Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Reactivity of Arynes toward Functionalized Alkenes: Intermolecular Alder-Ene vs. Addition Reactions

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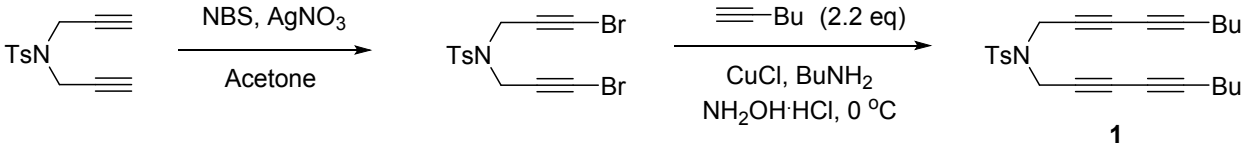
General Information

Reactions were carried out in oven-dried glassware unless otherwise noted. Compounds were purchased from Aldrich, Acros, Oakwood or TCI America unless otherwise noted. Anhydrous acetonitrile and methanol from Sigma-Aldrich were used as purchased. Toluene and dichloromethane were distilled over calcium hydride (CaH_2) under nitrogen. Tetrahydrofuran was dried over sodiumbenzophenone ketyl. Column chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040−0.063 mm). Yields refer to chromatographically and spectroscopically pure isolated compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to the residual proteated solvent peak ($CDCl_3$ (7.26 ppm)). ^{13}C chemical shifts (δ) are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$ (77.2 ppm)). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet) or m (multiplet). ^{1}H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a range of chemical shift values corresponding to the peak or center of the peak. Coupling constants, J, are reported in Hz (Hertz). Electrospray ionization (ESI) and Electron impact (EI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima and Micromass 70-VSE, respectively in the University of Illinois at Urbana-Champaign.

Experimental Details

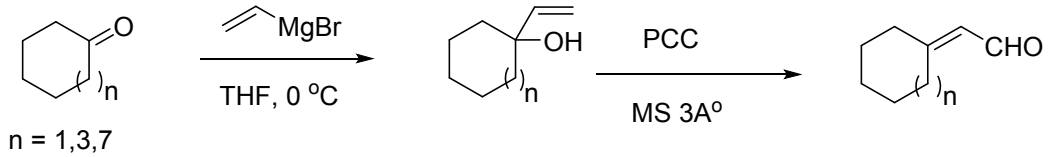
Preparation of tetaryne 1



1

Tetrayne **1** was prepared by following the published procedure.[1]

Preparation of Cycloalkylidene Carboxaldehyde[2]

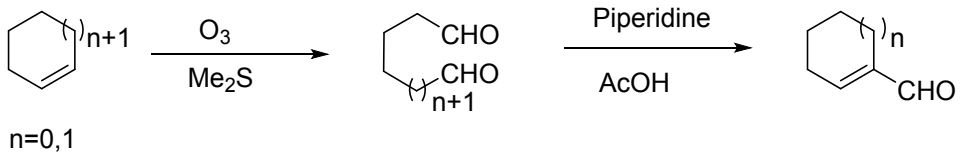


n = 1,3,7

To a THF solution of a cycloalkanone (2 mmol) was added vinylmagnesium bromide (1 M in THF, 2.2 mL) at 0 °C. After completion, the reaction mixture was quenched by addition of sat. NH_4Cl solution and extracted with Et_2O (x2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 10:1) to

obtain alkynyl alcohol as colorless oil. The alcohol (1.4 mmol) was dissolved in CH_2Cl_2 and 3 A° MS (1.5 g) was added followed by Pyridinium Chlorochromate (2.1 mmol) in portions and stirred for 14 h. The reaction mixture was filtered over celite, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 10:1) to obtain the corresponding enal as white solid.

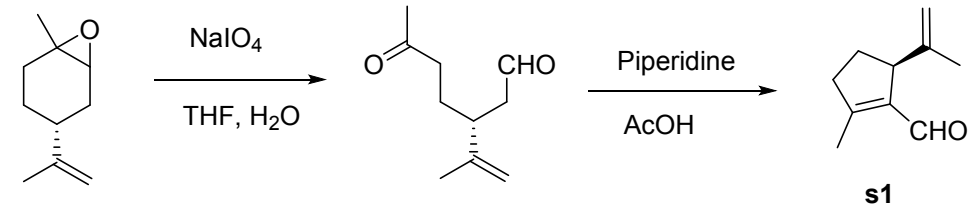
Preparation of Cyclopalkenylcarboxaldehydes



n=0,1

Cycloalkene (2 mmol) was dissolved in MeOH (20 mL) and cooled to –78 °C and a stream of ozone gas was passed until the appearance of blue color. The excess ozone was removed by a stream of nitrogen and Me_2S (20 mmol) and the reaction mixture was slowly warmed to room temperature and stirred for 14 h. The reaction mixture was concentrated and dissolved in EtOAc and the organic layer was washed with brine (x4), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 5:1). The dialdehyde (1.5 mmol) was dissolved in dichloromethane followed by addition of Piperidine (2 ml) and AcOH (1.5 mL) and stirred for 15 min at ambient temperature. The reaction was quenched by adding water and organic layer washed with 1 M HCl (x1), sat. $NaHCO_3$ (x1) and brine (x1). The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 20:1) to obtain the desired cyclopalkenylcarboxaldehydes as colorless oil.

Preparation of Limonene-Oxide derived aldehyde s1

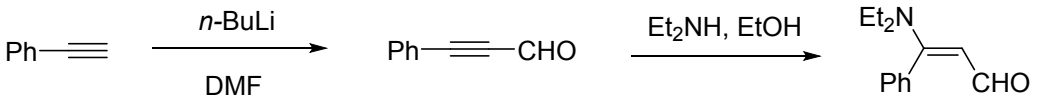


Limonene Oxide

s1

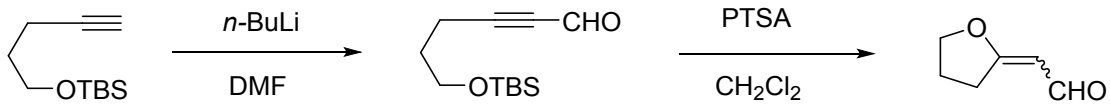
The substrate **s1** was prepared from limonene oxide by following known literature procedures[3]

Preparation of β-diethylamino cinnamaldehyde



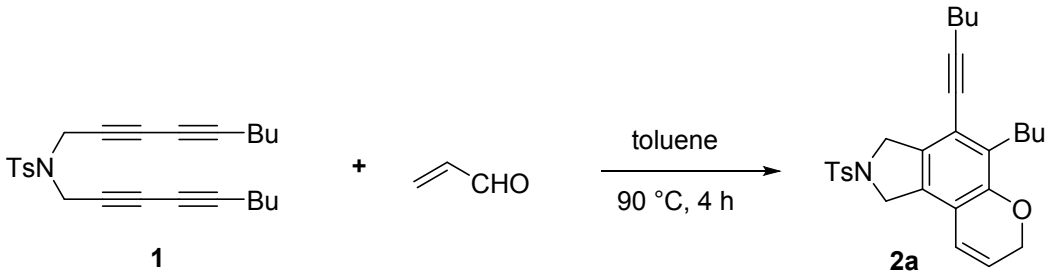
Phenylacetylene (5 mmol) was dissolved in dry THF and cooled to –40 °C and *n*-BuLi (2.5 M in Hexanes) was added dropwise while maintaining temperature between –40 °C to –35 °C and stirred for 45 min at same temperature. Then DMF (50 mmol) was added dropwise at –40 °C and stirred for 45 min and slowly warmed to room temperature and stirred for another 1 h. The reaction mixture was poured into 100 ml of 1M HCl solution and the biphasic solution was transferred to a separatory funnel. The organic layer was washed with brine (x4), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 10:1). The alkynyl aldehyde (1.2 mmol) was dissolved in EtOH and treated with Et_2NH (1.4 mmol) and stirred at room temperature for 16 h. EtOH was removed under reduced pressure and the residue was dissolved in EtOAc and washed with brine (x5). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to obtain β-diethylamino cinnamaldehyde as red oil, which was carried to the next step without further purification.

Preparation of 2-(dihydrofuran-2(3H)-ylidene)acetaldehyde



The alkynyl aldehyde (1 mmol) prepared by the method described above was dissolved in dichloromethane, followed by addition of *p*-toluenesulfonic acid and stirred for 14 h. The deep purple solution was washed with brine (x2), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography to obtain 2-(dihydrofuran-2(3H)-ylidene)acetaldehyde (SiO_2, hexanes–EtOAc, 2:1) as a colorless oil (76% yield, *Z/E* = 3:1).

Representative Procedure for the Tandem HDDAR–Intermolecular Alder-ene/Addition Reaction with a 1.0 mmol Scale



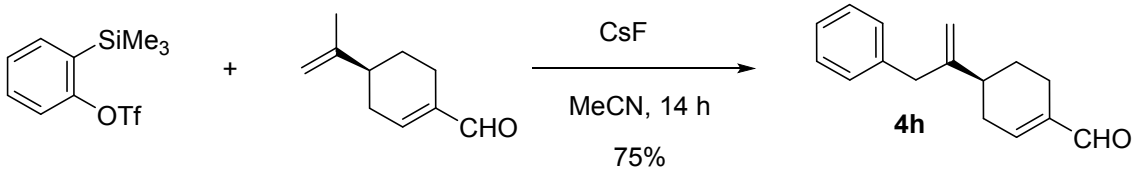
1 **2a**

To a toluene solution (0.05 M) of tetrayne **1** (410 mg, 1 mmol) in a Shlenk tube was added acrolein (0.3 ml, 5.0 mmol). The reaction mixture was heated at 90 °C for 4 h, bought to room temperature, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexanes–EtOAc, 4:1), providing product **2a** (324 mg, 72%) as white solid.

General Procedure for the Tandem HDDAR–Intermolecular Alder-ene/ Addition Reactions[4]

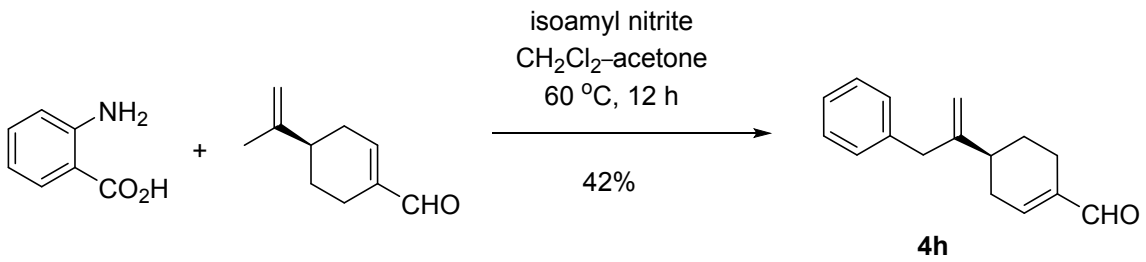
To a toluene solution (0.03–0.05 M) of tetrayne (0.05–0.06 mmol) in a Shlenk tube was added functionalized alkene (5 equiv). The reaction mixture was heated at 90 °C for 4 h, bought to room temperature, and concentrated under reduced pressure. The product was isolated by column chromatography (SiO_2, hexanes–EtOAc, 4:1, for alder-ene products) and (SiO_2, hexanes–EtOAc, 10:1, for addition product).

Reaction of perillaldehyde with benzyne generated from Kobayashi's precursor



2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (30 mg, 0.1 mmol) was dissolved in MeCN under N_2 and subsequently perillaldehyde (60 mg, 0.4 mmol) and CsF (62 mg, 0.4 mmol) were added. After stirring the mixture for 14 h at ambient temperature, MeCN was removed under reduced pressure and EtOAc (10 mL) was added and the organic layer was washed with brine (x2). The organic layer dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography (SiO_2, hexanes–EtOAc, 20:1) to obtain **4h** (30 mg, 75% yield) as yellow solid.

Reaction of perillaldehyde with benzyne generated from anthranilic acid



4h

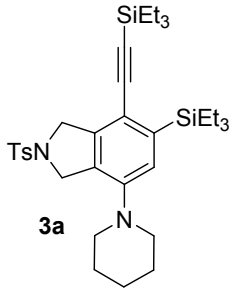
A solution of perillaldehyde (602.4 mg, 4.0 mmol) and isoamyl nitrite (0.293 ml, 2.2 mmol) in CH_2Cl_2 was taken in a three-necked flask equipped with a refluxing condenser and a dropping funnel and heated to 60 °C. Anthranilic acid (250 mg, 1.82 mmol) was dissolved in 8 mL acetone and added dropwise through the dropping funnel over 30 min. The mixture was refluxed for additional 12 h. After completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, hexanes–EtOAc, 20:1) to obtain **4h** (173 mg, 42% yield) as yellow solid.

References/Notes:

1. Lee, N. M.; Yun, S. Y.; Mamidipalli, P.; Salzman, R. M.; Lee, D.; Zhou, T.; Xia, Y. *J. Am. Chem. Soc.*, **2014**, *136*, 4363–4368.
2. Michno, D. M.; Dauben, W. G. *J. Org. Chem.* **1977,** 42, 682–685.
3. Wolinsky, J.; Slabaugh, M. R.; Gibson, T. *J. Org. Chem*., **1964,** *29*, 3740–3742.

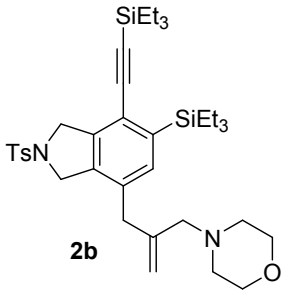
4. For 2H-chromene products **3k-o, 3p and 3r** have similar R_f values to that of residual aldehydes. Thus, each crude reaction mixture was treated with $NaBH_4$ to convert the aldehydes to the corresponding alcohols for complete separation. For the isolation of pure **3s**, the corresponding alcohol generated by treating the crude reaction mixture with $NaBH_4$ was isolated and re-oxidized with DMP.

Characterization Data



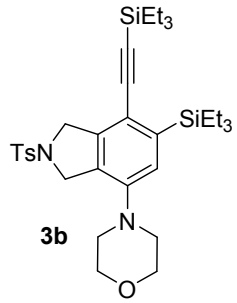
3a

3a: This compound was isolated in (62% yield, 15 mg) as a colorless oil.[1]H NMR (CDCl3, 500 MHz): 7.75 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 4.57–4.60 (m, 4H), 2.88–2.92 (m, 4H), 2.40 (s, 3H), 1.64–1.70 (m, 4H), 1.60–1.54 1.04 (t, *J* = 7.8 Hz, 9H), 0.88–0.93 (m, 15H), 0.67 (q, *J* = 7.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 500 MHz): 147.9, 143.5, 141.8, 140.6, 133.9, 129.8, 128.7, 127.6, 123.1, 116.0, 104.6, 98.0, 54.4, 53.8, 51.7, 26.3, 24.2, 21.5, 7.52, 7.48, 4.42, 3.25; **HRMS** (ESI) calcd for $C_{34}H_{53}N_2O_3SSi_2$ $[M+H]^+$ 609.3366, found 609.3348.



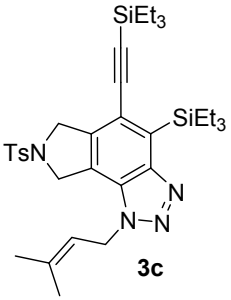
2b

2b: This compound was isolated in (15% yield, 6 mg) as a yellow oil. **^{1}H NMR** (CDCl3, 500 MHz): 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.14 (s, 1H), 4.98 (s, 1H), 4.81 (s, 1H), 4.63 (s, 2H), 4.61 (s, 2H), 3.63–3.68 (m, 4H), 3.25 (s, 2H), 2.40 (s, 3H), 2.26–2.32 (m, 4H), 1.05 (t, *J* = 7.9 Hz, 2H), 0.86–0.93 (m, 15H), 0.68 (q, *J* = 7.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 143.6, 140.3, 139.0, 136.2, 135.8, 134.0, 133.4, 122.8, 121.4, 115.1, 104.1, 99.5, 67.1, 63.5, 54.4, 53.5, 53.4, 38.3 21.5, 7.5, 4.3, 3.1; **HRMS** (ESI) calcd for $C_{33}H_{51}N_2O_3SSi_2$ $[M+H]^+$ 611.3125, found 611.3135.



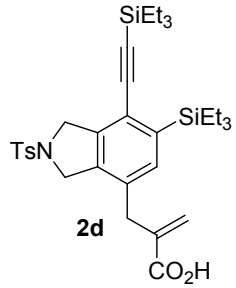
3b

3b: This compound was isolated in (45% yield, 18 mg) as a yellow oil. **^{1}H NMR** (CDCl3, 500 MHz): 7.77 (d, *J* = 7.9, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 4.59 (s, 4H), 3.78–3.84 (m, 4H), 2.91–2.97 (m, 4H), 2.41 (s, 3H), 1.04 (t, *J* = 7.8 Hz, 2H), 0.88–0.93 (m, 15H), 0.68 (q, *J* = 8.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 146.5, 143.7, 142.1, 141.0, 133.8, 129.8, 128.7, 127.6, 122.8, 117.2, 104.2, 98.7, 67.1, 54.2, 53.7, 50.7, 21.5, 7.50, 7.47, 4.4, 3.2; **HRMS** (ESI) calcd for $C_{33}H_{51}N_2O_3SSi_2$ $[M+H]^+$ 611.3125, found 611.3135.



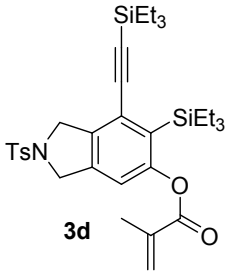
3c

3c: This compound was isolated in (76% yield, 26 mg) as a colorless oil. **^{1}H NMR** (CDCl3, 500 MHz): 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.33–5.26 (m, 1H), 5.18 (d, *J* = 6.2 Hz, 1H), 4.97 (s, 2H), 4.74 (s, 2H), 2.4 (s, 3H), 1.89 (s, 3H), 1.78 (s, 3H), 1.99 (q, *J* = 8.1 Hz, 6H), 1.08 (t, *J* = 7.2 Hz, 9H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.72 (q, *J* = 7.5 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 152.1, 144.0, 139.7, 138.3, 134.2, 133.7, 129.9, 127.5, 127.0, 120.4, 118.9, 117.6, 115.7, 104.1, 99.9, 54.9, 53.4, 47.4, 25.7, 21.5, 18.4, 7.6, 7.5, 4.4, 4.3; **HRMS** (ESI) calcd for $C_{34}H_{51}N_4O_2SSi_2$ $[M+H]$ 635.3271, found 635.3257.



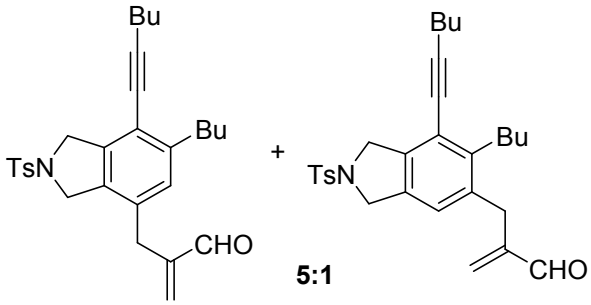
2d

2d: This compound was isolated in (33% yield, 12 mg) as a yellow oil. **^{1}H NMR** (CDCl3, 500 MHz): 7.75 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.11 (s, 1H), 6.34 (s, 1H), 4.64 (s, 2H), 4.59 (s, 2H), 3.44 (s, 2H), 2.39 (s, 3H), 1.05 (t, *J* = 8.0 Hz, 9H), 0.88 – 0.91 (m, 15H), 0.69 (q, *J* =7.9 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 170.1, 143.6, 140.6, 139.6, 137.4, 136.0, 135.7, 133.9, 131.8, 129.8, 128.5, 127.6, 122.1, 103.9, 99.9, 54.4, 53.4, 35.0, 21.5, 7.4, 4.3, 3.1; **HRMS** (ESI) calcd for $C_{33}H_{48}NO_4SSi_2$ $[M+H]^+$ 610.2843, found 610.2842.



3d

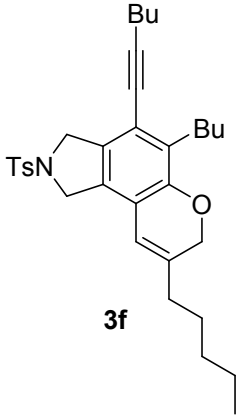
3d: This compound was isolated in (40% yield, 14 mg) as a yellow solid.^{1}H NMR (CDCl3, 500 MHz): 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.72 (s, 1H), 6.27 (s, 1H), 5.75 (t, *J* = 1.3 Hz, 1H), 4.64 (s, 2H), 4.59 (s, 2H), 2.42 (s, 3H), 2.03 (s, 3H), 1.06 (t, *J* = 8.1 Hz, 9H), 0.86–0.94 (m, 15H), 0.70 (q, *J* = 8.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 500 MHz): 166.5, 156.3, 143.8, 138.8, 138.0, 136.0, 133.6, 130.3, 129.9, 127.7, 125.4, 117.1, 103.6, 102.2, 54.3, 21.5, 18.4, 7.6, 7.4, 4.30, 4.25; **HRMS** (ESI) calcd for $C_{33}H_{48}NO_4SSi_2$ $[M+H]^+$ 610.2843, found 610.2841.



5:1

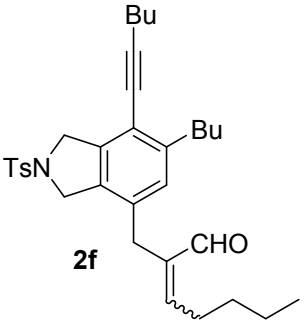
2e

2e: This compound was isolated in (55% yield, 16 mg, colorless oil) as a 5:1 regioisomeric mixture. Characterization data for the major isomer is given. **^{1}H NMR** (CDCl3, 500 MHz): δ 9.58 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.81 (s, 1H), 6.05 (s, 1H), 5.94 (s, 1H), 4.63 (s, 2H), 4.50 (s, 2H), 3.36 (s, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 1.62–1.56 (m, 2H), 1.54–1.46 (m, 4H), 1.36–1.28 (m, 2H), 0.96 (t, *J* = 7.8 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 193.6, 149.3, 147.7, 144.9, 143.6, 139.2, 135.0, 132.4, 131.3, 129.8, 129.3, 127.6, 116.9, 98.5, 75.9, 54.4, 53.2, 33.8, 32.9, 31.5, 30.8, 22.5, 21.9, 21.5, 19.3, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{29}H_{36}NO_3S$ $[M+H]^+$ 478.2416, found 478.2401.



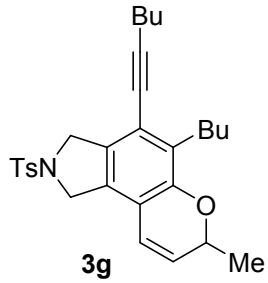
3f

2f: This compound was isolated in (23% yield, 11 mg) as colorless oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 9.43 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* =7.8 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.62 (s, 4H), 3.39 (s, 2H), 2.60 (t, *J* = 7.5, 2H), 2.46–2.40 (m, 2H), 2.41 (s, 3H), 2.29 (q, *J* = 7.5 Hz, 2H), 1.60–1.54 (m, 2H), 1.51–1.40 (m, 6H), 1.34–1.24 (m, 6H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.91–0.86 (m, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 194.2, 157.1, 144.6, 143.6, 140.6, 138.9, 133.9, 132.3, 132.0, 129.8, 127.6, 127.3, 120.2, 116..3, 98.2, 76.0, 54.4, 53.5, 33.9, 32.9, 30.9, 30.5, 29.2, 26.7, 22.5, 21.9, 21.5, 19.3, 13.8; **HRMS** (ESI) calcd for $C_{33}H_{44}NO_3S$ $[M+H]^+$ 534.3042, found 534.3063.



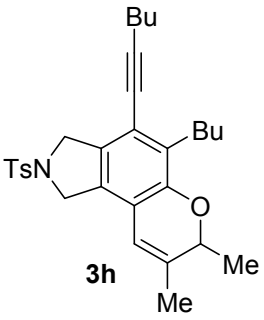
2f

3f: This compound was isolated in (23% yield, 11 mg, colorless oil) as a 10:1 regioisomeric mixture. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.93 (s, 1H), 4.59 (s. 2H), 4.59 (s, 2H), 4.56 (s, 4H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.09 (t, *J* = 7.5 Hz, 2H), 1.61–1.55 (m, 2H), 1.53–1.41 (m, 6H), 1.37–1.28 (m, 6H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.92–0.88 (m, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.0, 143.5, 137.7, 134.0, 131.4, 131.1, 129.8, 128.4, 127.6, 117.6, 117.2, 115.1, 98.1, 76.6, 68.2, 54.2, 53.0, 33.4, 31.9, 31.5, 30.9, 27.5, 26.5, 22.8, 22.4, 21.9, 21.5, 19.3, 14.0, 13.6 ; **HRMS** (ESI) calcd for $C_{33}H_{44}NO_3S$ $[M+H]^+$ 534.3042, found 534.3037.



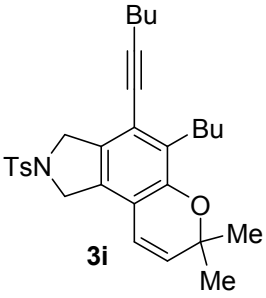
3g

3g: This compound was isolated in (71% yield, 25 mg) as a white solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.17 (dd, *J* = 1.7, 8.3 Hz, 1H), 5.72 (dd, *J* = 3.6, 6.7 Hz, 1H), 4.924.86 (m, 1H), 4.60–4.49 (m, 4H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.45 (t, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.61–1.56 (m, 2H), 1.51–1.41 (m, 4H), 1.37 (d, *J* = 5.9 Hz, 3H), 0.96 (t, J = 6.5 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.4, 143.6, 134.0, 132.1, 130.7, 129.8, 129.0, 128.3, 127.6, 120.1, 118.7, 115.8, 98.5, 76.6, 71.1, 54.2, 52.9, 31.7, 30.9, 27.4, 22.7, 21.9, 21.5, 20.8, 19.3, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{28}H_{34}NO_3S$ $[M+H]^+$ 464.2259, found 464.2251.



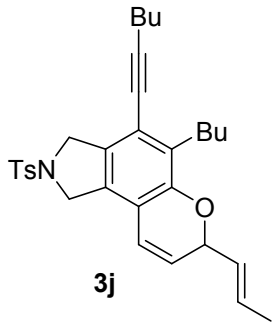
3h

3h: This compound was isolated in (65% yield, 24 mg) as yellow solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.9 (s, 1H), 4.75 (q, *J* = 6.3 Hz, 1H), 4.59–4.51 (m, 4H), 2.67 (t, *J* =7.5 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.82 (s, 3H), 1.61–1.54 (m, 2H), 1.52–1.43 (m, 4H), 1.38–1.32 (m, 2H), 1.28 (d, *J* = 6.8, 3H), 0.96 (t, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 7.3, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 148.2, 143.4, 137.3, 134.0, 131.9, 129.8, 128.1, 127.6, 117.6, 116.6, 115.2, 98.0, 76.6, 74.7, 54.2, 53.0, 31.8, 30.9, 27.5, 22.8, 21.9, 21.5, 19.5, 19.3, 18.4, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{30}H_{38}NO_3S$ $[M+H]^+$ 492.2572, found 492.2562.



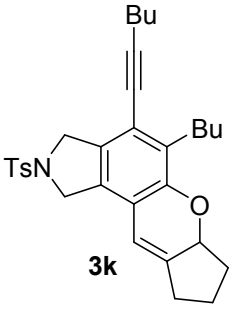
3i

3i: This compound was isolated in (86% yield, 29 mg) as white solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, J = 7.5 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 6.10 (d, *J* = 10.2 Hz, 1H), 5.63 (d, *J* = 11.8 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.62–1.54 (m, 2H), 1.52–1.43 (m, 4H), 1.37 (s, 6H), 1.39–1.31 (m, 2H), 0.96 (t, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 149.9, 143.5, 133.9, 132.3, 131.9, 130.4, 129.8, 128.9, 127.6, 118.7, 118.6, 115.1, 98.3, 76.6, 75.9, 54.2, 52.9, 31.7, 30.9, 27.6, 27.3, 22.7, 21.9, 21.5, 19.3, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{25}H_{38}N_3O_5S$ $[M+H]^+$ 534.3042, found 534.3037.



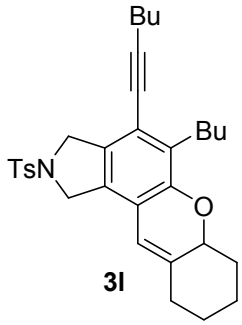
3j

3j: This compound was isolated in (84% yield, 28 mg) as colorless oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.21 (d, *J* = 9.5 z, 1H), 5.96–5.69 (m, 2H), 5.62–5.54 (m, 1H), 5.17–5.12 (s, 1H), 4.59–4.57 (m, 4H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.45 (t, J = 6.5 Hz, 2H), 2.41 (s, 3H), 1.68 (d, *J* = 5.6 Hz, 2H), 1.61–1.54 (m, 2H), 1.52–1.41 (m, 4H), 1.36–1.29 (m, 2H), 0.96 (t, J = 6.5 Hz, 3H), 0.90 (t, J =7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.1, 143.6, 133.9, 132.1, 129.8, 129.2,128.8, 127.6, 126.0, 120.2, 118.7, 115.8, 98.6, 76.6, 75.0, 54.2, 52.9, 31.7, 30.8, 27.5, 22.7, 21.9, 21.5, 19.3, 17.7, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{31}H_{38}NO_3S$ $[M+H]^+$ 504.2572, found 504.2565.



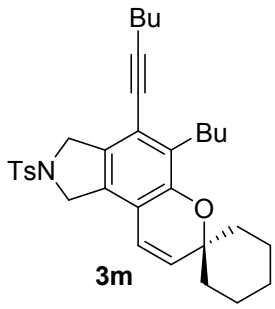
3k

3k: This compound was isolated in (56% yield, 22 mg) as a colorless oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.76 (d, *J* =7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.02–5.99 (m, 1H), 4.75–4.69 (m, 1H), 4.65–4.46 (m, 4H), 2.69 (t, *J* =7.5 Hz, 2H), 2.45 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 2.34–2.29 (m, 1H), 1.94–1.84 (m, 2H), 1.73–1.64 (m, 1H), 1.61–155 (m, 2H), 1.51–1.43 (m, 4H), 1.38–1.31 (m, 2H), 0.96 (t, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.9, 143.5, 143.2, 133.9, 131.9, 131.2, 129.8, 128.7, 127.6, 118.6, 117.6, 113.4, 98.1, 78.9, 76.7, 54.3, 53.2, 32.2, 31.9, 30.9, 28.4, 27.6, 22.6, 21.9, 21.7, 21.5, 19.4, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{31}H_{38}NO_3S$ $[M+H]^+$ 504.2572, found 504.2578.



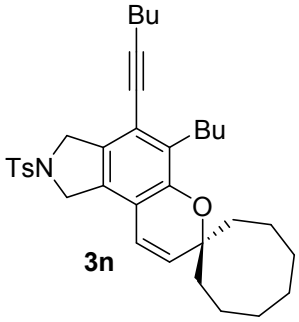
3l

3l: This compound was isolated in (62% yield, 29 mg) as a colorless oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.80–5.77 (m, 1H), 4.87–4.81 (m, 1H), 4.56–4.49 (m, 4H), 2.65–2.60 (m, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.22–2.15 (m, 1H), 2.07–1.99 (m, 1H), 1.91–1.83 (m, 1H), 1.82–1.76 (m, 1H), 1.74–1.65 (m, 1H), 1.60–1.53 (m, 2H), 1.51–138 (m, 6H), 1.36–1.29 (m, 2H), 1.27–1.22 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 149.7, 143.5, 139.9, 134.0, 130.7, 130.4, 129.8, 128.1, 127.6, 117.5, 115.6, 112.8, 97.8, 77.2, 76.0, 54.2, 52.9, 34.9, 33.1, 31.7, 30.9, 27.3, 26.7, 24.2, 24.2, 22.7, 21.9, 21.5, 19.3, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{33}H_{42}NO_3S$ $[M+H]^+$ 532.2885, found 532.2885.



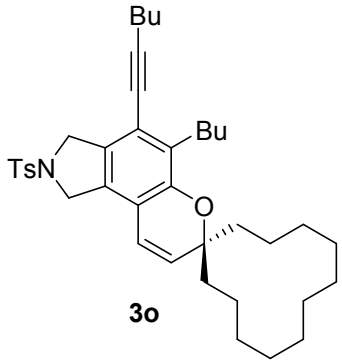
3m

3m: This compound was isolated in (75% yield, 25 mg) as a white solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.10 (d, *J* = 9.8 Hz, 2H), 5.62 (d, *J* = 9.9 Hz, 2H), 4.56 (s, 4H), 2.73 (t, *J* = 8.1 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.94–1.86 (m, 2H), 1.73–1.66 (m, 2H), 1.62–1.54 (m, 3H), 1.53–1.45 (m, 7H), 1.44–1.35 (m, 3H), 1.31–1.25 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.93 (t, J = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.1, 143.6, 134.0, 132.1, 130.8, 129.8, 129.2, 129.1, 128.7, 127.6, 125.9, 120.2, 118.7, 115.8, 98.6, 76.6, 75.0, 54.2, 52.9, 31.7, 30.8, 27.4, 22.7, 21.9, 21.5, 19.3, 17.7, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{33}H_{42}NO_3S$ $[M+H]^+$ 532.2885, found 532.2885.



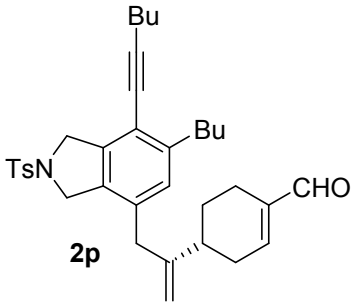
3n

3n: This compound was isolated in (65% yield, 26 mg) as a white solid. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.08 (d, J =9.9 Hz, 1H), 5.73 (d, J = 9.8 Hz, 1H), 4.55 (s, 4H), 2.72-2.67 (m, 2H), 2.45 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 2.09-1.98 (m, 2H), 1.75-1.62 (m, 6H), 1.60-1.53 (m, 4H), 1.53-1.43 (m, 8H), 1.40-1.32 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 149.6, 143.5, 134.0, 132.3, 131.5, 130.2, 129.8, 128.9, 127.6, 118.5, 118.4, 115.6, 98.3, 80.3, 76.6, 54.2, 53.0, 34.2, 31.7, 30.9, 28.1, 27.5, 24.8, 22.9, 21.9, 21.5, 21.2, 19.3, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{35}H_{46}NO_3S$ $[M+H]^+$ 560.3198, found 560.3198.



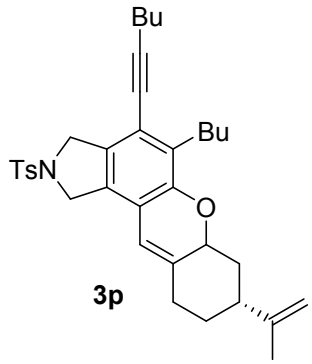
3o

3o: This compound was isolated in (68% yield, 25 mg) as a white solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.69 (d, *J* = 10.9 Hz, 1H), 4.55 (s, 4H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 1.80–1.72 (m, 2H), 1.68–1.61 (m, 2H), 1.60–1.55 (m, 2H), 1.52–1.43 (m, 4H), 1.39–1.32 (m, 20H), 0.96 (t, J = 7.6 Hz, 3H), 0.92 (t, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 149.8, 143.5, 134.0, 132.2, 131.1, 130.3, 129.8, 128.9, 127.6, 118.5, 115.9, 98.3, 80.5, 76.7, 54.2, 52.9, 32.6, 31.6, 30.9, 27.5, 26.3, 26.0, 22.8, 22.5, 22.1, 21.9, 21.5, 19.3, 18.9, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{39}H_{54}NO_3S$ $[M+H]^+$ 616.3824, found 616.3835.



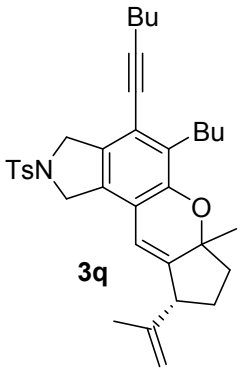
2p

2p: This compound was isolated in (24% yield, 11 mg, colorless oil) as a 10:1 regioisomeric mixture. Characterization data for major isomer is given. **^{1}H NMR** (CDCl3, 500 MHz): 9.43 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.7, 2H), 6.82 (s, 1H), 6.79–6.76 (m, 1H), 4.85 (s, 1H), 4.63–4.60 (m, 2H), 4.59 (s, 1H), 4.56–4.47 (m, 2H), 3.22 (s, 2H), 2.67 (t, *J* = 7.1 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.26–2.14 (m, 2H), 2.14–2.02 (m, 2H), 1.91–1.84 (m, 1H), 1.62–155 (m, 4H), 1.54–144 (m, 4H), 1.34–1.28 (m, 2H), 0.96 (t, *J* = 7.7 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 193.7, 150.0, 149.6, 143.6, 141.2, 139.1, 133.9, 132.8, 132.5, 129.8, 129.4, 127.5, 116.5, 111.1, 98.4, 76.0, 54.4, 53.3, 39.2, 38.7, 33.8, 32.9, 32.2, 30.9, 26.7, 22.5, 21.9, 21.6, 21.5, 19.3, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{35}H_{44}NO_3S$ $[M+H]^+$ 558.3018, found 558.3029.



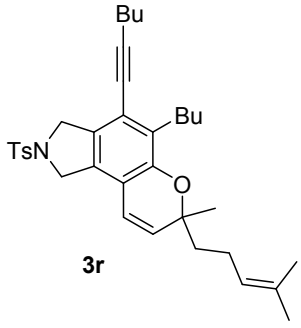
3p

3p: This compound was isolated in (34% yield, 14 mg) as yellow oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.83 (s, 1H), 4.99–4.95 (m, 1H), 4.92 (s, 1H), 4.83 (s, 1H), 4.58–4.48 (m, 4H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.61–2.56 (m, 1H), 2.44 (t, J = 5.6 Hz, 2H), 2.40 (s, 3H), 2.27–2.21 (m, 2H), 2.01–1.93 (m, 2H), 1.77 (s, 3H), 1.70–1.62 (m, 1H), 1.60–1.54(m, 2H), 1.52–1.41 (m, 4H), 1.36–1.29 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 2H), 0.91 (t, J = 7.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 150.0, 146.1, 143.5, 139.7, 133.9, 130.6, 129.8, 128.1,127.6, 117.4, 116.3, 113.4, 111.1, 109.5, 97.9, 76.7, 73.4, 54.2, 52.9, 38.7, 35.7, 31.7, 30.9, 28.1, 27.8, 27.2, 22.6, 22.2, 21.9, 21.5, 19.3, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{35}H_{44}NO_3S$ $[M+H]^+$ 558.3042, found 558.3040.



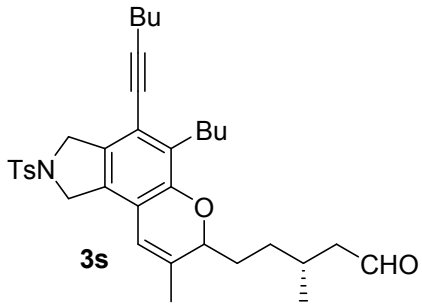
3q

3q: This compound was isolated in (55% yield, 20 mg, yellow oil) as a 1:1 diastereomeric mixture. **^{1}H NMR** (CDCl3, 500 MHz) (all discernable signals for all isomers): δ 7.78 (d, *J* = 8.2 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 5.92 (d, *J* = 2.3 Hz, 1H), 5.79 (d, *J* = 2.5 Hz, 1H), 4.87–4.80 (m, 4H), 4.63–4.46 (m, 8H), 3.44–3.34 (m, 2H), 2.74–2.36 (m, 4H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.24–2.20 (m, 1H), 2.18–213 (m, 1H), 2.08–2.01 (m, 4H), 1.72 (s, 3H), 1.68 (s, 3H), 1.61–1.55 (m, 4H), 1.52–144 (m, 8H), 1.38–1.32 (m, 4H), 1.28–1.24 (m, 2H), 1.22 (s, 3H), 1.21 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 6H), 0.93–0.89 (m, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz) (all discernable signal for both isomers): δ 149.5, 147.5, 146.6, 145.8, 145.5, 143.5, 134.1, 132.4, 132.4, 130.8, 129.8, 129.6, 128.9, 127.7, 127.6, 117.7, 117.4, 117.1, 113.9, 113.0, 112.2, 111.3, 98.1, 98.06, 87.6, 85.3, 83.2, 82.7, 54.2, 53.2, 53.2, 53.2, 48.8, 47.9, 46.5, 38.7, 38.4, 36.6, 31.8, 30.9, 28.1, 27.6, 27.1, 22.8, 22.7, 22.0, 21.5, 20.1, 19.4, 18.7, 14.0, 13.6; **HRMS** (ESI) calcd for $C_{39}H_{44}NO_3S$ $[M+H]^+$ 558.3042 found 558.3056.



