Synthesis of γ-Substituted Carbonyl Compounds from DMSO-Mediated Oxidation of Enynamides: Mechanistic Insights and Carbon- and Hetero-Functionalizations

Quynh Huong Nguyen, Nguyen Hoang Nguyen, Hanbyul Kim, and Seunghoon Shin*

Department of Chemistry, Research Institute for Natural Sciences and Center for New Directions in Organic Synthesis (CNOS), Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 04763 (Korea)
sshin@hanyang.ac.kr

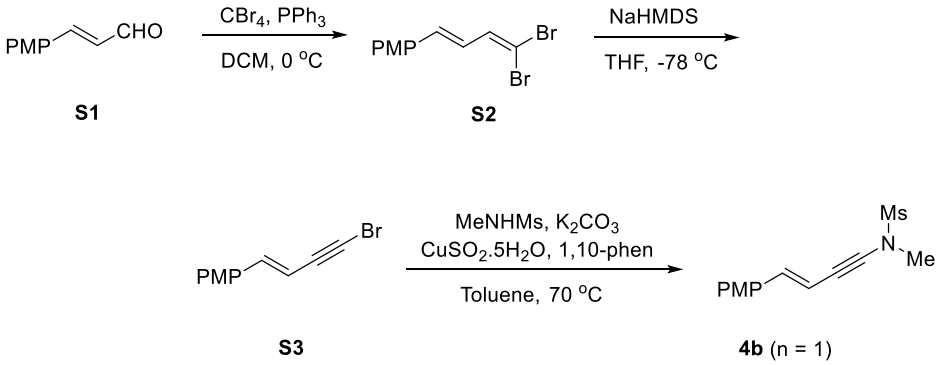
Table of Contents

1. General Information

All solvents and DMSO were dried and distilled according to standard methods before use.[1] Enynamides[2] were prepared according to the literature procedures. All other chemicals were purchased from commercial sources and was used as received; $HNTf_2$ was purchased from Aldrich and was kept in the Ar-atmosphere glove box for storage. TLC (thin-layer chromatography) analysis was carried out on Merck silica gel 60 F254 TLC plates and was visualized with UV lamp and $KMnO_4$ solution. Flash chromatography was performed on Kieselgel 60 (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer with TMS as an internal standard. GC calibration curve were obtained by an Agilent Technologies 7890B GC system with dodecane as an internal standard. High resolution mass spectra (HRMS) were obtained from Korea Basic Science Institute (KBSI, Daegu).

2. General Procedure

2.1. Synthesis of enynamides and dienynamides substrates



Synthesis of **S2**: To a solution of triphenylphosphine (6.47g, 24.7 mmol) in CH_2Cl_2 (50 mL) was added carbon tetrabromide (4.09 g, 12.3 mmol) at 0°C. The reaction mixture was stirred for 10 min before addition of the aldehyde **S1** (1.0 g, 6.17 mmol). The resulting mixture was stirred at 0 °C for 1 hour. The triphenylphosphine oxide was removed by filtration through a celite pad, rinsed with diethyl ether (x3) and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (EtOAc:Hex = 1:10) to afford **S2** (1.84g, 94%) as a white solid.

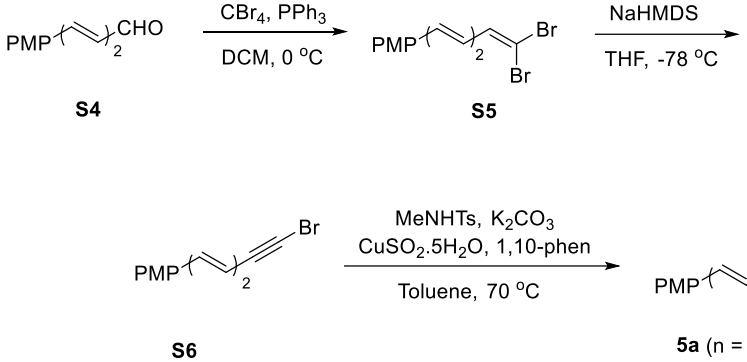
Synthesis of **S3**: To a stirred solution of **S2** (1.84g, 5.79 mmol) in THF (30 mL) was add NaHMDS (6.94 mL, 6.94 mmol, 1.0 M in THF) slowly at -78°C under Ar atmosphere. The resulting solution was stirred at -78°C for 1 h, before quenching with saturated aq. solution of NH_4Cl. The aqueous layer was separated and extracted with ether (x3). The combined organic layers were dried by $MgSO_4$, filtered and the residue was purified by

[1] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; Elsevier: Oxford, **2009**.

[2] (a) Silvi, M.; Verrier, C. Rey, Y.P.; Buzzetti, L.; Melchiorre, P. *Nature Chem.* **2017**, *9*, 868. (b) Mou, C.; Zhu, T.; Zhang, P.; Yang, S.; Song, B.-A.; Chi, Y.R. *Adv. Synth. Catal.* **2016**, *358*, 707.

chromatography to afford the desired bromoalkyne **S3** (1.25 g, 91%) as a yellow solid.

Synthesis of **4b**: To a solution of **S3** (1.25 g, 5.27 mmol) in toluene (10 mL) was added *N*-methylmethanesulfonamide (690.2 mg, 6.32 mmol), potassium carbonate (1.46g, 10.54 mmol), copper(II) sulfate (132.3 mg, 0.53 mmol) and 1,10-phenanthroline (189.9 mg, 1.05 mmol). The reaction mixture was heated to 70 °C for 14 h. The solution was cooled to room temperature, filtered through Celite, and concentrated in vacuo. The residue was purified by flash chromatography (EtOAc:Hex = 1:3) to afford **4b** (1.26 g, 90%) as a white solid.



Synthesis of **S5**: To a solution of triphenylphosphine (3.45 g, 13.16 mmol) in CH_2Cl_2 (30 mL) was added carbon tetrabromide (2.18 g, 6.58 mmol) at 0°C. The reaction mixture was stirred for 10 min before addition of the aldehyde **S4** (620.0 mg, 3.29 mmol).[2a] The resulting mixture was stirred at 0 °C for 1 hour. The triphenylphosphine oxide was removed by filtration through a celite pad, rinsed with diethyl ether (x3) and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (EtOAc:Hex = 1:10) to afford **S5** (1.02 g, 90%) as a white solid.

Synthesis of **S6**: To a stirred solution of **S5** (1.02 g, 2.96 mmol) in THF (15 mL) was add NaHMDS (3.55 mL, 3.55 mmol, 1.0 M in THF) slowly at -78°C under Ar atmosphere. The resulting solution was stirred at -78°C for 1 h, before quenching with saturated aq. solution of NH_4Cl. The aqueous layer was separated and extracted with ether (x3). The combined organic layers were dried by $MgSO_4$, filtered and the residue was purified by chromatography to afford the desired bromoalkyne **S6** (685.0 mg, 88%) as a brown solid.

Synthesis of **5a**: To a solution of **S6** (685.0 mg, 2.60 mmol) in toluene (5.2 mL) was added *N*-methyltoluenesulfonamide (577.9 mg, 3.12 mmol), potassium carbonate (718.6 mg, 5.2 mmol), copper(II) sulfate (64.9 mg, 0.26 mmol) and 1,10-phenanthroline (93.7 mg, 0.52 mmol). The reaction mixture was heated to 70 °C for 12 h. The solution was cooled to room temperature, filtered through Celite, and concentrated in vacuo. The residue was purified by flash chromatography (EtOAc:Hex = 1:3) to afford **5a** (773.6 mg, 81%) as a pale yellow solid.

2.2. Representative Procedure

General Procedure A (a representative example for the formation of 8ba, Table 2): Enynamide **4b** (53.1 mg, 0.20 mmol), DMSO (18.9 mg, 0.24 mmol) and *N*-Me-indole (31.5 mg, 0.24 mmol) were mixed in CH_2Cl_2 (1.0 mL) in a 4 mL screw-capped vial. A stock of $HNTf_2$ (100 µL of 14.0 mg/mL in CH_2Cl_2; 2.5 mol%) which

was prepared inside a glovebox was then added and the resulting mixture was allowed to stir at RT for 3 h. At this point, the crude ^{1}H NMR spectra of an aliquot showed the ratio of isomeric products to be α:γ =1:10. Solvent was removed under vacuum and the residue was purified by flash column chromatography (EtOAc:*n*Hex = 1:8~1:2) to yield **8ba** (76.1 mg, 97%) as a white foamy solid.

A gram-scale reaction was also conducted for the synthesis of **8ba**: In an oven-dried 50 mL rb flask was added **4b** (1.00 g, 3.77 mmol), DMSO (321.2 µL, 4.52 mmol, 1.2 equiv.) and *N*-methylindole (564.7 µL, 4.52 mmol, 1.2 equiv.). The reaction mixture was dissolved in CH_2Cl_2 (15 mL) and $HNTf_2$ (26.5 mg, 0.094 mmol, 2.5 mol%) was added. The resulting mixture was stirred at room temperature. After 3 hours, the TLC indicated that the reaction was complete. The mixture was concentrated and the residue was purified by flask chromatography (EtOAc:*n*Hex = 1:8 ~ 1:2) to afford 1.45 g (93%) of **8ba**. The crude ^{1}H NMR for the larger scale reactions had the same α/γ ratio (1:10).

General Procedure B (representative reactions of silyl enol ethers for the formation of 11bb, Table 3): Similar procedure to General Procedure A was followed using enynamides **4b** (0.2 mmol), except the following: DMSO (31.3 mg, 0.4 mmol, 2.0 equiv.), silyl enol ether **10b** (149.1 mg, 0.6 mmol, 3.0 equiv.) and $HNTf_2$ (200 µL of 14.0 mg/mL in CH_2Cl_2; 5.0 mol%). The resulting mixture was allowed to stir at 40°C for 40 h. At this point, the crude ^{1}H NMR spectra of an aliquot showed only a γ isomer with a ratio of diastereomeric products to be 1:1.6. Solvent was removed under vacuum and the residue was purified by flash column chromatography (EtOAc:*n*Hex = 1:10~1:4) to yield **11bb** (68.3 mg, 82%) as a pale yellow oil.

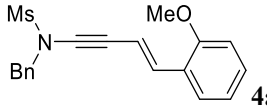
General Procedure C (representative example for the formation of 12ba, Table 4): Similar procedure to General Procedure A was followed using enynamides **4b** (0.2 mmol), except the following: DMSO (62.5 mg, 0.8 mmol, 4.0 equiv.), benzyl alcohol (64.9 mg, 0.6 mmol, 3.0 equiv.) and $HNTf_2$ (100 µL of 14.0 mg/mL in CH_2Cl_2; 2.5 mol%) was added dropwise over 3 minutes. The resulting mixture was allowed to stir at RT for 1 h. The crude ^{1}H NMR spectra of an aliquot showed only the γ product **12ba**. Solvent was removed under vacuum and the residue was purified by flash column chromatography (EtOAc:*n*Hex = 1:10~1:4) to yield **12ba** (52.3 mg, 67%) as a colorless oil.

General Procedure C (representative example for the formation of 14ba, Table 5): Similar procedure to General Procedure A was followed using enynamides **4b** (0.2 mmol), except the following: 1-propanethiol (18.3 mg, 0.24 mmol, 1.2 equiv.) was used as a nucleophile. The resulting mixture was allowed to stir at RT for 3 h. The crude ^{1}H NMR spectra of an aliquot showed only the γ product. Solvent was removed under vacuum and the residue was purified by flash column chromatography (EtOAc:*n*Hex = 1:8~1:2) to yield **14ba** (49.2 mg, 69%) as a colorless oil.

General Procedure D (representative example for the formation of 16ba, Table 5): Similar procedure to General Procedure A was followed using enynamides **4b** (0.2 mmol), except the following: *p*-toluenesulfonyl hydrazide (44.7 mg, 0.24 mmol, 1.2 equiv.) was used as a nucleophile. The resulting mixture was allowed to stir at RT for 6 h. The crude ^{1}H NMR spectra of an aliquot showed only the γ product. Solvent was removed under

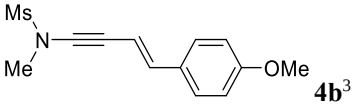
vacuum and the residue was purified by flash column chromatography (EtOAc:*n*Hex = 1:8~1:2) to yield **16ba** (66.5 mg, 71%) as a white solid.

3. Characterization of Substrates and Products



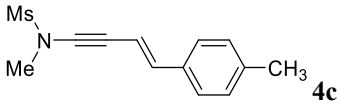
4a

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.44 (m, 2H), 7.43-7.34 (m, 4H), 7.24 (td, *J* = 7.4, 1.7 Hz, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.31 (d, *J* = 16.4 Hz, 1H), 4.68(s, 2H), 3.85 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 135.5, 134.7, 129.5, 128.9, 128.8, 128.7, 126.8, 125.3, 120.7, 111.0, 107.8, 83.5, 71.8, 56.0, 55.5, 39.0; LRMS (APCI) Calcd for $C_{19}H_{20}NO_3S^+$ $[M+H]^+$ 342.1, found 342.0.



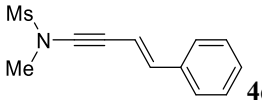
4b[3]

White solid: mp = 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.09 (d, J = 16.2 Hz, 1H), 3.81 (s, 3H), 3.25 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 140.2, 129.1, 127.5, 114.2, 104.6, 84.0, 69.2, 55.3, 39.3, 36.7; LRMS (APCI) Calcd for $C_{13}H_{16}NO_3S^+$ $[M+H]^+$ 266.1, found 266.1.



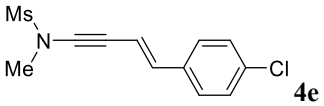
4c

White solid: mp = 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.12 (d, J = 8.0, 2H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.18 (d, *J* = 16.2 Hz, 1H), 3.24 (s, 3H), 3.08 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 138.6, 133.5, 129.4, 126.1, 106.0, 84.6, 69.2, 39.2, 36.7, 21.3; LRMS (APCI) Calcd for $C_{13}H_{16}NO_2S^+$ $[M+H]^+$ 250.1, found 250.0.



4d[3]

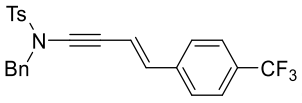
White solid: mp = 95-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.28 (m, 5H), 6.91(d, *J* = 16.2 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 3.31 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 136.3, 128.7, 128.5, 126.1, 107.1, 85.0, 69.2, 39.2, 36.8; LRMS (APCI) Calcd for $C_{12}H_{14}NO_2S^+$ $[M+H]^+$ 236.1, found 236.0.



4e

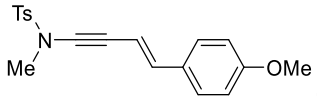
[3] Gawade, S. A.; Huple, D. B.; Liu, R.-S. *J. Am. Chem. Soc.* **2014**, *136*, 2978.

Pale yellow solid: mp = 89-91 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 4H), 6.81 (d, *J* = 16.2 H, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 3.25 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 134.8, 134.1, 128.9, 127.3, 107.9, 85.6, 69.0, 39.2, 36.9; LRMS (APCI) Calcd for $C_{12}H_{12}ClNO_2S^+$ $[M+H]^+$ 270.1, found 270.2.



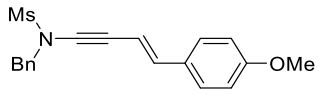
4f

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.34-7.26 (m, 7H), 6.67 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 4.55 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 139.8, 137.1, 134.7, 134.4, 129.9, 129.7 (q, *J* = 32 Hz), 128.8, 128.6, 128.4, 128.2, 127.7, 126.1, 125.6 (q, *J* = 4Hz), 124.0 (q, *J* = 270 Hz), 110.4, 86.4, 71.0, 55.7, 21.7; LRMS (APCI) Calcd for $C_{25}H_{19}F_3NO_2S^-$ $[M-H]^-$ 454.1, found 454.0.



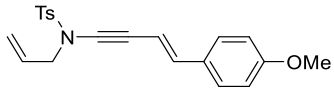
4g[3]

Pale yellow solid; mp = 88-90 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 16.1 Hz, 1H), 6.06 (d, *J* = 16.1 Hz, 1H), 3.71 (s, 3H), 3.11 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 144.8, 139.7, 133.3, 129.9, 129.2, 127.8, 127.5, 114.2, 105.0, 85.2, 68.8, 55.3, 39.4, 21.7; LRMS (APCI) Calcd for $C_{19}H_{19}NO_3S^+$ $[M+H]^+$ 342.1, found 342.2.



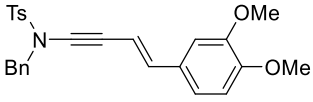
4h

White solid: mp = 64-66 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.44 (m, 2H), 7.43-7.34 (m, 3H), 7.29 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 6.07 (d, *J* = 16.1 Hz, 1H), 4.67 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 140.1, 134.6, 129.1, 128.9, 128.85, 128.7, 127.4, 114.2, 104.8, 83.1, 71.3, 55.9, 55.3, 39.0; LRMS (APCI) Calcd for $C_{19}H_{20}NO_3S^+$ $[M+H]^+$ 342.1, found 342.2.



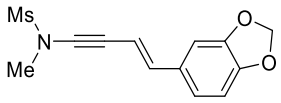
4i

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 16.1 Hz, 1H), 6.07 (d, *J* = 16.1 Hz, 1H), 5.75 (tdd, *J* = 6.3, 10.2, 17.0 Hz, 1H), 5.28 (dd, *J* = 1.3, 17.0 Hz, 1H), 5.22 (dd, *J* = 1.2, 10.2 Hz, 1H), 4.01 (dt, *J* = 6.3, 2.4 Hz, 1H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 144.6, 139.6, 134.7, 131.1, 129.8, 129.3, 127.8, 127.4, 120.0, 114.3, 105.1, 83.5, 70.6, 55.3, 54.4, 21.7; LRMS (APCI) Calcd for $C_{21}H_{22}NO_3S^+$ $[M+H]^+$ 368.1, found 368.2.



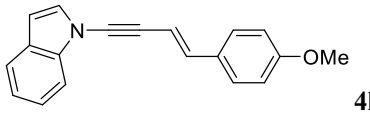
4j

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32-7.27 (m, 7H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.84 (s, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.66 (d, *J* = 16.1 Hz, 1H), 6.01 (d, *J* = 16.1 Hz, 1H), 4.53 (s, 2H), 3.84 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 149.8, 144.6, 139.6, 134.8, 134.6, 129.8, 129.5, 128.7, 128.5, 128.3, 127.7, 119.7, 111.1, 108.2, 105.4, 84.1, 71.0, 55.9, 55.8, 55.7, 21.7; LRMS (APCI) Calcd for $C_{26}H_{26}NO_4S^+$ $[M+H]^+$ 448.2, found 448.2.



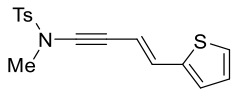
4k

White solid: mp = 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (s, 1H) 6.83-6.72 (m, 3H), 6.04 (d, *J* = 16.2 Hz, 1H), 5.96 (s, 2H), 3.25 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 140.1, 130.8, 121.5, 108.5, 105.15, 105.07, 101.3, 84.5, 69.1, 39.2, 36.8; LRMS (APCI) Calcd for $C_{13}H_{14}NO_4S^+$ $[M+H]^+$ 280.1, found 280.2.



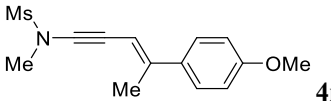
4l

Off-white solid: mp = 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.33 (t, *J* = 8.3 Hz, 1H), 7.25-7.18 (m, 2H), 6.98 (d, *J* = 16.2 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 3.3 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 139.7, 138.1, 129.3, 128.9, 127.8, 127.5, 123.5, 121.9, 121.2, 114.2, 111.3, 105.5, 104.8, 82.1, 70.4, 55.4; LRMS (APCI) Calcd for $C_{19}H_{15}NO^+$ $[M+H]^+$ 274.1, found 274.2.



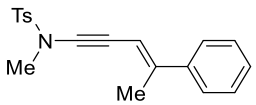
4m[3]

Yellow solid: mp = 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18-7.16 (m, 1H), 7.00-6.96 (m, 2H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 3.10 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 141.5, 133.3, 132.8, 129.9, 127.8, 127.7, 126.6, 125.1, 106.7, 86.3, 68.4, 39.3, 21.7; LRMS (APCI) Calcd for $C_{16}H_{16}NO_2S_2^+$ $[M+H]^+$ 318.1, found 318.0.



4n

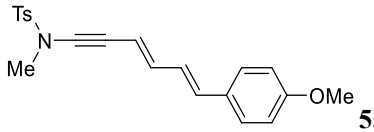
White solid: mp = 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.87 (d, *J* = 1.0 Hz, 1H), 3.81 (s, 3H), 3.28 (s, 3H), 3.11 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 146.8, 133.3, 126.6, 113.8, 103.6, 87.8, 68.5, 55.3, 39.4, 36.6, 18.6; LRMS (APCI) Calcd for $C_{14}H_{18}NO_3S^+$ $[M+H]^+$ 280.1, found 280.1.



4o

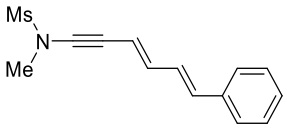
White solid: mp = 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.45-7.26 (m, 7H), 5.92

(s, 1H), 3.14 (s, 3H), 2.46 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 144.8, 140.9, 133.4, 129.8, 128.4, 127.9, 127.8, 125.3, 105.7, 89.3, 68.0, 39.5, 21.7, 18.5; LRMS (APCI) Calcd for $C_{19}H_{20}NO_2S^+$ $[M+H]^+$ 326.1, found 326.2.



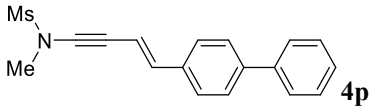
5a

Pale yellow solid: mp = 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 10.6, 24.5 Hz, 1H), 6.63 (dd, *J* = 10.6, 24.3 Hz, 1H), 6.53 (d, *J* = 14.9 Hz, 1H), 5.71 (d, *J* = 14.8 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 144.8, 140.9, 133.6, 133.3, 129.8, 129.6, 127.9, 127.8, 126.1, 114.2, 109.4, 86.5, 69.1, 55.3, 39.4, 21.7; LRMS (APCI) Calcd for $C_{21}H_{22}NO_3S^+$ $[M+H]^+$ 368.1, found 368.2.



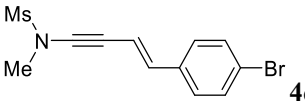
5b

White solid: mp = 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 10.8, 15.5 Hz, 1H), 6.69 (dd, *J* = 11.0, 15.0 Hz, 1H), 6.59 (d, *J* = 15.4 Hz, 1H), 3.25 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 136.7, 134.3, 128.7, 1281, 128.0, 126.6, 110.3, 86.0, 69.5, 39.3, 36.9; LRMS (APCI) Calcd for $C_{14}H_{16}NO_2S^+$ $[M+H]^+$ 262.1, found 262.1.



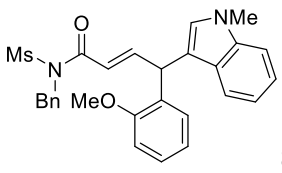
4p

Pale yellow solid: mp = 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.53 (m, 4H), 7.48-7.40 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 3.27 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 135.2, 131.9, 127.6, 122.3, 108.0, 85.7, 69.0, 39.2, 37.0; LRMS (APCI) Calcd for $C_{18}H_{17}NO_2S^+$ $[M+H]^+$ 312.1, found 312.1.



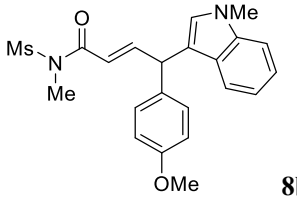
4q

Pale yellow solid: mp = 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 3.28 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.4, 139.6, 135.3, 128.9, 127.5, 127.4, 126.9, 126.6, 107.1, 85.2, 69.3, 39.3, 36.9; LRMS (APCI) Calcd for $C_{12}H_{12}BrNO_2S^+$ $[M+H]^+$ 313.0, found 313.0.



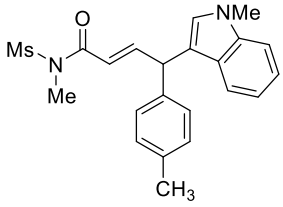
8aa

Yellow oil; (92.7 mg, 95%); (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 6.2, 15.0 Hz, H), 7.37-7.28 (m, 2H), 7.30-7.20 (m, 4H), 7.19 (t, *J* = 7.0 Hz, H), 7.10-7.07 (m, 2H), 7.01 (t, *J* = 7.0 Hz, H), 6.96 (dd, *J* = 7.0, 1.7 Hz, H), 6.87 (d, *J* = 8.2 Hz, H), 6.83 (t, *J* = 7.5, 1.0 Hz, H), 6.63 (s, H), 6.23 (dd, *J* = 1.7, 15.0 Hz, H), 5.56 (d, *J* = 6.1 Hz, H), 4.89 (d of ABq, *J* = 16.4 Hz, H), 4.81 (d of ABq, *J* = 16.4 Hz, H), 3.76 (s, 3H), 3.70 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 156.7, 153.0, 137.4, 136.5, 129.4, 129.1, 128.8, 128.1, 127.7, 127.4, 127.0, 121.8, 121.1, 120.7, 119.5, 119.0, 114.1, 110.6, 109.3, 55.5, 49.0, 42.9, 38.0, 32.8; HRMS (EI) Calcd for $C_{28}H_{28}N_2O_4S^+$ 488.1764; found 488.1764.



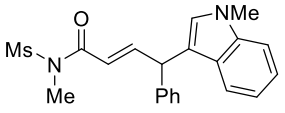
8ba

White foamy solid; (80.1 mg, 97%); (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.2, 15.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.23-7.17 (m, 3H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.72 (s, 1H), 6.49 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.11 (d, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.22 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.6, 152.5, 137.4, 133.1, 129.4, 127.5, 126.8, 121.9, 121.0, 119.5, 119.2, 115.0, 114.1, 109.4, 55.3, 44.9, 41.7, 32.8, 32.6; HRMS (EI) Calcd for $C_{22}H_{24}N_2O_4S^+$ 412.1451; found 412.1452.



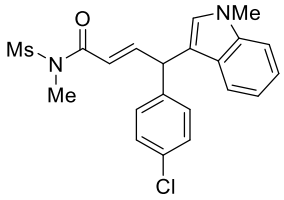
8ca

Brown oil; (65.6 mg, 83%); (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.2, 15.0 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 9.1 Hz, 1H), 7.20 (td, *J* = 8.1, 1.1 Hz, 1H), 7.15 (d of ABq, *J* = 8.2 Hz, 1H), 7.12 (d of ABq, *J* = 8.1 Hz, 1H), 7.02 (td, *J* = 7.0, 1.0 Hz, 1H), 6.72 (s, 1H), 6.48 (dd, *J* = 15.0, 1.4 Hz, 1H), 5.11 (d, *J* =7.2, 1H), 3.73 (s, 3H), 3.22 (s, 3H), 3.09 (s, 3H), 2.32 (s, 3H); HRMS (EI) Calcd for $C_{22}H_{24}N_2O_3S^+$ 396.1502, found 396.1504.



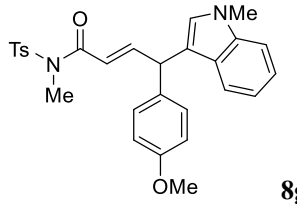
8da

Brown oil; (47.3 mg, 62%); (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.57-7.51 (dd, *J* = 7.2, 15.0 Hz, 4H), 7.36-7.18 (m, 23H), 7.14 (t, J = 8.0 Hz, 1H), 7.07 (s, 1H), 7.03 (t, J = 8.0 Hz, 2H), 6.73 (s, 1H), 6.63-6.57 (dd, J = 7.5, 15.9 Hz, 1H), 6.51-6.46 (m, 2H), 5.29 (d, *J* = 7.5 Hz, 1H), 5.15 (d, *J* =7.2, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.28 (s, 3H), 3.22 (s, 3H), 3.14 (s, 3H), 3.09 (s, 3H); HRMS (EI) Calcd for $C_{21}H_{22}N_2O_3S^+$ 382.1346, found 382.1345.



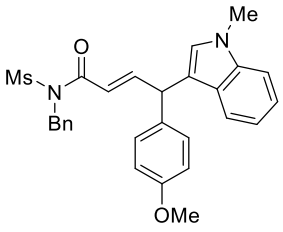
8ea

Brown oil; (52.4 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$): δ (**γ-isomer**) 7.51 (dd, *J* = 7.2, 15.0 Hz, H), 7.7.33-7.18 (m, 8 H), 7.04 (t, *J* = 6.8 Hz, 1H), 6.73 (s, 1H), 6.49 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 3.23 (s, 3H), 3.10 (s, 3H); (**α-isomer**) 7.64 (d, *J* = 8.0 Hz, 1H), 7.40-7.20 (m, 6H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.59 (dd, *J* = 7.6, 15.9 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 3H), 3.12 (s, 3H); HRMS (EI) Calcd for $C_{21}H_{21}N_2O_3S^+$ 416.0956; found 416.0958.



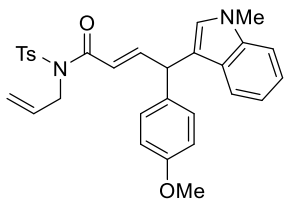
8ga

Brown oil; (92.7 mg, 95%); (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 6.8, 15.0 Hz, 1H), 7.33-7.29 (m, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.16-7.12 (m, 4H), 7.02 (t, *J* = 6.9 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 1H), 6.64 (dd, *J* = 1.5, 15.0 Hz, 1H), 5.07 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.28 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 158.5, 151.2, 144.6, 137.4, 136.4, 133.4, 129.8, 129.5, 127.5, 127.2, 126.9, 122.3, 121.9, 119.6, 119.1, 115.1, 114.0, 109.3, 55.3, 44.7, 33.0, 32.8, 21.6; HRMS (EI) Calcd for $C_{28}H_{28}N_2O_4S^+$ 488.1764; found 488.488.1766.



8ha

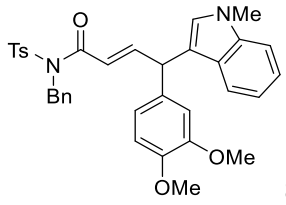
Brown oil; (85.1 mg, 87%); (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 6.6, 14.9 Hz, 1H), 7.30-7.24 (m, 6H), 7.11-7.08 (m, 2H), 7.06 (d, *J* = .7 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 6.26 (dd, *J* = 1.5, 14.9 Hz, 1H), 5.05 (d, *J* = 6.4 Hz, 1H), 4.90 (d of ABq, *J* = 16.4 Hz, 1H), 4.82 (d of ABq, *J* = 16.4 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 158.6, 152.9, 137.4, 136.4, 132.9, 129.5, 128.8, 127.8, 127.6, 127.4, 126.8, 121.9, 121.4, 119.4, 119.2, 114.8, 109.4, 55.3, 49.0, 44.7, 43.0, 32.8; HRMS (EI) Calcd for $C_{28}H_{28}N_2O_4S^+$ 488.1764; found 488.1765.



8ia

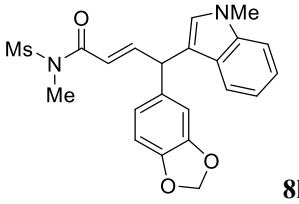
Brown oil; (90.8 mg, 88%); (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.41

(dd, *J* = 6.6, 15.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H) 7.10 (d, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.68 (s, 1H), 6.38 (dd, *J* = 1.6, 15.0 Hz, 1H), 5.82 (ddd, *J* = 5.6, 10., 17.0 Hz, 1H), 5.15 (d, *J* = 10.1 Hz, 1H), 5.11 (d, *J* = 17.3 Hz, 1H), 5.01 (d, *J* = 6.5 Hz, 1H), 4.49-4.35 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 158.5, 151.8, 144.5, 137.3, 136.8, 133.2, 133.0, 129.6, 129.5, 127.9, 127.5, 126.9, 122.0, 121.9, 119.5, 119.1, 118.2, 115.0, 114.0, 109.3, 55.3, 48.6, 44.7, 32.8, 21.6; HRMS (EI) Calcd for $C_{30}H_{30}N_2O_4S^+$ 514.1921; found 514.1925.



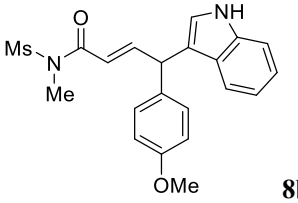
8ja

Brown oil; (101.2 mg, 85%) (spectra of γ-isomer) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 6.4, 15.0 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 7H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.07, (d, *J* = 8.0 Hz, 2H), 7.00 (dt, *J* = 1.0, 8.0 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.69-6.68 (m, 2H), 6.64 (s, 1H), 6.38 (dd, *J* = 1.6, 15.0 Hz, 1H), 5.07 (d of ABq, *J* = 15.8 Hz, 1H), 00 (d of ABq, *J* = 15.8 Hz, 1H), 4.97 (d, *J* = 4.6 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 151.6, 149.0, 147.9, 144.5, 137.3, 136.9, 136.8, 133.6, 129.5, 128.6, 127.9, 127.7, 127.6, 127.5, 126.9, 122.3, 121.9, 120.6, 119.5, 119.1, 114.7, 111.8, 111.1, 109.3, 55.9, 55.8, 49.4, 45.1, 32.8, 21.6; HRMS (EI) Calcd for $C_{35}H_{34}N_2O_5S^+$ 594.2183; found 594.2184.



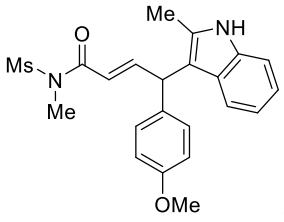
8ka

Brown oil; (71.7 mg, 84%) (spectra of the γ isomer) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.2, 15.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.77-6.73 (m, 4H), 6.49 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.95-5.91 (m, 2H), 5.10 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 3.23 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 152.1, 147.9, 146.5, 137.4, 134.9, 127.4, 126.7, 122.0, 121.5, 121.0, 119.4, 119.2, 114.7, 109.4, 108.9, 108.3, 101.0, 45.3, 41.7, 32.8, 32.5; HRMS (EI) Calcd for $C_{22}H_{22}N_2O_5S^+$ 426.1244; found 426.1243.



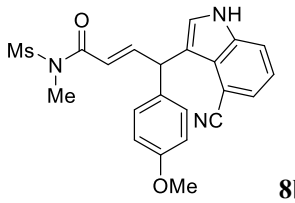
8bb

Brown oil; (72.6 mg, 91%) (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.56 (dd, *J* = 7.1, 15.0 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.19-7.15 (m, 3H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.86-6.83 (m, 3H), 6.48 (dd, *J* = 1.5, 15.0 Hz, 1H), 5.12 (d, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 3.22 (s, 3H), 3.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.6, 152.4, 136.6, 132.9, 129.4, 126.3, 122.8, 122.4, 121.1, 119.7, 119.4, 116.6, 114.1, 111.4, 55.3, 44.9, 41.7, 32.6; HRMS (EI) Calcd for $C_{21}H_{22}N_2O_4S^+$ 398.1295; found 398.1294.



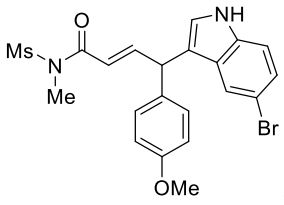
8bc

Brown oil; (77.8 mg, 94%); (spectra of the γ isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.65 (dd, *J* = 7.0, 15.0 Hz, 1H), 7.31-7.23 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.48 (dd, *J* = 1.6, 15.0 Hz, 1H), 5.12 (d, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 3.22 (s, 3H), 3.08 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.3, 152.4, 135.3, 133.2, 132.2, 129.1, 127.7, 127.5, 121.2, 121.1, 119.5, 119.0, 113.9, 110.5, 55.3, 44.0, 41.7, 32.6, 12.4; HRMS (EI) Calcd for $C_{22}H_{24}N_2O_4S^+$ 412.1451; found 412.1450.



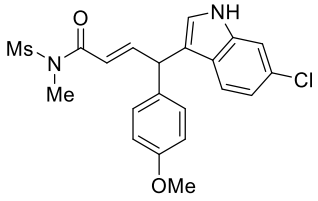
8bd

Brown oil; (71.3 mg, 84%); (spectra of γ-isomer) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 7.0, 15.0 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.22-7.16 (m, 3H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.44 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.67 (d, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 3.25 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 158.7, 152.6, 136.7, 132.7, 129.7, 126.7, 126.4, 125.6, 121.9, 121.5, 119.5, 116.7, 116.6, 114.1, 101.8, 55.3, 43.3, 41.7, 32.7; HRMS (EI) Calcd for $C_{22}H_{21}N_3O_4S^+$ 423.1247; found 423.1246.



8be

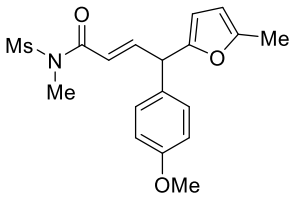
Brown oil; (84.1 mg, 88%); (spectra of the γ isomer) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.50 (dd, *J* = 7.0, 15.0 Hz, 2H), 7.47 (s, 1H), 7.28-7.23 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.87-6.83 (m, 3H), 6.48 (dd, *J* = 15.0, 1.4 Hz, 1H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 3.23 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.7, 152.0, 135.3, 132.4, 129.4, 128.1, 125.2, 124.1, 121.8, 121.3, 116.2, 114.2, 113.0, 112.9, 55.3, 44.7, 41.7, 32.6; HRMS (EI) Calcd for $C_{21}H_{21}BrN_2O_4S^+$ 476.0400; found 476.0398.



8bf

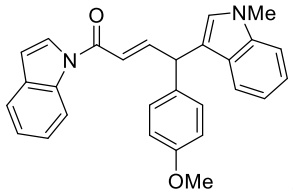
Brown oil; (71.1 mg, 82%) (spectra of the γ isomer) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.52 (dd, *J* =

7.2, 15.0 Hz, 1H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.99 (dd, *J* = 1.8, 8.5 Hz, 1H), 6.86-6.83 (m, 3H), 6.47 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.06 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.23 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.7, 152.1, 137.0, 132.6, 129.4, 128.2, 127.7, 124.9, 123.5, 121.2, 120.3, 116.6, 114.5, 111.4, 55.3, 44.8, 41.7, 32.6.; HRMS (EI) Calcd for $C_{22}H_{21}ClN_2O_4S^+$ 432.0905; found 432.0905.



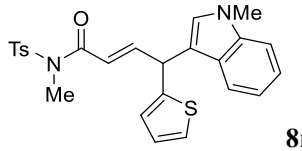
8bg

Colorless oil; (46.8 mg, 64%); (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.33 (dd, *J* = 7.2, 15.0 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.50 (dd, *J* = 1.5, 15.0 Hz, 1H), 5.92 – 5.8 (m, 2H), 4.81 (d, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.27 (s, 3H), 3.28 (s, 3H),); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 158.8, 152.1, 151.9, 149.9, 131.0, 129.3, 121.7, 114.2, 108.8, 106.1, 55.3, 47.1, 41.7, 32.7, 13.5; HRMS (EI) Calcd for $C_{18}H_{21}NO_5S^+$ 363.1135; found 363.1136.



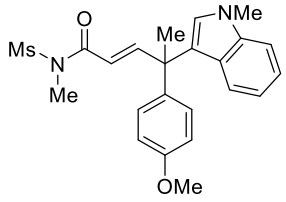
8la

Brown oil; (55.7 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 6.6, 15.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.35-6.99 (m, 5H),7.23 (d, *J* = 8.7 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.76 (s, 1H), 6.57 (d, *J* = 3.8 Hz, 1H), 6.56 (dd, *J* = 1.6, 15.0 Hz, 1H), 5.20 (d, *J* = 6.5 Hz, 1H) 3.80 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 158.6, 152.3, 137.4, 135.8, 133.2, 130.6, 129.6, 127.5, 126.9, 124.9, 124.8, 123.7, 122.0, 121.5, 120.8, 119.6, 119.3, 116.7, 115.2, 114.1, 109.4, 108.9, 55.3, 45.0, 32.8; HRMS (EI) Calcd for $C_{28}H_{24}N_2O_2^+$ 420.1832; found 420.1836.



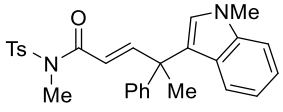
8ma

Brown oil; (86.3 mg, 93%); (spectra of γ-isomer) ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.0, 15.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26-7.23 (m, 1H), 7.20 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 3.5, 5.1 Hz, 1H), 6.88-6.87 (m, 2H), 6.80 (dd, *J* = 1.4, 15.0 Hz, 1H), 5.36 (d, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 3.27 (s, 3H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.2, 149.9, 145.2, 144.7, 137.3, 136.3, 129.9, 129.5, 127.5, 127.4, 126.9, 126.6, 125.4, 122.3, 122.0, 119.4, 119.3, 114.5, 109.5, 40.5, 33.0, 32.9, 21.6; HRMS (EI) Calcd for $C_{25}H_{24}N_2O_3S_2^+$ 464.1223; found 464.1222.



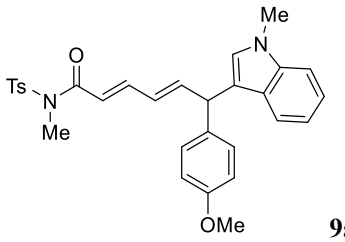
8na

Brown oil; (82.0 mg, 96%) (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 15.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 6.39 (d, *J* = 15.2 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.19 (s, 3H), 3.05 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 158.2, 157.3, 137.8, 137.5, 128.4, 127.2, 126.0, 121.6, 121.4, 119.6, 118.9, 118.6, 113.7, 109.5, 55.2, 45.4, 41.7, 32.8, 32.6, 27.6; HRMS (EI) Calcd for $C_{23}H_{26}N_2O_4S^+$ 426.1608; found 426.1609.



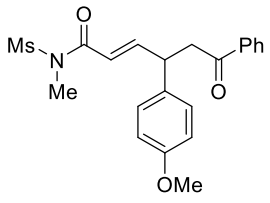
8oa

Brown oil; (71.1 mg, 75%); (spectra of γ-isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 15.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.35+-7.12 (m, 5H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.82 (s, 1H), 6.62 (d, *J* = 15.2 Hz, 1H), 3.75 (s, 3H), 3.27 (s, 3H), 2.38 (s, 3H), 1.90 (s, 3H); HRMS (EI) Calcd for $C_{28}H_{28}N_2O_3S^+$ 472.1815; found 472.1817.



9aa

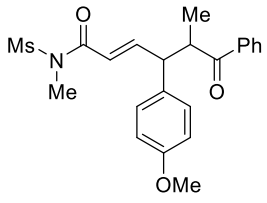
Yellow oil; (74.1 mg, 72%); (spectra of the ε-isomer); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.41-7.34 (m, 2H), 7.30-7.28 (m, 3H), 7.23-7.16 (m, 3H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 14.8 Hz, 1H), 6.67 (s, 1H), 6.63 (dd, *J* = 7.2, 15.1 Hz, 1H), 6.21 (ddd, *J* = 0.6, 11.2, 15.1 Hz, 1H), 5.02 (d, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.25 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 158.4, 147.2, 146.2, 144.7, 137.4, 136.2, 134.3, 129.9, 129.4, 128.8, 127.3, 127.0, 121.8, 120.3, 119.7, 119.0, 116.1, 114.0, 109.3, 55.3, 45.3, 33.0, 32.8, 21.6; HRMS (EI) Calcd for $C_{30}H_{30}N_2O_4S^+$ 514.1921; found 514.1925.



11ba

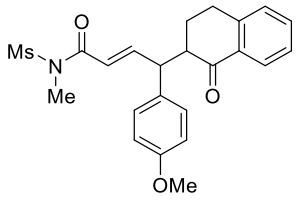
Colorless oil; (42.8 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.9, 2H), 7.20 (dd, *J* = 7.4, 15.1, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.58 (dd, *J* = 1.3, 15.1 Hz, 1H), 4.33 (ddd, *J* = 6.6, 7.3, 13.9 Hz, 1H), 3.79 (s, 3H), 3.50 (8.1, 17.3 Hz, 1H), 3.42 (dd, *J* = 5.9, 17.3 Hz, 1H), 3.25 (s, 3H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 166.4, 158.8, 152.5, 133.7, 133.4, 132.9, 128.8, 128.7, 128.0, 120.7, 114.4, 55.3, 43.7, 42.7, 41.6, 32.5; HRMS (EI) Calcd for $C_{21}H_{23}NO_5S^+$ 401.1291;

found 401.1292.



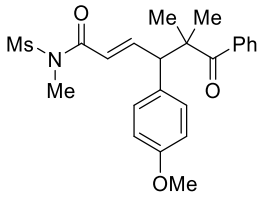
11bb

Pale yellow oil; (68.3mg, 82%); (major diastereomer) ^{1}H NMR (400 MHz, C_6D_6): δ 8.0 (d, *J* = 8.2 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.11 (dd, *J* = 7.6, 15.1 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.49 (dd, *J* = 1.1, 15.2 Hz, 1H), 4.03-3.86 (m, 2H), 3.81 (s, 3H), 3.14 (s, 3H), 2.99 (s, 3H), 1.01 (d, *J* = 6.7 Hz, 3H); (minor diastereomer) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.27 (dd, *J* = 9.4, 14.9 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 14.9 Hz, 1H), 4.08-3.89 (m, 2H), 3.70 (s, 3H), 3.30 (s, 3H), 3.19 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): (major) δ 202.7, 166.1, 158.9, 151.8, 136.3, 133.5, 131.2, 129.5, 128.9, 128.3, 120.7, 114.4, 55.3, 50.4, 44.9, 41.5, 32.4, 17.2; HRMS (EI) Calcd for $C_{22}H_{25}NO_5S^+$ 415.1453; found 415.1451.



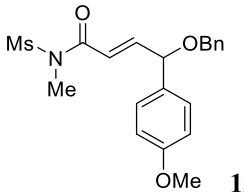
11bc

Pale yellow oil; (61.8 mg, 72%); (for a mixture of diastereomers) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.50-7.44 (m, 2H), 7.38-7.20 (m, 5H), 7.20 (d, *J* = 8.6. Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.68 (dd, *J* = 1.0, 15.0 Hz, 1H), 6.59 (dd, *J* = 1.2, 15.1 Hz, 1H), 4.52 (dd, *J* = 4.5, 8.8 Hz, 1H), 4.15 (t, *J* = 7.8 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.27 (s, 6H), 3.21 (s, 3H), 3.20 (s, 3H), 3.05-2.90 (m, 6 H), 2.25-2.18 (m, 1H), 2.17-1.98 (m, 2H), 1.82-1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 197.6, 166.5, 166.3, 158.7, 158.6, 152.5, 149.8, 143.7, 143.5, 133.6, 132.6, 132.4, 131.1, 129.7, 129.2, 128.8, 128.7, 127.5, 126.8, 122.8, 120.7, 114.3, 114.2, 55.3, 53.7, 52.0, 46.7, 46.2, 41.8, 41.7, 32.6, 32.5, 29.0, 27.8, 26.0, 24.8; HRMS (EI) Calcd for $C_{23}H_{25}NO_5S^+$ 427.1448; found 427.1448.



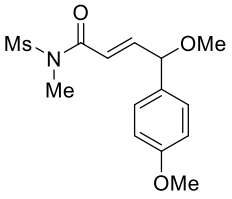
11bd

Colorless oil; (46.4 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 9.6, 14.9 Hz, 1H), 7.44-7.40 (m, 1H), 7.38-7.29 (m, 4H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.55 (dd, *J* = 0.9, 14.9 Hz, 1H), 4.21 (d, *J* = 9.6 Hz, 1H), 3.79 (s, 3H), 3.25 (s, 3H), 3.14 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6, 166.2, 158.8, 149.7, 139.6, 133.4, 130.7, 130.6, 130.4, 128.1, 126.9, 122.8, 113.8, 55.2, 54.6, 52.0, 41.7, 32.5, 24.5, 23.8; HRMS (EI) Calcd for $C_{23}H_{27}NO_5S^+$ 429.1604; found 429.1607.



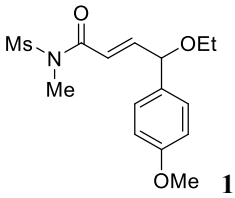
12ba

Pale yellow oil; (52.3 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.11 (dd, *J* = 4.8, 15.1 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.88 (dd, *J* = 1.6, 15.1 Hz, 1H), 4.99 (dd, *J* = 1.6, 4.8 Hz, 1H), 4.55 (d opf ABq, *J* = 12.1 Hz, 1H), 4.42 (d of ABq, *J* = 12.1 Hz, 1H), 3.82 (s, 3H), 3.32 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.8, 149.8, 137.9, 130.4, 128.7, 128.5, 127.8, 127.6, 119.4, 114.3, 79.2, 70.2, 55.4, 41.7, 32.7; HRMS (EI) Calcd for $C_{20}H_{23}NO_5S^+$ 389.1291; found 389.1292.



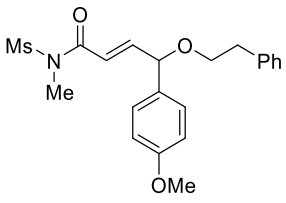
12bb

Colorless oil; (39.4 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.6 Hz, 2H), 7.06 (dd, *J* = 4.8, 15.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.79 (dd, *J* = 1.7, 15.1 Hz, 1H), 4.79 (dd, *J* = 1.6, 4.8 Hz, 1H), 3.81 (s, 3H), 3.33 (s, 3H), 3.30 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.8, 149.7, 130.3, 128.6, 119.1, 114.2, 82.0, 56.5, 55.3, 41.7, 32.7; HRMS (EI) Calcd for $C_{14}H_{19}NO_5S^+$ 313.0978; found 313.0978.



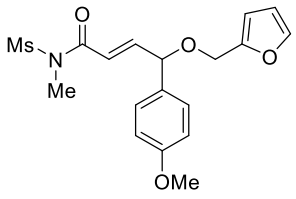
12bc

Colorless oil; (40.1 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.7 Hz, 2H), 7.09 (dd, *J* = 5.0, 15.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.82 (dd, *J* = 1.6, 15.1 Hz, 1H), 4.91 (dd, *J* = 1.5, 5.0 Hz, 1H), 3.80 (s, 3H), 3.46 (q, *J* = 7.0 Hz, 2H), 3.33 (s, 3H), 3.22 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.6, 150.2, 131.0, 128.4, 119.1, 114.2, 80.2, 64.3, 55.3, 41.7, 32.7, 15.2; HRMS (EI) Calcd for $C_{15}H_{21}NO_5S^+$ 327.1135; found 327.1135.



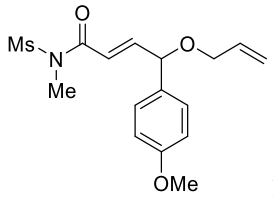
12bd

Pale yellow oil; (62.2 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.23-7.17 (m, 3H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.03 (dd, *J* = 4.6, 15.0 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.75 (dd, *J* = 1.7, 15.0 Hz, 1H), 4.89 (dd, *J* = 1.6, 4.6 Hz, 1H), 3.79 (s, 3H), 3.60 (t, *J* = 6.8Hz, 2H), 3.26 (s, 3H), 3.18 (s, 3H), 2.96-2.82 (m, 2H) 4-6); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 159.7, 149.9, 139.0, 130.6, 129.1, 128.5, 128.3, 126.3, 118.9, 114.2, 80.4, 69.6, 55.3, 41.7, 36.4, 32.6, 30.1; HRMS (EI) Calcd for $C_{21}H_{25}NO_5S^+$ 403.1448; found 403.1449.



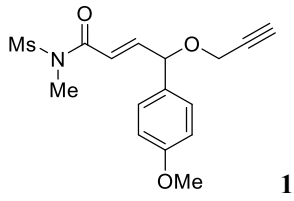
12be

Pale yellow oil; (31.0 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 0.8, 1.8 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.08 (dd, *J* = 4.9, 15.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.82 (dd, *J* = 1.6, 15.0 Hz, 1H), 6.35 (dd, *J* = 1.8, 3.2 Hz, 1H), 6.30 (d, *J* = 3.1 Hz, 1H), 5.01 (dd, *J* = 1.6, 4.9 Hz, 1H), 4.48 (d of ABq, *J* = 12.9 Hz, 1H), 4.38 (d of ABq, *J* = 12.9 Hz, 1H), 3.81 (s, 3H), 3.32 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.8, 151.3, 149.5, 142.9, 130.1, 128.8, 119.5, 114.3, 110.3, 109.7, 78.9, 62.2, 55.33, 41.7, 32.7; HRMS (EI) Calcd for $C_{18}H_{21}NO_6S^+$ 379.1084; found 379.1085.



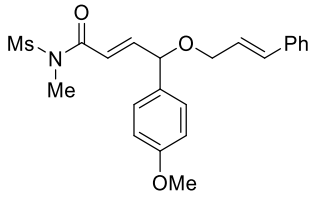
12bf

Colorless oil; (50.3 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.6 Hz, 2H), 7.08 (dd, *J* = 4.8, 15.1 Hz, 1H), 6.89 (d, *J* = 8.8Hz, 2H), 6.84 (dd, *J* = 1.6, 15.1 Hz, 1H), 5.95-5.85 (m, 1H), 5.28 (qd, *J* = 1.7, 17.2 Hz, 1H), 5.20 (qd, *J* = 1.6, 10.4 Hz, 1H), 4.98 (dd, *J* = 1.6, 4.8 Hz, 1H), 3.99 (tdd, *J* = 1.6, 5.2, 13.0 Hz, 1H), 3.91 (tdd, *J* = 1.4, 5.8, 13.0 Hz, 1H), 3.81 (s, 3H), 3.32 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.7, 149.9, 134.3, 130.5, 128.6, 119.2, 117.2, 114.2, 79.3, 69.3, 55.3, 41.7, 32.7; HRMS (EI) Calcd for $C_{16}H_{21}NO_5S^+$ 339.1135; found 339.1136.



12bg

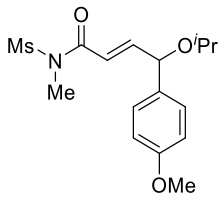
Colorless oil; (41.7 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.6 Hz, 2H), 7.08 (dd, *J* = 4.8, 15.1 Hz, 1H), 6.91 (d, *J* = 8.8Hz, 2H), 6.84 (dd, *J* = 1.7, 15.1 Hz, 1H), 5.23 (dd, *J* = 1.6, 4.8 Hz, 1H), 4.20 (dd, *J* = 2.4, 15.9 Hz, 1H), 4.00 (dd, *J* = 2.4, 15.9 Hz, 1H), 3.81 (s, 3H), 3.34 (s, 3H), 3.23 (s, 3H), 2.46 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 160.0, 149.0, 129.2, 129.0, 119.7, 114.3, 79.2, 78.4, 75.0, 55.3, 55.3, 41.8, 32.7; HRMS (EI) Calcd for $C_{16}H_{19}NO_5S^+$ 337.0978; found 337.0981.



12bh

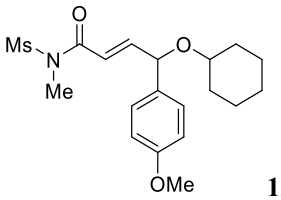
Pale yellow oil; (69.9 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 7H), 7.11 (dd, *J* = 4.9, 15.1 Hz,

1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.88 (dd, *J* = 1.6, 15.1 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.27 (td, *J* = 6.0, 15.9 Hz, 1H), 5.04 (dd, *J* = 1.3, 4.8 Hz, 1H), 4.17 (ddd, *J* = 1.4, 5.6, 12.8 Hz, 1H), 4.18 (ddd, *J* = 1.2, 6.3, 12.8 Hz, 1H), 3.81 (s, 3H), 3.32 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.8, 149.8, 136.6, 132.7, 130.5, 128.7, 128.6, 127.8, 126.5, 125,6, 119.3, 114.3, 79.4, 69.0, 55.4, 41.7, 32.7; HRMS (EI) Calcd for $C_{22}H_{25}NO_5S^+$ 415.1448; found 415.1447.



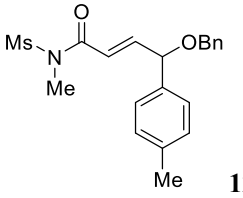
12bi

Pale yellow oil; (37.0 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.7 Hz, 2H), 7.09 (dd, *J* = 4.9, 15.0Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.80 (dd, *J* = 1.4, 15.1 Hz, 1H), 5.03 (dd, *J* = 1.3, 4.8 Hz, 1H), 3.80 (s, 3H), 3.63 (septet, *J* = 6.0 Hz, 1H), 3.32 (s, 3H), 3.21 (s, 3H), 1.20 (d, 6.0 Hz, 3H), 1.15 (d, 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 159.5, 151.0, 131.6, 128.3, 119.0, 114.2, 69.5, 55.3, 41.7, 32.7, 22.7, 21.8; HRMS (EI) Calcd for $C_{16}H_{23}NO_5S^+$ 341.1291; found 341.1288.



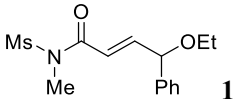
12bj

Pale yellow oil; (39.8 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.7 Hz, 2H), 7.10 (dd, *J* = 4.8, 15.0 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.84 (dd, *J* = 1.6, 15.0 Hz, 1H), 5.09 (dd, *J* = 1.5, 4.8 Hz, 1H), 3.80 (s, 3H), 3.35-3.27 (m, 1H),3.32 (s, 3H), 3.21 (s, 3H), 1.91-1.87 (m, 1H), 1.75-1.70 (m, 2H), 1.50-1.21 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 159.5, 151.2, 131.7, 128.3, 118.9, 114.1, 75.2, 55.3, 41.7, 32.8, 32.6, 31.9, 25.7, 24.0, 23.9; HRMS (EI) Calcd for $C_{19}H_{27}NO_5S^+$ 381.1604; found 381.1605.



12ca

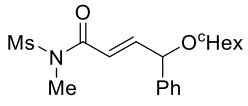
Colorless oil; (49.4 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.25 (m, 5H), 7.257.15 (m, 4H), 7.09 (dd, *J* = 4.8, 15.0 Hz, 1H), 6.88 (dd, *J* = 1.6, 15.0 Hz, 1H), 4.99 (dd, *J* = 1.5, 4.8 Hz, 1H), 4.56 (d of ABq, J = 12.1 Hz, 1H), 4.43 (d of ABq, J = 12.0 Hz, 1H), 3.31 (s, 3H), 3.20 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 149.8, 138.4, 137.9, 135.4, 129.6, 128.5, 127.8, 127.6, 127.3, 119.4, 79.6, 70.3, 41.7, 32.7, 21.2; HRMS (EI) Calcd for $C_{20}H_{23}NO_4S^+$ 373.1342; found 373.1344.



12dc

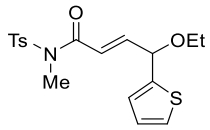
Pale yellow oil; (36.5 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.27 (m, 5H), 7.09 (dd, *J* = 5.0, 15.0 Hz, 1H), 6.83 (dd, *J* = 1.6, 15.1 Hz, 1H), 4.96 (dd, *J* = 1.5, 5.0 Hz, 1H), 3.49 (q, *J* = 7.0 Hz, 2H), 3.32 (s, 3H), 3.21 (s,

3H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 150.0, 139.0, 128.8, 128.3, 127.1, 119.4, 80.7, 64.6, 41.7, 32.7, 15.2; HRMS (EI) Calcd for $C_{14}H_{19}NO_4S^+$ 297.1029; found 297.1031.



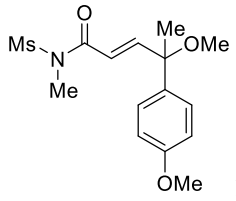
12dj

Pale yellow oil; (31.3 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4-7.28 (m, 5H), 7.10 (dd, J = 4.8, 15.0 Hz, 1H), 6.84 (dd, J = 1.6, 15.0 Hz, 1H), 5.13 (dd, J = 1.5, 4.7 Hz, 1H), 3.40-3.30 (m, 1H), 3.32 (s, 3H), 3.20 (s, 3H), 1.99-1.85 (br, 1H), 1.85-1.65 (m, 2H), 1.55-1.14 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 151.0, 139.8, 128.7, 128.1, 126.9, 119.2, 77.6, 75.6, 41.7, 32.7, 32.6, 31.9, 25.7, 24.0, 23.9; HRMS (EI) Calcd for $C_{18}H_{25}NO_4S^+$ 351.1499; found 351.1500.



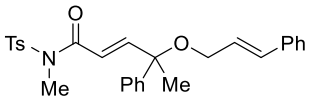
12mc

Pale yellow oil; (53.1 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.34-7.27 (m, 3H), 7.08 (dd, J = 1.4, 15.1 Hz, 1H), 7.01-6.92 (m, 2H), 6.95 (dd, J = 5.2, 15.0 Hz, 1H), 5.18 (dd, J = 0.7, 5.2 Hz, 1H), 3.60-3.47 (m, 2H), 3.31 (s, 3H), 2.43 (s, 3H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 147.4, 144.9, 142.8, 136.2, 129.9, 127.4, 126.8, 126.0, 125.7, 121.7, 76.2, 64.7, 33.0, 21.6, 15.2; HRMS (EI) Calcd for $C_{18}H_{21}NO_4S_2^+$ 379.0907; found 379.0907.



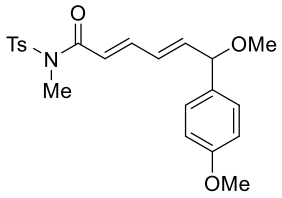
12nb

Pale yellow oil; (38.7 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 9.0 Hz, 2H), 7.10 (d, J = 15.0 Hz, 1H), 6.89 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 15.0 Hz, 1H), 3.81 (s, 3H), 3.34 (s, 3H), 3.23 (s, 3H), 3.11 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 159.2, 154.8, 133.1, 128.0, 117.5, 113.9, 78.5, 55.3, 50.8, 41.8, 32.7, 22.7; HRMS (EI) Calcd for $C_{15}H_{21}NO_5S^+$ 327.1135; found 327.1134.



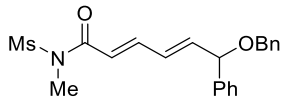
12oh

Colorless oil; (58.1 mg, 61%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.42-7.20 (m, 12 H), 7.10 (d, J = 150.1 Hz, 1H), 6.98 (d, J = 15.1 Hz, 1H), 6.69 (d, J = 15.9 Hz, 1H), 6.29 (td, J = 5.4, 15.9 Hz, 1H), 3.99 (ddd, J = 1.6, 5.5, 12.7Hz, 1H), 3.89 (ddd, J = 1.6, 5.4, 12.6 Hz, 1H), 3.33 (s, 3H), 2.37 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 152.7, 144.8, 142.0, 137.0, 136.5, 131.2, 129.9, 128.6, 128.5, 127.8, 127.6, 127.4, 126.6, 126.5, 119.8, 79.0, 64.0, 33.0, 23.8, 21.6; HRMS (EI) Calcd for $C_{28}H_{29}NO_4S^+$ 475.1812; found 475.1813.



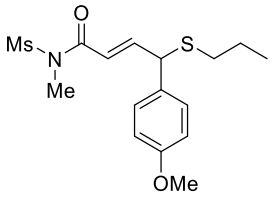
13ab

Colorless oil; (62.3 mg, 77%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 11.2, 14.8 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 15.0 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.43 (td, *J* = 0.6, 11.2, 15.2 Hz, 1H), 6.20 (dd, *J* = 6.0, 15.3 Hz, 1H), 4.71 (d, *J* = 5.9 Hz, 1H), 3.81 (s, 3H), 3.29 (s, 3H), 3.26 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.3, 159.5, 145.1, 144.8, 143.8, 136.2, 131.7, 129.9, 128.4, 128.2, 127.3, 121.8, 114.1, 82.8, 56.4, 55.3, 33.0, 21.6.; HRMS (EI) Calcd for $C_{22}H_{25}NO_5S^+$ 415.1448; found 415.1450.



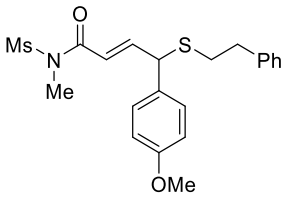
13ba

Pale yellow oil; (54.1 mg, 70%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47-7.22 (m, 11H), 6.67 (d, *J* = 14.8 Hz, 1H), 6.49 (dd, *J* = 11.2, 15.2 Hz, 1H), 6.31 (dd, *J* = 5.6, 15.2 Hz, 1H), 4.98 (d, *J* = 5.6 Hz, 1H), 4.53 (d of ABq, *J* = 11.8 Hz, 1H), 4.46 (d of ABq, *J* = 11.8 Hz, 1H), 3.31 (s, 3H), 3.19 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.5, 146.1, 144.5, 139.7, 138.0, 128.8, 128.5, 128.3, 128.0, 127.8, 127.2, 120.6, 80.5, 70.4, 41.6, 32.6; HRMS (EI) Calcd for $C_{21}H_{23}NO_4S^+$ 385.1342; found 385.1339.



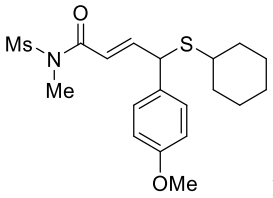
14ba

Colorless oil; (49.2 mg, 69%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6 Hz, 2H), 7.20 (dd, *J* = 8.8, 14.9 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.63 (dd, *J* = 1.0, 14.8 Hz, 1H), 4.53 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.31 (s, 3H), 3.20 (s, 3H), 2.49-2.35 (m, 2H), 1.68-1.51 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.1, 159.2, 149.1, 130.4, 129.0, 120.2, 114.3, 55.3, 50.2, 41.7, 33.8, 32.7, 22.6, 13.5; HRMS (EI) Calcd for $C_{16}H_{23}NO_4S_2^+$ 357.1063; found 357.1066.



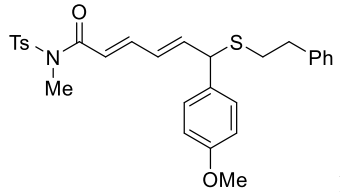
14bb

Colorless oil; (58.8 mg, 70%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 6.9 Hz, 2H), 7.23-7.14 (m, 6H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.60 (dd, *J* = 1.0, 14.9 Hz, 1H), 4.40 (d, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 3.28 (s, 3H), 3.16 (s, 3H), 2.90-2.80 (m, 2H), 2.68 (t, *J* = 7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.0, 159.3, 148.7, 140.2, 130.2, 129.0, 128.7, 128.5, 126.5, 120.5, 114.3, 55.4, 50.4, 41.7, 36.2, 33.1, 32.7; HRMS (EI) Calcd for $C_{21}H_{25}NO_4S_2^+$ 419.1220; found. 419.1217.



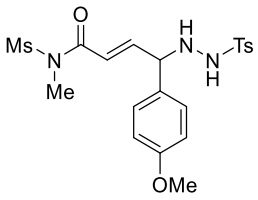
14bc

Pale yellow oil; (64.7 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.7, 14.9 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.63 (dd, *J* = 0.9, 14.8 Hz, 1H), 4.64 (d, *J* = 8.7 Hz, 1H), 3.79 (s, 3H), 3.30 (s, 3H), 3.19 (s, 3H), 2.62-2.50 (m, 1H), 1.99-1.85 (m, 2H), 1.80-1.68 (m, 2H), 1.62-1.55 (m, 1H), 1.42-1.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 159.2, 149.6, 130.7, 129.0, 119.9, 114.3, 55.3, 48.7, 43.4, 41.7, 33.4 (d, 31Hz), 32.7, 25.9, 25.7; HRMS (EI) Calcd for $C_{19}H_{27}NO_4S_2^+$ 397.1376; found 397.1375.



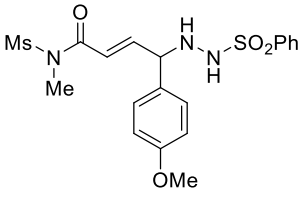
15ab

Colorless oil; (77.3 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.32-7.20 (m, 6H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.90 (d, *J* = 15.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.31-6.18 (m, 2H), 4.41 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.25 (s, 3H), 2.87-2.83 (m, 2H), 2.68-2.64 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 159.1, 144.9, 144.8, 143.1, 140.3, 136.1, 131.3, 130.0, 128.9, 128.8, 128.6, 128.5, 127.2, 126.5, 121.7, 114.2, 55.3, 51.3, 36.2, 33.2, 33.0, 21.6; HRMS (EI) Calcd for $C_{29}H_{31}NO_4S_2^+$ 521.1689; found 521.1690.



16ba

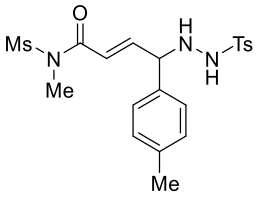
White solid; (66.5 mg, 71%); mp = 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.91 (dd, *J* = 6.4, 15.2 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.76 (dd, *J* = 1.2, 15.2 Hz, 1H), 6.14 (s, 1H), 4.56 (d, *J* = 6.2 Hz, 1H), 3.84 (s br, 1H), 3.78 (s, 3H), 3.29 (s, 3H), 3.22 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 159.8, 147.8, 144.4, 134.9, 129.8, 129.3, 129.1, 128.1, 122.3, 114.4, 64.8, 55.3, 41.7, 32.7, 21.6; HRMS (EI) Calcd for $C_{20}H_{25}N_3O_6S_2^+$ 467.1179; found. 467.1179.



16bb

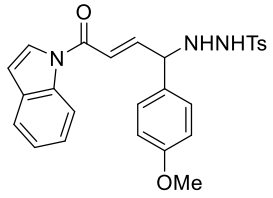
White foamy solid; (68.2 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.94 (dd, *J* = 6.6, 15.2 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.74 (dd, *J* = 1.1, 15.2 Hz, 1H), 6.15 (s, 1H), 4.55 (t, *J* = 4.9 Hz, 1H), 3.87 (s br, 1H), 3.78 (s, 3H), 3.29 (s, 3H),

3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 159.9, 147.8, 138.0, 133.4, 129.2, 129.14, 129.1, 128.1, 122.4, 114.5, 64.9, 55.3, 41.7, 32.7; HRMS (EI) Calcd for $C_{19}H_{23}N_3O_6S_2^+$ 453.1023; found 453.1025.



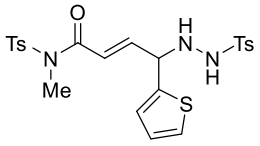
16ca

White foamy solid; (49.8 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.93 (dd, *J* = 6.4, 15.2 Hz, 1H), 6.77 (dd, *J* = 1.2, 15.2 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 4.58 (t, *J* = 5.6 Hz, 1H), 3.83 (dd, *J* = 2.1, 5.4 Hz, 1H), 3.30 (s, 3H), 3.22 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 147.7, 144.4, 138.7, 134.9, 134.3, 129.8, 129.76, 128.1, 127.8, 122.4, 65.1, 41.7, 32.7, 21.6, 21.2; HRMS (EI) Calcd for $C_{20}H_{25}N_3O_5S_2^+$ 451.1230; found 451.1228.



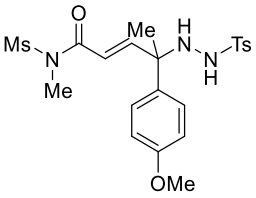
16la

White solid; (60.1 mg, 63%); mp = 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 3.8 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 3H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 6.2, 15.2 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.81 (dd, *J* = 1.2, 15.2 Hz, 1H), 6.65 (d, *J* = 3.8 Hz, 1H), 5.94 (s, 1H), 4.65 (d, *J* = 6.2 Hz, 1H), 3.80 (s, 1H), 3.79 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 160.0, 147.6, 144.5, 135.8, 135.1, 130.7, 129.8, 129.3, 129.2, 128.1, 125.0, 124.9, 123.9, 122.3, 120.9, 116.8, 114.5, 109.3, 64.9, 55.4, 21.6; HRMS (EI) Calcd for $C_{26}H_{25}N_3O_4S^+$ 475.1560; found 475.1560.



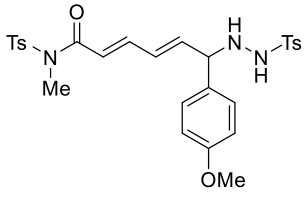
16ma

White solid; (77.1 mg, 74%); mp = 103-104 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 4H), 7.28 (dd, *J* = 1.2, 5.1 Hz, 1H), 6.99-6.95 (m, 2H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.75 (dd, *J* = 6.6, 15.2 Hz, 1H), 6.05 (d, *J* = 2.0 Hz, 1H), 4.79 (t, *J* = 6.7 Hz, 1H), 3.85 (dd, *J* = 2.1, 6.8 Hz, 1H), 3.27 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 145.2, 145.1, 144.4, 140.5, 135.9, 134.9, 130.1, 129.8, 128.2, 127.4, 127.1, 126.3, 126.2, 124.4, 60.9, 33.0, 21.7; HRMS (EI) Calcd for $C_{23}H_{25}N_3O_5S_3^+$ 519.0951; found 519.0952.



16na

White foamy solid; (73.3 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H),7.22 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 15.4 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 5.98 (s, 1H), 3.77 (s, 3H), 3.33 (s, 3H), 3.25 (s, 3H), 2.42 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 159.2, 152.4, 144.1, 134.7, 134.0, 129.6, 128.3, 127.5, 121.1, 114.0, 62.7, 55.3, 41.7, 32.8, 23.8, 21.6; HRMS (EI) Calcd for $C_{21}H_{27}N_3O_6S_2^+$ 481.1336; found 481.1336.



17aa

White solid; (90.2 mg, 79%); mp = 118-119 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.34-7.32 (m, 4H), 7.14 (dd, *J* = 11.2, 14.8 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.87-6.83 (m, 3H), 6.18 (dd, *J* = 11.0, 15.4 Hz, 1H), 5.94 (dd, *J* = 7.0, 13.3 Hz, 1H), 5.79 (s, 1H), 4.37 (d, *J* = 7.0 Hz, 1H), 3.90 (s br, 1H), 3.79 (s, 3H), 3.25 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 159.6, 145.0, 144.7, 144.3, 142.1, 136.0, 135.4, 130.3, 130.0, 129.7, 128.9, 128.2, 127.2, 122.1, 114.4, 65.3, 55.3, 33.0, 21.6; (EI) HRMS Calcd for $C_{28}H_{31}N_3O_6S_2^+$ 569.1649; found 569.1650.

4. Kinetic Study

4.1. General

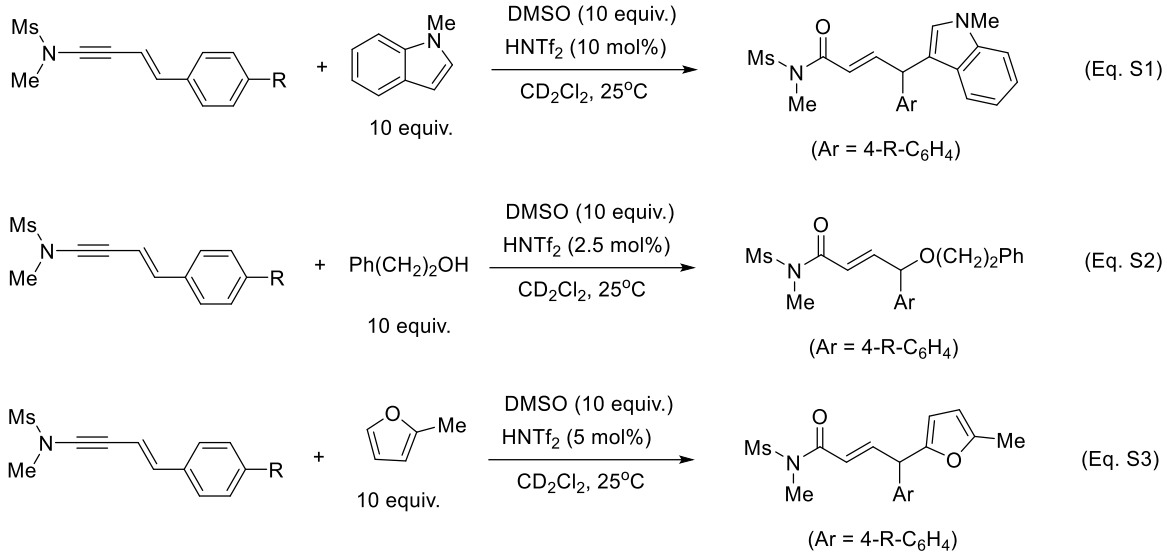
The reaction mixture was prepared in an NMR tube by adding: enynamides **4** (0.05 mmol), DMSO (0.50 mmol), *N*-Me-indole (0.50 mmol) and 1,2-diethylphthalate (internal reference) in CD_2Cl_2 (1.0 mL). To this mixture was added a stock solution of $HNTf_2$ (2.5 mol%; 50 μL of a stock made of 35.0 mg of $HNTf_2$ in 5.00 mL $CDCl_3$) and the progress of the reaction was monitored by ^1H NMR spectrometer (probe temperature at 298 K). For volumetric measurements, Finnpipette F1 from Thermo Scientific was used.

4.2. Hammett plot

A set of enynamides, **4b** (4-OMe), **4c** (4-Me), **4d** (4-H), **4e** (4-Cl), **4p** (4-Ph), and **4q** (4-Br) was chosen for a Hammett study to probe the electronic influence of the aryl substituent at C4 of enynamides (Table S1). Firstly, the k_{obs}'s of the reaction of enynamides **4** with *N*-Me-indole were measured at 298 K under the general conditions in 4.1 (Eq. S1). Similarly, the rates of the reactions of enynamides **4b-e, 4p-q** with $Ph(CH_2)_2OH$ and 2-methylfuran were obtained (Eq. S2 and S3, respectively). A plot of $\log(k_R/k_H)$ thus obtained was linearly proportional to the σ^+ values, with a slope of ρ = -1.32, -3.73, and -0.80 for the reactions with *N*-Me-indole, $Ph(CH_2)_2OH$, and 2-Me-furan, respectively. The negative ρ value (-1.3) with *N*-Me-indole indicated positive charge is developing in the transition state. The ρ value depended on the type of nucleophiles: from the highest negative ρ value (-3.7) with $Ph(CH_2)_2OH$, the corresponding turnover-limiting transition state has the most developed cationic charge. In contrast, less negative ρ value (-0.8) with 2-methylfuran indicated less buildup of positive charge in the transition state.

Table S1. Hammett analysis

R	σ_p	σ^+	σ^-	k_R (s^{-1}) for rxn (a)	$\log(k_R/k_H)$ for rxn (a)	k_R (s^{-1}) for rxn (b)	$\log(k_R/k_H)$ for rxn (b)	k_R (s^{-1}) for rxn (c)	$\log(k_R/k_H)$ for rxn (c)
p-OMe	-0.27	**-0.78**	-0.26	1.33×10^{-3}	0.996747	3.25×10^{-3}	2.937852	8.00×10^{-4}	0.552842
p-Me	0.14	**-0.31**	0.17	4.04×10^{-4}	0.479277	1.39×10^{-4}	1.568984	4.15×10^{-4}	0.267800
p-Ph	0.01	**-0.18**	0.02	2.53×10^{-4}	0.276016	4.53×10^{-5}	1.082067	3.82×10^{-4}	0.231815
p-H	0	**0**	0	1.34×10^{-4}	0.000000	3.75×10^{-6}	0.000000	2.24×10^{-4}	0.000000
p-Cl	0.24	**0.11**	0.19	9.88×10^{-5}	-0.132348	2.08×10^{-6}	-0.255968	1.38×10^{-4}	-0.210369
p-Br	0.23	**0.15**	0.25	7.67×10^{-5}	-0.242309	1.32×10^{-6}	-0.453457		


Ms
N
Me
R
+
Me
N
10 equiv.
DMSO (10 equiv.)
HNTf2 (10 mol%)
CD2Cl2, 25°C
O
NMe
Ms
N
Me
Ar
(Ar = 4-R-C6H4)
(Eq. S1)
Ms
N
Me
R
+
Ph(CH2)2OH
10 equiv.
DMSO (10 equiv.)
HNTf2 (2.5 mol%)
CD2Cl2, 25°C
O
Ms
N
Me
O(CH2)2Ph
Ar
(Ar = 4-R-C6H4)
(Eq. S2)
Ms
N
Me
R
+
O
Me
10 equiv.
DMSO (10 equiv.)
HNTf2 (5 mol%)
CD2Cl2, 25°C
O
Ms
N
Me
O
Me
Ar
(Ar = 4-R-C6H4)
(Eq. S3)

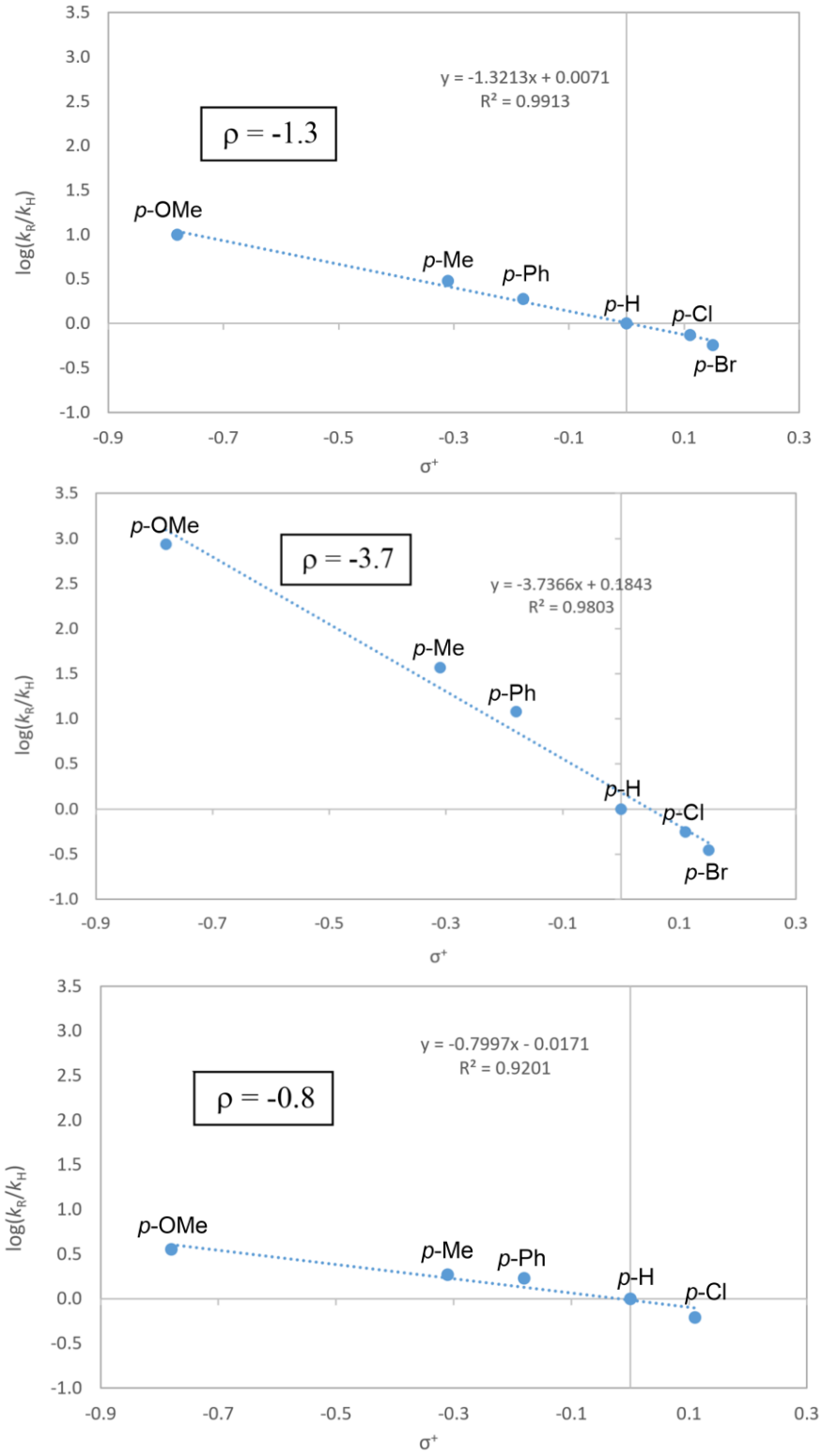
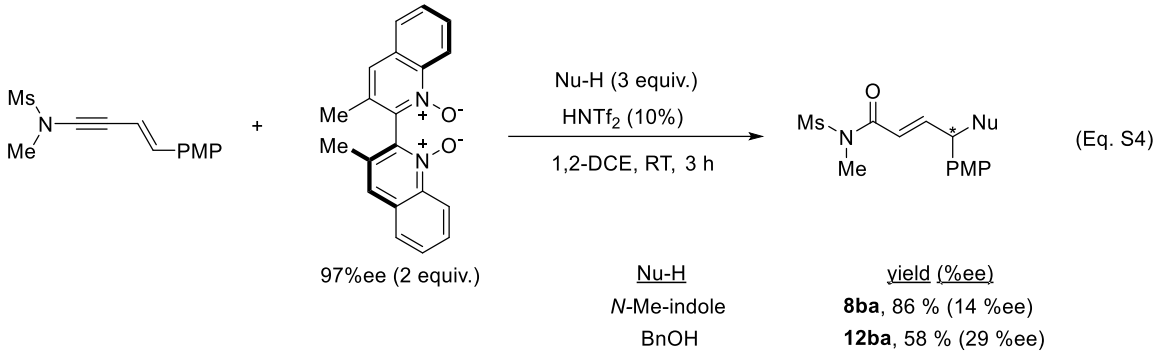


Figure S1. Hammett Plot

4.3. Asymmetric Induction Experiment

The reaction of enynamides **4b** was repeated with an enantiomerically enriched *N,N'*-dioxide[4a] as reported in our previous paper.[4] As shown in Eq. S4, a low level of asymmetric induction was observed (14%ee for **8ba**, and 29%ee for **12ba**) was obtained (For comparison, a similar reaction with ynamide gave 83 %ee of asymmetric induction).[4b]



4.4. Eyring analysis

The first-order rate constant was measured at each 298, 308, 318 and 328 K with a catalyst loading (5 mol%). The kinetic data and the corresponding plots of ln[**4b**] vs. time are given in Table S2 and Figure S2, respectively. These obtained first-order rate constants (k_{obs}) were plotted according to Eyring equation (Eq. S5) as in Figure S3.

$$\ln(k_{obs}/T) = -(\Delta H^{\ddagger}/R)(1/T) + \ln(k_B/h) + \Delta S^{\ddagger}/R \quad \text{.....(Eq. S5)}$$

where k_{obs} (observed rate constant), T (temperature, K), k_B (Boltzmann const.), h (Planck const.), R (molar gas constant)

From the slope and the y-intercept, activation enthalpy and entropy was measured to be $\Delta H^{\ddagger}$ = 83.5 kJmol^{-1} and $\Delta S^{\ddagger}$ = -37.6 JK^{-1}mol^{-1}, respectively (Figure S3).

