Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# One step construction of taxane-like skeleton by diendiyne metathesis cyclization reaction

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## Supporting Information

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# I. Figures

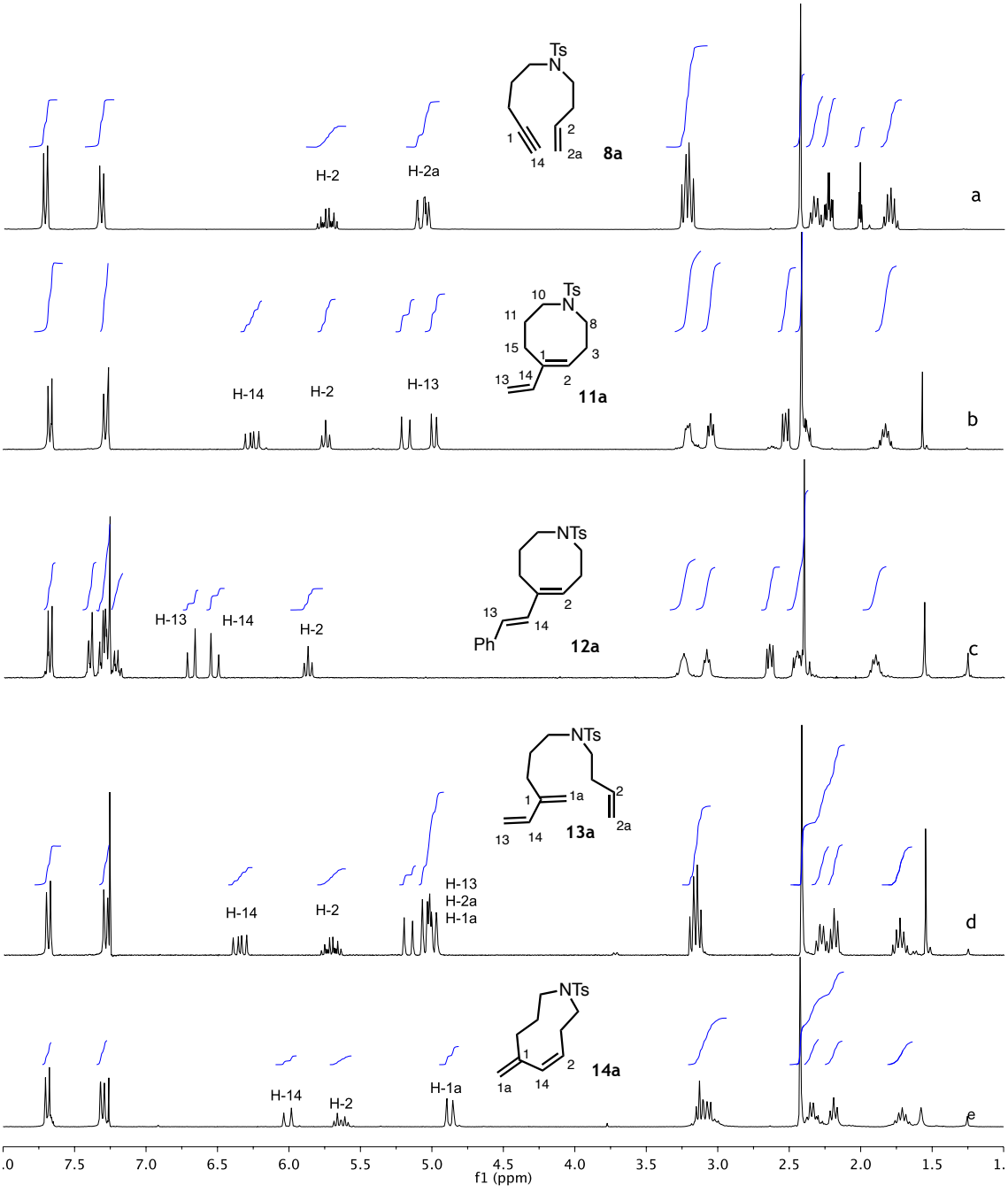



**Figure 1SI.** $^{1}$H-NMR spectra (8.00-1.00 ppm) of resulting derivatives (**11a**, **12a**, **13a** and **14a**) obtained in the metathesis reaction of enyne **8a**.

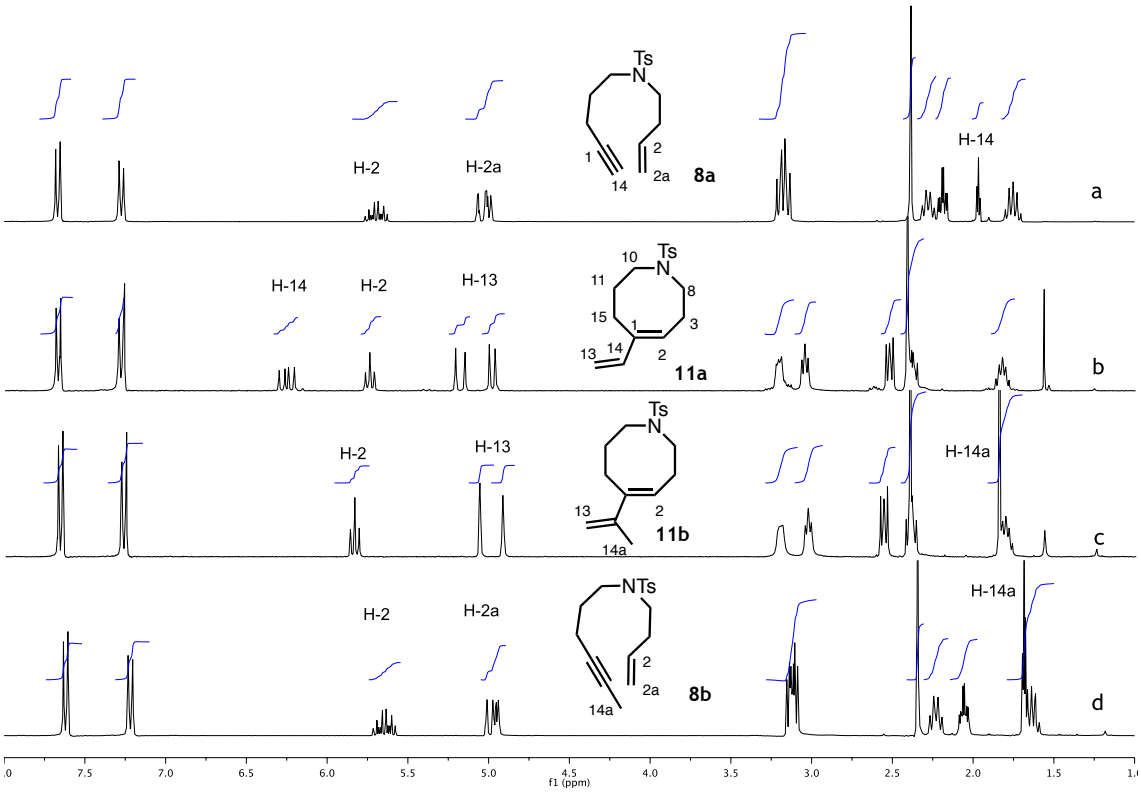



**Figure 2SI.** $^{1}$H-NMR spectra (8.00-1.00 ppm) of enynes precursors **8a** and **8b** and the corresponding cyclization products (**11a** and **11b**).

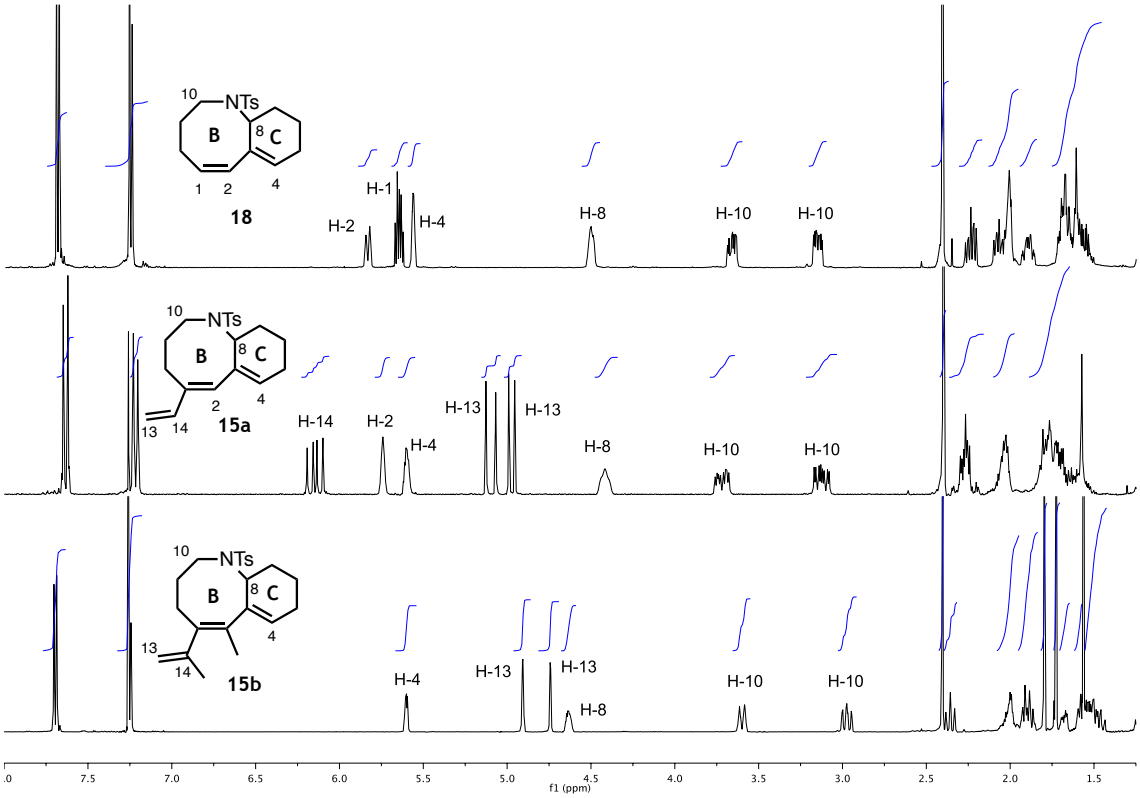



**Figure 3SI.** $^{1}$H-NMR spectra (8.00-1.00 ppm) of bicyclic compounds **18**, **15a** y **15b**.

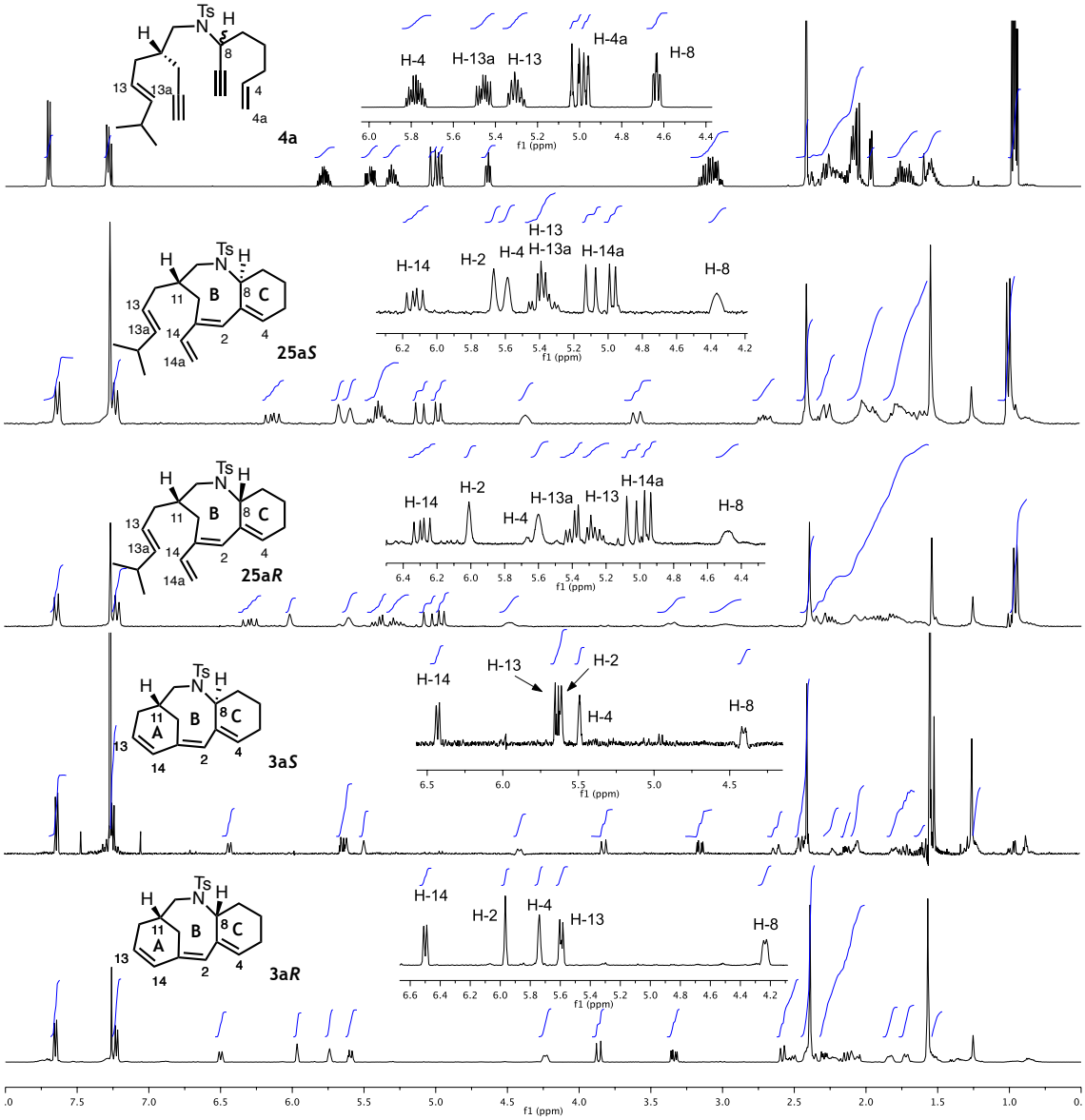



**Figure 4SI.** $^{1}$H-NMR spectra (8.00-0.00 ppm) of diendiyne precursor **4a** and tetraenes **25a*S***, **25a*R*** and tricycles **3a*S***, **3a*R***.

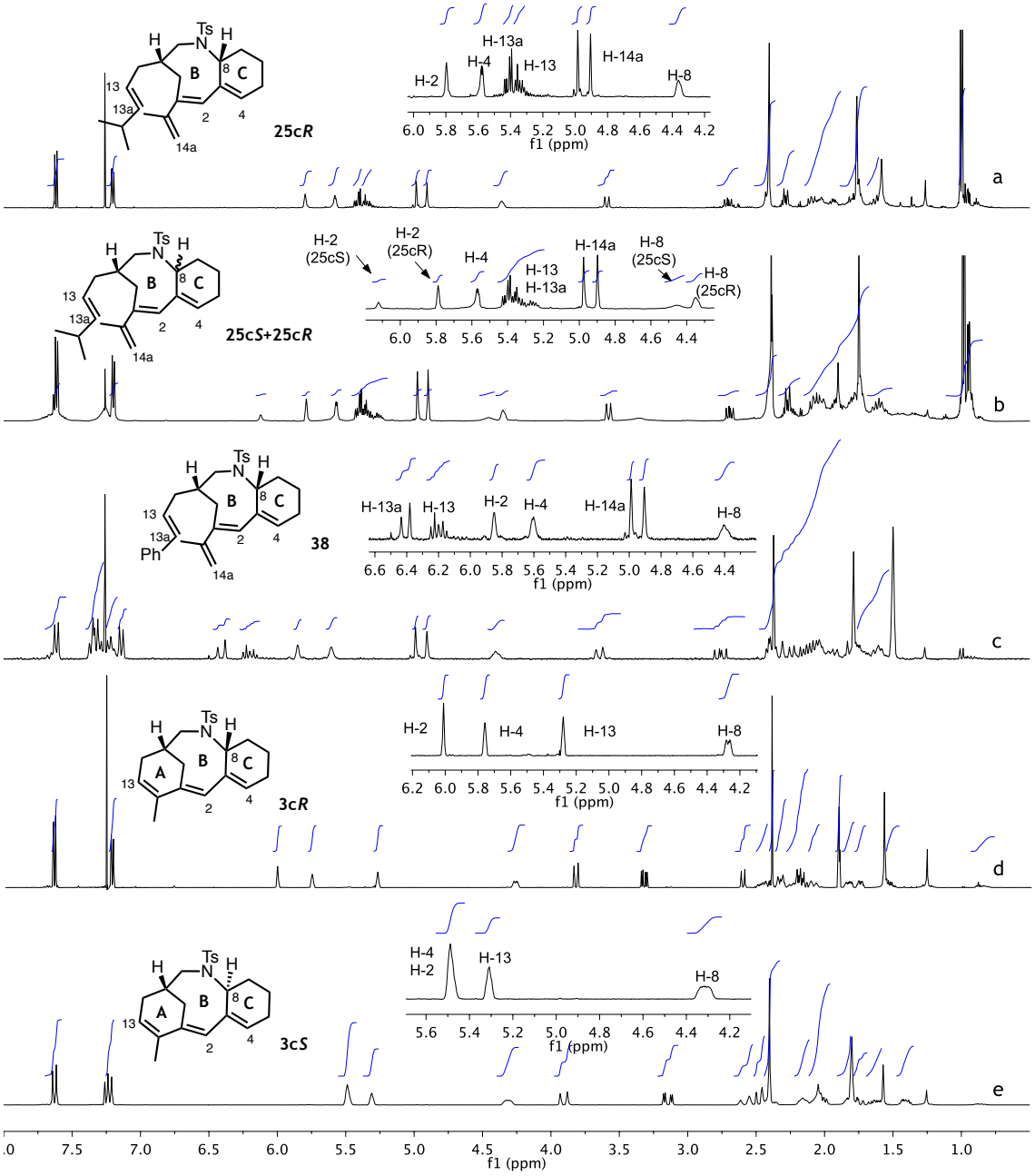



**Figure 5SI.** $^{1}$H-NMR spectra (8.00-0.00 ppm) of polycycles **25c*R*** (a), **25c*R*** y **25c*S*** (b), **38** (c), **3c*R*** (d) y, **3c*S*** (e).

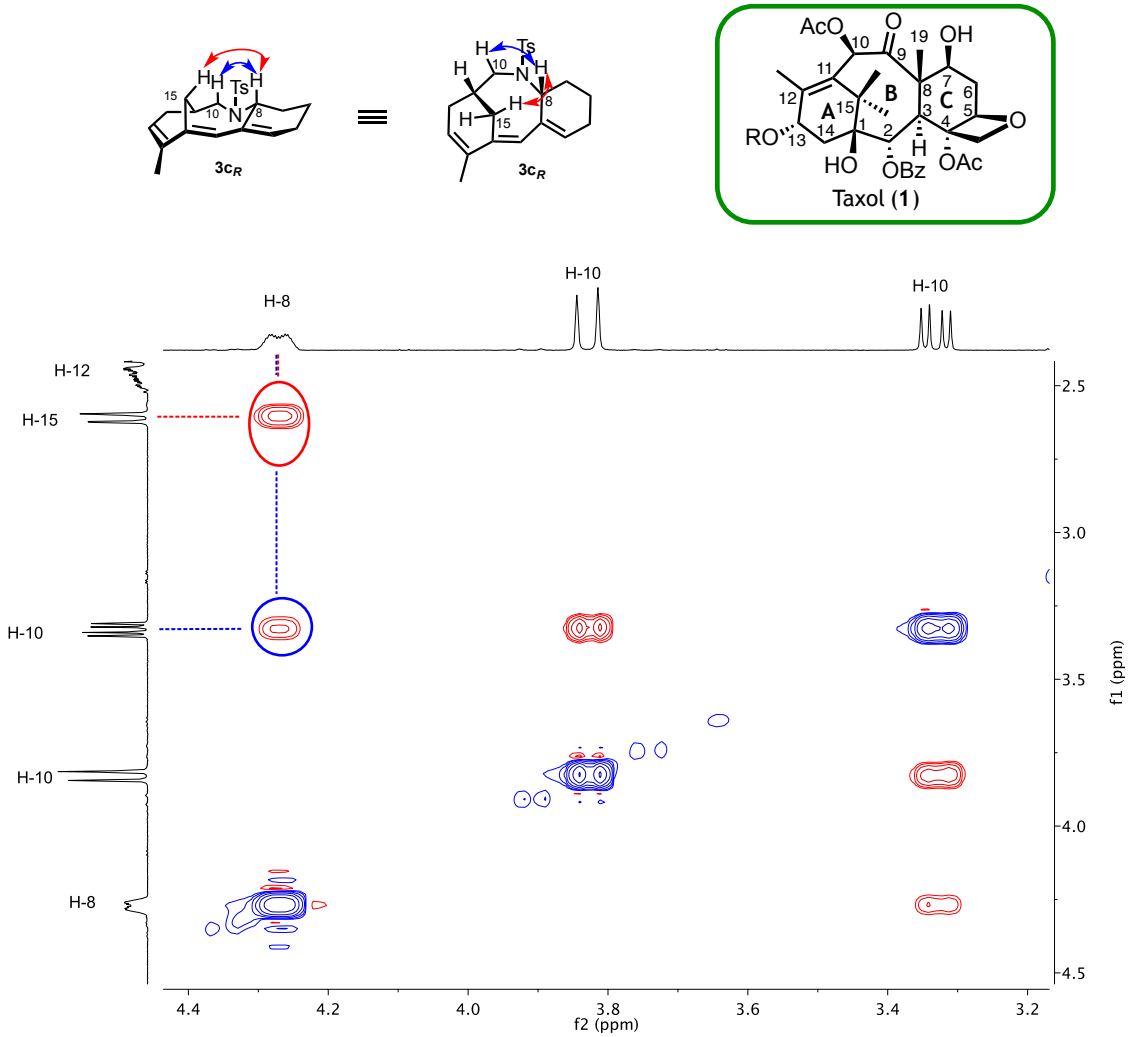



**Figure 6SI.** Observed nOe cross peaks at NOESY experiment on tricycle **3c*R***.

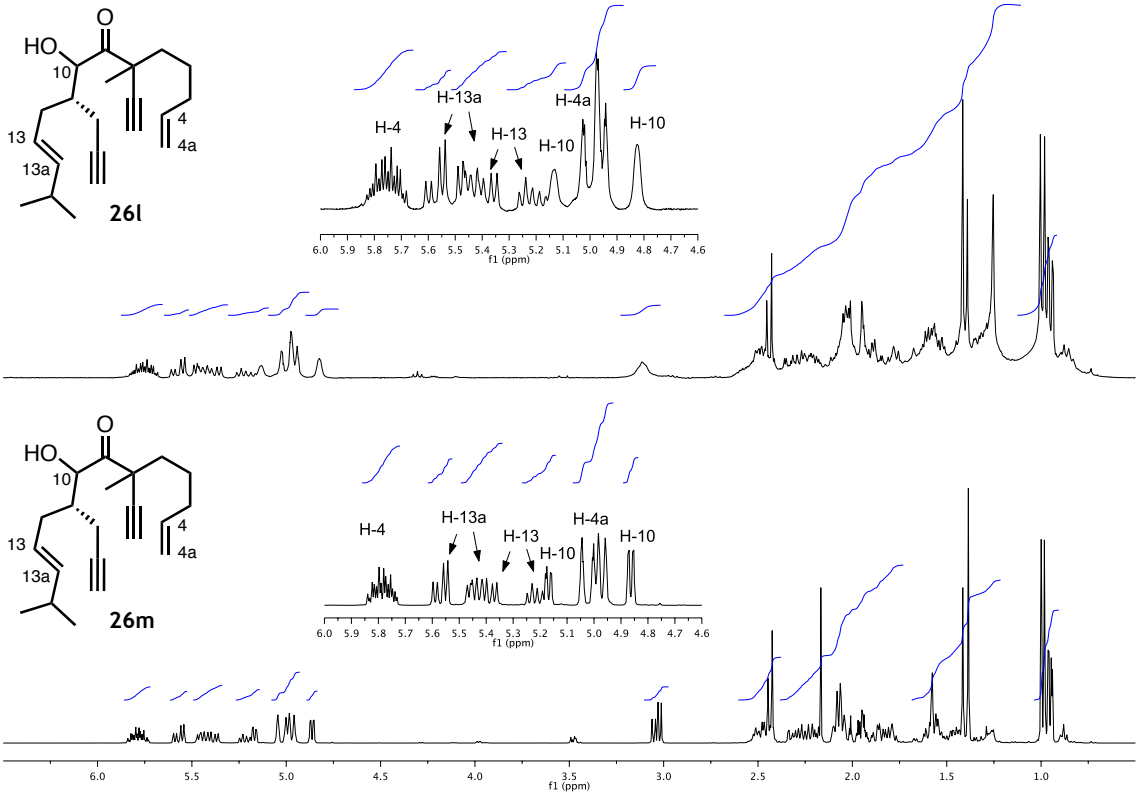



**Figure 7SI.** $^{1}$H-NMR spectra (8.00-0.00 ppm) of both pairs of stereoisomers separated by column chromatography and asigned as **26l,** for the less polar fraction, and **26m**, for the most polar fraction**.**

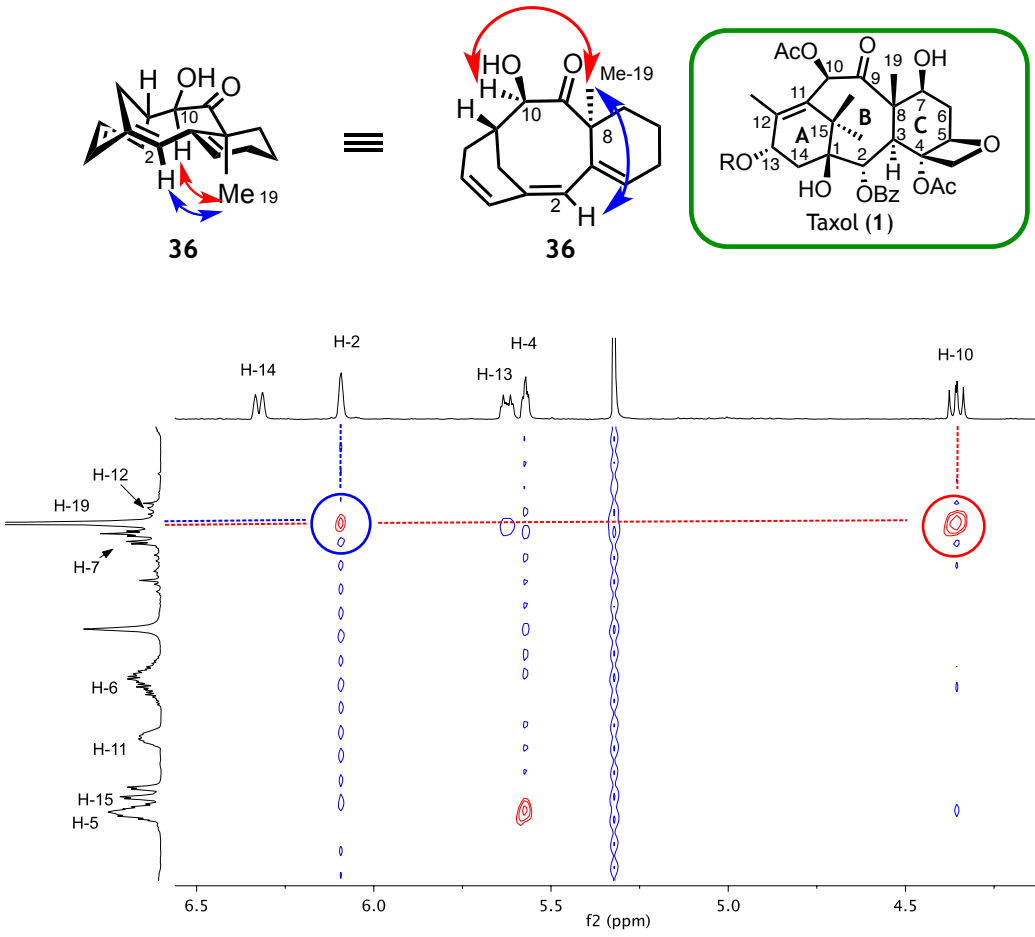
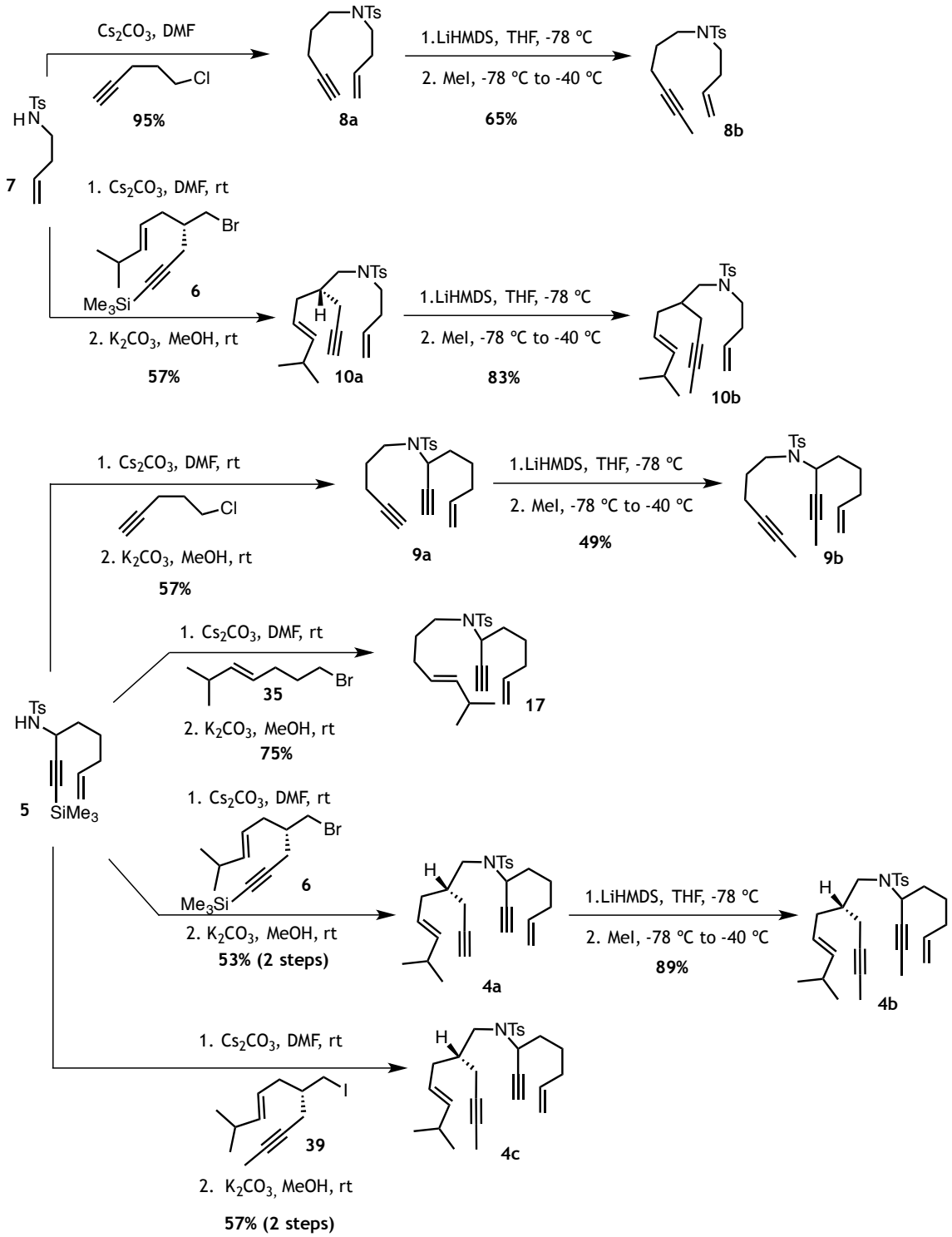



**Figure 8SI.** Observed nOe cross peaks at NOESY experiment on taxane **30**.

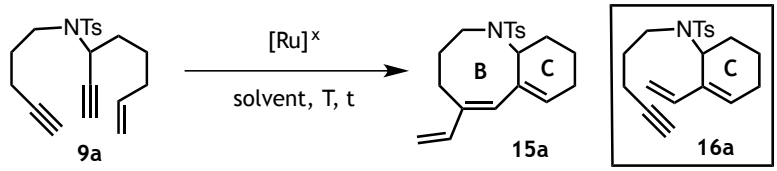
# II. Schemes




**Scheme 1SI**. General scheme for synthesis of precursors.

## III. Tables

**Table 1SI.** Studies for the formation of the BC-ring system using endiyne **9a**.

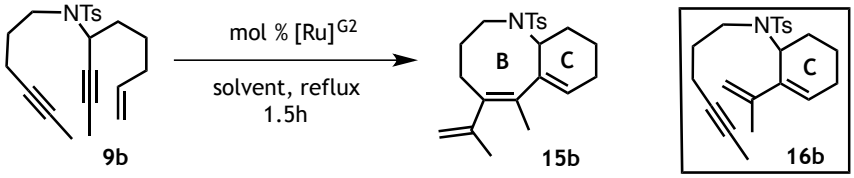



**9a** **15a** **16a**

| Entry | mol%[Ru]$^X$ | Solvent[a] | T(°C) | t (h) | 9a/15a[b] | Yield |
|---|---|---|---|---|---|---|
| 1 | 10% G2 | $CH_2Cl_2$ | 40 | 1.5 | 5/1 | -[c] |
| 2 | 20% G2 | $CH_2Cl_2$ | 40 | 1.5 | 1/1 | -[c] |
| 3 | 30% G2 | $CH_2Cl_2$ | 40 | 1.5 | 0/1 | 20% |
| 4 | 10% G2 | $CH_2Cl_2$ | 40 | 4 | 2/1 | -[c] |
| 5 | 10% G2 | bencene | 80 | 1.5 | 1/1 | -[c] |
| 6 | 10% G2 | toluene | 110 | 1.5 | 1/1 | -[c] |
| 7 | 20% G2 | bencene | 80 | 1.5 | 0/1 | 20% |
| 8 | 30% G1 | toluene | 110 | 1.5 | 0/1 | 37% |

[a] 5 mM solution of endiyne **9a**. [b] Ratio determined by $^1$H-NMR in crude mixtures. [c] not purified.

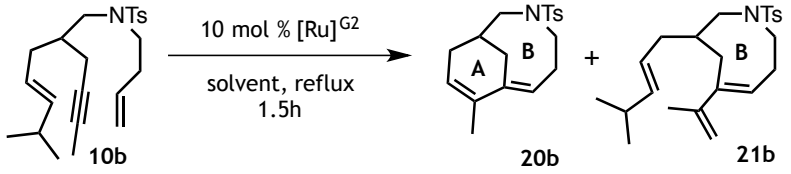
**Table 2SI.** Studies for the formation of the BC-ring system using endiyne **9b**.




| Entry | Precursor | [Ru]$^{G2}$ | solvent[a] | 9b/15b[b] | Yield[c] |
|---|---|---|---|---|---|
| 1 | 9a | 10 % | $CH_2Cl_2$ | 1/2 | -[d] |
| 2 | mixture 1[e] | 10 % | bencene | 0/1 | 56% |
| 3 | 9a | 12 % | bencene | 0/1 | 63% |

[a] 5 mM solution. [b] Ratio determined by $^1$H-NMR in crude mixtures. [c] Isolated yields. [d] Inseparable mixture. [e] Mixture of **15b** and **9b** obtained from entry 1.

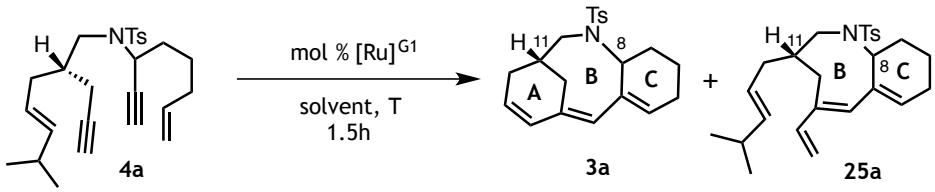
**Table 3SI.** Studies for the formation of the AB-ring system using dienyne **10b**.




| Entry | precursor | solvent[a] | 20b/21b[b] | Yield 20b (%)[c] |
|---|---|---|---|---|
| 1 | 10b | $CH_2Cl_2$ | 3.5/1 | -[d] |
| 2 | mixture 1[e] | $CH_2Cl_2$ | 7/1 | -[d] |
| 3 | mixture 2[f] | bencene | 1/0 | 72 |
| 4 | 10b | bencene | 1/0 | 75 |

[a] 5 mM solution of endiyne. [b] Ratio determined by $^1$H-NMR in crude mixtures. [c] Isolated yields. [d] Inseparable mixture. [e] Mixture of **10b** and **21b** obtained from entry 1. [f] Mixture of **10b** and **21b** obtained from entry 2.

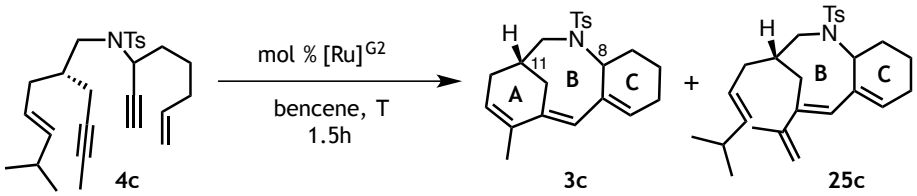
**Table 4SI.** Studies for cascade metathesis reaction of diendiyne **4a**.




| Entry | [Ru]$^{G1}$ | solvent[a] | T (°C) | 3a/25a[b] | 3a*S*/3a*R*/25a*S*/25a*R*[b][c] |
|---|---|---|---|---|---|
| 1 | 30 mol % | toluene | 110 | 0/1 | 0/0/1/1 |
| 2 | 30 mol % | bencene | 80 | 1/6 | 0/1/3/3 |
| 3 | 30 mol % | bencene | 100 | 4/13 | 1/3/8/5 |
| 4 | 30 mol % | bencene | 120 | 3/7 | 1/2/5/2 |
| 5 | 30 mol % | bencene | 140 | 3/7 | 1/2/5/2 |
| 6 | 40 mol % | bencene | 80 | 1/4 | 0/1/2/2 |
| 7 | 40 mol % | bencene | 120 | 6/10 | 1/5/10/0 |
| 8 | 50 mol % | bencene | 120 | -[d] | -[d] |
| 9 | 30 mol % | dichloroethane | 120 | 1/4 | 1/1/5/3 |

[a] 5 mM solution of diendiyne. [b] Ratio determined by $^1$H-NMR in crude mixtures. [c] Mixtures in which ***R*** and ***S*** denoted the proposed configuration for C8. [d] Decomposition of the mixture.

**Table 5SI.** Studies for cascade metathesis reaction of diendiyne **4c**.




| Entry | [Ru]$^{G2}$ | T (°C) | 3c/25c[a] | 3c*R*/3c*S*/25c*R*/25c*S*[a] | Yield 3c/25c (%) |
|---|---|---|---|---|---|
| 1 | 10 mol % | 80 | 0/1 | 0/0/1/1 | 0/67 |
| 2 | 20 mol % | 80 | 1.2/1 | 1/3.8/3/1 | -[b] |
| 3 | 40 mol % | 80 | 5/2.2 | 1/4/2/0.2 | -[b] |
| 4 | 60 mol % | 80 | 4/1.5 | 1/3/1.5/0 | 21/19 |
| 5 | 80 mol % | 80 | -[c] | -[c] | -[c] |
| 6 | 20 mol % | 120 | 1.7+x[d]/3 | x[d]/1.7/2/1 | -[b] |

[a] Ratio determined by $^{1}$H-RMN in crude mixtures. [b] Not isoltaed [c] Descomposition of the mixture [d] Ratio could not be determined by $^{1}$H-NMR due to overlapping between signals.

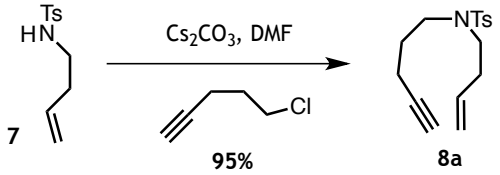
# IV. General methods

Dry solvents were freshly distilled under argon from an appropriate drying agent before use. Dry THF was obtained using Solvent Purification System (SPS). Benzene, toluene, DMF, dichloroethane and $CH_2Cl_2$ were purchased from Aldrich. All chemicals were purchased from commercial suppliers and used as received. Reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. Reactions at room temperature were carried out between 20-25 °C, reactions at different temperatures were maintained using Thermowatch-controlled silicone oil baths (high temperatures) and dry ice-acetone, water-ice or a Cryocool-Inmersion Cooler equipped with temperature controller (low temperatures). All indicated temperatures are referred to external bath temperature. Where possible, reactions were monitored by thin layer chromatography (TLC) performed on commercially prepared glass plates precoated with Merck silica gel 60 F254 or aluminium oxide 60 F254. Visualisation was by the quenching of UV fluorescence ($\nu_{max}$ = 254 nm) or by staining with *p*-anisaldehyde or cerium nitrate solutions. Column chromatography was performed using slurry-packed silica gel (200-400 mesh) as the stationary phase unless otherwise stated. Dryings were performed with anhydrous $Na_2SO_4$ or $MgSO_4$. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by residual solvent removal under high vacuum. NMR spectra were recorded in $CDCl_3$, at 250 MHZ (Bruker), at 300 MHz (Varian), at 400MHz (Varian) or 500 MHz (Bruker). Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestreNova NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, dd, double doublet; td, triple doublet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) or electrospray ionization (ESI) and were recorded at the CACTUS facility of the University of Santiago de Compostela.

# V. Experimental procedures

## V.1. Synthesis of precursors with terminal alkynes

### V.1.1 Enyne 8a



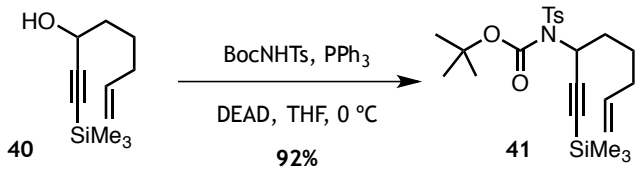

To a solution of the sulfonamide **7** (385 mg, 1.71 mmol)[1] in dimethylformamide (17 mL) was added $Cs_2CO_3$ (1.115 g, 3.42 mmol). After 30 min, 5-chloro-1-pentyne (0.3 mL, 2.56 mmol) was added dropwise. The reaction mixture was stirred for 19 h and then quenched by addition of water (50 mL). The mixture was extracted with $Et_2O$ (3 x 70 mL), the combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (15-20% EtOAc/hexanes) to afford benzenesulfonamide **8a** [476 mg, 95%, $R_f$= 0.7 (25% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.80-5.30 (m, 1H), 5.16-4.97 (m, 2H), 3.34-3.08 (m, 4H), 2.43 (s, 3H), 2.39-2.18 (m, 4H), 2.03-1.99 (m, 1H), 1.86-1.73 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.2 (C), 136.6 (C), 134.6 (CH), 129.6 (CH), 127.1 (CH), 117.1 ($CH_2$), 83.1 (C), 69.1 (CH), 48.1 ($CH_2$), 47.4 ($CH_2$), 33.2 ($CH_2$), 27.6 ($CH_2$), 21.5 ($CH_3$), 15.8 ($CH_2$); **MS** (*m/z*, ESI): 292 ($MH^+$), 155, 136; **HRMS:** calculated for $C_{16}H_{22}NO_2S$ ($MH^+$): 292.1366, found: 292.1369.

[1] Prepared according: D. Belmessieri, D. B. Cordes, A. M. Z. Slawin, A. Smith, *Org. Lett.* 2013, **15**, 3472-3475.

## V.1.2 Precursors of bicycle BC: endiyne 9 and dienyne 17

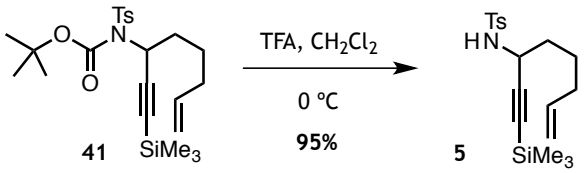
### V.1.2.1 Preparation of tosylamide 5

**Preparation of *tert*-butyl *N*-(*p*-toluenesulfonyl)-*N*-[1-(trimethylsilyl)oct-7-en-1-yn-3-yl]carbamate (41)**[2]




To a solution of alcohol **40** (253 mg, 1.29 mmol)[3] in THF (4.3 mL) were added successively *tert*-butyltosylcarbamate (420 mg, 1.55 mmol) and triphenylphosphine (880 mg, 3.35 mmol). The resulting solution was cooled at 0 °C and then ethyl azodicarboxylate (0.5 mL, 3.22 mmol) was added dropwise. The reaction mixture was stirred for 10 h and the solvent was removed. The resulting residue was purified by flash chromatographic (5-6% EtOAc/hexanes) to afford **41** [535 mg, 92%, $R_f$= 0.5 (15% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.88 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.82-5.71 (m, 1H), 5.25 (t, *J* = 7.8 Hz, 1H), 5.10-4.87 (m, 2H), 2.41 (s, 3H), 2.21-1.94 (m, 4H), 1.63-1.49 (m, 2H), 1.33 (s, 9H), 0.14 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 150.2 (C), 144.0 (C), 138.2 (CH), 137.3 (C), 129.1 (CH), 127.9 (CH), 115.0 ($CH_2$), 103.5 (C), 88.3 (C), 84.5 (C), 50.6 (CH), 34.3 ($CH_2$), 32.9 ($CH_2$), 27.9 ($CH_3$), 25.7 ($CH_2$), 21.6 ($CH_3$), -0.1 ($CH_3$); **MS** (*m/z*, I): 472 ($MNa^+$, 100), 394 (69), 372 (40); **HRMS:** calculated for $C_{23}H_{35}NO_4SSiNa$ ($MNa^+$): 472.1948, found: 472.1944.

