Supporting information:

The use of (cyclopentadienone)iron tricarbonyl complexes for C-N bond-formation reactions between amines and alcohols.

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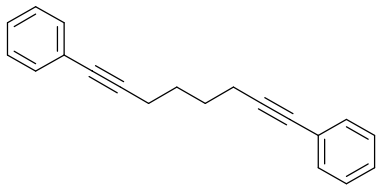
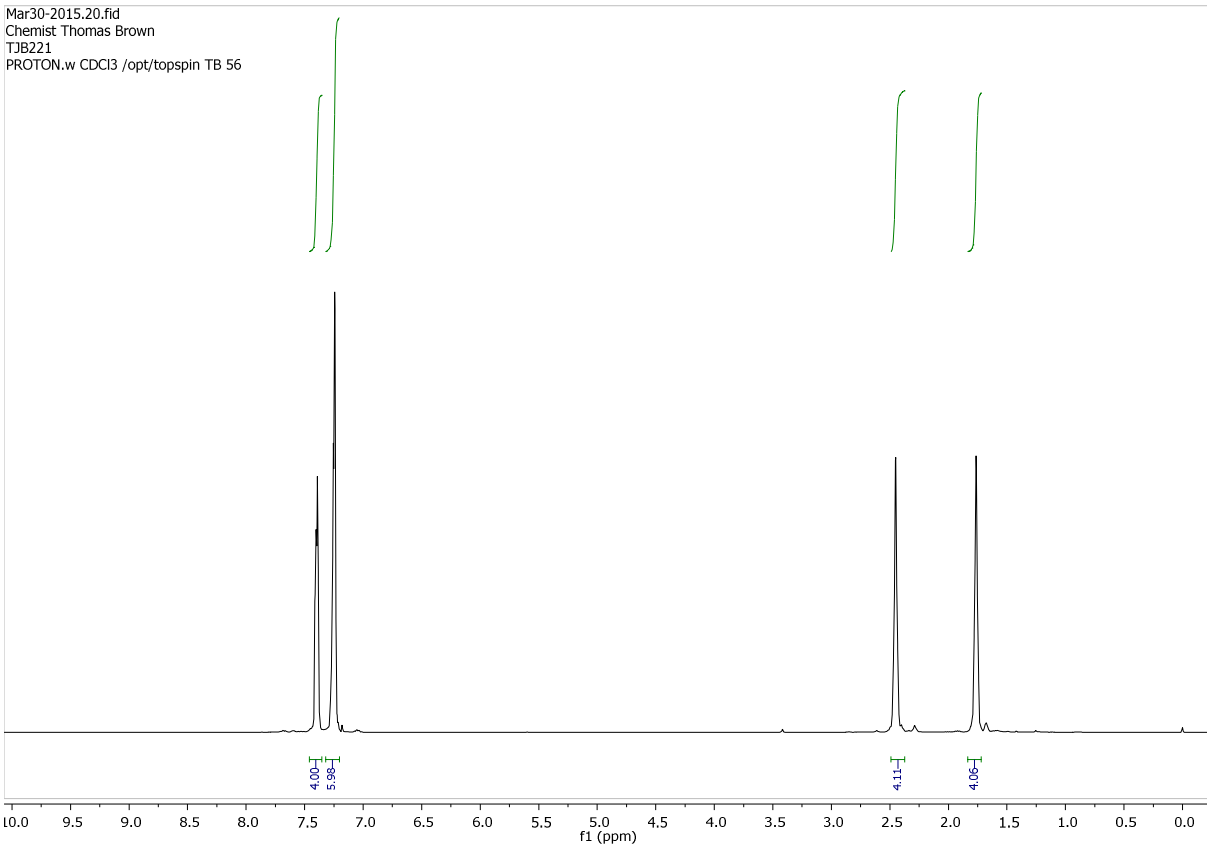
Contents:

1H and 13C NMR Spectra:

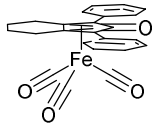
1,8-Diphenylocta-1,7-diyne **10**.



^{1}H NMR (400 MHz, $CDCl_3$)

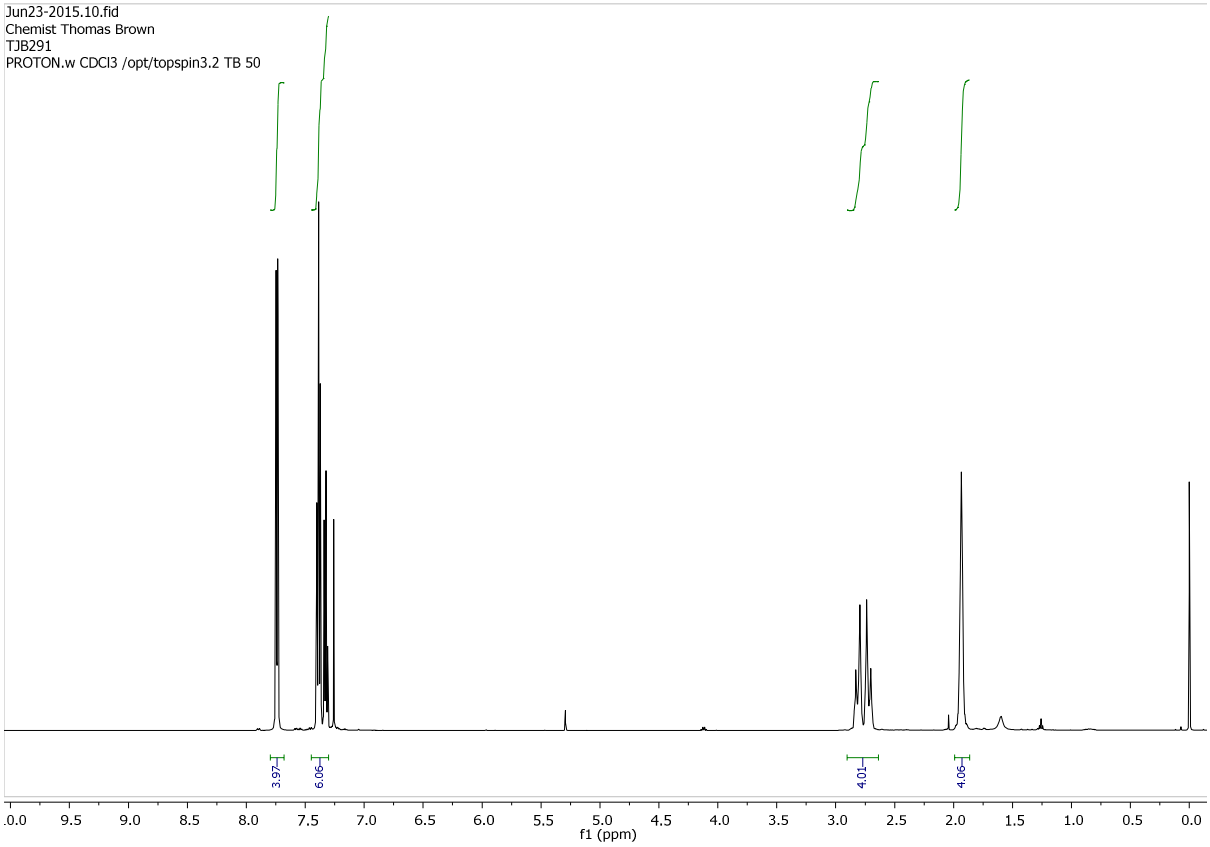


Tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron **5**.

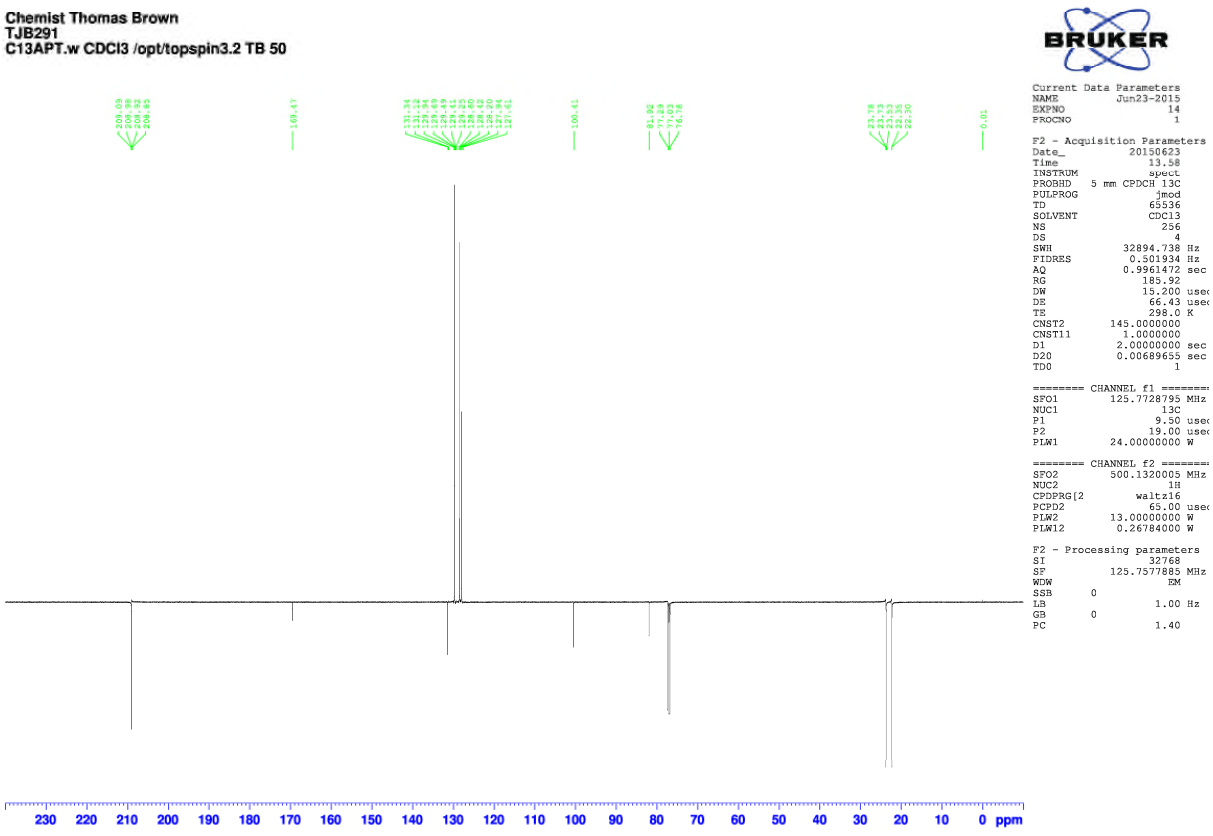


TJB291

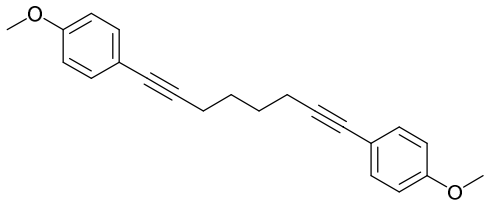
^{1}H NMR (500 MHz, $CDCl_3$)



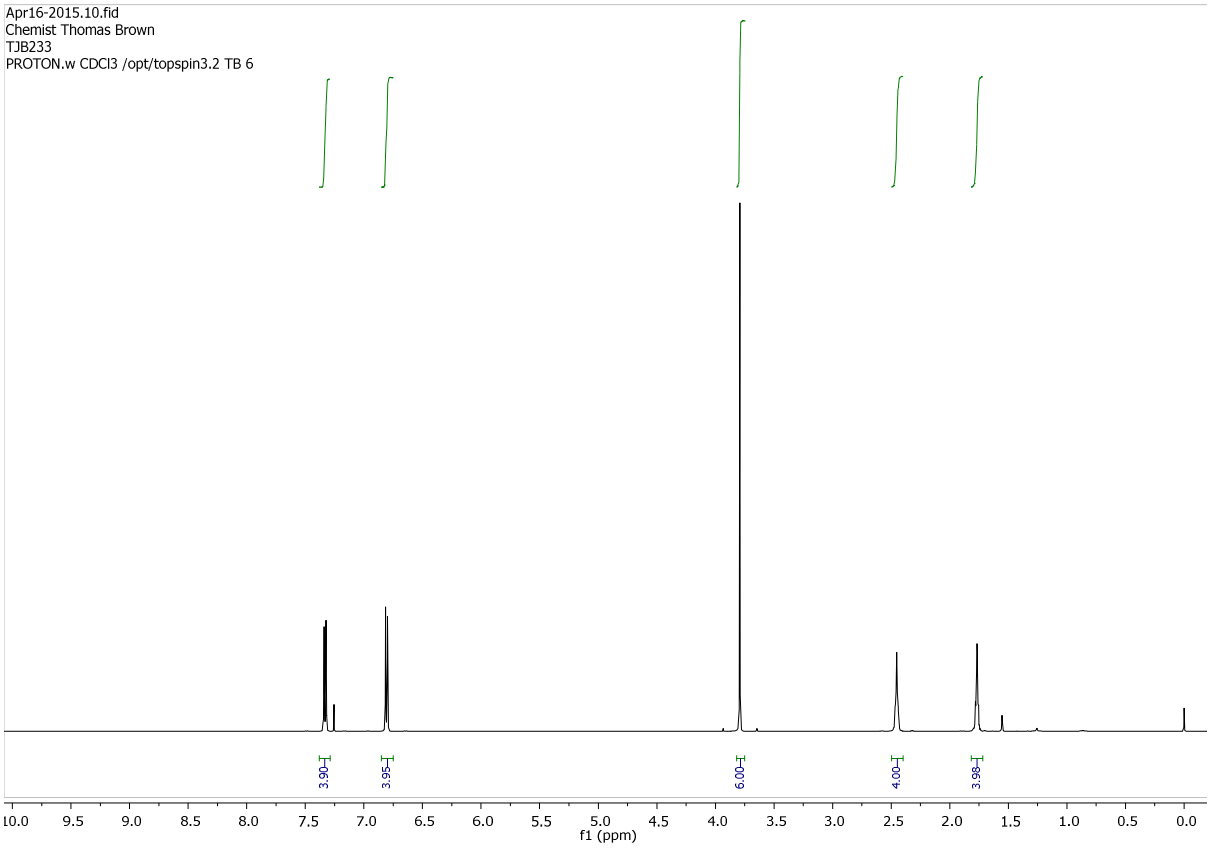
^{13}C NMR (126 MHz, $CDCl_3$)



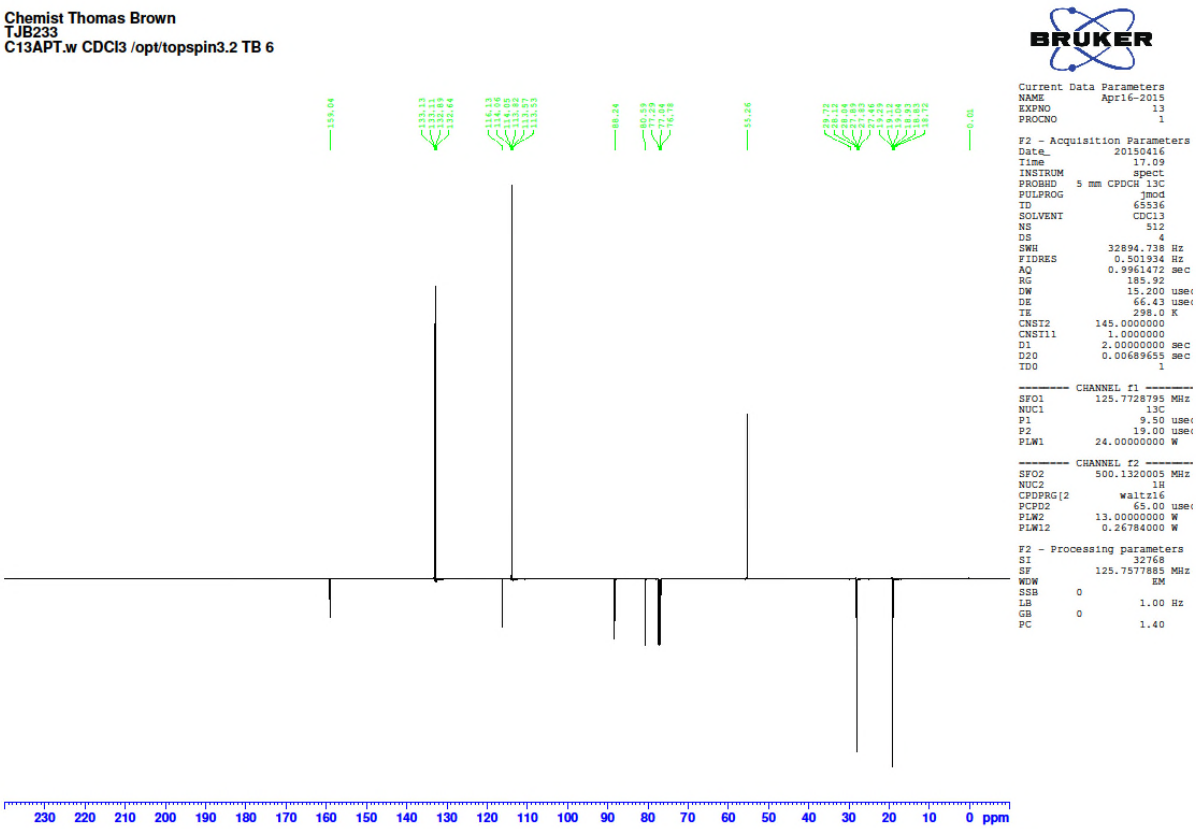
1,8-Bis(4-methoxyphenyl)octa-1,7-diyne **11**.



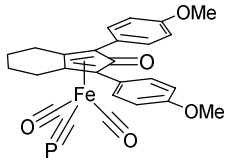
^{1}H NMR (500 MHz, $CDCl_3$).



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

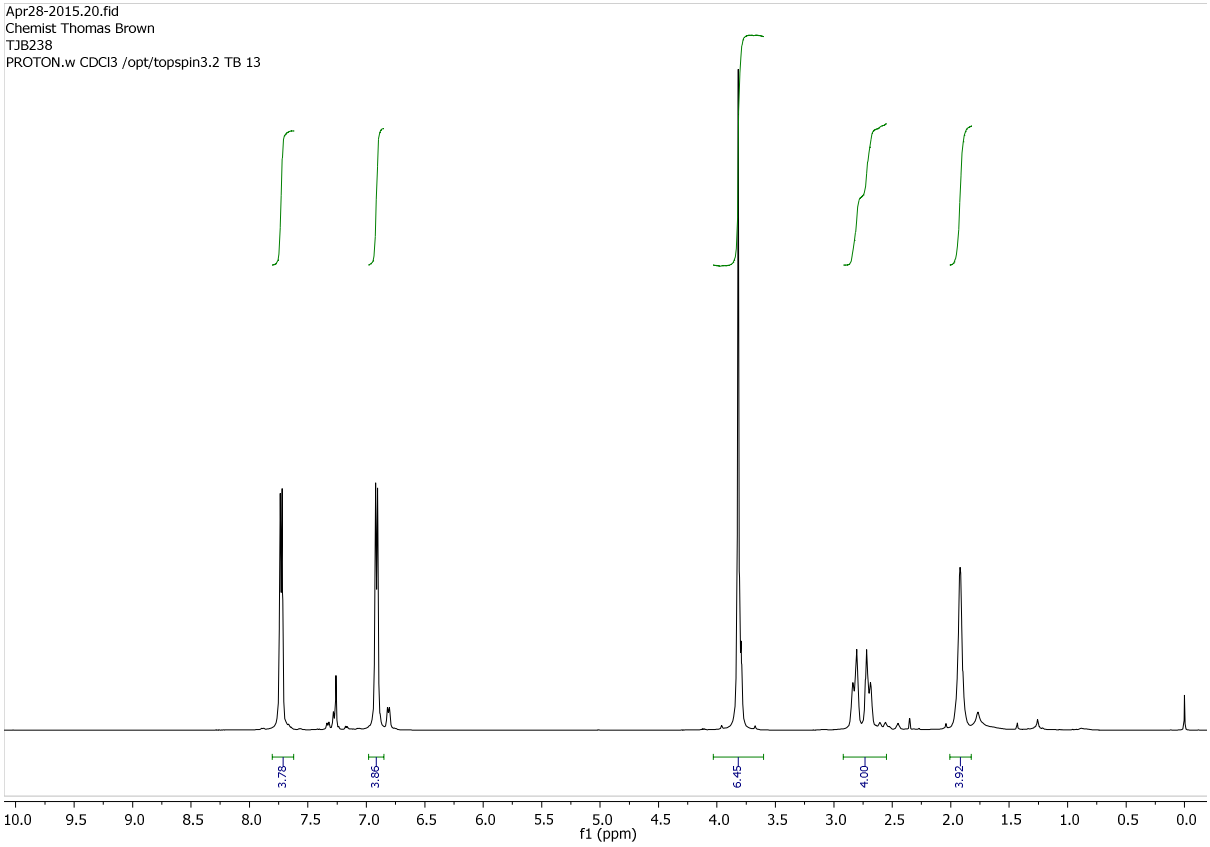


Tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron **6**.

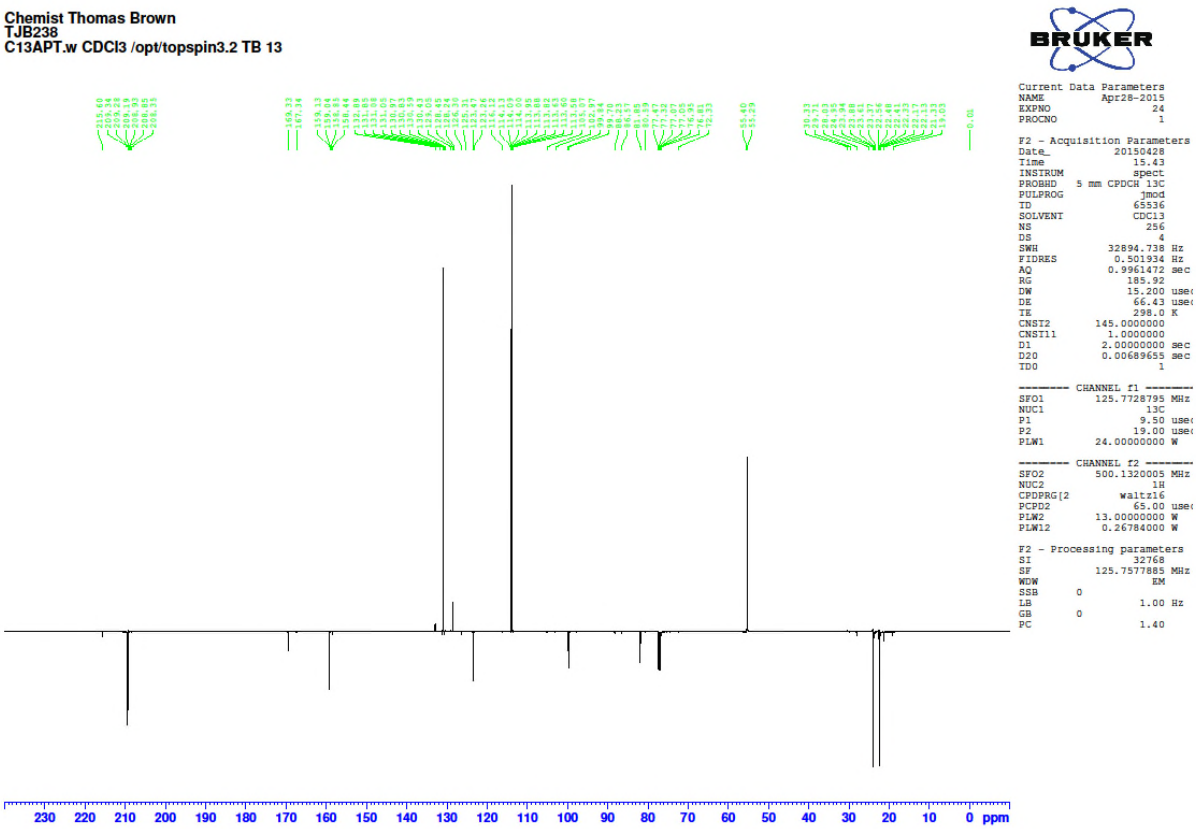


TJB238

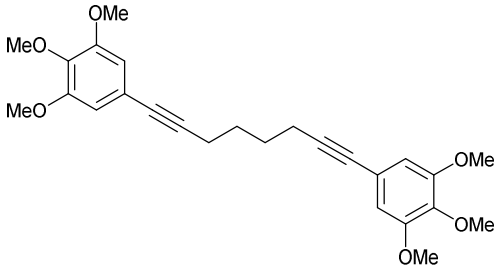
^{1}H NMR (500 MHz, $CDCl_3$).



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

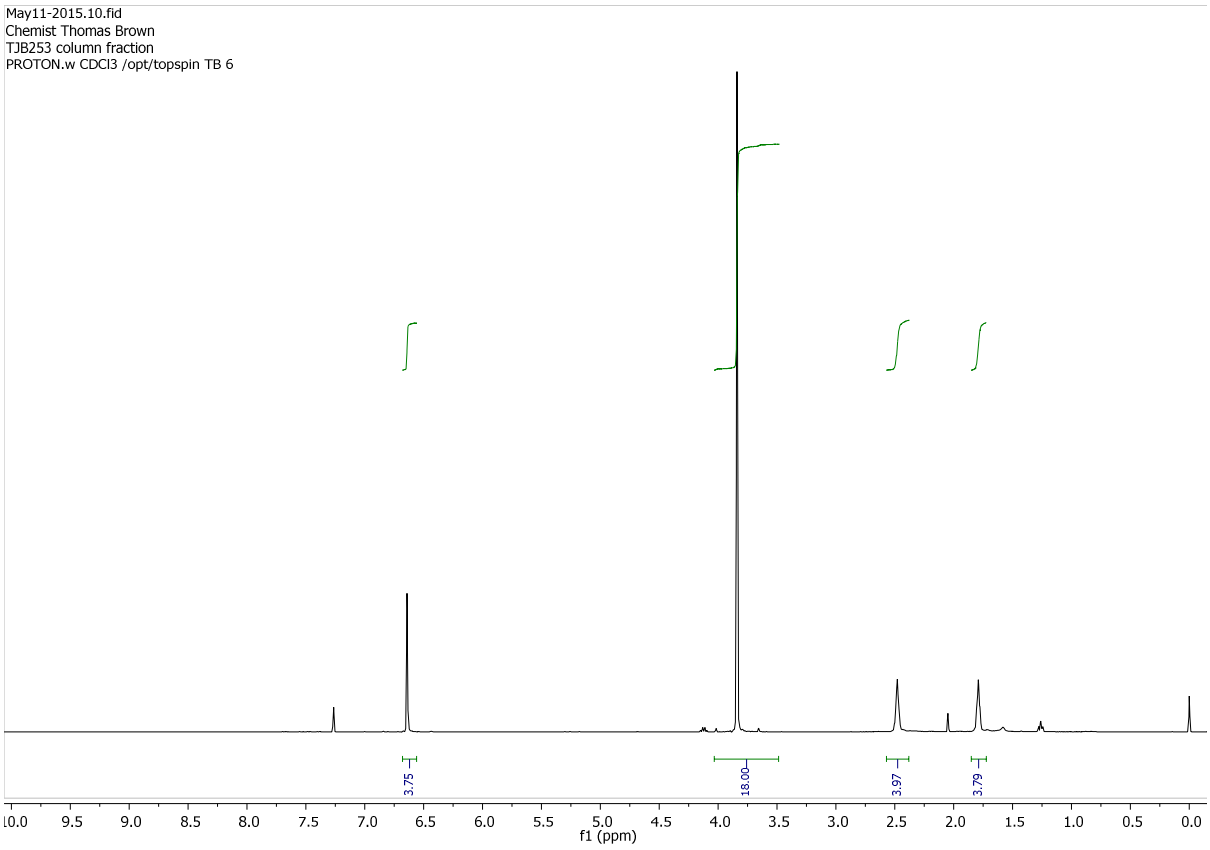


1,8-Bis(3,4,5-trimethoxybenzene)octa-1,7-diyne **12**.

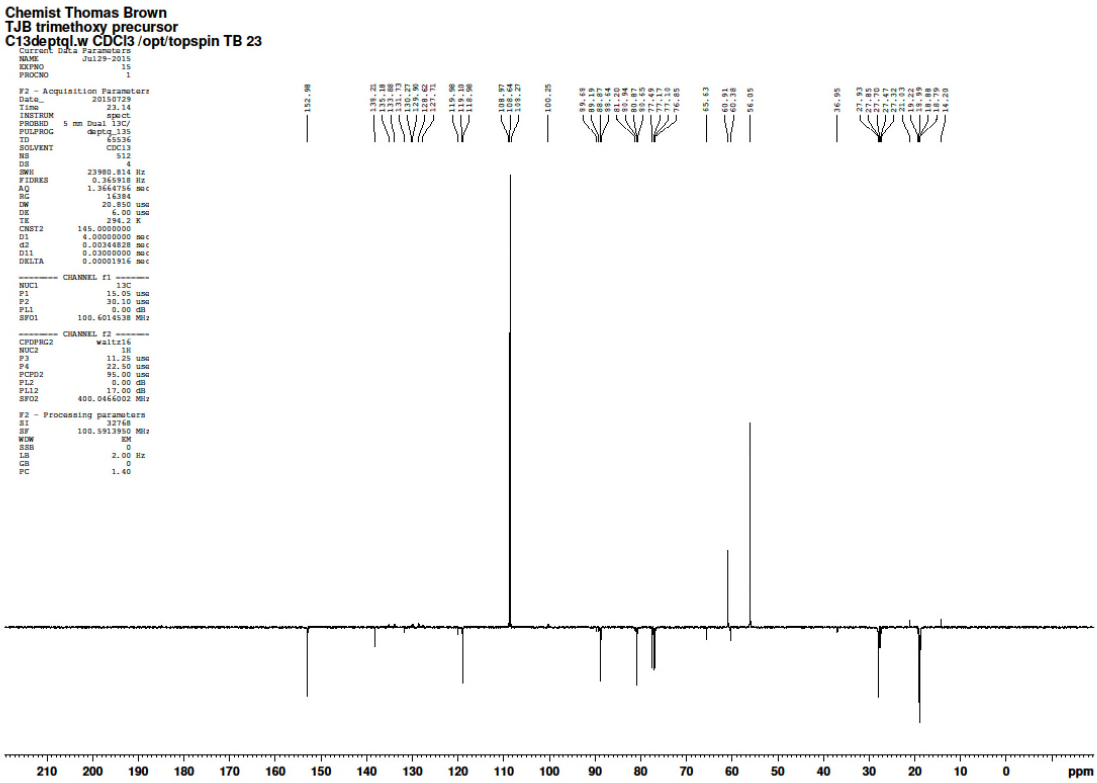


TJB253

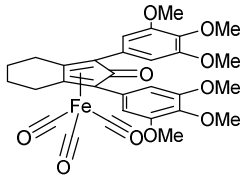
^{1}H NMR (400 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

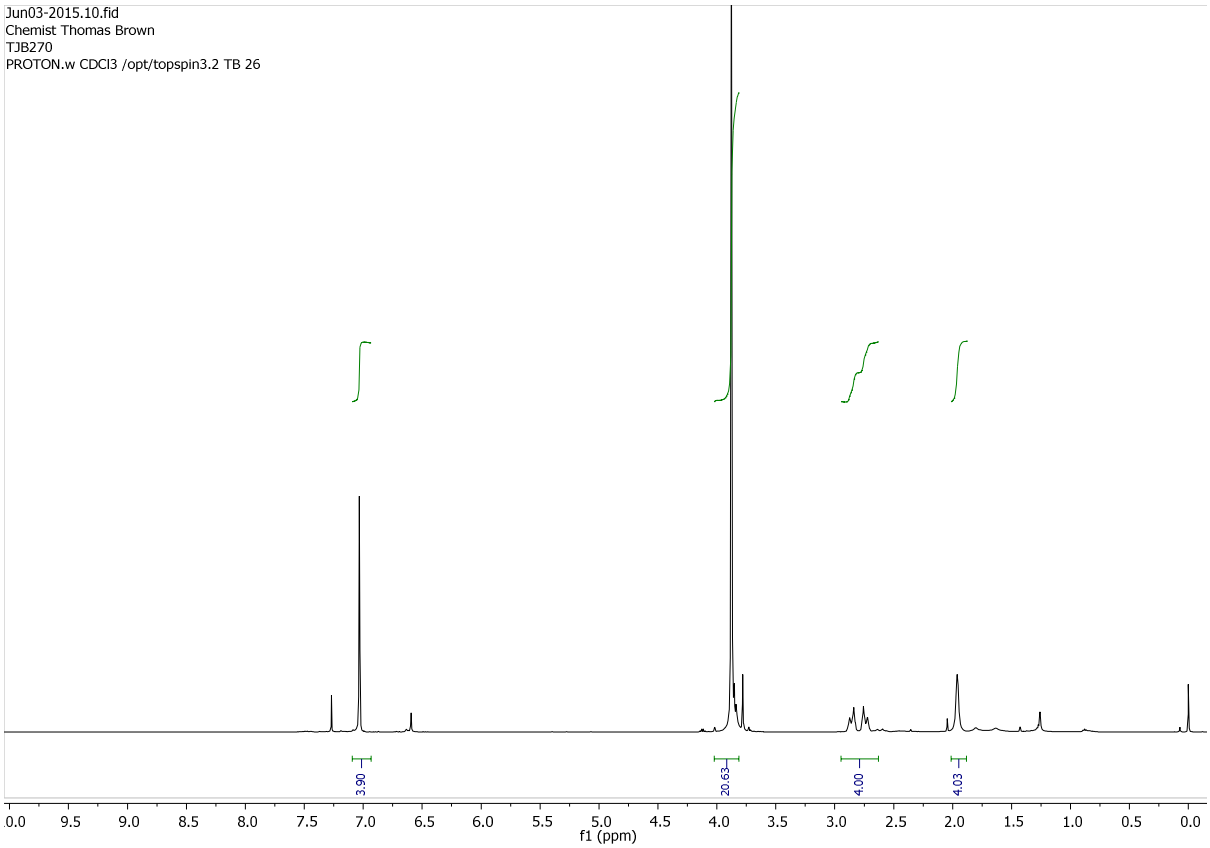


Tricarbonyl(1,3-di(3,4,5-trimethoxyphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron **7**.

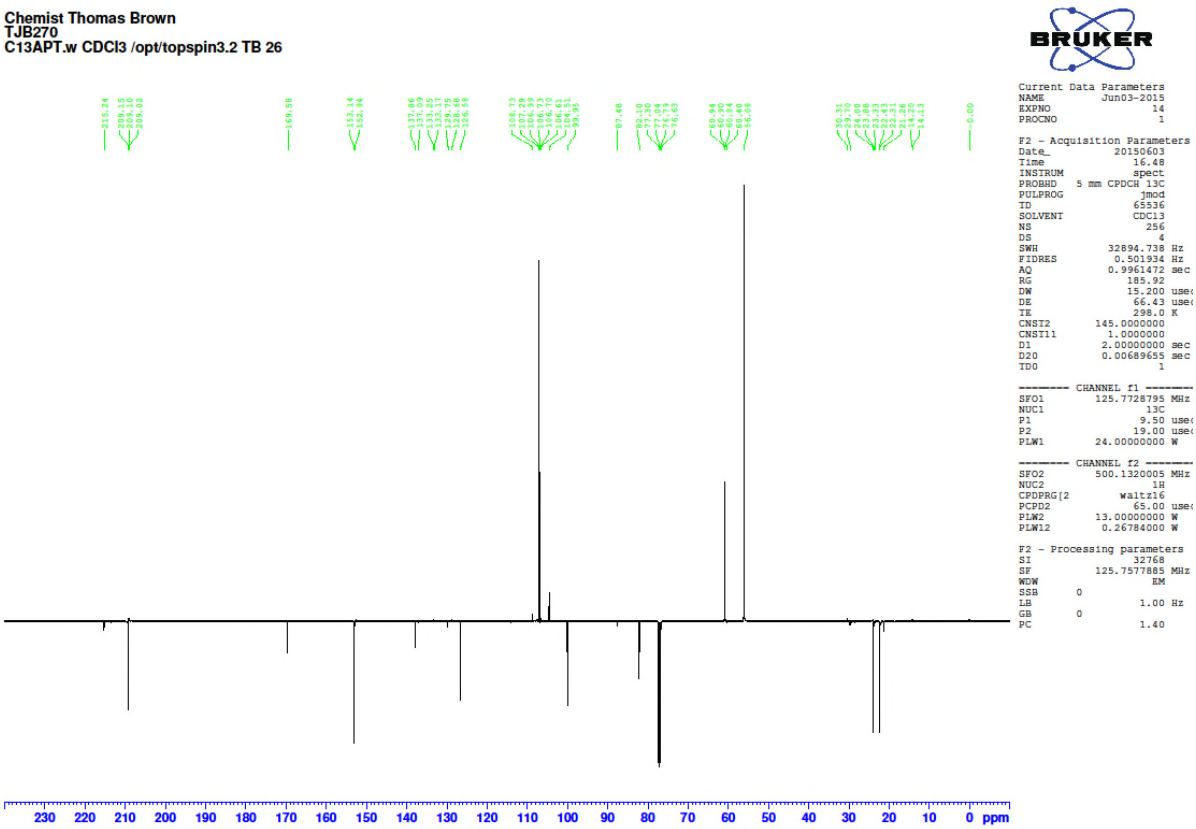


TJB270.

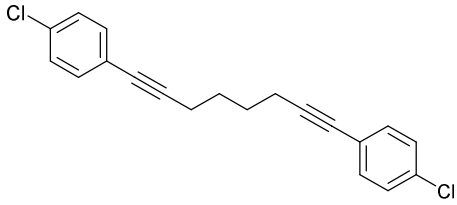
^{1}H NMR (500 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

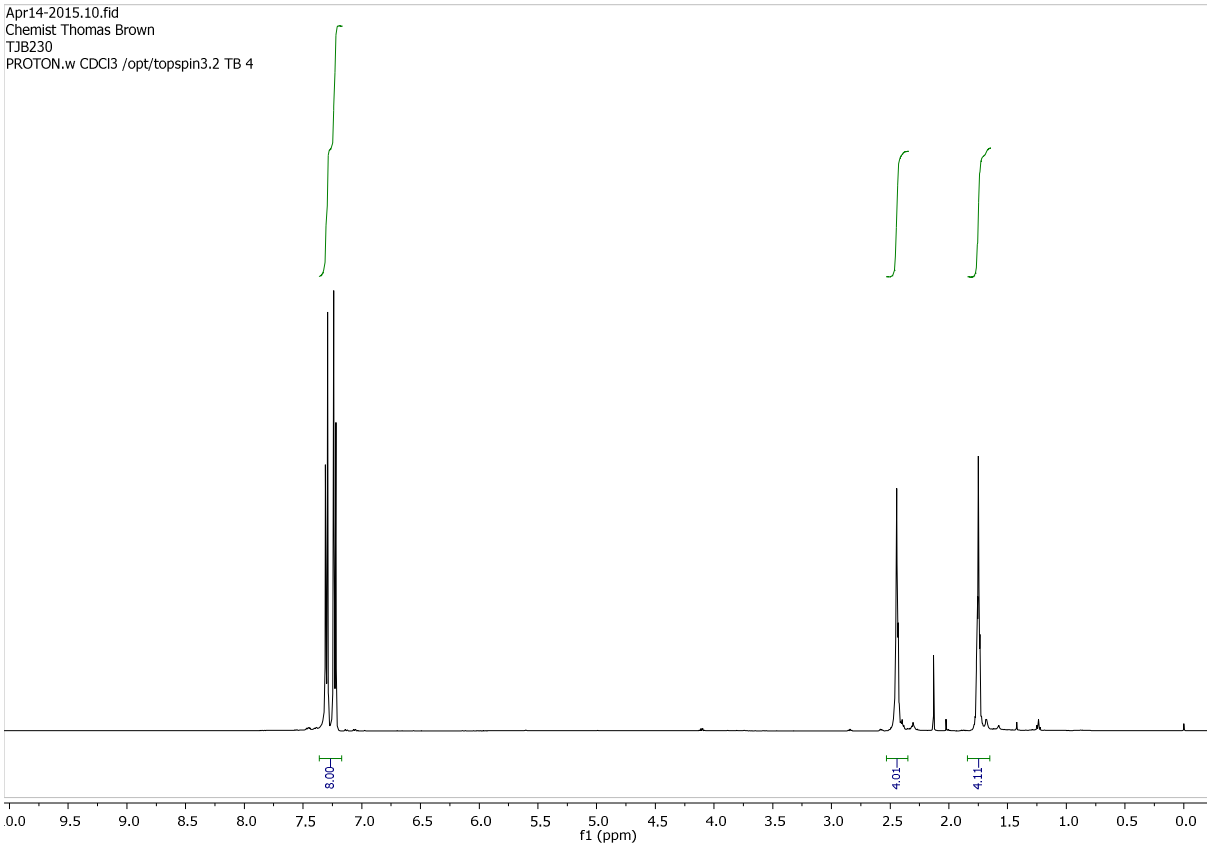


1,8-(4-Chlorophenyl)octa-1,7-diyne **13**.

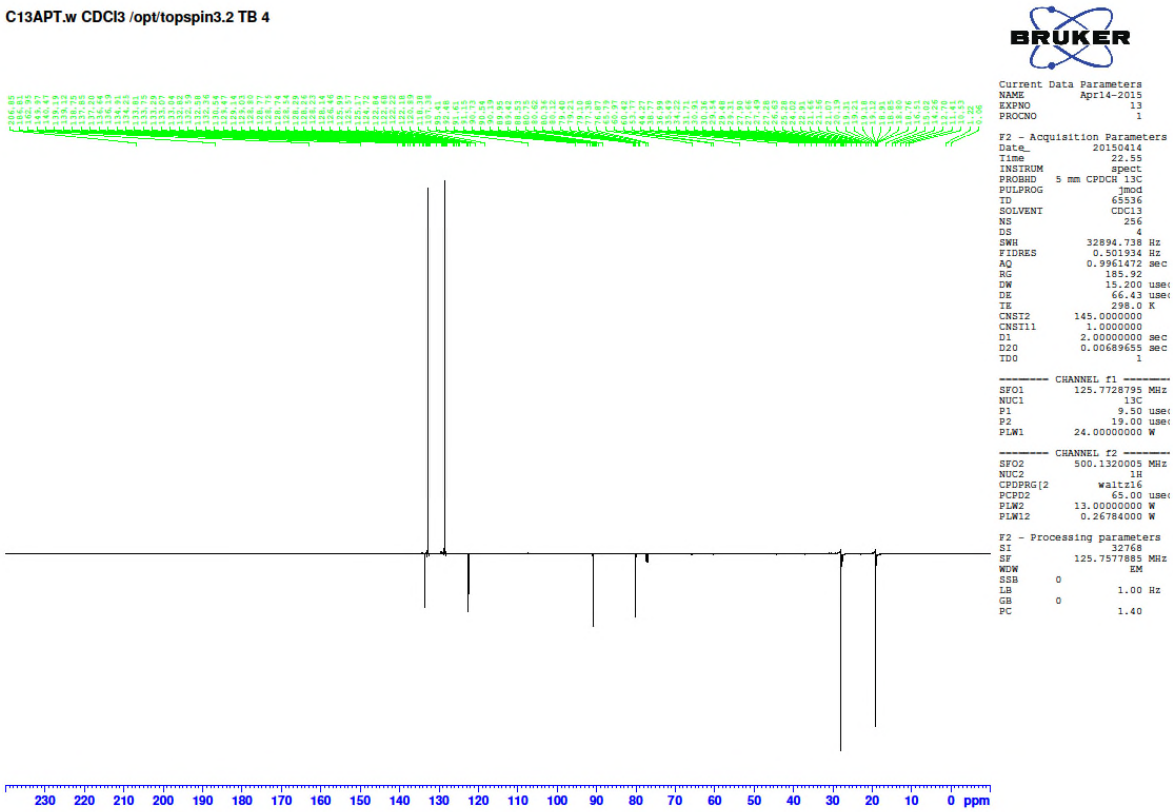


TJB230

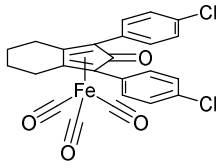
^{1}H NMR (500 MHz, $CDCl_3$).



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

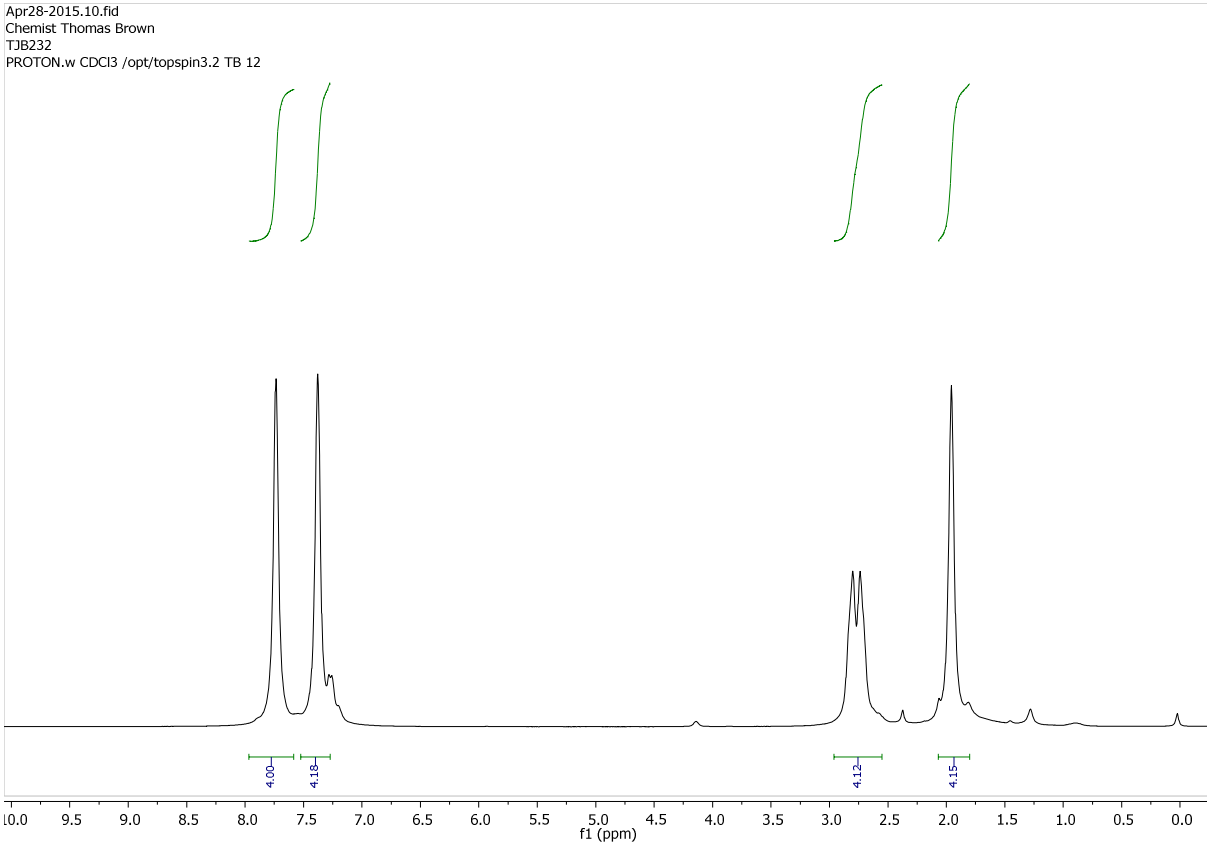


Tricarbonyl(1,3-di(4-chloro)phenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron **8**.

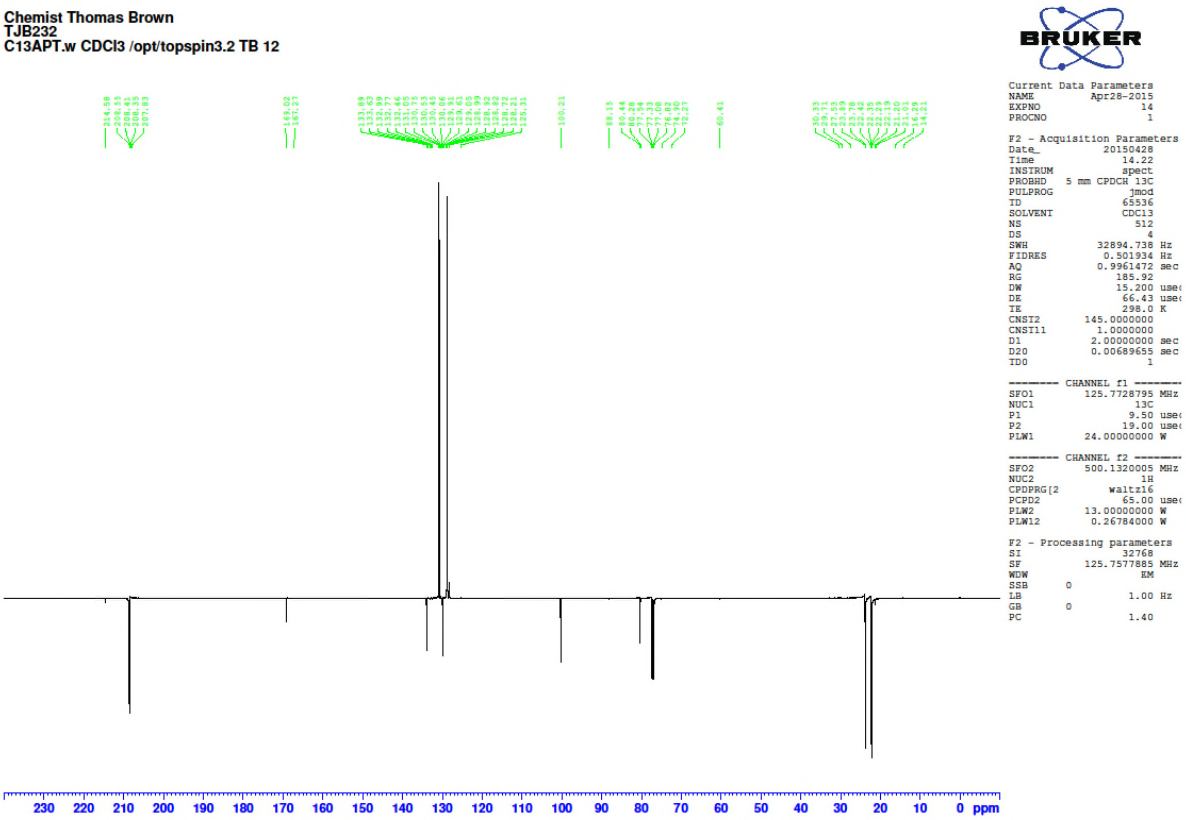


TJB232

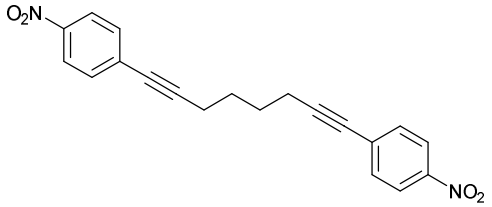
^{1}H NMR (500 MHz, $CDCl_3$).



