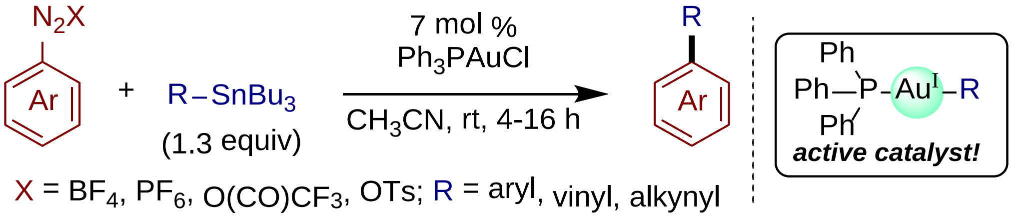
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Gold(I)-Catalyzed Cross-Coupling Reactions of Aryldiazonium Salts with Organostannanes

Manjur O. Akram, Popat S. Shinde, Chetan C. Chintawar and Nitin T. Patil*



Contents

1. General information

1.1 Practical considerations:

All reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere, unless otherwise specified. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. Unless otherwise stated, all gold catalyzed reactions were carried out under argon atmosphere. All experiments were monitored by analytical thin layer chromatography (TLC) or Gas Chromatography by using 1,2-dibromobutane as an internal standard. TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ and charring on a hot plate. Solvents were removed in vacuum and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet ether and equilibrated with the appropriate solvent mixture prior to use. The elution was assisted by applying pressure with an air pump.

1.2 Instrumentation:

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV, 400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^1H NMR signals are designated as s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), sep (septet), m (multiplet) etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Gas chromatography (GC) was performed on a Perkin Elmer Arnel Clarus 500 instrument equipped with a hydrogen flame ionization detector; HP5 columns (polar) (12 m×0.32 mm×1.0 μm) were used with helium as the carrier gas at a flow rate of 1 mL/min.

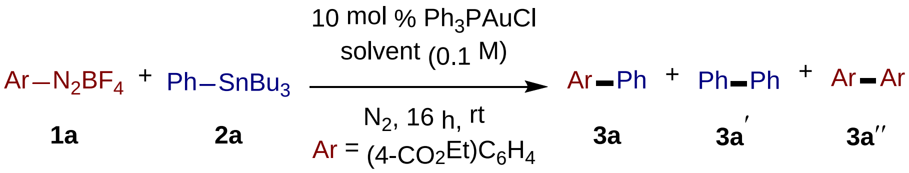
1.3 Materials:

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was distilled from Na/benzophenone under an atmosphere of N_2. Solvents, e.g. MeOH, MeCN, DCM, DCE, $CHCl_3$, DMF, 1,4-dioxane were dried using standard protocol under N_2. All the diazonium salts and organostannens were prepared by using standard methods. Gold and silver salts were purchased from Sigma-Aldrich and stored under inert atmosphere.

2. Optimization of the reactions conditions:

To an oven-dried screw-cap vial containing a stir bar were added 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**, 0.1 mmol), tributylphenylstannae (**2a**), [Au] cat and degassed solvent (0.1 M). The reaction vial was fitted with a cap, evacuated and back filled with nitrogen and stirred at room temperature for 16 h. The mixture was then diluted with diethyl ether (5 mL) and the residue was subsequently purified by chromatography on silica gel using petroleum ether and ethyl acetate to yield the cross-coupled product **3a**. The GC yields were determined by using 1,2-dibromobutane as an internal standard.

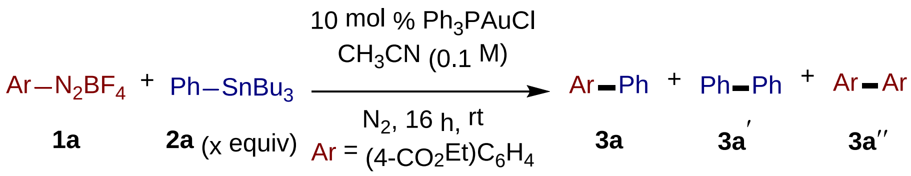
2.1 Solvent screening:[a]



entry	solvent	yield (%)[b] **3a**:**3a'**:**3a''**
1	MeOH	49(46):26:8
2	$CHCl_3$	17:8:≤5
3	DCM	35:8:≤5
4	DCE	44:14:8
5	THF	44:8:≤5
6	DMF	45:14:11
7	**CH_3CN**	**59(55[c]):17:≤5**
8	1,4-dioxane	49:14:≤5

[a] **Reaction conditions**: 0.10 mmol **1a**, 0.10 mmol **2a**, 10 mol % Ph_3PAuCl, degassed 0.1 (M) solvent, N_2, rt, 16 h. [b] Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c] Isolated yields.

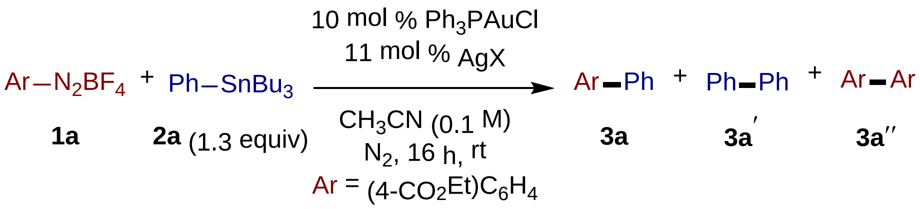
2.2 Studies on stoichimetry of 2a:[a]



entry	x equiv	yield (%)^{b,c} **3a:3a':3a''**
1	**1.3**	**73(69^{d}):13:≤5**
2	1.5	71(66^{d}):15:≤5
3	2	66:14:≤5

[a] **Reaction conditions**: 0.10 mmol **1a**, x equiv **2a**, 10 mol % Ph_3PAuCl, degassed 0.1 (M) CH_3CN, N_2, rt, 16 h. [b] Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c] Yields of **3a'** was based on **2a**. [d] Isolated yields.

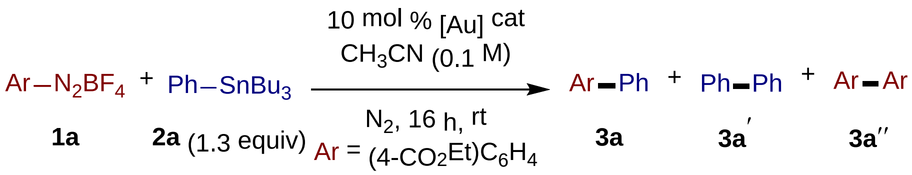
2.3 Screening of counter anions on Au center:[a]



entry	X	yield (%)^{b,c} **3a:3a':3a''**
1	NTf_2	53:16:≤5
2	OTf	48:14:≤5
3	BF_4	53:8:≤5
4	SbF_6	41:14:≤5

[a] **Reaction conditions**: 0.10 mmol **1a**, 0.13 mmol **2a**, 10 mol % Ph_3PAuCl, 11 mol % AgX (X = NTf_2, OTf, BF_4, SbF_6), degassed 0.1 (M) CH_3CN, N_2, rt, 16 h. [b] Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c] Yields of **3a'** was based on **2a**.

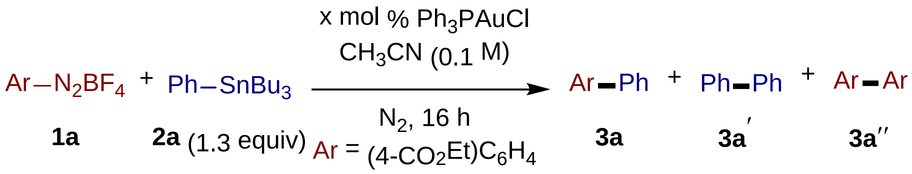
2.4 Screening of Au-complexes:[a]



entry	[Au] cat	yield (%)[b,c] **3a:3a':3a''**
1	AuCl	NR
2	$AuCl_3$	NR
3	IPrAuCl	NR
4	(*p*-Me-C_6H_4)$_3$PAuCl	52:11:≤5
5	(*p*-OMe-C_6H_4)$_3$PAuCl	55:16:≤5
6	(*p*-F-C_6H_4)$_3$PAuCl	57:19:≤5
7	(*p*-CF_3-C_6H_4)$_3$PAuCl	65:13:≤5
8	(C_6F_5)$_3$PAuCl	17:14:≤5
9	JohnPhosAuCl	NR
10	CyJohnPhosAuCl	NR
11	dppmAu_2Cl_2	61:11:≤5

[a] **Reaction conditions**: 0.10 mmol **1a**, 0.13 mmol **2a**, 10 mol % [Au], degassed 0.1 (M) CH_3CN, N_2, rt, 16 h. [b] Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c] Yields of **3a'** was based on **2a**. NR = no reaction.

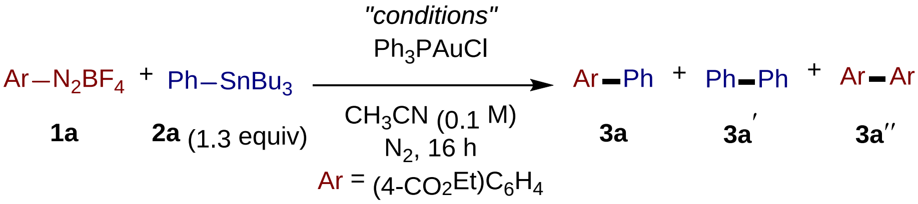
2.5 Effect of catalyst loadings:[a]



entry	x mol %	yield (%)[b,c] **3a:3a':3a''**
1	10	73(69[d]):13:≤5
2	7	72(69[d]):13:≤5
3	5	66(59[d]):11:≤5

[a]**Reaction conditions**: 0.10 mmol **1a**, 0.13 mmol **2a**, x mol % Ph_3AuCl, degassed 0.1 (M) CH_3CN, N_2, rt, 16 h. [b]Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c]Yields of **3a'** was based on **2a**. [d]Isolated yields.

2.6 Control experiments:[a]



entry	*"conditions"*	yield (%)[b,c] **3a**:**3a'**:**3a''**
1	2 mol % $Ru(bpy)_3(PF_6)_2$, 23 W CFL bulb, rt	49:21:11
2	2 equiv bipyridine	56:15:00
3	2 equiv CsF	41:11:9
4	2 equiv KF	39:15:6
5	23 W CFL bulb	65:15:8
6	3 W blue LEDs	65:13:7
7	dark	67:13:≤5
8	heated at 50 °C	51:16:8

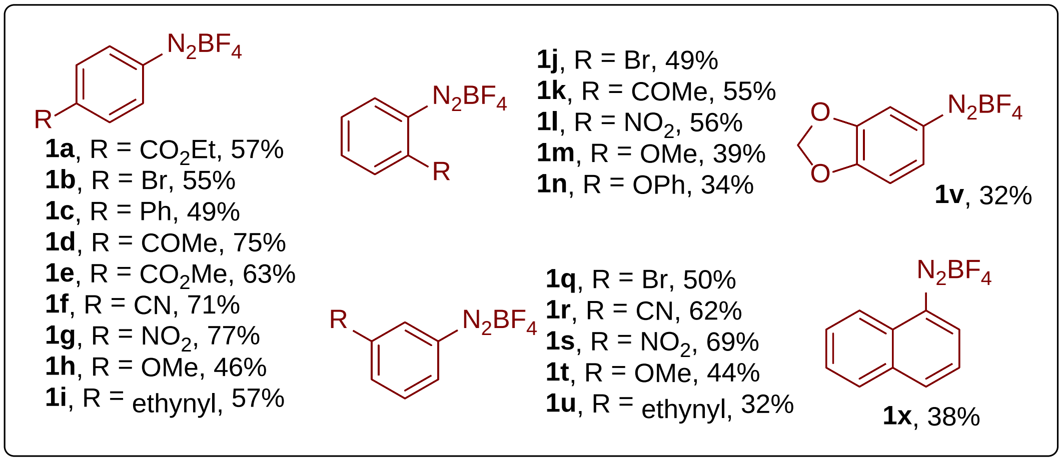
[a]**Reaction conditions**: 0.10 mmol **1a**, 0.13 mmol **2a**, 7 mol % Ph_3PAuCl, degassed 0.1 (M) CH_3CN, N_2, rt, 16 h. [b]Yields were calculated by GC using 1,2-dibromobutane as an internal standard. [c]Yields of **3a'** was based on **2a**.

3. General procedures

3.1 Preparation of starting materials:

3.1.1 Experimental procedure for the synthesis of aryl diazonium salts (ArN_2X):

Representative procedure A:[1] To a suspension of ethyl 4-aminobenzoate (10.0 mmol) in water, HBF_4 (48% in water, 20.0 mmol, 2.0 equiv) was added at rt and the reaction mixture was stirred for 2 min. The reaction mixture was cooled to 0 °C and a saturated aqueous solution of $NaNO_2$ (10.0 mmol, 1.0 equiv) was added drop-wise. The reaction mixture was stirred for 15 min at 0 °C. The resultant solid was filtered, washed with ice-cold water (5 mL) and diethyl ether (10 mL) to give the crude product which was further purified by precipitation with diethyl ether from an acetone solution to obtain ethyl 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**1a**) as white solid in 57% yield. Aryl diazonium salts **1b-1n**, **1q-1v** and **1x** were prepared by procedure A.



Representative procedure B:[2] To a saturated solution of 3-aminoquinoline (10.0 mmol) in ethanol, HBF_4 (48% in water, 20.0 mmol, 2.0 equiv) was added at rt and the reaction mixture was stirred for 2 min. The mixture was then cooled to 0 °C and *tert*-butyl nitrite (10.0 mmol, 1.0 equiv) was added in drop-wise manner. The mixture was stirred for 15 min at 0 °C and then for 1 h at rt. Diethyl ether (20 mL) was added to the reaction mixture and the resulting solid was filtered, washed with diethyl ether (3 x 20 mL) and dried under high vacuum to afford the

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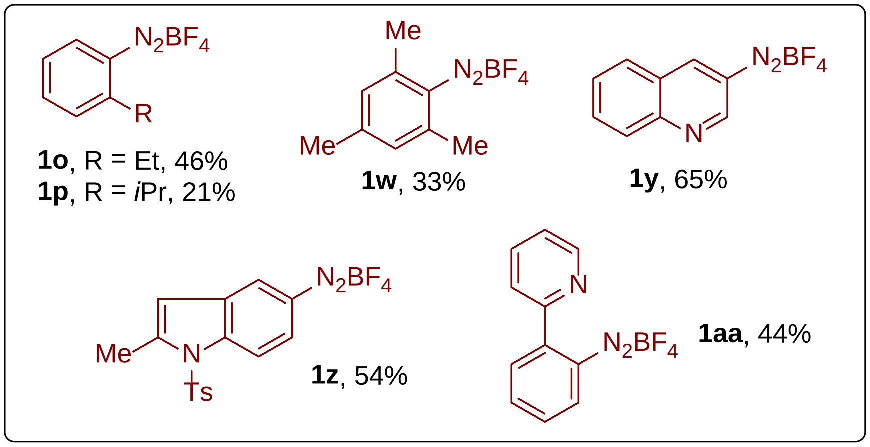
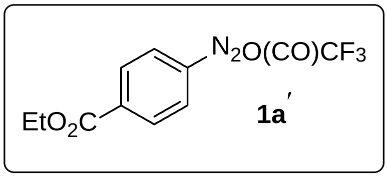
[1] W. Erb, A. Hellal, M. Albini, J. Rouden, J. Blanchet, *Chem. Eur. J.*, 2014, **20**, 6608.

[2] J. Wu, Y. Gu, X. Leng, Q. Shen, *Angew. Chem.*, *Int. Ed.*, 2015, **54**, 7648.

aryldiazonium salt **1y** as white solid in 46% yield. Aryl diazonium salts **1o**, **1p**, **1w**, **1z** and **1aa** were prepared by procedure B.



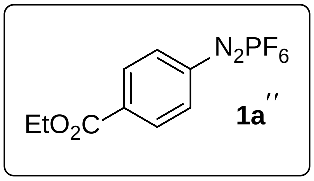
Synthesis of 1a':[1]



To a solution of ethyl 4-aminobenzoate (1.65 g, 10.0 mmol) in dry CH_2Cl_2 (20 mL) trifluoroacetic acid (1.6 mL, 2.39 g, 21.0 mmol, 2.1 equiv) was added at rt. The reaction mixture was then cooled to 0 °C and isopentyl nitrite (1.6 mL, 1.41 g, 12.0 mmol, 1.2 equiv) was added drop-wise. The reaction mixture was stirred for 1 h at 0 °C before being cooled to −78 °C. Ice-cold diethyl ether (20 mL) was added drop-wise and the resulting solid was filtered using a sintered glass funnel. The crude product was washed with cold diethyl ether (3 x 20 mL) and dried under high vacuum to give the title **1a'** as a white solid (1.36 g, 47%).

^{1}H NMR: (**400 MHz**, **DMSO-d$_6$**) δ = 8.84 (d, *J* = 7.9 Hz, 2 H), 8.42 (d, *J* = 7.9 Hz, 2 H), 4.40 (d, *J* = 6.1 Hz, 2 H), 1.35 (br. s., 3 H); **^{13}C NMR**: (**100 MHz**, **DMSO-d$_6$**) δ = 163.3, 158.7-157.7 (q, *J* = 32.4 Hz), 139.4, 133.2, 131.2, 120.3, 62.4, 13.9 (one peak was not observed); **^{19}F NMR**: (**375 MHz**, **DMSO-d$_6$**) δ = −74.2.

<u>Synthesis of 1a''</u>:[3]

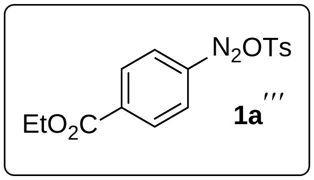


1a''

To a suspension of ethyl 4-aminobenzoate (1.65 g, 10.0 mmol) in water (10 mL) HPF_6 (65% in water, 4.9 mL, 2.92 g, 20.0 mmol, 2.0 equiv) was added at rt and the reaction mixture was stirred for 2 min. The mixture was then cooled to 0 °C and a solution of $NaNO_2$ (0.7 g, 10.00 mmol, 1.0 equiv) in water (3.5 mL) was added drop-wise. The reaction mixture was stirred for 15 min and the resultant solid was filtered and washed with ice-cold water (2 x 2 mL) followed by cold diethyl ether (3 x 10 mL). Resultant mass was dried under high vacuum to give the product **1a''** as a white solid (1.9 g, 59%).

^{1}H NMR: (**400 MHz**, **DMSO-d$_6$**) δ = 8.79 (d, *J* = 7.9 Hz, 2 H), 8.44 (d, *J* = 7.9 Hz, 2 H), 4.41 (q, *J* = 6.7 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **DMSO-d$_6$**) δ = 163.3, 139.5, 133.2, 131.2, 120.2, 62.4, 13.9; **^{31}P NMR**: (**162 MHz**, **DMSO-d$_6$**) δ = −70.2 (d, *J* = 711.8 Hz); **^{19}F NMR**: (**375 MHz**, **DMSO-d$_6$**) δ = −144.2 (sep, *J* = 711.3 Hz).

<u>Synthesis of 1a'''</u>:[3]



1a'''

Ethyl 4-aminobenzoate (1.65 g, 10.0 mmol) was dissolved in a mixture of 50% (V/V) glacial acetic acid (5 mL) and water (5 mL). *p*-Toluenesulfonic acid monohydrate (2.1 g, 11.0 mmol, 1.1 equiv) was added to the solution. After cooling to 0 °C, isopentyl nitrite (1.6 mL, 1.43 g, 12.0 mmol, 1.2 equiv) was added drop-wise. The mixture was then stirred for 30 min and stirred at 25 °C for another 30 min. Diethyl ether (200 mL) was poured into the solution and the and the resultant precipitate was collected by filtration. The precipitate was dissolved in minimum amount of methanol and then precipitated by the addition of diethyl ether. The product **1a'''** was obtained as brown solid (1.43 g, 41%).

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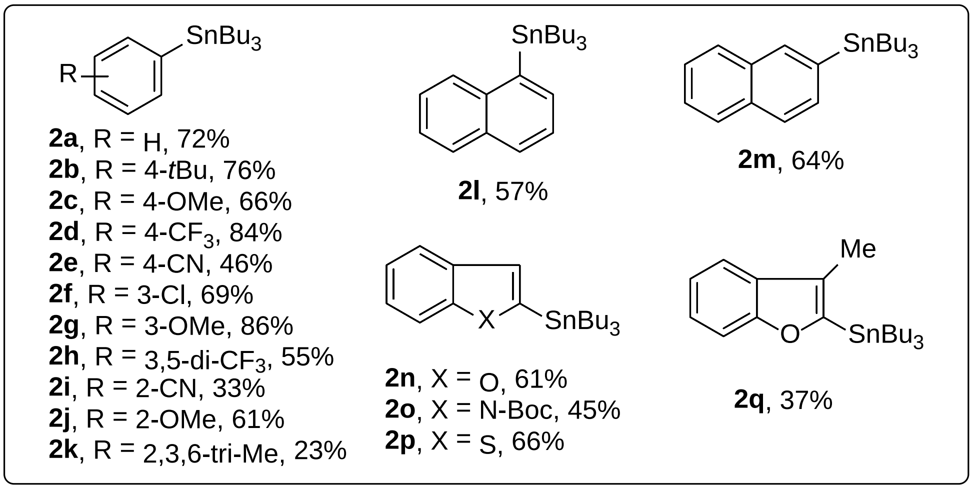
[3] S. Kim, J. Rojas-Martin, F. D. Toste, *Chem. Sci.* 2016, **7**, 85.

^{1}H NMR: (**500 MHz**, **DMSO-d$_6$**) δ = 8.92 - 8.69 (m, 2 H), 8.53 - 8.29 (m, 2 H), 7.58 - 7.34 (m, 2 H), 7.21 - 6.98 (m, 2 H), 4.50 - 4.30 (m, 2 H), 2.28 (br. s., 3 H), 1.36 (br. s., 3 H); **^{13}C NMR**: (**125 MHz**, **DMSO-d$_6$**) δ = 163.3, 145.7, 139.3, 137.6, 133.2, 131.1, 128.0, 125.5, 120.2, 62.4, 20.7, 13.9.

3.1.2 Preparation of organostannanes:

3.1.2a Synthesis of tributyl(aryl)stannanes:



Representative procedure A: To a flame dried two neck round-bottom flask equipped with a stir bar under nitrogen atmosphere, THF (5.0 mL) and activated magnesium turnings (360 mg, 15.0 mmol), was added. A solution of bromobenzene (1.05 mL, 10.0 mmol) in THF (5.0 mL) was added drop-wise over 5 minutes under gentle reflux conditions. The mixture slowly turned dark brown and the mixture was stirred for 1 h at ambient temperature. To this mixture, Bu_3SnCl (2.4 mL, 9.0 mmol) was added drop-wise at 0 ºC. The mixture was then stirred at room temperature for 16 h which is followed by addition of 14 mL aqueous 1 M NaOH. An hour later, the mixture was transferred to a separating funnel and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine (2 × 40 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography to afford the tributyl(phenyl)stannane (**2a**) in 63% yield (2.32 g). All literature known compound **2b-2d**, **2f-2h** and **2j-2m** were prepared by this procedure.

Representative procedure B: A solution of benzofuran (1.18 g, 10.0 mmol) in dry Et_2O (20 mL) *n*-BuLi (1.6 M in hexane, 7 mL, 11.0 mmol) was added in drop-wise manner at 0 °C. After

1 h, the mixture was cooled to -78 °C and a solution of tributyltin chloride (2.4 mL, 9.0 mmol) was slowly added. The mixture was then allowed to warm to room temperature and stirred for 16 h. Upon completion of the reaction, cold water (50 mL) was added and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine (2 × 30 mL), dried over Na_2SO_4, filtered and solvents were removed under reduced pressure. The residue was purified by silica gel chromatography (1% triethylamine/hexane) to give 2-(tri-*n*-butylstannyl)furan **2n** in 74% yield (1.28 g, 3.6 mmol). Compound **2e**, **2i** and **2n-2q** were prepared by this protocol. Characterization for unknown compound **2q** is given below.

Compound 2q: **R_f**: 0.90 (pet. ether); 156 mg, yield: 37%; colourless liquid; **^{1}H NMR**: (**400 MHz**, **$CDCl_3$**) δ = 7.52 - 7.48 (m, 1 H), 7.44 (d, *J* = 7.3 Hz, 1 H), 7.24 - 7.16 (m, 2 H), 2.27 (s, 3 H), 1.65 - 1.57 (m, 6 H), 1.39 - 1.33 (m, 6 H), 1.21 - 1.16 (m, 6 H), 0.90 (t, *J* = 7.3 Hz, 9 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 161.0, 158.9, 129.4, 126.4, 123.2, 121.5, 118.6, 110.8, 29.0, 27.2, 13.6, 10.1, 9.3.

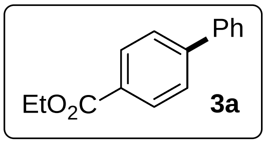
The references for the known compounds are given below in tabular form.

Stannanes	References
2a, **2c**, **2l** and **2m**	*Tetrahedron* **2015**, *71*, 1705
2b	*Org. Lett.* **2010**, *12*, 2848
2d	*J. Am. Chem. Soc.* **2007**, *129*, 14193
2f	*Org. Lett.* **2017**, *19*, 5968
2g	*Org. Biomol. Chem.* **2005**, *3*, 216
2h	*Organometallics* **2004**, *23*, 3184
2e, **2i** and **2k**	*J. Am. Chem. Soc.* **2010**, *132*, 12150
2j	*J. Organomet. Chem.* **2013**, *741*, 24
2n and **2p**	*Bioorg. Med. Chem* **2012**, *20*, 2762
2o	*Bioorg. Chem.* **2005**, *33*, 439

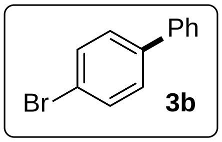
3.2 General procedure for the gold(I)-catalyzed cross-coupling reactions of aryl diazonium salts with organostannanes:

To an oven-dried screw-cap vial containing a stir bar were added diazonium salt **1** (0.2 mmol), organo-stannane **2** (0.26 mmol) and Ph_3PAuCl (7 mg, 0.014 mmol, 7 mol %) and degassed CH_3CN (0.1 M). The reaction vial was fitted with a cap, evacuated and back filled with argon and stirred at room temperature for 4-16 h. The mixture was then diluted with diethyl ether (5 mL) and the residue was subsequently purified by chromatography on silica gel using petroleum ether and ethyl acetate to yield the cross-coupled product **3**. NMR yields are calculated for the literature known compounds **3j**, **3k**, **3o**, **3p**, **3w** and **3ai** (NMR spectra are not shown herein).

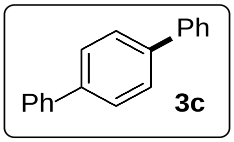
Characterization data:


3a

Compound 3a:[4] **R*f***: 0.30 (pet. ether/EtOAc = 98/02); 31 mg, yield: 69%; **physical appearance**: colourless solid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 8.13 (d, *J* = 8.4 Hz, 2 H), 7.71 - 7.61 (m, 4 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.44 - 7.36 (m, 1 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 166.5, 145.5, 140.1, 130.0, 129.2, 128.9, 128.1, 127.3, 127.0, 61.0, 14.4.


3b

Compound 3b:[4] **R*f***: 0.90 (pet. ether); 22 mg, yield: 48%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 7.60 - 7.55 (m, 4 H), 7.50 - 7.41 (m, 4 H), 7.41 - 7.33 (m, 1 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 140.1, 140.0, 131.8, 128.9, 128.7, 128.5, 127.6, 126.9, 121.5.


3c

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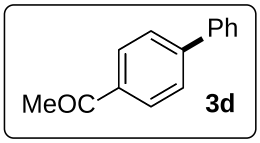
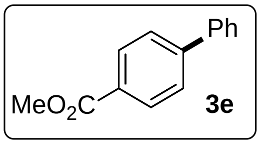
[4] T. Kawamoto, A. Sato, I. Ryu, *Org. Lett.* 2014, **16**, 2111.

Compound 3c:[4] **R*f***: 0.60 (pet. ether); 21 mg, yield: 46%; **physical appearance**: white solid; **^{1}H NMR**: (5**00 MHz**, **CDCl$_3$**) δ = 7.71 (s, 4 H), 7.68 (d, *J* = 7.6 Hz, 4 H), 7.49 (t, *J* = 7.6 Hz, 4 H), 7.44 - 7.36 (m, 2 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.



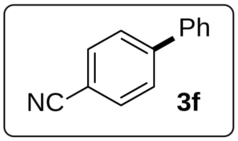
3d

Compound 3d:[5] **R*f***: 0.40 (pet. ether/EtOAc = 98/02); 24 mg, yield: 61%; **physical appearance**: white solid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.05 (d, *J* = 7.9 Hz, 2 H), 7.70 (d, *J* = 7.9 Hz, 2 H), 7.64 (d, *J* = 7.3 Hz, 2 H), 7.52 - 7.45 (m, 2 H), 7.45 - 7.37 (m, 1 H), 2.65 (s, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 197.7, 145.8, 139.9, 135.8, 128.9, 128.9, 128.2, 127.3, 127.2, 26.7.



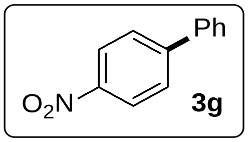
3e

Compound 3e:[6] **R*f***: 0.60 (pet. ether/EtOAc = 95/05); 26 mg, yield: 62%; **physical appearance**: colourless solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.12 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 7.2 Hz, 2 H), 7.52 - 7.45 (m, 2 H), 7.45 - 7.36 (m, 1 H), 3.96 (s, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 167.0, 145.6, 140.0, 130.1, 128.9, 128.1, 127.3, 127.0, 52.1.



3f

Compound 3f:[7] **R*f***: 0.60 (pet. ether/EtOAc = 95/05); 18 mg, yield: 49%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.7 (s), 7.7 (s), 7.6 (br. s.), 7.5 (br. s.), 7.4 (br. s.); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 145.6, 139.1, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9.



3g

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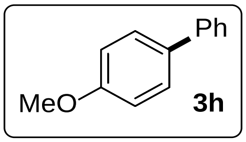
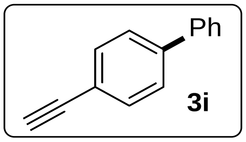
[5] J.-Y. Lee, D. Ghosh, J.-Y. Lee, S.-S. Wu, C.-H. Hu, S.-D. Liu, H. M. Lee, *Organometallics*, 2014, **33**, 6481.
[6] S. Thapa, A. S. Vangala, R. Giri, *Synthesis*, 2016, **48**, 504.
[7] G. R. Rosa, C. H. Rosa, F. Rominger, J. Dupont, A. L. Monteiro, *Inorg. Chim. Acta*, 2006, **359**, 1947.

Compound 3g:[7] **R$_f$**: 0.40 (pet. ether/EtOAc = 98/02); 22 mg, yield: 55%; **physical appearance**: colourless solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.39 - 8.24 (m, *J* = 8.8 Hz, 2 H), 7.78 - 7.72 (m, *J* = 8.8 Hz, 2 H), 7.64 (d, *J* = 7.2 Hz, 2 H), 7.54 - 7.49 (m, 2 H), 7.49 - 7.43 (m, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 147.6, 147.1, 138.8, 129.1, 128.9, 127.8, 127.4, 124.1.



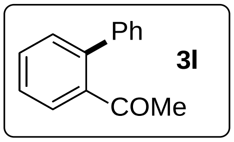
3h

Compound 3h:[4] **R$_f$**: 0.40 (pet. ether/EtOAc = 98/02); 15 mg, yield: 40%; **physical appearance**: colourless solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.57 - 7.54 (m, 4 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.36 - 7.28 (m, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 3.87 (s, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 159.1, 140.8, 133.8, 128.7, 128.2, 126.7, 126.6, 114.2, 55.3.



3i

Compound 3i:[8] **R$_f$**: 0.70 (pet. ether); 13 mg, yield: 37%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.60 (d, *J* = 7.2 Hz, 2 H), 7.57 (s, 4 H), 7.49 - 7.44 (m, 2 H), 7.39 - 7.36 (m, 1 H), 3.14 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 141.6, 140.3, 132.5, 128.9, 127.7, 127.1, 127.0, 121.0, 83.5, 77.7.



3l

Compound 3l:[9] **R$_f$**: 0.40 (pet. ether/EtOAc = 98/02); 20 mg, yield: 50%; **physical appearance**: pale yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.53 (s, 1 H), 7.56 (s, 1 H), 7.42 (br. s., 5 H), 7.36 (br. s., 2 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 204.9, 140.9, 140.7, 140.5, 130.7, 130.2, 128.8, 128.7, 127.9, 127.4, 30.4.

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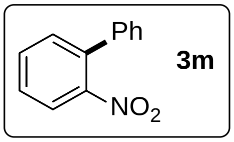
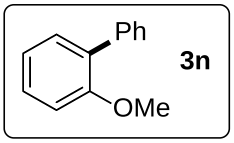
[8] A. Hosseini, A. Pilevar, E. Hogan, B. Mogwitz, A. S. Schulze, P. R. Schreiner, *Org. Biomol. Chem.*, 2017, **15**, 6800.

[9] L. Candish, M. Freitag, T. Gensch, F. Glorius, *Chem. Sci.*, 2017, **8**, 3618.



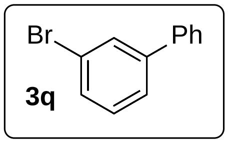
3m

Compound 3m: [10] **R*f***: 0.60 (pet. ether/EtOAc = 95/05); 20 mg, yield: 51%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.88 - 7.86 (m, 1 H), 7.65 - 7.61 (m, 1 H), 7.52 - 7.48 (m, 1 H), 7.48 - 7.41 (m, 4 H), 7.34 (dd, *J* = 1.7, 7.4 Hz, 2 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 149.3, 137.4, 136.4, 132.2, 131.9, 128.7, 128.2, 128.1, 127.9, 124.1.



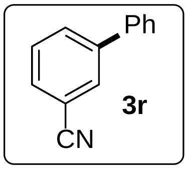
3n

Compound 3n:[4] **R*f***: 0.50 (pet. ether/EtOAc = 98/02); 11 mg, yield: 31%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.54 (d, *J* = 7.2 Hz, 2 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.36 - 7.31 (m, 3 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 7.02 - 6.98 (m, 1 H), 3.83 (s, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 156.5, 138.5, 130.9, 130.7, 129.5, 128.6, 128.0, 126.9, 120.8, 111.2, 55.6.



3q

Compound 3q:[9] **R*f***: 0.90 (pet. ether); 20 mg, yield: 44%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.75 (s, 1 H), 7.57 (d, J = 7.2 Hz, 2 H), 7.53 (d, J = 7.6 Hz, 1 H), 7.51 - 7.44 (m, 3 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.32 (t, J = 7.8 Hz, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 143.3, 139.7, 130.3, 130.2, 130.2, 128.9, 127.9, 127.1, 125.8, 122.9.



3r

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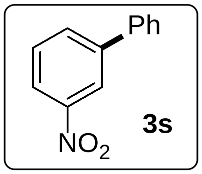
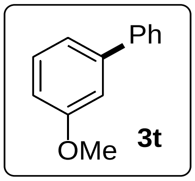
[10] E. A. Weitz, J. Y. Chang, A. H. Rosenfield, V. C. Pierre, *J. Am. Chem. Soc.*, 2012, **134**, 16099.

Compound 3r:[11] **R$_f$**: 0.30 (pet. ether/EtOAc = 95/05); 22 mg, yield: 62%; **physical appearance**: colourless solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.88 (s, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.59 - 7.54 (m, 3 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.45 - 7.41 (m, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 142.4, 138.8, 131.5, 130.7, 130.7, 129.6, 129.1, 128.4, 127.1, 118.8, 112.9.



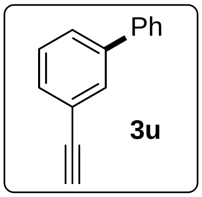
3s

Compound 3s:[12] **R$_f$**: 0.40 (pet. ether/EtOAc = 95/05); 21 mg, yield: 52%; **physical appearance**: yellow solid; **^{1}H NMR**: (500 MHz, CDCl$_3$) δ = 8.47 (s, 1 H), 8.23 - 8.19 (m, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.66 - 7.61 (m, 3 H), 7.53 - 7.49 (m, 2 H), 7.47 - 7.43 (m, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 148.7, 142.9, 138.6, 133.0, 129.7, 129.1, 128.5, 127.1, 122.0, 121.9.



3t

Compound 3t:[4] **R$_f$**: 0.50 (pet. ether/EtOAc = 98/02); 15 mg, yield: 42%; **physical appearance**: pale yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.60 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.37 (dt, *J* = 4.2, 7.6 Hz, 2 H), 7.20 (d, *J* = 7.6 Hz, 1 H), 7.16 - 7.12 (m, 1 H), 6.91 (dd, *J* = 2.1, 8.2 Hz, 1 H), 3.88 (s, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 159.9, 142.8, 141.1, 129.7, 128.7, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3.



3u

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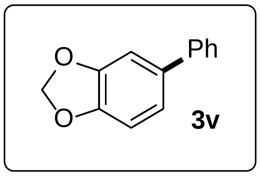
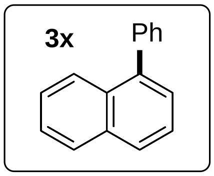
[11] P. Klumphu, B. H. Lipshutz, *J. Org. Chem.*, 2014, **79**, 888.

[12] V. Gauchot, A. Lee, *Chem. Commun.*, 2016, **52**, 10163.

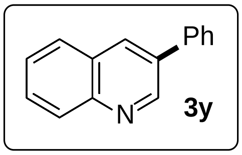
Compound 3u:[13] **R$_f$**: 0.80 (pet. ether); 18 mg, yield: 51%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.75 (s, 1 H), 7.59 (d, *J* = 7.6 Hz, 3 H), 7.52 - 7.43 (m, 3 H), 7.43 - 7.35 (m, 2 H), 3.12 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 141.4, 140.2, 130.9, 128.8, 128.8, 127.7, 127.1, 122.6, 83.6.



Compound 3v:[14] **R$_f$**: 0.70 (pet. ether/EtOAc = 95/05); 12 mg, yield: 31%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.53 (d, *J* = 7.2 Hz, 2 H), 7.42 (t, *J* = 7.8 Hz, 2 H), 7.37 - 7.30 (m, 1 H), 7.14 - 7.02 (m, 2 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.01 (s, 2 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 148.1, 147.0, 140.9, 135.6, 128.7, 126.9, 126.9, 120.6, 108.6, 107.7, 101.1.



Compound 3x:[4] **R$_f$**: 0.70 (pet. ether); 17 mg, yield: 41%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 7.93 (d, *J* = 7.9 Hz, 2 H), 7.88 (d, *J* = 7.9 Hz, 1 H), 7.57 - 7.49 (m, 6 H), 7.47 - 7.41 (m, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 140.8, 140.3, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4.



Compound 3y:[15] **R$_f$**: 0.60 (pet. ether/EtOAc = 80/20); 8 mg, yield: 19%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 9.21 (s, 1 H), 8.32 (d, *J* = 1.9 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.77 - 7.71 (m, 3 H), 7.63 - 7.58 (m, 1 H), 7.55 (t,

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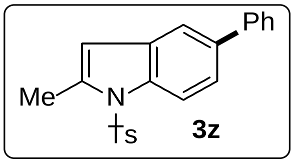
[13] S. Singh, J.-I. Goo, H. Noh, S. J. Lee, M. W. Kim, H. Park, H. B. Jalani, K. Lee, C. Kim, W.-K. Kim, C. Ju, Y. Choi, *Bioorg. Med. Chem.*, 2017, **25**, 1394.

[14] A. Affrose, P. Suresh, I. A. Azath, K. Pitchumani, *RSC Adv.*, 2015, **5**, 27533.

[15] J.-F. Soulé, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.*, 2013, **135**, 10602.

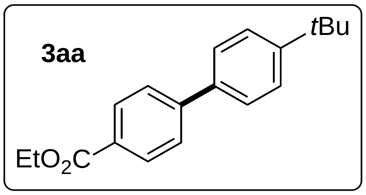
J = 7.6 Hz, 2 H), 7.49 - 7.43 (m, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 150.0, 147.4, 137.9, 133.9, 133.2, 129.4, 129.3, 129.2, 128.1, 128.0, 128.0, 127.4, 127.0.



3z

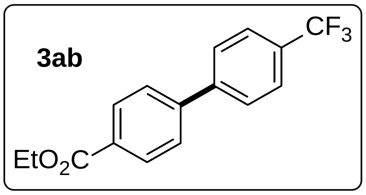
Compound 3z: **R*f***: 0.60 (pet. ether/EtOAc = 90/10); 40 mg, yield: 56%; **physical appearance**: thick liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.21 (d, *J* = 8.4 Hz, 1 H), 7.75 - 7.67 (m, *J* = 8.0 Hz, 2 H), 7.67 - 7.56 (m, 3 H), 7.50 (dd, *J* = 1.5, 8.8 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.38 - 7.31 (m, 1 H), 7.25 - 7.21 (m, *J* = 8.4 Hz, 2 H), 6.39 (s, 1 H), 2.62 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 144.8, 141.3, 138.0, 136.8, 136.4, 136.3, 130.2, 129.9, 128.7, 127.3, 126.9, 126.4, 123.2, 118.4, 114.7, 109.7, 21.6, 15.8; **HRMS**: (**ESI**) calcd 362.1209 for $C_{22}H_{20}O_2NS$ $[M + H]^+$ found 362.1202.

3aa



Compound 3aa: [16] **R*f***: 0.70 (pet. ether/EtOAc = 95/05); 37 mg, yield: 66%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.11 (d, *J* = 8.5 Hz, 2 H), 7.67 (d, *J* = 7.9 Hz, 2 H), 7.59 (d, *J* = 7.9 Hz, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 4.41 (q, *J* = 7.3 Hz, 2 H), 1.42 (t, *J* = 7.0 Hz, 3 H), 1.40 - 1.35 (m, 9 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.6, 151.3, 145.4, 137.1, 130.0, 129.0, 126.9, 126.8, 125.9, 60.9, 34.6, 31.3, 14.4.

3ab



Compound 3ab: [17] **R*f***: 0.30 (pet. ether/EtOAc = 98/02); 36 mg, yield: 61%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.20 - 8.10 (m, *J* = 8.0 Hz, 2 H),

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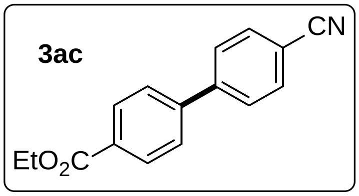
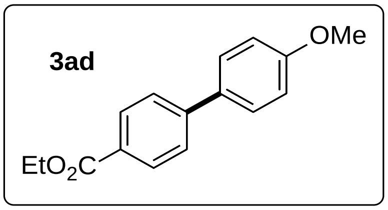
[16] D.-Y. Wang, M. Kawahata, Z.-K. Yang, K. Miyamoto, S. Komagawa, K. Yamaguchi, C. Wang, M. Uchiyama, *Nat. Commun.*, 2016, **7**, 12937.

[17] D. Wu, J.-L. Tao, Z.-X. Wang, *Org. Chem. Front.*, 2015, **2**, 265.

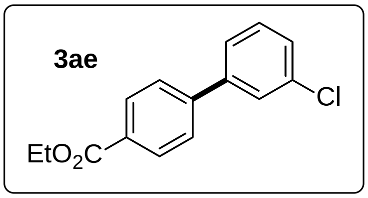
7.73 (s, 4 H), 7.69 - 7.63 (m, *J* = 8.4 Hz, 2 H), 4.43 (q, *J* = 7.2 Hz, 2 H), 1.43 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.3, 143.9, 143.6, 130.2 (2 C), 130.0, 127.6, 127.2, 126.3 (q, *J* = 272.8 Hz), 125.9 (q, *J* = 2.9 Hz), 61.1, 14.3; **^{19}F NMR** (**375 MHz**, **CDCl$_3$**) δ = –62.6.


3ac

Compound 3ac:[18] 20 **R**$_f$: 0.60 (pet. ether/EtOAc = 80/20); 31 mg, yield: 61%; **Physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.19 - 8.12 (m, 2 H), 7.79 - 7.74 (m, 2 H), 7.74 - 7.70 (m, 2 H), 7.69 - 7.63 (m, 2 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.1, 144.5, 143.3, 132.7, 130.5, 130.3, 127.9, 127.2, 118.6, 111.8, 61.2, 14.3.


3ad

Compound 3ad:[16] **R**$_f$: 0.50 (pet. ether/EtOAc = 95/05); 20 mg, yield: 39%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.10 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 4.41 (q, *J* = 7.0 Hz, 2 H), 3.87 (s, 3 H), 1.42 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.6, 159.8, 145.1, 132.5, 130.0, 128.6, 128.4, 126.4, 114.4, 60.9, 55.4, 14.4.


3ae

Compound 3ae:[16] **R**$_f$: 0.60 (pet. ether/EtOAc = 95/05); 37 mg, yield: 71%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.13 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.61 (s, 1 H), 7.50 (d, *J* = 7.2 Hz, 1 H), 7.44 - 7.34 (m, 2 H), 4.42 (q, *J* = 7.2 Hz,

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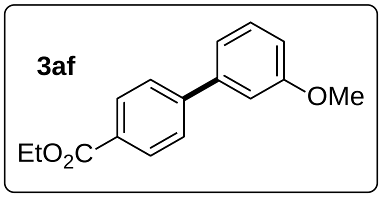
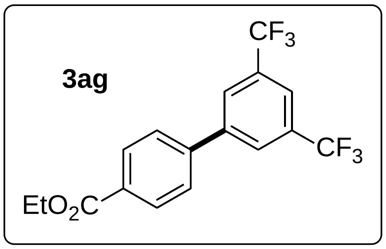
[18] S. Bernhardt, Z.-L. Shen, P. Knochel, *Chem. Eur. J.*, 2013, **19**, 828.

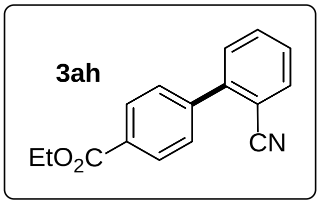
2 H), 1.43 (t, *J* = 7.1 Hz, 3 H); ^{13}**C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.3, 144.0, 141.9, 134.8, 130.1, 129.8, 128.1, 127.4, 127.0, 125.4, 61.1, 14.3.



Compound 3af:[19] **R*f***: 0.40 (pet. ether/EtOAc = 95/05); 33 mg, yield: 64%; **physical appearance**: white solid; ^{1}**H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.16 - 8.07 (m, *J* = 8.4 Hz, 2 H), 7.71 - 7.61 (m, *J* = 8.0 Hz, 2 H), 7.44 - 7.34 (m, 1 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.16 (s, 1 H), 6.95 (dd, *J* = 2.1, 8.2 Hz, 1 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 3.89 (s, 3 H), 1.43 (t, *J* = 7.1 Hz, 3 H); ^{13}**C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.5, 160.0, 145.4, 141.5, 130.0, 129.9, 129.4, 127.0, 119.7, 113.4, 113.0, 61.0, 55.3, 14.3.



Compound 3ag:[20] **R*f***: 0.40 (pet. ether/EtOAc = 98/02); 43 mg, yield: 59%; **physical appearance**: white solid; ^{1}**H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.19 (d, *J* = 8.5 Hz, 2 H), 8.05 (s, 2 H), 7.91 (s, 1 H), 7.69 (d, *J* = 7.9 Hz, 2 H), 4.44 (q, *J* = 7.3 Hz, 2 H), 1.44 (t, *J* = 7.3 Hz, 3 H); ^{13}**C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.0, 142.3, 142.2, 132.4 (q, *J* = 33.1), 130.9, 130.5, 127.4, 127.2, 121.7 (q, *J* = 272.8 Hz), 121.7 (m), 61.3, 14.3; ^{19}**F NMR** (**375 MHz**, **CDCl$_3$**) δ = –62.9.



Compound 3ah:[20] **R*f***: 0.50 (pet. ether/EtOAc = 80/20); 21 mg, yield: 42%; **Physical appearance**: white solid; ^{1}**H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.20 - 8.16 (m, 2 H), 7.83 - 7.77 (m,

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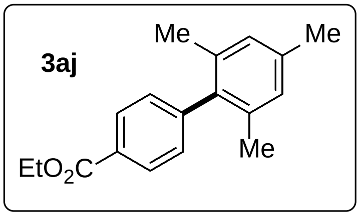
[19] Z.-L. Shen, K. Sommer, P. Knochel, *Synthesis*, 2015, **47**, 2617.
[20] A. Castelló-Micó, S. A. Herbert, T. León, T. Bein, P. Knochel, *Angew. Chem., Int. Ed.*, 2016, **55**, 401.

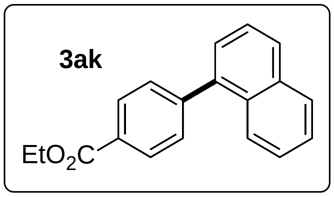
1 H), 7.71 - 7.67 (m, 1 H), 7.66 - 7.63 (m, 2 H), 7.56 - 7.53 (m, 1 H), 7.50 (dt, *J* = 1.1, 7.6 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.1, 144.4, 142.3, 133.8, 132.9, 130.7, 130.0, 129.9, 128.8, 128.2, 118.3, 111.3, 61.1, 14.3.

3aj



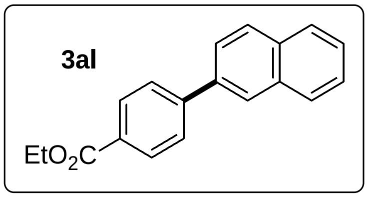
Compound 3aj:[16] **R*f***: 0.60 (pet. ether/EtOAc = 95/05); 13 mg, yield: 25%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.11 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 6.96 (s, 2 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 2.34 (s, 3 H), 1.99 (s, 6 H), 1.43 (t, *J* = 6.9 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.7, 146.2, 138.0, 137.1, 135.5, 129.7, 129.4, 128.8, 128.2, 60.9, 21.0, 20.6, 14.4.

3ak



Compound 3ak:[21] **R*f***: 0.70 (pet. ether/EtOAc = 95/05); 41 mg, yield: 74%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.24 - 8.14 (m, *J* = 8.4 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 7.62 - 7.58 (m, *J* = 8.4 Hz, 2 H), 7.57 - 7.51 (m, 2 H), 7.48 - 7.43 (m, 2 H), 4.45 (q, *J* = 7.1 Hz, 2 H), 1.46 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 166.6, 145.4, 139.2, 133.8, 131.2, 130.1, 129.5, 129.4, 128.4, 128.2, 126.9, 126.3, 125.9, 125.6, 125.3, 61.0, 14.4.

3al



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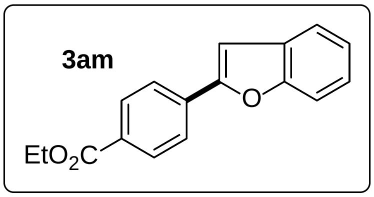
[21] Z.-L. Shen, P. Knochel, *ACS Catal.* 2015, **5**, 2324.

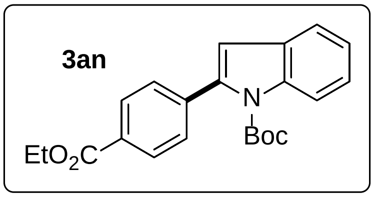
Compound 3al:[22] **R$_f$**: 0.70 (pet. ether/EtOAc = 95/05); 31 mg, yield: 56%; **physical appearance**: white solid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.18 (d, *J* = 7.9 Hz, 2 H), 8.10 (s, 1 H), 7.97 - 7.88 (m, 3 H), 7.83 - 7.74 (m, 3 H), 7.58 - 7.49 (m, 2 H), 4.44 (q, *J* = 6.9 Hz, 2 H), 1.45 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.5, 145.4, 137.3, 133.6, 133.0, 130.1, 129.3, 128.6, 128.3, 127.7, 127.2, 126.5, 126.4, 126.3, 125.2, 61.0, 14.4.

3am



Compound 3am:[23] **R$_f$**: 0.50 (pet. ether/EtOAc = 95/05); 29 mg, yield: 54%; **physical appearance**: white solid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.16 - 8.09 (m, *J* = 7.9 Hz, 2 H), 7.97 - 7.90 (m, *J* = 7.9 Hz, 2 H), 7.63 (d, *J* = 7.3 Hz, 1 H), 7.56 (d, *J* = 7.9 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.30 - 7.24 (m, 1 H), 7.17 (s, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 1.44 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.2, 155.2, 154.7, 134.4, 130.1, 128.9, 125.0, 124.6, 123.2, 121.3, 111.3, 103.4, 61.1, 14.3.

3an



Compound 3an:[24] **R$_f$**: 0.50 (pet. ether/EtOAc = 90/10); 31 mg, yield: 43%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.22 (d, *J* = 8.4 Hz, 1 H), 8.02 - 8.14 (m, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.47 - 7.54 (m, *J* = 8.0 Hz, 2 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.29 (s, 4 H), 6.63 (s, 1 H), 4.42 (q, *J* = 7.0 Hz, 2 H), 1.43 (t, *J*=7.2 Hz, 3 H), 1.35 (s, 9 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ =171.2, 166.4, 150.0, 139.4, 139.4, 137.7, 129.4, 129.1, 128.5, 124.8, 123.1, 120.7, 115.3, 111.0, 83.9, 61.1, 27.6, 14.3.

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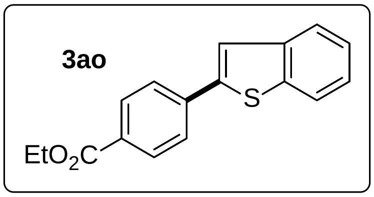
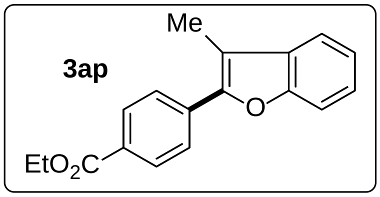
[22] E. Shirakawa, F. Tamakuni, E. Kusano, N. Uchiyama, W. Konagaya, R. Watabe, T. Hayashi, *Angew. Chem., Int. Ed.*, 2014, **53**, 521.

[23] T. Dao-Huy, M. Haider, F. Glatz, M. Schnurch, M. D. Mihovilovic, *Eur. J. Org. Chem.*, 2014, **2014**, 8119.

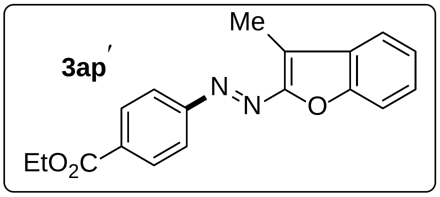
[24] S. E. Denmark, J. D. Baird, *Org. Lett.*, 2006, **8**, 793.



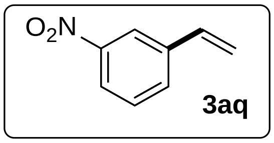
Compound 3ao:[23] **R$_f$**: 0.50 (pet. ether/EtOAc = 95/05); 32 mg, yield: 56%; **physical appearance**: white solid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.10 (d, *J* = 8.5 Hz, 2 H), 7.90 - 7.73 (m, 4 H), 7.66 (s, 1 H), 7.37 (quin, *J* = 6.6 Hz, 2 H), 4.42 (q, *J* = 7.3 Hz, 2 H), 1.43 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.1, 142.8, 140.4, 139.8, 138.4, 130.2, 129.9, 126.1, 124.9, 124.7, 123.9, 122.3, 121.0, 61.1, 14.3.



Compound 3ap: **R$_f$**: 0.60 (pet. ether/EtOAc = 95/05); 17 mg, yield: 31%; **physical appearance**: thick liquid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.16 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 7.9 Hz, 2 H), 7.58 (d, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 7.9 Hz, 1 H), 7.35 (t, *J* = 7.3 Hz, 1 H), 7.29 (d, *J* = 7.3 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 2.54 (s, 3 H), 1.44 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.3, 149.5, 135.5, 130.9, 129.9, 129.3, 126.1, 125.1, 122.6, 119.6, 113.5, 111.1, 85.7, 61.1, 14.4, 9.7; **HRMS**: (**ESI**) calcd 280.1172 for $C_{18}H_{17}O_3$ [M + H]$^+$ found 280.1169.

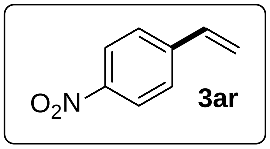


Compound 3ap': **R$_f$**: 0.60 (pet. ether/EtOAc = 90/10); 10 mg, yield: 16%; **physical appearance**: red solid; mp: 73 ºC; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.20 (d, *J* = 7.9 Hz, 2 H), 8.04 (d, *J* = 8.5 Hz, 2 H), 7.72 (d, *J* = 7.3 Hz, 1 H), 7.58 (d, *J* = 7.9 Hz, 1 H), 7.50 (t, *J* = 7.9 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 4.43 (q, *J* = 6.7 Hz, 2 H), 2.75 (s, 3 H), 1.44 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 166.0, 156.2, 155.9, 153.3, 131.8, 130.6, 129.7, 129.4, 126.1, 123.4, 122.6, 121.2, 112.4, 61.2, 14.3, 8.9; **HRMS**: (**ESI**) calcd 309.1234 for $C_{18}H_{17}O_3N_2$ [M + H]$^+$ found 309.1231.



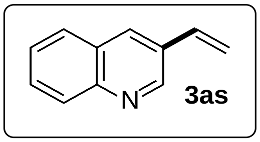
3aq

Compound 3aq:[25] **R_f**: 0.60 (pet. ether/EtOAc = 98/02); 8 mg, yield: 27%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 8.27 (s, 1 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 1 H), 6.78 (dd, *J* = 10.7, 17.5 Hz, 1 H), 5.91 (d, *J* = 17.5 Hz, 1 H), 5.46 (d, *J* = 11.1 Hz, 1 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 148.6, 139.3, 134.7, 132.1, 129.4, 122.4, 120.9, 117.1.



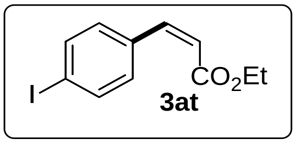
3ar

Compound 3ar:[26] **R_f**: 0.60 (pet. ether/EtOAc = 98/02); 7 mg, yield: 24%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**400 MHz**, **$CDCl_3$**) δ = 8.20 (d, *J* = 8.5 Hz, 2 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 6.79 (dd, *J* = 11.0, 17.7 Hz, 1 H), 5.94 (d, *J* = 17.7 Hz, 1 H), 5.51 (d, *J* = 10.4 Hz, 1 H); **^{13}C NMR**: (**100 MHz**, **$CDCl_3$**) δ = 147.1, 143.8, 135.0, 126.8, 124.0, 118.6.



3as

Compound 3as:[27] **R_f**: 0.60 (pet. ether/EtOAc = 90/10); 10 mg, yield: 31%; **physical appearance**: pale yellow liquid; **^{1}H NMR**: (**400 MHz**, **$CDCl_3$**) δ = 9.03 (s, 1 H), 8.20 - 8.01 (m, 2 H), 7.81 (d, *J* = 7.9 Hz, 1 H), 7.69 (t, *J* = 7.6 Hz, 1 H), 7.62 - 7.47 (m, 1 H), 6.88 (dd, *J* = 11.0, 17.7 Hz, 1 H), 6.00 (d, *J* = 17.7 Hz, 1 H), 5.48 (d, *J* = 11.0 Hz, 1 H); **^{13}C NMR**: (**100 MHz**, **$CDCl_3$**) δ = 149.1, 147.6, 133.8, 132.5, 130.3, 129.3, 129.2, 127.9, 126.9, 116.4.



3at

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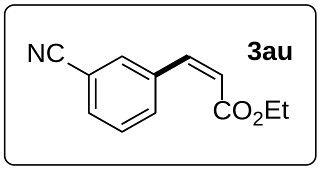
[25] W. Susanto, C.-Y. Chu, W. J. Ang, T.-C. Chou, L.-C. Lo, Y. Lam, *J. Org. Chem.*, 2012, **77**, 2729.

[26] E. Emer, L. Pfeifer, J. M. Brown, V. Gouverneu, *Angew. Chem.*, *Int. Ed.*, 2014, **53**, 4181.

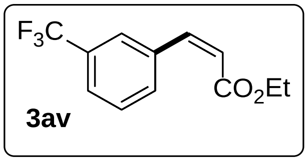
[27] T. M. Gøgsig, L. S. Søbjerg, A. T. Lindhardt, K. L. Jensen, T. Skrydstrup, *J. Org. Chem.* 2008, **73**, 3404.

Compound 3at:[28] **R_f**: 0.60 (pet. ether/EtOAc = 90/10); 35 mg, yield: 58%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 7.69 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 6.86 (d, J = 12.6 Hz, 1 H), 5.98 (d, J = 13.0 Hz, 1 H), 4.18 (q, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.2 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 165.9, 142.0, 137.1, 134.3, 131.4, 120.6, 95.2, 60.4, 14.1.



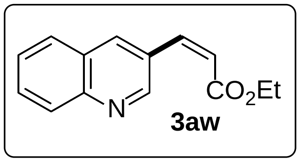
3au

Compound 3au: **R_f**: 0.40 (pet. ether/EtOAc = 90/10); 27 mg, yield: 67%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 7.86 (s, 1 H), 7.78 (d, J = 7.6 Hz, 1 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.47 (t, J = 7.8 Hz, 1 H), 6.93 (d, J = 12.6 Hz, 1 H), 6.08 (d, J = 12.6 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 165.4, 140.6, 136.1, 133.7, 133.0, 132.1, 128.8, 122.4, 118.5, 112.3, 60.7, 14.0.



3av

Compound 3av:[29] **R_f**: 0.60 (pet. ether/EtOAc = 90/10); 24 mg, yield: 53%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 7.81 (s, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.59 (d, J = 7.6 Hz, 1 H), 7.48 (t, J = 7.8 Hz, 1 H), 6.98 (d, J = 12.6 Hz, 1 H), 6.06 (d, J = 12.6 Hz, 1 H), 4.18 (q, J = 7.1 Hz, 2 H), 1.24 (t, J = 7.1 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 165.7, 141.2, 135.6, 132.7, 130.8 - 130.0 (q, J C-F = 32.4 Hz), 128.4, 126.4 - 126.3 (q, J C-F = 3.8 Hz), 125.4 - 125.3 (q, J C-F = 3.8 Hz), 125.1 - 122.9 (d, J C-F = 272.8 Hz), 121.8, 60.6, 14.0; **^{19}F NMR**: (**375 MHz**, **$CDCl_3$**) δ = 62.8.



3aw

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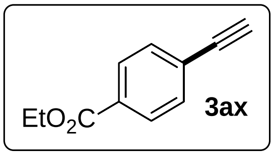
[28] Z. Liu, B. Liu, X.-F. Zhao, Y.-B. Wu, X. Bi, *Eur. J. Org. Chem.*, 2017, **2017**, 928.

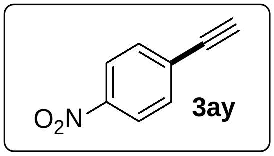
[29] K. Nishikawa, H. Fukuda, M. Abe, K. Nakanishi, T. Taniguchi, T. Nomura, C. Yamaguchi, S. Hiradate, Y. Fujii, K. Okuda, M. Shindo, *Phytochemistry*, 2013, **96**, 132.

Compound 3aw:[30] **R$_f$**: 0.60 (pet. ether/EtOAc = 80/20); 25 mg, yield: 55%; **physical appearance**: pale yellow liquid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 8.96 (s, 1 H), 8.59 (s, 1 H), 8.10 (d, *J* = 8.5 Hz, 1 H), 7.86 (d, *J* = 8.5 Hz, 1 H), 7.74 (t, *J* = 7.6 Hz, 1 H), 7.57 (t, *J* = 7.3 Hz, 1 H), 7.11 (d, *J* = 12.8 Hz, 1 H), 6.16 (d, *J* = 12.8 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 1.28 - 1.24 (m, 3 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 165.8, 151.5, 147.7, 139.7, 136.7, 134.5, 130.2, 129.2, 128.4, 128.0, 126.9, 122.2, 60.6, 14.1.



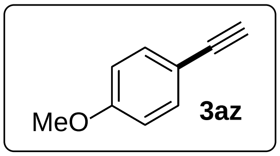
3ax

Compound 3ax:[31] **R$_f$**: 0.40 (pet. ether/EtOAc = 95/05); 18 mg, yield: 52%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.02 – 8.00 (d, *J* = 8.0 Hz, 2 H), 7.56 - 7.55 (d, *J* = 8.0 Hz, 2 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 3.23 (s, 1 H), 1.41 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 165.9, 132.0, 130.5, 129.4, 126.6, 82.8, 79.9, 61.2, 14.3.



3ay

Compound 3ay:[32] **R$_f$**: 0.40 (pet. ether/EtOAc = 95/05); 20 mg, yield: 68%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.22 - 8.20 (d, *J* = 8.8 Hz, 2 H), 7.66 - 7.64 (d, *J* = 8.4 Hz, 2 H), 3.37 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 147.5, 133.0, 128.9, 123.5, 82.3, 81.6.



3az

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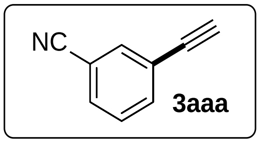
[30] S. Rommel, C. Belger, J. M. Begouin, B. Plietker, *ChemCatChem*, 2015, **7**, 1292.

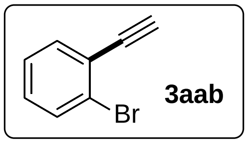
[31] T.-F. Liu, D. Feng, Y.-P. Chen, L. Zou, M. Bosch, S. Yuan, Z. Wei, S. Fordham, K. Wang, H.-C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 413.

[32] Y.-S. Feng, C.-Q. Xie, W.-L. Qiao, H.-J. Xu, *Org. Lett.*, 2013, **15**, 936.

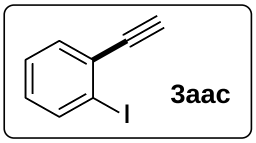
Compound 3az:[33] **R*f***: 0.2 (pet. ether); 12 mg, yield: 42%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 7.44 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 3.82 (s, 3 H), 3.01 (s, 1 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 159.9, 133.6, 114.1, 113.9, 83.6, 75.7, 55.3.



Compound 3aaa:[34] **R*f***: 0.60 (pet. ether/EtOAc = 95/05); 14 mg, yield: 57%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.77 (s, 1 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 3.20 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 136.2, 135.5, 132.0, 129.3, 123.8, 117.9, 112.9, 81.2, 79.8.



Compound 3aab:[35] **R*f***: 0.85 (pet. ether); 17 mg, yield: 47%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 7.60 (d, *J* = 7.9 Hz, 1 H), 7.54 (d, *J* = 7.9 Hz, 1 H), 7.32 - 7.27 (m, 1 H), 7.24 - 7.19 (m, 1 H), 3.39 (s, 1 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 134.1, 132.5, 130.0, 127.0, 125.6, 124.3, 81.9, 81.8.



