SUPPORTING INFORMATION

Nickel-Catalyzed Allylic Alkylation with Diarylmethane Pronucleophiles: Development and Mechanistic Insight

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General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. The solvent (DME) was sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with neutral alumina. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI America, Strem Chemicals or Matrix Scientific, and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wavelength ultraviolet light as well as by treatment potassium permanganate ($KMnO_4$) stain or iodine. Silica gel (230–400 mesh, Silicycle) was used for flash chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained using a Brüker AM-500 Fourier transform NMR spectrometer at 500 and 126 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC–TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of Diarylmethanes.

Compounds **4d**[1], **4e**[2], **7b**[3] were prepared according to literature procedures.

Preparation of Allylic Electrophiles.

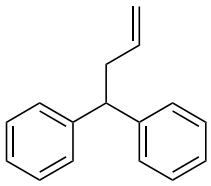
Compounds **2a**[4], **2b**[5], **2c**[6] were prepared according to literature procedures.

General Procedure A: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (100 mg, 0.50 mmol, 5 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Ni(COD)_2$ (2.06 mg, 0.0075 mmol) and DPPF (8.31 mg, 0.015 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, diphenylmethane (**1a**) (17 μL,

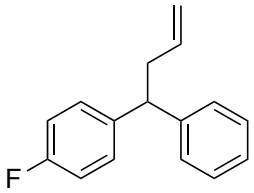
0.1 mmol, 1 equiv) was added to the reaction mixture followed by allylOBoc (**2a**) (51 μL, 0.3 mmol, 3 equiv). Note that the diarylmethanes or allylic OBoc in a solid form was added to the reaction vial prior to $KN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 24 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7 mL of ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes.

General Procedure B: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Ni(COD)_2$ (1.37 mg, 0.005 mmol) and DPPF (5.54 mg, 0.010 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, 2-benzylpyridine (**4a)** (16 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by allylOBoc (**2a**) (20.4 μL, 0.12 mmol, 1.2 equiv). Note that the diarylmethanes or alylic OBoc in a solid form was added to the reaction vial prior to $NaN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 24 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7 mL of ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes.

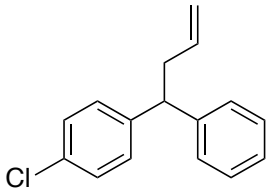
General Procedure C: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Ni(COD)_2$ (1.37 mg, 0.005 mmol) and enantioenriched phosphine ligand **L1** (3.65 mg, 0.005 mmol) in 1 mL of dry DME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, di(pyridin-3-yl)methane (**4d)** (17 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by cyclohexenyl OBoc (**2b)** (40 μL, 0.2 mmol, 2 equiv). Note that the di(pyridin-3-yl)methane (**4d) or** *tert*-butyl ((1S,3S)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl) carbonate (**2c)** was added to the reaction vial prior to $NaN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 0 °C, quenched with two drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional 7mL of ethyl acetate, and the solution was concentrated *in vacuo*. The crude material was loaded onto a silica gel column and purified by flash chromatography eluting with EtOAc/hexanes.



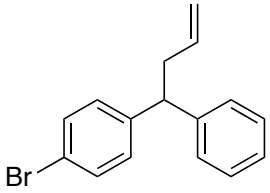
But-3-ene-1,1-diyldibenzene (3aa): The reaction was performed following General Procedure A with diphenylmethane (**1a)** (17 µL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and allylOBoc (**2a)** (51 µL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (18.3 mg, 88% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[7]



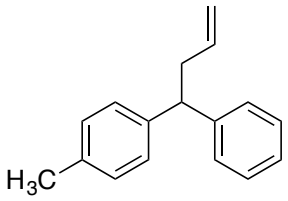
1-Fluoro-4-(1-phenylbut-3-en-1-yl)benzene (3ba): The reaction was performed following General Procedure A with 1-benzyl-4-fluorobenzene (**1b)** (17 μL, 0.1 mmol), $KN(SiMe_3)_2$ (80 mg, 0.40 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (15.2 mg, 67% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[8]



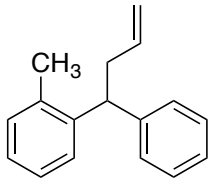
1-Chloro-4-(1-phenylbut-3-en-1-yl)benzene (3ca): The reaction was performed following General Procedure A with 1-benzyl-4-chlorobenzene (**1c)** (18 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (91 mg, 0.50 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (23.8 mg, 98% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[7]



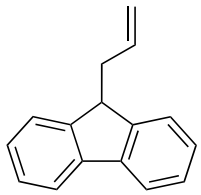
1-Bromo-4-(1-phenylbut-3-en-1-yl)benzene (3da): The reaction was performed following General Procedure A with 1-benzyl-4-bromobenzene (**1d)** (18.5 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (91 mg, 0.50 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (25.5 mg, 89% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[8]



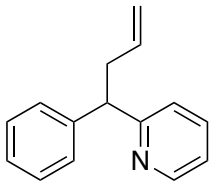
1-Methyl-4-(1-phenylbut-3-en-1-yl)benzene (3ea):The reaction was performed following General Procedure A with 1-benzyl-4-methylbenzene (**1e)** (18.5 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (13.5 mg, 61% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[7]



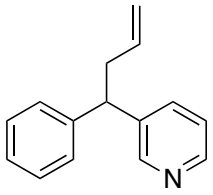
1-Methyl-2-(1-phenylbut-3-en-1-yl)benzene (3fa):The reaction was performed following General Procedure A with 1-benzyl-2-methylbenzene (**1f)** (18.5 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.50 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (14.4 mg, 65% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[9]



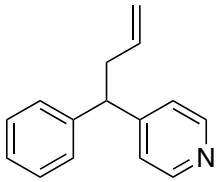
9-Allyl-9*H*-fluorene (3ga): The reaction was performed following General Procedure A with 9*H*-fluorene **(1g)** (16.7 mg, 0.1 mmol), LiO^tBu (12 mg, 0.15 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (17.1 mg, 83% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[10]



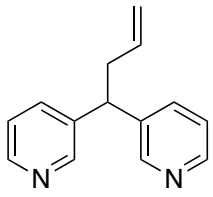
2-(1-Phenylbut-3-en-1-yl)pyridine (5aa): The reaction was performed following General Procedure B with 2-benzylpyridine (**4a)** (16 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (36 mg, 0.20 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 10:90) to give the product (19 mg, 91% yield) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 10:90); The NMR spectral data match the previously published data.[8]



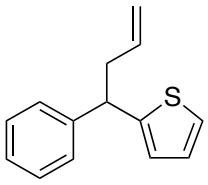
3-(1-Phenylbut-3-en-1-yl)pyridine (5ba): The reaction was performed following General Procedure B with 3-benzylpyridine **(4b)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.30 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 30:70) to give the product (19 mg, 91% yield) as a yellow oil. R_f = 0.40 (EtOAc:hexanes = 40:60); The NMR spectral data match the previously published data.[8]



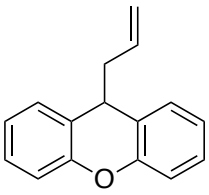
4-(1-Phenylbut-3-en-1-yl)pyridine (5ca): The reaction was performed following General Procedure B with 4-benzylpyridine **(4c)** (16 μL, 0.1 mmol), $LiN(SiMe_3)_2$ (34 mg, 0.20 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 30:70) to give the product (19.5 mg, 93% yield) as a yellow oil. R_f = 0.30 (EtOAc:hexanes = 40:60); The NMR spectral data match the previously published data.[8]



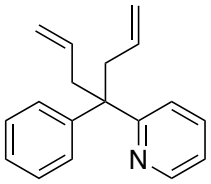
3,3'-(But-3-ene-1,1-diyl)dipyridine (5da): The reaction was performed following General Procedure B with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (51 mg, 0.30 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (18.9 mg, 90% yield) as a yellow oil. R_f = 0.30 (MeOH:DCM = 2.5:97.5); The NMR spectral data match the previously published data.[8]



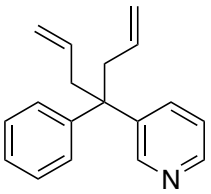
2-(1-Phenylbut-3-en-1-yl)thiophene (5ea): The reaction was performed following General Procedure B with 2-benzylthiophene (**4e)** (16 μL, 0.1 mmol), $NaN(SiMe_3)_2$ (36 mg, 0.20 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (17.6 mg, 82% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[12]



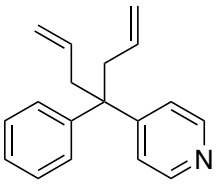
9-Allyl-9*H*-xanthene (5fa): The reaction was performed following General Procedure B with xanthene (**4f)** (18.2 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (55 mg, 0.30 mmol) and allylOBoc (**2a)** (20.4 μL, 0.12 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (18 mg, 81% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[11]



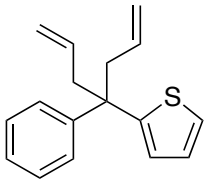
2-(4-Phenylhepta-1,6-dien-4-yl)pyridine (6aa): The reaction was performed following General Procedure B with 2-benzylpyridine **(4a)** (16 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (21 mg, 84% yield) as a colorless oil. R_f = 0.30 (EtOAc:hexanes = 5:95); The NMR spectral data match the previously published data.[8]



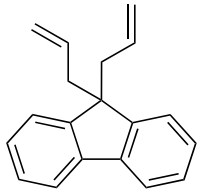
3-(4-Phenylhepta-1,6-dien-4-yl)pyridine (6ba): The reaction was performed following General Procedure B with 3-benzylpyridine **(4b)** (17 mg, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 20:80) to give the product (19.5 mg, 78% yield) as a colorless oil. R_f = 0.20 (EtOAc:hexanes = 20:80); The NMR spectral data match the previously published data.[8]



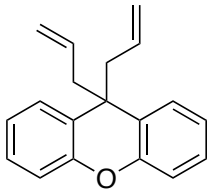
4-(4-Phenylhepta-1,6-dien-4-yl)pyridine (6ca): The reaction was performed following General Procedure B with 4-benzylpyridine **(4c)** (16 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 40:60) to give the product (18.7 mg, 75% yield) as a colorless oil. R_f = 0.25 (EtOAc:hexanes = 40:60); The NMR spectral data match the previously published data.[8]



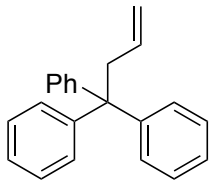
2-(4-Phenylhepta-1,6-dien-4-yl)thiophene (6da): The reaction was performed following General Procedure B with 2-benzylthiophene (**4e)** (16 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (21.1 mg, 83% yield) as a colorless oil. R_f = 0.30 (hexanes); The NMR spectral data match the previously published data.[8]



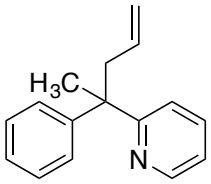
9,9-Diallyl-9*H*-fluorene (6ea): The reaction was performed following General Procedure B with 9*H*-fluorene **(1g)** (16.7 mg, 0.1 mmol), KO^{t}Bu (56 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (22.2 mg, 90% yield) as a colorless oil. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data.[20]



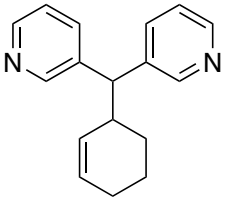
9,9-Diallyl-9*H*-xanthene (6fa): The reaction was performed following General Procedure B with xanthene (**4f)** (18.2 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (91 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (23.3 mg, 89% yield) as a colorless oil. R_f = 0.25 (hexanes); The NMR spectral data match the previously published data.[8]



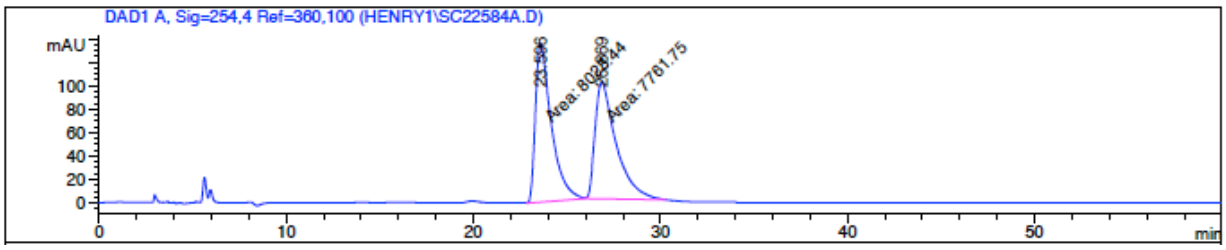
But-3-ene-1,1,1-triyltribenzene (8aa): The reaction was performed following General Procedure B with triphenylmethane (**7a)** (24.4 mg, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (25.5 mg, 90% yield) as white solid. R_f = 0.20 (hexanes); The NMR spectral data match the previously published data. [21]



2-(2-Phenylpent-4-en-2-yl)pyridine (8ba): The reaction was performed following General Procedure A with 2-(1-phenylethyl)pyridine **(7b)** (18 μL, 0.1 mmol), $KN(SiMe_3)_2$ (100 mg, 0.5 mmol) and allylOBoc (**2a)** (51 μL, 0.3 mmol). The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (20.5 mg, 92% yield) as a colorless oil. R_f = 0.20 (EtOAc:hexanes = 5:95); The NMR spectral data match the previously published data.[8]

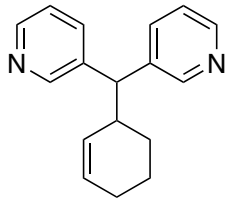


3,3'-(Cyclohex-2-en-1-ylmethylene)dipyridine (9db) (from DPPF): The reaction was performed following General Procedure B with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and cyclohexenyl OBoc (**2b)** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (22.5 mg, 91% yield) as a yellow oil. R_f = 0.25 (MeOH:DCM = 2.5:97.5); The NMR spectral data match the previously published data.[8] The enantiomers were resolved by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, major tr= 23.6 min, minor tr = 26.9 min).



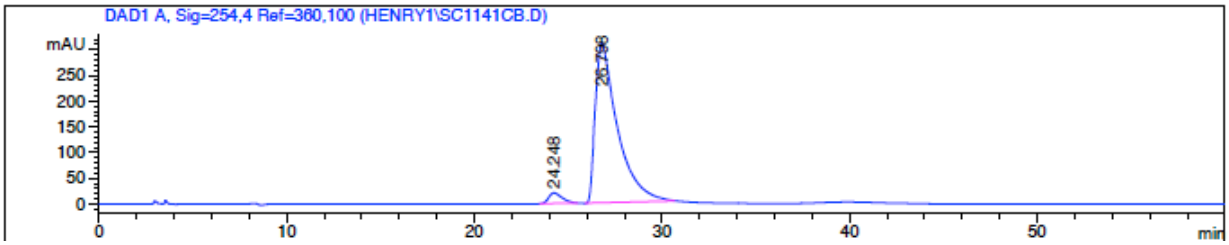
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.596	MM	0.9899	8028.43848	135.16833	50.8445
2	26.869	MM	1.3019	7761.75195	99.36530	49.1555
Totals :				1.57902e4	234.53363	



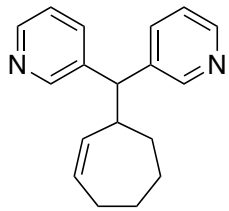
3,3'-(Cyclohex-2-en-1-ylmethylene)dipyridine (9db) [from L1 (SL-J204-1)]: The reaction was performed following General Procedure C with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and cyclohexenyl OBoc (**2b)** (40 μL, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (22.5 mg, 91% yield, 92% e.e.) as a yellow oil. R_f = 0.25 (MeOH:DCM = 2.5:97.5); The NMR spectral data match the previously published data.[8]

The ee was determined by HPLC with a Daicel Chiralpak AD-H column (10% isopropanol in hexanes, 1 mL/min, 254 nm, minor tr= 24.2 min, major tr = 26. 8 min).



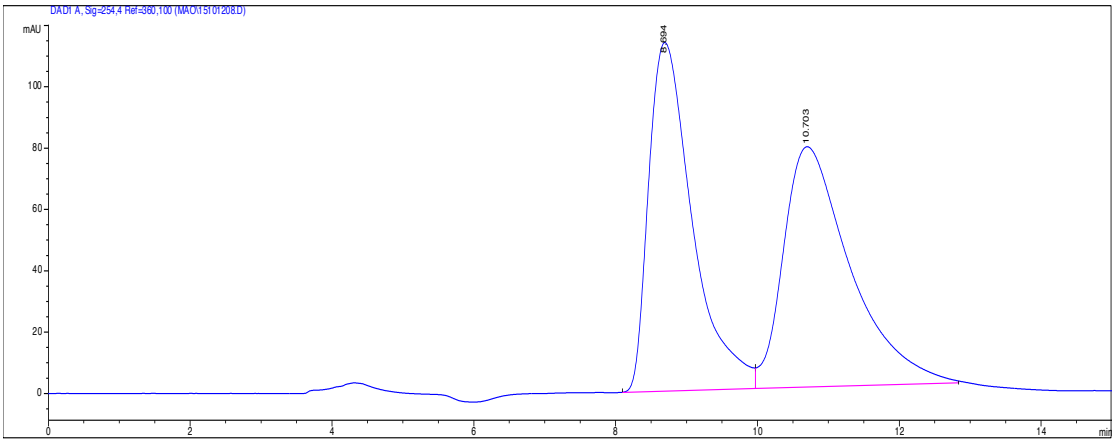
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.248	PB	0.7350	1024.41492	20.71267	3.8563
2	26.798	PB	1.1770	2.55403e4	312.02063	96.1437
Totals :				2.65648e4	332.73330	

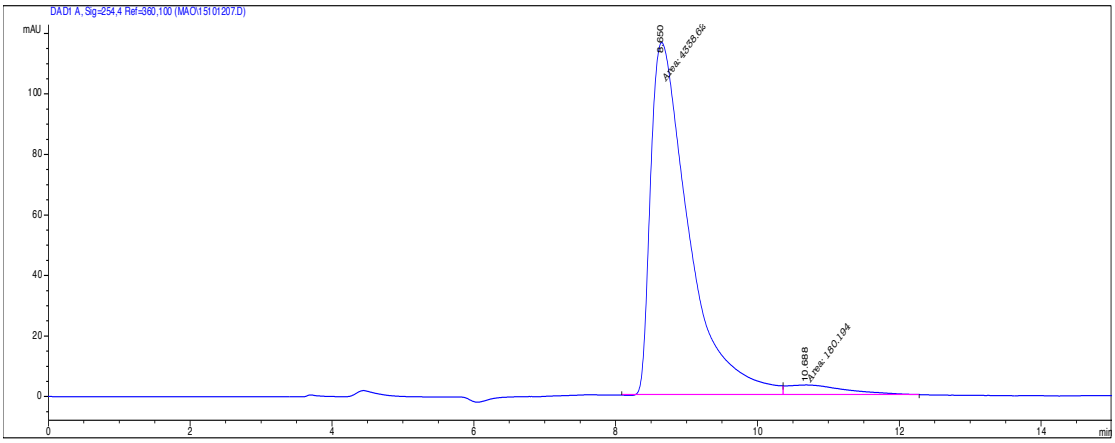


3,3'-(Cyclohept-2-en-1-ylmethylene)dipyridine (9dd) [from L1 (SL-J204-1)]: The reaction was performed following General Procedure B with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and cycloheptenyl OBoc **(2d)** (53 mg, 0.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (22.5 mg, 85% yield) as a yellow oil. R_f = 0.25 (MeOH:DCM = 2.5:97.5); ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.55 (t, J = 3.0, 2H), 8.45-8.42 (m, 2H), 7.56 (ddt, J = 11.8, 8.0, 1.8, 2H), 7.21 (dt, J = 8.2, 4.2, 2H), 5.76 (dtd, J = 11.0, 6.5, 2.0, 1H), 5.40 (dd, J =

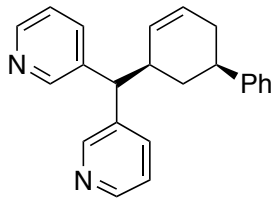
11.1, 4.5, 1H), 3.89 (d, J = 11.1, 1H), 3.21-3.16 (m, 1H), 2.19-2.15 (m, 2H), 1.90 (dtd, J = 11.3, 5.7, 3.2, 1H), 1.70-1.65 (m, 1H), 1.59-1.49 (m, 2H), 1.32 (dtd, J = 9.9, 6.5, 3.3, 1H), 1.26-1.23 (m, 1H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 150.2, 149.9, 148.09, 148.01, 138.9, 138.5, 135.6, 135.3, 134.8, 132.5, 123.7, 123.6, 52.1, 42.6, 31.3, 30.5, 28.5, 26.2. IR: 2924, 2853, 1735, 1575, 1478, 1422, 1377, 1107, 1025, 799, 720. HRMS : calcd for $C_{18}H_{20}N_2$ $[M+H]^+$ 265.1705, found 265.1704. $[\alpha]_D^{25}$ = 59.9. The ee was determined by HPLC with a Daicel Chiralpak AS-H column (20% isopropanol in hexanes, 0.8 mL/min, 254 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.694	BB	0.6568	4879.19727	113.67563	48.6841
2	10.703	BB	0.9616	5142.96191	78.36824	51.3159
Totals :				1.00222e4	192.04387	

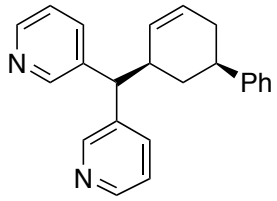


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.650	MF	0.6216	4338.62305	116.32966	96.0124
2	10.688	FM	0.9468	180.19398	3.17186	3.9876
Totals :				4518.81703	119.50152	



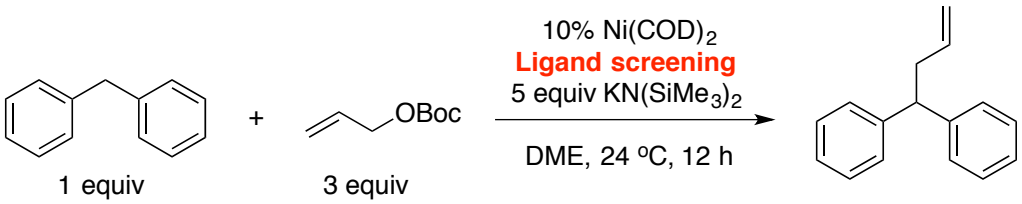
3,3'-(((1*R*,3*R*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)methylene)dipyridine (10dc)(from DPPF): The reaction was performed following General Procedure B with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and *tert*-butyl ((1S,3S)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl) carbonate (**2c)** (54 μL, 0.2 mmol, *cis:trans* > 30:1). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (29 mg, 89% yield, *cis:trans* = 15:1) as a pale yellow oil. R_f = 0.20 (MeOH:DCM = 2.5:97.5); The NMR spectral data match the previously published data.[8]

Stereochemistry was assigned by ^{1}H NMR analysis.[6]

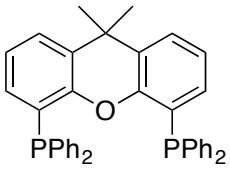


3,3'-(((1*R*,3*R*)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)methylene)dipyridine (10dc) [from L1 (SL-J204-1)]: The reaction was performed following General Procedure C with di(pyridin-3-yl)methane **(4d)** (17 mg, 0.1 mmol), $NaN(SiMe_3)_2$ (55 mg, 0.3 mmol) and *tert*-butyl ((1S,3S)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl) carbonate (**2c)** (54 μL, 0.2 mmol, *cis:trans* > 30:1). The crude material was purified by flash chromatography on silica gel (eluted with MeOH:DCM = 2.5:97.5) to give the product (28.4 mg, 87% yield, *cis:trans* = 15:1) as a pale yellow oil. R_f = 0.20 (MeOH:DCM = 2.5:97.5); The NMR spectral data match the previously published data.[8]

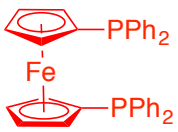
Screening Results of Achiral Ligands



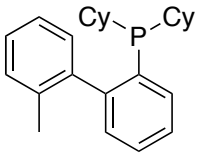
Control: Xantphos
Assay Yield/ Internal Standard



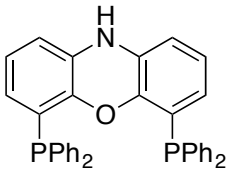
Xantphos: 22



DPPF: 46



MePhos: 11



NiXantphos: 20

24 Achiral Ligands
2-(Di-tert-butylphosphino)biphenyl (JohnPhos)
4-(Di-tert-butylphosphino)-N,N-dimethylaniline (Ataphos)
2-Dicyclohexylphosphino-2'-(N,N-dimethylamino)biphenyl (Dave Phos)
2-Di-tert-butylphosphino-3,4,5,6-tetramethyl-2',4',6'-triisopropyl-1,1'-biphenyl (Me4tBuXPhos)
Dicyclohexyl-[3,6-dimethoxy-2-(2,4,6-triisopropylphenyl)phenyl]phosphane (BrettPhos)
1,1'-Bis(diphenylphosphino)ferrocene (Dppf)
9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (XantPhos)
2-Dicyclohexylphosphino-2′-methylbiphenyl (MePhos)
N-(dicyclohexylphosphino)-2-2'-tolylindole (Indole ligand)
P(O-Tol)3
$P^tBu_3HBF_4$
2-(Dicyclohexylphosphino)-1-phenyl-1H-pyrrole (CataCXium Pcy)
4,6-Bis(diphenylphosphino)phenoxazine (NIXANTPHOS)
Di(1-adamantyl)-2-dimethylaminophenylphosphine (Me-Dalphos)
2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (Sphos)
Butyldi-1-adamantylphosphine (CataCXium A)
PCy_3HBF_4
2-Di-tert-butylphosphino-3-Methoxy-6-Methyl-2'-4'-6'-triisopropylbiphenyl (RockPhos)
1,2,3,4,5-Pentaphenyl-1'-(di-t-butylphosphino)ferrocene (Qphos)
PPh_3
1-[2-[Bis(tert-butyl)phosphino]phenyl]-3,5-diphenyl-1H-pyrazole (Trippy Phos)
2-(Dicyclohexylphosphino)biphenyl (CyJohnPhos)
2-Dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl (Xphos)
Di(1-adamantyl)-2-morpholinophenylphosphine (Mor-DalPhos)

