Supporting Information

Divergent Gold-catalysed Reactions of Cyclopropenylmethyl Sulfonamides with Tethered Heteroaromatics

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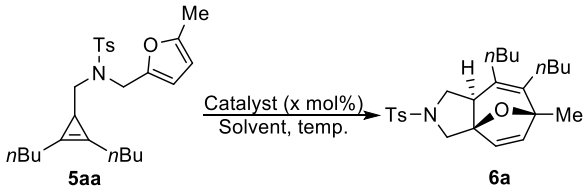
Table of Contents

1. Optimisation of the Gold-Catalysed (4 + 3) Cycloaddition Rearrangement of Cyclopropenyl Furyl Sulfonamide **5aa** 2
2. General Information 3
3. General Procedures 4
4. Preparation of Alkynes 6
5. Preparation of 1*H*-indole-2-carbaldehydes 8
6. Preparation of Sulfonamides 9
7. Preparation of Cyclopropenyl Carboxylates 12
8. Preparation of Cyclopropenyl Alcohols 14
9. Preparation of Cyclopropenyl Sulfonamides 15
10. Au(I)-Catalysed Reactions of Cyclopropenyl Sulfonamides 29
11. Chemical Transformations on Heterocycles 42
12. NMR Spectra 46

1. Optimisation of the Gold-Catalysed (4 + 3) Cycloaddition Rearrangement of Cyclopropenyl Furyl Sulfonamide 5aa

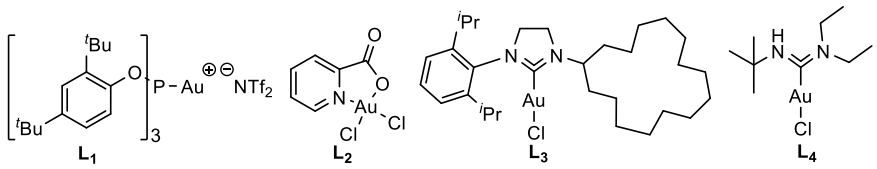
Table S1. Optimisation of the gold(I)-catalysed reaction of cyclopropenyl furyl sulfonamide **5aa** to 5,7-fused heterocycle **6a**



Entry[a]	Catalyst	Catalyst Loading	Solvent	Temp.	NMR Yield[b]
1	IPrAuNTf$_2$	5 mol%	DCE	rt	53%
2	IMesAuNTf$_2$	5 mol%	DCE	rt	36%[c]
3	PPh$_3$AuCl/AgNTf$_2$	5 mol%	DCE	rt	4%
4	JohnPhosAuNCMeSbF$_6$	5 mol%	DCE	rt	2%
5	**L$_1$**	5 mol%	DCE	rt	13%
6[d]	AuCl	5 mol%	DCE	rt	≤1% (62%)[e]
7[d]	AuCl$_3$	5 mol%	DCE	rt	≤1% (50%)[e]
8	**L$_2$**	5mol%	DCE	rt	≤1% (4%)[e]
9	**L$_3$**/AgNTf$_2$	5mol%	DCE	rt	30%
10	**L$_4$**/AgNTf$_2$	5mol%	DCE	rt	13%
11	IPrAuNTf$_2$	5 mol%	CHCl$_3$	rt	40%
12	IPrAuNTf$_2$	5 mol%	DCM	rt	48%
13	IPrAuNTf$_2$	5 mol%	PhMe	rt	36%
14	IPrAuNTf$_2$	5 mol%	THF	rt	30%
15	IPrAuNTf$_2$	5 mol%	MeCN	rt	9%
16	IPrAuNTf$_2$	5 mol%	MeOH	rt	10%
17	IPrAuNTf$_2$	5 mol%	DCE	0 °C	57%
18[f]	IPrAuNTf$_2$	5 mol%	DCE	–30 to –20 °C	56%
19	IPrAuCl/AgSbF$_6$	5 mol%	DCE	0 °C	57%

20	IPrAuCl/AgOTf	5 mol%	DCE	0 °C	60%
21	IPrAuCl/$AgBF_4$	5 mol%	DCE	0 °C	71% (75%)[g]
22[f]	IPrAuCl/$AgBF_4$	2.5 mol%	DCE	0 °C	60%
23[f]	IPrAuCl/$AgBF_4$	1 mol%	DCE	0 °C	46% (5%)[e]
24[f]	IPrAuCl	5 mol%	DCE	0 °C	0% (76%)[e]
25[f]	$AgBF_4$	5 mol%	DCE	0 °C	0%
26[d]	$HNTf_2$	5 mol%	DCE	0 °C	0%[h] (59%)[e]

[a]All reactions were performed over 0.75-2 h at a concentration of 0.1 mol/L unless otherwise specified; [b] mesitylene used as the internal standard and integrations of singlet at δ 6.8 ppm for mesitylene and the doublet at δ 6.2 ppm for heterocycle **6a** were compared to calculate NMR yields; [c] reaction also attempted using IMesAuCl/$AgNTf_2$ and the same yield was obtained; [d] reaction time 18-22 h; [e] starting material was recovered; [f] reaction time 4-5 h; [g] isolated yield corrected for the presence of cyclobutene; [h] cleavage product obtained



2. General Information

Chemicals and solvents were purchased from commercial sources and were used without further purification. All air/moisture sensitive reactions were performed with oven (120 °C) dried glassware under a nitrogen or argon atmosphere. Dry solvents were either obtained from commercial sources or were preparing by passing the solvent through a column of activated alumina. Solvents were then stored under nitrogen with 3Å or 4Å molecular sieves. Thin-layer chromatography (TLC) was performed using Merck TLC Silica gel 60 F_{254} aluminium backed sheets. Reaction spots were viewed under a UV lamp (wavelength 254 nm) before being stained with one of the following: anisaldehyde (4 mL 4-methoxybenzaldehyde, 2 mL glacial acetic acid, 5 mL concentrated H_2SO_4 and 150 mL ethanol (EtOH)) or potassium permanganate stain (1.5 g $KMnO_4$, 10 g K_2CO_3 and 1.25 mL NaOH (10% w/v solution) and 200 mL water). Flash column chromatography was conducted with Davisil chromatographic silica media (40-63 μm) purchased from Grace Davison Discovery Science. The mobile phase in all cases were mixtures of *n*-hexane (hex), ethyl acetate (EtOAc), pentane (pent), diethyl ether (Et_2O), petroleum ether (PE) and triethylamine (Et_3N). ^1H and ^{13}NMR spectra were collected at room temperature (rt) in

deuterated chloroform ($CDCl_3$ or $CDCl_3$ with 0.1% v/v TMS, Sigma Aldrich). NMR spectrometry experiments were run on a a Bruker 300 (300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR), 400 (400 MHz ^{1}H NMR, 100 MHz ^{13}C NMR) or 500 (500 MHz ^{1}H NMR, 125 MHz ^{13}C NMR) spectrometer. When reported the NMR chemical shifts were expressed in parts per million (ppm) and the coupling constants were expressed in Hertz (Hz). Depending on the solvent, chemical shifts in the ^{1}H NMR spectra were referenced to either $CDCl_3$ (7.26 ppm) or TMS (0.00 ppm). All chemical shifts in the ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). The multiplicities of the ^{1}H NMR peaks were assigned as either a singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), doublet of triplets (dt), triplet of doublets (td), triplet or triplets (tt), quartet (q), quartet of doublets (qd), pentet (p), or as a multiplet (m). For NMR characterisation data for compounds that occurred as two inseparable isomers, signals were assigned to the major and the minor isomers based on data collected from HSQC and HMBC 2D spectra. High-resolution mass spectrometry (HRMS) was performed with a Waters Xevo G1 QTOF instruments. All solvents used in the mass spectrometry experiments were of HPLC grade. Infrared spectra (IR) (pwere collected using Bruker Vertex 70 spectrometer and values are reported in cm^{-1} units. Melting points (MP) were obtained using a Buchi Melting point M-560 appartus, with temperatures increasing by 3 °C/min. Values are reported in °C.