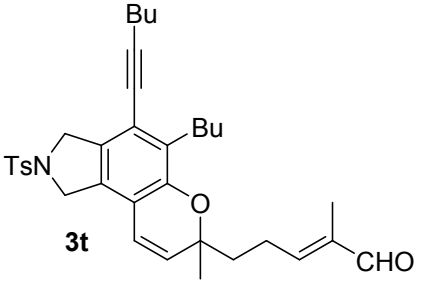
3r

3r: This compound was isolated in (62%, 24 mg) yield. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.13 (d, *J* = 9.7 Hz, 1H), 5.59 (d, J = 9.9 Hz, 1H), 5.08 (t, J = 3.1 Hz, 1H), 4.59–4.51 (m, 4H), 2.67 (t, J = 7.4 Hz, 2H), 2.45 (t, J = 6.9 Hz, 2H), 2.40 (s, 3H), 1.99–2.14 (m, 2H), 1.62–1.74 (m, 2H), 1.66 (s, 3H), 1.60–1.55 (m, 2H), 1.56 (s, 3H), 1.51–1.42 (m, 4H), 1.38–1.32 (m, 2H), 1.31 (s, 3H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 8.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.1, 143.5, 133.9, 131.9, 130.9, 130.2, 129.8, 128.9, 127.6, 123.9, 119.1, 118.6, 114.8, 98.3, 78.3, 76.6, 54.19, 53.0, 41.3, 31.7, 30.9, 27.4, 26.0, 25.7, 22.8, 22.0, 21.5, 19.4, 17.6, 14.0. **HRMS** (ESI) calcd for $C_{35}H_{46}NO_3S$ $[M+H]^+$ 560.3198, found 560.3210.



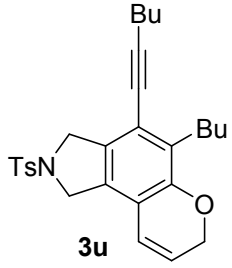
3s

3s: This compound was isolated in (46% yield, 14 mg, colorless oil) as 1: 1 diastereomeric mixture. **^{1}H NMR** (CDCl3, 500 MHz):9.74–9.71 (m, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz. 2H), 5.92 (s, 1H), 4.61–4.46 (m, 5H), 2.70–2.61 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.28–2.19 (m, 1H), 2.08–1.99 (m, 1H), 1.82 (s, 3H), 1.62–1.54 (m, 4H), 1.52–1.45 (m, 6H), 1.38–1.32 (m, 3H), 0.97–0.88 (m, 9H). **^{13}C NMR** ($CDCl_3$, 500 MHz) (all discernable signal for both isomers): 202.42, 148.2, 148.1, 143.5, 135.8, 135.0, 134.0, 131.6, 130.8, 129.8, 127.6, 117.7, 116.5, 115.92, 115.89, 98.2, 78.7, 78.6, 76.6, 54.2, 52.9, 51.1, 50.8, 32.7, 31.94, 31.92, 29.89, 29.78, 29.7, 28.0, 28.88, 27.57, 22.96, 21.5, 20.0, 19.7, 19.3, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{35}H_{46}NO_4S$ $[M+H]^+$ 576.3148, found 576.3147.



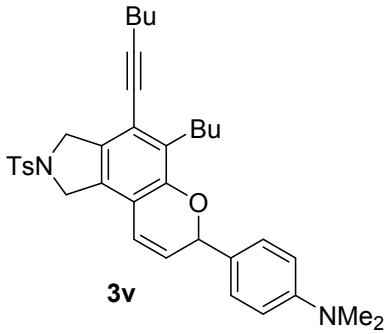
3t

3t: This compound was isolated in (72% yield, 26 mg) as a yellow oil. **^{1}H NMR** (CDCl3, 500 MHz): δ 9.36 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.47 (t, *J* = 7.2 Hz, 1H), 6.19 (d, *J* = 9.9 Hz, 1H), 5.59 (d, *J* = 9.9 Hz, 1H), 4.56 (s, 4H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.92–1.77 (m, 2H), 1.69 (s, 3H), 1.62–1.54 (m, 3H), 1.53–1.41 (m, 4H), 1.39–1.32 (m, 1H), 1.35 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 195.1, 153.8, 149.7, 139.5, 133.9, 131.9, 130.6, 129.9, 129.8, 129.2, 127.6, 119.9, 119.0, 114.5, 98.7, 78.1, 76.5, 54.1, 52.9, 39.7, 31.7, 30.8, 27.4, 26.2, 24.1, 22.8, 21.9, 21.5, 19.3, 14.0, 13.6, 9.1; **HRMS** (ESI) calcd for $C_{35}H_{44}NO_4S$ $[M+H]^+$ 574.2991, found 574.2998.



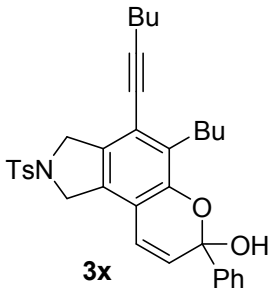
3u

3u: This compound was isolated in (72% yield, 324 mg) as a white solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.2 Hz), 6.22 (d, *J* = 10.4, 1H), 5.85–5.80 (m, 1H), 4.74–4.70 (m, 2H), 4.57–4.53 (m, 4H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.61–154 (m, 2H), 1.53–1.40 (m, 4H), 1.37–1.30 (m, 2H), 0.96 (t, *J* = 7.7 Hz, 3H), 0.90 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 151.2, 143.6, 133.9, 11.9, 131.1, 129.8, 129.2, 127.6, 123.4, 121.2, 118.7, 116.5, 98.6, 76.5, 65.2, 54.1, 52.9, 31.8, 30.8, 27.5, 22.8, 22.0, 21.5, 19.3, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{28}H_{34}NO_3S$ $[M+H]^+$ 464.2259, found 464.2251.



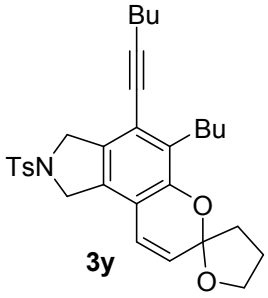
3v

3v: This compound was isolated in (74% yield, 28 mg) as a yellow solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.32 (*d*, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 1H), 5.87 (dd, *J* = 3.7, 5.8 Hz, 1H), 5.77–5.74 (m, 1H), 4.60 (s, 2H), 4.55 (s, 2H), 2.92 (s, 6H), 2.59 (t, J = 6.7 Hz, 2H), 2.44–2.38 (m, 5H), 1.58–1.52 (m, 4H), 1.49–1.43 (m, 2H), 1.24–1.18 (m, 2H), 0.94 (t, *J* = 6.7 Hz, 3H), 0.8 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 150.7, 150.1, 143.5, 134.0, 132.2, 130.6, 129.8, 128.4, 127.2, 126.4, 126.4, 124.6, 120.3, 118.7, 115.8, 112.2, 98.4, 76.4, 76.4, 54.2, 53.0, 40.4, 31.6, 30.8, 27.4, 22.6, 21.9, 21.5, 19.3, 14.0, 13.6. **HRMS** (ESI) calcd for $C_{36}H_{43}N_2O_3S$ $[M+H]^+$ 583.2994, found 583.2988.



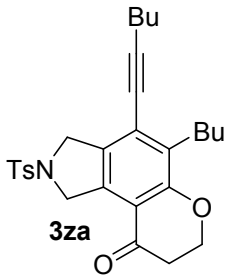
3x

3x: This compound was isolated in (54% yield, 18 mg) as white solid. **^{1}H NMR** (CDCl3, 500 MHz): 7.78 (d, *J* =7.8 Hz, 2H), 7.62 (d, *J* = 6.0 Hz, 2H), 7.44–7.37 (m, 3H), 7.32 (d, *J* = 6.64, 2H), 6.47 (d, *J* =9.7 Hz, 2H), 5.94 (d, *J* = 10.3 Hz, 2H), 4.73–4.56 (m, 4H), 3.12 (s, 1H, –OH, D_2O exchangeable) 2.84–2.78 (m, 2H), 2.47 (t, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.64–1.57 (m, 2H), 1.54–1.46 (m, 4H), 1.37–1.31 (m, 2H), 0.97 (t, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 145.7, 143.6, 142.7, 141.9, 140.8, 129.8, 128.7, 128.4, 127.6, 125.6, 124.4, 124.3, 121.4, 116.5, 111.7, 96.9, 96.4, 75.9, 54.8, 52.2, 33.1, 30.9, 30.0, 22.9, 22.0, 19.3, 13.9, 13.6. **HRMS** (ESI) calcd for $C_{34}H_{38}NO_4S$ $[M+H]^+$ 556.2522, found 556.2527.



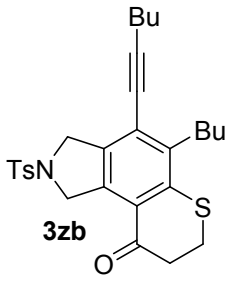
3y

3y: This compound was isolated in (92% yield, 30 mg) as white solid. **^{1}H NMR** (CDCl3, 500 MHz): 7.76 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.49 (d, *J* = 9.1 Hz, 1H), 5.79 (d, *J* = 9.5 Hz, 1H), 4.73–4.49 (m, 4H), 4.08–4.02 (m, 1H), 4.07–4.02 (m, 1H), 3.96–3.91 (m, 1H), 2.78–2.67 (m, 2H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 2.48–2.38 (m, 1H), 2.37–2.32 (m, 1H), 2.13–2.05 (m, 1H), 2.04–1.96 (m, 1H), 1.61-1.57 (m, 2H), 1.53-1.43 (m, 4H), 1.39-1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 148.8, 143.6, 133.8, 132.6, 130.9, 129.8, 129.3, 127.5, 123.5, 123.3, 118.9, 114.5, 104.9, 98.8, 76.6, 68.4, 54.3, 53.1, 38.9, 31.8, 30.8, 27.6, 24.6, 22.9, 21.9, 21.5, 19.4, 14.0, 13.6. **HRMS** (ESI) calcd for $C_{31}H_{38}NO_4S$ $[M+H]^+$ 520.2522, found 520.2509.



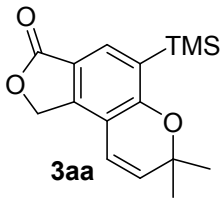
3za

3za: This compound was isolated in (56% yield, 20 mg) as a yellow solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 4.90–4.86 (m, 2H), 4.56–4.51 (m, 2H), 4.47 (t, *J* = 6.7 Hz, 2H), 2.75–2.69 (m, 4H), 2.49 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.64–1.57 (m, 2H), 1.52–1.42 (m, 4H), 1.38–1.31 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.6 Hz, 2H) ;**^{13}C NMR** ($CDCl_3$, 500 MHz): δ 192.1, 159.7, 143.4, 134.2, 134.1, 133.7, 131.7, 129.8, 127.6, 125.3, 115.7, 102.4, 76, 67.0, 55.9, 53.1, 37.8, 31.6, 30.6, 27.7, 22.8, 22.0, 21.5, 19.5, 13.9, 13.6; **HRMS** (ESI) calcd for $C_{28}H_{34}NO_4S$ $[M+H]^+$ 488.2209, found 488.2202.



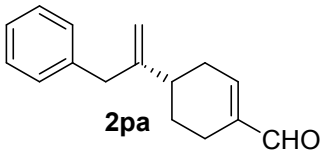
3zb

3zb: This compound was isolated in (51% yield, 17 mg) as a yellow solid. **^{1}H NMR** (CDCl3, 500 MHz): 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* =8.2 Hz, 2H), 4.92 (s, 2H), 4.92 (s, 2H), 3.17-3.12 (m, 2H), 2.92-2.87 (m, 2H), 2.86-2.81 (m, 2H), 2.50 (t, *J* = 7.04 Hz, 2H), 2.39 (s, 3H), 1.64-1.57 (m, 2H), 1.52-1.46 (m, 4H), 1.44-1.36 (m, 2H), 0.99-092 (m, 6H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 194.8, 143.5, 141.8, 141.1, 136.8, 136.4, 133.9, 129.8, 127.6, 125.2, 123.5, 102.6, 76.2, 56.9, 39.8, 32.1, 25.8, 23.0, 22.0, 21.5, 19.5, 13.8, 13.6; **HRMS** (ESI) calcd for $C_{28}H_{34}NO_4S$ $[M+H]^+$ 488.2209, found 488.2202; **HRMS** (ESI) calcd for $C_{28}H_{34}NO_3S_2$ $[M+H]^+$ 496.1980, found 496.1997.



3aa

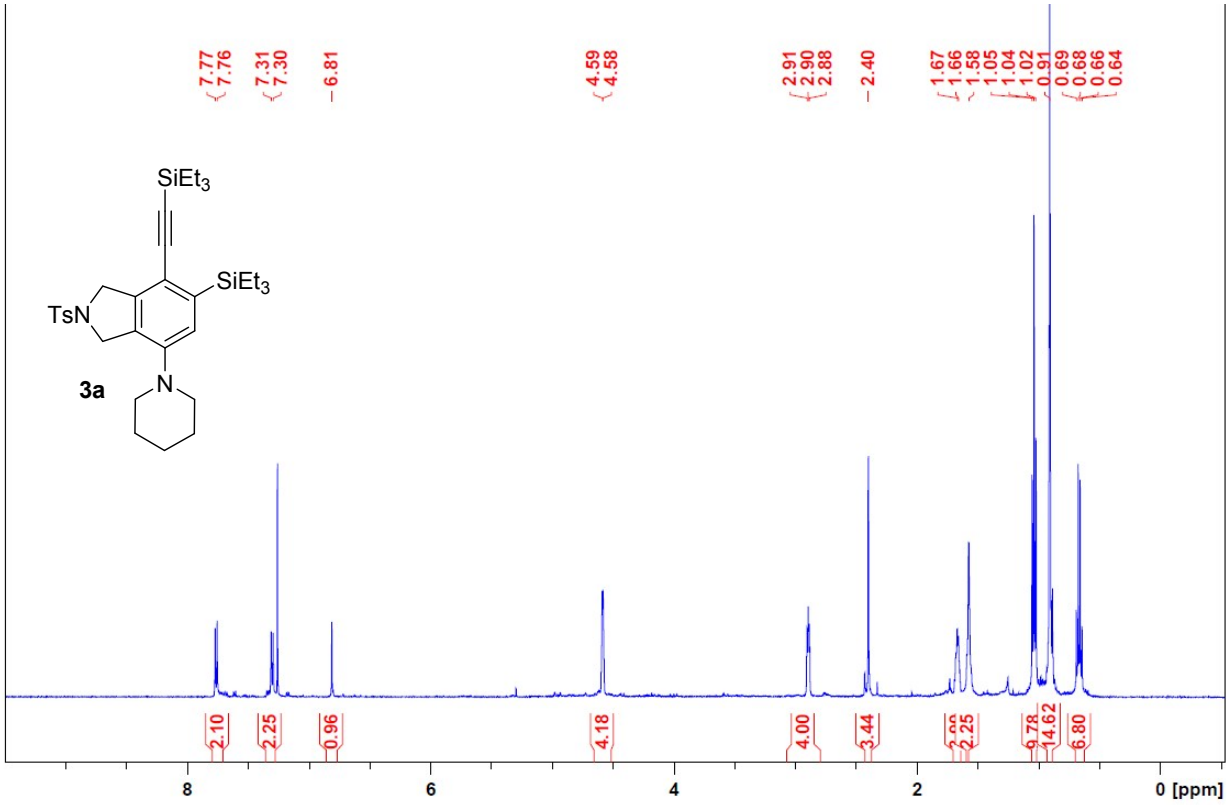
3aa: This compound was isolated in (86% yield, 28 mg) as a white solid. **^{1}H NMR** (CDCl3, 500 MHz): 7.75 (s, 1H), 6.21 (d, *J* = 10.2 Hz, 1H), 5.72 (d, *J* = 9.7 Hz, 1H), 5.21 (s, 2H), 1.5 (s, 6H), 0.3 (s, 9H); **^{13}C NMR** ($CDCl_3$, 500 MHz): 171.2, 162.2, 144.9, 132.2, 131.6, 129.3, 117.5, 116.9, 113.4, 77.9, 69.3, 67.8, 28.3, -1.06; **HRMS** (ESI) calcd for $C_{16}H_{21}O_3Si$ $[M+H]^+$ 298.1260, found 298.1265.

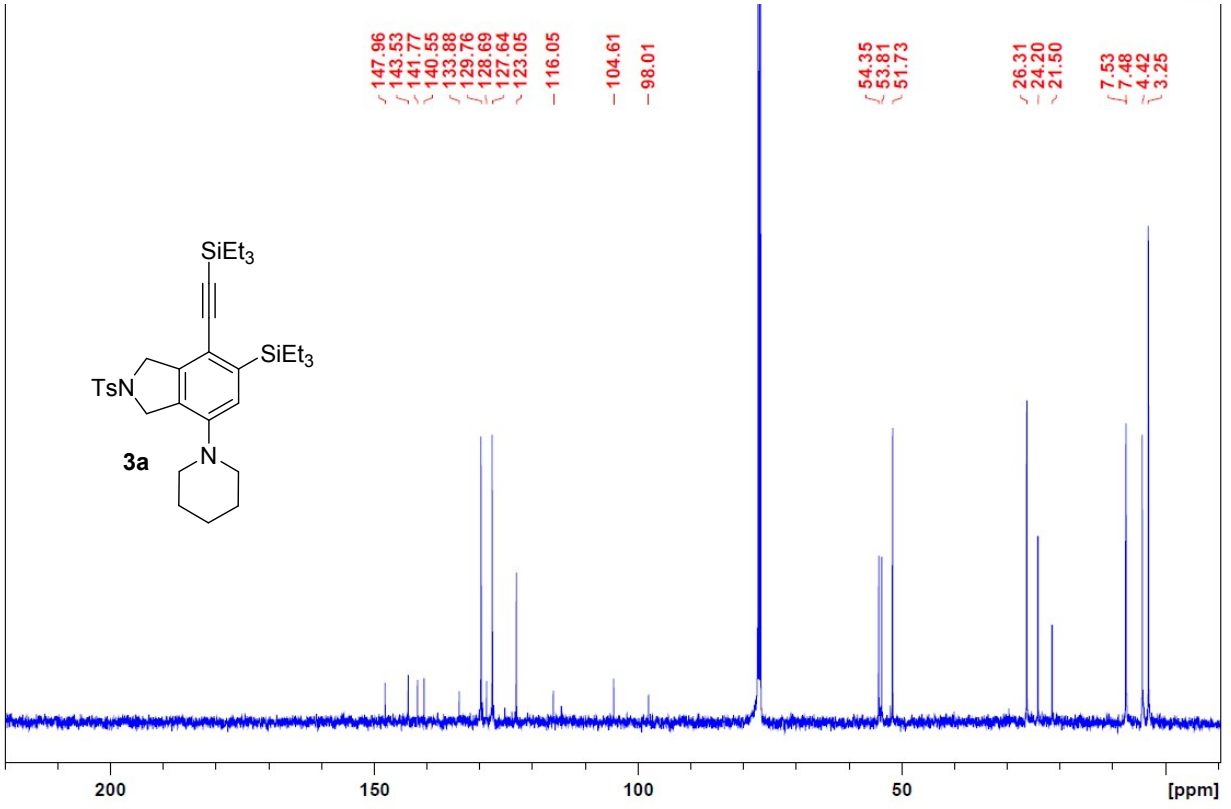


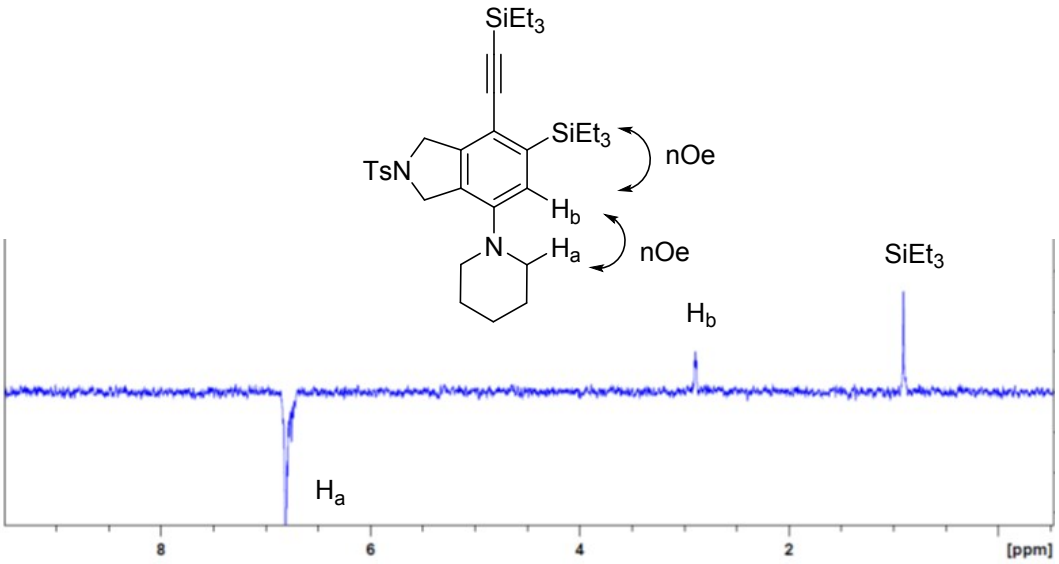
2pa

2pa: This compound was isolated in (75% yield, 38 mg) as a yellow solid. **^{1}H NMR** (CDCl3, 500 MHz): δ 9.41 (s, 1H), 7.31–7.27 (m, 2H), 6.79–6.76 (m, 1H), 4.90 (s, 1H), 4.81 (s, 1H), 3.42 (s, 2H), 2.51–2.37 (m, 2H), 2.28–2.16 (m, 2H), 2.12–2.01 (m, 1H), 1.95–1.88 (m, 1H), 1.52–1.42 (m, 1H); **^{13}C NMR** ($CDCl_3$, 500 MHz): δ 193.8, 151.9, 150.5, 141.2, 139.5, 129.0, 128.4, 126.2, 110.9, 42.0, 38.4, 32.4, 26.7, 21.6; **HRMS** (ESI) calcd for $C_{16}H_{18}O$ $[M+H]^+$ 226.1357, found 226.1359.

