Electronic Supplementary Information (ESI)

One-step Formation of Fused Tetracyclic Skeletons from Cyclohexene-diynes and Carbon Monoxide through Rh(I)-Catalyzed [2+2+2+1] Cycloaddition Reaction

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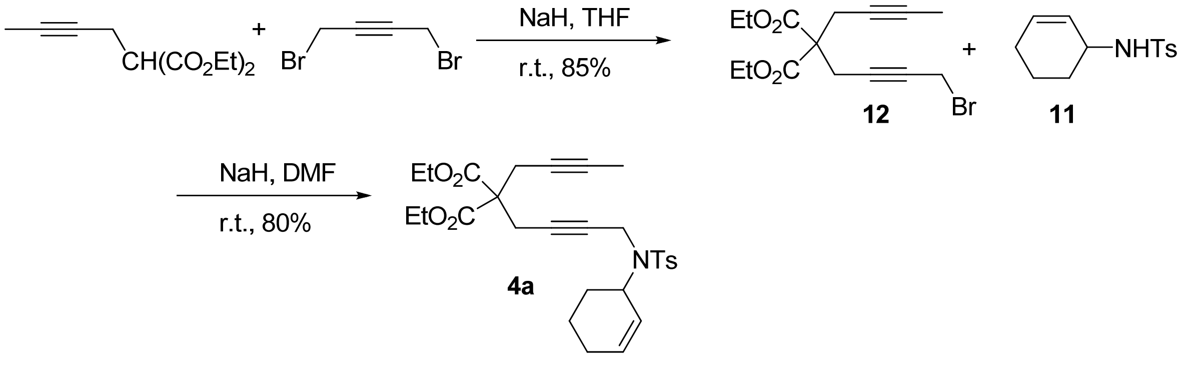
Contents:

General Methods. All reactions were carried out under nitrogen or carbon monoxide in oven dried glassware using standard Schlenk techniques unless otherwise noted. All reactions were monitored by thin layer chromatography (TLC) using E. Merck 60F254 precoated silica gel plates. Flash chromatography was performed with the indicated solvents using Fisher silica gel (particle size 170-400 Mesh). Yields refer to chromatographically and spectroscopically pure compounds. Analytical high performance liquid chromatography (HPLC) was performed with a Shimadzu LC 2010A system using a phenomenex Jupiter 10μ proteo 90A column (4.5 x 250 mm/mm) and gradient from 100% acetonitrile to 95:5 acetonitrile:water over 24 min with a flow rate of 1mL/min. Preparative HPLC was carried out on a Shimadzu semi-preparative LC-6AD HPLC system using a phenomenex Jupiter 10μ proteo 90A column (21.2 x 250 mm/mm) and gradient from 100% acetonitrile to 95:5 acetonitrile:water over 24 min with a flow rate of 20 mL/min. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Shimadzu FTIR-84005 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova-400 (400 MHz) or a Gemini-300 (300 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform (δ = 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova-400 (100 MHz) or a Gemini-300 (75 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform (δ = 77.0 ppm). High resolution mass spectrometry (HRMS) was carried out at the Mass Spectrometry Facility, the University of Illinois Urbana Champaign. **Caution:** Carbon monoxide is a toxic gas and thus all reactions should be carried out in a fume hood with sufficient ventilation.

Materials. Solvents were reagent grade and freshly distilled before use. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from DrySolv® and used without further purification. Dichloroethane (DCE) and trifluoroethanol (TFE) were purchased from Aldrich and used without purification. Carbon monoxide was purchased from Liquid Carbonic Specialty Gases, Oak Brook, Illinois and passed through Drierite® before use. $[Rh(CO)_2Cl]_2$ was prepared by the literature method.[1]

1-Aza-1-(cyclohex-2-en-1-yl)-6,6-dicarbethoxy-1-(4-methylbenzenesulfonyl)nona-3,8-diyne (4a)



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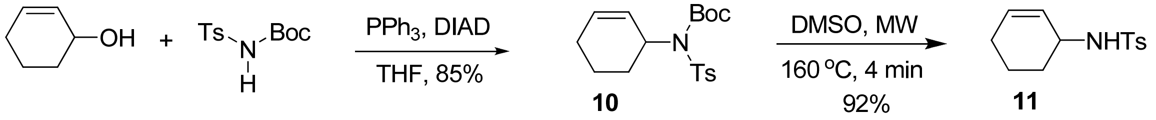
[1] J. A. McCleverty, and G. Wilkinson, *Inorg. Syn.*, **8**, 211-214.

(i) *Preparation of N-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide* (**11**)



A mixture of triphenylphosphine (4.41 g, 16.83 mmol) and diisopropylazodicarboxylate (DIAD) (3.58 g, 16.83 mmol) in THF (50 cm^3) was stirred for 10 min until a precipitate formed. Then, *N*-Boc-*N*-tosylamide (4.15 g, 15.28 mmol) in 30 cm^3 of THF was added dropwise, followed by cyclohex-3-enol (1.50 g, 15.28 mmol) in 30 cm^3 of THF. The resulting mixture was stirred overnight. The mixture was concentrated and purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eleunt to give **10** (4.57 g, 85%) as a white solid. This product (6.14 g, 17.47 mmol) was dissolved in DMSO (30 cm^3) and heated in a microwave reactor at 160 ^{o}C for 4 min. Water was added and the mixture extracted with ether (3 x 50 mL). The organic layers were combined, washed with water, brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eleuent to give **11** (4.04 g, 92%) as a white solid; mp 100 -101 ^{o}C (lit.[2,3] 101-102 ^{o}C). All spectral data were consistent with that reported in the literature.[3] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60-1.52 (m, 3H), 1.79-1.76 (m, 1H), 1.93-1.91 (m, 2H), 2.43 (s, 1H), 3.85-3.79 (m, 1H), 4.48 (d, 1H, *J* = 8.4 Hz), 5.37-5.32 (m, 1H), 5.78-5.74 (m, 1H), 7.32 (d, 2H, *J* = 8.7 Hz), 7.78 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.27 (CH_2), 21.51 (CH_3), 24.48 (CH_2), 30.28 (CH_2), 48.96 (CH), 126.97 (CH), 127.03 (CH), 129.68 (CH), 131.59 (CH), 138.37 (C), 143.24 (C).

(ii) *Preparation of diethyl 2-(but-2-ynyl)-2-(4-bromobut-2-yn-1-yl)malonate (**12**)*:

Diethyl 2-(but-2-ynyl)malonate[4] (5.00 g, 23.6 mmol) was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 1.00 g, 23.6 mmol) in 80 cm^3 of THF. The resulting mixture was stirred for 1 h at room temperature. The mixture was then transferred to a solution of 1,4-dibromobut-2-yne (15.00 g, 70.7 mmol) in 100 cm^3 of THF *via* canula over 2.5 h. The mixture was then stirred at room temperature for 18 h. The mixture was diluted with water and extracted with ether. The organic layer was dried over $MgSO_4$, filtered and concentrated to yield yellow oil. The excess dibromobutyne was recovered by distillation (100 ^{o}C/4 mmHg). The residue was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent to give product **12** as yellow oil (6.88 g, 85%); TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.52$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, 6H, *J* = 7.2 Hz), 1.75 (t, 2H, *J* = 2.7 Hz), 2.88 (q, 2H, *J* = 2.7 Hz), 3.02 (t, 2H, *J* = 2.1 Hz), 3.87 (t, 2H, *J* = 2.1 Hz), 4.25 (q, 4H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.45 (CH_3), 14.02 (CH_3), 14.69 (CH_2), 22.74 (CH_2), 22.99 (CH_2), 56.70 (C), 61.69 (CH_2), 61.87 (CH_2), 72.94 (C), 78.20 (C), 79.14 (C), 82.23 (C), 168.86 (C).

(iii) *Preparation of **4a** through coupling of **11** and **12***:

N-Cyclohexenyl-*N*-tosylamide **11** (0.40 g, 1.59 mmol) in 4 cm^3 of DMF was added dropwise to a suspension of NaH, (60% dispersion in mineral oil, 82 mg, 2.07 mol) in 3 cm^3 of DMF. The resulting solution was stirred at room temperature for 45 min and then **12** (0.55 g, 1.59 mmol) in 5 cm^3 of DMF was added dropwise and the mixture was stirred for an additional 5 h. Water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave cyclohexenediyne **4a** as light yellow oil (0.65 g,

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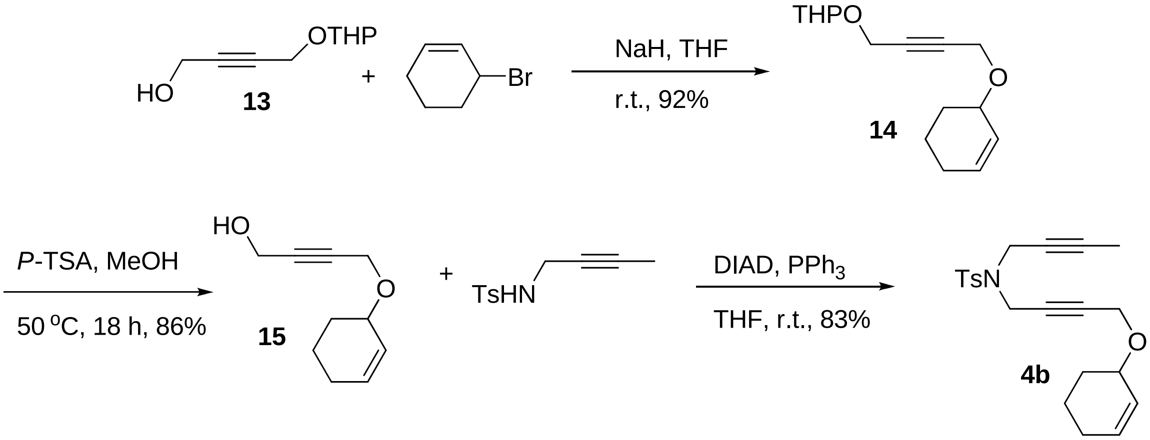
[2] K.B. Sharpless and T. Hori, *J. Org. Chem.* 1976, **41,** 176-177.
[3] J.G. Taylor, N. Whittall and K.K. Hii, *Org. Lett.* 2006, **8**, 3561-3564.
[4] K.M. Brummond, H. Chen, P. Sill and L. You, *J. Am. Chem. Soc.* 2002, **124**, 15186-15187.

80 %); TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.46$); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.24-1.21 (m, 6H), 1.48-1.55 (m, 2H), 1.74-1.67 (m, 5H), 1.94-1.93 (m, 2H), 2.42 (s, 3H) 2.79 (t, 2H, *J* = 2.0 Hz), 2.86 (t, 2H, *J* = 2.0 Hz), 3.90 (dt, 1H, *J* = 2.0 Hz), 4.10 (dt, 1H, *J* = 2.0 Hz), 4.22-4.15 (m, 4H), 4.43-4.40 (m, 1H), 5.30 (d, 1H, *J* = 10.4 Hz), 5.86-5.83 (m, 1H), 7.30 (d, 2H, *J* = 8.8 Hz), 7.78 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.42 (CH_3), 13.95 (CH_3), 21.45 (CH_3), 22.70 (CH_2), 22.75 (CH_2), 22.88 (CH_2), 24.32 (CH_2), 27.86 (CH_2), 32.89 (CH_2), 54.87 (CH), 56.55 (C), 61.66 (CH_2), 61.70 (CH_2), 73.09 (C), 78.42 (C), 78.83 (C), 79.89 (C), 127.28 (CH), 127.35 (CH), 129.39 (CH), 132.74 (CH), 138.13 (C), 142.99 (C), 168.93 (C); IR (neat, cm^{-1}) 2979, 2921, 1734, 1326, 1290, 1209, 1161, 1095, 1051; HRMS (ES) m/z calcd for $C_{28}H_{36}NO_6S$ $(M + H)^+$ 514.2263, found 514.2255 (Δ = -0.8 ppm).

6-Aza-1-(4-cyclohex-2-en-1-yl)-6-(4-methylbenzenesulfonyl)-1-oxadeca-3,8-diyne (4b)



1-Tetrahydropyranyl(THP)butyne-1,4-diol[5] (**13**) (775 mg, 4.56 mmol) in 15 cm^3 of THF was added dropwise to a suspension of NaH, (60% dispersion in mineral oil, 237 mg, 5.93 mmol) in THF (5 cm^3). The resulting solution was stirred at room temperature for 30 min and then 3-bromocyclohex-1-ene (734 mg, 4.56 mmol) in 10 cm^3 of THF was added dropwise and the mixture was stirred overnight. Water was added and the mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave 1-THP-4-(cyclohex-2-en-1-yl)but-2-yne-1,4-diol (**14**) (1.05 g, 92%) as light yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.64); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.84-1.49 (m, 10H), 1.98-1.95 (m, 1H), 2.04-2.00 (m, 1H), 3.54-3.49 (m, 1H), 3.86-3.80 (m, 1H), 4.07-4.05 (m, 1H), 4.24-4.23 (m, 2H), 4.28-4.27 (m, 1H), 4.32-4.30 (m, 1H), 4.81 (t, 1H, *J* = 3.2 Hz), 5.79-5.74 (m, 1H), 5.89-5.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.04 (CH_2), 19.06 (CH_2), 25.15 (CH_2), 25.33 (CH_2), 28.04 (CH_2), 30.23 (CH_2), 54.43 (CH_2), 55.56 (CH_2), 62.01 (CH_2), 71.67 (CH), 81.74 (C), 82.58 (C), 96.83 (CH), 127.13 (CH), 131.41 (CH).

p-Toluenesulfonic acid (*p*-TSA, 372 mg, 1.96 mmol) was added to a solution of eneyne-THP ether **14** (980 mg, 3.91 mmol) in MeOH (50 cm^3). The solution was then heated at 50 °C overnight. The solution was cooled to room temperature and then solid $NaHCO_3$ was added portionwise. The mixture was then diluted with water and extracted with ether. The organic layer was washed with sat. $NaHCO_3$, water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 25% EtOAc in hexanes as eluent gave 1-(cyclohex-2-en-1-yl)but-2-yne-1,4-diol **(15)** (559 mg, 86 %) as yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.24); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59- 1.54 (m, 1H), 1.83-1.64 (m, 3H),

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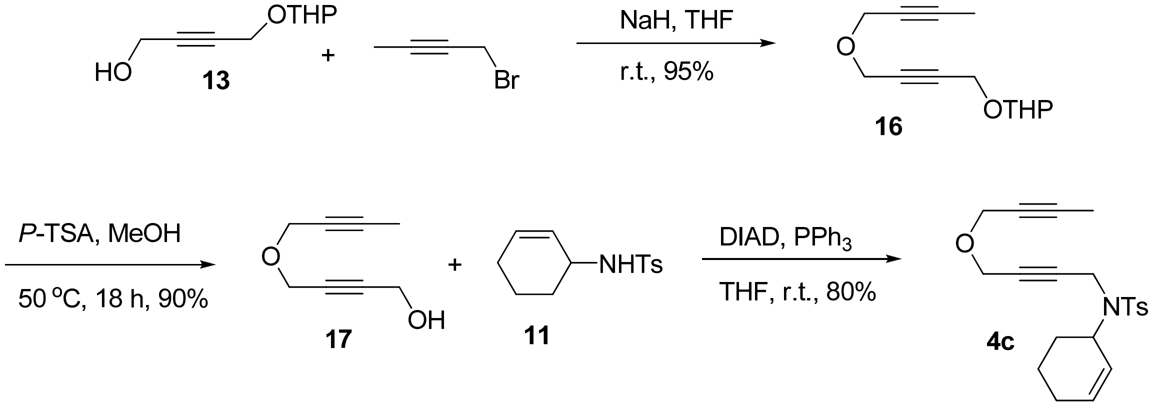
[5] A.T. Khan, L.H. Choudhury and S. Ghosh, *Tetrahedron Lett.* 2004, **45**, 7891-7894.

2.04-1.95 (m, 2H), 4.07-4.03 (m, 1H), 4.24-4.17 (m, 2H), 4.31-4.29 (m, 2H), 5.79-5.74 (m, 1H), 5.90-5.85 (m, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 19.01 (CH$_2$), 25.13 (CH$_2$), 28.00 (CH$_2$), 51.11 (CH$_2$), 55.47 (CH$_2$), 71.87 (CH), 82.37 (C), 84.07 (C), 126.96 (CH), 131.57 (CH).

Diisopropyl azodicarboxylate (DIAD) (694 mg, 3.26 mmol) was added to a solution of triphenylphosphine (856 mg, 3.26 mmol) in 10 cm^3 of THF. After formation of a solid, *N*-(but-2-ynyl)-*N*-(4-methylbenzene)sulfonamide (583 mg, 2.61 mmol) in 10 cm^3 of THF was added, followed by the addition of eneynol **15** (434 mg, 2.61 mmol) in 5 cm^3 of THF. The resulting mixture was stirred overnight and then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eleuent to give **4b** (802 mg, 83%) as colorless oil; TLC (SiO$_2$, hexanes:EtOAc = 3:1, $R_f = 0.48$); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.61-1.55 (m, 1H), 1.65-1.63 (m, 4H), 1.75-1.67 (m, 2H), 2.03-1.96 (m, 2H), 2.41 (s, 3H), 3.92 (m, 1H), 4.08 (m, 4H), 4.17(t, 2H, J = 1.8 Hz), 5.71-5.66 (1H), 5.88-5.83 (m, 1H), 7.30 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 3.36 (CH$_3$), 18.97 (CH$_2$), 21.50 (CH$_3$), 25.13 (CH$_2$), 27.99 (CH$_2$), 36.51 (CH$_2$), 36.79 (CH$_2$), 55.28(CH$_2$), 71.43 (C), 71.59 (C), 78.42 (CH), 81.89 (C), 82.25 (C), 126.96 (CH), 127.97 (CH), 129.33 (CH), 131.50 (CH), 135.48 (C), 143.56 (C); IR (neat, cm^{-1}) 3026, 2929, 2179, 1596, 1350, 1163; HRMS (ES) m/z calcd for $C_{21}H_{26}NO_3S$ $(M + H)^+$ 372.1633, found 372.1638 (Δ = 0.5 ppm).

1-(Cyclohex-3-en-1-yl)-1-(4-methylbenzenesulfonyl)-6-oxadeca-3,8-diyne (4c)

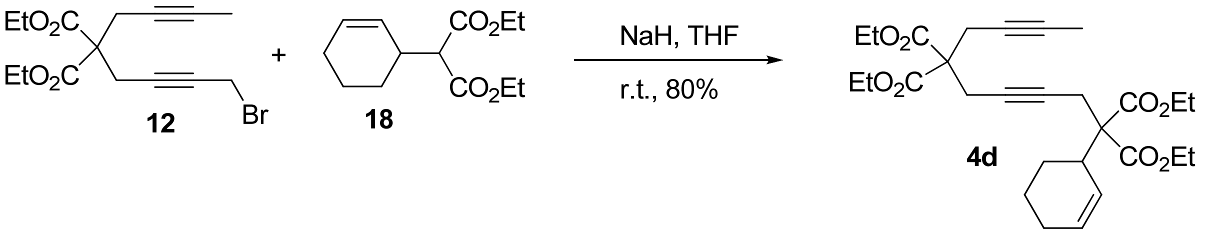


1-Tetrahydropyranyl(THP)-butynediol **13** (2.00 g, 11.75 mmol) in 25 cm^3 of THF was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 0.611 g, 15.28 mmol) in THF (10 cm^3). The resulting solution was stirred at room temperature for 30 min and then 1-bromobut-2-yne (1.56 g, 11.75 mmol) in 15 cm^3 of THF was added dropwise and the mixture was stirred overnight. Water was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave 1-THP-*O*-5-oxanona-2,7-diyne (**16**, 2.48 g, 95%) as light yellow oil; TLC (SiO$_2$, hexanes:EtOAc = 2:1, $R_f = 0.66$); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.65 (m, 4H), 1.81 (m, 2H), 1.85 (t, 3H, J = 2.4 Hz), 3.55-3.50 (m, 1H), 3.86-3.78 (m, 1H), 4.19 (q, 2H, J = 2.4 Hz), 4.31-4.27 (m, 3H), 4.35 (t, 1H, J = 1.8 Hz), 4.80 (t, 1H, J = 2.4 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 3.56 (CH$_3$), 19.01 (CH$_2$), 25.32 (CH$_2$), 30.21 (CH$_2$), 54.24 (CH$_2$), 56.63 (CH$_2$), 57.13 (CH$_2$), 61.98 (CH$_2$), 74.31 (C), 81.34 (C), 82.68 (C), 83.08 (C), 96.83 (CH).

p-Toluenesulfonic acid (*p*-TSA) (1.28 g, 6.73 mmol) was added to a solution of **16** (2.35 g, 10.57 mmol) in MeOH (40 cm^3). The solution was then heated at 50 °C overnight. The resulting solution was cooled to room temperature and then solid NaHCO$_3$ was added portionwise. The mixture was diluted with water and extracted with ether. The organic layer was washed with sat. $NaHCO_3$, water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 25% EtOAc in hexanes as eluent gave 1-hydroxy-5-oxanona-2,7-diyne (**17**) (1.32 g, 90%) as yellow oil. TLC (SiO_2, hexanes:EtOAc = 2:1, $R_f = 0.30$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.81 (t, 3H, *J* = 1.2 Hz), 3.01 (bs, 1H), 4.16 (q, 2H, *J* = 1.2 Hz), 4.22 (t, 2H, *J* = 1.8 Hz), 4.25 (t, 2H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.53 (CH_3), 50.97 (CH_2), 56.50 (CH_2), 57.17 (CH_2), 74.15 (C), 81.09 (C), 83.23 (C), 84.92 (C).

DIAD (614 mg, 3.04 mmol) was added to a solution of triphenylphosphine (796 mg, 3.04 mmol) in 10 cm^3 of THF. After formation of a solid, **11** (637 mg, 2.53 mmol) in 10 cm^3 of THF and then hydroxydiyne **17** (350 mg, 2.53 mmol) in 10 cm^3 of THF were added. The resulting mixture was stirred overnight and then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eleuent to give **4c** (752 mg, 80%) as light yellow viscous oil; TLC (SiO_2, hexanes:EtOAc = 2:1, $R_f = 0.52$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.55-1.61 (m, 2H), 1.79-1.69 (m, 2H), 1.87 (t, 3H, *J* = 2.4 Hz), 1.97-1.93 (m, 2H), 2.42 (s, 3H), 3.99 (dt, 1H, *J* = 2.1 Hz), 4.09 (q, 2H, *J* = 2.4 Hz), 4.18-4.12 (m, 3H), 4.55-4.48 (m, 1H), 5.32 (d, 1H, *J* = 10.3 Hz), 5.85-5.83 (m, 1H), 7.31 (d, 2H, *J* = 8.4 Hz), 7.81 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.57 (CH_3), 21.42 (CH_3), 21.48 (CH_2), 24.34 (CH_2), 27.98 (CH_2), 32.94 (CH_2), 55.03 (CH), 56.52 (CH_2), 56.96 (CH_2), 74.31 (C), 79.19 (C), 82.97 (C), 83.32 (C), 127.19 (CH), 127.38 (CH), 129.40 (CH), 133.01 (CH), 138.12 (C), 143.11 (C); IR (neat, cm^{-1}) 2921, 1627, 1340, 1161, 1095, 1074, 1031; HRMS (ES) m/z calcd for $C_{21}H_{26}NO_3S$ $(M + H)^+$ 372.1633, found 372.1648 (Δ = 1.5 ppm).

1-(Cyclohex-2-en-1-yl)-,1,16,6-tetracarbethoxydeca-3,8-diyne (4d)



Diethyl 2-(cyclohex-2-en-1-yl)malonate[6] (**18**) (0.65 g, 2.73 mmol) in 10 cm^3 of THF was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 0.13 g, 3.28 mmol) in THF (10 cm^3). The resulting solution was stirred at room temperature for 30 min and then **12** (0.94 g, 2.73 mmol) in 10 cm^3 of THF was added dropwise and the mixture was stirred for additional 5 h. Water was added and the mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave **4d** (1.10 g, 80%) as yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.52$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28-1.20 (m, 12H), 1.59-1.52 (m, 2H), 1.74 (t, 3H, *J* = 2.7 Hz), 1.80-1.76 (m, 2H), 1.94-1.90 (m, 2H), 2.82 (dt, 2H, *J* = 2.4 Hz), 2.90-2.85 (m, 4H), 3.08-3.03 (m, 1H), 4.25-4.12 (m, 8H), 5.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.44 (CH_3), 13.97 (CH_3), 14.01 (CH_3), 14.05 (CH_3), 22.25 (CH_2), 22.70 (CH_2), 22.76 (CH_2), 24.16 (CH_2), 24.89 (CH_2), 38.35 (CH), 56.71 (C), 60.06 (C), 61.16 (CH_2), 61.22 (CH_2), 61.68 (CH_2), 73.24 (C), 77.41 (C), 78.35 (C), 78.72 (C), 128.01 (CH), 128.47 (CH), 169.04 (C), 169.72 (C), 169.88 (C); IR (neat, cm^{-1}) 3033, 2979, 2935, 2181, 1737, 1733, 1367, 1193; HRMS (ES) m/z calcd for $C_{28}H_{39}O_8$ $(M + H)^+$ 503.2645, found 503.2638 (Δ = -0.7 ppm).

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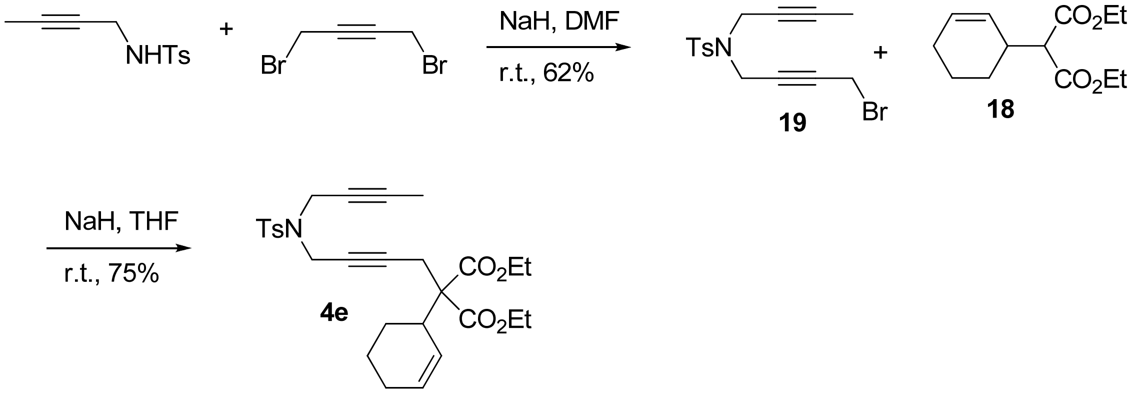
[6] F.A. Hicks, N.M. Kablaoui and S.L. Buchwald, *J. Am. Chem. Soc.* 1999, **121**, 5881-5898.

