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Electronic Supplementary Information

Lewis acidic $FeCl_3$ promoted 2-Aza-Cope Rearrangement to afford α-Substituted homoallylamines in dimethyl carbonate

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1 General information

Nuclear magnetic resonance (NMR) spectra were recorded at 400 (101) MHz on a Bruker Avance III HD spectrometer. Used $CDCl_3$ as solvent and TMS (= 0) as internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*-values) are expressed in hertz (Hz). Multiplicities are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; etc.

For high resolution mass-spectrometric (HRMS) analysis, samples were dissolved in acetonitrile and diluted to a concentration of approximately 10^{-5} M (50/50 CH_3CN/H_2O). 10 µL of each sample was injected using a CapLC system (Waters, Manchester, UK) and electrosprayed using a standard electrospray source. Samples were injected with an interval of 3 minutes. Positive ion mode accurate mass spectra were acquired using a Q-TOFF II instrument (Waters, Manchester, UK). The MS was calibrated prior to use with a 0.1% H_3PO_4 solution. The spectra were lock mass corrected using the known mass of the nearest H_3PO_4 cluster or a known background ion.

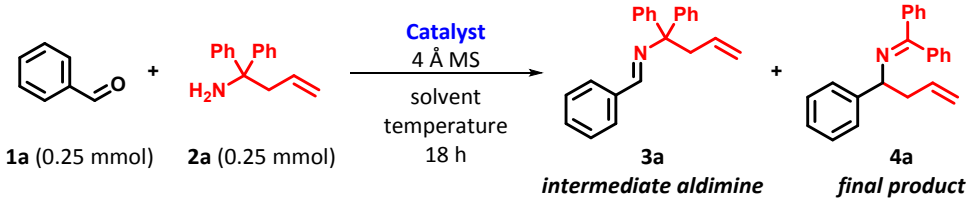
IR spectra of the pure compounds were recorded on a Bruker Alpha spectrometer, equipped with a platinum-ATR crystal. Melting points were determined by a BÜCHI B-545 capillary melting point apparatus and are uncorrected. Flash chromatography was performed on an automated chromatography system (Biotage®) with on-line UV detection using Alumina (Basic) Flash Cartridges (25 g, Interchim) and the indicated solvent system. Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used as received without additional purification. Commercially available molecular sieves (4Å) were dried in vacuum oven at 200 °C for 12 h before use.

2 Reaction optimization studies

2.1 Screening of Lewis acids

General procedure for Lewis acids screening reactions: In an oven-dried 10 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (56 mg, 0.25 mmol, 1.0 equiv), benzaldehyde (**1a**) (27 mg, 0.25 mmol, 1.0 equiv), catalyst (0.025 mmol, 10 mol%), 4Å molecular sieves (100 mg) and solvent (0.5 mL). The vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 50 °C (or at 90 °C) and stirred for 18 hours in the same temperature. Afterwards cooling to room temperature, the reaction mixture was diluted with 10 mL dichloromethane (or 10 mL EtOAc) and filtered through sintered glass funnel (molecular sieves can be separated here). Then, the filtrate was poured in 0.5N NaOH solution (10 mL) and extracted with dichloromethane (or EtOAc) (10, 10, 5 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. 1,3,5-Trimethoxybenzene (14.02 mg, 0.33 equiv.) was added, as internal standard, and everything was dissolved in $CDCl_3$. Subsequently, a ^1H NMR was recorded and signals were integrated versus the internal standard.

Table S-1. Lewis acid catalyst screening



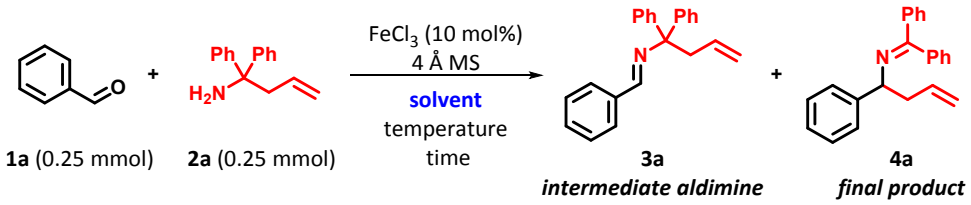
1a (0.25 mmol) **2a** (0.25 mmol) **3a** *intermediate aldimine* **4a** *final product*

Entry	Lewis acid (10 mol%)	Dichloromethane at 50 °C[a] NMR yield[c]		Dimethyl carbonate at 90 °C[b] NMR yield[c]	
		3a (%)	4a (%)	3a (%)	4a (%)
1	$Zn(OTf)_2$	44	51	1	94
2	$ZnCl_2$	15	50	0	85
3	$Cu(OTf)_2$	54	31	11	70
4	$CuCl_2$	79	0	37	15
5	Ag(OTf)	52	0	58	28
6	$AuPPh_3Cl$	8	0	73	9
7	$Ni(OTf)_2$	91	0	70	14
8	$Sc(OTf)_3$	11	83	0	76
9	$Yb(OTf)_3$	16	80	1	90
10	$In(OTf)_3$	11	85	1	84
11	$InCl_3$	3	88	0	94
12	$BiCl_3$	5	81	0	91
13	$Al(OTf)_3$	15	77	1	94
14[d]	$BF_3{\cdot}OEt_2$	2	38	0	81
15	$Fe(OTf)_3$	17	78	0	91
16	$FeCl_3{\cdot}6H_2O$	22	76	5	92
17	$FeCl_2$	38	44	2	81
18	$FeCl_3$	13	85	0	99

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), catalyst (0.025 mmol), 4 Å molecular sieves (100 mg), dichloromethane (0.5 mL), 50 °C, 18 h.
[b] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), catalyst (0.025 mmol), 4 Å molecular sieves (100 mg), dimethyl carbonate (0.5 mL), 90 °C, 18 h.
[c] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.
[d] 100 mol% of $BF_3{\cdot}OEt_2$ was used.

2.2 Screening of solvents

Table S-2. Solvent screening[a]



1a (0.25 mmol) **2a** (0.25 mmol) **3a** *intermediate aldimine* **4a** *final product*

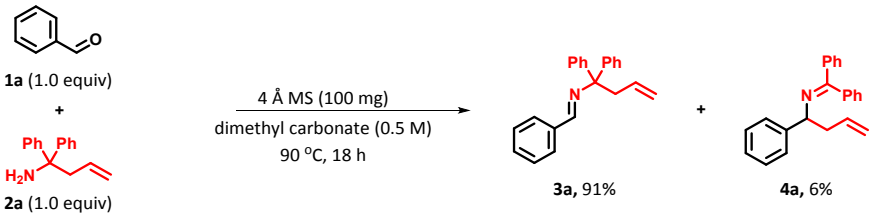
Entry	Solvent	Time [h]	T [°C]	NMR yield[b] 3a	NMR yield[b] 4a	Solvent Guide[1]
1[c]	Water	18	50	65	0	Recommended
2	DMSO	18	50	58	0	Problematic
3	DMF	18	50	47	0	Hazardous
4	Acetonitrile	18	50	83	6	Problematic
		18	82	0	94	
5	Methanol	18	50	47	11	Recommended
		18	65	84	14	
6	1,4-dioxane	18	50	28	5	Hazardous
		18	101	0	94	
7	EtOAc	18	50	45	52	Recommended
		18	80	0	89	
8	2-Me-THF	18	50	4	87	Problematic
		18	80	0	94	
9	n-BuOAc	18	50	10	84	Recommended
		18	126	0	94	
10	Dichloroethane	18	50	4	82	Highly Hazardous
		18	85	0	98	
11	Dichloromethane	18	50	13	85	Highly Hazardous
12	Toluene	18	50	5	58	Problematic
		18	110	0	91	
13[c]	Neat	18	50	48	0	Recommended
14	Dimethyl carbonate	18	25	9	71	Recommended
			50	3	90	
		18	90	0	99	
		6	90	0	99	
		3	90	26	71	

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), $FeCl_3$ (10 mol%), 4 Å molecular sieves (100 mg) and solvent (0.5 mL) at 50 °C (or at reflux) for 18 h.
[b] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.
[c] without molecular sieves.

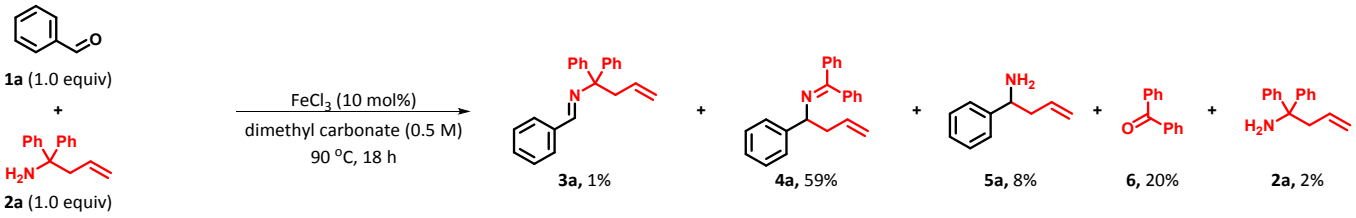
General procedure for solvent screening reactions: In an oven-dried 10 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (56 mg, 0.25 mmol, 1.0 equiv), benzaldehyde (**1a**) (27 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10mol%), 4Å molecular sieves (100 mg) and solvent (0.5 mL). The vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 50 °C (or at solvent boiling point temperature) and stirred for 18 h in the same temperature. Afterwards cooling to room temperature, the reaction mixture was diluted with 10 mL dichloromethane (or 10 mL EtOAc) and filtered through sintered glass funnel (molecular sieves can be separated here). Then, the filtrate was poured in 0.5N NaOH solution (10 mL) and extracted with dichloromethane (or EtOAc) (10, 10, 5 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. 1,3,5-Trimethoxybenzene (14.02 mg, 0.33 equiv.) was added, as internal standard, and everything was dissolved in $CDCl_3$. Subsequently, a ^1H NMR was recorded and signals were integrated versus the internal standard.

3 Control experiments for reaction mechanism [a]

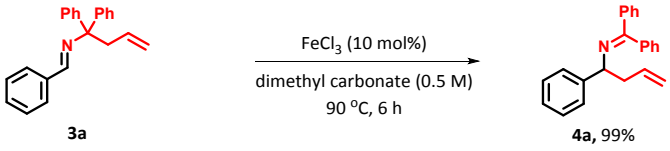
(i) Reaction carried out in the **absence of catalyst**



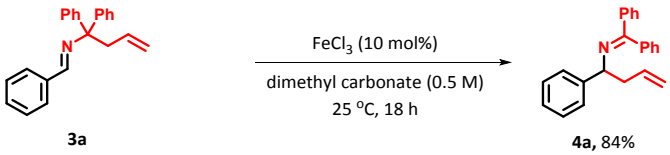
(ii) Reaction carried out in the **absence of molecular sieves**



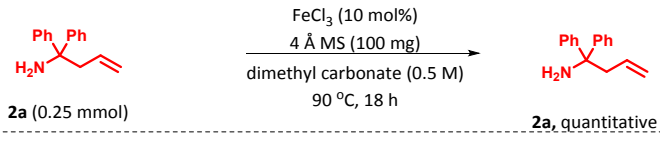
(iii) Reaction carried out **with pre-made aldimine**



(iv) Reaction carried out **with pre-made aldimine at room temperature**

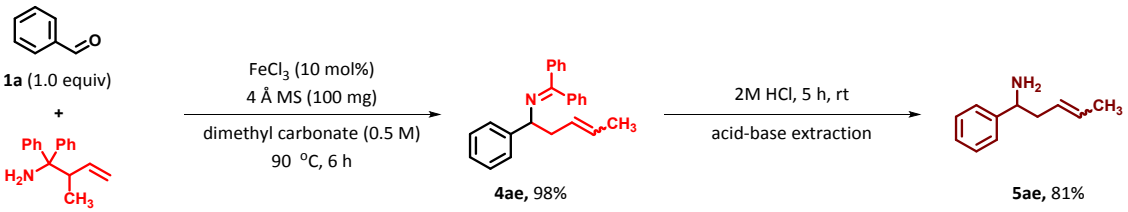


(v) Reaction carried out in the **absence of aldehyde** under the standard reaction condition



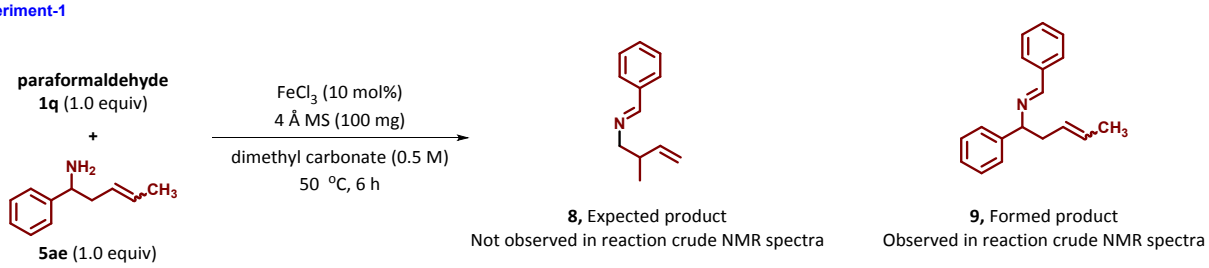
[a] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.

(vi) Synthesis of **δ-substituted homoallylamine** from **β-substituted homoallylamine**



(vii) Synthesis of **β-substituted homoallylamine** from **δ-substituted homoallylamine**

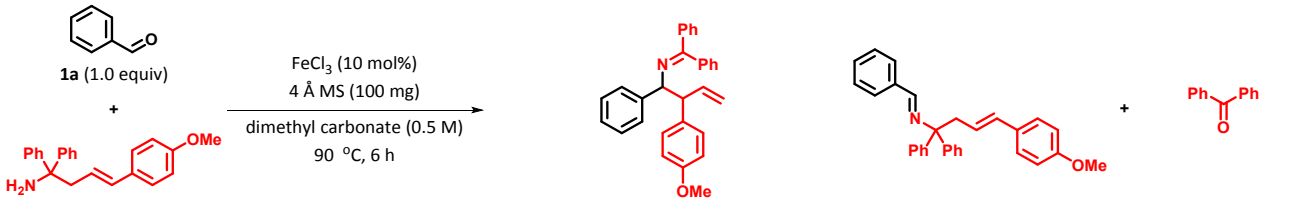
Experiment-1



8, Expected product
Not observed in reaction crude NMR spectra

9, Formed product
Observed in reaction crude NMR spectra

Experiment-2



10, Expected product
Not observed in reaction crude NMR spectra

11, Formed product

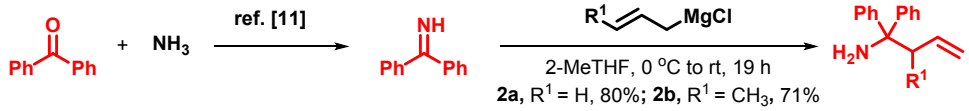
6, Formed product

Observed in reaction crude NMR spectra
NMR ratio of **11** and **6** = 39:61

The developed method was applied for the scope of β- and δ-substituted homoallylamines with aldehydes. In case of β- substituted homoallylamine **2b,** the expected product **4ae** was obtained in 98% yield under the standard optimized condition. On the other hand, the reaction with δ- substituted homoallylamines **5ae** and **2c** was unsuccessful under the standard optimized condition. In literature, 2-aza-Cope rearrangements for the synthesis of β-substituted homoallylamines from δ-substituted homoallylamines are very rarely known. In experiment-1, the expected product **8** was not observed. Instead, the unexpected product **9** was observed. Possibaly, product **9** was formed by the reaction between the starting material **5ae** and an *in situ* formed benzaldehyde (Benzaldehyde, which was formed by the hydrolysis of expected product **8**). In experiment-2, the expected product **10** was not observed. Instead, aldmine intermediate **11** and benzophenone **6** were formed. Possibaly, benzophenone **6** was formed by the hydrolysis of the expected product **10**.

4 Typical experimental procedure

4.1 Preparation of starting materials (1,1-diphenylhomoallylamines 2a and 2b)



1,1-diphenylhomoallylamines are easily prepared from benzophenone imine and allylmagnesium chlorides. Benzophenone imine is commercially available and can be easily synthesized by reaction of benzophenone with ammonia.[11]

General procedure A (Preparation of 1,1-diphenylbut-3-en-1-amine **2a**): Following modified reported procedure,[2-3] benzophenone imine (6 mL, 35.76 mmol, 1.0 equiv) was added to an oven-dried 2-neck roundbottom flask equipped with a pressure equalizing addition funnel and reflux condenser which had been evacuated and refilled with argon 3 times. 40 mL of dry 2-MeTHF was then added and the flask cooled to 0 °C. Allylmagnesium chloride (46 mL at 1.7 M in THF, 79 mmol, 2.2 equiv) was added into the additional funnel and then added dropwise to the stirring benzophenone imine solution over the course of 60 minutes. Subsequently, the reaction mixture was stirred up to room temperature and stirred for 18 hours, then it was cooled to 0 °C and queanched by the dropwise addition of ice cold solution of 1N NaOH, passed through a small plug of celite and concentrated in vacuo to remove solvent. Then, the resulting residue was dissolved in 30% aq. AcOH at room temperature. The mixture was stirred at room temperature for 1 hour, MTBE (15 mL) added, then partitioned in between MTBE and aqueous layer (2 times). The aqueous layer was then neutralized with 2N NaOH and extracted with ethyl acetate. The ethyl acetate fractions were combined, dried using $MgSO_4$ and concentrated under vacuum affording the pure desired 1,1-diphenylbut-3-en-1-amine **2a** (6.4 g, 80%).

General procedure B (Preparation of 2-methyl-1,1-diphenylbut-3-en-1-amine **2b**): Following modified reported procedure,[2-3] benzophenone imine (1.5 mL, 8.94 mmol, 1.0 equiv) was added to an oven-dried 2-neck roundbottom flask equipped with a pressure equalizing addition funnel and reflux condenser which had been evacuated and refilled with argon 3 times. 15 mL of dry 2-MeTHF was then added and the flask cooled to 0 °C. 2-Butenylmagnesium chloride (39.5 mL at 0.5 M in THF, 19.67 mmol, 2.2 equiv) was added into the additional funnel and then added dropwise to the stirring benzophenone imine solution over the course of 60 minutes. Subsequently, the reaction mixture was stirred up to room temperature and stirred for 18 hours, then it was cooled to 0 °C and quenched by the dropwise addition of ice cold solution of 1N NaOH, passed through a small plug of celite and concentrated in vacuo to remove solvent. Then, the resulting residue was dissolved in 30% aq. AcOH at room temperature. The

mixture was stirred at room temperature for 1 hour, MTBE (10 mL) added, then partitioned in between MTBE and aqueous layer (2 times). The aqueous layer was then neutralized with 2N NaOH and extracted with ethyl acetate. The ethyl acetate fractions were combined, dried using $MgSO_4$ and concentrated under vacuum affording the pure desired 2-methyl-1,1-diphenylbut-3-en-1-amine **2b** (1.5 g, 71%).

4.2 Synthesis of α-substituted homoallylamines 4a-4z, 4aa-4ah

General procedure C (4a-4l, 4y-4z and 4aa-4ah): In an oven-dried 10 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (or 2-methyl-1,1-diphenylbut-3-en-1-amine **2b**) (0.25 mmol, 1.0 equiv), aldehyde (0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 10 mol%), 4Å molecular sieves (100 mg) and dimethyl carbonate (0.5 mL). The vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 90 °C and stirred for 6 to 18 h at this temperature. Afterwards the mixture was cooled to room temperature, then diluted with 10 mL ethyl acetate and filtered through sintered glass funnel (to remove molecular sieves). Subsequently, the filtrate was poured in 0.5N NaOH solution (10 mL) and extracted with ethyl acetate (10, 10, 5 mL). The combined organic layer was dried using $MgSO_4$, filtered and concentrated under reduced pressure.

General procedure D (4m-4q): In an oven-dried 10 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (or 2-methyl-1,1-diphenylbut-3-en-1-amine **2b**) (0.25 mmol, 1.0 equiv), aldehyde (0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%), 4Å molecular sieves (100 mg) and dimethyl carbonate (0.5 mL). The vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 90 °C and stirred for 24 h at this temperature. Afterwards the mixture was cooled to room temperature, then diluted with 10 mL ethyl acetate and filtered through sintered glass funnel (to remove molecular sieves). Subsequently, the filtrate was poured in 0.5N NaOH solution (10 mL) and extracted with ethyl acetate (10, 10, 5 mL). The combined organic layer was dried using $MgSO_4$, filtered and concentrated under reduced pressure.

General procedure E (4r-4x): In an oven-dried 10 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (or 2-methyl-1,1-diphenylbut-3-en-1-amine **2b**) (0.25 mmol, 1.0 equiv), aldehyde (0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 10 mol%), 4Å molecular sieves (100 mg) and dimethyl carbonate (0.5 mL). The vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 50 °C and stirred for 2 to 6 h at this temperature. Afterwards the mixture was cooled to room temperature, then diluted with 10 mL ethyl acetate and filtered through sintered glass funnel (to remove molecular sieves). Subsequently, the filtrate was poured in 0.5N NaOH solution (10 mL) and extracted with ethyl acetate (10, 10, 5 mL). The combined organic layer was dried using $MgSO_4$, filtered and concentrated under reduced pressure.

Note-1: The most of the products are not required column chromatography purification. The products **4a**, **4c**, **4d**, **4e**, **4f**, **4g**, **4n**, **4o**, **4p**, **4q**, **4w**, **4aa** and **4ab** were purified by flash chromatography (1-20% EtOAc/Heptane gradient with 1% Et_3N).

Note-2: We can use an alternative method base on fitration over neutral alumina avoiding aqueous work-up: the reaction mixture was filtered through a bed of neutral alumina and the neutral alumina subsequently washed with EtOAc, then filtrate was concentrated in vacuo.

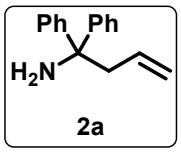
4.3 Gram scale experiment

General procedure F (4a): In an oven-dried 50 mL vial were added 1,1-diphenylbut-3-en-1-amine (**2a**) (1.117 g, 5 mmol, 1.0 equiv), benzaldehyde (0.531 g, 5 mmol, 1.0 equiv), $FeCl_3$ (81 mg, 10mol%), 4Å molecular sieves (2 g) and dimethyl carbonate (20 mL). The reaction mixture vial was sealed under an ambient atmosphere. Then, the reaction mixture was placed in a preheated oil-bath at 90 °C and stirred for 9 h at this temperature. Afterwards, the mixture was cooled to room temperature, then filtered through a bed of neutral alumina and the neutral alumina subsequently washed with dimethyl carbonate (3 x 30 mL). The filtrate was concentrated under reduced pressure to afford the pure 1,1-diphenyl-N-(1-phenylbut-3-en-1-yl)methanimine **2a** (1.464 g, 94%) and recovered dimethyl carbonate.

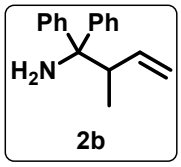
4.4 Hydrolysis of the ketimine and recovery of benzophenone

General procedure G (5a and 6): This general procedure was adapted from a literature procedure.[4] 1,1-diphenyl-N-(1-phenylbut-3-en-1-yl)methanimine (1.464 g, 4.7 mmol) was dissolved in 2-MeTHF (20 mL), followed by the addition of 2N aqueous HCl solution (10.0 mL). The mixture was stirred at room temperature for 5 h and monitored by TLC. Upon completion, 2-MeTHF was removed by rotary evaporation and another 10 mL of H_2O was added. The mixture was washed with EtOAc (4 x 5 mL) and the combined organic phase was extracted with H_2O (5 mL) which was then washed with EtOAc (1.0 mL). The EtOAc fractions were combined, dried using $MgSO_4$ and concentrated under vacuum affording the pure benzophenone **6** (0.782 g, 91 %). The combined aqueous phase was neutralized with 3N NaOH and extracted with ethyl acetate, the organic fractions were combined, dried using $MgSO_4$ and concentrated under vacuum affording the pure 1-phenylbut-3-en-1-amine **5a** (0.626g, 90 %).

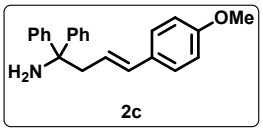
5 Characterization data for starting materials 2a-2c



1,1-diphenylbut-3-en-1-amine (2a):[5] The general procedure-A was applied using benzophenone imine and allylmagnesium chloride solution. After acid-base extraction, 1,1-diphenylbut-3-en-1-amine was obtained in 80% (6.4 g) yield. Pale yellow oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.39-7.37 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.1f9 (t, *J* = 7.3 Hz, 2H), 5.53 (ddt, *J* =17.2, 10.1, 7.1 Hz, 1H), 5.17-5.06 (m, 2H), 3.01 (d, *J* = 7.1 Hz, 2H), 1.81 (br s, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 148.2 (C), 134.2 (CH), 128.1 (CH), 126.6 (CH), 126.4 (CH), 119.1 (CH_2), 60.3 (C), 47.6 (CH_2) ppm. **IR** (ATR) (cm^{-1}): 3058, 3023, 1637, 1597, 1491, 1444, 1240, 1192, 1060, 1031, 999, 915, 858, 752, 720, 695, 610, 571. The spectroscopic data for **2a** is in agreement with literature.[5]

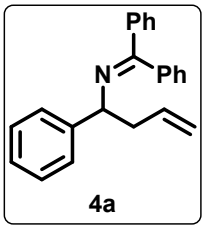


2-methyl-1,1-diphenylbut-3-en-1-amine (2b):[2] The general procedure-B was applied using benzophenone imine and 2-butenylmagnesium chloride solution. After acid-base extraction, 2-methyl-1,1-diphenylbut-3-en-1-amine was obtained in 71% (1.5 g) yield. Pale yellow oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 4H), 7.30-7.24 (m, 4H), 7.18-7.12 (m, 2H), 5.73 (ddd, *J* =17.1, 10.6, 6.2 Hz, 1H), 5.07 (dd, *J* = 6.2, 4.4 Hz, 2H), 3.51 (p, *J* = 6.6 Hz, 1H), 1.68 (br s, 2H), 1.00 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 147.6 (C), 146.9 (C), 139.9 (CH), 128.0 (CH), 127.9 (CH), 126.7 (CH), 126.6 (CH), 126.1 (CH), 126.0 (CH), 116.3 (CH_2), 63.1 (C), 44.4 (CH), 14.2 (CH_3) ppm. **IR** (ATR) (cm^{-1}): 3057, 3020, 1633, 1596, 1491, 1445, 1414, 1372, 1317, 1196, 1076, 1031, 1004, 965, 913, 873, 823, 764, 747, 697, 671, 628, 571, 506. The spectroscopic data for **2b** is in agreement with literature.[2]



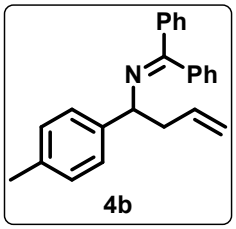
(*E*)-4-(4-methoxyphenyl)-1,1-diphenylbut-3-en-1-amine (2c):[10] The letirature procedure[10] was applied using 1,1-diphenylbut-3-en-1-amine, 1-iodo-4-methoxybenzene and $Pd(OAc)_2$ in DMF. After column chromatography purification, (*E*)-4-(4-methoxyphenyl)-1,1-diphenylbut-3-en-1-amine was obtained in 51% yield (168 mg; 1 mmol scale). Pale yellow oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 4H), 7.30 (t, J = 7.7 Hz, 4H), 7.23-7.19 (m, 2H), 7.16 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 6.44 (d, J = 15.8 Hz, 1H), 5.76 (dt, *J* =15.7, 7.2 Hz, 1H), 3.77j (s, 3H), 3.13 (dd, *J* = 7.3 Hz, 2H), 1.83 (br s, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 159.0 (C), 148.3 (C), 133.6 (CH), 130.2 (C), 128.1 (CH), 127.3 (CH), 126.7 (CH), 126.4 (CH), 123.4 (CH), 113.9 (CH), 60.8 (C), 55.3 (CH_3), 46.9 (CH_2) ppm. **IR** (ATR) (cm^{-1}): 3056, 3027, 2956, 2932, 2835, 1606, 1577, 1509, 1492, 1463, 1444, 1295, 1248, 1174, 1109, 1032, 968, 910, 837, 801, 755, 699, 640, 597, 525. The spectroscopic data for **2c** is in agreement with literature.[10]

6 Characterization data for products 4a-4z,4aa-4ah, 5a and 6



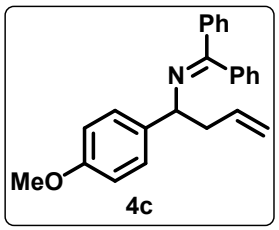
4a

1,1-diphenyl-*N*-(1-phenylbut-3-en-1-yl)methanimine (4a):[6-7] The general procedure-C was applied using benzaldehyde (1a) (27 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up and flash chromatography afforded 1,1-diphenyl-*N*-(1-phenylbut-3-en-1-yl)methanimine in 95% (74 mg) yield. White solid; ***mp***: 86-88 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.68-7.65 (m, 2H), 7.42-7.40 (m, 3H), 7.36-7.19 (m, 8H), 7.07-7.04 (m, 2H), 5.65 (ddt, *J* =17.2, 10.2, 7.1 Hz, 1H), 4.95 (ddd, *J* = 10.1, 9.2, 1.5 Hz, 2H), 4.43 (dd, *J* = 7.9, 5.5 Hz, 1H), 2.68 (dt, *J* = 14.0, 7.6 Hz, 1H, diastereotopic allyl-CH_2), 2.57 (ddd, *J* = 13.7, 6.7, 5.6 Hz, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.7 (C=N), 144.5 (C), 140.1 (C), 137.2 (C), 135.8 (CH), 130.7 (CH), 129.8 (CH), 128.6 (CH), 128.29 (CH), 128.27 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 126.7 (CH), 116.7 (CH_2), 66.5 (CH), 43.9 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3059, 3026, 1623, 1599, 1577, 1491, 1445, 1314, 1281, 1074, 1028, 993, 912, 770, 725, 696, 578; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{22}N$ $[M+H]^+$: 312.1747; found 312.1754. The spectroscopic data for **4a** is in agreement with literature.[6]

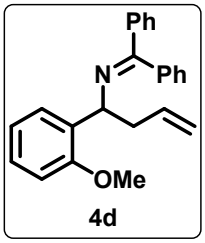


4b

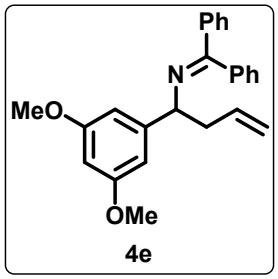
1,1-diphenyl-*N*-(1-(p-tolyl)but-3-en-1-yl)methanimin (4b):[7] The general procedure-C was applied using *p*-tolualdehyde (1b) (30 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 1,1-diphenyl-*N*-(1-(p-tolyl)but-3-en-1-yl)methanimin was obtained in 98% (80 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.34-7.28 (m, 3H), 7.22-7.19 (m, 2H), 7.10-7.04 (m, 4H), 5.64 (ddt, *J* =17.2, 10.1, 7.1 Hz, 1H), 4.99-4.92 (m, 2H), 4.40 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.67 (dt, *J* = 15.1, 7.6 Hz, 1H, diastereotopic allyl-CH_2), 2.59-2.53 (m, 1H, diastereotopic allyl-CH_2), 2.31 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.4 (C=N), 141.5 (C), 140.1(C), 137.2(C), 136.2(C), 135.9 (CH), 130.1 (CH), 129.8 (CH), 129.0 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 116.5 (CH_2), 66.2 (CH), 43.9 (CH_2), 21.1 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2921, 1621, 1597, 1576, 1511, 1489, 1444, 1313, 1278, 1177, 1106, 1073, 1020, 992, 940, 909, 814, 777, 724, 693, 657, 644, 624, 603, 541; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{24}N$ $[M+H]^+$: 326.1903; found 326.1913.



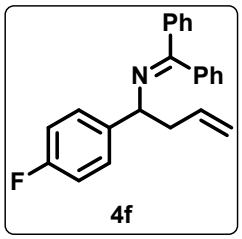
***N*-(1-(4-methoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4c):**[6] The general procedure-C was applied using *p*-anisaldehyde (1c) (34 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 18 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, *N*-(1-(4-methoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 93% (79 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.42-7.21 (m, 8H), 7.07-7.05 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 5.64 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 4.99-4.92 (m, 2H), 4.38 (dd, *J* = 7.7, 5.7 Hz, 1H), 3.78 (s, 3H), 2.65 (dt, *J* = 14.9, 7.5 Hz, 1H, diastereotopic allyl-CH_2), 2.58-2.51 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): 166.3 (C=N), 158.4 (C), 140.1 (C), 137.2 (C), 136.7 (C), 135.9 (CH), 129.8 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.95 (CH), 127.92 (CH), 116.6 (CH_2), 113.7 (CH), 65.9 (CH), 55.2 (CH_3), 43.9 (CH_2); **IR** (ATR) (cm^{-1}): 1610, 1577, 1508, 1489, 1462, 1443, 1313, 1285, 1242, 1172, 1073, 1033, 993, 909, 828, 810, 778, 693, 657, 641, 622, 603, 547; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852; found 342.1850. The spectroscopic data for **4c** is in agreement with literature.[6]



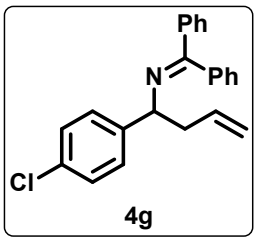
***N*-(1-(2-methoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4d):** The general procedure-C was applied using *o*-anisaldehyde (1d) (34 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 18 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, *N*-(1-(2-methoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 88% (75 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.68-7.66 (m, 3H), 7.37-7.29 (m, 6H), 7.19-7.15 (m, 1H), 7.01-6.99 (m, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.71 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 4.99-4.90 (m, 3H), 3.61 (s, 3H), 2.66-2.54 (m, 2H, overlapping diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.8 (C=N), 155.9 (C), 140.4 (C), 137.4 (C), 136.4 (CH), 133.4 (C), 129.7 (CH), 128.6 (CH), 128.3 (CH), 128.02 (CH), 128.00 (CH), 127.9 (CH), 127.2 (CH), 120.7 (CH), 116.1 (CH_2), 110.4 (CH), 58.9 (CH_3), 55.2 (CH), 42.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3059, 2933, 1621, 1597, 1584, 1488, 1461, 1438, 1351, 1313, 1285, 1238, 1178, 1159, 1098, 1073, 1048, 1028, 992, 908, 844, 779, 752, 724, 693, 639, 622, 589, 566, 511; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852; found 342.1853.



***N*-(1-(3,5-dimethoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4e):**[7] The general procedure-C was applied using 3,5-dimethoxybenzaldehyde (1e) (42 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 12 hours reaction time at 90 °C. After aqueous work-up, *N*-(1-(3,5-dimethoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 98% (91 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.43-7.38 (m, 3H), 7.36-7.29 (m, 3H), 7.08-7.06 (m, 2H), 6.50 (d, *J* = 2.3 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H), 5.65 (ddt, *J* =17.2, 10.1, 7.1 Hz, 1H), 4.96 (ddd, *J* = 11.2, 10.0, 1.5 Hz, 2H), 4.35 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.77 (s, 6H), 2.66 (dt, *J* = 15.1, 7.6 Hz, 1H, diastereotopic allyl-CH_2), 2.56 (ddd, *J* = 13.6, 6.7, 5.6 Hz, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.9 (C=N), 160.7 (C), 147.0 (C), 140.0 (C), 137.1 (C), 135.7 (CH), 129.9 (CH), 128.6 (CH), 128.3 (CH), 127.98 (CH), 127.96 (CH), 116.7 (CH_2), 105.2 (CH), 98.7 (CH), 66.6 (CH), 55.3 (CH_3), 43.9 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2934, 1660, 1593, 1459, 1445, 1427, 1347, 1312, 1286, 1202, 1149, 1059, 1028, 993, 939, 917, 834, 773, 735, 693, 637, 588, 538; **HRMS** (ESI) *m/z* calculated for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958; found 372.1951. The spectroscopic data for **4e** is in agreement with literature.[7]

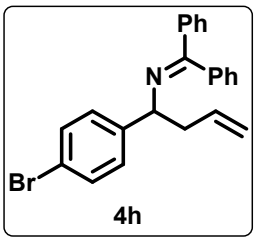


N*-(1-(4-fluorophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4f):**[7] The general procedure-C was applied using 4-fluorobenzaldehyde (1f) (31 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, *N*-(1-(4-fluorophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 94% (77 mg) yield. White solid; ***mp: 54-56 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.42-7.41 (m, 3H), 7.38-7.24 (m, 5H), 7.05-7.03 (m, 2H), 6.9z6 (t, *J* = 7.8 Hz, 1H), 5.62 (ddt, *J* =17.3, 10.2, 7.1 Hz, 1H), 4.98-4.93 (m, 2H), 4.40 (dd, *J* = 7.5, 5.8 Hz, 1H), 2.64 (dt, *J* = 14.8, 7.5 Hz, 1H, diastereotopic allyl-CH_2), 2.57-2.50 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.8 (C=N), 161.7 (d, *J* = 243 Hz, C-F), 140.2 (d, *J* = 3.1 Hz, C), 139.9 (C), 137.0 (C), 135.5 (CH), 130.0 (CH), 128.6 (CH), 158.58 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 116.9 (CH_2), 115.0 (d, *J* = 21 Hz, CH), 65.7 (CH), 44.0 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2958, 2908, 1614, 1602, 1573, 1505, 1442, 1415, 1314, 1287, 1259, 1238, 1216, 1177, 1153, 1092, 1073, 1025, 1014, 999, 958, 917, 849, 834, 794, 782, 769, 726, 695, 681, 659, 639, 623, 604, 546; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{21}NF$ $[M+H]^+$: 330.1653; found 330.1653. The spectroscopic data for **4f** is in agreement with literature.[7]



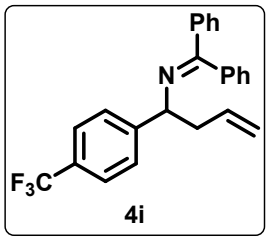
4g

N*-(1-(4-chlorophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4g):** The general procedure-C was applied using 4-chlorobenzaldehyde (1g) (35 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, *N*-(1-(4-chlorophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 90% (78 mg) yield. White solid; ***mp: 59-61 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.42-7.40 (m, 3H), 7.37-7.29 (m, 3H), 7.27-7.22 (m, 4H), 7.04-7.02 (m, 2H), 5.62 (ddt, *J* =17.4, 10.3, 7.1 Hz, 1H), 4.98-4.93 (m, 2H), 4.39 (dd, *J* = 7.6, 5.7 Hz, 1H), 2.63 (dt, *J* = 14.8, 7.5 Hz, 1H, diastereotopic allyl-CH_2), 2.57-2.50 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.1 (C=N), 143.0 (C), 140.0 (C), 137.0 (C), 135.3 (CH), 132.3 (C), 130.0 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.38 (CH), 128.0 (CH), 127.8 (CH), 117.0 (CH_2), 65.8 (CH), 43.9 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1621, 1596, 1575, 1488, 1444, 1407, 1313, 1284, 1088, 1073, 1028, 1013, 992, 911, 825, 778, 770, 730, 692, 654, 636, 618, 591, 538; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{21}NCl$ $[M+H]^+$: 346.1357; found 346.1362.



4h

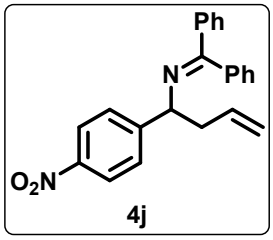
***N*-(1-(4-bromophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4h):** The general procedure-C was applied using 4-bromobenzaldehyde (1g) (46 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, *N*-(1-(4-bromophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 90% (88 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.41-7.30 (m, 8H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 3.0 Hz, 2H), 5.67-5.56 (m, 1H), 4.98-4.93 (m, 2H), 4.39-4.36 (m, 1H), 2.63 (dt, *J* = 14.4, 7.4 Hz, 1H, diastereotopic allyl-CH_2), 2.56-2.49 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.1 (C=N), 143.5 (C), 139.8 (C), 136.9 (C), 135.3 (CH), 131.4 (CH), 130.0 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 120.4 (C), 117.0 (CH_2), 65.9 (CH), 43.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1621, 1597, 1576, 1485, 1444, 1403, 1314, 1277, 1070, 1028, 1009, 940, 913, 820, 779, 769, 728, 692, 652, 636, 616, 587, 537; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{21}NBr$ $[M+H]^+$: 390.0852; found 390.0863.



4i

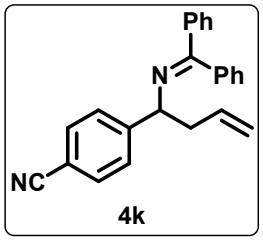
1,1-diphenyl-*N*-(1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)methanimine (4i):[3] The general procedure-C was applied using 4-(trifluoromethyl)benzaldehyde (1i)

(44 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 1,1-diphenyl-*N*-(1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)methanimine was obtained in 93% (88 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.47-7.30 (m, 8H), 7.03 (d, *J* = 3.5 Hz, 2H), 5.68-5.58 (m, 1H), 4.99-4.95 (m, 2H), 4.48 (dd, *J* = 7.5, 5.8 Hz, 1H), 2.67 (dt, *J* = 14.6, 7.4 Hz, 1H, diastereotopic allyl-CH_2), 2.59-2.53 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.5 (C=N), 148.5 (C), 139.8 (C), 136.9 (C), 135.0 (CH), 130.1 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.5 (C), 125.2 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270 Hz, CF_3), 117.2 (CH_2), 66.1 (CH), 43.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1661, 1618, 1598, 1577, 1445, 1417, 1322, 1280, 1162, 1119, 1065, 1017, 993, 941, 910, 838, 779, 733, 693, 667, 652, 638, 604; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{21}NF_3$ $[M+H]^+$: 380.1621; found 380.1632. The spectroscopic data for **4i** is in agreement with literature.[3]



4j

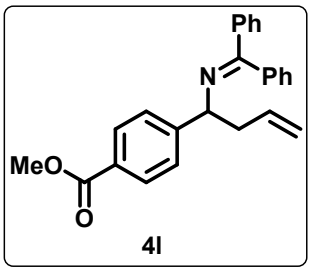
***N*-(1-(4-nitrophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4j):[7]** The general procedure-C was applied using 4-nitrobenzaldehyde (1j) (38 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, *N*-(1-(4-nitrophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 92% (82 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.44-7.32 (m, 6H), 7.02 (d, *J* = 3.4 Hz, 2H), 5.68-5.58 (m, 1H), 4.99-4.94 (m, 2H), 4.55-4.51 (m, 1H), 2.66 (dt, *J* = 14.3, 7.3 Hz, 1H, diastereotopic allyl-CH_2), 2.59-2.53 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.1 (C=N), 152.0 (C), 146.9 (C), 139.5 (C), 136.7 (C), 134.5 (CH), 130.3 (CH), 128.64 (CH), 128.62 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 123.6 (CH), 117.6 (CH_2), 65.9 (CH), 43.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1622, 1596, 1517, 1489, 1444, 1341, 1313, 1279, 1107, 1013, 993, 915, 852, 829, 780, 770, 752, 726, 693, 654, 637, 617, 591, 535; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{21}N_2O_2$ $[M+H]^+$: 357.1598; found 357.1590. The spectroscopic data for **4j** is in agreement with literature.[7]



4k

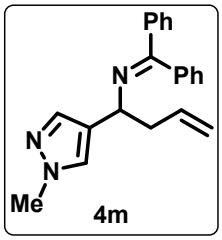
4-(1-((diphenylmethylene)amino)but-3-en-1-yl)benzonitrile (4k):[6] The general procedure-C was applied using 4-cyanobenzaldehyde (1k) (33 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl

carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 4-(1-((diphenylmethylene)amino)but-3-en-1-yl)benzonitrile was obtained in 97% (82 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.43-7.31 (m, 8H), 7.02 (dd, *J* = 6.4, 2.8 Hz, 2H), 5.62 (ddt, *J* =17.8, 9.3, 7.1 Hz, 1H), 4.98-4.94 (m, 2H), 4.47 (dd, *J* = 7.3, 5.9 Hz, 1H), 2.64 (dt, *J* = 14.7, 7.4 Hz, 1H, diastereotopic allyl-CH_2), 2.57-2.50 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.9 (C=N), 149.9 (C), 139.6 (C), 136.7 (C), 134.7 (CH), 132.2 (CH), 130.3 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 119.0 (C), 117.5 (CH_2), 110.6 (C), 66.1 (CH), 43.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3072, 2916, 2853, 2229, 1619, 1606, 1574, 1501, 1488, 1444, 1401, 1339, 1315, 1305, 1290, 1273, 1173, 1075, 1036, 1019, 1001, 988, 951, 855, 829; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{21}N_2$ $[M+H]^+$: 337.1699; found 337.1687. The spectroscopic data for **4k** is in agreement with literature.[6]



4l

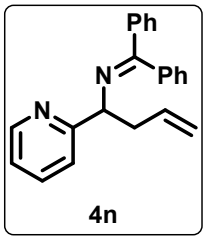
methyl 4-(1-((diphenylmethylene)amino)but-3-en-1-yl)benzoate (4l):[7] The general procedure-C was applied using Methyl 4-formylbenzoate (1l) (41 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, methyl 4-(1-((diphenylmethylene)amino)but-3-en-1-yl)benzoate was obtained in 99% (91 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.67 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.42-7.31 (m, 8H), 7.03 (dd, *J* = 4.3, 0.9 Hz, 2H), 5.69-5.58 (m, 1H), 4.98-4.94 (m, 2H), 4.47 (dd, *J* = 9.2, 3.8 Hz, 1H), 3.89 (s, 3H), 2.71-2.64 (m, 1H, diastereotopic allyl-CH_2), 2.60-2.54 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.5 (C=N), 167.1 (C), 149.8 (C), 139.8 (C), 136.9 (C), 135.2 (CH), 130.1 (CH), 129.7 (CH), 128.6 (CH), 128.43 (CH), 128.40 (CH), 128.0 (CH), 127.8 (CH), 127.2 (CH), 117.1 (CH_2), 66.3 (CH), 52.0 (CH_3), 43.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1719, 1609, 1575, 1489, 1434, 1414, 1312, 1273, 1190, 1175, 1109, 1074, 1018, 994, 967, 910, 855; **HRMS** (ESI) *m/z* calculated for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802; found 370.1799. The spectroscopic data for **4l** is in agreement with literature.[7]



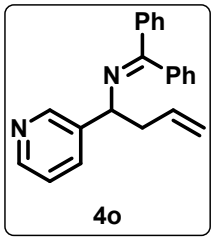
4m

***N*-(1-(1-methyl-1H-pyrazol-4-yl)but-3-en-1-yl)-1,1-diphenylmethanimine (4m):** The general procedure-D was applied using 1-Methyl-1H-pyrazole-4-carboxaldehyde (1m) (28 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%) and 4 Å molecular sieves (100 mg) in

dimethyl carbonate over 24 hours reaction time at 90 °C. After aqueous work-up, *N*-(1-(1-methyl-1H-pyrazol-4-yl)but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 94% (74 mg) yield. White solid; ***mp***: 78-81 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.44-7.41 (m, 3H), 7.39-7.29 (m, 4H), 7.12-7.10 (m, 2H), 5.69 (ddt, *J* =17.3, 10.2, 7.1 Hz, 1H), 5.03-4.97 (m, 2H), 4.45 (dd, *J* = 7.6, 5.5 Hz, 1H), 3.85 (s, 3H), 2.65-2.51 (m, 2H, overlapping diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.9 (C=N), 140.0 (C), 137.4 (CH), 136.9 (C), 135.6 (CH), 130.1 (CH), 129.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.8 (CH), 124.9 (C), 116.9 (CH_2), 58.2 (CH), 43.2 (CH_2), 38.9 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 1657, 1622, 1595, 1574, 1561, 1488, 1446, 1439, 1417, 1392, 1312, 1277, 1178, 1160, 1073, 1047, 1018, 988, 931, 920, 865, 851; **HRMS** (ESI) *m/z* calculated for $C_{21}H_{22}N_3$ $[M+H]^+$: 316.1808; found 316.1802.

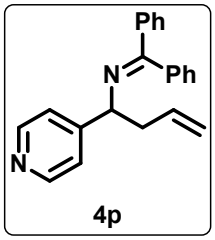


1,1-diphenyl-*N*-(1-(pyridin-2-yl)but-3-en-1-yl)methanimine (4n): The general procedure-D was applied using 2-pyridinecarboxaldehyde (1n) (27 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 24 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, 1,1-diphenyl-*N*-(1-(pyridin-2-yl)but-3-en-1-yl)methanimine was obtained in 81% (63 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.51 (dd, *J* = 4.8, 0.8 Hz, 2H), 7.71-7.69 (m, 2H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.40-7.31 (m, 6H), 7.12 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 7.07 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.69 (ddt, *J* =17.2, 10.1, 7.2 Hz, 1H), 5.00-4.93 (m, 2H), 4.68 (dd, *J* = 7.8, 5.0 Hz, 1H), 2.78-2.65 (m, 2H, overlapping diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.1 (C=N), 163.4 (C), 148.9 (CH), 140.1 (C), 136.8 (C), 136.4 (CH), 135.5 (CH), 130.0 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 121.9 (CH), 121.8 (CH), 116.9 (CH_2), 67.8 (CH), 42.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3058, 2924, 1623, 1588, 1570, 1489, 1470, 1445, 1432, 1314, 1278, 1048, 992, 912, 780; **HRMS** (ESI) *m/z* calculated for $C_{22}H_{21}N_2$ $[M+H]^+$: 313.1699; found 313.1696.

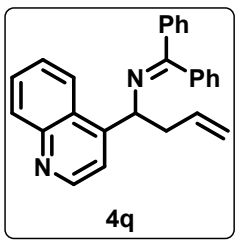


1,1-diphenyl-*N*-(1-(pyridin-3-yl)but-3-en-1-yl)methanimine (4o):[6] The general procedure-D was applied using 3-pyridinecarboxaldehyde (1o) (27 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 24 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, 1,1-diphenyl-*N*-(1-(pyridin-3-yl)but-3-en-1-yl)methanimine was obtained in 84% (66 mg) yield. Pale yellow solid; ***mp***: 80-82 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 3.7 Hz, 1H), 8.43 (s, 1H), 7.74 (dt, *J* = 7.9,

1.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.44-7.42 (m, 3H), 7.40-7.30 (m, 3H), 7.25-7.21 (m, 1H), 7.04 (dd, *J* = 6.4, 2.9 Hz, 2H), 5.64 (ddt, *J* = 20.3, 9.6, 7.1 Hz, 1H), 4.99-4.95 (m, 2H), 4.47 (dd, *J* = 7.5, 5.8 Hz, 1H), 2.68 (dt, *J* = 14.8, 7.4 Hz, 1H, diastereotopic allyl-CH_2), 2.60-2.54 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.7 (C=N), 148.9 (CH), 148.3 (CH), 139.8 (C), 139.7 (C), 136.8 (C), 134.9 (CH), 134.8 (CH), 130.1 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 123.4 (CH), 117.4 (CH_2), 64.1 (CH), 43.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2930, 2895, 1644, 1619, 1593, 1573, 1488, 1473, 1443, 1421, 1313, 1286, 1192, 1177, 1152, 1124, 1104, 1074, 1025, 1000, 931, 912, 870, 836; **HRMS** (ESI) *m/z* calculated for $C_{22}H_{21}N_2$ $[M+H]^+$: 313.1699; found 313.1703. The spectroscopic data for **4o** is in agreement with literature.[6]

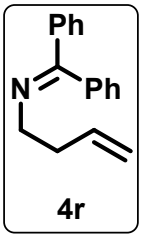


1,1-diphenyl-*N*-(1-(pyridin-4-yl)but-3-en-1-yl)methanimine (4p): The general procedure-D was applied using 4-pyridinecarboxaldehyde (1p) (27 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 24 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, 1,1-diphenyl-*N*-(1-(pyridin-4-yl)but-3-en-1-yl)methanimine was obtained in 83% (65 mg) yield. Brown solid; ***mp***: 93-95 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 5.5 Hz, 2H), 7.68-7.66 (m, 2H), 7.43-7.32 (m, 6H), 7.24 (d, *J* = 5.5 Hz, 2H), 7.03 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.69-5.58 (m, 1H), 4.99-4.95 (m, 2H), 4.41 (dd, *J* = 7.5, 5.6 Hz, 1H), 2.65 (dt, *J* = 14.8, 7.5 Hz, 1H, diastereotopic allyl-CH_2), 2.58-2.52 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.1 (C=N), 153.1 (C), 149.8 (CH), 139.6 (C), 136.7 (C), 134.7 (CH), 130.3 (CH), 128.6 (CH), 128.55 (CH), 128.49 (CH), 128.1 (CH), 127.7 (CH), 122.4 (CH), 117.5 (CH_2), 65.4 (CH), 43.4 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1621, 1593, 1574, 1442, 1407, 1315, 1275, 1258, 1178, 992, 921, 809; **HRMS** (ESI) *m/z* calculated for $C_{22}H_{21}N_2$ $[M+H]^+$: 313.1699; found 313.1697.

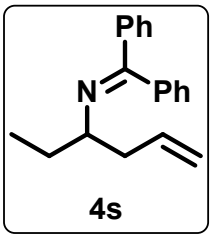


1,1-diphenyl-*N*-(1-(quinolin-4-yl)but-3-en-1-yl)methanimine (4q): The general procedure-D was applied using 4-Quinolinecarboxaldehyde (1q) (39 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (10.14 mg, 25 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 24 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, 1,1-diphenyl-*N*-(1-(quinolin-4-yl)but-3-en-1-yl)methanimine was obtained in 80% (72 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.87 (d, *J* = 4.5 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.74-7.69 (m, 3H), 7.67-7.63 (m, 1H), 7.44-7.31 (m, 7H), 6.95 (d, *J* = 6.9 Hz, 2H), 5.71 (ddt, *J*

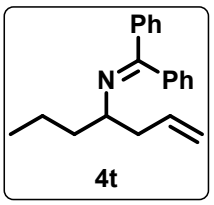
=17.2, 10.2, 7.1 Hz, 1H), 5.21 (dd, *J* = 8.0, 4.7 Hz, 1H), 5.00-4.95 (m, 2H), 2.81 (dt, *J* = 15.1, 7.6 Hz, 1H, diastereotopic allyl-CH_2), 2.73-2.67 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.2 (C=N), 150.4 (CH), 150.3 (C), 148.6 (C), 139.6 (C), 136.6 (C), 135.0 (CH), 130.3 (CH), 130.2 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.7 (CH), 126.1 (CH), 125.8 (C), 123.4 (CH), 119.7 (CH), 117.3 (CH_2), 62.1 (CH), 43.3 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3059, 1621, 1587, 1570, 1507, 1489, 1444, 1314, 1284, 1239, 1180, 1158, 1074, 1048, 1029, 993, 915, 869, 850; **HRMS** (ESI) *m/z* calculated for $C_{26}H_{23}N_2$ $[M+H]^+$: 363.1856; found 363.1849.



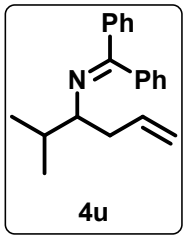
***N*-(but-3-en-1-yl)-1,1-diphenylmethanimine (4r):** The general procedure-E was applied using Paraformaldehyde (1r) (8.3 mg, 0.275 mmol, 1.1 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 2 hours reaction time at 50 °C. After aqueous work-up, *N*-(but-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 89% (52 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.47-7.29 (m, 6H), 7.17-7.15 (m, 2H), 5.82 (ddt, *J* =17.0, 10.2, 6.8 Hz, 1H), 5.06-4.96 (m, 2H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.44 (q, J = 7.0 Hz, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.2 (C=N), 140.0 (C), 137.0 (C), 136.8 (CH), 129.8 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 115.7 (CH_2), 53.4 (CH_2), 35.7 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2916, 1621, 1598, 1576, 1490, 1445, 1314, 1276, 1177, 1153, 1073, 1028, 998, 940, 909, 778; **HRMS** (ESI) *m/z* calculated for $C_{17}H_{18}N$ $[M+H]^+$: 236.1434; found 236.1424.



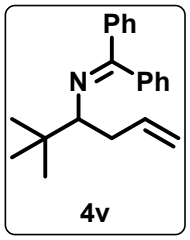
***N*-(hex-5-en-3-yl)-1,1-diphenylmethanimine (4s):** The general procedure-E was applied using Propionaldehyde (1s) (15 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 2 hours reaction time at 50 °C. After aqueous work-up, *N*-(hex-5-en-3-yl)-1,1-diphenylmethanimine was obtained in 92% (61 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 6.8 Hz, 2H), 7.44-7.29 (m, 6H), 7.15-7.13 (m, 2H), 5.75-5.64 (m, 1H), 5.02-4.96 (m, 2H), 3.31-3.24 (m, 1H), 2.31 (t, *J* = 6.7 Hz, 2H), 1.63-1.56 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.7 (C=N), 140.4 (C), 137.7 (C), 136.3 (CH), 130.1 (CH), 129.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 116.3 (CH_2), 63.3 (CH), 41.0 (CH_2), 29.0 (CH_2), 11.0 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2961, 2928, 1621, 1598, 1577, 1445, 1349, 1314, 1276, 1177, 1073, 1028, 981, 941, 910, 777; **HRMS** (ESI) *m/z* calculated for $C_{19}H_{22}N$ $[M+H]^+$: 264.1747; found 264.1745.



***N*-(hept-1-en-4-yl)-1,1-diphenylmethanimine (4t):** The general procedure-E was applied using butyraldehyde (1t) (18 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 2 hours reaction time at 50 °C. After aqueous work-up, *N*-(hept-1-en-4-yl)-1,1-diphenylmethanimine was obtained in 92% (64 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.43-7.28 (m, 6H), 7.15-7.13 (m, 2H), 5.76-5.65 (m, 1H), 5.02-4.96 (m, 2H), 3.39-3.33 (m, 1H), 2.31 (t, *J* = 6.7 Hz, 2H), 1.65-1.47 (m, 2H), 1.34-1.09 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.5 (C=N), 140.4 (C), 137.6 (C), 136.3 (C), 130.1 (CH), 129.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 116.3 (CH_2), 66.7 (CH), 41.4 (CH_2), 38.5 (CH_2), 19.8 (CH_2), 14.2 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2955, 2929, 2870, 1622, 1598, 1576, 1489, 1445, 1314, 1279, 1178, 1073, 1028, 996, 908, 769; **HRMS** (ESI) *m/z* calculated for $C_{20}H_{24}N$ $[M+H]^+$: 278.1903; found 278.1893.

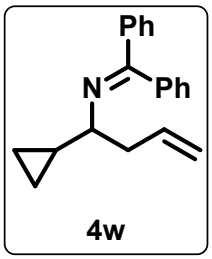


***N*-(2-methylhex-5-en-3-yl)-1,1-diphenylmethanimine (4u):** The general procedure-E was applied using isobutyraldehyde (1u) (18 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 50 °C. After aqueous work-up, *N*-(2-methylhex-5-en-3-yl)-1,1-diphenylmethanimine was obtained in 91% (63 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.43-7.28 (m, 6H), 7.14 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.70 (ddt, *J* =17.3, 10.1, 7.3 Hz, 1H), 5.02-4.95 (m, 2H), 3.17-3.13 (m, 1H), 2.40-2.29 (m, 2H), 1.90-1.78 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.3 (C=N), 140.5 (C), 137.6 (C), 136.7 (CH), 129.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 116.2 (CH_2), 67.0 (CH), 38.5 (CH_2), 32.9 (CH), 19.7 (CH_3), 18.6 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2957, 2869, 1623, 1597, 1577, 1489, 1468, 1444, 1382, 1365, 1314, 1279, 1178, 1073, 1028, 992, 954, 908, 768; **HRMS** (ESI) *m/z* calculated for $C_{20}H_{24}N$ $[M+H]^+$: 278.1903; found 278.1909.

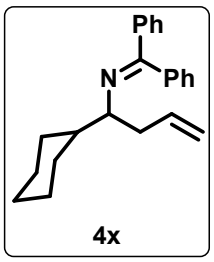


***N*-(2,2-dimethylhex-5-en-3-yl)-1,1-diphenylmethanimine (4v):** The general procedure-E was applied using pivalaldehyde (1v) (22 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%)

and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 50 °C. After aqueous work-up, *N*-(2,2-dimethylhex-5-en-3-yl)-1,1-diphenylmethanimine was obtained in 86% (63 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 6.9 Hz, 2H), 7.39-7.30 (m, 6H), 7.16 (d, *J* = 6.0 Hz, 2H), 5.67-5.57 (m, 1H), 4.99-4.94 (m, 2H), 3.10-3.07 (m, 1H), 2.40-2.37 (m, 2H), 0.91 (s, 9H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 165.6 (C=N), 140.7 (C), 138.1 (CH), 137.4 (C), 129.4 (CH), 128.8 (CH), 128.5 (CH), 127.9 (CH), 127.86 (CH), 127.82 (CH), 116.0 (CH_2), 69.9 (CH), 36.1 (CH_2), 35.5 (C), 27.0 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2952, 2865, 1624, 1597, 1578, 1488, 1477, 1445, 1391, 1361, 1311, 1277, 1178, 1073, 1028, 992, 955, 909, 777; **HRMS** (ESI) *m/z* calculated for $C_{21}H_{26}N$ $[M+H]^+$: 292.2060; found 292.2050.

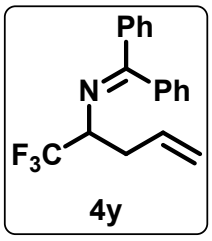


***N*-(1-cyclopropylbut-3-en-1-yl)-1,1-diphenylmethanimine (4w):** The general procedure-E was applied using Cyclopropanecarboxaldehyde (1w) (20 mg, 0.285 mmol, 1.14 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 50 °C. After aqueous work-up and flash chromatography, *N*-(1-cyclopropylbut-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 89% (61 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.42-7.28 (m, 6H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 2H), 5.75 (ddt, *J* =17.3, 10.1, 7.3 Hz, 1H), 5.04-4.95 (m, 2H), 2.78 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.50-2.40 (m, 2H), 1.18-1.09 (m, 1H), 0.46-0.34 (m, 2H), 0.15-0.03 (m, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.2 (C=N), 140.3 (C), 137.4 (C), 136.3 (CH), 129.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 128.01 (CH), 127.99 (CH), 116.2 (CH_2), 65.9 (CH), 41.6 (CH_2), 17.0 (CH), 2.7 (CH_2), 2.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3077, 3002, 1623, 1597, 1577, 1489, 1444, 1313, 1282, 1178, 1073, 1018, 993, 956, 907, 820, 768; **HRMS** (ESI) *m/z* calculated for $C_{20}H_{22}N$ $[M+H]^+$: 276.1747; found 276.1751.