^{1}H, ^{13}C NMRs and Selected nOE Spectra



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Ha
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Hb
Ha
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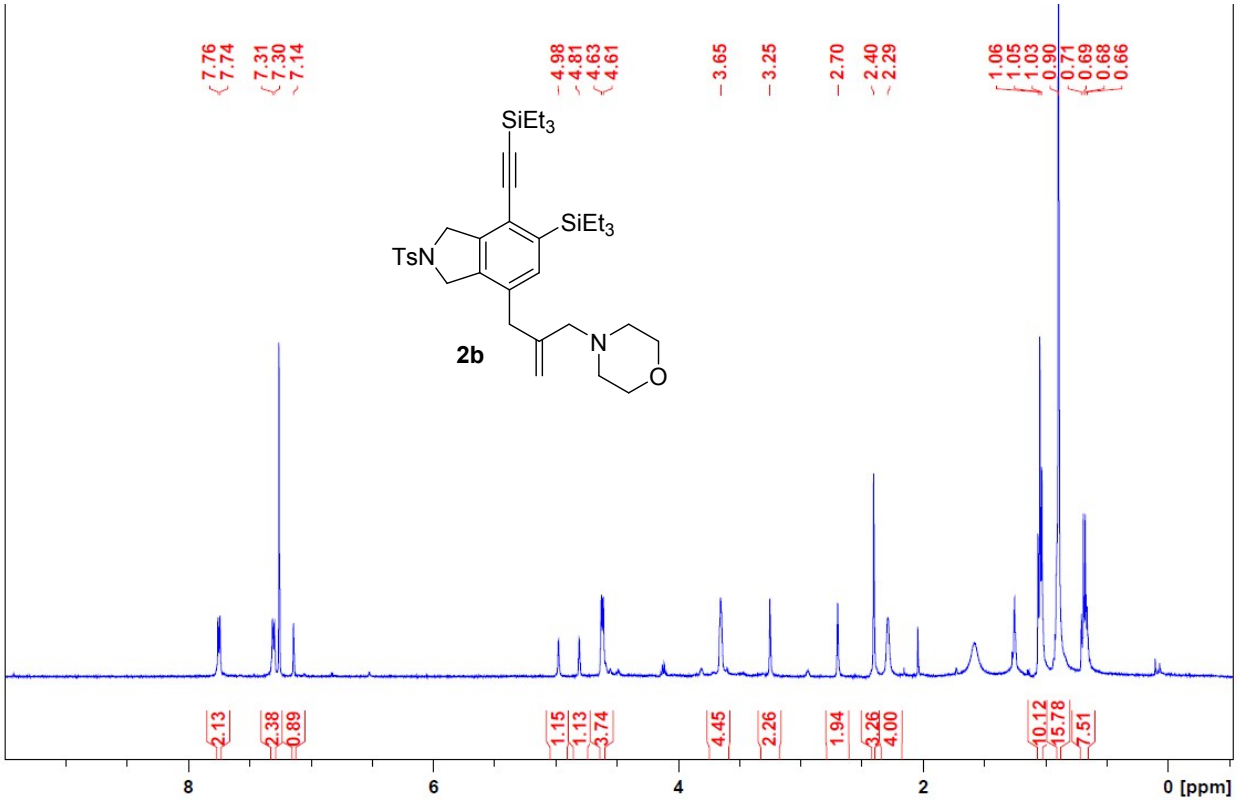
4
2
[ppm]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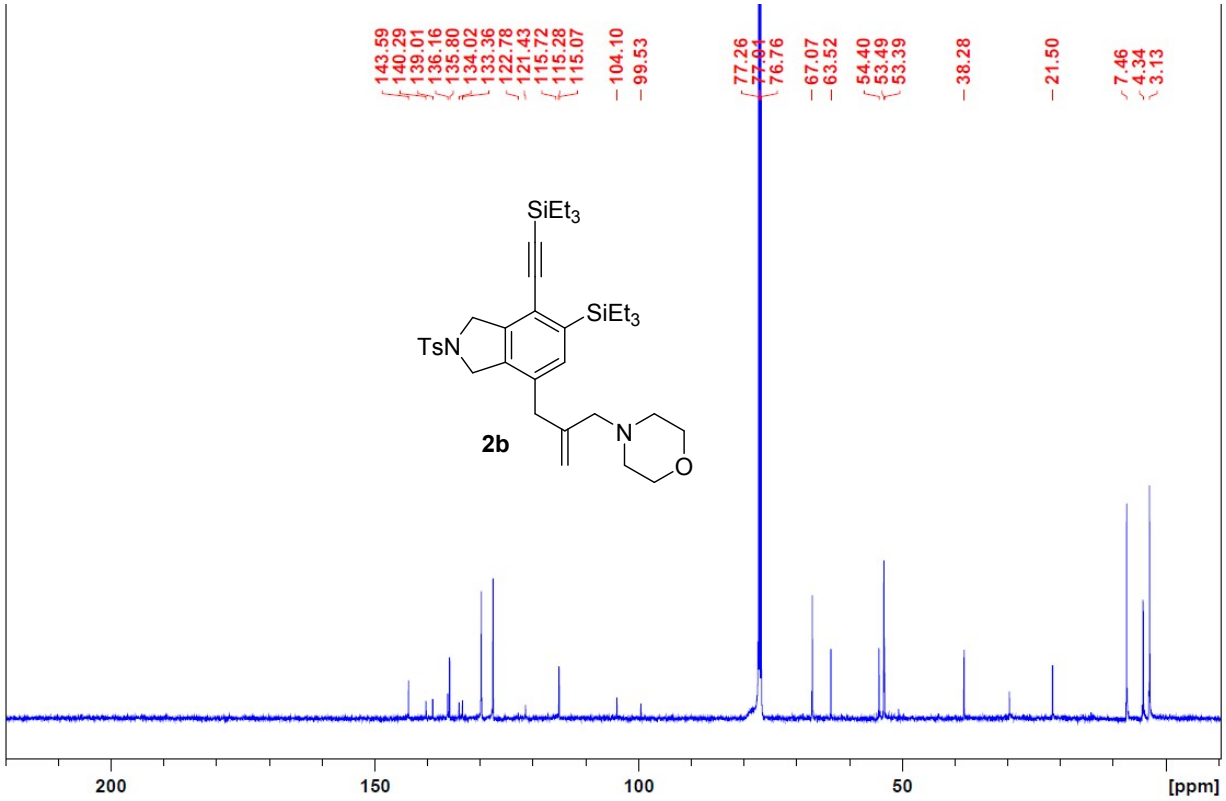
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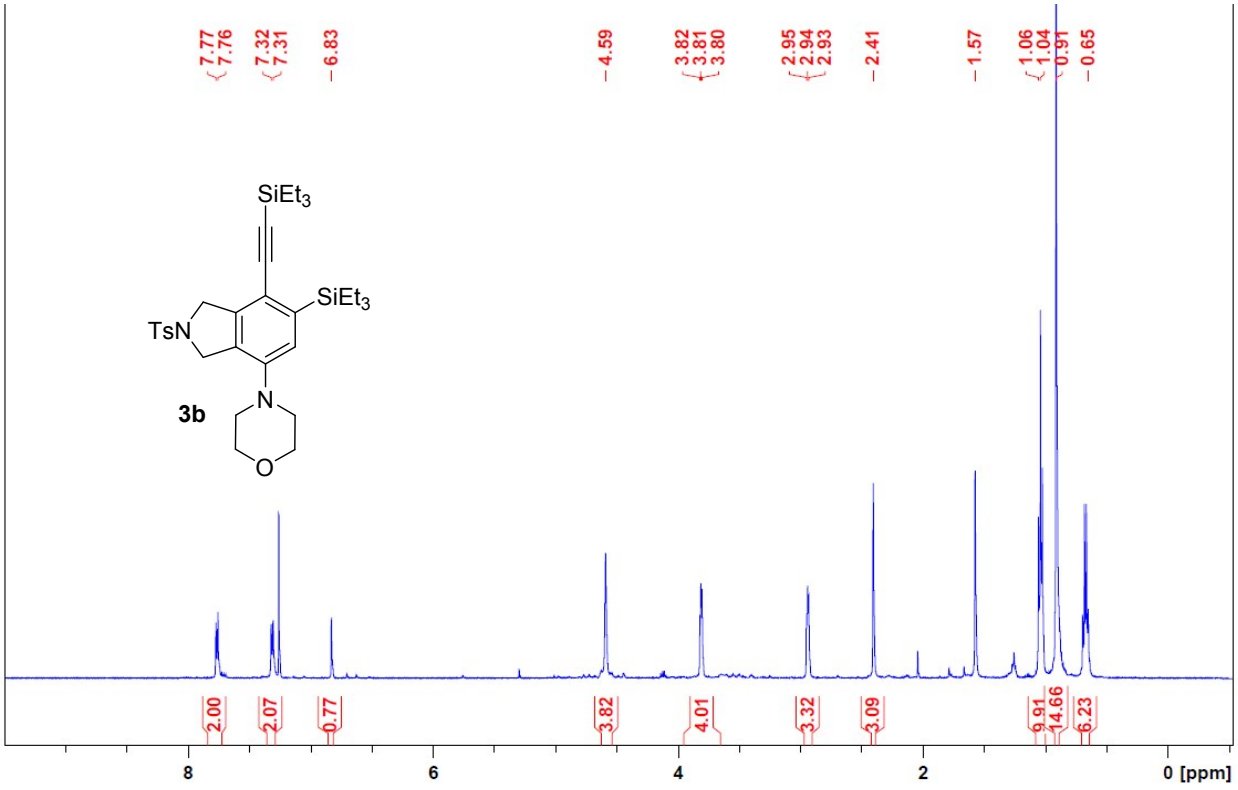
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SiEt3
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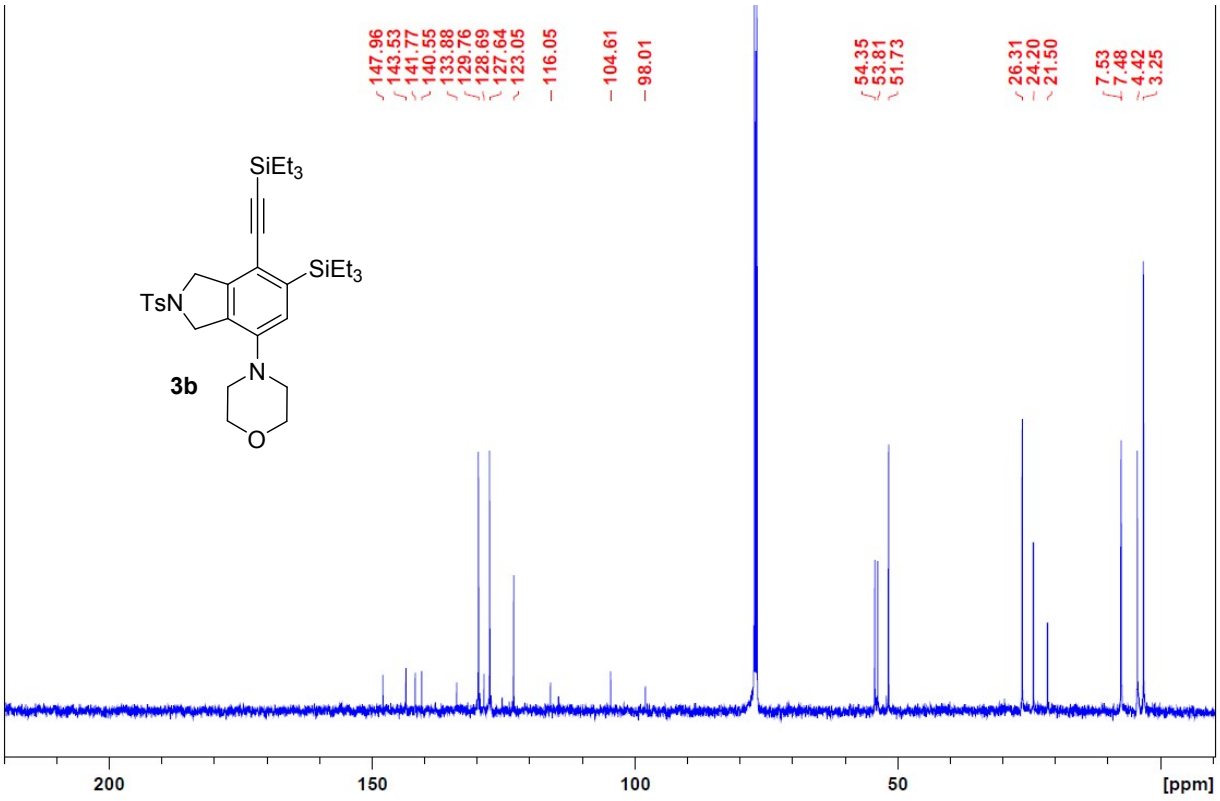
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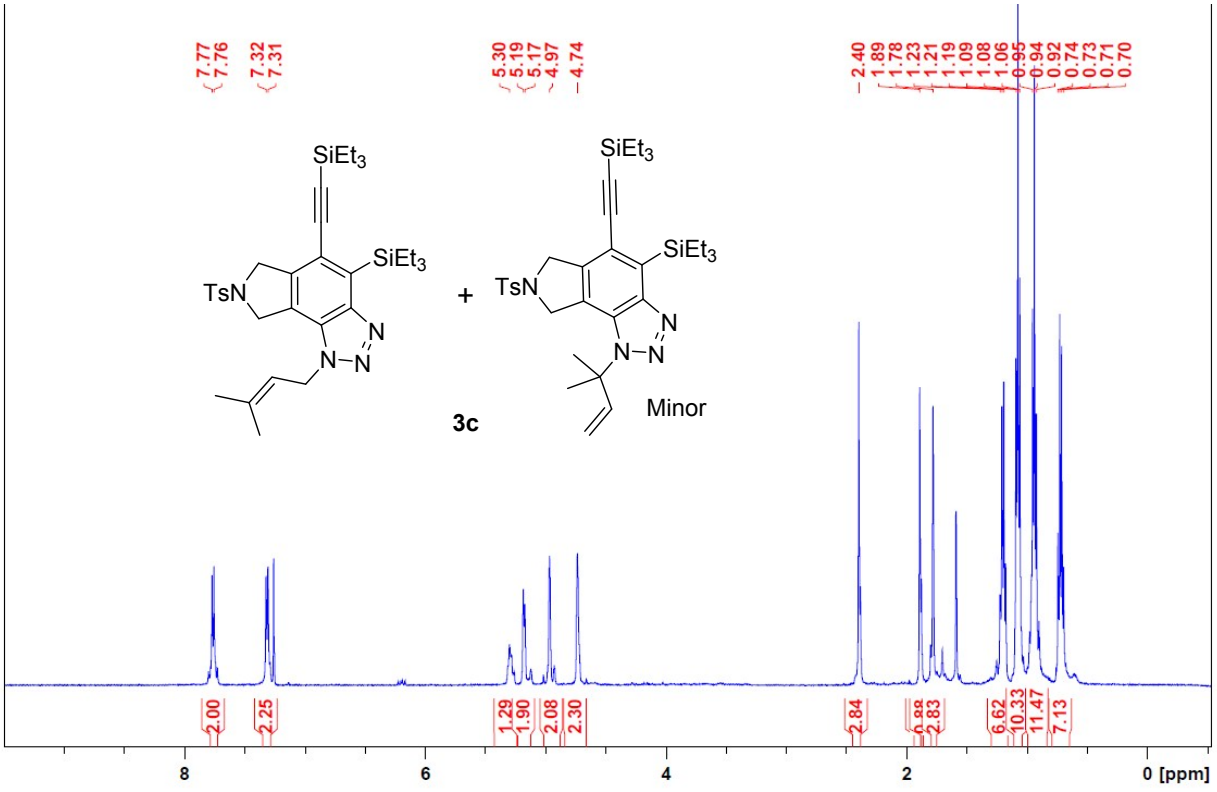
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Minor
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11.47
7.13
8
6
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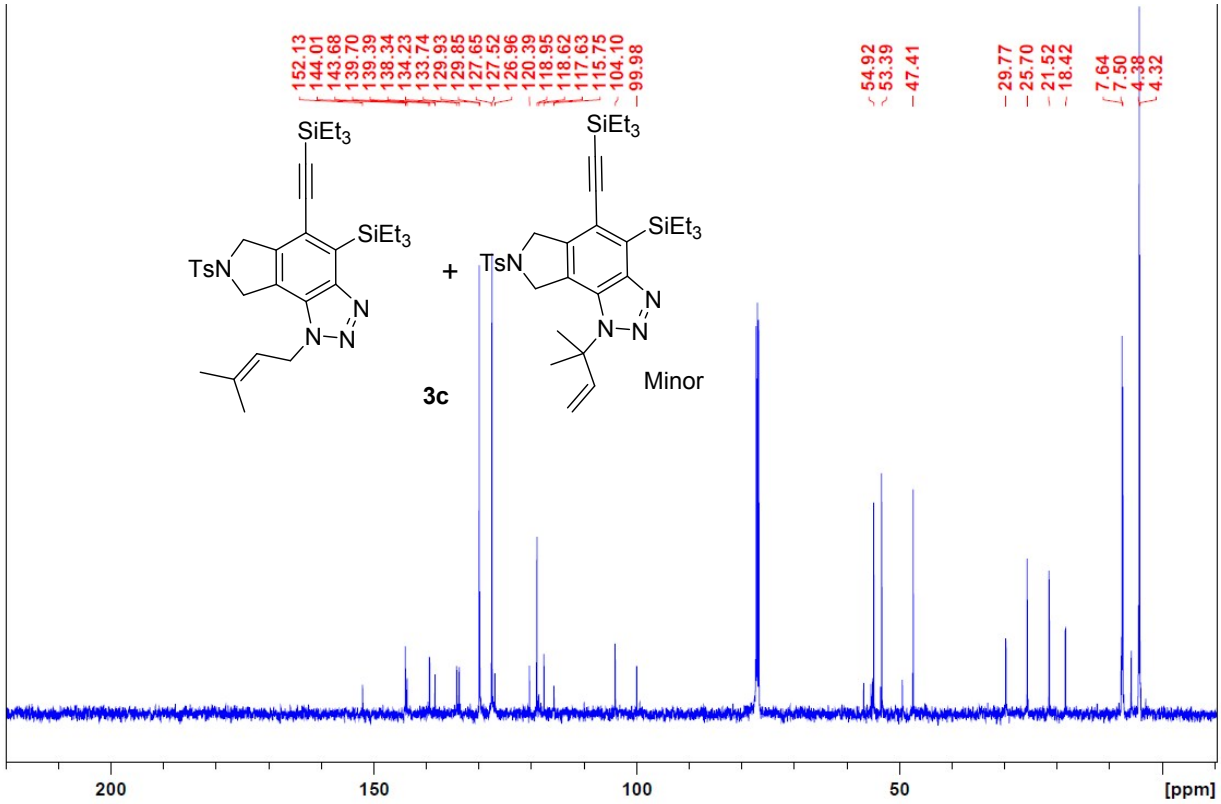
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127.52
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118.95
118.62
117.63
115.75
104.10
99.98
54.92
53.39
47.41
29.77
25.70
21.52
18.42
7.64
7.50
4.38
4.32
SiEt3
SiEt3
TsN
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+
SiEt3
SiEt3
TsN
N
N–N
Minor
3c
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100
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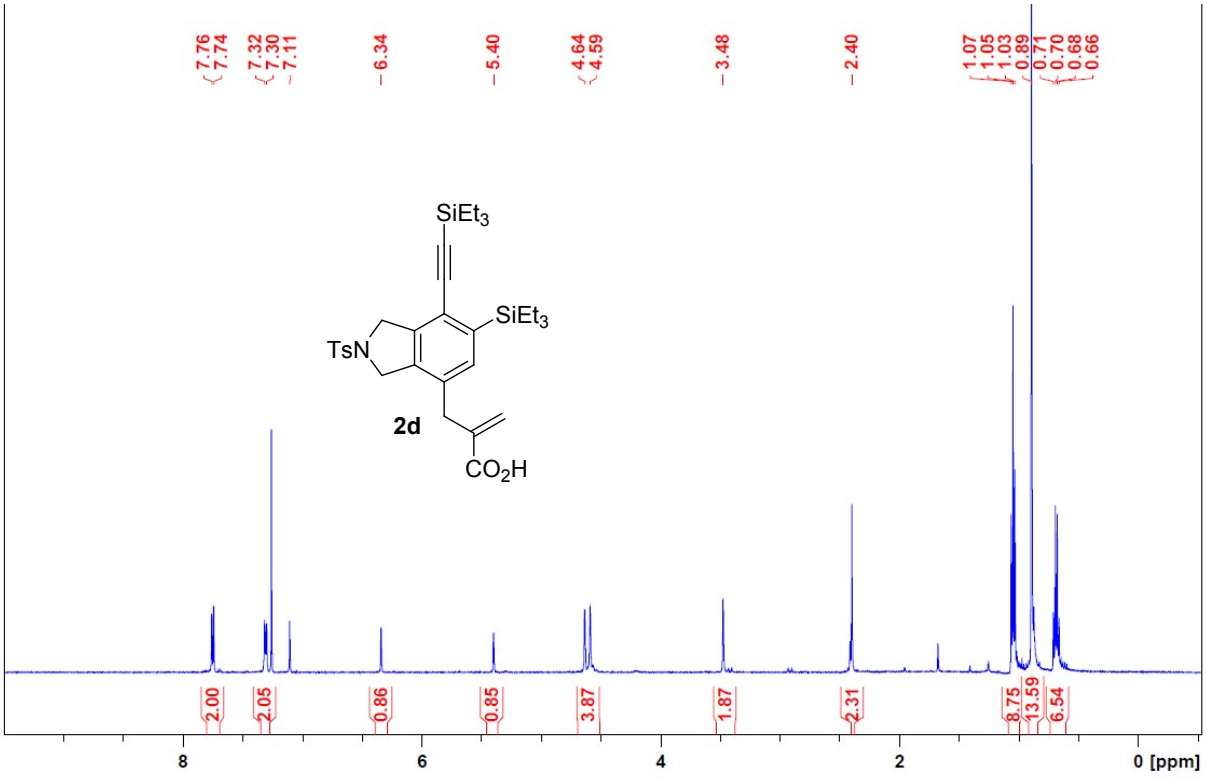
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4.64
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3.48
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1.05
1.03
0.89
0.71
0.70
0.68
0.66
SiEt3
SiEt3
TsN
2d
CO2H
2.00
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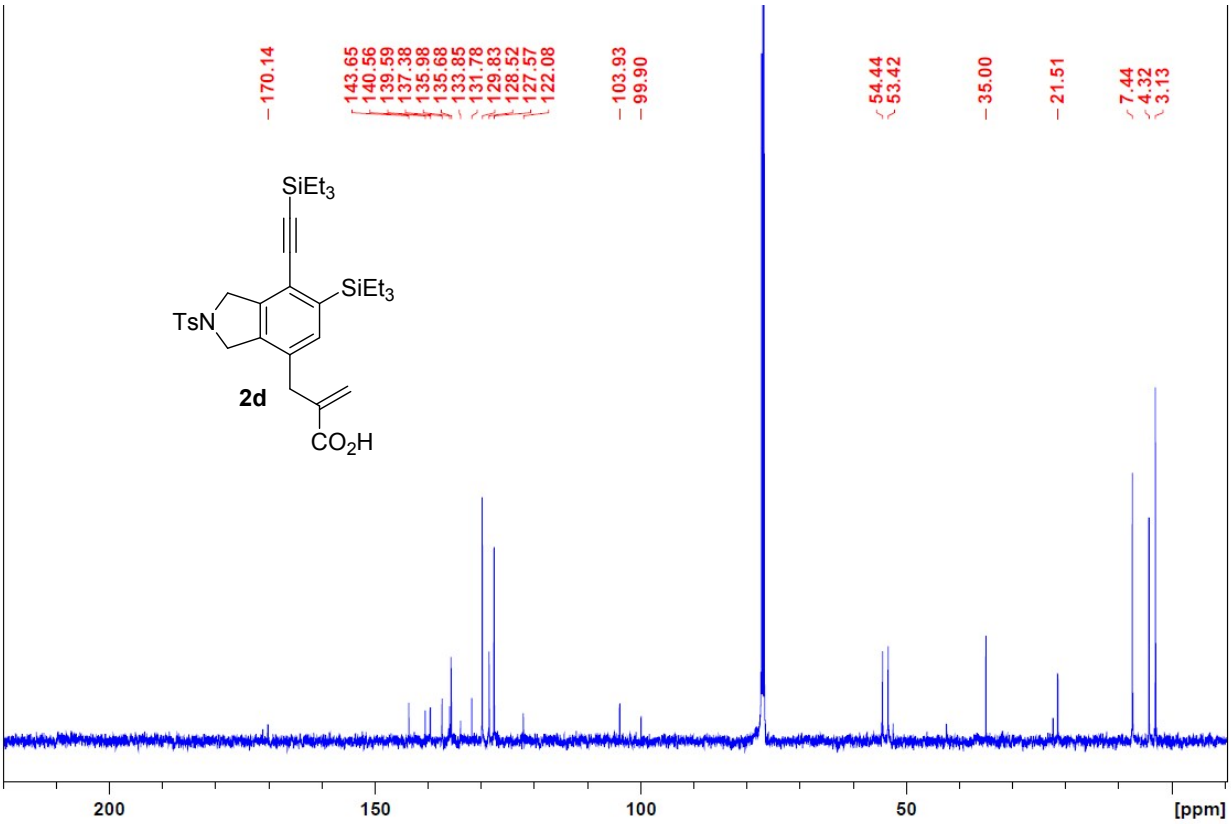
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53.42
35.00
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3.13
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SiEt3
TsN
2d
CO2H
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100
50
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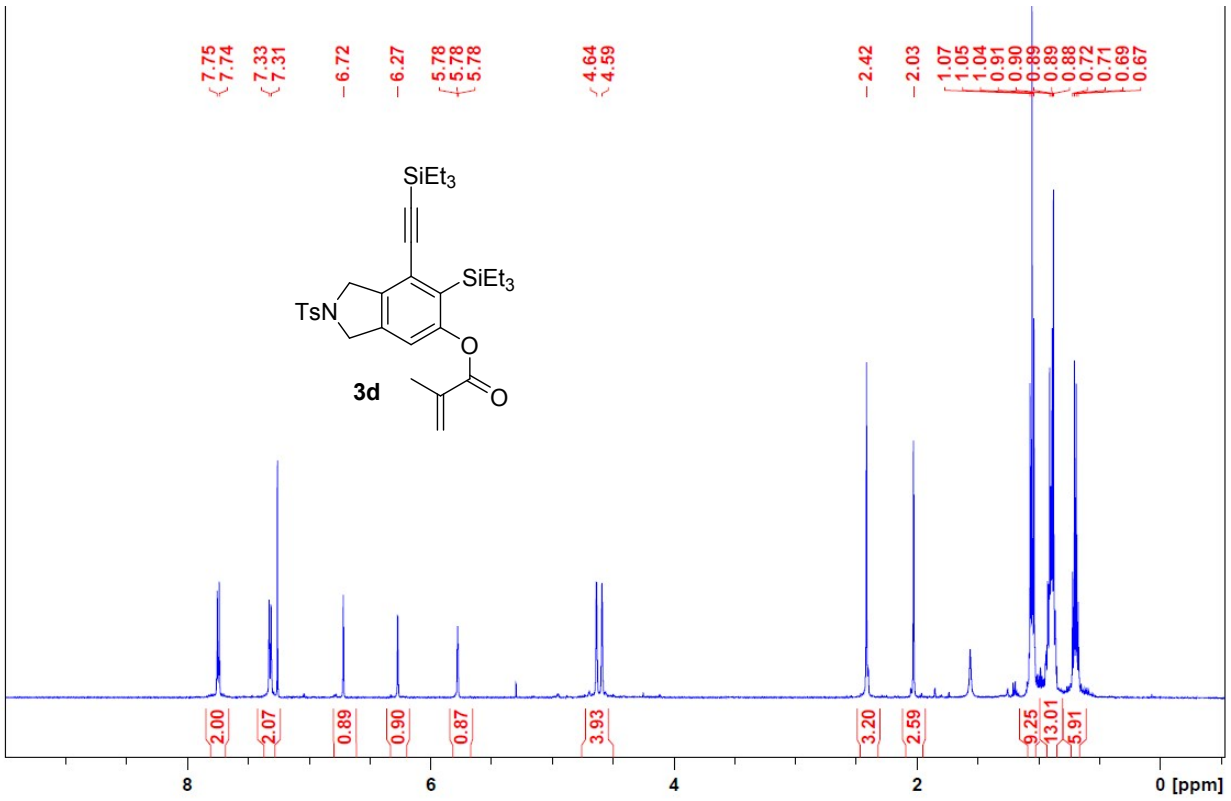
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5.78
5.78
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4.59
2.42
2.03
1.07
1.05
1.04
0.91
0.90
0.89
0.89
0.88
0.72
0.71
0.69
0.67
SiEt3
SiEt3
TsN
O
O
3d
2.00
2.07
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3.93
3.20
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5.91
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4
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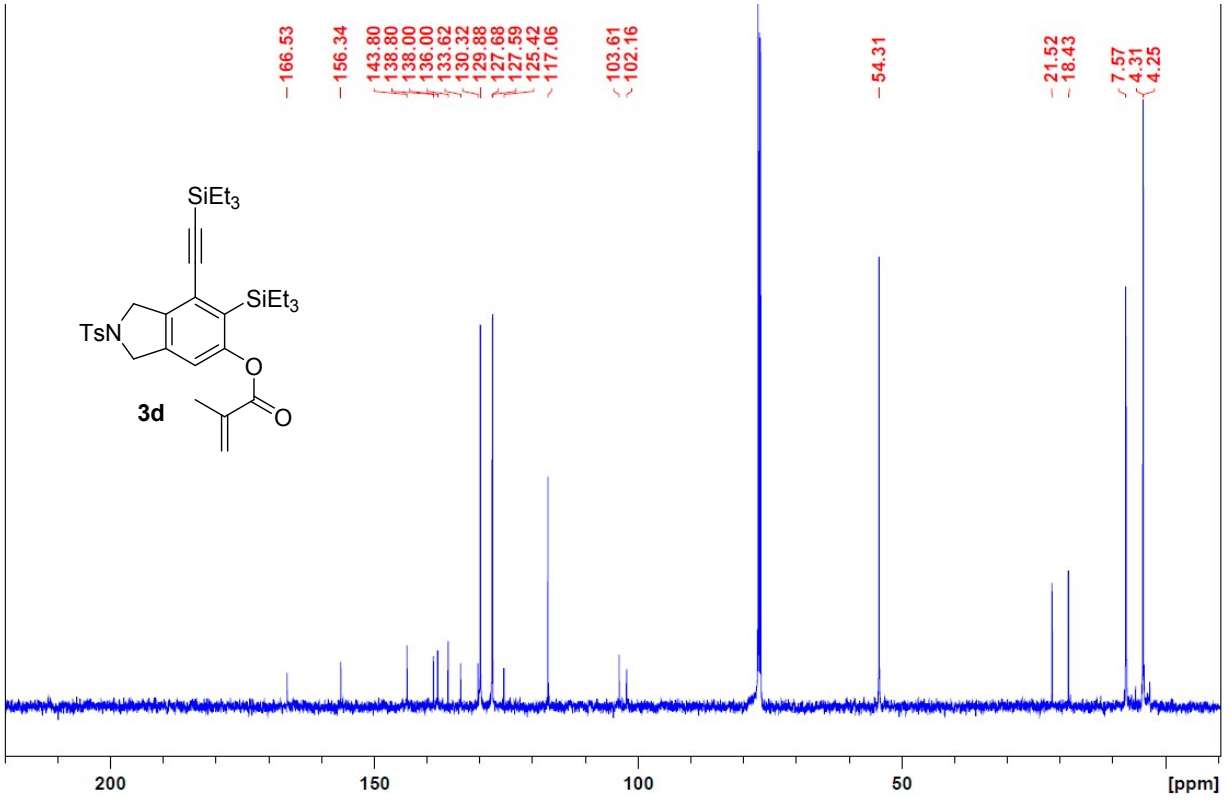
0 [ppm]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127.68
127.59
125.42
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102.16
54.31
21.52
18.43
7.57
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4.25
SiEt3
SiEt3
TsN
O
O
3d
200
150
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50
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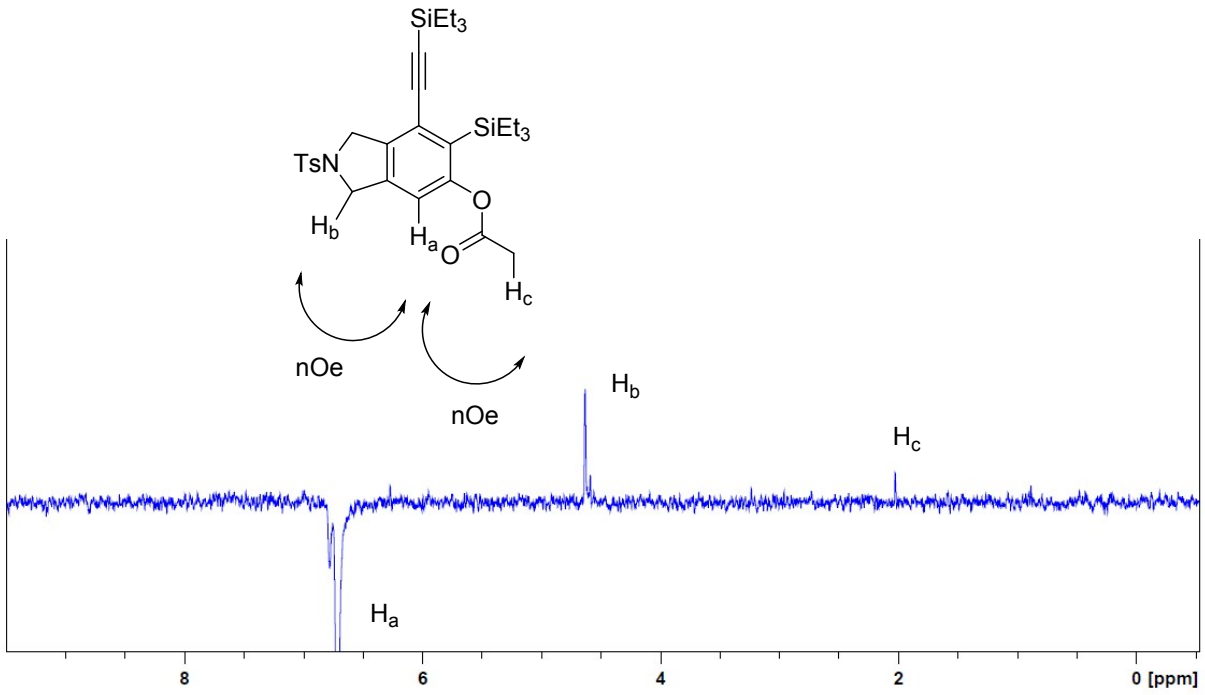
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SiEt3
TsN
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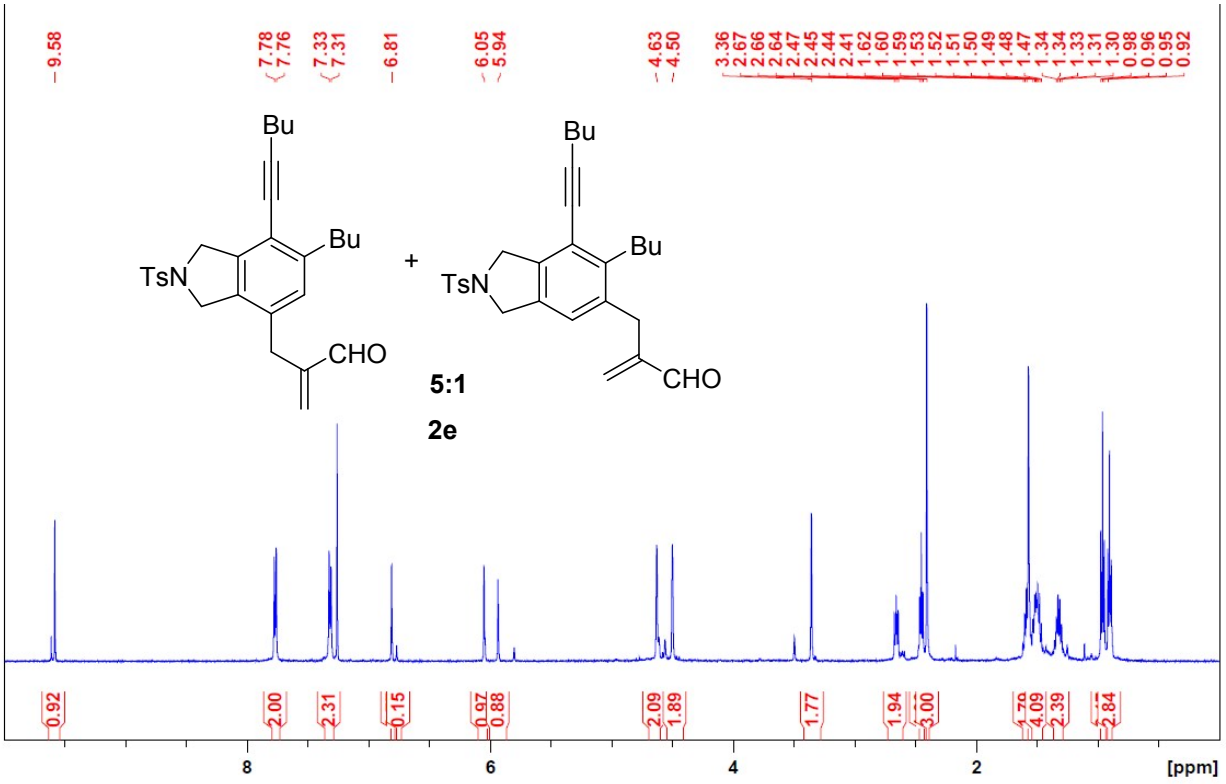
O
Hc
nOe
nOe
Hb
Hc
Ha
8
6
4
2
0 [ppm]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2.64
2.47
2.45
2.44
2.41
1.62
1.60
1.59
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.34
1.34
1.33
1.31
1.30
0.98
0.96
0.95
0.92
Bu
Bu
TsN
CHO
+
Bu
Bu
TsN
CHO
5:1
2e
0.92
2.00
2.31
0.15
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1.89
1.77
1.94
3.00
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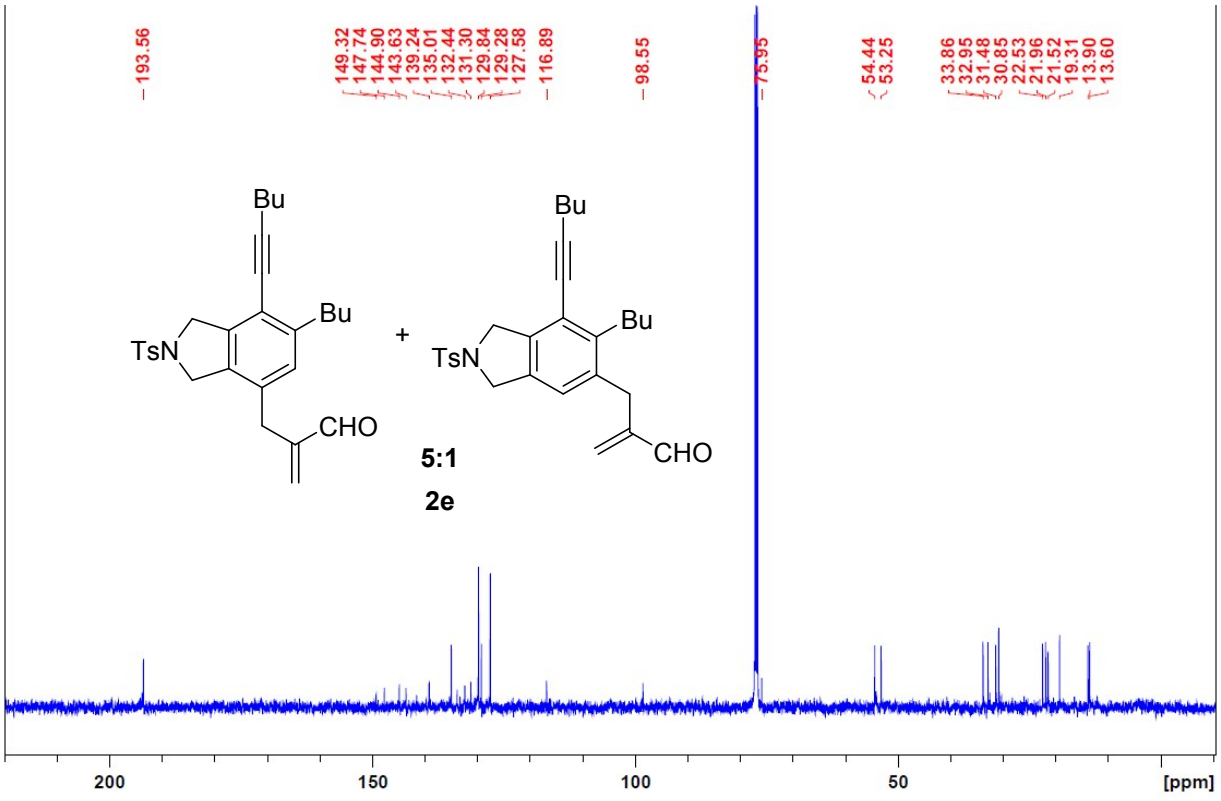
4
2
[ppm]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135.01
132.44
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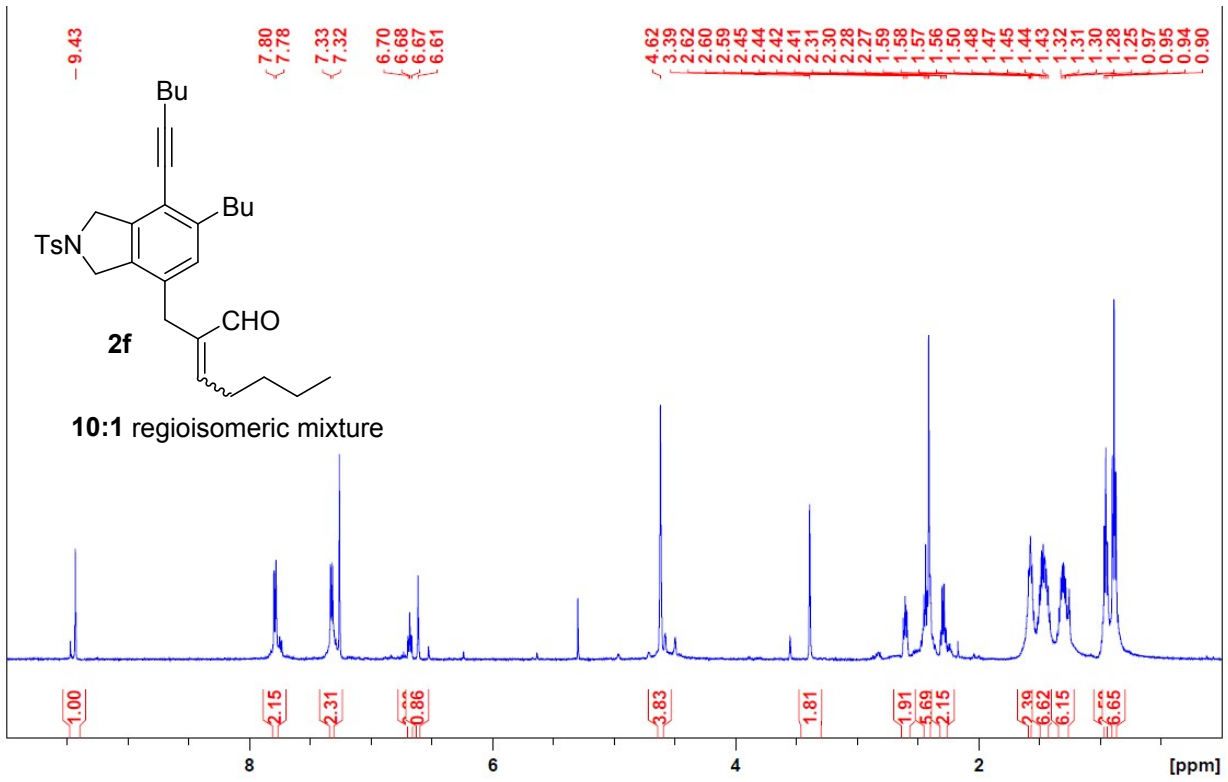
129.84
129.28
127.58
116.89
98.55
75.95
54.44
53.25
33.86
32.95
31.48
30.85
22.53
21.96
21.52
19.31
13.90
13.60
Bu
Bu
TsN
CHO
+
Bu
Bu
TsN
CHO
5:1
2e
200
150
100
50
[ppm]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3.39