Compound 3aac:[36] **R*f***: 0.9 (pet. ether); 20 mg, yield: 44%; **physical appearance**: white solid; **^{1}H NMR**: (**400 MHz**, **CDCl$_3$**) δ = 7.86 (d, *J* = 6.9 Hz, 1 H), 7.59 - 7.46 (m, 1 H), 7.32 (br. s., 1 H), 7.05 (br. s., 1 H), 3.40 (br. s., 1 H); **^{13}C NMR**: (**100 MHz**, **CDCl$_3$**) δ = 138.8, 133.4, 130.0, 128.7, 127.8, 100.4, 85.1, 81.0.

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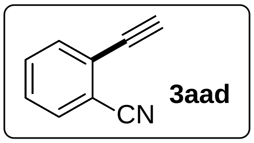
[33] P. C. Chen, R. E. Wharton, P. A. Patel, A. K. Oyelere, *Bioorganic Med. Chem.*, 2007, **15**, 7288.

[34] Q. H. Sodji, V. Patil, J. R. Kornacki, M. Mrksich, A. K. Oyelere, *J. Med. Chem.*, 2013, **56**, 9969.

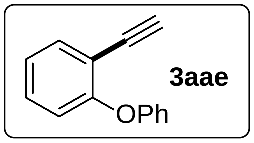
[35] A. Riss, S. Wickenburg, P. Gorman, L. Z. Tan, H.-Z. Tsai, D. G. de Oteyza, Y.-C. Chen, A. J. Bradley, M. M. Ugeda, G. Etkin, S. G. Louie, F. R. Fischer, M. F. Crommie, *Nano Lett.*, 2014, **14**, 2251.

[36] Y. Li, J. Zhang, W. Wang, Q. Miao, X. She, X. Pan, *J. Org. Chem.*, 2005, **70**, 3285.



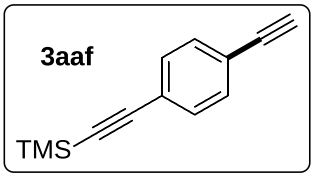
3aad

Compound 3aad:[37] **R$_f$**: 0.30 (pet. ether/EtOAc = 95/05); 14 mg, yield: 35%; **physical appearance**: white solid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.68 (d, *J* = 7.6 Hz, 1 H), 7.65 - 7.61 (m, 1 H), 7.61 - 7.55 (m, 1 H), 7.48 - 7.44 (m, 1 H), 3.49 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 133.0, 132.7, 132.4, 129.0, 126.0, 117.2, 115.9, 83.8, 79.6.



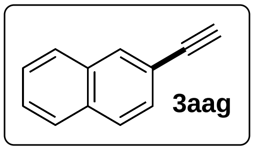
3aae

Compound 3aae:[38] **R$_f$**: 0.70 (pet. ether/EtOAc = 98/02); 00 mg, yield: 36%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.56 (d, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.30 (t, *J* = 7.8 Hz, 1 H), 7.13 (t, *J* = 7.4 Hz, 1 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 1 H), 3.23 (s, 1 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 158.4, 156.9, 134.3, 130.2, 129.7, 123.5, 123.2, 118.9, 118.5, 114.2, 81.7, 79.3.



3aaf

Compound 3aaf:[39] **R$_f$**: 0.80 (pet. ether); 11 mg, yield: 29%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.42 (s, 4 H), 3.17 (s, 1 H), 0.26 (s, 9 H); **^{13}C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 131.9, 131.8, 123.6, 122.1, 104.3, 96.5, 83.2, 78.9, -0.1.



3aag

Compound 3aag:[33] **R$_f$**: 0.8 (pet. ether); 17 mg, yield: 57%; **physical appearance**: colourless liquid; **^{1}H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.38 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 7.6 Hz, 2 H),

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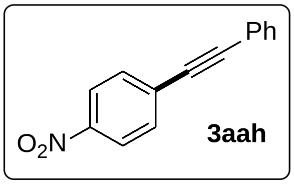
[37] C. Chen, L. Chu, F.-L. Qing, *J. Am. Chem. Soc.*, 2012, **134**, 12454.

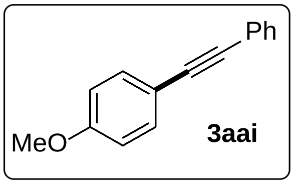
[38] L. F. Tietze, T. Hungerland, A. Düfert, I. Objartel, D. Stalke, *Chem. Eur. J.*, 2012, **18**, 3286.

[39] S. Marqués-González, M. Parthey, D. S. Yufit, J. A. K. Howard, M. Kaupp, P. J. Low, *Organometallics*, 2014, **33**, 4947.

7.75 (d, *J* = 6.5 Hz, 1 H), 7.59 (d, *J* = 7.2 Hz, 1 H), 7.55 (d, *J* = 6.9 Hz, 1 H), 7.44 (t, *J* = 7.1 Hz, 1 H), 3.49 (br. s., 1 H); ^{13}**C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 133.5, 133.1, 131.2, 129.3, 128.3, 126.9, 126.5, 126.0, 125.1, 119.7, 81.9, 81.7.



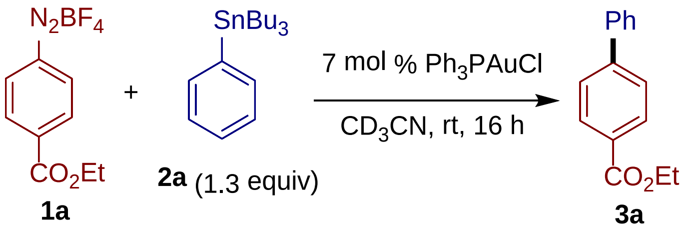
Compound 3aah:[25] **R*f***: 0.30 (pet. ether/EtOAc = 98/02); 18 mg, yield: 41%; **physical appearance**: yellow solid; ^{1}**H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 8.23 (d, *J* = 8.5 Hz, 2 H), 7.68 (d, *J* = 8.5 Hz, 2 H), 7.60 - 7.55 (m, 2 H), 7.43 - 7.37 (m, 3 H); ^{13}**C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 147.0, 132.3, 131.8, 130.3, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5.



Compound 3aai:[11] **R*f***: 0.30 (pet. ether/EtOAc = 98/02); 14 mg, yield: 33%; **physical appearance**: yellow solid; ^{1}**H NMR**: (**500 MHz**, **CDCl$_3$**) δ = 7.52 (d, *J* = 6.5 Hz, 2 H), 7.50 - 7.45 (m, *J* = 8.8 Hz, 2 H), 7.38 - 7.29 (m, 3 H), 6.94 - 6.85 (m, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H); ^{13}**C NMR**: (**125 MHz**, **CDCl$_3$**) δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

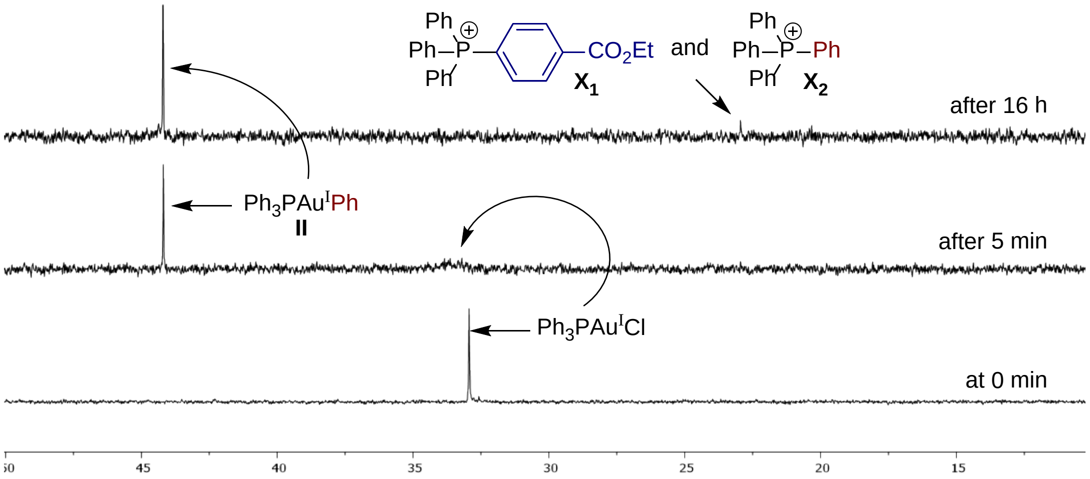
4. Mechanistic Investigations

4.1 In situ monitoring of the reaction of 1a with 2a under standard conditions by ^{1}H NMR, ^{31}P NMR spectroscopy and HRMS analysis:



The reaction of **1a** (0.1 mmol) with 1.3 equiv of **2a** (0.13 mmol) in CD_3CN (1.0 mL) was conducted under 7 mol % Ph_3PAuCl in J Young NMR tube. The ^{1}H NMR and ^{31}P NMR was accounted after 5 min and 16 h. During the time period of 0-5 min, the peak (at δ 22.9 ppm) in ^{31}P NMR corresponding to Ph_3PAuCl disappeared and a new peak started appearing at δ 44.2 ppm (scheme 4.1a). After complete conversion of the aryldiazonium salt **1a** (^{1}H NMR), another new peak appeared at δ 44.2 ppm in ^{31}P NMR.

a) ^{31}P NMR Studies of the standard reaction:



The new peak at δ 44.2 ppm was accounted for the species Ph_3PAuPh (**II**).[40] Further the intermediacy of Ph_3PAuPh (**II**) was confirmed, when the standard reaction proceeded smoothly in presence of 7 mol % Ph_3PAuPh as catalyst instead of Ph_3PAuCl (scheme 4.1b). Further, the new peak at δ 22.9 can be assigned as phosphonium salts. HRMS analysis of the reaction mass

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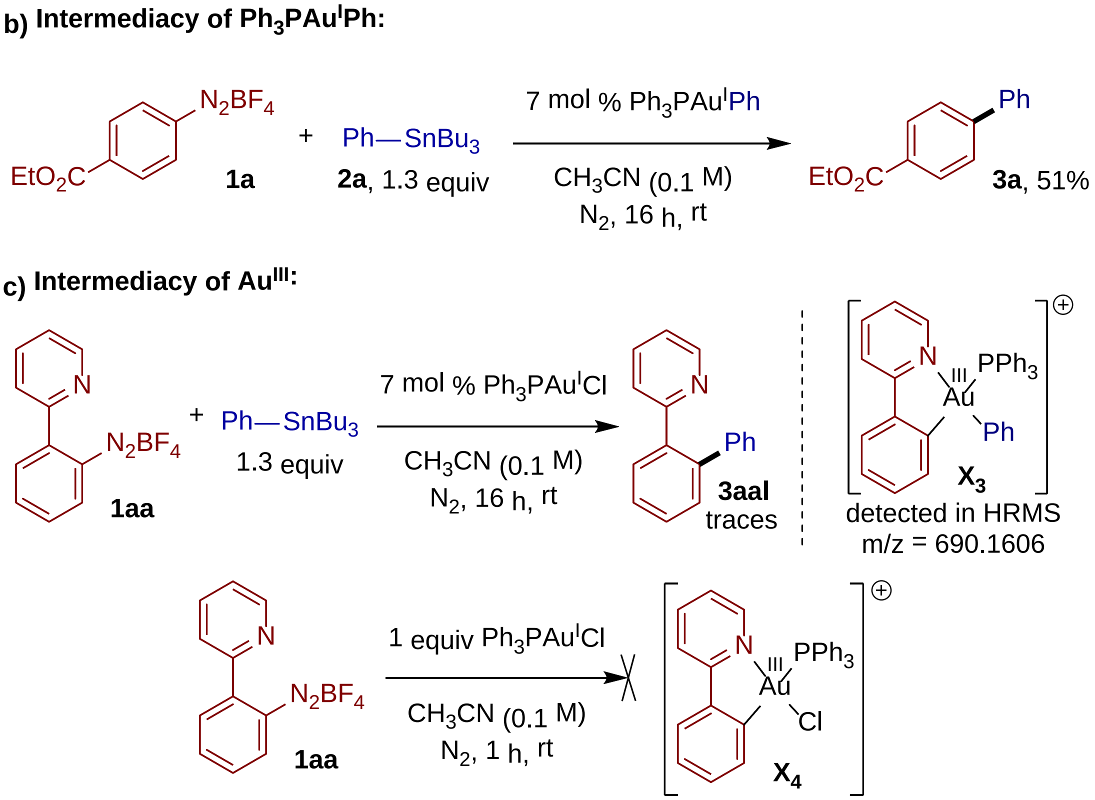
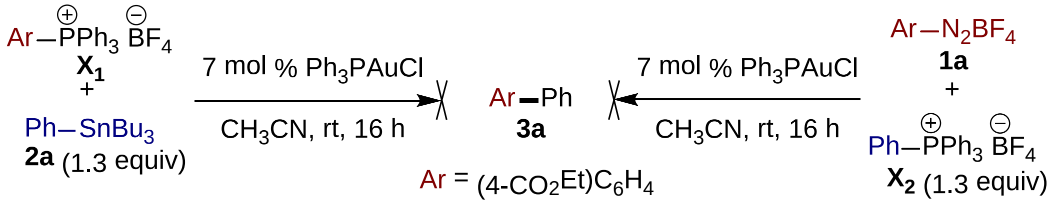
[40] T. Cornilleau, P. Hermange, E. Fouquet, *Chem. Commun.* 2016, **52**, 10040.

provided two peaks at m/z = 411.1501 and 339.1287 which can be accounted for the species $[P(Ar)Ph_3]^+$ (**X_1**) and $[PPh_4]^+$ (**X_2**). Notably, these phosphonium species (**X_1** and **X_2**) was not observed in appreciable amount in ^{31}P NMR as a large excess of stannane **2a** (1.3 equiv) was used in the standard reaction conditions. When **X_1** and **X_2** were prepared separately and characterized; it showed same chemical shifts in ^{31}P NMR. Thus, the formation of phosphonium salts **X_1** and **X_2** in the reaction implies the potent formation of Au(III)-intermediates via the oxidation of gold(I)-precursors. Further, when diazonium salt **1aa** was treated under standard reaction condition (Scheme 4.1c), species **X_3** was detected in HRMS (m/z = 690.1606) after 10 min. Conversely, diazonium salt **1aa** was unable to oxidize Ph_3PAuCl in absence of $PhSnBu_3$ as we were unable to detect **X_4** in HRMS. This observation clearly indicates the intermediacy of Ph_3PAu^IPh species (**II**) along with the fact that the reaction is proceeding via the transmetalation/oxidation sequence.



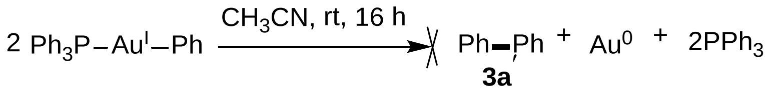
Next, to know the whether phosphonium salt **X_1** is the active intermediate, a control experiment was performed as shown below (Scheme 4.1d). However, product **3a** was not observed indicating that the species **X_1** could not be the catalytically active species.

d) Intermediacy of phosphonium salts:

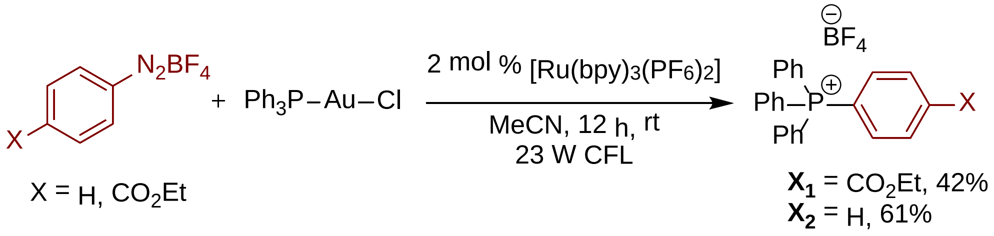


Further, when Ph_3PAuPh (**II**) was stirred for 16 h in CH_3CN, it didn't provide **3a'** (Scheme 4.1e). Thus a possible disproportionation reaction of Ph_3PAuPh (**II**) to form **3a'** was discarded. Which eventually suggests that the formation of **3a'** is thus an outcome of Au(I)/Au(III) catalysis.

e) Disproportionation of Ph_3PAu^IPh:



4.2 General procedure for the synthesis of phosphonium salts [(*p*-CO_2Et-C_6H_4)PPh_3]BF_4 (X_1) and [PPh_4] BF_4 (X_2):



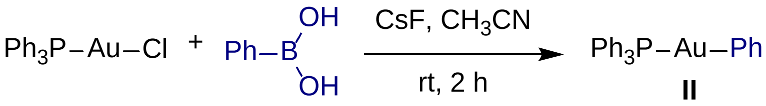
A Schlenk tube was loaded with the Ph_3PAuCl (50 mg, 0.1 mmol), diazonium salt **1** (0.11 mmol, 1.1 equiv) and [$Ru(bpy)_3(PF_6)_2$] (2 mg, 0.002 mmol, 2 mol %). The reaction vessel was wrapped with aluminium foil before 1 mL CH_3CN was added at 0 °C. The reaction mixture was degassed using 3 freeze-pump-thaw cycles. The foil was then removed and the reaction mixture was stirred for 12 h at room temperature under light irradiation using 23 W CFL bulb. The mixture was then diluted with diethyl ether (25 mL) and the resultant precipitate was filtered out. The crude solid was recrystallized with DCM/diethyl ether to afford the corresponding phosphonium salts.

Compound X_1: 21 mg, yield: 42%; brown solid, mp: 141 °C; **^{1}H NMR**: (**500 MHz, CD_3CN**) δ = 7.9 (dd, *J* = 8.39, 3.05 Hz, 2 H), 7.6 - 7.7 (m, 3 H), 7.5 (dd, *J* = 8.39 Hz, 4.20 Hz, 1 H), 7.4-7.3

(m, 12 H), 4.1 (q, *J*=7.25 Hz, 2 H), 1.1 (t, *J*=7.25 Hz, 3 H); ^{13}**C NMR**: (**125 MHz**, **CD_3CN**) δ = 165.9, 137.6 (d, *J* = 2.9 Hz), 136.7 (d, *J* = 2.9 Hz), 136.2 (d, *J* = 10.5 Hz), 135.9 (d, *J* = 10.5 Hz), 133.4 (s), 131.5 (d, *J* = 12.4 Hz), 124.0 (d, *J* = 88.7 Hz), 118.4 (d, *J* = 89.7 Hz), 63.1, 14.5; ^{31}**P NMR**: (**202 MHz**, **CD_3CN**) δ = 23.0; ^{11}**B NMR**: (**128 MHz**, **CD_3CN**) δ = −1.2; ^{19}**F NMR**: (**375 MHz**, **CD_3CN**) δ = −151.8; **HRMS**: (**ESI**) calcd 411.1508 for $C_{27}H_{24}OP$ M^+ found 411.1501.

Compound X_2:[41] 26 mg, yield: 61%; yellow solid; ^{1}**H NMR**: (**400 MHz**, **CD_3CN**) δ = 7.70 - 7.51 (m, 3 H), 7.51 - 7.28 (m, 12 H); ^{13}**C NMR**: (**100 MHz**, **CD_3CN**) δ = 136.7 (d, J = 3.1), 135.6 (d, J = 10.8), 131.3 (d, J = 13.1), 119.5; ^{31}**P NMR**: (**162 MHz**, **CD_3CN**) δ = 22.9; **HRMS**: (**ESI**) calcd 339.1297 for $C_{24}H_{20}P$ M^+ found 339.1292.

4.3 Procedure for the synthesis of Ph_3PAuPh (II):[40]



In a vial was added PPh_3AuCl (49.5 mg, 0.1 mmol, 1 equiv), dried CsF (30.4 mg, 0.2 mmol, 2 equiv) and phenylboronic acid (12.2 mg, 0.1 mmol, 1 equiv) in anhydrous CH_3CN (1 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed and 5 mL benzene was added to the residue. The resulting mixture was filtered through a Celite pad and the filtrate was evaporated under reduced pressure and triturated with pentane to precipitate the product. The resulting white suspension was filtered to afford PPh_3AuPh (34 mg, 63%) as a white solid. ^{1}H-NMR spectrum was in accordance with the data previously reported.

Compound II: 34 mg, yield: 63%; white solid; ^{1}**H NMR**: (**400 MHz**, **CD_3CN**) δ = 7.46 - 7.37 (m, 6 H), 7.37 - 7.26 (m, 10 H), 7.25 - 7.16 (m, 3 H), 6.98 (t, *J* = 7.0 Hz, 2 H), 6.80 (t, *J* = 7.3 Hz, 1 H); ^{31}**P NMR**: (**162 MHz**, **CD_3CN**) δ = 43.1.

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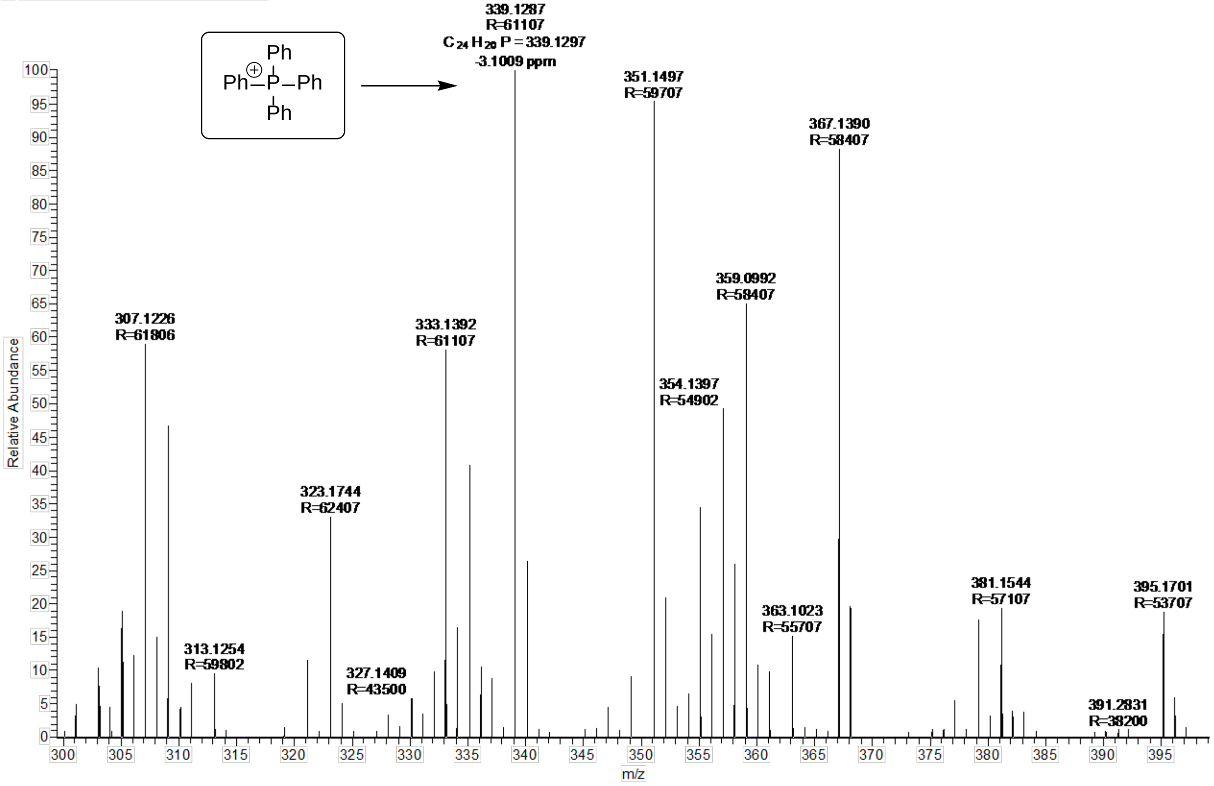
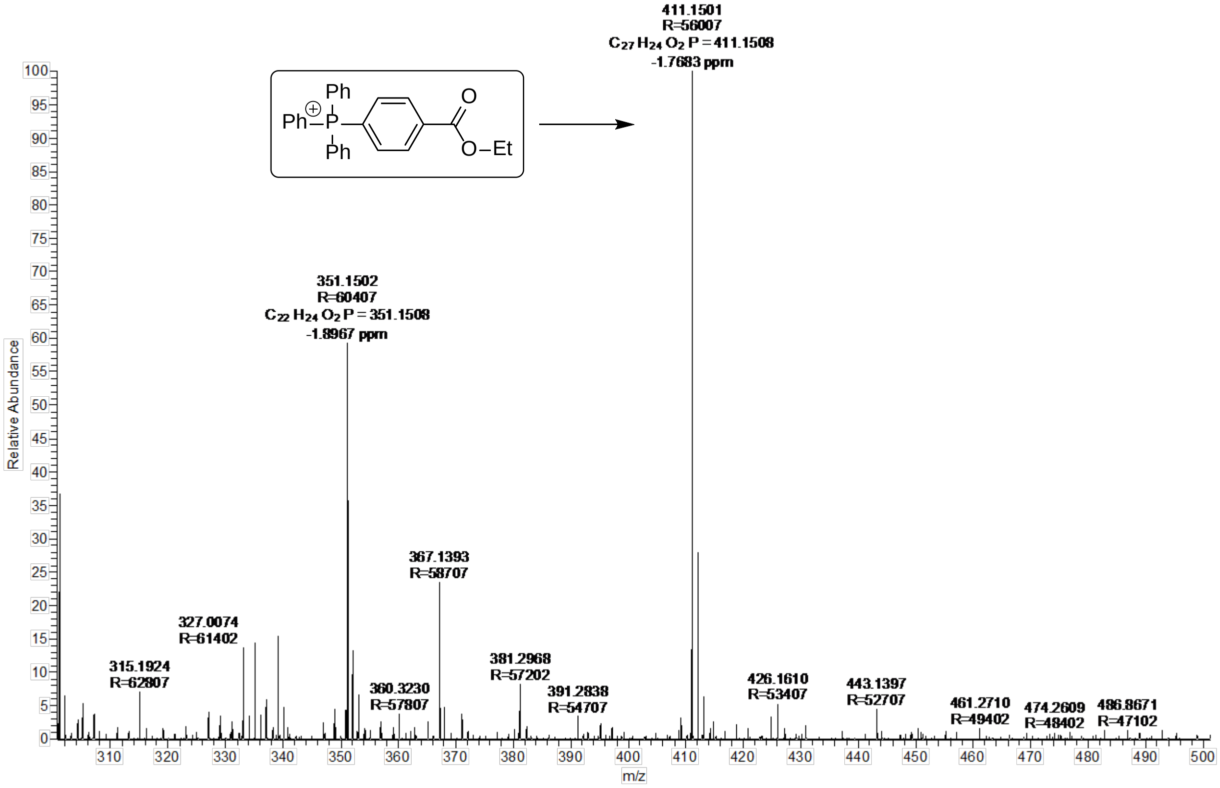
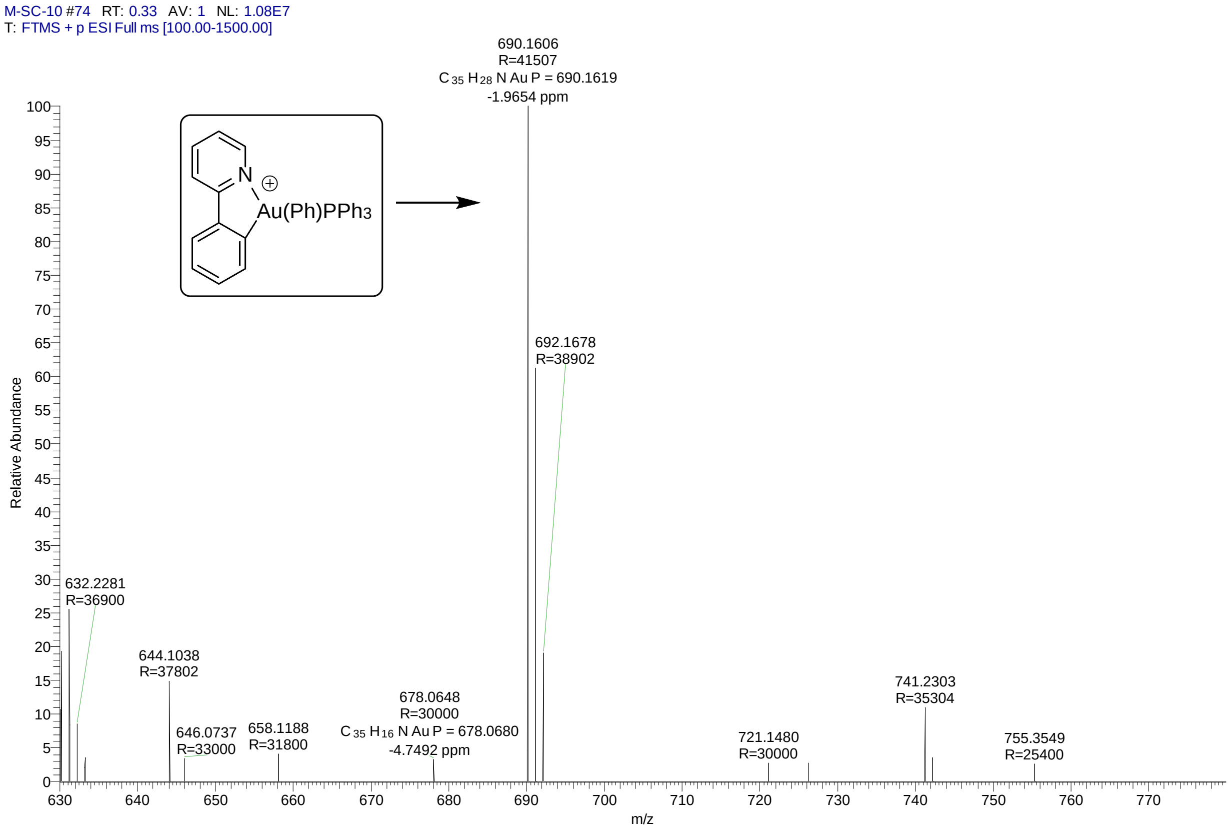
[41] X.-Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.*, 2014, **136**, 5844.

5. HRMS spectra:



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-1.9654 ppm
N
⊕
Au(Ph)PPh3
692.1678
R=38902
632.2281
R=36900
644.1038
R=37802
646.0737
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658.1188
R=31800
678.0648
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C 35 H 16 N Au P = 678.0680
-4.7492 ppm
721.1480
R=30000
741.2303
R=35304
755.3549
R=25400
Relative Abundance
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100
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90
85
80
75
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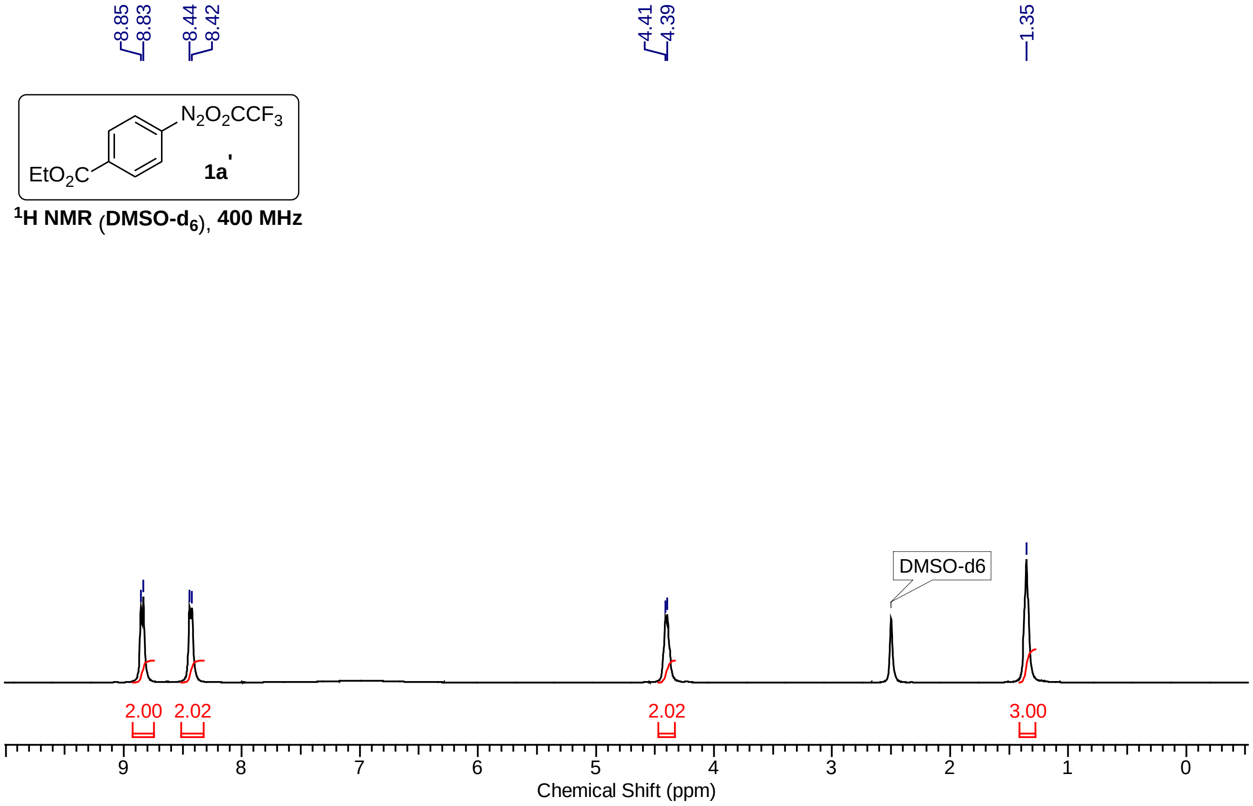
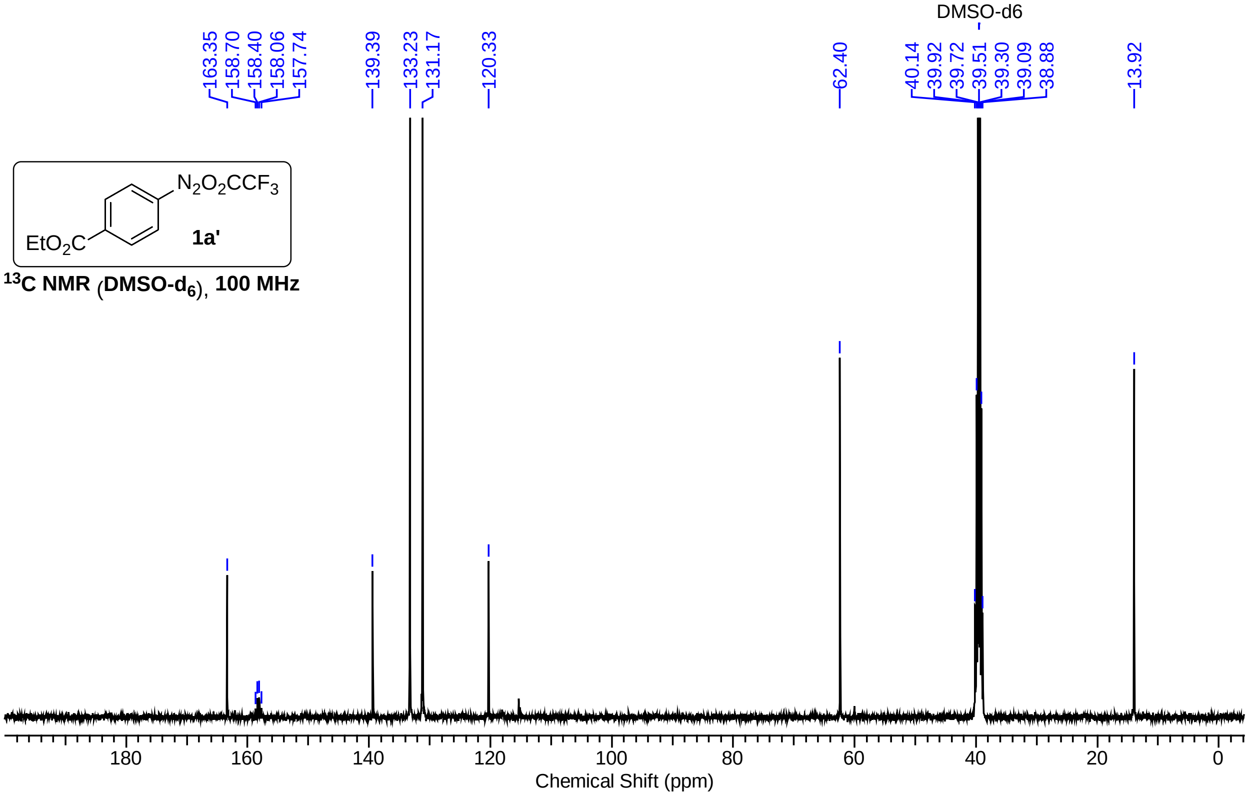
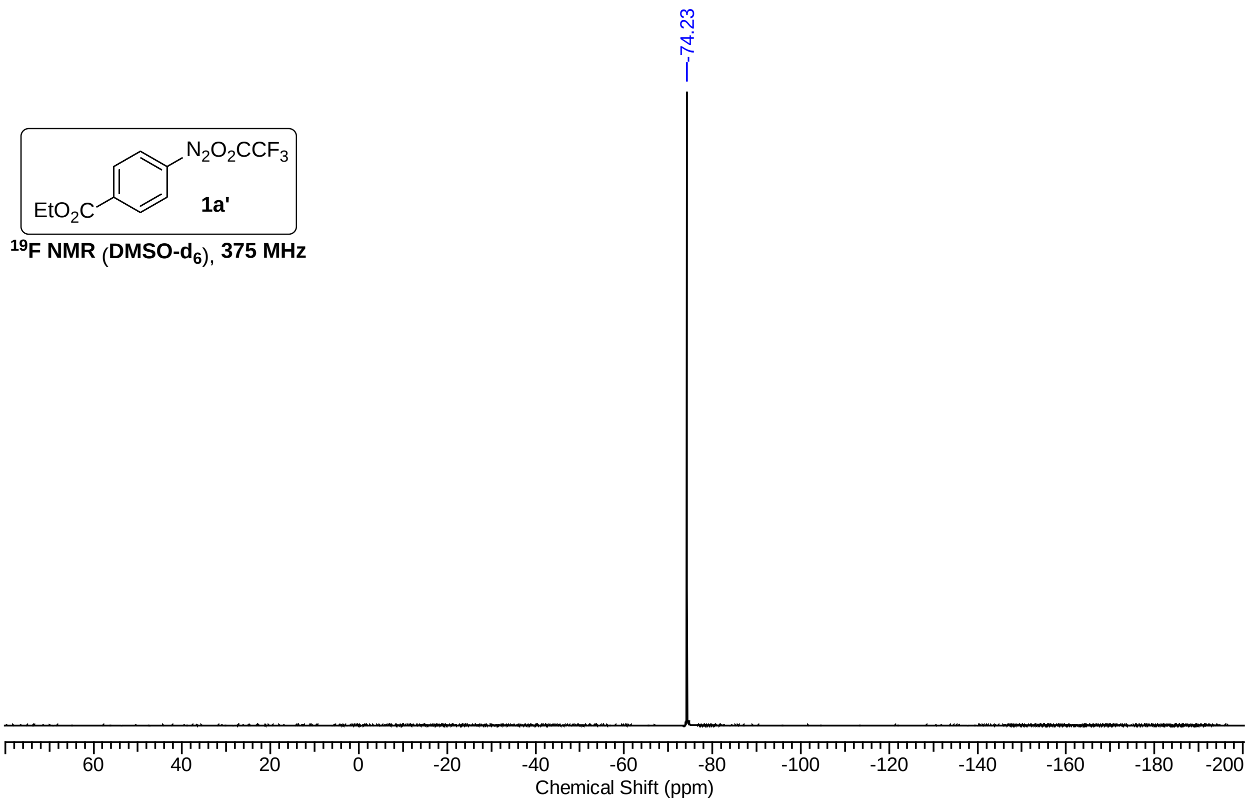
6. NMR Spectra



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EtO2C
1a'
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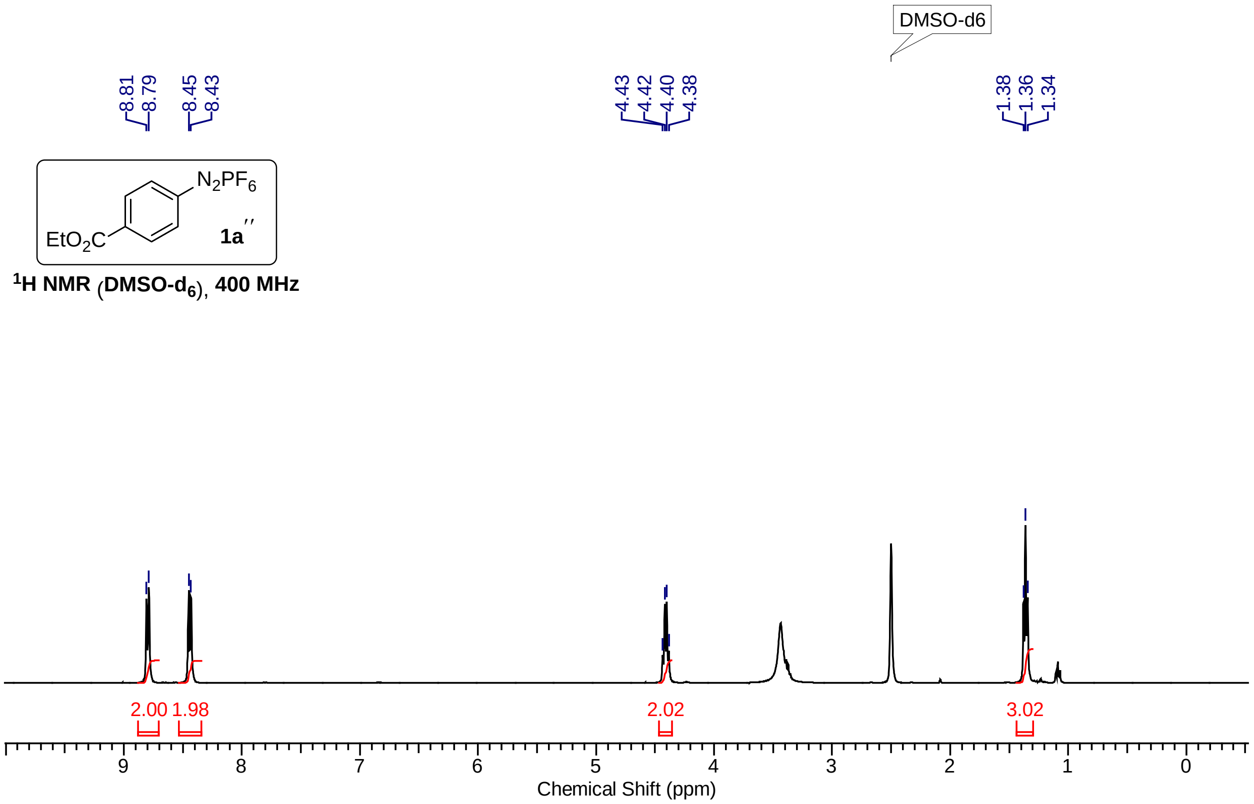
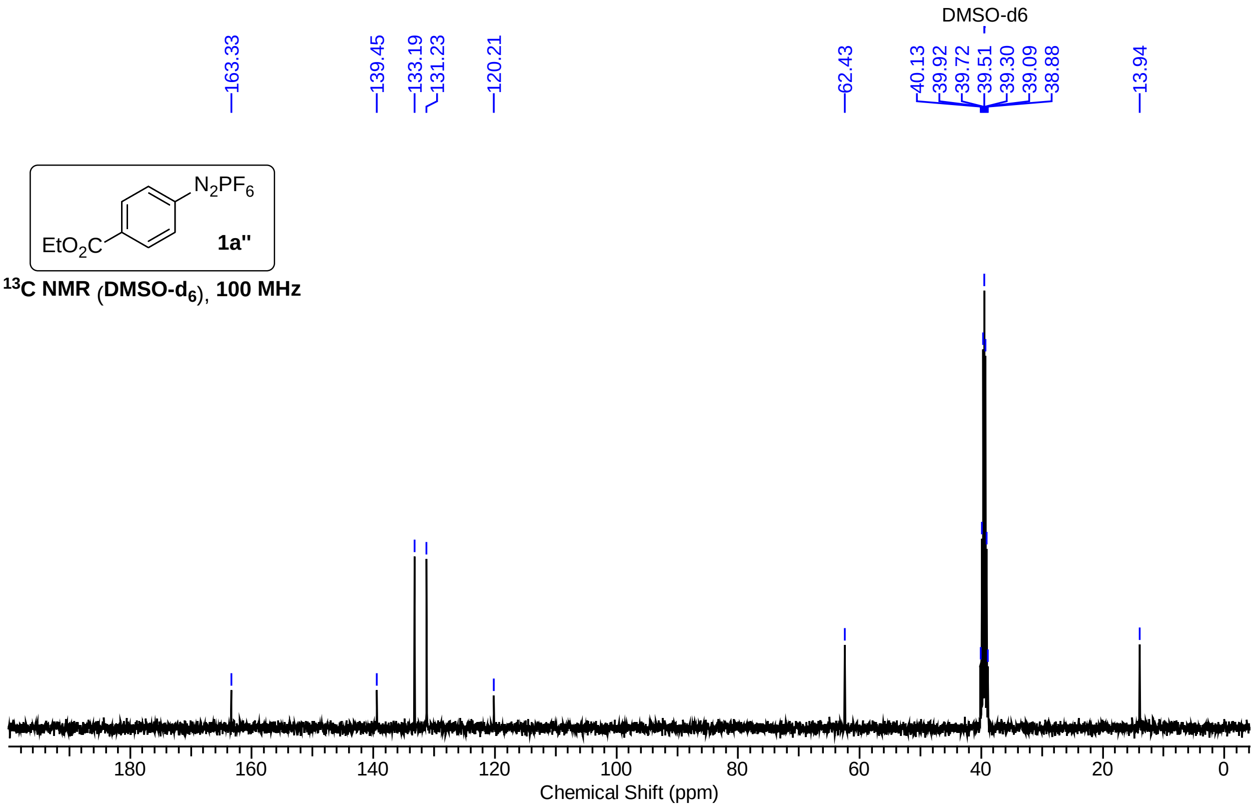
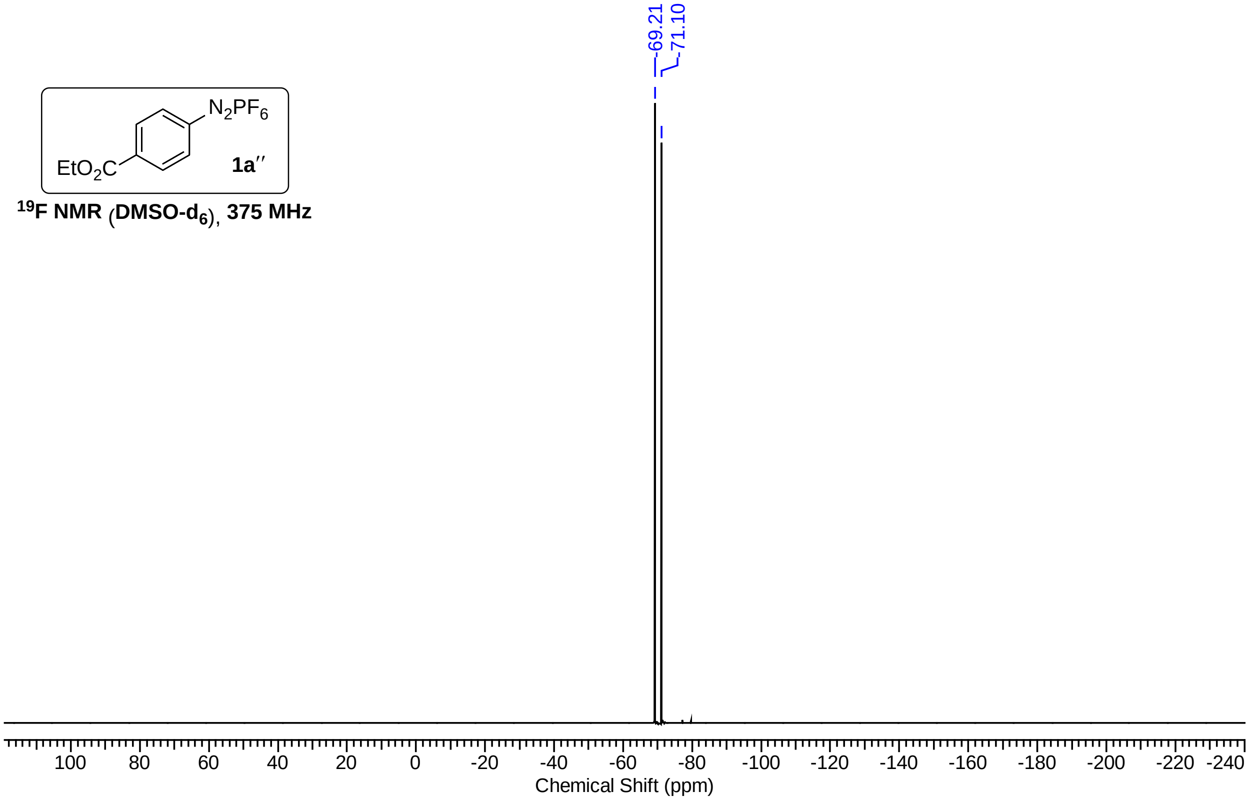
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

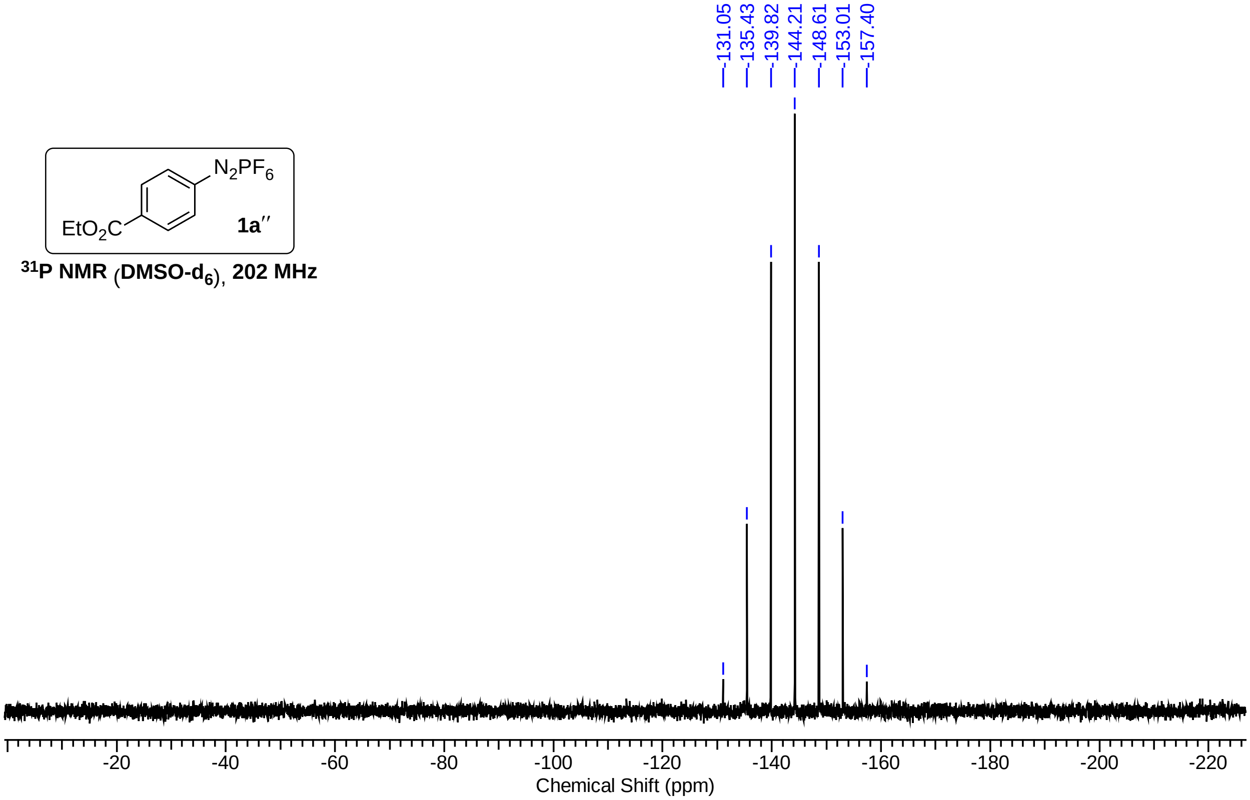


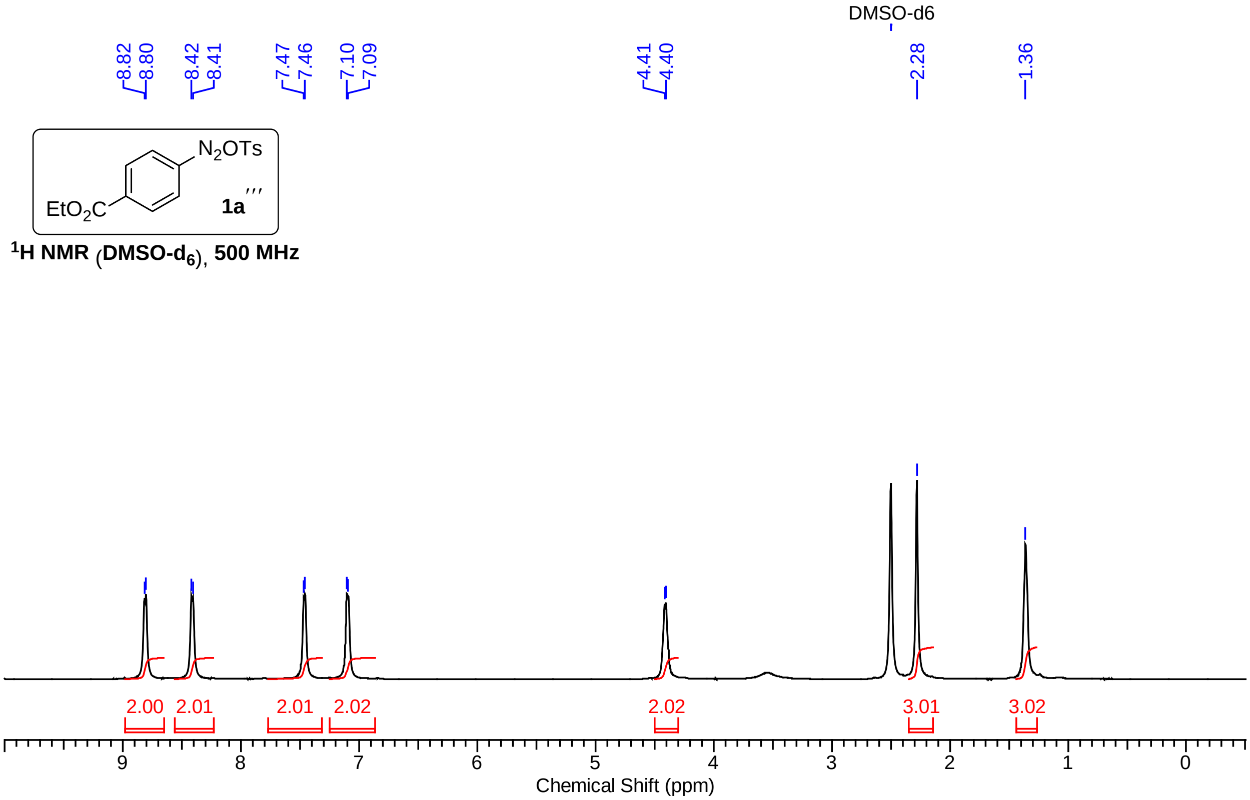
^{1}H NMR (DMSO-d$_6$), 400 MHz



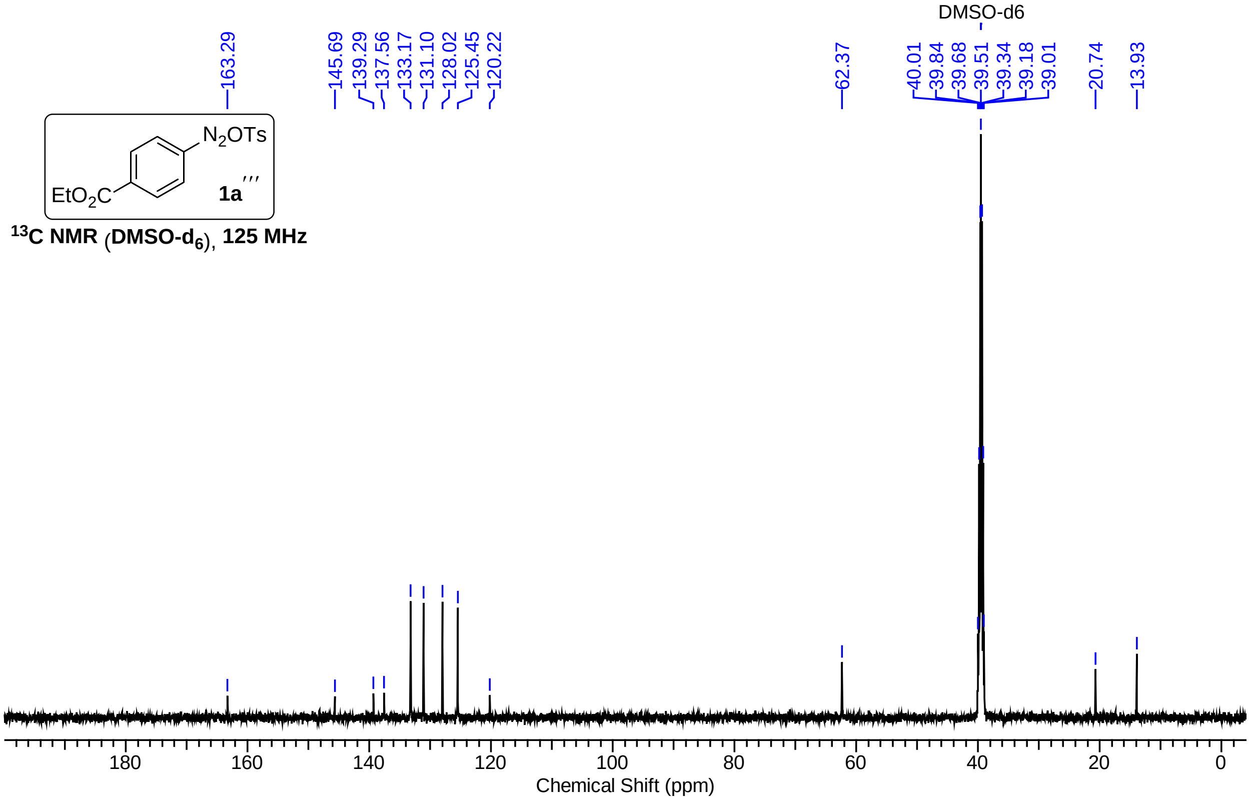
^{13}C NMR (DMSO-d$_6$), 100 MHz


-69.21
-71.10
N_2PF_6
EtO_2C
1a″
^{19}F NMR (DMSO-d$_6$), 375 MHz
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
Chemical Shift (ppm)

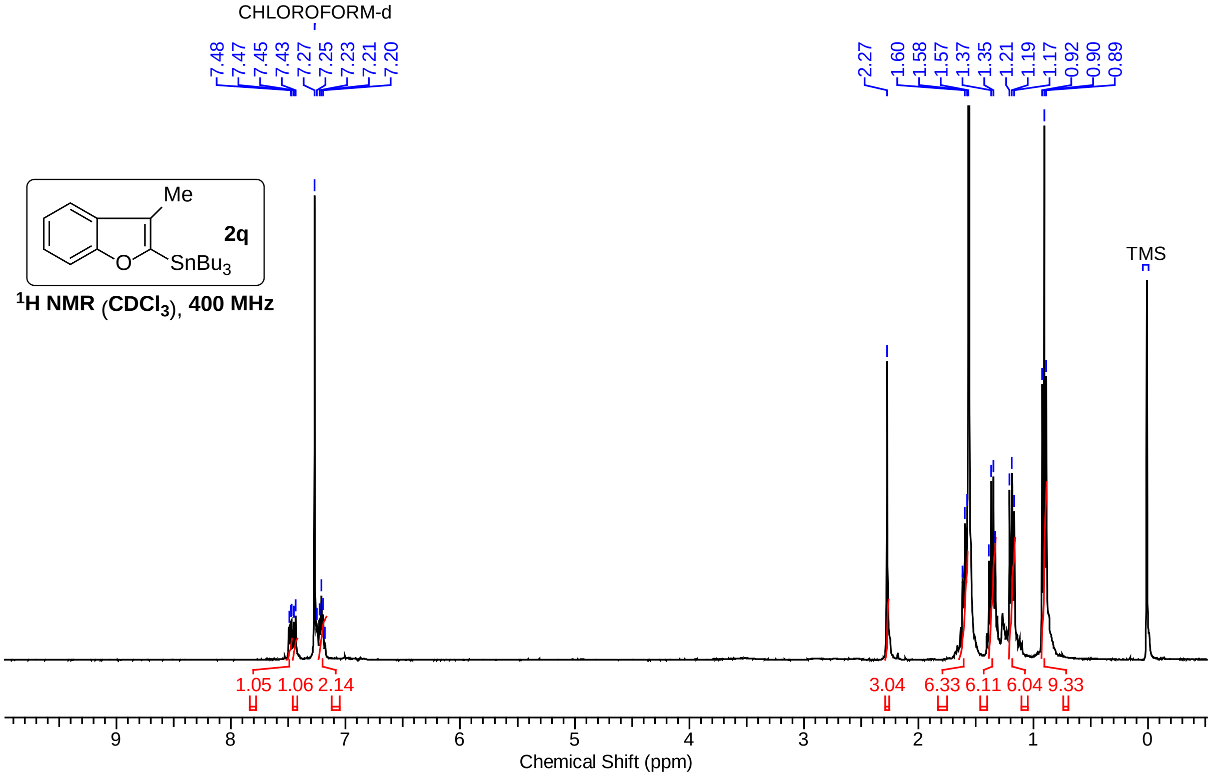

-131.05
-135.43
-139.82
-144.21
-148.61
-153.01
-157.40
N_2PF_6
EtO_2C
1a″
^{31}P NMR (DMSO-d$_6$), 202 MHz
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)



