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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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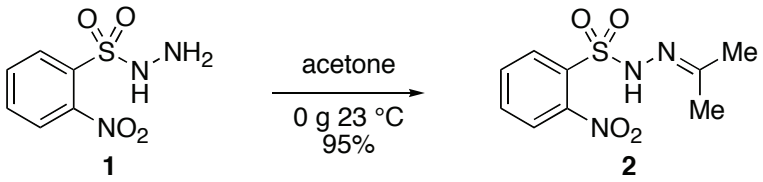
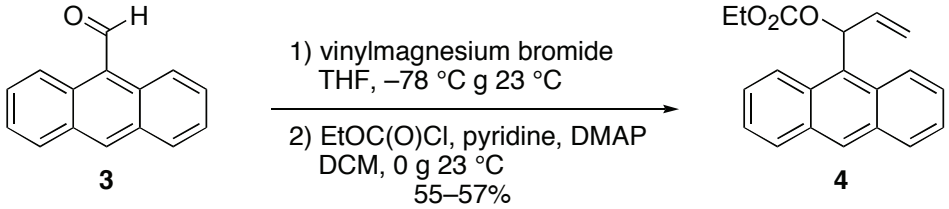
Preparation of *n*-Isopropylidene-*n'*-2-Nitrobenzenesulfonyl Hydrazine (IPNBSH) and Its Use in Palladium–catalyzed Synthesis of Monoalkyl Diazenes. Synthesis of 9-Allylanthracene

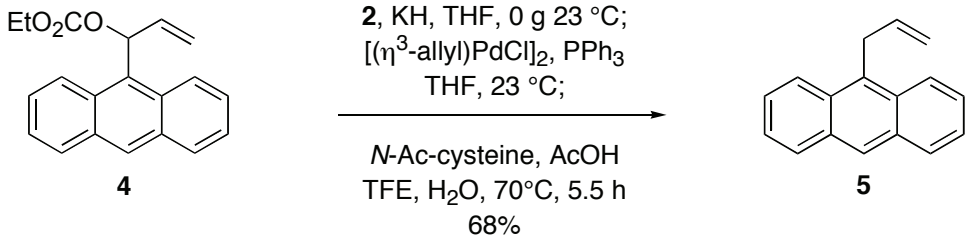
A.



B.



C.



Submitted by Jens Willwacher, Omar K. Ahmad, and Mohammad Movassaghi.[1]
Checked by Juliane Keilitz and Mark Lautens.

Potassium hydride is a pyrophoric solid and must not be allowed to come into contact with the atmosphere. This reagent should only be handled by individuals trained in its proper and safe use.

1. Procedure

*A. N-Isopropylidene-N'-2-nitrobenzenesulfonyl hydrazine (**2**).* An oven-dried 1-L, two-necked, round-bottomed flask, equipped with a 3 cm football-shaped stir bar, a rubber septum and inert gas inlet connected to a manifold, is charged with *o*-nitrobenzenesulfonyl hydrazide (**1**) (Note 1) (20.0 g,

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shaped stir bar, a rubber septum and inert gas inlet connected to a manifold, is charged with *o*-nitrobenzenesulfonyl hydrazide (**1**) (Note 1) (20.0 g, 92.1 mmol, 1 equiv) under an argon atmosphere. Acetone (Note 2) (300 mL) is added via cannula and the resulting solution stirred at room temperature (24 °C). After 10 min, TLC (Note 3) analysis of the reaction mixture indicated full conversion of the starting material (hexanes:ethyl acetate = 1:2; Rf_{SM} = 0.2, R$f_{product}$ = 0.5, visualized with ceric ammonium molybdate). Aliquots of the solution are transferred to a 500-mL one-necked flask and the solvent is removed with a rotary evaporator (200 mmHg, 40 °C) to afford a yellow powder. Hexanes (100 mL), acetone (20 mL), and a 3-cm football-shaped stir bar are added and the suspension stirred for 10 min at room temperature. The white solid is collected by vacuum filtration (40 mm, Büchner funnel with fritted disc, medium porosity) and washed with hexanes (2 × 60 mL, 24 °C). The white solid is then transferred to a 250-mL flask and dried in vacuo (7 mmHg, 24 °C) for 24 h to afford *N*-isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine (**2**) (Note 4) (22.5 g, 87.4 mmol, 95%) as an off-white solid.

*B. 1-(Anthracen-9-yl)allyl ethyl carbonate (**4**)*. A flame-dried 1-L, three-necked round-bottomed flask, equipped with a thermometer, a rubber septum, a 3-cm football-shaped stir bar, and an inert gas inlet connected to a manifold, is charged with anthracene-9-carboxaldehyde (Note 5) (18.0 g, 87.3 mmol, 1 equiv). Anhydrous THF (Note 6) (360 mL) is added via cannula. The resulting dark brown solution is cooled to –78 °C (dry-ice–acetone bath, internal temperature) and stirred for 15 min at –78 °C. Vinyl magnesium bromide (Note 5) (1.0 M in THF, 96.0 mmol, 96.0 mL, 1.10 equiv) is added to the reaction mixture slowly via cannula over 14 min during which the internal temperature increased to –65 °C. The reaction mixture is stirred for one hour in the dry-ice–acetone bath and another hour after removal of the cooling bath (internal temperature: 15 °C). TLC analysis (hexanes:ethyl acetate = 17:3; Rf_{SM} = 0.3, R$f_{product}$ = 0.2, visualized with ceric ammonium molybdate) indicated complete conversion of the starting material. The reaction mixture is cooled to 0 °C (ice–water bath, internal temperature), excess Grignard reagent is quenched with saturated aqueous ammonium chloride solution (500 mL, 23 °C) and the reaction mixture is diluted with CH_2Cl_2 (600 mL). The aqueous and organic layers are separated in a 3-L separatory funnel and the aqueous layer is further extracted with CH_2Cl_2 (2 × 350 mL). The combined organic layers are washed with water (700 mL) and brine (700 mL), dried over anhydrous sodium sulfate (110 g),

and concentrated with a rotary evaporator (200 mmHg, 40 °C) in a 1-L round-bottomed flask. The flask is equipped with a magnetic stir bar for continuous agitation, and the residue is further dried in vacuo (6.5 mmHg, 23 °C) for 10 h. The crude alcohol is dissolved in anhydrous CH_2Cl_2 (Note 5) (360 mL) and the flask is fitted with a rubber septum and connected to a manifold via a needle. After addition of pyridine (Note 5) (10.6 mL, 131 mmol, 1.50 equiv) and *N*,*N*-dimethylpyridine-4-amine (Note 7) (1.1 g, 8.7 mmol, 0.10 equiv), the solution is cooled to 0 °C (ice–water bath, internal temperature). After 30 min, ethyl chloroformate (Note 7) (10.4 mL, 109 mmol, 1.25 equiv) is added dropwise via a syringe over 17 min, resulting in a dark red reaction mixture and a temperature increase to 6 °C. After 30 min, the ice–water bath is removed and the reaction mixture is allowed to warm to 23 °C. After 90 min, TLC analysis (hexanes:ethyl acetate = 17:3, Rf_{SM} = 0.2, $Rf_{product}$ = 0.35 (Note 8), visualized with ceric ammonium molybdate) indicated complete consumption of the starting material. The reaction mixture is diluted with a mixture of water and saturated aqueous ammonium chloride solution (1:1, 400 mL) and the aqueous and organic layers are separated in a 2-L separatory funnel. The aqueous layer is further extracted with CH_2Cl_2 (2 × 300 mL). The combined organic layers are washed with water (550 mL) and brine (550 mL), dried over anhydrous sodium sulfate (110 g), filtered and concentrated with a rotary evaporator (200 mmHg, 40 °C). The brown residue is then dissolved in a mixture of hexanes–ethyl acetate (6:1, 100 mL) and CH_2Cl_2 (40 mL), loaded on a short pad of silica gel (Note 9) (70 g, 9 × 5 cm) and flushed with hexanes–ethyl acetate (6:1, 400 mL). The resulting yellow solution is concentrated on a rotary evaporator (200 mmHg, 40 °C), and transferred to a 250-mL flask, and equipped with a magnetic stir bar. The residue is dried in vacuo (6.5 mmHg, 23 °C, 30 min) and the flask is fitted with a reflux condenser. The orange solid is dissolved in a mixture of hexanes and ethyl acetate (1:1, 42 mL, 70 °C, oil bath, external temperature), the stir bar is removed and the sealed flask is allowed to cool to –20 °C in a freezer for 16 h to allow crystallization of the desired product. The solvent is decanted and the yellow crystals are washed with hexanes–ethyl acetate (3 × 15 mL, 0 °C) and dried in vacuo (6.5 mmHg, 23 °C, 24 h) to afford carbonate **4** (Note 10) (14.7–15.2 g, 48.0–49.7 mmol, 55–57% yield) (Note 11).