Screening Results of Chiral Ligands

Chiral Ligands P1-52 ligands	Assay Yield (%)	ee[a] (%)
(S,S)-bpm2: (2S,4S)-tBu-(-)-4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)pyrrolidine carboxylate	62	16
Catasium D: (3S,4S)-(-)-1-Benzyl-3,4-bis(diphenylphosphino)pyrrolidine	35	10
(R,R)-SL-M004-1: (SP,S'P)-1,1'-Bis[bis(4-methoxy-3,5-dimethylphenyl)phosphino]-2,2'-bis[(R)-alpha-(dimethylamino)benzyl]ferrocene	59	21
SL-W009-1: [2-[2-[(1S)-1-bis(3,5-dimethylphenyl)phosphanylethyl]cyclopentyl]phenyl]-bis(3,5-dimethylphenyl)phosphane;cyclopentane;iron	78	30
(R,R)-SL-W021-1: dimethoxy-2'-(Diphenylphosphino)phenyl]ferrocenyl}ethyl di(bis-(3,5-trifluoromethyl)phenyl)-phosphine	74	30
(S,S)-DIOP: (4S,5S)-2,2-Dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane	46	5
(S,S)-SL-M001-1: (aR,aR)-2,2'-Bis(a-N,N-dimethylaminophenylmethyl)-(S,S)-1,1'-bis(diphenylphosphino)-ferrocene	64	35
(S,S)-SL-M002-1: (aR,aR)-2,2'-Bis(a-N,N-dimethylaminophenylmethyl)-(S,S)-1,1'-bis(dicyclohexylphosphino)-ferrocene	64	14
(S,S)-SL-M003-1: (aR,aR)-2,2'-Bis(a-N,N-dimethylaminophenylmethyl)-(S,S)-1,1'-bis[di-(bis(3,5-trifluoromethyl)-phenyl)phosphino]-ferrocene	27	11
(S)-BINAPINE: (3S,3'S,4S,4'S,11bS,11'bS)-(+)-4,4'-Di-t-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho[2,1-c:1',2'-e]phosphepine	27	11
(S,S)-SL-T001-1: (S)-1-Diphenylphosphino-2-[(S)-a-(N,N-dimethyl-amino)-o-(diphenylphosphinophenyl)methyl]-ferrocene	71	20
(R,S)-SL-T002-1**:** (R)-1-Dicyclohexylphosphino-2-[(R)-a-(N,N-dimethylamino)-o-(dicyclohexylphosphinophenyl)-methyl]-ferrocene	65	12
(S)-CTH-JAFAPHOS: (R)-CTH-JAFAPHOS;(R)-(+)-1,1'-BIS(DIPHENYLPHOSPHINO)-2,2'-BIS(N,N-DIISOPROPYLAMIDO)FERROCENE	51	20
(R,R)-Me-DuPhos: 1,2-bis((2R,5R)-2,5-dimethylphospholano)benzene	76	60
(R,R)-i-Pr-DUPHOS: (+)-1,2-Bis((2R,5R)-2,5-di-i-propylphospholano)benzene	48	13
(R,R) Et-DuPhos: (-)-1,2-BIS((2R,5R)-2,5-DIETHYLPHOSPHOLANO)BENZENE	67	15
(R)-Prophos: (R)-(+)-BIS-(1,2-DIPHENYLPHOSPHINO)PROPANE	15	-
SL-J011-1: (R)-1-[(S)-2-Di-(4-trifluoromethylphenylphos-phino)ferrocenyl]-ethyl-di-tert.-butylphosphine	56	20
SL-J412-1: (R)-1-[(S)-2-bis(3,5-dimethylphenyl)phosphino)ferrocenyl]ethyl bis[bis-(3,5-trifluoro- methyl)phenyl]-phosphine	49	12
SL-W022-1: (R)-1-{(RP)-2-[2-(Diphenylphosphino)phenyl]ferrocenyl}ethyldi(2-norbornyl)phosphine	68	-
SL-F011-2: (Twinphos, analog of Me-BoPhoz)	76	6
SL-F013-2: (Twinphos, analog of P(cyco)-BoPhoz)	80	44
(S,S)-Ph-BPE: (+)-1,2-Bis((2S,5S)-2,5-diphenylphospholano)ethane	59	50
(+)-catASium I: [(1R,2R,3S)-(+)-1,2-Dimethyl-2,3-bis(diphenylphosphinomethyl)cyclopentyl]methanol	71	37
(S,S)-CHIRAPHOS: (2S,3S)-(-)-Bis(diphenylphosphino)butane	31	9
(R,R)-SL-W002-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-diphenylphosphine	78	3
(S,S)-DIPAMP: (S,S)-(+)-1,2-Bis[(2-methoxyphenyl)(phenyl)phosphino]ethane	59	20
(1S,1'S,2R,2'R)-DuanPhos: (1S,1'S,2R,2'R)-2,2'-Di-tert-butyl-2,3,2',3'-tetrahydro-1H,1'H-(1,1')biisophosphindolyl	62	17
(R)-BINAPHANE: (R,R)-(-)-1,2-Bis{(R)-4,5-dihydro-3H-binaphtho[1,2-c:2',1'-e]phosphepino}benzene	71	5
(S,S,S,S)-Me-Ketalphos	71	3

(S,S,R,R)-TANGPHOS: (1S,1'S,2R,2'R)-(+)-1,1'-Di-t-butyl-[2,2']-diphospholane	29	-
SL-W006-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-di-3,5-xylylphosphine	74	20
(-)-MOD DIOP: ((4S,5S)-2,2-diMethyl-1,3-dioxolane-4,5-diyl)bis(Methylene)bis(bis(3,5-diMethylphenyl)phosphine	53	13
SL-W003-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-dicyclohexylphosphine	72	5
CTH-(R)-SpiroP: 1R,5R,6R-(+)-1,6-Bis(diphenylphosphinoxy)spiro[4.4]nonane	74	3
SL-W001-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-di-bis(3,5-trifluoromethyl-phenyl)phosphine	73	15
CARBOPHOS: METHYL-ALPHA-D-GLUCOPYRANOSIDE-2,6-DIBENZOATE-3,4-DI(BIS(3,5-DIMETHYLPHENYL)PHOSPHINITE)	76	7
(1S,2S)-(-)-Bis(methylphenylphosphino)benzene	59	-
SL-W008-1: (R)-1-[(R)-2-(2'-Dicyclohexylphosphinophenyl)-ferrocenyl]-ethyl-di-bis(3,5-trifluoromethyl)-phenyl)phosphine	72	45
(S)-Me-f-Ketalphos: 1,1′-Bis[(3a*S*,4*S*,6*S*,6a*S*)-tetrahydro-2,2,4,6-tetramethyl-5*H*-phospholo[3,4-*d*]-1,3-dioxol-5-yl]ferrocene, 1,1-Bis[(2*S*,3*S*,4*S*,5*S*)-2,5-dimethyl-3,4-*O*-isopropylidene-3,4-dihydroxyphospholanyl]ferrocene	76	30
SL-W005-1: (*R*)-1-{(R_P)-2-[2-[Bis(4-methoxy-3,5-dimethylphenyl)phosphino]phenyl]ferrocenyl}ethylbis[3,5-bis(trifluoromethyl)phenyl]phosphine	72	28
(R,R)-NORPHOS: (2R,3R)-(-)-2,3-BIS(DIPHENYLPHOSPHINO)BICYCLO[2.2.1]HEPT-5-ENE	40	9
catASium D (R):(3R,4R)-(+)-1-BENZYL-3,4-BIS(DIPHENYLPHOSPHINO)PYRROLIDINE	54	4
M012-1: (S,S)-(-)-2,2'-BIS[(R)-(N,N-DIMETHYLAMINO)(PHENYL)METHYL]-1,1'-BIS(DI(2-METHYLPHENYL)PHOSPHINO)FERROCENE	46	22
CTH-(R)-3,5-xylyl-PHANEPHOS: (R)-(-)-4,12-Bis(di(3,5-xylyl)phosphino)-[2.2]-paracyclophane	54	27
(S,S)-BDPP: (2S,4S)-(-)-2,4-BIS(DIPHENYLPHOSPHINO)PENTANE	24	9
(R,R)-QuinoxP*: (R,R)--2,3-Bis(tert-butylmethylphosphino)quinoxaline	37	-
SL-J005-1: (R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine	48	25
SL-J216-1: (R)-1-[(S)-2-(Di-1-naphtylphosphino)ferrocenyl]-ethyl-di-tert.-butylphosphine	40	20
SL-J404-1: (R)-1-[(S)-2-(Di-1-naphtylphosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine	61	31
SL-J502-1: (R)-1-[(S)-2-(Di-tert.-butylphosphino)ferrocenyl]-ethyl-diphenylphosphine	64	7
SL-J505-1: (R)-1-[(S)-2-(Di-tert.-butylphosphino)ferrocenyl]-ethyl-di-2-methylphenylphosphine	26	23

Chiral Ligands P2-70 ligands	Assay Yield (%)	ee[a] (%)
(R,R)-Me-BPE: (+)-1,2-Bis[(2R,5R)-2,5-dimethylphospholano]ethane	22	13
(R,R)-Et-BPE: (+)-1,2-Bis((2R,5R)-2,5-diethylphospholano)ethane	41	-
(R,R)-iPr-BPE: 1,2-BIS[(2R,5R)-2,5-DIISOPROPYLPHOSPHOLANO]ETHANE	46	9
(R,R)-Me-Ferrolane: 1,1'-BIS[(2R,5R)-2,5-DIMETHYLPHOSPHOLANO]FERROCENE	62	11
(R,R)-Et-Ferrolane: 1,1'-BIS[(2R,5R)-2,5-DIETHYLPHOSPHOLANO]FERROCENE	64	20
(R,R)-iPr-Ferrolane: 1,1'-Bis[(2R,5R)-2,5-diisopropylphospholano]ferrocene	63	4
SL-F131-1 (Trifer): 1,1'-BIS[(R)-[(RP)-2-[(S)-1-(DIMETHYLAMINO)ETHYL]FERROCENYL]PHENYLPHOSPHINO]FERROCENE	52	20
SL-F356-1 (Chenphos): 1-DICYCLOHEXYLPHOSPHINO-1'-[(R)-[(RP)-2-[(S)-1-(DIMETHYLAMINO)ETHYL]FERROCENYL]PHENYLPHOSPHINO]FERROCENE	71	9

SL-J681-1: (S, Rp, SSPO)-1-tert.-butylphosphinoyl)-2-[1-(diphenylphosphino)ethyl]ferrocene	53	15
SL-J688-1: (RP)-1-[(S)-1-(DI-TERT-BUTYLPHOSPHINO)ETHYL]-2-[(S)-PHENYLPHOSPHINOYL]FERROCENE	58	45
(R)-PhanePhos: (R)-(-)-4,12-BIS(DIPHENYLPHOSPHINO)-[2.2]-PARACYCLOPHANE	52	7
(R)-An-PhanePhos: (R)-4,12-Bis[di(4-methoxyphenyl)phosphino]-[2.2]-paracyclophane	62	3
(1S,1'S)-ethane-1,2-diylbis(tert-butyl(methyl)phosphonium) tetrafluoroborate	68	13
(R,R)-miniPHOS 2HBF4: (1R,1'R)-methylenebis(tert-butyl(methyl)phosphonium) tetrafluoroborate	25	25
(R)-di-tert-butyl((tert-butyl(methyl)phosphonio)methyl)phosphonium tetrafluoroborate	27	51
(S)-MaxPhos HBF4: (S)-(tert-butylmethylphosphonium)(di-tert-butylphosphino)amine tetrafluoroborate	21	30
(R,R)-(+)-1,2-Bis(t-butylmethylphosphino)benzene	3	-
(R,R)-Nap-DIPAMP: 1,2-bis((R)-naphthalen-1-yl(phenyl)phosphino)ethane	59	-
(R,R)-Tol-DIPAMP: 1,2-bis((R)-phenyl(o-tolyl)phosphino)ethane	19	10
(S,S)-iPr-DIPAMP: 1,2-bis((S)-(2-isopropylphenyl)(phenyl)phosphino)ethane	44	47
(S,S)-Ph2-DIPAMP: 1,2-bis((S)-[1,1'-biphenyl]-2-yl(phenyl)phosphino)ethane	19	31
catASium T1 (R): (1R,AR)-3-DIPHENYLPHOSPHINO-2-(4-DIPHENYLPHOSPHINO-2,5-DIMETHYL-3-THIENYL)-1,7,7-TRIMETHYL-BICYCLO[2.2.1]HEPT-2-ENE	17	44
catASium T3 (R): (1R,AR)-3-DIPHENYLPHOSPHINO-2-(4-BIS(3,5-DIMETHYLPHENYL)PHOSPHINO-2,5-DIMETHYL-3-THIENYL)-1,7,7-TRIMETHYLBICYCLO[2.2.1]HEPT-2-ENE	21	27
(R)-Tol-Binap: (R)-(+)-2,2'-BIS(DI-P-TOLYLPHOSPHINO)-1,1'-BINAPHTHYL	66	13
(R)-Hexaphemp	43	7
(S)-Me-Soniphos: (S)-(-)-6,6'-Bis(diphenylphosphino)-1,1'-biphenyl-2,2'-diylbis(acetate)	64	9
(R)-Cl,MeO-Biphep: (R)-(+)-5,5'-DICHLORO-6,6'-DIMETHOXY-2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BIPHENYL	64	33
SL-J203-2	63	71
SL-A109-2: (S)-2,2'-Bis(di(3,5-di-tert-butyl-4-methoxyphenyl)phosphino)-6,6'-dimethoxy-1,1'-biphenyl	21	37
(R)-P-Phos: (R)-(+)-2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine	71	37
(R)-DTBM-SEGPHOS: (*R*)-(−)-5,5′-Bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole, [(4*R*)-(4,4′-bi-1,3-benzodioxole)-5,5′-diyl]bis[bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine]	22	27
(S)-Binap: (S)-(+)-2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL	65	3
(R)-xyl-binap: (R)-(+)-2,2'-BIS[DI(3,5-XYLYL)PHOSPHINO]-1,1'-BINAPHTHYL	68	25
(R)-DM-SEGPHOS: (*R*)-(+)-5,5′−Bis[di(3,5-xylyl)phosphino]-4,4′-bi-1,3-benzodioxole, [(4*R*)-(4,4′-bi-1,3-benzodioxole)-5,5′-diyl]bis[bis(3,5-dimethylphenyl)phosphine]	62	20
(R)-Difluorophos: (R)-(-)-5,5'-Bis(diphenylphosphino)-2,2,2',2'-tetrafluoro-4,4'-bi-1,3-benzodioxole	72	20
SL-A120-2: (S)-2,2'-Bis[bis(3,5-dimethyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl	58	23
(R)-H8-BINAP: (*R*)-(+)-2,2′-Bis(diphenylphospino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl, [(1*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalene]-2,2′-diyl]bis[diphenylphosphine]	34	47
(S)-Xylyl-P-Phos: (S)-(-)-2,2',6,6'-Tetramethoxy-4,4'-bis(di(3,5-xylyl)phosphino)-3,3'-bipyridine	65	27
(S)-cHex-Soniphos: (S)-(-)-6,6'-Bis(diphenylphosphino)-1,1'-biphenyl-2,2'-diylbis(cyclohexylcarboxylate),	57	11
SL-A102-1: (R)-2,2'-Bis(di-p-tolylphosphino)-6,6'-dimethoxy-1,1'-biphenyl	58	23
SL-A107-1: (R)-2,2'-Bis[bis(3,5-diisopropyl-4-dimethylaminophenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl	24	13
SL-A104-1: (R)-2,2'-Bis[bis(3,4,5-trimethoxyphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl	47	53
SL-A121-1: (R)-2,2'-Bis[bis(3,5-di-tert-butyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl	24	14

SL-A108-1: (R)-(+)-2,2'-Bis(di-2-furylphosphino)-6,6'-dimethoxy-1,1'-biphenyl	64	7
SL-A116-1: (R)-2,2'-Bis(diisopropylphosphino)-6,6'-dimethoxy-1,1'-biphenyl	28	5
SL-A118-1: (R)-2,2'-Bis(dicyclobutylphosphino)-6,6'-dimethoxy-1,1'-biphenyl	72	35
(R,R)-DACH-Phenyl Trost Ligand: (1*R*,2*R*)-(+)-1,2-Diaminocyclohexane-*N*,*N*′-bis(2-diphenylphosphinobenzoyl)	55	20
(R,R)-DACH-Naphthyl Trost Ligand: (1*R*,2*R*)-(+)-1,2-Diaminocyclohexane-*N*,*N*′-bis(2-diphenylphosphino-1-naphthoyl)	44	11
SL-N003-2 ((S)-4-Isopropyl-2-[(S)-2-(diphenylphosphino)ferrocen-1-yl]oxazoline)	56	14
SL-N008-2 ((S)-4-Isopropyl-2-[(S)-2-(bis(3,5.dimethyl-4-methoxyphenyl)phosphino)ferrocen-1-yl]oxazoline)	56	12
SL-N011-2 ((S)-4-Isopropyl-2-[(S)-2-(bis(1-naphtyl)phosphino)ferrocen-1-yl]oxazoline)	51	25
SL-N012-2 ((S)-4-Isopropyl-2-[(S)-2-(bis(2-methoxyphenyl)phosphino)ferrocen-1-yl]oxazoline)	17	53
SL-N004-2: (S)-4-tert.-Butyl-2-[(S)-2-(bis(1-phenyl)-phosphino)ferrocen-1-yl]oxazoline	58	29
(S)-Xyl-SDP: (*S*)-(–)-7,7′-Bis[di(3,5-dimethylphenyl)phosphino]-1,1′-spirobiindane, (*S*)-(–)-7,7′-Bis[di(3,5-dimethylphenyl)phosphino]-2,2′,3,3′-tetrahydro-1,1′-spirobiindene	26	32
(S)-Tol-SDP: (*S*)-(–)-7,7′-Bis[di(4-methylphenyl)phosphino]-2,2′,3,3′-tetrahydro-1,1′-spirobiindene, (*S*)-(–)-7,7′-Bis[di(*p*-methylphenyl)phosphino]-1,1′-spirobiindane	24	23
SL-J001-1: (R)-(-)-1-[(S)-2-(DIPHENYLPHOSPHINO)FERROCENYL]ETHYLDICYLCOHEXYLPHOSPHINE	63	25
SL-J002-1: (R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]-ethyl-di-tert.-butylphosphine	65	40
SL-J004-1: (R)-(-)-1-[(S)-2-(DICYCLOHEXYLPHOSPHINO)FERROCENYL]ETHYLDIPHENYLPHOSPHINE	43	32
SL-J006-1: (R)-1-[(S)-2-Di-(3,5-bis(trifluoromethyl)phenyl-phosphino)ferrocenyl]-ethyl-dicyclohexylphosphine	76	44
SL-J008-1: (R)-1-[(S)-2-Di-(3,5-bis(trifluoromethyl)phenyl-phosphino)-ferrocenyl]-ethyl-di-3,5-xylylphosphine	51	30
SL-J204-1	75	70
SL-J013-1: (R)-1-[(S)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-di-tert.-butyl-phosphine	65	40
SL-J212-1: (R)-1-[(S)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-tert.-butylphosphine	71	40
SL-J425-1: (R)-1-[(S)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-di-2-methylphenyl-phosphine	52	27
SL-J452-1: (R)-1-[(S)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-2-methylphenylphosphine	75	29
SL-J003-1: (R)-(-)-1-[(S)-2-(DICYCLOHEXYLPHOSPHINO)FERROCENYL]ETHYLDICYCLOHEXYLPHOSPHINE	67	20
SL-J007-1:(R)-1-[(S)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-dicyclohexylphosphine	64	-
SL-J009-1: (R)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]-ethyldi-tert.-butylphosphine	29	44
SL-J015-2: (S)-1-[(R)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine	66	3
SL-J418-1: (R)-1-[(S)-2-Di-(4-methoxy-3,5-dimethylphenyl-phosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine	53	28

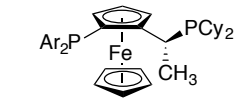
Chiral Ligands P3-56 ligands	Assay Yield (%)	Ee[a] (%)
(R)-MonoPhos: (R)-(-)-[4-N,N-DIMETHYLAMINO]DINAPHTHO[2,1-D:1',2'-F][1,3,2]DIOXAPHOSPHEPINE	45	10
(S)-N-Me-N-Bn-MonoPhos: (S)-(+)-(3,5-DIOXA-4-PHOSPHA-CYCLOHEPTA[2,1-A:3,4-A']DINAPHTHALEN-4-YL)BENZYL(METHYL)AMINE	56	7
(S)-PipPhos: (S)-(+)-(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a']dinapthalen-4-yl)piperidine	53	3
(S)-2,6-Me-MonoPhos: (S)-(+)-(2,6-Dimethyl-3,5-dioxa-4-phospha-cyclohepta[2,1-a;3,4-	52	23

a']dinaphthalen-4-yl)dimethylamine		
(S,R)-(a-MeBn)-MonoPhos: (S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)[(1R)-1-phenylethyl]amine	21	13
(S,R,R)-(a-MeBn)2-MonoPhos: (S)-(+)-(3,5-DIOXA-4-PHOSPHA-CYCLOHEPTA[2,1-A;3,4-A']DINAPHTHALEN-4-YL)BIS[(1R)-1-PHENYLETHYL]AMINE, DICHLOROMETHANE ADDUCT	37	9
(S,S,S)-(a-MeBn)2-MonoPhos: (S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis[(1S)-1-phenylethyl]amine	40	8
(S)-H8-MonoPhos: (S)-(+)-(8,9,10,11,12,13,14,15-OCTAHYDRO-3,5-DIOXA-4-PHOSPHA-CYCLOHEPTA[2,1-A;3,4-A']DINAPHTHALEN-4-YL)DIMETHYLAMINE	41	16
(S)-H8-PipPhos: 1-[(11bS)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl]piperidine	20	26
(R)-BINOL-P-OiPr: (R)-BINAPHTHYLISOPROPYLPHOSPHITE	13	60
(R)-BINOL-P-OiBu: (R)-BINAPHTHYLISOBUTYLPHOSPHITE	14	-
(R,R)-TADDOL-P-NMe2: (3aR,8aR)-(-)-(2,2-Dimethyl-4,4,8,8-tetraphenyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)dimethylamine	21	-
(R)-SIPHOS (11aR)-(+)-10,11,12,13-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-dimethylamine	53	3
(R)-SIPHOS-PE: (11aR)-(+)-10,11,12,13-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-bis[(R)-1-phenylethyl]amine	33	27
(R)-ShiP: (11aR)-(+)-10,11,12,13-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-5-phenoxy	2	57
(S,S)-Mikami Ligand: 2,10-dimethyl-N,N-bis[(1S)-1-phenylethyl]-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin-6-amine	32	27
(S,S)-tBu-Mikami Ligand: 4,8-di-tert-butyl-2,10-dimethyl-N,N-bis[(1S)-1-phenylethyl]-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin-6-amine	19	29
(R)-Quinap: (R)-1-(2-DIPHENYLPHOSPHINO-1-NAPHTHYL)ISOQUINOLINE	37	3
(R)-N-PINAP: (R)-(+)-4-[2-(DIPHENYLPHOSPHINO)-1-NAPHTHALENYL]-N-[(R)-1-PHENYLETHYL]-1-PHTHALAZINAMINE	31	11
(R)-MOP: (*R*)-(+)-2-(Diphenylphosphino)-2′-methoxy-1,1′-binaphthyl	21	9
(R,R)-Me-DuPhos Monoxide: (2R,5R)-1-[2-[(2R,5R)-2,5-DIMETHYLPHOSPHOLAN-1-YL]PHENYL]-2,5-DIMETHYLPHOSPHOLANE 1-OXIDE	26	3
(S,S)-Me-RajPhos: (2S,5S)-(+)-1-(2-(1,3-DIOXOLAN-2-YL)PHENYL)-2,5-DIMETHYLPHOSPHOLANE	39	11
(S,S)-Et-RajPhos: (2S,5S)-(-)-1-(2-(1,3-DIOXOLAN-2-YL)PHENYL)-2,5-DIETHYLPHOSPHOLANE	30	7
(S,S,S)-DiazaPhos-PPE: 2,2'-[(1S,3S)-2,3,5,10-tetrahydro-5,10-dioxo-2-phenyl-1H-[1,2,4]diazaphospholo[1,2b]phthalazine-1,3-diyl]bis[N-(1S)-1-phenylethyl]benzamide	26	20
(S)-BINAP: (S)-(+)-2,2'-BIS(DIPHENYLPHOSPHINO)-1,1'-BINAPHTHYL	66	3
(R)-xyl-BINAP: (R)-(+)-2,2'-BIS[DI(3,5-XYLYL)PHOSPHINO]-1,1'-BINAPHTHYL	69	23
(R)-SegPhos: (R)-(+)-5,5'-BIS(DIPHENYLPHOSPHINO)-4,4'-BI-1,3-BENZODIOXOLE	65	31
SL-J002-1: (R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]-ethyl-di-tert.-butylphosphine	52	47
SL-J212-1: (R)-1-[(S)-2-(Di-2-furylphosphino)ferrocenyl]-ethyl-di-tert.-butylphosphine	76	45
SL-J005-1: (R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]-ethyl-di-3,5-xylylphosphine	39	13
SL-J009-1: (R)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]-ethyldi-tert.-butylphosphine	31	31
SL-J006-2: (S)-1-[(R)-2-Di-(3,5-bis(trifluoromethyl)phenyl-phosphino)ferrocenyl]-ethyl-dicyclohexylphosphine	77	53
(S,S)-Me-DuPhos: (+)-1,2-BIS[(2S,5S)-2,5-DIMETHYLPHOSPHOLANO]BENZENE	75	55
(1S,1'S,2R,2'R)-DuanPhos: (1S,1'S,2R,2'R)-2,2'-Di-tert-butyl-2,3,2',3'-tetrahydro-1H,1'H-(1,1')biisophosphindolyl	57	11
SL-J003-2: (*S*)-1-[(R_P)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine	68	16
SL-W001-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-di-bis(3,5-trifluoromethyl-phenyl)phosphine	70	24
SL-W003-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-dicyclohexylphosphine	76	17

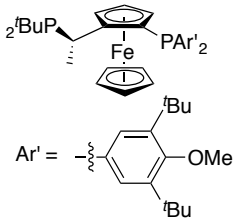
SL-W006-1: (R)-1-[(R)-2-(2'-Diphenylphosphinophenyl)-ferrocenyl]-ethyl-di-3,5-xylylphosphine	75	26
(R,R)-QuinoxP*: (R,R)-2,3-Bis(tert-butylmethylphosphino)quinoxaline	35	4
(S)-(–)-7,7'-Bis(diphenylphosphino)-2,2',3,3'-tetrahydro-1,1'-spirobiindene	22	26
SL-T001-1: (R)-1-Diphenylphosphino-2-[(R)-a-(N,N-dimethyl-amino)-o-(diphenylphosphinophenyl)methyl]-ferrocene	72	15
(+)-Cy-SEGPHOS	30	30
(S)-BINAPINE: (3S,3'S,4S,4'S,11bS,11'bS)-(+)-4,4'-Di-t-butyl-4,4',5,5'-tetrahydro-3,3'-bi-3H-dinaphtho[2,1-c:1',2'-e]phosphepine	28	5
(S)-PipPhos: (S)-(+)-(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a']dinapthalen-4-yl)piperidine	54	13
K15-0026: (1R,2R)-N,N'-BIS[2-(DIPHENYLPHOSPHINO)BENZYL]CYCLOHEXANE-1,2-DIAMINE	55	4
K15-0088: (1R,2R)-N,N-Bis(2-(di-p-tolylphosphino)-benzyl)cyclohexane-1,2-diamine	49	30
K15-0090: (1R,2R)-N,N-Bis(2-(bis(3,5-dimethylphenyl)-phosphino)benzyl)cyclohexane-1,2-diamine	22	20
K15-0020: 2,2'-BIS[(R-1,1'-BINAPHTHYL-2,2'-DIMETHYL)PHOSPHINO]DIETHYLAMINE	79	5
K15-0129: (R)-1-(DIPHENYLPHOSPHINO)-2-AMINO-3-METHYLBUTANE	34	9
K15-0131: (R)-1-(DIPHENYLPHOSPHINO)-2-AMINO-3,3-DIMETHYLBUTANE	39	15
K15-0128: (S)-1-AMINO-8-(DIPHENYLPHOSPHINO)-1,2,3,4-TETRAHYDRONAPHTHALENE	72	9
K15-0051: 2-[(11BS)-3H-BINAPHTHO[2,1-C:1',2'-E]PHOSPHEPIN-4(5H)-YL]ETHANAMINE	47	14
K15-0046: (1R,2R)-2-(DIPHENYLPHOSPHINO)-1,2-DIPHENYLETHYLAMINE	26	23
K15-0137: (1R,2R)-2-(DIPHENYLPHOSPHINO)-1-AMINOCYCLOHEXANE	42	15
K15-0100: (1R,2R)-1-[(4S,11BR)-3,5-DIHYDRO-4H-DINAPHTHO[2,1-C:1',2'-E]PHOSPHEPIN-4-YL]-1-PHENYLPROPAN-2-AMINE	38	-
(1S,2S)-(2-METHYLAMINO-1-PHENYLPROPYL)DIPHENYLPHOSPHINE	24	-

[a] Absolute value was calculated on e.e.

Repeat hits on lab scales with e.e >70%

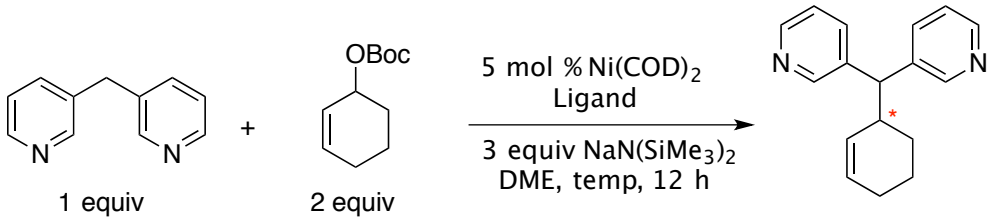


SL-J204-1
Assay yield: 75%
e.e. = 70%



SL-J203-2
Assay yield: 63%
e.e. = 71%

Lab Scale and Optimization



1 equiv 2 equiv

entry	Ligand	Ni/Ligand (mol %)	temp(°C)	yield[b](%)	e.e.[c](%)
1	SL-J203-2	5/10	24	66	70
2	SL-J204-1	5/10	24	85	73
3	SL-J204-1	5/10	0	80	93
4	SL-J204-1	5/7.5	0	93	92
5	SL-J204-1	5/5	0	92(91)[d]	92

[a] Reaction conducted on a 0.1 mmol scale.[b]Yield determined by ^{1}H NMR spectroscopy of the crude reaction mixture.[c] Crude e.e. determined by chiral-HPLC. [d] Isolated yield.