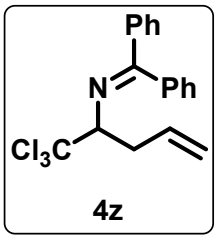
***N*-(1-cyclohexylbut-3-en-1-yl)-1,1-diphenylmethanimine (4x):** The general procedure-E was applied using Cyclohexanecarboxaldehyde (1x) (28 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 50 °C. After aqueous work-up, *N*-(1-cyclohexylbut-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 94% (75 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 6.5 Hz, 2H), 7.43-7.29 (m, 6H), 7.14-7.13 (m, 2H), 5.76-5.65 (m, 1H), 5.01-4.96 (m, 2H), 3.15 (dd, *J* = 12.3, 5.9 Hz, 1H), 2.40-2.28 (m, 2H), 1.79-1.62 (m, 5H), 1.26-1.01 (m, 5H), 0.95-0.86 (m, 1H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.1 (C=N), 140.5 (C), 137.6 (C), 136.7 (CH), 129.5

(CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 116.2 (CH_2), 66.5 (CH), 42.9 (CH), 38.3 (CH_2), 30.2 (CH_2), 29.3 (CH_2), 26.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2922, 2850, 1623, 1445, 1313, 1277, 1073, 1028, 992, 907, 777; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{28}N$ $[M+H]^+$: 318.2216; found 318.2211.



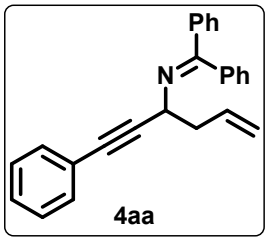
4y

1,1-diphenyl-*N*-(1,1,1-trifluoropent-4-en-2-yl)methanimine (4y): The general procedure-C was applied using trifluoracetaldehyde monohydrate (1y) (29 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 1,1-diphenyl-*N*-(1,1,1-trifluoropent-4-en-2-yl)methanimine was obtained in 98% (74 mg) yield. *(Note: In place of trifluoracetaldehyde monohydrate, Trifluoroacetaldehyde methyl hemiacetal is also tried, delivered simillar result).* White solid, ***mp***: 50-52 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.48-7.31 (m, 6H), 7.16-7.13 (m, 2H), 5.54 (ddt, *J* =17.2, 10.0, 7.3 Hz, 1H), 5.08-5.02 (m, 2H), 3.95-3.87 (m, 1H), 2.64-2.51 (m, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 172.5 (C=N), 139.1 (C), 135.9 (C), 133.2 (CH), 130.7 (CH), 128.9 (d, *J* = 15.8 Hz, CH), 128.6 (CH), 128.1 (d, *J* = 9.3 Hz, CH), 126.95, 122.8 (q, *J* = 278 Hz, CF_3), 118.5 (CH_2), 63.6 (q, *J* = 80.8 Hz, CH), 34.5 (d, *J* = 2.0 Hz, CH_2) ppm; **IR** (ATR) (cm^{-1}): 1624, 1577, 1447, 1434, 1376, 1316, 1263, 1228, 1162, 1142, 1101, 1075, 1059, 1017, 997, 952, 911, 864, 785; **HRMS** (ESI) *m/z* calculated for $C_{18}H_{17}NF_3$ $[M+H]^+$: 304.1308; found 304.1308.



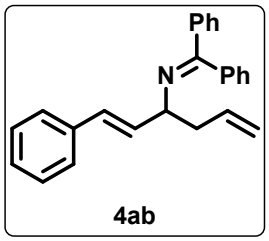
4z

1,1-diphenyl-*N*-(1,1,1-trichloropent-4-en-2-yl)methanimine (4z): The general procedure-C was applied using chloral hydrate (1z) (41 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 1,1-diphenyl-*N*-(1,1,1-trichloropent-4-en-2-yl)methanimine was obtained in 97% (86 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.45-7.32 (m, 6H), 7.26-7.24 (m, 2H), 5.57 (ddt, *J* = 17.1, 9.9, 7.5 Hz, 1H), 5.11-5.04 (m, 2H), 4.13 (dd, *J* = 8.9, 2.9 Hz, 1H), 2.91-2.85 (m, 1H, diastereotopic allyl-CH_2), 2.77-2.69 (m, 1H, diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 171.0 (C=N), 139.6 (C), 136.0 (C), 134.2 (CH), 130.6 (CH), 130.1 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 118.6 (CH_2), 103.2(CCl_2), 75.8 (CH), 37.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1624, 1597, 1576, 1445, 1314, 1278, 993, 918, 810, 776, 763, 720, 692, 665, 652; **HRMS** (ESI) *m/z* calculated for $C_{18}H_{17}NCl_3$ $[M+H]^+$: 352.0421; found 352.0419.



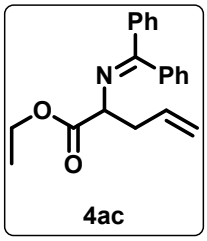
4aa

1,1-diphenyl-*N*-(1-phenylhex-5-en-1-yn-3-yl)methanimine (4aa): The general procedure-C was applied using phenylpropargyl aldehyde (1aa) (33 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, 1,1-diphenyl-*N*-(1-phenylhex-5-en-1-yn-3-yl)methanimine was obtained in 93% (78 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.50-7.37 (m, 6H), 7.34-7.25 (m, 7H), 5.84 (ddt, *J* =17.2, 10.2, 7.1 Hz, 1H), 5.14-5.05 (m, 2H), 4.36-4.33 (m, 1H), 2.72-2.60 (m, 2H, overlapping diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 169.6 (C=N), 139.8 (C), 136.5 (C), 134.7 (CH), 131.8 (CH), 130.3 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 123.5 (C), 117.4 (CH_2), 90.1 (C), 83.6 (C), 54.6 (CH), 41.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1618, 1597, 1577, 1489, 1445, 1316, 1274, 1220, 1195, 1176, 1150, 1105, 1073, 1028, 999, 940, 917; **HRMS** (ESI) *m/z* calculated for $C_{25}H_{22}N$ $[M+H]^+$: 336.1747; found 336.1749.

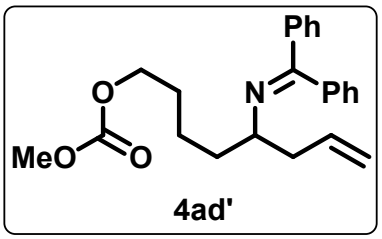


4ab

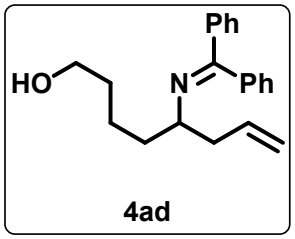
(*E*)-1,1-diphenyl-*N*-(1-phenylhexa-1,5-dien-3-yl)methanimine (4ab):[3] The general procedure-C was applied using *trans*-cinnamaldehyde (1ab) (33 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up and flash chromatography, (*E*)-1,1-diphenyl-*N*-(1-phenylhexa-1,5-dien-3-yl)methanimine was obtained in 91% (77 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.45-7.41 (m, 3H), 7.37-7.26 (m, 7H), 7.21-7.16 (m, 3H), 6.39 (dd, *J* = 16.0, 6.2 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 7.64 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.07-4.98 (m, 2H), 4.08 (dd, *J* = 12.8, 6.3 Hz, 1H), 2.57-2.43 (m, 2H, overlapping diastereotopic allyl-CH_2) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.6 (C=N), 140.1 (C), 137.4 (C), 137.2 (C), 135.5 (CH), 132.1 (CH), 130.0 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.2 (CH), 126.3 (CH), 116.8 (CH_2), 64.7 (CH), 41.8 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 1659, 1619, 1597, 1576, 1491, 1445, 1314, 1276, 1177, 1154, 1072, 1028, 988, 964, 940, 912, 808; **HRMS** (ESI) *m/z* calculated for $C_{25}H_{24}N$ $[M+H]^+$: 338.1903; found 338.1905. The spectroscopic data for **4ab** is in agreement with literature.[3]



ethyl 2-((diphenylmethylene)amino)pent-4-enoate (4ac):[6] The general procedure-C was applied using ethyl glyoxylate, ca 50% solution in toluene (1ac) (51.2 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, ethyl 2-((diphenylmethylene)amino)pent-4-enoate was obtained in 98% (76 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.3 Hz, 2H), 7.46-7.30 (m, 6H), 7.18-7.17 (m, 2H), 5.74-5.64 (m, 1H), 5.09-5.00 (m, 2H), 4.21-4.11 (m, 3H), 2.73-2.59 (m, 2H, overlapping diastereotopic allyl-CH_2), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 171.8 (C), 170.5 (C), 139.7 (C), 136.5 (C), 134.4 (CH), 130.3 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 128.0 (CH), 117.5 (CH_2), 65.4 (CH), 60.9 (CH_2), 38.2 (CH_2), 14.2 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 1735, 1656, 1597, 1577, 1446, 1316, 1274, 1176, 1150, 1074, 1027, 999, 940, 918, 809; **HRMS** (ESI) *m/z* calculated for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1645; found 308.1639. The spectroscopic data for **4ac** is in agreement with literature.[6]

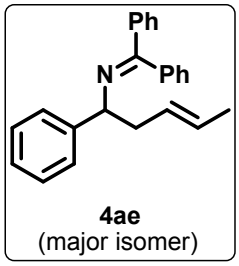


5-((diphenylmethylene)amino)oct-7-en-1-yl methyl carbonate (4ad'): The general procedure-C was applied using 5-hydroxypentanal (1ad) (26 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 5-((diphenylmethylene)amino)oct-7-en-1-yl methyl carbonate was obtained in 96% yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.58-7.12 (m, 10 H), 5.70-5.68 (m, 1H), 5.11-4.98 (m, 2H), 4.14-4.08 (m, 2H), 3.74 (s, 3H), 3.36-3.35 (m, 1H), 2.31-2.30 (m, 2H), 1.57-1.21 (m, 6H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.8 (C=N), 155.9 (C=O), 140.2 (C), 137.5 (C), 130.1 (CH), 129.7 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 116.6 (CH_2), 68.1 (CH_2), 61.6 (CH), 54.6 (CH_3), 41.2 (CH_2), 35.6 (CH_2), 28.8 (CH_2), 22.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 2937, 1745, 1660, 1622, 1598, 1577, 1442, 1387, 1315, 1260, 1177, 1153, 1073, 1028, 998, 941, 916, 791; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{28}NO_3$ $[M+H]^+$: 366.2064; found 366.2048.



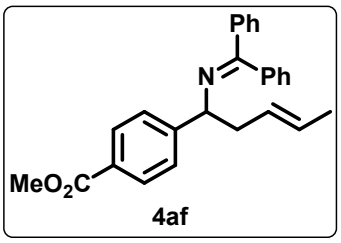
5-((diphenylmethylene)amino)oct-7-en-1-ol (4ad): The general procedure-C was applied using 5-hydroxypentanal (1ad) (26 mg, 0.25 mmol, 1.0 equiv), 1,1-diphenylbut-3-en-1-amine (2a) (56 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in **propylene**

carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, 5-((diphenylmethylene)amino)oct-7-en-1-ol was obtained in 94% (72 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.45-7.28 (m, 6H), 7.14-7.12 (m, 2H), 5.69 (ddt, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.02-4.96 (m, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 3.40-3.33 (m, 1H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.69-1.52 (m, 3H), 1.51-1.39 (m, 2H), 1.38-1.16 (m, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.9 (C=N), 140.2 (C), 137.5 (C), 136.1 (CH), 129.7 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 128.0 (CH), 116.5 (CH_2), 62.7 (CH_2), 61.7 (CH), 41.3 (CH_2), 35.7 (CH_2), 32.8 (CH_2), 22.6 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3340,,3059, 2932, 2860, 1620, 1598, 1576, 1489, 1444, 1353, 1314, 1282, 1178, 1073, 1054, 1028, 994, 908, 768; **HRMS** (ESI) *m/z* calculated for $C_{21}H_{26}NO$ $[M+H]^+$: 308.2009; found 308.1998.



4ae
(major isomer)

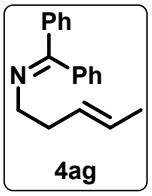
(*E*)-1,1-diphenyl-*N*-(1-phenylpent-3-en-1-yl)methanimine (4ae): The general procedure-C was applied using benzaldehyde (1a) (27 mg, 0.25 mmol, 1.0 equiv), 2-methyl-1,1-diphenylbut-3-en-1-amine (2b) (59 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, (*E*)-1,1-diphenyl-*N*-(1-phenylpent-3-en-1-yl)methanimine was obtained in 98% (80 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.41-7.40 (m, 3H), 7.35-7.18 (m, 8H), 7.07 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.47-5.33 (m, 1H), 5.27-5.21 (m, 1H), 4.40 (dd, *J* = 7.6, 5.9 Hz, 1H), 2.71-2.47 (m, 2H, overlapping diastereotopic allyl-CH_2) 1.49 (d, *J* = 11.9 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.4 (C=N), 144.7 (C), 140.1 (C), 137.2 (C), 129.8 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 125.7 (CH), 66.6 (CH), 36.9 (CH_2), 12.9 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 3022, 1622, 1598, 1576, 1490, 1445, 1313, 1278, 1177, 1073, 1027, 1000, 967, 942, 910, 770; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{24}N$ $[M+H]^+$: 326.1903; found 326.1891.



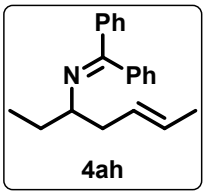
4af

methyl (*E*)-4-(1-((diphenylmethylene)amino)pent-3-en-1-yl)benzoate (4af): The general procedure-C was applied using methyl 4-formylbenzoate (1l) (41 mg, 0.25 mmol, 1.0 equiv), 2-methyl-1,1-diphenylbut-3-en-1-amine (2b) (59 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, methyl (*E*)-4-(1-((diphenylmethylene)amino)pent-3-en-1-yl)benzoate was obtained in 93% (89 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.68-7.65 (m, 2H), 7.42-7.30 (m, 8H), 7.05-7.03 (m, 2H), 5.51-5.37 (m, 1H), 5.26-5.19 (m, 1H),

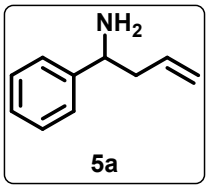
4.43 (dd, *J* = 11.1, 6.4 Hz, 1H), 3.89 (s, 3H), 2.70-2.45 (m, 2H, overlapping diastereotopic allyl-CH_2), 1.46 (dd, *J* =3.7, 3.1 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 167.2 (C=N), 150.0 (C), 139.8 (C), 136.9 (C), 130.0 (CH), 129.6 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH),127.7 (CH), 127.6 (CH), 127.2 (CH), 126.5 (CH), 126.2 (CH), 66.4 (CH), 52.0 (CH_3), 36.8 (CH_2), 12.9(CH_3) ppm; **IR** (ATR) (cm^{-1}): 1719, 1609, 1575, 1434, 1415, 1312, 1273, 1190, 1174, 1109, 1074, 1018, 1000, 965, 909, 856; **HRMS** (ESI) *m/z* calculated for $C_{26}H_{26}NO_2$ $[M+H]^+$: 384.1958; found 384.1959.



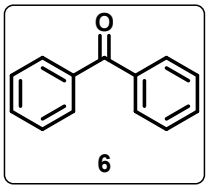
(*E*)-*N*-(pent-3-en-1-yl)-1,1-diphenylmethanimine (4ag): The general procedure-C was applied using paraformaldehyde (1r) (9 mg, 0.30 mmol, 1.2 equiv), 2-methyl-1,1-diphenylbut-3-en-1-amine (2b) (59 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, (*E*)-*N*-(pent-3-en-1-yl)-1,1-diphenylmethanimine was obtained in 96% (60 mg) yield. Brown oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2H), 7.47-7.29 (m, 6H), 7.17-7.15 (m, 2H), 5.52-5.43 (m, 1H), 5.42-5.35 (m, 1H), 3.41 (t, *J* = 7.3 Hz, 1H), 2.43 (q, *J* = 7.2 Hz, 2H), 1.59 (dd, *J* = 6.3, 1.0 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 168.2 (C=N), 140.0 (C), 137.0 (C), 129.8 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 125.2 (CH), 53.7 (CH_2), 28.9 (CH_2), 12.87 (CH_3) ppm; **IR** (ATR) (cm^{-1}): 2915, 1621, 1598, 1577, 1489, 1444, 1314, 1276, 1177, 1073, 1028, 940, 910, 778; **HRMS** (ESI) *m/z* calculated for $C_{18}H_{20}N$ $[M+H]^+$: 250.1590; found 250.1582.



(*E*)-*N*-(hept-5-en-3-yl)-1,1-diphenylmethanimine (4ah): The general procedure-C was applied using propionaldehyde (1s) (15 mg, 0.25 mmol, 1.0 equiv), 2-methyl-1,1-diphenylbut-3-en-1-amine (2b) (59 mg, 0.25 mmol, 1.0 equiv), $FeCl_3$ (4.05 mg, 0.025 mmol, 10 mol%) and 4 Å molecular sieves (100 mg) in dimethyl carbonate over 6 hours reaction time at 90 °C. After aqueous work-up, (*E*)-*N*-(hept-5-en-3-yl)-1,1-diphenylmethanimine was obtained in 95% (66 mg) yield. Brownoil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2H), 7.43-7.28 (m, 6H), 7.15-7.13 (m, 2H), 5.51-5.41 (m, 1H), 5.38-5.27 (m, 1H), 3.29-3.18 (m, 1H), 2.30 (t, *J* = 6.5 Hz, 2H), 1.63-1.54 (m, 4H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 166.5 (C=N), 140.4 (C), 137.7 (C), 129.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 126.6 (CH), 125.3 (CH), 63.5 (CH), 33.9 (CH_2), 29.0 (CH_2), 13.0 (CH_3), 11.1 (CH_3), ppm; **IR** (ATR) (cm^{-1}): 2960, 2917, 2872, 1622, 1598, 1577, 1445, 1314, 1284, 1073, 1028, 987, 947, 910, 777; **HRMS** (ESI) *m/z* calculated for $C_{20}H_{24}N$ $[M+H]^+$: 278.1903; found 278.1895.



1-phenylbut-3-en-1-amine (5a):[8] The general procedure-G was applied using 1,1-diphenyl-*N*-(1-phenylbut-3-en-1-yl)methanimine (4a) (1.464 g, 4.7 mmol, 1.0 equiv), after aqueous work-up, 1-phenylbut-3-en-1-amine was obtained in 90% (0.626 g) yield. Pale yellow oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 4H), 7.27-7.22 (m, 1H), 5.75 (dddd, *J* =16.7, 10.2, 7.9, 6.3 Hz, 1H), 5.14-5.05 (m, 2H), 3.99 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.51-2.40 (m, 1H, diastereotopic allyl-CH_2), 2.41-2.32 (m, 1H, diastereotopic allyl-CH_2), 1.69 (bs, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 145.9 (C), 135.5 (CH), 128.4 (CH), 127.0 (CH), 126.3 (CH), 117.6 (CH_2), 55.4 (CH), 44.2 (CH_2) ppm; **IR** (ATR) (cm^{-1}): 3269, 3063, 3029, 2977, 2929, 1640, 1542, 1493, 1452, 1435, 1372, 1296, 1072, 1027, 993, 914, 840, 757. The spectroscopic data for **5a** is in agreement with literature.[8]



benzophenone (6):[9] The general procedure-G was applied using 1,1-diphenyl-*N*-(1-phenylbut-3-en-1-yl)methanimine (4a) (1.464 g, 4.7 mmol, 1.0 equiv), after aqueous work-up, benzophenone was obtained in 91% (0.782 mg) yield. Colourless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.61-7.56 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 196.7 (C=O), 137.7 (C), 132.4 (CH), 130.1 (CH), 128.3 (CH) ppm; **IR** (ATR) (cm^{-1}): 1655, 1597, 1446, 1316, 1274, 940, 918, 763, 695. The spectroscopic data for **6** is in agreement with literature.[9]

7 References

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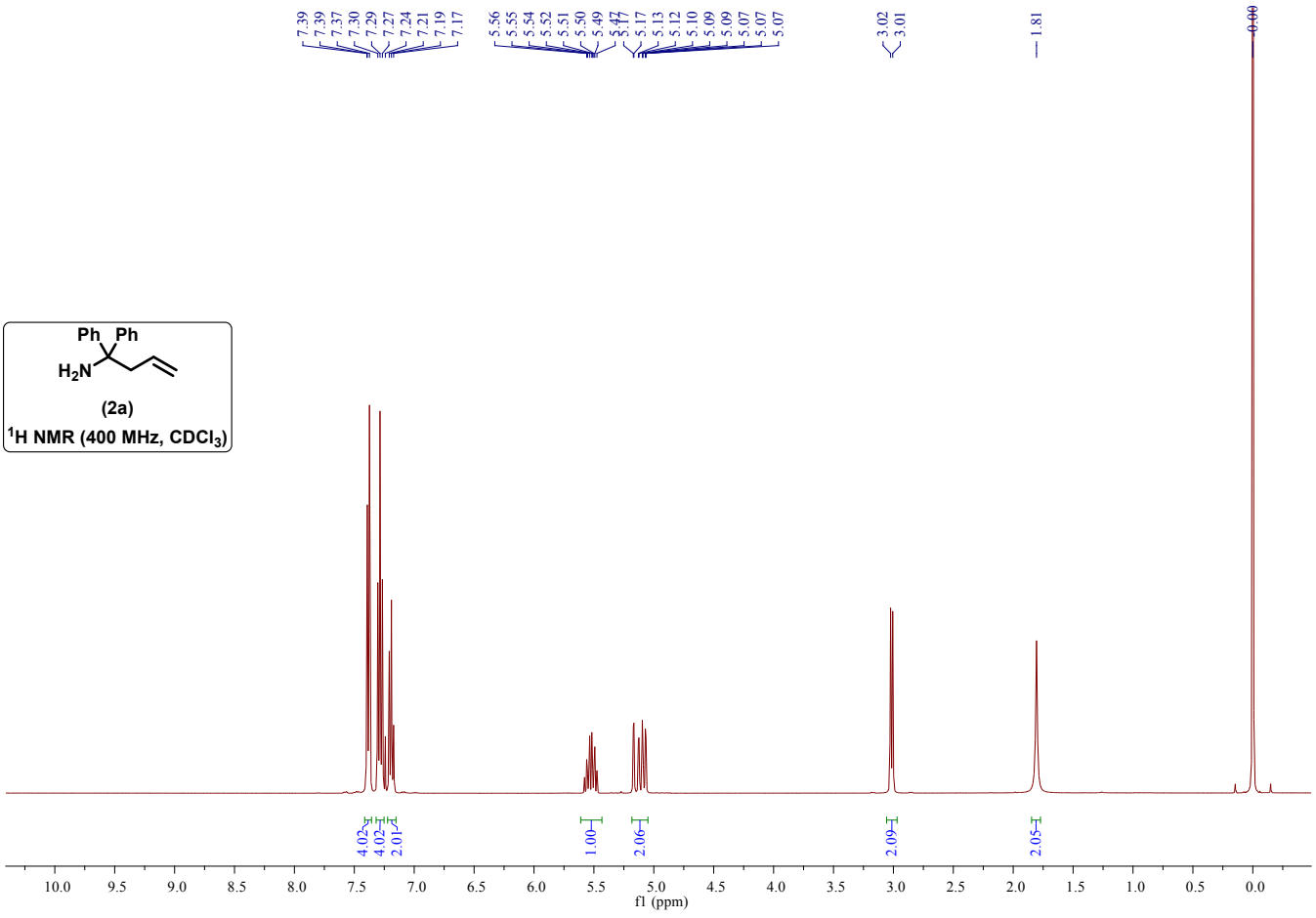
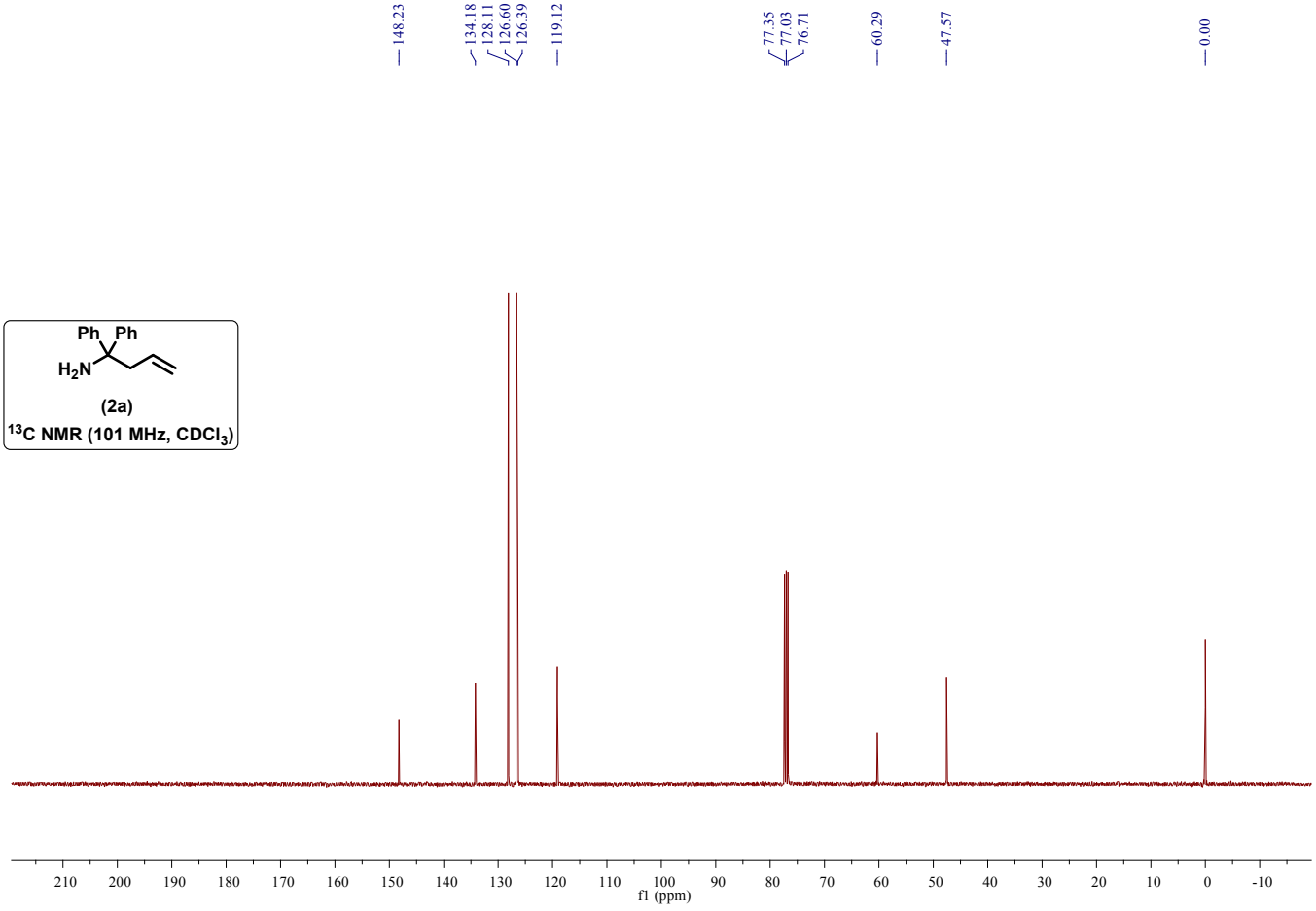
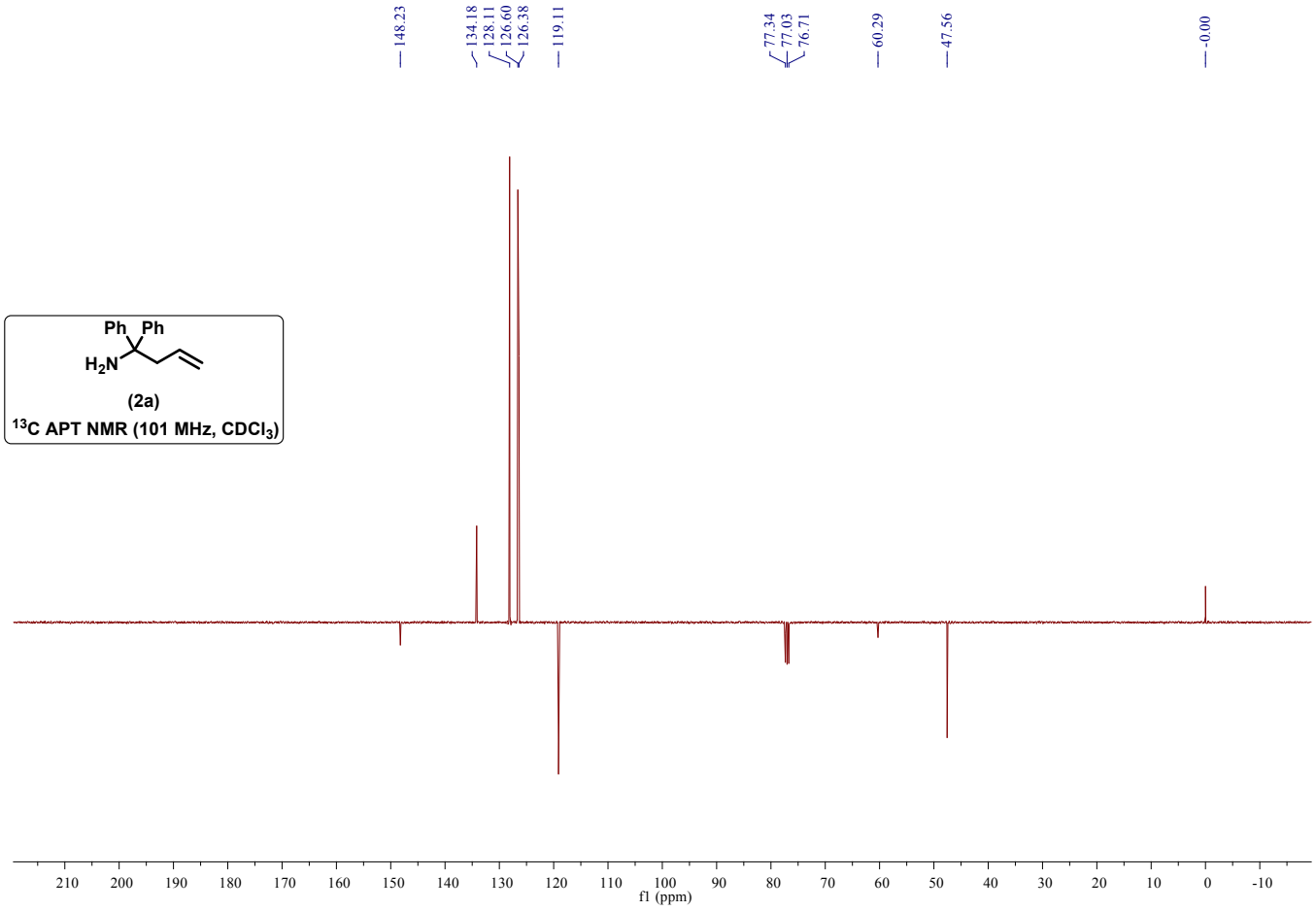
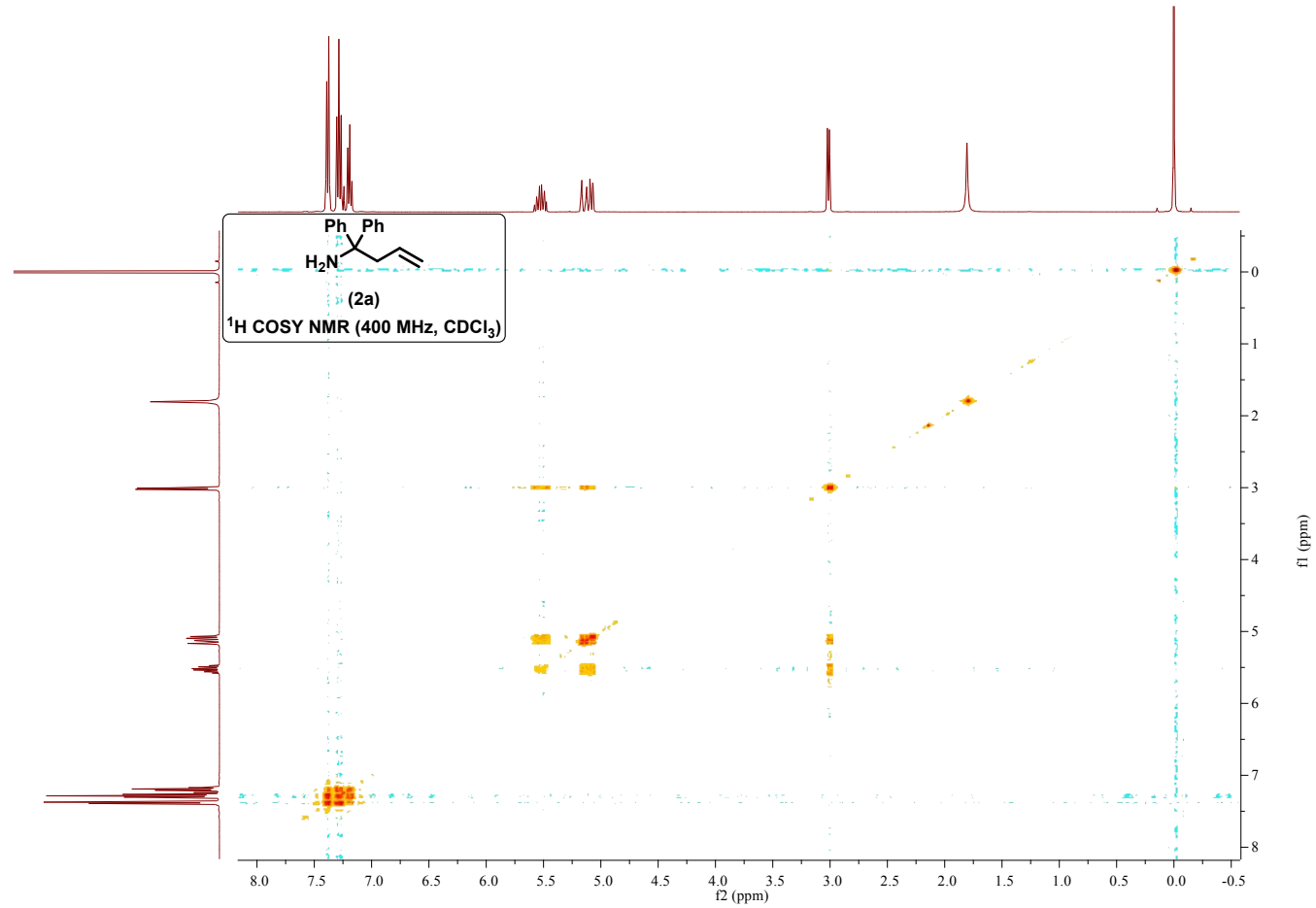
Copies of NMR spectra



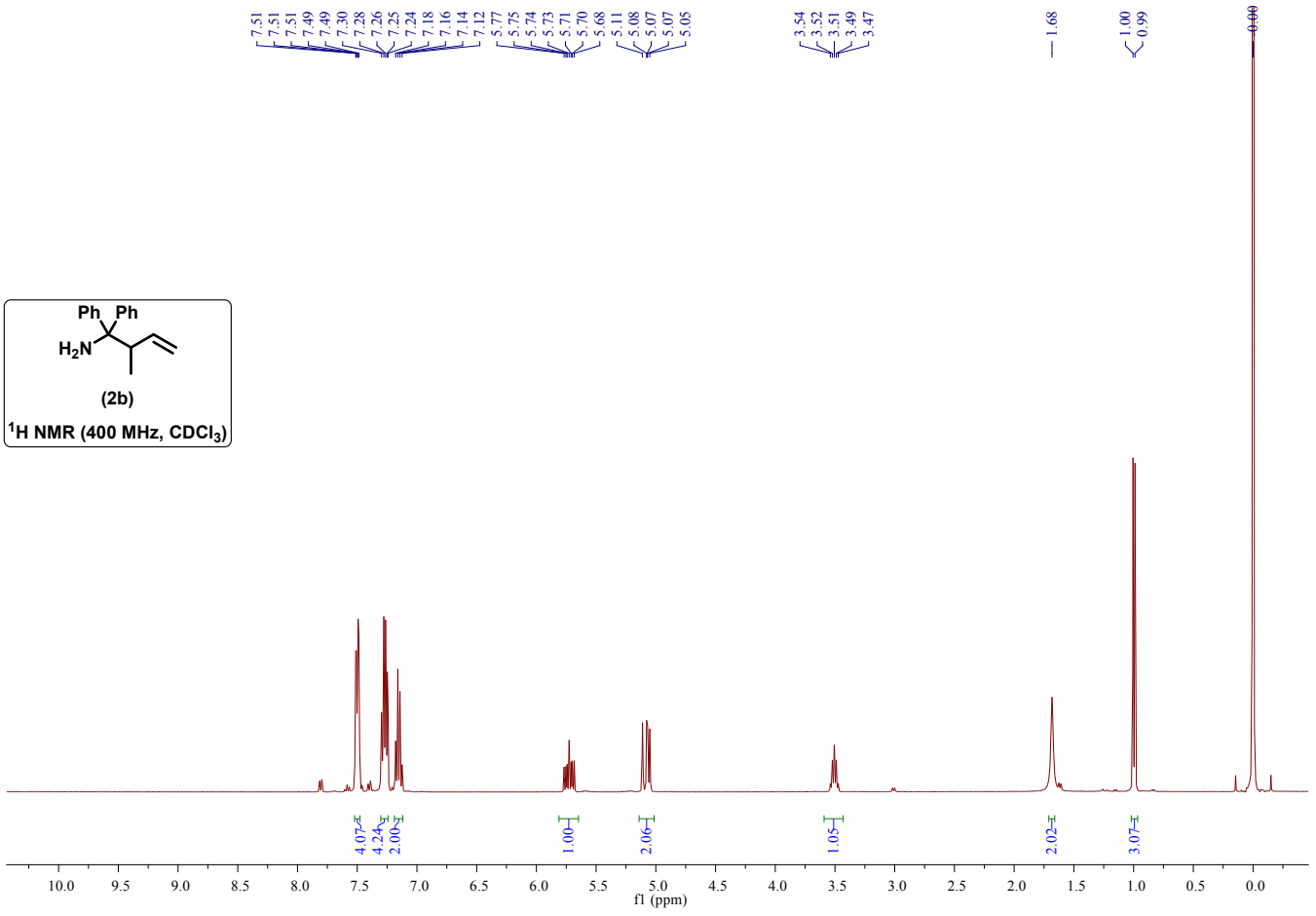


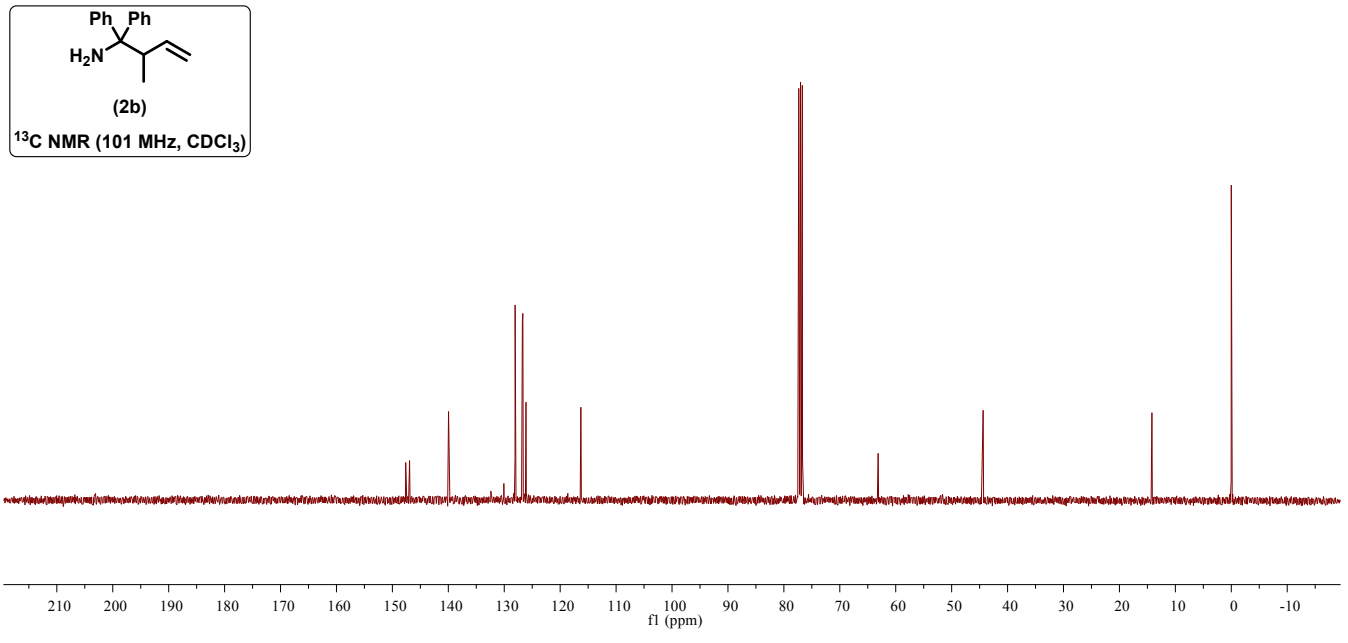
Copies of NMR spectra



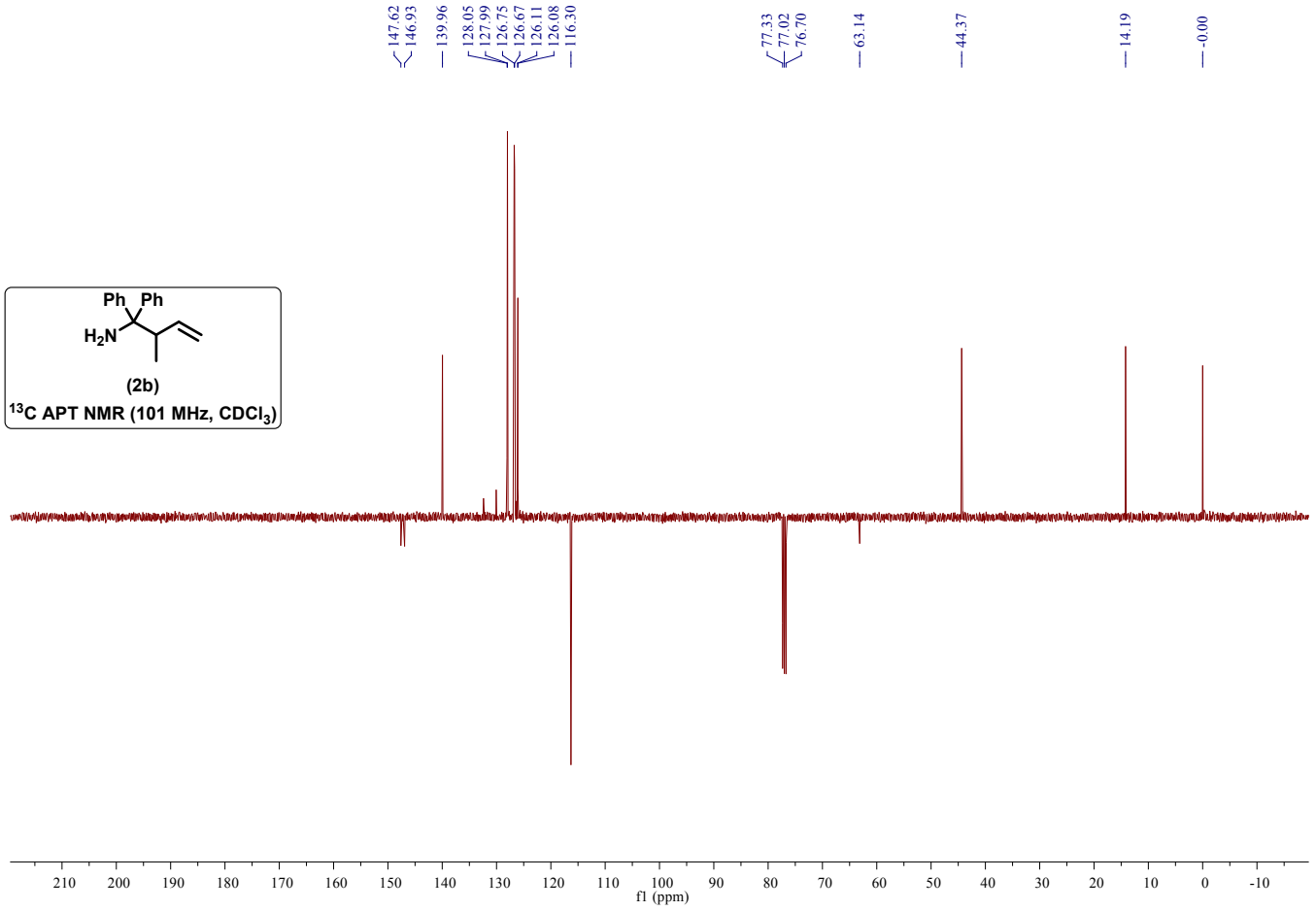


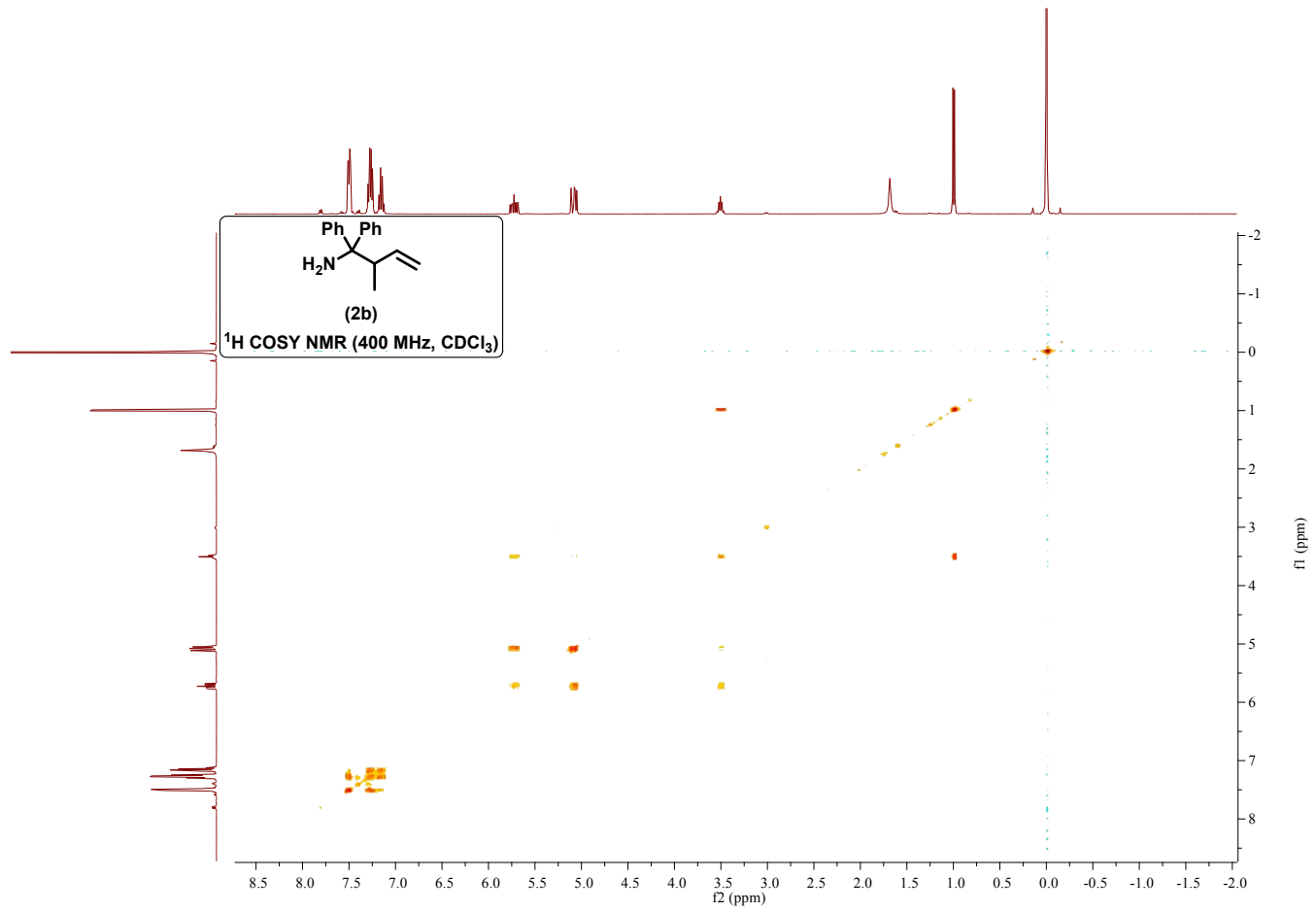
Copies of NMR spectra



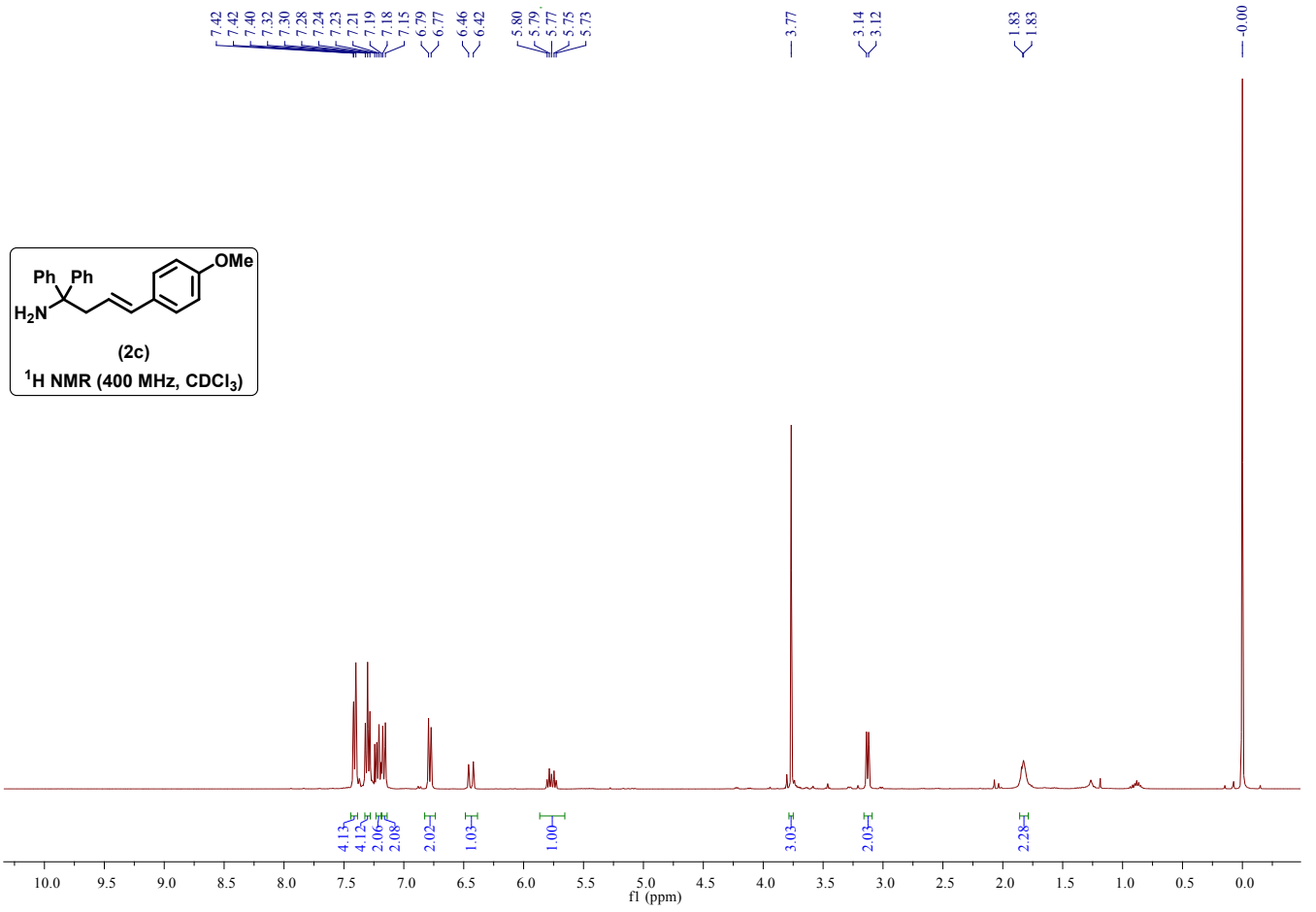


Copies of NMR spectra



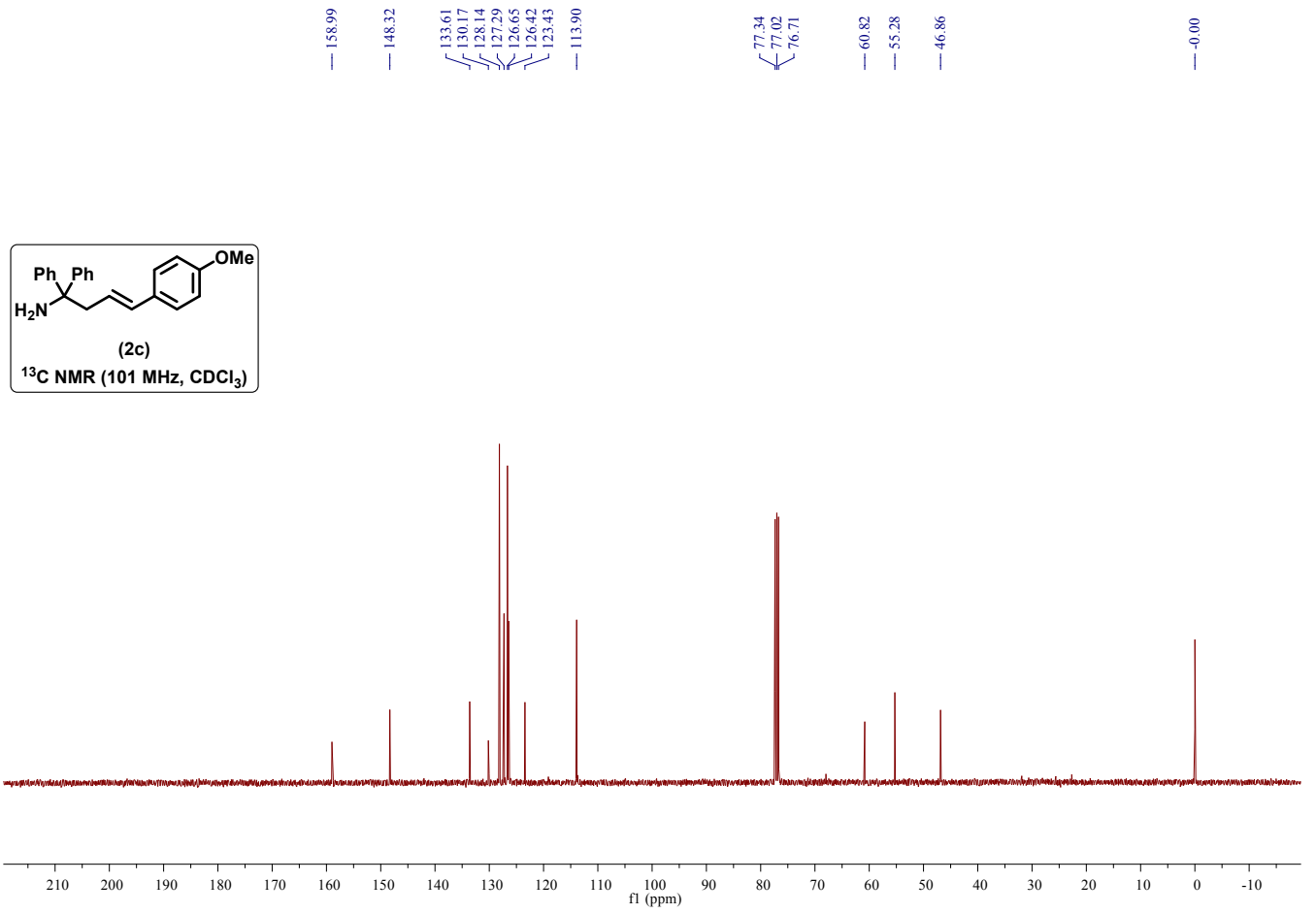


Copies of NMR spectra



(2c)

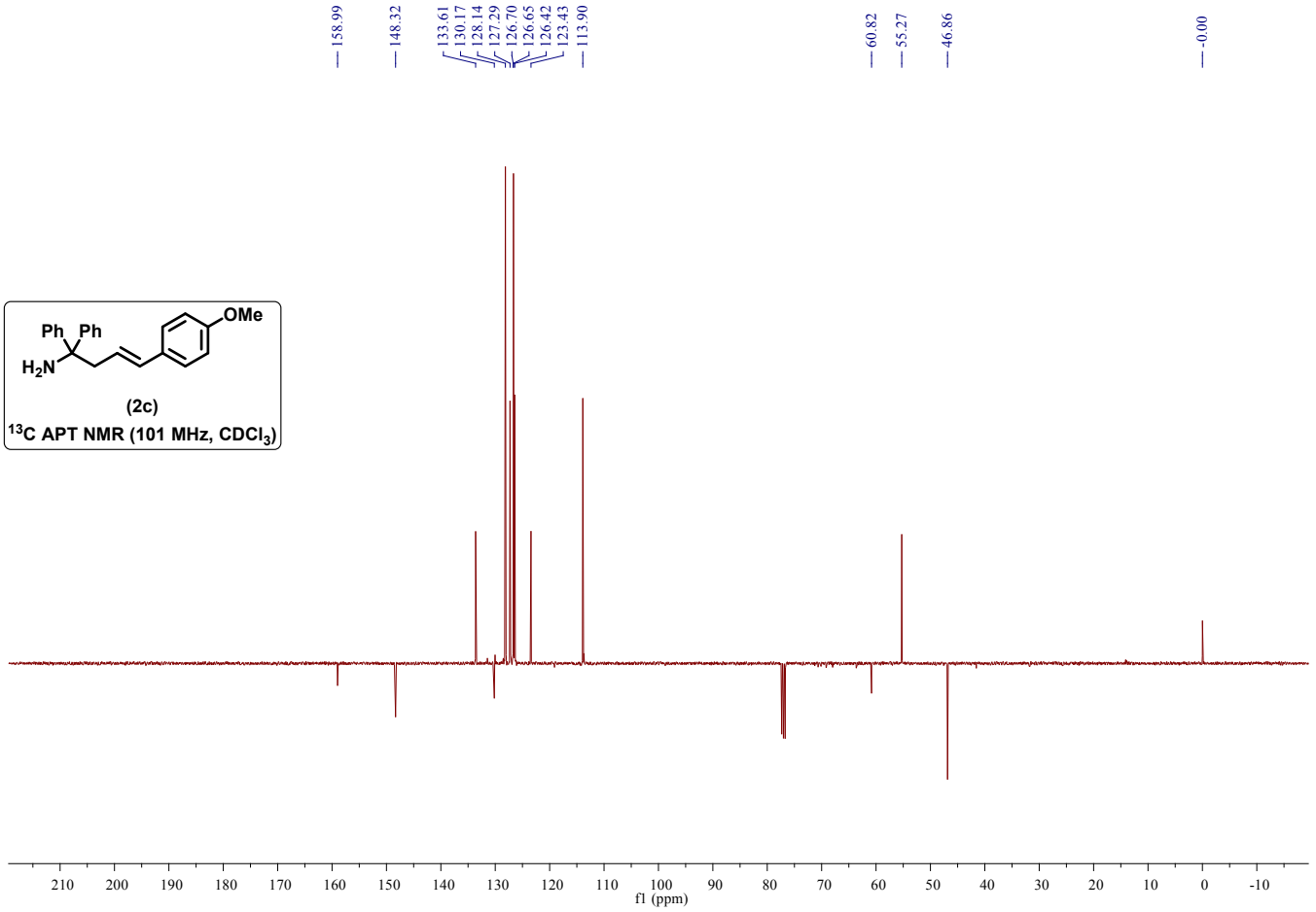
^{1}H NMR (400 MHz, $CDCl_3$)