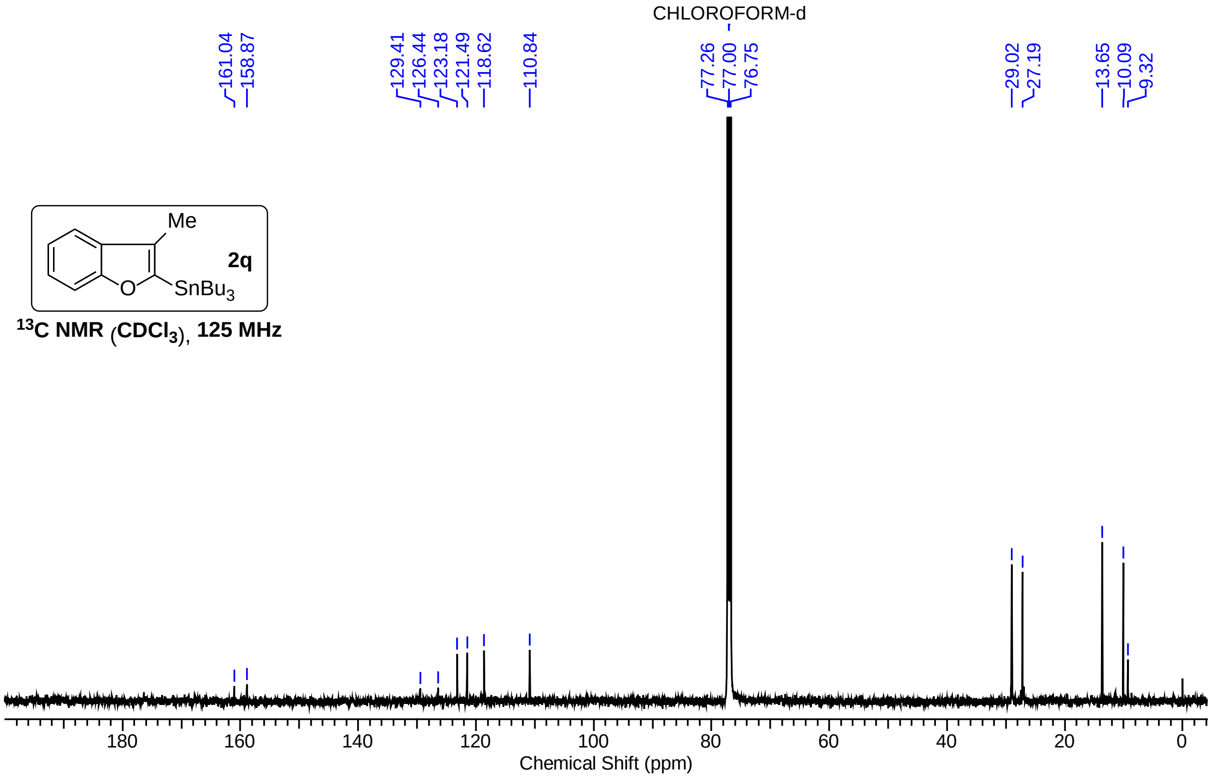
^{1}H NMR (DMSO-d$_6$), 500 MHz



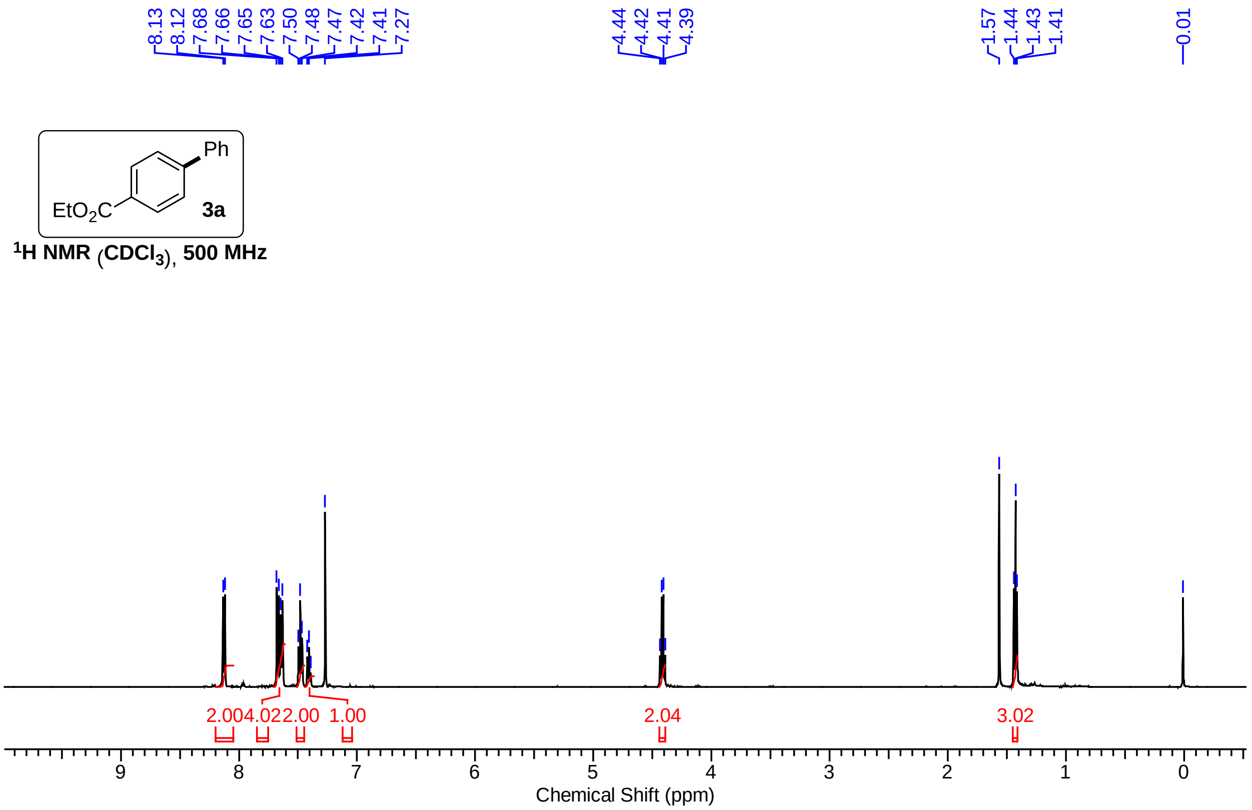
^{13}C NMR (DMSO-d$_6$), 125 MHz



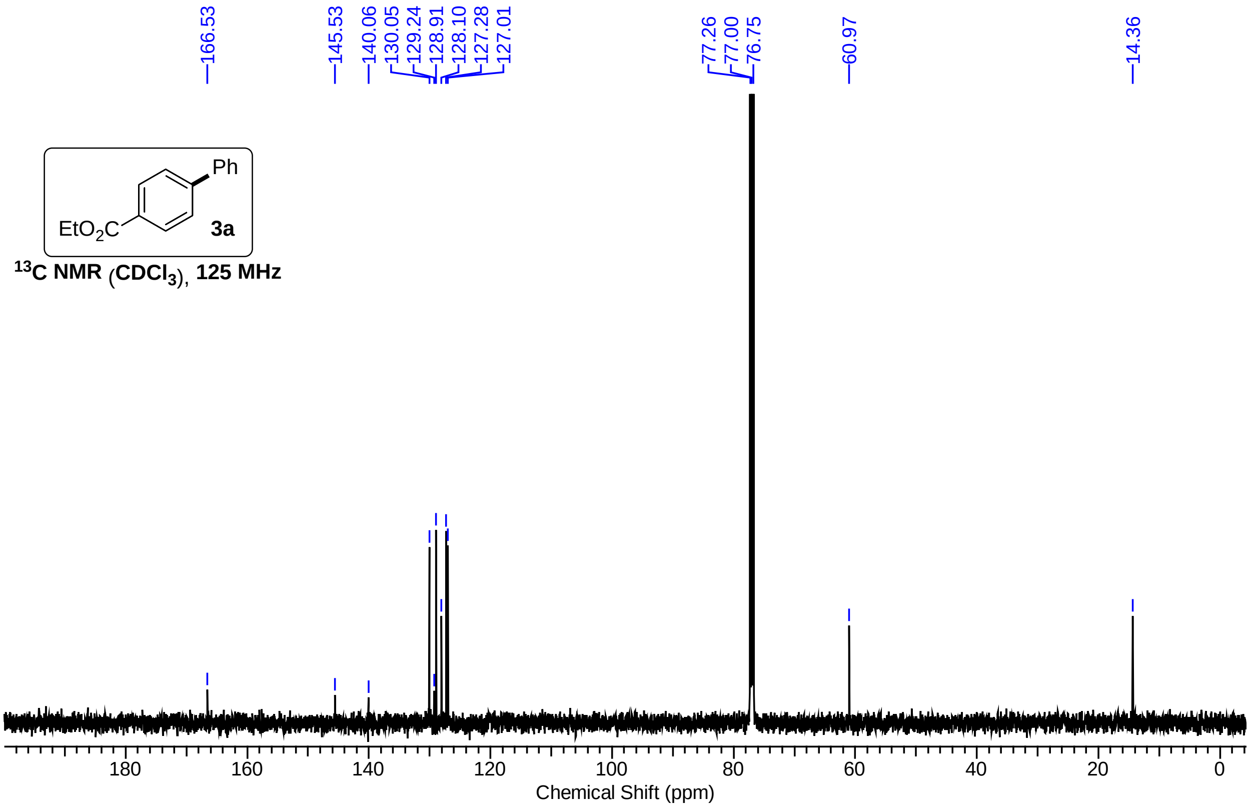
^{1}H NMR (CDCl$_3$), 400 MHz



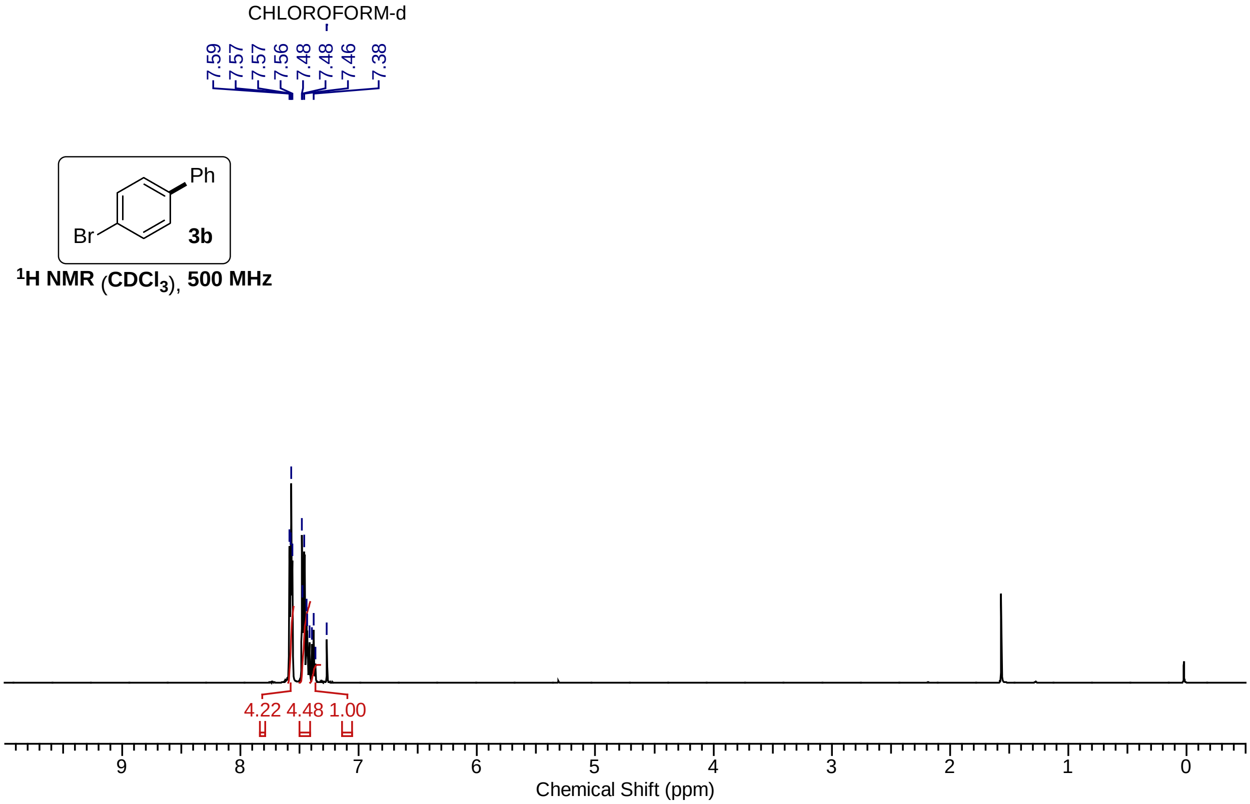
^{13}C NMR (CDCl$_3$), 125 MHz



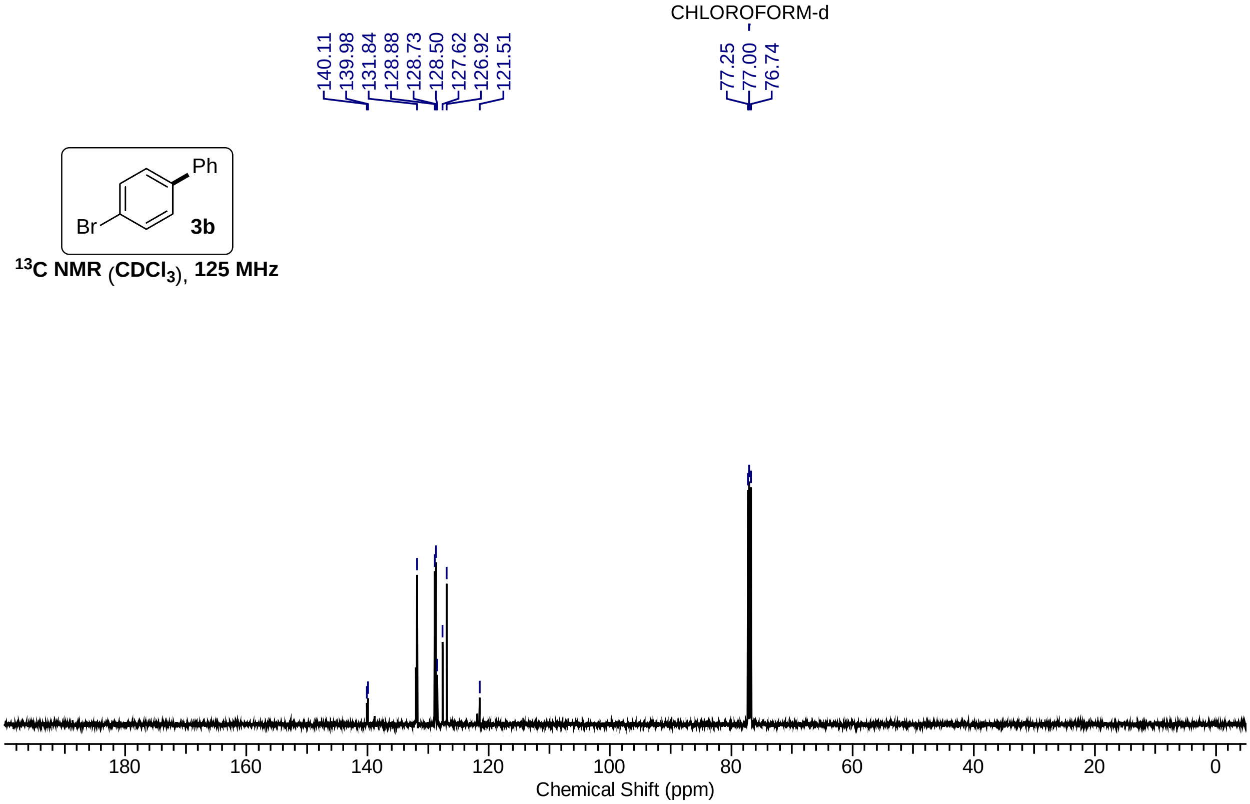
^{1}H NMR (CDCl$_3$), 500 MHz



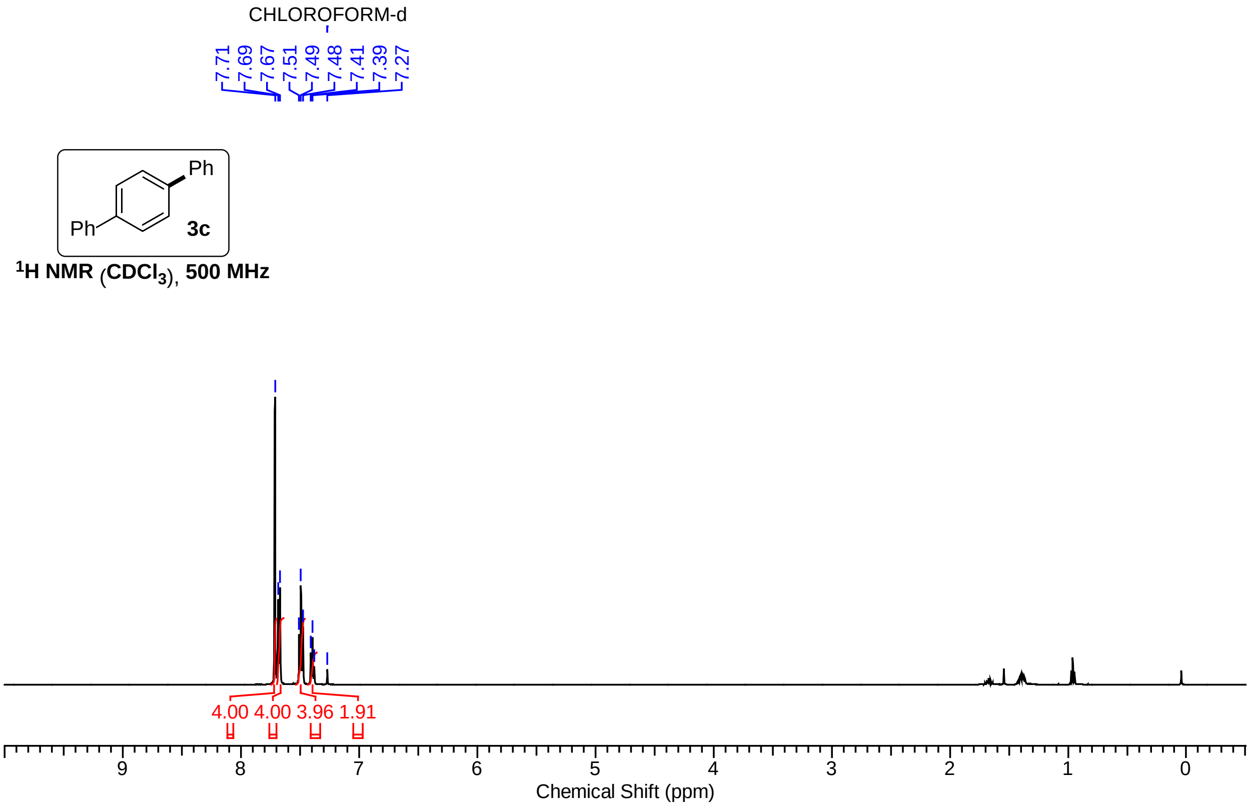
^{13}C NMR (CDCl$_3$), 125 MHz



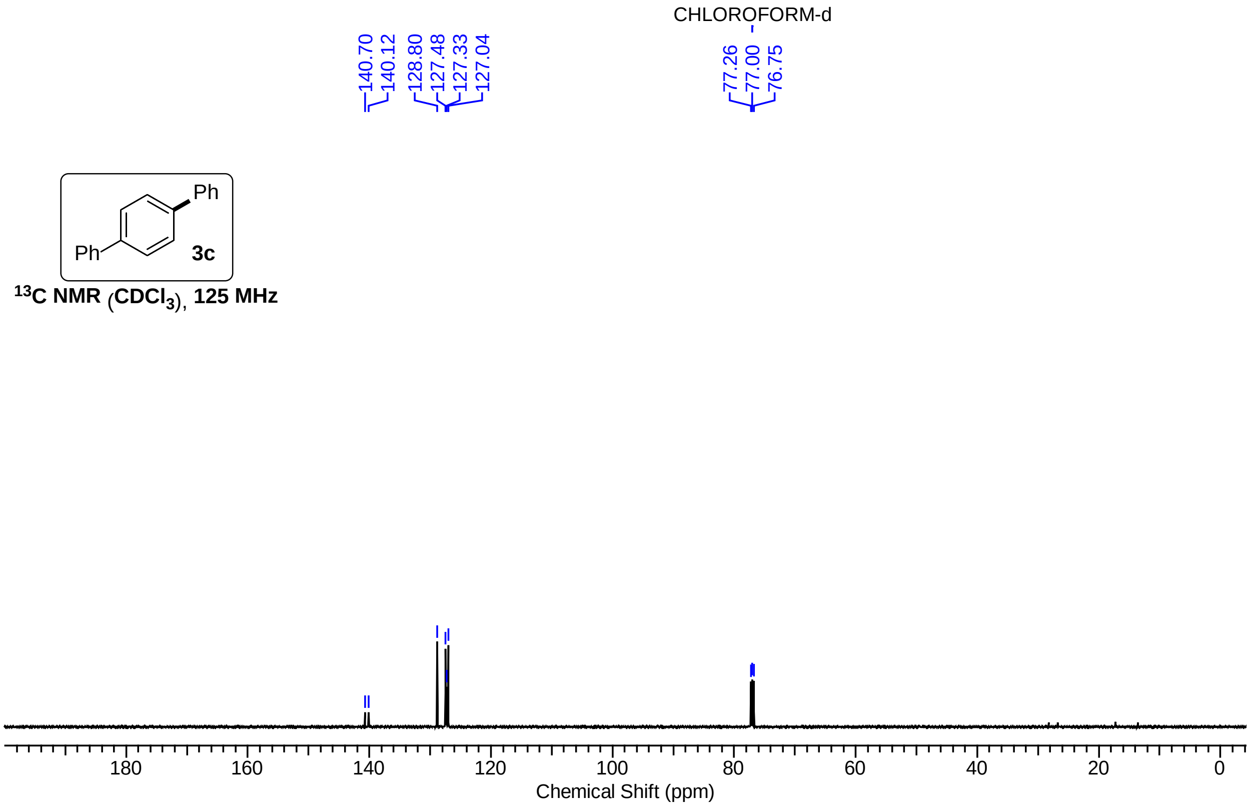
^{1}H NMR (CDCl$_3$), 500 MHz



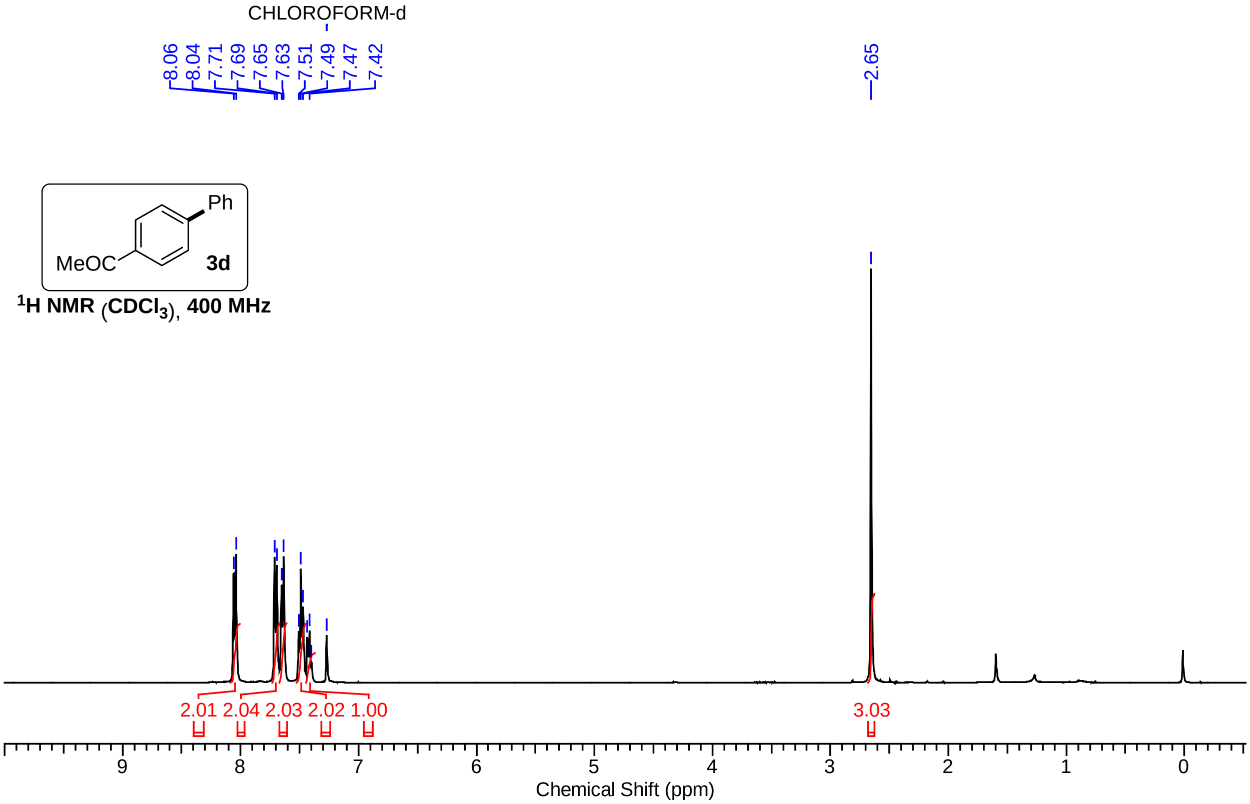
^{13}C NMR (CDCl$_3$), 125 MHz



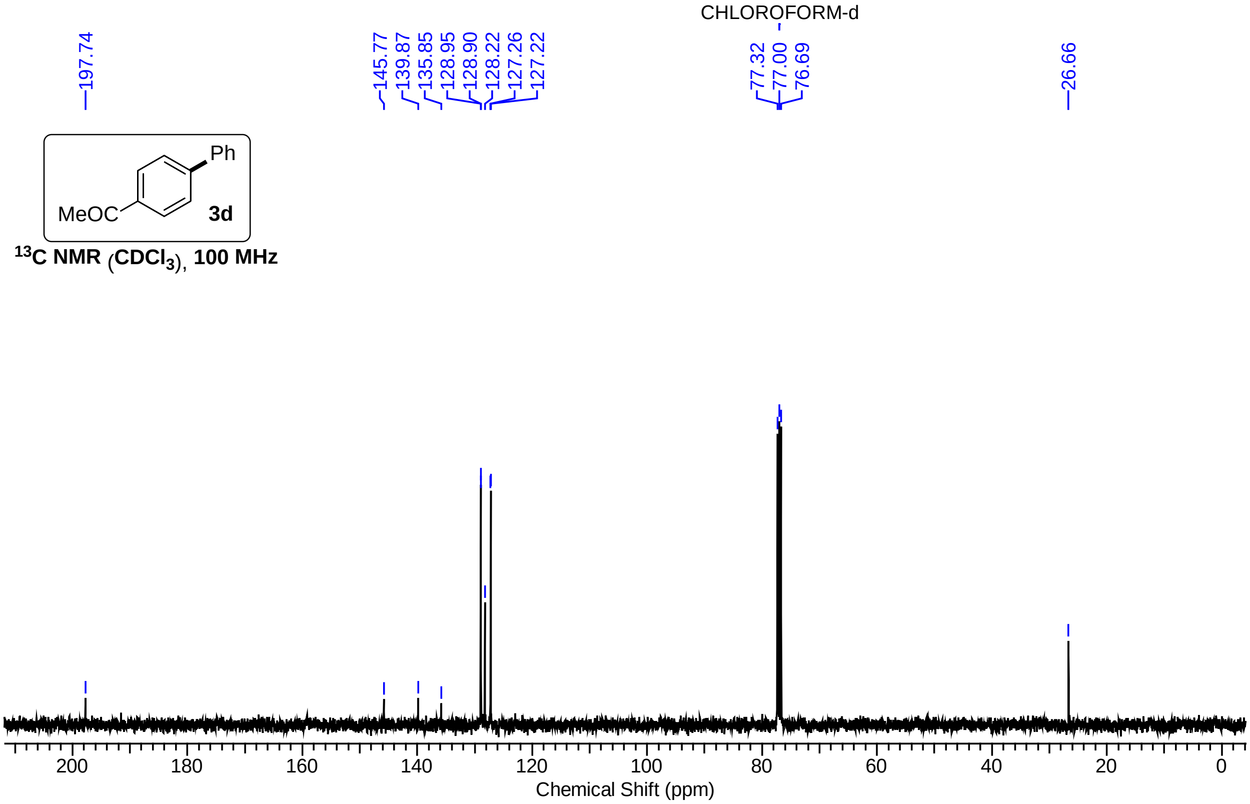
^{1}H NMR (CDCl$_3$), 500 MHz



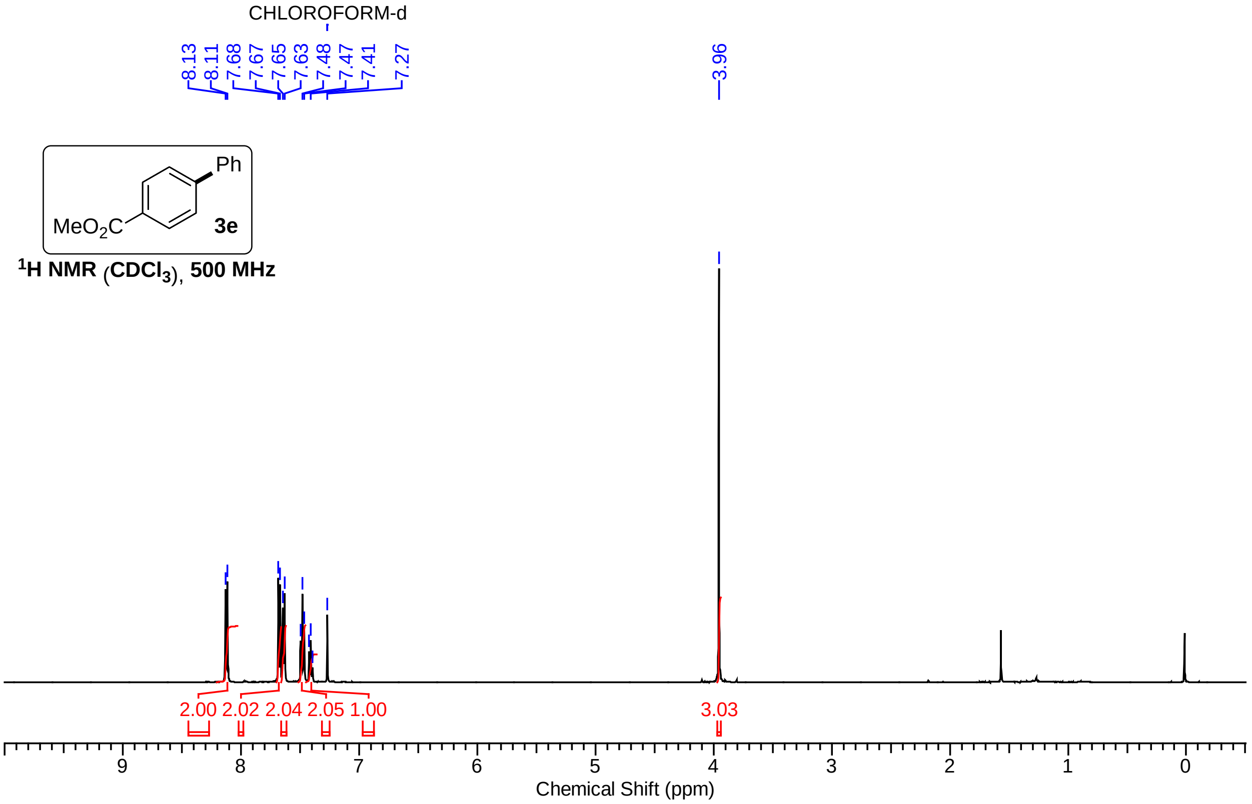
^{13}C NMR (CDCl$_3$), 125 MHz



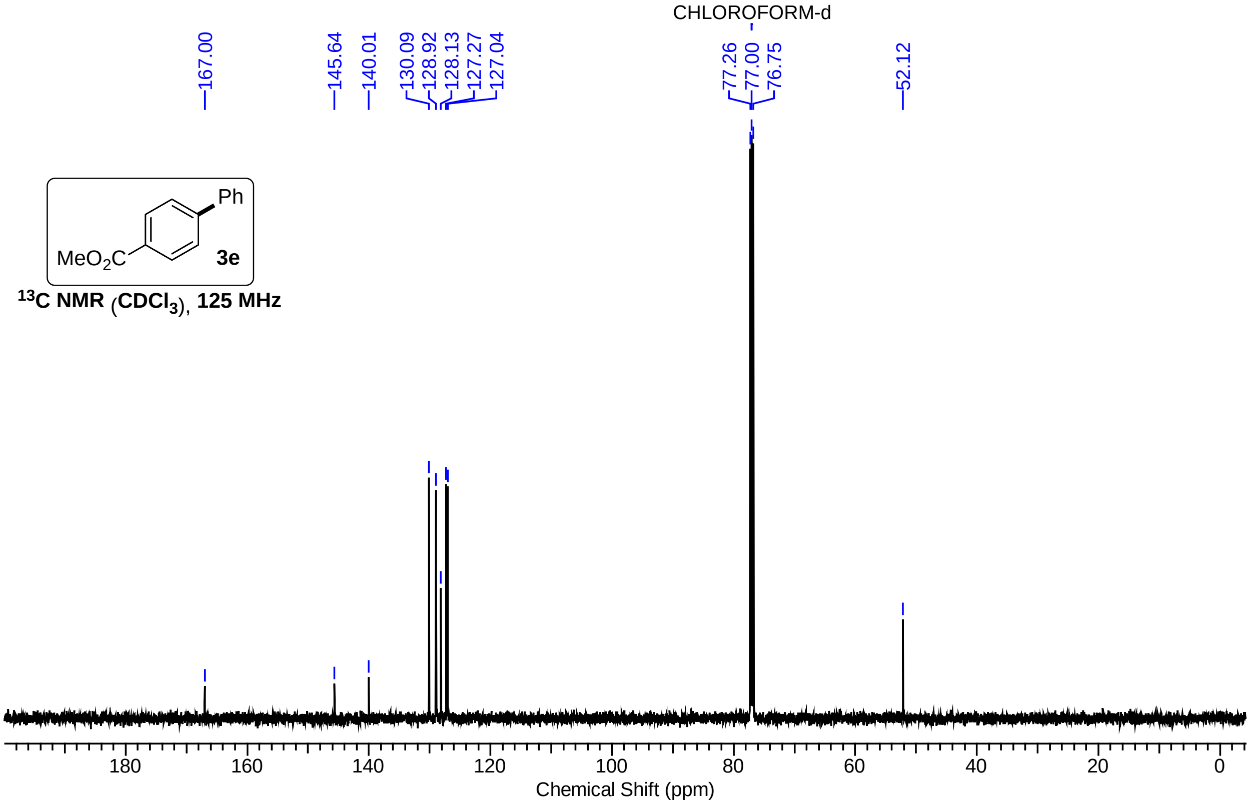
^{1}H NMR (CDCl$_3$), 400 MHz



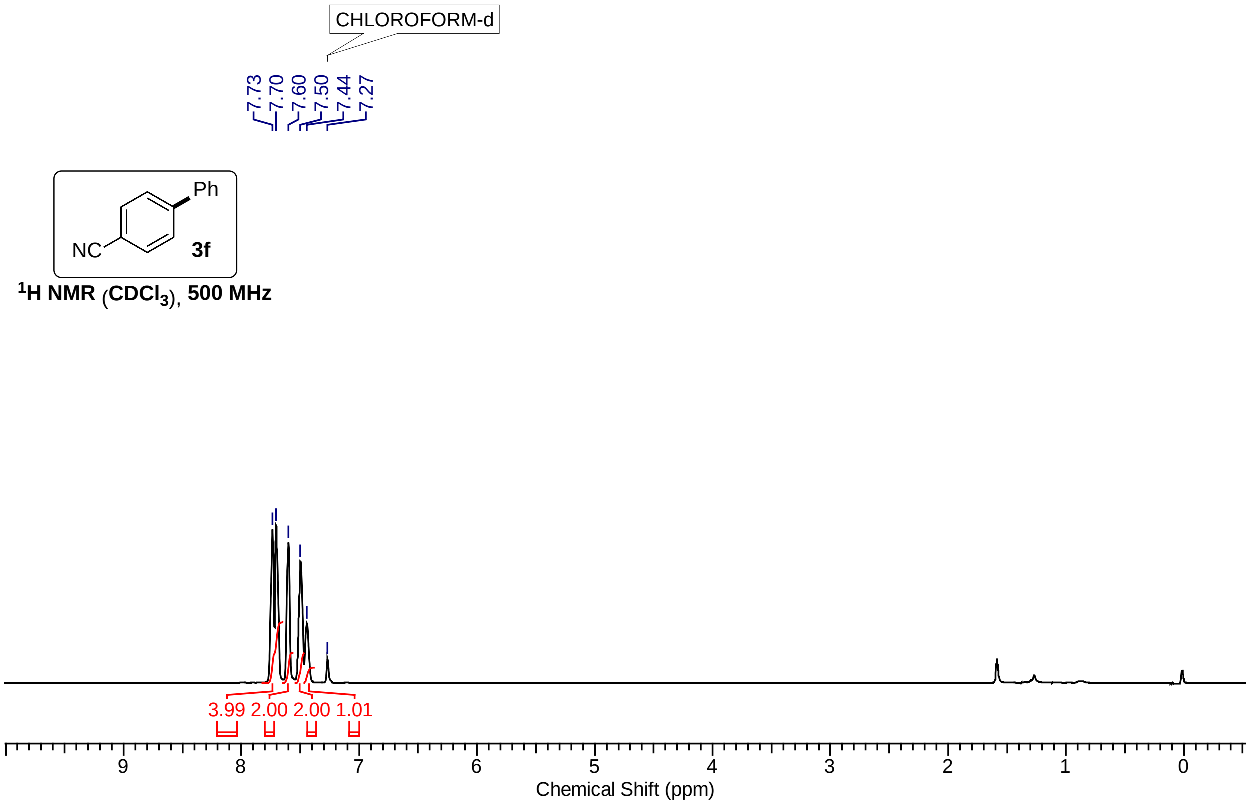
^{13}C NMR (CDCl$_3$), 100 MHz



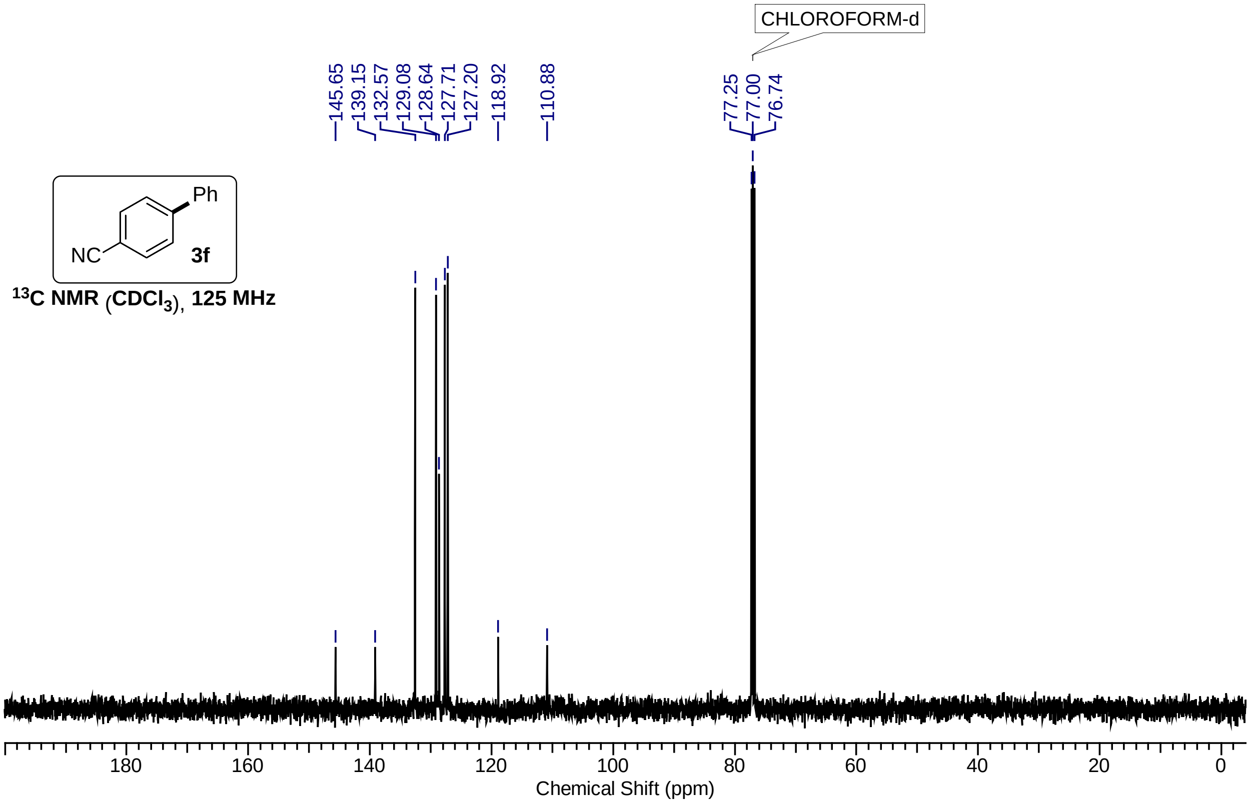
^{1}H NMR (CDCl$_3$), 500 MHz



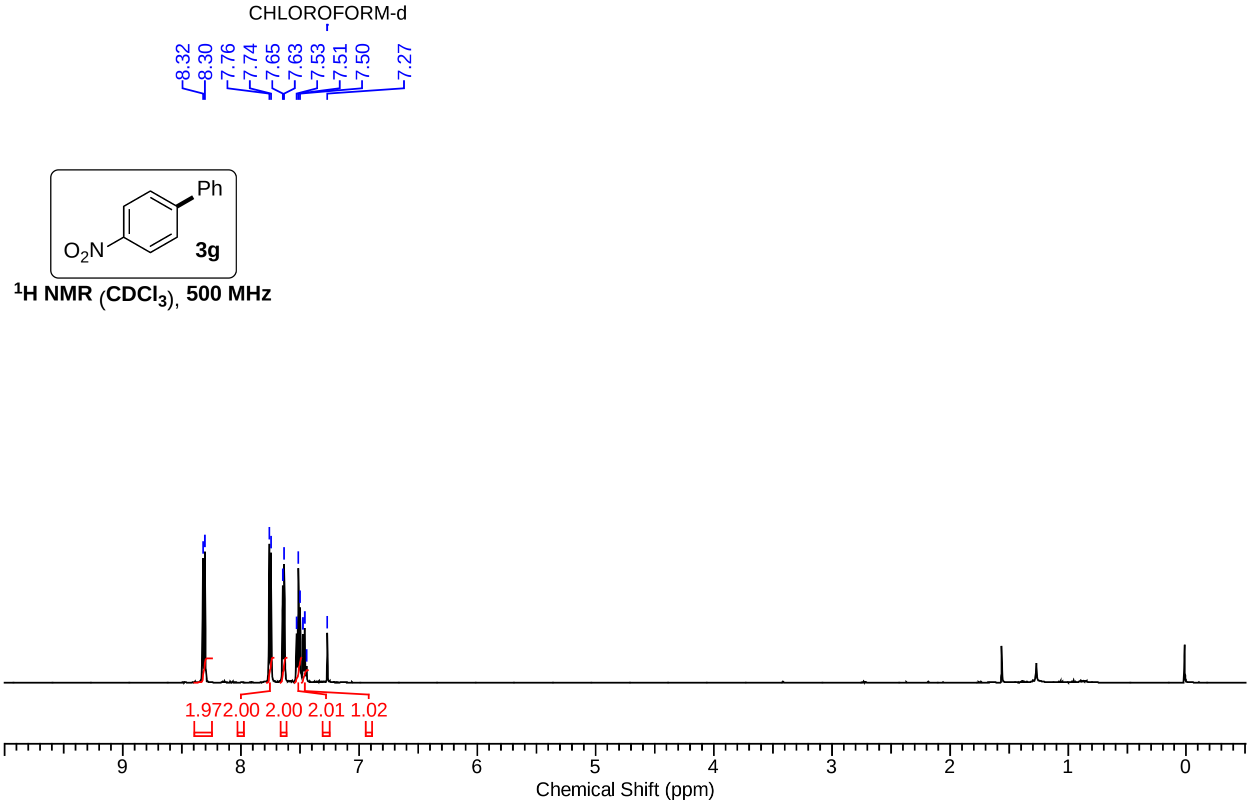
^{13}C NMR (CDCl$_3$), 125 MHz



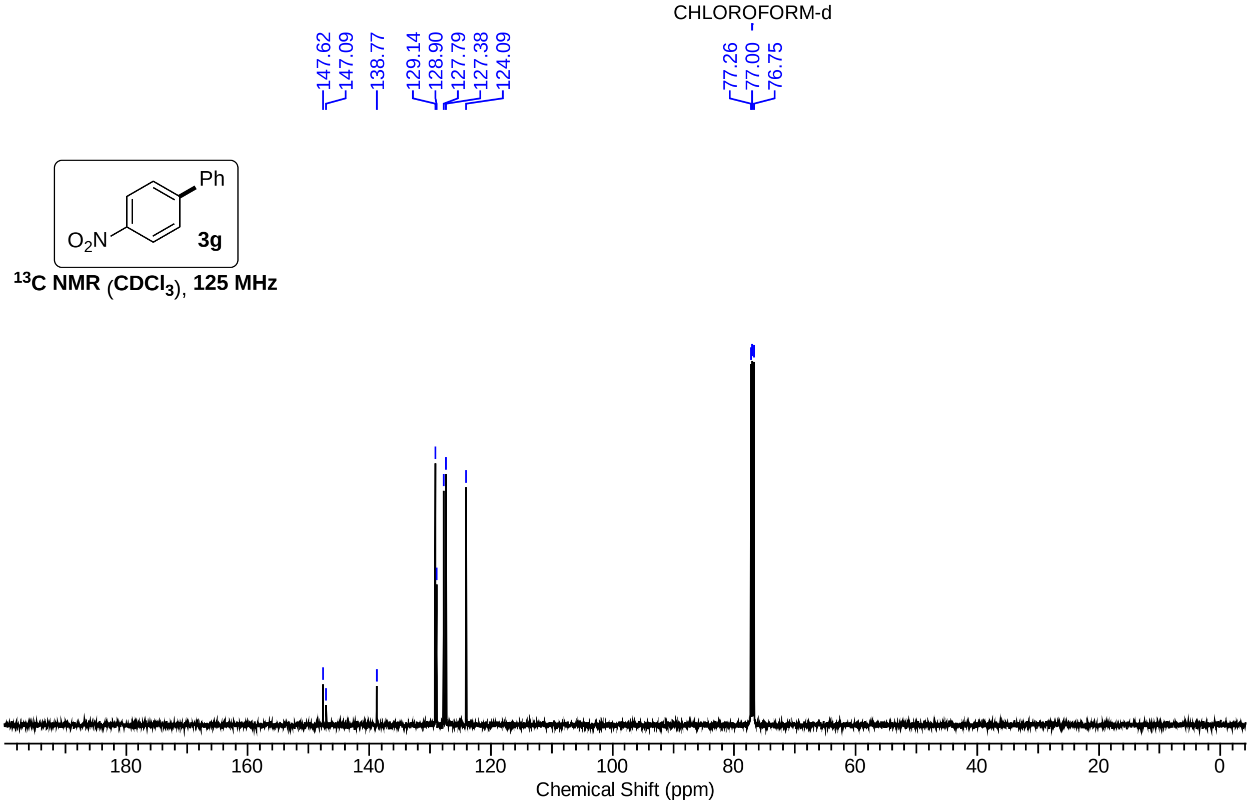
^{1}H NMR (CDCl$_3$), 500 MHz



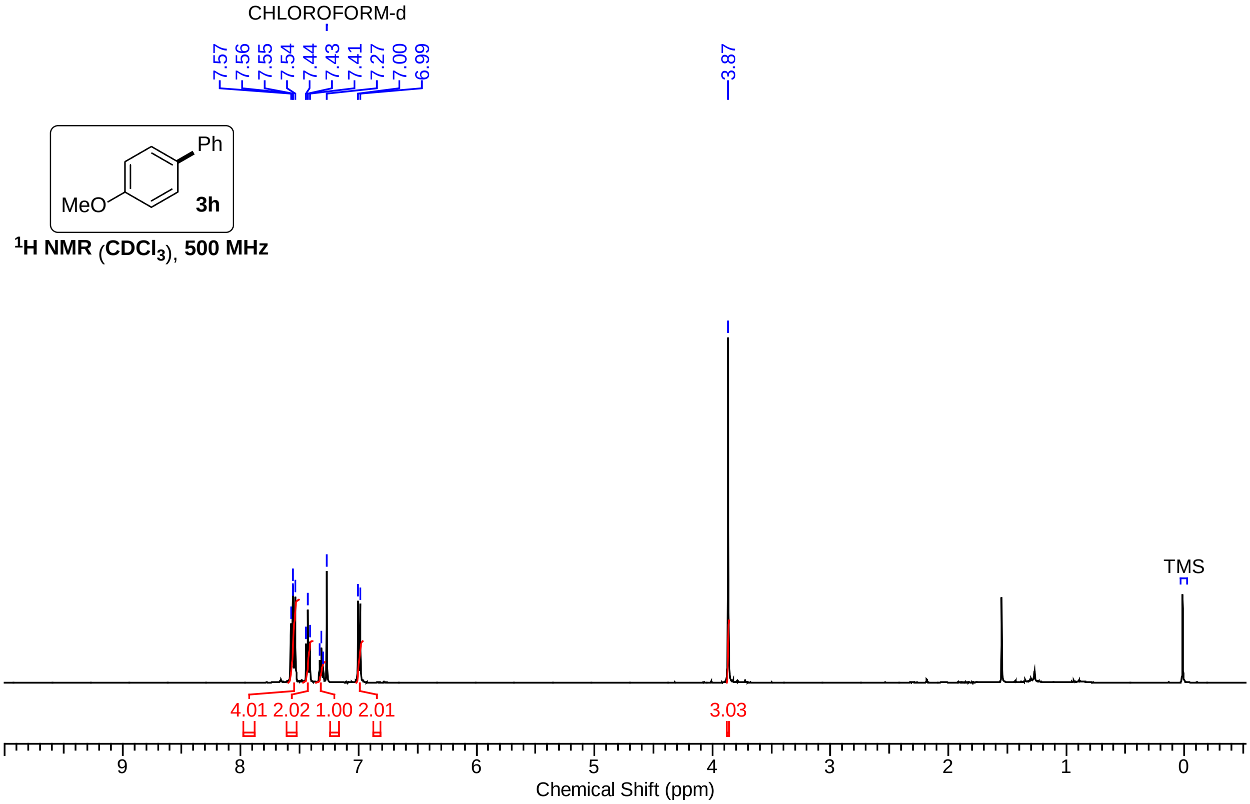
^{13}C NMR (CDCl$_3$), 125 MHz



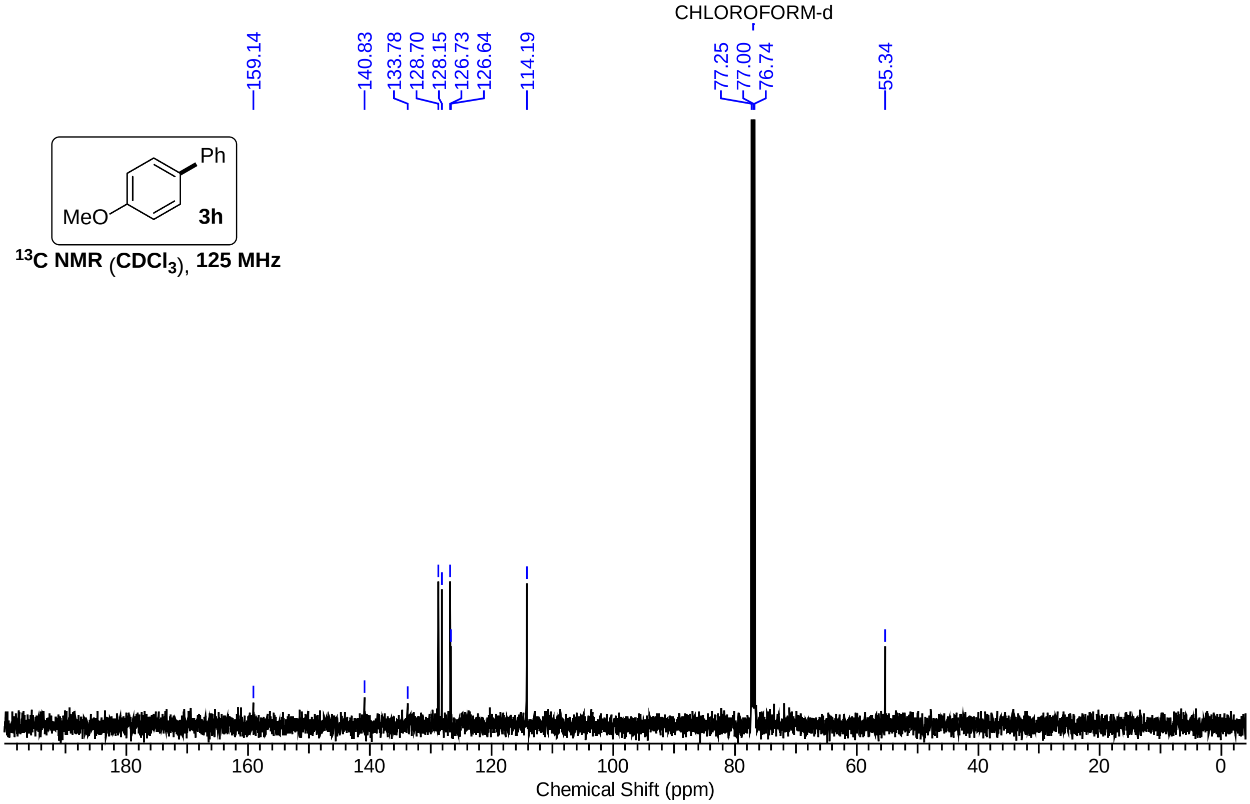
^{1}H NMR ($CDCl_3$), 500 MHz



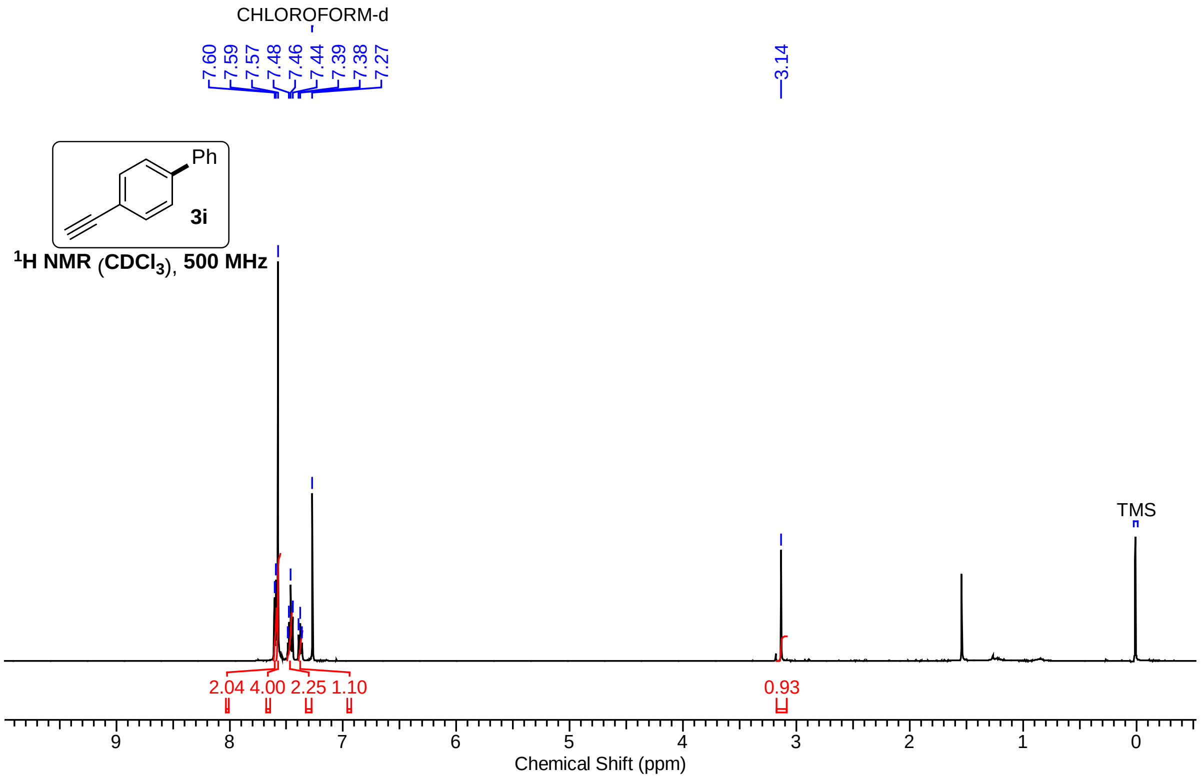
^{13}C NMR ($CDCl_3$), 125 MHz

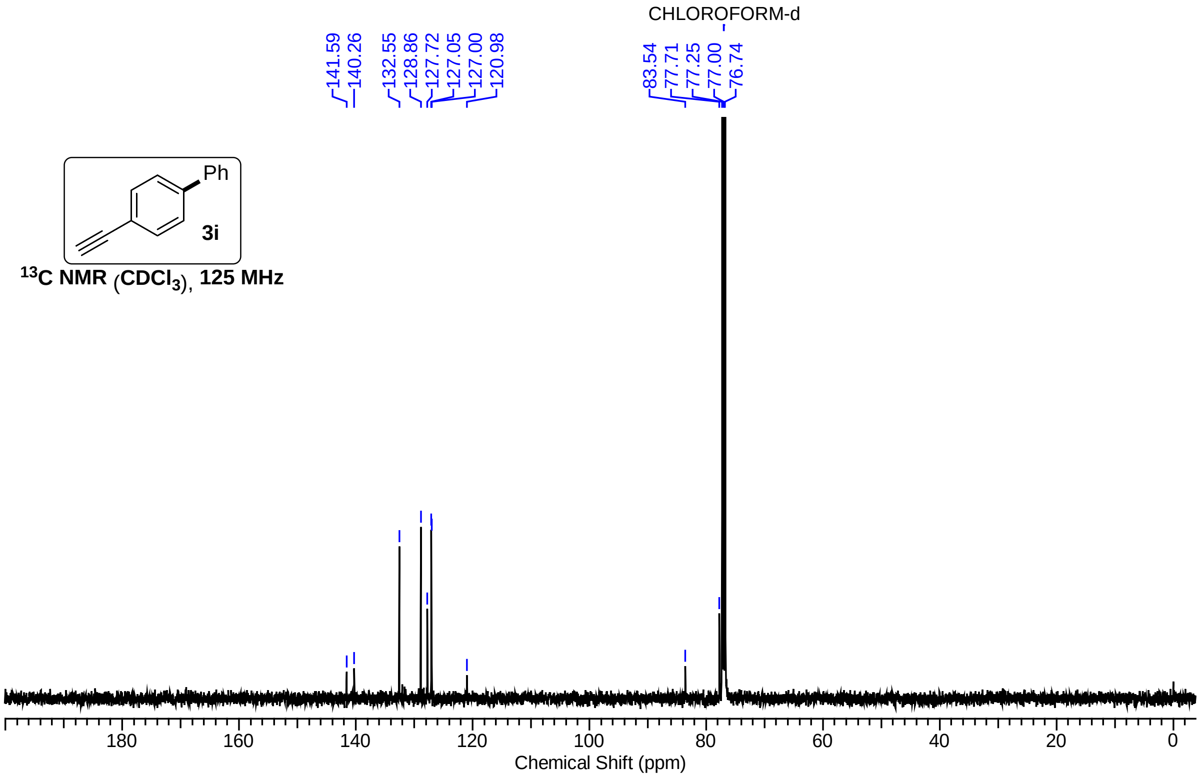


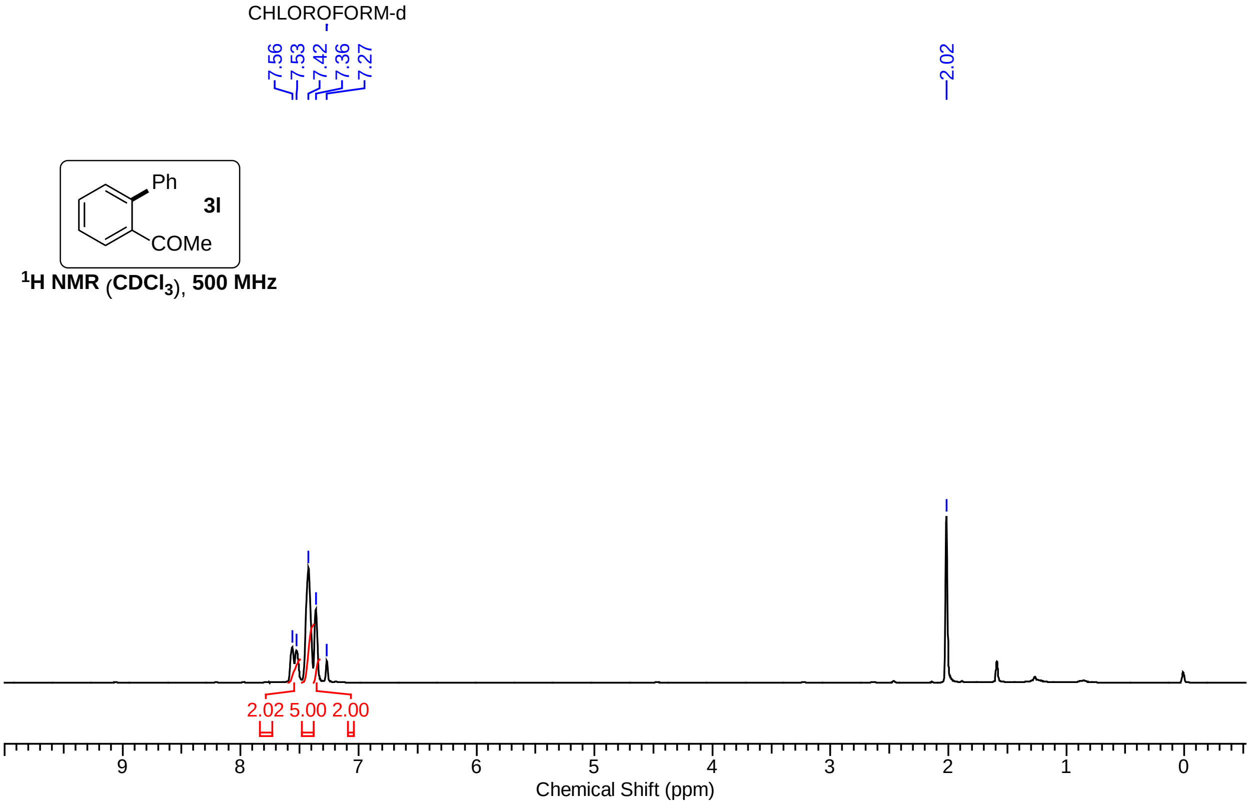
^{1}H NMR (CDCl$_3$), 500 MHz

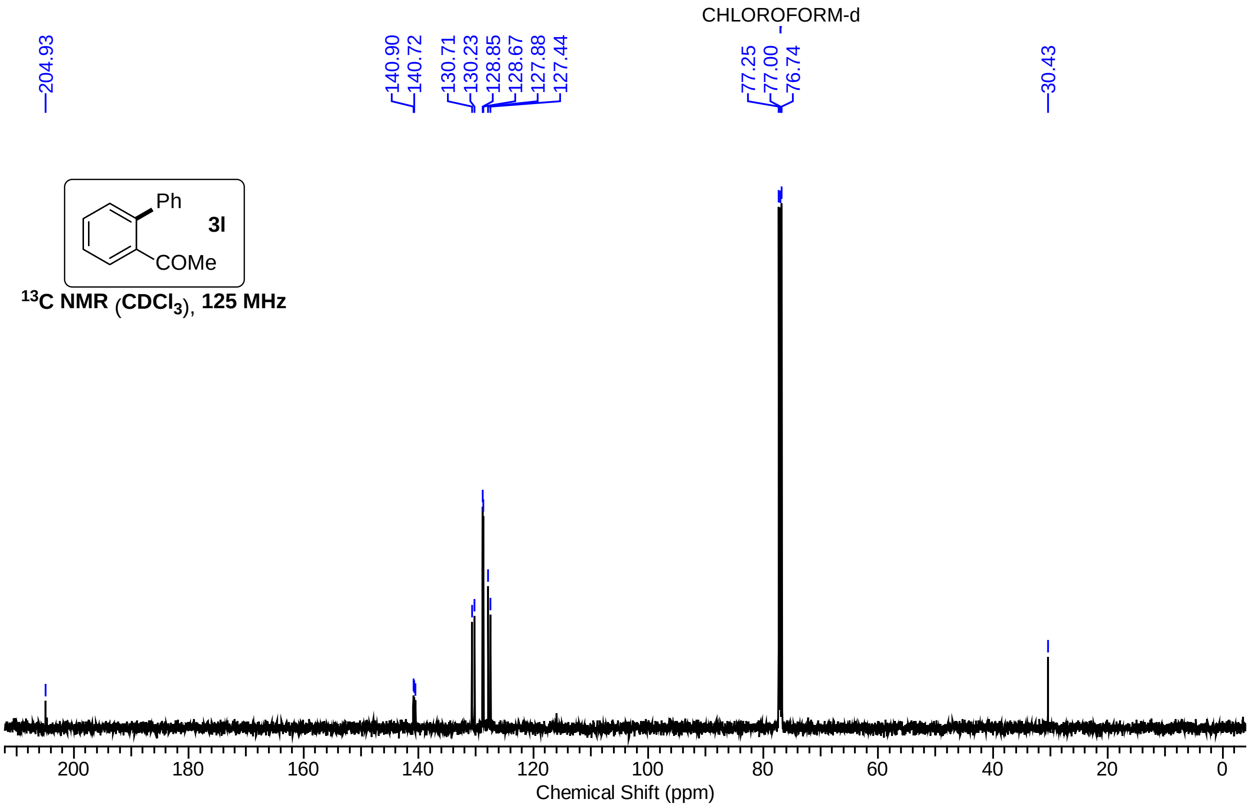


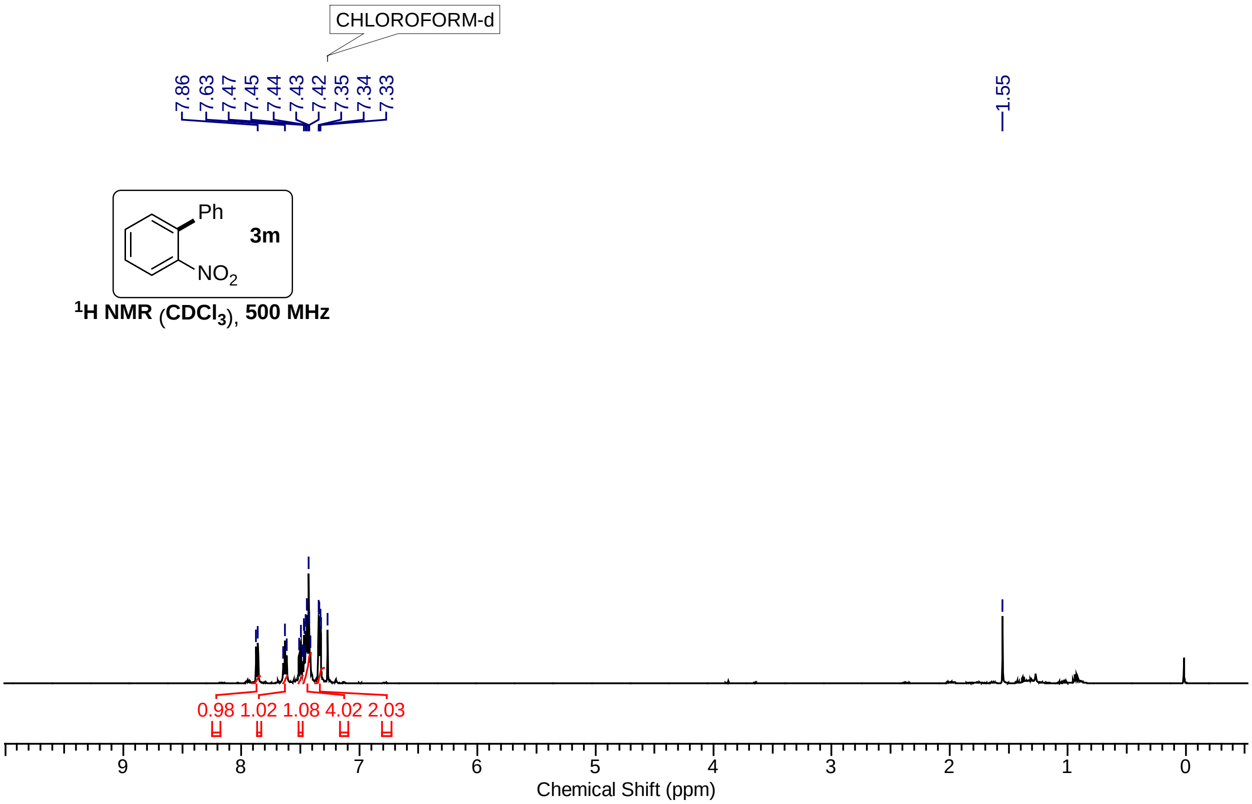
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
7.60
7.59
7.57
7.48
7.46
7.44
7.39
7.38
7.27
3.14
Ph
3i
^{1}H NMR (CDCl$_3$), 500 MHz
TMS
2.04
4.00
2.25
1.10
0.93
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
141.59
140.26
132.55
128.86
127.72
127.05
127.00
120.98
83.54
77.71
77.25
77.00
76.74
Ph
3i
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