*C. 9-Allylanthracene (**5**).* A flame-dried 500-mL, two-necked round-bottomed flask, equipped with an inert gas inlet connected to a manifold, a rubber septum and a 3-cm football-shaped stir bar, is charged with IPNBSH

(**2**) (11.8 g, 45.8 mmol, 1.10 equiv). Anhydrous THF (Note 6) (160 mL) is added via cannula and the resulting solution is cooled to 0 °C (ice–water bath, external temperature). A flame-dried 1-L, three-necked round-bottomed flask, equipped with a thermometer, an inert gas inlet, a rubber septum and magnetic stir bar is charged with potassium hydride (Note 12) (5.83 g of the suspension in oil, 1.75 g, 43.7 mmol, 1.05 equiv) under an argon atmosphere. Potassium hydride is washed with anhydrous hexane (3 x 20 mL) and dried in vacuo (6.5 mmHg, 23 °C, 30 min). Anhydrous THF (Note 6) (50 mL) is added via cannula and the resulting suspension is cooled to 0 °C (ice–water bath, internal temperature). The cold solution of IPNBSH is transferred to the suspension of potassium hydride via cannula over 15 min at 0 °C under an argon atmosphere, resulting in formation of a beige precipitate. The IPNBSH source flask is rinsed with anhydrous THF (Note 6) (25 mL, 0 °C) to complete the transfer to the reaction mixture. After 15 min, the ice–water bath is removed, and the reaction mixture is allowed to warm to 16 °C over 20 min. A flame-dried 250-mL, two-necked flask, equipped with an inert gas inlet, rubber septum and magnetic stir bar, is charged with carbonate **4** (12.7 g, 41.6 mmol, 1 equiv), allylpalladiumchloride dimer (Note 13) (228 mg, 0.624 mmol, 0.015 equiv) and triphenylphosphine (Note 13) (655 mg, 2.50 mmol, 0.06 equiv). Anhydrous THF (Note 6) (100 mL) is added via cannula and the resulting dark red solution is transferred slowly via cannula over 12 min to the solution of the potassium sulfonamide prepared above. The flask is rinsed with anhydrous THF (Note 6) (25 mL) to complete the transfer. After 30 min, TLC analysis indicated the complete consumption of the carbonate and formation of the intermediate arenesulfonyl hydrazone (hexanes:ethyl acetate = 17:3, Rf_{SM} = 0.35, $Rf_{hydrazone}$ = 0.05, visualized with ceric ammonium molybdate). *N*-Acetyl cysteine (Note 13) (543 mg, 3.33 mmol, 0.08 equiv) is added as a solid and glacial acetic acid (Note 14) (5.2 mL, 91.5 mmol, 2.2 equiv) is added via syringe. After 10 min, a mixture of 2,2,2-trifluoroethanol (Note 15) and deionized water (1:1, 180 mL, deoxygenated by purging with argon for 10 min) is added via cannula. The flask is fitted with a reflux condenser and heated to 70 °C (oil bath, external temperature). After 5.5 h, TLC analysis indicated consumption of the hydrazone–adduct (hexanes:ethyl acetate = 17:3, $Rf_{hydrazone}$ = 0.05, $Rf_{product}$ = 0.6, visualized with ceric ammonium molybdate). The reaction mixture is cooled to 23 °C, diluted with hexanes (250 mL) and excess acid is quenched with a mixture of saturated aqueous bicarbonate solution and water (1:1, 500 mL). The

aqueous and organic layers are separated in a 3-L separatory funnel and the aqueous layer is further extracted with hexanes (2 × 350 mL). The combined organic layers are washed with water (450 mL) and brine (450 mL), dried over anhydrous sodium sulfate (110 g) and filtered. Volatiles are removed with a rotary evaporator (200 mmHg, 40 °C) and the residue dried in vacuo (6.5 mmHg, 10 h). The remaining orange residue is purified by flash column chromatography (Note 16). All product fractions are combined, concentrated with a rotary evaporator (200 mmHg, 40 °C) and dried in vacuo (6.5 mmHg, 23 °C, 5 h) to afford the reduction product **5** as a pale green solid (Note 17) (6.21 g, 28.4 mmol, 68% yield).

2. Notes

1. For the preparation of *o*-nitrobenzenesulfonyl hydrazide, see: *Organic Syntheses*, **1999**, *76*, 178; *Coll. Vol. 10,* **2004**, 165.

2. Acetone (Chromasolv for HPLC, ≥ 99%) and hexanes (mixture of isomers, Chromasolv for HPLC, ≥98.5%) were purchased from Aldrich and used as received.

3. TLC was performed on EMD Chemicals Inc. Silica Gel 60 F_{254} plates.

4. In different runs of this step, the yield varied from 95 to 96%. Analytical data for IPNBSH (**2**) are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.90 (s, 3 H), 1.93 (s, 3 H), 7.73–7.79 (m, 2 H), 7.81–7.87 (m, 2 H), 8.22–8.28 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.9, 25.2, 125.1, 131.7, 132.7, 133.1, 134.1, 148.2, 158.7; IR (neat): 3265, 1553, 1374, 1347, 1177 cm^{-1}; HRMS calc'd for $C_9H_{12}N_3O_4S$ [M+H]: 258.05485, found: 258.05382; mp 133–134 °C (with decomposition); Anal. calcd. for $C_9H_{11}N_3O_4S$: C, 42.02; H, 4.31; N, 16.33, found: C, 42.06; H, 4.56; N, 16.32. IPNBSH (**2**) can be stored under an argon atmosphere at 23 °C for several months.

5. Anthracene-9-carbaldehyde (97%) and vinyl magnesium bromide in THF (1.0 M) were purchased from Aldrich Chemical Company, Inc. and used as received.

6. Anhydrous tetrahydrofuran was distilled from Na/benzophenone, anhydrous dichloromethane was obtained from a Solvent Purification System Mbraun MB-SPS, and anhydrous pyridine was purchased from Aldrich Chemical Company, Inc. and used as received. The submitters purchased tetrahydrofuran, dichloromethane, and pyridine from J.T. Baker

(Cycletainer™) and dried the solvents by the method reported by Grubbs[2] et al. under positive argon pressure.

7. *N*,*N*-Dimethylpyridine-4-amine (99 %) and ethyl chloroformate (97%) were purchased from Aldrich Chemical Company, Inc. and used as received.

8. It is recommended to dilute the sample for TLC analysis due to decomposition of the carbonate on silica gel at high concentrations; one major decomposition product can be seen with an R*f* = 0.2.

9. SiliCycle Silia*Flash*® P60 silica gel, 60-63 μm, 60 Å; the submitters used Zeochem® Silicagel Zeoprep 60HYD, 40–63 μm was used for flash column chromatography.

10. Analytical data for carbonate **4** are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, *J* = 7.0 Hz, 3 H), 4.10 (dq, *J* = 10.5, 7.0 Hz, 1 H), 4.21 (dq, *J* = 10.5, 7.0 Hz, 1 H), 5.26–5.34 (m, 2 H), 6.51 (ddd, *J* = 17.2, 10.6, 4.3 Hz, 1 H), 7.46–7.52 (m, 2 H), 7.57 (ddd, *J* = 9.0, 6.7, 1.6 Hz, 2 H), 7.74 (dt, *J* = 4.7, 2.0 Hz, 1 H), 8.01–8.05 (m, 2 H), 8.49 (s, 1 H), 8.57 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 64.2, 75.6, 117.6, 124.9, 124.9, 126.2, 128.8, 129.2, 129.3, 129.9, 131.6, 136.1, 154.9; IR (neat): 3053, 2985, 1742, 1448, 1369, 1256, 1007, 877, 789, 731 cm^{-1}; HRMS calcd. for $C_{20}H_{18}O_3$ $[M]^+$: 306.1256, found 306.1259; mp 92–93 °C; Anal. calcd. for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92, found: C, 78.03; H, 5.99.

11. The submitters reported a higher yield (17.9 g, 58.4 mmol, 67%), but the checkers were not able to reproduce this result. However, the checkers noted that after decantation of the solvent and washing of the crystals, the residual solution contained a significant amount of carbonate **4** (determined by ^{1}H NMR) which could not be crystallized, but accounts for the missing product.