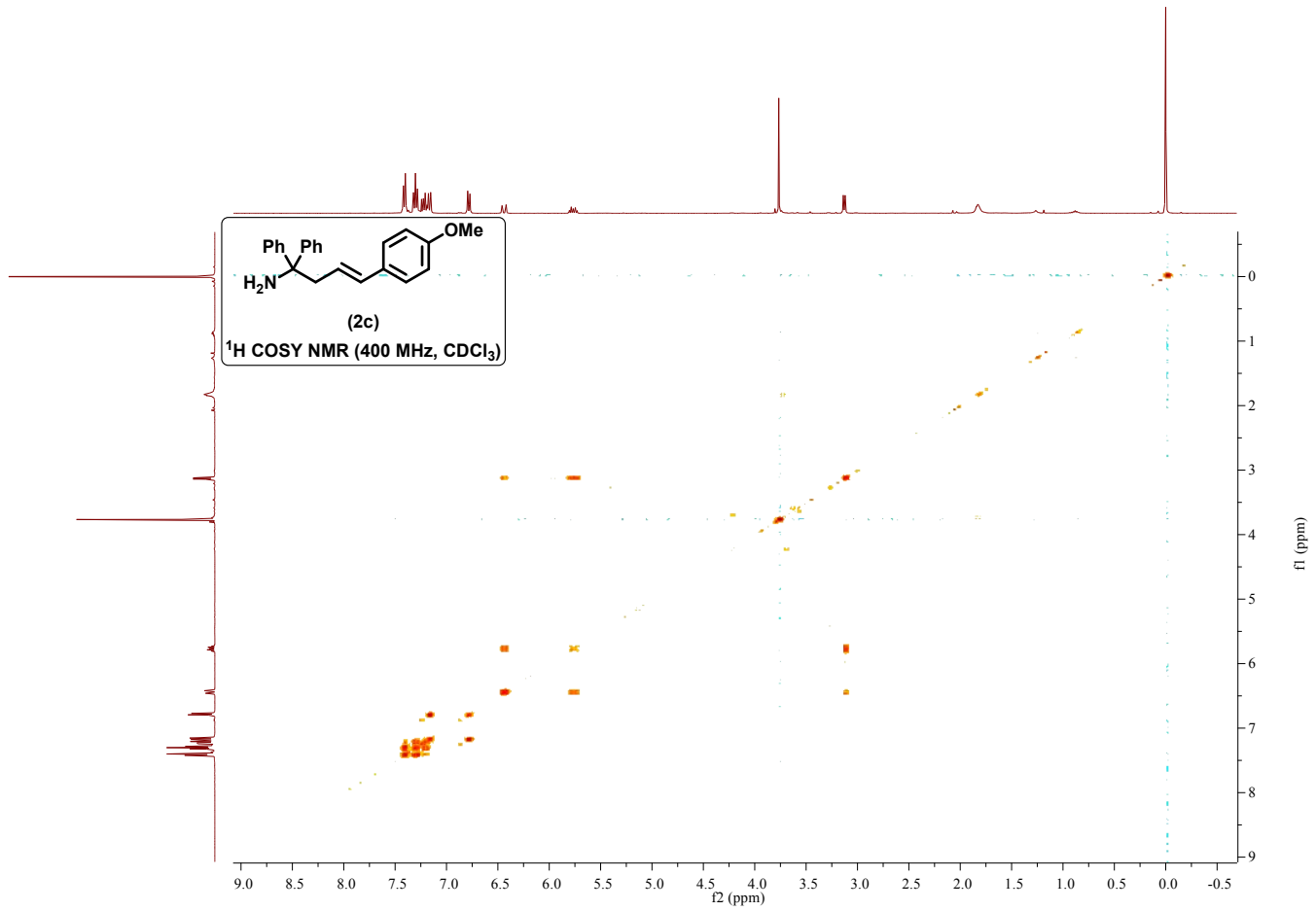


(2c)

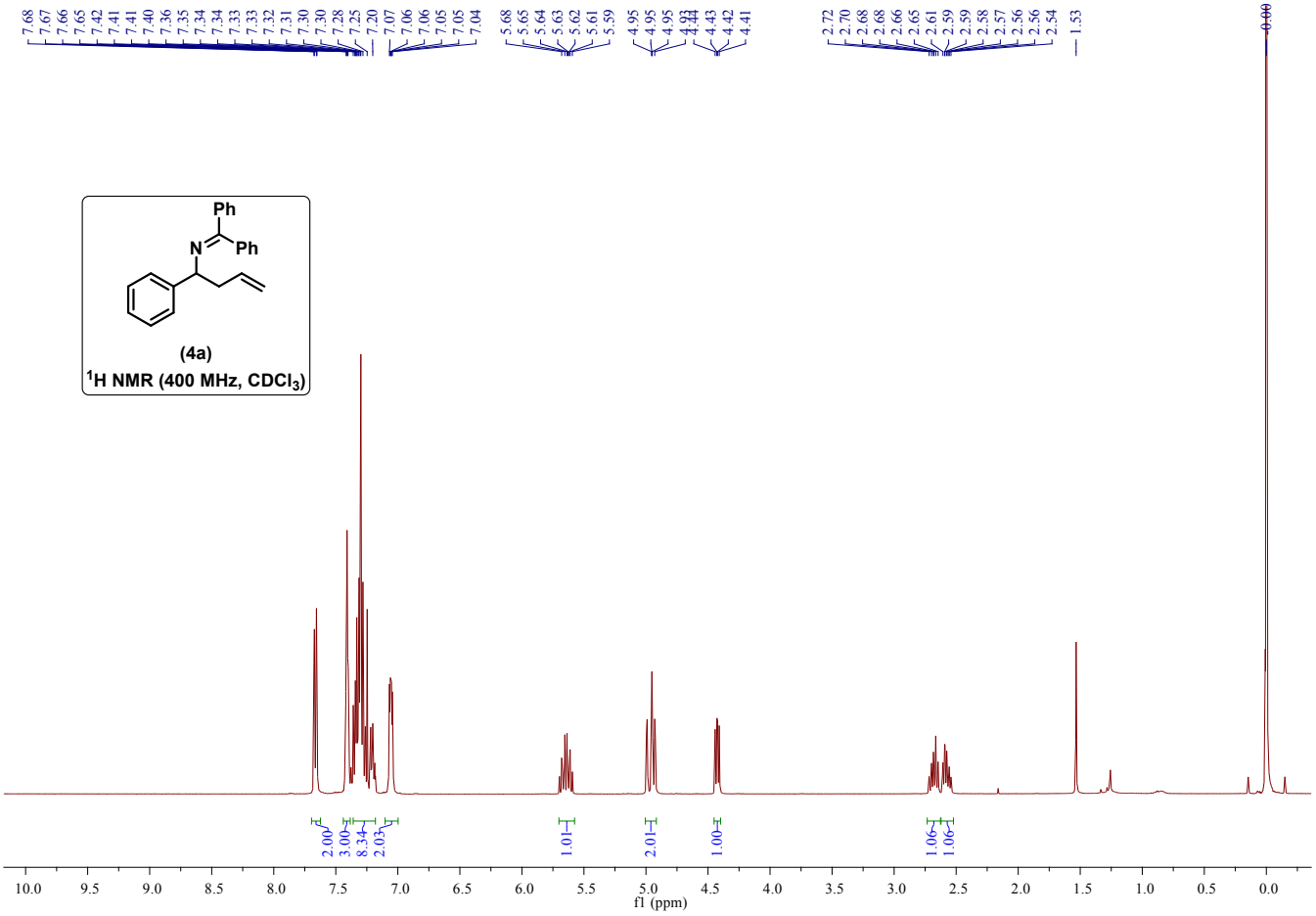
^{13}C NMR (101 MHz, $CDCl_3$)

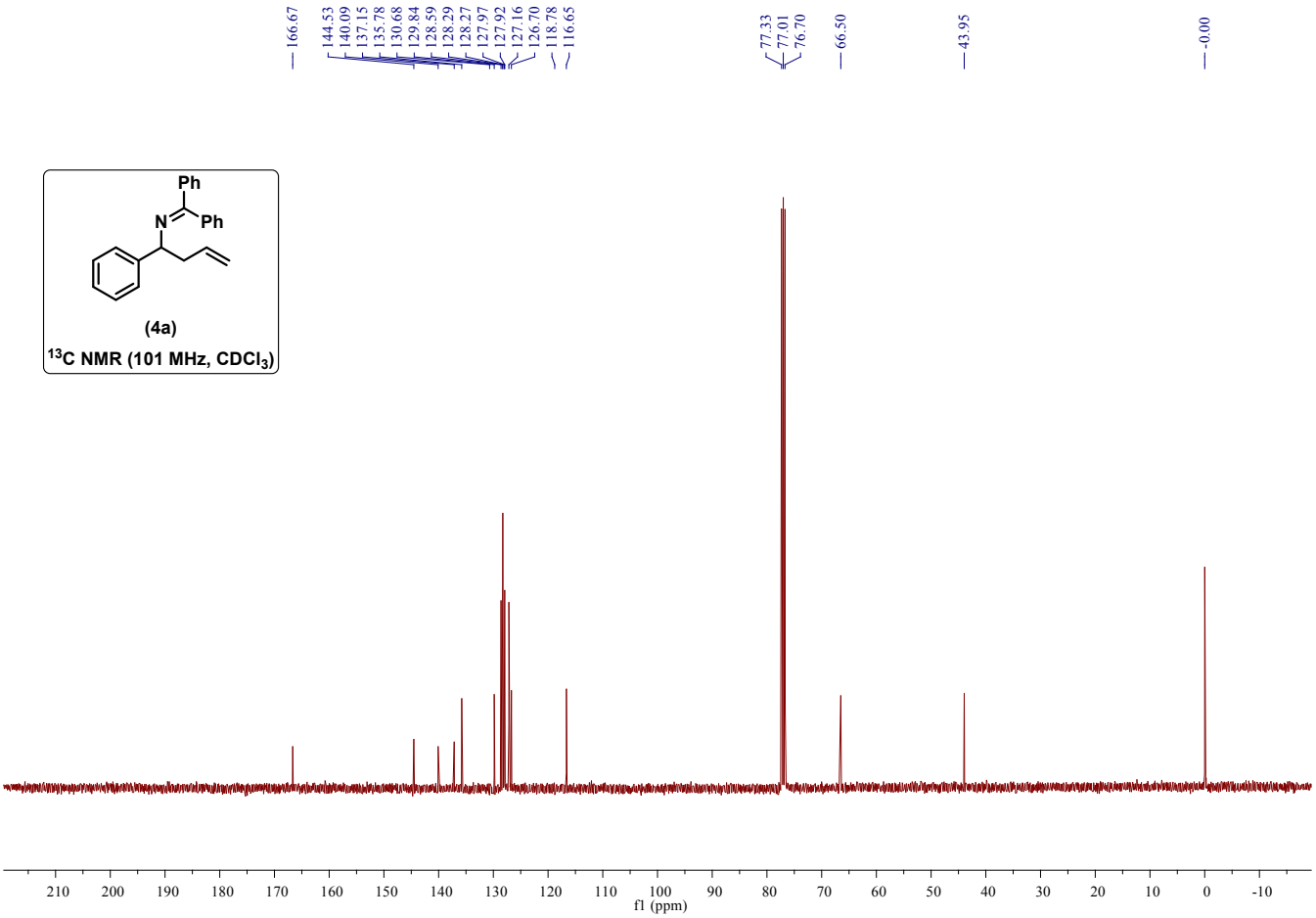
Copies of NMR spectra



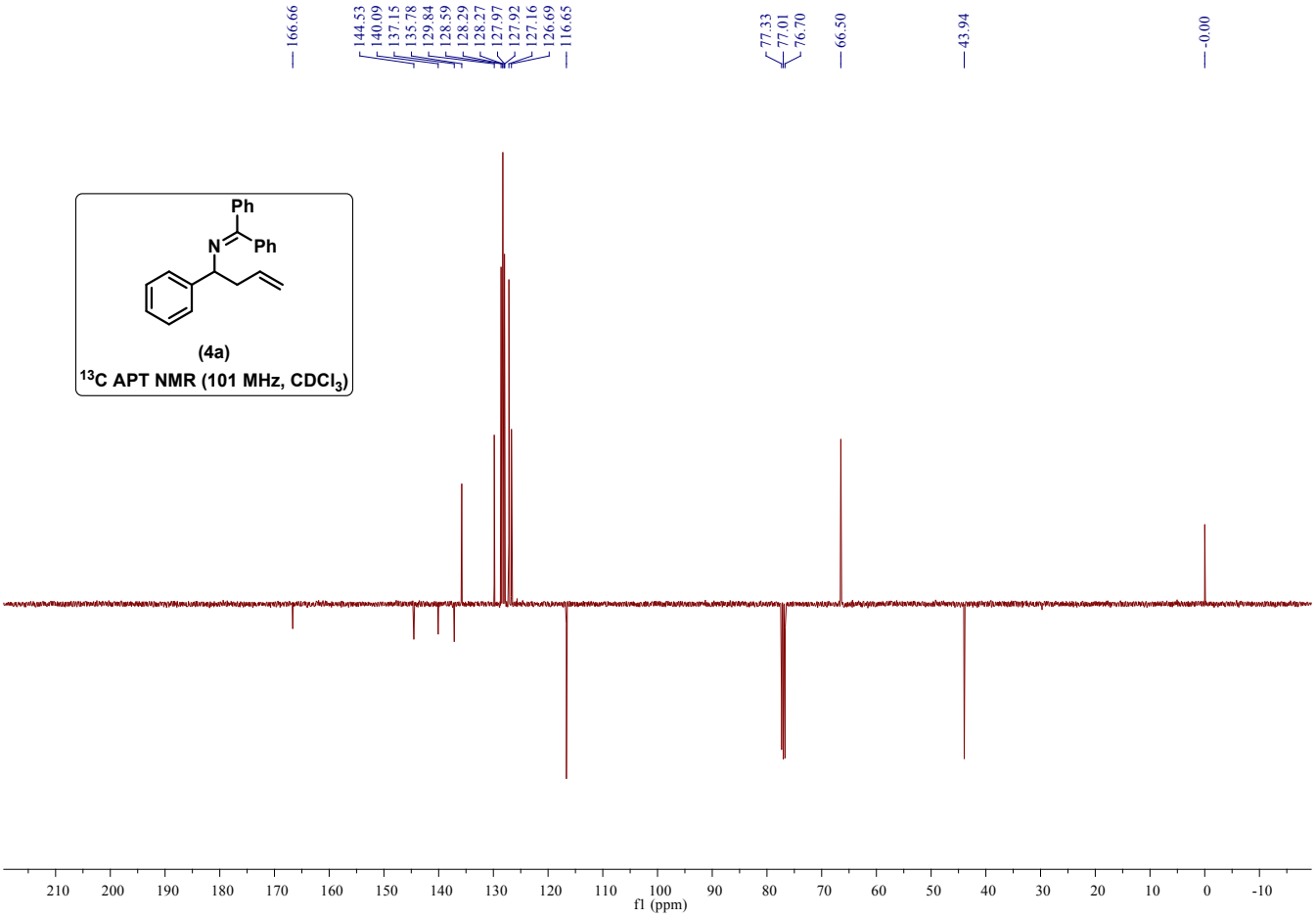


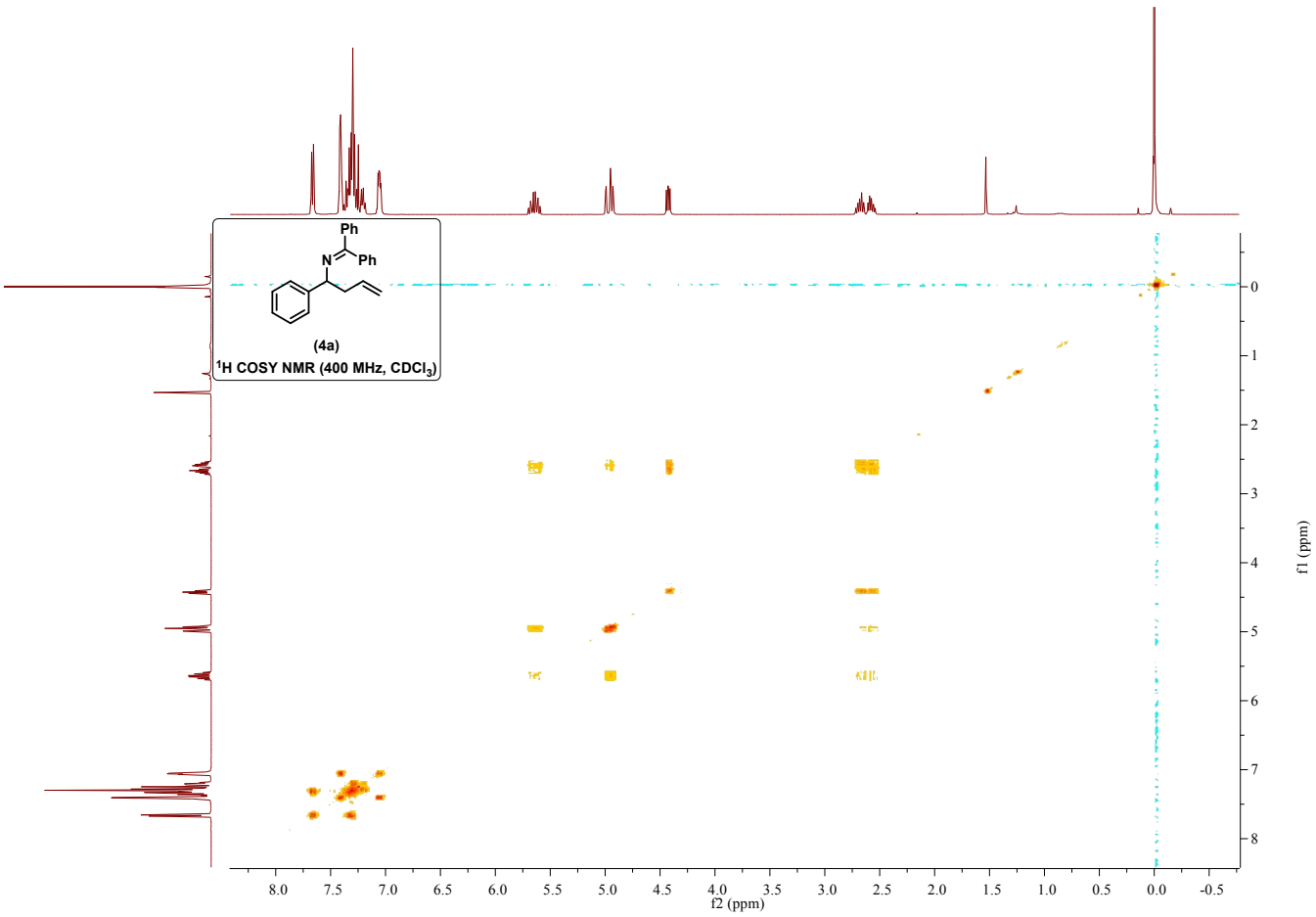
Copies of NMR spectra



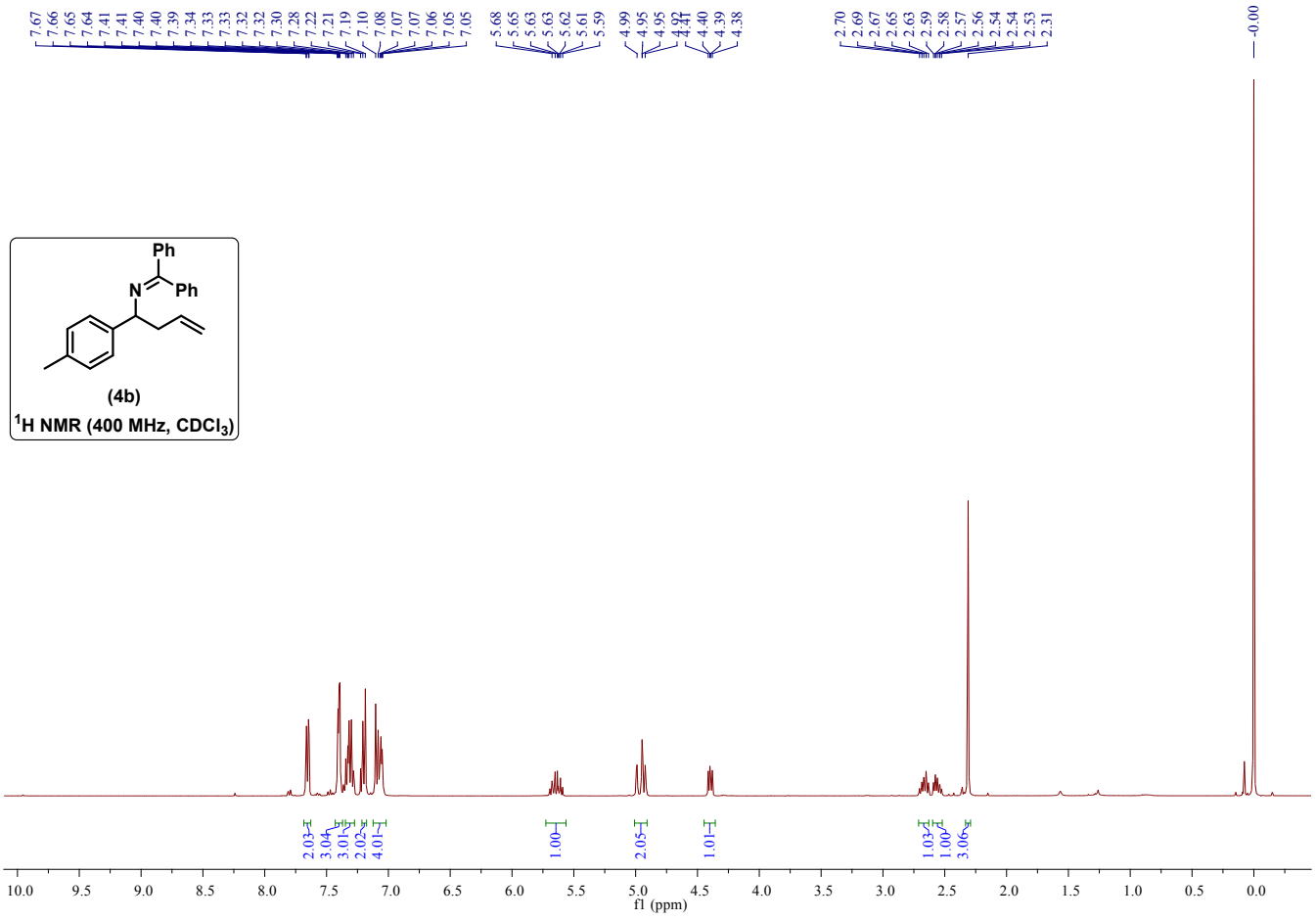


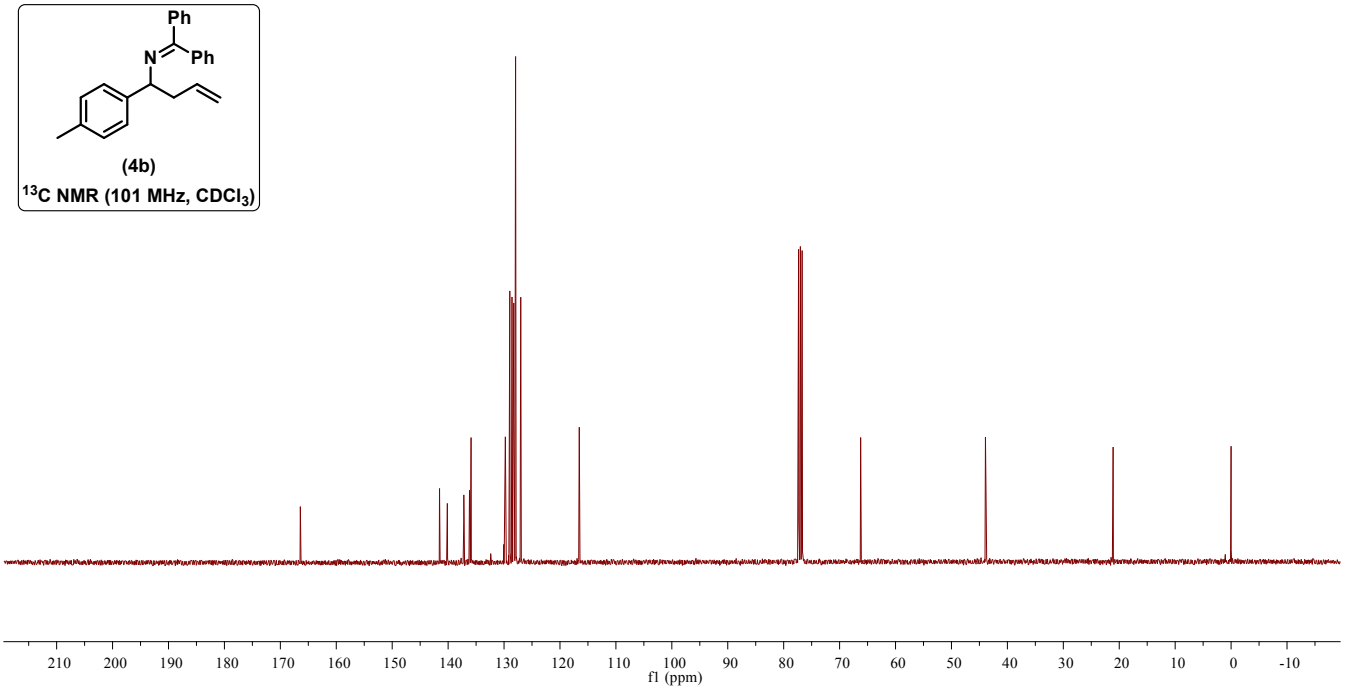
Copies of NMR spectra



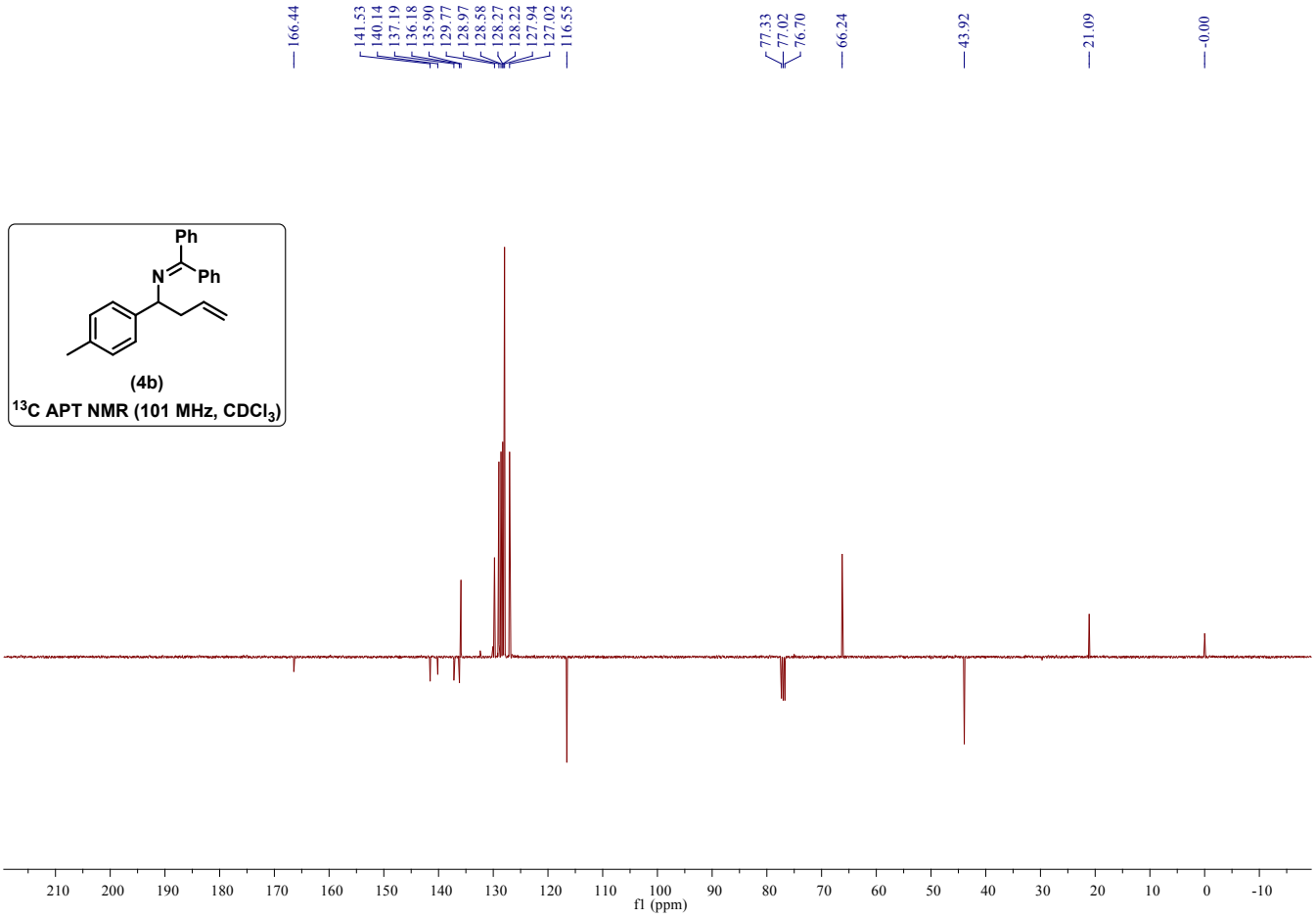


Copies of NMR spectra

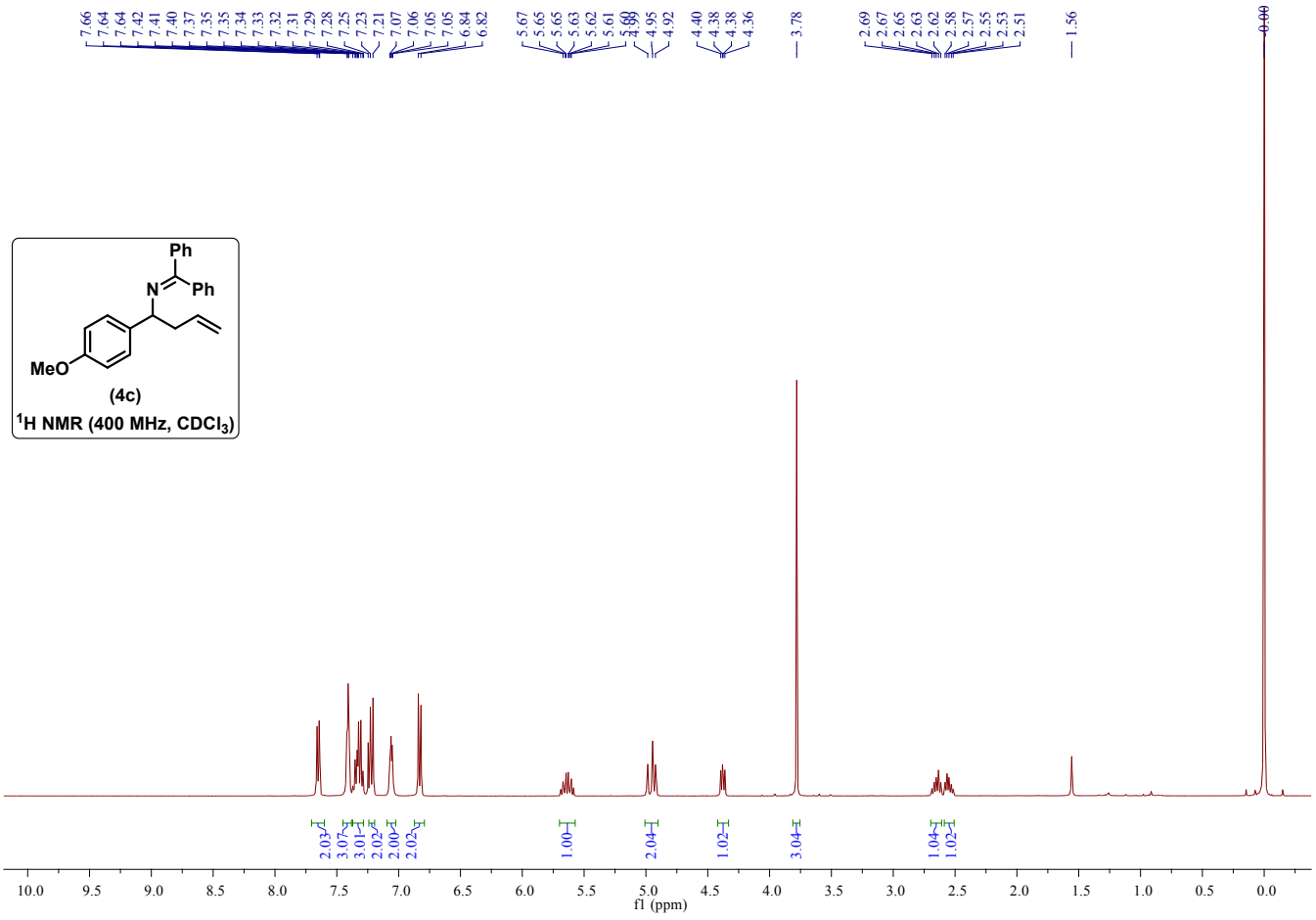


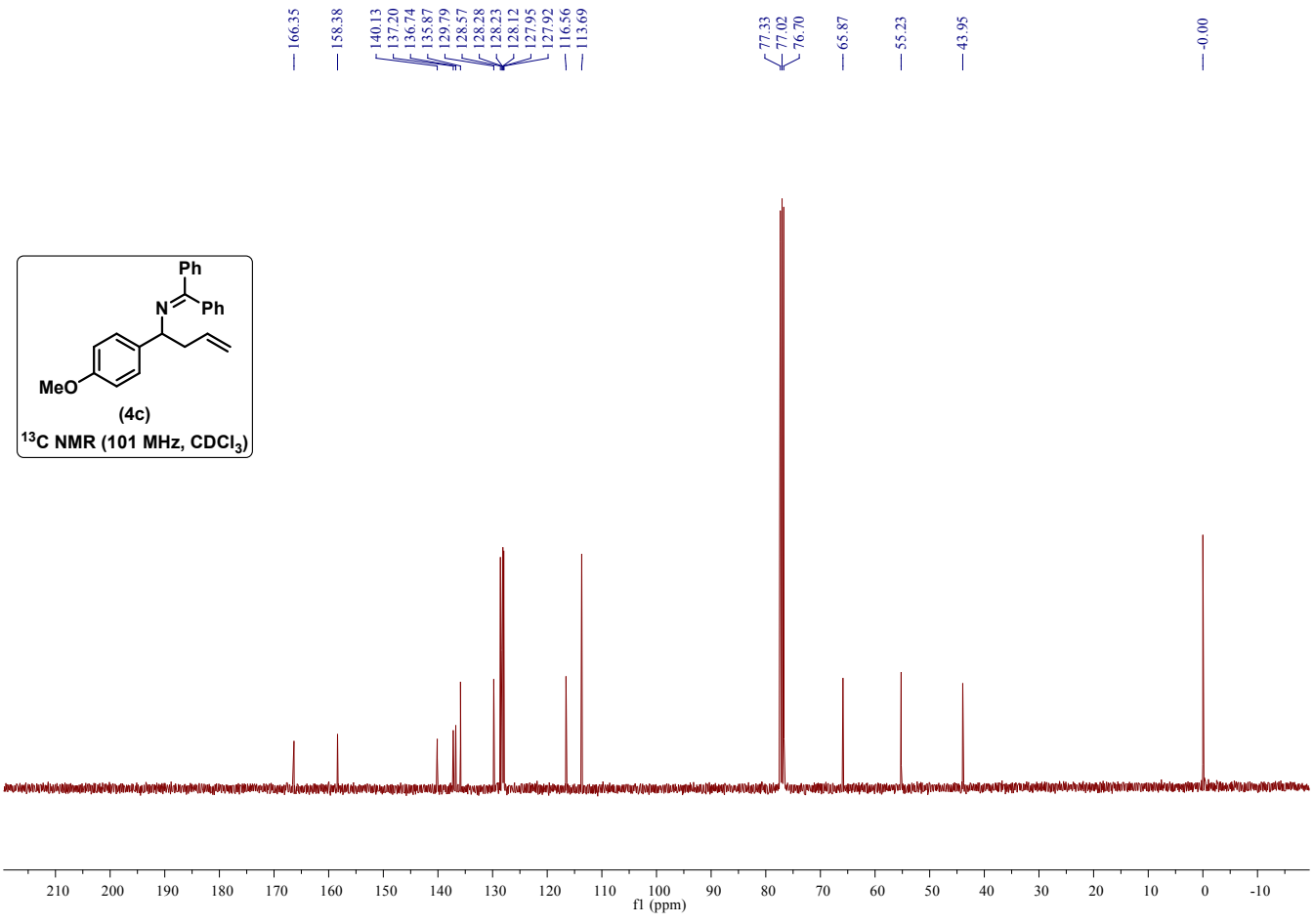


Copies of NMR spectra

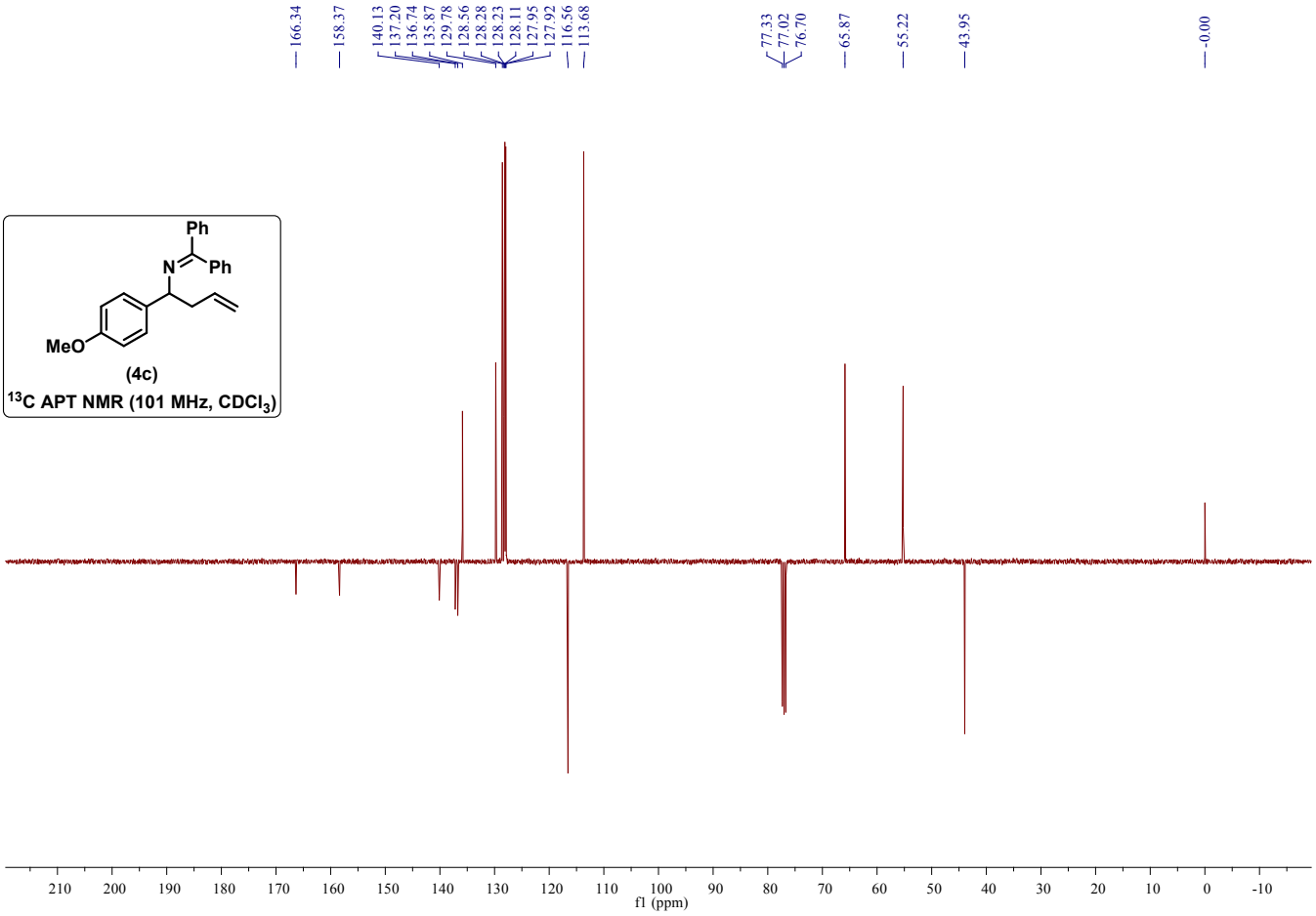


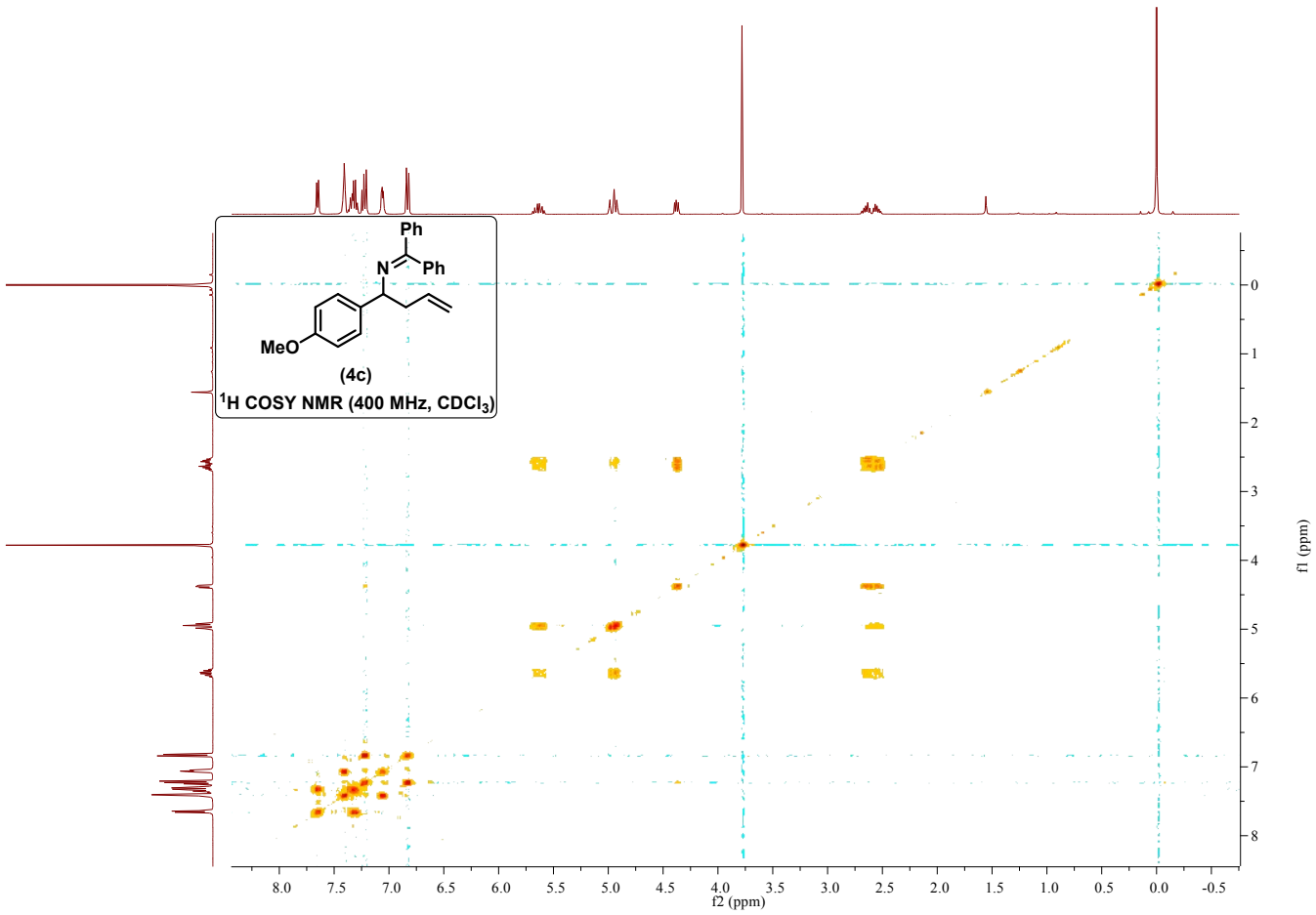
Copies of NMR spectra



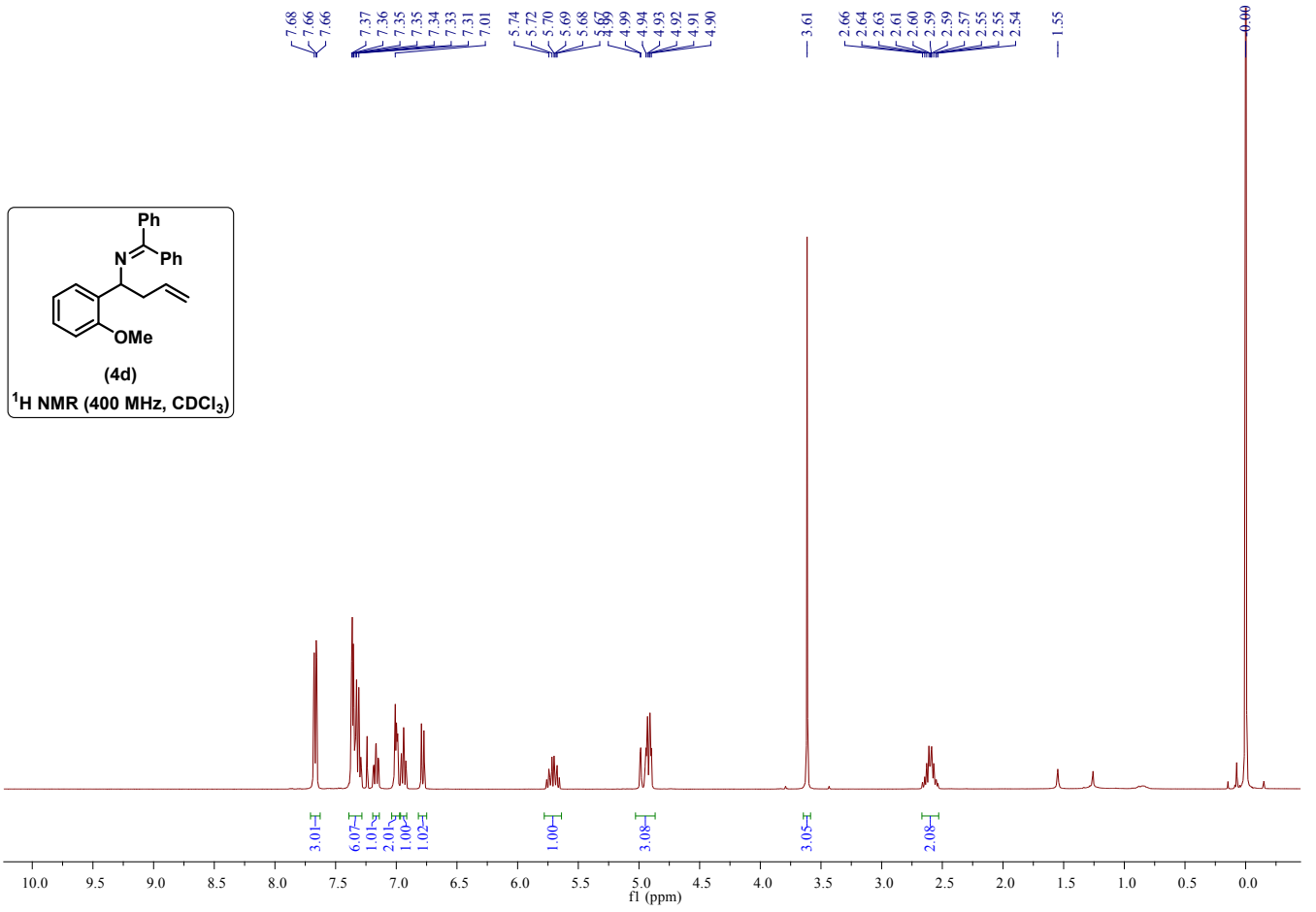


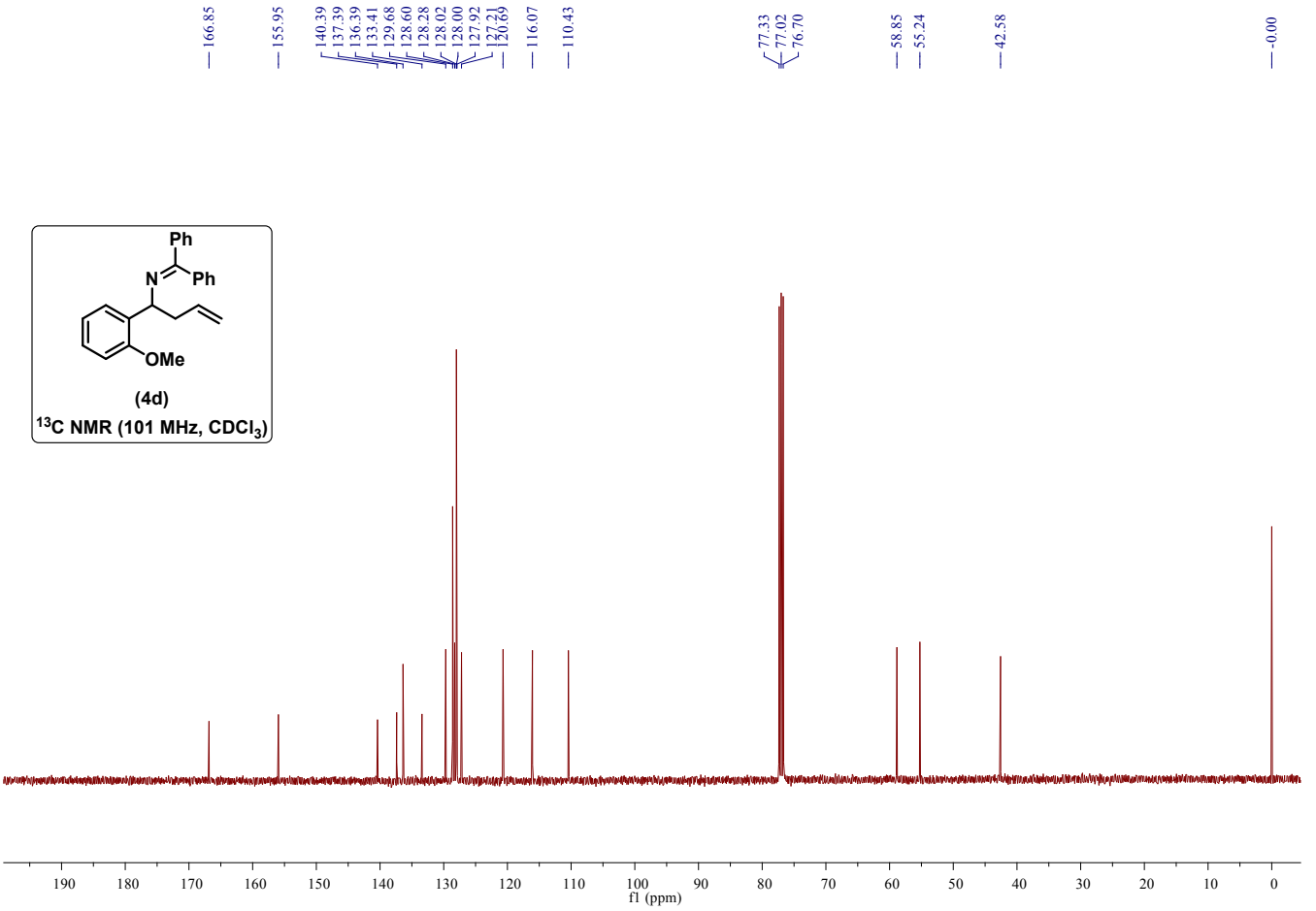
Copies of NMR spectra



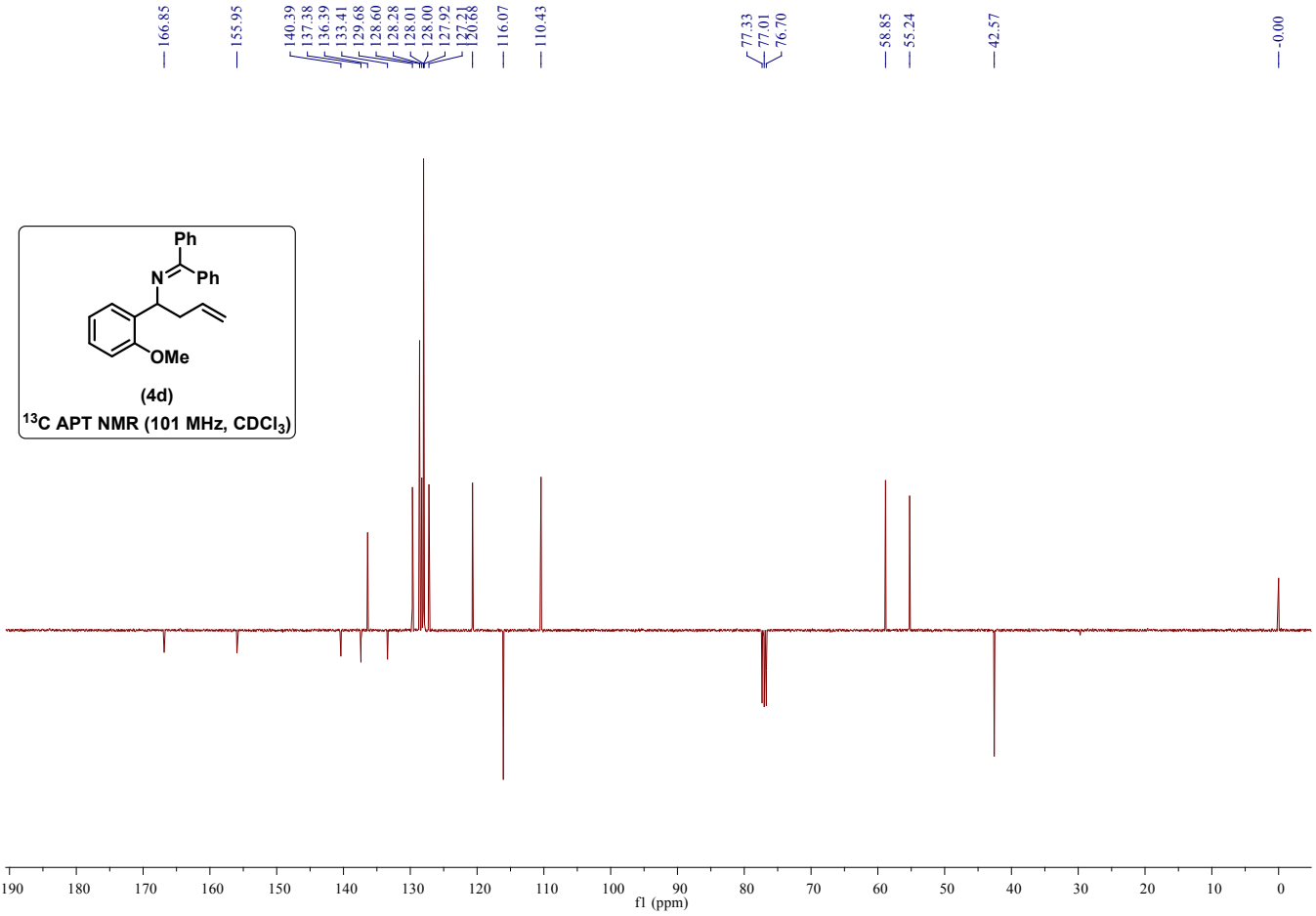


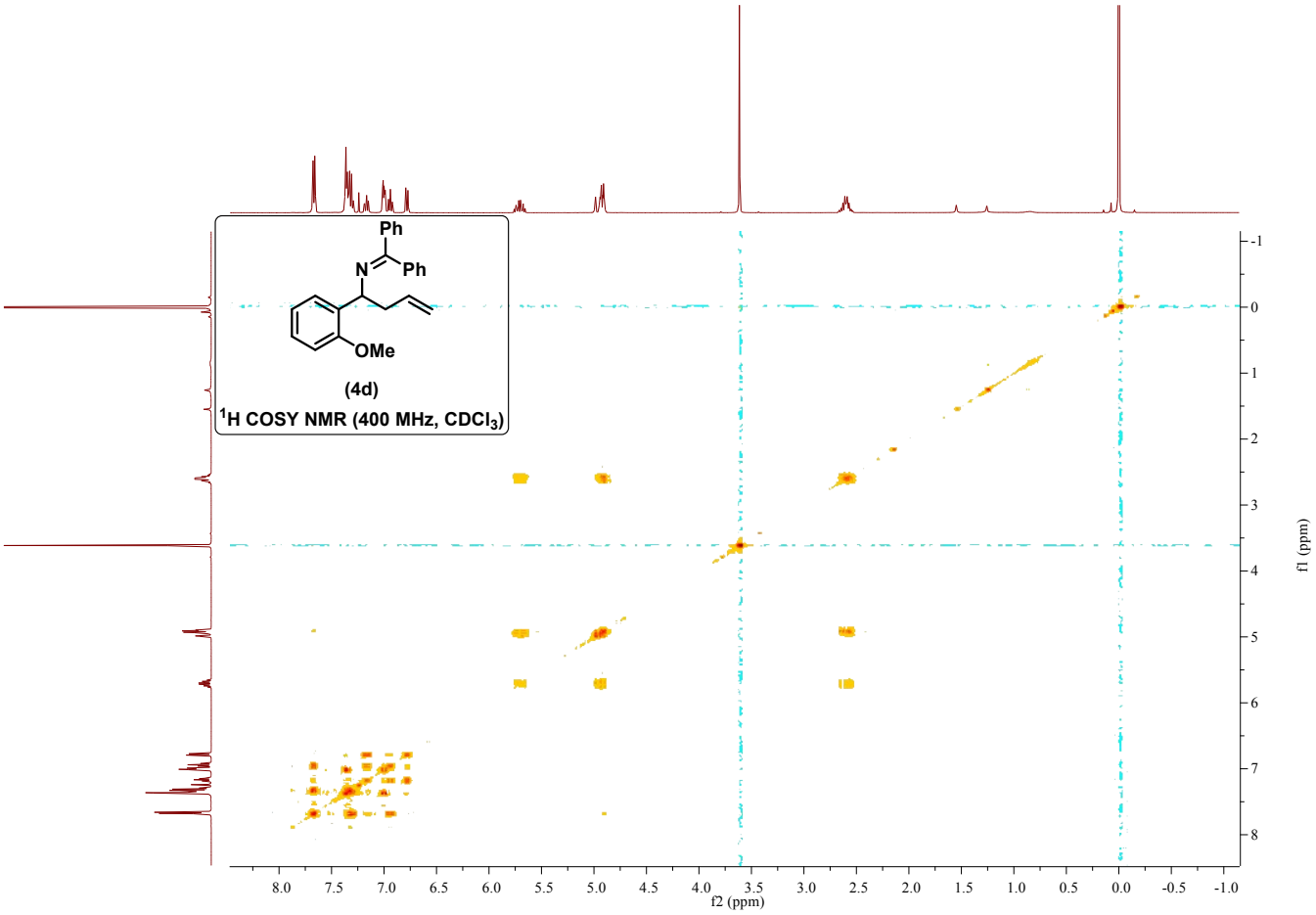
Copies of NMR spectra



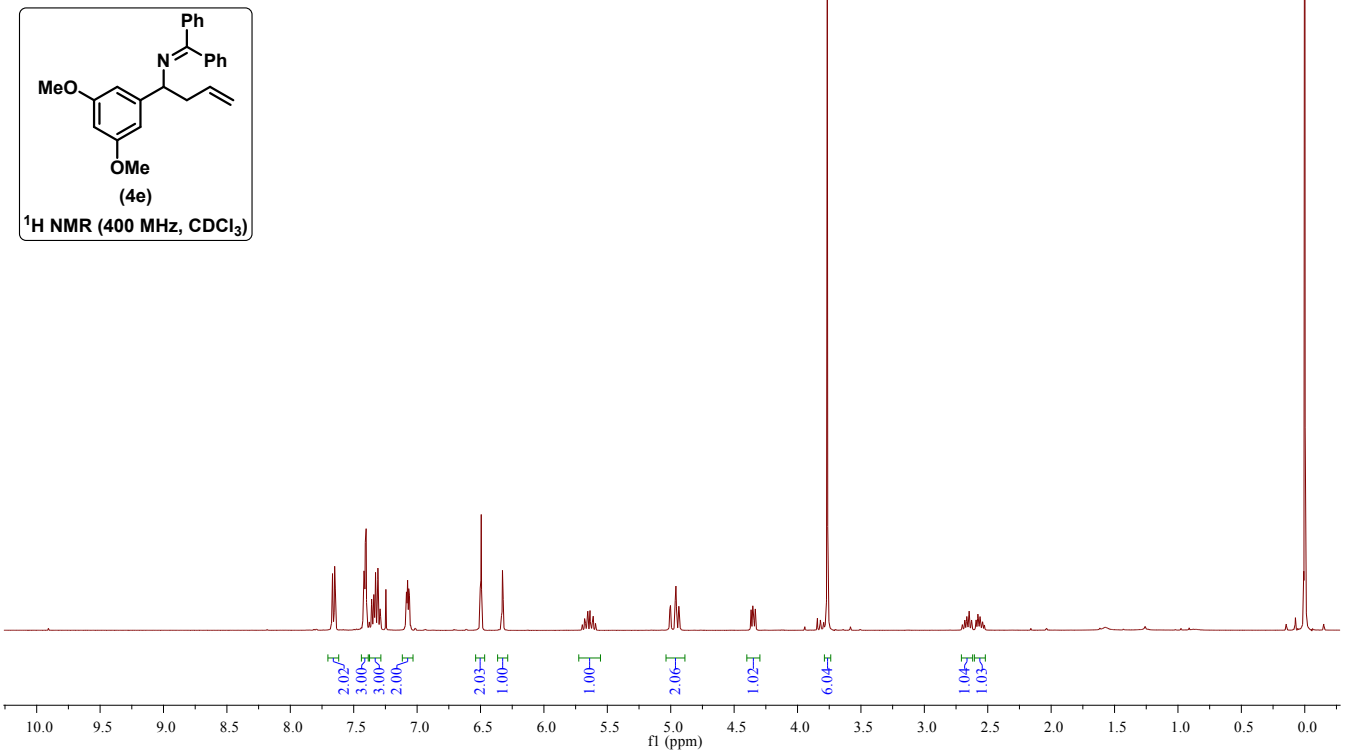


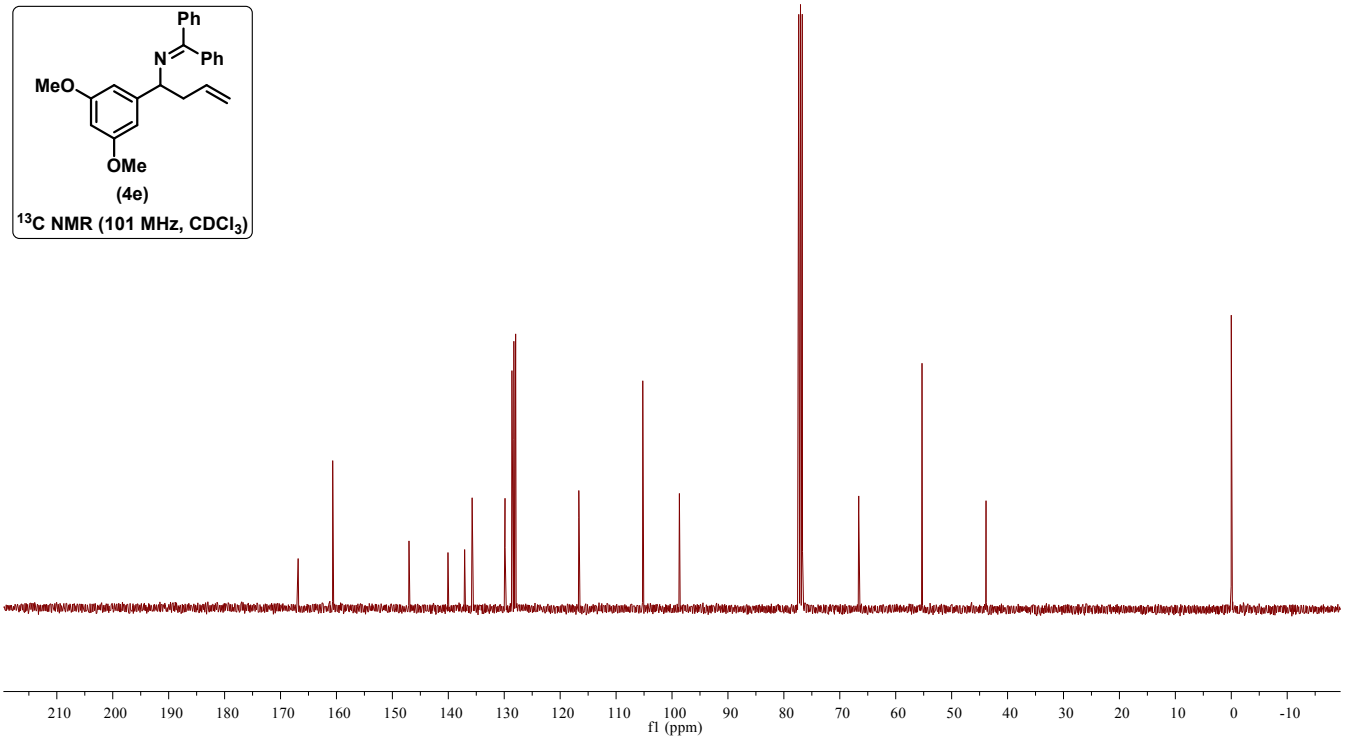
Copies of NMR spectra



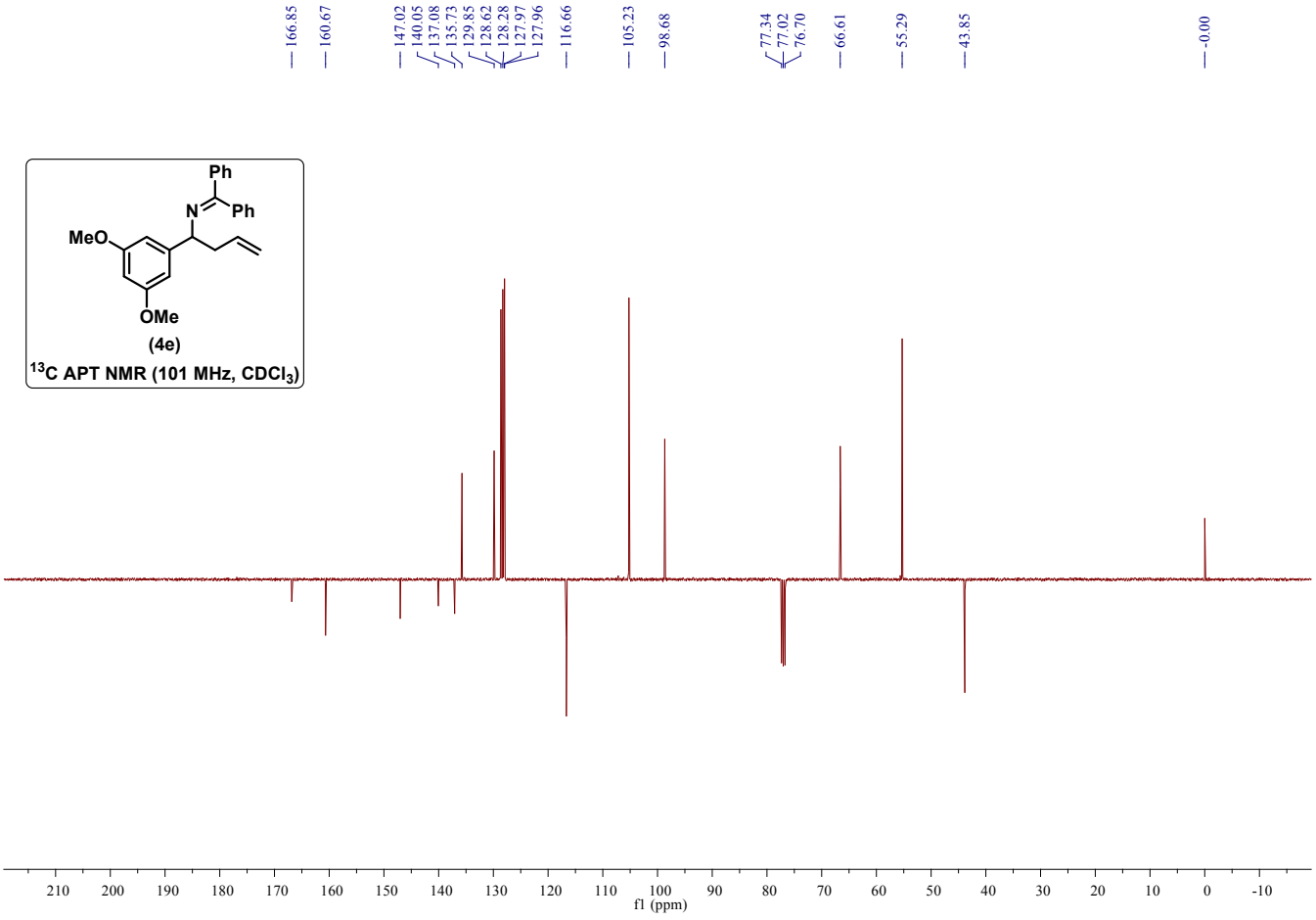


Copies of NMR spectra

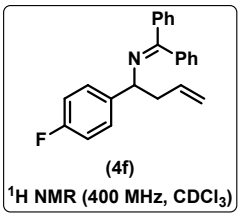




Copies of NMR spectra

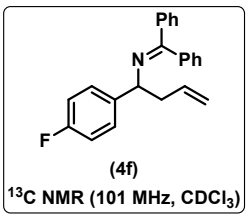


Copies of NMR spectra



(4f)