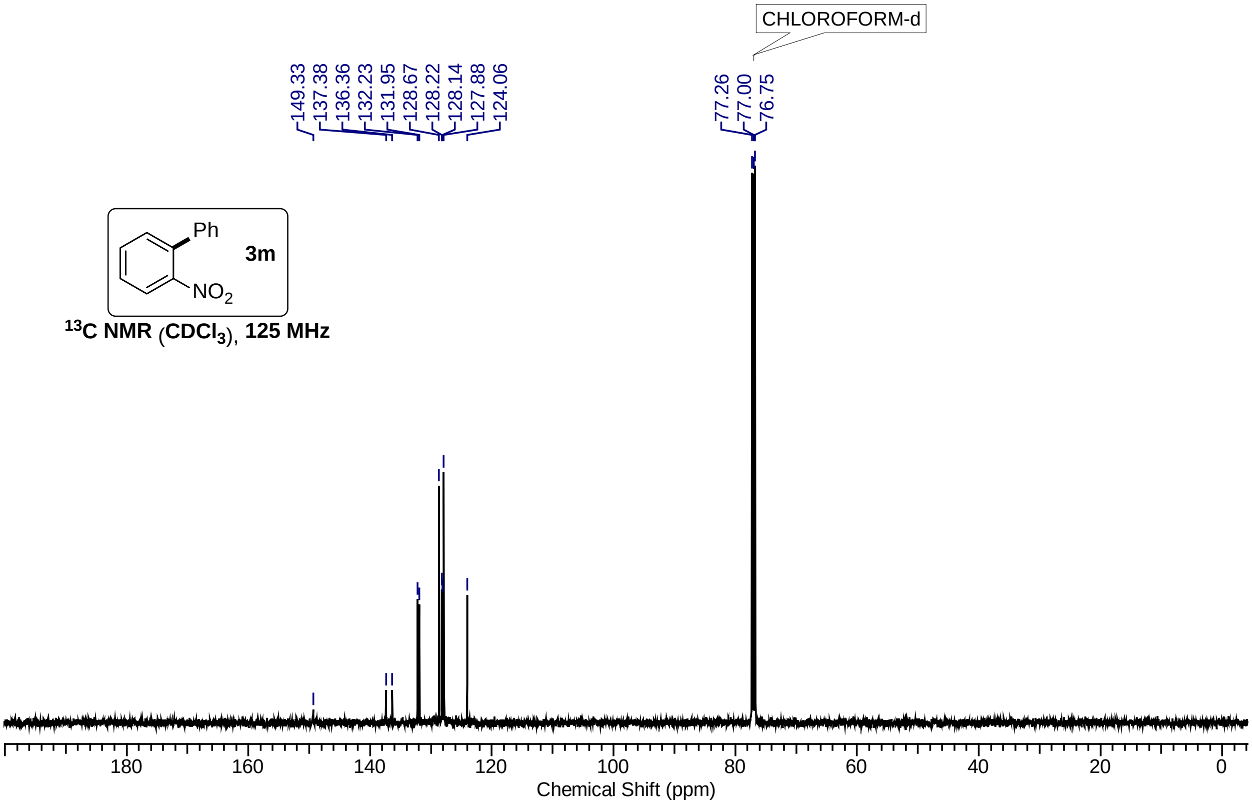

CHLOROFORM-d
7.56
7.53
7.42
7.36
7.27
2.02
Ph
3l
COMe
1H NMR (CDCl3), 500 MHz
2.02
5.00
2.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
204.93
140.90
140.72
130.71
130.23
128.85
128.67
127.88
127.44
77.25
77.00
76.74
30.43
Ph
3l
COMe
13C NMR (CDCl3), 125 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



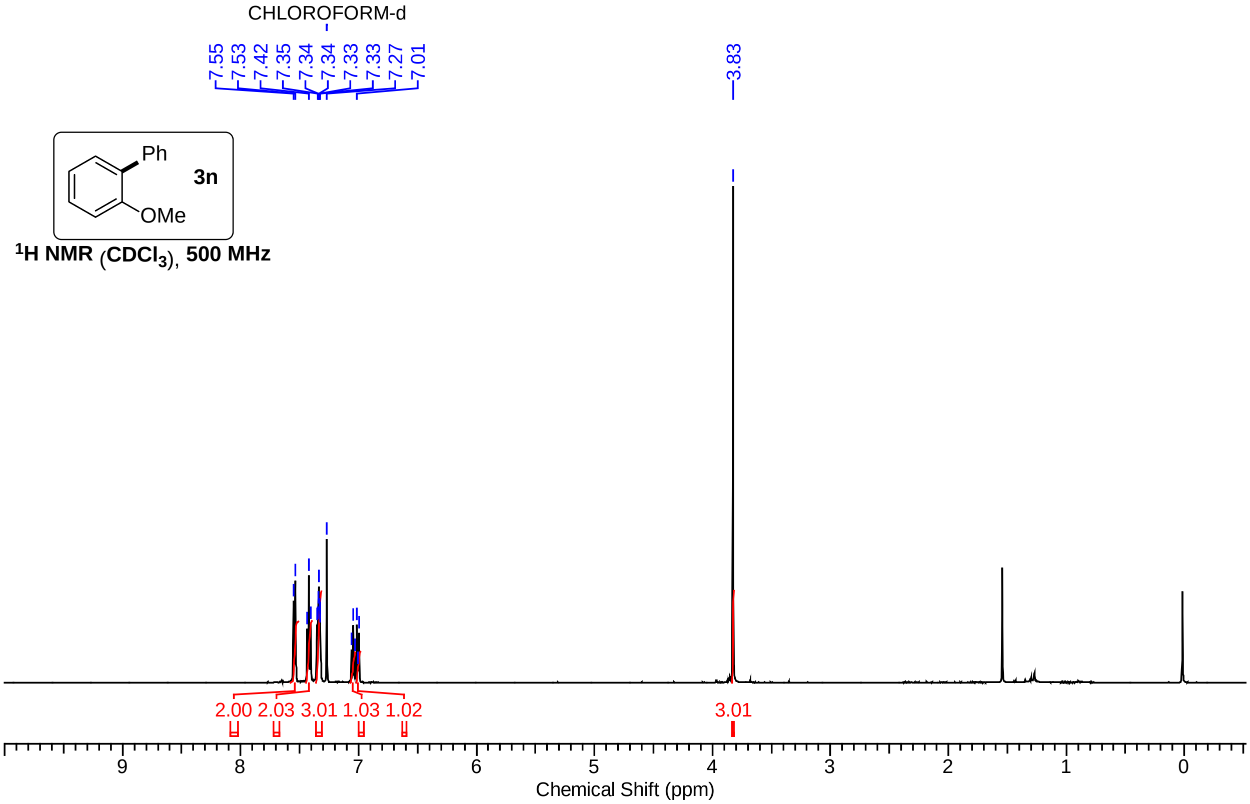
3m

^{1}H NMR ($CDCl_3$), 500 MHz

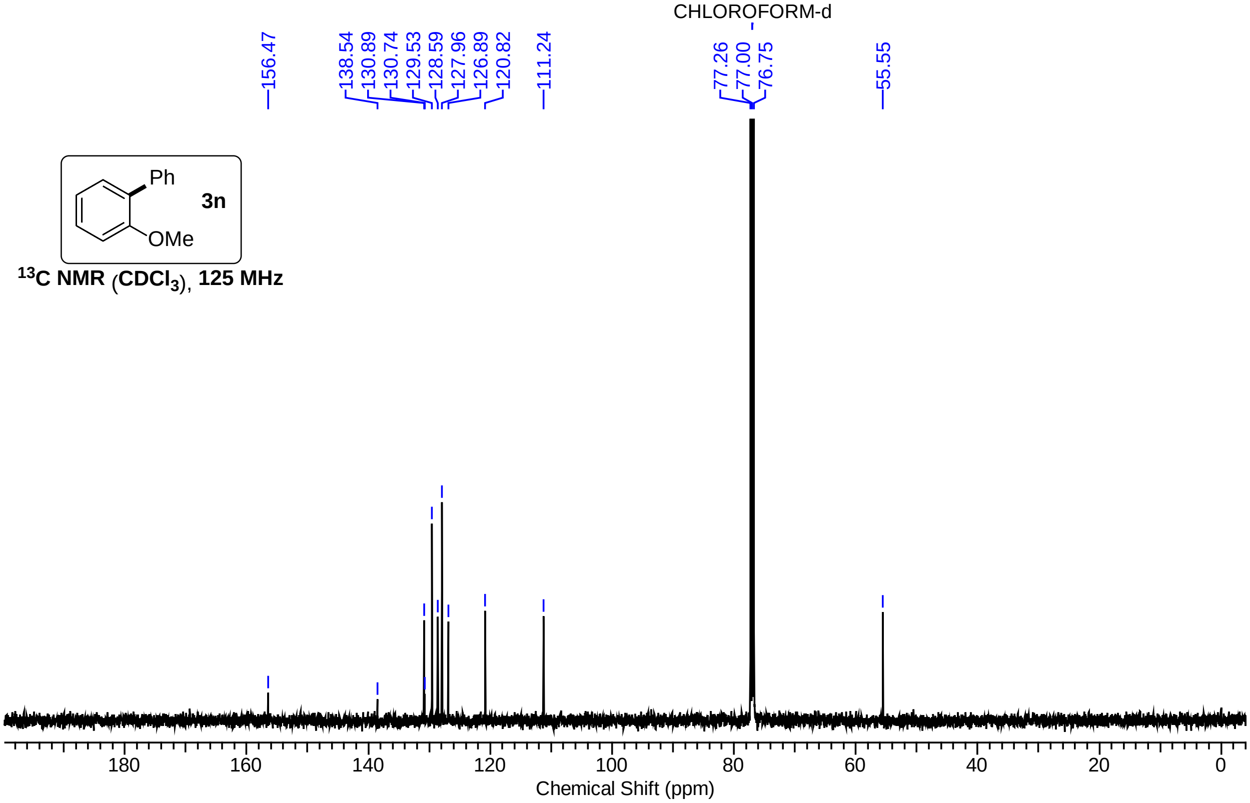


3m

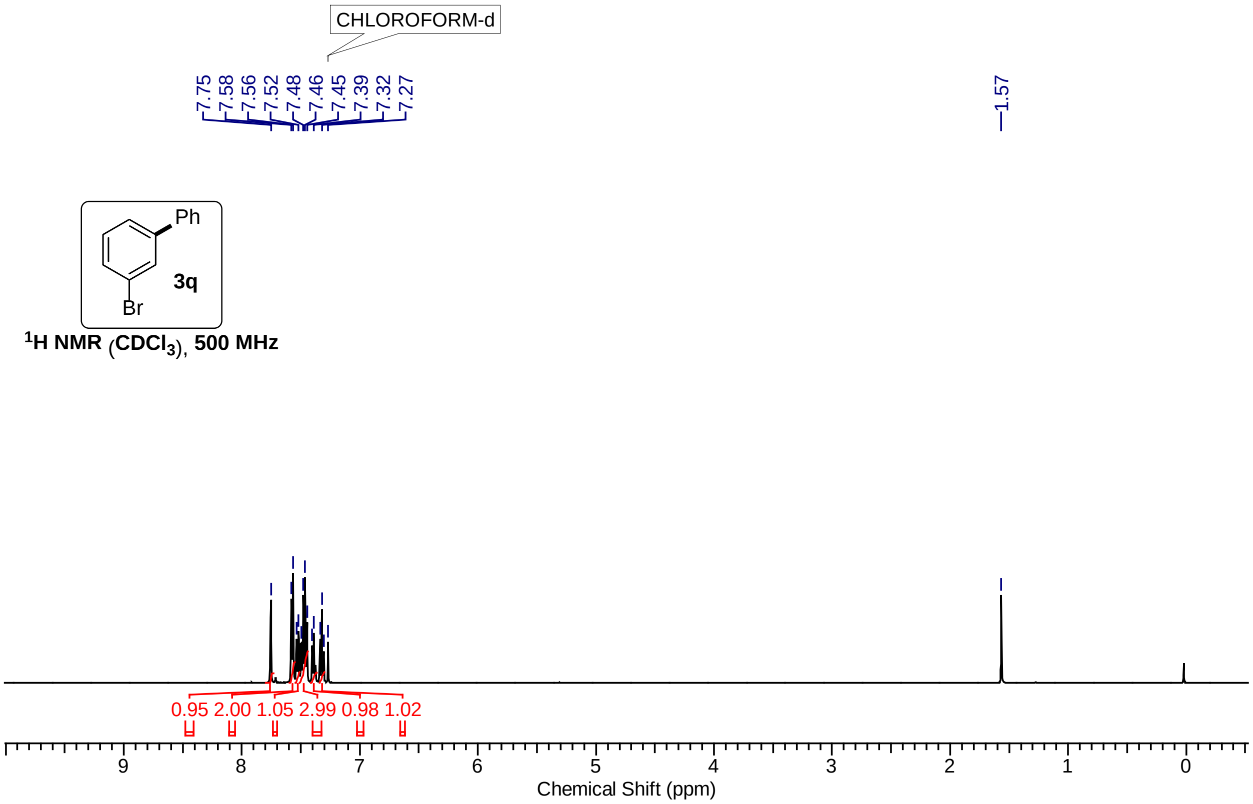
^{13}C NMR ($CDCl_3$), 125 MHz

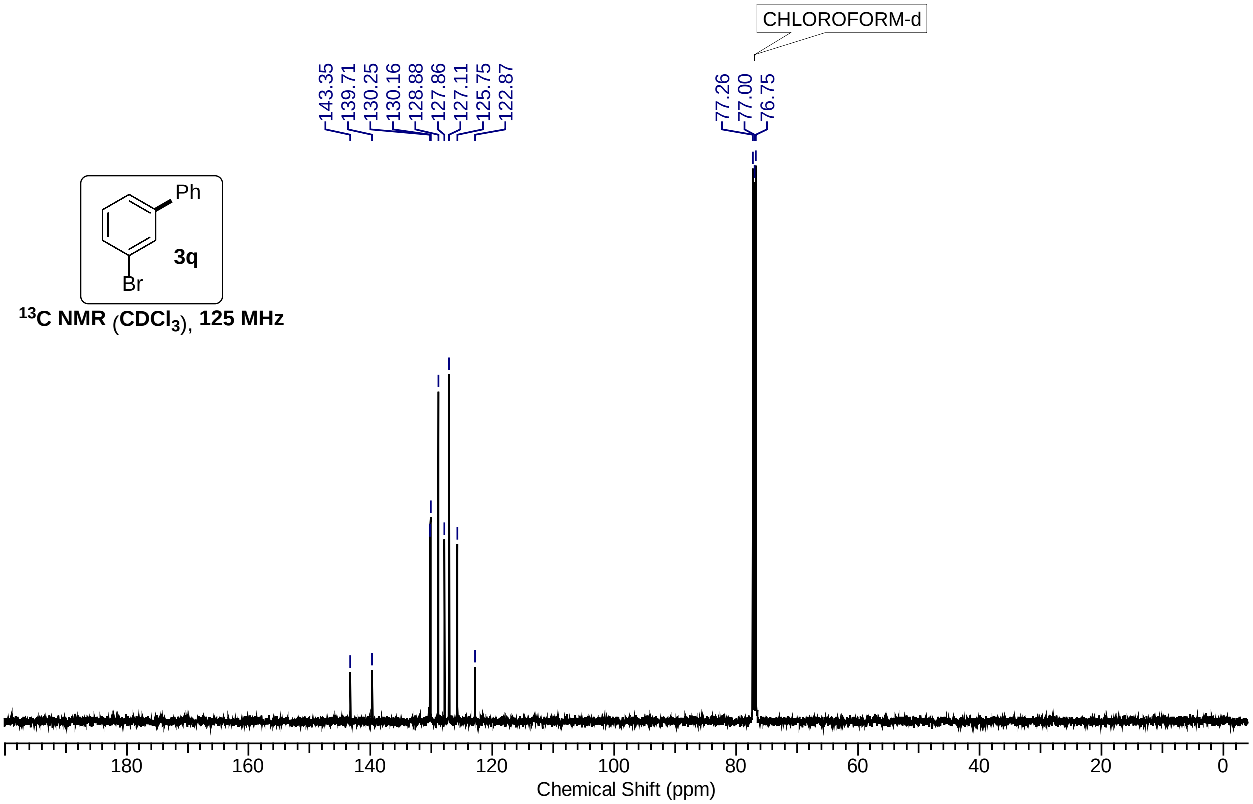


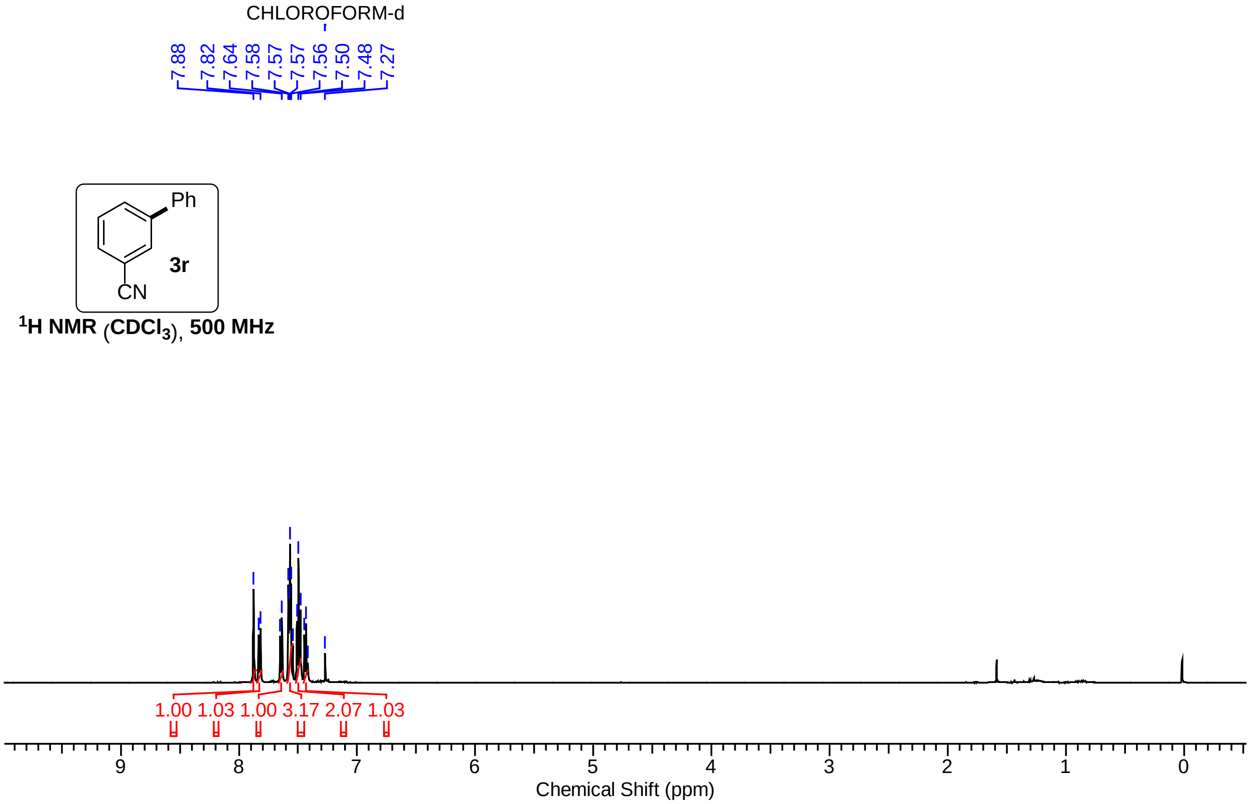
^{1}H NMR (CDCl$_3$), 500 MHz



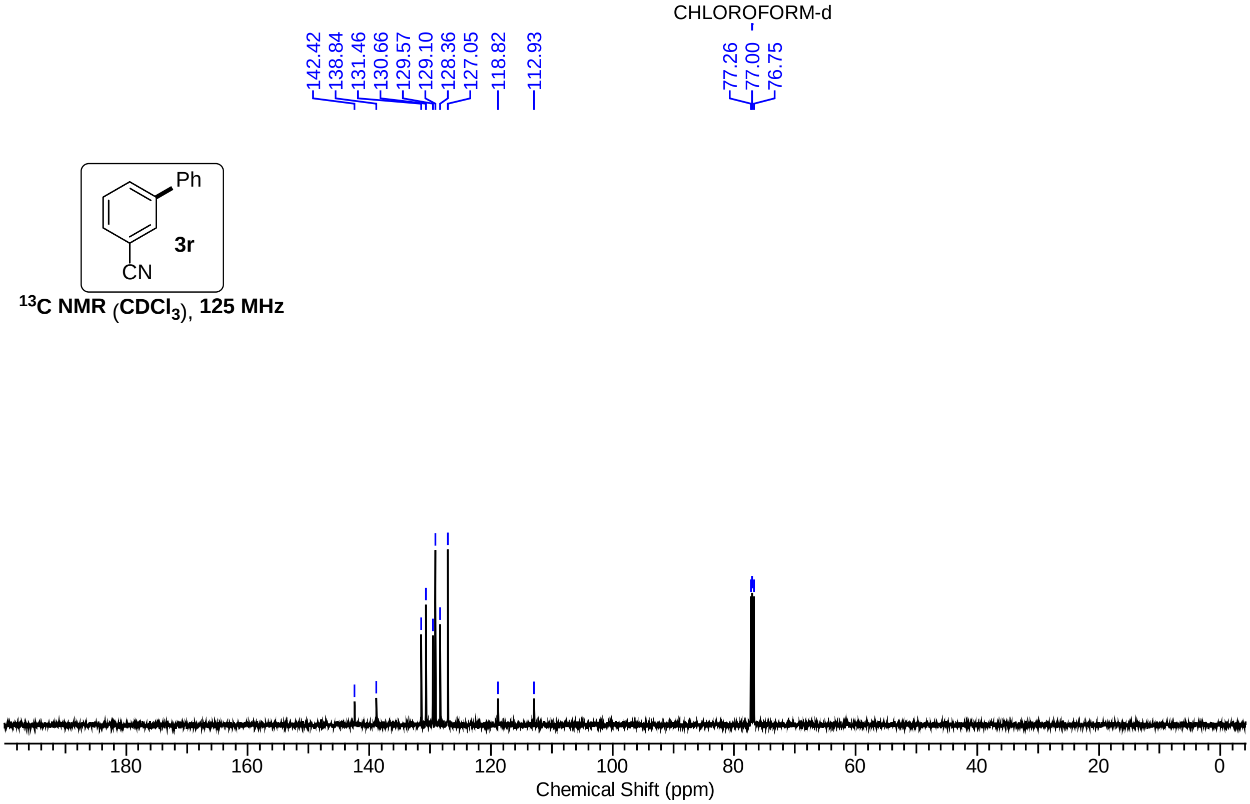
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
7.75
7.58
7.56
7.52
7.48
7.46
7.45
7.39
7.32
7.27
1.57
Ph
3q
Br
^{1}H NMR (CDCl$_3$), 500 MHz
0.95
2.00
1.05
2.99
0.98
1.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

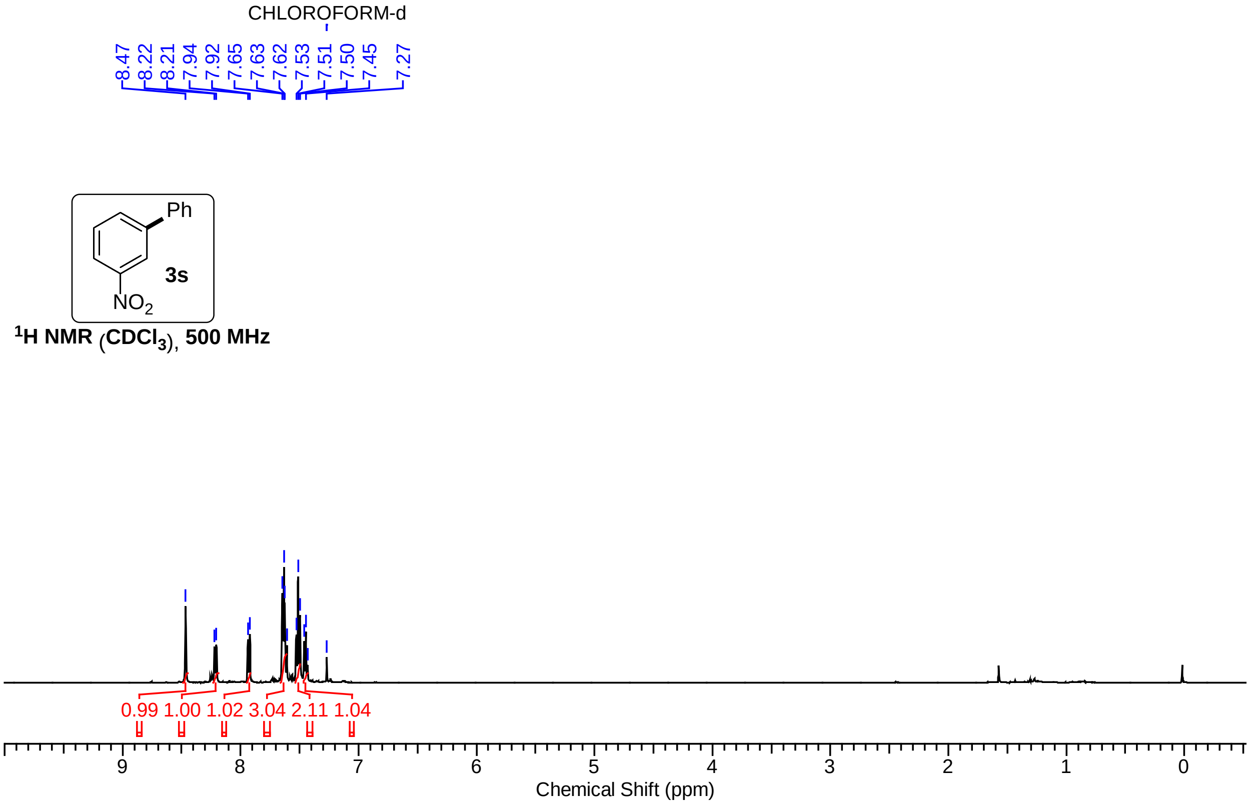

CHLOROFORM-d
143.35
139.71
130.25
130.16
128.88
127.86
127.11
125.75
122.87
77.26
77.00
76.75
Ph
3q
Br
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