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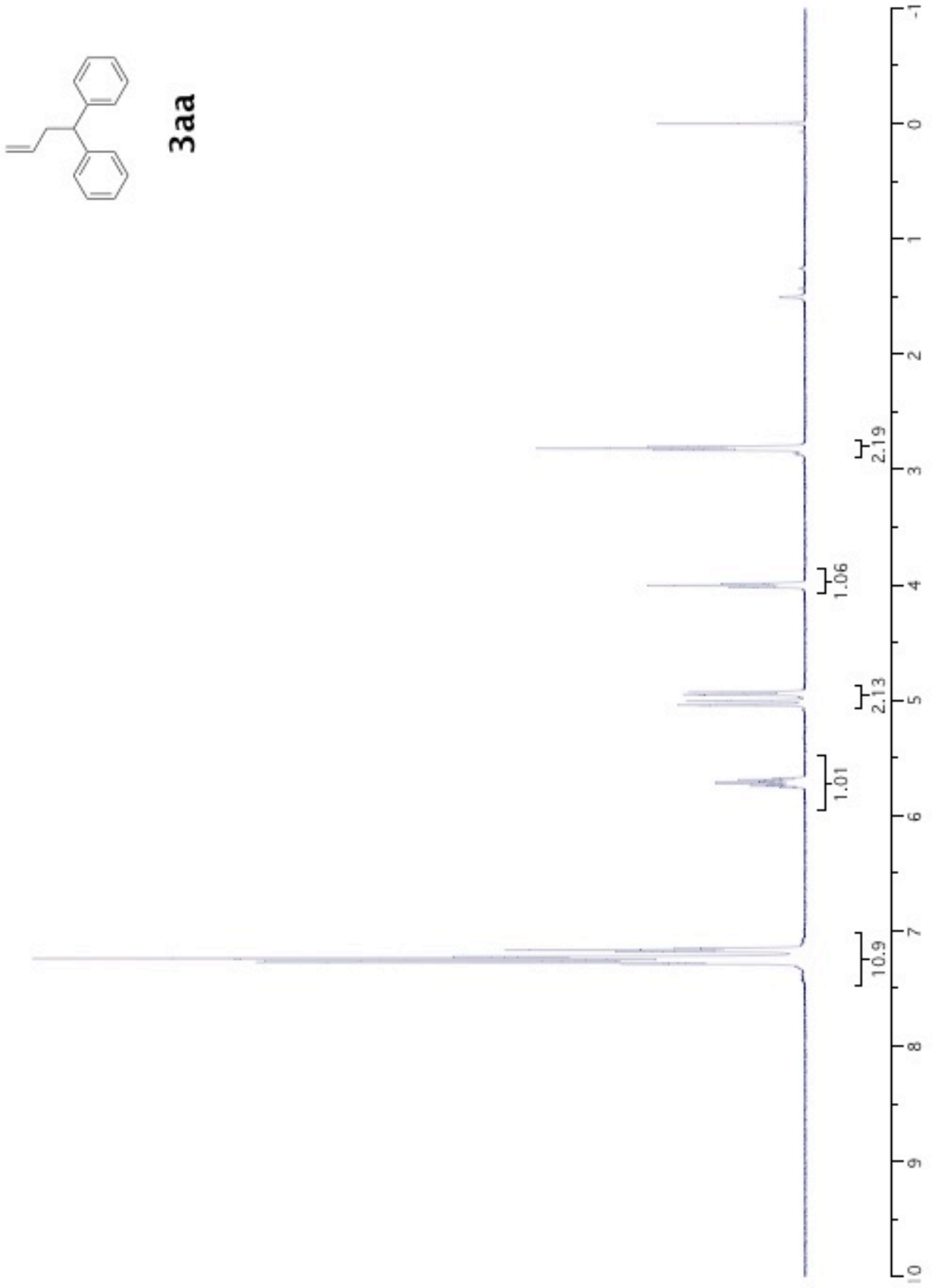
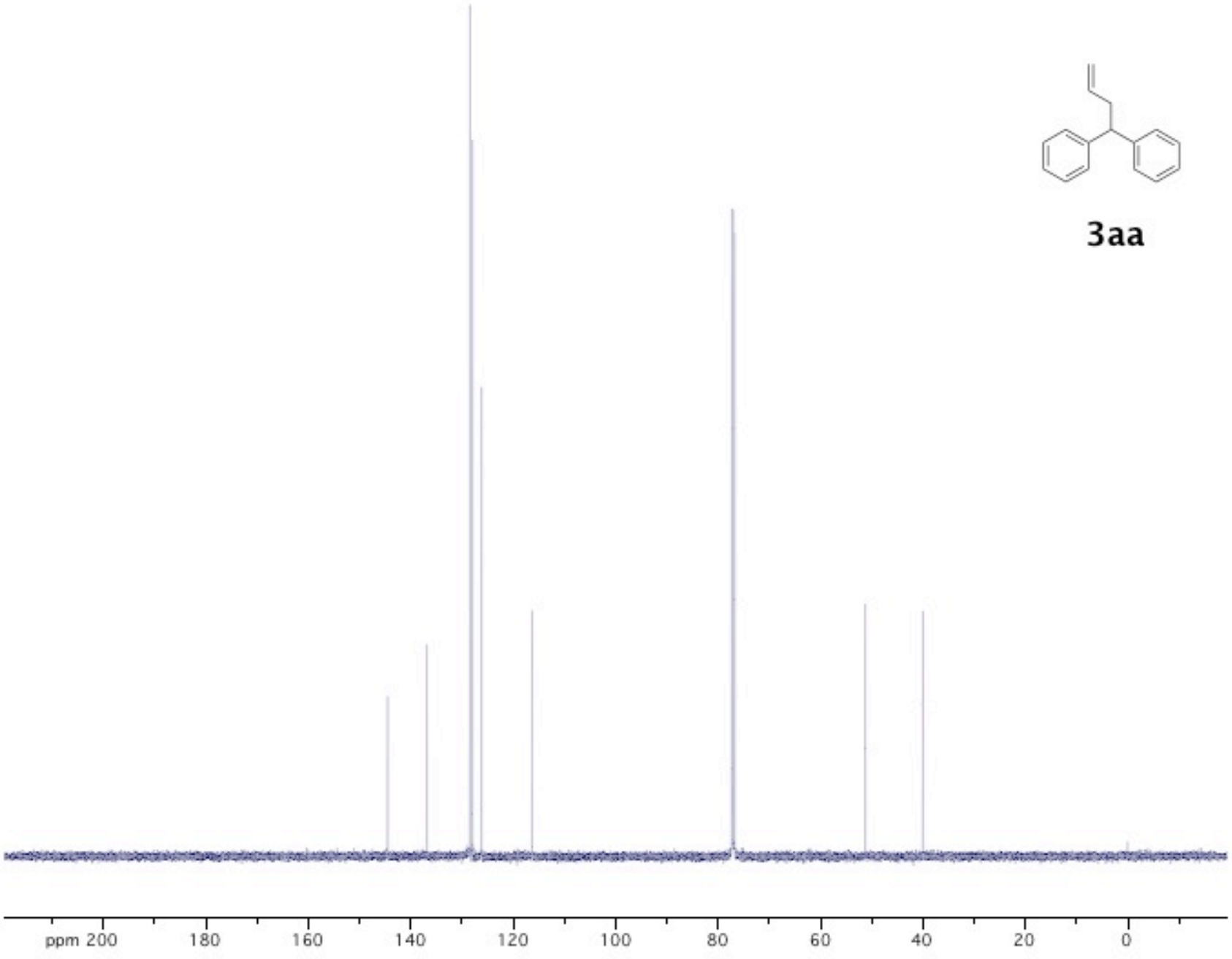
NMR Spectra

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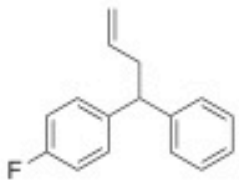
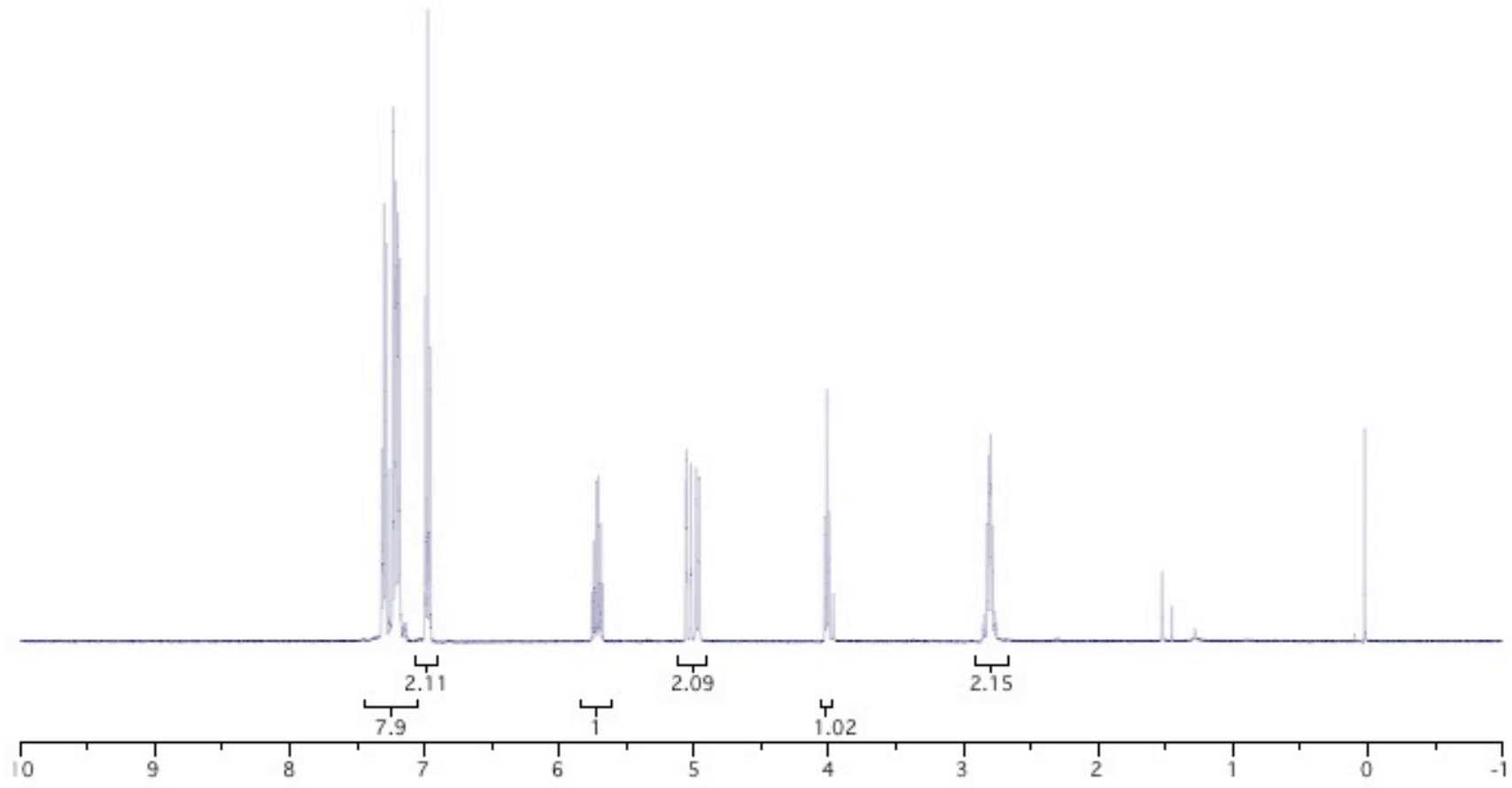
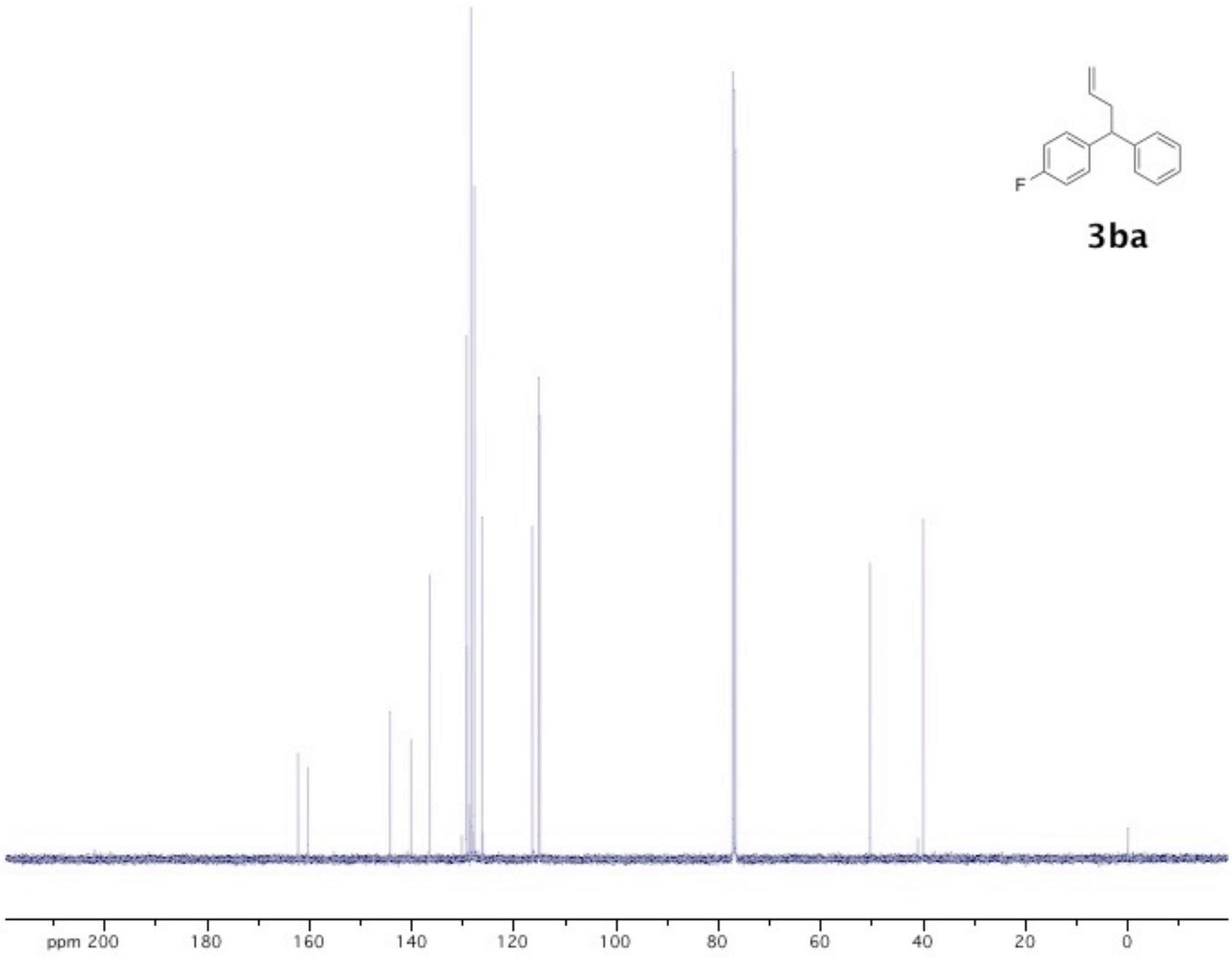


3ba

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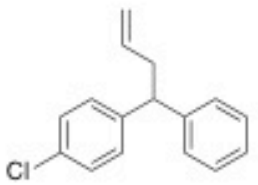

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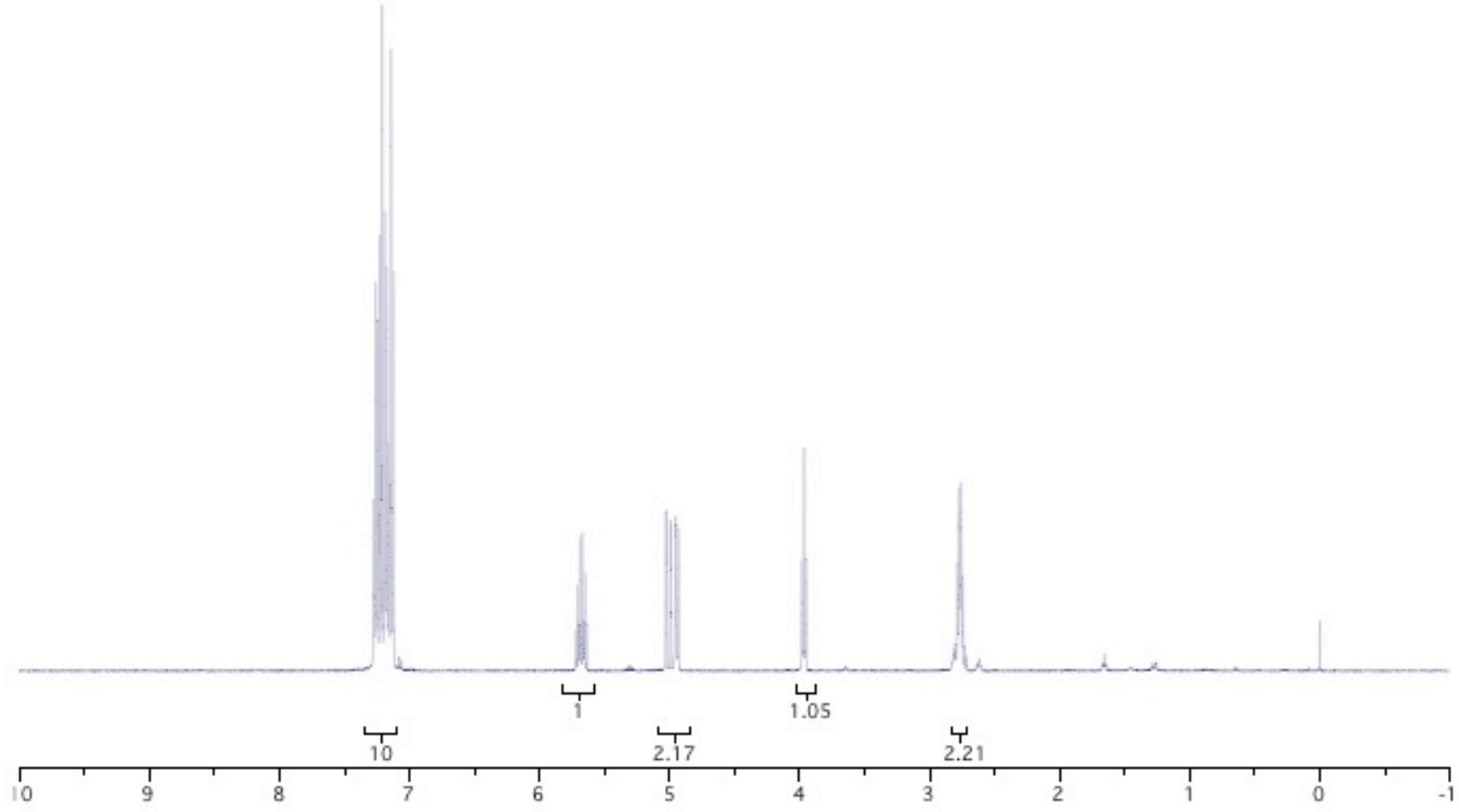

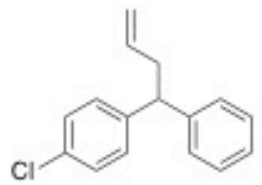

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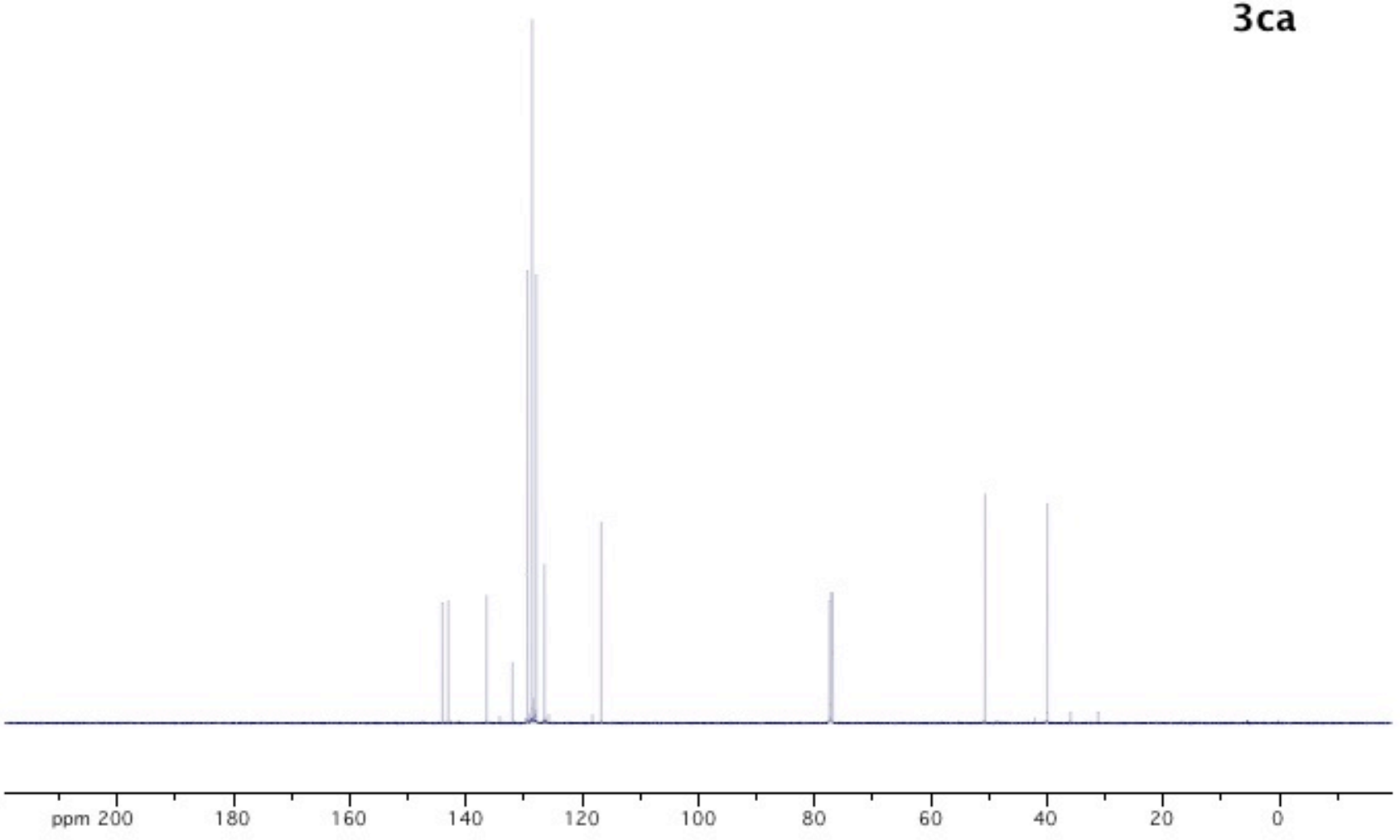

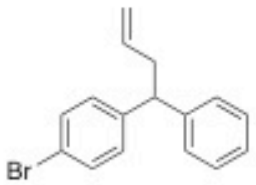

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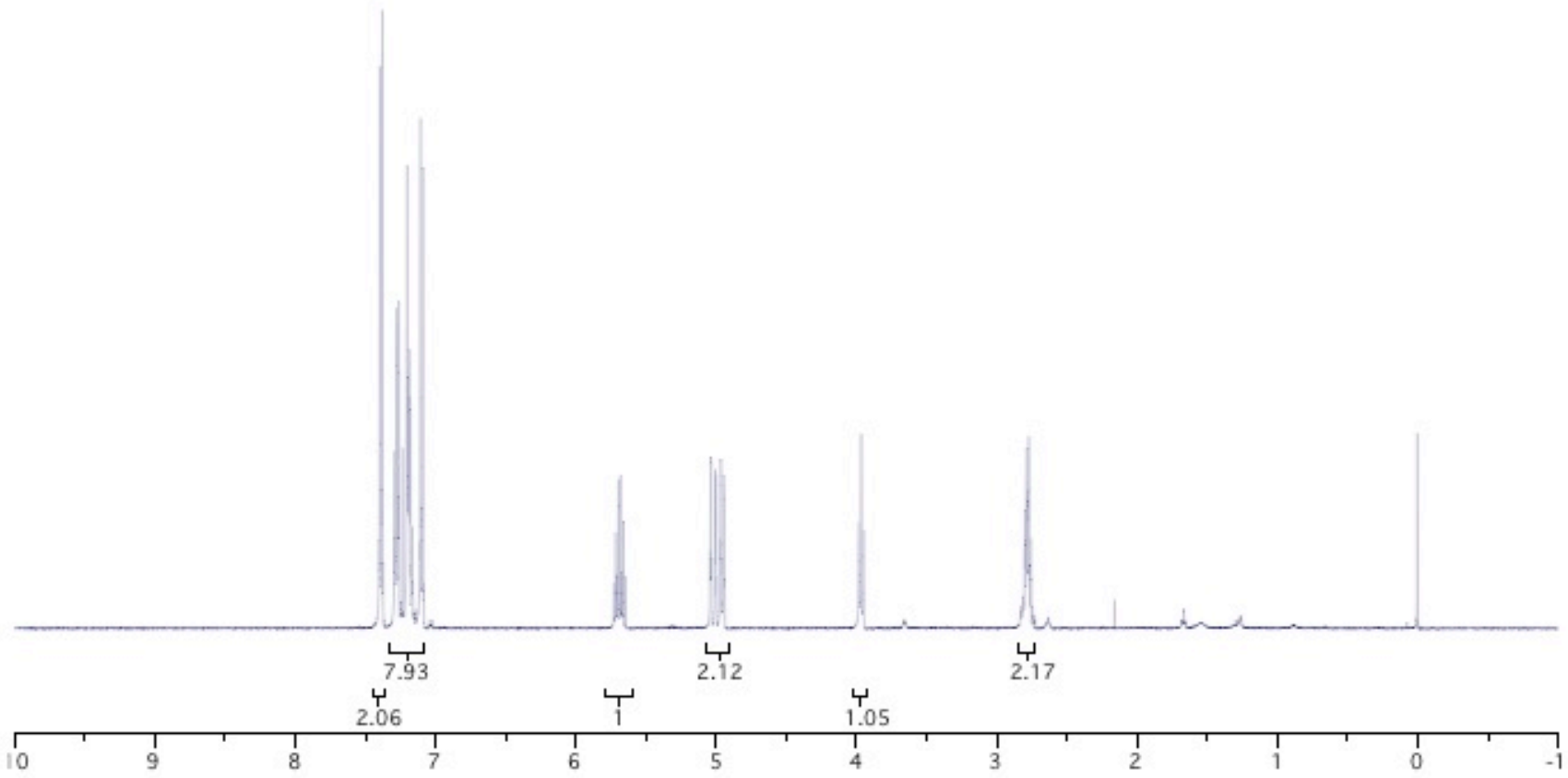