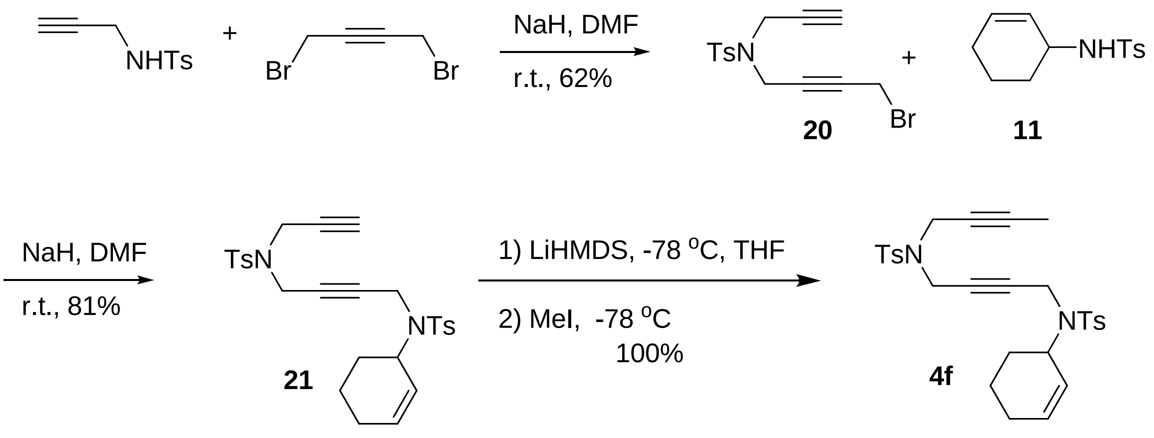
6-Aza-1-(cyclohex-2-en-1-yl)-,1,1-dicarbethoxy-6-(4-methylbenzenesulfonyl)deca-3,8-diyne (4e)



N-(But-2-ynyl)-4-methylbenzenesulfonamide (500 mg, 2.24 mmol) in 5 cm^3 of DMF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 107 mg, 2.69 mmol) in 5 cm^3 of DMF. The resulting mixture was stirred for 1 h at room temperature. The mixture was then transferred to a solution of 1,4-dibromobut-2-yne (1.50 g, 7.07 mmol) in 5 cm^3 of DMF via cannula and the resulting mixture stirred at room temperature for 18 h. The mixture was diluted with water and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated to yield yellow oil. The excess dibromobutyne was recovered by distillation (100 ^{o}C/4 mmHg). The residue was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent to give bromodiyne **19** as viscous yellow oil (490 mg, 62%). TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.50$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (t, 3 H, J = 2.4 Hz), 2.43 (s, 3 H), 3.72 (t, 2 H, J = 2.1 Hz), 4.06 (q, 2 H, J = 2.4 Hz), 4.21 (d, 2 H, J = 2.1 Hz), 7.32 (d, 2 H, J = 8.4 Hz), 7.72 (d, 2 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.38 (CH_3), 13.69 (CH_2), 21.51 (CH_3), 36.49 (CH_2), 36.96 (CH_2), 71.33 (C), 79.63 (C), 80.43 (C), 82.02 (C), 127.89 (CH), 129.42 (CH), 135.30 (C), 143.72 (C).

Diethyl 2-(cyclohex-2-enyl)malonate **18** (0.41 g, 1.69 mmol) in 5 cm^3 of THF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 88 mg, 2.20 mmol) in THF (5 cm^3). The resulting solution was stirred at room temperature for 30 min and then bromodiyne **19** (0.60 g, 1.69 mmol) in 5 cm^3 of THF was added dropwise and the mixture was stirred for an additional 5 h. Water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave **4e** (0.65 g, 75%) as a white solid; mp 69-70 ^{o}C; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.40$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29-1.19 (m, 7H), 1.54-1.48 (m, 1H), 1.62 (t, 3 H, J = 2.4 Hz), 1.76-1.69 (m, 2H), 1.94-1.91 (m, 2H), 2.41 (s, 3H), 2.69 (dt, 1H, J = 2.1 Hz), 2.78 (dt, 1H, J = 2.1 Hz), 3.02-2.98 (m, 1H), 4.07-4.02 (m, 4H), 4.22-4.12 (m, 4H), 5.70-5.64 (m, 2H), 7.32 (d, 2H, J = 8.7 Hz), 7.70 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.31 (CH_3), 14.04 (CH_3), 21.47 (CH_3), 22.24 (CH_2), 22.52 (CH_2), 24.16 (CH_2), 24.84 (CH_2), 36.46 (CH_2) 36.52 (CH_2), 38.63 (CH), 59.94 (C), 61.29 (CH_2), 61.33 (CH_2), 71.39 (C), 75.53 (C), 81.30 (C), 81.64 (C), 127.66 (CH), 127.89 (CH), 128.71 (CH), 129.29 (CH), 135.49 (C), 143.47 (C), 169.54 (C), 169.73 (C); IR (in $CHCl_3$, cm^{-1}) 2979, 2933, 2178, 1726, 1352, 1163; HRMS (ES) m/z calcd for $C_{28}H_{36}NO_6S$ $(M + H)^+$ 514.2263, found 514.2261 (Δ - 0.2 ppm).

1,6-Bis(4-methylphenylsulfonyl)-1-(cyclohex-2-en-1-yl)- 1,6-diazadeca-3,8-diyne (4f)



N-(Prop-2-ynyl)-4-methylbenzenesulfonamide[7] (4.30 g, 20.05 mmol) in 25 cm^3 of DMF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 1.15 g, 28.70 mmol) in 40 cm^3 of DMF. The resulting mixture was stirred for 1 h at room temperature. The mixture was then transferred to a solution of 1,4-dibromobut-2-yne (13.05 g, 61.5 mmol) in 20 cm^3 of DMF via cannula. The mixture was then stirred at room temperature for 18 h. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated to yield yellow oil. The excess dibromobutyne was recovered by distillation (100 $^oC/4$ mmHg). The residue was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent to give bromodiyne **20** as a yellow oil (4.23 g, 62%); TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.48); ^1H NMR (300 MHz, $CDCl_3$) δ 2.08 (t, 1 H, *J* = 2.4 Hz), 2.43 (s, 3 H), 2.44 (s, 3 H), 3.71 (d, 2 H, *J* = 6.6 Hz), 3.89 (d, 2 H, *J* = 2.4 Hz), 3.90 (d, 1 H, *J* = 2.4 Hz), 3.91 (d, 1 H, *J* = 2.4 Hz), 3.96 (d, 1 H, *J* = 2.4 Hz), 3.97 (d, 1 H, *J* = 2.4 Hz), 5.18 (dd, 1 H, *J* = 1.5 Hz / *J* = 11.4 Hz), 5.20 (dd, 1 H, *J* = 1.5 Hz / *J* = 17.7 Hz), 5.68 (ddt, 1 H, *J* = 11.4 Hz / *J* = 17.7 Hz / *J* = 6.6 Hz), 7.26 (d, 2 H, *J* = 12.6 Hz), 7.30 (d, 2 H, *J* = 16.8 Hz), 7.64 (d, 2 H, *J* = 13.5 Hz), 7.68 (d, 2 H, *J* = 13.5 Hz).

Cyclohexenylsulfonamide **11** (1.22 g, 4.84 mmol) in 10 cm^3 of DMF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 0.24 g, 6.05 mmol) in DMF (5 cm^3). The resulting solution was stirred at room temperature for 45 min and then bromodiyne **20** (2.06 g, 6.05 mmol) in 10 cm^3 of DMF was added dropwise and the mixture was stirred for an additional 5 h. Water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 15% EtOAc in hexanes as eluent gave cyclohexenediyne **21** (2.01 g, 81%) as a white solid: mp 96-98 ^oC; TLC (SiO_2, hexanes:EtOAc = 4:1, R_f = 0.25); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.69-1.54 (m, 2H), 1.75-1.71 (m, 2H), 1.95-1.92 (m, 2H), 2.09 (t, 1H, *J* = 2.7 Hz), 2.43 (s, 3H), 3.87 (dt, 1H, *J* = 2.4 Hz), 4.02 (dt, 1H, *J* = 2.4 Hz), 4.03 (d, 4H, *J* = 2.4 Hz), 4.43-4.47 (m, 1H), 5.27 (dd, 1H, *J* = 10.5, 1.8 Hz), 5.86-5.83 (m, 1H), 7.31 (dd, 4H, *J* = 9.0, 2.4 Hz), 7.76 (m 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.64 (CH_3), 21.78 (CH_3), 24.59 (CH_2), 28.18 (CH_2), 32.95 (CH_2), 36.34 (CH_2), 36.69 (CH_2), 55.18 (CH), 74.11 (C), 74.16 (C), 76.45 (C), 82.76 (C), 127.37 (CH), 127.52 (CH), 128.06 (CH), 129.79 (CH), 133.25 (CH), 135.45 (CH), 138.22 (CH), 143.57 (C), 144.19 (C); IR (in $CHCl_3$, cm^{-1}) 3272, 2929, 1596, 1448, 1350, 1163, 1095, 1031.

To a cold solution of **21** (0.50 g, 0.098 mmol) in 10 cm^3 of THF was added dropwise 1.2 M LiHMDS (1.63 cm^3) in THF at -78 ^oC. The resulting mixture was stirred at -78 ^oC for 45 min and then

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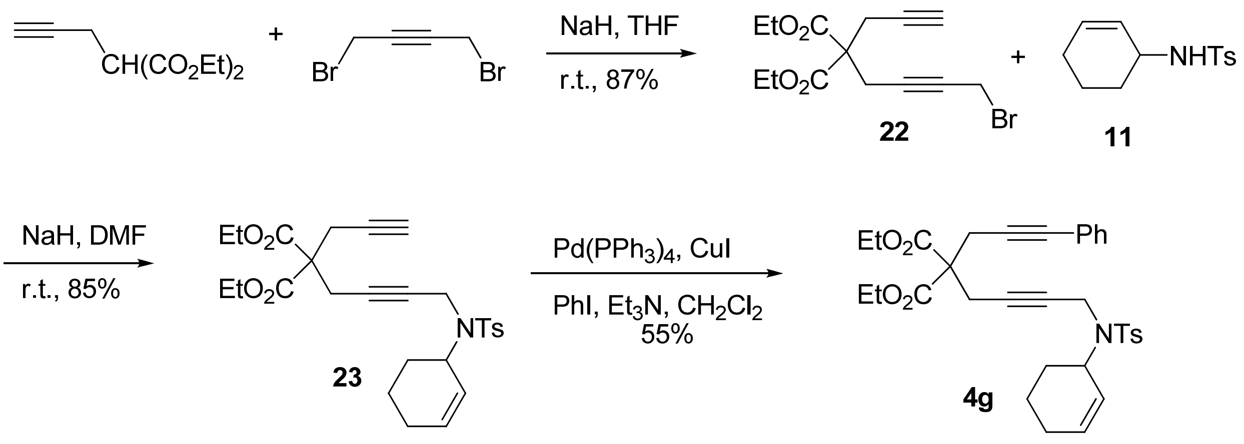
[7] S. Cerezo, J. Cortès, D. Galvan, E. Lago, C. Marchi, E. Molins, M. Moreno-Mañas, R.J.T. Pleixats and A. Vallribera, *Eur. J. Org. Chem.* 2001, **2001,** 329-337.

methyl iodide (0.56 g, 3.92 mmol) was added dropwise. The resulting mixture was warmed slowly to -40 °C and stirred for 4 h. The reaction mixture was diluted with ether, followed by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eleuent to give methyl-terminal cyclohexenediyne **4f** (0.513 g, 100% yield) as viscous yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.31$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.53-1.46 (m, 5H), 1.67-1.64 (m, 2H), 1.86 (bs, 2H), 2.34 (s, 6H), 3.76 (dt, 1H, $J = 2.4$ Hz), 3.92 (m, 5H), 4.38-4.37 (m, 1H), 5.22 (d, 1H, $J = 10.0$ Hz), 5.78-5.75 (m, 1H), 7.38 (d, 4H, $J = 8.0$ Hz), 7.62 (d, 2H, $J = 8.0$ Hz), 7.69 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.19 (CH_3), 21.24 (CH_3), 21.36 (CH_3), 24.19 (CH_2), 27.75 (CH_2), 32.62 (CH_2), 36.28 (CH_2), 36.52 (CH_2), 54.77 (CH), 71.11 (C), 76.44 (C), 81.71 (C), 82.03 (C), 126.96 (CH), 127.12 (CH), 127.74 (CH), 129.24 (CH), 129.39 (CH), 132.84 (CH), 135.19 (CH), 137.82 (CH), 143.19 (C), 143.56 (C); IR (in $CHCl_3$, cm^{-1}) 3028, 2921, 1627, 1596, 1348, 1161, 1095, 1031; HRMS (ES) m/z calcd for $C_{28}H_{33}N_2O_4S_2$ $(M + H)^+$ 525.1882, found 525.1902 (Δ 2.0 ppm).

1-Aza-1-(cyclohex-2-en-1-yl)-6,6,-dicarbethoxy-1-(4-methylbenzenesulfonyl)-9-phenylnona-3,8-diyne (4g)

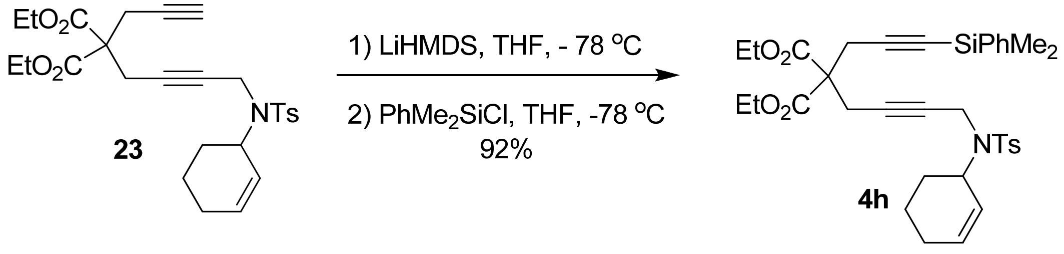


Diethyl 2-(prop-2-ynyl)malonate[4] (6.50 g, 32.80 mmol) in 40 cm^3 of THF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 1.70 g, 42.36 mmol) in 30 cm^3 of THF. The resulting mixture was stirred for 1 h at room temperature. The mixture was then transferred to a solution of dibromobut-2-yne (17.68 g, 83.43 mmol) in 50 cm^3 of THF via cannula over the period of 2.5 h. The mixture was then stirred at room temperature for 18 h. The reaction mixture was diluted with water and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated to yield dark oil. The excess dibromobutyne was recovered by distillation (100 °C/4 mmHg). The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent to give bromodiyne **22** as light yellow oil (9.39 g, 87%); TLC (SiO_2, hexanes:EtOAc = 4:1, $R_f = 0.33$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, 6 H, $J = 7.1$ Hz), 2.03 (t, 1 H, $J = 2.7$ Hz), 2.97 (d, 2 H, $J = 2.7$ Hz), 3.05 (t, 2 H, $J = 2.2$ Hz), 3.87 (t, 2 H, $J = 2.5$ Hz), 4.24 (q, 4 H, $J = 7.1$ Hz).

Cyclohexenylsulfonamide **11** (2.26 g, 8.99 mmol) in 20 cm^3 of DMF was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 0.44 g, 10.9 mmol) in 10 cm^3 of DMF. The resulting solution was stirred at room temperature for 45 min and then bromodiyne **22** (2.96 g, 8.99 mmol) in 25 cm^3 of DMF was added dropwise and the mixture was stirred for an additional 5 h. Water was added and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent gave cyclohexenediyne **23** (3.81 g, 85% yield) as yellow oil: TLC (SiO_2, hexanes:EtOAc = 4:1, $R_f = 0.34$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, 6H, *J* = 7.2 Hz), 1.48-1.55 (m, 2H), 1.72-1.65 (m, 2H), 1.95-1.92 (m, 2H), 1.99 (t, 1H, *J* = 2.4 Hz), 2.39 (s, 3H) 2.79 (t, 2H, *J* = 2.0 Hz), 2.84 (d, 2H, *J* = 2.4 Hz), 2.87 (t, 2H, *J* = 2.1 Hz), 3.90 (dt, 1H, *J* = 2.1 Hz), 4.10 (dt, 1H, *J* = 2.1 Hz), 4.21-4.15 (m, 4H), 4.43-4.40 (m, 1H), 5.29 (dd, 1H, *J* = 10.5, 1.8 Hz), 5.86-5.81 (m, 1H), 7.29 (d, 2H, *J* = 8.7 Hz), 7.77 (d, 2H, *J* = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.87 (CH_3), 21.38 (CH_2), 21.39 (CH_3), 22.46 (CH_2), 22.67 (CH_2), 24.26 (CH_2), 27.82 (CH_2), 32.78 (CH_2), 54.82 (CH), 56.15 (C), 61.85 (CH_2), 71.43 (CH), 77.99 (C), 78.46 (C), 80.08 (C), 126.84 (CH), 127.17 (CH), 127.23 (CH), 129.36 (CH), 129.54 (CH), 132.73 (CH), 138.04, (C) 142.97 (C), 168.49 (C); IR (neat, cm^{-1}) 3276, 2935, 1737, 1596, 1444, 1334, 1288, 1209, 1161, 1095, 1053, 1031.

Iodobenzene (0.24 g, 1.20 mmol) in 4 cm^3 of CH_2Cl_2 was added to a mixture of $Pd(PPh_3)_4$ (0.035 g, 0.05 mmol) and CuI (0.02 g, 0.10 mmol) in 10 cm^3 of CH_2Cl_2 and 5 cm^3 of Et_3N. Then cyclohexenediyne **23** (0.50 g, 1.0 mmol) in 4 cm^3 of CH_2Cl_2 was added dropwise via syringe. The resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and then washed with saturated NH_4Cl solution. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in hexanes as eluent to yield phenyl-terminal cyclohexenediyne **4g** (0.32 g, 55% yield) as yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.47$); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29 (dt, 6H, *J* = 7.2. 0.8 Hz), 1.56-1.54 (m, 2H), 1.77-1.71 (m, 2H), 1.95-1.92 (m, 2H), 2.35 (s, 3H) 2.95 (t, 2H, *J* = 2.0 Hz), 3.10 (s, 2H), 3.95 (dd, 1H, *J* = 18.4, 1.6 Hz), 4.14 (dd, 1H, *J* = 18.4, 1.6 Hz), 4.27-4.20 (m, 4H), 4.45-4.41 (m, 1H), 5.25 (d, 1H, *J* = 10.4 Hz), 5.89-5.86 (m, 1H), 7.30 (m, 5H), 7.37 (m, 2H), 7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.01 (CH_3), 21.38 (CH_2), 21.46 (CH_3), 22.95 (CH_2), 23.49 (CH_2), 24.35 (CH_2), 27.90 (CH_2), 32.90 (CH_2), 54.90 (CH), 56.63 (C), 61.89 (CH_2), 78.30 (C), 80.15 (C), 83.58 (C), 84.00 (C), 123.05 (C), 127.29 (CH), 127.32 (CH), 128.02 (CH), 128.19 (CH), 129.40 (CH), 131.57 (CH), 132.78 (CH), 138.11 (C), 143.06 (C), 168.74 (C); IR (neat, cm^{-1}) 3026, 2935, 1733, 1730, 1652, 1596, 1558, 1490, 1423, 1328, 1193, 1161, 1095, 1051, 1031; HRMS (ES) m/z calcd for $C_{33}H_{38}NO_6S$ $(M + H)^+$ 576.2420, found 576.2410 (Δ - 1.0 ppm).

1-Aza-1-(cyclohex-2-en-1-yl)-6,6,-dicarbethoxy-9-dimethylphenylsilyl-1-(4-methylbenzene-sulfonyl)nona-3,8-diyne (4h)

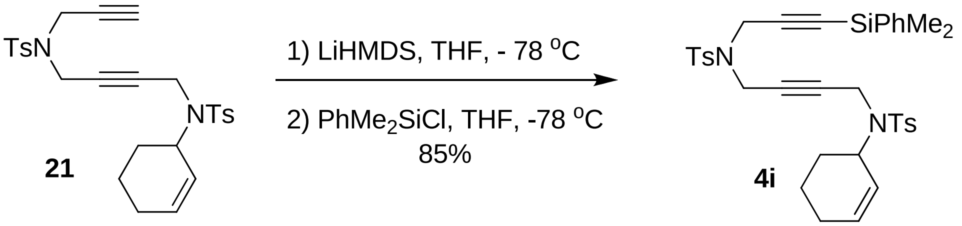


To a cold solution of cyclohexenyldiyne **23** (0.93 g, 1.85 mmol) in 20 cm^3 of THF was added dropwise 1 M LiHMDS (2.80 cm^3) in THF at -78 °C. The resulting mixture was stirred at -78 °C for 45 min and then dimethylphenylsilyl chloride (0.47 g, 2.78 mmol) in 10 cm^3 of THF was added dropwise. The resulting mixture was then warmed slowly to -40 °C and stirred for 4 h. The reaction mixture was diluted with ether, followed by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using

10% EtOAc in hexanes as eleuent to afford silyl-terminal cyclohexenediyne **4h** (1.07 g, 92% yield) as yellow oil; TLC (SiO_2, hexanes:EtOAc = 4:1, $R_f = 0.40$); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.37 (s, 6H), 1.25 (t, 6H, *J* = 7.2), 1.56-1.54 (m, 2H), 1.77-1.71 (m, 2H), 1.95-1.92 (m, 2H), 2.38 (s, 3H) 2.91 (t, 2H, *J* = 1.8 Hz), 2.95 (s, 2H), 3.93 (dd, 1H, *J* = 14.1, 2.1 Hz), 4.19-4.05 (m, 5H), 4.42-4.40 (m, 1H), 5.31 (d, 1H, *J* = 10.2 Hz), 5.87-5.83 (m, 1H), 7.34-7.41 (m, 5H), 7.57-7.61 (m, 2H), 7.76-7.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ – 0.84 (CH_3), 13.98 (CH_3), 21.47 (CH_3), 22.88 (CH_2), 24.05 (CH_2), 24.37 (CH_2), 27.92 (CH_2), 32.91 (CH_2), 54.91 (CH), 56.54 (C), 61.91 (CH_2), 78.22 (C), 80.14 (C), 86.23 (C), 102.88 (C), 127.28 (CH), 127.34 (CH), 127.81 (CH), 129.37 (CH), 129.44 (CH), 132.81 (CH), 133.59 (CH), 136.89 (C), 138.12 (C), 143.07 (C), 168.59 (C); IR (neat, cm^{-1}) 2979, 2937, 2358, 2179, 1735, 1334, 1207, 1161; HRMS (ES) m/z calcd for $C_{35}H_{44}NO_6SSi$ $(M + H)^+$ 634.2659, found 634.2687 (Δ 2.8 ppm).

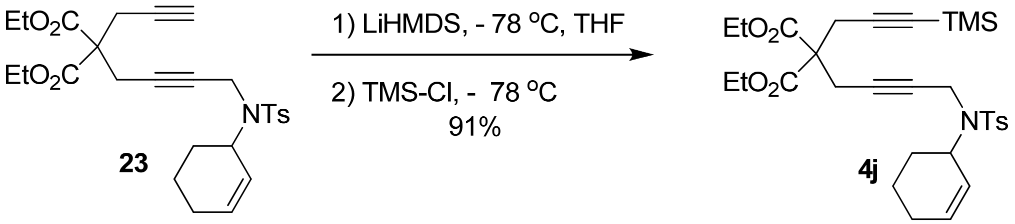
In the same manner other 9-silyl derivatives of **21** and **23** were synthesized.

1,6-Bis(4-methylbenzenesulfonyl)-1-(cyclohex-2-en-1-yl)-1,6-diaza-9-dimethylphenylsilylnona-3,8-diyne (4i):



85% yield; yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.43$); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.27 (s, 6H), 1.60-1.56 (m, 2H), 1.74-1.71 (m, 2H), 1.92-1.90 (m, 2H), 2.34 (s, 3H), 2.40 (s, 3H), 3.88 (dt, 1H, *J* = 2.1 Hz), 4.00-4.13 (m, 5H), 4.46-4.40 (m, 1H), 5.28 (dd, 1H, *J* = 12.0, 1.5 Hz), 5.87-5.81 (m, 1H), 7.21 (d, 2H, *J* = 8.1 Hz), 7.48-7.37 (m, 7 H), 7.69 (d, 2H, *J* = 8.1 Hz), 7.78 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ – 1.15 (CH_3), 21.38 (CH_3), 21.49 (CH_3), 24.34 (CH_2), 27.94 (CH_2), 32.76 (CH_2), 36.51 (CH_2), 37.13 (CH_2), 54.92 (CH), 76.36 (C), 82.36 (C), 89.27 (C), 99.14 (C), 127.15 (CH), 127.28 (CH), 127.78 (CH), 127.88 (CH), 129.56 (CH), 129.59 (CH), 129.68 (CH), 133.01 (CH), 133.49 (CH), 135.27 (C), 136.20 (C), 137.98 (C), 143.35 (C), 143.80 (C); IR (neat, cm^{-1}) 2952, 2929, 2177, 1597, 1429, 1334, 1163; HRMS (ES) m/z calcd for $C_{35}H_{41}N_2O_4S_2Si$ $(M + H)^+$ 645.2277, found 645.2247 (Δ - 3.0 ppm).

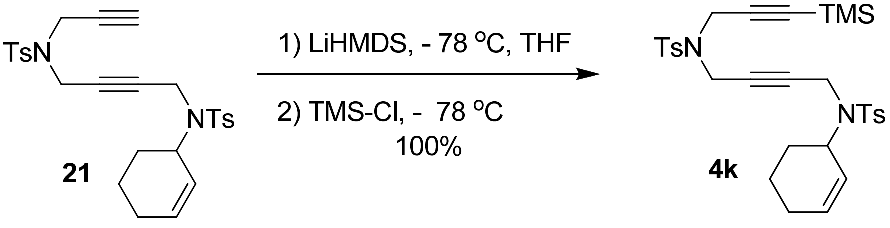
1-Aza-1-(cyclohex-2-en-1-yl)-6,6,-dicarbethoxy-9-trimethylsilyl-1-(4-methylbenzene-sulfonyl)nona-3,8-diyne (4j):



91% yield; yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.52$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.12 (s, 9H), 1.26 (t, 6H, *J* = 7.2 Hz), 1.48-1.55 (m, 2H), 1.74-1.65 (m, 2H), 1.95-1.92 (m, 2H), 2.43 (s, 3H) 2.89 (m, 4H), 3.91 (dt, 1H, *J* = 2.0 Hz), 4.11 (dt, 1H, *J* = 2.0 Hz), 4.21-4.14 (m, 4H), 4.44-4.41 (m, 1H), 5.31 (dd, 1H, *J* = 10.0, 2.0 Hz), 5.89-5.84 (m, 1H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.79 (d, 2H, *J* = 8.0

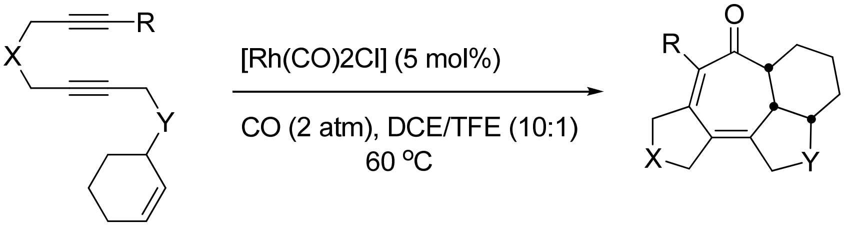
Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.06 (CH_3), 14.03 (CH_3), 21.52 (CH_3), 22.79 (CH_2), 23.94 (CH_2), 24.39 (CH_2), 27.92 (CH_2), 32.94 (CH_2), 54.92 (CH), 56.57 (C), 61.87 (CH_2), 78.29 (C), 80.04 (C), 88.19 (C), 100.97 (C), 127.29 (CH), 127.36 (CH), 129.45 (CH), 132.79 (CH), 138.14 (C), 143.05 (C), 168.61 (C); IR (neat, cm^{-1}) 2979, 2937, 2177, 1739, 1336, 1207, 1163; HRMS (ES) m/z calcd for $C_{30}H_{42}NO_6SSi$ $(M + H)^+$ 572.2502, found 572.2501 (Δ - 0.1 ppm).