3. General Procedures

General Procedure A

A round bottom flask was charged with the desired alcohol or amine (1 equiv.) and Cs_2CO_3 (2.5 equiv.) and the flask was put under a nitrogen atmosphere. Dry acetonitrile (MeCN, 0.2 M) was added and the reaction was stirred at 50 °C for 30 mins before the selected electrophile (1.4-2.5 equiv.) was added. The reaction was left to stir at 50 °C until complete according to TLC analysis. If necessary, additional electrophile was added to push the reaction the completion. Once complete, the reaction was filtered to remove the solids and was washed thoroughly with additional MeCN. The filtrate was evaporated to dryness, redissolved in DCM and filtered to remove any further solids. The filtrate was then concentrated under reduced pressure and the resulting products were either used directly or were purified by flash column chromatography.

General Procedure B

Following a modified literature procedure,[1] to a flame-dried flask was added the desired carboxylate (1 equiv.) and either dry THF (0.2 M) or dry DCM under nitrogen. The mixture was cooled to −78 °C and to this was added diisobutylaluminium hydride (DIBAL-H, 3 equiv.), dropwise. The reaction was either maintained at −78 °C or was allowed to gradually warm to rt. Once complete according to TLC, the reaction was quenched with NH_4Cl and was stirred at rt for a few mins. The reaction mixture was then treated with aqueous HCl (2M) until the white gel was dissolved. The aqueous phase was extracted with Et_2O (3x) and the combined organic layers were washed with brine and dried over Na_2SO_4. The residue was filtered, concentrated under reduced pressure and either used in the next reaction immediately or was purified by flash column chromatography (10:90 EtOAc:hex) using silica gel that had been pre-treated with 1% Et_3N.

General Procedure C

In accordance with the literature procedure,[2] the selected alcohol (1 equiv.) was dissolved in dry DCM under nitrogen and to this was added activated MnO_2 (10 equiv.) and the reaction was left to stir until complete. Once complete according to TLC analysis, the reaction was filtered through a pad of celite and the solvent was evaporated under reduced pressure to afford the corresponding aldehyde. Aldehydes were purified by flash column chromatography (20:80 EtOAc:hex).

General Procedure D

Following a modified literature procedure,[3] to a round bottom equipped with a reflux condenser was added tosyl amide (1 equiv.), the selected aldehyde (1 equiv.) and $Si(OEt)_4$ (1.1 equiv.). The reaction mixture was heated to 140-150 °C and the reaction was monitored by TLC until complete. Following the completion of the reaction, the solvent was removed under reduced pressure, and if necessary, tituration with pentane was performed to isolate the resulting imines which were used without further purification. The imine was dissolved in THF/MeOH (ratio 5:1,

[1] Li, C.; Zhang, H.; Feng, J.; Zhang, Y.; Wang, J. *Org. Lett.* **2010**, *12*, 3082

[2] Ye, Q.; Chourey, S.; Wang, R.; Chintam, N. R.; Gravel, S.; Powell, W. S.; Rokach, J. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 4770

[3] Sun, Y.-W.; Tang, X.-Y.; Shi, M. *Chem. Commun.* **2015**, *51*, 13937.

0.2 M) and to this was added $NaBH_4$ (0.5-1 equiv.). Reaction were typically complete after 30 mins, the reaction was quenched with saturated NH_4Cl and extracted with EtOAc (3x). The organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (typically 30:70 EtOAc:hex), was then used to obtain the final product over a two-step process.

General Procedure E

In accordance with the literature,[1] a round bottom flask was charged with the selected alkyne (1.5 equiv.), $Rh_2(OAc)_4$ (0.5 mol%) and DCM (2 M) under a nitrogen atmosphere. A solution of ethyl diazoacetate (1 equiv.) in DCM (4 M) was prepared and added to the reaction via syringe pump at a rate of 1 mL/h. Following the complete addition of the ethyl diazoacetate, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (4:96 EtOAc:hex) on silica that had first been treated with the eluent and 1% Et_3N.

General Procedure F

Following a modified literature procedure,[1] a round bottom flask was charged with the desired alcohol (1 equiv.), sulfonamide (1-1.1 equiv.), PPh_3 (1.3 equiv.) and THF (0.1 M) under a nitrogen atmosphere. While stirring at rt., diisopropyl azodicarboxylate (DIAD, 1.3 equiv.) was added to the reaction dropwise. The resulting mixture was stirred at rt overnight (15-18 h) and TLC analysis was used to confirm the reaction was complete. The solvent was removed under reduced pressure and the residue was typically absorbed to celite and purified by flash column chromatography (5:95 EtOAc:hex) using silica gel that was pre-treated with 1% Et_3N, unless otherwise specified.

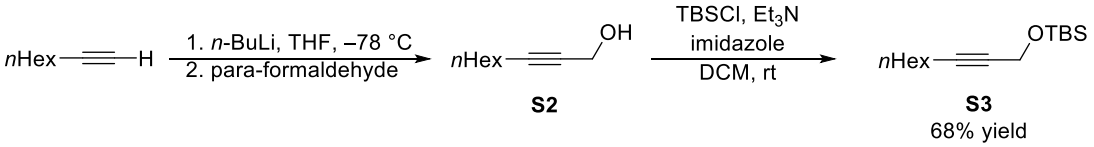
General Procedure G

Cyclopropenyl sulfonamides **5** (1 equiv.), were dissolved in DCE (0.1 M) and were cooled down to 0 °C under nitrogen. To this was added chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I) (IPrAuCl, 5mol%) and $AgBF_4$ (5 mol%) with stirring. The reaction was left to stir at 0 °C until the reaction was complete. Once completed, the solvent was removed under reduced pressure and the crude residue was absorbed to silica and purified by flash column chromatography (10:90 EtOAc:hex).