Table S2. Kinetic data for temperature dependence study.

298 K		308 K		318 K		328 K	
Time (s)	ln[**4b**]	Time (s)	ln[**4b**]	Time (s)	[**4b**]	Time (s)	[**4**]
185	-3.024	230	-3.075	184	-3.182	184	-3.491
435	-3.055	390	-3.157	245	-3.254	245	-3.713
915	-3.123	570	-3.245	305	-3.337	305	-3.967
1515	-3.210	765	-3.307	365	-3.435	365	-4.177
2115	-3.291	1095	-3.464	425	-3.476	425	-4.397
3015	-3.447	1455	-3.628	545	-3.691	485	-4.623
3915	-3.581	1815	-3.808	725	-3.905	548	-4.888
5115	-3.787	2175	-3.990	905	-3.181	605	-5.010
6315	-4.957	2535	-4.141	1085	-3.383		
7515	-4.168	3015	-4.362	1325	-4.804		
k_{obs}	1.56 x 10^{-4}	k_{obs}	4.63 x 10^{-4}	k_{obs}	1.40 x 10^{-3}	k_{obs}	3.69 x 10^{-3}

[4] (a) Nakajima, M.; Saito, M.; Shiro, S. M.; Hashimoto, S.-I. *J. Am. Chem. Soc.* **1998**, *120*, 6419. (b) Patil, D. V.; Kim, S. W.; Nguyen, Q. H.; Kim, H.; Wang, S.; Hoang, T.; Shin, S. *Angew. Chem. Int. Ed.* **2017**, *56*, 3670.

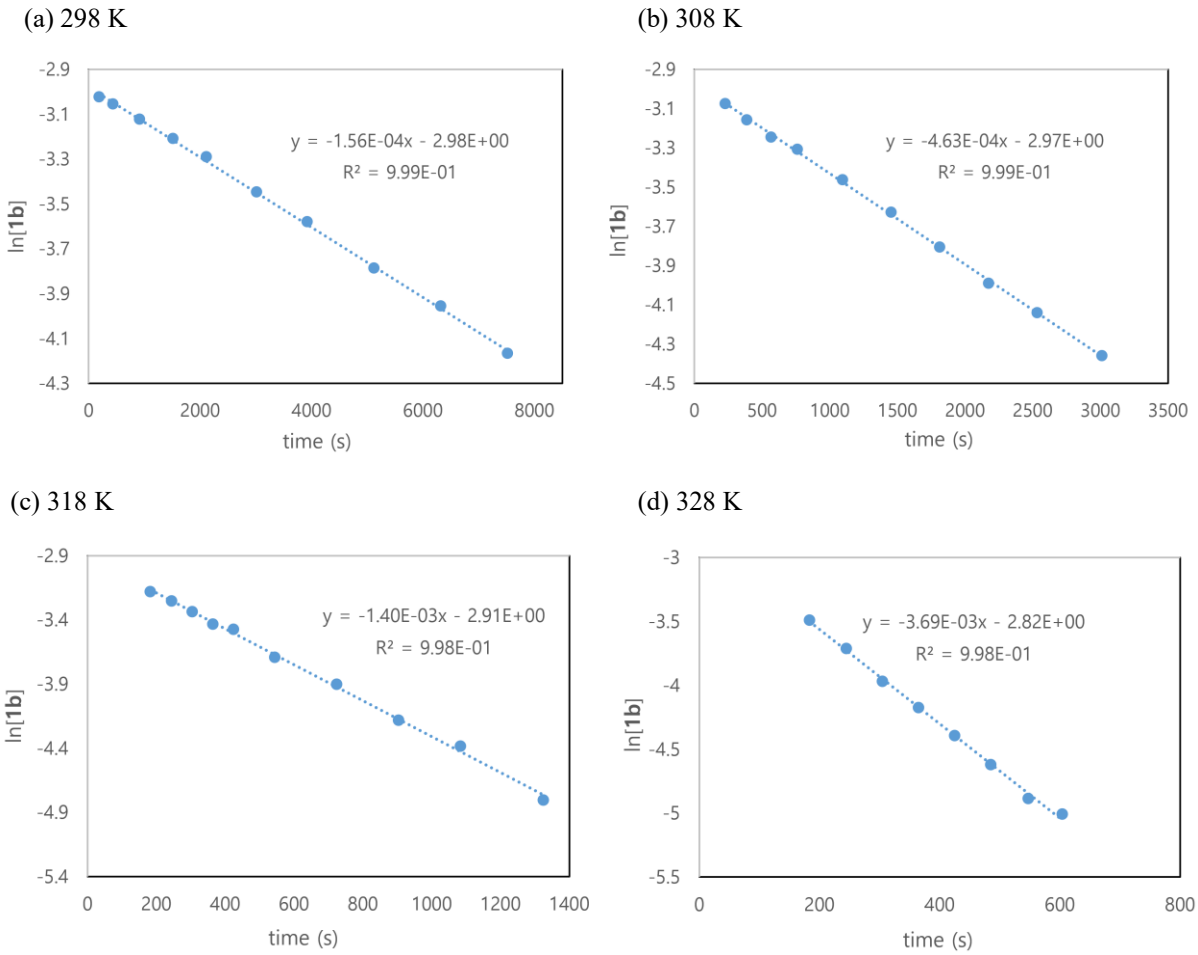


Figure S2. A plot of ln[**4b**] vs. time at (a) 298 K, (b) 308 K, (c) 318 K, and (d) 328 K.

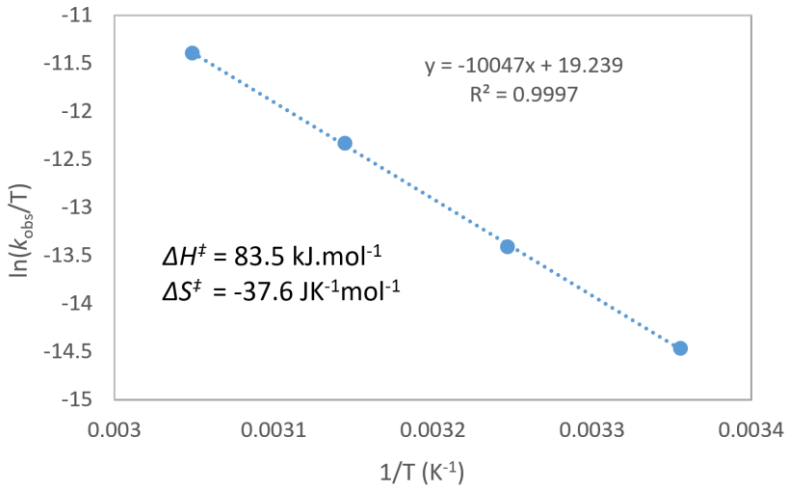


Figure S3. Eyring Plot: The reactions of enynamides **4b** with *N*-Me-indole

4.5. Reaction order

The dependence of k_{obs} on the concentration of DMSO and nucleophile (*N*-Me-indole) was studied under the following conditions: (**Figure S4**) for the reaction order in DMSO, **4b** (0.05 mmol), *N*-Me-indole (0.105 mmol), DMSO (0.06~0.12 mmol) and $HNTf_2$ (1.25 mol%) in CD_2Cl_2 (1.0 mL) at 298 K; (**Figure S5**) for the reaction order in *N*-Me-indole, **4b** (0.05 mmol), *N*-Me-indole (0.054-0.109 mmol), DMSO (0.06 mmol) and $HNTf_2$ (1.25 mol%) in CD_2Cl_2 at 298 K; (**Figure S6**) for the reaction order in $Ph(CH_2)_2OH$, **4b** (0.05 mmol), DMSO (0.20 mmol), $HNTf_2$ (1.25 mol%) and $Ph(CH_2)_2OH$ (0.15-0.30 mmol) in CD_2Cl_2 (2.0 mL) at 298 K. The results of these analysis are shown in Figure S4-6, respectively.

DMSO (equiv.)	[DMSO] (M)	k_{obs} (s^{-1})
1.2	0.060	1.94×10^{-4}
1.6	0.080	2.68×10^{-4}
2.0	0.100	2.36×10^{-4}
2.4	0.120	2.00×10^{-4}

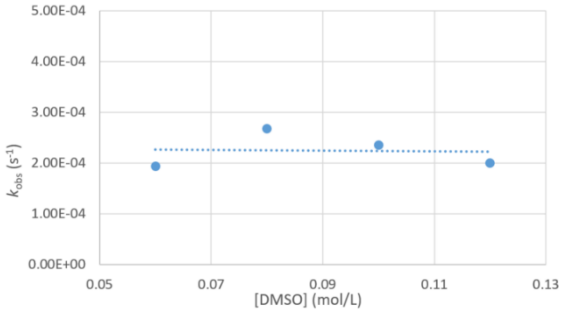


Figure S4. Reaction order with respect to DMSO

[*N*-Me-indole] (M)	k_{obs} (s^{-1})
0.0545	3.93×10^{-4}
0.0681	3.45×10^{-4}
0..0818	2.59×10^{-4}
0..0954	1.94×10^{-4}
0.1091	1.54×10^{-4}

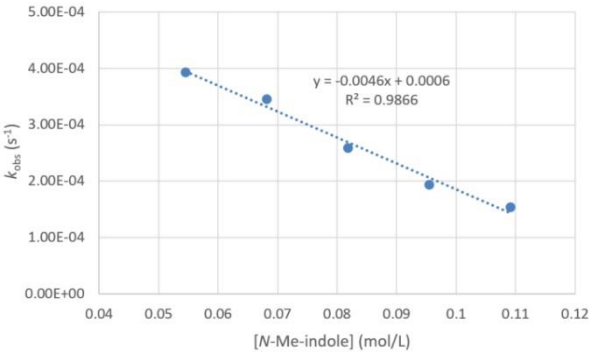


Figure S5. Reaction order with respect to *N*-Me-indole

[$Ph(CH_2)_2OH$] (M)	k_{obs} (s^{-1})
0.075	2.90×10^{-3}
0.100	3.73×10^{-3}
0.125	2.97×10^{-3}
0.150	3.48×10^{-3}

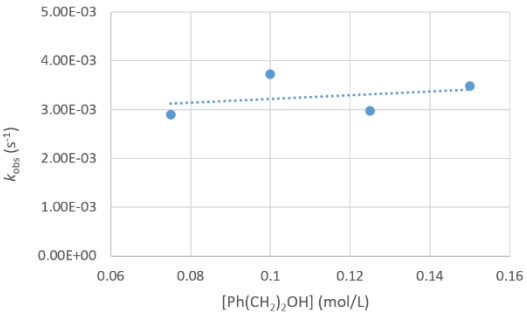


Figure S6. Reaction order with respect to $Ph(CH_2)_2OH$

[$HNTf_2$] (mol%)	k_{obs} (s^{-1})
1.25	1.29 x 10^{-4}
1.75	2.44 x 10^{-4}
2.25	5.09 x 10^{-4}
2.75	7.60 x 10^{-4}
3.25	8.67 x 10^{-4}

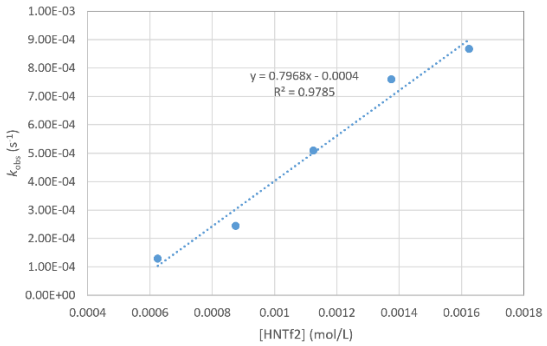
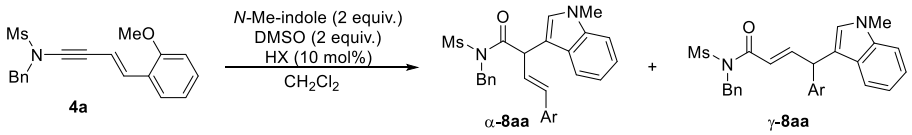


Figure S7. Reaction order with respect to $HNTf_2$

4.7. Test of other Brønsted acids

Considering the strong acidity of $HNTf_2$ in CH_2Cl_2 and there a number of potential Brønsted bases in the reaction mixture, including nucleophiles, oxidants, byproducts of oxidants and the products derived from the nucleophiles, it was of interest whether the corresponding conjugate acids (for example, protonated *N*-Me-indole or an oxonium ion from 2-phenylethanol) can catalyze the reaction. To elucidate this aspect, we conducted screening of Brønsted acids of varying pKa's and compared the outcome through crude ^{1}H NMR analysis. It turned out that Brønsted acids weaker than *p*-NO_2-$C_6H_4SO_3H$ (pKa = 6.4 in CH_3CN[5a]) do not catalyze the reaction of **4a** effectively and affords the **8aa** in only trace amount. Assuming that the conjugate acids of *N*-Me-indole (pKa = -2.30 in $HClO_4$[5b]) is a weaker acid than *p*-NO_2-$C_6H_4SO_3H$, the conjugate acid of *N*-Me-indole is not likely to be a true catalyst.

Table S3. Comparison of Brønsted acids cayalyst.[a]



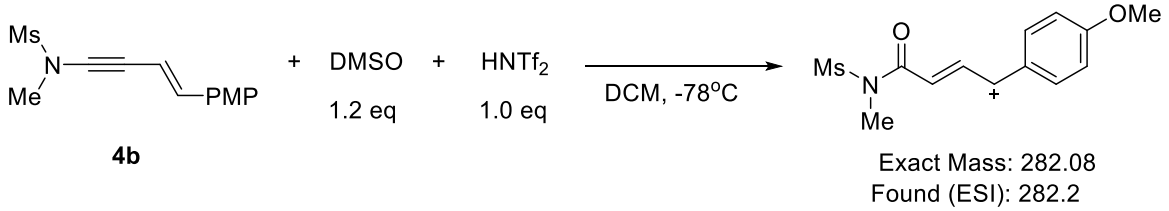
Entry	HX	Conditions	Yield	α : γ
1	$HNTf_2$	RT, 5 min	95%	1:5.6
2	TfOH	RT, 30 min	90%	1:5.0
3	*p*-$NO_2C_6H_4SO_3H$	RT, 1 h	36%	1:5.0
4	*p*-$ClC_6H_4SO_3H$	RT, 1 h	<35%	1:4.9
5	$TsOH{\cdot}H_2O$	40 °C, 24 h	<30%	1:4.9
6	(*S*)-CSA	40 °C, 24 h	<30%	1:5.9
7	MsOH	40 °C, 24 h	<30%	1:4.3
8	*p*-$NO_2C_6H_4CO_2H$	80 °C, 12 h	NR	-

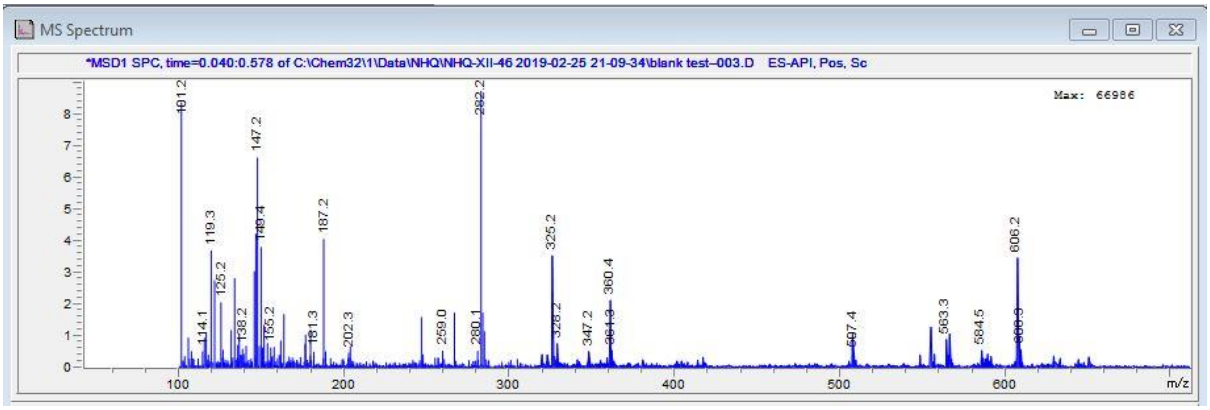
[a]The yield and the regioisomeric ratio (α/γ) was determined from the crude ^{1}H NMR with 1,2-diethylphthalate as an internal standard.

[5] (a) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391-395. (b) Hinman, R. L.; Lang, J. *J. Am. Chem. Soc.* **1964**, *86*, 3796-3806.

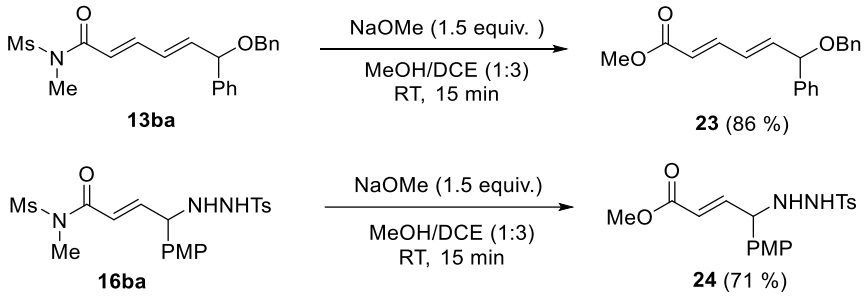
4.8. Mass analysis

To probe whether we can detect the dienolonium carbocation in the reaction mixture, we prepared a solution composed of enynamide **4b**, DMSO and $HNTf_2$ at -78 °C and subject it to ESI-MS analysis. The sample was prepared in the following manner: In a 4 mL vial was added enynamide **4b** (0.025 mmol, 6.6 mg) and DMSO (0.03 mmol, 2.3 mg) in 1 mL dichloromethane. A stock solution of $HNTf_2$ was made using $HNTf_2$ (0.025 mmol, 7.0 mg) in 1 mL CH_2Cl_2. Both solutions were cooled to -78 °C, followed by rapid addition of stock solution of $HNTf_2$ to the reaction mixture. LCMS sample was made by diluting 0.1 mL of reaction solution with 0.9 mL of pre-cooled (at -78°C) acetonitrile followed by injection to LCMS. A peak at m/z 282.2 was assigned as the dienolonium carbocation species.





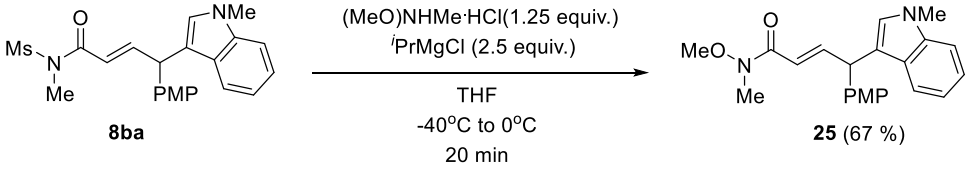
5. Synthetic Applications



In a 4-mL vial, **13ba** (or **16ba**) (0.05 mmol) was dissolved in a mixture of methanol and 1,2-dichloroethane (1:3), followed by the addition of NaOMe (4.1 mg, 0.075 mmol). The reaction mixture was stirred at room temperature for 15 minutes and purified by flash column chromatography.

23 (86 %); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (m, 11H), 6.41 (dd, *J* = 11.1, 15.3 Hz, 1H), 6.21 (dd, *J* = 6.0, 15.3 Hz, 1H), 5.90 (d, *J* = 15.4 Hz, 1H), 4.94 (d, *J* = 6.0 Hz, 1H), 4.49 (dd, *J* = 12.0, 21.5 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 144.0, 142.6, 140.0, 138.1, 128.8, 128.5, 128.3, 128.2, 127.8, 127.2, 121.5, 80.6, 70.3, 51.6; LRMS (ESI) Calcd for $C_{20}H_{20}O_3Na^+$ $[M+Na]^+$ 331.1; found 331.3.

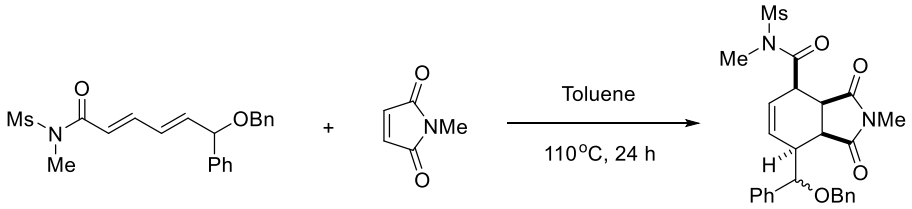
24 (71 %); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.85-6.80 (m, 3H), 5.82 (dd, *J* = 1.4, 15.8 Hz, 1H), 5.76 (s, 1H), 4.44 (d, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 159.8, 146.2, 144.4, 135.3, 129.8, 129.4, 129.0, 128.2, 122.6, 114.4, 64.4, 55.3, 51.7, 21.7; LRMS (ESI) Calcd for $C_{19}H_{22}N_2O_5SNa^+$ $[M+Na]^+$ 413.1; found 413.2.



In a flame-dried rb flask, *N,O*-dimethylhydroxylamine hydrochloride (7.3mg, 0.075 mmol) was dissolved in THF (2.4 ml), the solution was cooled to -20 °C before addition of isopropylmagnesium chloride (2.0 M in THF, 75 μL, 0.150 mmol). The mixture was stirred at -20 °C for 15 minutes and then at -40 °C, which generated a solution of (MeO)MeNMgCl. In another rb flask, substrate **8ba** (25.0 mg, 0.060 mmol) was dissolved in THF (1.8 ml) and the rb flask was placed in an ice-bath, before addition of (MeO)MeNMgCl solution above. The reaction mixture was stirred at 0°C until completion was indicated by TLC. The reaction mixture was quenched with saturated aq. ammonium chloride (3.0 mL) and extracted with ethyl acetate (3 x 3 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The residue purified by flash column chromatography (EtOAc:*n*Hex = 1:2~1:1) to afford 14.7 mg (67%) of **25** as pale-yellow oil.

25 (67 %); Pale-yellow oil.; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 15.3, 7.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.20 (m, 3H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.37 (d, *J* = 15.4 Hz, 1H), 5.08 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.55 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.0, 158.3, 148.8, 137.4, 134.1, 129.4, 127.3, 127.0, 121.7, 119.7, 119.1, 118.9, 115.9, 113.9,

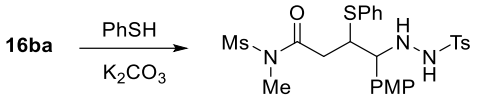
109.2, 61.7, 55.3, 44.8, 32.7; LRMS (APCI) Calcd for $C_{22}H_{24}N_2O_3$ $[M+H]^+$ 364.2, found. 365.2.



13ba 5.0 equiv. **26** (39 %, dr 8:1)

In a flame-dried 4 mL vial was dissolved **13ba** (20 mg, 0.052 mmol) in toluene, followed by addition of N-methylmaleimide (28.9 mg, 0.26 mmol). Reaction mixture was heated to 110 ºC for 24 h and purified by flash column chromatography (EtOAc:*n*Hex = 1:5~1:1).

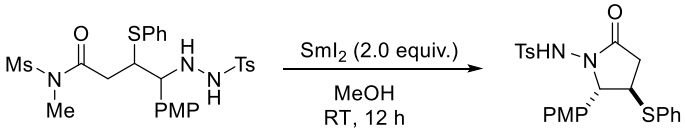
26 (39%); Colorless oil; (only spectra of major product) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.26 (m, 10H), 6.16 (dt, *J* = 2.9, 9.7 Hz, 1H), 5.62 (dt, *J* = 9.6, 3.2 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.52 (d, J = 10.4 Hz, 1H), 4.33 (d, J = 10.4 Hz, 1H), 3.92 (dd, *J* = 5.5, 8.3 Hz, 1H), 3.84-3.73 (m, 2H), 3.35 (s, 3H), 3.26 (s, 3H), 2.93 (s, 3H), 2.71-2.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 177.3, 176.5, 171.5, 140.2, 138.4, 129.3, 128.8, 128.5, 128.4, 128.2, 127.9, 127.7, 126.6, 80.7, 71.0, 43.7, 42.9, 42.2, 41.1, 40.6, 33.2, 24.9; LRMS (APCI) Calcd for $C_{26}H_{29}N_2O_6S^+$ $[M+H]^+$ 497.2, found. 497.2.



27 (81 %, dr 2:1)

Hydrazide **16ba** (150.0 mg, 0.32 mmol) and benzenethiol (42.0 mg, 0.38 mmol) was dissolved in dichloromethane, followed by K_2CO_2 (88.4 mg, 0.64mmol). The reaction mixture was stirred at room temperature for 4 hours (monitored by TLC). After completion, the reaction mixture was filtered, and the filtrate was concentrated and purified by column chromatography (EtOAc:*n*Hex = 1:3~1:2) to afford 150.3 mg (81%) of **27** as white solid.

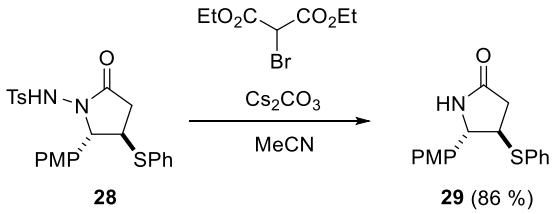
27 (81 %) White solid; (dr 2:1) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.31-7.18 (m, 10H), 7.11 (d, J = 8.6 Hz, 1H), 7.05 (d, J = 8.7 Hz, 2H), 6.83-6.79 (m, 3H), 5.65 (d, J = 1.7 Hz, 0.5H), 5.45 (d, J = 1.0 Hz, 1H), 4.49 (dd, J = 1.8, 6.6 Hz, 0.5H), 4.21 (t, J = 6 Hz, 0.5H), 4.06 (dd, J = 1.2, 8.7 Hz, 1H), 3.95-3.90 (m, 1H), 3.89-3.78 (m, 1.5H), 3.79 (s, 3H), 3.78 (s, 1.5H), 3.20 (s, 3H), 3.18 (s, 1.5H), 3.15 (s, 1.5H), 3.11 (s, 3H) 3.09-3.03 (m, 1.5H), 2.90-2.78 (m, 1.5H), 2.45 (s, 1.5H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.4, 171.7, 159.8, 159.6, 144.2, 135.7, 135.4, 134.1, 133.8, 132.2, 131.6, 129.8, 129.5, 129.1, 129.0, 128.9, 128.1, 127.9, 127.6, 127.4, 114.3, 114.1, 67.1, 66.2, 55.3, 50.1, 48.2, 41.4, 41.3, 39.8, 39.7, 32.4, 21.6; LRMS (APCI) Calcd for $C_{26}H_{31}N_3O_6S_3$ $[M+H]^+$ 577.1, found. 578.0.



27 (dr 2:1) **28** (58%, single dr)

In a flame-dried 4 mL vial was dissolved **27** (10 mg, 0.017 mmol) in MeOH (2ml). followed by addition of SmI_2 (0.1 M in THF, 0.35 mL, 0.0346 mmol). The reaction mixture was stirred at 35ºC for 12 hours. The reaction mixture was concentrated and purified by column chromatography (EtOAc:*n*Hex = 1:5~1:1) to afford 4.7 mg (58%) of **28** as white solid.

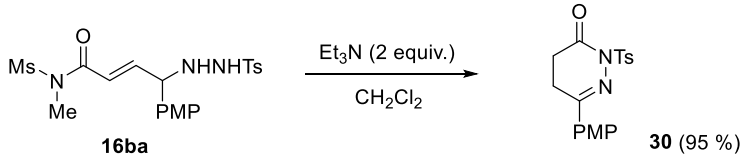
28 (58 %); White solid (single dr) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.52-7.50 (m, 2H), 7.41-7.36 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.09 (d, *J* = 1.9 Hz, 1H), 3.78 (s, 3H), 3.64 (dt, *J* =2.6, 8.1 Hz, 1H), 2.83 (dd, *J* =8.5, 18.3 Hz, 1H) 2.46 (s, 3H), 2.28 (dt, *J* =2.8, 18.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.2, 160.0, 145.2, 133.9, 133.5, 133.0, 129.8, 129.6, 129.4, 129.0, 128.6, 127.7, 114.7, 68.4, 55.5, 45.8, 33.7, 22.0; LRMS (APCI) Calcd for $C_{24}H_{24}N_2O_4S_2$ $[M+H]^+$ 468.1, found. 469.1.



28 **29** (86 %)

In a flame-dried 4 mL vial **28** (4.7 mg, 0.01 mmol) and Cs_2CO_3 (8.2 mg, 0.025 mmol) was dissolved in acetonitrile (0.2 ml), followed by addition of diethyl bromomalonate (3.4 μL, 0.02 mmol). The reaction mixture was stirred at 35°C for 36 hours. The reaction mixture was quenched with saturated aq. ammonium chloride (0.4 mL) and extracted with ethyl acetate (3 x 0.5 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The residue purified by flash column chromatography (EtOAc:*n*Hex = 1:5~1:1) to afford 1.0 mg (86%) of **29** as colorless oil.

29 (86 %); Colorless oil; (Single dr) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.30-7.27 (m, 3H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 1H), 4.57 (d, *J* = 5.2 Hz, 1H), 3.80 (s, 3H), 3.65 (ddd, *J* = 8.4, 6.6, 5.2 Hz, 1H), 2.90 (dd, *J* = 17.5, 8.4 Hz, 1H), 2.46 (dd, *J* =17.5, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 175.1, 159.7, 133.1, 132.7, 132.0, 129.2, 127.9, 127.2, 114.3, 63.5, 55.4, 50.8, 37.2; LRMS (APCI) Calcd for $C_{17}H_{17}NO_2S$ $[M+H]^+$ 299.1, found. 300.2.



16ba **30** (95 %)

In a 4-mL vial, **16ba** (5.0 mg, 0.01 mmol) was dissolved in dichloromethane(0.4ml), followed by the addition of Triethylamine (3.0 μL, 0.02 mmol). The reaction mixture was stirred at room temperature for 36 hours. The reaction mixture was concentrated and purified by column chromatography (EtOAc:*n*Hex = 1:1) to afford 3.3 mg (95%) of **30** as white solid.

30 (95 %); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 161.8, 154.3, 145.2, 134.8, 129.5, 129.0, 128.2, 126.9, 114.1, 55.5, 29.4, 22.4, 21.7; LRMS (APCI) Calcd for $C_{18}H_{18}N_2O_4S$ $[M+H]^+$ 358.1, found. 359.0.

5. Single Crystal X-ray Crystallographic Data on 16ma

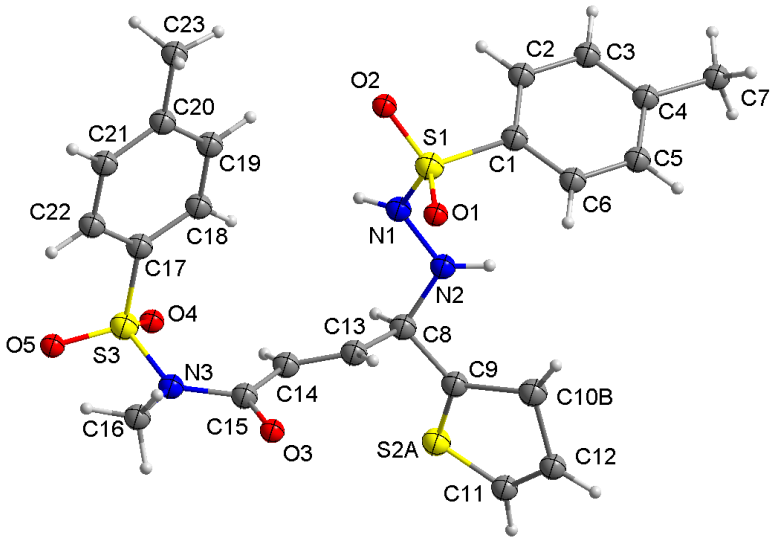


Figure S8. ORTEP Drawing of **16ma**

Table S4. Crystal data and structure refinement for NHQ-IX-58 (**16ma**).

Identification code	NHQ-IX-58	
Empirical formula	C23 H25 N3 O5 S3	
Formula weight	519.64	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7689(3) Å	α= 84.839(3)°.
	b = 12.7180(6) Å	β= 81.171(2)°.
	c = 12.8936(6) Å	γ = 79.286(3)°.
Volume	1234.43(10) $Å^3$	
Z	2	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	0.340 mm^{-1}	
F(000)	544	
Crystal size	0.274 x 0.132 x 0.067 mm^3	
Theta range for data collection	1.602 to 28.239°.	
Index ranges	-10<=h<=9, -16<=k<=16, -17<=l<=17	
Reflections collected	21026	
Independent reflections	6081 [R(int) = 0.0412]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Multi-scan SADABS	
Max. and min. transmission	0.7457 and 0.7097	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6081 / 0 / 307	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1408	
R indices (all data)	R1 = 0.0741, wR2 = 0.1535	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.712 and -0.652 e.$Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for NHQ-IX-58. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6834(1)	7956(1)	1402(1)	29(1)
S(2A)	2904(1)	10308(1)	4027(1)	32(1)
C(10A)	2488(2)	8968(2)	5865(2)	62(1)
S(2B)	2488(2)	8968(2)	5865(2)	62(1)
C(10B)	2904(1)	10308(1)	4027(1)	32(1)
S(3)	2712(1)	4147(1)	3853(1)	40(1)
O(1)	5175(2)	8346(2)	1030(2)	40(1)
O(2)	7992(2)	7051(1)	949(2)	38(1)
O(3)	-69(2)	6881(2)	3268(2)	40(1)
O(4)	3611(3)	4422(2)	4642(2)	49(1)
O(5)	1926(3)	3207(2)	4019(2)	61(1)
N(1)	6454(3)	7590(2)	2662(2)	28(1)
N(2)	5493(3)	8453(2)	3264(2)	29(1)
N(3)	1041(3)	5159(2)	3667(2)	35(1)
C(1)	8002(3)	9029(2)	1330(2)	27(1)
C(2)	9826(3)	8803(2)	1309(2)	29(1)
C(3)	10753(3)	9629(2)	1336(2)	33(1)
C(4)	9861(4)	10680(2)	1402(2)	35(1)
C(5)	8041(4)	10886(2)	1409(2)	39(1)
C(6)	7099(4)	10076(2)	1371(2)	34(1)
C(7)	10856(5)	11571(2)	1491(2)	51(1)
C(8)	4242(3)	8098(2)	4123(2)	26(1)
C(9)	3288(3)	9071(2)	4684(2)	26(1)
C(11)	1554(3)	10176(2)	5952(2)	33(1)
C(12)	1714(4)	10856(2)	5094(2)	36(1)
C(13)	2924(3)	7585(2)	3699(2)	26(1)
C(14)	2529(3)	6638(2)	4052(2)	28(1)
C(15)	1104(3)	6256(2)	3638(2)	28(1)
C(16)	-410(4)	4897(3)	3164(3)	52(1)
C(17)	4114(4)	4089(2)	2648(2)	36(1)
C(18)	5373(4)	4751(2)	2415(2)	40(1)
C(19)	6436(4)	4700(2)	1460(3)	45(1)

C(20)	6278(4)	3998(2)	719(2)	46(1)
C(21)	4995(4)	3356(2)	969(3)	52(1)
C(22)	3924(4)	3388(2)	1924(3)	47(1)
C(23)	7466(5)	3936(3)	-318(3)	67(1)

Table S6. Bond lengths [Å] and angles [°] for NHQ-IX-58.

S(1)-O(1)	1.4302(18)
S(1)-O(2)	1.4320(18)
S(1)-N(1)	1.647(2)
S(1)-C(1)	1.762(2)
S(2A)-C(12)	1.665(3)
S(2A)-C(9)	1.716(2)
C(10A)-C(9)	1.557(3)
C(10A)-C(11)	1.578(3)
C(10A)-H(10A)	0.9500
S(2B)-C(9)	1.557(3)
S(2B)-C(11)	1.578(3)
C(10B)-C(12)	1.665(3)
C(10B)-C(9)	1.716(2)
C(10B)-H(10B)	0.9500
S(3)-O(4)	1.421(2)
S(3)-O(5)	1.426(2)
S(3)-N(3)	1.678(2)
S(3)-C(17)	1.754(3)
O(3)-C(15)	1.218(3)
N(1)-N(2)	1.427(3)
N(1)-H(1A)	0.8800
N(2)-C(8)	1.455(3)
N(2)-H(2A)	0.8800
N(3)-C(15)	1.403(3)
N(3)-C(16)	1.484(3)
C(1)-C(6)	1.387(3)
C(1)-C(2)	1.389(3)
C(2)-C(3)	1.385(3)
C(2)-H(2B)	0.9500
C(3)-C(4)	1.390(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.388(4)
C(4)-C(7)	1.506(4)
C(5)-C(6)	1.378(4)
C(5)-H(5A)	0.9500

C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.503(3)
C(8)-C(13)	1.503(3)
C(8)-H(8A)	1.0000
C(11)-C(12)	1.347(4)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.322(3)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.474(3)
C(14)-H(14A)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.387(4)
C(17)-C(22)	1.389(4)
C(18)-C(19)	1.372(4)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.399(4)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.385(5)
C(20)-C(23)	1.503(5)
C(21)-C(22)	1.375(5)
C(21)-H(21A)	0.9500
C(22)-H(22A)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

O(1)-S(1)-O(2)	119.80(11)
O(1)-S(1)-N(1)	108.60(11)
O(2)-S(1)-N(1)	104.38(11)
O(1)-S(1)-C(1)	108.62(12)
O(2)-S(1)-C(1)	109.05(11)

N(1)-S(1)-C(1)	105.45(11)
C(12)-S(2A)-C(9)	91.94(13)
C(9)-C(10A)-C(11)	96.81(18)
C(9)-C(10A)-H(10A)	131.6
C(11)-C(10A)-H(10A)	131.6
C(9)-S(2B)-C(11)	96.81(18)
C(12)-C(10B)-C(9)	91.94(13)
C(12)-C(10B)-H(10B)	134.0
C(9)-C(10B)-H(10B)	134.0
O(4)-S(3)-O(5)	119.46(13)
O(4)-S(3)-N(3)	107.99(12)
O(5)-S(3)-N(3)	105.08(13)
O(4)-S(3)-C(17)	109.63(14)
O(5)-S(3)-C(17)	108.59(14)
N(3)-S(3)-C(17)	105.10(12)
N(2)-N(1)-S(1)	112.07(15)
N(2)-N(1)-H(1A)	124.0
S(1)-N(1)-H(1A)	124.0
N(1)-N(2)-C(8)	112.36(18)
N(1)-N(2)-H(2A)	123.8
C(8)-N(2)-H(2A)	123.8
C(15)-N(3)-C(16)	114.6(2)
C(15)-N(3)-S(3)	126.10(17)
C(16)-N(3)-S(3)	116.34(18)
C(6)-C(1)-C(2)	120.6(2)
C(6)-C(1)-S(1)	120.35(19)
C(2)-C(1)-S(1)	118.90(18)
C(3)-C(2)-C(1)	119.9(2)
C(3)-C(2)-H(2B)	120.1
C(1)-C(2)-H(2B)	120.1
C(2)-C(3)-C(4)	120.2(2)
C(2)-C(3)-H(3A)	119.9
C(4)-C(3)-H(3A)	119.9
C(5)-C(4)-C(3)	118.8(2)
C(5)-C(4)-C(7)	121.0(3)
C(3)-C(4)-C(7)	120.3(3)
C(6)-C(5)-C(4)	121.8(2)

C(6)-C(5)-H(5A)	119.1
C(4)-C(5)-H(5A)	119.1
C(5)-C(6)-C(1)	118.7(2)
C(5)-C(6)-H(6A)	120.6
C(1)-C(6)-H(6A)	120.6
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(2)-C(8)-C(9)	107.63(19)
N(2)-C(8)-C(13)	110.17(19)
C(9)-C(8)-C(13)	109.29(19)
N(2)-C(8)-H(8A)	109.9
C(9)-C(8)-H(8A)	109.9
C(13)-C(8)-H(8A)	109.9
C(8)-C(9)-S(2B)	120.69(19)
C(8)-C(9)-C(10A)	120.69(19)
C(8)-C(9)-S(2A)	121.32(17)
C(10A)-C(9)-S(2A)	117.82(16)
C(8)-C(9)-C(10B)	121.32(17)
S(2B)-C(9)-C(10B)	117.82(16)
C(12)-C(11)-C(10A)	118.4(2)
C(12)-C(11)-S(2B)	118.4(2)
C(12)-C(11)-H(11)	120.8
C(10A)-C(11)-H(11)	120.8
C(11)-C(12)-S(2A)	115.0(2)
C(11)-C(12)-C(10B)	115.0(2)
C(11)-C(12)-H(12)	122.5
S(2A)-C(12)-H(12)	122.5
C(14)-C(13)-C(8)	123.8(2)
C(14)-C(13)-H(13A)	118.1
C(8)-C(13)-H(13A)	118.1
C(13)-C(14)-C(15)	118.9(2)
C(13)-C(14)-H(14A)	120.5
C(15)-C(14)-H(14A)	120.5

O(3)-C(15)-N(3)	117.7(2)
O(3)-C(15)-C(14)	121.3(2)
N(3)-C(15)-C(14)	121.0(2)
N(3)-C(16)-H(16A)	109.5
N(3)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(3)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	120.5(3)
C(18)-C(17)-S(3)	120.3(2)
C(22)-C(17)-S(3)	119.2(2)
C(19)-C(18)-C(17)	119.1(3)
C(19)-C(18)-H(18A)	120.4
C(17)-C(18)-H(18A)	120.4
C(18)-C(19)-C(20)	121.5(3)
C(18)-C(19)-H(19A)	119.2
C(20)-C(19)-H(19A)	119.2
C(21)-C(20)-C(19)	118.0(3)
C(21)-C(20)-C(23)	120.8(3)
C(19)-C(20)-C(23)	121.2(3)
C(22)-C(21)-C(20)	121.4(3)
C(22)-C(21)-H(21A)	119.3
C(20)-C(21)-H(21A)	119.3
C(21)-C(22)-C(17)	119.4(3)
C(21)-C(22)-H(22A)	120.3
C(17)-C(22)-H(22A)	120.3
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2 x 10^3$) for NHQ-IX-58. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

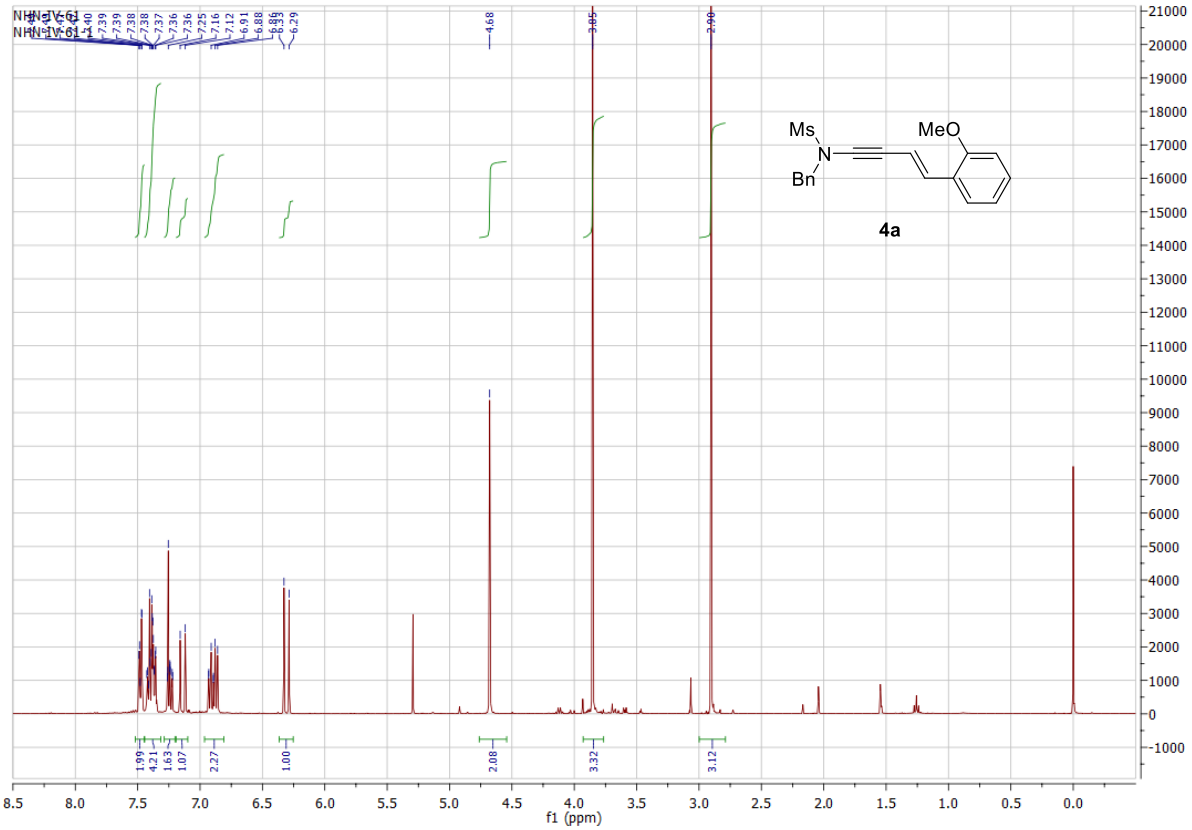
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	24(1)	30(1)	34(1)	-10(1)	-3(1)	-6(1)
S(2A)	33(1)	31(1)	31(1)	-4(1)	-1(1)	-7(1)
C(10A)	42(1)	74(1)	74(1)	-38(1)	-1(1)	-11(1)
S(2B)	42(1)	74(1)	74(1)	-38(1)	-1(1)	-11(1)
C(10B)	33(1)	31(1)	31(1)	-4(1)	-1(1)	-7(1)
S(3)	49(1)	25(1)	51(1)	7(1)	-18(1)	-10(1)
O(1)	31(1)	48(1)	45(1)	-10(1)	-14(1)	-7(1)
O(2)	36(1)	34(1)	46(1)	-18(1)	4(1)	-9(1)
O(3)	30(1)	38(1)	56(1)	4(1)	-18(1)	-7(1)
O(4)	63(1)	37(1)	51(1)	7(1)	-30(1)	-4(1)
O(5)	75(2)	31(1)	80(2)	14(1)	-15(1)	-24(1)
N(1)	24(1)	24(1)	36(1)	-4(1)	-1(1)	-4(1)
N(2)	26(1)	26(1)	36(1)	-8(1)	4(1)	-9(1)
N(3)	32(1)	29(1)	48(1)	2(1)	-13(1)	-14(1)
C(1)	29(1)	27(1)	26(1)	-4(1)	-2(1)	-6(1)
C(2)	28(1)	31(1)	29(1)	-5(1)	0(1)	-4(1)
C(3)	30(1)	43(1)	28(1)	-2(1)	-2(1)	-14(1)
C(4)	48(2)	36(1)	25(1)	4(1)	-8(1)	-21(1)
C(5)	53(2)	27(1)	37(2)	1(1)	-10(1)	-5(1)
C(6)	32(1)	30(1)	39(1)	0(1)	-6(1)	-2(1)
C(7)	75(2)	44(2)	44(2)	6(1)	-15(2)	-33(2)
C(8)	24(1)	28(1)	28(1)	0(1)	-5(1)	-6(1)
C(9)	23(1)	29(1)	29(1)	-4(1)	-4(1)	-8(1)
C(11)	32(1)	39(1)	30(1)	-9(1)	0(1)	-14(1)
C(12)	38(2)	36(1)	39(1)	-5(1)	-7(1)	-12(1)
C(13)	23(1)	29(1)	26(1)	-2(1)	-2(1)	-6(1)
C(14)	25(1)	27(1)	34(1)	1(1)	-6(1)	-5(1)
C(15)	26(1)	28(1)	30(1)	2(1)	-5(1)	-8(1)
C(16)	45(2)	45(2)	74(2)	-8(2)	-22(2)	-20(1)
C(17)	36(1)	22(1)	54(2)	-4(1)	-19(1)	-3(1)
C(18)	35(2)	31(1)	58(2)	-12(1)	-14(1)	-5(1)
C(19)	33(2)	36(2)	66(2)	-9(1)	-10(1)	-1(1)

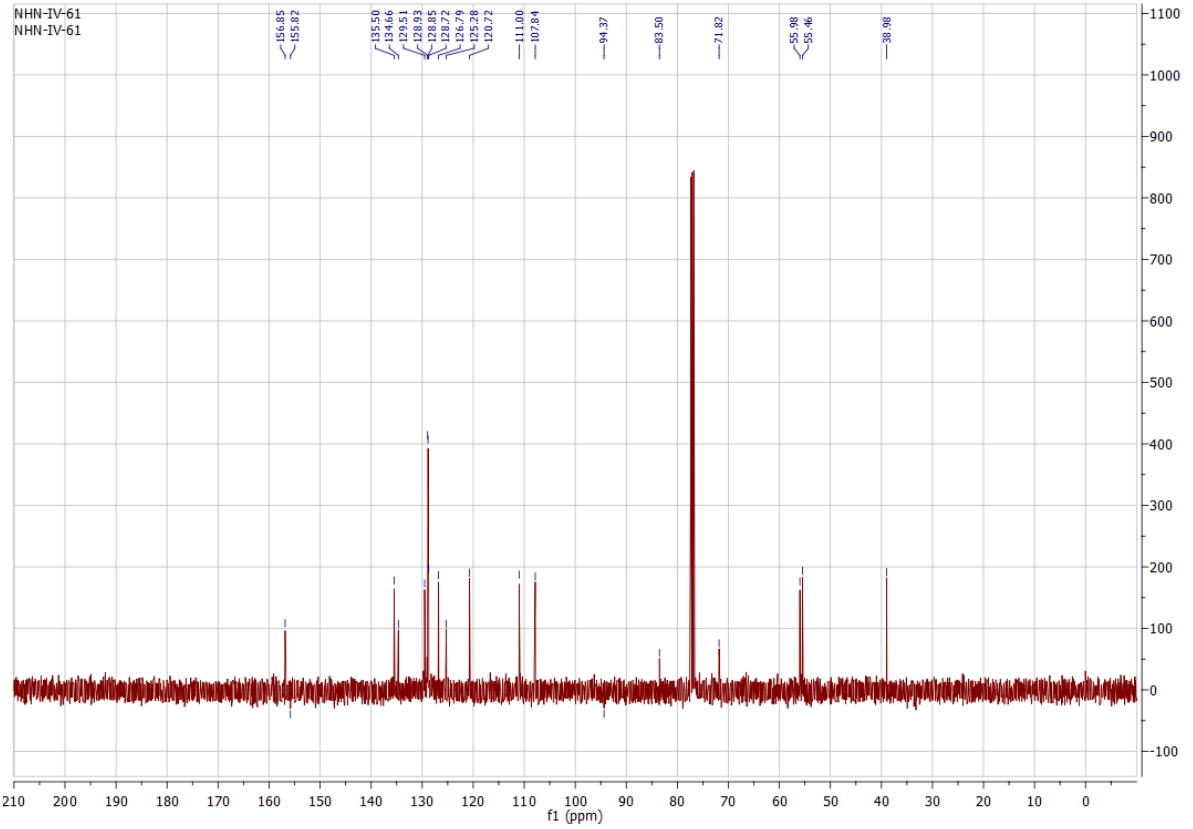
C(20)	40(2)	39(2)	56(2)	-8(1)	-14(1)	13(1)
C(21)	51(2)	38(2)	71(2)	-24(2)	-29(2)	7(1)
C(22)	45(2)	32(1)	71(2)	-14(1)	-24(2)	-7(1)
C(23)	55(2)	65(2)	68(2)	-11(2)	-10(2)	26(2)

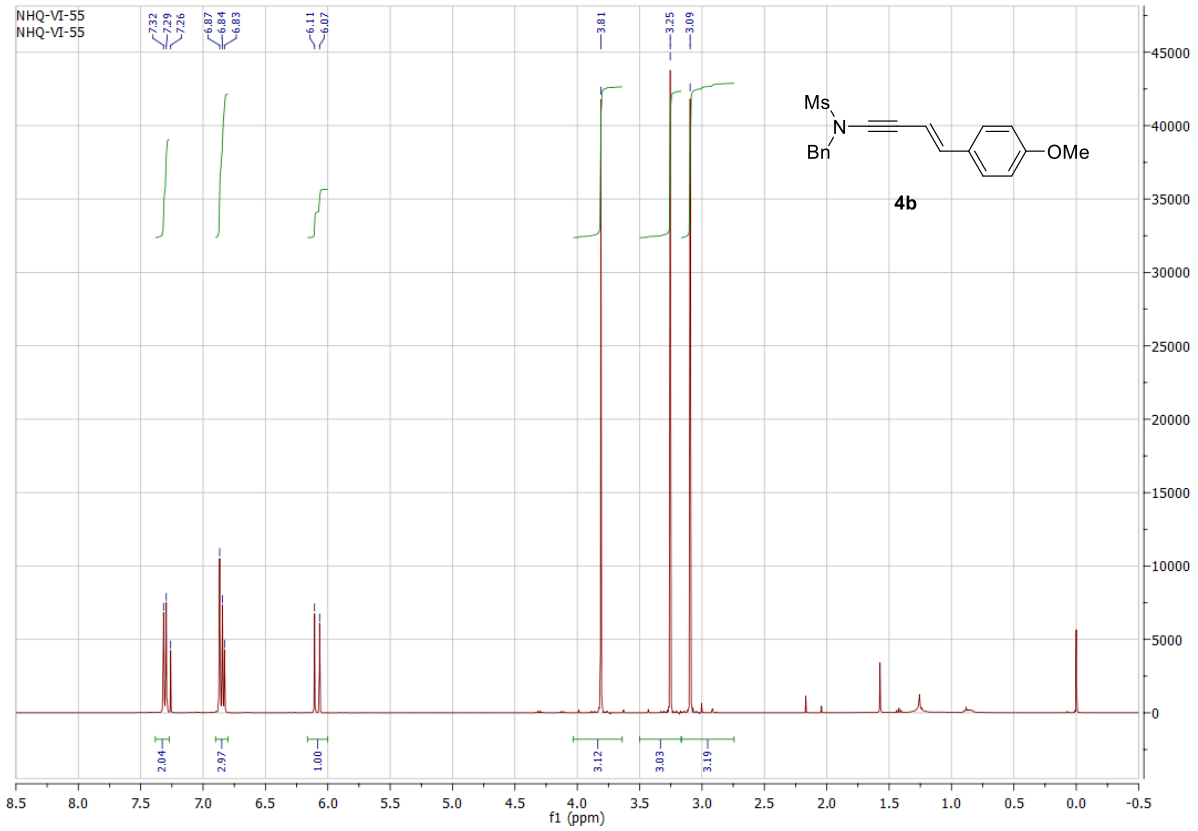
Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10^{-3}) for NHQ-IX-58.

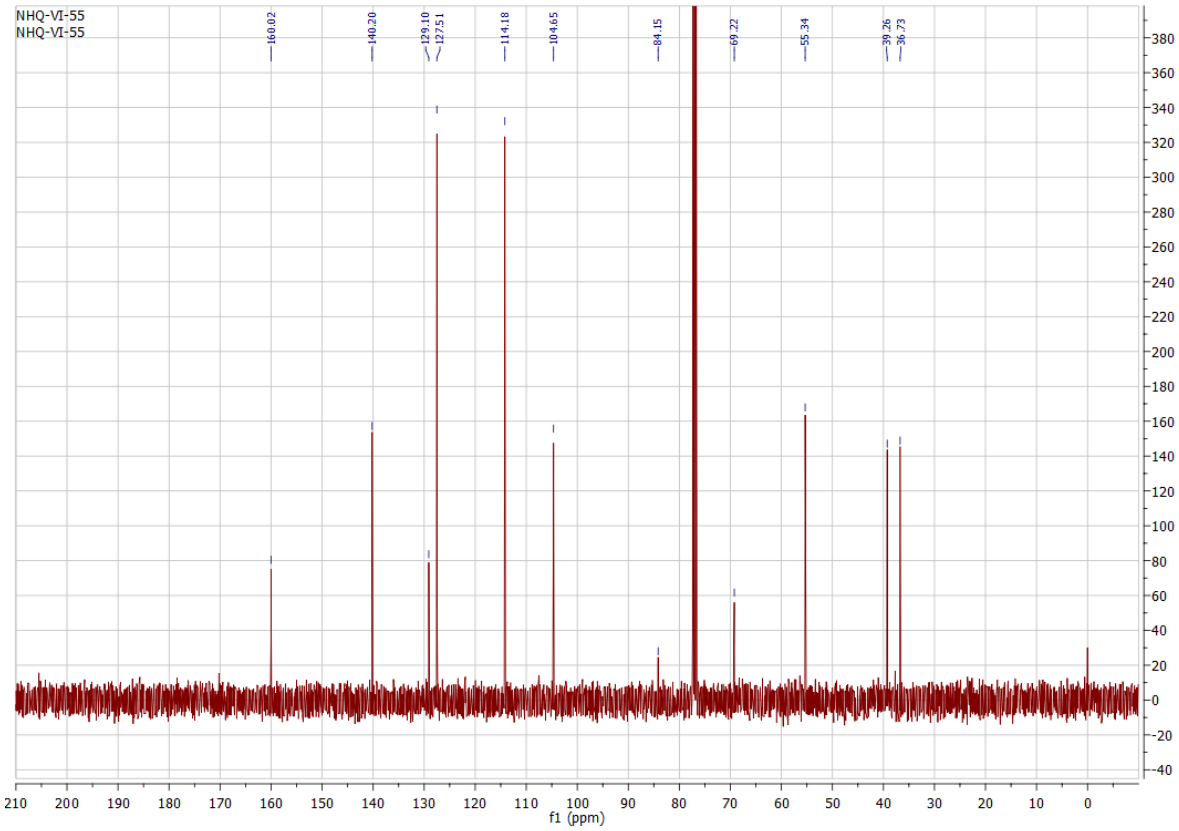
	x	y	z	U(eq)
H(10A)	2545	8373	6368	74
H(10B)	3239	10576	3328	38
H(1A)	6802	6939	2932	34
H(2A)	5641	9124	3132	35
H(2B)	10436	8084	1277	35
H(3A)	12003	9476	1308	39
H(5A)	7429	11605	1440	47
H(6A)	5854	10233	1374	40
H(7A)	12119	11276	1472	77
H(7B)	10689	12106	902	77
H(7C)	10408	11909	2156	77
H(8A)	4887	7576	4619	32
H(11)	893	10418	6596	40
H(12)	1188	11592	5096	44
H(13A)	2341	7962	3145	31
H(14A)	3152	6210	4564	34
H(16A)	-360	4119	3218	77
H(16B)	-1551	5247	3521	77
H(16C)	-275	5154	2422	77
H(18A)	5498	5232	2910	48
H(19A)	7299	5152	1299	54
H(21A)	4852	2884	470	62
H(22A)	3063	2935	2087	57
H(23A)	8285	4443	-357	100
H(23B)	8140	3207	-380	100
H(23C)	6748	4117	-892	100

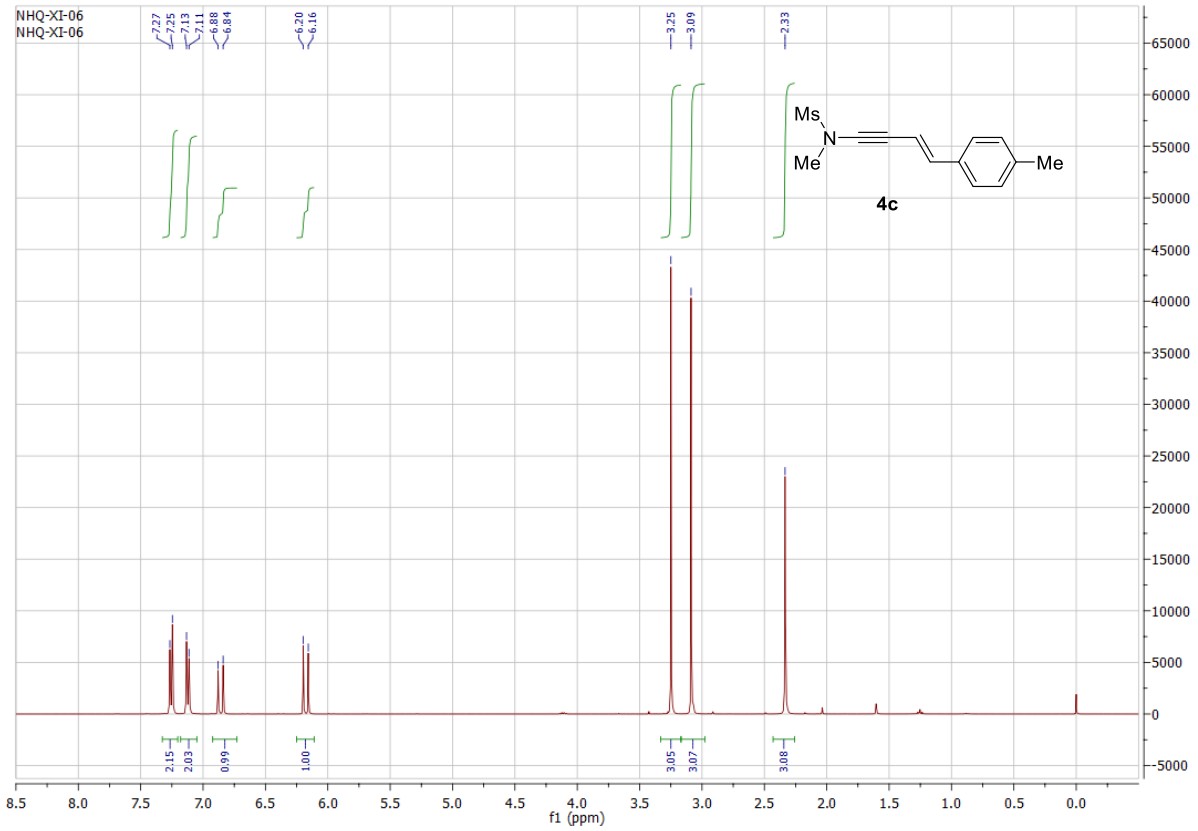
6. Copy of ^{1}H and ^{13}C NMR Spectra

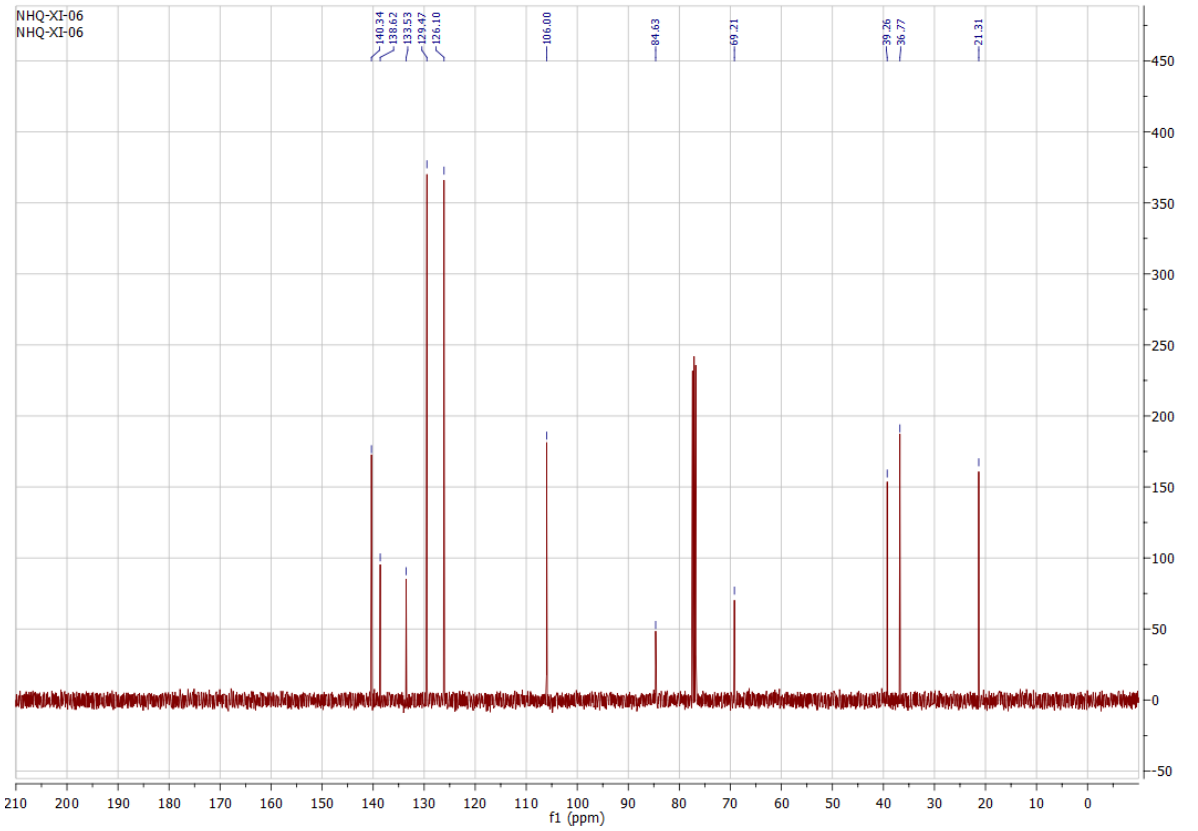

NHN-IV-61
NHN-IV-61
Ms
N
Bn
MeO
4a
f1 (ppm)

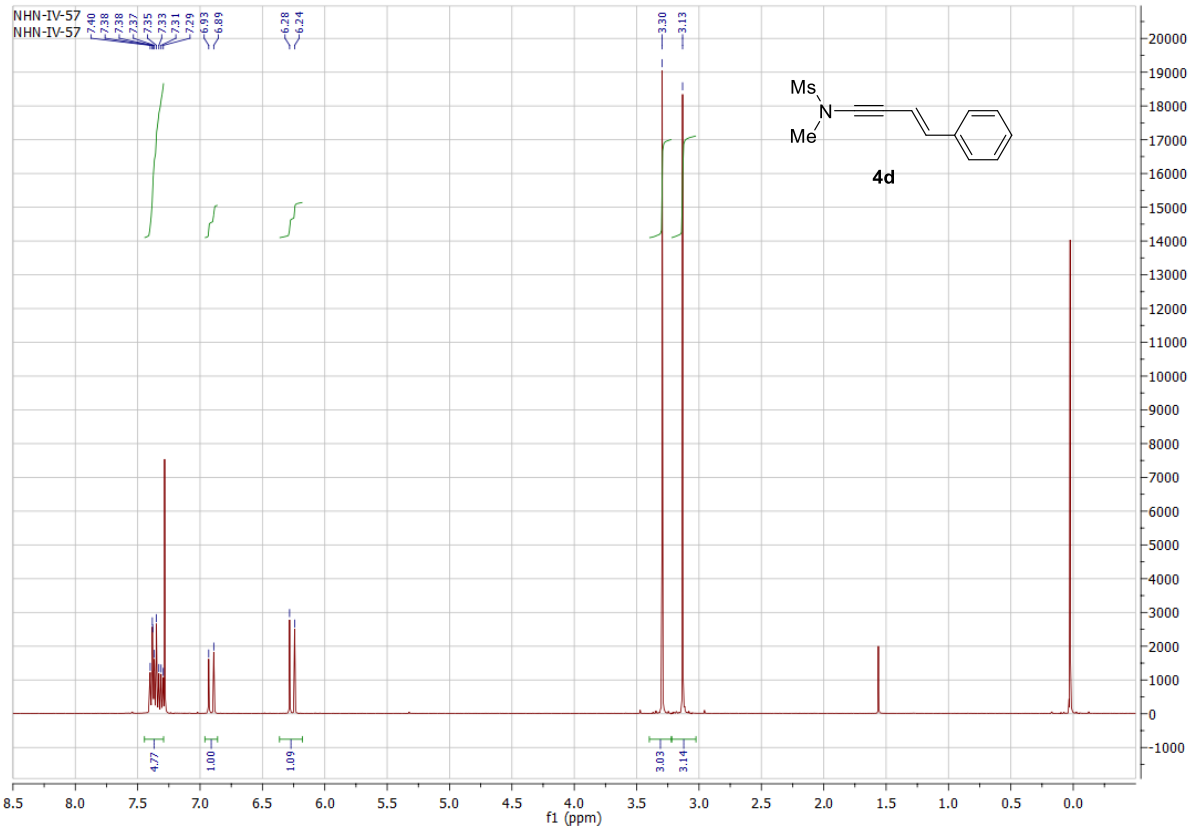

NHN-IV-61
NHN-IV-61
f1 (ppm)

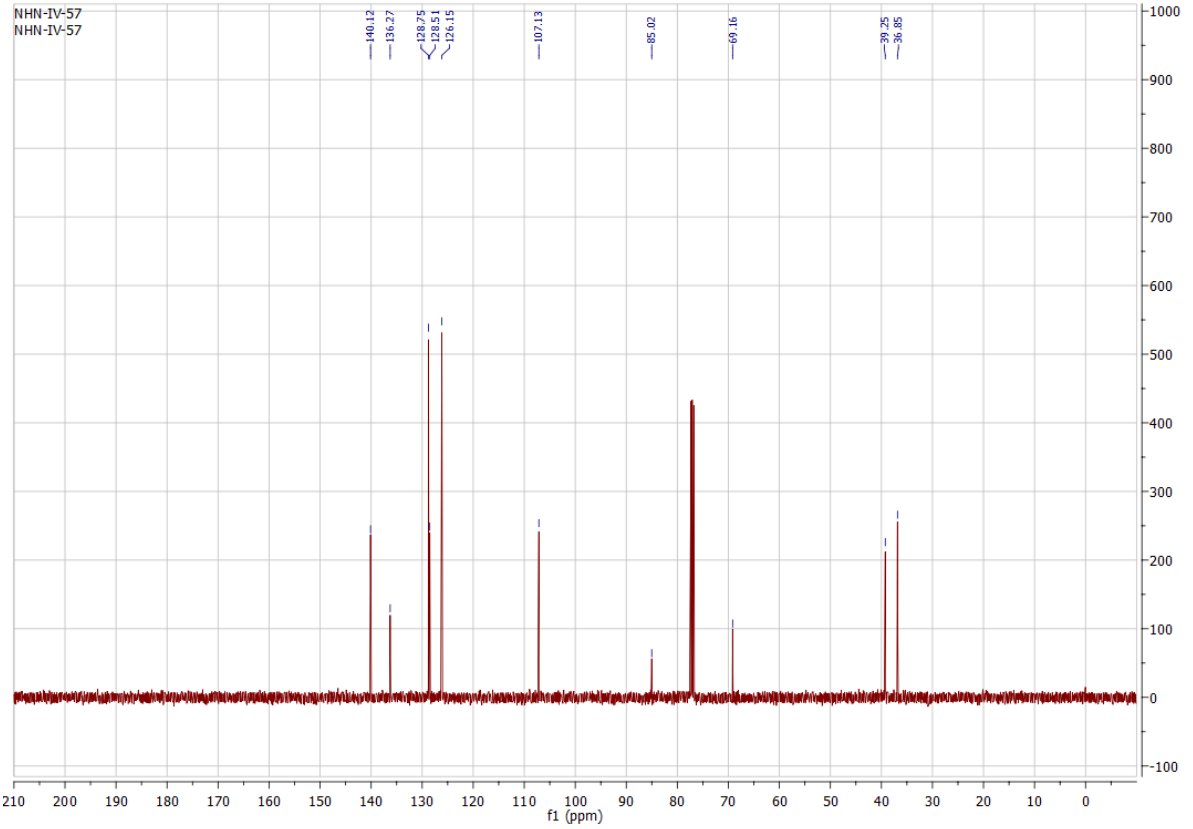

NHQ-VI-55
NHQ-VI-55
7.32
7.29
7.26
6.87
6.84
6.83
6.11
6.07
3.81
3.25
3.09
Ms
N
Bn
OMe
4b
2.04
2.97
1.00
3.12
3.03
3.19
f1 (ppm)

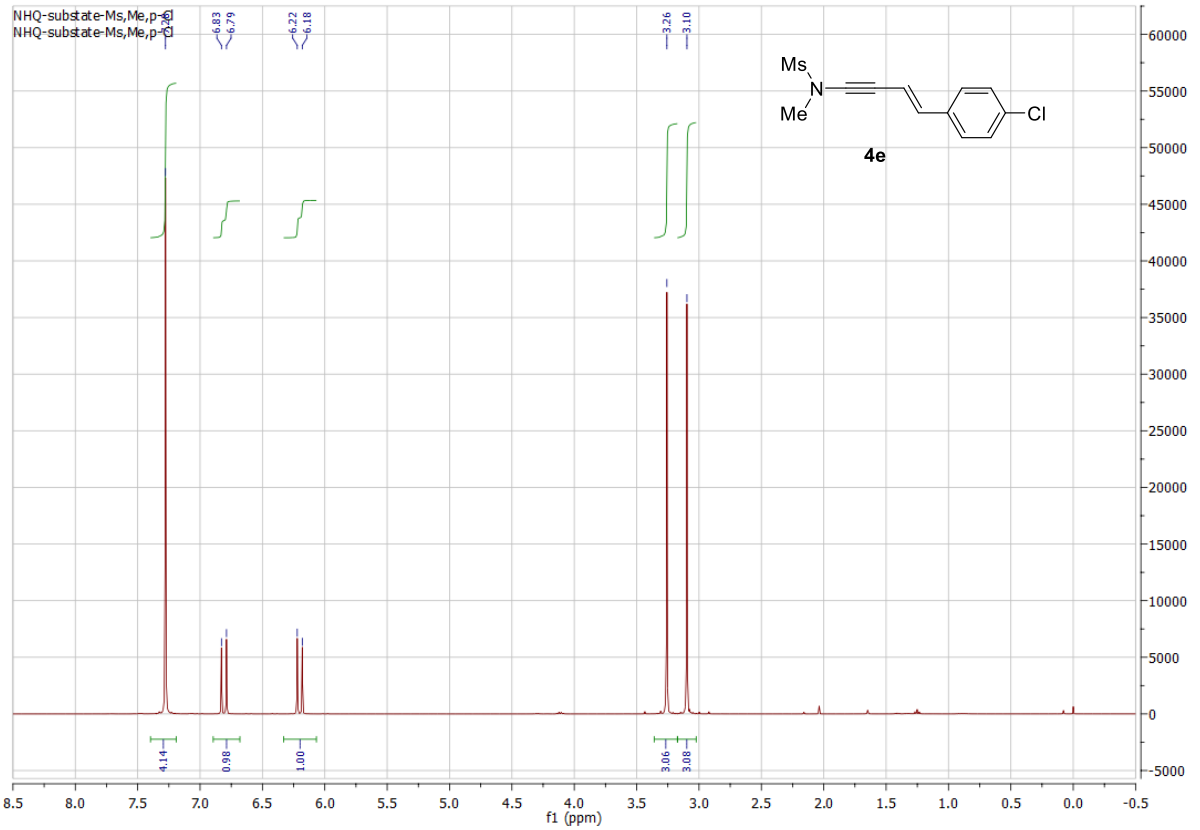

NHQ-VI-55
NHQ-VI-55
160.02
140.20
129.10
127.51
114.18
104.65
84.15
69.22
55.34
39.26
36.73
f1 (ppm)

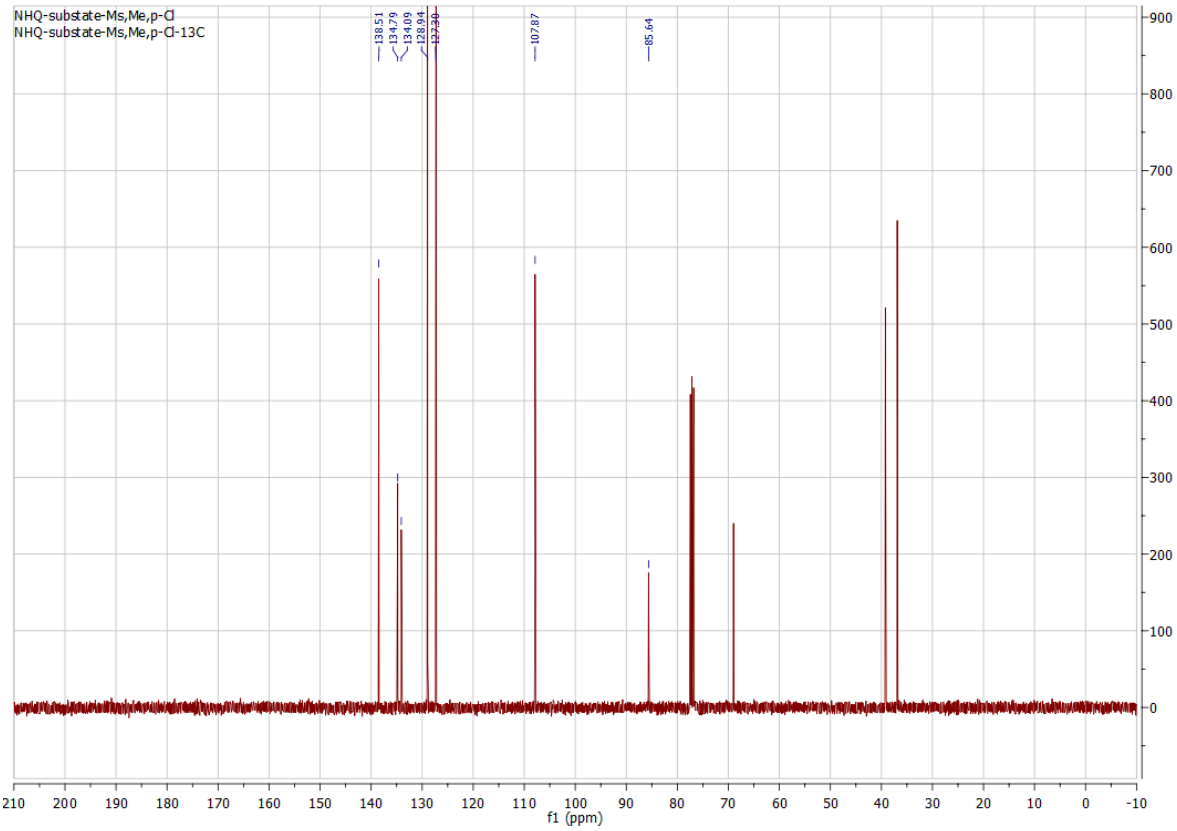

NHQ-XI-06
NHQ-XI-06
7.27
7.25
7.13
7.11
6.88
6.84
6.20
6.16
3.25
3.09
2.33
Ms
N
Me
Me
4c
2.15
2.03
0.99
1.00
3.05
3.07
3.08
f1 (ppm)

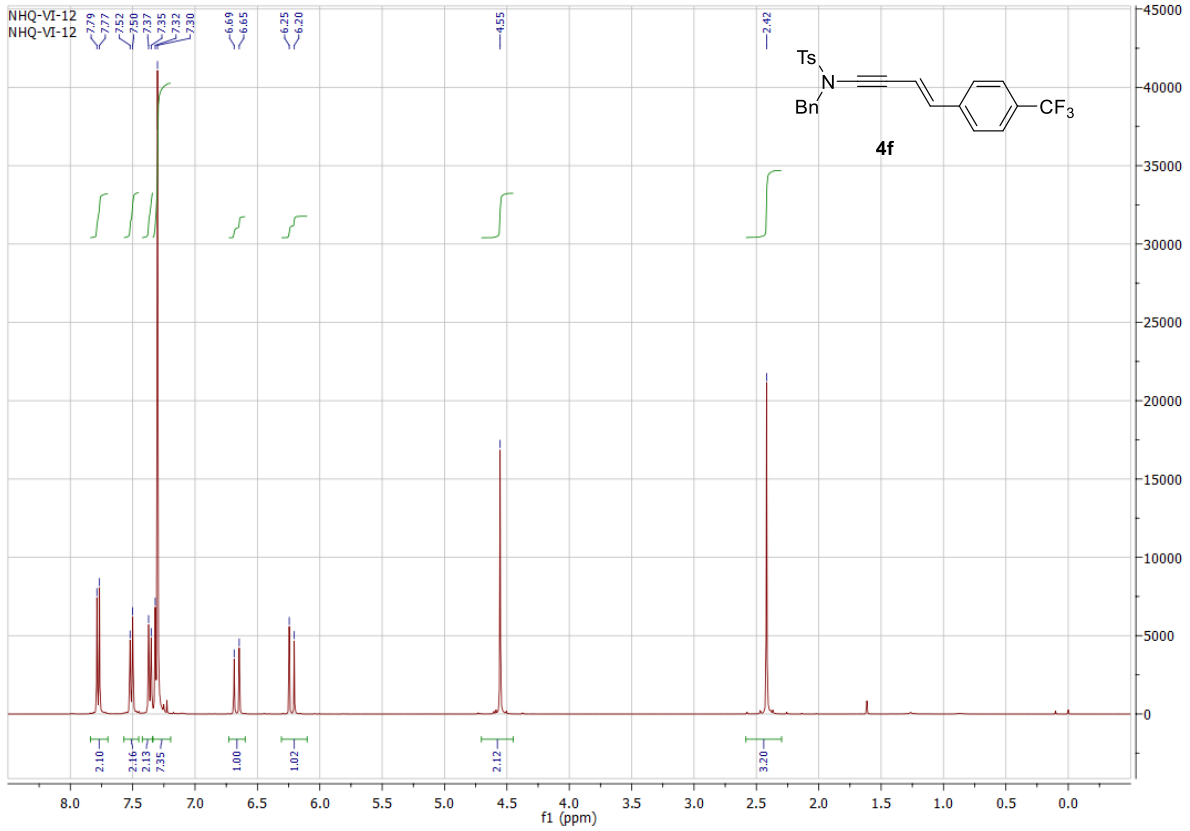

NHQ-XI-06
NHQ-XI-06
140.34
138.62
133.53
129.47
126.10
106.00
84.63
69.21
39.26
36.77
21.31
f1 (ppm)

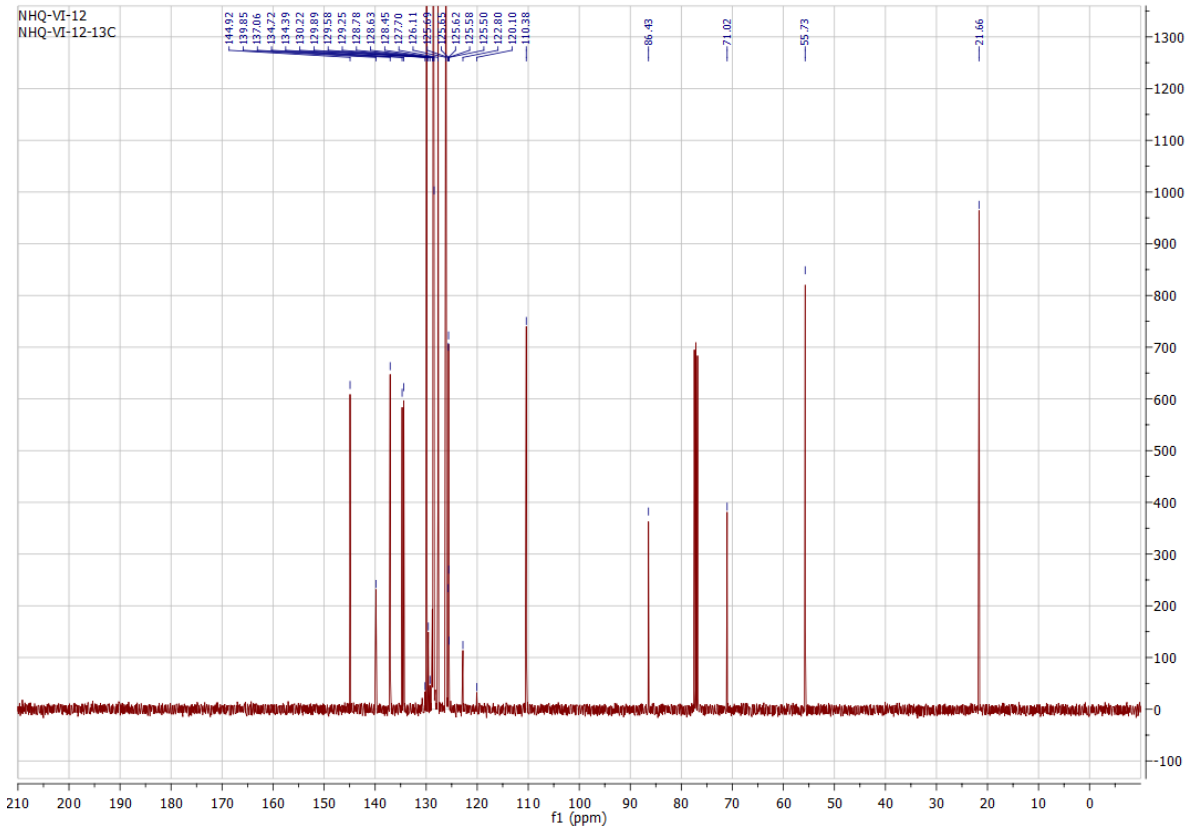

NHN-IV-57
NHN-IV-57
7.40
7.38
7.38
7.37
7.35
7.33
7.31
7.29
6.93
6.89
6.28
6.24
3.30
3.13
Ms
N
Me
4d
4.77
1.00
1.09
3.03
3.14
f1 (ppm)