1,6-Bis(4-methylbenzenesulfonyl)-1-(cyclohex-2-en-1-yl)-1,6-diaza-9-trimethylsilylnona-3,8-diyne (4k):



100% yield; white solid; mp = 88-89 °C; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.43); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 1.56-1.51 (m, 2H), 1.71-1.62 (m, 2H), 1.89 (bs, 2H), 2.36 (s, 3H), 2.38 (s, 3H), 3.83 (dt, 1H, *J* = 2.4 Hz), 4.00 (m, 5H), 4.43-4.40 (m, 1H), 5.24 (dd, 1H, *J* = 12.0, 1.5 Hz), 5.82-5.78 (m, 1H), 7.38 (m, 4H), 7.64 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.40 (CH_3), 21.41 (CH_3), 21.53 (CH_3), 24.36 (CH_2), 27.93 (CH_2), 32.76 (CH_2), 36.43 (CH_2), 37.06 (CH_2), 54.91 (CH), 76.46 (C), 82.25 (C), 91.18 (C), 97.34 (C), 127.21 (CH), 127.32 (CH), 127.85 (CH), 129.59 (CH), 133.04 (CH), 135.39 (CH), 138.04 (C), 143.36 (C), 143.78 (C); IR (in $CHCl_3$, cm^{-1}) 3026, 2958, 2177, 1647, 1596, 1494, 1350, 1249, 1163, 1095, 1032; HRMS (ES) m/z calcd for $C_{30}H_{39}N_2O_4S_2Si$ $(M + H)^+$ 583.2121, found 583.2104 (Δ - 1.7 ppm).

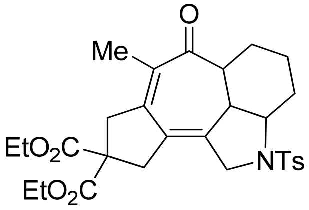
[2+2+2+1] Cycloaddition Reactions



Typical procedure is described for the reaction of cyclohexene-diyne **4a**: A 25 cm^3 round bottomed flask charged with **4a** (100 mg, 0.19 mmol) in DCE/TFE (10:1) (3.90 cm^3, [0.05 M] and $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.009 mmol) was transferred to a 125 cm^3 stainless steel autoclave and purged with CO and released (4x) (**Caution must be done in a well ventilated fume hood**) and then charged with CO to 2 atm. The autoclave was immersed in an oil bath at 60 °C for 20 h. The autoclave was allowed to cool to room temperature, followed by release of the gas in a well ventilated fume hood. The reaction mixture was concentrated under reduced pressure and the resulting crude product was purified by column chromatography on silica gel using EtOAc/hexanes (15/85) as eluent to give fused tetracyclic product **5a-1** (86 mg, 82%) as light yellow oil.

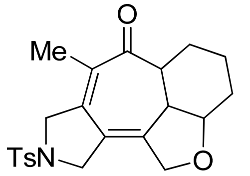
For **5h**-**5k** arising from 9-silyl-cyclohexene-diynes **4h**-**4k**, two regioisomers were separated by preparative HPLC using a phenomenex Jupiter 10μ proteo 90A column (21.2 x 250 mm/mm) and gradient from 100% acetonitrile to 95:5 acetonitrile:water over 24 min with a flow rate of 20 cm^3/min.

Diethyl-7-methyl-2-[(4-methylphenyl)sulfonyl]-6-oxo-2,2a,3,4,5,5a,6,8,10,10c-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (5a-1):



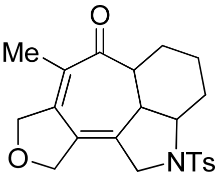
82% yield; yellow oil; TLC (SiO_2, hexanes:EtOAc = 2:1, R_f = 0.36); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28-1.22 (m, 6H), 1.45-1.38 (m, 2H), 1.71-1.63 (m, 3H), 1.85 (s, 3H), 1.96-1.87 (m, 1H), 2.41 (s, 3H), 2.65-2.62 (m, 1H), 2.84-2.80 (m, 2H), 3.16-3.00 (m, 3H), 3.97-3.94 (m, 1H), 4.08 (s, 2H), 4.24-4.15 (m, 4H), 7.31 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.99 (CH_3), 17.12 (CH_3), 21.52 (CH_2), 22.39 (CH_3), 23.79 (CH_2), 28.19 (CH_2), 39.86 (CH_2), 41.89 (CH_2), 43.76 (CH), 50.51 (CH_2), 50.72 (CH), 57.03 (C), 60.69 (CH), 61.95 (CH_2), 127.02 (CH), 129.95 (CH), 130.23 (C), 130.65 (C), 136.29 (C), 136.92 (C), 143.68 (C), 145.03 (C), 170.47 (C), 170.86 (C), 200.72 (C); IR (neat, cm^{-1}) 2979, 2860, 1730, 1734, 1652, 1596, 1444, 1344, 1261, 1161, 1093; HRMS (ES) m/z calcd for $C_{29}H_{36}NO_7S$ $(M + H)^+$ 542.2212, found 542.2206 (Δ - 0.6 ppm).

7-Methyl-9-[(4-methylphenyl)sulfonyl]-1,2a,3,4,5,5a,8,9,10,10c-decahydro-6*H*-[1]benzofuro[3',4':3,4,5]cyclohepta[1,2-*c*]pyrrol-6-one (5b-1):



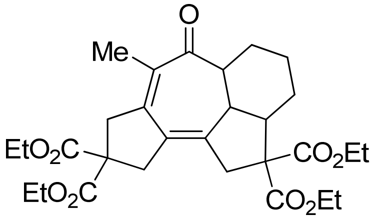
91% yield; white solid; mp = 182-183 °C; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.12); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28-1.18 (m, 3H), 1.44-1.38 (m, 1H), 1.69-1.63 m, 1H), 1.81 (s, 3H), 2.45-2.39 (m, 4H), 2.79-2.72 (m, 1H), 3.23 (bs, 1H), 3..67-3.61 (m, 1H), 4.38-3.95 (m, 5H), 7.36 (d, 2H, *J* = 7.8 Hz), 7.74 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.55 (CH_3), 21.56 (CH_2), 21.92 (CH_3), 23.84 (CH_2), 26.57 (CH_2), 44.27 (CH), 49.86 (CH), 51.91 (CH_2), 53.90 (CH2), 68.91 (CH_2), 79.10 (CH), 124.37 (C), 127.79 (CH), 129.74 (C), 129.87 (C), 129.95 (CH), 141.34 (C), 141.77 (C), 144.24 (C), 199.41 (C); IR (in $CHCl_3$, cm^{-1}) 2939, 2864, 1724, 1596, 1346, 1163; HRMS (ES) m/z calcd for $C_{22}H_{26}NO_4S$ $(M + H)^+$ 400.1583, found 400.1569 (Δ - 1.4 ppm).

7-Methyl-2-[(4-methylphenyl)sulfonyl]-2,2a,3,4,5,5a,10,10c-octahydro-1*H*-furo[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(8*H*)-one (5c-1):



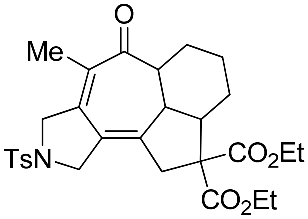
74% yield; white solid; mp = 191-193 °C; TLC (SiO_2, hexanes:EtOAc = 2:1, Rf = 0.24); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30-1.22 (m, 2H), 1.52-1.46 (m, 2H), 1.75 (s, 3H), 2.01-1.96 (m, 2H), 2.42 (s, 3H), 2.74-2.66 (m, 1H), 2.88 (bs, 1H), 4.07-3.94 (m, 3H), 4.38 (dt, 1H, *J* = 2.1 Hz)), 4.67-4.49 (m, 3H), 7.31 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.97 (CH_3), 21.51 (CH_3), 22.35 (CH_2), 23.99 (CH_2), 28.31 (CH_2), 43.99 (CH), 49.69 (CH), 50.48 (CH_2), 60.42 (CH), 72.18(CH_2), 73.58(CH_2), 127.0 (CH), 127.85 (C), 129.63 (C), 130.00 (CH), 135.05 (C), 136.14 (C), 143.81 (C), 144.46 (C), 199.74 (C); IR (in $CHCl_3$, cm^{-1}) 2929, 2856, 1721, 1654, 1596, 1342, 1159; HRMS (ES) m/z calcd for $C_{22}H_{26}NO_4S$ $(M + H)^+$ 400.1583, found 400.1569 (Δ - 1.4 ppm).

Tetraethyl-7-methyl-6-oxo-1,2a,3,4,5,5a,6,8,10,10c-decahydrobenzo[*cd*]cyclopenta[*h*]azulene-2,2,9,9-tetracarboxylate (5d-1):



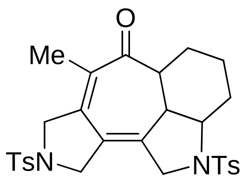
85% yield; light yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.30$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26-1.21 (m, 13H), 1.46-1.37 (m, 3H), 1.78-1.70 (m, 2H), 1.86 (s, 3H), 2.76 (m, 2H), 2.86 (d, 1H, *J* = 20 Hz), 2.97 (d, 1H, *J* = 16.4 Hz), 3.25-3.06 (m, 4H), 3.43 (d, 1H, *J* = 20 Hz), 4.24- 4.10 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.93 (CH_3), 13.97 (CH_3), 14.07 (CH_3), 16.87 (CH_3), 23.69 (CH_2), 23.87 (CH_2), 23.90 (CH_2), 38.36 (CH_2), 40.33 (CH_2), 42.49 (CH_2), 44.07 (CH), 45.22 (CH), 51.16 (CH), 57.02 (C), 1.62 (CH_2), 61.69 (CH_2), 61.75 (CH_2), 62.29 (C), 129.25 (C), 129.97 (C), 140.69 (C), 146.49 (C), 169.12 (C), 170.87 (C), 170.98 (C), 171.18 (C), 201.13 (C); IR (neat, cm^{-1}) 2979, 2935, 1731, 1367, 1257, 1159; HRMS (ES) m/z calcd for $C_{29}H_{39}O_9$ $(M + H)^+$ 531.2594, found 531.2576 (Δ - 1.8 ppm).

Diethyl-7-methyl-9-[(4-methylphenyl)sulfonyl]-6-oxo-2a,3,4,5,5a,6,8,9,10,10c-decahydrobenzo[1,8]azuleno[4,5-*c*]pyrrole-2,2(1*H*)-dicarboxylate (5e-1):



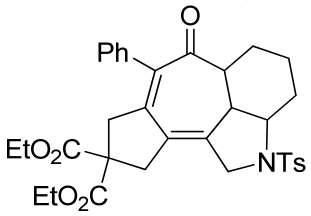
83% yield; white solid; mp = 86-88 °C; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.28$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27-1.21 (m, 8H), 1.42-1.39 (m, 2H), 1.71-1.67 (m, 2H), 1.78 (s, 3H), 2.43 (s, 3H), 2.79-2.71 (m, 3H), 3.21 (d, 1H, *J* = 12.0 Hz), 3.32 (d, 1H, *J* = 12.0 Hz), 3.89 (d, 1H, *J* = 13.2 Hz), 4.02 (d, 1H, *J* = 16 Hz), 4.26-4.09 (m, 6H), 7.36 (d, 2H, *J* = 8.0 Hz), 7.75 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.91 (CH_3), 14.06 (CH_3), 16.29 (CH_3), 21.51 (CH_3), 23.59 (CH_2), 23.65 (CH_2), 23.75 (CH_2), 37.79 (CH_2), 44.16 (CH), 45.04 (CH), 50.62 (CH_2), 52.81 (CH_2), 54.34 (CH), 61.79 (CH_2), 61.87 (CH_2), 62.31 (C), 126.64 (C), 127.79 (CH), 128.75 (C), 129.84 (CH), 132.63 (C), 141.37 (C), 141.85 (C), 144.06 (C), 168.70 (C), 170.69 (C), 200.04 (C); IR (in $CHCl_3$, cm^{-1}) 2983, 2906, 2255, 1741, 1731, 1373, 1266, 1096, 1046; HRMS (ES) m/z calcd for $C_{29}H_{36}NO_7S$ $(M + H)^+$ 542.2212, found 542.2192 (Δ - 2.0 ppm).

7-Methyl-2,9-bis[(4-methylphenyl)sulfonyl]-2,2a,3,4,5,5a,8,9,10,10c-decahydropyrrolo[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(1*H*)-one (5f-1):



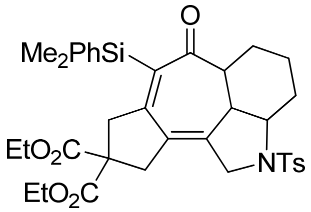
85% yield; white solid; mp = 200 -201 °C; TLC (SiO_2, hexanes:EtOAc = 2:1, R_f = 0.20); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22-1.11 (m, 3H), 1.40-1.38 (m, 1H), 1.71-1.62 (m, 1H), 1.77 (s, 3H), 1.95-1.91 (m, 2H), 2.42 (s, 3H), 2.43 (s, 3H), 2.65-2.62 (m, 1H), 2.79 (bs, 1H), 3.37 (d, 1H, *J* = 10 Hz), 3.99-3.89 (m, 3H), 4.10 (d, 1H, *J* = 14 Hz), 4.24 (d, 1H, *J* = 14 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 7.36 (d, 2H, *J* = 8.4 Hz), 7.71 (d, 2H, *J* = 8.4 Hz), 7.73 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.58 (CH_3), 21.55 (CH_3), 22.17 (CH_3), 23.64 (CH_2), 27.95 (CH_2), 29.67 (CH_2), 43.92 (CH), 50.06 (CH_2), 52.20 (CH), 53.81 (CH_2), 60.44 (CH), 126.83 (C), 127.07 (CH), 127.79 (CH), 129.97 (CH), 130.02 (CH), 130.25 (C), 132.39 (C), 136.08 (C), 137.58 (C), 140.73 (C), 143.91 (C), 144.33 (C), 199.52 (C); IR (in $CHCl_3$, cm^{-1}) 2923, 2854, 1733, 1596, 1346, 1163; HRMS (ES) m/z calcd for $C_{29}H_{33}N_2O_5S_2$ $(M + H)^+$ 553.1831, found 553.1818 (Δ - 1.3 ppm).

Diethyl-7-phenyl-2-[(4-methylphenyl)sulfonyl]-6-oxo-2,2a,3,4,5,5a,6,8,10,10c-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (**5g-1**):



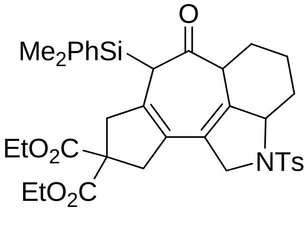
44% yield; light yellow oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.23); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (t, 6H, *J* = 7.2 Hz), 1.66-1.56 (m, 4H), 1.79-1.75 (m, 1H), 2.01-1.97 (m, 1H), 2.44 (s, 3H), 2.75-2.67 (m, 1H), 2.94-2.87 (m, 4H), 3.09 (d, 1H, *J* = 14.0 Hz), 4.03-3.99 (m, 1H), 4.19-4.12 (m, 6H), 7.04 (dd, 2H, *J* = 8.4, 1.5 Hz), 7.37-7.27 (m, 5H), 7.75 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.93 (CH_3), 13.99 (CH_3), 21.54 (CH_3), 22.23 (CH_2), 23.69 (CH_2), 28.37 (CH_2), 40.05 (CH_2), 42.62 (CH), 44.24 (CH_2), 50.19 (CH_2), 50.82 (CH), 57.32 (CH), 60.66 (C), 61.89 (CH_2), 127.04 (CH), 127.43 (CH), 128.42 (CH), 128.68 (CH), 130.01 (CH), 130.15 (C), 136.08 (C), 136.21 (C), 138.66 (C), 138.71 (C), 143.77 (C), 145.31 (C), 170.22 (C), 170.59 (C), 200.37 (C); IR (neat, cm^{-1}) 2960, 2860, 2358, 1735, 1728, 1723, 1650, 1444, 1365, 1344, 1263, 1159, 1093, 1053, 1016; HRMS (ES) m/z calcd for $C_{34}H_{38}NO_7S$ $(M + H)^+$ 604.2369, found 604.2348 (Δ - 2.1 ppm).

Diethyl-7-[dimethyl(phenyl)silyl]-2-[(4-methylphenyl)sulfonyl]-6-oxo 2,2a,3,4,5,5a,6,8,10,10c-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (5h-1):



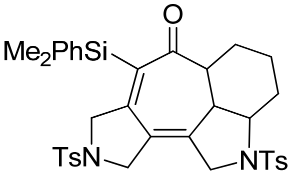
Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.28); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.46 (d, 6H, *J* = 6.6 Hz), 1.02-0.83 (m, 2H), 1.22-1.13 (m, 6H), 1.64-1.56 (m, 3H), 2.15-1.97 (m, 3H), 2.42 (s, 3H), 2.90-2.58 (m, 3H), 3.06-2.99 (m, 1H), 3.43 (d, 1H, *J* = 11.4 Hz), 3.81 (d, 1H, *J* = 11.4 Hz), 7.33-7.29 (m, 5H), 7.53 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -2.53 (CH$_3$), -1.76 (CH$_3$), 13.88 (CH$_3$), 21.45 (CH$_3$), 28.66 (CH$_2$), 29.97 (CH$_2$), 36.40 (CH$_2$), 36.85 (CH$_2$), 40.33 (CH), 41.27(CH$_2$), 46.87 (CH$_2$), 55.92 (CH), 58.47 (CH$_2$), 59.86 (C), 61.77 (CH$_2$), 62.21 (CH), 127.15 (CH), 127.74 (CH), 127.83 (CH), 129.17 (CH), 129.71 (CH), 133.93 (CH), 134.94 (C), 136.09 (C), 137.39 (C), 142.48 (C), 143.33 (C), 143.37 (C), 170.73 (C), 171.27 (C), 200.71 (C); IR (neat, cm^{-1}) 2941, 1762, 1731, 1348, 1251, 1164; HRMS (ES) m/z calcd for $C_{36}H_{44}NO_7SiS$ (M + H)$^+$ 662.2608, found 662.2609 (Δ 0.1 ppm).

Diethyl-7-[dimethyl(phenyl)silyl]-2-[(4-methylphenyl)sulfonyl]-6-oxo-2,2a,3,4,5,5a,6,7,8,10-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (5h-2):



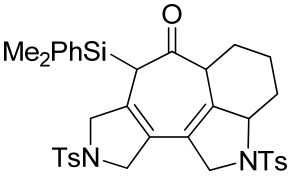
Colorless oil; TLC (SiO$_2$, hexanes:EtOAc = 3:1, R$_f$ = 0.28); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.40 (d, 6H, *J* = 7.8 Hz), 1.28-1.10 (m, 8H), 1.61-1.45 (m, 4H), 1.76-1.72 (m, 1H), 2.09-2.02 (m, 1H), 2.43 (s, 3H), 2.53-2.49 (m, 1H), 2.87-2.70 (m, 4H), 4.15-3.92 (m, 6H), 7.33-7.29 (m, 5H), 7.54 (d, 2H, *J* = 8.7 Hz), 7.72 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -1.49 (CH$_3$), -1.15 (CH$_3$), 13.86 (CH$_3$), 13.94 (CH$_3$), 21.52 (CH$_3$), 21.62 (CH$_2$), 23.72 (CH$_2$), 28.76 (CH$_2$), 39.25 (CH), 42.17 (CH$_2$), 44.98 (CH$_2$), 48.97 (CH$_2$), 50.79 (CH), 57.35 (C), 60.51 (CH), 61.77 (CH$_2$), 61.81 (CH$_2$), 127.00 (CH), 127.92 (CH), 129.16 CH), 129.99 (CH), 132.07 CH), 133.85 (CH), 136.04 (C), 137.25 (C), 137.82 (C), 143.74 (C), 150.55 (C), 179.18 (C), 170.57 (C), 207.10 (C); IR (neat, cm^{-1}) 2977, 2929, 1734, 1731, 1664, 1251, 1161; IR (neat, cm^{-1}) 2935, 1743, 1731, 1662, 1301, 1251, 1161; HRMS (ES) m/z calcd for $C_{36}H_{44}NO_7SiS$ (M + H)$^+$ 662.2608, found 662.2609 (Δ 0.1 ppm).

7-[Dimethyl(phenyl)silyl]-2,9-bis[(4-methylphenyl)sulfonyl]-2,2a,3,4,5,5a,8,9,10,10c-decahydropyrrolo[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(1*H*)-one (5i-1):



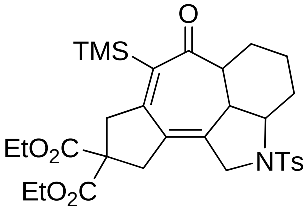
Colorless oil; TLC (SiO$_2$, hexanes:EtOAc = 3:1, R$_f$ = 0.24); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.40 (s, 3H), 0.43 (s, 3H), 1.13-0.85 (m, 3H), 1.54 (t, 1H, *J* = 9.6 Hz), 1.62-1.59 (m, 1H), 2.04-1.93 (m, 2H), 2.17-2.13 (m, 1H), 2.42 (s, 3H), 2.45 (s, 3H), 3.27 (d, 1H, *J* = 11.2 Hz), 3.68-3.63 (m, 1H), 3.89-3.75 (m, 5H), 7.23 (d, 2H, *J* = 8.0 Hz), 7.43-7.27 (m, 9H), 7.73 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz) δ -3.11 (CH$_3$), -1.43 (CH$_3$), 21.54 (CH$_3$), 28.49 (CH$_2$), 30.12 (CH$_2$), 36.93 (CH$_2$), 41.16 (CH), 47.00 (CH$_2$), 50.34 (CH), 53.69 (CH$_2$), 55.44 (CH$_2$), 58.39 (C), 61.39 (CH), 127.05 (CH), 127.15 (CH), 128.14 (CH), 129.62 (CH), 129.87 (CH), 133.71 (CH), 134.02 (C), 135.61 (C), 136.72 (C), 140.12 (C), 141.35 (C), 143.59 (C), 143.86 (C), 199.65 (C); HRMS (ES) m/z calcd for $C_{36}H_{41}N_2O_5SiS_2$ (M + H)$^+$ 673.2226, found 673.2242 (Δ 1.6 ppm).

7-[Dimethyl(phenyl)silyl]-2,9-bis[(4-methylphenyl)sulfonyl]-2,2a,3,4,5,5a,7,8,9,10-decahydropyrrolo[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(1*H*)-one (5i-2):



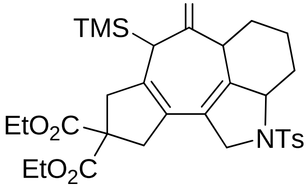
Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.24); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.34 (s, 3H), 0.45 (s, 3H), 1.22-1.09 (m, 3H), 1.52-1.48 (m, 1H), 1.66-1.62 (m, 1H), 2.01-1.96 (m, 1H), 2.41 (s, 3H), 2.43 (s, 3H), 2.54-2.48 (m, 1H), 2.67 (bs, 1H), 3.53 (s, 2H), 3.64-3.55 (m, 1H), 3.80-3.73 (m, 1H), 3.96-3.85 (m, 2H), 7.23 (d, 2H, *J* = 7.8 Hz), 7.35-7.29 (m, 4H), 7.53-7.38 (m, 5H), 7.70 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -2.14 (CH_3), -1.69 (CH_3), 21.44 (CH_3), 21.54 (CH_3), 23.31(CH_2), 28.48 (CH_2), 45.12 (CH), 48.67 (CH), 50.21 (CH_2), 51.33 (CH_2), 53.78 (CH_2), 60.17 (CH), 127.03 (CH), 127.79 (CH), 128.28 (CH), 128.93 (CH), 129.66 (CH), 129.74 (CH), 130.05 (CH), 131.86 (CH), 134.02 (C), 135.76 (C), 136.88 (C), 137.21 (C), 138.40 (C), 143.96 (C), 146.45 (C), 206.12 (C); IR (neat, cm^{-1}) 3066, 2941,1718,1666, 1596, 1448, 1305, 1163; HRMS (ES) m/z calcd for $C_{36}H_{41}N_2O_5SiS_2$ $(M + H)^+$ 673.2226, found 673.2205 (Δ - 2.1 ppm).

Diethyl-2-[(4-methylphenyl)sulfonyl]-6-oxo-7-(trimethylsilyl)-2,2a,3,4,5,5a,6,8,10,10c-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (5j-1):



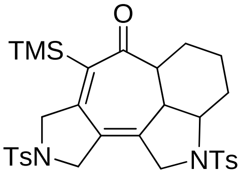
Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, R_f = 0.37); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9H), 1.07-0.85 (m, 3H), 1.26 (t, 6H, *J* = 7.2 Hz), 1.64 (t, 2H, *J* = 9.6 Hz), 2.01 (m, 2H), 2.16-2.09 (m, 1H), 2.43 (s, 3H), 2.83-2.77 (m, 2H), 3.06 (dd, 1H, *J* = 1.8 Hz), 3.35 (dd, 1H, *J* = 1.8 Hz), 3.40 (d, 1H, *J* = 11.4 Hz), 3.79 (d, 1H, *J* = 11.4 Hz), 3.96-3.87 (m, 1H), 4.22-4.13 (m, 4H), 7.33 (d, 2H, *J* = 8.4 Hz), 7.75 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.02 (CH_3), 13.97 (CH_3), 21.65 (CH_3), 28.54 (CH_2), 30.14 (CH_2), 36.43 (CH_2), 36.49 (CH_2), 40.33 (CH_2), 41.32 (CH), 46.87 (CH_2), 55.76 (CH), 58.41(CH_2), 60.16 (C), 61.88 (CH_2), 61.95 (CH_2), 62.25 (CH), 127.16 (CH), 129.73 (CH), 136.03 (C), 142.78 (C), 143.41(C), 143.52 (C), 170.98 (C), 171.27 (C), 201.15 (C); IR (neat, cm^{-1}) 2948, 2869, 2256, 1766, 1728, 1598, 1463, 1348, 1251, 1164, 1093, 1058; HRMS (ES) m/z calcd for $C_{31}H_{42}NO_7SiS$ $(M + H)^+$ 600.2451, found 600.2454 (Δ 0.3 ppm).

