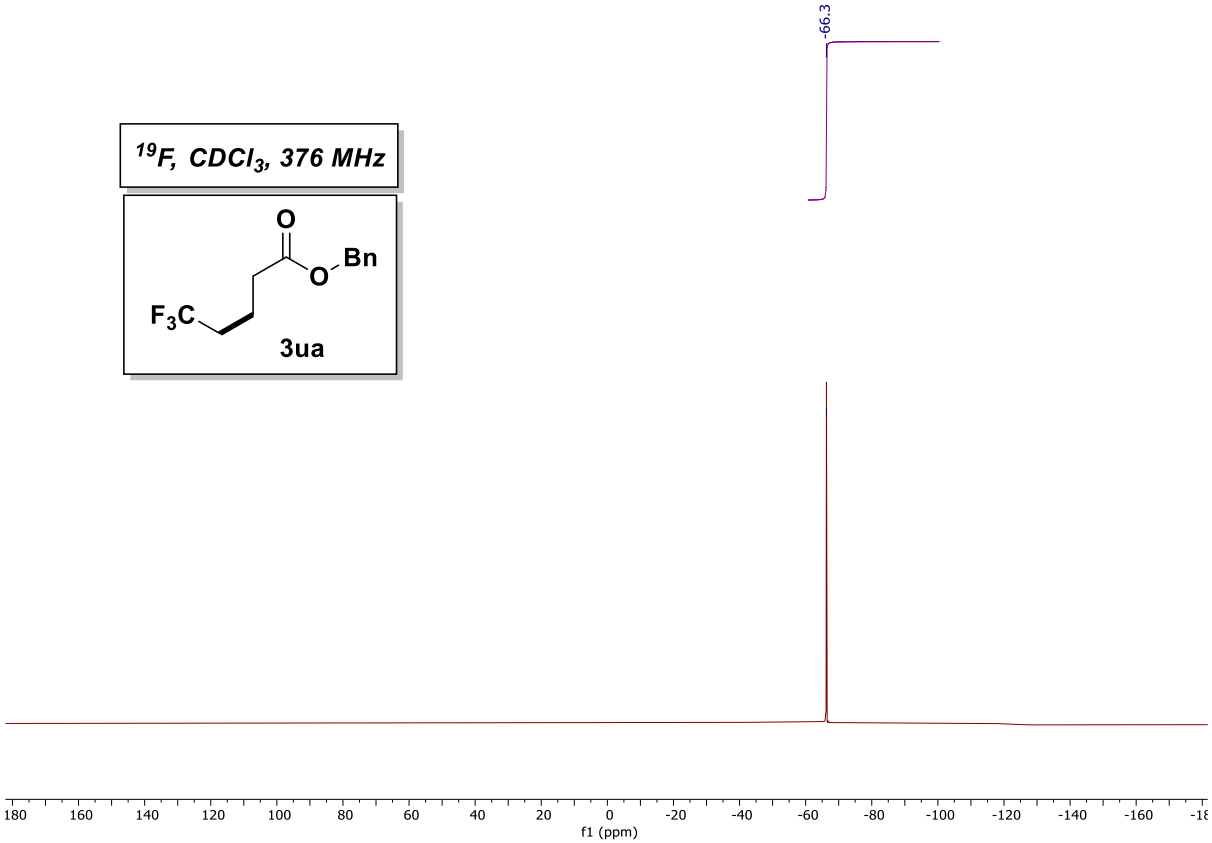

173.4
136.1
128.7
128.5
128.4
66.4
34.2
33.6
32.5
27.8
24.2
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Br
3sa
f1 (ppm)

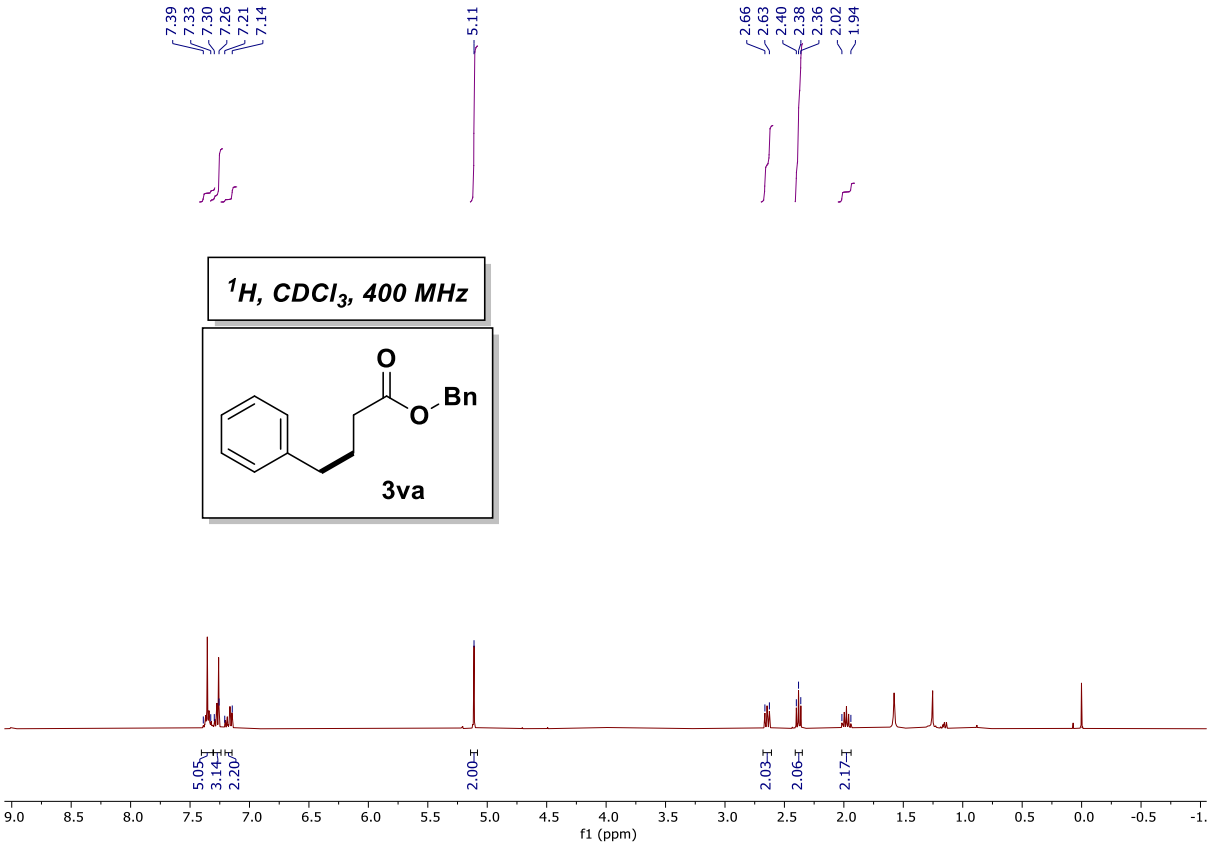

7.36
7.31
5.10
3.52
3.50
3.48
2.37
2.35
2.34
1.78
1.71
1.69
1.61
1.47
1.39
1.36
1.30
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
Cl
3ta
4.88
2.00
2.17
2.32
2.08
2.19
2.20
2.54
f1 (ppm)

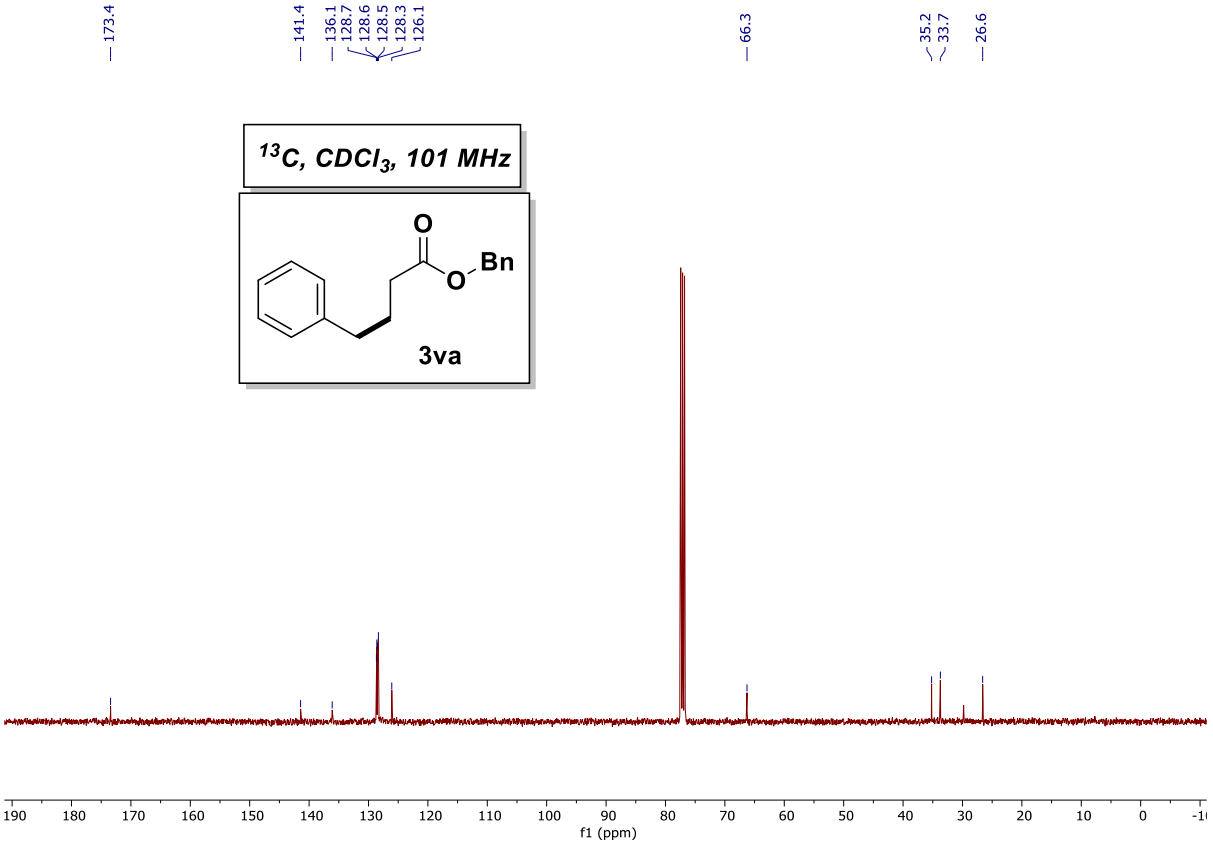

173.6
136.2
128.7
128.4
66.3
45.1
34.3
32.5
28.5
26.6
24.9
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
Cl
3ta
f1 (ppm)