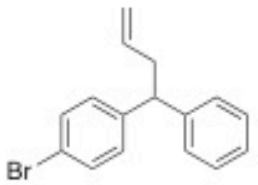

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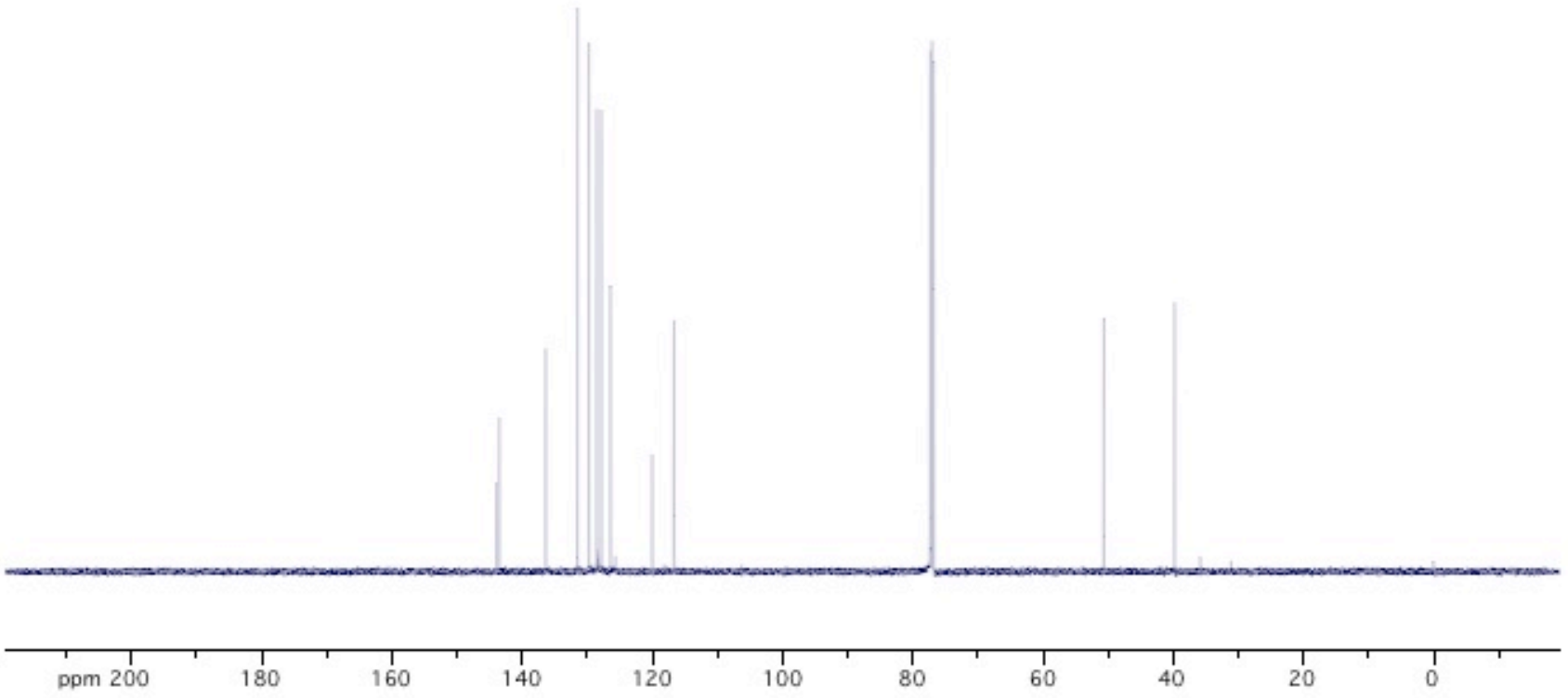

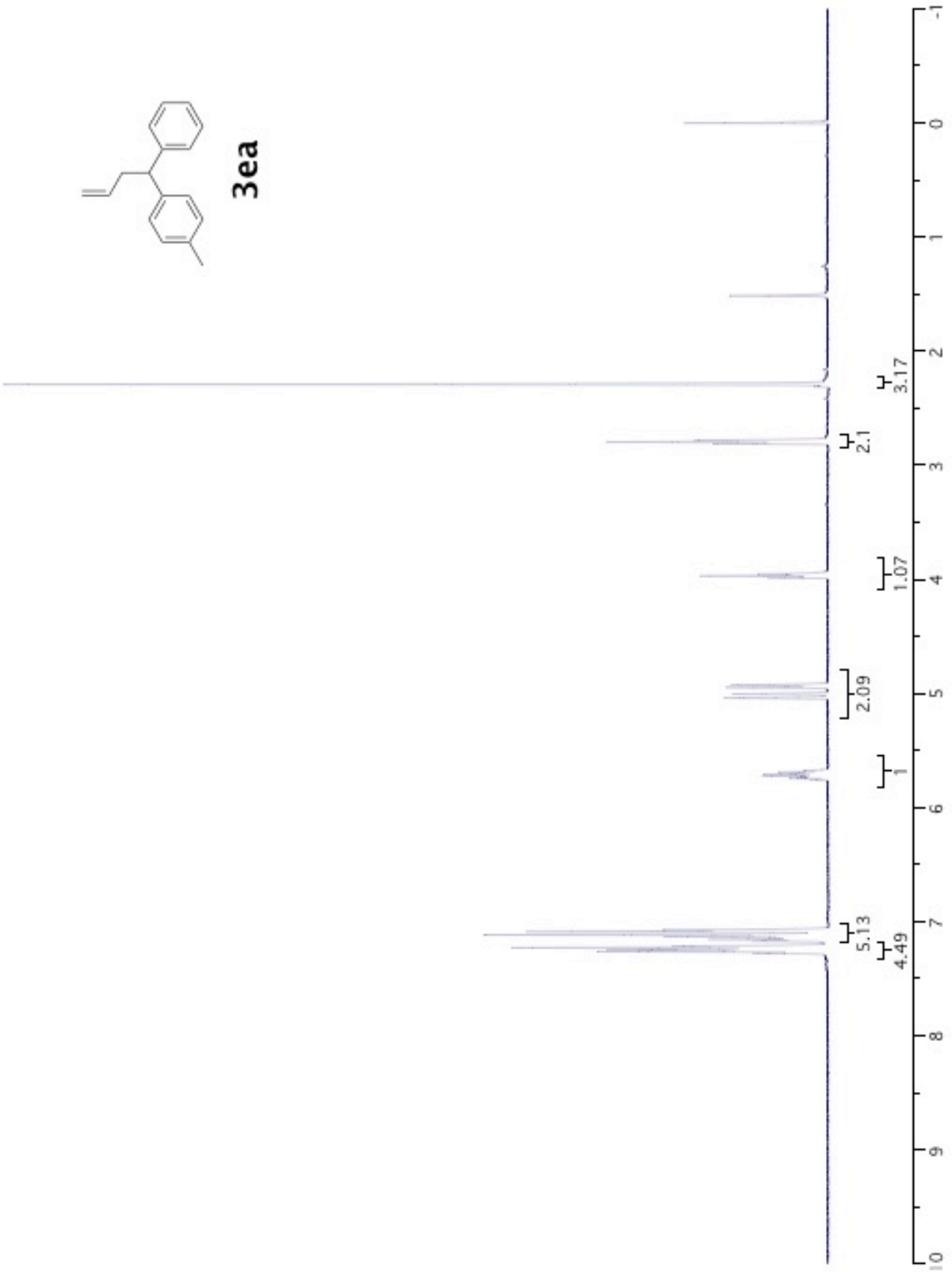
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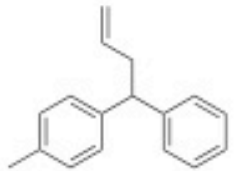

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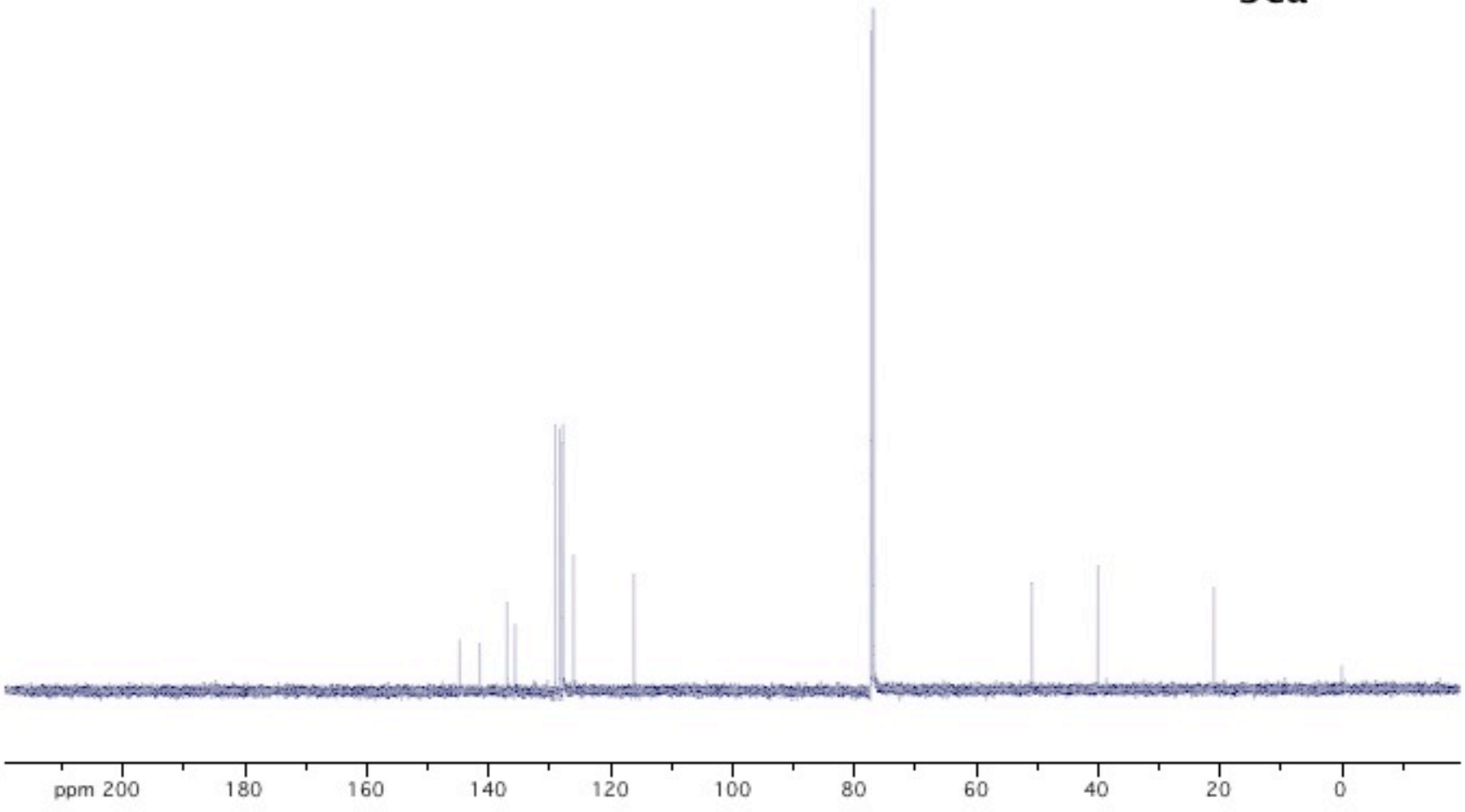

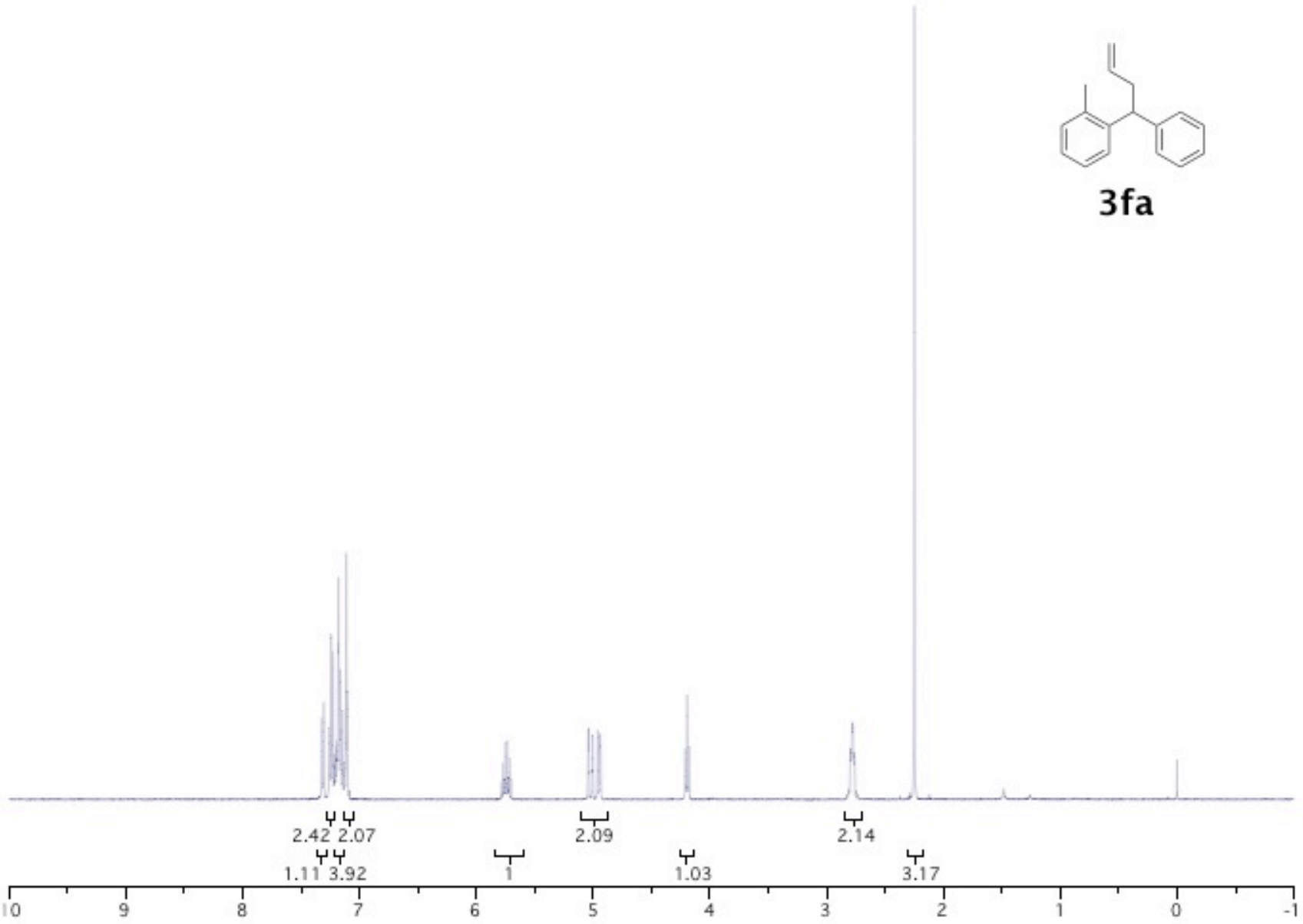
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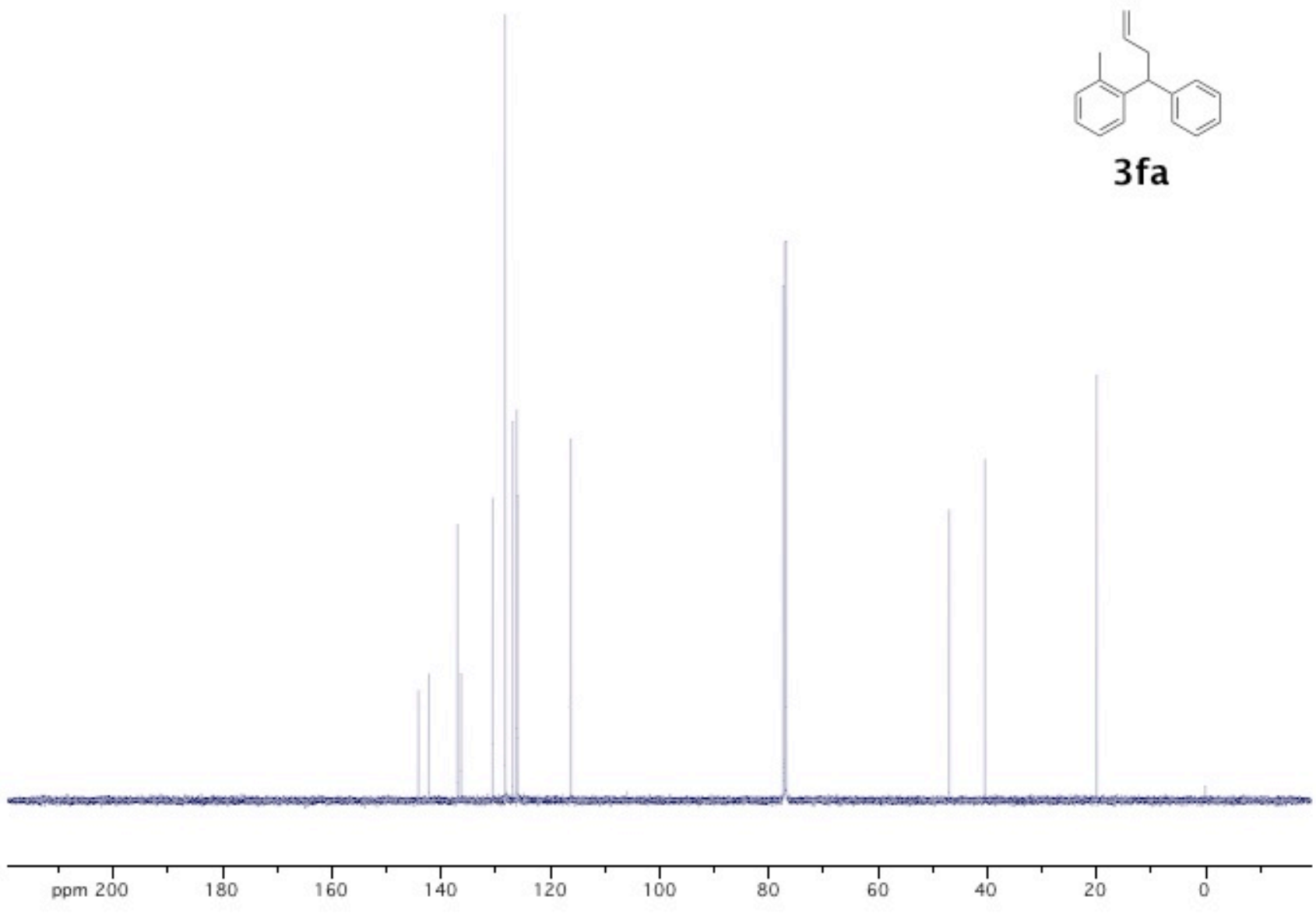
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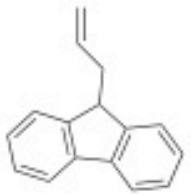

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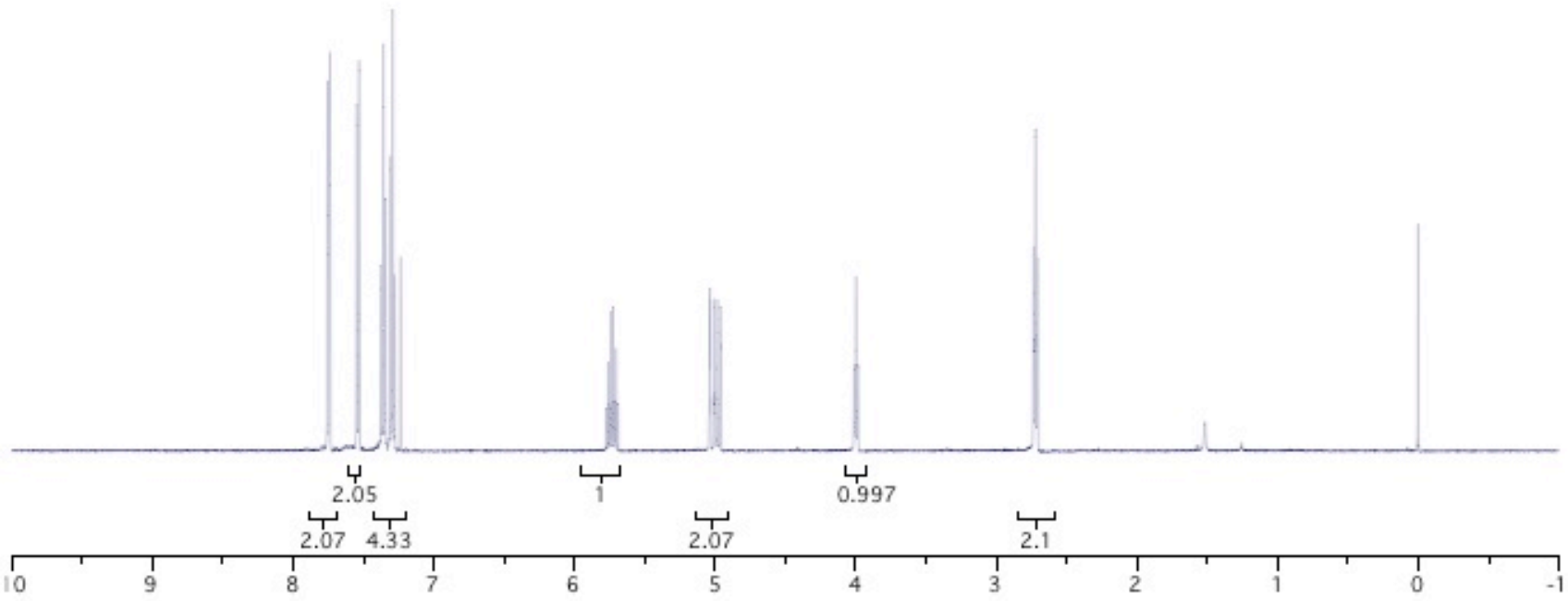

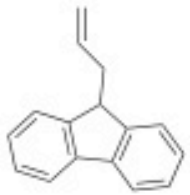

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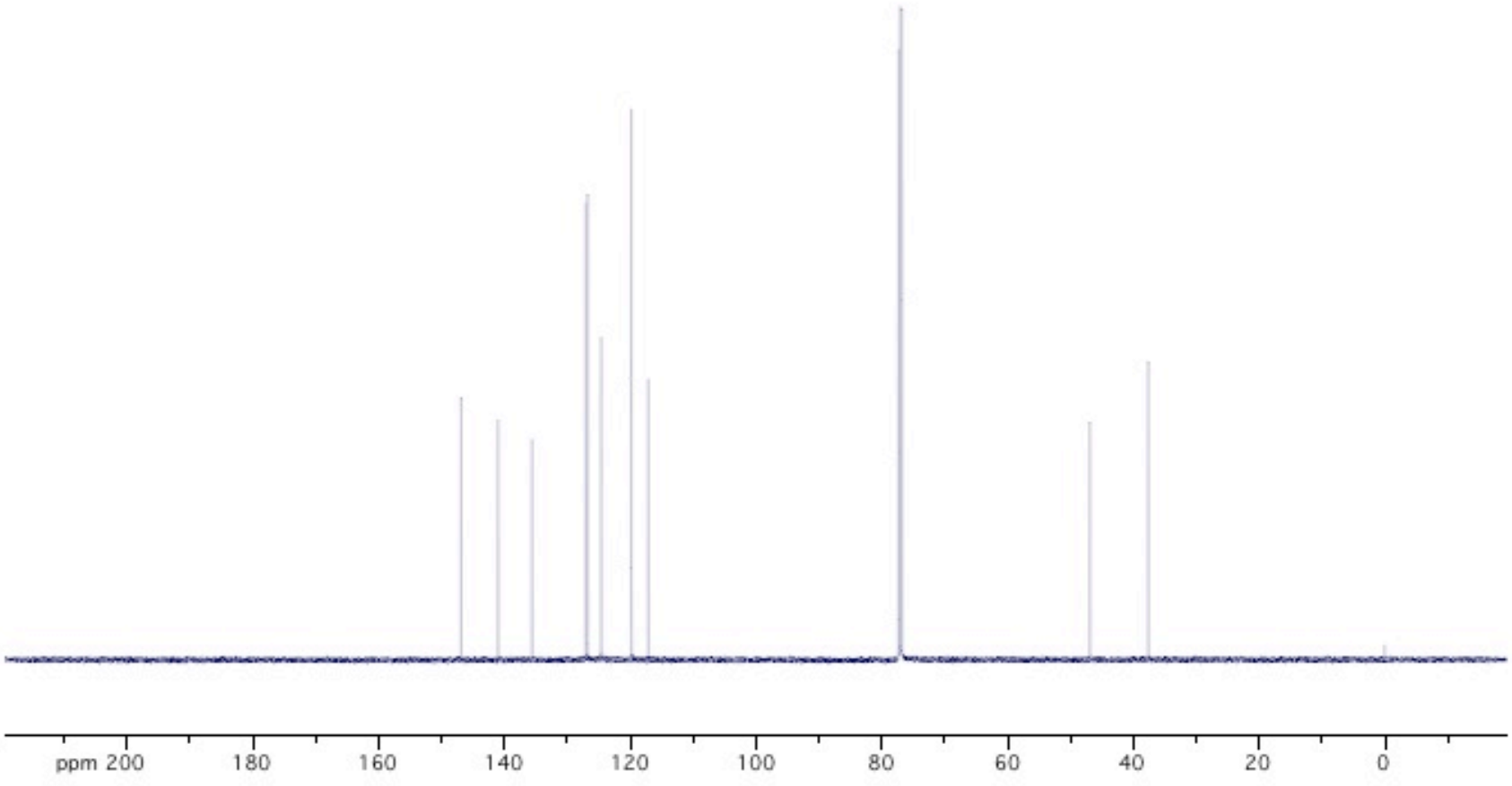

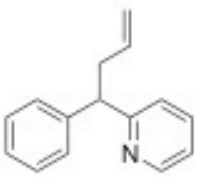

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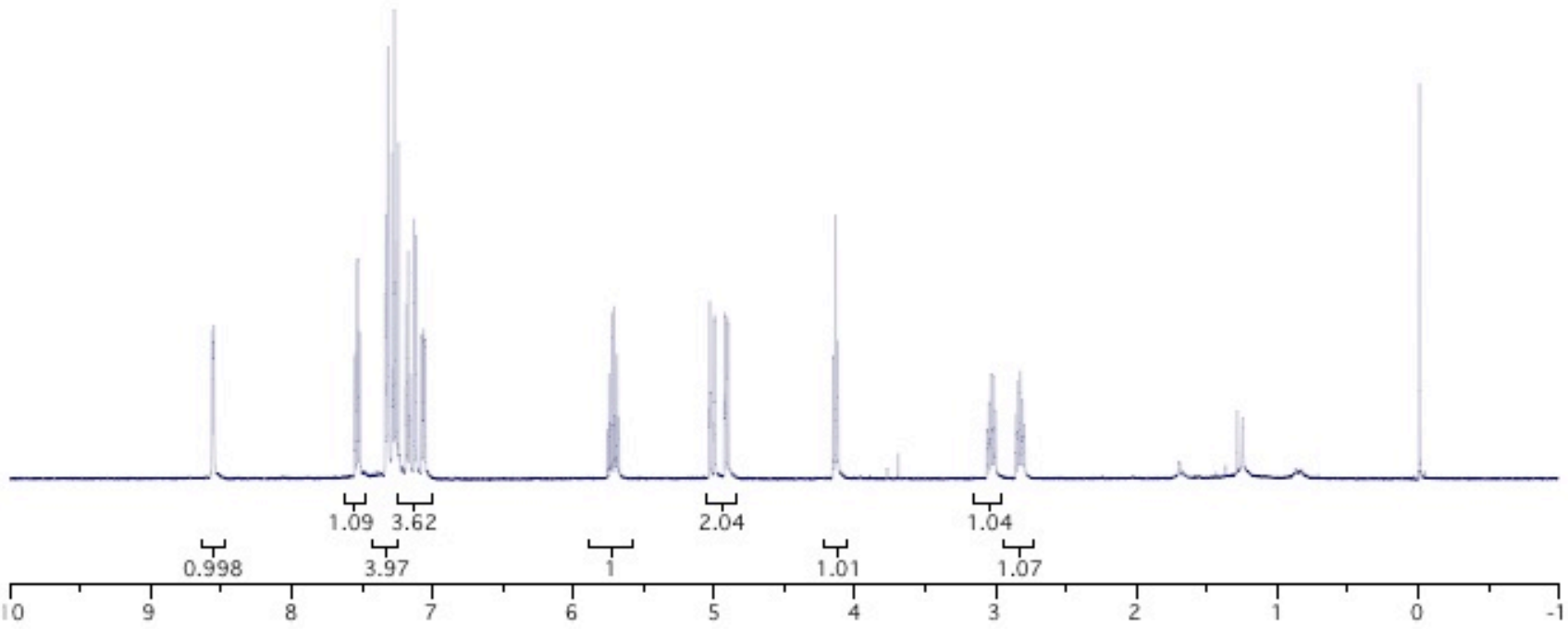