4. Preparation of Alkynes

Alkyne **S1** was prepared according to the literature and the characterisation data obtained was consistent with that previously reported.[4]

<u>*tert*-Butyldimethyl(non-2-yn-1-yloxy)silane **S3**</u>



In accordance with the literature procedure,[5] 1-octyne (3.2 mL, 21.7 mmol) was dissolved in dry THF (17.5 mL) under a nitrogen atmosphere and the mixture was cooled to –78 °C. To this was added *n*-BuLi (2.5 M in hexanes, 11 mL, 27.5 mmol) dropwise and the reaction allowed to warm to 0 °C and was stirred at this temperature for 1 h. The reaction was again cooled to –78 °C and paraformaldehyde (781.4 mg, 26.0 mmol) was added. The reaction warmed to rt and was stirred for 16 h. Following completion of the reaction, NH_4Cl was added and the aqueous layer was extracted with Et_2O (3x). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure and the crude residue of alkynol **S2** was used immediately in the next step without purification. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.89 (t, 3H, J = 7.0 Hz, CH_3), 1.24-1.42 (m, 6H, 3CH_2), 1.50 (p, 2H, J = 7.2 Hz, CH_2), 2.20 (tt, 2H, J = 7.2, 2.3 Hz, CH_2), 4.21-4.24 (m, 2H, CH_2) ppm.

In accordance with the literature procedure,[6] the crude residue of alkynol **S2** was dissolved in dry DCM (44 mL) under nitrogen at rt. This was then treated with Et_3N (3 mL, 21.5 mmol), imidazole (148.4 mg, 2.18 mmol) and TBSCl (3.5399 g, 23.5 mmol) and was left to stir the 3.5 h. Once complete, the reaction was quenched with H_2O and the two phases were separated. The organic layer was washed with H_2O (3x) and dried over Na_2SO_4. The crude residue was then filtered, concentrated under reduced pressure and purified by flash column chromatography (100% hex)

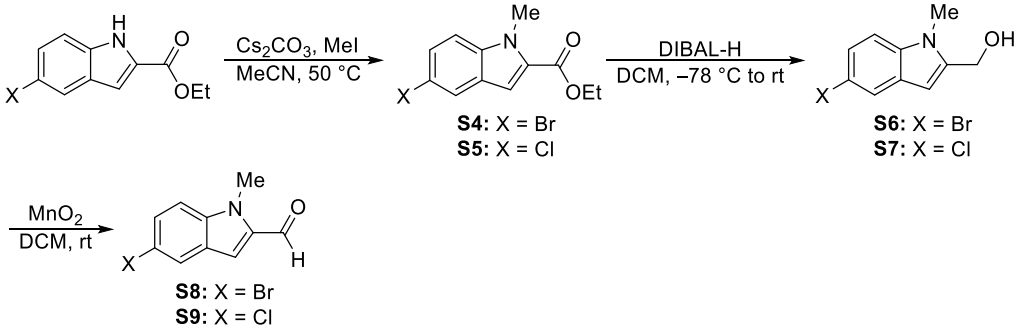
[4] Liddon, J. T. R.; James, M. J.; Clarke, A. K.; O'Brien, P.; Taylor, R. J. K.; Unsworth, W. P. *Chem. Eur. J.* **2016**, *22*, 8777

[5] Köpfer, A.; Breit, B. *Angew. Chem. Int. Ed.* **2015**, *54*, 6913

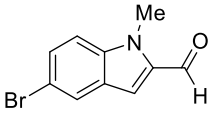
[6] Haase, R. G.; Schobert, R. *Org. Lett.* **2016**, *18*, 6352

to give the title compound **S3** as a colourless oil (3.7690 g, 14.8 mmol) in 68% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.12 (s, 6H, Si(CH_3)$_2$), 0.87-0.92 (m, 12H, 4CH_3), 1.24-1.42 (m, 6H, 3CH_2), 1.45-1.54 (m, 2H, CH_2), 2.19 (tt, 2H, J = 7.2, 2.2 Hz, CH_2), 4.30 (t, 2H, J = 2.2 Hz, CH_2) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = -5.1, 14.0, 18.3, 18.8, 22.5, 25.8, 28.5, 28.6, 31.3, 52.0, 78.6, 85.5 ppm; **MS:** *m/z* signal could not be detected by ESI or EI methods; **IR (ATR):** 2958, 2929, 2857, 1471, 1256, 1080, 834, 775 cm^{-1}.

5. Preparation of 1*H*-indole-2-carbaldehydes



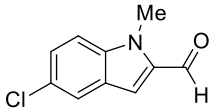
5-Bromo-1-methyl-1*H*-indole-2-carbaldehyde **S8**



Precursors **S4** and **S6** were prepared by general procedures A and B, respectively and characterisation data was consistent with that reported in the literature.[7] Following general procedure C, the crude 1*H*-indole alcohol **S6** (770.7 mg, 3.21 mmol) was dissolved in DCM (8.4 mL) and to this was added activated MnO_2 (2.8423 g, 27.8 mmol). After 4 h the reaction was worked up and purified to give the title compound **S8** as an off white solid (657.0 mg, 2.76 mmol) in 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.08 (s, 3H, CH_3), 7.17 (s, 1H, CH_{Het}), 7.24-7.31 (m, overlapped with $CHCl_3$, 1H, CH_{Het}), 7.48 (d, 1H, J = 8.8 Hz, CH_{Het}), 7.86 (s, 1H, CH_{Het}), 9.89 (s, 1H, C*H*O) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 31.7, 111.9, 114.1, 116.1, 125.5, 127.7, 129.7, 136.3, 139.3, 182.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{10}H_9(^{79}Br)NO$ $[M + H]^+$ 237.9862, found 237.9873; **IR (ATR):** 1663, 1473, 1401, 1126, 859, 795, 728 cm^{-1}; **MP:** 136.8–137.5 °C.

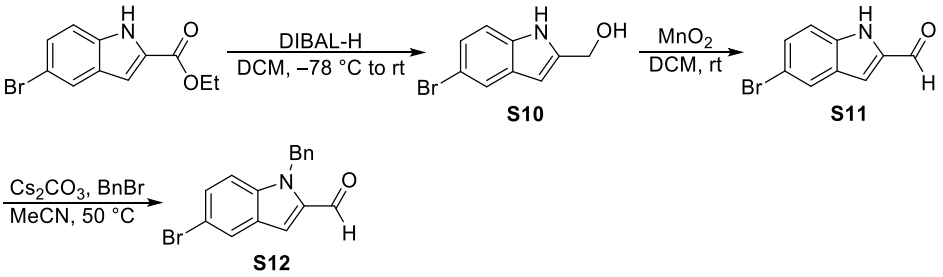
[7] Lubriks, D.; Sokolovs, I.; Suna, E. *J. Am. Chem. Soc.* **2012**, *134*, 15436; A. Branstrom, V. P. V. N. Josyula, M. A. Arnold, A. I. Gerasyuto, G. Karp, J. Wang, in *PCT Int. Appl., Vol. WO 2013033258*, PTC Therapeutics, Inc., USA, USA, **2013**, p. 337.