Diethyl-2-[(4-methylphenyl)sulfonyl]-6-oxo-7-(trimethylsilyl)-2,2a,3,4,5,5a,6,7,8,10-decahydroazuleno[4,5,6-*cd*]indole-9,9(1*H*)-dicarboxylate (5j-2):



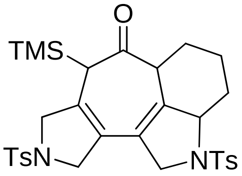
Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.37$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 1.28-1.18 (m, 8H), 1.52-1.32 (m, 2H), 1.70-1.68 (m, 1H), 2.02-1.98 (m, 1H), 2.42 (s, 3H), 2.49-2.45 (m, 1H), 2.93-2.67 (m, 3H), 3.04 (d, 1H, *J* = 16.5 Hz), 3.21 (d, 1H, *J* = 16.5 Hz), 4.00-3.89 (m, 3H), 4.24-4.14 (m, 4H), 7.31 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.03 (CH_3), 13.97 (CH_3), 14.03 (CH_3), 21.49 (CH_2), 21.54 (CH_3), 23.58 (CH_2), 28.74 (CH_2), 39.35 (CH), 42.01 (CH_2), 44.98 (CH_2), 48.81 (CH_2), 50.74 (CH), 57.69 (C), 60.45 (CH), 61.94 (CH_2), 61.97 (CH_2), 126.99 (CH), 129.97 (CH), 131.85 (C), 136.03 (C), 137.18 (C), 139.13 (C), 143.70 (C), 148.84 (C), 170.22 (C), 170.69 (C), 207.64 (C); IR (neat, cm^{-1}) 2937, 2538, 1734, 1731, 1662, 1446, 1346, 1249, 1161; HRMS (ES) m/z calcd for $C_{31}H_{42}NO_7SiS$ $(M + H)^+$ 600.2451, found 600.2438 (Δ - 1.3 ppm).

2,9-Bis[(4-methylphenyl)sulfonyl]-7-(trimethylsilyl)-2,2a,3,4,5,5a,8,9,10,10c-decahydropyrrolo-[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(1*H*)-one (5k-1):

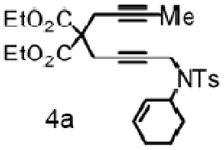


Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.20$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.09 (s, 9H), 1.03-0.82 (m, 3H), 1.63-1.51 (m, 2H), 1.94-1.89 (m, 2H), 2.15-2.10 (m, 1H), 2.43 (s, 3H), 2.46 (m, 3H), 3.29 (d, 1H, *J* = 11.4 Hz), 3.77 (d, 1H, *J* = 11.4 Hz), 3.89-3.84 (m, 2H), 4.15-4.06 (m, 2H), 4.31-4.24 (m, 1H), 7.32 (d, 2H, *J* = 7.8 Hz), 7.36 (d, 2H, *J* = 7.5 Hz), 7.63 (d, 2H, *J* = 7.5 Hz), 7.74 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -1.04 (CH_3), 21.53 (CH_3), 28.35 (CH_2), 30.11 (CH_2), 36.44 (CH_2), 41.12 (CH), 47.07 (CH_2), 50.54 (CH), 53.66 (CH_2), 55.16 (CH_2), 58.24 (CH), 61.40 (CH), 127.10 (CH), 127.16 (CH), 129.83 (CH), 129.93 (CH), 134.21 (C), 135.63 (C), 140.68 (C), 141.22 (C), 143.77 (C), 143.94 (C), 199.92 (C); IR (neat, cm^{-1}) 2948, 2867, 1770, 1596, 1346, 1163, 1091; HRMS (ES) m/z calcd for $C_{31}H_{39}N_2O_5SiS_2$ $(M + H)^+$ 611.2070, found 611.2042 (Δ - 2.8 ppm).

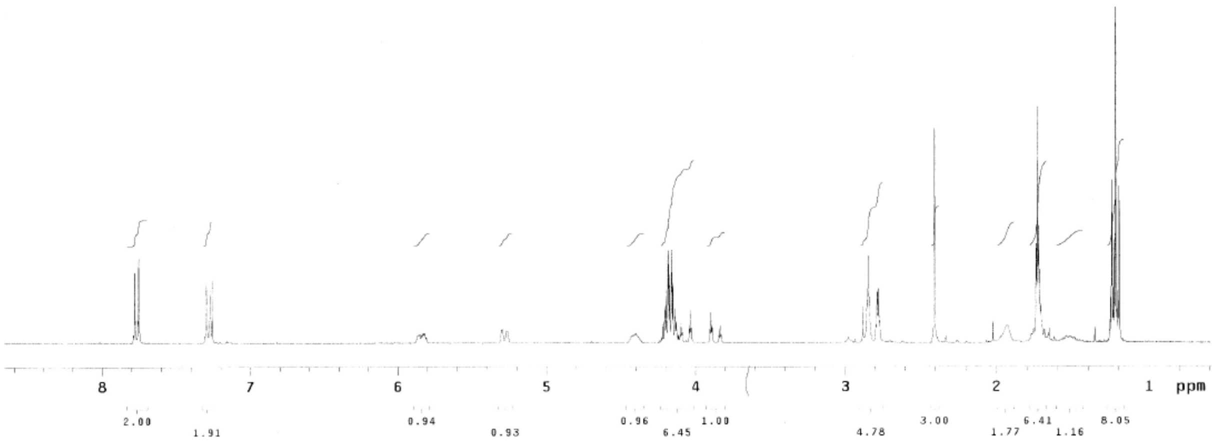
2,9-Bis[(4-methylphenyl)sulfonyl]-7-(trimethylsilyl)-2,2a,3,4,5,5a,7,8,9,10-decahydropyrrolo-[3',4':6,7]cyclohepta[1,2,3-*cd*]indol-6(1*H*)-one (5k-2):



Colorless oil; TLC (SiO_2, hexanes:EtOAc = 3:1, $R_f = 0.20$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.14 (s, 9H), 1.18-1.05 (m, 3H), 1.45-1.41 (m, 1H), 1.63-1.59 (m, 1H), 2.01-1.93 (m, 1H), 2.49-2.43 (m, 7H), 2.64 (bs, 1H), 3.71-3.65 (m, 1H), 3.96-3.87 (m, 5H), 4.23 (d, 1H, 15.3 Hz), 7.35-7.29 (m, 4H), 7.71-7.67 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.05 (CH_3), 21.38 (CH_3), 21.49 (CH_3), 23.18 (CH_2), 28.49 (CH_2), 45.23 (CH), 48.55 (CH_2), 50.19 (CH), 51.47 (CH_2), 53.45 (CH_2), 60.11 (CH), 127.06 (CH), 127.84 (CH), 128.89 (CH), 129.95 (CH), 130.06 (CH), 132.41 (C), 135.78 (C), 137.85 (C), 138.92 (C), 143.96 (C), 144.30 (C), 145.10 (C), 206.69 (C); IR (neat, cm^{-1}) 2945, 2358, 1662, 1346, 1163; HRMS (ES) m/z calcd for $C_{31}H_{39}N_2O_5SiS_2$ $(M + H)^+$ 611.2070, found 611.2079 (Δ 0.9 ppm).


EtO$_2$C
EtO$_2$C
Me
NTs

4a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7
6
5
4
3
2
1
ppm
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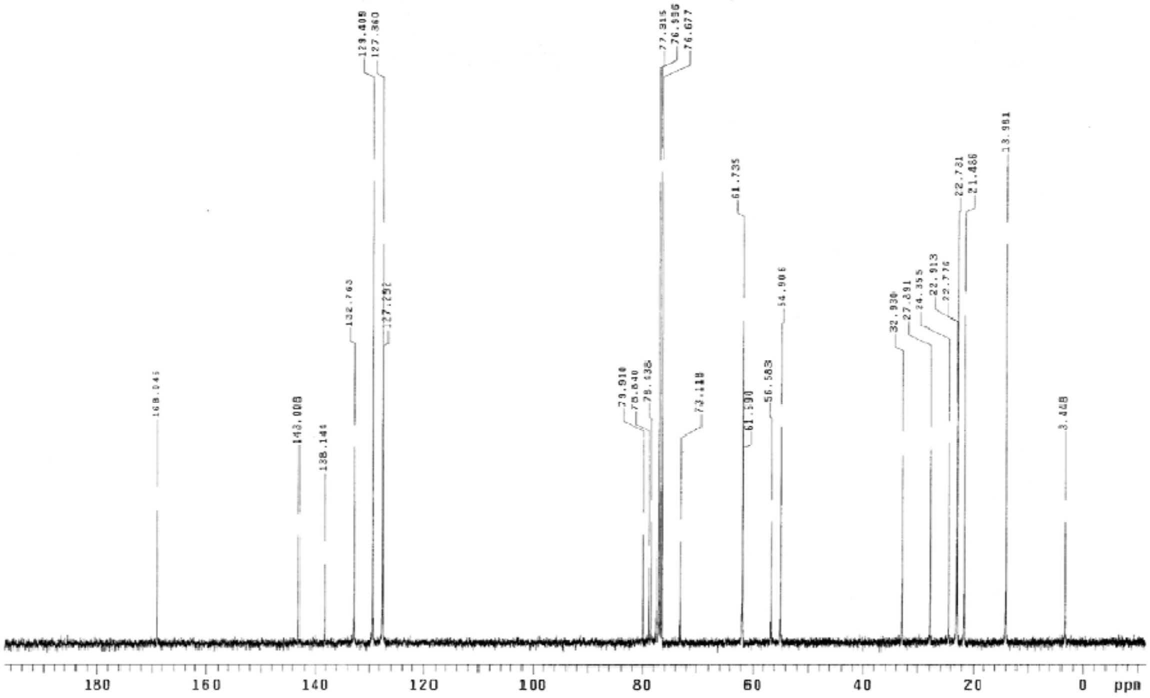
1.91
0.94
0.93
0.96
6.45
1.00
4.78
3.00
1.77
6.41
1.16
8.05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76.996
76.677
73.118
61.735
61.590
56.583
54.906
32.930
27.891
24.355
22.913
22.776
22.731
21.466
13.981
3.448
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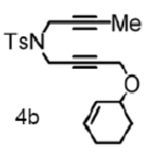
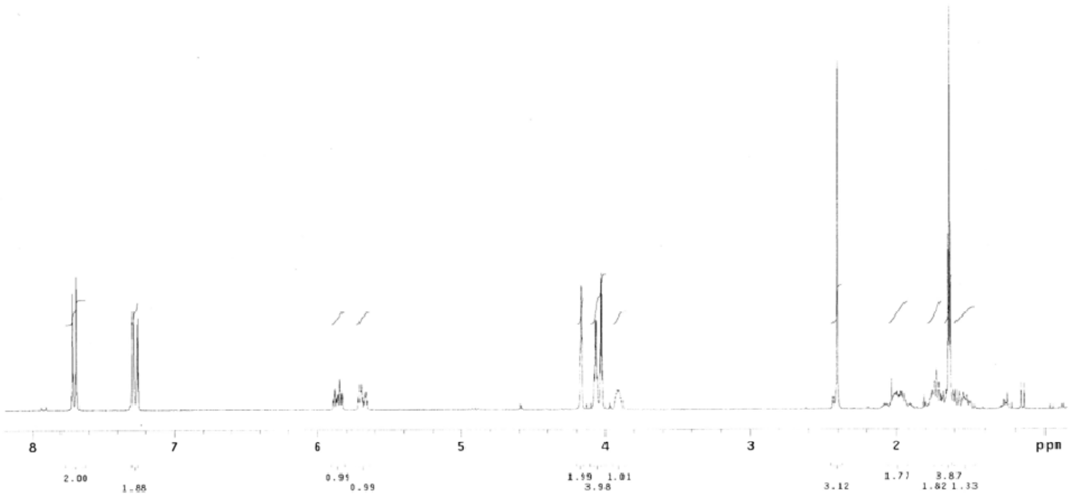
120
100
80
60
40
20
0
ppm


TsN
Me
O

4b


8
7
6
5
4
3
2
ppm
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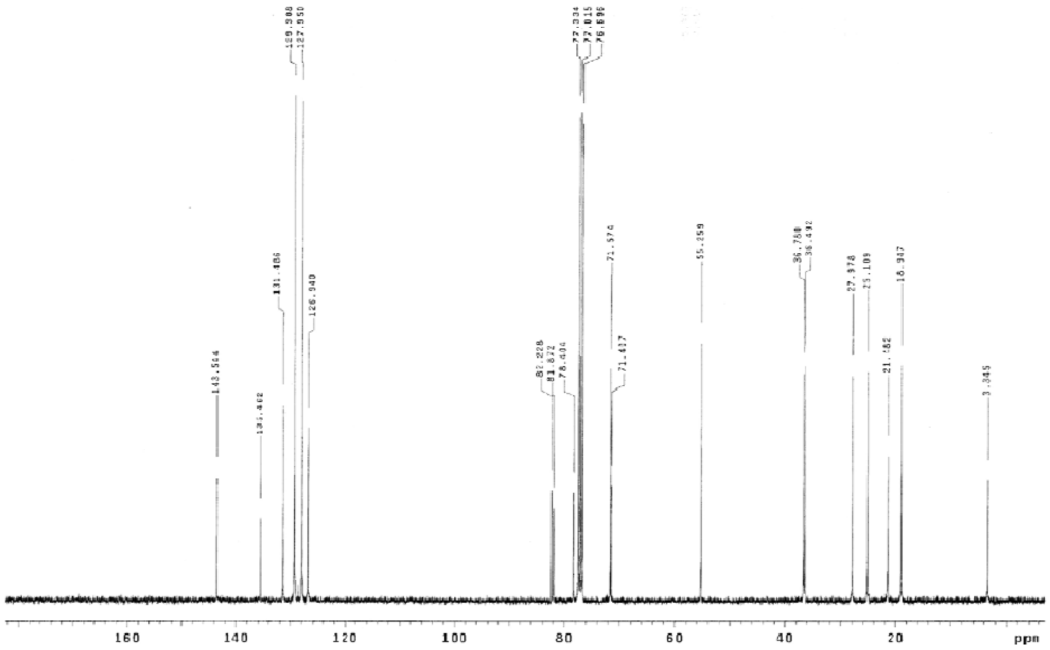
0.99
0.99
1.99
1.01
3.98
3.12
1.77
3.87
1.82
1.33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77.334
77.015
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71.417
55.259
36.780
36.492
27.978
25.109
21.582
18.947
3.345
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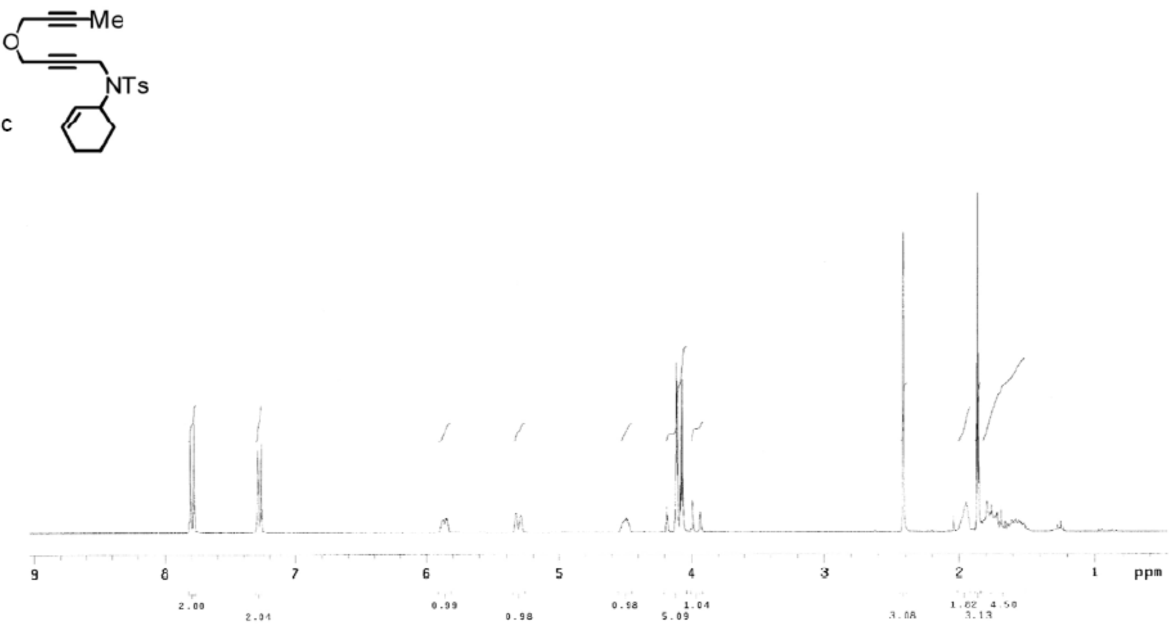
140
120
100
80
60
40
20
ppm

4c


Me
O
NTs
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8
7
6
5
4
3
2
1
ppm
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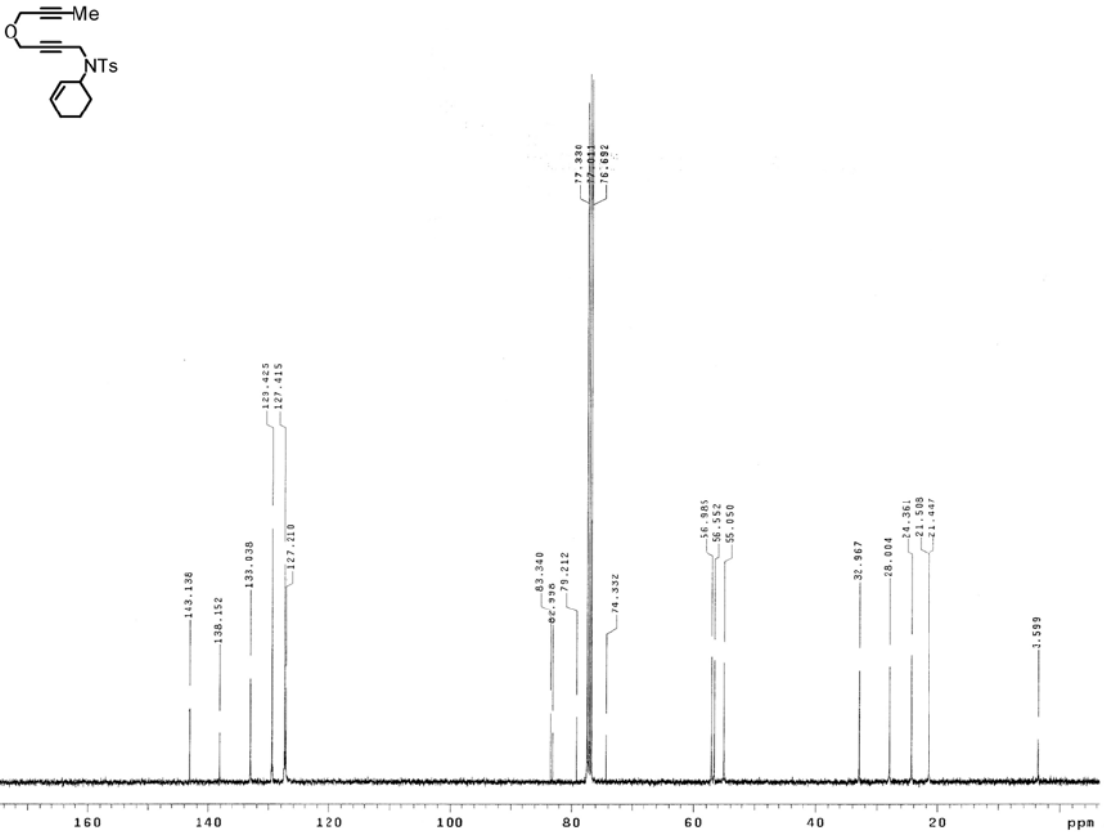
2.04
0.99
0.98
0.98
1.04
5.09
3.08
1.82
4.50
3.13

4c


Me
O
NTs
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77.011
76.692
129.425
127.415
127.210
133.038
143.138
138.152
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74.332
56.985
56.552
55.050
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24.361
21.508
21.447
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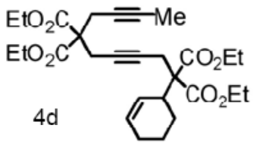
140
120
100
80
60
40
20
ppm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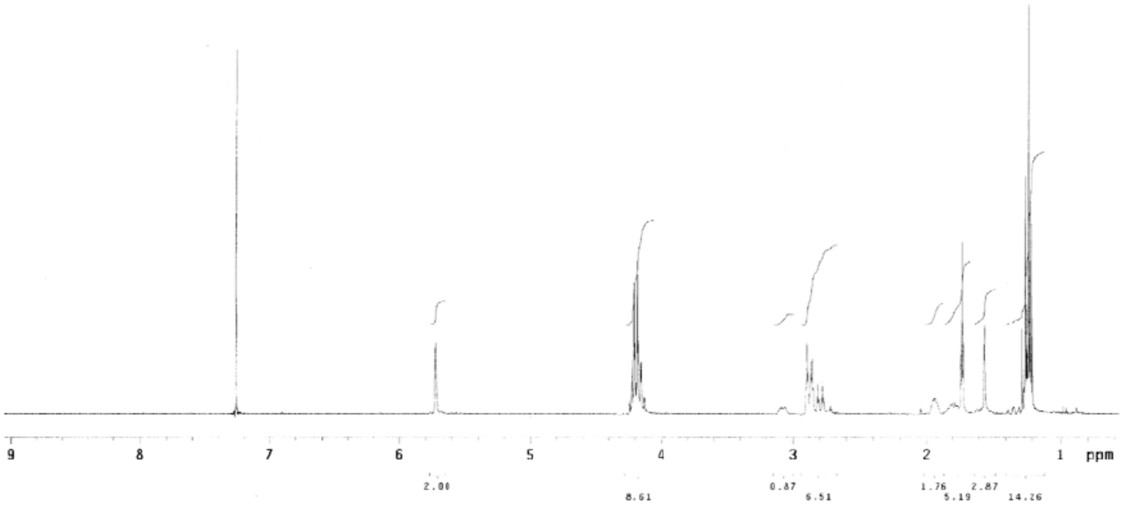
EtO2C
Me
CO2Et
CO2Et

4d


9
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7
6
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4
3
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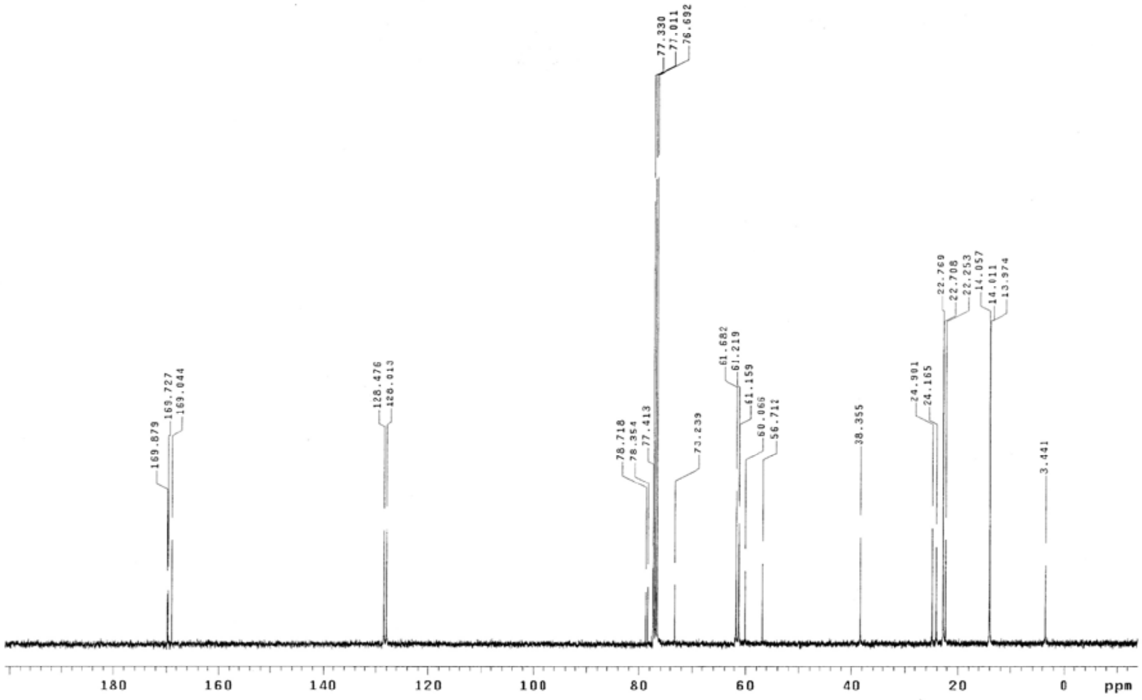
5.19
2.87
14.26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128.013
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77.330
77.011
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61.219
61.159
60.066
56.712
38.355
24.901
24.165
22.769
22.708
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14.011
13.974
3.441
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120
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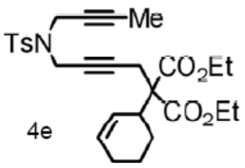
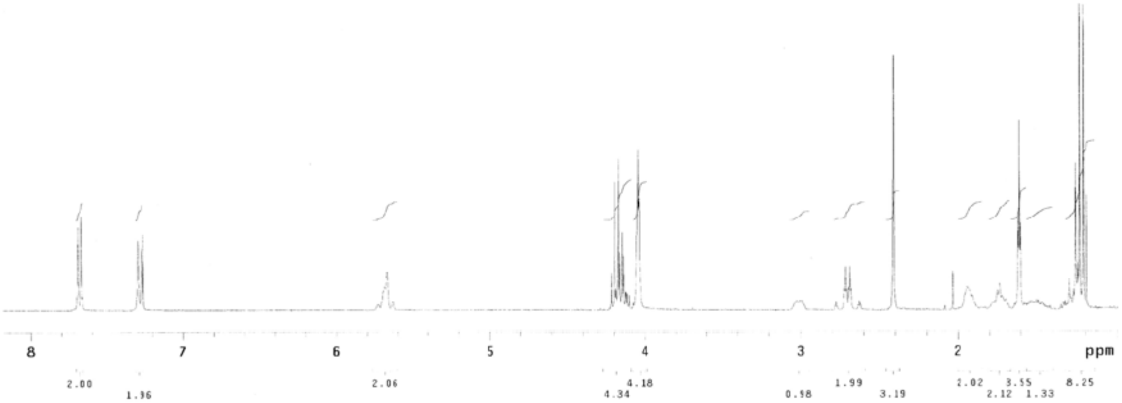
20
0
ppm