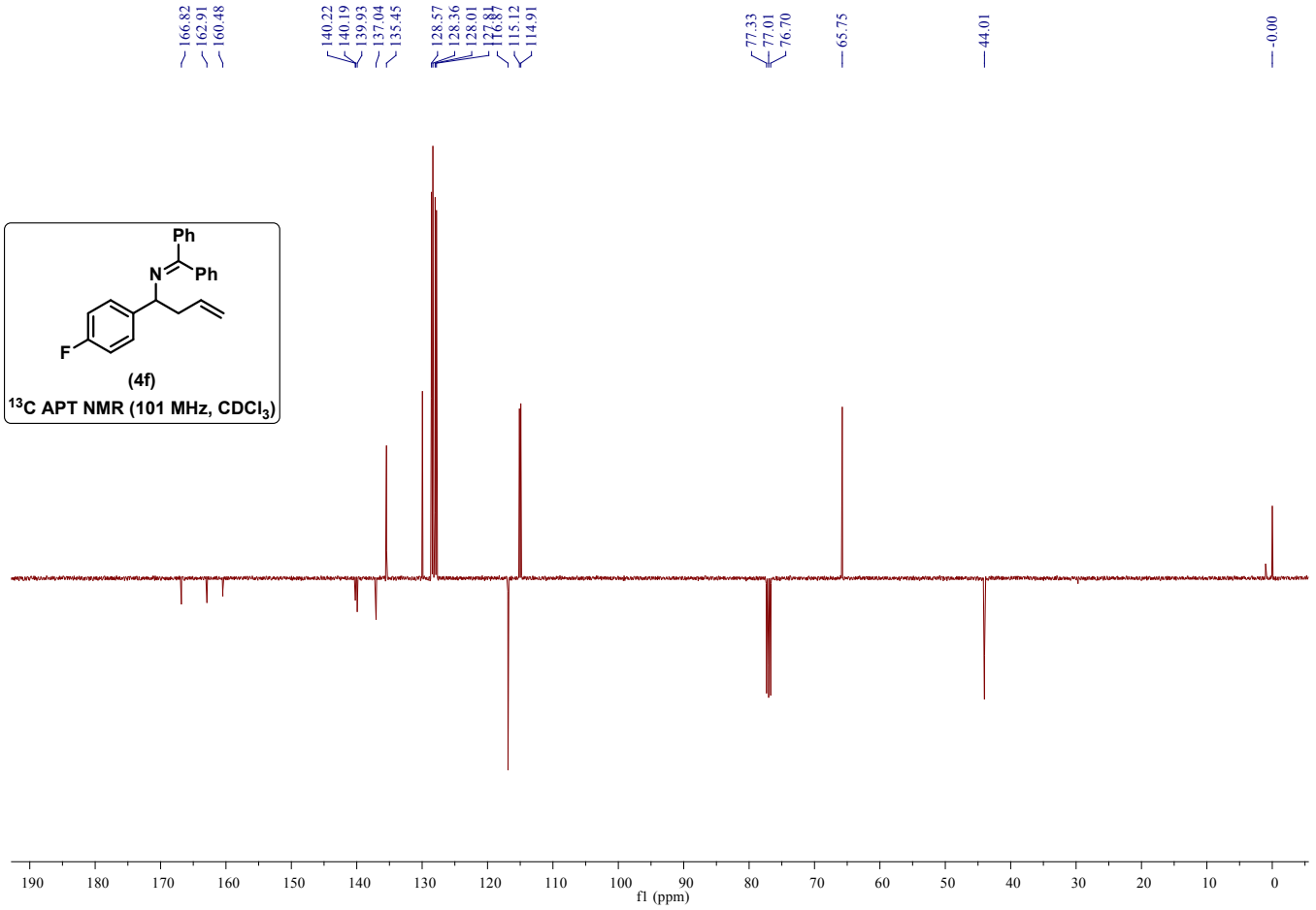
^{1}H NMR (400 MHz, $CDCl_3$)

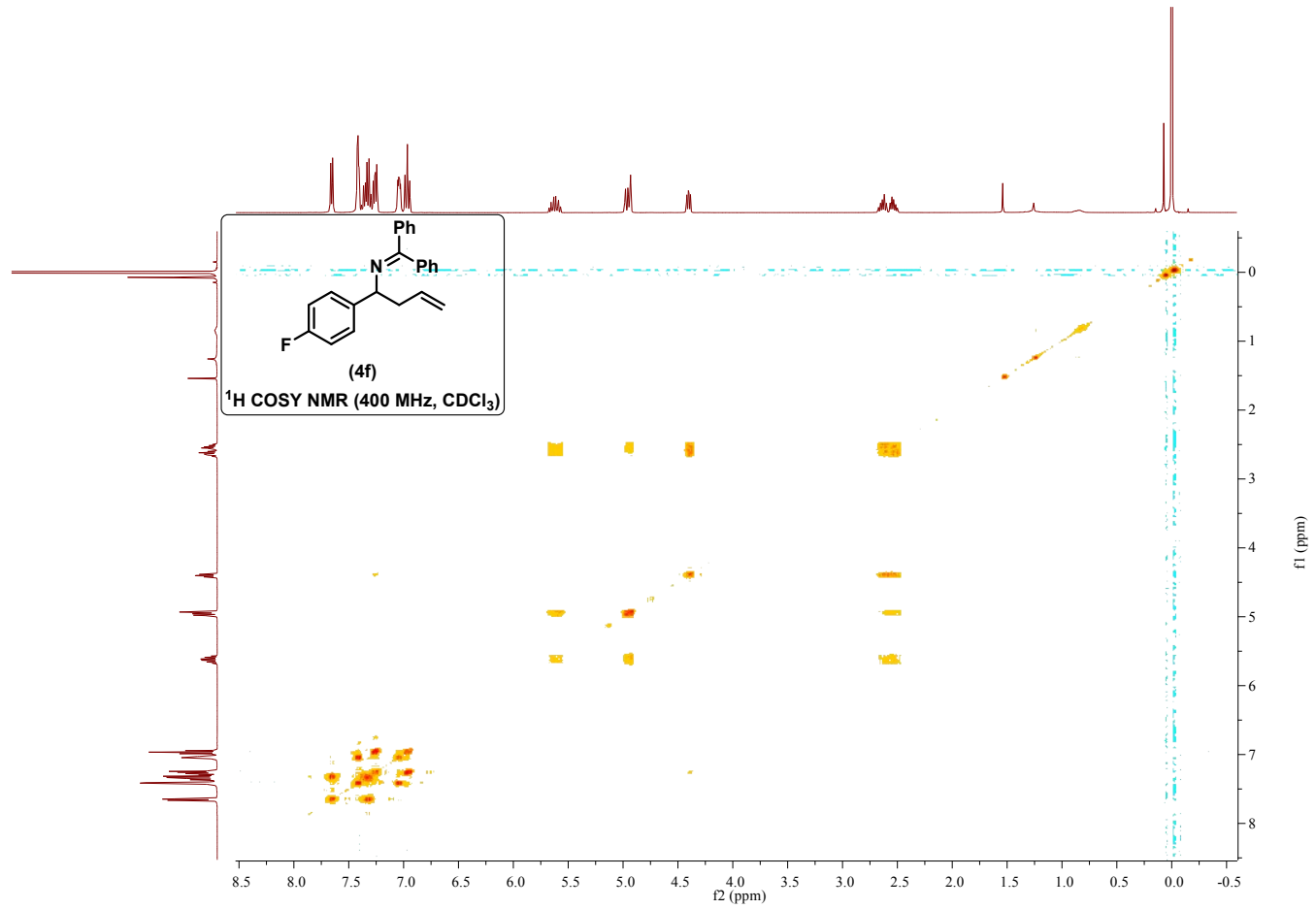


(4f)

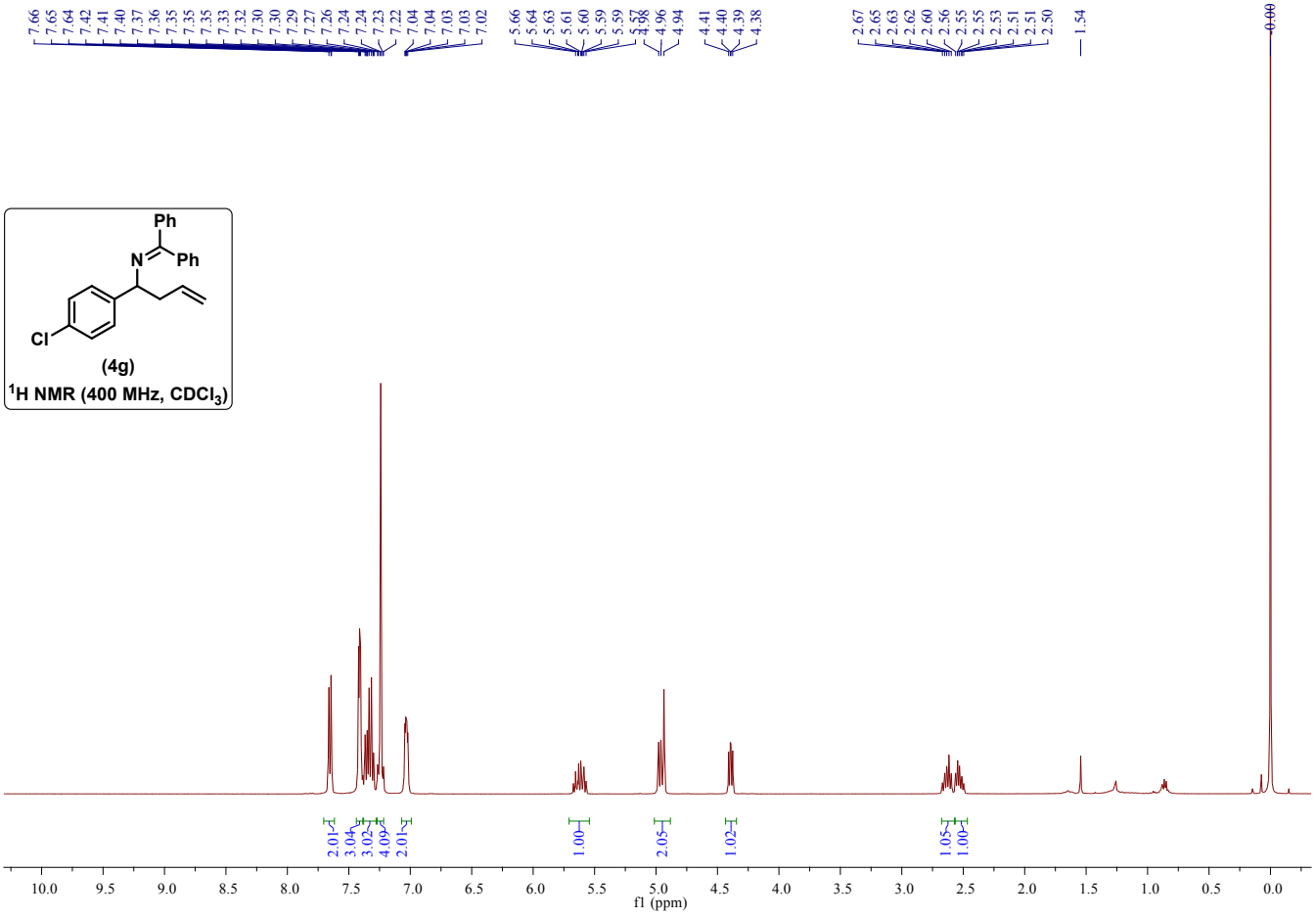
^{13}C NMR (101 MHz, $CDCl_3$)

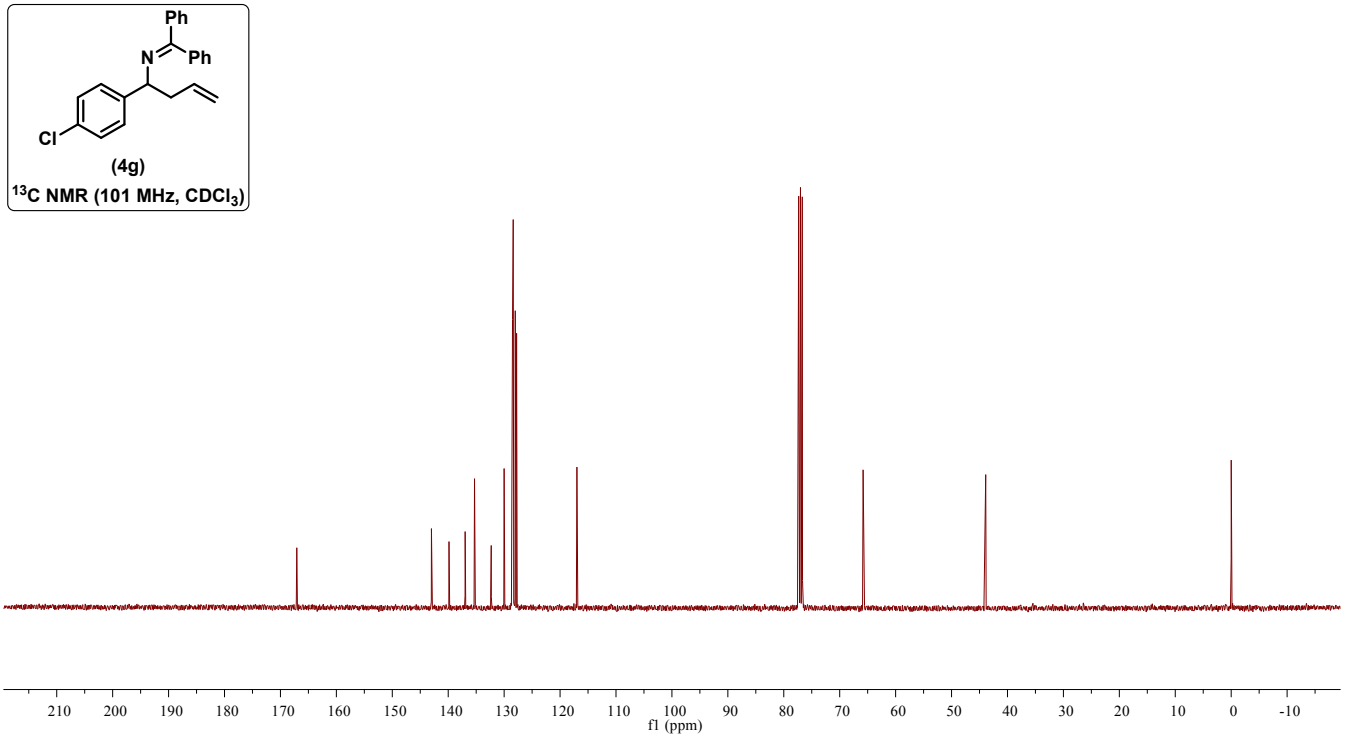
Copies of NMR spectra



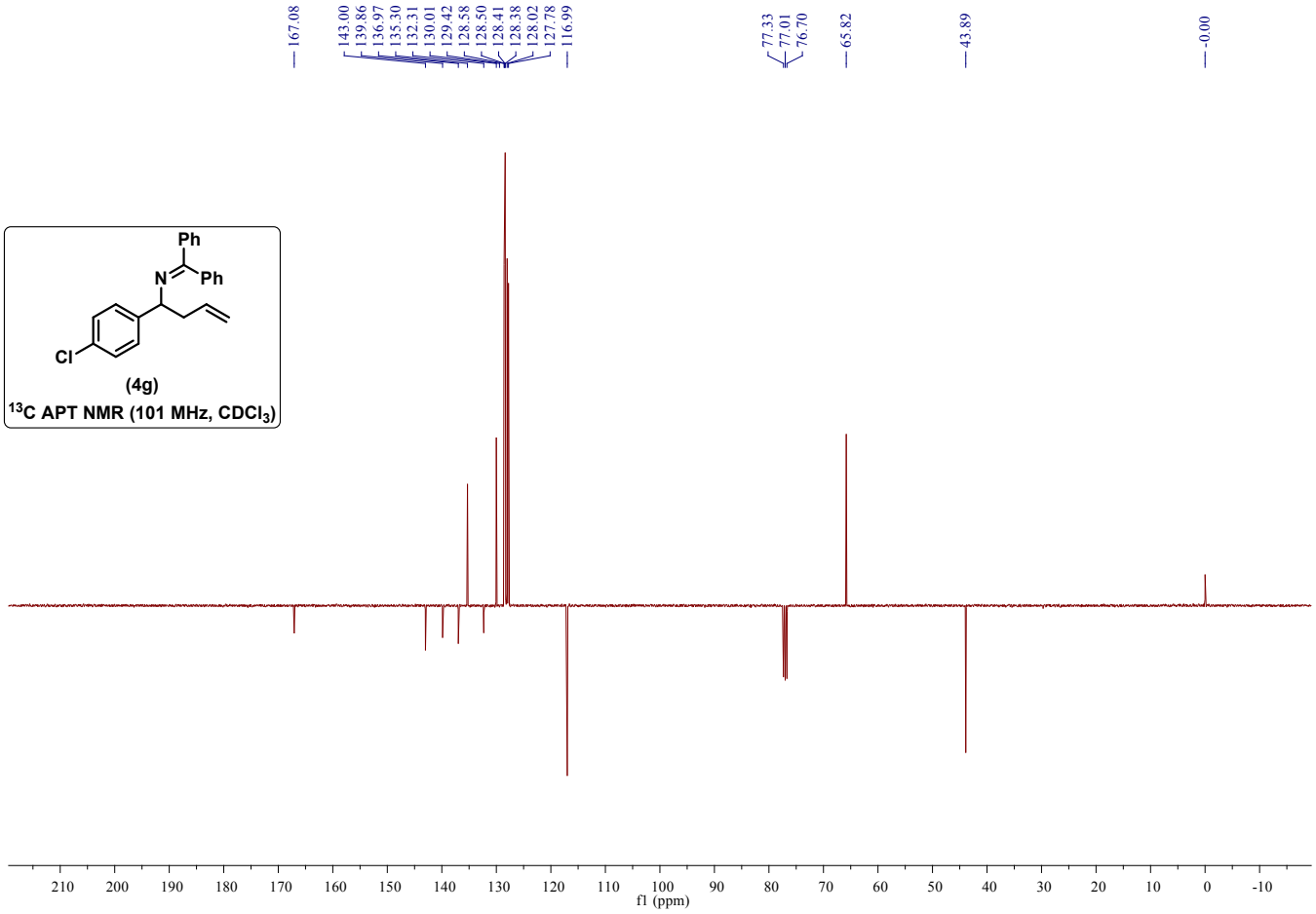


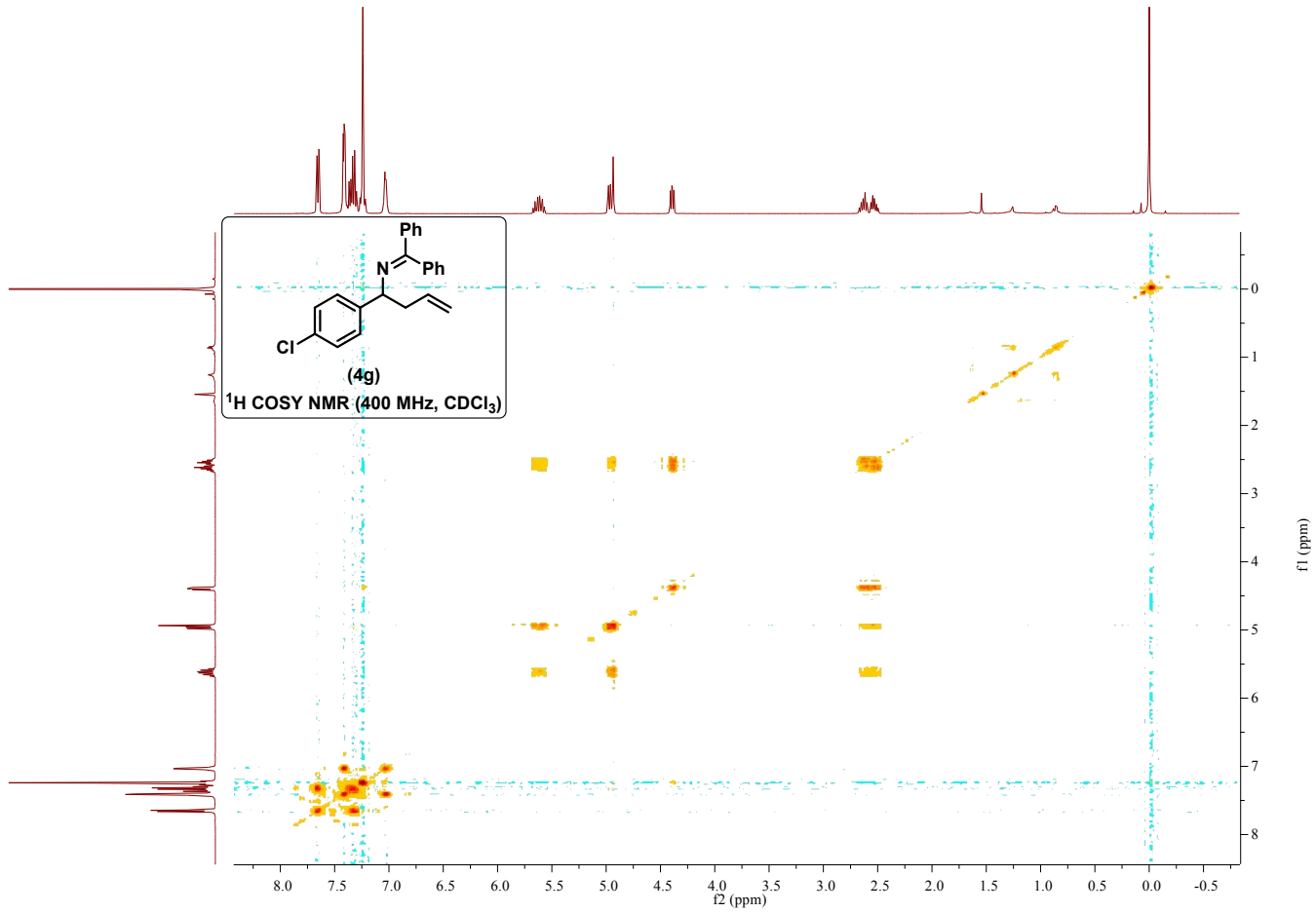
Copies of NMR spectra

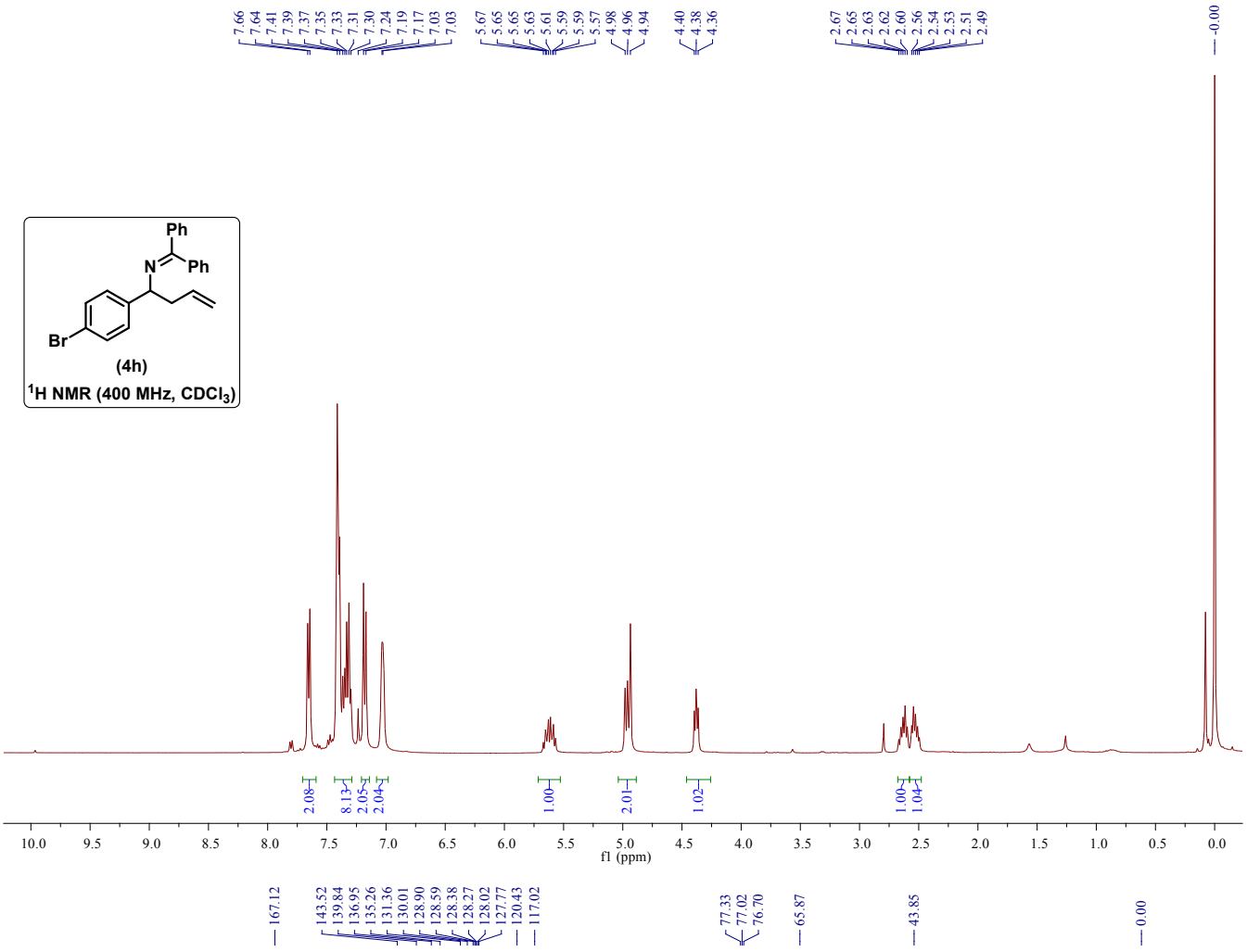


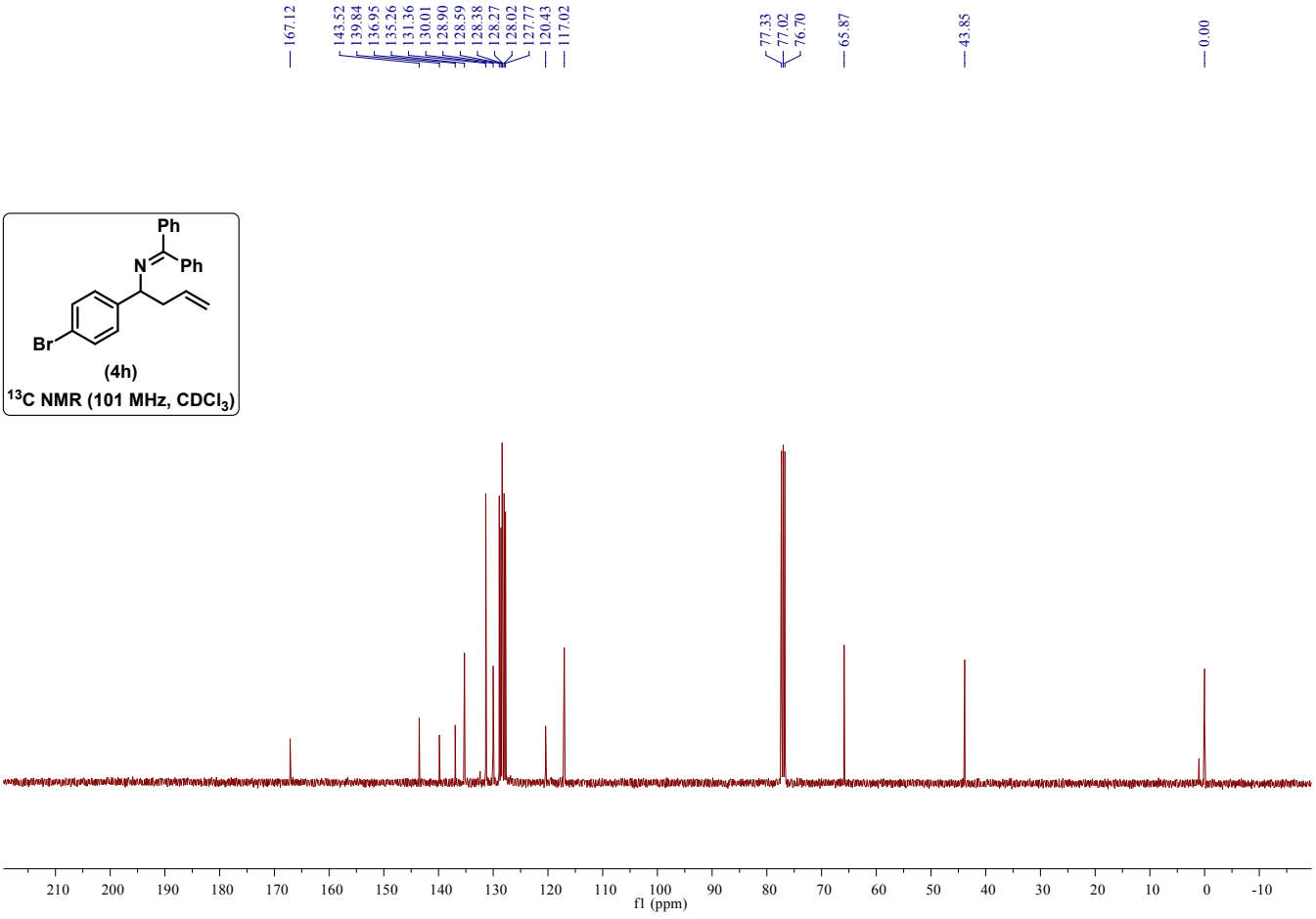


Copies of NMR spectra

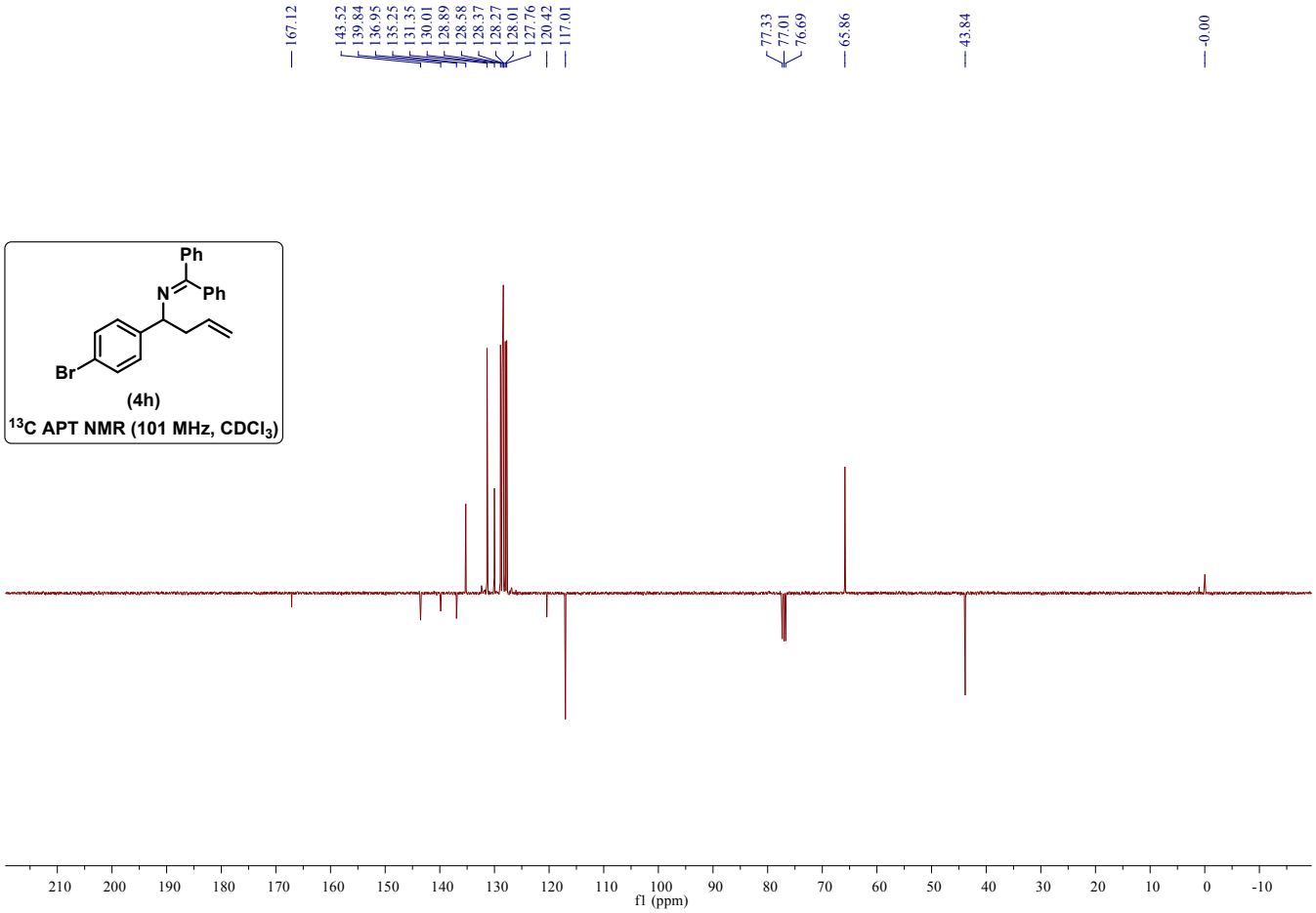




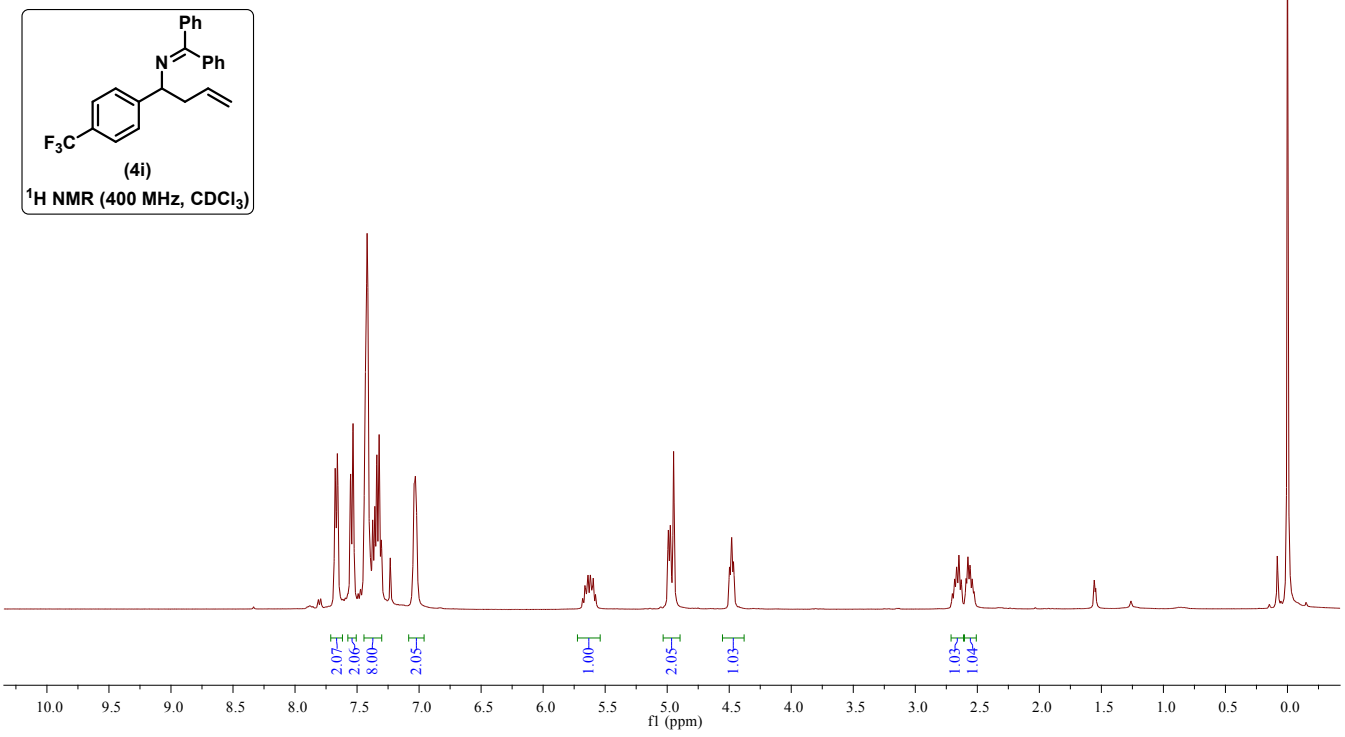

7.66
7.64
7.41
7.39
7.37
7.35
7.33
7.31
7.30
7.24
7.19
7.17
7.03
7.03
5.67
5.65
5.65
5.63
5.61
5.59
5.59
5.57
4.98
4.96
4.94
4.40
4.38
4.36
2.67
2.65
2.63
2.62
2.60
2.56
2.54
2.53
2.51
2.49
-0.00
Ph
N
Ph
Br
(4h)
1H NMR (400 MHz, CDCl3)
2.08
8.13
2.05
2.04
1.00
2.01
1.02
1.00
1.04
f1 (ppm)

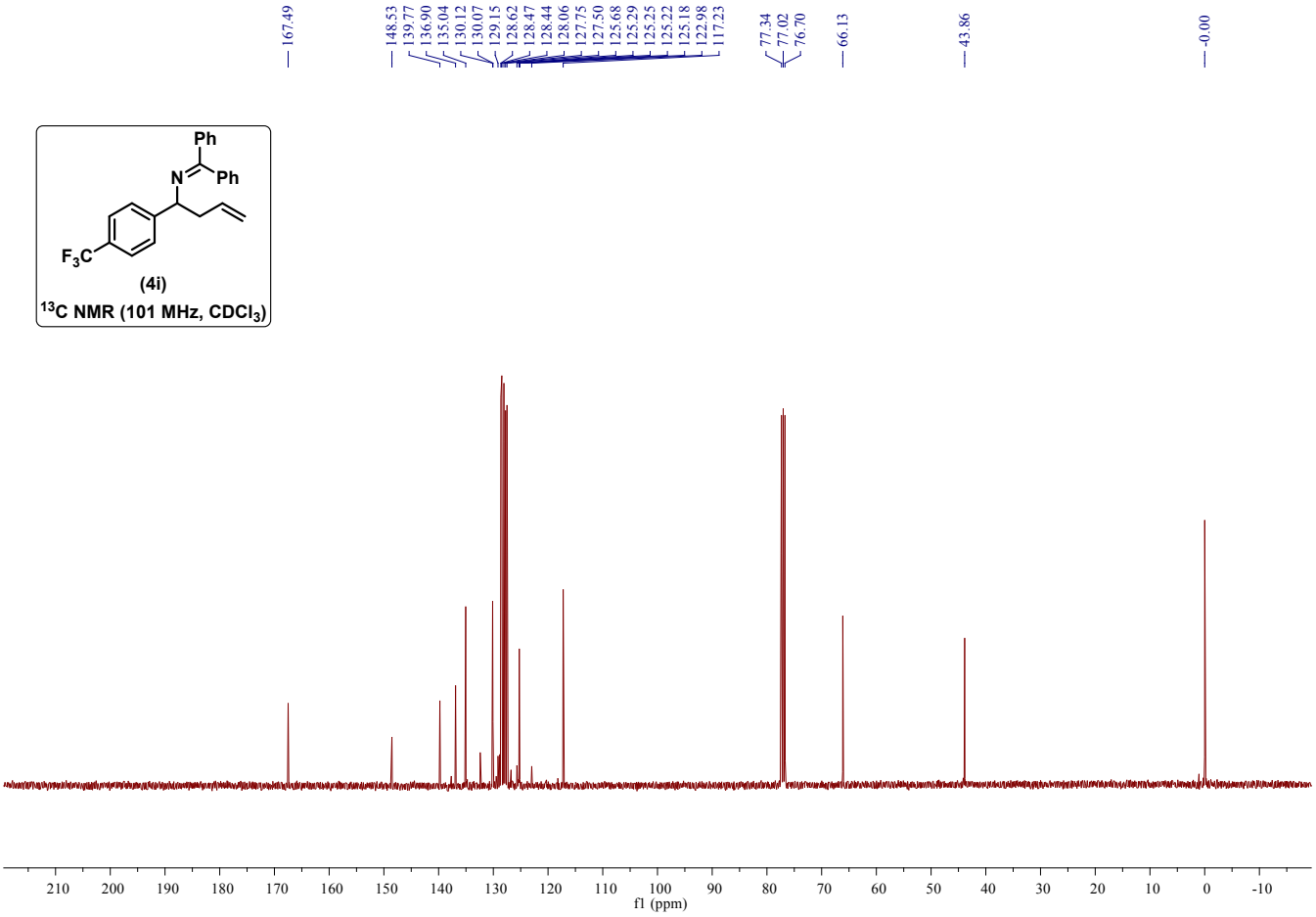

167.12
143.52
139.84
136.95
135.26
131.36
130.01
128.90
128.59
128.38
128.27
128.02
127.77
120.43
117.02
77.33
77.02
76.70
65.87
43.85
0.00
Ph
N
Ph
Br
(4h)
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Copies of NMR spectra