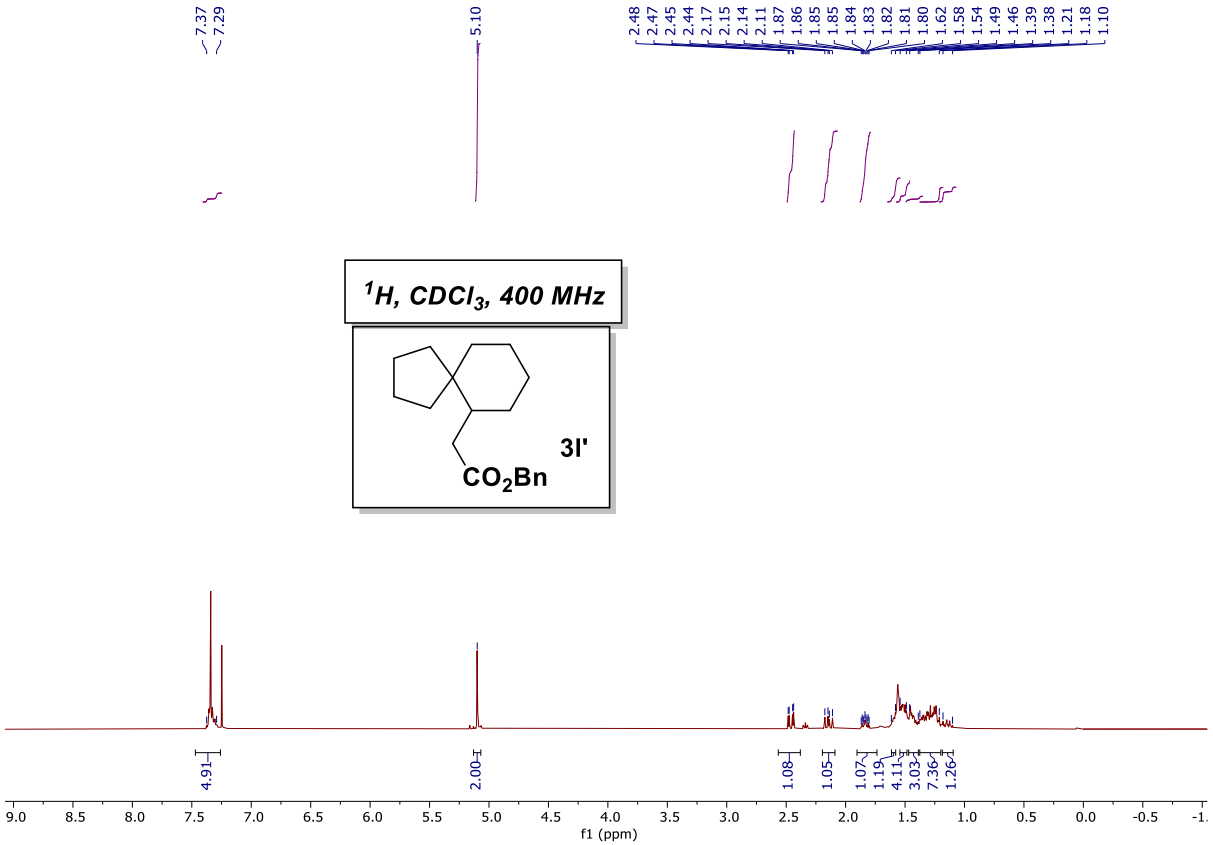

7.40
7.32
5.13
2.48
2.46
2.44
2.19
2.09
1.95
1.88
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
F_3C
3ua
4.95
2.00
2.19
2.16
2.21
f1 (ppm)

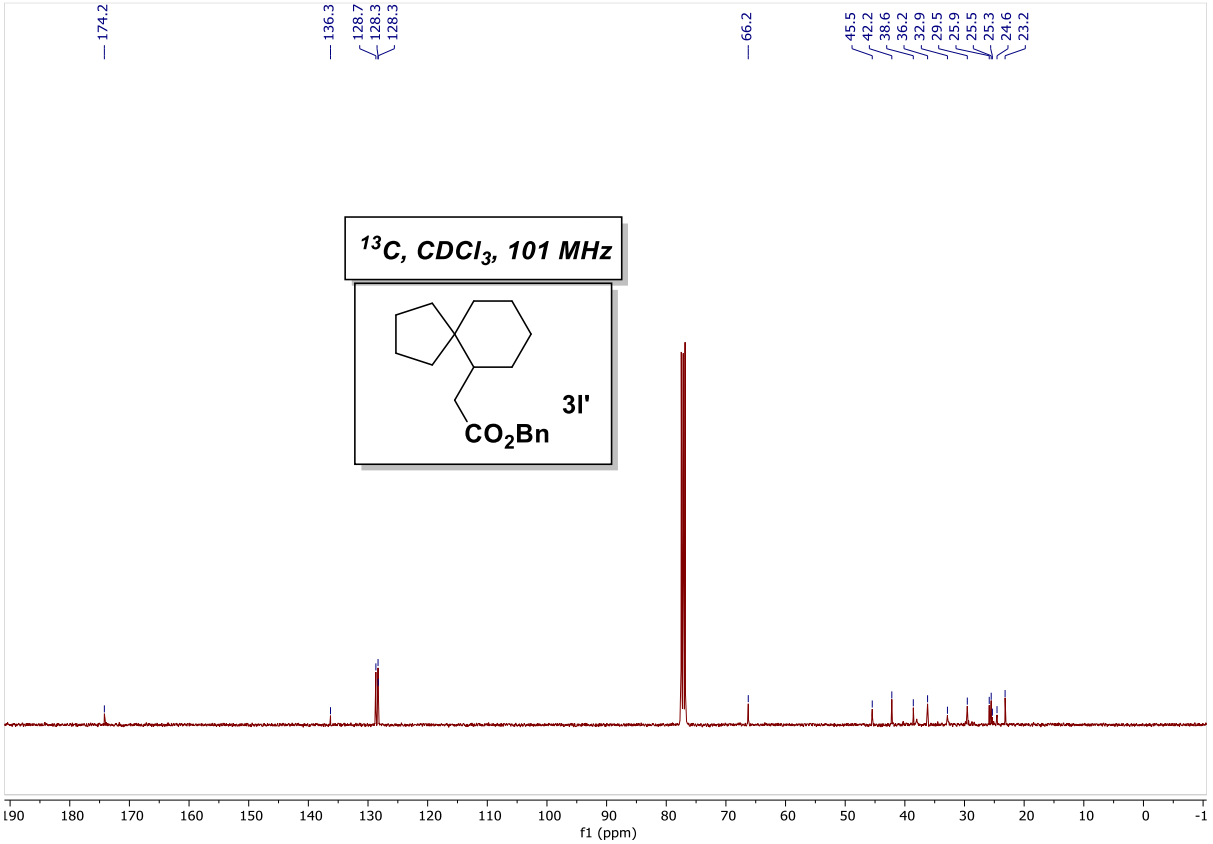

172.4
135.9
128.8
128.5
128.5
128.4
66.6
33.2
32.9
17.5
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
F_3C
3ua
f1 (ppm)

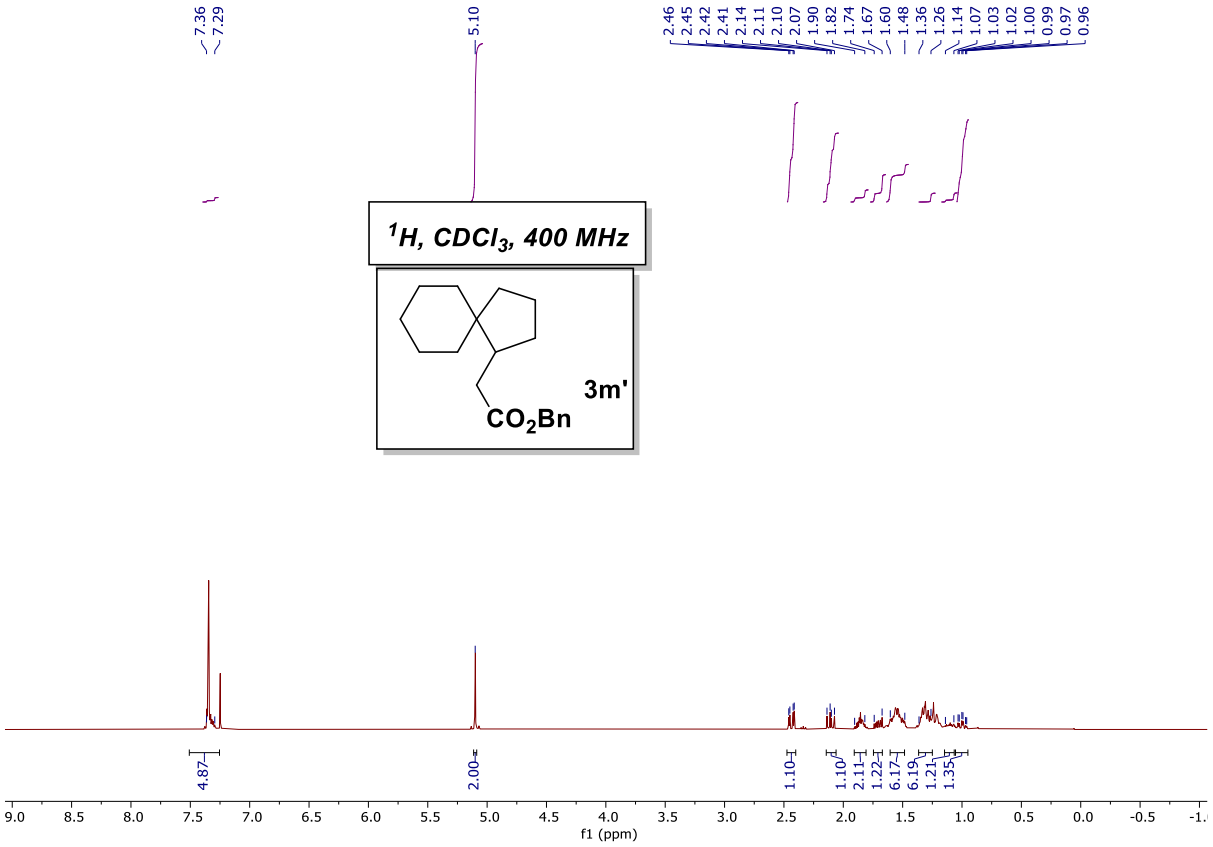

-66.3
^{19}F, $CDCl_3$, 376 MHz
O
O
Bn
F_3C
3ua
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (ppm)