5-Chloro-1-methyl-1*H*-indole-2-carbaldehyde **S9**



Precursors **S5** and **S7** and the title compound **S9** were prepared by general procedures A, B and C respectively and the characterisation data was consistent with that reported in the literature.[2]

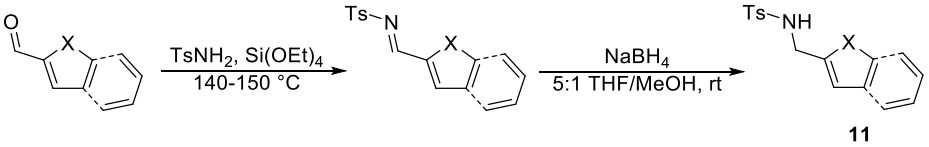
1-Benzyl-5-bromo-1*H*-indole-2-carbaldehyde **S12**



Precursors **S10** and **S11** were prepared by general procedures B and C, respectively and the characterisation data was consistent with the reported literature.[8] Following general procedure A, 1*H*-indole-2-carbaldehyde **S8** (176.5 mg, 0.788 mmol), Cs_2CO_3 (681.5 mg, 2.09 mmol) and MeCN (8.4 mL) were added to a flask and after 30 mins of heating, benzyl bromide (0.15 mL, 1.26 mmol) was injected. The reaction was heated for 20 h after which the reation was worked up to give the title compound **S12** as a solid (173.6 mg, 0.553 mmol) in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.80 (s, 2H, CH_2), 7.02-7.07 (m, 2H, 2CH_{Ar}), 7.19-7.28 (m, overlapped with $CHCl_3$, 5H, 3CH_{Ar}, 2CH_{Het}), 7.43 (dd, 1H, J = 9.2, 2.0 Hz, CH_{Het}), 7.89 (d, 1H, J = 2.0 Hz, CH_{Het}), 9.90 (s, 1H, C*H*O) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 48.1, 112.6, 114.4, 117.0, 125.7, 126.5, 127.5, 128.0, 128.7, 130.0, 136.0, 137.2, 139.1, 182.6 ppm; **IR (ATR):** 1745, 1668, 1454, 1243, 1125, 801, 720, 697 cm^{-1}; **MP:** 113.1–116.7 °C.

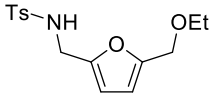
[8] Jiang, X.; Yang, J.; Zhang, F.; Yu, P.; Yi, P.; Sun, Y.; Wang, Y. *Adv. Synth. Catal.* **2016**, *358*, 2678; Ashalatha, B. V.; Vijaya Raj, K. K. *Org. Chem. Ind. J.* **2006**, *2*, 5.

6. Preparation of Sulfonamides



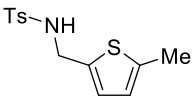
Sulfonamides **11a**, **11b**, **11d**, **11f**, **11g**, **11i** were all prepared by general procedure D and the characterisation data was consistent with that reported in the literature.[9,3]

N-((5-(Ethoxymethyl)furan-2-yl)methyl)-4-methylbenzenesulfonamide **11c**



Following general procedure D, 5-(ethoxymethyl)furan-2-carbaldehyde (0.45 mL, 3.21 mmol), tosyl amide (499.5 mg, 2.92 mmol) and $Si(OEt)_4$ (0.72 mL, 3.22 mmol) were heated overnight to obtain the corresponding imine. The crude imine was dissolved in THF (12.5 mL) and MeOH (2.5 mL), and reacted with $NaBH_4$ (61.8 mg, 1.63 mmol). The crude residue was purified to give the title compound **11c** as a fluffy, yellow solid (93.7 mg, 0.303 mmol) in 10% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.20 (t, 3H, J = 7.0 Hz, CH_3), 2.42 (s, 3H, CH_3), 3.48 (q, 2H, J = 7.0 Hz, CH_2), 4.16 (d, 2H, J = 6.0 Hz, CH_2), 4.28 (s, 2H, CH_2), 4.72 (t, 1H, J = 6.0 Hz, N*H*), 6.05 (d, 1H, J = 3.0 Hz, CH_{Het}), 6.14 (d, 1H, J = 3.0 Hz, CH_{Het}), 7.26-7.29 (m, overlapped with $CHCl_3$, 2H, 2CH_{Ar}), 7.69-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 15.1, 21.5, 40.3, 64.4, 65.7, 108.8, 109.8, 127.2, 129.6, 136.9, 143.5, 149.7, 152.0 ppm; **HRMS (ESI):** *m/z* calcd for $C_{15}H_{19}NNaO_4S$ $[M + Na]^+$ 332.0927, found 332.0942; **IR (ATR):** 3304, 3184, 2973, 2866, 1378, 1327, 1160, 1093, 1048 cm^{-1}; **MP:** 79.6–82.1 °C.

4-Methyl-*N*-((5-methylthiophen-2-yl)methyl)benzenesulfonamide **11e**

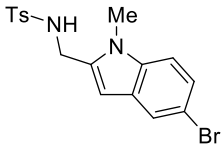


Following general procedure D, 5-methyl-2-thiophenecarboxaldehyde (0.60 mL, 5.56 mmol), tosyl amide (954.5 mg, 5.57 mmol) and $Si(OEt)_4$ (1.37 mL, 6.14 mmol) were heated overnight to

[9] Zhang, W.-B.; Xiu, S.-D.; Li, C.-Y. *Org. Chem. Front.* **2015**, *2*, 47; Shang, H.; Tian, Y.; Luo, J.; Li, L.; Tang, Y.; Zou, Z. *RSC Adv.* **2016**, *6*, 30835; Bandini, M.; Gualandi, A.; Monari, M.; Romaniello, A.; Savoia, D.; Tragni, M. *J. Organomet. Chem.* **2011**, *696*, 338

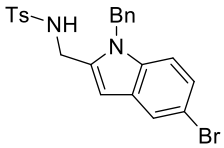
obtain the corresponding imine. The crude imine was dissolved in THF (23.2 mL) and MeOH (4.6 mL), and reacted with $NaBH_4$ (107.6 mg, 2.84 mmol). The crude residue was purified to give the title compound **11e** as a yellow solid (1.3034 g, 4.63 mmol) in 83% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.23 (d, 2H, J = 6.0 Hz, CH_2), 4.71 (bs, 1H, N*H*), 6.49-6.52 (m, 1H, CH_{Het}), 6.62 (d, 1H, J = 3.4 Hz, CH_{Het}), 7.30 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.73-7.77 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 15.3, 21.5, 42.4, 124.8, 126.5, 127.2, 129.7, 136.3, 136.8, 140.7, 143.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{13}H_{15}NNaO_2S_2$ $[M + Na]^+$ 304.0436, found 304.0436; **IR (ATR):** 3280, 1416, 1324, 1165, 1092, 1057, 1041, 861, 809 cm^{-1}; **MP:** 114.4–117.0 °C.