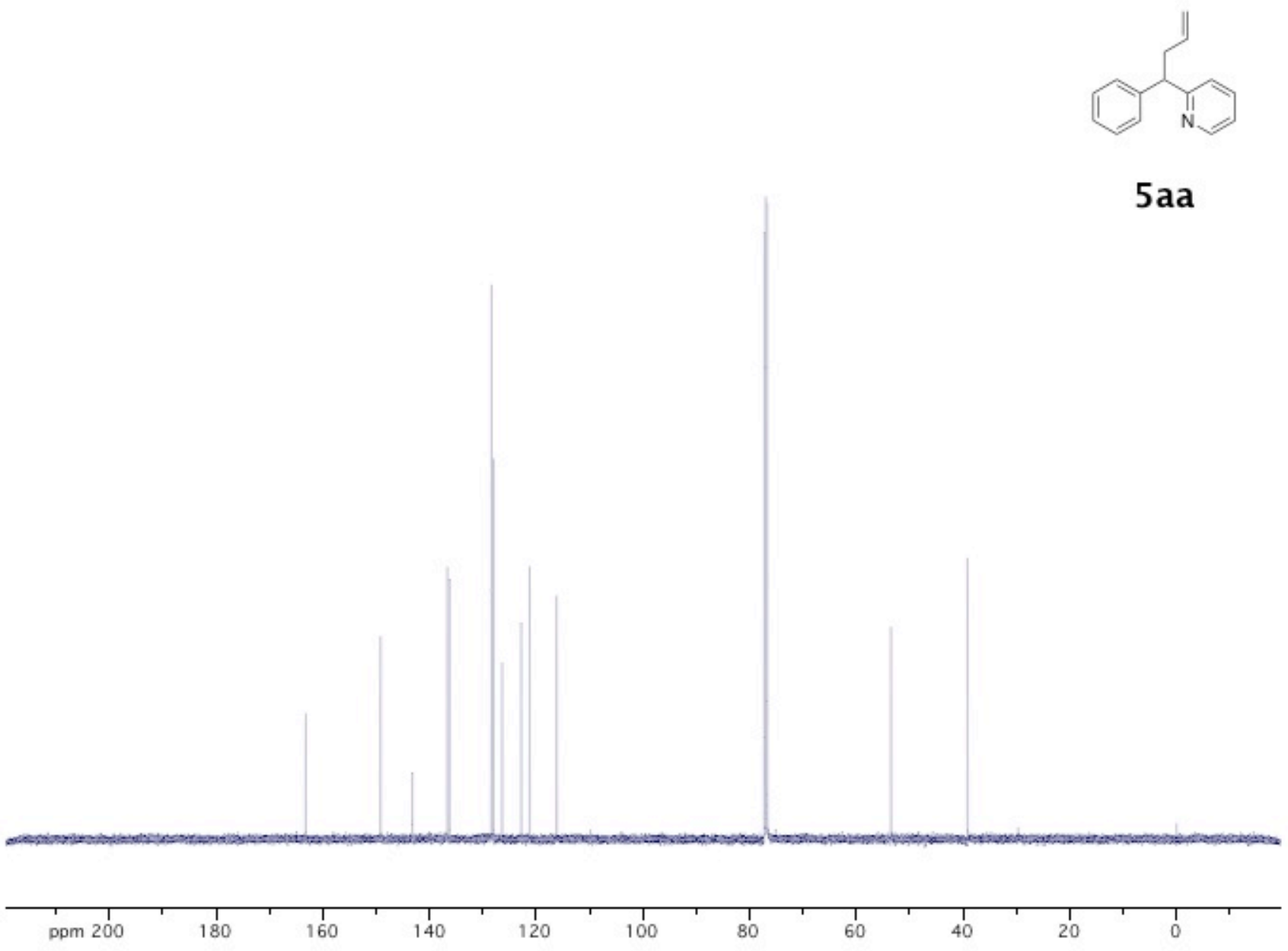
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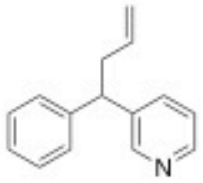

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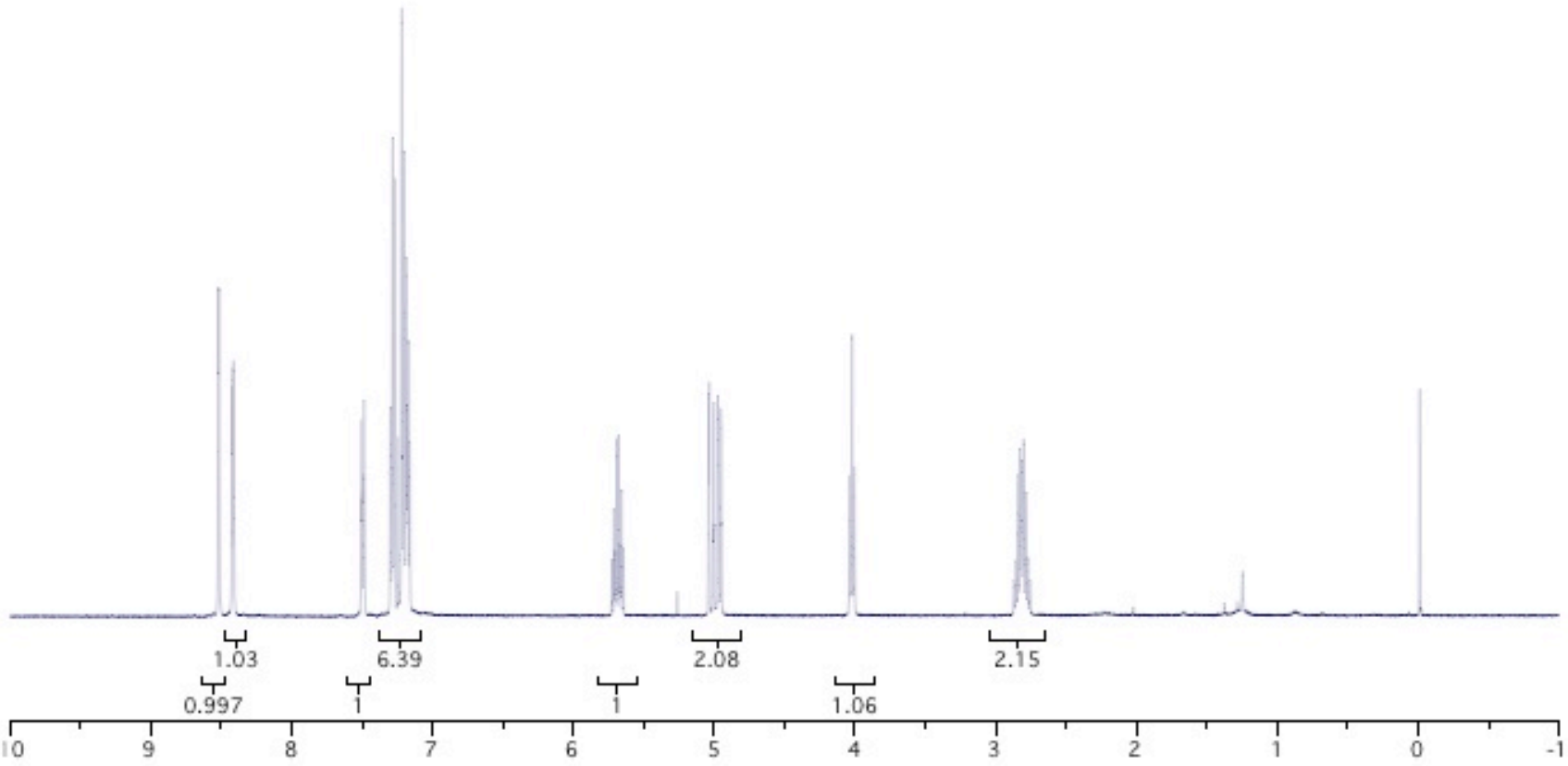

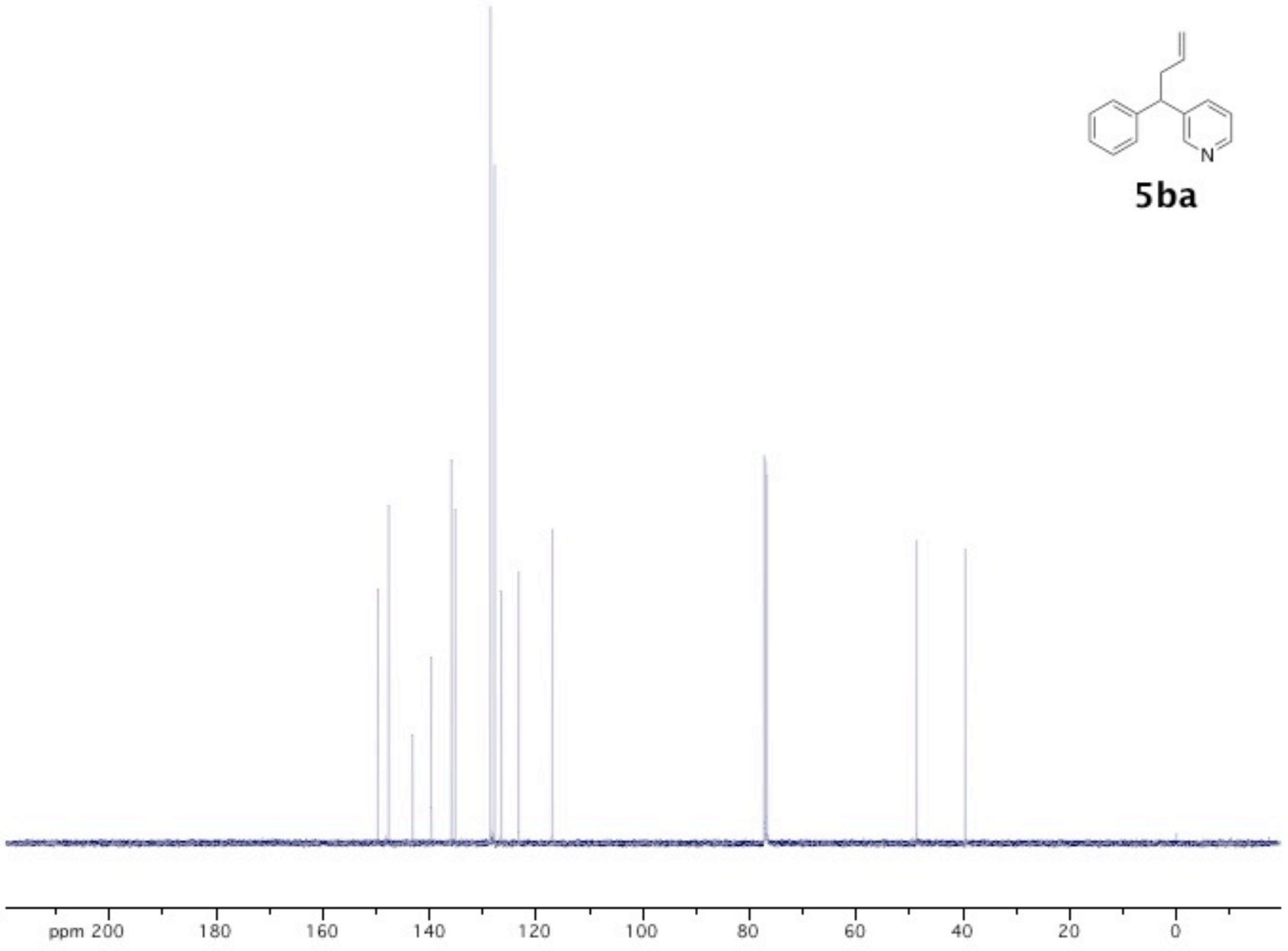
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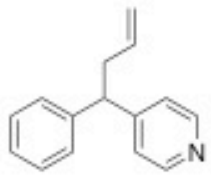

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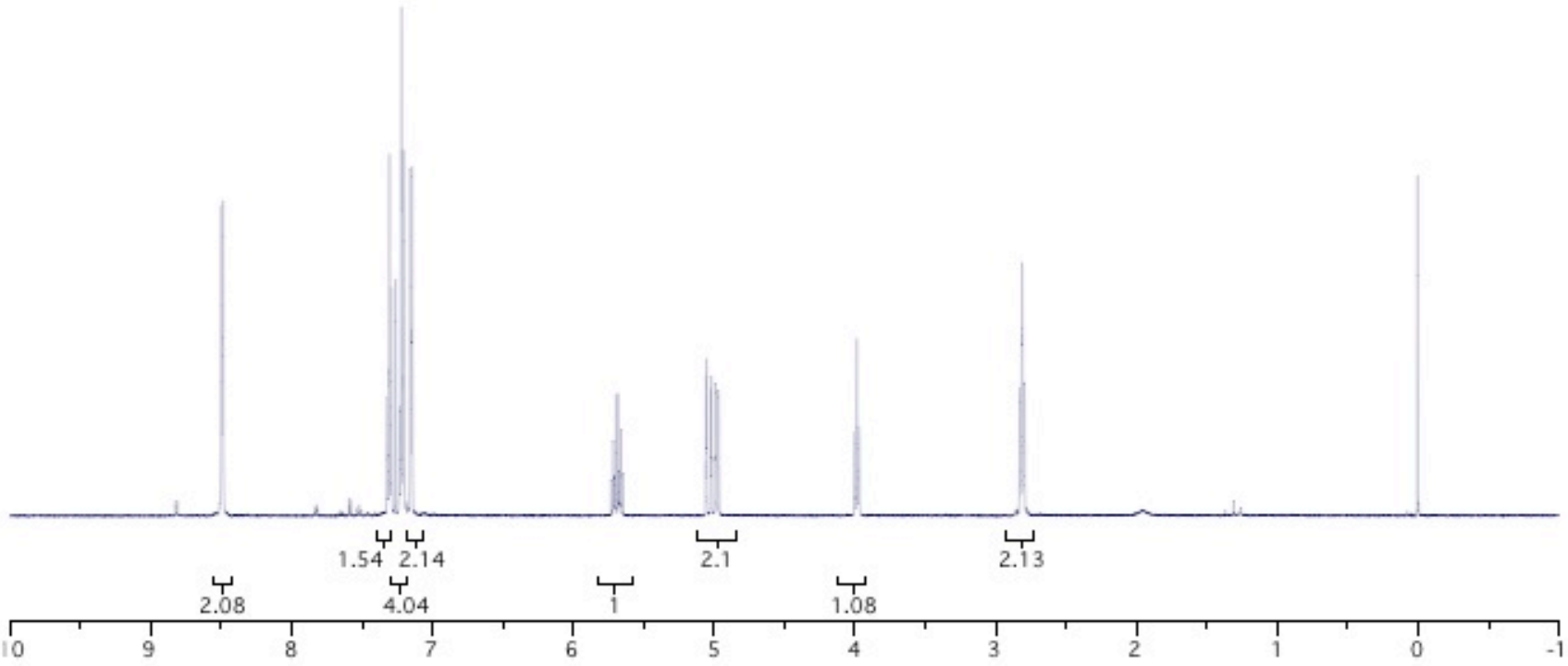

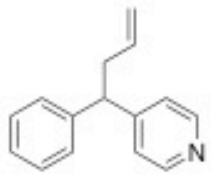

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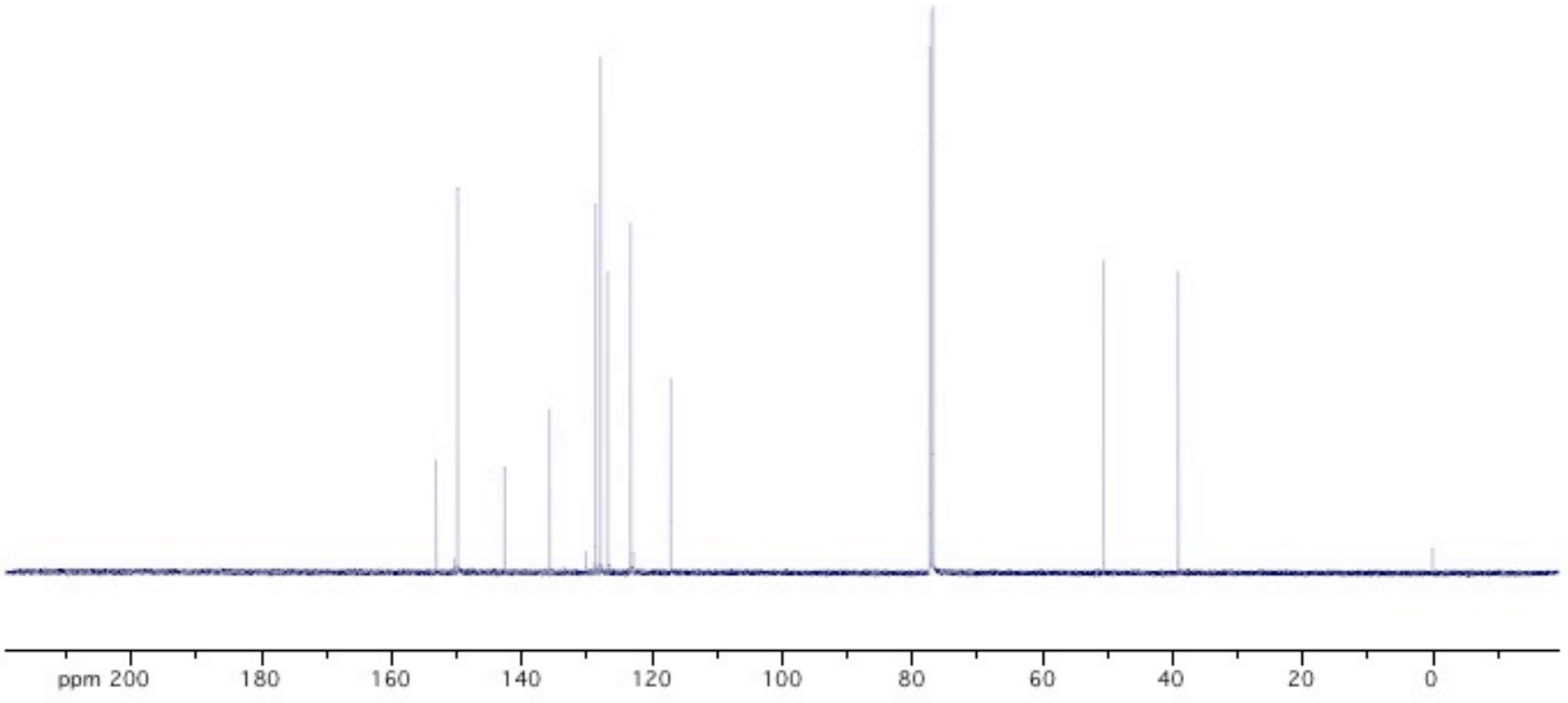

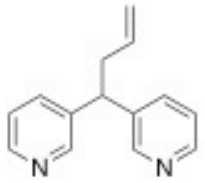

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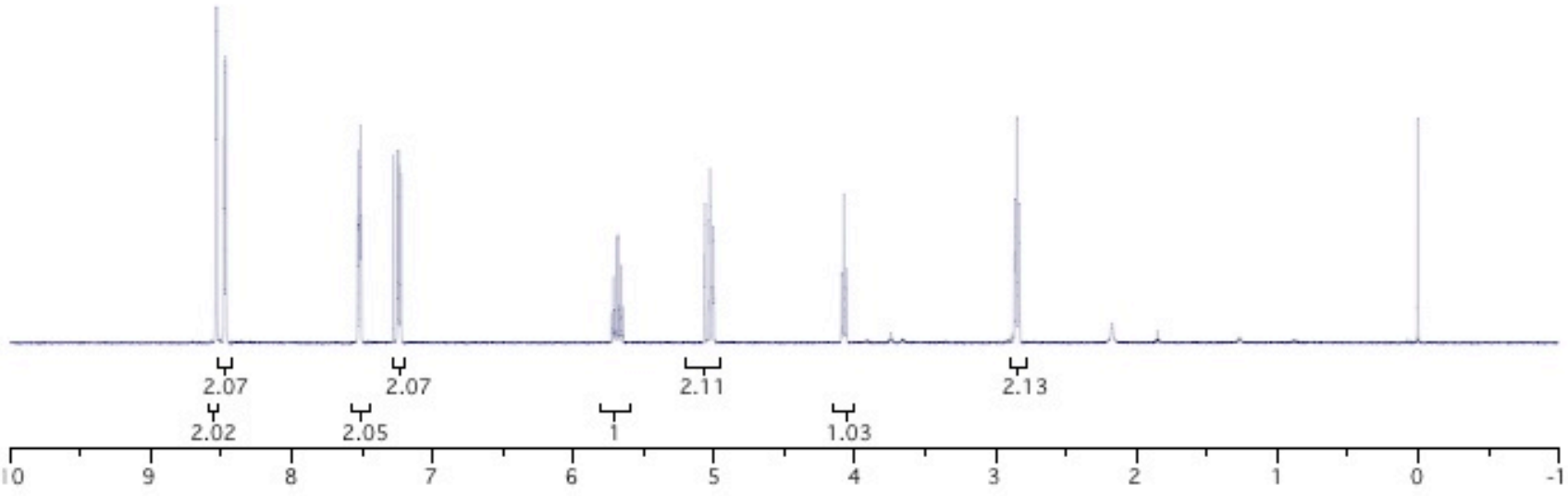

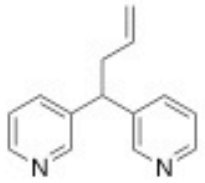

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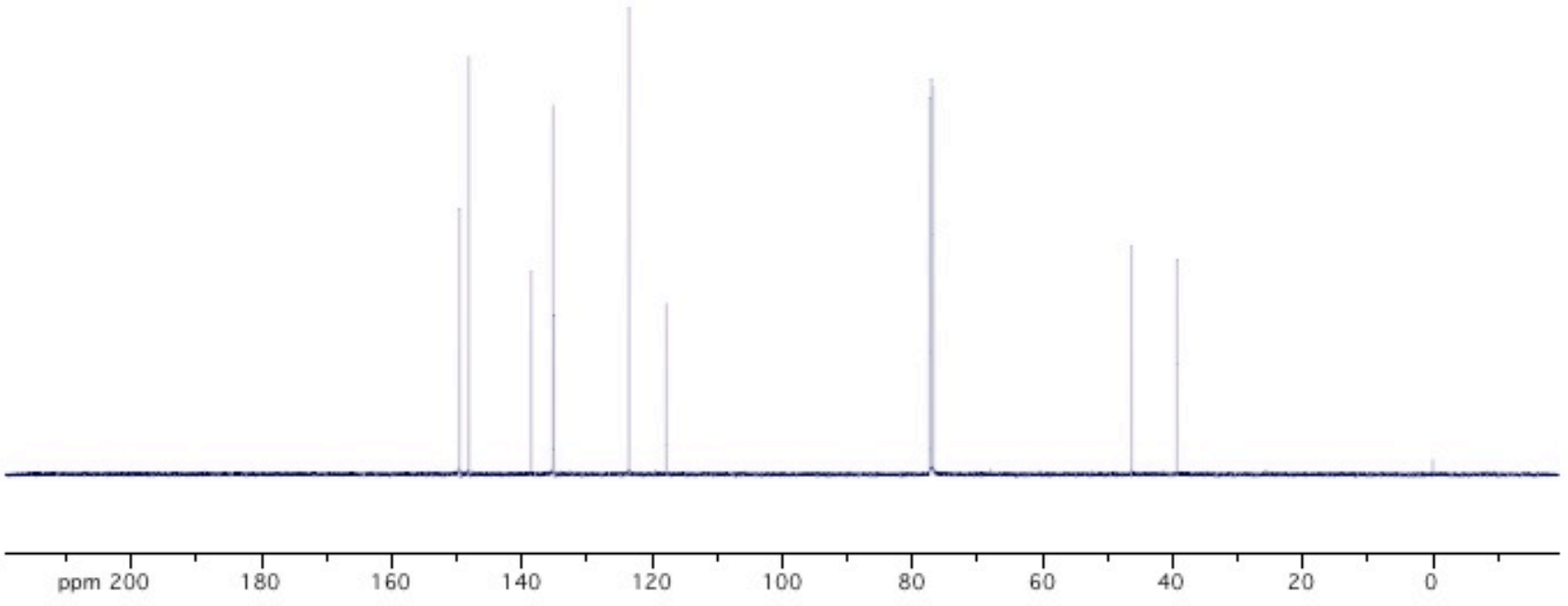