12. Potassium hydride (30% by weight in mineral oil) was purchased from Aldrich Chemical Company, Inc and was used as received. In order to use the correct amount of KH for the reaction, the flask was weighed before addition of the KH suspension in oil and after the washing procedure and drying in high vacuum. If necessary, the amount of the starting material and reagents was adjusted to the amount of KH used. The submitters report that KH was washed with anhydrous hexanes prior to use and stored in a glovebox. *Note that potassium hydride is a pyrophoric solid and must be handled with care.*

13. Allylpalladiumchloride dimer (98%), triphenylphosphine (99%, Reagent Plus) and *N*-acetyl-L-cysteine (Sigma grade) were purchased from Aldrich Chemical Company, Inc. and used as received.

14. Glacial acetic acid (99.7 %) was purchased from Mallinckrodt Chemicals and used as received.

15. 2,2,2-Trifluoroethanol was purchased from Aldrich Chemical Company, Inc. and used as received.

16. Flash column chromatography (7 cm diameter, 20 cm height) was performed using silica gel (350 g). The residue was dissolved in DCM (100 mL) and silica gel (10 g) was added. The solvent was removed with a rotary evaporator (200 mmHg, 40 °C) and the silica gel with the product was loaded on the column. It was first eluted with hexanes (3 L), continued with hexanes–acetone (99:1, 2 L; then 98:2, 1 L). The first 1 L was discarded, collection of 50-mL fractions was begun. Fractions #39–100 contained the desired product. Mixed fractions #24–38 were collected separately, concentrated, and purified again by flash column chromatography (200 g SiO_2, 5 × 18 cm); loaded with hexanes (5 mL). While eluting with hexanes (1500 mL), collection of 20-mL fractions was begun, fractions #61-95 contained the desired product. TLC analysis during flash column chromatography was performed using 100% hexanes as the eluent ($Rf_{byproduct}$ = 0.4 (only visible under UV light), $Rf_{product}$ = 0.3, visualized with ceric ammonium molybdate).

17. In different runs of this step, the yield varied from 63 to 68%. Analytical data for 9-allylanthracene (**5**) are as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.41 (dt, *J* = 5.5, 2.0 Hz, 2 H), 5.03 (dq, *J* = 17.2, 2.0 Hz, 1 H), 5.12 (dq, *J* = 10.2, 1.6 Hz, 1 H), 6.25 (ddt, *J* = 17.2, 10.2, 5.5 Hz, 1 H), 7.47–7.58 (m, 4 H), 8.02–8.07 (m, 2 H), 8.26–8.31 (m, 2 H), 8.41 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.9, 115.9, 124.5, 124.8, 125.6, 126.2, 129.1, 130.0, 131.5, 131.6, 136.4; IR (neat): 3081, 3052, 3004, 1638, 1623, 1446, 1157, 912, 883, 789, 730 cm^{-1}; HRMS calcd for $C_{17}H_{15}$ [M+H]: 219.11738, found: 219.11749; mp 43–44 °C; Anal. calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46, found: C, 93.29; H 6.75.

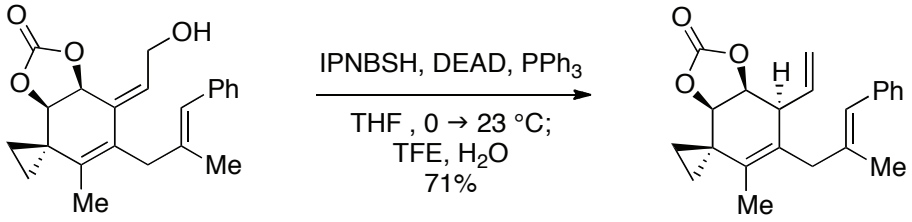
Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with “Prudent Practices in the Laboratory”; National Academies Press; Washington, DC, 2011.

3. Discussion

Monoalkyl diazenes have been used as key intermediates in a wide range of organic transformations.[3] Many of these methods involve condensation of carbonyl compounds with arenesulfonyl hydrazides as a prelude to monoalkyl diazene formation. Myers discovered an efficient, mild, and stereospecific method for the reduction of allylic, benzylic and saturated alcohols using the reagent 2-nitrobenzenesulfonyl hydrazide (NBSH).[4] Inspired by these reports we developed the complementary reagent *N*-isopropylidene-*N*′-2-nitrobenzene-sulfonyl hydrazine (IPNBSH)[5] that offers thermal stability both in the solid state and in solution. We initially used IPNBSH in a key reductive transposition for the total synthesis of (–)-acylfulvene and (–)-irofulvene (Scheme 1).[6]

Scheme 1



We recognized the utility of IPNBSH for generation of monoalkyl diazenes under basic reaction conditions.[5a] These observations prompted our development of IPNBSH as a diimide surrogate in palladium catalyzed allylic substitution reaction.[5b] Scheme 2 illustrates the proposed mechanism for the reduction of allylic carbonates as described in this procedure. The formation of a π-allyl complex[7] is followed by reaction with the potassium salt of IPNBSH to give the corresponding hydrazone-adduct. In situ hydrolysis and elimination of the arenesulfinic acid leads to the regioselective formation of the transient allylic monoalkyl diazene, that upon sigmatropic loss of dinitrogen affords the desired reduction product.

The reduction of allylic carbonates via the corresponding allylic monoalkyl diazene as described here is applicable to a broad range of substrates (Table 1). Both primary and secondary allylic carbonates undergo the reductive transformation to afford the desired products in good yields and high selectivity (*E*/*Z*, >96:4).[5]

Scheme 2

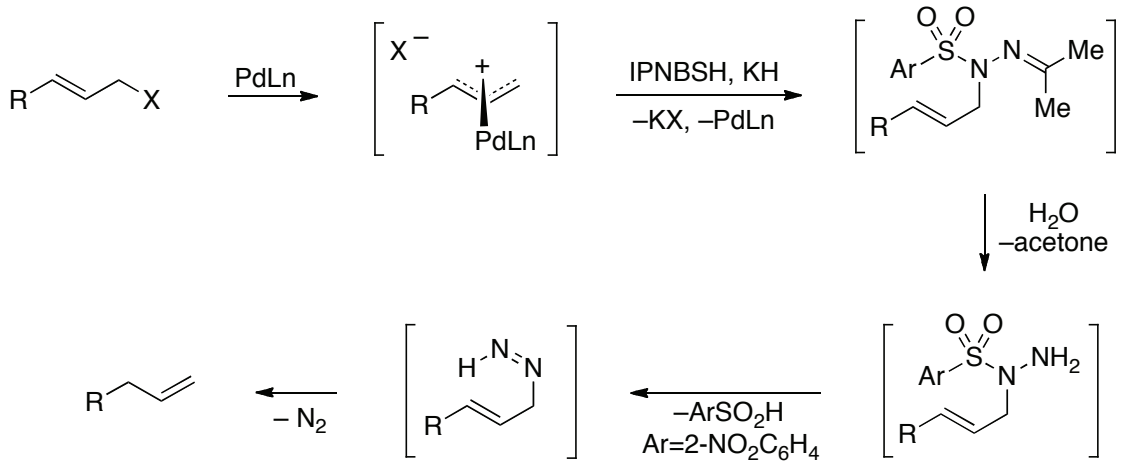
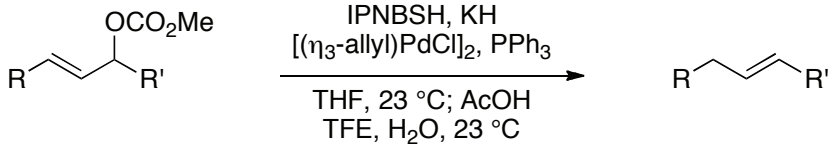
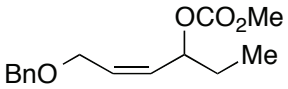
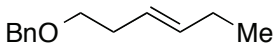
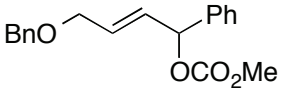
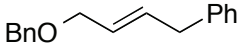
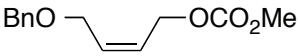
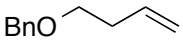
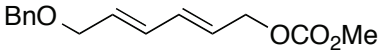
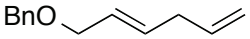
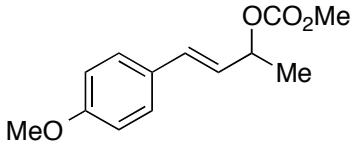
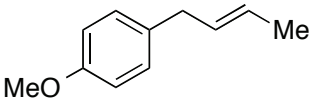