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

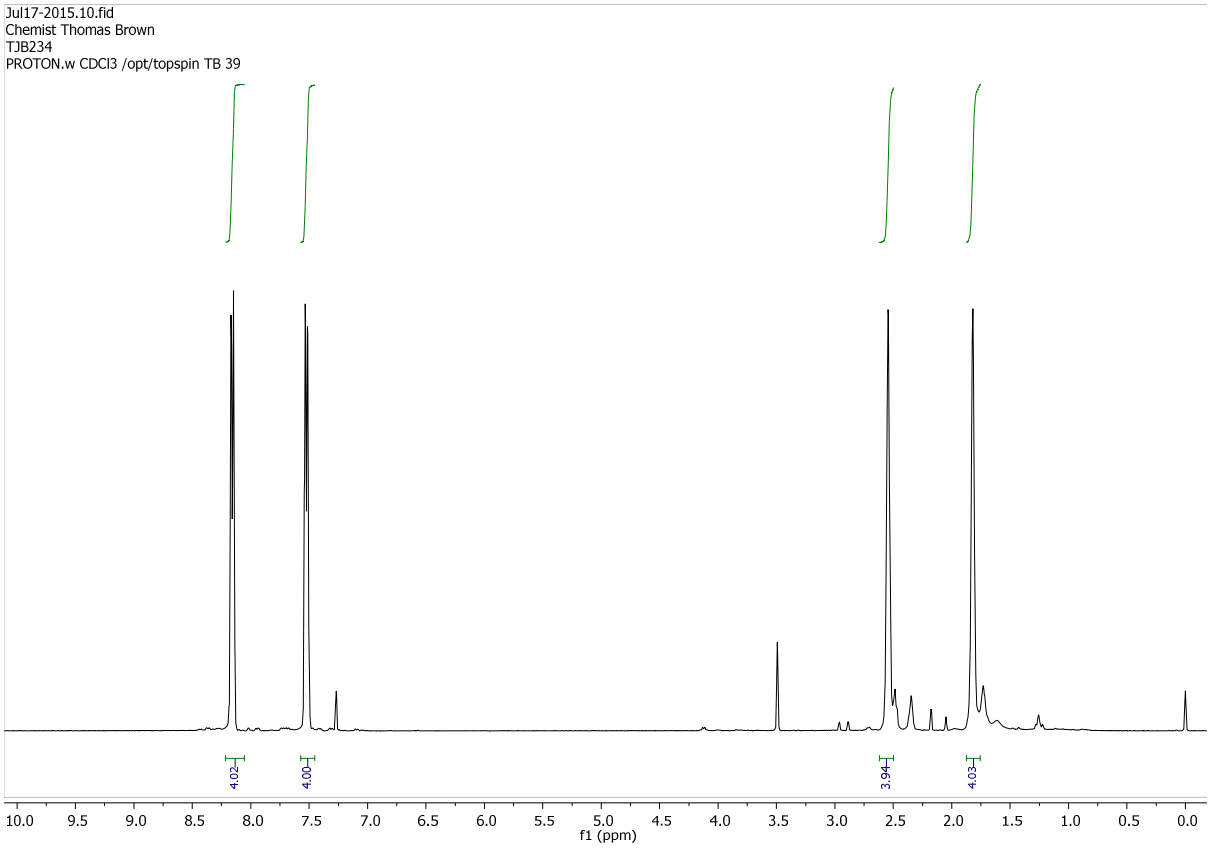


1,8-Bis(4-nitrophenyl)octa-1,7-diyne **14**.

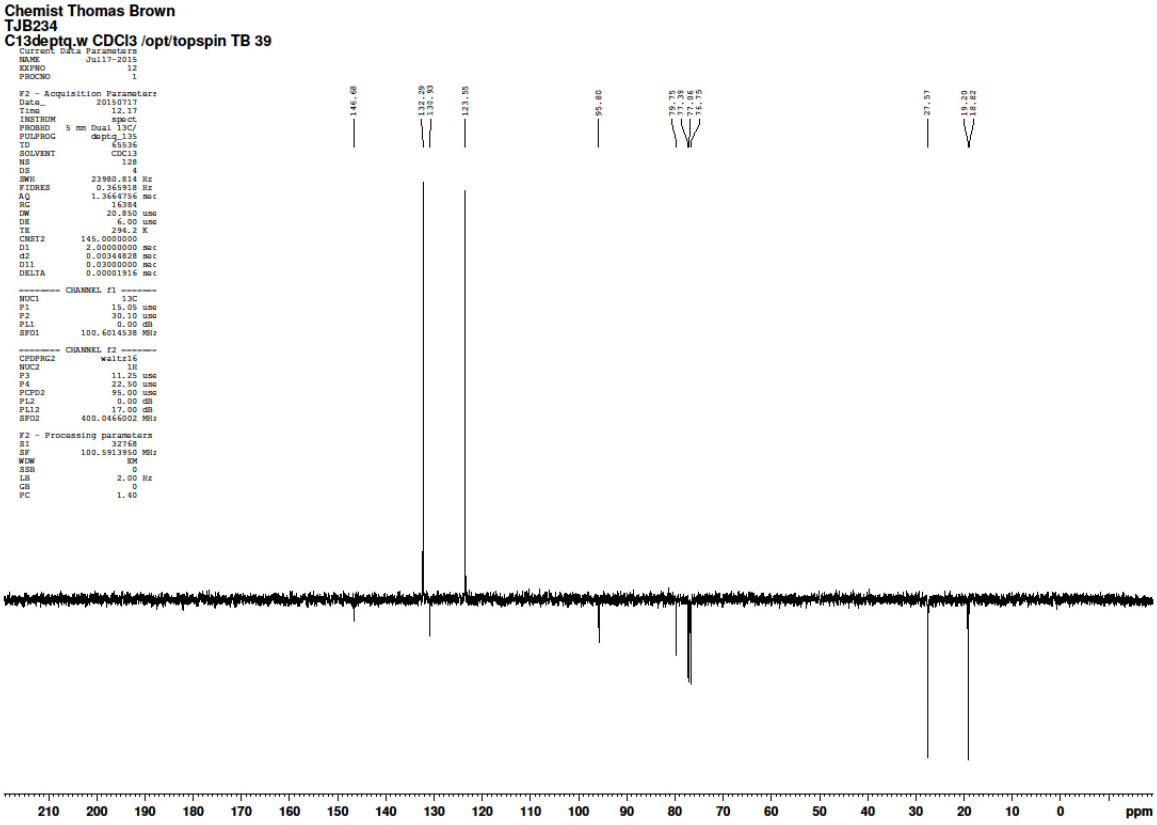


TJB234

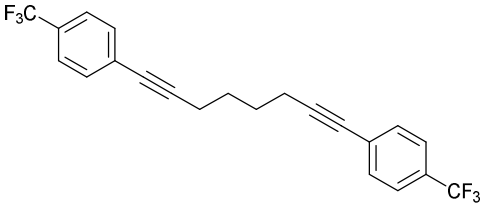
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

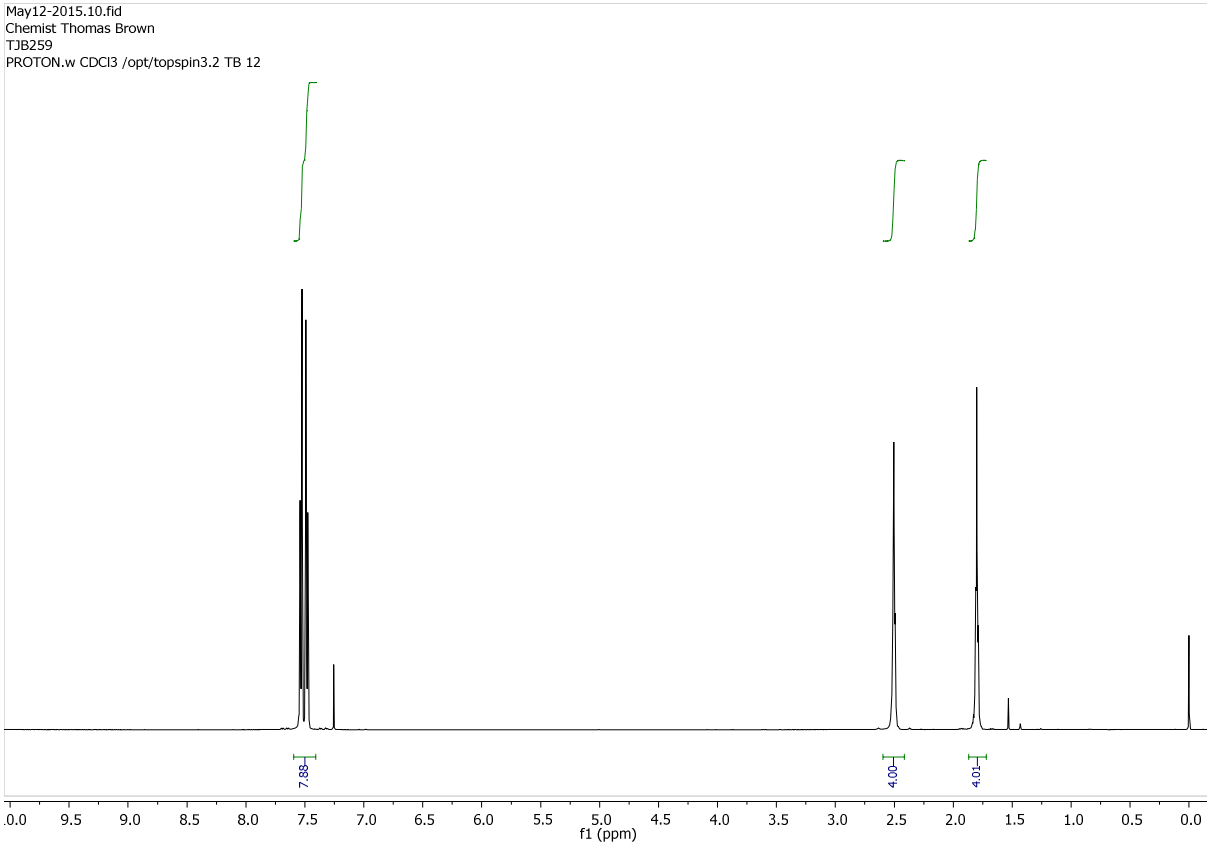


1,8-Bis(4-(trifluoromethyl)phenyl)octa-1,7-diyne **15**.

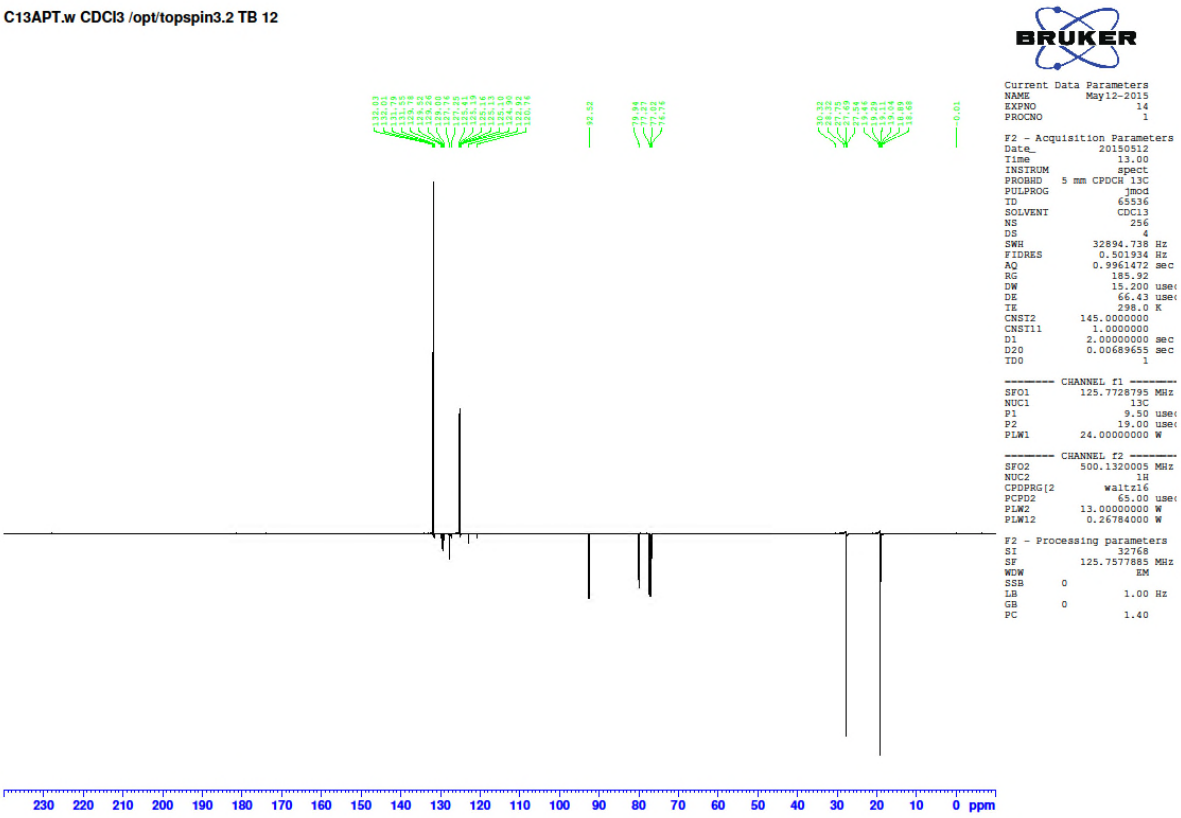


TJB259

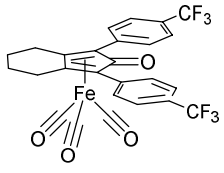
^{1}H NMR (500 MHz, $CDCl_3$).



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

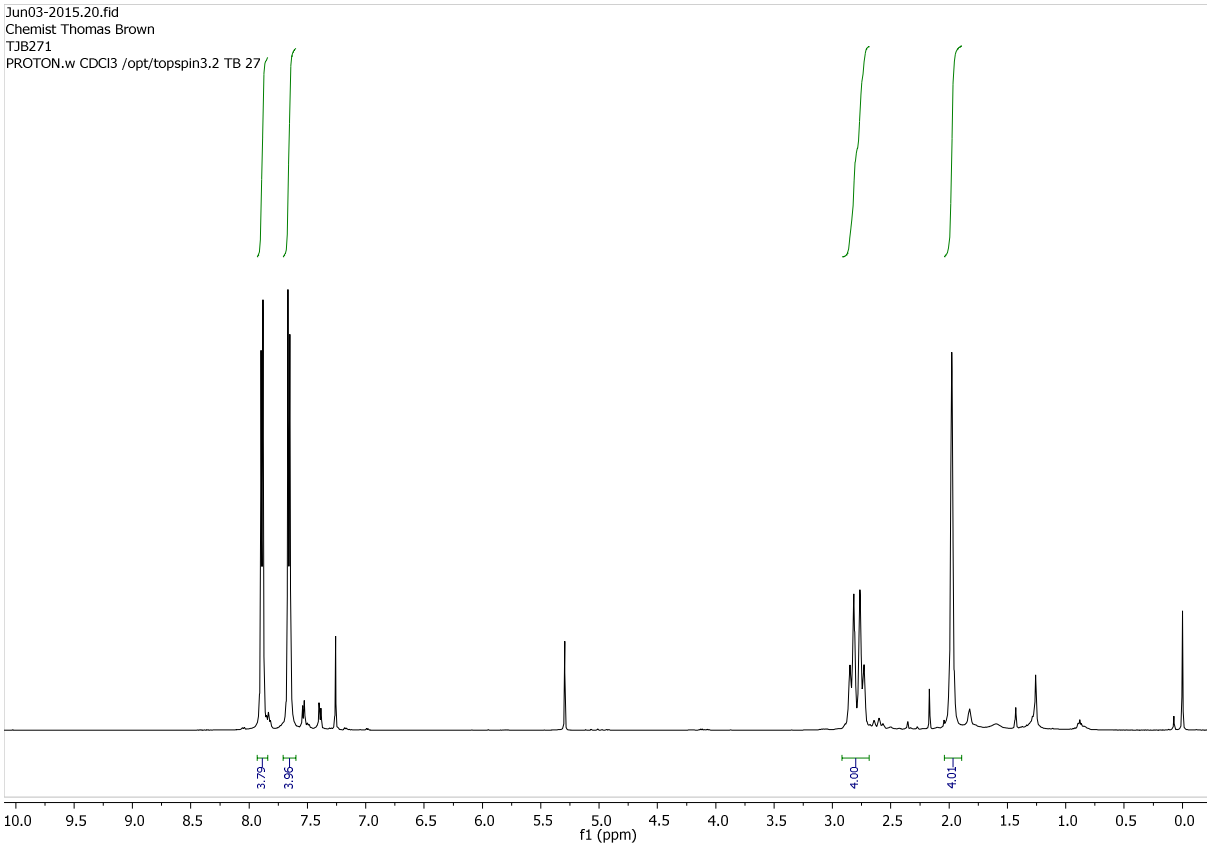


Tricarbonyl(1,3-di(4-trifluoromethylphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron **16**.

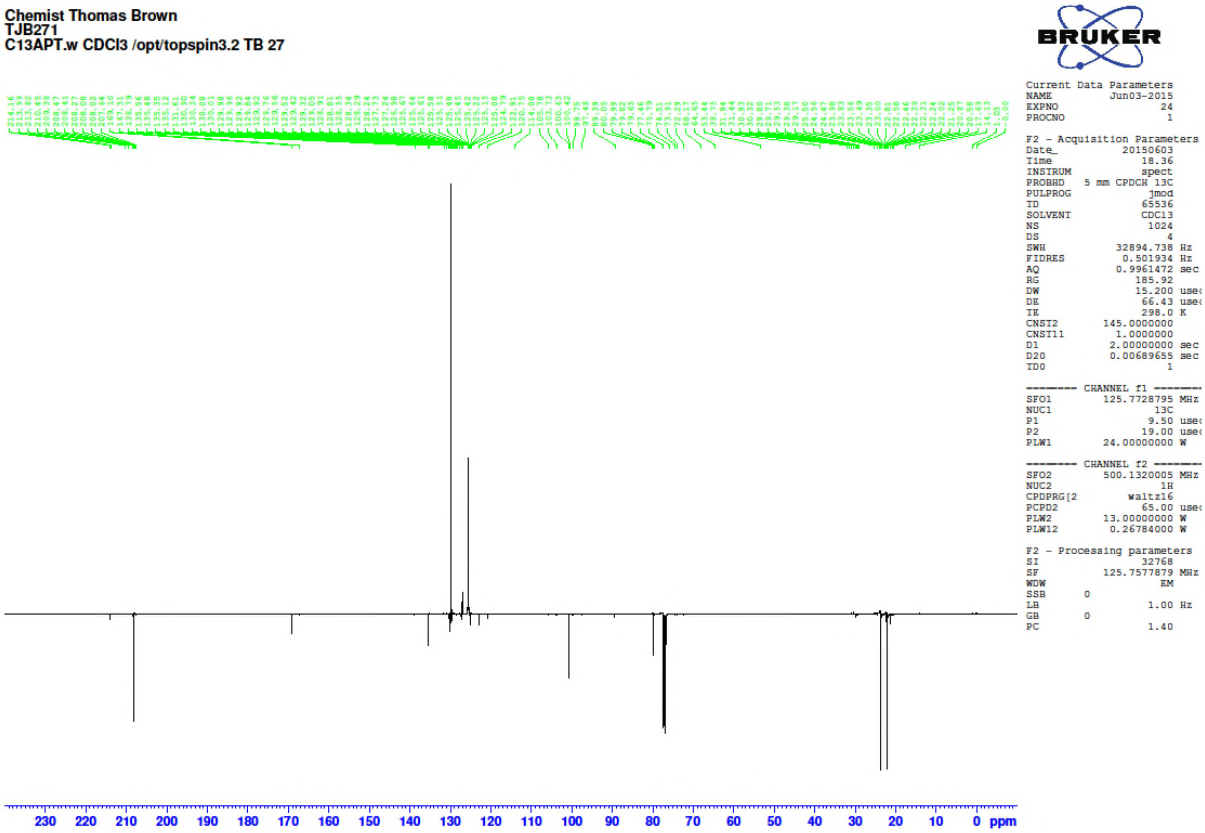


TJB271

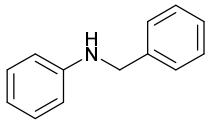
^{1}H NMR (500 MHz, $CDCl_3$).



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

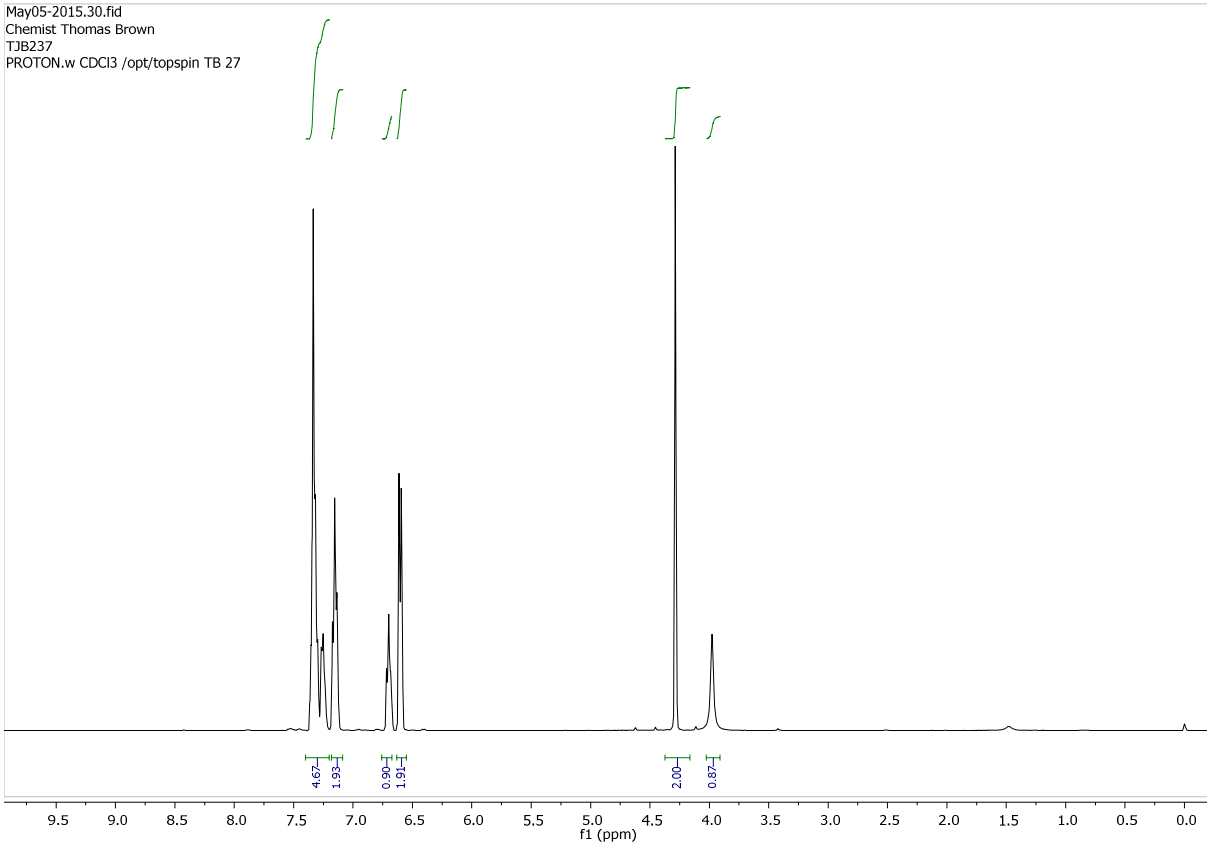


N-Benzylaniline **19.**

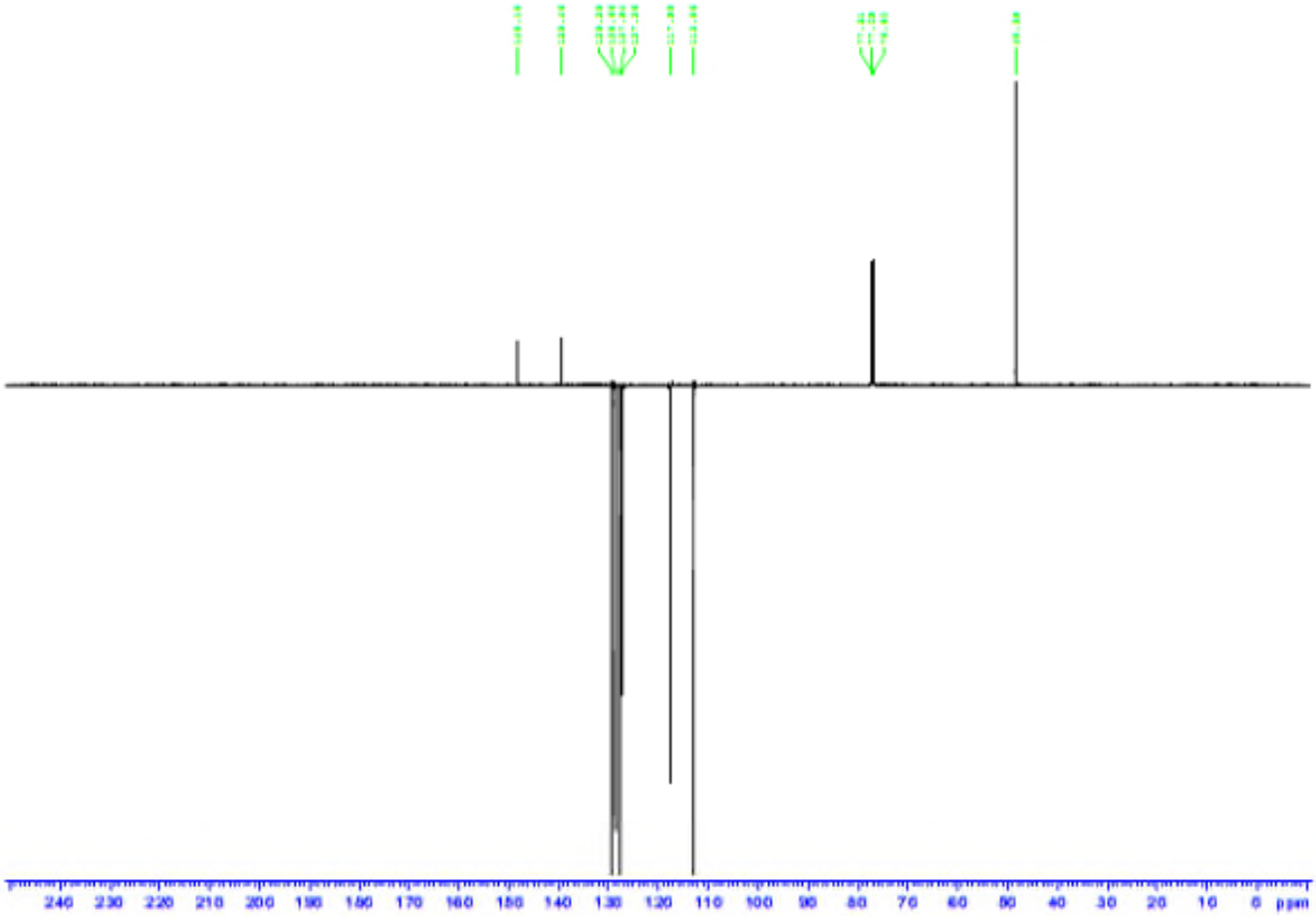


N-benzylaniline TJB237

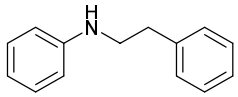
^{1}H NMR (400 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

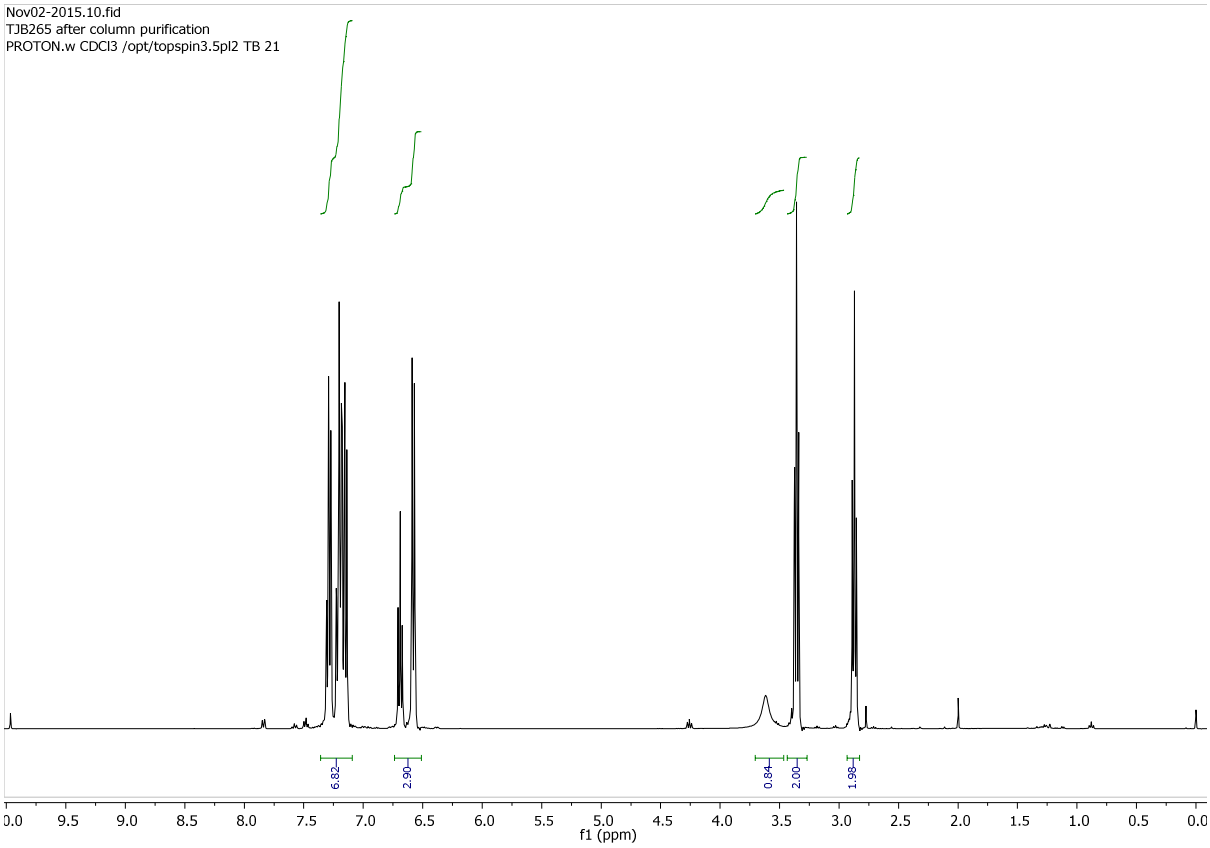


N-Phenethylaniline **20**.

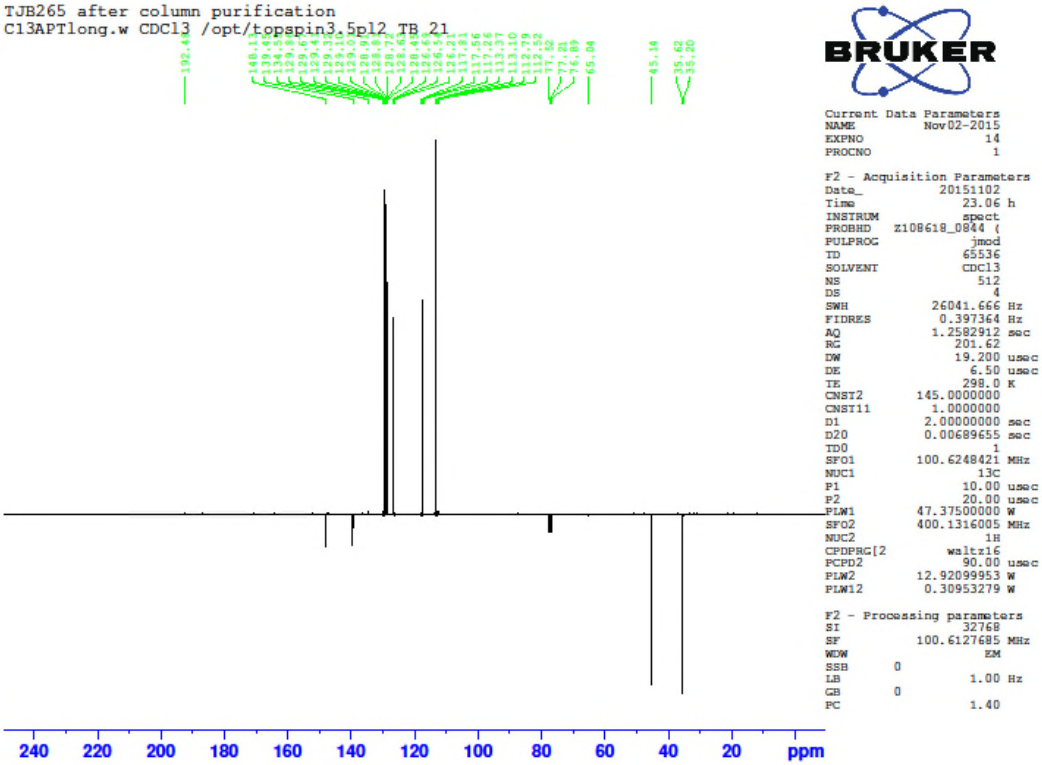


N-phenethylaniline TJB365

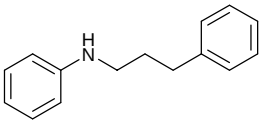
^{1}H NMR (500 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

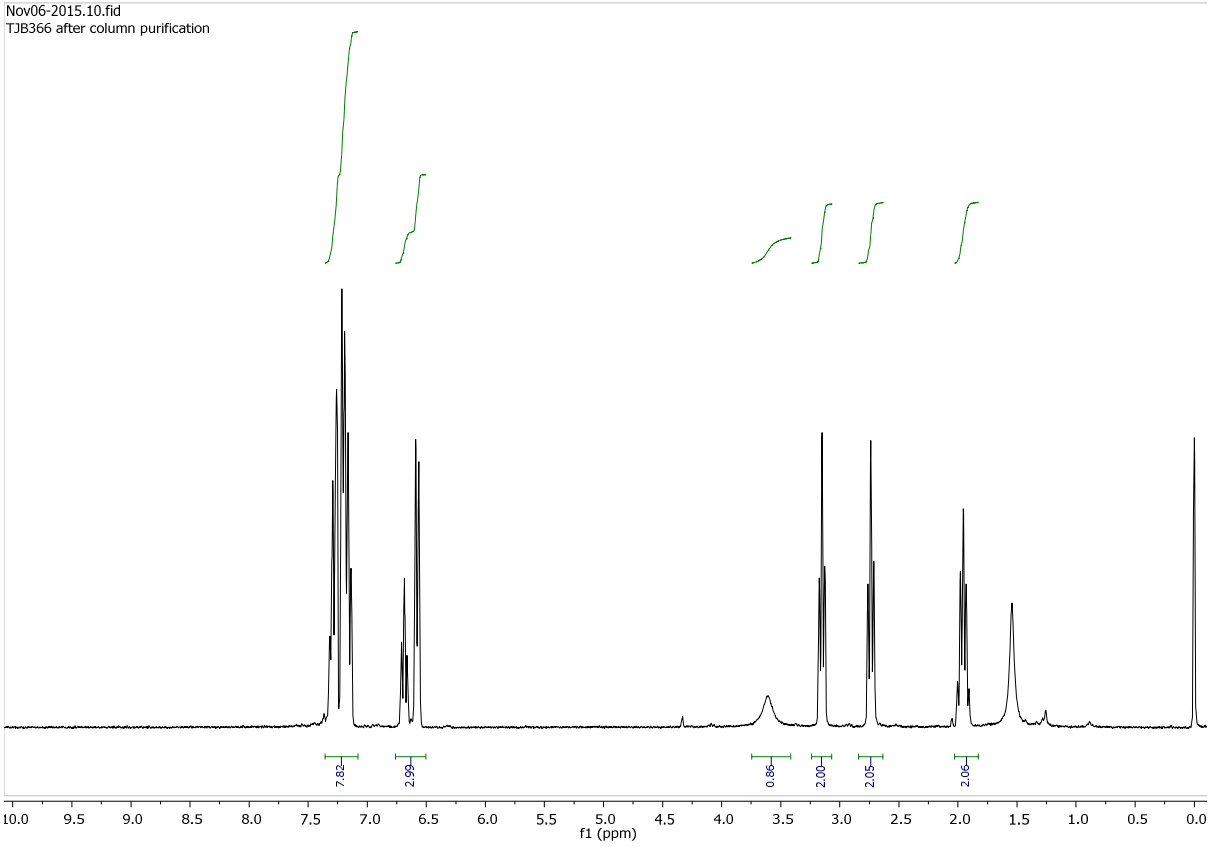


N-(3-Phenylpropyl)aniline **21**.

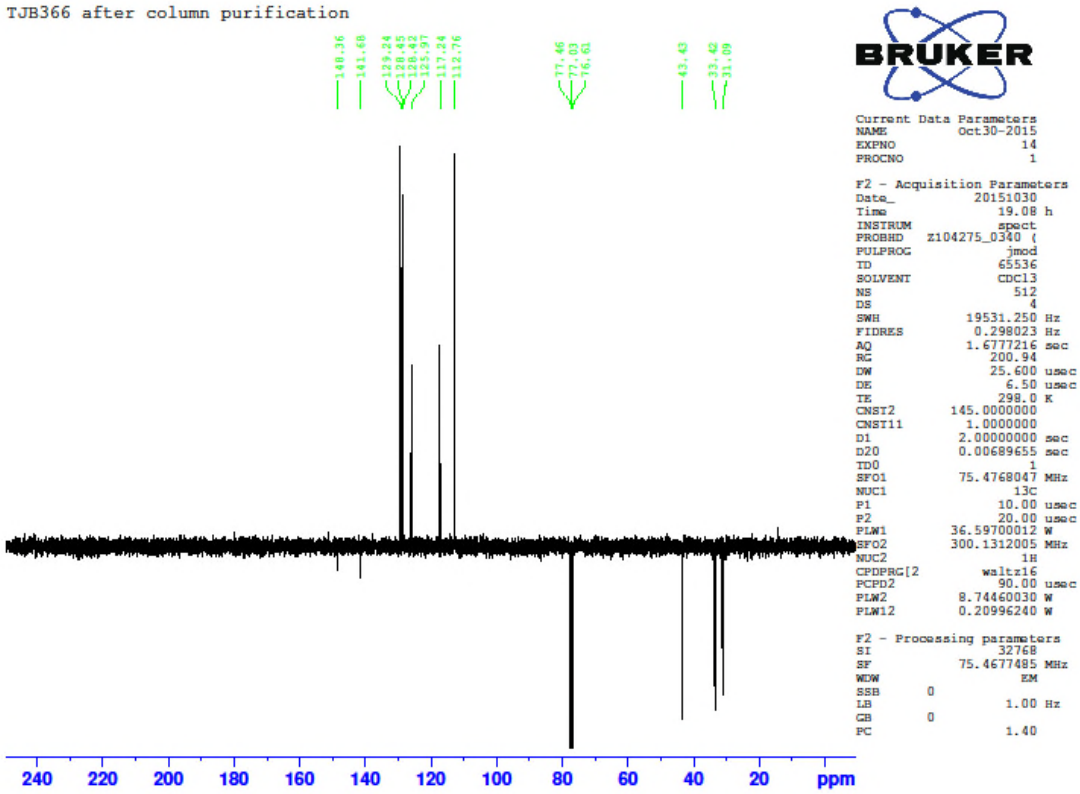


N-(3-phenylpropyl)aniline TJB366.

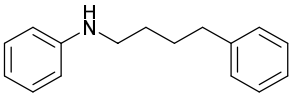
^{1}H NMR (300 MHz, $CDCl_3$).



^{13}C NMR (75 MHz, $CDCl_3$).

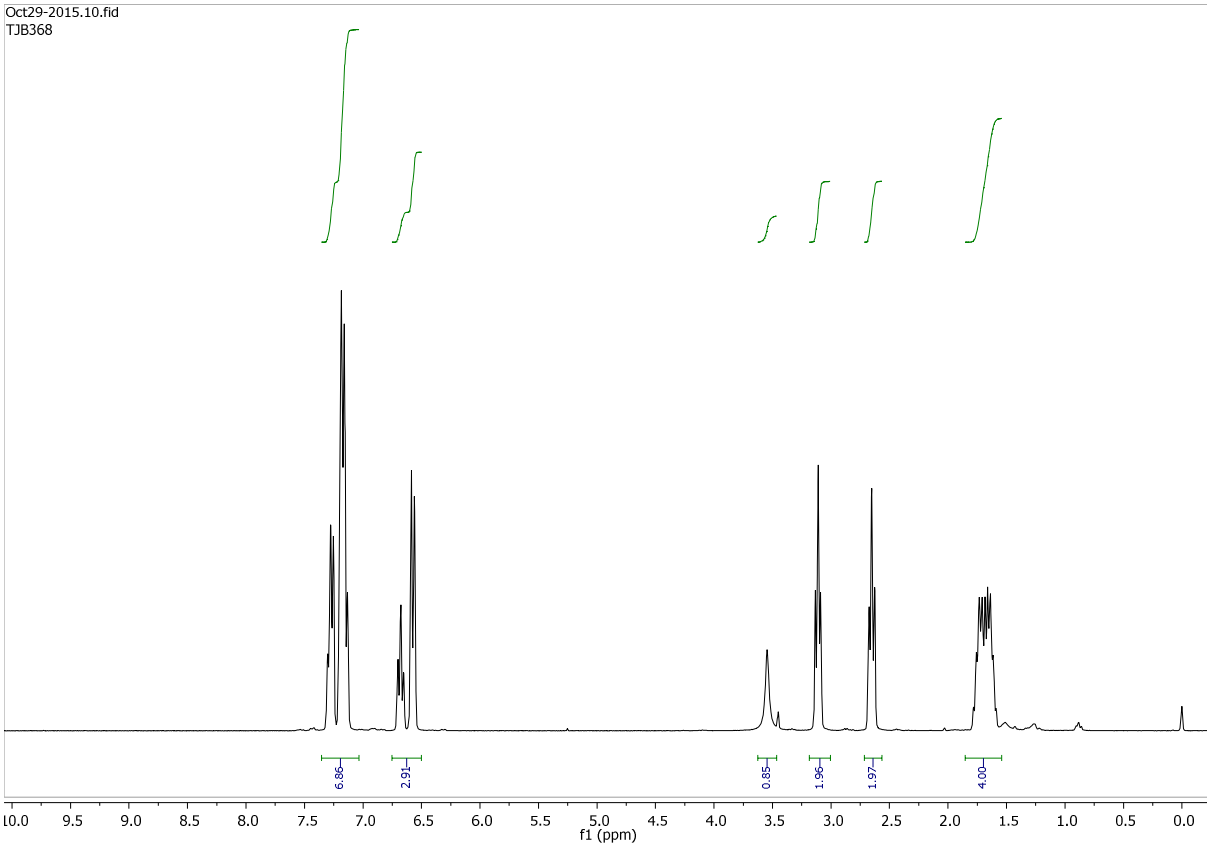


N-(4-Phenylbutyl)aniline **22**.

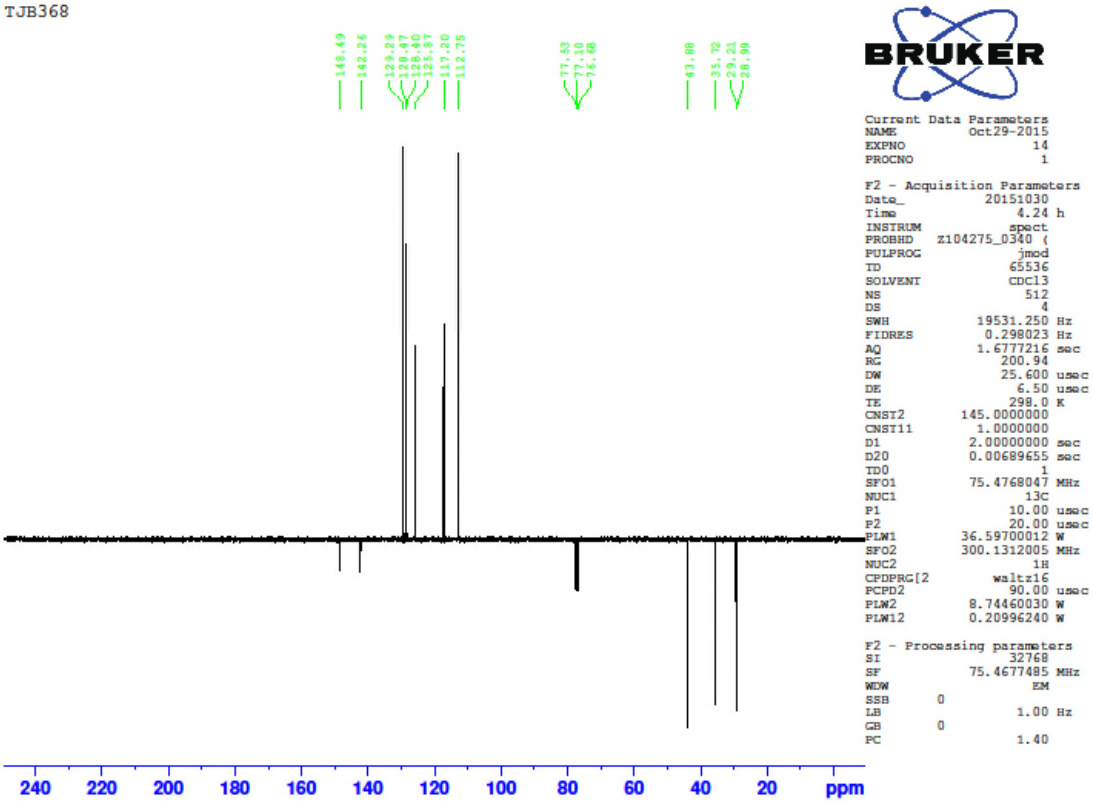


N-(4-phenylbutyl)aniline TJB368.

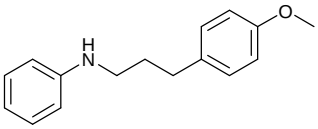
^{1}H NMR (300 MHz, $CDCl_3$).



^{13}C NMR (75 MHz, $CDCl_3$).