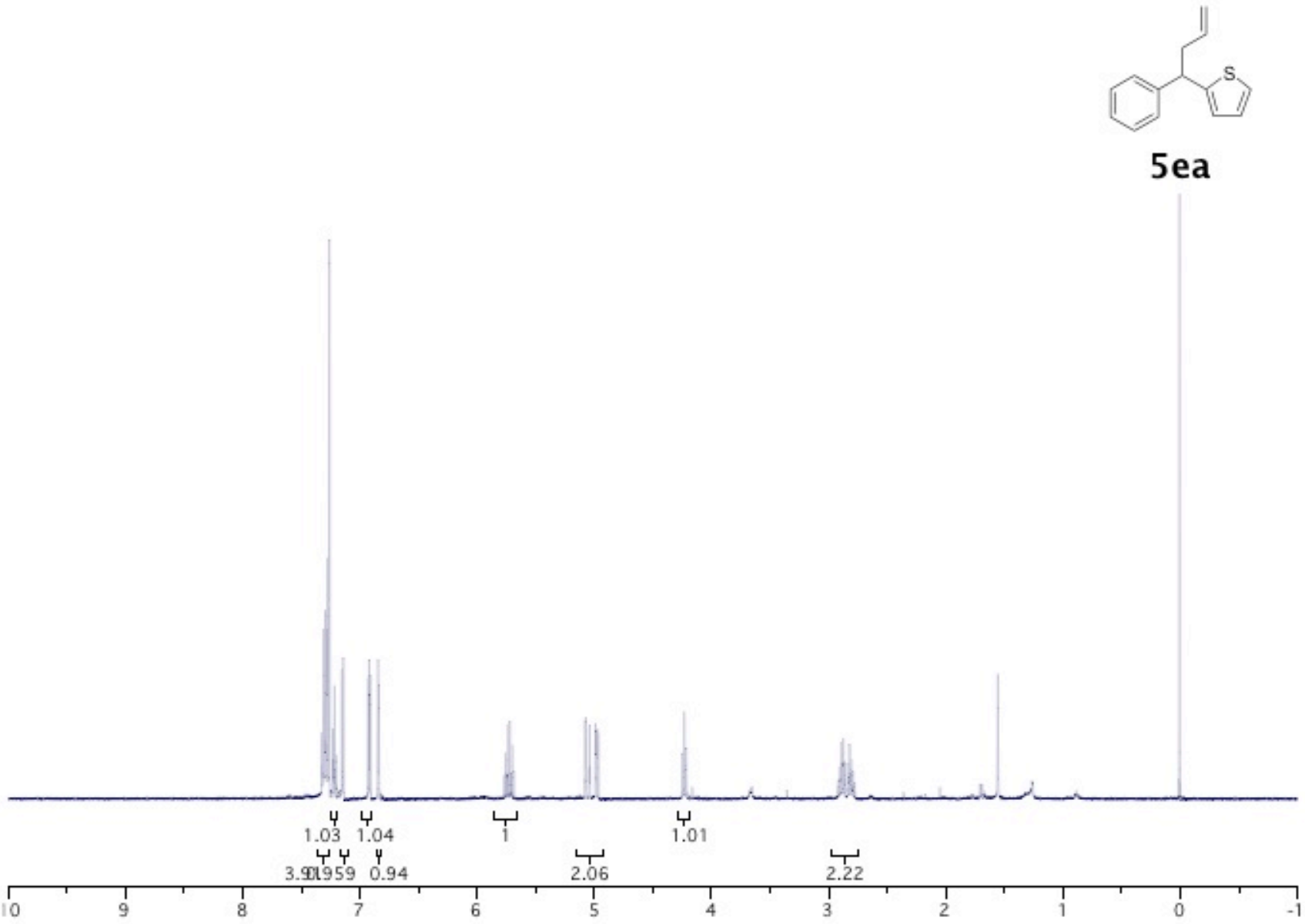
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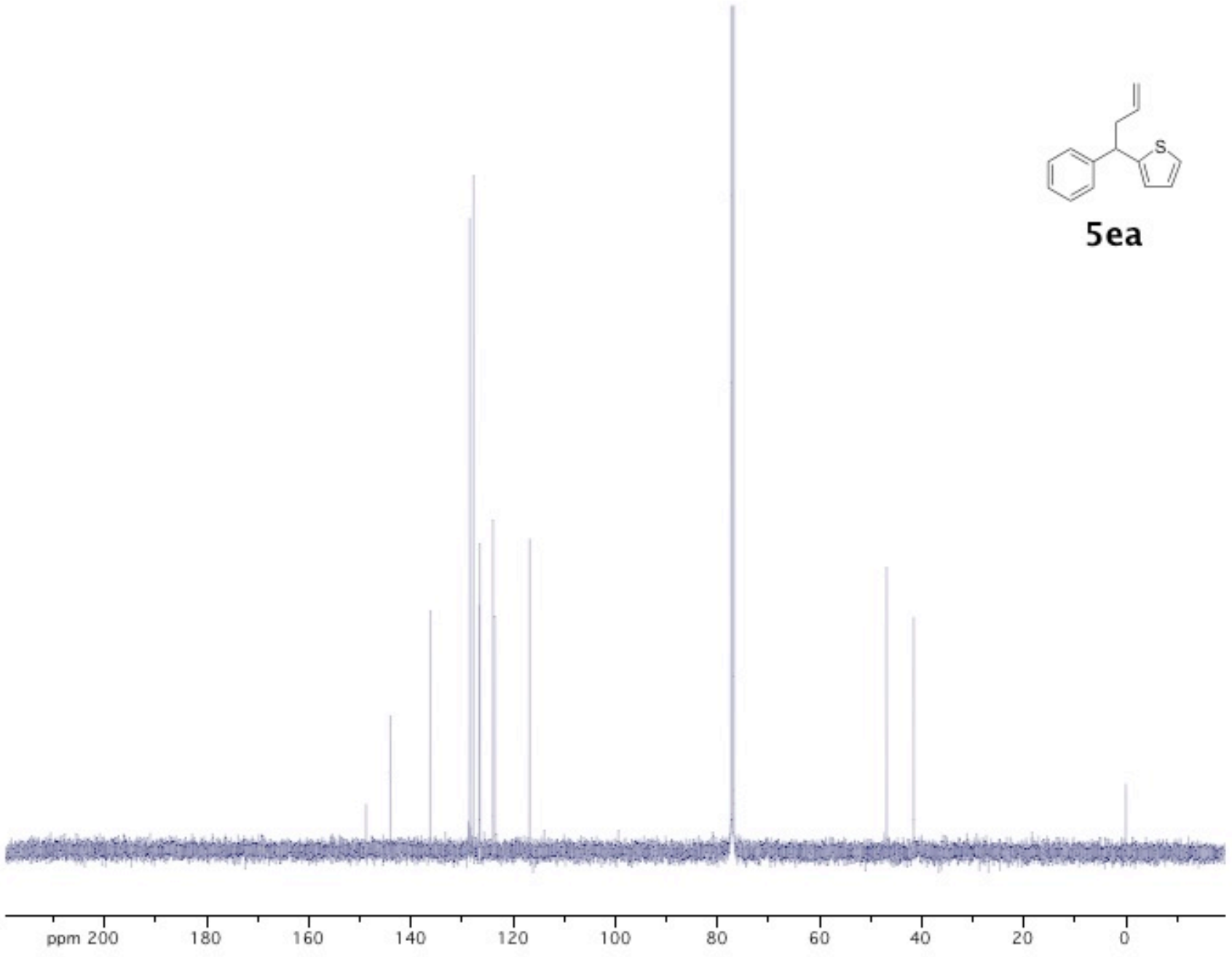
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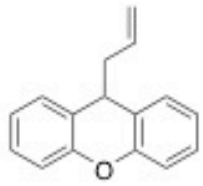

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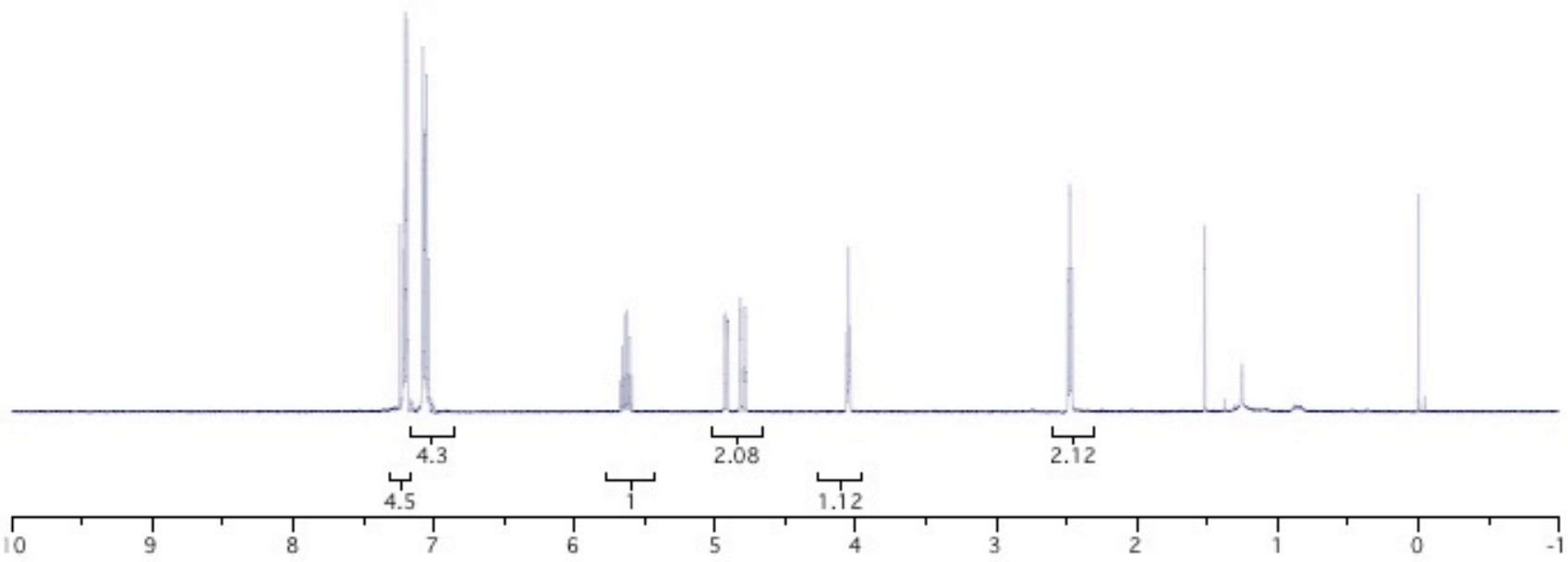

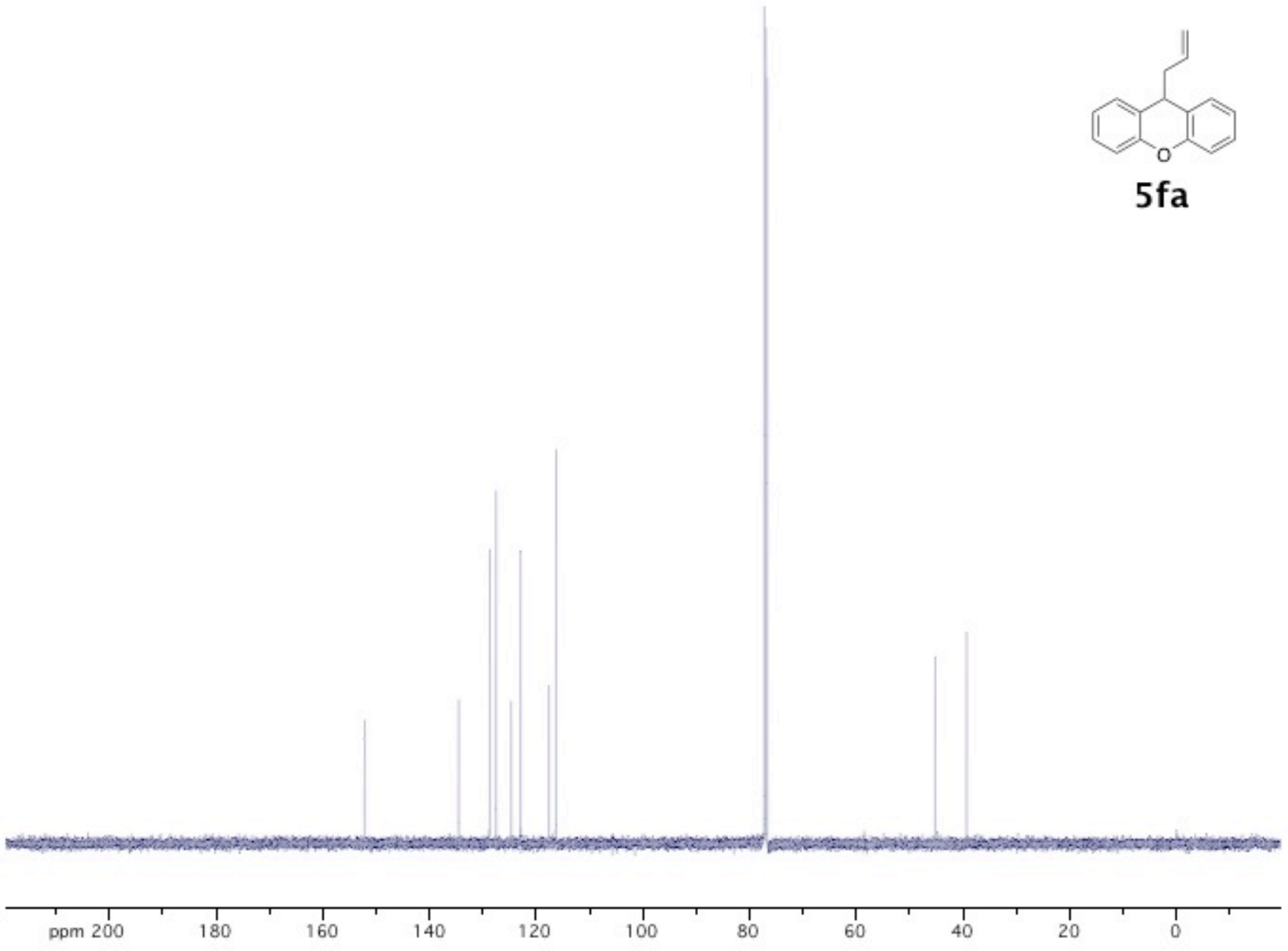
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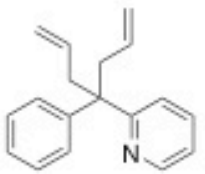

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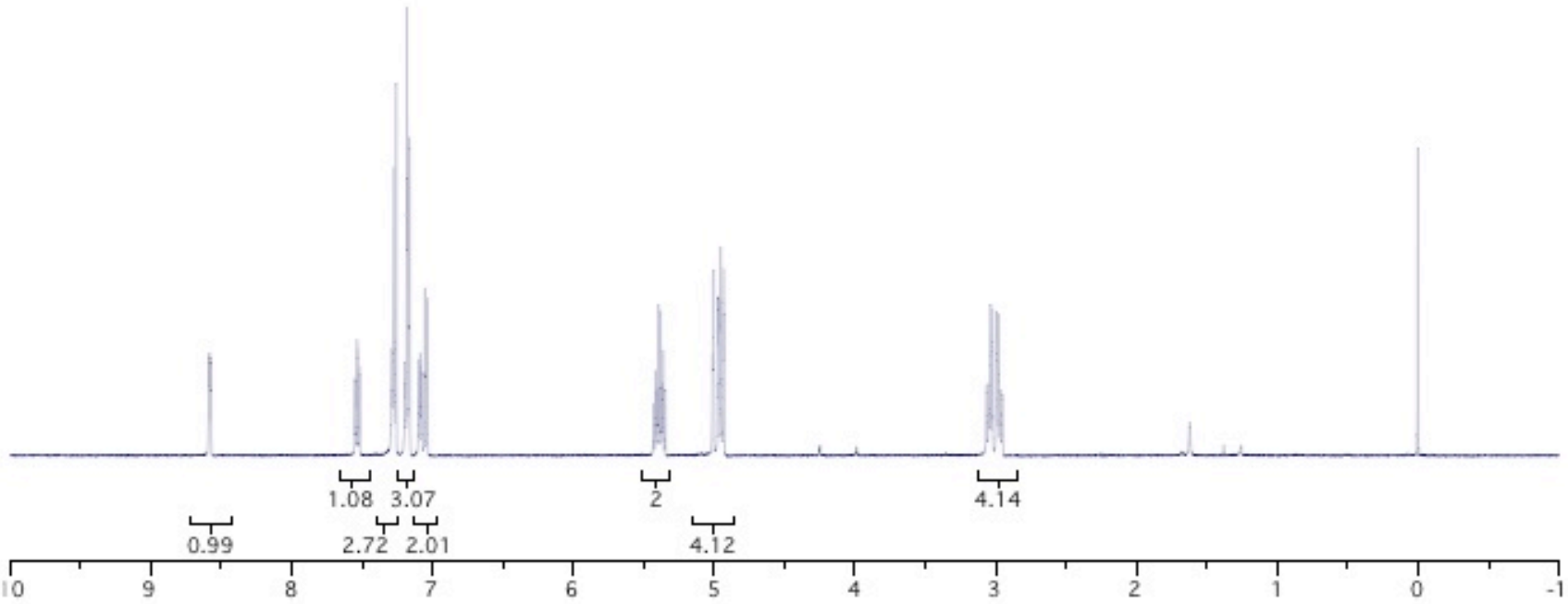

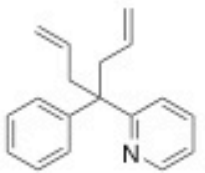

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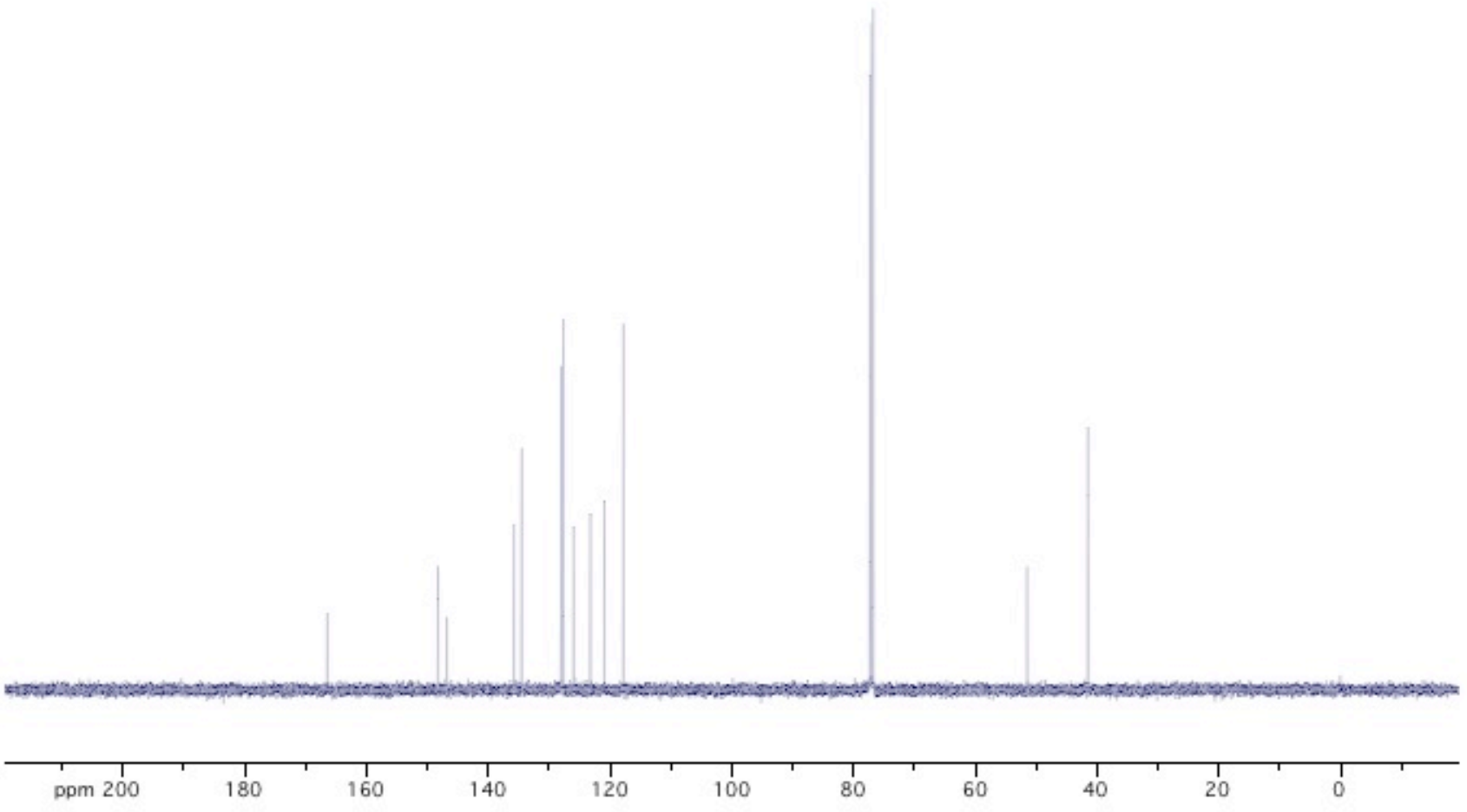

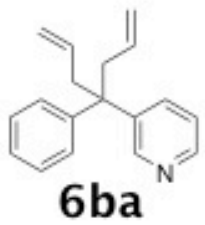

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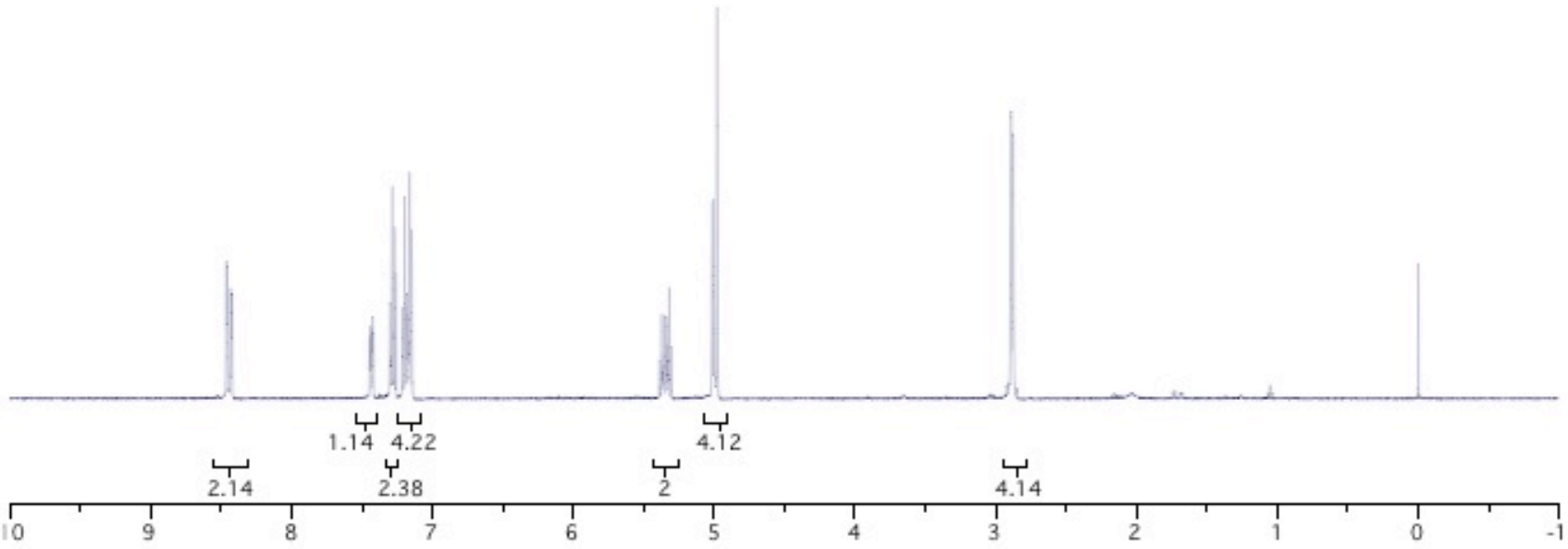

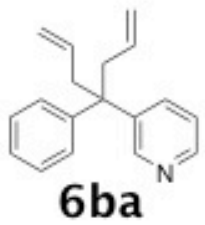

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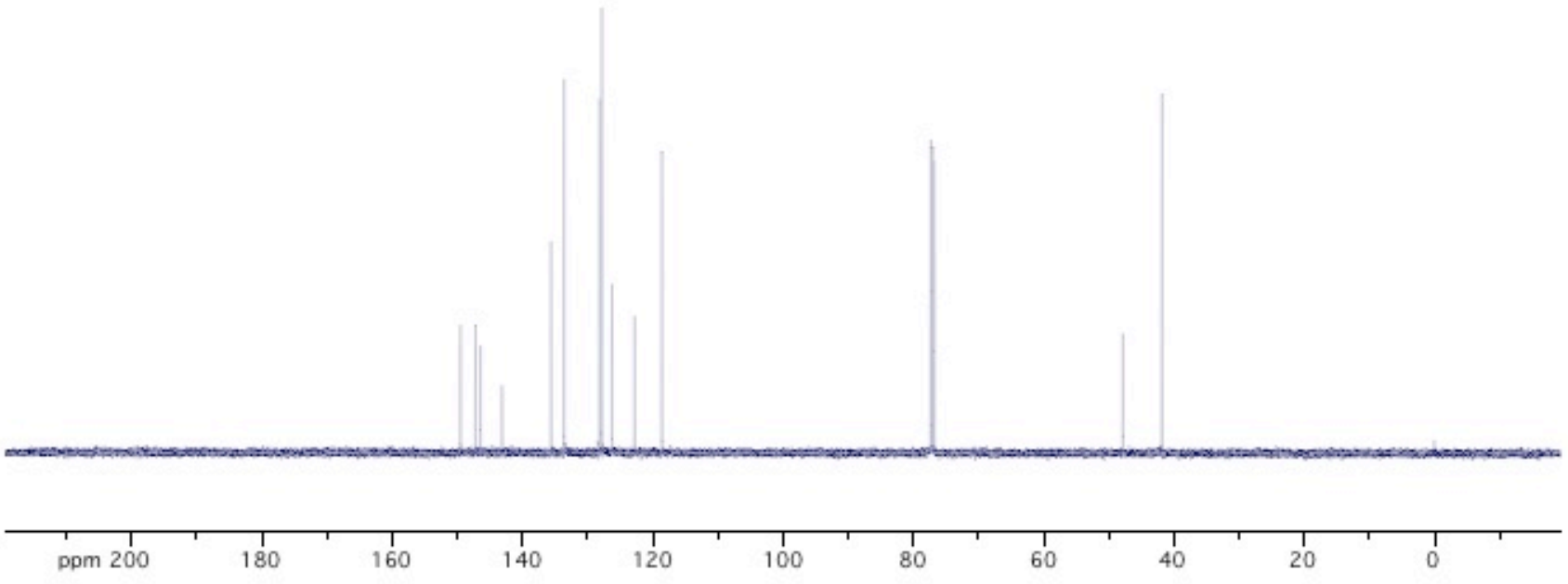

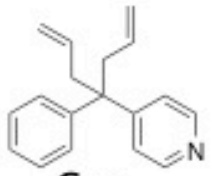

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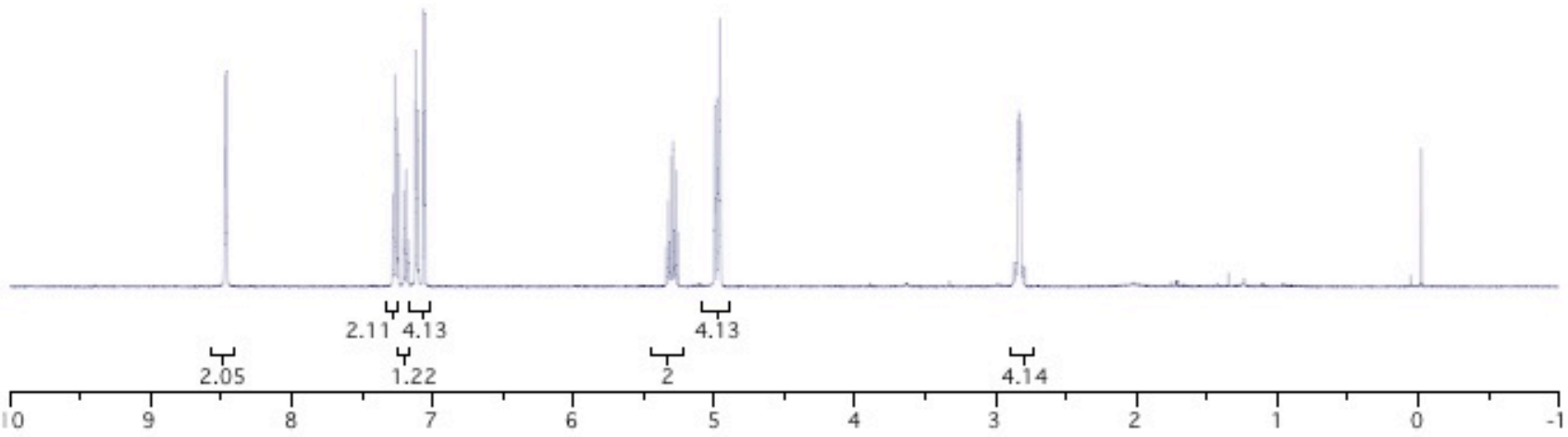

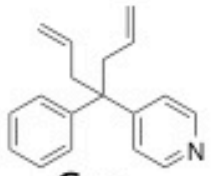

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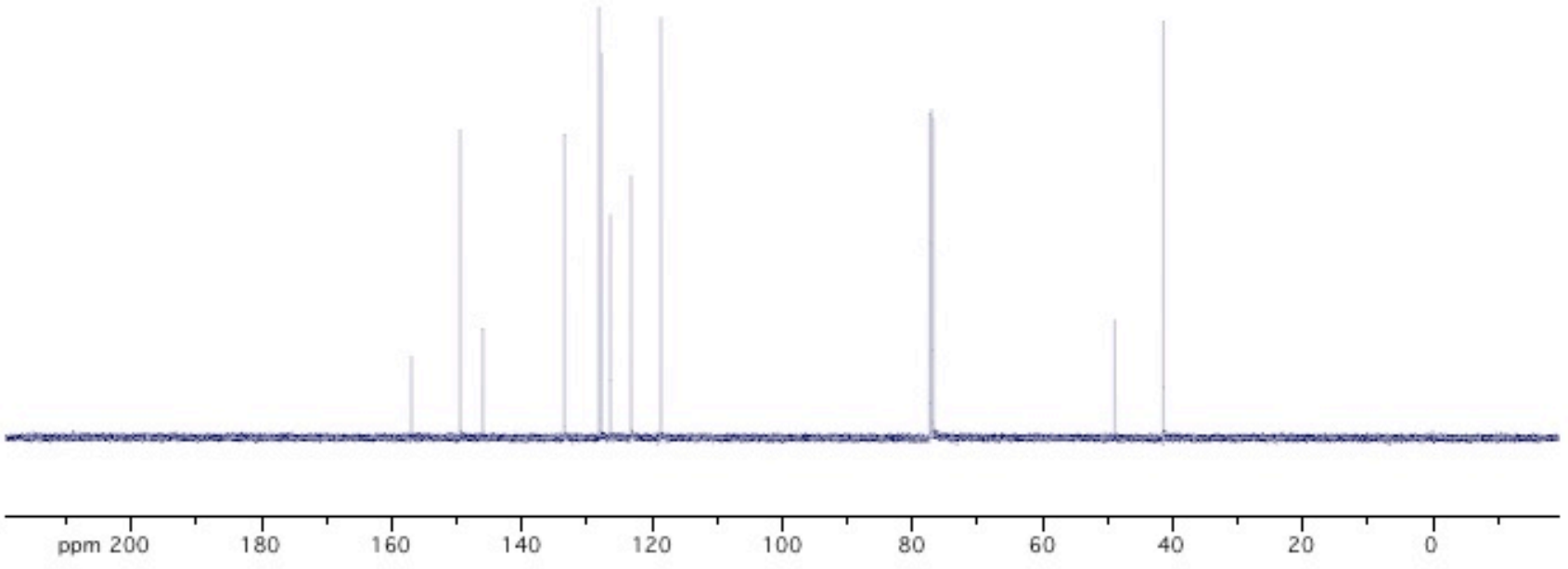