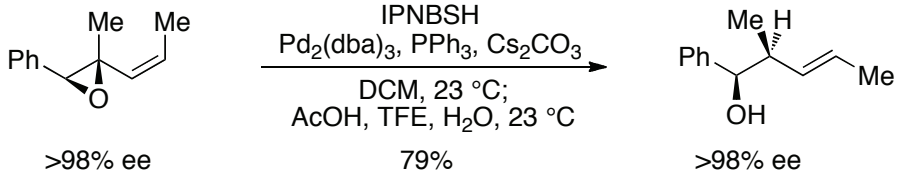
Table 1 Selected examples of IPNBSH-mediated reduction of allylic carbonates



Entry	Substrate	Product	Yield
1			76
2			82
3			91
4			68
5			59

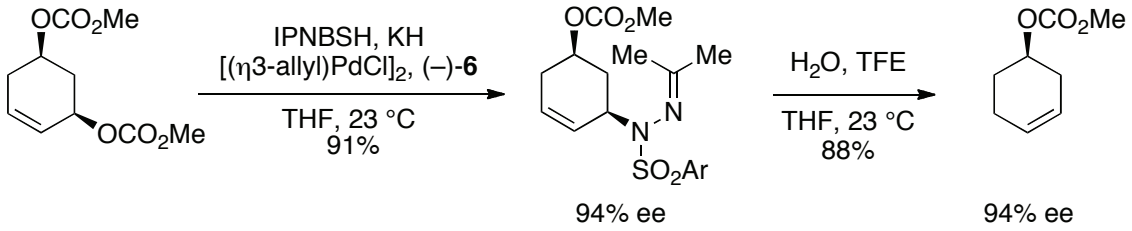
IPNBSH is further used for the reduction of vinyl epoxides to afford the corresponding homoallylic alcohols.[5b] Use of enantioenriched substrates did not lead to loss of enantiomeric excess during the reduction (Scheme 3).

Scheme 3



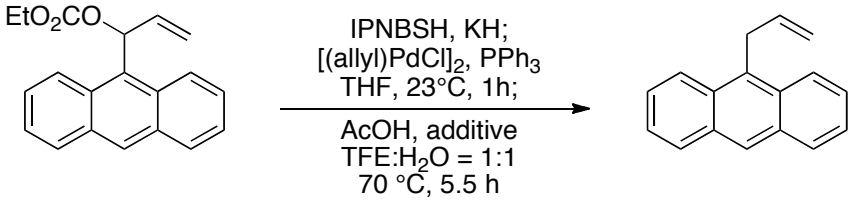
Modification of this palladium-catalyzed diazene synthesis led to the development of an asymmetric version by using a chiral catalyst system. Racemic carbonates were converted into enantiomerically enriched sulfonyl hydrazones using Trost's[8] ligand (*1S*,*2S*)-(–)-1,2-diaminocyclohexane-*N,N'*-bis(2'-diphenylphospinobenzoyl) ((–)-**6**) and $[(\eta^3\text{-allyl})PdCl]_2$. Mild hydrolysis of these hydrazones provided enantiomerically enriched reductively transposed products (Scheme 4).

Scheme 4



During the development of the procedure described here, we observed lower yields for the one-pot hydrazone formation and hydrolysis using 1-(anthracen-9-yl)allyl ethyl carbonate (**4**) as a substrate on large scale. After much experimentation, we recognized that this is due to interference of an active palladium species with the hydrazone adduct, resulting in formation of undesired by-products during the one-pot hydrolysis. We therefore developed a modification to the procedure to deactivate the palladium species after the formation of the hydrazone adduct. The best result was obtained using *N*-acetyl-L-cysteine as the palladium scavenger as described in the procedure above (Table 2). This additive prevents further activity of the palladium catalyst during the hydrazone hydrolysis step.

Table 2 Optimization studies for the synthesis of 9-allylanthracene



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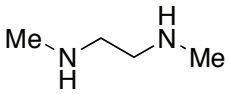
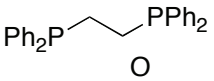
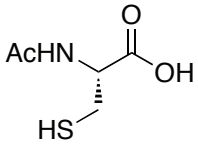
2		65%
3		68%
4		77%

1. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. We are grateful for generous financial support by NIH-NIGMS (GM074825). M.M. is a Camille Dreyfus Teacher-Scholar.

2. Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.

3. For representative examples, see: (a) Szmant, H. H.; Harnsberger, H. F.; Butler, T. J.; Barie, W. P. *J. Am. Chem. Soc.* **1952**, *74*, 2724. (b) Nickon, A.; Hill, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 1152. (c) Corey, E. J.; Cane, D. E.; Libit, L. *J. Am. Chem. Soc.* **1971**, *93*, 7016. (d) Hutchins, R. O.; Kacher, M.; Rua, L. *J. Org. Chem.* **1975**, *40*, 923. (e) Kabalka, G. W.; Chandler, J. H. *Synth. Commun.* **1979**, *9*, 275. (f) Corey, E. J.; Wess, G.; Xiang, Y. B.; Singh, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 4717. (g) Myers, A. G.; Kukkola, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 8208. (h) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9641. (i) Guziec, F. S., Jr.; Wei, D. *J. Org. Chem.* **1992**, *57*, 3772. (j) Wood, J. L.; Porco, J. A., Jr.; Taunton, J.; Lee, A. Y.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 5898. (k) Bregant, T. M.; Groppe, J.; Little, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 3635. (l) Ott, G. R.; Heathcock, C. H. *Org. Lett.* **1999**, *1*, 1475. (m) Chai, Y.; Vicic, D. A.; McIntosh, M. C. *Org. Lett.* **2003**, *5*, 1039. (n) Sammis, G. M.;

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5. (a) Movassaghi, M.; Ahmad, O. K. *J. Org. Chem.* **2007**, *72*, 1838. (b) Movassaghi, M.; Ahmad, O. K. *Angew. Chem., Int. Ed.* **2008**, *47*, 8909.
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Appendix
Chemical Abstracts Nomenclature; (Registry Number)