N-((5-Bromo-1-methyl-1*H*-indol-2-yl)methyl)-4-methylbenzenesulfonamide **11h**



Following general procedure D, 1*H*-indole-2-carbaldehyde **S8** (531.5 mg, 2.23 mmol), tosyl amide (346.4 mg, 2.02 mmol) and $Si(OEt)_4$ (2 mL, 8.96 mmol) were heated overnight to obtain the corresponding imine. The crude imine was dissolved in THF (9.5 mL) and MeOH (2 mL), and reacted with $NaBH_4$ (47.0 mg, 1.24 mmol). The crude residue was purified to give the title compound **11h** as a yellow solid (236.0 mg, 0.600 mmol) in 27% yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 4.26 (d, 2H, J = 6.0 Hz, CH_2), 4.47 (t, 1H, J = 6.0 Hz, N*H*), 6.23 (s, 1H, CH_{Het}), 7.13 (d, 1H, J = 8.5 Hz, CH_{Het}), 7.29 (dd, 1H, J = 8.5, 2.0 Hz, CH_{Het}), 7.31 (d, 2H, J = 8.0, 2CH_{Ar}), 7.63 (d, 1H, J = 1.5 Hz, CH_{Het}), 7.74-7.77 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 21.5, 30.0, 39.9, 101.9, 110.7, 113.0, 123.0, 125.0, 127.1, 128.5, 129.9, 134.6, 136.2, 136.7, 144.0 ppm; **HRMS (ESI):** *m/z* calcd for $C_{17}H_{18}(^{79}Br)N_2O_2S$ $[M + H]^+$ 393.0267, found 393.0279; **IR (ATR):** 3357, 3256, 2920, 2852, 1471, 1423, 1319, 1306, 1153, 1089, 1031 cm^{-1}; **MP:** 195 °C decomp.

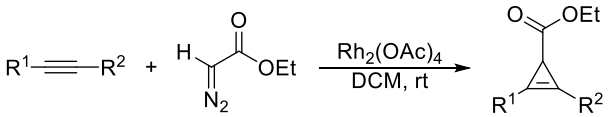
N-((1-Benzyl-5-bromo-1*H*-indol-2-yl)methyl)-4-methylbenzenesulfonamide **11j**



Following general procedure D, 1*H*-indole-2-carbaldehyde **S12** (147.7 mg, 0.470 mmol), tosyl amide (79.8 mg, 0.466 mmol) and $Si(OEt)_4$ (0.24 mL, 1.07 mmol) were heated for 44 h to obtain the corresponding imine. The crude imine was dissolved in THF (2 mL) and MeOH (0.4 mL), and

reacted with $NaBH_4$ (11.2 mg, 0.296 mmol). The reaction was worked up to give the title compound **11j** as a brown solid (223.3 mg) in quantitative yield over two steps. Sulfonamide **11j** was used in the next reaction without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.42 (s, 3H, CH_3), 4.16 (d, 2H, J = 6.5 Hz, CH_2), 4.47 (bs, 1H, NH), 5.31 (s, 2H, CH_2), 6.32 (s, 1H, CH_{Het}), 6.84-6.88 (m, 2H, 2CH_{Ar}), 7.08 (d, 1H, J = 8.5 Hz, CH_{Het}), 7.22-7.28 (m, overlapped with $CHCl_3$, 6H, 5CH_{Ar}, CH_{Het}), 7.64-7.68 (m, 3H, 2CH_{Ar}, CH_{Het}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 21.5, 39.8, 46.7, 102.8, 111.2, 113.2, 123.2, 125.3, 125.9, 127.2, 127.6, 128.8, 128.9, 129.8, 134.7, 136.1, 136.5, 137.0, 143.9 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{21}(^{79}Br)N_2NaO_2S$ $[M + Na]^+$ 491.0399, found 491.0417; **IR (ATR):** 3278, 1429, 1313, 1149, 1090, 1049, 884 cm^{-1}; **MP:** 142.8 °C decomp.

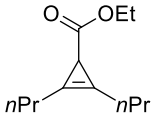
7. Preparation of Cyclopropenyl Carboxylates



12

Cyclopropenyl carboxylates **12a**, **12e** and were prepared by general procedure E and the characterisation data was consistent with that reported in the literature. [1,10] Cyclopropenyl carboxylate **12f** was prepared according to a different literature procedure.[1]

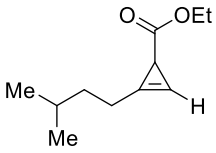
Ethyl 2,3-dipropylcycloprop-2-ene-1-carboxylate **12b**



Following general procedure E, 4-octyne (5.8 mL, 39.5 mmol), $Rh_2(OAc)_4$ (58.9 mg, 0.133 mmol) and DCM (13 mL) were added to a round bottom flask. Ethyl diazoacetate (87% solution in DCM, 3.2 mL, 26.5 mmol) in DCM (6.6 mL) was added and after the completion of the reaction, the crude residue was purified to give the title compound **12b** as a yellow oil (3.2278 g, 16.4 mmol) in 62% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.96 (t, 6H, J = 7.5 Hz, 2CH_3), 1.24 (t, 3H, J = 7.0 Hz, CH_3), 1.53-1.64 (m, 4H, 2CH_2), 2.03 (s, 1H, CH), 2.39 (t, 4H, J = 7.5 Hz, 2CH_2), 4.11 (q, 2H, J = 7.0 Hz, CH_2) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.8, 14.4, 20.4, 22.2, 26.5, 59.7, 105.7, 177.1 ppm; **HRMS (ESI):** *m/z* calcd for $C_{12}H_{20}NaO_2$ $[M + Na]^+$ 219.1356, found 219.1355; **IR (ATR):** 2961, 2935, 2874, 1719, 1461, 1334, 1173, 1039 cm^{-1}.

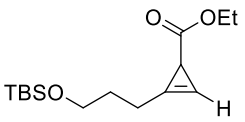
[10] Ueda, M.; Doi, N.; Miyagawa, H.; Sugita, S.; Takeda, N.; Shinada, T.; Miyata, O. *Chem. Commun.* **2015**, *51*, 4204.

Ethyl 2-isopentylcycloprop-2-ene-1-carboxylate **12c**



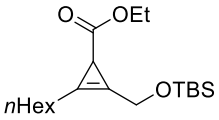
Following general procedure E, 5-methylhex-1-yne (0.87 mL, 6.59 mmol), $Rh_2(OAc)_4$ (10.0 mg, 22.6 μmol) and DCM (2.2 mL) were added to a round bottom flask. Ethyl diazoacetate (87% solution in DCM, 0.5 mL, 4.14 mmol) in DCM (1.1 mL) was added and after the completion of the reaction, the crude residue was purified to give the title compound **12c** as a pale yellow oil (445.1 mg, 2.44 mmol) in 59% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.91 (d, 6H, *J* = 6.5 Hz, 2CH_3), 1.25 (t, 3H, *J* = 7.0 Hz, CH_3), 1.48 (q, 2H, *J* = 7.5 Hz, CH_2), 1.63 (nonet, 1H, *J* = 6.5 Hz, C*H*), 2.12 (d, 1H, *J* = 1.5 Hz, C*H*), 2.50 (t, 2H, *J* = 7.5 Hz, CH_2), 4.09-4.18 (m, 2H, CH_2), 6.32 (m, 1H, C*H*) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.3, 19.3, 22.16, 22.25, 22.9, 27.4, 35.5, 60.1, 93.8, 115.7, 176.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{11}H_{19}O_2$ $[M + H]^+$ 183.1380, found 183.1389; **IR (ATR):** 2958, 2871, 1725, 1468, 1368, 1251, 1177, 1030 cm^{-1}.