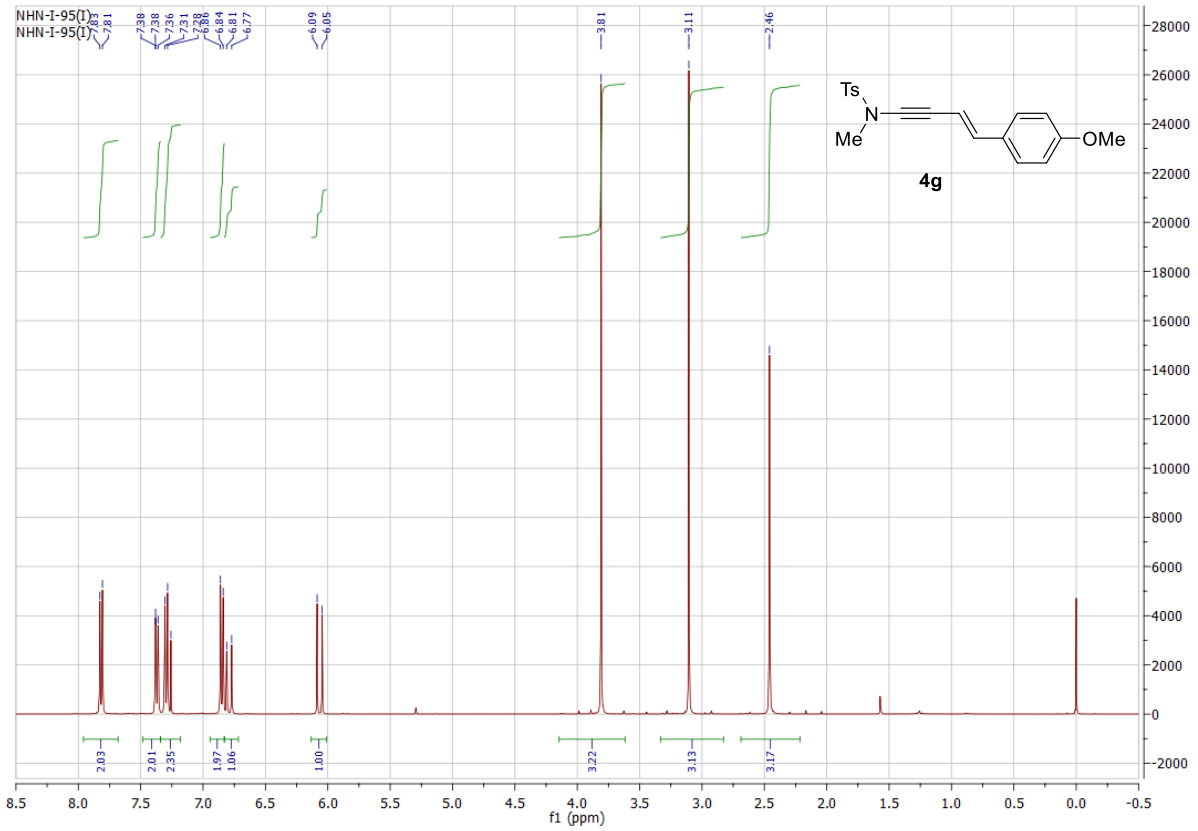

NHN-IV-57
NHN-IV-57
140.12
136.27
128.75
128.51
126.15
107.13
85.02
69.16
39.25
36.85
f1 (ppm)

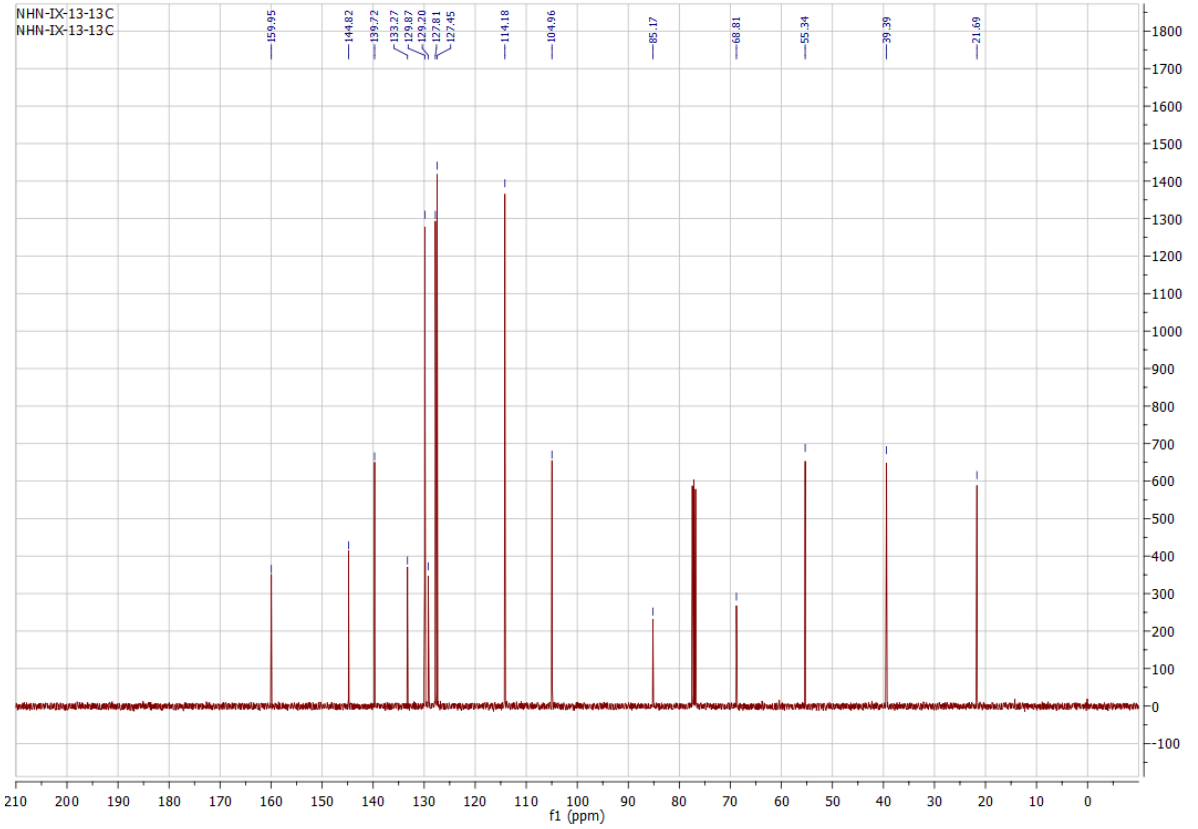

NHQ-substate-Ms,Me,p-Cl
NHQ-substate-Ms,Me,p-Cl
7.26
6.83
6.79
6.22
6.18
3.26
3.10
Ms
N
Me
Cl
4e
4.14
0.98
1.00
3.06
3.08
f1 (ppm)

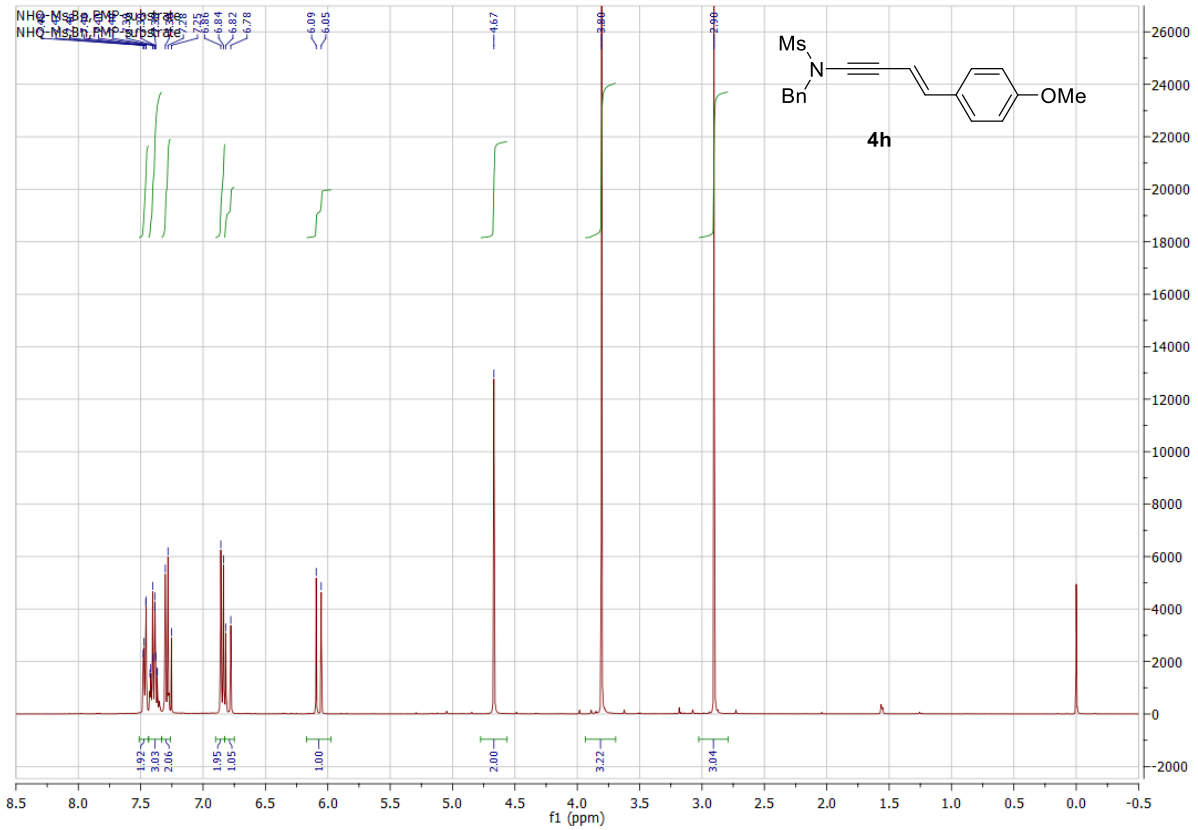

NHQ-substate-Ms,Me,p-Cl
NHQ-substate-Ms,Me,p-Cl-13C
138.51
134.79
134.09
128.94
127.30
107.87
85.64
f1 (ppm)

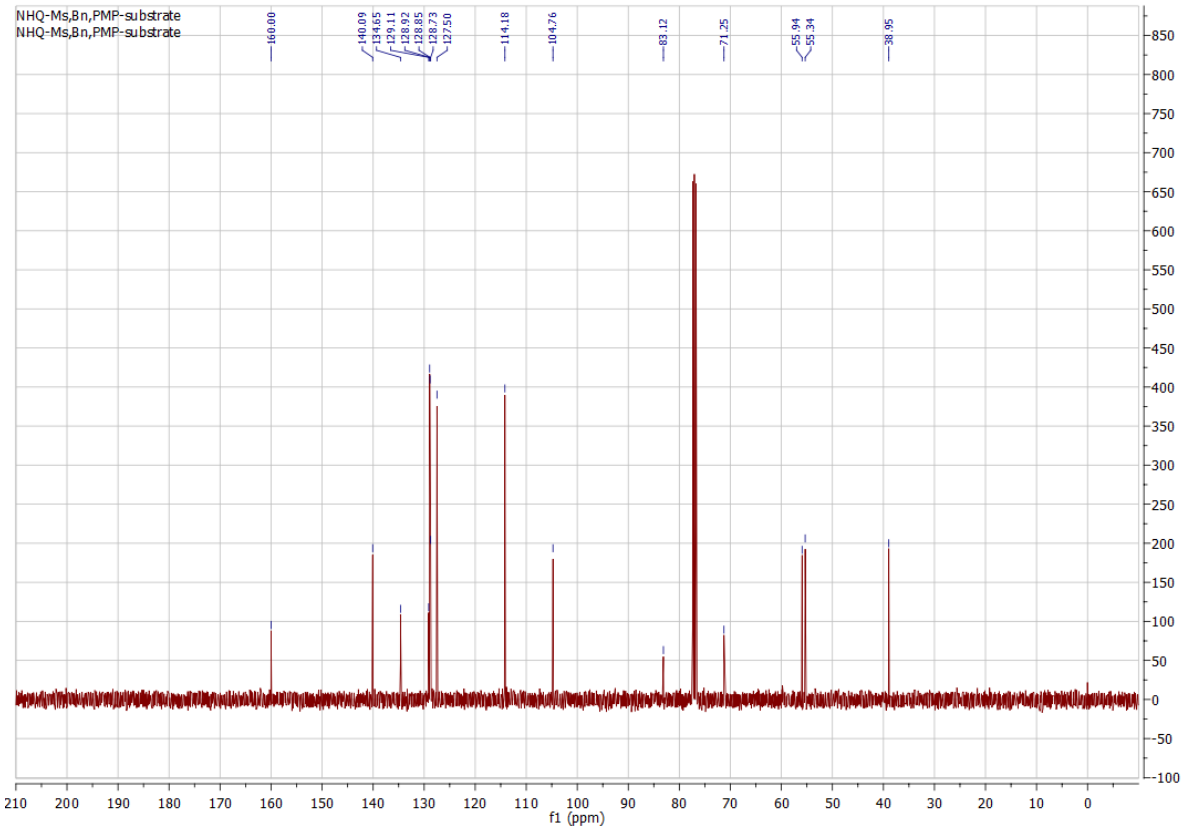

NHQ-VI-12
NHQ-VI-12
7.79
7.77
7.52
7.50
7.37
7.35
7.32
7.30
6.69
6.65
6.25
6.20
4.55
2.42
Ts
N
Bn
CF3
4f
2.10
2.16
2.13
7.35
1.00
1.02
2.12
3.20
f1 (ppm)

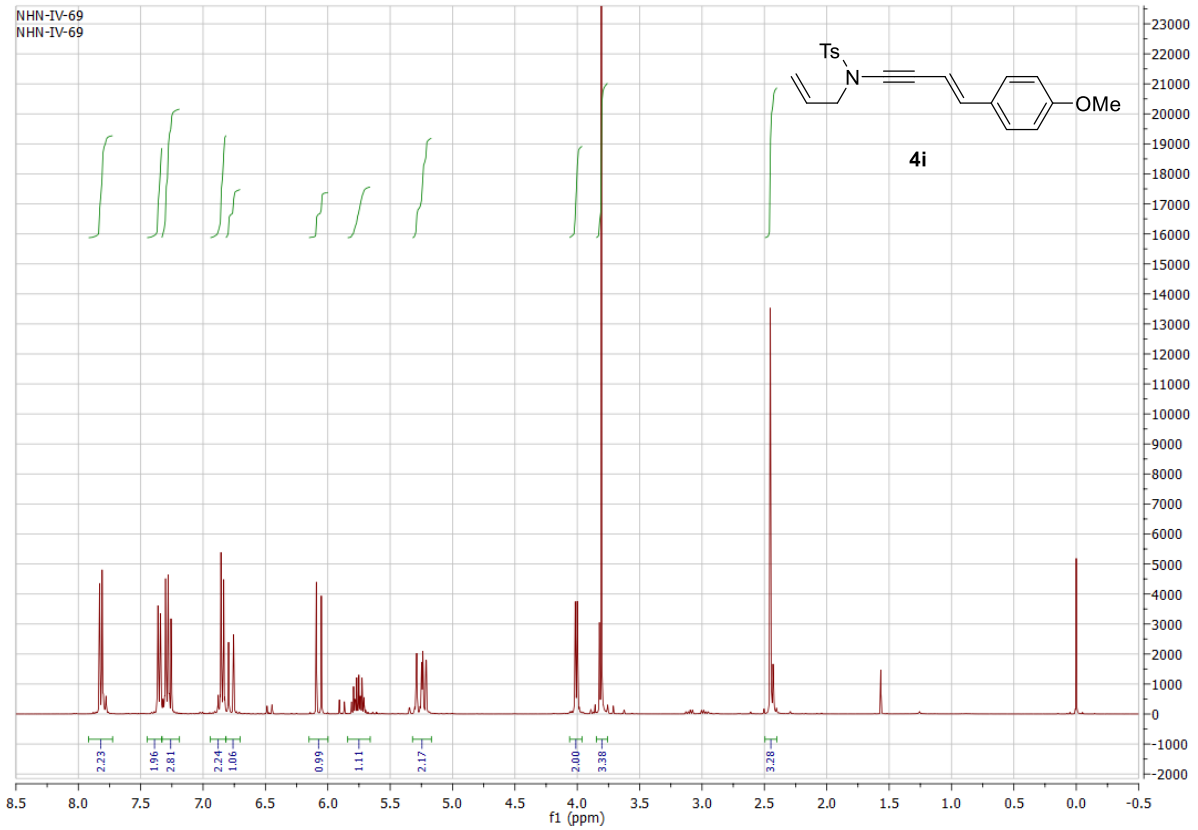

NHQ-VI-12
NHQ-VI-12-13C
144.92
139.85
137.06
134.72
134.39
130.22
129.89
129.58
129.25
128.78
128.63
128.45
127.70
126.11
125.65
125.62
125.58
125.50
122.80
120.10
110.38
86.43
71.02
55.73
21.66
f1 (ppm)

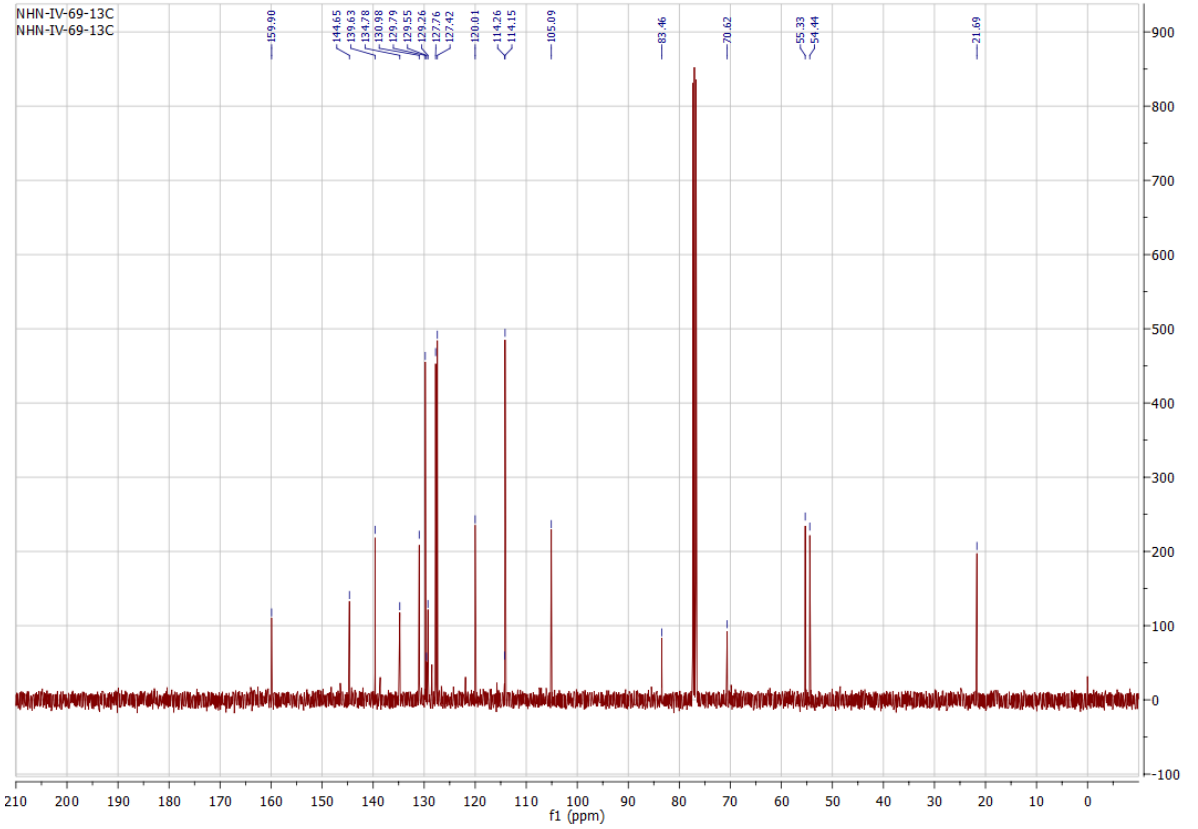

NHN-I-95(I)
NHN-I-95(I)
7.83
7.81
7.38
7.38
7.36
7.31
7.28
6.86
6.84
6.81
6.77
6.09
6.05
3.81
3.11
2.46
Ts
N
Me
OMe
4g
2.03
2.01
2.35
1.97
1.06
1.00
3.22
3.13
3.17
f1 (ppm)

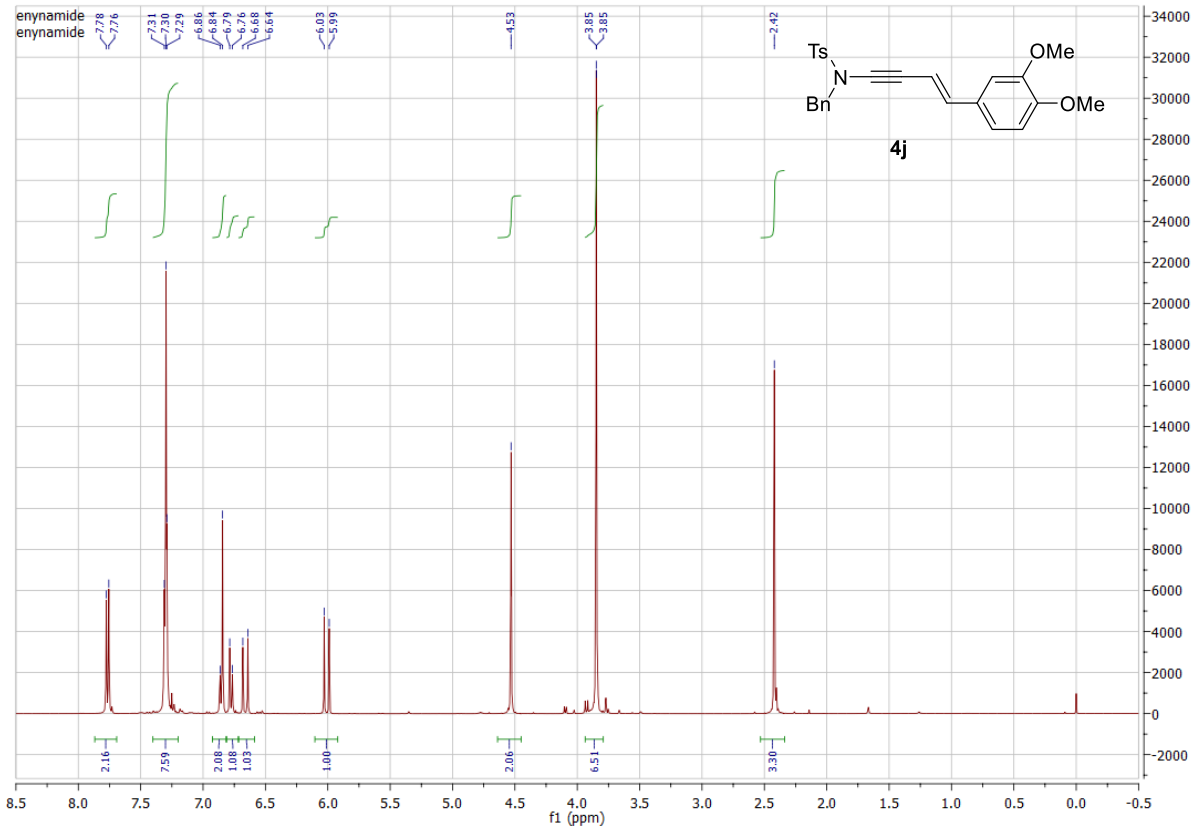

NHN-IX-13-13C
NHN-IX-13-13C
159.95
144.82
139.72
133.27
129.87
129.20
127.81
127.45
114.18
104.96
85.17
68.81
55.34
39.39
21.69
f1 (ppm)

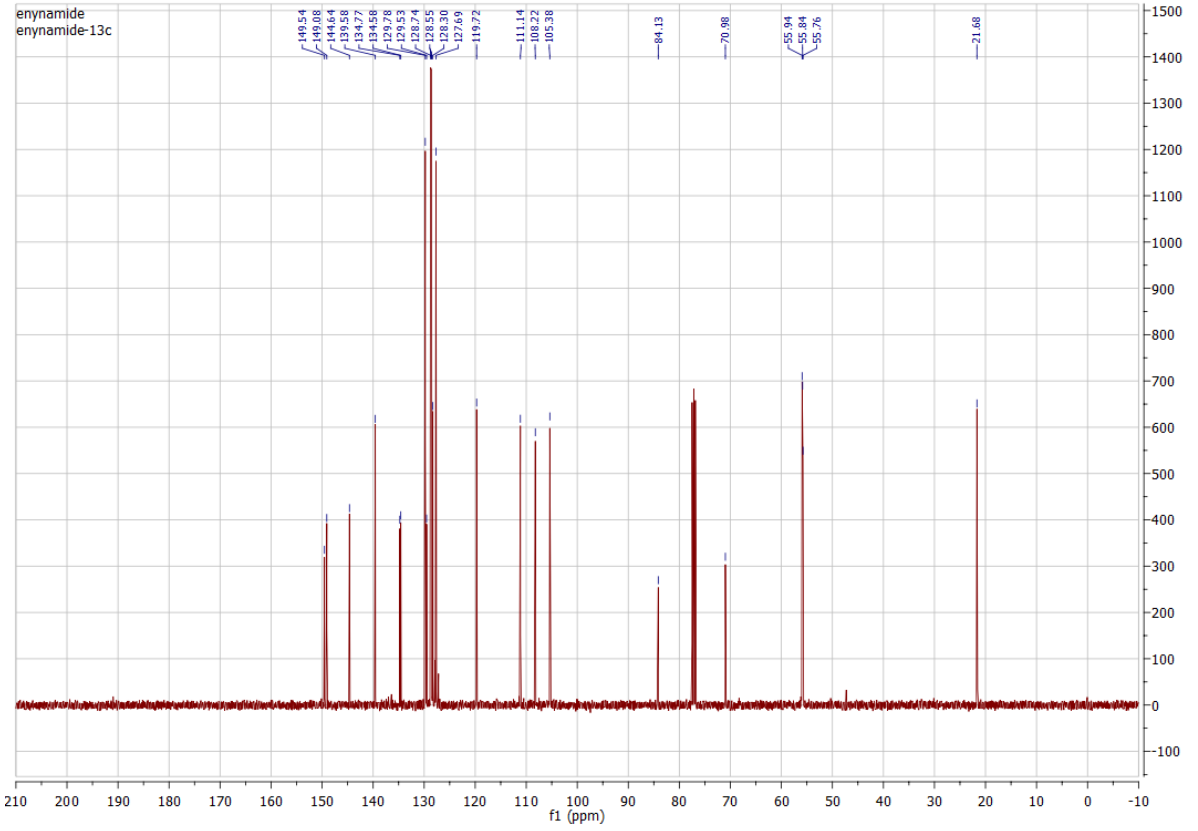

Ms
N
Bn
OMe
4h
f1 (ppm)

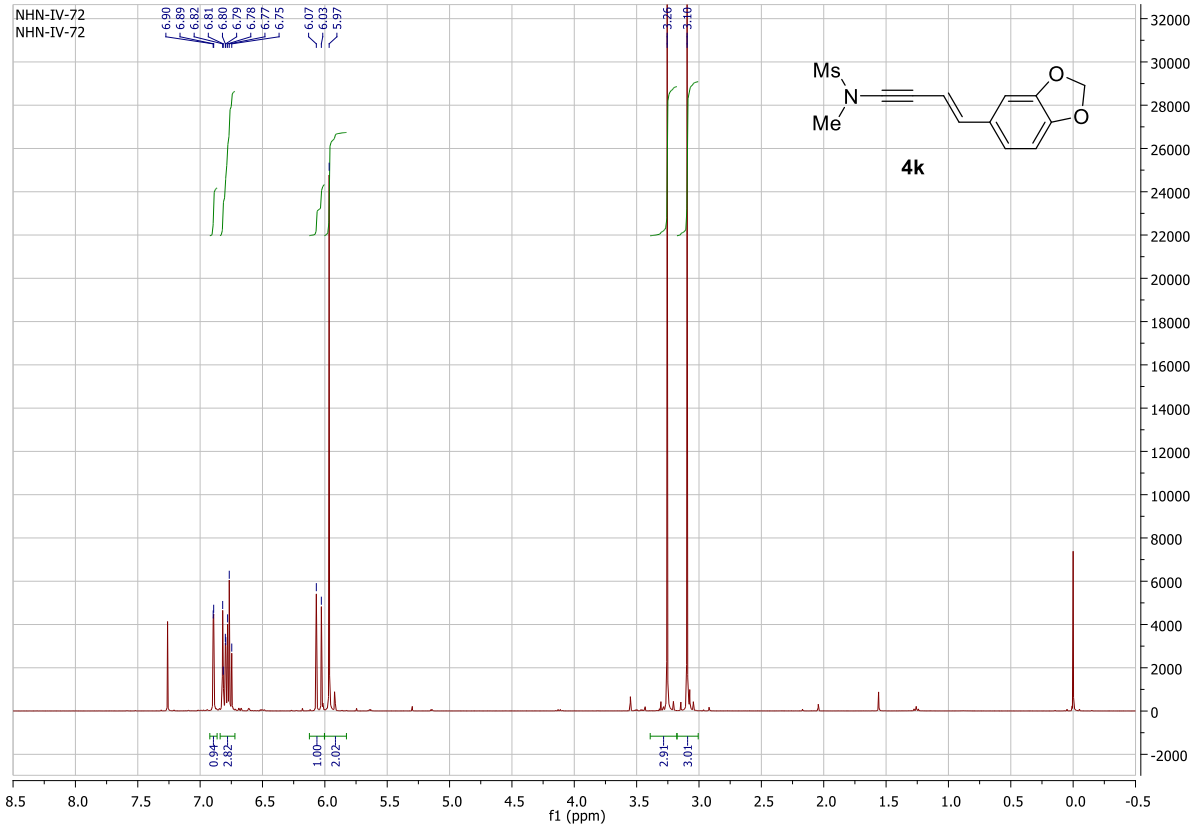

NHQ-Ms,Bn,PMP-substrate
NHQ-Ms,Bn,PMP-substrate
f1 (ppm)

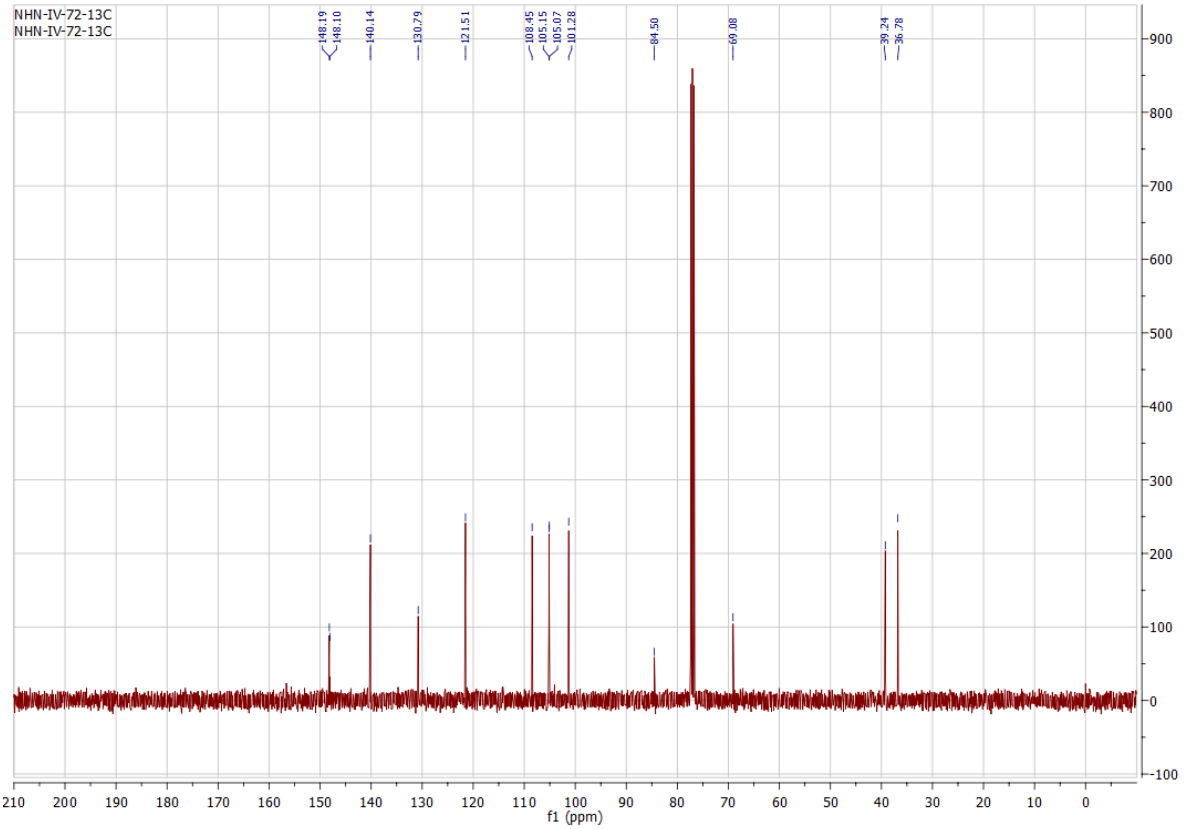

NHN-IV-69
NHN-IV-69
Ts
N
OMe
4i
2.23
1.96
2.81
2.24
1.06
0.99
1.11
2.17
2.00
3.38
3.28
f1 (ppm)

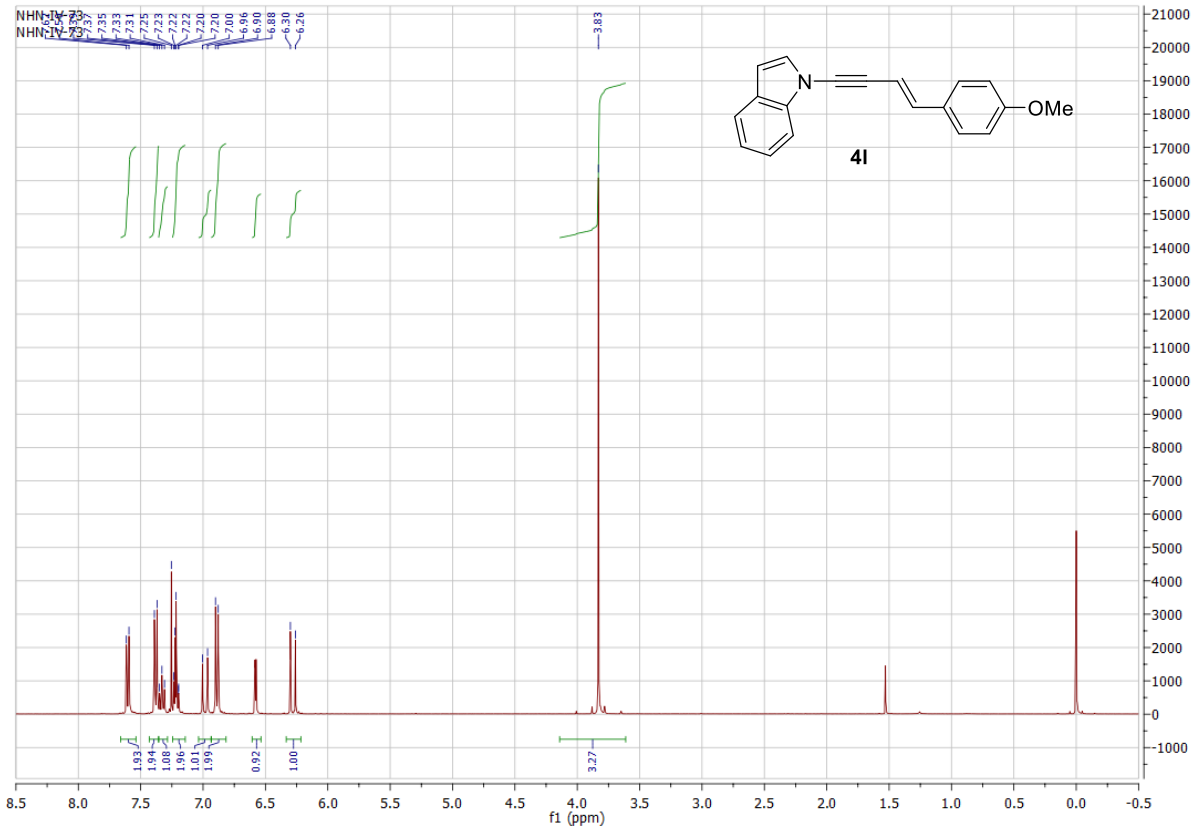

NHN-IV-69-13C
NHN-IV-69-13C
159.90
144.65
139.63
134.78
130.98
129.79
129.55
129.26
127.76
127.42
120.01
114.26
114.15
105.09
83.46
70.62
55.33
54.44
21.69
f1 (ppm)

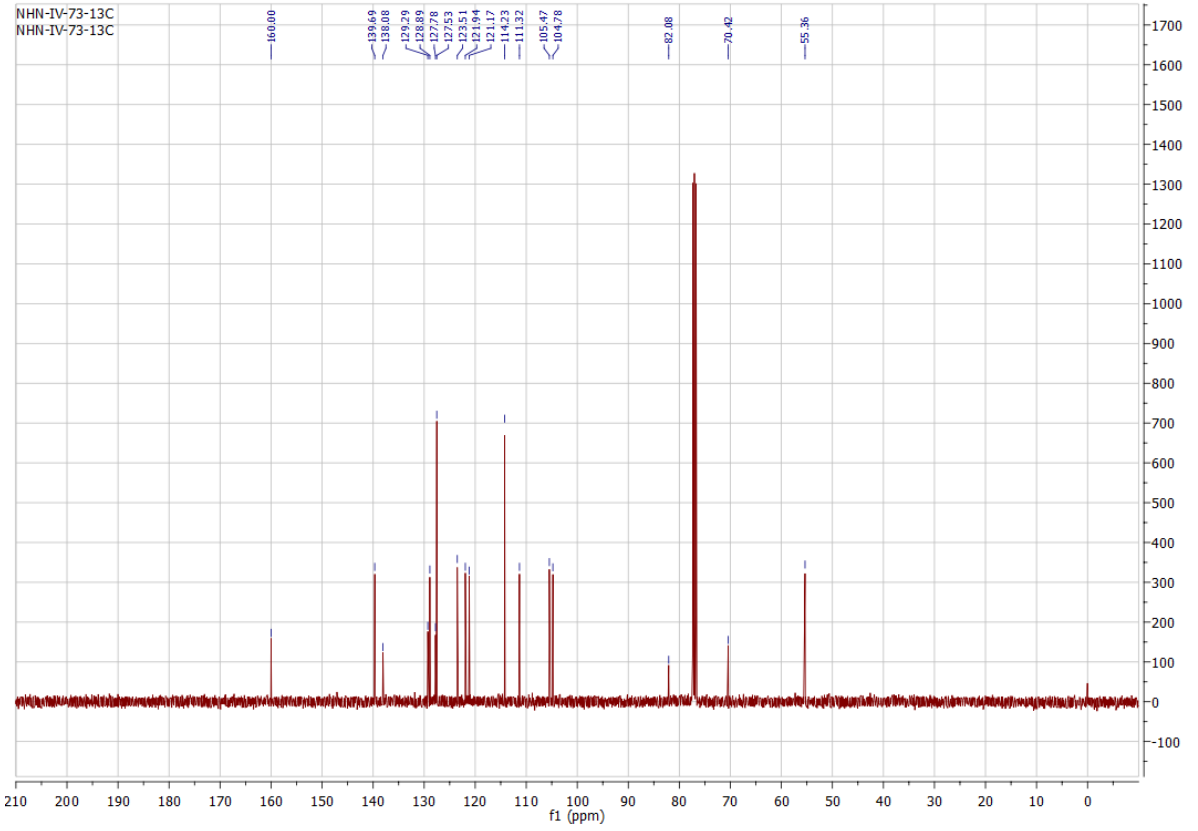

enynamide
enynamide
7.78
7.76
7.31
7.30
7.29
6.86
6.84
6.79
6.76
6.68
6.64
6.03
5.99
4.53
3.85
3.85
2.42
Ts
N
Bn
OMe
OMe
4j
2.16
7.59
2.08
1.08
1.03
1.00
2.06
6.51
3.30
f1 (ppm)

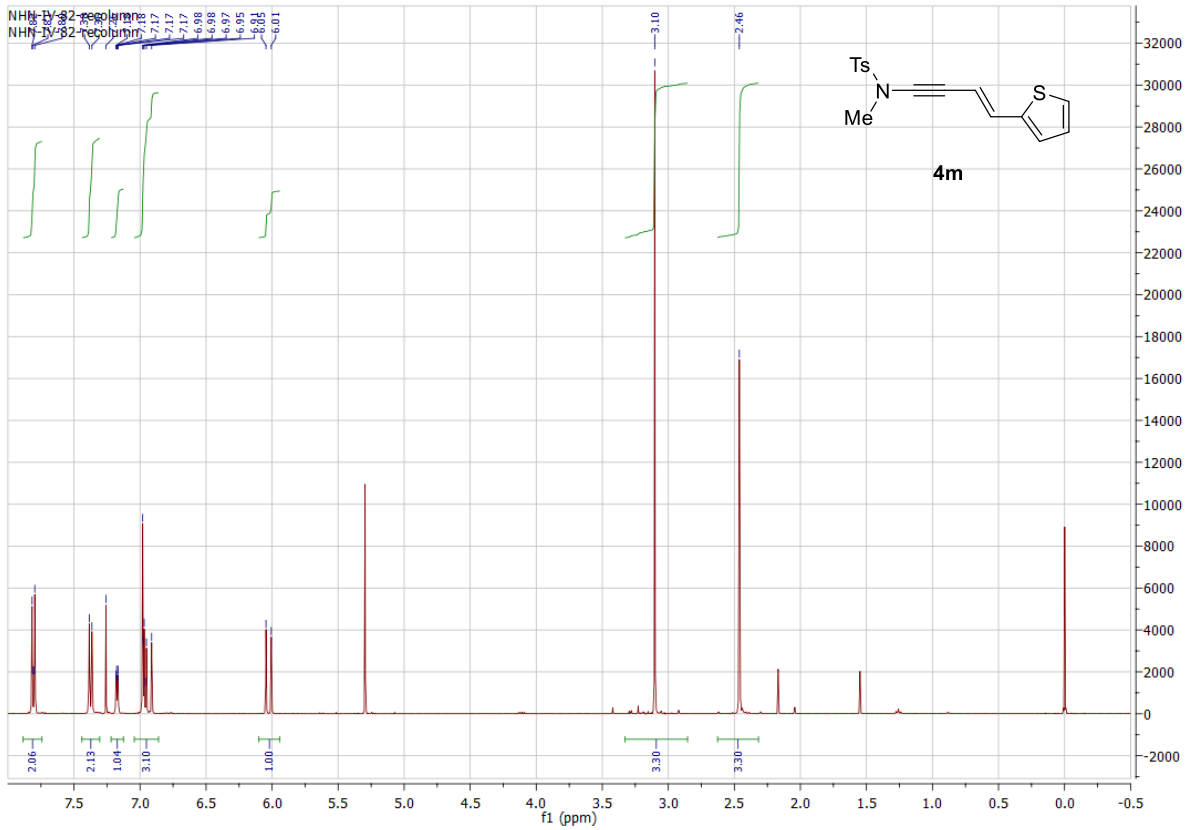

enynamide
enynamide-13c
149.54
149.08
144.64
139.58
134.77
134.58
129.78
129.53
128.74
128.55
128.30
127.69
119.72
111.14
108.22
105.38
84.13
70.98
55.94
55.84
55.76
21.68
f1 (ppm)

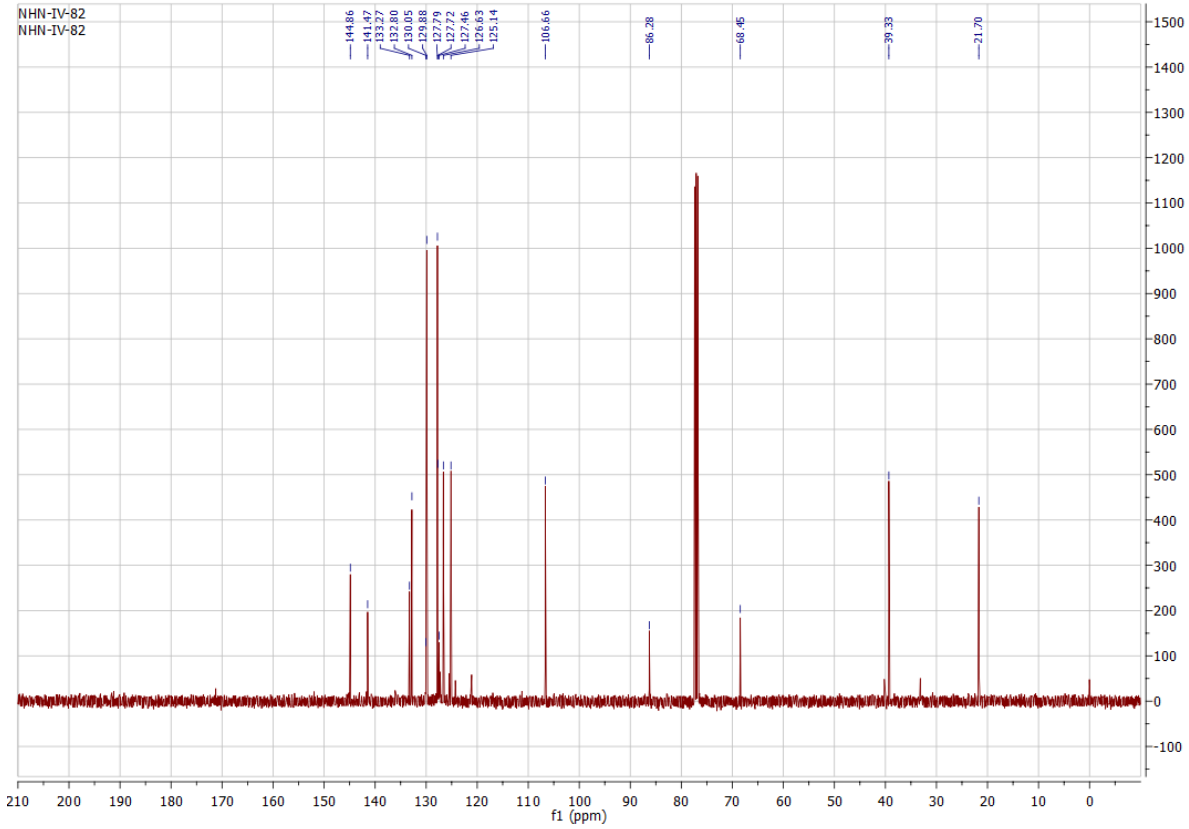

NHN-IV-72
NHN-IV-72
6.90
6.89
6.82
6.81
6.80
6.79
6.78
6.77
6.75
6.07
6.03
5.97
3.26
3.10
Ms
N
Me
O
O
4k
0.94
2.82
1.00
2.02
2.91
3.01
f1 (ppm)

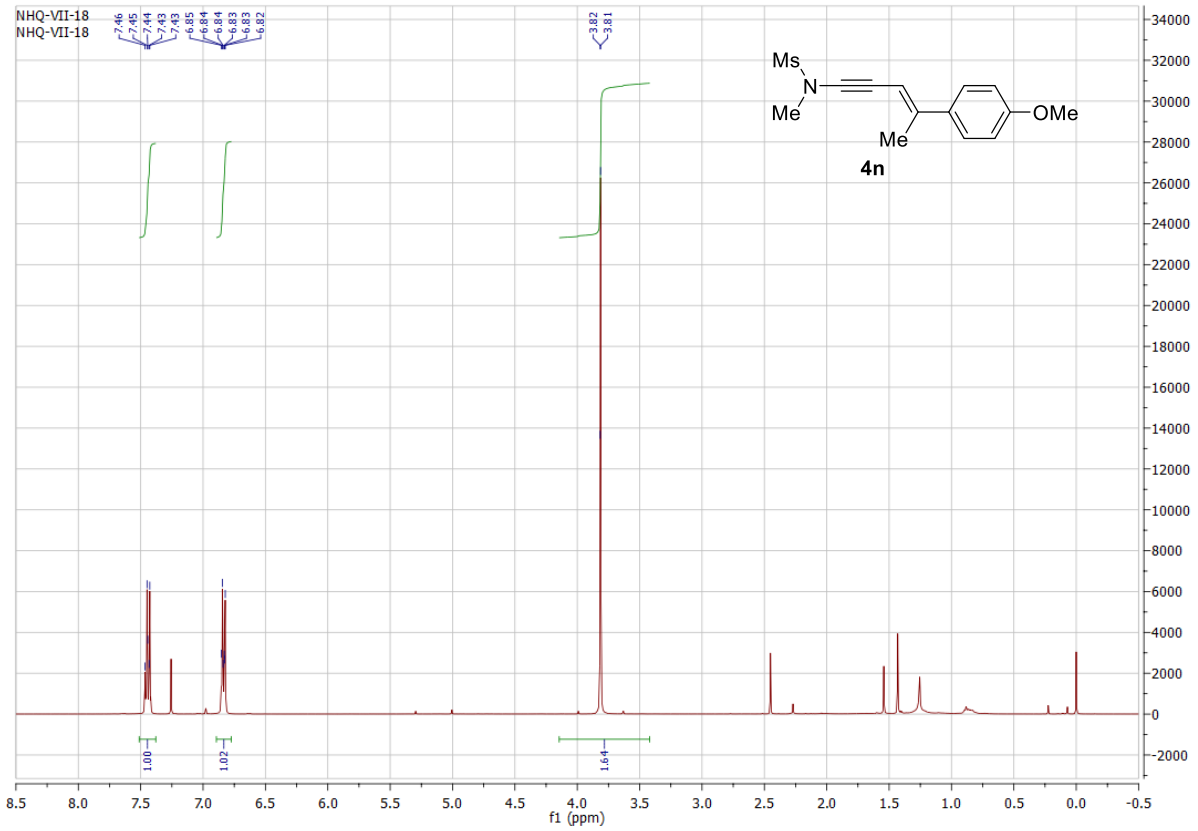

NHN-IV-72-13C
NHN-IV-72-13C
148.19
148.10
140.14
130.79
121.51
108.45
105.15
105.07
101.28
84.50
69.08
39.24
36.78
f1 (ppm)

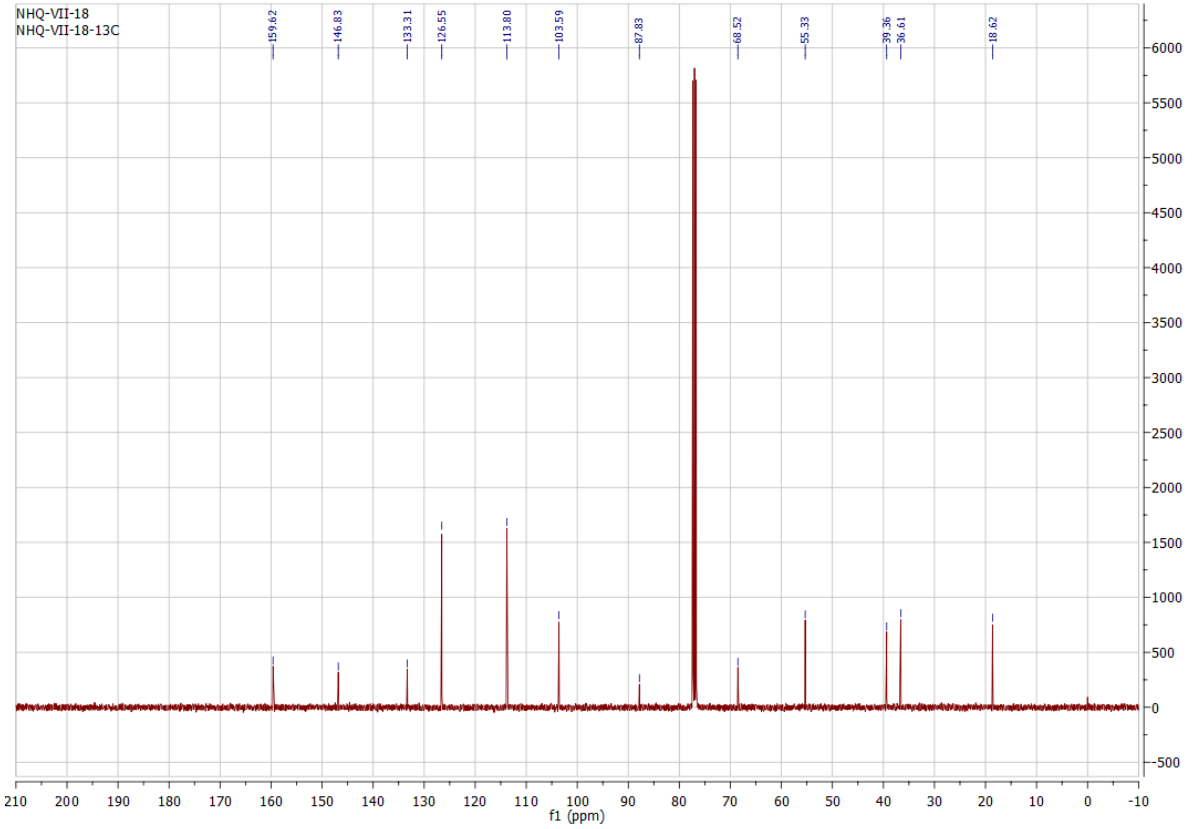

NHN-IV-73
7.37
7.35
7.33
7.31
7.25
7.23
7.22
7.22
7.20
7.20
7.00
6.96
6.90
6.88
6.30
6.26
3.83
N
OMe
4l
1.93
1.94
1.08
1.96
1.01
1.99
0.92
1.00
3.27
f1 (ppm)

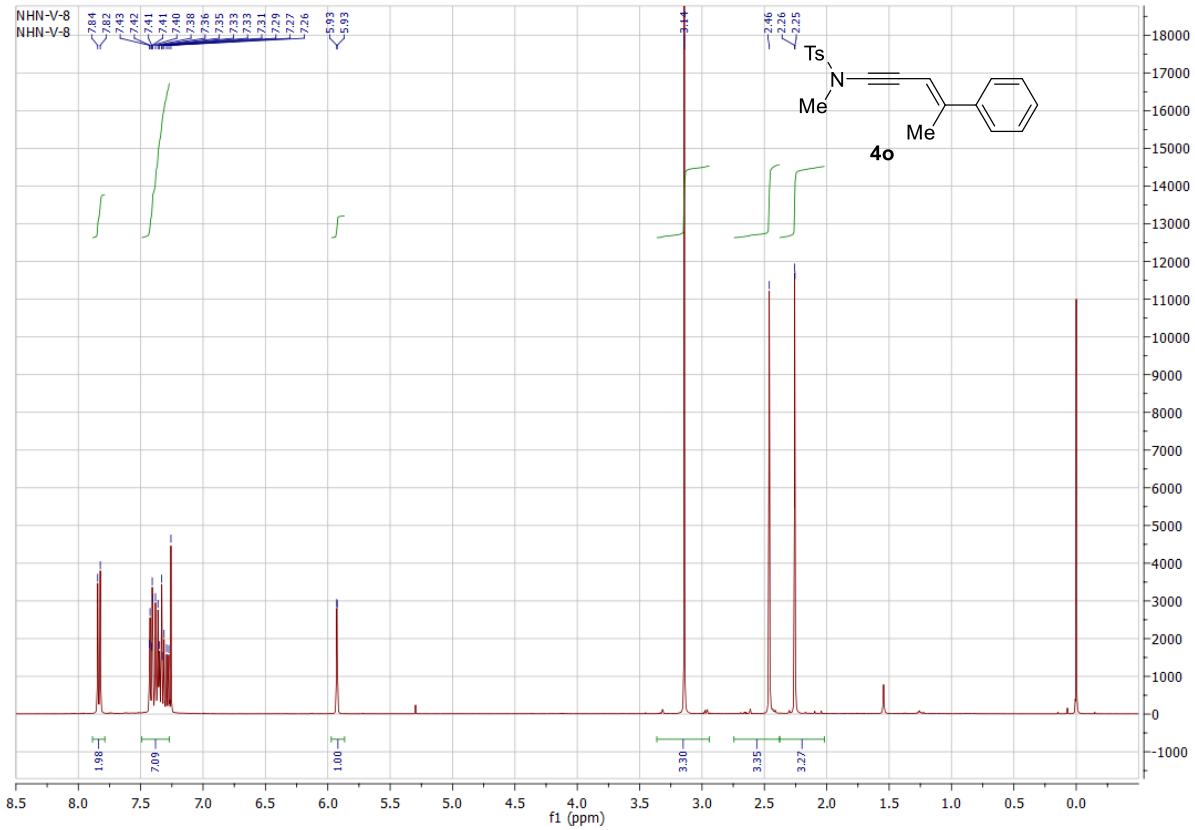

NHN-IV-73-13C
NHN-IV-73-13C
160.00
139.69
138.08
129.29
128.89
127.78
127.53
123.51
121.94
121.17
114.23
111.32
105.47
104.78
82.08
70.42
55.36
f1 (ppm)

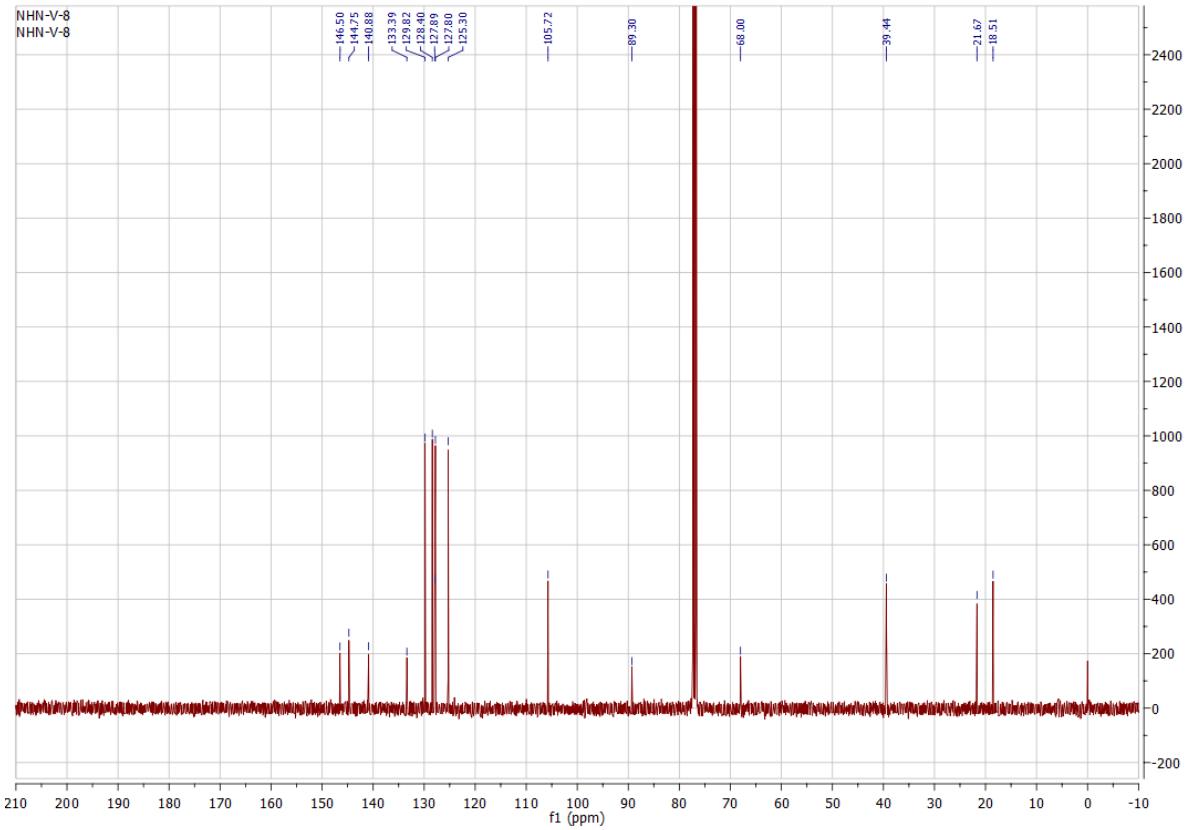

NHN-IV-82-recolumn
NHN-IV-82-recolumn
Ts
N
Me
S
4m
f1 (ppm)

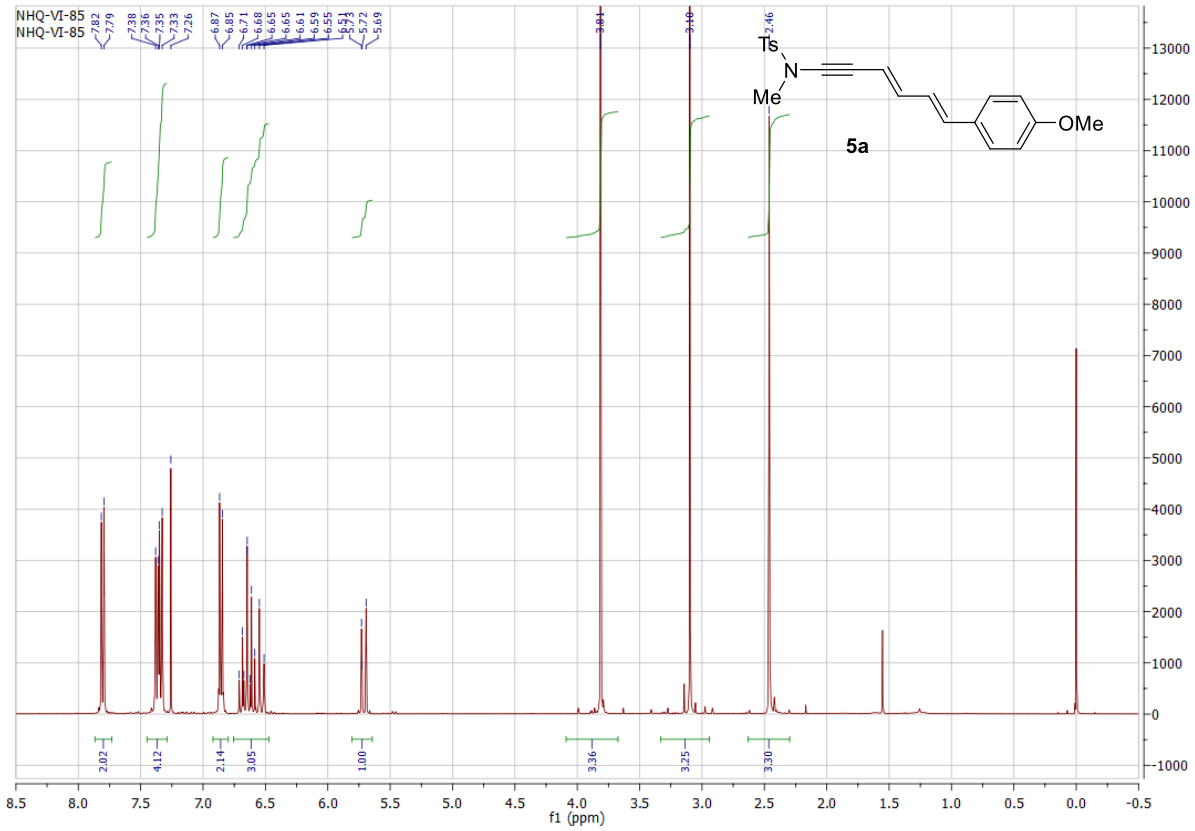

NHN-IV-82
NHN-IV-82
144.86
141.47
133.27
132.80
130.05
129.88
127.79
127.72
127.46
126.63
125.14
106.66
86.28
68.45
39.33
21.70
f1 (ppm)

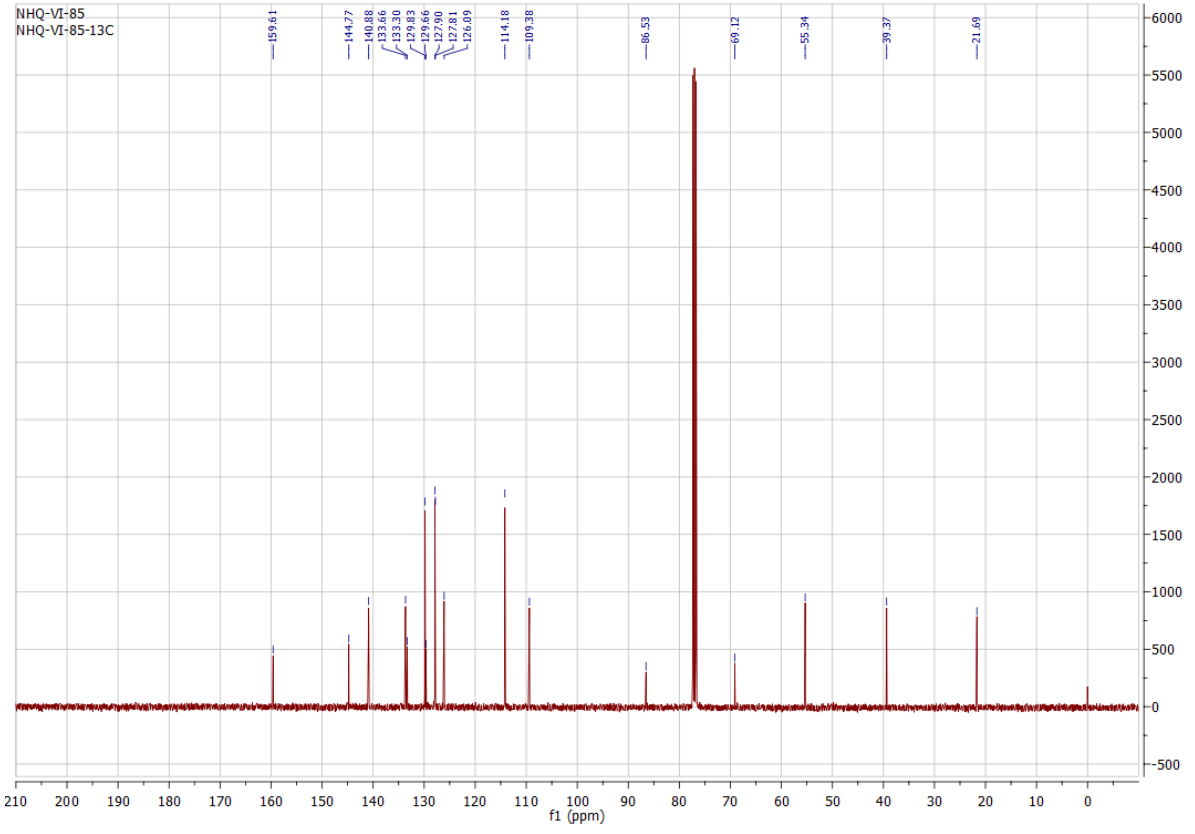

NHQ-VII-18
NHQ-VII-18
7.46
7.45
7.44
7.43
7.43
6.85
6.84
6.84
6.83
6.83
6.82
3.82
3.81
Ms
N
Me
Me
OMe
4n
1.00
1.02
1.64
f1 (ppm)

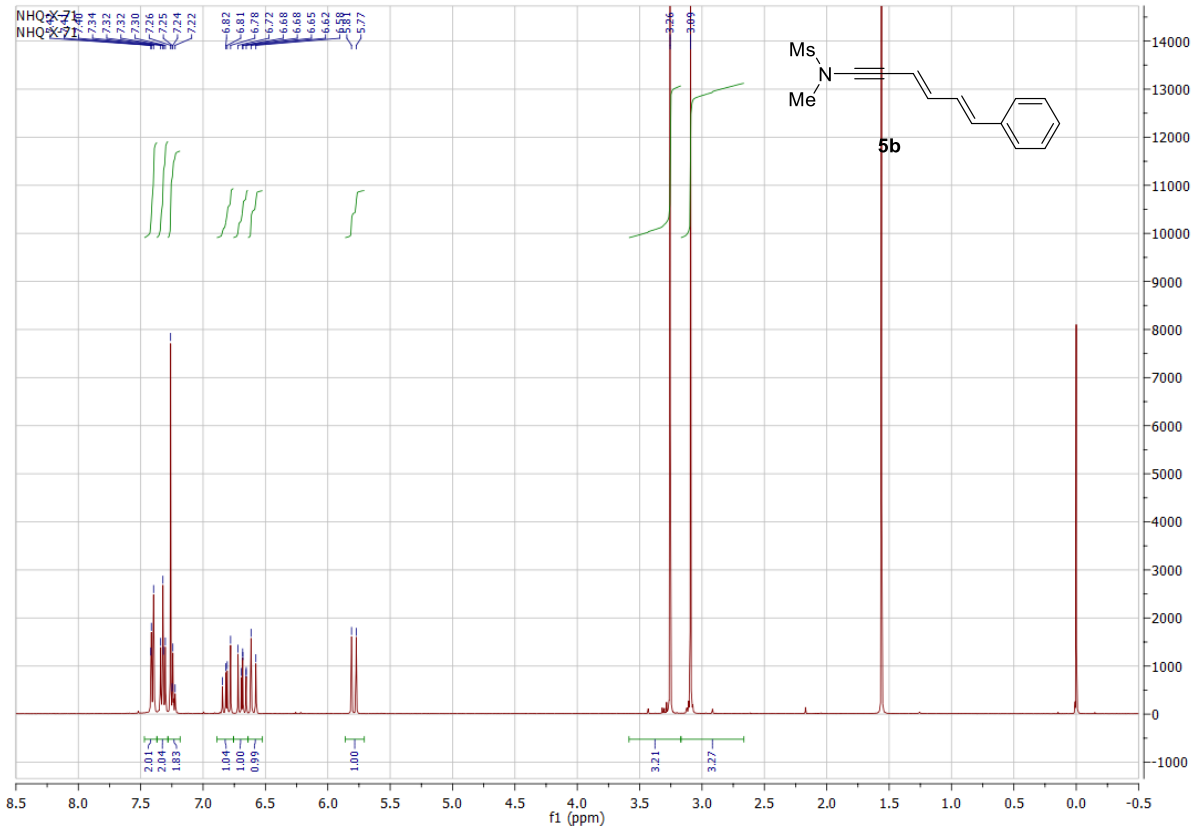

NHQ-VII-18
NHQ-VII-18-13C
159.62
146.83
133.31
126.55
113.80
103.59
87.83
68.52
55.33
39.36
36.61
18.62
f1 (ppm)

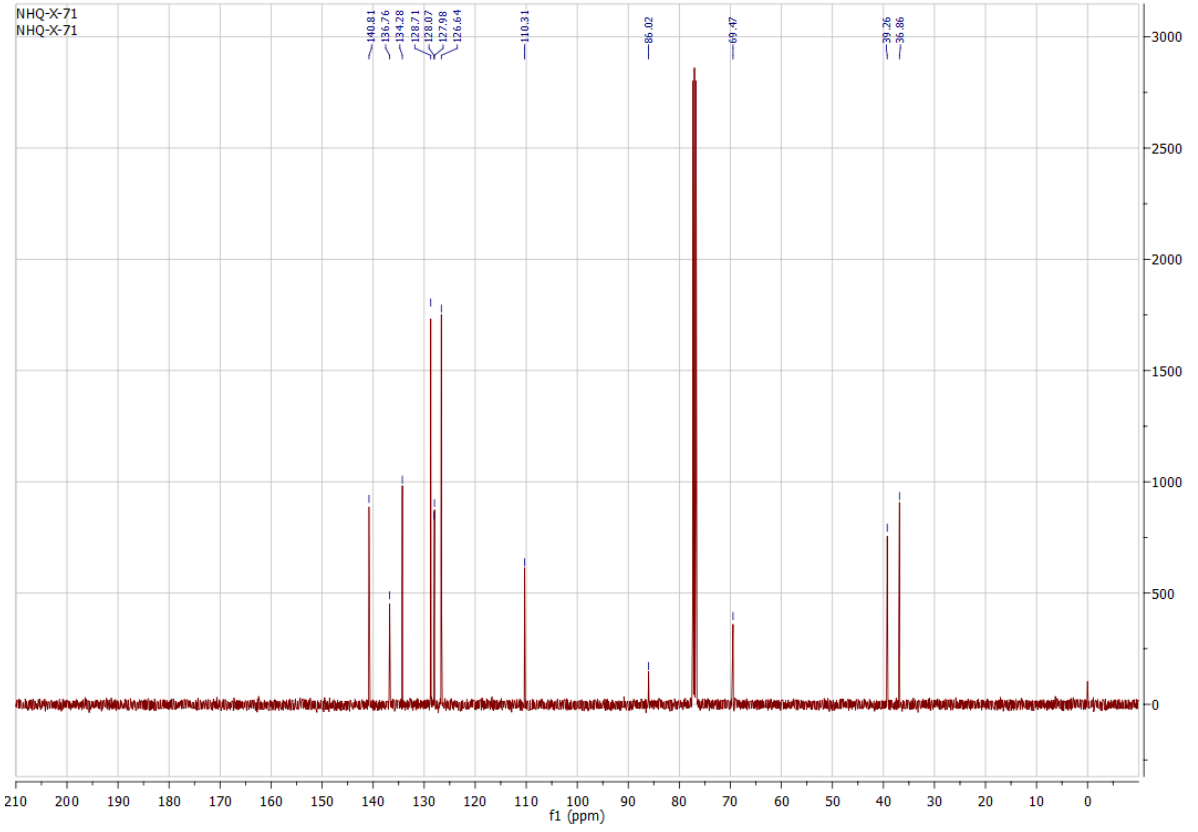

NHN-V-8
NHN-V-8
Ts
N
Me
Me
4o
f1 (ppm)

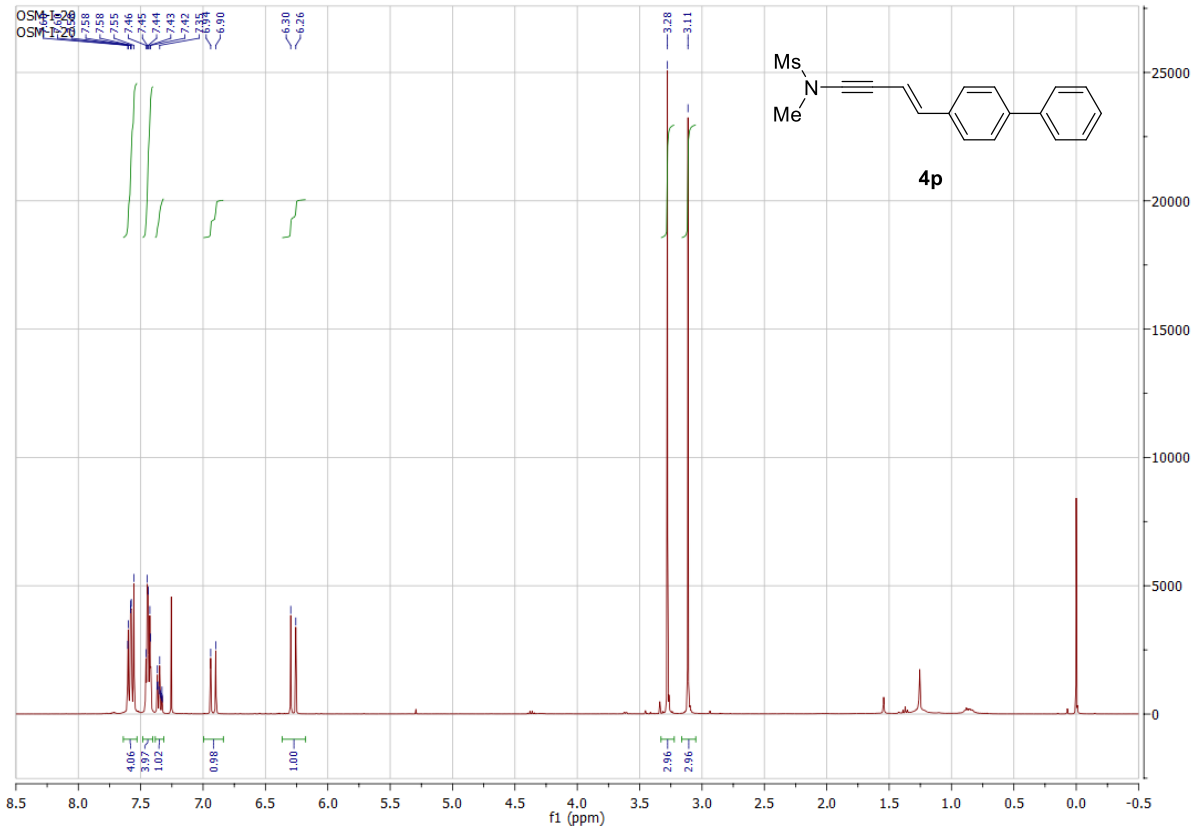

NHN-V-8
NHN-V-8
f1 (ppm)

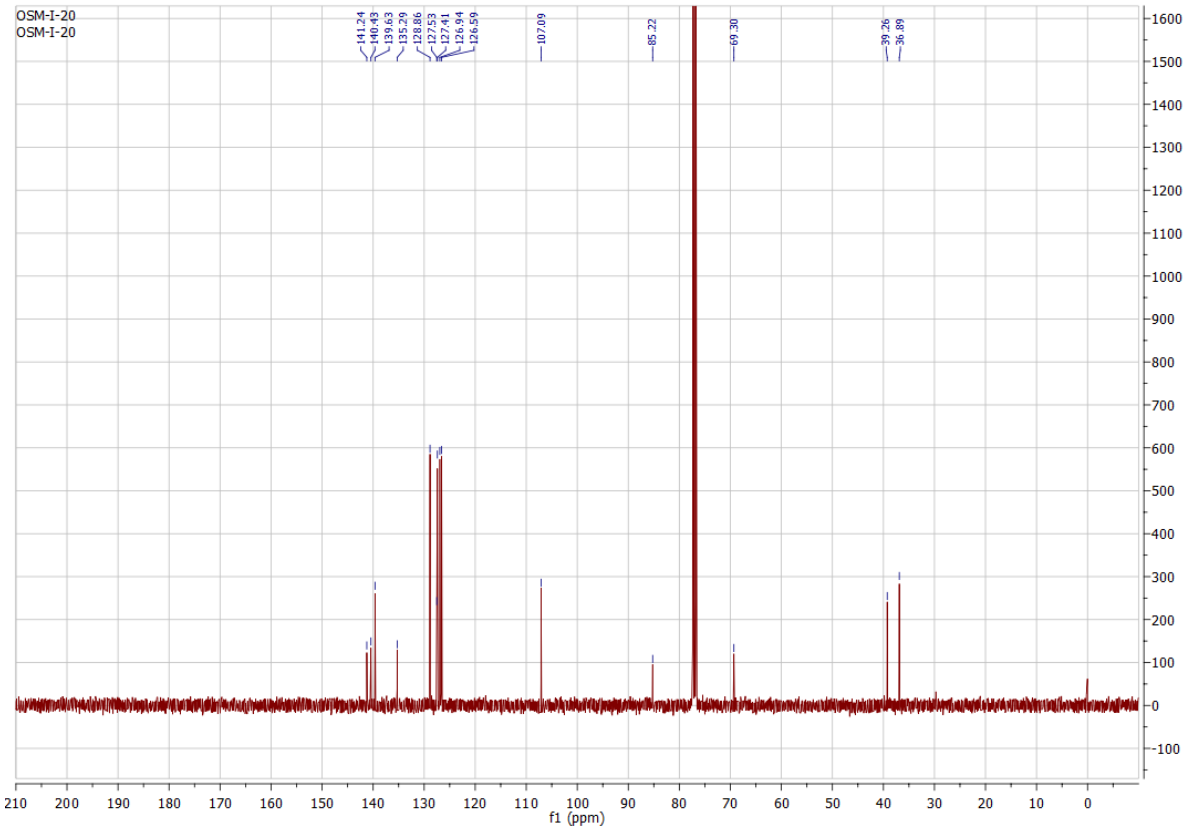

NHQ-VI-85
NHQ-VI-85
Ts
N
Me
OMe
5a
f1 (ppm)

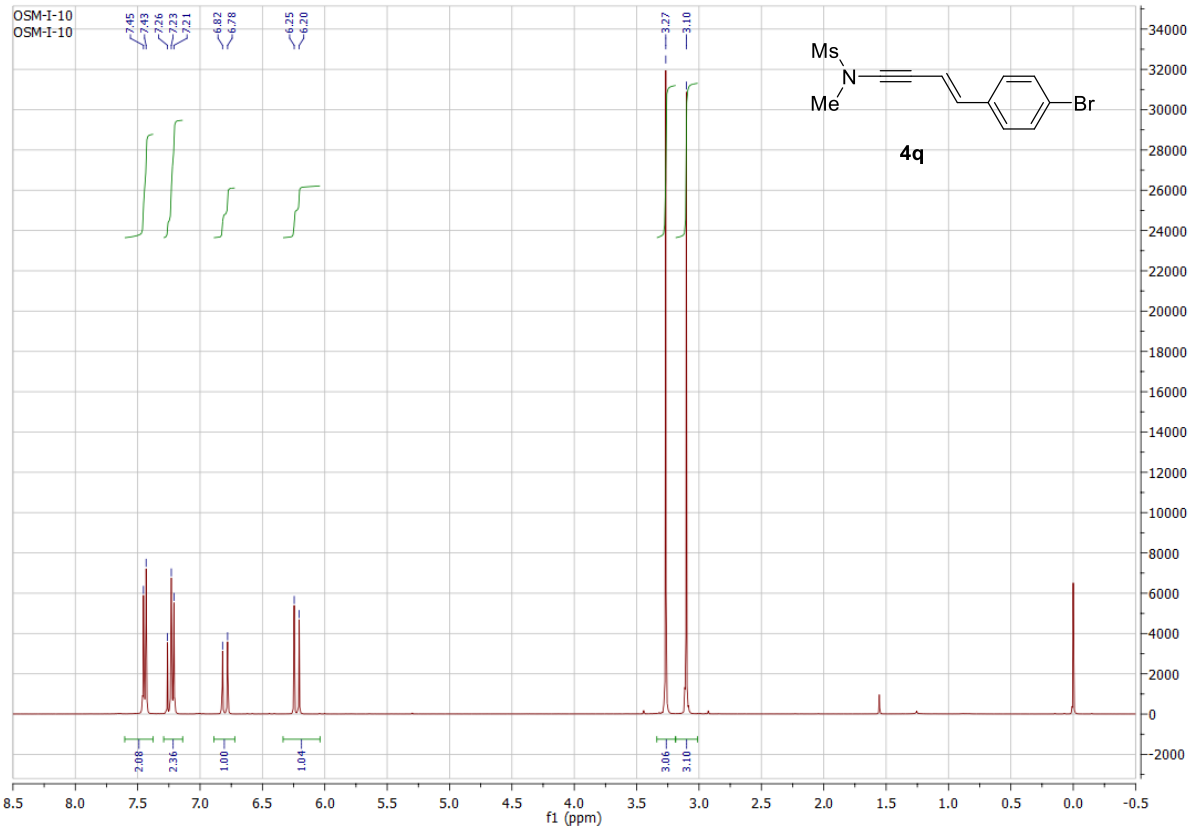

NHQ-VI-85
NHQ-VI-85-13C
f1 (ppm)

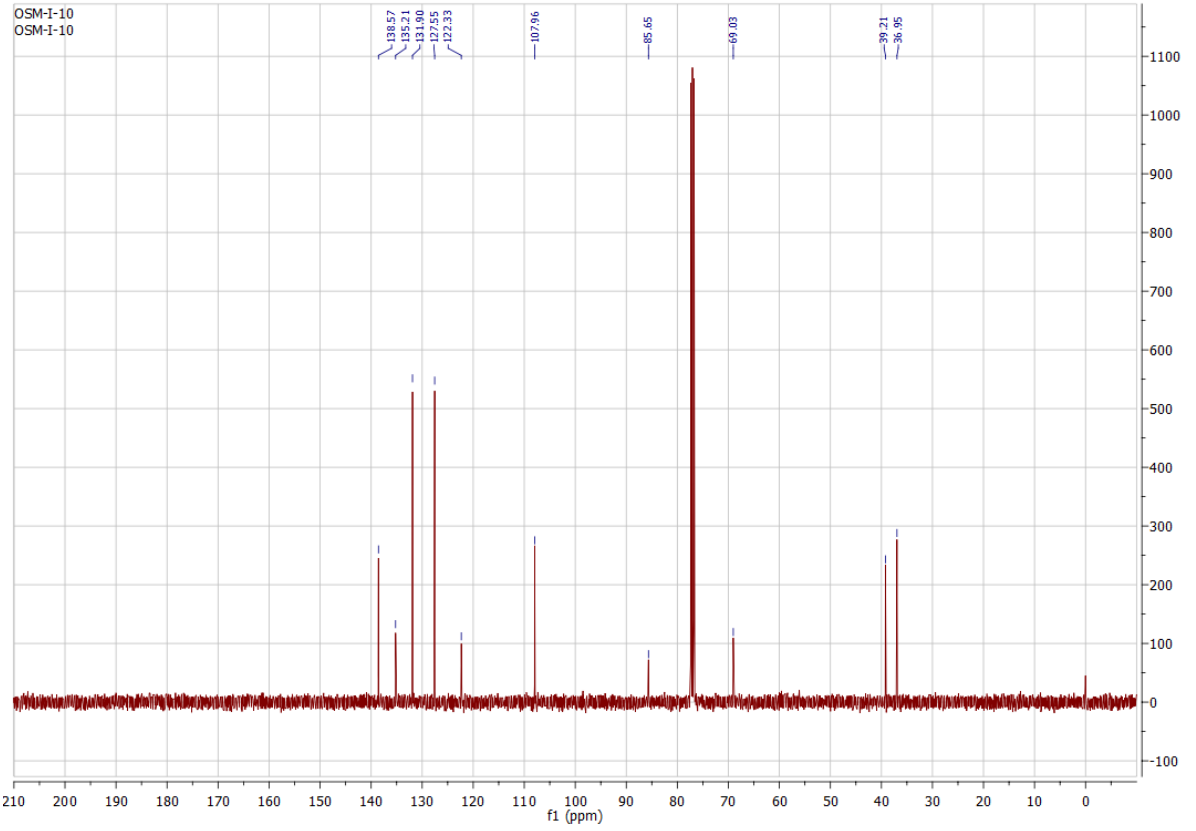

NHQ-X-71
NHQ-X-71
Ms
N
Me
5b
f1 (ppm)