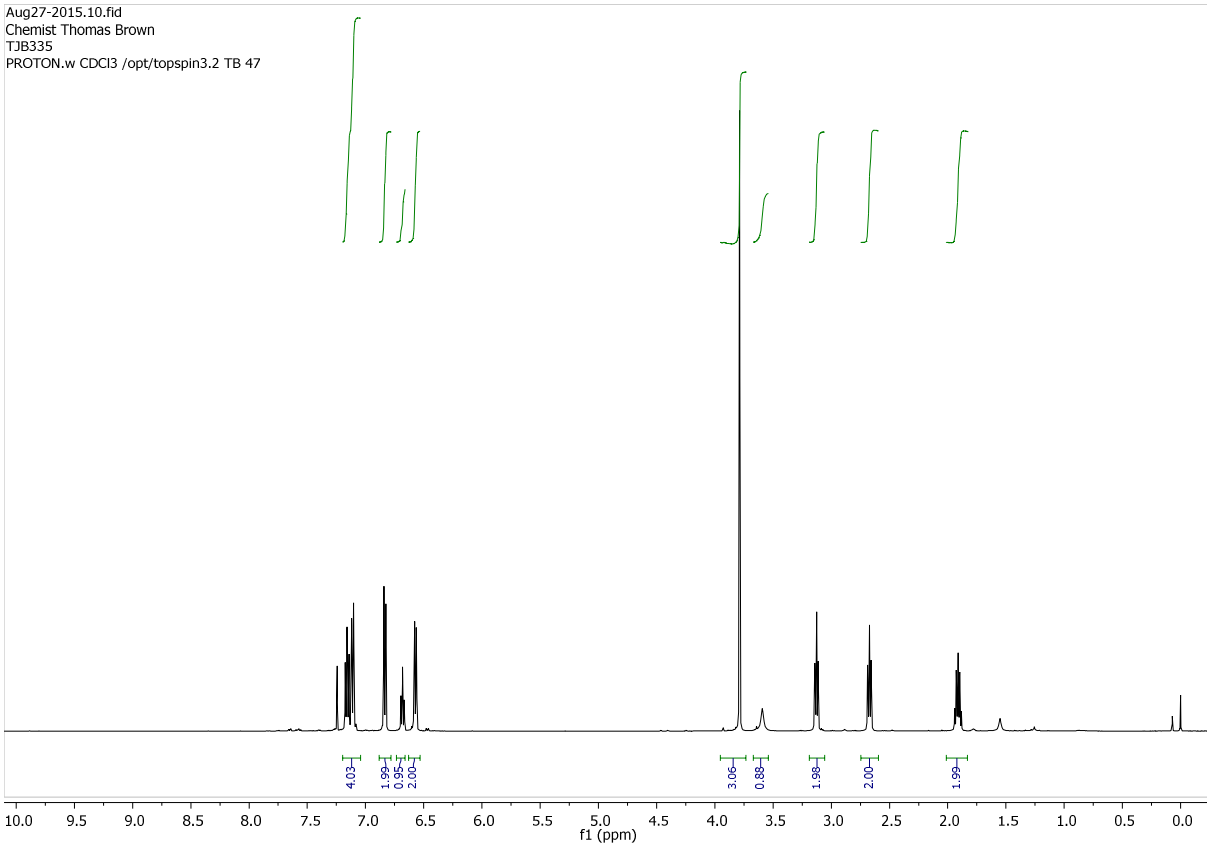


N-(3-(4-Methoxyphenyl)propyl)aniline **23**.

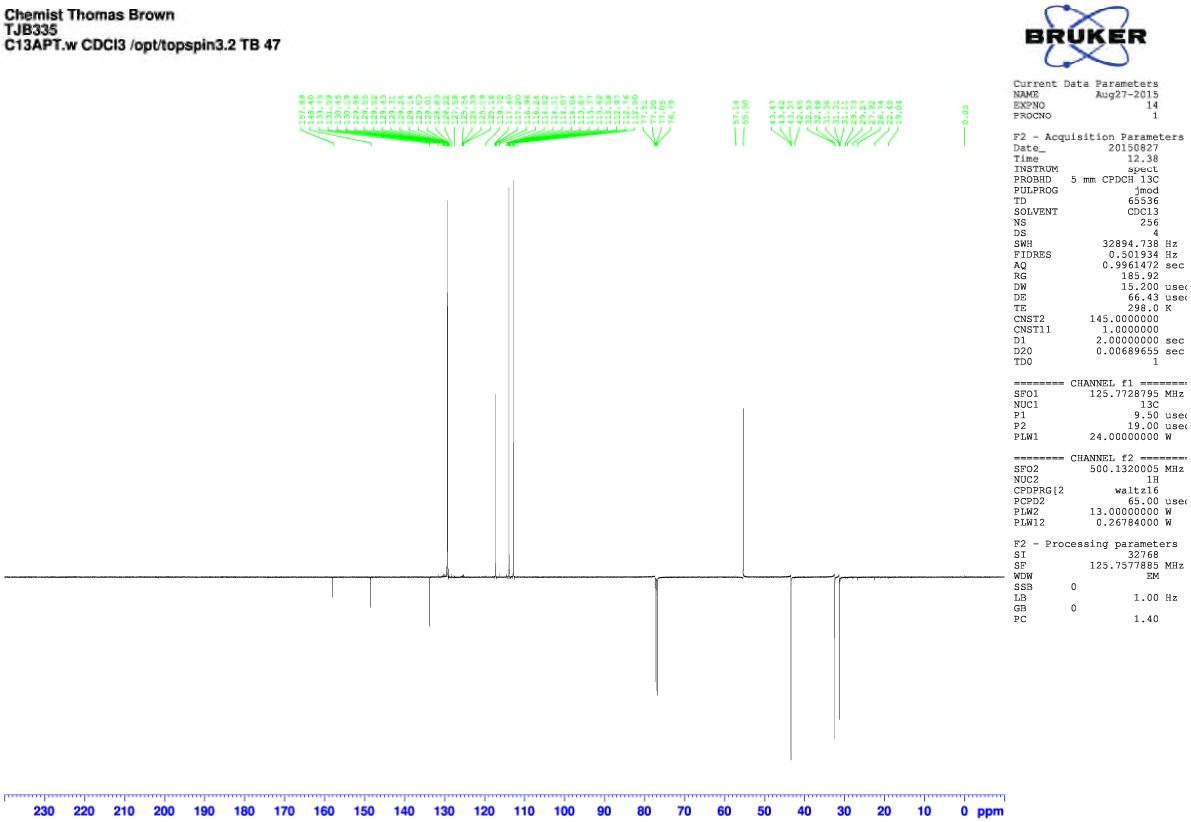


N-(3-(4-methoxyphenyl)propyl)aniline TJB335

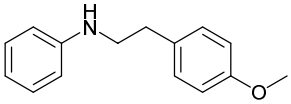
^{1}H NMR (500 MHz, $CDCl_3$).



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

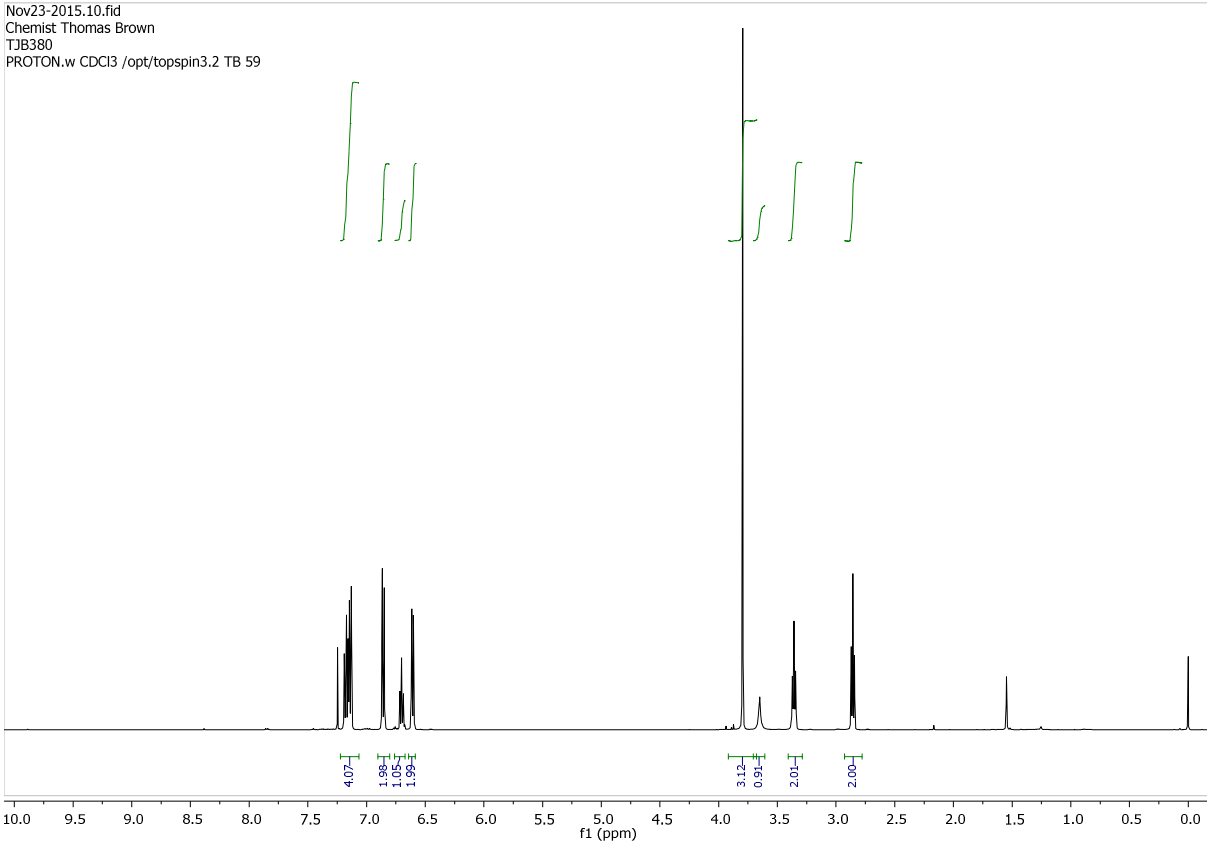


N-(4-Methoxyphenethyl)aniline **24**.

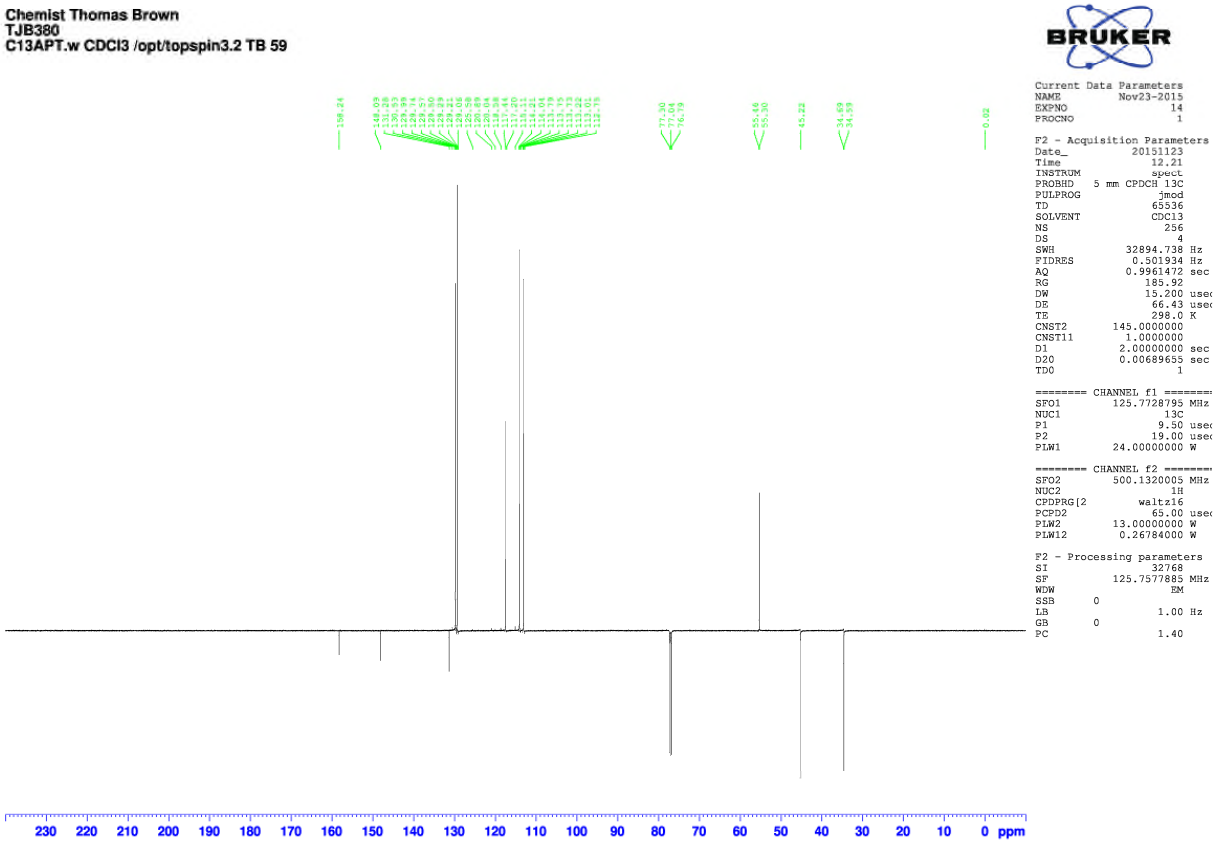


TJB367, 380. 380.

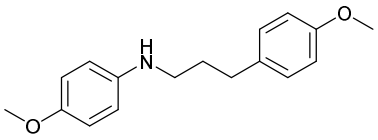
^{1}H NMR (500 MHz, $CDCl_3$).



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

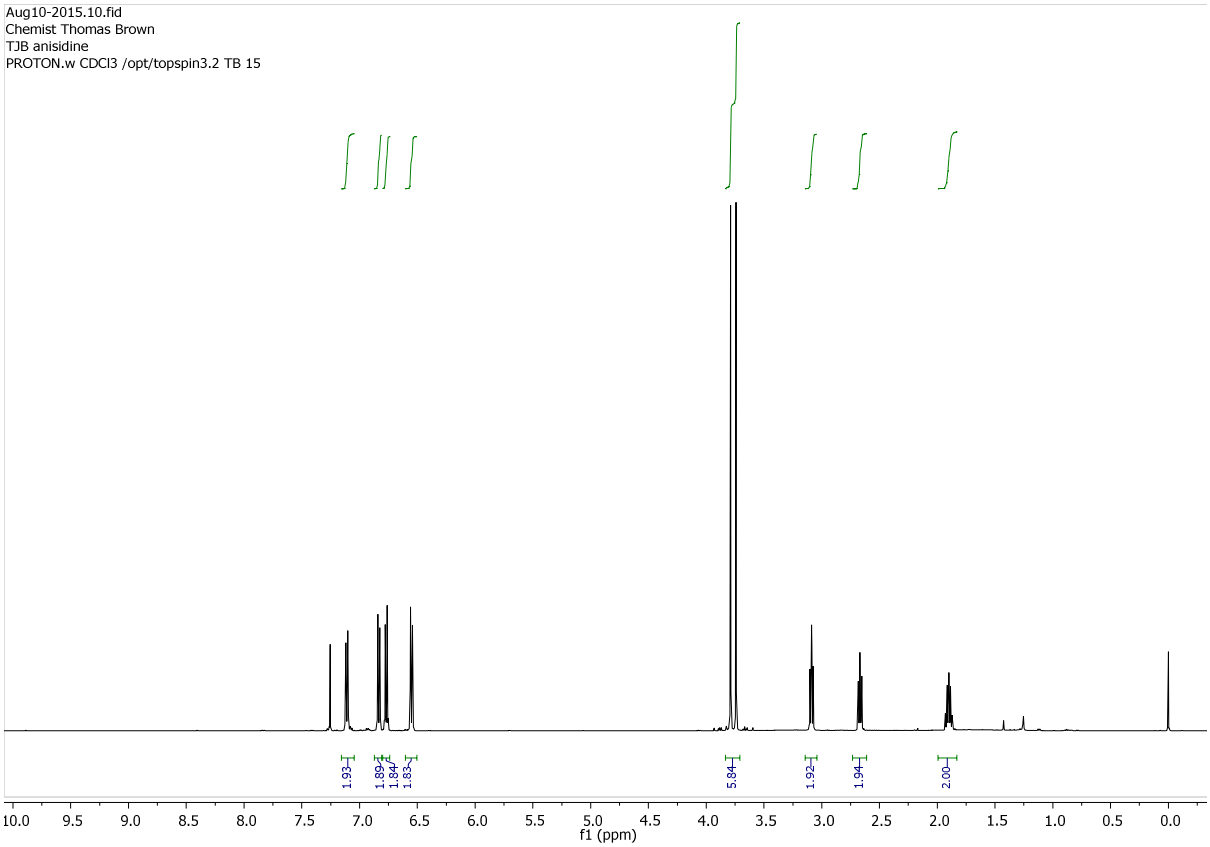


4-Methoxy-*N*-(3-(4-methoxyphenyl)propyl)aniline **25**.

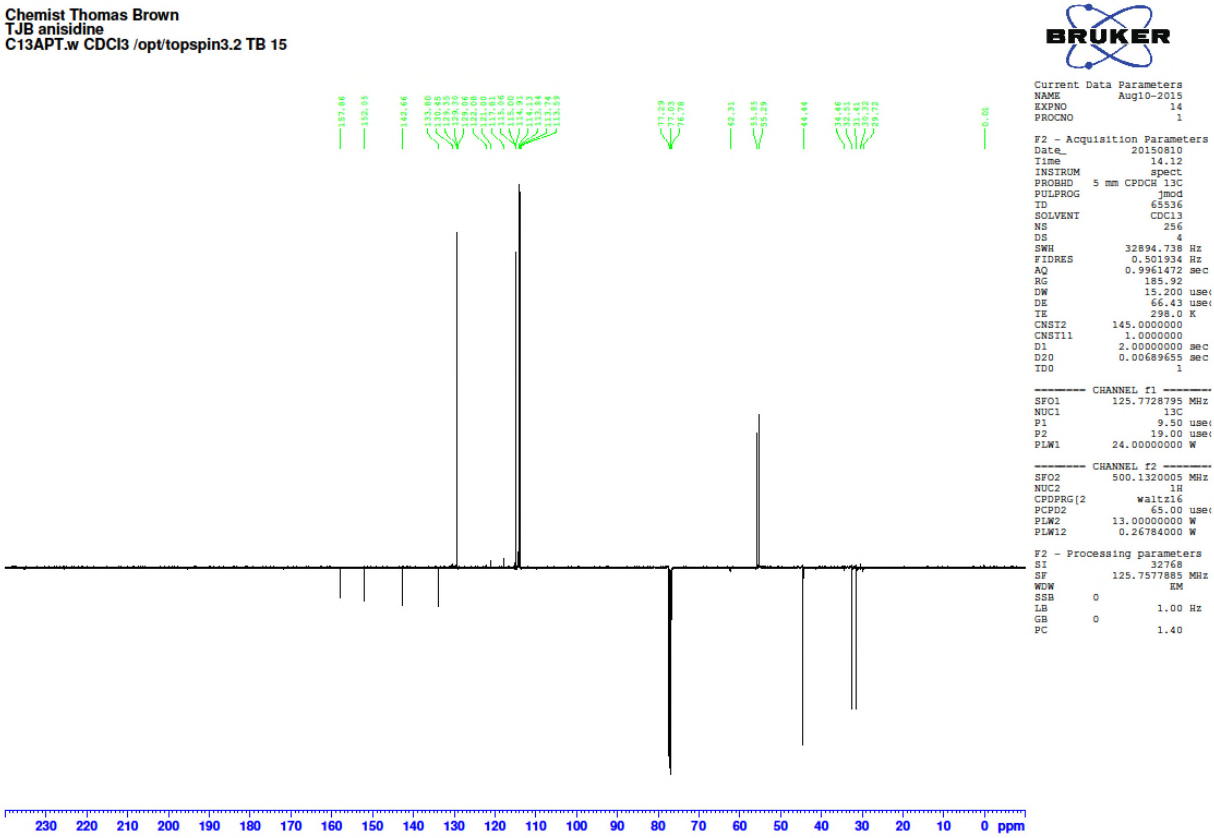


TJB319.

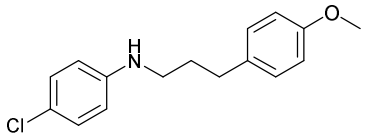
^{1}H NMR (500 MHz, $CDCl_3$).



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

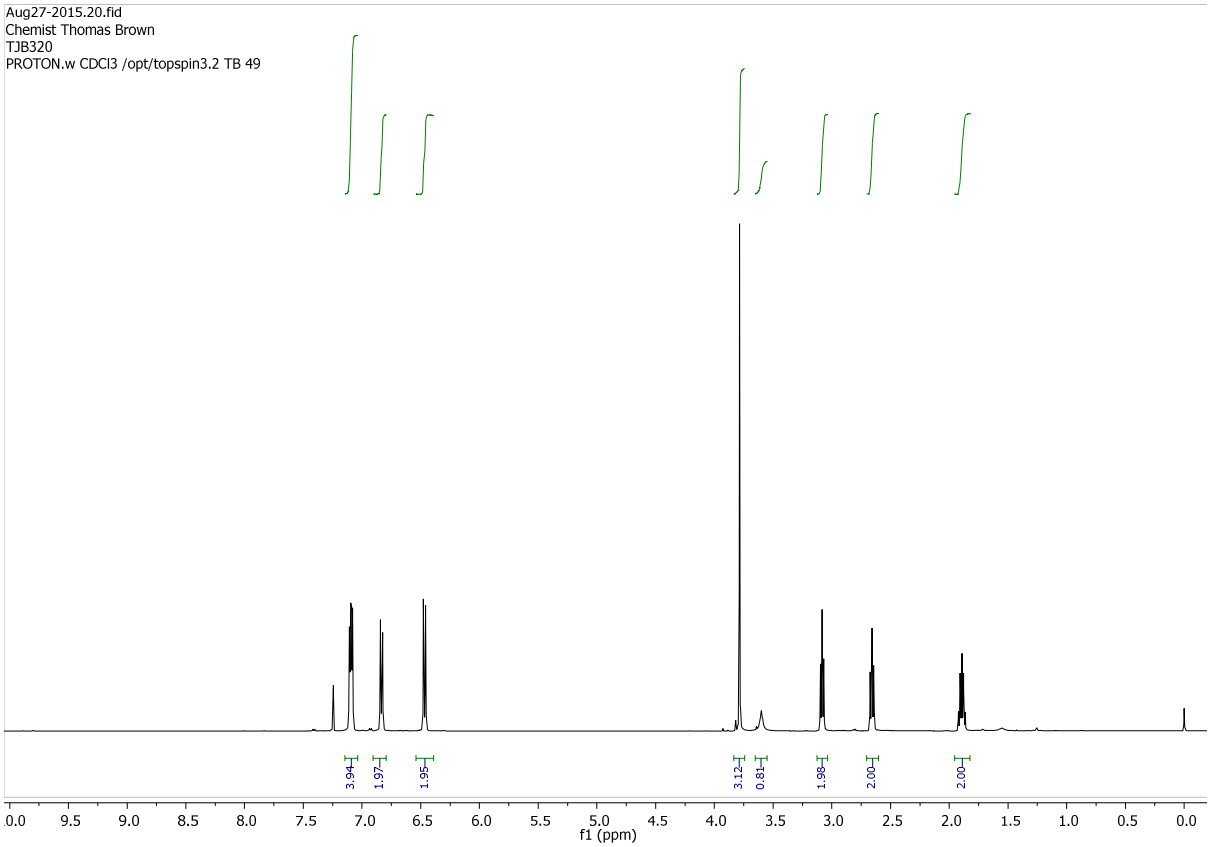


4-Chloro-*N*-(3-(4-methoxyphenyl)propyl)aniline **26**.

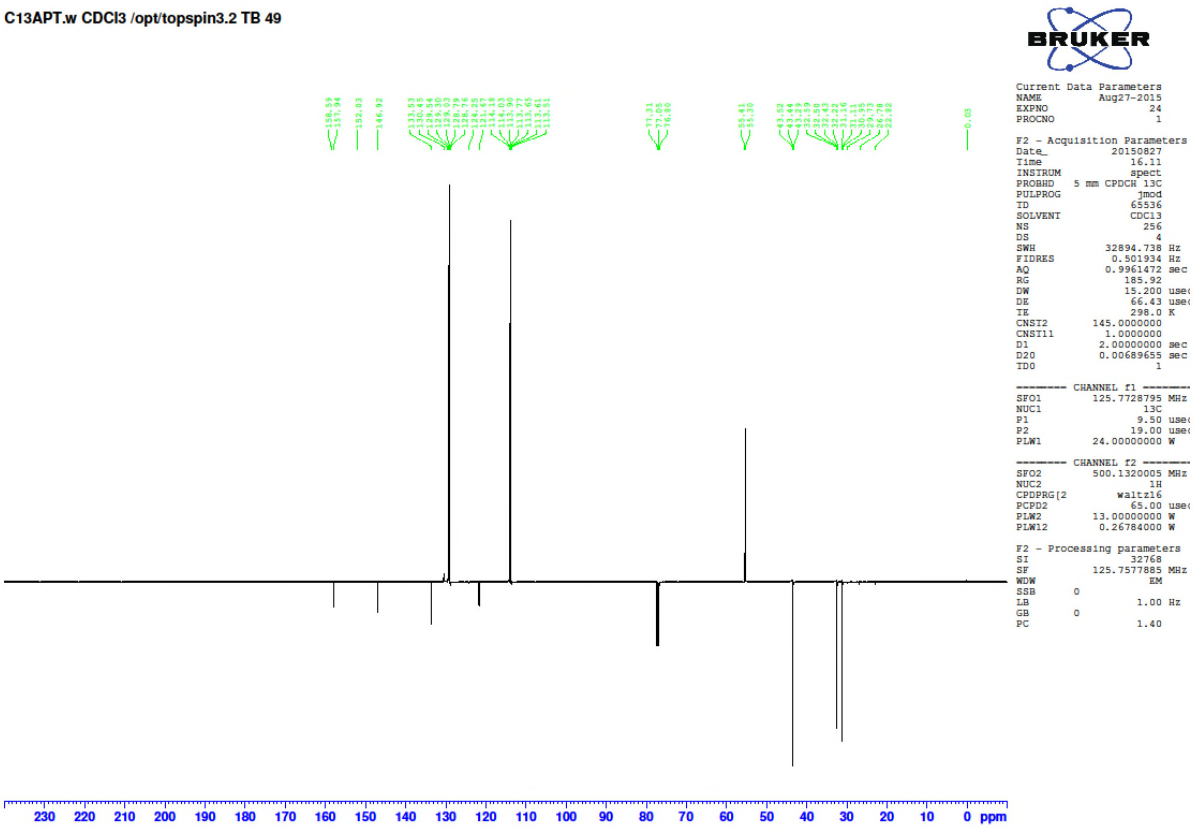


TJB320.

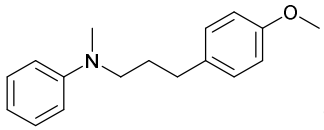
^{1}H NMR (500 MHz, $CDCl_3$).



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

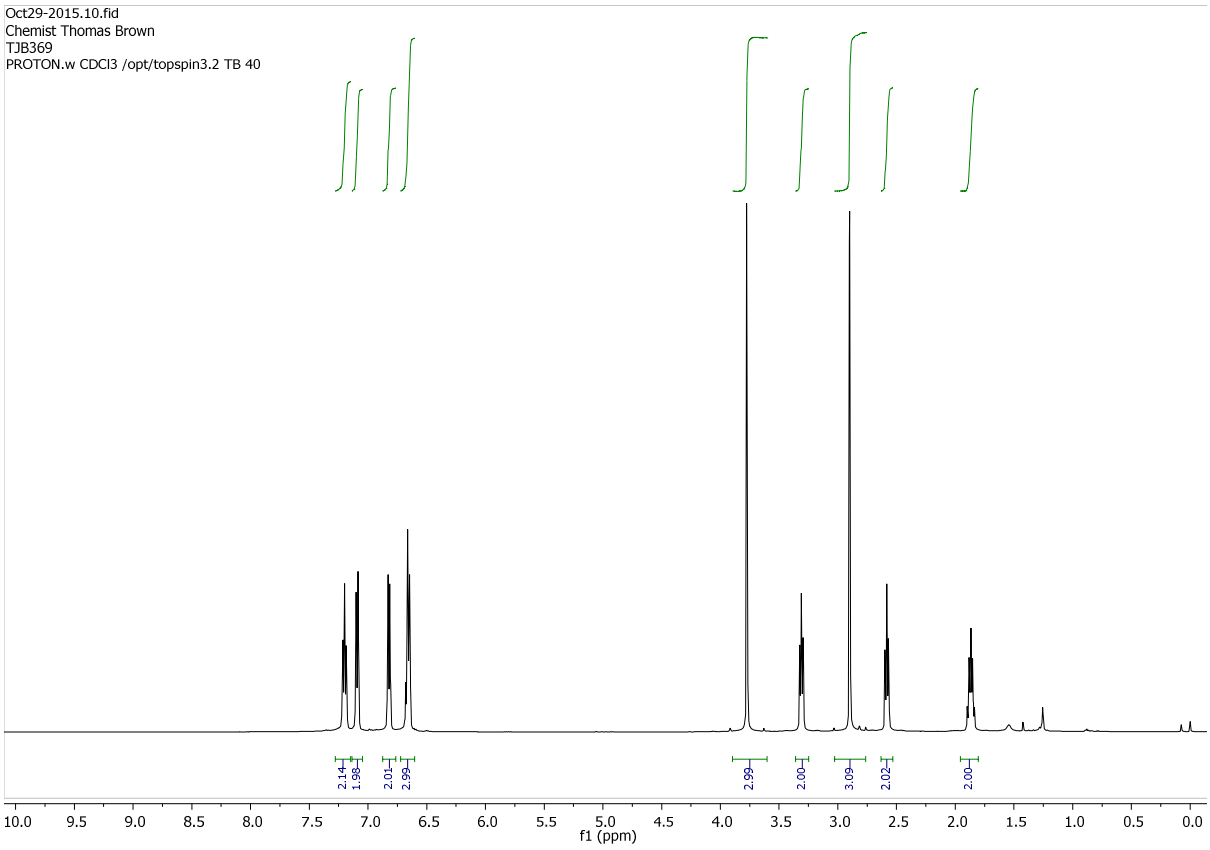


N-(3-(4-Methoxyphenyl)propyl)-*N*-methylaniline **27**.

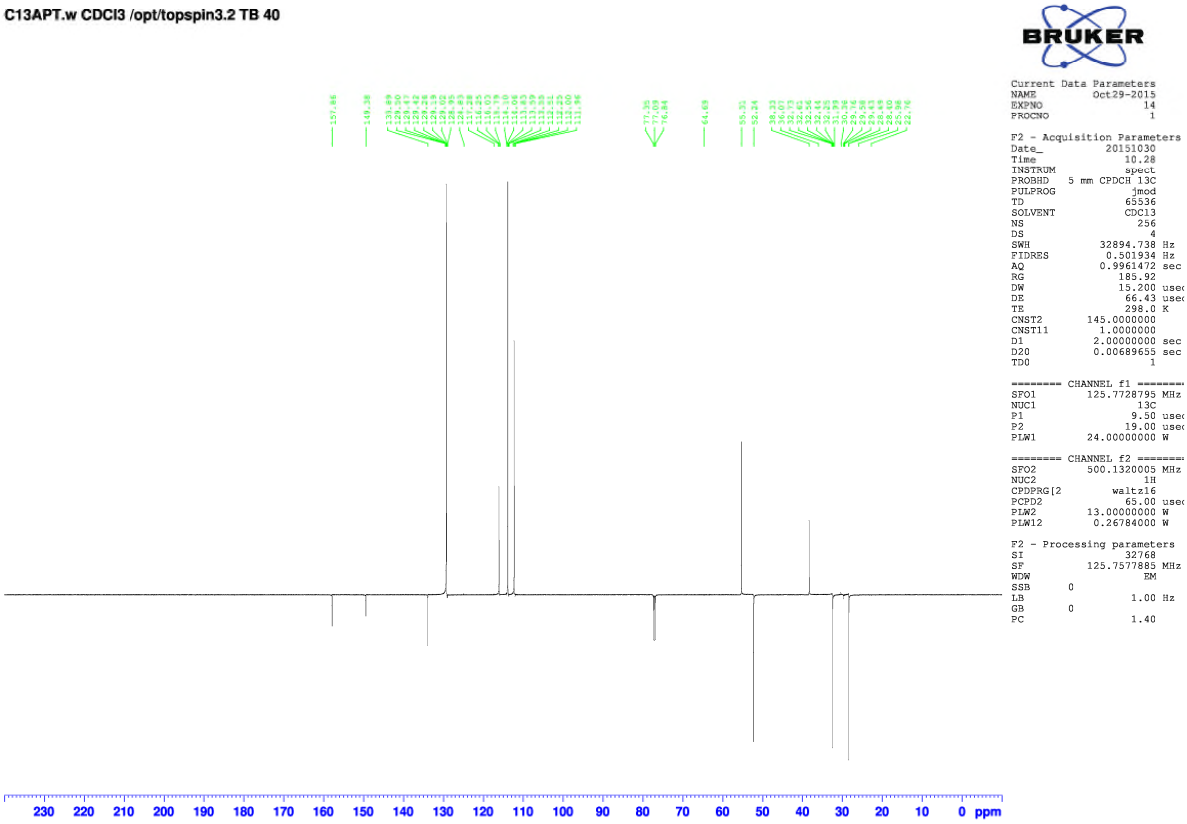


TJB369

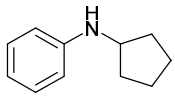
^{1}H NMR (500 MHz, $CDCl_3$).



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

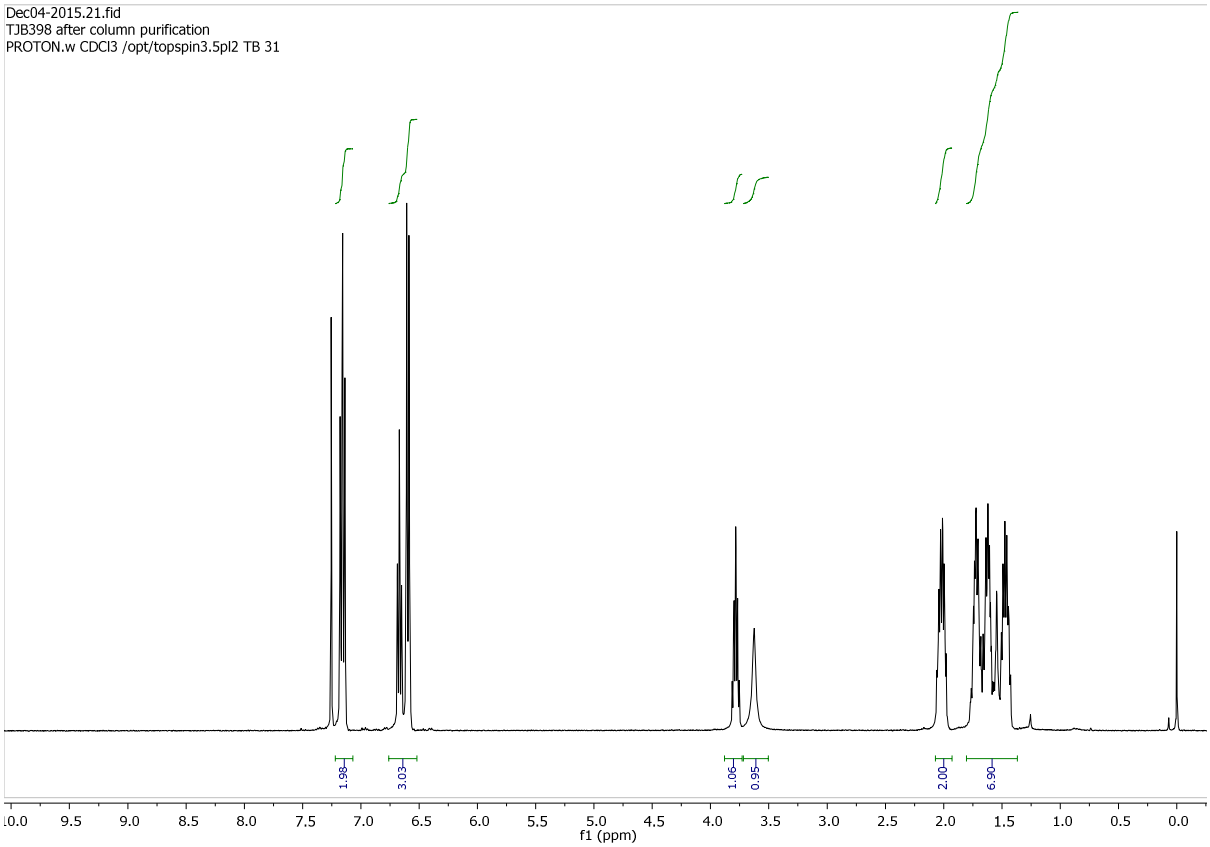


N-Cyclopentylaniline **28**.

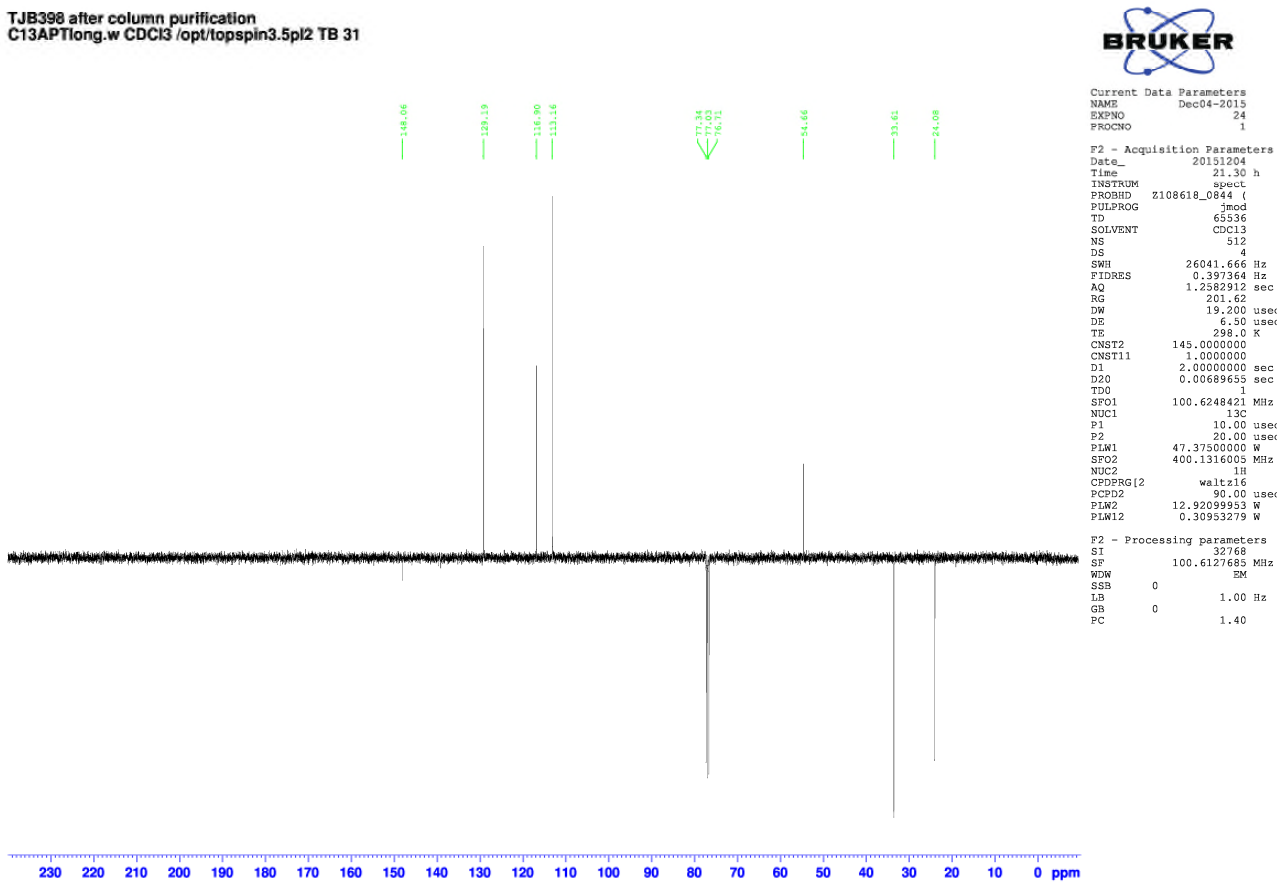


TJB398.

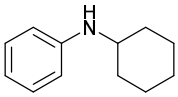
^{1}H NMR (400 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

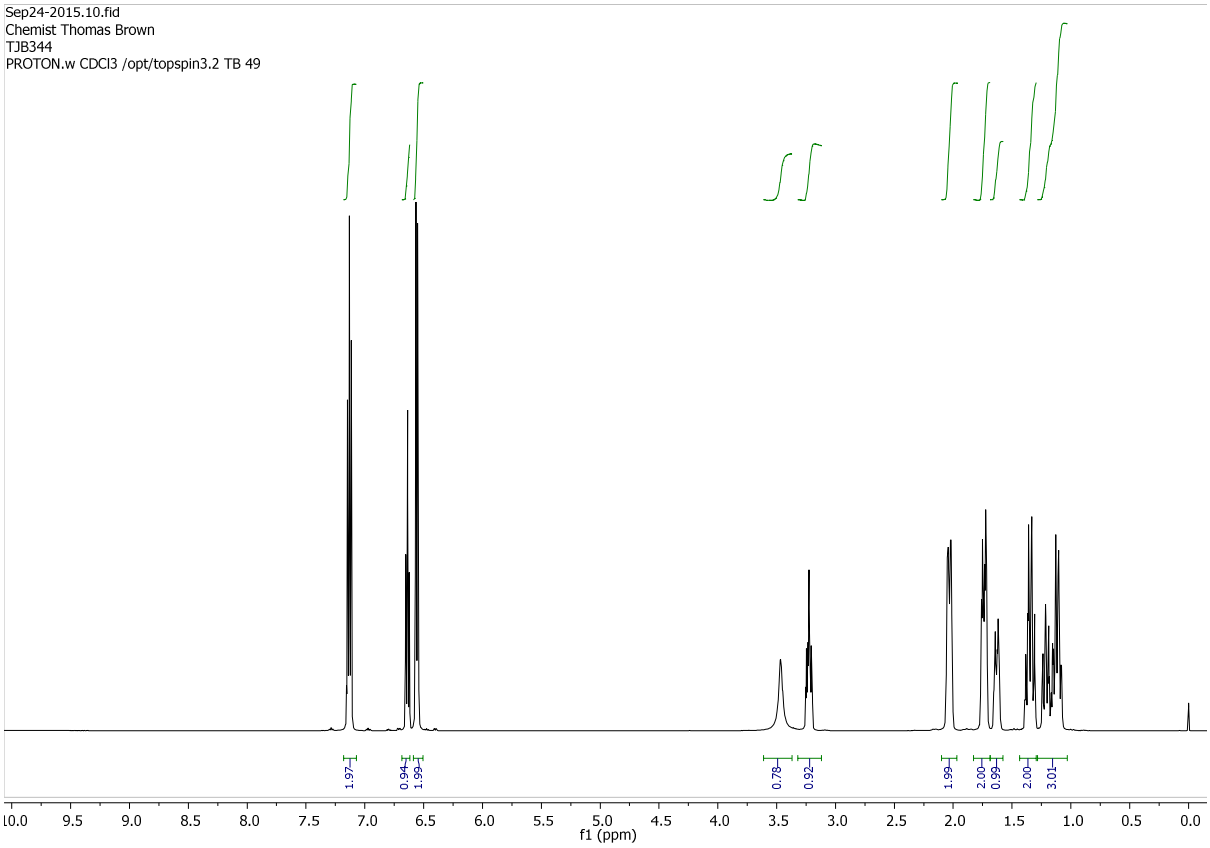


N-Cyclohexylaniline **29**.

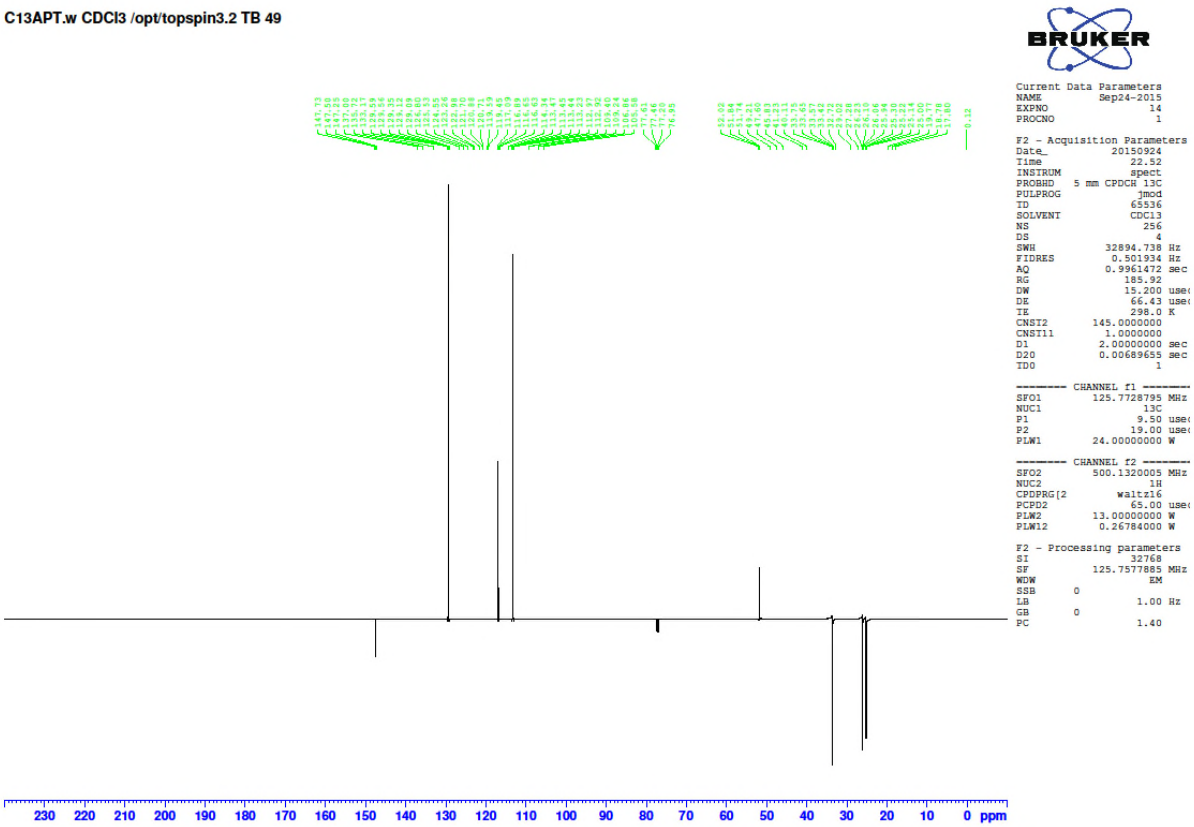


TJB344.

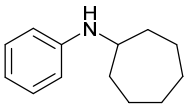
^{1}H NMR (500 MHz, $CDCl_3$).



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

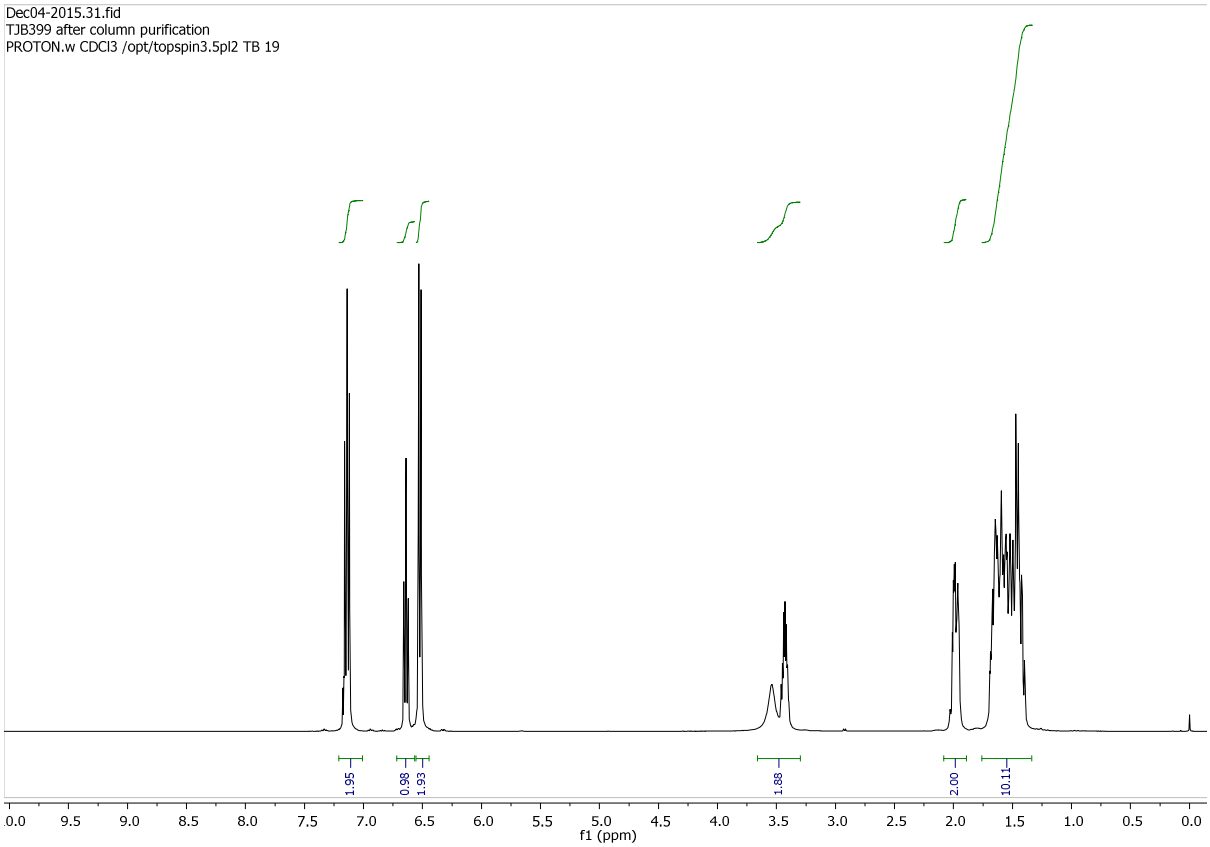


N-Phenylcycloheptanamine **30**.