Ethyl 2-(3-((*tert*-butyldimethylsilyl)oxy)propyl)cycloprop-2-ene-1-carboxylate **12d**



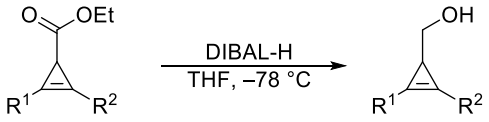
Following general procedure E, alkyne **S1** (2.4836 g, 12.5 mmol), $Rh_2(OAc)_4$ (20.9 mg, 47.3 μmol) and DCM (4 mL) were added to a round bottom flask. Ethyl diazoacetate (87% solution in DCM, 1 mL, 8.27 mmol) in DCM (2 mL) was added and after the completion of the reaction, the crude residue was purified to give the title compound **12d** as a yellow oil (1.6501 g, 5.80 mmol) in 70% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.05 (s, 6H, Si(CH_3)$_2$), 0.89 (s, 9H, C(CH_3)$_3$), 1.25 (t, 3H, *J* = 7.0 Hz, CH_3), 1.76-1.83 (m, 2H, CH_2), 2.13 (d, 1H, *J* = 1.5 Hz, C*H*), 2.58 (tt, 2H, *J* = 7.0, 1.5 Hz, CH_2), 3.61-3.70 (m, 2H, CH_2), 4.09-4.17 (m, 2H, CH_2), 6.34 (appar. q, 1H, *J* = 1.5 Hz, C*H*) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.4, 14.3, 18.3, 19.7, 21.5, 25.9, 29.8, 60.1, 61.9, 94.3, 115.3, 176.5 ppm; **HRMS (ESI):** *m/z* calcd for $C_{15}H_{28}NaO_3Si$ $[M + Na]^+$ 307.1700, found 307.1716; **IR (ATR):** 2954, 2930, 2857, 1723, 1251, 1178, 109, 833 cm^{-1}.

Ethyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3-hexylcycloprop-2-ene-1-carboxylate **12h**



Following general procedure E, alkyne **S3** (3.1599 g, 12.4 mmol), $Rh_2(OAc)_4$ (18.5 mg, 41.9 μmol) and DCM (4 mL) were added to a round bottom flask. Ethyl diazoacetate (87% solution in DCM, 1 mL, 8.27 mmol) in DCM (2 mL) was added and after the completion of the reaction, the crude residue was purified to give the title compound **12h** as an oil (1.1490 g, 3.37 mmol) in 41% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.09 (s, 6H, Si(CH_3)$_2$), 0.86-0.90 (m, 3H, CH_3), 0.91 (s, 9H, C(CH_3)$_3$), 1.24 (t, 3H, J = 7.0 Hz, CH_3), 1.26-1.37 (m, 6H, 3CH_2), 1.53-1.59 (m, overlapped with H_2O, 2H, CH_2), 2.18 (s, 1H, C*H*), 2.44 (tt, 2H, J = 7.5, 1.5 Hz, CH_2), 4.07-4.14 (m, 2H, CH_2), 4.53 (dt, 1H, J = 15.5, 1.5 Hz, C$\underline{H_a}H_b$), 4.61 (dt, 1H, J = 15.5, 1.5 Hz, C$H_a\underline{H_b}$) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.5, -5.4, 14.0, 14.4, 18.3, 22.5, 22.8, 24.4, 25.8, 26.9, 28.9, 31.5, 57.5, 59.9, 104.6, 108.2, 176.1 ppm; **HRMS (ESI):** *m/z* calcd for $C_{19}H_{37}O_3Si$ $[M + H]^+$ 341.2506, found 341.2500; **IR (ATR):** 2929, 2856, 1723, 1463, 1254, 1180, 1085, 834 cm^{-1}.

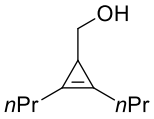
8. Preparation of Cyclopropenyl Alcohols



12 **13**

Cyclopropenyl alcohol **13a** and **13f** were prepared by general procedure B and the characterisation data was consistent with that reported in the literature.[1]

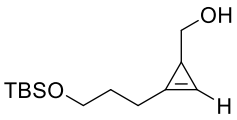
(2,3-Dipropylcycloprop-2-en-1-yl)methanol **13b**



Following general procedure B, cyclopropenyl carboxylate **12b** (1.0017 g, 5.10 mmol) was dissolved in THF (26 mL) and to this was added DIBAL-H (1 M solution in THF, 15.5 mL, 15.5 mmol). After 30 mins at –78 °C, the reaction was worked-up and purified to give the title compound **13b** as a colourless oil (646.8 mg, 4.19 mmol) in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.95 (t, 6H, J = 7.4 Hz, 2CH_3), 1.26 (bs, 1H, O*H*), 1.52-1.62 (m, 5H, 2CH_2, C*H*), 2.39 (td, 4H, J = 7.2, 1.4 Hz, 2CH_2), 3.52 (d, 2H, J = 4.4 Hz, CH_2) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.0, 21.0,

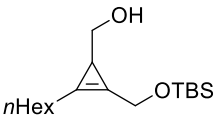
22.6, 27.7, 69.1, 114.1 ppm; **HRMS (ESI):** *m/z* calcd for $C_{10}H_{19}O$ $[M + H]^+$ 155.1430, found 155.1429; **IR (ATR):** 3335 (br), 2959, 2929, 2902, 2872 1457, 1009 cm^{-1}.

(2-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cycloprop-2-en-1-yl)methanol **13d**



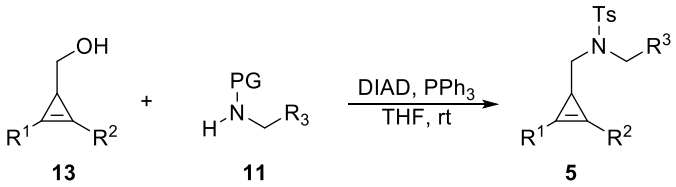
Following general procedure B, cyclopropenyl carboxylate **12d** (1.1591 g, 4.07 mmol) was dissolved in THF (20 mL) and to this was added DIBAL-H (1 M solution in THF, 10.4 mL, 10.4 mmol). After 1 h at –78 °C, the reaction was worked-up and purified to give the title compound **13d** as a colourless oil (799.3 mg, 3.30 mmol) in 81% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.05 (s, 6H, Si(CH_3)$_2$), 0.90 (m, 9H, C(CH_3)$_3$), 1.71 (td, 1H, *J* = 4.5, 1.5 Hz, C*H*), 1.80 (tt, 2H, *J* = 7.0, 6.0 Hz, CH_2), 2.57 (td, 2H, *J* = 7.0, 1.5 Hz, CH_2), 3.50 (ddd, 1H, *J* = 10.5, 4.5, 1.0 Hz, C$\underline{H_a}H_b$), 3.55 (dd, 1H, *J* = 10.5, 4.5 Hz, C$H_a\underline{H_b}$), 3.65-3.71 (m, 2H, CH_2), 6.65 (s, 1H, C*H*) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.3, 18.3, 20.5, 22.6, 25.9, 30.2, 62.1, 68.7, 102.0, 125.4 ppm; **HRMS (ESI):** *m/z* calcd for $C_{13}H_{26}NaO_2Si$ $[M + Na]^+$ 265.1594, found 265.1607; **IR (ATR):** 3344 (br), 2928, 2856, 1471, 1253, 1100, 1006, 832, 773 cm^{-1}.