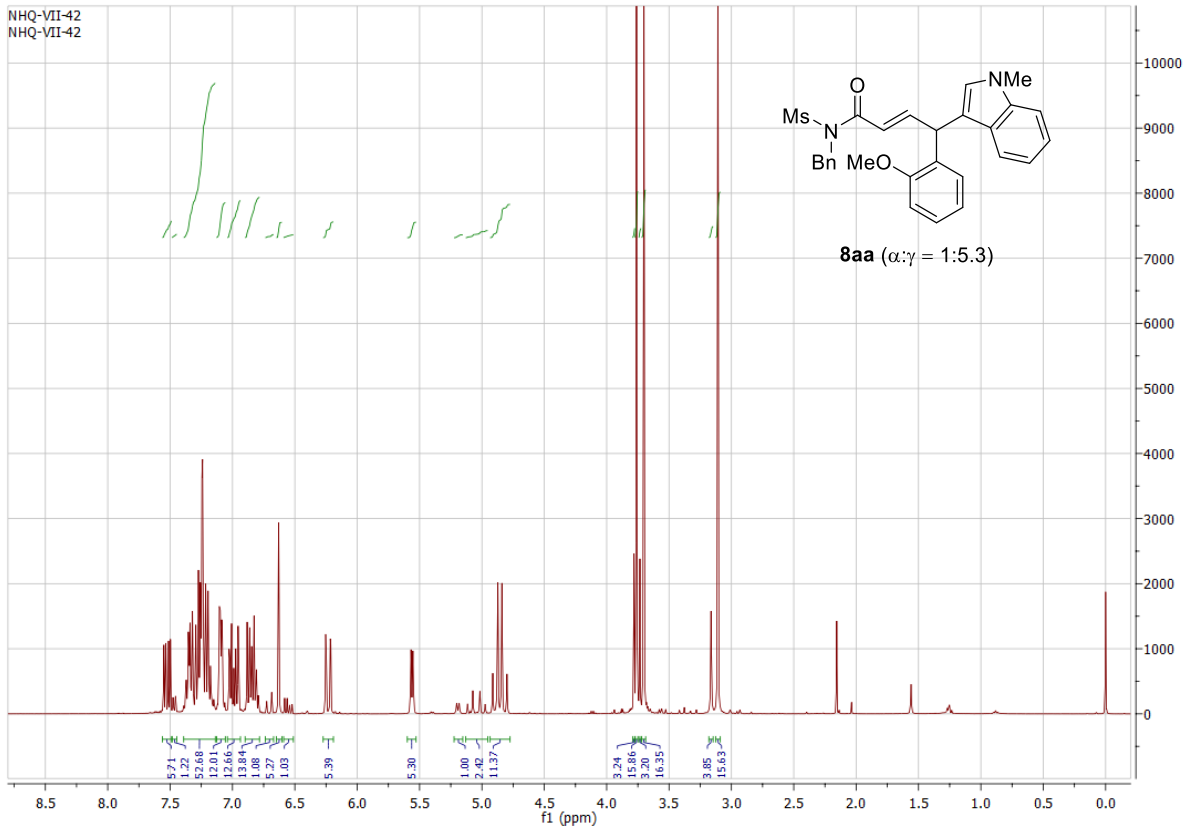

NHQ-X-71
NHQ-X-71
f1 (ppm)

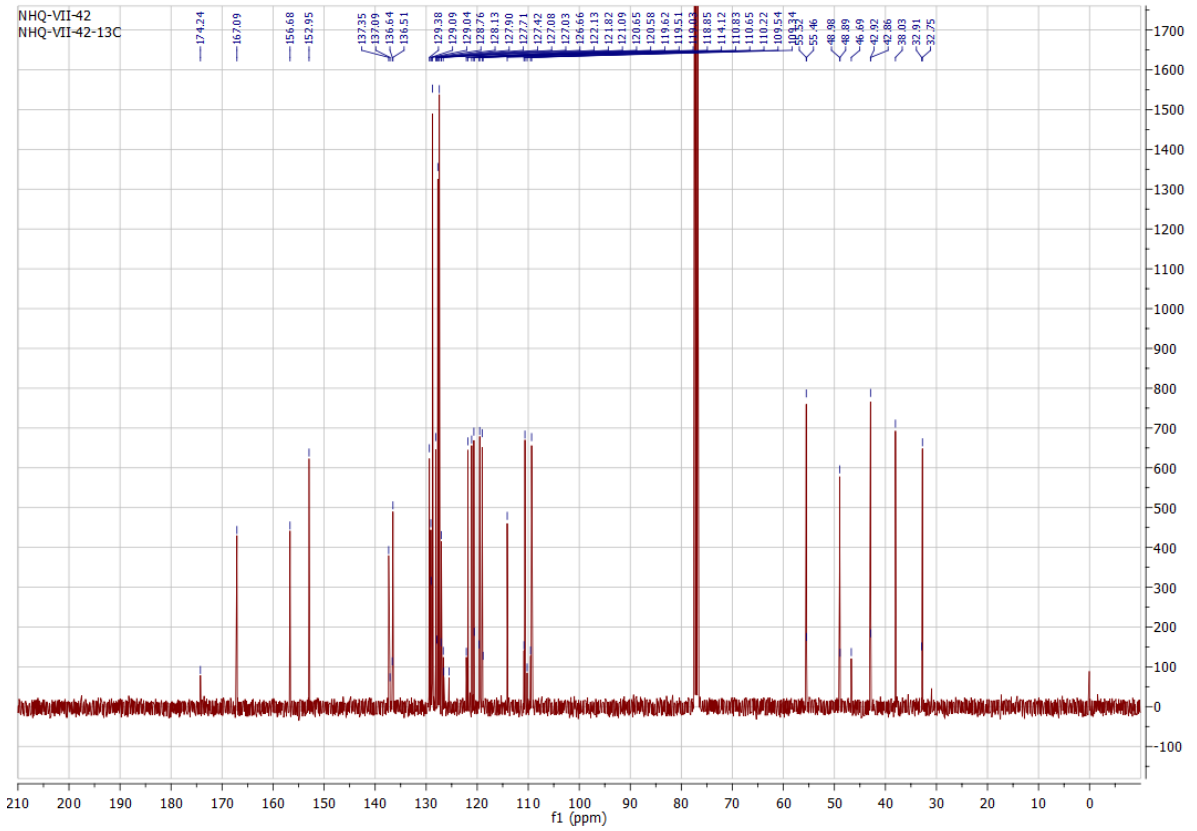

Ms
N
Me
4p
f1 (ppm)

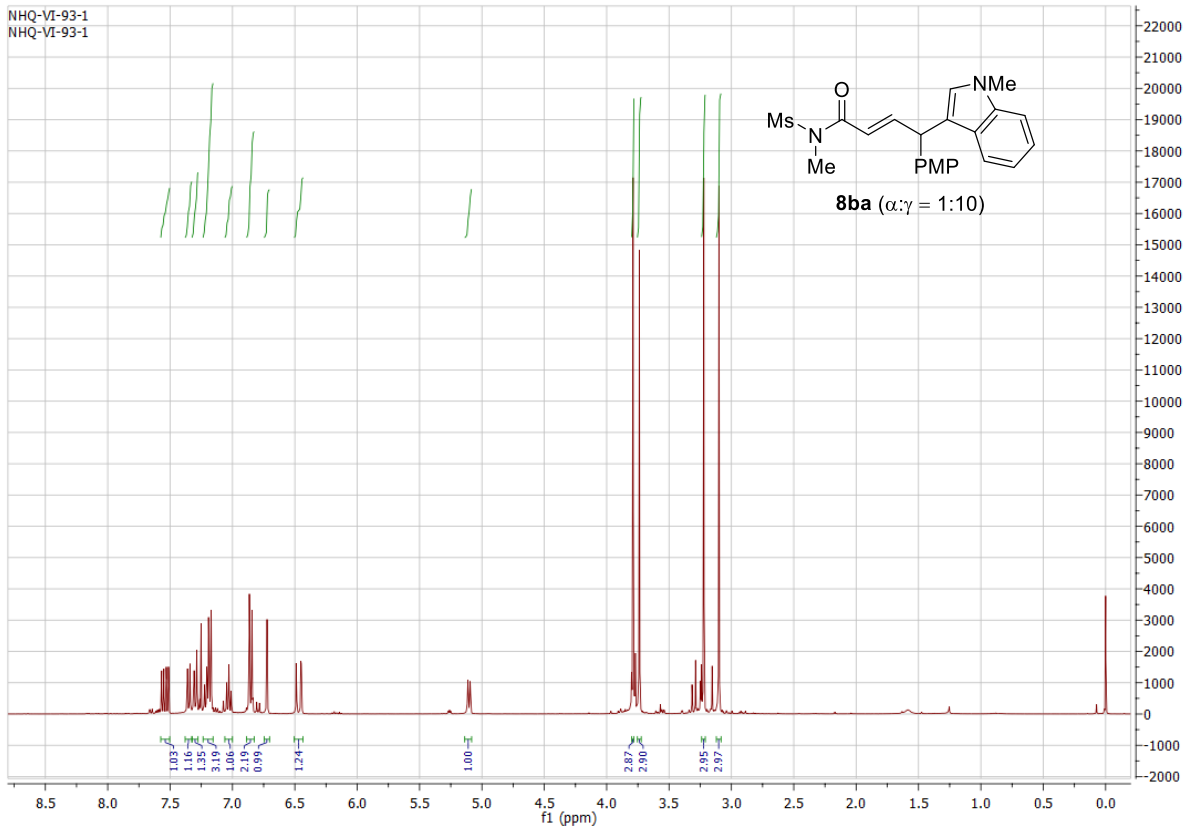

OSM-I-20
OSM-I-20
f1 (ppm)

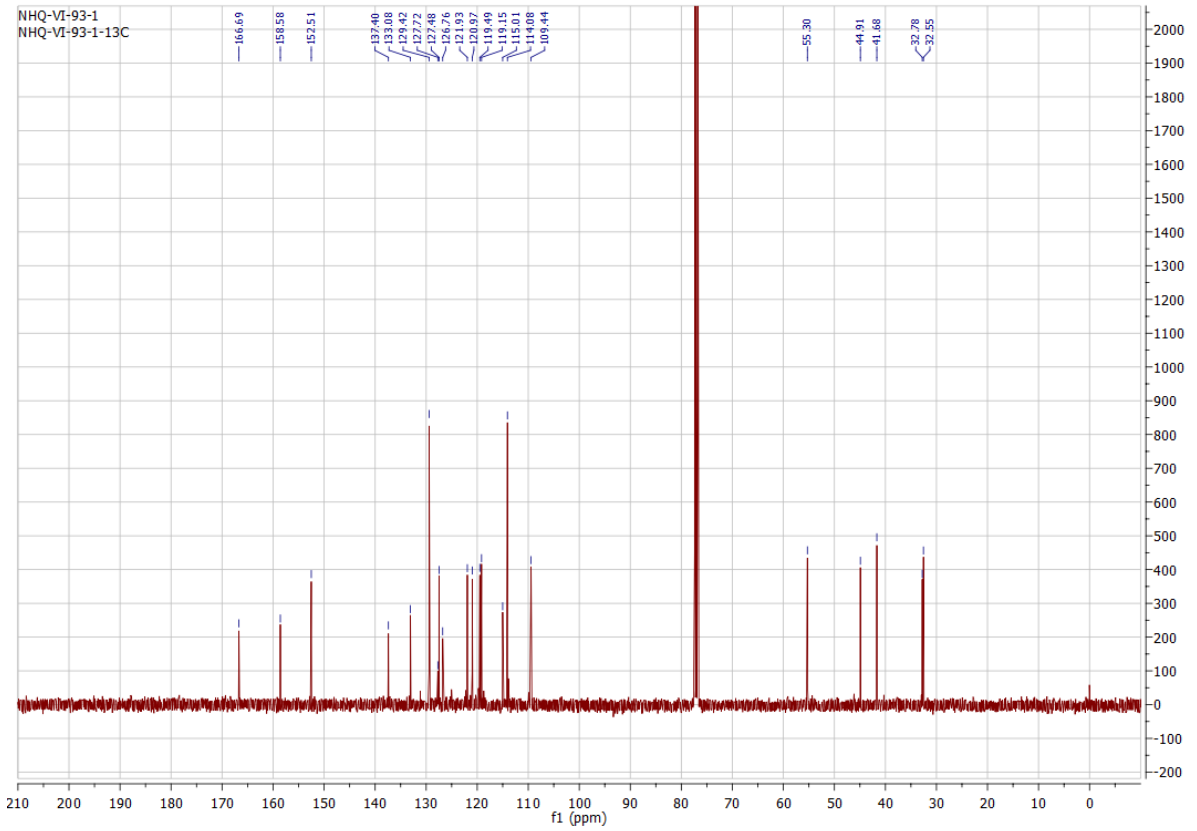

OSM-I-10
OSM-I-10
7.45
7.43
7.26
7.23
7.21
6.82
6.78
6.25
6.20
3.27
3.10
Ms
N
Me
Br
4q
2.08
2.36
1.00
1.04
3.06
3.10
f1 (ppm)

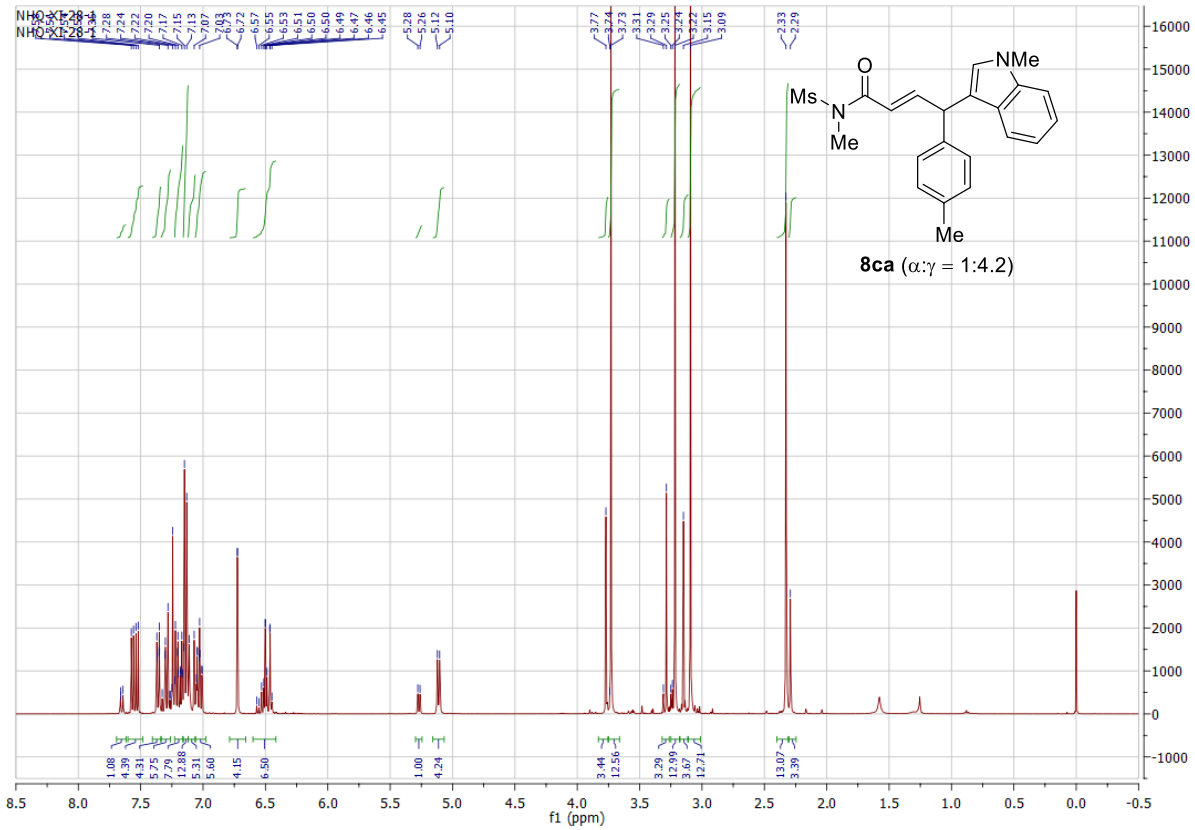

OSM-I-10
OSM-I-10
138.57
135.21
131.90
127.55
122.33
107.96
85.65
69.03
39.21
36.95
f1 (ppm)

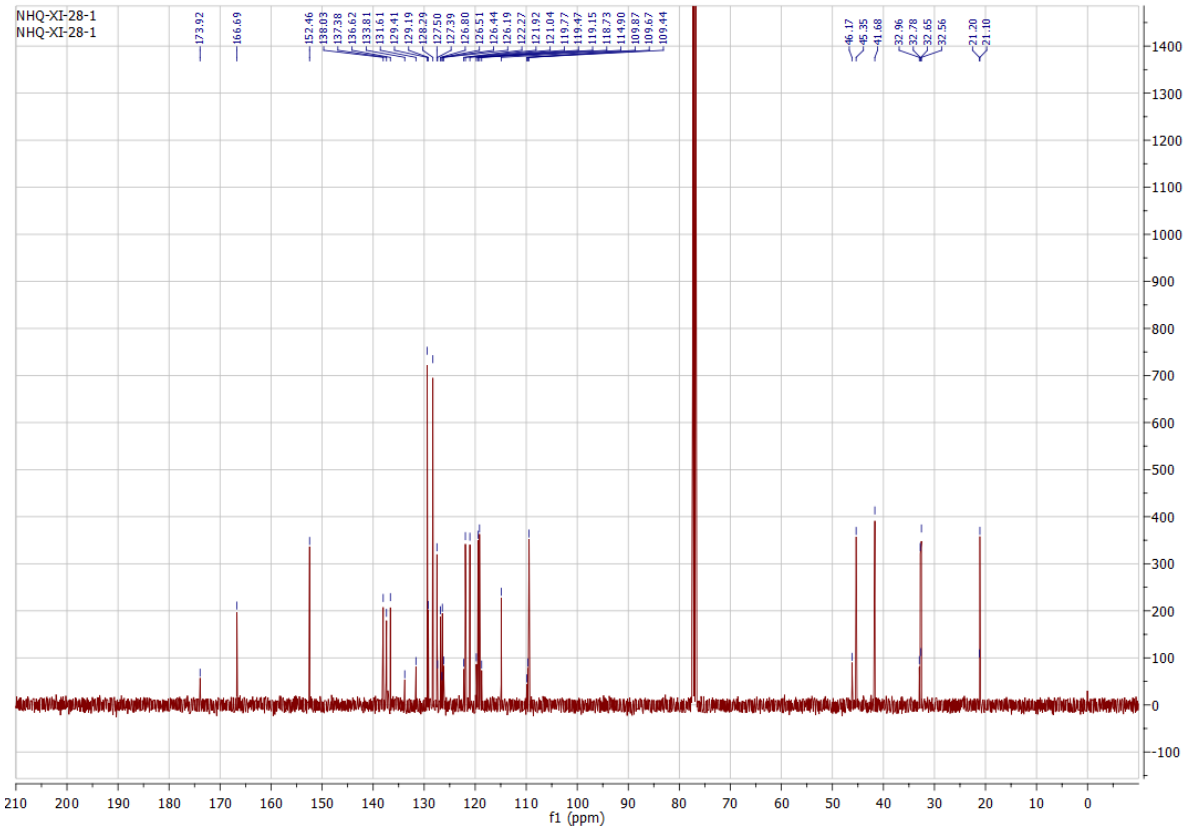

NHQ-VII-42
NHQ-VII-42
Ms
N
Bn
O
MeO
NMe
8aa (α:γ = 1:5.3)
f1 (ppm)

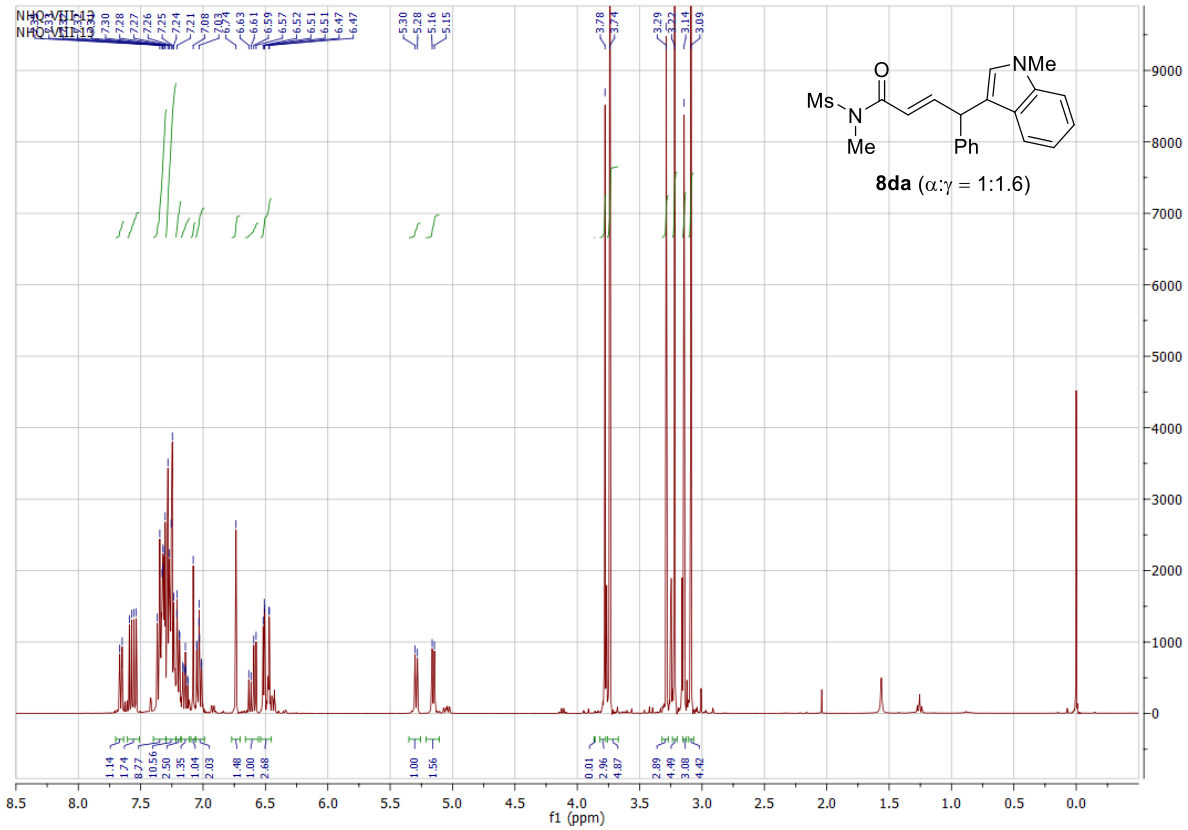

NHQ-VII-42
NHQ-VII-42-13C
f1 (ppm)

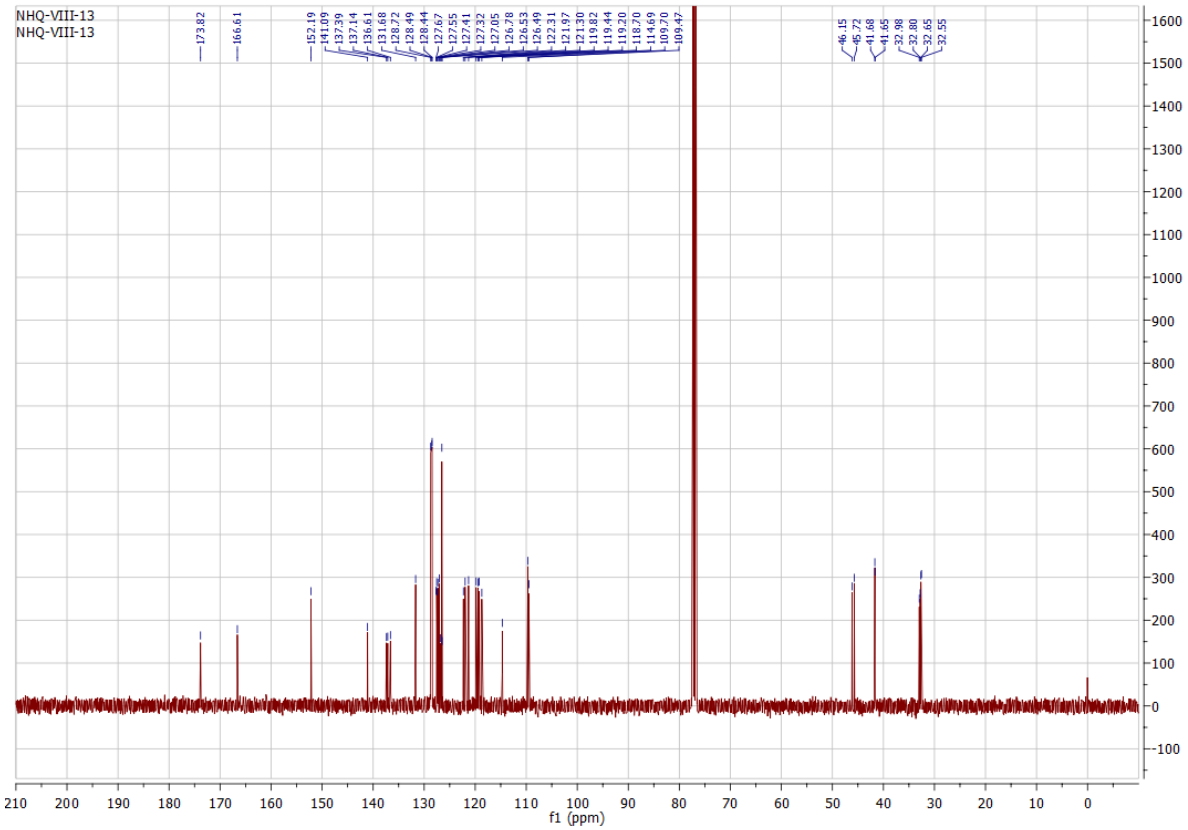

NHQ-VI-93-1
NHQ-VI-93-1
Ms
N
Me
O
NMe
PMP
8ba (α:γ = 1:10)
f1 (ppm)

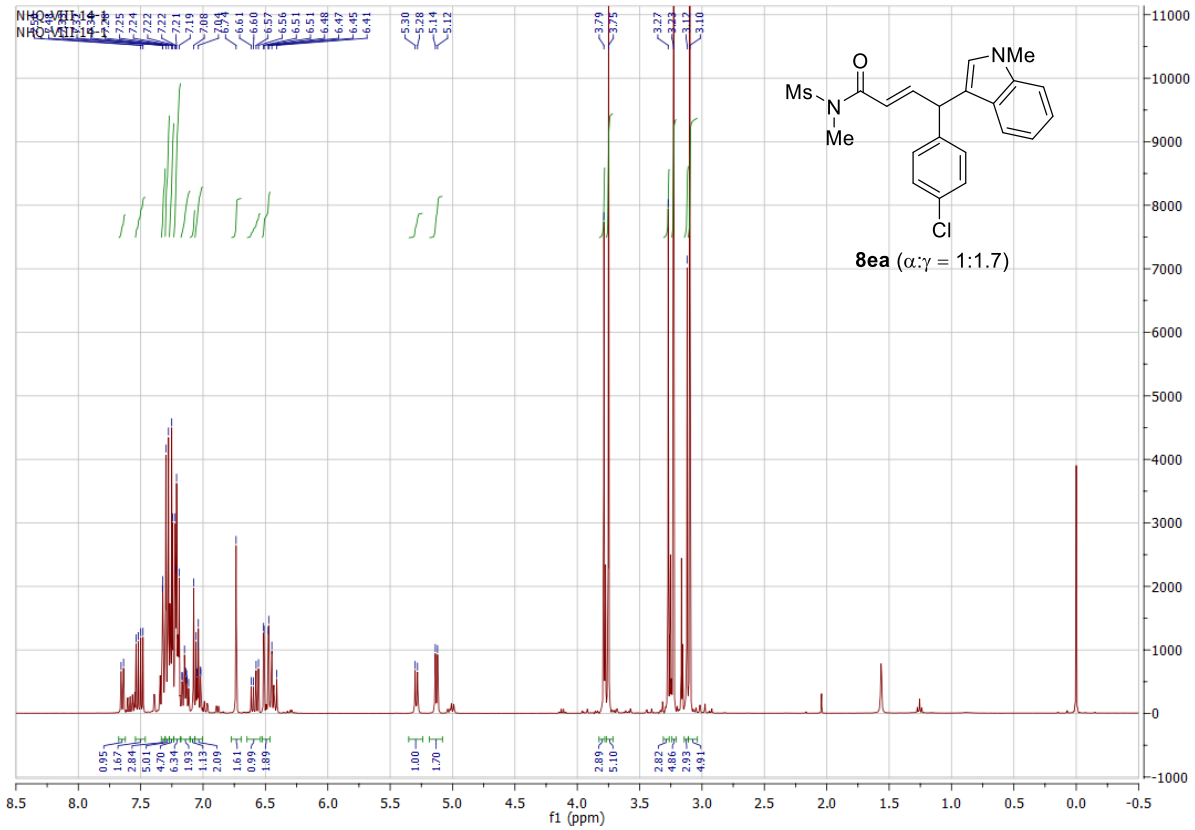

NHQ-VI-93-1
NHQ-VI-93-1-13C
166.69
158.58
152.51
137.40
133.08
129.42
127.72
127.48
126.76
121.93
120.97
119.49
119.15
115.01
114.08
109.44
55.30
44.91
41.68
32.78
32.55
f1 (ppm)

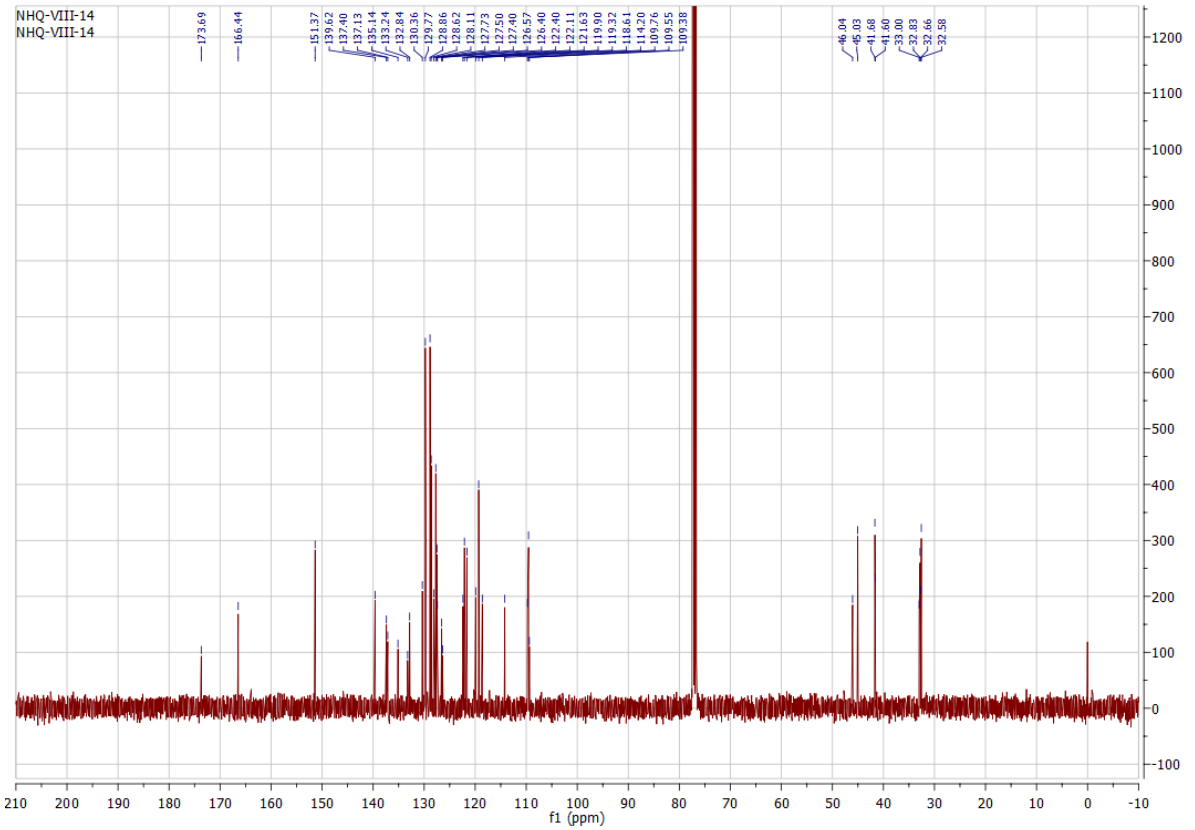

NHQ-XI-28-1
NHQ-XI-28-1
Ms
N
Me
O
NMe
Me
8ca (α:γ = 1:4.2)
f1 (ppm)

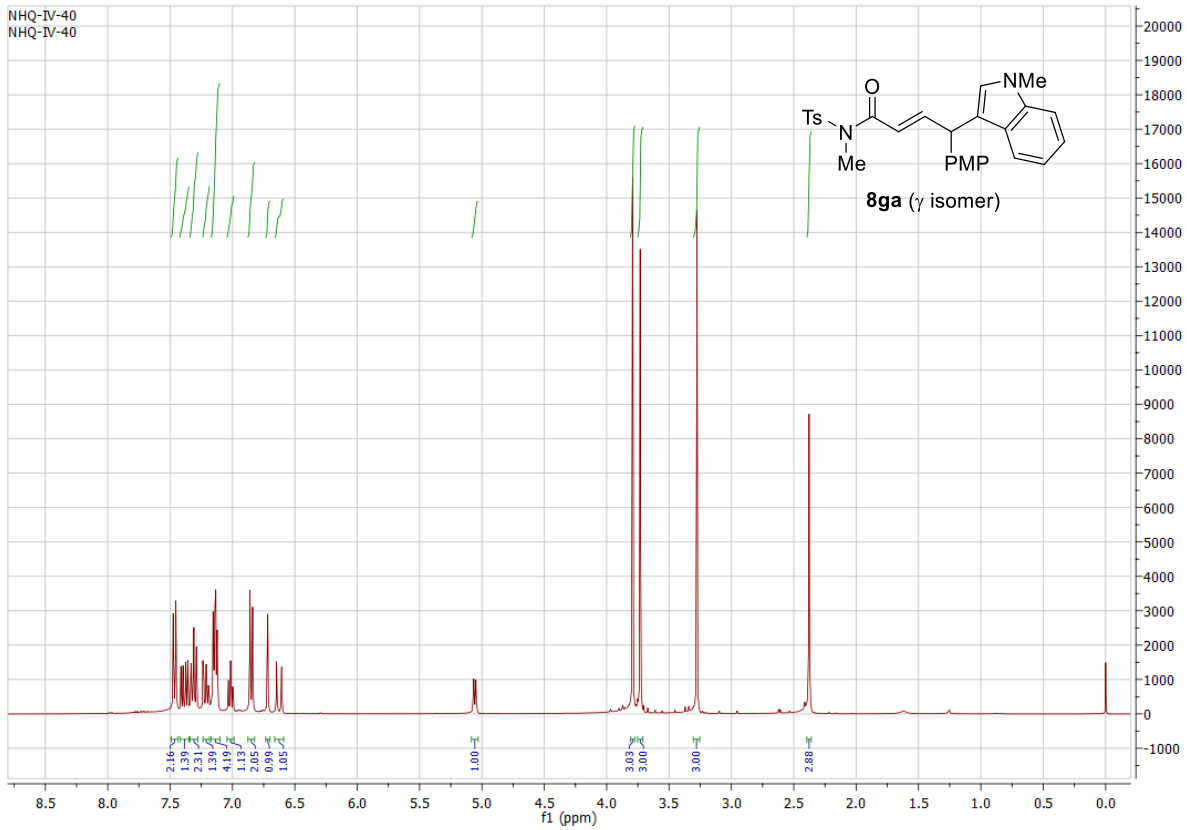

NHQ-XI-28-1
NHQ-XI-28-1
f1 (ppm)

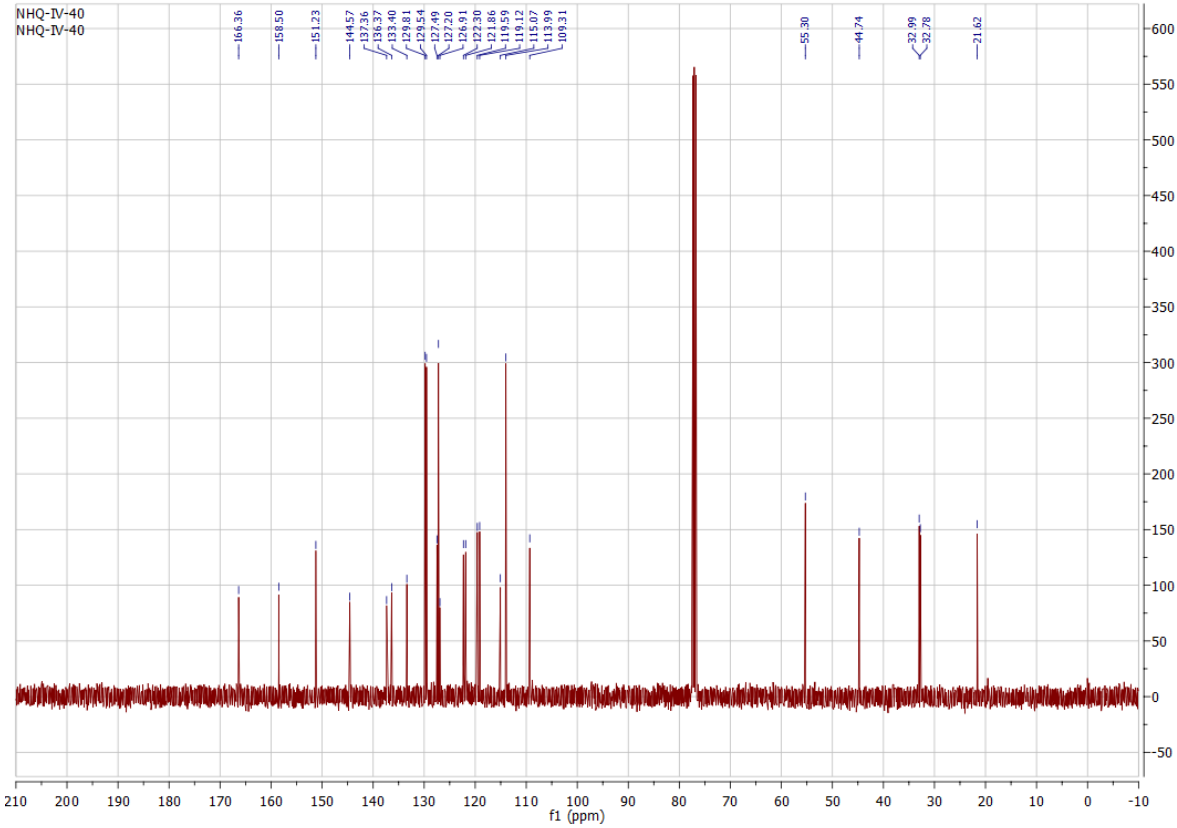

NHQ-VIII-13
NHQ-VIII-13
Ms
N
Me
O
NMe
Ph
8da (α:γ = 1:1.6)
f1 (ppm)

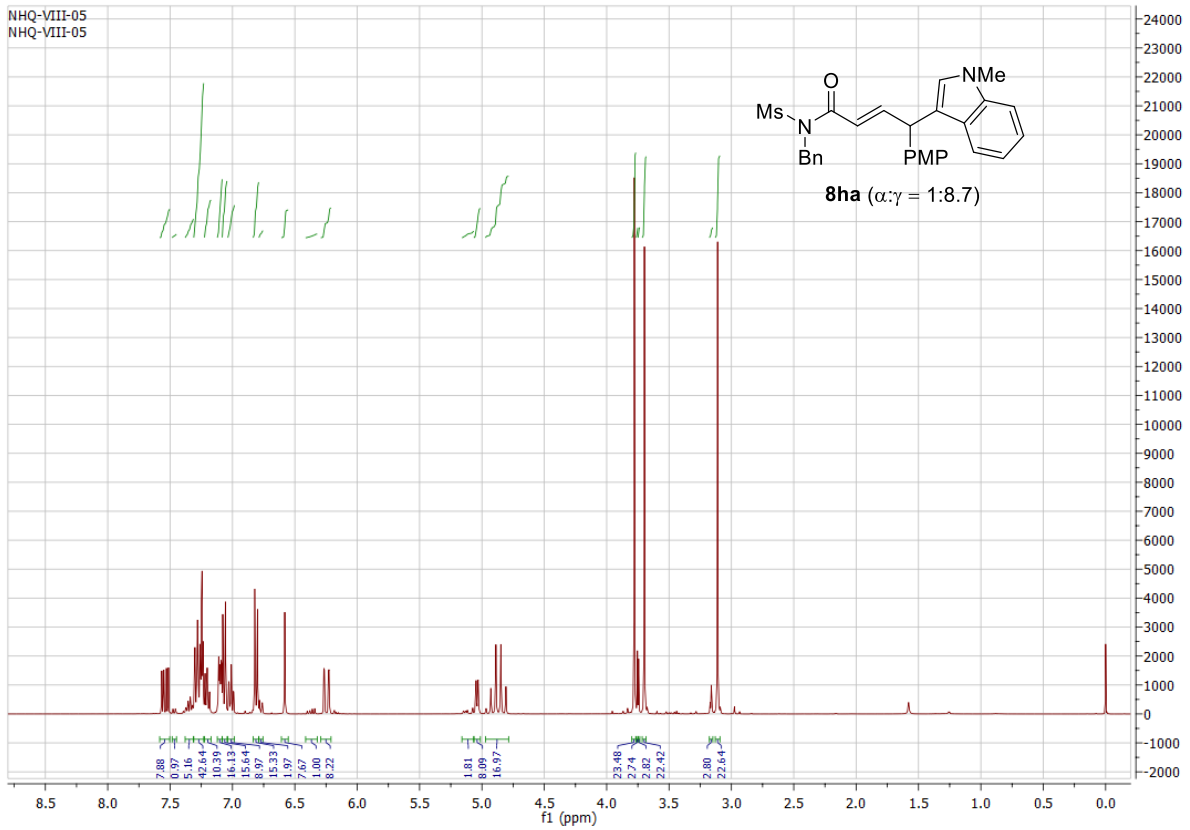

NHQ-VIII-13
NHQ-VIII-13
f1 (ppm)

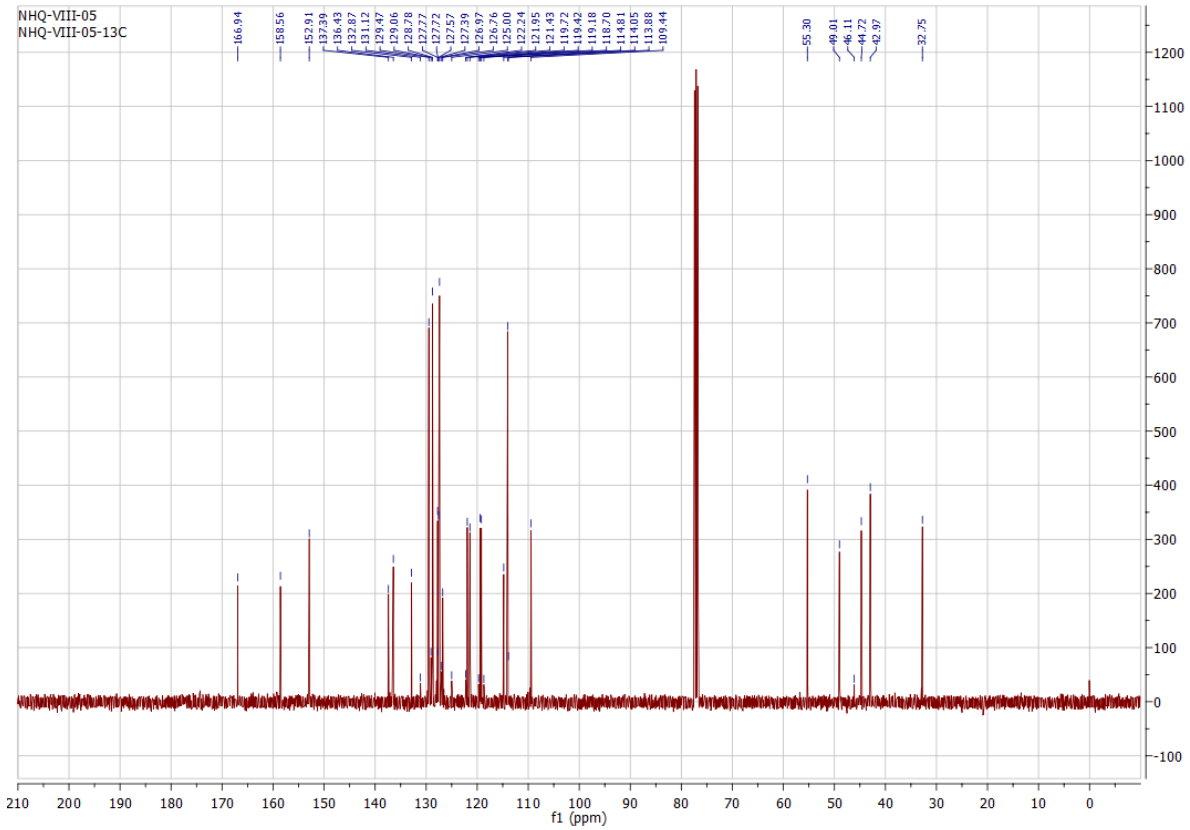

NHQ-VIII-14
NHQ-VIII-14
Ms
N
Me
O
NMe
Cl
8ea (α:γ = 1:1.7)
f1 (ppm)

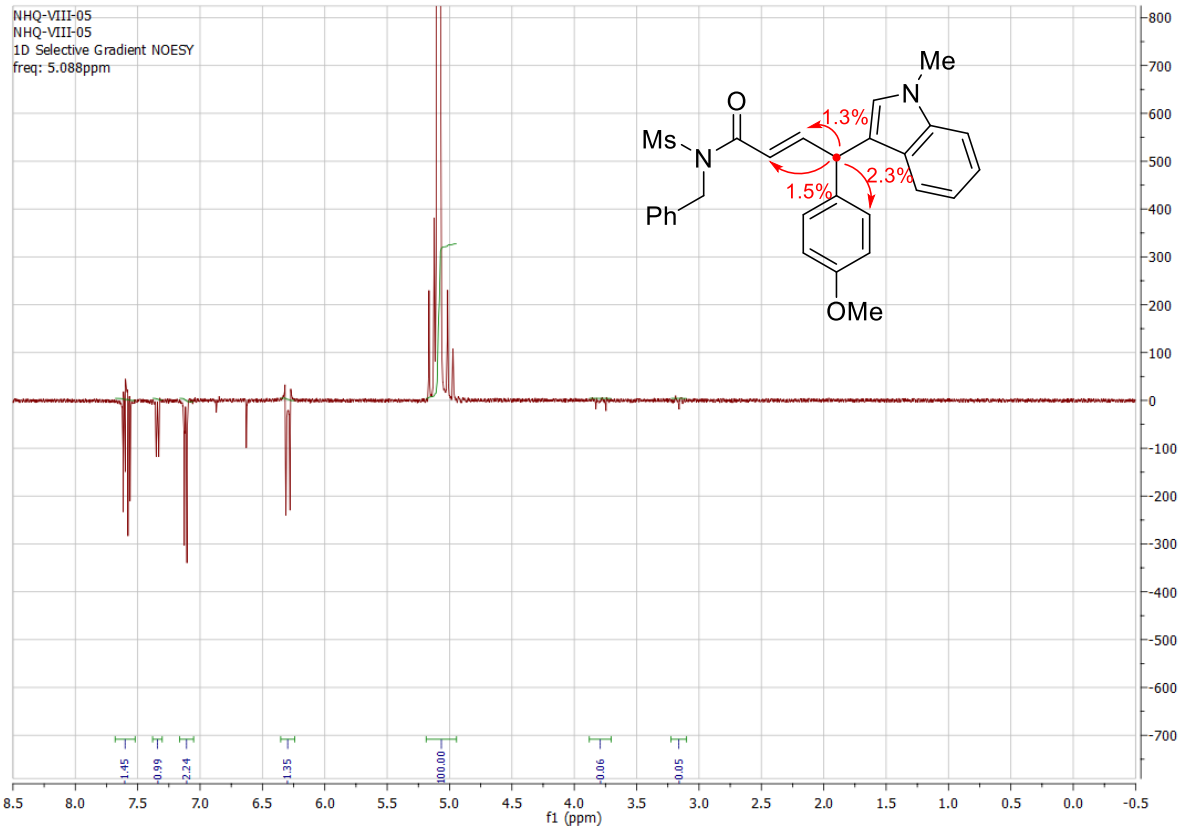

NHQ-VIII-14
NHQ-VIII-14
f1 (ppm)


NHQ-IV-40
NHQ-IV-40
Ts
N
Me
O
NMe
PMP
8ga (γ isomer)
f1 (ppm)

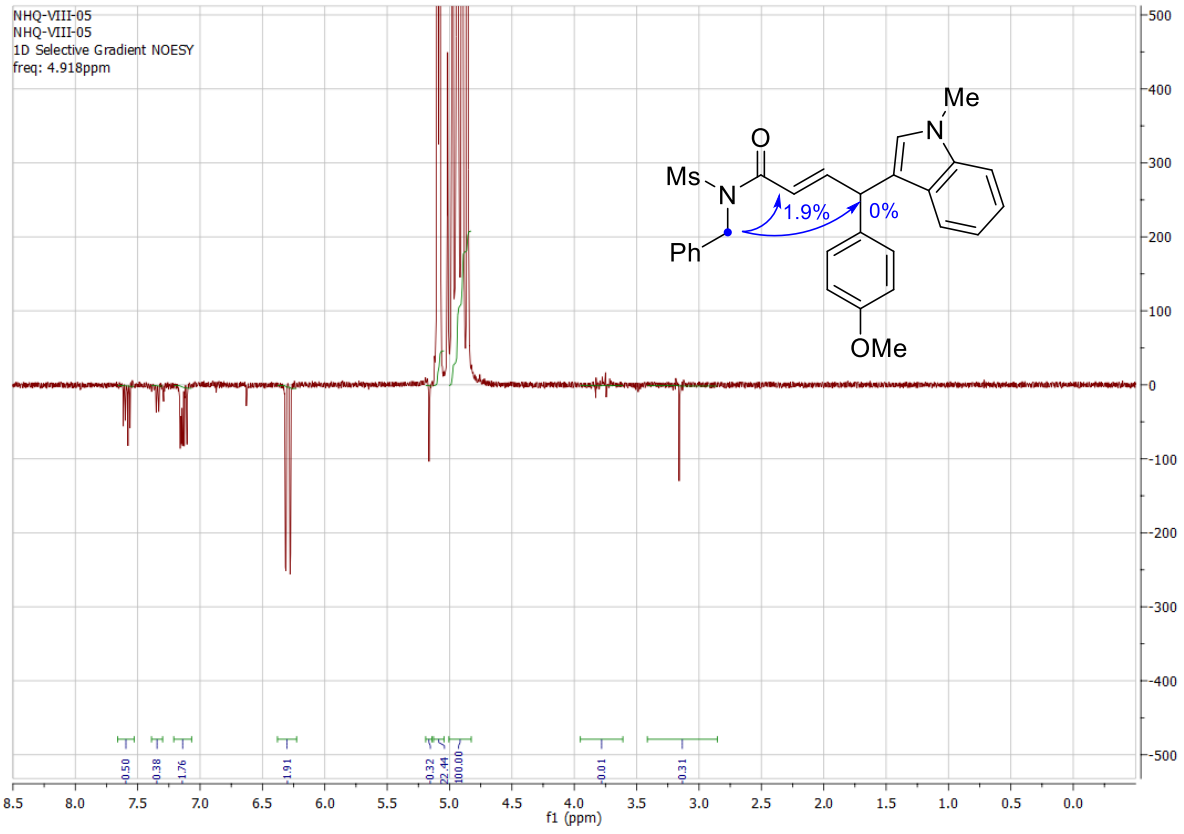

NHQ-IV-40
NHQ-IV-40
166.36
158.50
151.23
144.57
137.36
136.37
133.40
129.81
129.54
127.49
127.20
126.91
122.30
121.86
119.59
119.12
115.07
113.99
109.31
55.30
44.74
32.99
32.78
21.62
f1 (ppm)

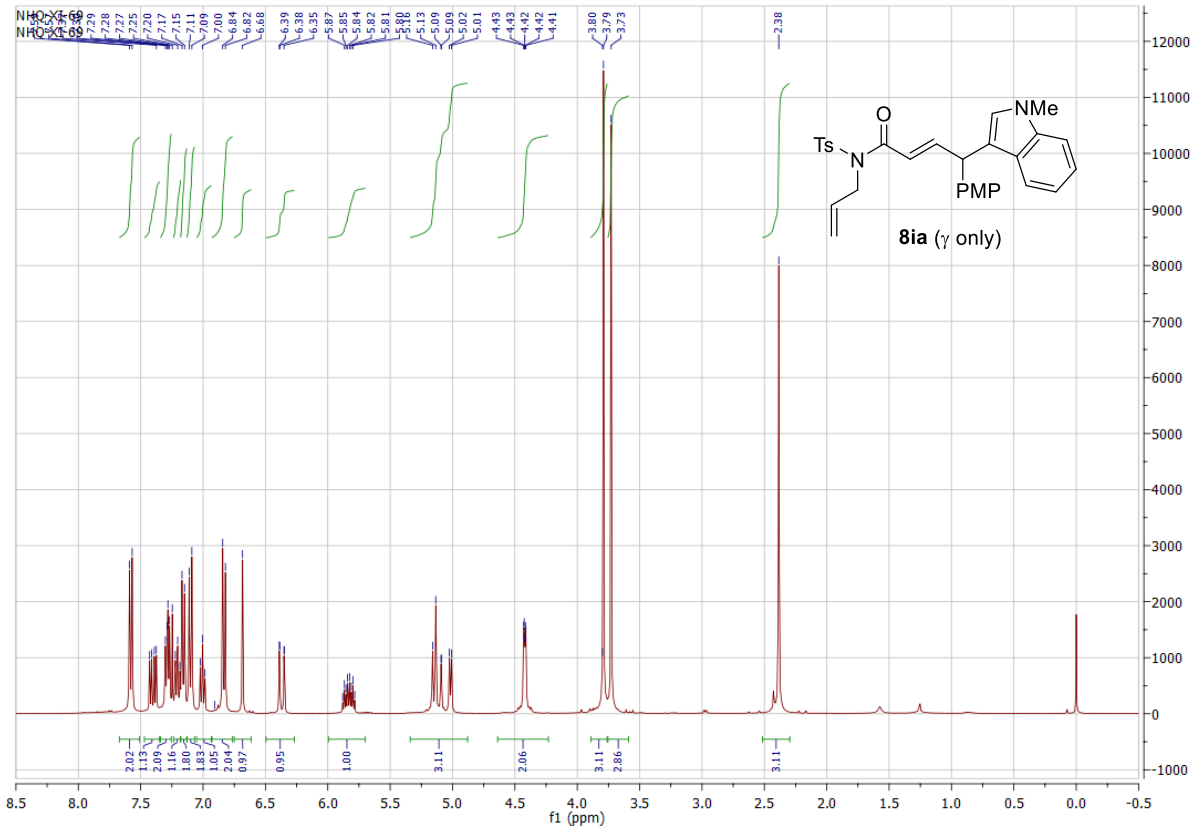

NHQ-VIII-05
NHQ-VIII-05
NMe
O
Ms
N
Bn
PMP
8ha (α:γ = 1:8.7)
f1 (ppm)

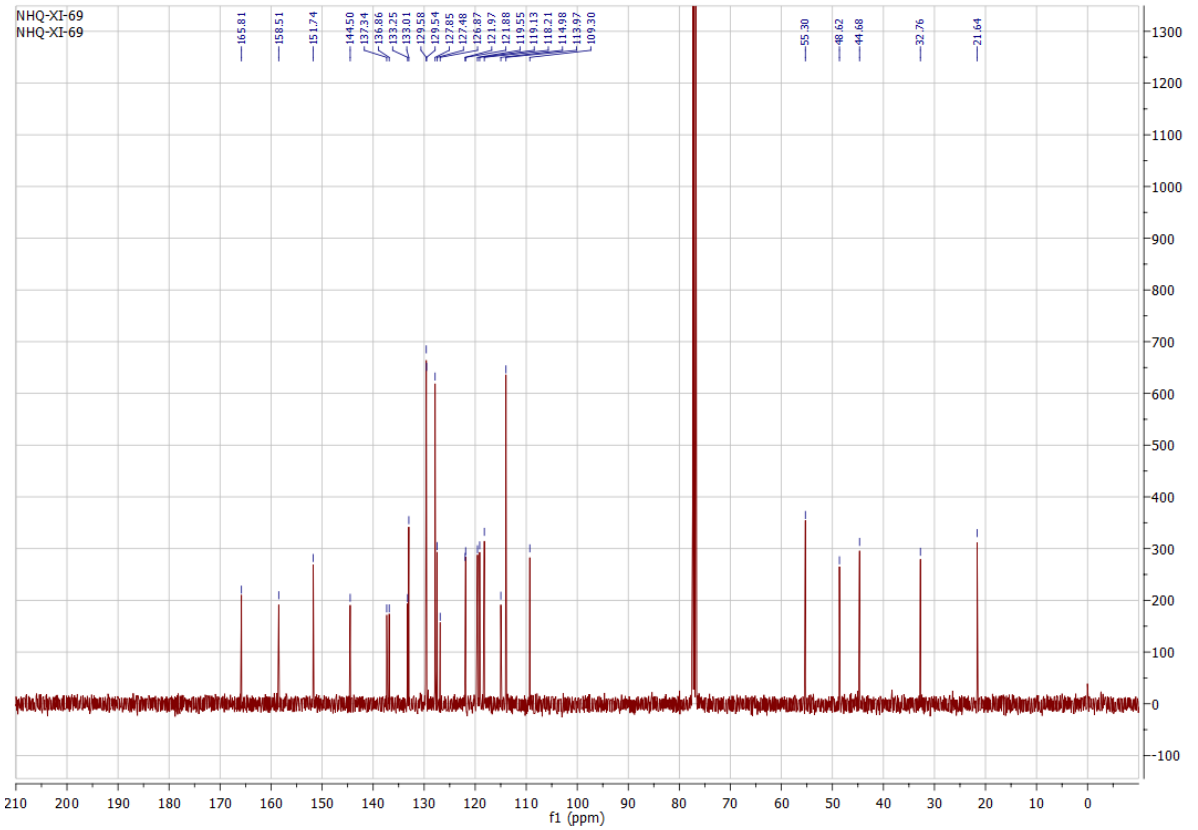

NHQ-VIII-05
NHQ-VIII-05-13C
f1 (ppm)

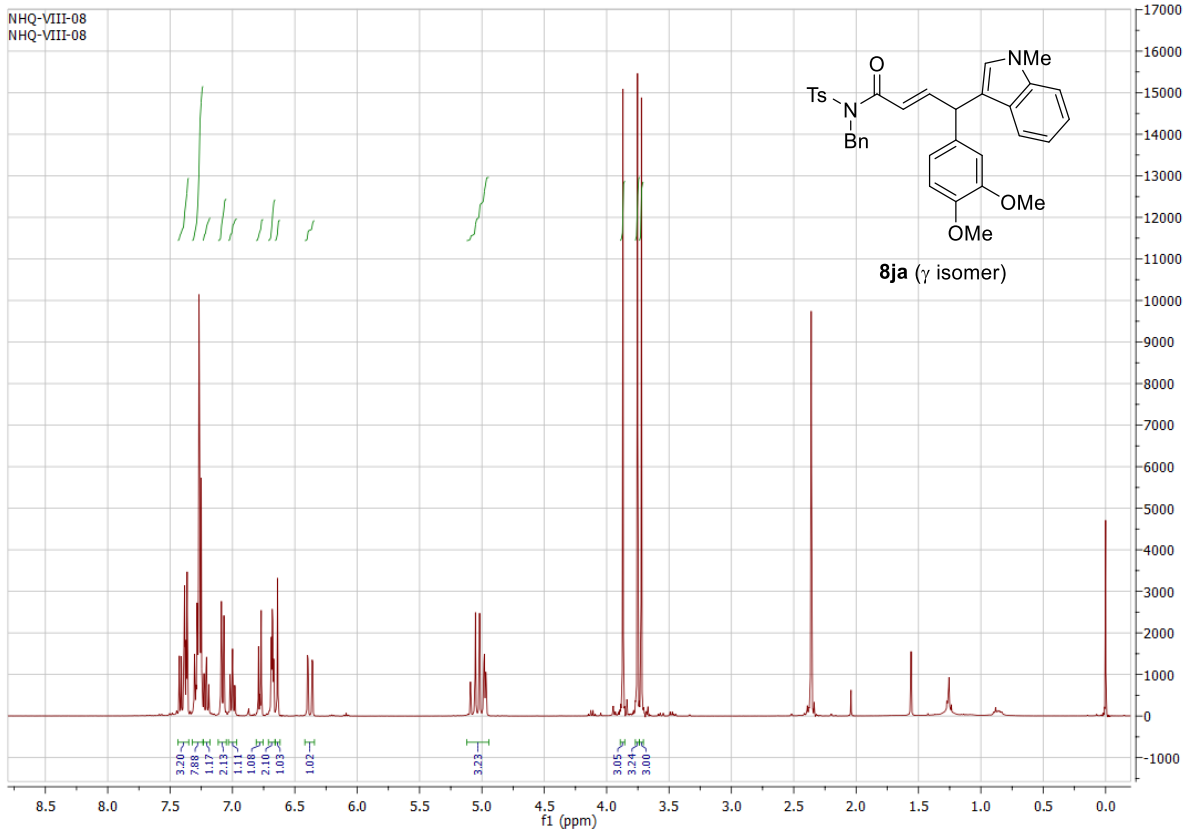


NOE at 4.9 ppm (2ha)

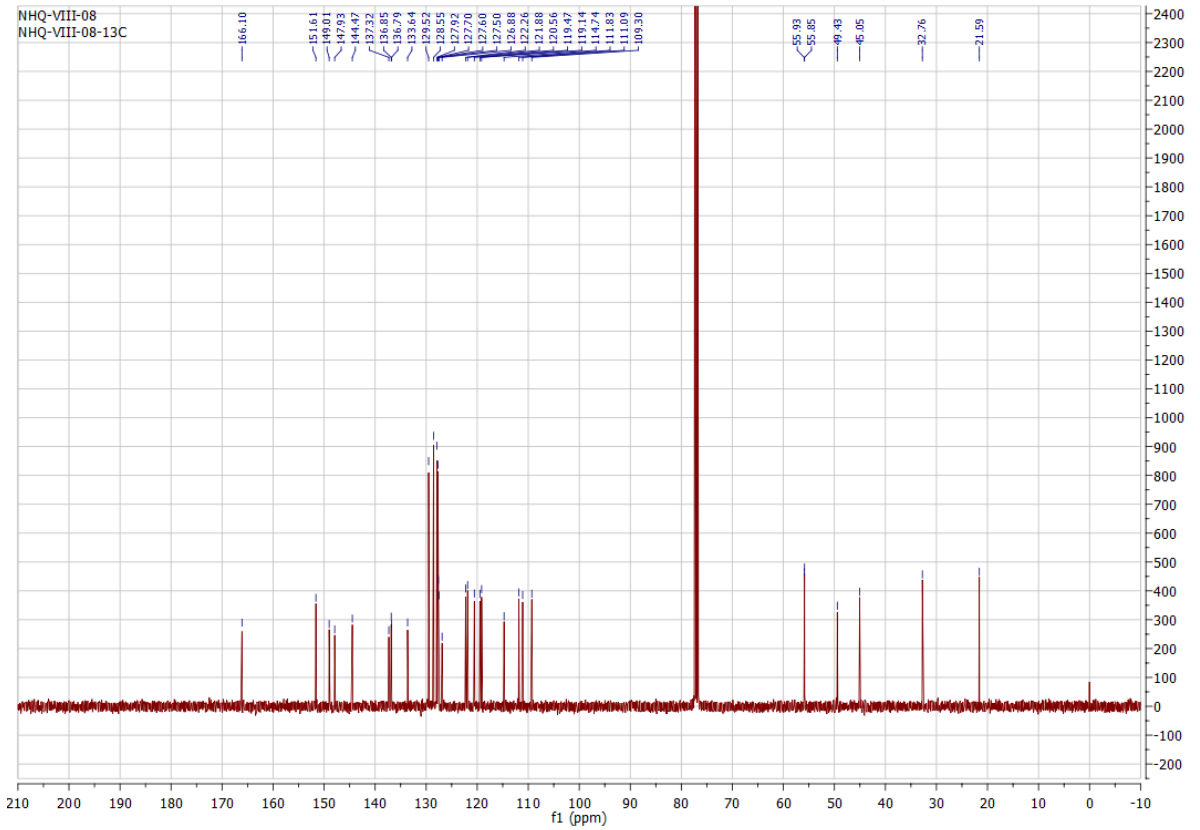


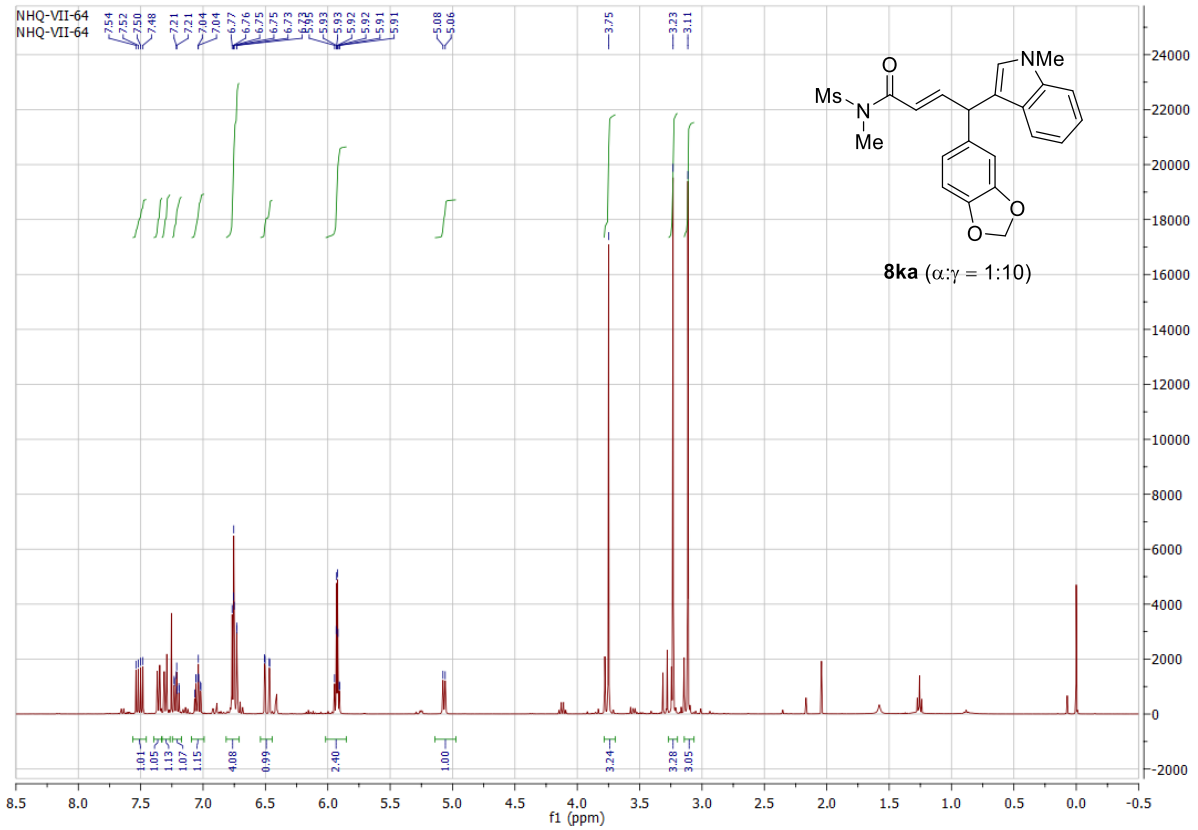

NHQ-XI-69
NHQ-XI-69
Ts
N
O
NMe
PMP
8ia (γ only)
f1 (ppm)

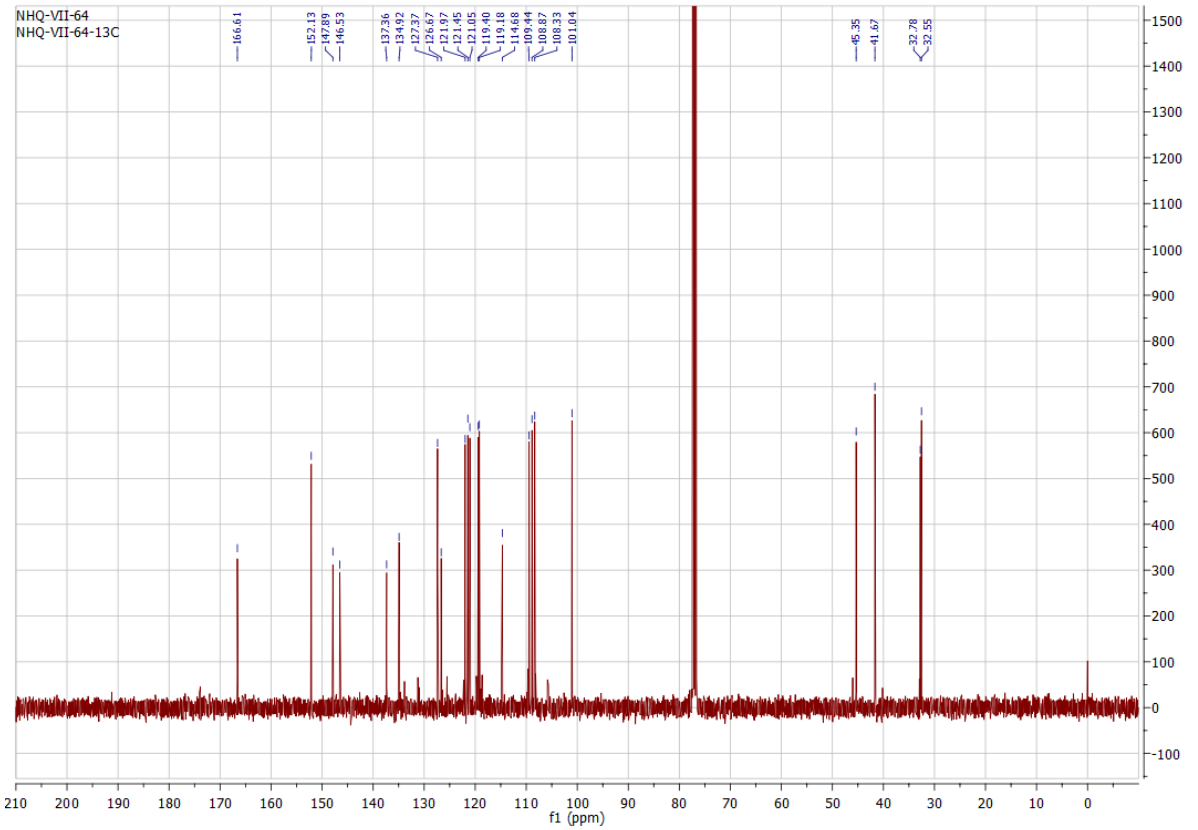

NHQ-XI-69
NHQ-XI-69
f1 (ppm)

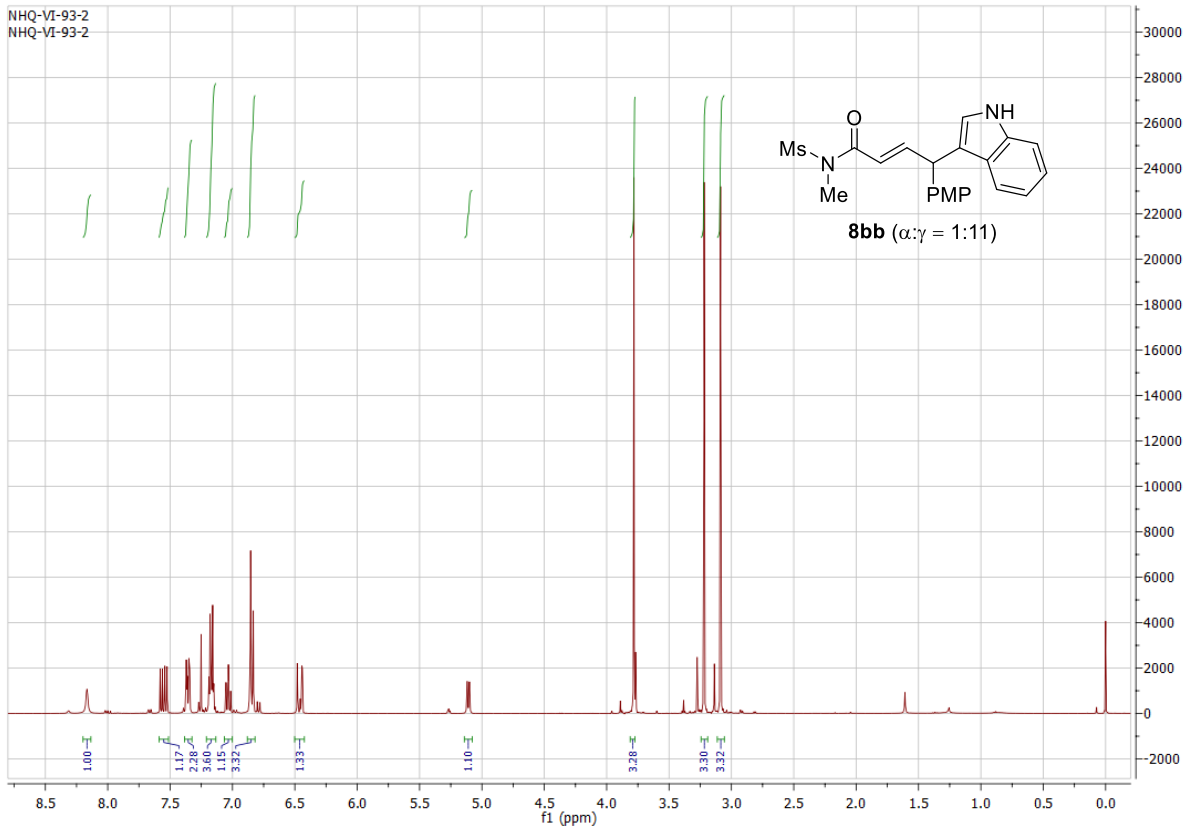


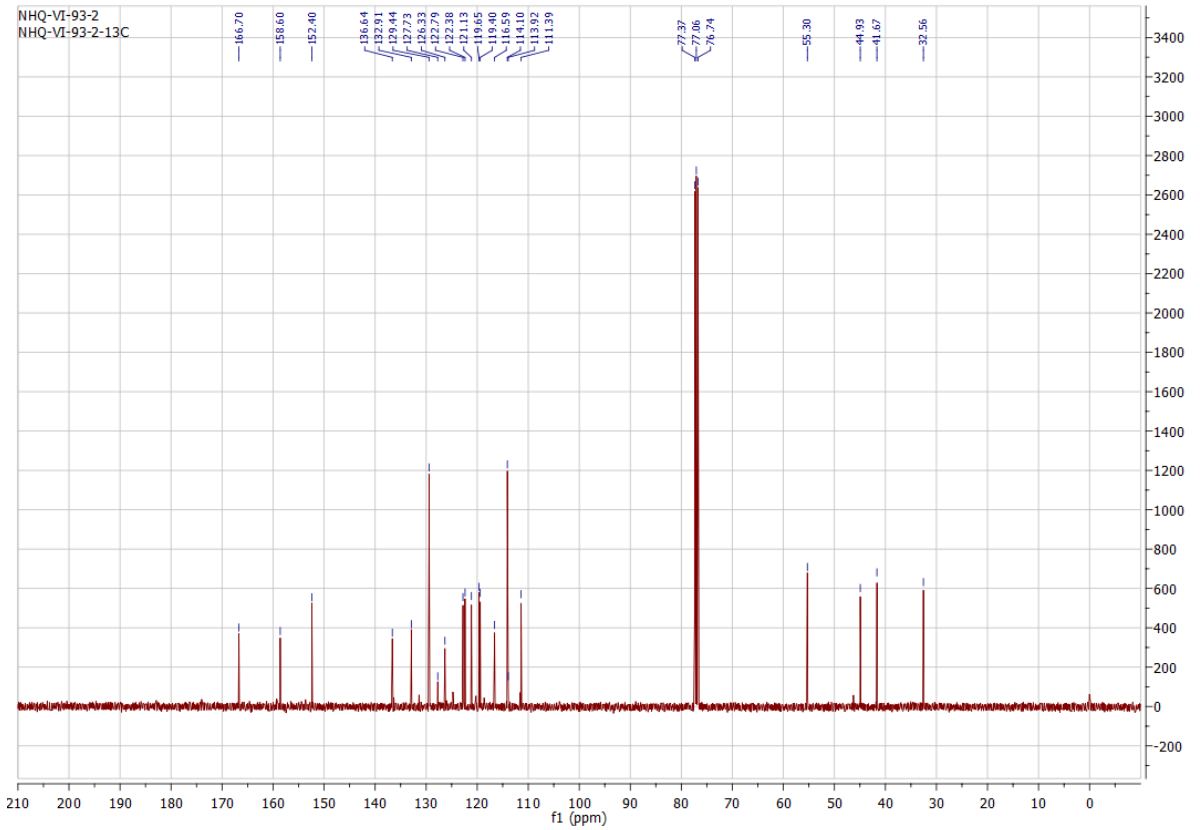
8ja (γ isomer)

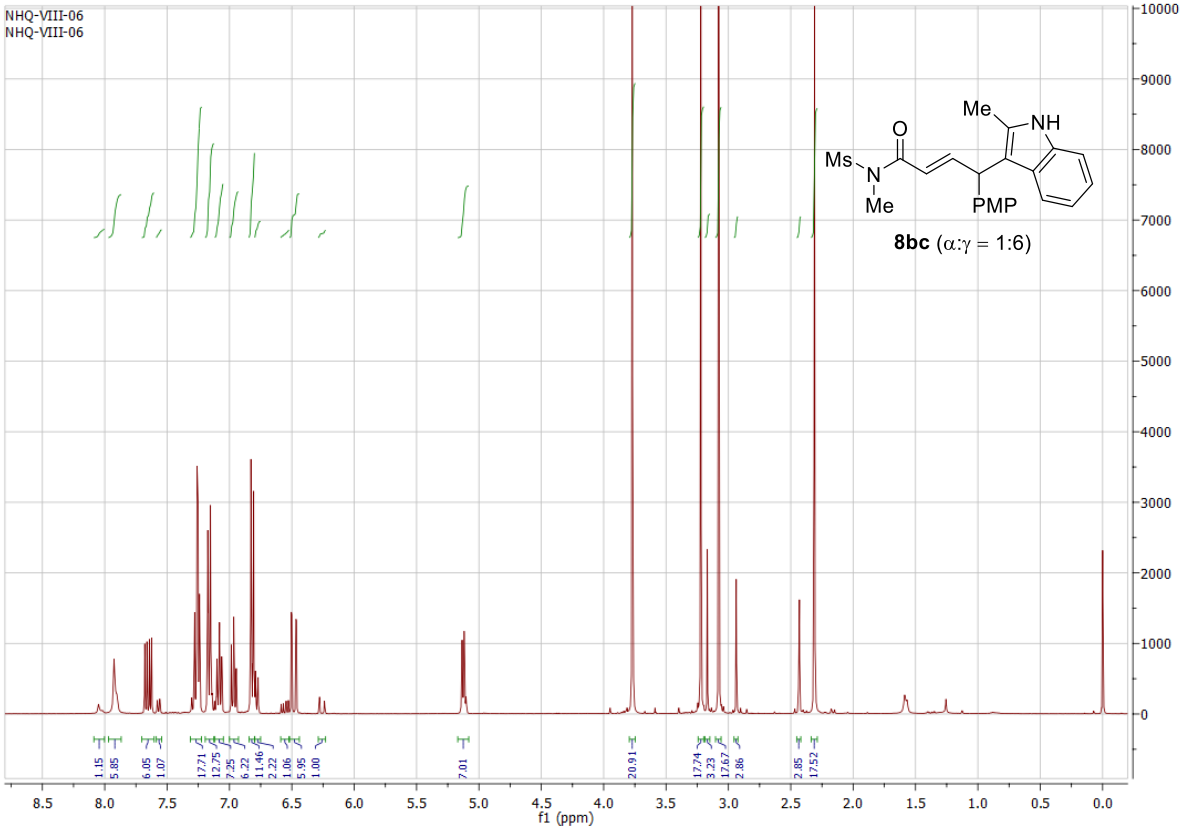


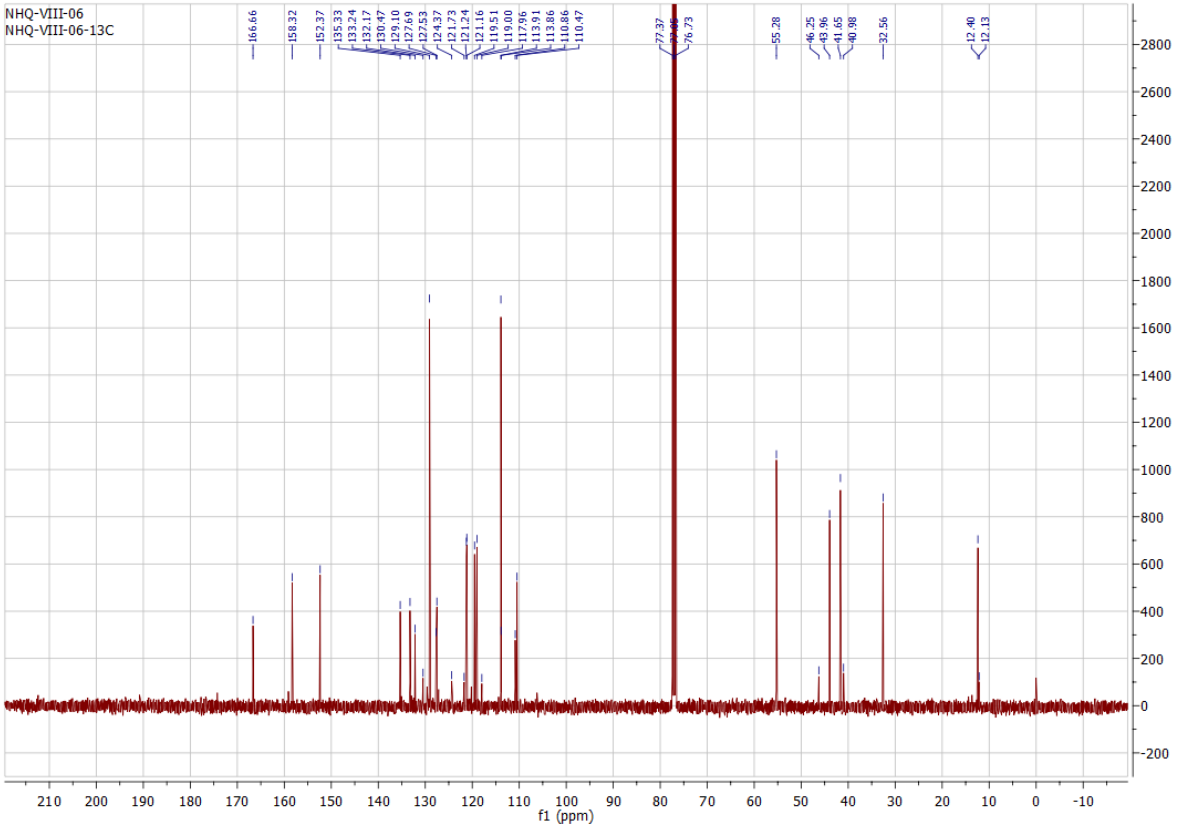

NHQ-VII-64
NHQ-VII-64
7.54
7.52
7.50
7.48
7.21
7.21
7.04
7.04
6.77
6.76
6.75
6.75
6.73
5.95
5.93
5.93
5.92
5.92
5.91
5.91
5.08
5.06
3.75
3.23
3.11
1.01
1.05
1.13
1.07
1.15
4.08
0.99
2.40
1.00
3.24
3.28
3.05
f1 (ppm)
Ms
N
Me
O
NMe
O
O
8ka (α:γ = 1:10)

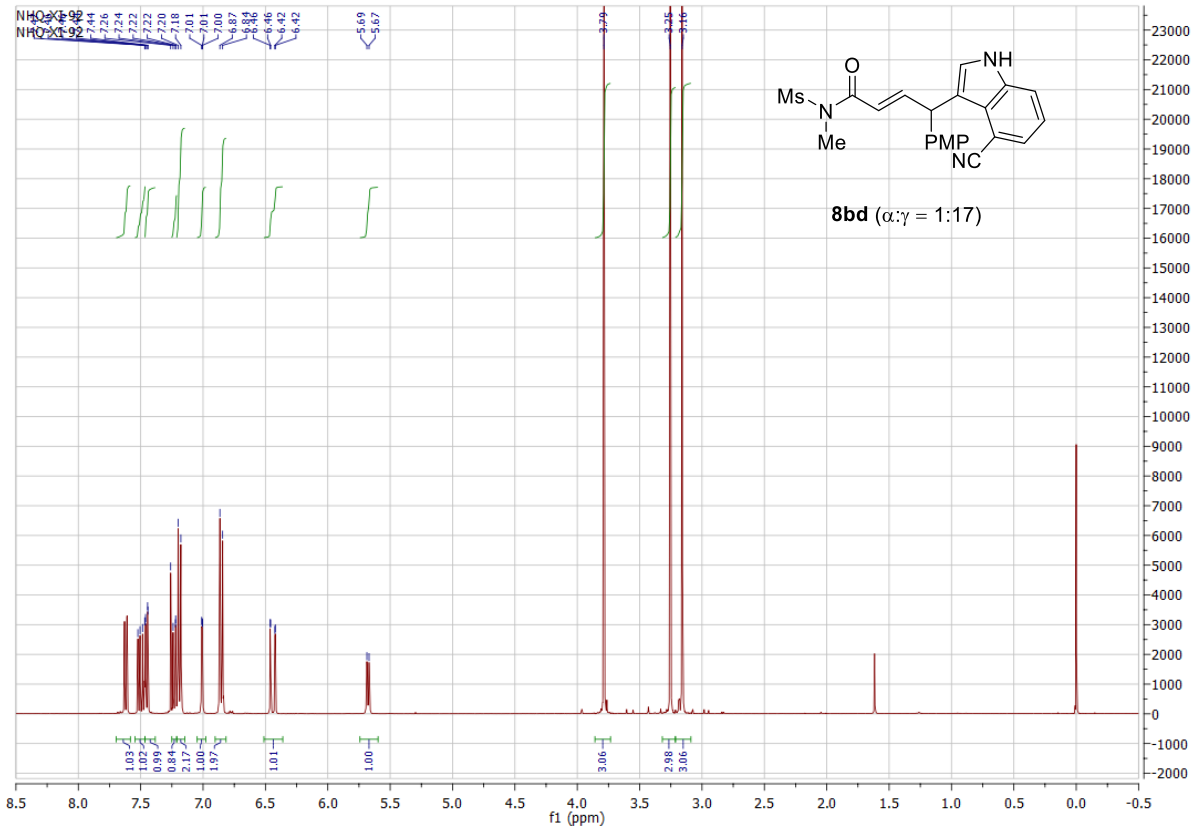

NHQ-VII-64
NHQ-VII-64-13C
166.61
152.13
147.89
146.53
137.36
134.92
127.37
126.67
121.97
121.45
121.05
119.40
119.18
114.68
109.44
108.87
108.33
101.04
46.35
41.67
32.78
32.55
f1 (ppm)