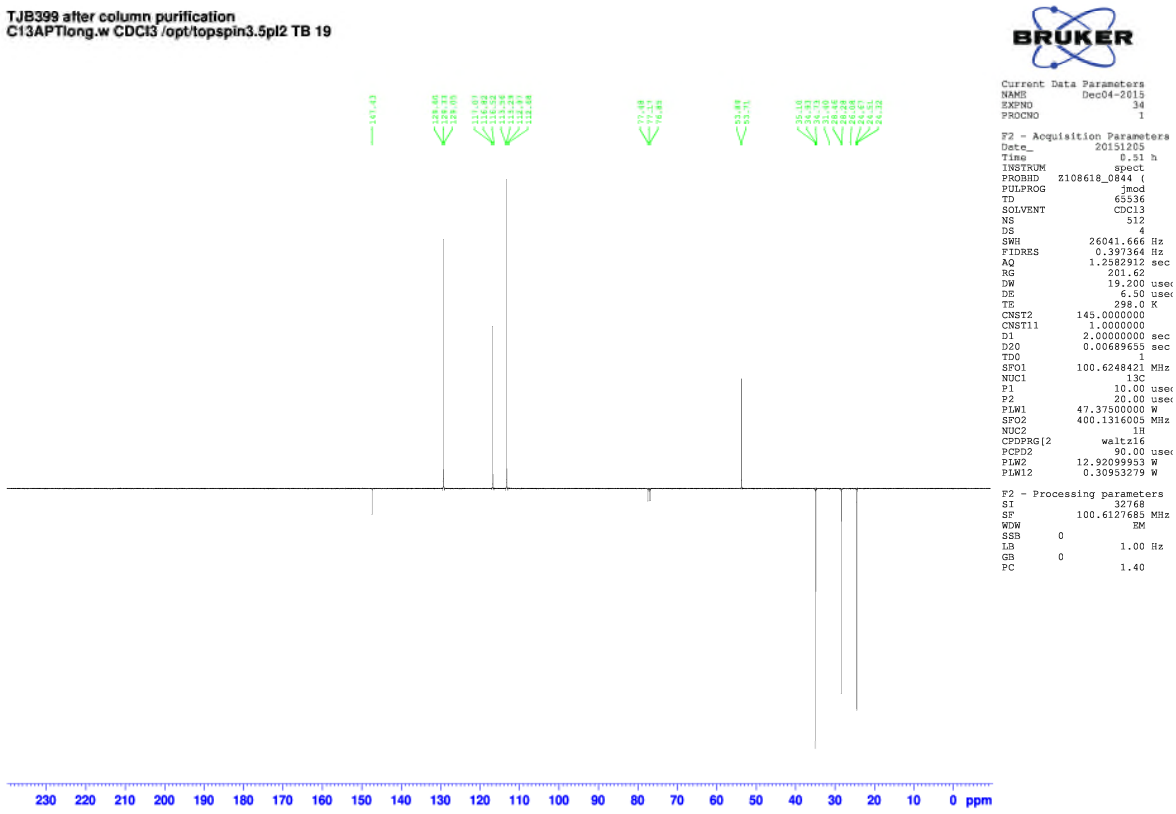


TJB399.

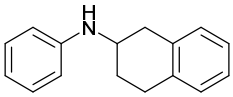
^{1}H NMR (400 MHz, $CDCl_3$).



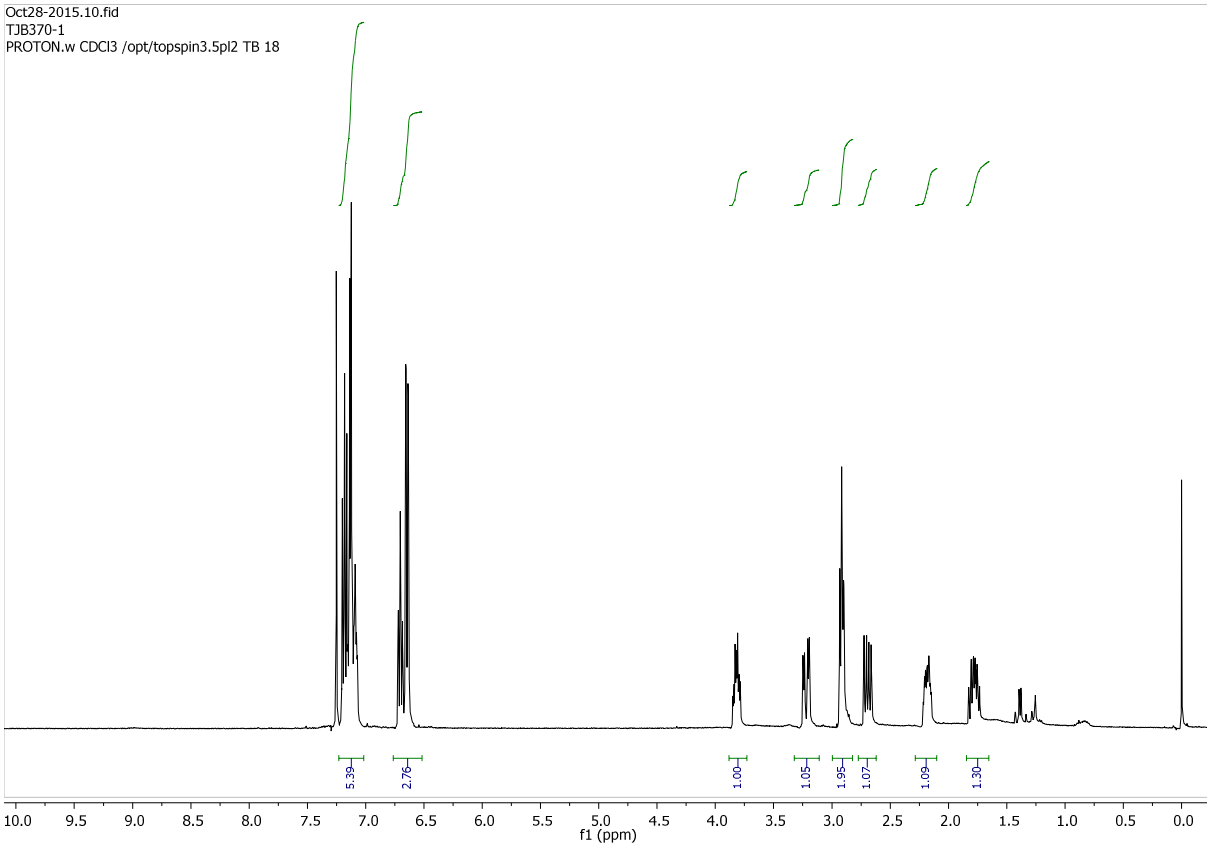
^{13}C NMR (100 MHz, $CDCl_3$).



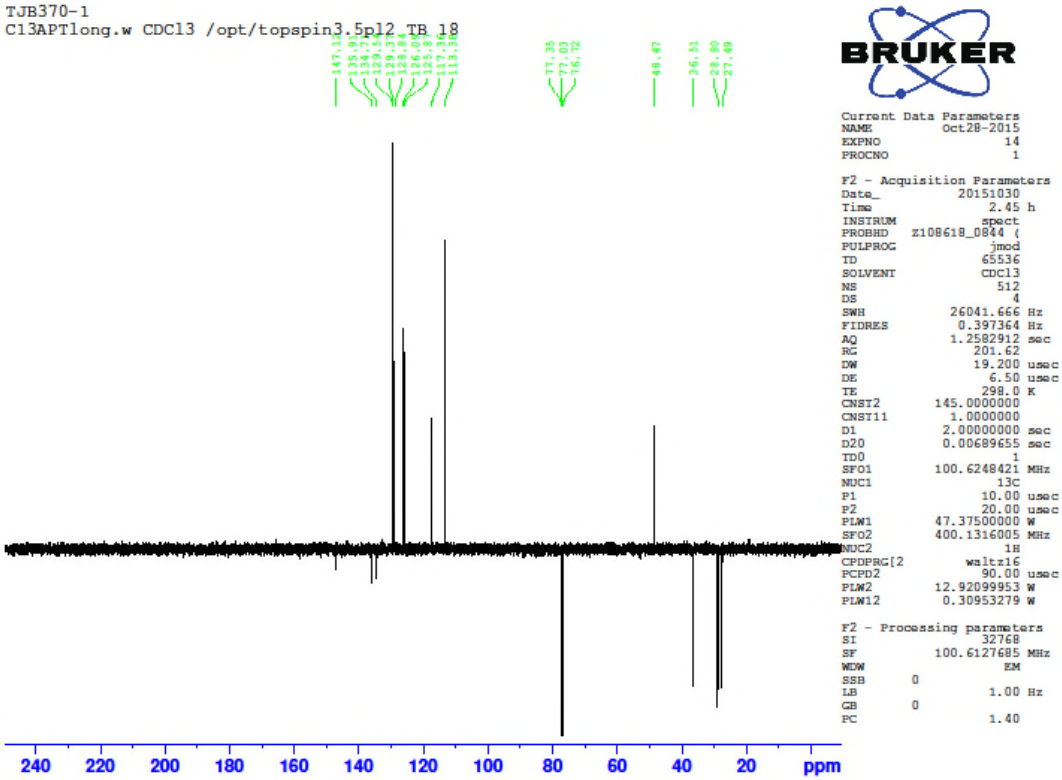
N-Phenyl-1,2,3,4-tetrahydronaphthalen-2-amine **31**.


TJB370.

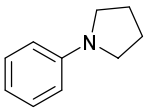
^{1}H NMR (400 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

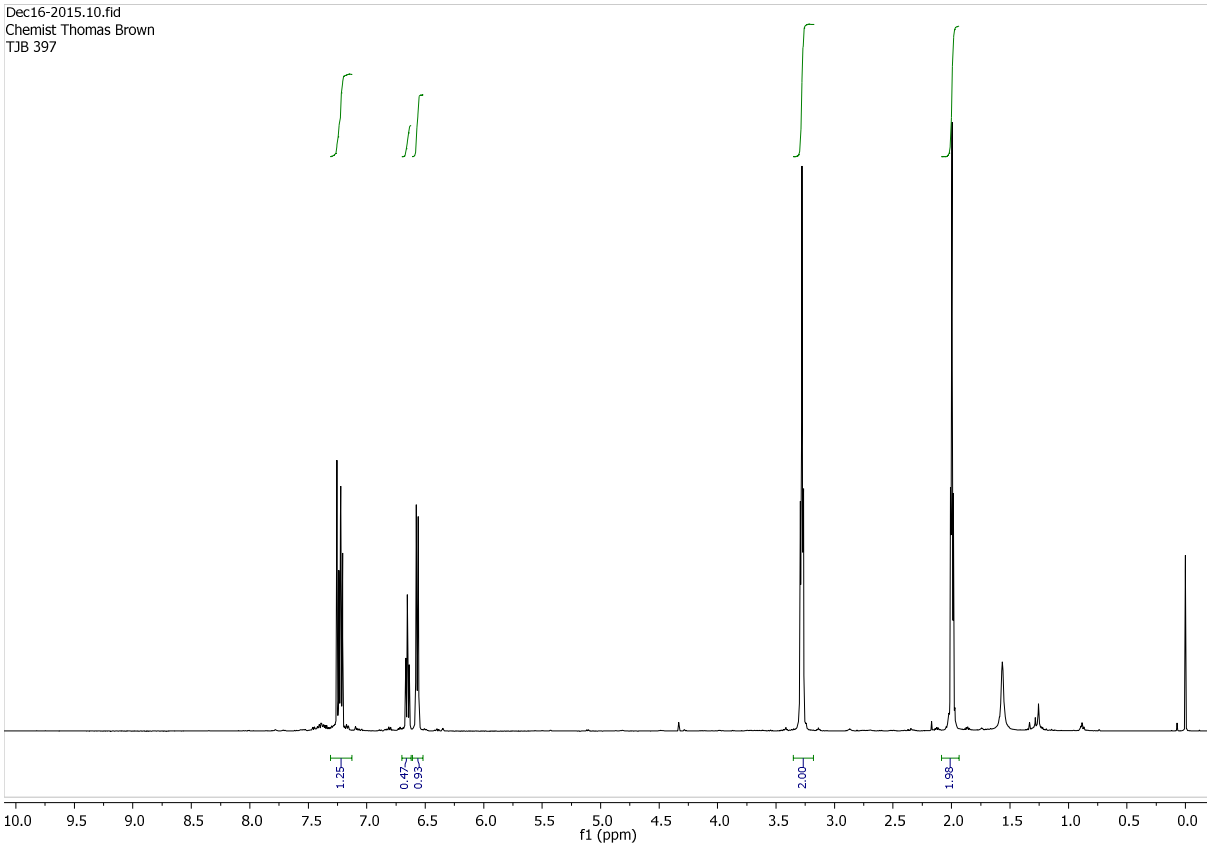


1-Phenylpyrrolidine **32**.

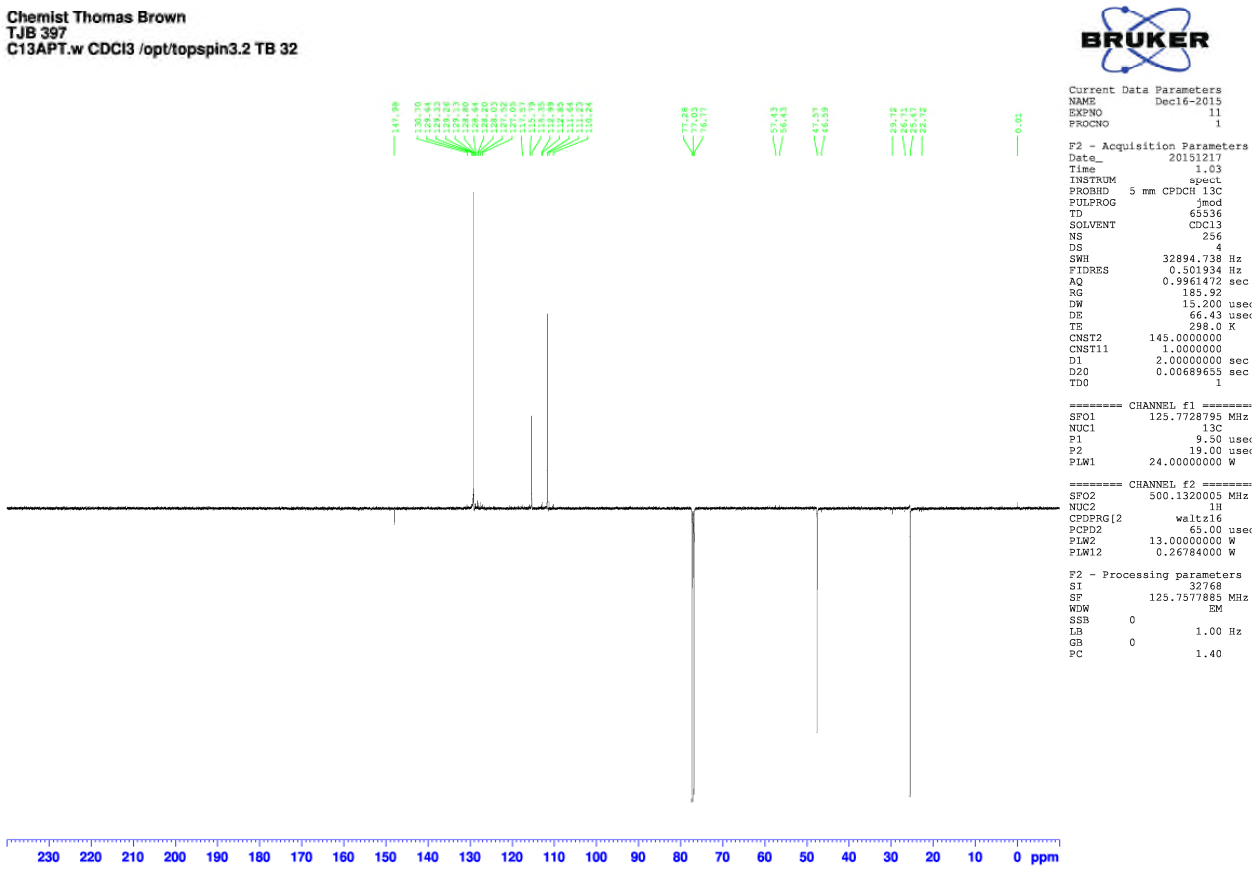


TJB395 original pdf spectra below –filename says 397.

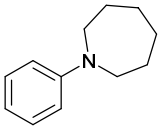
^{1}H NMR (500 MHz, $CDCl_3$).



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

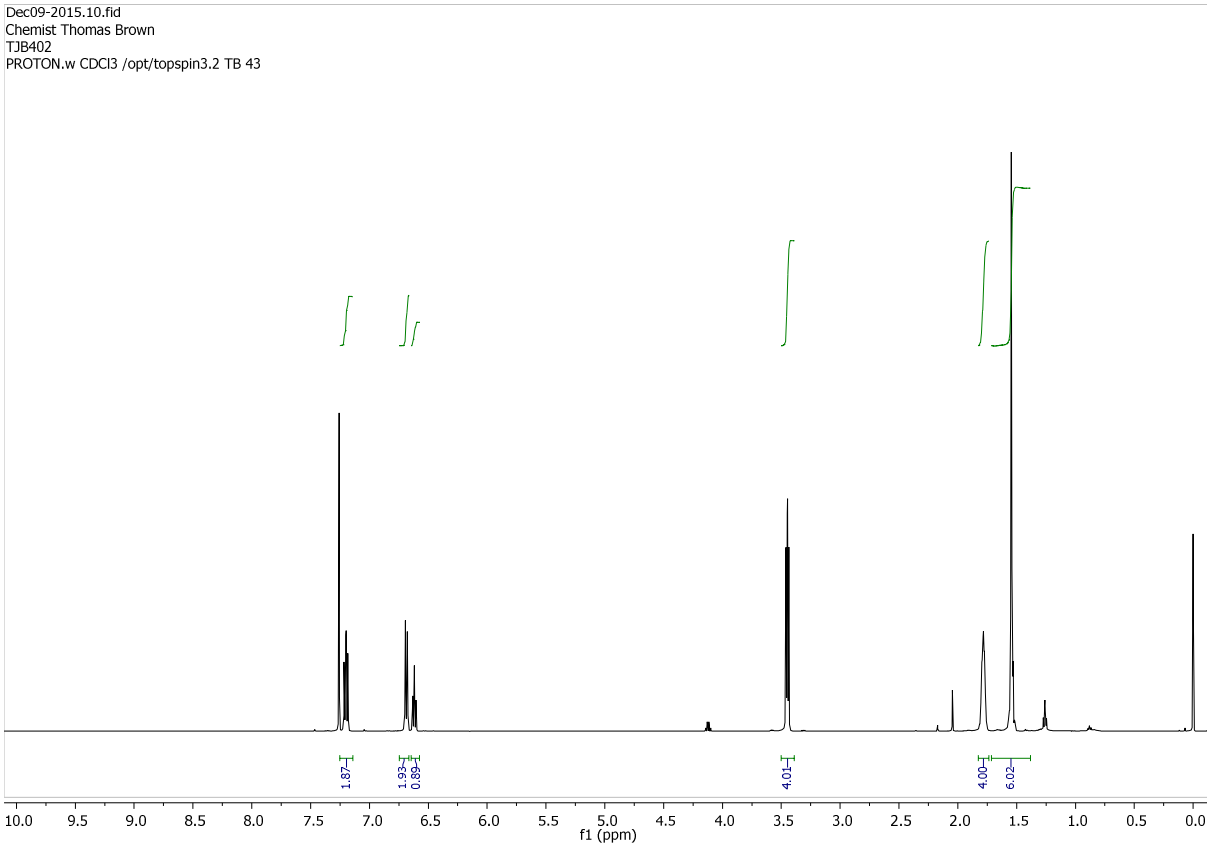


1-Phenylazapine **33**.

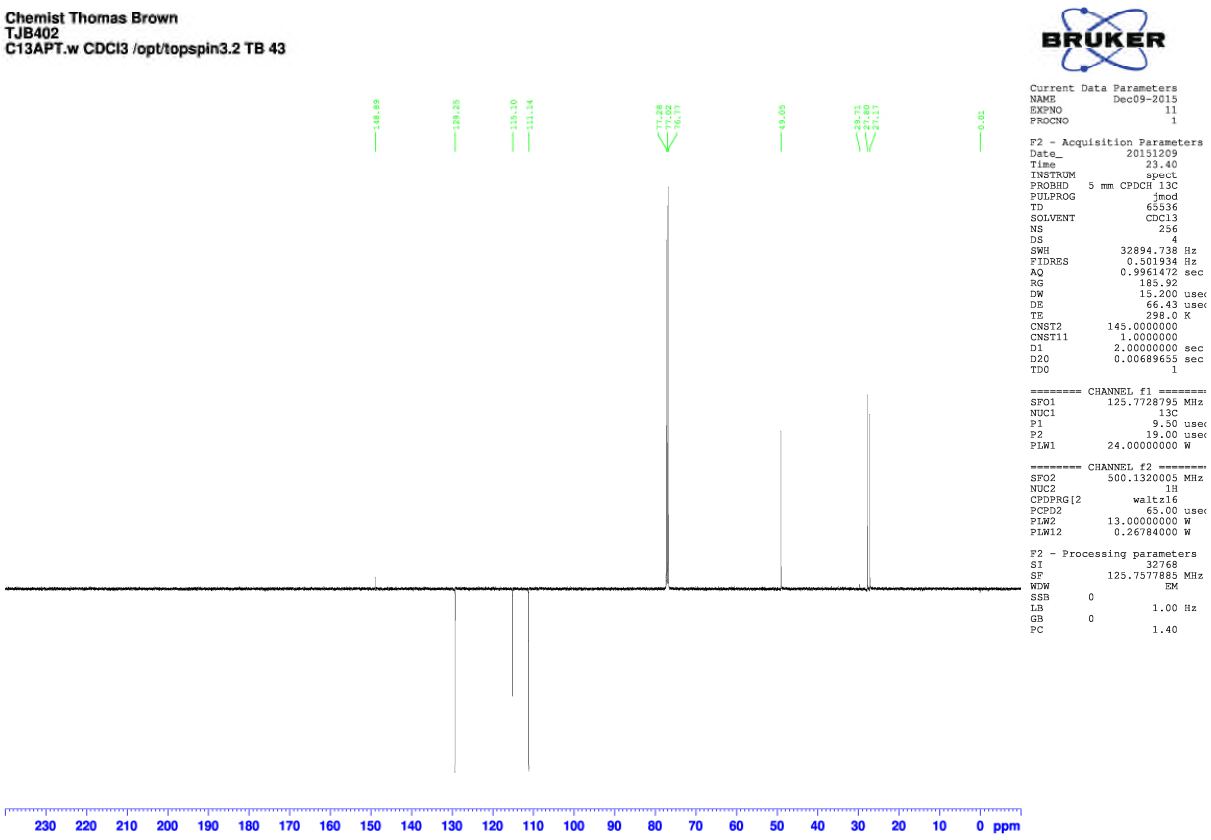


TJB402.

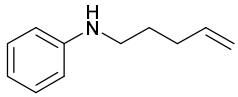
^{1}H NMR (500 MHz, $CDCl_3$).



^{13}C NMR (100 MHz, $CDCl_3$).

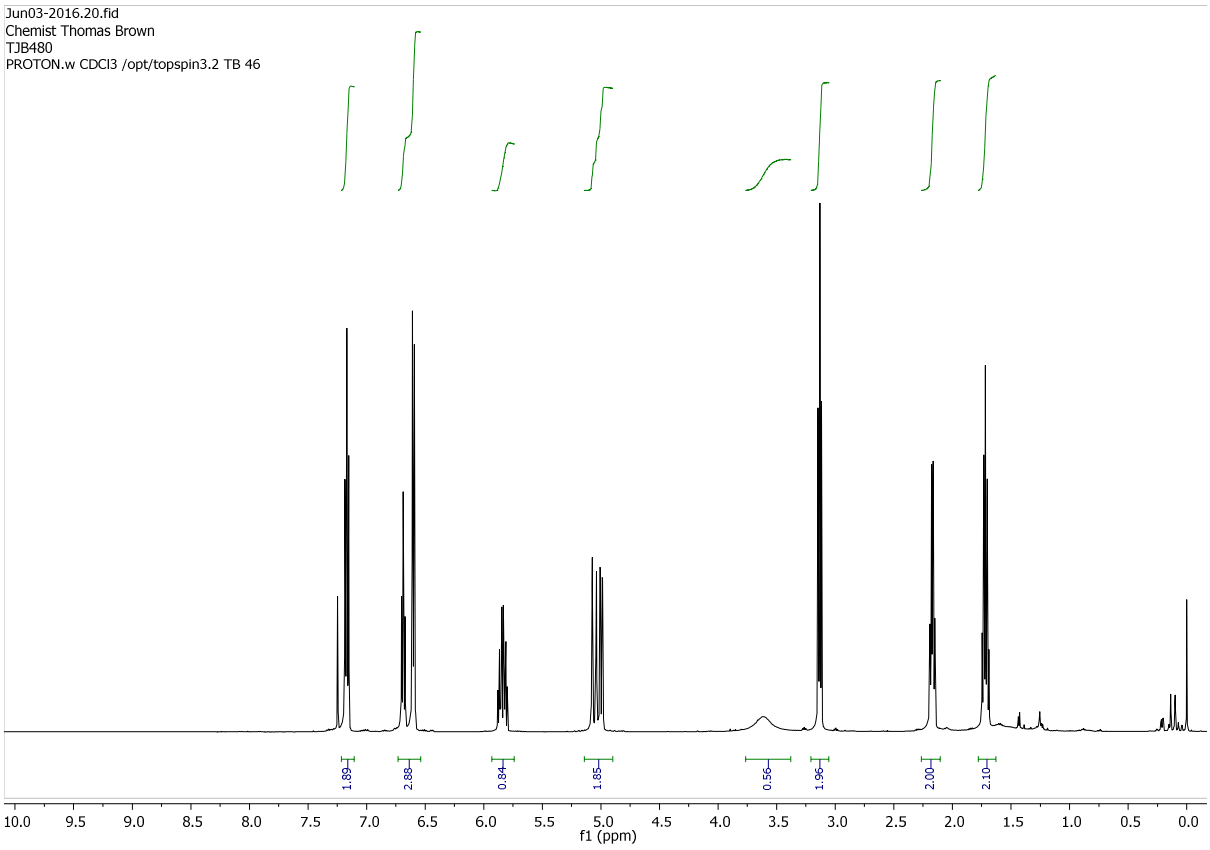


N-(Pent-4-en-1-yl)aniline **37**.

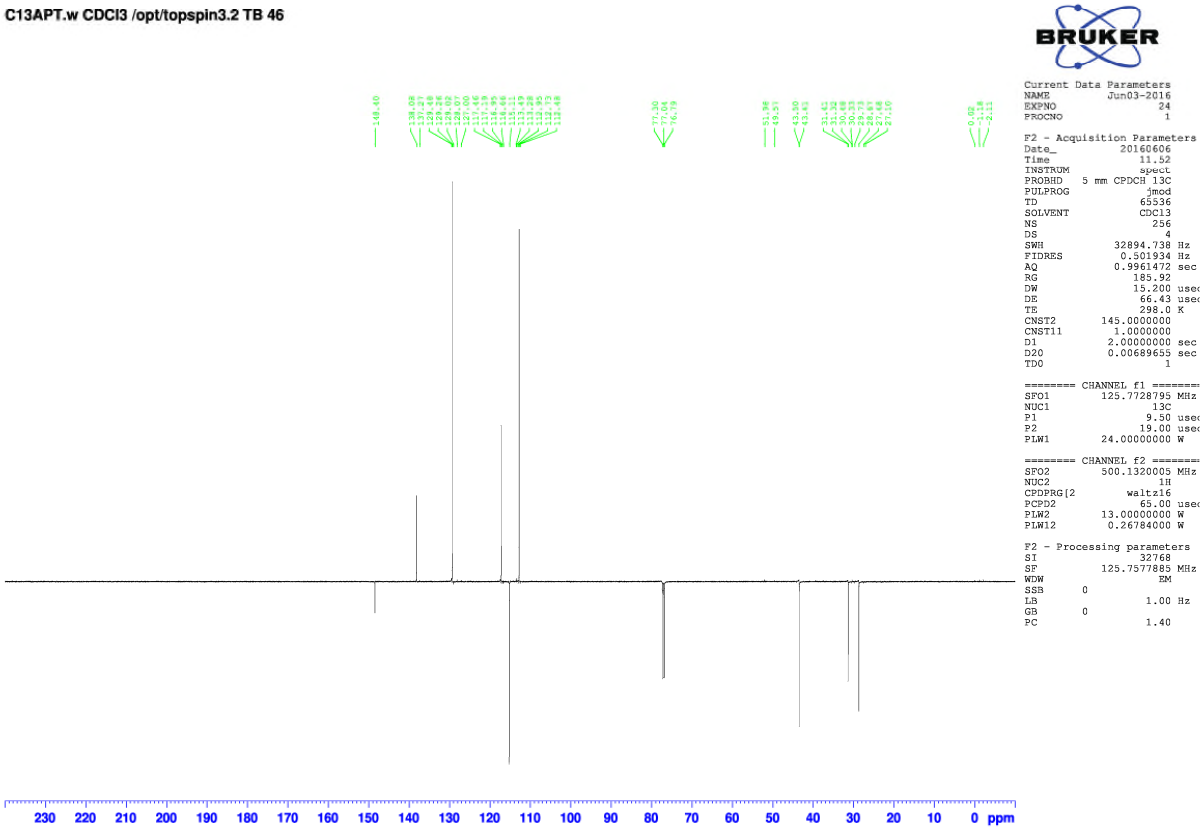


TJB480.

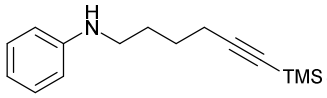
^{1}H NMR (500 MHz, $CDCl_3$).



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

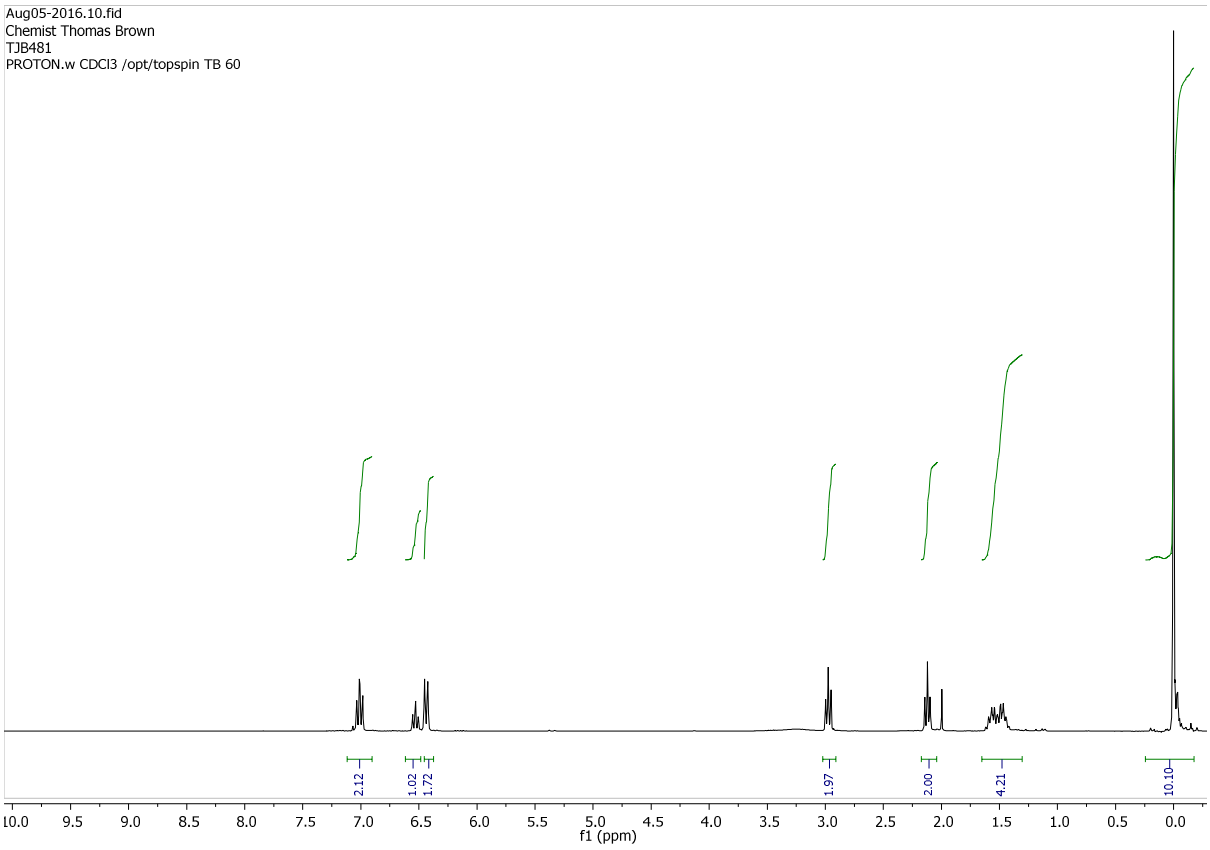


N-(6-(trimethylsilyl)hex-5-yn-1-yl)aniline **38**.

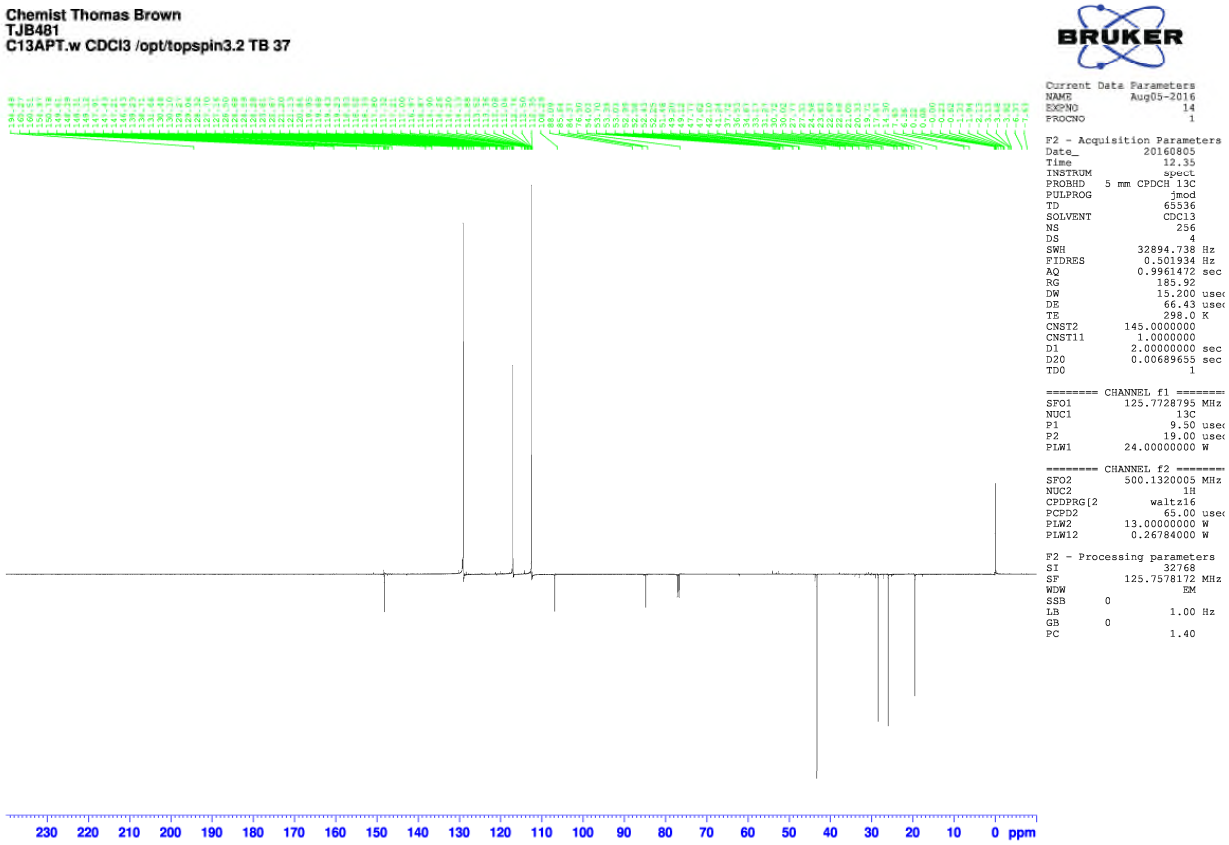


TJB481.

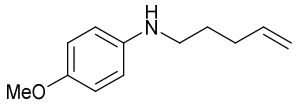
^{1}H NMR (500 MHz, $CDCl_3$).



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

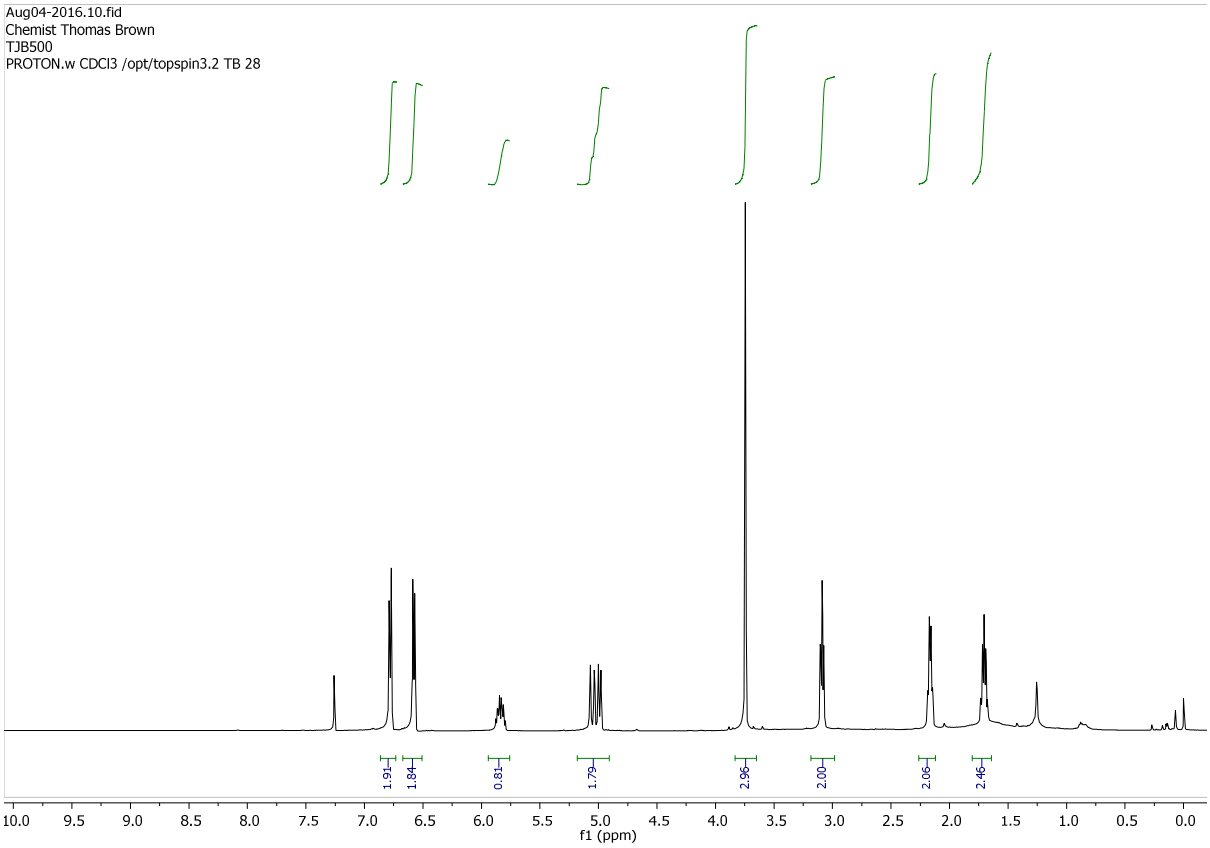


4-Methoxy-*N*-(pent-4-en-1-yl)aniline **39**.

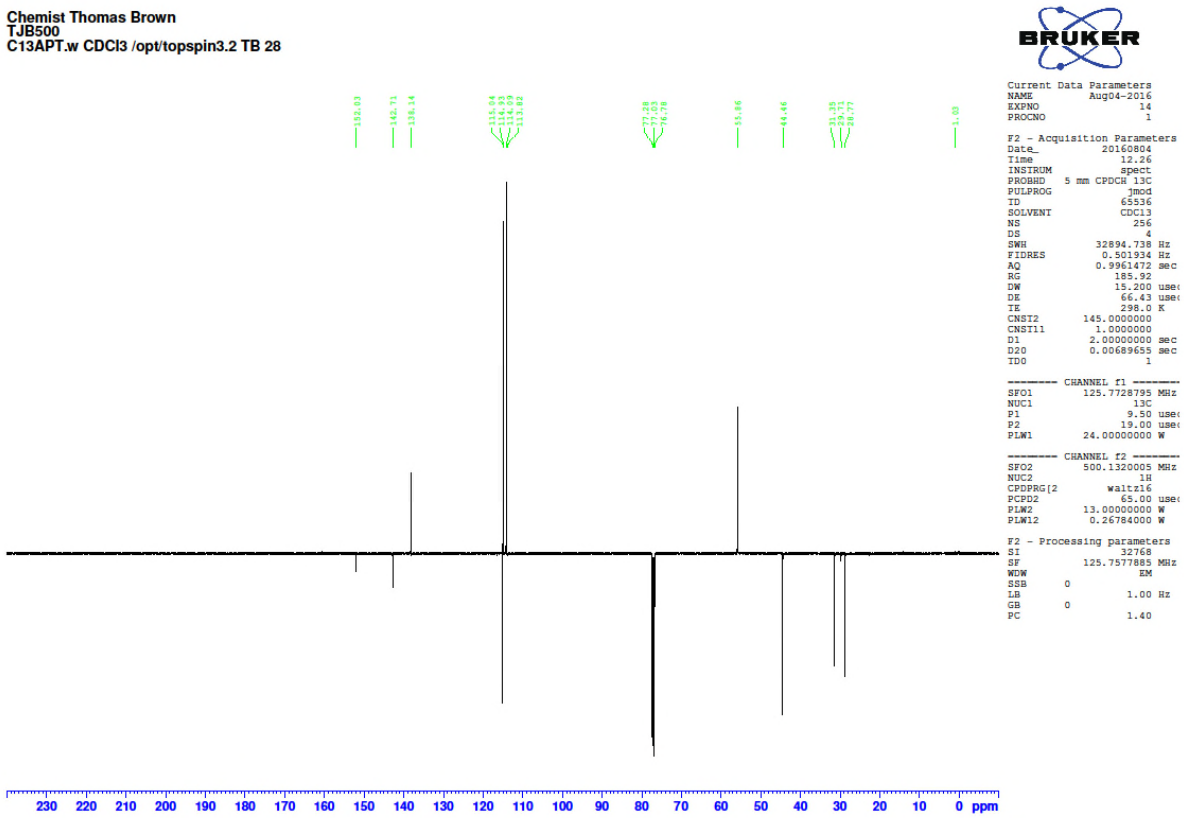


TJB500.

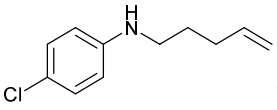
^{1}H NMR (500 MHz, $CDCl_3$).



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

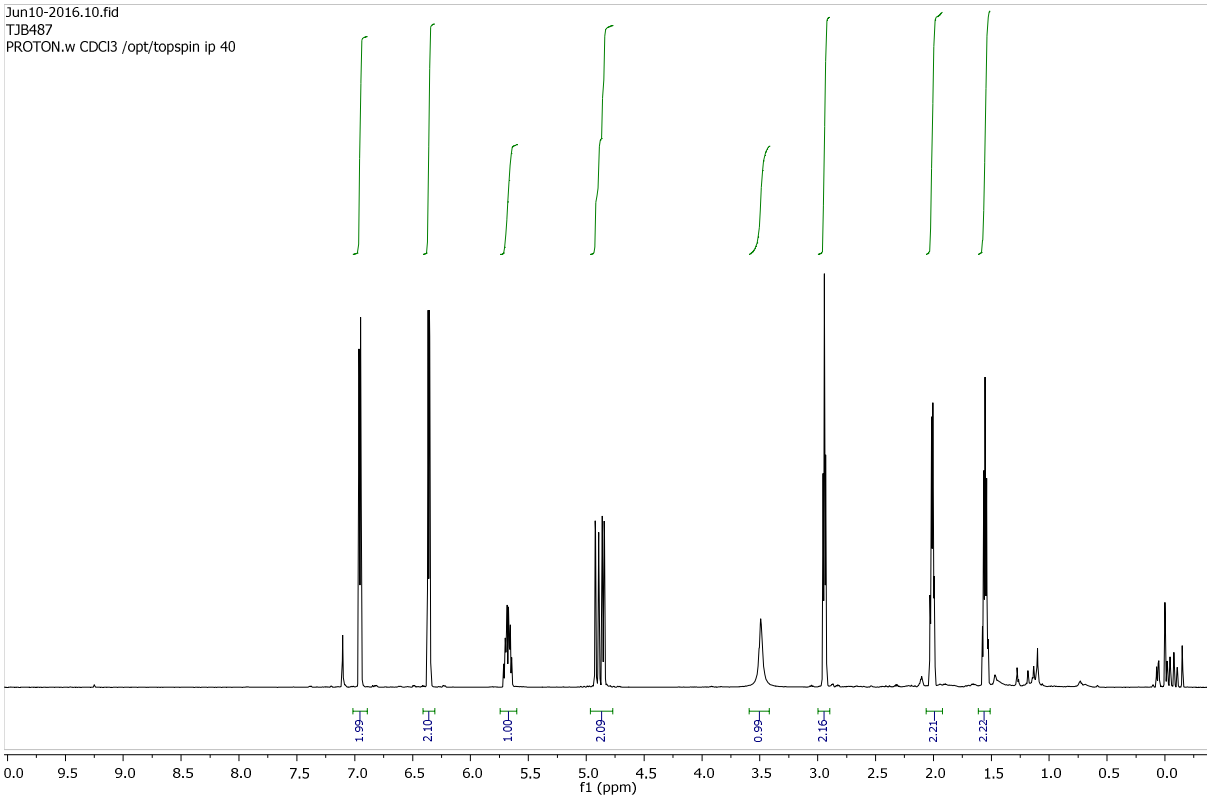


4-Chloro-*N*-(pent-4-en-1-yl)aniline **40**.

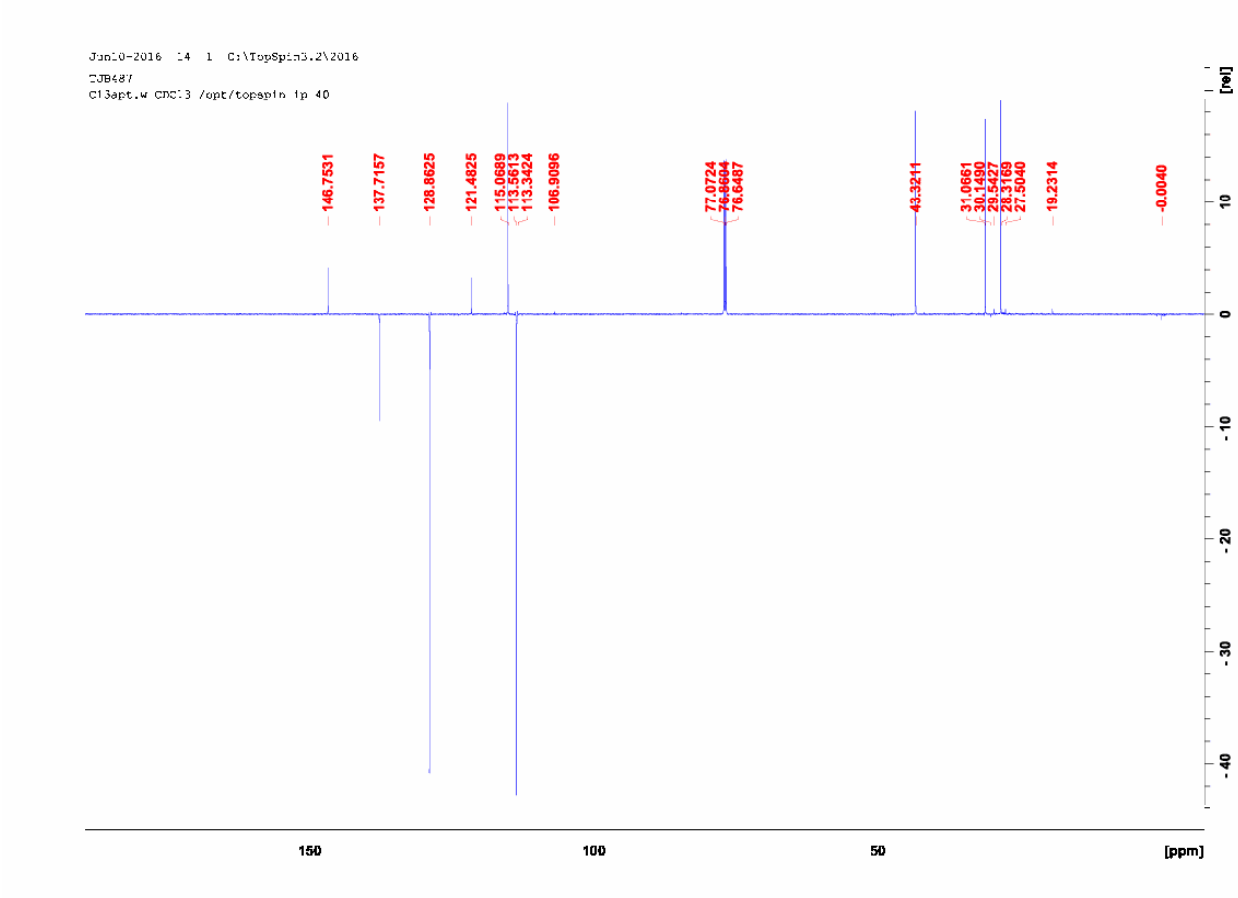


TJB487.