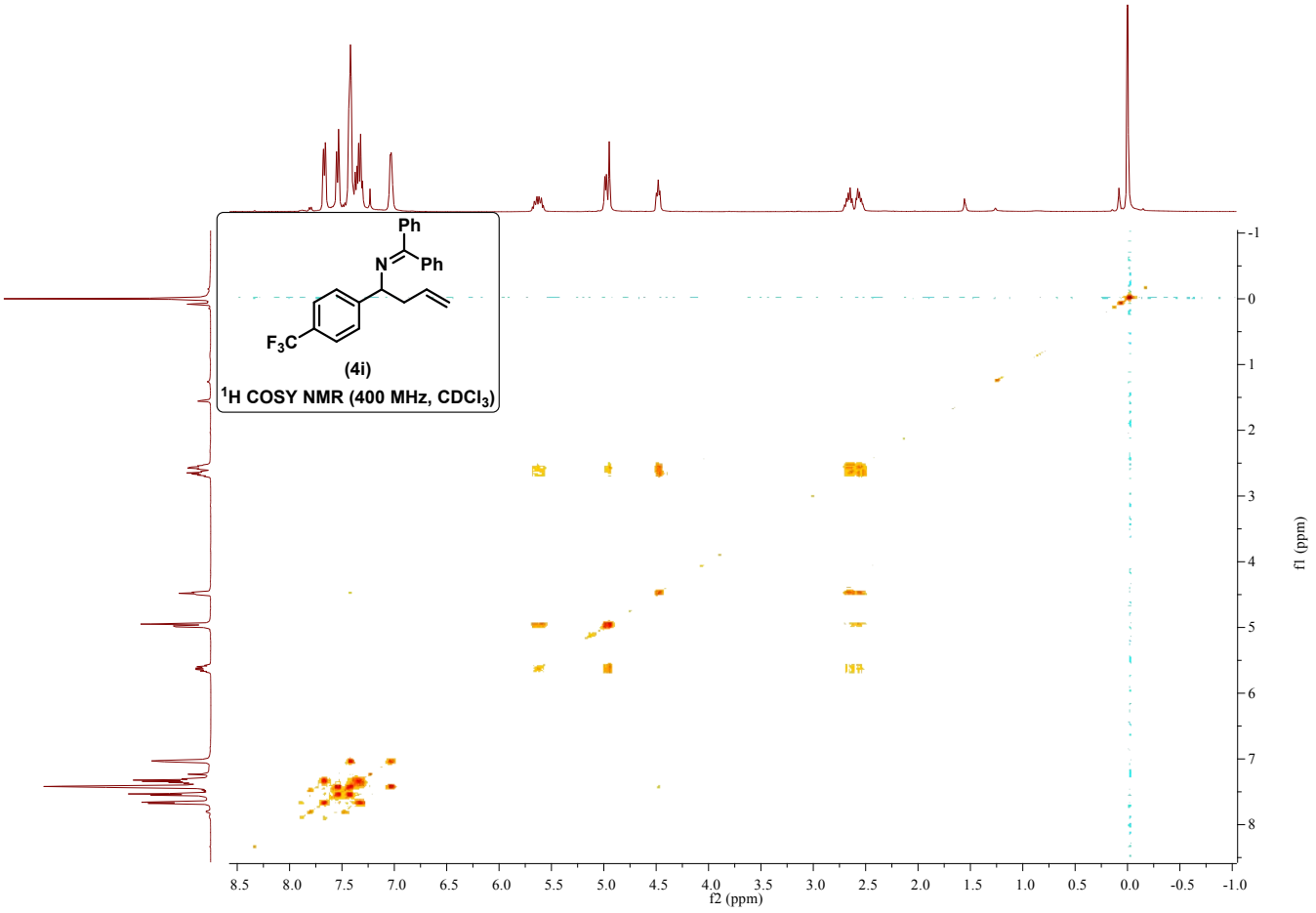


Copies of NMR spectra

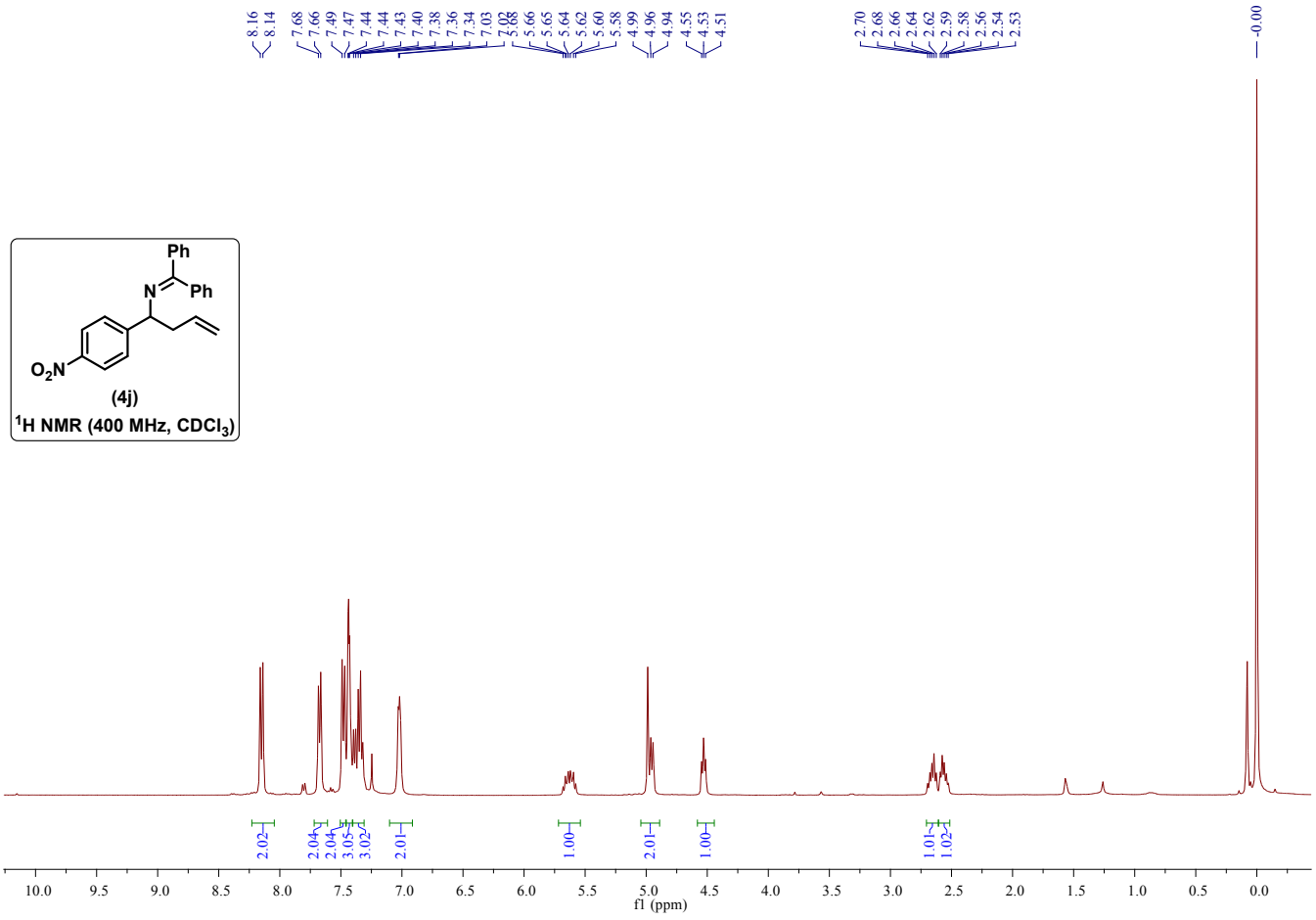


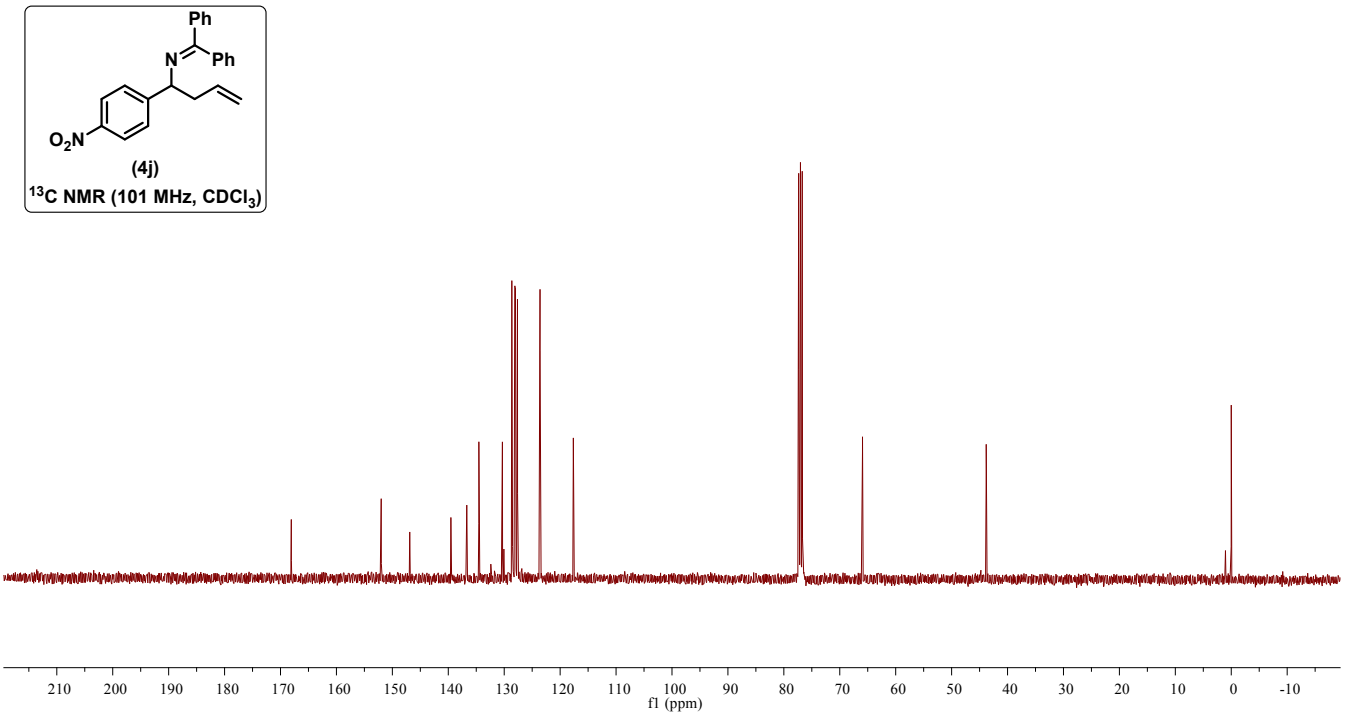


Copies of NMR spectra

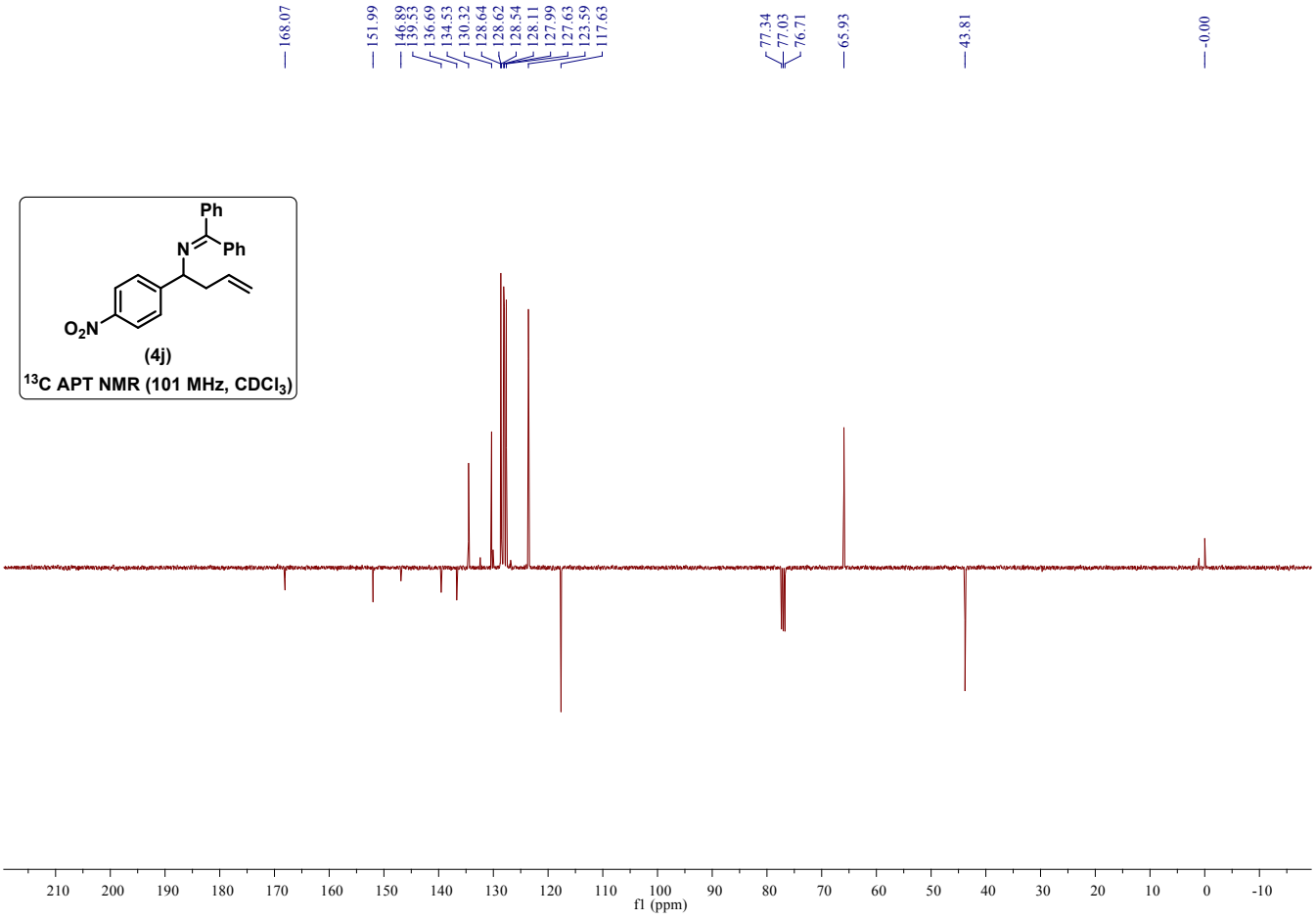


Copies of NMR spectra

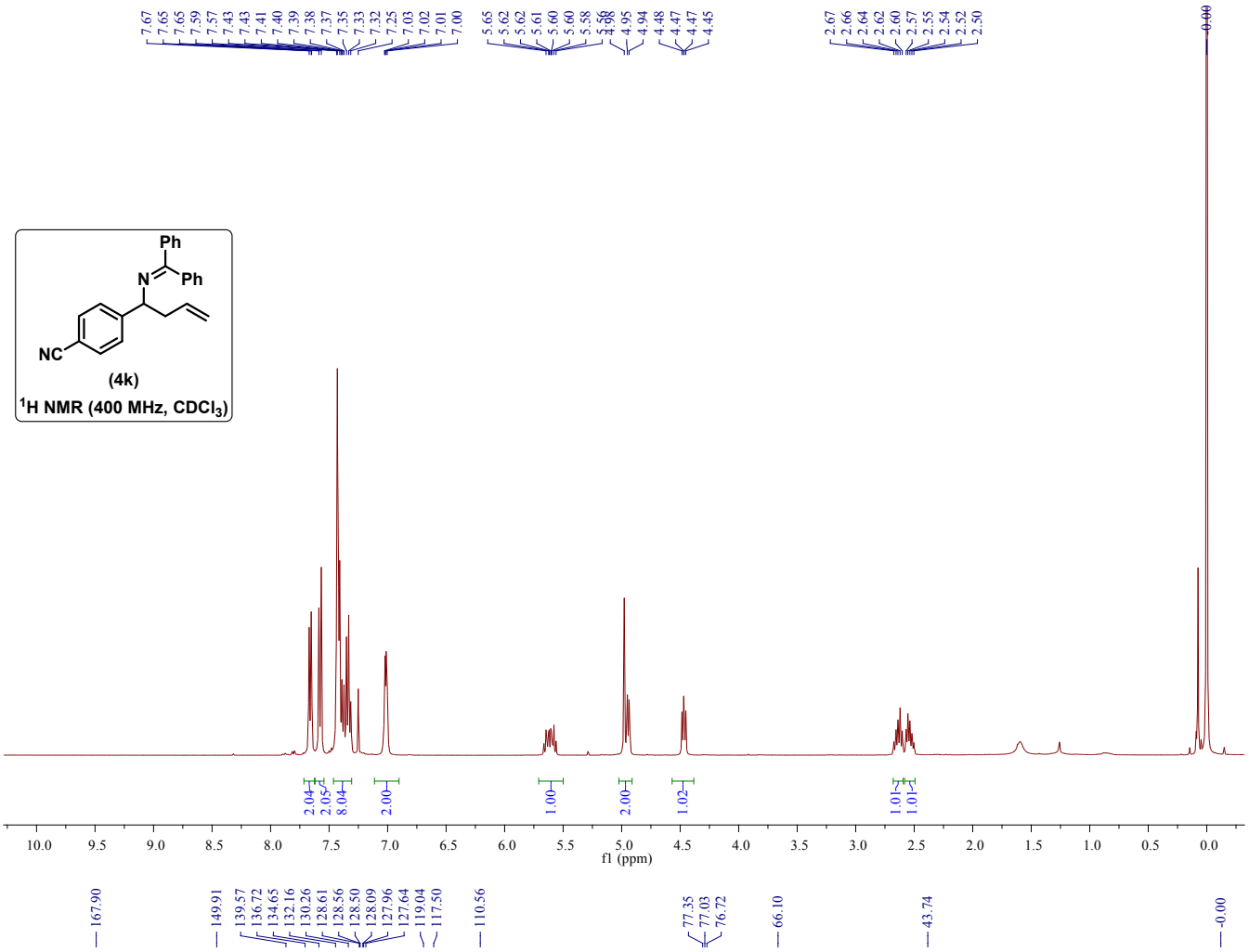


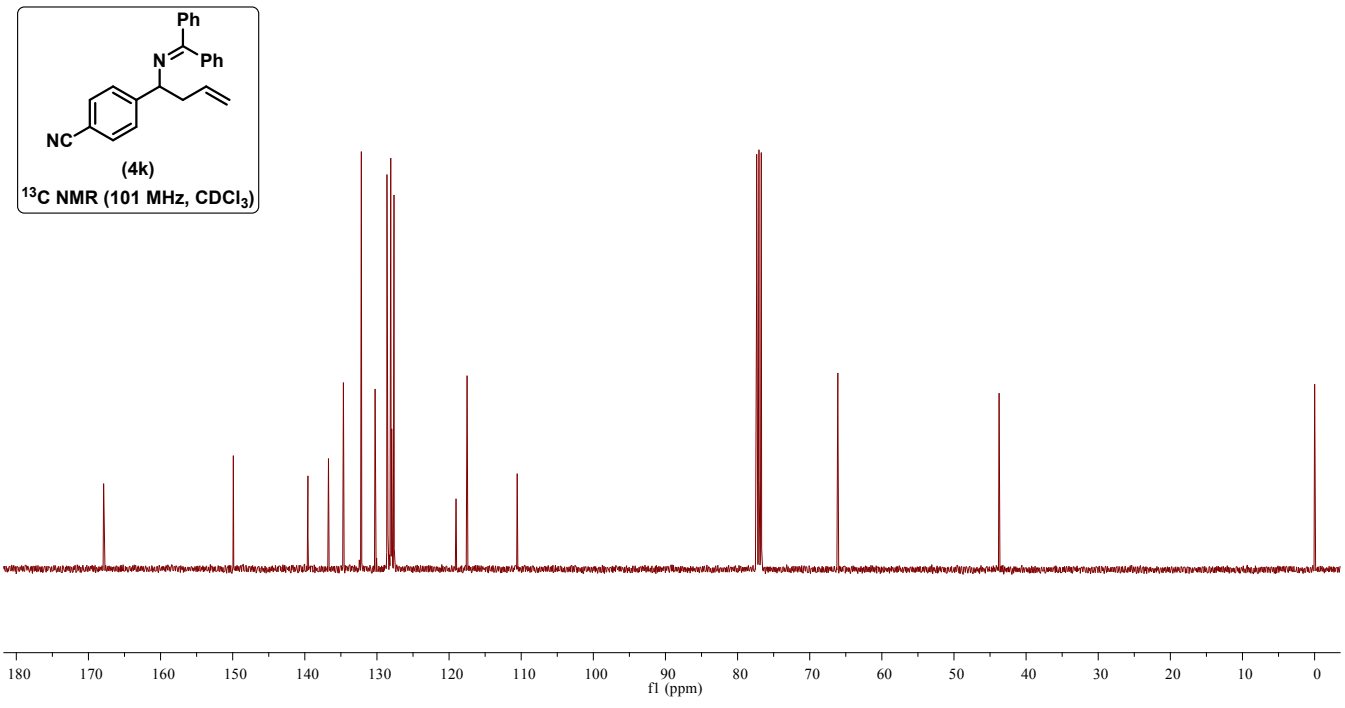


Copies of NMR spectra



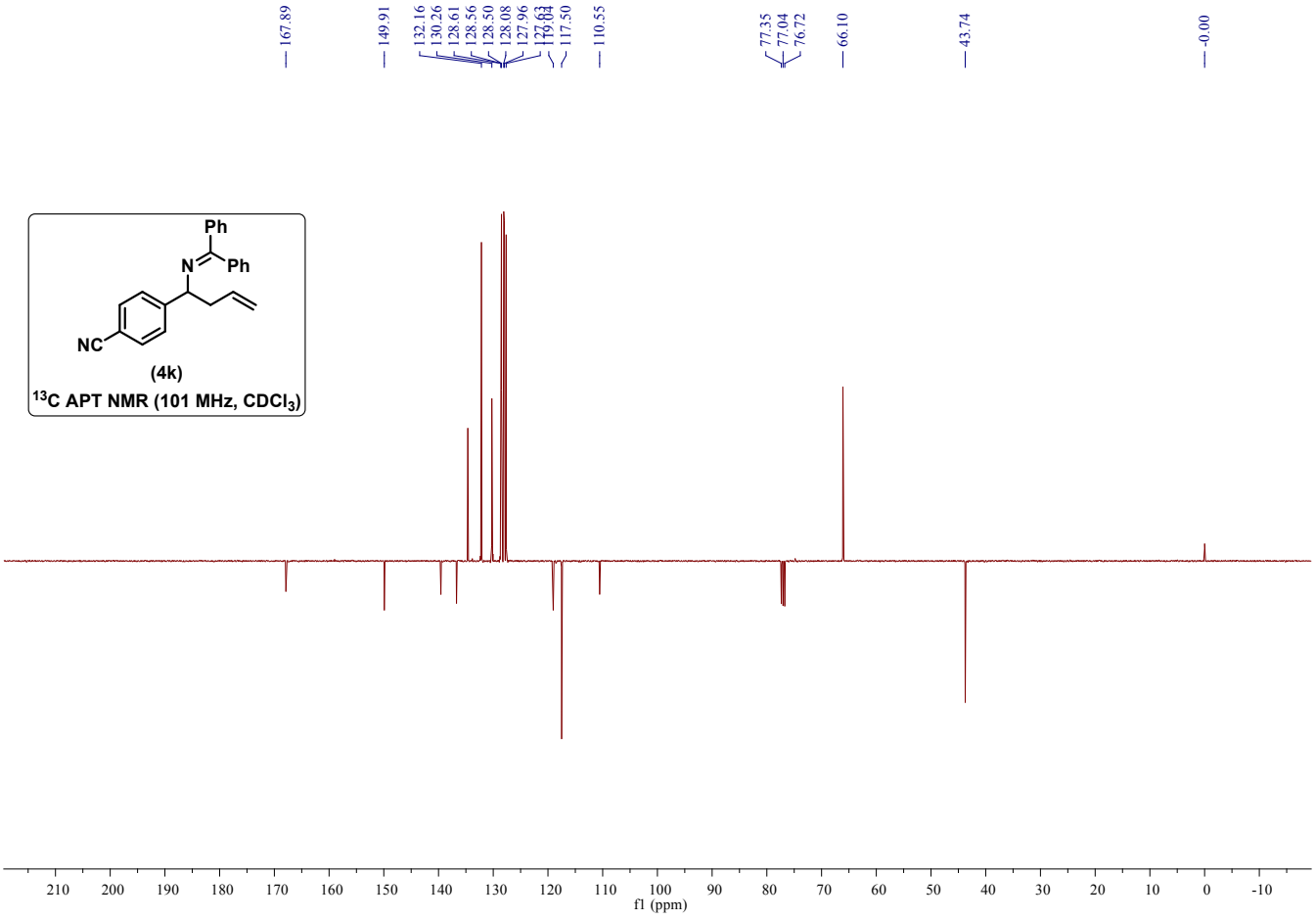
Copies of NMR spectra



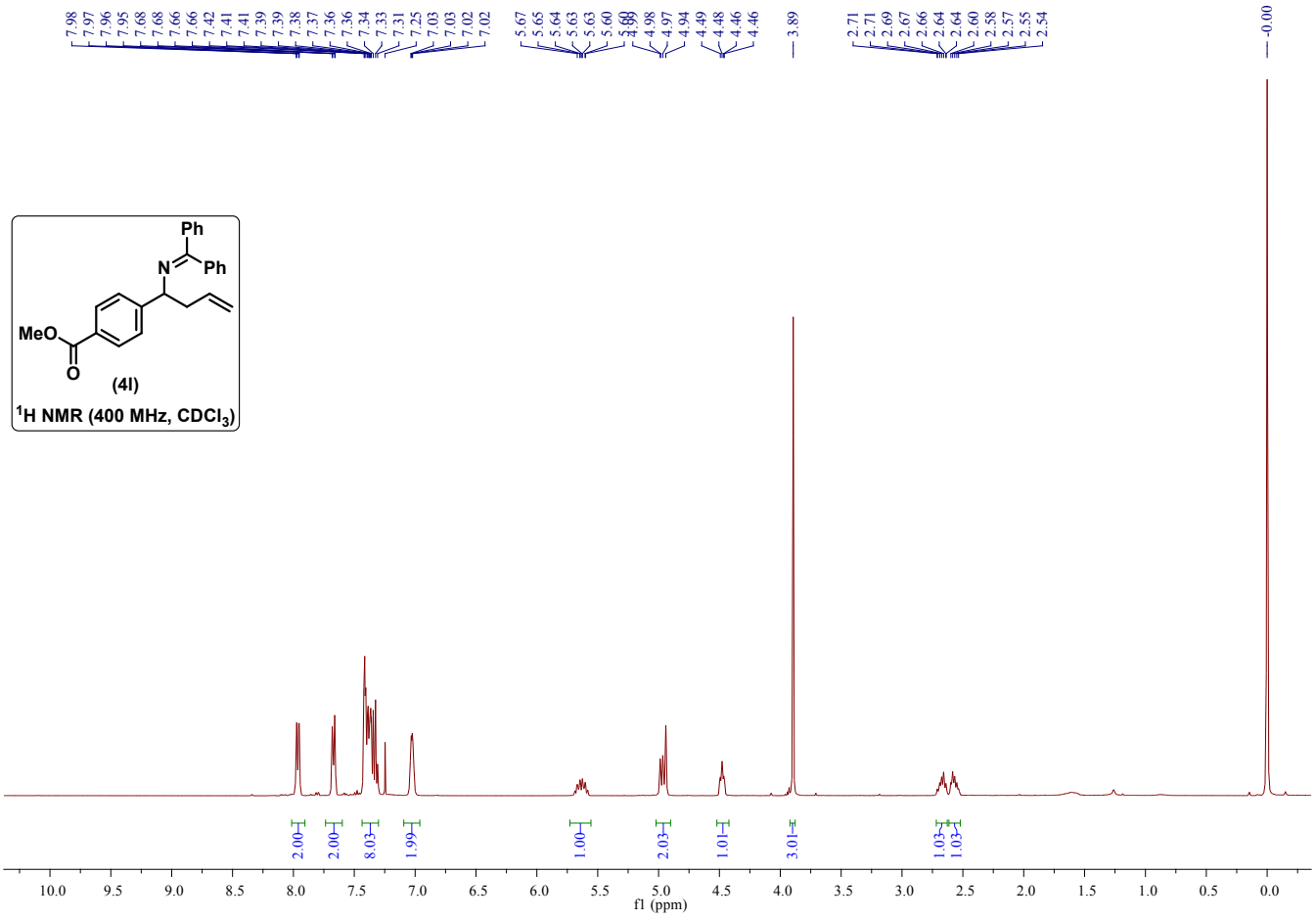


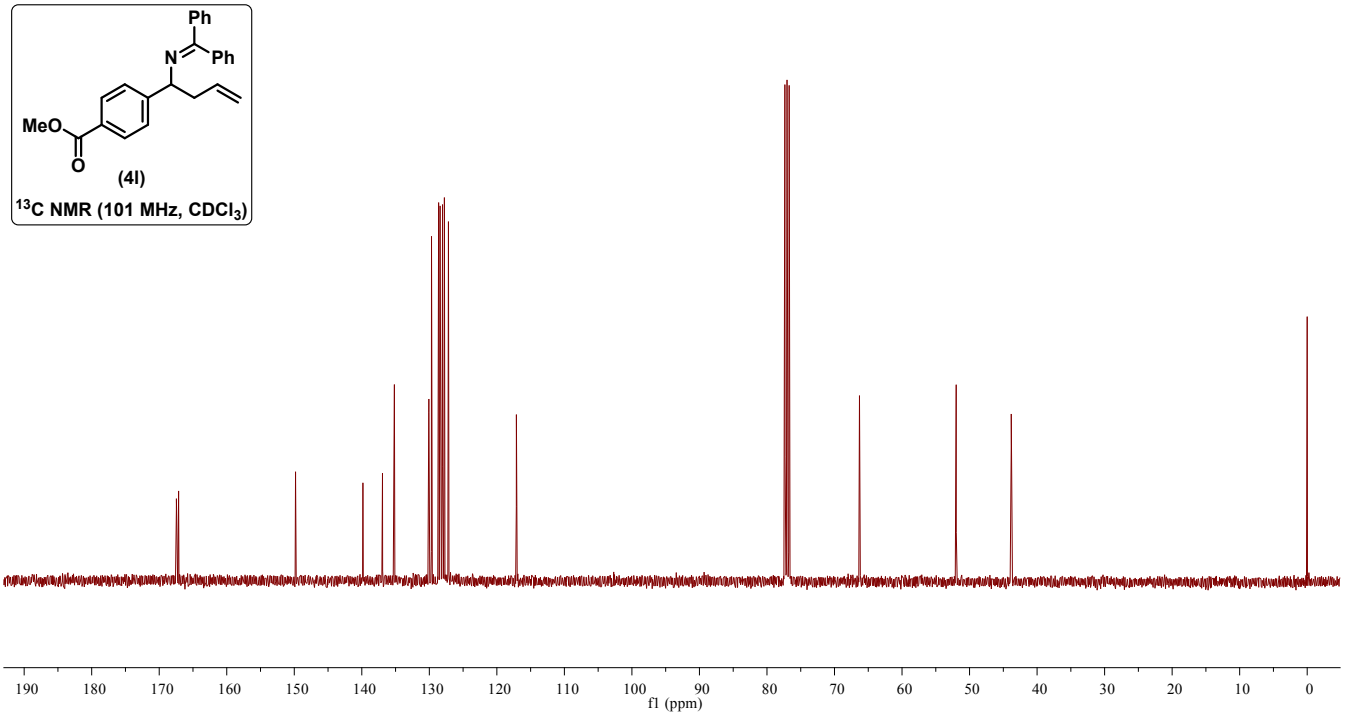
Copies of NMR spectra

z

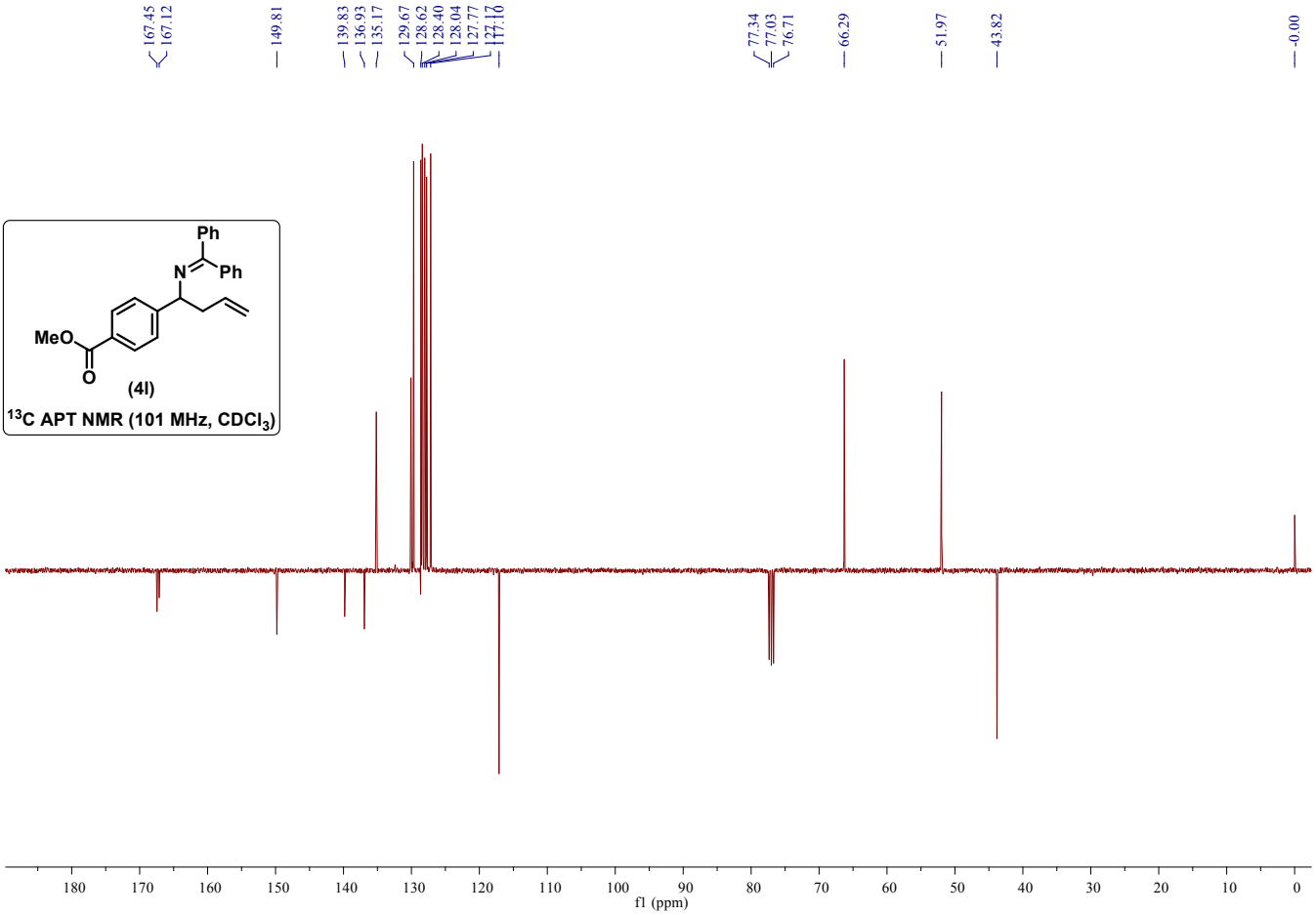


Copies of NMR spectra

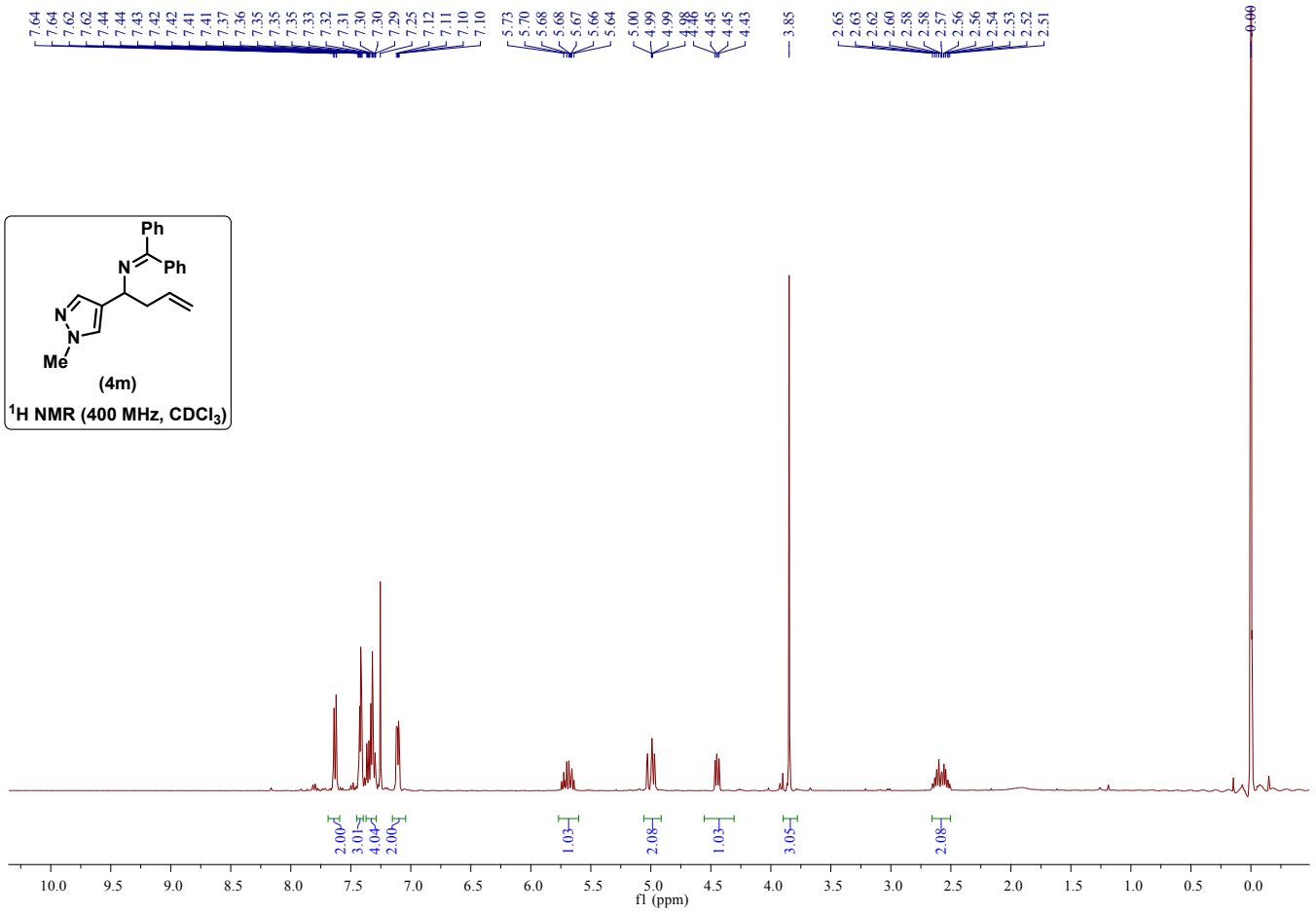


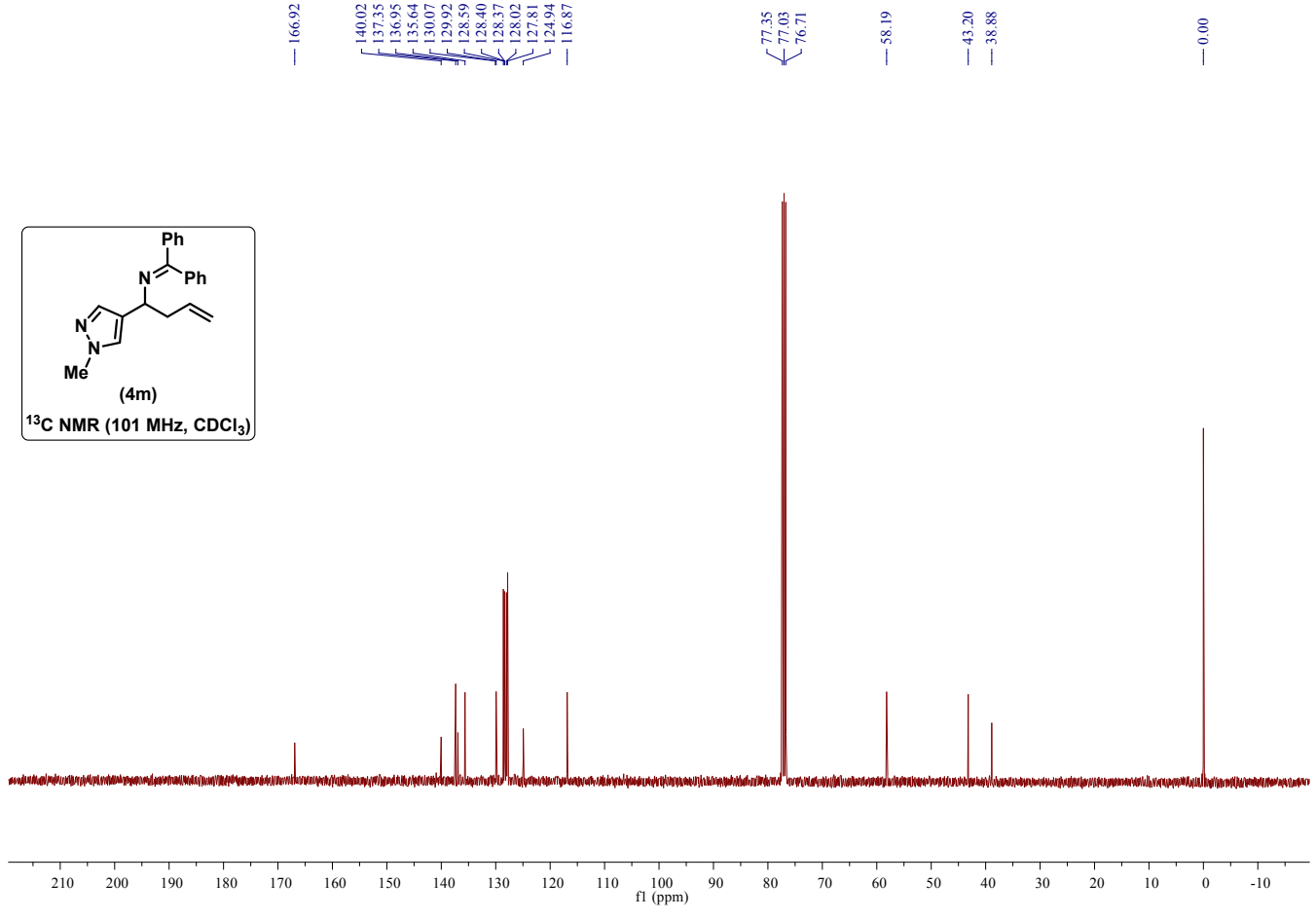


Copies of NMR spectra

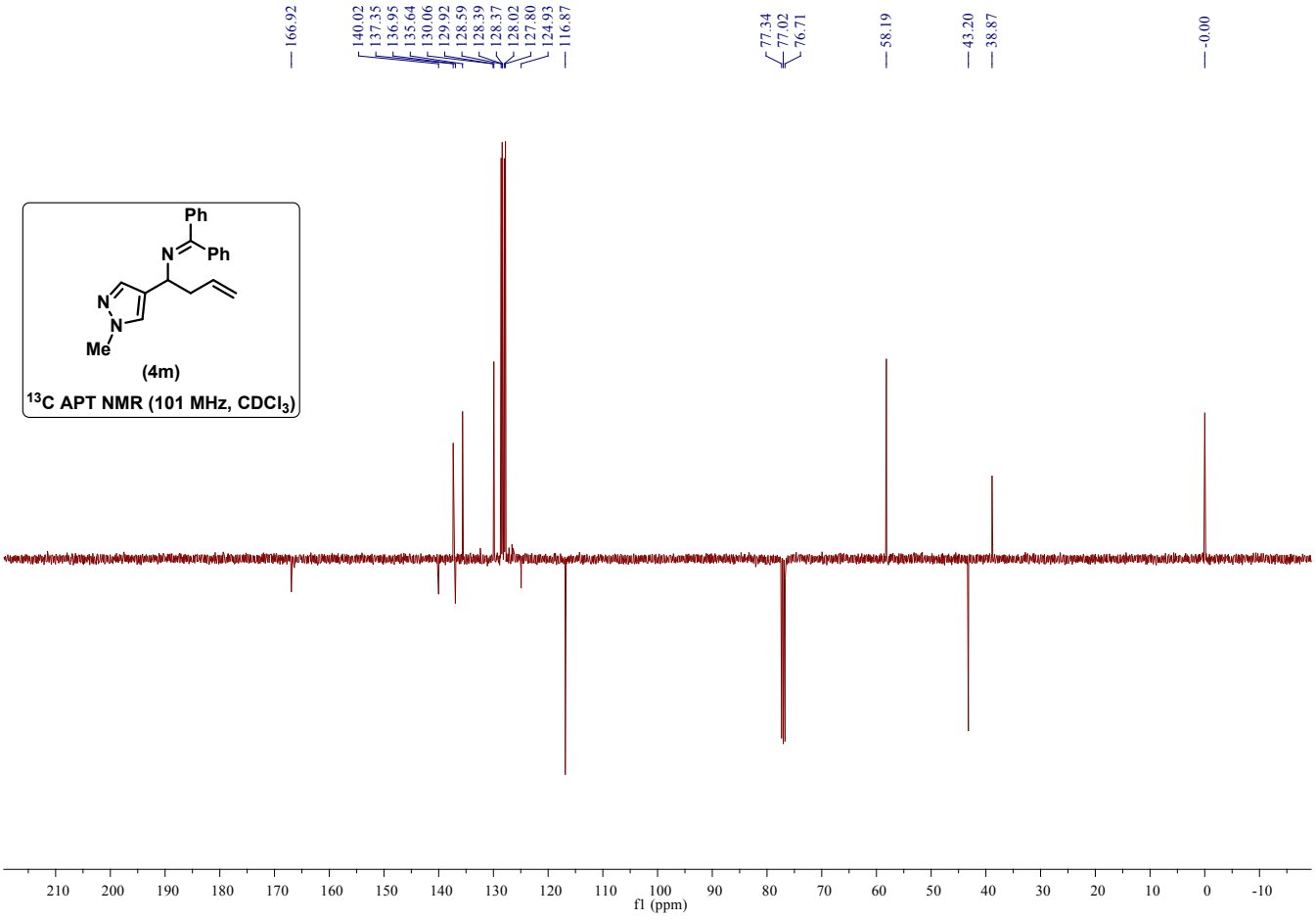


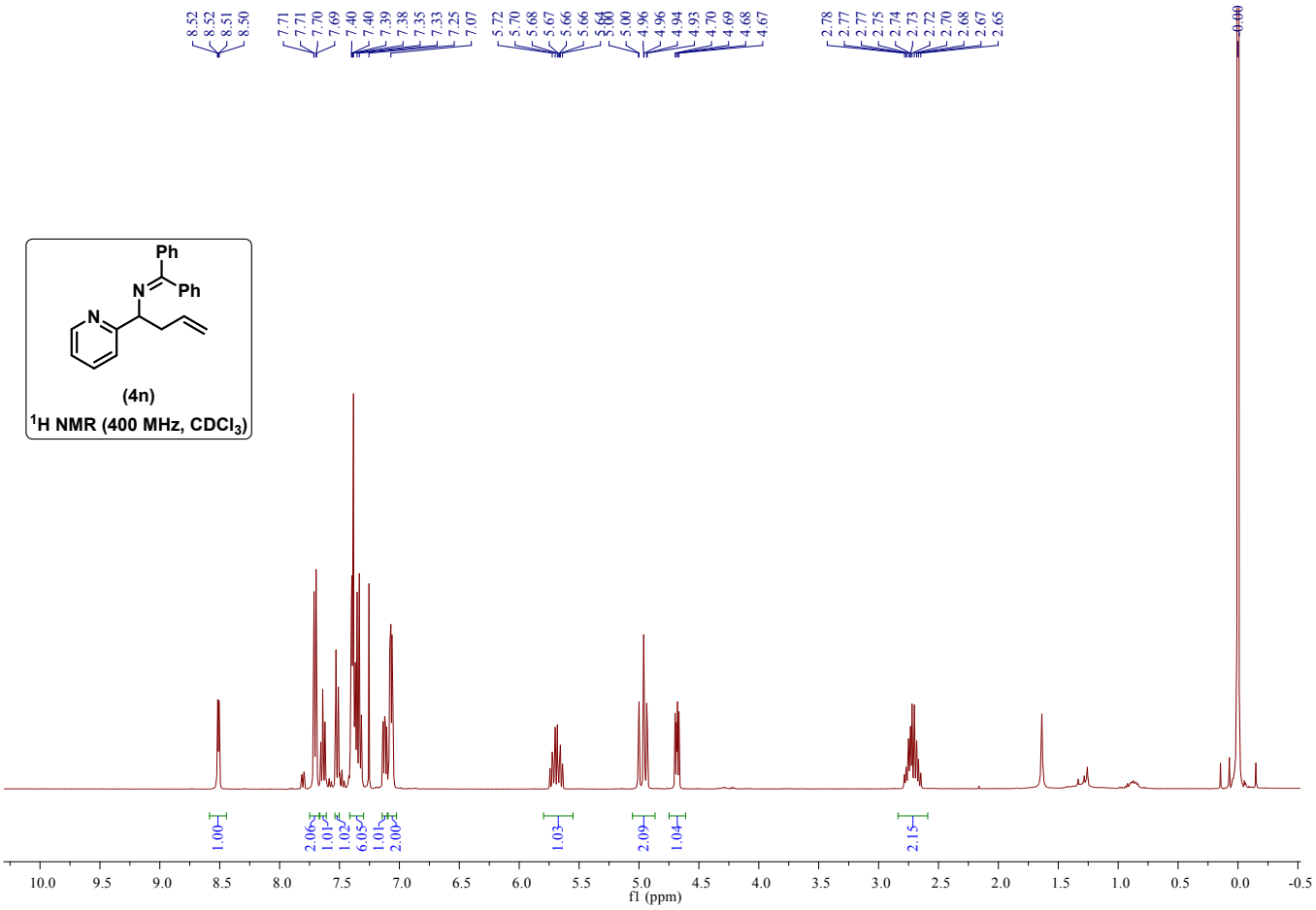
Copies of NMR spectra

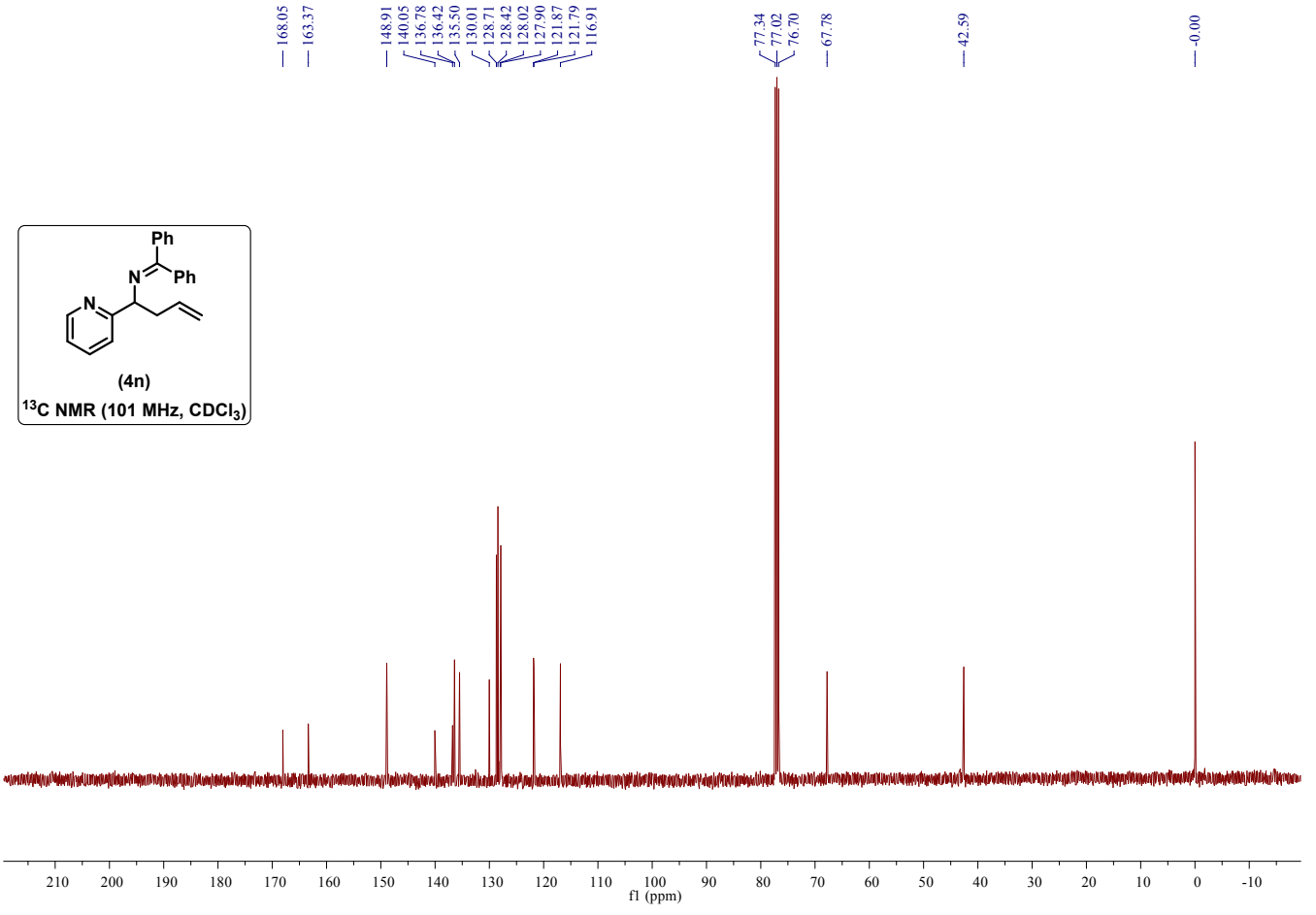




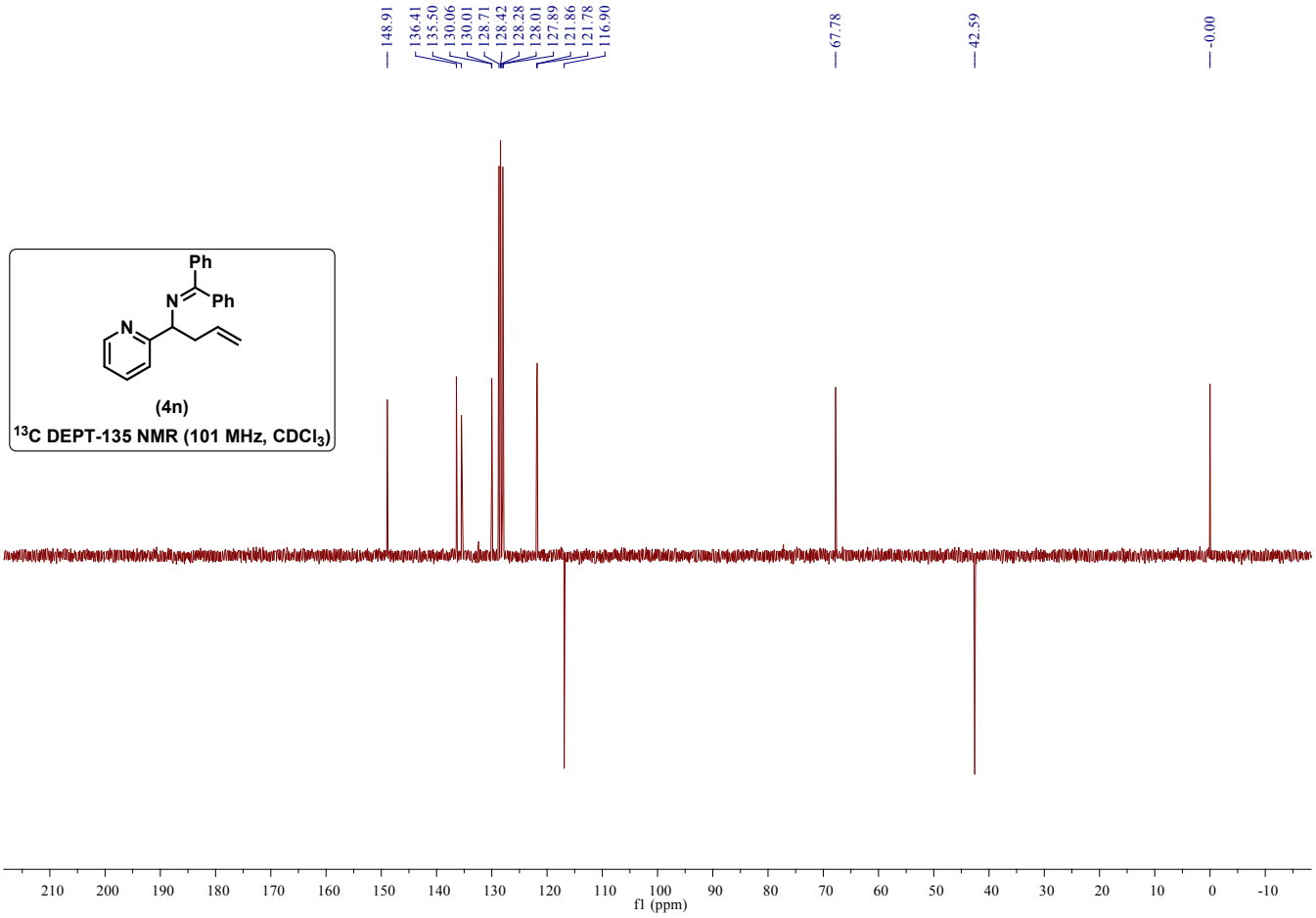
Copies of NMR spectra

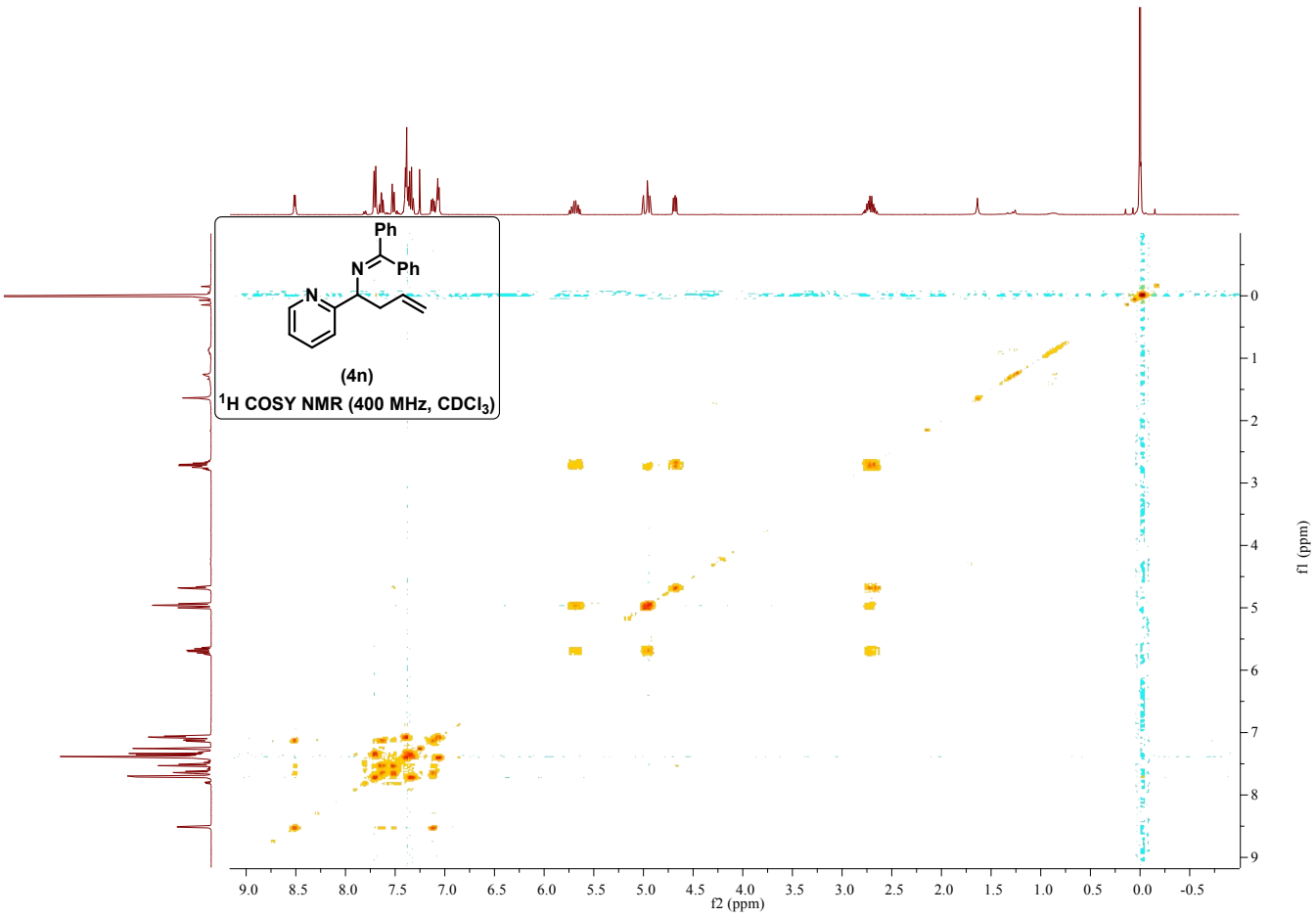



(4n)
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

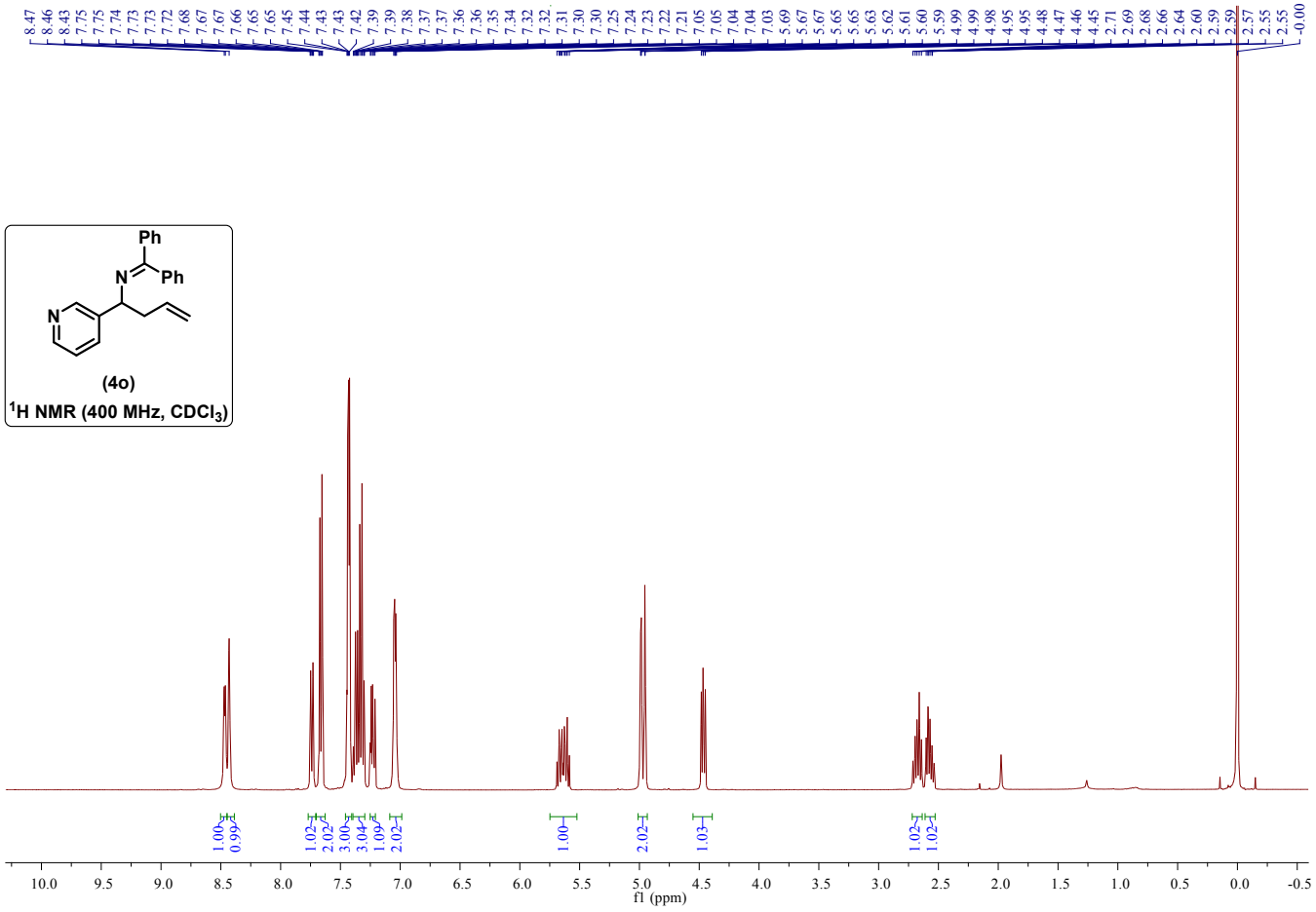

(4n)
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

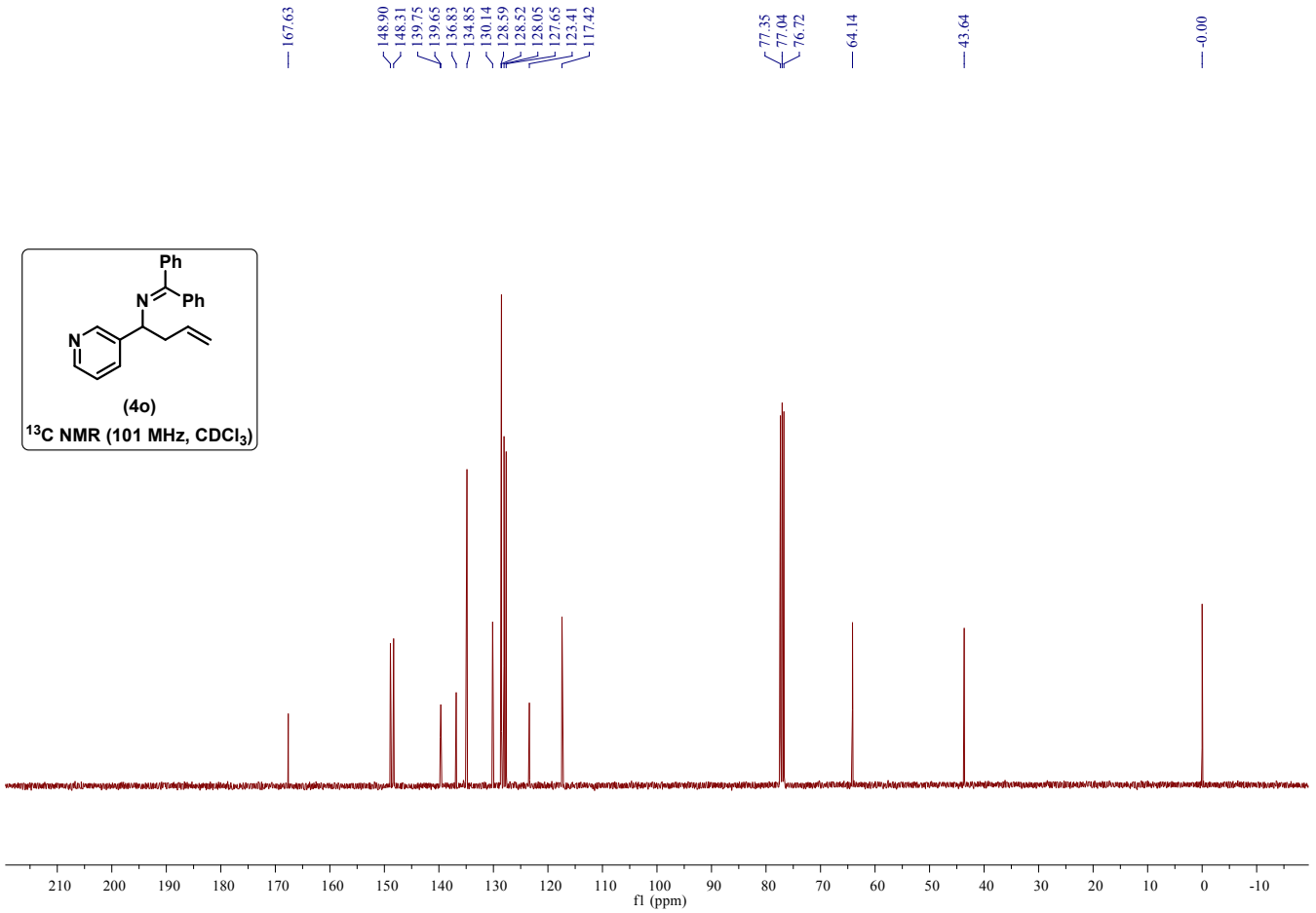
Copies of NMR spectra



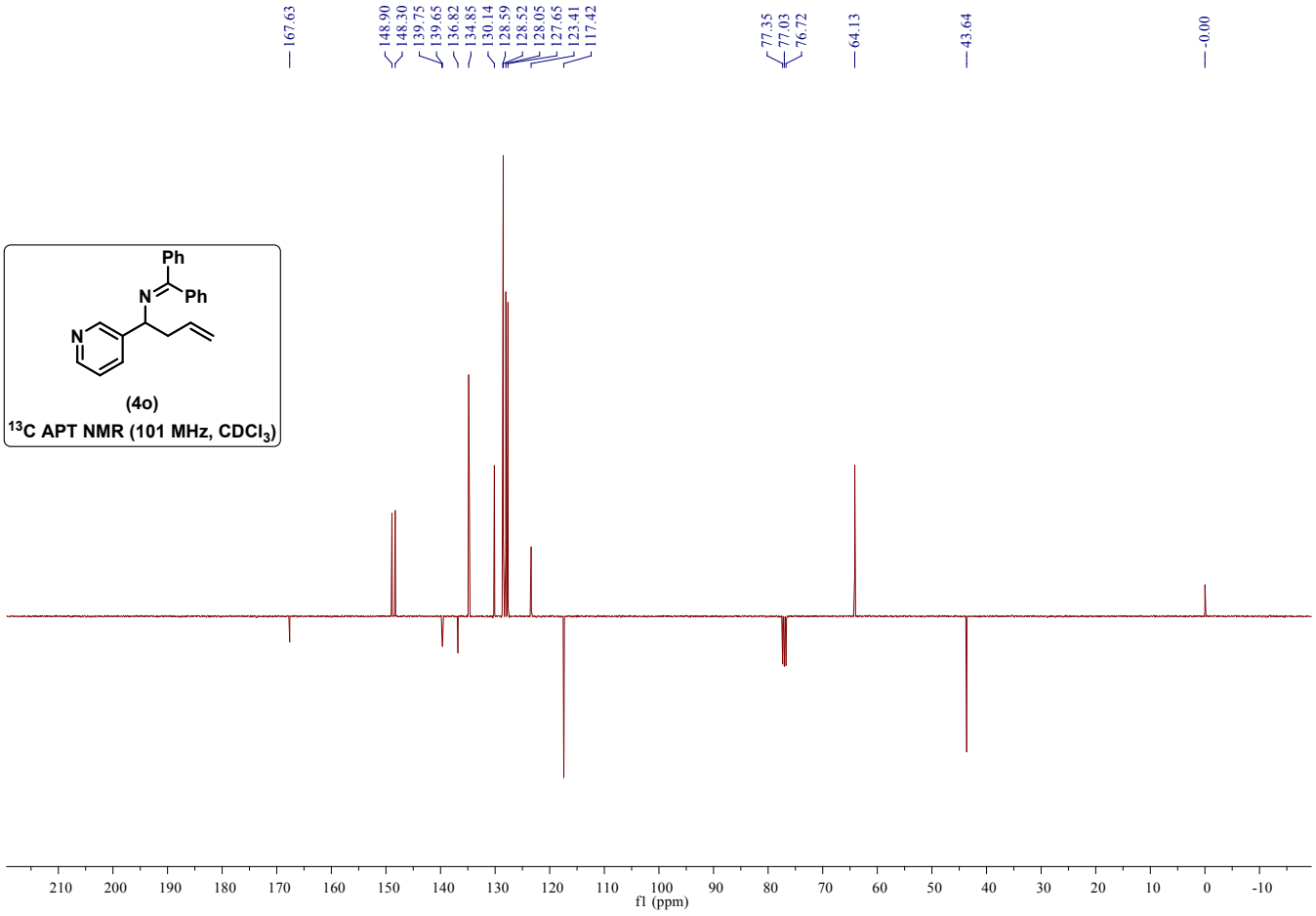