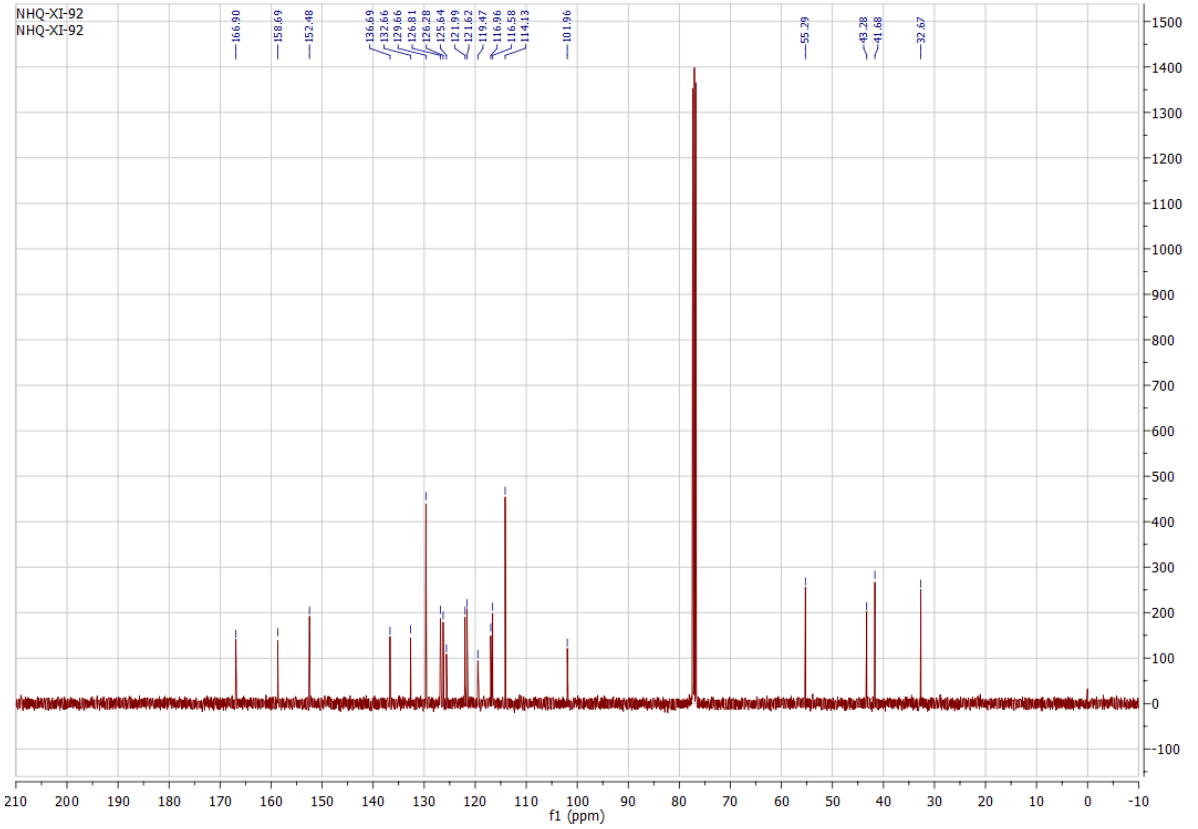

NHQ-VI-93-2
NHQ-VI-93-2
NH
O
Ms
N
Me
PMP
8bb (α:γ = 1:11)
1.00
1.17
2.28
3.60
1.15
3.32
1.33
1.10
3.28
3.30
3.32
f1 (ppm)

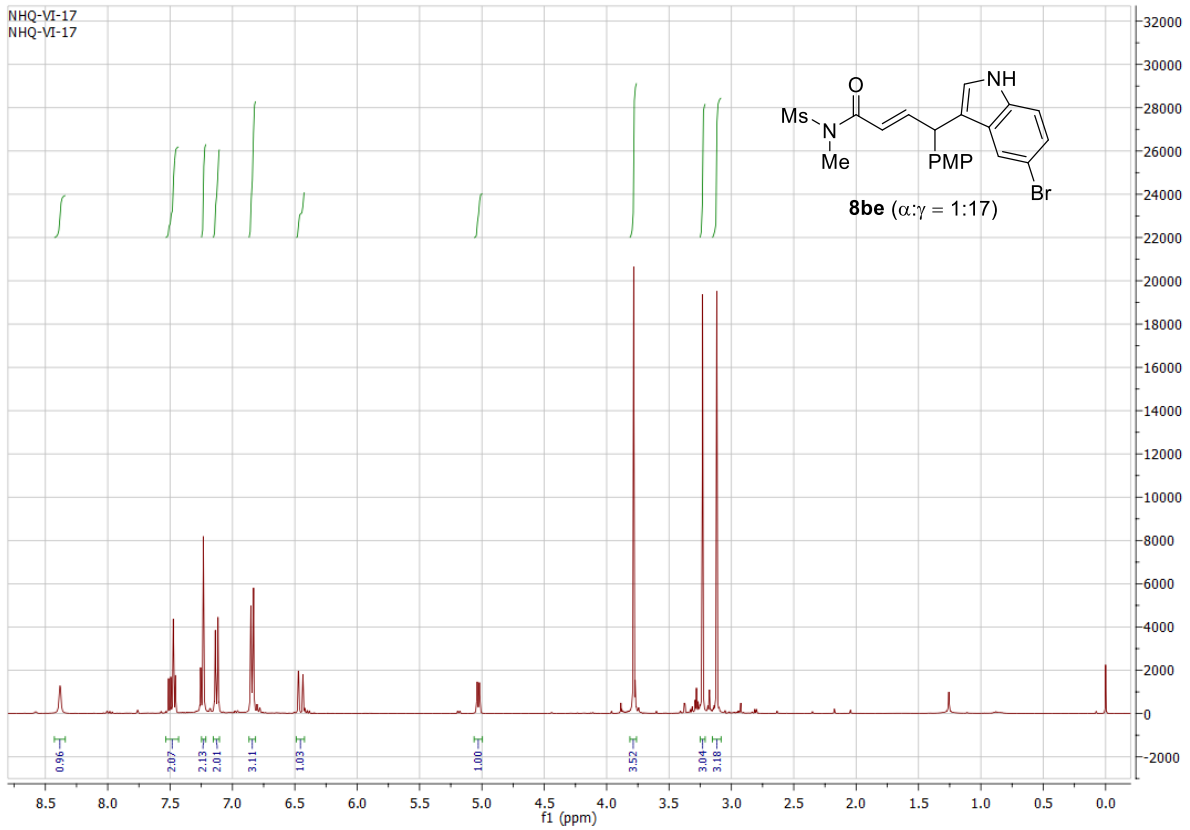

NHQ-VI-93-2
NHQ-VI-93-2-13C
166.70
158.60
152.40
136.64
132.91
129.44
127.73
126.33
122.79
122.38
121.13
119.65
119.40
116.59
114.10
113.92
111.39
77.37
77.06
76.74
55.30
44.93
41.67
32.56
f1 (ppm)

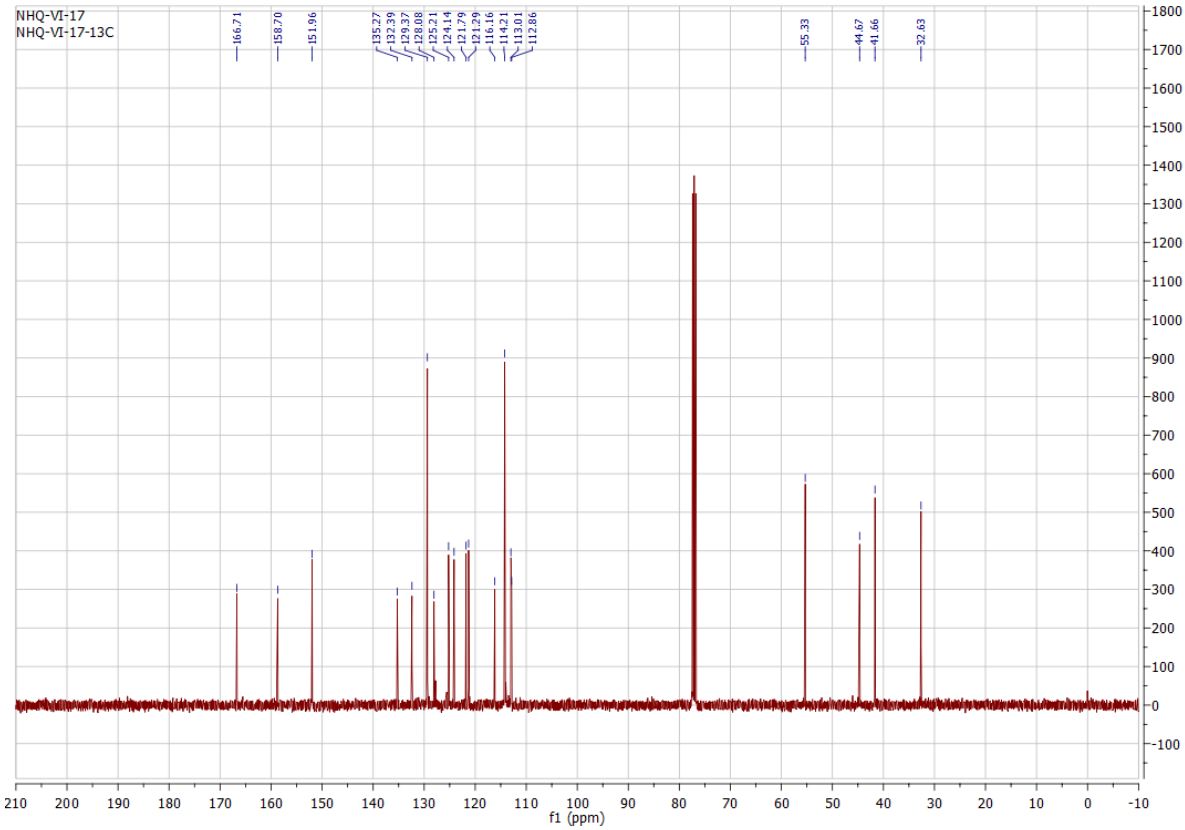

NHQ-VIII-06
NHQ-VIII-06
Me
NH
O
Ms
N
Me
PMP
8bc (α:γ = 1:6)
f1 (ppm)

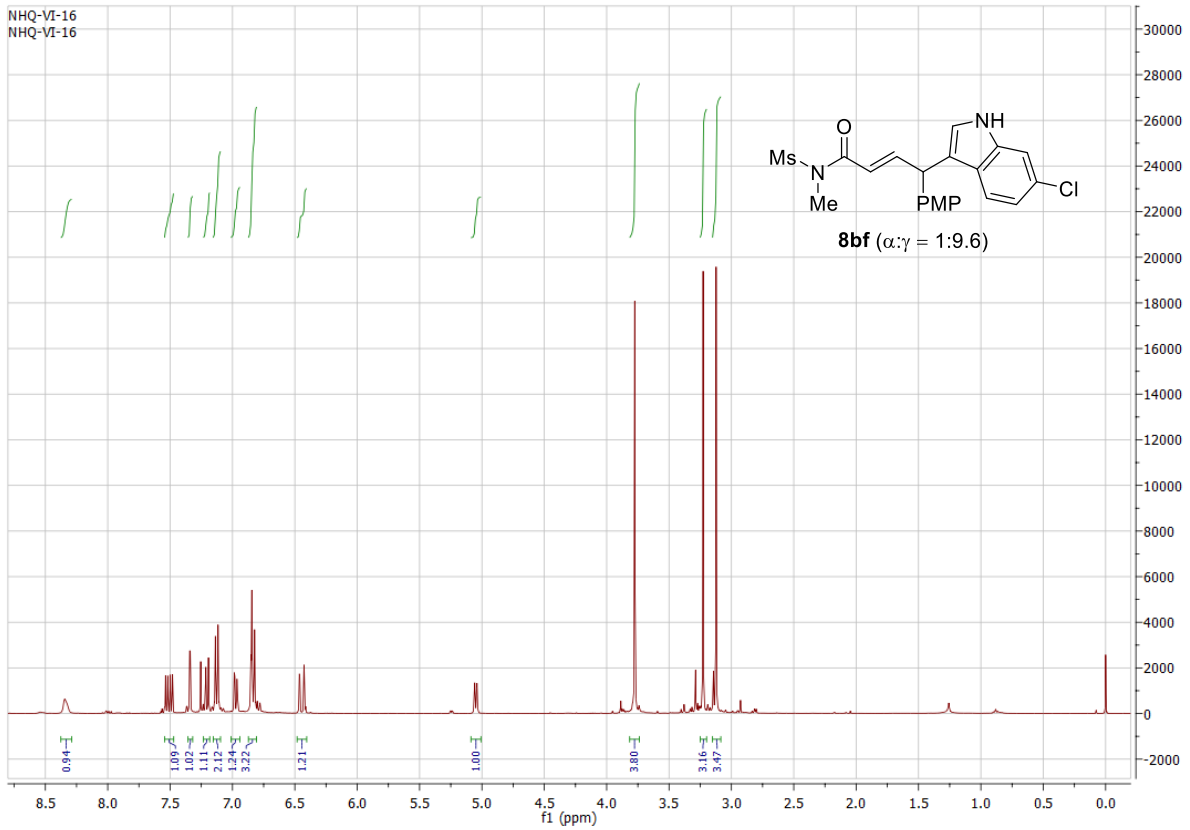

NHQ-VIII-06
NHQ-VIII-06-13C
f1 (ppm)

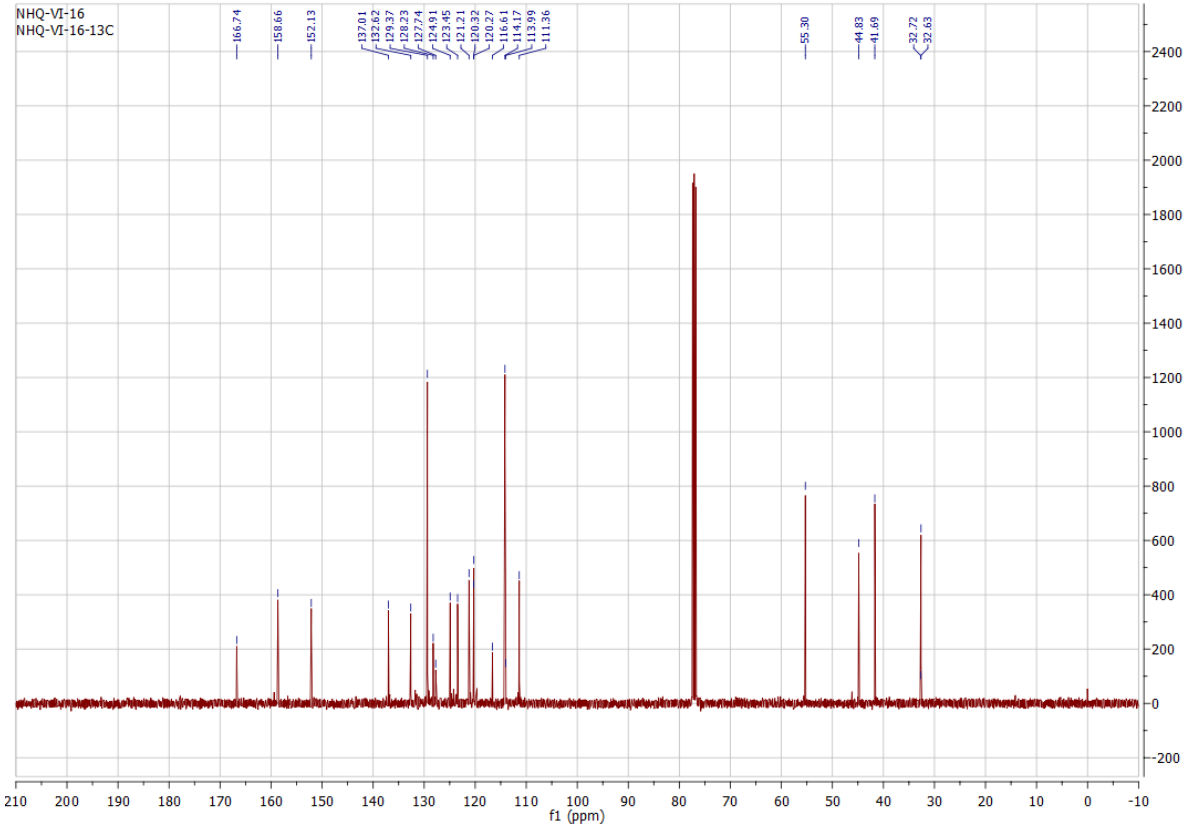

NHQ-XI-92
NHQ-XI-92
Ms
N
Me
O
NH
PMP
NC
8bd (α:γ = 1:17)
f1 (ppm)

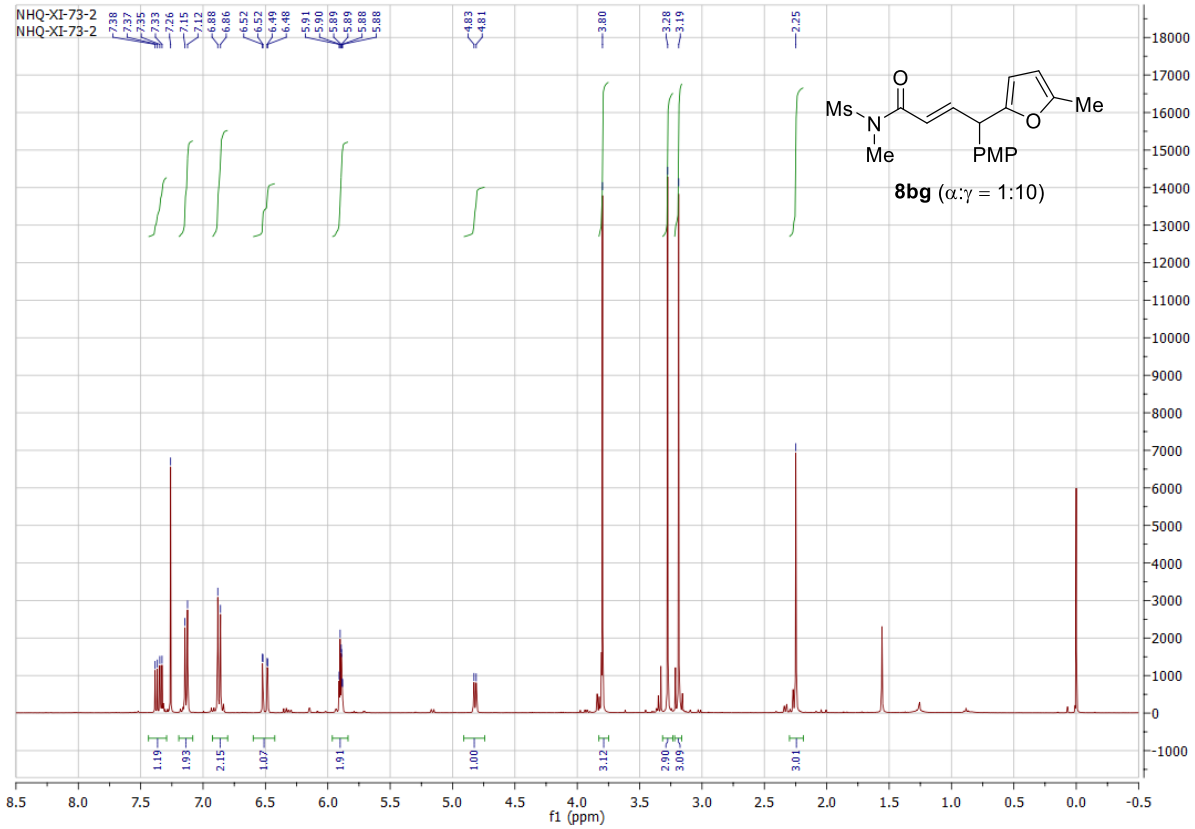

NHQ-XI-92
NHQ-XI-92
f1 (ppm)

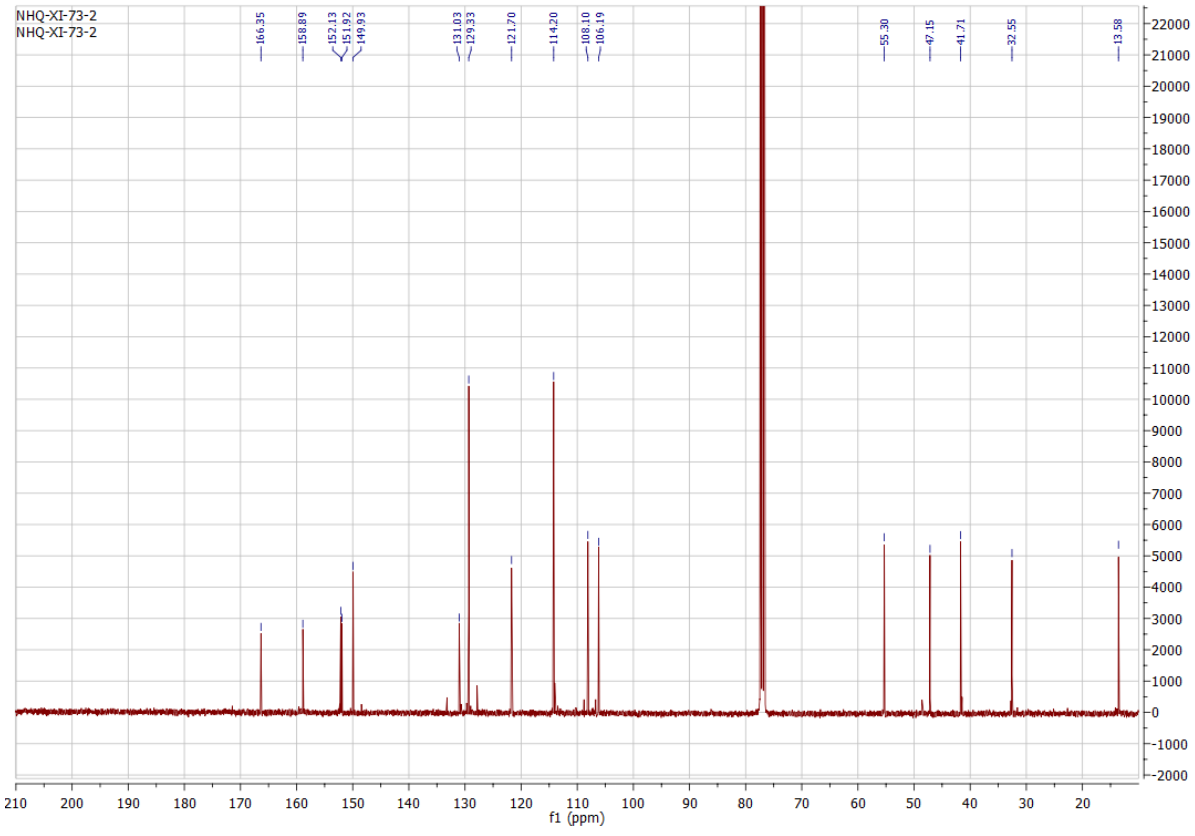

NHQ-VI-17
NHQ-VI-17
Ms
N
Me
O
NH
PMP
Br
8be (α:γ = 1:17)
f1 (ppm)

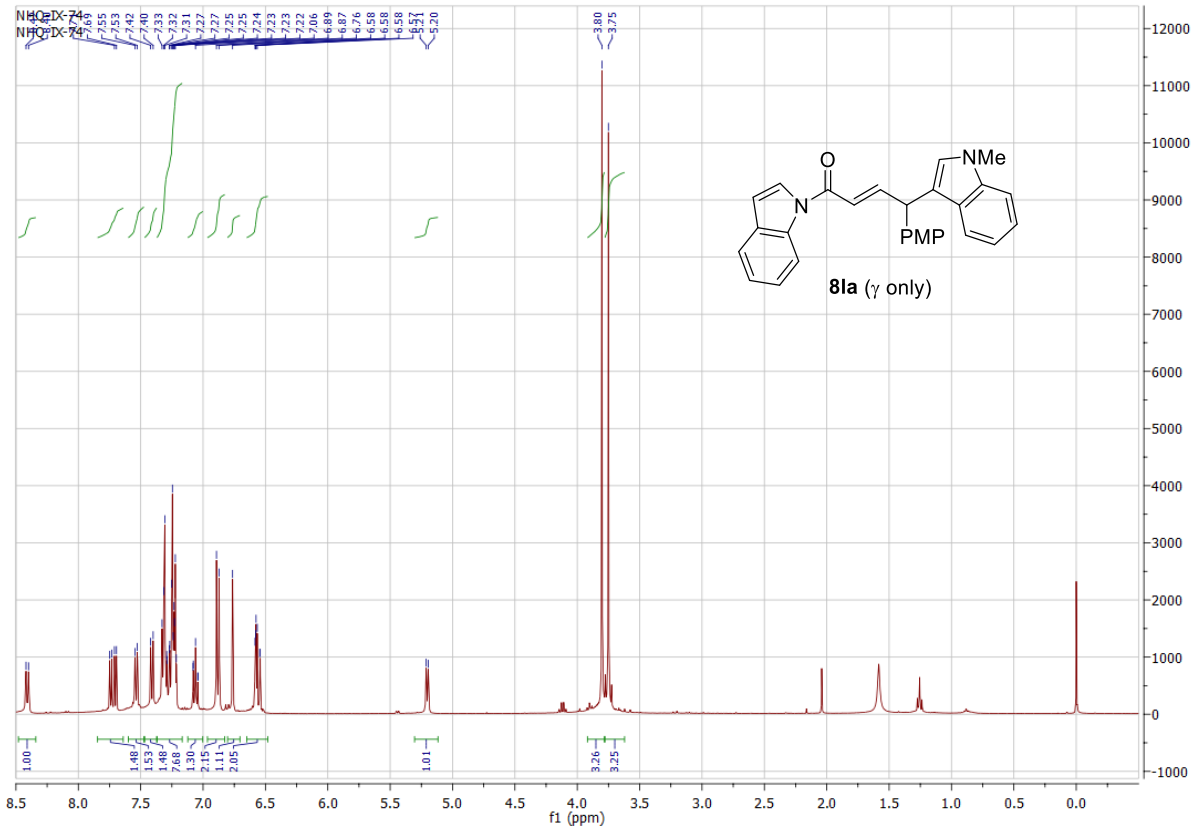

NHQ-VI-17
NHQ-VI-17-13C
166.71
158.70
151.96
135.27
132.39
129.37
128.08
125.21
124.14
121.79
121.29
116.16
114.21
113.01
112.86
55.33
44.67
41.66
32.63
f1 (ppm)

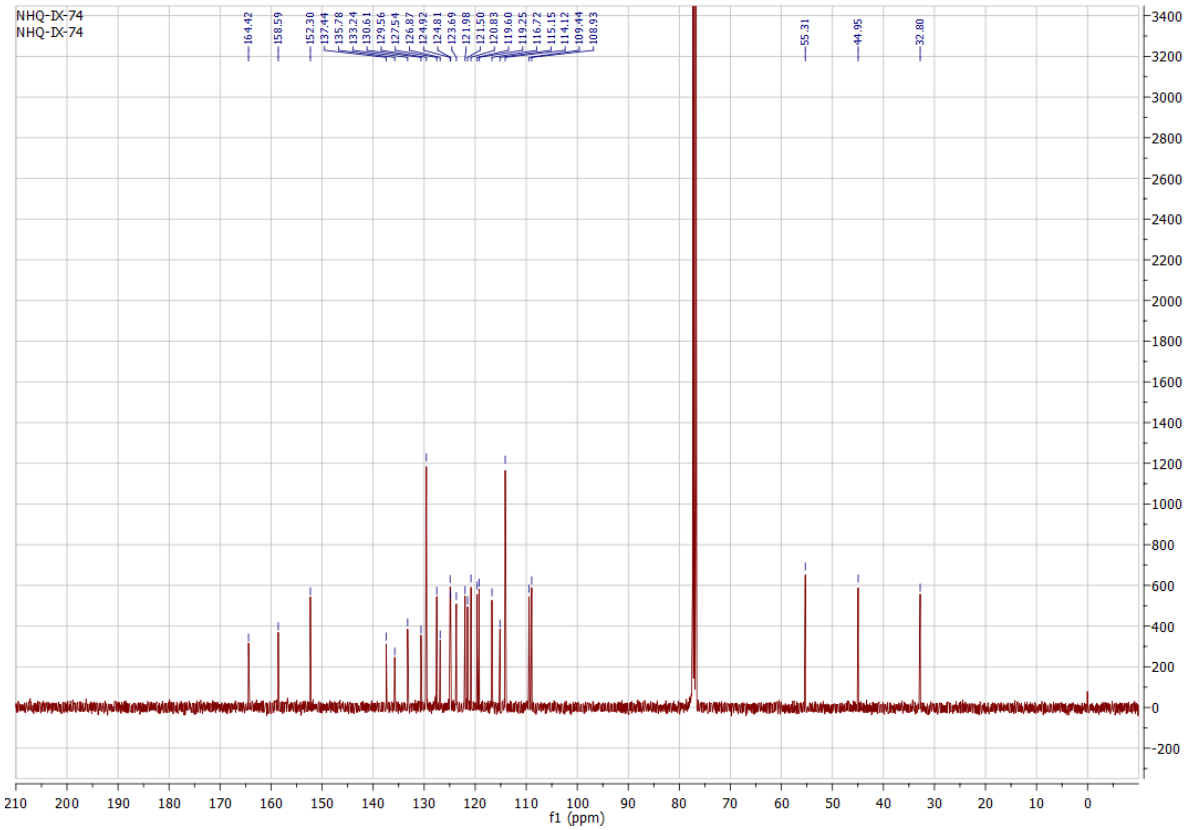

NHQ-VI-16
NHQ-VI-16
O
NH
Ms
N
Me
PMP
Cl
8bf (α:γ = 1:9.6)
f1 (ppm)

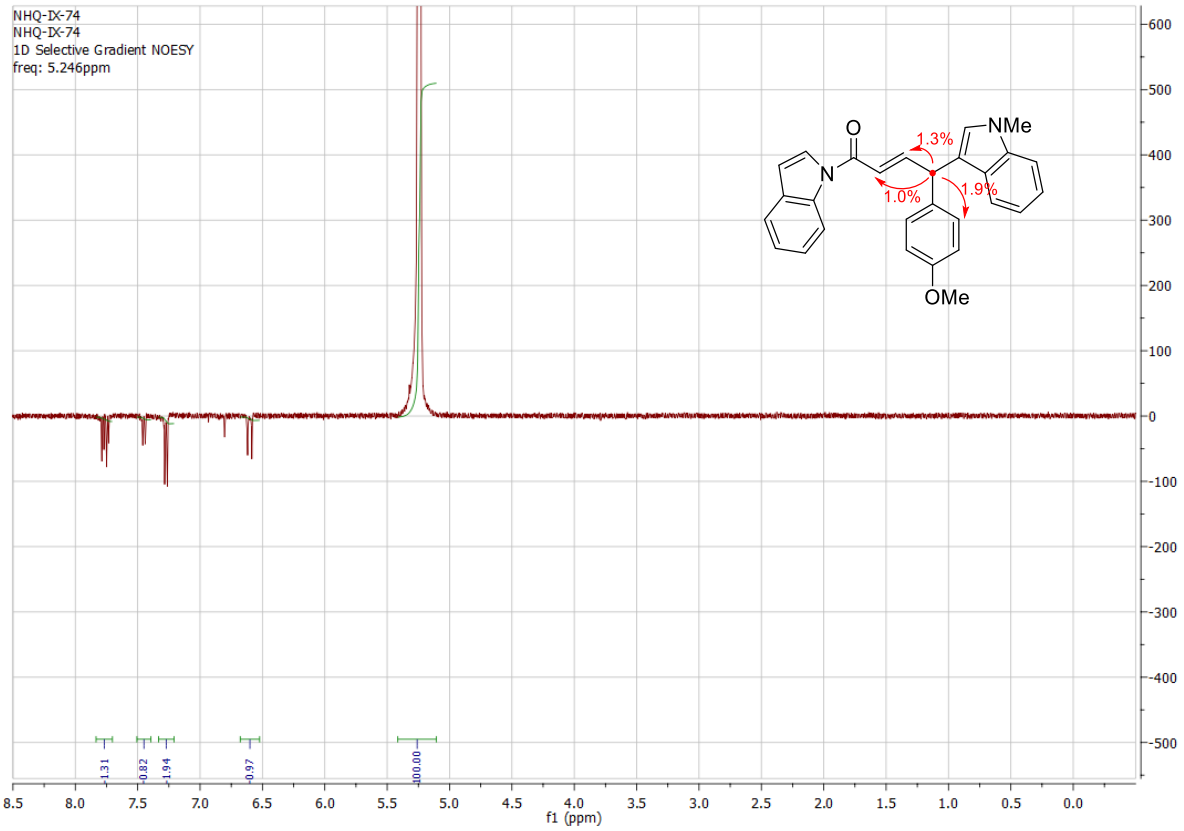

NHQ-VI-16
NHQ-VI-16-13C
166.74
158.66
152.13
137.01
132.62
129.37
128.23
127.74
124.91
123.45
121.21
120.32
120.27
116.61
114.17
113.99
111.36
55.30
44.83
41.69
32.72
32.63
f1 (ppm)

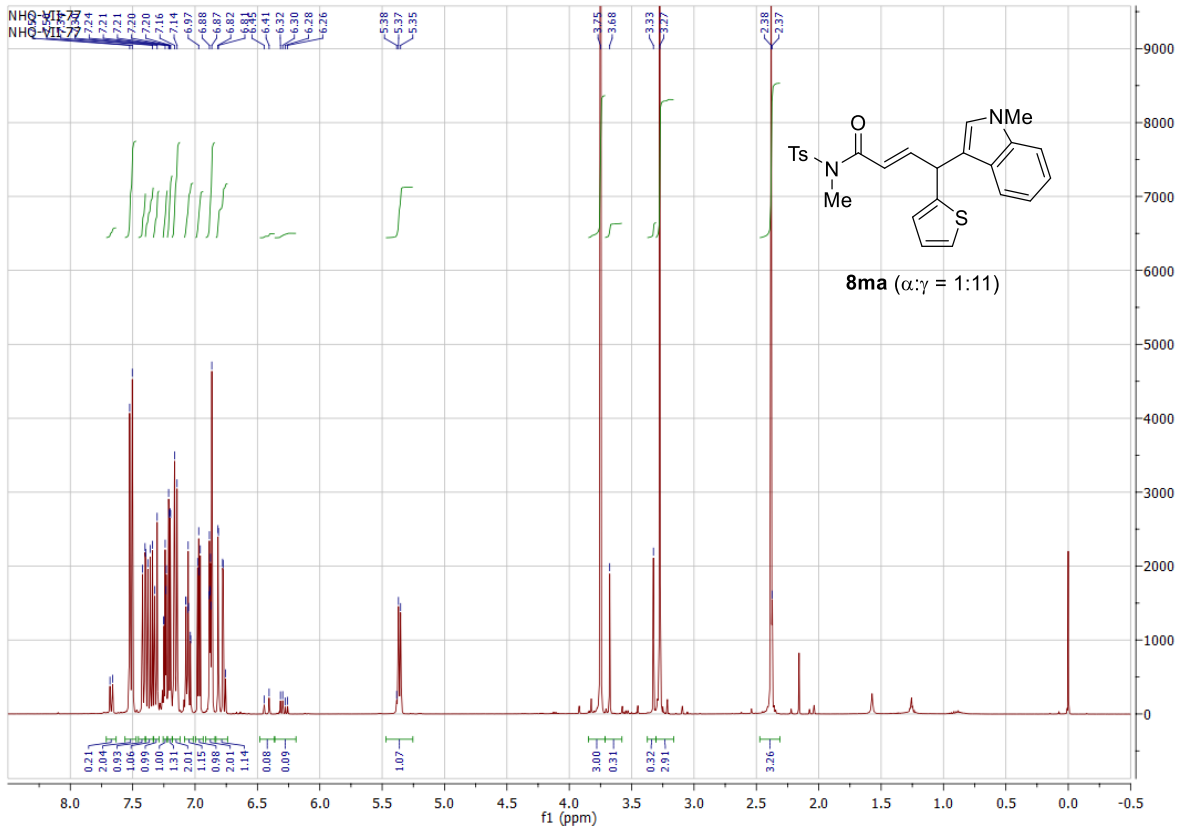

NHQ-XI-73-2
NHQ-XI-73-2
Ms
N
Me
O
O
Me
PMP
8bg (α:γ = 1:10)
f1 (ppm)

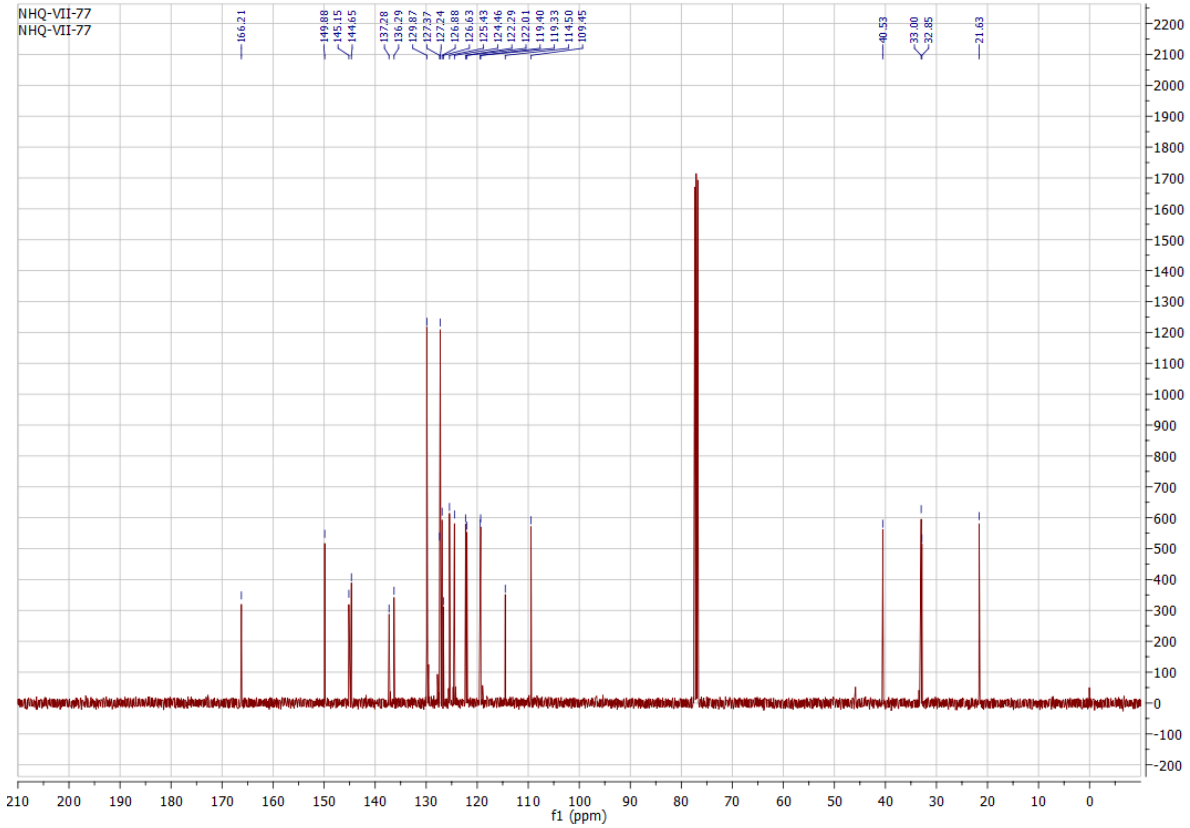

NHQ-XI-73-2
NHQ-XI-73-2
f1 (ppm)

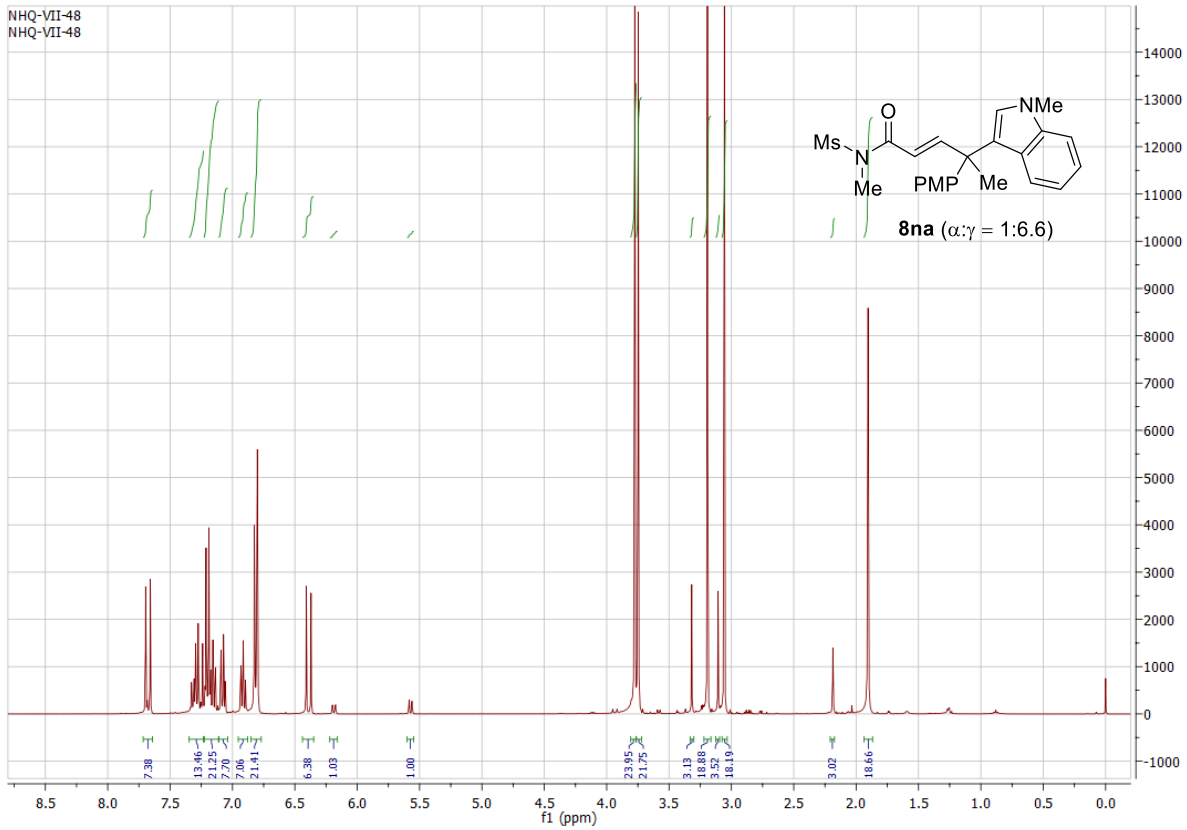

NHQ-IX-74
NHQ-IX-74
O
N
NMe
PMP
8la (γ only)
f1 (ppm)

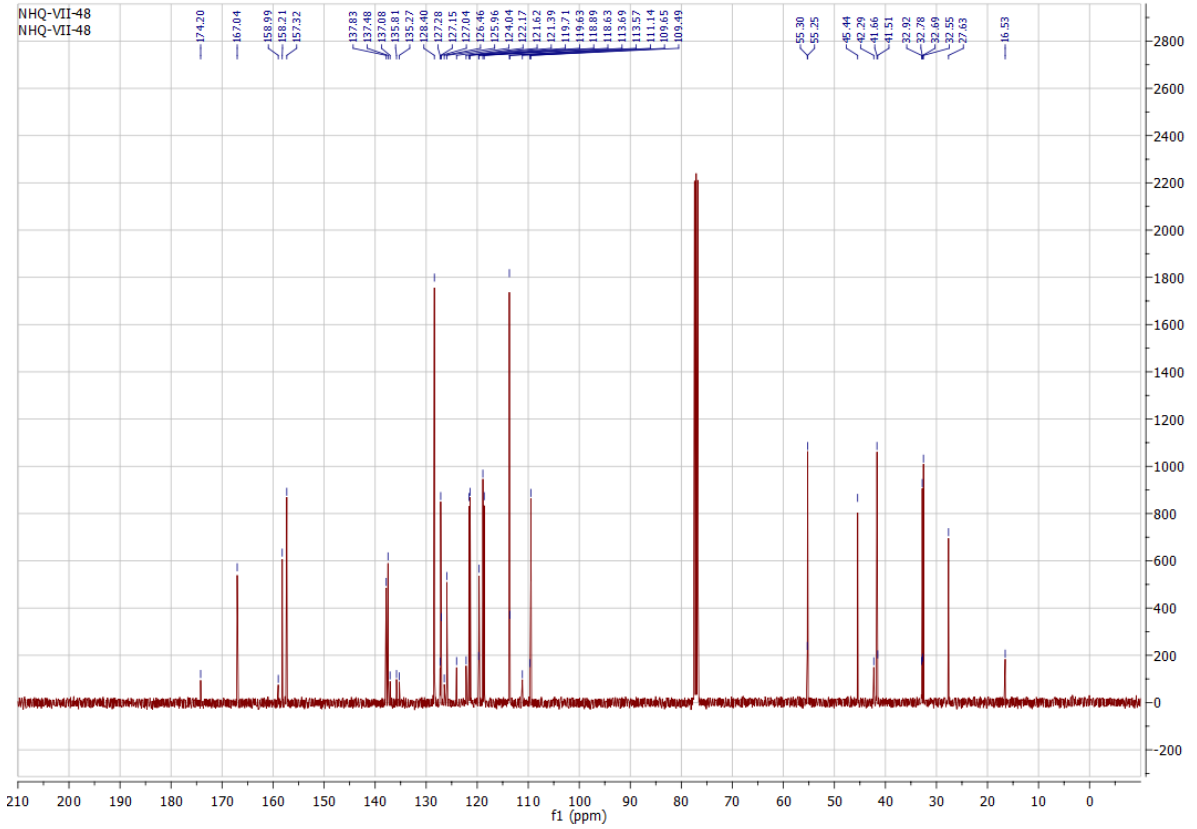

NHQ-IX-74
NHQ-IX-74
f1 (ppm)

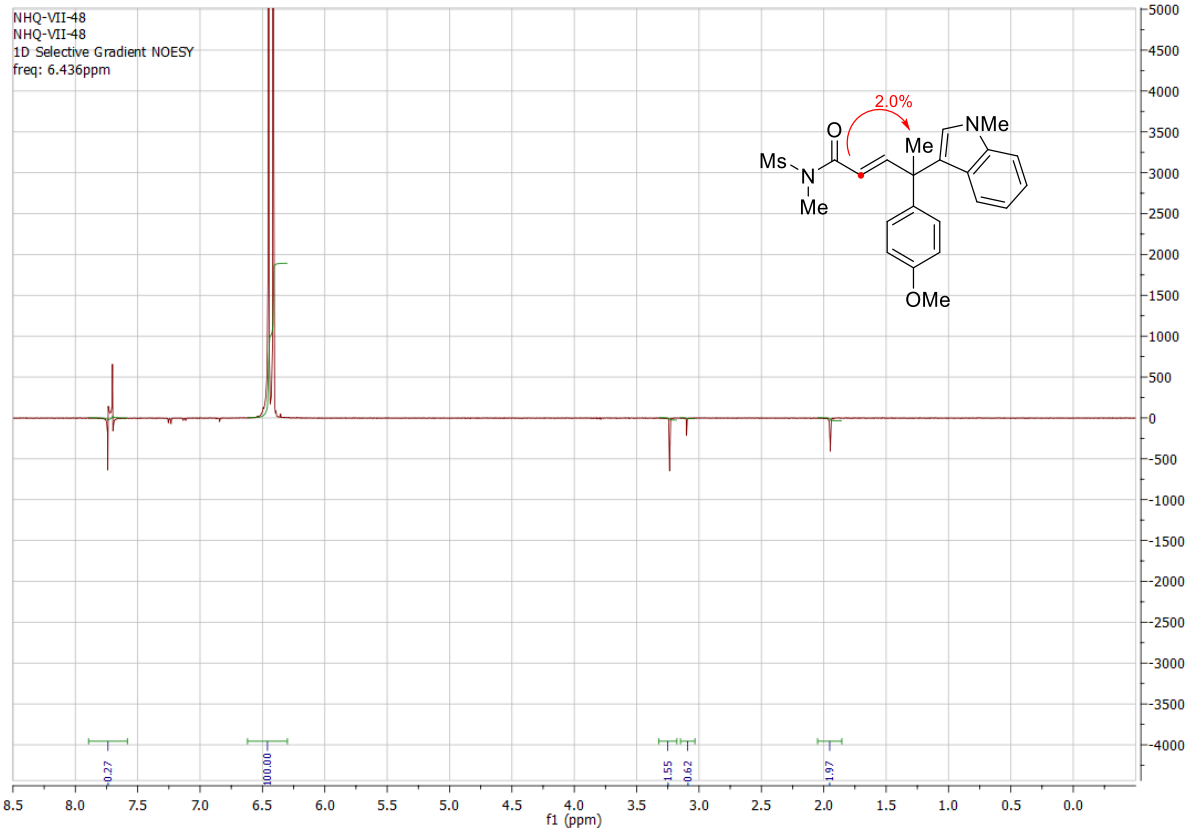

NHQ-IX-74
NHQ-IX-74
1D Selective Gradient NOESY
freq: 5.246ppm
O
N
NMe
OMe
1.3%
1.0%
1.9%
1.31
0.82
1.94
0.97
100.00
f1 (ppm)

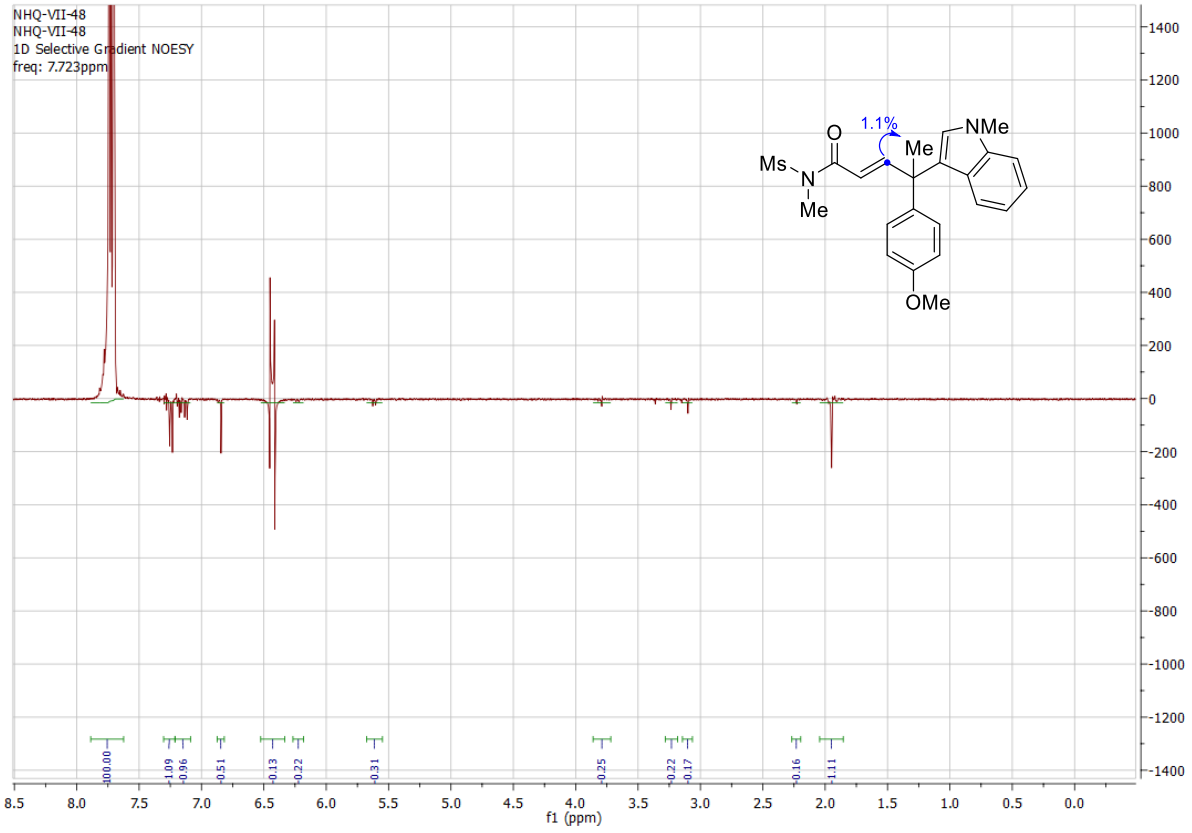

NHQ-VII-77
Ts
N
Me
O
NMe
S
8ma (α:γ = 1:11)
f1 (ppm)

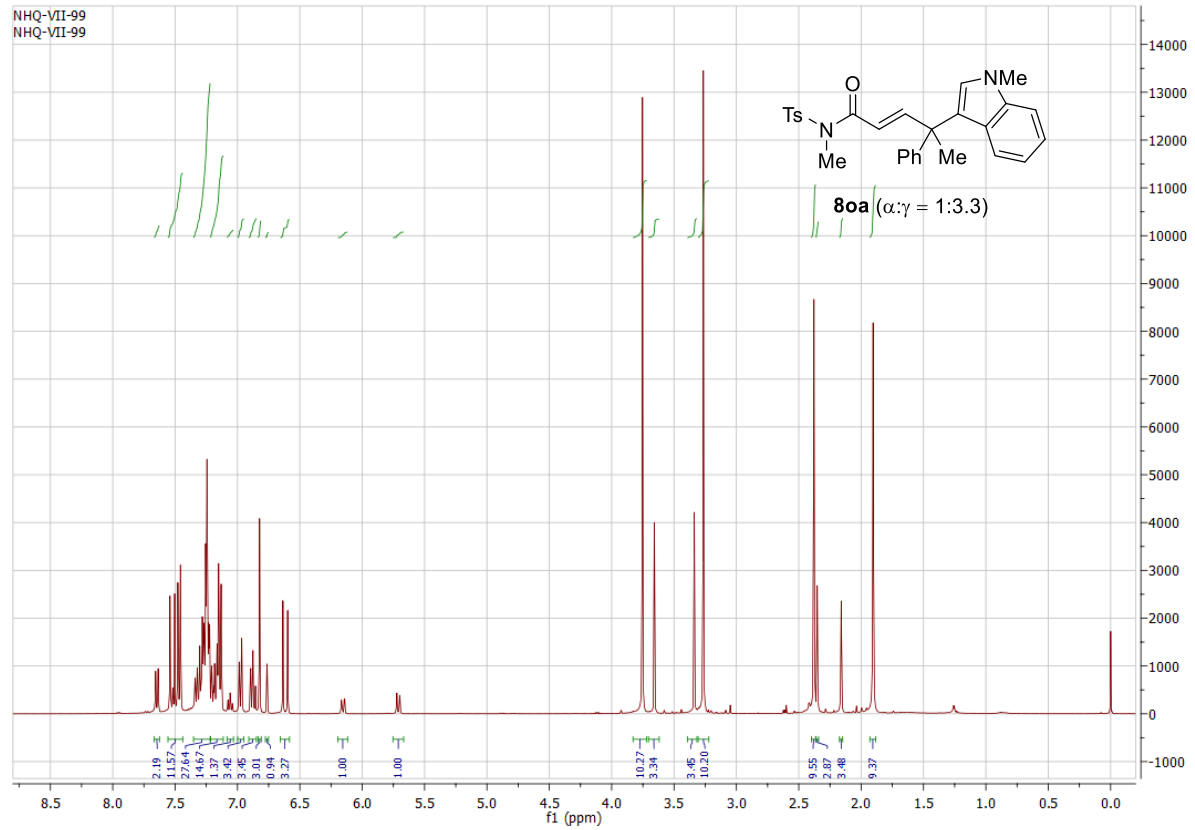

NHQ-VII-77
NHQ-VII-77
f1 (ppm)

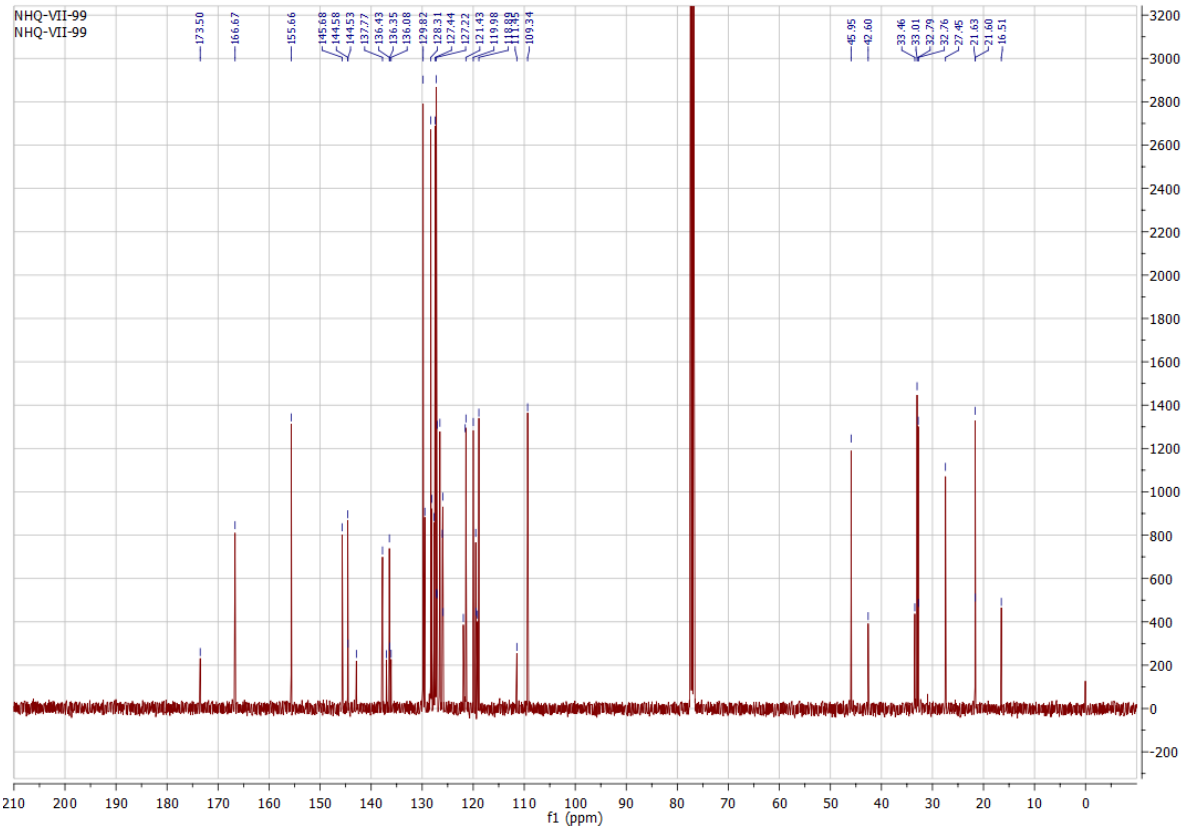

NHQ-VII-48
NHQ-VII-48
Ms
N
Me
O
NMe
PMP
Me
8na (α:γ = 1:6.6)
f1 (ppm)

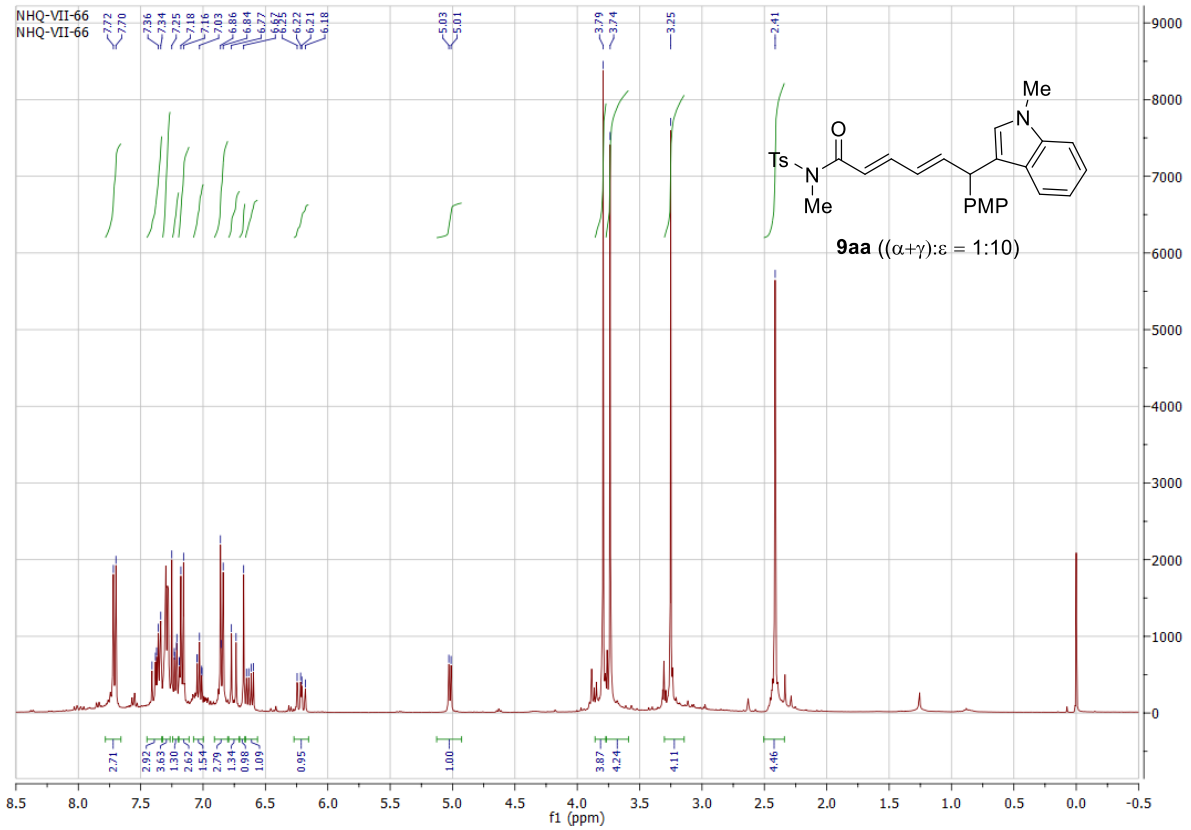

NHQ-VII-48
NHQ-VII-48
f1 (ppm)

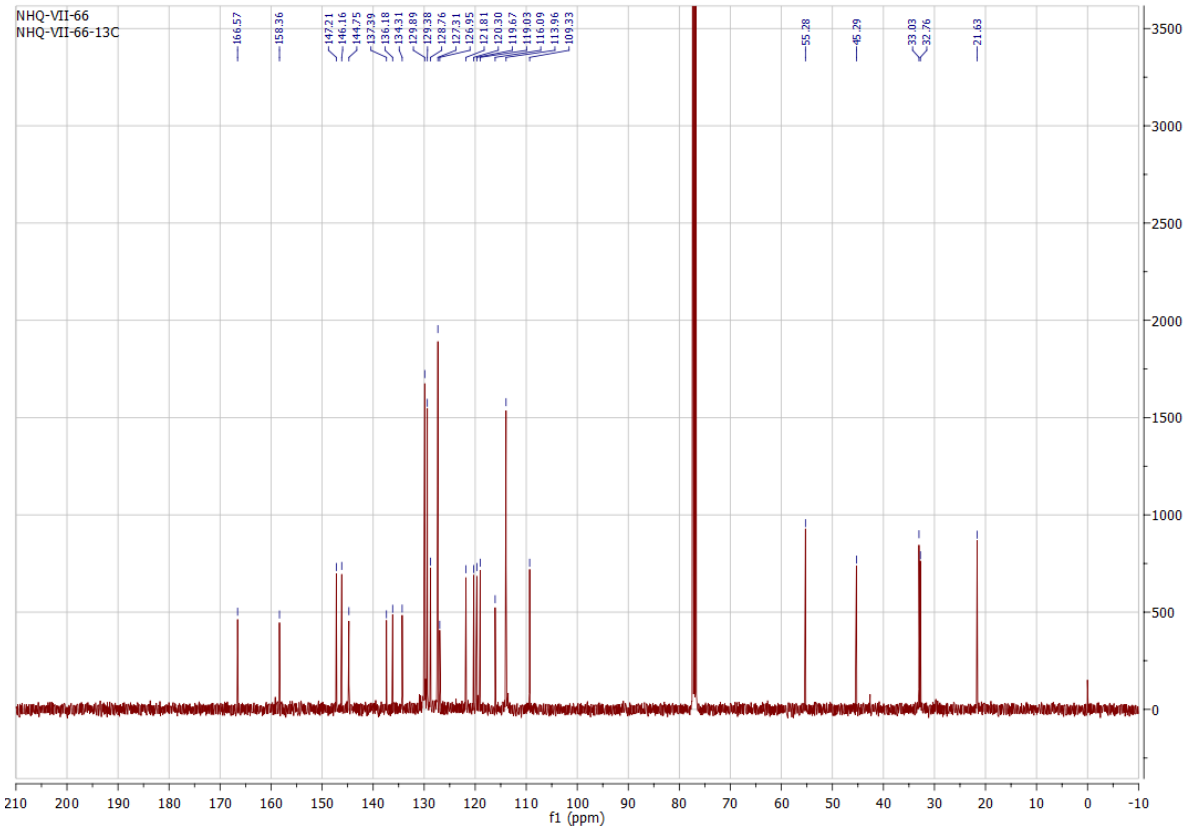

NHQ-VII-48
NHQ-VII-48
1D Selective Gradient NOESY
freq: 6.436ppm
2.0%
O
NMe
Me
Ms
N
Me
OMe
0.27
100.00
1.55
0.62
1.97
f1 (ppm)

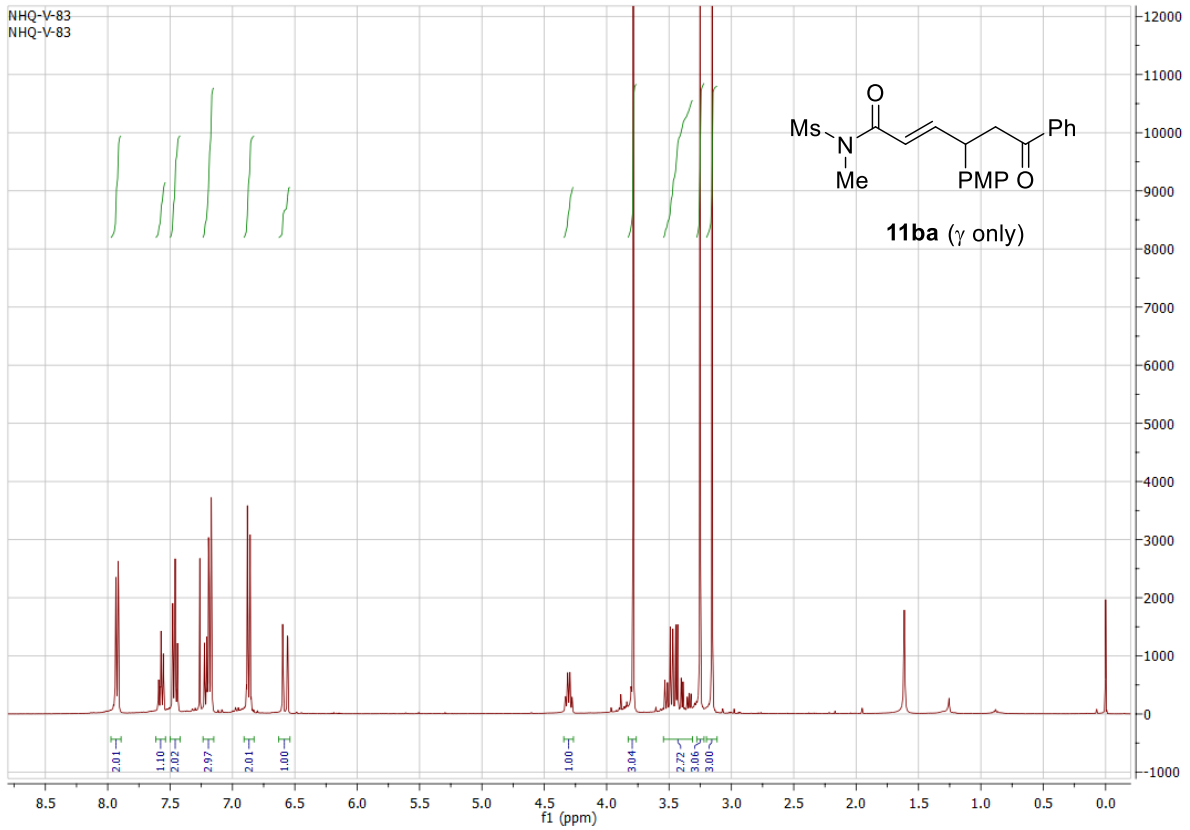

NHQ-VII-48
NHQ-VII-48
1D Selective Gradient NOESY
freq: 7.723ppm
1.1%
O
NMe
Me
Ms
N
Me
OMe
100.00
1.09
0.96
0.51
0.13
0.22
0.31
0.25
0.22
0.17
0.16
1.11
f1 (ppm)

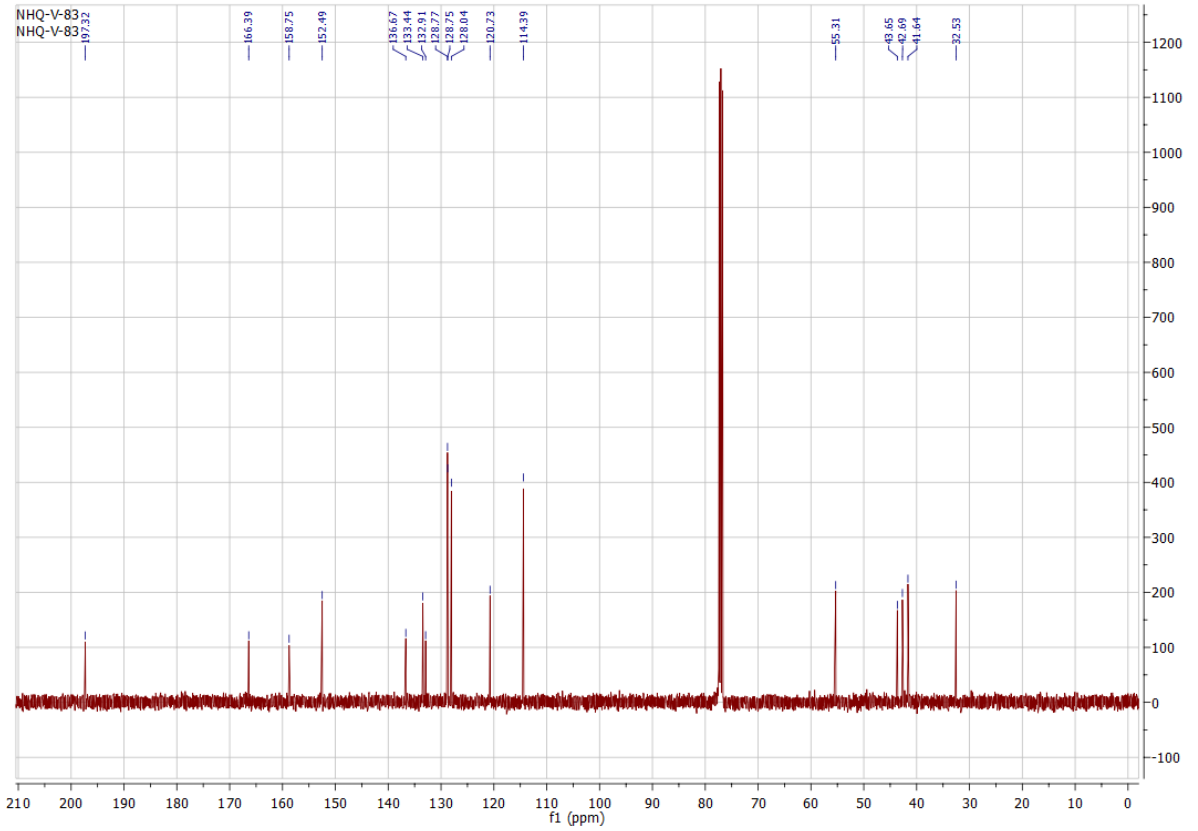

NHQ-VII-99
NHQ-VII-99
O
NMe
Ts
N
Me
Ph
Me
8oa (α:γ = 1:3.3)
f1 (ppm)

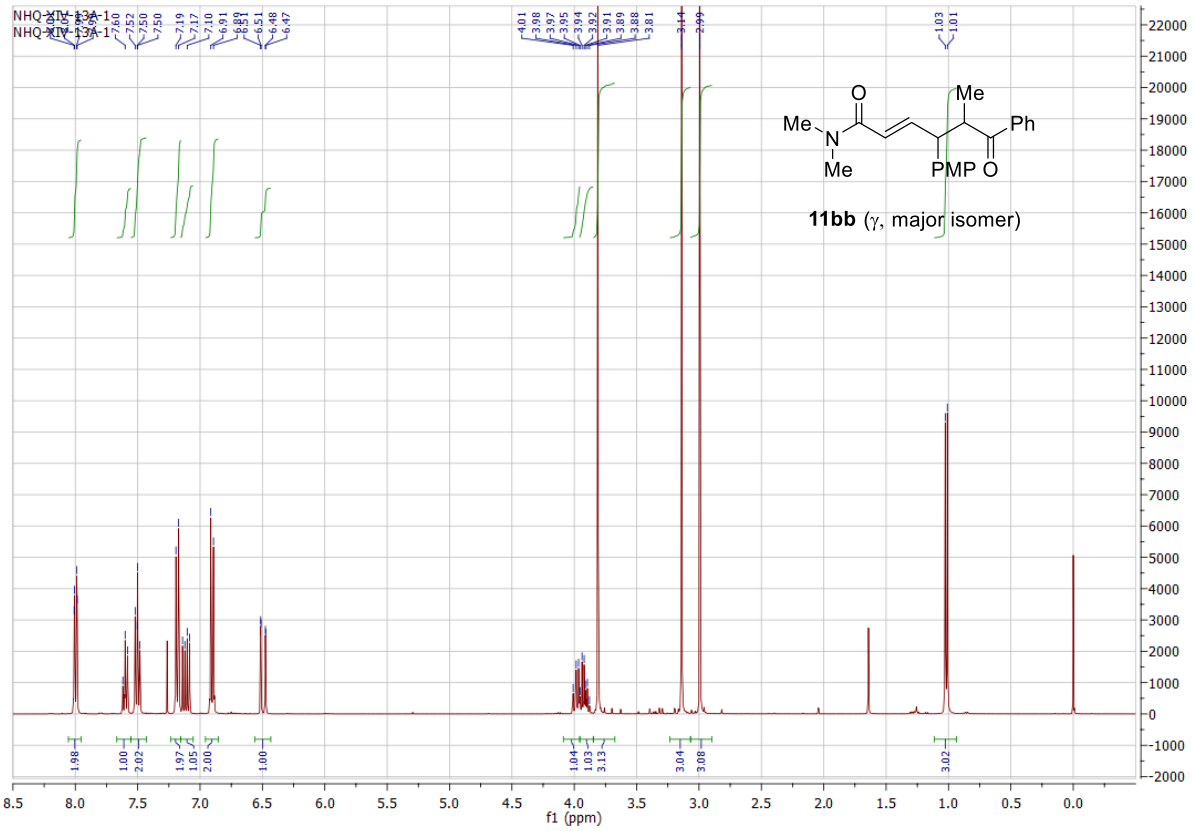

NHQ-VII-99
NHQ-VII-99
f1 (ppm)

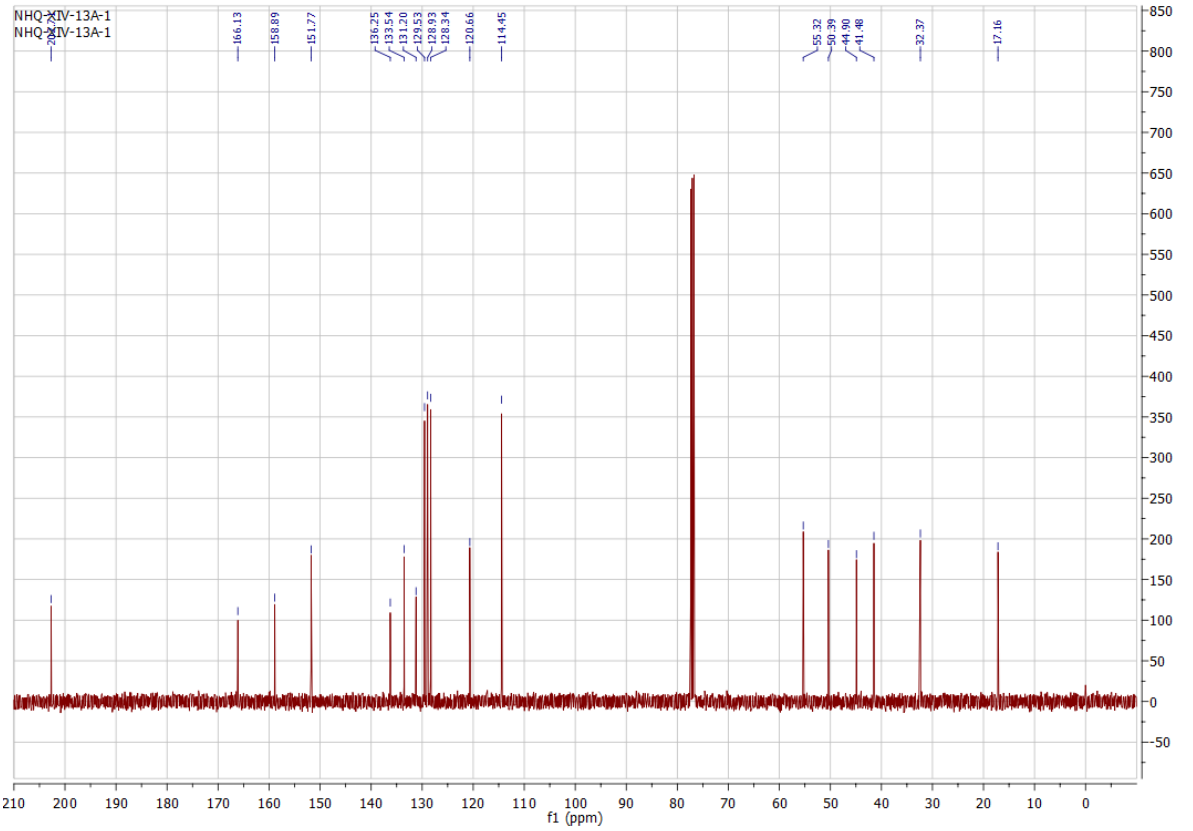

NHQ-VII-66
NHQ-VII-66
Me
N
O
Ts
N
Me
PMP
9aa ((α+γ):ε = 1:10)
f1 (ppm)

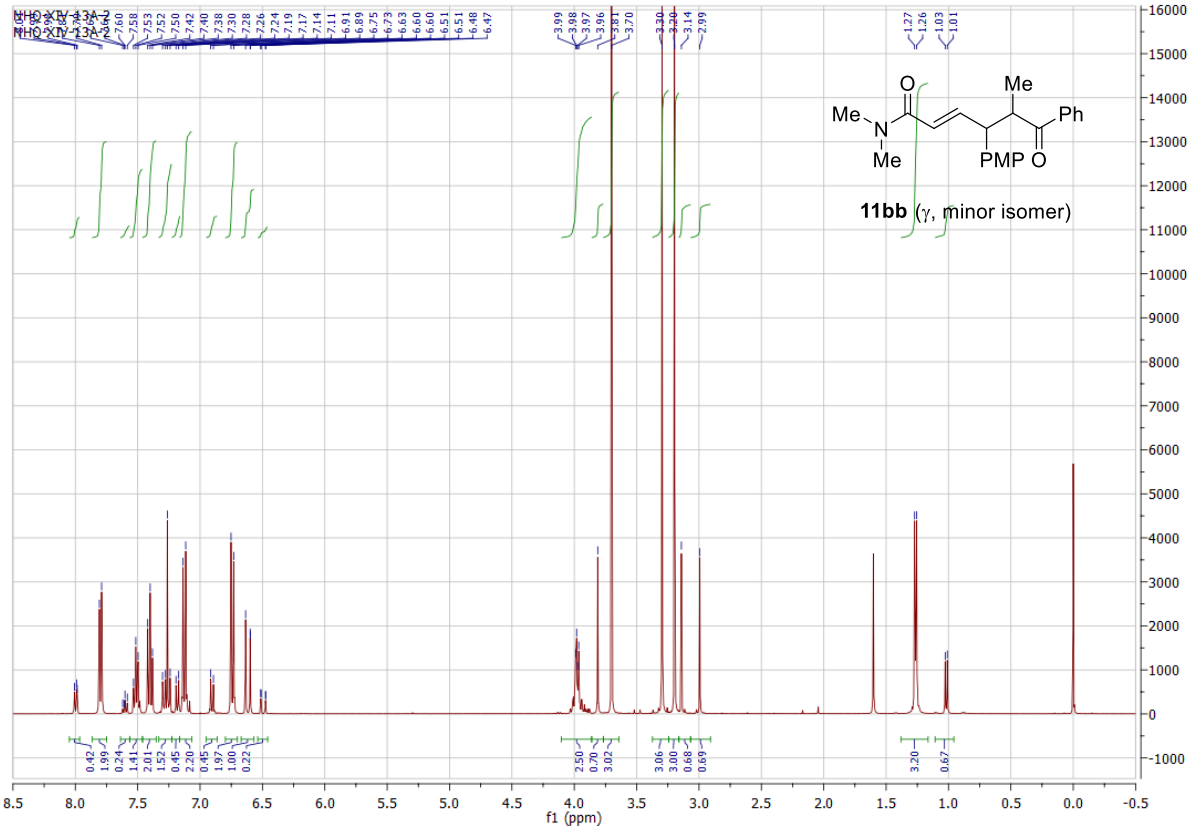

NHQ-VII-66
NHQ-VII-66-13C
f1 (ppm)

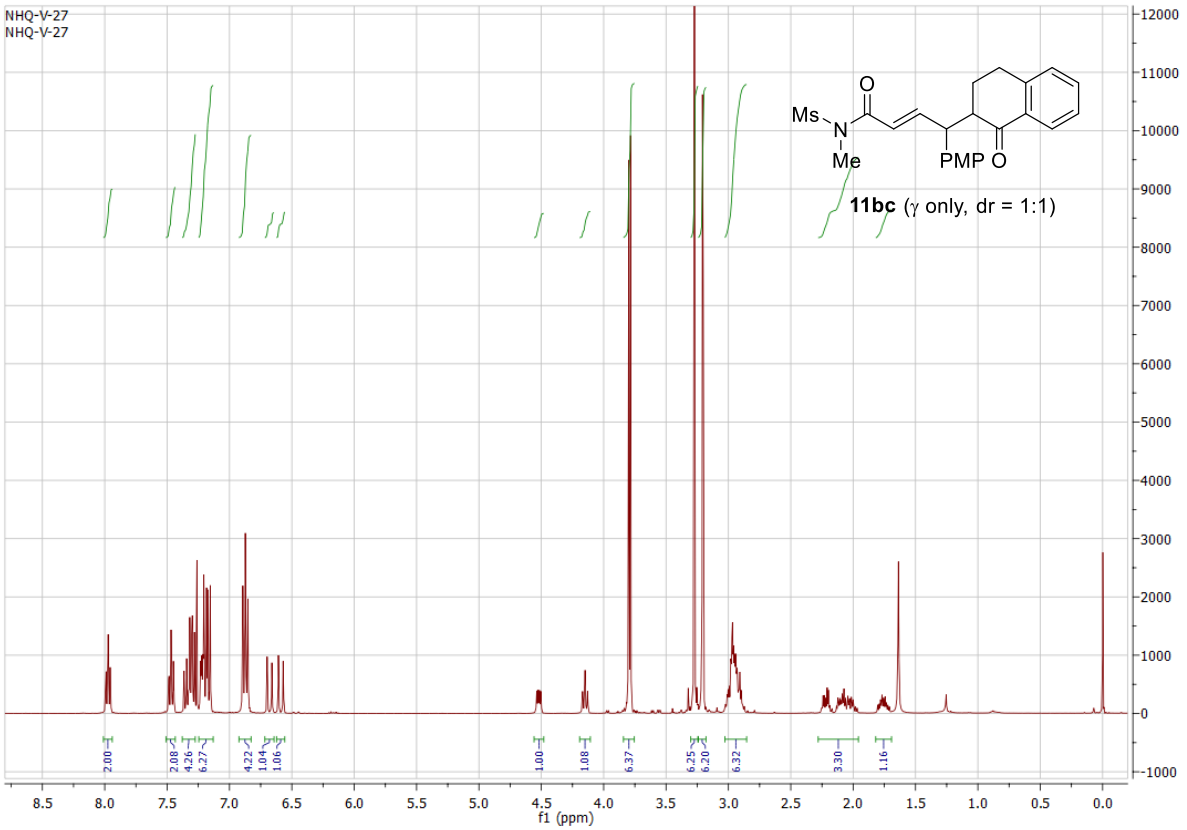

NHQ-V-83
NHQ-V-83
Ms
N
Me
O
Ph
PMP O
11ba (γ only)
f1 (ppm)