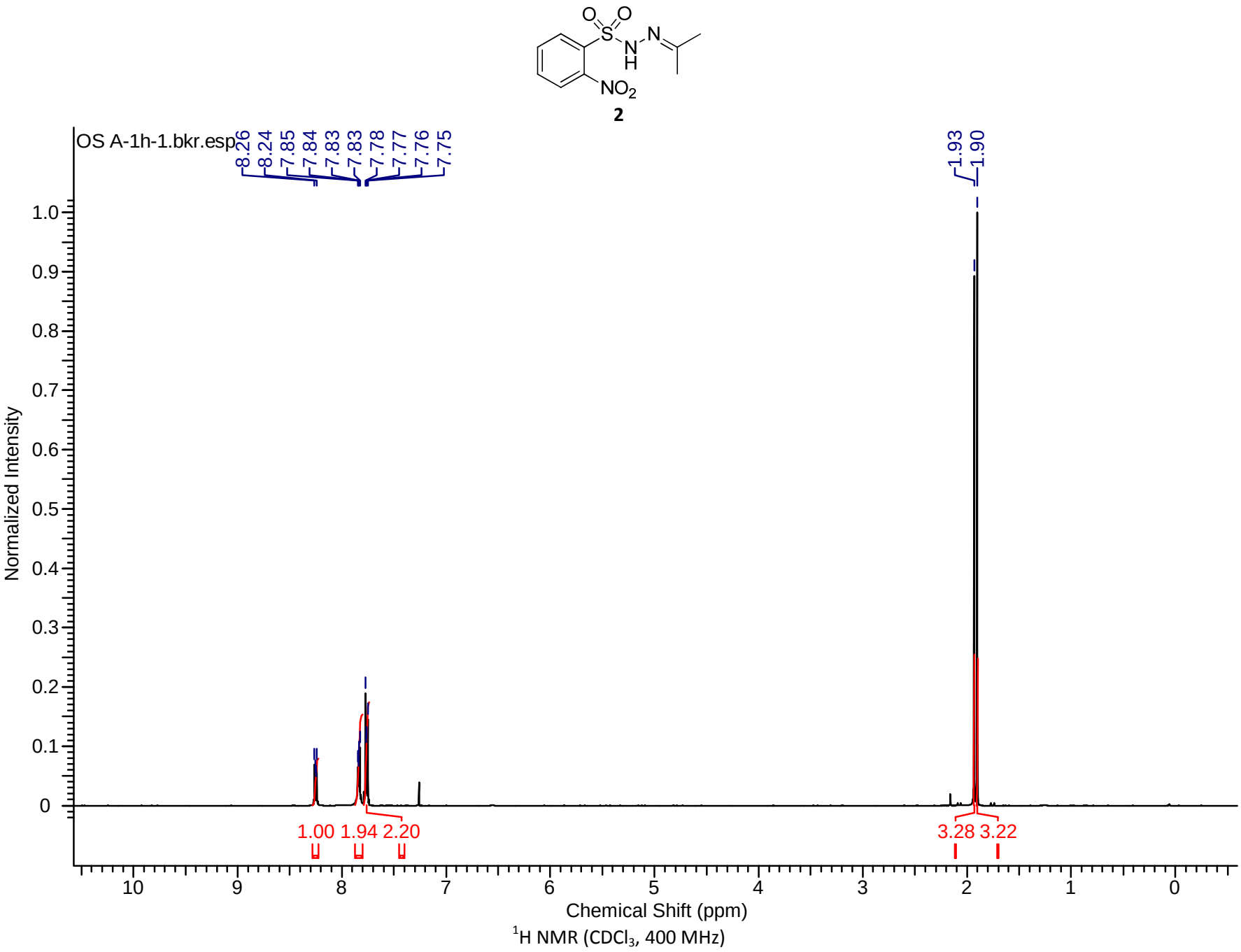
o-Nitrobenzenesulfonyl hydrazide; (5906-99-0)
N-Isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine; (6655-27-2)
Anthracene-9-carboxaldehyde; (642-31-9)
Vinylmagnesium bromide; (1826-67-1)
N,*N*-Dimethylpyridine-4-amine; (1122-58-3)
Ethyl chloroformate; (541-41-3)
9-Allylanthracene: 9-(2-propeny-1-yl)anthracene; (23707-65-5)
Potassium hydride; (7693-26-7)
Allylpalladiumchloride dimer; (12012-95-2)
Triphenylphosphine; (603-35-0)
N-Acetyl cysteine; (616-91-1)

Mohammad Movassaghi carried out his undergraduate research with Professor Paul A. Bartlett at UC Berkeley, where he received his BS degree in chemistry in 1995. Mo then joined Professor Andrew G. Myers' group for his graduate studies and was a Roche Predoctoral Fellow at Harvard University. In 2001, Mo joined Professor Eric N. Jacobsen's group at Harvard University as a Damon Runyon–Walter Winchell Cancer Research Foundation postdoctoral fellow. In 2003, he joined the chemistry faculty at MIT where his research program has focused on the total synthesis of alkaloids in concert with the discovery and development of new reactions for organic synthesis.

Jens Willwacher was born in 1986 and grew up in Leverkusen, Germany. After receiving his high-school degree in 2005 and completing military service in 2006, he started studying chemistry at the Westfaelische Wilhems-Universitaet Muenster, Germany. During his undergraduate program, he joined the laboratories of Professor Mohammad Movassaghi at Massachusetts Institute of Technology during the summer 2010 as a visiting student. He conducted his diploma thesis with Professor Frank Glorius with the focus on rhodium-catalyzed C-H activation olefinations and recently joined Professor Alois Fürstner's group for his Ph.D. program.

Omar K. Ahmad pursued his undergraduate studies at Brown University, where he received his Sc.B. degree in chemistry in 2005. As an undergraduate he worked in the laboratories of Professor Dwight Sweigart and Professor Amit Basu. In 2005, Omar joined Professor Mohammad Movassaghi's research group at MIT for his graduate studies where his research has focused on the development of new methodologies for organic synthesis.