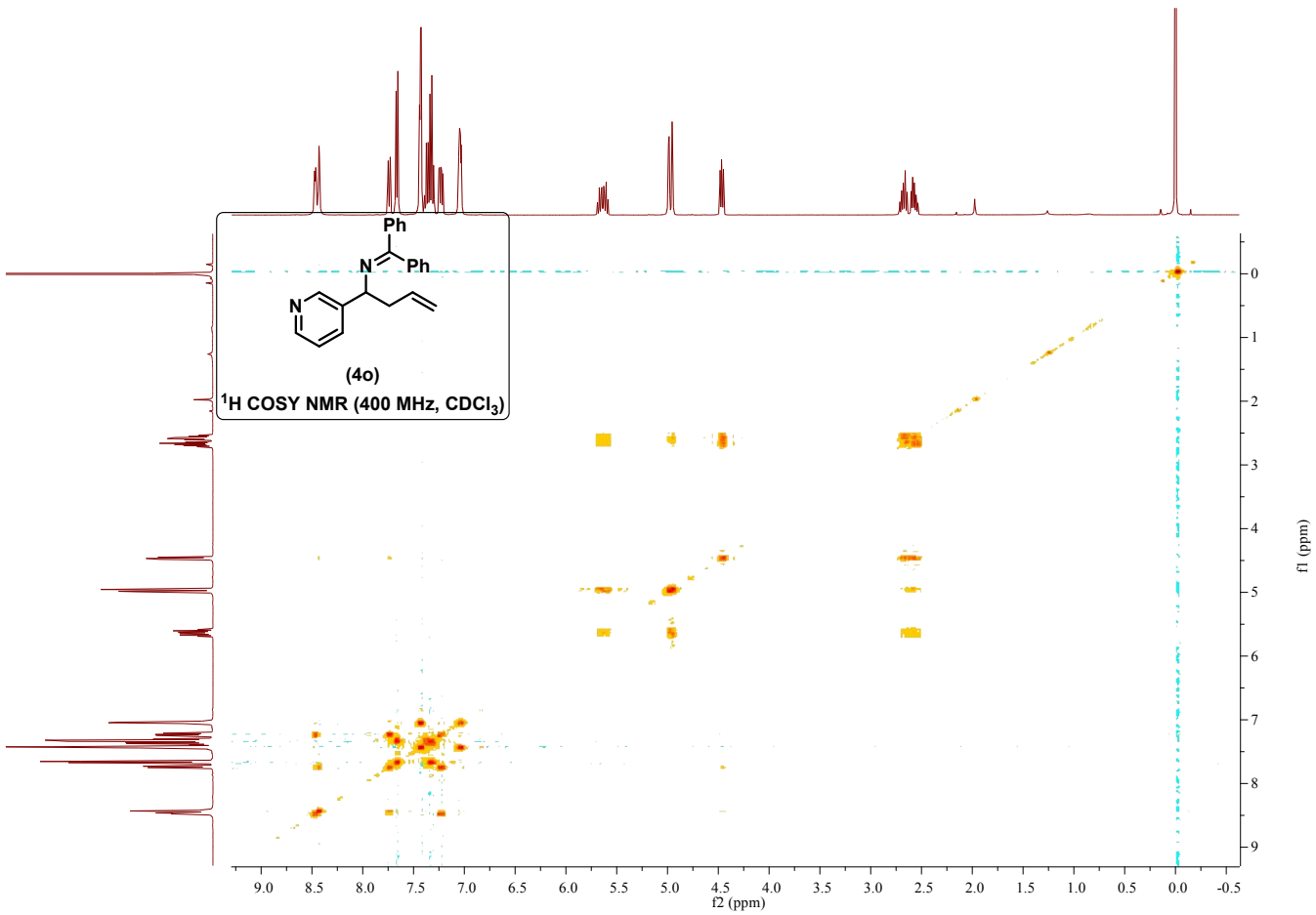
Copies of NMR spectra



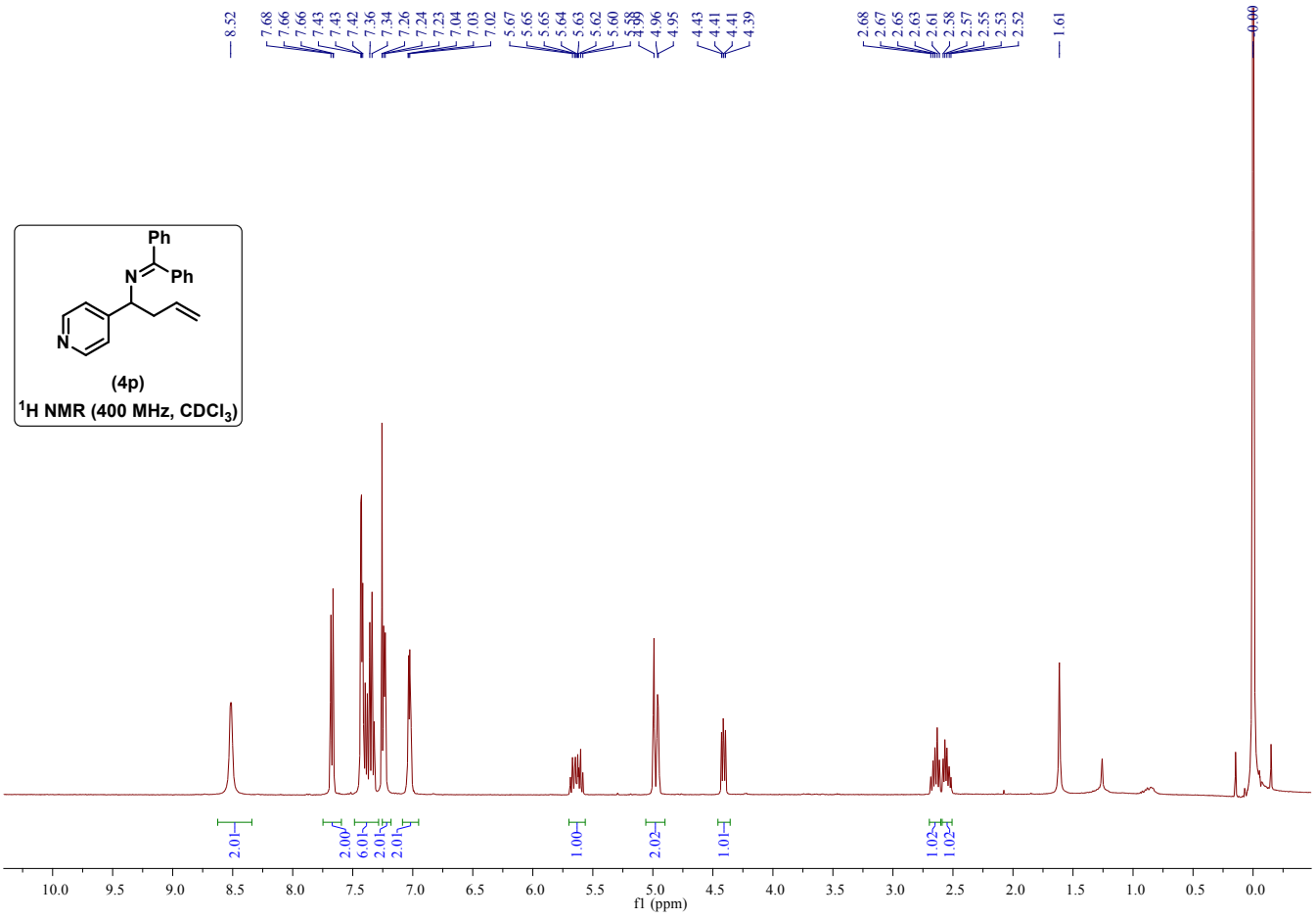


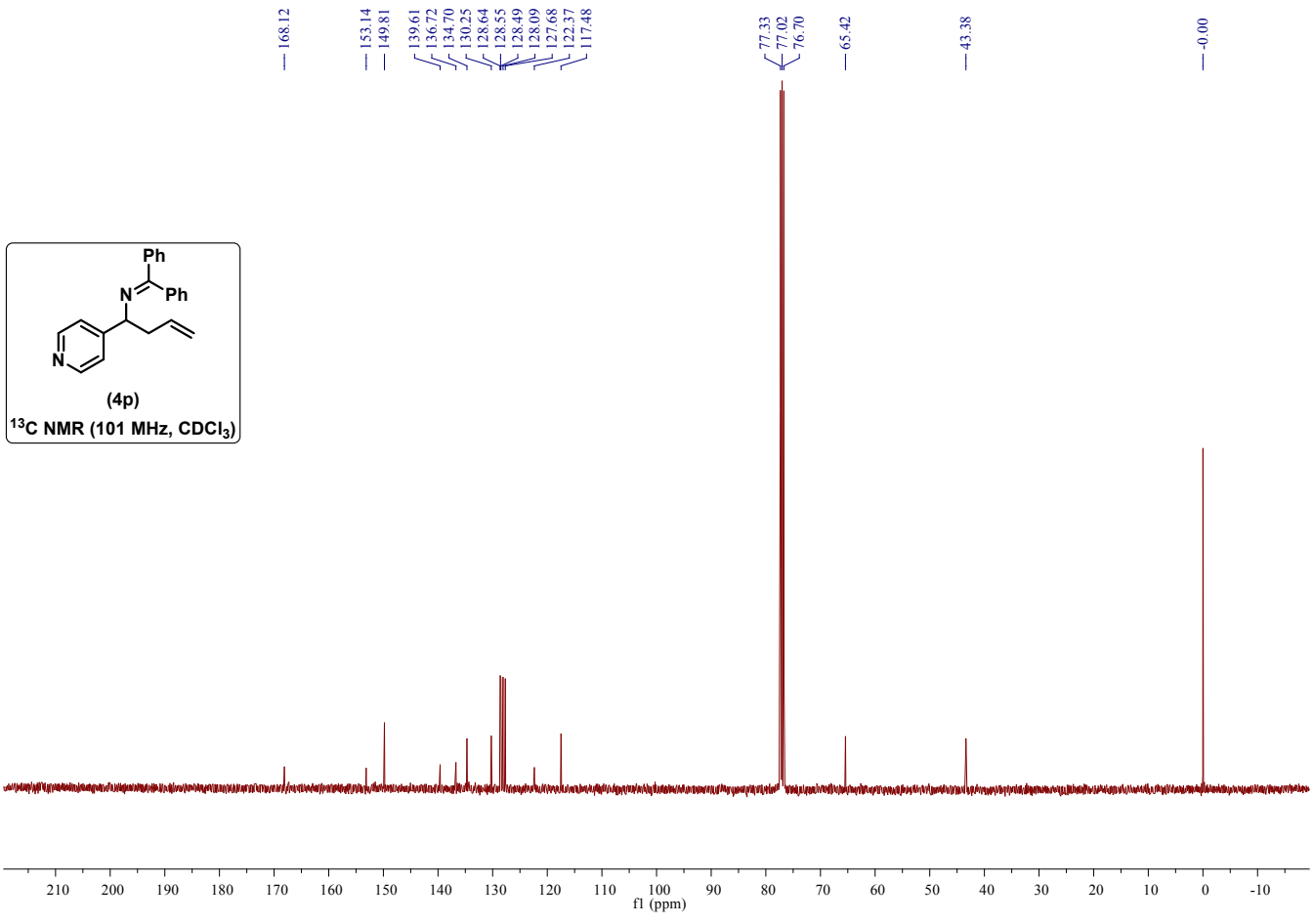
Copies of NMR spectra



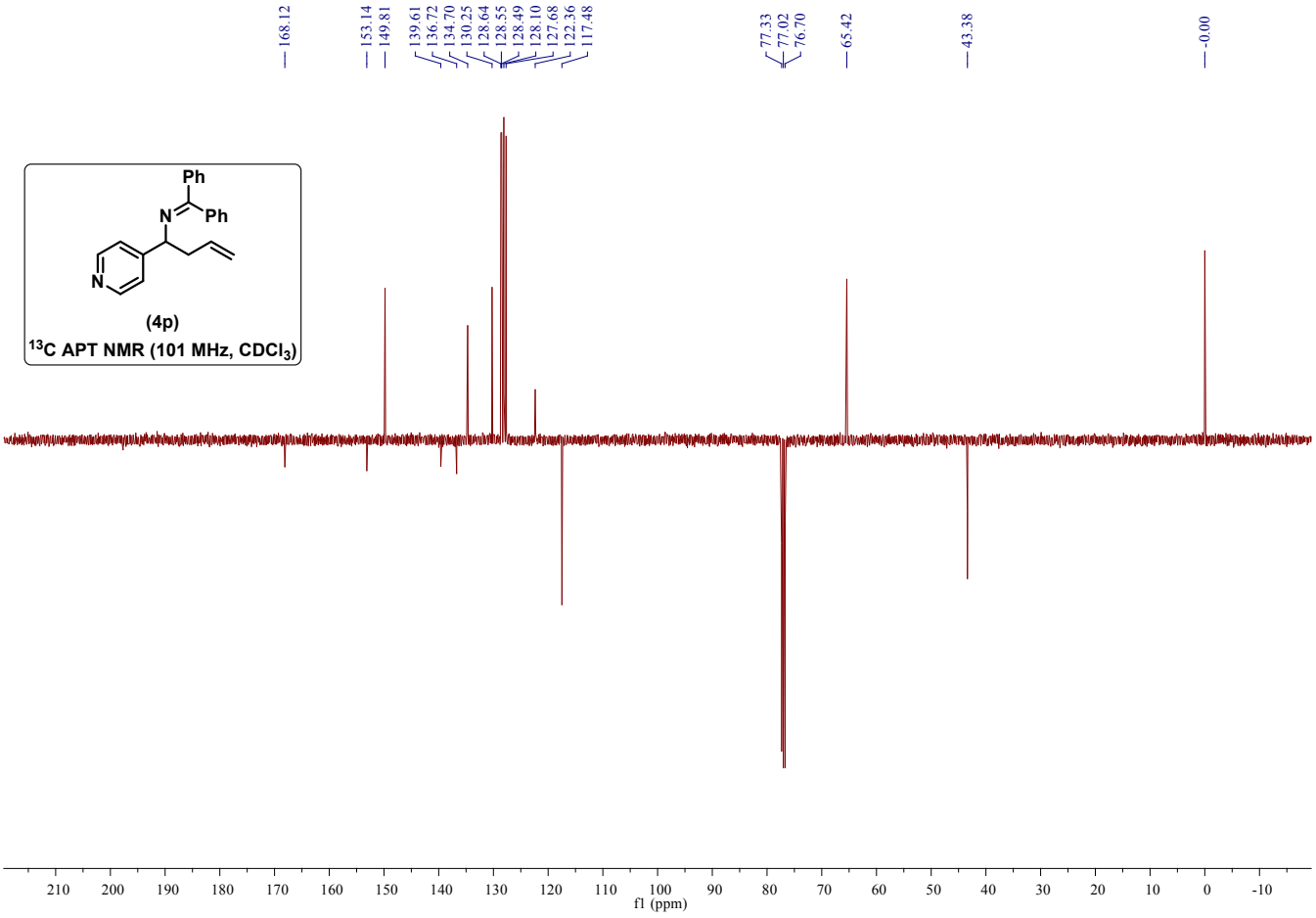


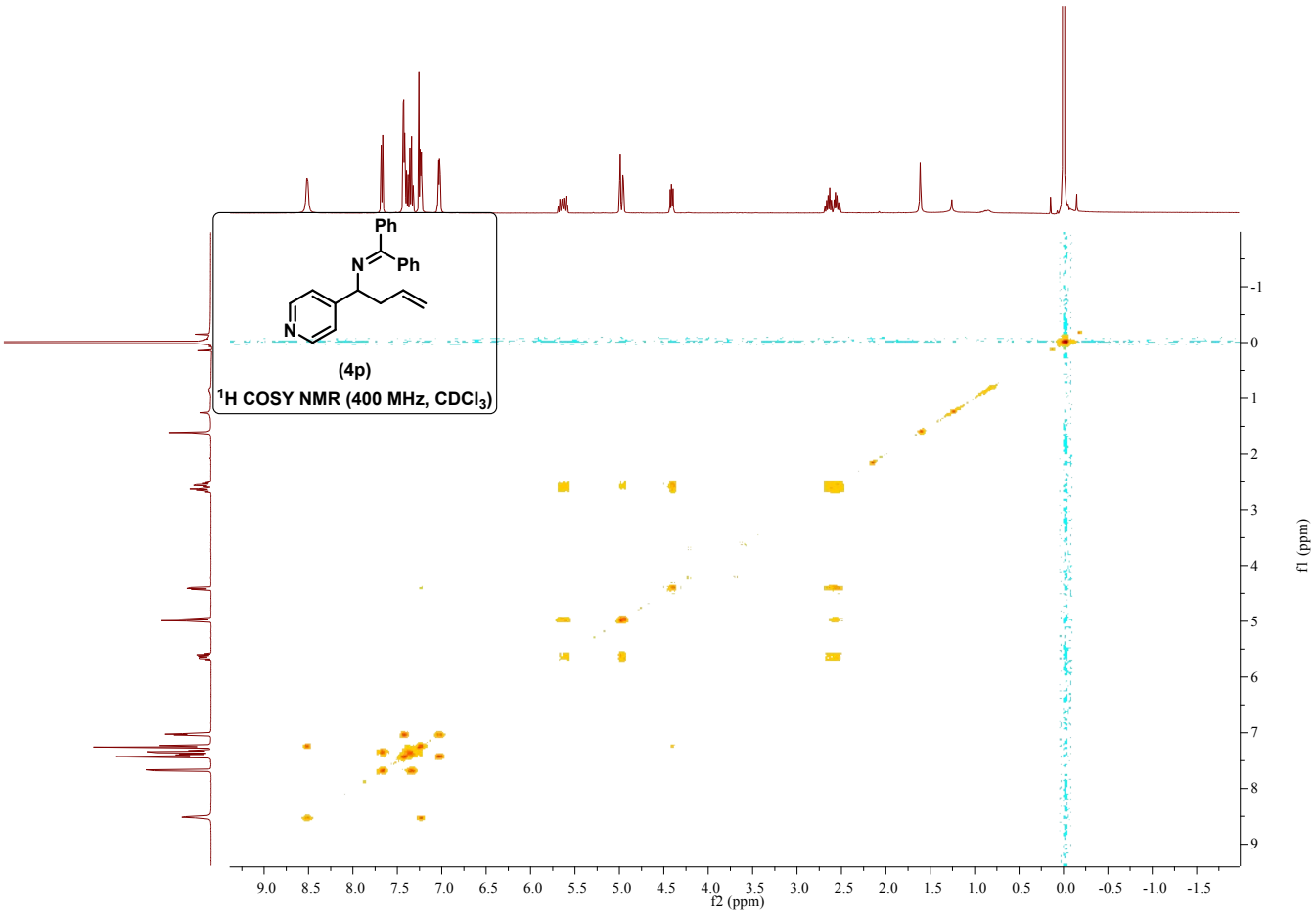
Copies of NMR spectra

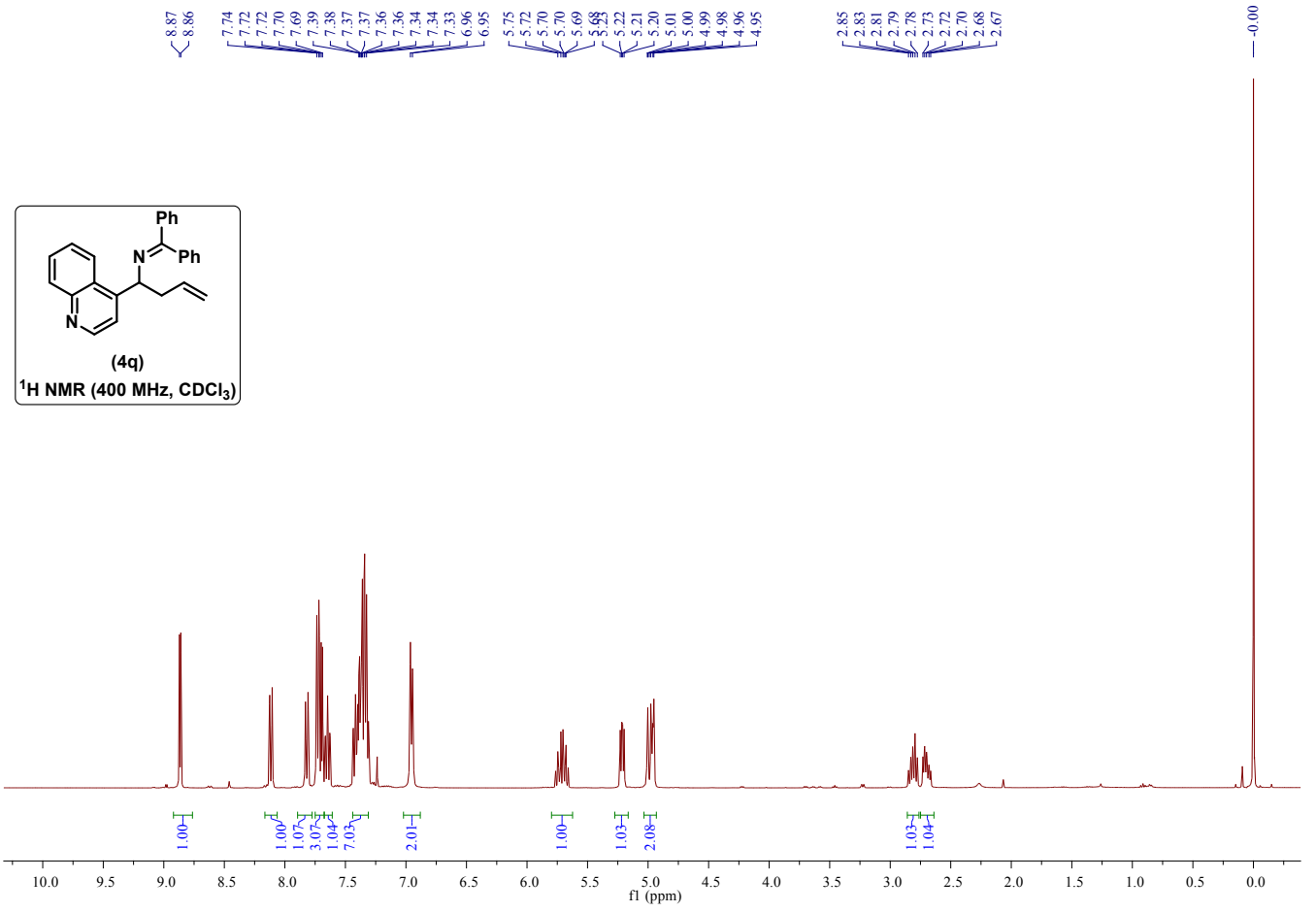


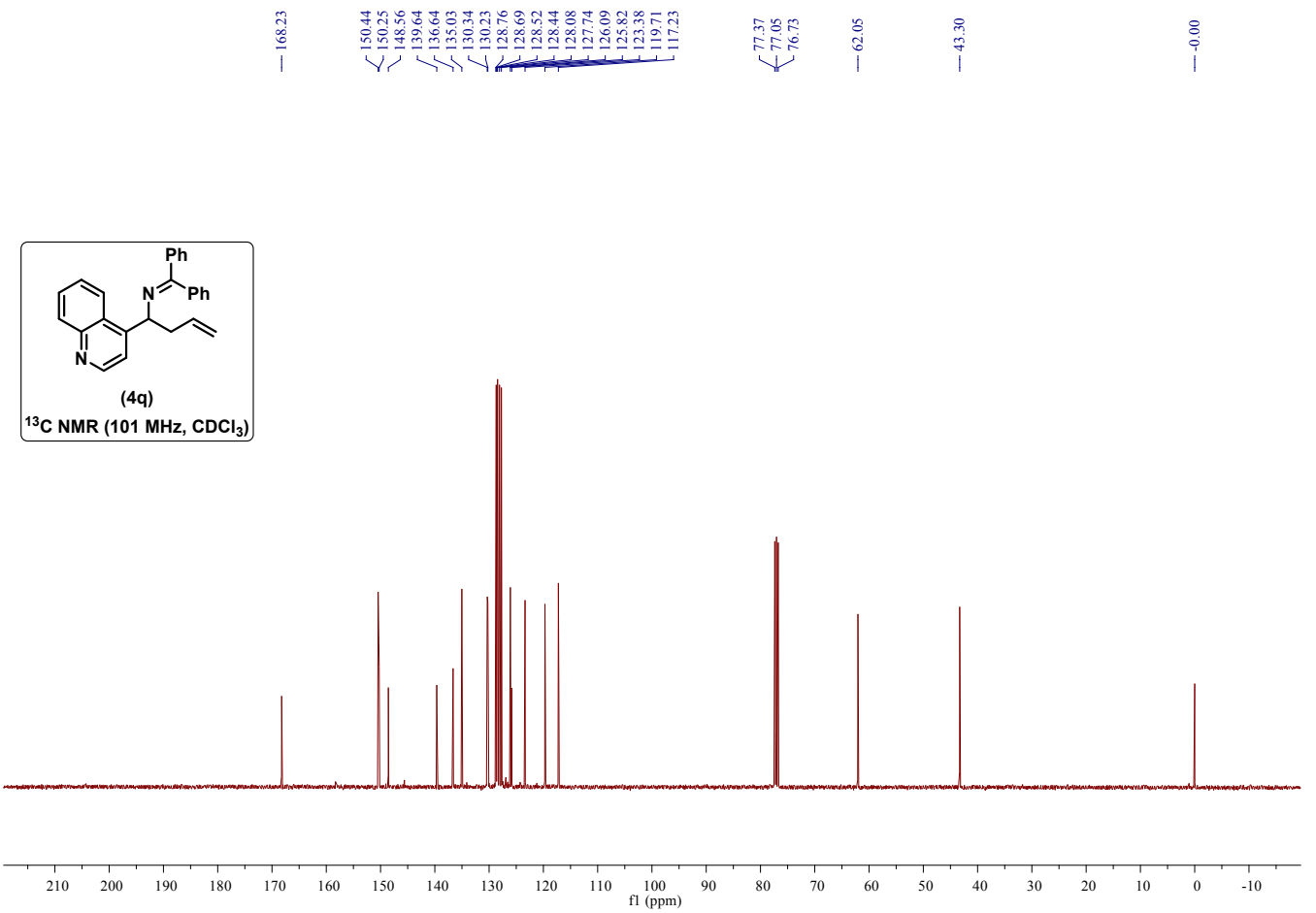


Copies of NMR spectra

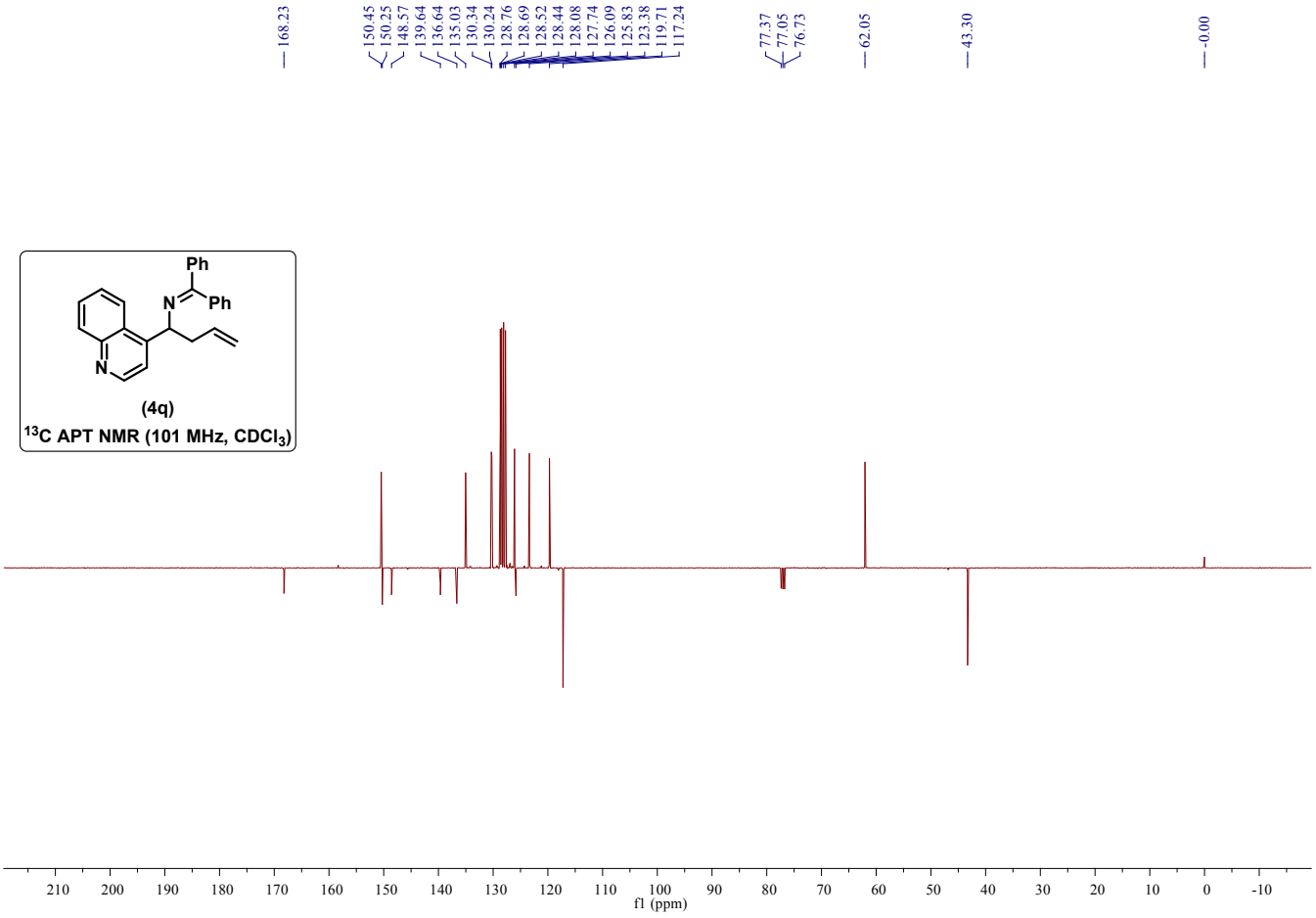


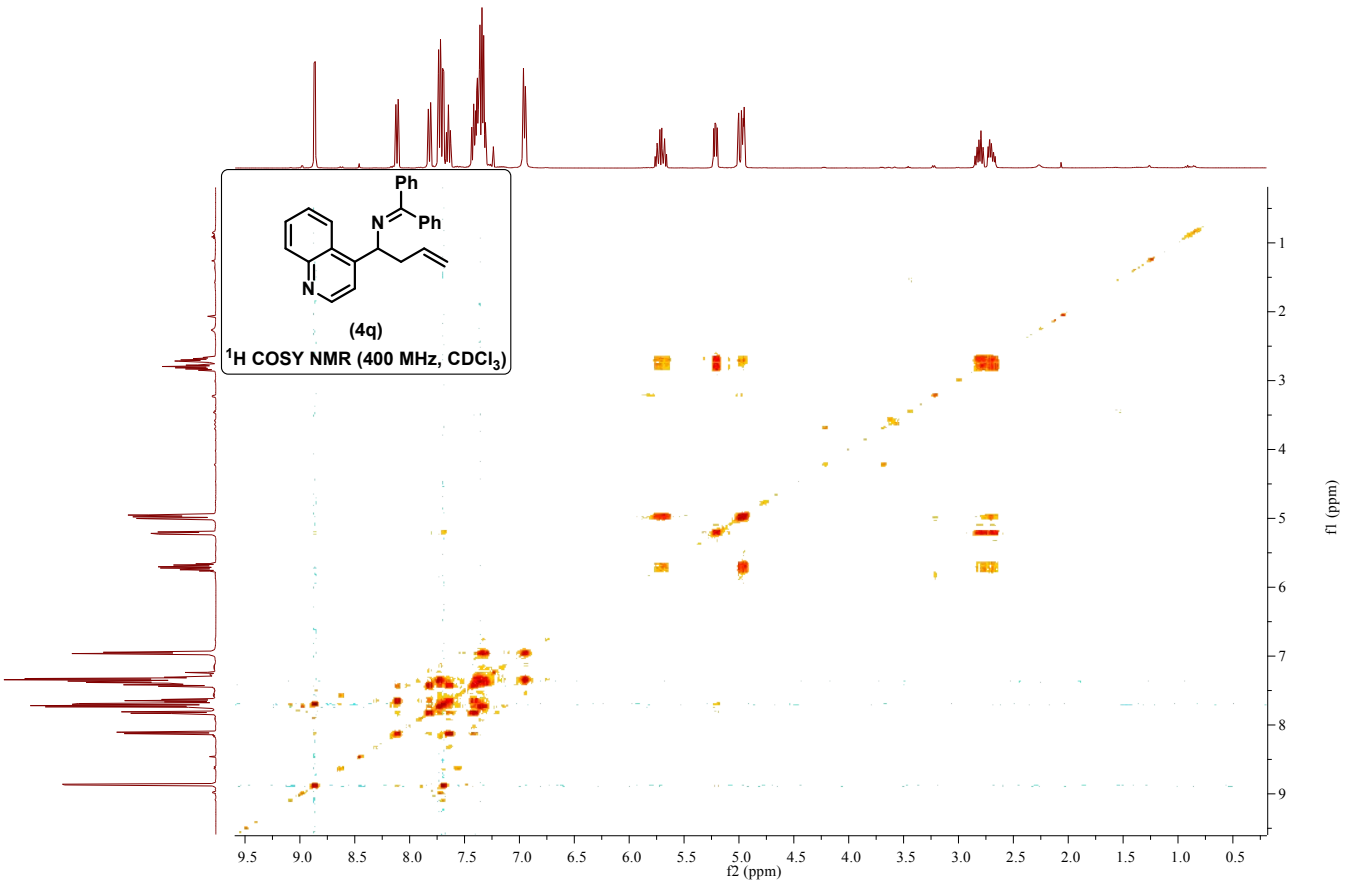



Ph
N
Ph
N
(4q)
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

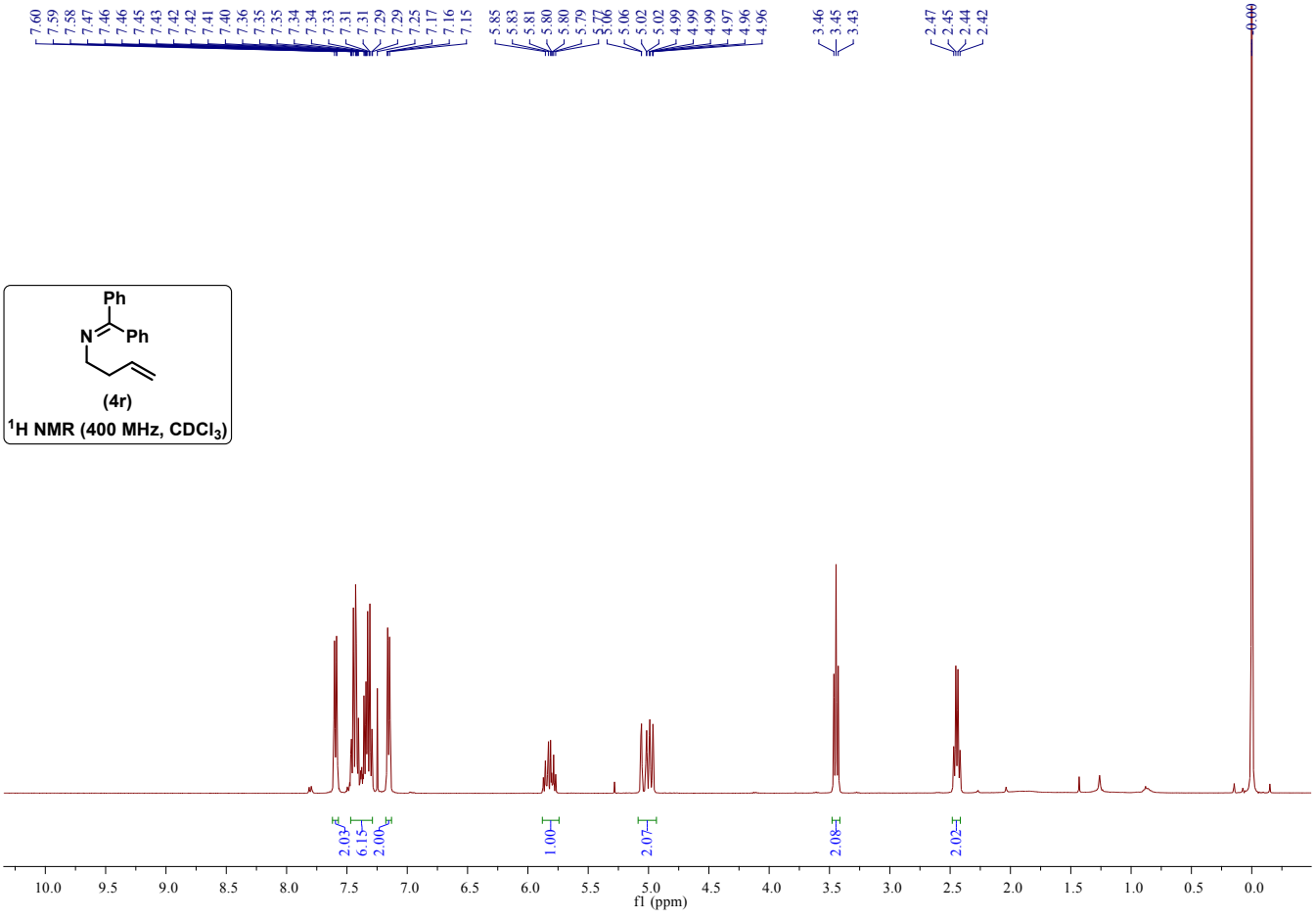

Ph
N
Ph
N
(4q)
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

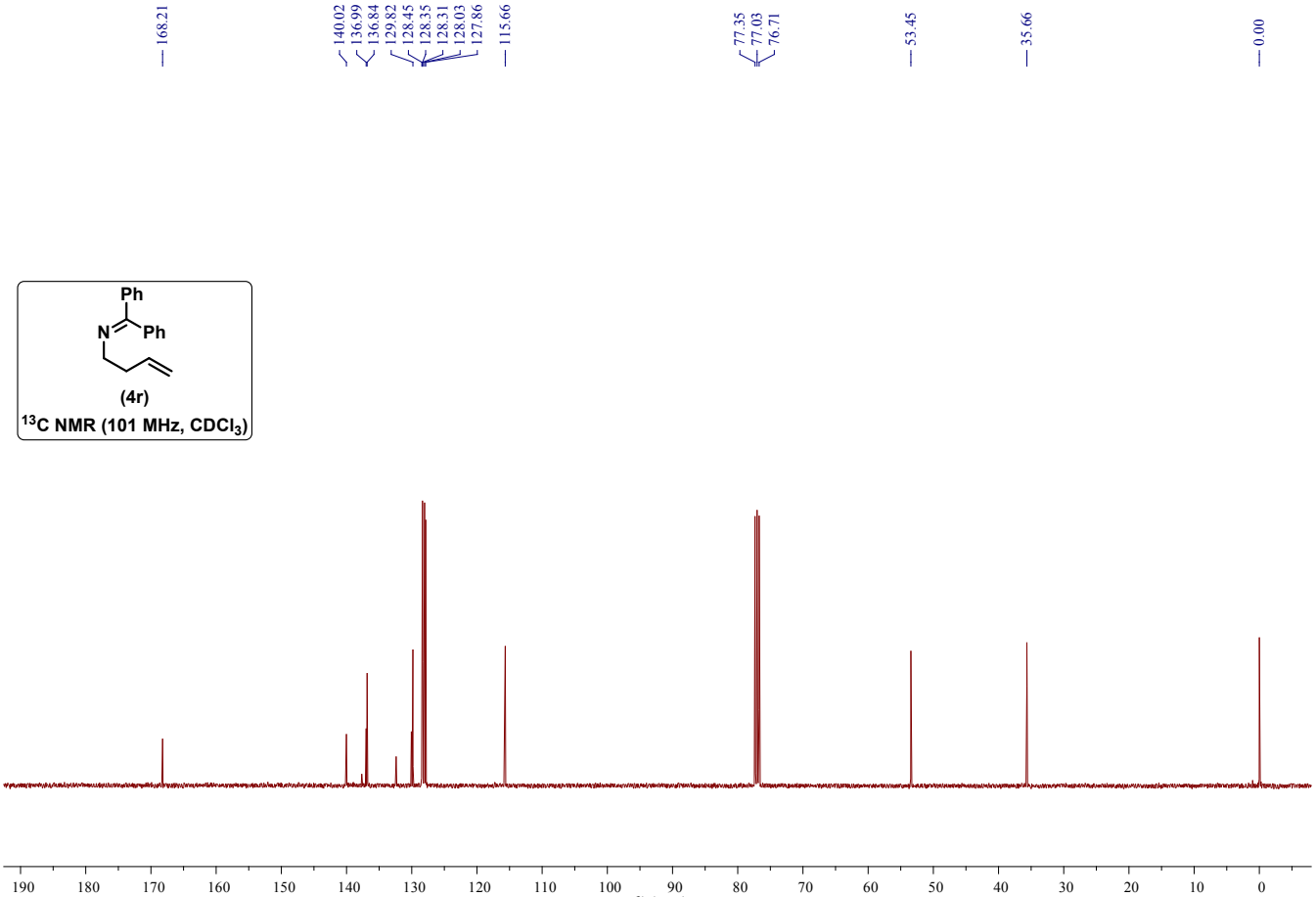
Copies of NMR spectra



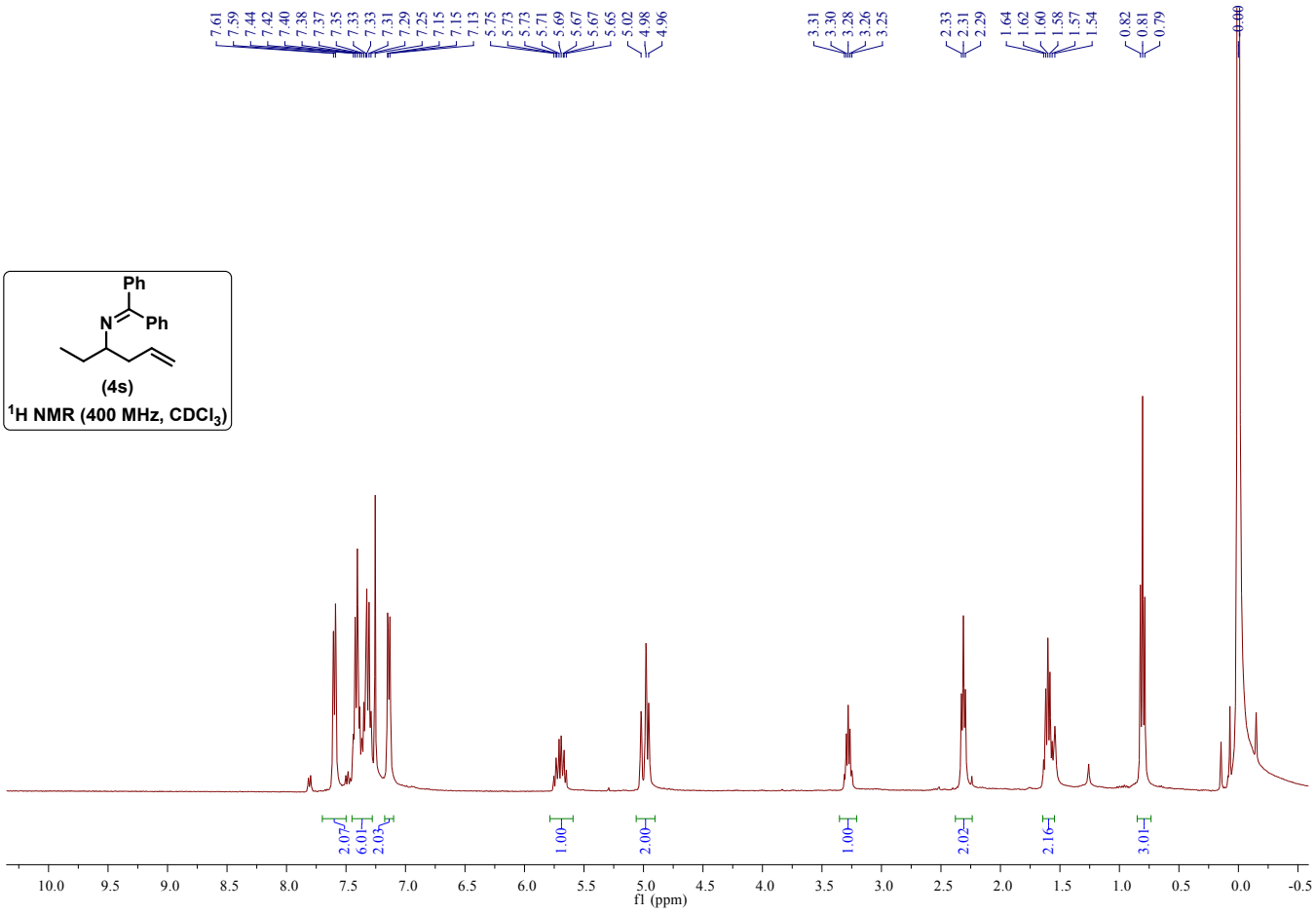


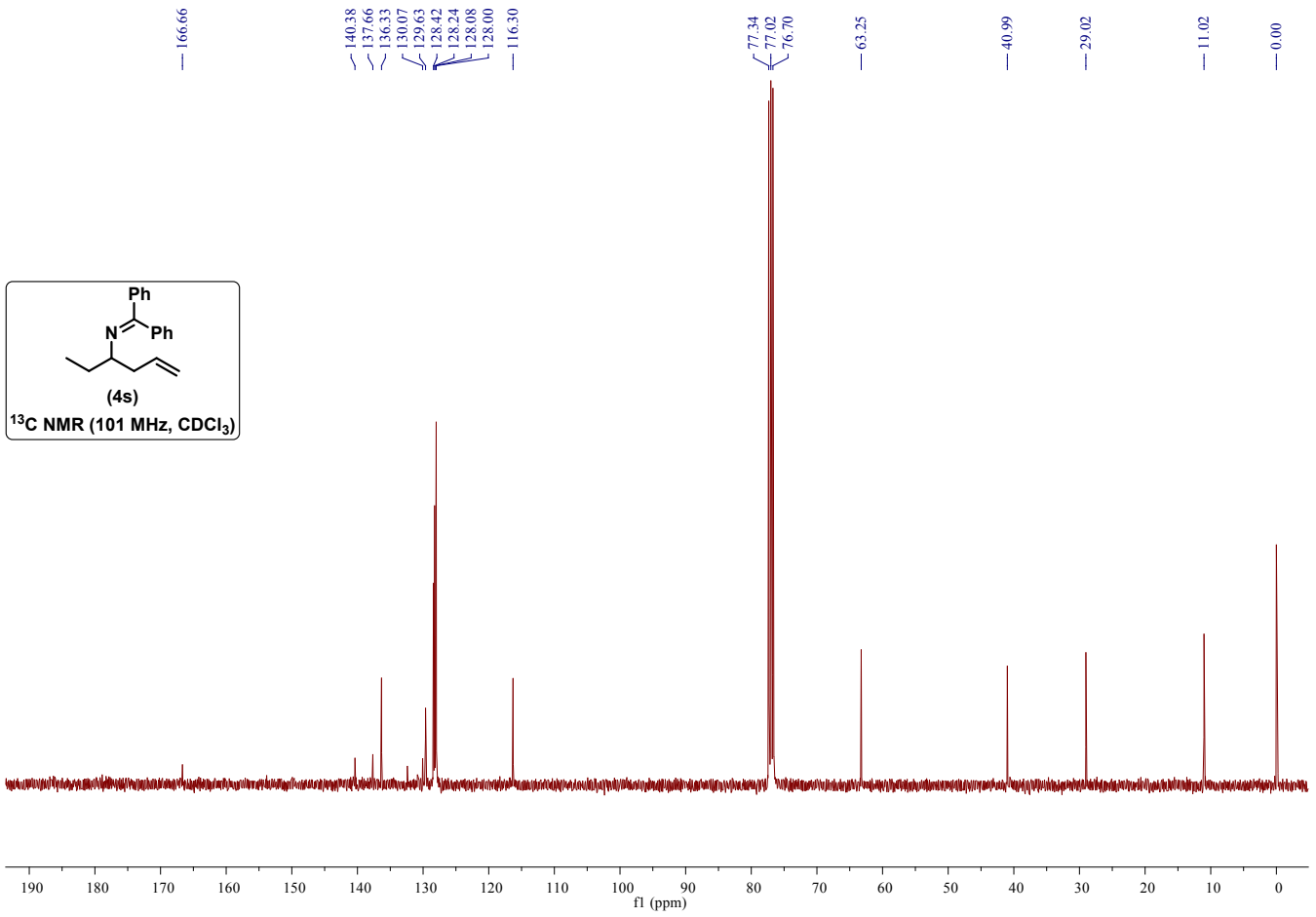
Copies of NMR spectra



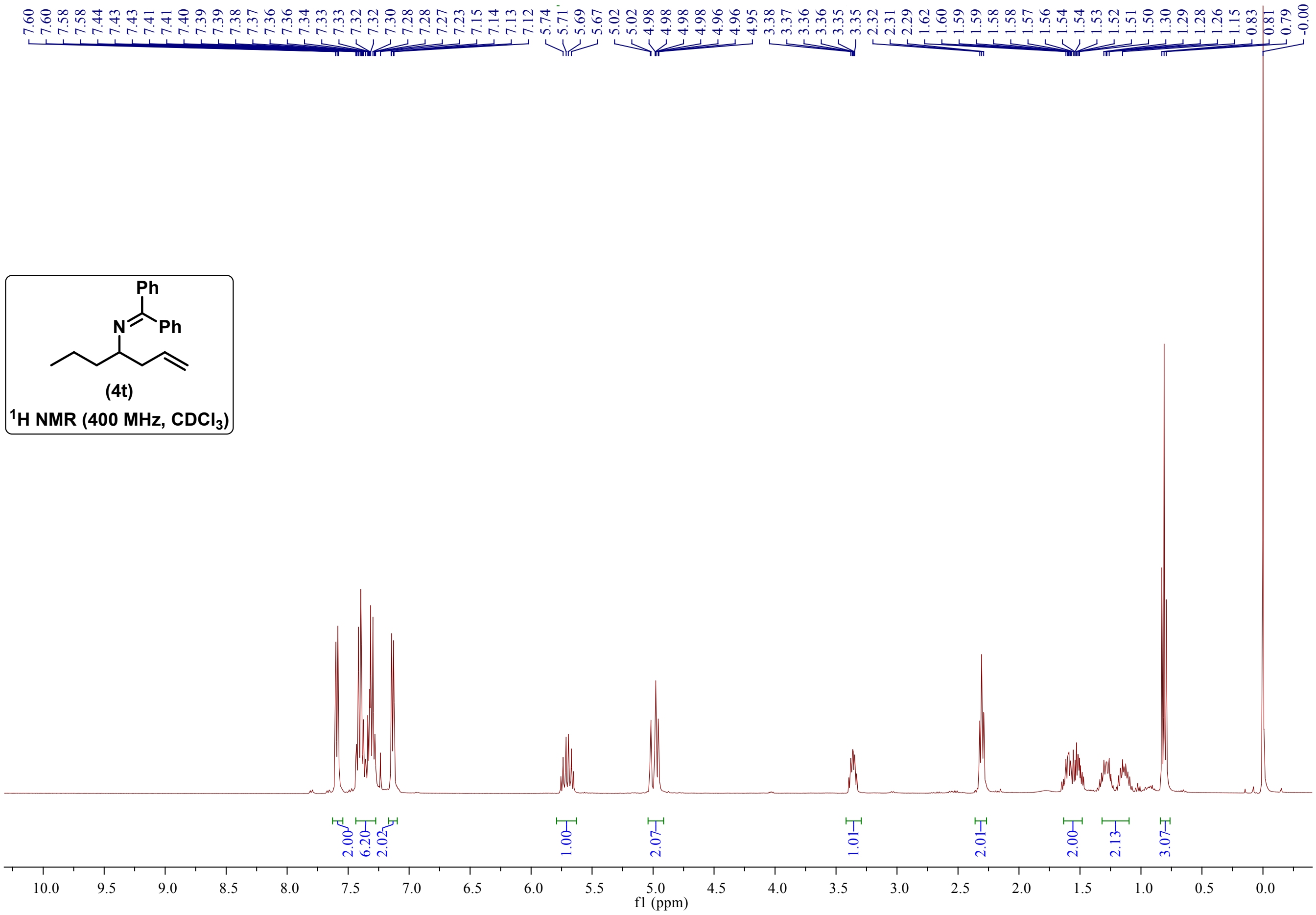


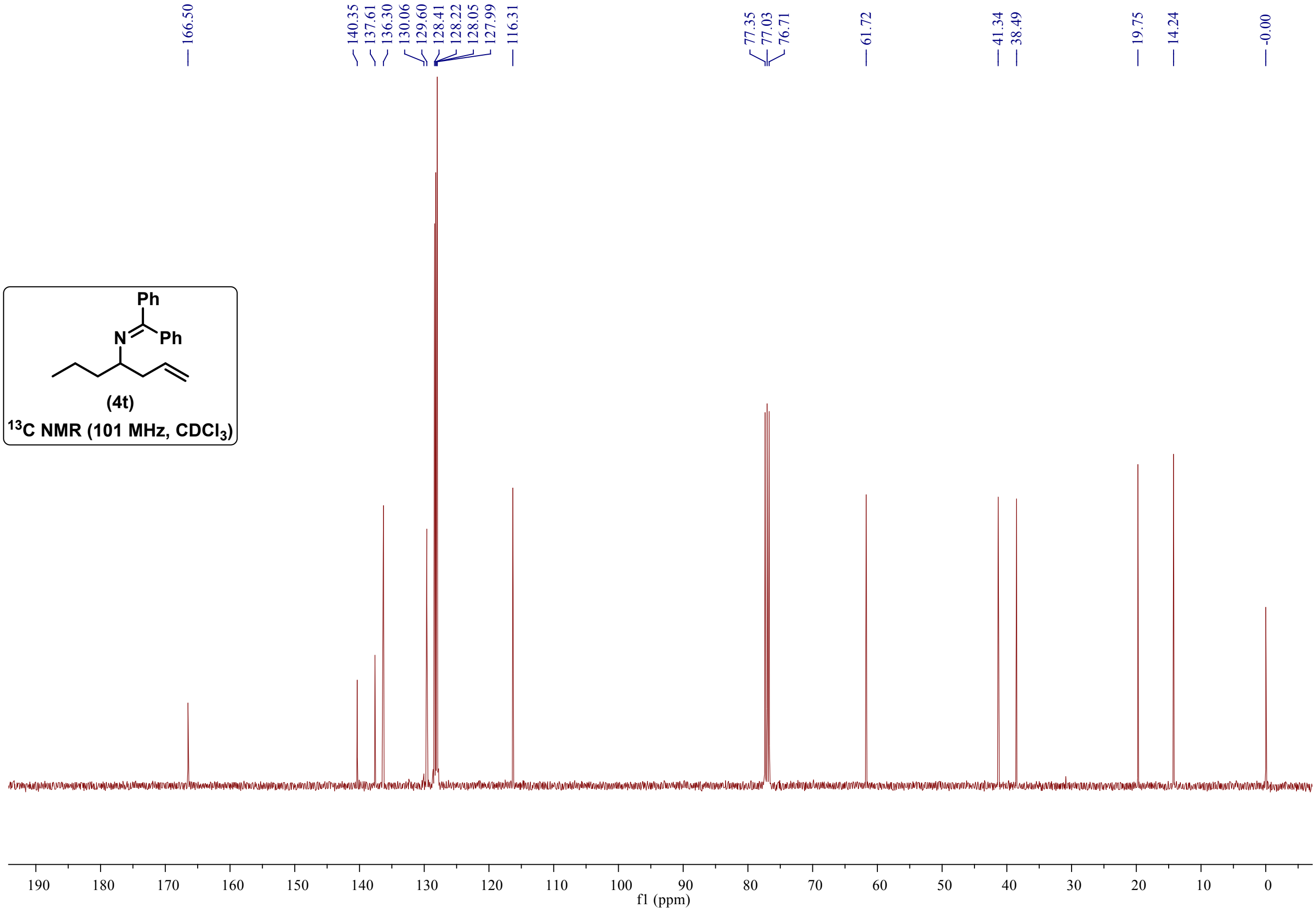
Copies of NMR spectra



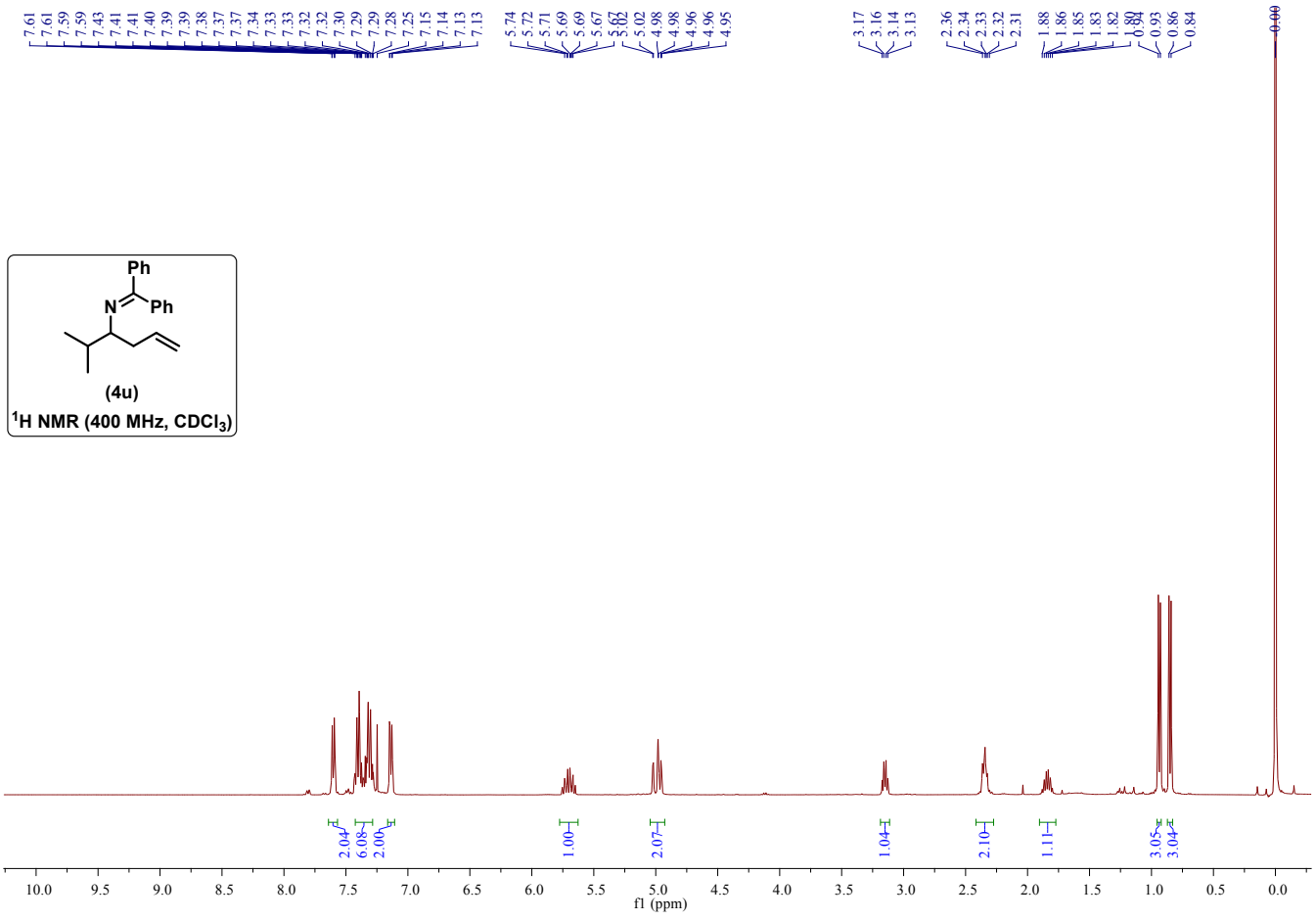


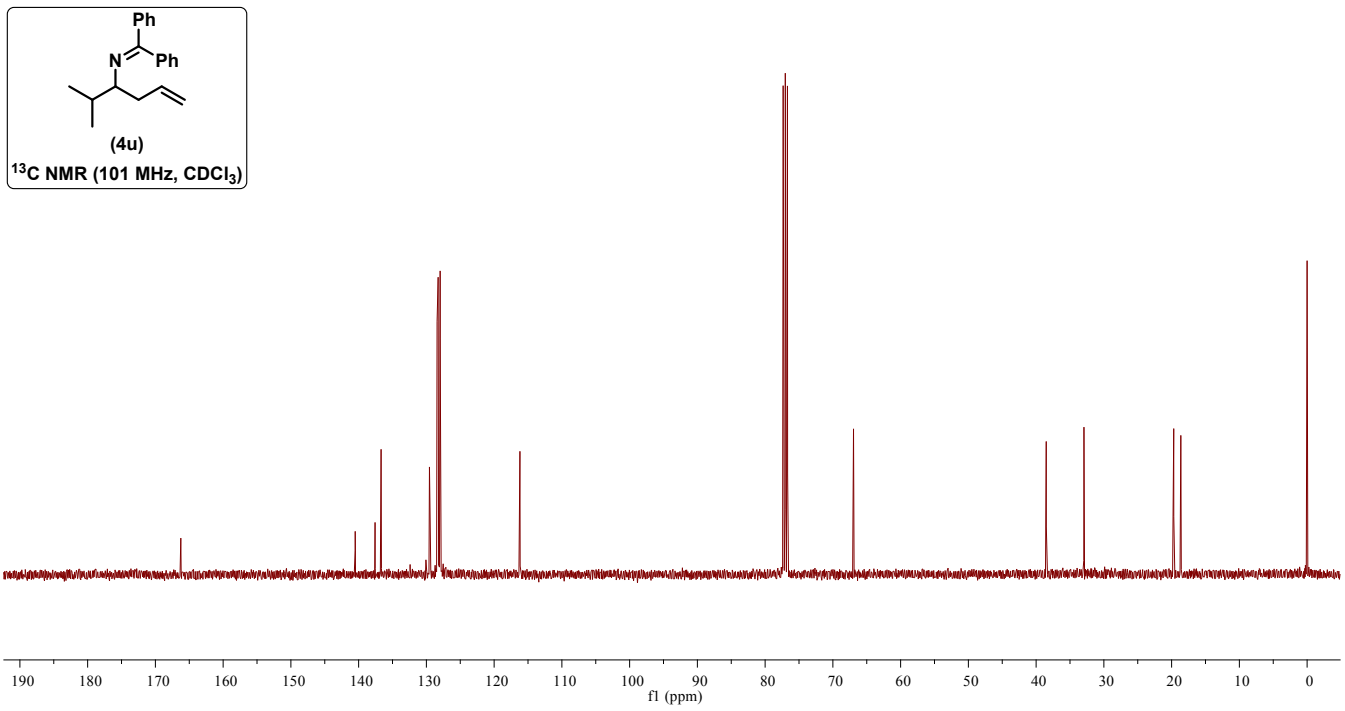
Copies of NMR spectra



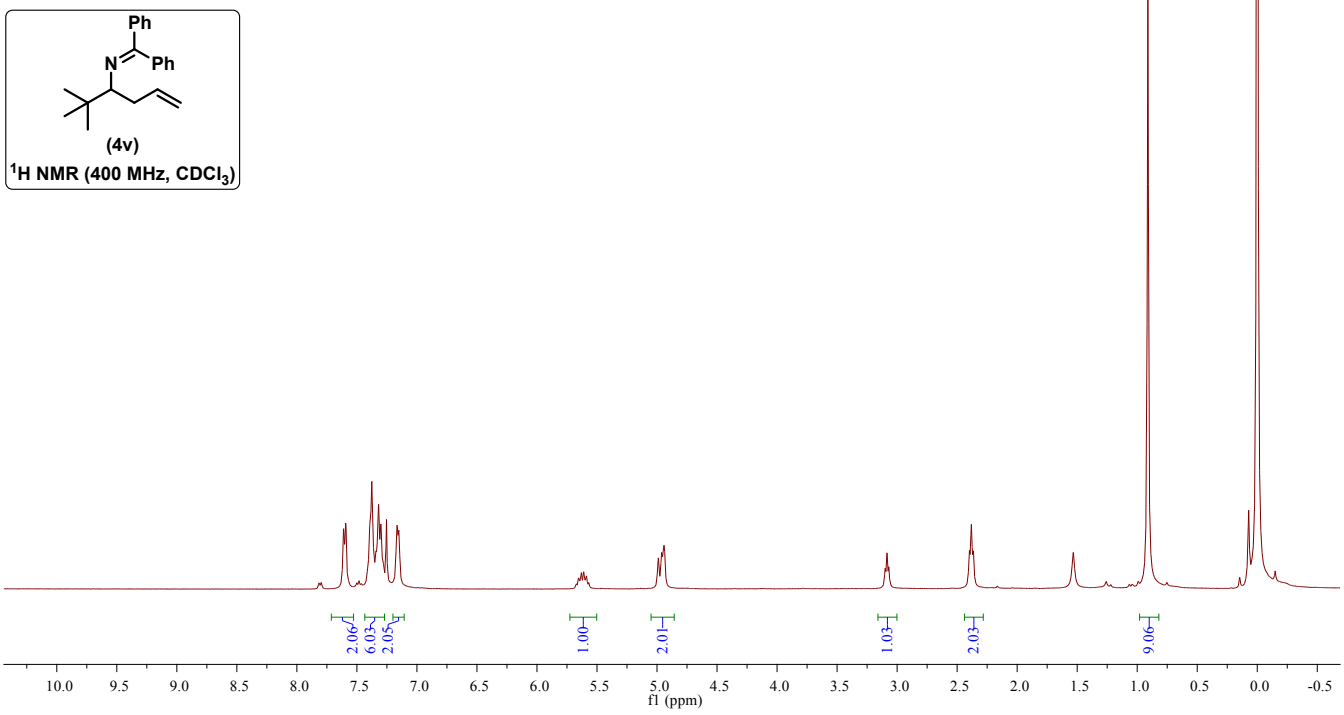


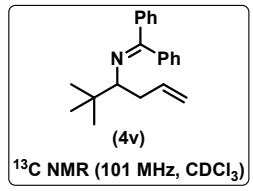
Copies of NMR spectra





Copies of NMR spectra





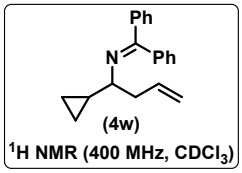
(4v)