2.62
2.60
2.59
2.45
2.44
2.42
2.41
2.31
2.30
2.28
2.27
1.59
1.58
1.57
1.56
1.50
1.48
1.47
1.45
1.44
1.43
1.32
1.31
1.30
1.28
1.25
0.97
0.95
0.94
0.90
Bu
Bu
TsN
CHO
2f
10:1 regioisomeric mixture
1.00
2.15
2.31
6.86
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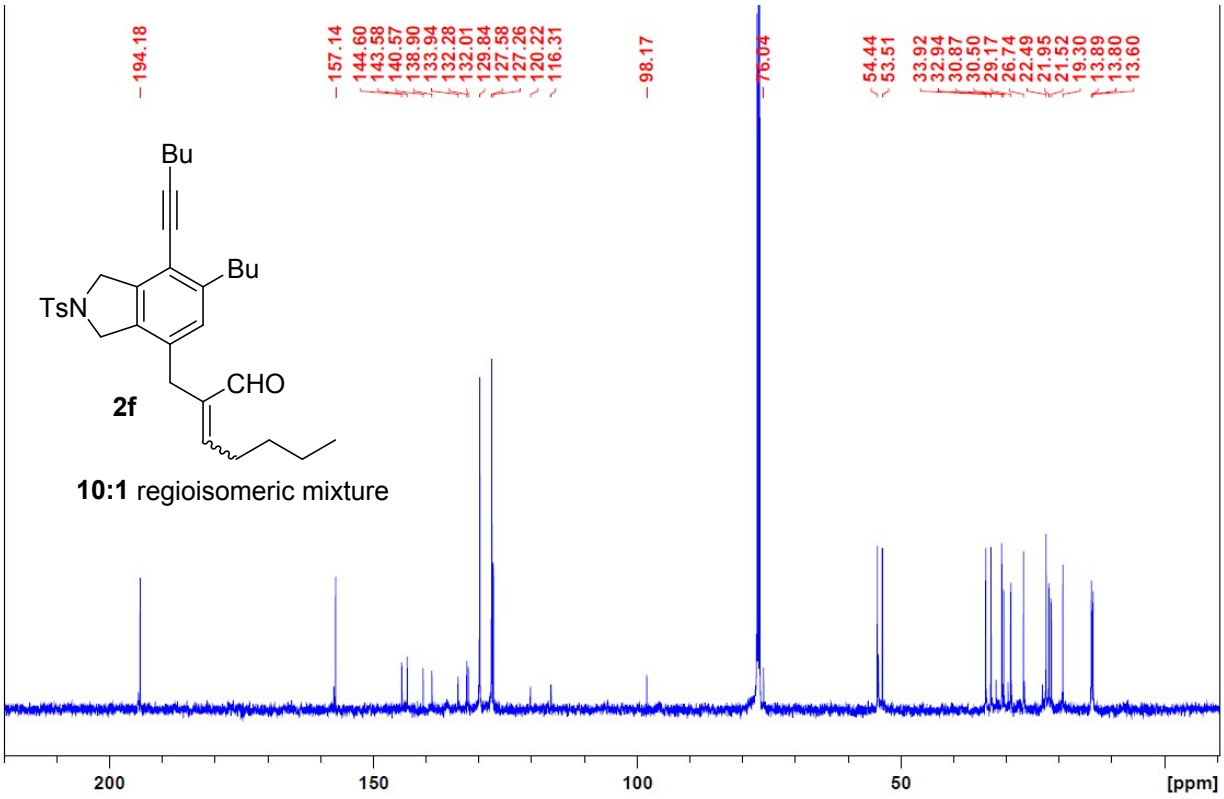
1.81
1.91
5.69
2.15
2.39
6.62
6.15
6.65
8
6
4
2
[ppm]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133.94
132.28
132.01
129.84
127.58
127.26
120.22
116.31
98.17
76.04
54.44
53.51
33.92
32.94
30.87
30.50
29.17
26.74
22.49
21.95
21.52
19.30
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Bu
Bu
TsN
CHO
2f
10:1 regioisomeric mixture
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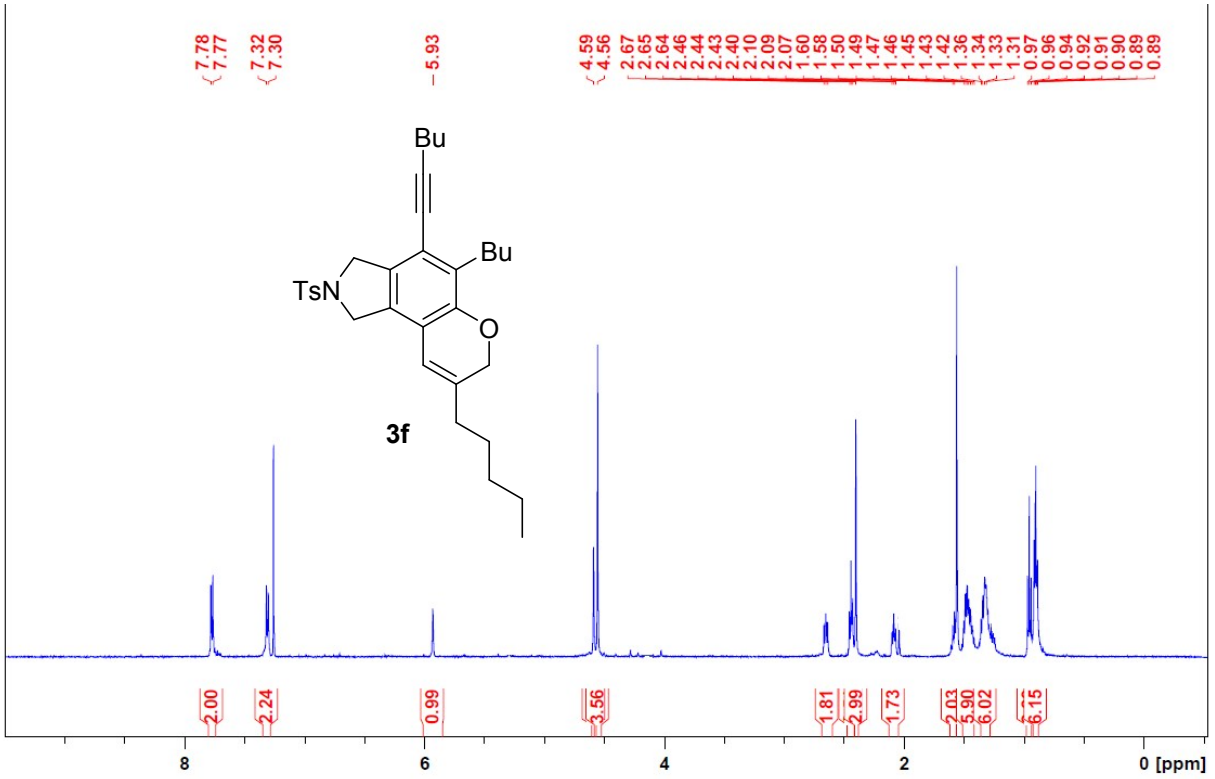
150
100
50
[ppm]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4.59
4.56
2.67
2.65
2.64
2.46
2.44
2.43
2.40
2.10
2.09
2.07
1.60
1.58
1.50
1.49
1.47
1.46
1.45
1.43
1.42
1.36
1.34
1.33
1.31
0.97
0.96
0.94
0.92
0.91
0.90
0.89
0.89
Bu
Bu
TsN
O
3f
2.00
2.24
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2.99
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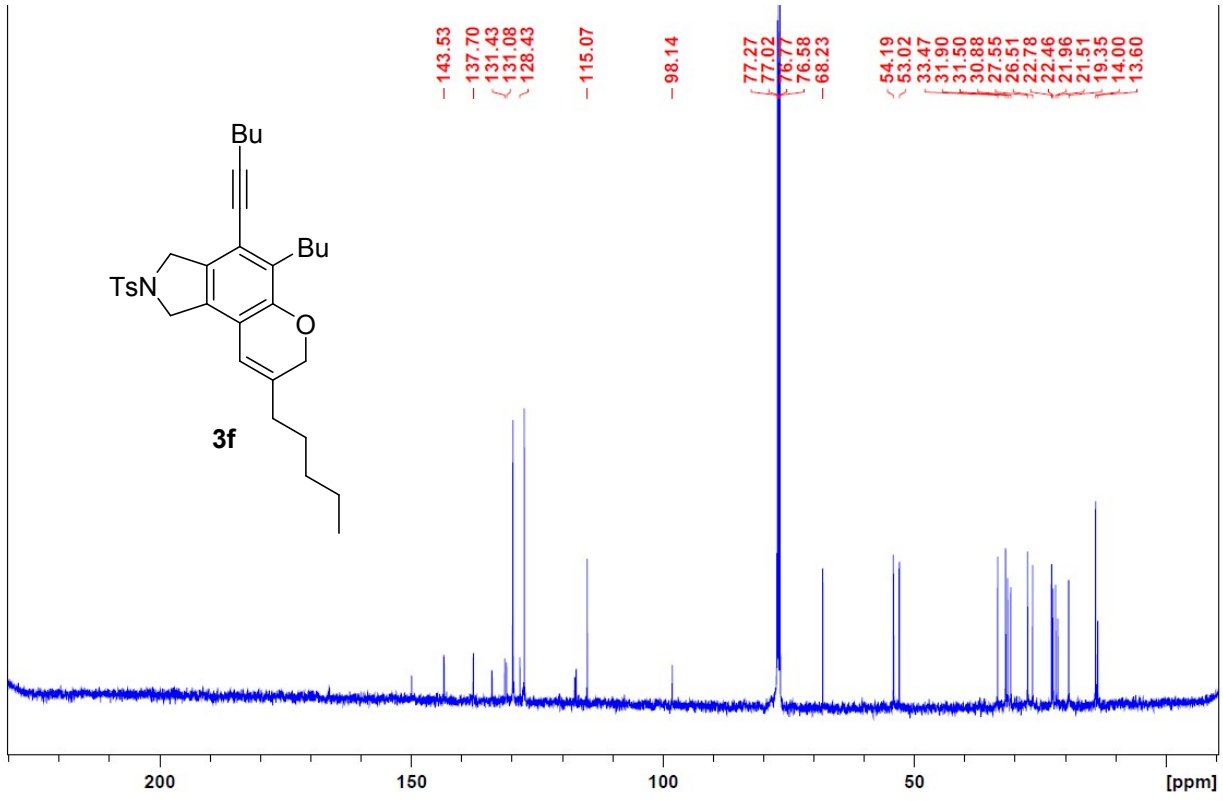
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77.02
76.77
76.58
68.23
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53.02
33.47
31.90
31.50
30.88
27.55
26.51
22.78
22.46
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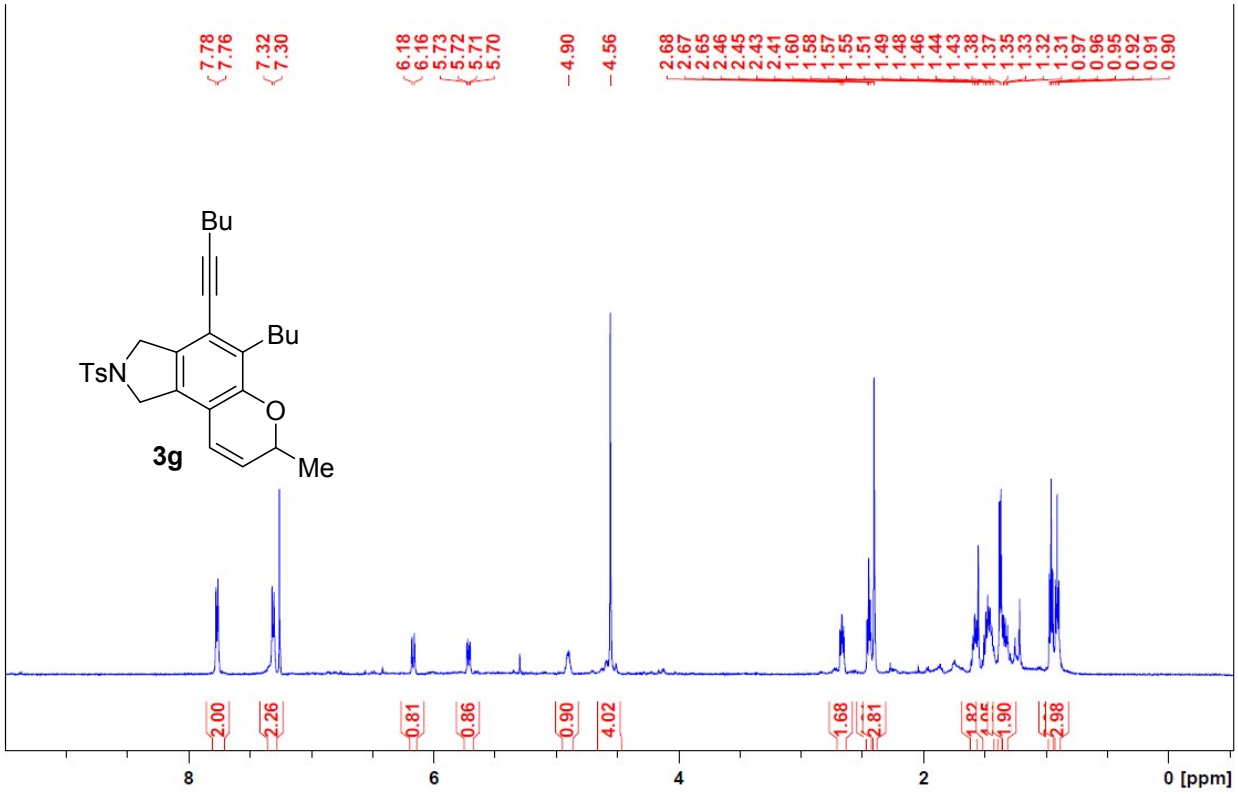
19.35
14.00
13.60
Bu
Bu
TsN
O
3f
200
150
100
50
[ppm]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5.70
4.90
4.56
2.68
2.67
2.65
2.46
2.45
2.43
2.41
1.60
1.58
1.57
1.55
1.51
1.49
1.48
1.46
1.44
1.43
1.38
1.37
1.35
1.33
1.32
1.31
0.97
0.96
0.95
0.92
0.91
0.90
Bu
Bu
TsN
O
Me
3g
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0.90
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2.98
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4
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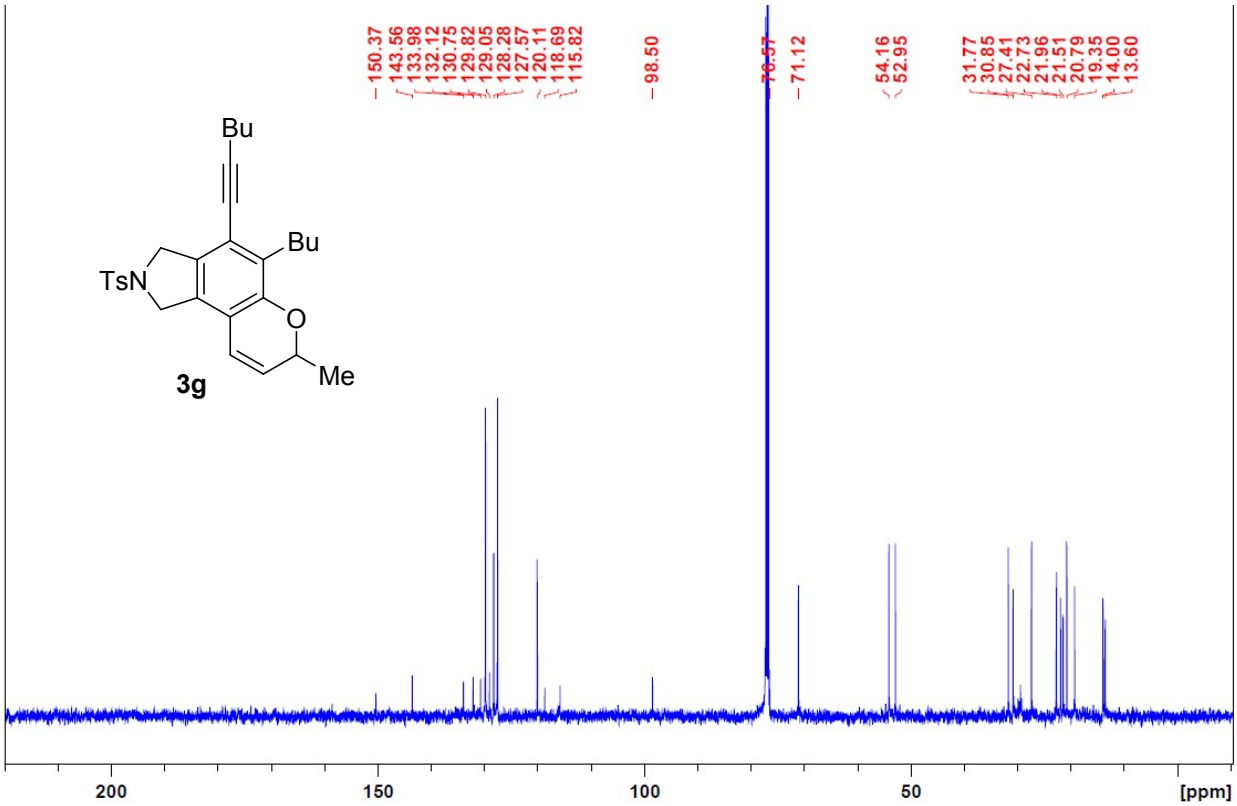
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31.77
30.85
27.41
22.73
21.96
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Bu
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3g
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100
50
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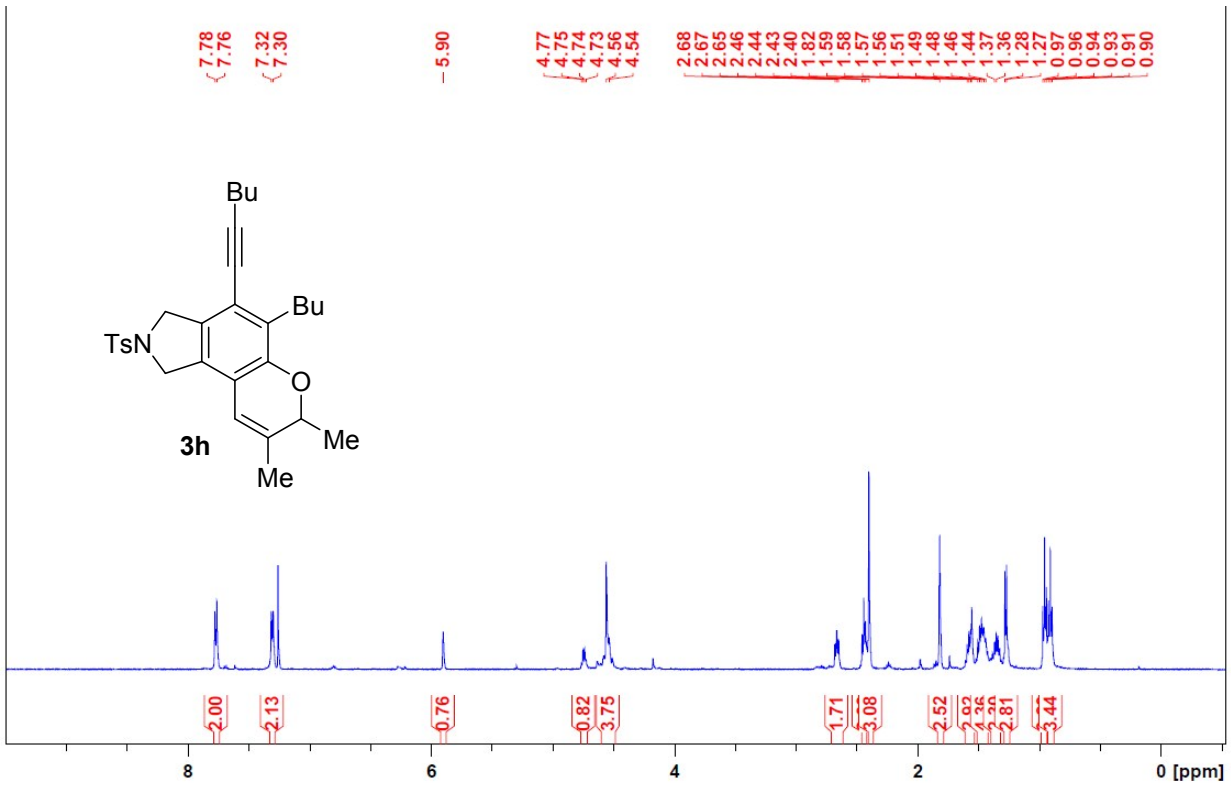
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4.56
4.54
2.68
2.67
2.65
2.46
2.44
2.43
2.40
1.82
1.59
1.58
1.57
1.56
1.51
1.49
1.48
1.46
1.44
1.37
1.36
1.28
1.27
0.97
0.96
0.94
0.93
0.91
0.90
Bu
Bu
TsN
O
Me
Me
3h
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1.71
3.08
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3.44
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4
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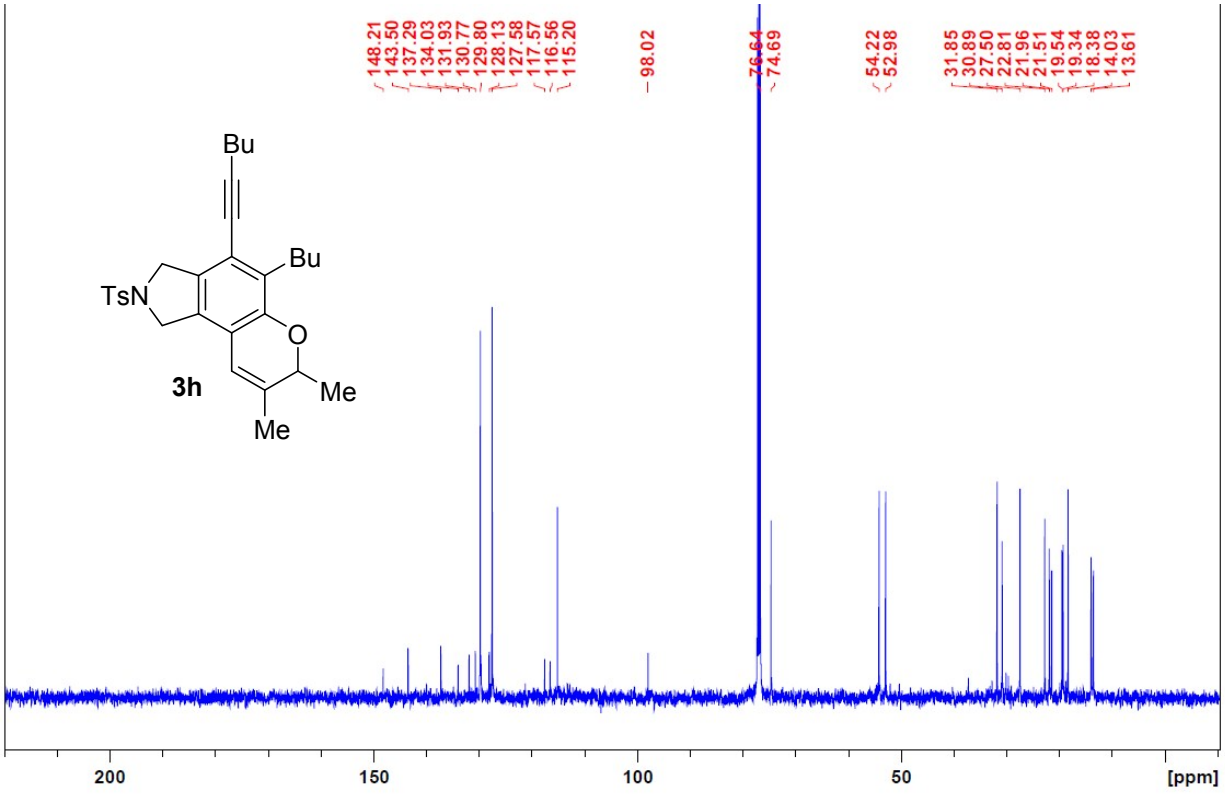
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27.50
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21.96
21.51
19.54
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Bu
TsN
O
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Me
3h
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150
100
50
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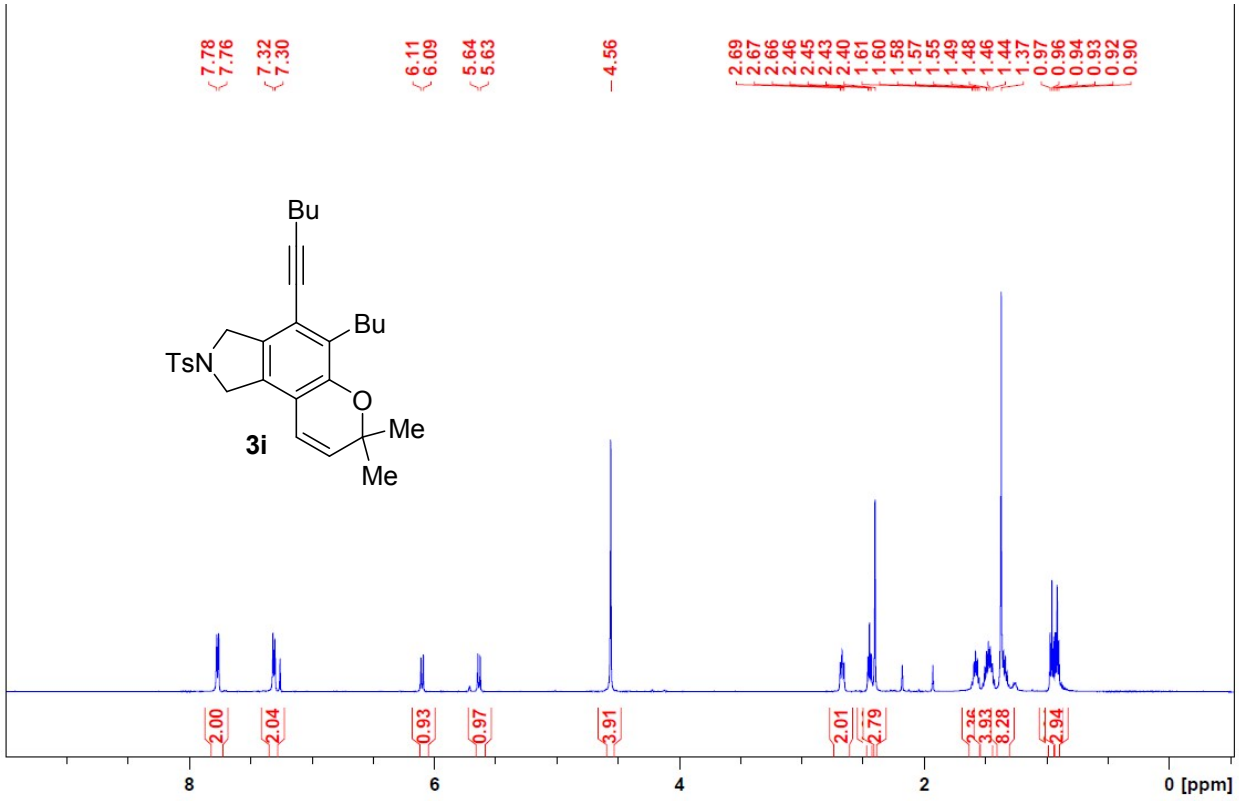
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1.57
1.55
1.49
1.48
1.46
1.44
1.37
0.97
0.96
0.94
0.93
0.92
0.90
Bu
Bu
TsN
O
Me
Me
3i
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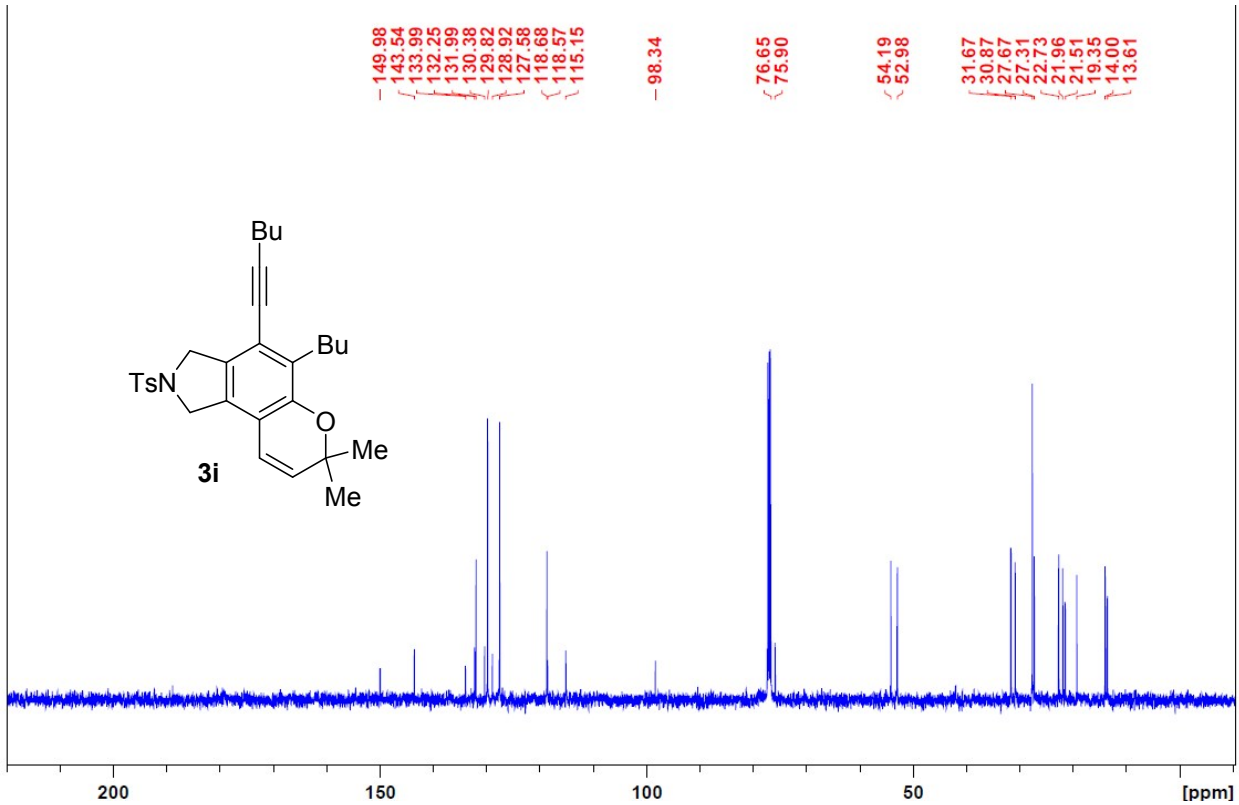
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118.57
115.15
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27.31
22.73
21.96
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13.61
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Bu
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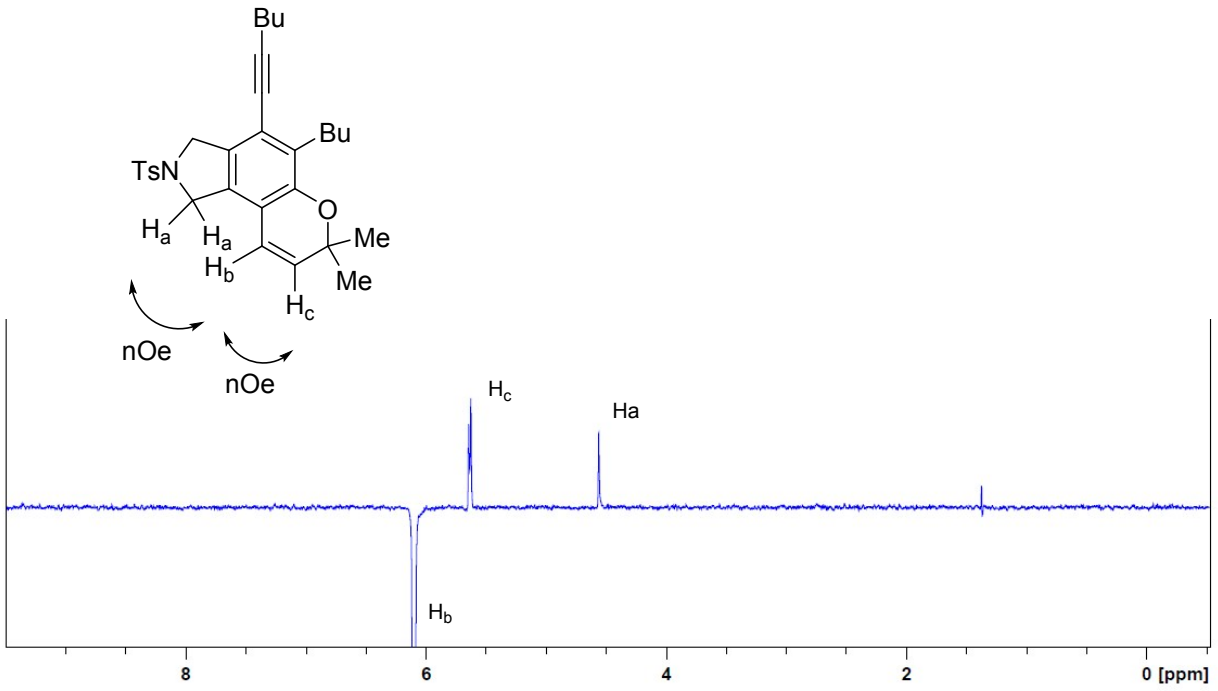
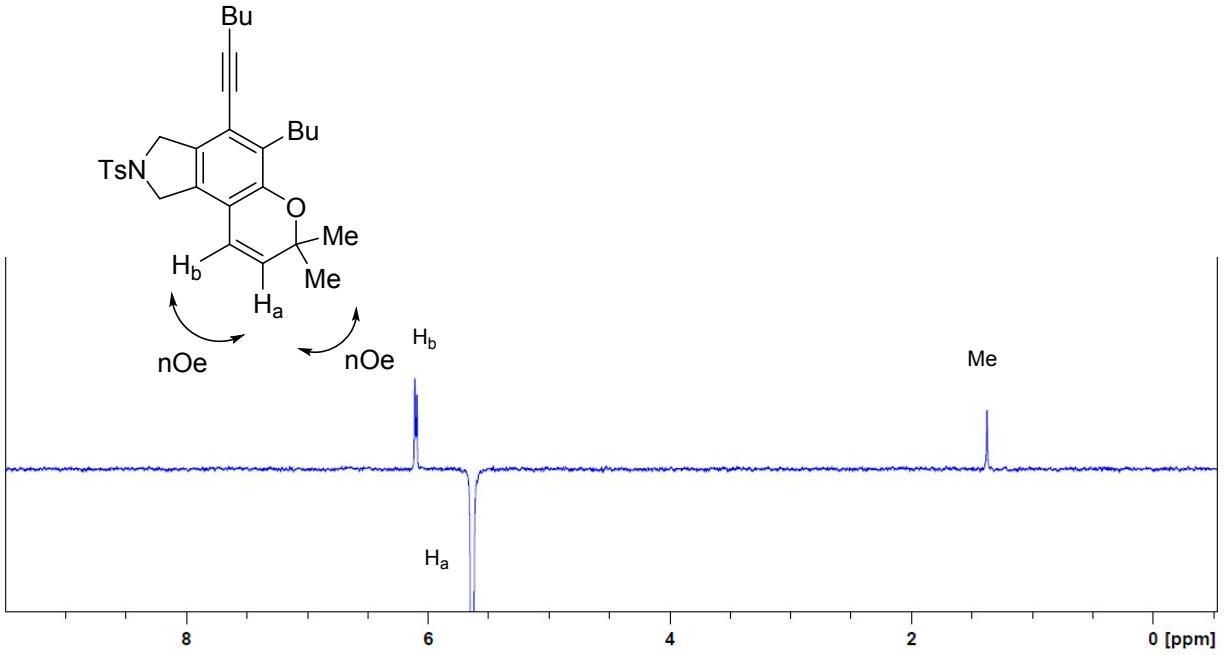
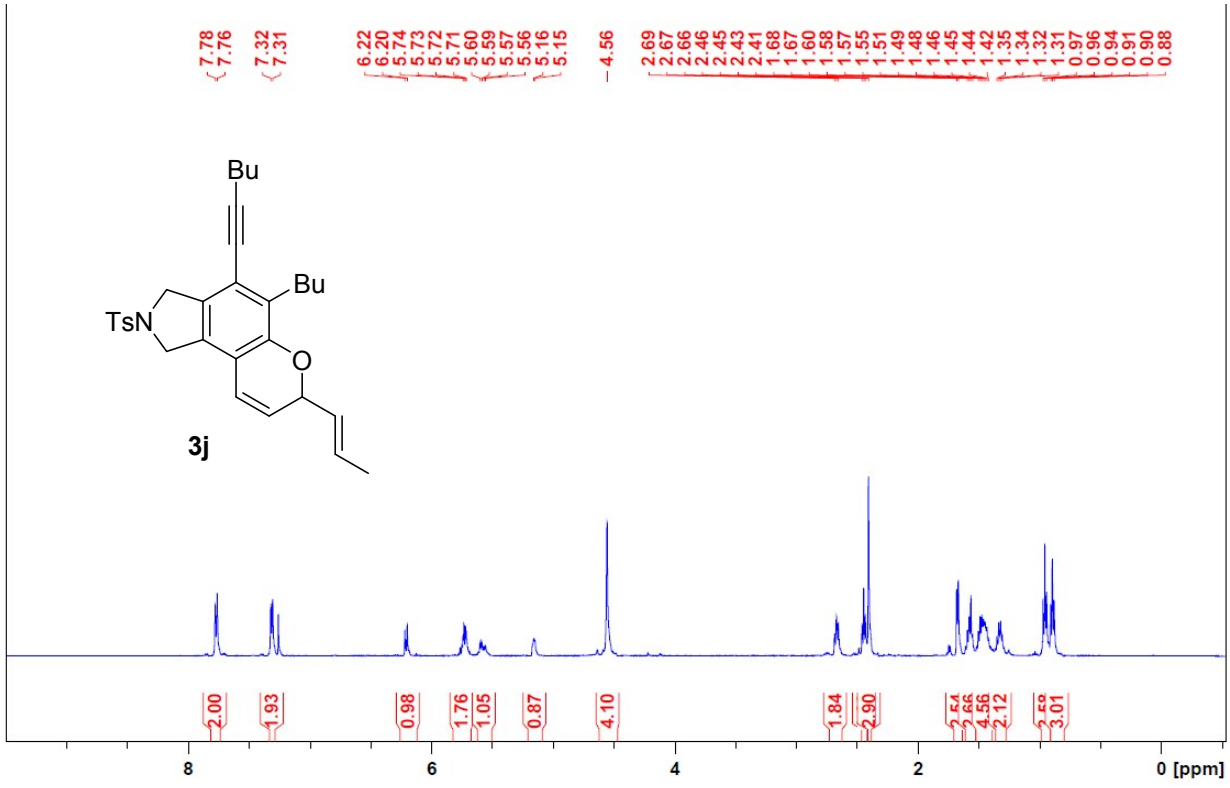
O
Me
Me
3i
200
150
100
50
[ppm]