Juliane Keilitz was born in 1981 in Berlin, Germany. She studied chemistry at the Freie Universität Berlin, where she received her Ph.D. in 2010 under the supervision of Prof. Rainer Haag. After working on the development and application of polymer-supported catalysts, she is now pursuing post-doctoral research in the group of Prof. Mark Lautens at the University of Toronto. Her research focuses on the desymmetrization of cyclohexadienones.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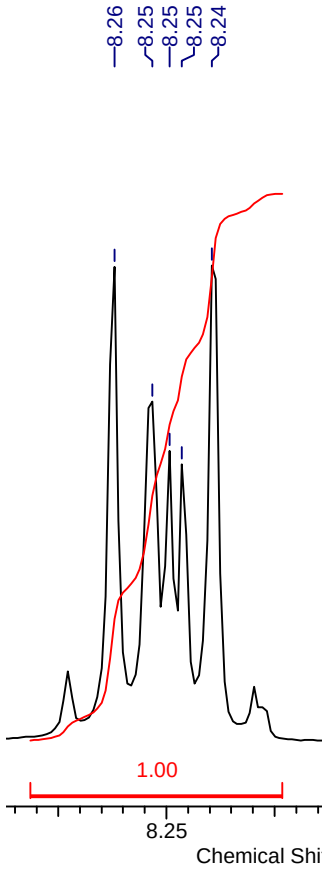
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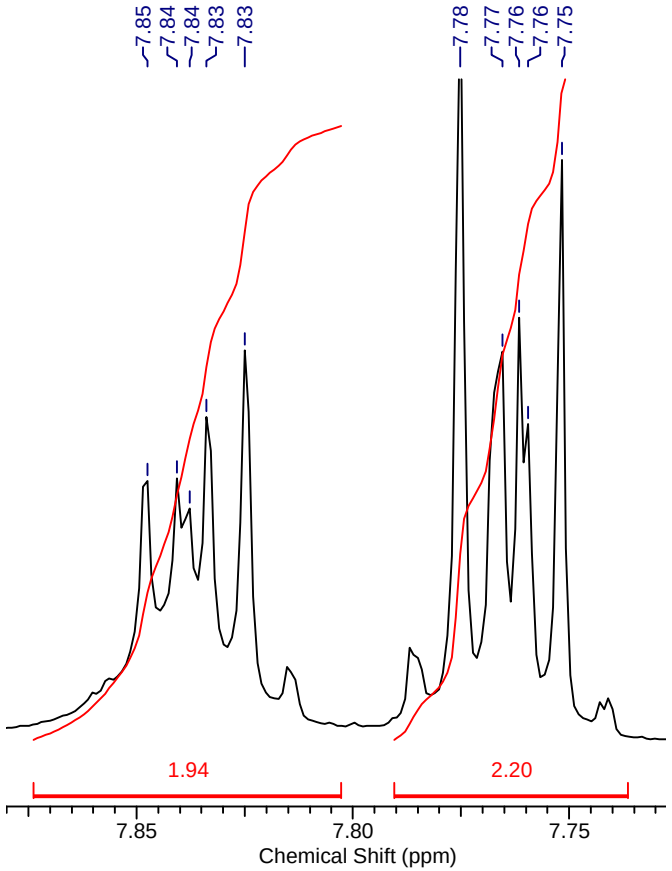
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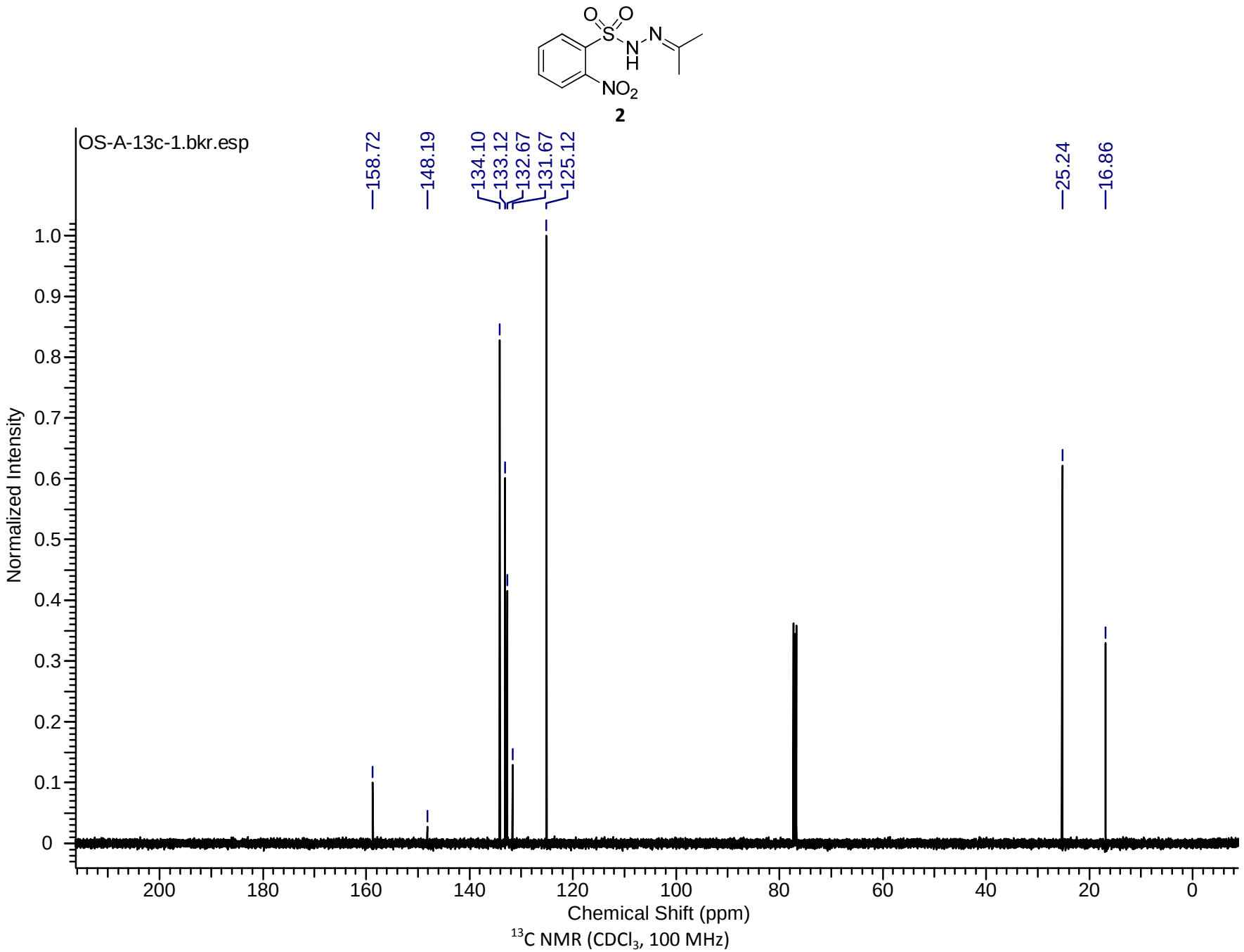
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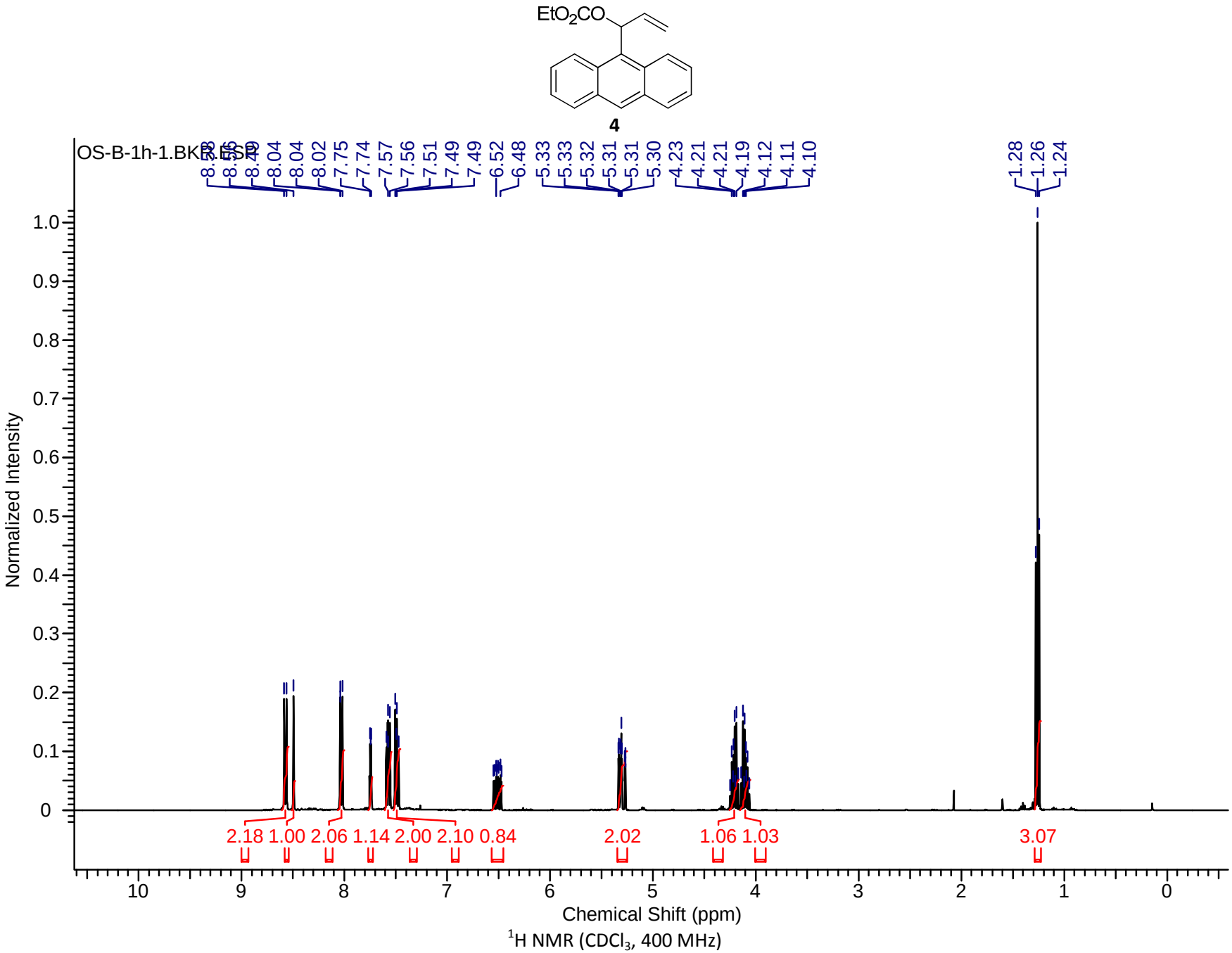
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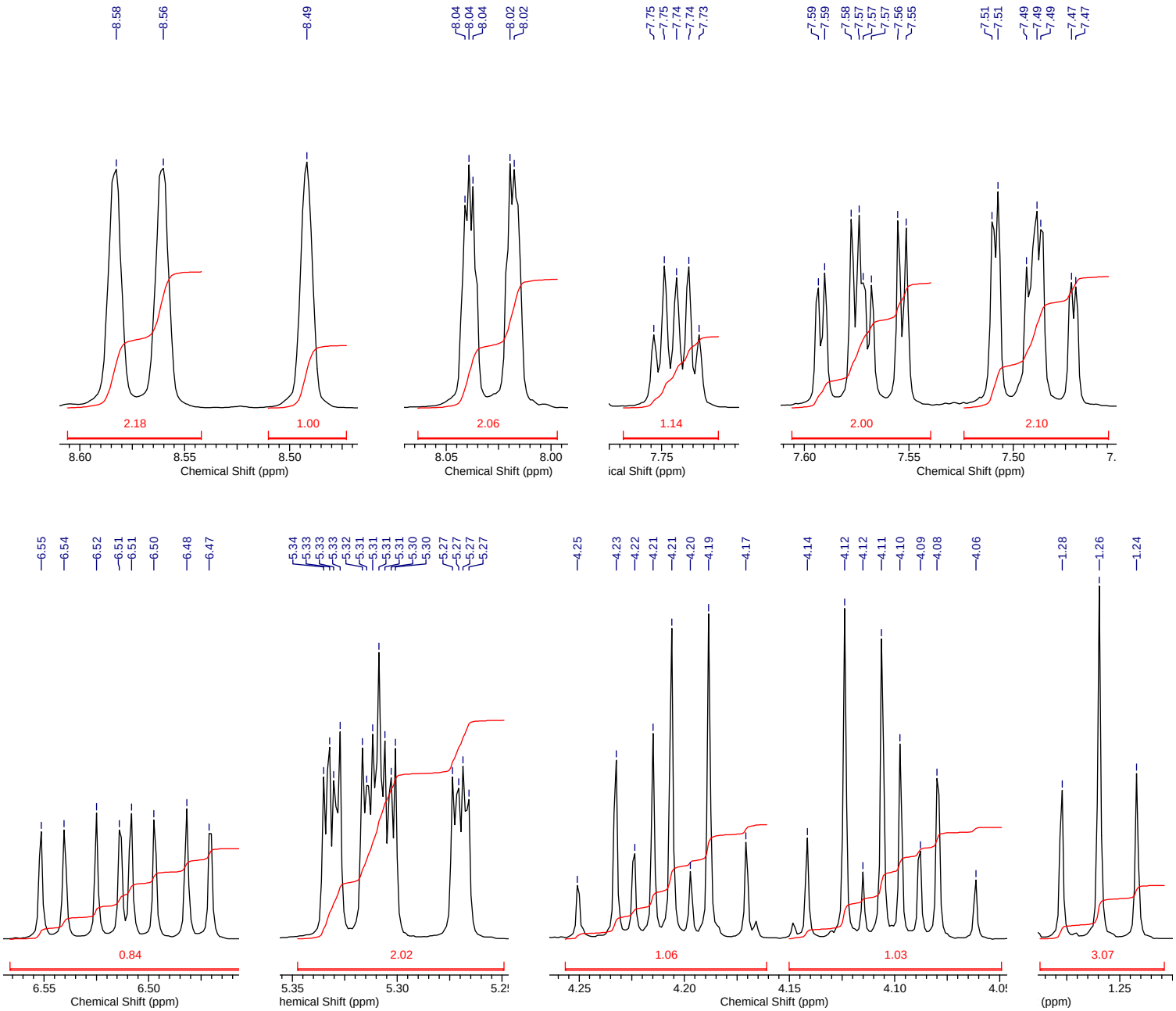