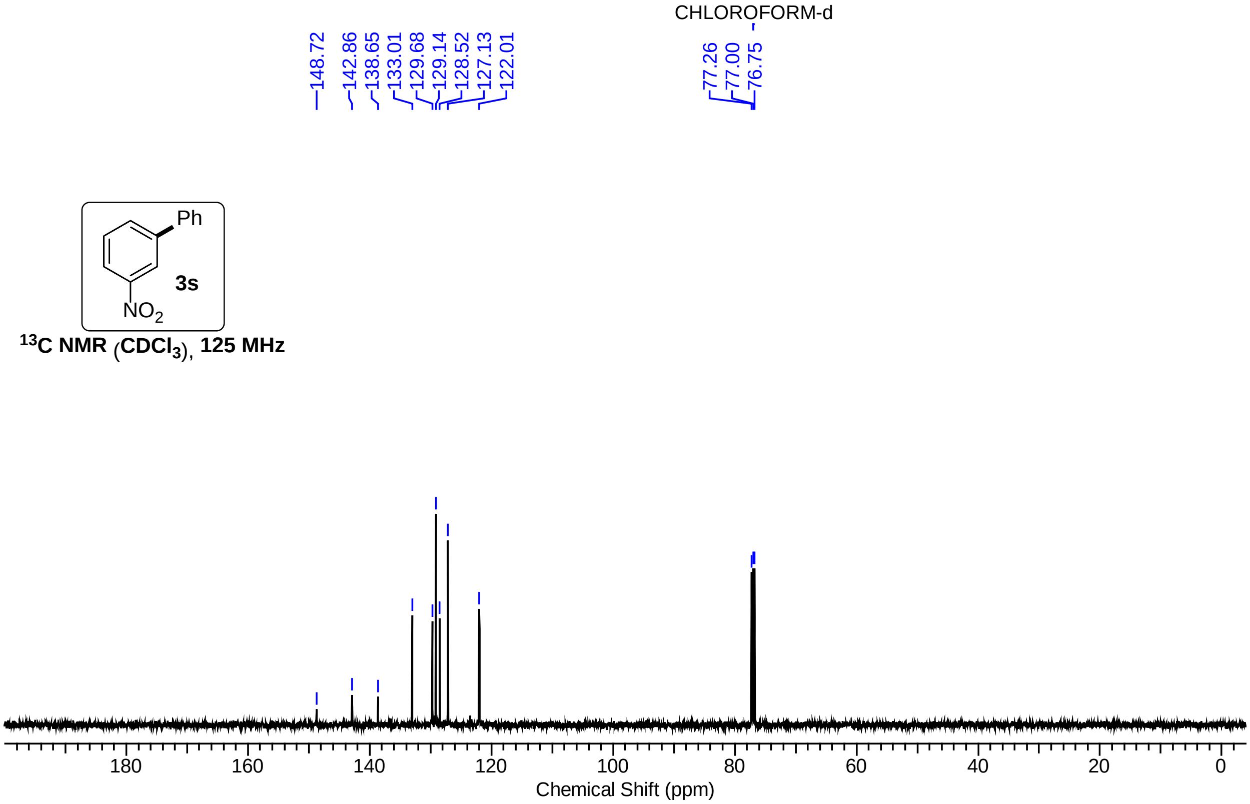
^{1}H NMR (CDCl$_3$), 500 MHz



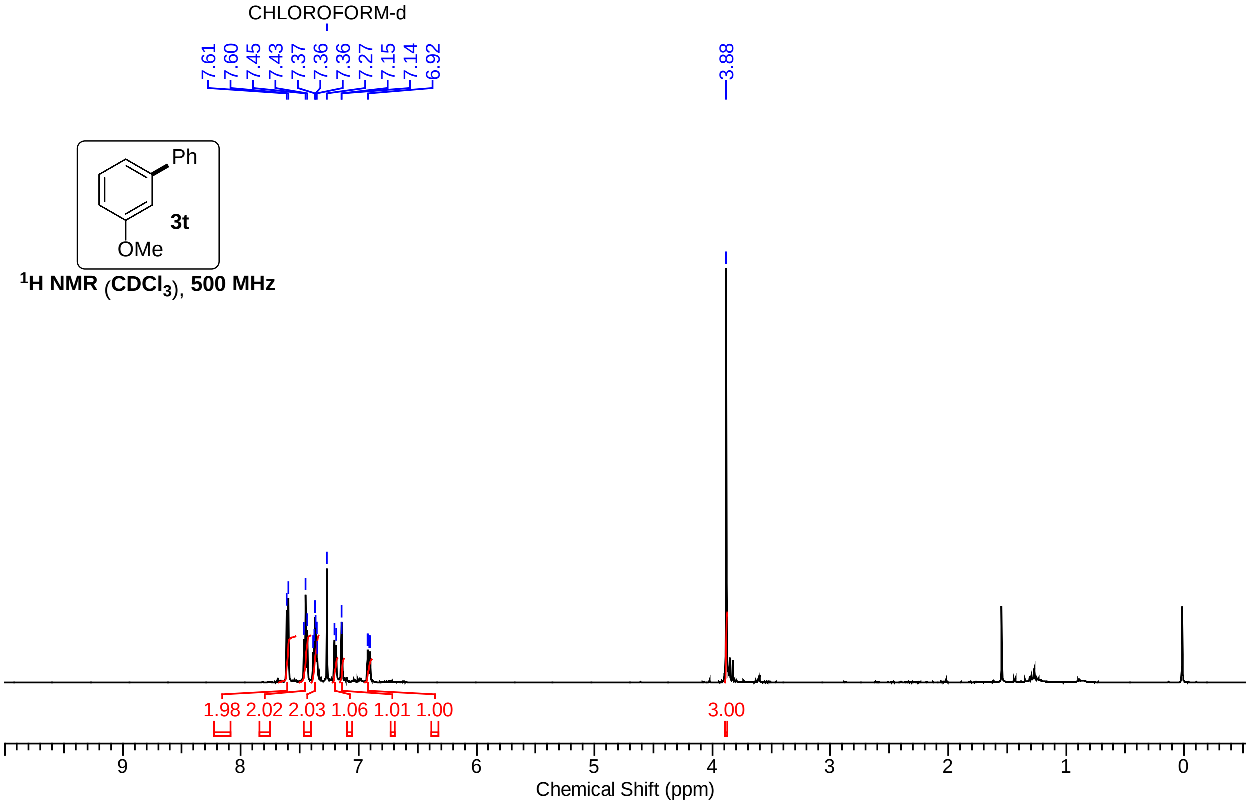
^{13}C NMR (CDCl$_3$), 125 MHz



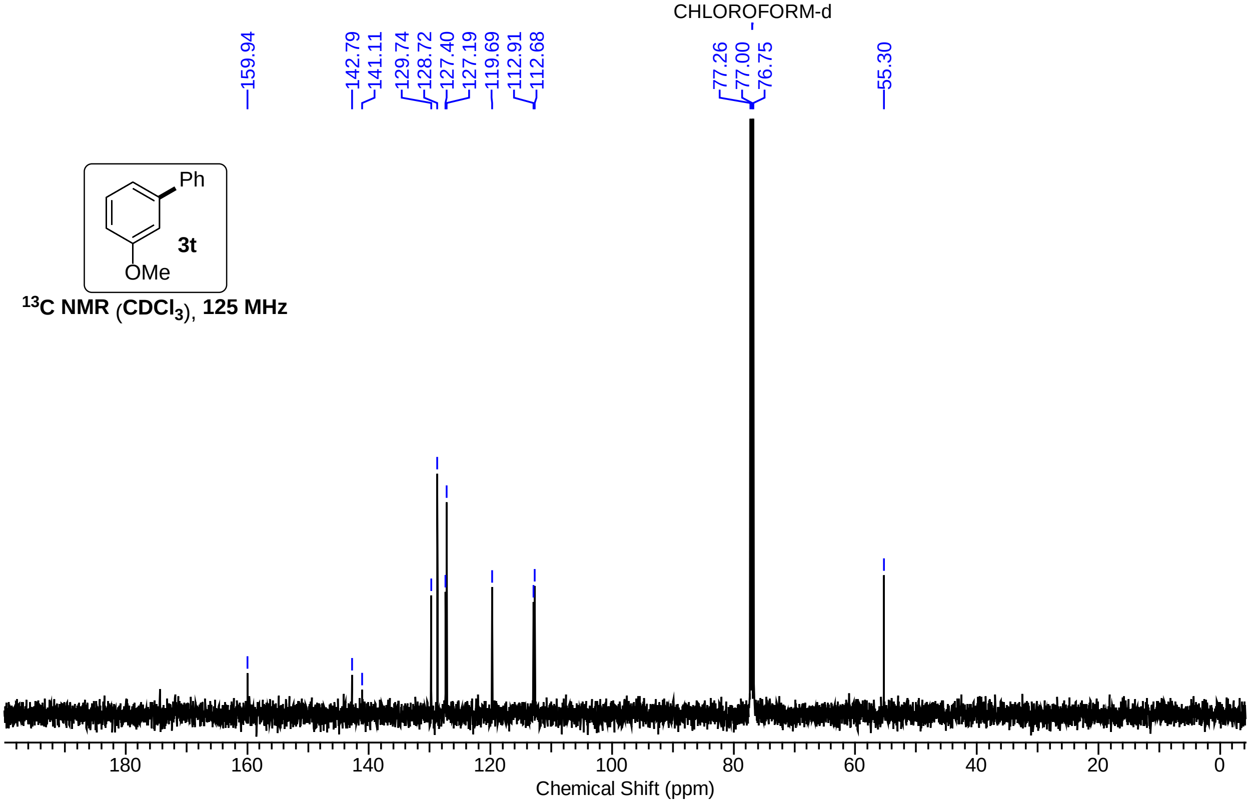
^{1}H NMR (CDCl$_3$), 500 MHz



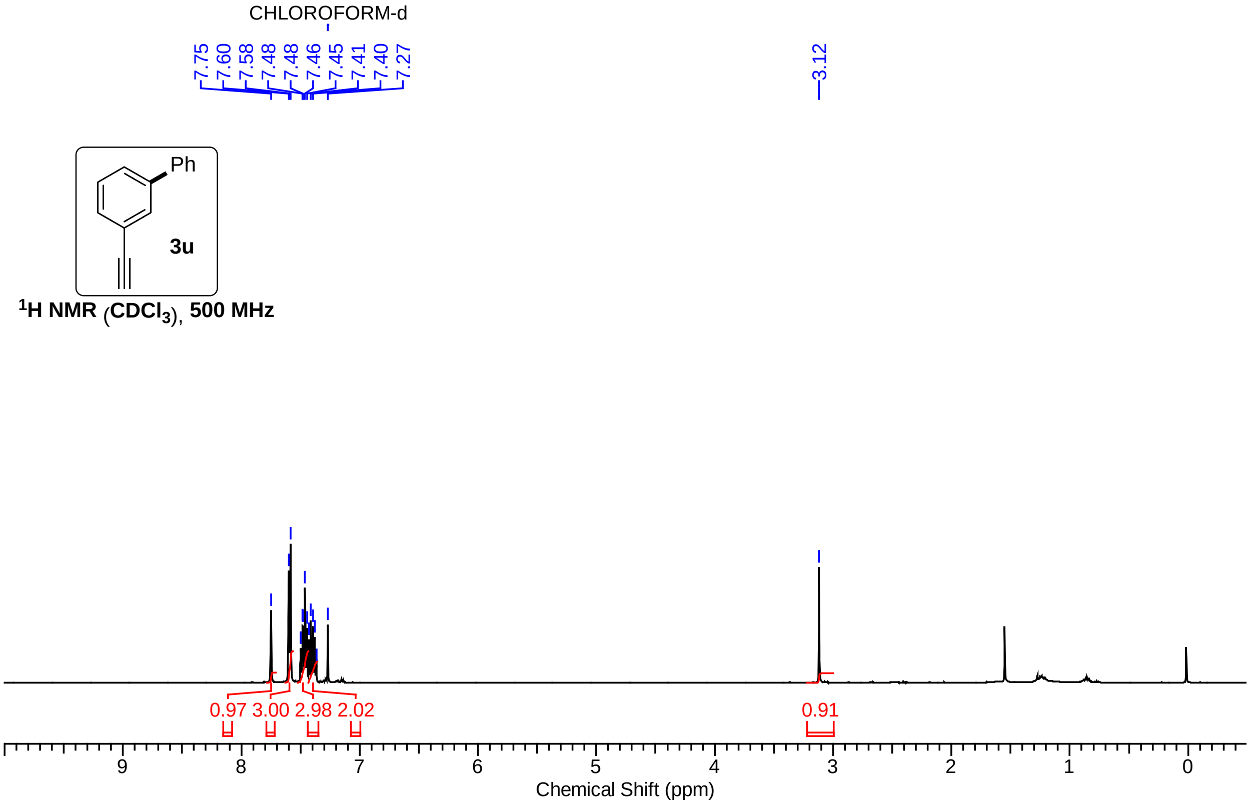
^{13}C NMR (CDCl$_3$), 125 MHz



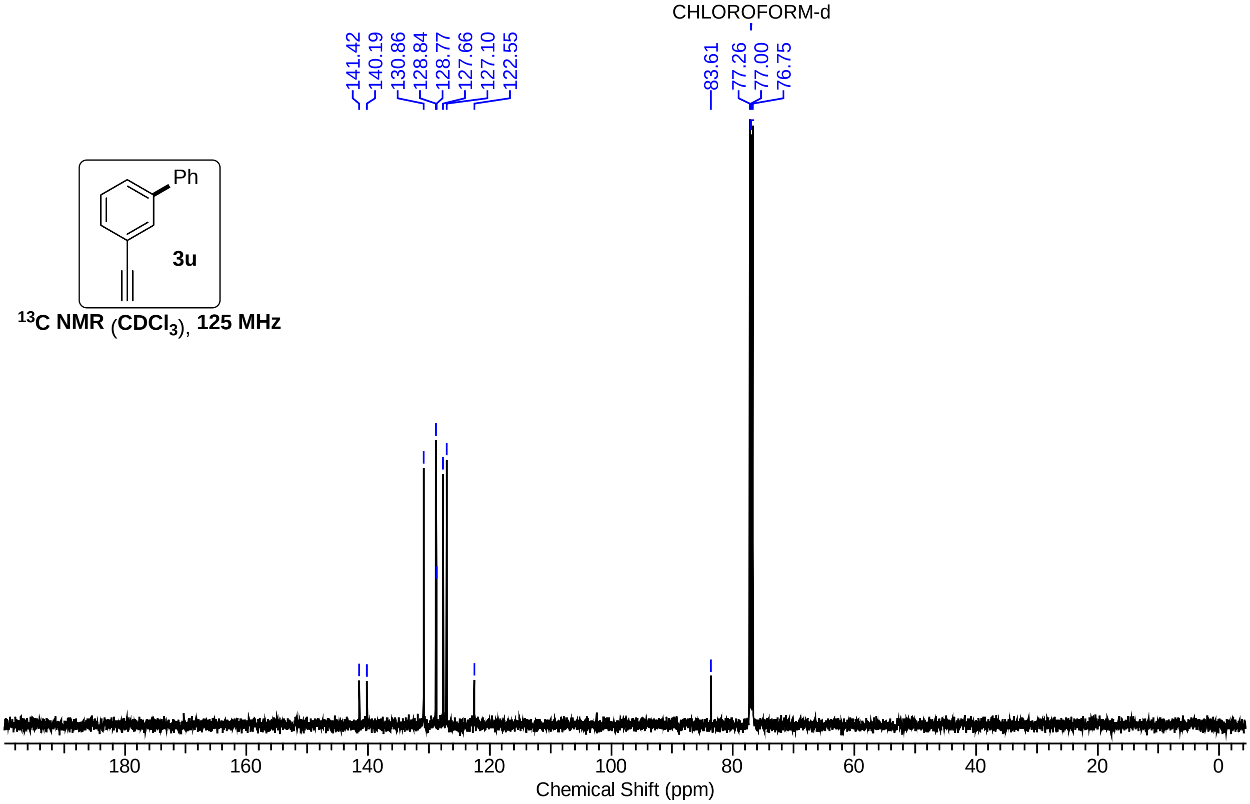
^{1}H NMR (CDCl$_3$), 500 MHz



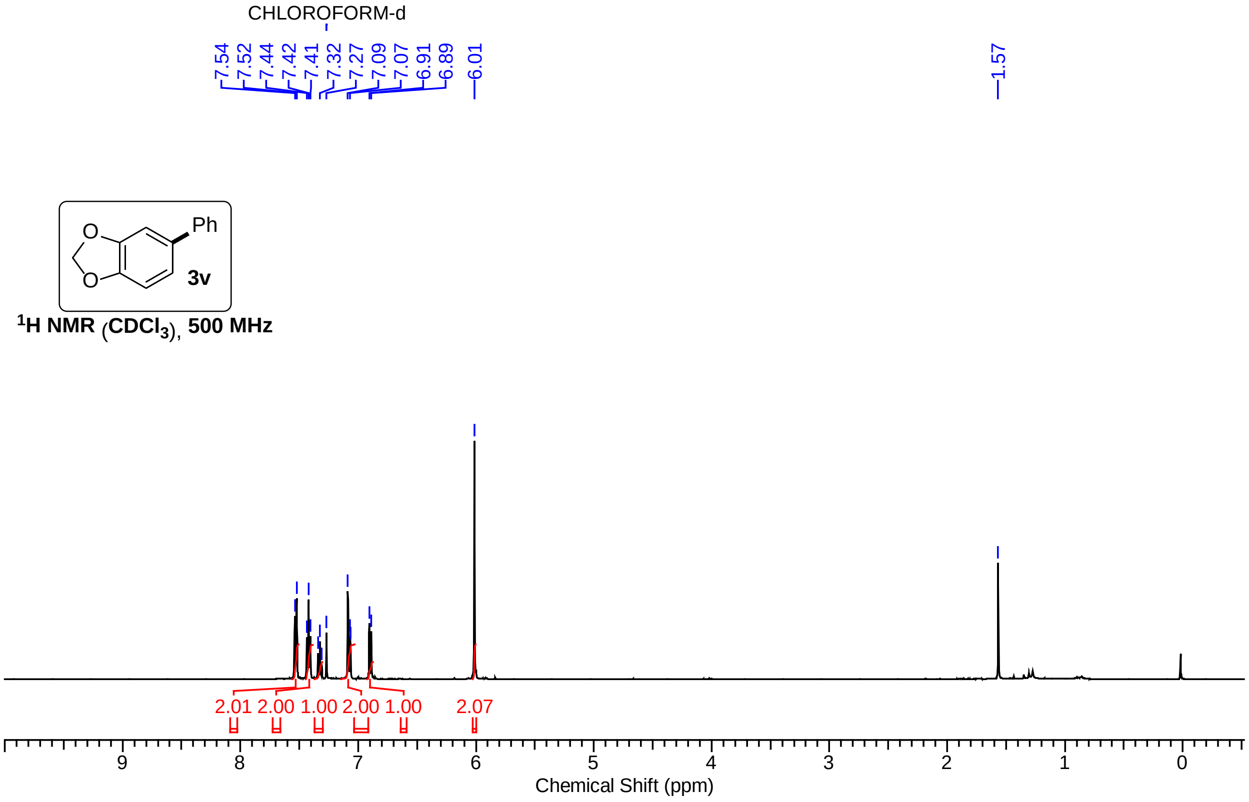
^{13}C NMR (CDCl$_3$), 125 MHz



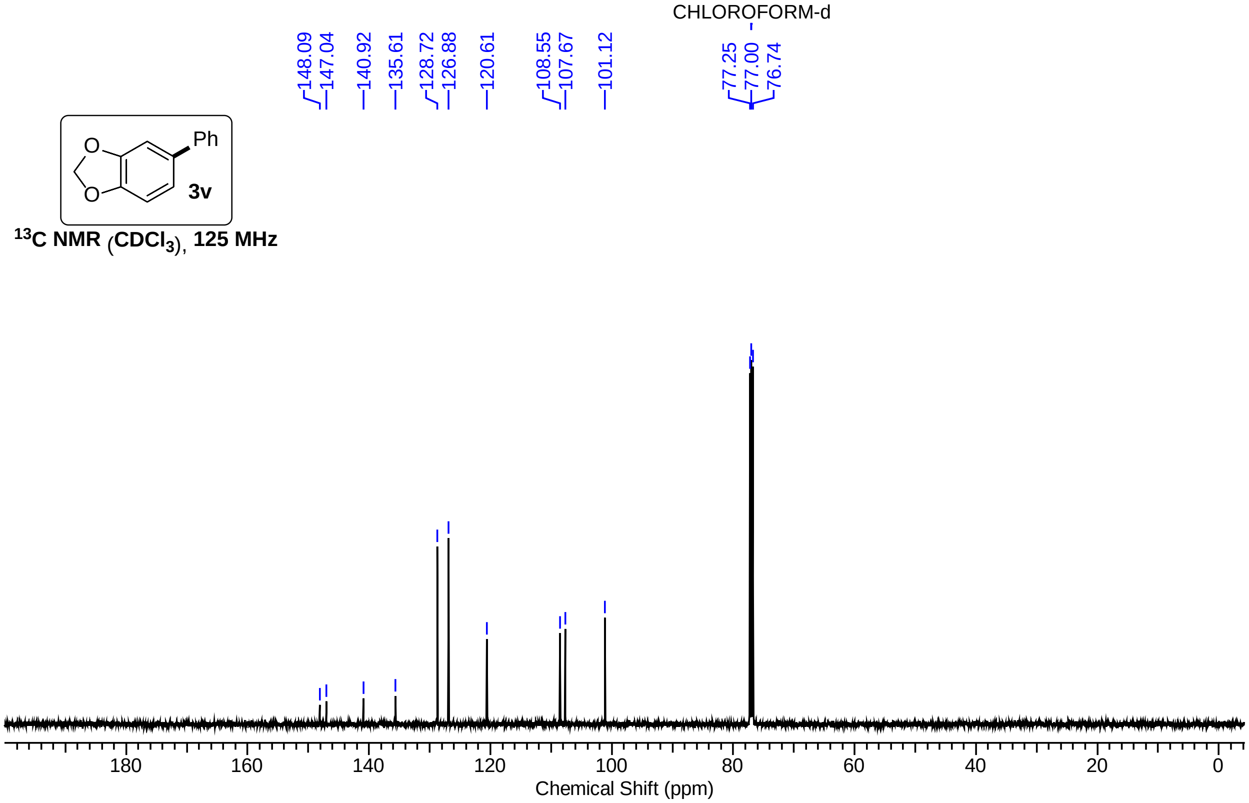
^{1}H NMR (CDCl$_3$), 500 MHz



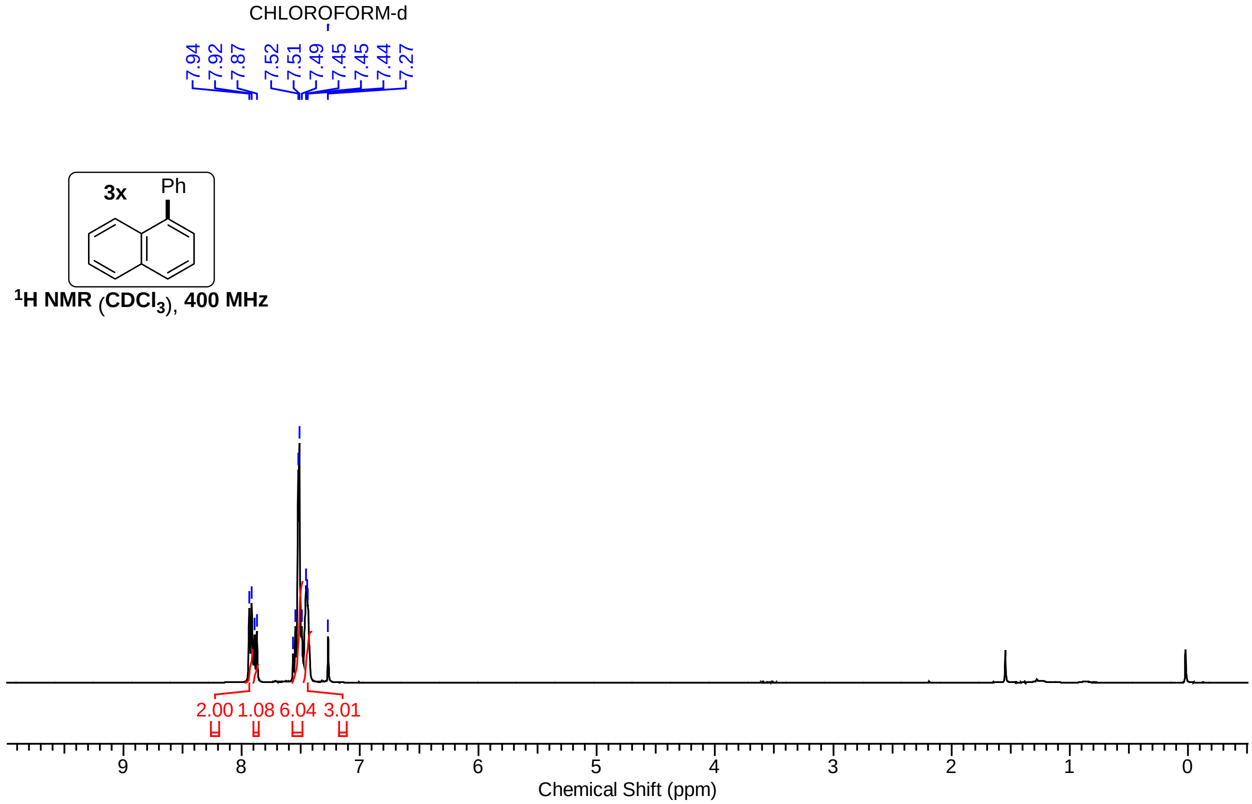
^{13}C NMR (CDCl$_3$), 125 MHz



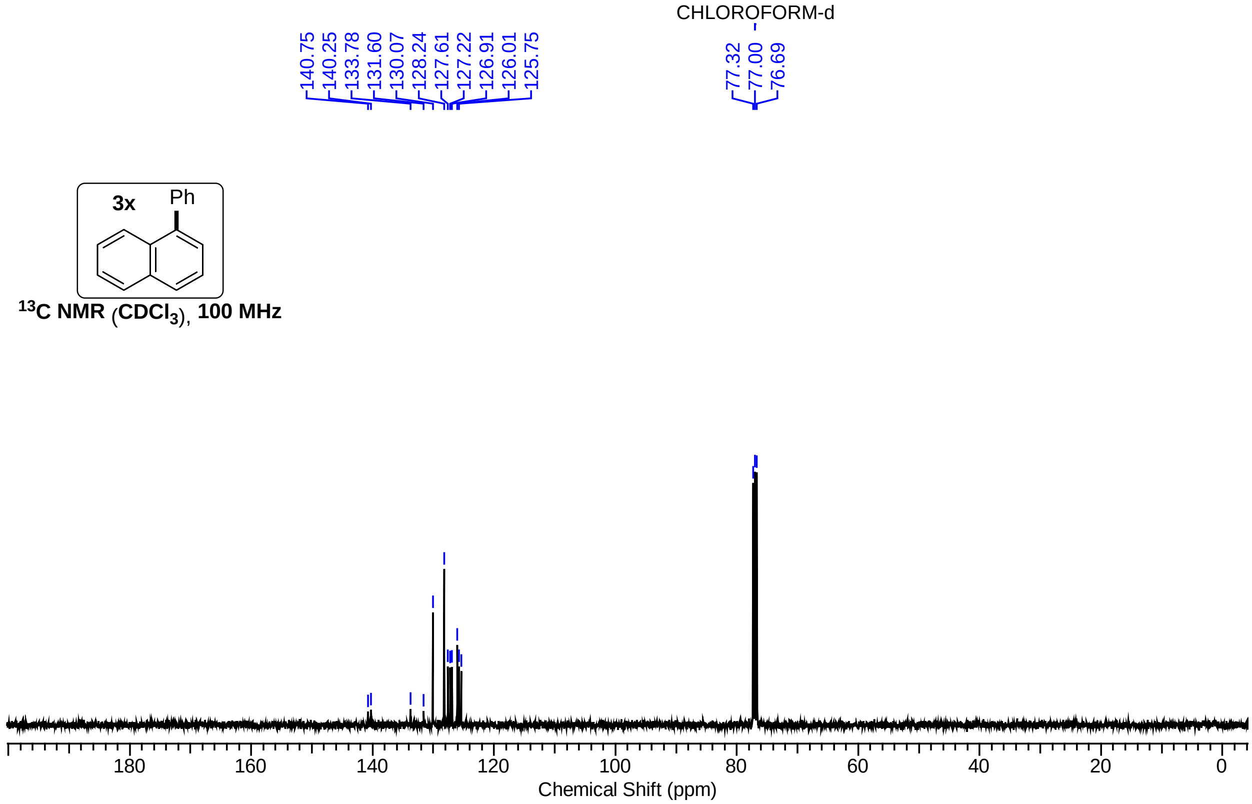
^{1}H NMR (CDCl$_3$), 500 MHz



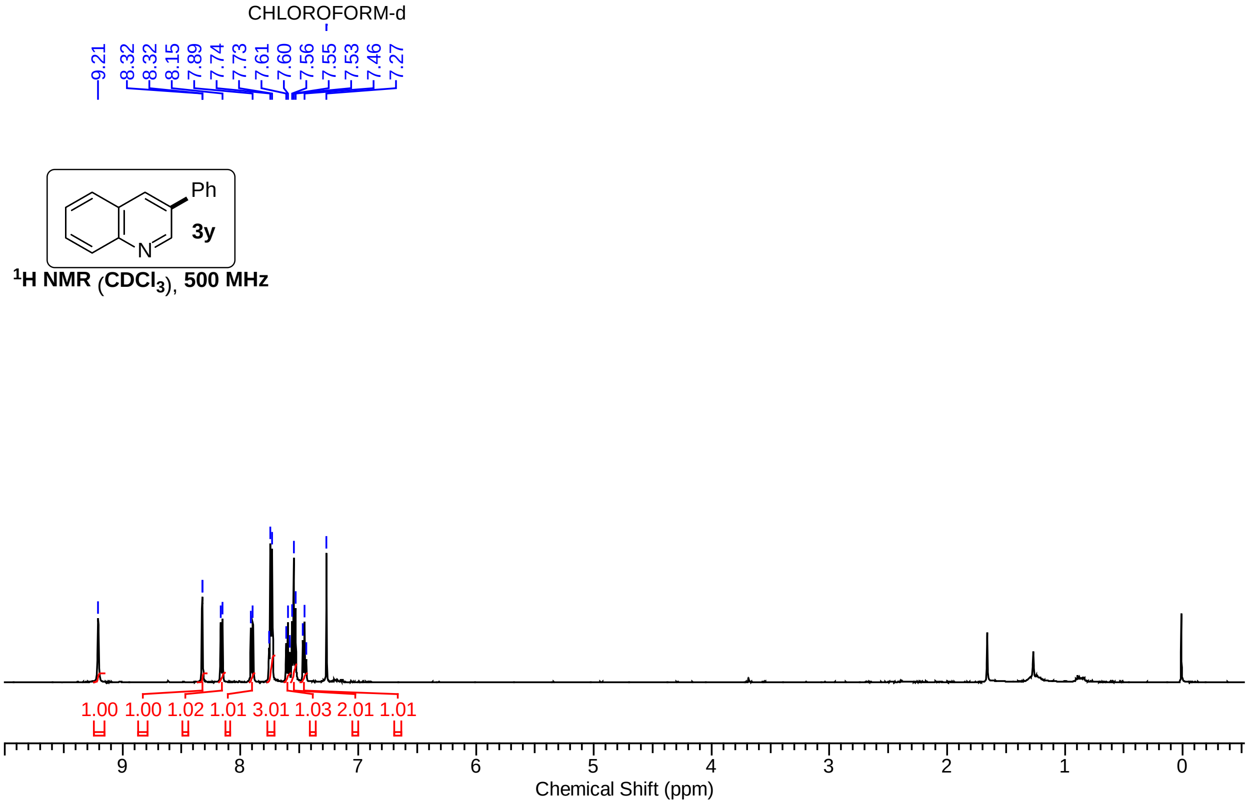
^{13}C NMR (CDCl$_3$), 125 MHz



^{1}H NMR (CDCl$_3$), 400 MHz

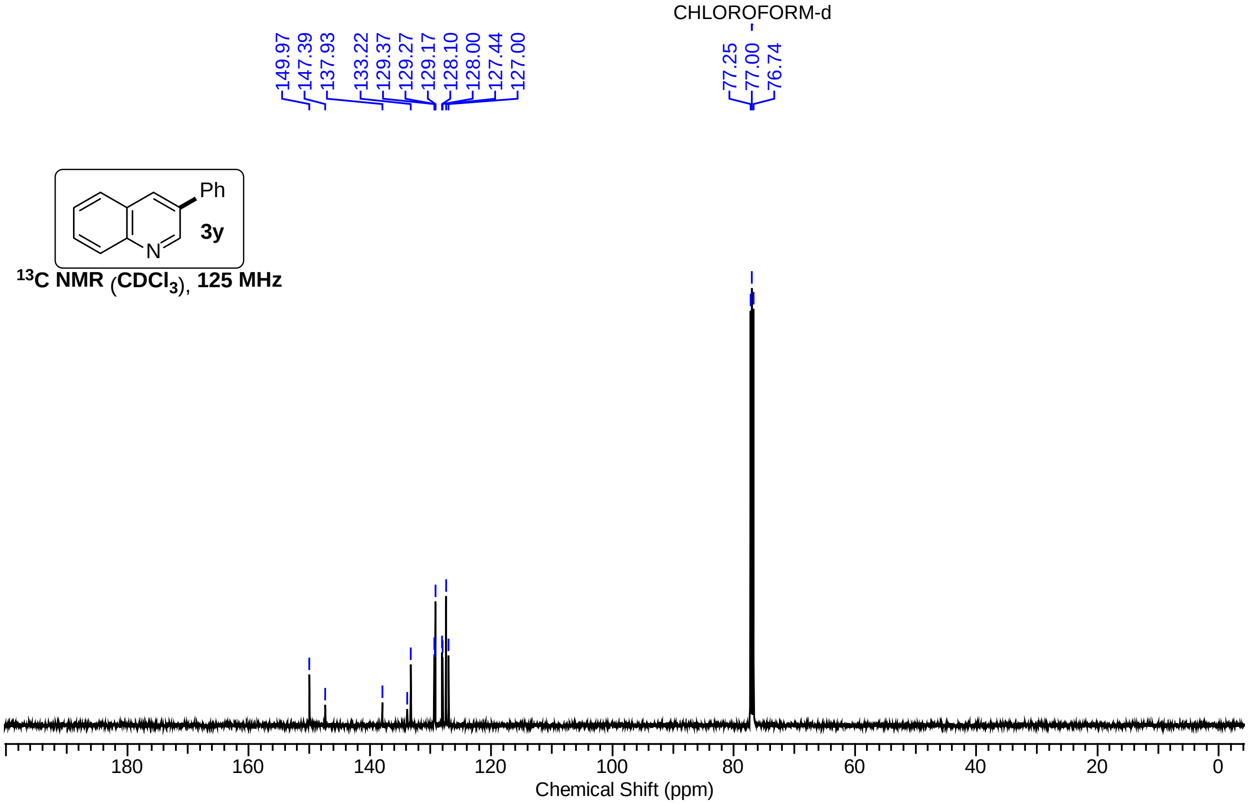


^{13}C NMR (CDCl$_3$), 100 MHz



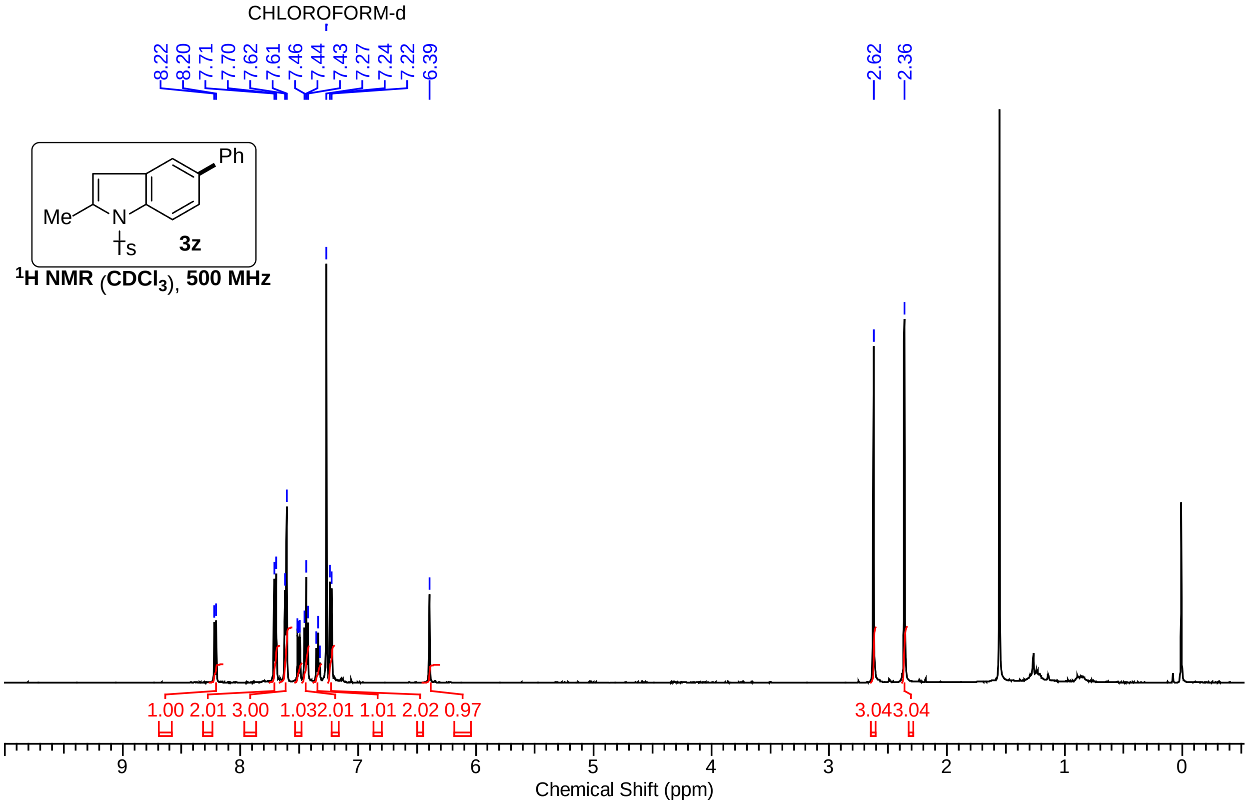
3y

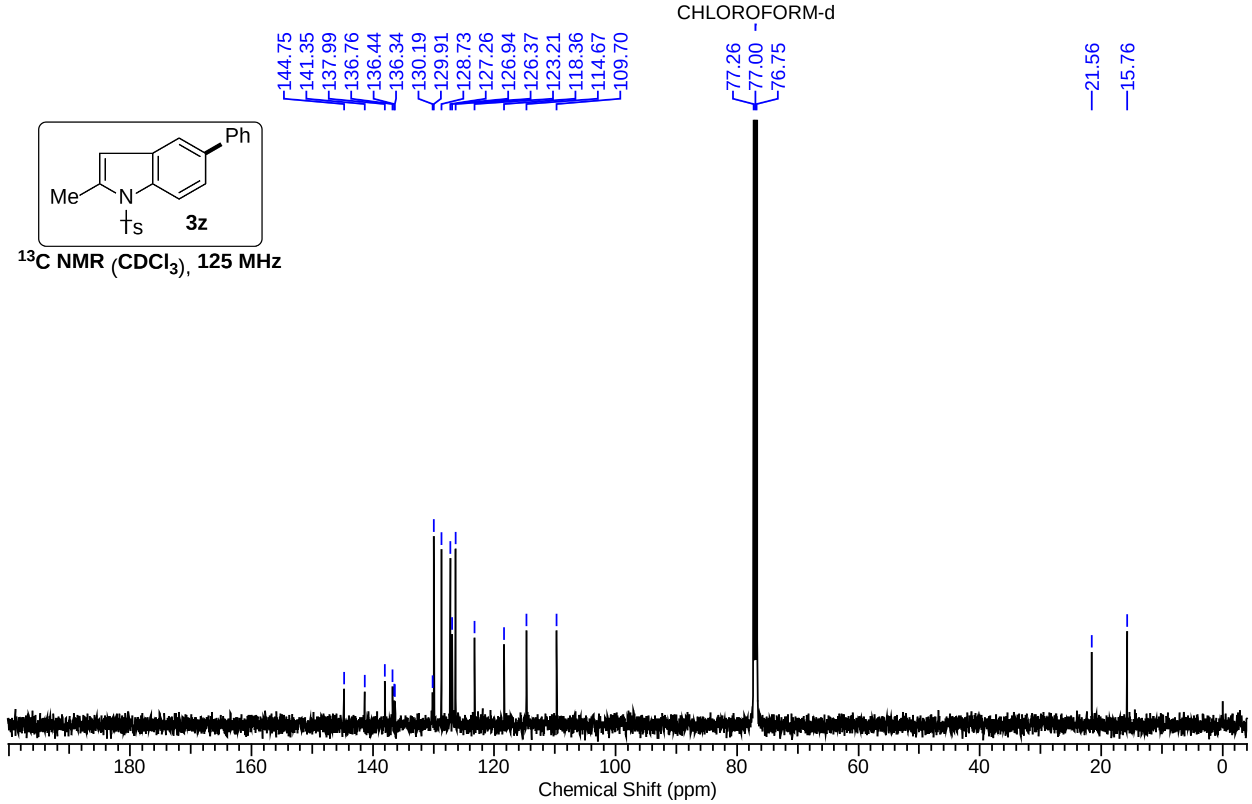
^{1}H NMR (CDCl$_3$), 500 MHz

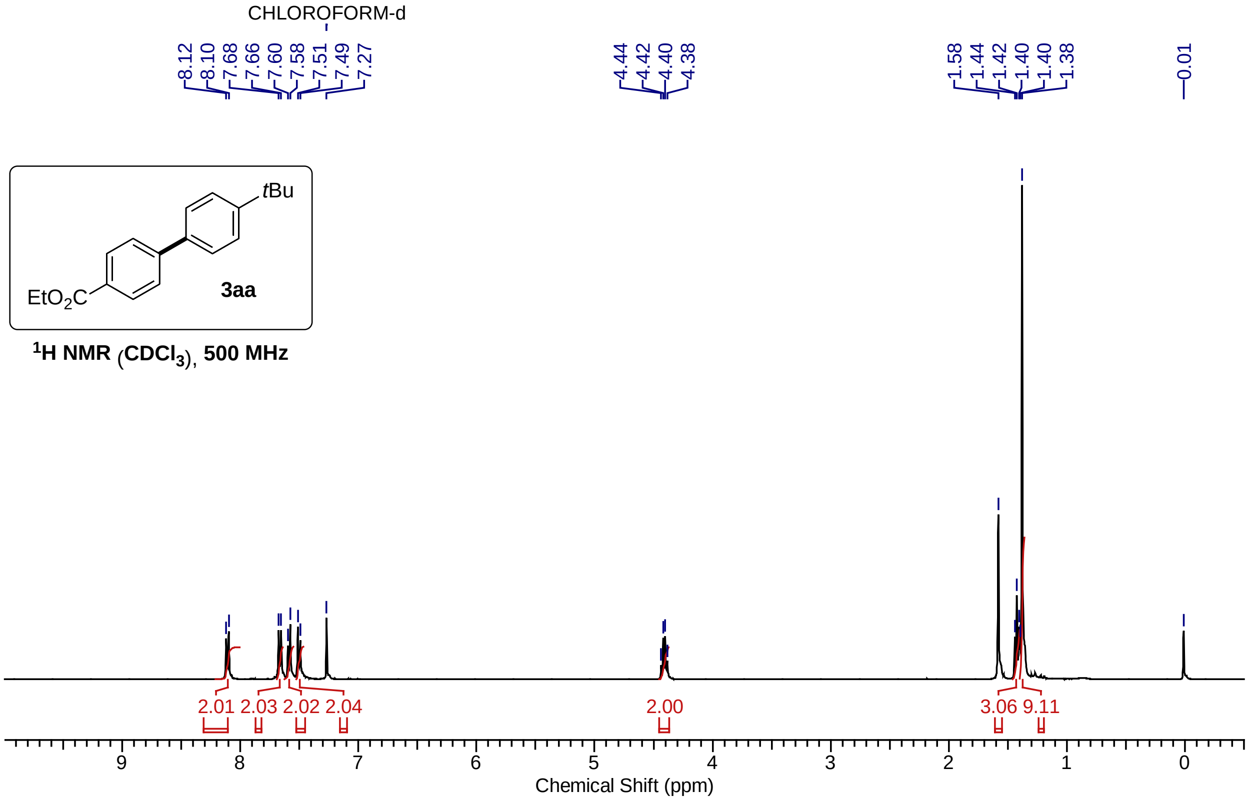


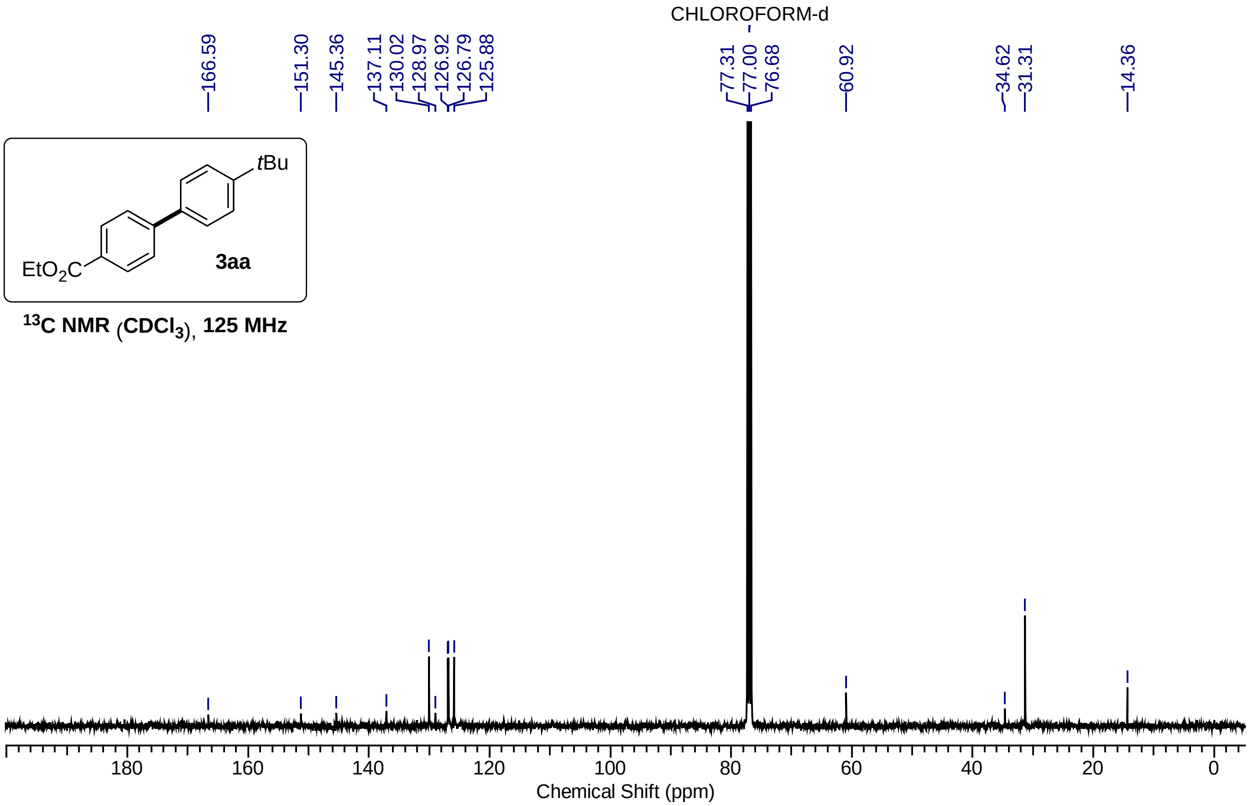
3y

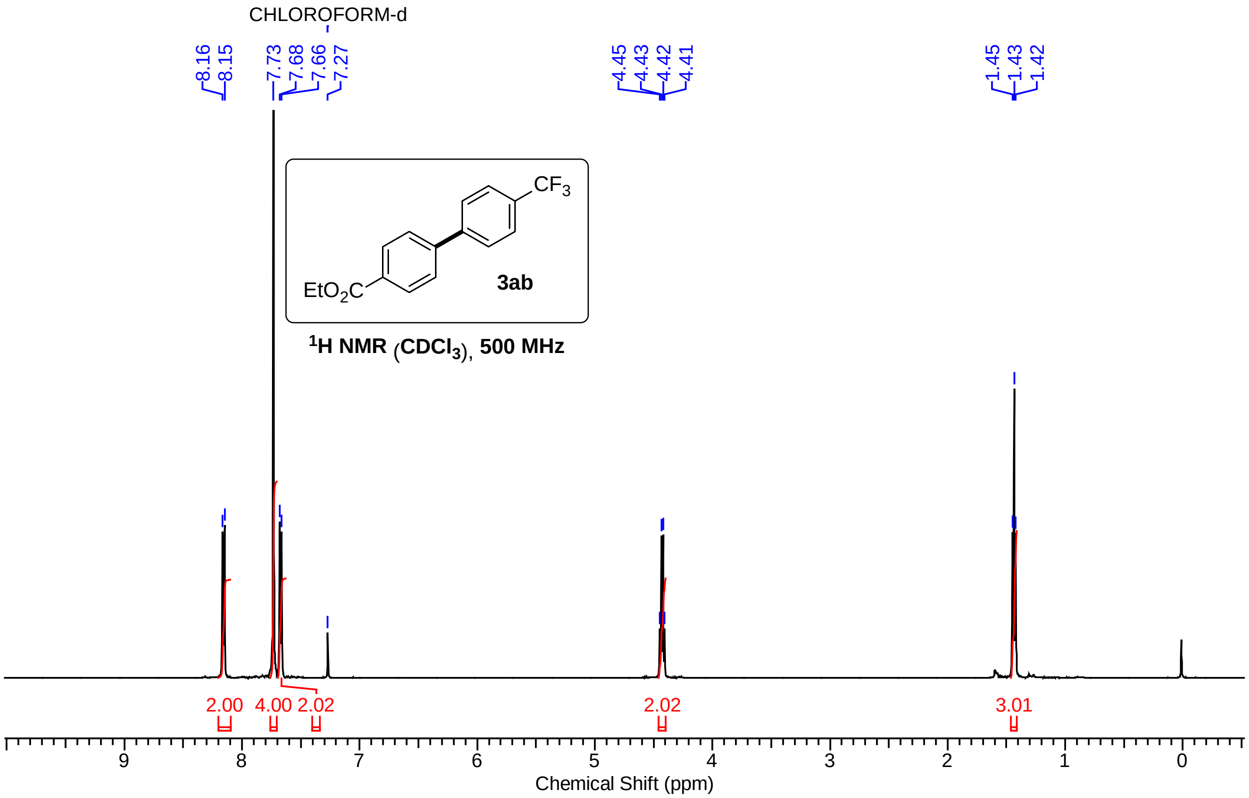
^{13}C NMR (CDCl$_3$), 125 MHz

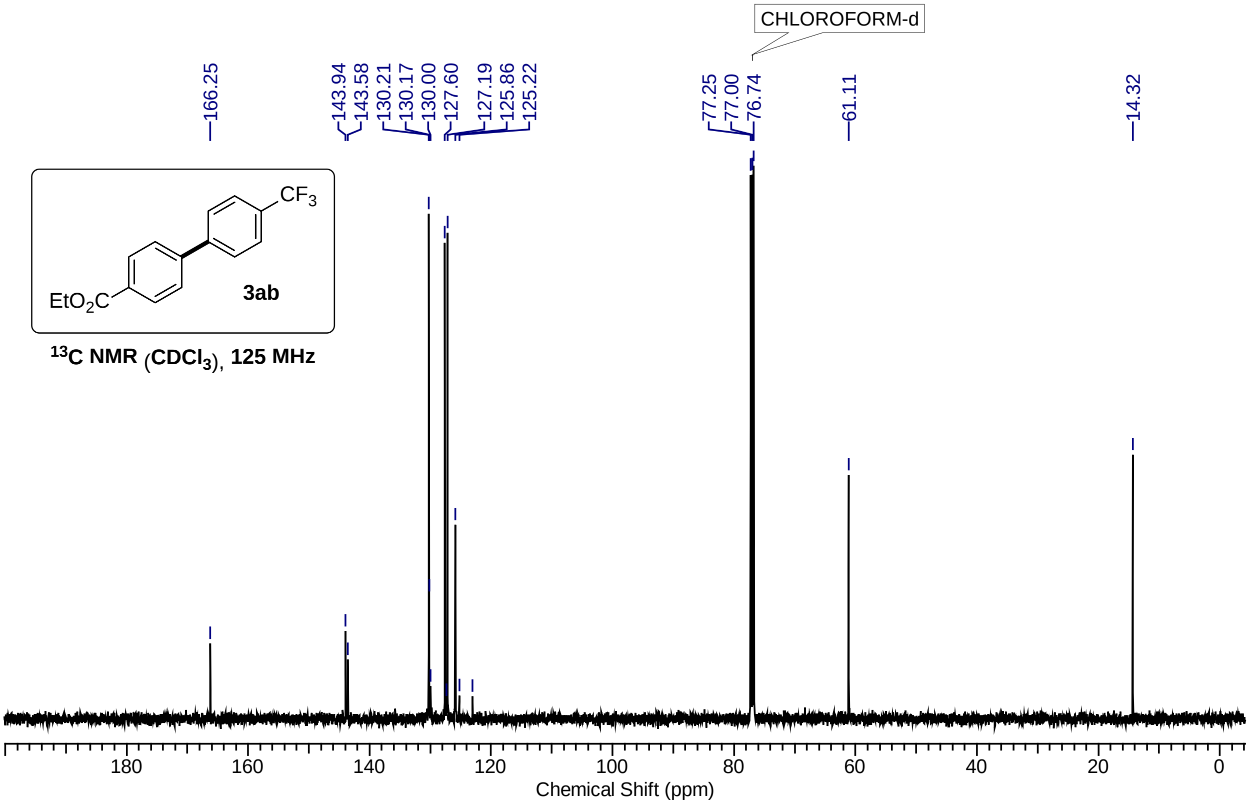

CHLOROFORM-d
8.22
8.20
7.71
7.70
7.62
7.61
7.46
7.44
7.43
7.27
7.24
7.22
6.39
2.62
2.36
Ph
Me
N
Ts
3z
^{1}H NMR (CDCl$_3$), 500 MHz
1.00
2.01
3.00
1.03
2.01
1.01
2.02
0.97
3.04
3.04
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
144.75
141.35
137.99
136.76
136.44
136.34
130.19
129.91
128.73
127.26
126.94
126.37
123.21
118.36
114.67
109.70
77.26
77.00
76.75
21.56
15.76
Ph
Me
N
Ts
3z
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
8.12
8.10
7.68
7.66
7.60
7.58
7.51
7.49
7.27
4.44
4.42
4.40
4.38
1.58
1.44
1.42
1.40
1.40
1.38
0.01
tBu
EtO2C
3aa
1H NMR (CDCl3), 500 MHz
2.01
2.03
2.02
2.04
2.00
3.06
9.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

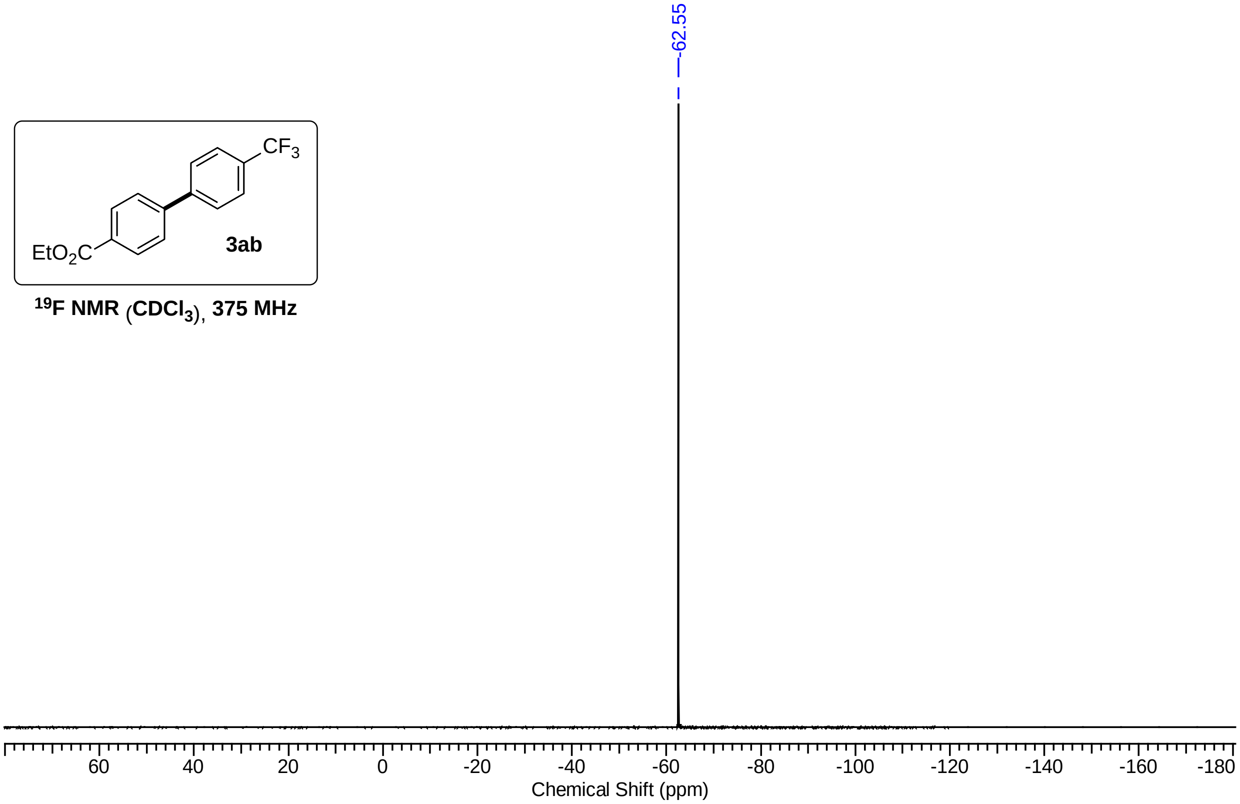

CHLOROFORM-d
166.59
151.30
145.36
137.11
130.02
128.97
126.92
126.79
125.88
77.31
77.00
76.68
60.92
34.62
31.31
14.36
tBu
EtO2C
3aa
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

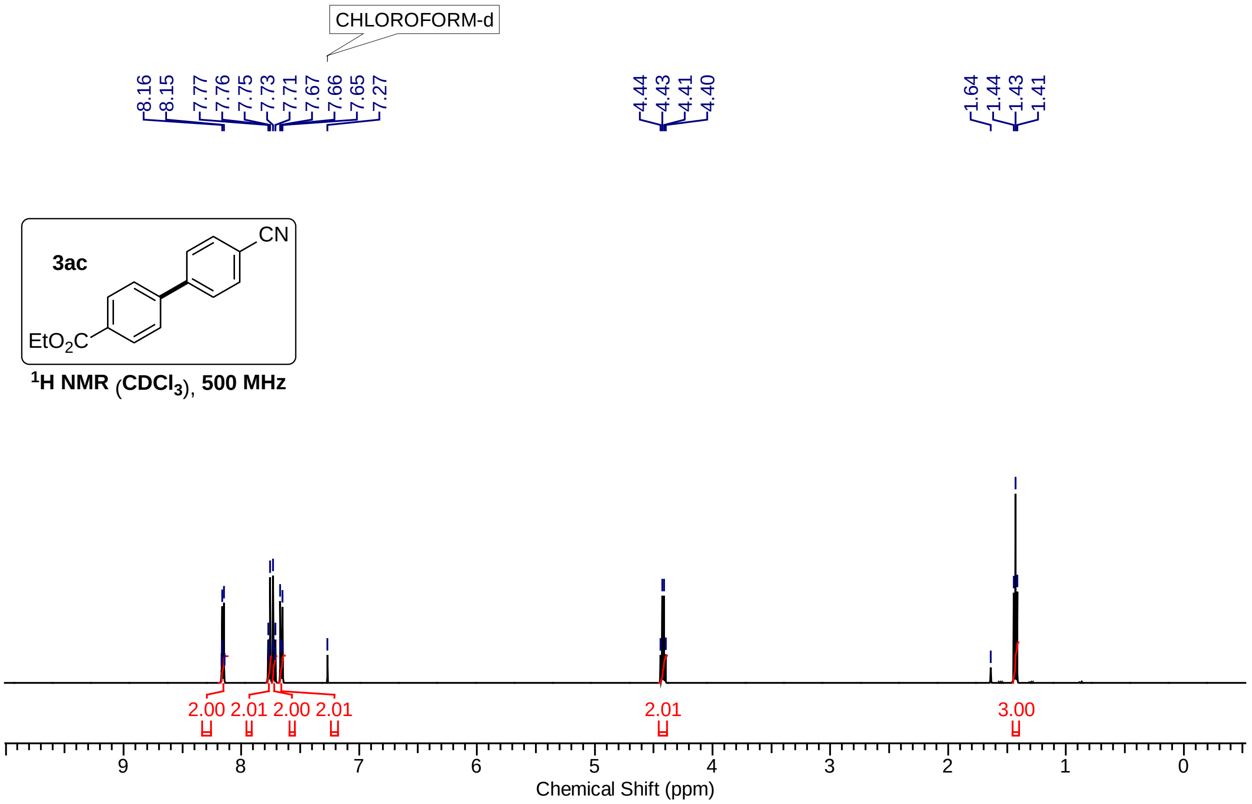

CHLOROFORM-d
8.16
8.15
7.73
7.68
7.66
7.27
4.45
4.43
4.42
4.41
1.45
1.43
1.42
CF3
EtO2C
3ab
1H NMR (CDCl3), 500 MHz
2.00
4.00
2.02
2.02
3.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

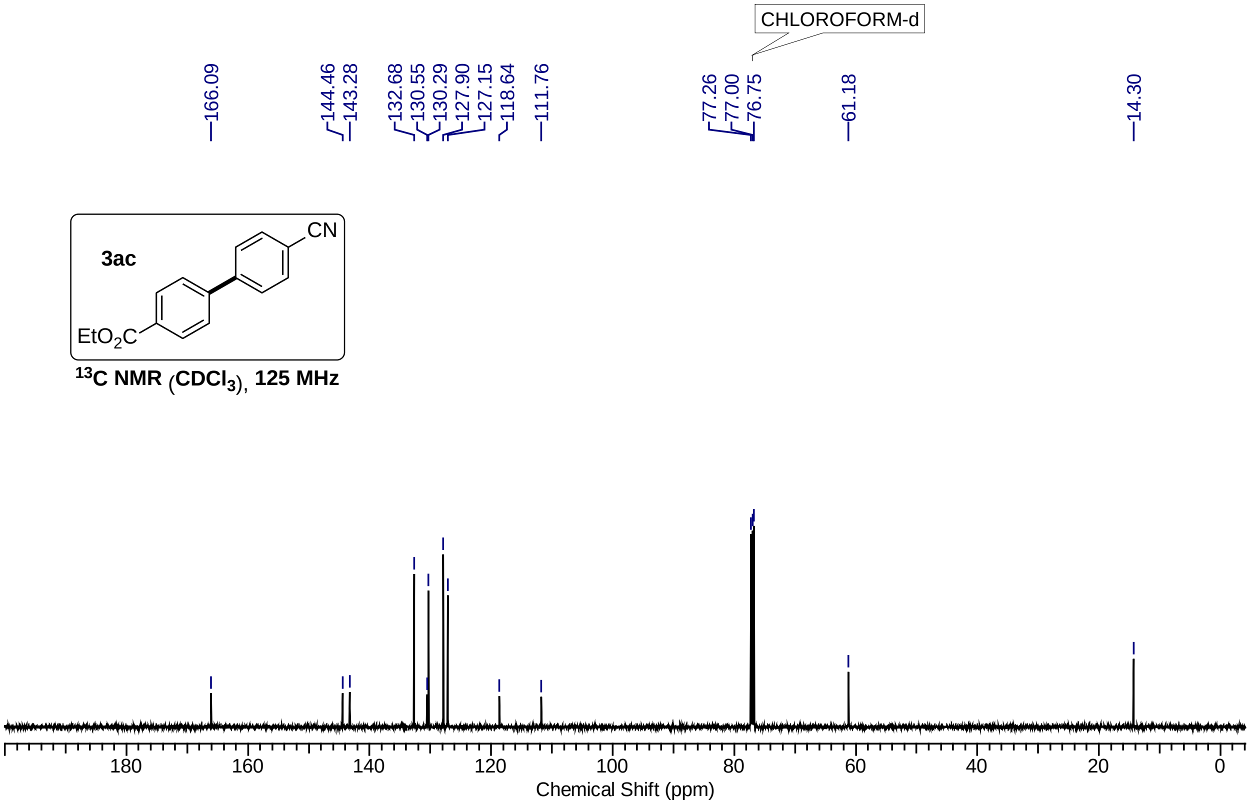

CHLOROFORM-d
166.25
143.94
143.58
130.21
130.17
130.00
127.60
127.19
125.86
125.22
77.25
77.00
76.74
61.11
14.32
CF3
EtO2C
3ab
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

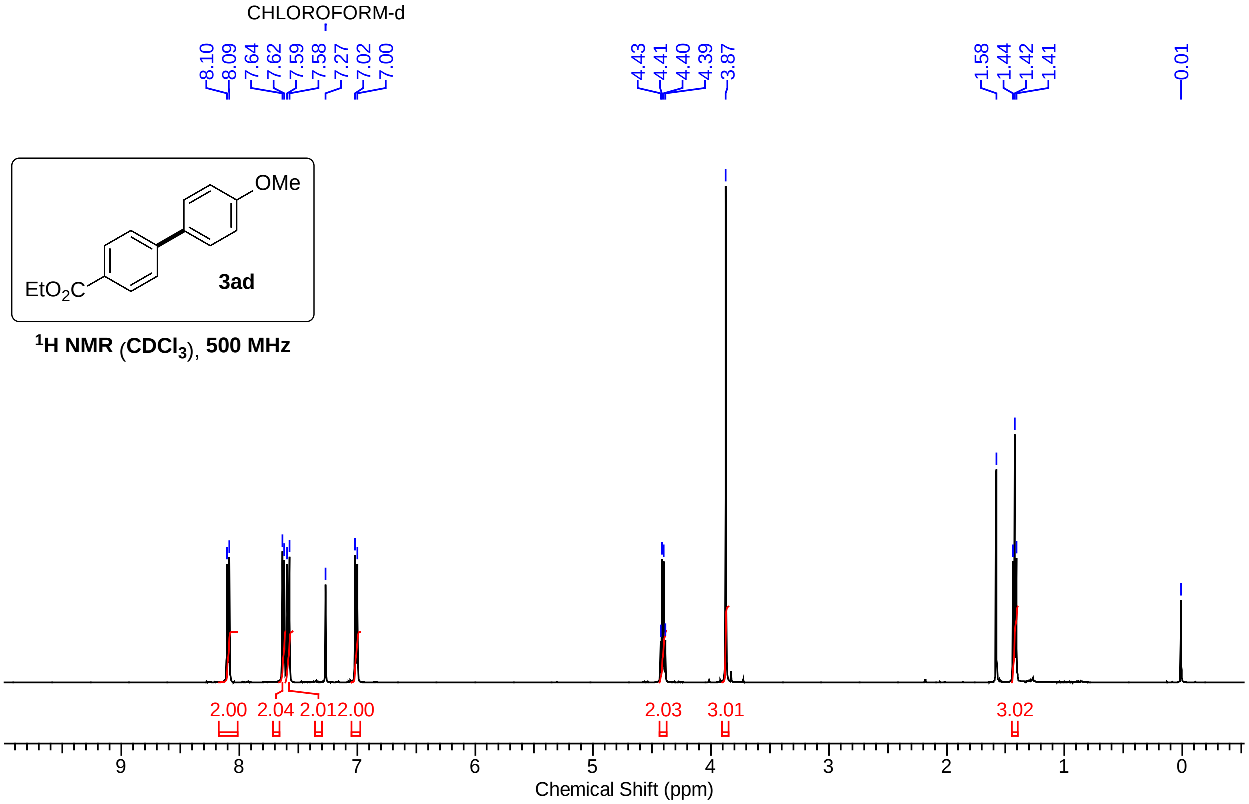
3ab

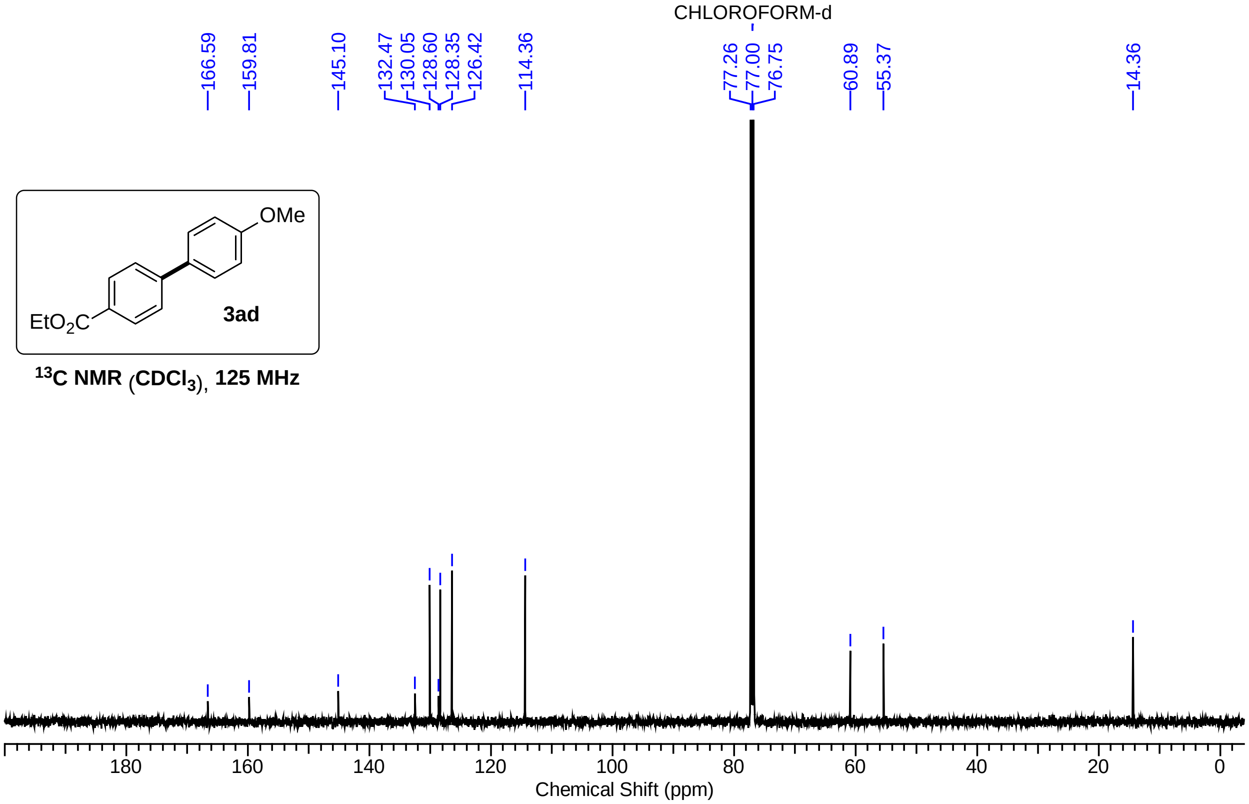
^{19}F NMR (CDCl$_3$), 375 MHz

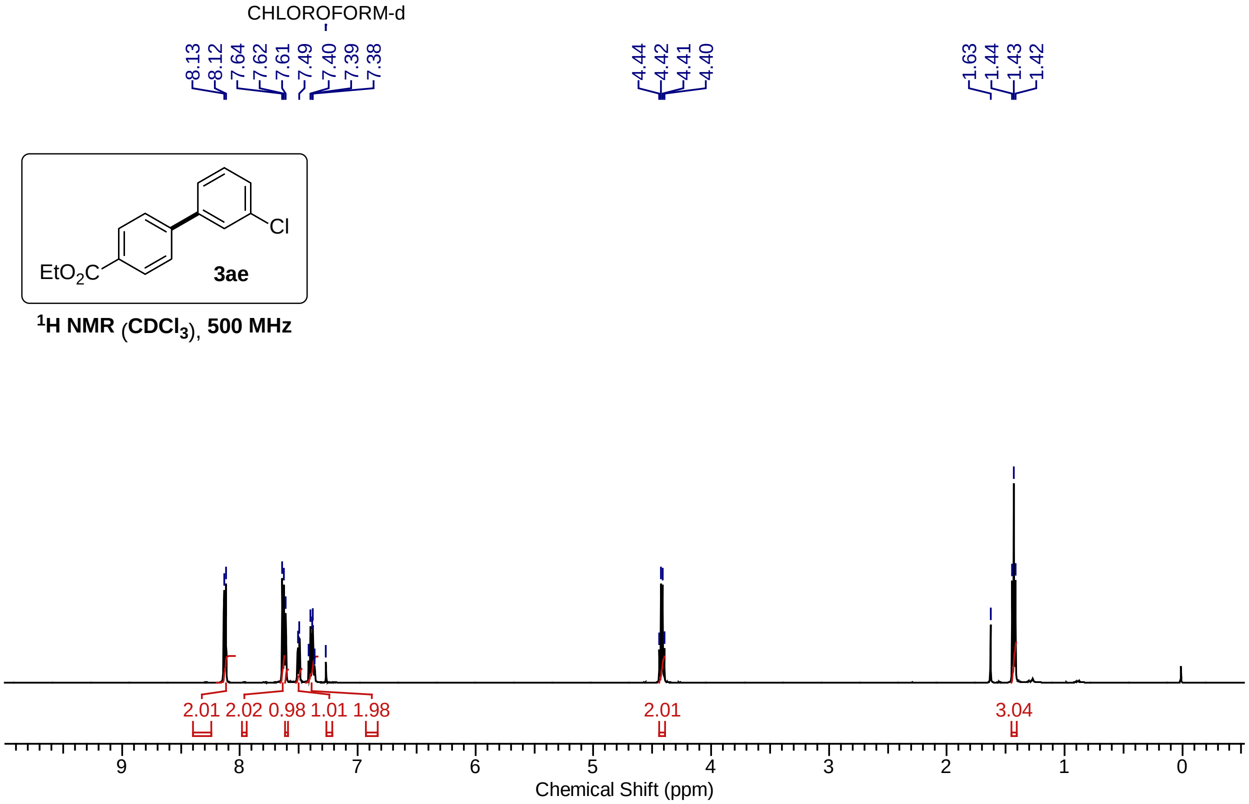



CHLOROFORM-d
8.16
8.15
7.77
7.76
7.75
7.73
7.71
7.67
7.66
7.65
7.27
4.44
4.43
4.41
4.40
1.64
1.44
1.43
1.41
3ac
CN
EtO$_2$C
^{1}H NMR (CDCl$_3$), 500 MHz
2.00
2.01
2.00
2.01
2.01
3.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
166.09
144.46
143.28
132.68
130.55
130.29
127.90
127.15
118.64
111.76
77.26
77.00
76.75
61.18
14.30
3ac
CN
EtO$_2$C
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

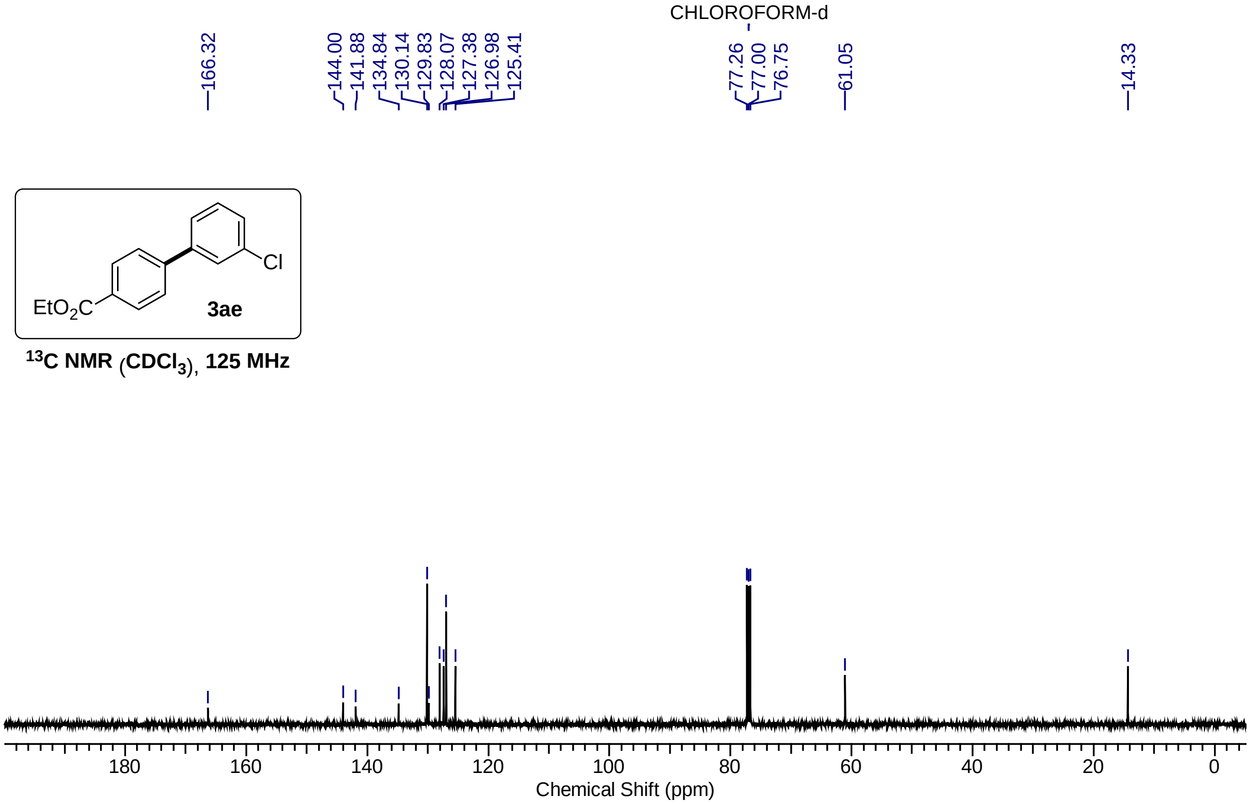

CHLOROFORM-d
8.10
8.09
7.64
7.62
7.59
7.58
7.27
7.02
7.00
4.43
4.41
4.40
4.39
3.87
1.58
1.44
1.42
1.41
0.01
OMe
EtO2C
3ad
1H NMR (CDCl3), 500 MHz
2.00
2.04
2.01
2.00
2.03
3.01
3.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
166.59
159.81
145.10
132.47
130.05
128.60
128.35
126.42
114.36
77.26
77.00
76.75
60.89
55.37
14.36
OMe
EtO2C
3ad
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



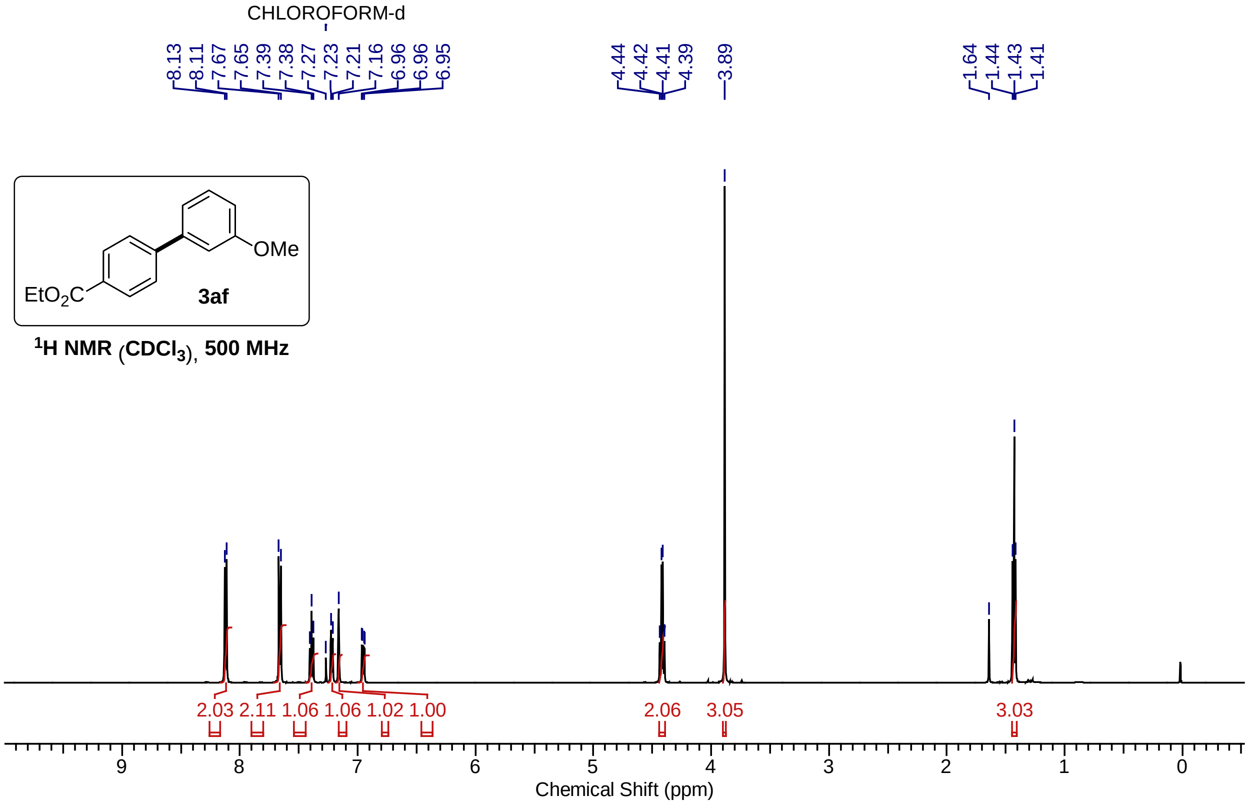
3ae

^{1}H NMR (CDCl$_3$), 500 MHz

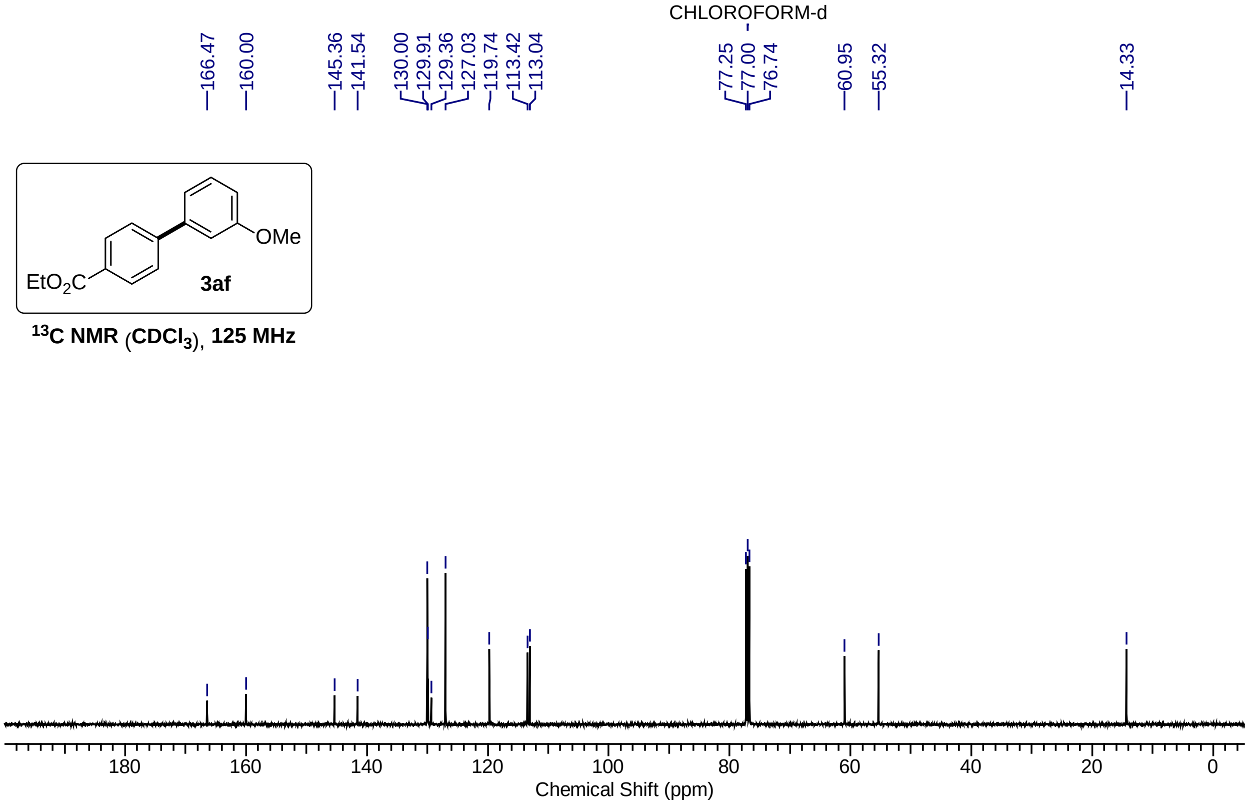


3ae

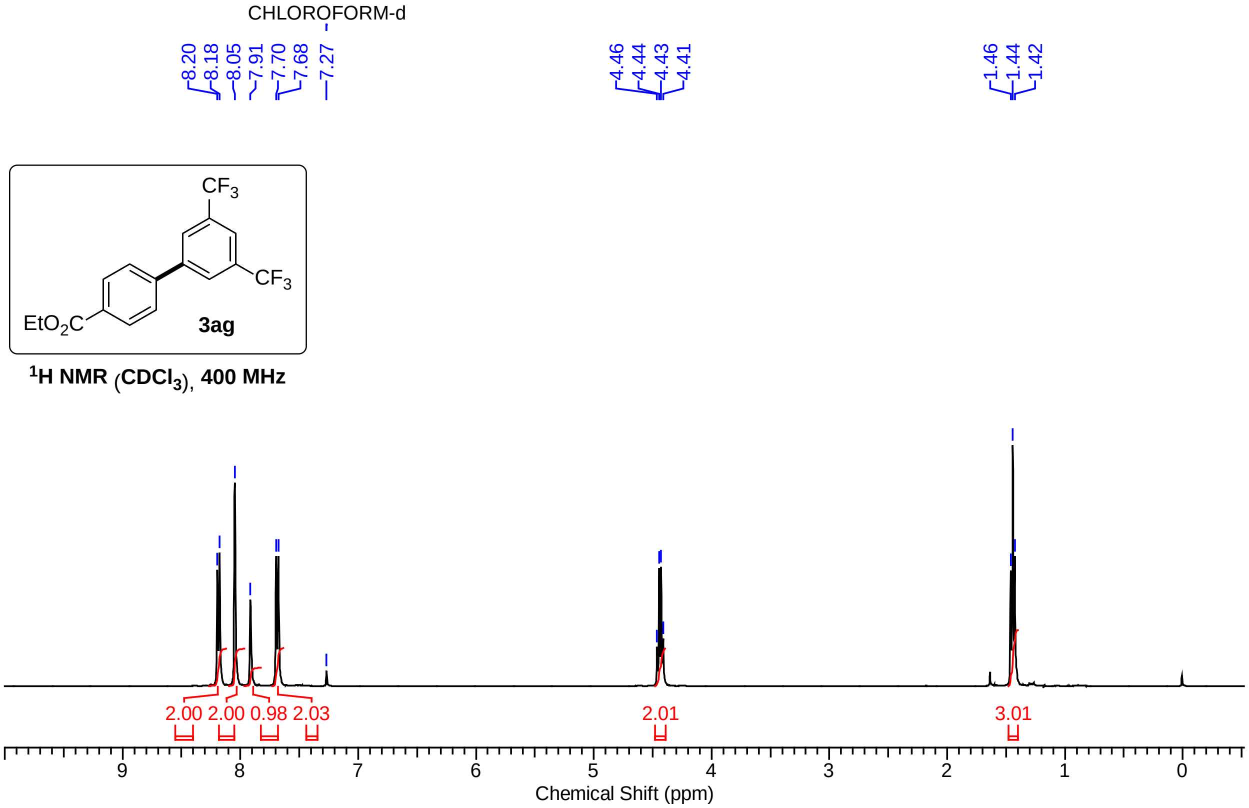
^{13}C NMR (CDCl$_3$), 125 MHz

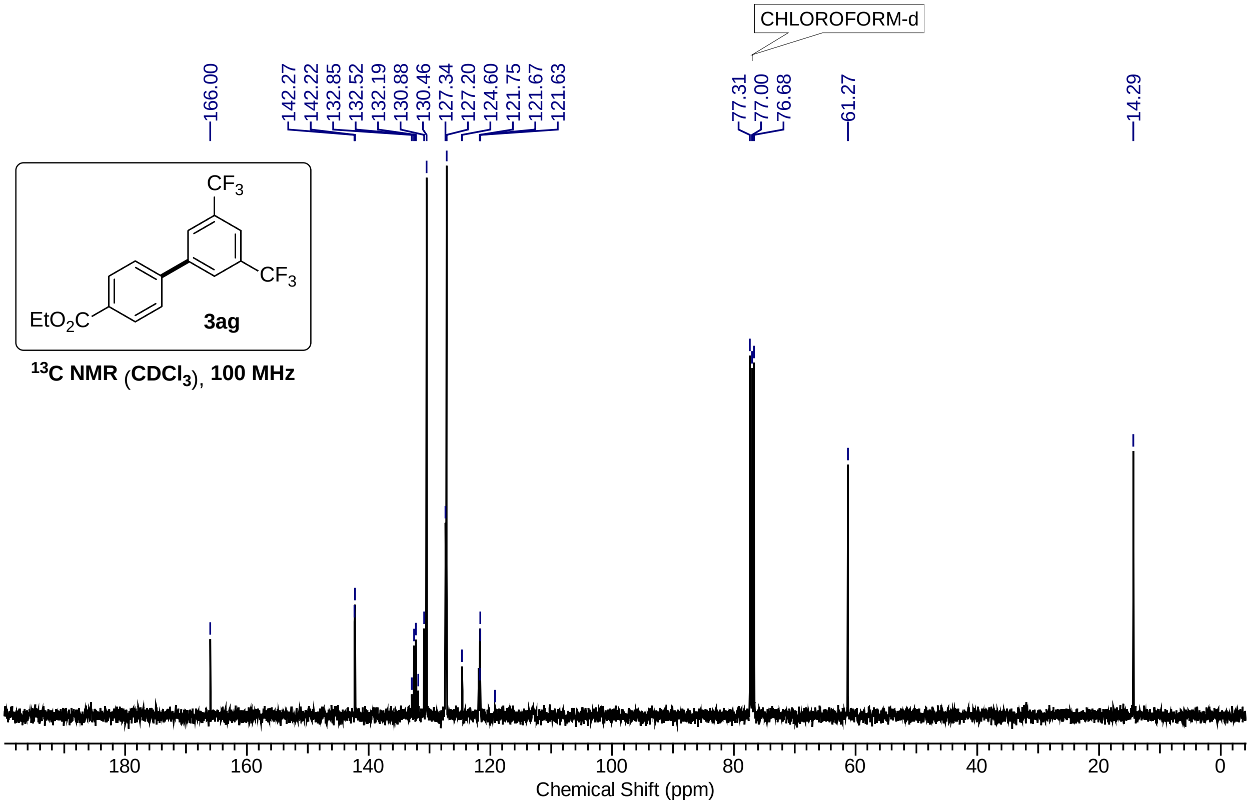


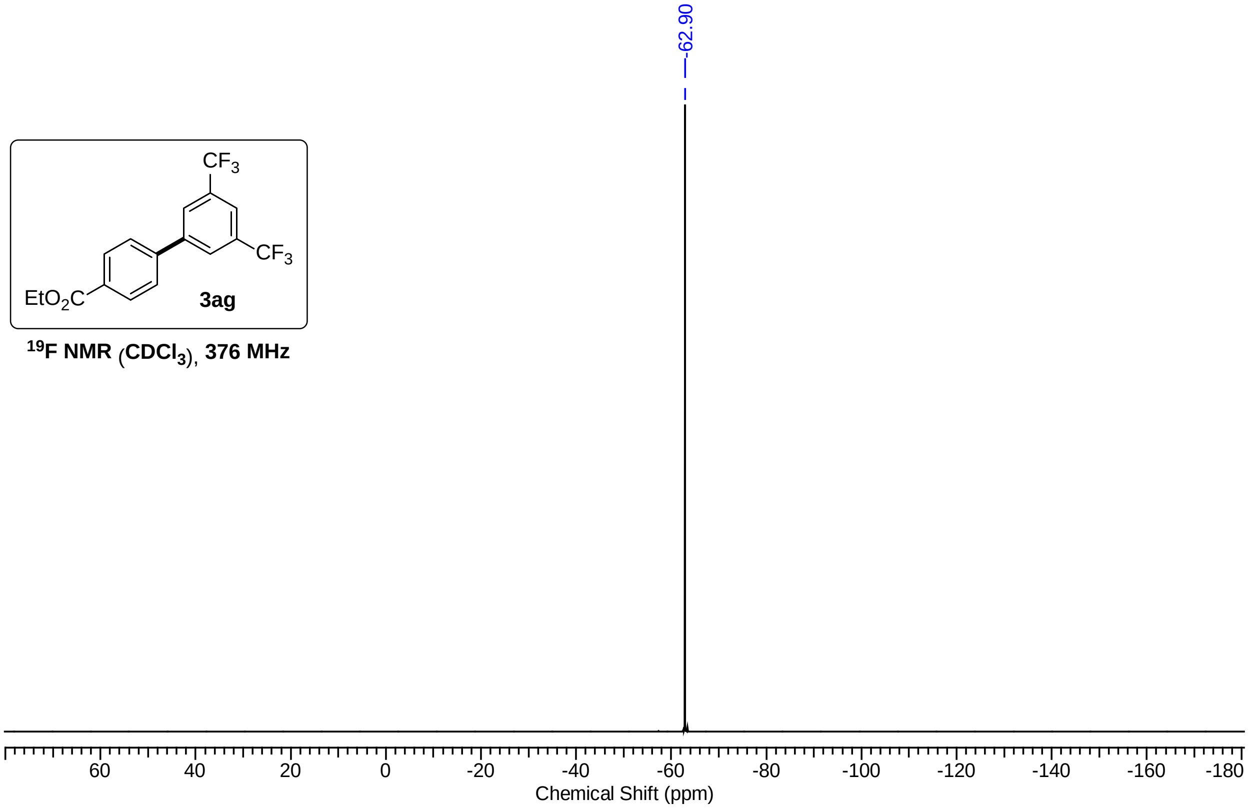
^1H NMR ($CDCl_3$), 500 MHz



^{13}C NMR ($CDCl_3$), 125 MHz

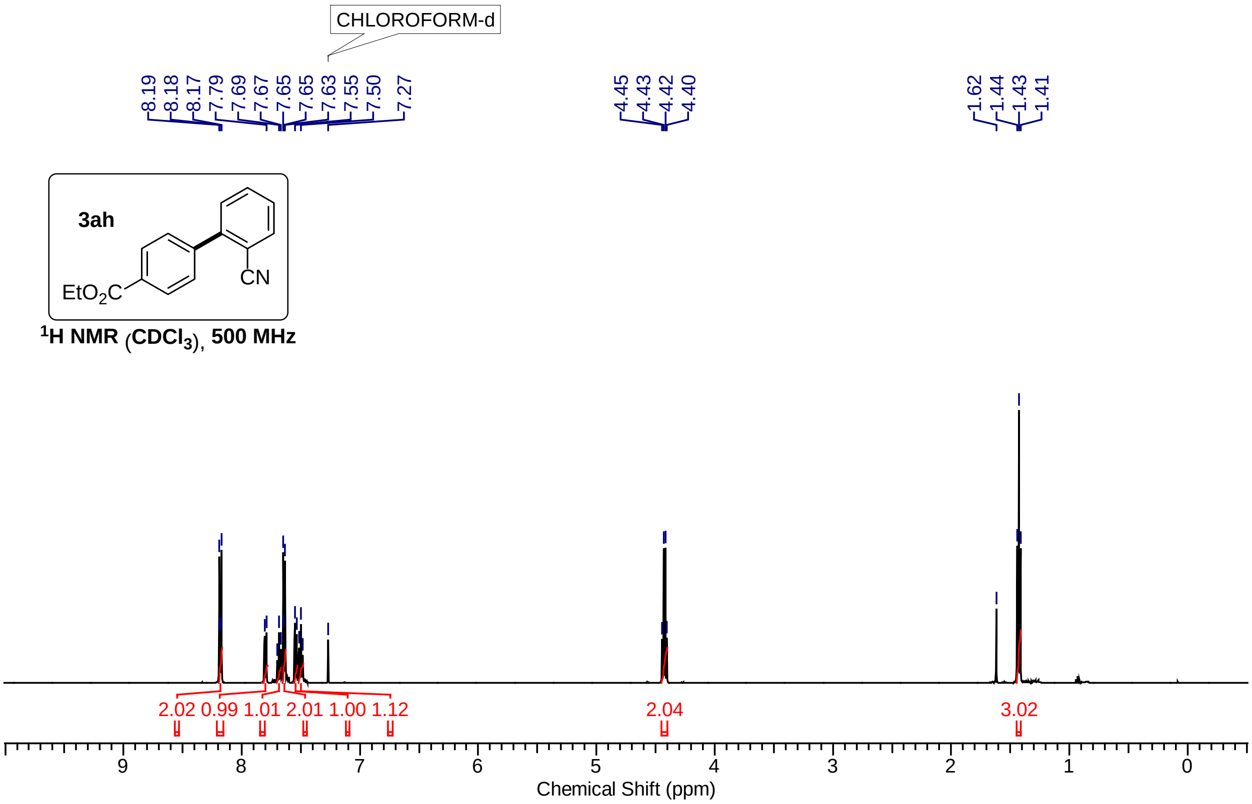

CHLOROFORM-d
8.20
8.18
8.05
7.91
7.70
7.68
7.27
4.46
4.44
4.43
4.41
1.46
1.44
1.42
CF3
CF3
EtO2C
3ag
1H NMR (CDCl3), 400 MHz
2.00 2.00 0.98 2.03
2.01
3.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
166.00
142.27
142.22
132.85
132.52
132.19
130.88
130.46
127.34
127.20
124.60
121.75
121.67
121.63
77.31
77.00
76.68
61.27
14.29
CF3
CF3
EtO2C
3ag
13C NMR (CDCl3), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