**Preparation of 4-methyl-*N*-(1-(trimethylsilyl)oct-7-en-1-yn-3-yl)benzenesulfonamide (5)**[4]




A solution of carbamate **41** (190 mg, 0.42 mmol) in $CH_2Cl_2$ (3 mL) cooled to 0 °C was treated with triflouroacetic acid (0.3 mL, 4.2 mmol). After 4 h, the reaction was quenched by addition of aqueous solution of $NaHCO_3$ (sat. sol., 20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3x50 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chormatography (10-15% EtOAc/hexanes) to afford benzenesulfonamide **5** [139 mg, 95%, $R_f$= 0.5 (10% EtOAc/hexanes), white solid]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.81-5.17 (m, 1H), 5.13-4.74 (m, 3H), 4.17-3.94 (m, 1H), 2.41 (s, 3H), 2.18-1.93 (m, 2H), 1.73-1.57 (m, 2H), 1.59-1.43 (m, 2H), -0.04 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.4 (C), 138.1 (CH), 137.6

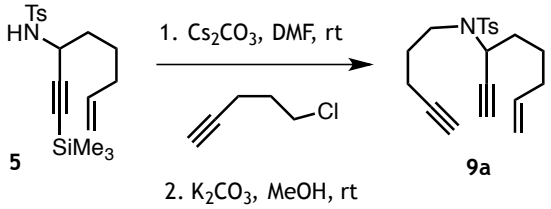
[2] B. M. Trost, M. R. Machacek, B. D. Faulk, *J. Am. Chem. Soc.* 2006, **128**, 6745-6754.

[3] Prepared according: N. Ortega, V. S. Martín, T. Martín, *J. Org. Chem.* 2010, **75**, 6660-6672.

[4] T. Kitamura, Y. Sato, M. Mori, *Adv. Synth. Catal.* 2002, **344**, 678-693.

(C), 129.6 (CH), 127.5 (CH), 115.0 ($CH_2$), 103.4 (C), 89.0 (C), 46.2 (CH), 36.1 ($CH_2$), 32.9 ($CH_2$), 24.6 ($CH_2$), 21.6 ($CH_3$), -0.3 ($CH_3$); **MS** (*m/z*, ESI): 350 ($MH^+$), 244, 179; **HRMS:** calculated for $C_{18}H_{28}NO_2SSi$ ($MH^+$): 350.1605, found: 350.1615.

### V.1.2.2 Preparation of endiyne 9a

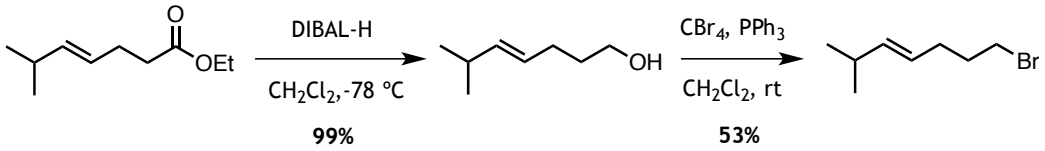



**57%**

***General procedure for sulfonamide alkylation*** applied to sulfonamide **5**: A solution of sulfonamide **5** (1.01 g, 2.90 mmol) in anhydrous DMF (29 mL) was treated with $Cs_2CO_3$ (2.84 g, 8.71 mmol) in several portions. The reaction mixture was stirred for 1 h and 5-chloro-1-pentyne (0.6 mL, 5.80 mmol) was added dropwise. After 12 hours, the reaction was quenched by adition of water (30 mL). The mixture was extracted with $Et_2O$ (3 x 70 mL) and the combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting crude was dissolved in MeOH (29 mL), then treated with $K_2CO_3$ (615 mg, 5.80 mmol) and stirred vigorously. When complete disappearance of starting material was observed (TLC, 5 h), the reaction was quenched by addition of water (30 mL) and diluted with $Et_2O$ (50 mL). The phases were separated and the aqueous phase was extracted with $Et_2O$ (3x50 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (10-15% EtOAc/hexanes) to afford 4-methyl-*N*-(oct-7-en-1-yn-3-yl)-*N*-(pent-4-yn-1-yl)benzenesulfonamide **9a** [563 mg, 57%, $R_f$= 0.5 (25% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.90-5.70 (m, 1H), 5.16-4.89 (m, 2H), 4.74-4.60 (m, 1H), 3.30-3.15 (m, 2H), 2.44 (s, 3H), 2.30-2.20 (m, 2H), 2.18-2.01 (m, 4H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.95-1.50 (m, 5H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.5 (C), 138.0 (CH), 135.9 (C), 129.5 (CH), 127.8 (CH), 115.2 ($CH_2$), 83.4 (C), 80.6 (C), 73.8 (CH), 69.1 (CH), 50.9 (CH), 44.5 ($CH_2$), 35.2 ($CH_2$), 33.0 ($CH_2$), 29.8 ($CH_2$), 25.3 ($CH_2$), 21.6 ($CH_3$), 16.2 ($CH_2$); **MS** (*m/z*, ESI): 366 ($MNa^+$), 238, 188; **HRMS:** calculated for $C_{20}H_{25}NO_2SNa$ ($MNa^+$): 366.1498, found: 366.1507.

### V.1.2.3 Preparation of dienyne 17

**Preparation of *(E)*-7-bromo-2-methylhept-3-ene**




A solution of ethyl (*E*)-6-methylhept-4-enoate (2.00 g, 11.76 mmol)[5] in $CH_2Cl_2$ (24 mL) cooled at -78 °C was dropwise treated with a commercial solution of diisobutylaluminum hydride (1M, 29.5 mL, 29.5 mmol). After 1 h, the reaction was quenched by adition of $H_2O$ (20 mL) at low temperature, reaching rt with vigorous stirring for 10 hours. The phases were separated and the aqueous phase was extracted with $CH_2Cl_2$ (3x100 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$, filtered and concentrated. The obtained crude was purified by flash chromatography (25% $Et_2O$/hexanes) to afford (*E*)-6-methylhept-4-en-1-ol [1.5 g, 99%, $R_f$= 0.5 (25% EtOAc/hexanes), colorless oil], whose spectroscopic data consistent with those described in the literature.[6]

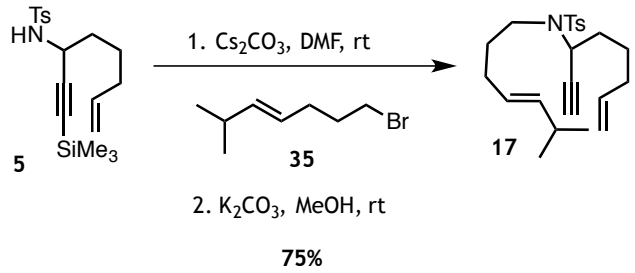
Then, a solution of (*E*)-6-methylhept-4-en-1-ol (585 mg, 4.57 mmol) in $CH_2Cl_2$ (26 mL) was treated with triphenylphosphine (1.23 g, 4.68 mmol). The resulting solution was cooled to 0 °C and carbon tetrabromide (1.42 g, 4.29 mmol) was added. After 1.5 h, the reaction mixture was diluted with $Et_2O$ (25 mL) and concentrated. The residue was purified by flash chromatography (10% $Et_2O$/hexanes), to afford (*E*)-7-bromo-2-methylhept-3-ene [461 mg, 53%, $R_f$= 0.9 (25% EtOAc/hexanes), slightly yellow oil], whose spectroscopic data are consistent with those described in the literature.[7]

[5] M. J. Aldegunde, R. García-Fandiño, L. Castedo, J. R. Granja, *Chem. Eur. J.* 2007, **13**, 5135-5150.

[6] S. E. Denmark, D. J. P. Kornfilt, T. Vogler, *J. Am. Chem. Soc.* 2011, **133**, 15308-15311.

[7] D. Becker, M. Nagler, Y. Sahali, N. Haddad, *J. Org. Chem.* 1991, **56**, 4537-4543.

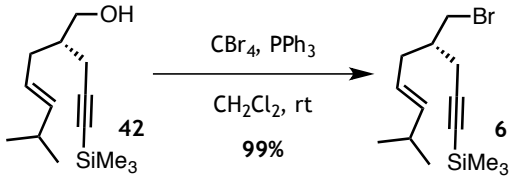
**Preparation of (*E*)-4-methyl-*N*-(6-methylhept-4-en-1-yl)-*N*-(oct-7-en-1-yn-3-yl)benzenesulfonamide (17)**




Dienyninic tosylamide **17** was prepared following the ***general procedure for sulfonamide alkylation*** using enyne **5** and bromide **35**: [250 mg, 75%, $R_f$= 0.7 (15% EtOAC/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.71 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.82-5.69 (m, 1H), 5.47-5.22 (m, 2H), 5.11-4.90 (m, 2H), 4.72-4.58 (m, 1H), 3.19-2.90 (m, 2H), 2.40 (s, 3H), 2.28-2.17 (m, 2H), 2.15-1.47 (m, 11H), 0.96 (d, *J* = 6.7 Hz, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.3 (C), 138.7 (CH), 138.1 (CH), 136.3 (C), 129.5 (CH), 127.7 (CH), 125.8 (CH), 115.2 ($CH_2$), 80.8 (C), 73.6 (CH), 50.8 (CH), 45.0 ($CH_2$), 35.4($CH_2$), 33.0 ($CH_2$), 31.1(CH), 31.0 ($CH_2$), 29.9 ($CH_2$), 25.3 ($CH_2$), 22.7($CH_3$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 410, 388 ($MH^+$), 282; **HRMS:** calculated for $C_{23}H_{34}NO_2S$ ($MH^+$): 388.2305, found: 388.2305.

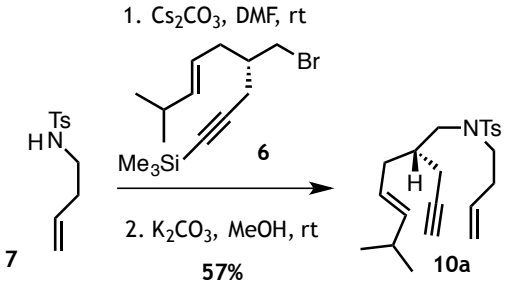
### V.1.3 Precursors of bicycle AB: dienyne 10a

**Preparation of bromide 6**



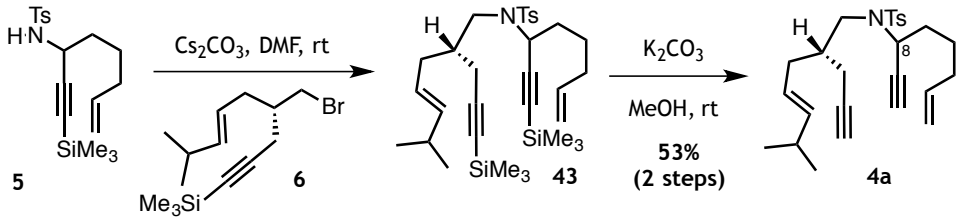

Bromide **6** was obtained using the same procedure as in preparation of bromide (*E*)-7-bromo-2-methylhept-3-ene. [130 mg, 99%, *Rf*= 0.9 (20% $Et_2O$/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 5.97-5.87 (m, 1H), 5.74-5.68 (m, 1H), 4.04-3.79 (m, 2H), 2.80-2.79 (m, 2H), 2.77-2.60 (m, 1H), 2.59-2.52 (m, 2H), 2.38-2.24 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 6H), 0.58 (s, 9H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 141.3 (CH), 123.1 (CH), 104.4 (C), 86.7 (C), 39.8 (CH), 37.5 ($CH_2$), 35.2 ($CH_2$), 31.2 (CH), 23.2 ($CH_2$), 22.7 ($CH_3$), 0.27 ($CH_3$); **MS** (*m/z*, I): 301 ($MH^+$, 1), 303 ($MH^+$, 1), 149 (109).

**Preparation of (*S*,*E*)-*N*-(but-3-en-1-yl)-4-methyl-*N*-(6-methyl-2-(prop-2-yn-1-yl)hept-4-en-1-yl)benzenesulfonamide (10a)**




Dienyne **10a** was prepared following the ***general procedure for sulfonamide alkylation*** using tosylamide **7** and bromide **6** [37%, $R_f$= 0.5 (10% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.68 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.74-5.60 (m, 1H), 5.45 (dd, *J* = 15.3 and 6.5 Hz, 1H), 5.34-5.21 (m, 1H), 5.09-4.95 (m, 2H), 3.26-3.07 (m, 2H), 3.04 (d, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.34-1.85 (m, 9H), 0.95 (d, *J* = 6.7 Hz, 6H); **$^{13}$C RMN** (75 MHz, $CDCl_3$, δ): 143.3 (C), 140.9 (CH), 136.4 (C), 134.7 (CH), 129.7 (CH), 127.4 (CH), 123.5 (CH), 117.1 ($CH_2$), 82.1 (C), 70.2 (CH), 51.8 ($CH_2$), 49.0 ($CH_2$), 36.8 (CH), 34.1 ($CH_2$), 33.1 ($CH_2$), 31.2 (CH), 22.7 ($CH_3$), 21.6 ($CH_3$), 20.4 ($CH_2$); **MS** (*m/z*, ESI): 396 ($MNa^+$), 374 ($MH^+$), 218; **HRMS:** calculated for $C_{22}H_{32}NO_2S$ ($MH^+$): 374.2148, found: 374.2140 .

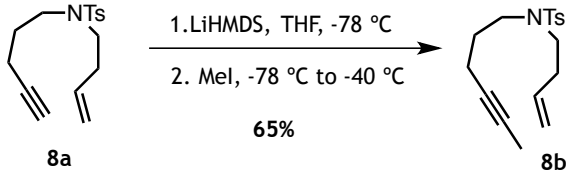
### V.1.4 Precursor of taxanic tricycle ABC: diendiyne 4a




Diendiyne **4a** was prepared following the ***general procedure for sulfonamide alkylation*** using tosylamide **5** and bromide **6** [445 mg, 53%, $R_f$= 0.5 (15% EtOAc/hexanes), colorless oil, mixture of 2 isomers at C8]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.86-5.70 (m, 1H), 5.54-5.38 (m, 1H), 5.38-5.23 (m, 1H), 5.08-4.90 (m, 2H), 4.68-4.58 (m, 1H), 3.24-2.96 (m, 2H), 2.42 (s, 3H), 2.39-2.02 (m, 9H), 1.99-1.92 (m, 1H), 1.84-1.64 (m, 2H), 1.62-1.44 (m, 2H), 1.00-0.92 (m, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 143.6 (C), 143.6 (C), 140.8 (CH), 140.6 (CH), 138.2 (CH), 138.1 (CH), 135.7 (C), 135.3 (C), 129.5 (CH), 128.1 (CH), 128.0 (CH), 124.0 (CH), 123.8 (CH), 115.3 ($CH_2$), 115.2 ($CH_2$), 82.7 (C), 82.0 (C), 80.2 (C), 80.2 (C), 74.3 (CH), 74.1 (CH), 70.5 (CH), 69.8 (CH), 51.5 (CH), 51.4 (CH), 49.1 ($CH_2$), 48.9 ($CH_2$), 37.9 (CH), 37.0 (CH), 35.4 ($CH_2$), 35.1 ($CH_2$), 34.5 ($CH_2$), 34.3 ($CH_2$), 33.1 ($CH_2$), 33.1 ($CH_2$), 31.2 (CH), 25.6 ($CH_2$), 25.5 ($CH_2$), 22.7 ($CH_3$), 22.7 ($CH_3$), 21.7 ($CH_3$), 21.0 ($CH_2$), 20.4 ($CH_2$); **MS** (*m/z*, ESI): 448, 426 ($MH^+$), 320; **HRMS:** calculated for $C_{26}H_{36}NO_2S$ ($MH^+$): 426.2461, found: 426.2468.

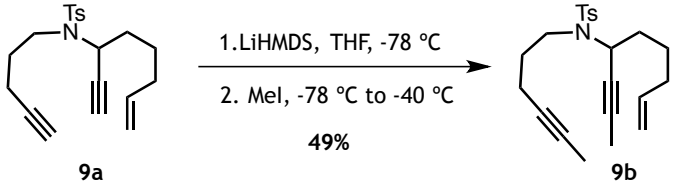
## V.2. Synthesis of precursors with methylated alkynes

### V.2.1 Precursor of cycle B: enyne 8b



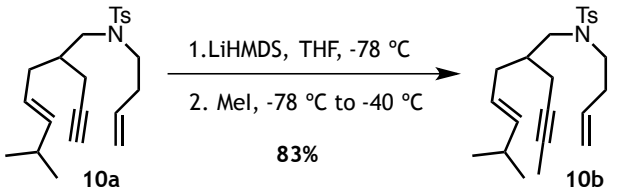

***General procedure for alkyne methylation*** applied to enyne **8a**: A solution lithium bis(trimethylsilyl)amide (1 M in THF, 1.0 mL, 1.00 mmol) was added dropwise to a solution of tosylamide **8a** (150 mg, 0.51 mmol) in THF (1.3 mL) at -78 °C. After 20 min, MeI (160 uL, 2.57 mmol) was added at -78 °C and after further 10 min of stirring, the temperature was increased to -40 °C and the mixture was stirred for 12 h. After this time, the solvent was removed and the resulting crude was purified by flash chromatography (10% EtOAc/hexanes) to afford an inseparable mixture of N-(but-3-en-1-yl)-N-(hex-4-yn-1-yl)-4-methylbenzenesulfonamide **8b**, and starting material (**8a**). After repeating the same procedure with this mixture N-(but-3-en-1-yl)-N-(hex-4-yn-1-yl)-4-methylbenzenesulfonamide **8b** was obtained exclusively [102.5 mg, 65%, $R_f$= 0.6 (10% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.62 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.74-5.53 (m, 1H), 5.07-4.88 (m, 2H), 3.23-3.00 (m, 4H), 2.34 (s, 3H), 2.31-2.16 (m, 2H), 2.10-2.01 (m, 2H), 1.67-1.58 (m, 5H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.2 (C), 136.9 (C), 134.8 (CH), 129.7 (CH), 127.2 (CH), 117.1 ($CH_2$), 77.9 (C), 76.4 (C), 48.1 ($CH_2$), 47.6 ($CH_2$), 33.3 ($CH_2$), 28.2 ($CH_2$), 21.6 ($CH_3$), 16.2 ($CH_2$), 3.5 ($CH_3$); **MS** (*m/z*, ESI): 328, 306 ($MH^+$); **HRMS:** calculated for $C_{17}H_{24}NO_2S$ ($MH^+$): 306.1522, found: 306.1524.

### V.2.2 Precursor of bicycle BC: endiyne 9b



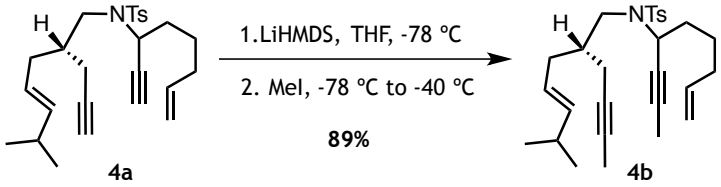

Endiyne **9b** was prepared following the ***general procedure for alkyne methylation*** using tosylamide **9a** [32 mg, 49%, $R_f$= 0.4, (15% Acetone/hexanes), colorless oil]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.91-5.77 (m, 1H), 5.15-4.92 (m, 2H), 4.60-4.66 (m, 1H), 3.23-3.14 (m, 2H), 2.47 (s, 3H), 2.27-2.17 (m, 2H), 2.17-2.12 (m, 2H), 2.08-1.96 (m, 1H), 1.87-1.51 (m, 11H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 143.1 (C), 138.3 (CH), 136.2 (C), 129.3 (CH), 128.0 (CH), 115.0 ($CH_2$), 81.4 (C), 78.3(C), 76.2(C), 76.1 (C), 51.5 (CH), 44.6 ($CH_2$), 35.5 ($CH_2$), 33.2 ($CH_2$), 30.5 ($CH_2$), 25.5 ($CH_2$), 21.6 ($CH_3$), 16.6 ($CH_2$), 3.6 ($CH_3$), 3.4 ($CH_3$); **MS** (*m/z*, ESI): 394 ($MNa^+$), 252, 217; **HRMS:** calculated for $C_{22}H_{29}NO_2SNa$ ($MNa^+$): 394.1811, found: 394.1809.

### V.2.3 Precursor ocf bicycle AB: dienine 10b




Dienyne **10b** was prepared following the ***general procedure for alkyne methylation*** fusing tosylamide **10a**.[8] [65 mg, 83%, *Rf*= 0.5 (15% Acetone/hexanes), colorless oil]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.68 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.72-5.63 (m, 1H), 5.42 (dd, *J* = 15.3 and 6.6 Hz, 1H), 5.31-5.23 (m, 1H), 5.08-4.96 (m, 2H), 3.26-2.99 (m, 4H), 2.41 (s, 3H), 2.33-2.19 (m, 3H), 2.17-1.97 (m, 4H), 1.93-1.82 (m, 1H), 1.78-1.74 (m, 3H), 0.98-0.94 (m, 6H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.2 (C), 140.6 (CH), 136.7 (C), 134.9 (CH), 129.7 (CH), 127.5 (CH), 123.9 (CH), 117.1 ($CH_2$), 77.3 (C), 76.8 (C), 51.9 ($CH_2$), 48.8 ($CH_2$), 37.2 (CH), 34.3 ($CH_2$), 33.0 ($CH_2$), 31.2 (CH), 22.7 ($CH_3$), 21.6 ($CH_3$), 20.9 ($CH_2$), 3.6 ($CH_3$); **MS** (*m/z*, ESI): 410, 388 ($MH^+$), 192; **HRMS:** calculated for $C_{23}H_{34}NO_2S$ ($MH^+$): 388.2305, found: 388.2311.

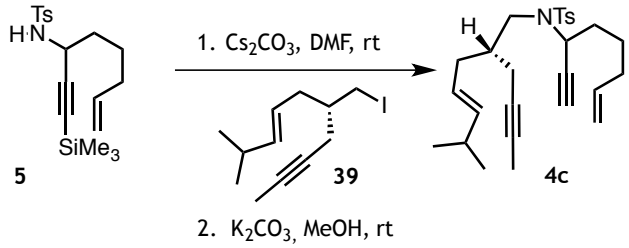
### V.2.4 Precursor of taxanic tricycle ABC: diendiyne 4b




Diendiyne **4b** was prepared following the ***general procedure for alkyne methylation*** using tosylamide **4a**. [101.3 mg, 89%, $R_f$= 0.5 (15% Acetone/hexanes), colorless oil]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.70 (2d, *J* = 8.3 Hz, 2H), 7.27 (2d, *J* = 8.3 Hz, 2H), 5.83-5.70 (m, 1H), 5.49-5.36 (m, 1H), 5.35-5.23 (m, 1H), 5.07-4.86 (m, 2H), 4.57-4.49 (m, 1H), 3.12-2.92 (m, 2H), 2.40 (s, 3H), 2.33-1.94 (m, 8H), [1.79 (t, *J* = 2.5 Hz) + 1.76 (t, *J* = 2.5 Hz), 3H], 1.75–1.58 (m, 2H), [1.54 (d, *J* = 2.3 Hz) + 1.52 (d, *J* = 2.3 Hz), 3H], 1.51-1.43 (m, 2H), 0.98-0.94 (m, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 143.2 (C), 143.1 (C), 140.5 (CH), 140.3 (CH), 140.1 (CH), 138.4 (CH), 138.3 (CH), 136.0 (C), 135.6 (C), 129.2 (CH), 128.1 (CH), 128.0 (CH), 124.5 (CH), 124.3 (CH), 115.0 ($CH_2$), 114.9 ($CH_2$), 81.7 (C), 81.6 (C), 77.5 (C), 77.4 (C), 76.7 (C), 75.7 (C), 75.6 (C), 70.3 (C), 52.0 (CH), 51.8 (CH), 49.1 ($CH_2$), 49.0 ($CH_2$), 38.3 (CH), 37.7 (CH), 35.5 ($CH_2$), 35.4 ($CH_2$), 34.8 ($CH_2$), 34.5 ($CH_2$), 33.2 ($CH_2$), 33.1 ($CH_2$), 31.2 (CH), 31.2 (CH), 25.8 ($CH_2$), 25.7 ($CH_2$), 22.7 ($CH_3$), 22.6 ($CH_3$), 21.6 ($CH_3$), 21.4 ($CH_2$), 20.8 ($CH_2$), 3.7 ($CH_3$), 3.6 ($CH_3$), 3.4 ($CH_3$), 3.3 ($CH_3$); **MS** (*m/z*, ESI): 454 ($MH^+$), 642; **HRMS:** calculated for $C_{28}H_{40}NO_2S$ ($MH^+$): 454.2774, found: 454.2772.

[8] In this case only one reation was required for complete methylation of terminal alkyne.

## V.2.5 Precursor of taxanic tricycle ABC: diendiyne 4c



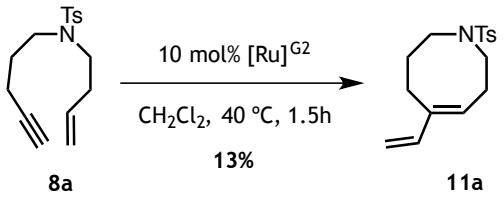

Diendiyne **4c** was prepared following the ***general procedure for sulfonamide alkylation*** using sulfonamide **5** and iodide **39**.[9] [298 mg, 57% (2 steps), $R_f$= 0.5 (15% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.63 (2d, *J* = 8.3 Hz, 2H), 7.21 (2d, *J* = 8.3 Hz, 2H), 5.80-5.63 (m, 1H), 5.44-5.31 (m, 1H), 5.29-5.17 (m, 1H), 4.99-4.85 (m, 2H), 4.60-4.52 (m, 1H), 3.16-2.88 (m, 2H), 2.34 (s, 3H), 2.27-1.89 (m, 9H), 1.75-1.36 (m, 7H), 0.93-0.84 (m, 6H); **$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 143.5 (C), 143.4 (C), 140.3 (CH), 140.2 (CH), 138.1 (CH), 138.0 (CH), 135.8 (C), 135.4 (C), 129.4 (CH), 128.0 (CH), 127.9 (CH), 124.3 (CH), 124.1 (CH), 115.2 ($CH_2$), 115.1 ($CH_2$), 80.3 (C), 80.2 (C), 77.3 (C), 76.8 (C), 76.6 (C), 74.1 (CH), 74.0 (CH), 51.5 (CH), 51.2 (CH), 49.3 ($CH_2$), 49.1 ($CH_2$), 38.2 (CH), 37.6 (CH), 35.2 ($CH_2$), 35.1 ($CH_2$), 34.6 ($CH_2$), 34.4 ($CH_2$), 33.1 ($CH_2$), 33.0 ($CH_2$), 31.2 (CH), 25.6 ($CH_2$), 25.5 ($CH_2$), 22.7 (CH), 21.6 ($CH_3$), 21.3 ($CH_2$), 20.7 ($CH_2$), 3.6 ($CH_3$), 3.5 ($CH_3$); **MS** (*m/z*, ESI): 462, 440 ($MH^+$); **HRMS:** calculated for $C_{27}H_{38}NO_2S$ ($MH^+$): 440.2618, found: 440.2624.

[9] Iodide **39** was prepared according: M. J. Aldegunde, R. García-Fandiño, L. Castedo, J. R. Granja, *Chem. Eur. J.* 2007, **13**, 5135-5150.

## V.3. Cascade metathesis reaction studies for azataxanes

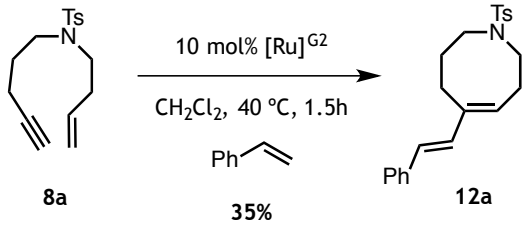
### V.3.1 B ring formation

#### V.3.1.1 Metathesis reaction of enyne 8a



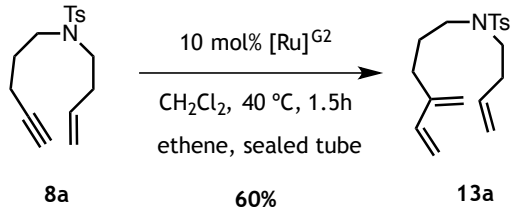

***General metathesis procedure A***, exemplified for preparation of diene **11a**: Second generation Grubbs catalyst **[Ru]$^{G2}$** (14.3 mg, 16.8 μmol, 10 mol%) was added to a solution of enyne **8a** (48.9 mg, 168 μmol) in $CH_2Cl_2$ (34 mL, 5mM). The resulting solution was sttirred at rt untyl became homogeneous and then was refluxed for 1.5 h. After this time the solvent was removed and the resulting residue was purified by flash chromatography (7% EtOAc/hexanes) to afford diene **11a** [6.3 mg, 13%, $R_f$= 0.3 (15% acetone/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.26 (dd, *J* = 17.6 and 10.7 Hz, 1H), 5.77-5.71 (m, 1H), 5.18 (d, *J* = 17.6 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 3.34-3.11 (m, 2H), 3.05 (t, *J* = 5.8 Hz, 2H), 2.61-2.47 (m, 2H), 2.43-2.34 (m, 5H), 1.91-1.76 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.1 (C), 140.8 (C), 138.9 (CH), 137.0 (C), 129.9 (CH), 129.7 (CH), 127.0 (CH), 112.1 ($CH_2$), 51.7 ($CH_2$), 48.5 ($CH_2$), 29.5($CH_2$), 29.2 ($CH_2$), 22.2 ($CH_2$), 21.6 ($CH_3$); **HRMS:** calculated for $C_{16}H_{232}NO_2S$ ($MH^+$): 292.1366, found: 292.1367.

#### V.3.1.2 Metathesis reaction of enyne 8a in presence of styrene




Second generation Grubbs catalyst **[Ru]$^{G2}$** (3.5 mg, 4 μmol, 10 mol%) was added a solution of enyne **8a** (11.7 mg, 40 μmol) and styrene (9.1 μL, 80 μmol) in $CH_2Cl_2$ (8 mL, 5 mM). The resulting solution was sttirred at rt untyl became homogeneous and then was refluxed for 1.5 h. After this time the solvent was removed and the resulting residue was purified by flash chromatography (7% EtOAc/hexanes) to afford diene **12a** [5.2 mg, 35%, $R_f$= 0.3 (15% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.68 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.35-7.27 (m, 4H), 7.25-7.18 (m, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 5.87 (t, *J* = 8.2 Hz, 1H), 3.31-3.17 (m, 2H), 3.08 (t, *J* = 5.7 Hz, 2H), 2.70-2.55 (m, 2H), 2.49-2.41 (m, 2H), 2.40 (s, 3H), 2.00-1.83 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.1 (C), 140.6 (C), 137.6 (C), 137.0 (C), 131.2 (CH), 130.7 (CH), 129.8 (CH), 128.7 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.4 (CH), 51.8 ($CH_2$), 48.5 ($CH_2$), 29.8 ($CH_2$), 29.4 ($CH_2$), 22.8 ($CH_2$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 297, 155, 126.

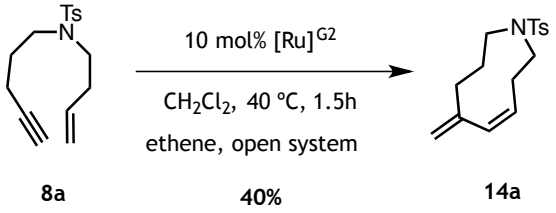
### V.3.1.3 Metathesis reaction of enyne 8a under ethene atmosphere (closed system)




**8a** **60%** **13a**

In a sealed tube, a solution of enyne **8a** (30.4 mg, 0.10 mmol) in $CH_2Cl_2$ (10 mL, 5 mM) was prepared and purged with ethylene for 10 minutes by bubbling the gas through the solution. On the other hand, a solution of **[Ru]$^{G2}$** catalyst (8.8 mg, 10.4 μmol, 10 mol%) in $CH_2Cl_2$ (8 mL) was prepared and also purged with ethylene for 10 minutes. This solution was added *via syringe* to the one containing the substrate and the flask was washed with of $CH_2Cl_2$ (2 mL). The resulting mixture was purged with ethylene for another 10 min and heated at 40 $^oC$ for 1.5 h. After this time the solvent was removed and the resulting crude was purified by flash chromatography (10% EtOAc/hexanes) to afford diene **13a** [17.9 mg, 60%, $R_f$= 0.3 (15% acetone/hexanes), slightly yellow oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.69 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.35 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.76-5.65 (m, 1H), 5.20-4.95 (m, 5H), 3.27-3.07 (m, 4H), 2.42 (s, 3H), 2.35-2.23 (m, 2H), 2.19 (t, *J* = 7.7 Hz, 2H), 1.82-1.65 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 145.2 (C), 143.2 (C), 138.7 (CH), 137.1 (C), 134.8 (CH), 129.7 (CH), 127.2 (CH), 117.1 ($CH_2$), 116.2 ($CH_2$), 113.5 ($CH_2$), 48.3 ($CH_2$), 47.8 ($CH_2$), 33.4 ($CH_2$), 28.5 ($CH_2$), 26.9 ($CH_2$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 342 ($MNa^+$), 238, 155; **HRMS:** calculated for $C_{18}H_{25}NO_2SNa$ ($MNa^+$): 342.1498, found: 342.1497.

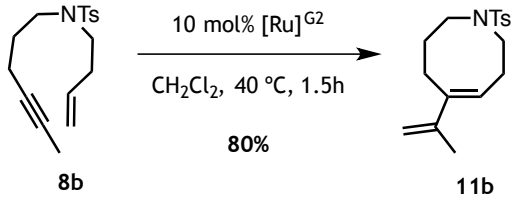
### V.3.1.4 Metathesis reaction of enyne 8a under ethene atmosphere (open system)




**8a** **40%** **14a**

In a round bottom flask a solution of enyne **8a** (36.1 mg, 0.12 mmol) in $CH_2Cl_2$ (25 mL, 5 mM) was prepared and purged with ethylene for 10 min by bubbling the gas through the solution and **[Ru]$^{G2}$** catalyst (10 mg, 11.7 μmol, 10 mol%) was added. The resulting mixture was purged with ethylene for 10 min and refluxed for 1.5 h. After this time the solvent was removed and the resulting crude mixture was purified by flash chromatography (20% acetone/hexanes) to afford diene **14a** [15.3 mg, 40%, $R_f$= 0.1 (15% acetone/hexanes), slightly yellow oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.69 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.01 (d, *J* = 16.0 Hz, 1H), 5.64 (dt, *J* = 15.8 and 6.9 Hz, 1H), 4.89 (s, 1H), 4.85 (s, 1H), 3.10 (dt, *J* = 16.8 and 7.2 Hz, 4H), 2.42 (s, 3H), 2.33 (dt, *J* = 10.4 and 4.9 Hz, 2H), 2.19 (t, *J* = 7.4 Hz, 2H), 1.72 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 144.9 (C), 143.3 (C), 136.5 (C), 133.4 (CH), 129.8 (CH), 127.4 (CH), 127.1 (CH), 115.3 ($CH_2$), 49.0 ($CH_2$), 48.5 ($CH_2$), 32.4 ($CH_2$), 30.0 ($CH_2$), 27.3 ($CH_2$), 21.6 ($CH_3$).

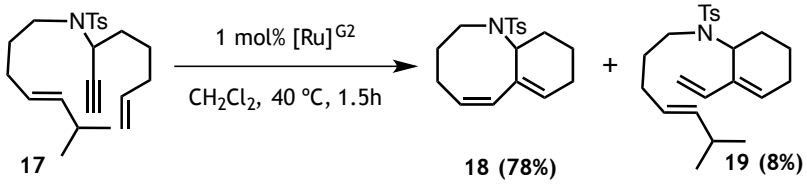
### V.3.1.5 Metathesis reaction of enyne 8b



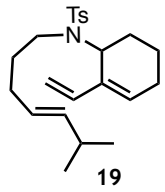

Diene **11b** was prepared following the ***general metathesis procedure A***: Solution of **8b** in $CH_2Cl_2$ (5mM), 10 mol% **[Ru]$^{G2}$** catalyst, 40 °C, 1.5 h to afford diene **11b** [24 mg, 80%, $R_f$= 0.4 (15% acetone/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.67 (d, *J* = 8.3 Hz, 2H), 7.2a (d, *J* = 8.3 Hz, 2H), 5.85 (t, *J* = 8.1 Hz, 1H), 5.07 (s, 1H), 4.93 (s, 1H), 3.29-3.16 (m, 2H), 3.04 (t, *J* = 5.8 Hz, 2H), 2.62-2.52 (m, 2H), 2.47-2.35 (m, 5H), 1.86 (s, 3H), 1.87-1.74 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 143.01 (C), 142.3 (C), 141.6 (C), 137.1 (C), 129.7 (CH), 127.0 (CH), 125.3 (CH), 112.3 ($CH_2$), 51.7 ($CH_2$), 48.5 ($CH_2$), 29.9 ($CH_2$), 29.7 ($CH_2$), 23.8 ($CH_2$), 21.6 ($CH_3$), 21.0 ($CH_3$; **MS** (*m/z*, ESI): 328, 306 ($MH^+$), 150; **HRMS:** calculated for $C_{17}H_{24}NO_2S$ ($MH^+$): 306.1522, found: 306.1523.

## V.3.2 Bicycle [6.4.0] formation. BC rings

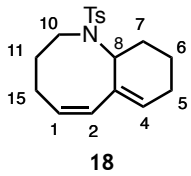
### V.3.2.1 Metathesis reaction of dienyne 17




Diene **18** was prepared following the ***general metathesis procedure A***: Solution of **17** (21.2 mg, 54.7 μmol) in $CH_2Cl_2$ (11 mL), 1 mol% of **[Ru]$^{G2}$** catalyst (0.5 mg, 5.0 μmol), 40 $^oC$, 1.5 h to afford triene **19** [1.7 mg, 8%, $R_f$= 0.5 (10% EtOAc/hexanes), colorless oil] and bicycle **18** [13.5 mg, 78%, $R_f$= 0.4, (10% EtOAc/hexanes), white solid].

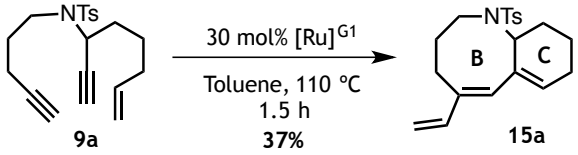



**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.75 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.10-5.97 (m, 2H), 5.33 (dd, *J* = 15.3 and 6.3 Hz, 1H), 5.27-5.18 (m, 2H), 4.87 (d, *J* = 11.3 Hz, 1H), 4.69-4.62 (m, 1H), 3.08-2.86 (m, 2H), 2.43 (s, 3H), 2.28-2.14 (m, 1H), 2.13-2.05 (m, 2H), 1.91-1.83 (m, 2H), 1.76-1.60 (m, 5H), 1.56-1.46 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 143.0 (C), 138.6 (C), 138.5 (CH), 137.2 (CH), 135.3 (C), 132.5 (CH), 129.6 (CH), 127.5 (CH), 126.0 (CH), 113.2 ($CH_2$), 54.3 (CH), 45.0 ($CH_2$), 31.1 (CH), 30.4 ($CH_2$), 30.2 ($CH_2$), 29.0 ($CH_2$), 25.3 ($CH_2$), 22.8 ($CH_3$), 21.6 ($CH_3$), 20.3($CH_2$); **MS** (*m/z*, ESI): 410 ($MNa^+$), 282, 256; **HRMS:** calculated for $C_{23}H_{33}NO_2SNa$ ($MNa^+$): 410.2124, found: 410.2125.



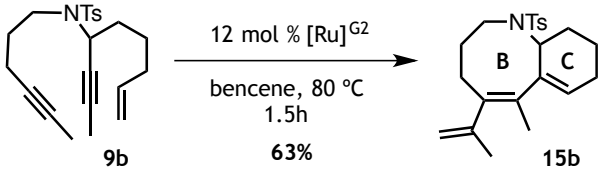

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.69 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.84 (d, *J* = 11.3Hz, 1H), 5.68-5.63 (m, 1H), 5.59-5.53 (m, 1H), 4.56-4.45 (m, 1H), 3.66 (ddd, *J* = 14.5, 8.2 and 3.8 Hz, 1H), 3.15 (ddd, *J* = 14.5, 7.0 and 3.3 Hz, 1H), 2.41 (s, 3H), 2.28-2.19 (m, 1H), 2.14-1.96 (m, 3H), 1.94-1.82 (m, 1H), 1.76-1.48 (m, 5H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.7 (C), 139.0 (C), 136.8 (C), 132.3 (CH), 129.5 (CH), 128.2 (CH), 127.8 (CH), 127.2 (CH), 56.7 ($CH_2$), 45.9 (CH), 27.9 ($CH_2$), 26.8 ($CH_2$), 26.3 ($CH_2$), 25.1 ($CH_2$), 21.8 ($CH_2$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 340 ($MNa^+$), 318, 178; **HRMS:** calculated for $C_{18}H_{23}NO_2SNa$ ($MNa^+$): 340.1342, found: 340.1352.

### V.3.2.2 Metathesis reaction of endiyne 9a



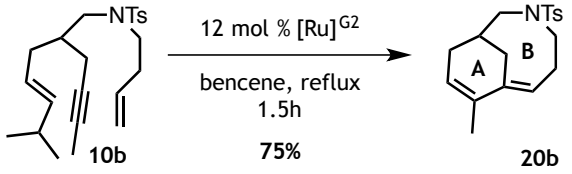

Bicycle **15a** was prepared following the ***general metathesis procedure A***: Solution of endiyne **9a** in toluene (5mM), 30 mol% of **[Ru]$^{G1}$** catalyst, 110 °C, 1.5 h to afford triene **15a** [6.2 mg, 37%, $R_f$= 0.3 (15% acetone/hexanes), white solid]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.64 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.15 (dd, *J* = 17.4 and 10.8 Hz, 1H), 5.76-5.74 (m, 1H), 5.65-5.56 (m, 1H), 5.10 (d, *J* = 17.4 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.46-4.37 (m, 1H), 3.72 (ddd, *J* = 15.0, 5.8 and 3.3 Hz, 1H), 3.13 (ddd, *J* = 15.0, 8.8 and 2.8 Hz, 1H), 2.40 (s, 3H), 2.37-2.18 (m, 2H), 2.13-1.95 (m, 2H), 1.90-1.51 (m, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.7 (C), 141.0 (C), 140.1 (CH), 138.6 (C), 136.6 (C), 130.8 (CH), 129.5 (CH), 128.6 (CH), 127.5 (CH), 111.8 ($CH_2$), 57.2 (CH), 45.9 ($CH_2$), 27.2 ($CH_2$), 27.0 ($CH_2$), 25.8 ($CH_2$), 25.1 ($CH_2$), 21.7 ($CH_2$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 366 ($MNa^+$), 188, 173, 155; **HRMS:** calculated for $C_{20}H_{25}NO_2SNa$ ($MH^+$): 366.1498, found: 366.1510.

### V.3.2.3 Metathesis reaction of endiyne 9b




Bicycle **15b** was prepared following the ***general metathesis procedure A***: Solution of endiyne **9b** in bencene (5mM), 12 mol% of **[Ru]$^{G2}$** catalyst, 80 °C, 1.5 h to afford triene **15b** [8.3 mg, 63%, $R_f$= 0.4 (15% acetone/hexanes), white solid]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.69 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.63-5.57 (m, 1H), 4.93-4.89 (m, 1H), 4.76-4.71 (m, 1H), 4.67-4.60 (m, 1H), 3.65-3.58 (m, 1H), 2.99-2.88 (m, 1H), 2.40 (s, 3H), 2.40-2.31 (m, 1H), 2.08-1.95 (m, 2H), 1.95-1.84 (m, 2H), 1.80 (s, 3H), 1.73 (s, 3H), 1.71-1.65 (m, 1H), 1.62-1.55 (m, 1H), 1.56-1.42 (m, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 146.4 (C), 142.7 (C), 141.9 (C), 139.3 (C), 139.1 (C), 130.9 (C), 129.6 (CH), 127.1 (CH), 127.1 (CH), 113.3 ($CH_2$), 55.9 (CH), 46.2 ($CH_2$), 31.4 ($CH_2$), 29.5 ($CH_2$), 26.5 ($CH_2$), 24.9 ($CH_2$), 22.4 ($CH_3$), 22.0 ($CH_2$), 21.6 ($CH_3$), 20.9 ($CH_3$); **MS** (*m/z*, ESI): 394, 372 ($MH^+$), 155; **HRMS:** calculated for $C_{22}H_{30}NO_2S$ ($MH^+$): 372.1992, found: 372.1988.