TsN
Me
CO2Et
CO2Et

4e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3
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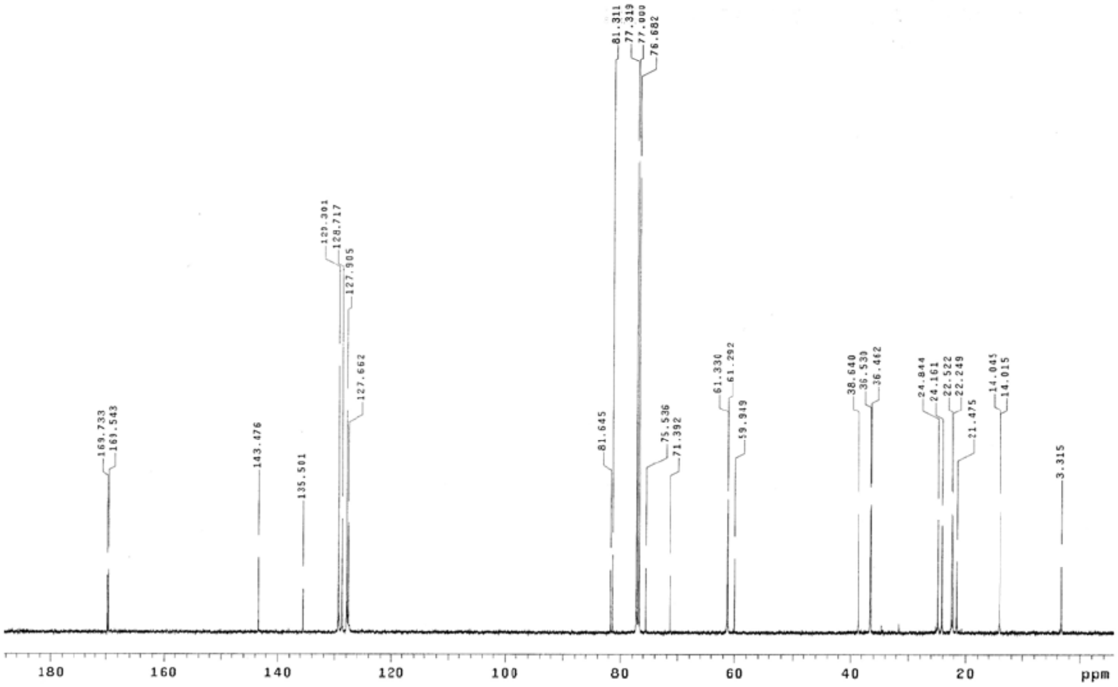
3.19
2.02
2.12
3.55
1.33
8.25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75.536
71.392
61.330
61.292
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38.640
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36.462
24.844
24.161
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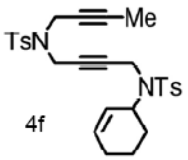
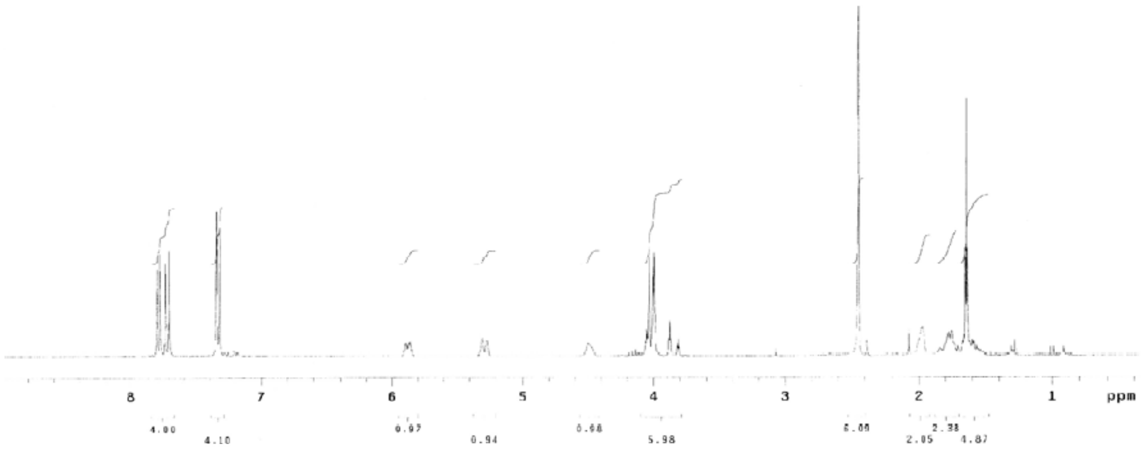

TsN
Me
NTs

4f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5.98
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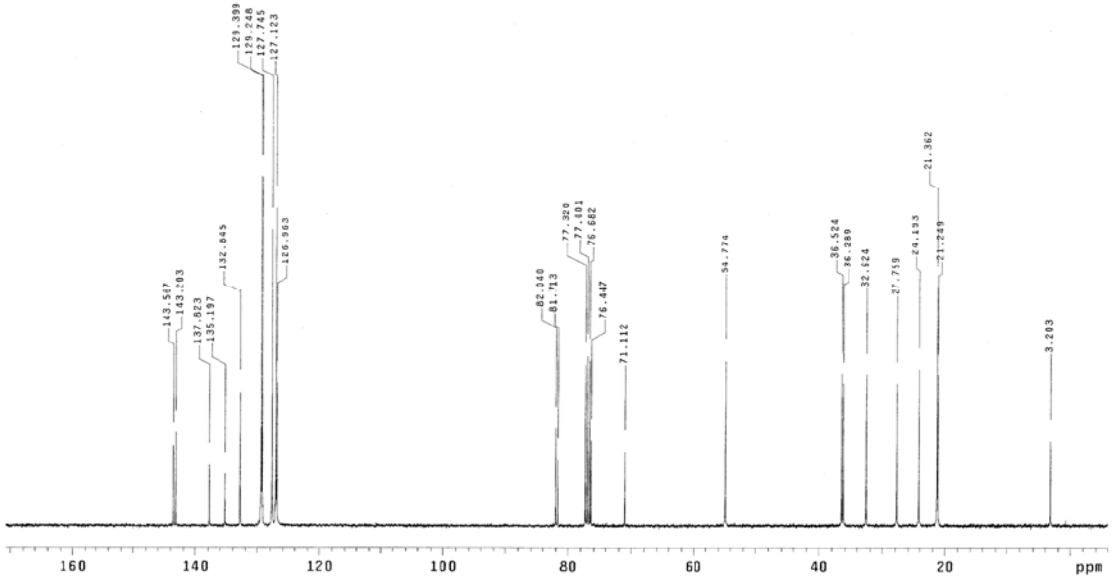
2.38
4.87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36.524
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21.249
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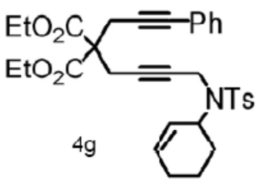
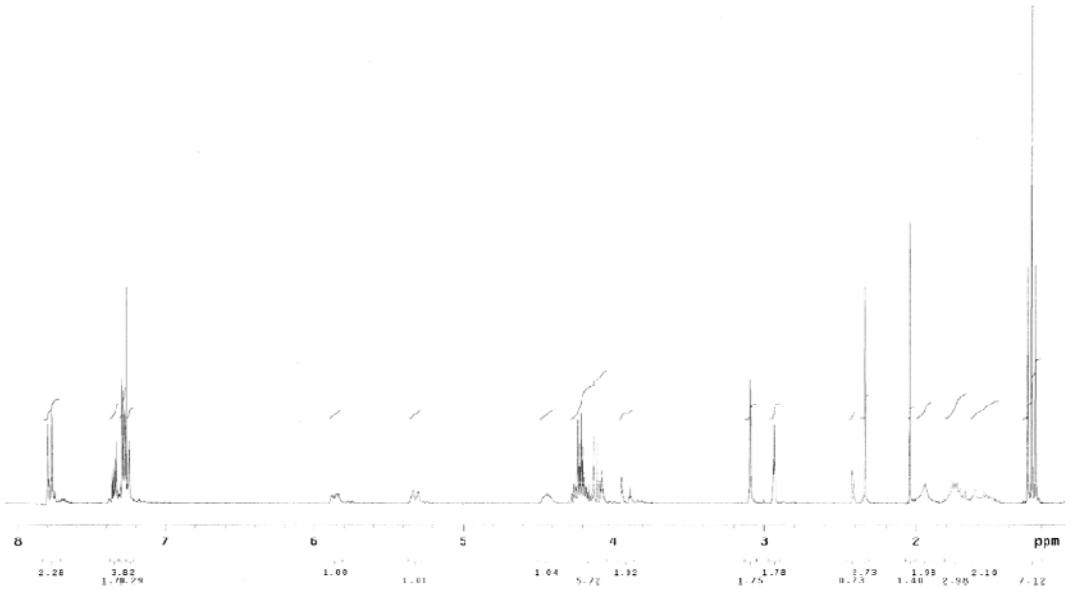
20
ppm


EtO2C
EtO2C
Ph
NTs

4g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7
6
5
4
3
2
ppm
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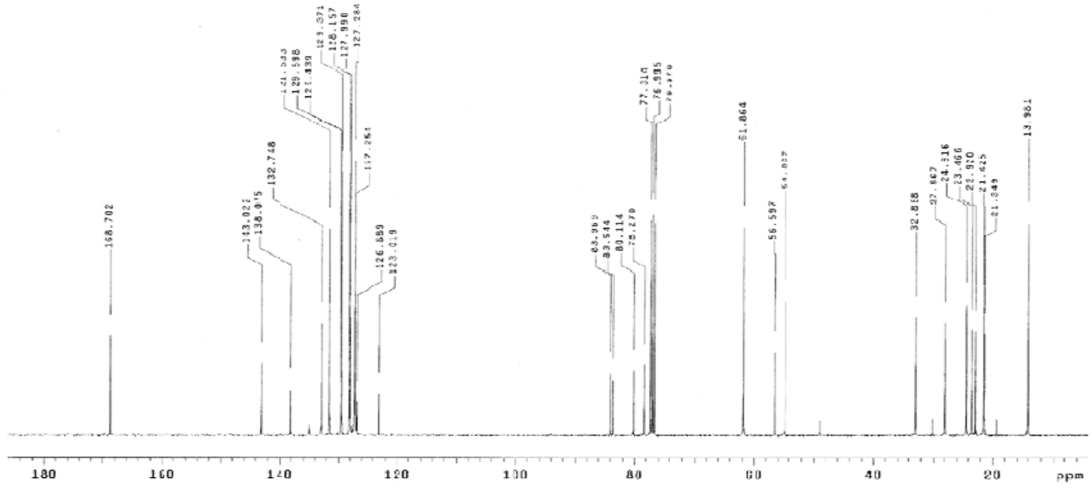
1.00
1.01
1.04
5.72
1.92
1.75
1.78
0.73
2.73
1.40
1.93
2.98
2.10
7.12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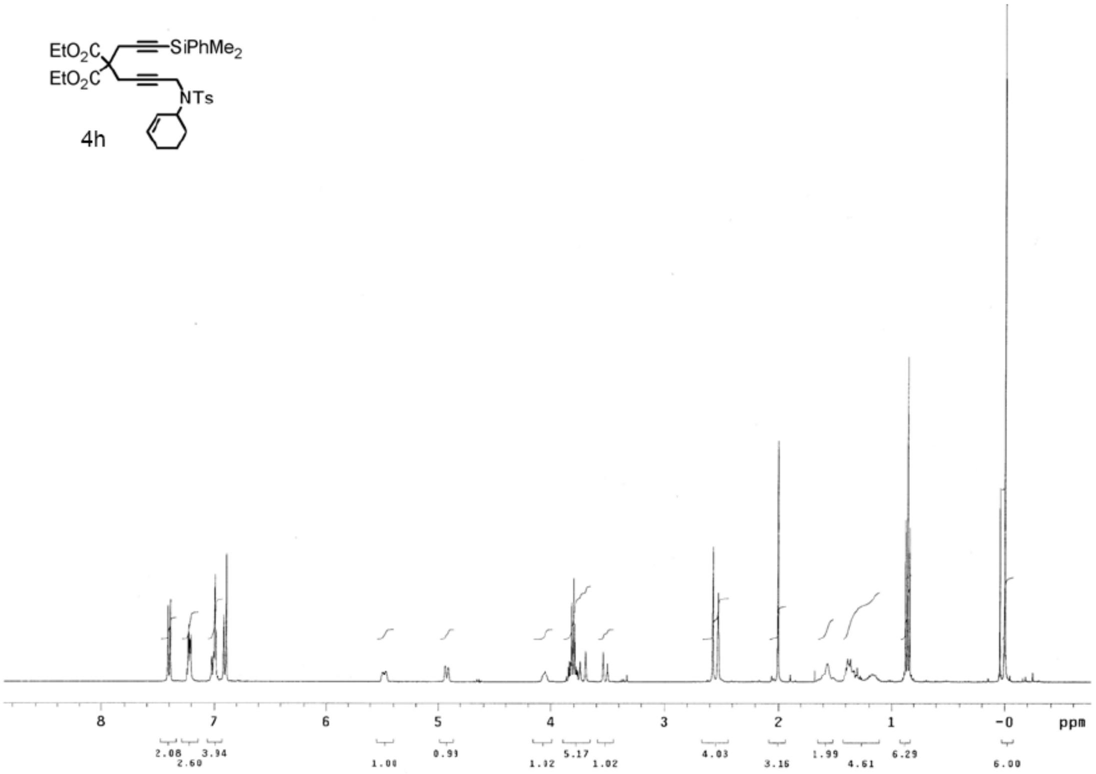
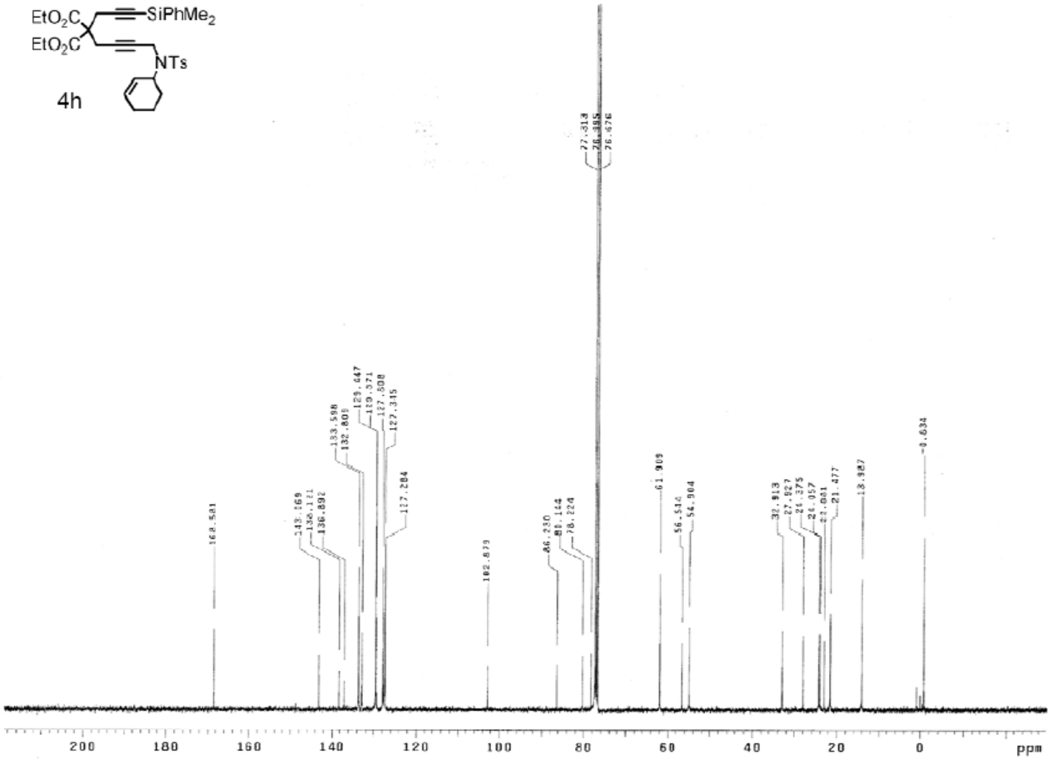
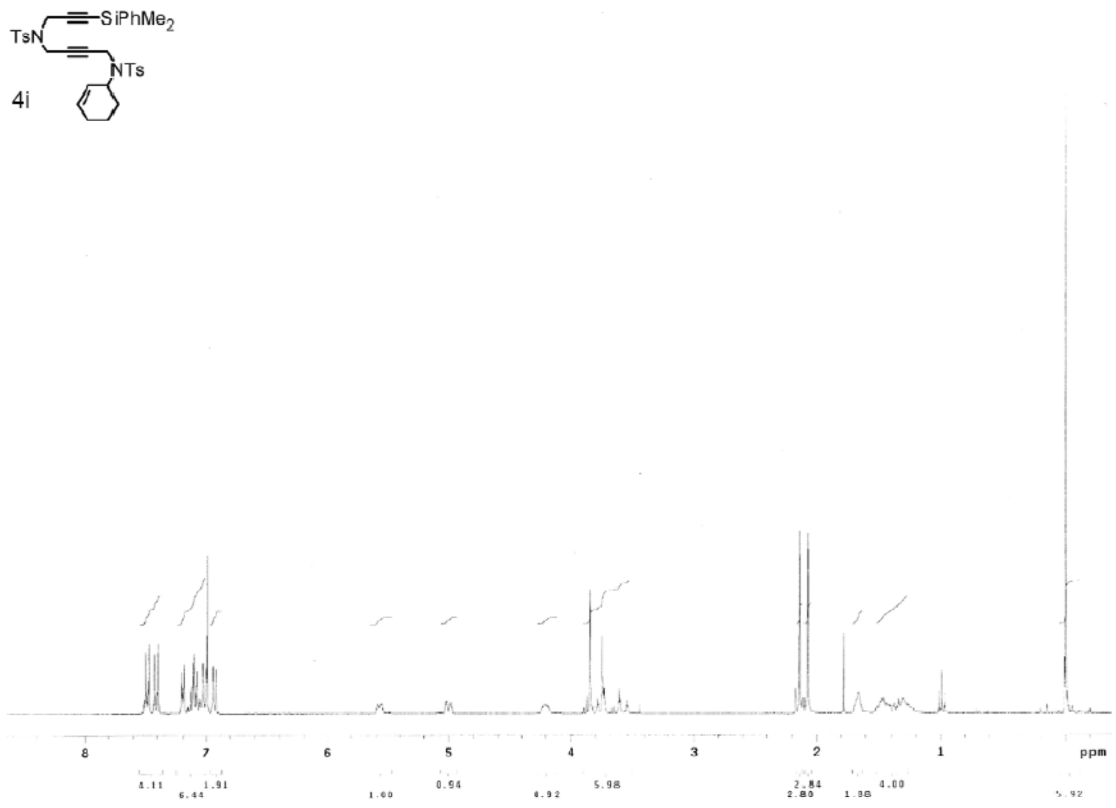
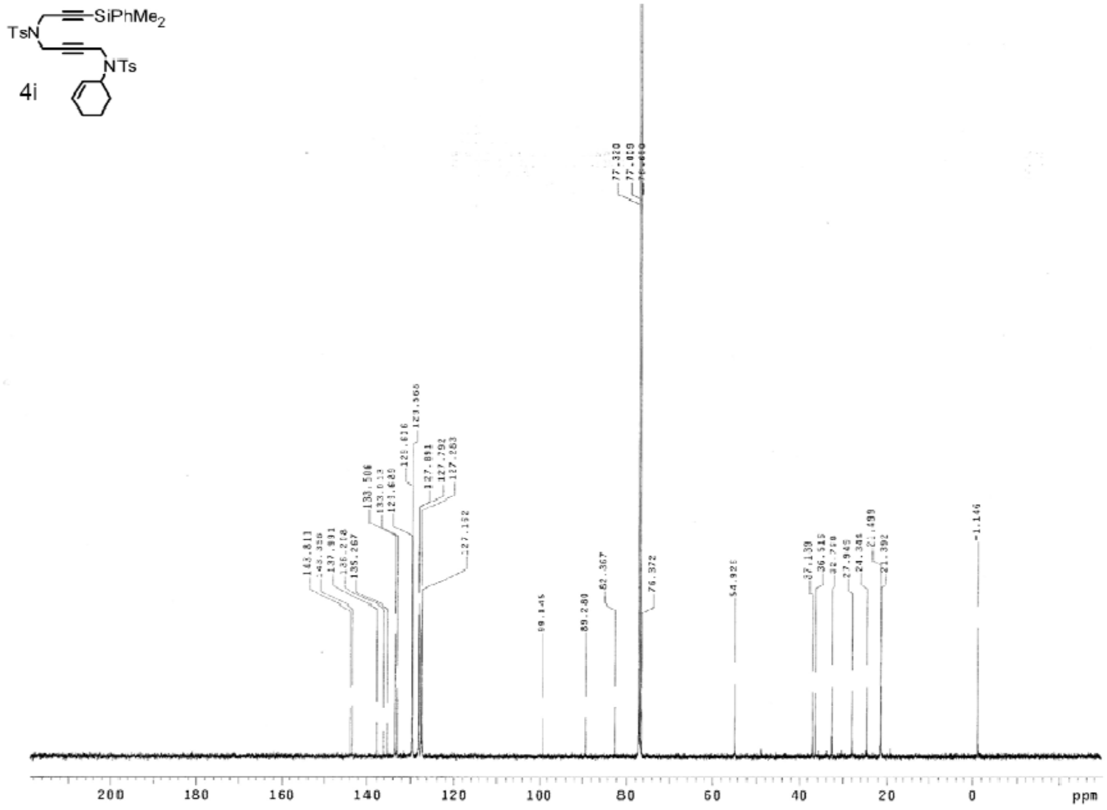
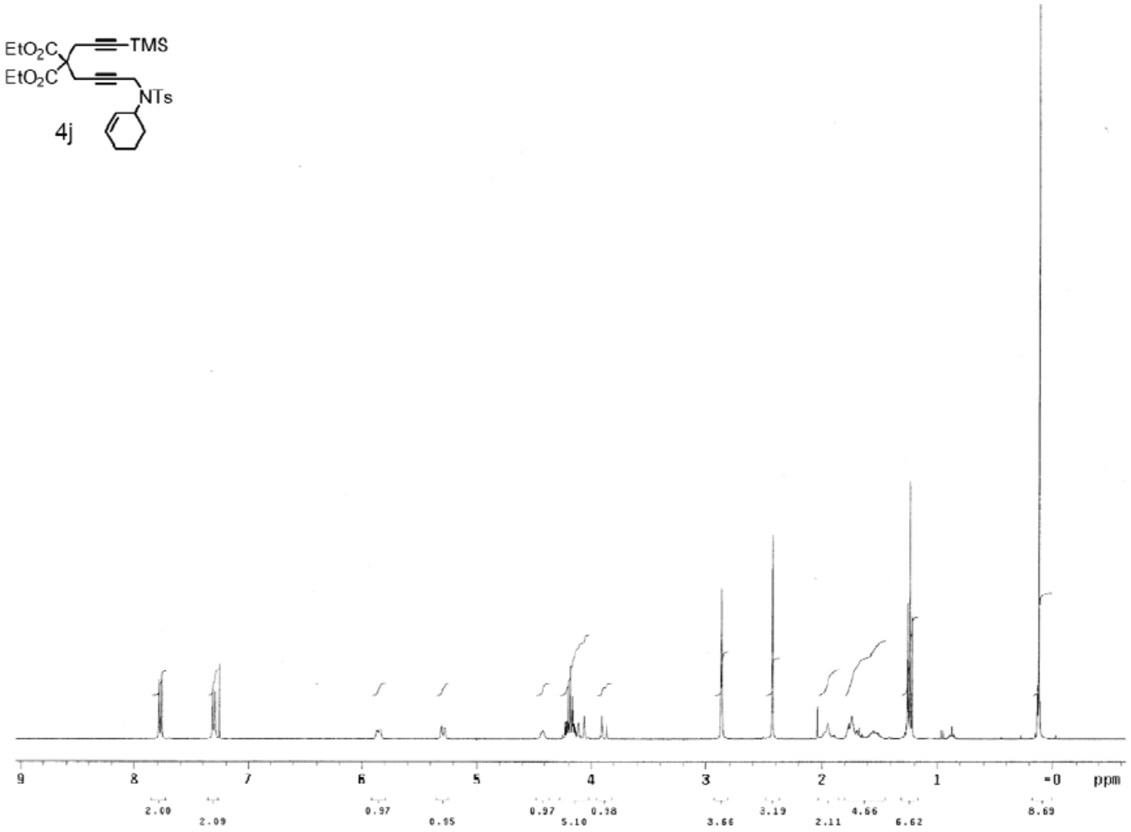
123.019
83.969
83.544
80.114
78.270
77.310
76.995
76.679
61.864
56.597
54.697
32.888
27.867
24.316
23.466
22.910
21.625
21.849
13.981
180
160
140
120
100
80
60
40
20
ppm

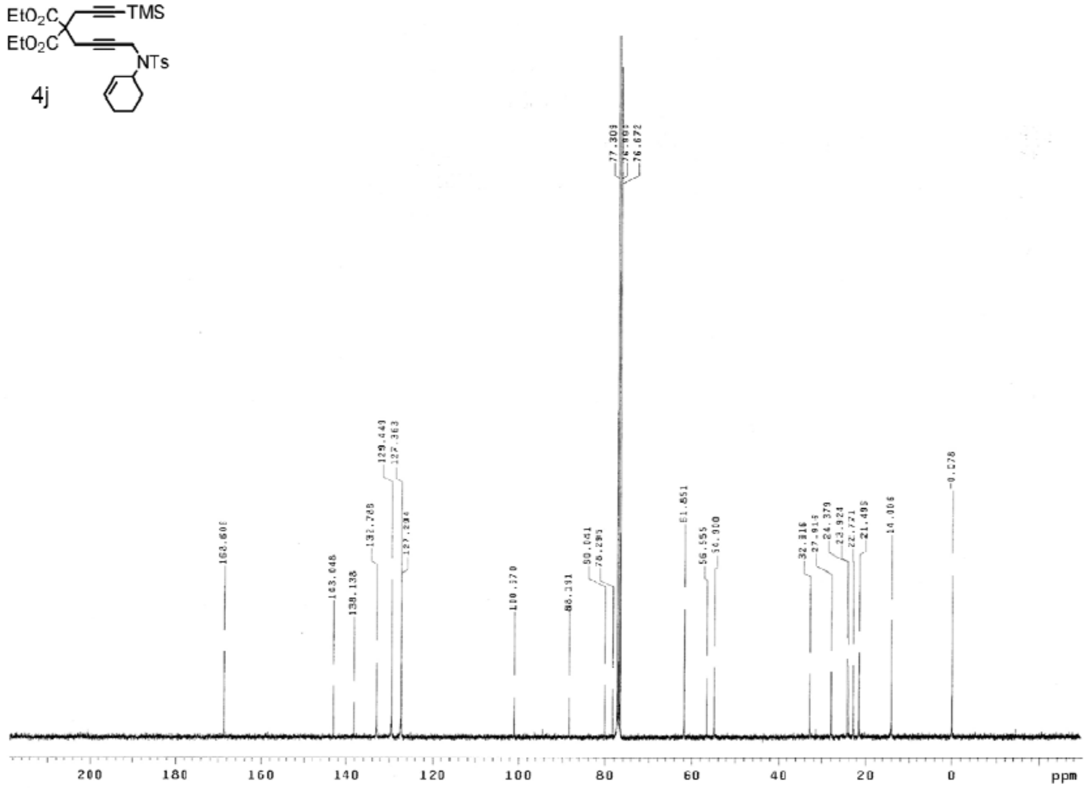

4h
EtO2C
EtO2C
SiPhMe2
NTs
8
7
6
5
4
3
2
1
-0
ppm
2.08
2.60
3.94
1.00
0.93
1.12
5.17
1.02
4.03
3.16
1.99
4.61
6.29
6.00

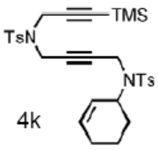

4h
EtO2C
EtO2C
SiPhMe2
NTs
168.581
143.169
138.121
136.892
133.598
132.809
129.447
129.371
127.508
127.345
127.284
102.879
86.230
80.144
78.224
77.318
76.895
76.676
61.909
56.514
54.904
32.913
27.927
24.375
24.057
22.081
21.477
13.987
-0.634
200
180
160
140
120
100
80
60
40
20
0
ppm


SiPhMe2
TsN
NTs
4i
8
7
6
5
4
3
2
1
ppm
4.11
6.44
1.91
1.00
0.94
0.92
5.98
2.84
2.80
1.88
4.00
5.92