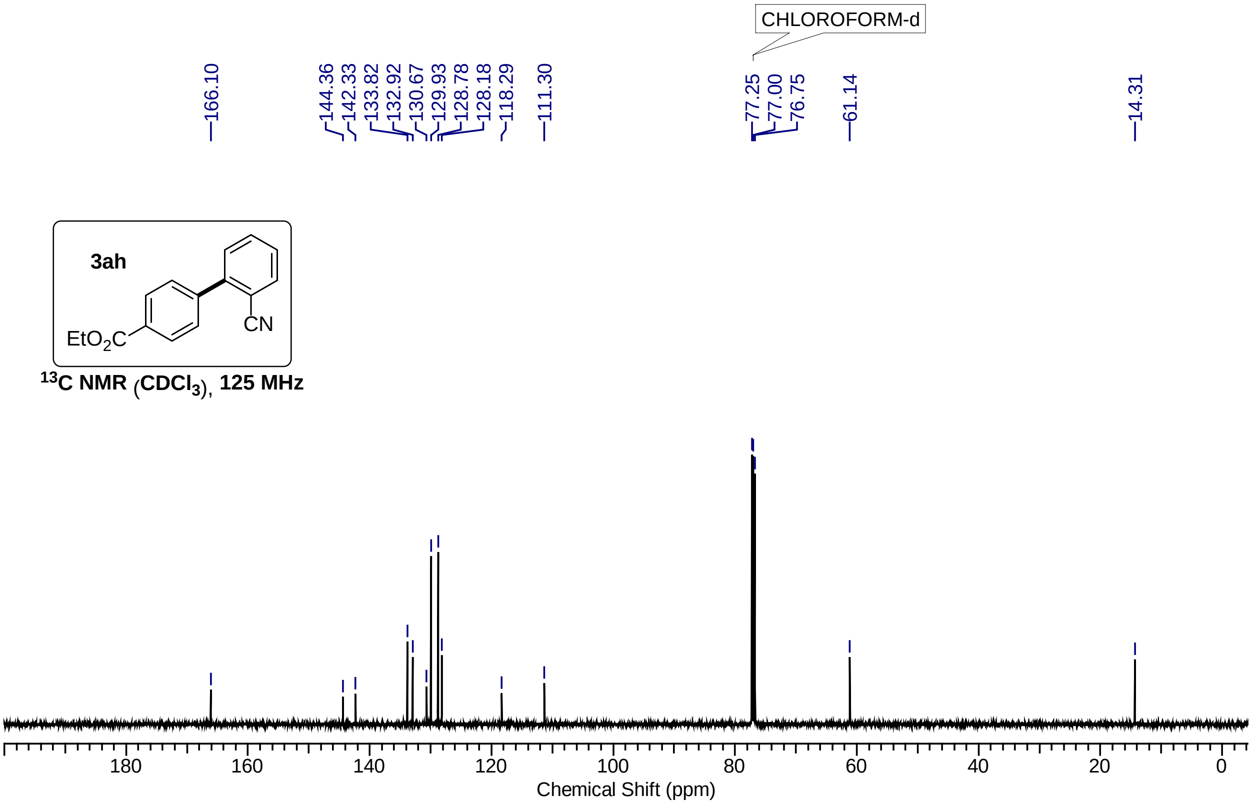


3ag

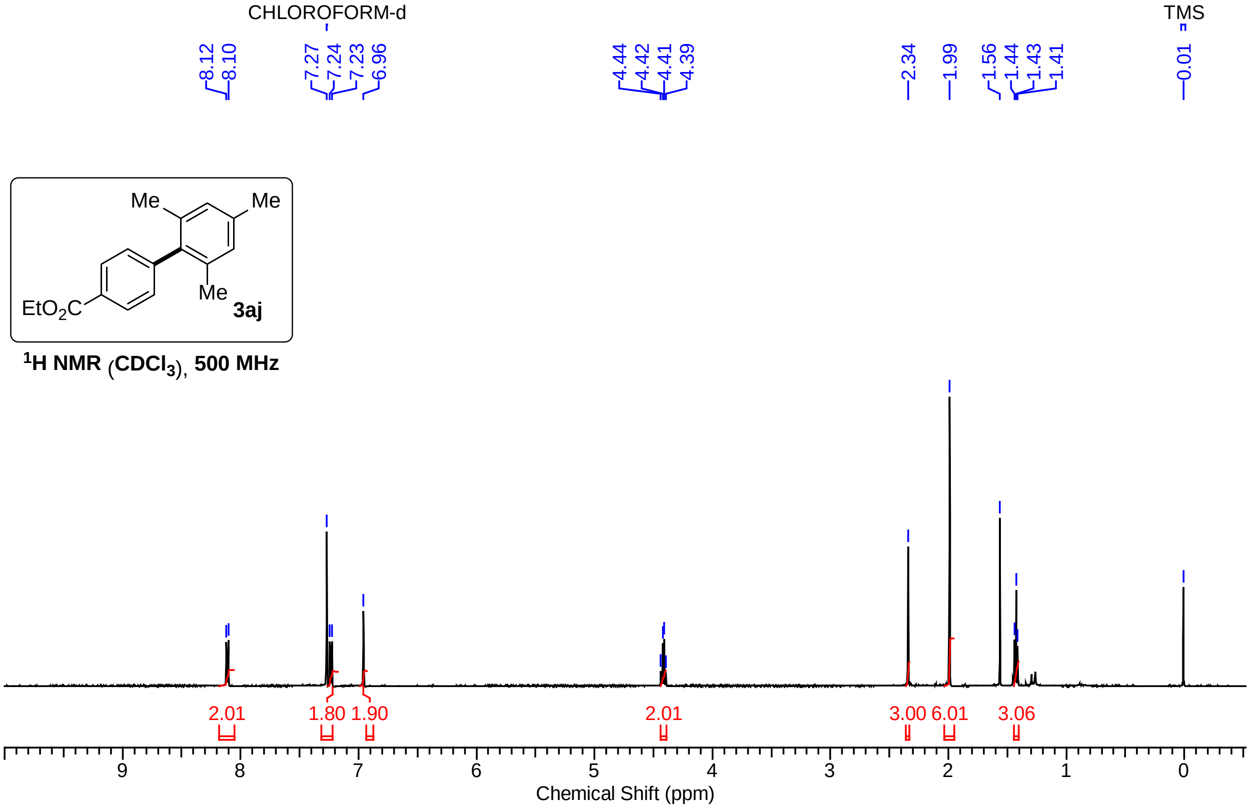
^{19}F NMR (CDCl$_3$), 376 MHz



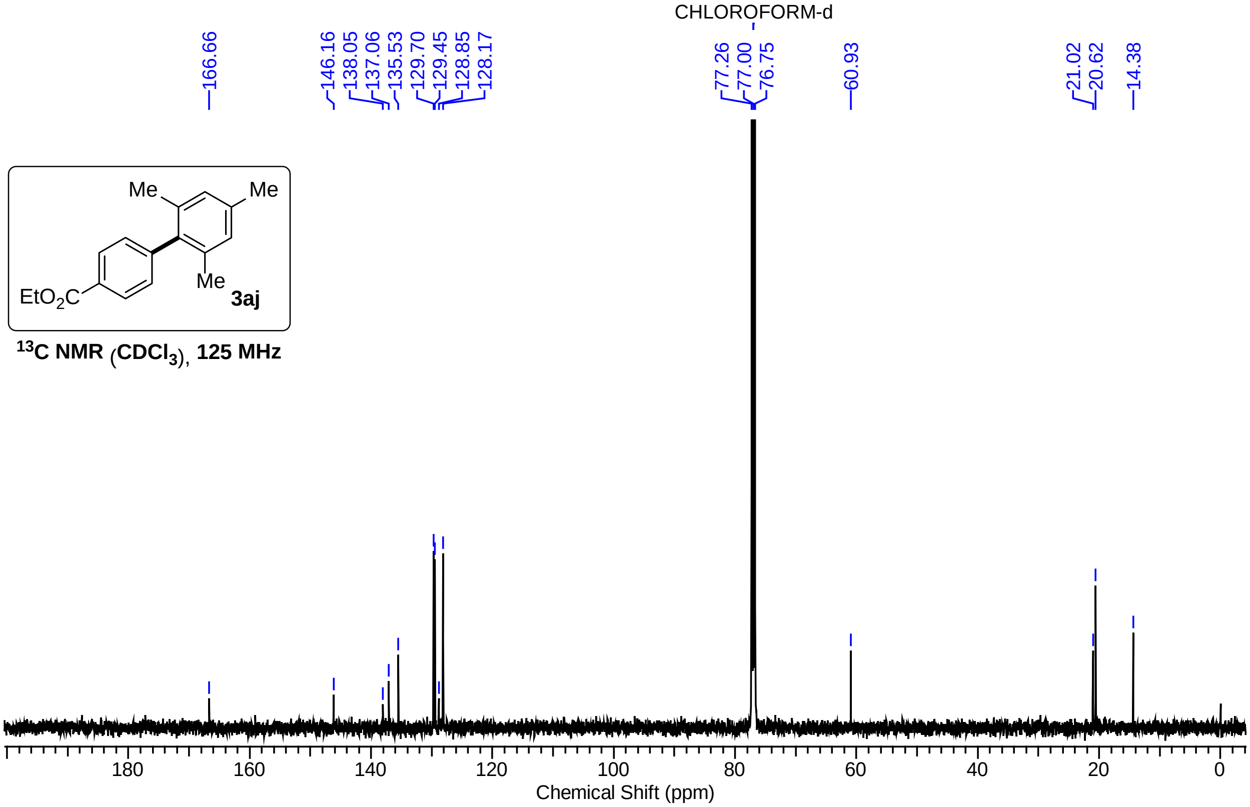
^{1}H NMR (CDCl$_3$), 500 MHz



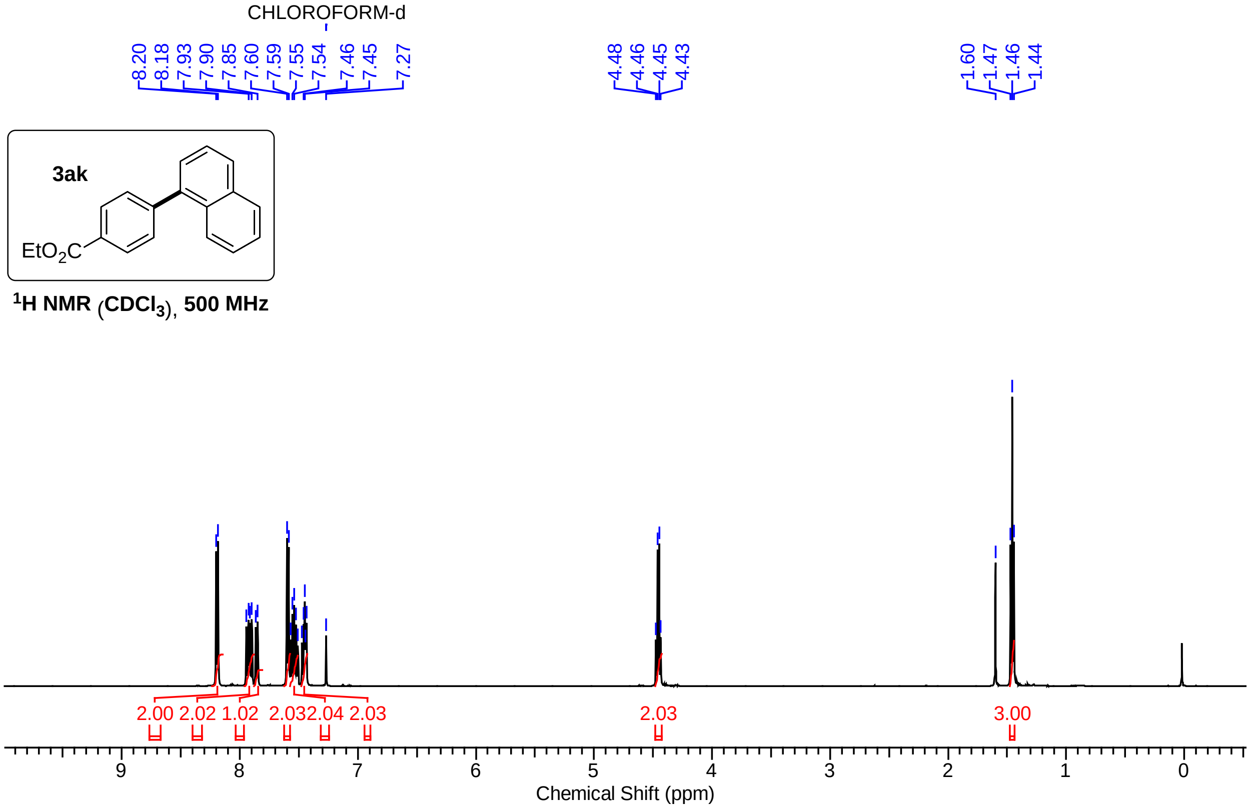
^{13}C NMR (CDCl$_3$), 125 MHz

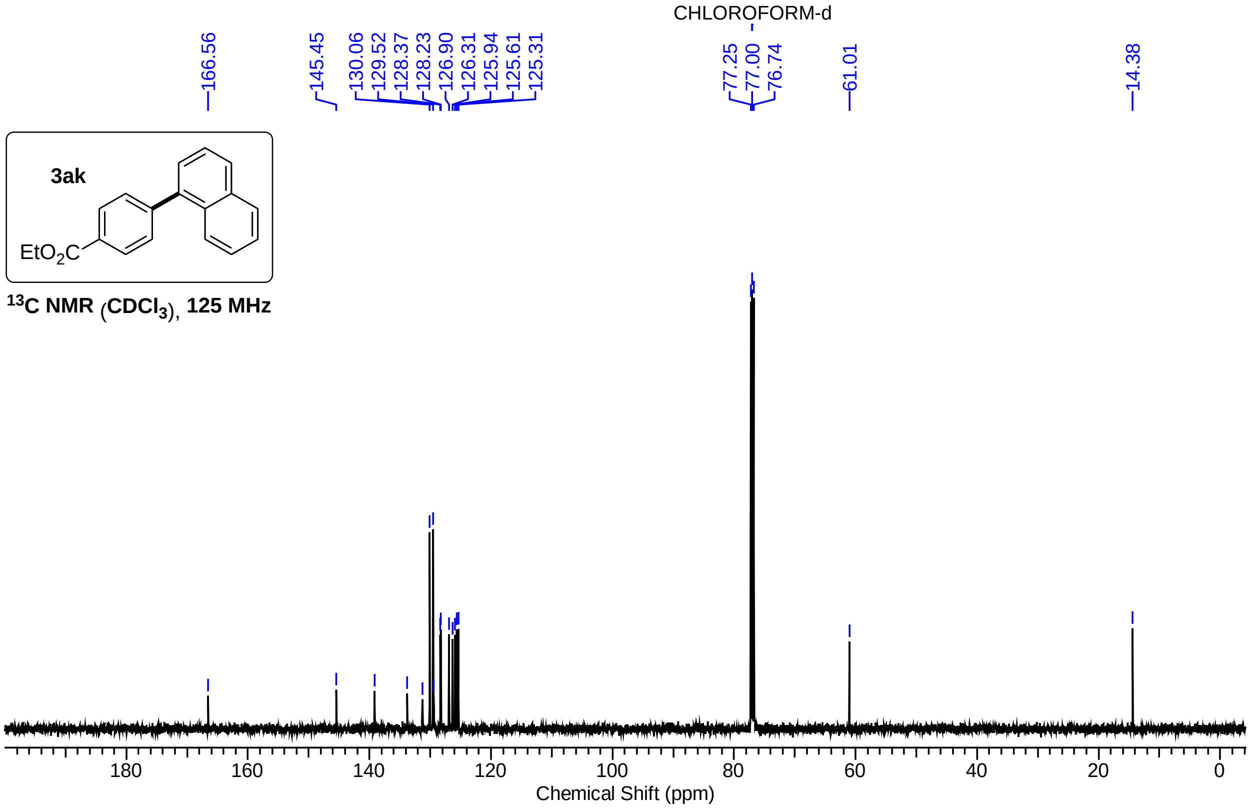


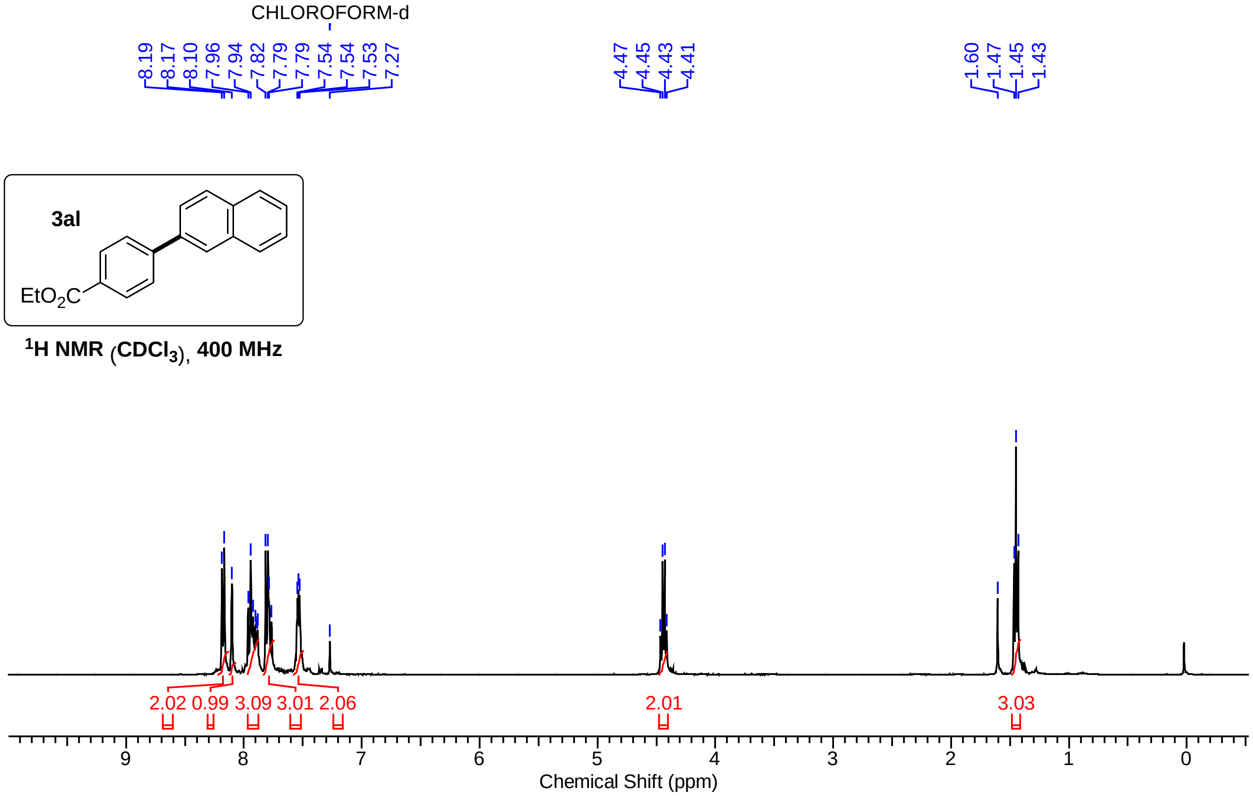
^{1}H NMR (CDCl$_3$), 500 MHz



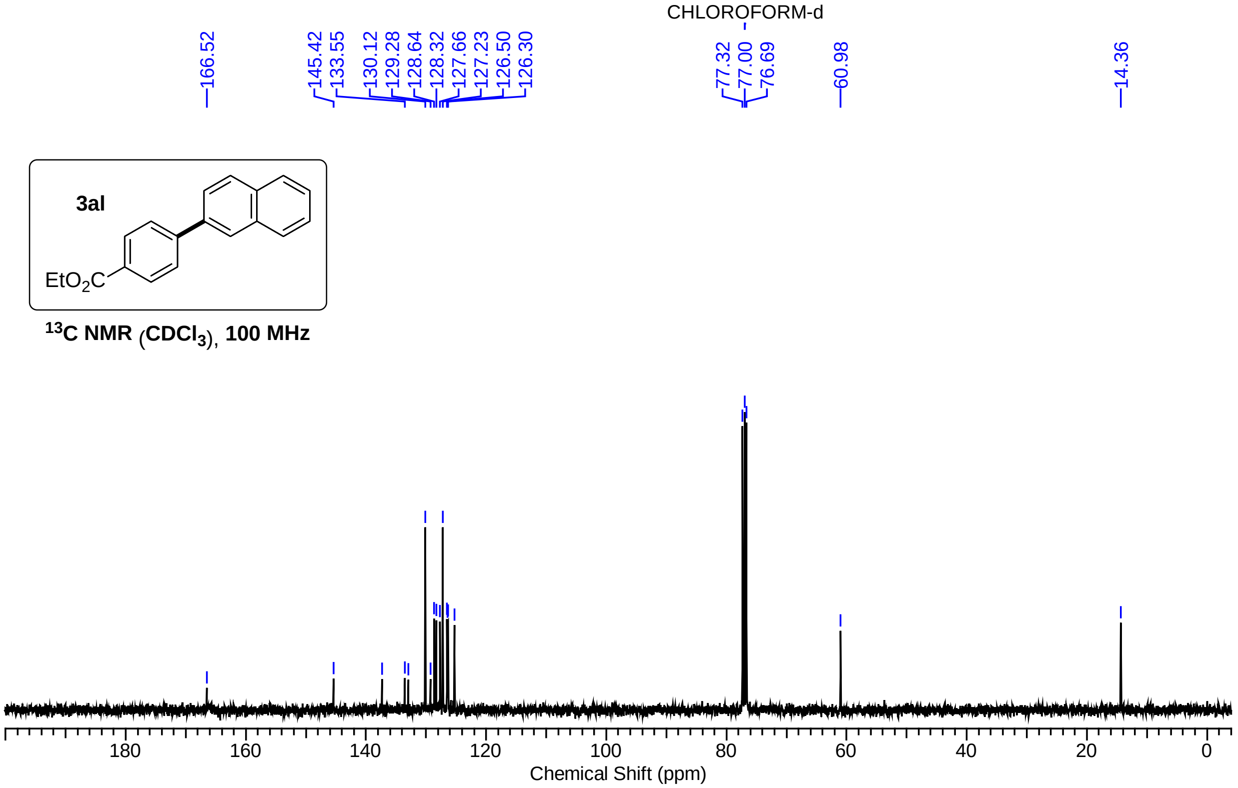
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
8.20
8.18
7.93
7.90
7.85
7.60
7.59
7.55
7.54
7.46
7.45
7.27
4.48
4.46
4.45
4.43
1.60
1.47
1.46
1.44
3ak
EtO$_2$C
^{1}H NMR (CDCl$_3$), 500 MHz
2.00
2.02
1.02
2.03
2.04
2.03
2.03
3.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

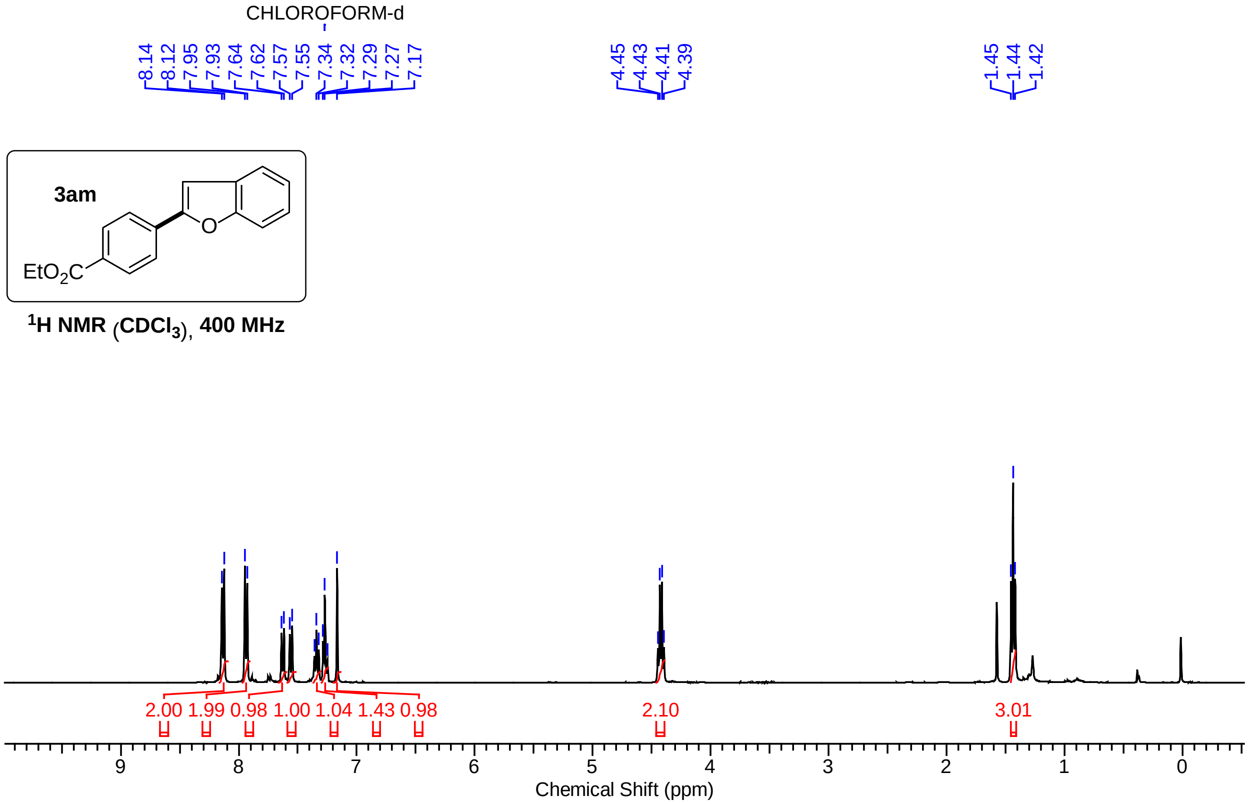

CHLOROFORM-d
166.56
145.45
130.06
129.52
128.37
128.23
126.90
126.31
125.94
125.61
125.31
77.25
77.00
76.74
61.01
14.38
3ak
EtO$_2$C
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

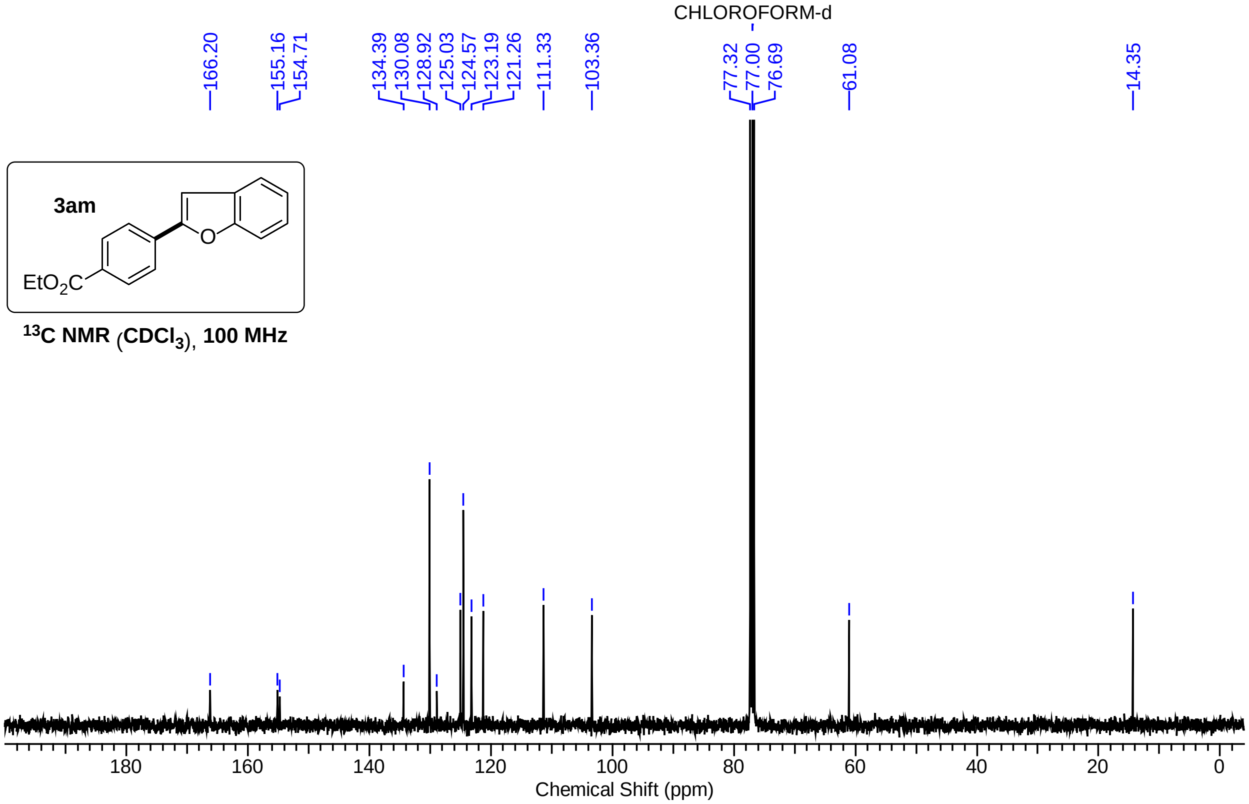


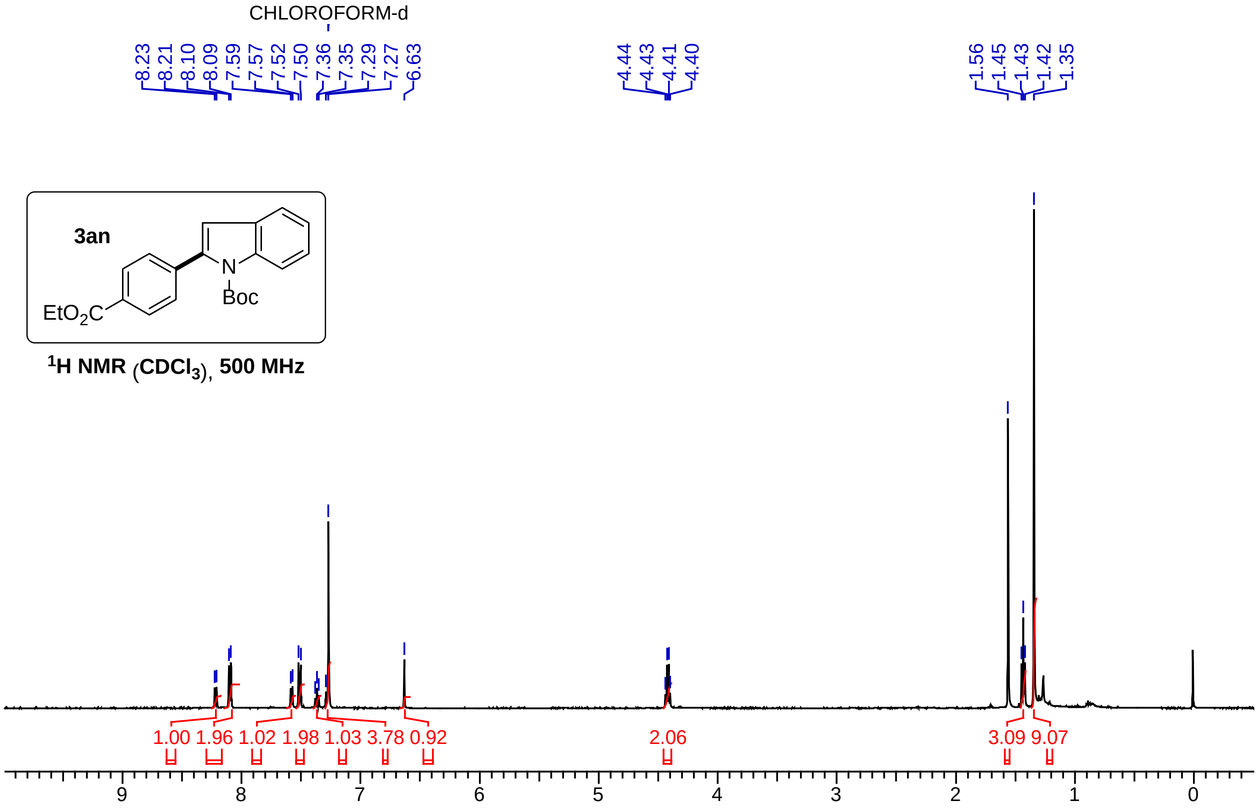
^{1}H NMR (CDCl$_3$), 400 MHz

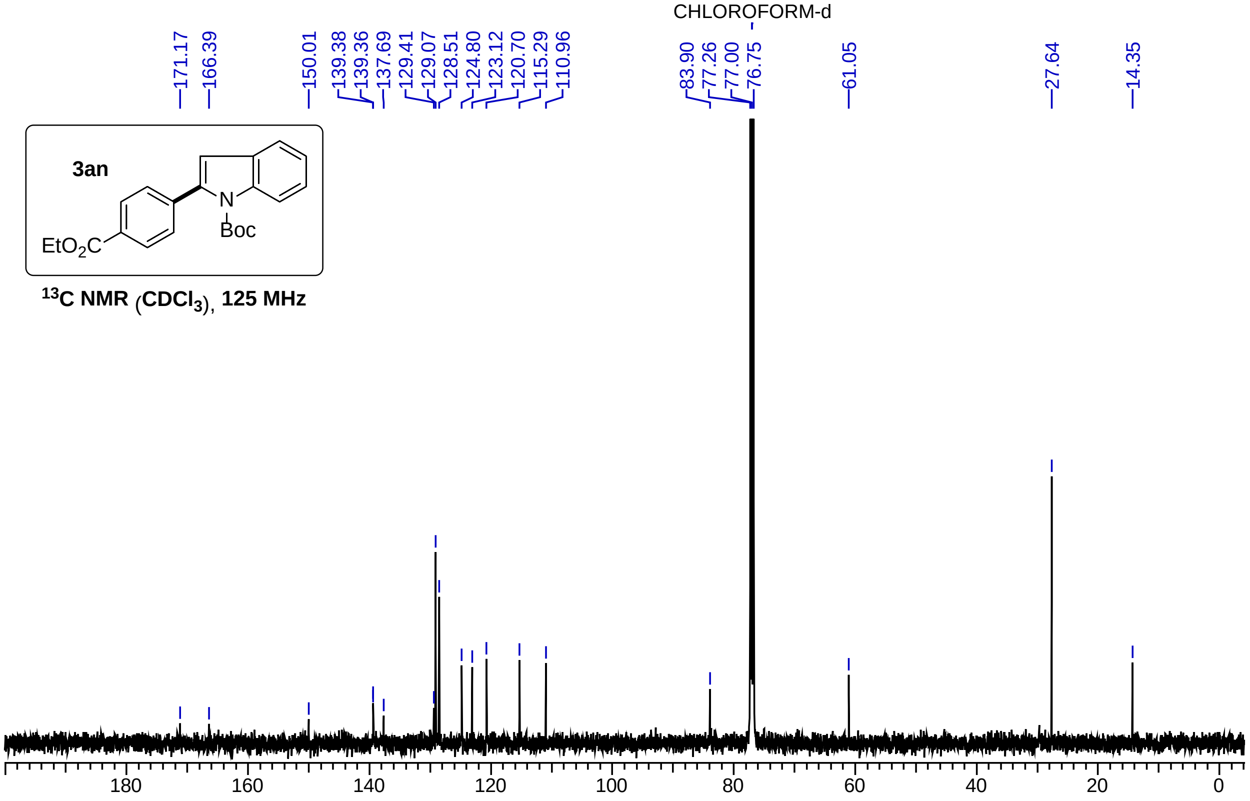


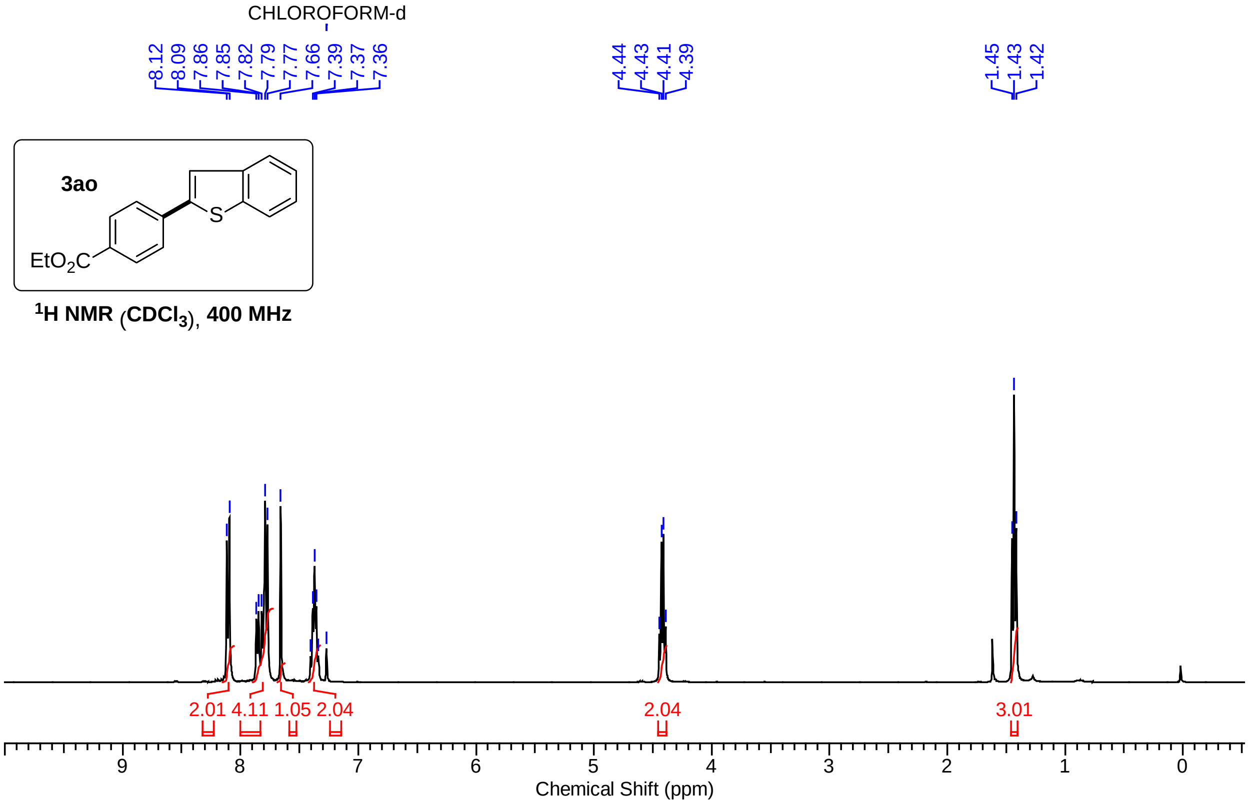
^{13}C NMR (CDCl$_3$), 100 MHz

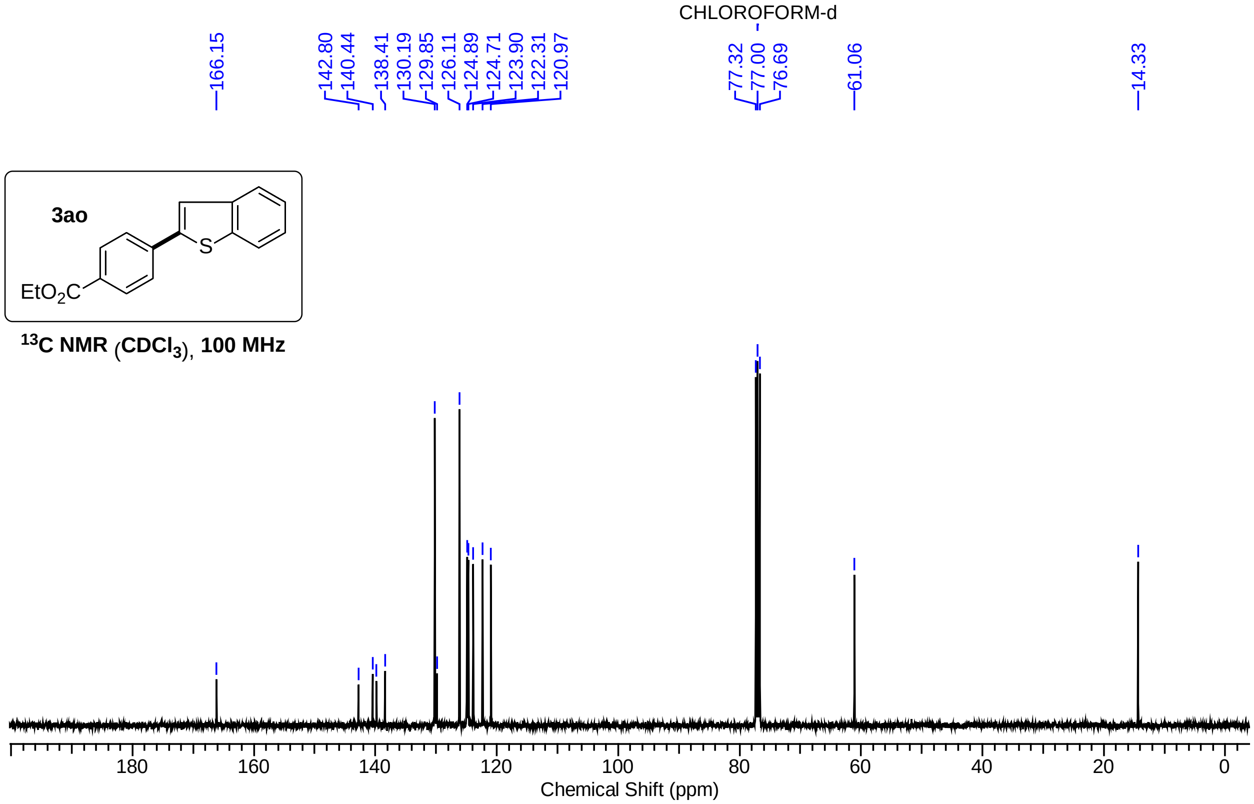

CHLOROFORM-d
8.14
8.12
7.95
7.93
7.64
7.62
7.57
7.55
7.34
7.32
7.29
7.27
7.17
4.45
4.43
4.41
4.39
1.45
1.44
1.42
3am
EtO_2C
O
^{1}H NMR (CDCl$_3$), 400 MHz
2.00
1.99
0.98
1.00
1.04
1.43
0.98
2.10
3.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

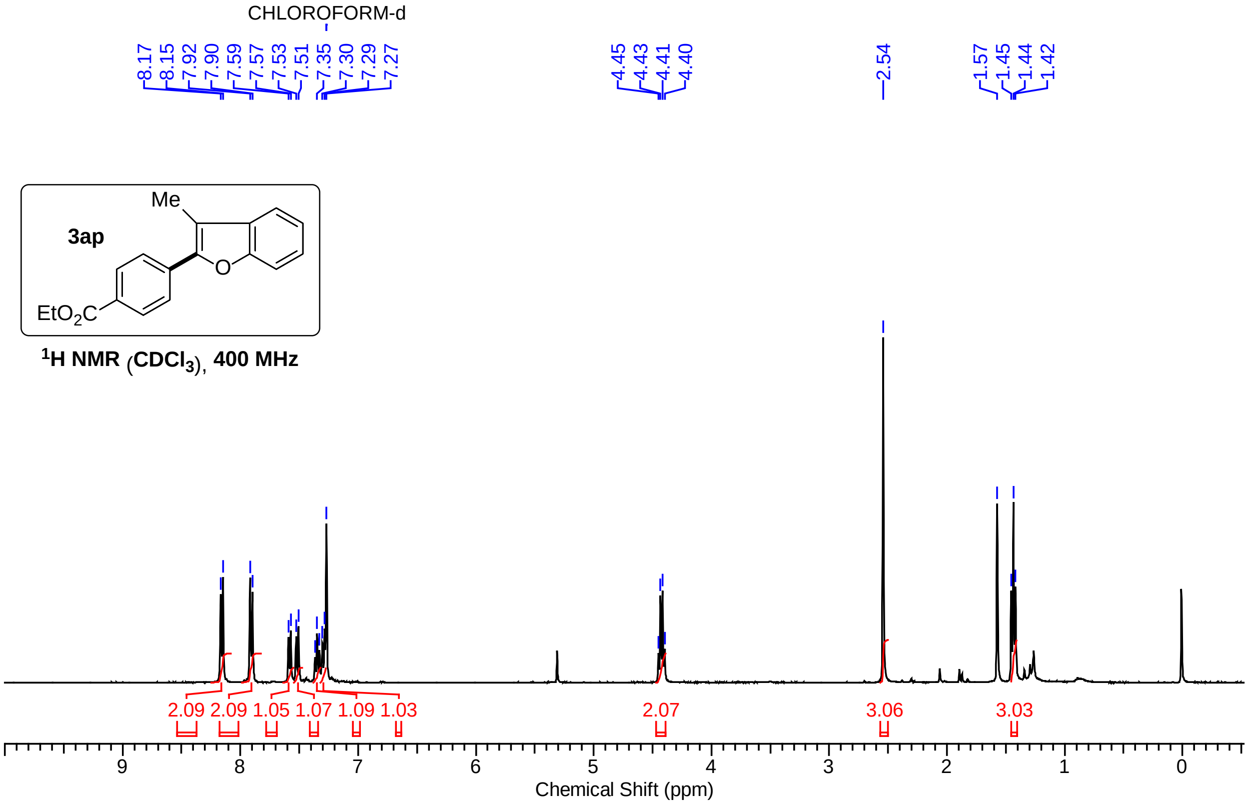

CHLOROFORM-d
166.20
155.16
154.71
134.39
130.08
128.92
125.03
124.57
123.19
121.26
111.33
103.36
77.32
77.00
76.69
61.08
14.35
3am
EtO_2C
O
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

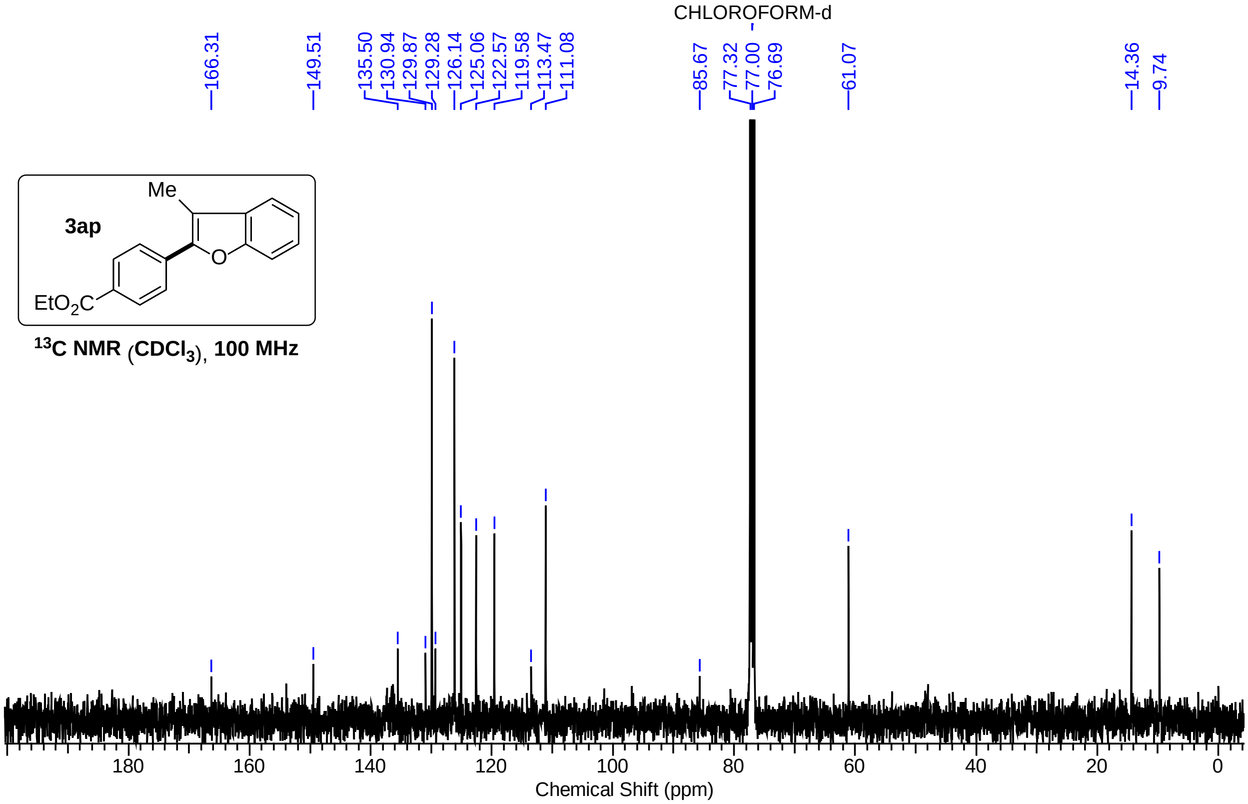

CHLOROFORM-d
8.23
8.21
8.10
8.09
7.59
7.57
7.52
7.50
7.36
7.35
7.29
7.27
6.63
4.44
4.43
4.41
4.40
1.56
1.45
1.43
1.42
1.35
3an
N
Boc
EtO2C
1H NMR (CDCl3), 500 MHz
1.00
1.96
1.02
1.98
1.03
3.78
0.92
2.06
3.09
9.07
9
8
7
6
5
4
3
2
1
0

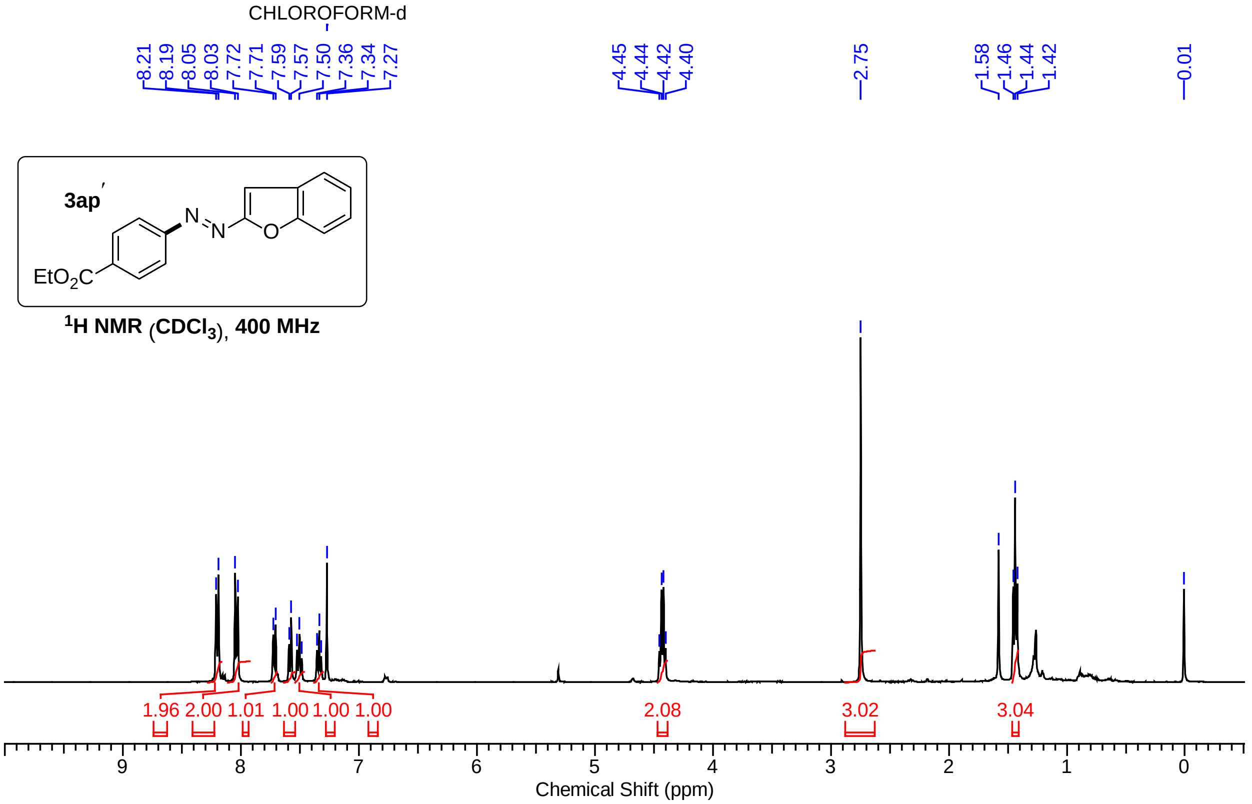

CHLOROFORM-d
171.17
166.39
150.01
139.38
139.36
137.69
129.41
129.07
128.51
124.80
123.12
120.70
115.29
110.96
83.90
77.26
77.00
76.75
61.05
27.64
14.35
3an
N
Boc
EtO2C
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0


CHLOROFORM-d
8.12
8.09
7.86
7.85
7.82
7.79
7.77
7.66
7.39
7.37
7.36
4.44
4.43
4.41
4.39
1.45
1.43
1.42
3ao
EtO$_2$C
S
^{1}H NMR (CDCl$_3$), 400 MHz
2.01
4.11
1.05
2.04
2.04
3.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

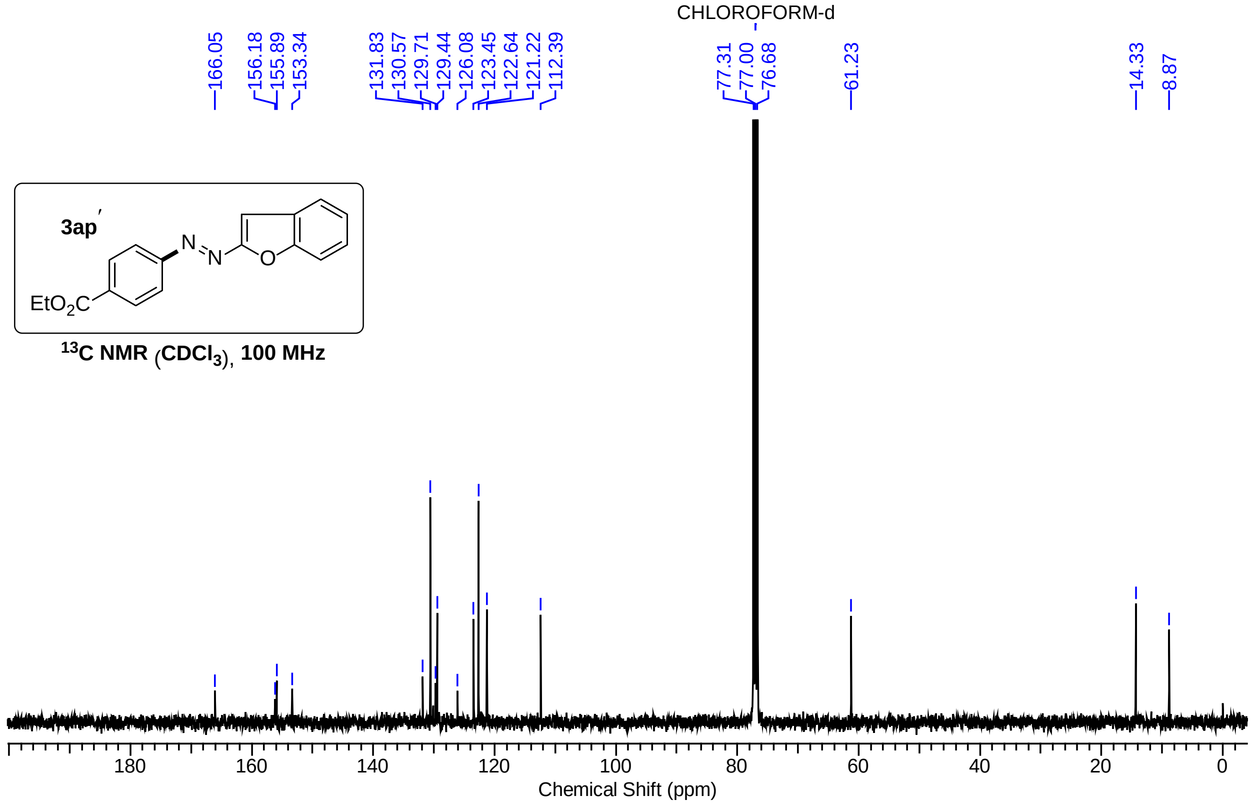

CHLOROFORM-d
166.15
142.80
140.44
138.41
130.19
129.85
126.11
124.89
124.71
123.90
122.31
120.97
77.32
77.00
76.69
61.06
14.33
3ao
EtO$_2$C
S
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
8.17
8.15
7.92
7.90
7.59
7.57
7.53
7.51
7.35
7.30
7.29
7.27
4.45
4.43
4.41
4.40
2.54
1.57
1.45
1.44
1.42
Me
3ap
O
EtO$_2$C
^{1}H NMR (CDCl$_3$), 400 MHz
2.09
2.09
1.05
1.07
1.09
1.03
2.07
3.06
3.03
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

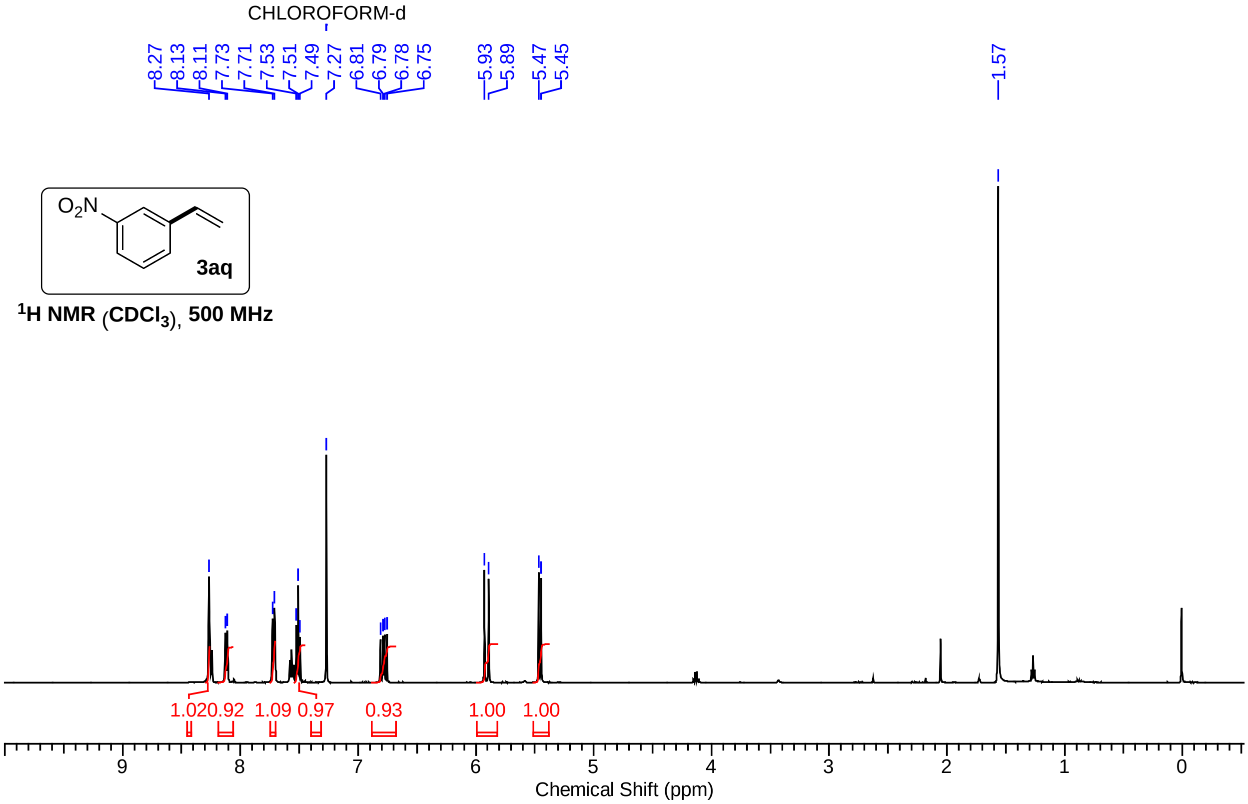

CHLOROFORM-d
166.31
149.51
135.50
130.94
129.87
129.28
126.14
125.06
122.57
119.58
113.47
111.08
85.67
77.32
77.00
76.69
61.07
14.36
9.74
Me
3ap
O
EtO$_2$C
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



^{1}H NMR (CDCl$_3$), 400 MHz

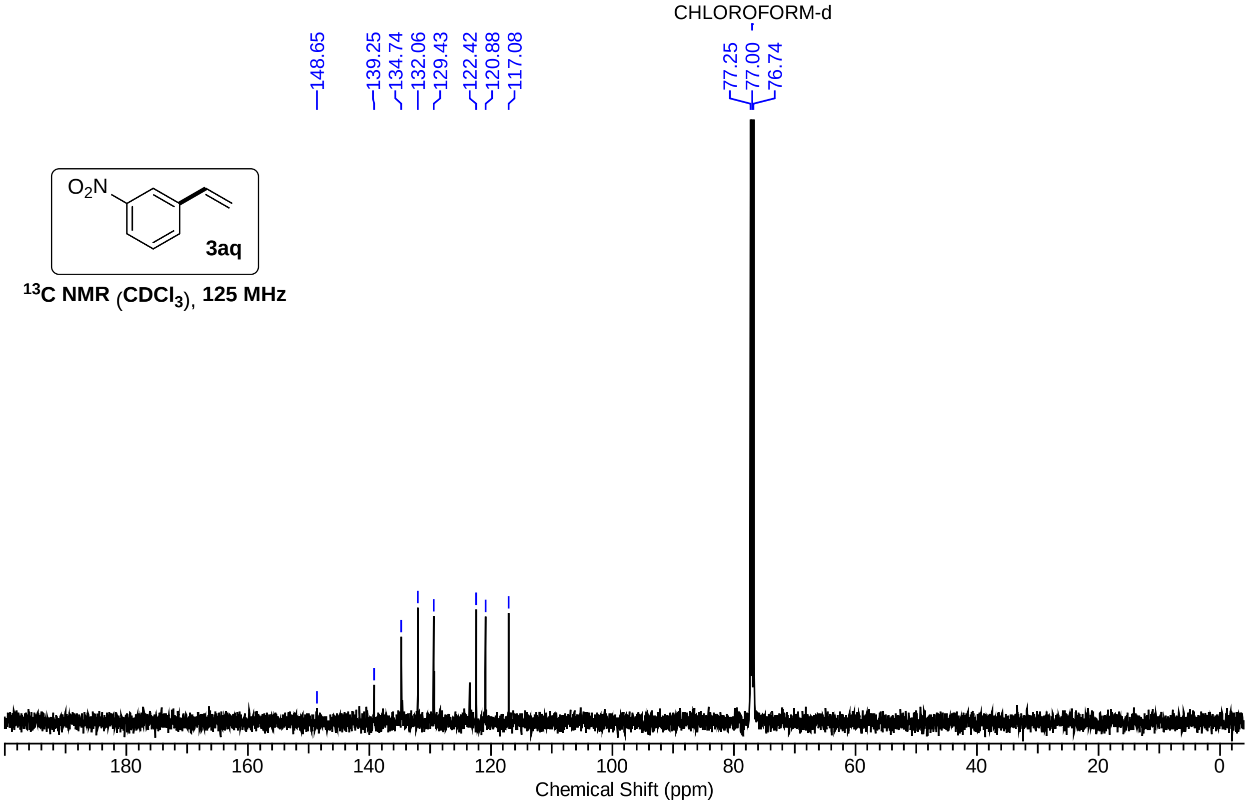


^{13}C NMR (CDCl$_3$), 100 MHz



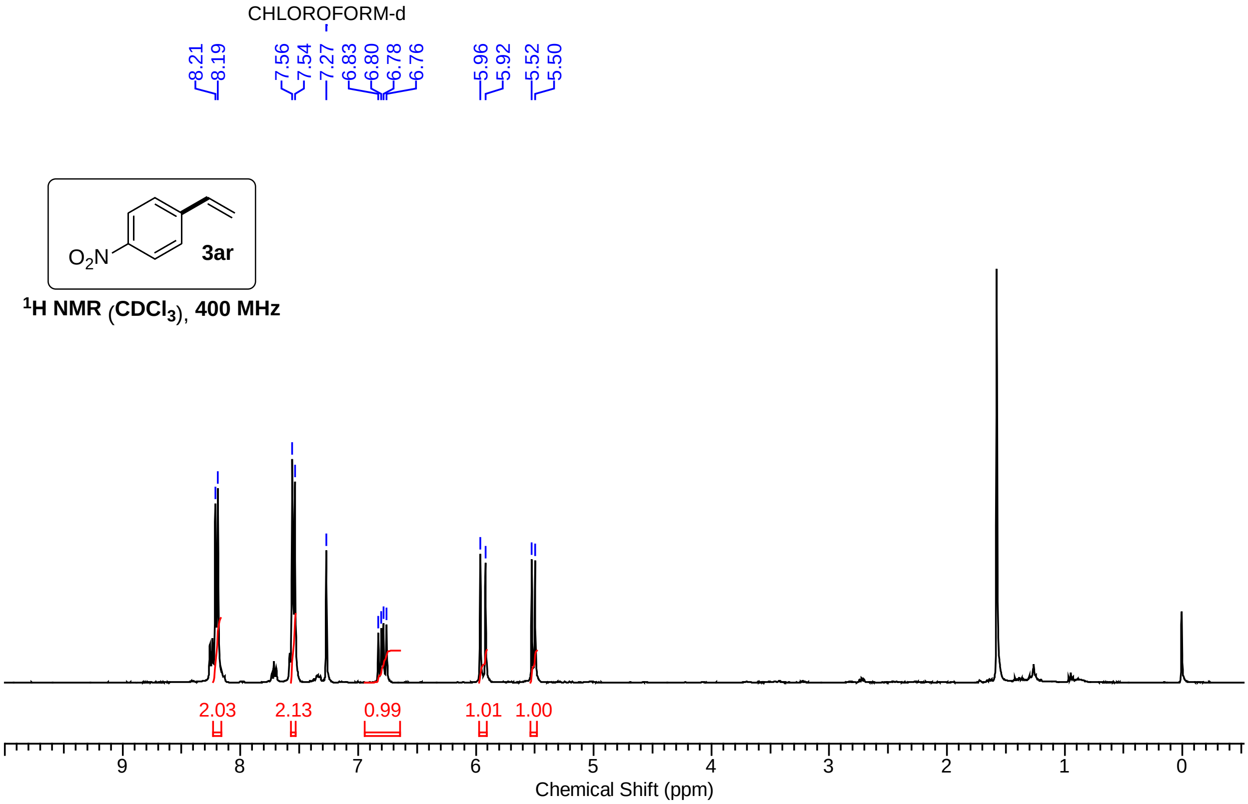
3aq

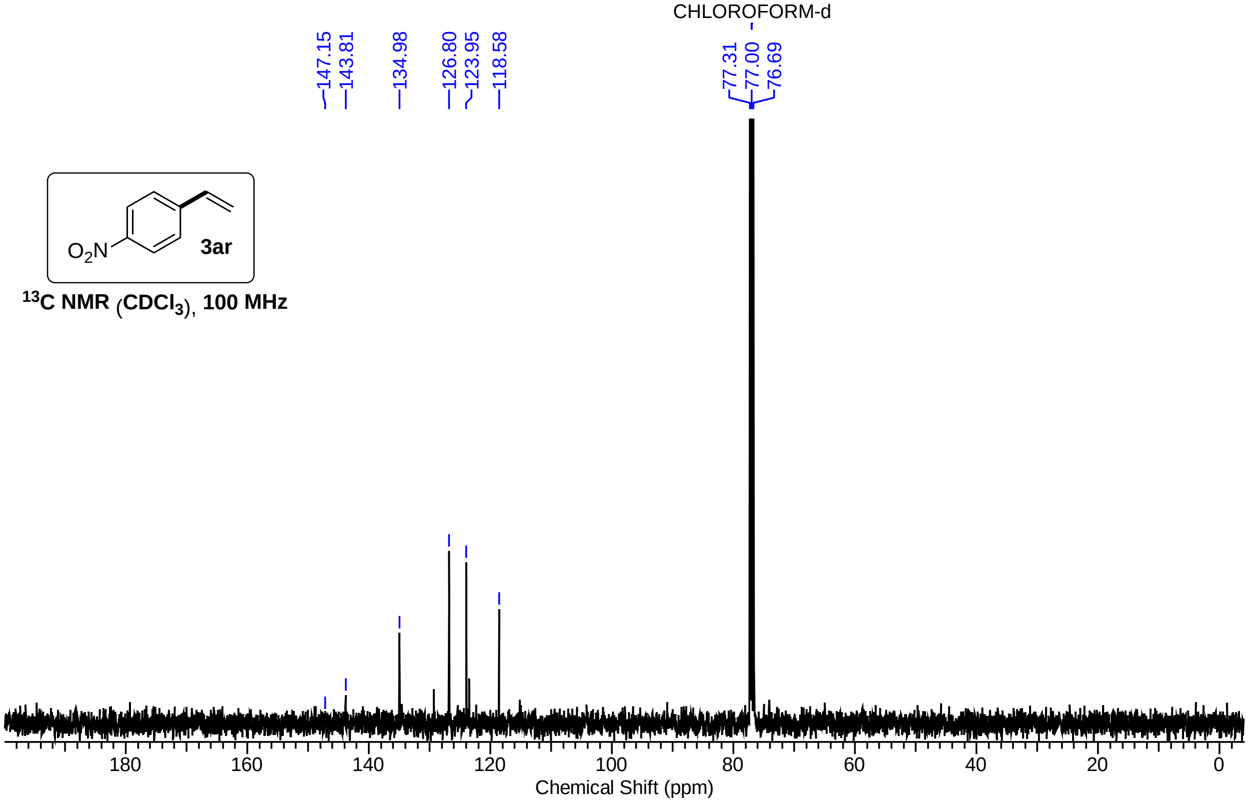
^{1}H NMR (CDCl$_3$), 500 MHz

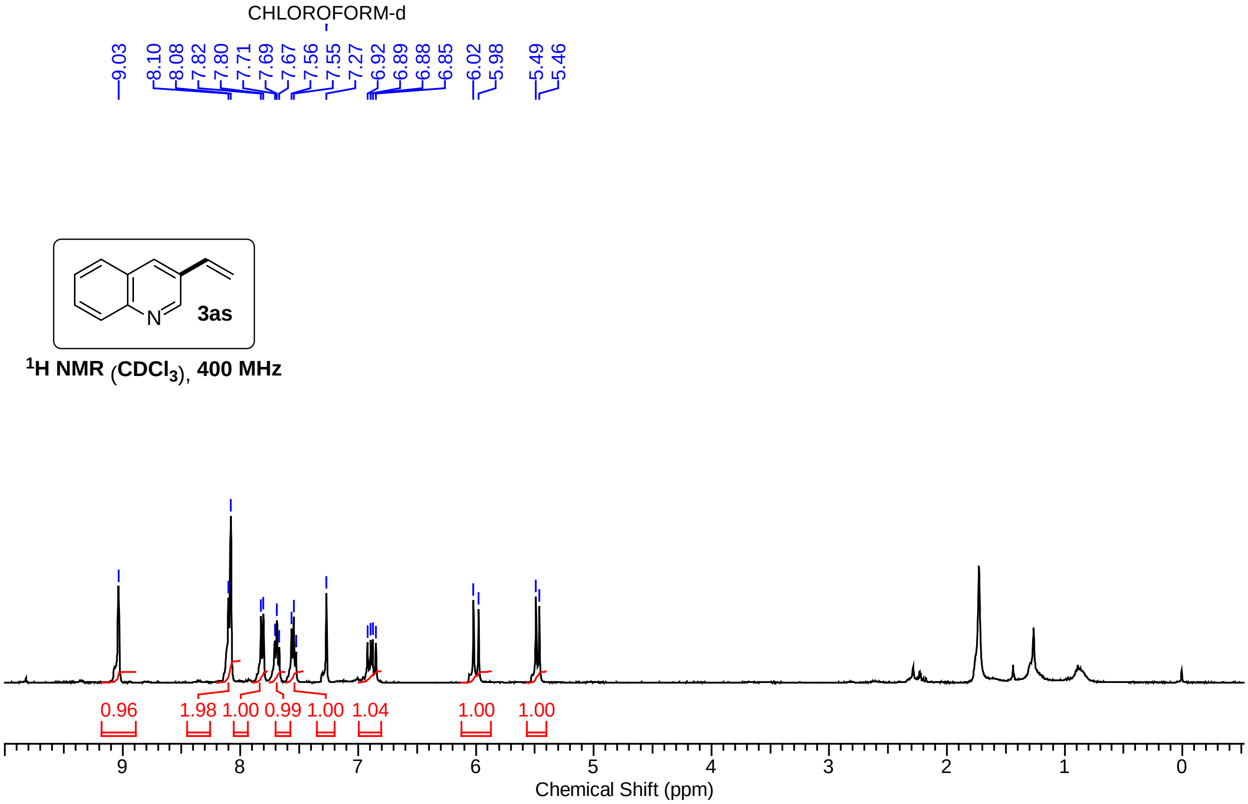


3aq

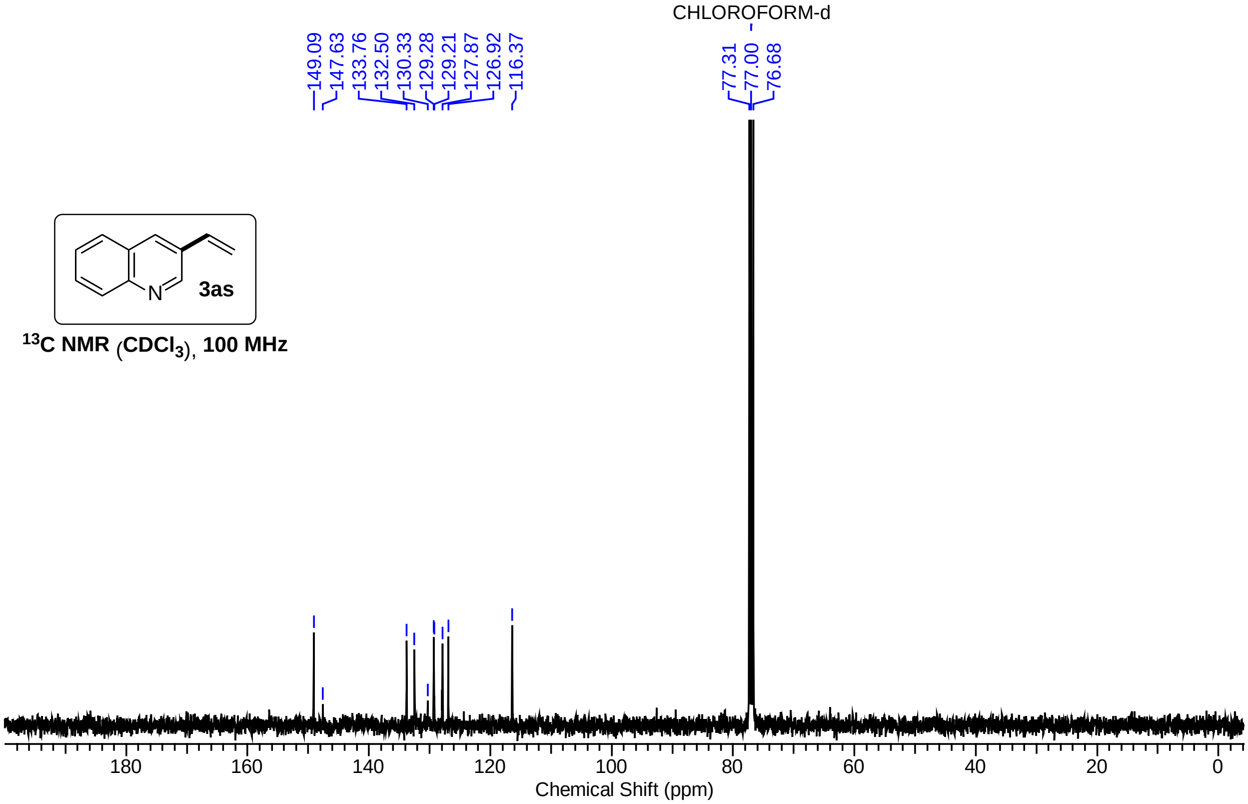
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
8.21
8.19
7.56
7.54
7.27
6.83
6.80
6.78
6.76
5.96
5.92
5.52
5.50
O_2N
3ar
^{1}H NMR (CDCl$_3$), 400 MHz
2.03
2.13
0.99
1.01
1.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