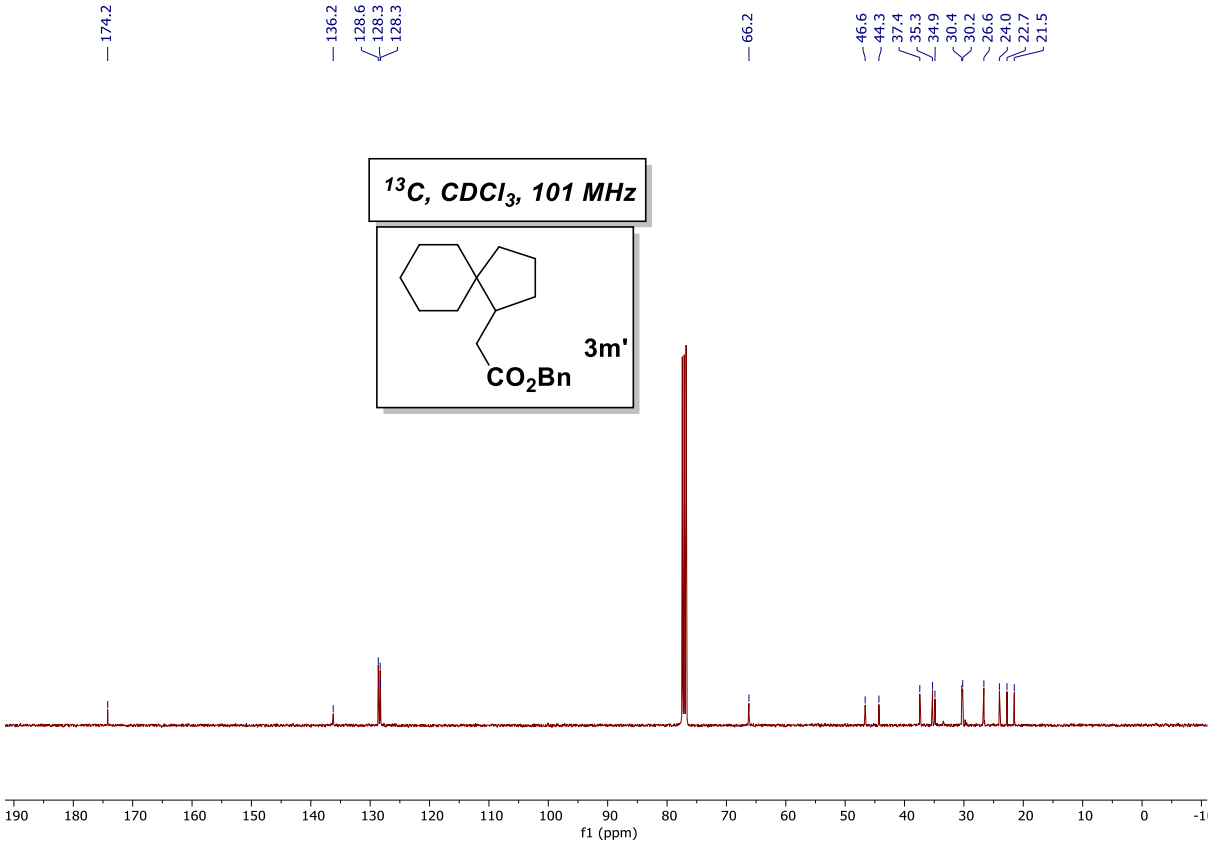

7.39
7.33
7.30
7.26
7.21
7.14
5.11
2.66
2.63
2.40
2.38
2.36
2.02
1.94
^{1}H, $CDCl_3$, 400 MHz
O
O
Bn
3va
5.05
3.14
2.20
2.00
2.03
2.06
2.17
f1 (ppm)

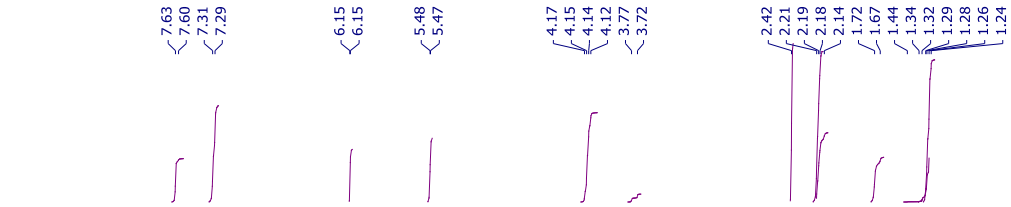

173.4
141.4
136.1
128.7
128.6
128.5
128.3
126.1
66.3
35.2
33.7
26.6
^{13}C, $CDCl_3$, 101 MHz
O
O
Bn
3va
f1 (ppm)


7.37
7.29
5.10
2.48
2.47
2.45
2.44
2.17
2.15
2.14
2.11
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.81
1.80
1.62
1.58
1.54
1.49
1.46
1.39
1.38
1.21
1.18
1.10
^{1}H, $CDCl_3$, 400 MHz
3l'
CO_2Bn
4.91
2.00
1.08
1.05
1.07
1.19
4.11
3.03
7.36
1.26
f1 (ppm)

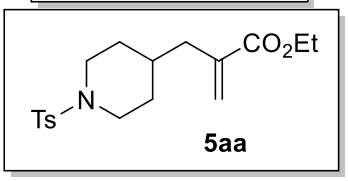

174.2
136.3
128.7
128.3
128.3
66.2
45.5
42.2
38.6
36.2
32.9
29.5
25.9
25.5
25.3
24.6
23.2
^{13}C, $CDCl_3$, 101 MHz
3l'
CO_2Bn
f1 (ppm)


7.36
7.29
5.10
2.46
2.45
2.42
2.41
2.14
2.11
2.10
2.07
1.90
1.82
1.74
1.67
1.60
1.48
1.36
1.26
1.14
1.07
1.03
1.02
1.00
0.99
0.97
0.96
^{1}H, $CDCl_3$, 400 MHz
3m'
CO_2Bn
4.87
2.00
1.10
1.10
2.11
1.22
6.17
6.19
1.21
1.35
f1 (ppm)

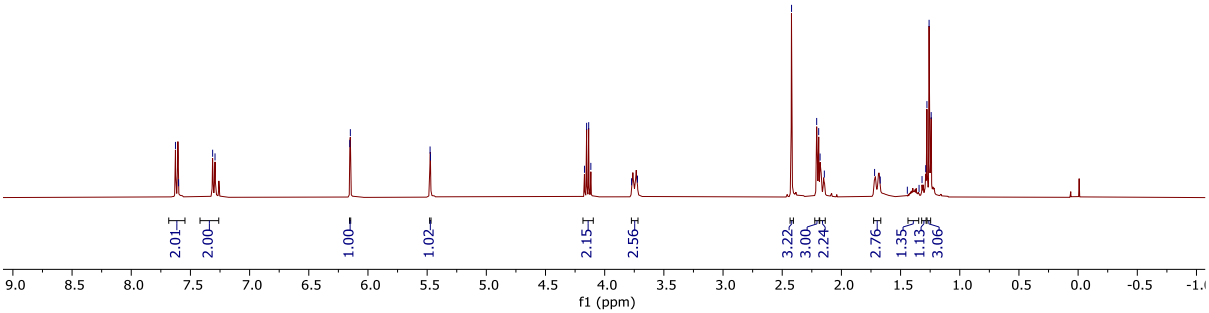

174.2
136.2
128.6
128.3
128.3
66.2
46.6
44.3
37.4
35.3
34.9
30.4
30.2
26.6
24.0
22.7
21.5
^{13}C, $CDCl_3$, 101 MHz
3m'
CO_2Bn
f1 (ppm)