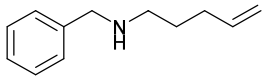
^{1}H NMR (600 MHz, $CDCl_3$).



^{13}C NMR (150 MHz, $CDCl_3$).

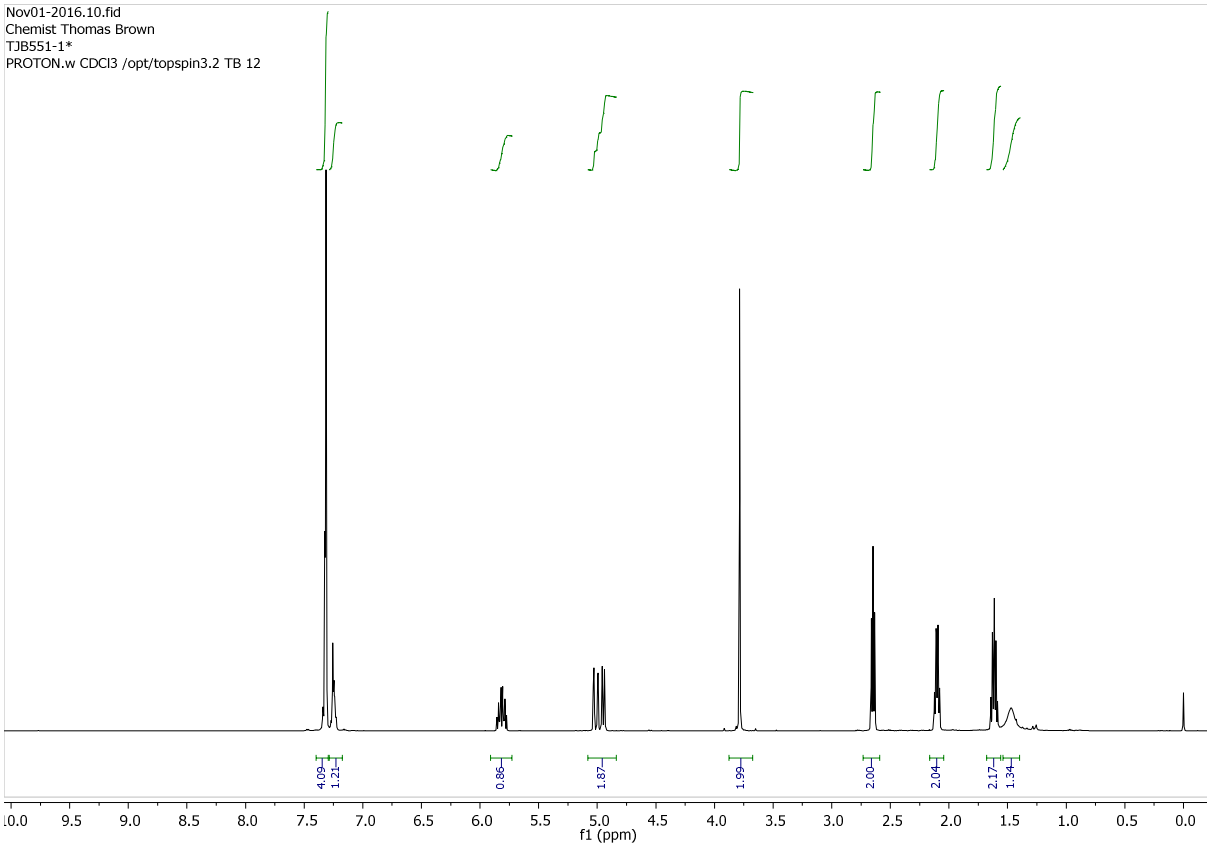


N-Benzylpent-4-en-1-amine **41**.

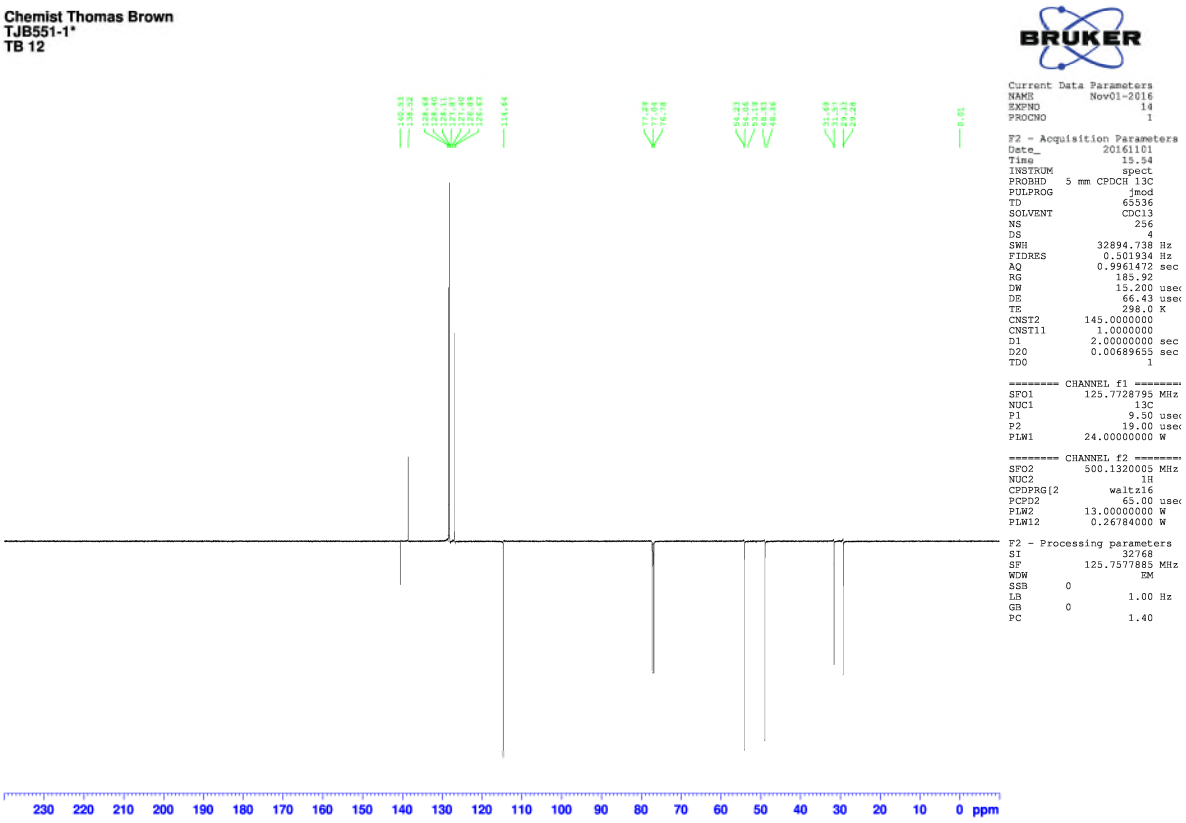


TJB551.

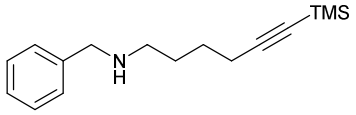
^{1}H NMR (500 MHz, $CDCl_3$).



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

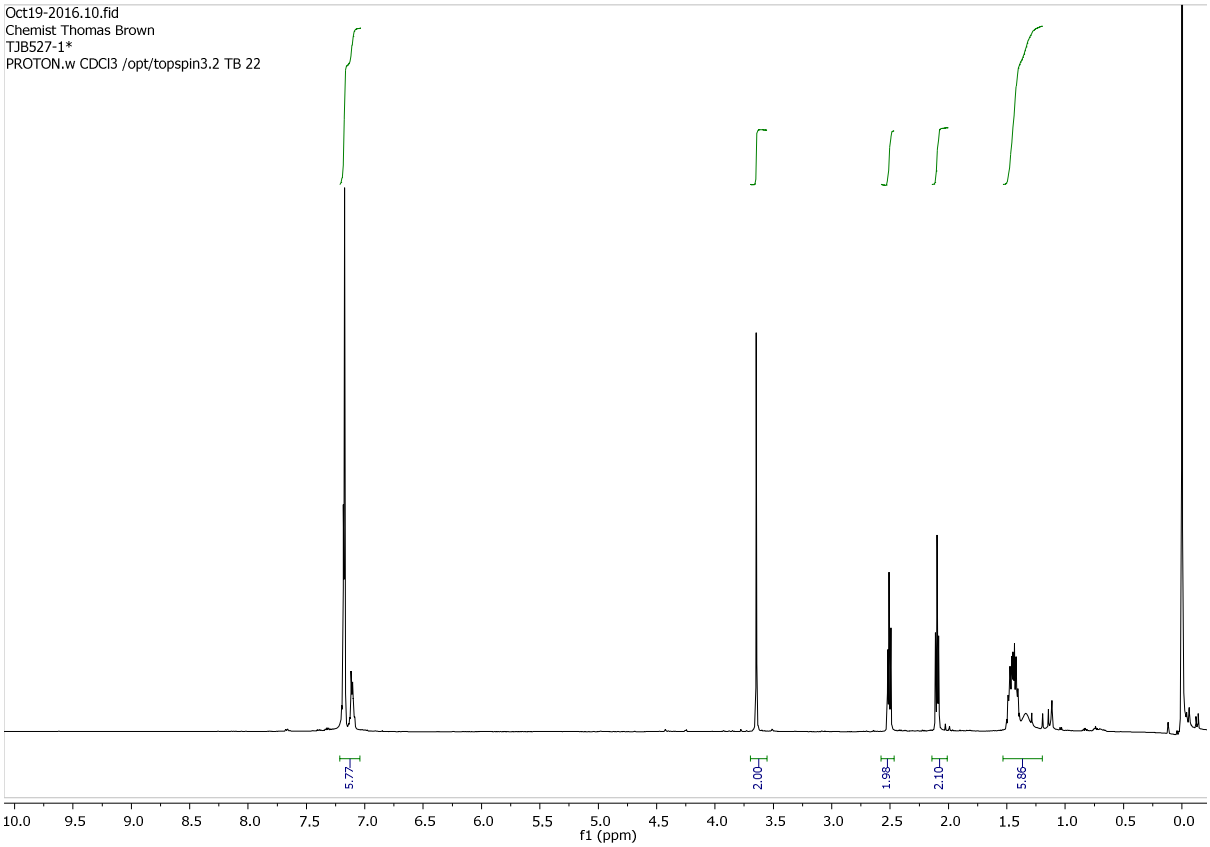


N-Benzyl-6-(trimethylsilyl)hex-5-yn-1-amine **42**.

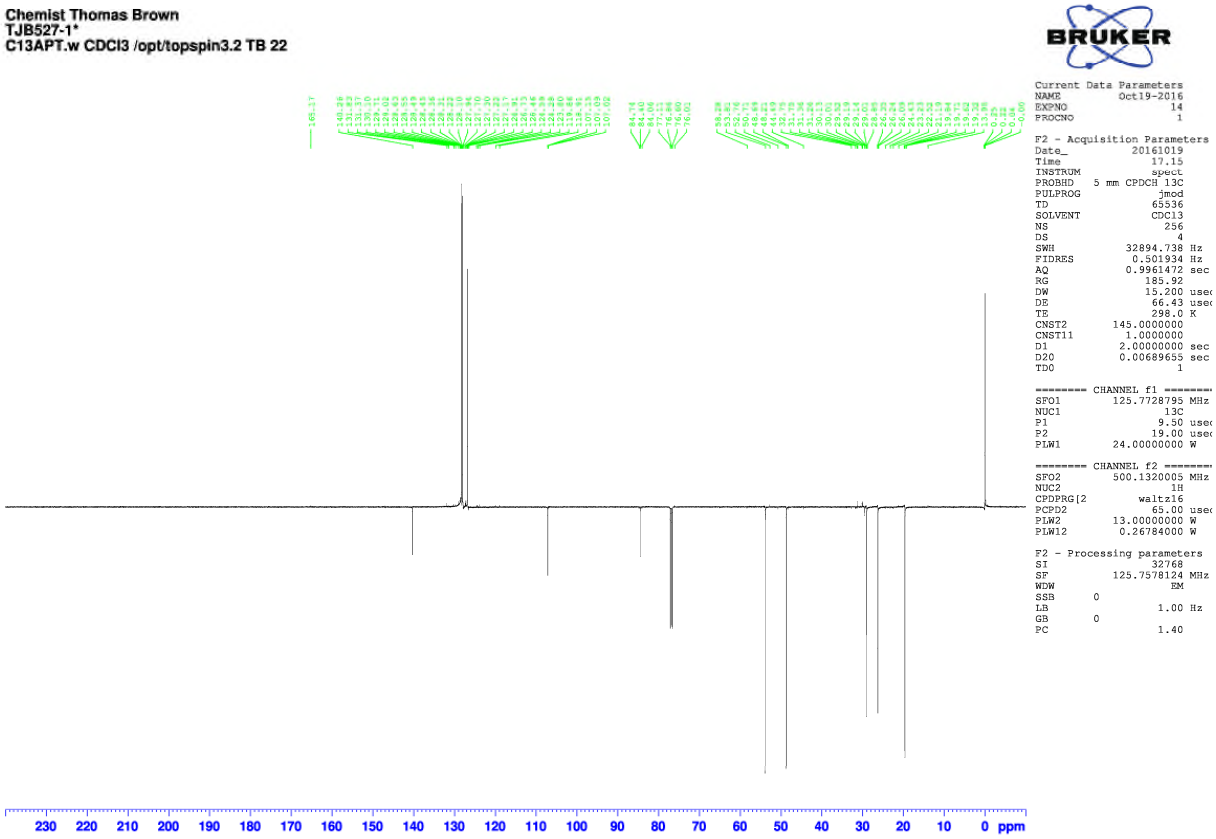


TJB527.

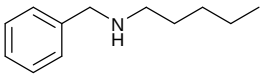
^{1}H NMR (500 MHz, $CDCl_3$).



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

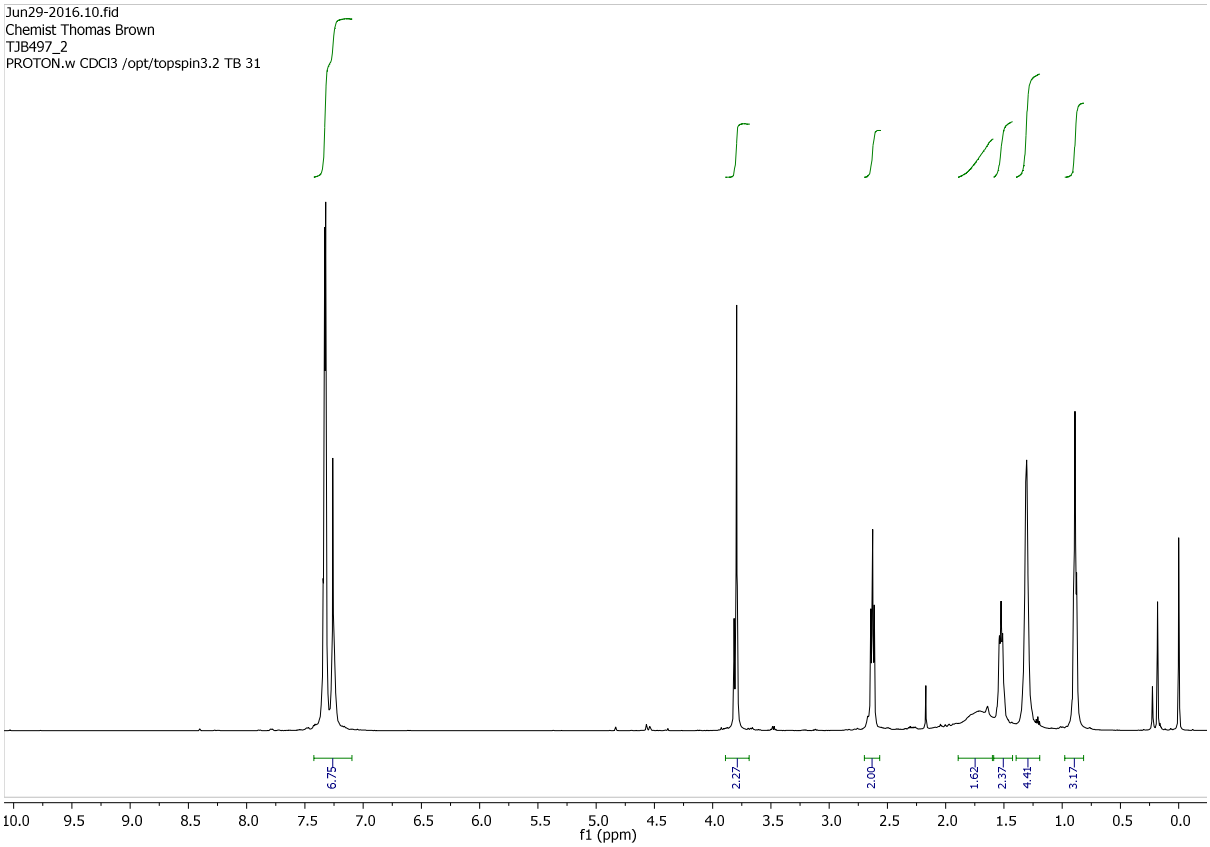


N-Benzylpentan-1-amine **43**.

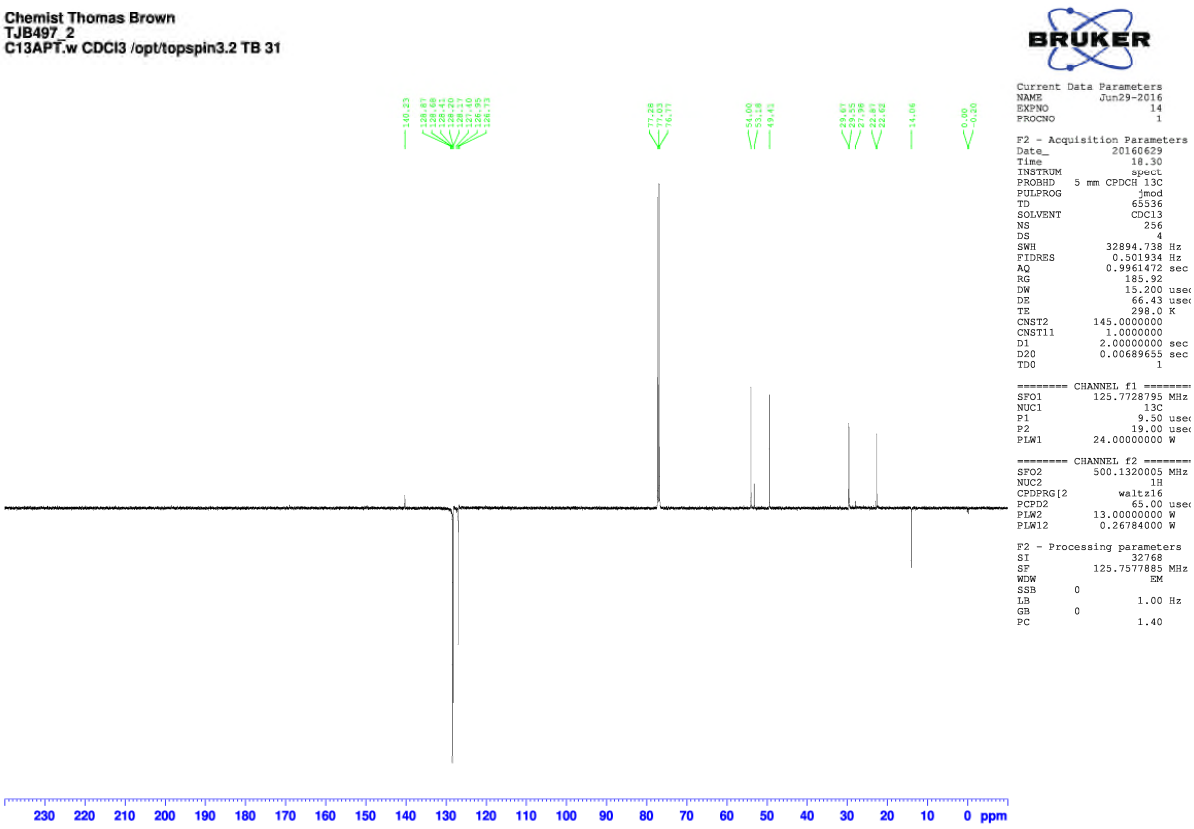


TJB497.

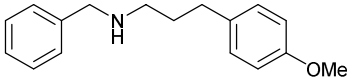
^{1}H NMR (500 MHz, $CDCl_3$).



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

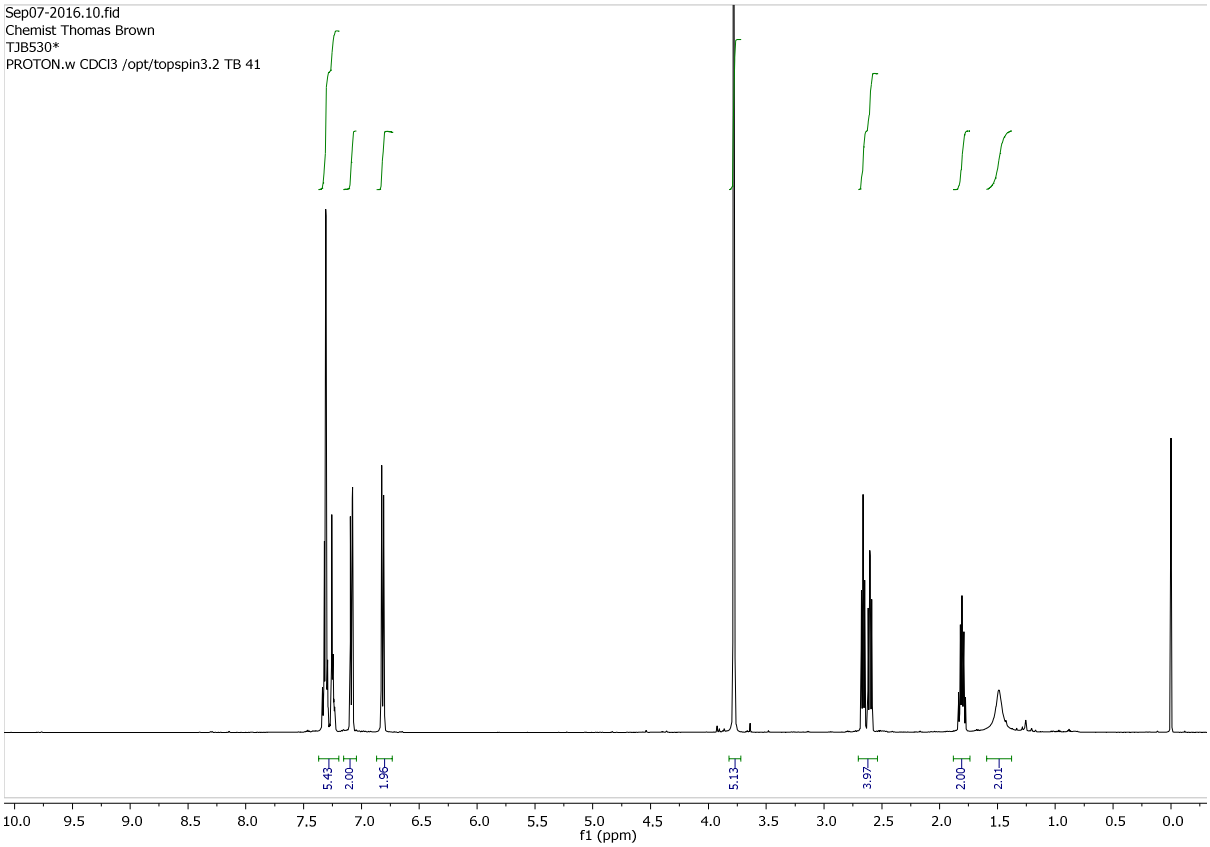


N-Benzyl-3-(4-methoxyphenyl)propan-1-amine **44**.

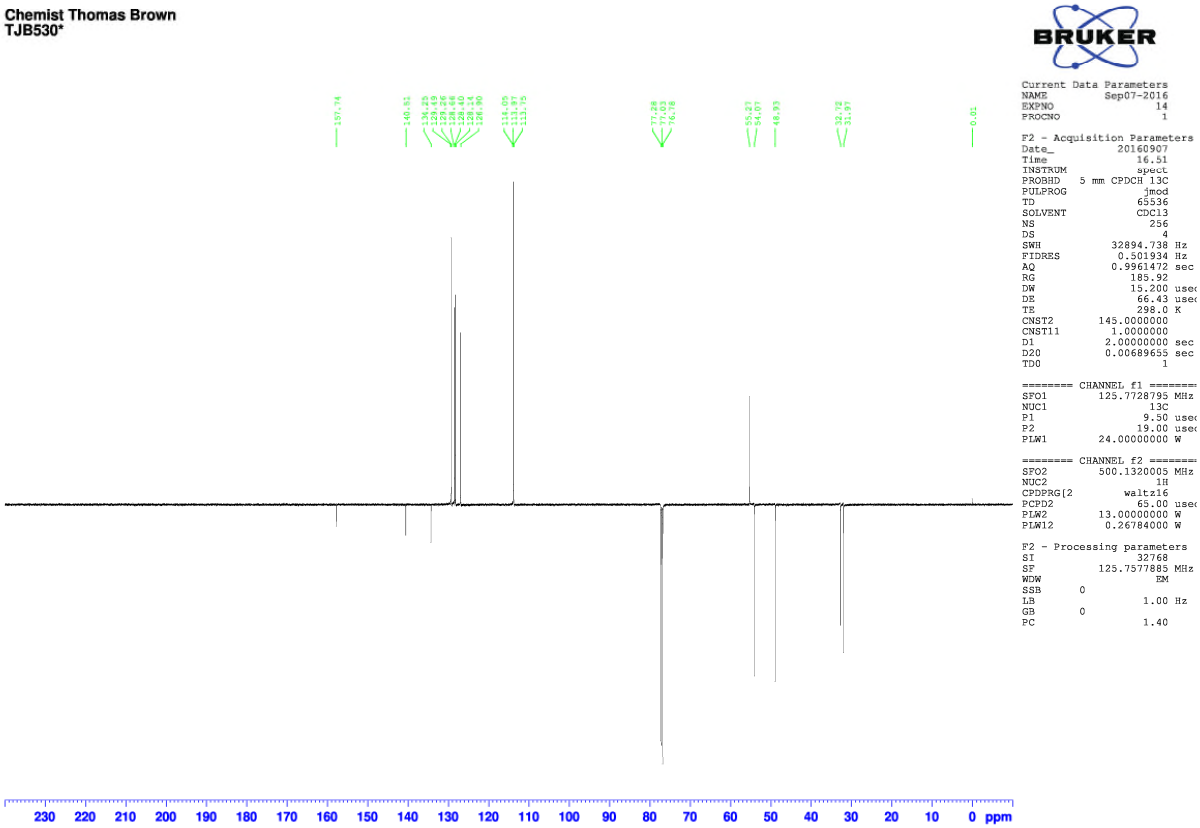


TJB530.

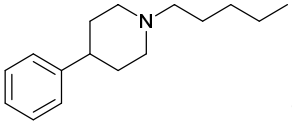
^{1}H NMR (500 MHz, $CDCl_3$).



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

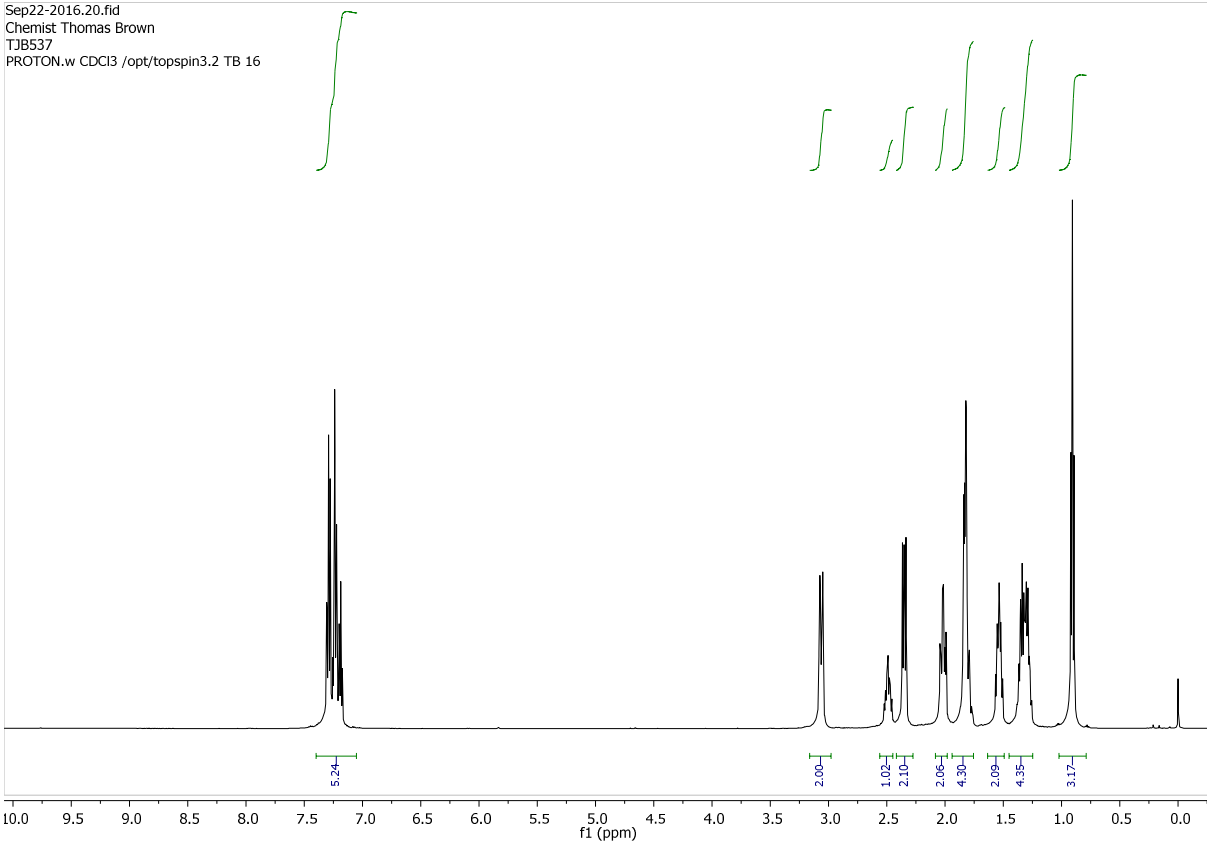


1-Pentyl-4-phenylpiperidine **45**.

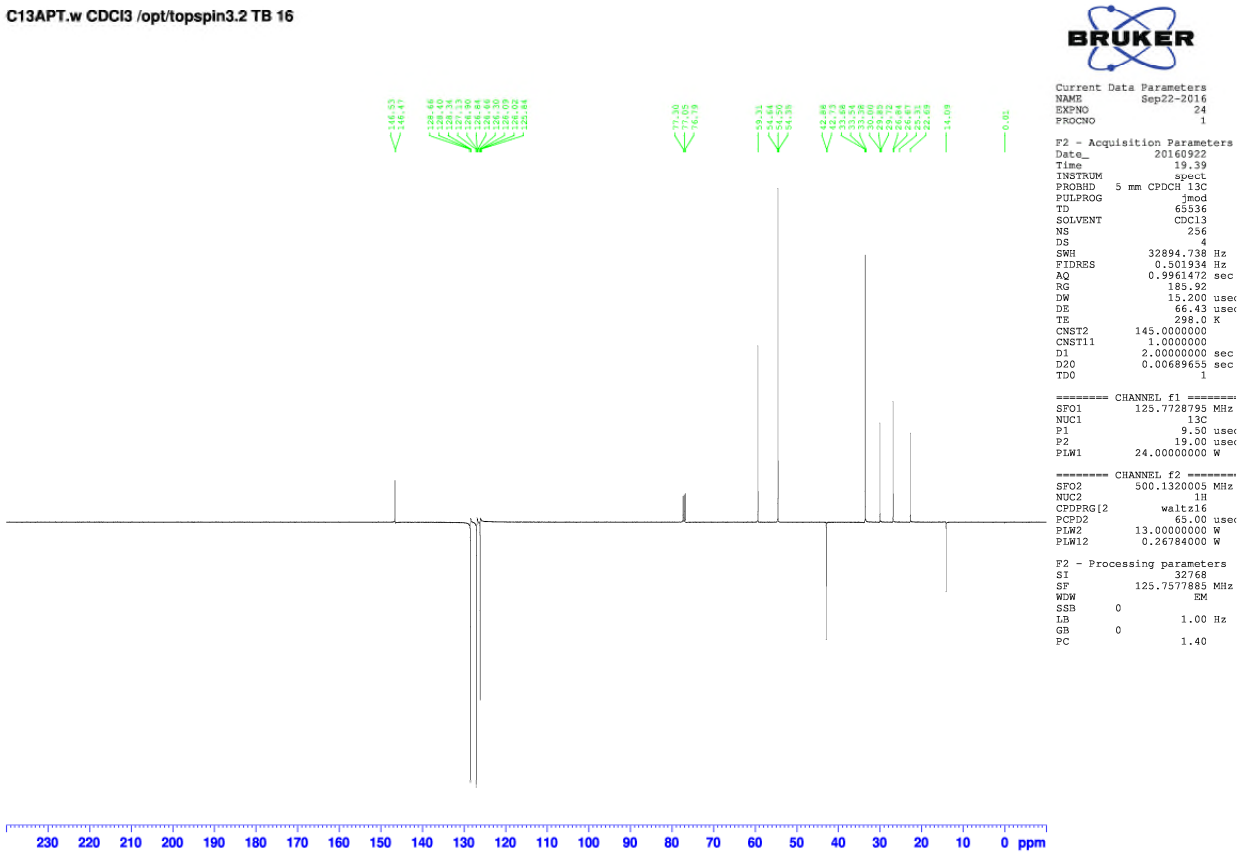


TJB537.

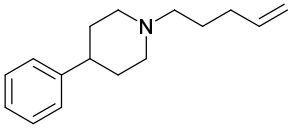
^{1}H NMR (500 MHz, $CDCl_3$).



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

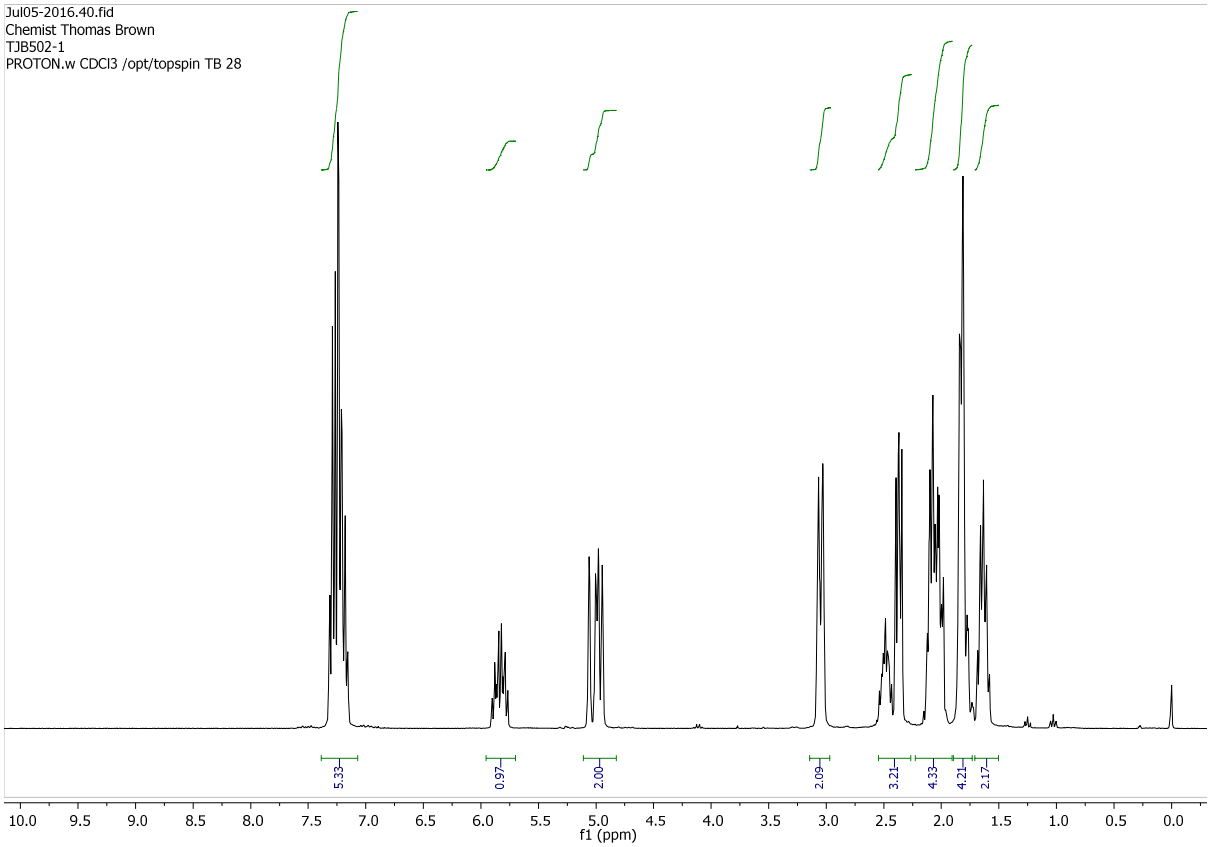


1-(Pent-4-en-1-yl)-4-phenylpiperidine **46**.

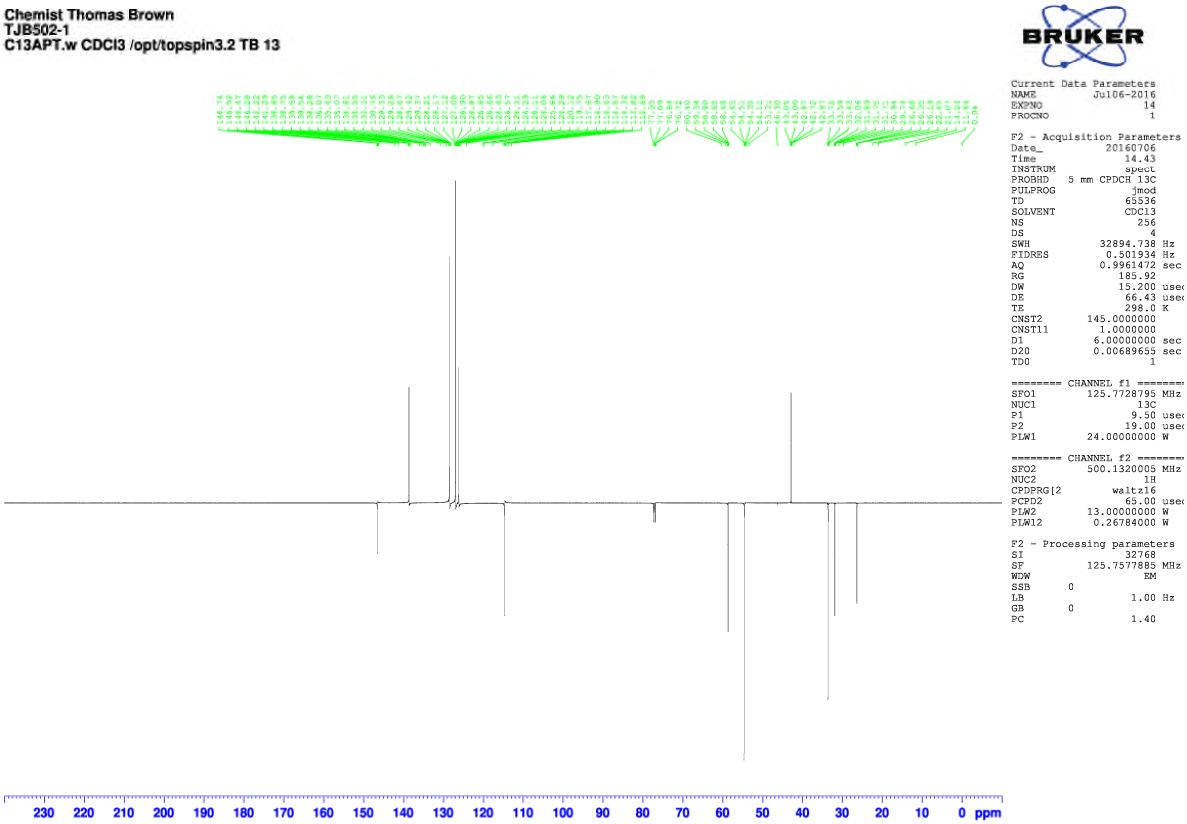


TJB502.

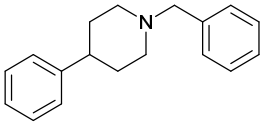
^{1}H NMR (300 MHz, $CDCl_3$).



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

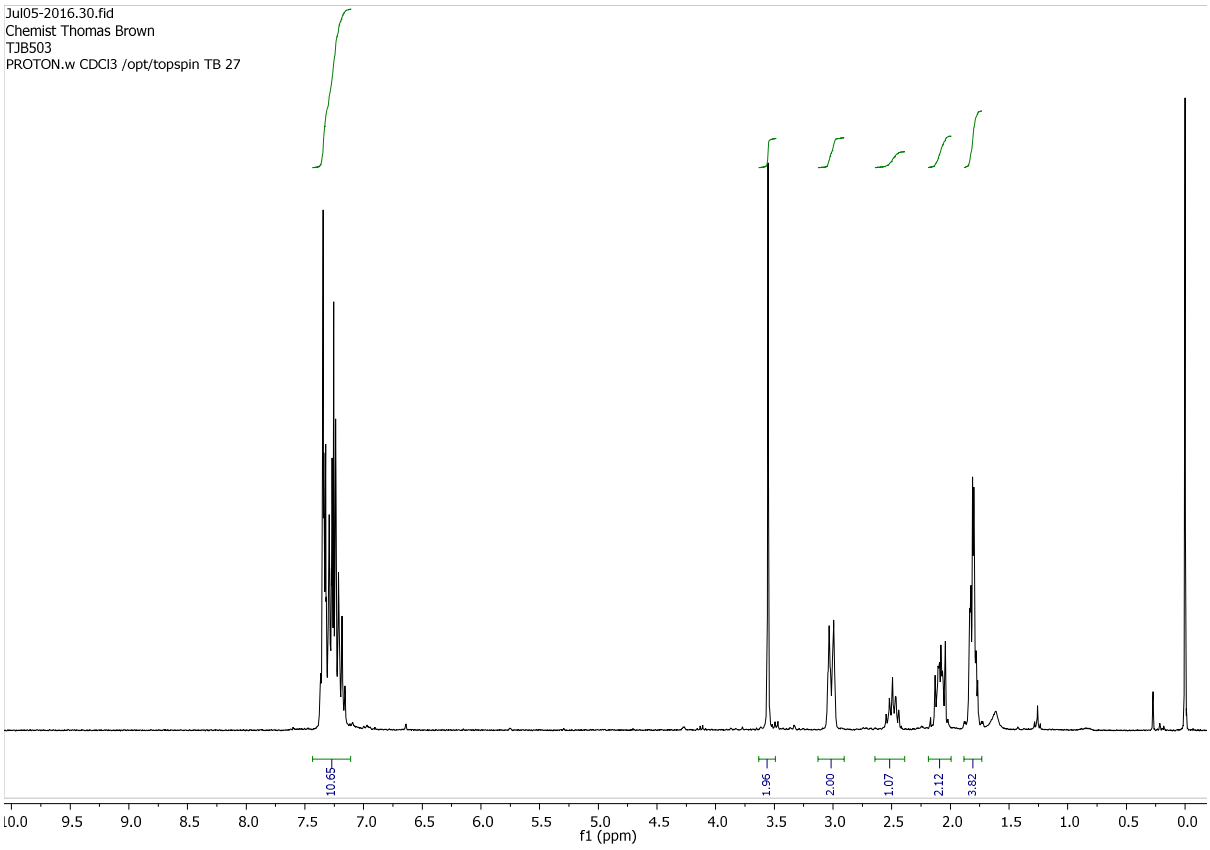


1-Benzyl-4-phenylpiperidine **47**.

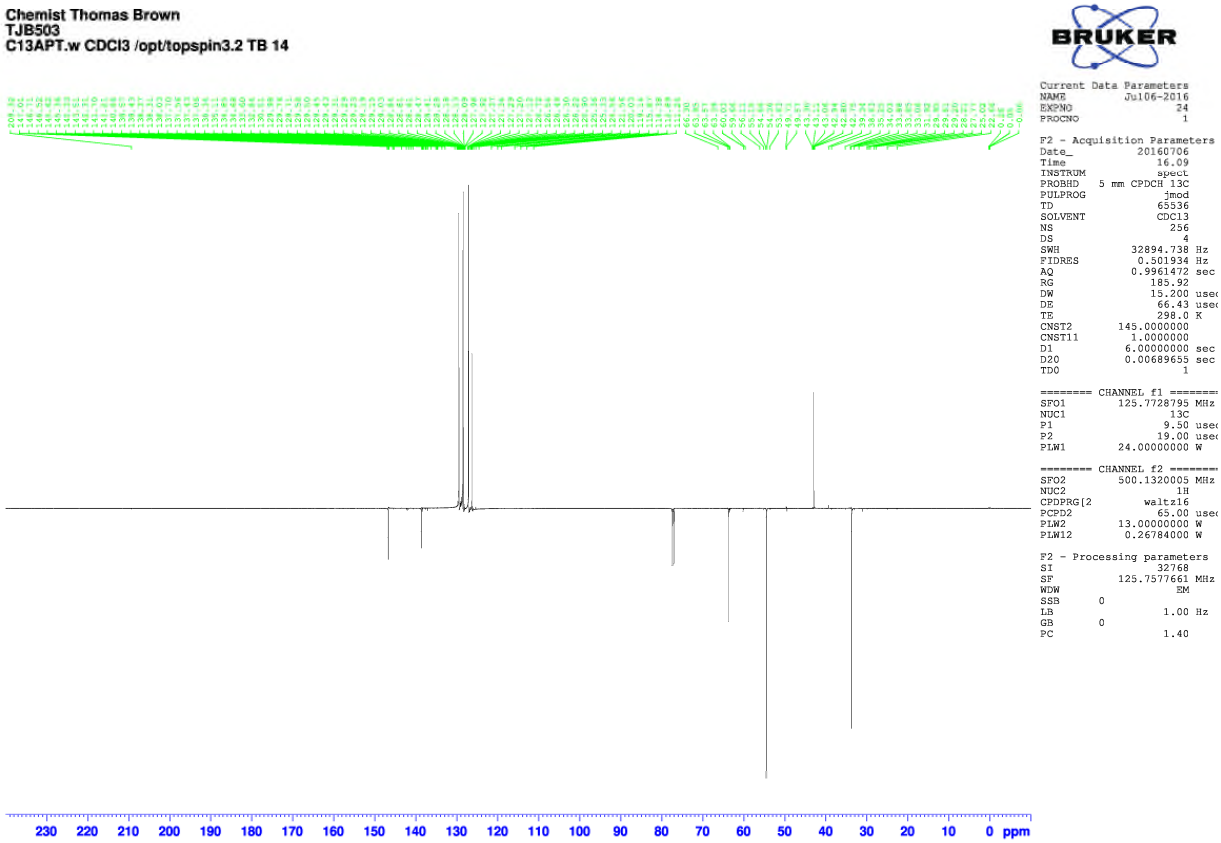


TJB503.

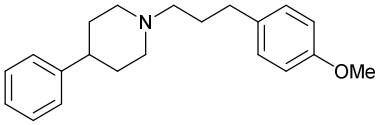
^{1}H NMR (300 MHz, $CDCl_3$).