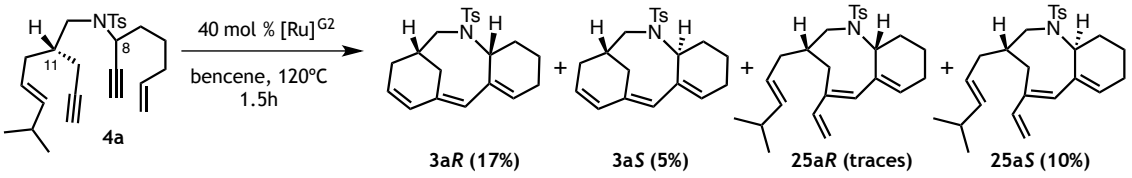
### V.3.3 Bicycle [5.3.1] formation. AB rings. Metathesis reaction of dienyne 10b



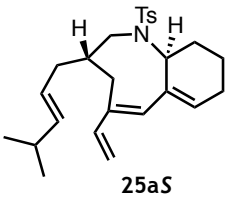

Bicycle **20b** was prepared following the ***general metathesis procedure A***: Solution of dienyne **10b** in bencene (5mM), 10 mol% of **[Ru]$^{G2}$** catalyst, 80 $^{o}$C, 1.5 h to afford diene **20b** [10.5 mg, 75%, $R_f$= 0.4 (15% acetone/hexanes), white solid]. **$^{1}$H NMR** (500 MHz, $CDCl_3$, δ): 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.63 (t, *J* = 7.9 Hz, 1H), 5.17-5.08 (m, 1H), 4.03-3.96 (m, 1H), 3.45-3.33 (m, 1H), 3.06 (dd, *J* = 11.8 and 3.8 Hz, 1H), 2.74-2.66 (m, 1H), 2.67-2.59 (m, 1H), 2.56-2.46 (m, 2H), 2.40 (s, 3H), 2.36-2.28 (m, 1H), 2.12-2.06 (m, 1H), 2.05-1.98 (m, 1H), 1.76 (s, 3H), 1.58 (d, *J* = 19.1 Hz, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 143.0 (C), 142.0 (C), 137.3 (C), 136.0 (C), 129.7 (CH), 126.9 (CH), 121.5 (CH), 121.0 (CH), 55.3 ($CH_2$), 53.1 ($CH_2$), 36.1 (CH), 29.4 ($CH_2$), 28.8 ($CH_2$), 28.2 ($CH_2$), 21.6 ($CH_3$), 18.6 ($CH_3$); **MS** (*m/z*, ESI): 340 ($MNa^+$), 184, 155; **HRMS:** calculated for $C_{18}H_{23}NO_2SNa$ ($MNa^+$): 340.1342, found: 340.1336.

## V.3.4 Taxane tricycle formation. ABC rings

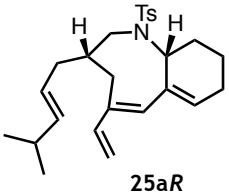
### V.3.4.1 Metathesis reaction of diendiyne 4a



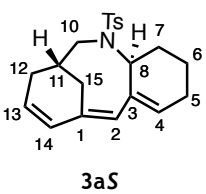

***General metathesis procedure B***, exemplified for preparation of tricycles **3a**: Catalyst **[Ru]**$^{G1}$ (38.7mg, 47 μmol, 40 mol%) was added to a solution of diendiyne **4a** (50 mg, 0.12 mmol) in benzene (24 mL, 5 mM). The resulting mixture was heated at 120 ºC in a sealed tube for 1.5 hours. After this time the solvent was removed and the residue was purified by flash chromatography (5% acetone/hexanes) to afford impure fractions of tetraenes **25a*S*** [4.9 mg, $R_f$= 0.5 (15% acetone/hexanes)] and **25a*R*** [traces, $R_f$= 0.4 (15% acetone/hexanes)],[10] in addition to tricarbocycles **3a*S*** [2.4 mg, 5%, $R_f$= 0.4 (15% acetone/hexanes)] and **3a*R*** [7.2 mg, 17%, $R_f$= 0.3 (15% Acetone/hexanes)] in 22% overall yield.




**$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.63 (d, *J*= 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.13 (dd, *J* = 17.5 and 10.7 Hz, 1H), 5.68 (s, 1H), 5.59 (s, 1H), 5.51-5.28 (m, 2H), 5.10 (d, *J* = 17.5 Hz, 1H), 4.97 (d, *J* = 10.7 Hz, 1H), 4.37 (s, 1H), 3.60 (d, *J* = 14.8 Hz, 1H), 2.80-2.64 (m, 1H), 2.41 (s, 3H), 2.26 (d, *J* = 11.4 Hz, 2H), 2.13-1.17 (m, 10H), 1.00 (d, *J* = 6.8 Hz, 6H).

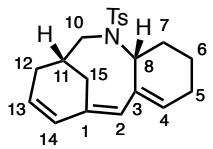



**$^1$H NMR** (300 MHz, $CDCl_3$, δ): 7.64 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.29 (dd, *J* = 17.5 and 10.8 Hz, 1H), 6.01 (s, 1H), 5.60 (s, 1H), 5.40 (dd, *J* = 15.3 and 6.8 Hz, 1H), 5.26 (dt, *J* = 15.3 and 6.7 Hz, 1H), 5.05 (d, *J*= 17.5 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.48 (s, 1H), 3.47-3.26 (m, 1H), 3.09-2.84 (m, 1H), 2.39 (s, 3H), 2.37-1.56 (m, 10H), 0.96 (d, *J* = 6.8 Hz, 6H).




**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.64 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.43 (d, *J* = 10.0 Hz, 1H), 5.59-5.68 (m, 2H), 5.50-5.45 (m, 1H), 5.61 (s, 1H), 4.47-4.36 (m, 1H), 3.85-3.78 (m, 1H), 3.15 (dd, *J* = 15.6 and 4.6 Hz, 1H), 2.62 (d, *J* = 19.6 Hz, 1H), 2.49-2.38 (m, 5H), 2.23 (m, 1H), 2.13 (dd, *J* = 12.4 and 6.5 Hz, 1H), 2.12-2.02 (m, 2H), 1.86-1.78 (m, 1H), 1.77-1.66 (m, 1H), 1.66-1.56 (m, 1H), 1.27-1.20 (m, 1H).

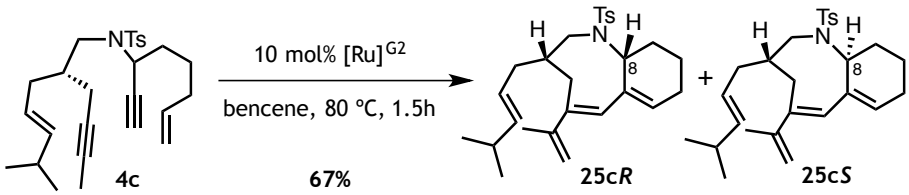
[10] Tretraene **25a*R*** could be isolated in higher quantities when **4a** was treated with 30 mol% of **[Ru]**$^{G1}$ in bencene, heating at 100 ºC using a similar procedure.



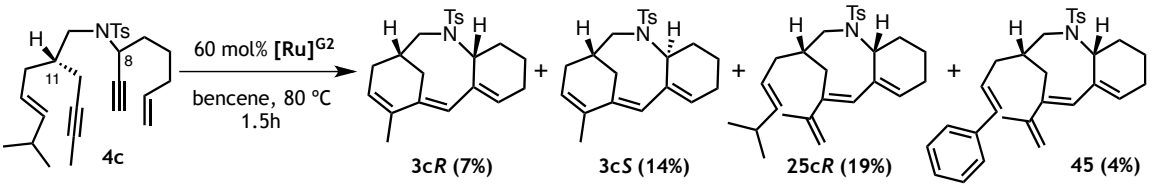

**3a*R***

**$^{1}$H NMR** (500 MHz, $CDCl_3$, δ): 7.65 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.50 (d, *J* = 10.1 Hz, 1H), 5.97 (bs, 1H), 5.74 (s, 1H), 5.59 (dt, *J* = 10.1, 3.6 Hz, 1H), 4.27-4.22 (m, 1H), 3.86 (d, *J* = 15.1 Hz, 1H), 3.41-3.29 (m, 1H), 2.62-2.45 (m, 2H), 2.47-2.33 (m, 5H), 2.34-2.05 (m, 4H), 1.88-1.81 (m, 1H), 1.75-1.69 (m, 1H), 1.60-1.48 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, $\delta$ ): 142.2 (C), 141.5 (C), 139.5 (C), 138.0 (C), 131.5 (CH), 129.5 (CH), 128.3 (CH), 126.6 (CH), 126.5 (CH), 122.8 (CH), 67.5 (CH), 59.7 ($CH_2$), 33.1 (CH), 31.7 ($CH_2$), 31.2 ($CH_2$), 28.7 ($CH_2$), 25.7 ($CH_2$), 23.3 ($CH_2$), 21.6 ($CH_3$); **MS** (*m/z*, ESI): 378 ($MNa^+$), 356 ($MH^+$), 297, 155; **HRMS:** calculated for $C_{21}H_{26}NO_2S$ ($MH^+$): 356.1679, found: 356.1688.

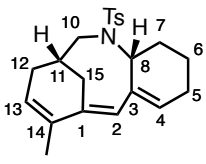
### V.3.4.2 Metathesis reaction of diendiyne 4c



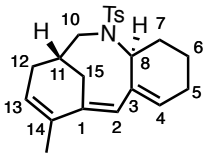

Tetraene **25c** was obteined using the ***general metathesis procedure A***: Solution of diendiyne **4c** in bencene (5mM), 10 mol% of **[Ru]$^{G2}$** catalyst, 80 °C, 1.5 h to afford biclycles **25c** [26 mg, 67%, 2 isomers, 1:2 ratio, $R_f$= 0.5 (15% acetone/hexanes), colorless oil]. **$^1$H NMR** (500 MHz, $CDCl_3$, δ, *major isomer*): 7.61 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.79 (s, 1H), 5.60-5.54 (m, 1H), 5.48-5.20 (m, 2H), 4.98 (s, 1H), 4.90 (s, 1H), 4.35 (s, 1H), 3.58 (d, *J* = 15.3 Hz, 1H), 2.69 (dd, *J* = 15.2 and 10.2 Hz, 1H), 2.39 (s, 3H), 2.32-2.18 (m, 2H), 2.13-1.20 (m, 13H), 0.98 (d, *J* = 6.8 Hz, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.9 (C), 142.7 (C), 142.5 (C), 140.5 (CH), 140.4 (CH), 138.4 (C), 137.1 (C), 129.5 (CH), 128.0 (CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 124.7 (CH), 124.2 (CH), 57.5 (CH), 51.1 ($CH_2$), 38.7 (CH), 38.2 ($CH_2$), 38.0 ($CH_2$), 33.0 ($CH_2$), 31.2 (CH), 27.0 ($CH_2$), 25.4 ($CH_2$), 24.9 ($CH_2$), 22.7 ($CH_3$), 22.1 ($CH_3$), 21.9 ($CH_2$), 21.6 ($CH_3$), 21.0 ($CH_3$); **MS** (*m/z*, ESI): 462 ($MNa^+$), 269, 155; **HRMS:** calculated for $C_{27}H_{37}NO_2SNa$ ($MNa^+$): 462.2437, found: 462.2428.




Taxane derivatives **3c** were prepared following the ***general metathesis procedure B***: Solution of diendiyne **4c** in bencene (5mM), 60 mol% of **[Ru]$^{G2}$** catalyst, 80 °C, 1.5 h to afford azataxanes **3c$_R$** [9.5 mg, 7%, $R_f$= 0.4 (10% EtOAc/hexanes)] and **3c$_S$** [19 mg, 14%, $R_f$= 0.4 (10% EtOAc/hexanes)] in addition to tetraenes **25c$_R$** [30 mg, 19%, $R_f$= 0.5 (10% EtOAc/hexanes)] and **45** [7.7 mg, 4%, $R_f$= 0.5 (10% EtOAc/hexanes)].

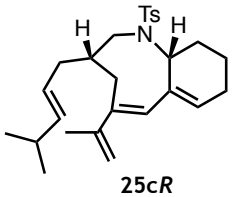



**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 7.64 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.01 (bs, 1H), 5.77-5.74 (m, 1H), 5.31-5.25 (m, 1H), 4.30-4.23 (m, 1H), 3.83 (d, *J* = 15.1 Hz, 1H), 3.33 (dd, *J* = 15.1 and 6.0 Hz, 1H), 2.61 (dd, *J* = 13.1 and 1.5 Hz, 1H), 2.54-2.38 (m, 1H), 2.40 (s, 3H), 2.38-2.05 (m, 6H), 1.91 (s, 3H), 1.90-1.69 (m, 2H), 1.60-1.48 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.2 (C), 141.4 (C), 139.9 (C), 139.4 (C), 137.7 (C), 129.4 (CH), 128.3 (CH), 126.5 (CH), 122.2 (CH), 120.9 (CH), 67.5 (CH), 59.5 ($CH_2$), 32.5 ($CH_2$), 32.3 (CH), 30.8 ($CH_2$), 28.8 ($CH_2$), 25.8 ($CH_2$), 23.3 ($CH_2$), 21.6 ($CH_3$), 18.6 ($CH_3$).



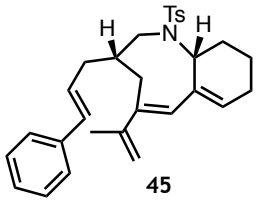
**3c*S***

**$^{1}$H NMR** (300 MHz, $CDCl_3$, δ): 7.63 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.49 (bs, 2H), 5.35-5.27 (m, 1H), 4.39-4.26 (m, 1H), 3.91 (d, *J* = 15.6 Hz, 1H), 3.14 (dd, *J* = 15.6 and 3.9 Hz, 1H), 2.58 (d, *J* = 19.2 Hz, 1H), 2.48 (dd, *J* = 12.3 and 1.3 Hz, 1H), 2.44-2.33 (m, 4H), 2.20-1.95 (m, 4H), 1.88-1.68 (m, 5H), 1.71-1.56 (m, 1H), 1.48-1.30 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 144.4 (C), 142.8 (C), 138.4 (C), 138.0 (C), 136.4 (C), 129.5 (CH), 127.4 (CH), 125.7 (CH), 122.8 (CH), 119.9 (CH), 61.3 (CH), 50.3 ($CH_2$), 33.6 (CH), 33.0 ($CH_2$), 28.7 ($CH_2$), 25.2 ($CH_2$), 25.0 ($CH_2$), 22.8 ($CH_2$), 21.6 ($CH_3$), 18.6($CH_3$); **MS** (*m/z*, ESI): 392 ($MNa^+$), 370 ($MH^+$), 199, 155; **HRMS:** calculated for $C_{22}H_{27}NO_2SNa$ ($MNa^+$): 392.1655, found: 392.1658.



**25c*R***

**$^{1}$H NMR** (300 MHz, $CDCl_3$, δ): 7.62 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.80 (s, 1H), 5.58 (m, 1H), 5.41 (dd, *J* = 15.3 and 6.3 Hz, 1H), 5.34 (m, 1H), 4.98 (s, 1H), 4.91 (s, 1H), 4.36 (m, 1H), 3.59 (d, *J* = 15.1 Hz, 1H), 2.71 (dd, *J* = 15.2 and 10.3 Hz, 1H), 2.42 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H), 2.35-2.22 (m, 2H), 2.15-1.69 (m, 9H), 1.64 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.9 (C), 142.7 (C), 142.5 (C), 140.5 (CH), 138.5 (C), 137.1 (C), 129.5 (CH), 127.9 (CH), 127.4 (CH), 126.8 (CH), 124.8 (CH), 112.4 ($CH_2$), 57.5 (CH), 51.1 ($CH_2$), 38.7 (CH), 38.1 ($CH_2$), 33.1 ($CH_2$), 31.2 (CH), 27.0 ($CH_2$), 24.9 ($CH_2$), 22.8 ($CH_3$), 22.7 ($CH_3$), 21.9 ($CH_2$), 21.62 ($CH_3$), 21.0 ($CH_3$).



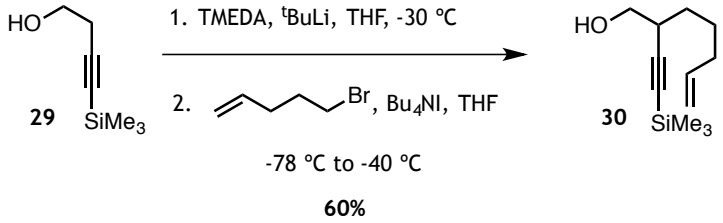
**45**

**$^{1}$H NMR** (300 MHz, $CDCl_3$, δ): 7.61 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32 (m, 2H), 7.23 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.2 Hz, 1H), 5.83 (s, 1H), 5.60 (m, 1H), 4.99 (s, 1H), 4.91 (s, 1H), 4.39 (s, 1H), 3.64 (d, *J* = 15.3 Hz, 1H), 2.76 (dd, *J* = 15.3 and 10.7 Hz, 1H), 2.40 (m, 2H), 2.38 (s, 3H), 2.34 (d, *J* = 13.7 Hz, 1H), 2.23 (d, *J* = 10.8 Hz, 1H), 2.16 (m, 1H), 2.12-1.90 (m, 3H), 1.86-1.70 (m, 5H), 1.60 (m, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$, δ): 142.9 (C), 142.7 (C), 142.3 (C), 138.3 (C), 137.6 (C), 137.0 (C), 132.3 (CH), 129.5 (CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.5 (CH), 127.2 (CH), 126.9 (CH), 126.2 (CH), 112.3 ($CH_2$), 57.5 (CH), 50.9 ($CH_2$), 38.9 (CH), 38.6 ($CH_2$), 33.5 ($CH_2$), 26.9 ($CH_2$), 24.9 ($CH_2$), 21.9 ($CH_2$), 21.6 ($CH_3$), 21.0 ($CH_3$).

## V.4. Synthesis of diendiyne 26

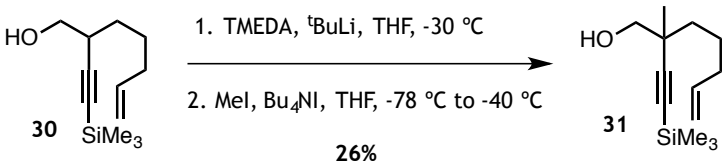
### V.4.1 Preparation of dithiane 27

**Preparation of 2-[2-(trimethylsilyl)ethynyl]hept-6-en-1-ol (30)[11]**




In a round bottom flask, flamed and purged with Ar, a solution of 4-(trimethylsilyl)-but-3-ynol (**29**, 2.9 mL, 17.57 mmol) and tetramethylethylenediamine (6.3 mL, 42.17 mmol) was prepared with freshly distilled THF (88 mL). The mixture was cooled to -30 ° C and a solution of *tert*-butyllithium (1.7 M, 22.7 mL, 38.65 mmol) was added dropwise. After 2.5h, this mixture was cooled to -78 °C and a previously prepared solution of 5-bromopentene (2.1 mL, 18.45 mmol) and tetrabutylammonium iodide (1.29 g, 3.51 mmol) in THF (74 mL) was added *via cannula*. After 12 h stirring and gradual increase in temperature to -40C, the reaction was quenched by adition of aqueous solution of $NH_4Cl$ (sat. Sol., 30 mL). The aqueous phase was extracted with $Et_2O$ (3 x 80 mL) and the combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting yellow oil was purified by flash chromatography (5% EtOAc/hexanes) to afford the homopropargylic alcohol **30** [2.19 g, 60%, $R_f$= 0.4 (15% EtOAc/hexanes), pale yellow oil]. **$^1$H NMR** (250 MHz, $CDCl_3$, δ): 5.85-5.72 (m, 1H), 5.84-5.08 (m, 2H), 3.65-3.48 (m, 2H), 2.66-2.51 (m, 1H), 2.12-2.01 (m, 2H), 1.90 (t, $J$ = 6.4 Hz, 1H), 1.52-1.38 (m, 4H), 0.15 (s, 9H,); **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 138.7 (CH), 114.9 ($CH_2$), 107.4 (C), 87.9 (C), 65.4 ($CH_2$), 36.4 (CH), 33.6 ($CH_2$), 30.6 ($CH_2$), 26.6 ($CH_2$), 0.4 ($CH_3$); **MS** (*m/z*, CI): 137.

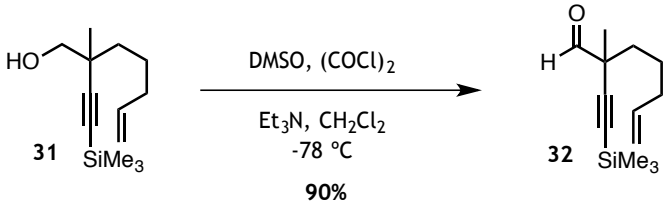
**Prepation of 2-methyl-2-((trimethylsilyl)ethynyl)hept-6-en-1-ol (31)**




Alcohol **31** was prepared using a procedure similar to the one described for alcohol **30**. Flash chromatographic purification (2% EtOAc/hexanes) of the crude mixture afforded the homopropargylic alcohol **31** [487 mg, 26%, $R_f$= 0.5 (10% EtOAc/hexanes), pale yellow oil]. **$^1$H NMR** (250 MHz, $CDCl_3$, δ): 5.91-5.69 (m, 1H), 5.20-4.74 (m, 2H), 3.46-3.30 (m, 2H), 2.35-1.71 (m, 3H), 1.67-1.40 (m, 3H), 1.41-1.19 (m, 1H), 1.14 (s, 3H), 0.13 (s, 9H); **$^{13}$C NMR** ( 63 MHz, $CDCl_3$, δ): 138.5 (CH), 114.5 ($CH_2$), 110.4 (C), 87.0 (C), 70.2 ($CH_2$), 37.1 ($CH_2$), 33.9 ($CH_2$), 23.6 ($CH_2$), 23.1 ($CH_3$), 0.1 ($CH_3$); **MS** (*m/z*, CI): 151.

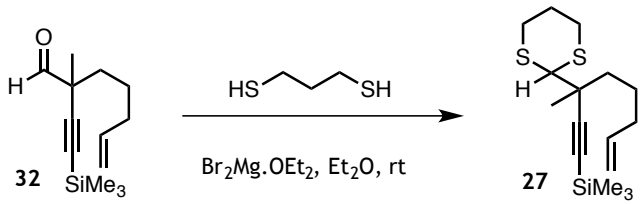
[11] Prepared optimizing the reaction conditions described in: N. V. Van Bac, Y. Langlois, *Tetrahedron Lett.* 1988, **29**, 2819-2822.

**Preparation of 2-methyl-2-((trimethylsilyl)ethynyl)hept-6-enal (32)[12]**




In a round bottom flask, flamed and purged with Ar, oxalyl chloride (90 uL, 1.07 mmol) was dissolved in $CH_2Cl_2$ (1.3 mL) and cooled to -78 and DMSO (150 uL, 2.14 mmol) was added dropwise at this temperature with vigorous stirring. After 40 min at this temperature, a solution of alcohol **31** (120 mg, 0.53 mmol) in $CH_2Cl_2$ (1 mL) was added. One hour later, triethylamine (0.37 mL, 2.68 mmol) was added and after stirring one additional hour, the reaction was quenched by the addition of water (10 mL). The aqueous phase was extracted with $CH_2Cl_2$ (3 x 25 mL) and the combined organic phases were washed with aqueous solutions of $NaHCO_3$ (sat. sol., 15 mL) and brine (15 mL). The organic phase was dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (2% EtOAc/hexanes) to afford aldehyde **32** [106 mg, 90%, $R_f$= 0.9 (15% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (250 MHz, $CDCl_3$, δ): 9.45 (s, 1H), 5.88-5.69 (m, 1H), 5.07-4.89 (m, 2H), 2.15-2.01 (m, 2H), 1.73-1.40 (m, 4H), 1.26 (s, 3H), 0.15 (s, 9H); **$^{13}$C NMR** (63 MHz, $CDCl_3$, δ): 198.8 (CO), 138.2 (CH), 115.1 ($CH_2$), 105.4 (C), 90.6 (C), 47.9 (C), 35.7 ($CH_2$), 33.8 ($CH_2$), 23.9 ($CH_2$), 21.1 ($CH_3$), 0.2 ($CH_3$); **MS** (*m/z*, CI): 223 ($MH^+$), 193, 149; **HRMS:** calculated for $C_{13}H_{22}OSi$ ($MH^+$): 223.1518, found: 223.1522.

**Preparation of thioacetal 27[13]**



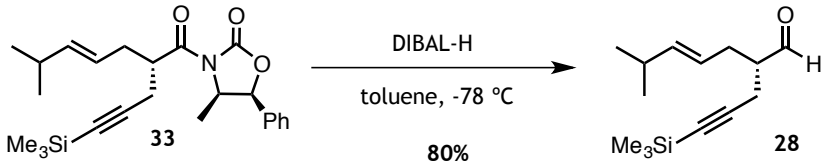

In a round bottom flask, 1,3-propanedithiol (250 uL, 2.49 mmol) was added to a suspension of $Br_2Mg.OEt_2$ (672 mg, 2.60 mmol) in $Et_2O$ (6 mL). After a few minutes, a solution of aldehyde **32** (482 mg, 2.16 mmol) in $Et_2O$ (2.5 mL) was also added. After stirring at rt for 1.5 h, the reaction was quenched by addition of water (15 mL). The resulting mixture was extracted with $Et_2O$ (3 x 40 mL) and the combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The residue was purified by flash chromatography (1% EtOAc/hexanes) to afford the dithiane **27** [484 mg, 71%, $R_f$= 0.3 (5% EtOAc/hexanes), colorless oil]. **$^1$H NMR** (250 MHz, $CDCl_3$, δ): 5.90-5.72 (m,

[12] Modification of the procedure described in: B. M. Trost, Y. Hu, D. B. Horne, *J. Am. Chem. Soc.* 2007, **129**, 11781-11790.

[13] V. A. Keller, J. R. Martinelli, E. R. Streiter, S. D. Burke, *Org. Lett.* 2002, **4**, 467-470.

1H), 5.16-4.79 (m, 2H), 4.10 (s, 1H), 3.11-2.66 (m, 4H), 2.15-1.95 (m, 3H), 1.95-1.42 (m, 5H), 1.32 (s, 3H), 0.13 (s, 9H); **$^{13}$C NMR** (63 MHz, $CDCl_3$, δ): 138.7 (CH), 114.6 ($CH_2$), 110.3 (C), 87.7 (C), 57.6 (CH), 41.1 (C), 38.9 ($CH_2$), 33.9 ($CH_2$), 31.0 ($CH_2$), 30.9 ($CH_2$), 26.1 ($CH_2$), 24.8 ($CH_3$), 24.1 ($CH_2$), 0.2 ($CH_3$); **MS** (*m/z*, CI): 335 ($MNa^+$), 201, 143.

### V.4.2 Preparation of aldehyde 28[14]

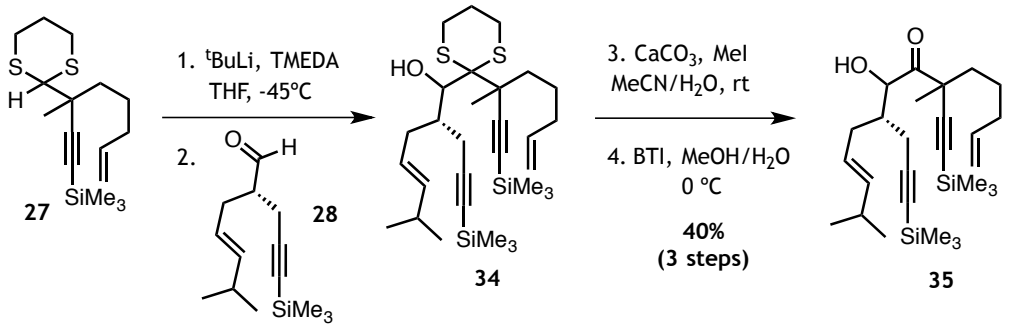



In a round bottom flask, a solution of the oxazolidinone **33** (48 mg, 0.11 mmol) in toluene (2.5 mL) was prepared and cooled to -78 °C and a solution of diisobutylaluminum hydride (1M, 220 uL, 22 umol) was added. The resulting mixture was stirred for 1 hour at this temperatura and then was quenched by addition of a aqueous solution potassium tartrate (sat. sol., 10 mL) at low temperature. The reaction mixture was allowed to reach rt with vigorous stirring and after 2 h was extracted with $Et_2O$ (2 x 50 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (1% EtOAc/hexanes) to give aldehyde **28** [22.3 mg, 80%, $R_f$= 0.6 (10% EtOAc/hexanes), colorless oil], whose spectroscopic data are consistent with those previously described by our group.[15]

[14] C. Faveau, M. Mondon, J.-P. Gesson, T. Mahnke, S. Gebhardt, U. Koert, *Tetrahedron Lett.* 2006, **47**, 8305-8308

[15] M. J. Aldegunde, R. García-Fandiño, L. Castedo, J. R. Granja, *Chem. Eur. J.* 2007, **13**, 5135-5150.

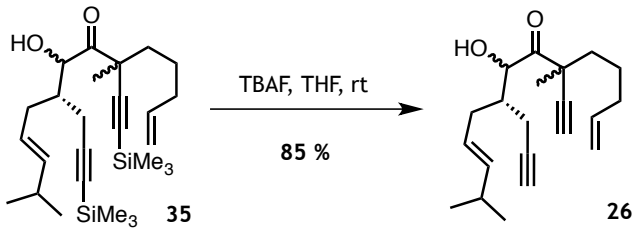
### V.4.3 Preparation of diendiyne 26[16]




In a flame-dried and purged under Ar round bottom flask, a solution of dithiane **27** (840 mg, 2.69 mmol) and tetramethylethylenediamine (0.4 mL, 2.69 mmol) in freshly dry THF (11 mL) was prepared. The mixture was cooled to -45 °C and a solution of *tert*-butyllithium (1.7 M, 1.50 mL, 2.55 mmol) was added dropwise. After 2 h of stirring at this temperatura, a solution of aldehyde **28** (250 mg, 1.00 mmol) in THF (4 mL) was added *via cannula*. The mixture was stirred for 3 h at this temperatura and then was quenched by the addition of aqueous solution of $NH_4Cl$ (sat. sol., 25 mL). The aqueous phase was extracted with $Et_2O$ (3 x 70 mL) and the combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting crude was dissolved in a mixture $MeCN/H_2O$ (4: 1, 50 mL) and calcium carbonate (500 mg, 5.00 mmol) and methyl iodide (3.74 mL, 60 mmol) were successively added. After 24 hours of stirring, the mixture was washed with an aqueous solution of $NaHCO_3$ (sat. sol., 30 mL). The aqueous phase was extracted with $Et_2O$ (3 x 100 mL). The combined organic phases were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting crude was purified by flash chromatography (1% EtOAc/hexanes) to afford an enriched fraction in the desired α-hydroxydithiane.

The resulting compound was dissolved in a $MeOH/H_2O$ mixture (9: 2, 100 mL) and cooled to 0 $^{o}$C and then bis(trifluoroacetoxy)iodobenzene (BTI, 1.29 g, 3.00 mmol) was added. The reaction was quenched after stirring 1.5 hours at rt by addition of an aqueous solution of $NaHCO_3$ (sat. sol., 30 mL). The aqueous phase was extracted with with $Et_2O$ (3 x 100 mL) and the combined organic phases were washed with aqueous solution of NaCl (sat. sol., 30 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by flash chromatography (1% EtOAc/hexanes) to afford the α-hydroxyketone **35** as an inseparable mixture of 4 isomers [185 mg, 40% (3 steps), $R_f$= 0.2 (5% AcOEt/hexanes), colorless oil]. **$^1$H NMR** (300 MHz, $CDCl_3$, δ): 5.92-5.64 (m, 1H), 5.59-5.19 (m, 2H), 5.09-4.92 (m, 2H), 5.09-4.66 (m, 3H), 3.21-3.10 (m, 1H), 2.61-1.14 (m, 15H), 1.01-0.92 (2d, *J*= 6.7 Hz, 6H), 0.21-0.12 (m, 18H); **MS** (*m/z*, ESI): 481 $(MNa)^+$, 459; **HRMS:** calculated for $C_{27}H_{46}O_2Si_2Na$ $(MNa^+)$: 481.2929, found: 481.2929.

[16] Modification of the conditions described in: L.-S. Deng, X.-P. Huang, G. Zhao, *J. Org. Chem.* 2006, **71**, 4625-4635. Conditions used for deprotection of thioacetals: T. E. La Cruz, S. D. Rychnovsky, *J. Org. Chem.* 2007, **72**, 2602-2611.



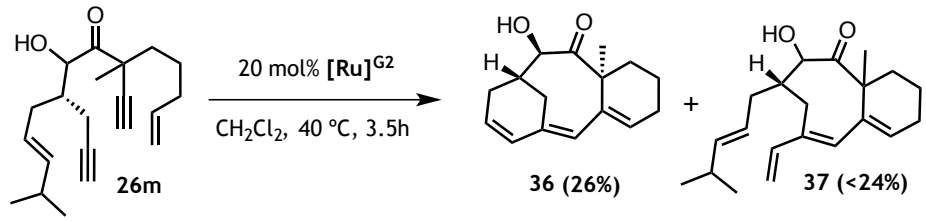

In a round bottom flask, a solution of tetrabutylammonium fluoride (1 M, 650 uL, 0.65 mmol) was added to a solution of **35** (100 mg, 0.21 mmol) in THF (4.5 mL). The reaction mixture was stirred for 1 hour and then was quenched by the addition of aqueous solution of $NH_4Cl$ (sat. sol., 15 mL). The aqueous phase was extracted with $Et_2O$ (3 x 40 mL). The combined organic phases were dried, filtered and concentrated. The resulting residue was purified by flash chromatography (1% acetone/hexane) to afford less polar fraction of diendiynes **26l** [35 mg, $R_f$= 0.25 (5% EtOAc/hexanes), colorless oil, isomer ratio 1: 1.4] and most polar fraction of diendiynes **26m** [23 mg, $R_f$= 0.2 (5% EtOAc/hexanes), colorless oil, isomer ratio 1: 1.5] in 85% overall yield.

**Mixture 26l:** $^1$**H NMR** (300 MHz, $CDCl_3$, δ): 5.93-5.65 (m, 1H), 5.63-5.17 (m, 2H), 5.17-4.80 (m, 3H), 3.11 (s, 1H), 2.65-0.77 (m, 23H); $^{13}$**C NMR** ( 75 MHz, $CDCl_3$, δ): 213.4 (C), 213.0 (C), 141.1 (CH), 141.0 (CH), 138.1 (CH), 124.1 (CH), 123.6 (CH), 115.2 ($CH_2$), 85.0 (C), 84.7 (C), 82.9 (C), 76.9 (CH), 76.1 (CH), 75.2 (C), 74.7 (C), 70.0 (C), 70.0 (C), 46.0 (C), 45.9 (C), 41.0 ($CH_2$), 40.9 ($CH_2$), 40.2 (CH), 39.8 (CH), 34.8 ($CH_2$), 33.7 ($CH_2$), 33.7 (CH), 31.2 (CH), 31.2 ($CH_2$), 31.1 ($CH_2$), 29.8 ($CH_2$), 26.2 (CH), 26.1 (CH), 24.5 ($CH_2$), 24.4 ($CH_2$), 22.7 ($CH_3$), 22.6 ($CH_3$), 20.4 ($CH_2$), 17.8 ($CH_2$).

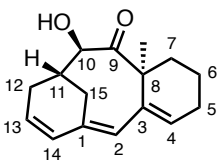
**Mixture 26m:** $^1$**H NMR** (400 MHz, $CDCl_3$, δ): 5.87-5.68 (m, 1H), [5.57 (dd, *J* = 15.4 and 6.4 Hz), 5.48-5.33 (m), 5.26-5.19 (m), 2H], [5.17 (dd, *J* = 7.1 and 1.8 Hz), 4.86 (dd, *J* = 6.9 and 1.9 Hz), 1H], 5.08-4.94 (m, 2H), [3.05 (d, *J* = 7.1 Hz), 3.02 (d, *J* = 6.9 Hz), 1H], 2.57-1.21 (m, 17H), [0.99 (d, *J* = 6.8 Hz), 0.95 (d, *J* = 6.8 Hz), 6H]; $^{13}$**C NMR** (101 MHz, $CDCl_3$, δ): 212.6 (C), 212.3 (C), 141.1 (CH), 140.9 (CH), 138.1 (CH), 124.1 (CH), 123.6 (CH), 115.2 ($CH_2$), 115.1 ($CH_2$), 85.0 (C), 84.7 (C), 83.0 (C), 82.8 (C), 75.7 (CH), 75.2 (CH), 74.9 (CH), 74.8 (CH), 70.0 (CH), 69.9 (CH), 46.2 (CH), 46.1 (CH), 39.9 (CH), 39.7 (CH), 38.3 ($CH_2$), 34.6 ($CH_2$), 33.8 ($CH_2$), 31.2 (CH), 31.2 (CH), 31.1 (CH), 30.9 ($CH_2$), 26.5 (CH), 26.5 (CH), 24.3 ($CH_2$), 24.3 ($CH_2$), 22.7 ($CH_3$), 22.6 ($CH_3$), 20.2 ($CH_2$), 17.8 ($CH_2$).

**MS** (*m/z*, ESI): 337 ($MNa^+$), 312; **HRMS:** calculated for $C_{21}H_{30}O_2Na$ ($MNa^+$): 337.2138, found: 337.2131.

## V.5. Cascade metathesis reaction for taxane 36

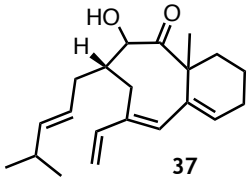



In a round bottom flask equipped with magnetic stirrer, catalyst **[Ru]$^{G2}$** (12 mg, 14.6 μmol, 20 mol%) was added to a solution of **26m** (23 mg, 73 μmol) in $CH_2Cl_2$ (15 mL). The resulting mixture was stirred at rt until became homogenous and then was refluxed for 3.5 hours. After this time the solvent was removed and the resulting residue was purified by flsh chromatography (3-15% $Et_2O$/hexanes) to afford bicycle **37** [5.6 mg, 24%, $R_f$= 0.4 ( 10% EtOAc/hexanes)] and expected tricycle **36** [4.7 mg, 26%, $R_f$= 0.3 (10% EtOAc/hexanes), white solid].



**36**

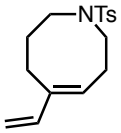
**$^1$H NMR** (500 MHz, $CD_2Cl_2$, δ): 6.32 (d, *J* = 10.0 Hz, 1H), 6.09 (bs, 1H), 5.66-5.59 (m, 1H), 5.60-5.54 (m, 1H), 4.36 (dd, *J* = 11.2 and 8.8 Hz, 1H), 2.47 (d, *J* = 11.2 Hz, 1H), 2.40-2.29 (m, 3H), 2.06-1.99 (m, 2H), 1.97 (dd, *J* = 12.6 and 2.7 Hz, 1H), 1.88-1.79 (m, 1H), 1.76-1.60 (m, 2H), 1.33-1.20 (m, 5H); **$^{13}$C NMR** (125 MHz, $CD_2Cl_2$, δ): 220.3 (C), 139.5 (C), 135.5 (C), 129.7 (CH), 129.6 (CH), 127.8 (CH), 124.7 (CH), 74.1 (CH), 46.2 (C), 41.7 (CH), 34.1 ($CH_2$), 30.5 ($CH_2$), 29.7 ($CH_2$), 26.1 ($CH_2$), 25.1 ($CH_3$), 20.4 ($CH_2$); **HRMS:** calculated for $C_{16}H_{20}O_2Na$ ($MNa^+$): 267.1356, found: 267.135.



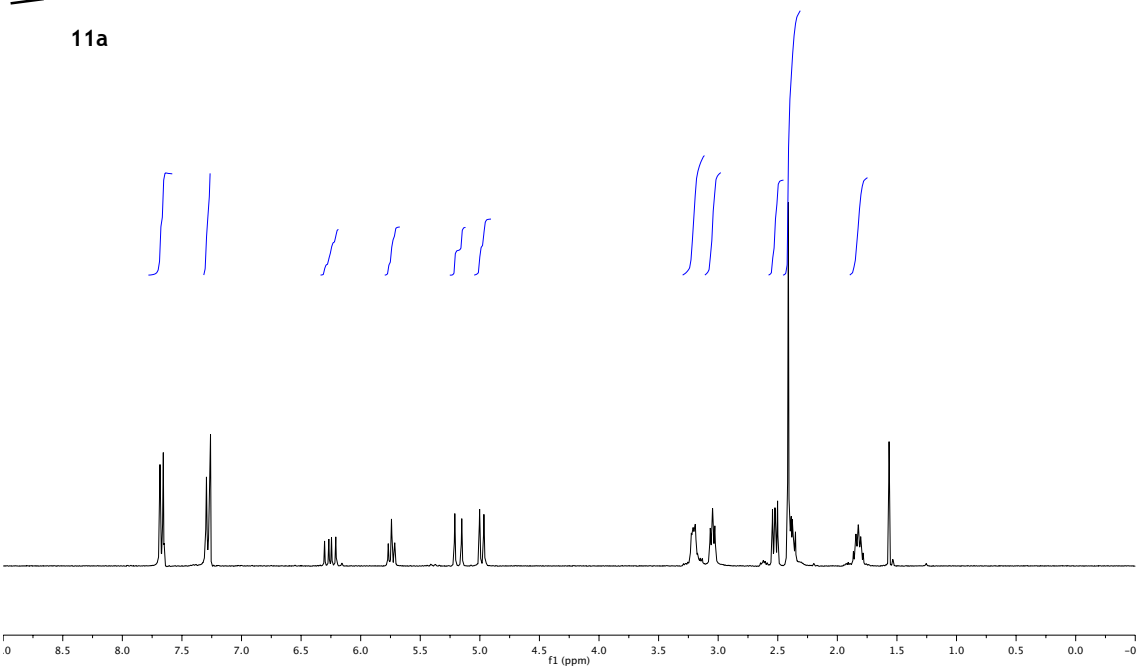
**37**

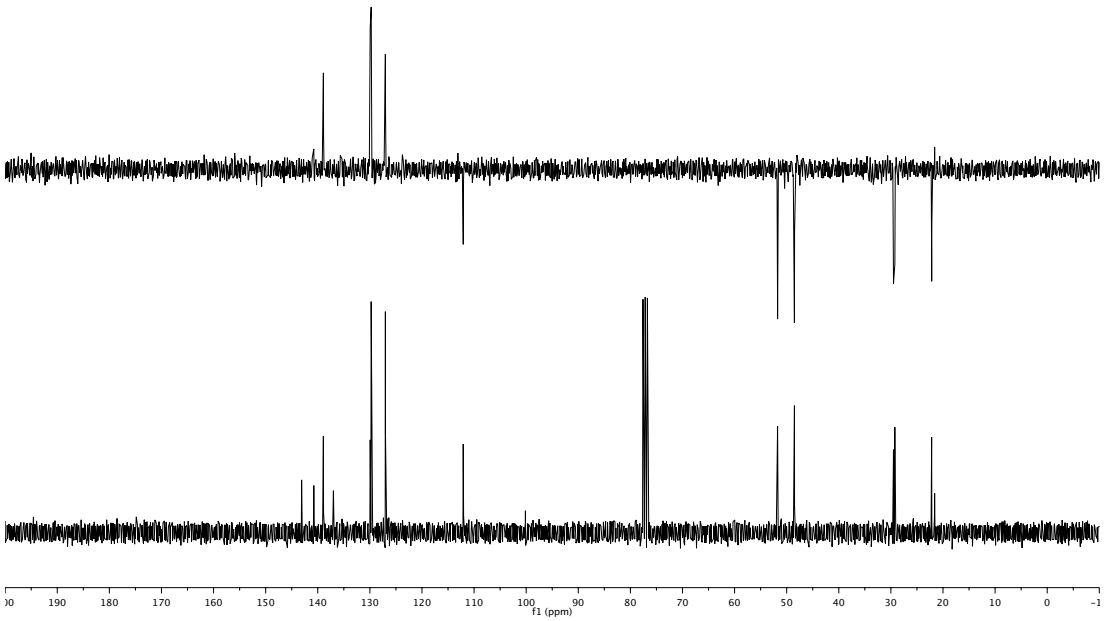
**$^1$H NMR** (400 MHz, $CD_2Cl_2$, δ): 6.35 (dd, *J* = 17.3 and 10.6 Hz, 1H), 6.24 (s, 1H), 5.68-5.60 (m, 1H), 5.47 (dd, *J* = 15.3 and 6.6 Hz, 1H), 5.41-5.30 (m, 1H), 5.24 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 10.6 Hz, 1H), 4.46 (dd, *J* = 10.2 and 4.0 Hz, 1H), 2.75 (d, *J* = 10.2 Hz, 1H), 2.60-2.47 (m, 1H), 2.41-2.02 (m, 8H), 1.96-1.78 (m, 1H), 1.74-1.58 (m, 4H), 1.33-1.24 (m, 4H), 1.22 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 6H); **$^{13}$C NMR** (125 MHz, $CD_2Cl_2$, δ): 140.8, 139.0, 133.4, 129.1, 125.6, 113.8, 77.1, 42.1, 34.7, 32.7, 31.7, 26.0, 24.6, 22.9, 19.9; **EMBR** (*m/z*, I): 337 ($MNa^+$, 70), 297 (100); **HRMS:** calculated for $C_{21}H_{30}O_2Na$ ($MNa^+$): 337.2138, found: 337.2126.