Bu
Bu
TsN
O
Me
Me
Ha
Ha
Hb
Hc
nOe
nOe
Hc
Ha
Hb
8
6
4
2
0 [ppm]


Bu
Bu
TsN
O
Me
Me
Hb
Ha
nOe
nOe
Hb
Me
Ha
8
6
4
2
0 [ppm]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5.60
5.59
5.57
5.56
5.16
5.15
4.56
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2.67
2.66
2.46
2.45
2.43
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1.67
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1.55
1.51
1.49
1.48
1.46
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1.42
1.35
1.34
1.32
1.31
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0.96
0.94
0.91
0.90
0.88
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Bu
TsN
O
3j
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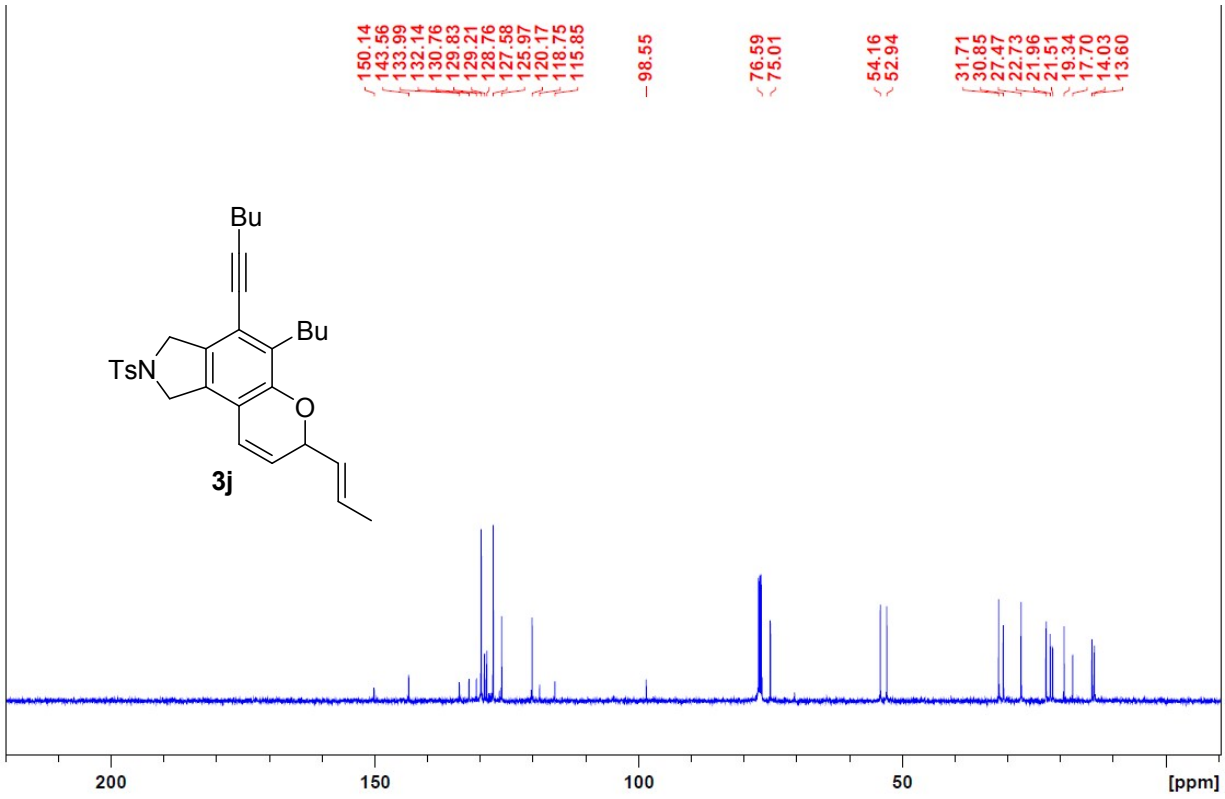
4
2
0 [ppm]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120.17
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115.85
98.55
76.59
75.01
54.16
52.94
31.71
30.85
27.47
22.73
21.96
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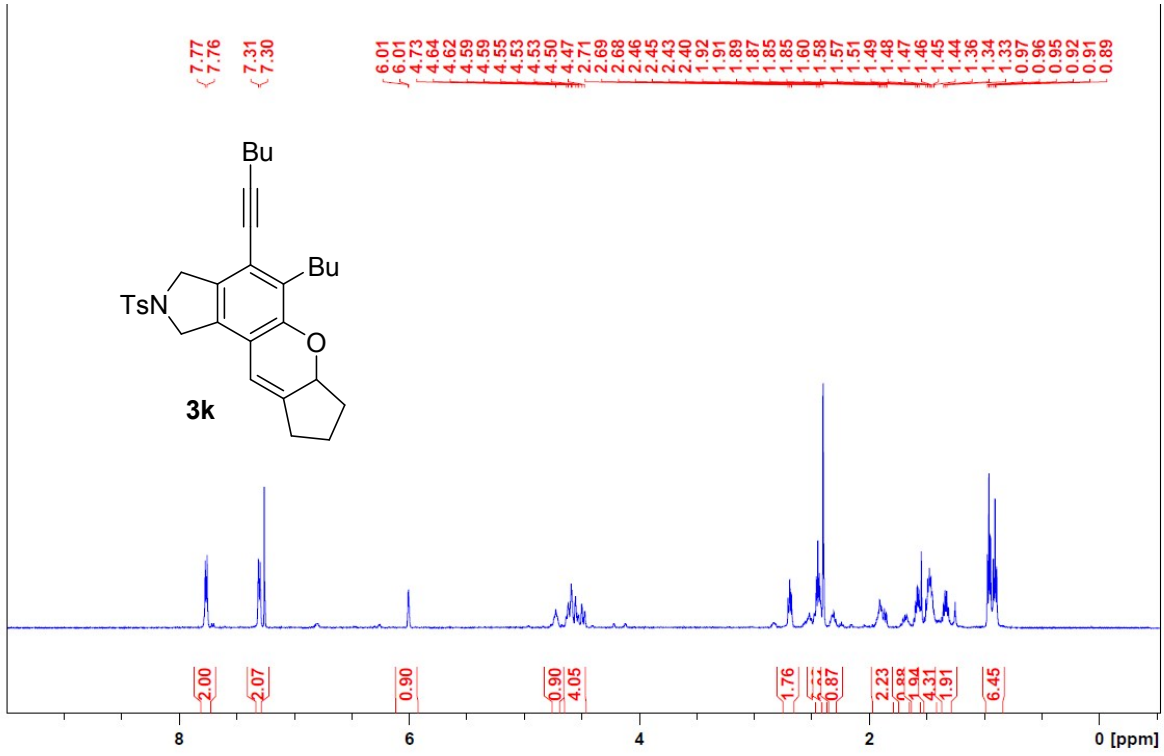
19.34
17.70
14.03
13.60
Bu
Bu
TsN
O
3j
200
150
100
50
[ppm]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4.53
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4.50
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4.71
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2.68
2.46
2.45
2.43
2.40
1.92
1.91
1.89
1.87
1.85
1.85
1.60
1.58
1.57
1.51
1.49
1.48
1.47
1.46
1.45
1.44
1.36
1.34
1.33
0.97
0.96
0.95
0.92
0.91
0.89
Bu
Bu
TsN
O
3k
2.00
2.07
0.90
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0.87
2.23
1.94
4.31
1.91
6.45
8
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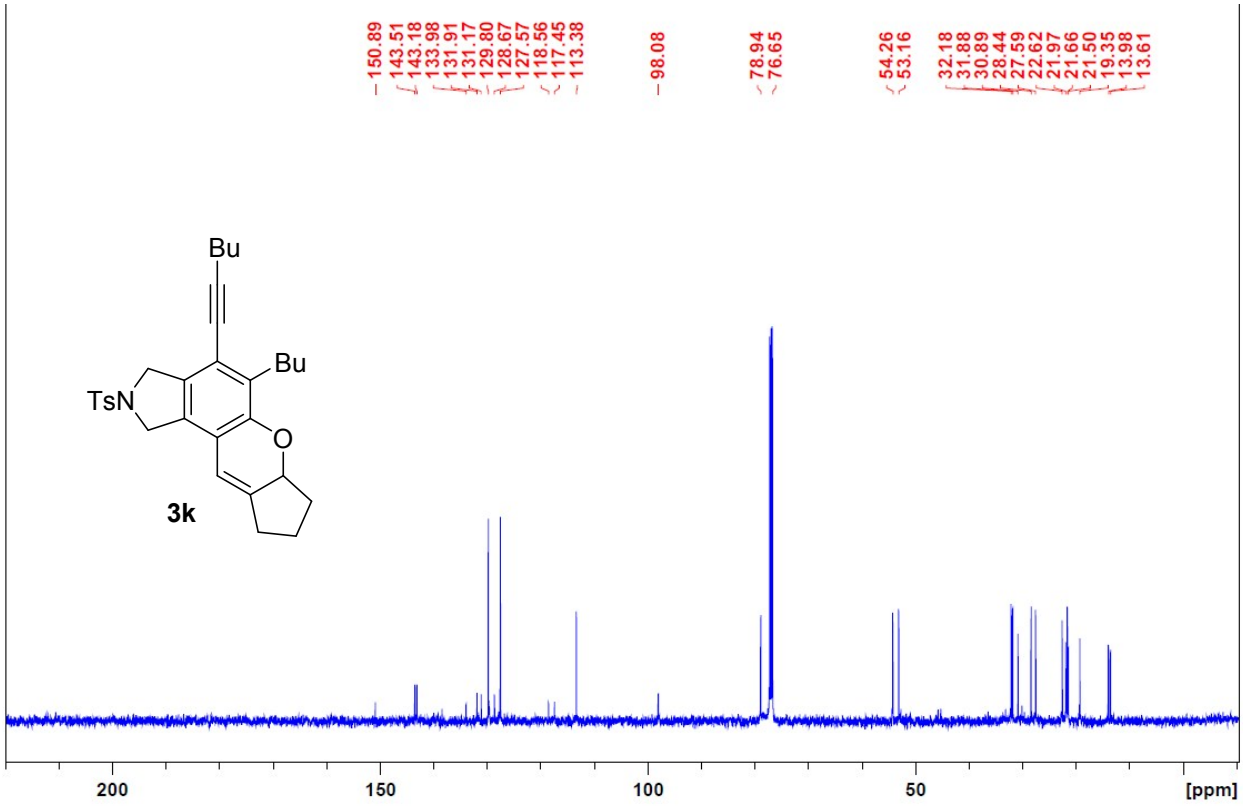
4
2
0 [ppm]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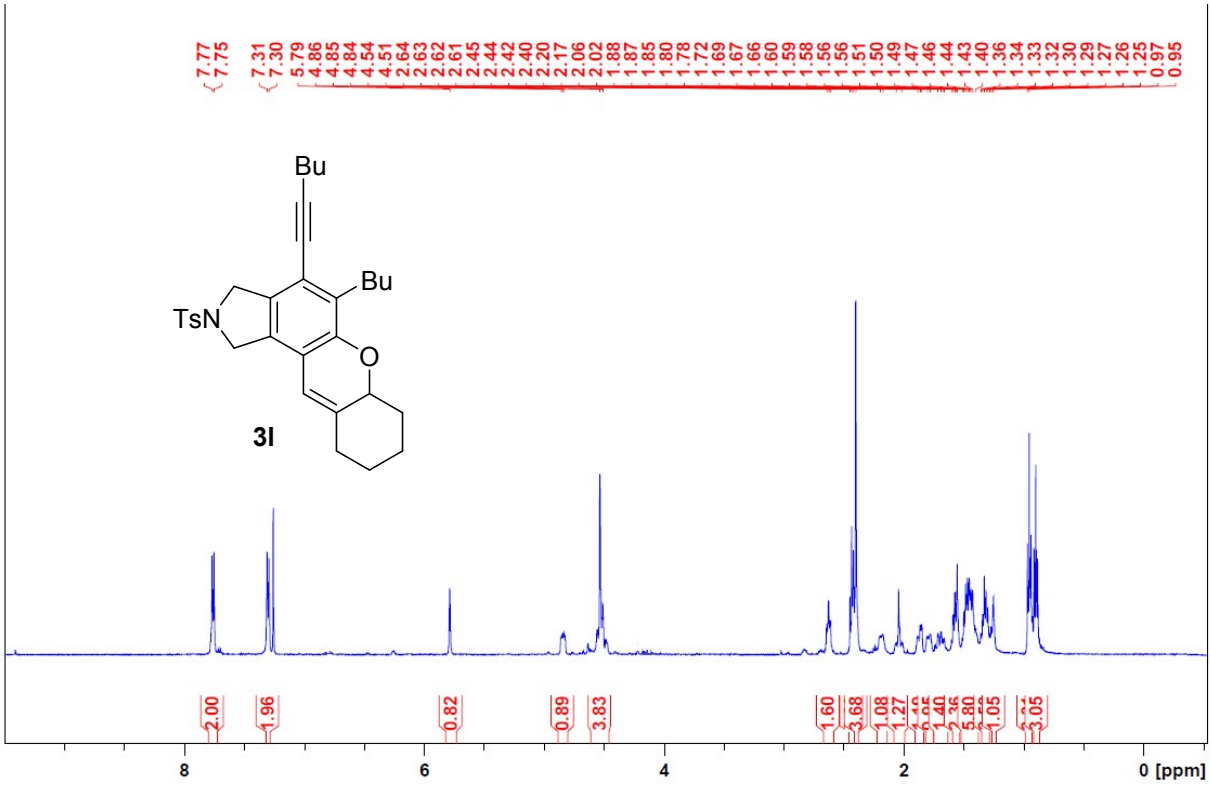
98.08
78.94
76.65
54.26
53.16
32.18
31.88
30.89
28.44
27.59
22.62
21.97
21.66
21.50
19.35
13.98
13.61
Bu
Bu
TsN
O
3k
200
150
100
50
[ppm]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Bu
TsN
O
3l
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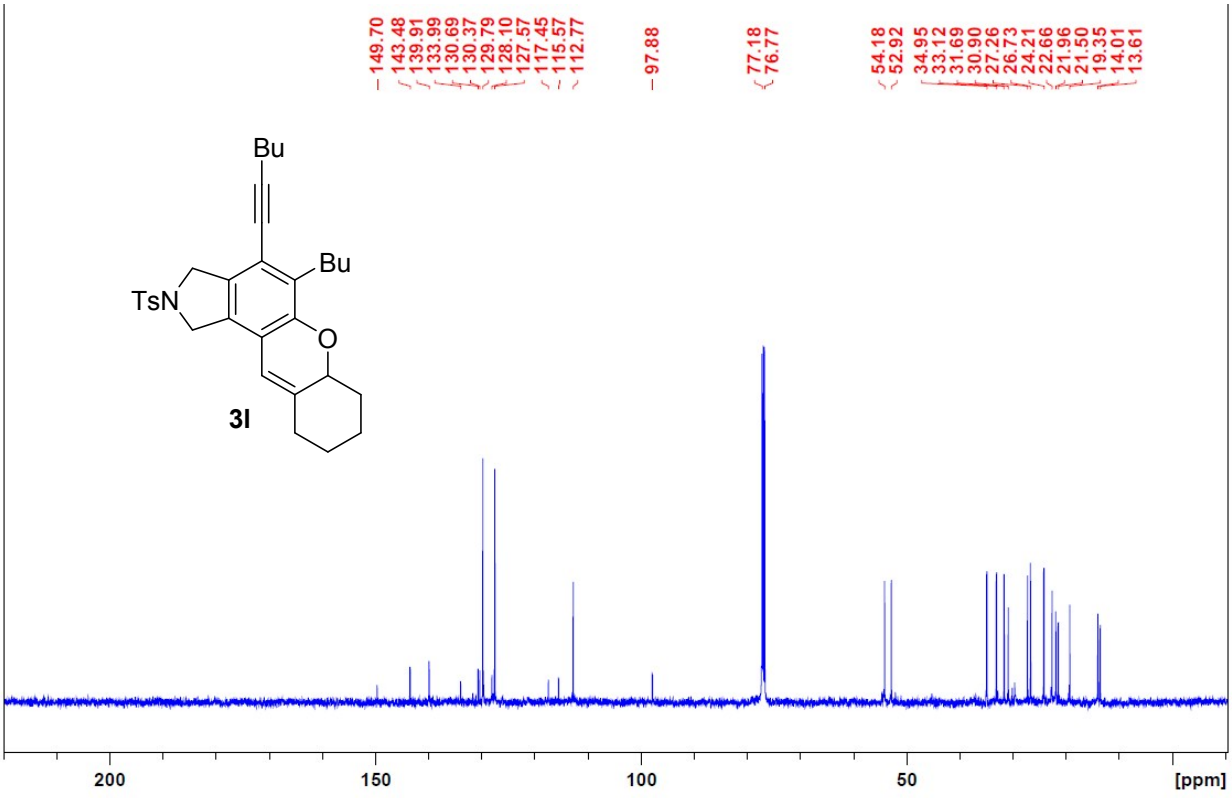
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Bu
TsN
O
3l
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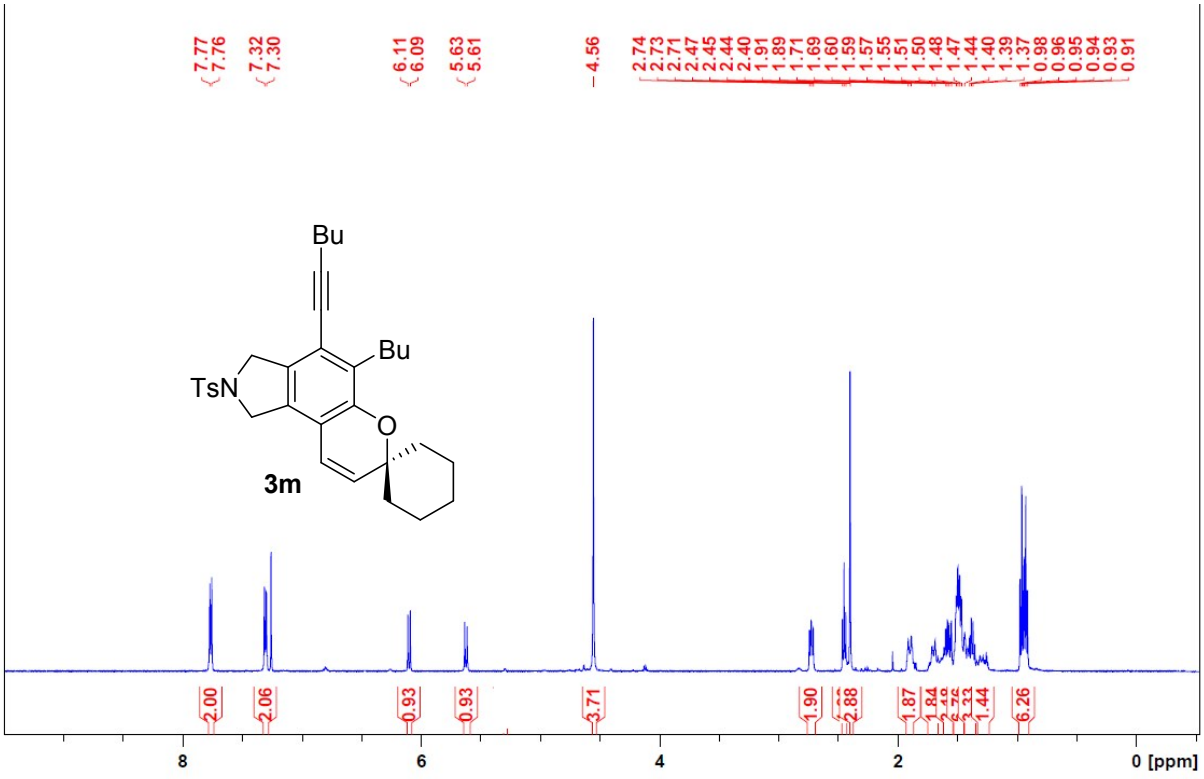
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2.73
2.71
2.47
2.45
2.44
2.40
1.91
1.89
1.71
1.69
1.60
1.59
1.57
1.55
1.51
1.50
1.48
1.47
1.44
1.40
1.39
1.37
0.98
0.96
0.95
0.94
0.93
0.91
Bu
Bu
TsN
O
3m
2.00
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3.71
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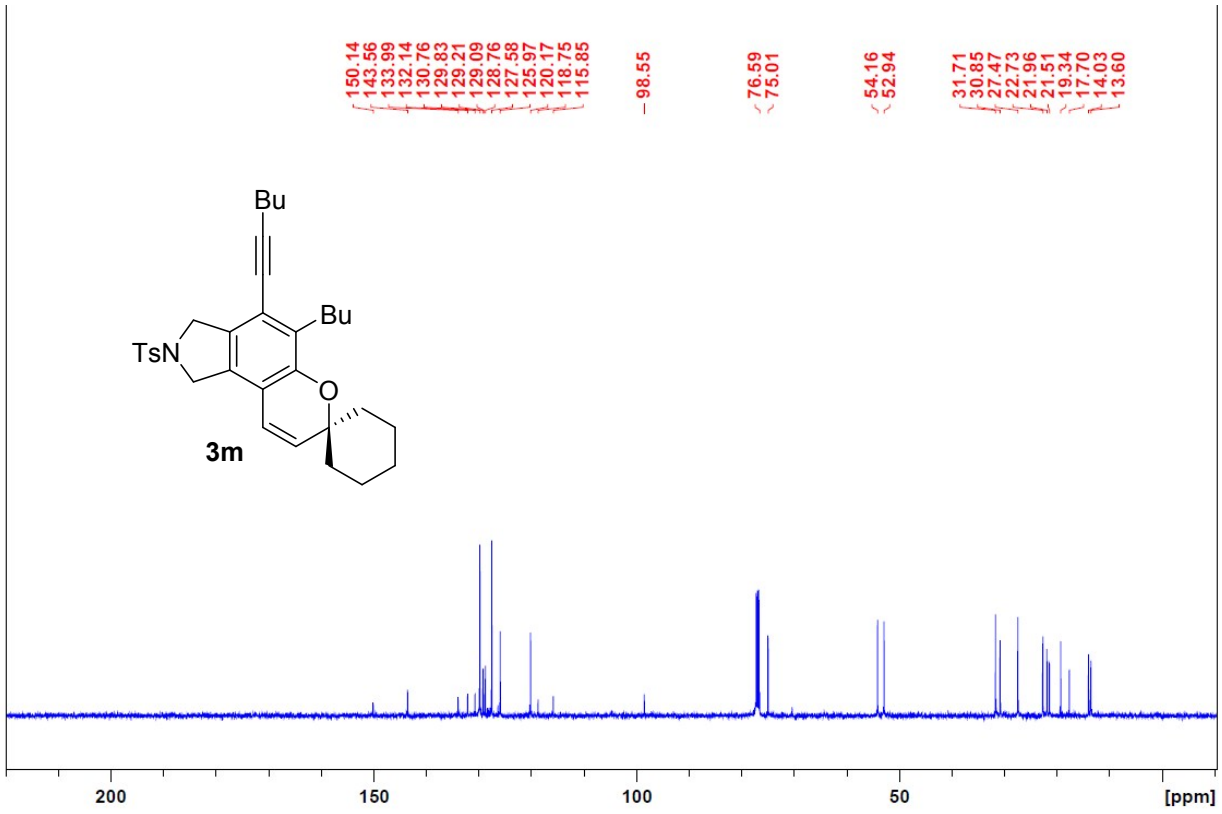
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127.58
125.97
120.17
118.75
115.85
98.55
76.59
75.01
54.16
52.94
31.71
30.85
27.47
22.73
21.96
21.51
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17.70
14.03
13.60
Bu
Bu
TsN
O
3m
200
150
100
50
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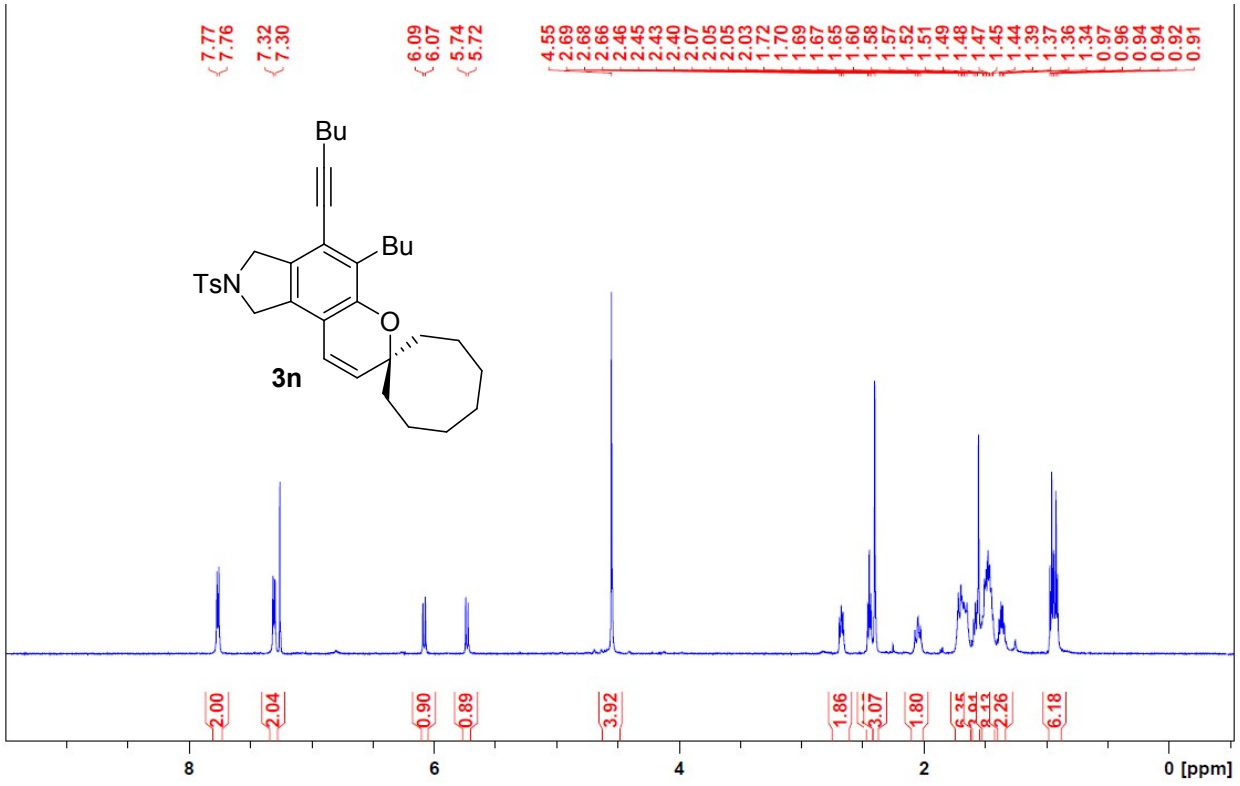
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5.72
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2.69
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2.66
2.46
2.45
2.43
2.40
2.07
2.05
2.05
2.03
1.72
1.70
1.69
1.67
1.65
1.60
1.58
1.57
1.52
1.51
1.49
1.48
1.47
1.45
1.44
1.39
1.37
1.36
1.34
0.97
0.96
0.94
0.94
0.92
0.91
Bu
Bu
TsN
O
3n
2.00
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1.80
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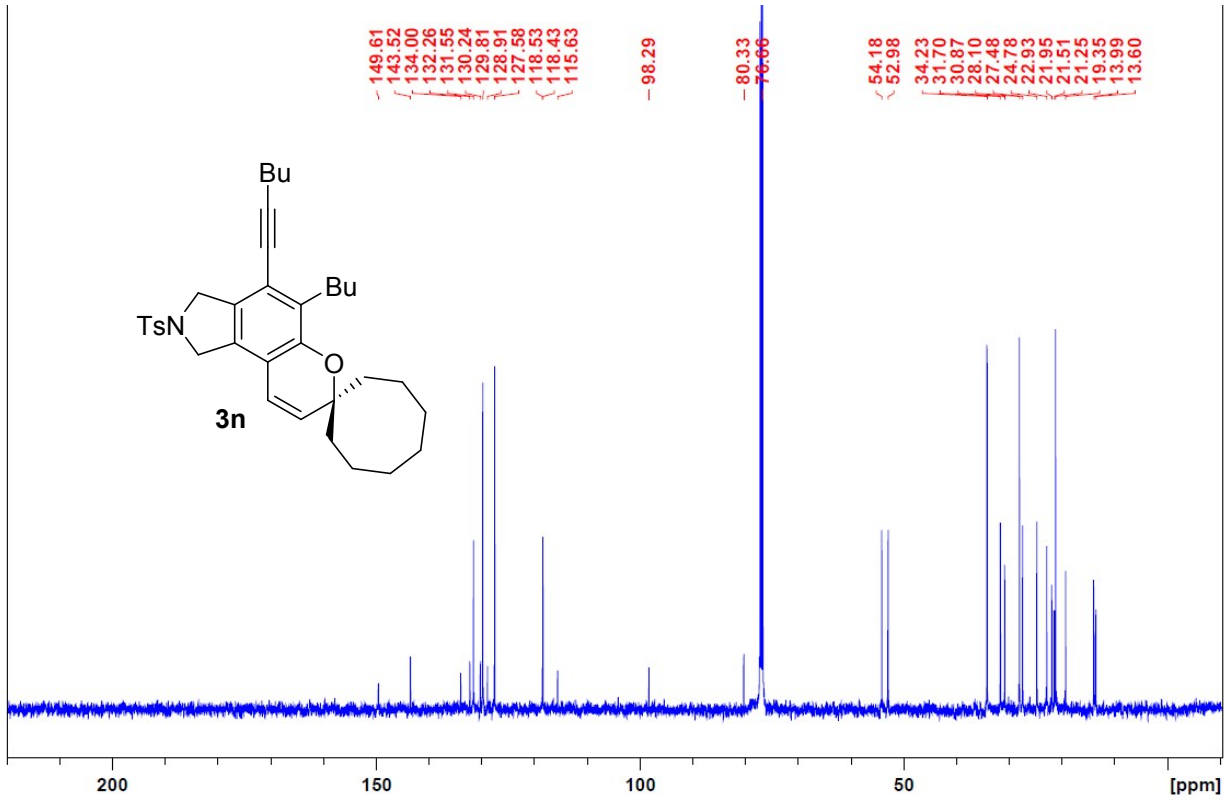
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128.91
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118.43
115.63
98.29
80.33
76.66
54.18
52.98
34.23
31.70
30.87
28.10
27.48
24.78
22.93
21.95
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Bu
TsN
O
3n
200
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100
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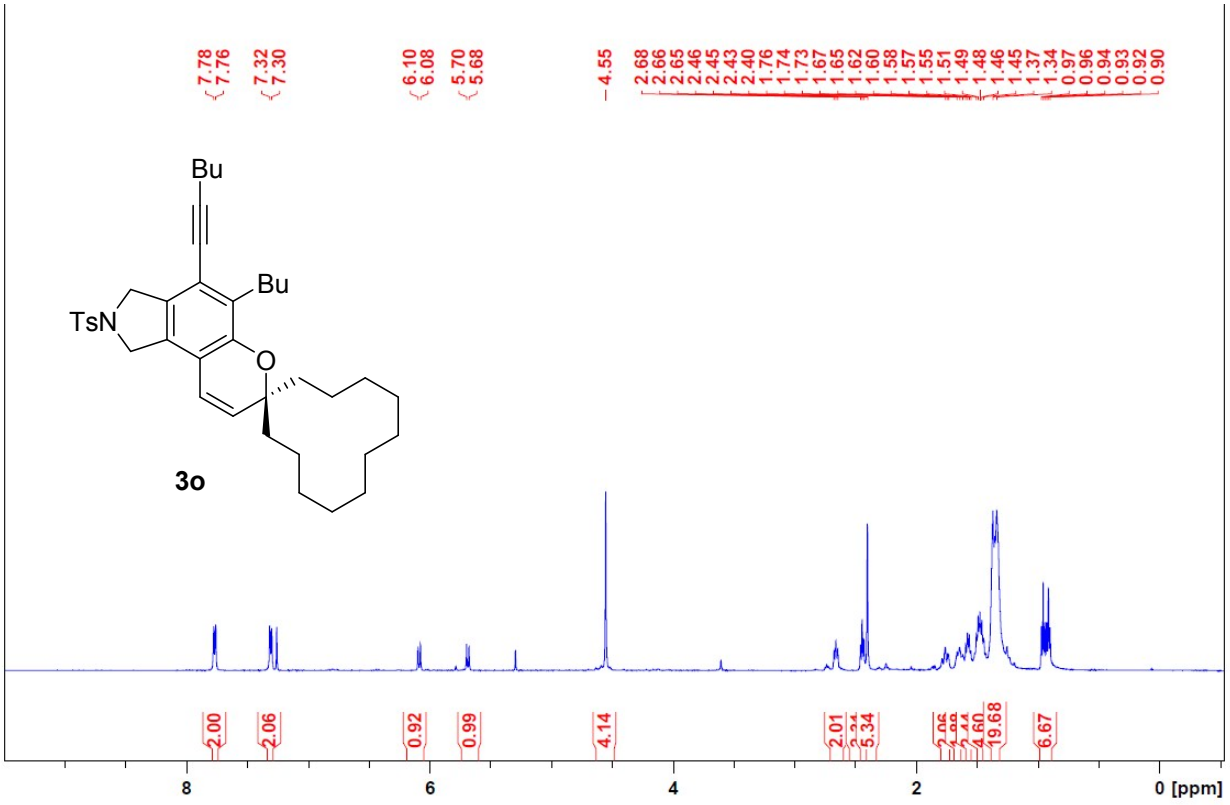
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2.68
2.66
2.65
2.46
2.45
2.43
2.40
1.76
1.74
1.73
1.67
1.65
1.62
1.60
1.58
1.57
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1.51
1.49
1.48
1.46
1.45
1.37
1.34
0.97
0.96
0.94
0.93
0.92
0.90
Bu
Bu
TsN
O
3o
2.00
2.06
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0.99
4.14
2.01
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6.67
8
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4
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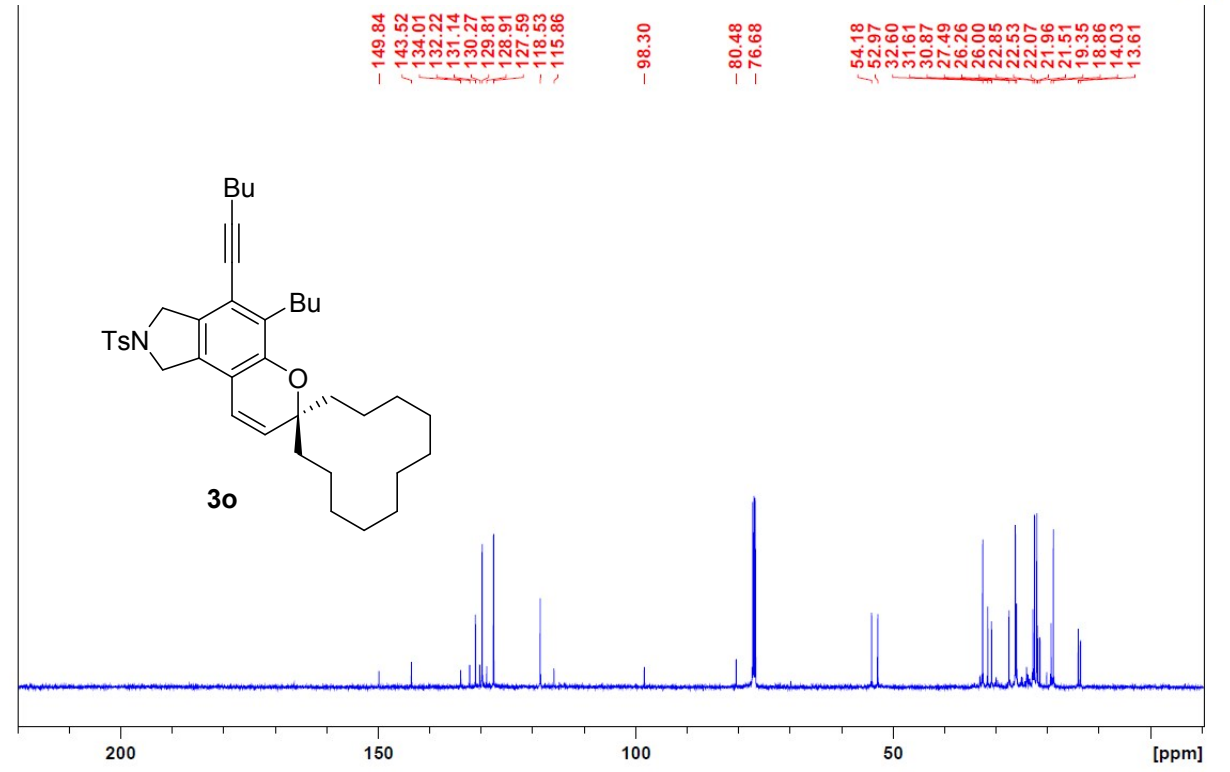
0 [ppm]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130.27
129.81
128.91
127.59
118.53
115.86
98.30
80.48
76.68
54.18
52.97
32.60
31.61
30.87
27.49
26.26
26.00
22.85
22.53
22.07
21.96
21.51
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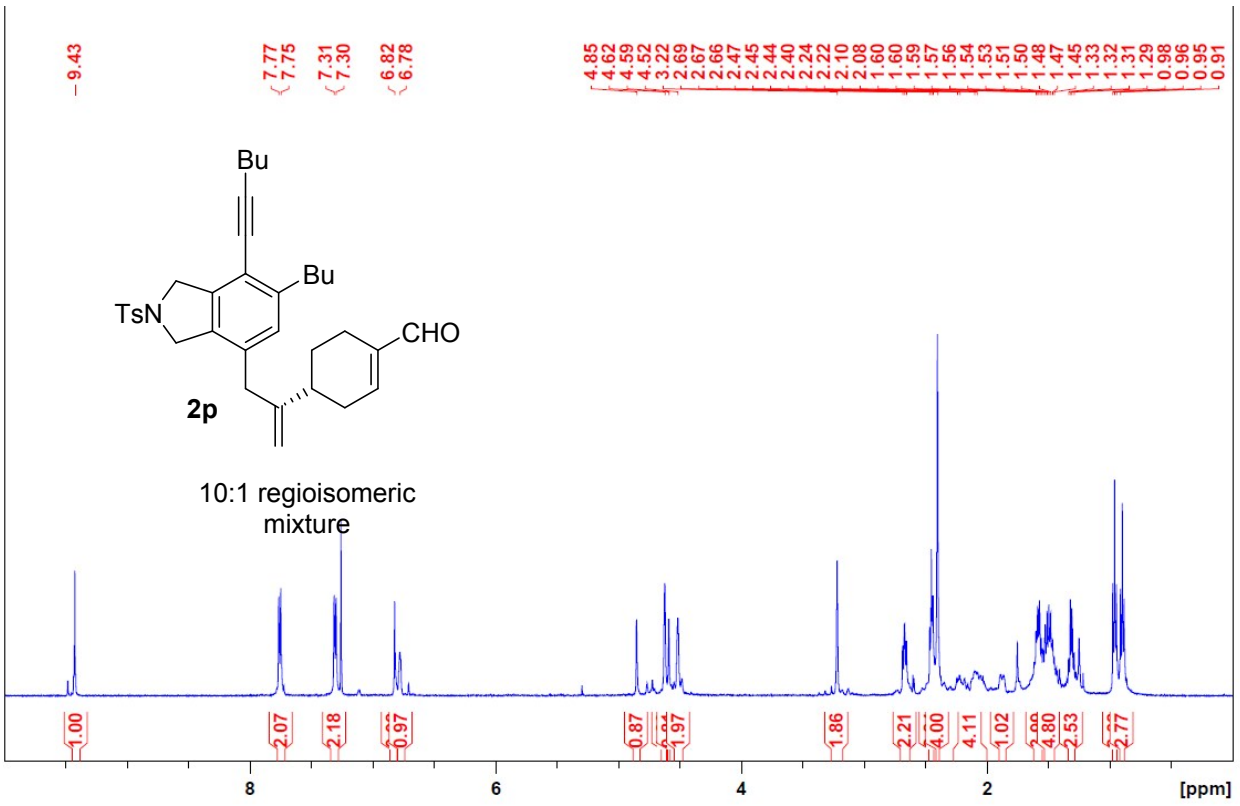
18.86
14.03
13.61
Bu
Bu
TsN
O
3o
200
150
100
50
[ppm]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7.75
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7.30
6.82
6.78
4.85
4.62
4.59
4.52
3.22
2.69
2.67
2.66
2.47
2.45
2.44
2.40
2.24
2.22
2.10
2.08
1.60
1.60
1.59
1.57
1.56
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1.51
1.50
1.48
1.47
1.45
1.33
1.32
1.31
1.29
0.98
0.96
0.95
0.91
Bu
Bu
TsN
CHO
2p
10:1 regioisomeric mixture
1.00
2.07
2.18
0.97
0.87
1.97
1.86
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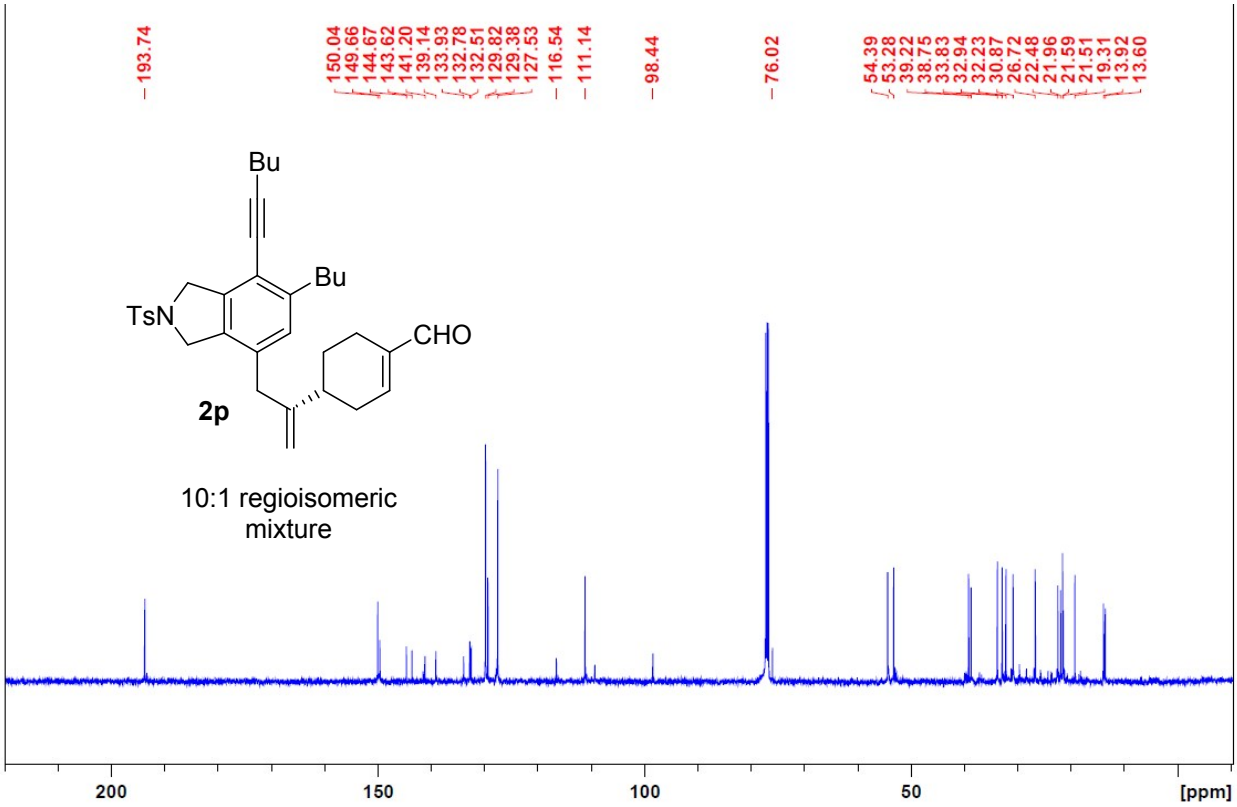
4.00
4.11
1.02
4.80
2.53
2.77
8
6
4
2
[ppm]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141.20
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133.93
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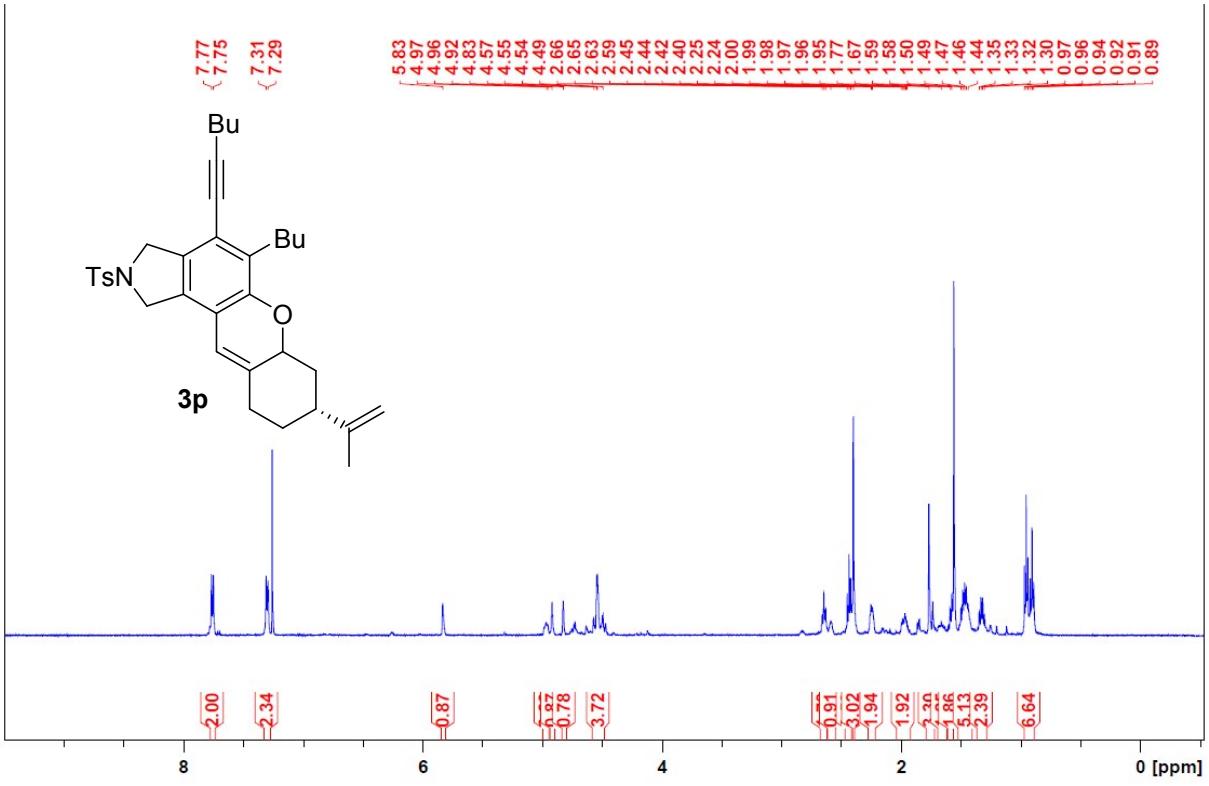
132.51
129.82
129.38
127.53
116.54
111.14
98.44
76.02
54.39
53.28
39.22
38.75
33.83
32.94
32.23
30.87
26.72
22.48
21.96
21.59
21.51
19.31
13.92
13.60
Bu
Bu
TsN
CHO
2p
10:1 regioisomeric mixture
200
150
100
50
[ppm]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7.75
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7.29
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4.97
4.96
4.92
4.83
4.57
4.55
4.54
4.49
2.66
2.65
2.63
2.59
2.45
2.44
2.42
2.40
2.25
2.24
2.00
1.99
1.98
1.97
1.96
1.95
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1.49
1.47
1.46
1.44
1.35
1.33
1.32
1.30
0.97
0.96
0.94
0.92
0.91
0.89
Bu
Bu
TsN
O
3p
2.00
2.34
0.87
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3.02
1.94
1.92
5.13
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6.64
8
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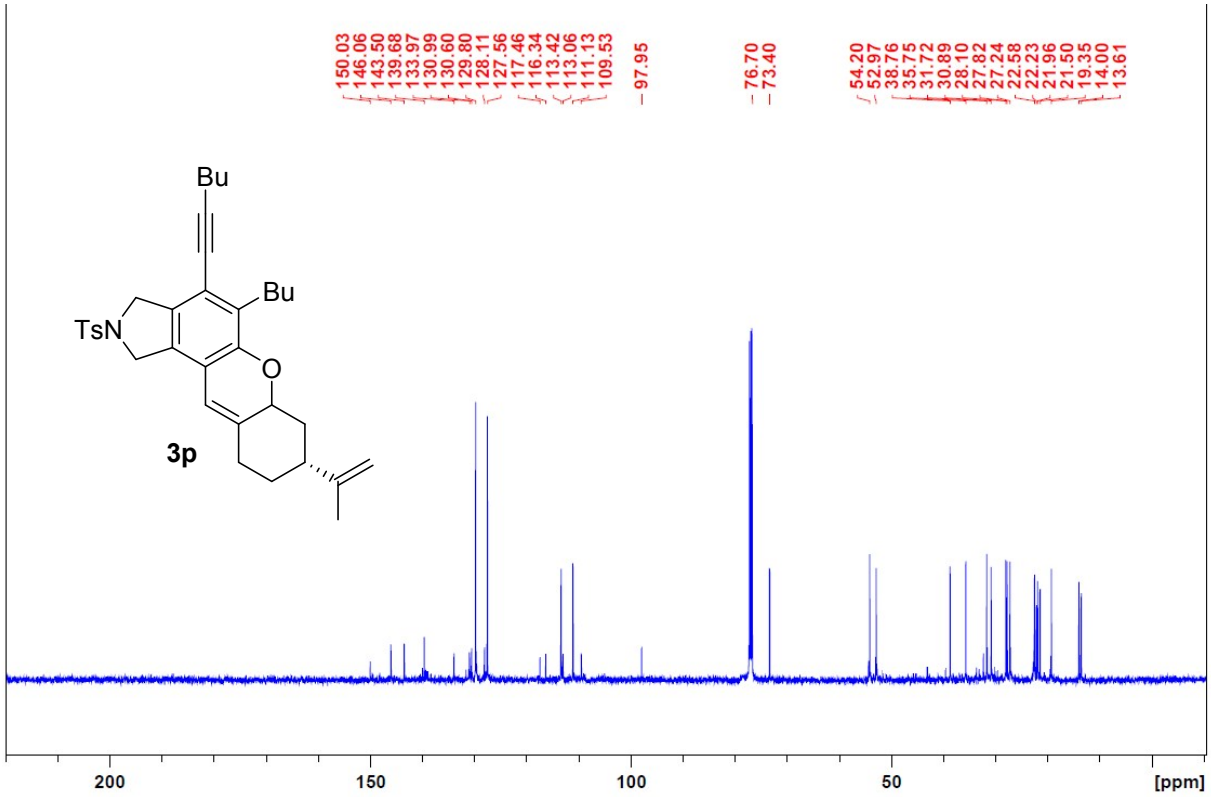
4
2
0 [ppm]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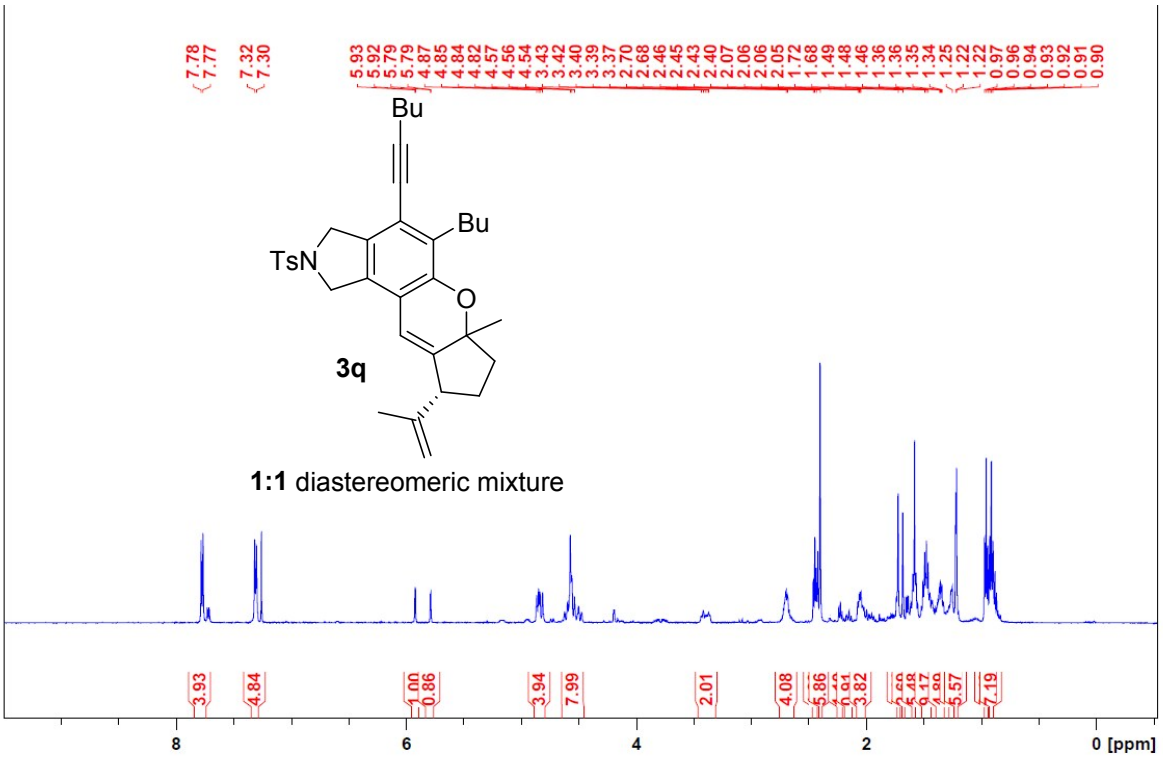
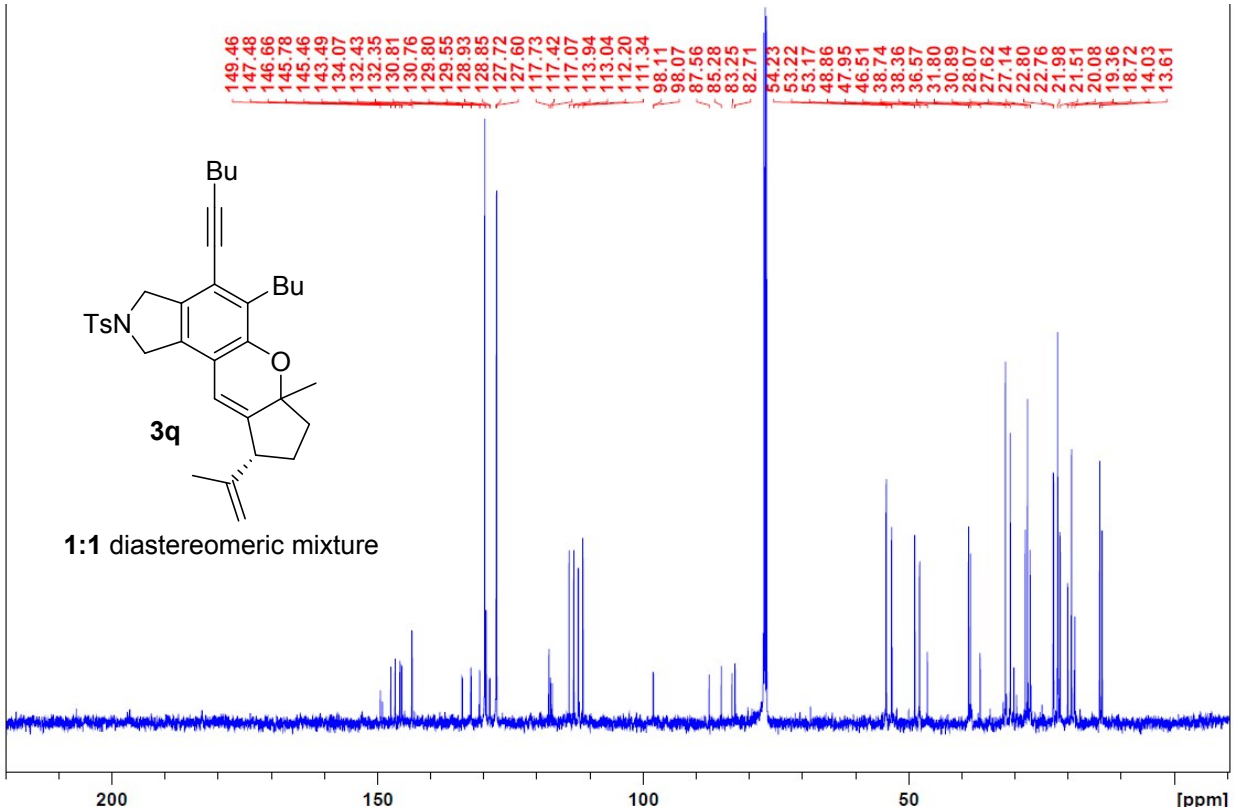
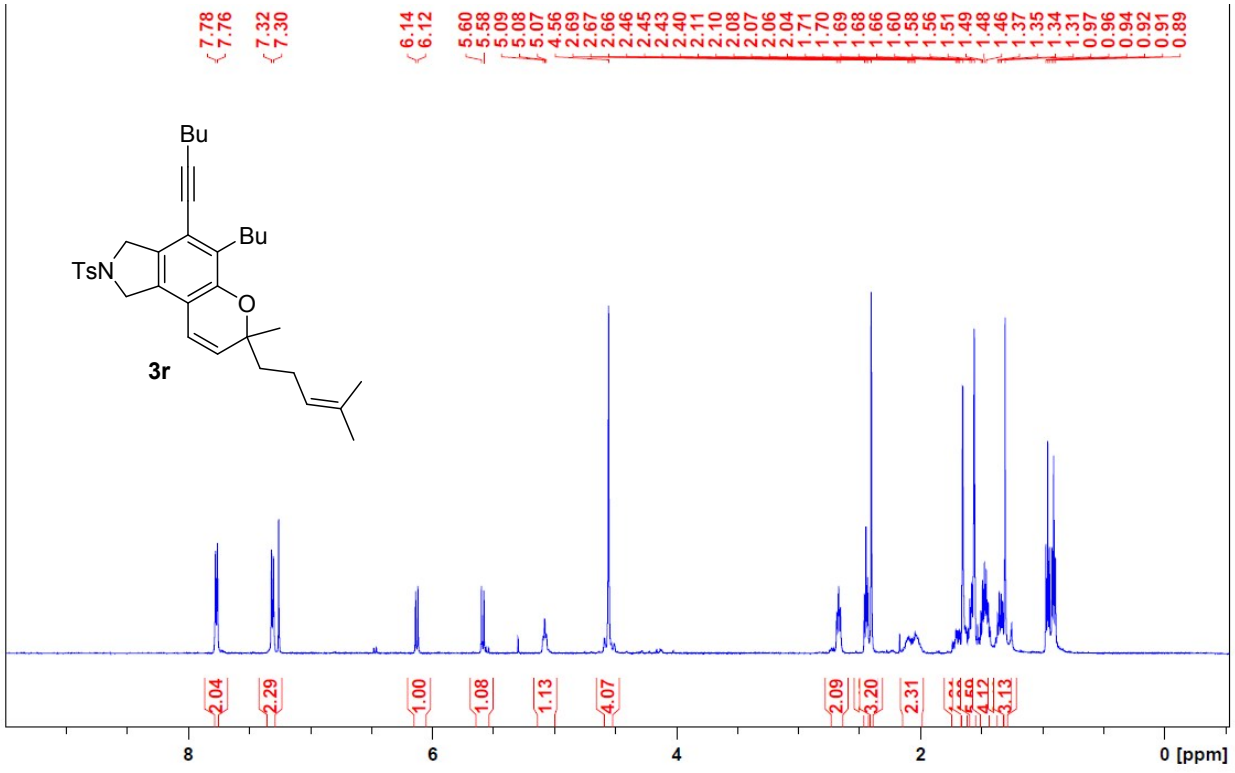
129.80
128.11
127.56
117.46
116.34
113.42
113.06
111.13
109.53
97.95
76.70
73.40
54.20
52.97
38.76
35.75
31.72
30.89
28.10
27.82
27.24
22.58
22.23
21.96
21.50
19.35
14.00
13.61
Bu
Bu
TsN
O
3p
200
150
100
50
[ppm]


Bu
Bu
TsN
O
3q
1:1 diastereomeric mixture
8
6
4
2
0 [ppm]


Bu
Bu
TsN
O
3q
1:1 diastereomeric mixture
200
150
100
50
[ppm]