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

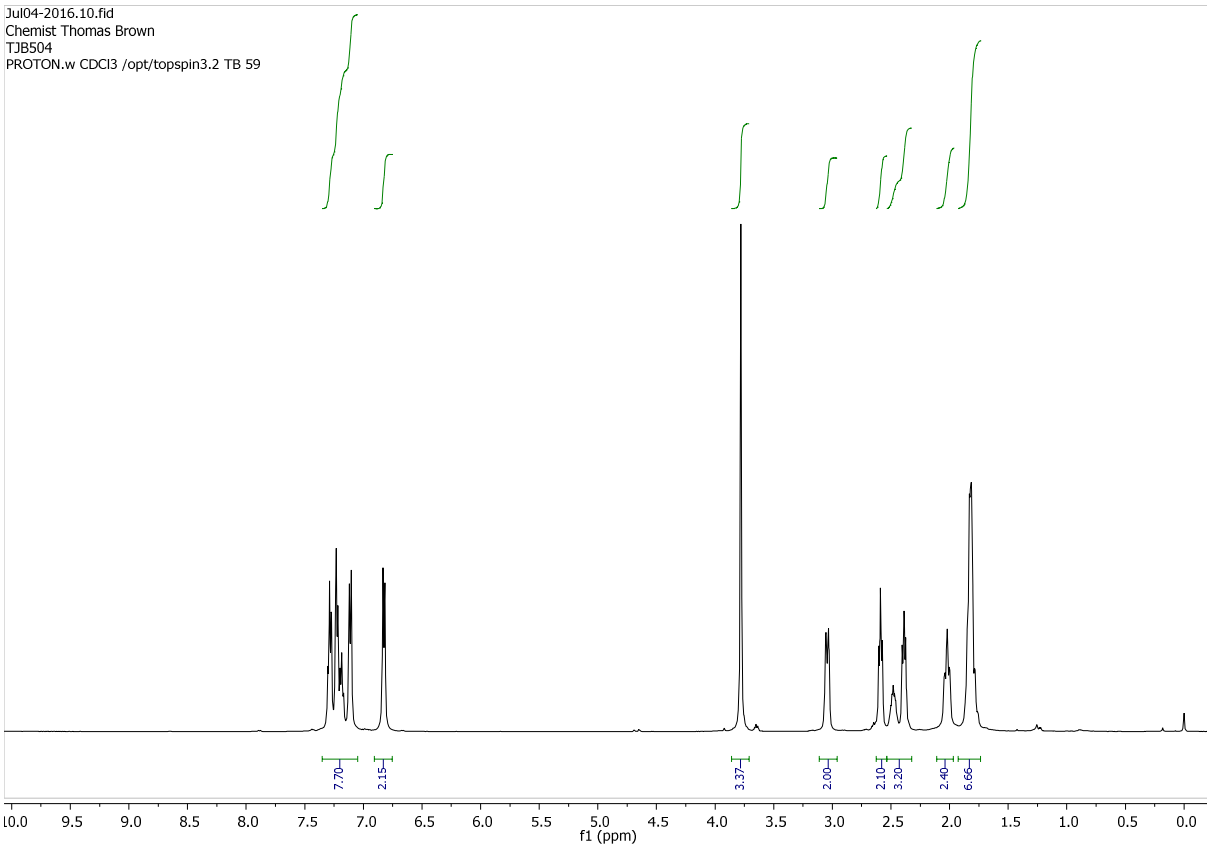


1-(3-(4-Methoxyphenyl)propyl)-4-phenylpiperidine **48**.

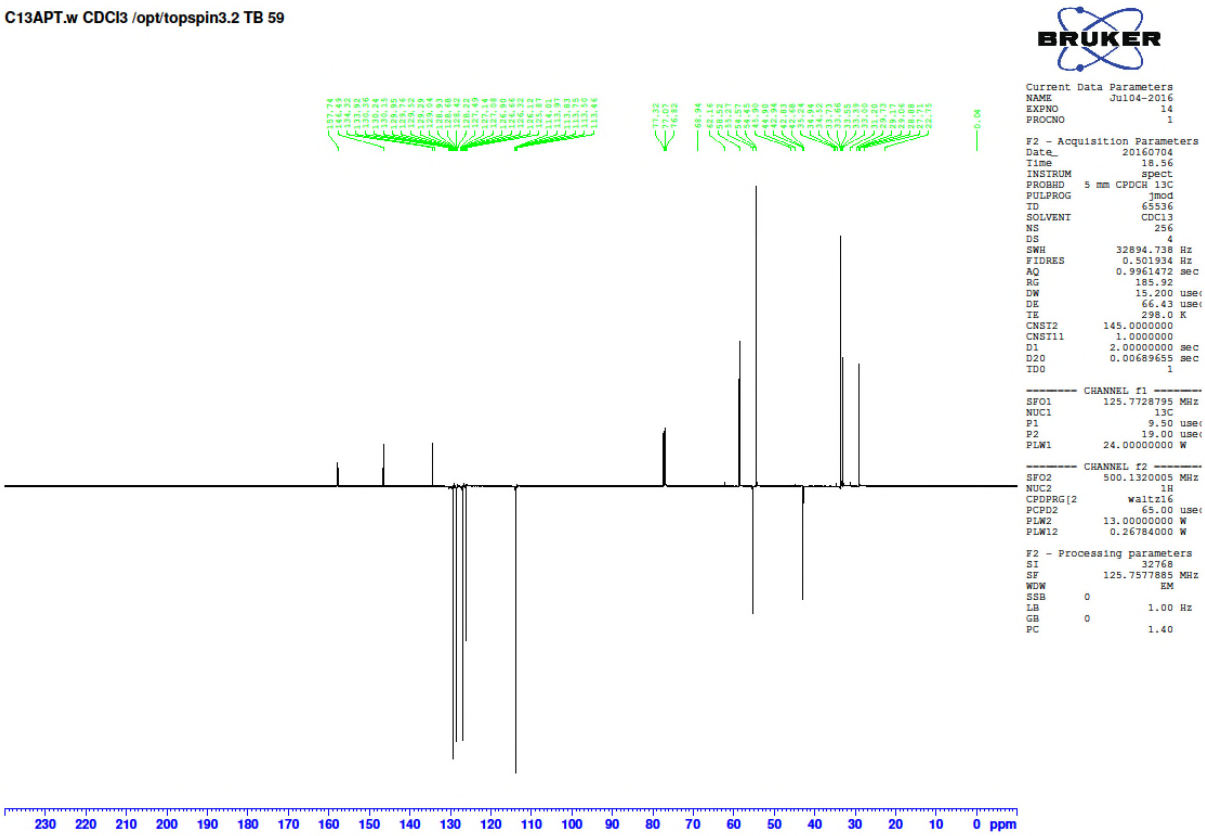


TJB504.

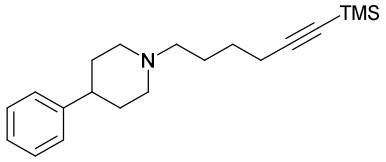
^{1}H NMR (500 MHz, $CDCl_3$).



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

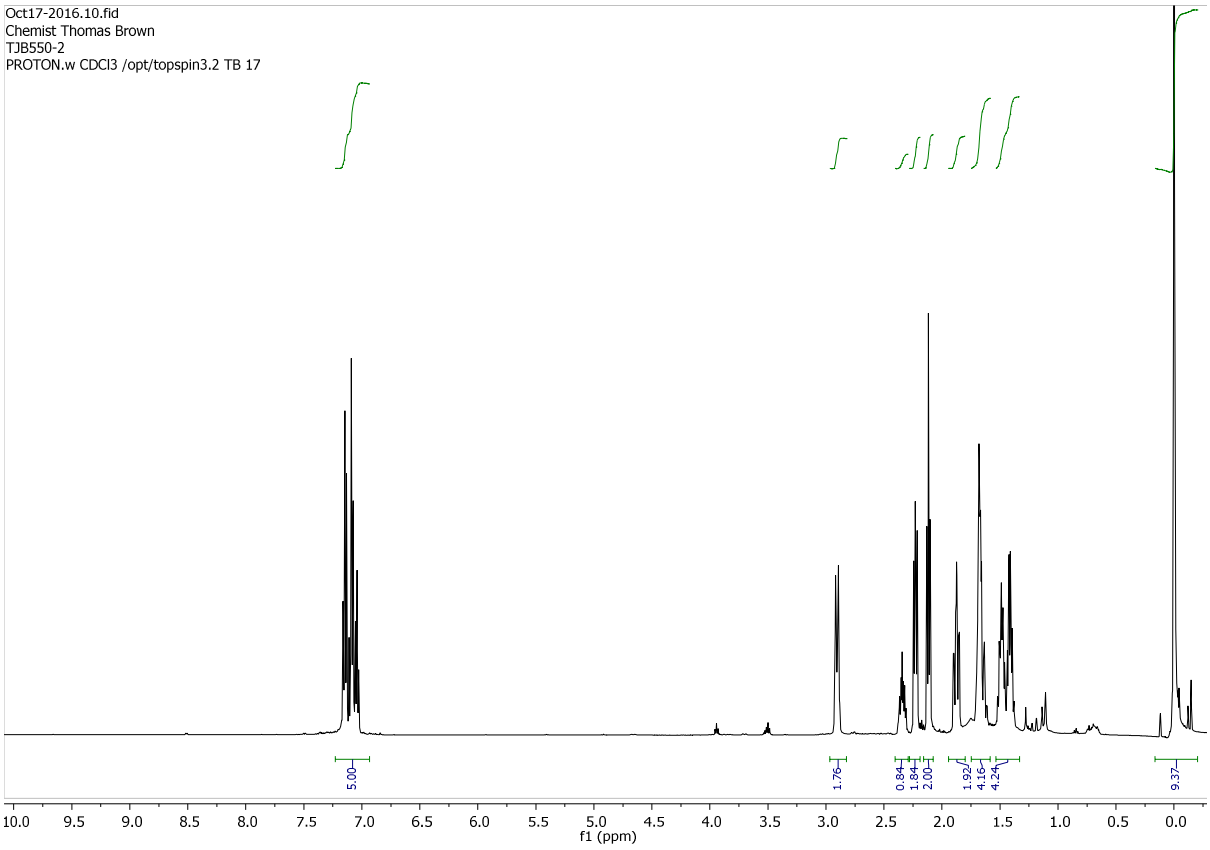


4-Phenyl-1-(6-(trimethylsilyl)hex-5-yn-1-yl)piperidine **49**.

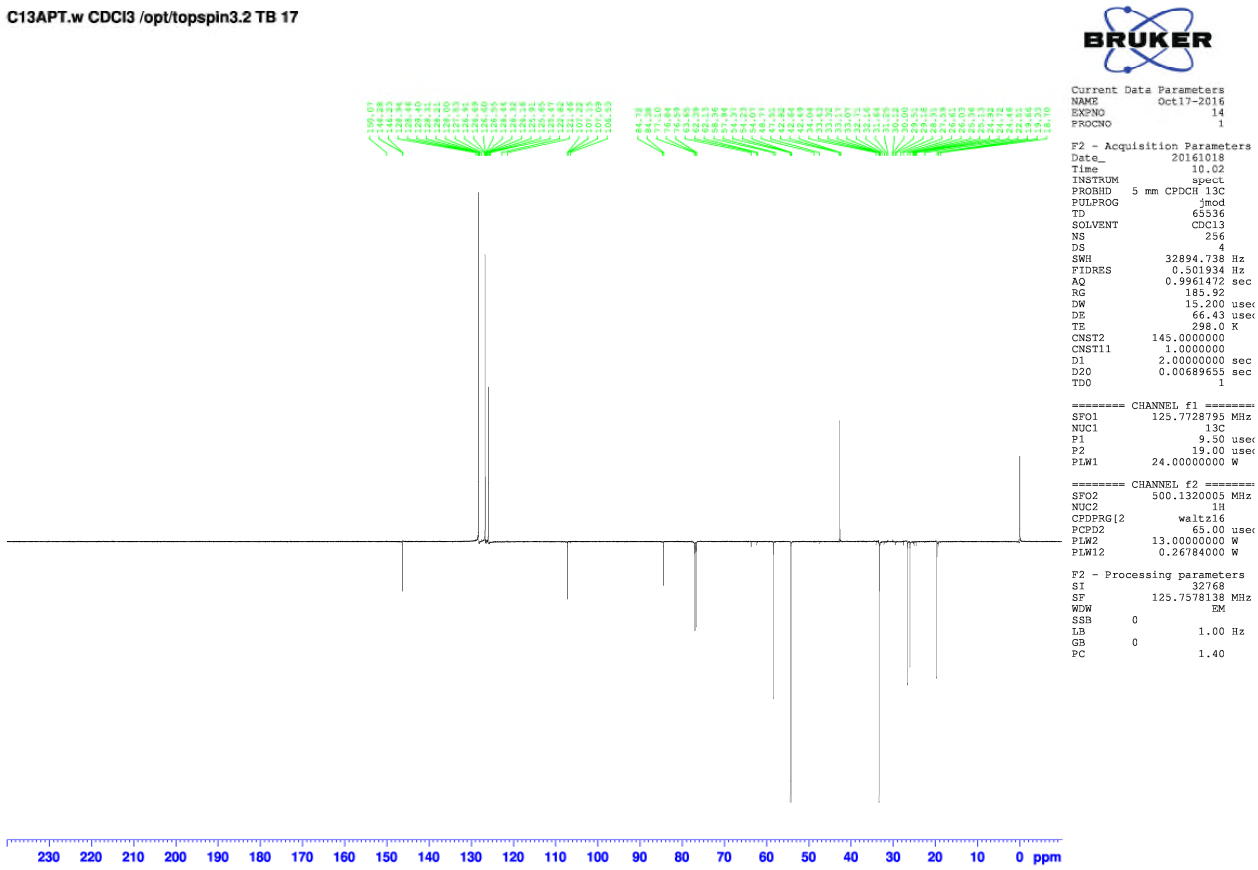


TJB550.

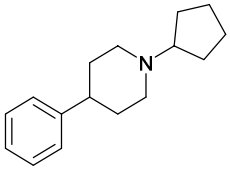
^{1}H NMR (500 MHz, $CDCl_3$).



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

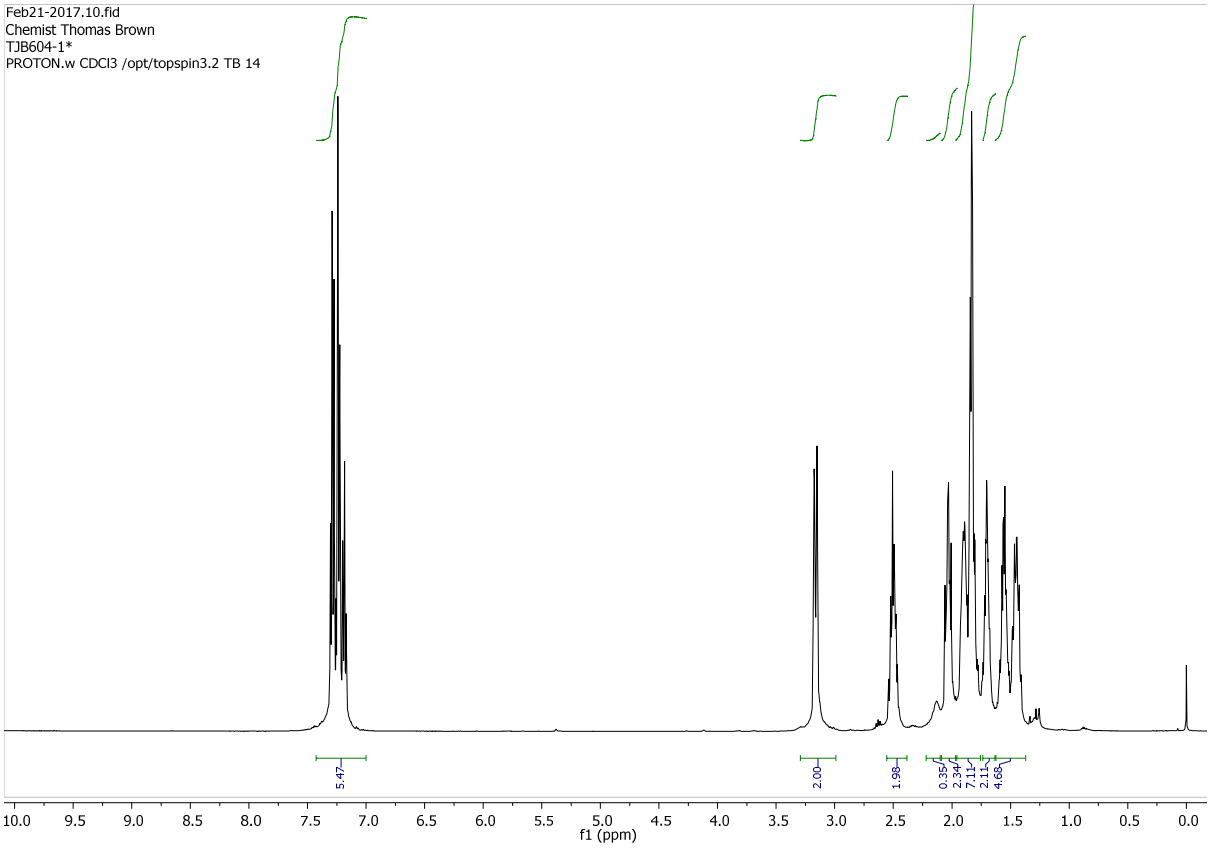


1-Cyclopentyl-4-phenylpiperidine **50**.

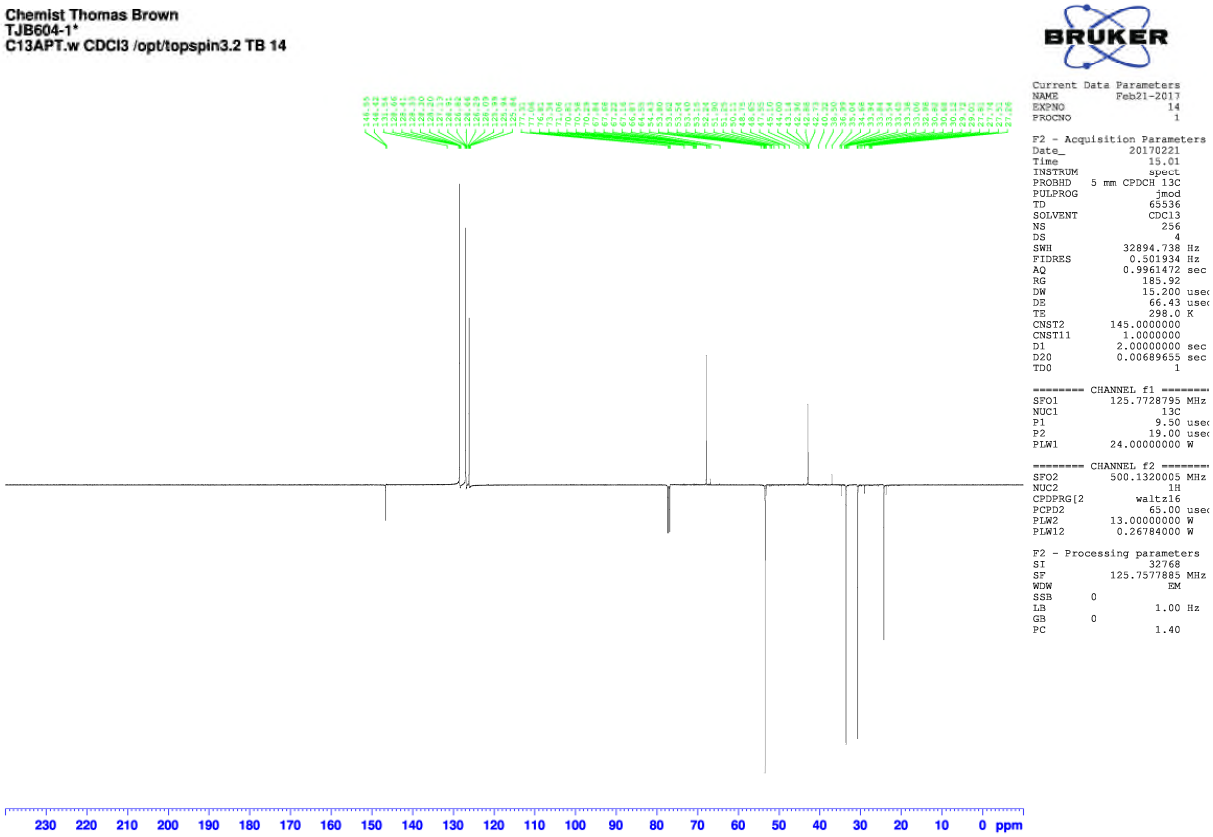


TJB604.

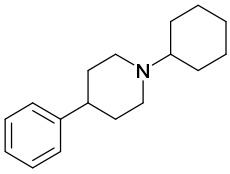
^{1}H NMR (500 MHz, $CDCl_3$).



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

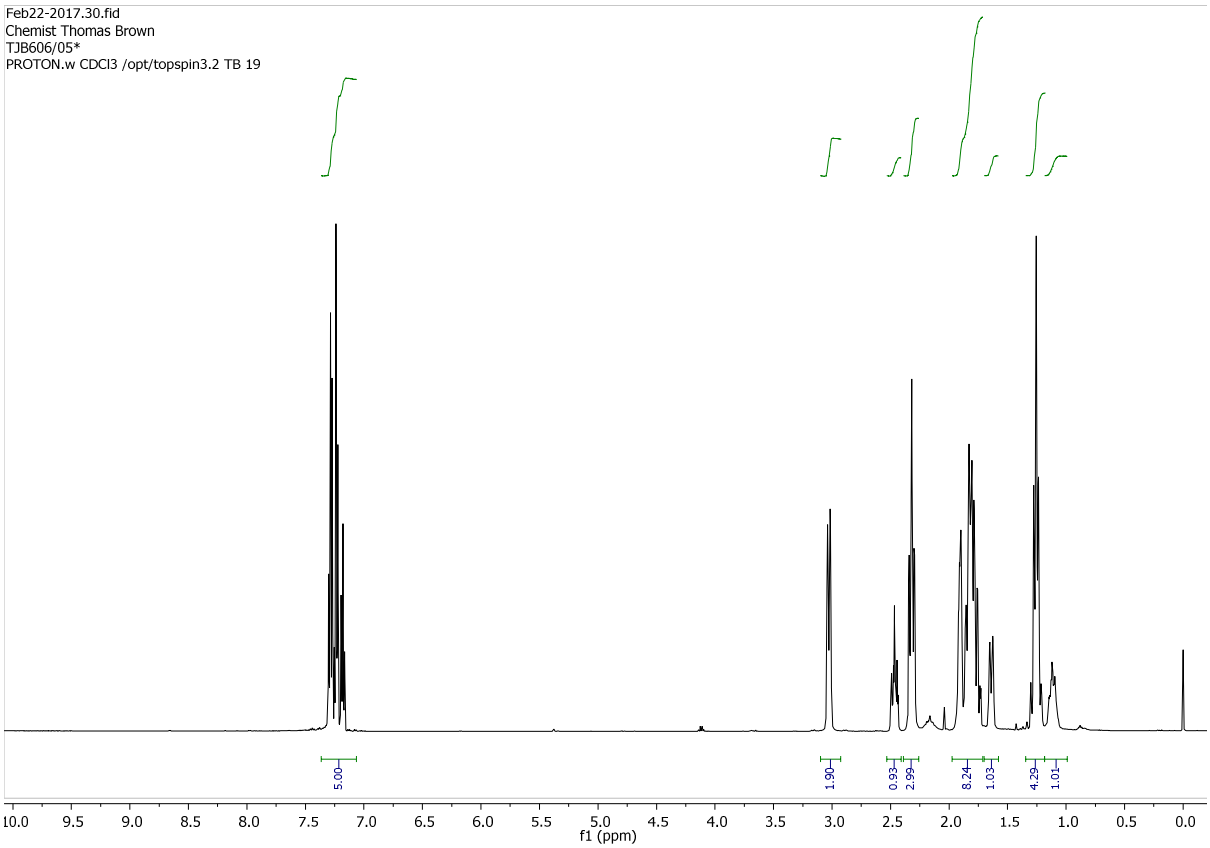


1-Cyclohexyl-4-phenylpiperidine **51**.

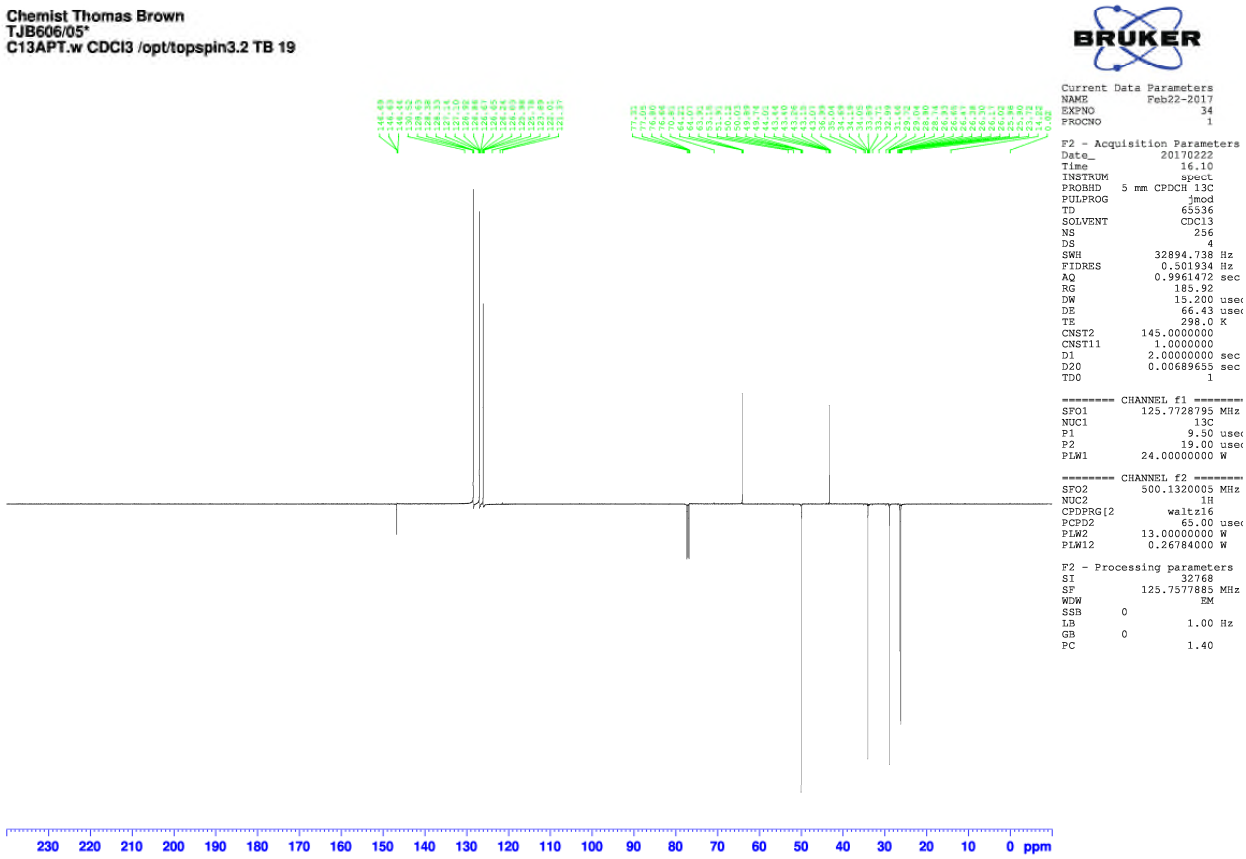


TJB605.

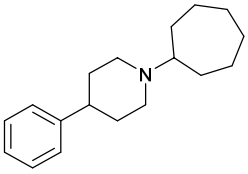
^{1}H NMR (500 MHz, $CDCl_3$).



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

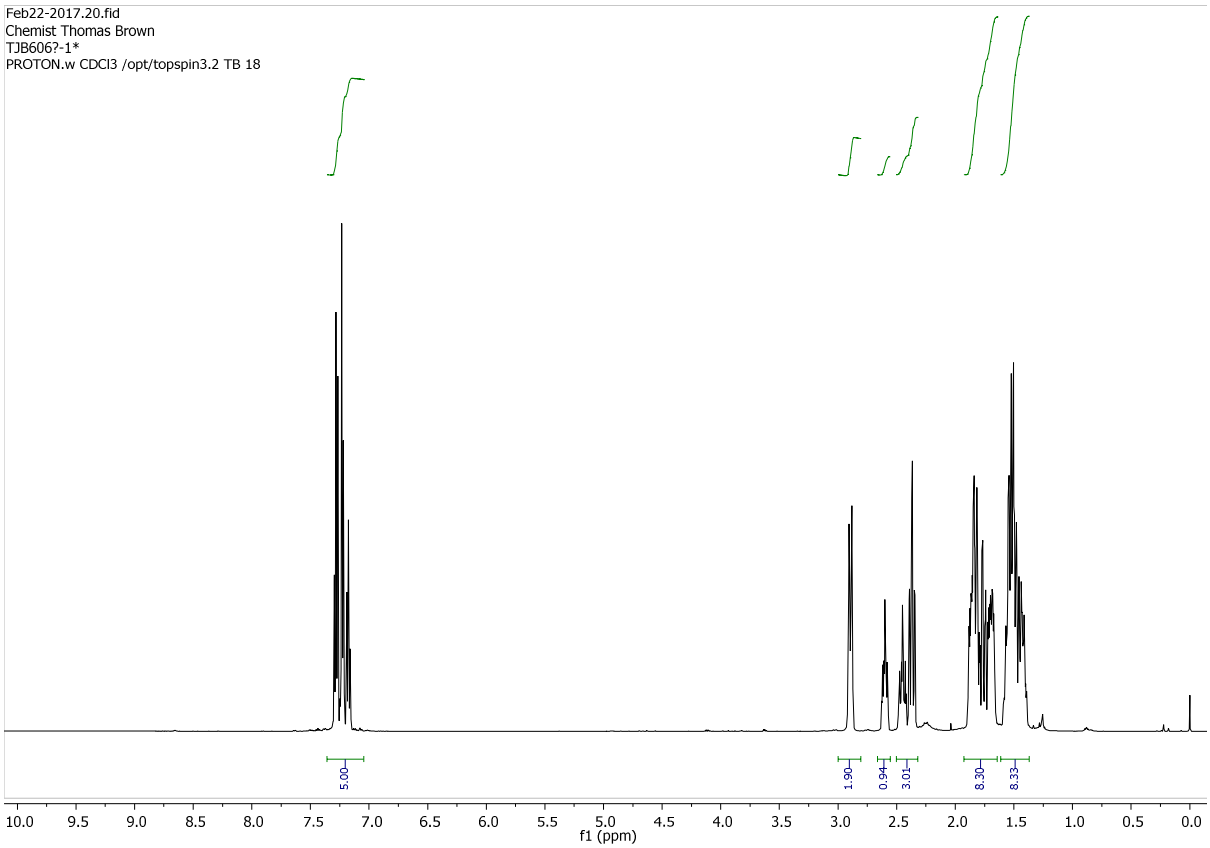


1-Cycloheptyl-4-phenylpiperidine **52**.

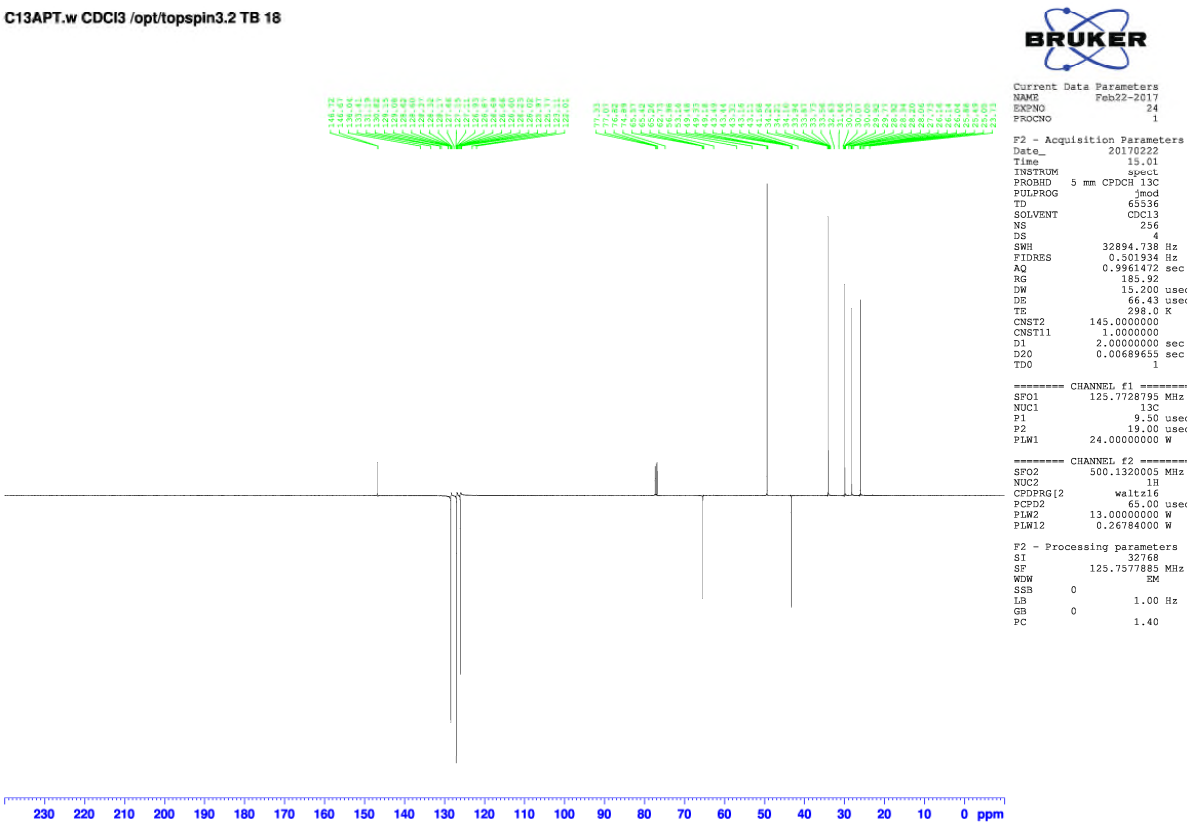


TJB606

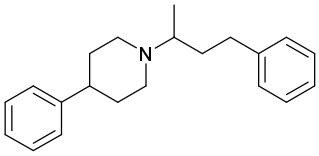
^{1}H NMR (500 MHz, $CDCl_3$).



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

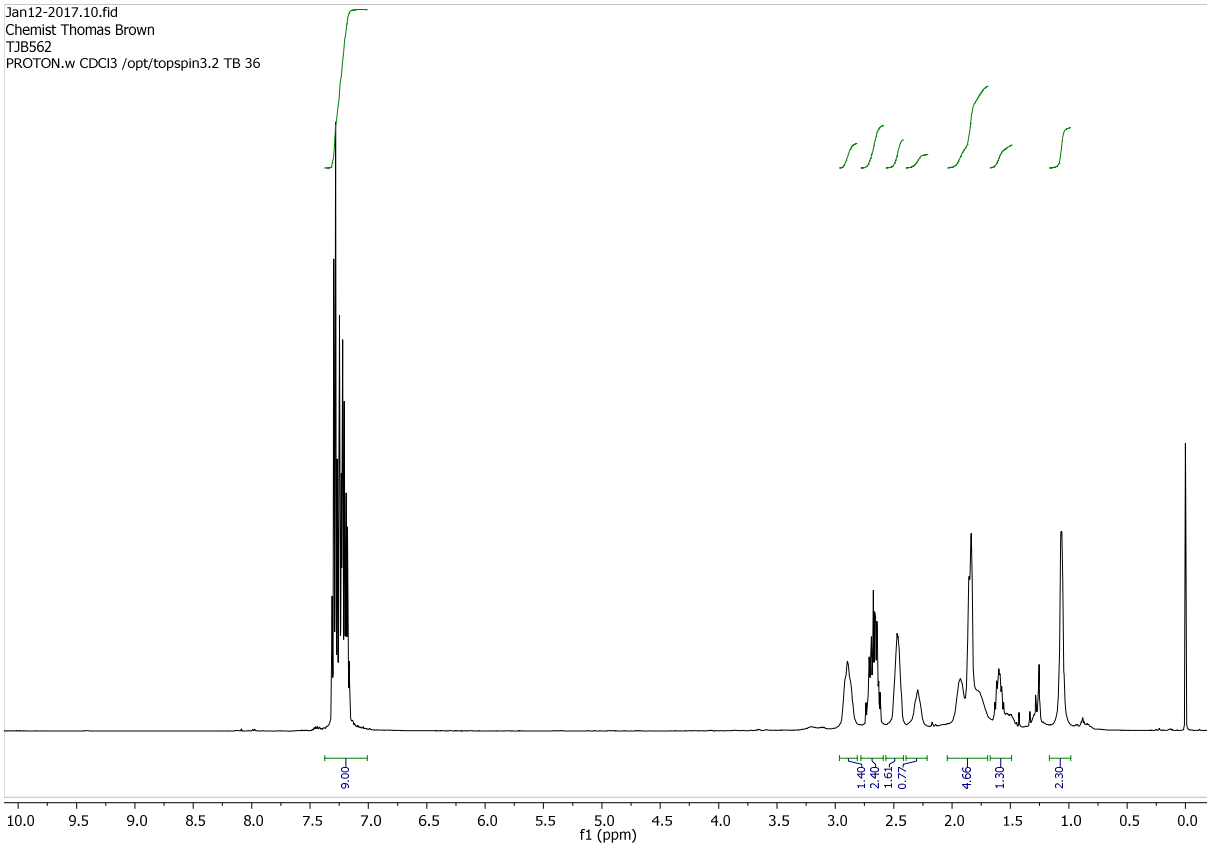


4-Phenyl-1-(4-phenylbutan-2-yl)piperidine **53**.

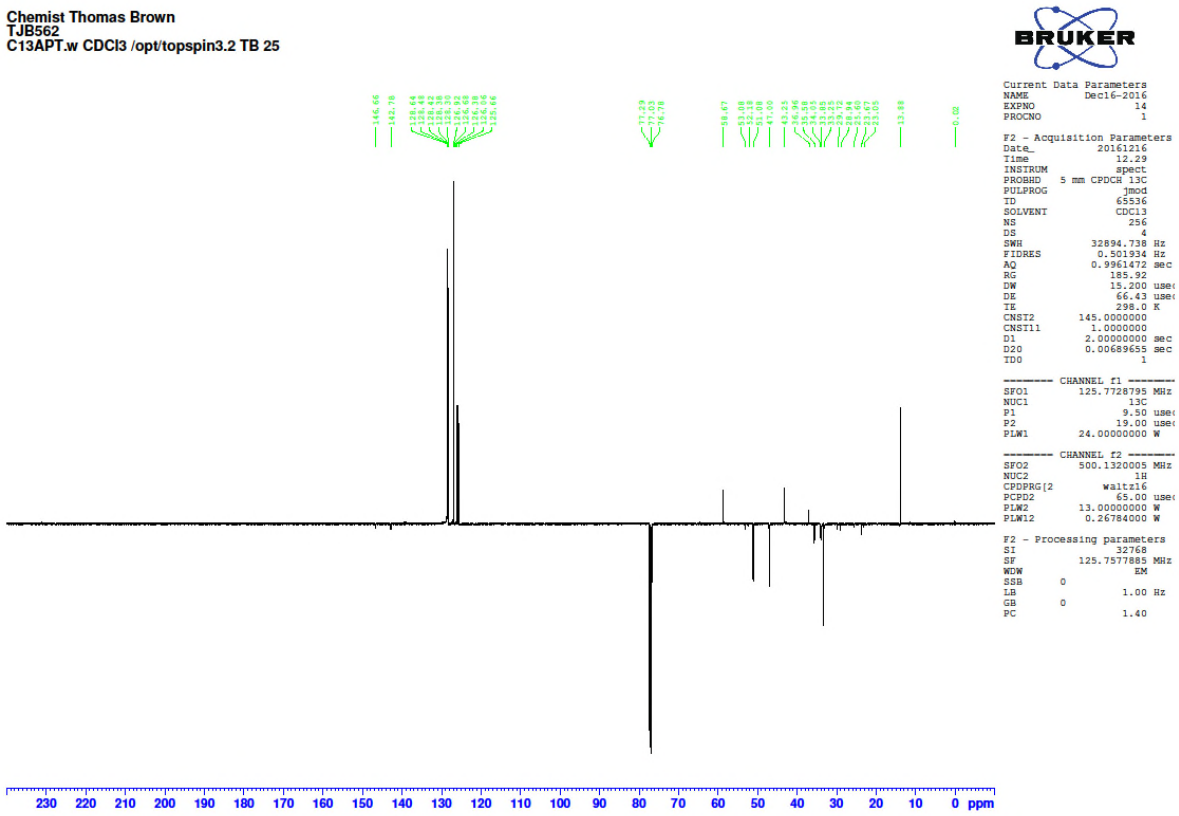


TJB562.

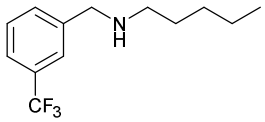
^{1}H NMR (500 MHz, $CDCl_3$).



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

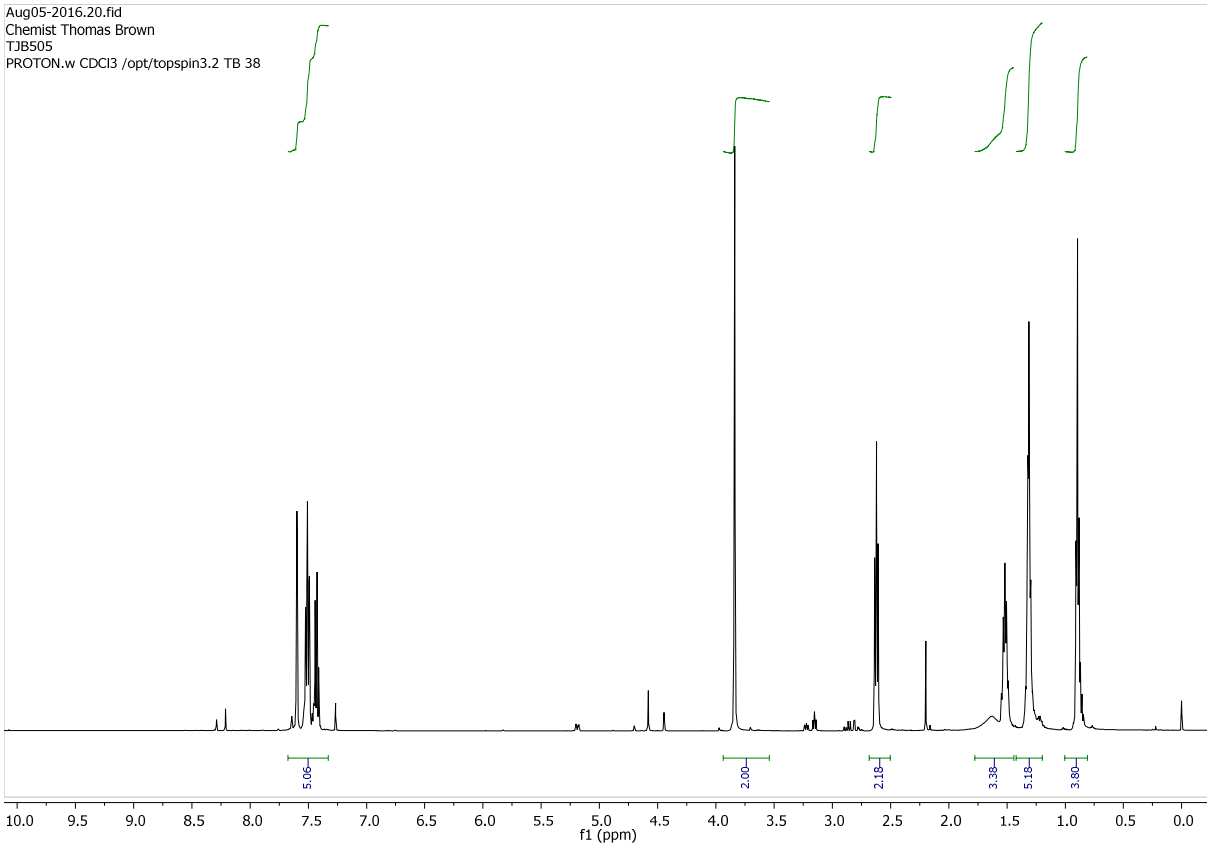


N-(3-(Trifluoromethyl)benzyl)pentan-1-amine **54**.

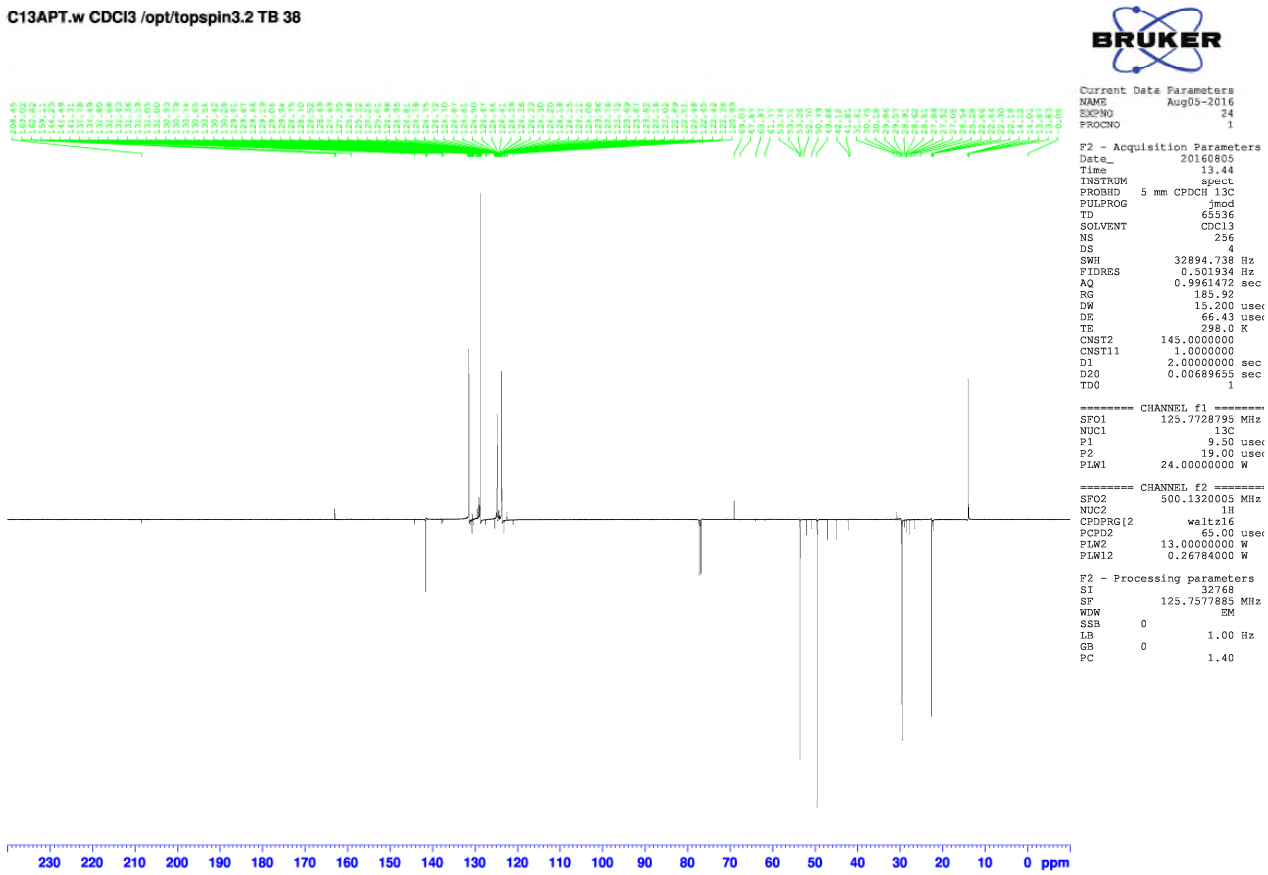


TJB505

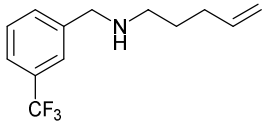
^{1}H NMR (500 MHz, $CDCl_3$).



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

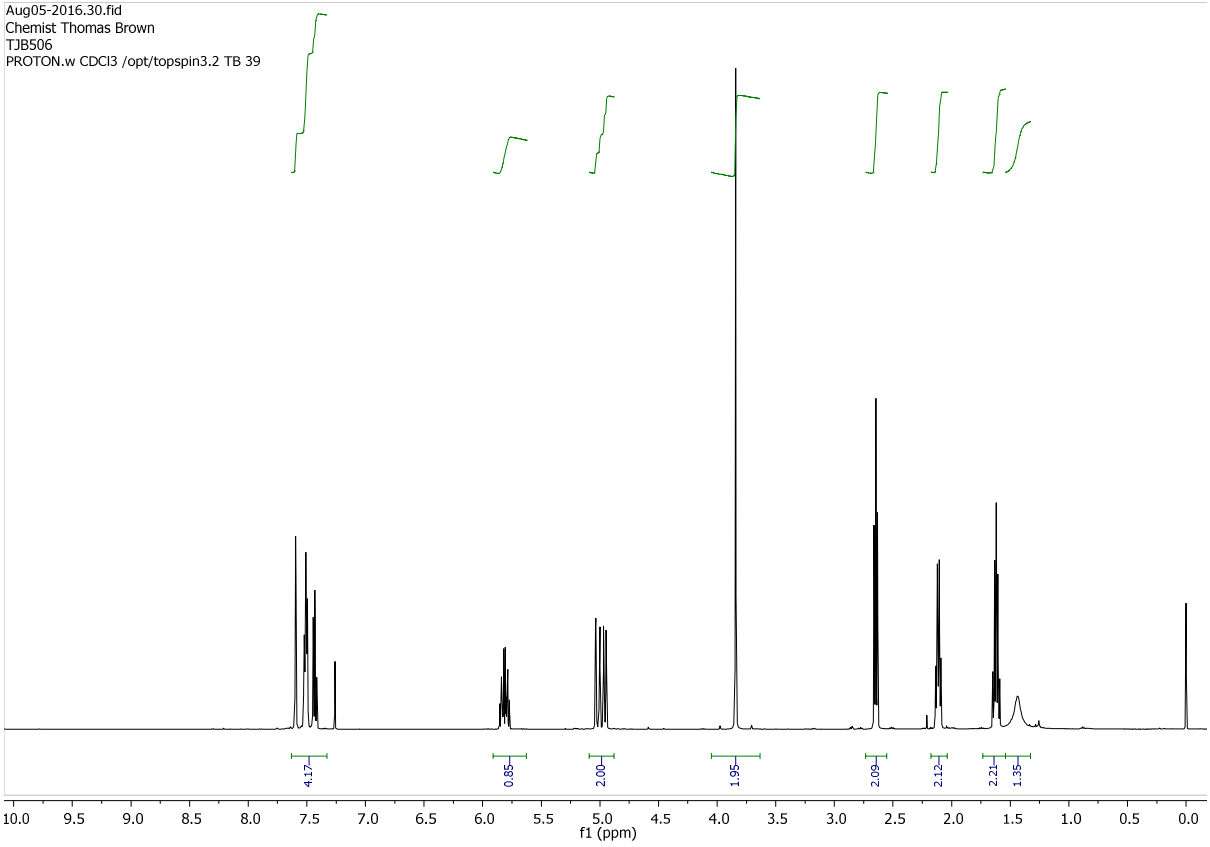


N-(3-(trifluoromethyl)benzyl)pent-4-en-1-amine **55**.