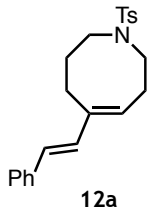
# VI. NMR spectra for cyclic compounds



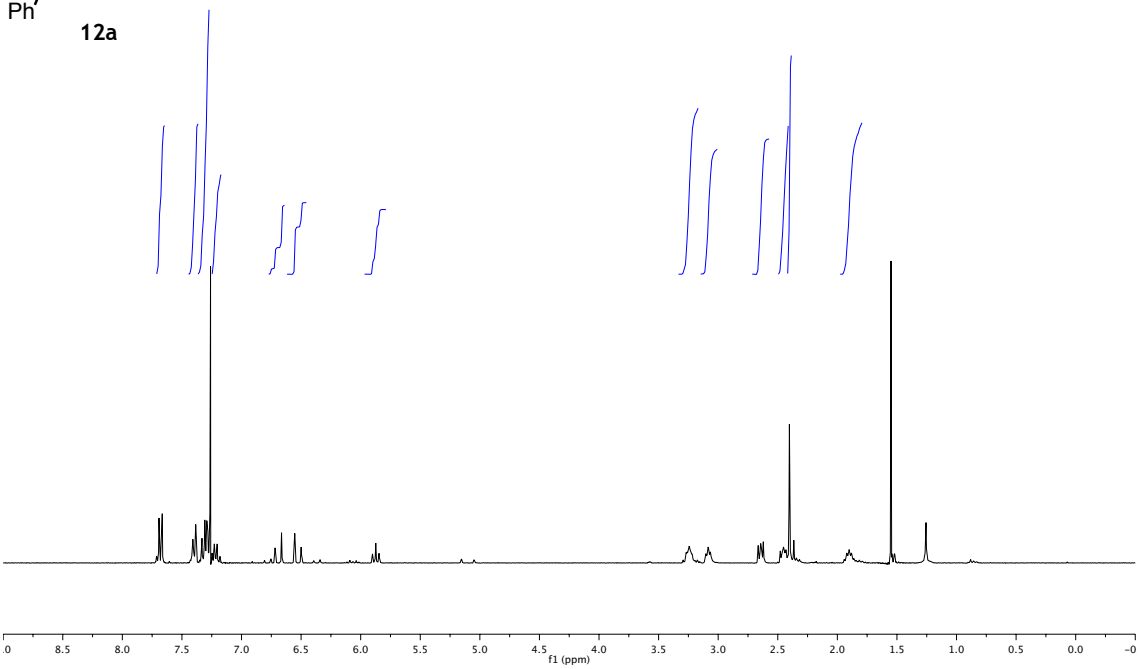

11a

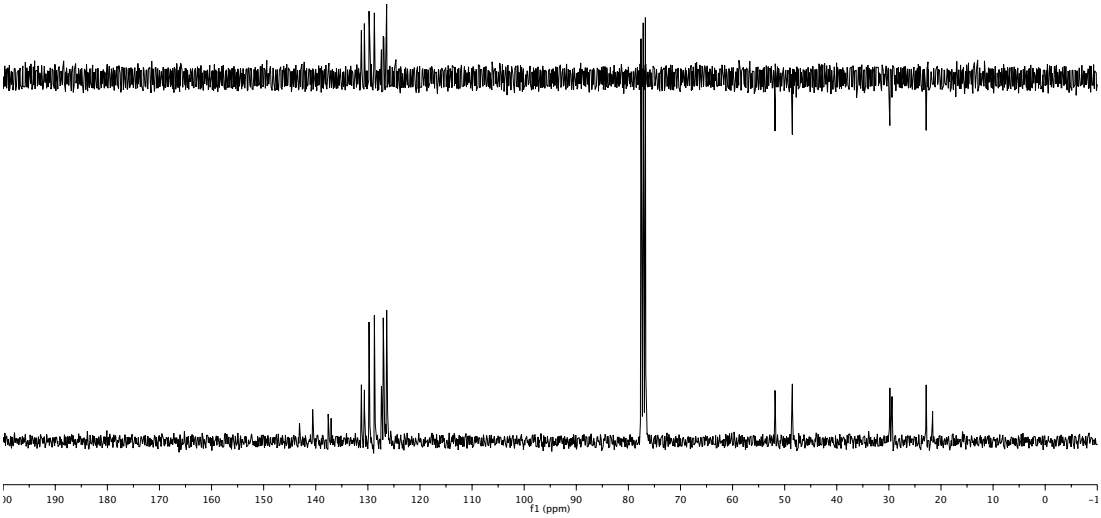


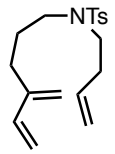






**12a**



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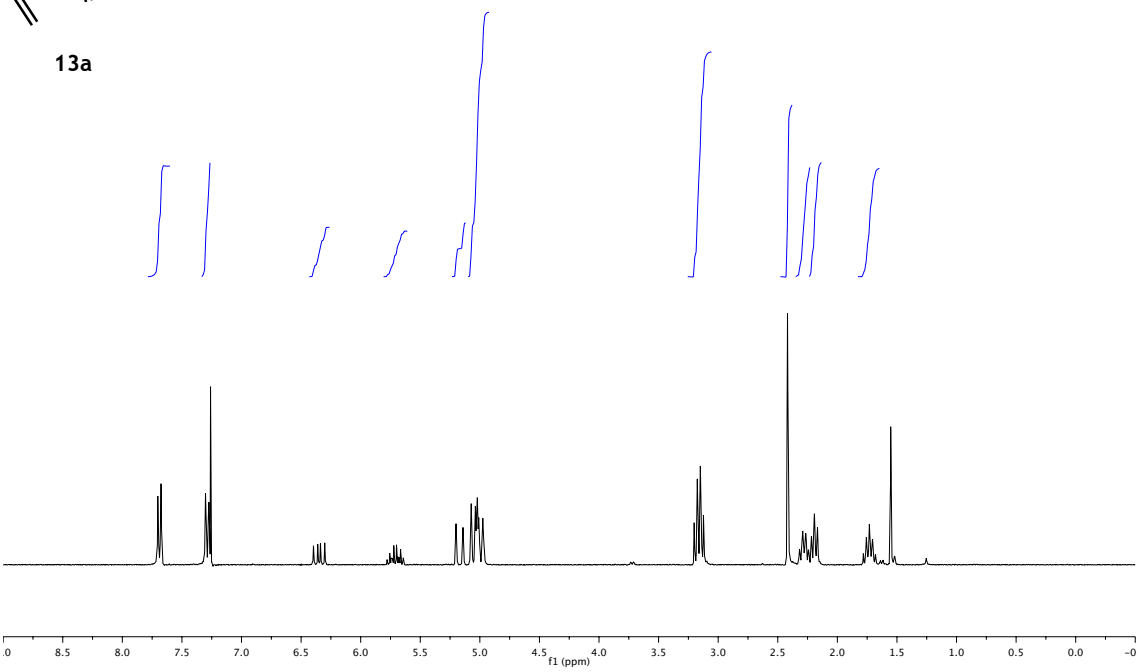
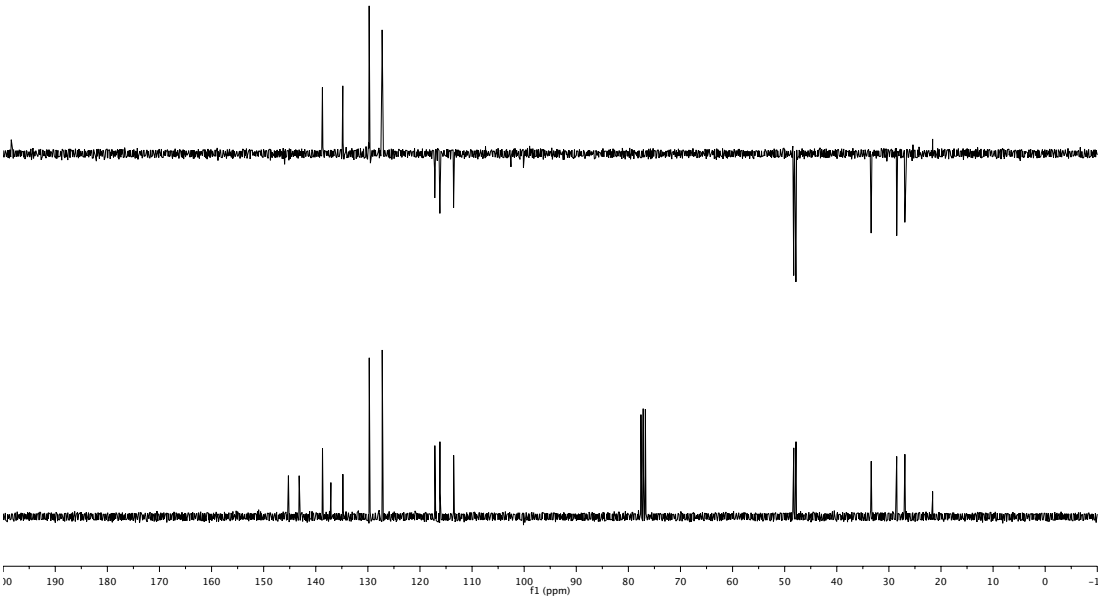
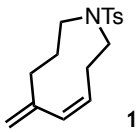
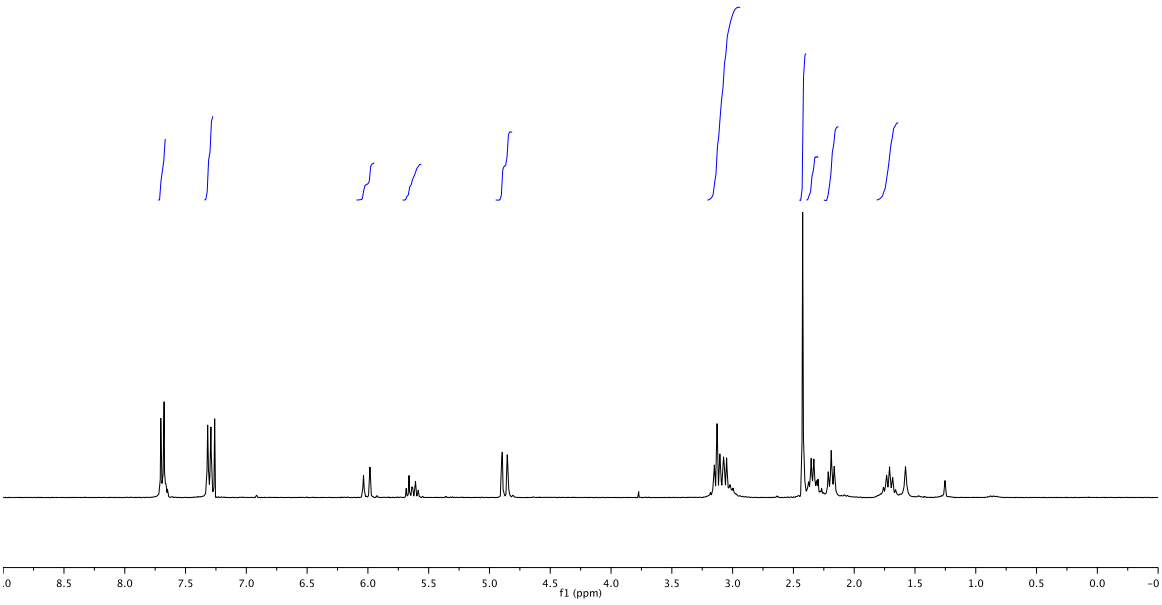
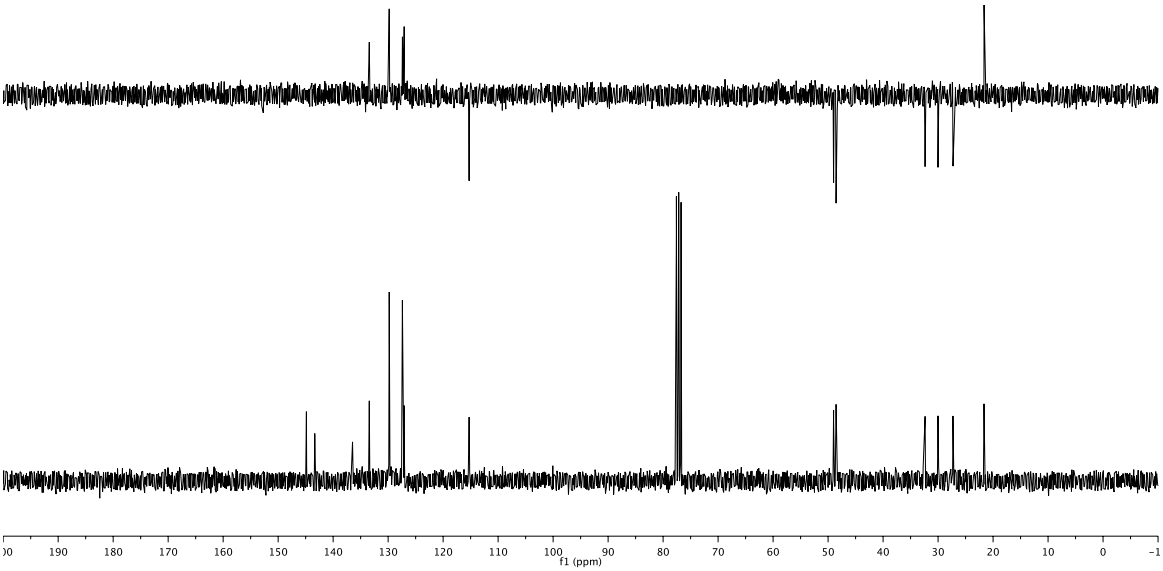


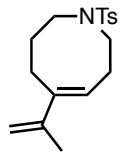





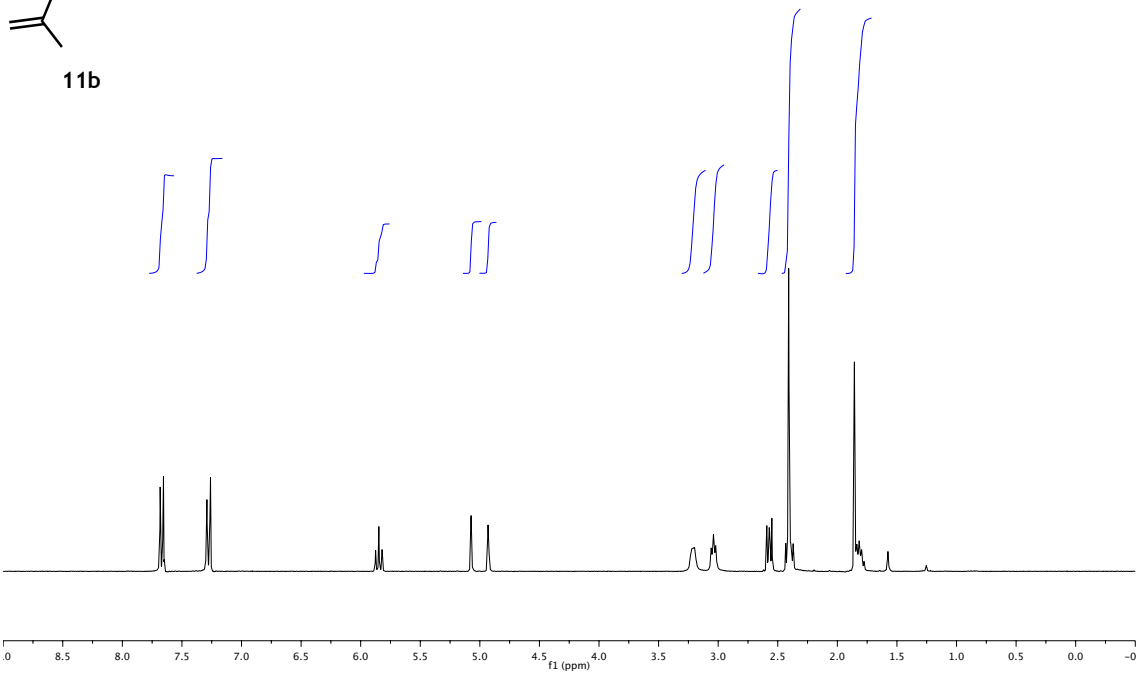

**14a**




NTs

**11b**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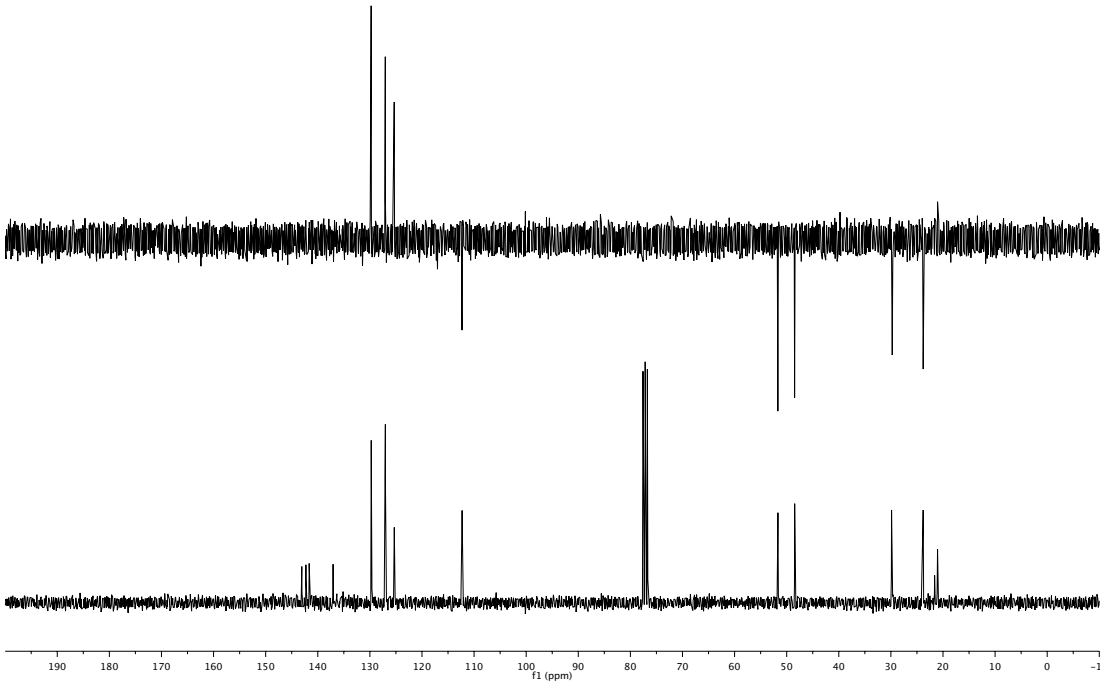
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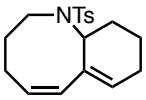
f1 (ppm)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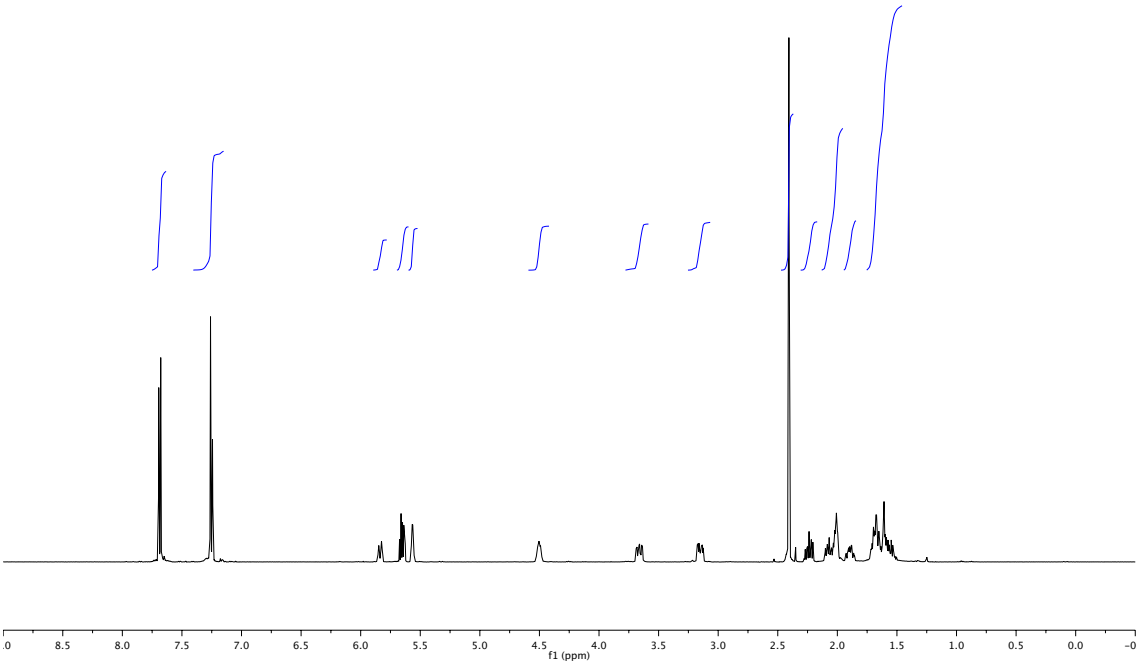
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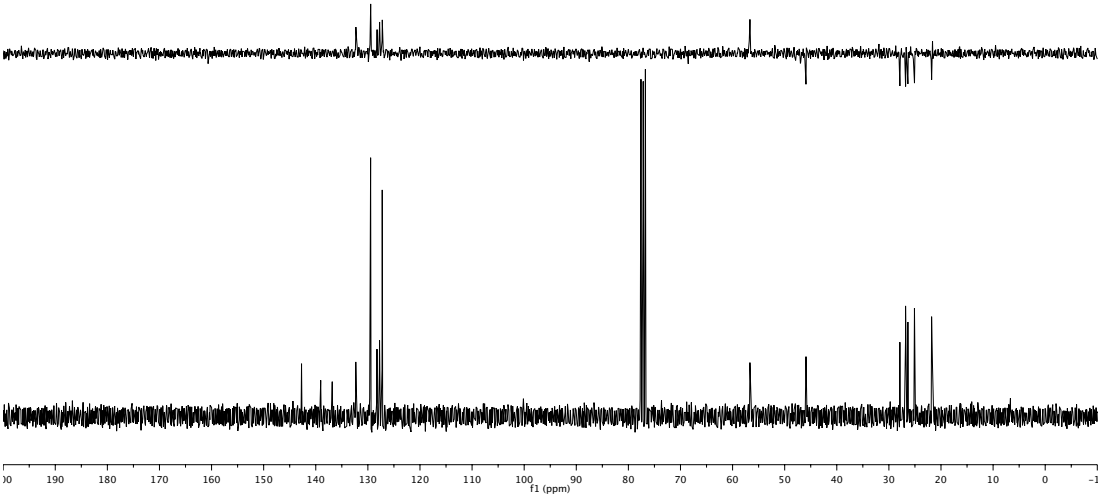
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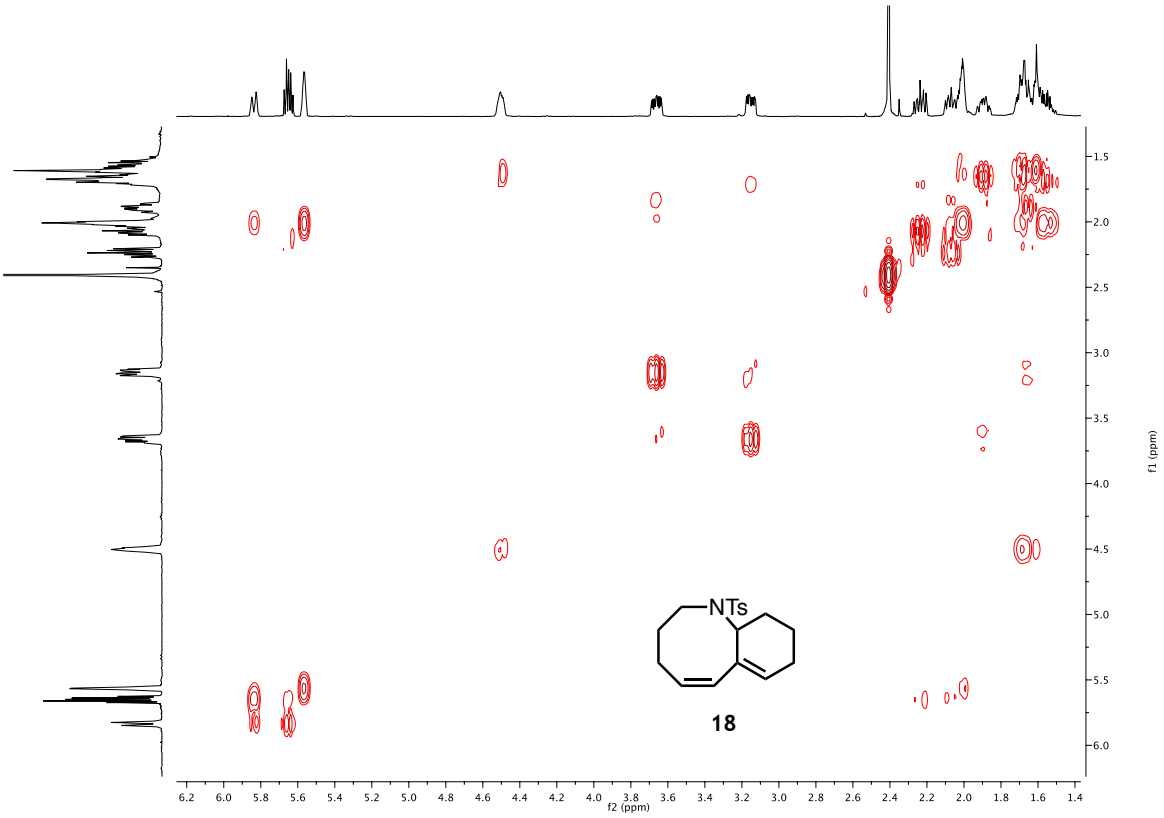
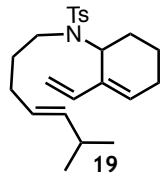
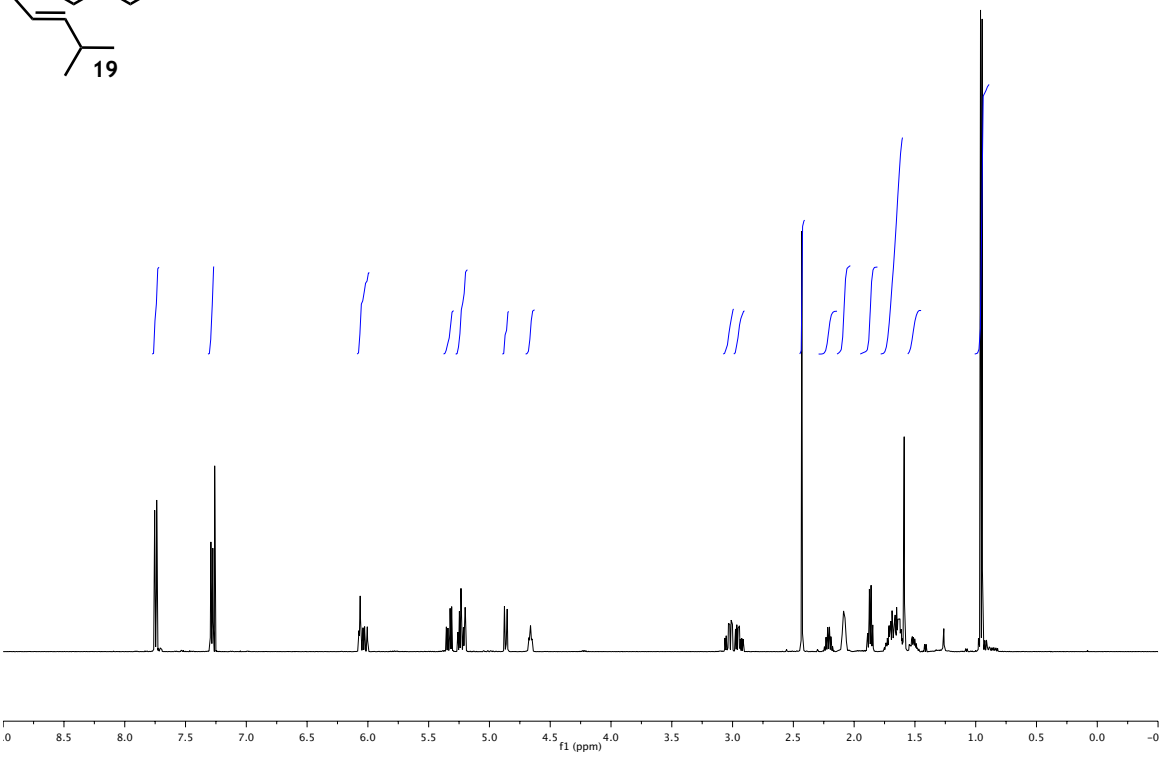
f1 (ppm)

**COSY-18**




Ts
N

**19**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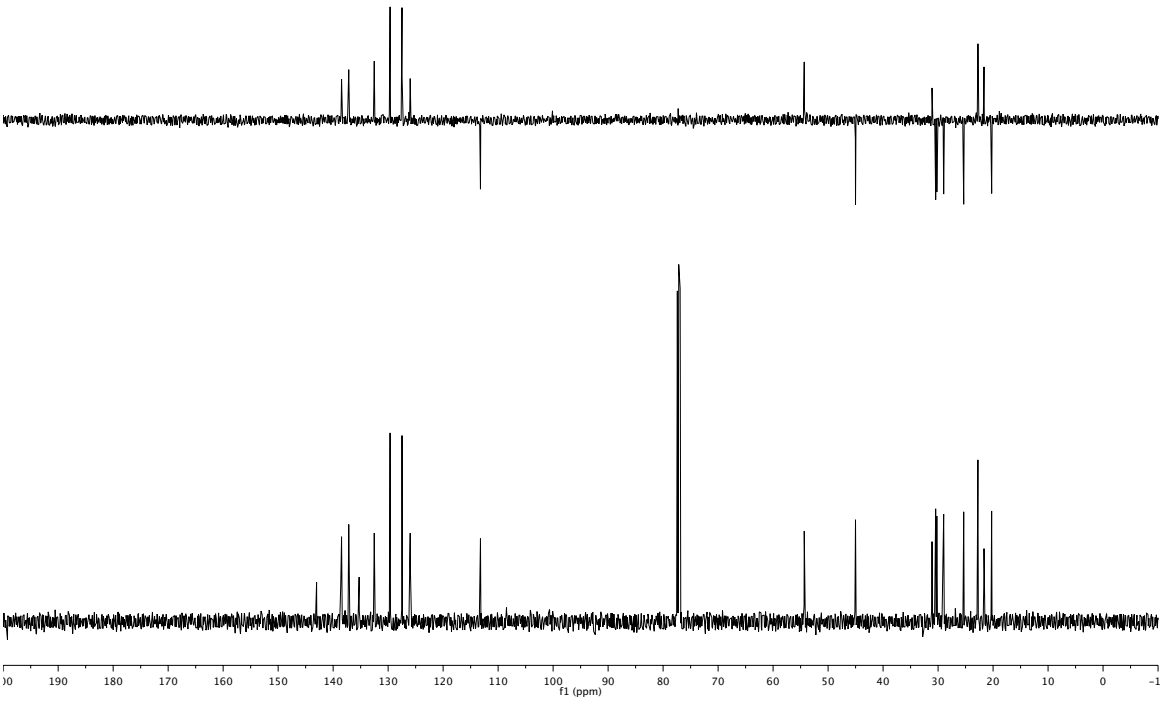
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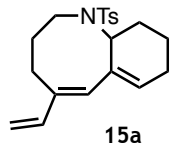
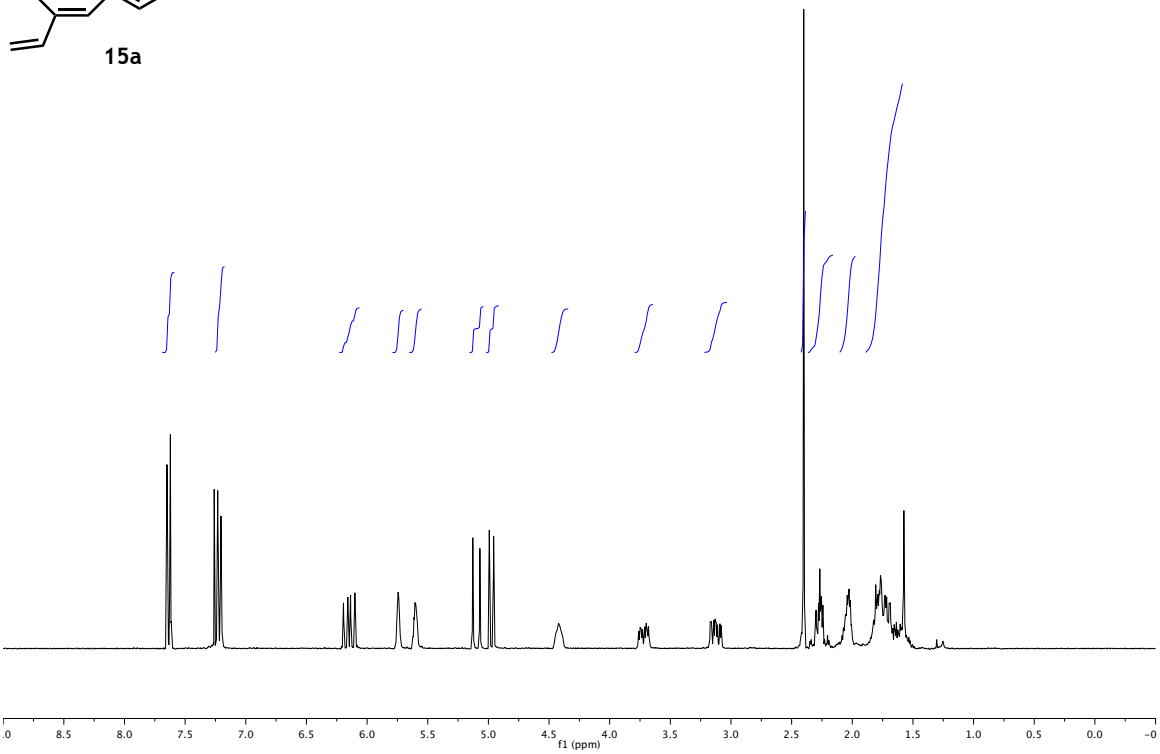
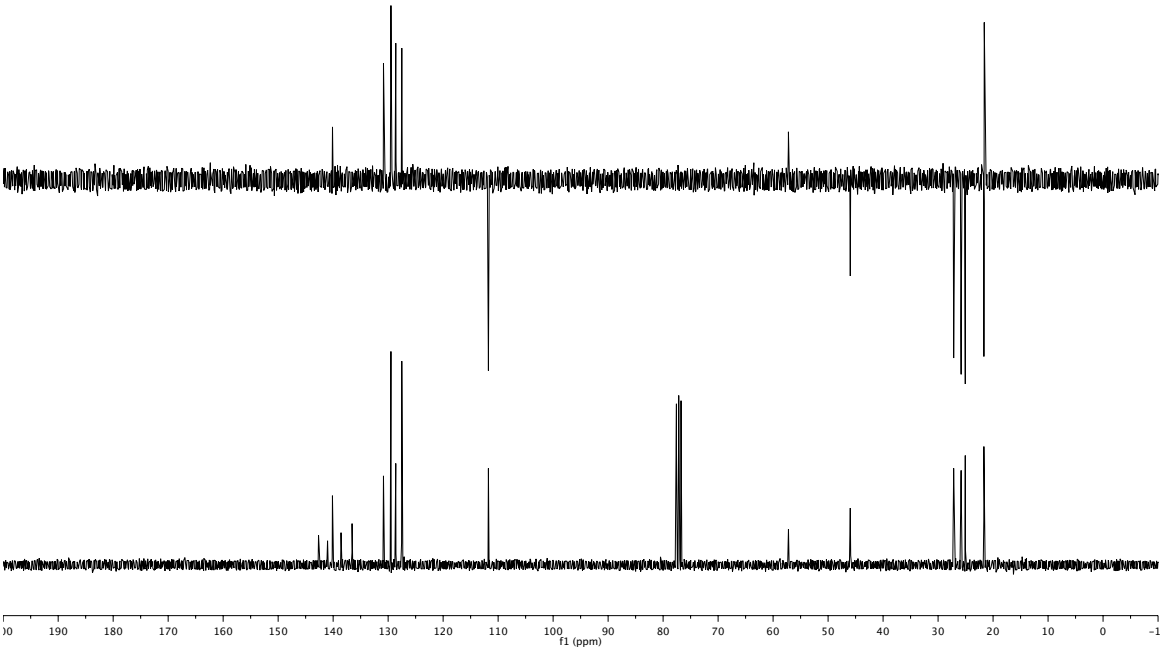
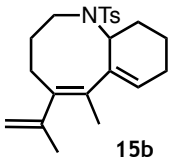