7.78
7.76
7.32
7.30
6.14
6.12
5.60
5.58
5.09
5.08
5.07
4.56
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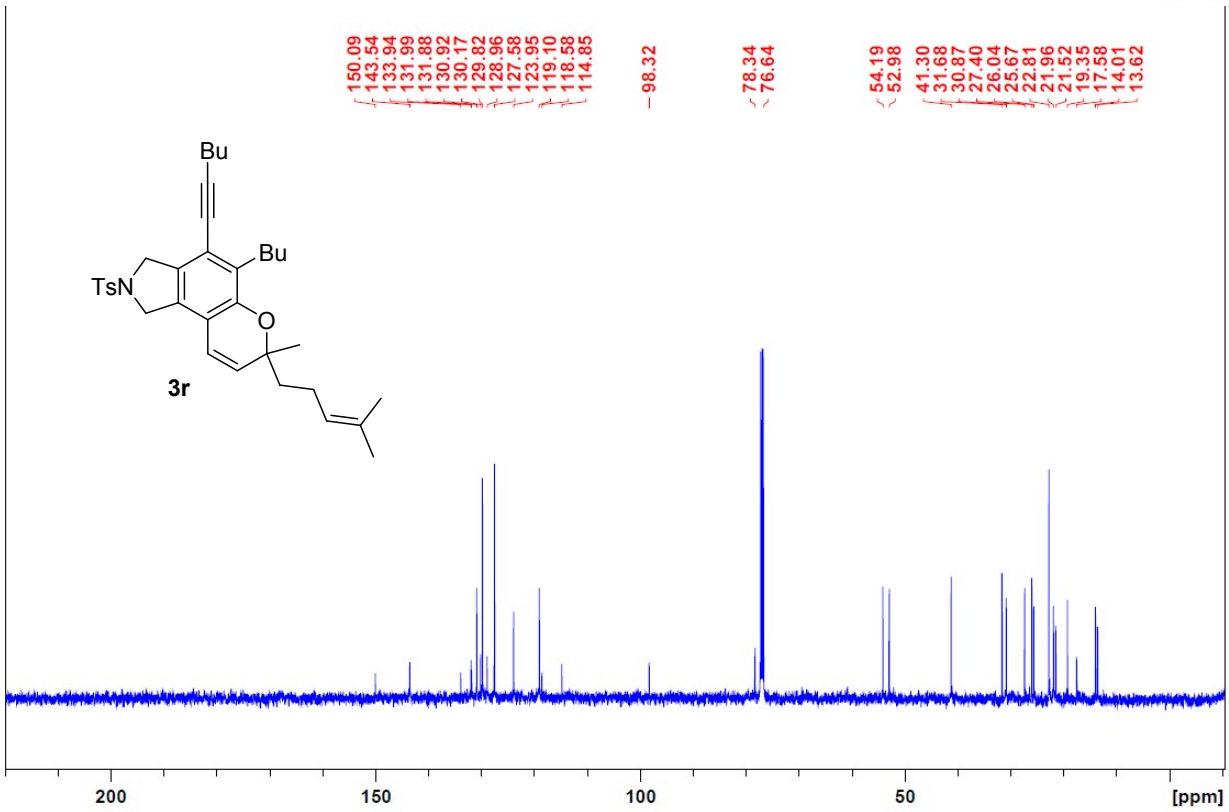
2.67
2.66
2.46
2.45
2.43
2.40
2.11
2.10
2.08
2.07
2.06
2.04
1.71
1.70
1.69
1.68
1.66
1.60
1.58
1.56
1.51
1.49
1.48
1.46
1.37
1.35
1.34
1.31
0.97
0.96
0.94
0.92
0.91
0.89
Bu
Bu
TsN
O
3r
2.04
2.29
1.00
1.08
1.13
4.07
2.09
3.20
2.31
4.12
3.13
8
6
4
2
0 [ppm]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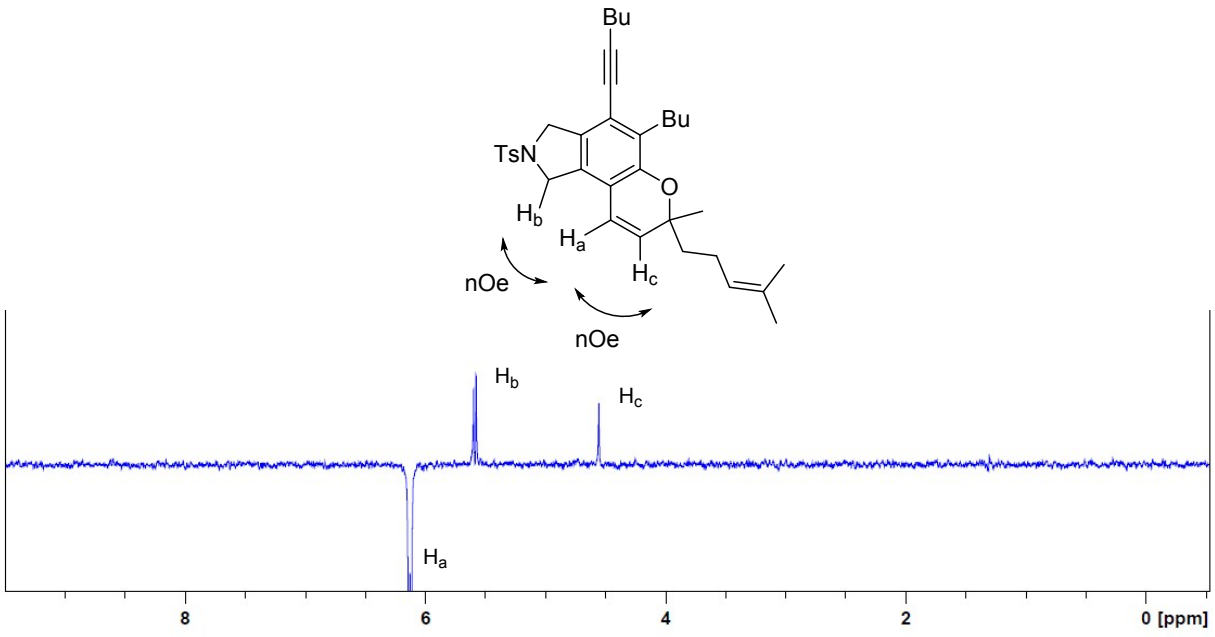
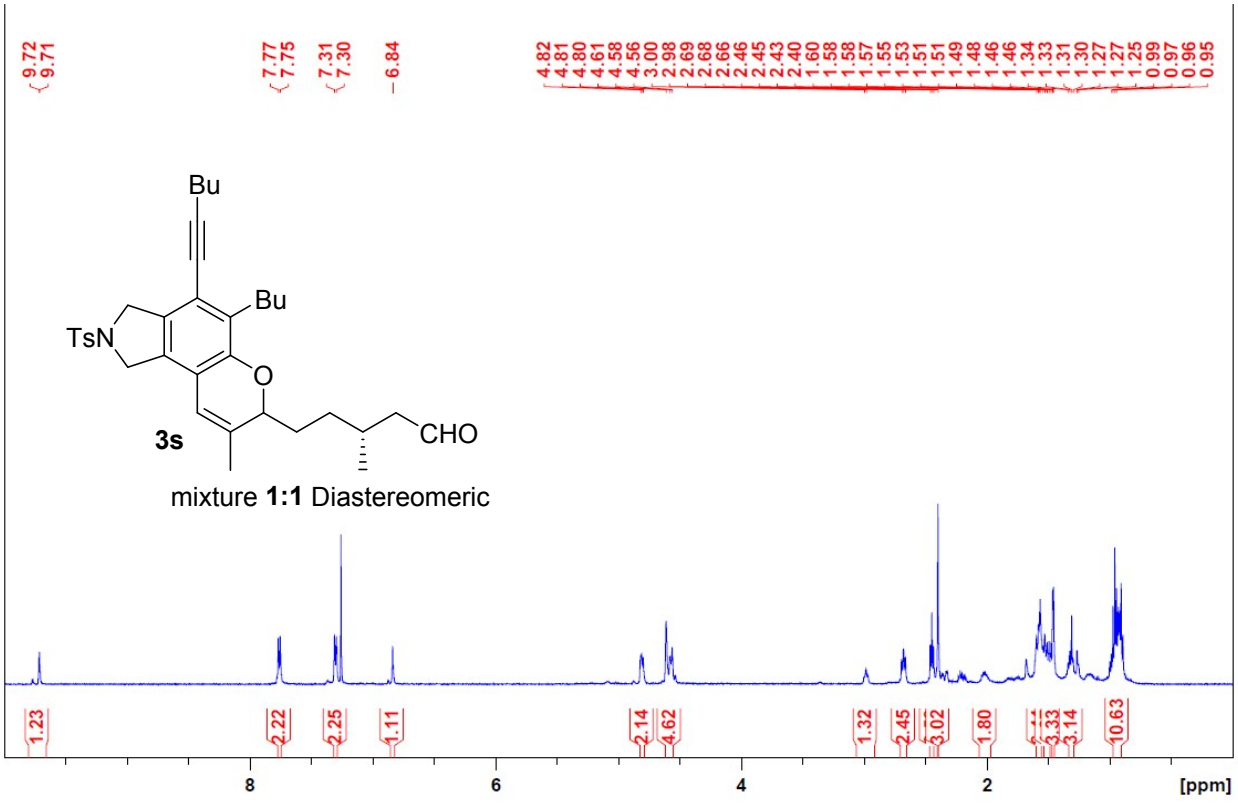
128.96
127.58
123.95
119.10
118.58
114.85
98.32
78.34
76.64
54.19
52.98
41.30
31.68
30.87
27.40
26.04
25.67
22.81
21.96
21.52
19.35
17.58
14.01
13.62
Bu
Bu
TsN
O
3r
200
150
100
50
[ppm]


Bu
Bu
TsN
O
H_b
H_a
H_c
nOe
nOe
H_b
H_c
H_a
8
6
4
2
0 [ppm]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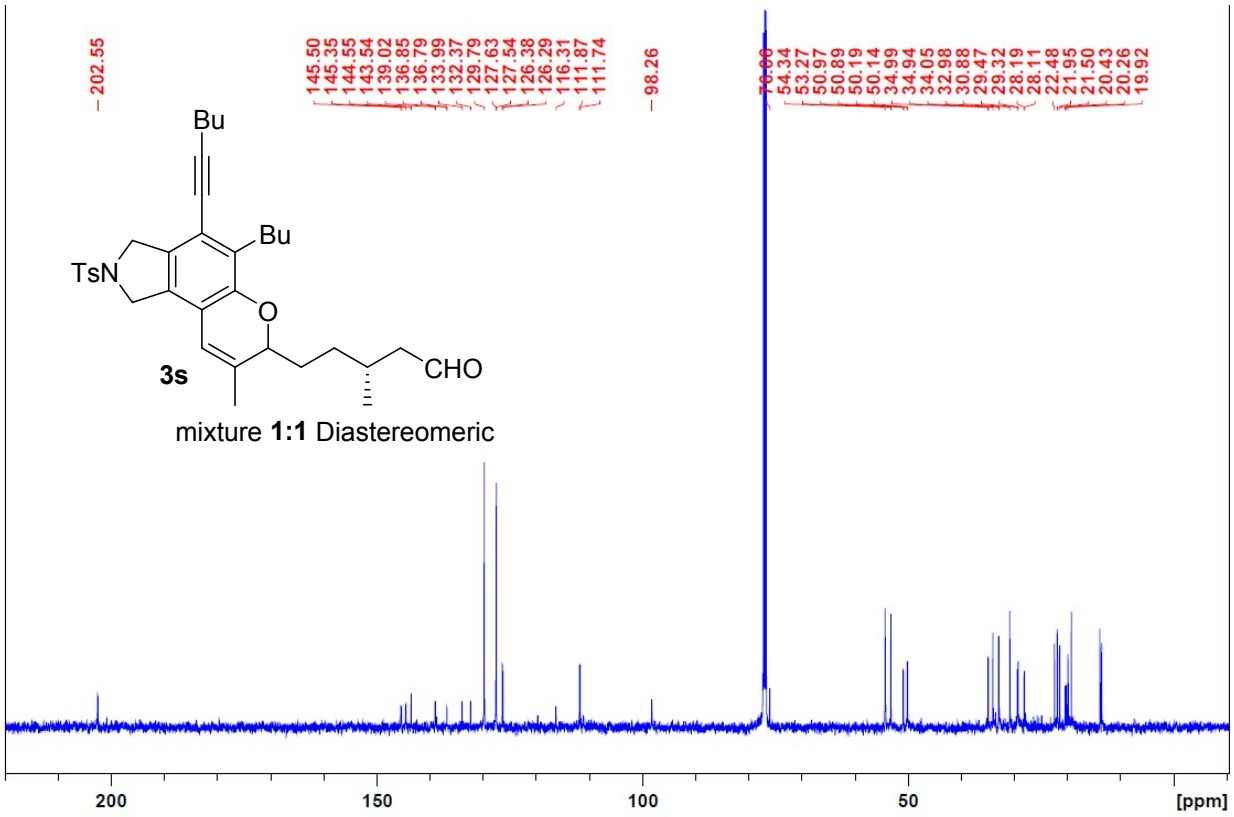
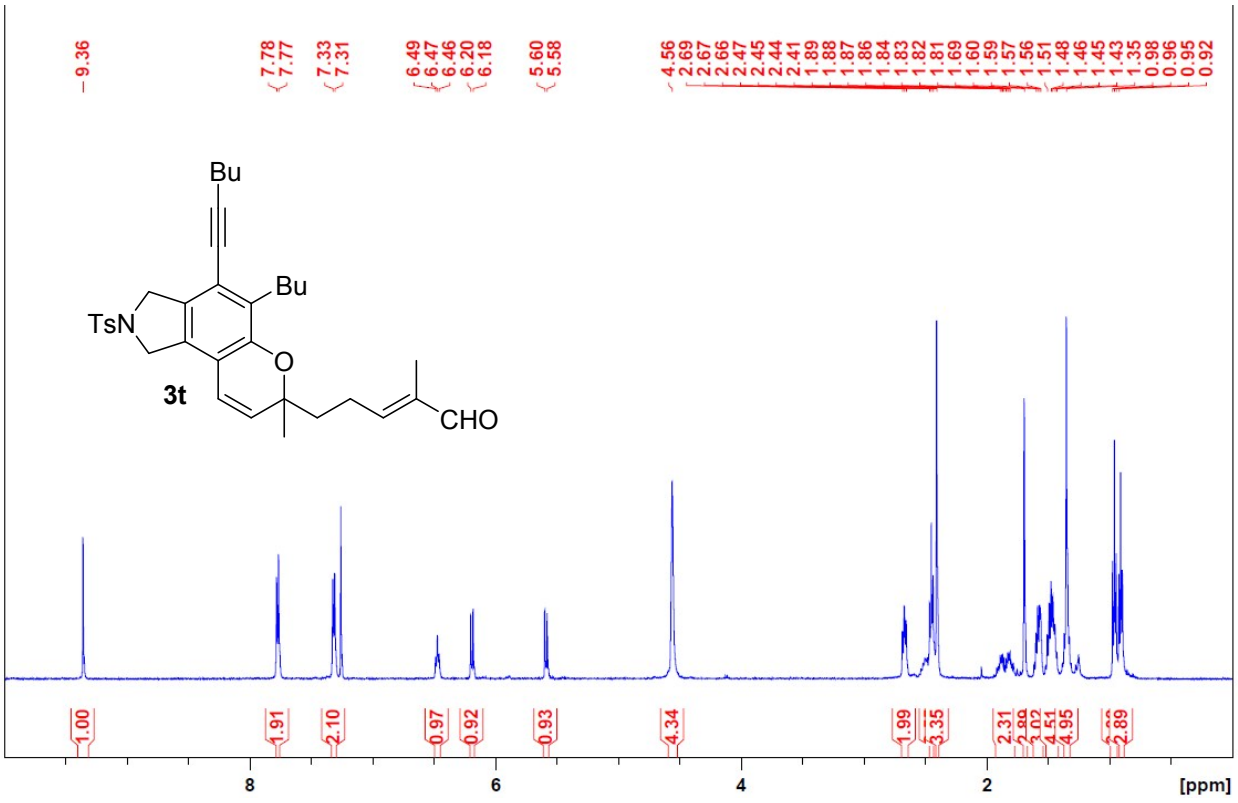
Bu
TsN
O
CHO
3s
mixture 1:1 Diastereomeric
[ppm]