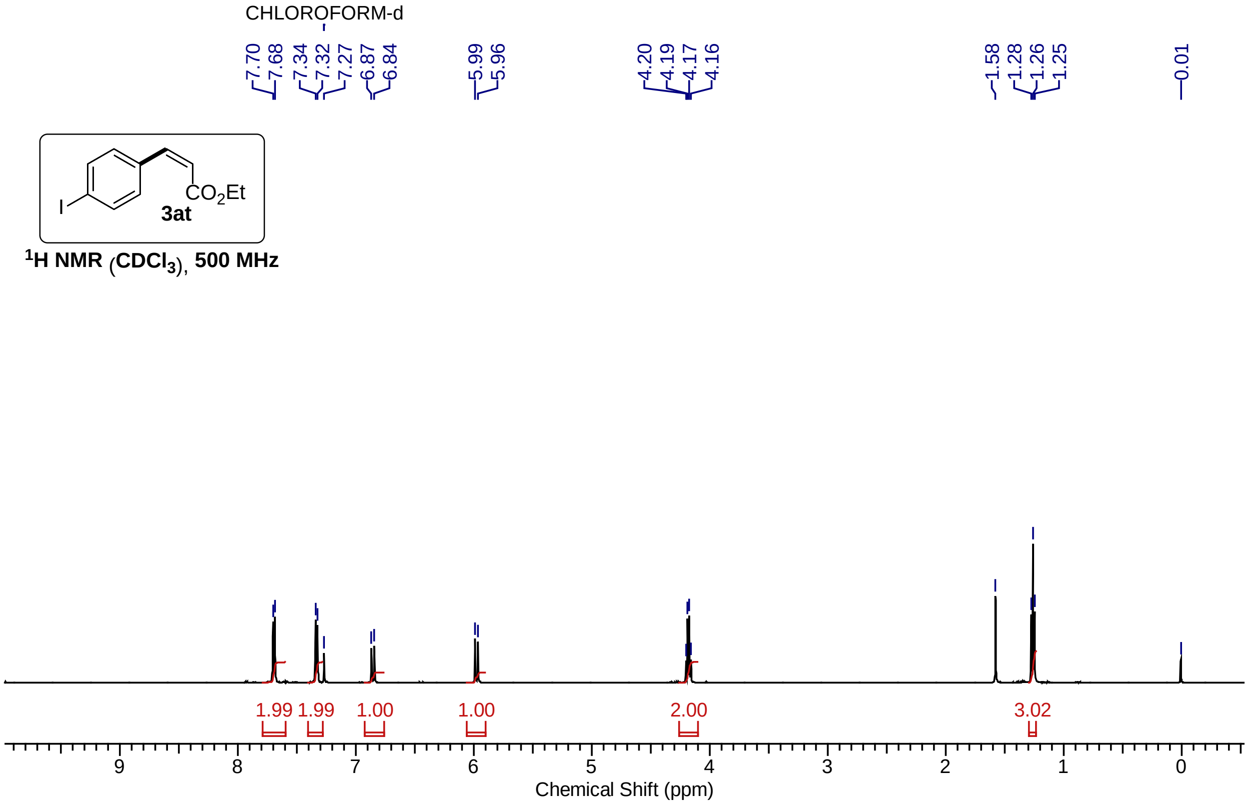

CHLOROFORM-d
147.15
143.81
134.98
126.80
123.95
118.58
77.31
77.00
76.69
O_2N
3ar
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

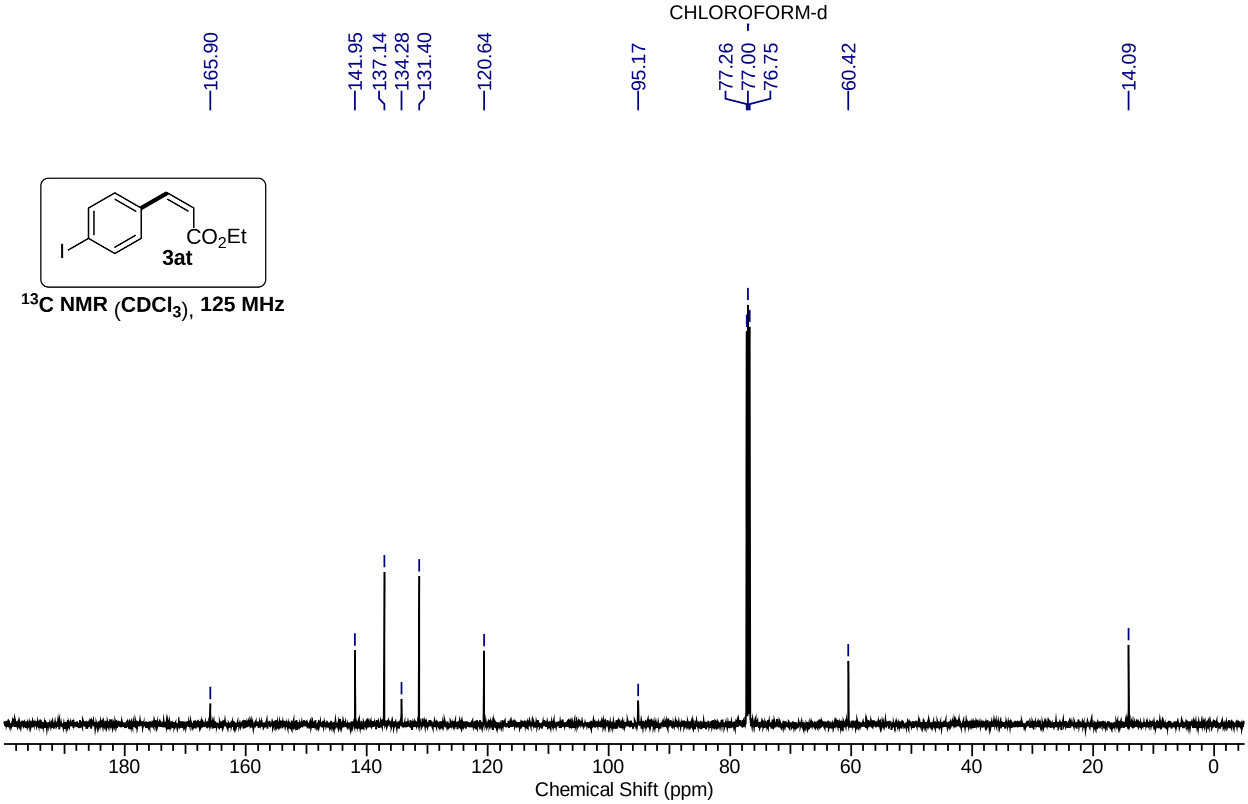


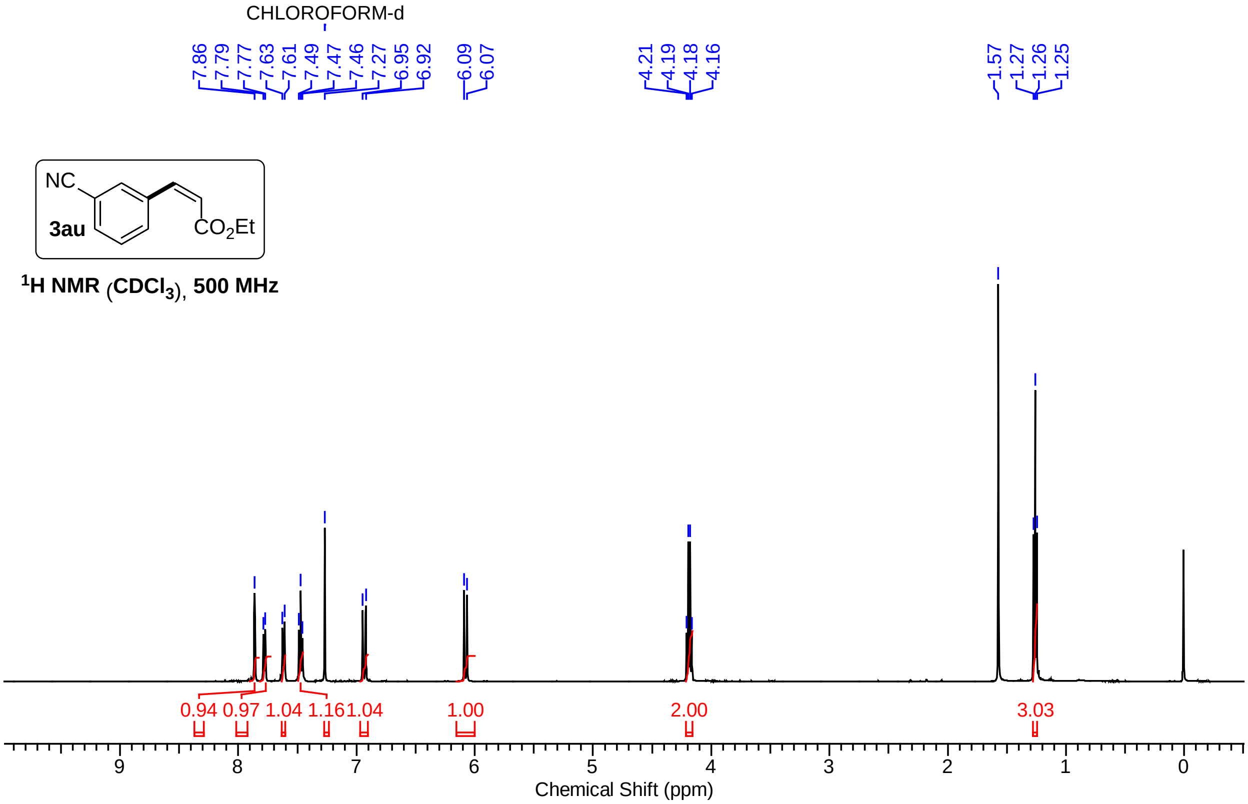
^{1}H NMR (CDCl$_3$), 400 MHz

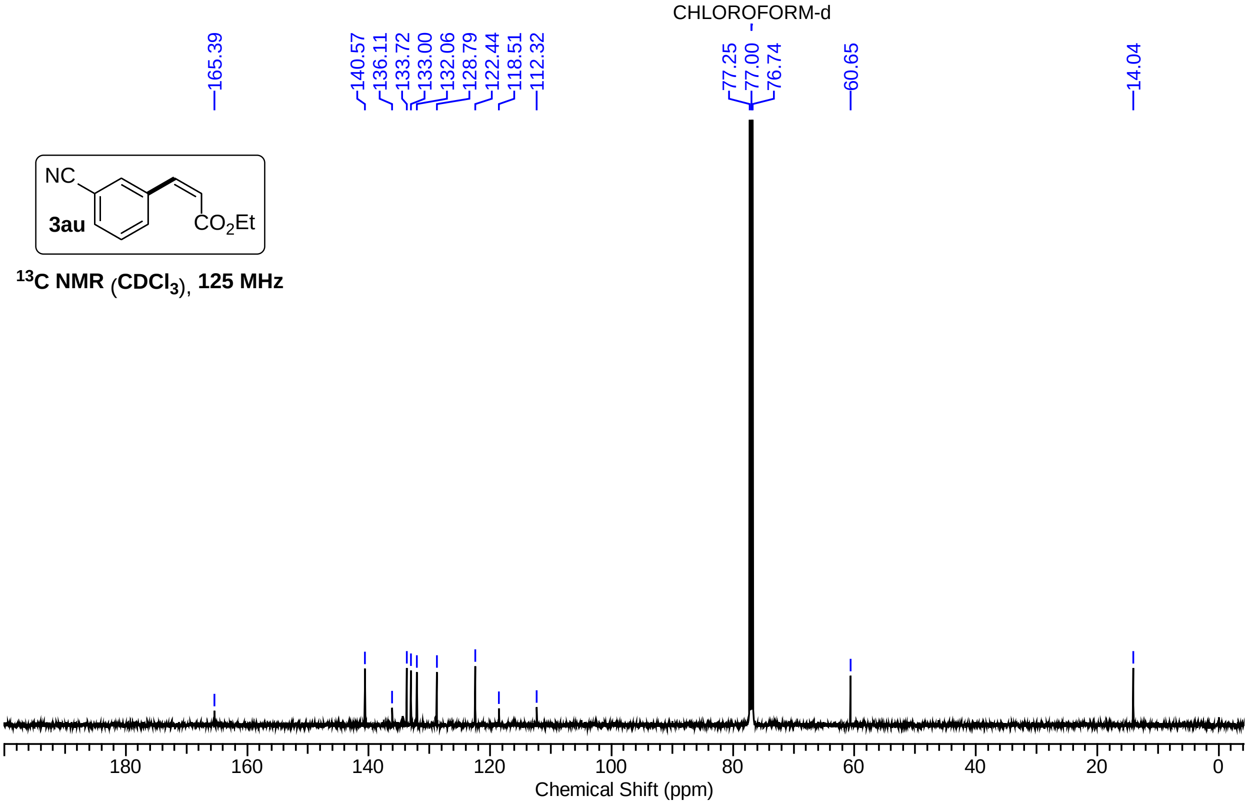


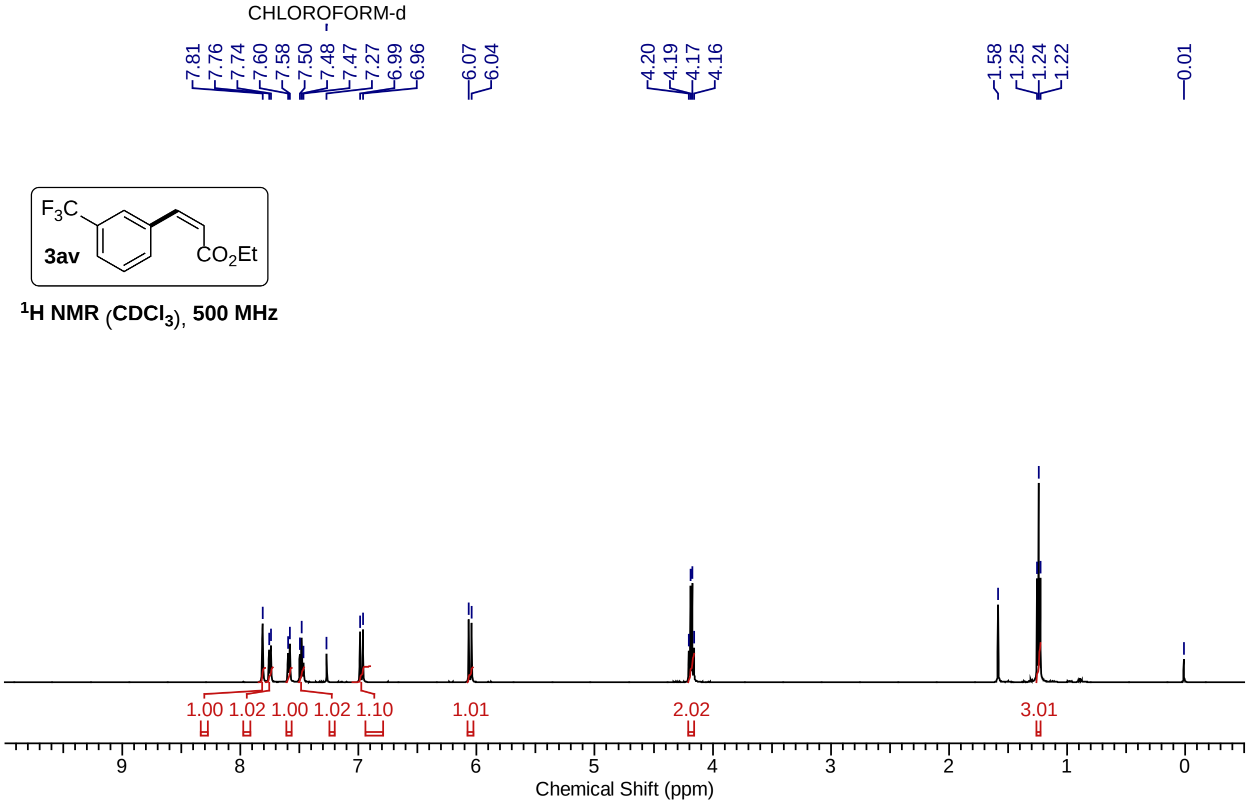
^{13}C NMR (CDCl$_3$), 100 MHz


CHLOROFORM-d
7.70
7.68
7.34
7.32
7.27
6.87
6.84
5.99
5.96
4.20
4.19
4.17
4.16
1.58
1.28
1.26
1.25
0.01
CO2Et
I
3at
1H NMR (CDCl3), 500 MHz
1.99
1.99
1.00
1.00
2.00
3.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
165.90
141.95
137.14
134.28
131.40
120.64
95.17
77.26
77.00
76.75
60.42
14.09
CO2Et
I
3at
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

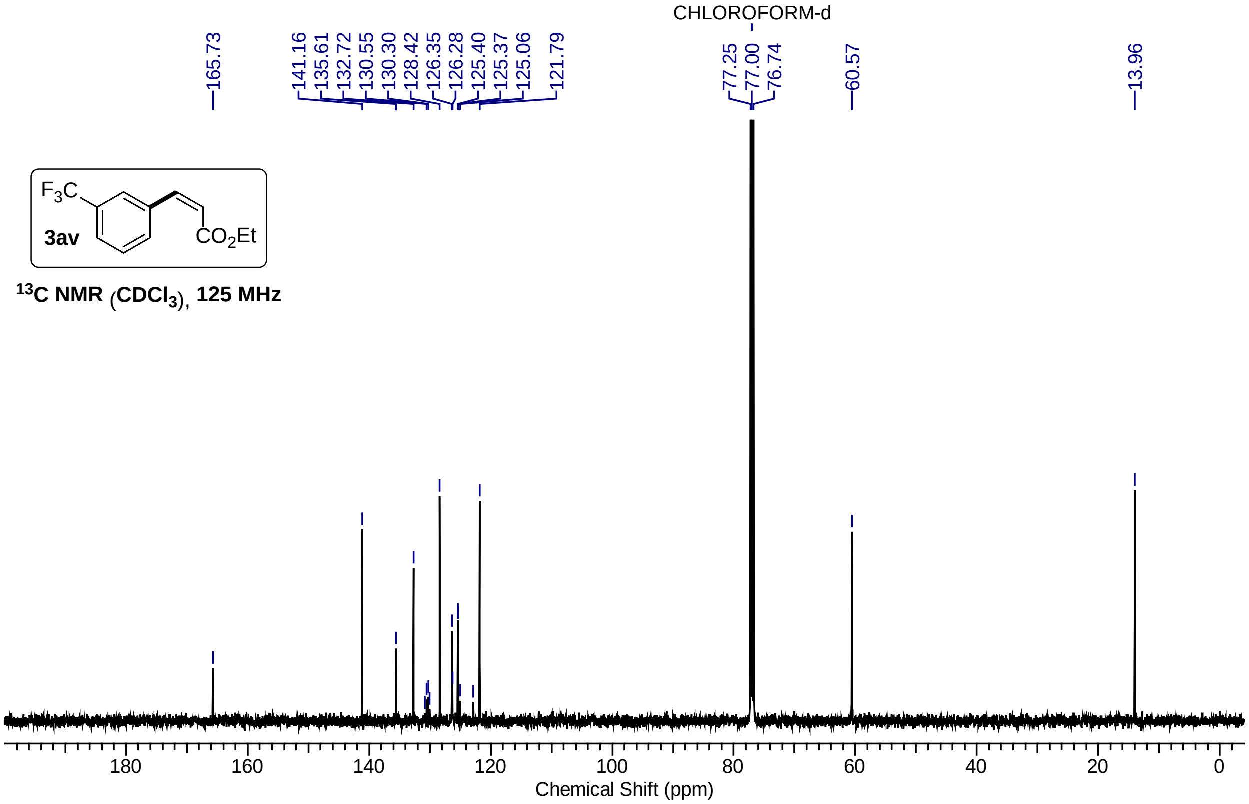

CHLOROFORM-d
7.86
7.79
7.77
7.63
7.61
7.49
7.47
7.46
7.27
6.95
6.92
6.09
6.07
4.21
4.19
4.18
4.16
1.57
1.27
1.26
1.25
NC
3au
CO2Et
1H NMR (CDCl3), 500 MHz
0.94
0.97
1.04
1.16
1.04
1.00
2.00
3.03
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
165.39
140.57
136.11
133.72
133.00
132.06
128.79
122.44
118.51
112.32
77.25
77.00
76.74
60.65
14.04
NC
3au
CO2Et
13C NMR (CDCl3), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



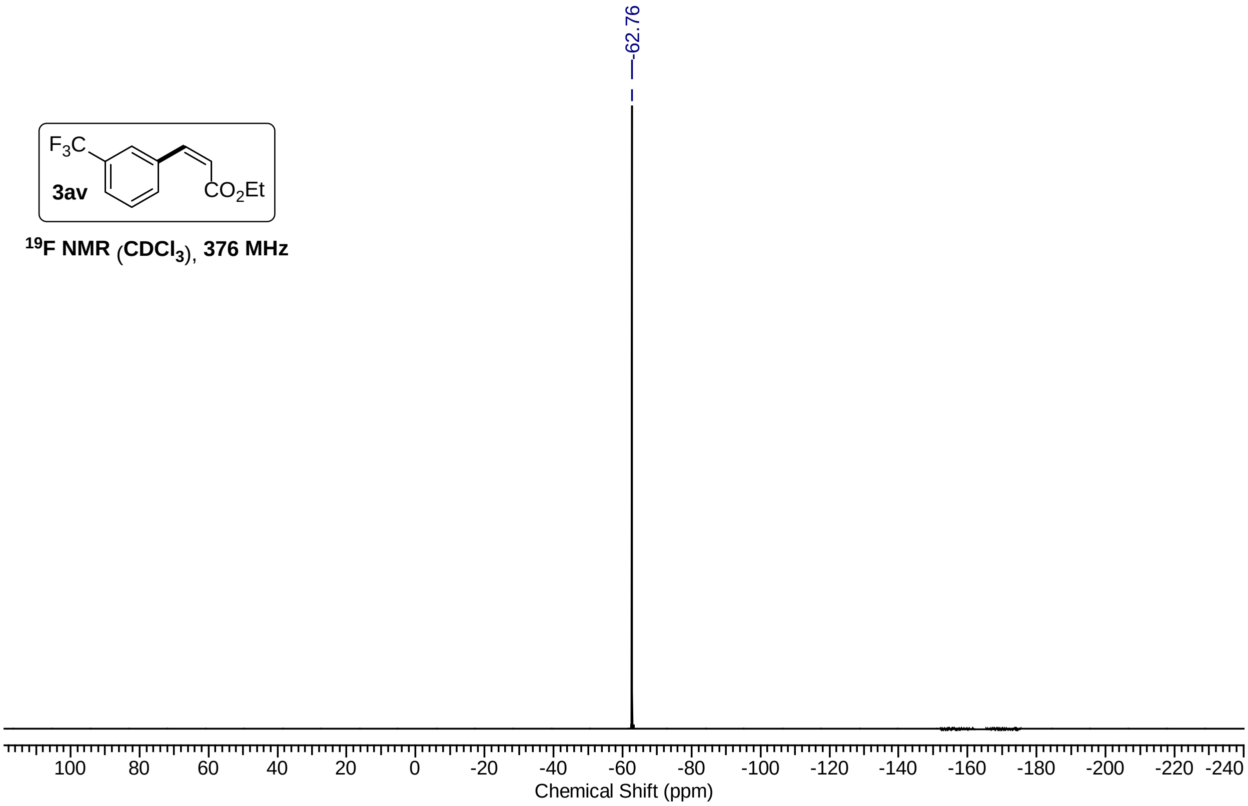
3av

^{1}H NMR (CDCl$_3$), 500 MHz

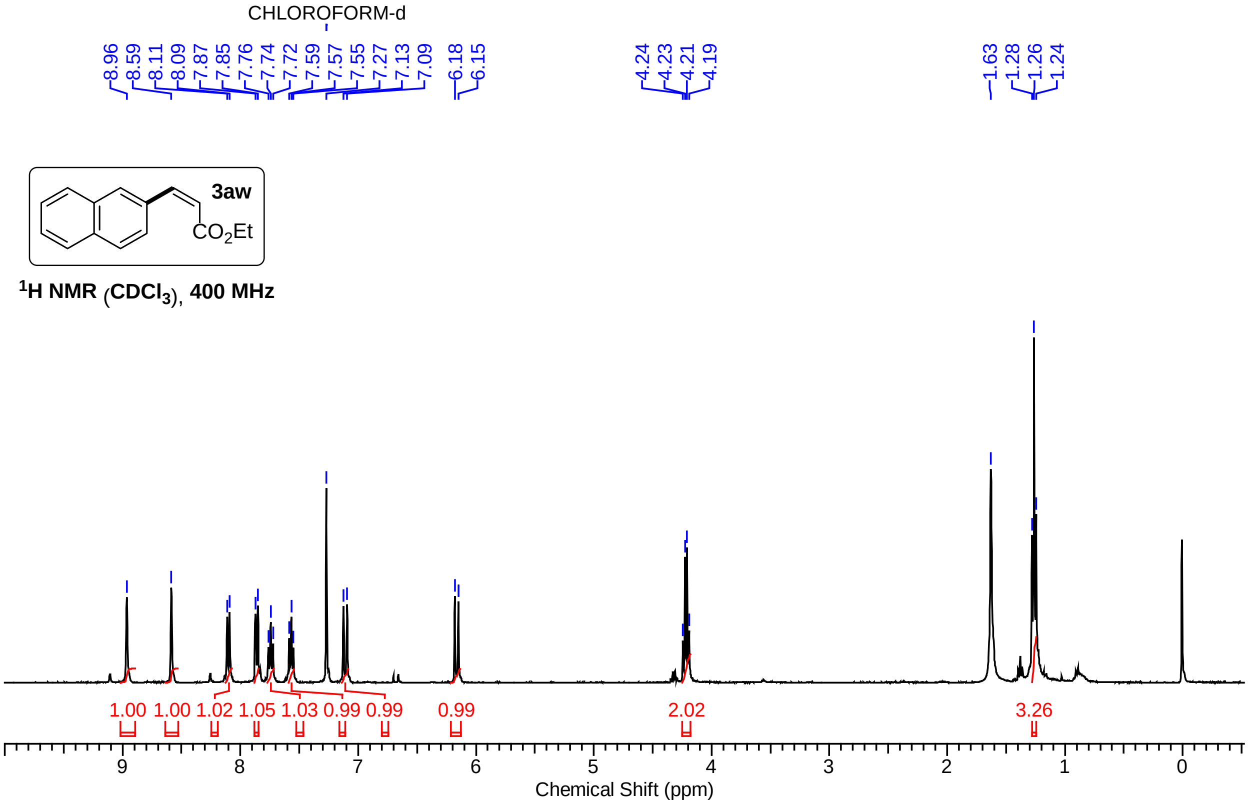


3av

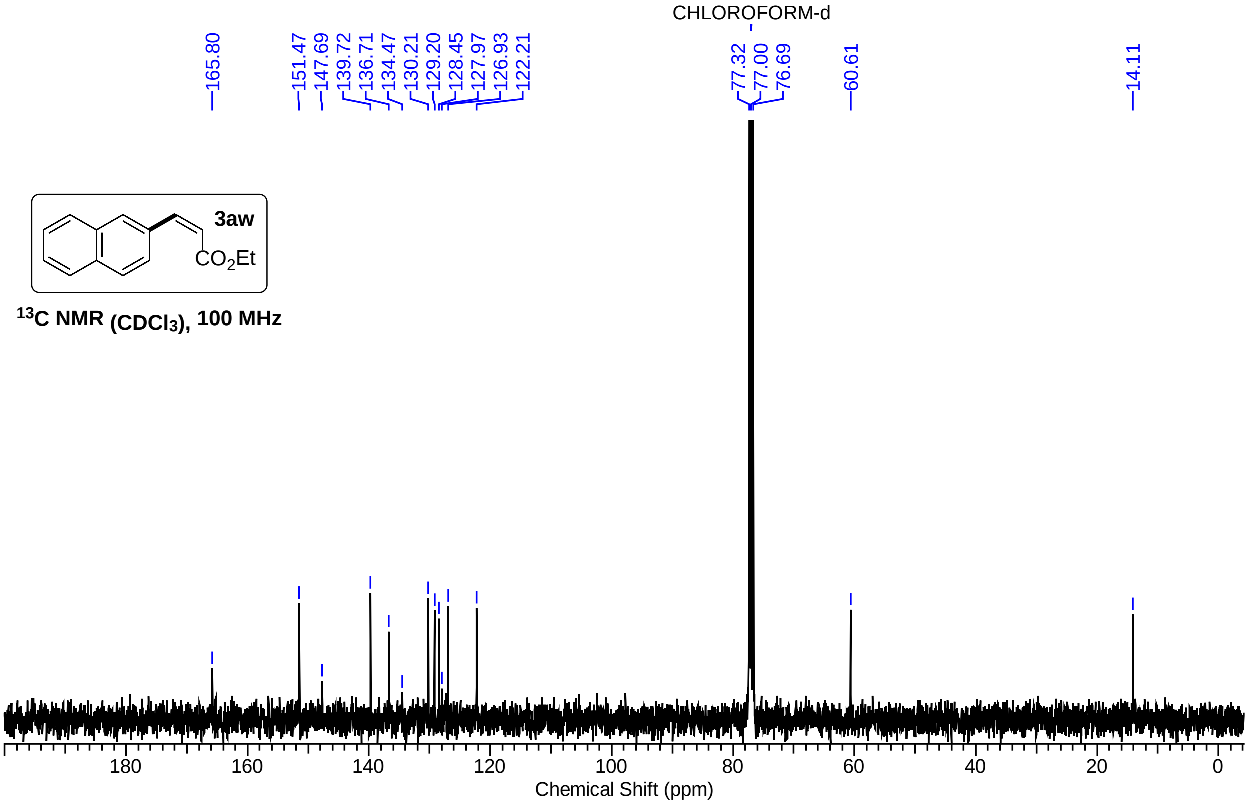
^{13}C NMR (CDCl$_3$), 125 MHz



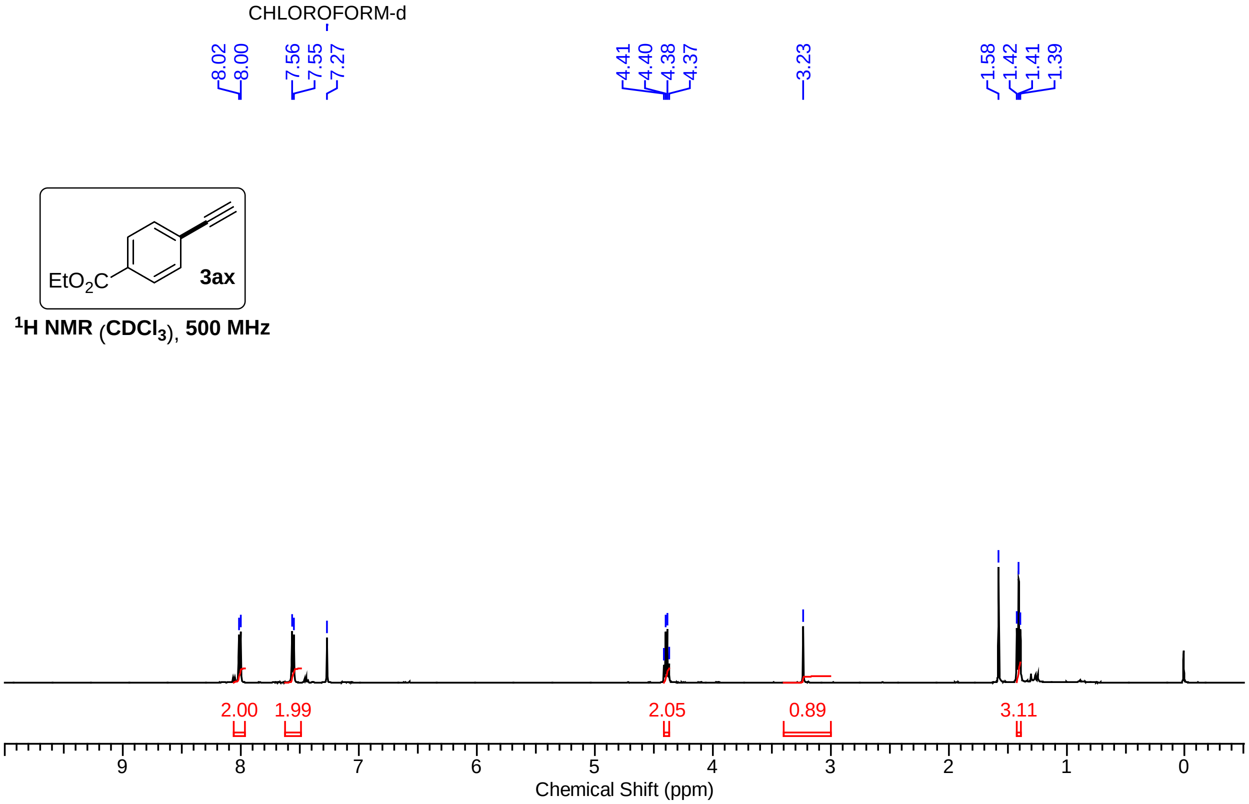
^{19}F NMR (CDCl$_3$), 376 MHz

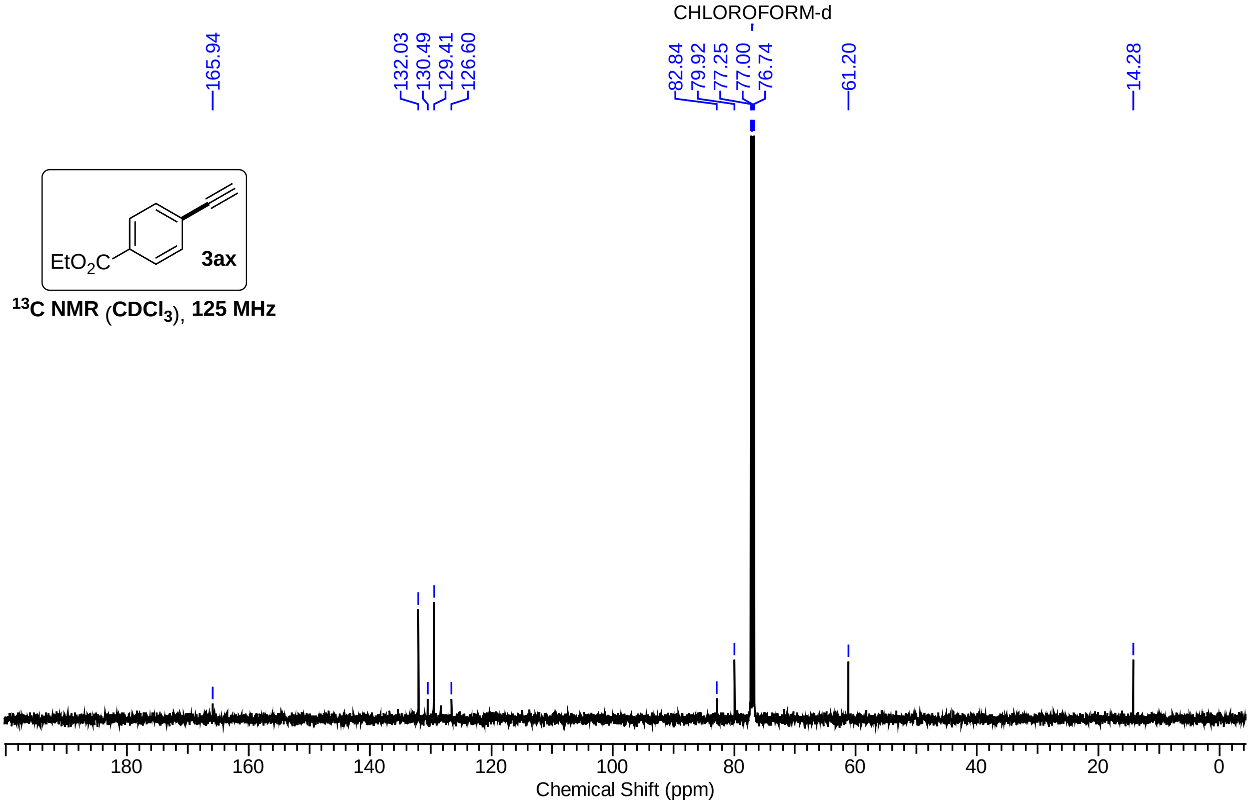


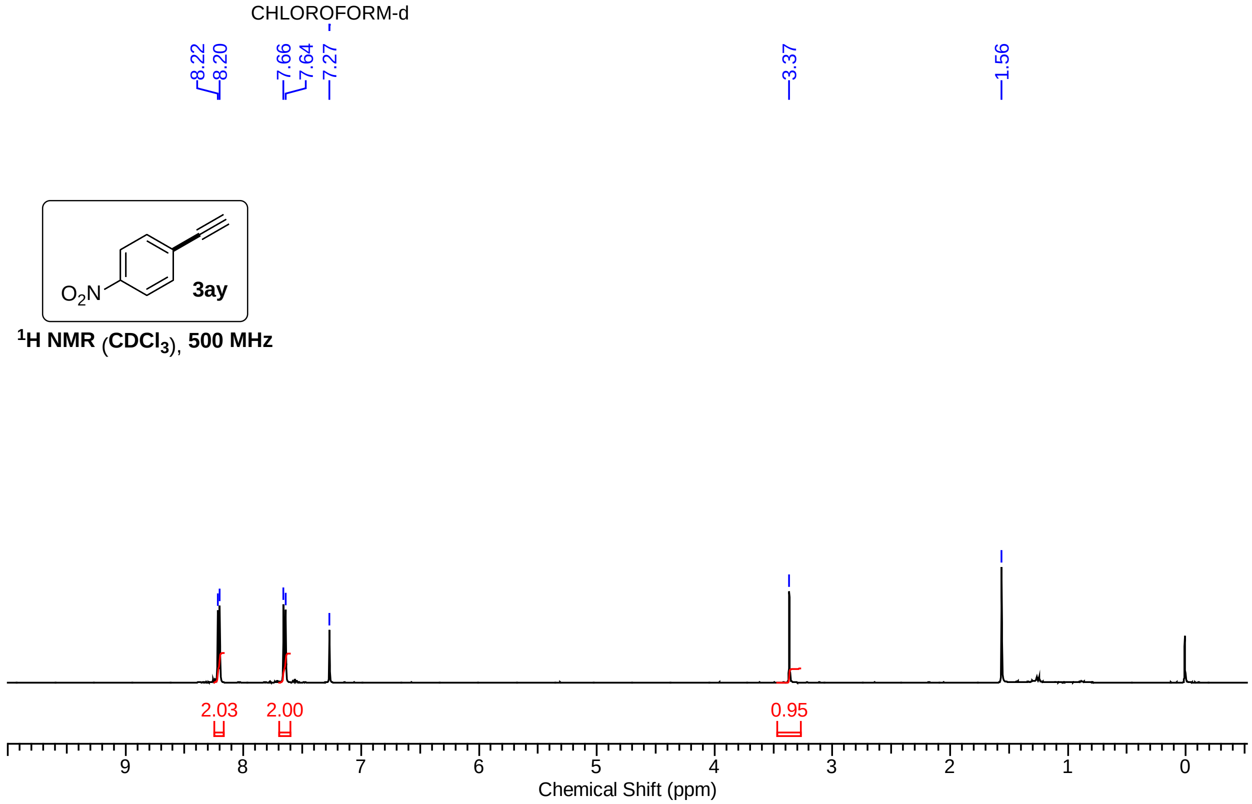
^{1}H NMR (CDCl$_3$), 400 MHz



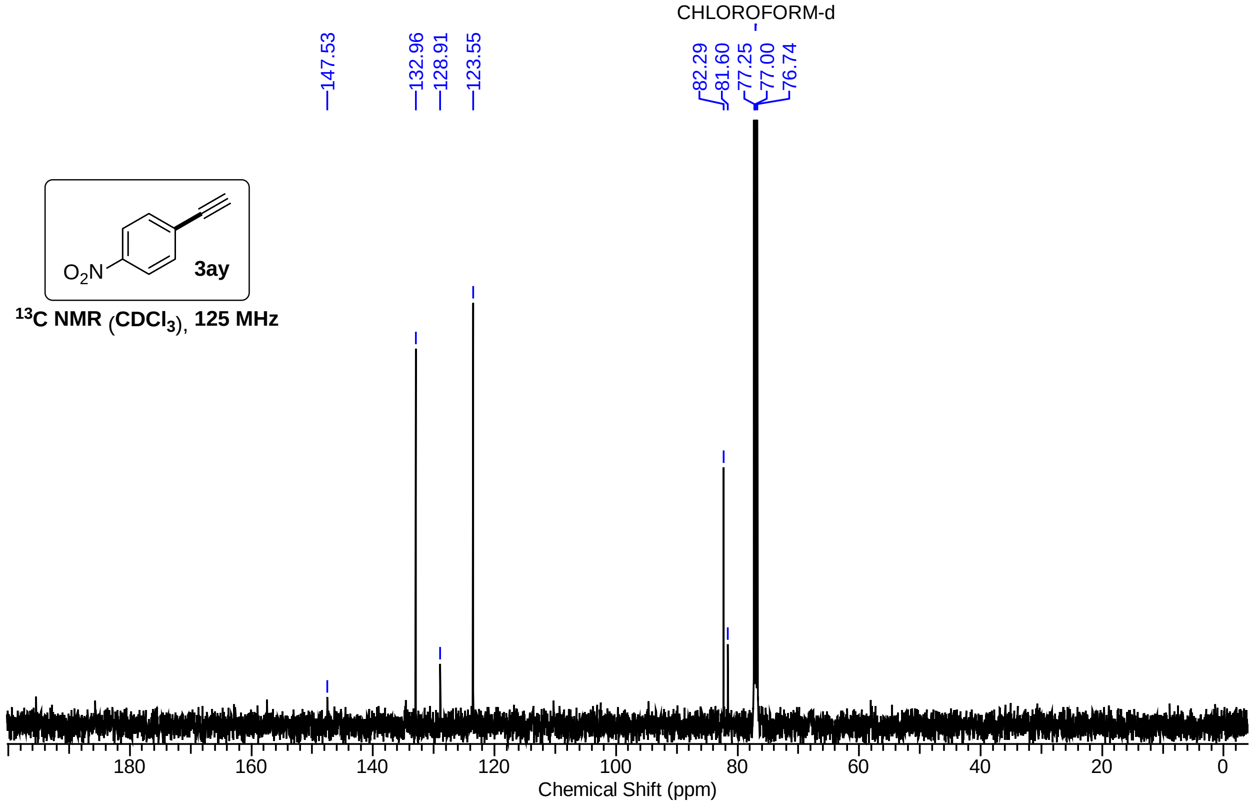
^{13}C NMR (CDCl$_3$), 100 MHz


CHLOROFORM-d
8.02
8.00
7.56
7.55
7.27
4.41
4.40
4.38
4.37
3.23
1.58
1.42
1.41
1.39
EtO$_2$C
3ax
^{1}H NMR (CDCl$_3$), 500 MHz
2.00
1.99
2.05
0.89
3.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

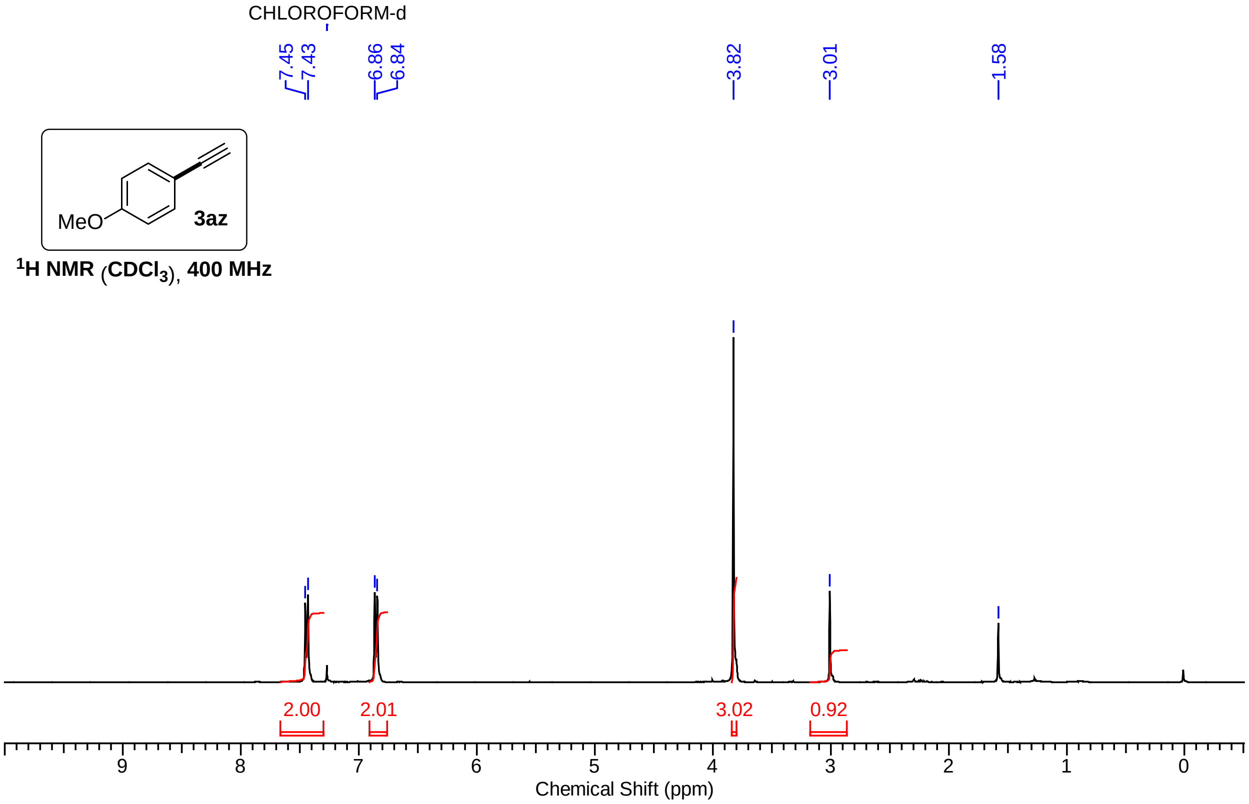

CHLOROFORM-d
165.94
132.03
130.49
129.41
126.60
82.84
79.92
77.25
77.00
76.74
61.20
14.28
EtO$_2$C
3ax
^{13}C NMR (CDCl$_3$), 125 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

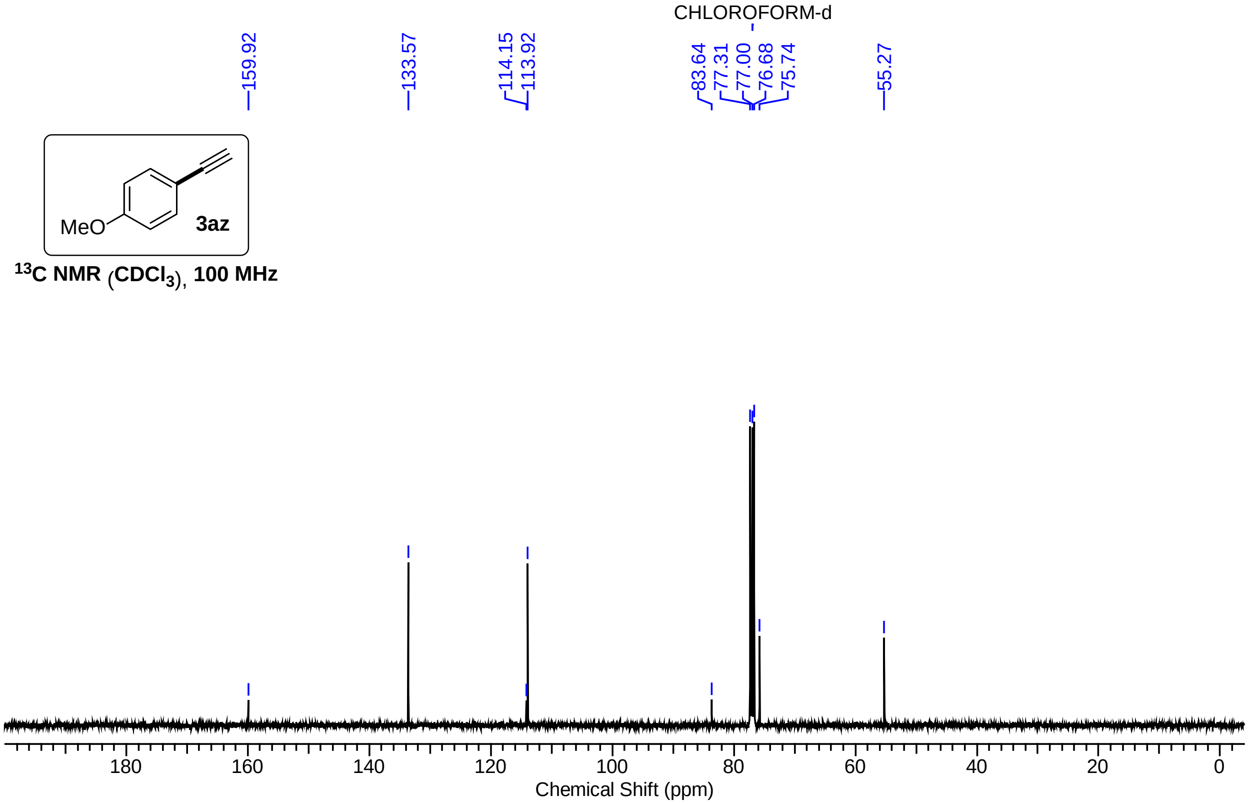


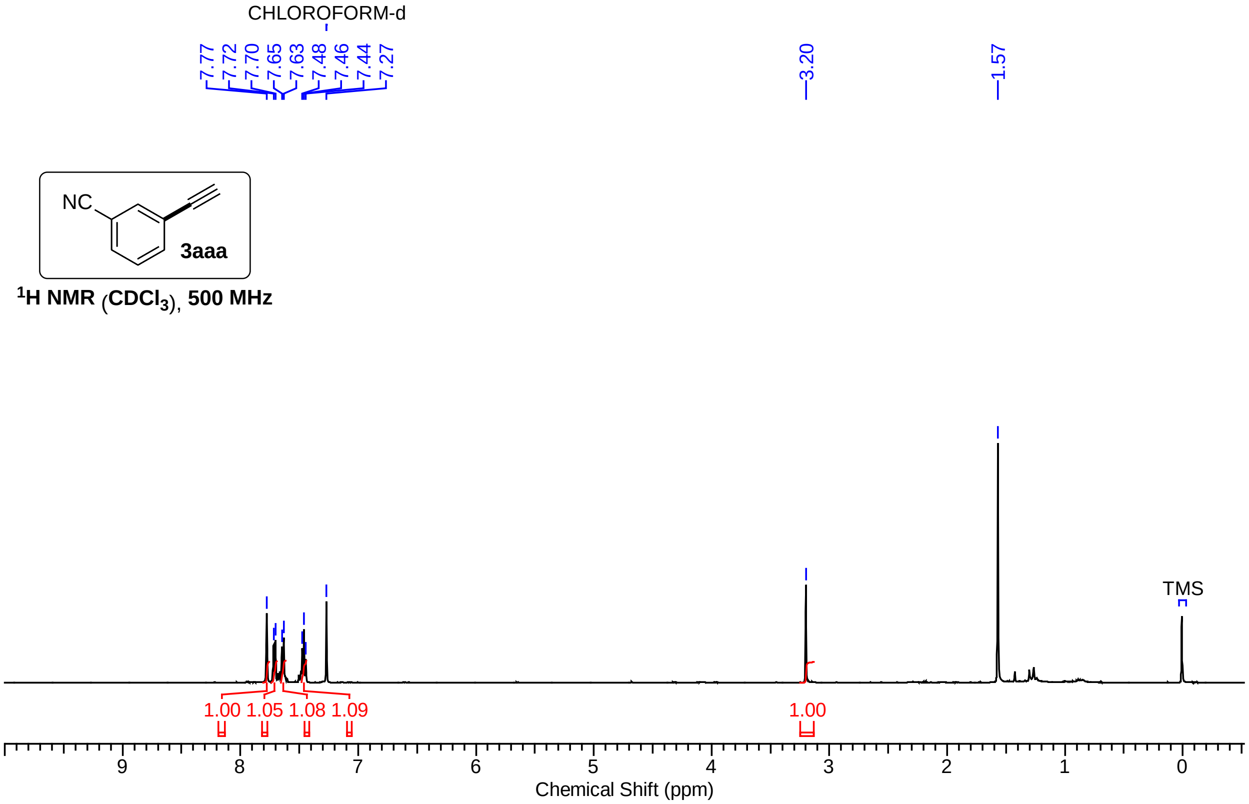
^{1}H NMR (CDCl$_3$), 500 MHz



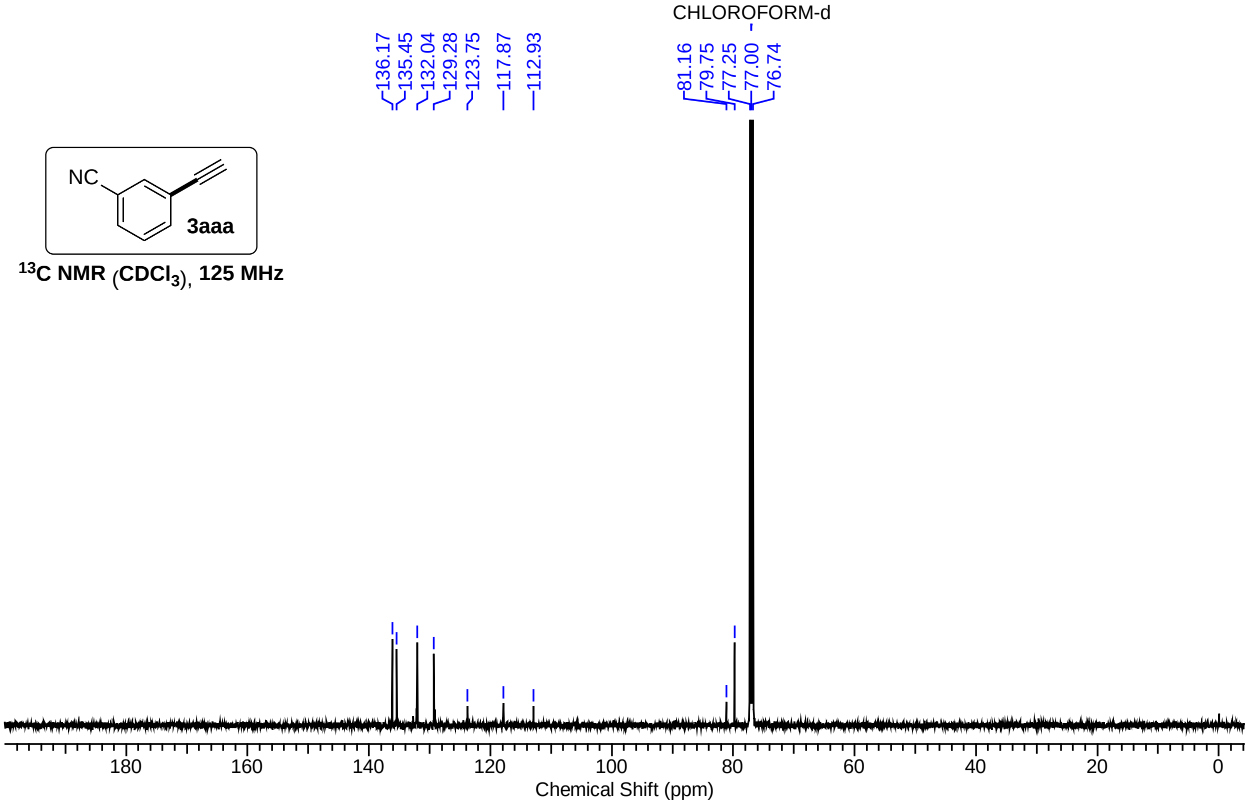
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
7.45
7.43
6.86
6.84
3.82
3.01
1.58
MeO
3az
^{1}H NMR (CDCl$_3$), 400 MHz
2.00
2.01
3.02
0.92
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

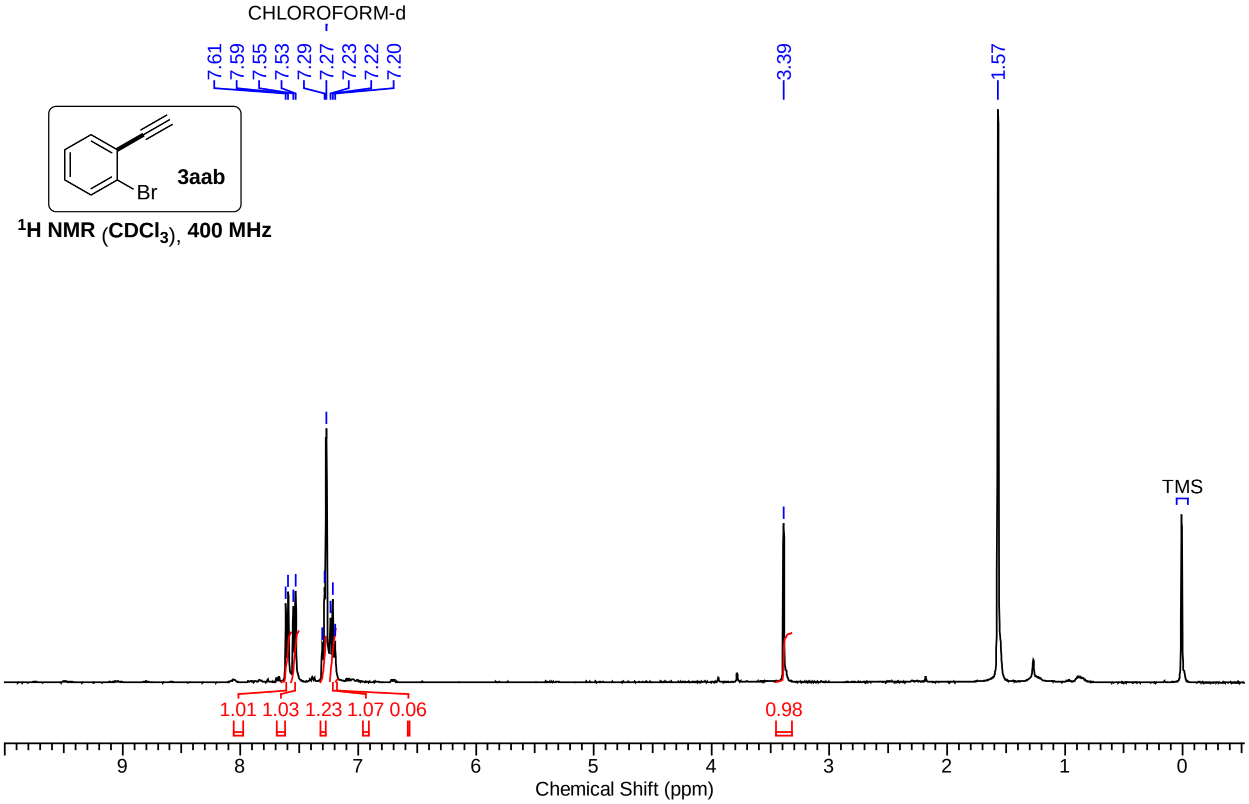

CHLOROFORM-d
159.92
133.57
114.15
113.92
83.64
77.31
77.00
76.68
75.74
55.27
MeO
3az
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

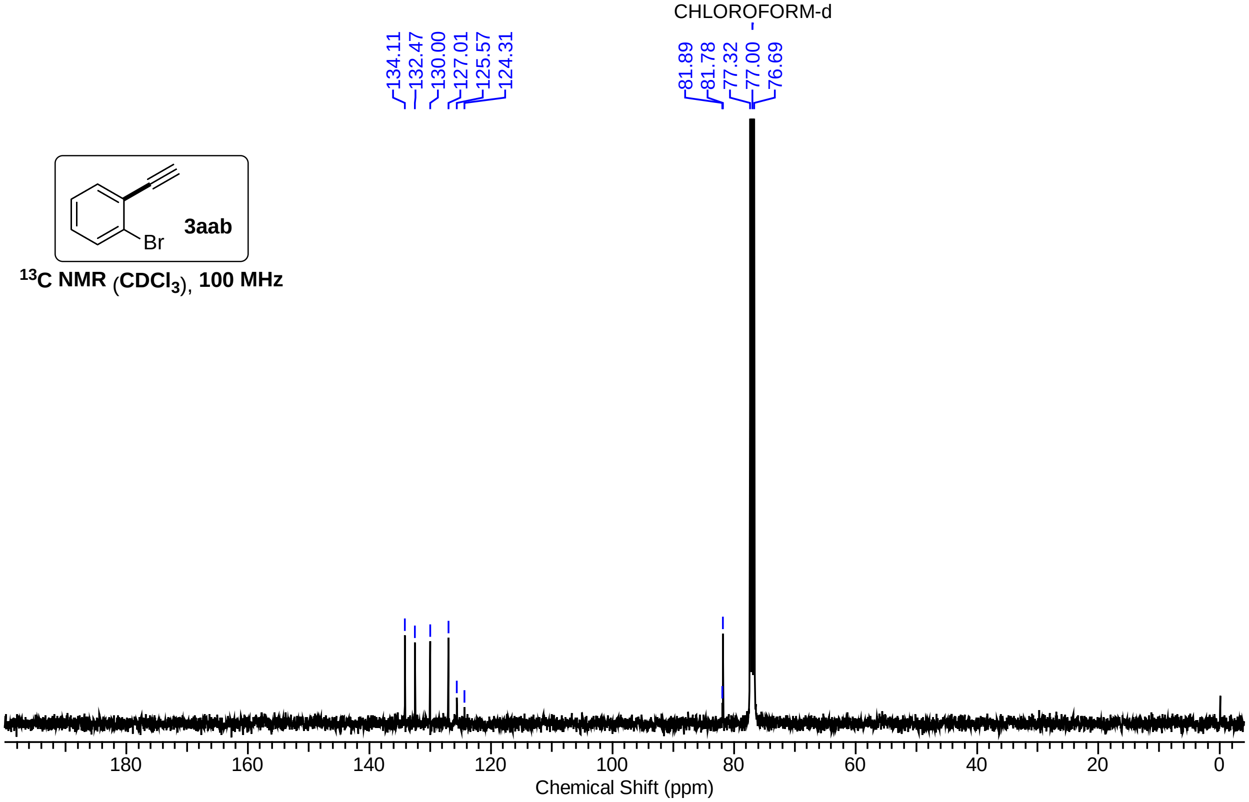


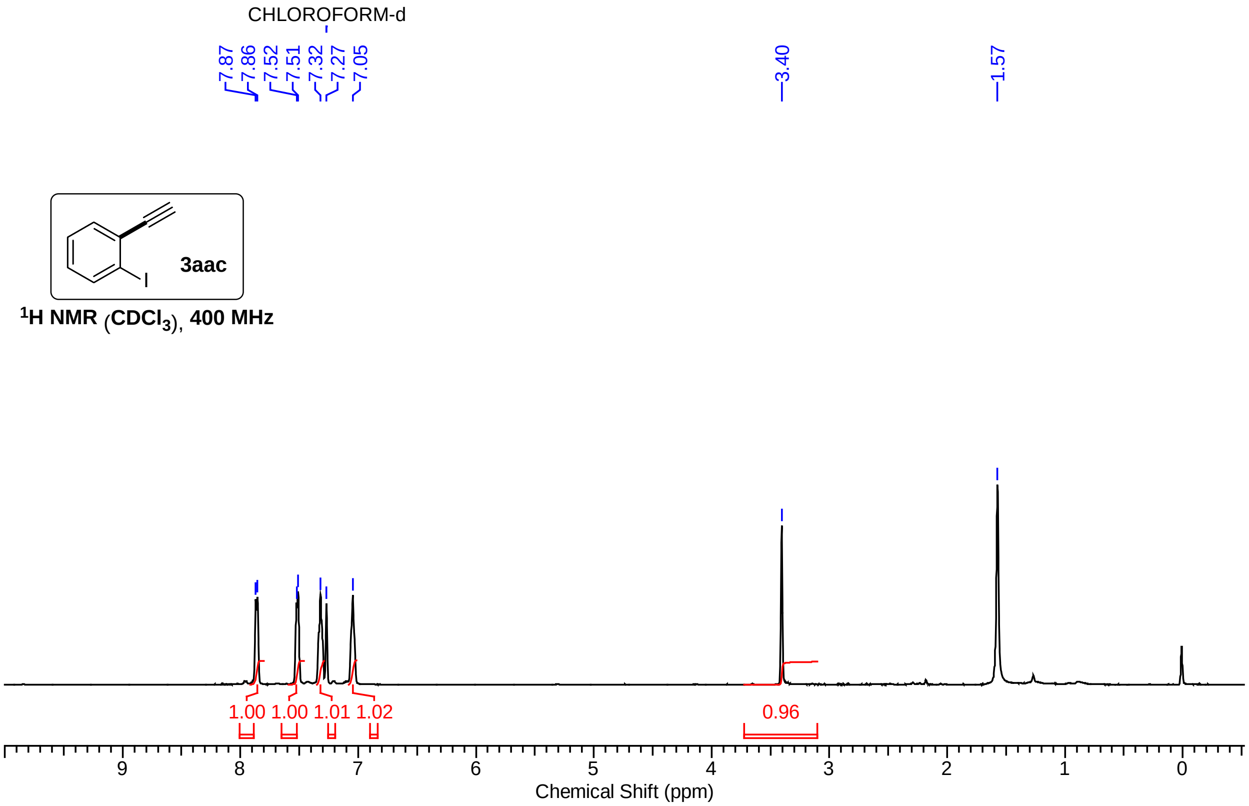
^{1}H NMR (CDCl$_3$), 500 MHz

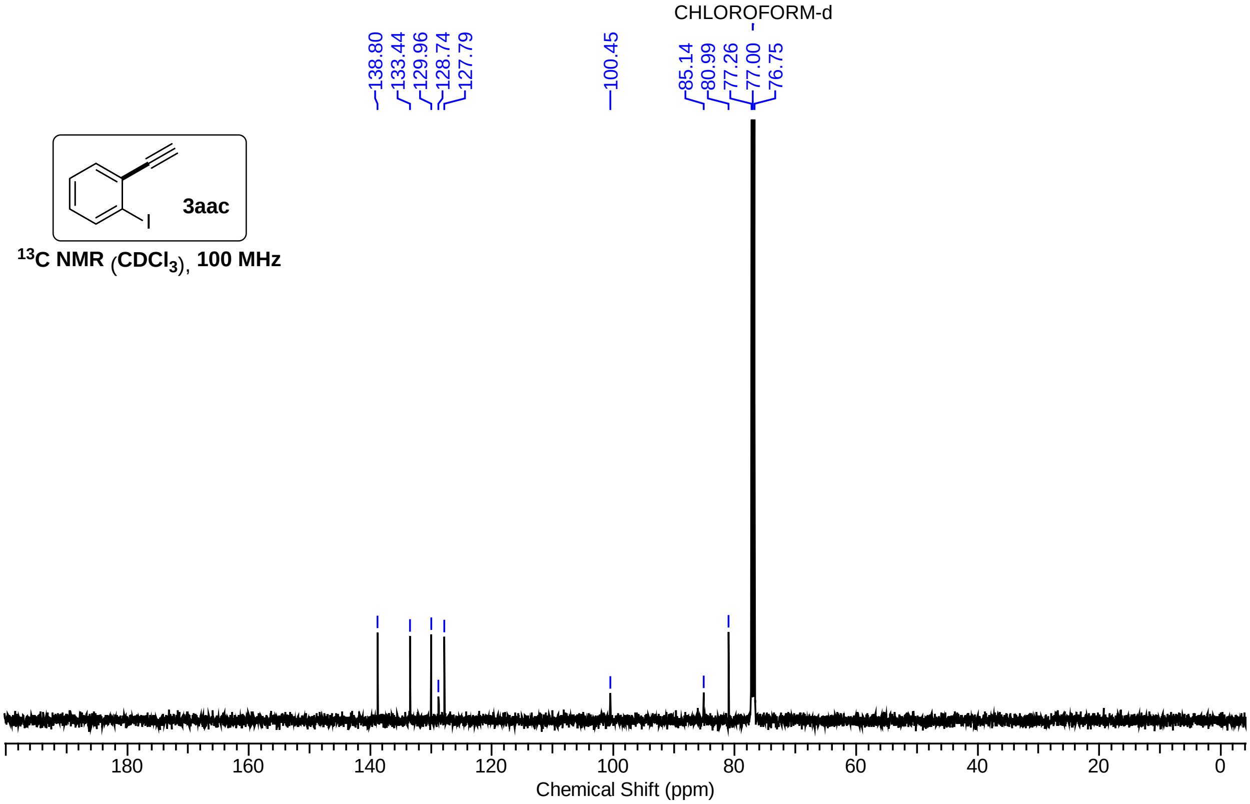


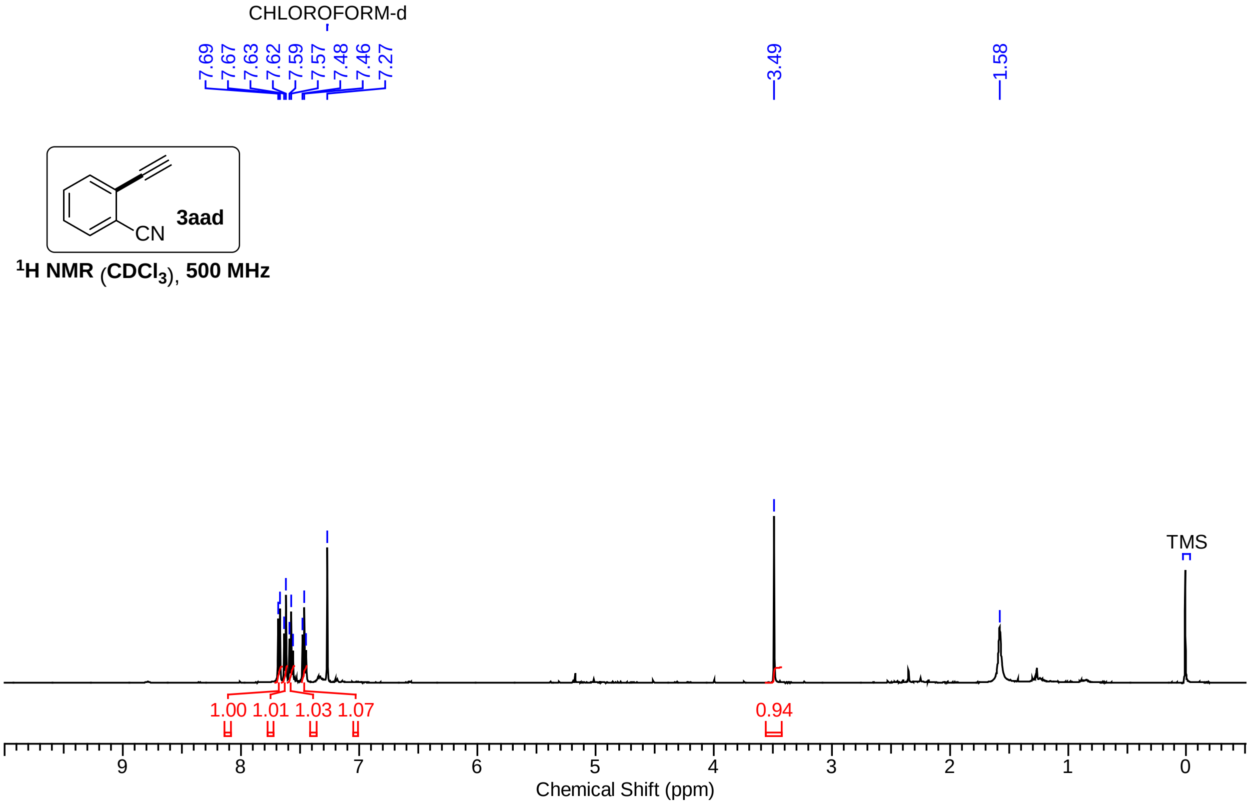
^{13}C NMR (CDCl$_3$), 125 MHz


CHLOROFORM-d
7.61
7.59
7.55
7.53
7.29
7.27
7.23
7.22
7.20
3.39
1.57
3aab
Br
^{1}H NMR (CDCl$_3$), 400 MHz
TMS
1.01
1.03
1.23
1.07
0.06
0.98
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
134.11
132.47
130.00
127.01
125.57
124.31
81.89
81.78
77.32
77.00
76.69
3aab
Br
^{13}C NMR (CDCl$_3$), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