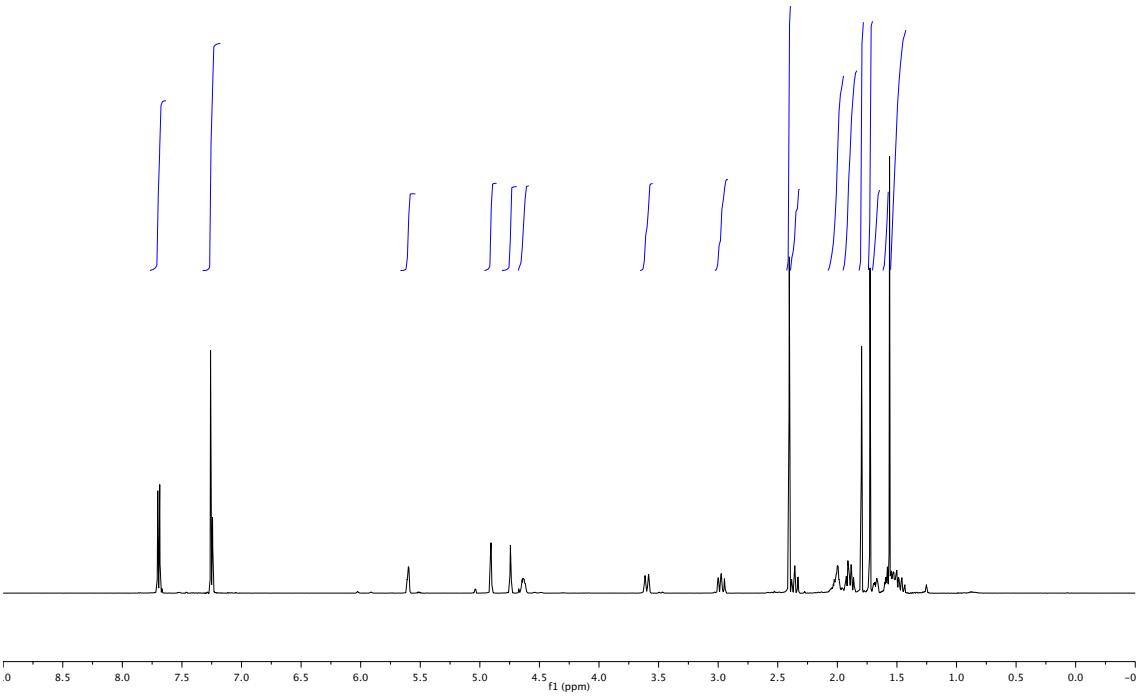

**15a**

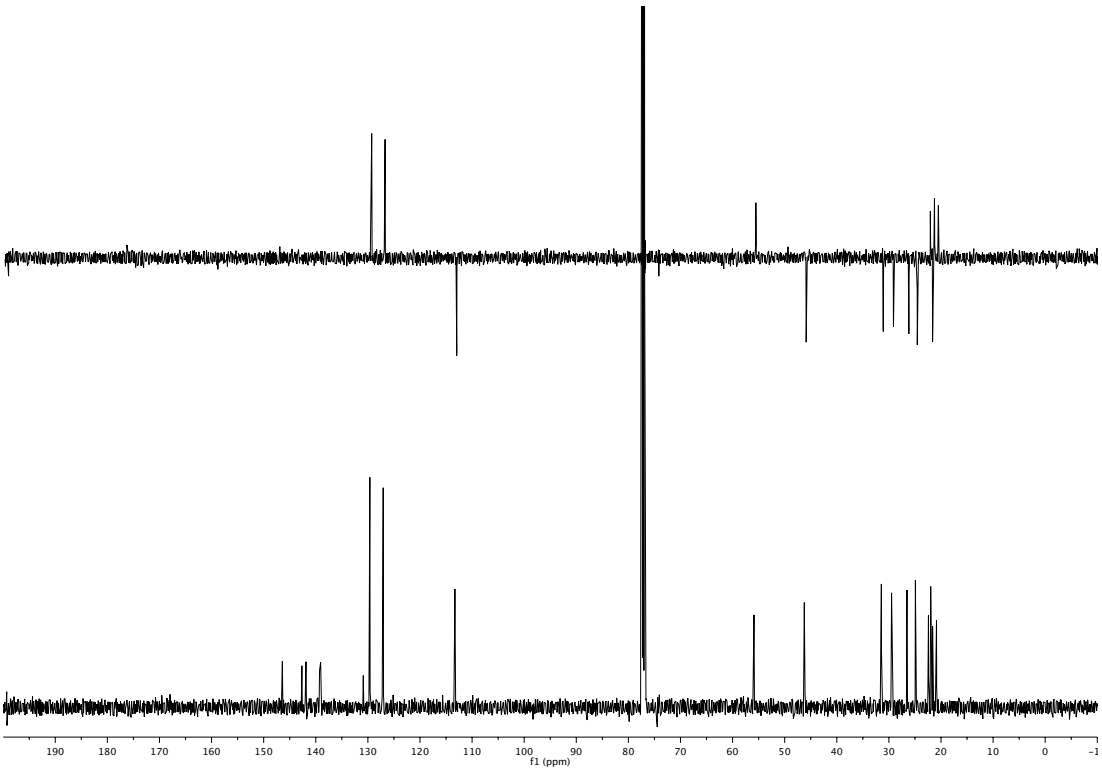


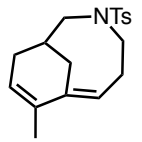





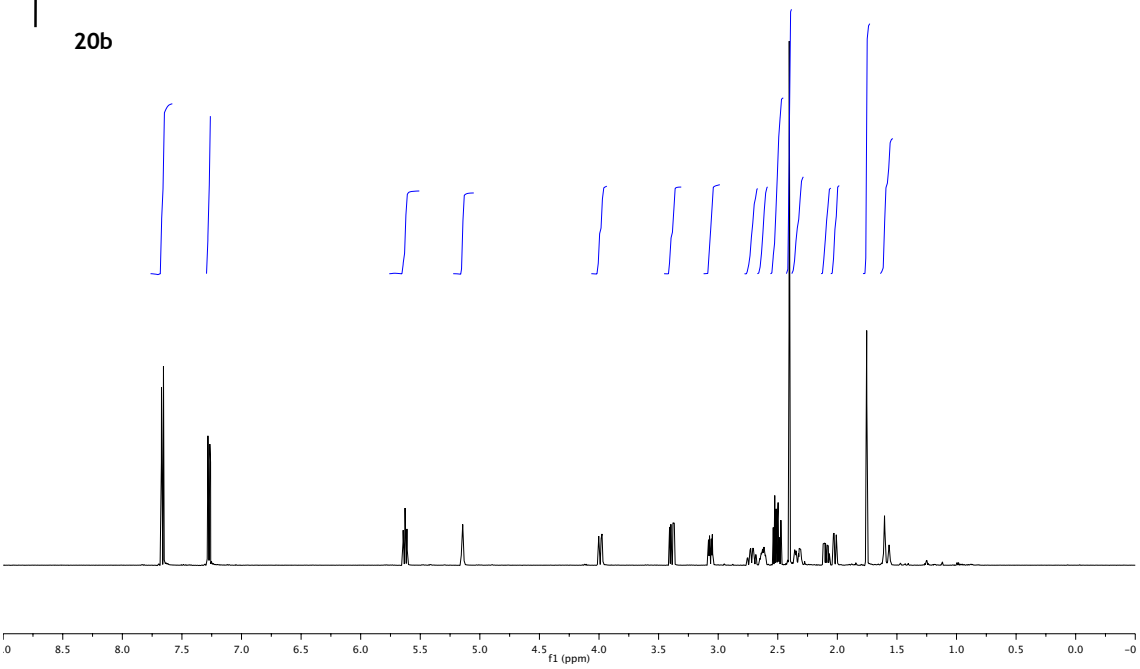

**15b**

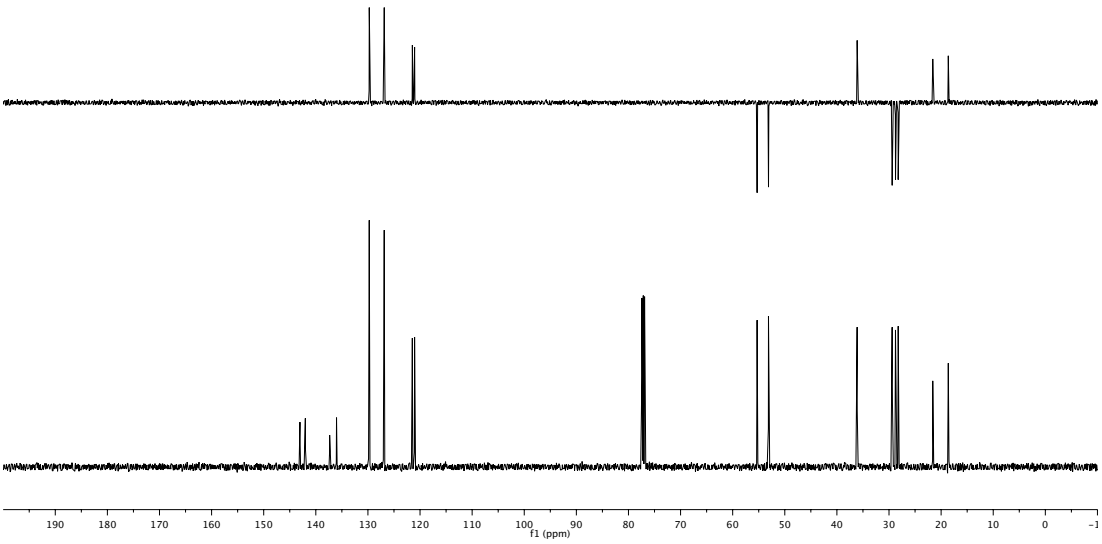


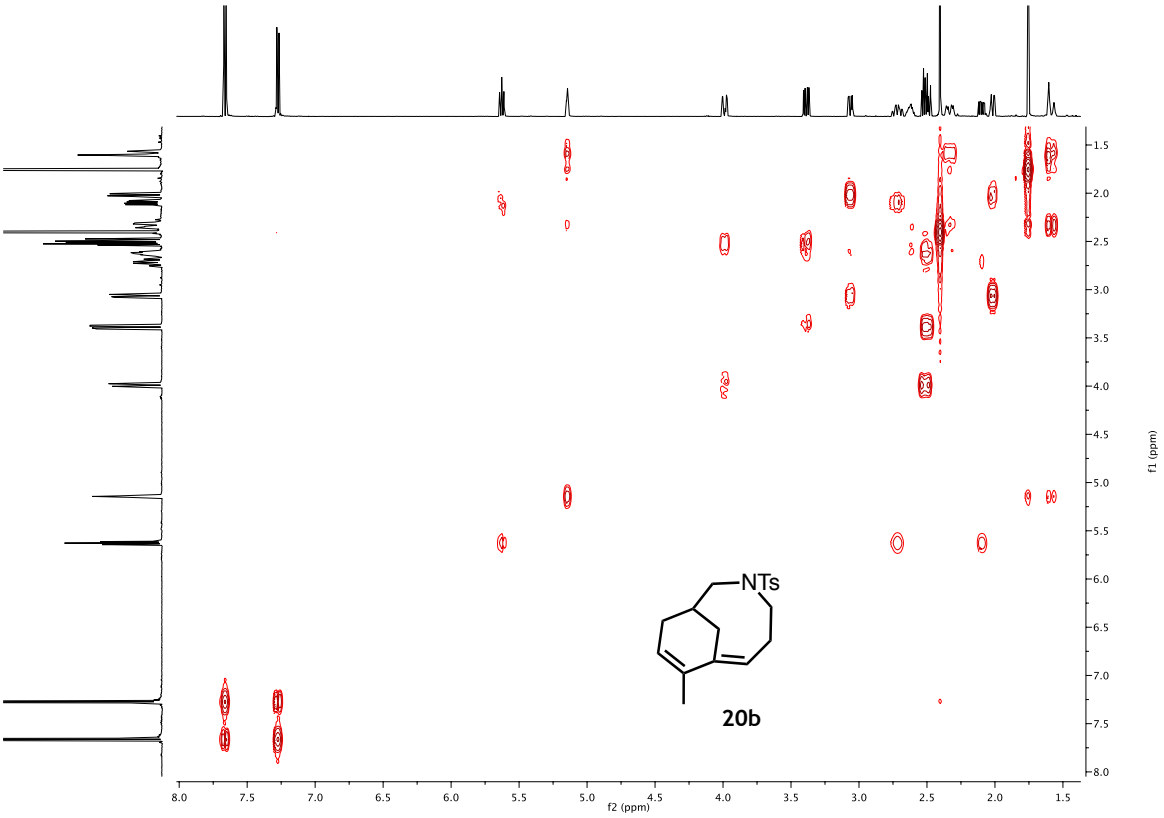


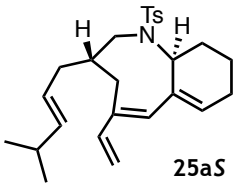

**20b**



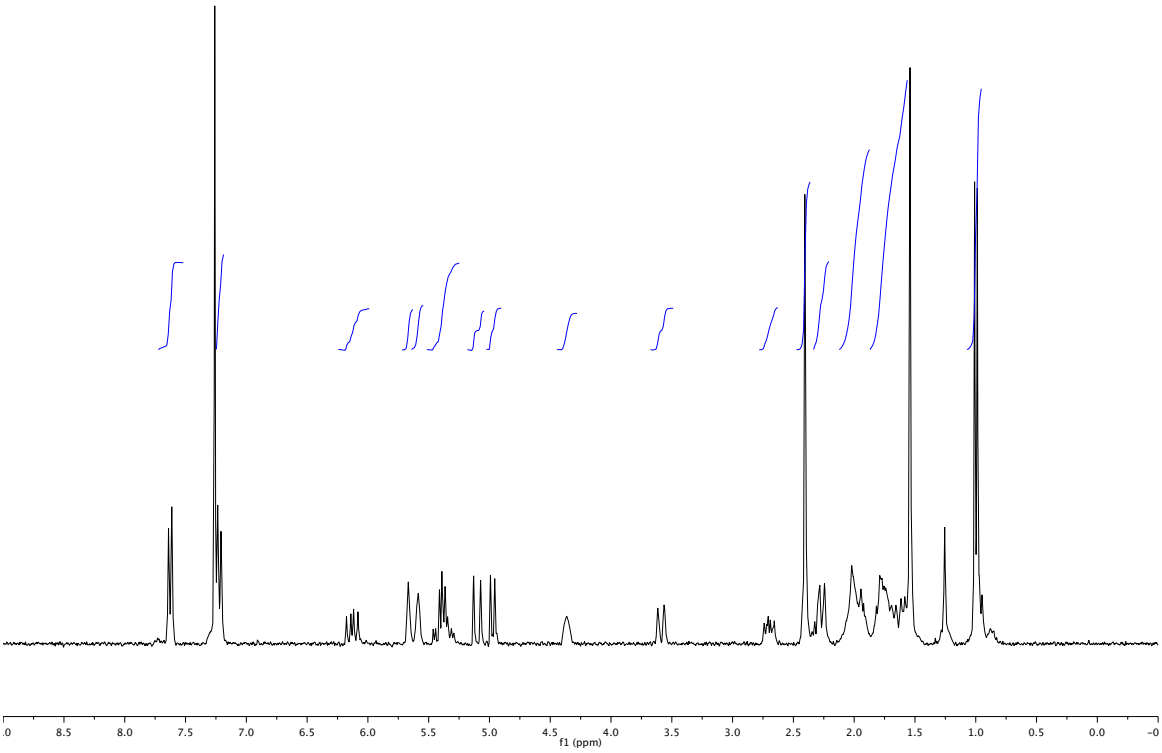



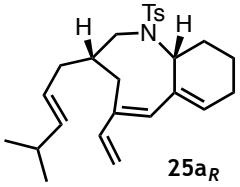
**COSY-20b**



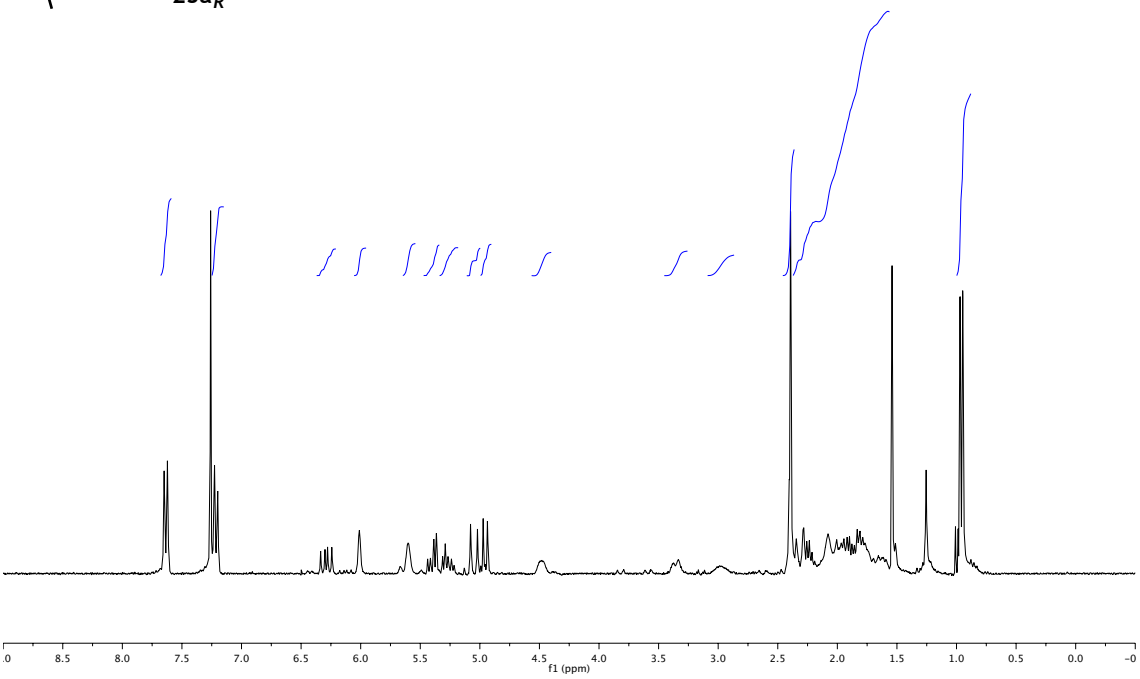

Ts
H
N
H

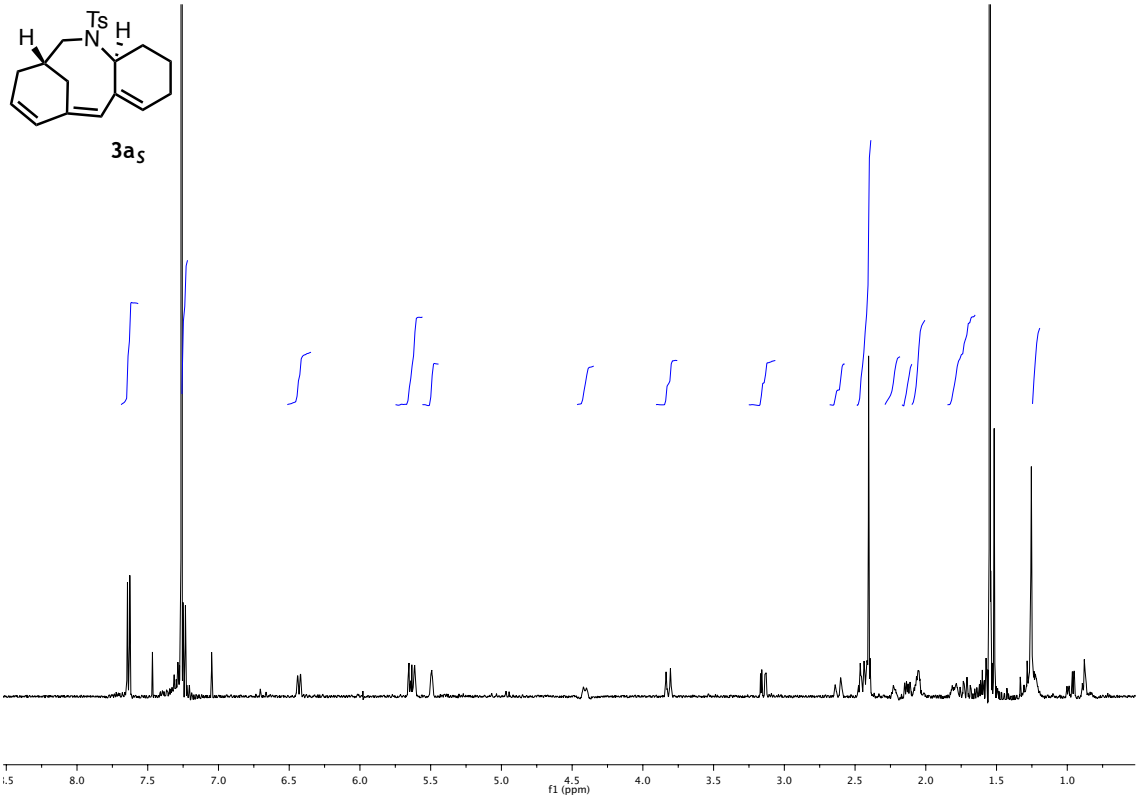
**25a*S***


.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

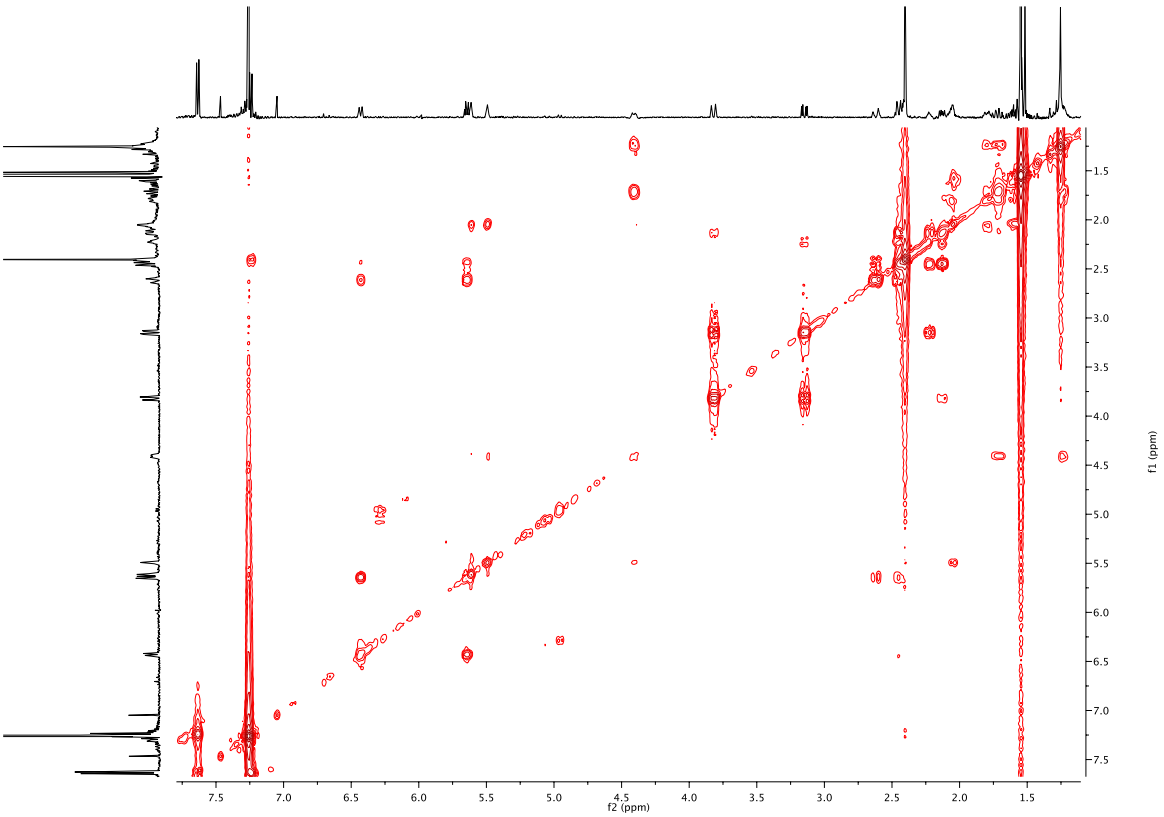

Ts
H
N
H

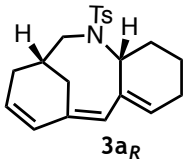
**25a*R***


.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

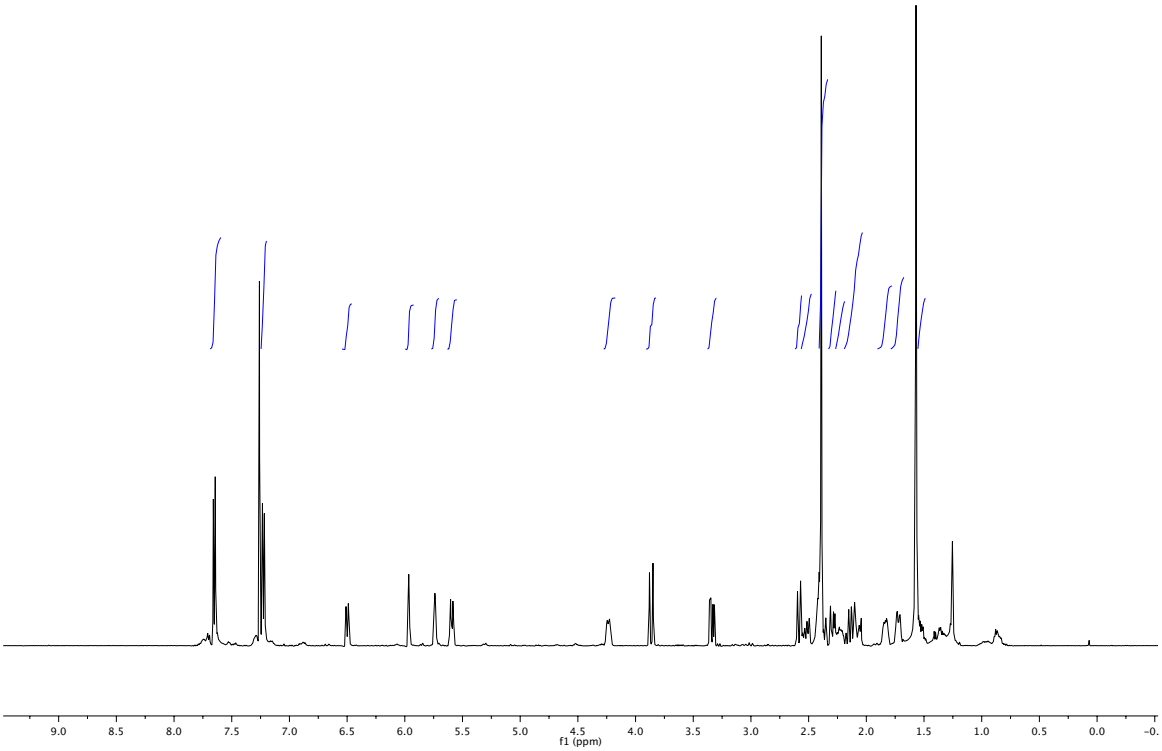


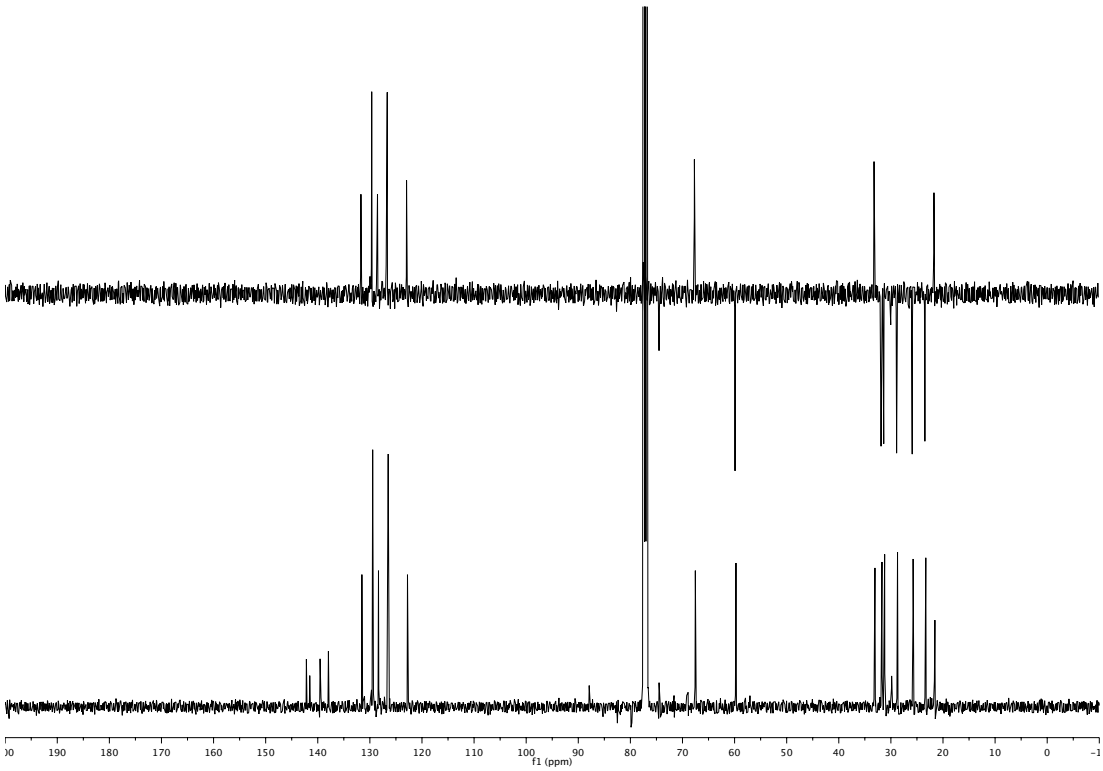

COSY-3a$_S$



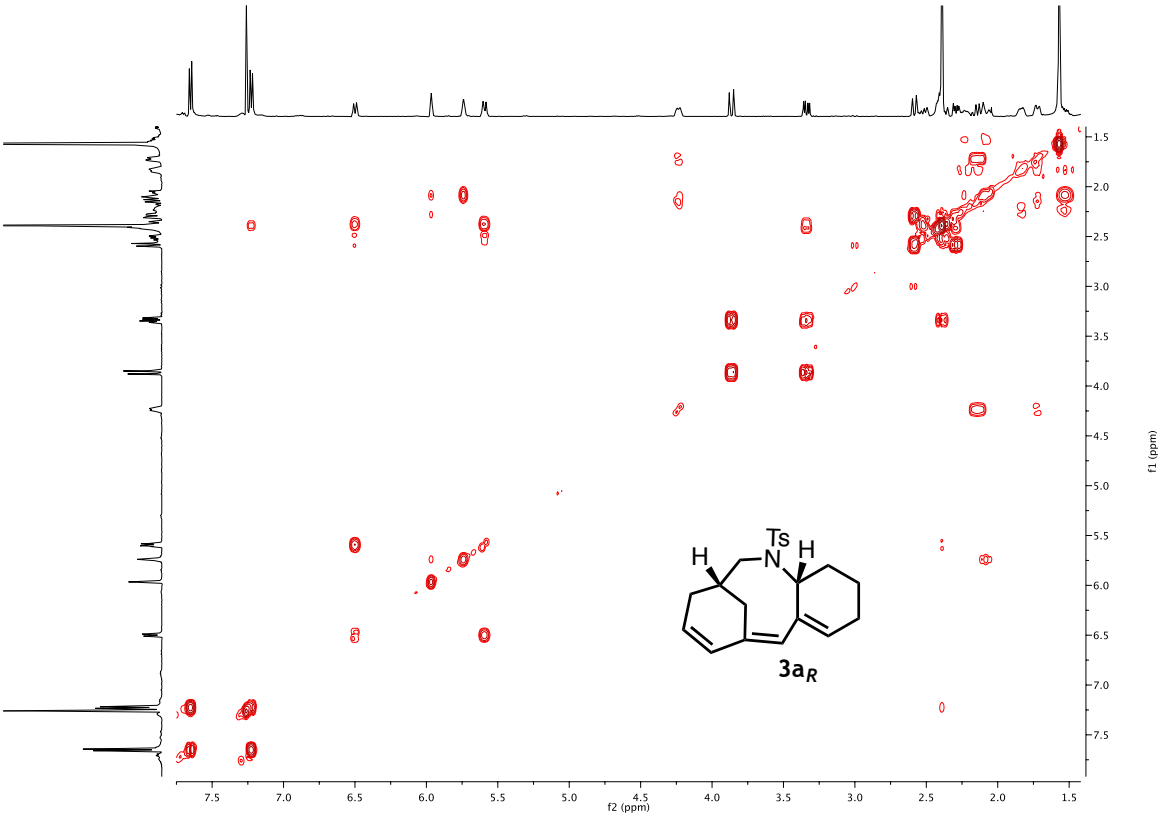

Ts
N
H
H

**3a$_R$**

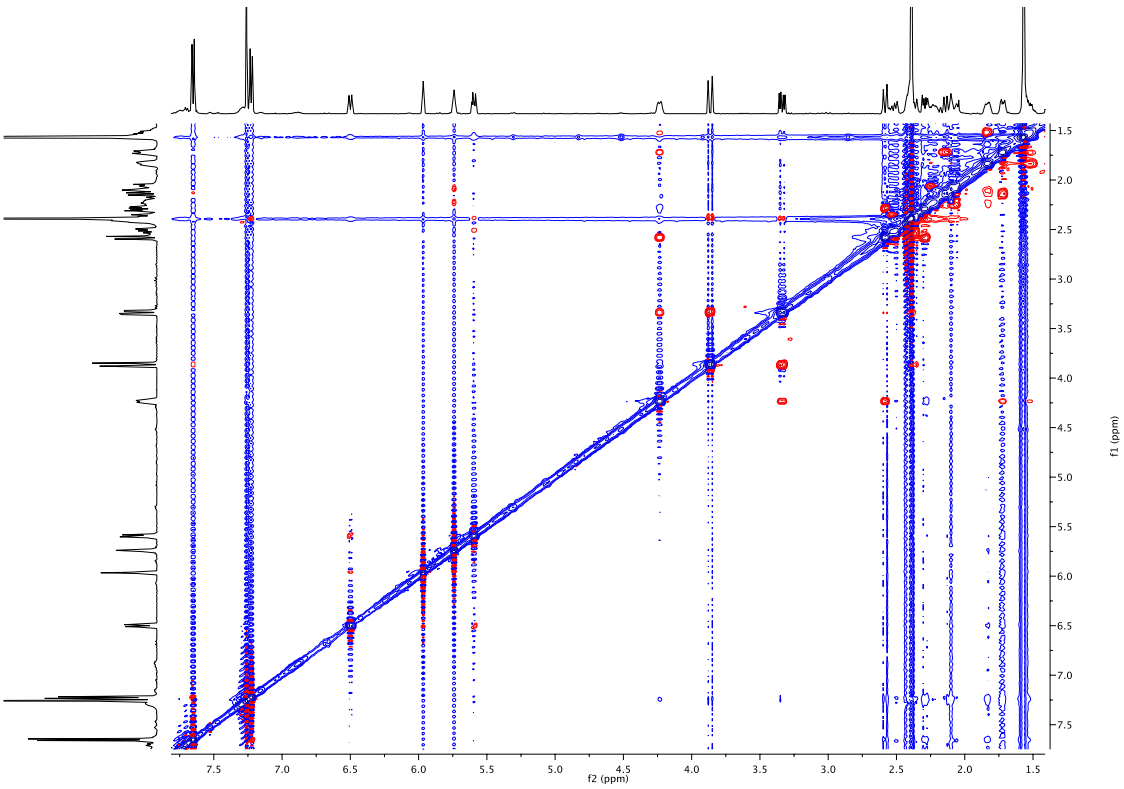

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

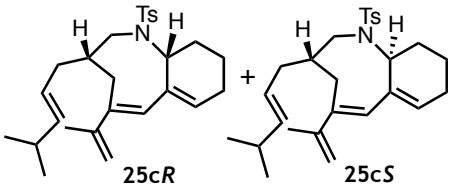

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**COSY-3a$_R$**

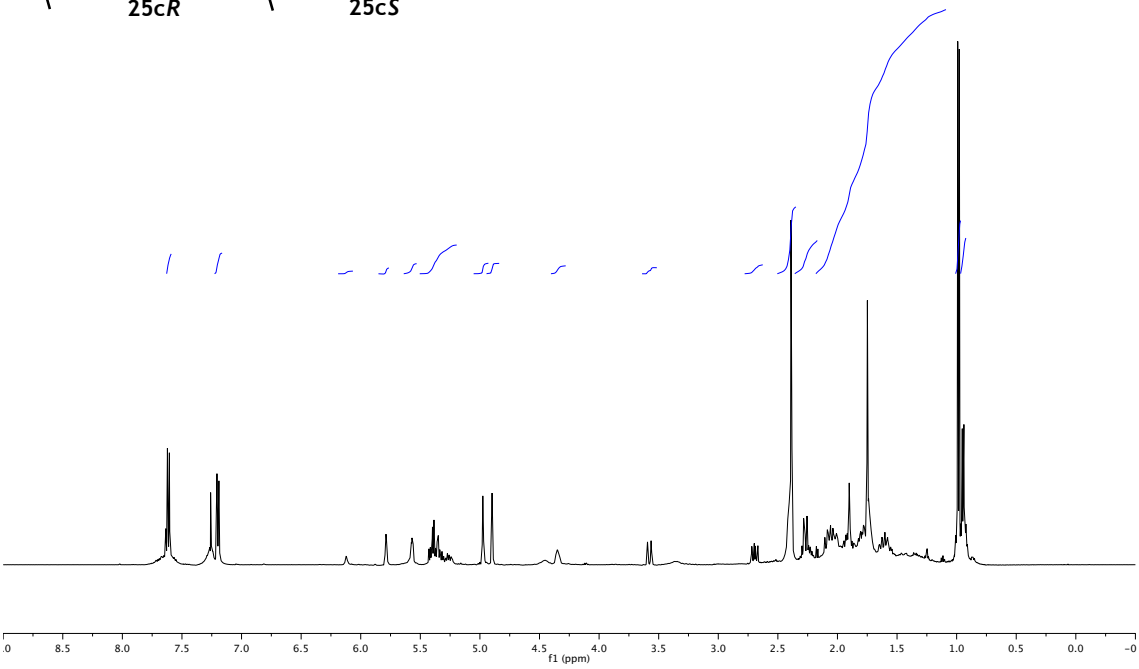


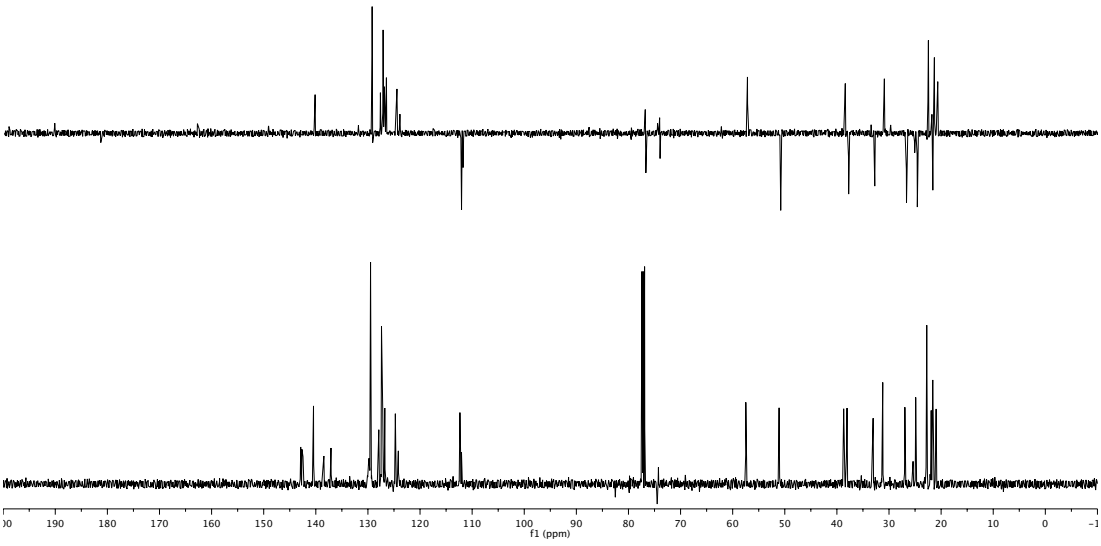

**NOESY-3a$_R$**

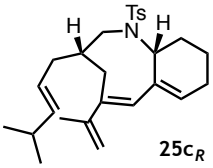




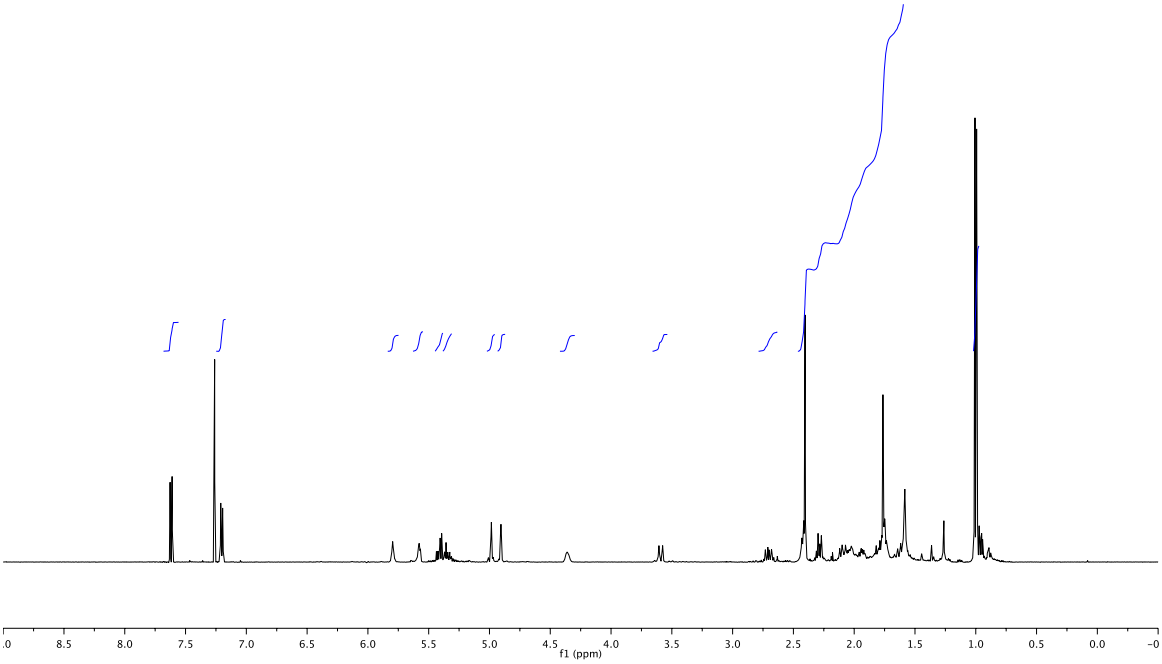

**25c*R*** **25c*S***

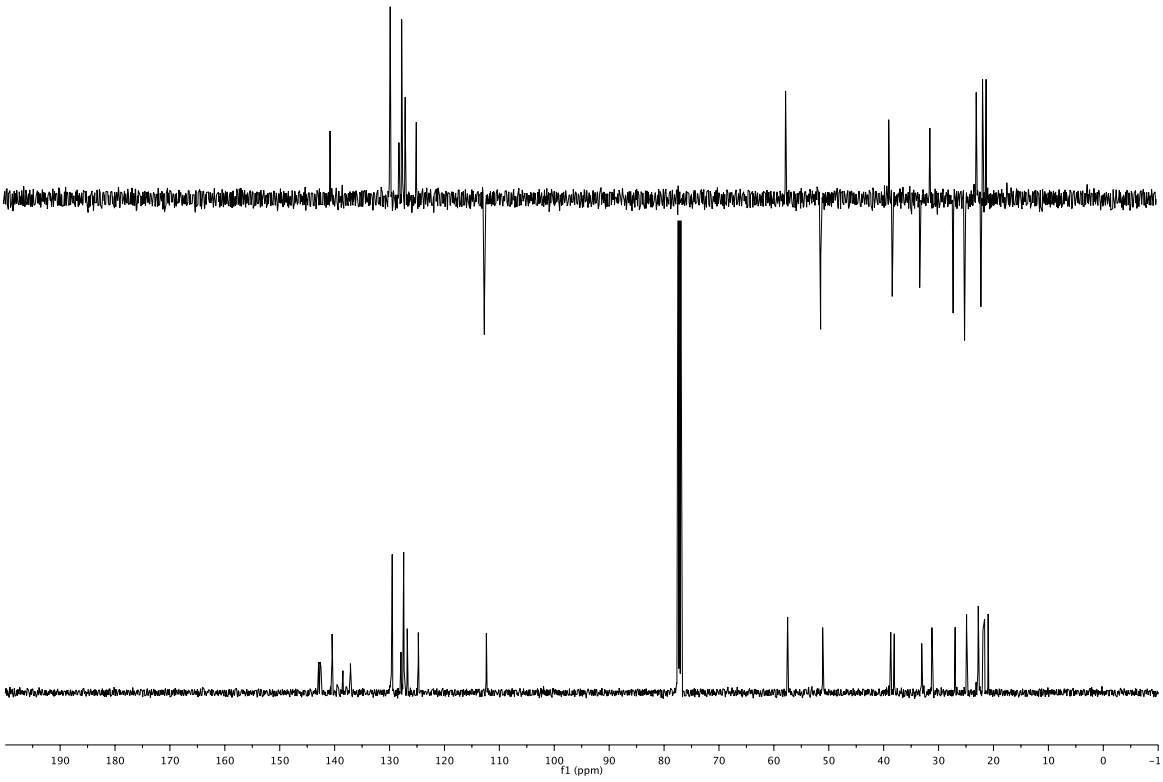


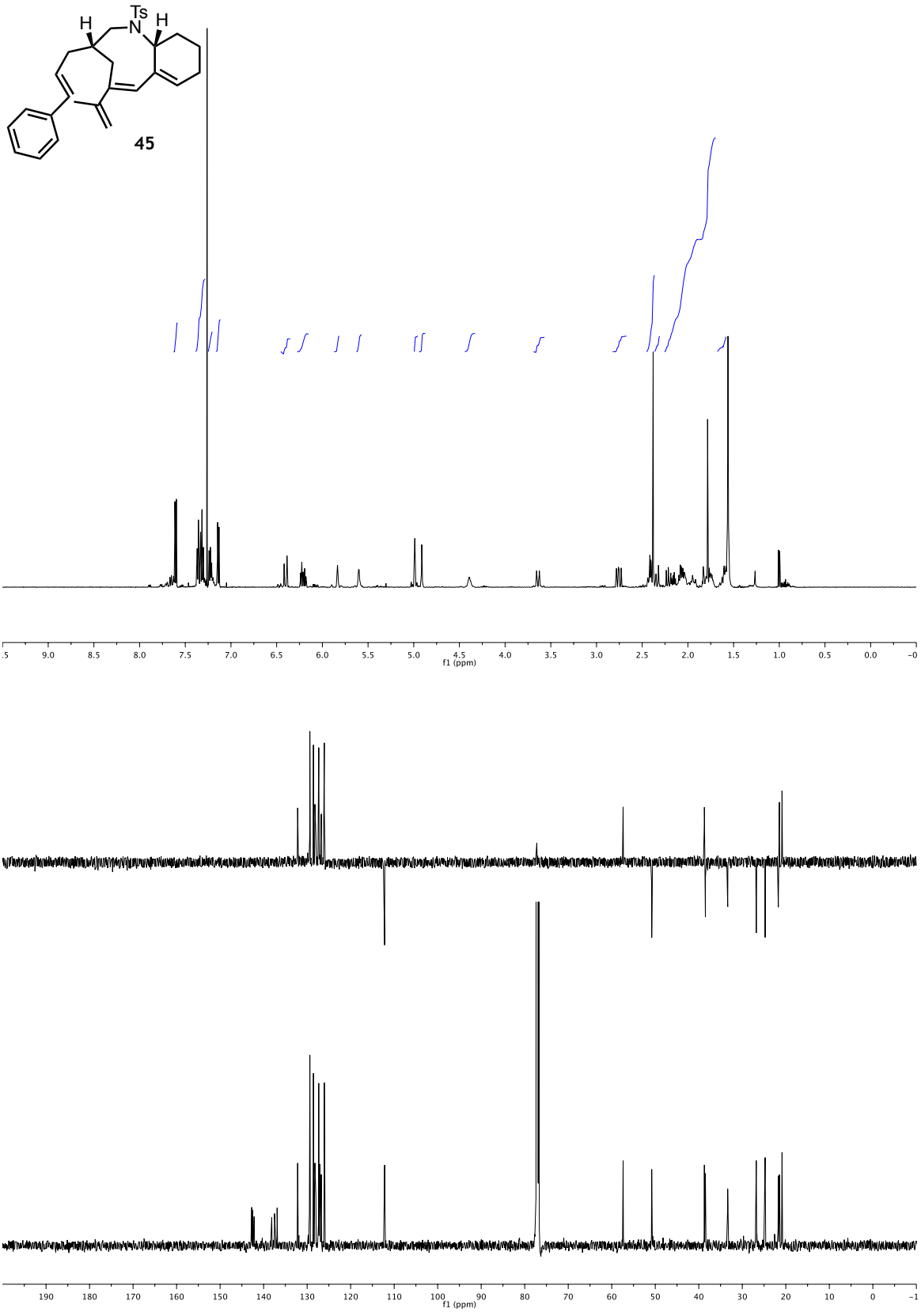



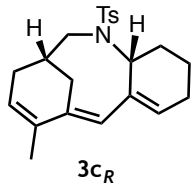



**25c**$_R$

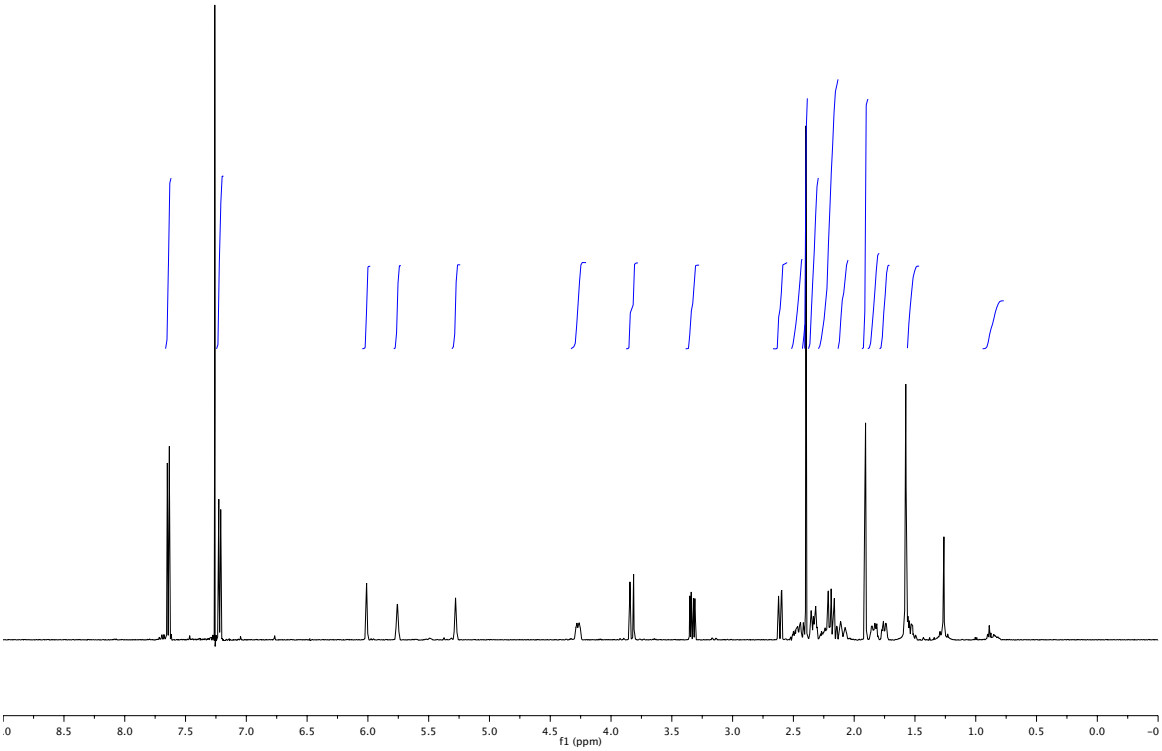


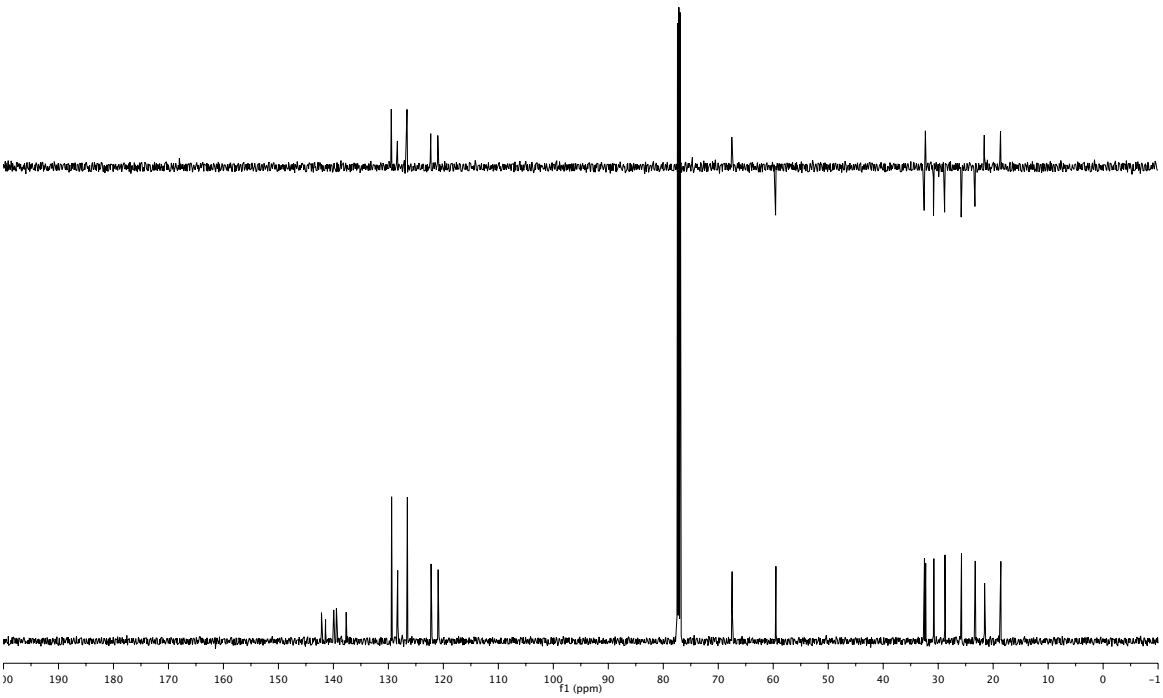




H
Ts
N
H
45
f1 (ppm)
f1 (ppm)