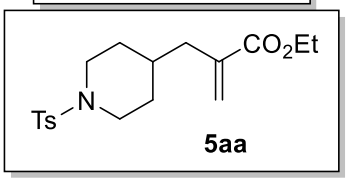
^{1}H, $CDCl_3$, 400 MHz



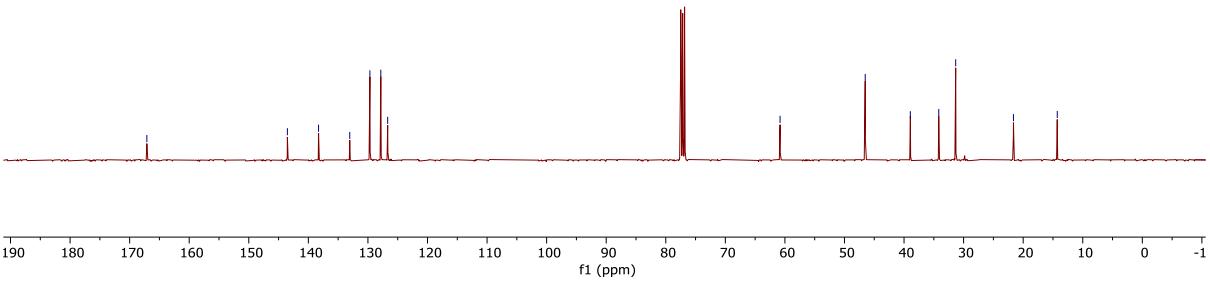
5aa

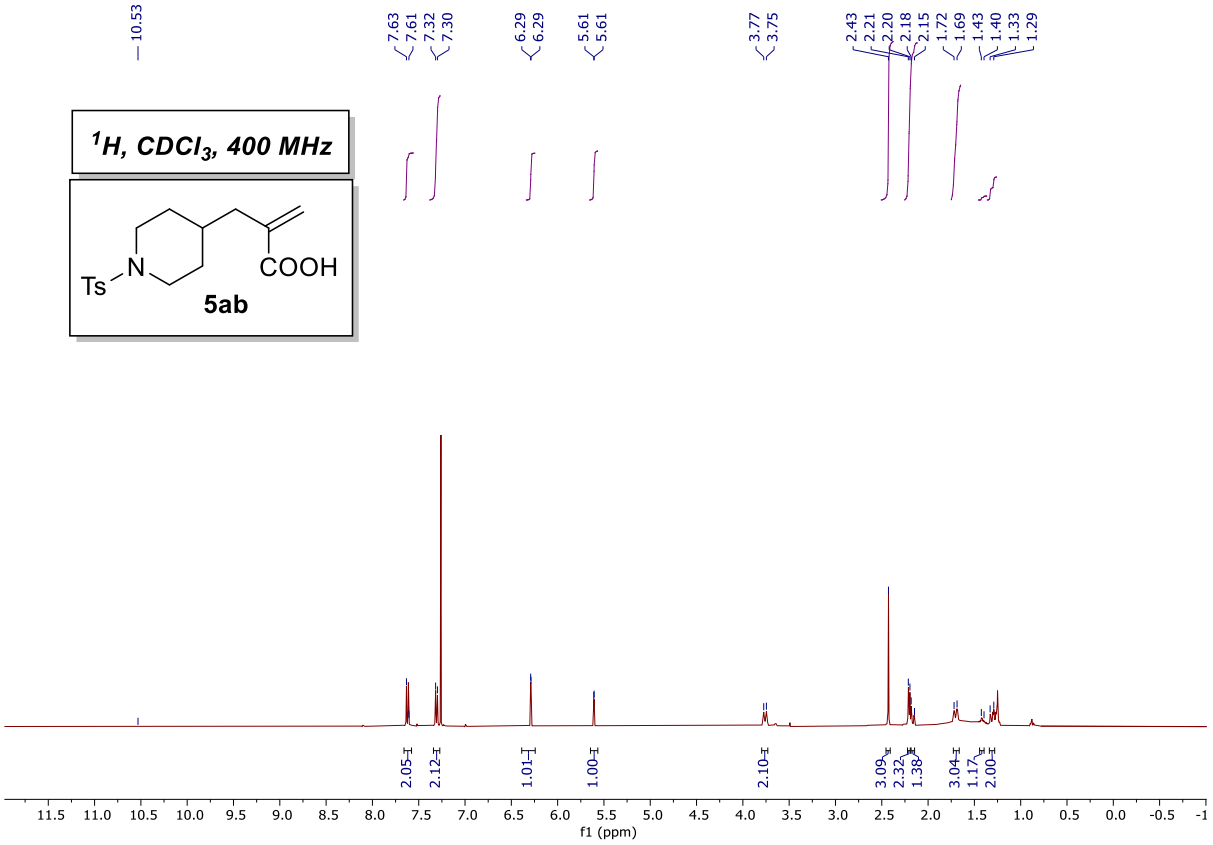


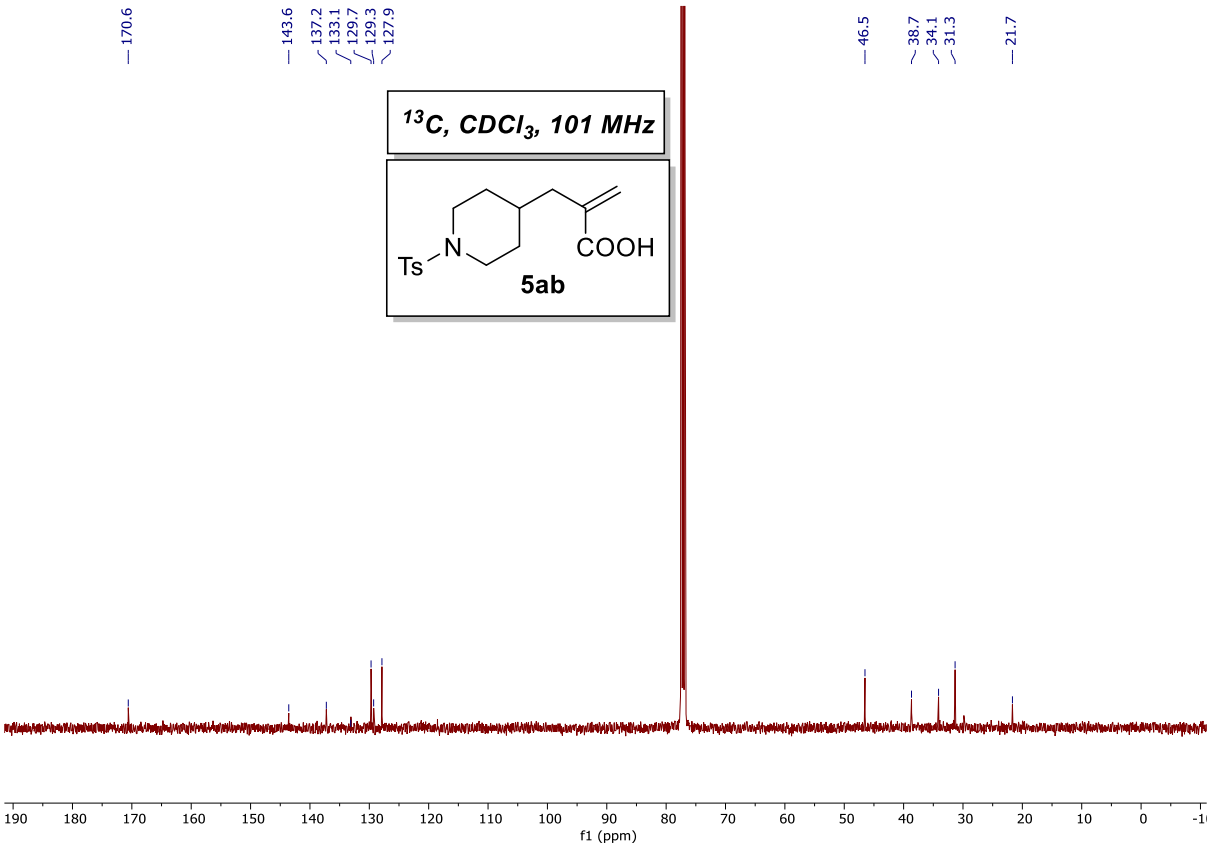
^{13}C, $CDCl_3$, 101 MHz

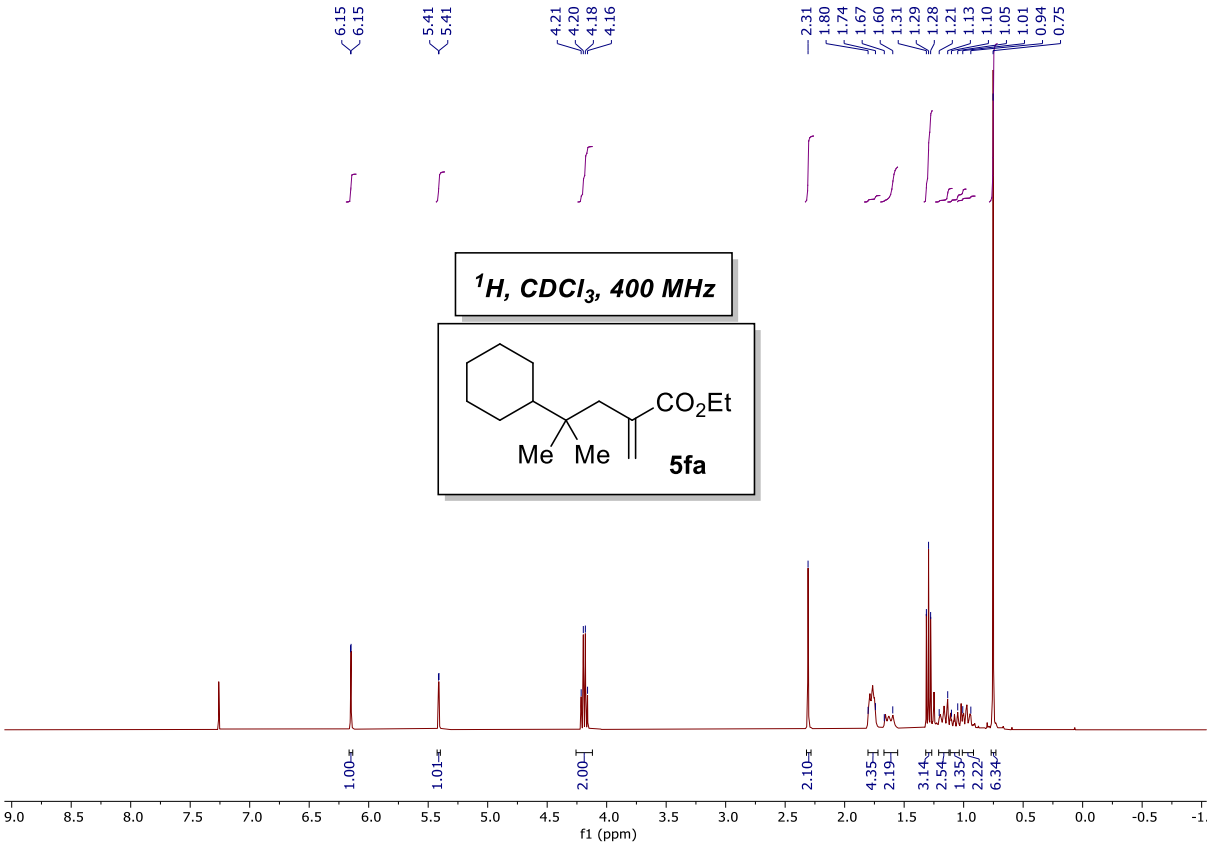


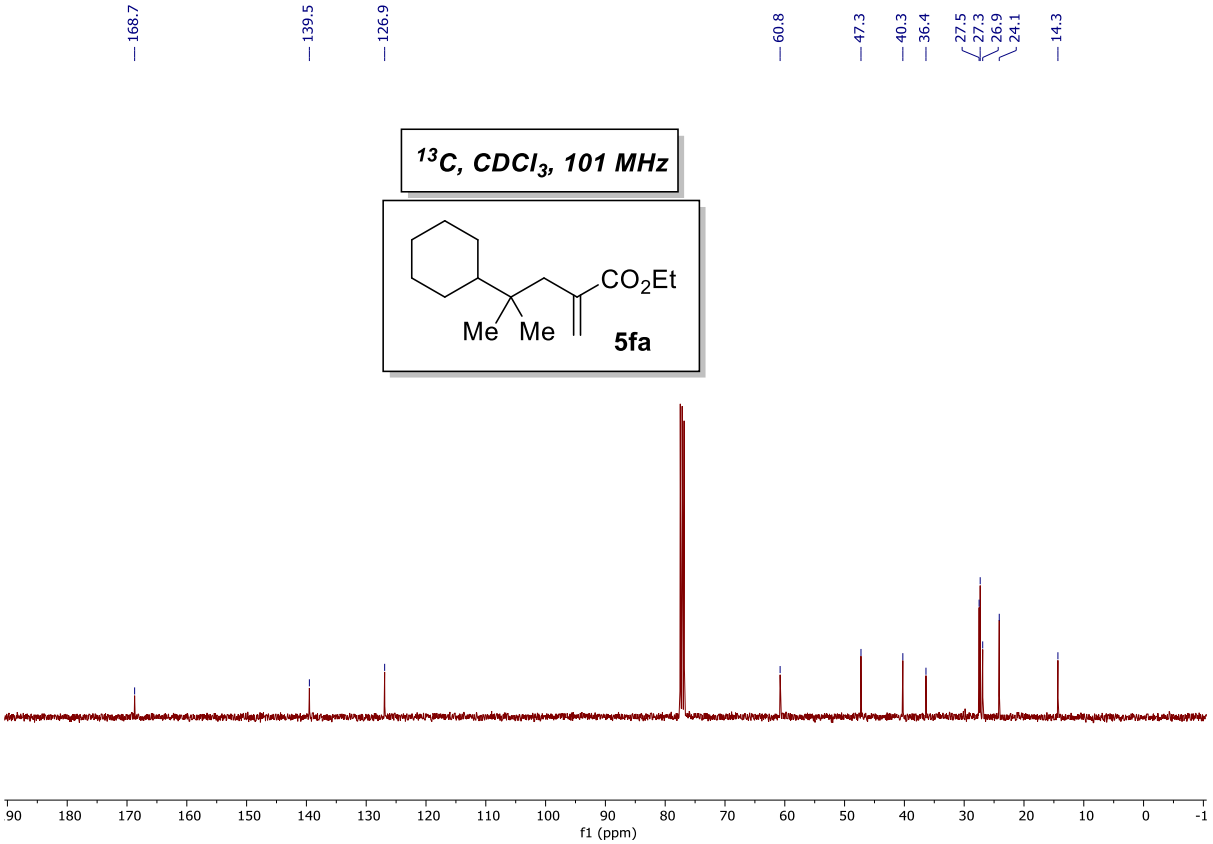