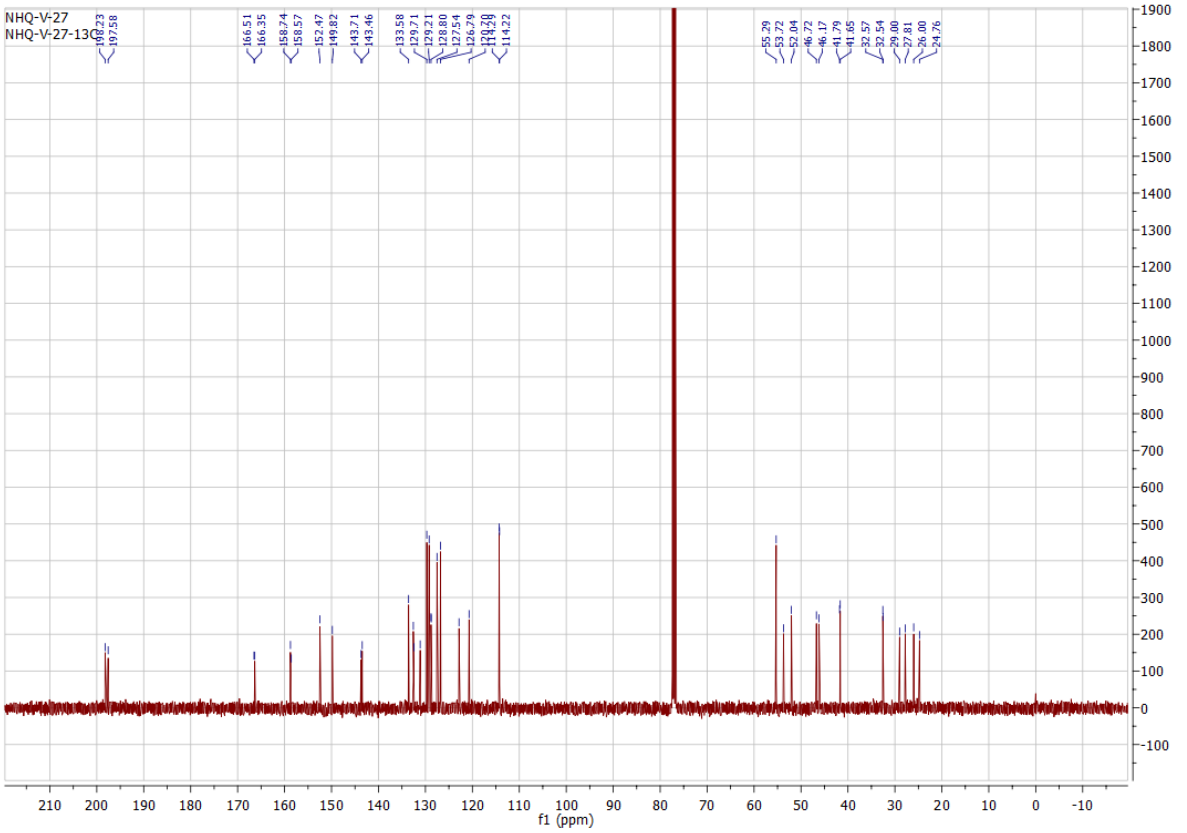

NHQ-V-83
NHQ-V-83
197.32
166.39
158.75
152.49
136.67
133.44
132.91
128.77
128.75
128.04
120.73
114.39
55.31
43.65
42.69
41.64
32.53
f1 (ppm)

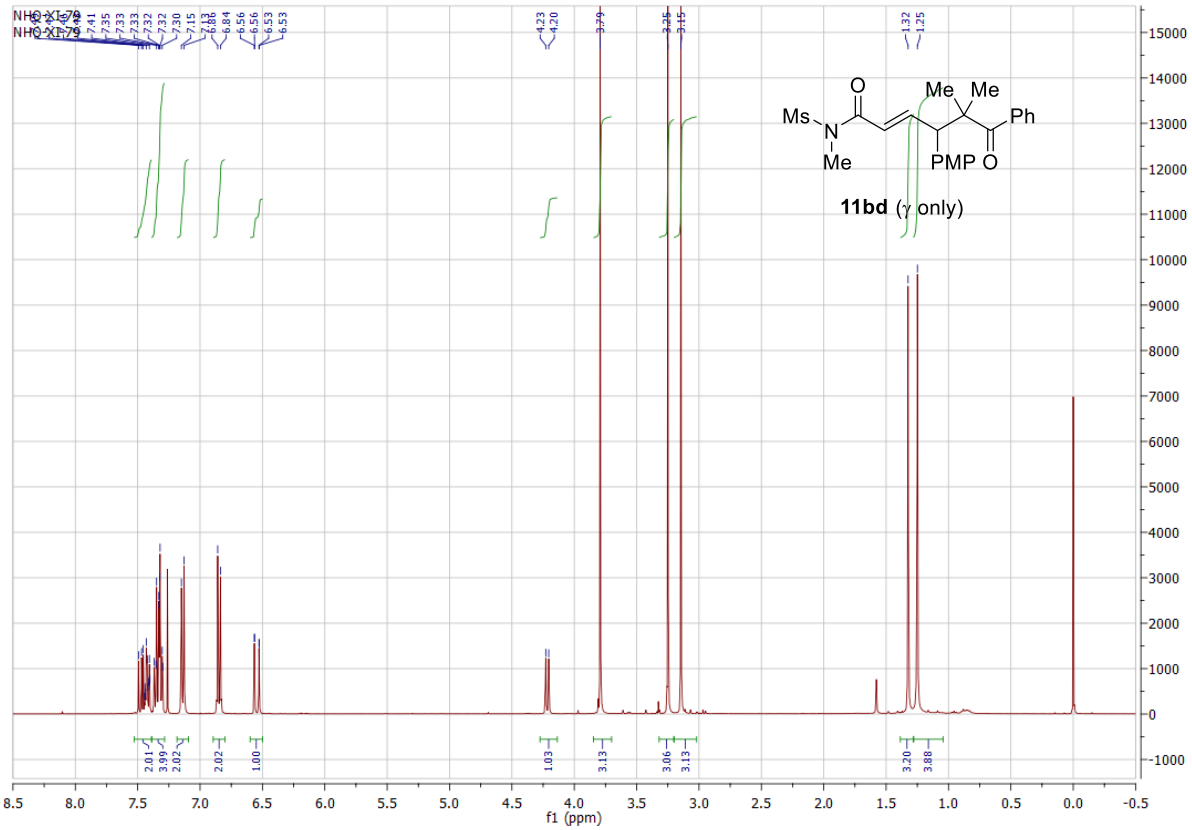

NHQ-XIV-13A-1
NHQ-XIV-13A-1
Me
O
Me
Me
N
Ph
Me
PMP O
11bb (γ, major isomer)
f1 (ppm)

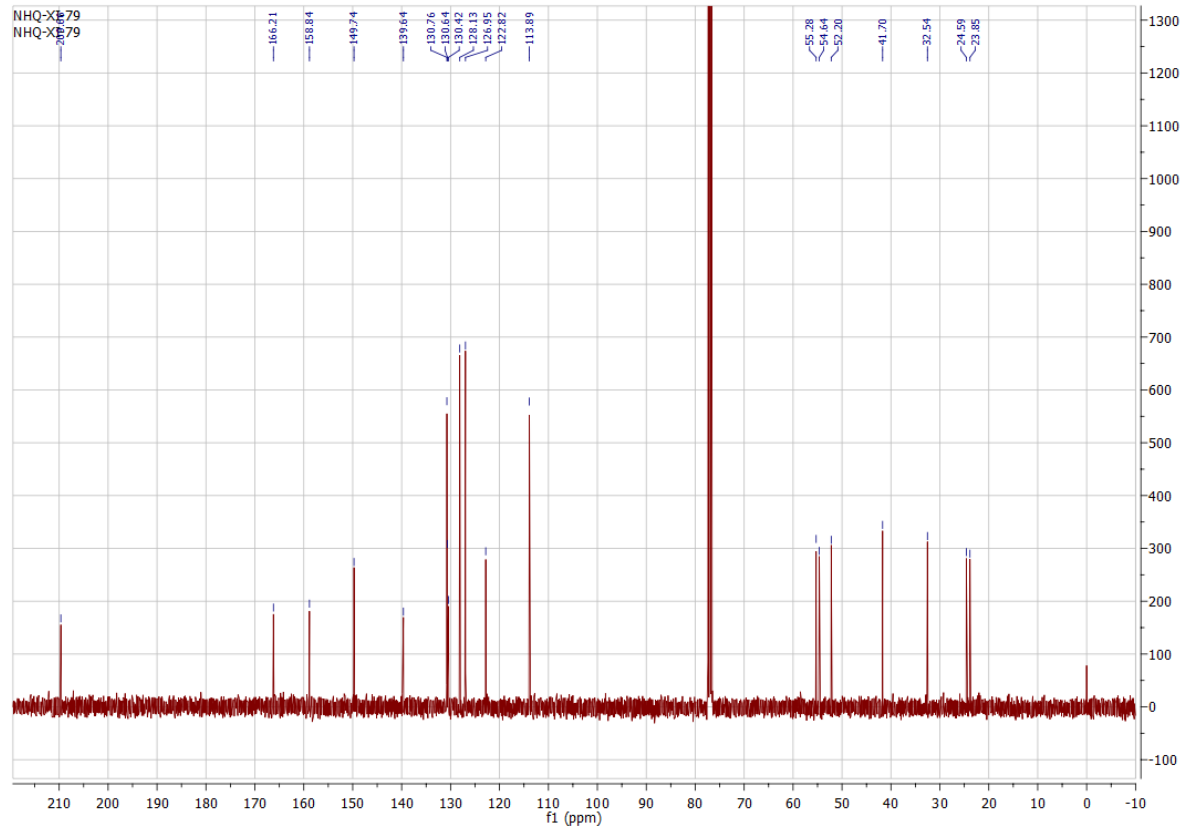

NHQ-XIV-13A-1
NHQ-XIV-13A-1
166.13
158.89
151.77
136.25
133.54
131.20
129.53
128.93
128.34
120.66
114.45
55.32
50.39
44.90
41.48
32.37
17.16
f1 (ppm)

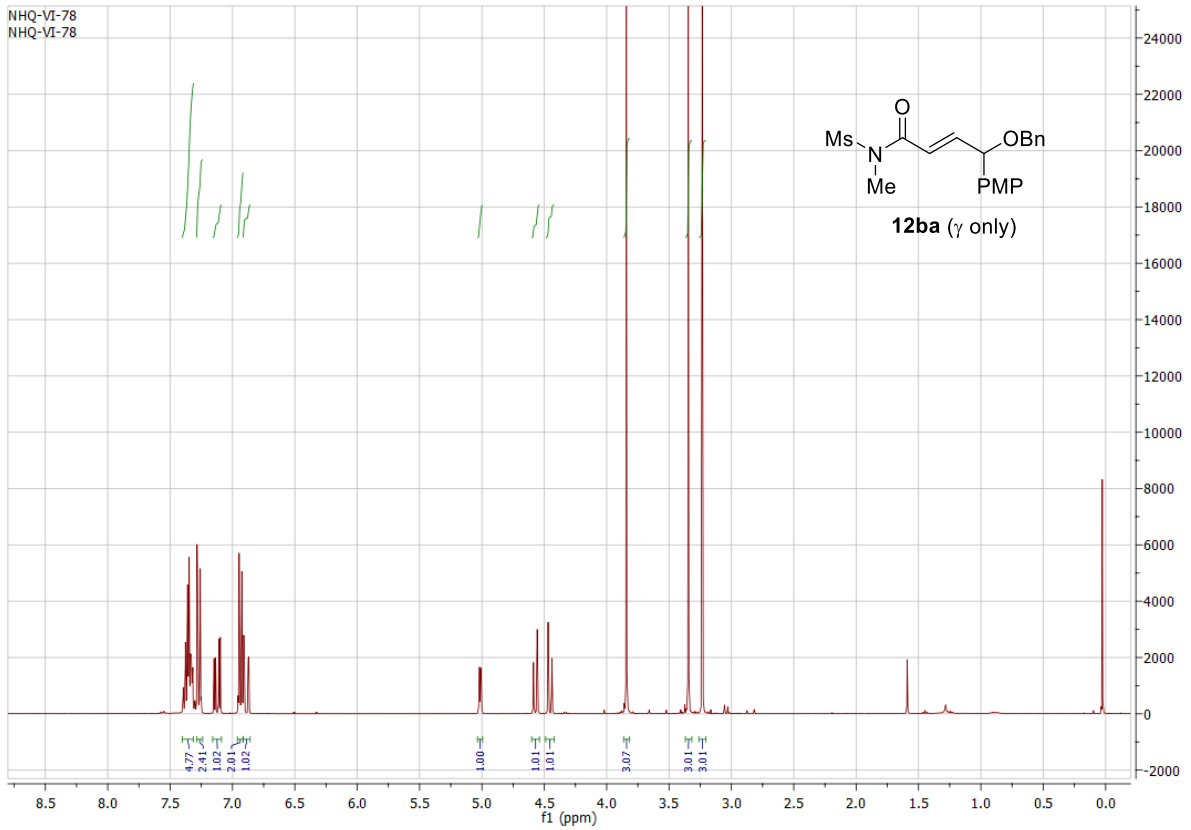

Me
O
Me
Ph
N
Me
PMP O
11bb (γ, minor isomer)
f1 (ppm)

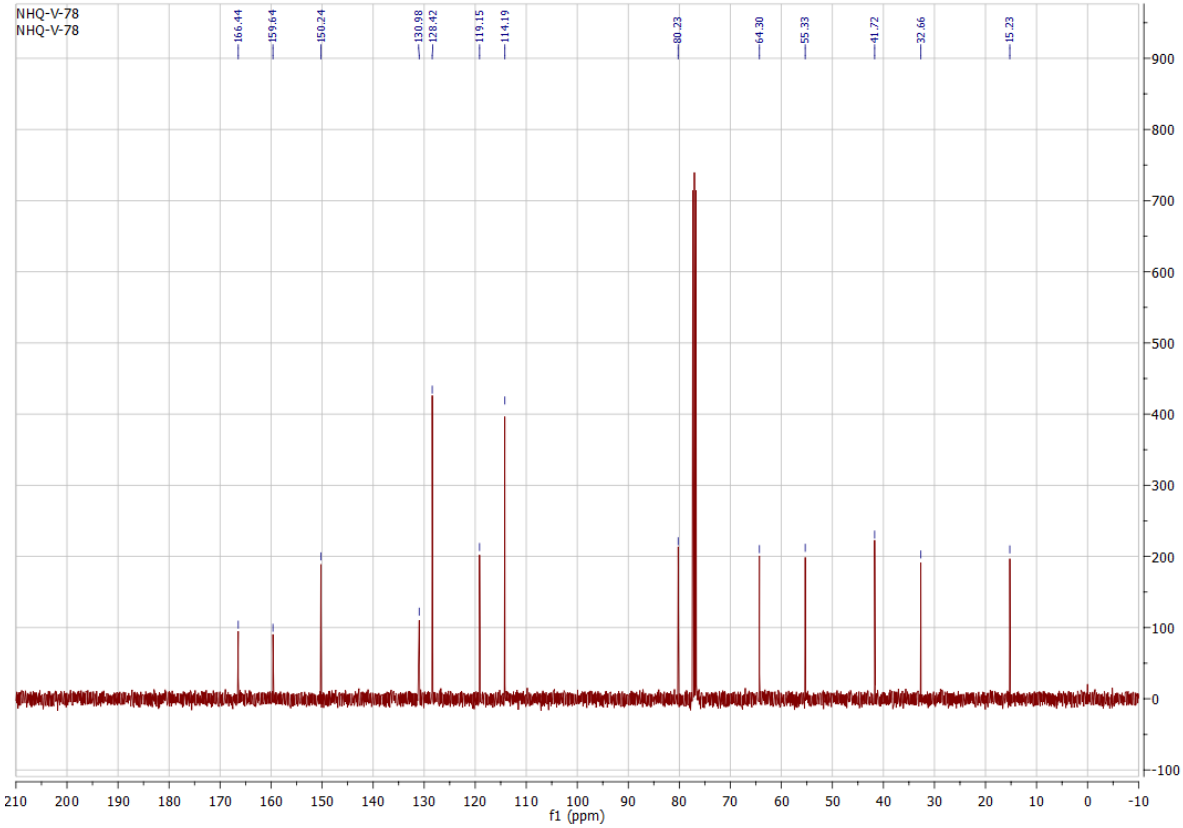

NHQ-V-27
NHQ-V-27
Ms
N
Me
O
PMP O
11bc (γ only, dr = 1:1)
f1 (ppm)

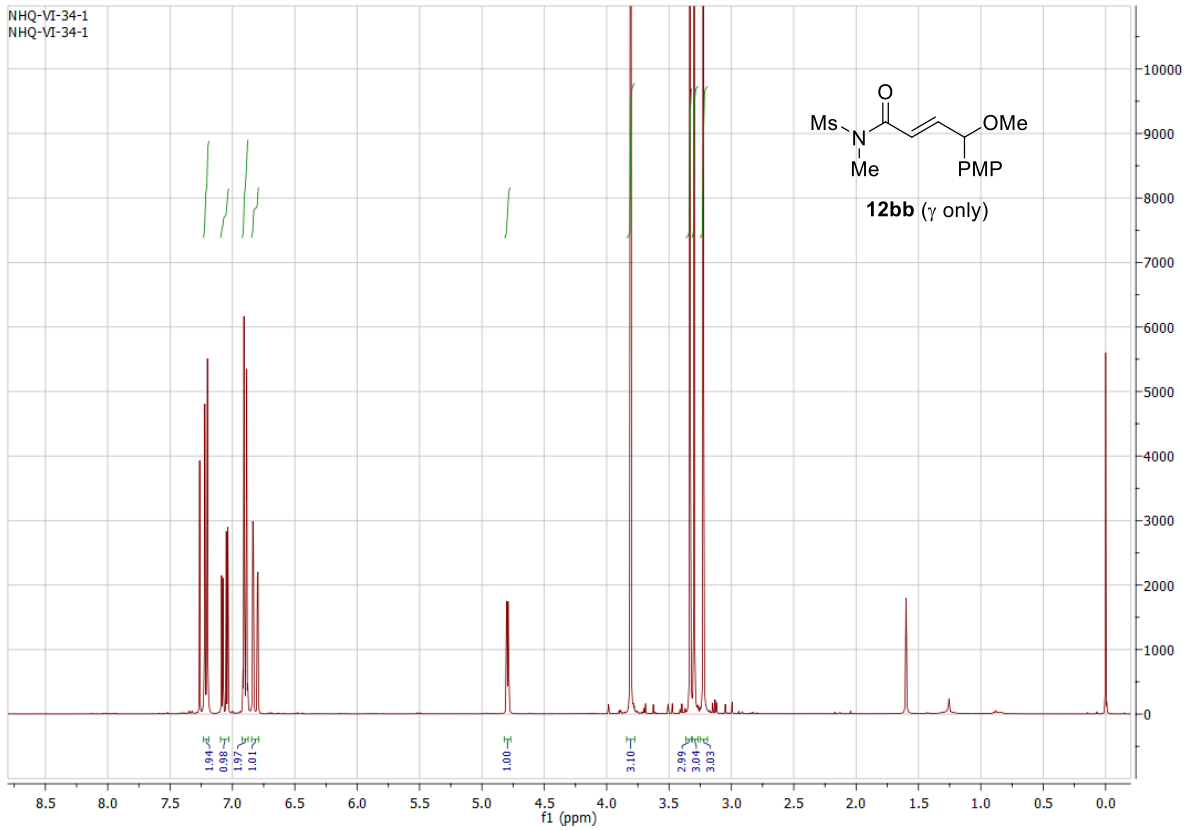

NHQ-V-27
NHQ-V-27-13C
f1 (ppm)

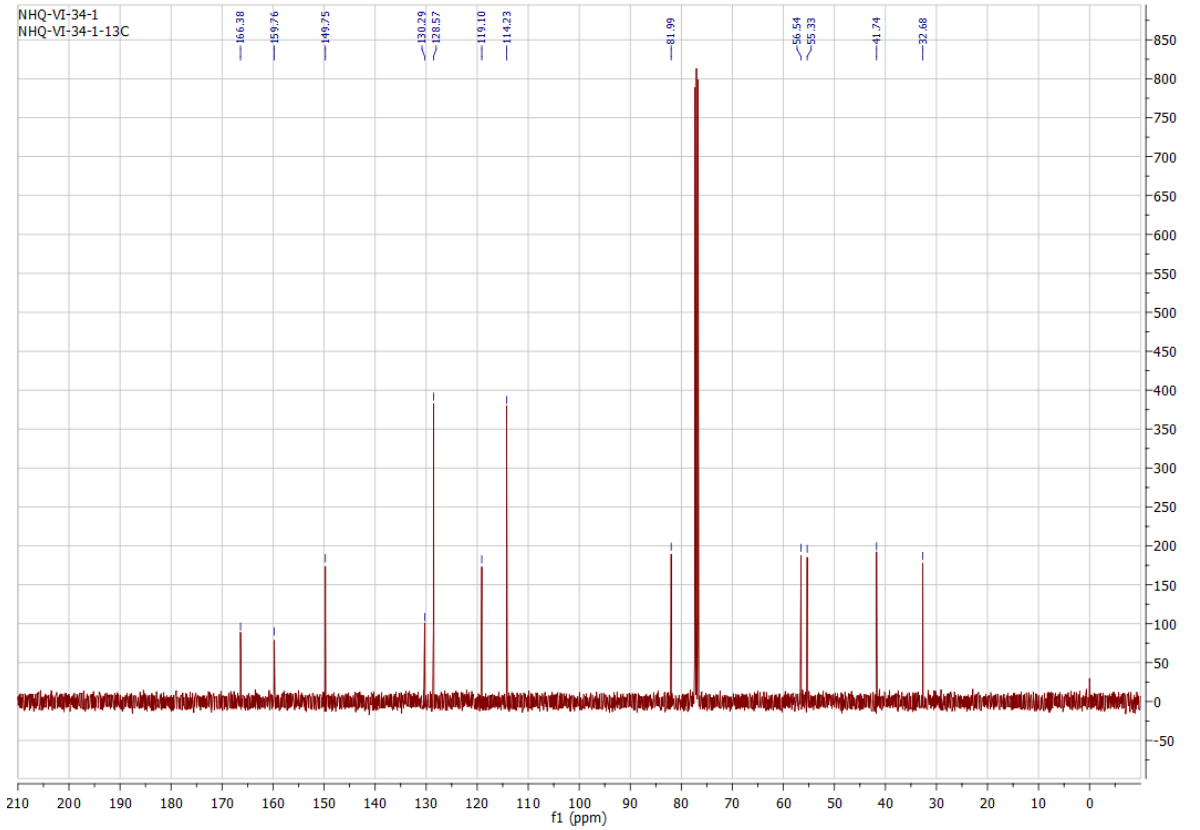

NHQ-XI-79
NHQ-XI-79
Ms
N
Me
O
Me
Me
Ph
PMP
O
11bd (γ only)
f1 (ppm)

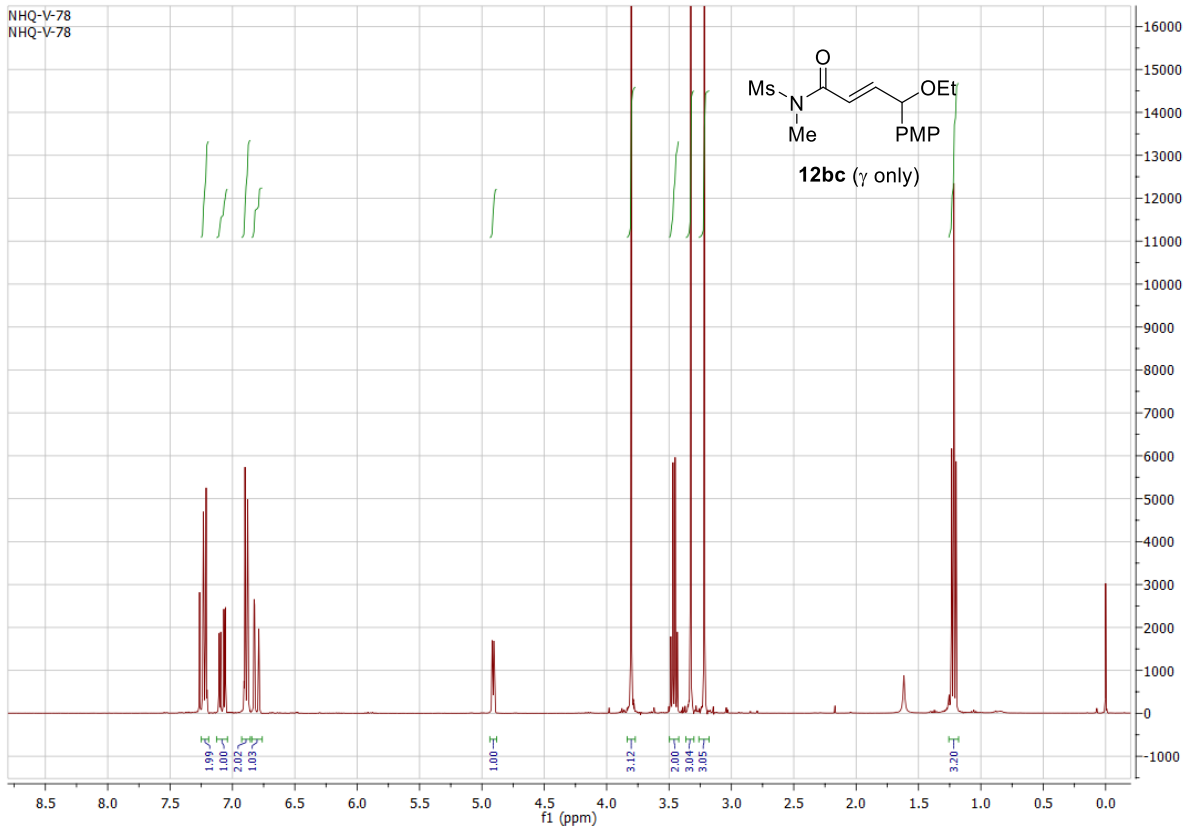

NHQ-XI-79
NHQ-XI-79
f1 (ppm)

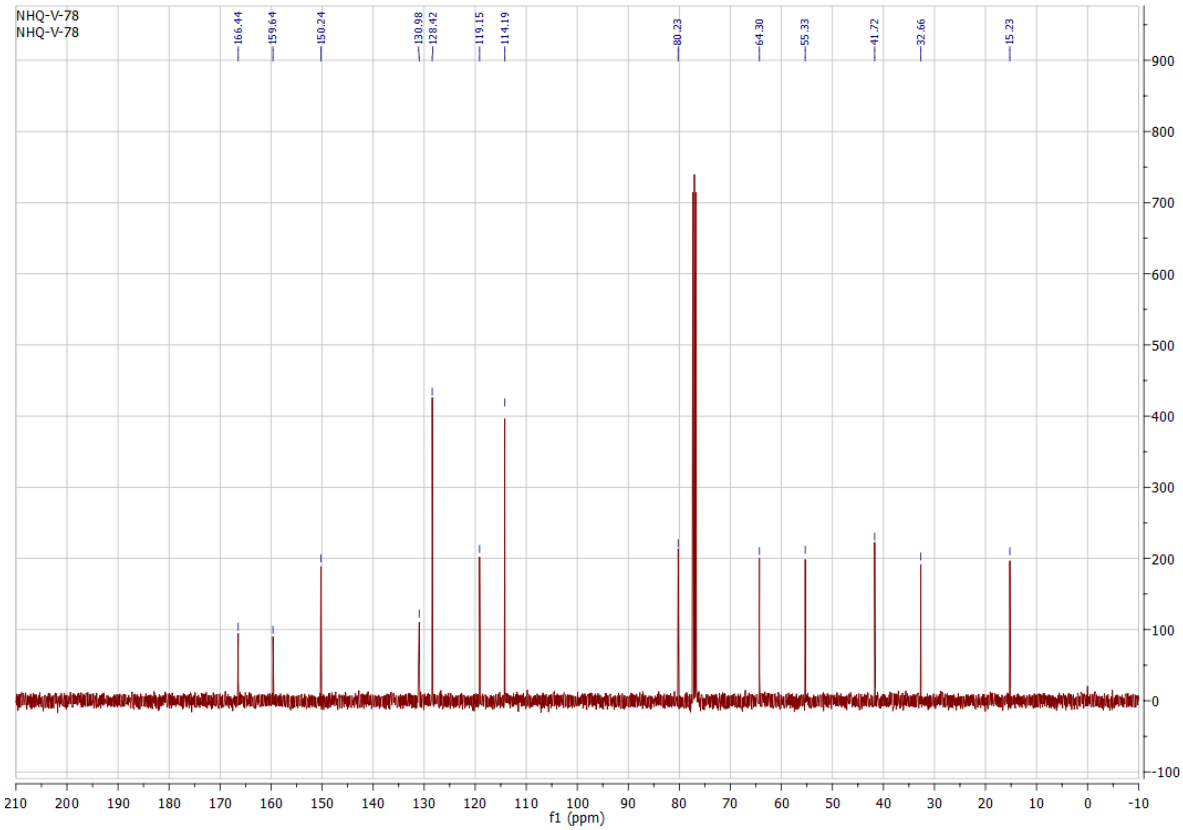

NHQ-VI-78
NHQ-VI-78
Ms
N
Me
O
OBn
PMP
12ba (γ only)
f1 (ppm)

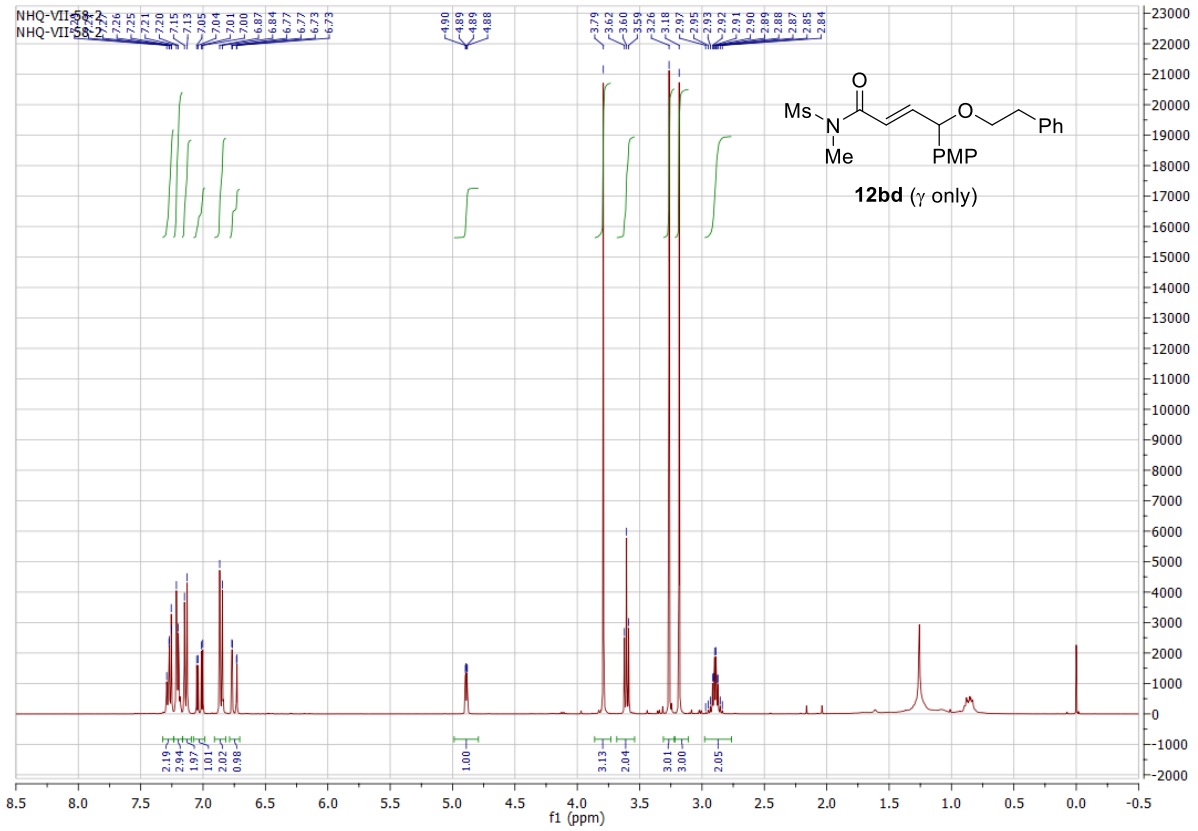

NHQ-V-78
NHQ-V-78
166.44
159.64
150.24
130.98
128.42
119.15
114.19
80.23
64.30
55.33
41.72
32.66
15.23
f1 (ppm)

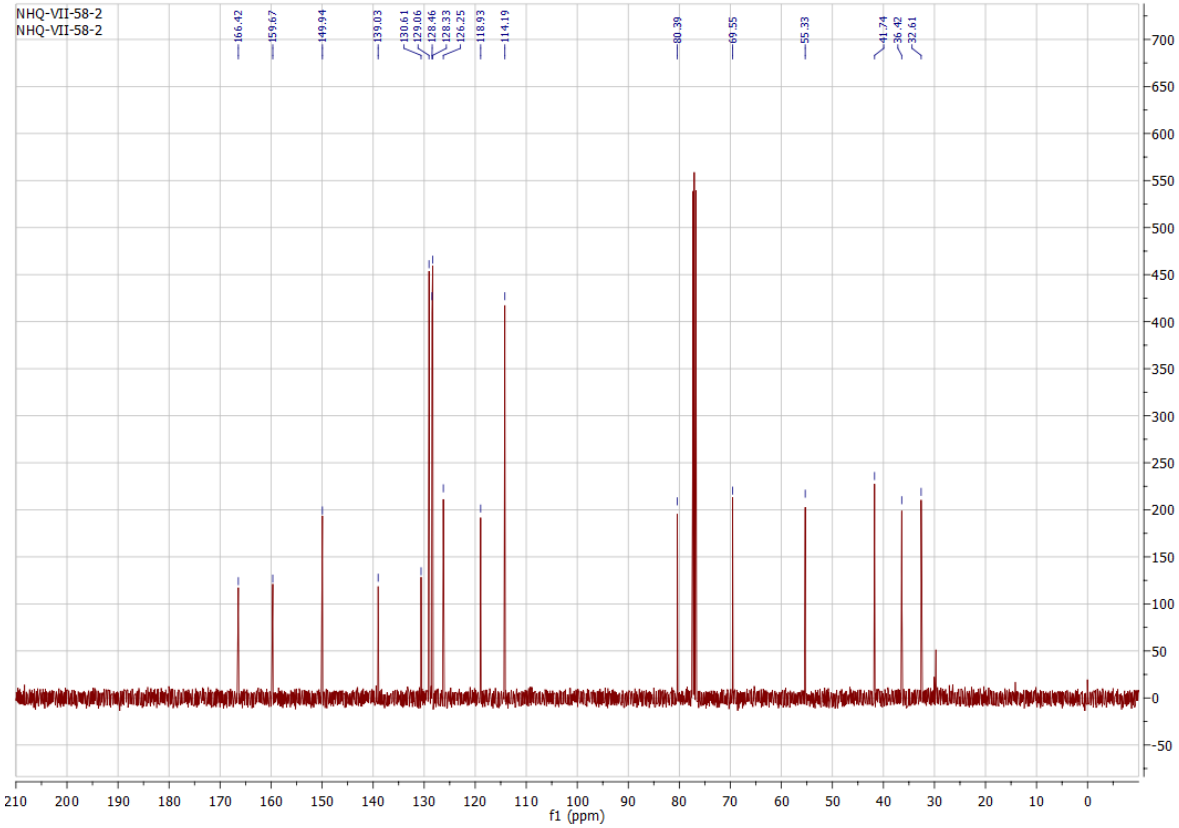

NHQ-VI-34-1
NHQ-VI-34-1
Ms
N
Me
O
OMe
PMP
12bb (γ only)
1.94
0.98
1.97
1.01
1.00
3.10
2.99
3.04
3.03
f1 (ppm)

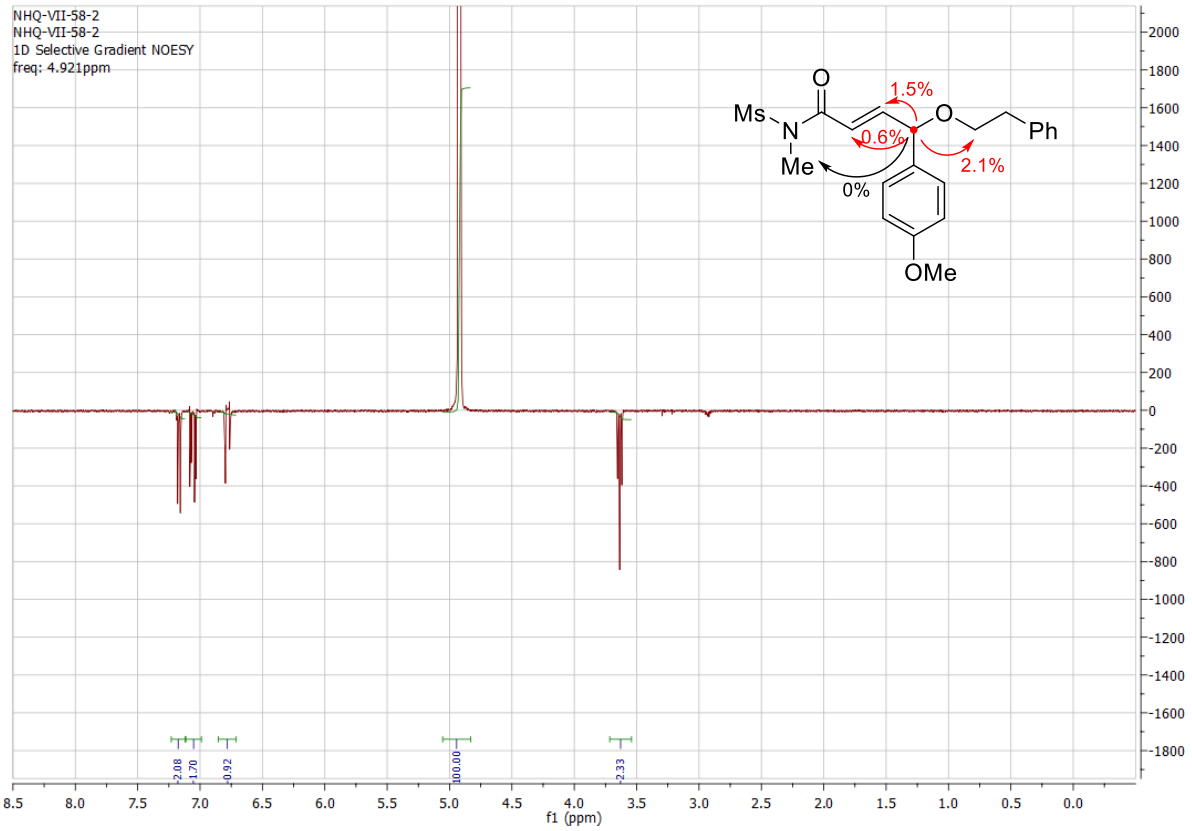

NHQ-VI-34-1
NHQ-VI-34-1-13C
166.38
159.76
149.75
130.29
128.57
119.10
114.23
81.99
56.54
55.33
41.74
32.68
f1 (ppm)

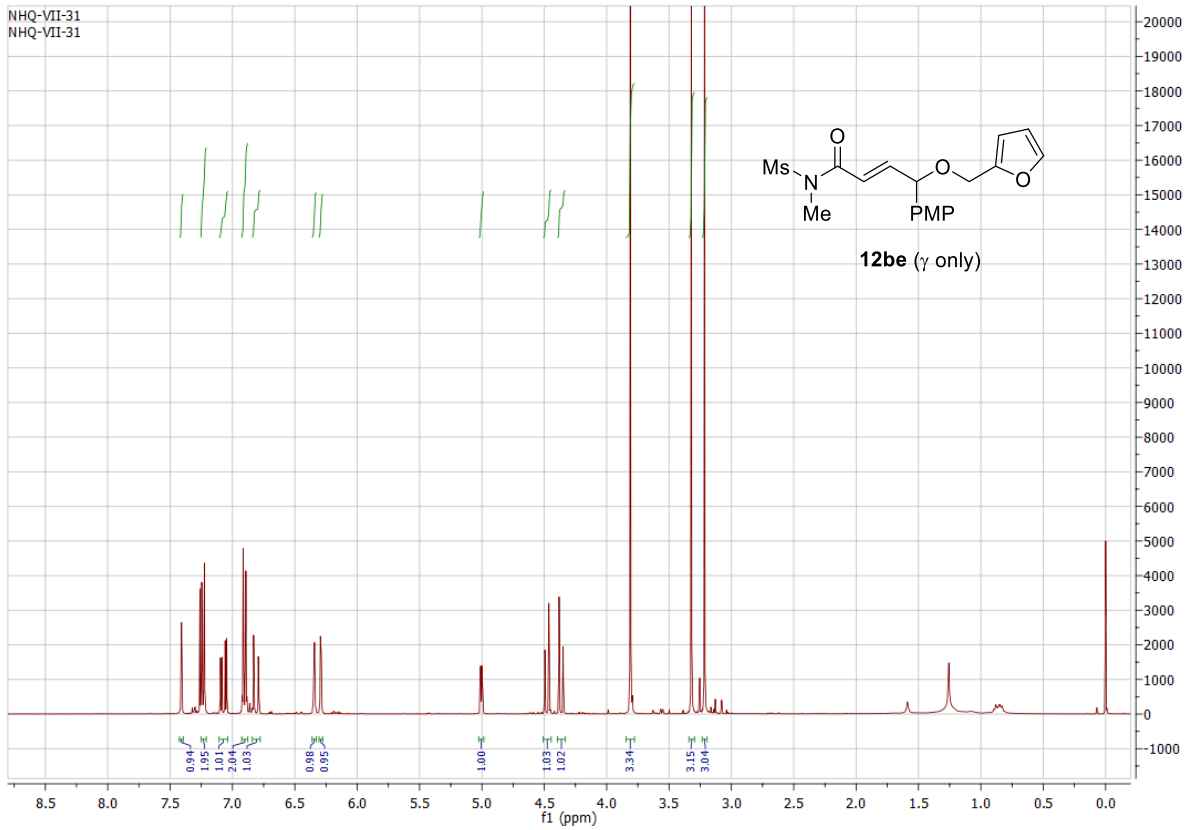

NHQ-V-78
NHQ-V-78
Ms
N
Me
O
OEt
PMP
12bc (γ only)
f1 (ppm)

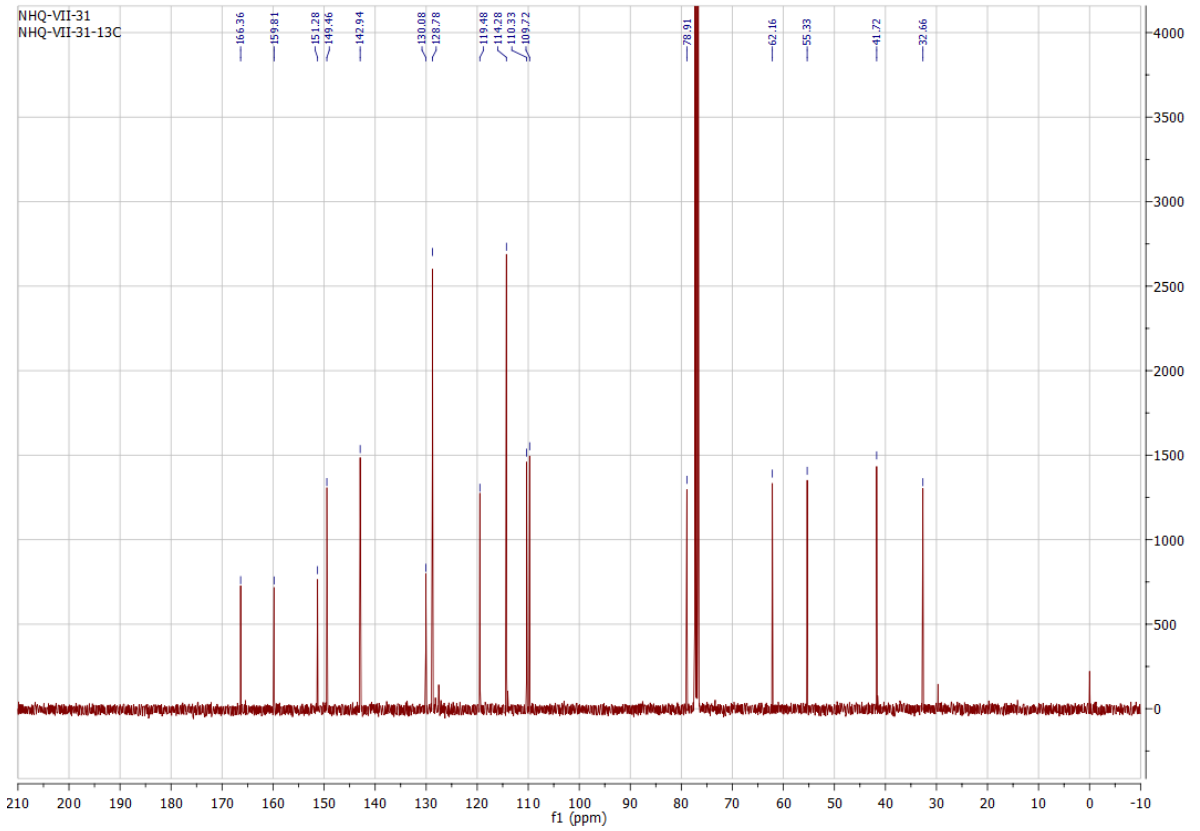

NHQ-V-78
NHQ-V-78
166.44
159.64
150.24
130.98
128.42
119.15
114.19
80.23
64.30
55.33
41.72
32.66
15.23
f1 (ppm)

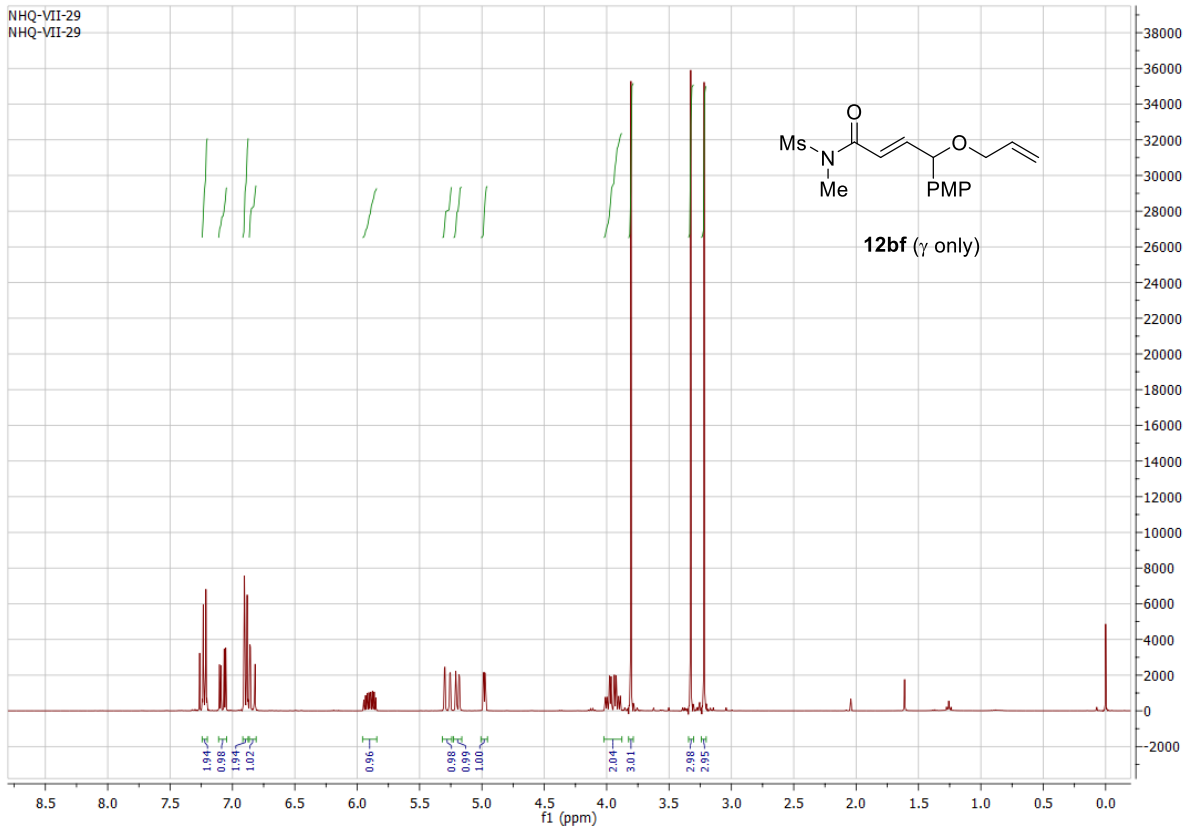

NHQ-VII-58-2
NHQ-VII-58-2
Ms
N
Me
O
O
Ph
PMP
12bd (γ only)
f1 (ppm)

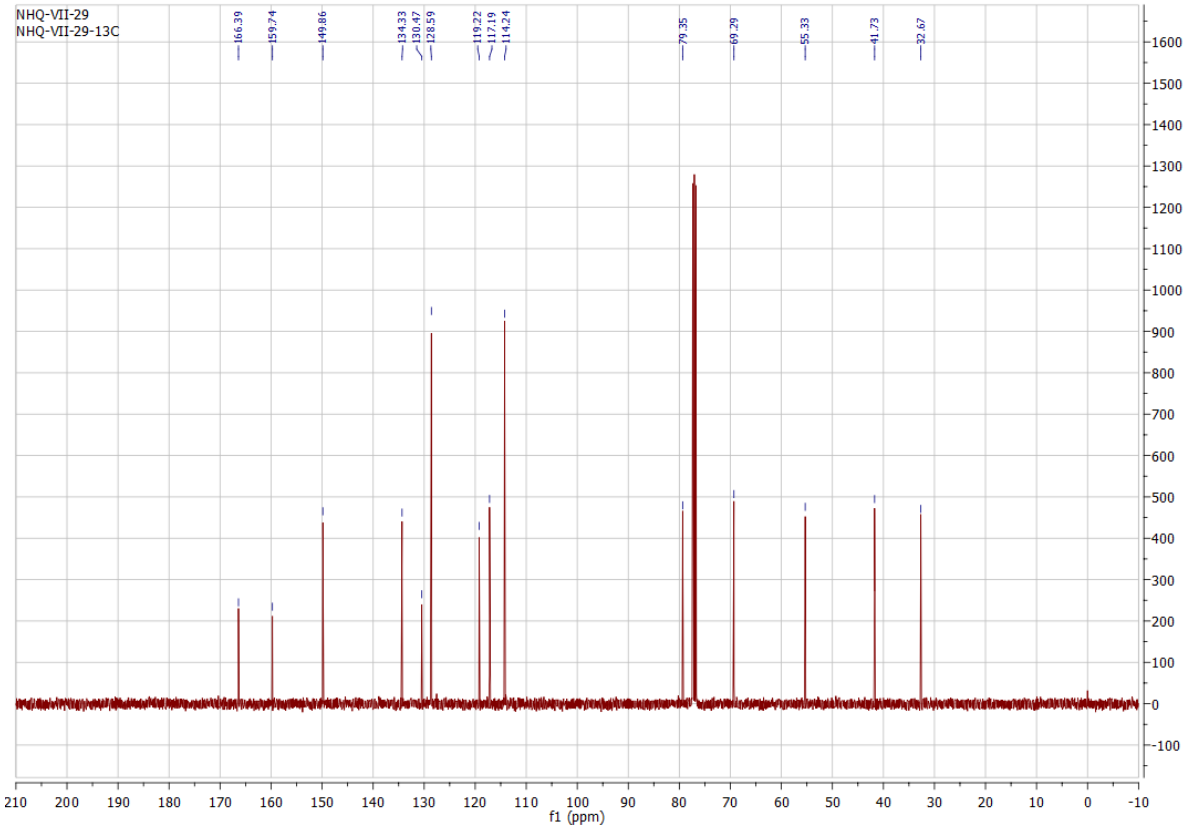

NHQ-VII-58-2
NHQ-VII-58-2
f1 (ppm)

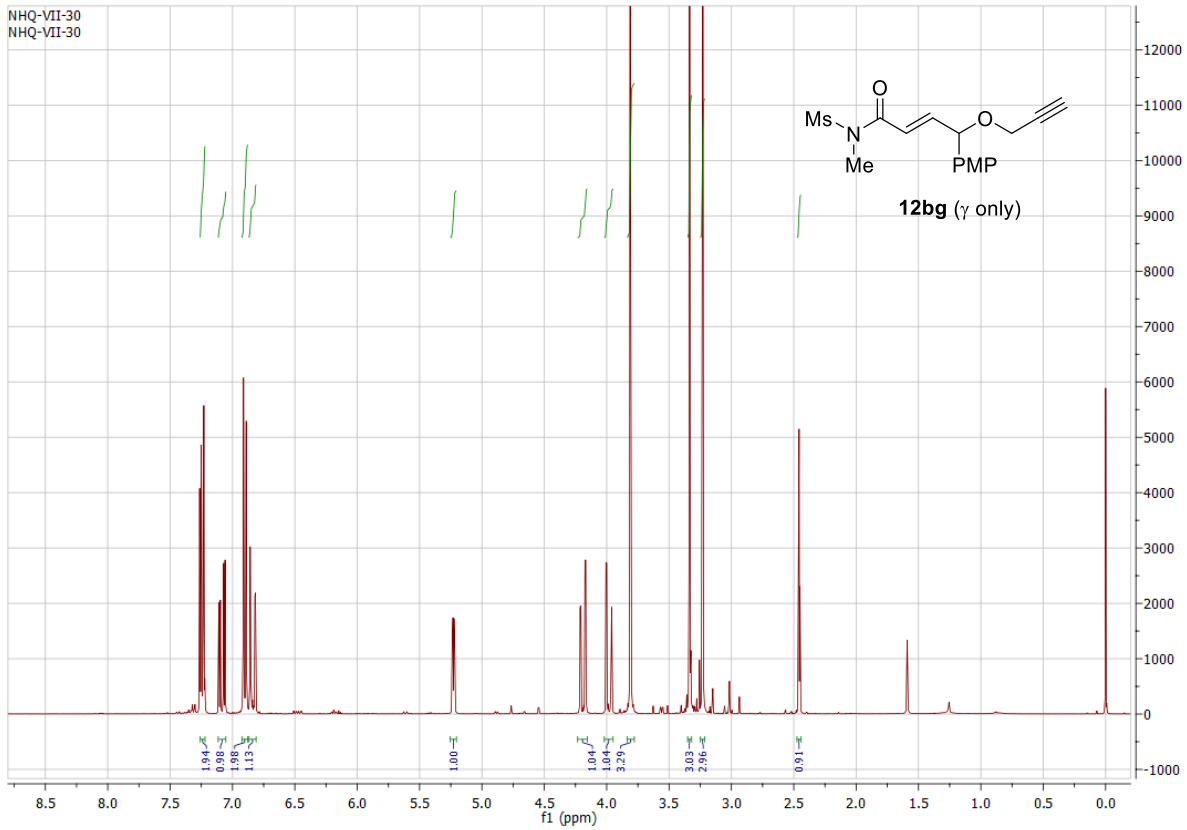

NHQ-VII-58-2
NHQ-VII-58-2
1D Selective Gradient NOESY
freq: 4.921ppm
O
Ms
N
Me
O
Ph
1.5%
0.6%
2.1%
0%
OMe
2.08
1.70
0.92
100.00
2.33
f1 (ppm)

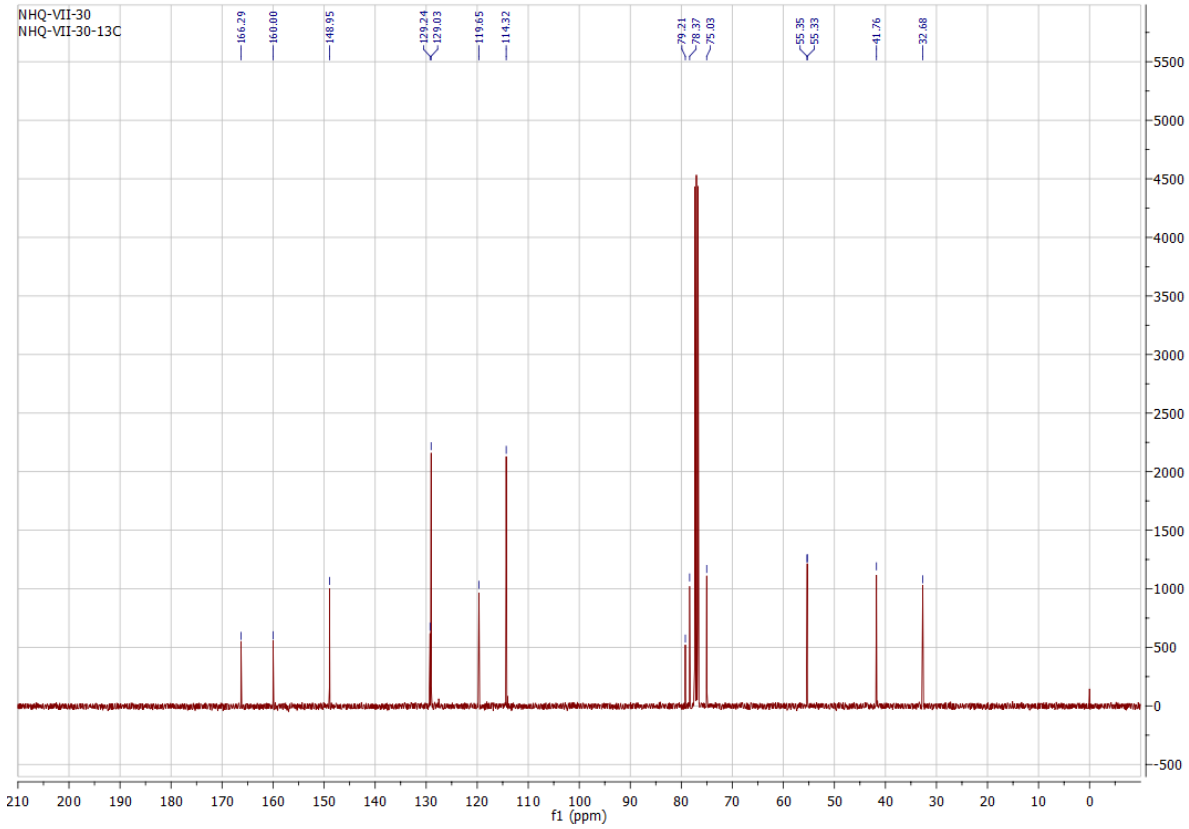

NHQ-VII-31
NHQ-VII-31
Ms
N
Me
O
O
O
PMP
12be (γ only)
f1 (ppm)

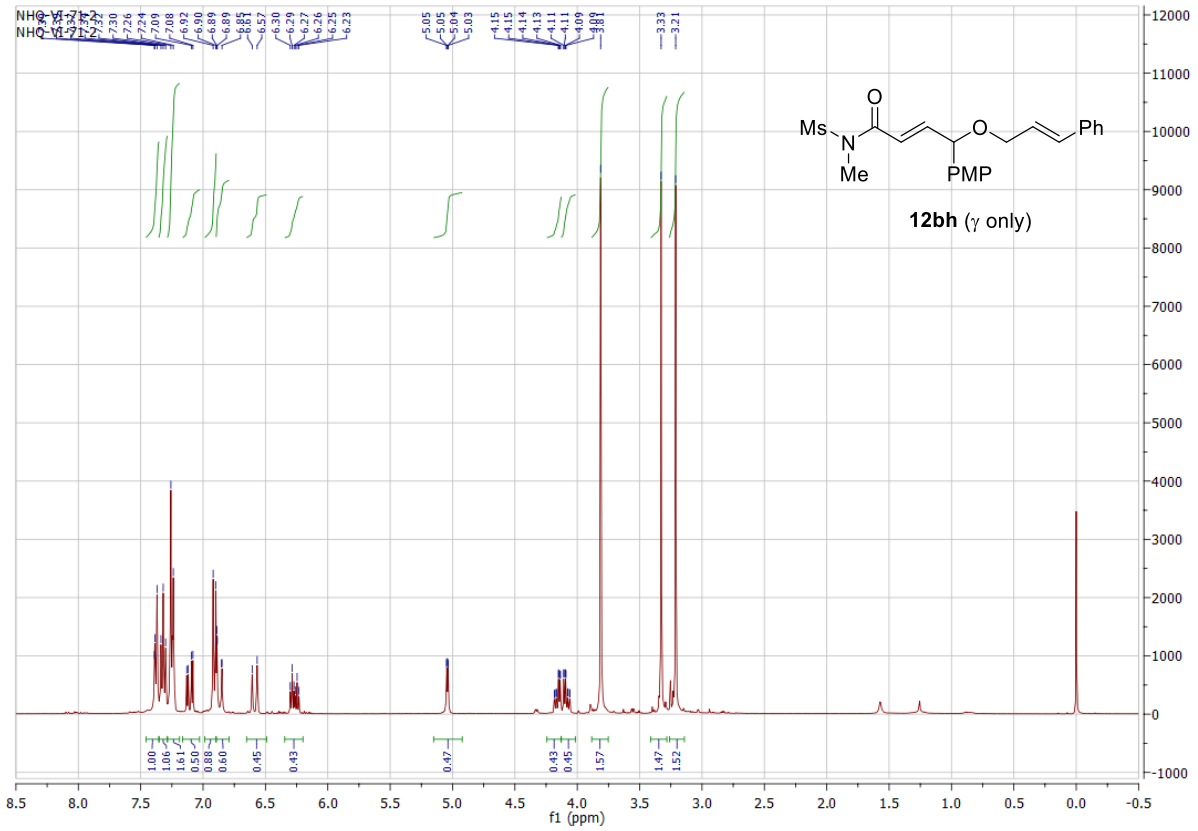

NHQ-VII-31
NHQ-VII-31-13C
166.36
159.81
151.28
149.46
142.94
130.08
128.78
119.48
114.28
110.33
109.72
78.91
62.16
55.33
41.72
32.66
f1 (ppm)

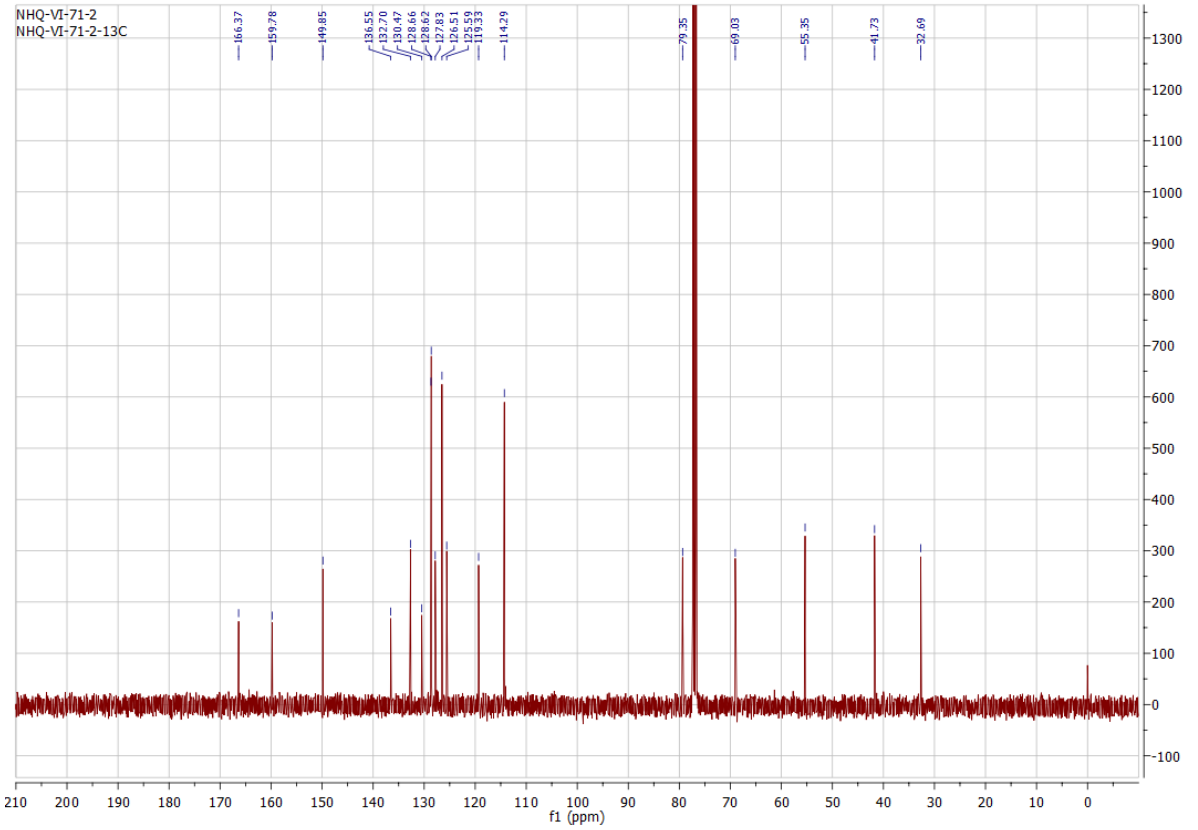

NHQ-VII-29
NHQ-VII-29
Ms
N
Me
O
O
PMP
12bf (γ only)
f1 (ppm)

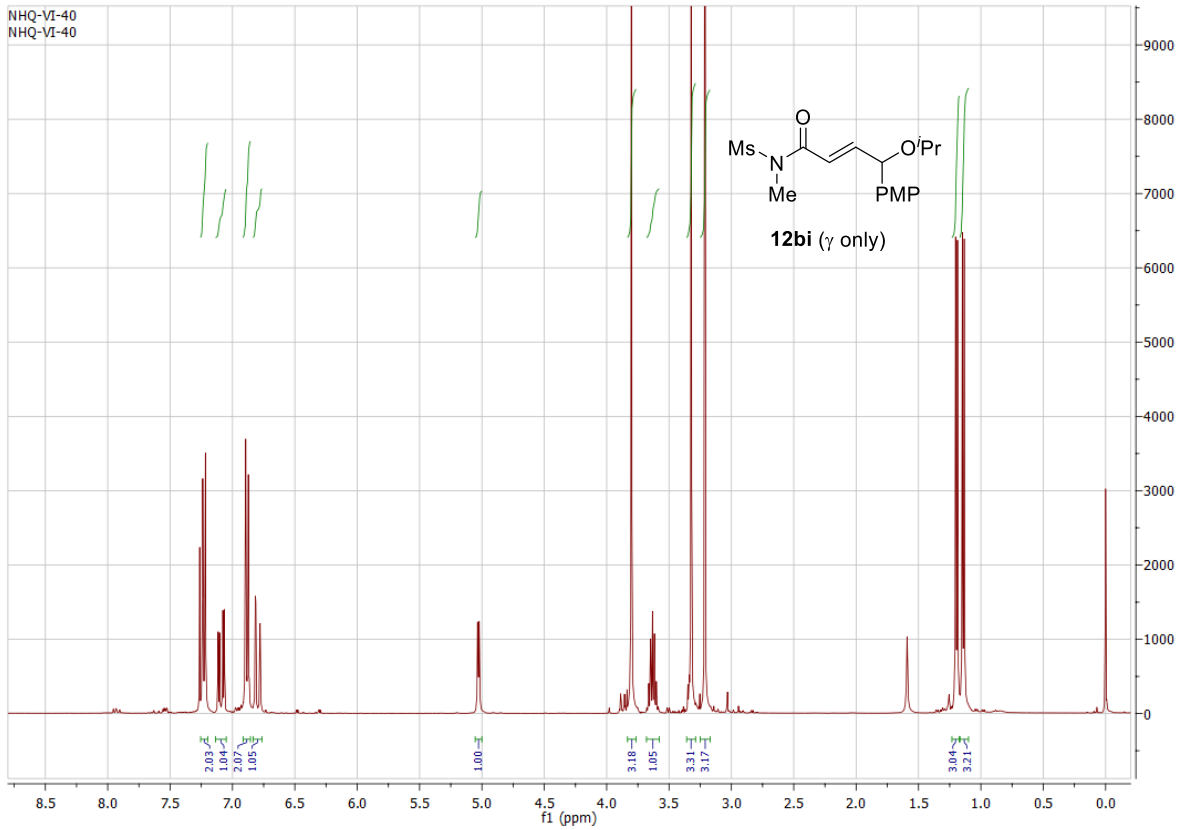

NHQ-VII-29
NHQ-VII-29-13C
166.39
159.74
149.86
134.33
130.47
128.59
119.22
117.19
114.24
79.35
69.29
55.33
41.73
32.67
f1 (ppm)

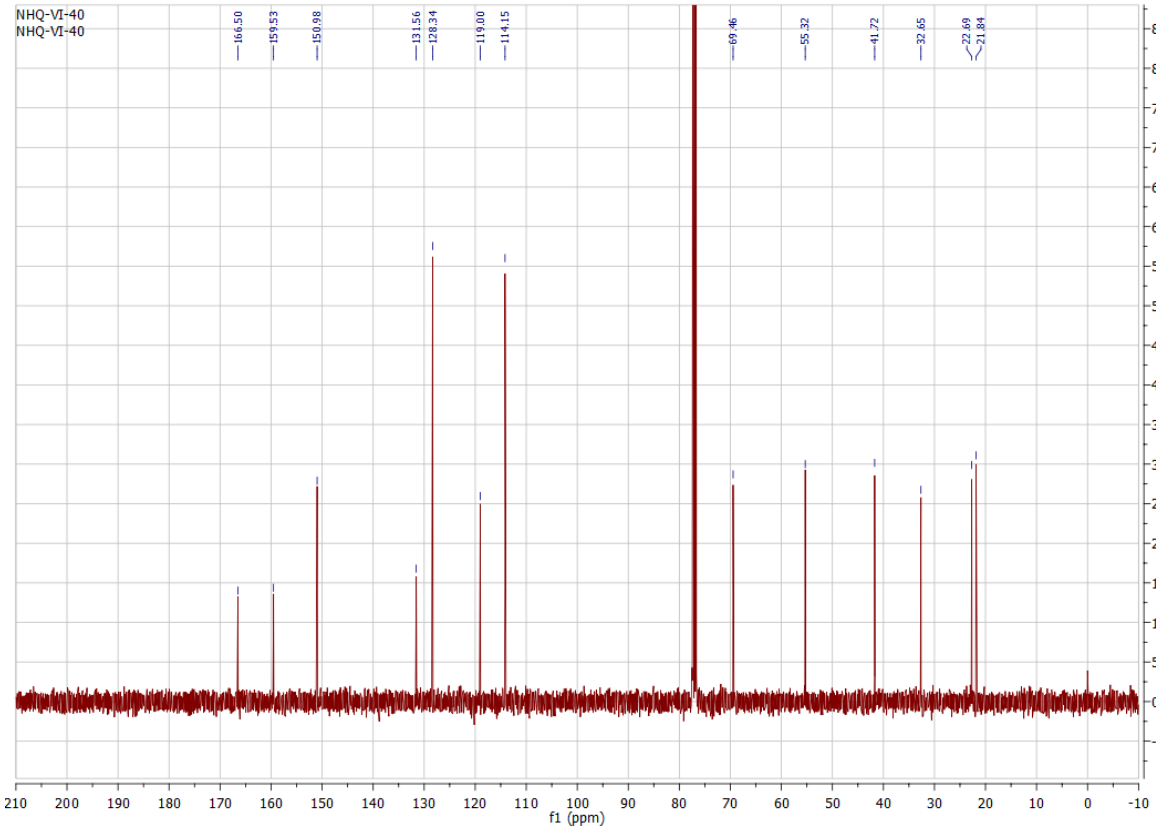

NHQ-VII-30
NHQ-VII-30
Ms
N
Me
O
O
PMP
12bg (γ only)
f1 (ppm)

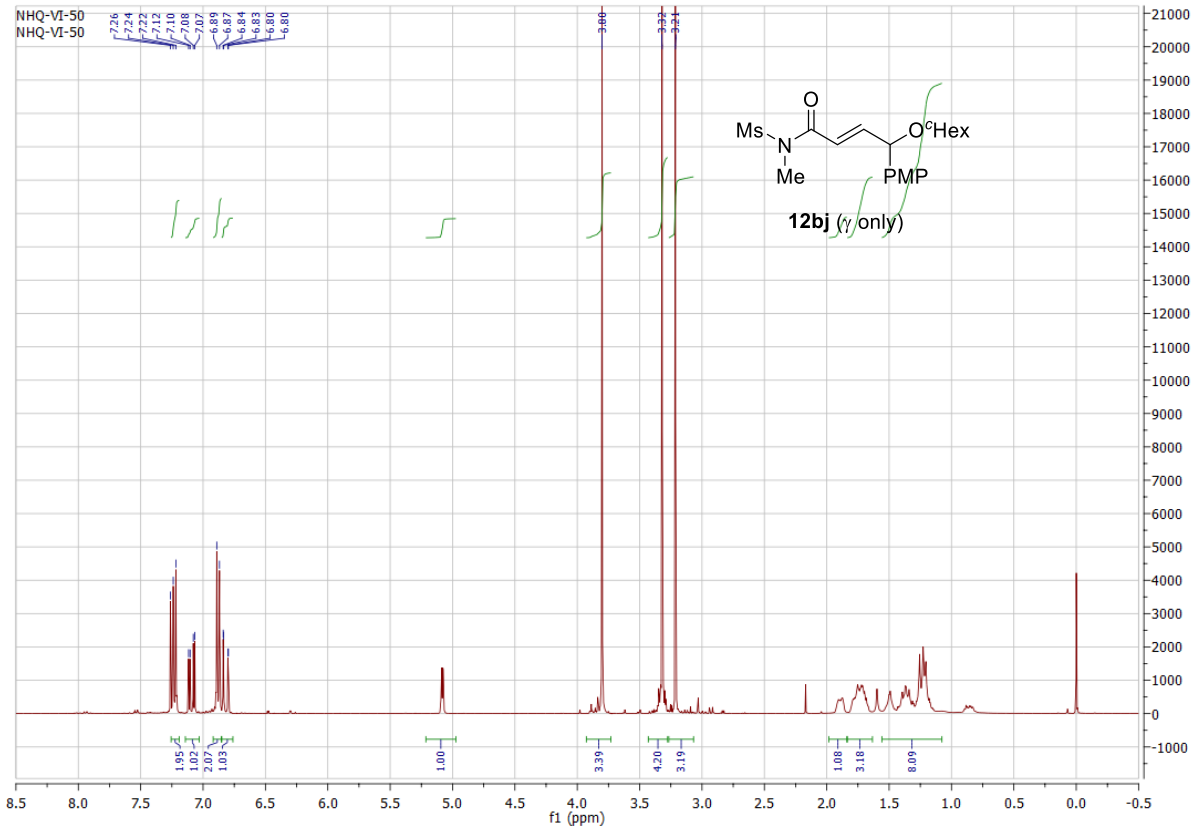

NHQ-VII-30
NHQ-VII-30-13C
166.29
160.00
148.95
129.24
129.03
119.65
114.32
79.21
78.37
75.03
55.35
55.33
41.76
32.68
f1 (ppm)

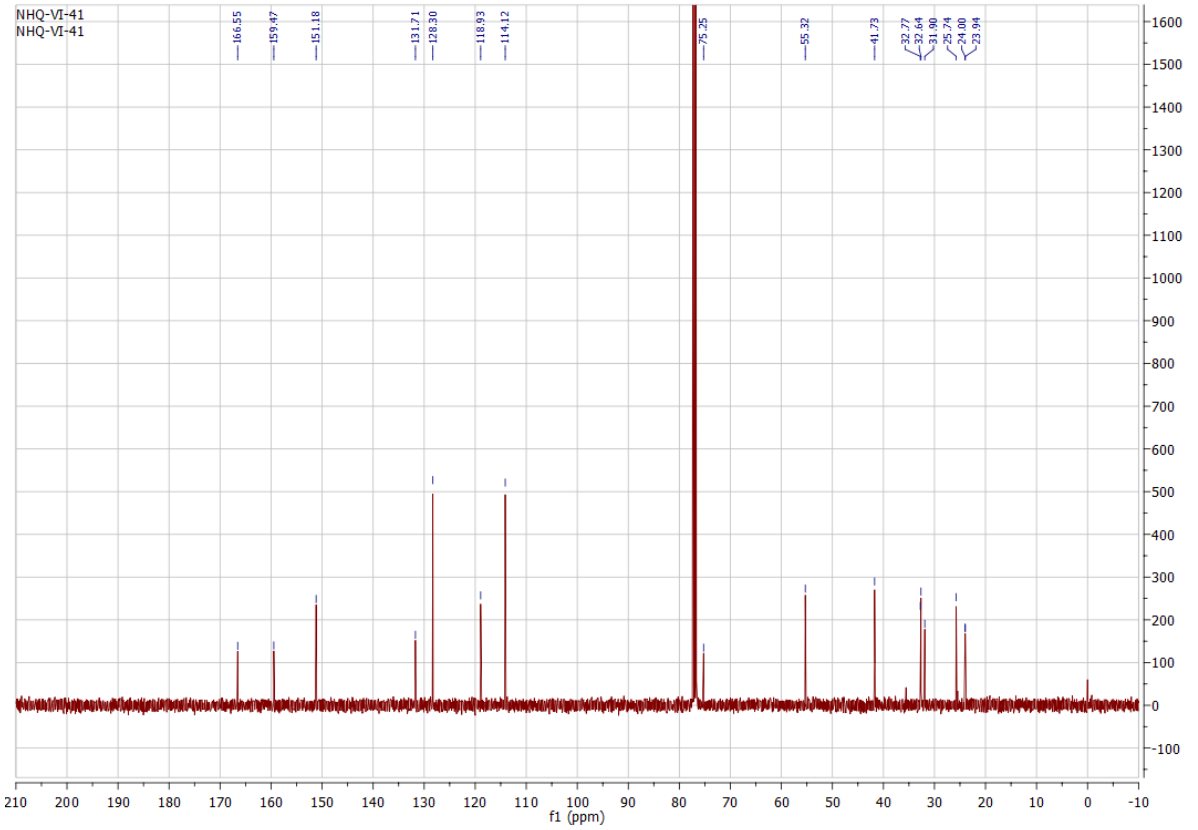

Ms
N
Me
O
O
PMP
Ph
12bh (γ only)
f1 (ppm)

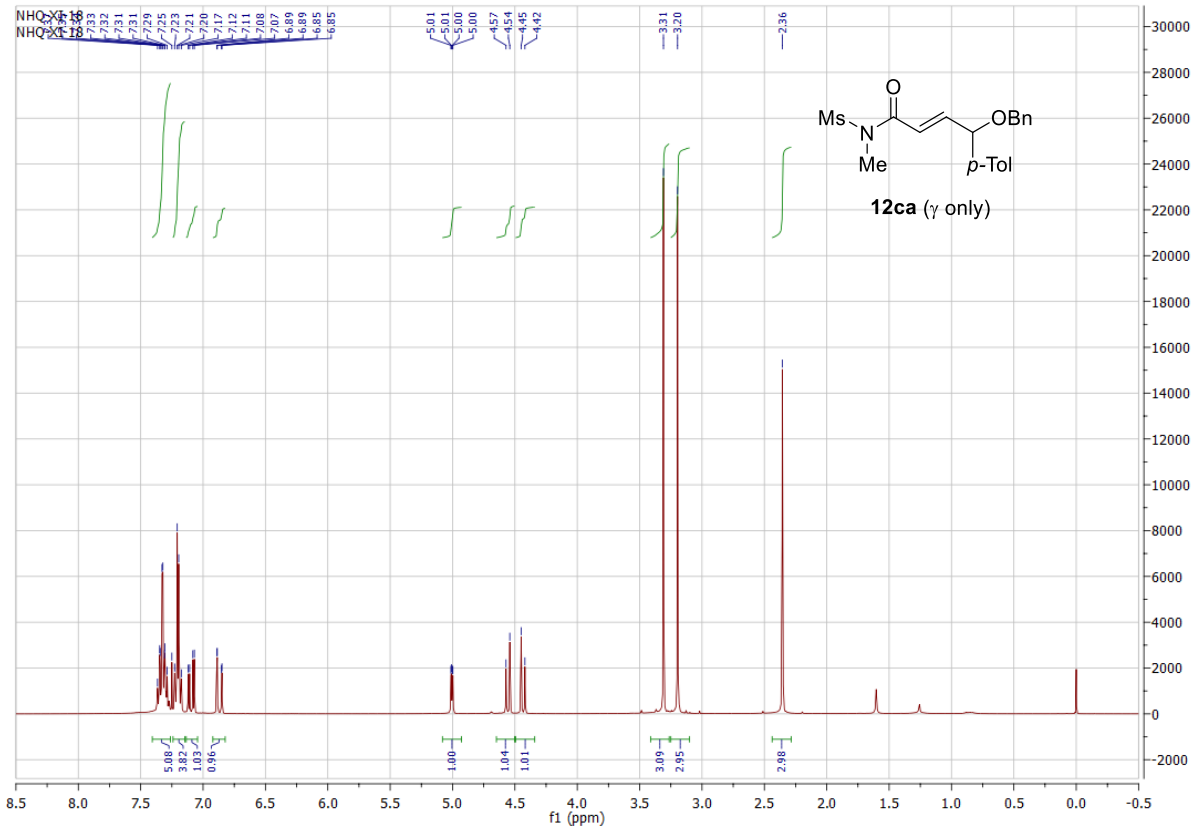

NHQ-VI-71-2
NHQ-VI-71-2-13C
f1 (ppm)

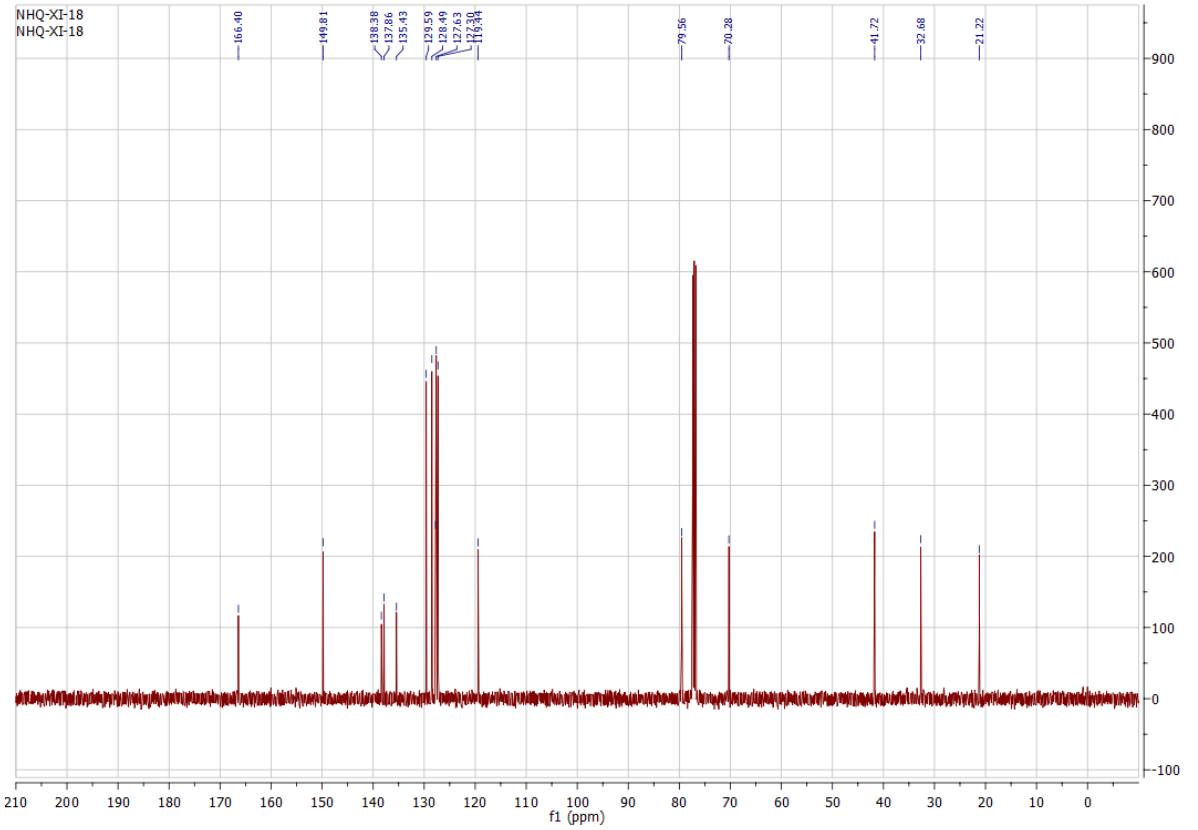

NHQ-VI-40
NHQ-VI-40
Ms
N
Me
O
O^{i}Pr
PMP
12bi (γ only)
f1 (ppm)

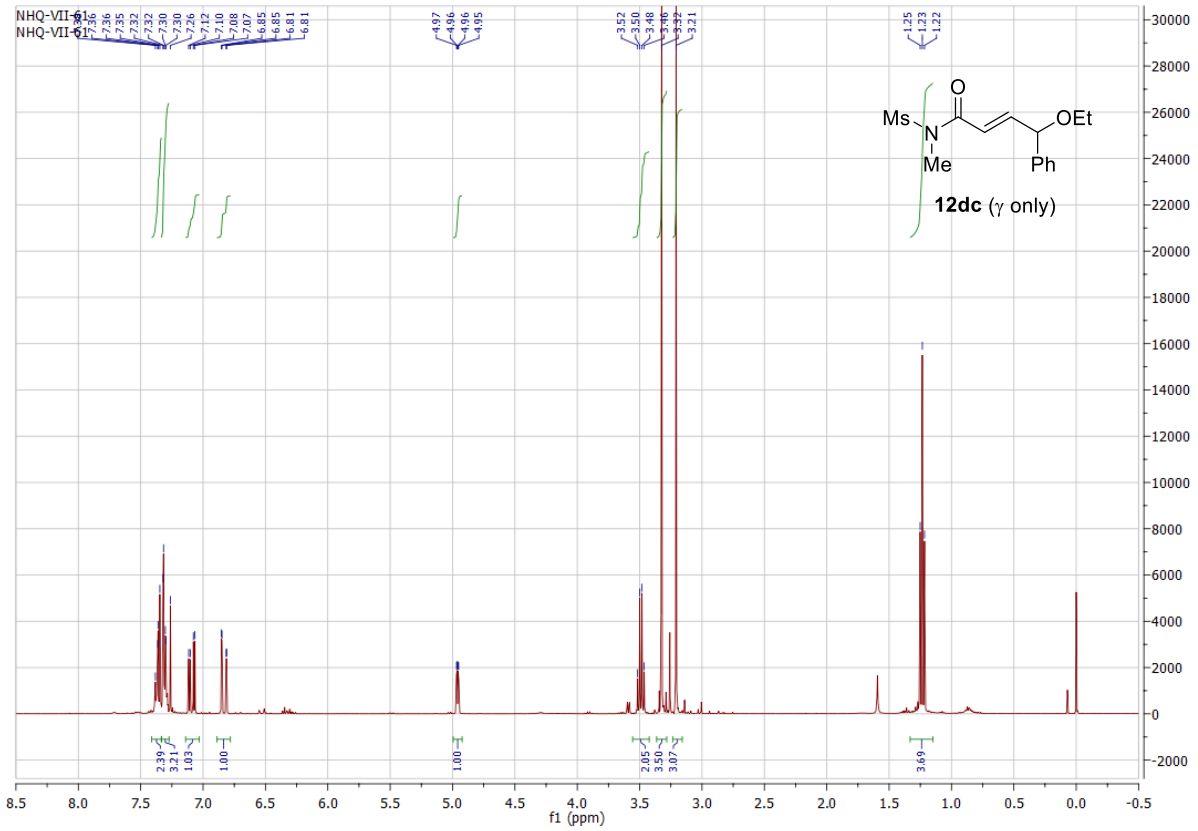

NHQ-VI-40
NHQ-VI-40
166.50
159.53
150.98
131.56
128.34
119.00
114.15
69.46
55.32
41.72
32.65
22.69
21.84
f1 (ppm)