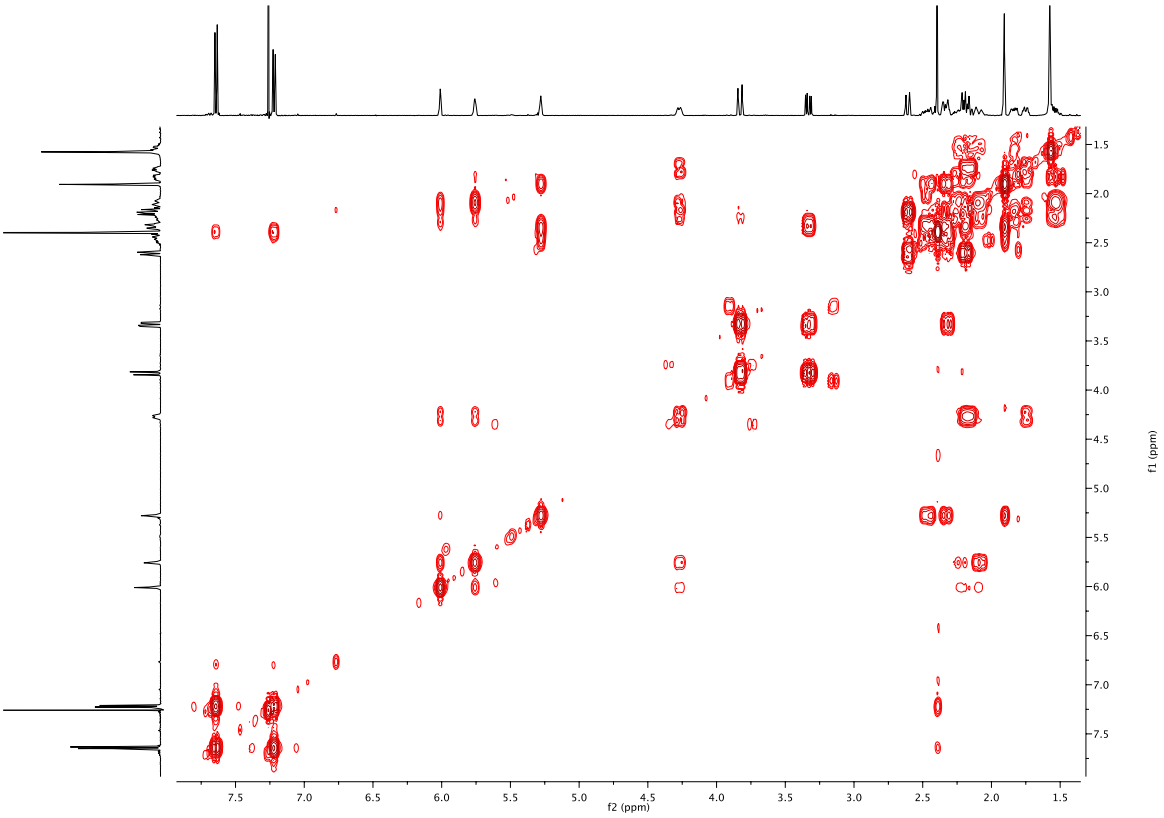

H
Ts
N
H

**3c**$_R$

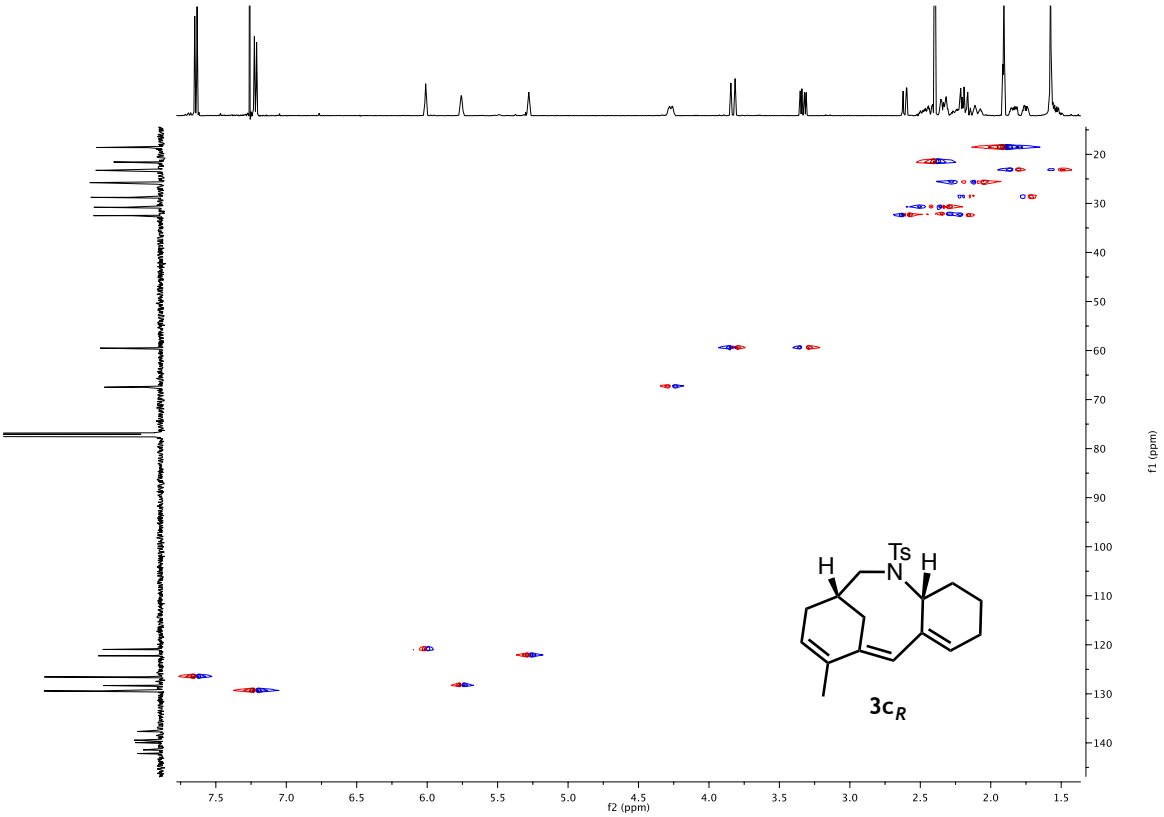

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

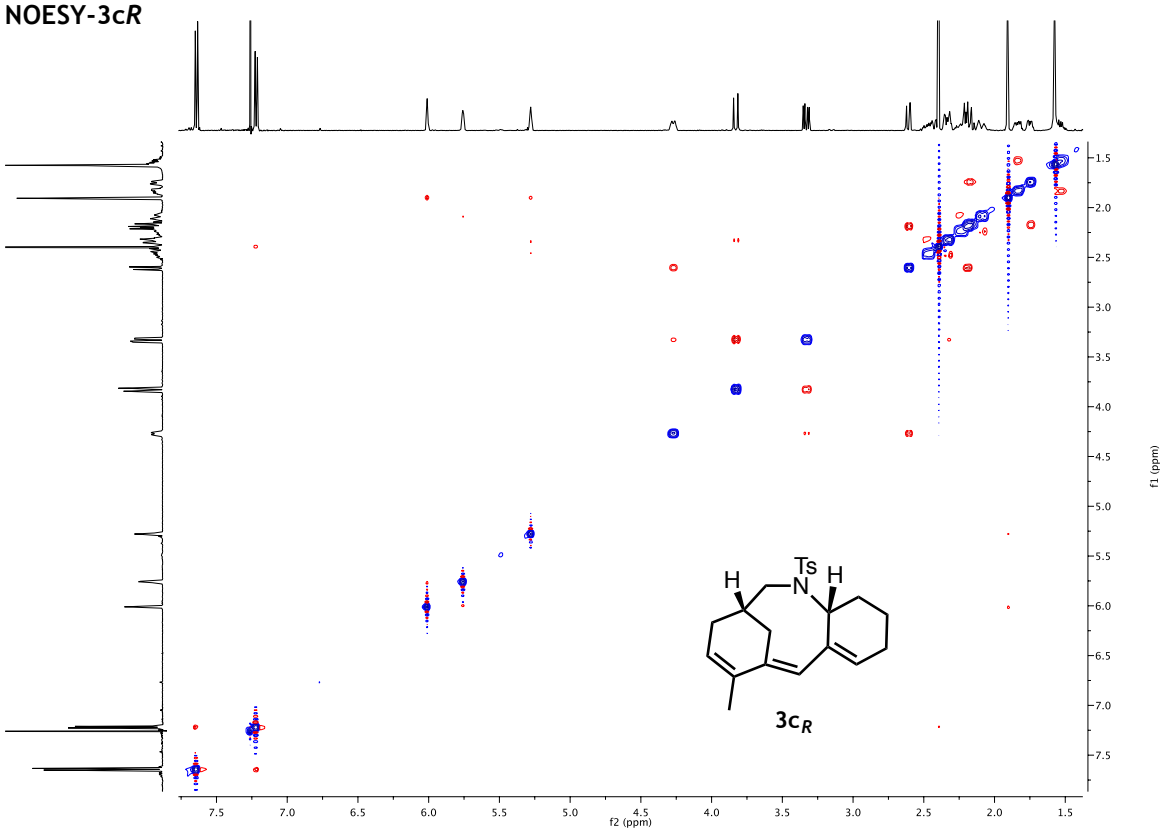
**COSY-3c*R***

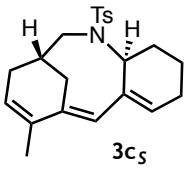



**HSQC-3c$_R$**

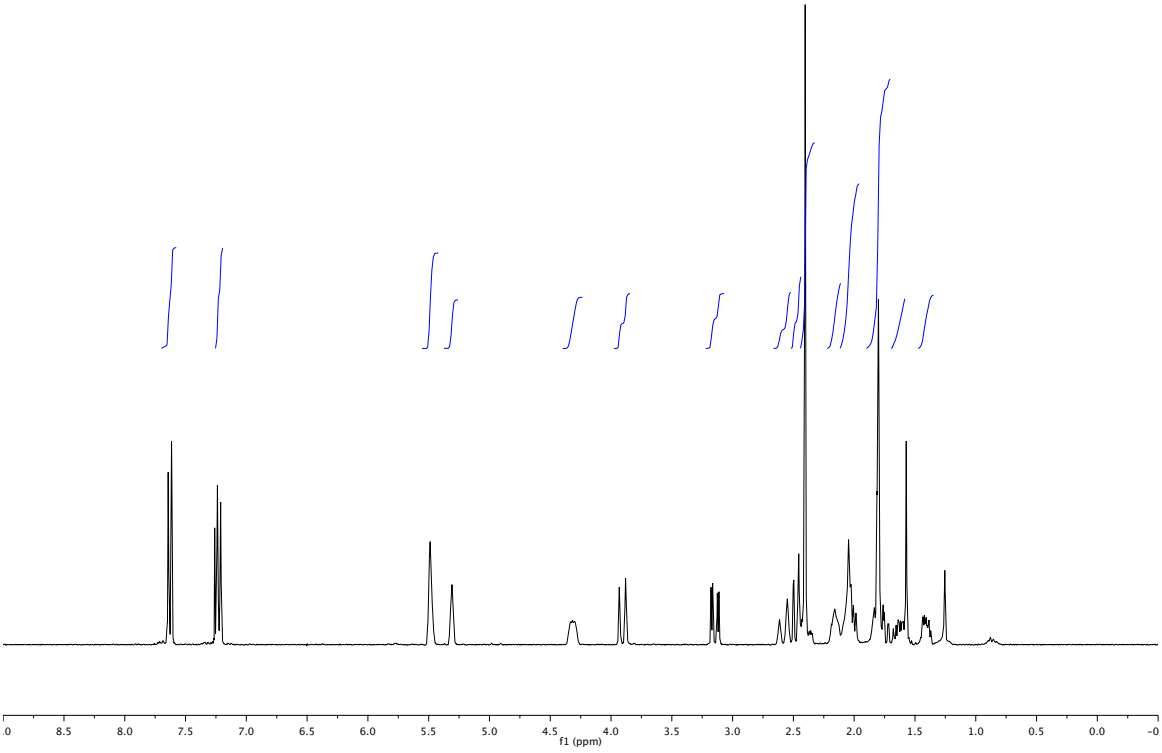


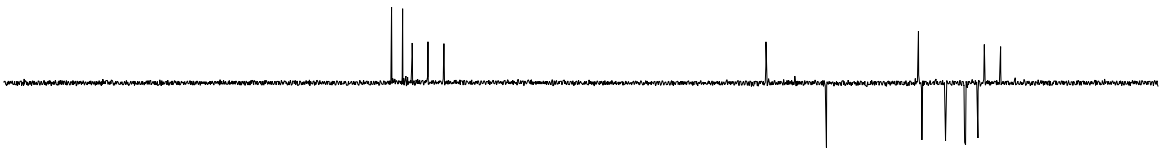
**NOESY-3c*R***

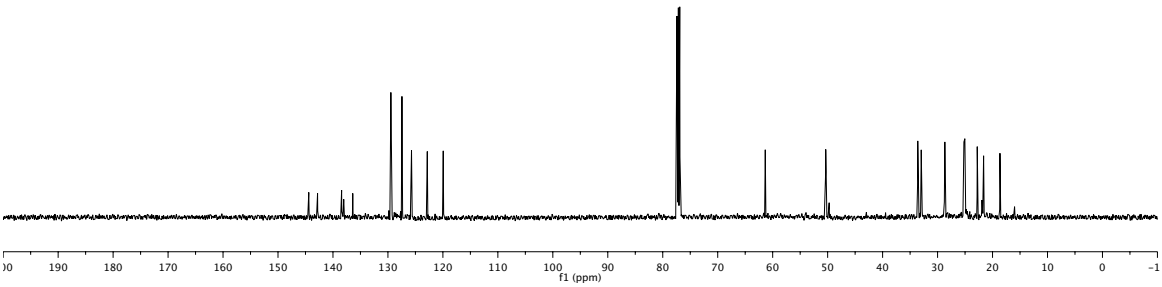



H
Ts
N
H

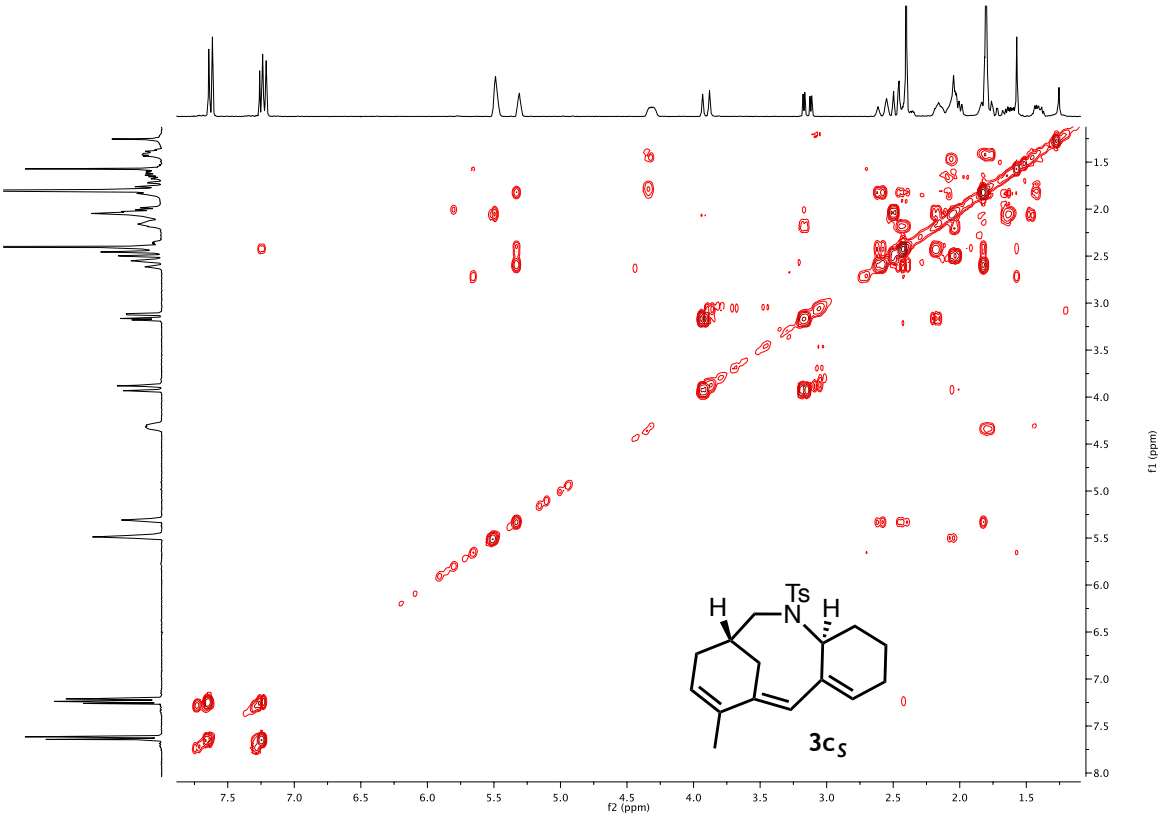
**3c$_S$**


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

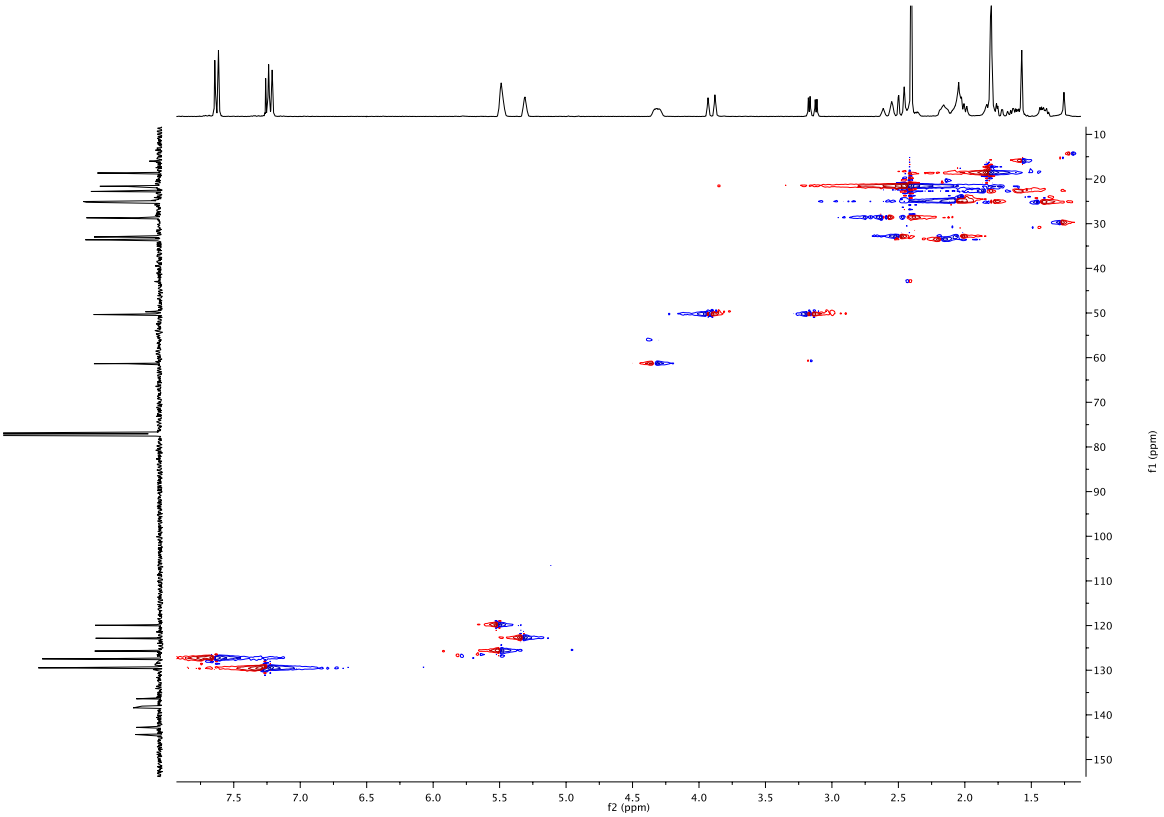



190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

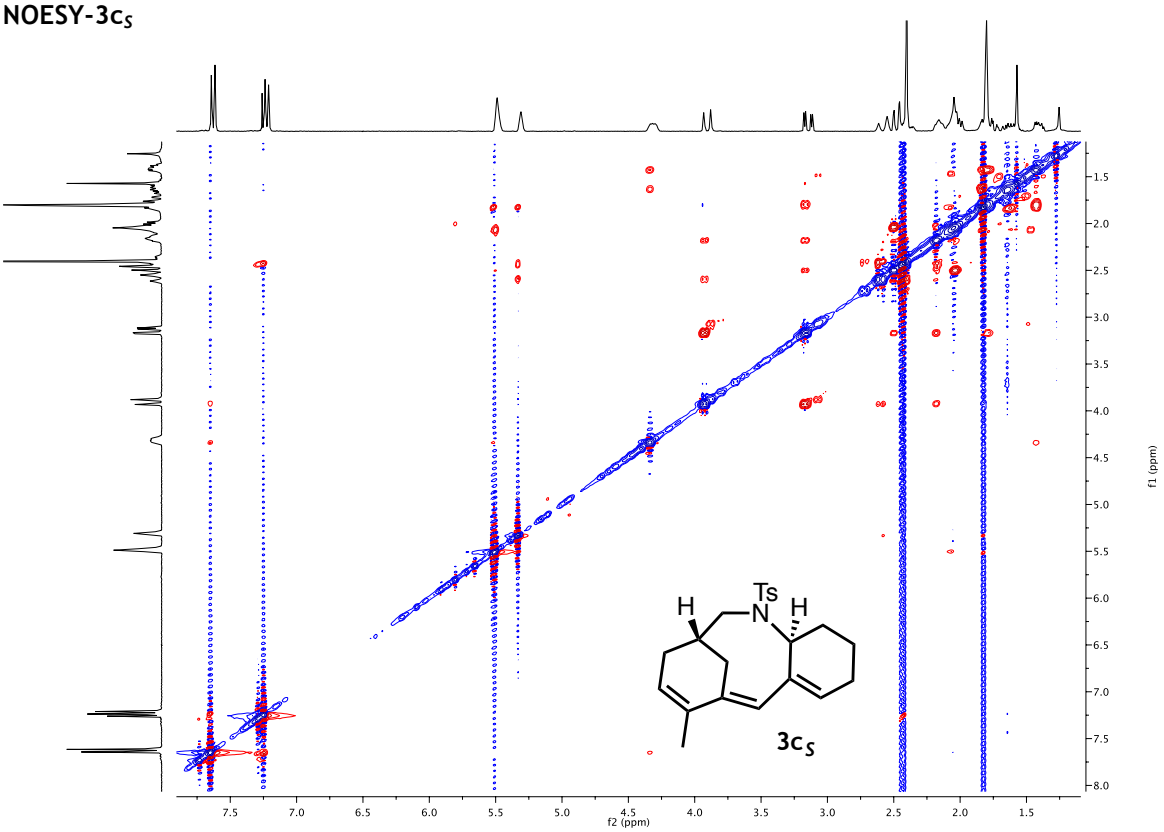
**COSY-3c$_S$**

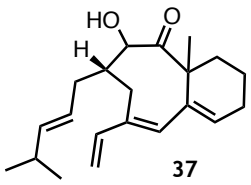



**HSQC-3c$_S$**

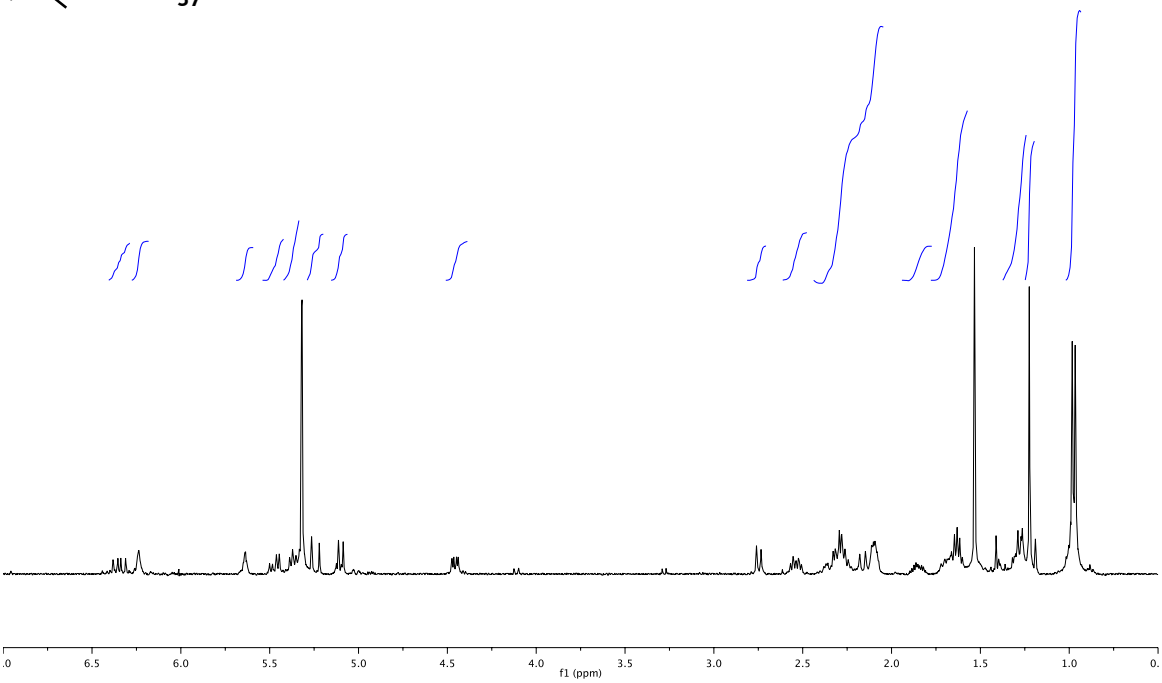


**NOESY-3c$_S$**

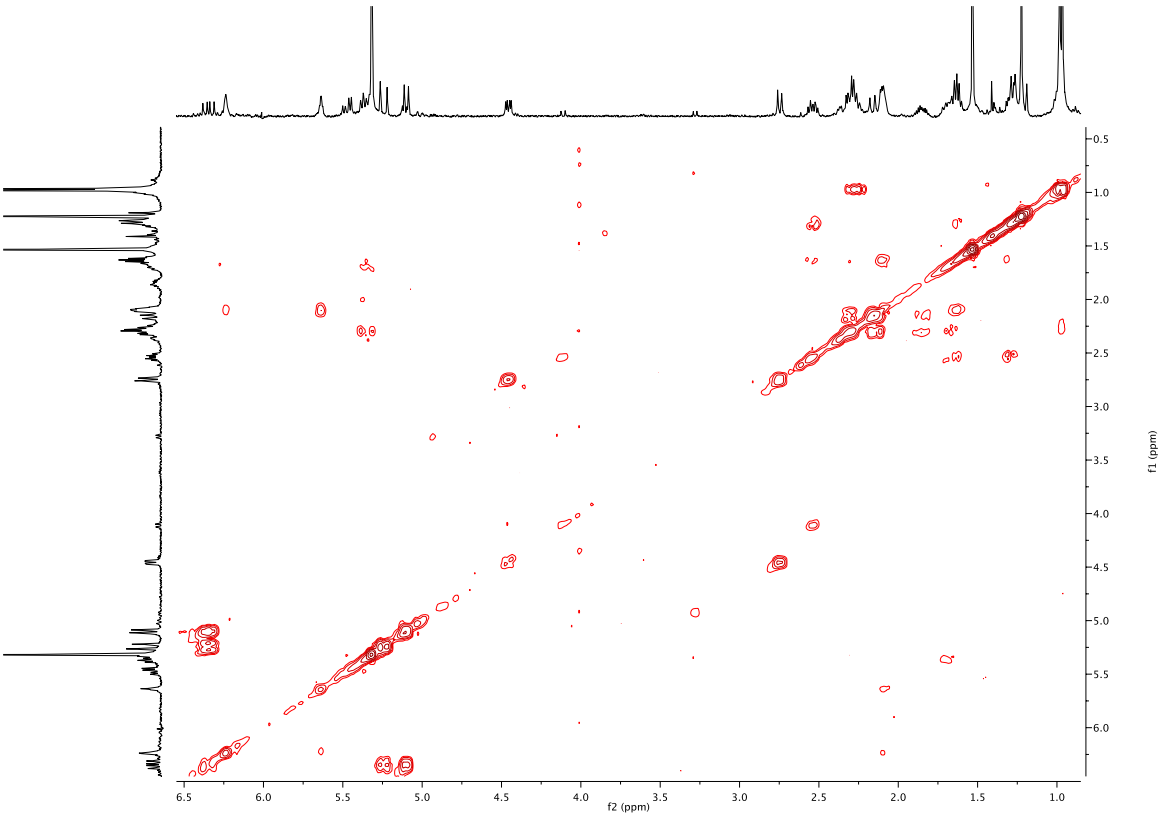


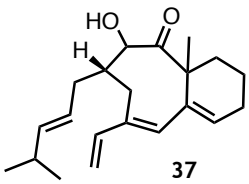



**37**



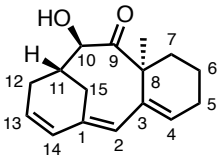

**COSY-37**



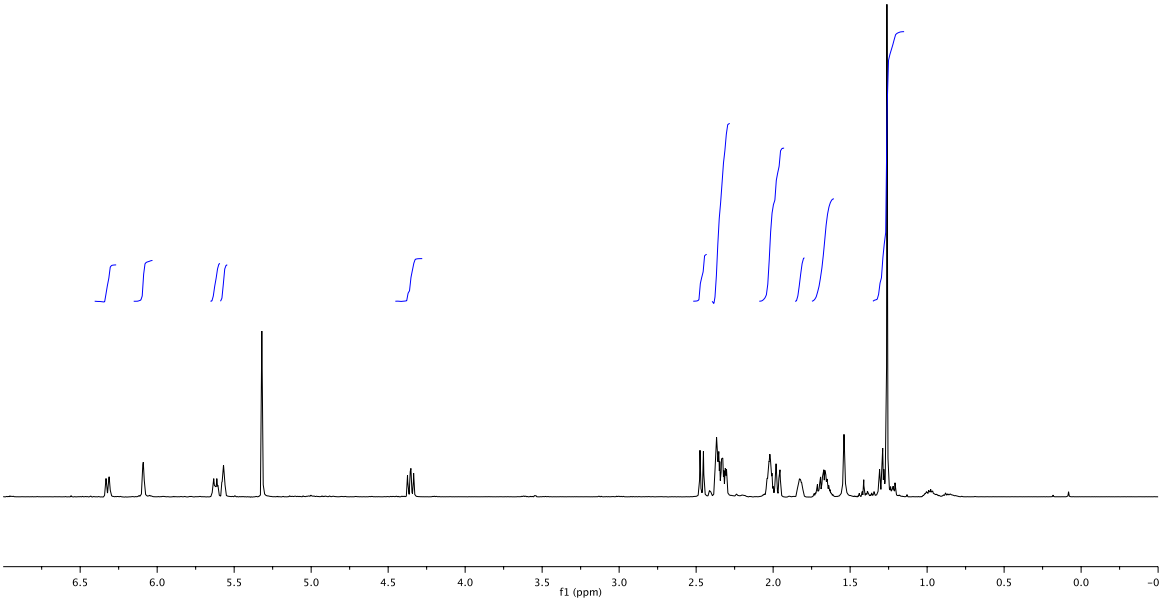

HO
O
H

**37**

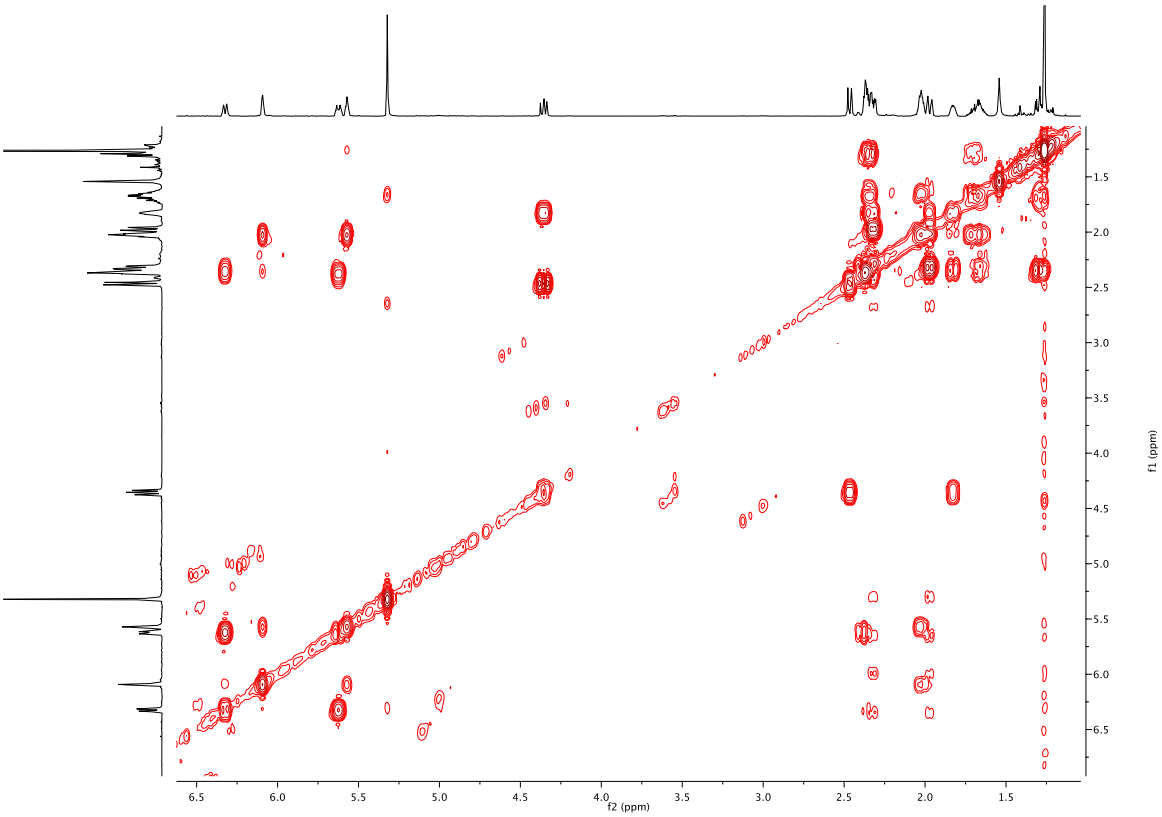

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

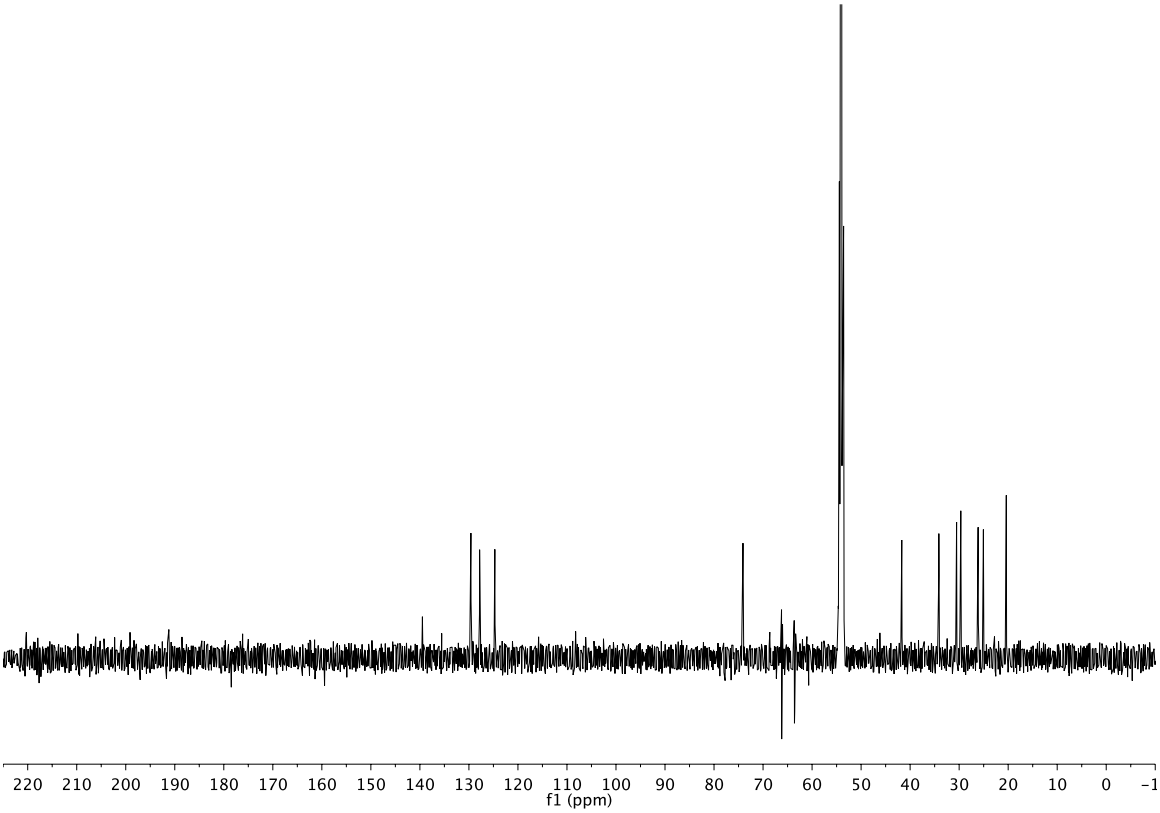

HO
O
H
7
6
5
10
9
8
12
11
15
13
3
4
1
2
14

**36**

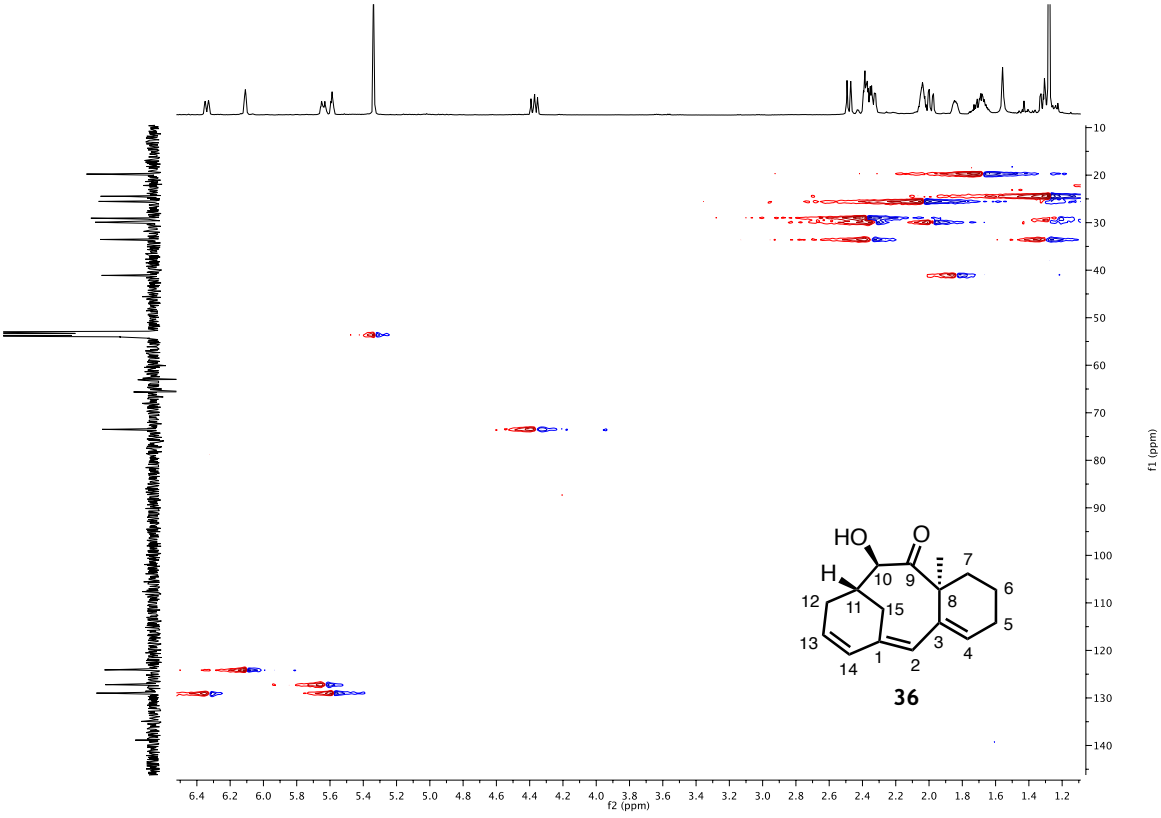

6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

**COSY-36**

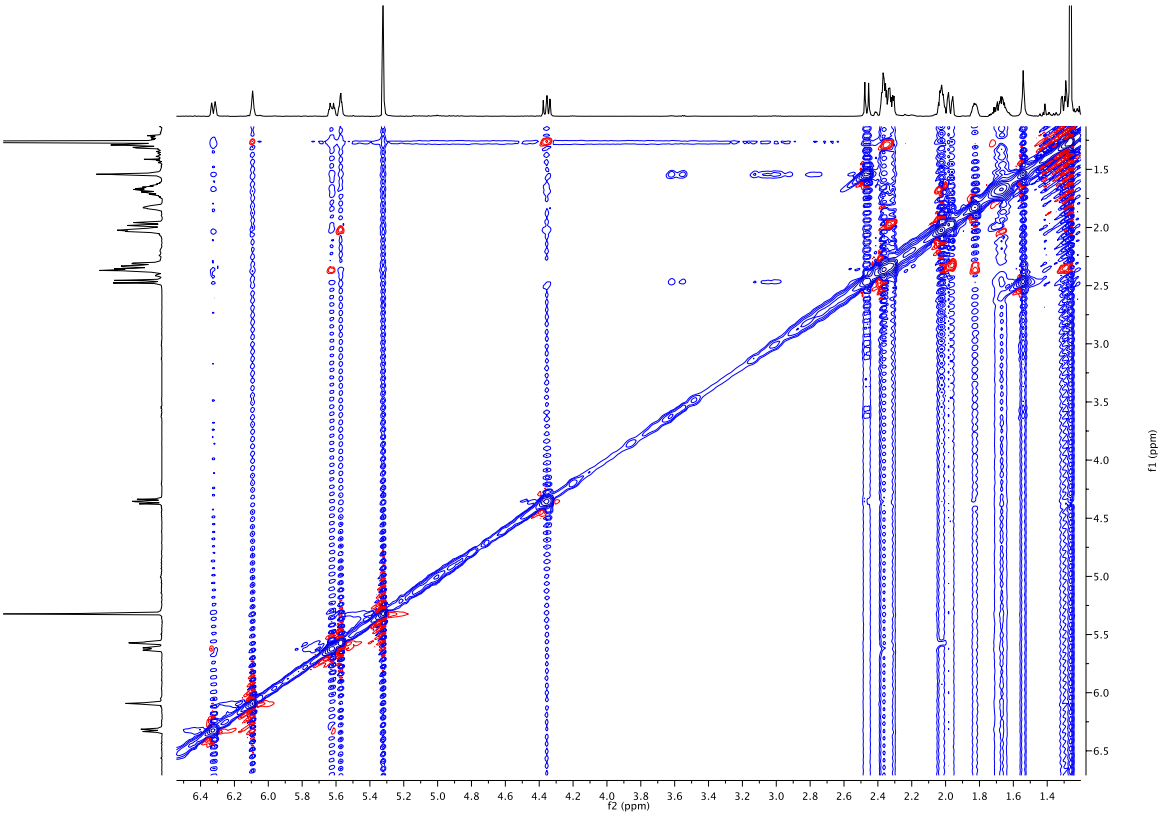

6.5
6.0
5.5
5.0
4.5
4.0
f2 (ppm)
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

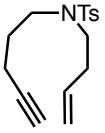
**HSQC-36**


6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110 120 130 140
f1 (ppm)
HO
O
H
7
6
10
9
8
12
11
15
5
13
3
4
1
2
14
36