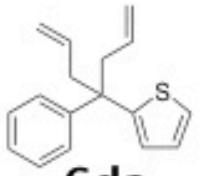

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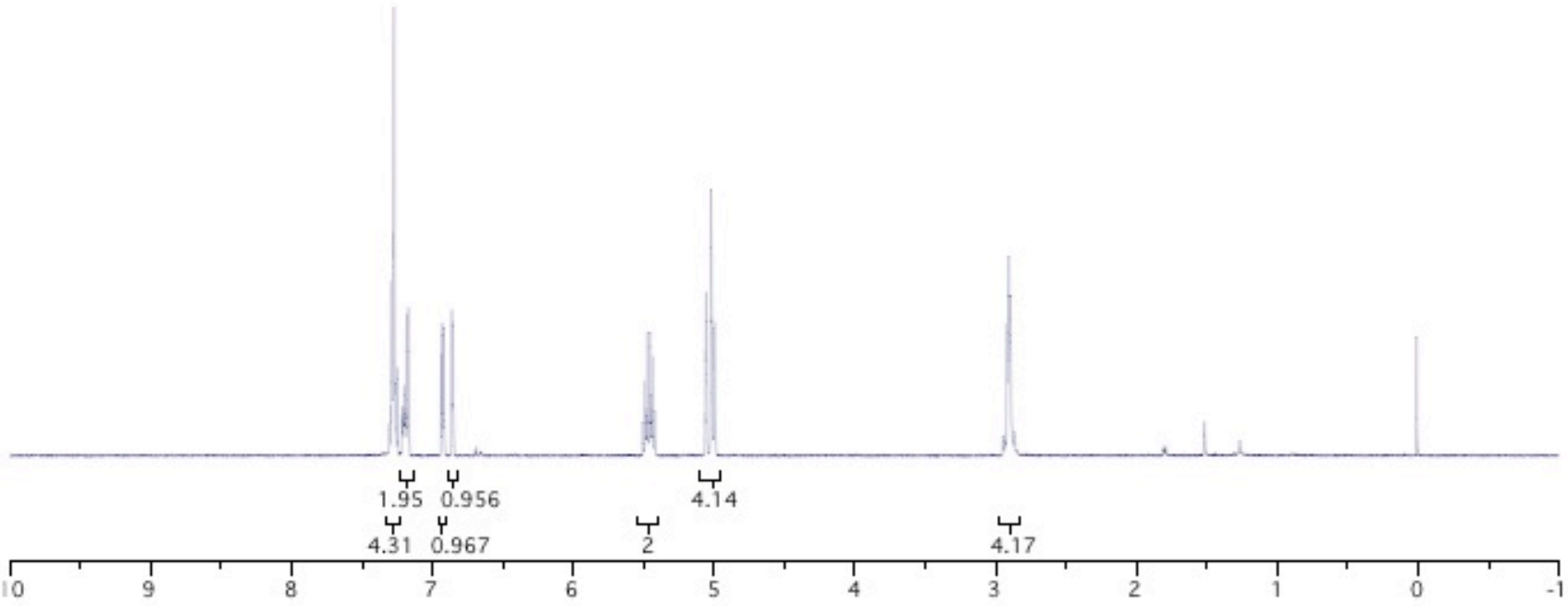

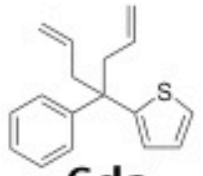

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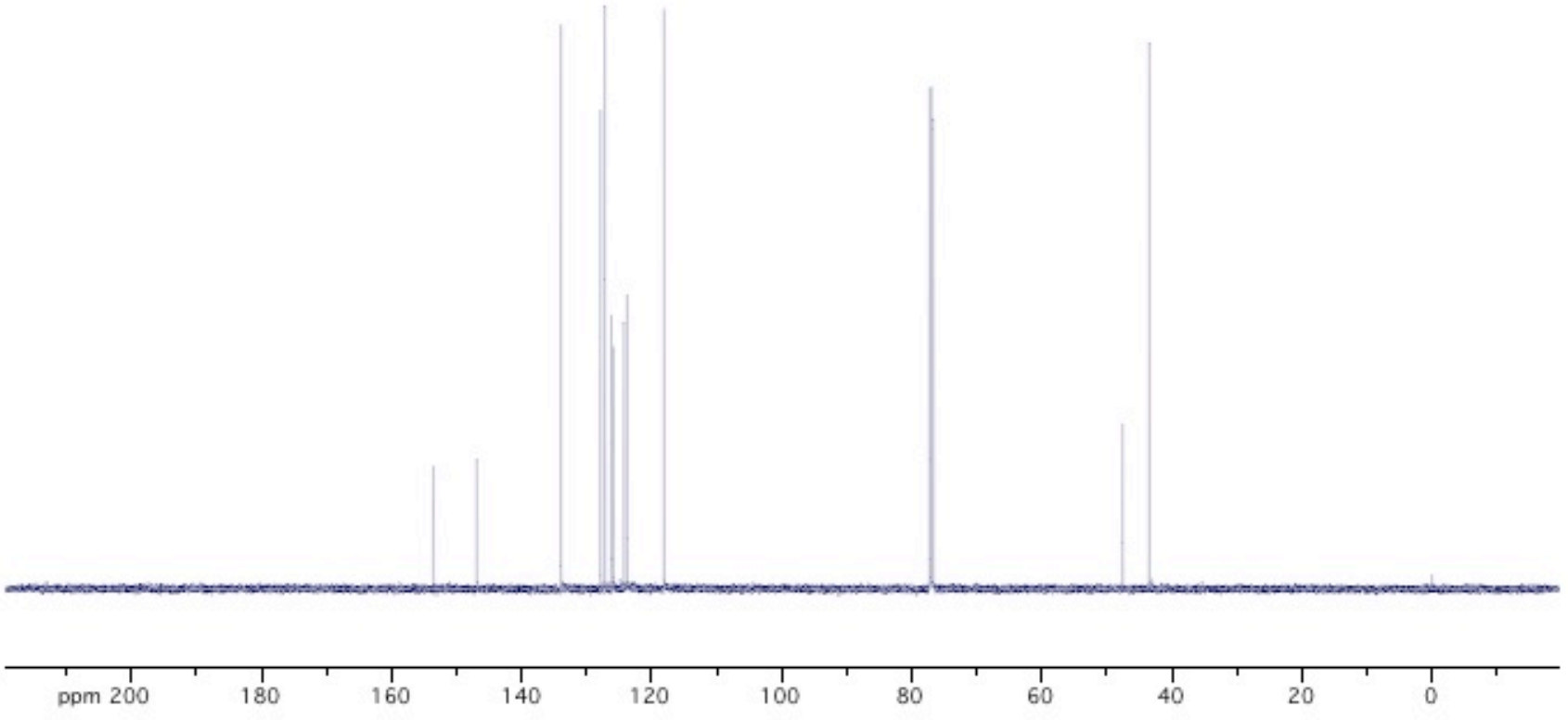

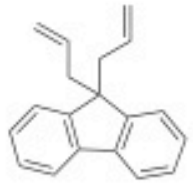

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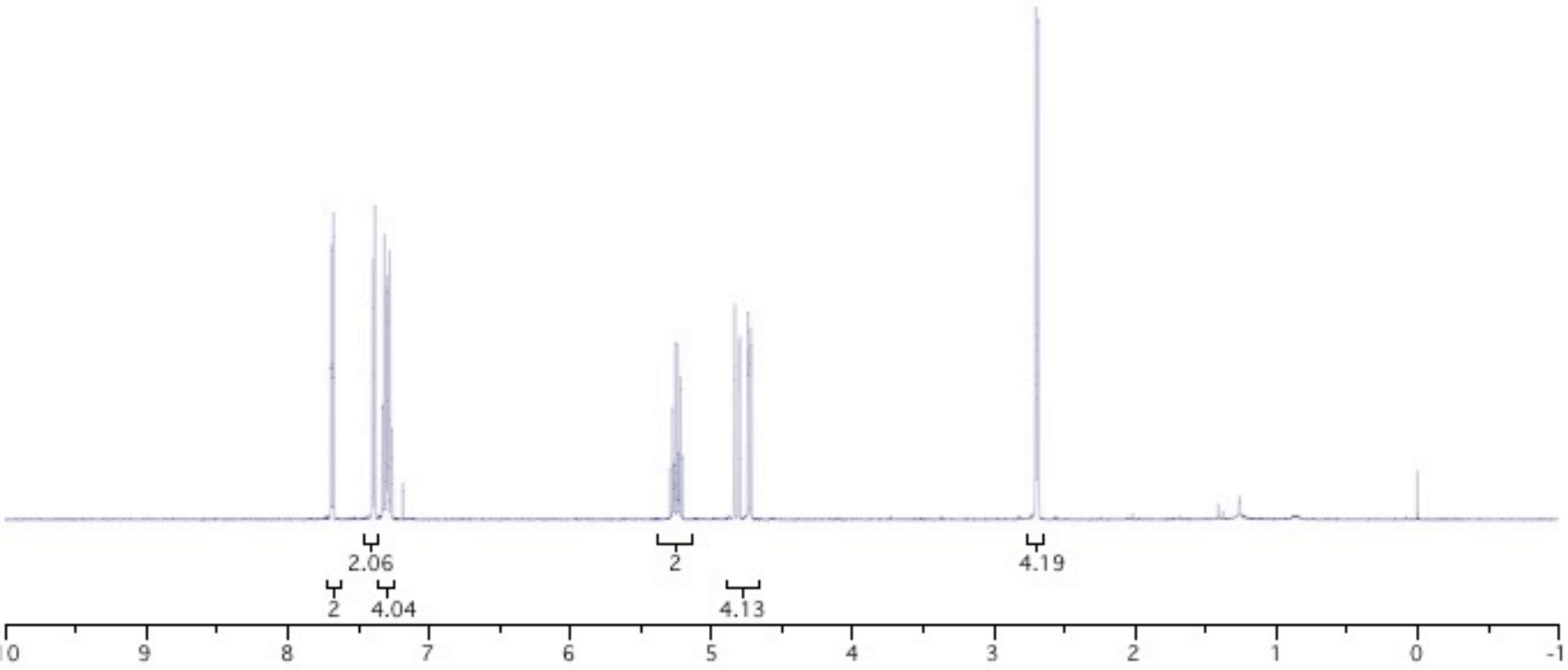

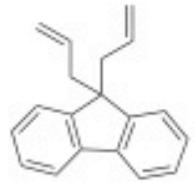

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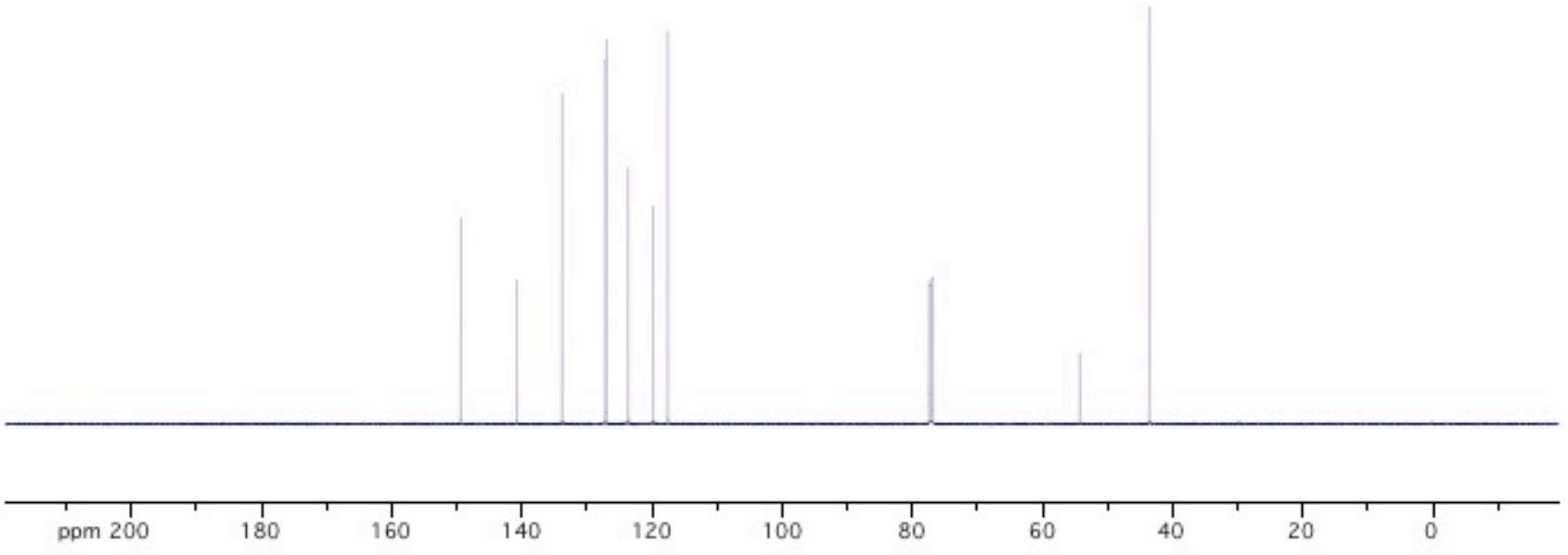

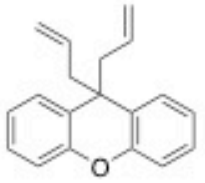

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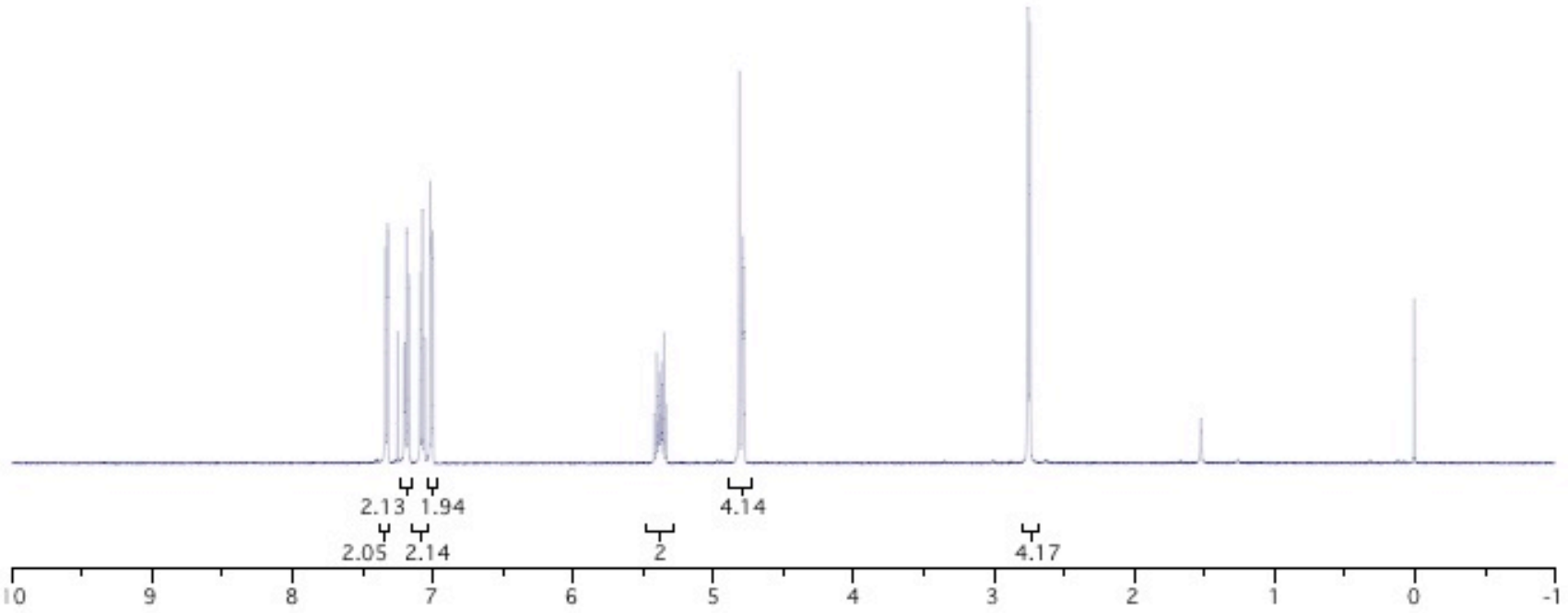

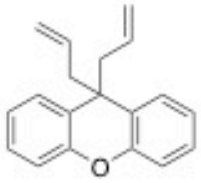

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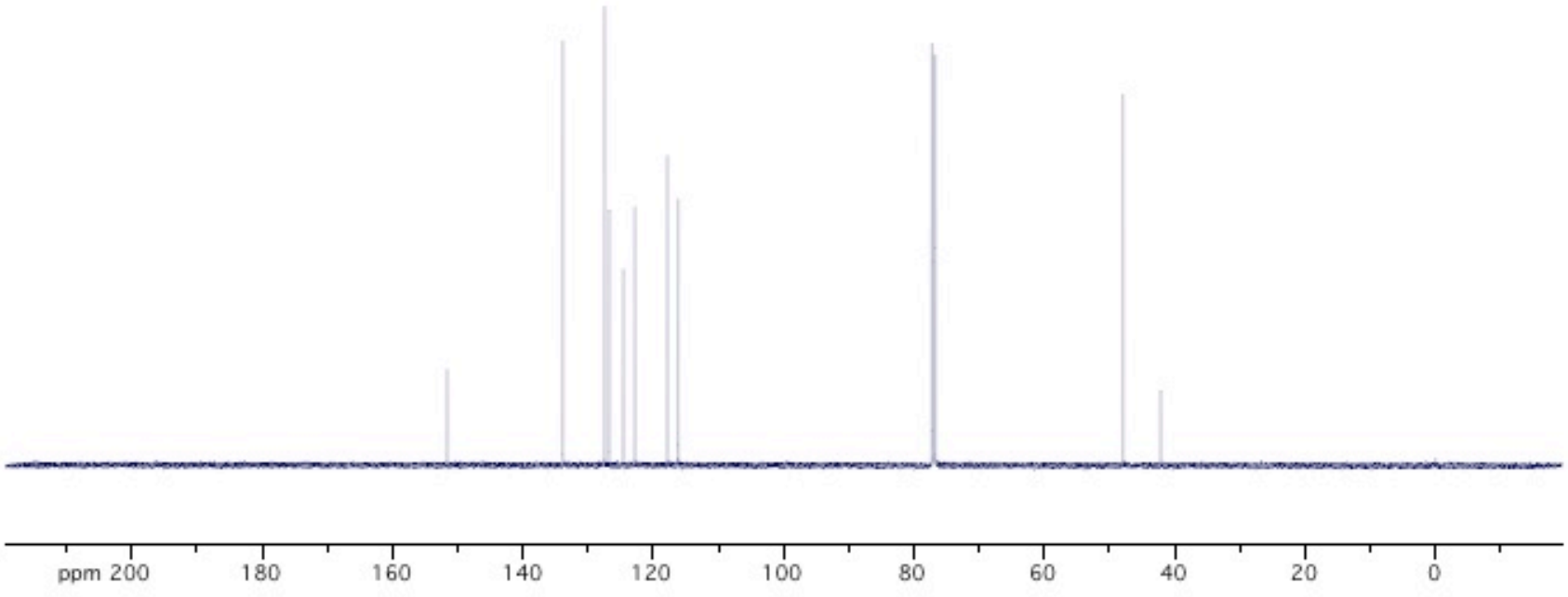

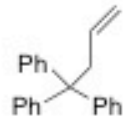

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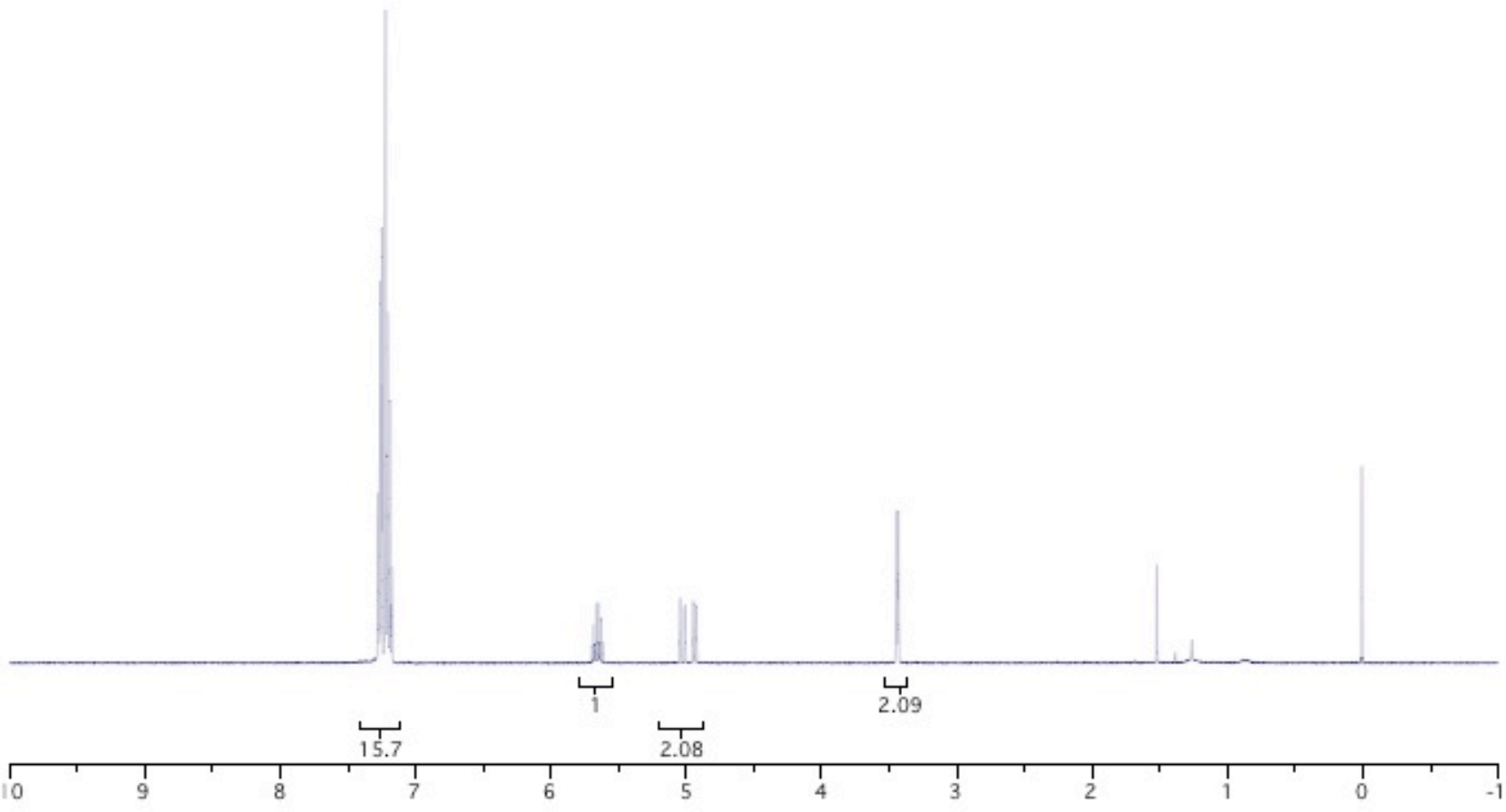