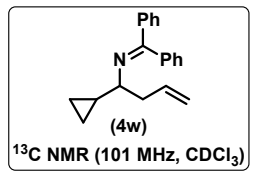
^{1}H NMR (400 MHz, $CDCl_3$)

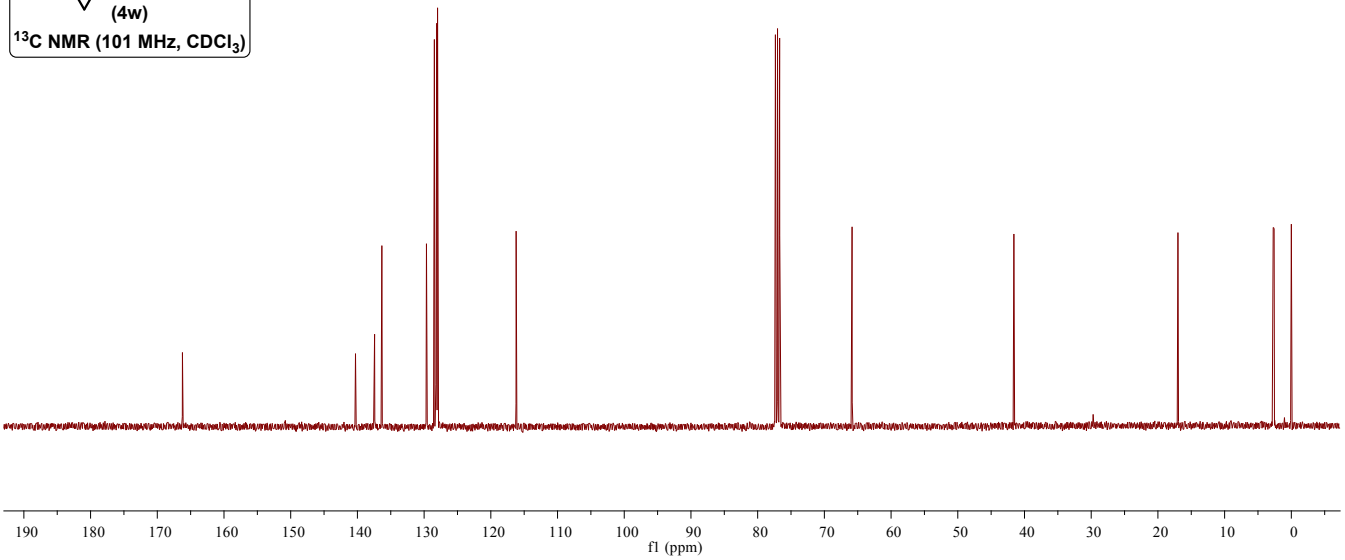
(4v)

^{13}C NMR (101 MHz, $CDCl_3$)

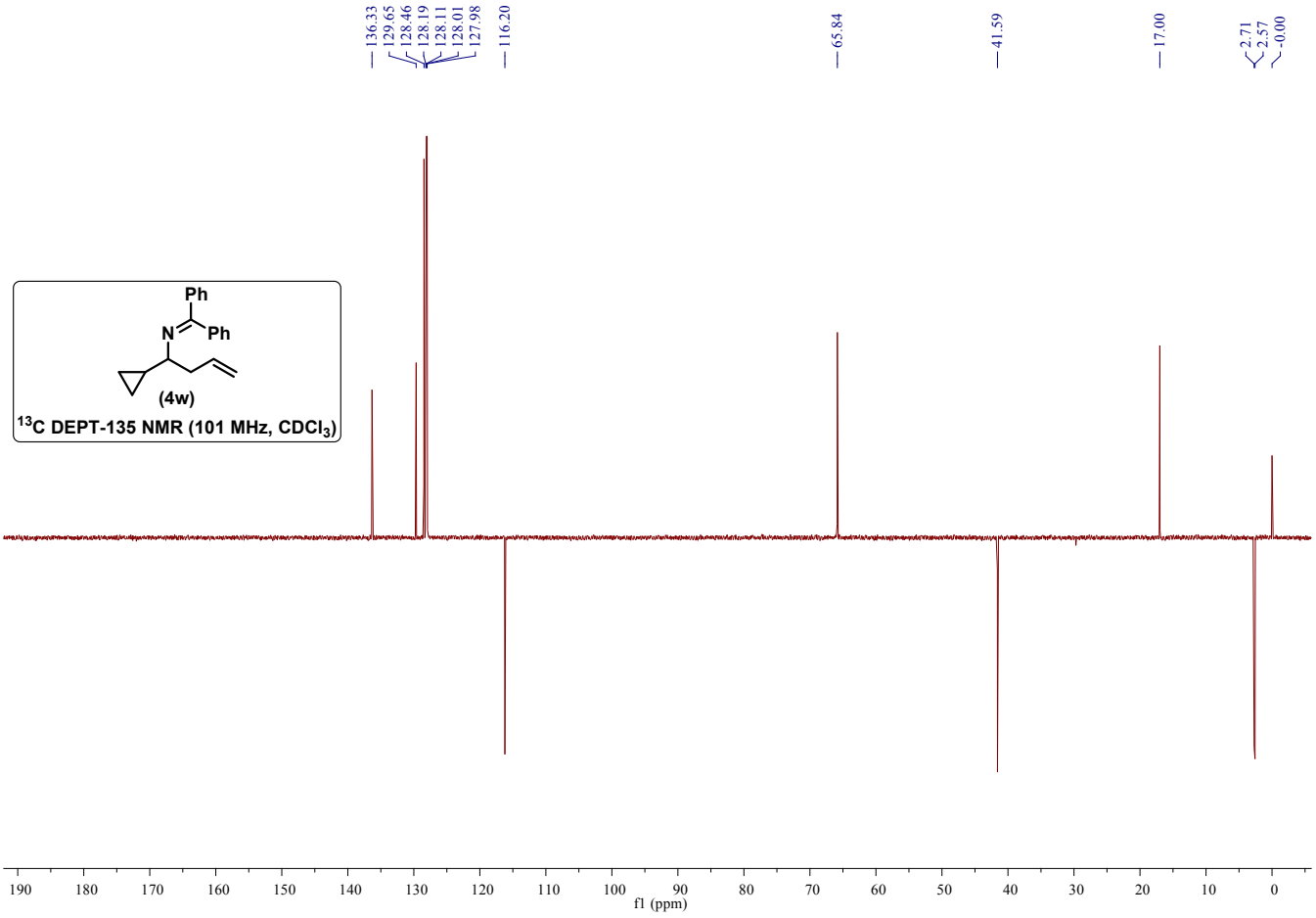
Copies of NMR spectra

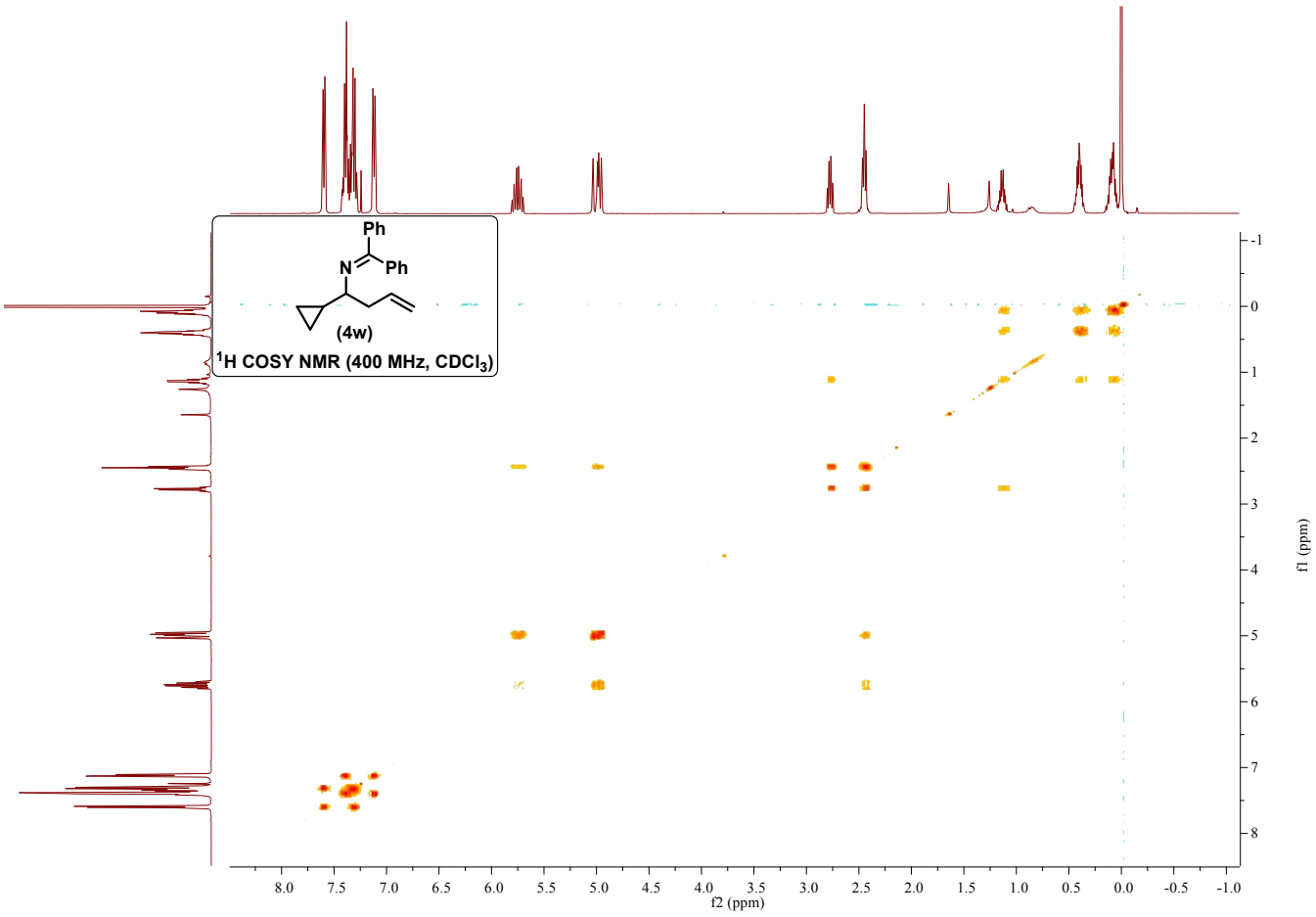




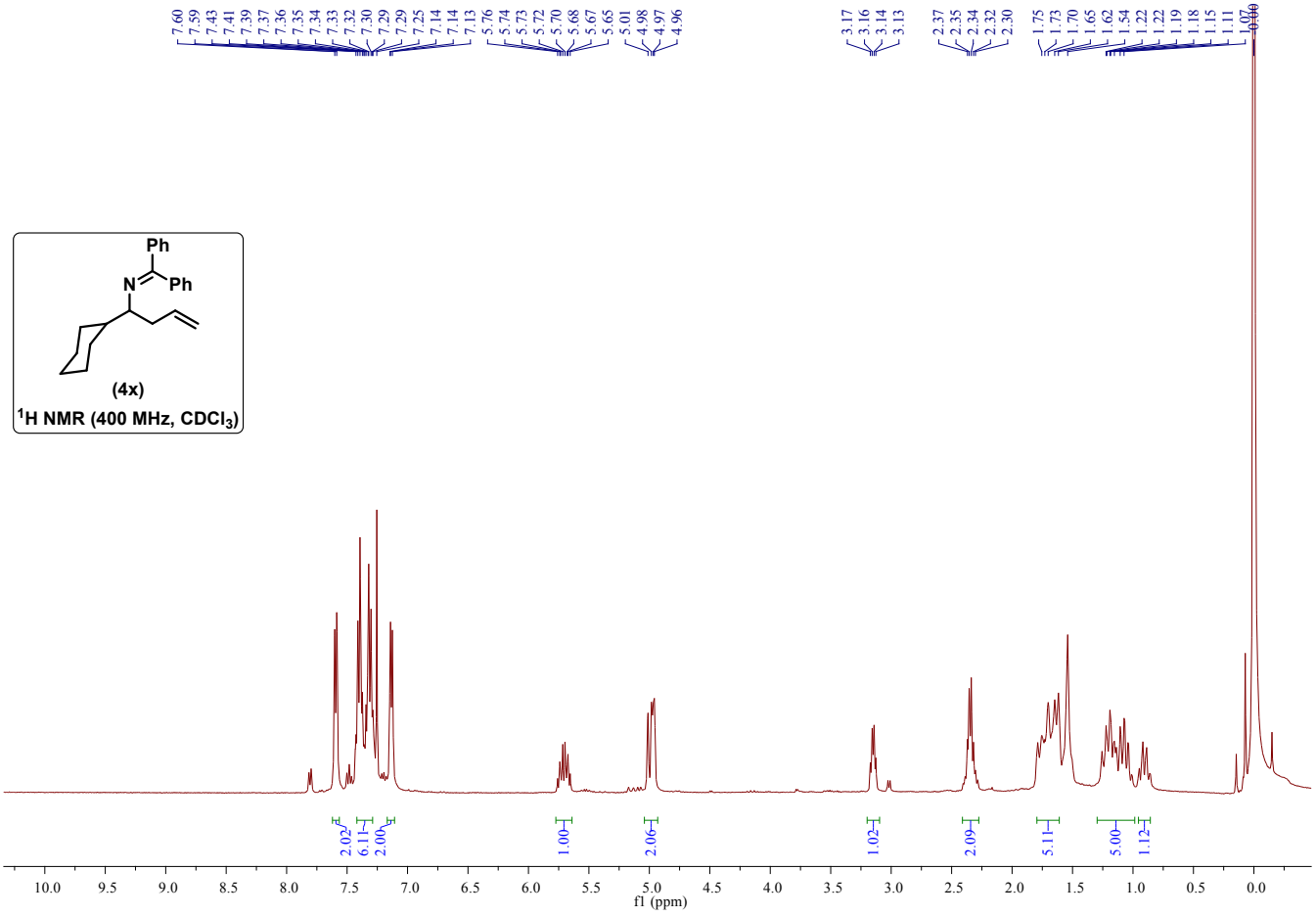


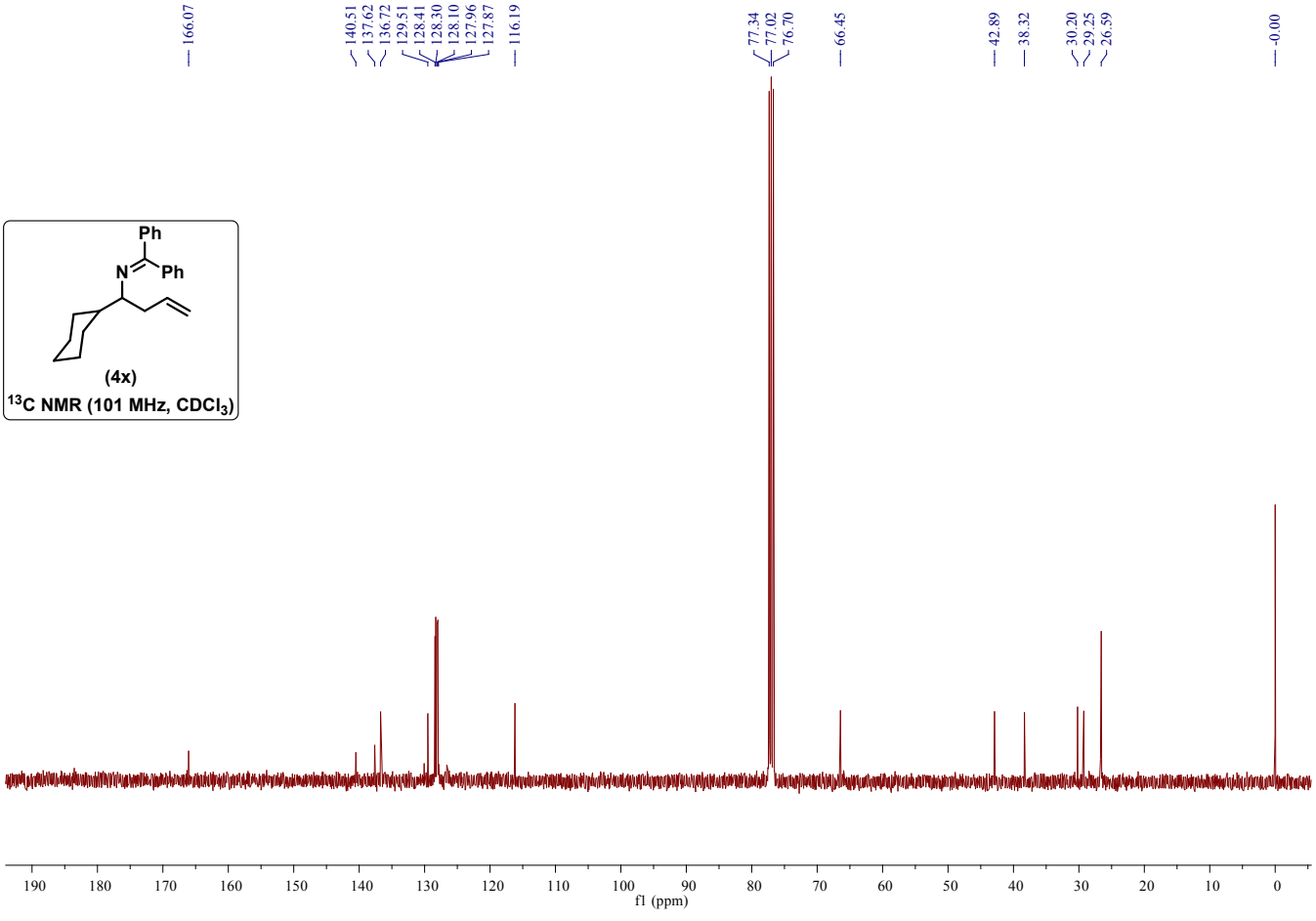
Copies of NMR spectra

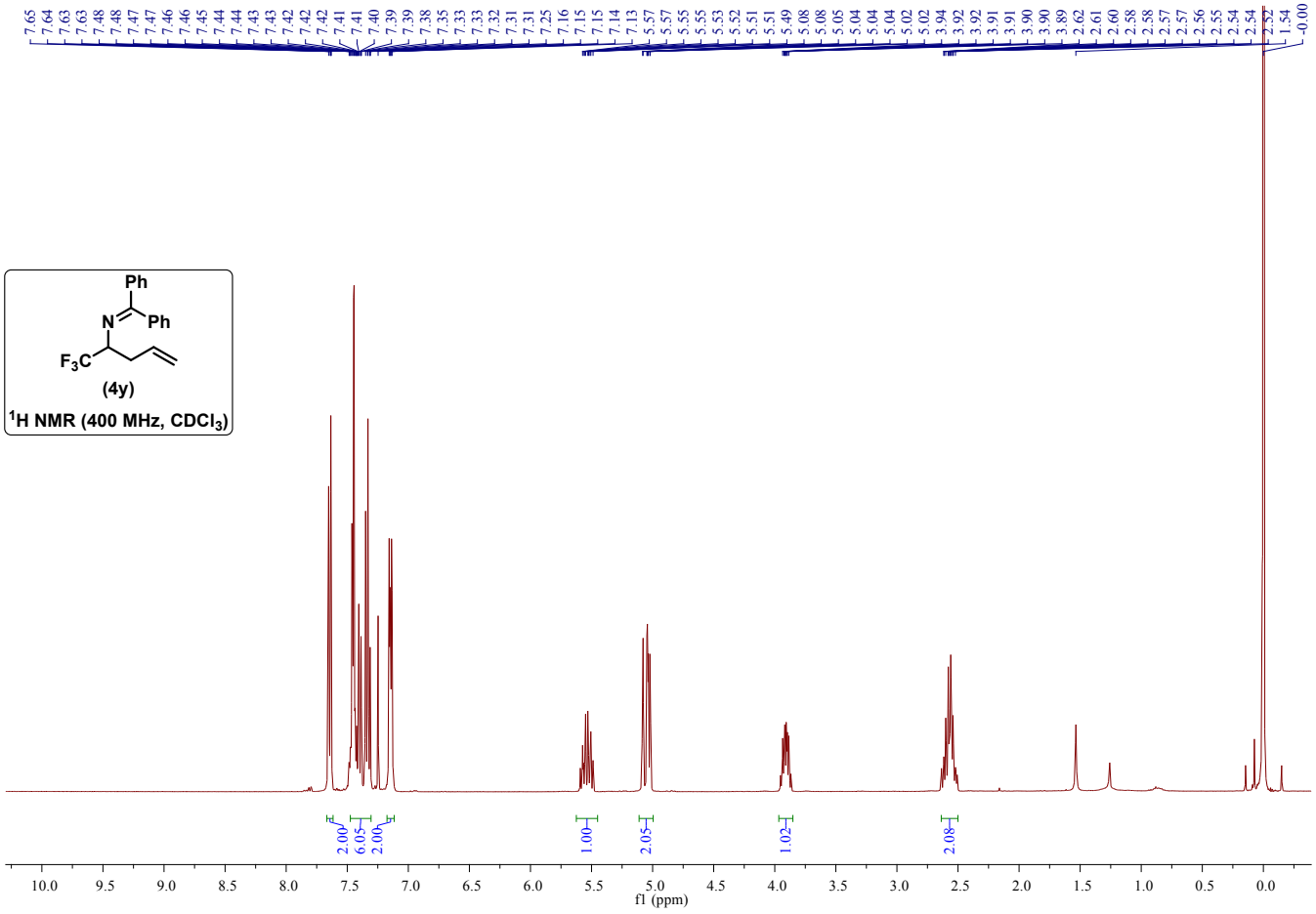


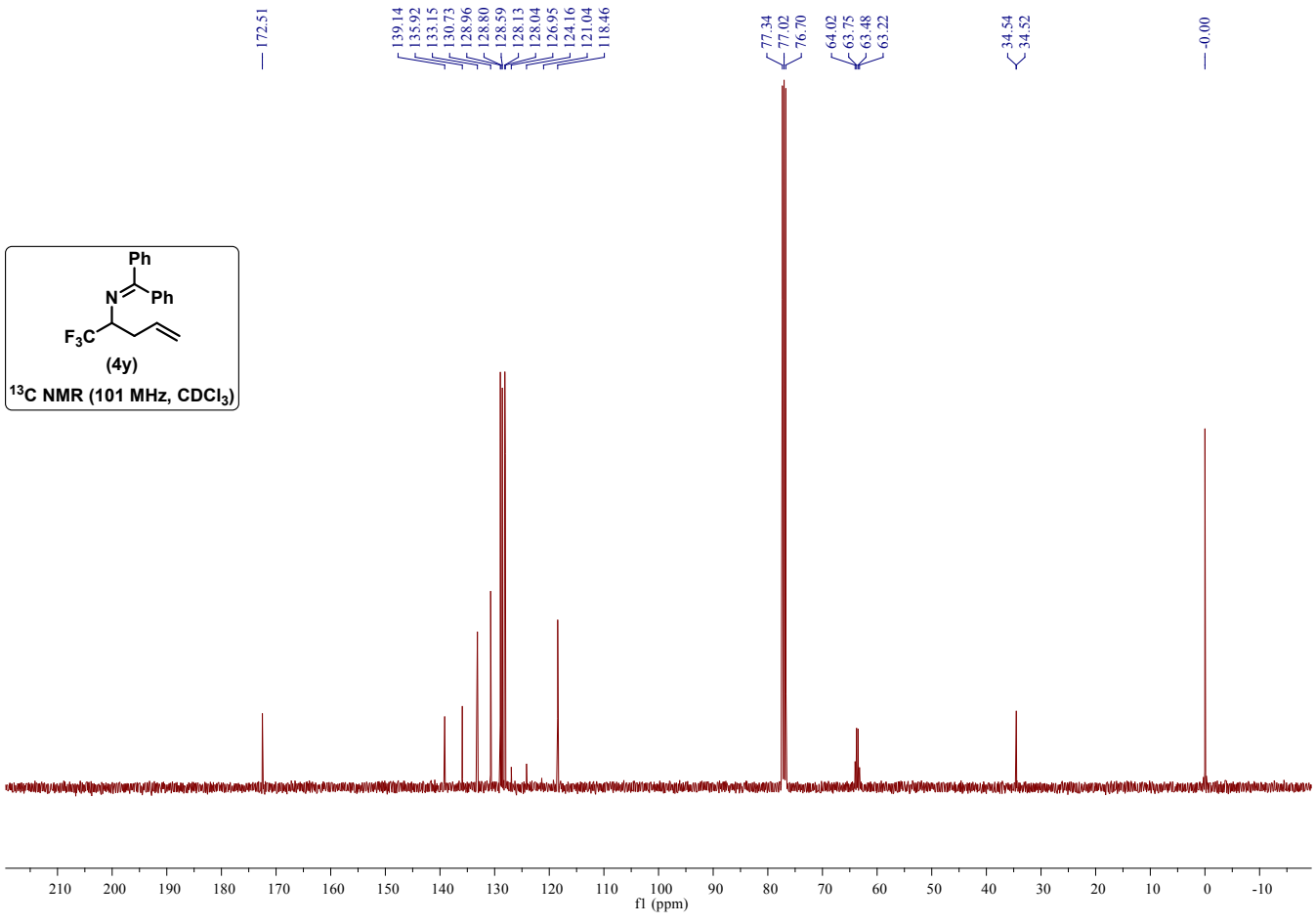


Copies of NMR spectra

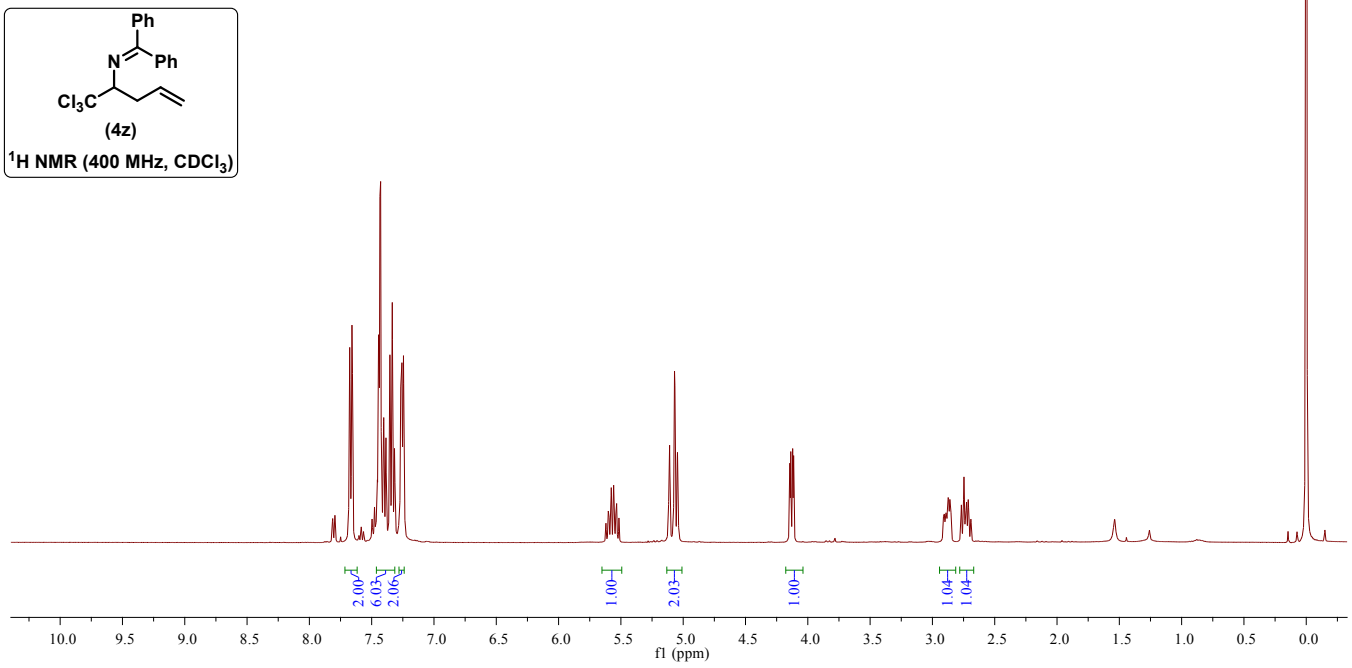


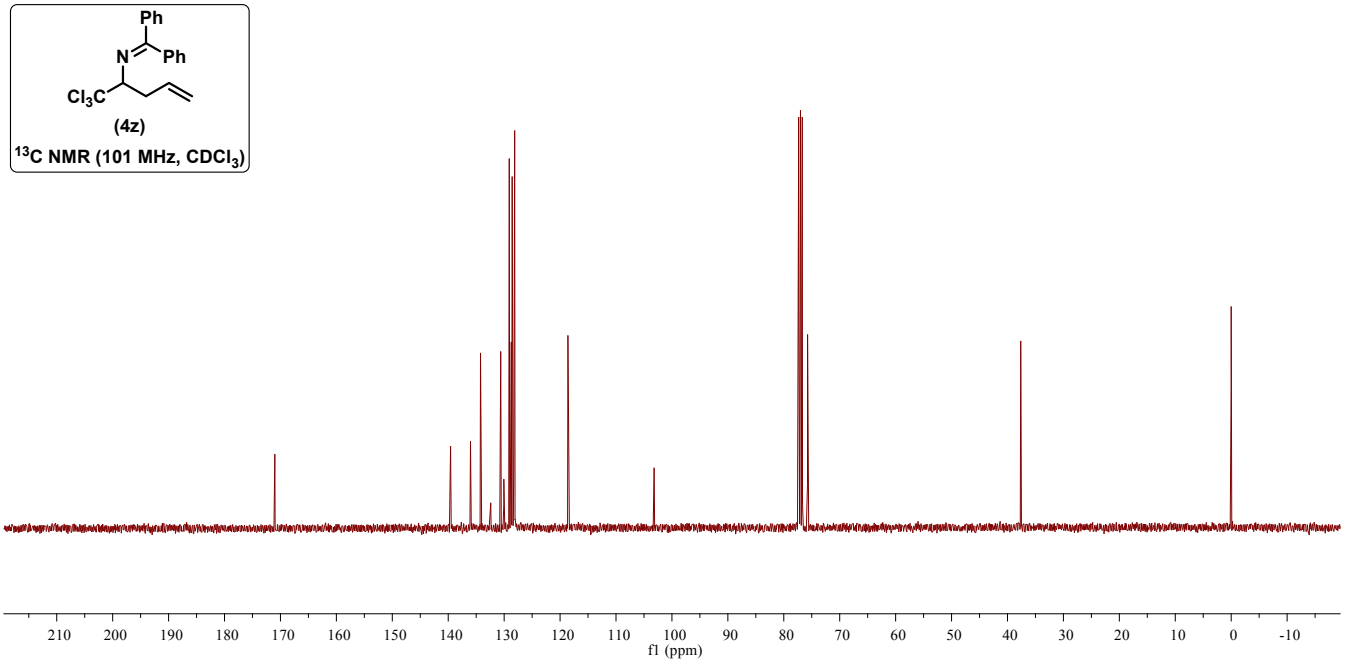



Ph
N
Ph
F3C
(4y)
1H NMR (400 MHz, CDCl3)
f1 (ppm)

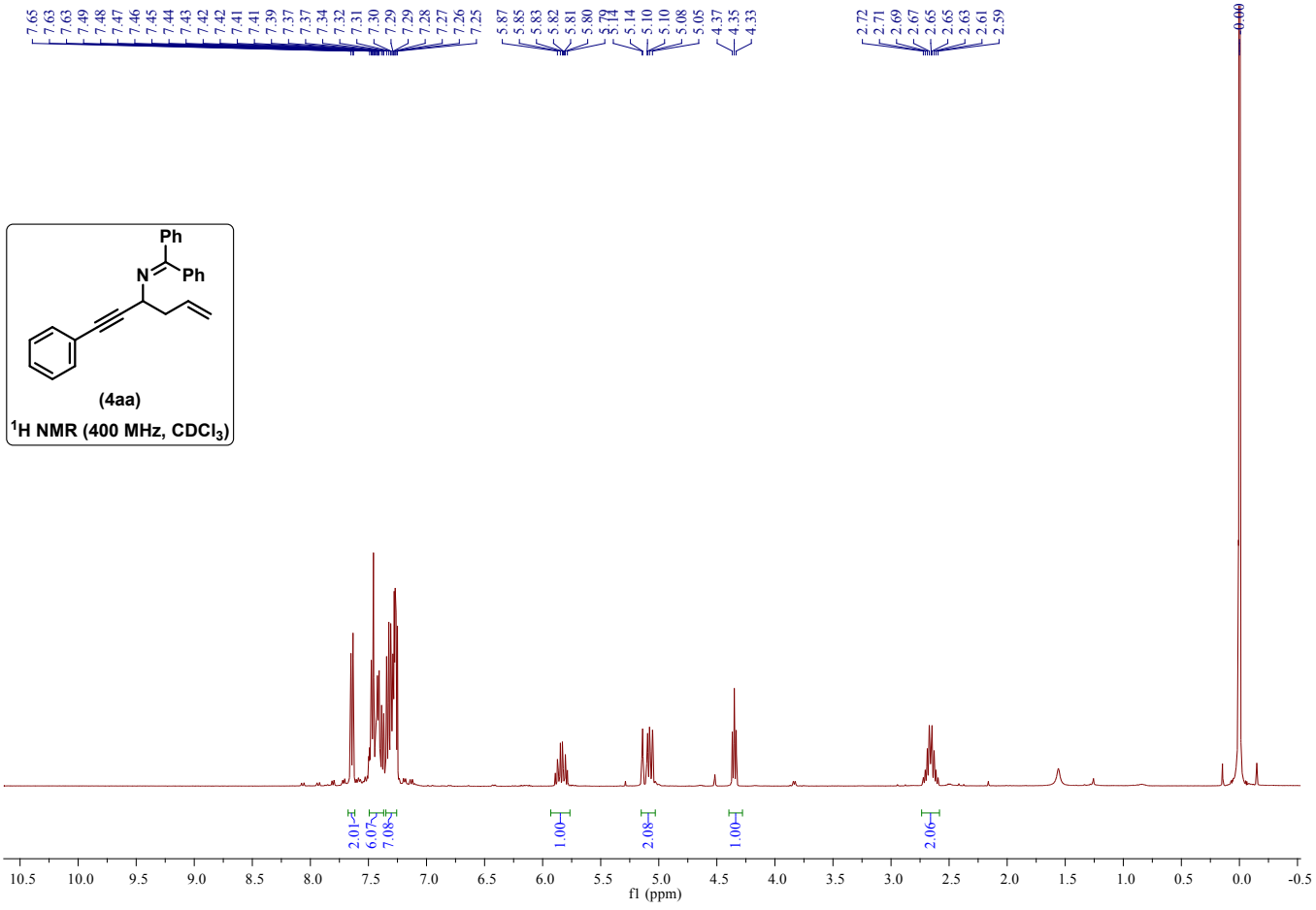

Ph
N
Ph
F3C
(4y)
13C NMR (101 MHz, CDCl3)
f1 (ppm)

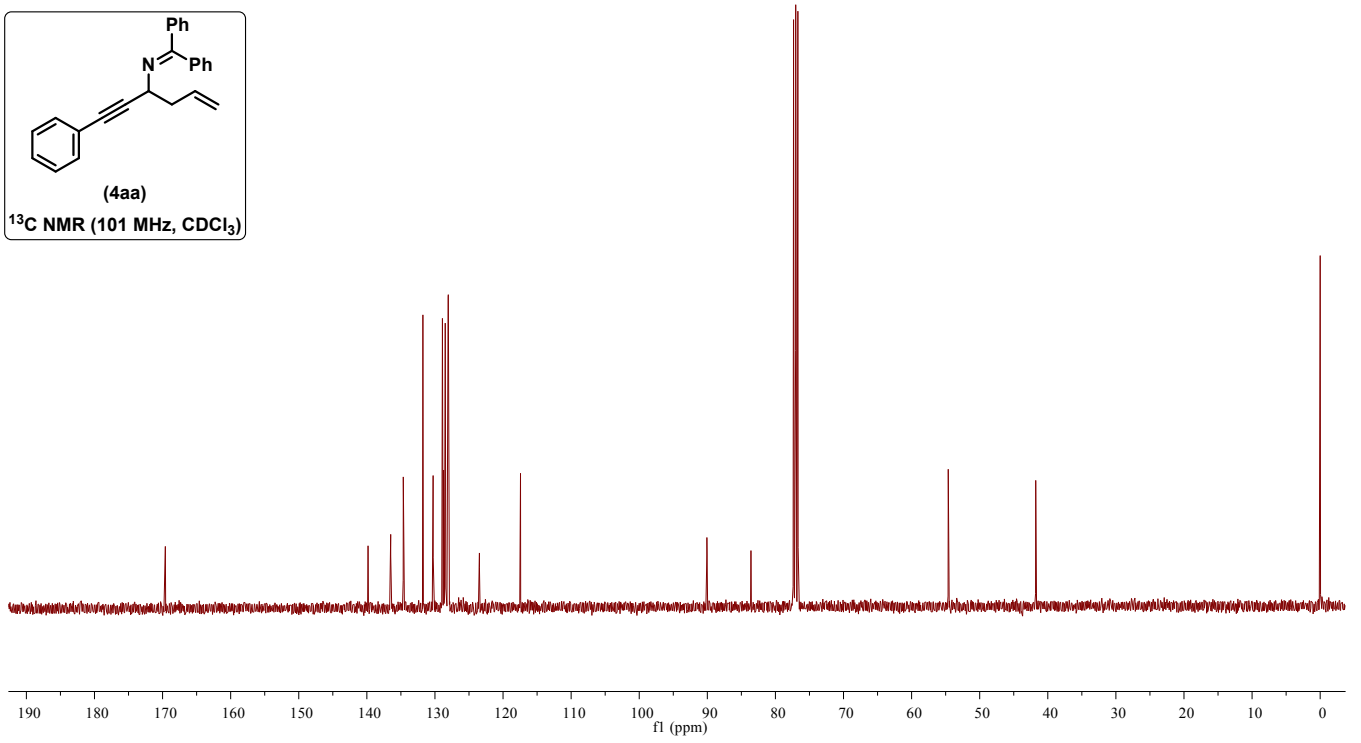
Copies of NMR spectra



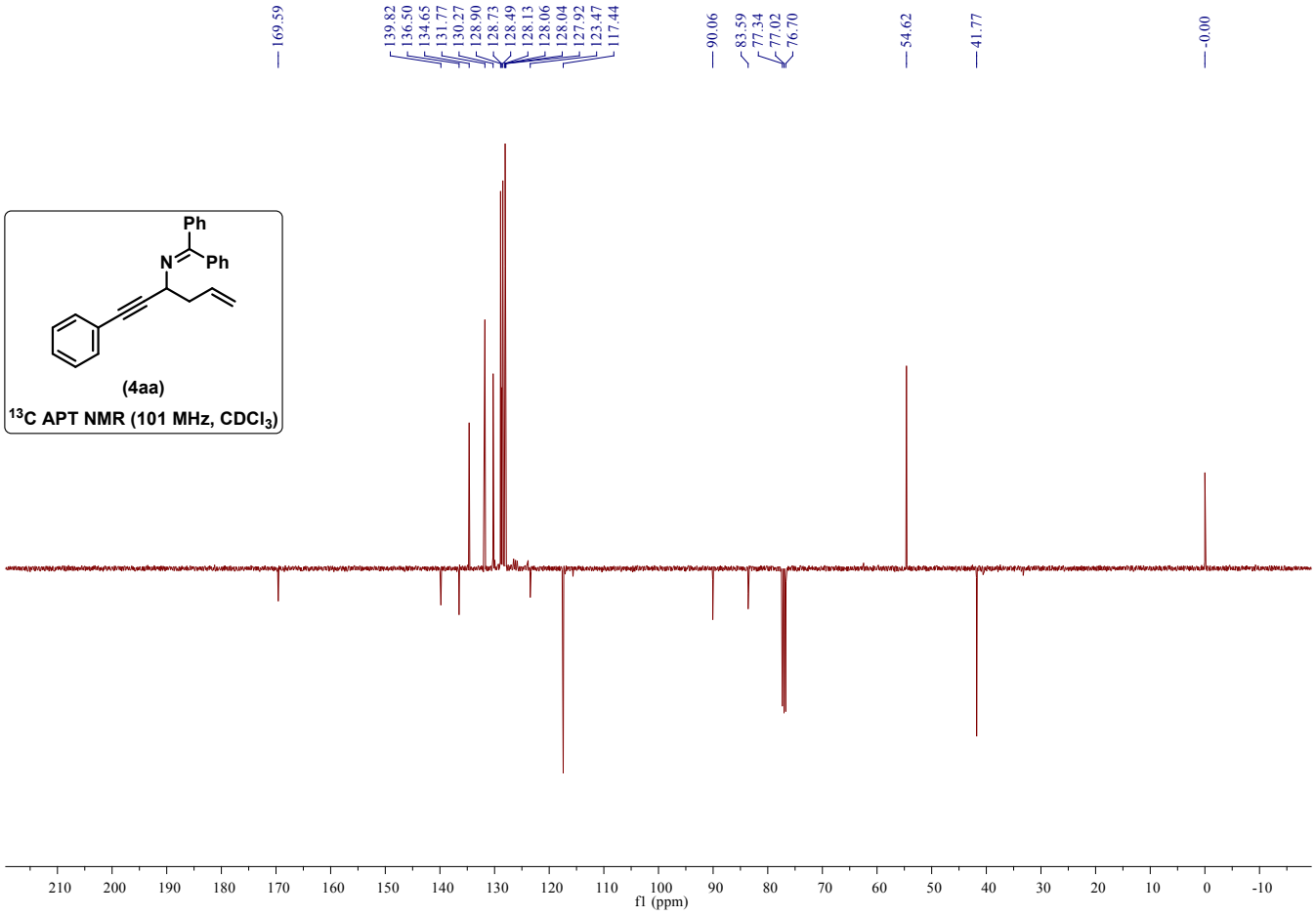


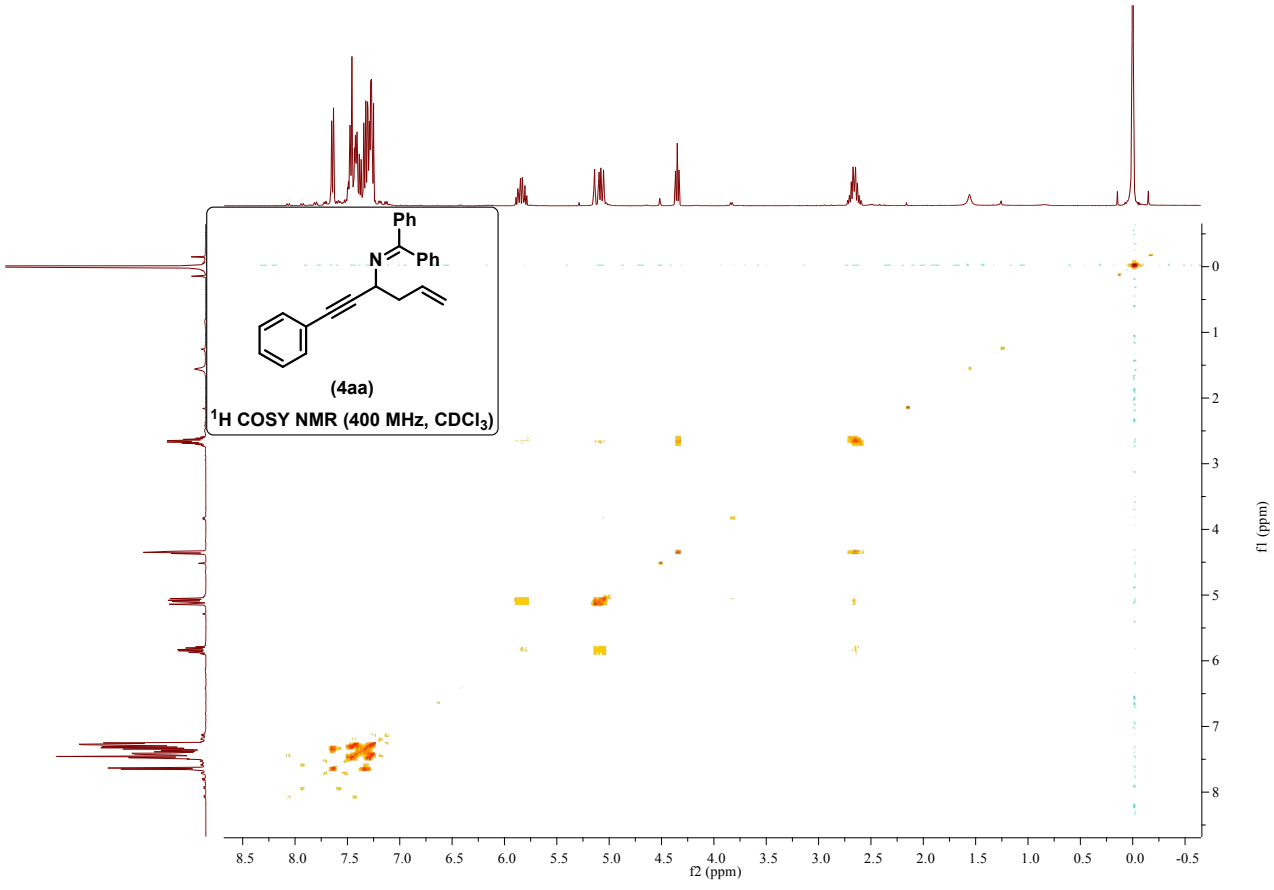
Copies of NMR spectra



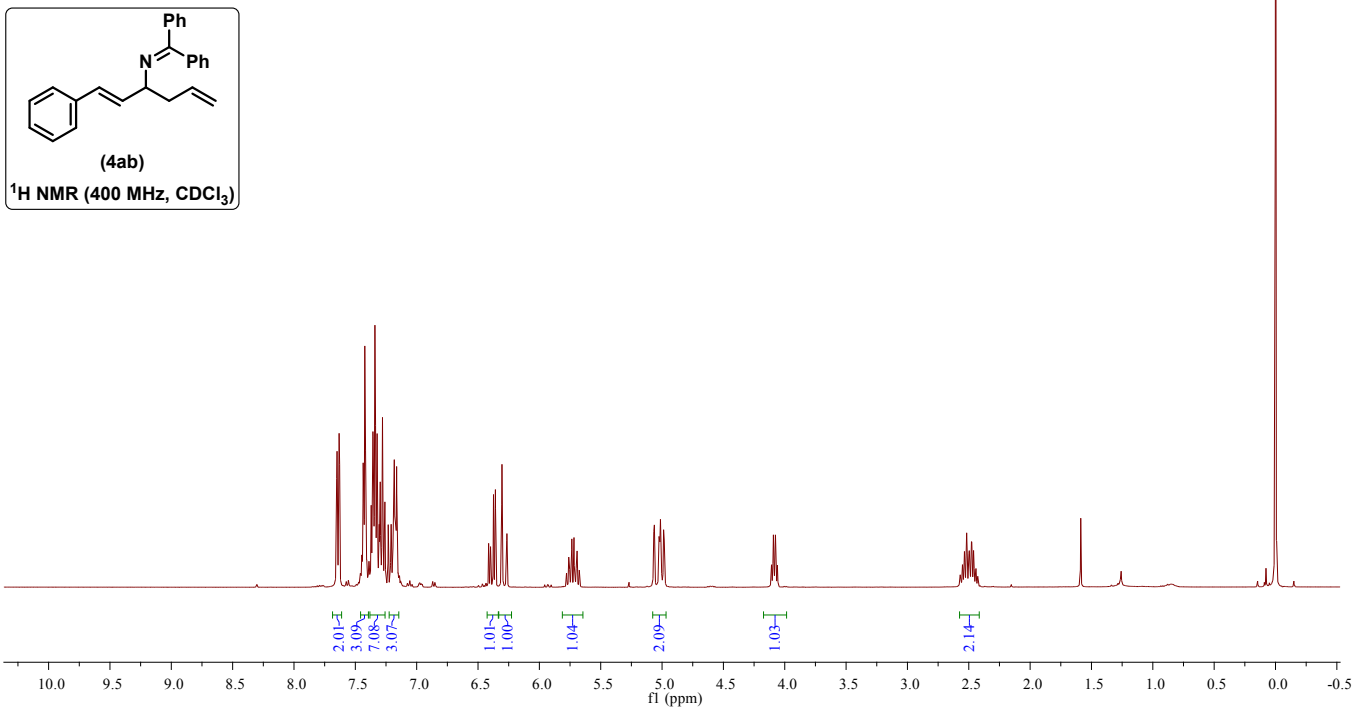


Copies of NMR spectra



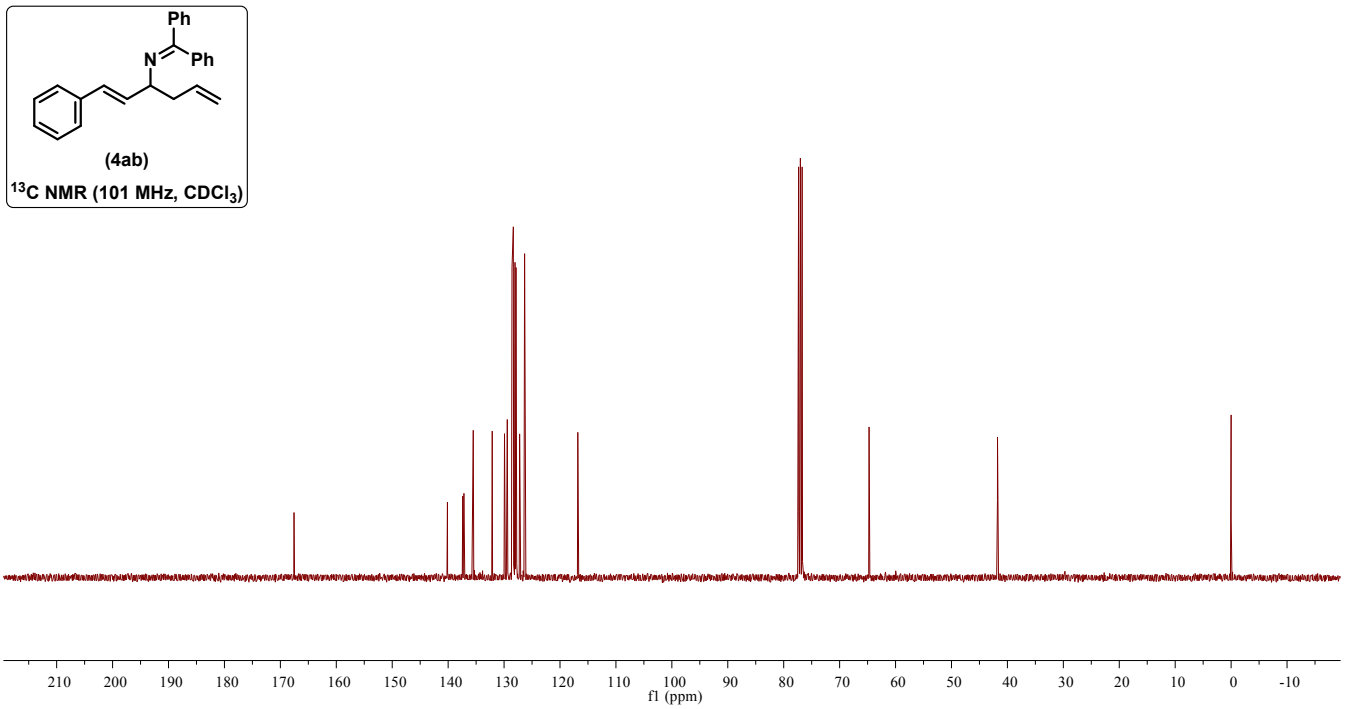


Copies of NMR spectra



(4ab)

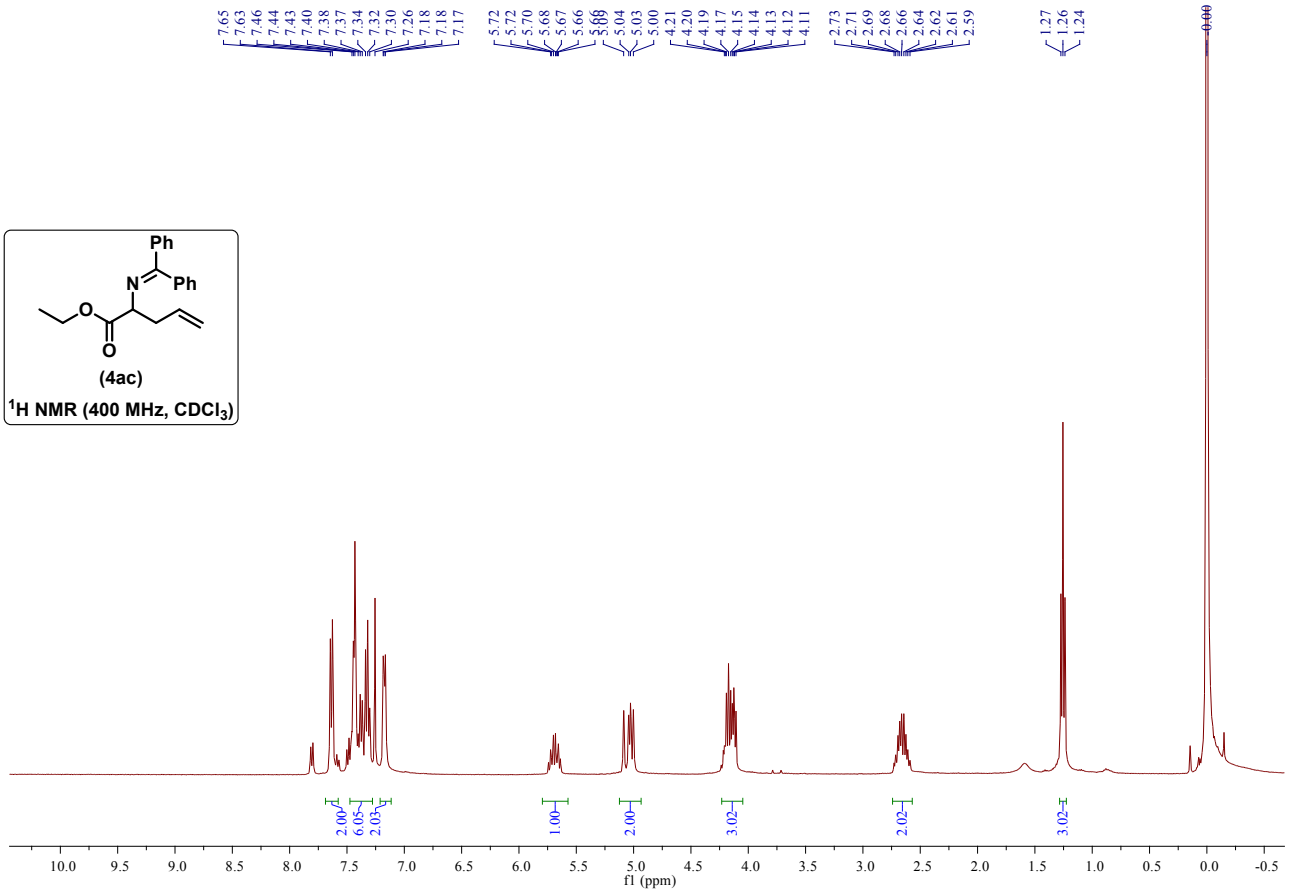
^{1}H NMR (400 MHz, $CDCl_3$)

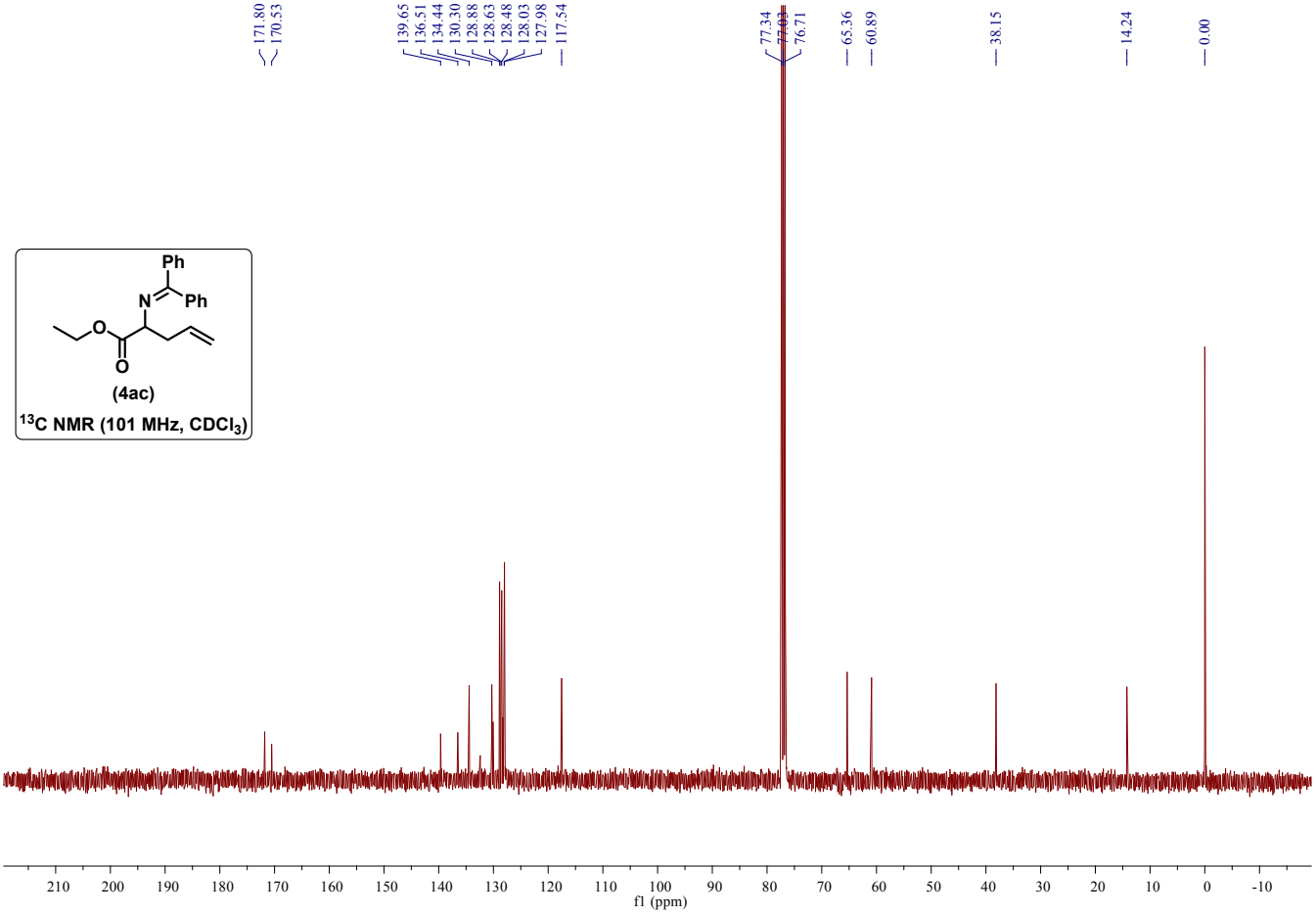


(4ab)

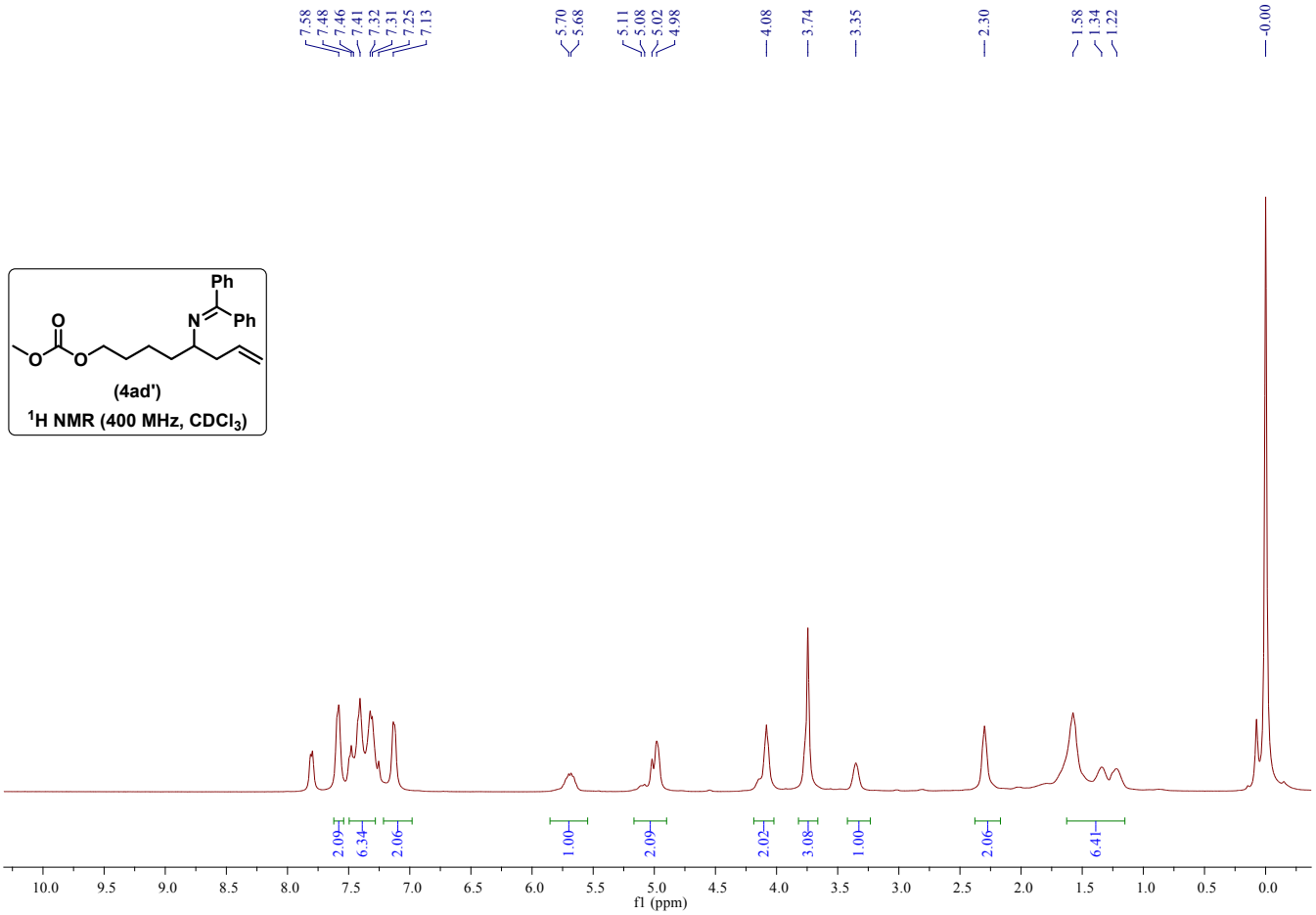
^{13}C NMR (101 MHz, $CDCl_3$)