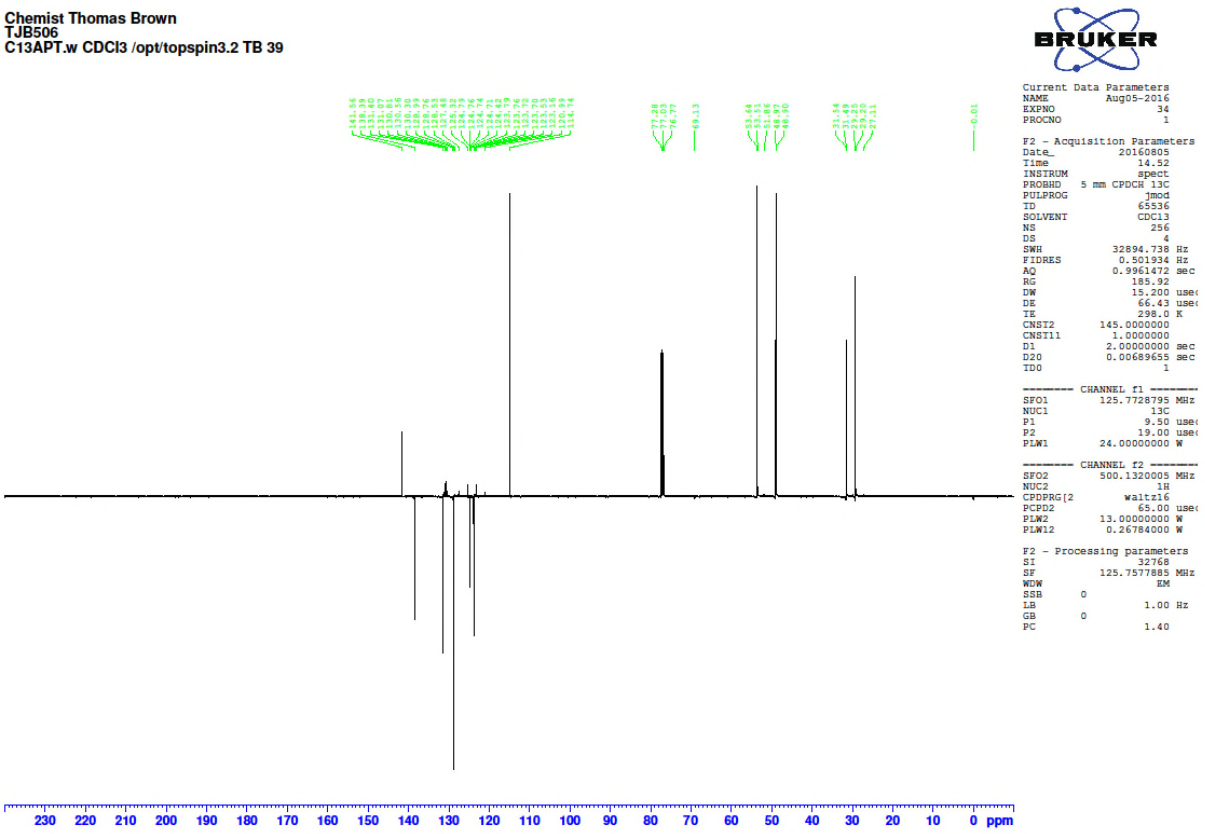


TJB506.

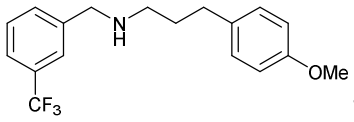
^{1}H NMR (500 MHz, $CDCl_3$).



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

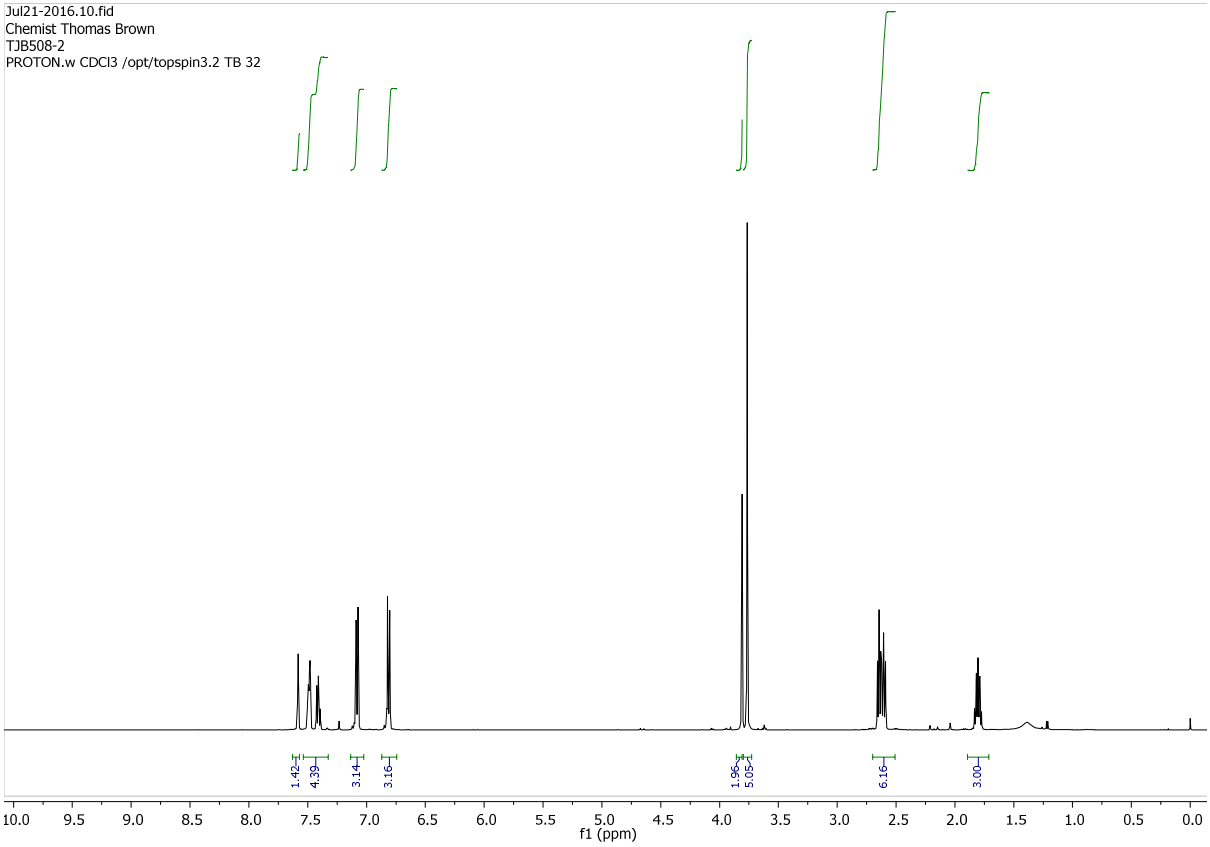


3-(4-Methoxyphenyl)-*N*-(3-(trifluoromethyl)benzyl)propan-1-amine **56**.

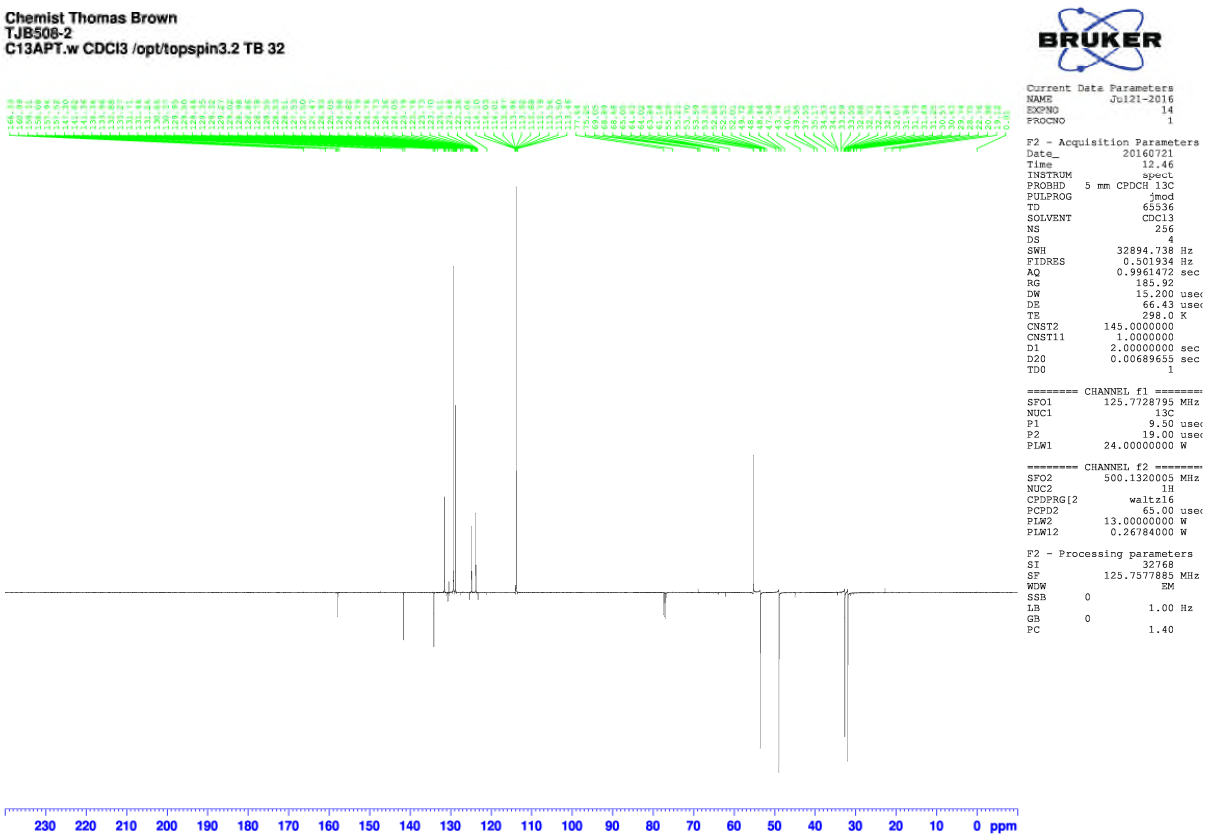


TJB508.

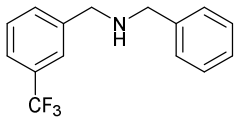
^{1}H NMR (500 MHz, $CDCl_3$).



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

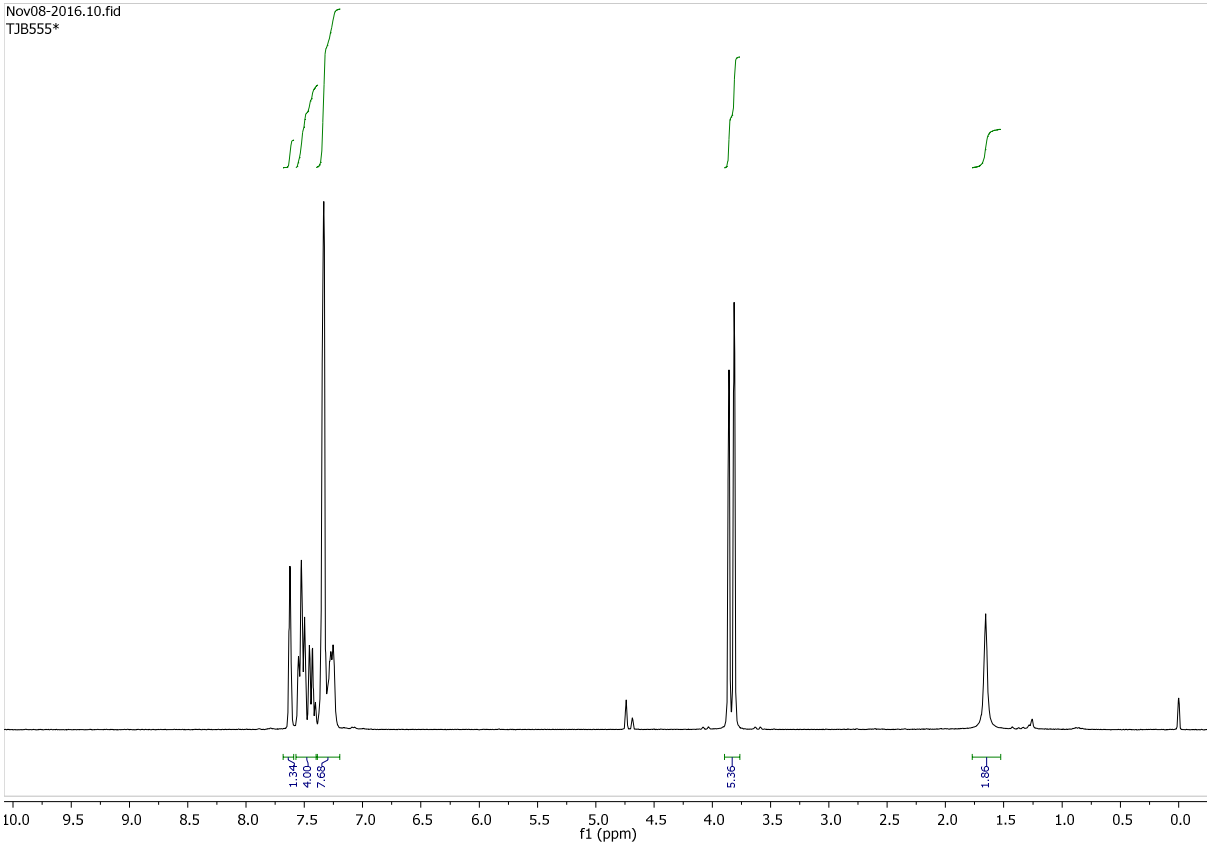


N-Benzyl-1-(3-(trifluoromethyl)phenyl)methanamine **57**.

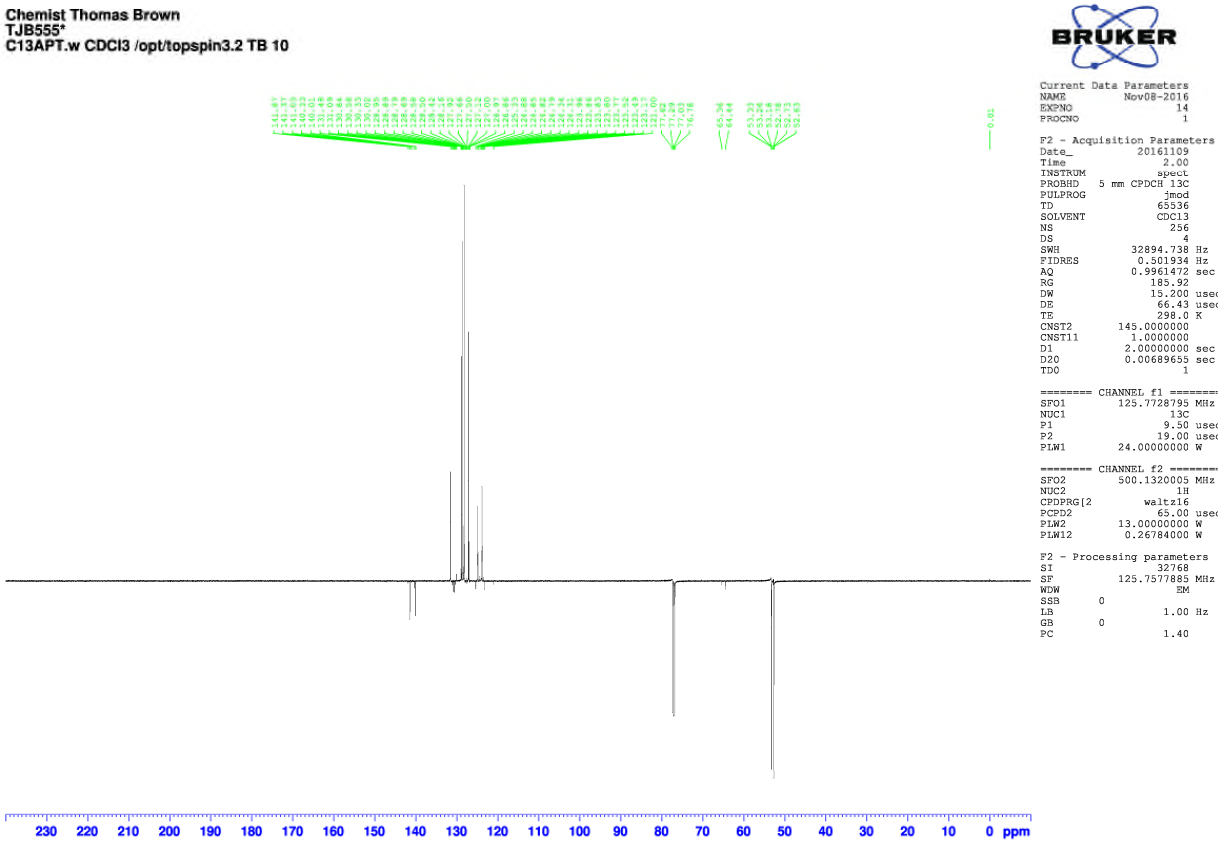


TJB555.

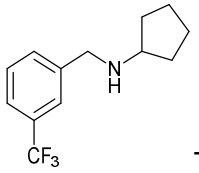
^{1}H NMR (500 MHz, $CDCl_3$).



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

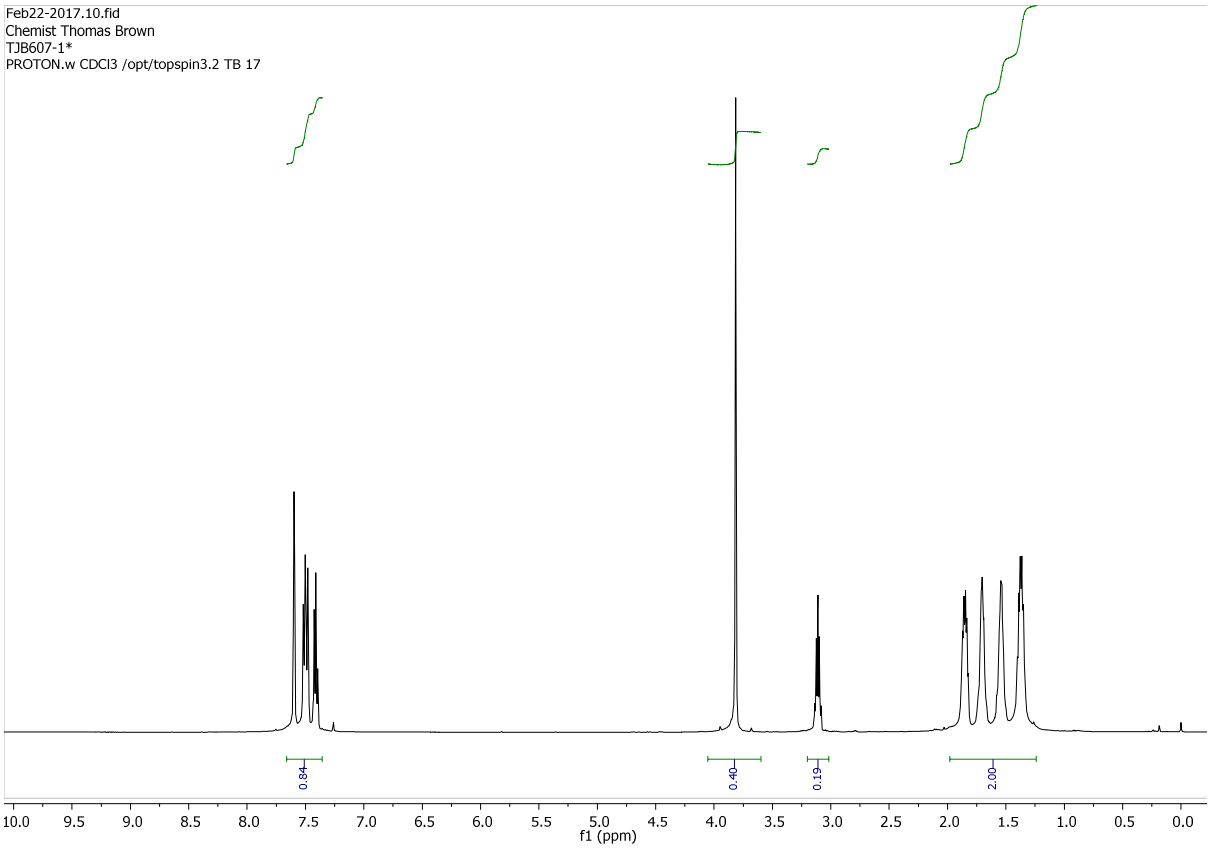


N-(3-(trifluoromethyl)benzyl)cyclopentanamine **58**.

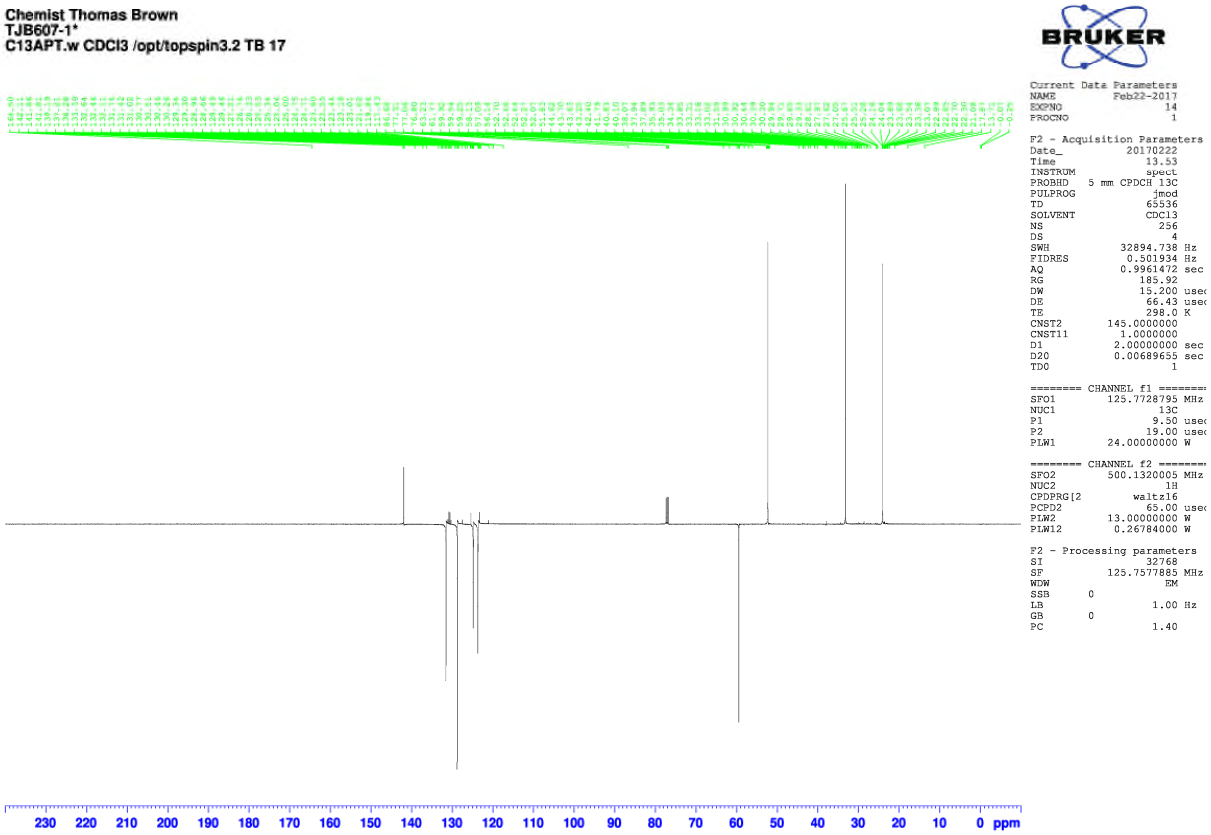


TJB607.

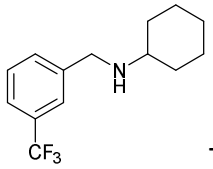
^{1}H NMR (500 MHz, $CDCl_3$).



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

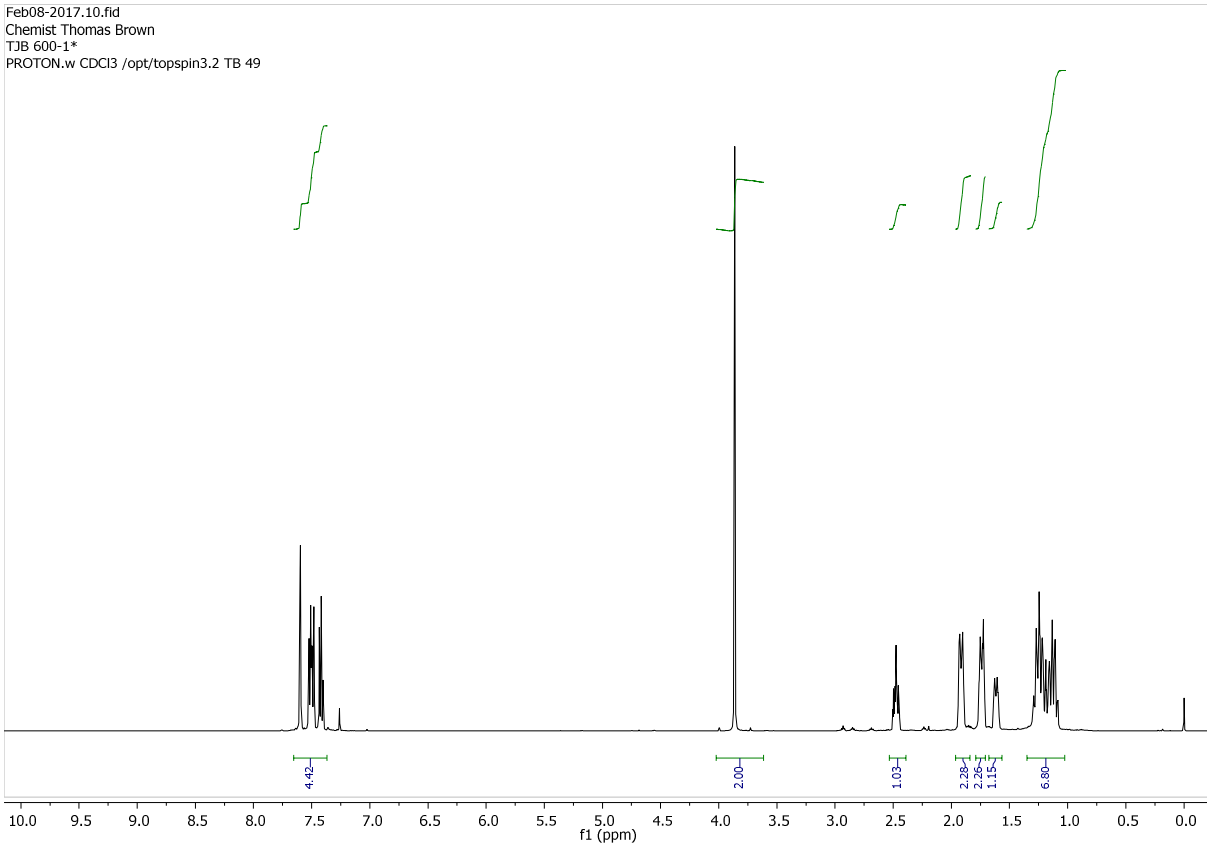


N-(3-(Trifluoromethyl)benzyl)cyclohexanamine **59**.

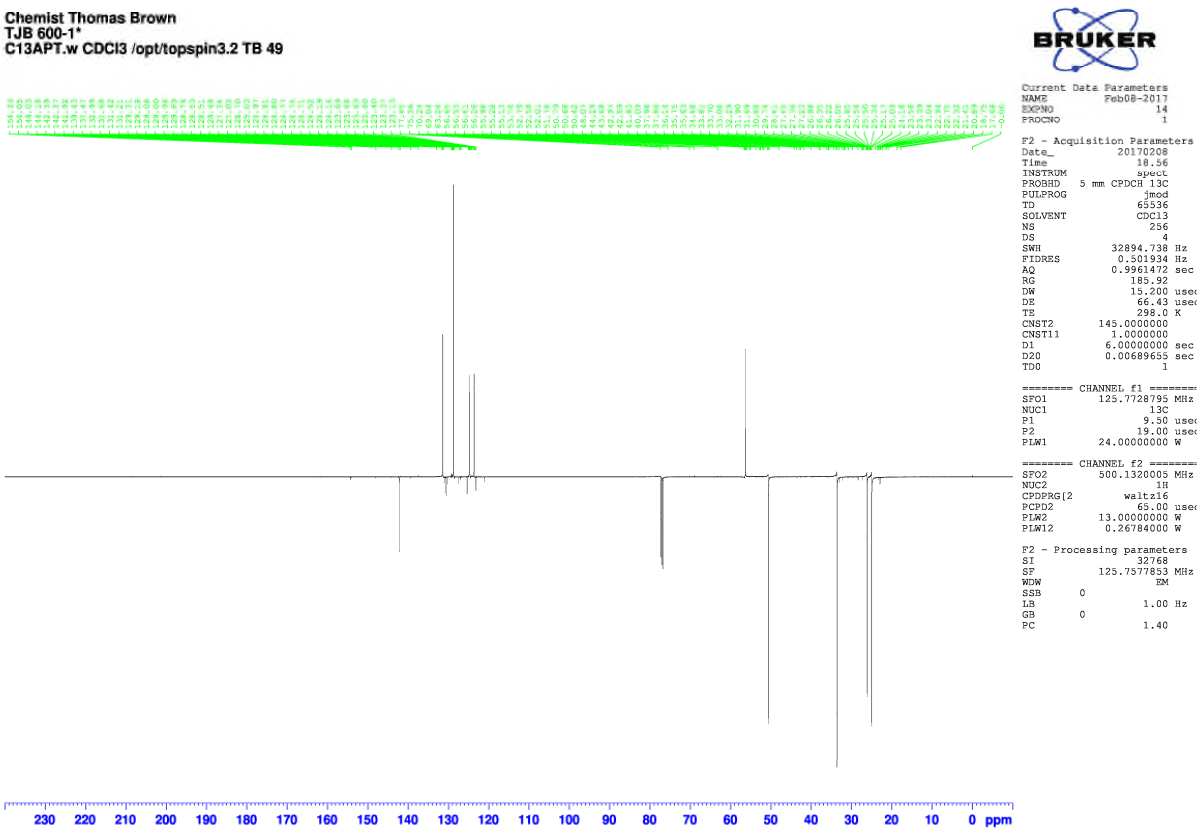


TJB600.

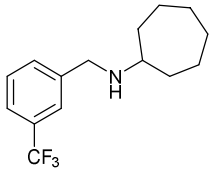
^{1}H NMR (500 MHz, $CDCl_3$).



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

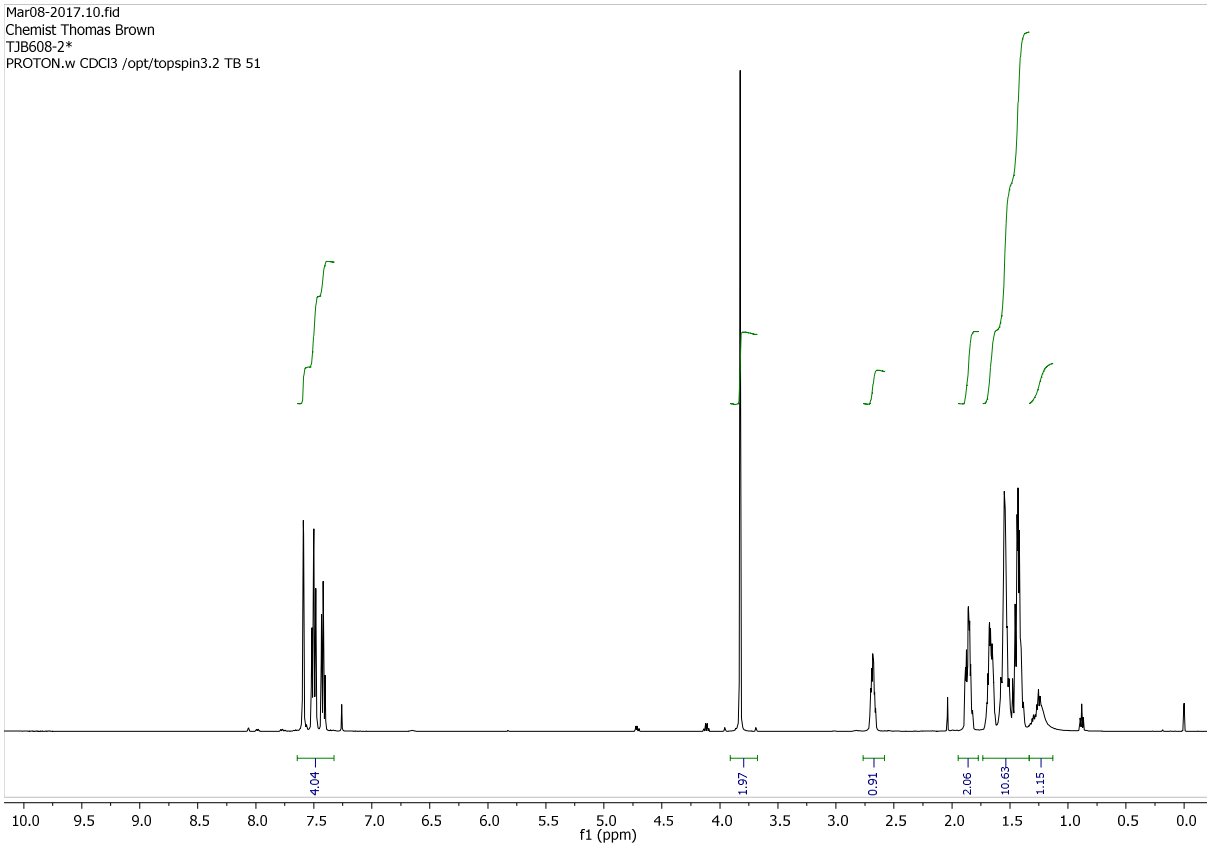


N-(3-(Trifluoromethyl)benzyl)cycloheptanamine **60**.

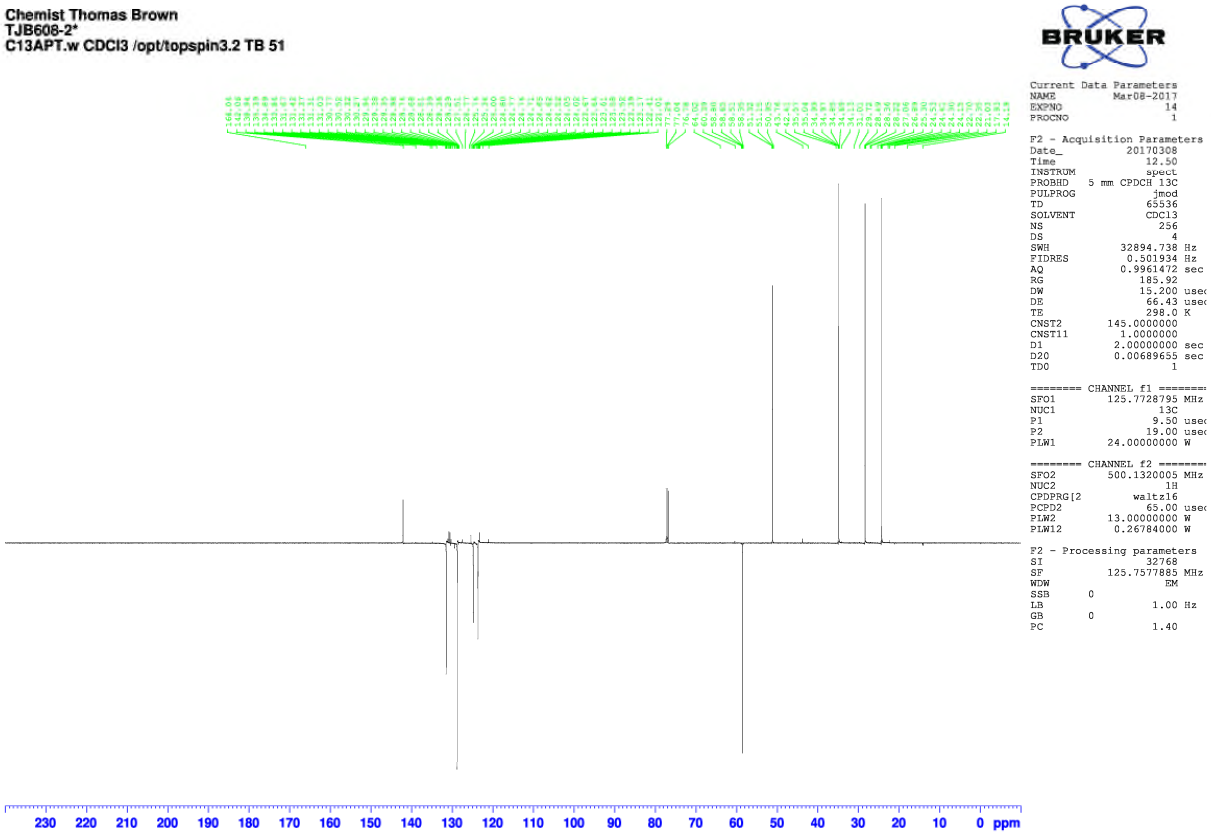


TJB608.

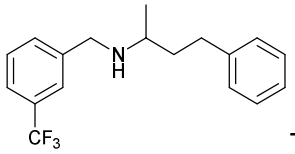
^{1}H NMR (500 MHz, $CDCl_3$).



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

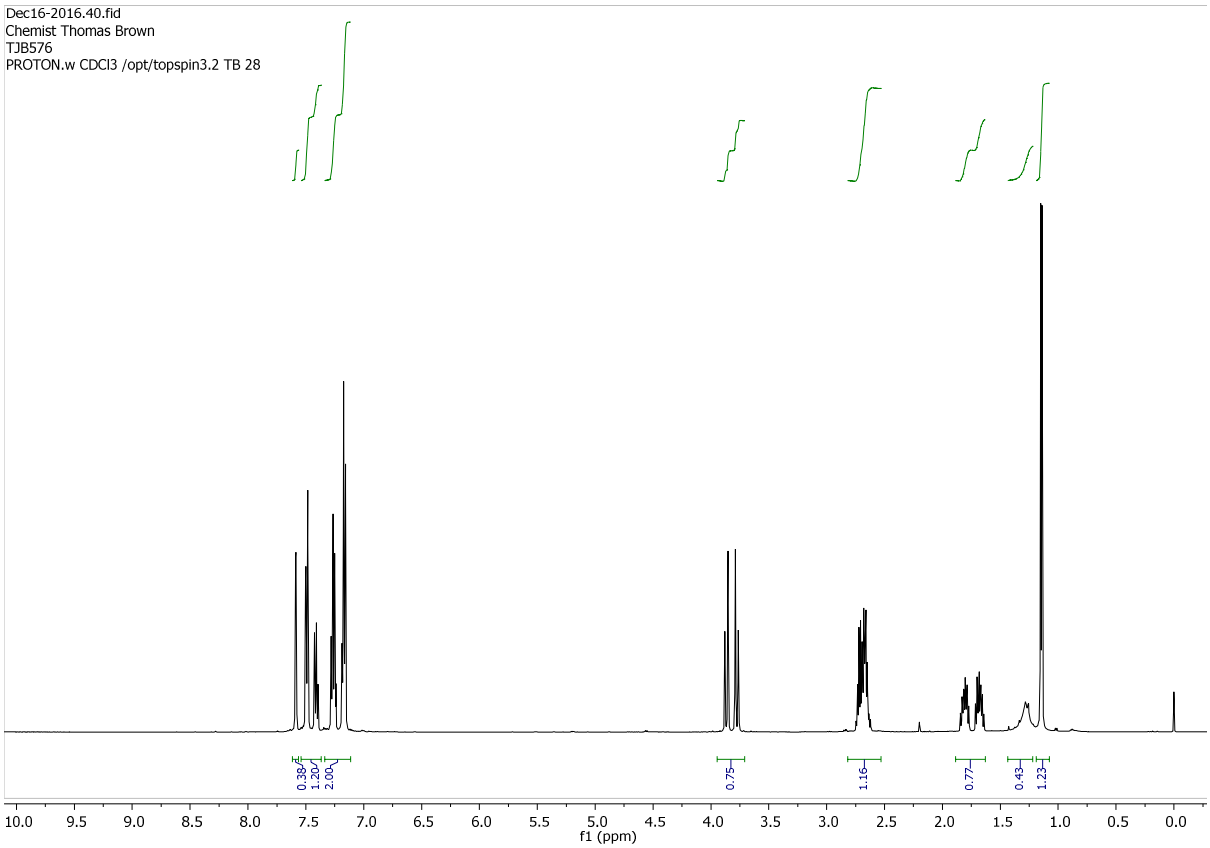


4-Phenyl-*N*-(3-(trifluoromethyl)benzyl)butan-2-amine **61**.

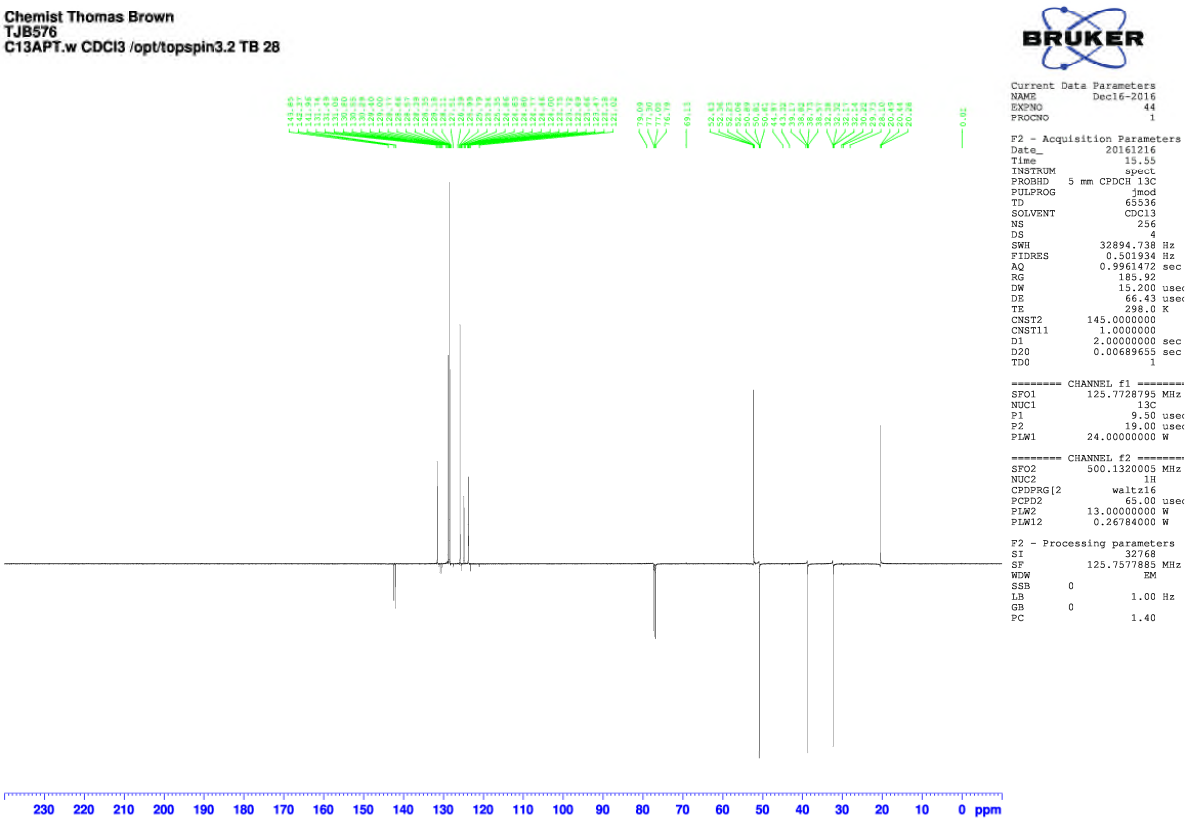


TJB576.

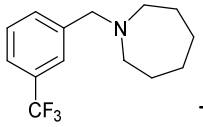
^{1}H NMR (500 MHz, $CDCl_3$).



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

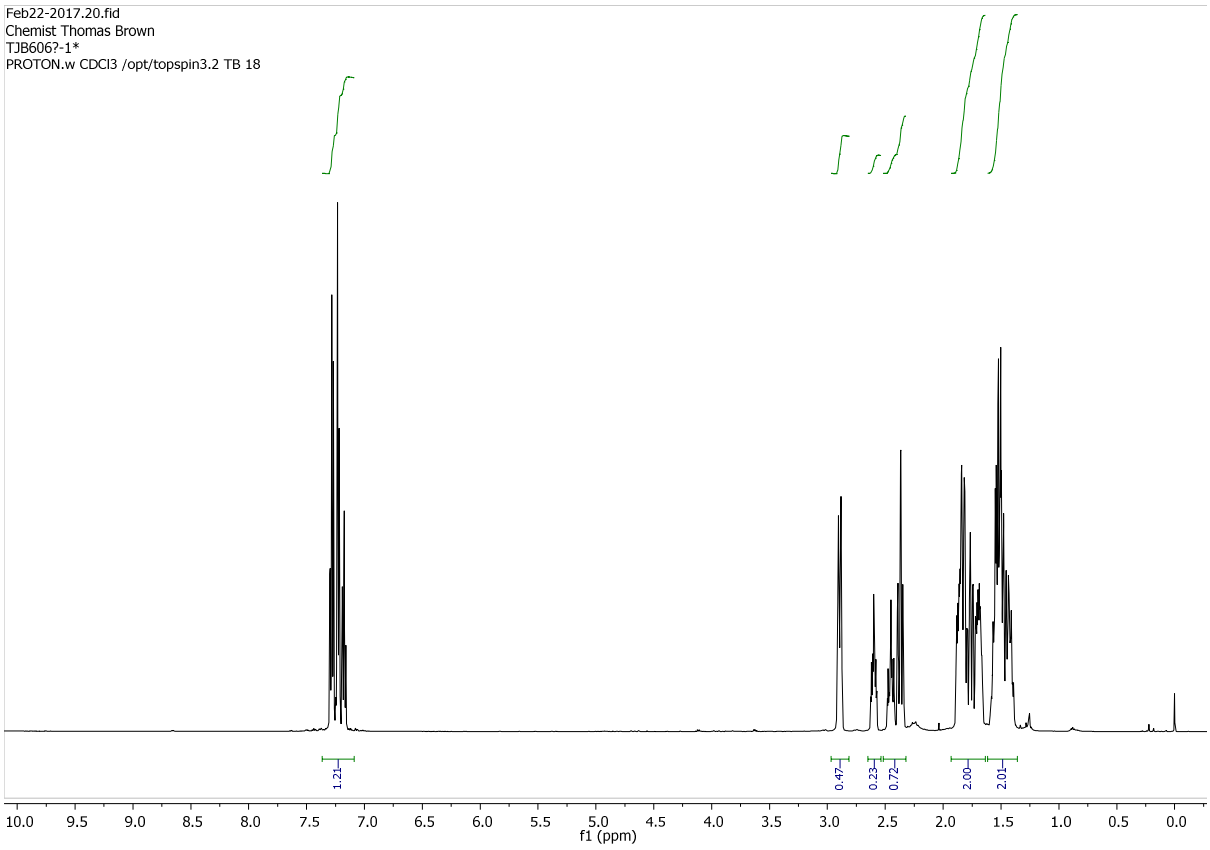


1-(3-(Trifluoromethyl)benzyl)azepane **62**.