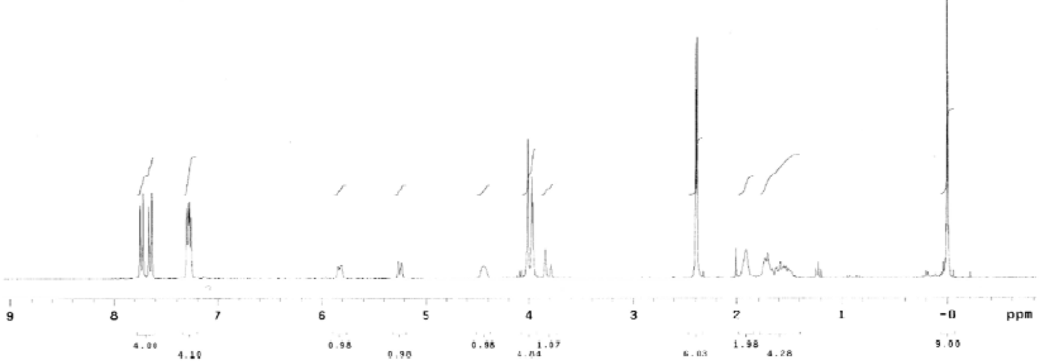

SiPhMe2
TsN
NTs
4i
77.330
77.010
76.680
143.811
143.358
137.991
136.218
135.267
133.506
133.013
131.685
128.616
129.366
127.891
127.792
127.263
127.152
99.145
89.260
82.367
76.372
54.928
37.139
36.515
32.750
27.945
24.388
21.499
21.392
-1.146
200
180
160
140
120
100
80
60
40
20
0
ppm

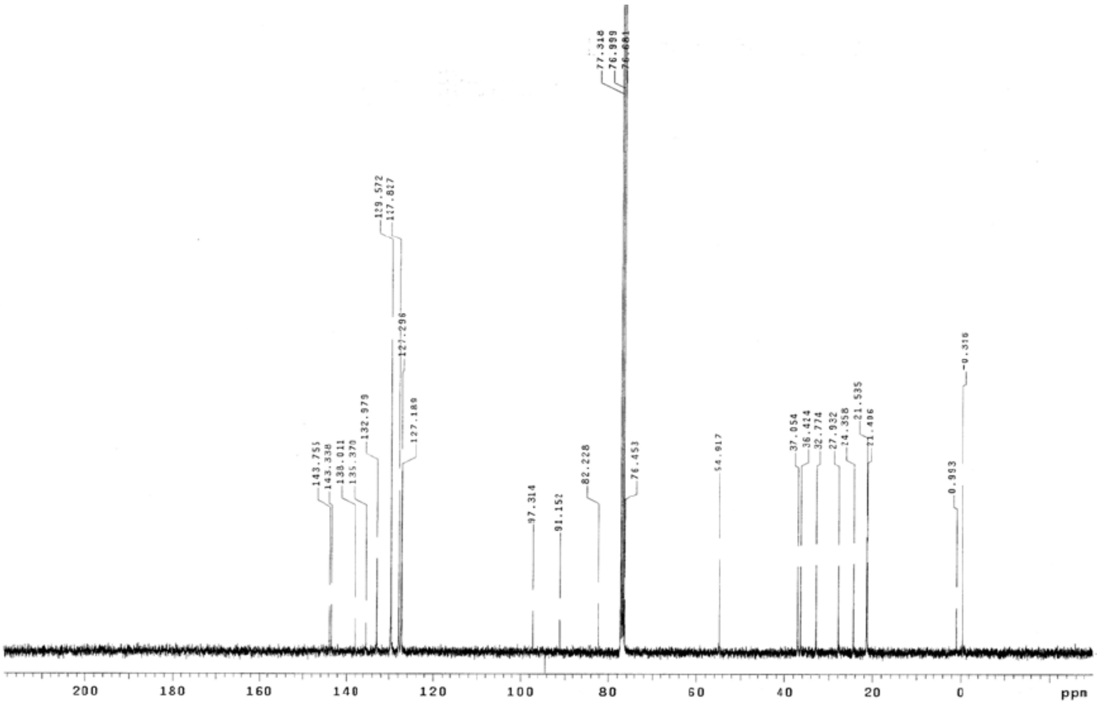

EtO2C
EtO2C
TMS
NTs
4j
9
8
7
6
5
4
3
2
1
=0
ppm
2.00
2.09
0.97
0.95
0.97
5.10
0.98
3.66
3.19
2.11
4.66
6.62
8.69

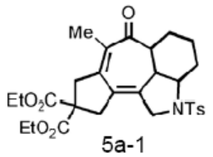

EtO2C
EtO2C
TMS
NTs
4j
77.309
76.982
76.672
168.606
143.048
138.138
132.788
129.449
127.363
127.294
100.370
88.391
80.041
78.295
61.851
56.555
54.900
32.316
27.915
24.379
23.924
22.771
21.495
14.006
-0.078
200
180
160
140
120
100
80
60
40
20
0
ppm


TMS
TsN
NTs

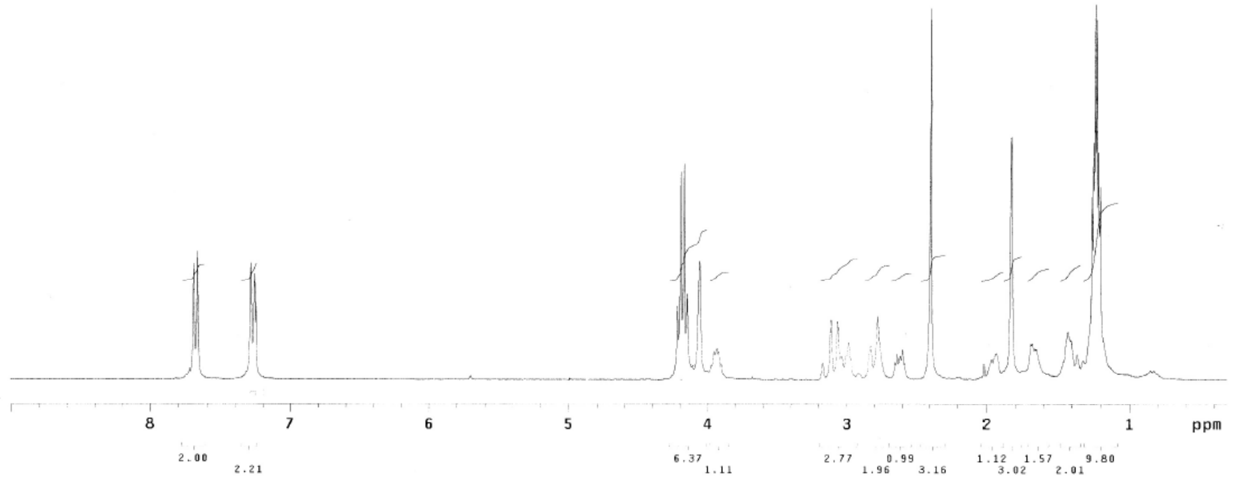
4k

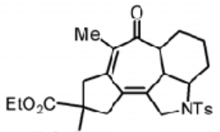

9
8
7
6
5
4
3
2
1
-0
ppm
4.00
4.10
0.98
0.90
0.98
4.04
1.07
6.03
1.98
4.28
9.00


77.318
76.999
76.681
129.572
127.817
127.296
127.189
143.755
143.338
138.011
135.370
132.979
97.314
91.152
82.228
76.453
54.917
37.054
36.424
32.774
27.932
24.358
21.535
21.406
0.993
-0.316
200
180
160
140
120
100
80
60
40
20
0
ppm

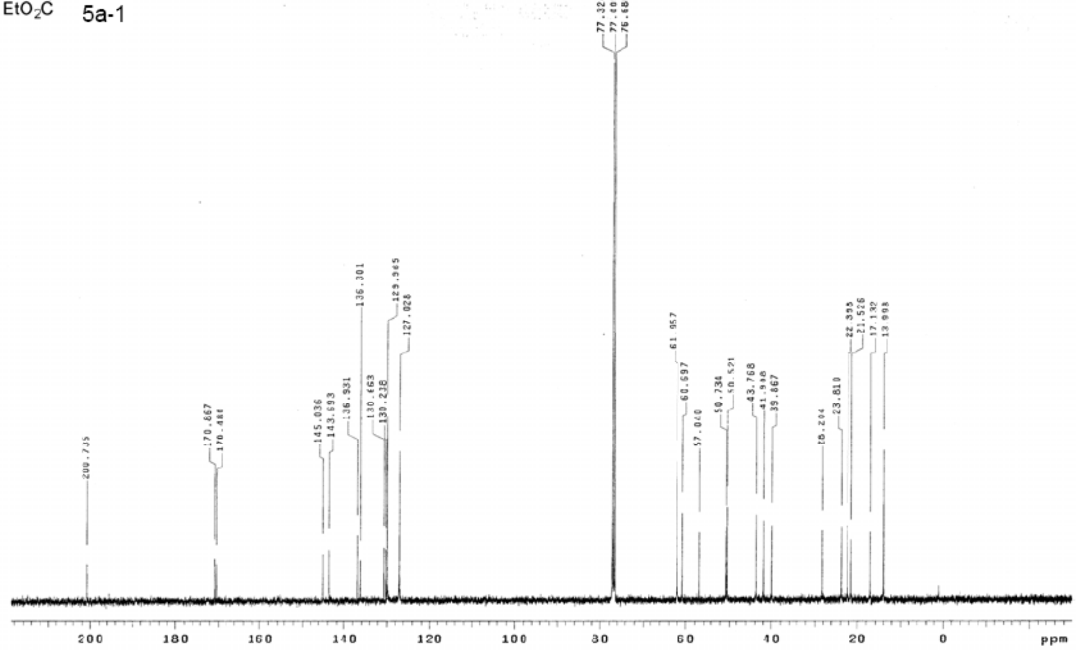

Me
O
EtO$_2$C
EtO$_2$C
NTs

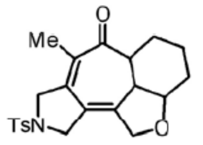
5a-1


8
7
6
5
4
3
2
1
ppm
2.00
2.21
6.37
1.11
2.77
1.96
0.99
3.16
1.12
3.02
1.57
2.01
9.80

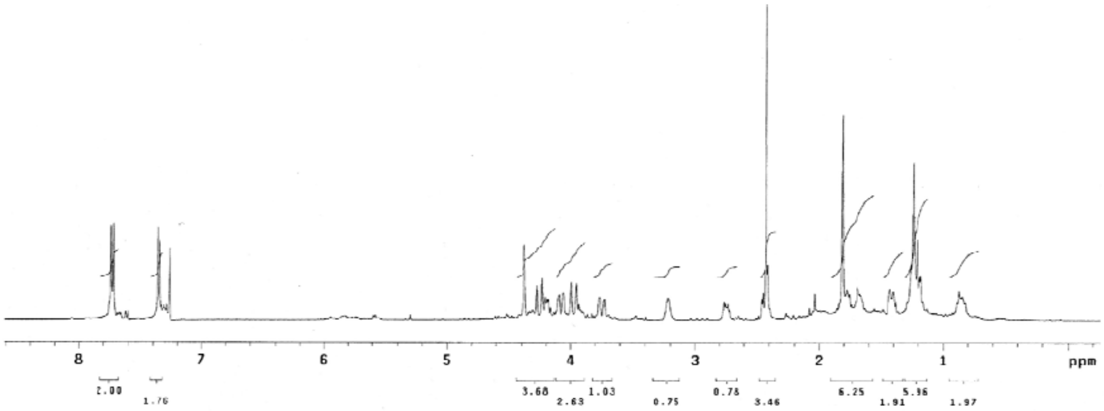

Me
O
EtO$_2$C
EtO$_2$C
NTs

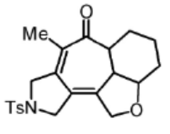
5a-1


200.735
170.667
170.488
145.036
143.693
136.931
136.301
130.463
130.238
129.965
127.028
77.324
77.005
76.686
61.957
60.697
57.040
50.734
50.521
43.768
41.998
39.867
28.204
23.810
22.395
21.526
17.132
13.998
200
180
160
140
120
100
80
60
40
20
0
ppm

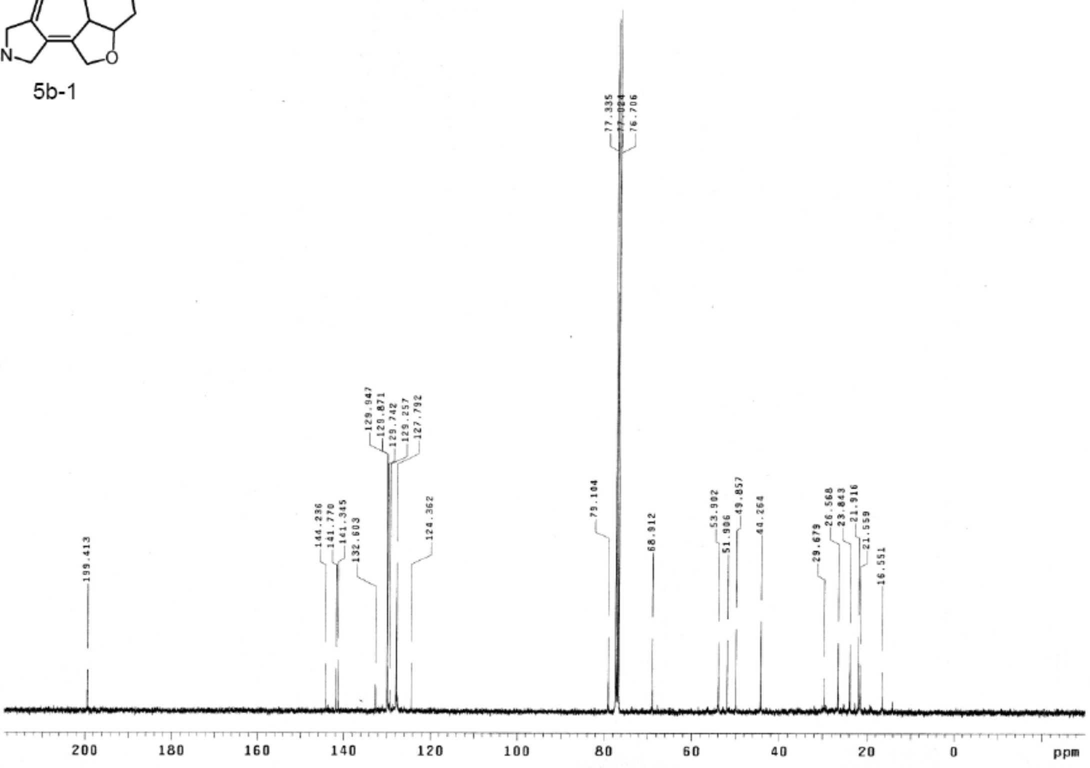

Me
O
TsN
O

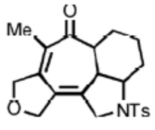
5b-1


8
7
6
5
4
3
2
1
ppm
2.00
1.76
3.68
2.63
1.03
0.75
0.78
3.46
6.25
1.91
5.36
1.97

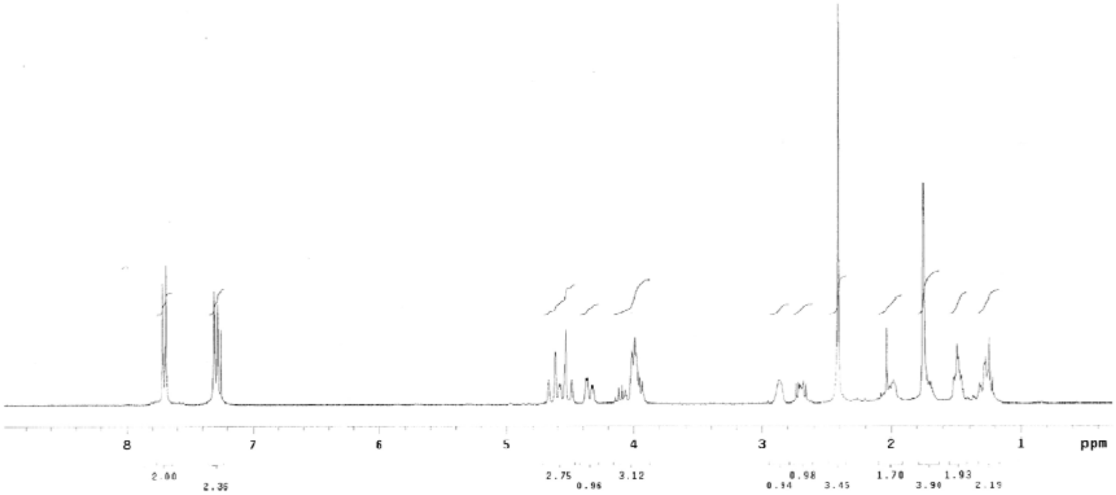

Me
O
TsN
O

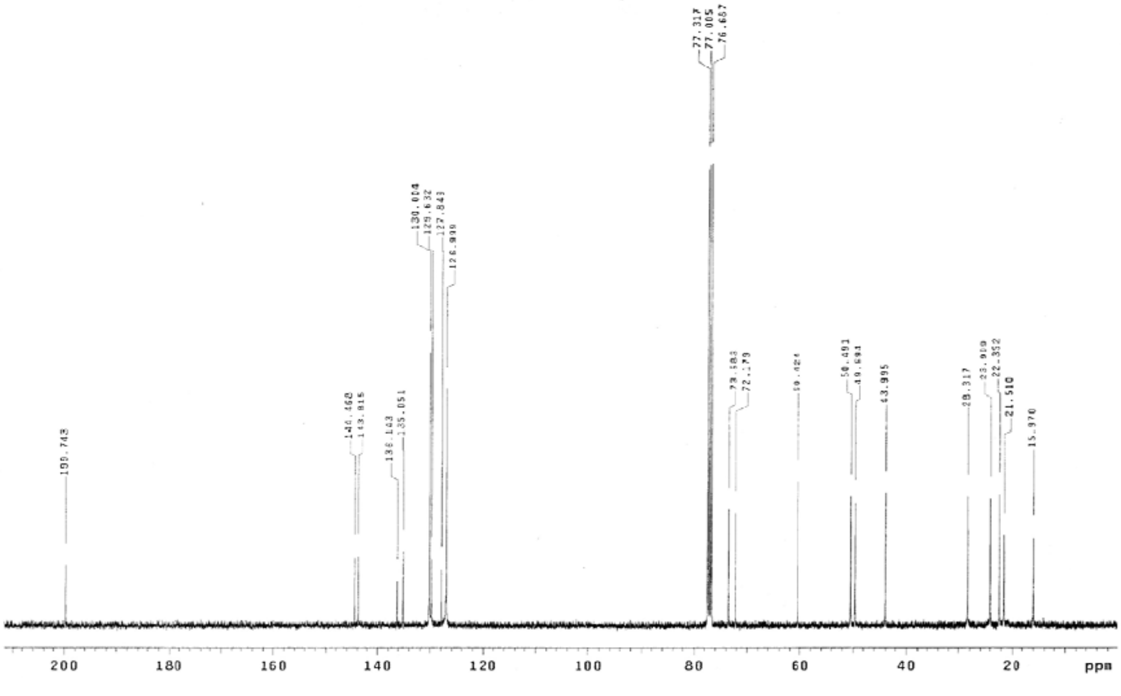
5b-1

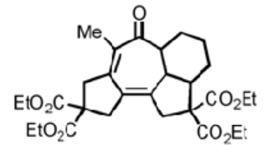

199.413
144.236
141.770
141.345
132.603
129.947
129.871
129.742
129.257
127.792
124.362
79.104
77.335
77.024
76.706
68.912
53.902
51.906
49.857
44.264
29.679
26.568
23.843
21.916
21.559
16.551
200
180
160
140
120
100
80
60
40
20
0
ppm


Me
O
O
NTs

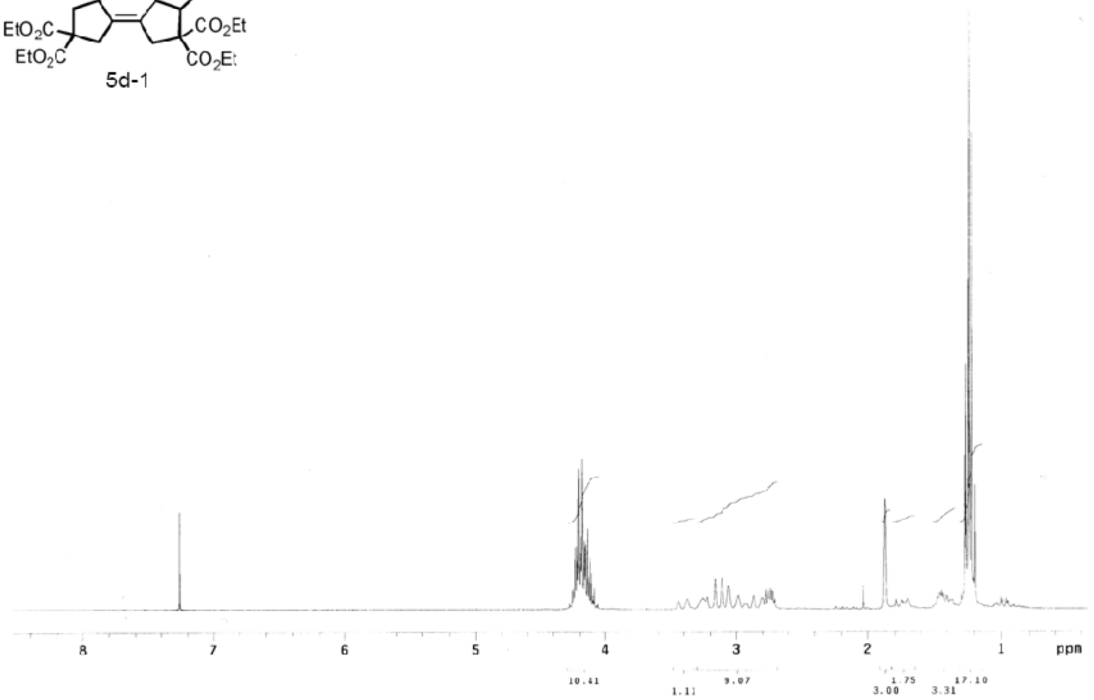
5c-1

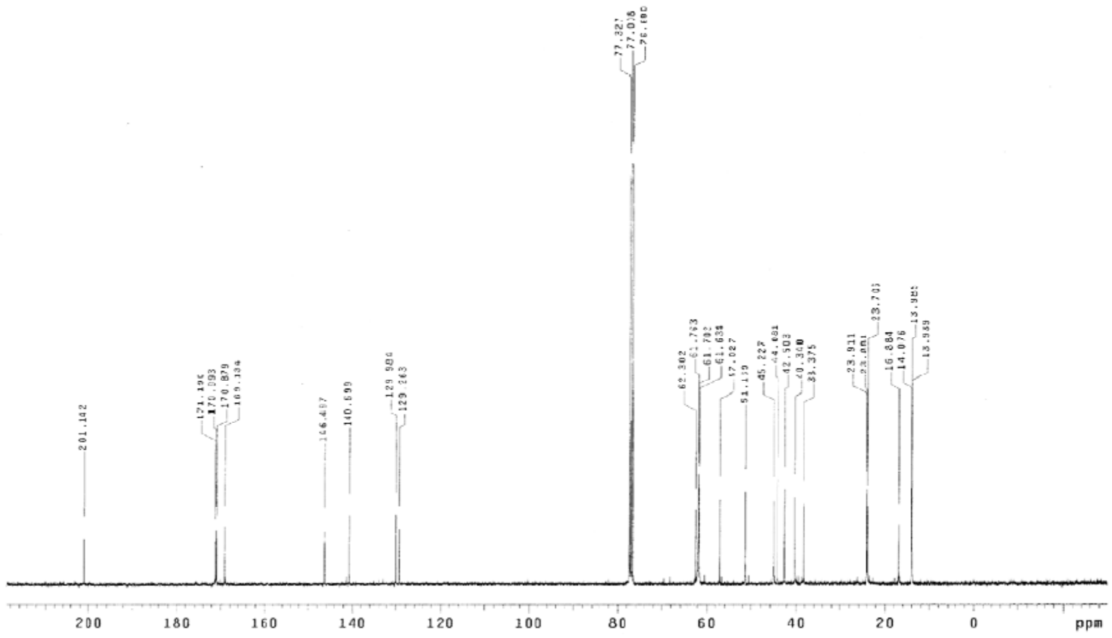

8
7
6
5
4
3
2
1
ppm
2.00
2.36
2.75
0.96
3.12
0.94
0.98
3.45
1.70
3.90
1.93
2.19

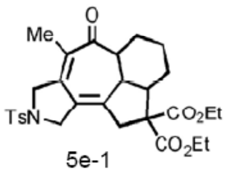

199.743
144.462
143.815
136.143
135.051
130.004
129.632
127.843
126.999
77.317
77.005
76.687
73.583
72.179
59.424
50.491
49.694
43.995
28.317
23.909
22.352
21.510
15.970
200
180
160
140
120
100
80
60
40
20
ppm