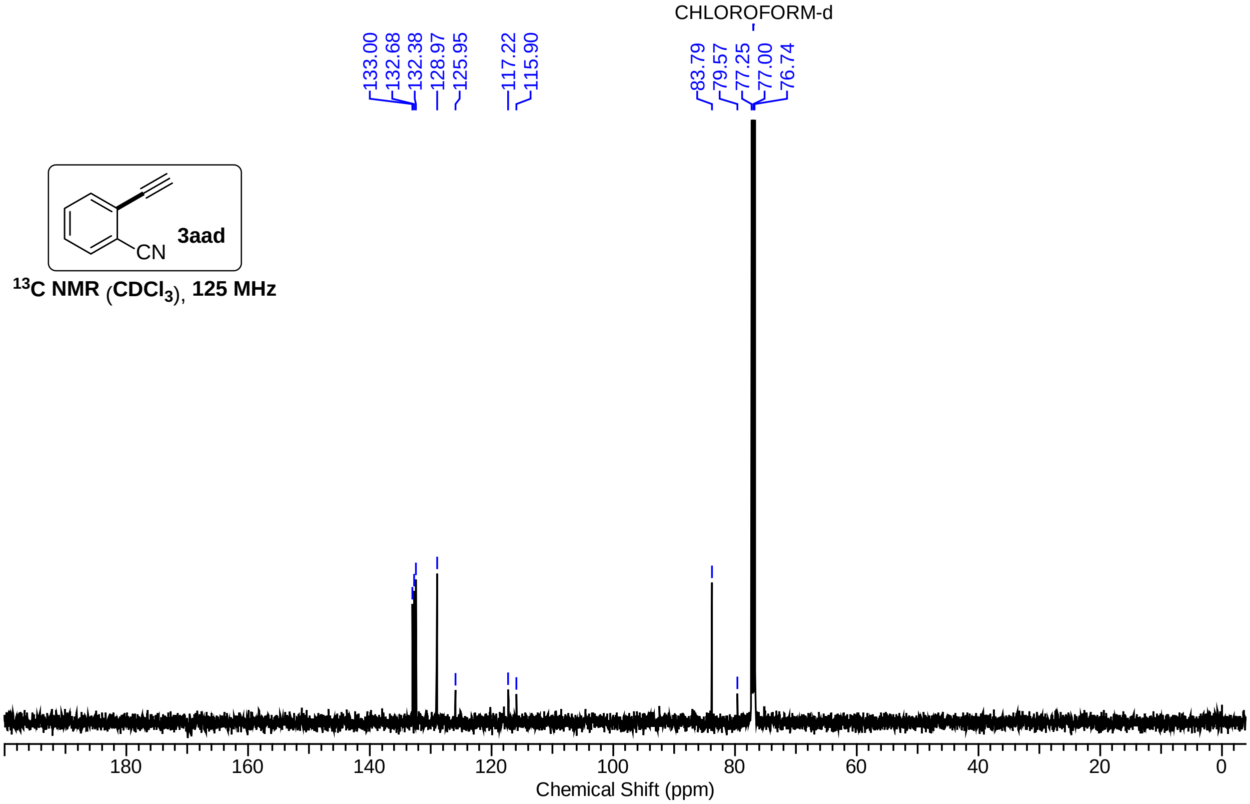

CHLOROFORM-d
7.87
7.86
7.52
7.51
7.32
7.27
7.05
3.40
1.57
3aac
1H NMR (CDCl3), 400 MHz
1.00
1.00
1.01
1.02
0.96
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CHLOROFORM-d
138.80
133.44
129.96
128.74
127.79
100.45
85.14
80.99
77.26
77.00
76.75
3aac
13C NMR (CDCl3), 100 MHz
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



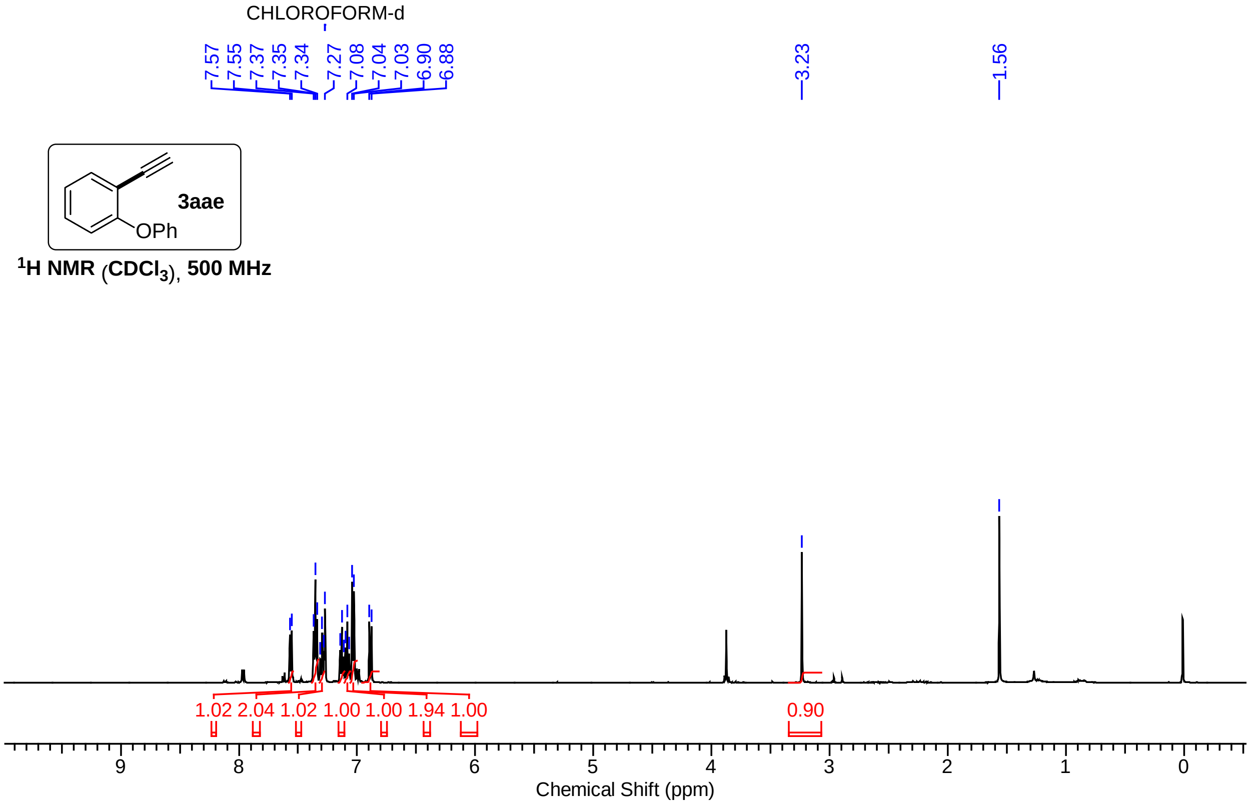
3aad

^{1}H NMR (CDCl$_3$), 500 MHz



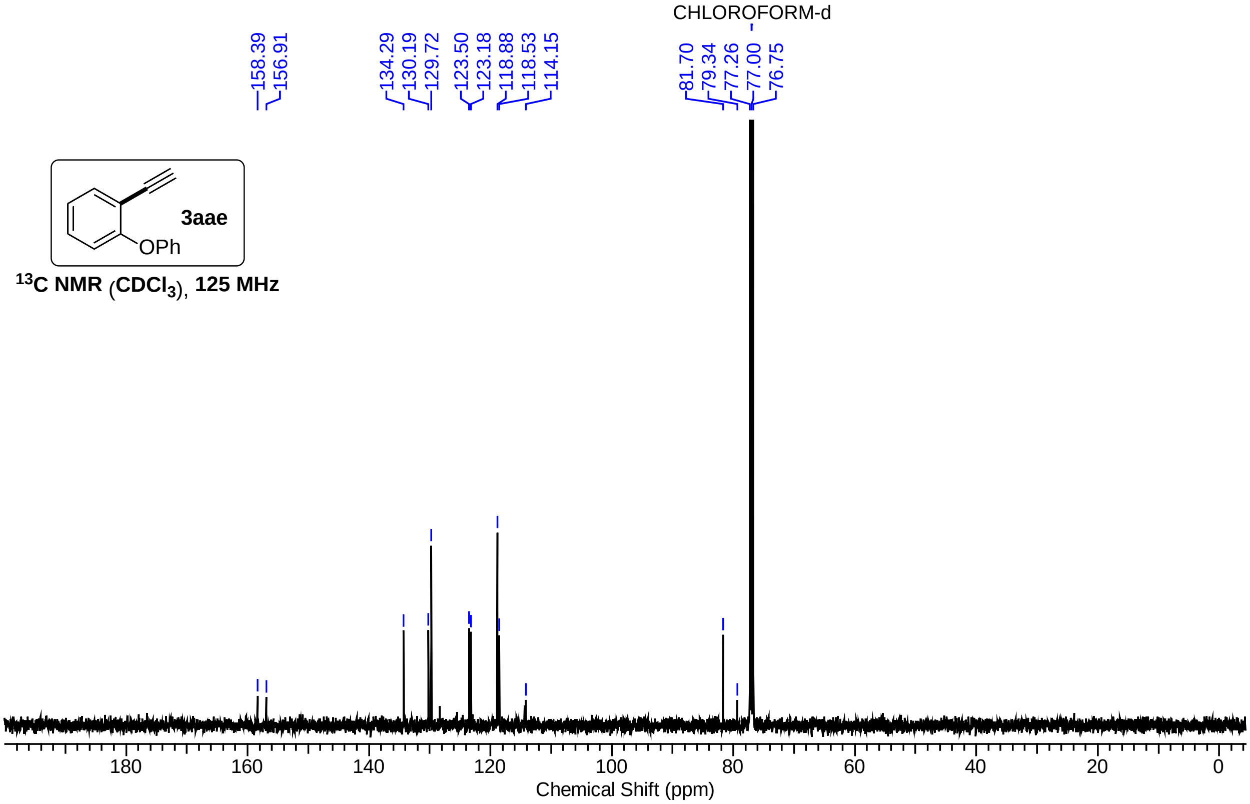
3aad

^{13}C NMR (CDCl$_3$), 125 MHz



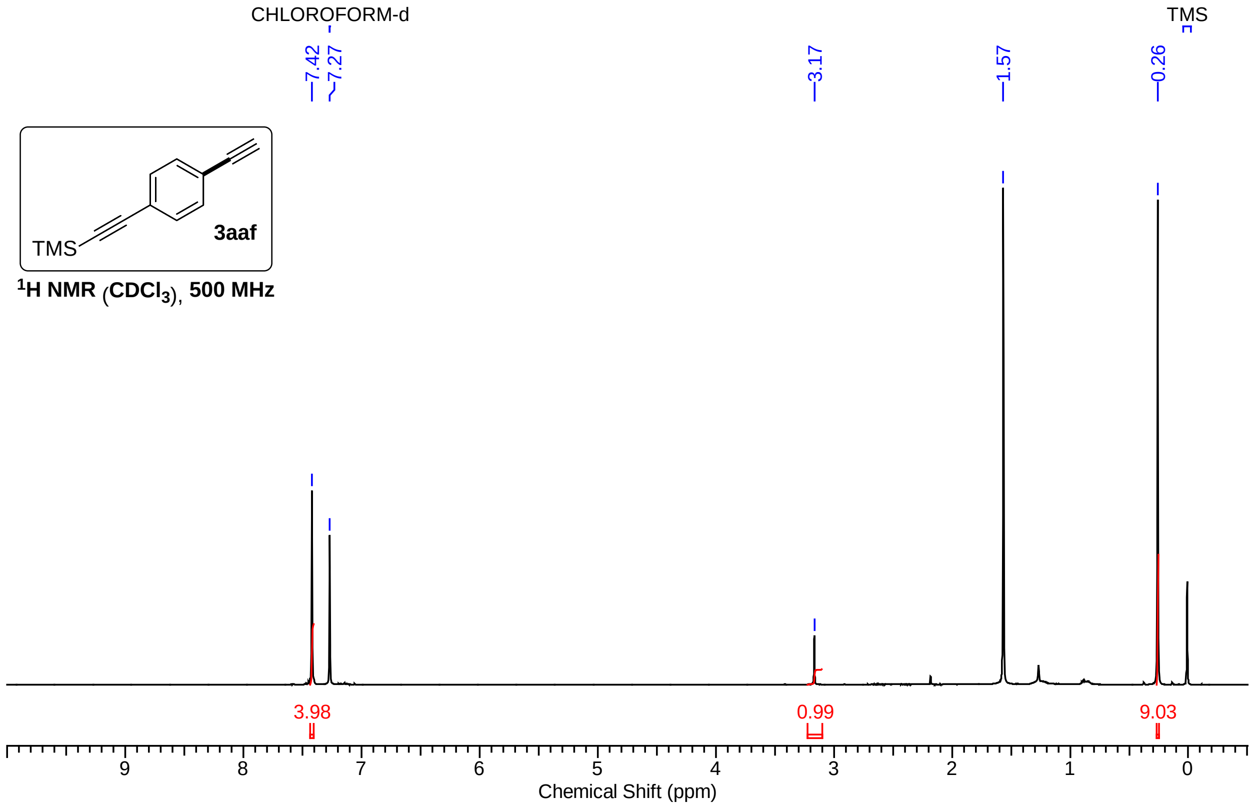
3aae

^{1}H NMR (CDCl$_3$), 500 MHz

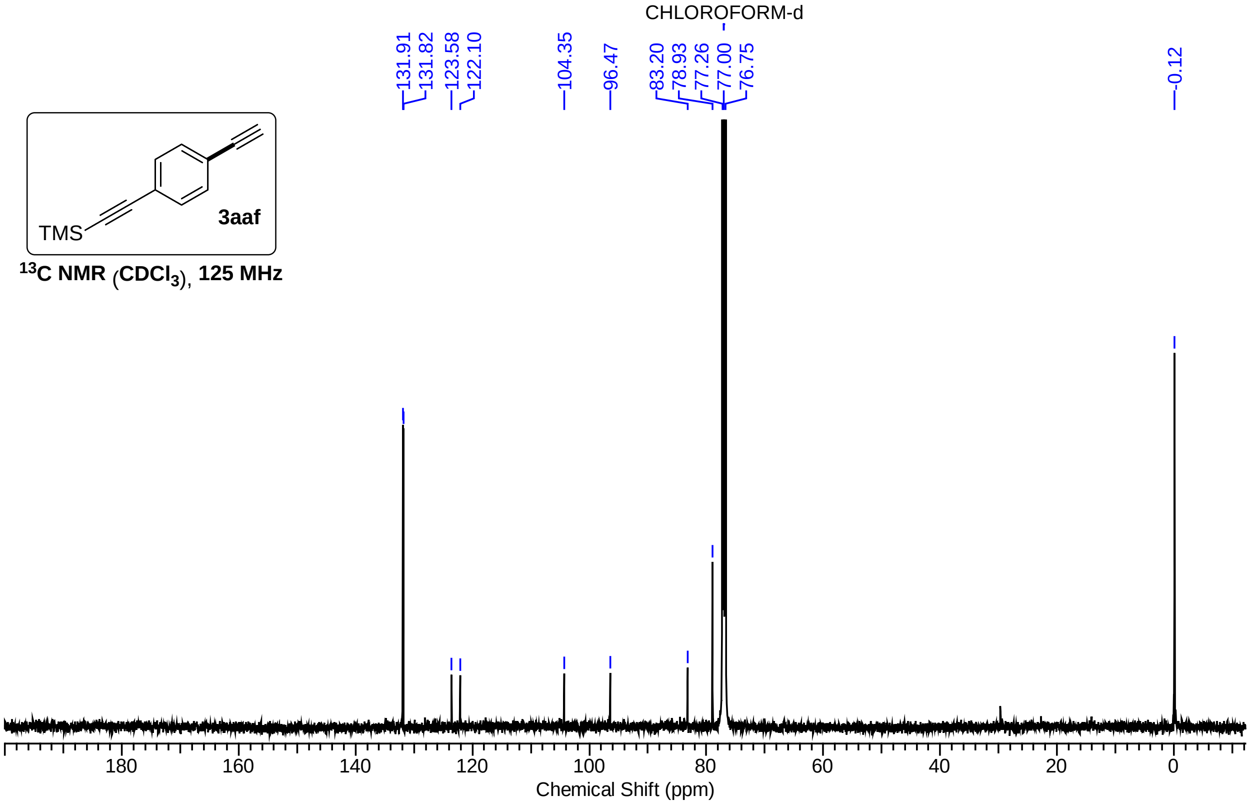


3aae

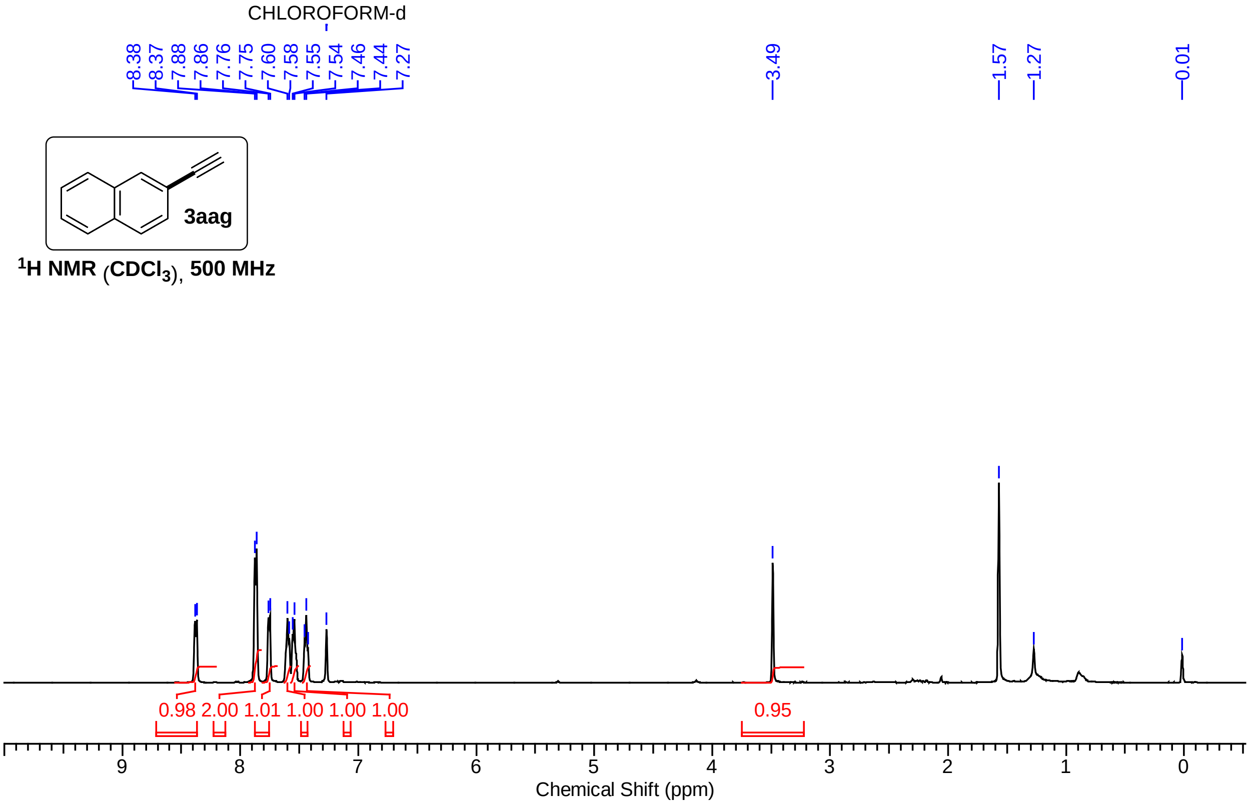
^{13}C NMR (CDCl$_3$), 125 MHz



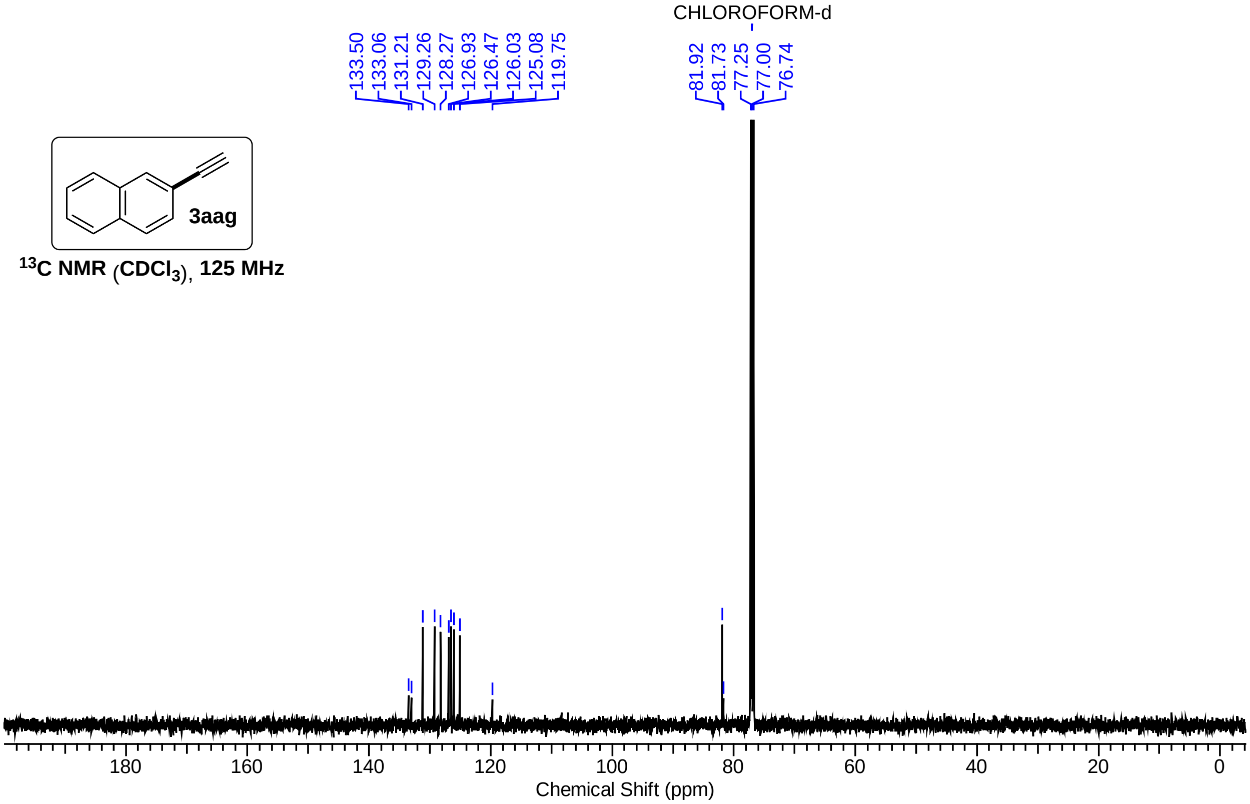
^{1}H NMR (CDCl$_3$), 500 MHz



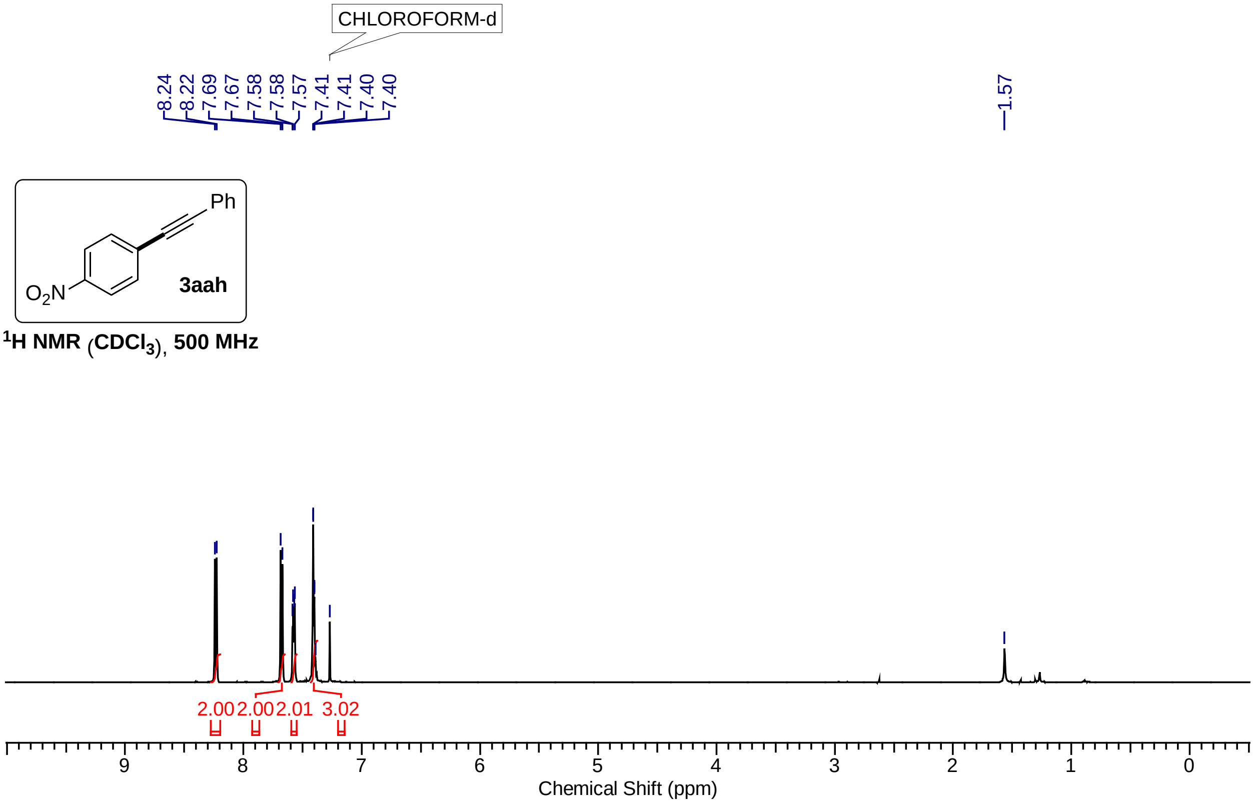
^{13}C NMR (CDCl$_3$), 125 MHz



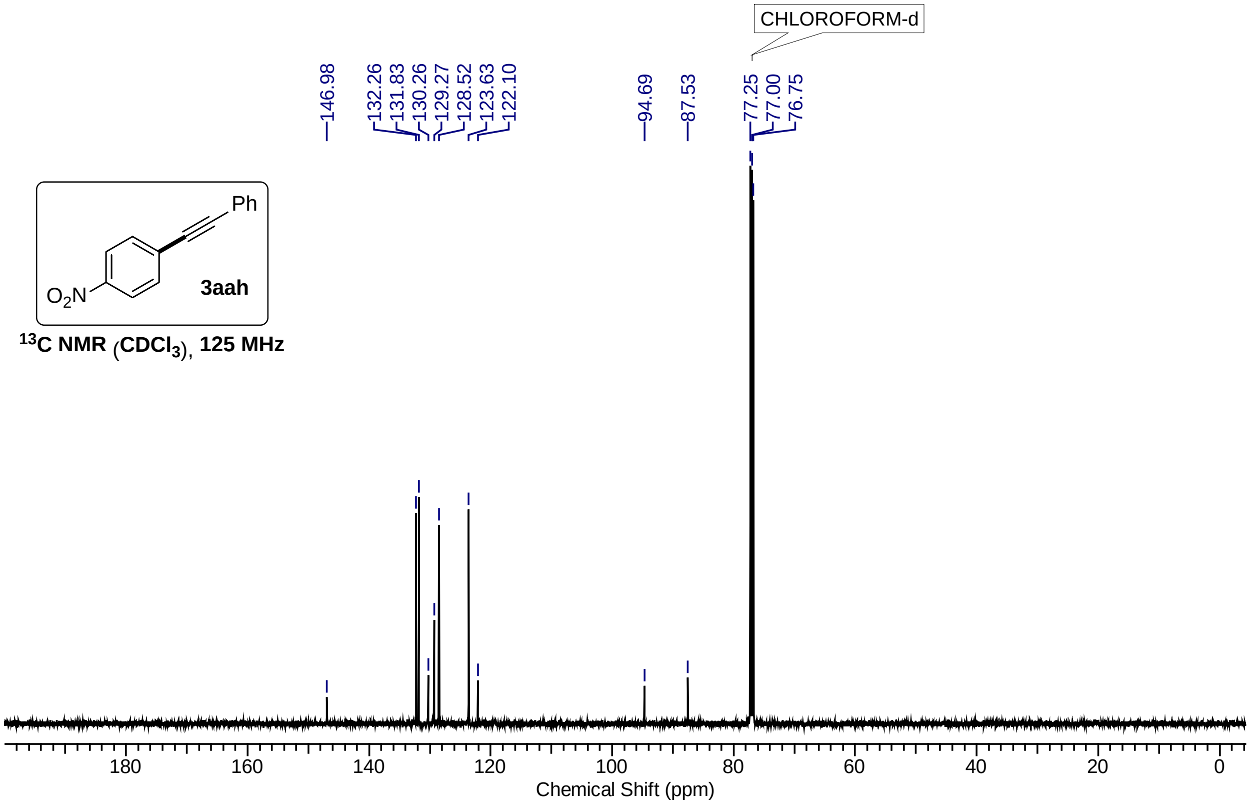
^{1}H NMR (CDCl$_3$), 500 MHz



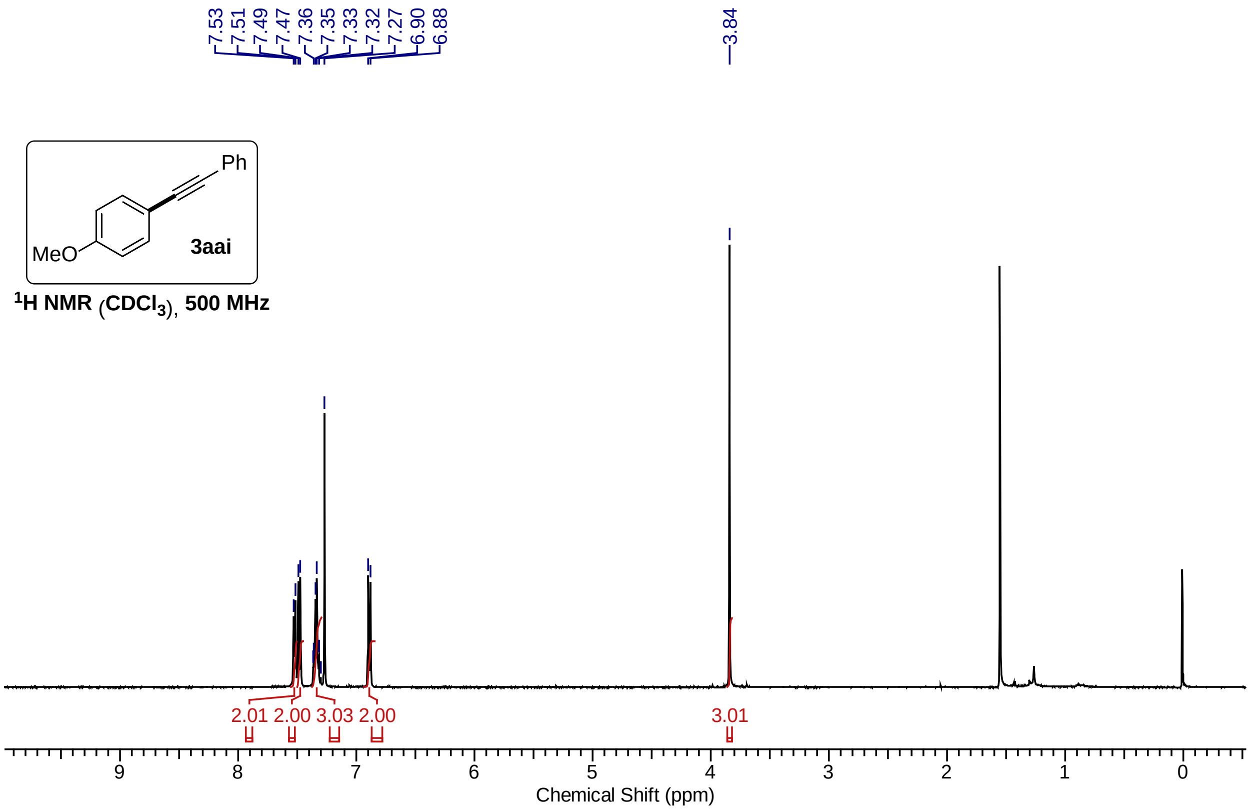
^{13}C NMR (CDCl$_3$), 125 MHz



^{1}H NMR (CDCl$_3$), 500 MHz

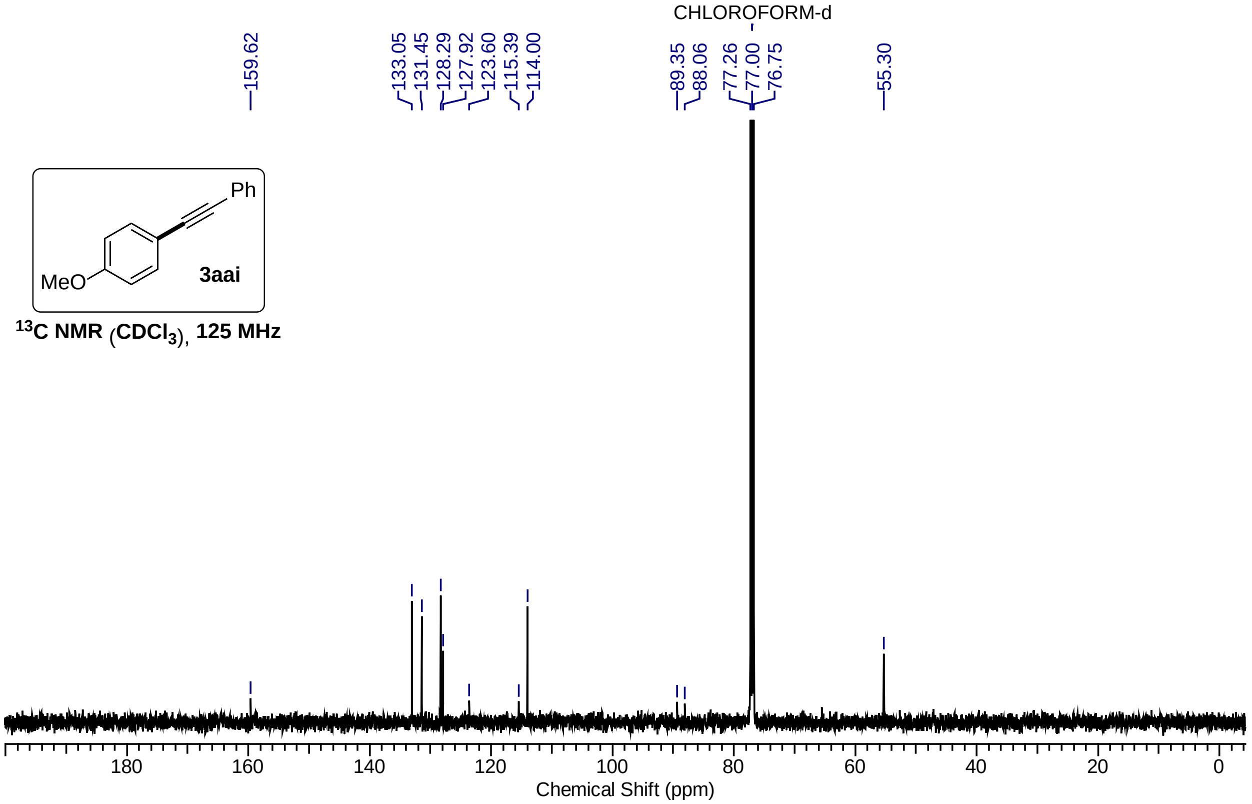


^{13}C NMR (CDCl$_3$), 125 MHz



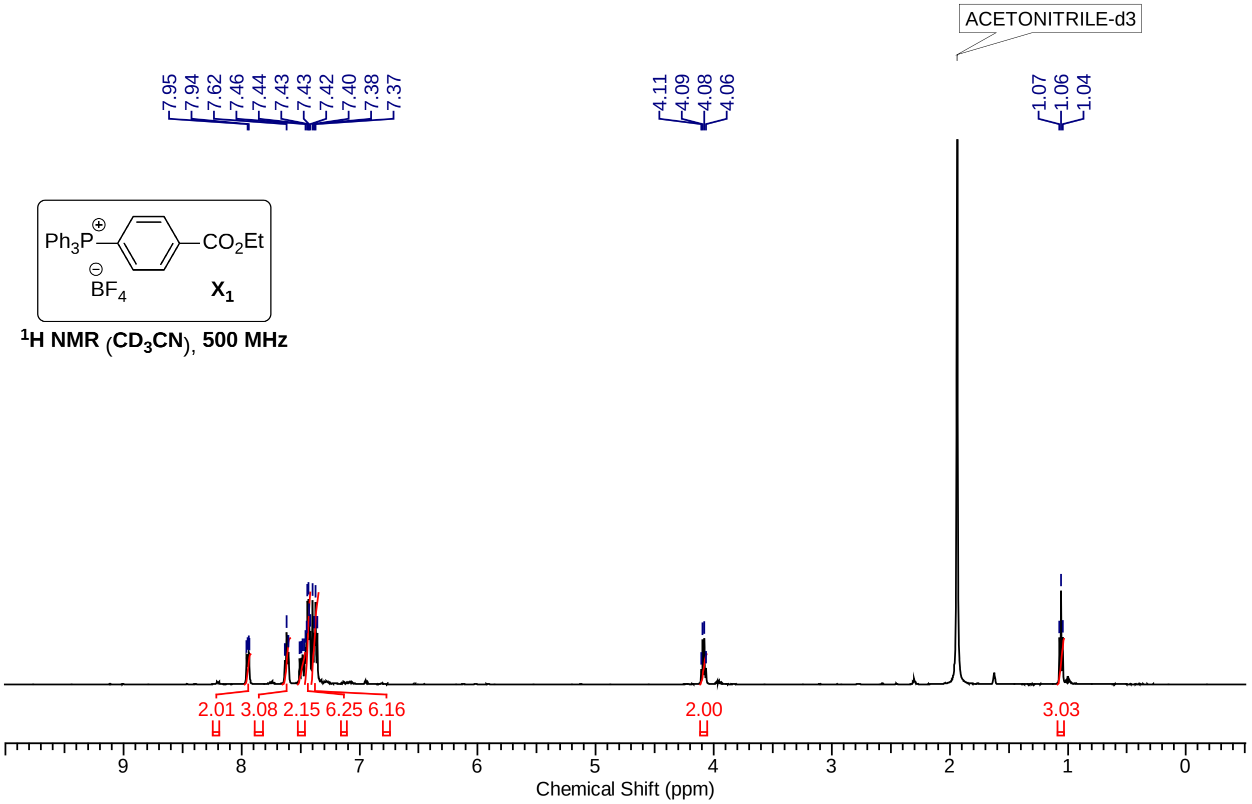
3aai

^{1}H NMR ($CDCl_3$), 500 MHz

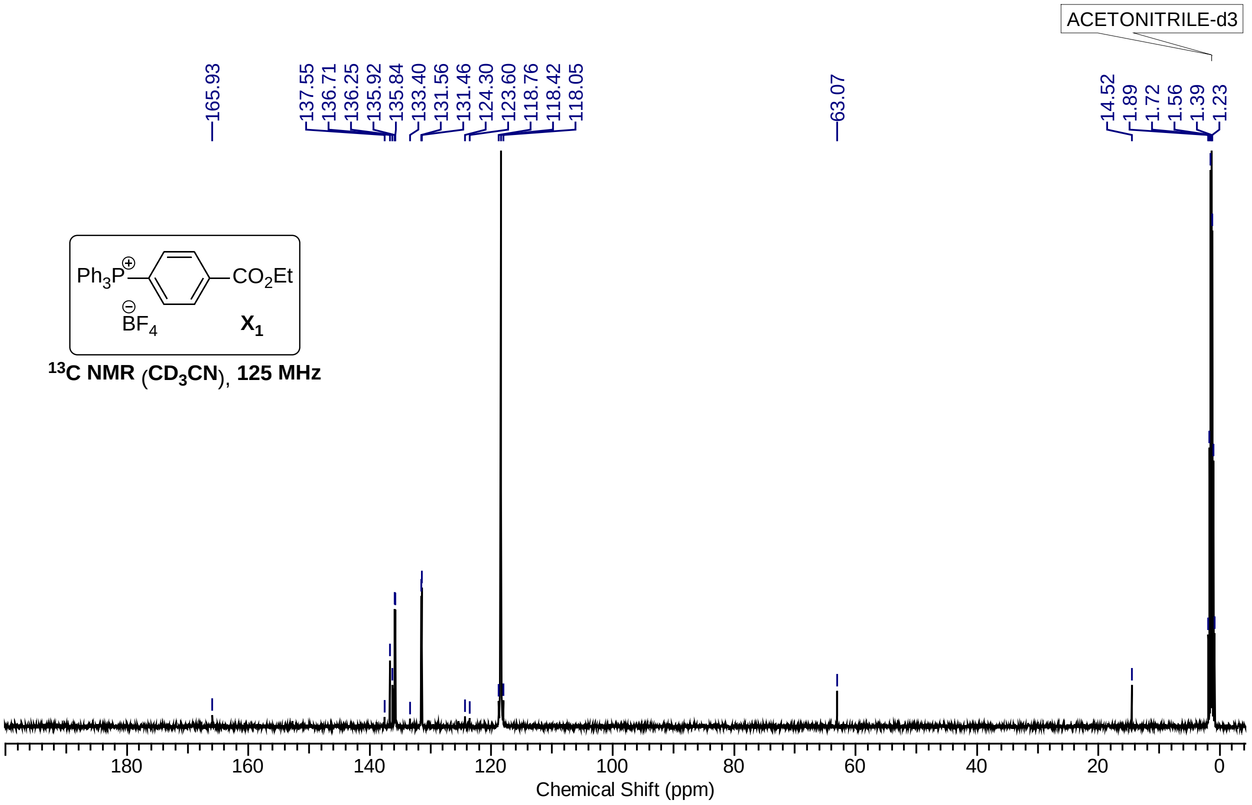


3aai

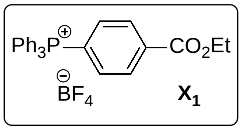
^{13}C NMR ($CDCl_3$), 125 MHz



^{1}H NMR (CD$_3$CN), 500 MHz

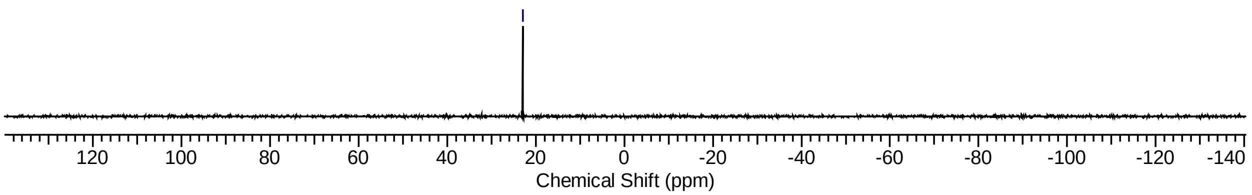


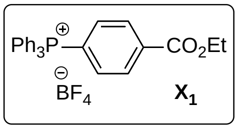
^{13}C NMR (CD$_3$CN), 125 MHz



X_1

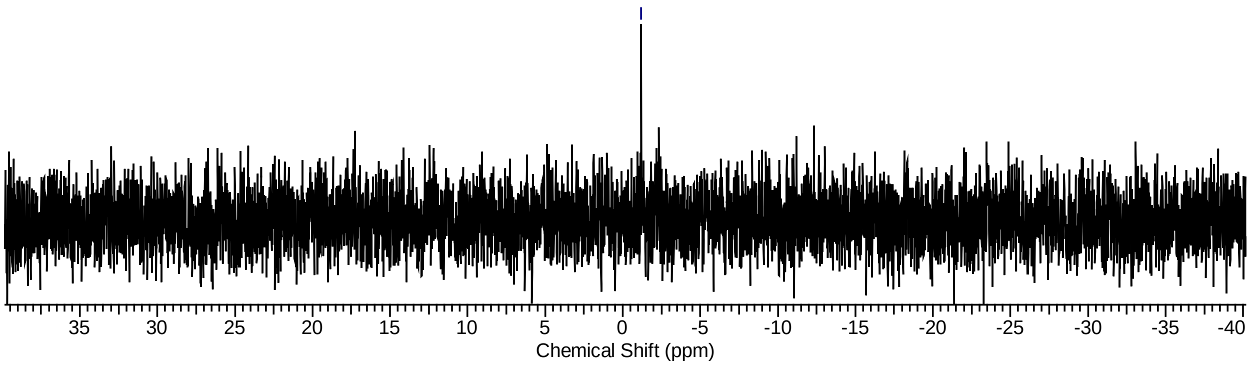
^{31}P NMR (CD$_3$CN), 202 MHz





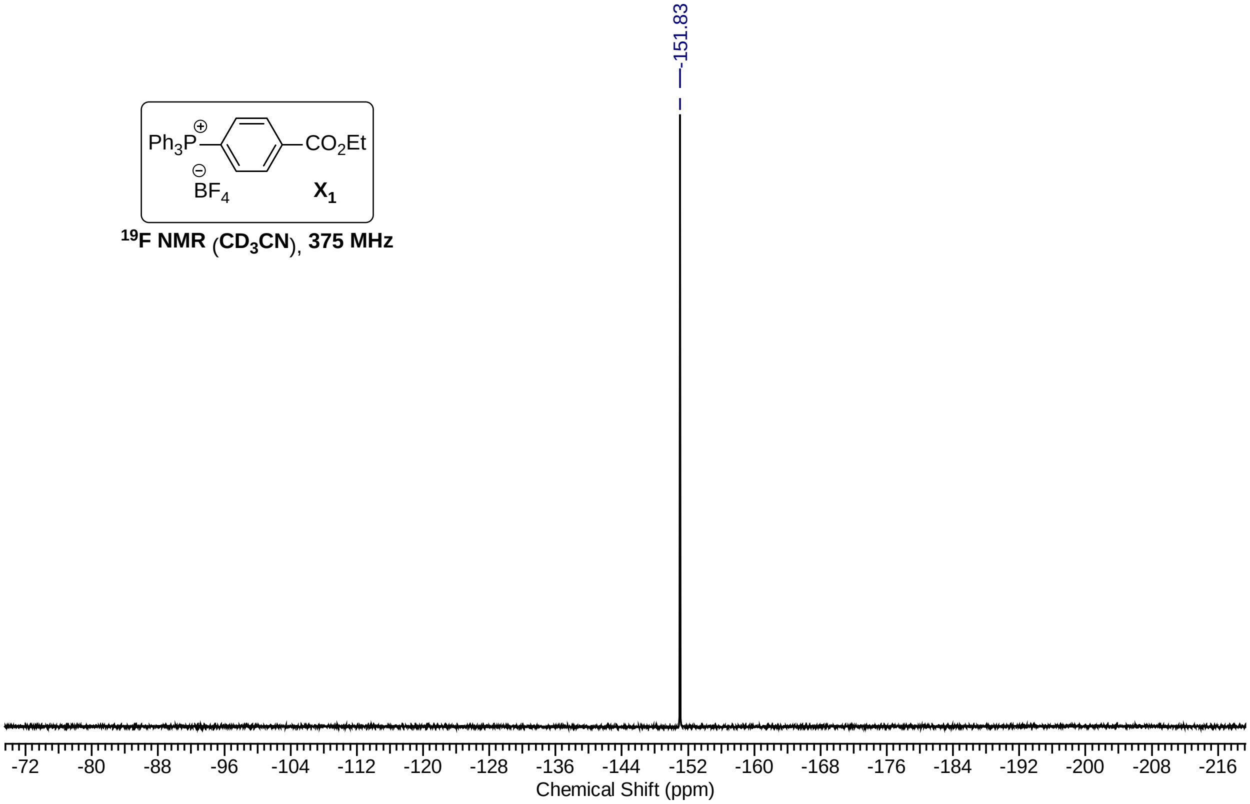
X_1

^{11}B NMR (CD$_3$CN), 128 MHz



X_1

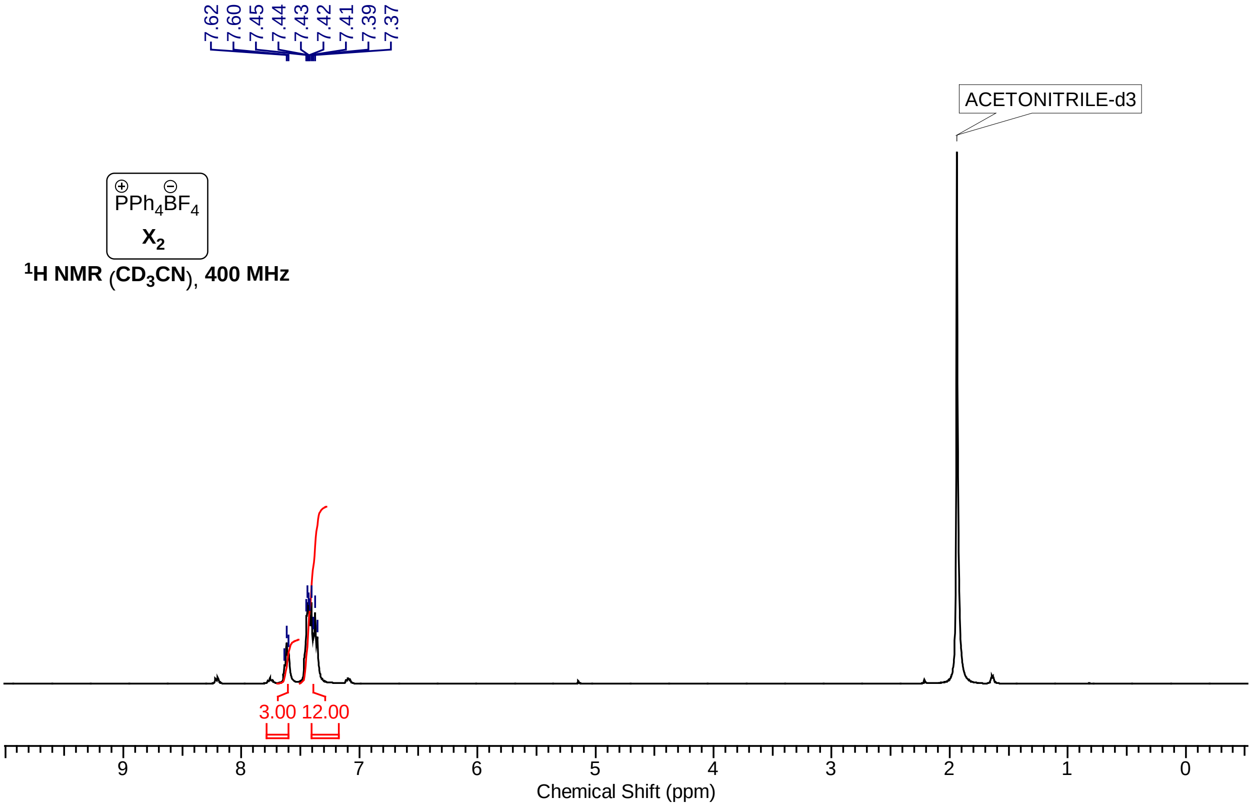
^{19}F NMR (CD_3CN), 375 MHz

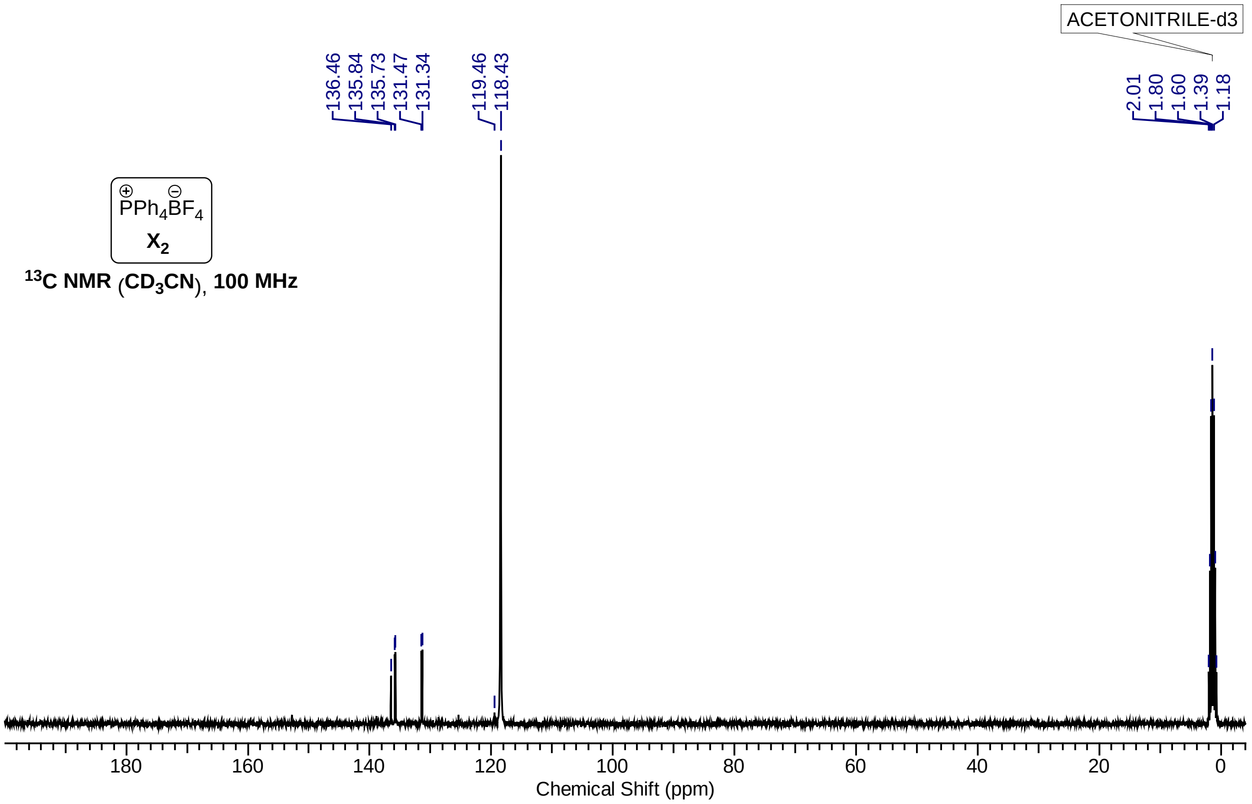


$\overset{\oplus}{P}Ph_4\overset{\ominus}{B}F_4$

X_2

^1H NMR (CD_3CN), 400 MHz

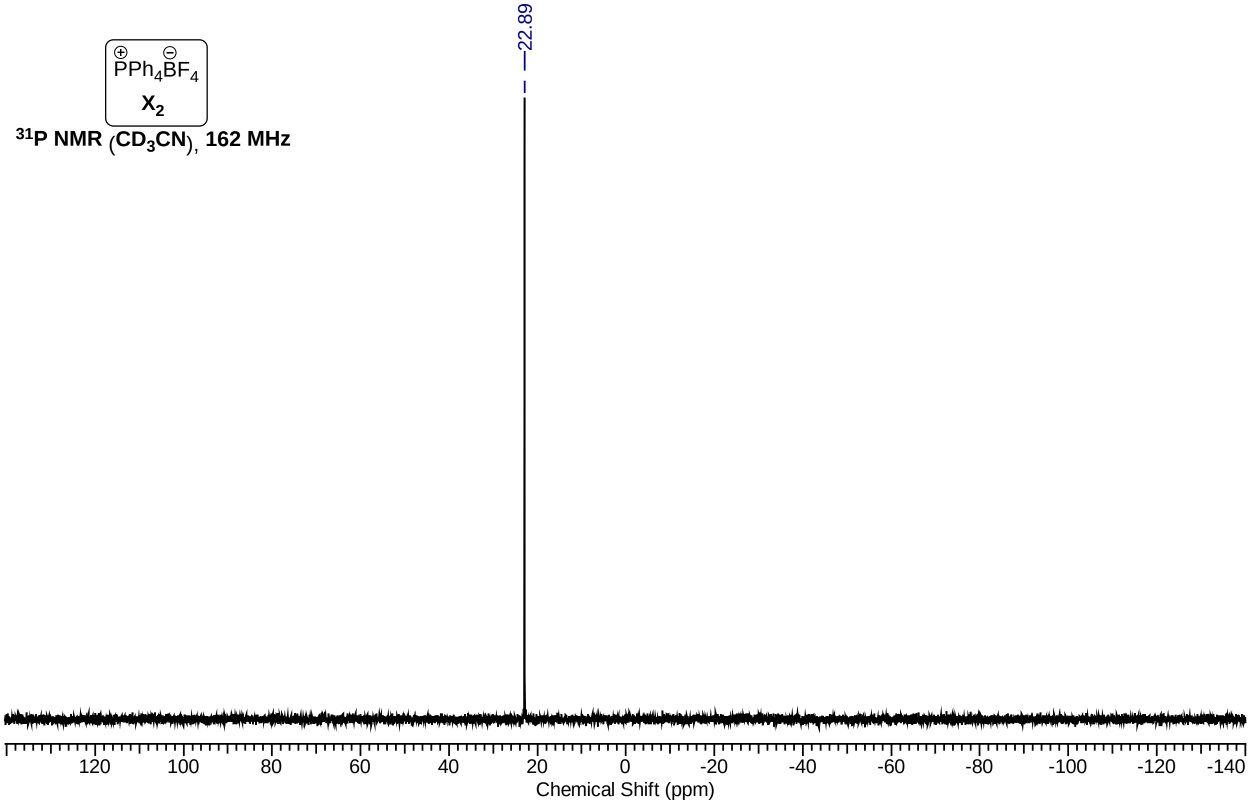




$\overset{\oplus}{P}Ph_4\overset{\ominus}{B}F_4$

X$_2$

^{13}C NMR (CD$_3$CN), 100 MHz



$\overset{\oplus}{P}Ph_4\overset{\ominus}{B}F_4$

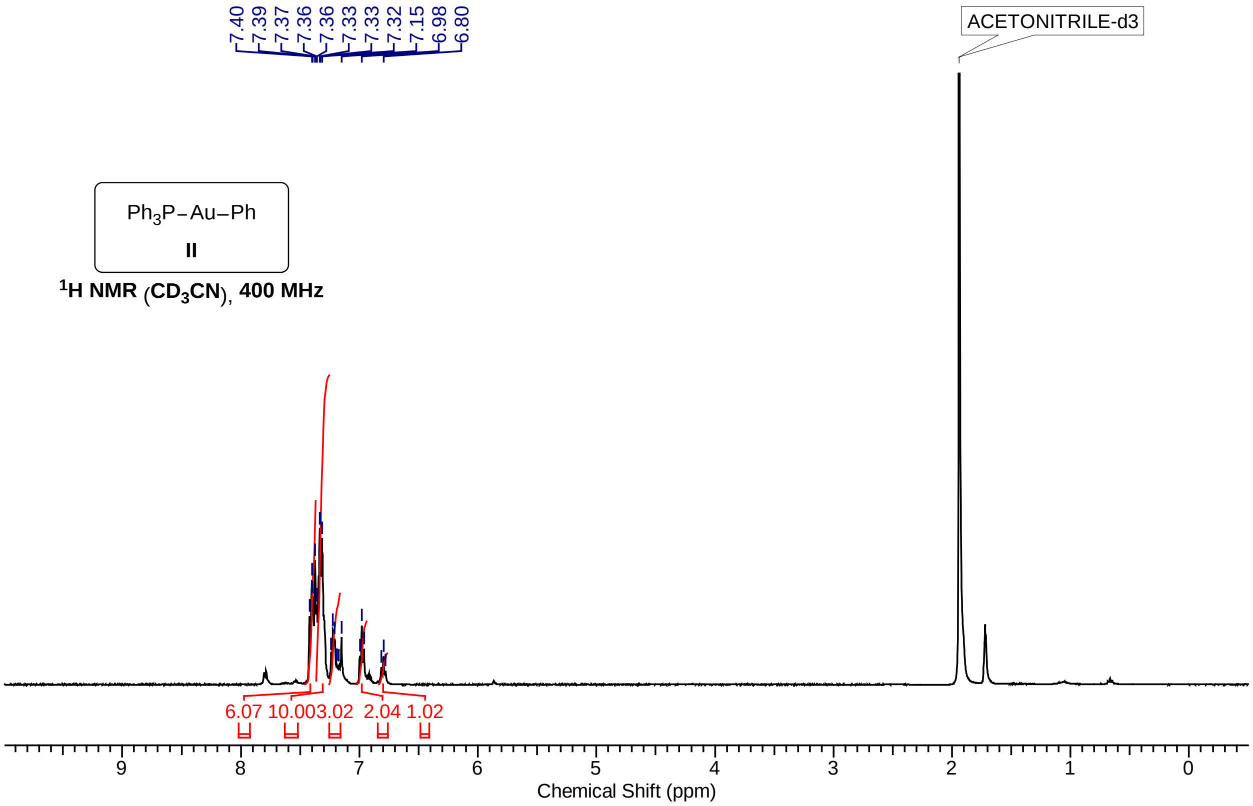
X$_2$

^{31}P NMR (CD$_3$CN), 162 MHz

$Ph_3P–Au–Ph$

II

^{1}H NMR (CD$_3$CN), 400 MHz



$Ph_3P–Au–Ph$

II

^{31}P NMR (CD$_3$CN), 162 MHz