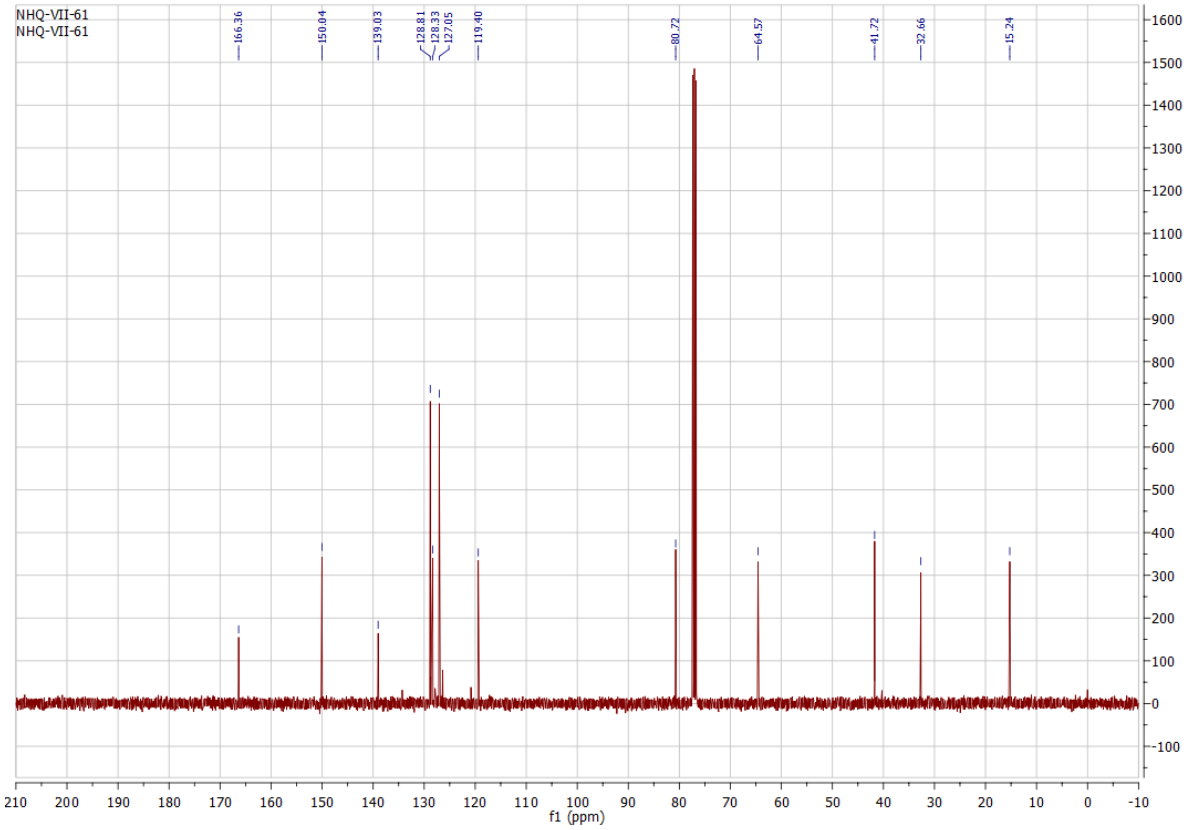

NHQ-VI-50
NHQ-VI-50
Ms
N
Me
O
OcHex
PMP
12bj (γ only)
f1 (ppm)

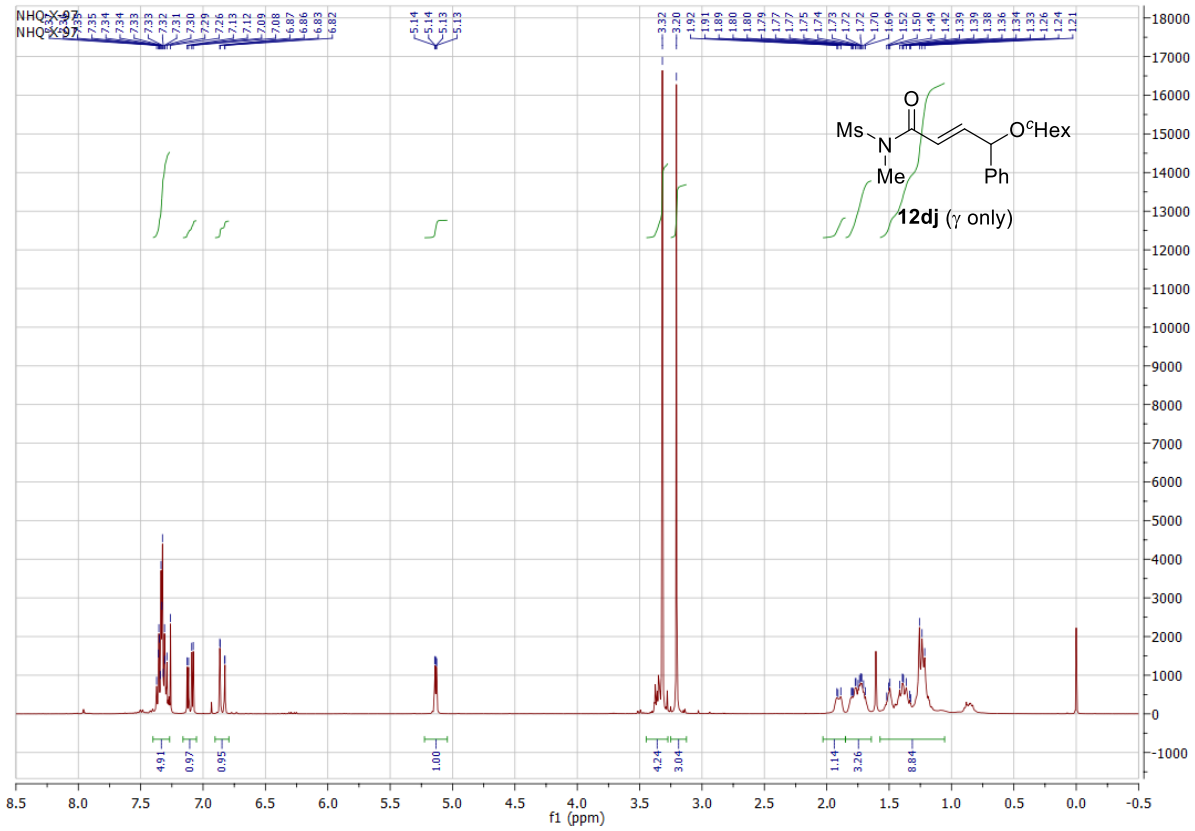

NHQ-VI-41
NHQ-VI-41
f1 (ppm)

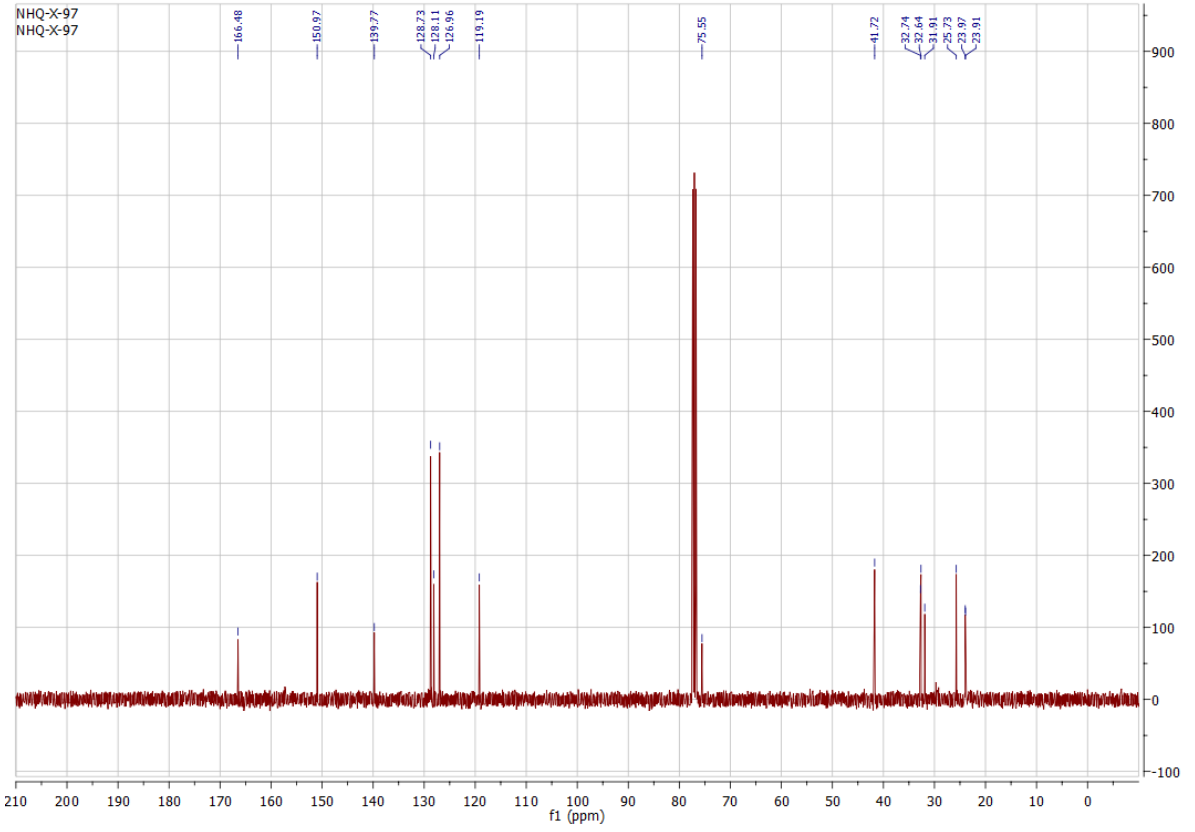

NHQ-XI-18
NHQ-XI-18
Ms
N
Me
O
OBn
p-Tol
12ca (γ only)
f1 (ppm)

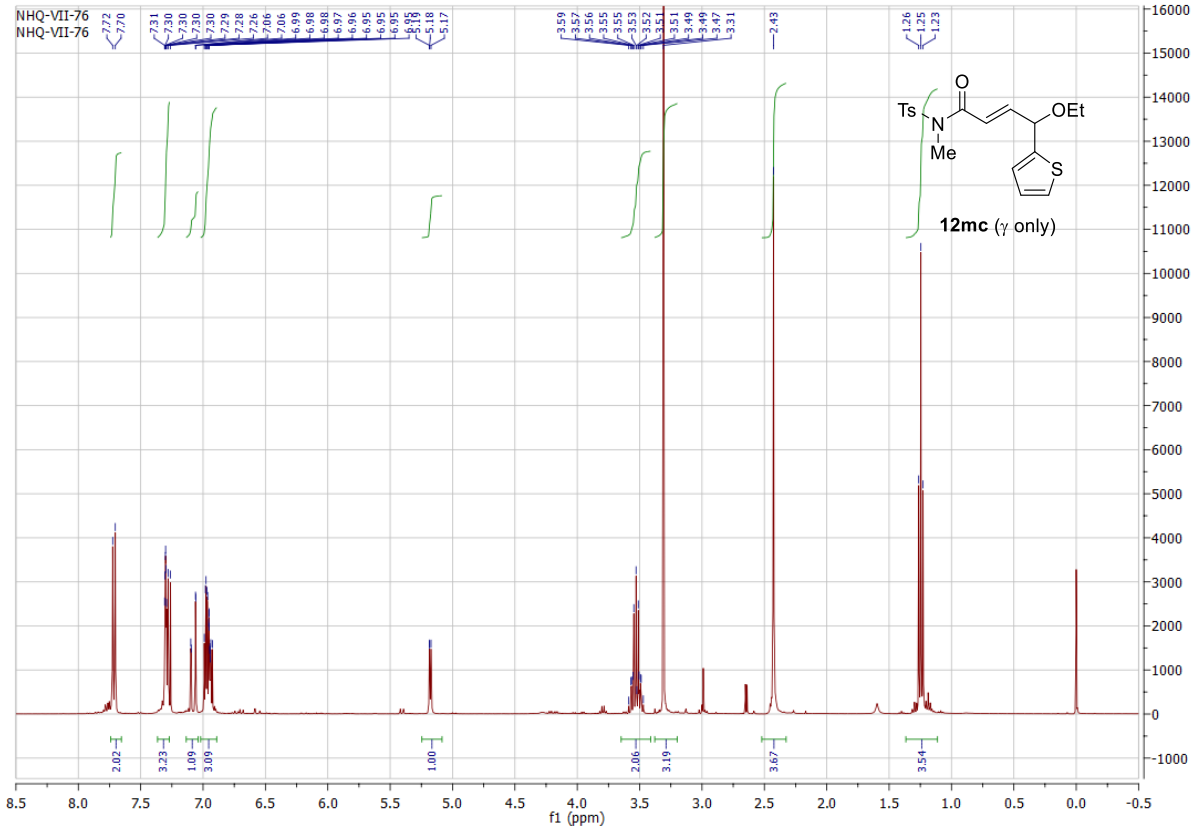

NHQ-XI-18
NHQ-XI-18
f1 (ppm)

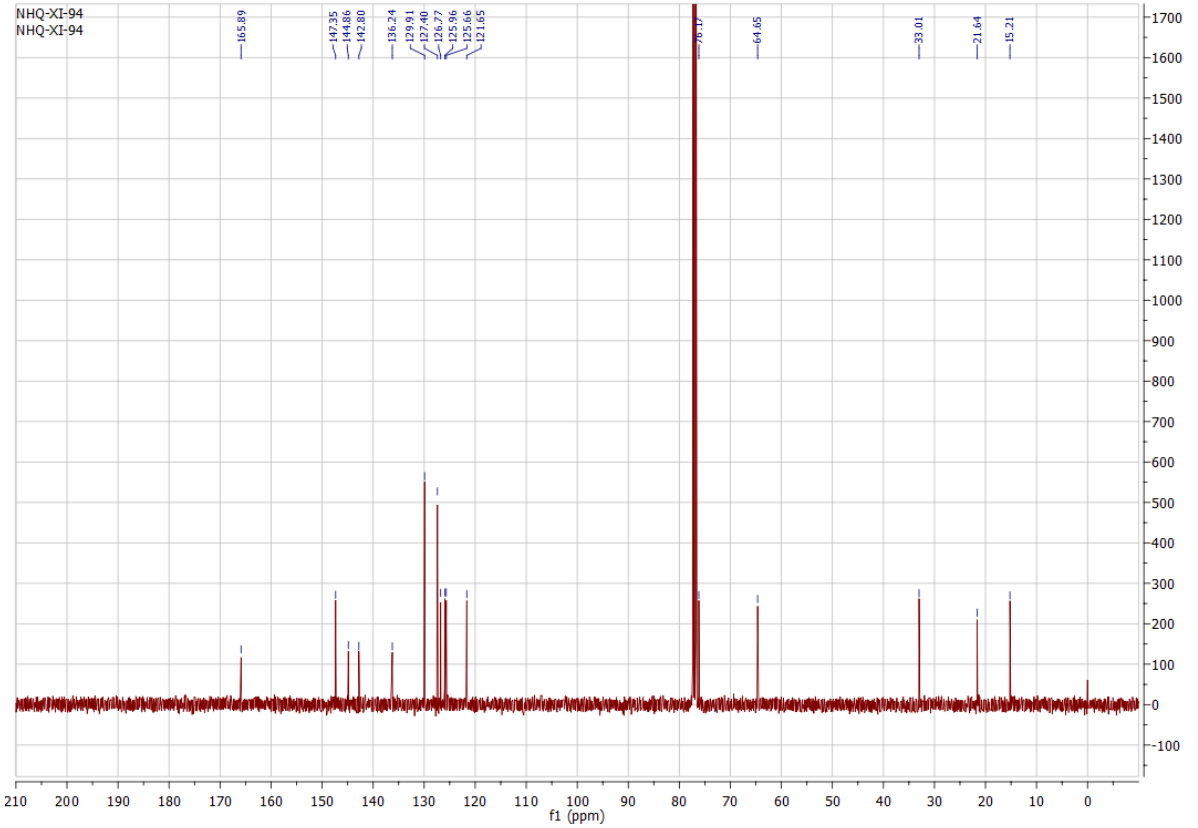

NHQ-VII-61
NHQ-VII-61
Ms
N
Me
O
OEt
Ph
12dc (γ only)
f1 (ppm)

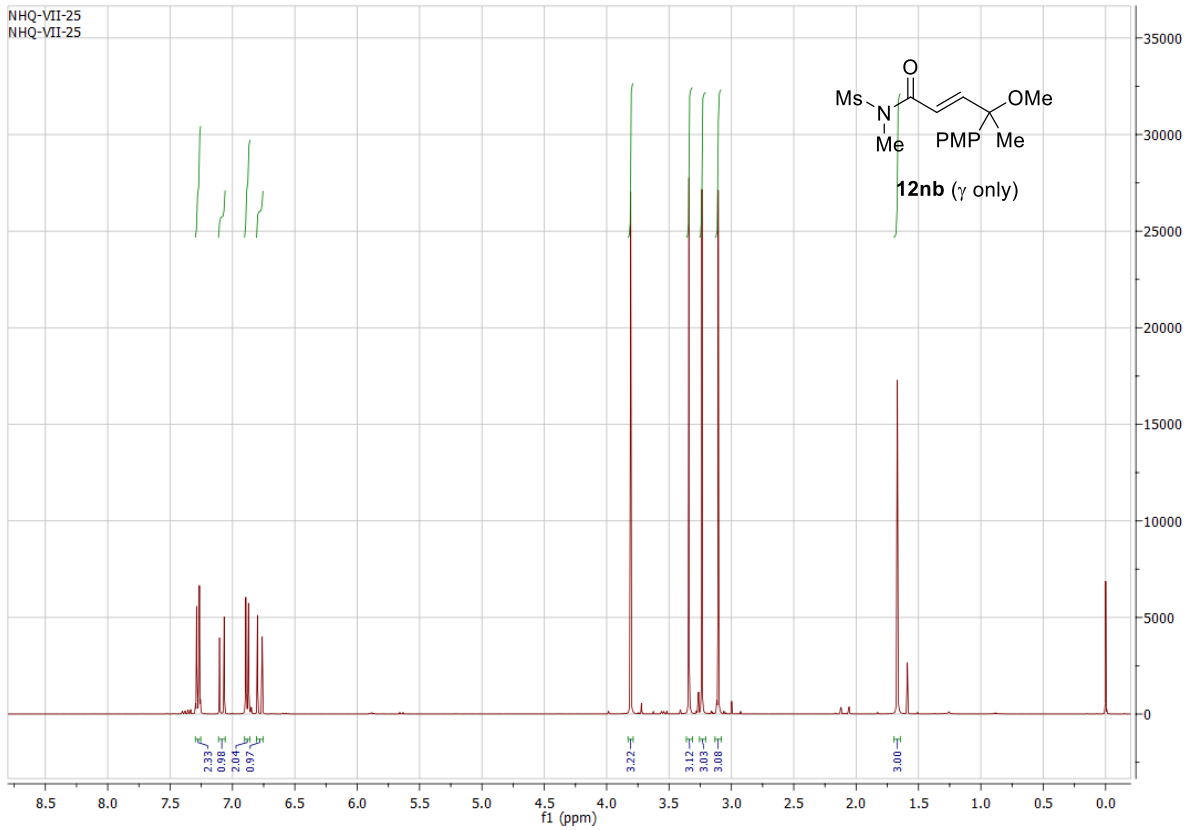

NHQ-VII-61
NHQ-VII-61
166.36
150.04
139.03
128.81
128.33
127.05
119.40
80.72
64.57
41.72
32.66
15.24
f1 (ppm)

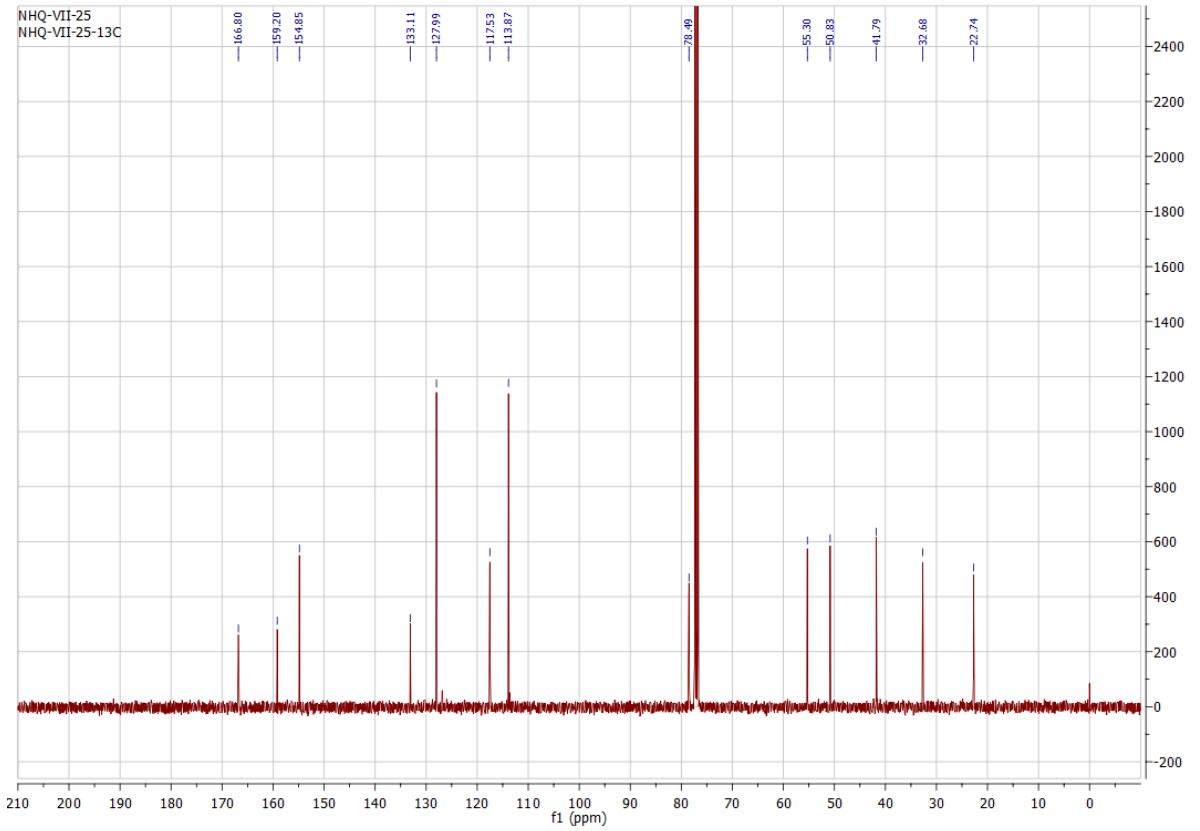

NHQ-X-97
NHQ-X-97
Ms
N
Me
O
O^cHex
Ph
12dj (γ only)
f1 (ppm)

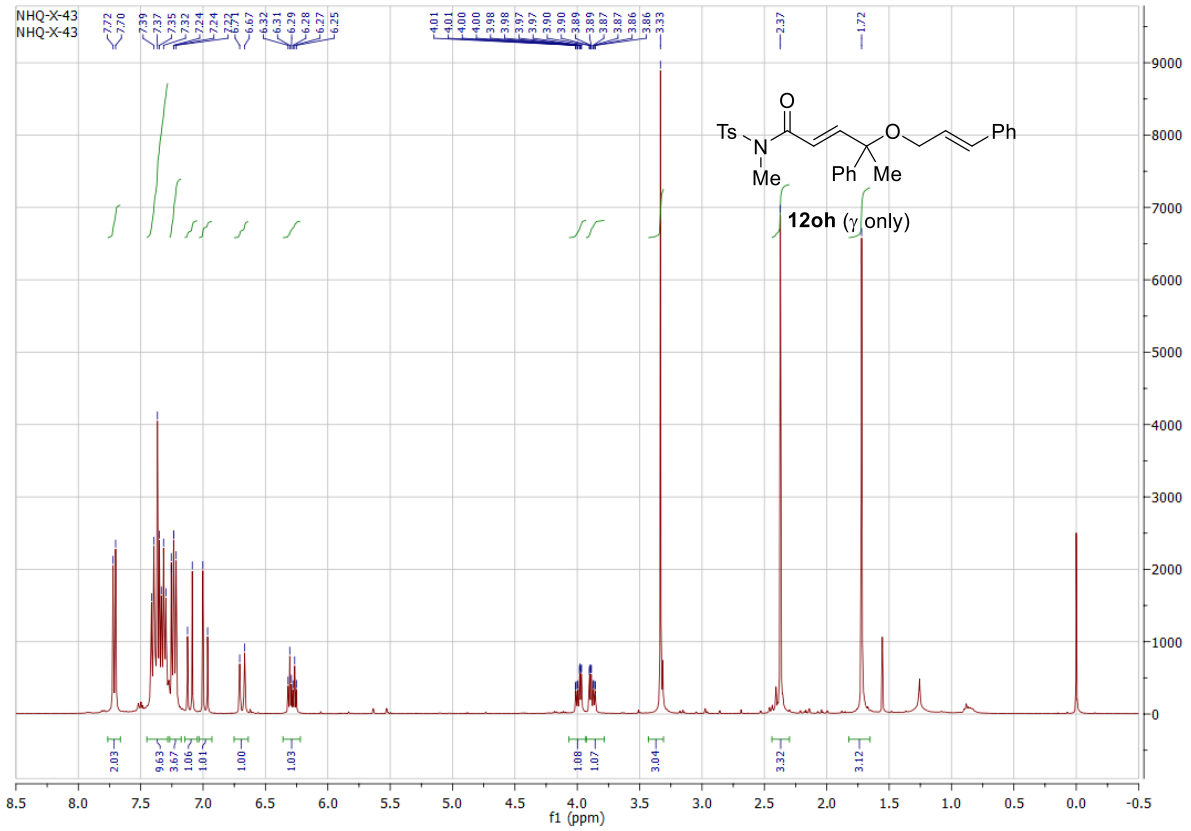

NHQ-X-97
NHQ-X-97
166.48
150.97
139.77
128.73
128.11
126.96
119.19
75.55
41.72
32.74
32.64
31.91
25.73
23.97
23.91
f1 (ppm)

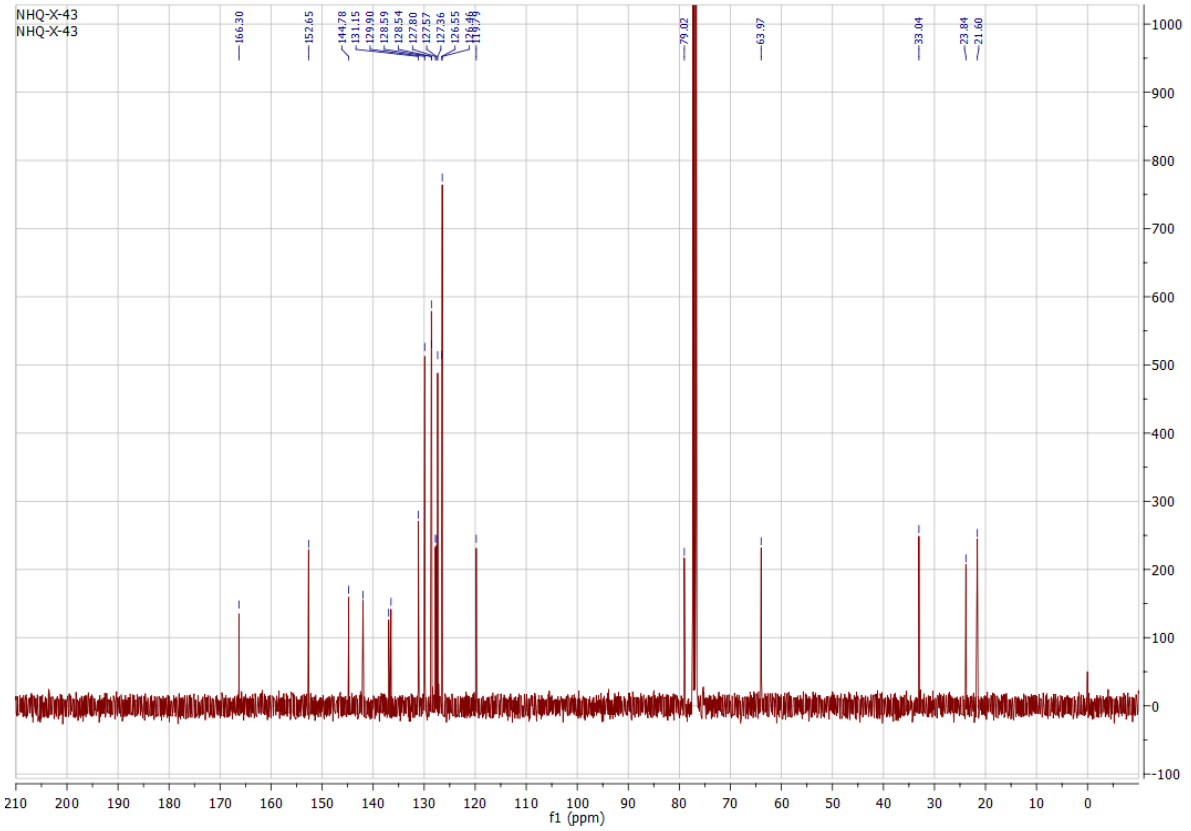

NHQ-VII-76
NHQ-VII-76
Ts
N
Me
O
OEt
S
12mc (γ only)
f1 (ppm)

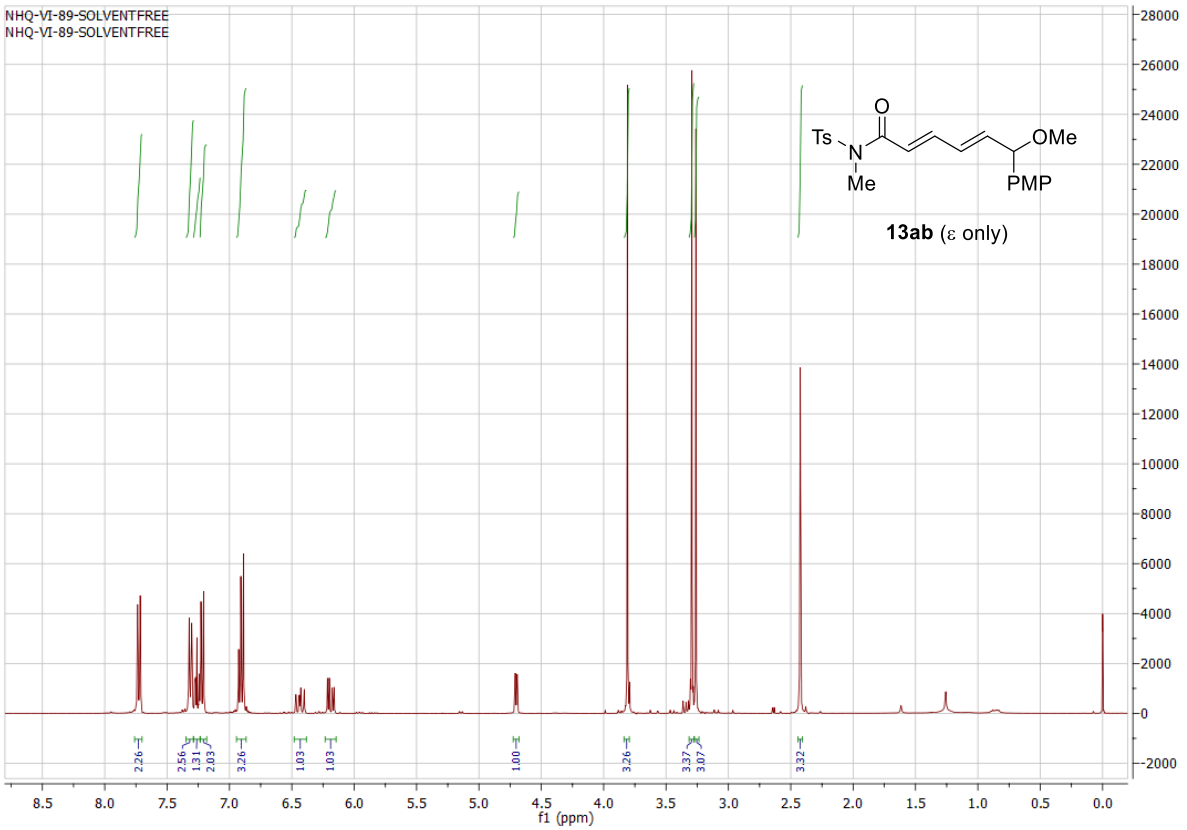

NHQ-XI-94
NHQ-XI-94
f1 (ppm)

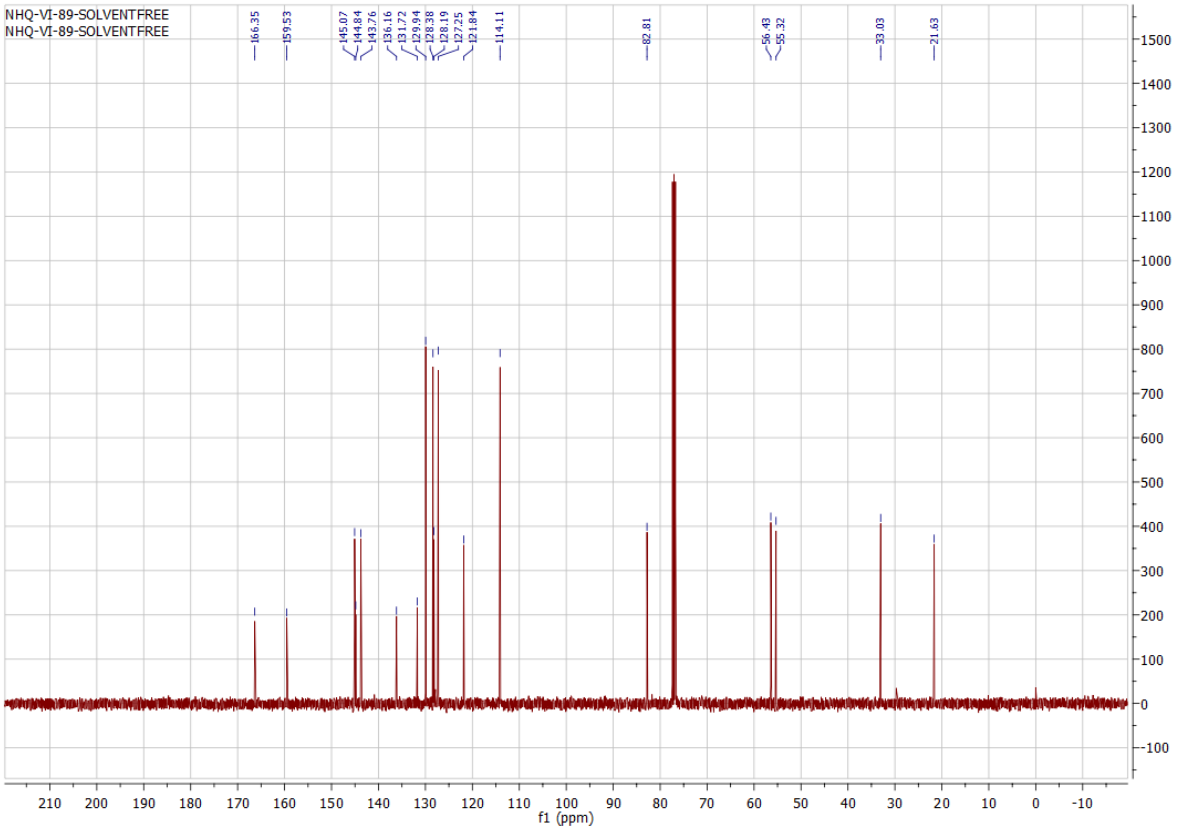

NHQ-VII-25
NHQ-VII-25
O
Ms
N
Me
OMe
PMP
Me
12nb (γ only)
2.33
0.98
2.04
0.97
3.22
3.12
3.03
3.08
3.00
f1 (ppm)

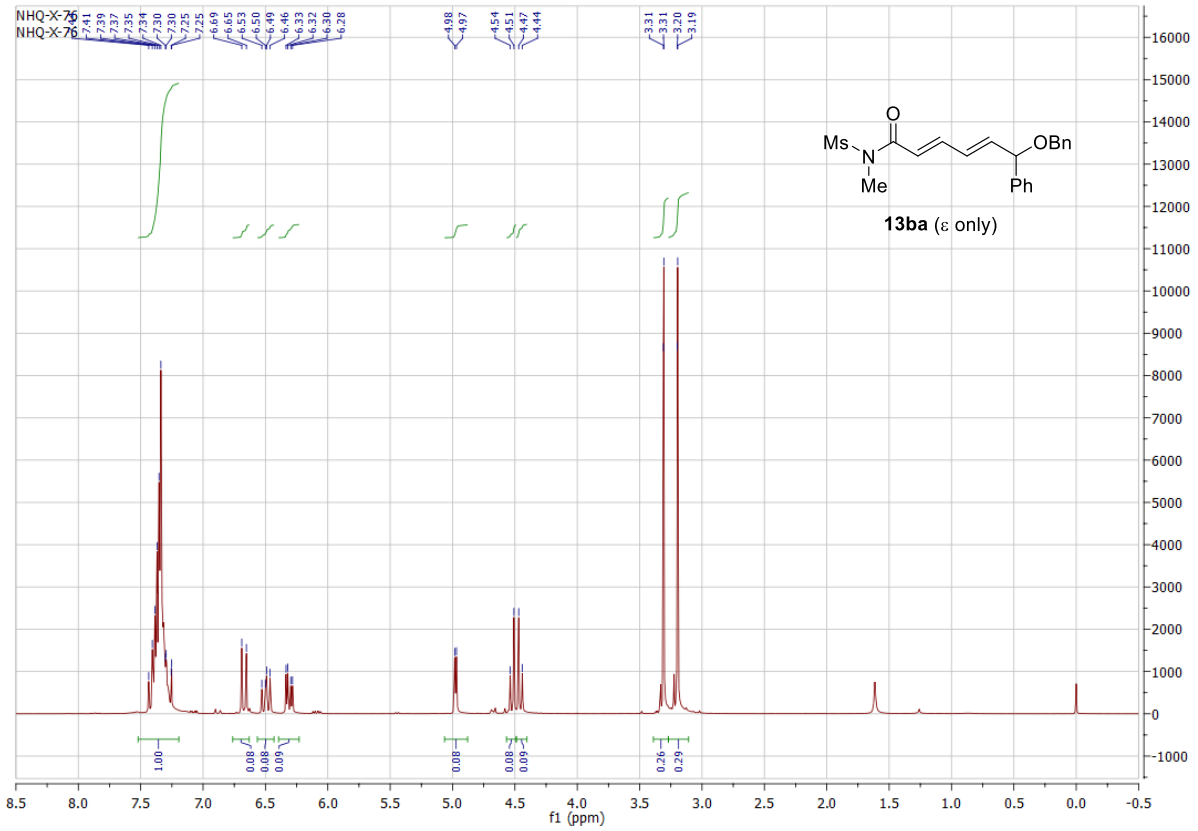

NHQ-VII-25
NHQ-VII-25-13C
166.80
159.20
154.85
133.11
127.99
117.53
113.87
78.49
55.30
50.83
41.79
32.68
22.74
f1 (ppm)

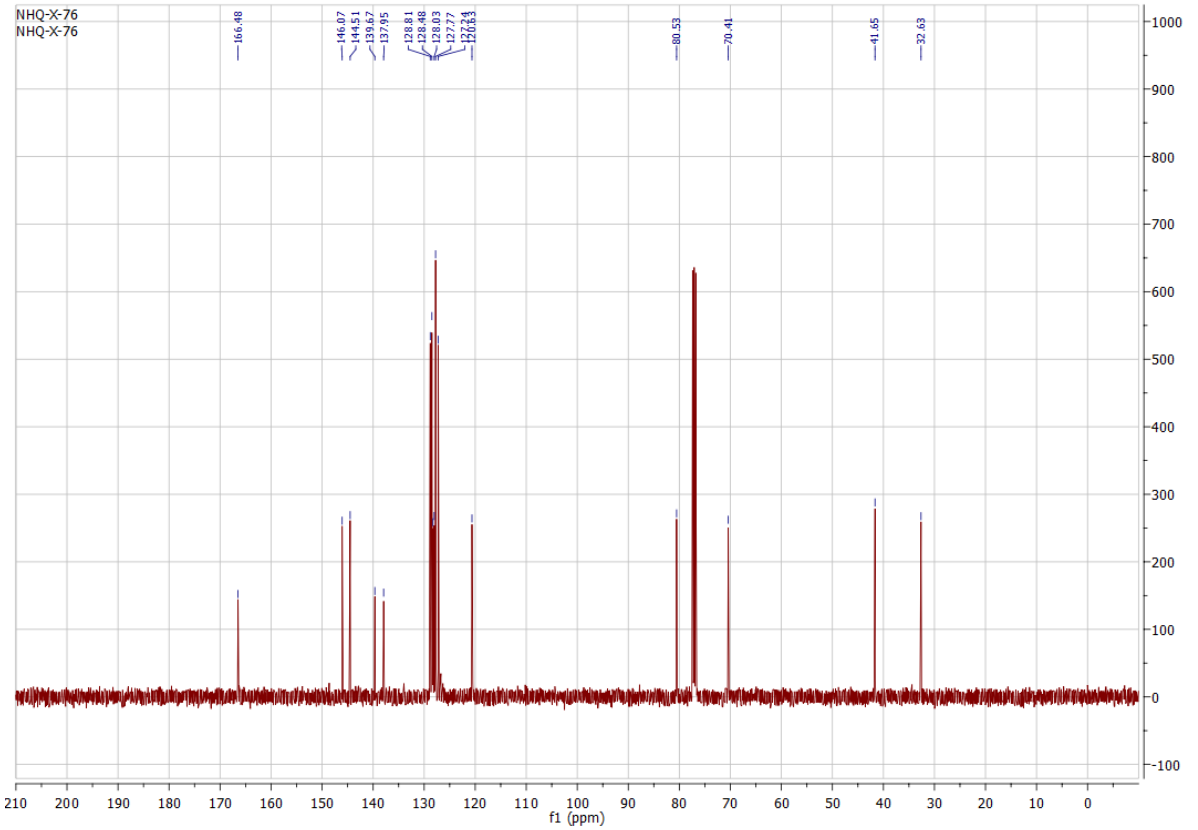

NHQ-X-43
NHQ-X-43
Ts
N
Me
O
O
Ph
Ph
Me
12oh (γ only)
f1 (ppm)

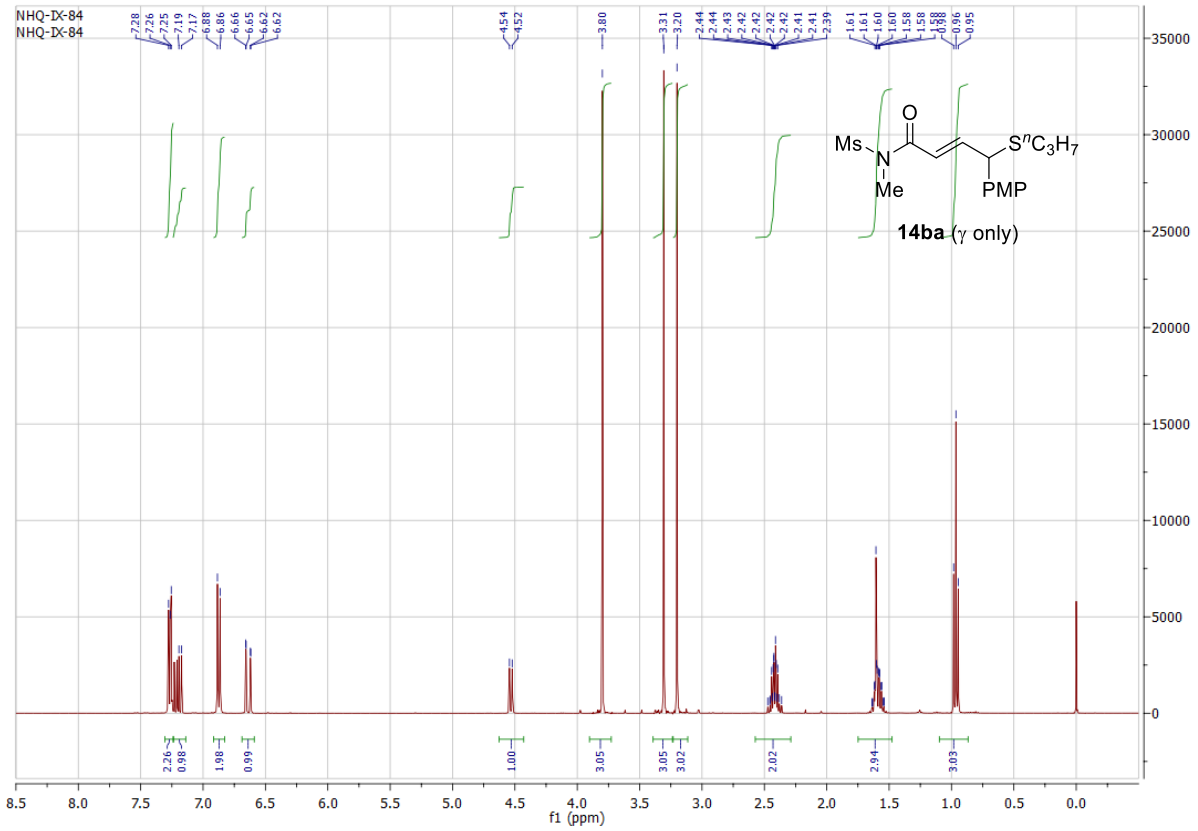

NHQ-X-43
NHQ-X-43
f1 (ppm)

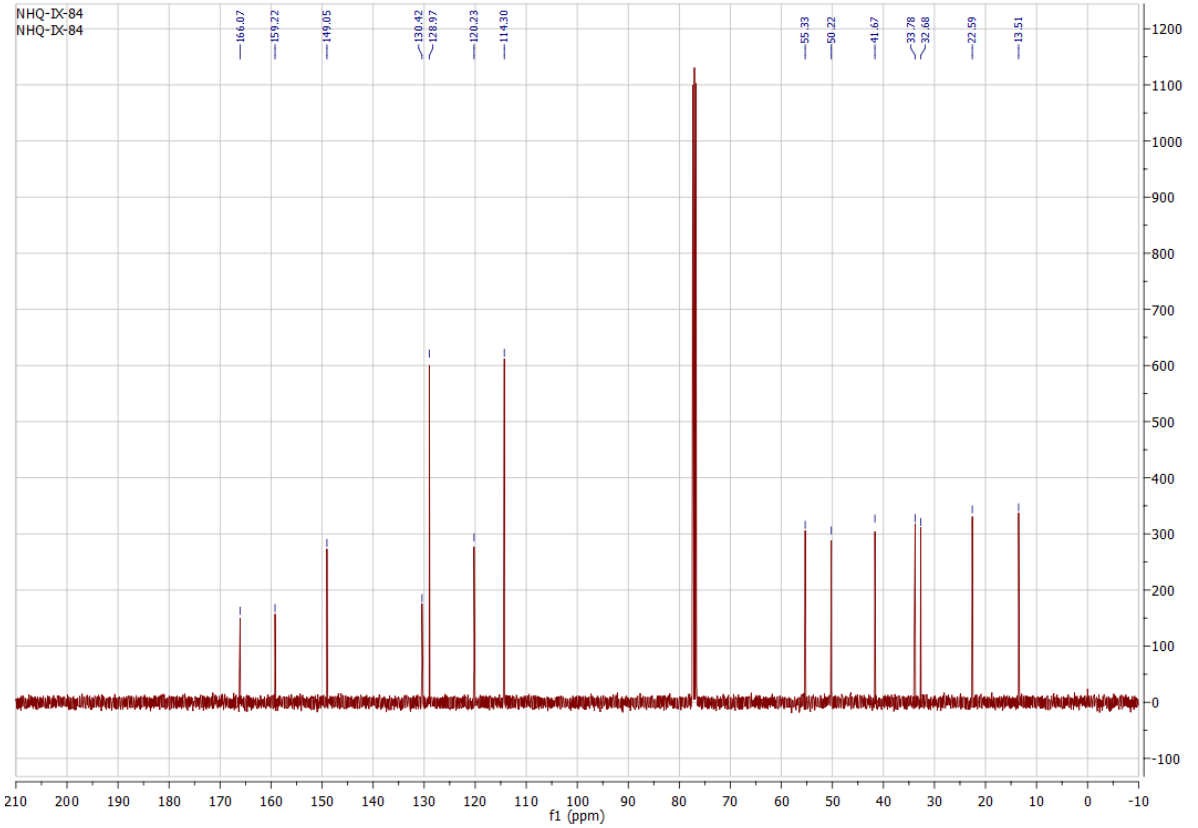

NHQ-VI-89-SOLVENTFREE
NHQ-VI-89-SOLVENTFREE
Ts
N
Me
O
OMe
PMP
13ab (ε only)
f1 (ppm)

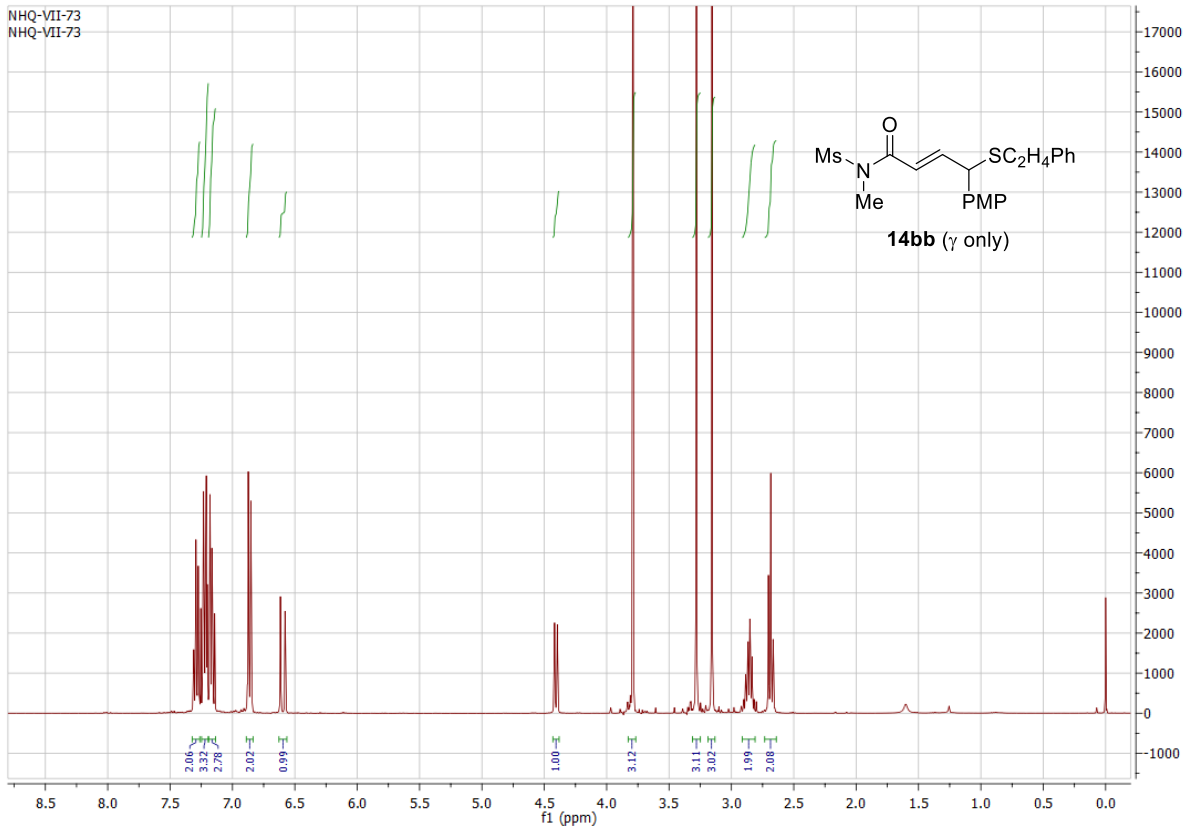

NHQ-VI-89-SOLVENTFREE
NHQ-VI-89-SOLVENTFREE
166.35
159.53
145.07
144.84
143.76
136.16
131.72
129.94
128.38
128.19
127.25
121.84
114.11
82.81
56.43
55.32
33.03
21.63
f1 (ppm)

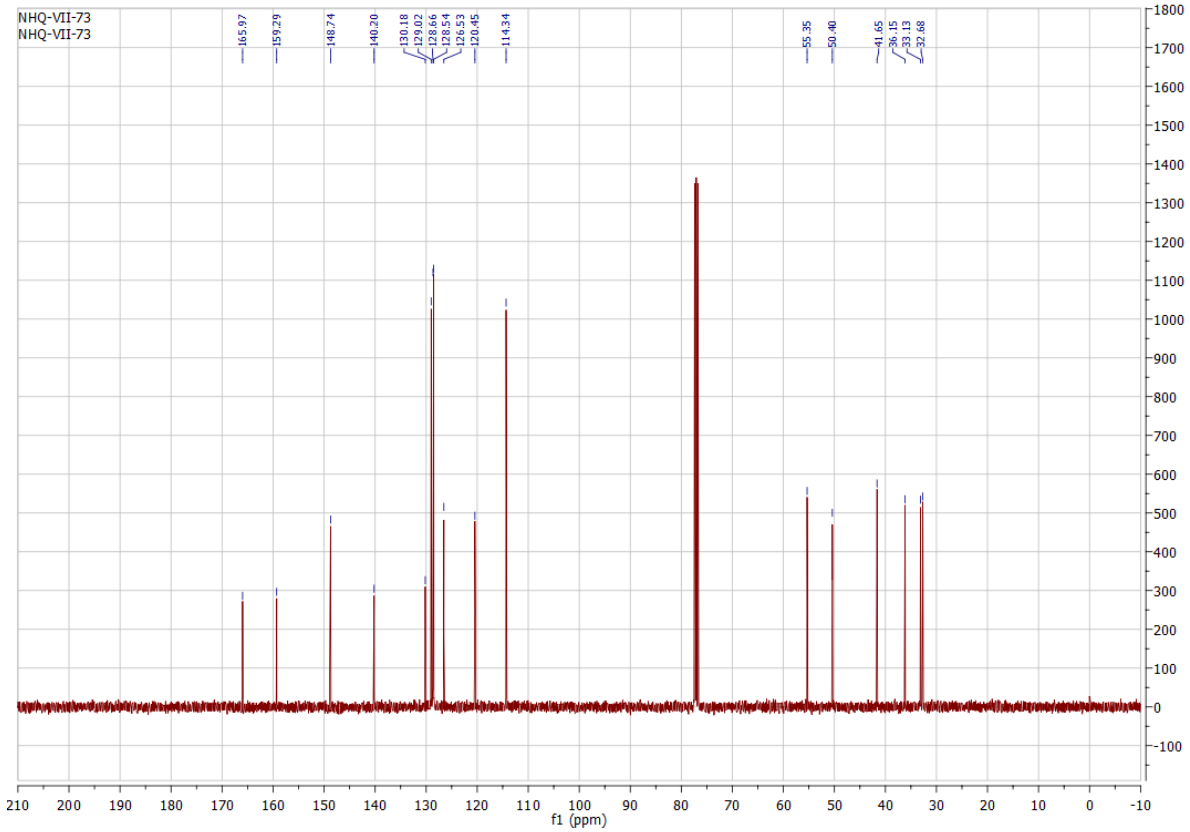

NHQ-X-76
NHQ-X-76
7.41
7.39
7.37
7.35
7.34
7.30
7.30
7.25
7.25
6.69
6.65
6.53
6.50
6.49
6.46
6.33
6.32
6.30
6.28
4.98
4.97
4.54
4.51
4.47
4.44
3.31
3.31
3.20
3.19
Ms
N
Me
O
OBn
Ph
13ba (ε only)
1.00
0.08
0.08
0.09
0.08
0.08
0.09
0.26
0.29
f1 (ppm)

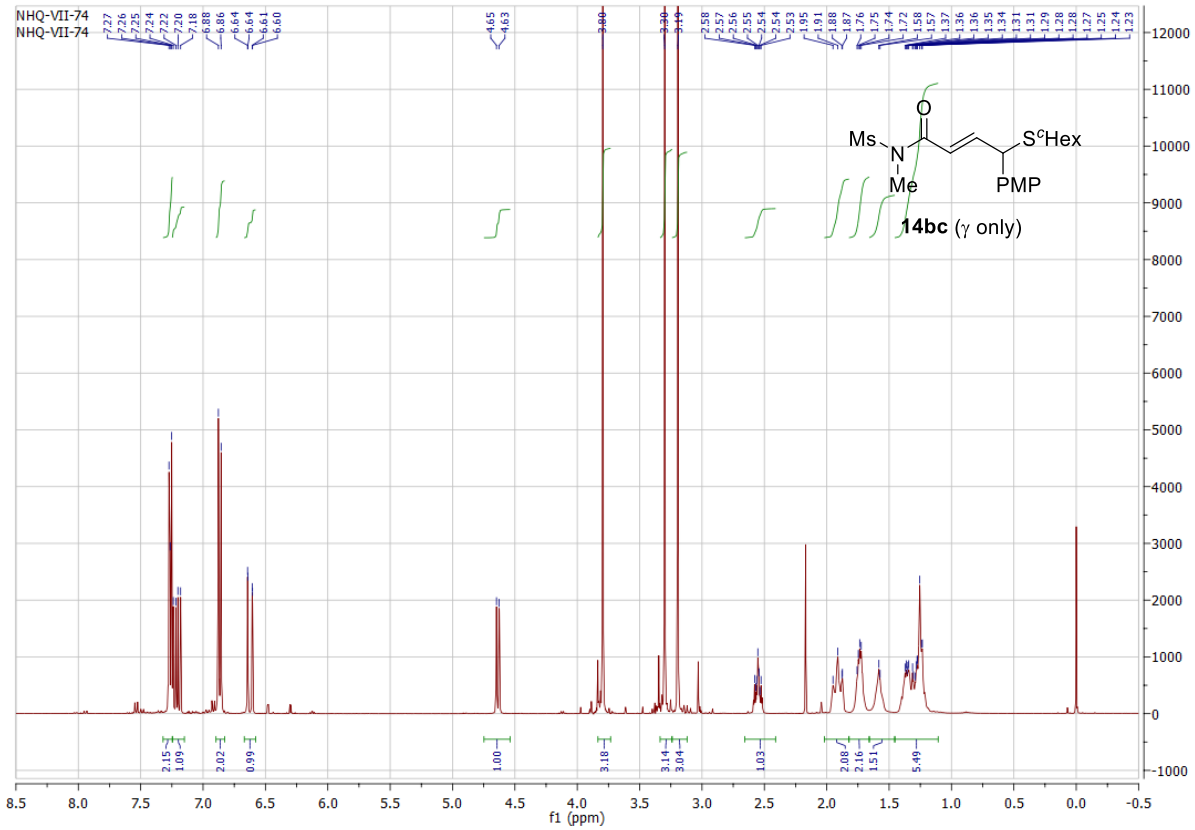

NHQ-X-76
NHQ-X-76
166.48
146.07
144.51
139.67
137.95
128.81
128.48
128.03
127.77
127.34
120.83
80.53
70.41
41.65
32.63
f1 (ppm)

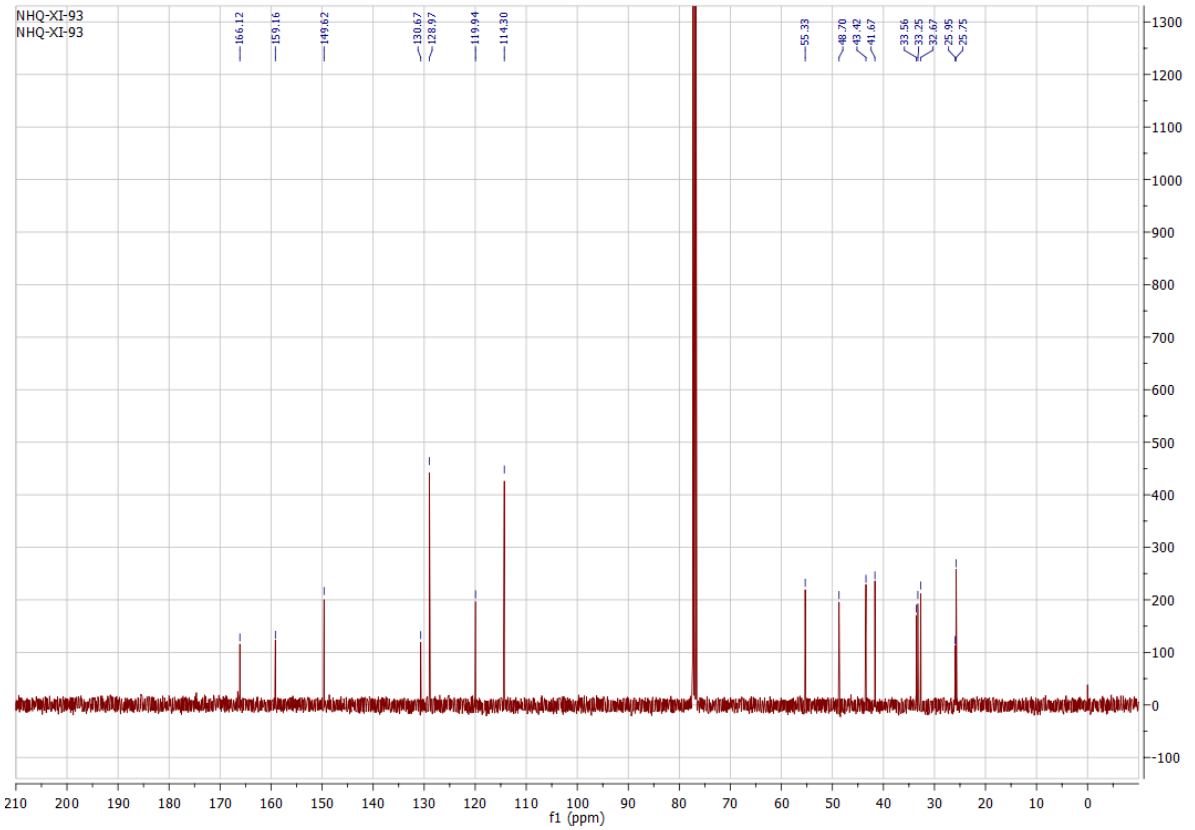

NHQ-IX-84
NHQ-IX-84
Ms
N
Me
O
S^{n}C$_3$H$_7$
PMP
14ba (γ only)
f1 (ppm)

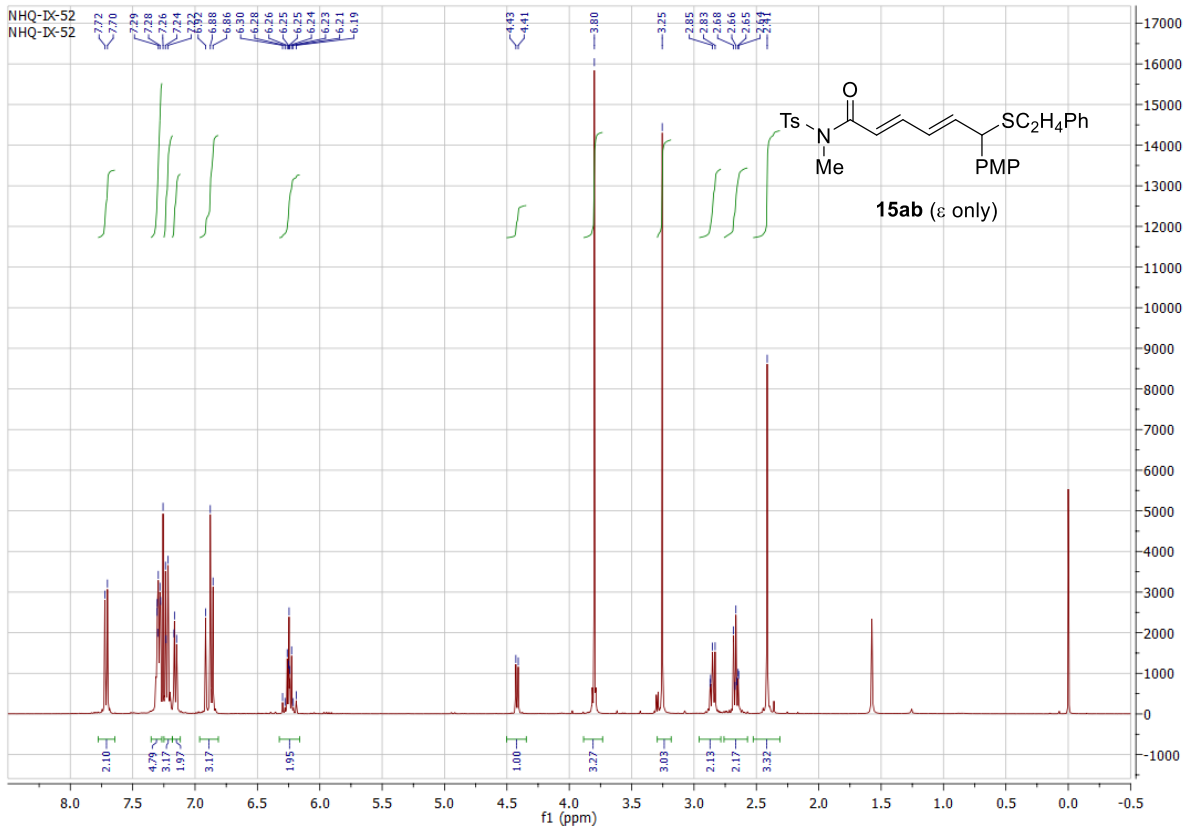

NHQ-IX-84
NHQ-IX-84
f1 (ppm)

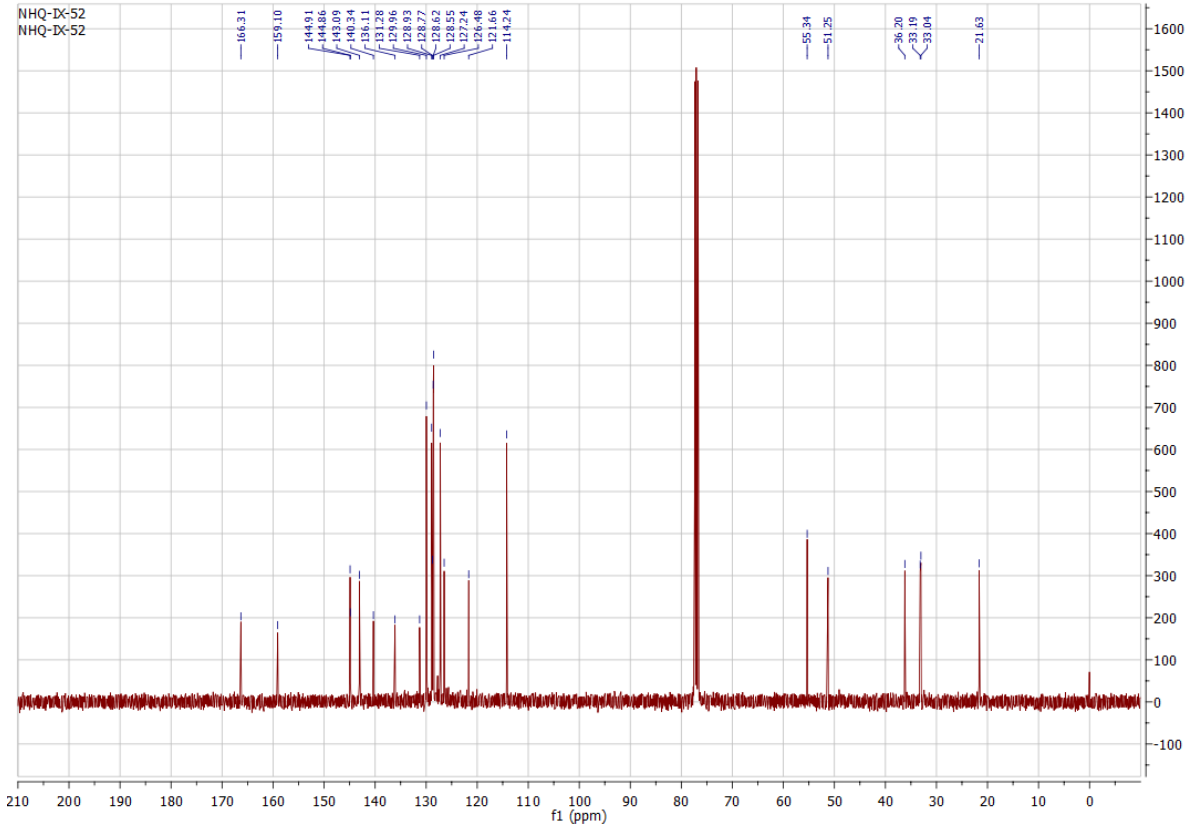

NHQ-VII-73
NHQ-VII-73
Ms
N
Me
O
SC2H4Ph
PMP
14bb (γ only)
2.06
3.32
2.78
2.02
0.99
1.00
3.12
3.11
3.02
1.99
2.08
f1 (ppm)

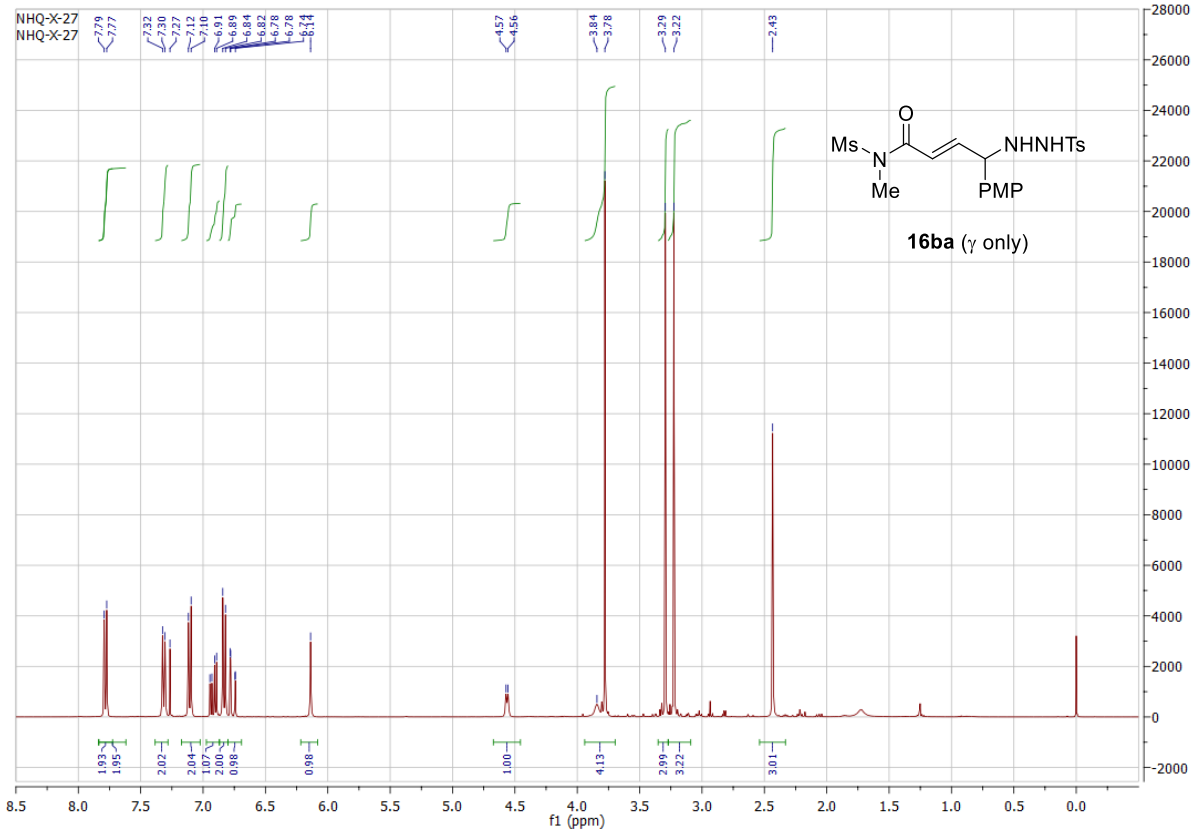

NHQ-VII-73
NHQ-VII-73
165.97
159.29
148.74
140.20
130.18
129.02
128.66
128.54
126.53
120.45
114.34
55.35
50.40
41.65
36.15
33.13
32.68
f1 (ppm)

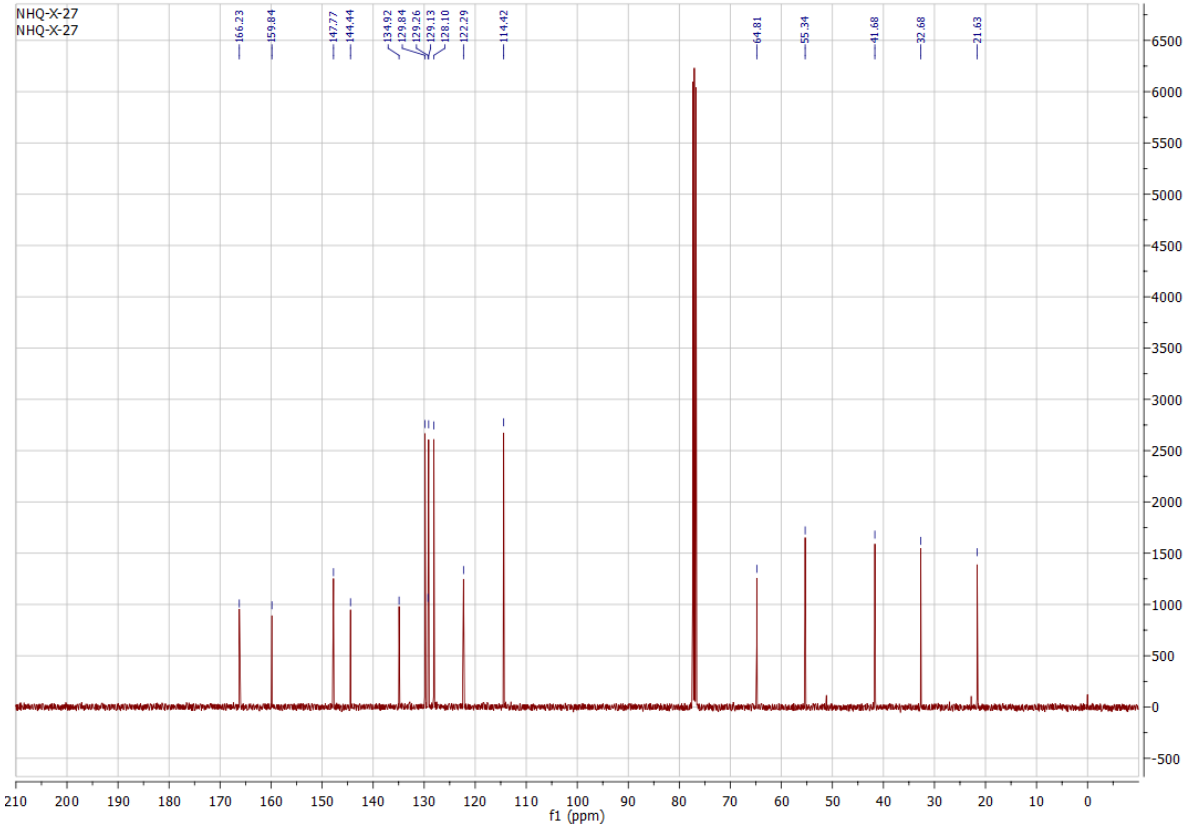

NHQ-VII-74
NHQ-VII-74
Ms
N
Me
O
S^cHex
PMP
14bc (γ only)
f1 (ppm)

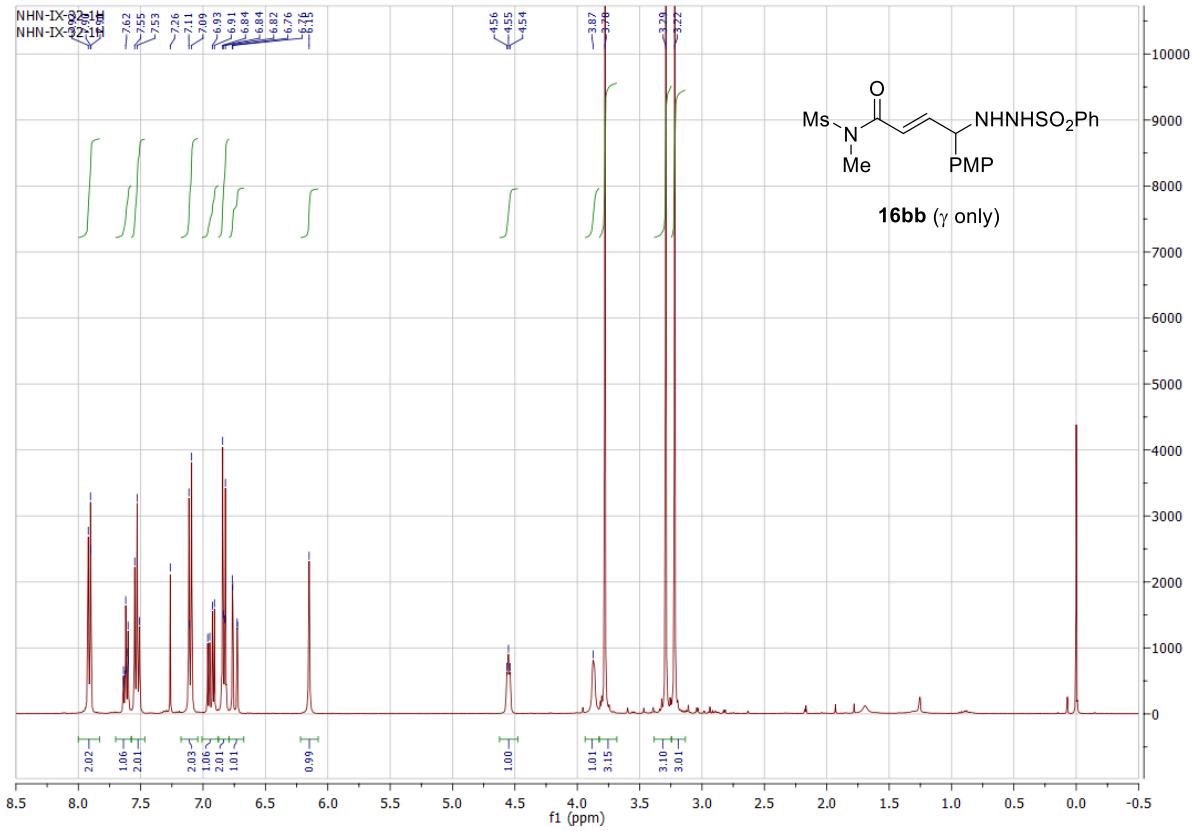

NHQ-XI-93
NHQ-XI-93
166.12
159.16
149.62
130.67
128.97
119.94
114.30
55.33
48.70
43.42
41.67
33.56
33.25
32.67
25.95
25.75
f1 (ppm)

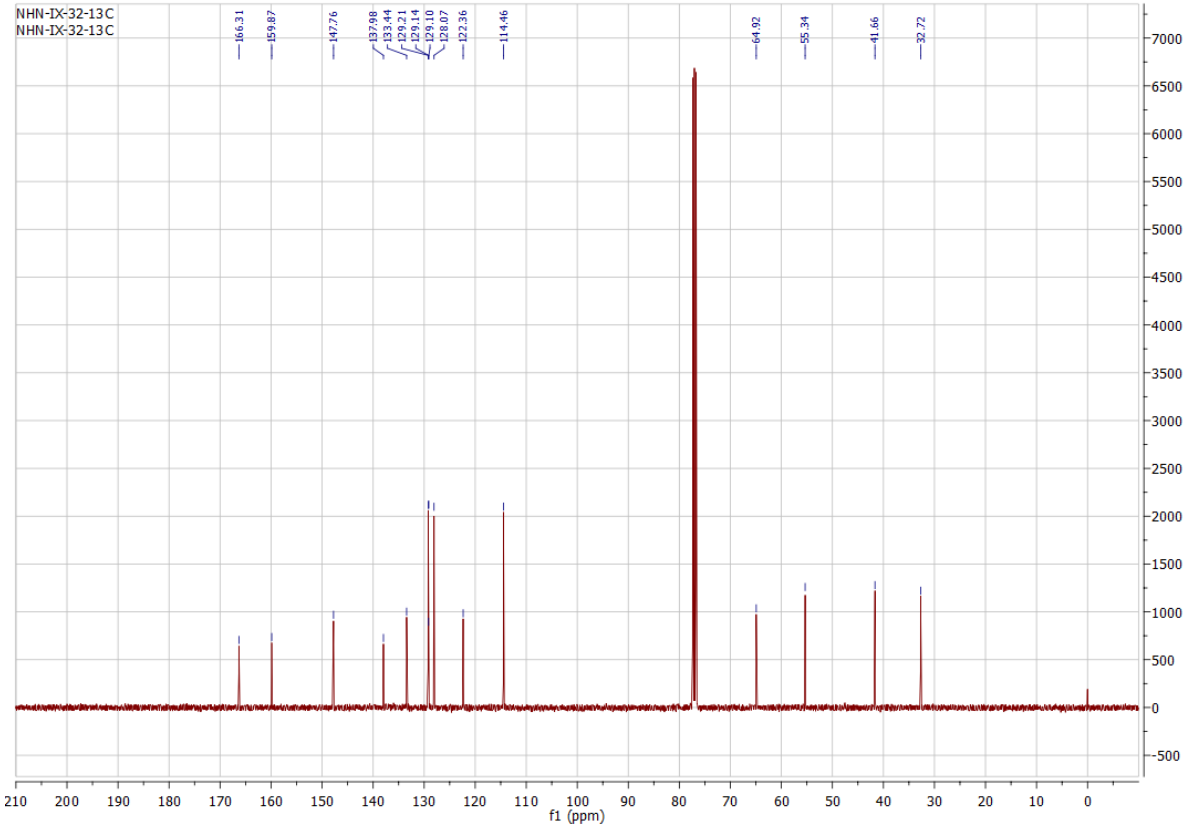

NHQ-IX-52
NHQ-IX-52
Ts
N
Me
O
SC2H4Ph
PMP
15ab (ε only)
f1 (ppm)

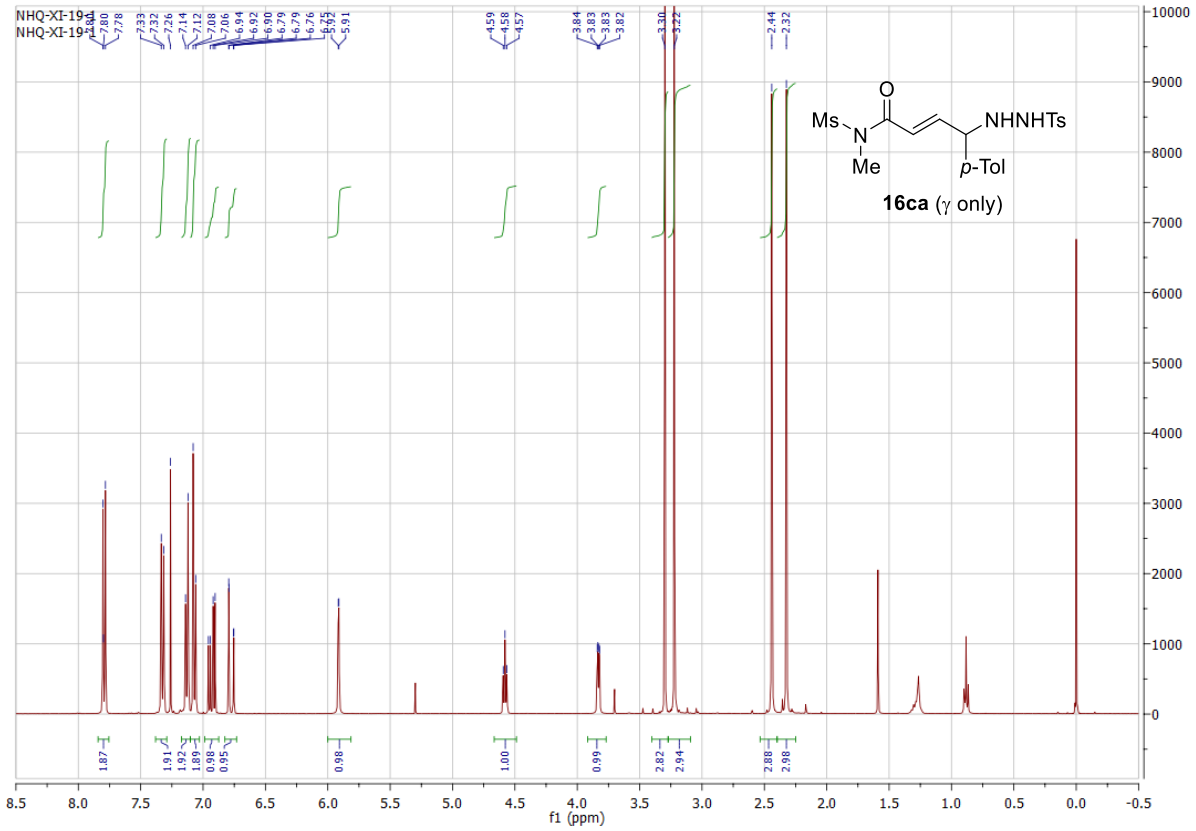

NHQ-IX-52
NHQ-IX-52
f1 (ppm)