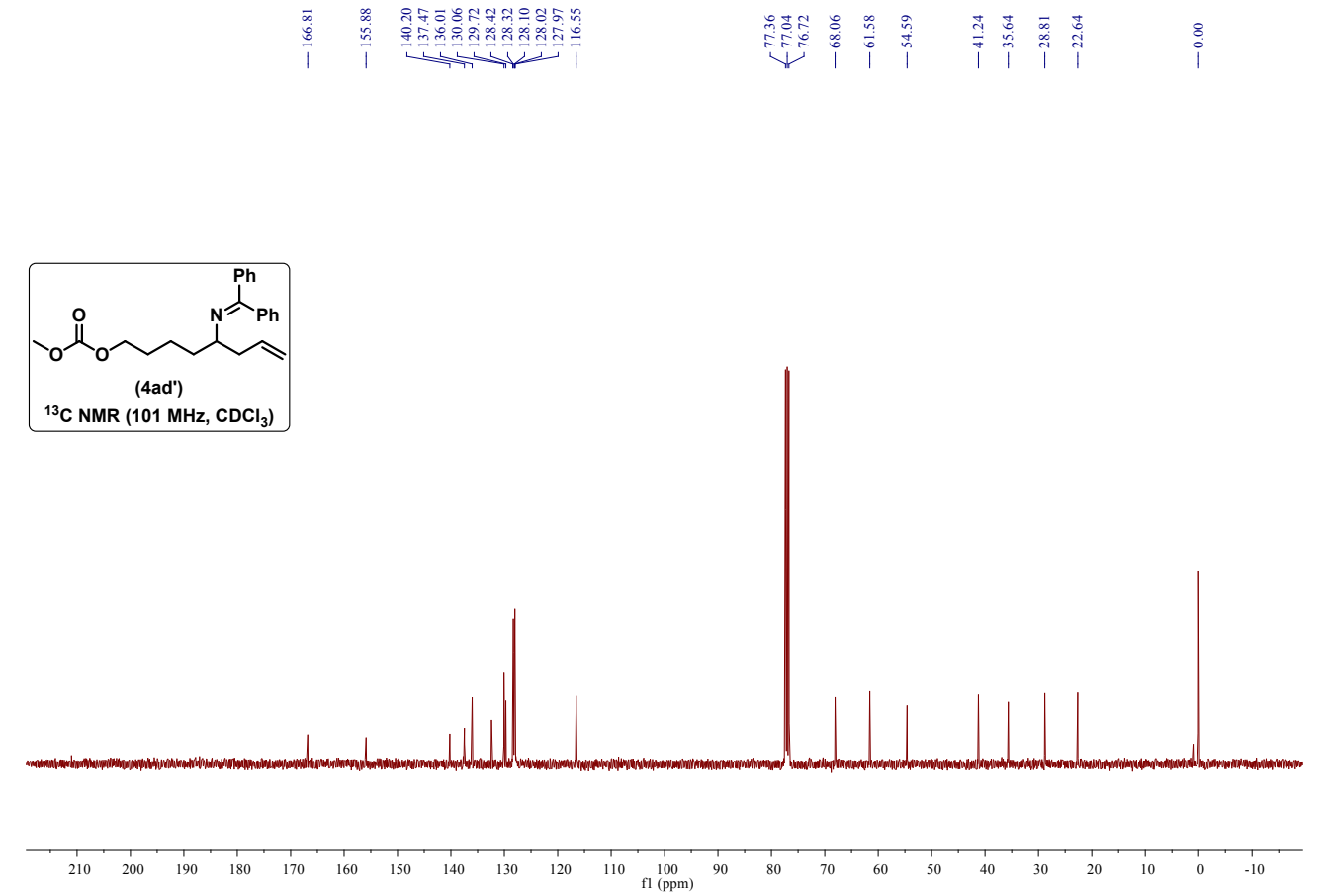
Copies of NMR spectra



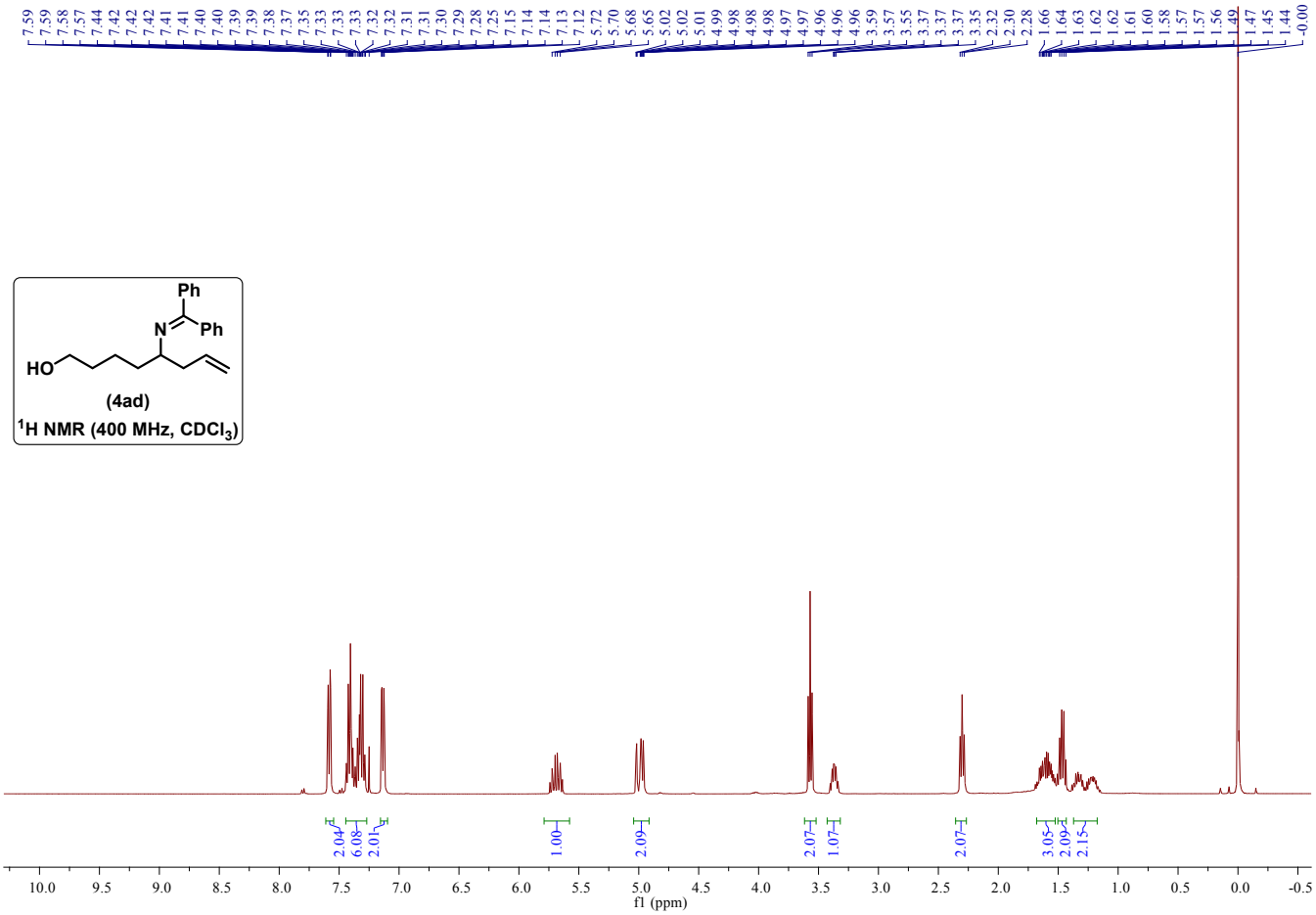


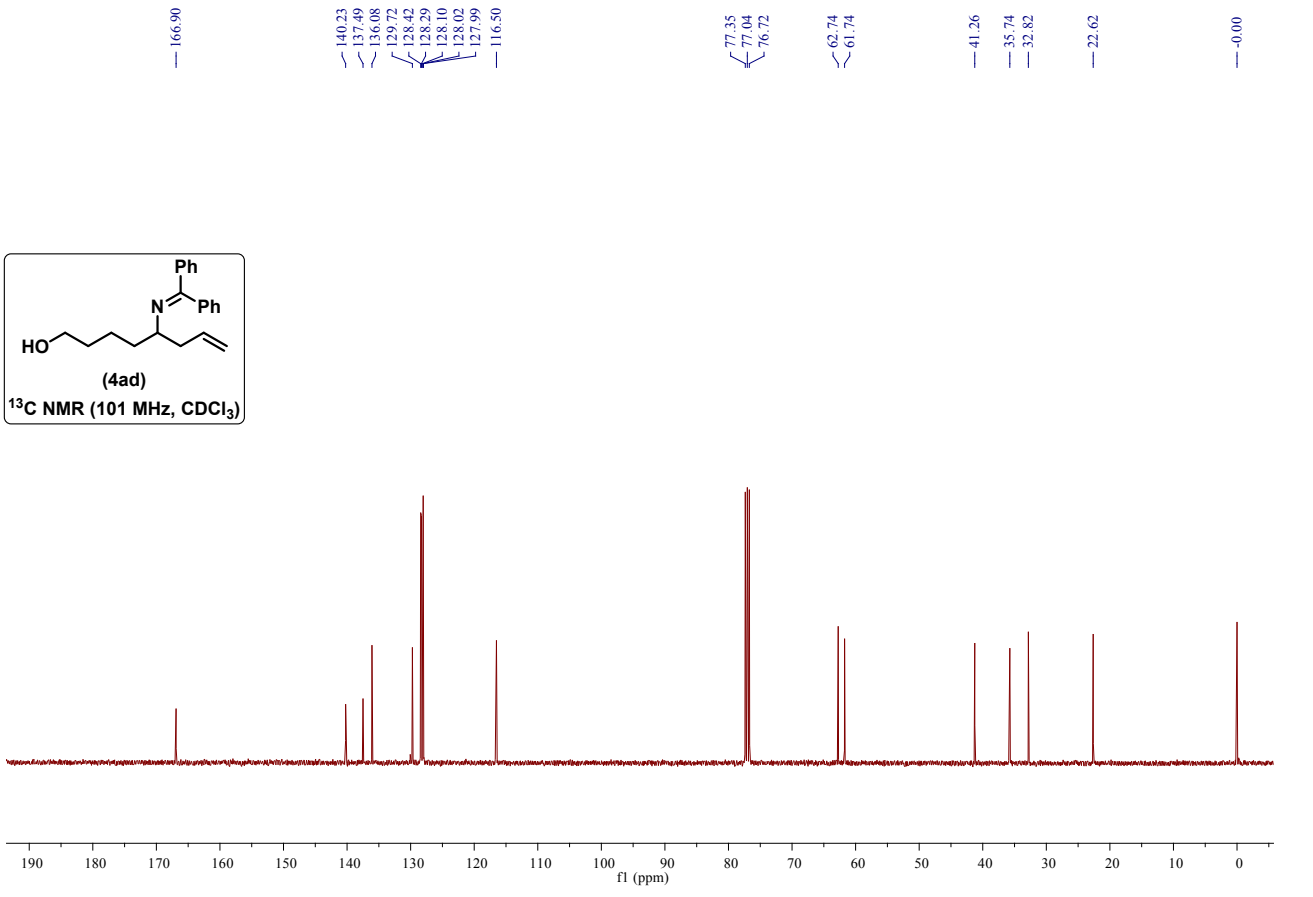
Copies of NMR spectra



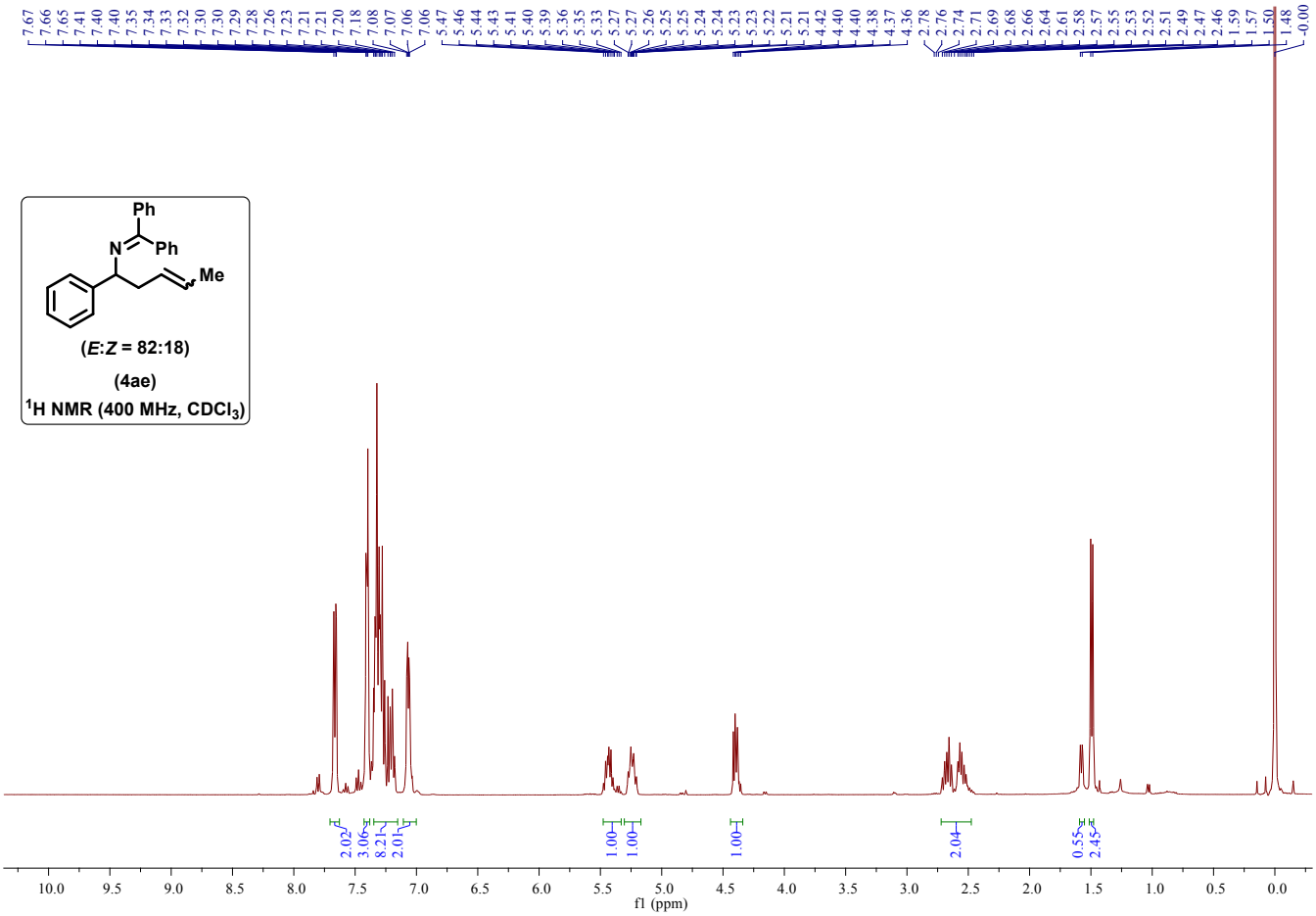


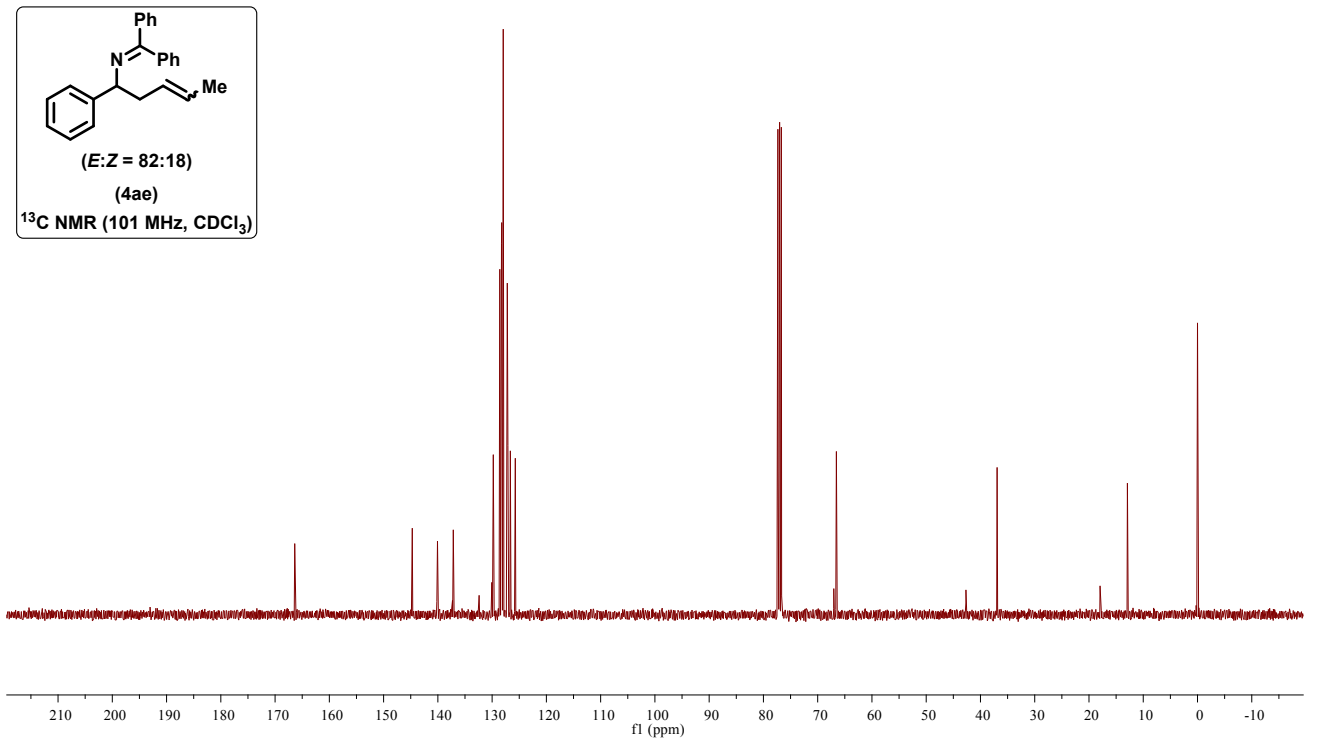
Copies of NMR spectra



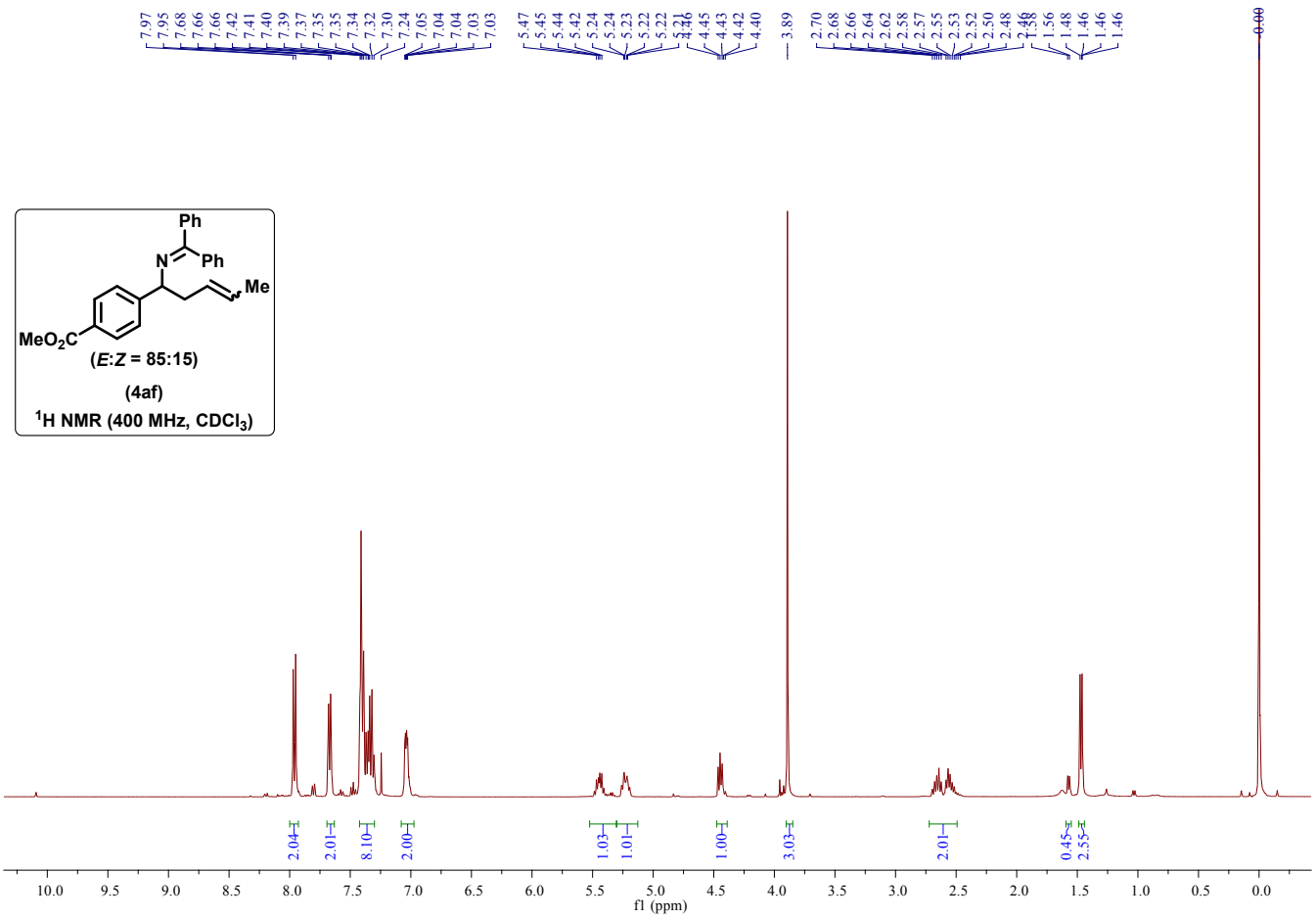


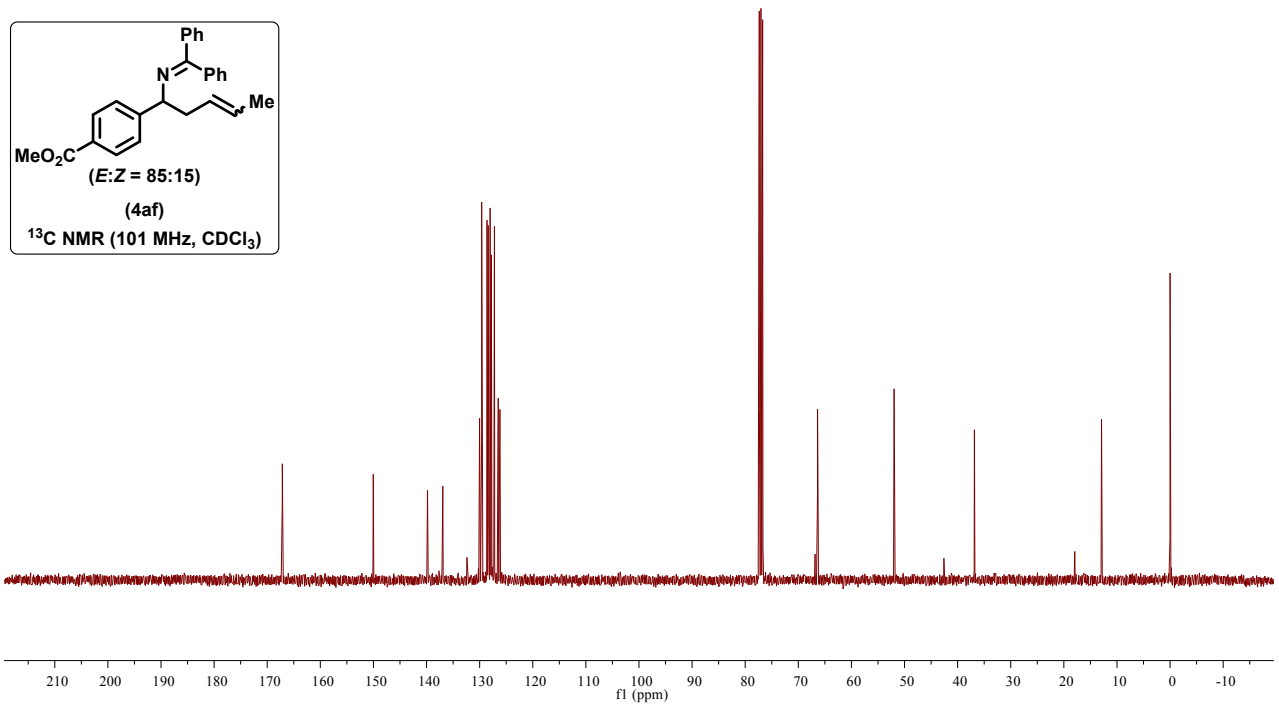
Copies of NMR spectra



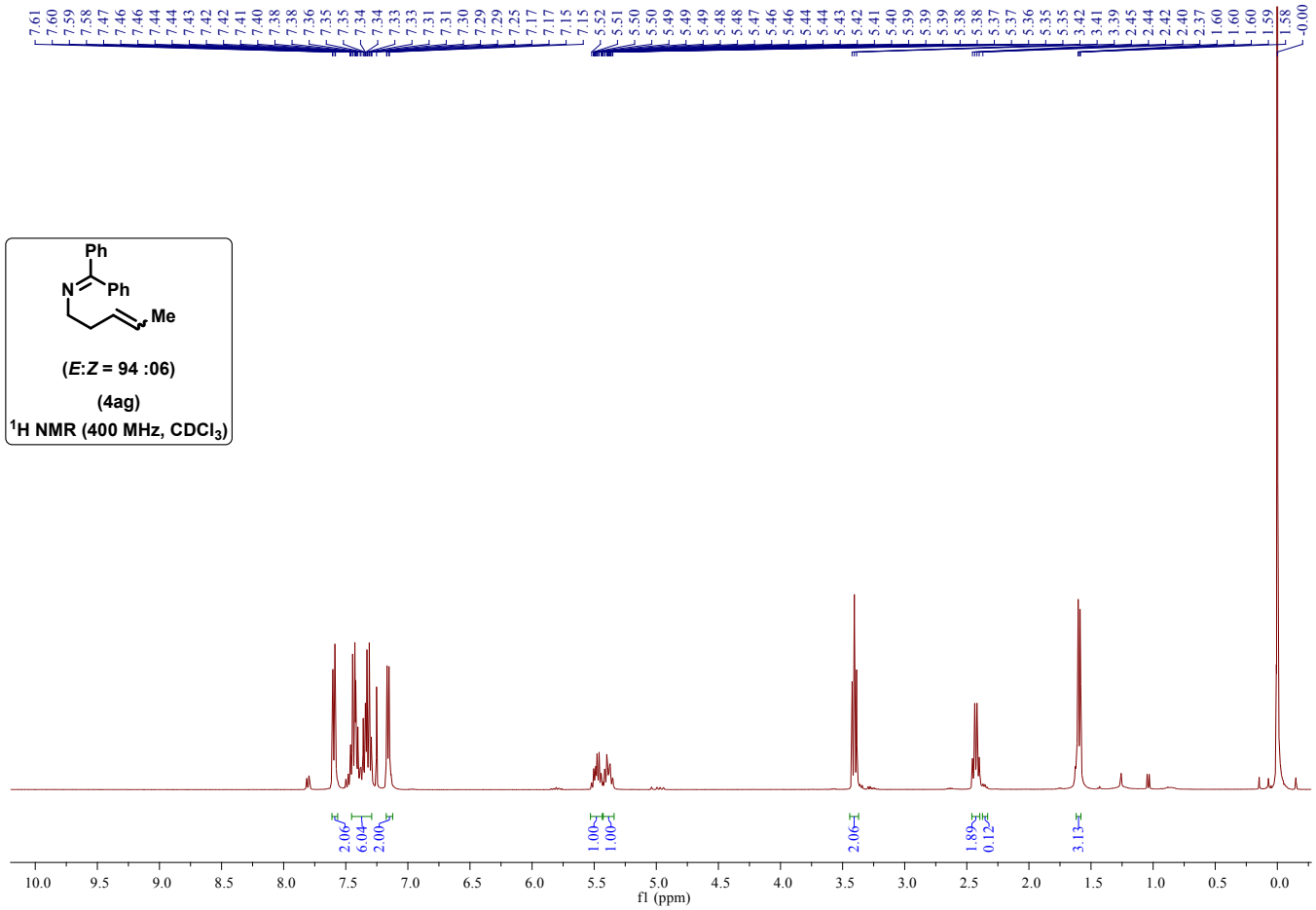


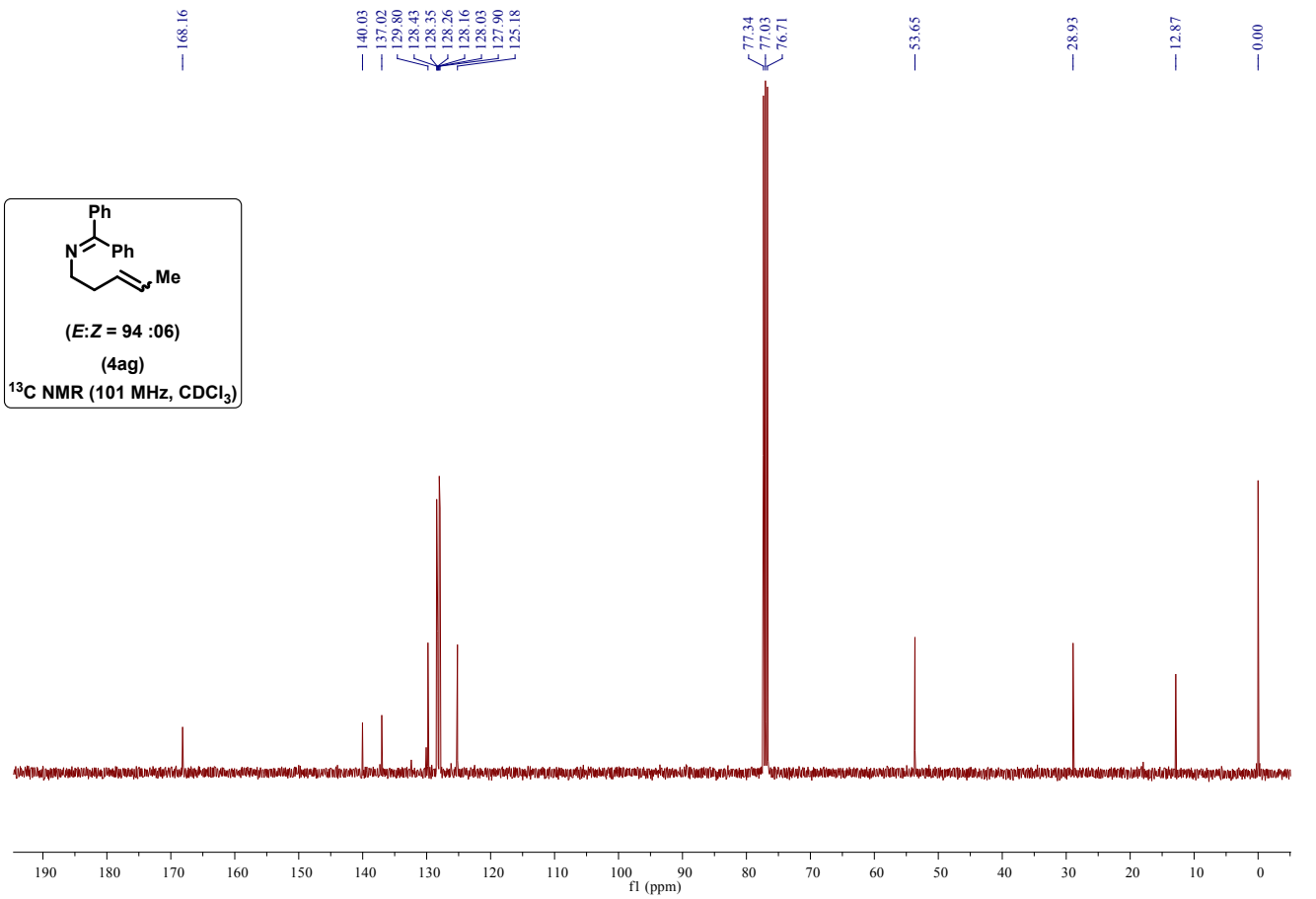
Copies of NMR spectra



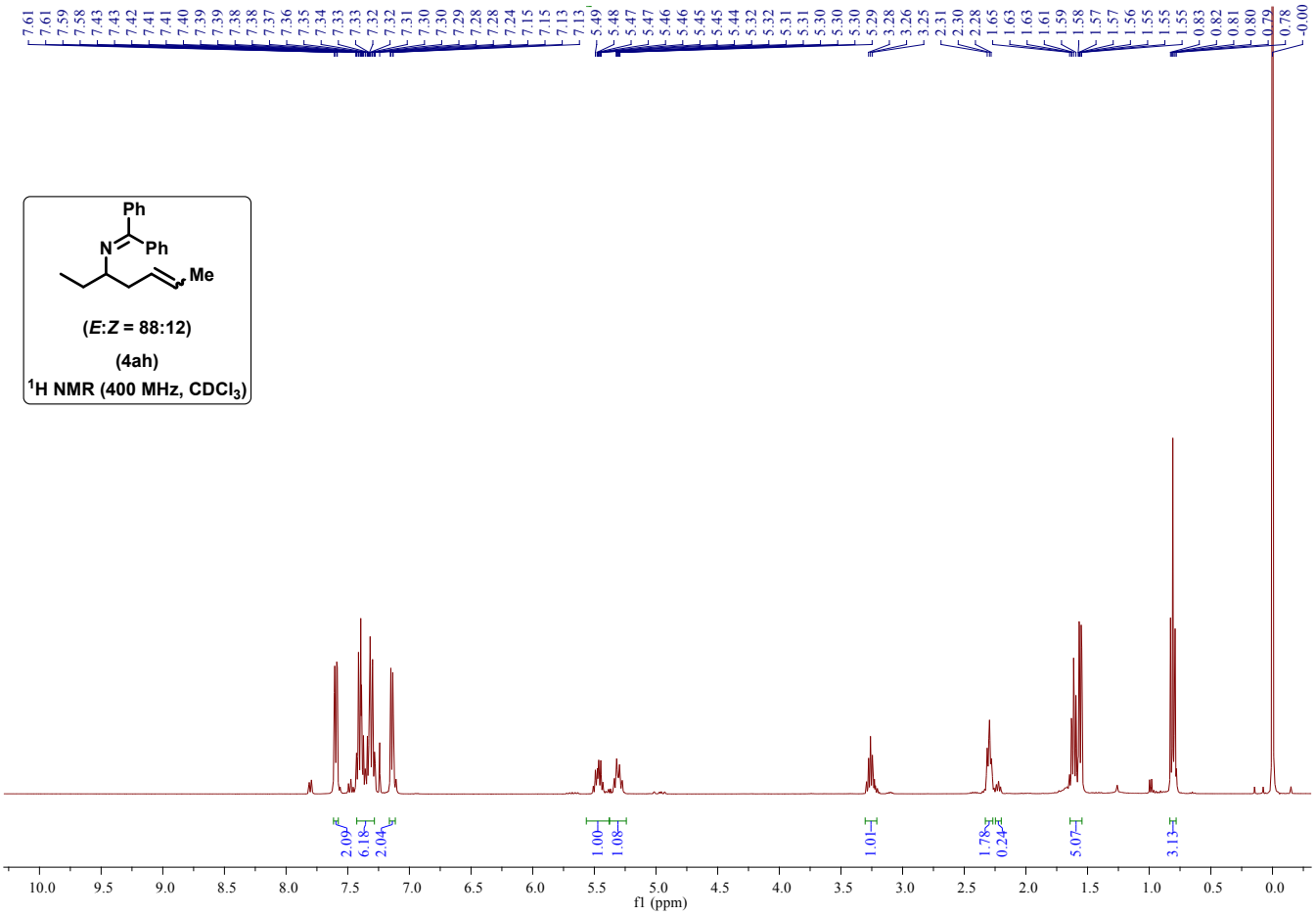


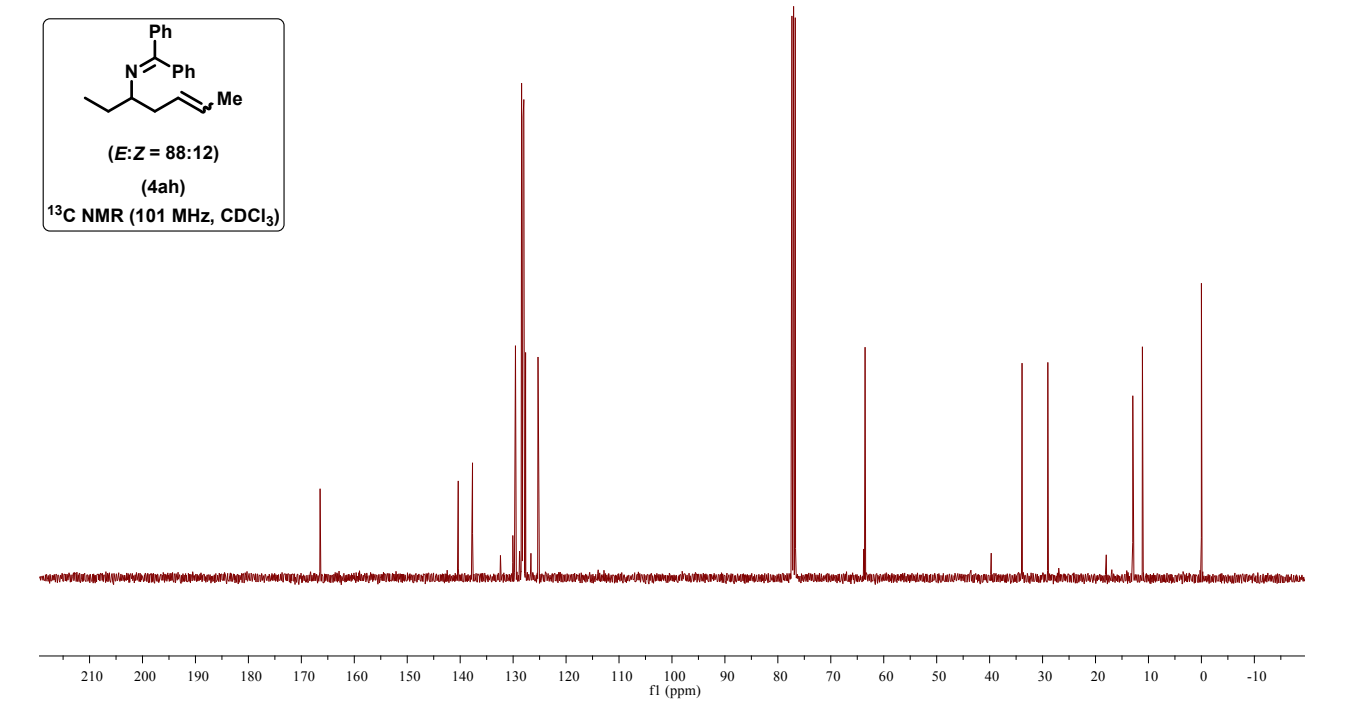
Copies of NMR spectra



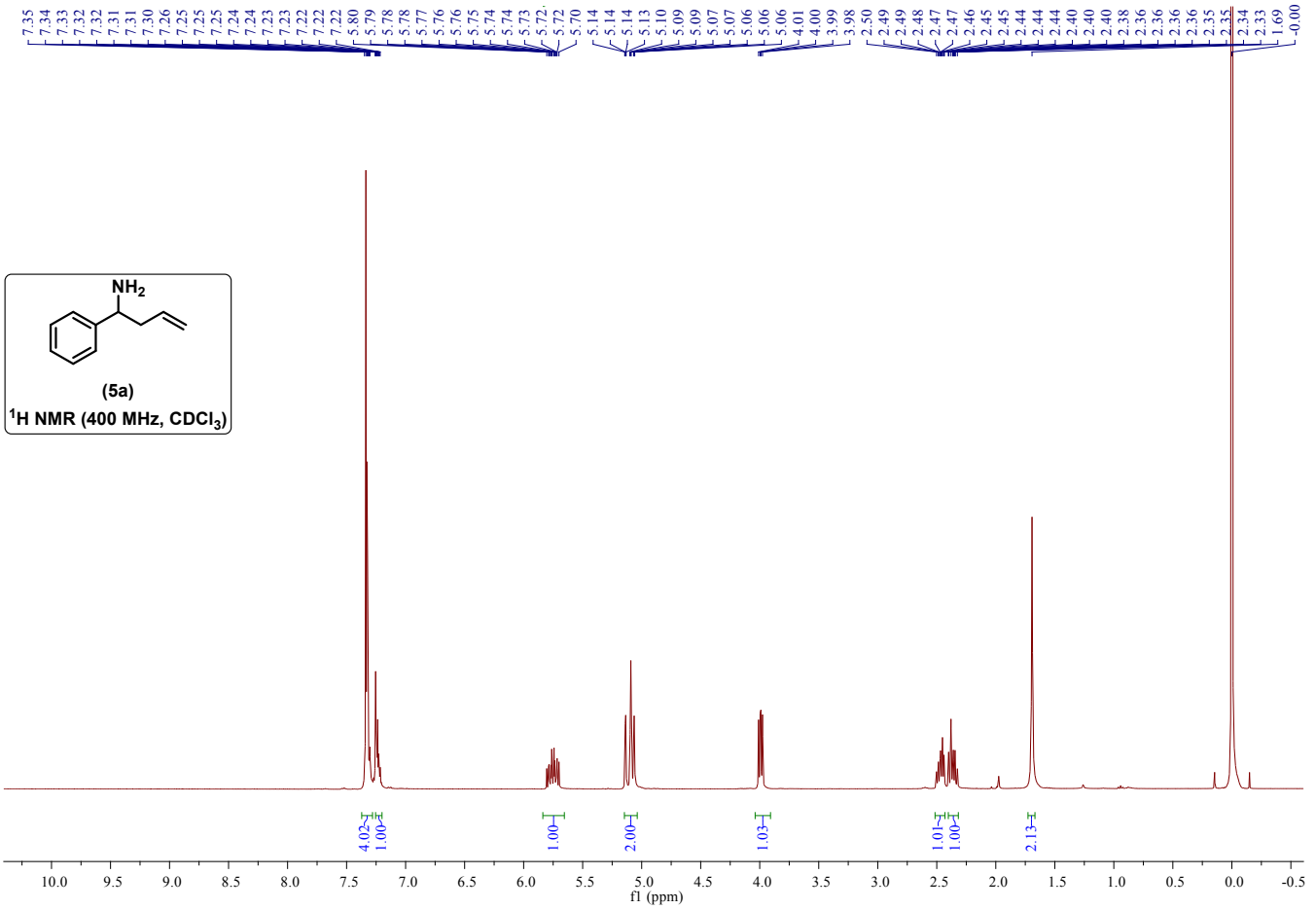


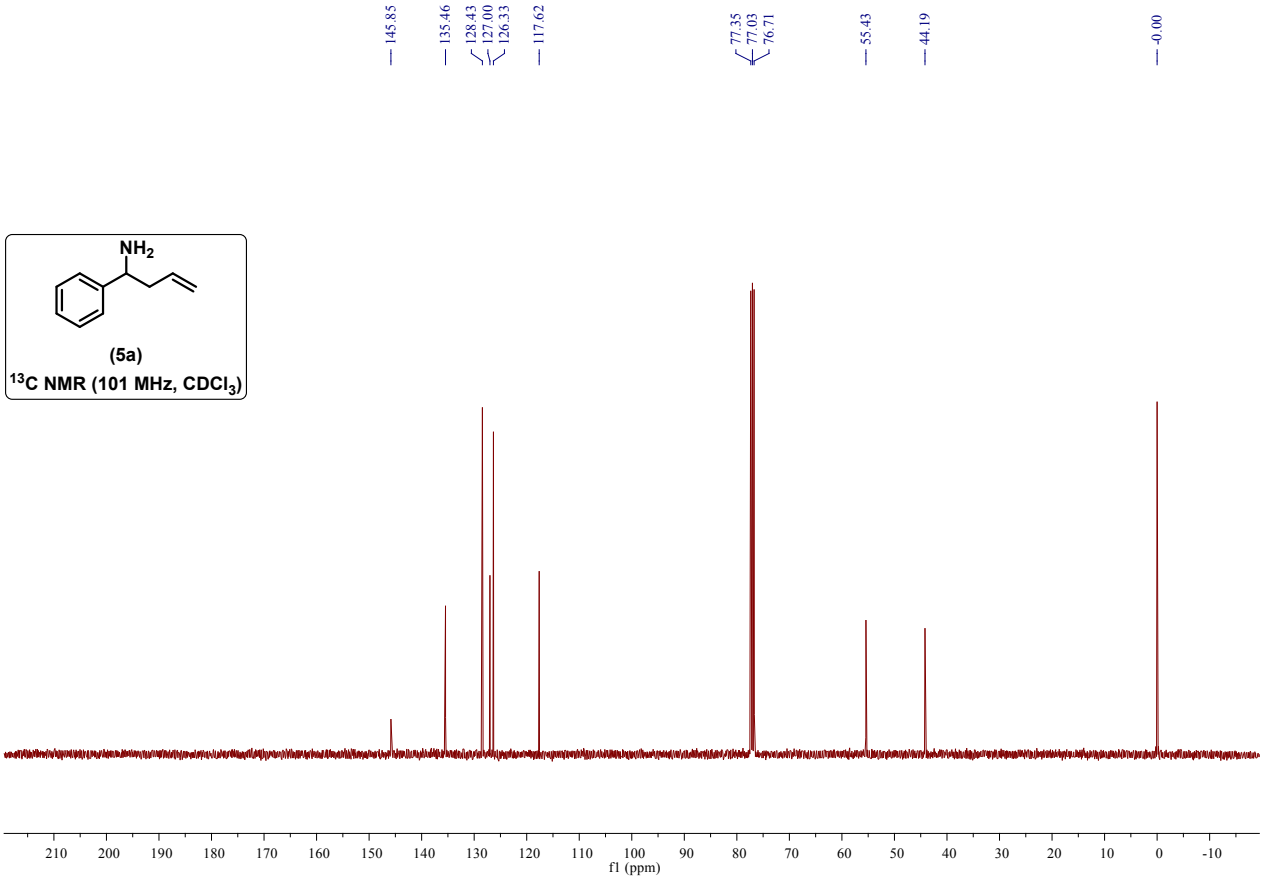
Copies of NMR spectra



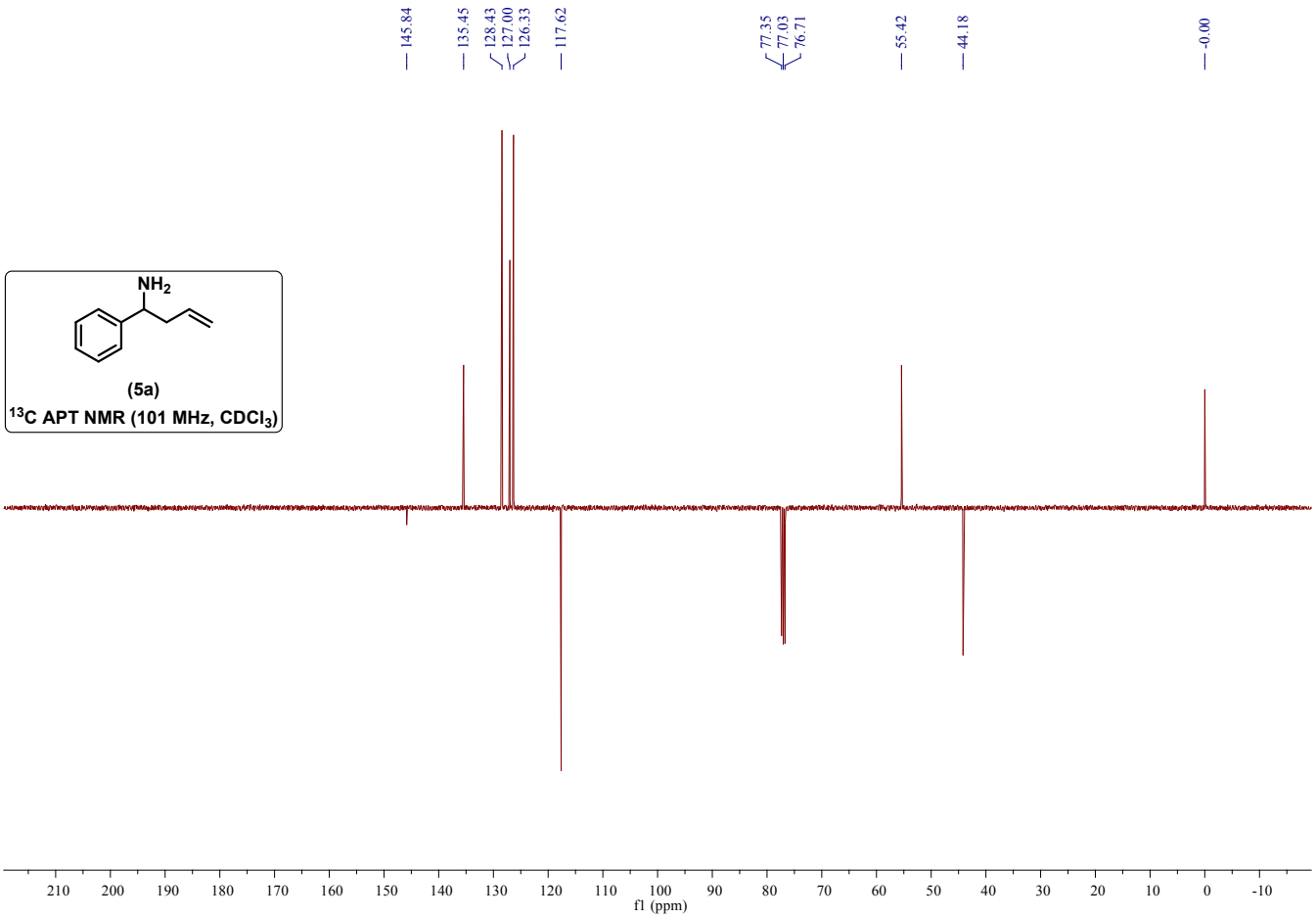


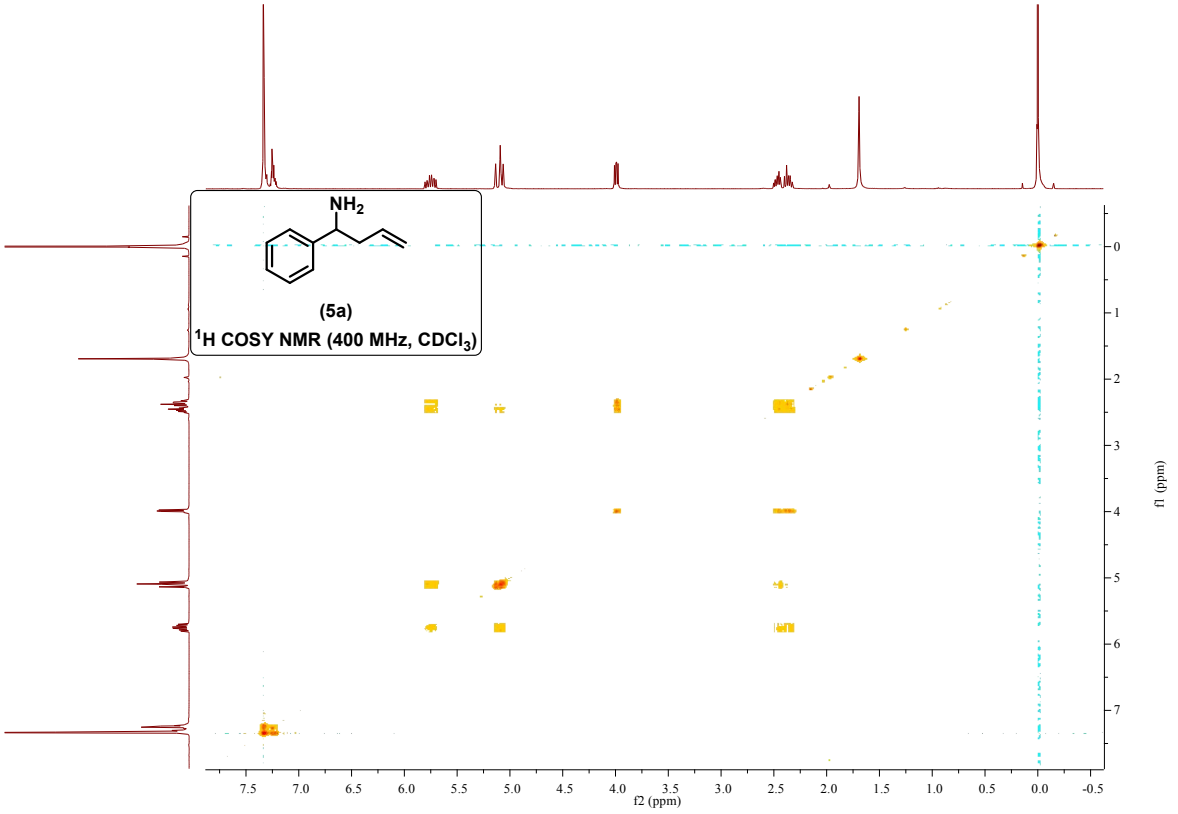
Copies of NMR spectra



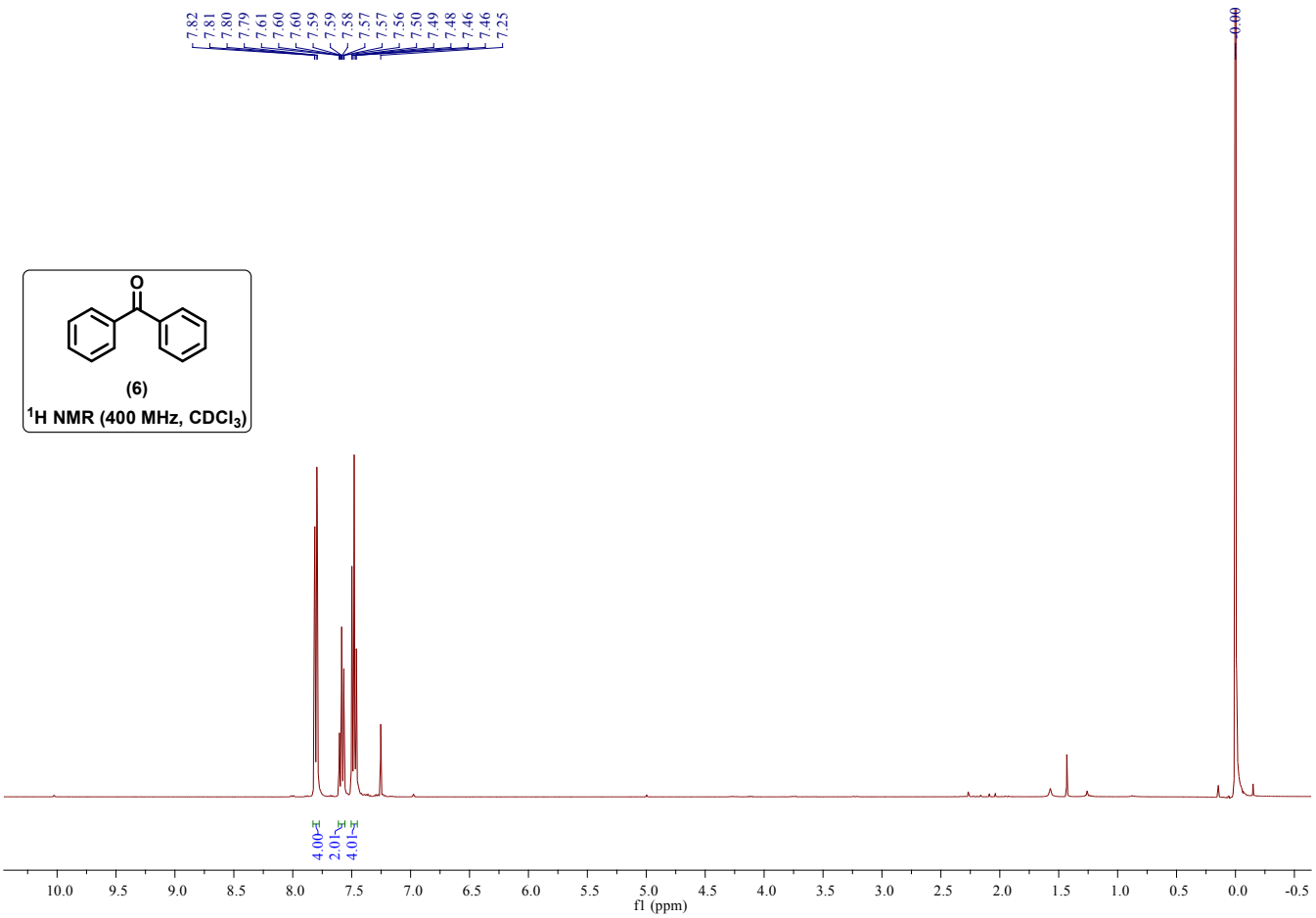


Copies of NMR spectra

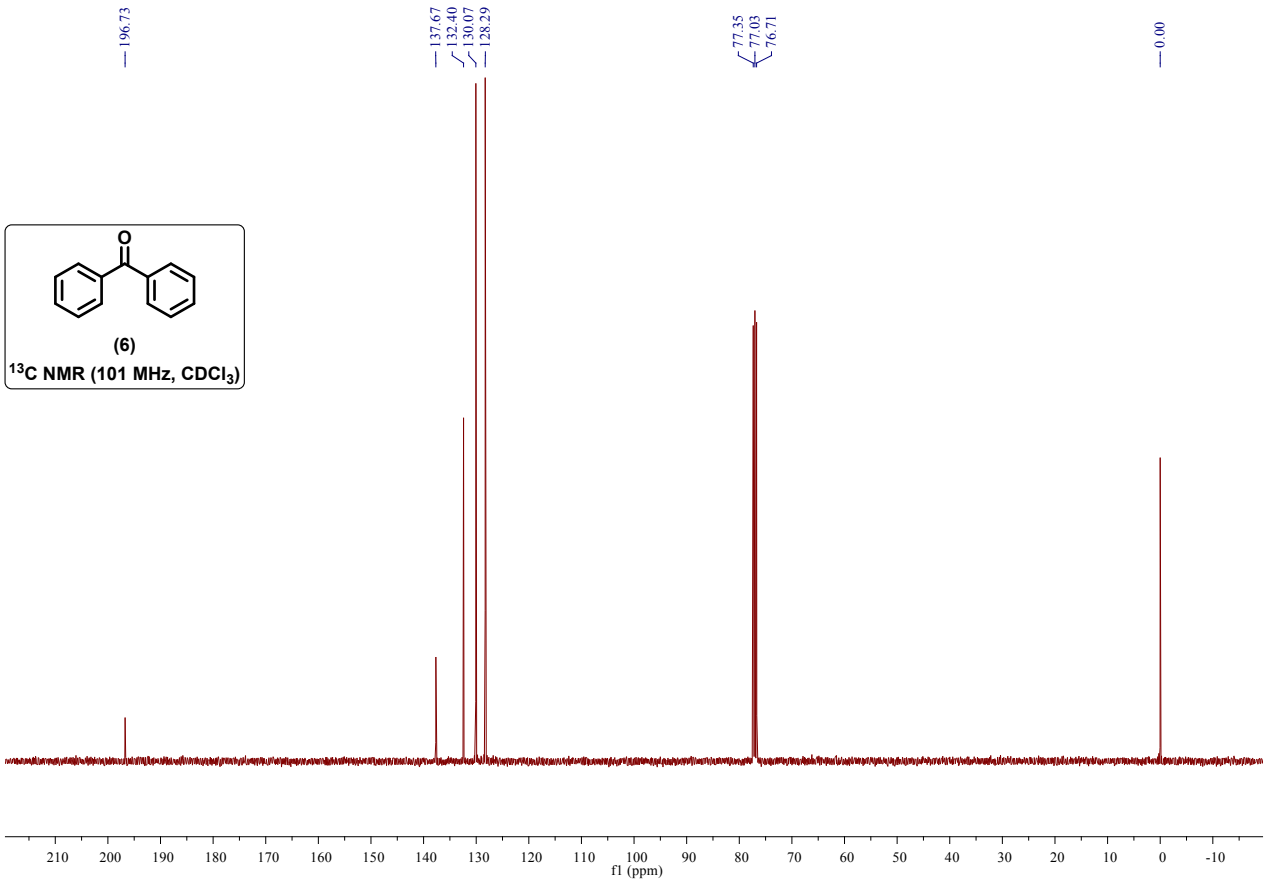




Copies of NMR spectra



(6)
^{1}H NMR (400 MHz, $CDCl_3$)



(6)
^{13}C NMR (101 MHz, $CDCl_3$)