Bu
Bu
TsN
O
CHO
3s
mixture 1:1 Diastereomeric
[ppm]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6.46
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6.18
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5.58
4.56
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2.67
2.66
2.47
2.45
2.44
2.41
1.89
1.88
1.87
1.86
1.84
1.83
1.82
1.81
1.69
1.60
1.59
1.57
1.56
1.51
1.48
1.46
1.45
1.43
1.35
0.98
0.96
0.95
0.92
Bu
Bu
TsN
O
3t
CHO
1.00
1.91
2.10
0.97
0.92
0.93
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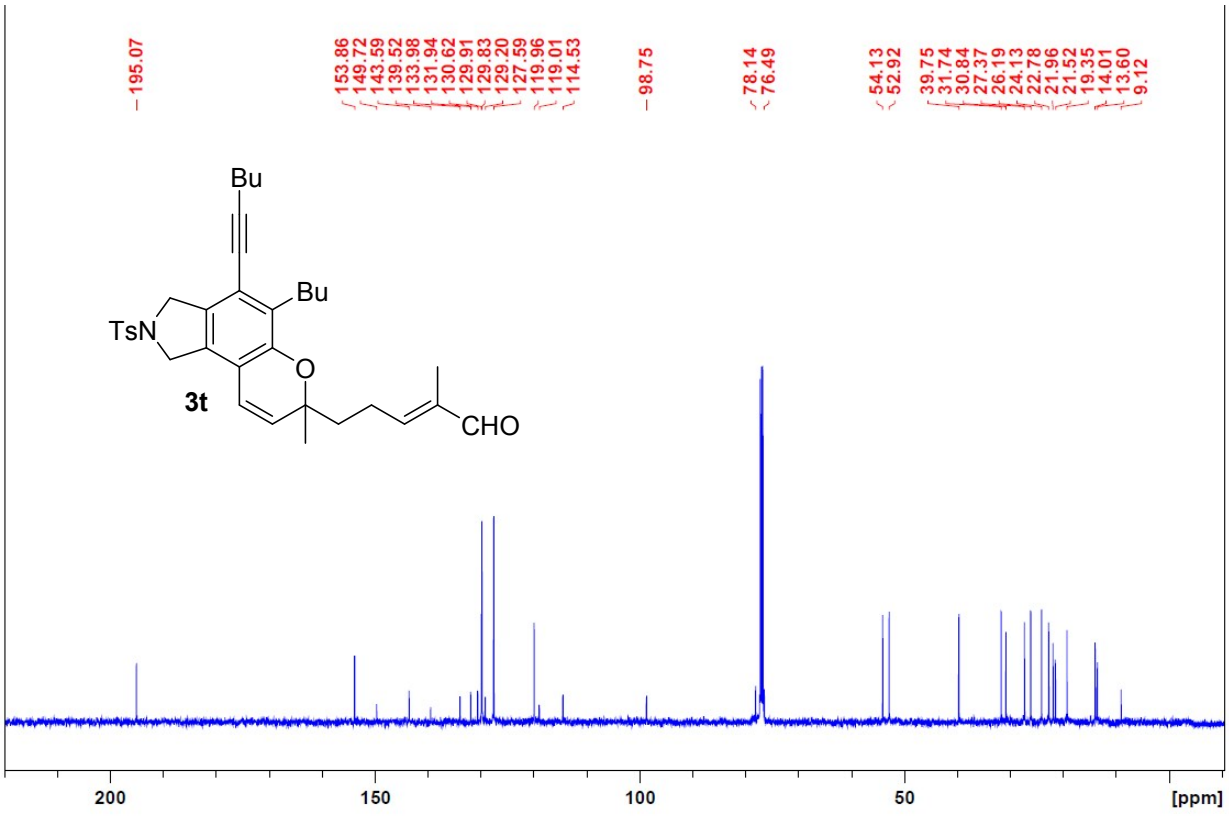
1.99
3.35
2.31
4.51
4.95
2.89
8
6
4
2
[ppm]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127.59
119.96
119.01
114.53
98.75
78.14
76.49
54.13
52.92
39.75
31.74
30.84
27.37
26.19
24.13
22.78
21.96
21.52
19.35
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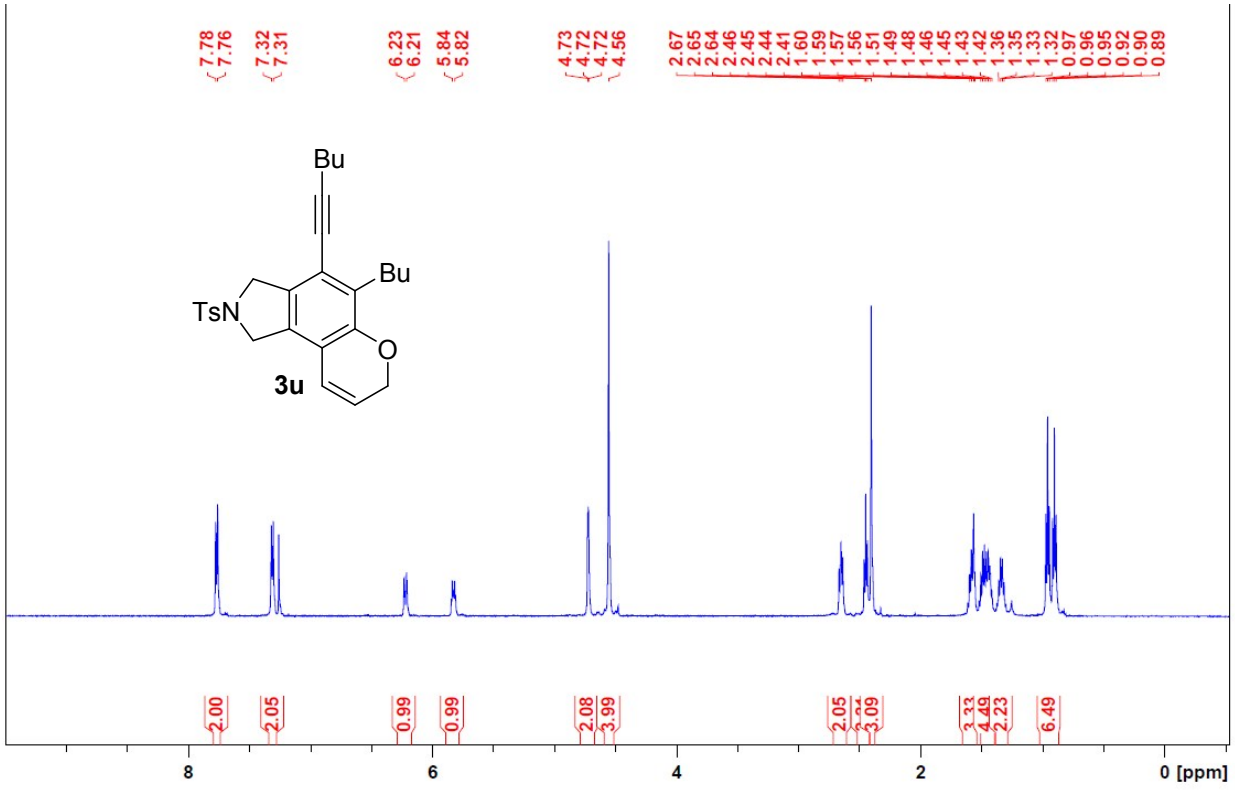
13.60
9.12
Bu
Bu
TsN
O
3t
CHO
200
150
100
50
[ppm]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7.31
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5.82
4.73
4.72
4.72
4.56
2.67
2.65
2.64
2.46
2.45
2.44
2.41
1.60
1.59
1.57
1.56
1.51
1.49
1.48
1.46
1.45
1.43
1.42
1.36
1.35
1.33
1.32
0.97
0.96
0.95
0.92
0.90
0.89
Bu
Bu
TsN
O
3u
2.00
2.05
0.99
0.99
2.08
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2.05
3.09
3.33
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2.23
6.49
8
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4
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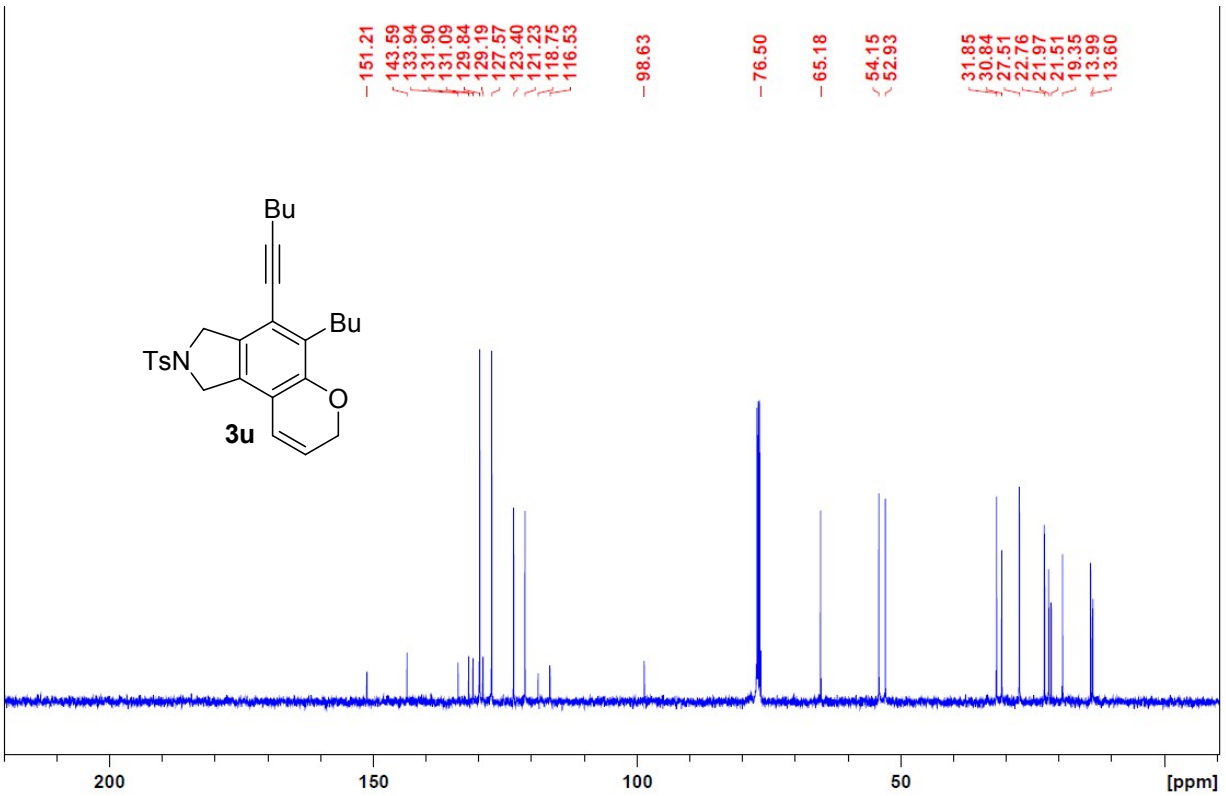
0 [ppm]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127.57
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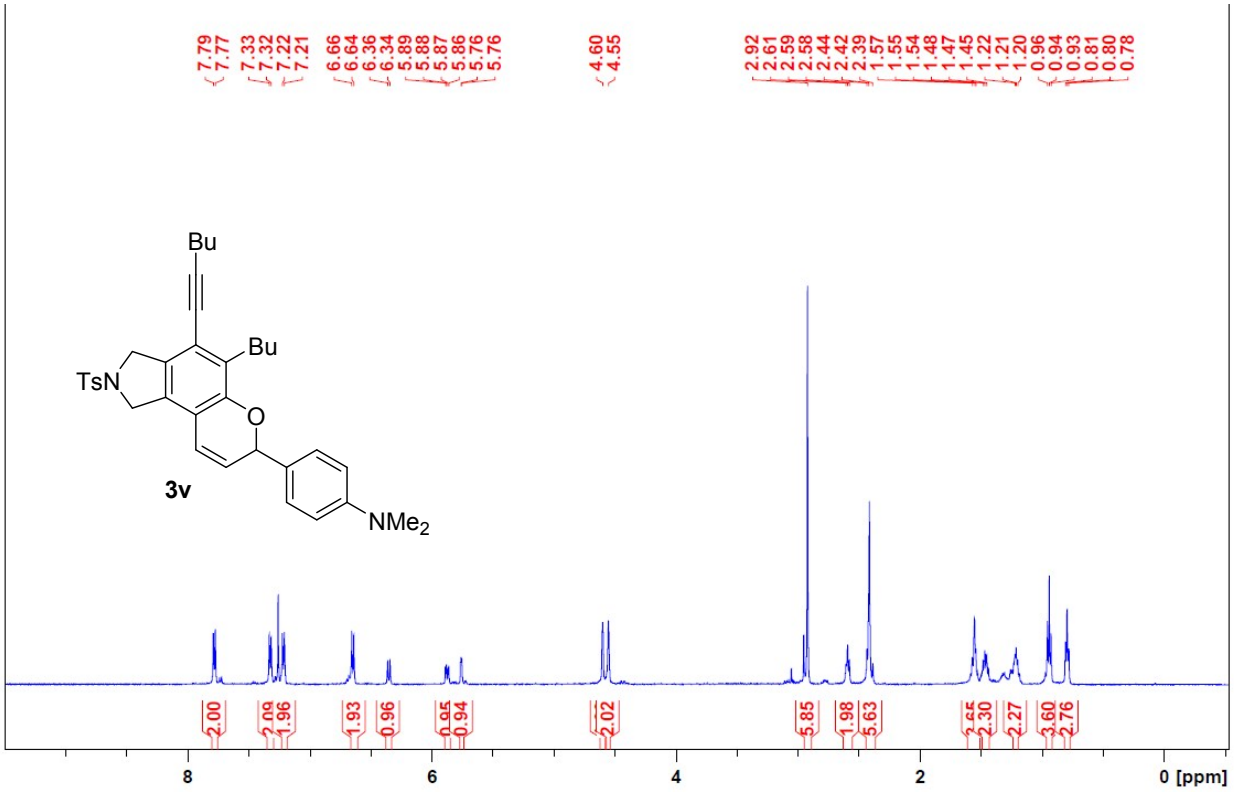
121.23
118.75
116.53
98.63
76.50
65.18
54.15
52.93
31.85
30.84
27.51
22.76
21.97
21.51
19.35
13.99
13.60
Bu
Bu
TsN
O
3u
200
150
100
50
[ppm]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7.21
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6.64
6.36
6.34
5.89
5.88
5.87
5.86
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5.76
4.60
4.55
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1.55
1.54
1.48
1.47
1.45
1.22
1.21
1.20
0.96
0.94
0.93
0.81
0.80
0.78
Bu
Bu
TsN
O
3v
NMe2
2.00
2.09
1.96
1.93
0.96
0.95
0.94
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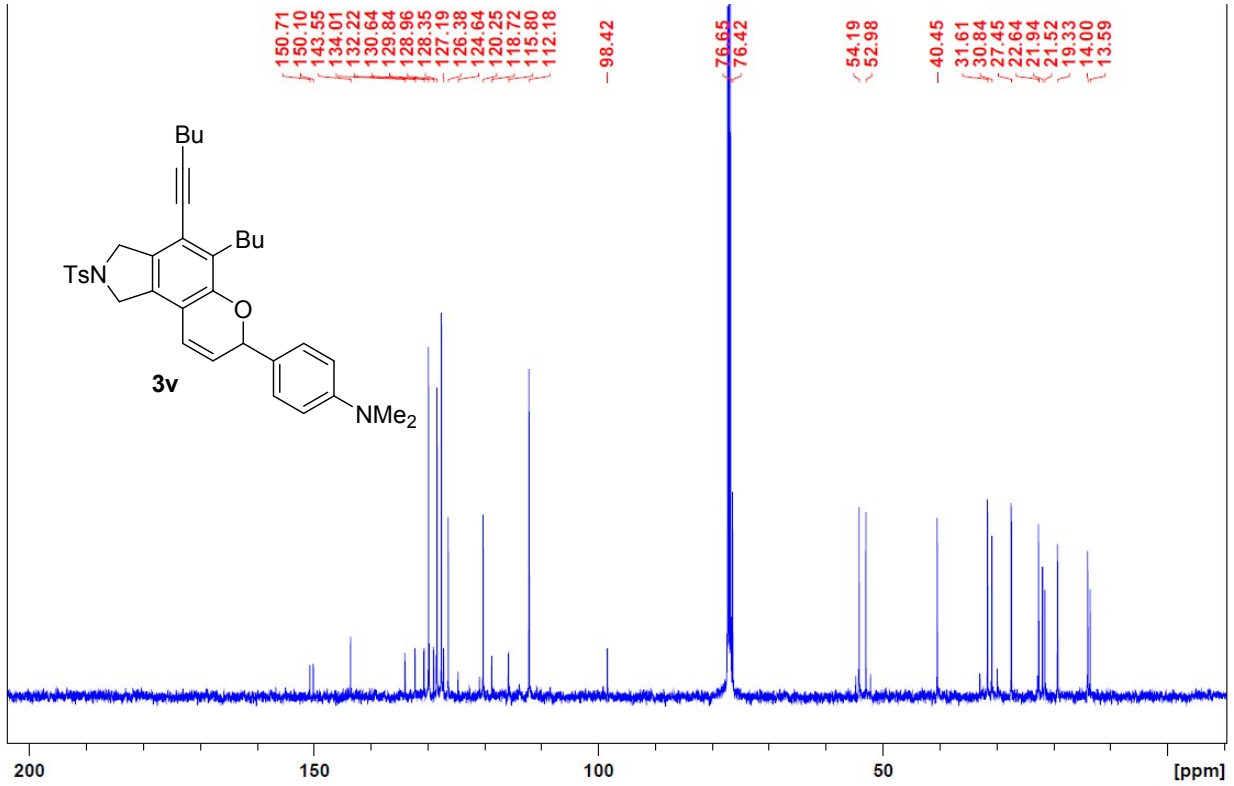
5.63
2.45
2.30
2.27
3.60
2.76
8
6
4
2
0 [ppm]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130.64
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128.35
127.19
126.38
124.64
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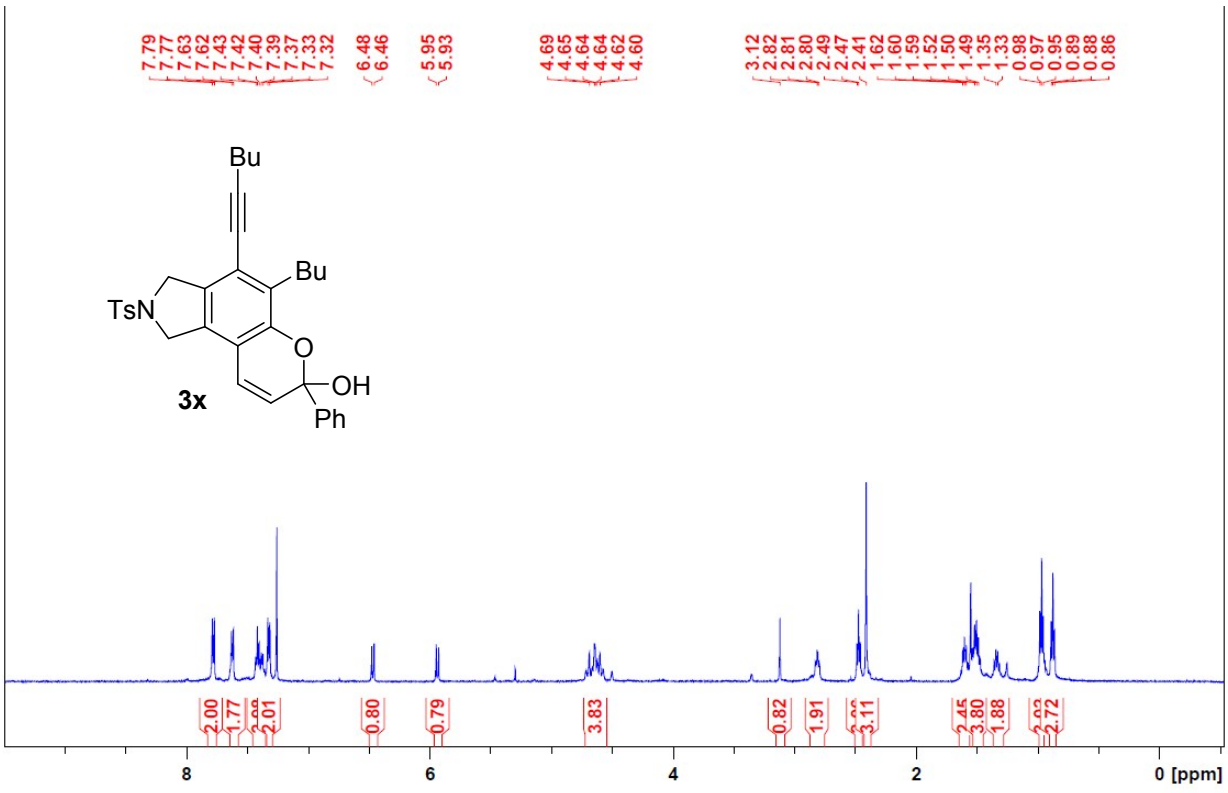
115.80
112.18
98.42
76.65
76.42
54.19
52.98
40.45
31.61
30.84
27.45
22.64
21.94
21.52
19.33
14.00
13.59
Bu
Bu
TsN
O
3v
NMe2
200
150
100
50
[ppm]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6.46
5.95
5.93
4.69
4.65
4.64
4.64
4.62
4.60
3.12
2.82
2.81
2.80
2.49
2.47
2.41
1.62
1.60
1.59
1.52
1.50
1.49
1.35
1.33
0.98
0.97
0.95
0.89
0.88
0.86
Bu
Bu
TsN
O
OH
Ph
3x
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2.01
0.80
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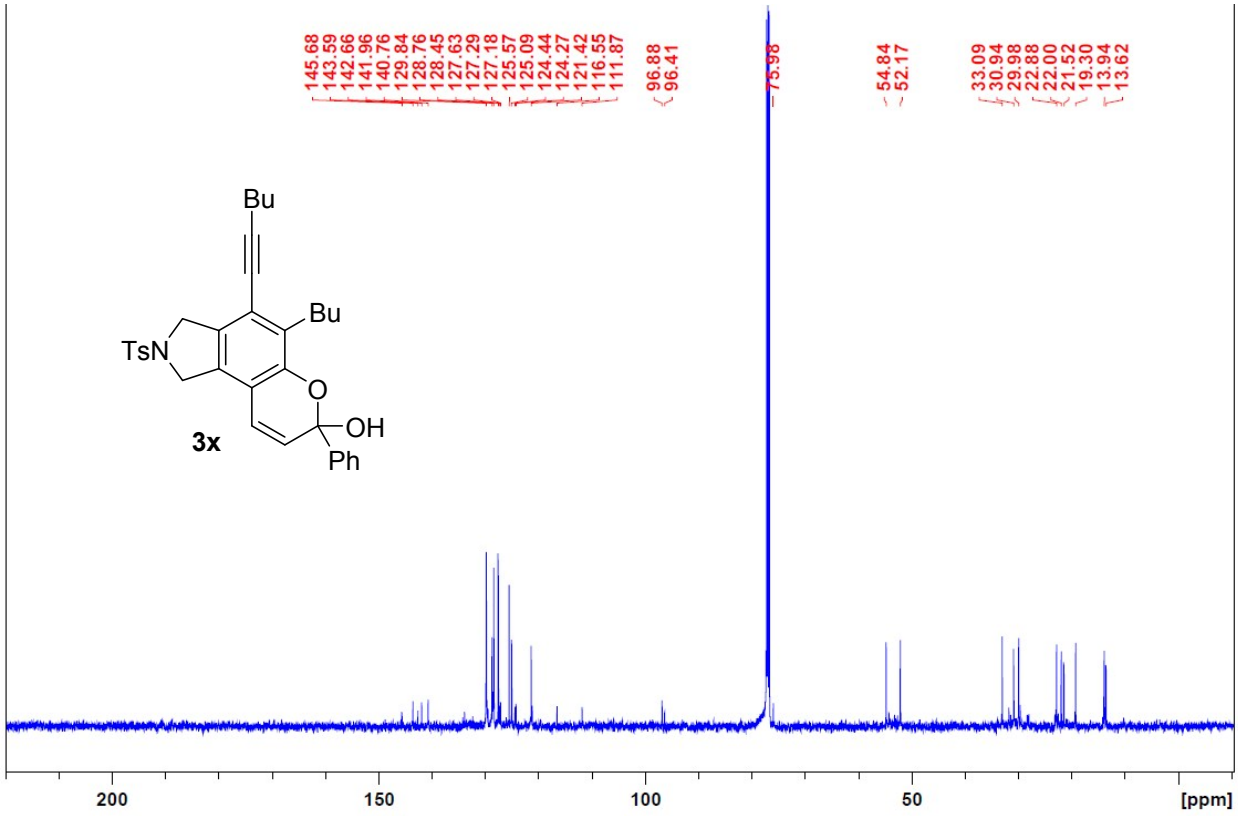
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124.44
124.27
121.42
116.55
111.87
96.88
96.41
75.98
54.84
52.17
33.09
30.94
29.98
22.88
22.00
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13.62
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Bu
TsN
O
OH
Ph
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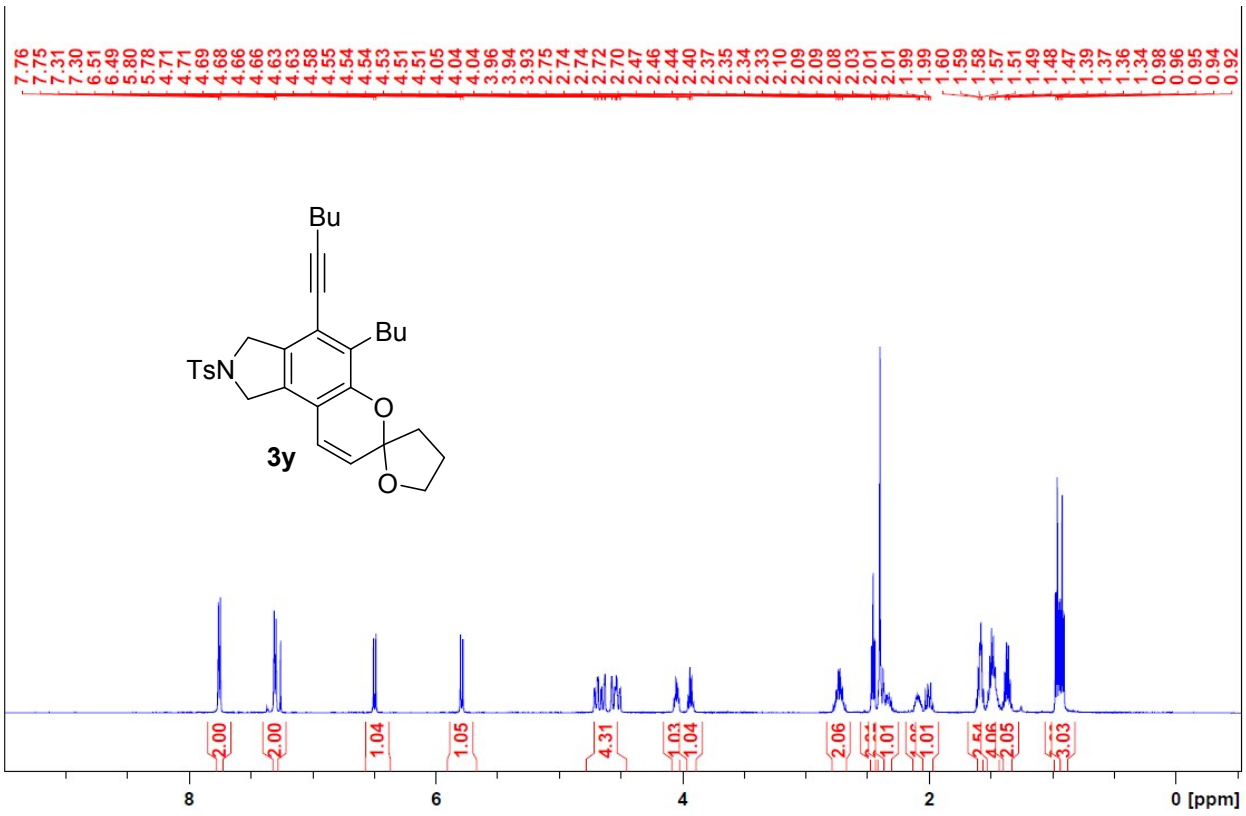
[ppm]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Bu
TsN
O
O
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8
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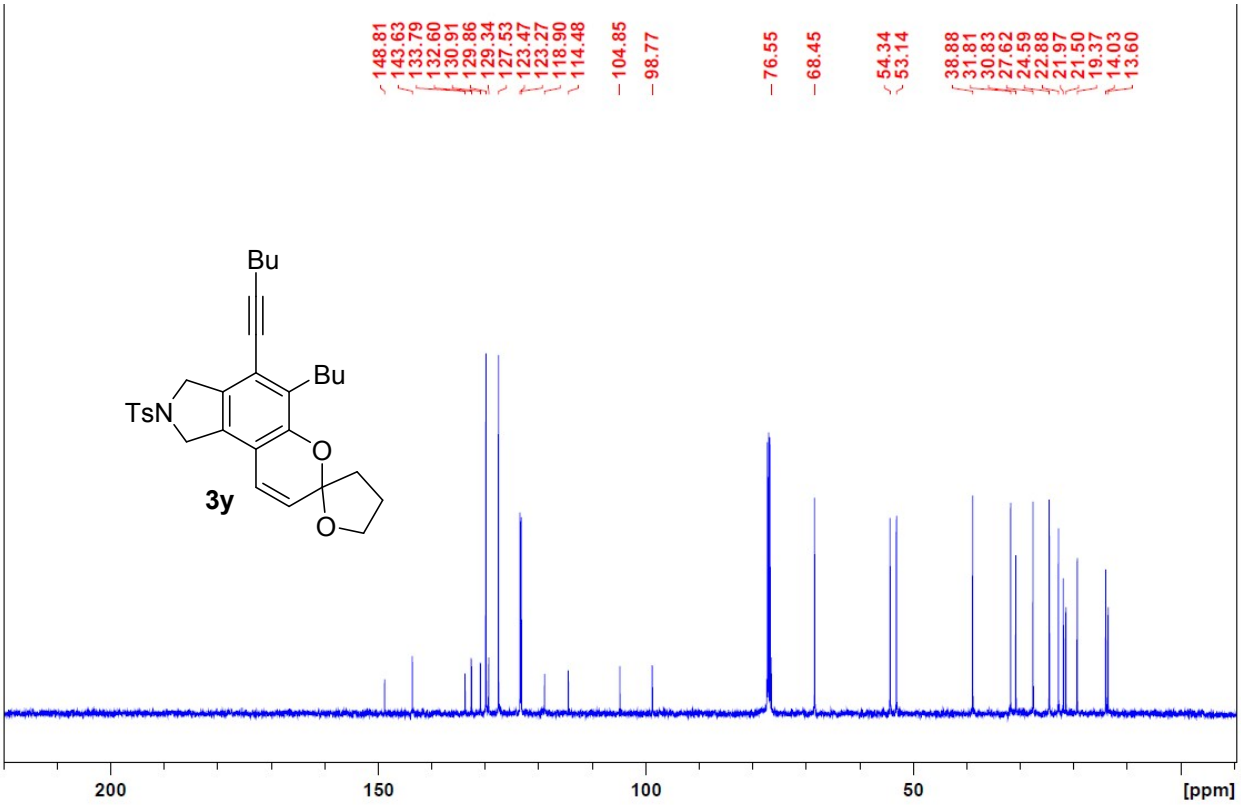
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Bu
TsN
O
O
3y
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150
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50
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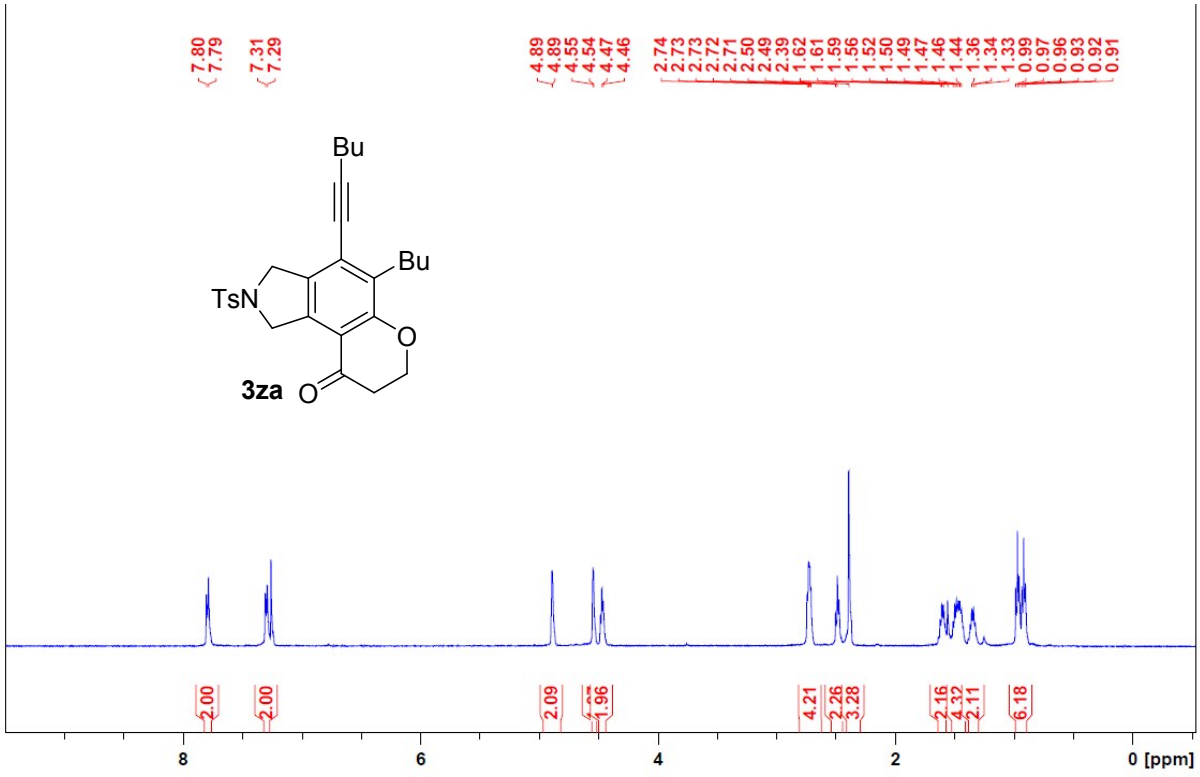
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1.52
1.50
1.49
1.47
1.46
1.44
1.36
1.34
1.33
0.99
0.97
0.96
0.93
0.92
0.91
Bu
Bu
TsN
O
3za
O
2.00
2.00
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2.26
3.28
2.16
4.32
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6.18
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4
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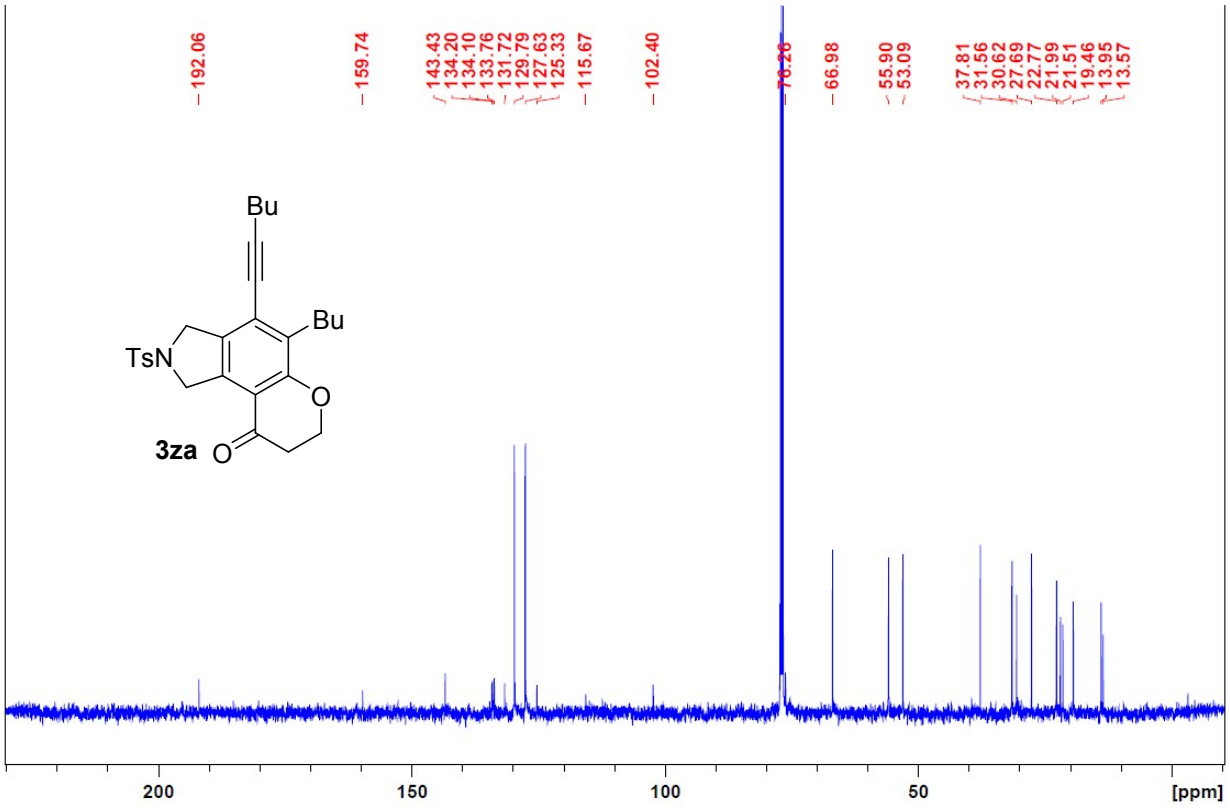
0 [ppm]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133.76
131.72
129.79
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125.33
115.67
102.40
78.20
66.98
55.90
53.09
37.81
31.56
30.62
27.69
22.77
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21.51
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13.95
13.57
Bu
Bu
TsN
O
3za
O
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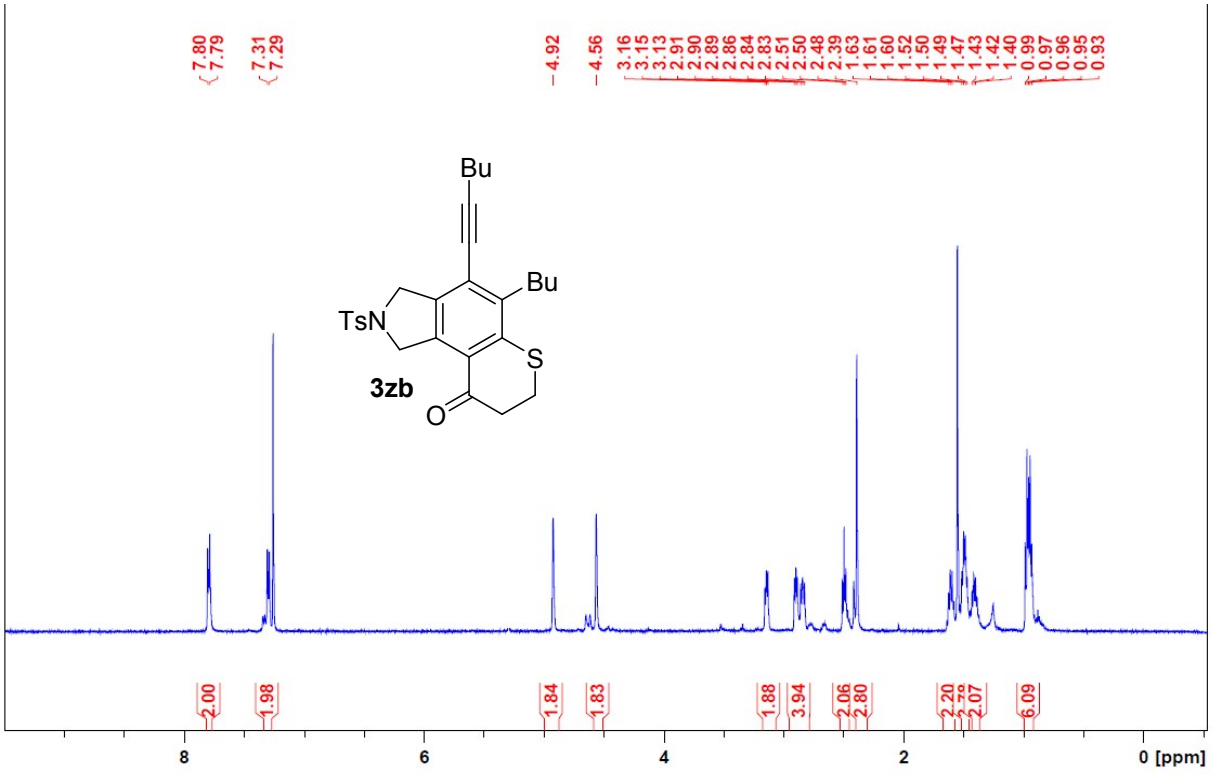
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1.61
1.60
1.52
1.50
1.49
1.47
1.43
1.42
1.40
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0.97
0.96
0.95
0.93
Bu
Bu
TsN
S
O
3zb
2.00
1.98
1.84
1.83
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3.94
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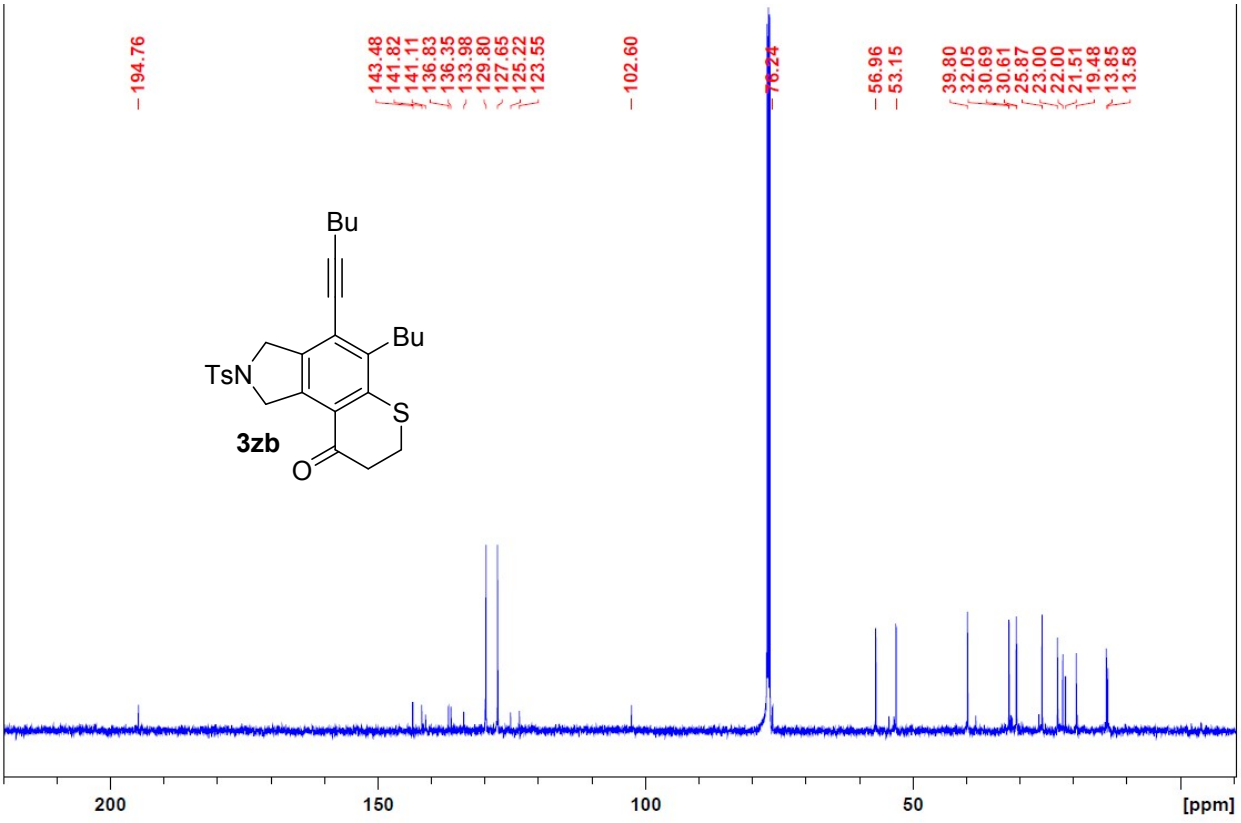
2.80
2.20
2.07
6.09
8
6
4
2
0 [ppm]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141.82
141.11
136.83
136.35
133.98
129.80
127.65
125.22
123.55
102.60
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56.96
53.15
39.80
32.05
30.69
30.61
25.87
23.00
22.00
21.51
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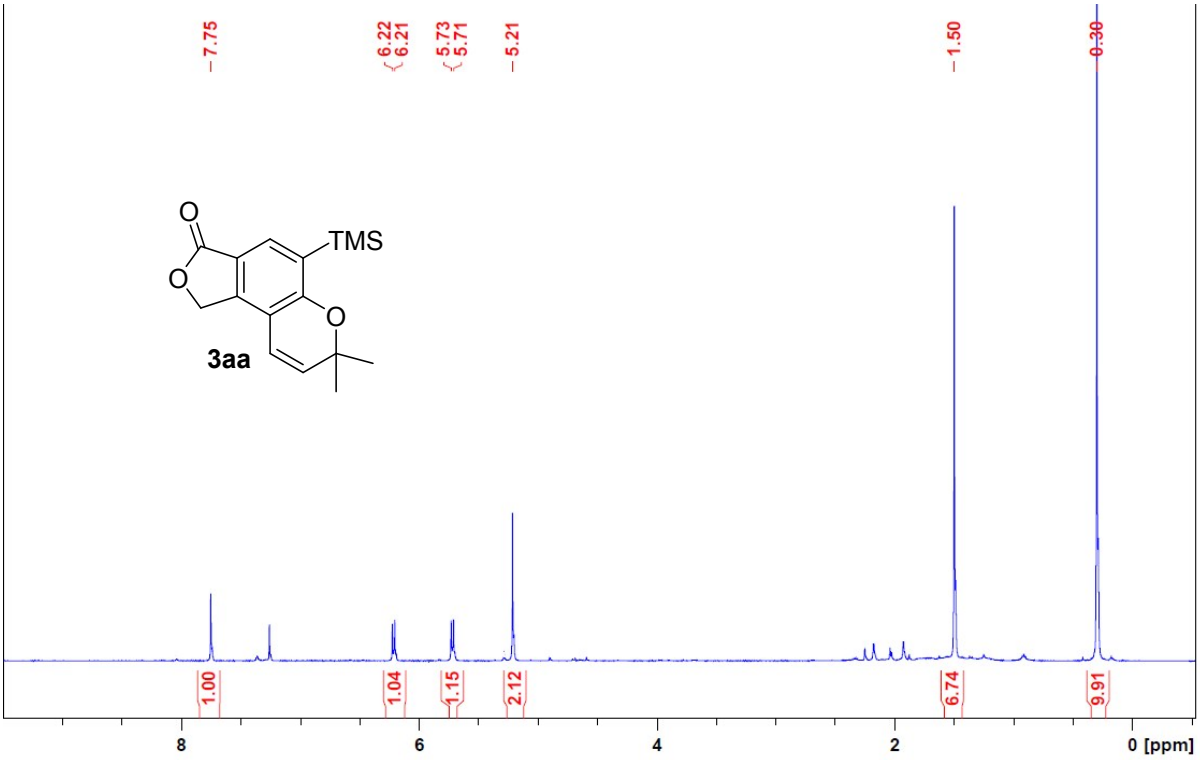
13.85
13.58
Bu
Bu
TsN
S
O
3zb
200
150
100
50
[ppm]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O
O
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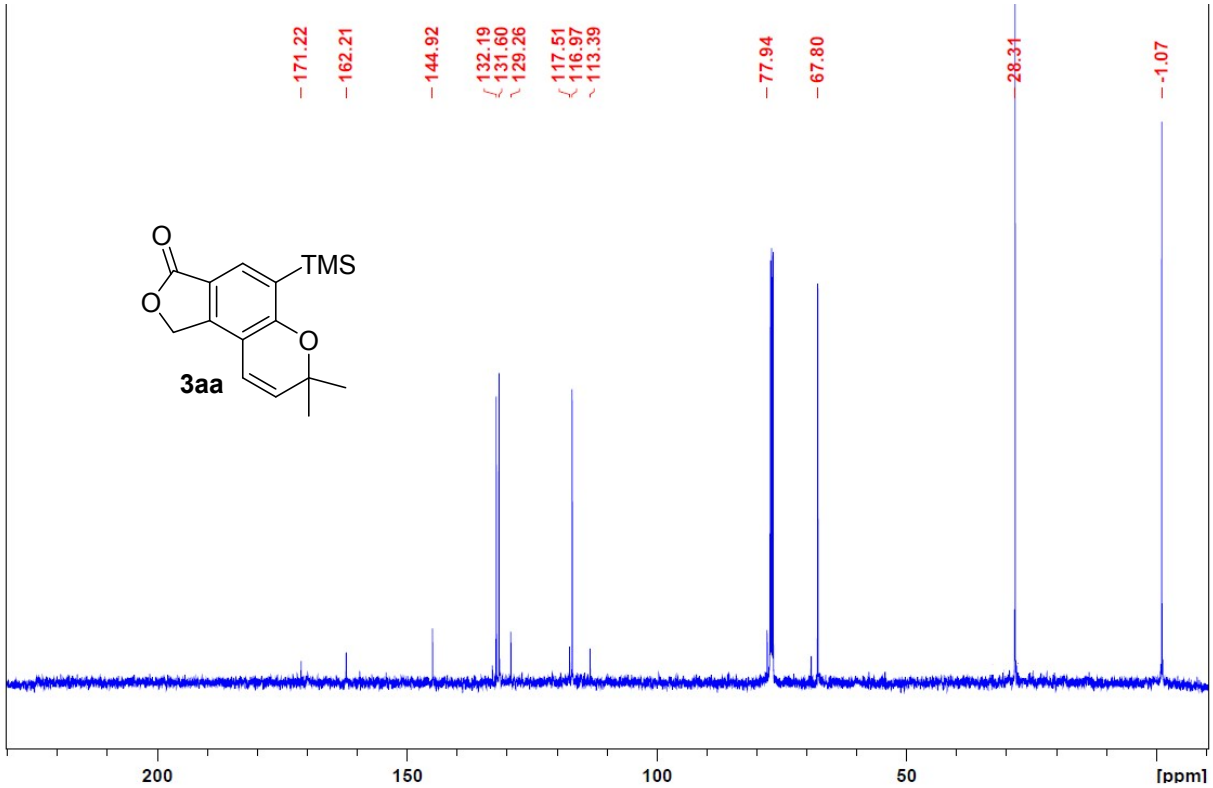
1.15
2.12
6.74
9.91
8
6
4
2
0 [ppm]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162.21
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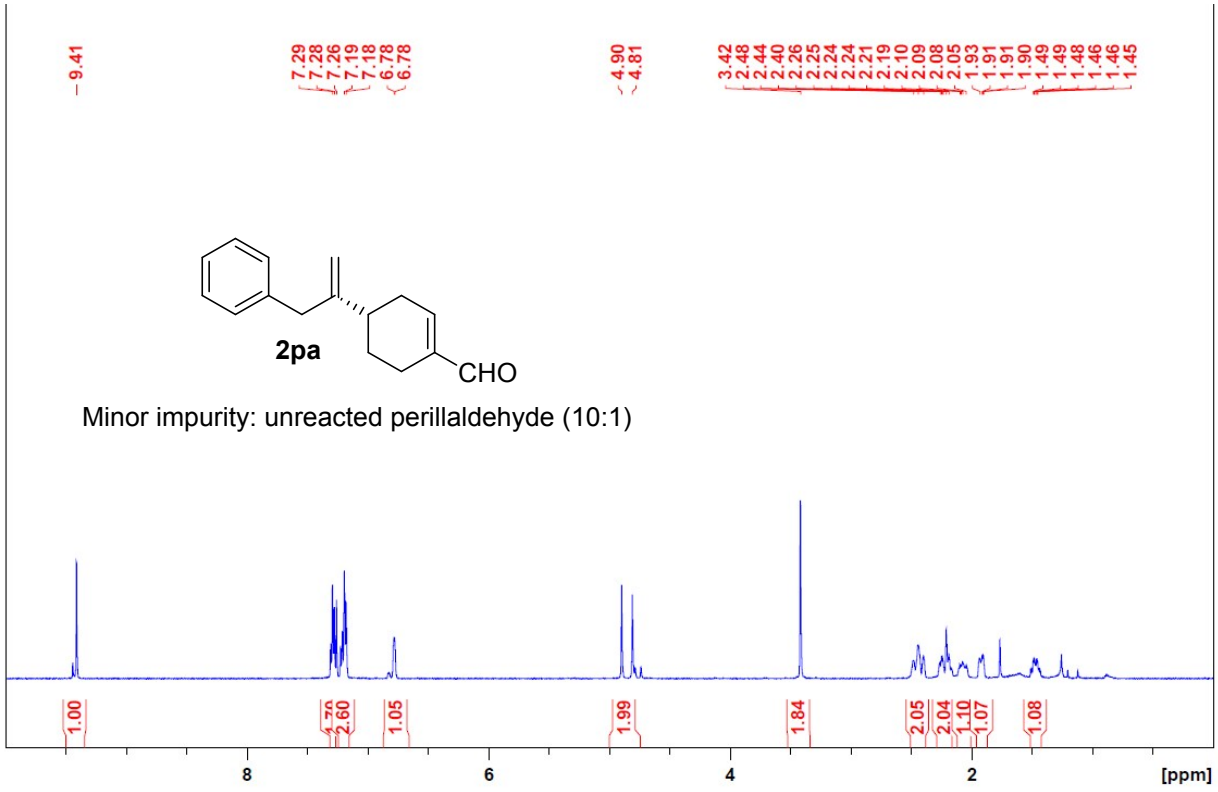
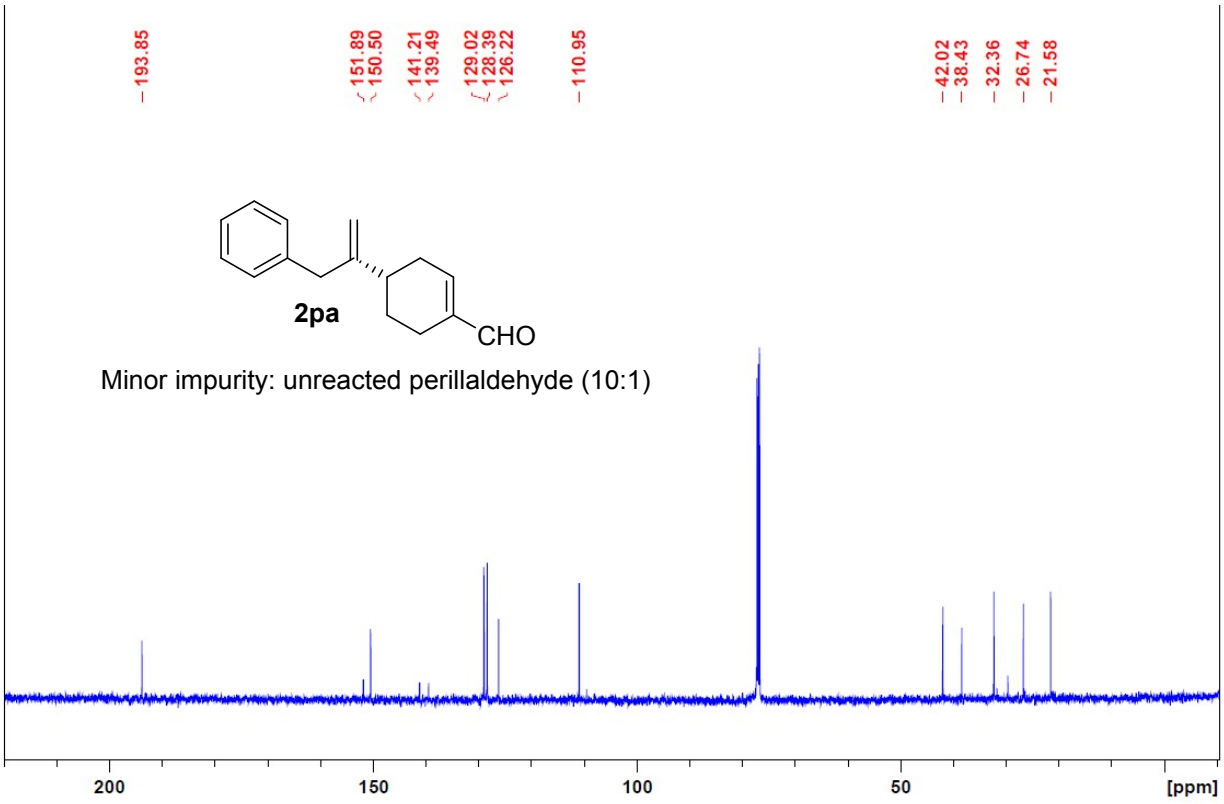
129.26
117.51
116.97
113.39
77.94
67.80
28.31
-1.07
TMS
O
O
O
3aa
200
150
100
50
[ppm]



2pa

Minor impurity: unreacted perillaldehyde (10:1)



2pa

Minor impurity: unreacted perillaldehyde (10:1)

Computational studies for the reaction of tiglyl aldehyde and an aryne generated from a tetrayne

1. Computational Details

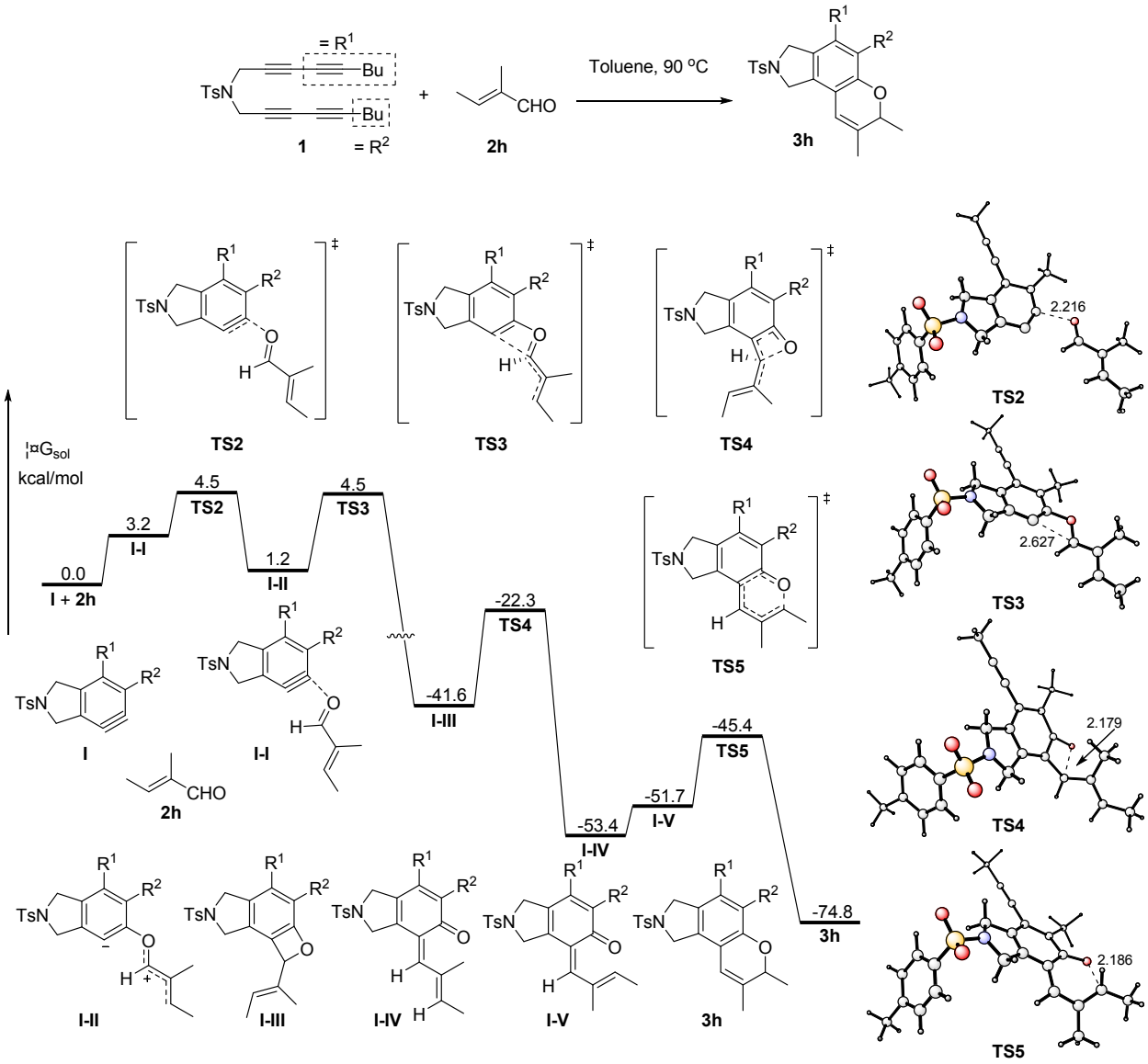
All DFT calculations were carried out with the Gaussian 09 suite of computational programs.[1] The geometries of all stationary points were optimized using the B3LYP hybrid functional[2] at the basis set level of 6-31+G(d). Frequencies were analytically computed at the same level of theory to obtain the free energies and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). The solvent effect of toluene was evaluated by using the SMD polarizable continuum model by carrying out single point calculations at the M06/6-311+G(d,p) level.[3] All transition state structures were confirmed to connect the proposed reactants and products by intrinsic reaction coordinate (IRC) calculations. All the energies given in the text are relative free energies corrected with solvation effects.