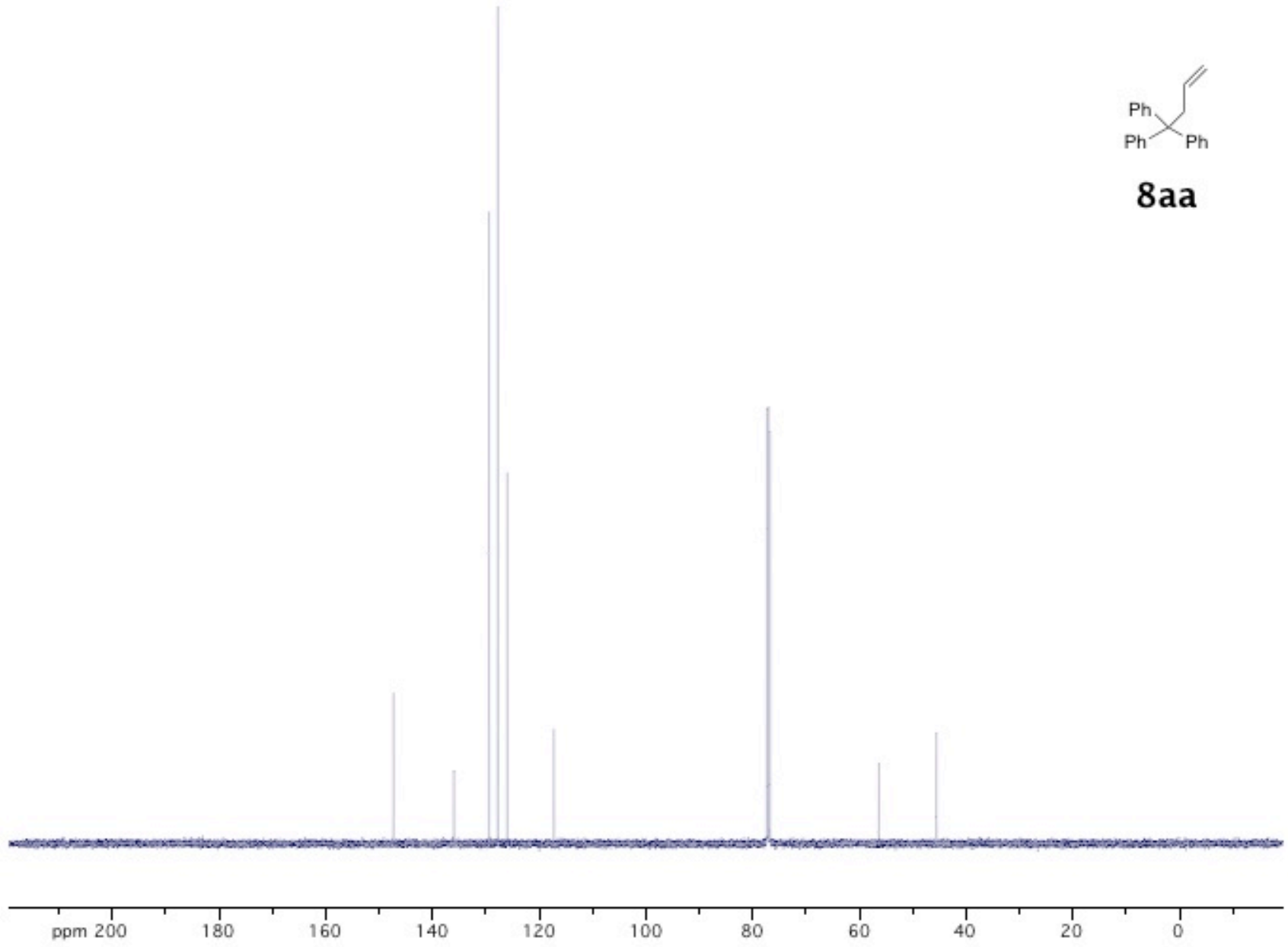
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Ph
Ph
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140
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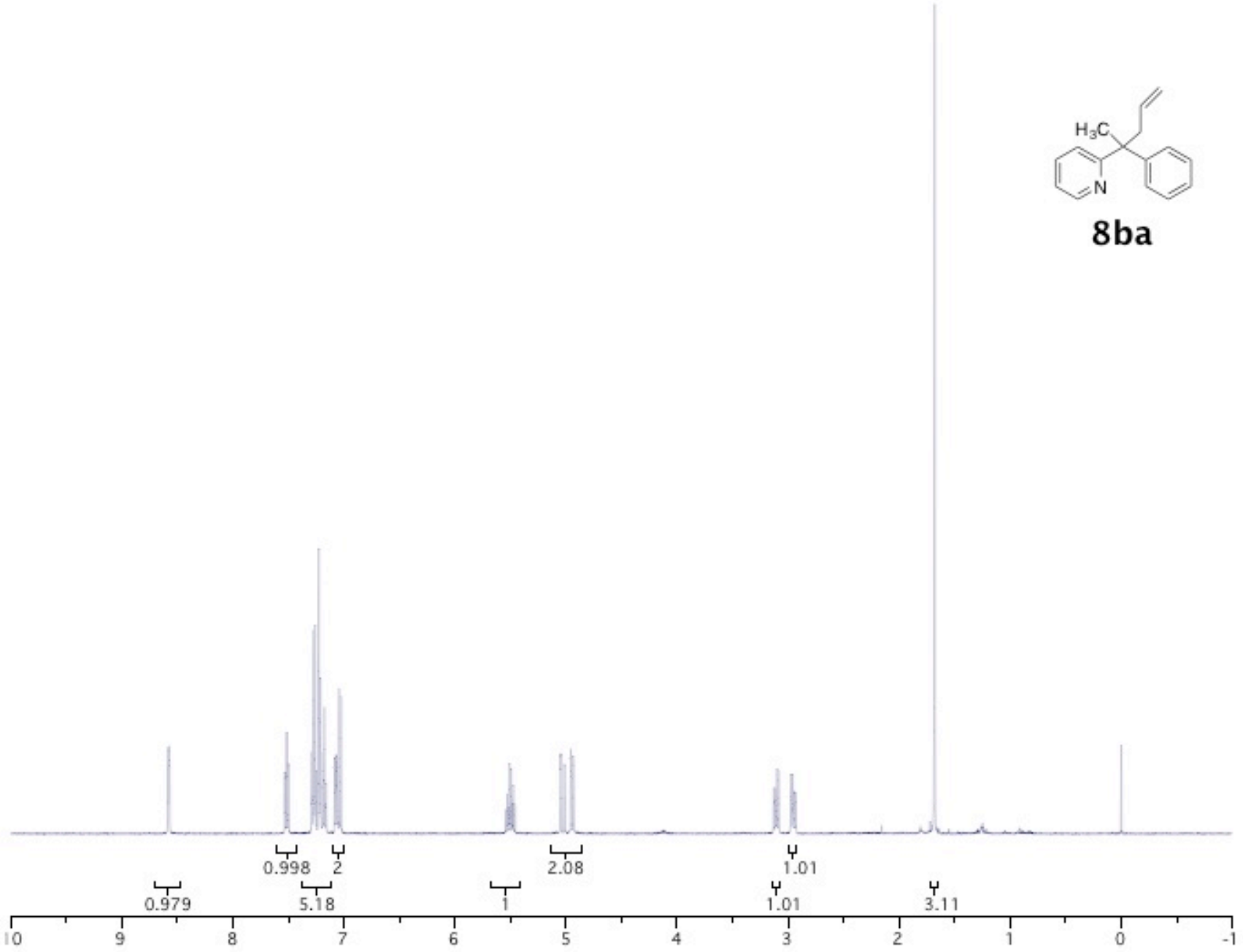
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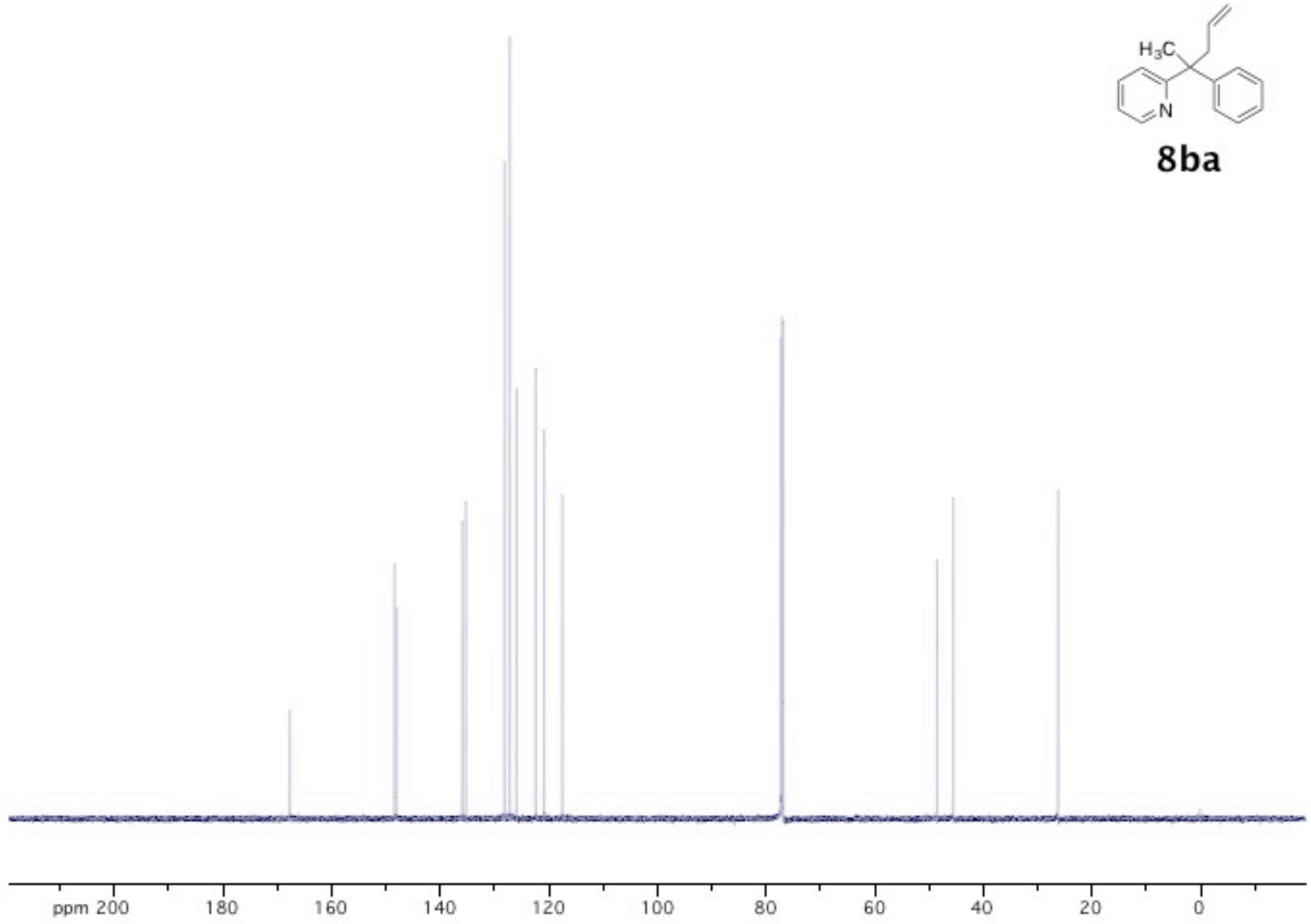
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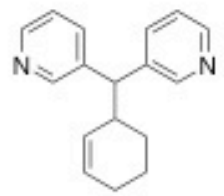

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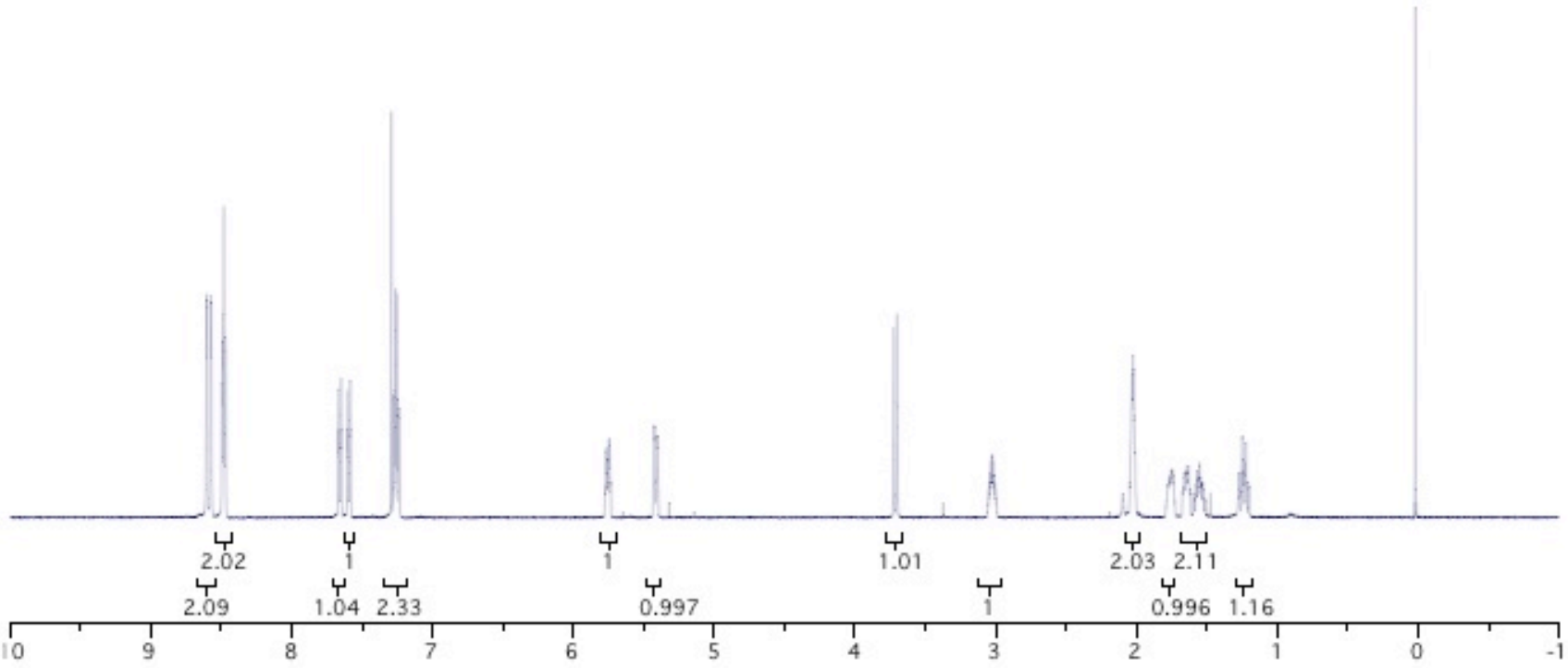

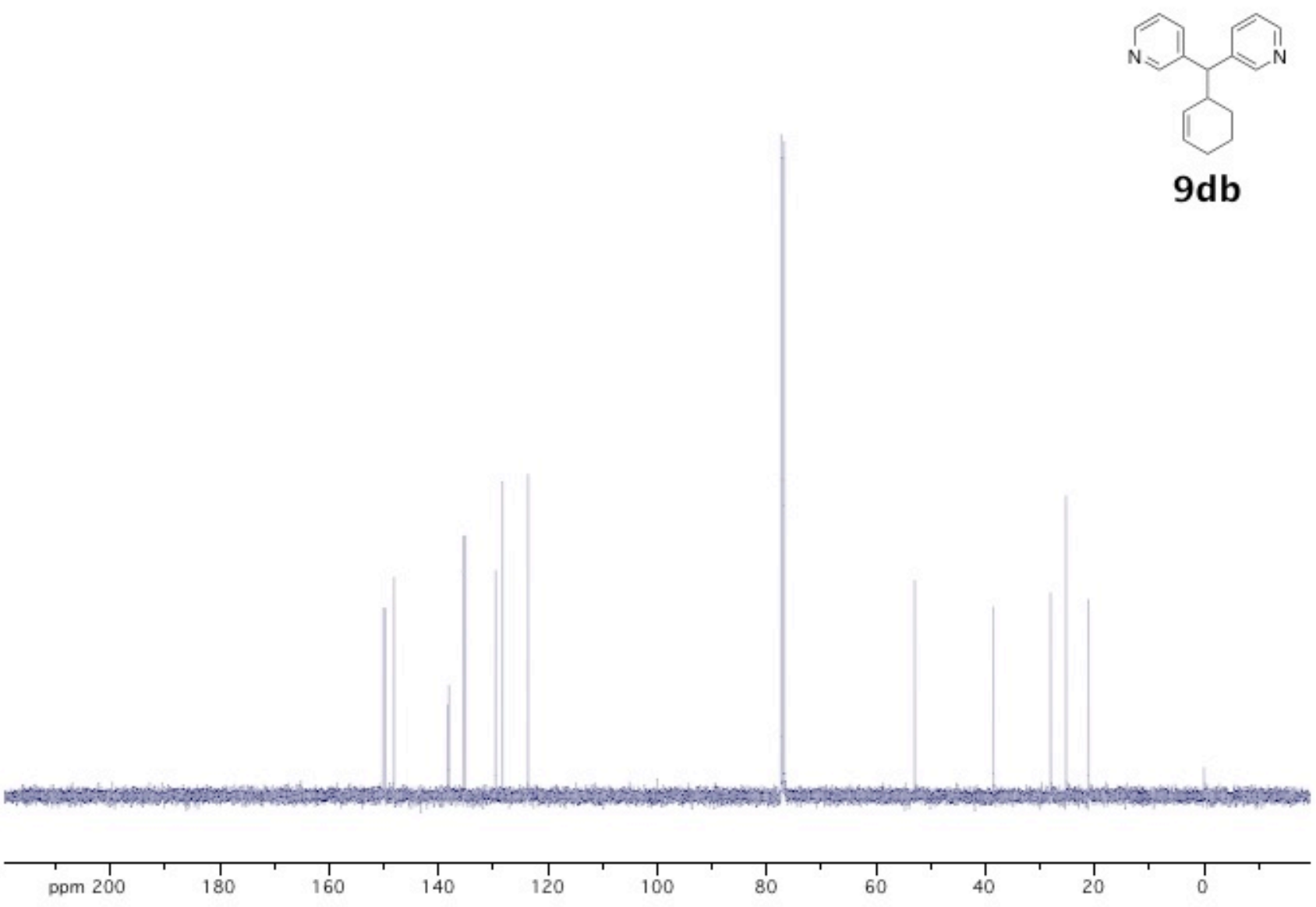
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N
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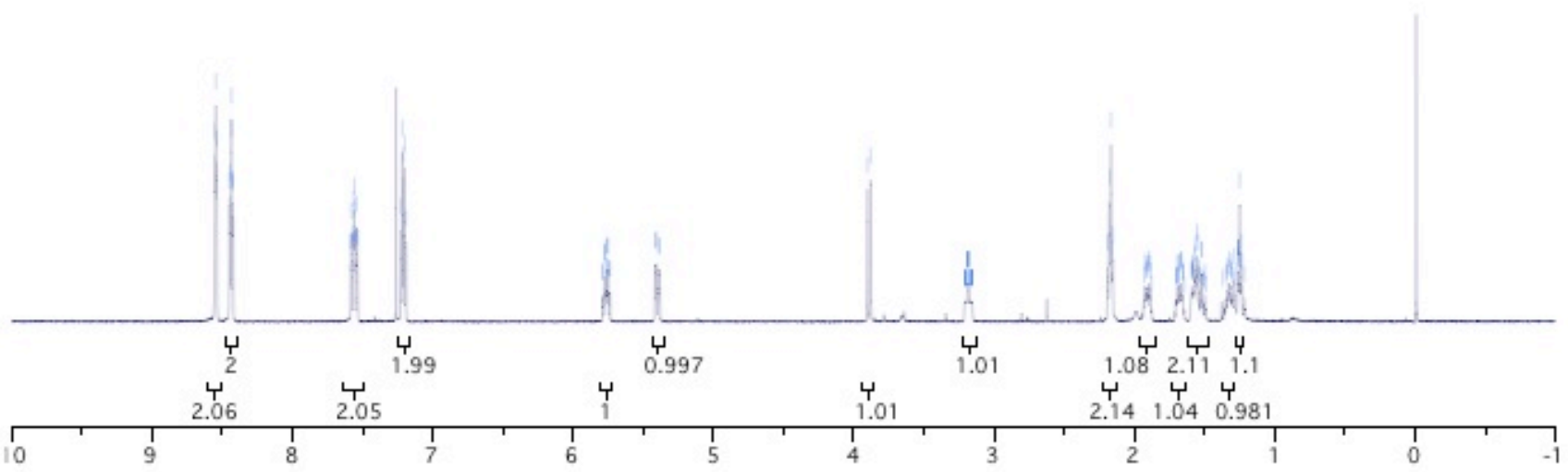
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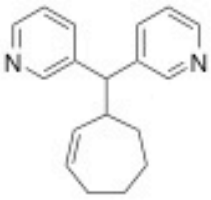

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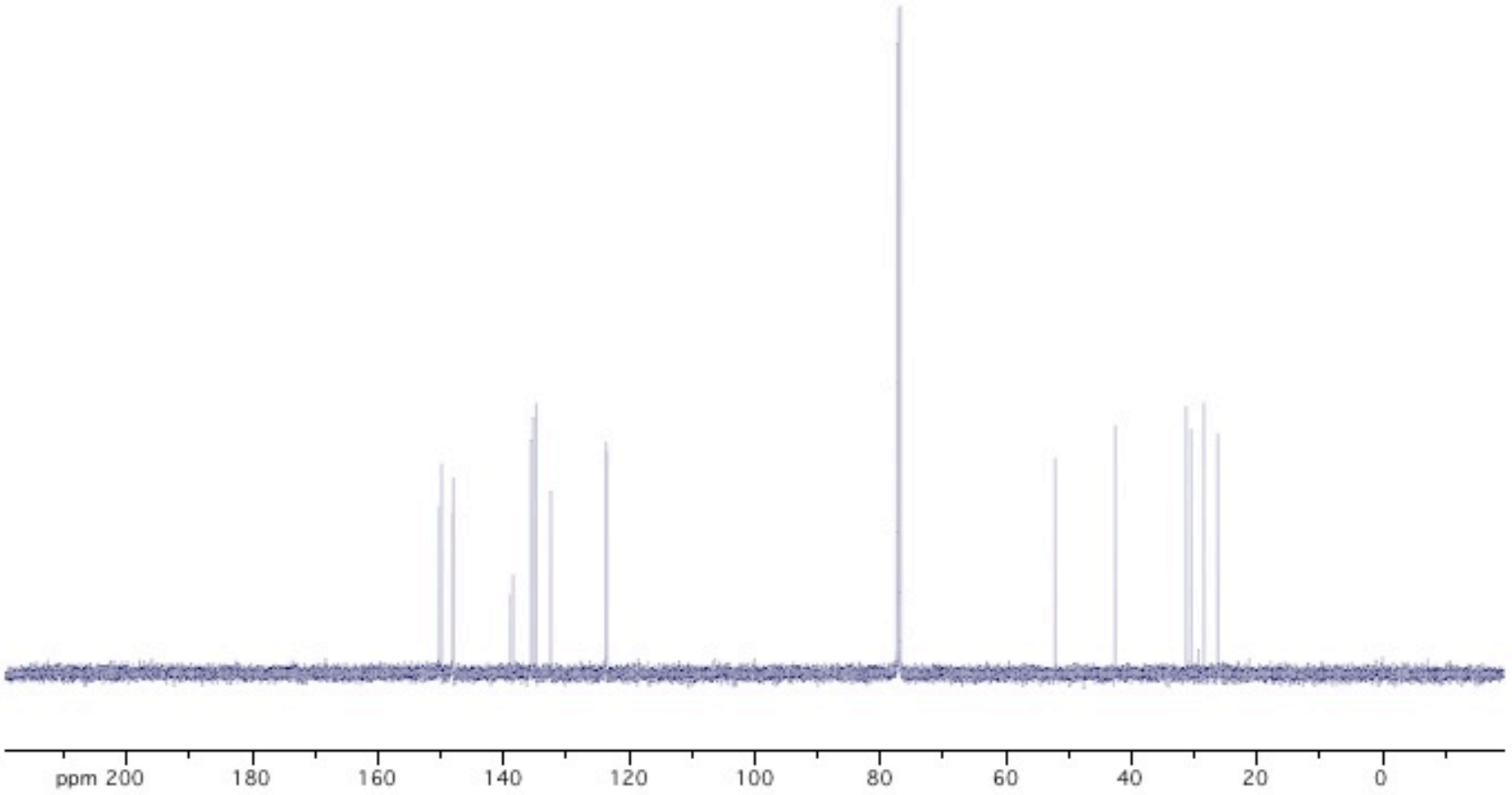

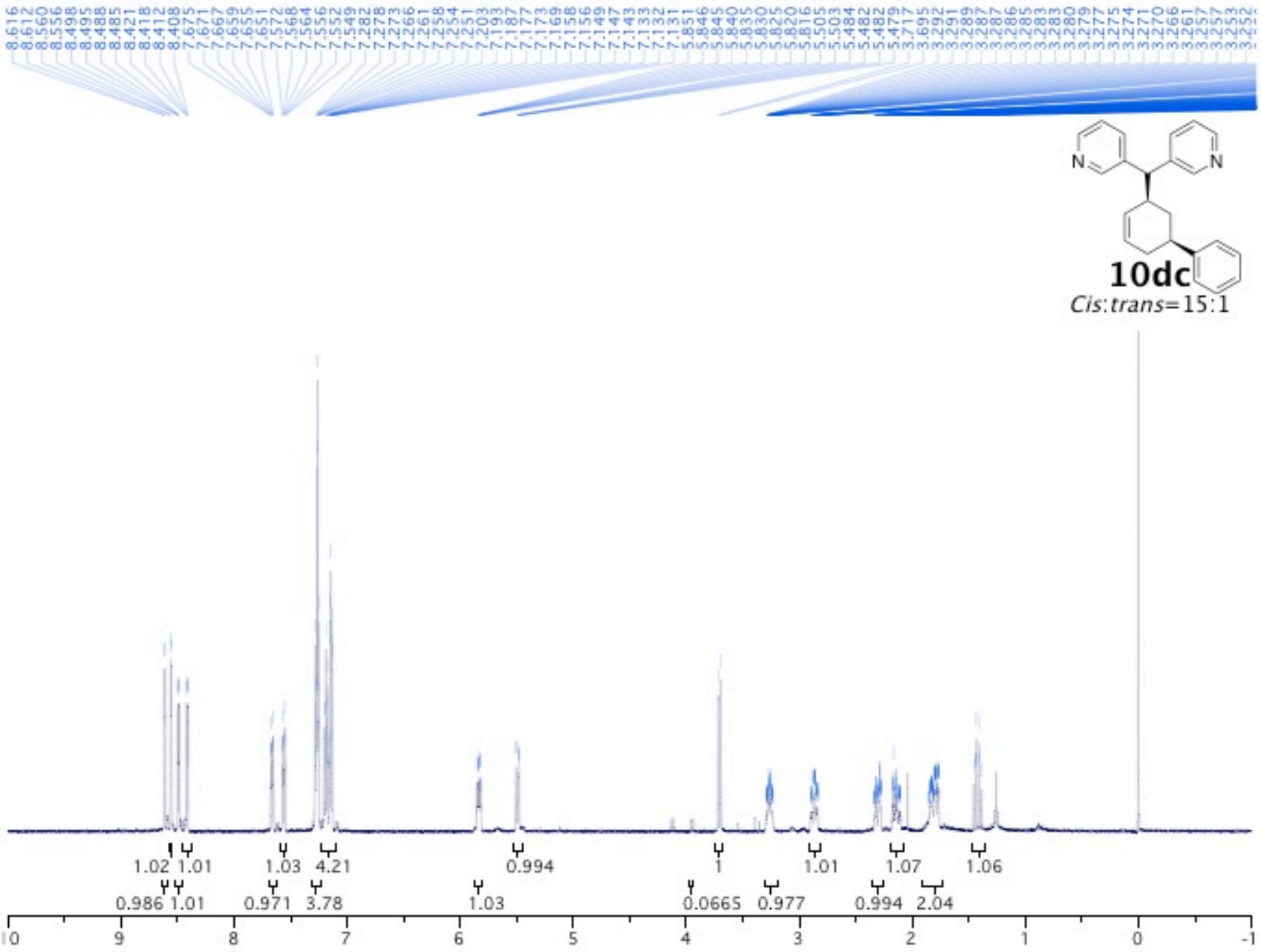
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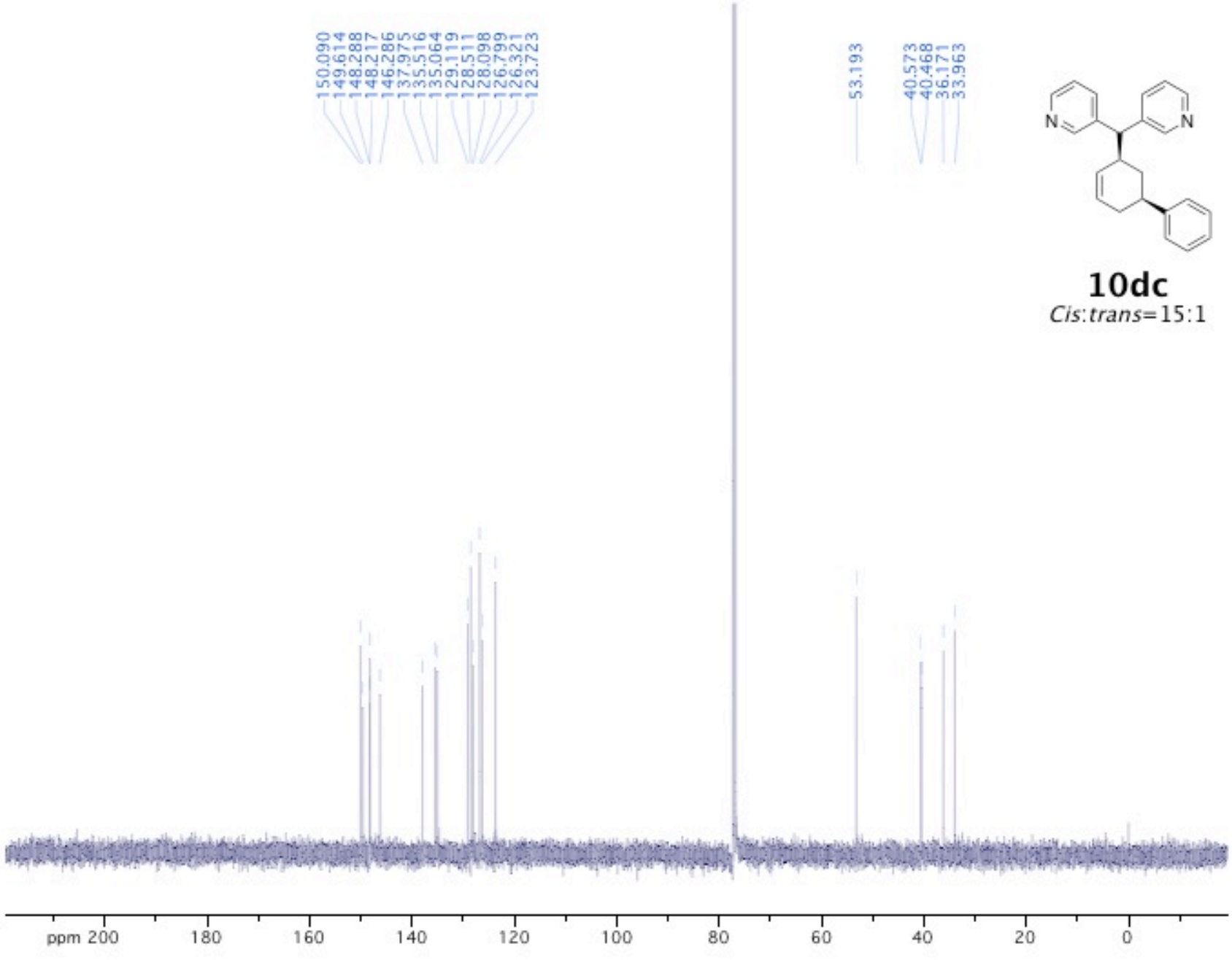
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