Me
O
EtO2C
EtO2C
CO2Et
CO2Et

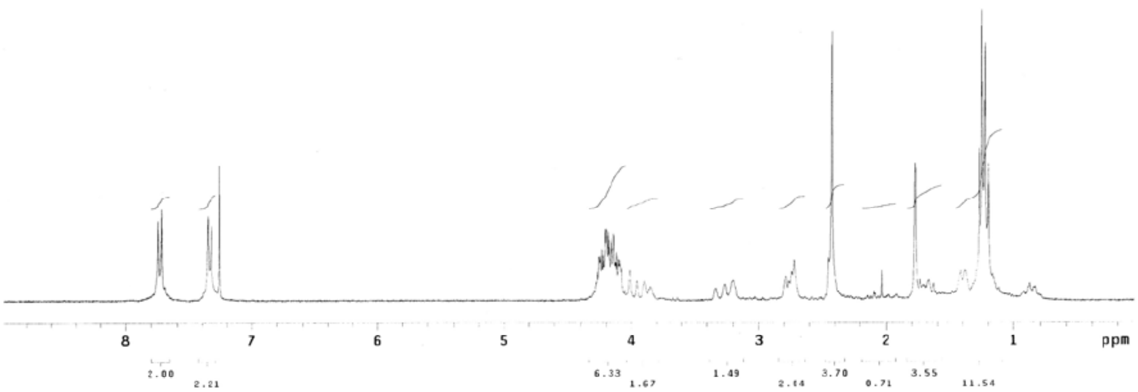
5d-1

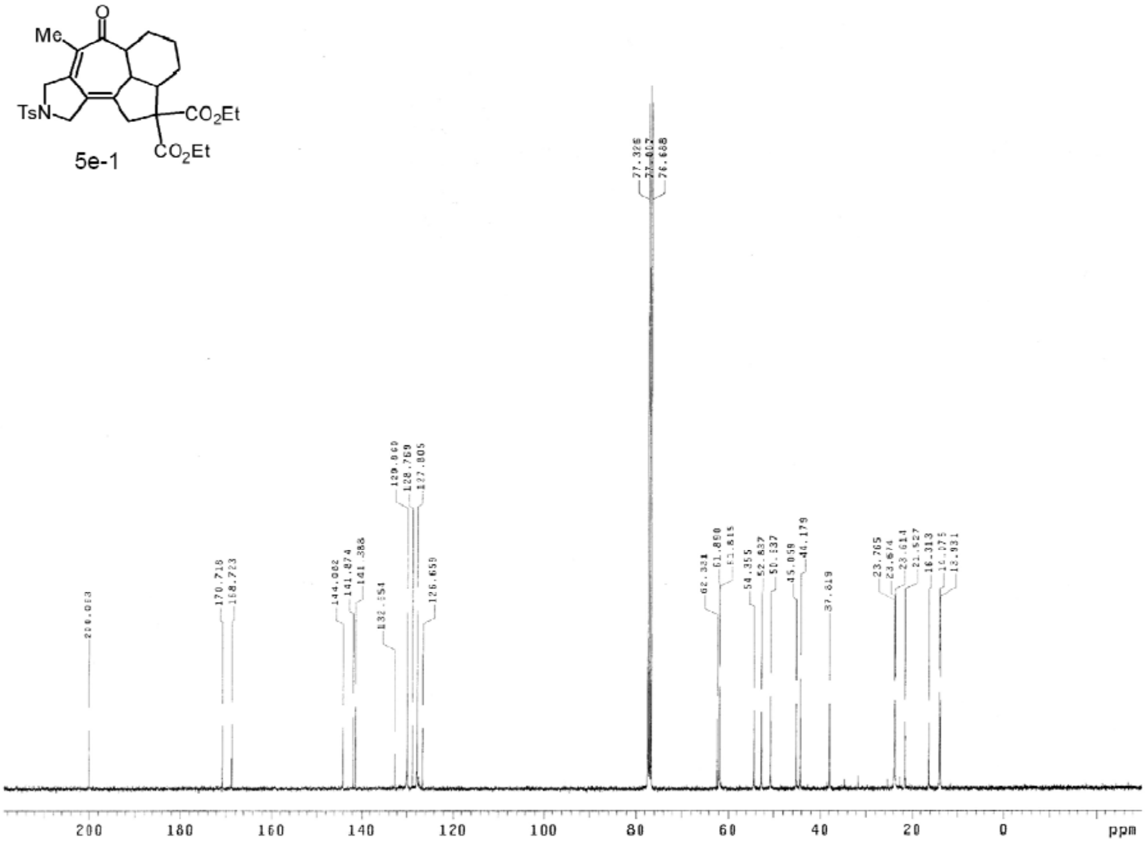

8
7
6
5
4
3
2
1
ppm
10.41
1.11
9.07
3.00
1.75
3.31
17.10


201.142
171.196
170.093
170.879
169.134
146.487
140.699
129.984
129.263
77.321
77.016
76.690
62.302
61.763
61.702
61.638
57.027
51.139
45.227
44.081
42.503
40.340
38.375
23.911
23.881
23.703
16.884
14.076
13.985
13.959
200
180
160
140
120
100
80
60
40
20
0
ppm

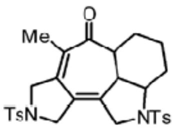

O
Me
TsN
CO$_2$Et
CO$_2$Et

5e-1

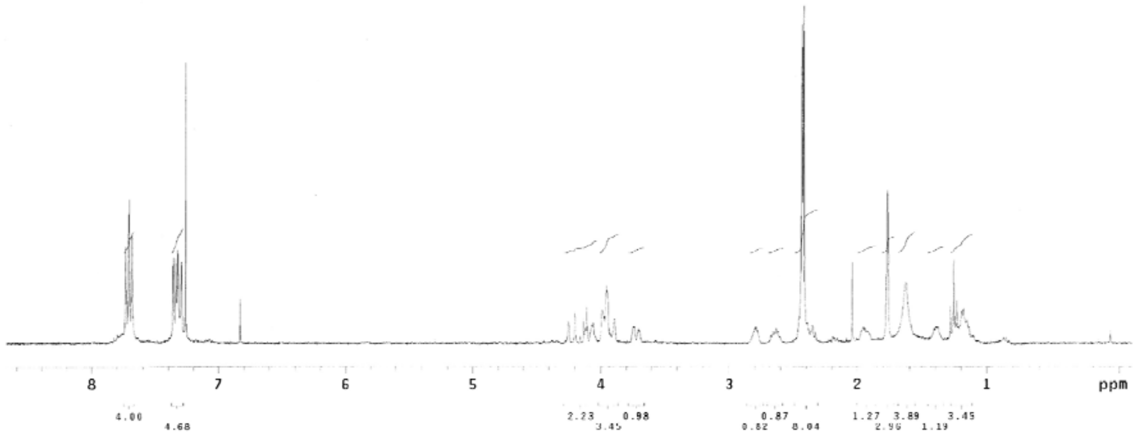

8
7
6
5
4
3
2
1
ppm
2.00
2.21
6.33
1.67
1.49
2.14
3.70
0.71
3.55
11.54

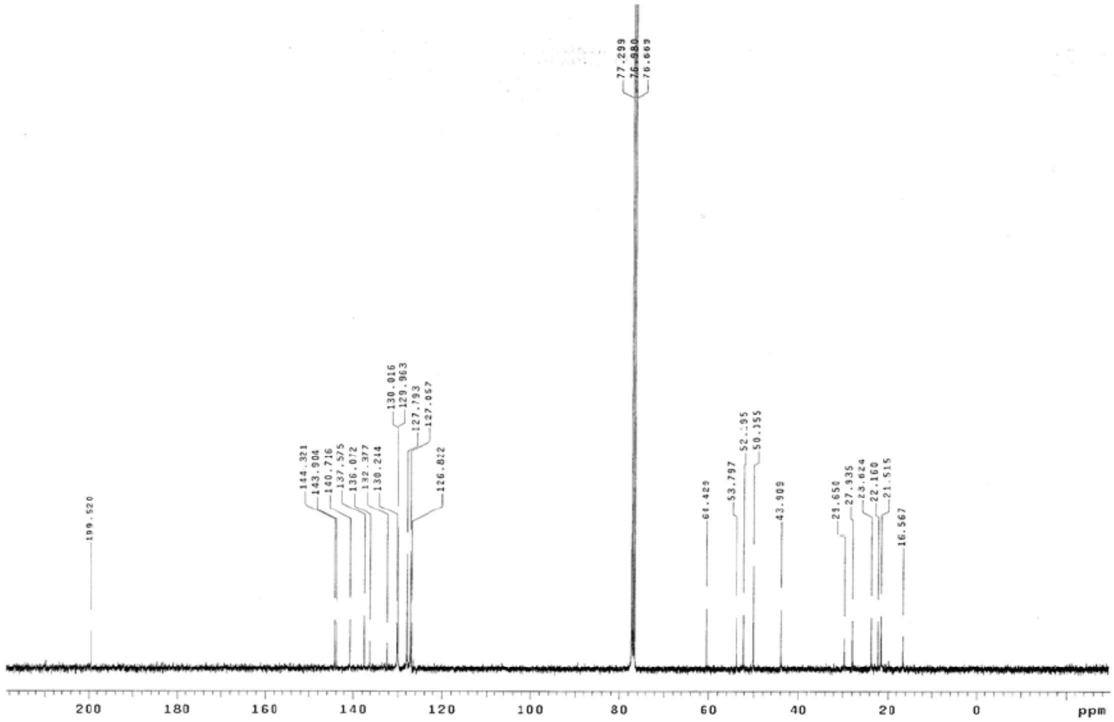

O
Me
TsN
CO$_2$Et
CO$_2$Et
77.326
77.007
76.688
200.063
170.718
168.723
144.062
141.874
141.388
132.554
129.069
128.769
127.805
126.659
62.331
61.890
61.815
54.355
52.837
50.137
45.059
44.179
37.819
23.765
23.674
23.614
21.527
16.313
14.075
13.931
200
180
160
140
120
100
80
60
40
20
0
ppm

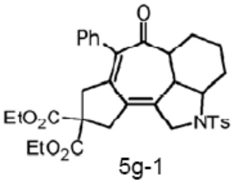
5e-1


Me
O
TsN
NTs

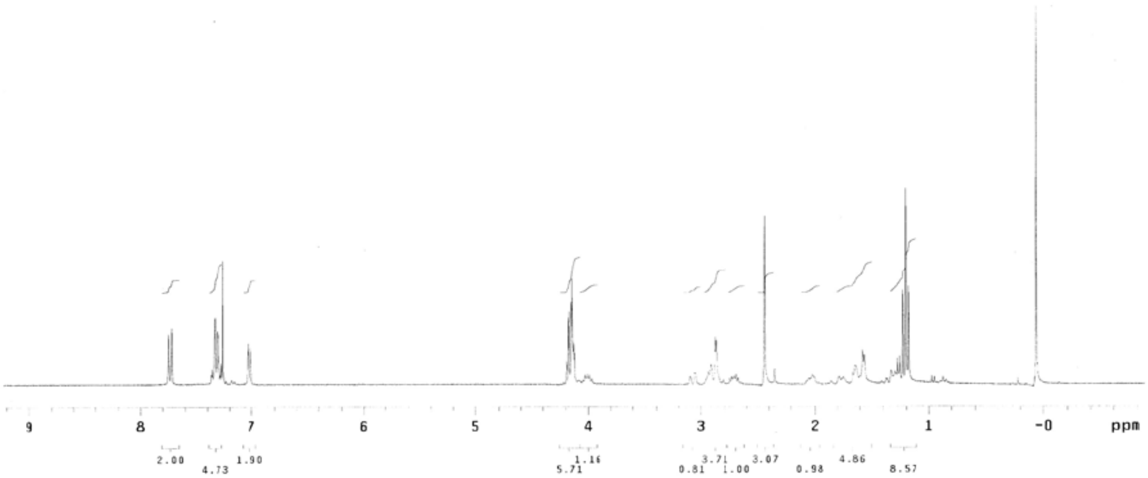
5f-1

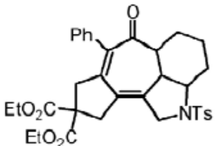

8
7
6
5
4
3
2
1
ppm
4.00
4.68
2.23
3.45
0.98
0.82
0.87
8.04
1.27
2.96
3.89
1.19
3.45


199.520
144.321
143.904
140.716
137.575
136.072
132.377
130.244
130.016
129.963
127.793
127.057
126.822
77.299
76.980
76.669
60.429
53.797
52.[illegible]95
50.355
43.909
29.650
27.935
23.024
22.160
21.515
16.567
200
180
160
140
120
100
80
60
40
20
0
ppm

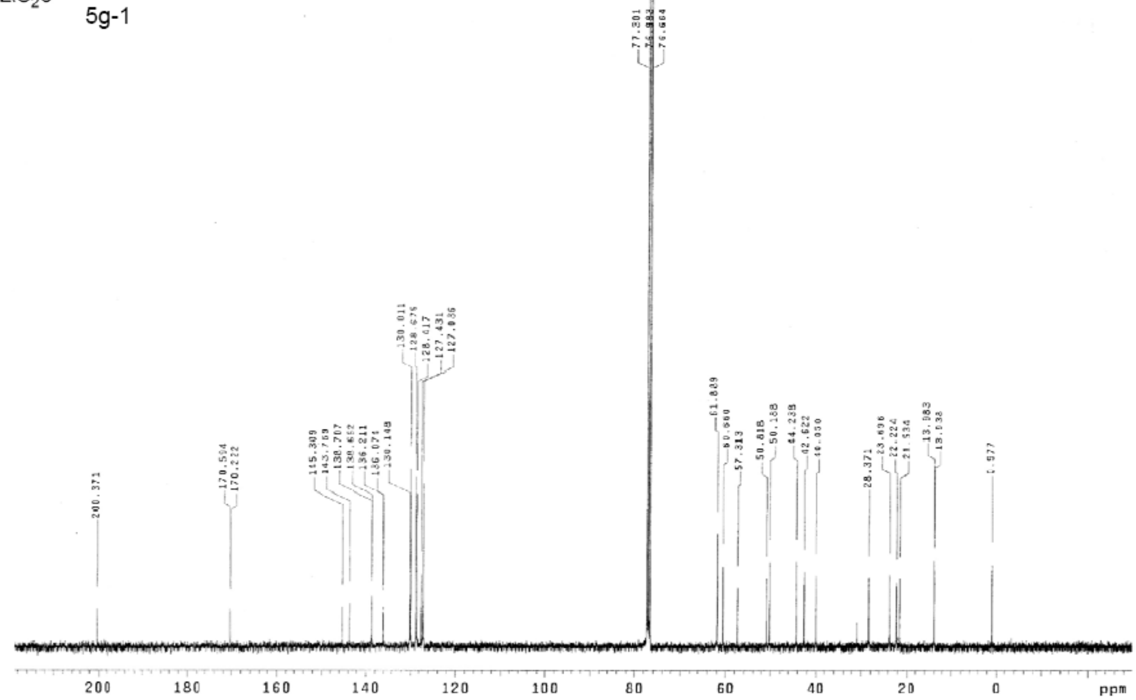

Ph
O
EtO2C
EtO2C
NTs

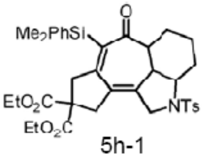
5g-1


9
8
7
6
5
4
3
2
1
-0
ppm
2.00
4.73
1.90
5.71
1.16
0.81
3.71
1.00
3.07
0.98
4.86
8.57

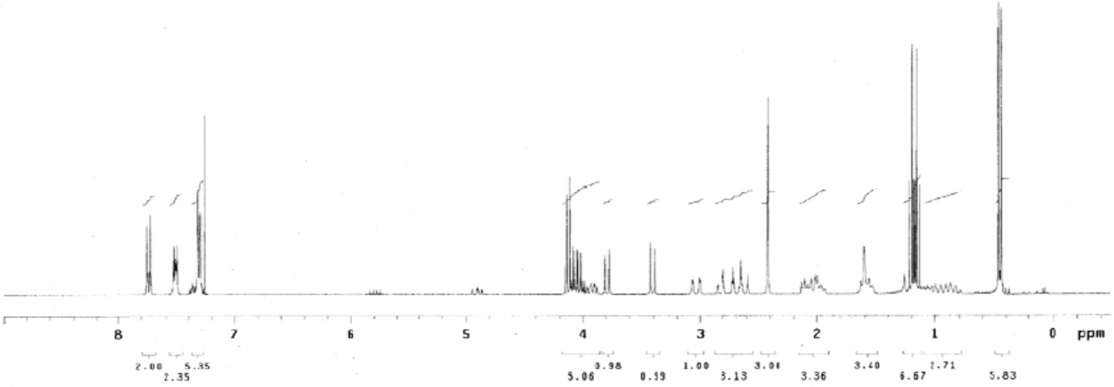

Ph
O
EtO2C
EtO2C
NTs

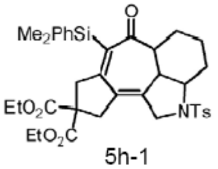
5g-1


200.371
170.504
170.222
145.309
143.769
138.707
138.662
136.211
136.071
130.148
130.011
128.675
128.617
127.431
127.086
77.201
76.883
76.664
61.889
60.660
57.313
50.818
50.188
44.238
42.622
40.050
28.371
23.696
22.224
21.534
13.983
13.938
1.577
200
180
160
140
120
100
80
60
40
20
0
ppm

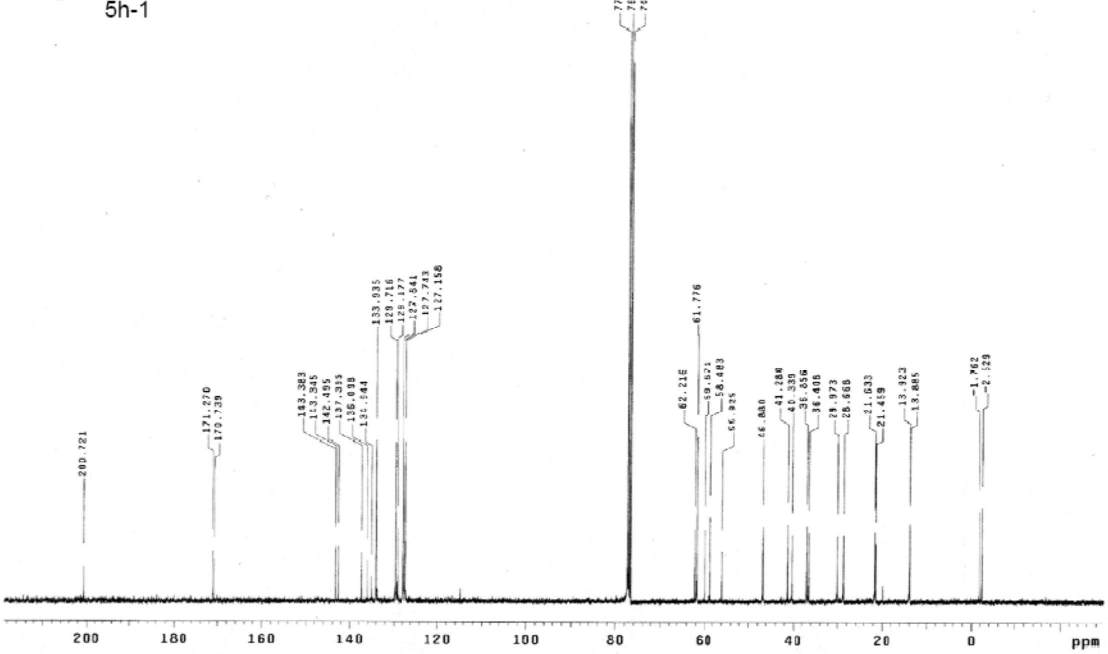

Me₂PhSi
O
EtO₂C
EtO₂C
NTs

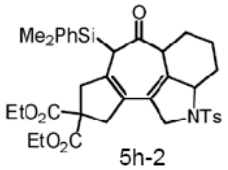
5h-1


8
7
6
5
4
3
2
1
0
ppm
2.00
2.35
5.35
5.06
0.98
0.19
1.00
3.13
3.04
3.36
3.40
6.67
2.71
5.83

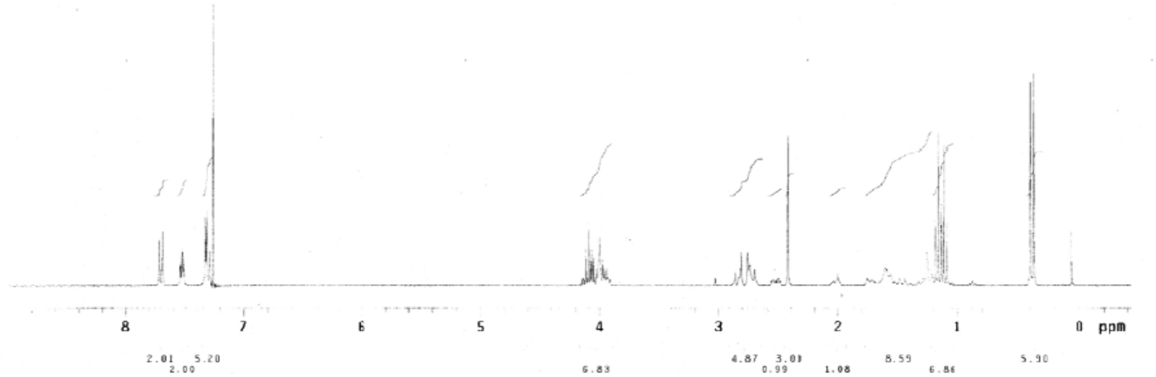

Me₂PhSi
O
EtO₂C
EtO₂C
NTs

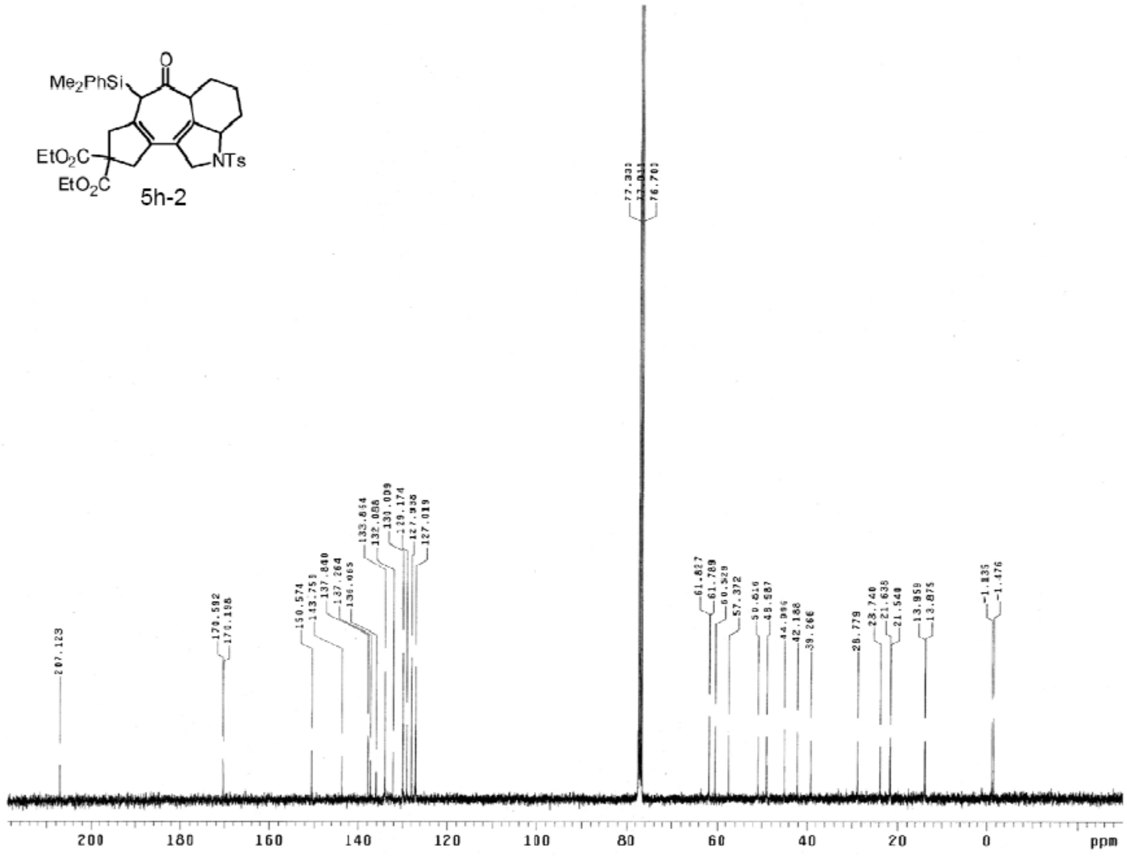
5h-1

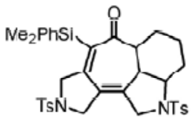

77.310
76.991
76.672
200.721
171.270
170.739
143.383
143.345
142.495
137.395
136.098
134.944
133.935
129.716
129.177
127.841
127.743
127.158
62.216
61.776
59.671
58.483
56.925
46.880
41.280
40.339
36.856
36.408
29.973
28.668
21.633
21.459
13.923
13.885
-1.762
-2.029
200
180
160
140
120
100
80
60
40
20
0
ppm



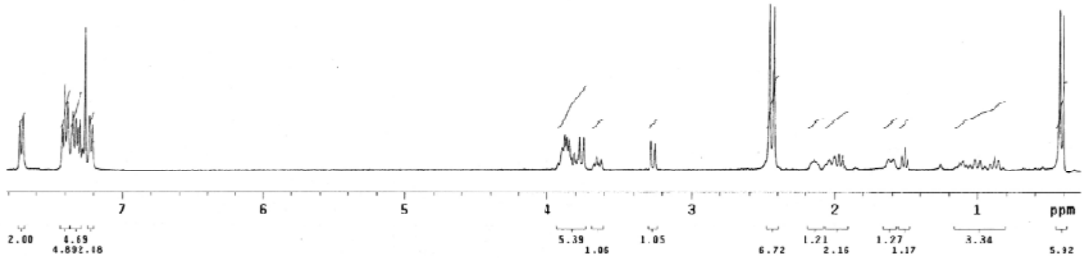
5h-2


8
7
6
5
4
3
2
1
0
ppm
2.01
2.00
5.20
6.83
4.87
0.99
3.01
1.08
8.59
6.86
5.90


Me2PhSi
O
EtO2C
EtO2C
NTs
5h-2
207.123
170.592
170.198
150.574
143.758
137.840
137.264
136.065
133.854
132.088
130.009
129.174
127.938
127.019
77.331
77.011
76.701
61.827
61.789
60.529
57.372
50.616
48.587
44.096
42.188
39.266
28.779
23.740
21.638
21.548
13.959
13.875
-1.835
-1.476
200
180
160
140
120
100
80
60
40
20
0
ppm

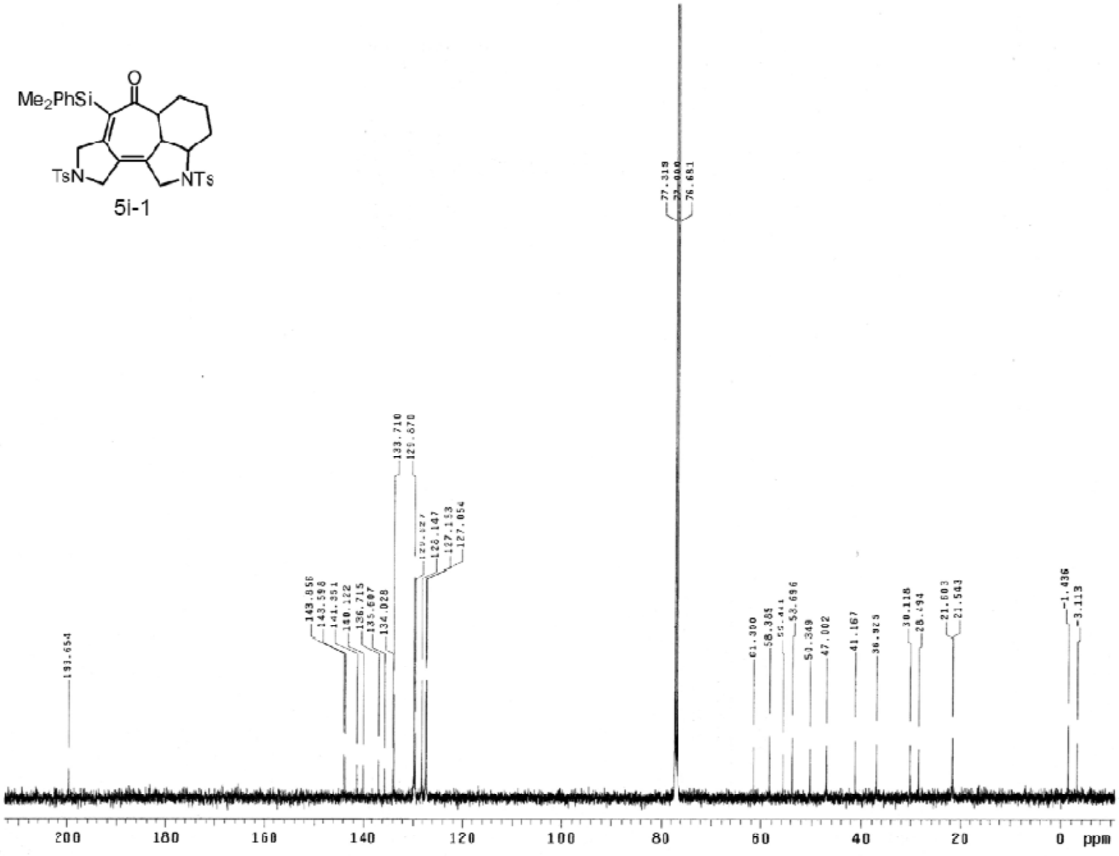

Me₂PhSi
O
TsN
NTs

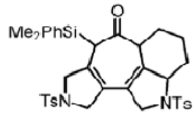
5i-1


7
6
5
4
3
2
1
ppm
2.00
4.69
4.89
2.18
5.39
1.06
1.05
6.72
1.21
2.16
1.27
1.17
3.34
5.32