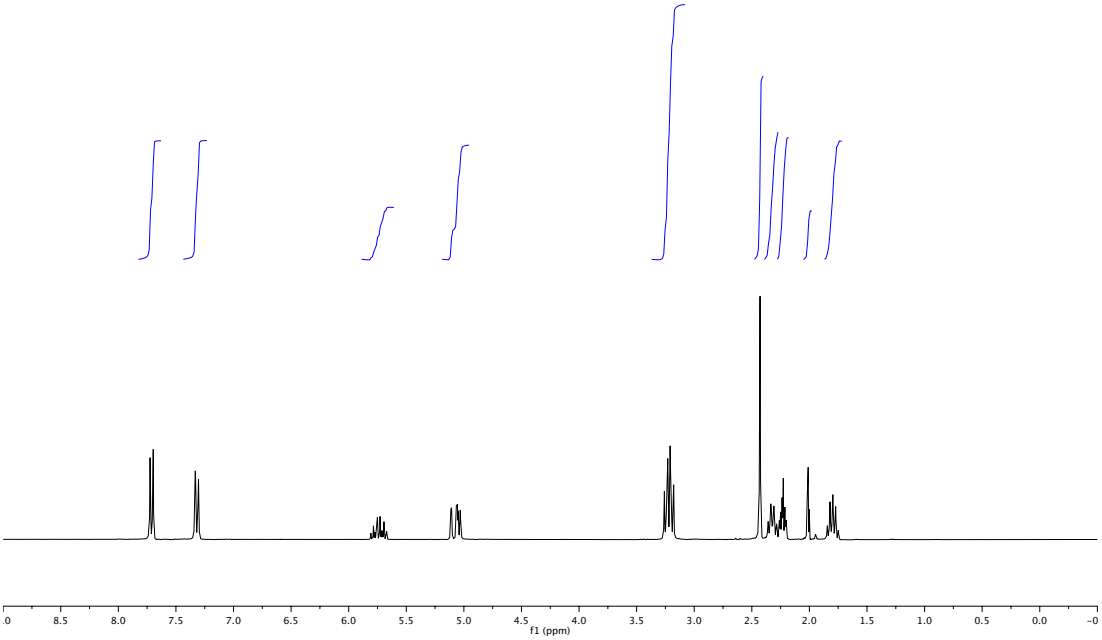
**NOESY-36**



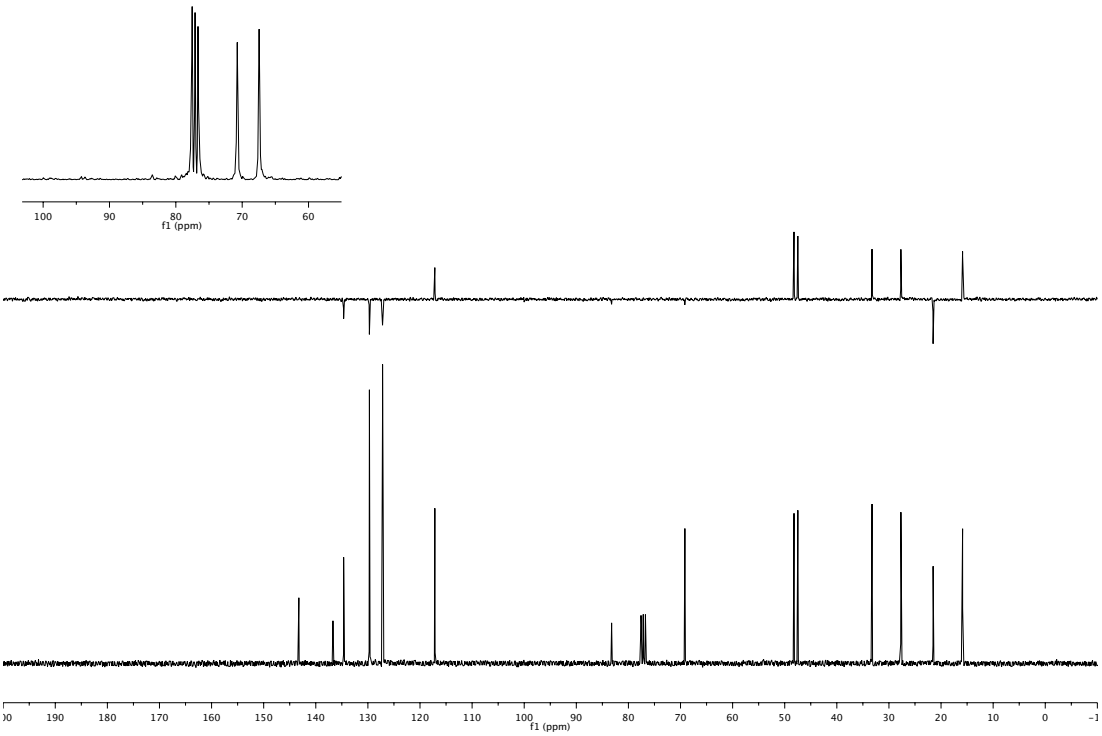
# VII. NMR spectra for precursors

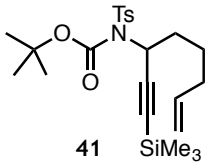



**8a**

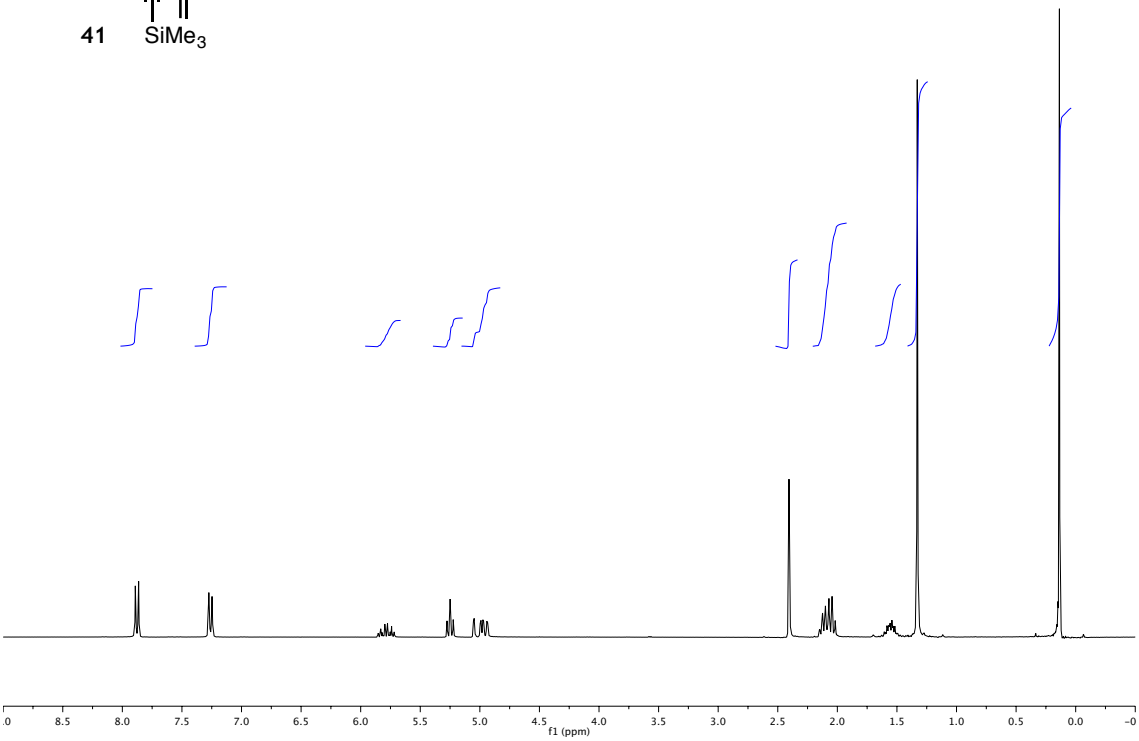


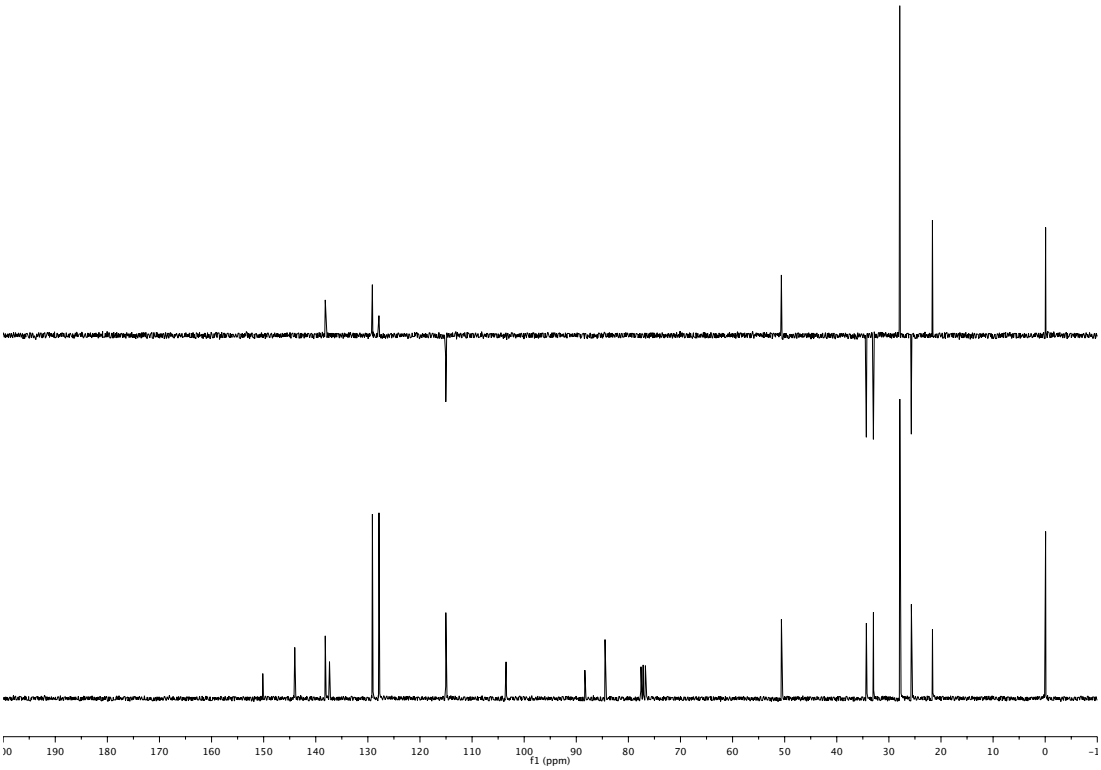

$^{1}$H-coupled $^{13}$C-NMR

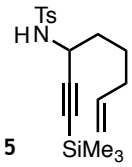




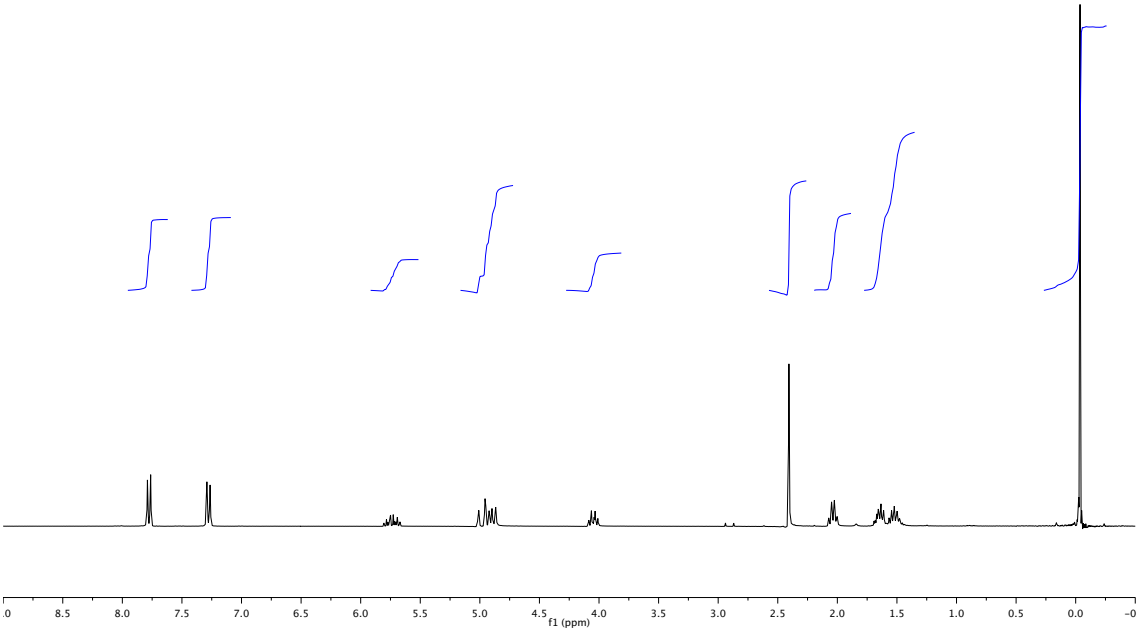

**41**




Ts
HN
SiMe3

**5**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1.0
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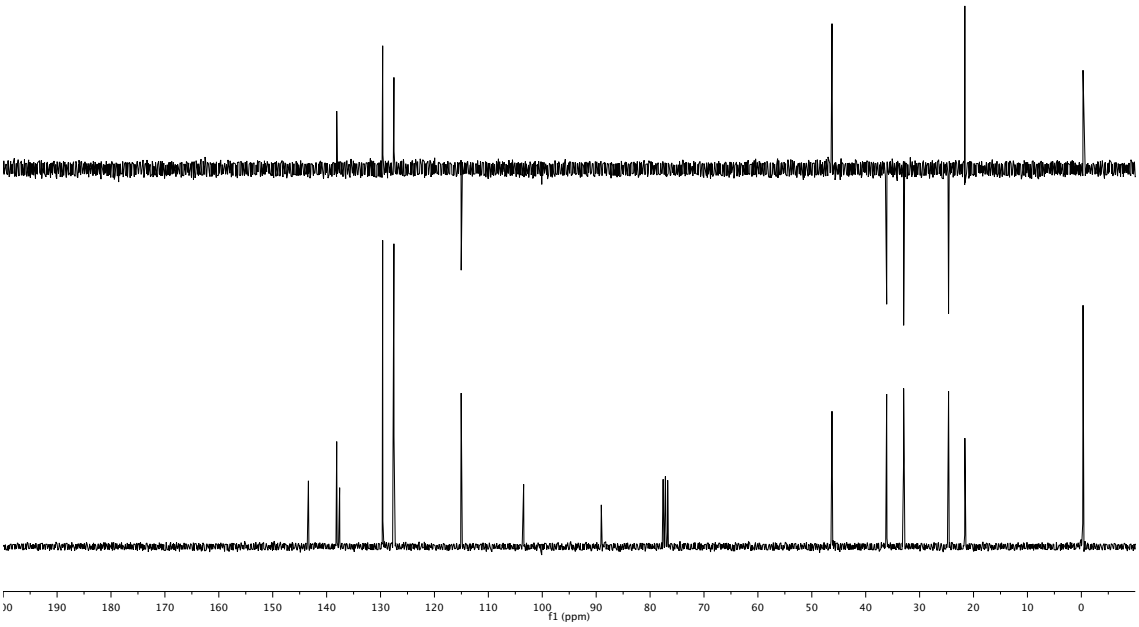
0.0
f1 (ppm)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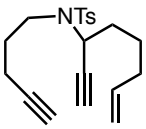
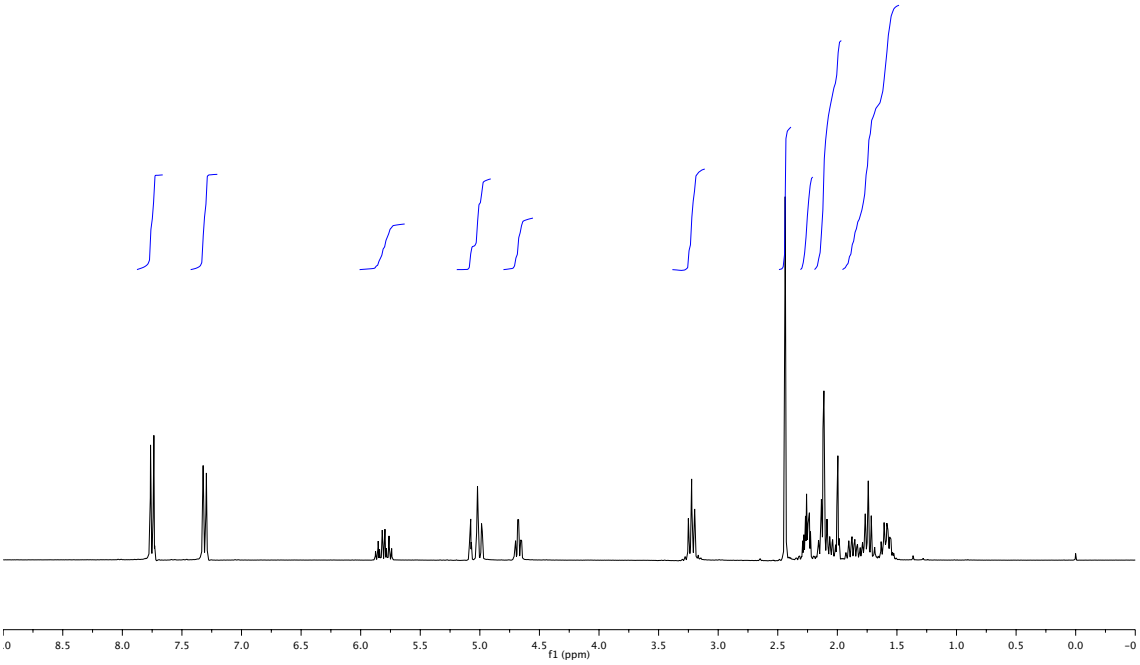
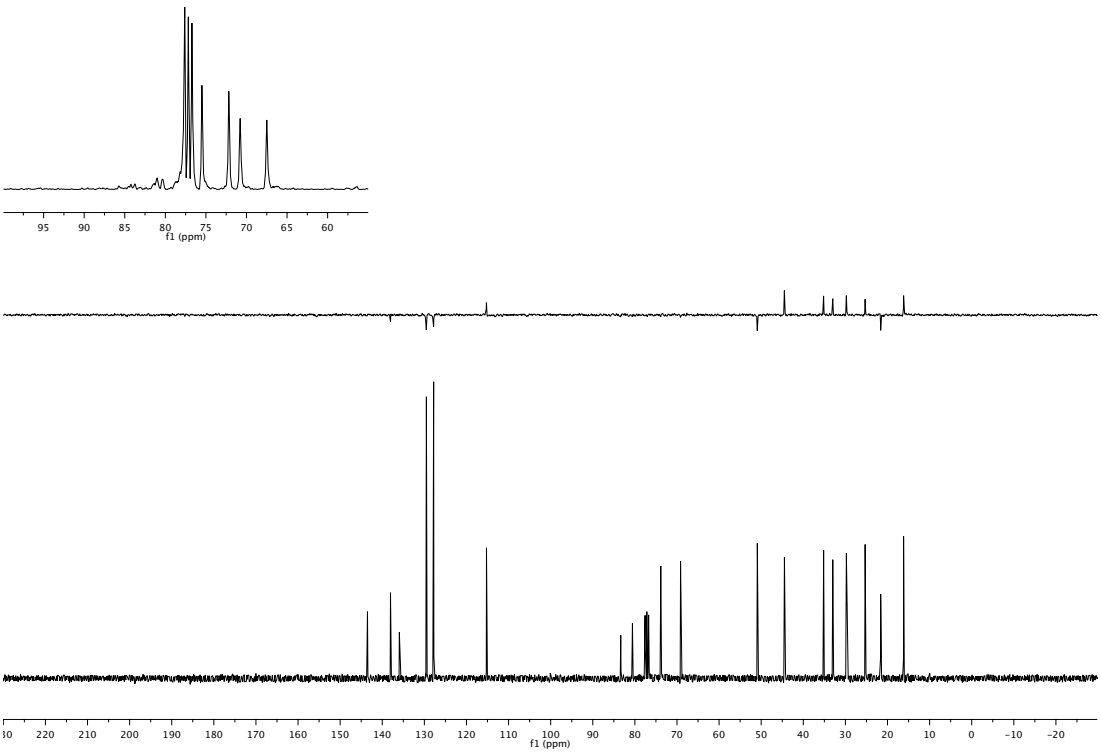
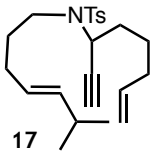



**9a**

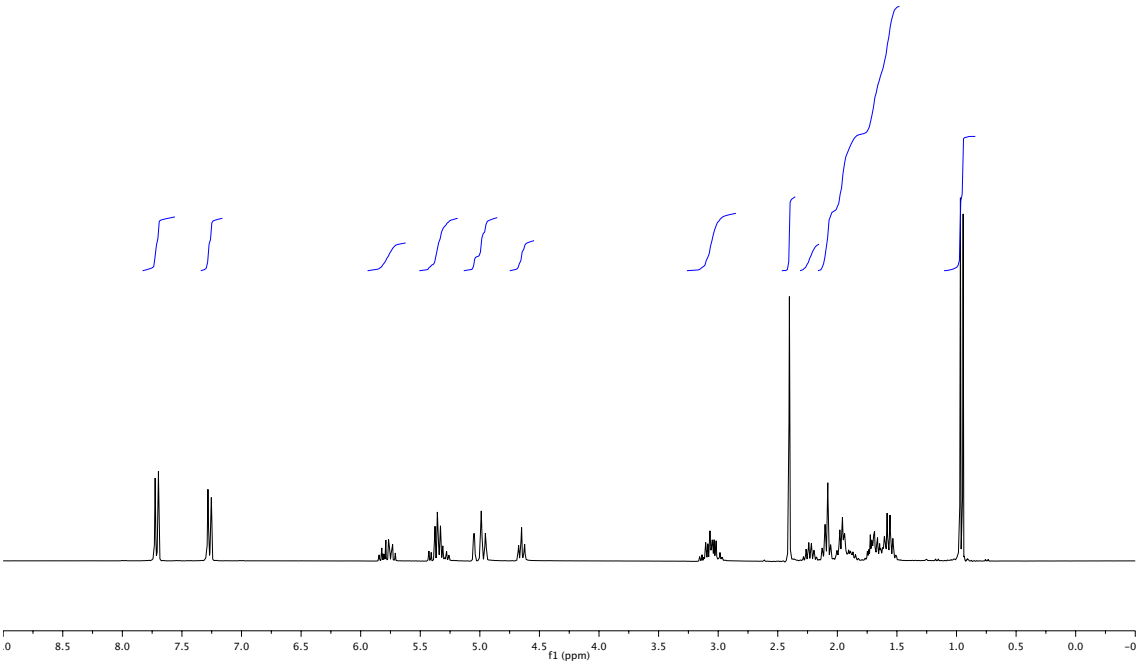



**$^{1}$H-coupled $^{13}$C-NMR**

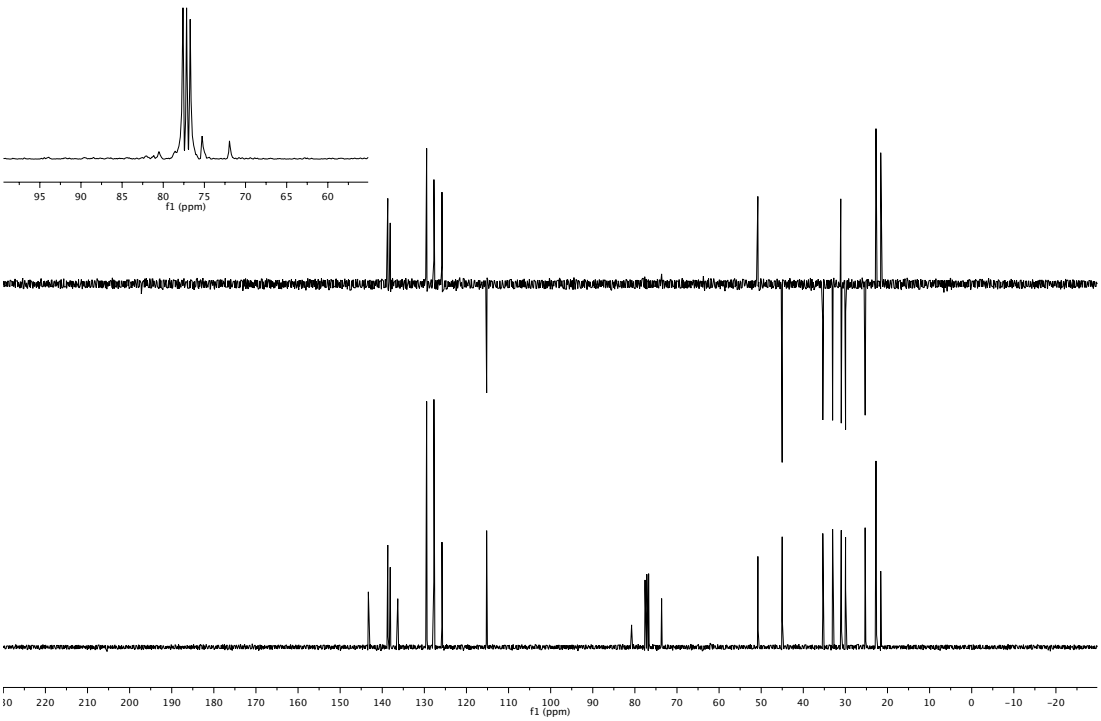


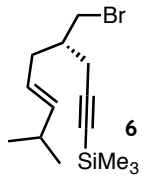



17

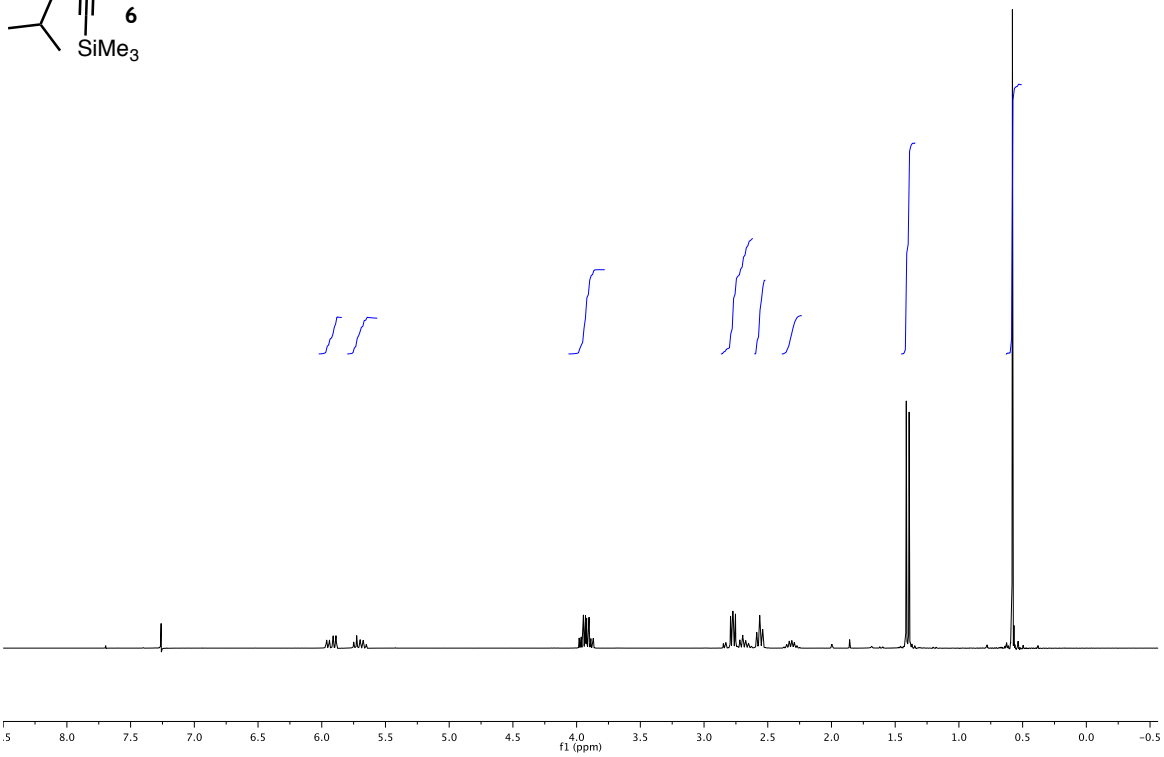



**$^{1}$H-coupled $^{13}$C-NMR**




Br
SiMe3

**6**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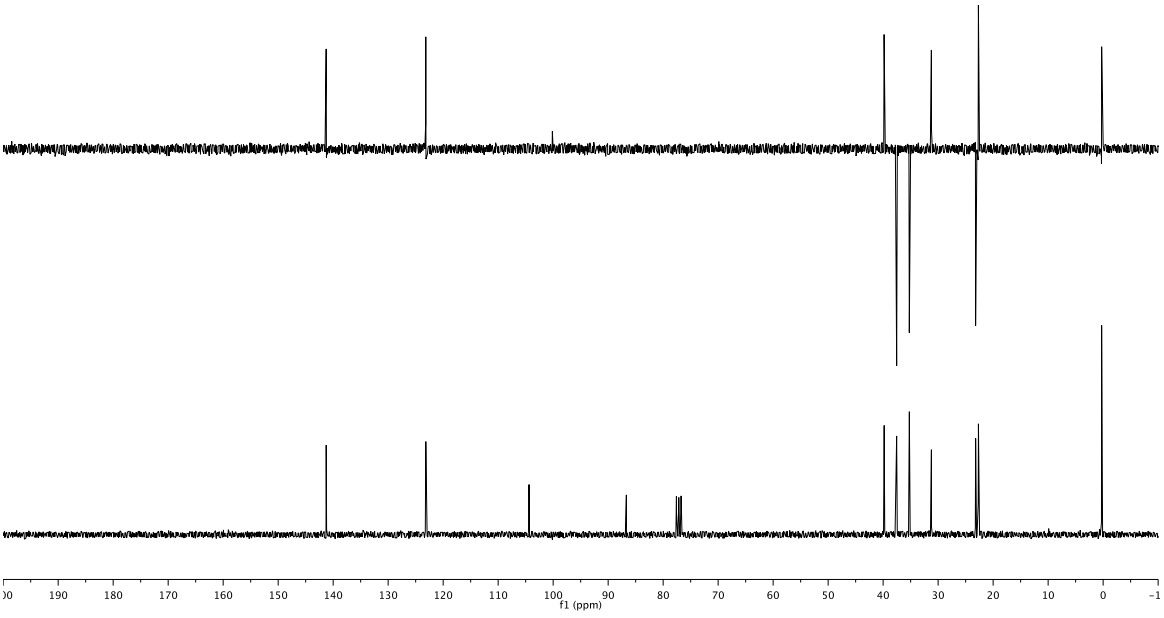
f1 (ppm)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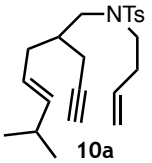
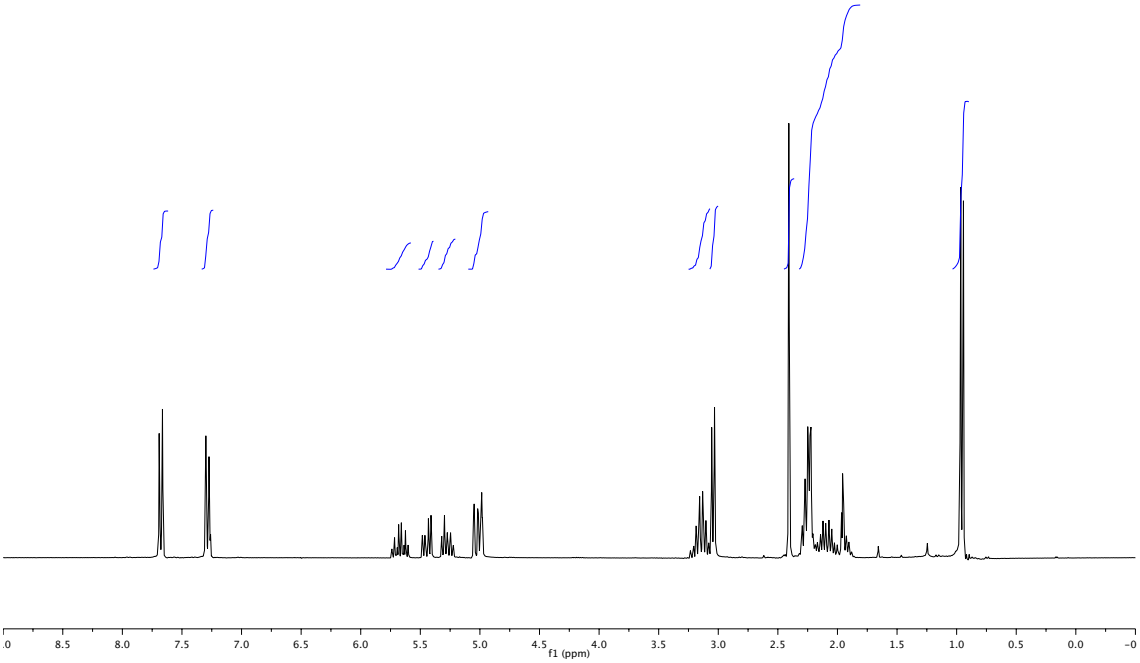
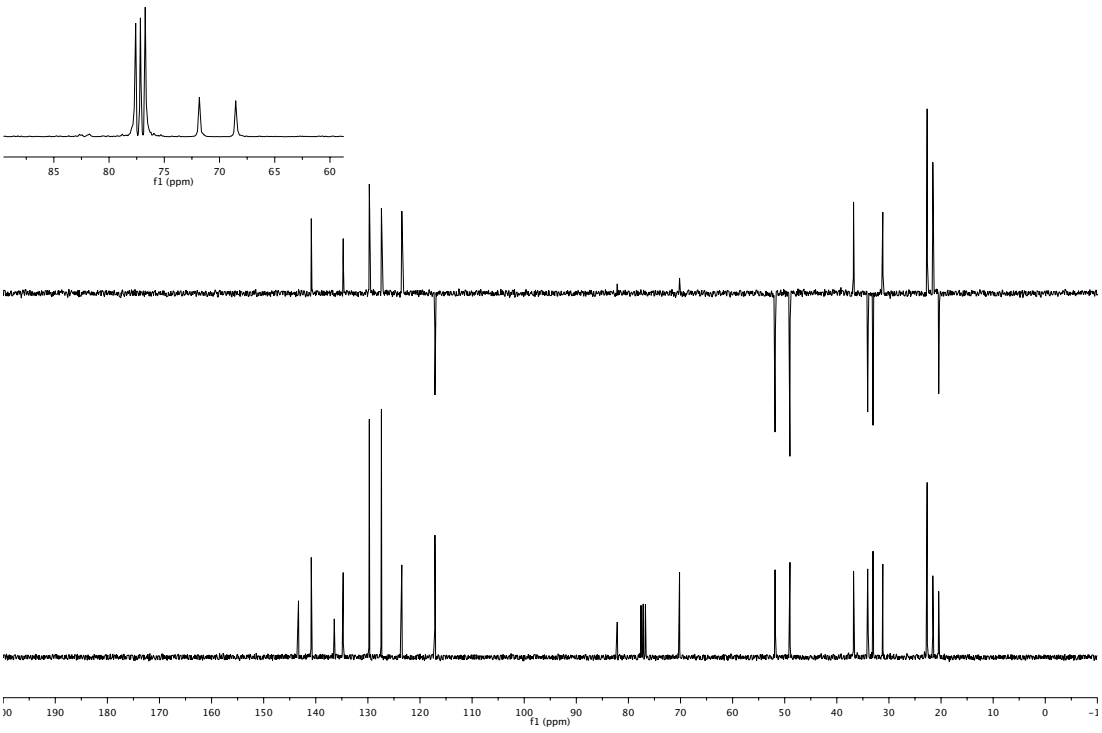
f1 (ppm)

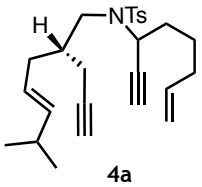



**10a**

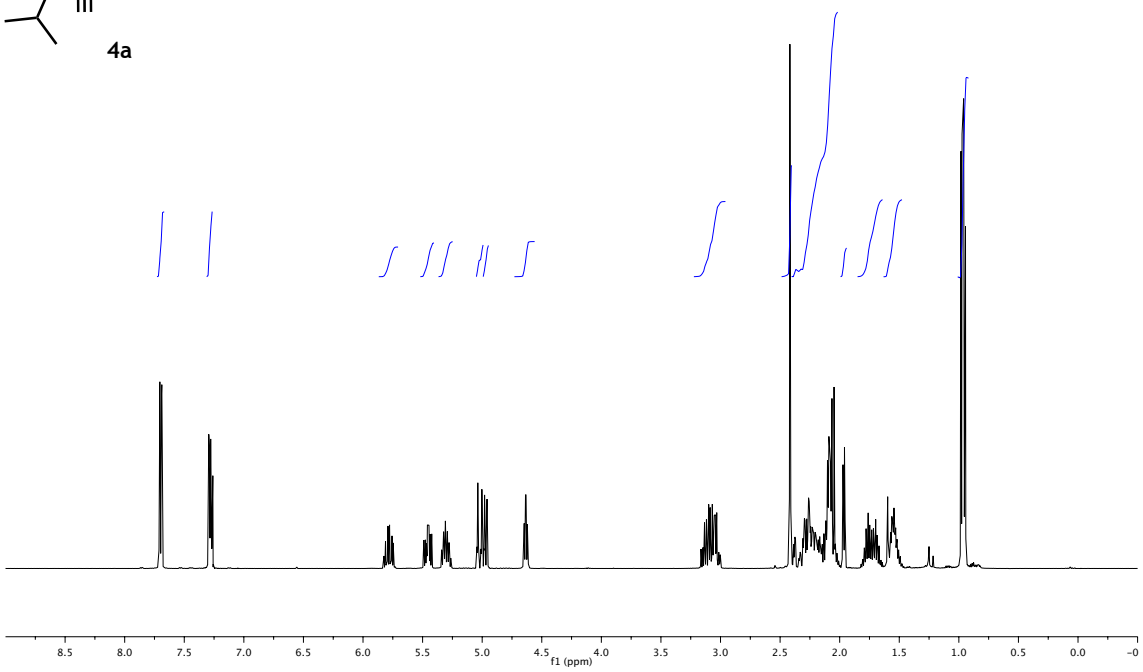



**$^{1}$H-coupled $^{13}$C-NMR**




H
NTs

**4a**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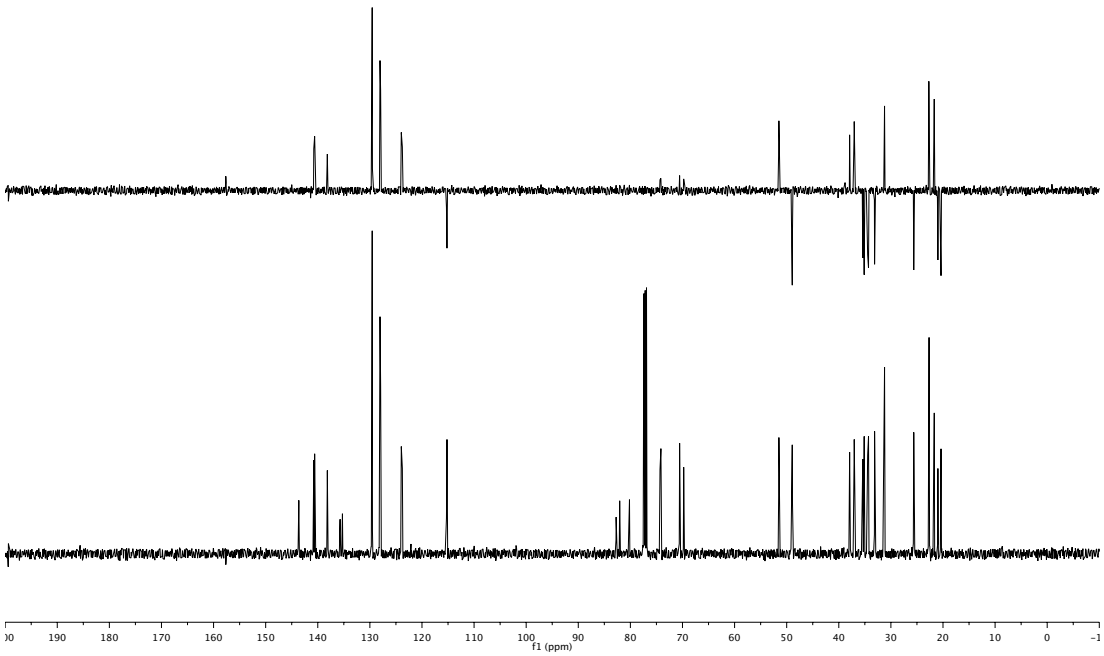
f1 (ppm)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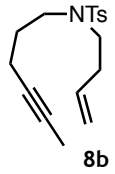
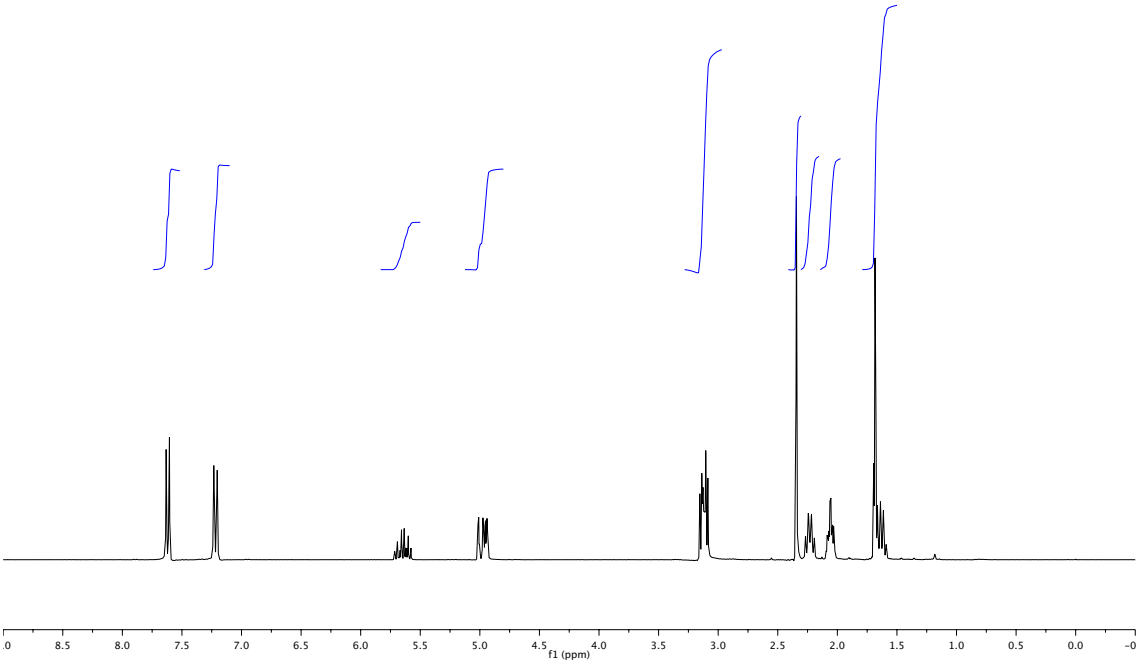
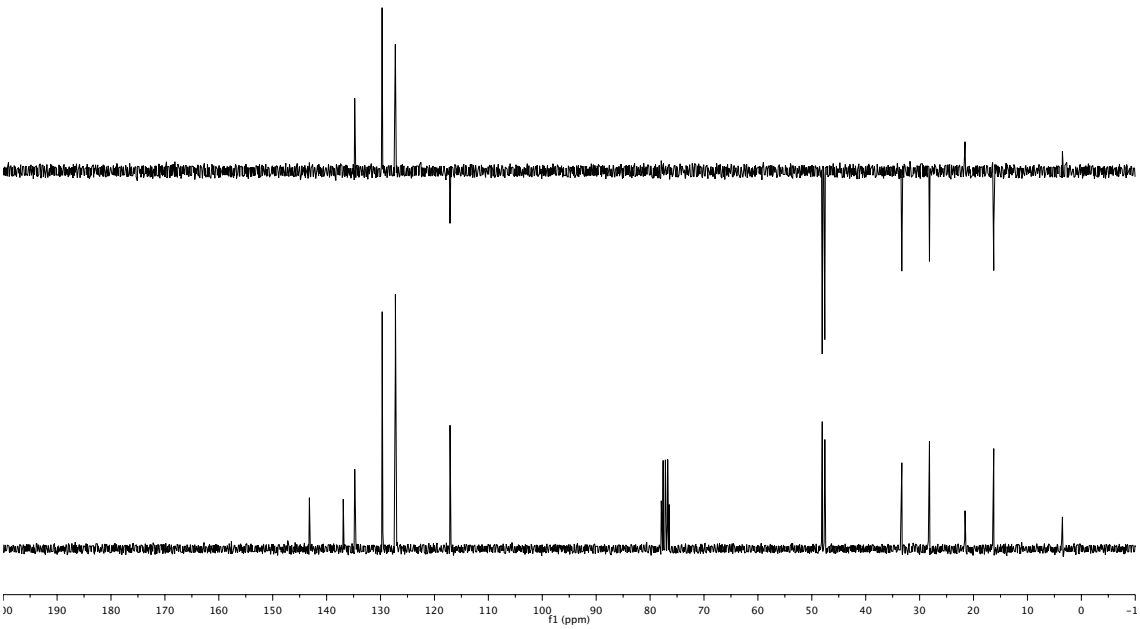
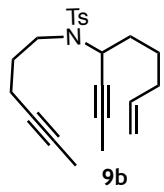
f1 (ppm)