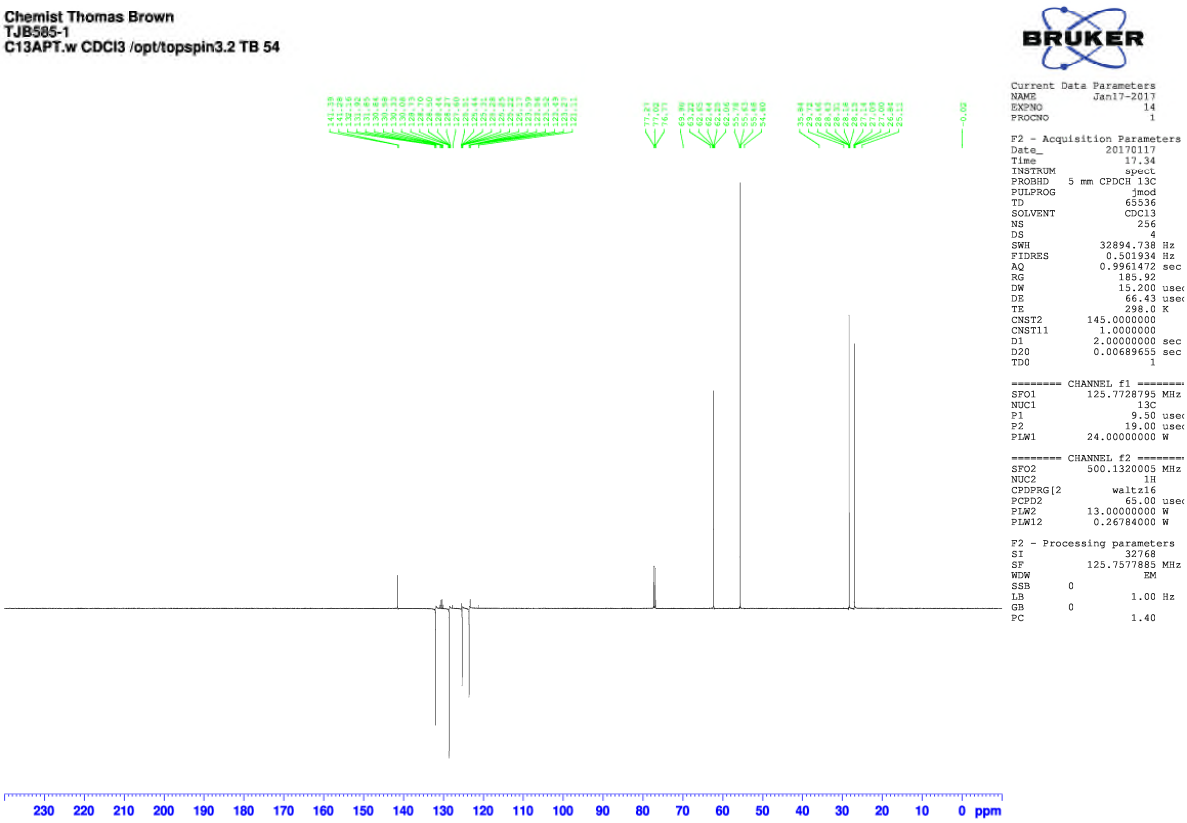


TJB585.

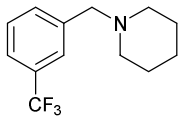
^{1}H NMR (500 MHz, $CDCl_3$).



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

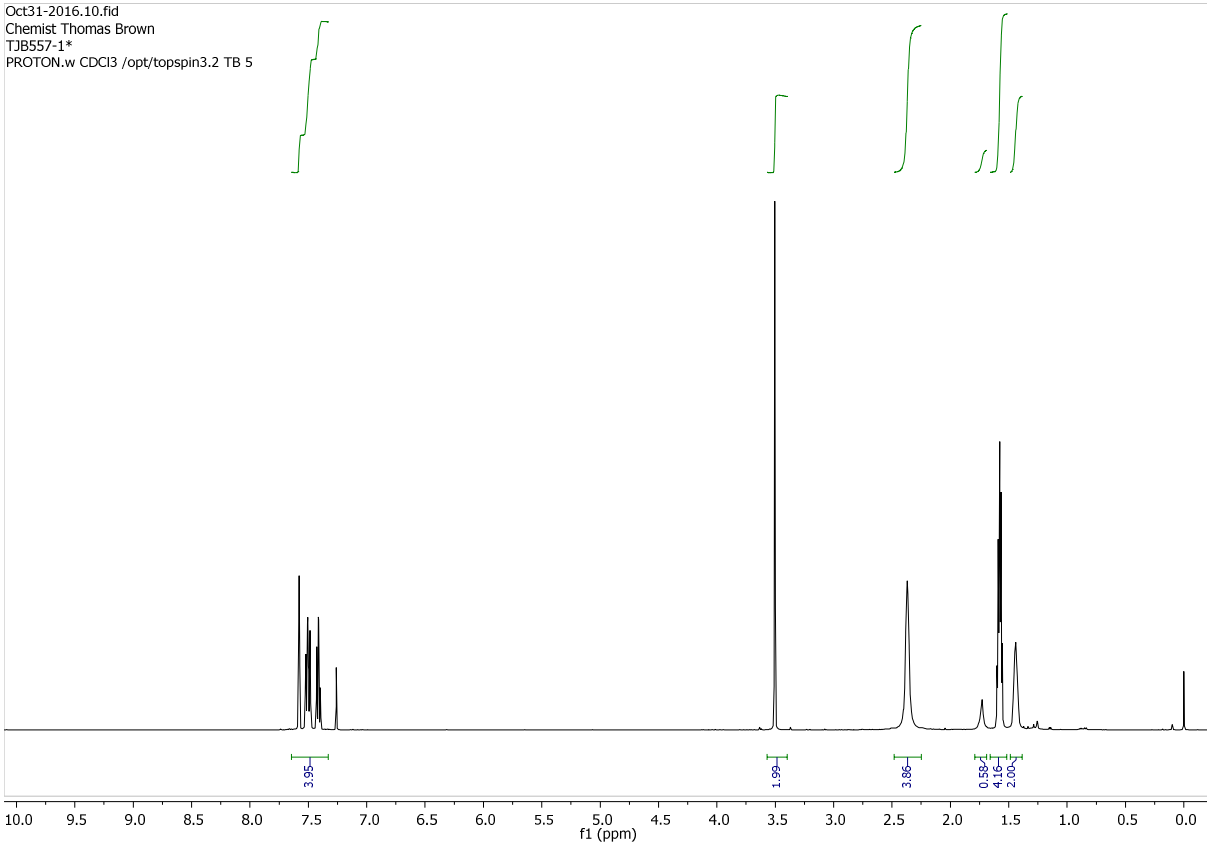


1-(3-(Trifluoromethyl)benzyl)piperidine **63**.

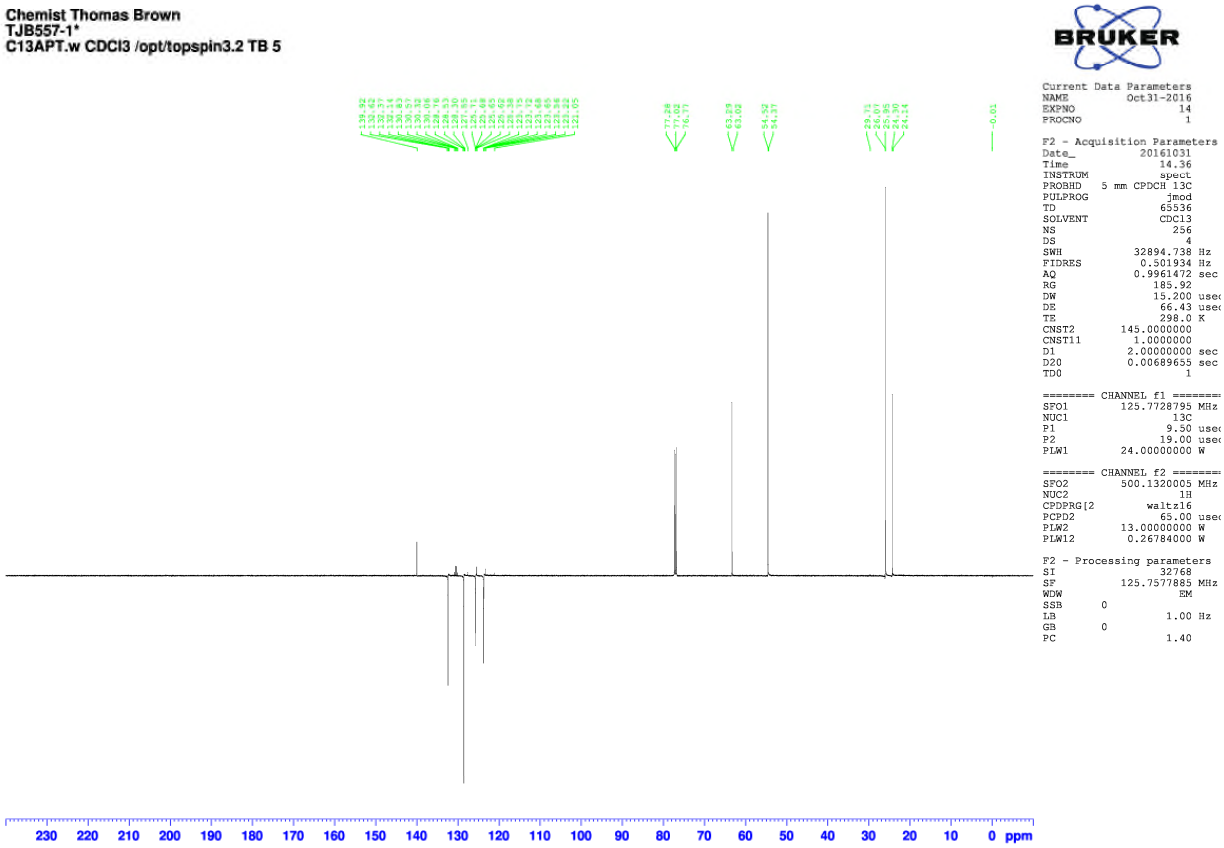


TJB557.

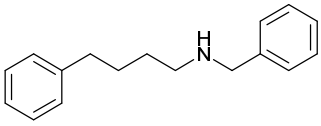
^{1}H NMR (500 MHz, $CDCl_3$).



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

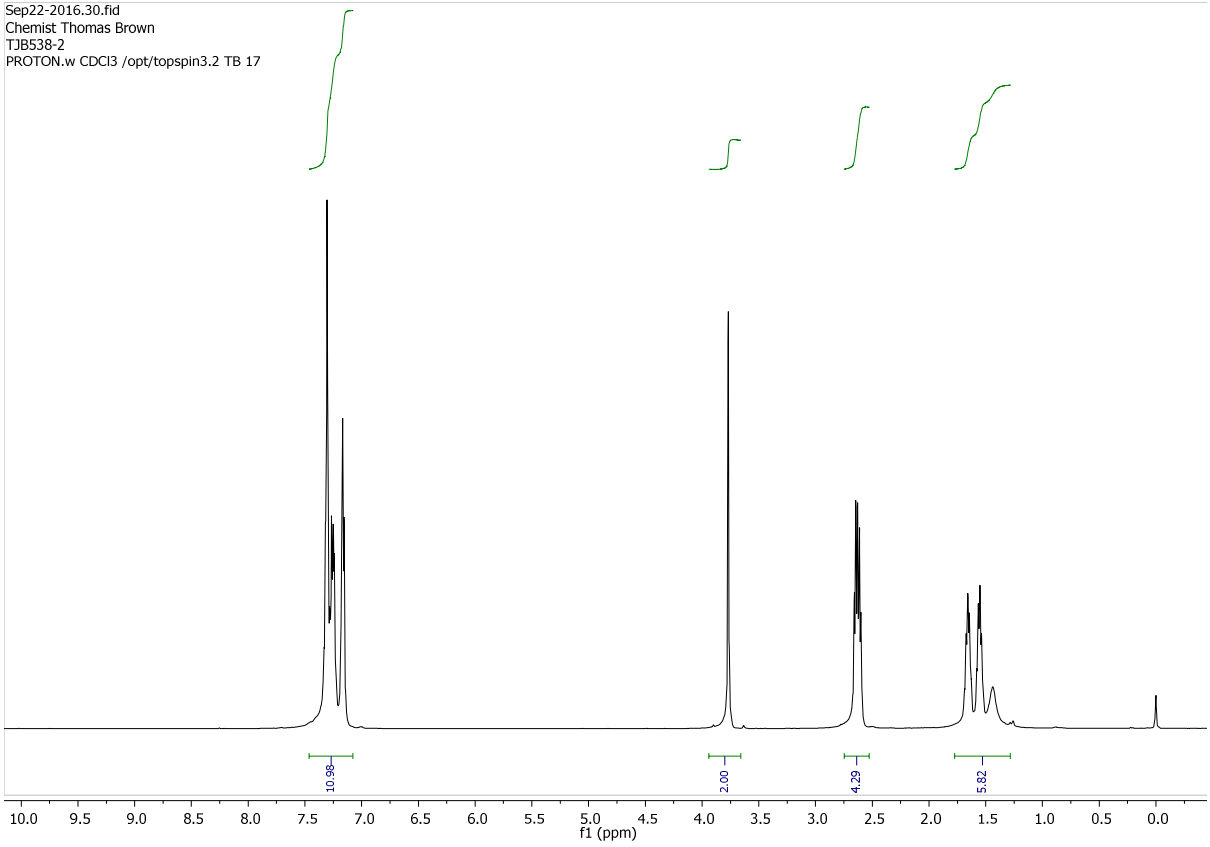


N-Benzyl-4-phenylbutan-1-amine **64**.

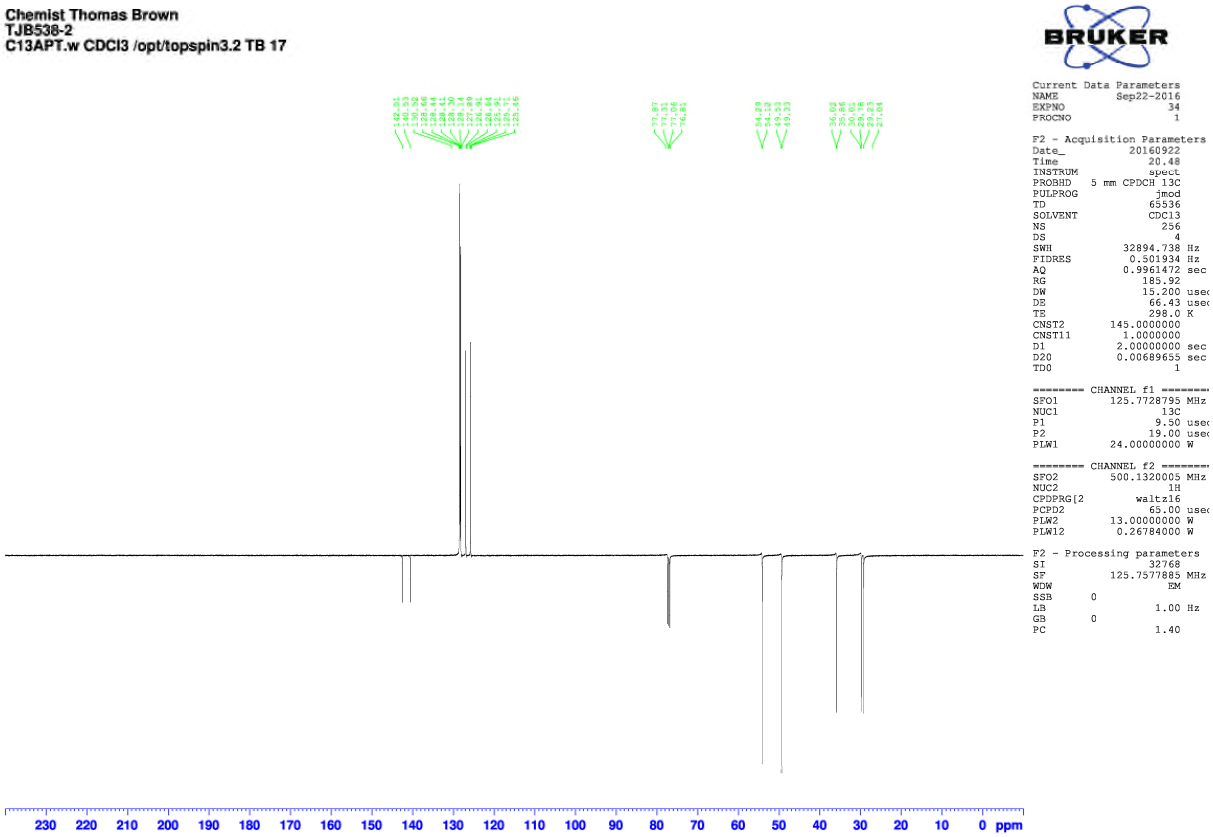


TJB538.

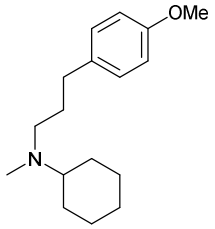
^{1}H NMR (500 MHz, $CDCl_3$).



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

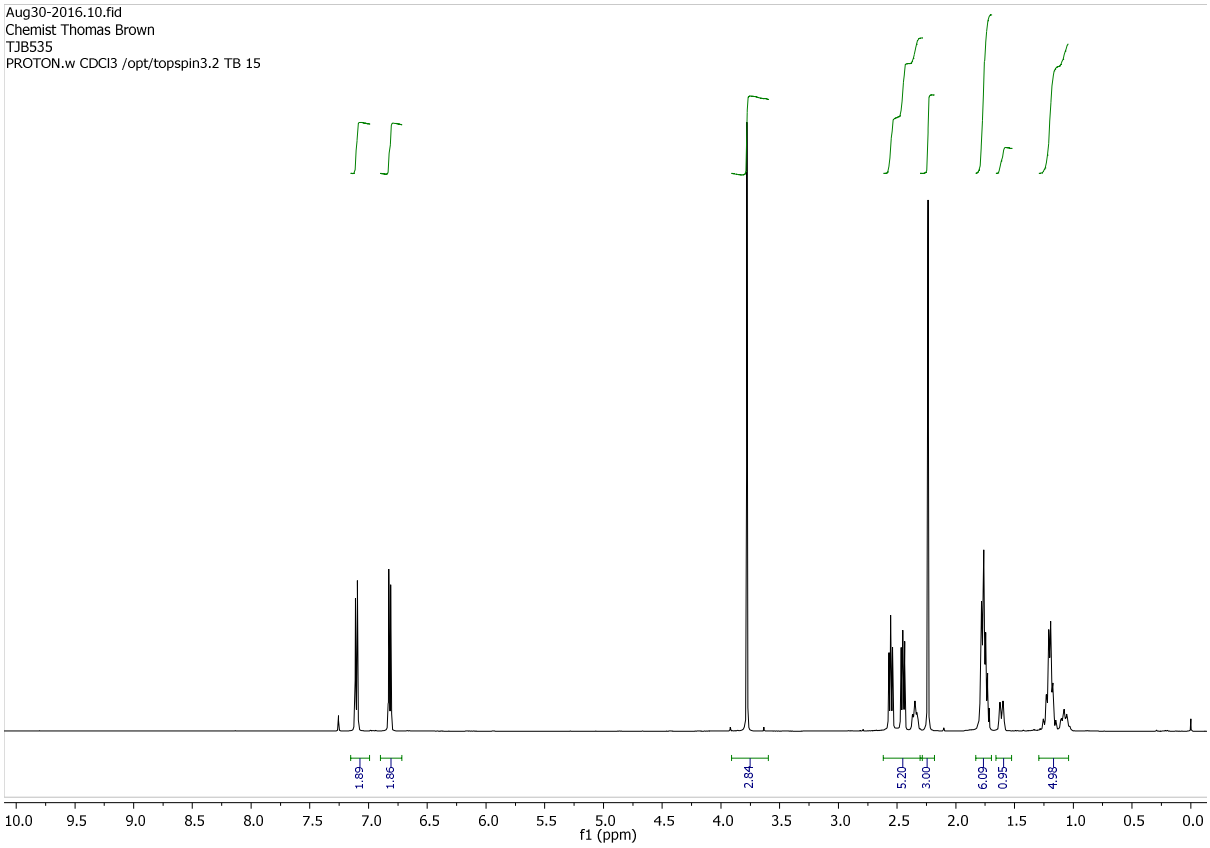


N-(3-(4-Methoxyphenyl)propyl-*N*-methylcyclohexanamine **65**.

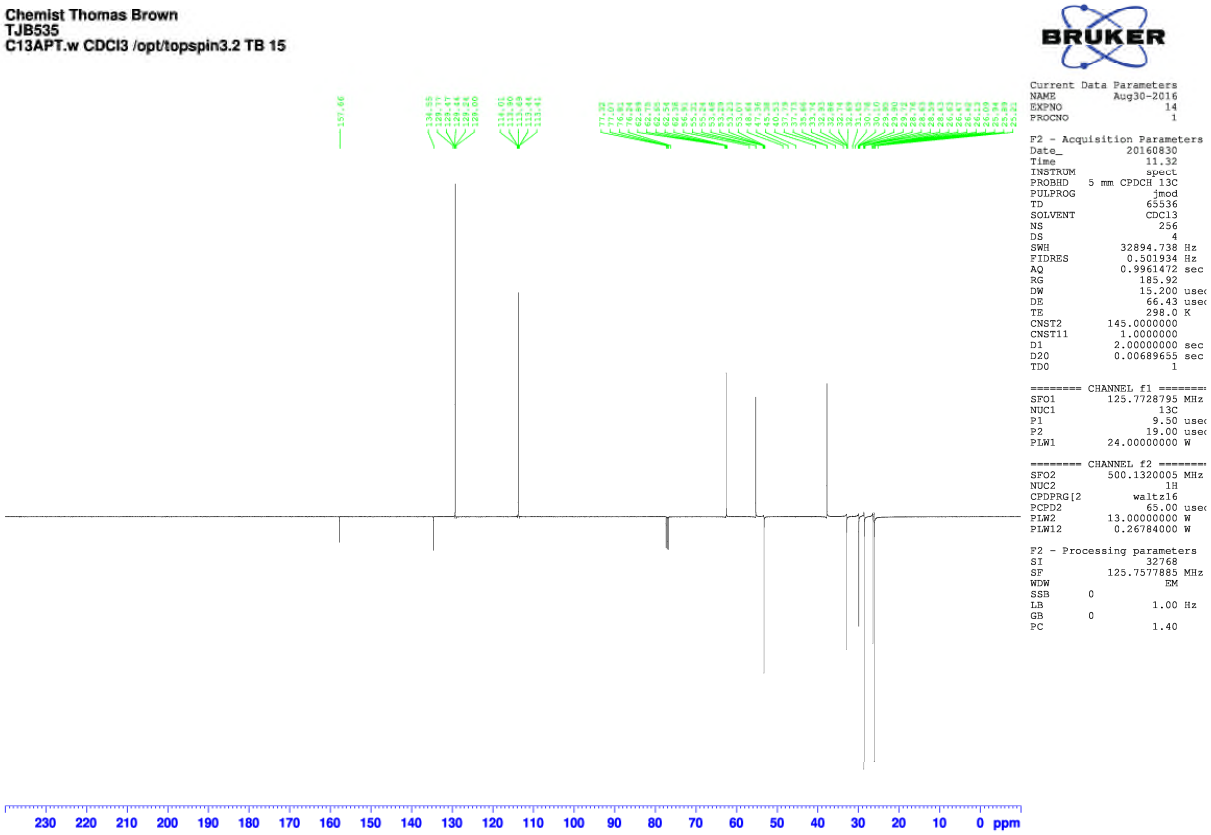


TJB535.

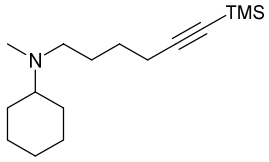
^{1}H NMR (500 MHz, $CDCl_3$).



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

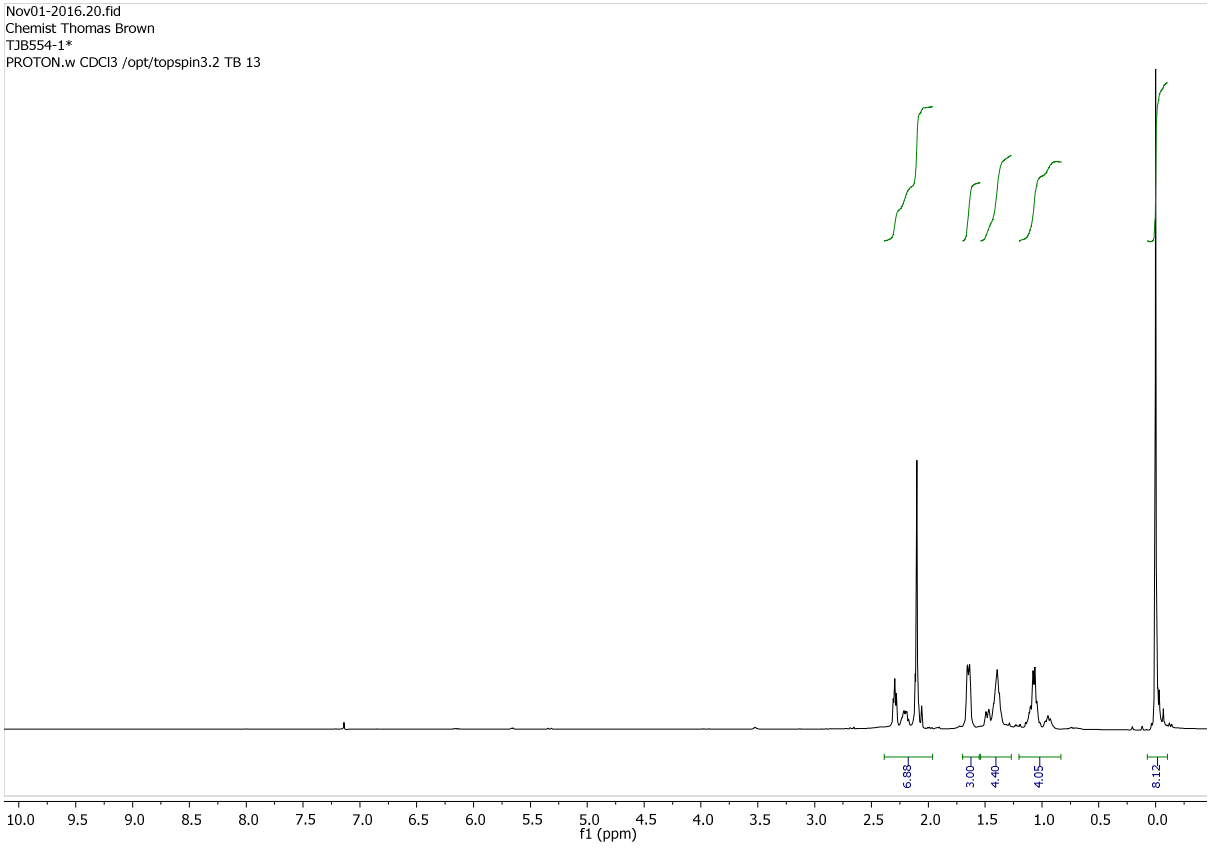


N-Methyl-*N*-(6-trimethylsilyl)hex-5-yn-1-yl)cyclohexanamine **66**.

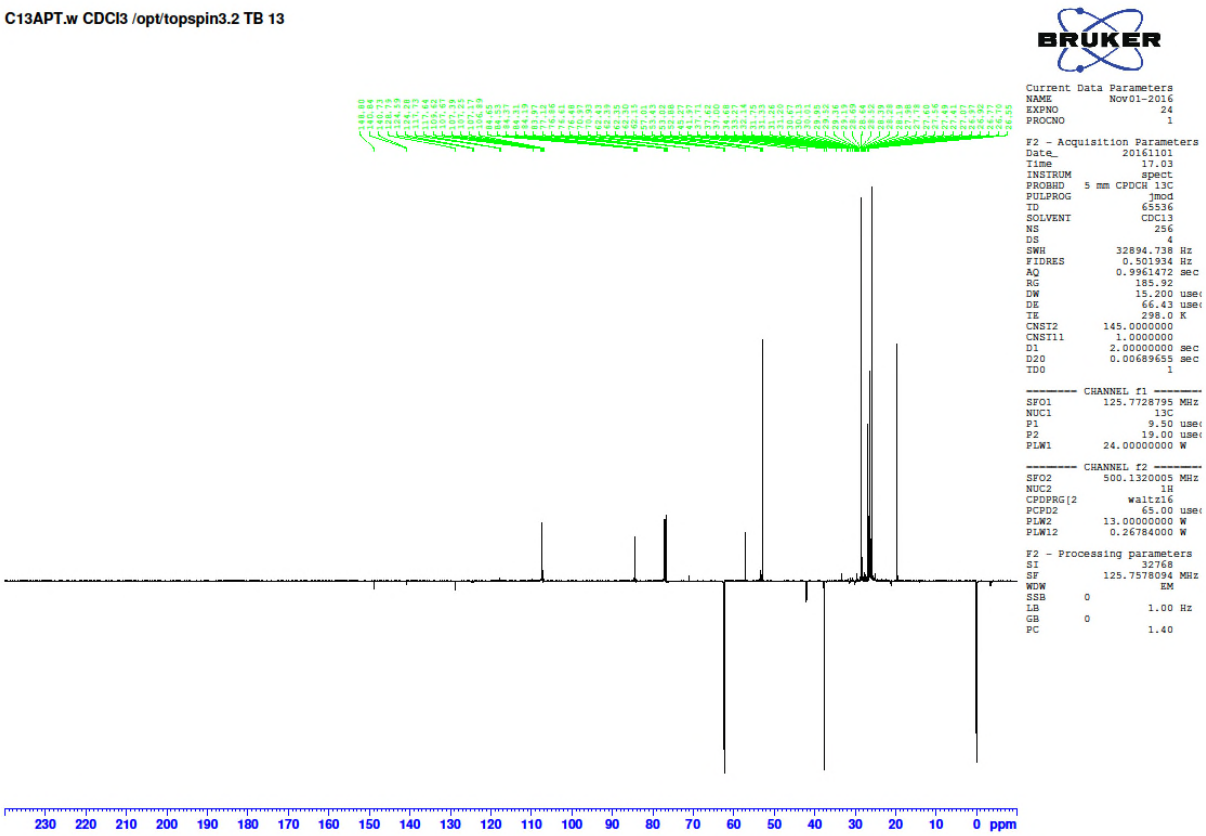


TJB554.

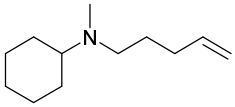
^{1}H NMR (500 MHz, $CDCl_3$).



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

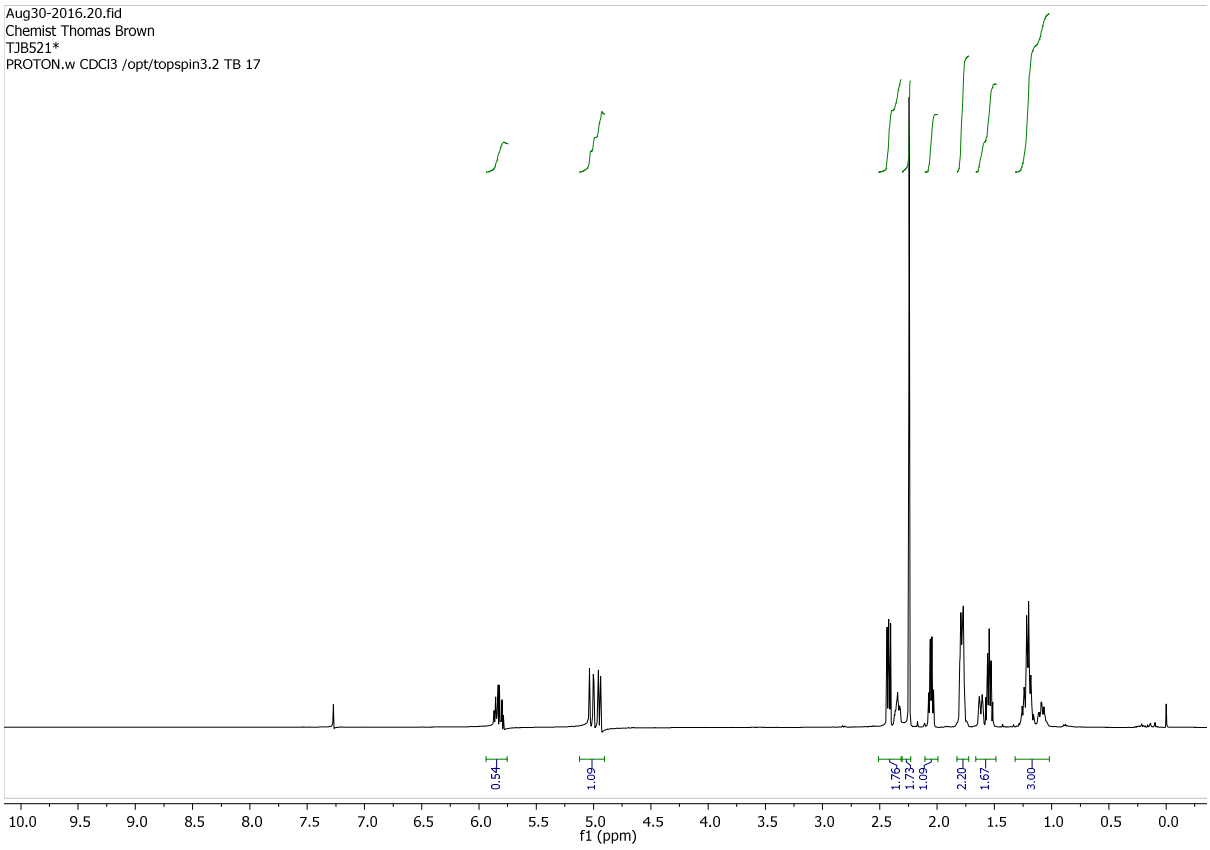


N-Methyl-*N*-(pent-4-en-1-yl)cyclohexanamine **67**.

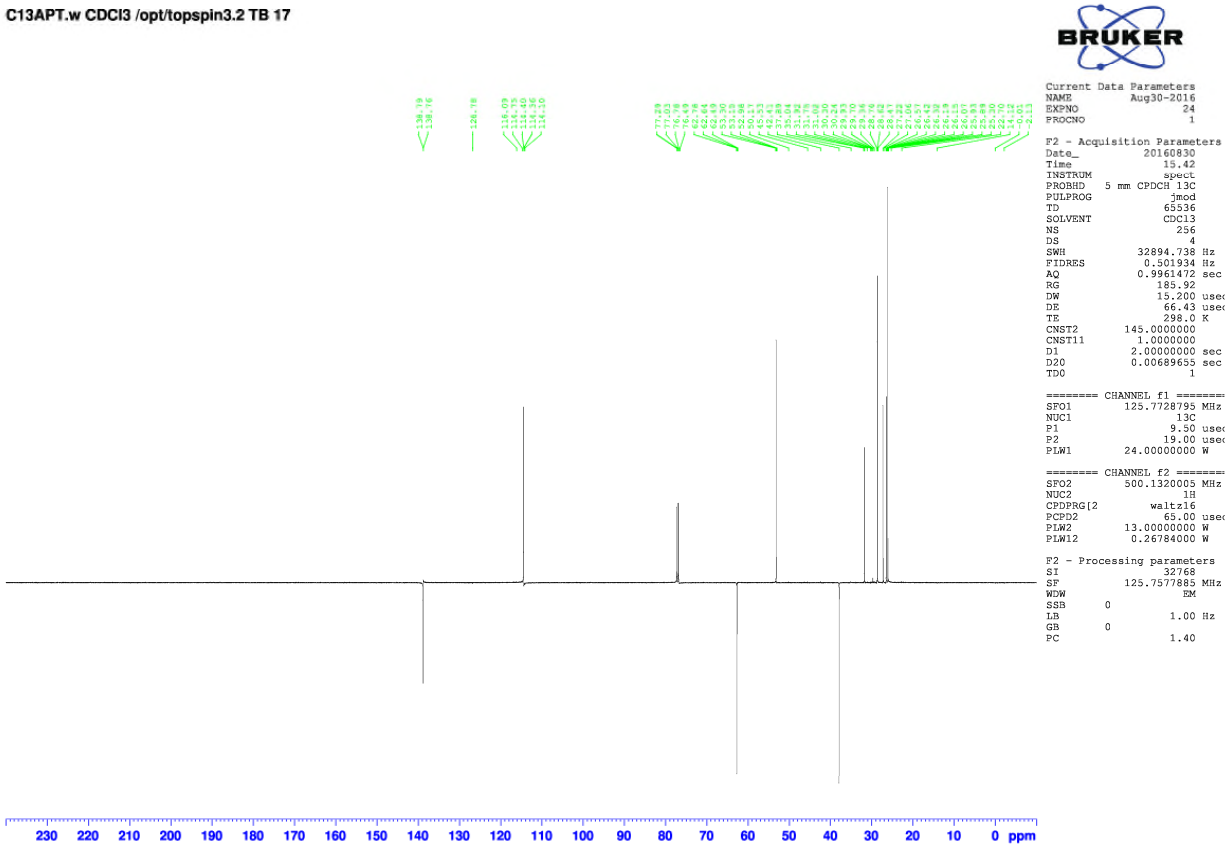


TJB521.

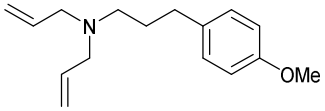
^{1}H NMR (500 MHz, $CDCl_3$).



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

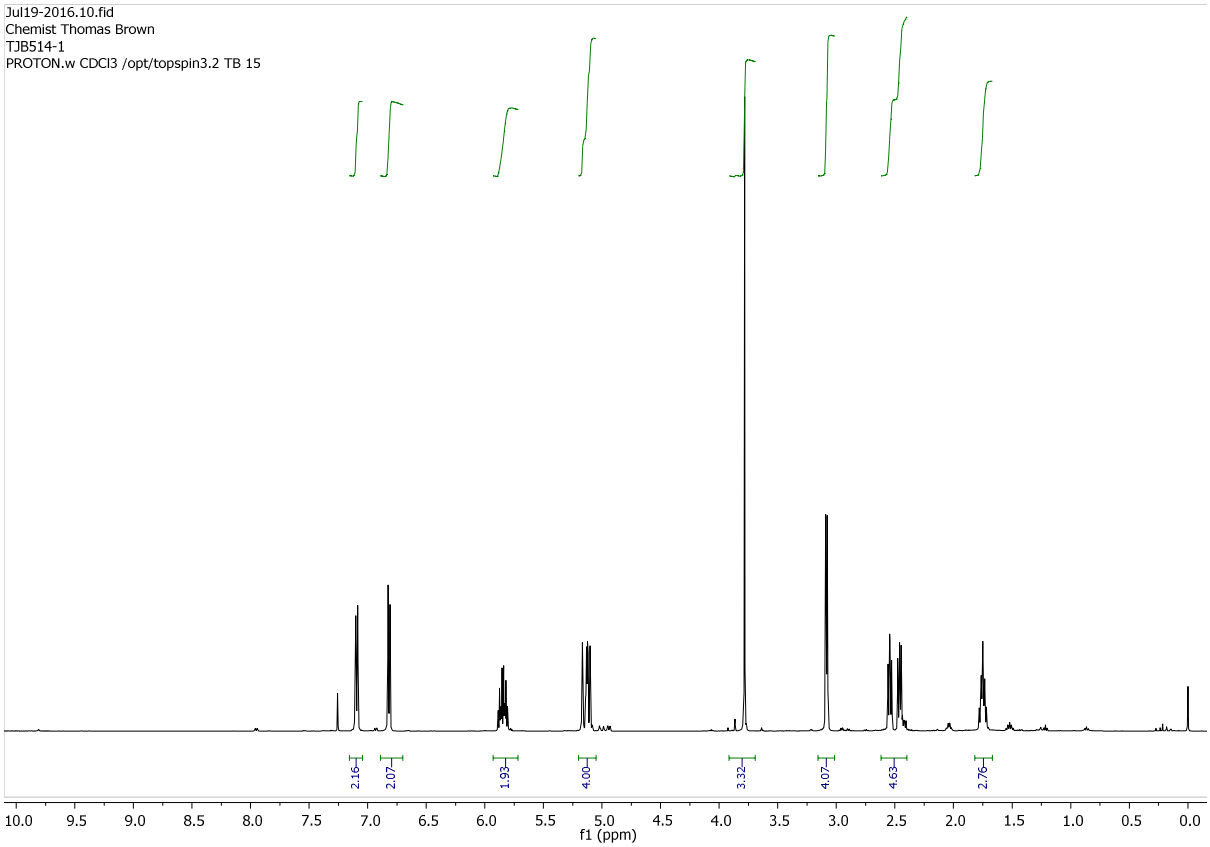


N-Allyl-*N*-(3-(4-Methoxyphenyl)propyl)prop-2-en-1-amine **68**.

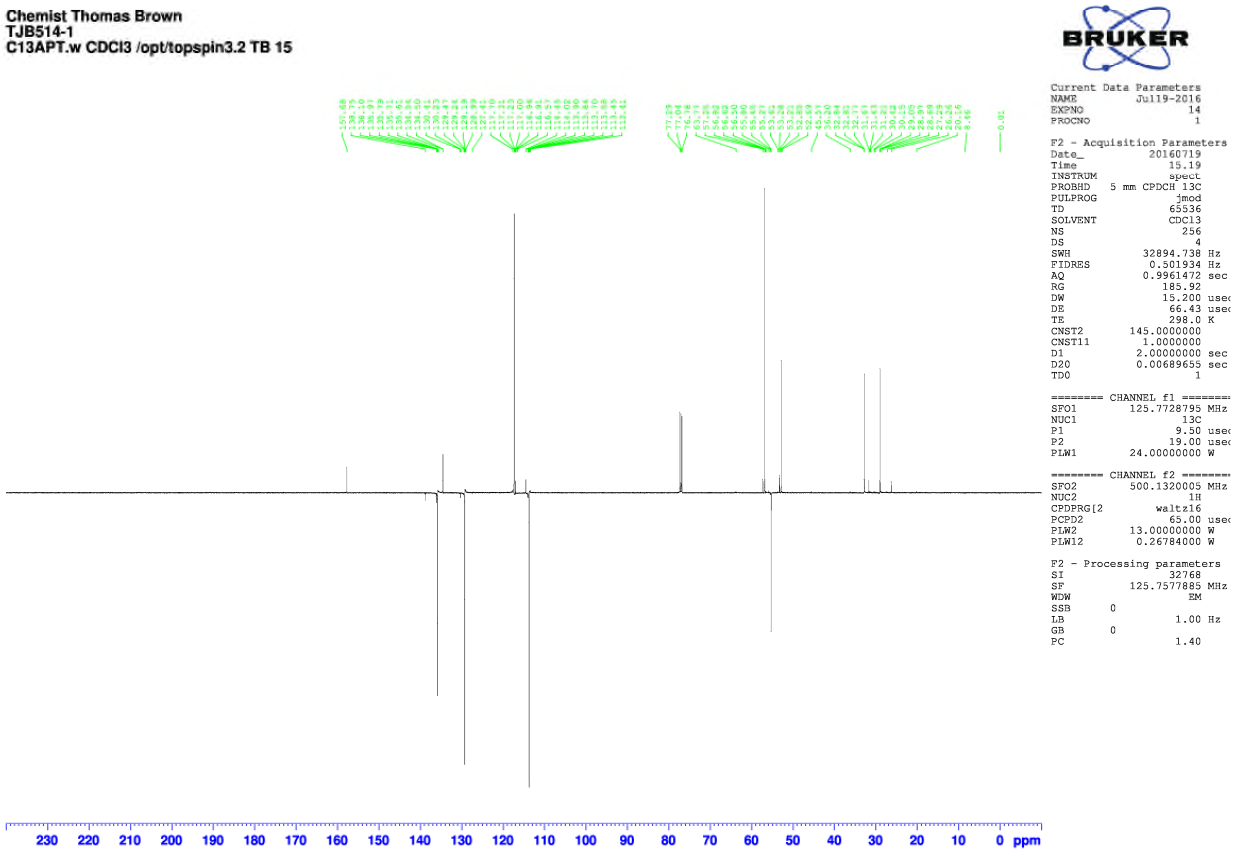


TJB514.

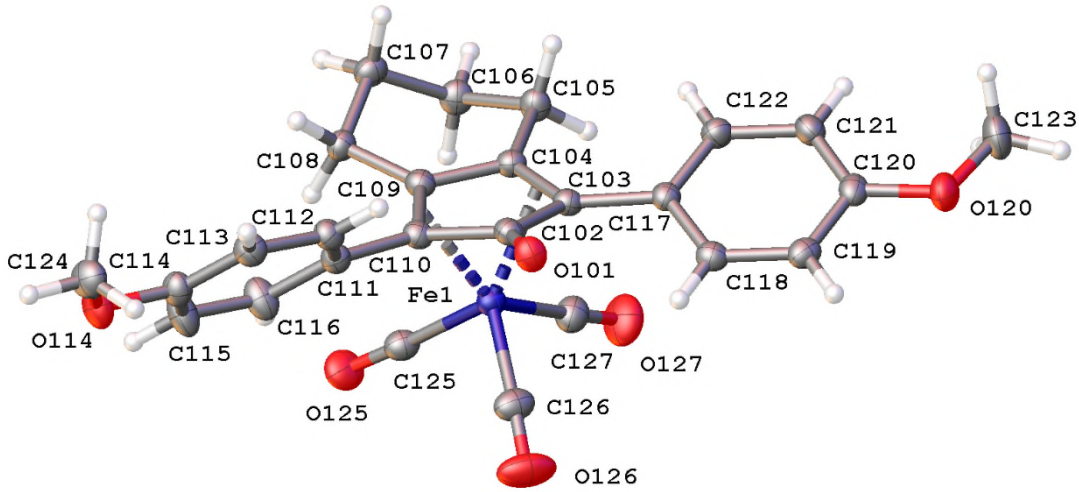
^{1}H NMR (500 MHz, $CDCl_3$).



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

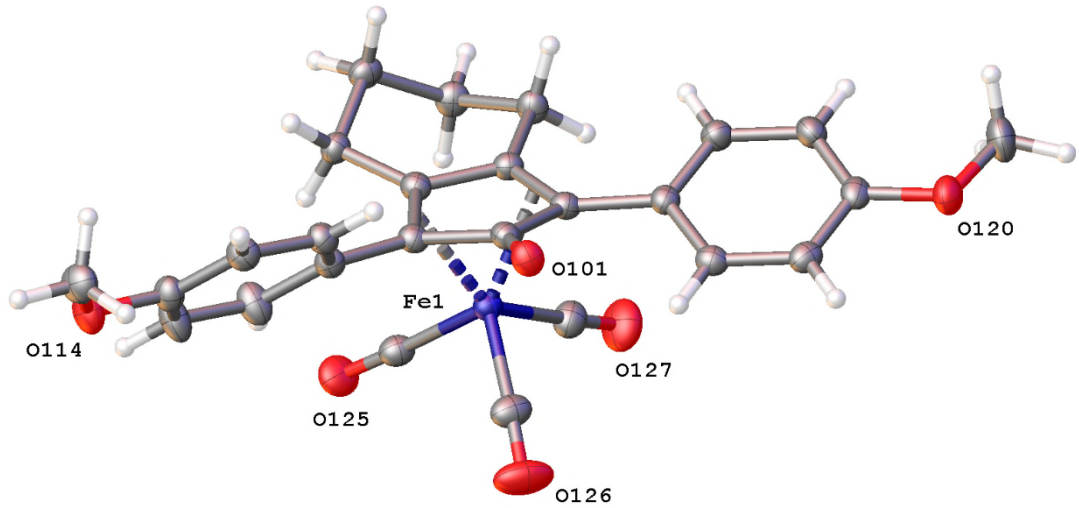


X-ray crystallographic data for tricarbonyl(1,8-bis(4-methoxyphenyl)octa-1,7-diyne)iron **6** (local code MC1), CCDC 1560655:



Solid state structure of one of the crystrallographically independent but chemically identical molecules in the asymmetric unit of mc1 with atom labeling and thermall ellipsoids drawn at 50% probability level.

Below is the same picture but just Fe and oxygen labeled.



Crystal structure determination of 6 (MC1).

The asymmetric unit contains two crystallographically independent but chemically identical Fe complexes. Four molecules in the unit cell. Nothing unusual to report with regards to the refinement or crystal packing.

Experimental

Single crystals of $C_{26}H_{22}FeO_6$ were grown from EtOAc. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program

using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3 Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{26}H_{22}FeO_6$ (M =486.28 g/mol): triclinic, space group P-1 (no. 2), a = 11.3053(2) Å, b = 13.6069(3) Å, c = 16.3832(4) Å, α = 105.526(2)°, β = 92.8266(19)°, γ = 109.973(2)°, V = 2254.47(10) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 5.709 mm^{-1}, *Dcalc* = 1.433 g/cm^3, 23003 reflections measured (7.254° ≤ 2Θ ≤ 156.258°), 9502 unique (R_{int} = 0.0322, R_{sigma} = 0.0383) which were used in all calculations. The final R_1 was 0.0359 (I > 2σ(I)) and wR_2 was 0.0994 (all data).

Table S1 Crystal data and structure refinement for 6 (MC1).

Identification code	MC1
Empirical formula	$C_{26}H_{22}FeO_6$
Formula weight	486.28
Temperature/K	150(2)
Crystal system	Triclinic
Space group	P-1
a/Å	11.3053(2)
b/Å	13.6069(3)
c/Å	16.3832(4)
α/°	105.526(2)
β/°	92.8266(19)
γ/°	109.973(2)
Volume/Å^3	2254.47(10)
Z	4
ρ_{calc}g/cm^3	1.433
μ/mm^{-1}	5.709
F(000)	1008.0
Crystal size/mm^3	0.4 × 0.25 × 0.08 yellow block
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	7.254 to 156.258
Index ranges	$-13 \leq h \leq 14$, $-17 \leq k \leq 16$, $-20 \leq l \leq 20$
Reflections collected	23003
Independent reflections	9502 [R_{int} = 0.0322, R_{sigma} = 0.0383]
Data/restraints/parameters	9502/0/599
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0973
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0994
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.39