(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-3-hexylcycloprop-2-en-1-yl)methanol **13h**

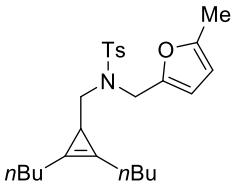


Following general procedure B, cyclopropenyl carboxylate **12h** (969.5 mg, 2.85 mmol) was dissolved in THF (14 mL) and to this was added DIBAL-H (1 M solution in THF, 8.5 mL, 8.50 mmol). After 1 h at –78 °C, the reaction was worked-up give the title compound **13h** as a colourless oil (694.5 mg, 2.33 mmol) in 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.115 (s, 3H, Si(CH_3)$_2$), 0.121 (s, 3H, Si(CH_3)$_2$), 0.86-0.91 (m, 3H, CH_3), 0.93 (s, 9H, C(CH_3)$_3$), 1.26-1.36 (m, 6H, 3CH_2), 1.49-1.58 (m, 2H, CH_2), 1.80 (dd, 1H, *J* = 5.8, 3.8 Hz, C*H*), 1.91 (bs, 1H, O*H*), 2.41 (tq 2H, *J* = 7.6, 2.0 Hz, CH_2), 3.19 (dd, 1H, *J* = 10.8, 6.0 Hz, C$\underline{H_a}H_b$), 3.75 (dd, 1H, *J* = 10.8, 3.6 Hz, C$H_a\underline{H_b}$), 4.46 (dtd, 1H, *J* = 14.0, 2.0, 0.8 Hz, C$\underline{H_a}H_b$), 4.65 (dt, 1H, *J* = 14.0, 1.2 Hz, C$H_a\underline{H_b}$) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = -5.4, 14.0, 18.3, 22.5, 23.9, 25.6, 25.8, 27.4, 29.0, 31.5, 57.6, 68.4, 112.7, 117.0 ppm; **HRMS (ESI):** *m/z* calcd for $C_{17}H_{34}NaO_2Si$ $[M + Na]^+$ 321.2220, found 321.2239; **IR (ATR):** 3359 (br), 2928, 2856, 1463, 1253, 1087, 1005, 833, 775 cm^{-1}.

9. Preparation of Cyclopropenyl Sulfonamides

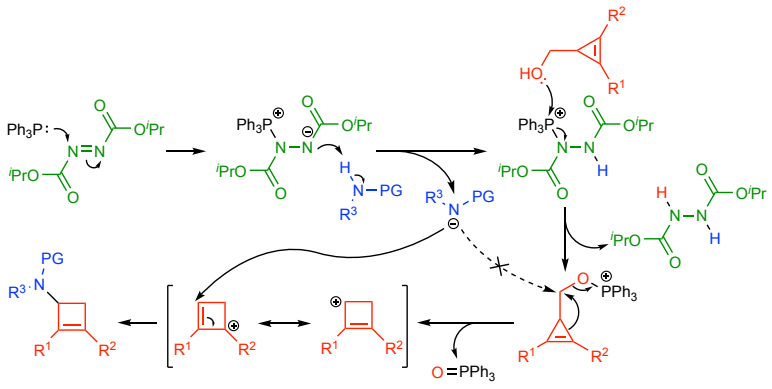


N-((2,3-Dibutylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide **5aa**



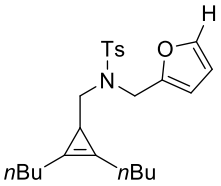
Following the general procedure F, cyclopropenyl alcohol **13a** (204.1 mg, 1.12 mmol), furyl sulfonamide **11a** (309.3 mg, 1.17 mmol), PPh_3 (392.7 mg, 1.50 mmol) and THF (11 mL) were added to a flask. DIAD (0.29 mL, 1.47 mmol) was added with stirring at rt. Following purification the title compound **5aa** was obtained as an oil (330.0 mg, 0.768 mmol) in 69% yield with a purity of 95%.[11] **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.3 Hz, 2CH_3), 1.25-1.39 (m, 4H, 2CH_2), 1.40-1.54 (m, 5H, 2CH_2, CH), 2.10 (s, 3H, CH_3), 2.30-2.44 (m, 7H, 2CH_2, CH_3), 3.08 (d, 2H, J = 4.9 Hz, CH_2), 4.44 (s, 2H, CH_2), 5.78 (dd, 1H, J = 3.1, 1.1 Hz, CH_{Het}), 5.96 (d, 1H, J = 3.1 Hz, CH_{Het}), 7.21 (d, 2H, J = 8.1 Hz, 2CH_{Ar}), 7.63 (d, 2H, J = 8.3 Hz, 2CH_{Ar}) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 13.3, 13.8,

[11] The contaminant was the cyclobutene constitutional isomer which has the same mass and R_f as the title compound and could not be separated. The cyclobutene isomer is inert to the gold(I)-catalysis conditions and does not affect the reaction in any way. The cyclobutene can be separated from the 5,7-fused heterocycle by column chromatography following the gold(I)-catalysed reaction. The proposed mechanism for the cyclobutene formation is:



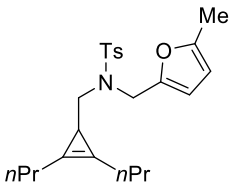
18.9, 21.4, 22.5, 25.1, 29.7, 43.1, 54.1, 106.0, 109.7, 114.5, 127.2, 129.1, 138.0, 142.4, 148.4, 151.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{25}H_{35}NNaO_3S$ $[M + Na]^+$ 452.2230, found 452.2232; **IR (ATR):** 2956, 2928, 2872, 1599, 1563, 1455, 1344, 1220, 1158, 1093, 1020 cm^{-1}.

N-((2,3-Dibutylcycloprop-2-en-1-yl)methyl)-*N*-(furan-2-ylmethyl)-4-methylbenzenesulfonamide **5ab**



Following general procedure F, cyclopropenyl alcohol **13a** (404.5 mg, 2.22 mmol), furyl sulfonamide **11b** (557.9 mg, 2.22 mmol), PPh_3 (754.1 mg, 2.88 mmol) and THF (22 mL) were added to a flask. DIAD (0.57 mL, 2.89 mmol) was added with stirring at rt. Following purification the title compound **5ab** was obtained as a colourless oil (614.1 mg, 1.48 mmol) in 67% yield with a purity of 94%.[11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 7.3 Hz, 2CH_3), 1.25-1.36 (m, 4H, 2CH_2), 1.40 (t, 1H, J = 5.0 Hz, CH), 1.42-1.51 (m, 4H, 2CH_2), 2.25-2.37 (m, 4H, 2CH_2), 2.38 (s, 3H, CH_3), 3.09 (d, 2H, J = 5.0 Hz, CH_2), 4.49 (s, 2H, CH_2), 6.10 (d, 1H, J = 3.1 Hz, CH_{Het}), 6.22-6.25 (m, 1H, CH_{Het}), 7.18-7.23 (m, 3H, 2CH_{Ar}, CH_{Het}), 7.61 (d, 2H, J = 8.4 Hz, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.8, 18.8, 21.4, 22.4, 25.1, 29.6, 43.0, 54.4, 108.7, 110.2, 114.4, 127.1, 129.3, 137.8, 141.9, 142.6, 150.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{24}H_{33}NNaO_3S$ $[M + Na]^+$ 438.2073, found 438.2072; **IR (ATR):** 2957, 2929, 2872, 1599, 1465, 1344, 1159, 1094, 1012 cm^{-1}.