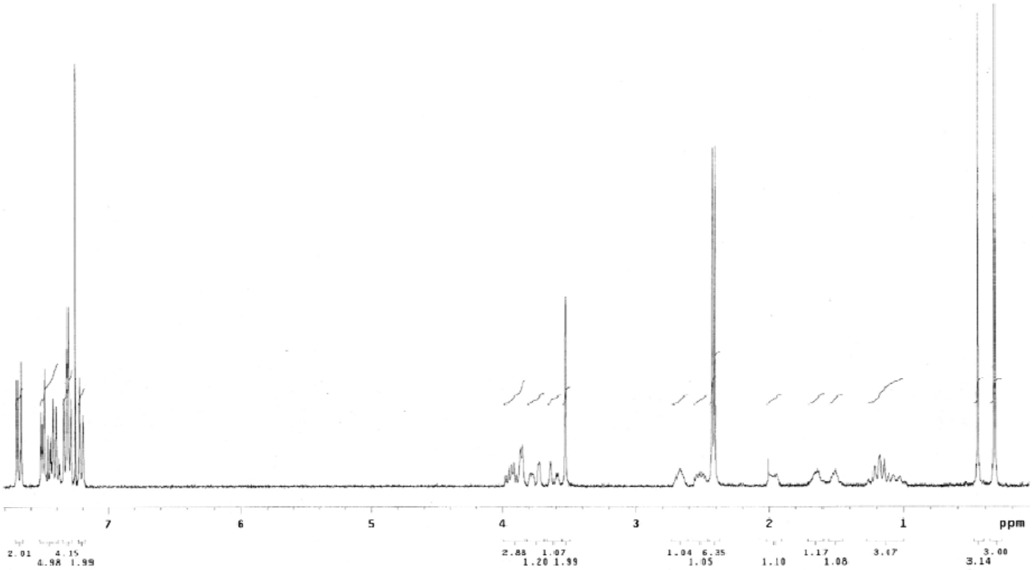
Me₂PhSi
O
TsN
NTs

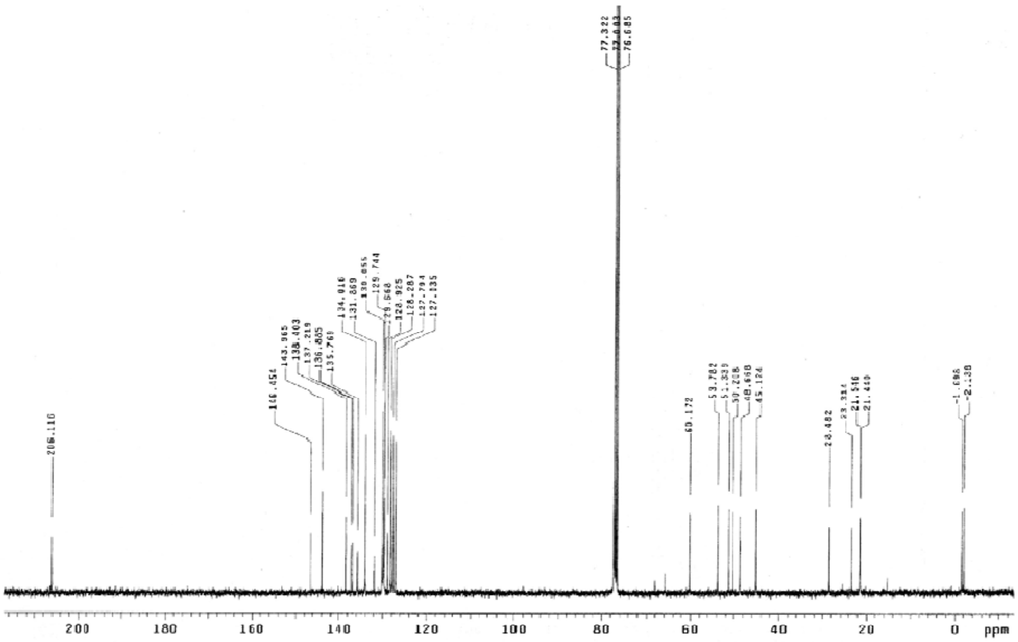
5i-1

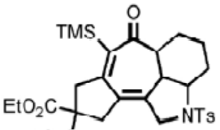

199.654
143.856
143.598
141.951
140.122
136.715
135.607
134.028
133.710
129.670
129.827
128.147
127.153
127.054
77.319
77.000
76.681
61.300
58.385
55.441
53.696
51.349
47.002
41.167
36.925
30.118
28.494
21.603
21.543
-1.436
-3.113
200
180
160
140
120
100
80
60
40
20
0
ppm


Me₂PhSi
O
TsN
NTs

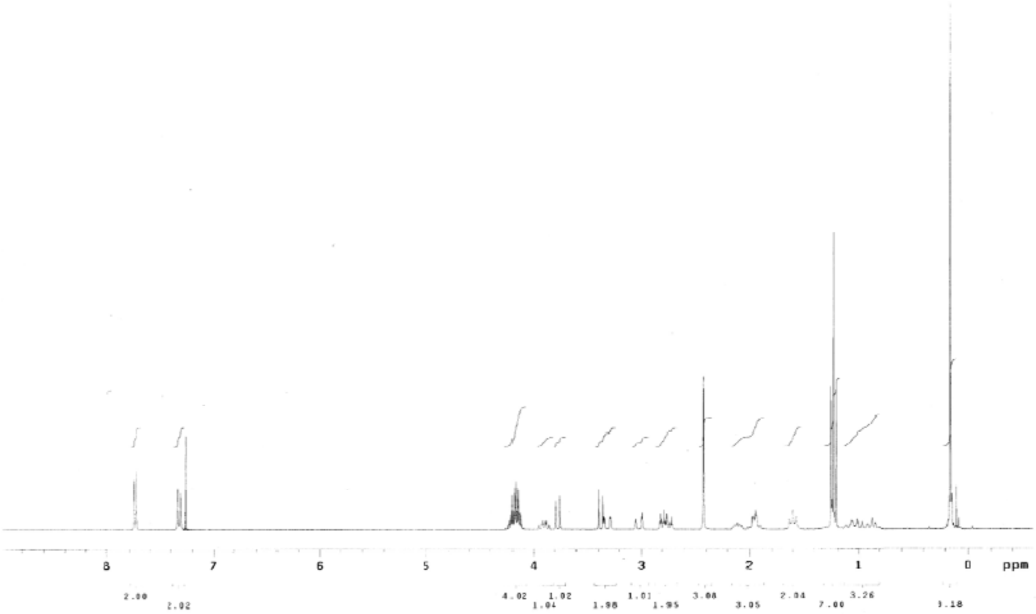
5i-2

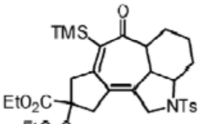

7
6
5
4
3
2
1
ppm
2.01
4.15
4.98
1.99
2.88
1.07
1.20
1.99
1.04
6.35
1.05
1.10
1.17
1.08
3.47
3.00
3.14


206.110
146.454
143.965
138.403
137.219
136.885
135.769
134.916
131.869
130.055
129.744
129.568
128.925
128.287
127.794
127.135
77.322
77.003
76.685
60.172
53.782
51.339
50.208
48.668
45.124
28.482
23.384
21.546
21.440
-1.686
-2.138
200
180
160
140
120
100
80
60
40
20
0
ppm

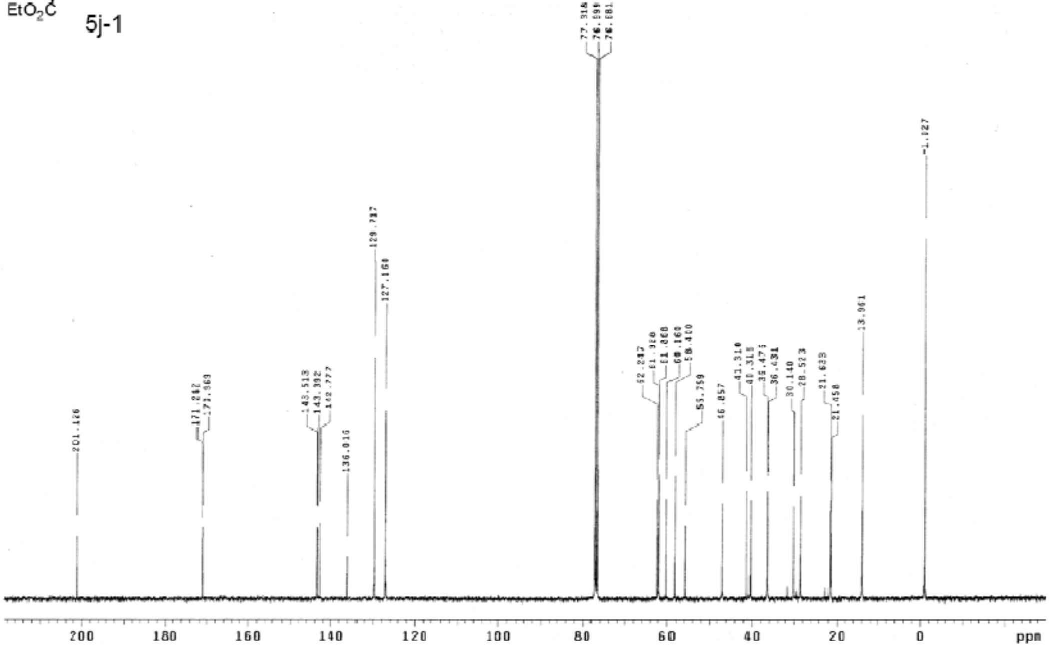

TMS
O
EtO2C
EtO2C
NTs

5j-1


8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
4.02
1.04
1.02
1.98
1.01
1.95
3.08
3.05
2.04
7.00
3.26
3.18


TMS
O
EtO2C
EtO2C
NTs

5j-1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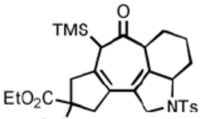
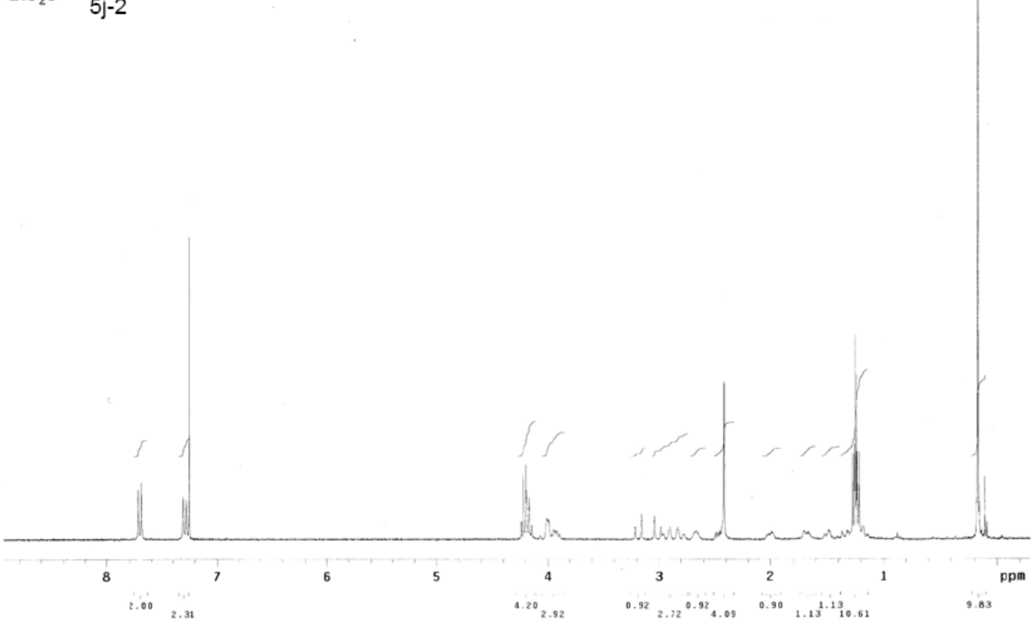
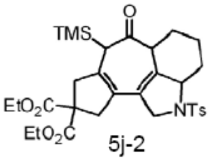
171.969
143.513
143.392
142.777
136.016
129.787
127.160
77.318
76.999
76.681
62.247
61.920
61.060
60.160
58.400
55.759
46.857
41.310
40.318
36.473
36.431
30.140
28.523
21.623
21.458
13.961
-1.127
200
180
160
140
120
100
80
60
40
20
0
ppm

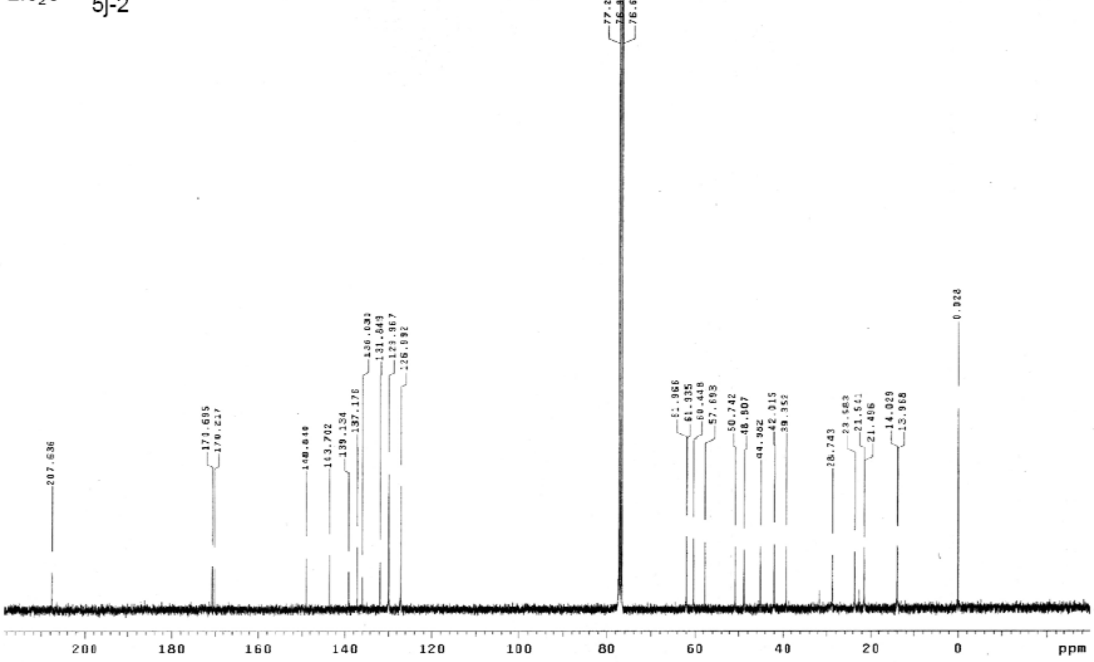

TMS
O
EtO$_2$C
EtO$_2$C
NTs

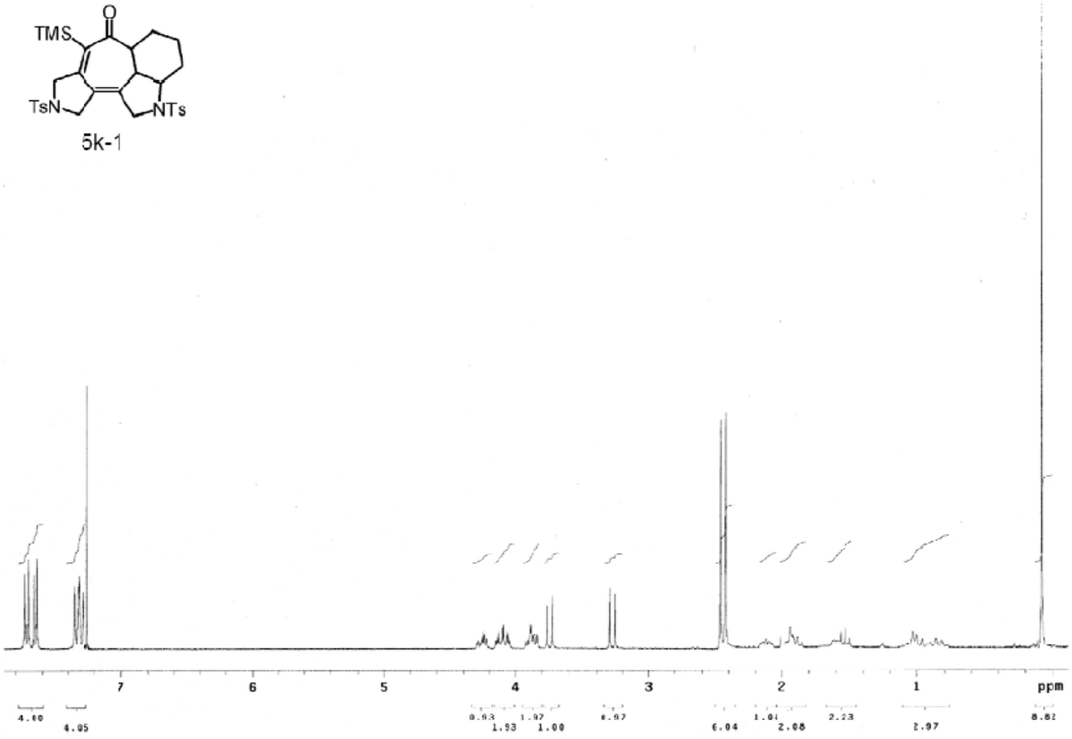
5j-2

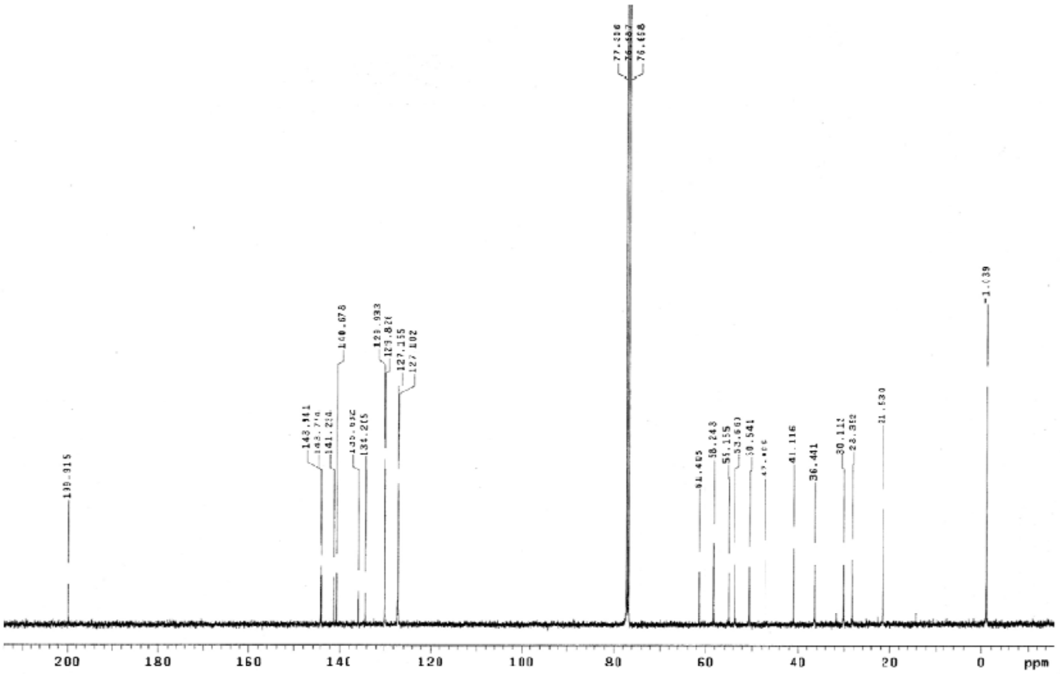

8
7
6
5
4
3
2
1
ppm
2.00
2.31
4.20
2.92
0.92
2.72
0.92
4.09
0.90
1.13
1.13
10.61
9.83

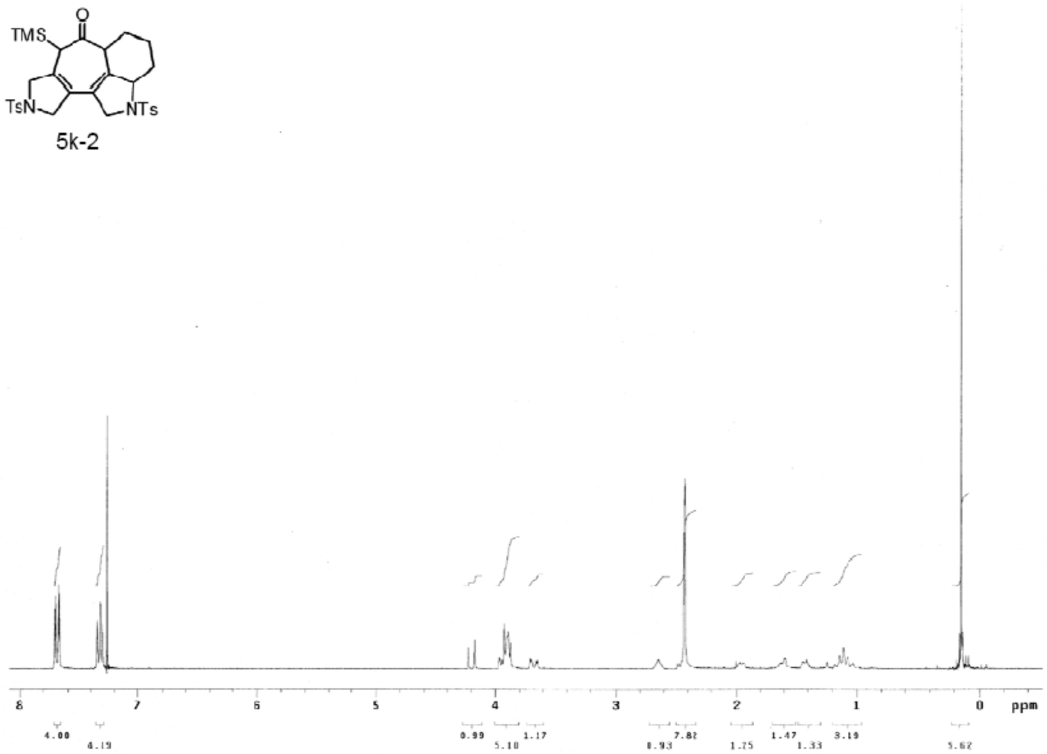

TMS
O
EtO$_2$C
EtO$_2$C
NTs

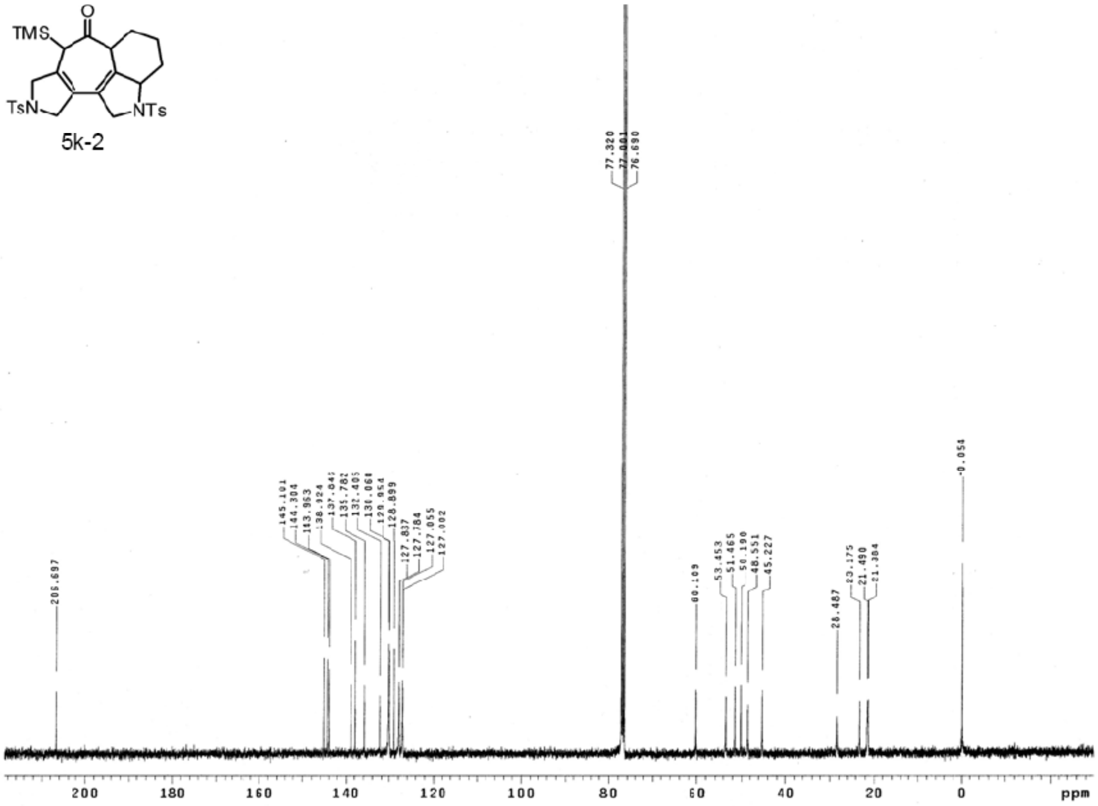
5j-2


207.636
171.695
170.217
148.848
143.702
139.134
137.176
136.033
131.849
129.967
126.092
77.235
76.883
76.665
61.966
61.935
60.448
57.693
50.742
48.807
44.982
42.015
39.352
28.743
23.583
21.541
21.496
14.029
13.968
0.028
200
180
160
140
120
100
80
60
40
20
0
ppm


TMS
O
TsN
NTs
5k-1
7
6
5
4
3
2
1
ppm
4.00
4.05
0.93
1.93
1.97
1.00
6.04
1.08
2.08
2.23
2.97
8.82


199.315
143.341
141.294
140.678
135.892
134.215
129.933
129.826
127.155
127.102
77.236
76.987
76.488
61.465
58.243
55.155
53.663
50.541
41.116
36.441
30.111
28.352
21.530
-1.039
200
180
160
140
120
100
80
60
40
20
0
ppm


TMS
O
TsN
NTs
5k-2
8
7
6
5
4
3
2
1
0
ppm
4.00
4.19
0.99
5.10
1.17
0.93
7.82
1.75
1.47
1.33
3.19
5.62


TMS
O
TsN
NTs
5k-2
206.697
145.101
144.304
143.963
138.924
137.843
135.782
132.405
130.068
129.954
128.899
127.837
127.784
127.055
127.002
77.320
77.001
76.690
60.109
53.453
51.465
50.190
48.551
45.227
28.487
23.175
21.490
21.384
-0.054
200
180
160
140
120
100
80
60
40
20
0
ppm