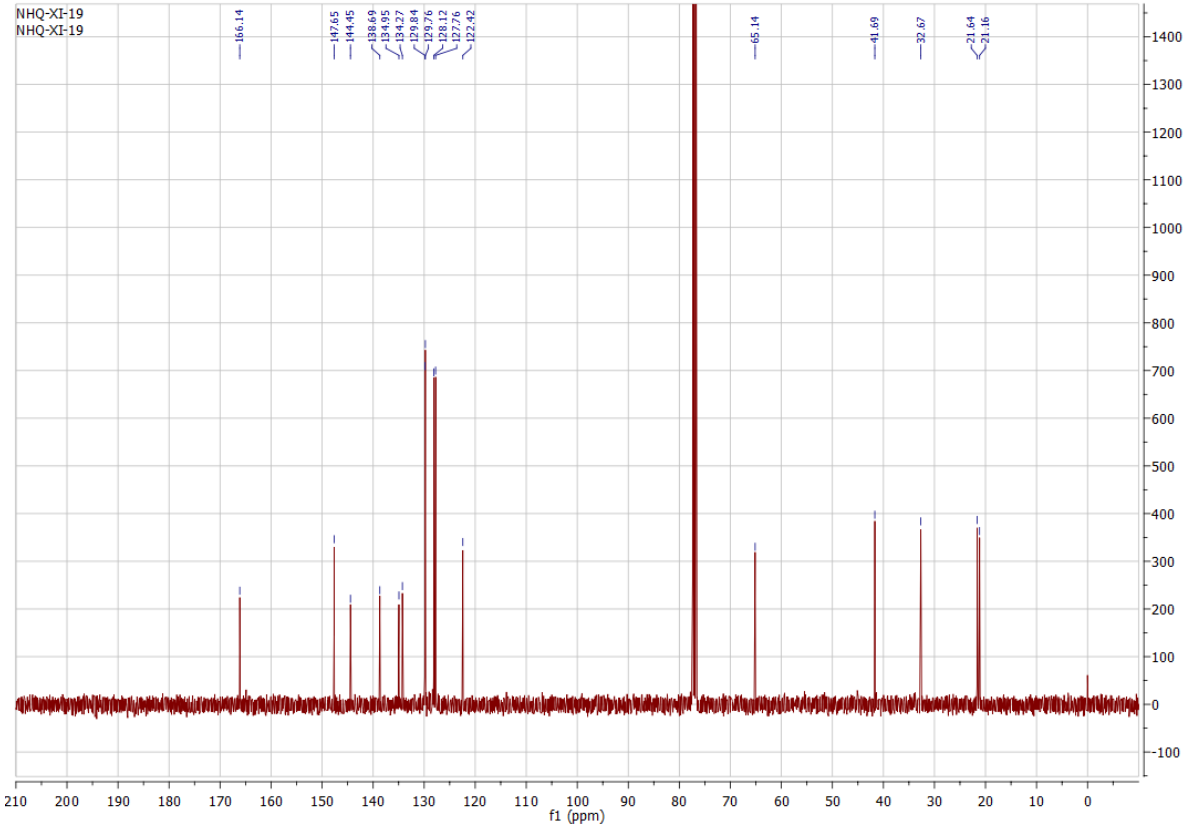

NHQ-X-27
NHQ-X-27
Ms
N
Me
O
NHNHTs
PMP
16ba (γ only)
f1 (ppm)

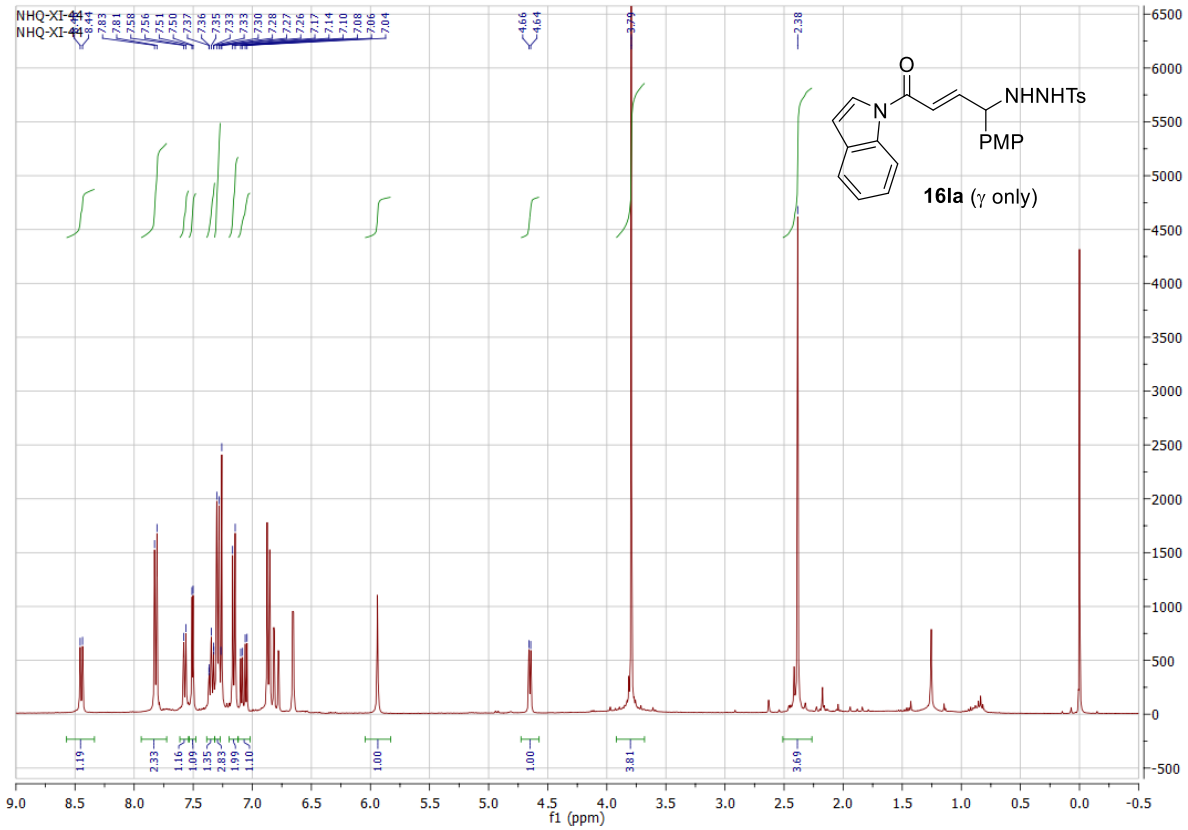

NHQ-X-27
NHQ-X-27
f1 (ppm)

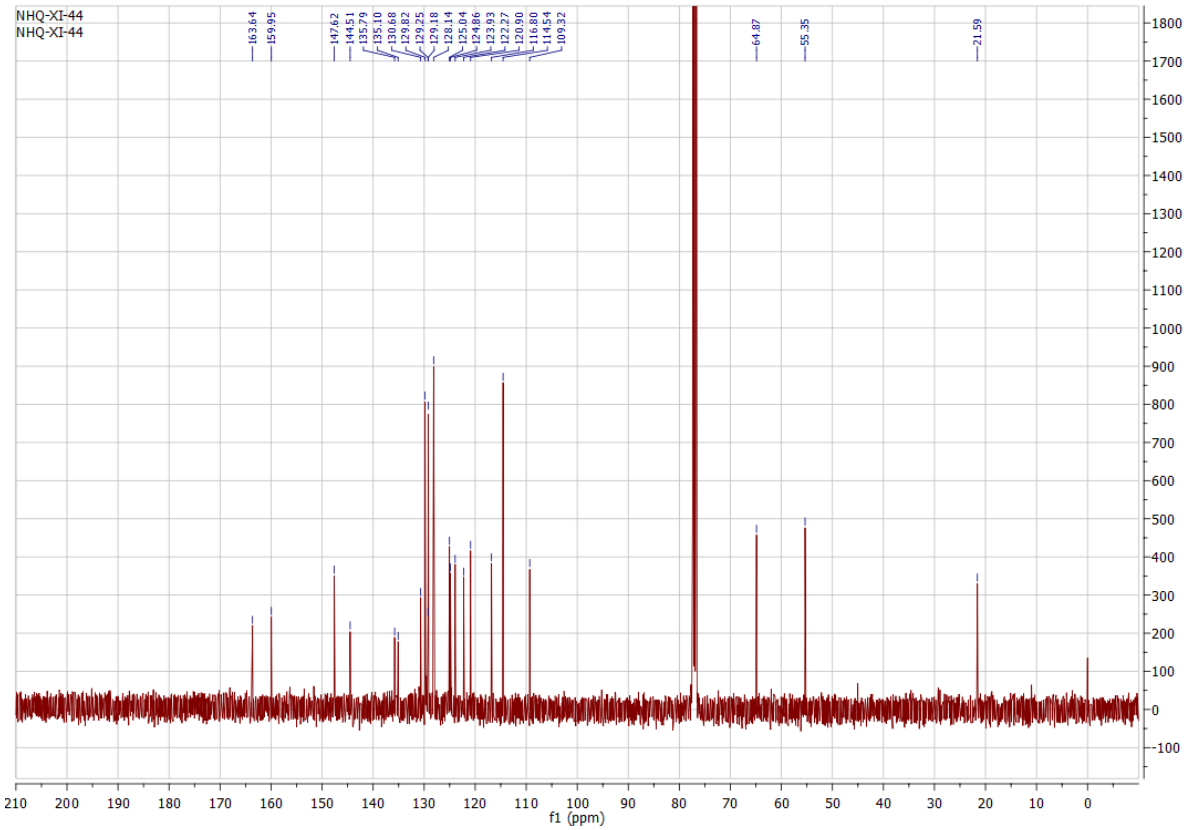

NHN-IX-32-1H
7.62
7.55
7.53
7.26
7.11
7.09
6.93
6.91
6.84
6.84
6.82
6.76
6.76
6.15
4.56
4.55
4.54
3.87
3.78
3.29
3.22
Ms
N
Me
O
NHNHSO2Ph
PMP
16bb (γ only)
2.02
1.06
2.01
2.03
1.06
2.01
1.01
0.99
1.00
1.01
3.15
3.10
3.01
f1 (ppm)

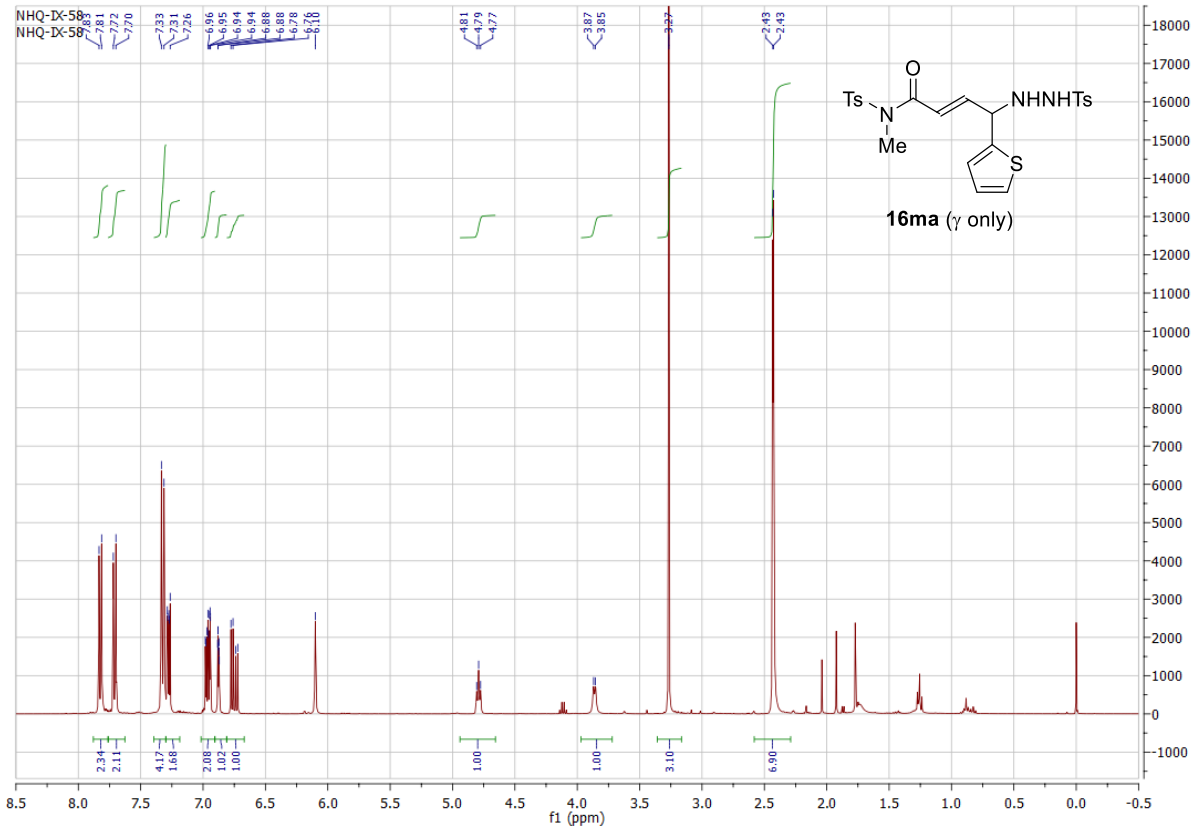

NHN-IX-32-13C
NHN-IX-32-13C
166.31
159.87
147.76
137.98
133.44
129.21
129.14
129.10
128.07
122.36
114.46
64.92
55.34
41.66
32.72
f1 (ppm)

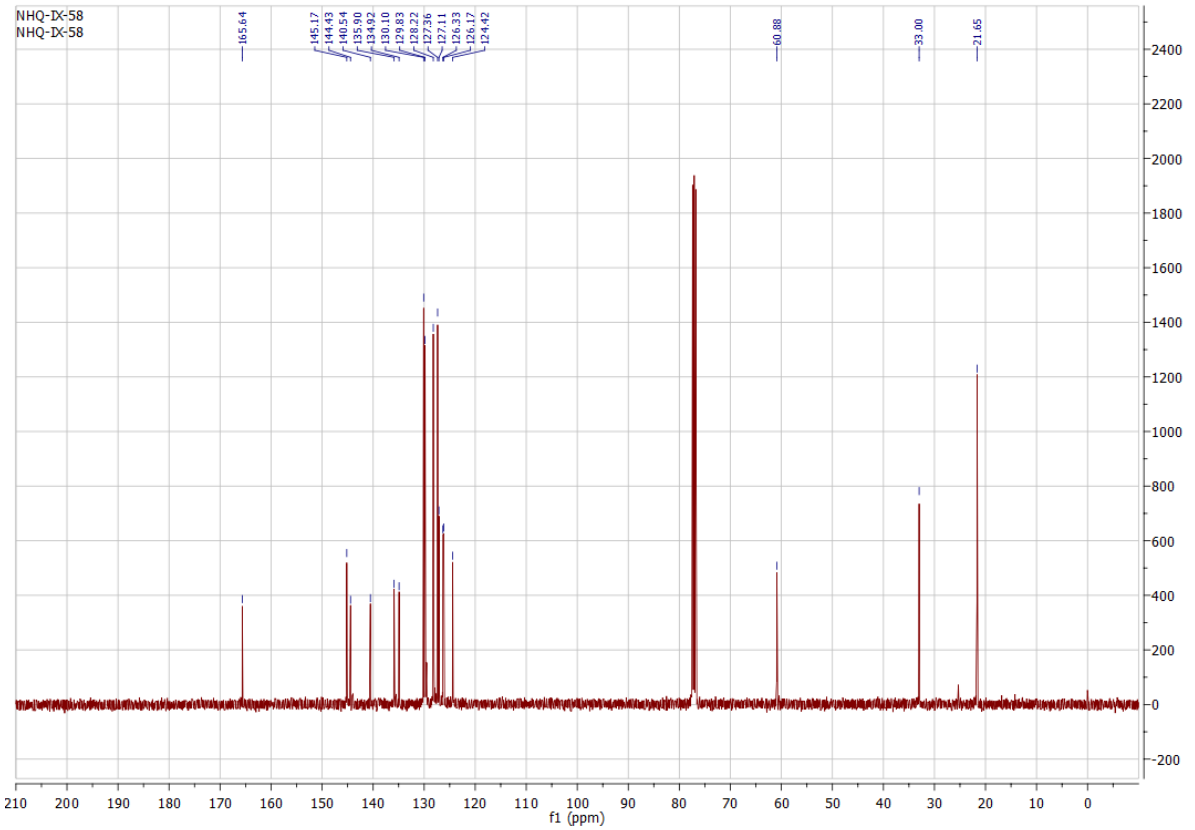

NHQ-XI-19
NHQ-XI-19
Ms
N
Me
O
NHNHTs
p-Tol
16ca (γ only)
f1 (ppm)

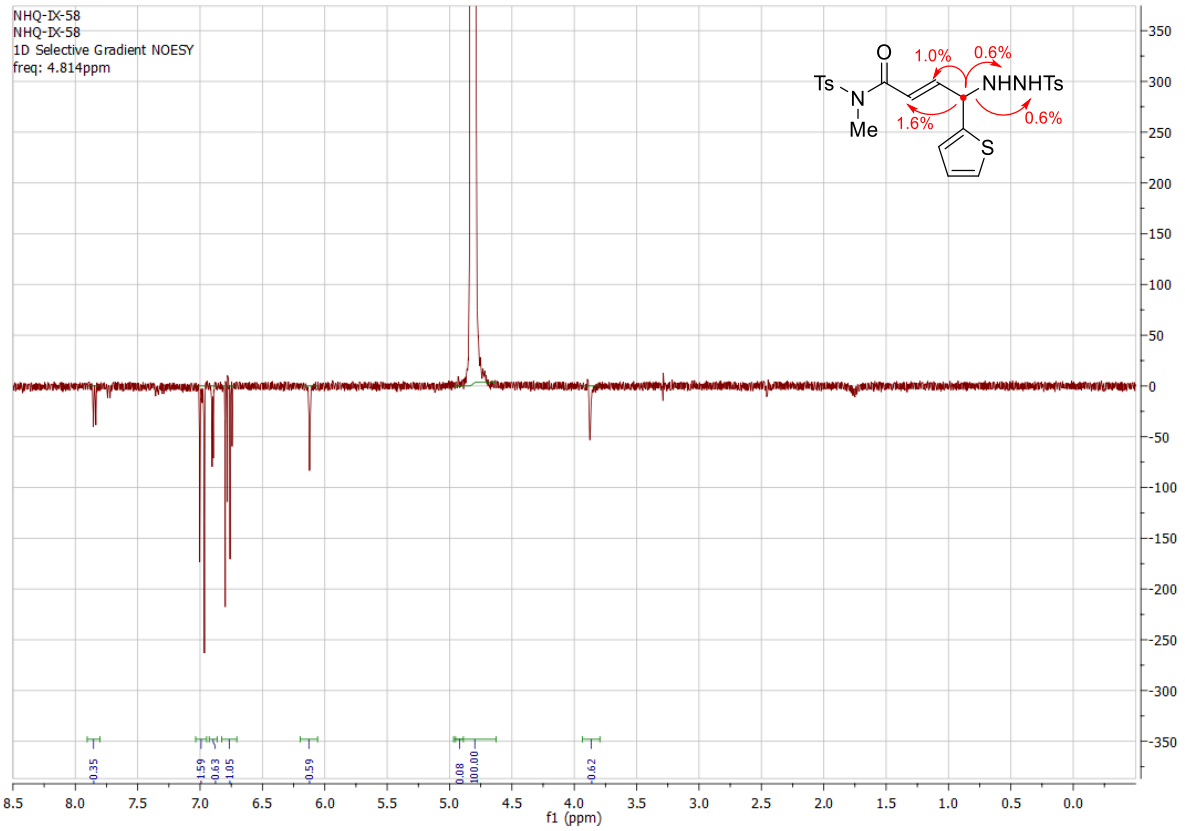

NHQ-XI-19
NHQ-XI-19
f1 (ppm)

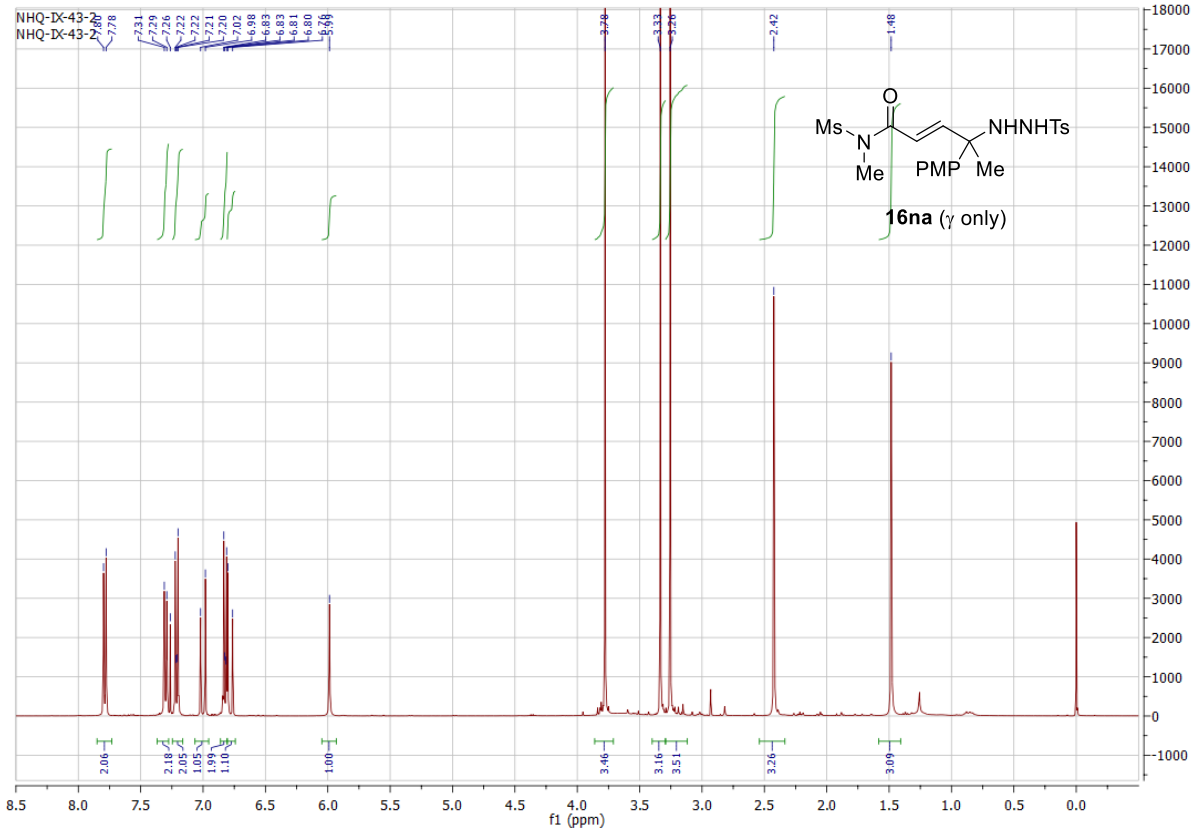

NHQ-XI-44
NHQ-XI-44
O
N
NHNHTs
PMP
16la (γ only)
f1 (ppm)

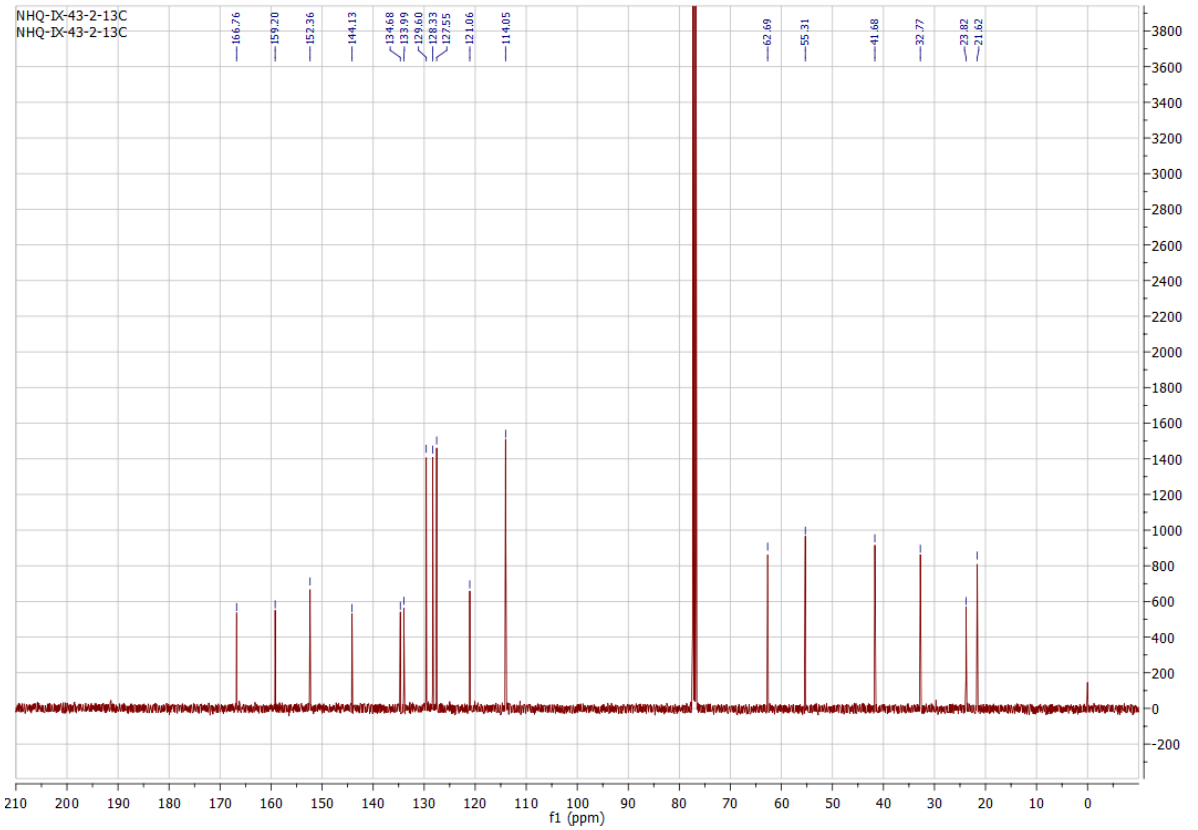

NHQ-XI-44
NHQ-XI-44
f1 (ppm)

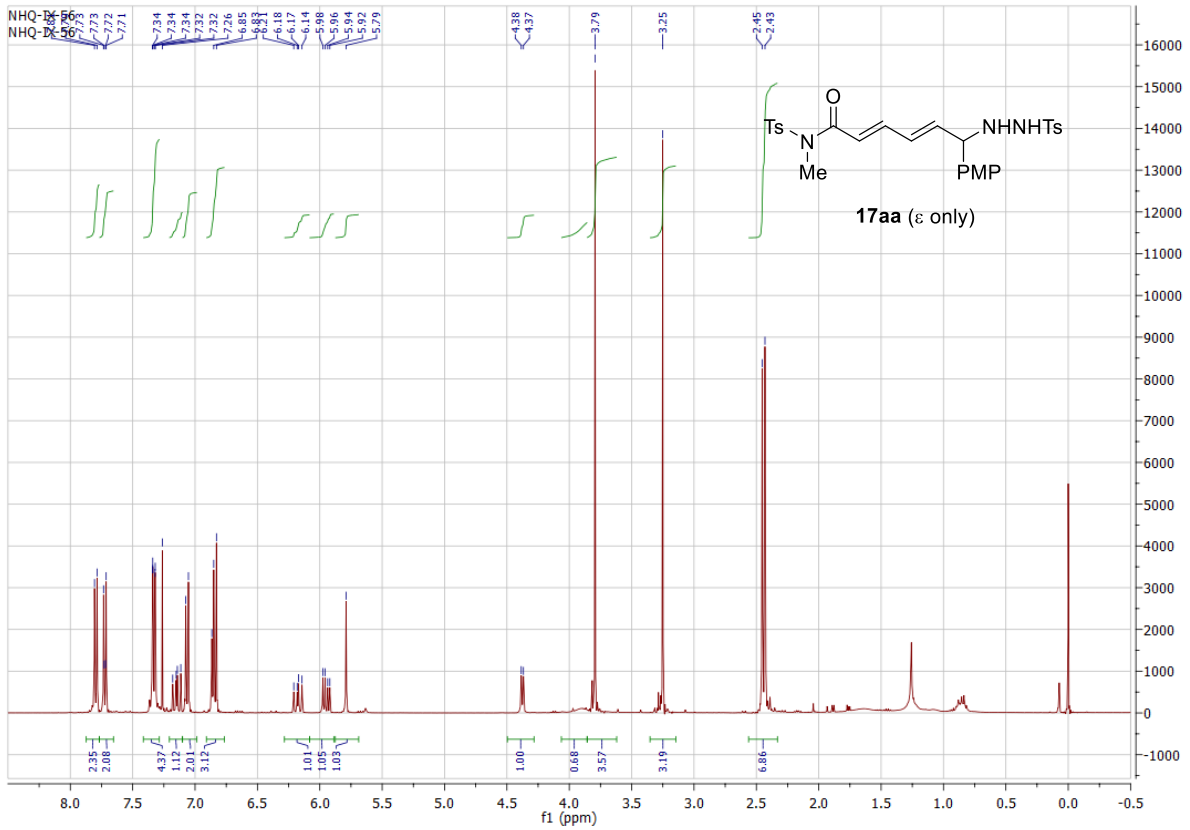

NHQ-IX-58
NHQ-IX-58
Ts
N
Me
O
NHNHTs
S
16ma (γ only)
f1 (ppm)

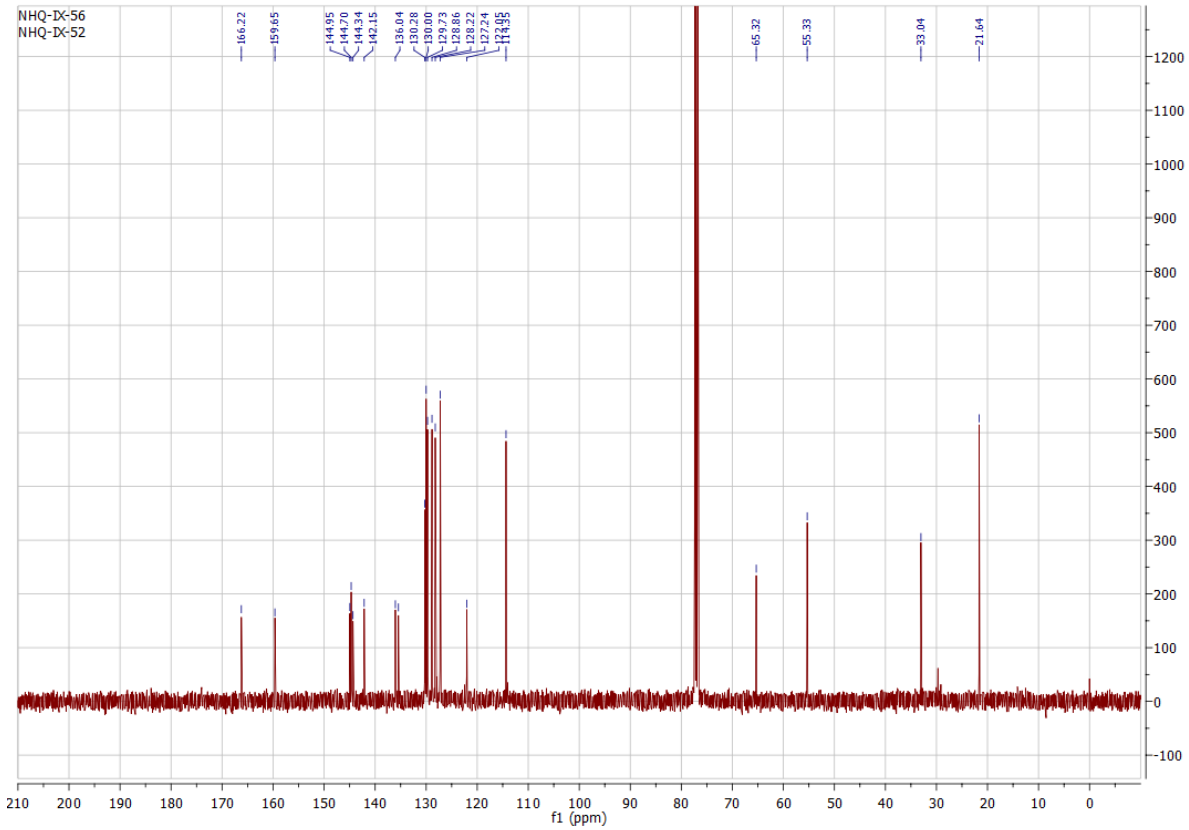

NHQ-IX-58
NHQ-IX-58
165.64
145.17
144.43
140.54
135.90
134.92
130.10
129.83
128.22
127.36
127.11
126.33
126.17
124.42
60.88
33.00
21.65
f1 (ppm)

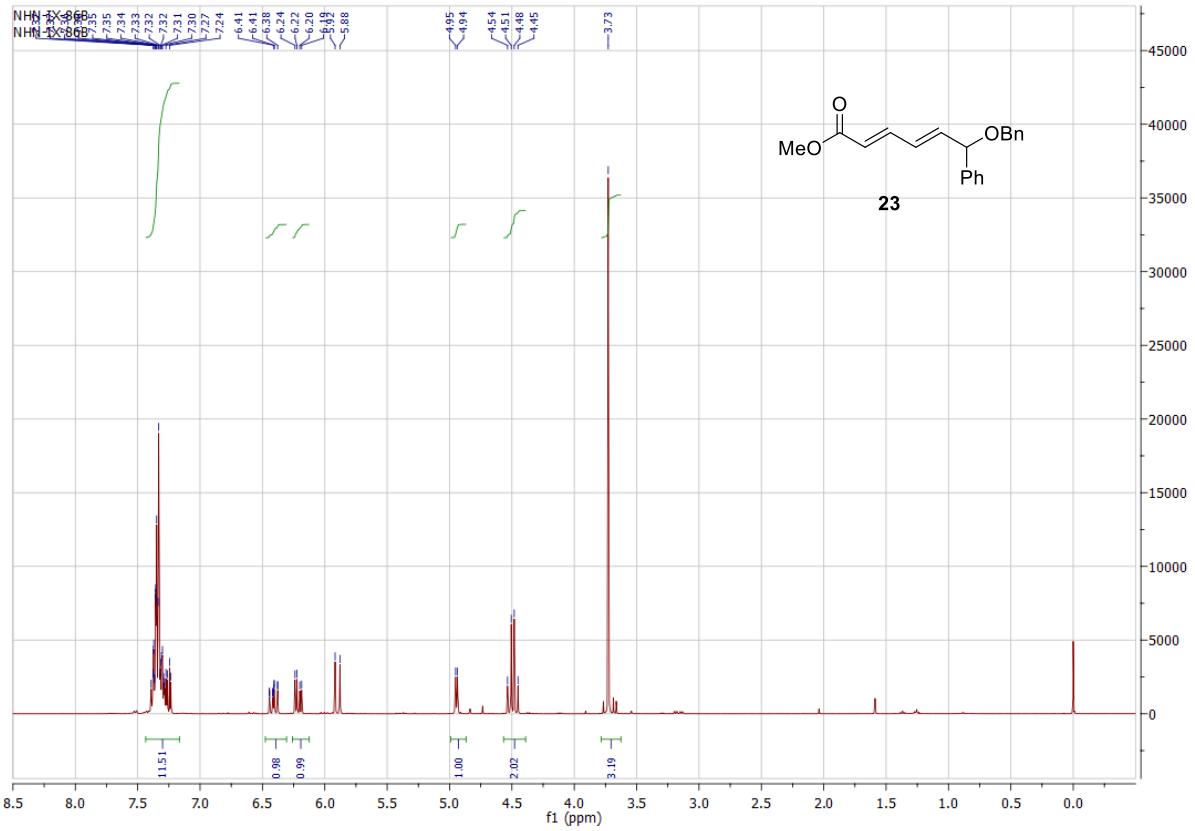

NHQ-IX-58
NHQ-IX-58
1D Selective Gradient NOESY
freq: 4.814ppm
O
Ts
N
Me
1.0%
0.6%
NHNHTs
1.6%
0.6%
S
f1 (ppm)

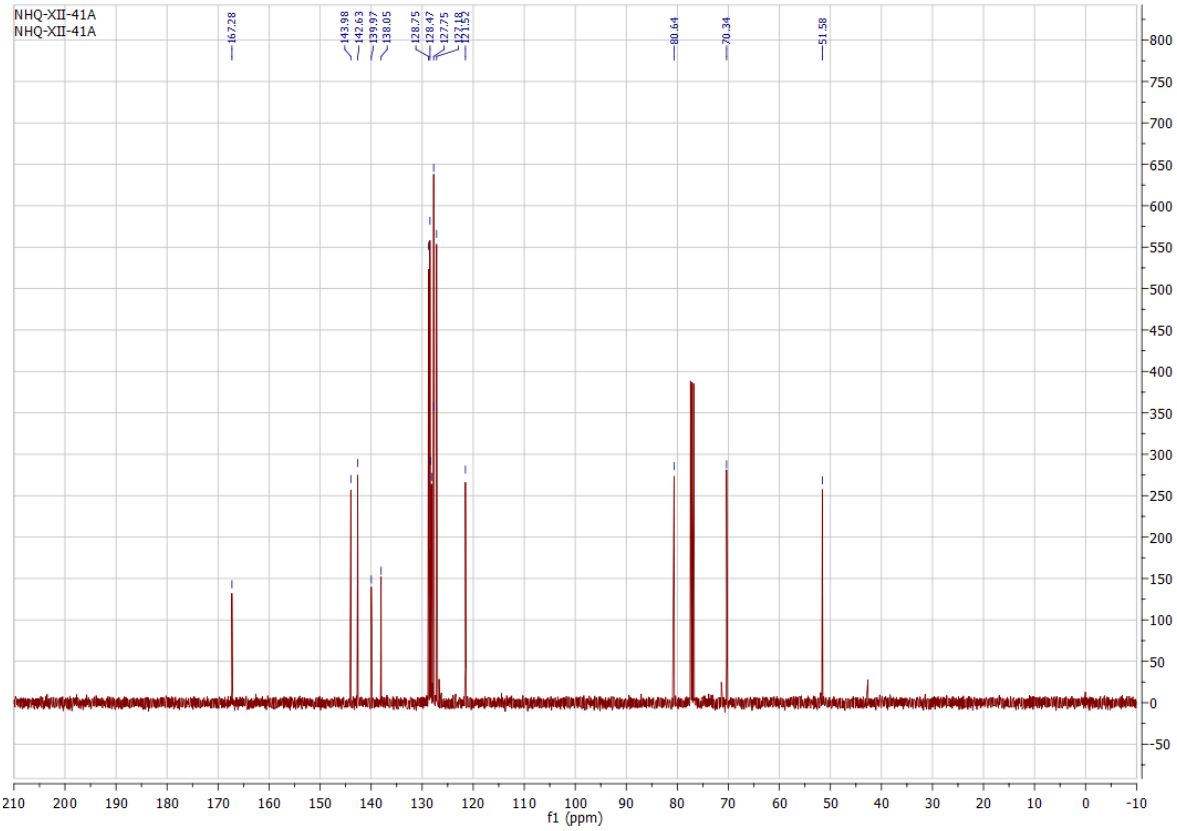

NHQ-IX-43-2
NHQ-IX-43-2
Ms
N
Me
O
NHNHTs
PMP
Me
16na (γ only)
f1 (ppm)

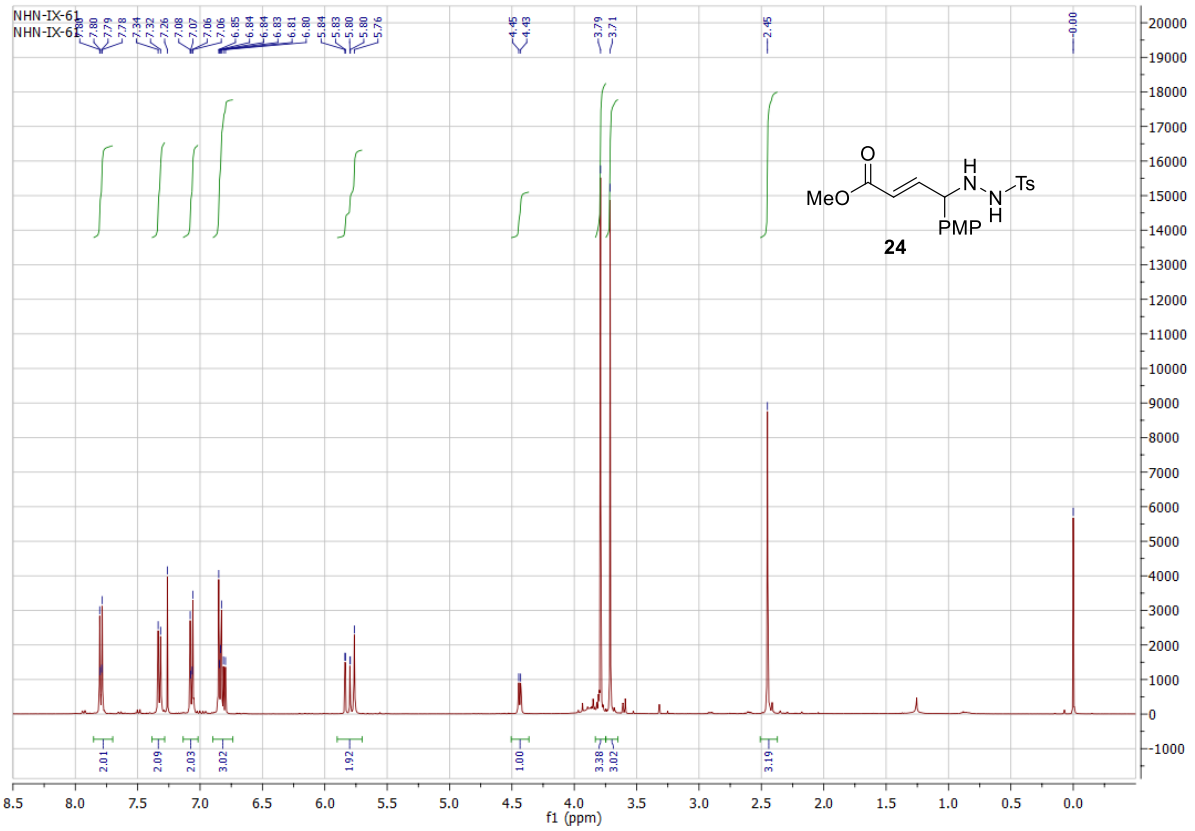

NHQ-IX-43-2-13C
NHQ-IX-43-2-13C
f1 (ppm)

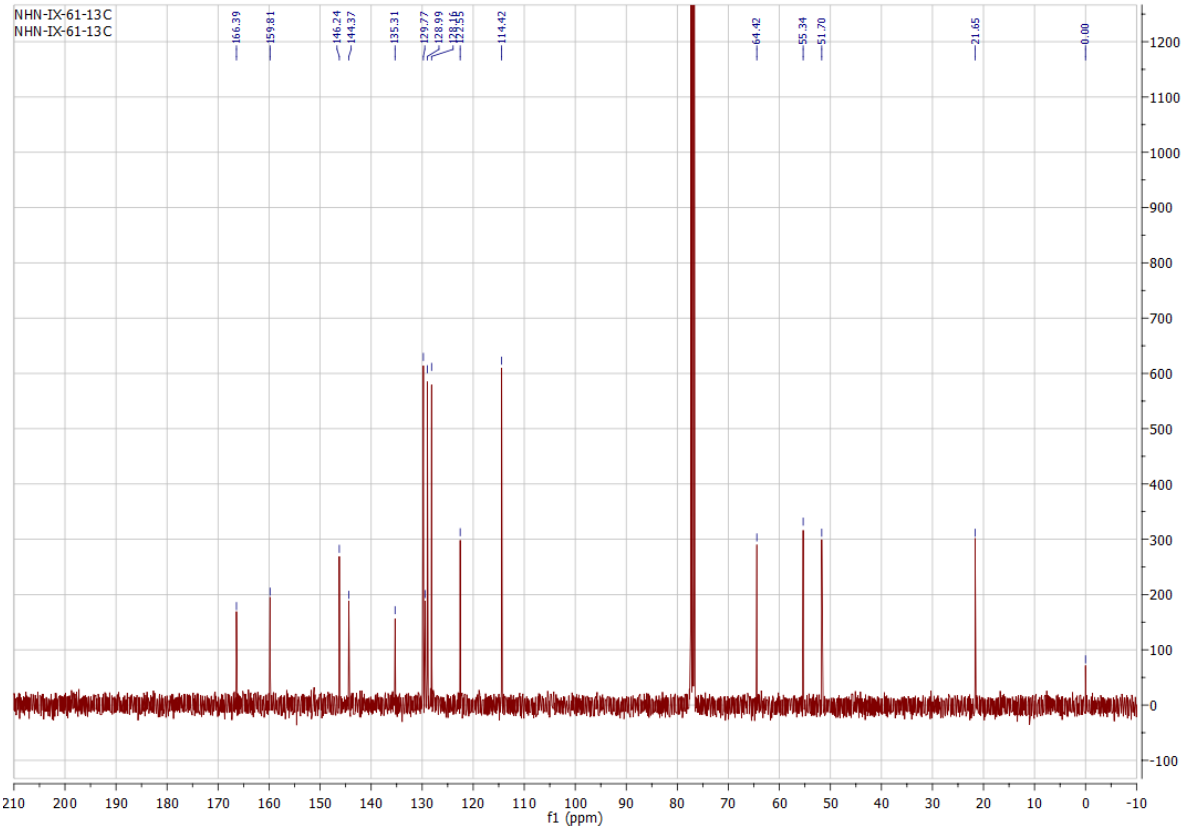

NHQ-IX-56
NHQ-IX-52
Ts
N
Me
O
NHNHTs
PMP
17aa (ε only)
f1 (ppm)

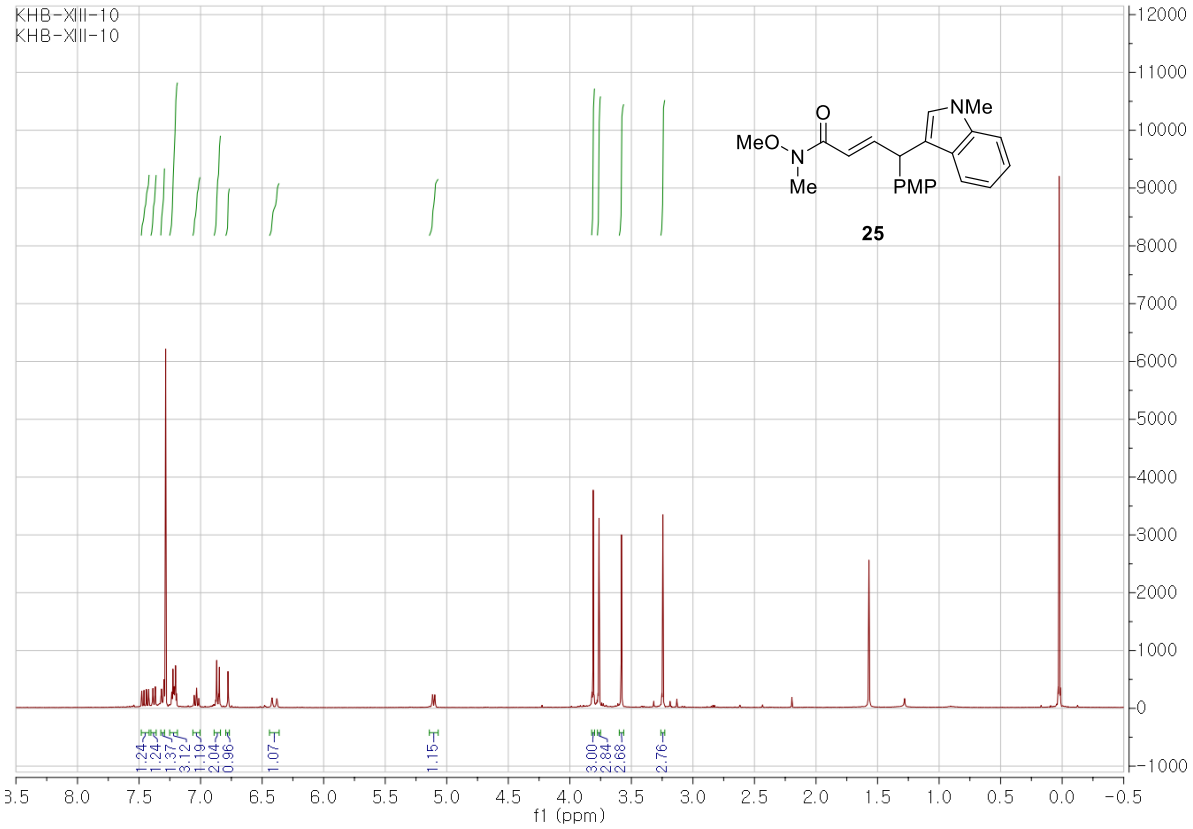

NHQ-IX-56
NHQ-IX-52
f1 (ppm)

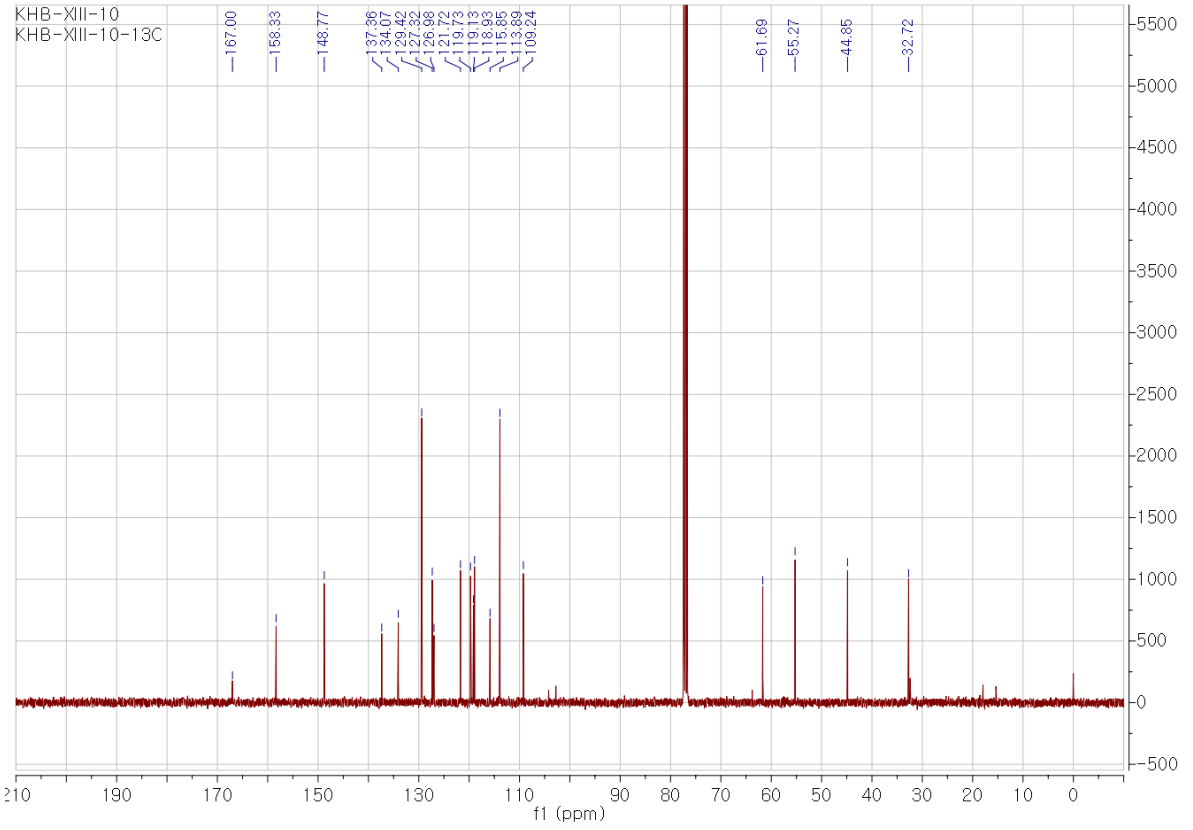

NHN-1X-86B
NHN-1X-86B
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.27
7.24
6.41
6.41
6.38
6.24
6.22
6.20
5.92
5.88
4.95
4.94
4.54
4.51
4.48
4.45
3.73
11.51
0.98
0.99
1.00
2.02
3.19
f1 (ppm)
O
MeO
OBn
Ph
23

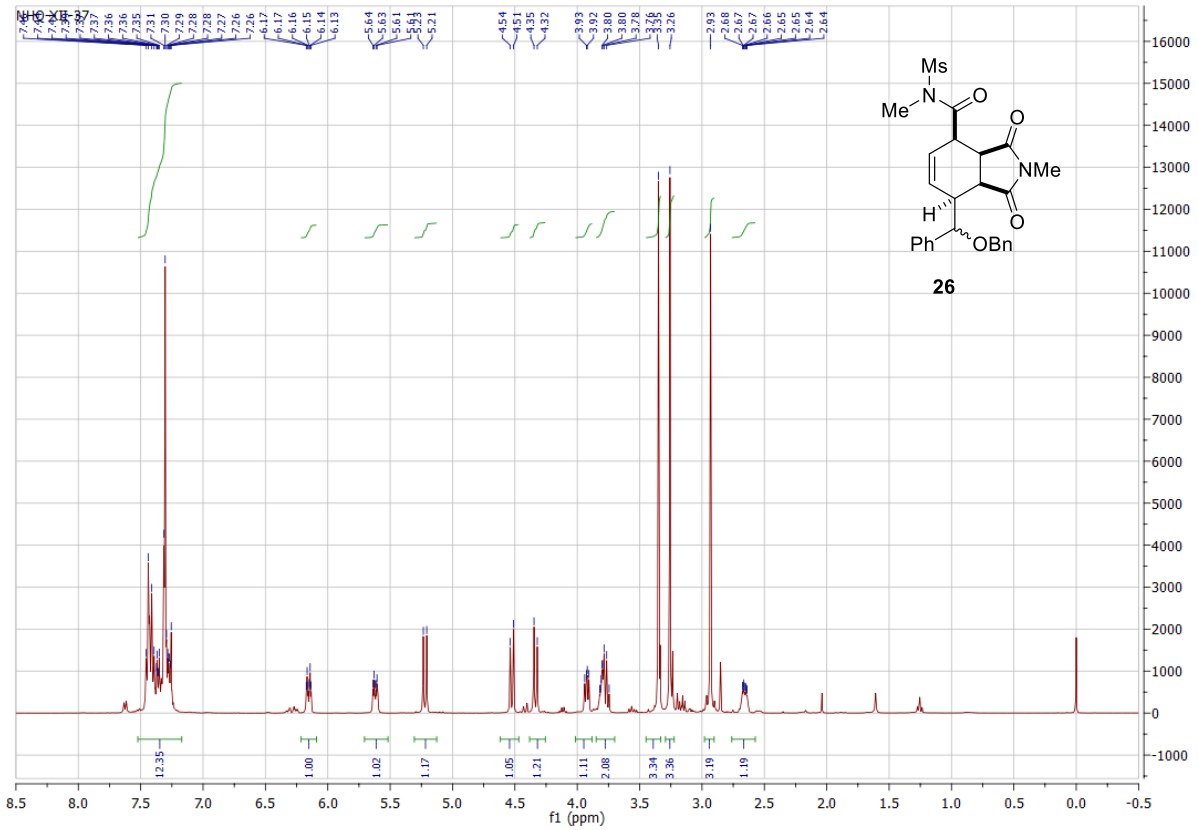

NHQ-XII-41A
NHQ-XII-41A
16.728
143.98
142.63
139.97
138.05
128.75
128.47
127.75
127.18
121.12
80.64
70.34
51.58
f1 (ppm)

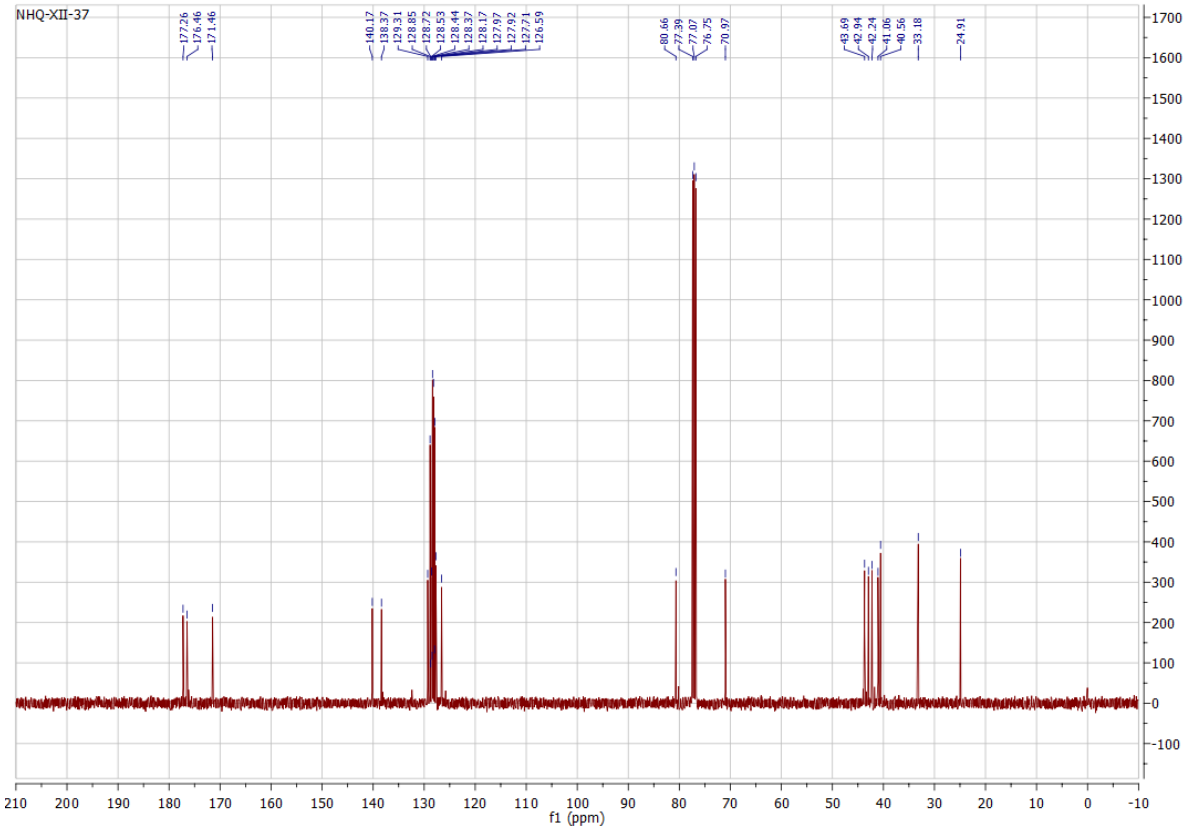

NHN-IX-61
NHN-IX-61
MeO
O
H
N
N
Ts
H
PMP
24
f1 (ppm)

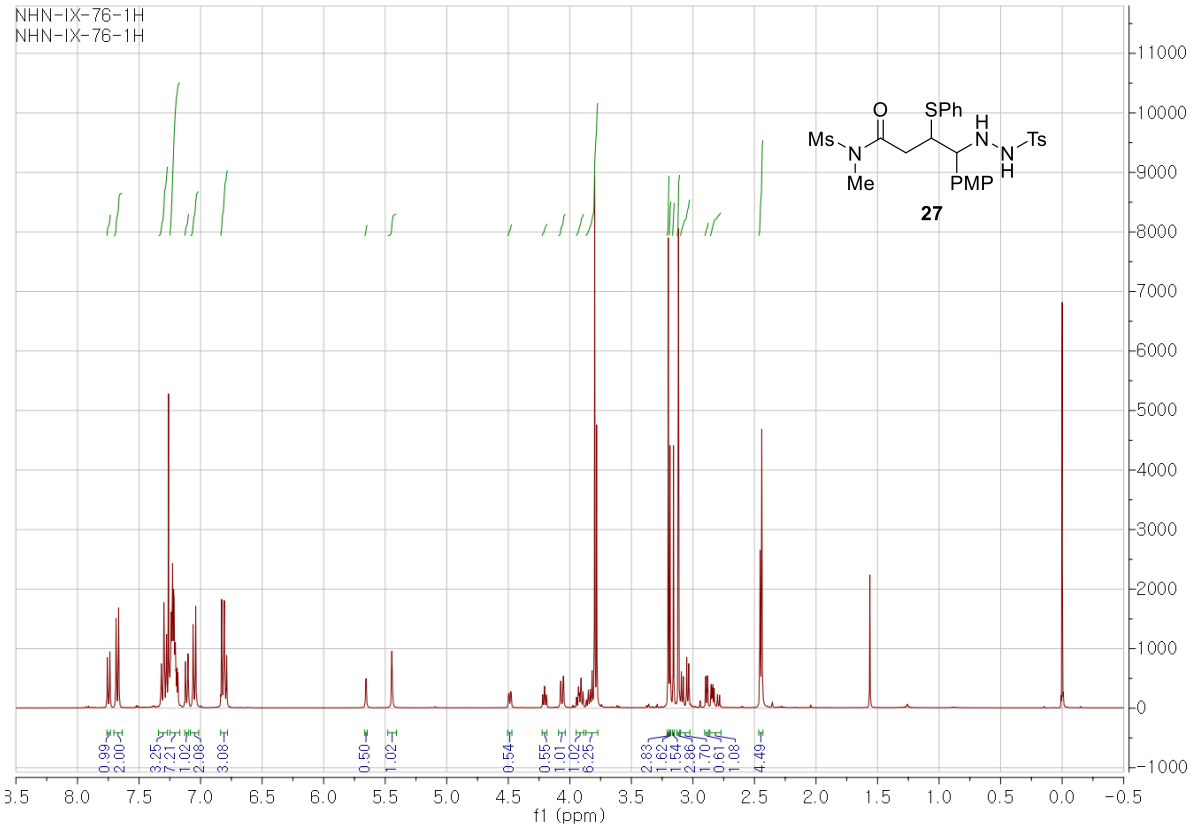

NHN-IX-61-13C
NHN-IX-61-13C
f1 (ppm)

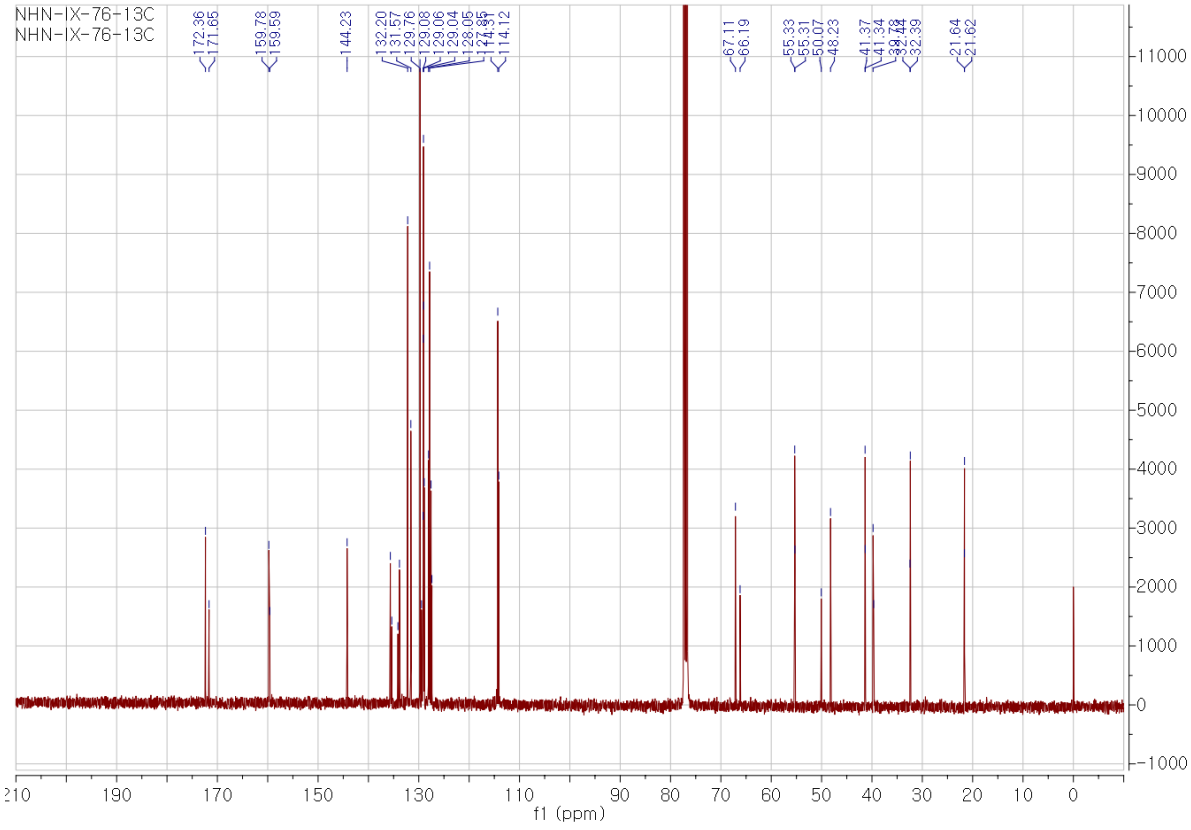

KHB-XIII-10
KHB-XIII-10
MeO
N
Me
O
NMe
PMP
25
f1 (ppm)

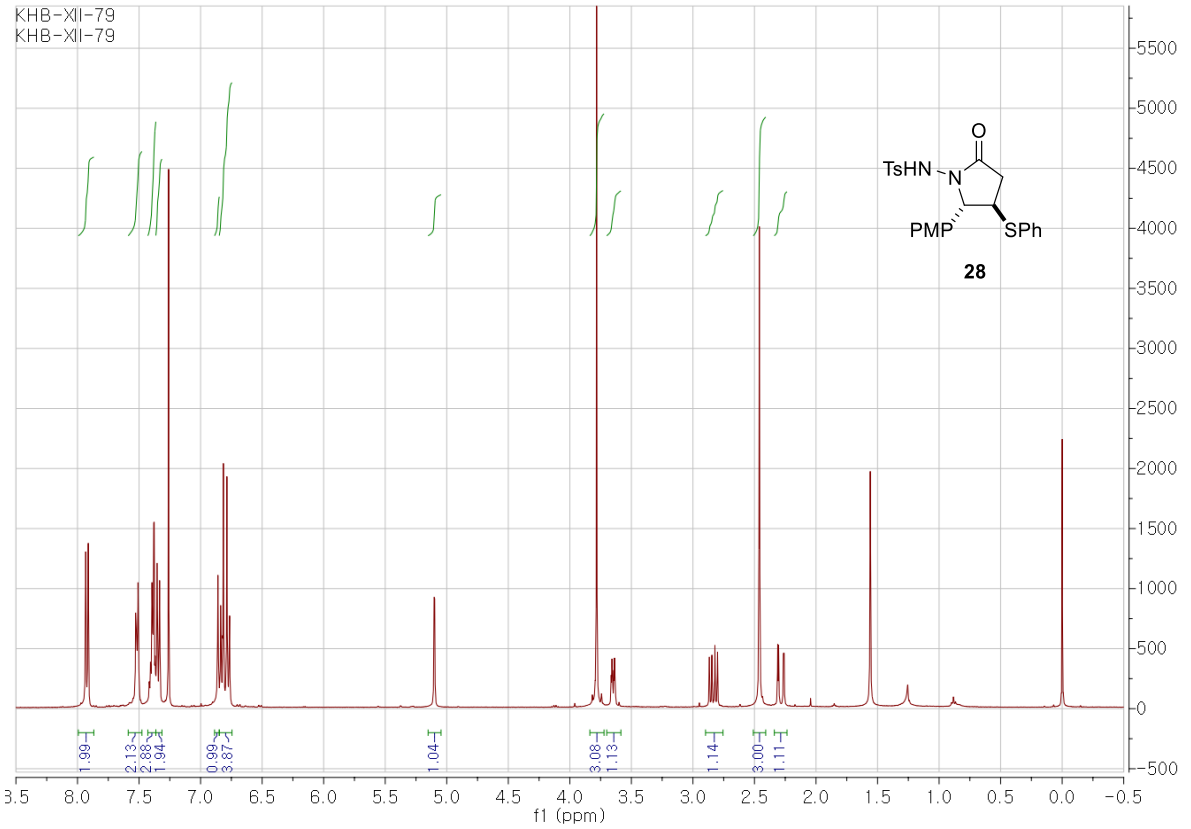

KHB-XIII-10
KHB-XIII-10-13C
167.00
158.33
148.77
137.36
134.07
129.42
127.32
126.98
121.72
119.73
119.13
118.93
115.85
113.89
109.24
61.69
55.27
44.85
32.72
f1 (ppm)

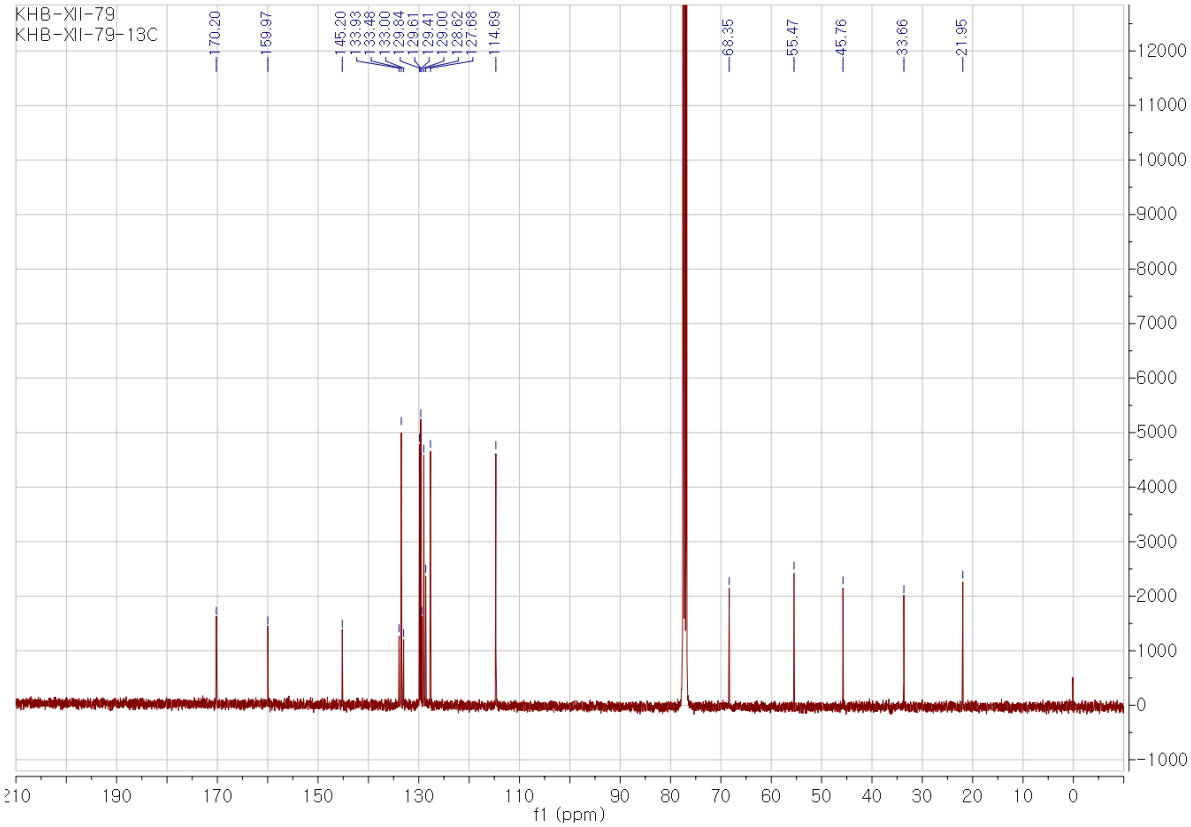

NHQ-XII-37
Ms
N
Me
O
O
NMe
O
H
Ph
OBn
26
f1 (ppm)

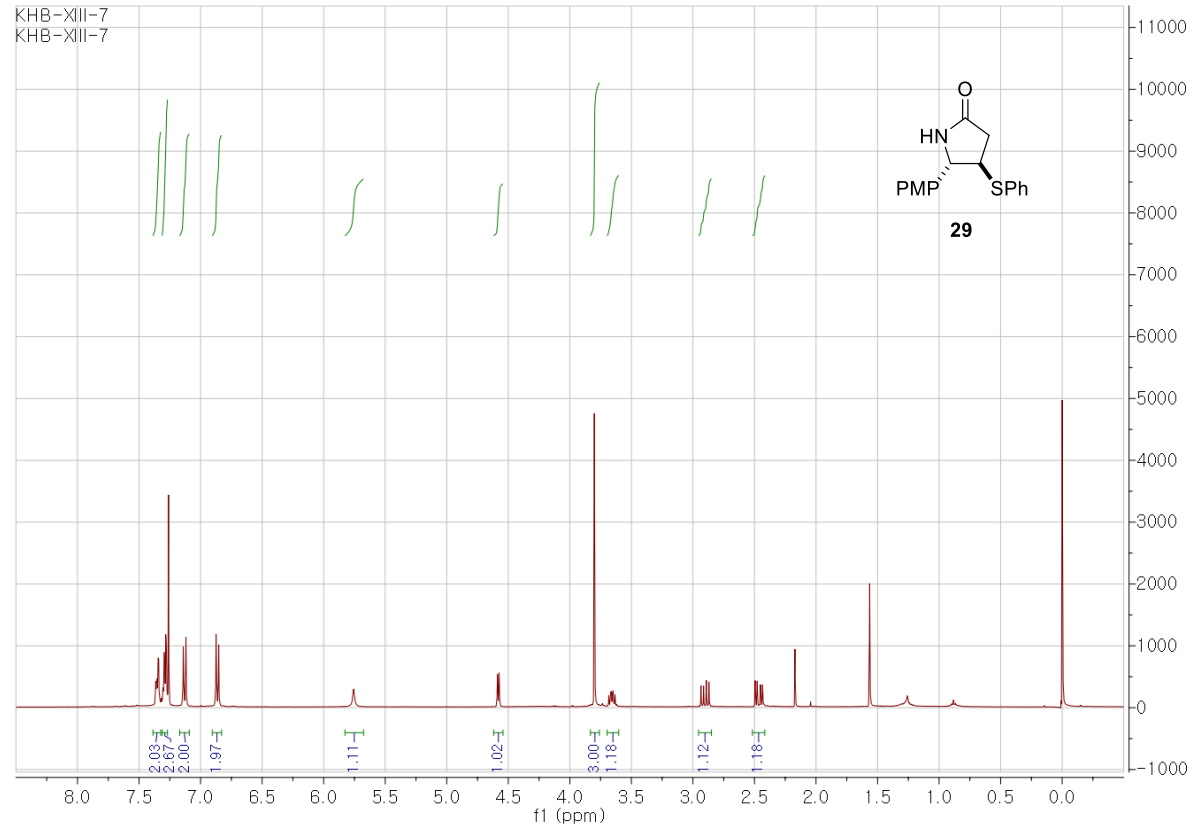

NHQ-XII-37
f1 (ppm)

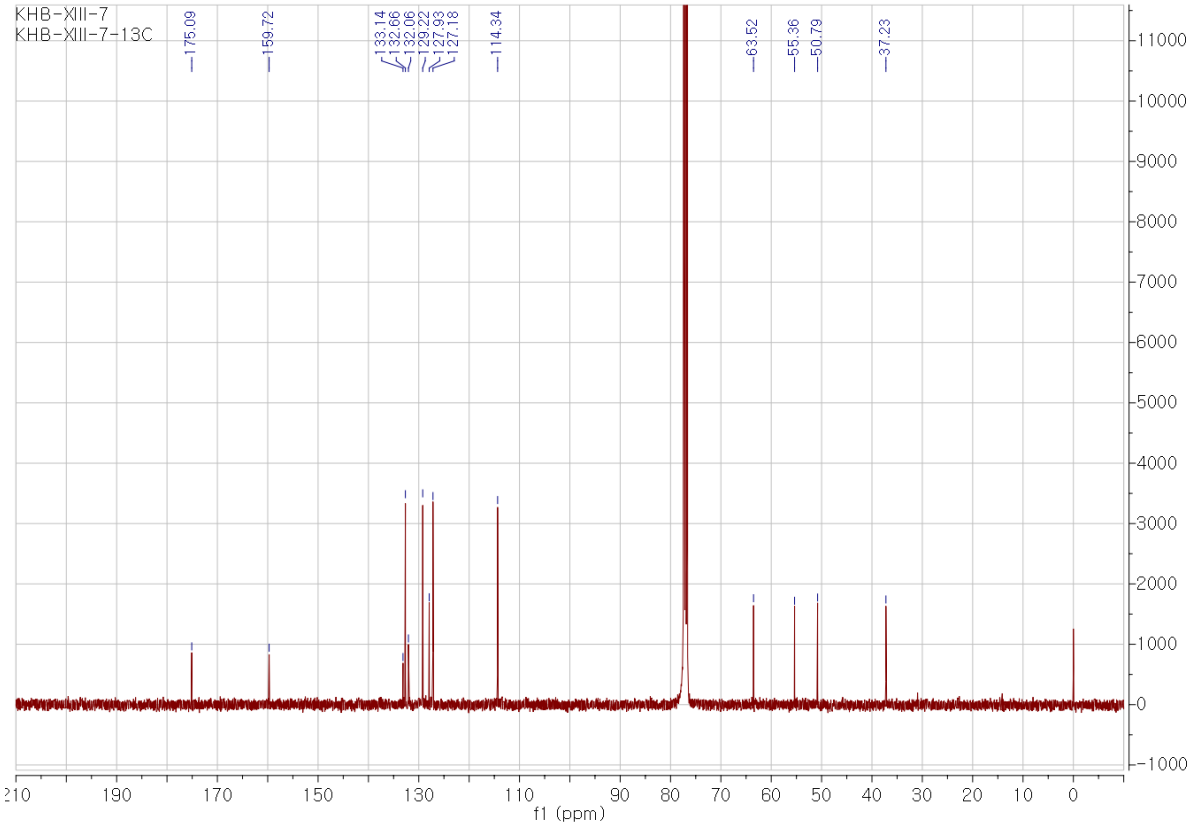

NHN-IX-76-1H
NHN-IX-76-1H
O
SPh
H
N
Ts
Ms
N
N
H
Me
PMP
27
f1 (ppm)

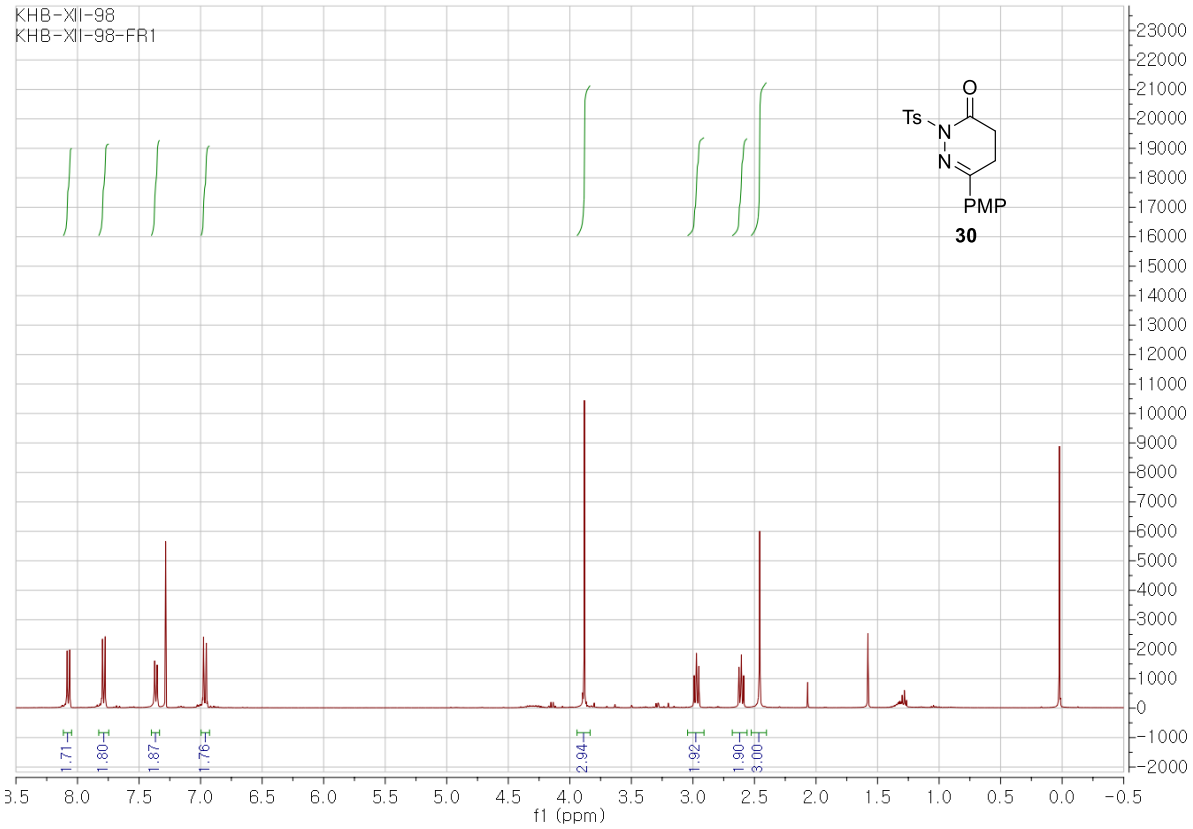

NHN-IX-76-13C
NHN-IX-76-13C
172.36
171.65
159.78
159.59
144.23
132.20
131.57
129.76
129.08
129.06
129.04
128.05
114.12
67.11
66.19
55.33
55.31
50.07
48.23
41.37
41.34
32.39
21.64
21.62
f1 (ppm)

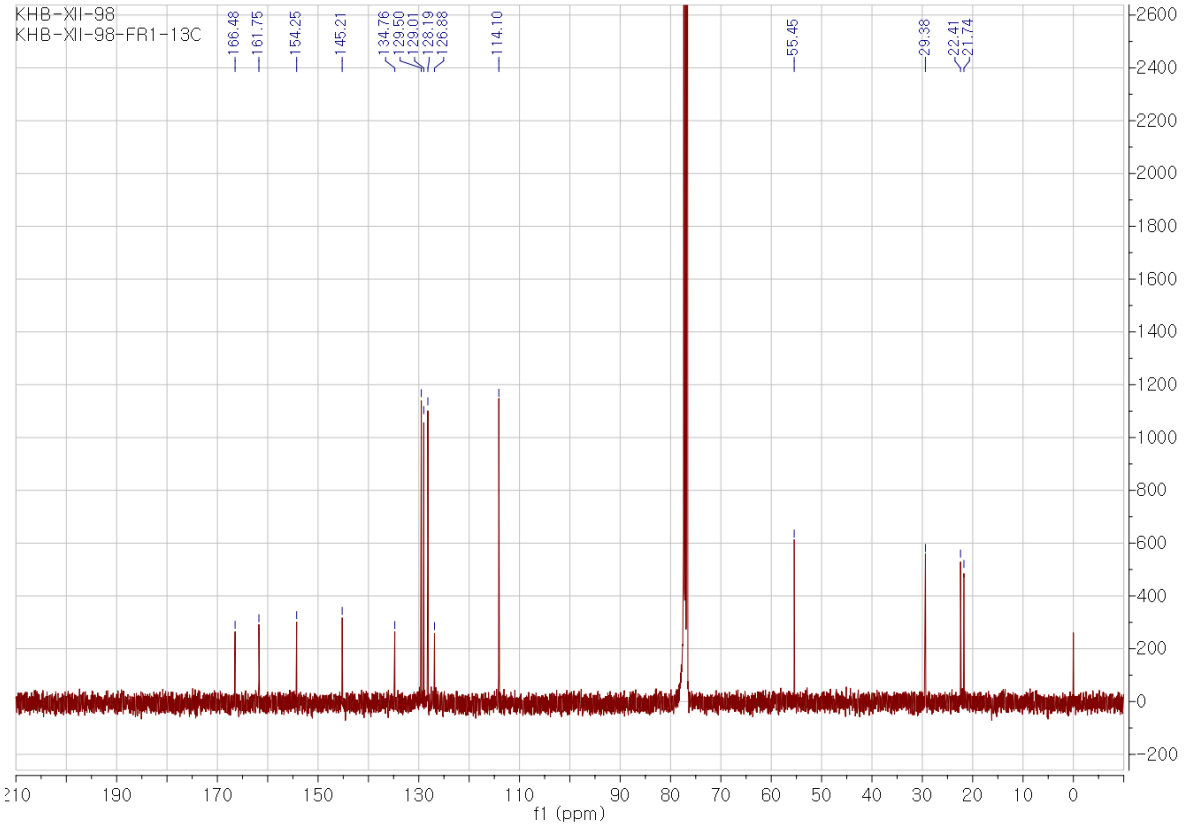

KHB-XII-79
KHB-XII-79
TsHN
N
O
PMP
SPh
28
1.99
2.13
2.88
1.94
0.99
3.87
1.04
3.08
1.13
1.14
3.00
1.11
f1 (ppm)


KHB-XII-79
KHB-XII-79-13C
170.20
159.97
145.20
133.93
133.48
133.00
129.84
129.61
129.41
129.00
128.62
127.68
114.69
68.35
55.47
45.76
33.66
21.95
f1 (ppm)


KHB-XIII-7
KHB-XIII-7
HN
O
PMP
SPh
29
2.03
2.67
2.00
1.97
1.11
1.02
3.00
1.18
1.12
1.18
f1 (ppm)


KHB-XIII-7
KHB-XIII-7-13C
175.09
159.72
133.14
132.66
132.06
129.22
127.93
127.18
114.34
63.52
55.36
50.79
37.23
f1 (ppm)


KHB-XII-98
KHB-XII-98-FR1
Ts
N
N
O
PMP
30
1.71
1.80
1.87
1.76
2.94
1.92
1.90
3.00
f1 (ppm)


KHB-XII-98
KHB-XII-98-FR1-13C
166.48
161.75
154.25
145.21
134.76
129.50
129.01
128.19
126.88
114.10
55.45
29.38
22.41
21.74
f1 (ppm)