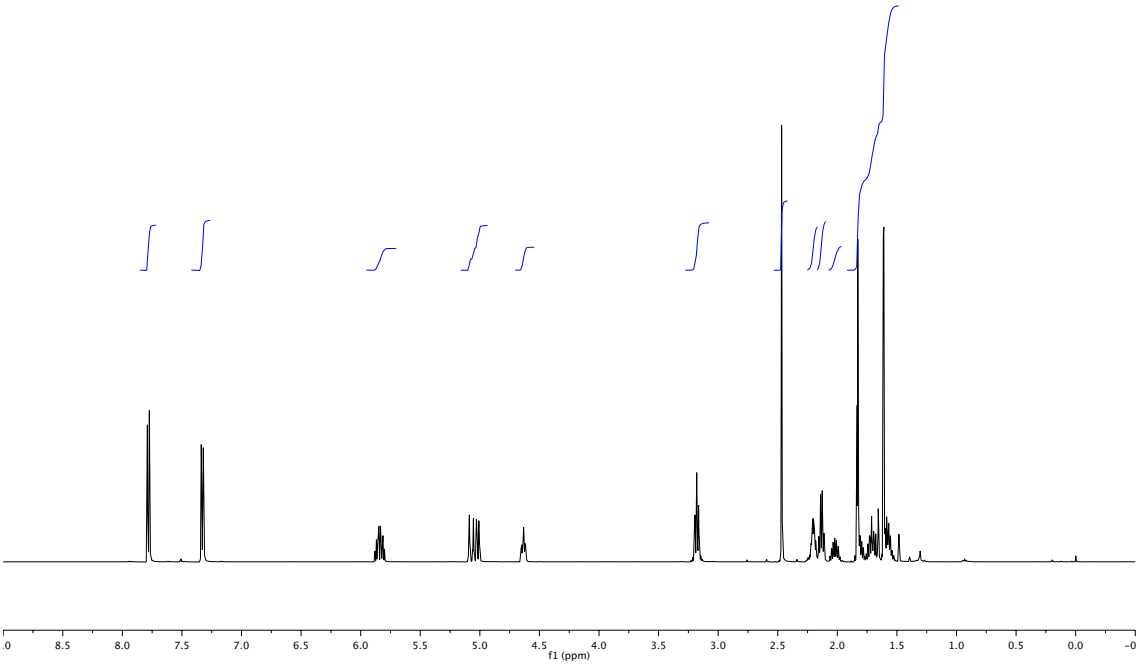

**8b**

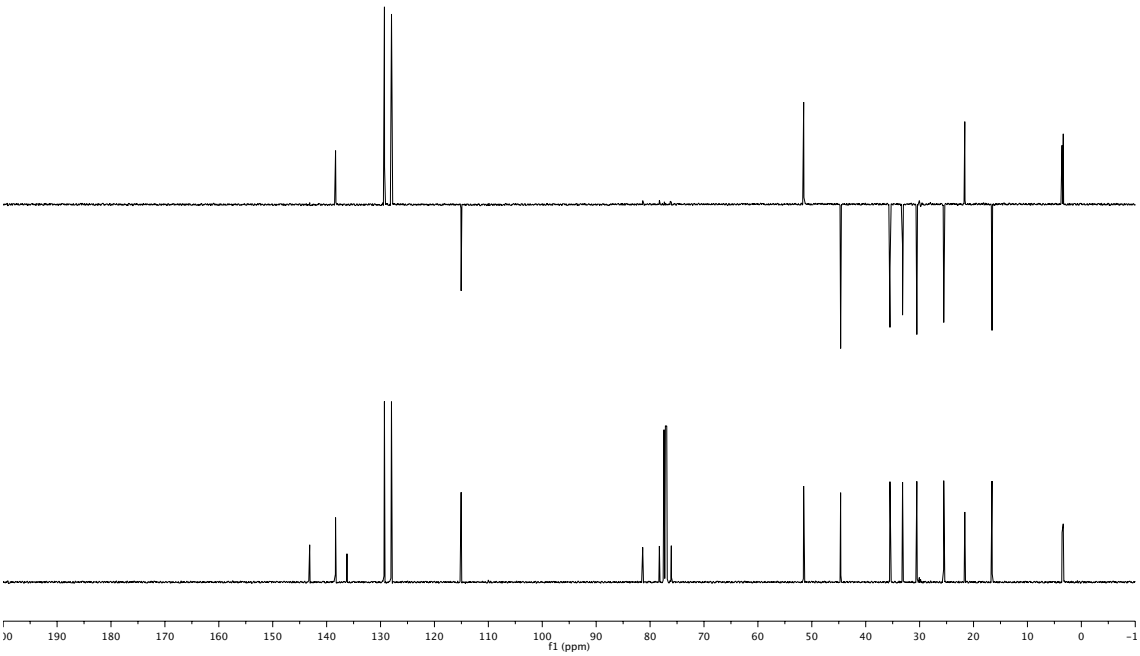


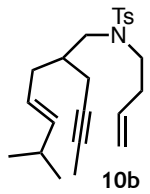





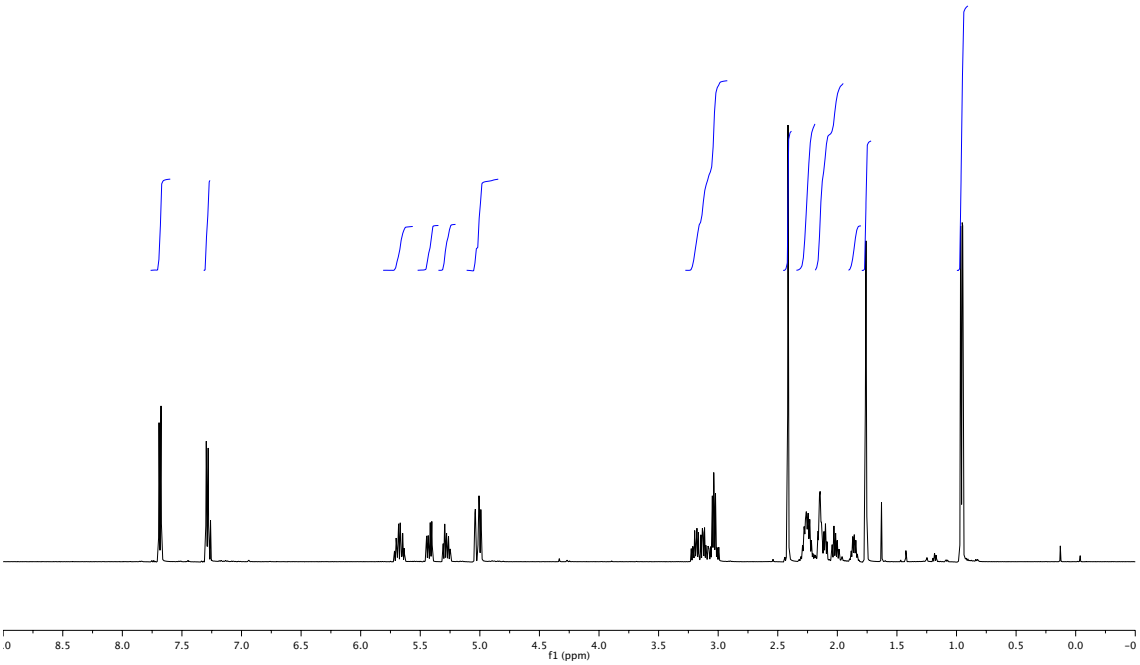

**9b**

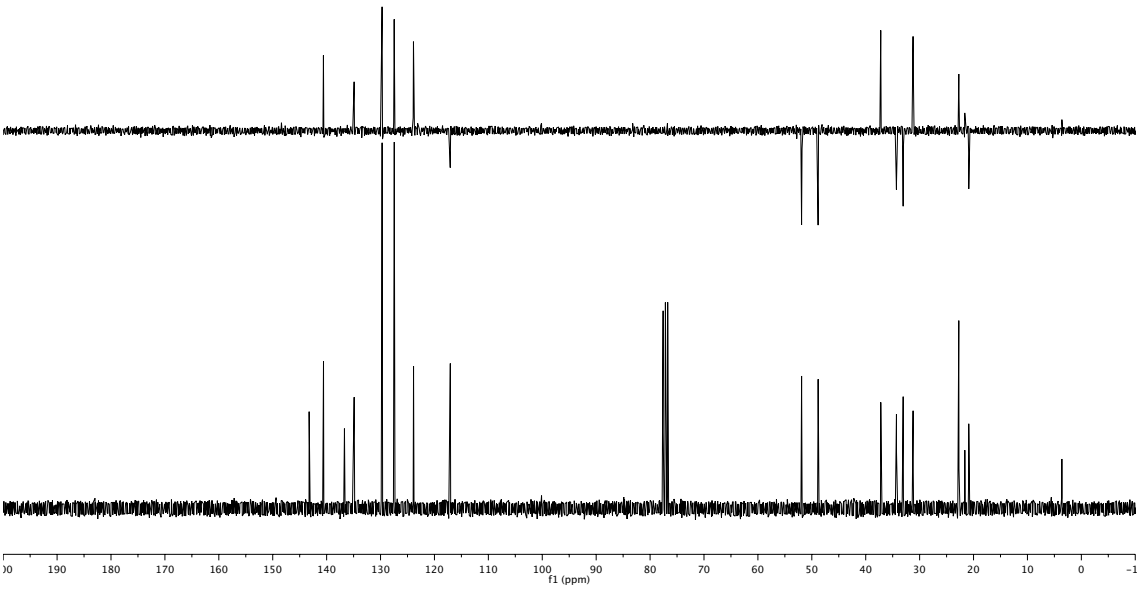


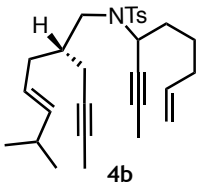





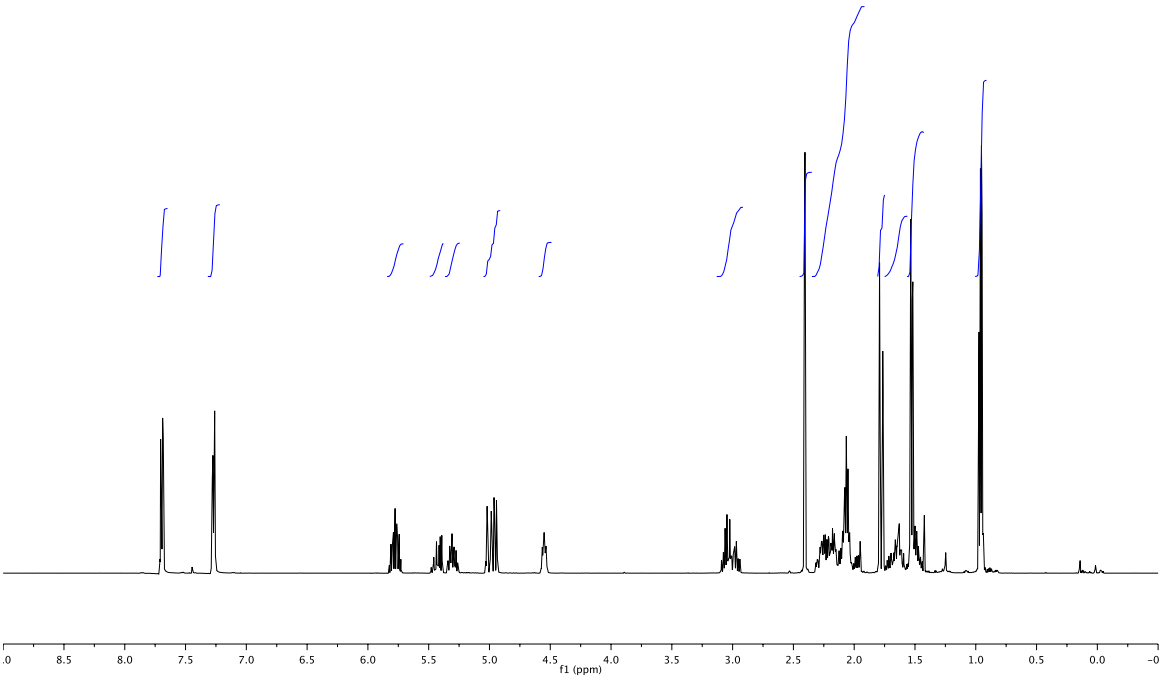

**10b**

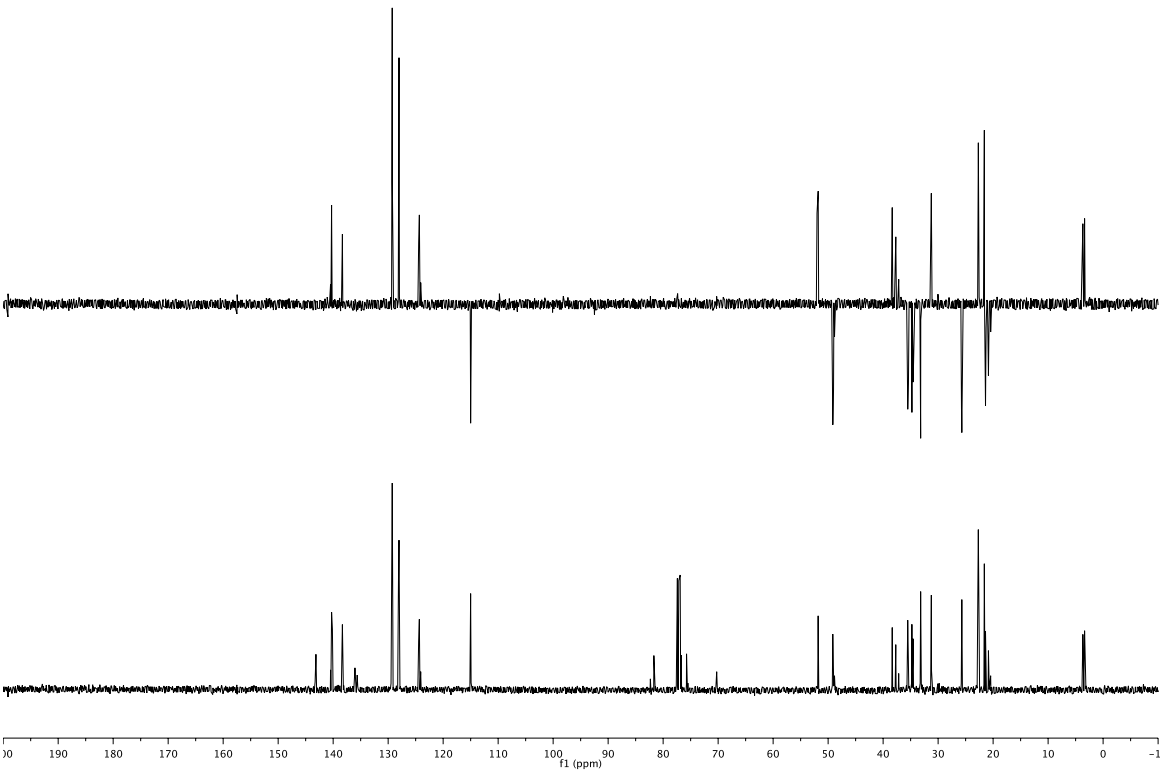


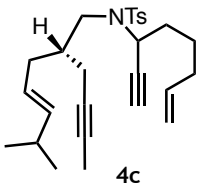





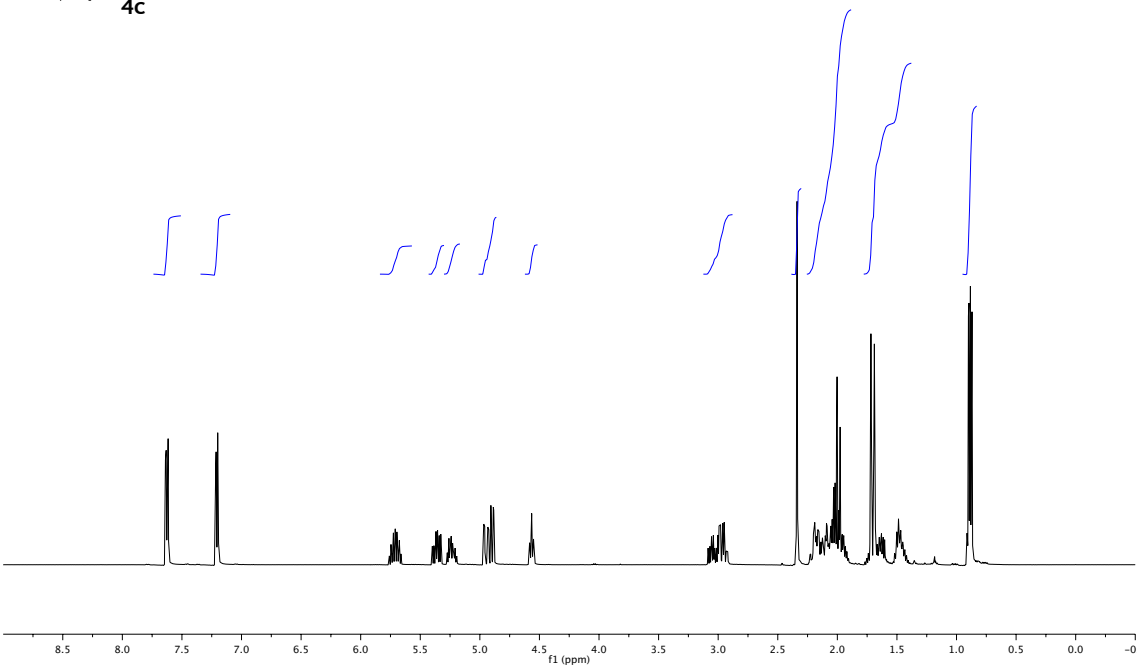

**4b**



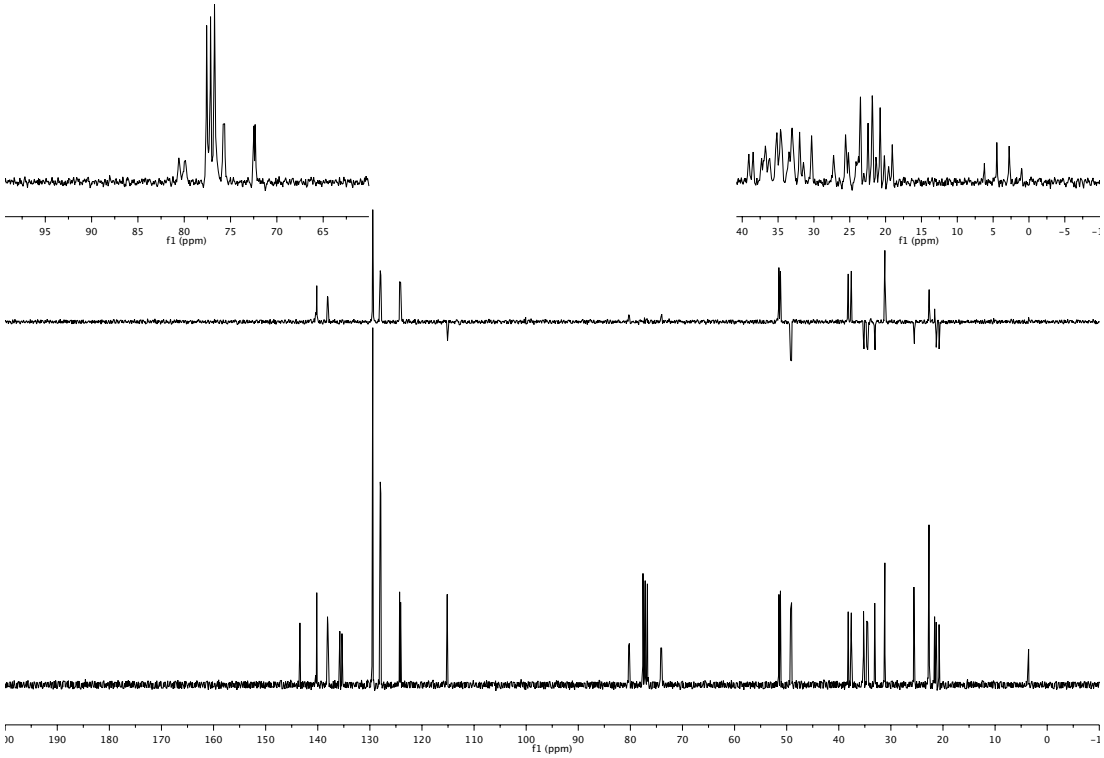



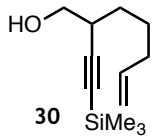


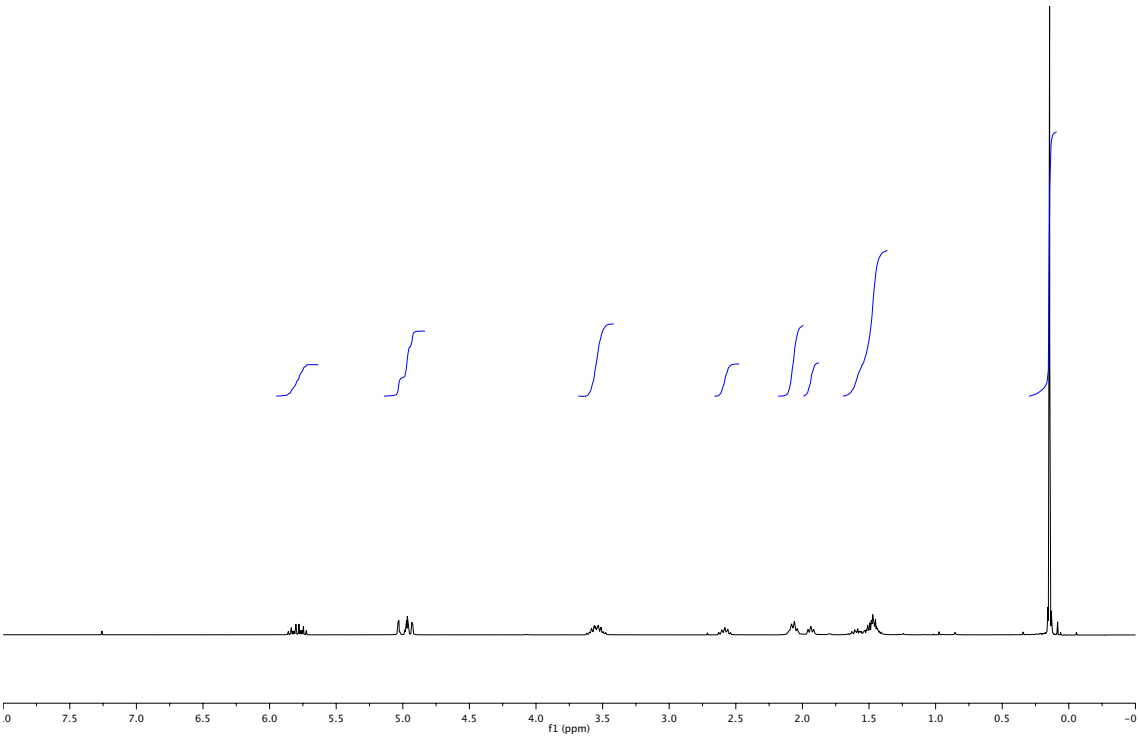

**4c**




**$^{1}$H-coupled $^{13}$C-NMR** **$^{1}$H-coupled $^{13}$C-NMR**




HO
30
SiMe3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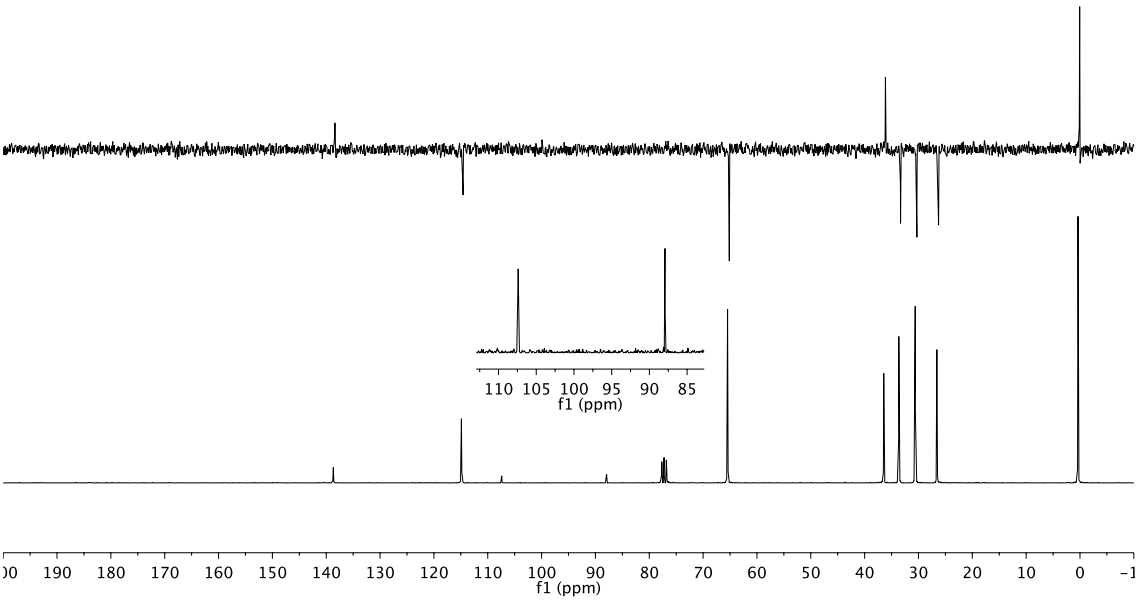
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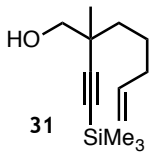
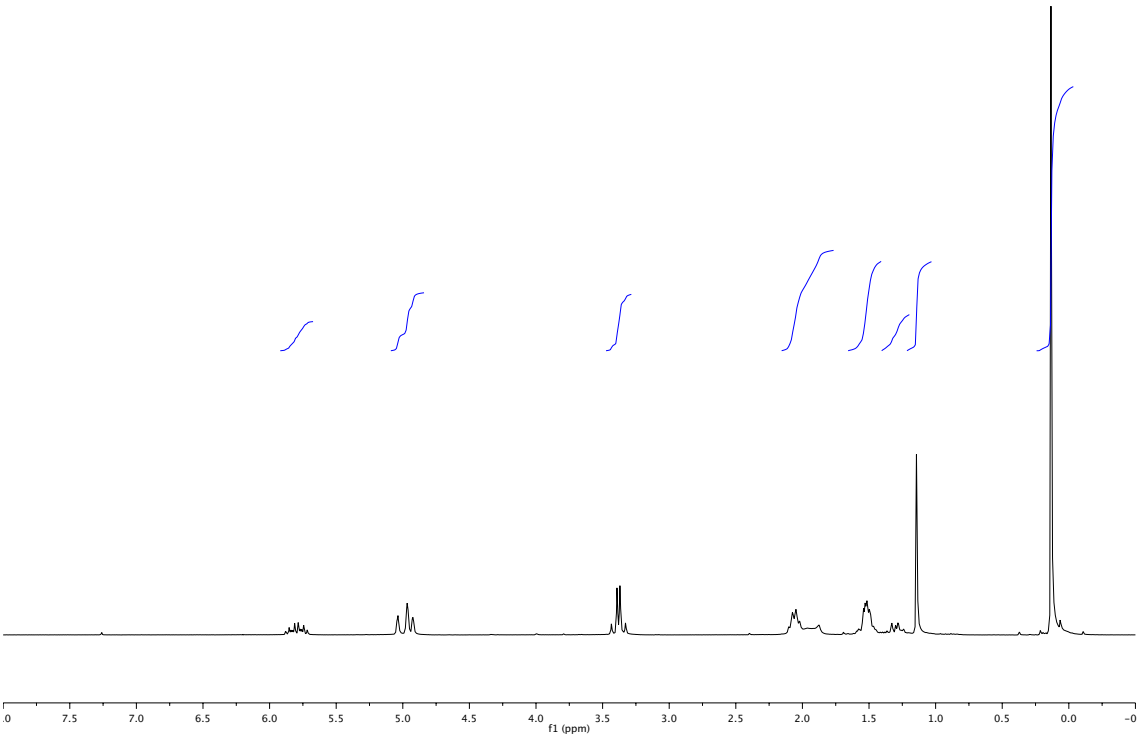
f1 (ppm)


HO
31
SiMe3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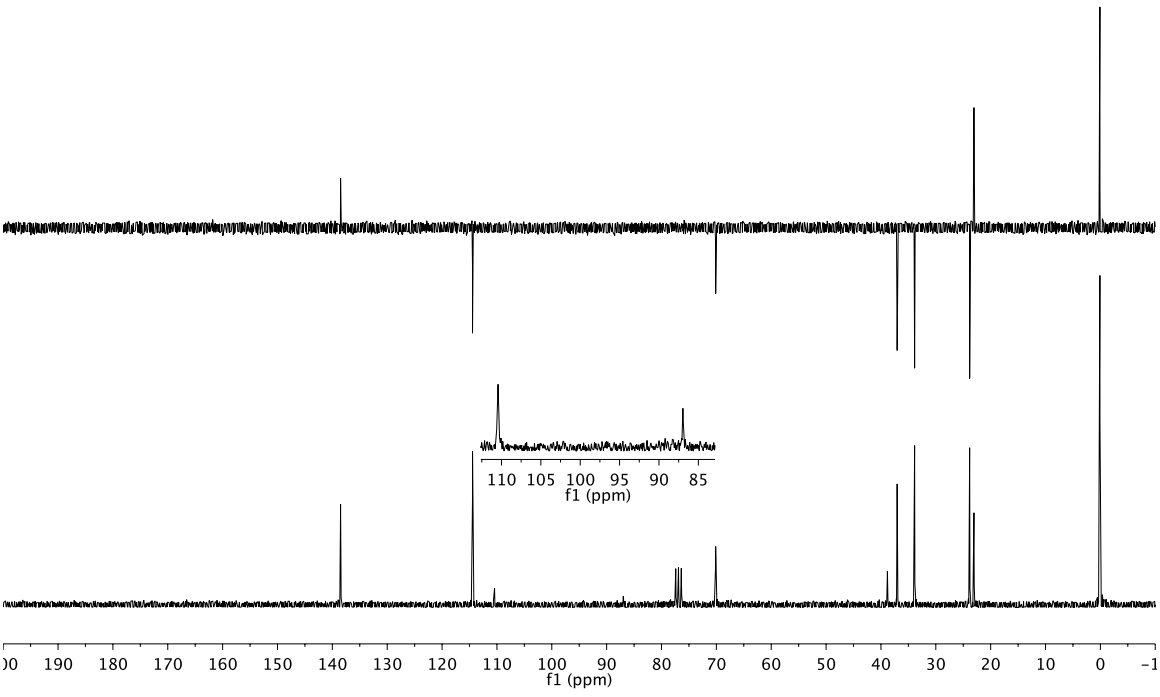
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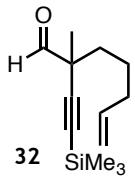
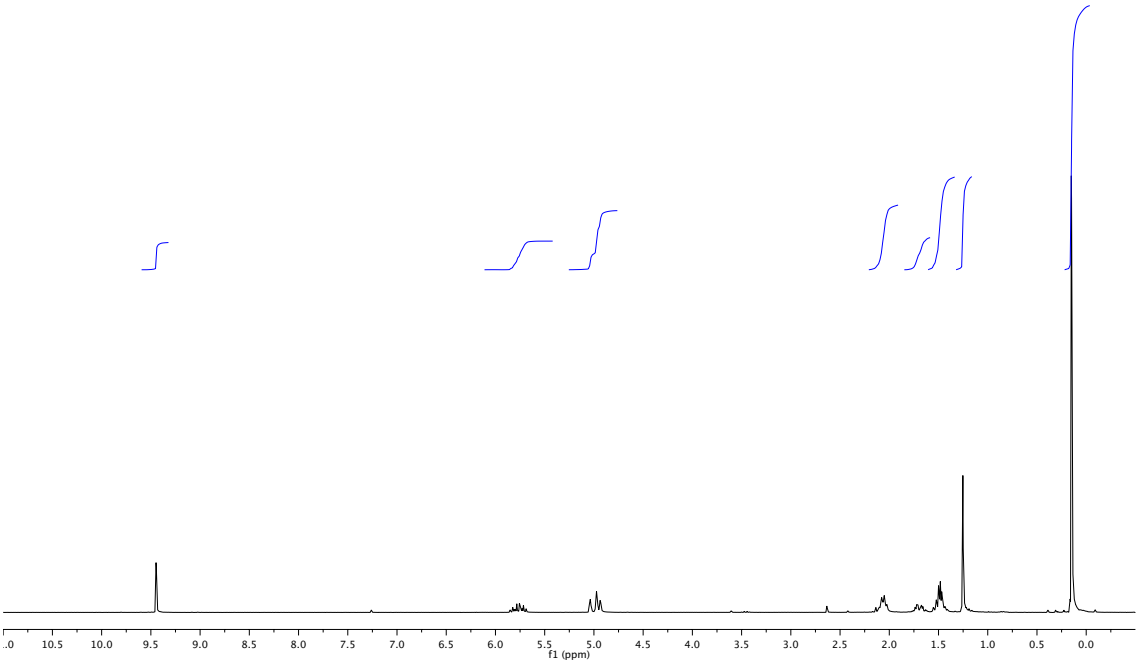
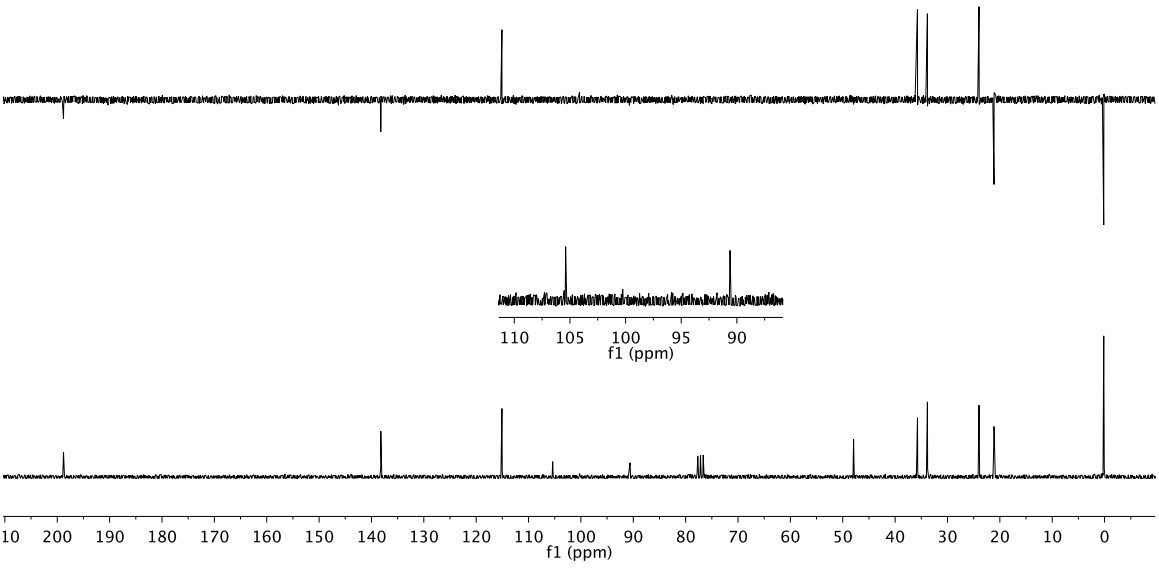
f1 (ppm)
f1 (ppm)


O
H
32
SiMe3


f1 (ppm)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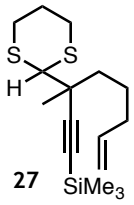
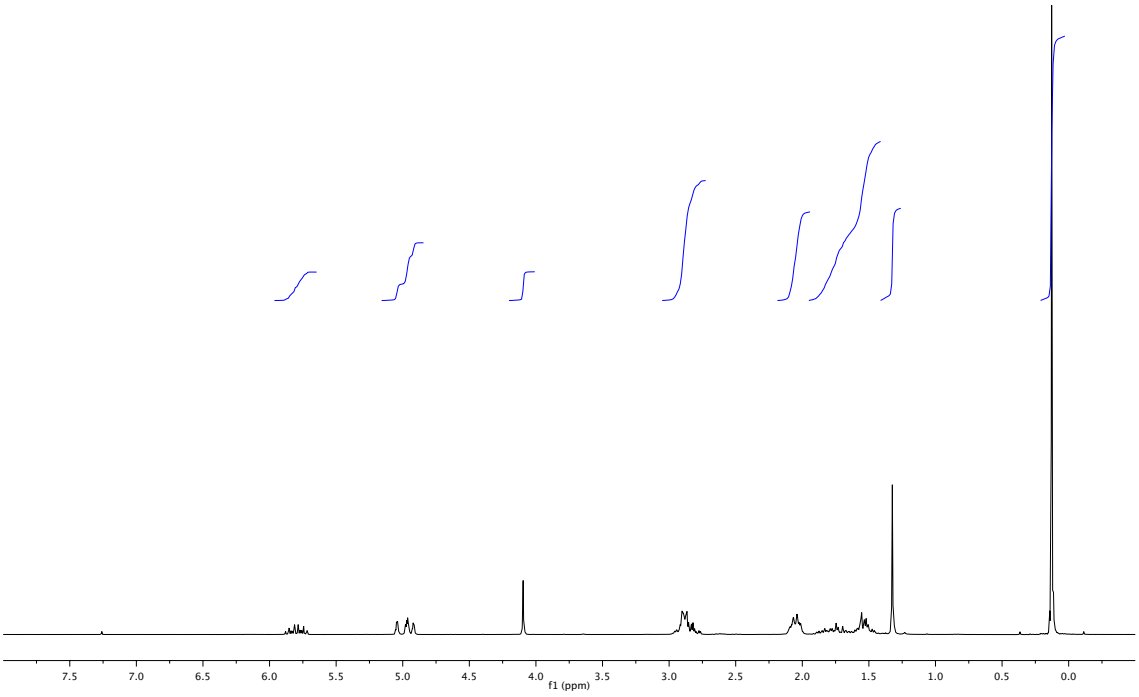
f1 (ppm)
f1 (ppm)


S
S
H
SiMe3

**27**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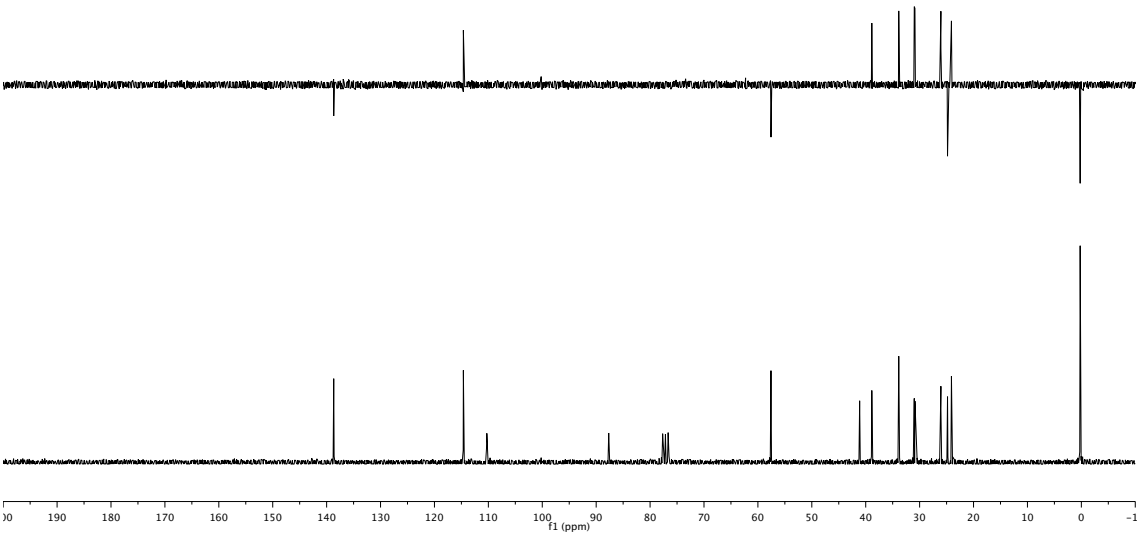
f1 (ppm)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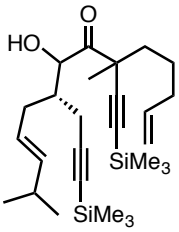
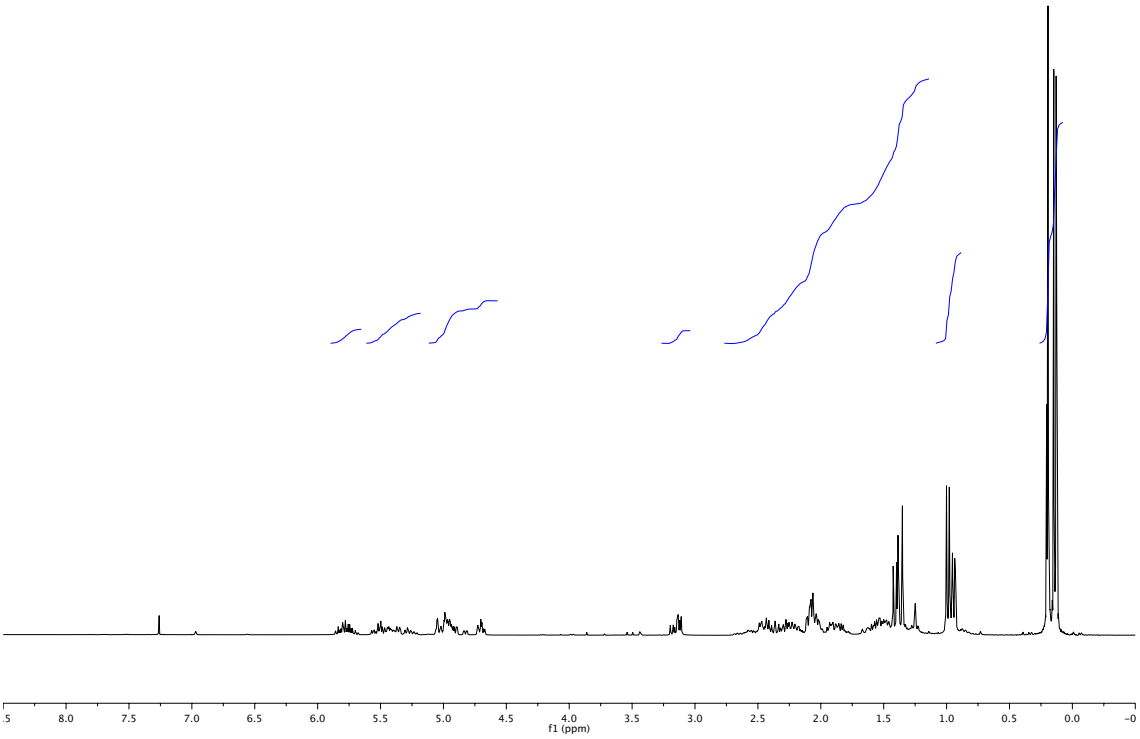
f1 (ppm)


HO
O
SiMe3
SiMe3

**35**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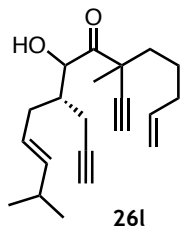
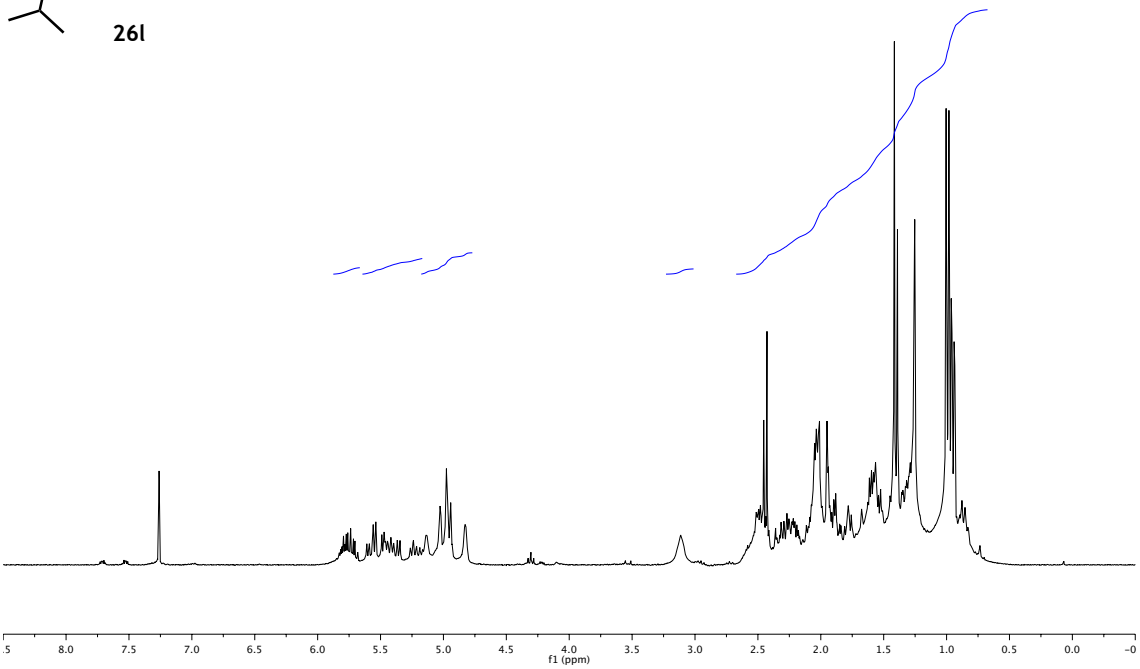
0.5
0.0
f1 (ppm)


HO
O

**26l**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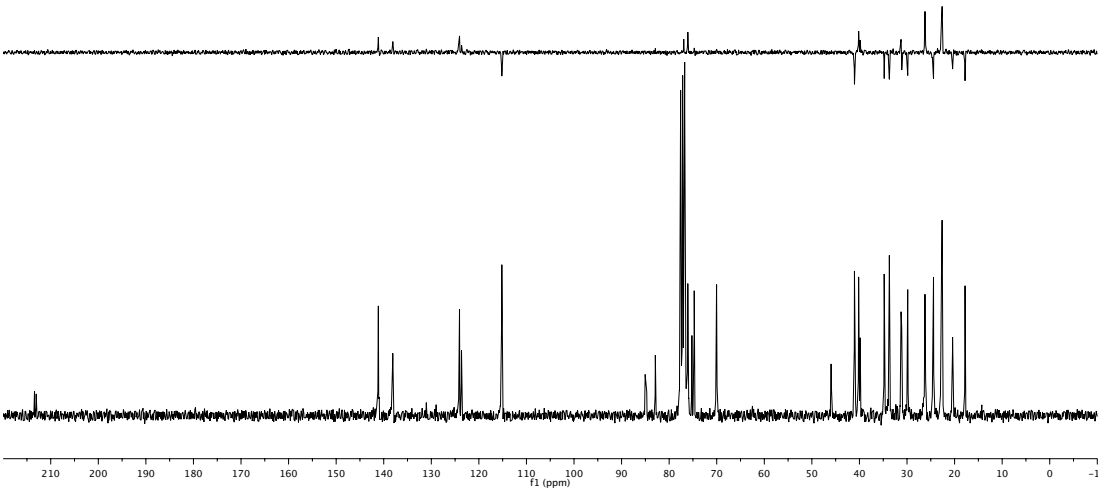
f1 (ppm)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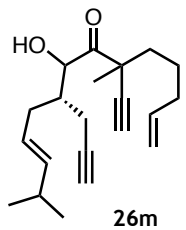
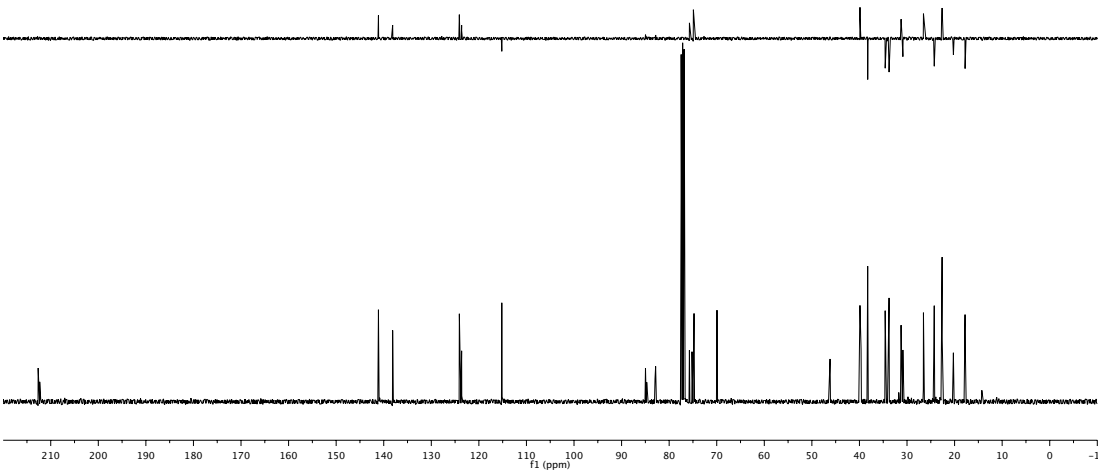
10
0
f1 (ppm)


HO
O

**26m**


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)