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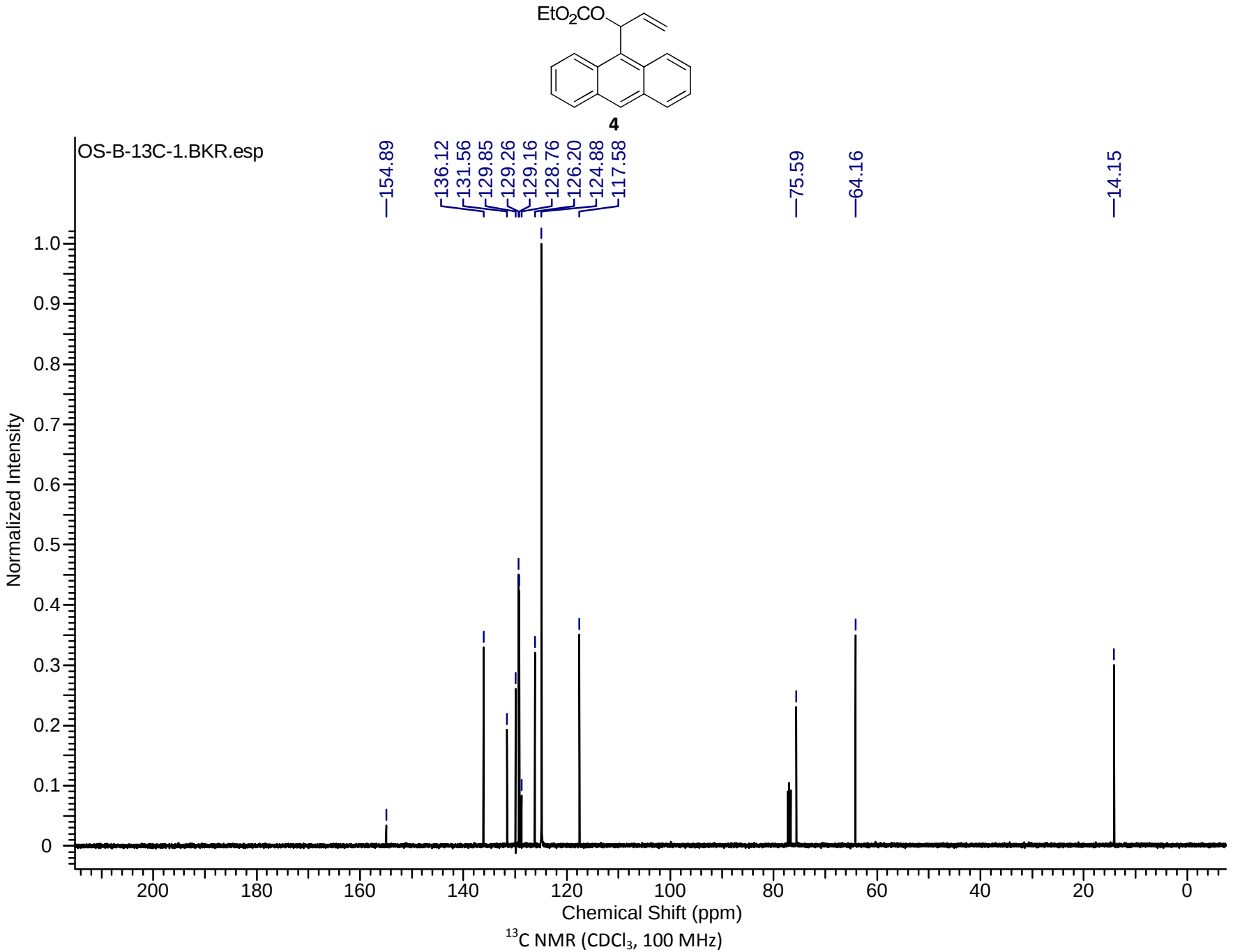
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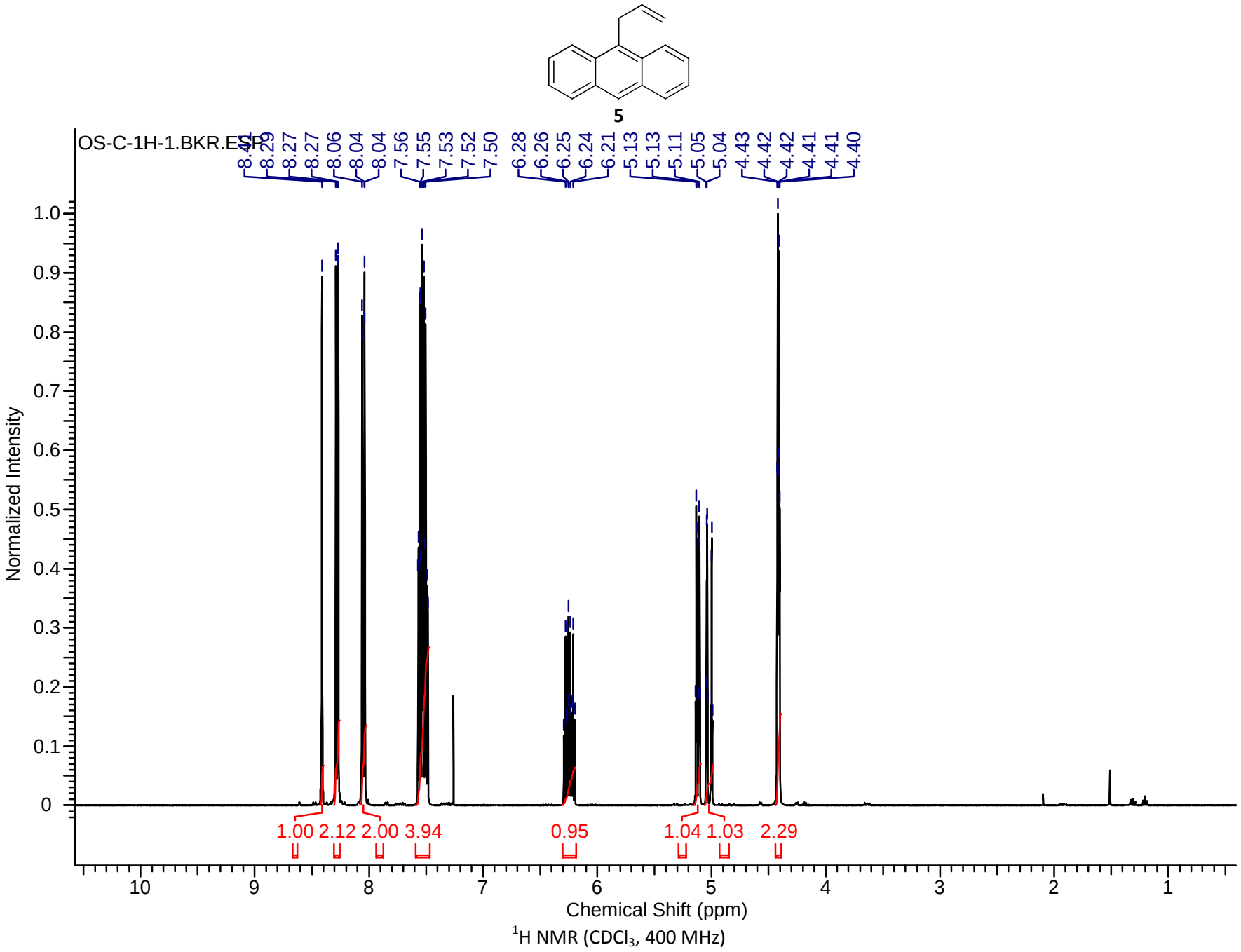
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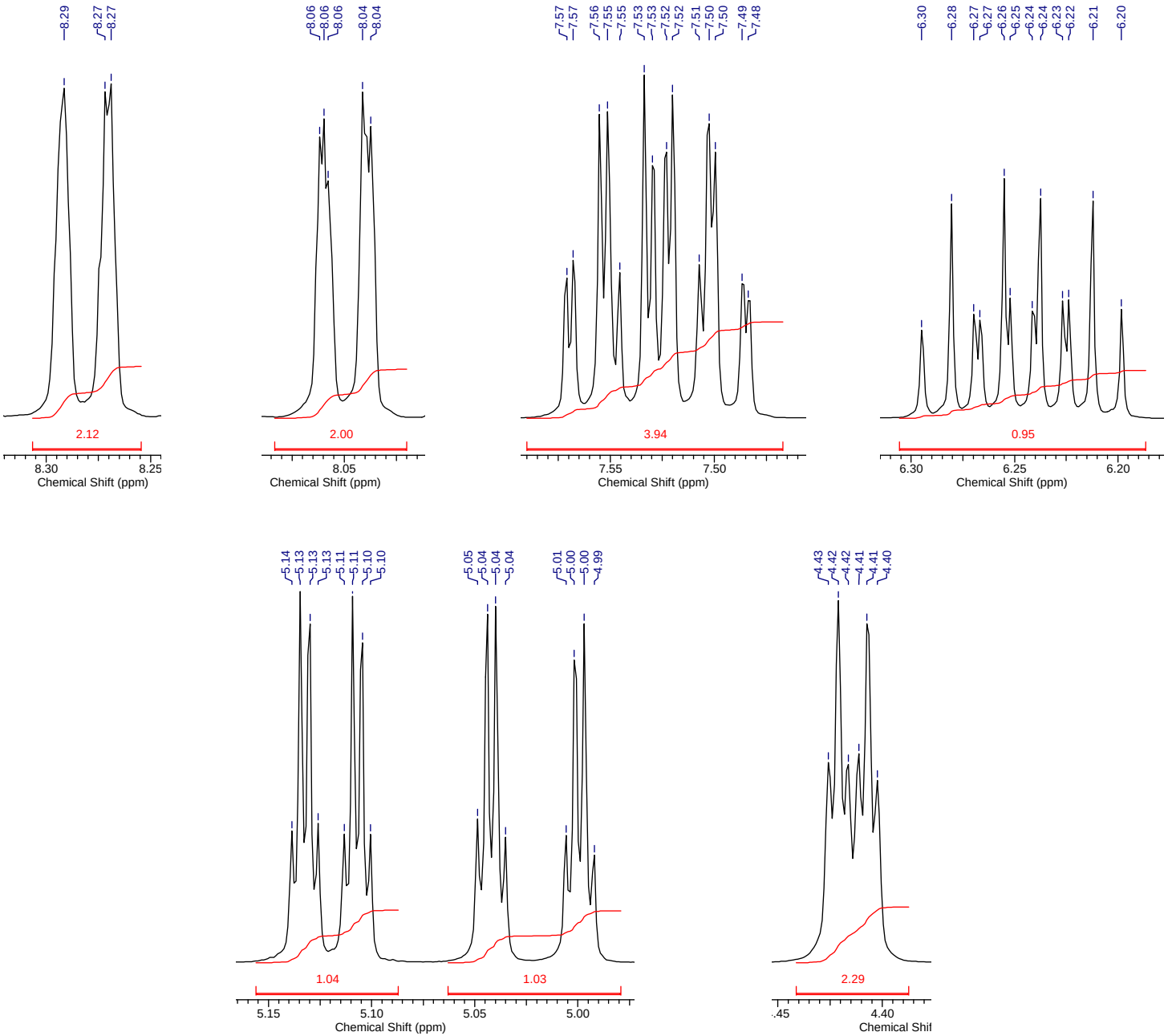
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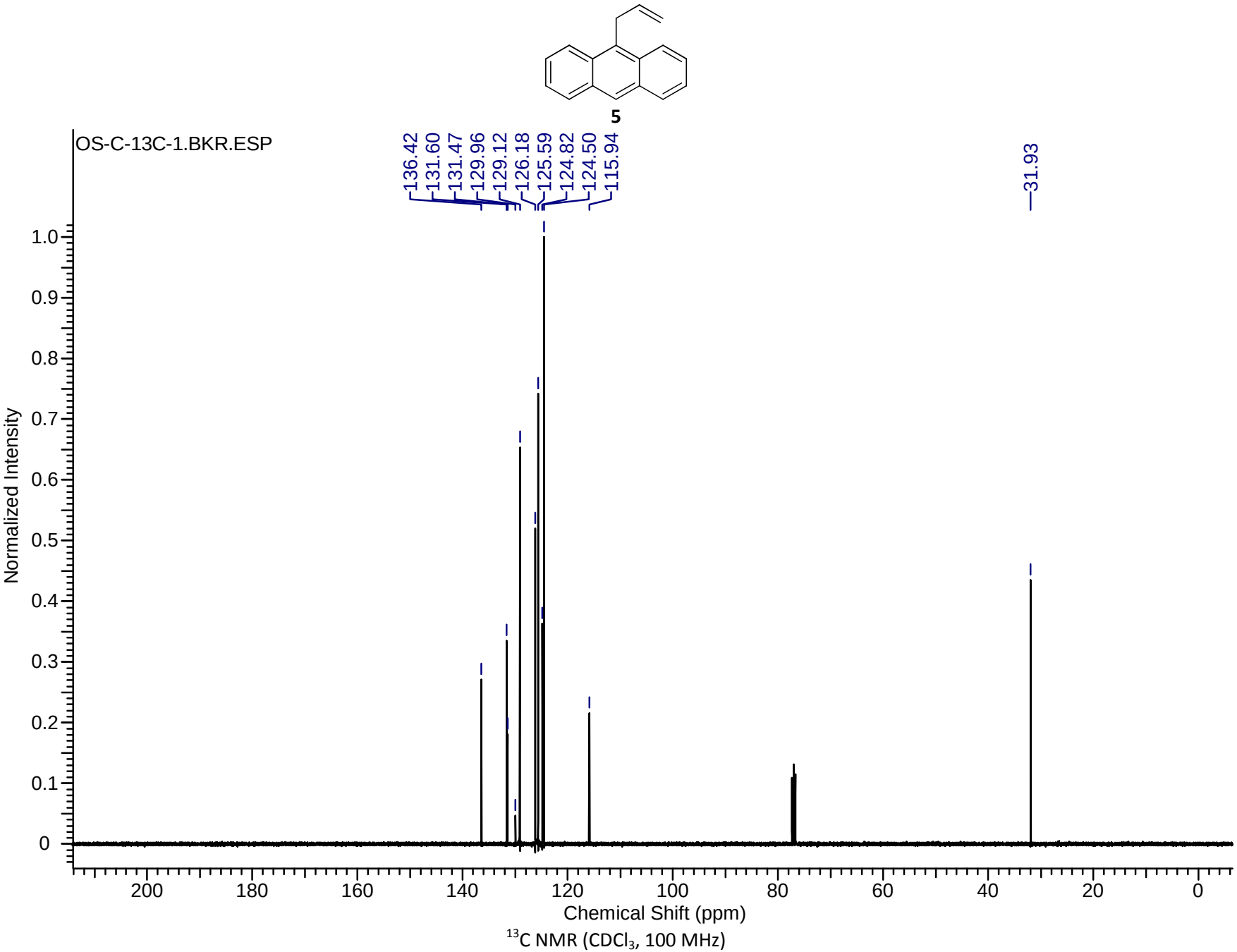
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