5aa

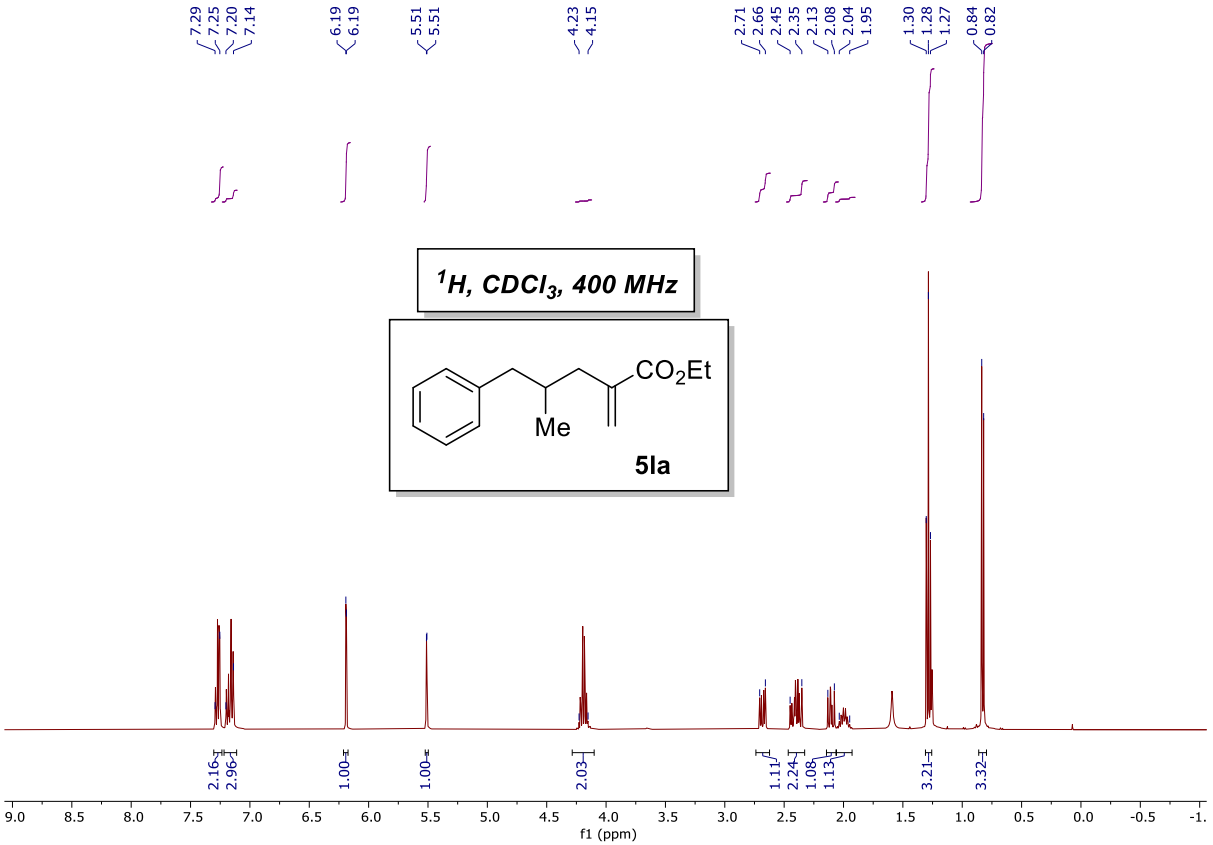


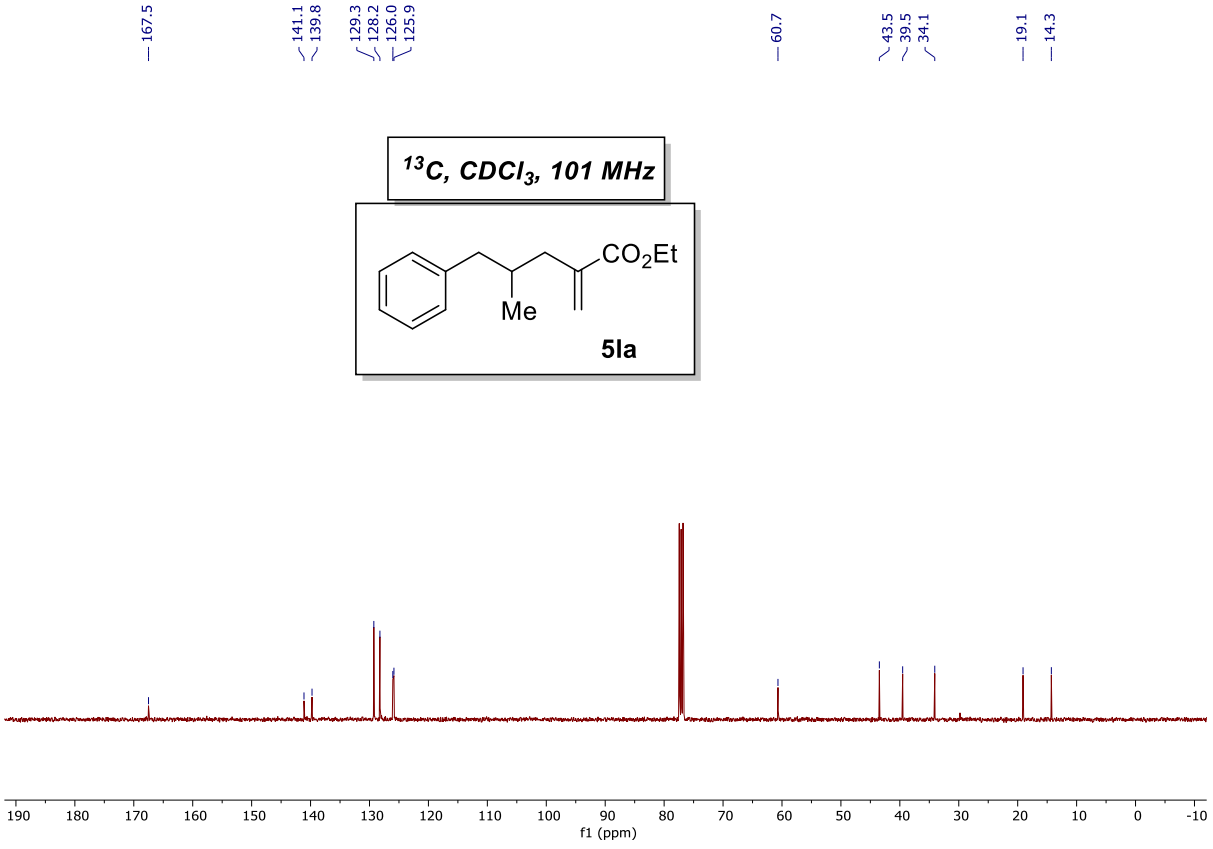

10.53
7.63
7.61
7.32
7.30
6.29
6.29
5.61
5.61
3.77
3.75
2.43
2.21
2.20
2.18
2.15
1.72
1.69
1.43
1.40
1.33
1.29
^{1}H, $CDCl_3$, 400 MHz
Ts
N
COOH
5ab
2.05
2.12
1.01
1.00
2.10
3.09
2.32
1.38
3.04
1.17
2.00
f1 (ppm)