[1] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[2] (a) Becke, A. D. J. *Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[3] (a) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

2. DFT-Calculated Reaction Mechanism



3. Cartesian Coordinates and Energies for All Species

Benzyne

C	2.68094300	7.58193200	-0.66947700
C	3.32903500	6.33765200	-0.55834700
C	4.66544700	6.40445200	-0.91673900
C	5.21764200	7.46606500	-1.29011400
C	4.73309000	8.74885400	-1.45139900
C	3.33470700	8.76272300	-1.09927000
C	1.23027500	7.43334500	-0.28478000
C	2.39215900	5.25861600	-0.09331300
H	0.90650300	8.14632400	0.47901400
H	2.75520200	4.71117500	0.78179000
H	0.57415700	7.55552200	-1.16112600
H	2.19344900	4.52946700	-0.89480500
N	1.19312500	6.05325600	0.25869800
C	2.60479000	9.98815200	-1.18185500
C	1.98361000	11.03022100	-1.25039200
S	-0.27009800	5.29333400	0.51034300
O	-1.17219000	6.32486500	1.03357900
O	0.03841500	4.06457400	1.24947200
C	-0.89605600	4.80163300	-1.10358800
C	-1.68926700	5.68785000	-1.83988400
C	-0.55969100	3.54720500	-1.62254600
C	-2.13250500	5.31356800	-3.10917700
H	-1.97436000	6.64327100	-1.41122200
C	-1.01224200	3.19057200	-2.89384600
H	0.02463700	2.85352400	-1.02651600
C	-1.80232600	4.06401600	-3.65734700
H	-2.75377500	6.00118300	-3.67885700
H	-0.75413500	2.21270100	-3.29426400
C	-2.31885300	3.65416100	-5.01692000
H	-3.30316300	3.17388200	-4.93274300
H	-2.43336300	4.51862100	-5.67993900
H	-1.64664000	2.93861000	-5.50241500
C	1.23339400	12.28180200	-1.32451200
H	1.89732300	13.12707400	-1.54262400
H	0.47146300	12.24224500	-2.11295300
H	0.72236200	12.49246200	-0.37697900
C	5.47653400	9.97309700	-1.90512300
H	5.01596900	10.40549600	-2.80179700
H	5.46242500	10.75161800	-1.13237000
H	6.51746200	9.72921200	-2.13214000

Energies:
Sum of electronic and zero-point Energies = -1337.111253
Sum of electronic and thermal Enthalpies = -1337.087596
Sum of electronic and thermal Free Energies = -1337.166620
Electronic energies = -1337.4226843
Single point energies in solution = -1336.99268980

2h

C	-3.27100600	-0.12439500	-0.00009500
C	-2.62377200	1.03914200	0.21885300
H	-1.56595100	0.95316000	0.46882900
C	-2.48993600	-1.38779300	0.11877700
O	-1.30525200	-1.47574500	0.39699000
H	-3.07603900	-2.31430500	-0.07069800
C	-4.72827500	-0.29195700	-0.35890700
H	-4.84114500	-0.80247200	-1.32505200
H	-5.25024200	-0.90672900	0.38697900
H	-5.25570100	0.66223000	-0.42666000
C	-3.16852900	2.43227900	0.16337000
H	-2.61579500	3.02668800	-0.57767900
H	-4.23145900	2.47798400	-0.08776700
H	-3.02295800	2.93571600	1.12945900

Energies:
Sum of electronic and zero-point Energies = -270.438301
Sum of electronic and thermal Enthalpies = -270.429899
Sum of electronic and thermal Free Energies = -270.469848
Electronic energies = -270.5560001
Single point energies in solution = -270.434172589

β,γ-unsaturated aldehyde

C	3.10416500	-1.95040000	0.77498200
O	2.69116000	-0.82098000	0.62133600
H	2.40835000	-2.76076200	1.09190200
C	4.53462400	-2.41487600	0.53635800
H	4.83670800	-2.95869800	1.44544600
C	5.48663600	-1.27676400	0.28437500
H	5.20480500	-0.58996300	-0.51292400
C	6.62302900	-1.07943900	0.95850500
H	6.93288400	-1.73676900	1.76981600
H	7.28501700	-0.24923400	0.72620500
C	4.51405200	-3.43423900	-0.63309800
H	3.78580100	-4.23497300	-0.45298600
H	4.25194800	-2.93959000	-1.57552400
H	5.50230800	-3.88961700	-0.74940800

Energies:
Sum of electronic and zero-point Energies = -270.425387
Sum of electronic and thermal Enthalpies = -270.417273
Sum of electronic and thermal Free Energies = -270.456713
Electronic energies = -270.5431296
Single point energies in solution = -270.421893330

TS1

C	2.59697200	-2.48036800	1.82992700
C	3.41584600	-1.88828500	2.77007300
C	4.30556400	-0.75668800	2.44696000
H	4.89557600	-0.44143200	3.31030400
H	4.95690200	-0.93785900	1.58639100
H	3.62176300	0.08906100	2.14830700
C	-1.11501500	-0.12821900	1.94543000
C	-0.20799200	-1.19091800	2.07165400
C	1.11108200	-0.81209200	1.88611100
C	1.50091400	0.38553400	1.65337900
C	0.68448300	1.49896800	1.48632400
C	-0.70695200	1.19543000	1.66319100
C	-2.52190200	-0.62262200	2.16603200
C	-0.91497700	-2.48605600	2.37126000
H	-2.93526500	-0.23421900	3.11006700
H	-0.69812800	-2.83418600	3.39425300
H	-3.21145600	-0.35202500	1.36114700
H	-0.66627600	-3.29769500	1.67945700
N	-2.33084300	-2.09354500	2.19954500
C	-1.68623000	2.23229500	1.56736600
C	-2.51793000	3.11428300	1.48347800
S	-3.54200000	-3.08334700	2.78284900
O	-3.10807200	-4.45477000	2.49251500
O	-4.79772600	-2.52752100	2.26850000
C	-3.56092900	-2.89356600	4.57185600
C	-2.76364800	-3.72662400	5.36545400
C	-4.34887300	-1.89647500	5.15387200
C	-2.74818900	-3.54138600	6.74757700
H	-2.19165500	-4.52622700	4.90565400
C	-4.32030100	-1.72637600	6.53978900
H	-4.99624700	-1.28575200	4.53274700
C	-3.51778400	-2.53633900	7.35687100
H	-2.13641600	-4.19591600	7.36466100
H	-4.94174700	-0.95747500	6.99291800
C	-3.47597000	-2.33695400	8.85397000
H	-4.29654900	-1.69843200	9.19668200
H	-3.54412500	-3.29277700	9.38633100
H	-2.53478500	-1.86154400	9.16058500
H	1.93523500	-3.26807600	2.19452000
C	-3.51899400	4.17336700	1.37754600
H	-4.28126000	3.92347300	0.62916100
H	-4.03147100	4.33315200	2.33444100
H	-3.05810300	5.12369400	1.08187700
C	1.15775500	2.89579200	1.18205100
H	0.71273800	3.27302600	0.25264300
H	0.86988600	3.59525600	1.97731100
H	2.24583300	2.91614400	1.08011900
C	3.18330800	-2.24552700	4.18334300
O	3.78418100	-1.76570600	5.13197200
H	2.40553000	-3.02183100	4.34996000
C	2.84050000	-2.48757700	0.34174400
H	1.91533100	-2.67192100	-0.21224000
H	3.27085300	-1.54852400	-0.01351700
H	3.53967600	-3.30129100	0.09844100

Energies:

Sum of electronic and zero-point Energies = -1607.545230
Sum of electronic and thermal Enthalpies = -1607.513829
Sum of electronic and thermal Free Energies = -1607.611762
Electronic energies = -1607.9753539
Single point energies in solution = -1607.42953892

Ene-P

C	2.23595900	-2.04587700	1.96671500
C	3.46571800	-1.65717000	2.77512800
C	4.72279400	-1.58118400	2.31120400
H	5.52980700	-1.30012000	2.98264300
H	4.98054000	-1.79523200	1.27884000
H	2.67023100	0.63516500	1.55631200
C	-1.08113700	-0.10900300	1.95809300
C	-0.15618900	-1.14705500	2.05582800
C	1.21457100	-0.90688600	1.91238600
C	1.61020000	0.41758100	1.66478700
C	0.70327500	1.47825300	1.55857400
C	-0.68262900	1.21424600	1.71073300
C	-2.48379900	-0.61368200	2.17072000
C	-0.86061100	-2.45362400	2.34261300
H	-2.89644100	-0.24937800	3.12525600
H	-0.64779300	-2.80894900	3.36493800
H	-3.17768700	-0.32555100	1.37562600
H	-0.60361700	-3.26102600	1.64975600
N	-2.28039200	-2.07999900	2.16677200
C	-1.65619500	2.25679400	1.61881500
C	-2.49384500	3.13346100	1.54088800
S	-3.48355200	-3.09822700	2.71354800
O	-3.03214900	-4.45736700	2.39403100
O	-4.74220700	-2.54509000	2.20311500
C	-3.52101600	-2.95335200	4.50698400
C	-2.71825100	-3.79347500	5.28758700
C	-4.33065500	-1.98418100	5.10591500
C	-2.71990300	-3.64343500	6.67411500
H	-2.12866200	-4.57175700	4.81362600
C	-4.31922400	-1.84921700	6.49603100
H	-4.98121600	-1.36822200	4.49333500
C	-3.51249500	-2.66722000	7.30074900
H	-2.10435700	-4.30417500	7.28086100
H	-4.95780900	-1.10231000	6.96196400
C	-3.49148600	-2.50741100	8.80311900
H	-4.31592800	-1.87657500	9.15075300
H	-3.56930600	-3.47682500	9.30908900
H	-2.55409400	-2.04241600	9.13612900
H	1.76171300	-2.87725600	2.51046000
C	-3.50096800	4.18755800	1.44152700
H	-4.24377900	3.95299100	0.66899900
H	-4.03673600	4.31558200	2.39040900
H	-3.04165300	5.14959800	1.18397400
C	1.18920500	2.88151700	1.29087600
H	0.76279400	3.28001200	0.36173100
H	0.88978900	3.56636600	2.09400400
H	2.28001500	2.91090900	1.20658600
C	3.21623900	-1.36631900	4.22229700
O	4.05845600	-0.99642400	5.01999100
H	2.16899000	-1.52176800	4.55870900
C	2.55438000	-2.55879800	0.54919100
H	1.63360200	-2.86935700	0.04468800
H	3.01604000	-1.77566800	-0.06269000
H	3.23238100	-3.41942300	0.58402800

Energies:

Sum of electronic and zero-point Energies = -1607.670696
Sum of electronic and thermal Enthalpies = -1607.640027
Sum of electronic and thermal Free Energies = -1607.735784
Electronic energies = -1608.106222
Single point energies in solution = -1607.56186009

TS2

C	5.07959800	-3.48124200	0.90737100
C	4.76810000	-2.21200700	0.54434100
C	5.68549700	-1.19947000	-0.09010700
H	5.75938000	-0.30301300	0.53676100
H	6.69206500	-1.59254500	-0.24780200
H	5.28663200	-0.87336800	-1.05790900
C	-1.45439900	-0.39256700	1.78129200
C	-0.76615300	-1.59673600	1.97192300
C	0.58188900	-1.70598400	1.59172700
C	1.02597000	-0.59894600	1.08482200
C	0.54156800	0.65985500	0.81109300
C	-0.83352400	0.73970900	1.20715200
C	-2.88129700	-0.50694800	2.24896100
C	-1.67621300	-2.63502600	2.58559600
H	-3.17683800	0.27246200	2.95782600
H	-1.26356200	-3.09340400	3.48927200
H	-3.58580200	-0.47466800	1.40245400
H	-1.90182600	-3.43962400	1.86756000
N	-2.87469800	-1.83050300	2.92124900
C	-1.56329200	1.95450100	1.02490500
C	-2.19235200	2.98345600	0.87451400
S	-4.31002400	-2.57503700	3.30391500
O	-5.20853400	-1.51599400	3.77967900
O	-3.96284000	-3.73759900	4.13000100
C	-5.00694600	-3.20736800	1.76675900
C	-5.86161100	-2.40015200	1.00935500
C	-4.66568100	-4.49025000	1.32665100
C	-6.36158800	-2.88135100	-0.20190600
H	-6.15257100	-1.42307400	1.38158400
C	-5.17491100	-4.95466100	0.11287000
H	-4.03579000	-5.12302600	1.94357900
C	-6.02238900	-4.15883600	-0.67377900
H	-7.03594800	-2.25664200	-0.78370200
H	-4.91801700	-5.95740000	-0.22192900
C	-6.54763100	-4.66042900	-1.99913200
H	-6.66360600	-5.74976800	-1.99841800
H	-7.51896900	-4.21488700	-2.23982200
H	-5.85902300	-4.40532700	-2.81629100
H	4.28133500	-4.07351800	1.35735400
C	-2.95131800	4.22046000	0.70151200
H	-3.36454100	4.56928400	1.65628100
H	-2.31706300	5.02045600	0.30006600
H	-3.79016100	4.08005000	0.00802300
C	1.27076300	1.82462500	0.19890500
H	0.77851900	2.14933100	-0.72619700
H	1.26837700	2.68596800	0.87830500
H	2.30474700	1.56218000	-0.02882500
C	3.39091100	-1.81567700	0.81098600
O	2.93953000	-0.69683400	0.54410100
H	2.69250400	-2.53972500	1.27697700
C	6.38854200	-4.18886800	0.77301700
H	6.73701700	-4.52424100	1.75963900
H	6.26381500	-5.09705400	0.16724300
H	7.17174300	-3.57699200	0.32019200

Energies:

Sum of electronic and zero-point Energies = -1607.557680
Sum of electronic and thermal Enthalpies = -1607.526138
Sum of electronic and thermal Free Energies = -1607.625296
Electronic energies = -1607.9891548
Single point energies in solution = -1607.44133497

I-2

C	5.24788200	-3.18221000	1.21831800
C	4.61637500	-2.12838500	0.62470500
C	5.18296100	-1.23567100	-0.45169600
H	5.13086000	-0.18435100	-0.14734300
H	6.22386500	-1.47422900	-0.67800500
H	4.59978100	-1.32843800	-1.37547500
C	-1.37736600	-0.50554400	1.75233300
C	-0.73174300	-1.73157100	1.93353200
C	0.59116600	-1.98119900	1.54373200
C	1.16746100	-0.84309100	1.02359800
C	0.63865300	0.43580500	0.79119400
C	-0.71355500	0.60055200	1.17932500
C	-2.81188000	-0.56458500	2.20285100
C	-1.69742600	-2.73298700	2.53301400
H	-3.08701100	0.23382500	2.89896300
H	-1.30745600	-3.22750000	3.42697200
H	-3.50465900	-0.51432600	1.34657300
H	-1.96153400	-3.51135500	1.79984700
N	-2.85758500	-1.87931000	2.88695800
C	-1.40611500	1.84201700	1.01465000
C	-2.03107300	2.87742100	0.89441200
S	-4.32234200	-2.55971300	3.27268000
O	-5.17486800	-1.46221700	3.74787600
O	-4.02851800	-3.73495400	4.10170900
C	-5.05136100	-3.16392400	1.73842200
C	-5.87990400	-2.32425200	0.98696300

C	-4.76137100	-4.45779100	1.29442200
C	-6.40626100	-2.78488200	-0.22091000
H	-6.13039700	-1.33710700	1.36195600
C	-5.29616900	-4.90151400	0.08364300
H	-4.15012700	-5.11449500	1.90504500
C	-6.11867500	-4.07391100	-0.69616800
H	-7.06044700	-2.13443400	-0.79772000
H	-5.07825700	-5.91236400	-0.25431900
C	-6.67157000	-4.55256900	-2.01881400
H	-6.77559800	-5.64282000	-2.03931400
H	-7.65371800	-4.11314700	-2.22551700
H	-6.00705100	-4.27112200	-2.84720900
H	4.68803300	-3.72403900	1.98133600
C	-2.77911800	4.12563800	0.75392900
H	-3.75066800	4.06064200	1.25921600
H	-2.23244200	4.96995300	1.19288400
H	-2.96796200	4.36357300	-0.30081000
C	1.45058600	1.56637900	0.20708100
H	0.81261400	2.42551000	-0.01433300
H	2.23173300	1.90077400	0.90333900
H	1.95297300	1.26140400	-0.71844600
C	3.27967700	-1.89546700	1.08496200
O	2.57651800	-0.95472900	0.58448600
H	2.77928600	-2.51579700	1.83513500
C	6.61517200	-3.71077400	0.94551200
H	7.21233800	-3.69882800	1.86823400
H	6.55400100	-4.76425300	0.63767800
H	7.15557500	-3.15656100	0.17548700

Energies:

Sum of electronic and zero-point Energies = -1607.560213
Sum of electronic and thermal Enthalpies = -1607.528658
Sum of electronic and thermal Free Energies = -1607.627056
Electronic energies = -1607.9927129
Single point energies in solution = -1607.44844283

TS2'

C	-1.71437000	-0.60233800	1.66798000
C	-1.02138400	-1.80619600	1.83340800
C	0.33322500	-1.94197000	1.48520700
C	0.80050700	-0.79977400	1.00279100
C	0.28834900	0.46476300	0.76648200
C	-1.08645000	0.54570600	1.14081500
C	-3.14174400	-0.72396100	2.12993500
C	-1.93654500	-2.85427000	2.42813200
H	-3.31854600	-0.13519800	3.04456900
H	-1.63961500	-3.09846500	3.46057200
H	-3.87617000	-0.40616000	1.38366800
H	-1.95899700	-3.78442000	1.85286200
N	-3.25740700	-2.18370100	2.37001500
C	-1.81290000	1.76596700	0.98089800
C	-2.44388600	2.79652300	0.85077500
S	-4.54857800	-2.78321900	3.22570900
O	-4.49602800	-4.24348400	3.08621800
O	-5.71778300	-1.99891800	2.80857300
C	-4.25549500	-2.41012900	4.96461900
C	-3.55316200	-3.32252400	5.76055400
C	-4.70552200	-1.20060400	5.50015900
C	-3.29408300	-3.00831000	7.09426900
H	-3.24225800	-4.27474500	5.34303100
C	-4.43651800	-0.90241200	6.83845300
H	-5.28254700	-0.51784400	4.88475100
C	-3.72565600	-1.79417600	7.65415600
H	-2.75643400	-3.72329200	7.71381500
H	-4.79566600	0.03555400	7.25596700
C	-3.43374400	-1.46842700	9.10096900
H	-2.35502200	-1.35865300	9.27256500
H	-3.91656900	-0.53446300	9.40632100
H	-3.78762000	-2.26427700	9.76790100
C	-3.20994400	4.03106900	0.69086200
H	-2.65663600	4.76565200	0.09273400
H	-4.16554700	3.84154900	0.18611700
H	-3.43283900	4.49163800	1.66179000
C	1.01498000	1.65275400	0.19008600
H	0.54314900	1.97970400	-0.74494600
H	0.97248100	2.50495000	0.87936600
H	2.06219700	1.42493300	-0.01399300
C	3.02660400	-1.95428000	0.71379400
O	2.48674600	-0.86011700	0.52164000
H	2.37772500	-2.73608300	1.16118600
C	4.45690700	-2.21350400	0.36049100
H	4.90048400	-1.28475500	-0.01500600
C	5.17403900	-2.65434200	1.62357200
H	4.87874800	-3.62331000	2.02723900
C	6.11871600	-1.93445900	2.23528300
H	6.43224000	-0.96115700	1.86278100
H	6.61661300	-2.30002100	3.12934200
C	4.51151700	-3.30529700	-0.73795400
H	4.05044500	-4.23867600	-0.39572600
H	3.99530100	-2.97804800	-1.64670800
H	5.55759100	-3.51109200	-0.98611000

Energies:

Sum of electronic and zero-point Energies = -1607.536819
Sum of electronic and thermal Enthalpies = -1607.505699
Sum of electronic and thermal Free Energies = -1607.603539
Electronic energies = -1607.968413
Single point energies in solution = -1607.42094478

I-2'

C	-1.70185600	-0.62827400	1.67086000
C	-1.02641000	-1.84291400	1.83100900
C	0.32172800	-2.02664900	1.48890800
C	0.83876600	-0.87566500	0.99716200
C	0.31247100	0.39661100	0.77520700
C	-1.05550800	0.50883100	1.14665000
C	-3.13053500	-0.72538400	2.13304500
C	-1.96275600	-2.87525400	2.42324900
H	-3.29434600	-0.13656700	3.05036700
H	-1.67069400	-3.12651900	3.45526000
H	-3.85949800	-0.38922800	1.38932100
H	-2.00028000	-3.80355400	1.84615500
N	-3.27312700	-2.18314200	2.36673700
C	-1.76086200	1.74227300	0.98963000
C	-2.37742000	2.78200000	0.86317200
S	-4.57373000	-2.76120400	3.22170700
O	-4.54893900	-4.22192000	3.07923700
O	-5.72969000	-1.95510400	2.80848500
C	-4.27246600	-2.39750200	4.96146100
C	-3.58131100	-3.32173700	5.75354500
C	-4.70417900	-1.18322900	5.50129000
C	-3.31497200	-3.01475300	7.08753100
H	-3.28431400	-4.27696800	5.33278900
C	-4.42840900	-0.89247000	6.83987800
H	-5.27253000	-0.49067800	4.88874200
C	-3.72834700	-1.79625700	7.65162000
H	-2.78590300	-3.73876800	7.70398500
H	-4.77358100	0.04928900	7.26069300
C	-3.42818400	-1.47801200	9.09846400
H	-2.34807300	-1.37475900	9.26563200
H	-3.90438600	-0.54254000	9.40960400
H	-3.78339200	-2.27448100	9.76391700
C	-3.12627800	4.02769800	0.70722000
H	-2.56119600	4.75816800	0.11502100
H	-4.08253900	3.85392100	0.19798800
H	-3.34672600	4.48625300	1.67969700
C	1.05326800	1.57962800	0.20168000
H	0.58355000	1.91557500	-0.73135600
H	1.01961500	2.43010200	0.89368600
H	2.09918400	1.34767100	-0.00646300
C	2.96503500	-2.02246500	0.73381800
O	2.36295700	-0.94496900	0.55852200
H	2.35264600	-2.82613300	1.18634200
C	4.39524300	-2.17934900	0.34752800
H	4.76620100	-1.22304200	-0.03811900
C	5.16363300	-2.56204600	1.60178000
H	4.95711800	-3.55421900	2.00361900
C	6.04813900	-1.76344700	2.20562100
H	6.27066500	-0.76519700	1.83373800
H	6.58685800	-2.08696200	3.09214700
C	4.51024400	-3.26993700	-0.74804900
H	4.12212100	-4.23183100	-0.39500500
H	3.95817400	-2.98439400	-1.64959000
H	5.56471900	-3.40080400	-1.01095600

Energies:

Sum of electronic and zero-point Energies = -1607.536611
Sum of electronic and thermal Enthalpies = -1607.504959
Sum of electronic and thermal Free Energies = -1607.604185
Electronic energies = -1607.9686699
Single point energies in solution = -1607.42273061

I-1

C	5.11245500	-3.58490700	0.91981500
C	4.88075100	-2.30619100	0.53825300
C	5.86537200	-1.35219900	-0.08495800
H	5.97009000	-0.45264200	0.53308500
H	6.85373300	-1.79864900	-0.21411600
H	5.50636700	-1.01658200	-1.06512800
C	-1.46076700	-0.37408000	1.78266700
C	-0.77435200	-1.58151100	1.97127500
C	0.57020600	-1.65023700	1.57653000
C	1.00619200	-0.55632700	1.07909000
C	0.53321500	0.70260400	0.80651300
C	-0.84483400	0.76445700	1.21116800
C	-2.88709600	-0.49481600	2.25166200
C	-1.67803100	-2.62368000	2.58271400
H	-3.18298700	0.28055900	2.96471700
H	-1.26466100	-3.08159500	3.48647400
H	-3.59199500	-0.45978800	1.40580700
H	-1.90098900	-3.42838400	1.86393900
N	-2.87779400	-1.82157900	2.91794000
C	-1.58322000	1.97512000	1.03807900
C	-2.21860700	3.00119800	0.89526900
S	-4.31238600	-2.57225300	3.29708100
O	-5.21441900	-1.51536400	3.77006100
O	-3.96083100	-3.73250700	4.12422000
C	-5.00200200	-3.20814900	1.75875900
C	-5.85001600	-2.40107100	0.99317200
C	-4.65462700	-4.49020000	1.32171800
C	-6.33837100	-2.88274700	-0.22226600
H	-6.13919000	-1.42100400	1.35890500
C	-5.15259400	-4.95518500	0.10325900
H	-4.02340300	-5.11954600	1.94079200
C	-5.99862800	-4.16274300	-0.68781000
H	-7.00109800	-2.25541100	-0.81456700
H	-4.88488000	-5.95436800	-0.23346000
C	-6.56191900	-4.68789800	-1.98818800
H	-5.90411100	-5.44115900	-2.43494500
H	-7.54089400	-5.16019300	-1.82906900
H	-6.70334300	-3.88314300	-2.71806900
H	4.27214200	-4.12623900	1.35802500
C	-2.98520100	4.23446800	0.73022800
H	-2.41754000	5.10470900	1.08271300
H	-3.24098500	4.40770000	-0.32284800
H	-3.92223200	4.19477800	1.29905900
C	1.26305900	1.86669000	0.19824100
H	0.76881100	2.19955700	-0.72272500
H	1.27071500	2.72368200	0.88299300
H	2.29347600	1.59308300	-0.03384600
C	3.51773300	-1.81922700	0.76802400
O	3.13651600	-0.68584100	0.48267800
H	2.78575100	-2.51501200	1.22726200
C	6.38254100	-4.36785900	0.82159000
H	6.22063900	-5.27590100	0.22450900
H	7.20689600	-3.80628100	0.37623000
H	6.69453300	-4.70738300	1.81894400

Energies:

Sum of electronic and zero-point Energies = -1607.557960
Sum of electronic and thermal Enthalpies = -1607.525355
Sum of electronic and thermal Free Energies = -1607.627656
Electronic energies = -1607.9892584
Single point energies in solution = -1607.44108841

TS3

C	4.12201900	-4.15037500	2.43769300
C	3.88090500	-2.80924600	2.51292600
C	4.84753400	-1.75657400	2.99851900
H	4.44740100	-1.24911200	3.88389100
H	5.82093800	-2.17896300	3.25461400
H	4.99943700	-0.98761000	2.23267300
C	-1.78699400	-0.35537000	2.10605000
C	-1.29920800	-1.55184900	2.64021400
C	0.06330400	-1.85699800	2.70796400
C	0.84779100	-0.88369000	2.09277100
C	0.46267500	0.33168500	1.50960300
C	-0.92780700	0.60257300	1.52837200
C	-3.28209500	-0.25434300	2.25176400
C	-2.44534700	-2.38010100	3.18067100
H	-3.61700600	0.65969900	2.75227600
H	-2.29473000	-2.69667200	4.21653300
H	-3.78133000	-0.29811700	1.27016600
H	-2.60637200	-3.28150200	2.56835100
N	-3.58632600	-1.43749700	3.09117900
C	-1.47383500	1.80560900	0.97831300
C	-1.98031400	2.81220400	0.52315900
S	-5.14821600	-1.98257000	3.22543100
O	-5.99800700	-0.78677800	3.28950500
O	-5.14359400	-2.99726900	4.28604300
C	-5.55235900	-2.83268200	1.68768000
C	-6.10852600	-2.11660100	0.62365600
C	-5.27615300	-4.19807300	1.55801100
C	-6.37564300	-2.77480800	-0.57872400
H	-6.35043800	-1.06586200	0.74725600
C	-5.54934100	-4.83929200	0.34930600
H	-4.87638400	-4.75023000	2.40245400
C	-6.10090900	-4.14141800	-0.73714400
H	-6.81335400	-2.21715100	-1.40385000
H	-5.33858700	-5.90231400	0.25203300
C	-6.42481400	-4.85570900	-2.02924100
H	-5.66758100	-5.61028000	-2.27071300
H	-7.39064500	-5.37439900	-1.96005900
H	-6.48762600	-4.15608700	-2.86953200
H	3.30653600	-4.77629900	2.07347200
C	-2.58706300	4.02706700	-0.01829200
H	-3.61337200	4.15125500	0.34868500
H	-2.01945400	4.91964500	0.27359500
H	-2.62636000	4.00137700	-1.11491100
C	1.46157600	1.26881800	0.87581100
H	1.88426600	0.84179700	-0.04395200
H	0.99125200	2.22052700	0.61620100
H	2.30107200	1.46981400	1.55184200
C	2.56592900	-2.40001900	2.12113600
O	2.25742000	-1.13887200	2.12093800
H	1.81950100	-3.10569500	1.77318600
C	5.35814200	-4.89010700	2.82489300
H	5.12605300	-5.62179200	3.61205300
H	5.73336000	-5.47134600	1.97073900
H	6.16243200	-4.24391800	3.18232000

Energies:

Sum of electronic and zero-point Energies = -1607.559065
Sum of electronic and thermal Enthalpies = -1607.528484
Sum of electronic and thermal Free Energies = -1607.623741
Electronic energies = -1607.9918202
Single point energies in solution = -1607.44547912

I-3

C	3.35528700	-4.10317400	2.61217700
C	2.83130100	-2.86298000	2.63114200
C	2.93792100	-1.87853600	3.77007600
H	1.96104300	-1.70992500	4.24191700
H	3.63123400	-2.21393500	4.54448000
H	3.28691100	-0.90710600	3.40120600
C	-1.23677500	-0.37930200	1.72618900
C	-0.58206200	-1.60061500	1.96856900
C	0.73930000	-1.66270100	1.58019200
C	1.35135400	-0.56690900	0.98863200
C	0.76709800	0.65675200	0.71081400
C	-0.60436400	0.72498800	1.11661600
C	-2.66921400	-0.45723500	2.19291700
C	-1.51390600	-2.59746200	2.60361100
H	-2.95706200	0.35562000	2.86591800
H	-1.11941200	-3.05389600	3.51653300
H	-3.37066300	-0.45513400	1.34322700
H	-1.76693400	-3.40891700	1.90181500
N	-2.68343900	-1.74784500	2.92449800
C	-1.34857700	1.92778800	0.90406000
C	-1.98709500	2.94625800	0.72697400
S	-4.13305100	-2.45655800	3.34271900
O	-5.00248900	-1.36523200	3.79483200
O	-3.78954500	-3.59686500	4.20033600
C	-4.85393900	-3.12307300	1.83306800
C	-5.68882500	-2.31848300	1.05028600
C	-4.54801700	-4.42874700	1.43691700
C	-6.20540800	-2.82739900	-0.14189200
H	-5.94693300	-1.31902300	1.38547000
C	-5.07396500	-4.92059700	0.24085800
H	-3.92887800	-5.05550500	2.07075300
C	-5.90731300	-4.13184000	-0.56713900

H	-6.85816100	-2.20231700	-0.74738800
H	-4.83954000	-5.93822300	-0.06360800
C	-6.50139900	-4.68430400	-1.84204600
H	-5.88231200	-5.48602000	-2.25845100
H	-7.50070900	-5.10217200	-1.65937600
H	-6.60879000	-3.90537500	-2.60497800
H	3.20634600	-4.69422400	1.70655100
C	-2.75547200	4.17168300	0.51841500
H	-3.56569400	4.25942000	1.25254400
H	-2.11829000	5.05937200	0.61471700
H	-3.20727800	4.19261000	-0.48147400
C	1.49193500	1.80190000	0.05704800
H	0.99919000	2.10419000	-0.87533300
H	1.51231300	2.68468800	0.70824600
H	2.52416900	1.52301400	-0.17489700
C	2.05974800	-2.41098400	1.42630600
O	2.60829100	-1.13387600	0.81361400
H	2.05456300	-3.17399600	0.64280300
C	4.12743800	-4.80545400	3.69211100
H	3.61515000	-5.73044900	3.99089400
H	5.11923400	-5.10246100	3.32434800
H	4.26813600	-4.19695200	4.58901500

Energies:

Sum of electronic and zero-point Energies = -1607.634257
Sum of electronic and thermal Enthalpies = -1607.603470
Sum of electronic and thermal Free Energies = -1607.699243
Electronic energies = -1608.0698548
Single point energies in solution = -1607.52159426

TS4

C	4.36299300	-2.75779400	2.14926100
C	3.51719500	-1.68395500	2.17986400
C	3.74453600	-0.46436800	3.03902100
H	2.79971400	0.03906600	3.25967100
H	4.22547600	-0.71720500	3.98815700
H	4.37867300	0.25328100	2.50653300
C	-1.00124000	0.00300700	1.70927700
C	-0.15313700	-1.09531200	1.81871900
C	1.16038200	-0.93538200	1.38653800
C	1.57462000	0.23628900	0.72947300
C	0.74763200	1.38561300	0.65749800
C	-0.57026900	1.23415400	1.14622400
C	-2.36397200	-0.31856400	2.26683500
C	-0.85909900	-2.26578100	2.45211200
H	-2.71133900	0.39037700	3.02465000
H	-0.33354100	-2.68805100	3.31516800
H	-3.12759900	-0.36155400	1.47359900
H	-1.02063700	-3.07914400	1.72553800
N	-2.13190500	-1.64738800	2.88706300
C	-1.50068600	2.31848100	1.06567700
C	-2.30176800	3.22991800	1.00245500
S	-3.42051400	-2.61197600	3.31314700
O	-4.42064700	-1.71835300	3.90694200
O	-2.84666200	-3.74797100	4.04537500
C	-4.12633100	-3.26463500	1.79008000
C	-5.12049100	-2.54439300	1.12285400
C	-3.65455900	-4.47614700	1.27105700
C	-5.63064500	-3.03743200	-0.08078500
H	-5.50721100	-1.62735800	1.55556300
C	-4.17608900	-4.95291900	0.06898000
H	-2.91355600	-5.04711900	1.82127000
C	-5.16666200	-4.24168400	-0.62907400
H	-6.40992100	-2.47975700	-0.59498900
H	-3.81631300	-5.89994500	-0.32817300
C	-5.72123000	-4.77529400	-1.92973200
H	-6.14567700	-5.77846900	-1.79851000
H	-6.50920000	-4.12678500	-2.32581800
H	-4.93640000	-4.85364300	-2.69285900
H	4.11213800	-3.57225600	1.46892000
C	-3.26125500	4.32967600	0.92927100
H	-3.78566700	4.46192400	1.88383300
H	-2.76142300	5.27556100	0.68732400
H	-4.01874700	4.14521200	0.15690700
C	1.25060700	2.65416900	0.02386700
H	0.83496800	2.79410000	-0.98391500
H	0.96985300	3.53490500	0.61261800
H	2.34015900	2.61918300	-0.07179900
C	2.36104800	-1.77743300	1.32994600
O	2.76564200	0.04237900	0.20260600
H	2.30037600	-2.71147300	0.76304400
C	5.62031600	-2.95099200	2.92992500
H	5.59819000	-3.90933300	3.46701300
H	6.47821100	-3.00566200	2.24304500
H	5.81407200	-2.15102000	3.64762700

Energies:

Sum of electronic and zero-point Energies = -1607.602784
Sum of electronic and thermal Enthalpies = -1607.571919
Sum of electronic and thermal Free Energies = -1607.668034
Electronic energies = -1608.0355614
Single point energies in solution = -1607.48766934

I-4

C	4.13636200	-3.22986400	0.67646600
C	3.66897200	-1.96545300	0.87868400
C	4.59766500	-0.77591100	0.99103000
H	4.17851100	-0.01646000	1.65614200
H	5.56160800	-1.08590200	1.40699600
H	4.76521700	-0.29099500	0.02586800
C	-0.88673900	0.03914700	1.59337800
C	-0.00421200	-0.98818500	1.51947200
C	1.33812800	-0.81185200	1.00562100
C	1.63053400	0.51191000	0.37055700
C	0.67448700	1.62222200	0.56793400
C	-0.55459400	1.38014900	1.14257000
C	-2.19796700	-0.38745400	2.19494800
C	-0.60347300	-2.25613100	2.07925900
H	-2.50096100	0.21455800	3.05807200
H	-0.01209900	-2.70645600	2.88435300
H	-3.01411900	-0.34326000	1.45641700
H	-0.73652600	-3.01945800	1.29513600
N	-1.89398100	-1.77293900	2.61457800
C	-1.54022900	2.40214200	1.30648000
C	-2.40985600	3.23570400	1.46670900
S	-3.12391000	-2.84655900	2.94300100
O	-4.14392700	-2.08229900	3.66903700
O	-2.47712100	-4.03595600	3.50933500
C	-3.84257100	-3.32951200	1.36486600
C	-4.89620600	-2.58472300	0.82785300
C	-3.32327200	-4.43028600	0.67307000
C	-5.41787500	-2.93899600	-0.41859500
H	-5.31969300	-1.76046700	1.39266700
C	-3.85681100	-4.76865200	-0.57008400
H	-2.53559400	-5.02809800	1.12038600
C	-4.90553500	-4.02724600	-1.13967500
H	-6.24468300	-2.36500000	-0.83054500
H	-3.46019100	-5.63089200	-1.10200200
C	-5.46379900	-4.40108200	-2.49309900
H	-5.69156600	-5.47225400	-2.54872200
H	-6.38243500	-3.84841400	-2.71474100
H	-4.74245900	-4.18143400	-3.29119600
H	3.40840600	-4.04283200	0.68348800
C	-3.44144700	4.25197200	1.65720200
H	-3.04525100	5.11797900	2.20183000
H	-3.82367800	4.61141000	0.69351100
H	-4.28898500	3.85444100	2.22826500
C	1.09353500	2.96229200	0.03508500
H	1.20226200	2.92756400	-1.05646400
H	0.36847900	3.73780600	0.29270700
H	2.07752700	3.24454900	0.42808800
C	2.22962800	-1.86057300	1.07531600
O	2.61877100	0.67672800	-0.35869400
H	1.78338400	-2.81014600	1.37098500
C	5.54472600	-3.65442400	0.40102300
H	5.89386600	-4.35969300	1.16944100
H	5.59599600	-4.19376000	-0.55546700
H	6.24757600	-2.81971300	0.35334300

Energies:

Sum of electronic and zero-point Energies = -1607.651868
Sum of electronic and thermal Enthalpies = -1607.620760
Sum of electronic and thermal Free Energies = -1607.717143
Electronic energies = -1608.0867313
Single point energies in solution = -1607.53933803

I-5

C	4.30168000	-1.43829400	-0.31422800

C	3.59416900	-2.07456500	0.66114200
C	4.15012100	-3.24899000	1.45535000
H	3.53880000	-4.14916800	1.30547500
H	5.17557100	-3.49951600	1.17955900
H	4.14264100	-3.03252700	2.53144000
C	-0.89712500	0.12158200	1.56652500
C	0.00605500	-0.88803400	1.48741200
C	1.32396300	-0.71413900	0.90368700
C	1.60185500	0.63102400	0.31205500
C	0.61818700	1.71602800	0.50496500
C	-0.60233700	1.45868900	1.09131000
C	-2.19242600	-0.32296000	2.18855500
C	-0.56957500	-2.16259200	2.06188400
H	-2.49681800	0.28345300	3.04794400
H	0.03754800	-2.60543300	2.85934800
H	-3.01775700	-0.30296700	1.45911700
H	-0.70639300	-2.92925200	1.28192000
N	-1.85476200	-1.69526400	2.62159700
C	-1.60661100	2.46292500	1.25133200
C	-2.49181900	3.28003000	1.41087300
S	-3.05738700	-2.78833000	2.98741500
O	-4.08202700	-2.03159900	3.71481300
O	-2.37810400	-3.95366300	3.56535100
C	-3.78771600	-3.31431700	1.42855300
C	-4.85438400	-2.58900000	0.88404500
C	-3.26660800	-4.42413700	0.75805500
C	-5.38372000	-2.97464100	-0.34675900
H	-5.27812800	-1.75511600	1.43434600
C	-3.81047900	-4.79577500	-0.47411600
H	-2.46834700	-5.00452800	1.20951500
C	-4.86905200	-4.07784200	-1.04862700
H	-6.21862000	-2.41609400	-0.76473600
H	-3.41065800	-5.66558200	-0.99028200
C	-5.45444300	-4.47863200	-2.38283300
H	-5.29629600	-3.69526900	-3.13521800
H	-4.99971800	-5.40025900	-2.75967800
H	-6.53665100	-4.64215500	-2.30932800
H	3.80772700	-0.62000900	-0.82279600
C	-3.54356700	4.27570900	1.59952100
H	-4.20250000	4.32350200	0.72326600
H	-4.16391700	4.03567100	2.47144300
H	-3.11847900	5.27524700	1.75180100
C	1.00945600	3.06439700	-0.02890800
H	1.13388200	3.03104900	-1.11874600
H	0.26064900	3.82091500	0.21690100
H	1.98031500	3.37231900	0.37691400
C	2.21495900	-1.77059100	1.01489000
O	2.63059100	0.87545700	-0.34150400
H	1.78724100	-2.60233300	1.57538800
C	5.69512300	-1.73032900	-0.77602600
H	5.69072100	-1.97052600	-1.84902600
H	6.31239000	-0.82615200	-0.67400500
H	6.19484400	-2.54469700	-0.24634300

Energies:

Sum of electronic and zero-point Energies = -1607.649989
Sum of electronic and thermal Enthalpies = -1607.618680
Sum of electronic and thermal Free Energies = -1607.716524
Electronic energies = -1608.0847482
Single point energies in solution = -1607.53528627

TS5

C	3.98725400	-0.92974700	0.07312400
C	3.11441500	-1.91892800	-0.37839400
C	3.45836500	-2.84917200	-1.52510700
H	2.80681000	-3.73030800	-1.50676300
H	3.31231900	-2.36400700	-2.50040200
H	4.49566200	-3.19916900	-1.48332100
C	-0.99313200	0.01111100	1.53891500
C	-0.11779300	-1.02402400	1.37258600
C	1.16283800	-0.85530000	0.76248900
C	1.54829300	0.52062400	0.38402400
C	0.52240200	1.55457500	0.40169700
C	-0.69524900	1.31934400	1.03500400
C	-2.26080000	-0.43406400	2.21746200
C	-0.70530900	-2.31171100	1.89522100
H	-2.50793000	0.14181300	3.11515100
H	-0.05574600	-2.83861500	2.60167800
H	-3.12558400	-0.37922000	1.53725300
H	-0.94311600	-3.00977000	1.07415600
N	-1.92263700	-1.82988000	2.58367400
C	-1.67114700	2.35037900	1.20574200
C	-2.52861300	3.19366900	1.38001600
S	-3.12447800	-2.90307600	3.00533500
O	-4.06998300	-2.14668600	3.83356800
O	-2.43928900	-4.10658400	3.49096600
C	-3.98828600	-3.35727700	1.49159100
C	-5.06667100	-2.58313300	1.05203000
C	-3.56070300	-4.46598100	0.75345600
C	-5.70481500	-2.91653300	-0.14381300
H	-5.41879700	-1.75311400	1.65605400
C	-4.21140400	-4.78455100	-0.43940900
H	-2.75335200	-5.08635100	1.12931900
C	-5.28557200	-4.01379500	-0.91193200
H	-6.55104800	-2.32047000	-0.47813100
H	-3.88664500	-5.65509600	-1.00526400
C	-5.96657000	-4.35337400	-2.21742100
H	-5.98681600	-5.43510000	-2.38992500
H	-6.99807100	-3.98613700	-2.23867300
H	-5.43802100	-3.89739600	-3.06568400
H	3.87907100	-0.60985100	1.10165100
C	-3.54912800	4.21907600	1.58304400
H	-4.17905900	4.33224600	0.69154100
H	-4.20425000	3.96458200	2.42501700
H	-3.09286700	5.19403300	1.79419600
C	0.90181300	2.90037600	-0.15348100
H	1.41504100	2.78434800	-1.11447400
H	0.02179900	3.53494200	-0.28539700
H	1.60483900	3.42247300	0.50968400
C	1.83838600	-1.96187400	0.20467700
O	2.71391400	0.84584400	-0.00062300
H	1.25119800	-2.87209900	0.06647900
C	5.27552200	-0.55294500	-0.57874700
H	5.29277800	-0.77451900	-1.64932900
H	5.45559100	0.51789400	-0.43461200
H	6.11132000	-1.08638700	-0.10004700

Energies:

Sum of electronic and zero-point Energies = -1607.641541
Sum of electronic and thermal Enthalpies = -1607.611324
Sum of electronic and thermal Free Energies = -1607.705617
Electronic energies = -1608.0756519
Single point energies in solution = -1607.52698582

3h

C	3.68665800	-0.38439800	-0.26253400
C	3.23302900	-1.83477900	-0.18711700
C	4.22605300	-2.92076700	-0.49499100
H	3.79426000	-3.90880700	-0.30539400
H	4.55625200	-2.88883700	-1.54163800
H	5.13069700	-2.82387900	0.12335700
C	-1.00519400	-0.08357100	1.45495600
C	-0.16297800	-1.16434800	1.22966900
C	1.06737500	-1.00123900	0.58119800
C	1.41344300	0.30505900	0.18193300
C	0.57971600	1.41654700	0.37545900
C	-0.66210100	1.21444100	1.03110900
C	-2.26698700	-0.51742900	2.15369600
C	-0.78027400	-2.44013000	1.74692800
H	-2.47889300	0.04526400	3.06782900
H	-0.13109200	-3.00302600	2.42535900
H	-3.14406900	-0.42692800	1.49339400
H	-1.06935100	-3.11168900	0.92155700
N	-1.95687000	-1.92873700	2.48556600
C	-1.56910600	2.29241400	1.27667200
C	-2.36920300	3.17822100	1.50442600
S	-3.17449400	-2.97280100	2.93475500
O	-4.07000500	-2.20119800	3.80357400
O	-2.50821000	-4.20124700	3.38311900
C	-4.09964500	-3.38374400	1.44509700
C	-5.17046400	-2.57542900	1.05009600
C	-3.72696700	-4.49437300	0.68130900
C	-5.85642000	-2.87747300	-0.12719800
H	-5.47927700	-1.74326800	1.67454000
C	-4.42519100	-4.78142500	-0.49277500
H	-2.92447800	-5.14029400	1.02290600
C	-5.49273500	-3.97679800	-0.92083400
H	-6.69635800	-2.25451300	-0.42666200
H	-4.14239200	-5.65324400	-1.07872200
C	-6.22498000	-4.28043000	-2.20730600

H	-6.22010600	-5.35332100	-2.42804400
H	-7.26724700	-3.94646600	-2.16405500
H	-5.75238400	-3.76930500	-3.05718200
H	4.12609800	-0.10605300	0.71432200
C	-3.32266800	4.25152400	1.77778300
H	-2.81789500	5.13440300	2.18946700
H	-3.84497800	4.56256600	0.86406200
H	-4.08027500	3.93131600	2.50337100
C	1.02052200	2.77013600	-0.12058300
H	1.11629800	2.77759800	-1.21390200
H	0.30615400	3.54467800	0.16731100
H	2.00598000	3.03376500	0.28099400
C	1.98420800	-2.08458200	0.25200100
O	2.58034700	0.51288900	-0.50743000
H	1.64112000	-3.11060200	0.37019800
C	4.70380800	-0.07700900	-1.35754700
H	4.31049600	-0.35117900	-2.34273400
H	4.92466700	0.99482100	-1.35972200
H	5.63898200	-0.61937700	-1.18557400

Energies:

Sum of electronic and zero-point Energies = -1607.688691
Sum of electronic and thermal Enthalpies = -1607.658888
Sum of electronic and thermal Free Energies = -1607.751320
Electronic energies = -1608.1261628
Single point energies in solution = -1607.57865360