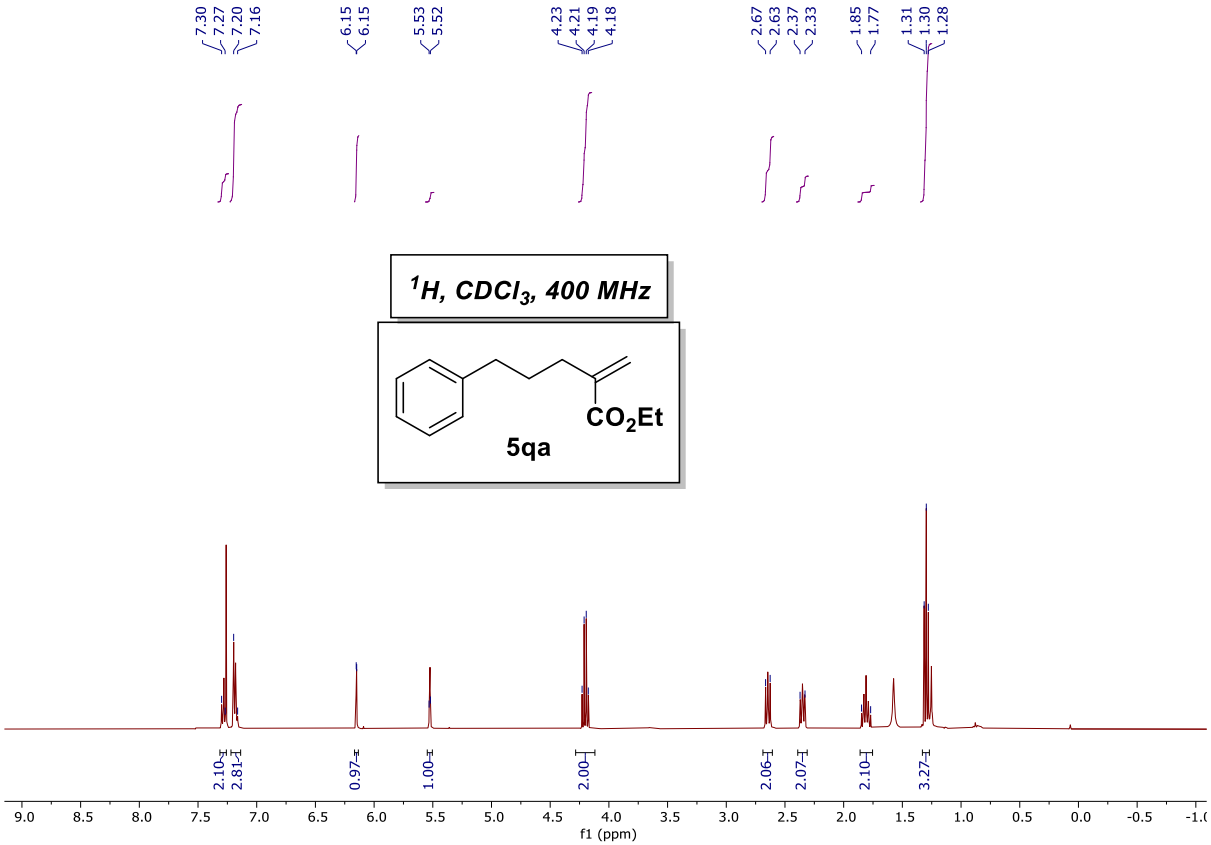

170.6
143.6
137.2
133.1
129.7
129.3
127.9
46.5
38.7
34.1
31.3
21.7
^{13}C, $CDCl_3$, 101 MHz
Ts
N
COOH
5ab
f1 (ppm)

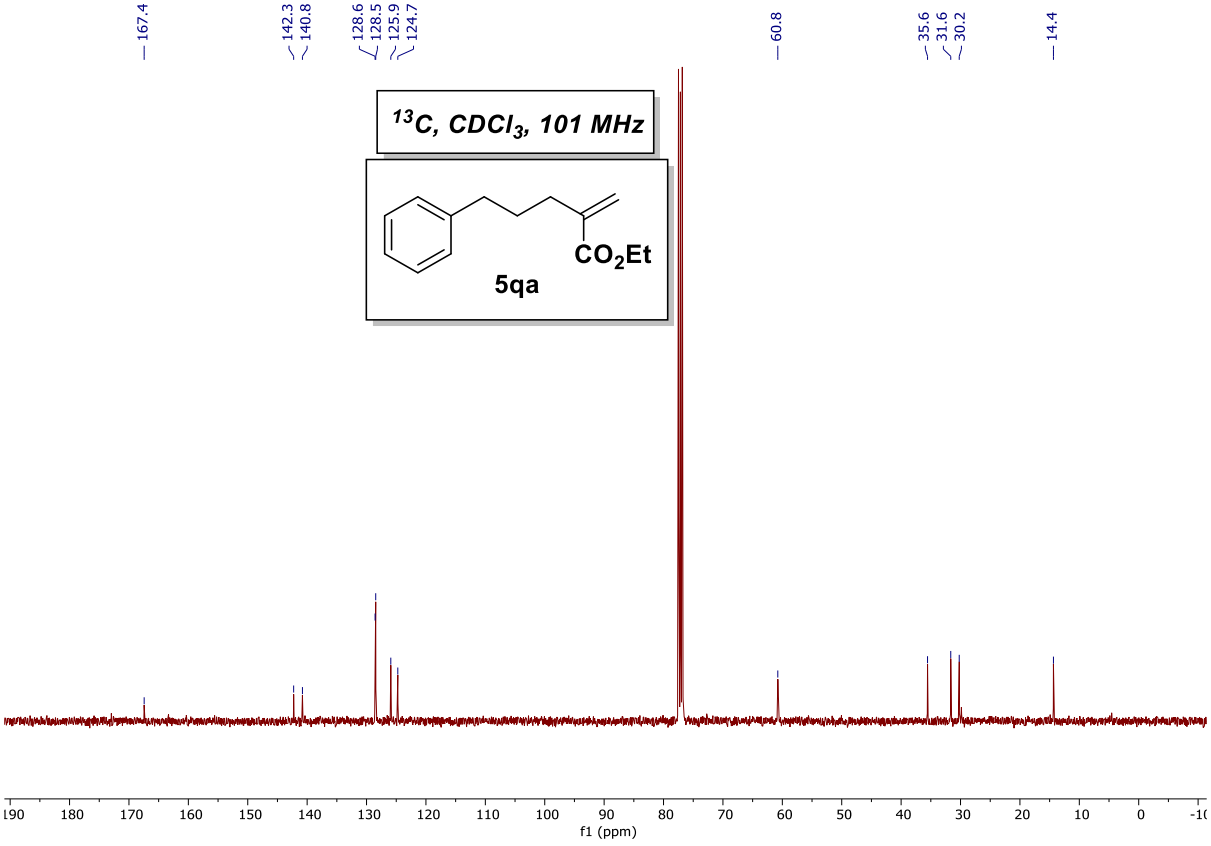

6.15
6.15
5.41
5.41
4.21
4.20
4.18
4.16
2.31
1.80
1.74
1.67
1.60
1.31
1.29
1.28
1.21
1.13
1.10
1.05
1.01
0.94
0.75
1H, CDCl3, 400 MHz
CO2Et
Me Me
5fa
1.00
1.01
2.00
2.10
4.35
2.19
3.14
2.54
1.35
2.22
6.34
f1 (ppm)

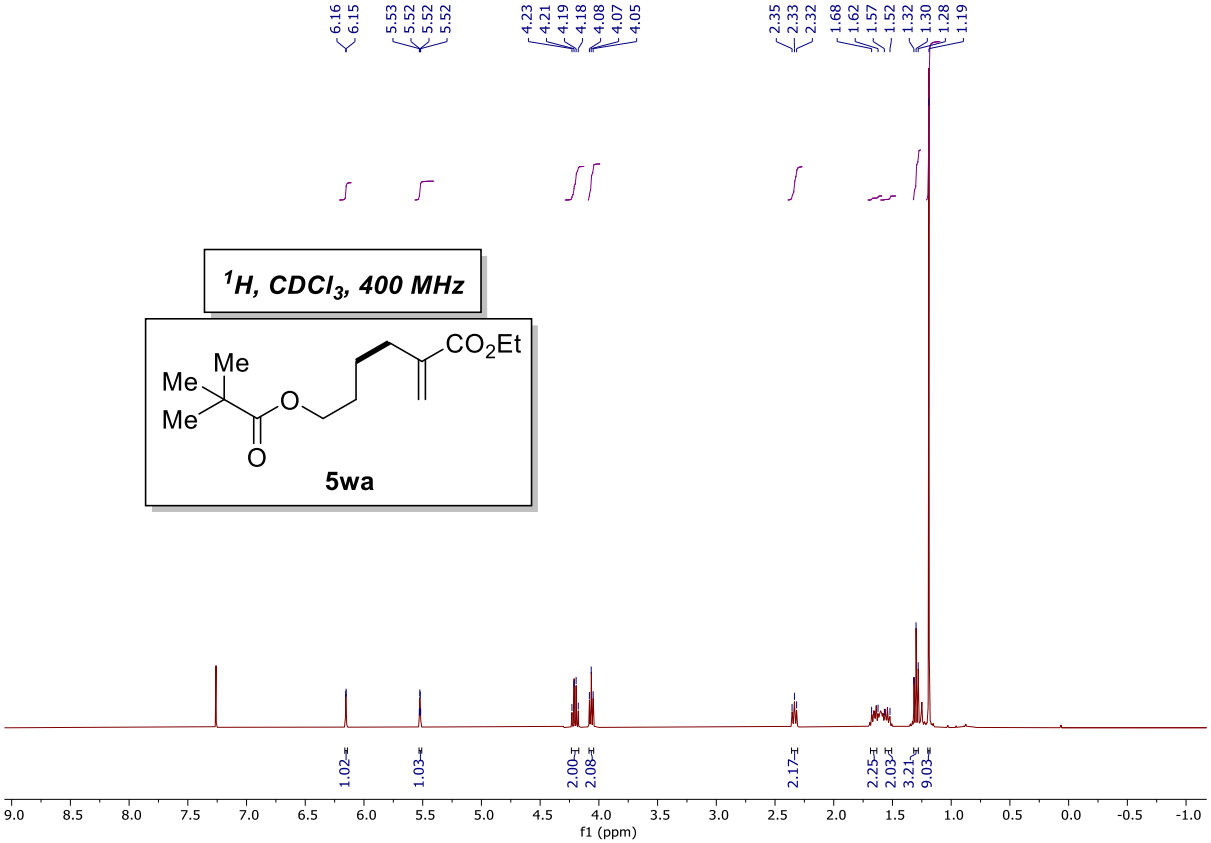

168.7
139.5
126.9
60.8
47.3
40.3
36.4
27.5
27.3
26.9
24.1
14.3
13C, CDCl3, 101 MHz
CO2Et
Me Me
5fa
f1 (ppm)

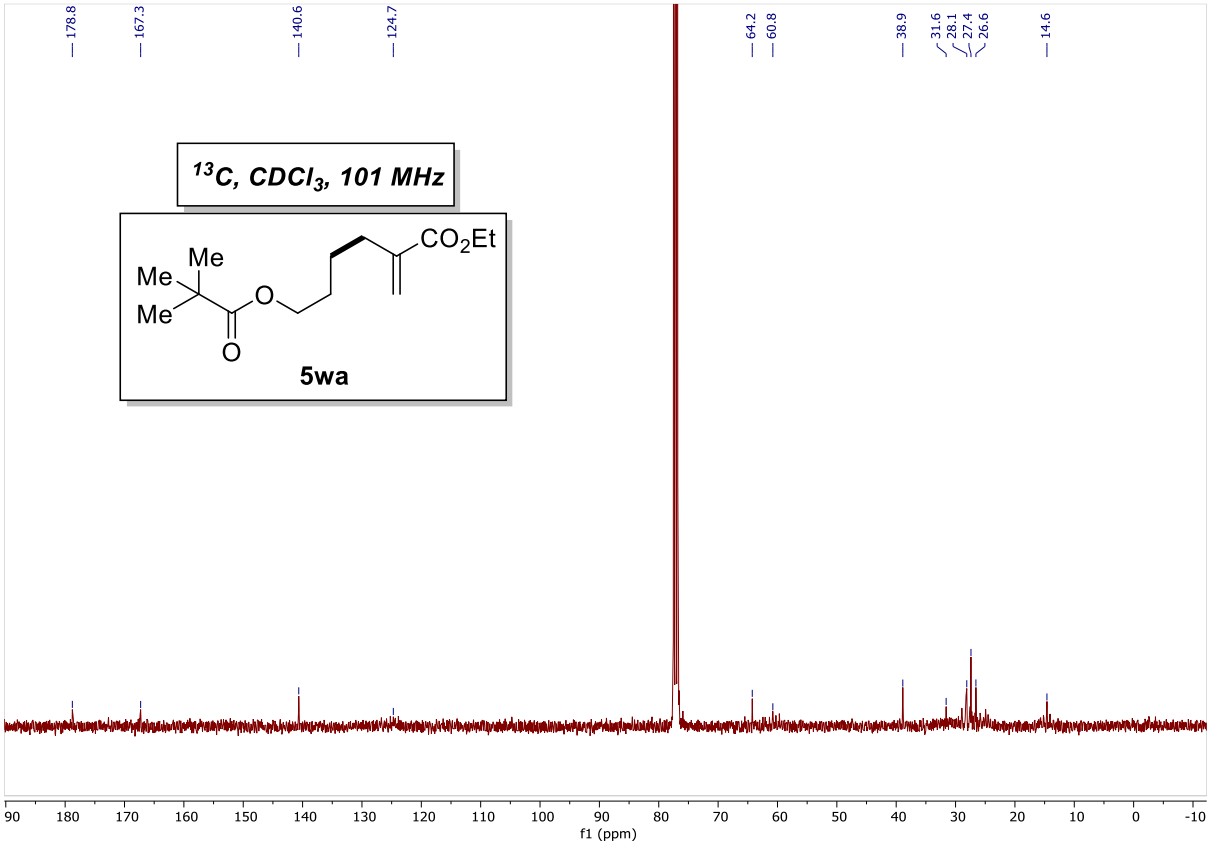

7.29
7.25
7.20
7.14
6.19
6.19
5.51
5.51
4.23
4.15
2.71
2.66
2.45
2.35
2.13
2.08
2.04
1.95
1.30
1.28
1.27
0.84
0.82
^{1}H, $CDCl_3$, 400 MHz
CO_2Et
Me
5la
2.16
2.96
1.00
1.00
2.03
1.11
2.24
1.08
1.13
3.21
3.32
f1 (ppm)

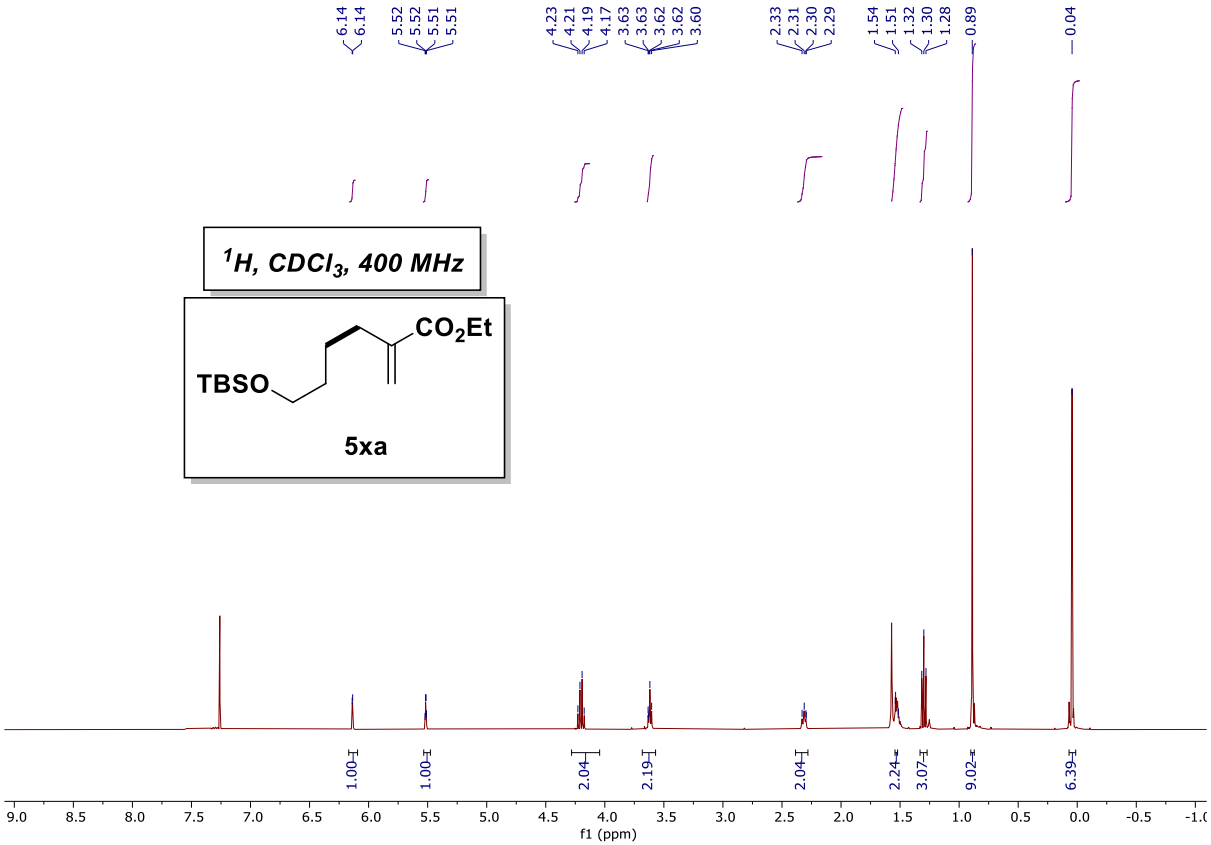

167.5
141.1
139.8
129.3
128.2
126.0
125.9
60.7
43.5
39.5
34.1
19.1
14.3
^{13}C, $CDCl_3$, 101 MHz
CO_2Et
Me
5la
f1 (ppm)

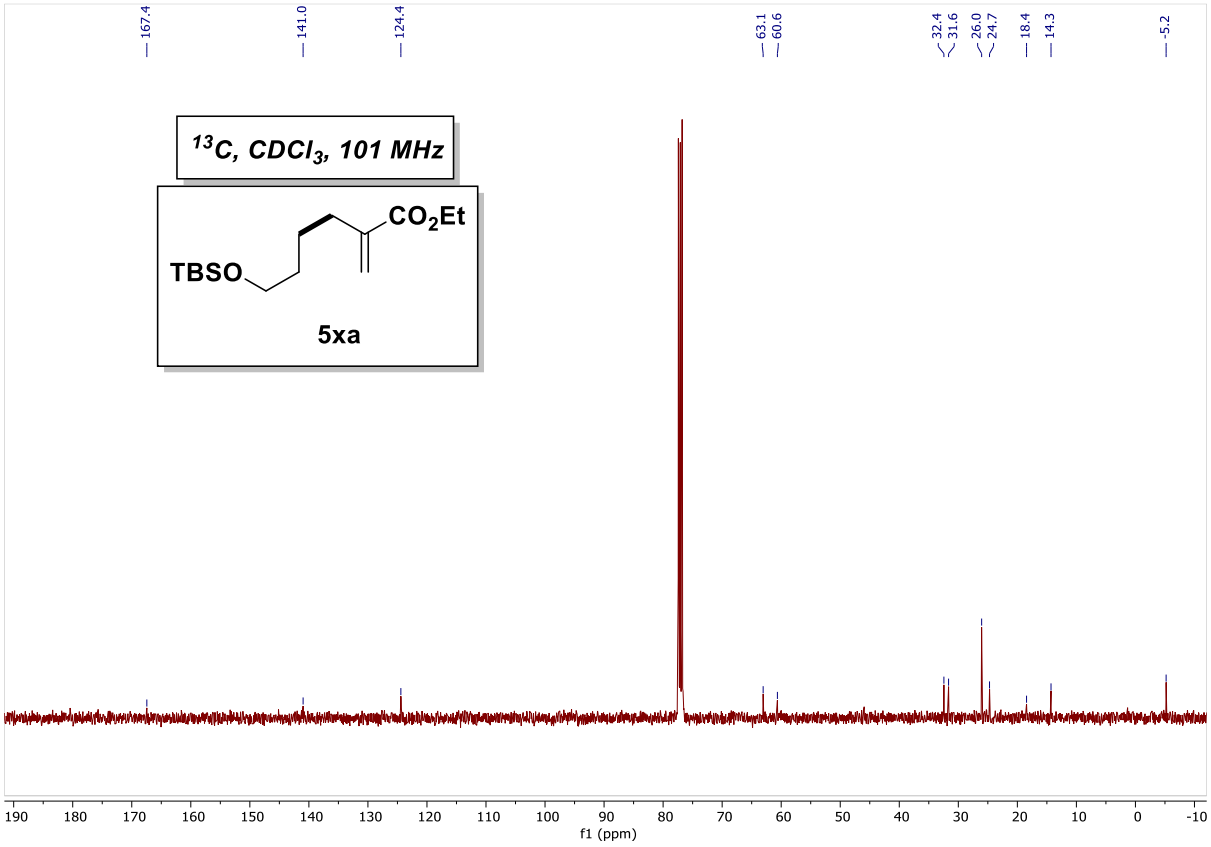

7.30
7.27
7.20
7.16
6.15
6.15
5.53
5.52
4.23
4.21
4.19
4.18
2.67
2.63
2.37
2.33
1.85
1.77
1.31
1.30
1.28
^{1}H, $CDCl_3$, 400 MHz
CO_2Et
5qa
2.10
2.81
0.97
1.00
2.00
2.06
2.07
2.10
3.27
f1 (ppm)

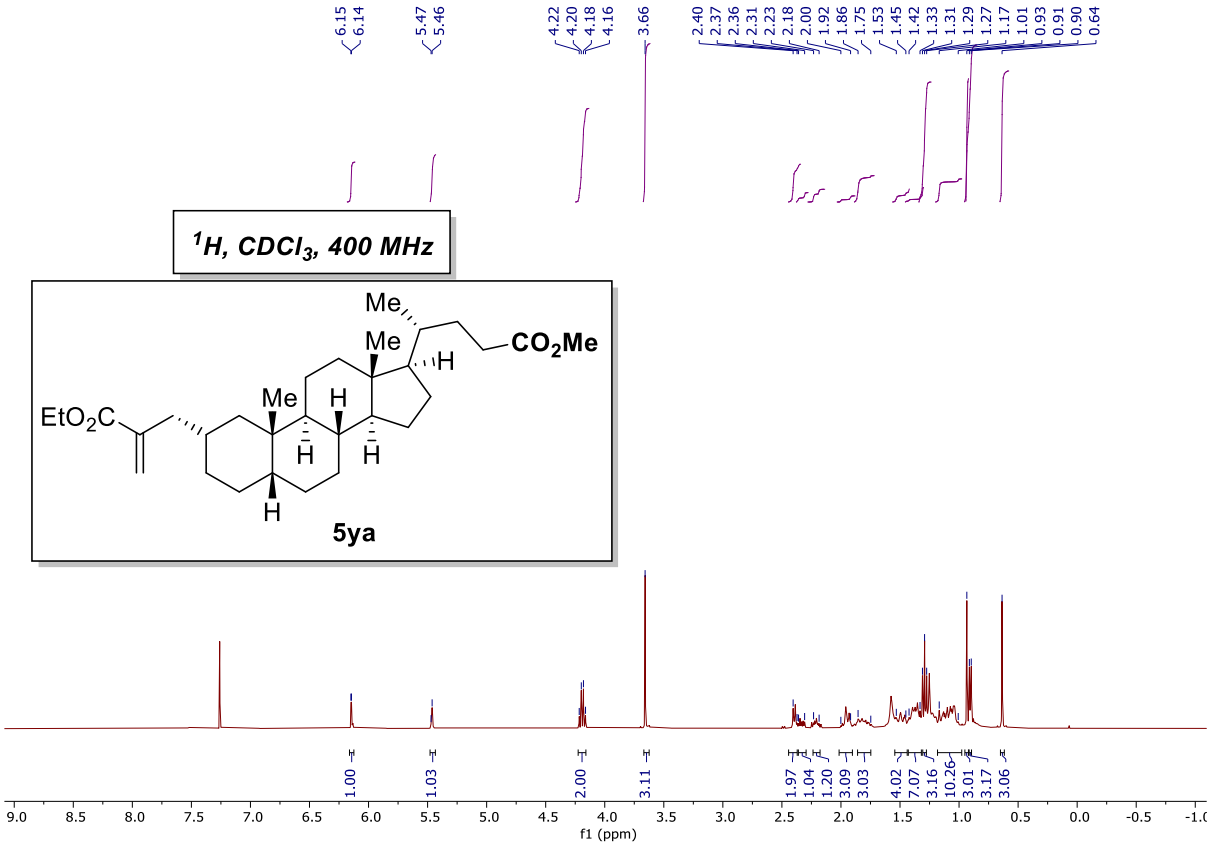

167.4
142.3
140.8
128.6
128.5
125.9
124.7
60.8
35.6
31.6
30.2
14.4
^{13}C, $CDCl_3$, 101 MHz
CO_2Et
5qa
f1 (ppm)

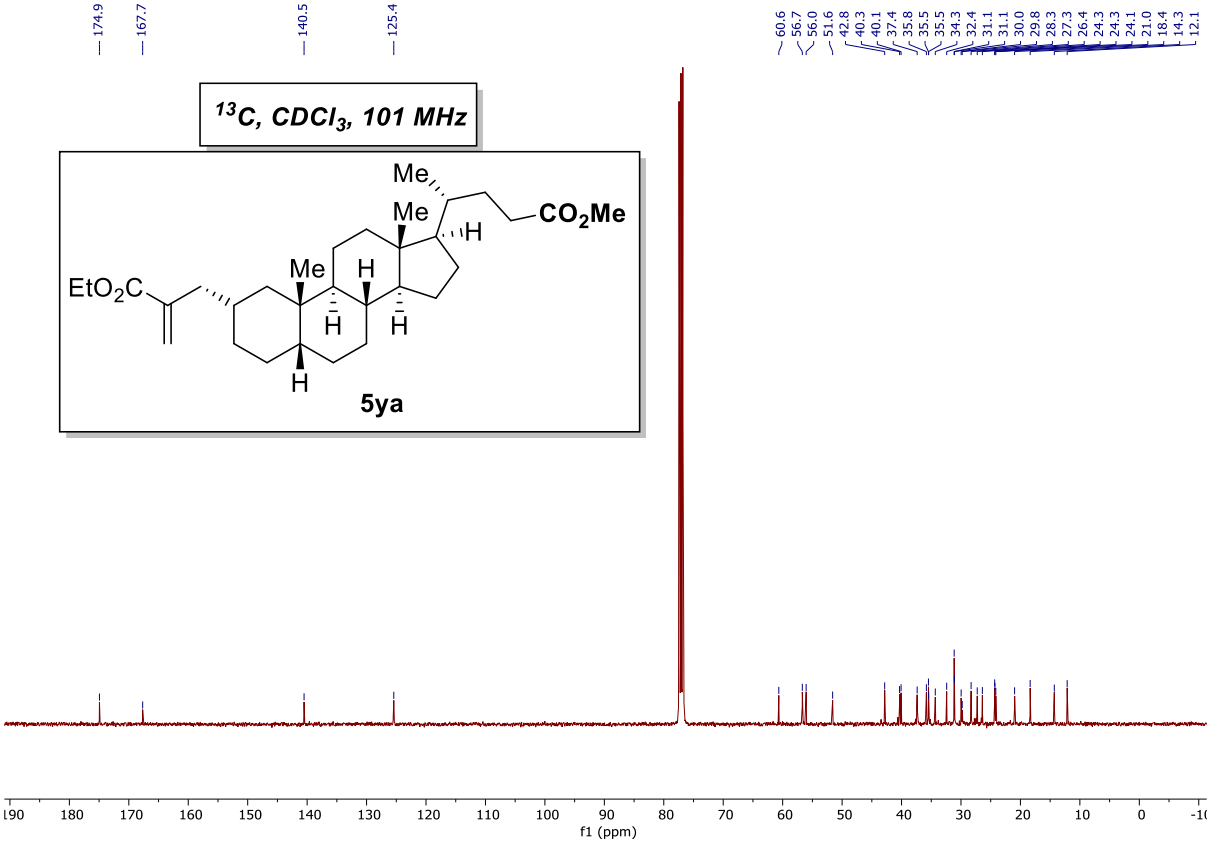

6.16
6.15
5.53
5.52
5.52
5.52
4.23
4.21
4.19
4.18
4.08
4.07
4.05
2.35
2.33
2.32
1.68
1.62
1.57
1.52
1.32
1.30
1.28
1.19
^{1}H, $CDCl_3$, 400 MHz
Me
Me
Me
O
O
CO_2Et
5wa
1.02
1.03
2.00
2.08
2.17
2.25
2.03
3.21
9.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


178.8
167.3
140.6
124.7
64.2
60.8
38.9
31.6
28.1
27.4
26.6
14.6
^{13}C, $CDCl_3$, 101 MHz
Me
Me
Me
O
O
CO_2Et
5wa
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


6.14
6.14
5.52
5.52
5.51
5.51
4.23
4.21
4.19
4.17
3.63
3.63
3.62
3.62
3.60
2.33
2.31
2.30
2.29
1.54
1.51
1.32
1.30
1.28
0.89
0.04
^{1}H, $CDCl_3$, 400 MHz
CO_2Et
TBSO
5xa
1.00
1.00
2.04
2.19
2.04
2.24
3.07
9.02
6.39
f1 (ppm)


167.4
141.0
124.4
63.1
60.6
32.4
31.6
26.0
24.7
18.4
14.3
-5.2
^{13}C, $CDCl_3$, 101 MHz
CO_2Et
TBSO
5xa
f1 (ppm)


6.15
6.14
5.47
5.46
4.22
4.20
4.18
4.16
3.66
2.40
2.37
2.36
2.31
2.23
2.18
2.00
1.92
1.86
1.75
1.53
1.45
1.42
1.33
1.31
1.29
1.27
1.17
1.01
0.93
0.91
0.90
0.64
^{1}H, $CDCl_3$, 400 MHz
Me
Me
CO_2Me
H
EtO_2C
Me
H
H
H
H
5ya
1.00
1.03
2.00
3.11
1.97
1.04
1.20
3.09
3.03
4.02
7.07
3.16
10.26
3.01
3.17
3.06
f1 (ppm)


174.9
167.7
140.5
125.4
60.6
56.7
56.0
51.6
42.8
40.3
40.1
37.4
35.8
35.5
35.5
34.3
32.4
31.1
31.1
30.0
29.8
28.3
27.3
26.4
24.3
24.3
24.1
21.0
18.4
14.3
12.1
^{13}C, $CDCl_3$, 101 MHz
Me
Me
CO_2Me
H
EtO_2C
Me
H
H
H
H
5ya
f1 (ppm)