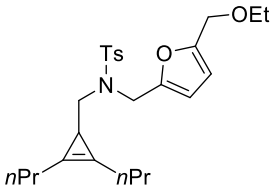
N-((2,3-Dipropylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide **5ac**



Following general procedure F, cyclopropenyl alcohol **13b** (155.1 mg, 1.01 mmol), furyl sulfonamide **11a** (278.1 mg, 1.05 mmol), PPh_3 (343.0 mg, 1.31 mmol) and THF (10 mL) were added to a flask. DIAD (0.26 mL, 1.32 mmol) was added with stirring at rt. Following purification the title compound **5ac** was obtained as a yellow oil (266.5 mg, 0.664 mmol) in 66% yield with a purity of 93%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.92 (t, 6H, J = 7.5 Hz, 2CH_3), 1.44 (t, 1H, J = 5.0 Hz, CH), 1.50-1.56 (m, 4H, 2CH_2), 2.10 (d, 3H, J = 1.0 Hz, CH_3), 2.30-2.36 (m, 4H, 2CH_2), 2.39 (s, 3H,

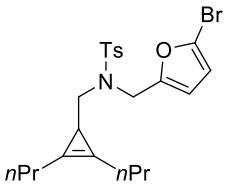
CH_3), 3.08 (d, 2H, J = 5.0 Hz, CH_2), 4.44 (s, 2H, CH_2), 5.77-5.79 (m, 1H, CH_{Het}), 5.96 (d, 1H, J = 3.0 Hz, CH_{Het}), 7.19-7.23 (m, 2H, 2CH_{Ar}), 7.61-7.64 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.3, 14.0, 18.9, 20.9, 21.4, 27.5, 43.1, 54.0, 106.0, 109.7, 114.5, 127.2, 129.1, 137.9, 142.4, 148.4, 151.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{32}NO_3S$ $[M + H]^+$ 402.2097, found 402.2098; **IR (ATR):** 2960, 2930, 2872, 1699, 1335, 1155, 1090, 814 cm^{-1}.

N-((2,3-Dipropylcycloprop-2-en-1-yl)methyl)-*N*-((5-(ethoxymethyl)furan-2-yl)methyl)-4-methylbenzenesulfonamide **5ad**



Following general procedure F, cyclopropenyl alcohol **13b** (40.6 mg, 0.263 mmol), furyl sulfonamide **11c** (84.1 mg, 0.272 mmol), PPh_3 (90.4 mg, 0.345 mmol) and THF (2.6 mL) were added to a flask. DIAD (70 µL, 0.356 mmol) was added with stirring at rt. Following purification the title compound **5ad** was obtained as a pale yellow oil (75.2 mg, 0.169 mmol) in 64% yield with a purity of 95%.[11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.91 (t, 6H, J = 7.4 Hz, 2CH_3), 1.18 (t, 3H, J = 7.0 Hz, CH_3), 1.42 (t, 1H, J = 4.8 Hz, CH), 1.46-1.57 (m, 4H, 2CH_2), 2.28-2.35 (m, 4H, 2CH_2), 2.39 (s, 3H, CH_3), 3.10 (d, 2H, J = 4.8 Hz, CH_2), 3.44 (q, 2H, J = 7.0 Hz, CH_2), 4.26 (s, 2H, CH_2), 4.48 (s, 2H, CH_2), 6.04 (d, 1H, J = 3.2 Hz, CH_{Het}), 6.15 (d, 1H, J = 3.2 Hz, CH_{Het}), 7.21 (d, 2H, J = 8.0 Hz 2CH_{Ar}), 7.61-7.65 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.0, 15.1, 18.8, 20.9, 21.4, 27.5, 43.2, 54.4, 64.4, 65.5, 109.4, 109.7, 114.5, 127.2, 129.3, 137.8, 142.5, 150.6, 151.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{25}H_{35}NNaO_4S$ $[M + Na]^+$ 468.2179, found 468.2191; **IR (ATR):** 2959, 2931, 2871, 1344, 1156, 1090, 1019 cm^{-1}.

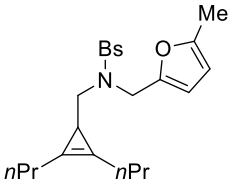
N-((5-Bromofuran-2-yl)methyl)-*N*-((2,3-dipropylcycloprop-2-en-1-yl)methyl)-4-methyl benzenesulfonamide **5ae**



Following general procedure F, cyclopropenyl alcohol **13b** (66.9 mg, 0.434 mmol), furyl sulfonamide **11d** (140.8 mg, 0.426 mmol), PPh_3 (147.2 mg, 0.561 mmol) and THF (4.4 mL) were added to a flask. DIAD (0.11 mL, 0.559 mmol) was added with stirring at rt. Following purification

the title compound **5ae** was obtained as an oil (124.8 mg, 0.268 mmol) in 63% yield with a purity of 88%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$) (contains cyclobutene by-product): δ = 0.81 (t, 3H, J = 7.5 Hz, CH_3, cyclobutene), 0.87 (t, 3H, J = 7.5 Hz, CH_3, cyclobutene), 0.92 (t, 6H, J = 7.5 Hz, 2CH_3, cyclopropene), 1.38 (appar. q, 2H, J = 7.5 Hz, CH_2, cyclobutene), 1.43 (t, 1H, J = 5.0 Hz, CH, cyclopropene), 1.48-1.58 (m, 4H, 2CH_2, cyclopropene), 2.29-2.36 (m, 4H, 2CH_2, cyclopropene), 2.40 (s, 3H, CH_3, cyclopropene), 2.41 (s, 3H, CH_3, cyclobutene), 3.10 (d, 2H, J = 5.0 Hz, CH_2, cyclopropene), 4.14 (d, 1H, J = 16.5 Hz, C$\underline{H_a}H_b$, cyclobutene), 4.20 (d, 1H, J = 16.5 Hz, C$H_a\underline{H_b}$, cyclobutene), 4.45 (s, 2H, CH_2, cyclopropene), 4.75-4.79 (m, 1H, CH, cyclobutene), 6.10 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclopropene), 6.13 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclopropene), 6.18 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclobutene), 6.27 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclobutene), 7.23 (d, 2H, J = 8.0 Hz, 2CH_{Ar}, cyclopropene and cyclobutene), 7.59-7.63 (m, 2H, 2CH_{Ar}, cyclopropene and cyclobutene) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (contains cyclobutene by-product marked with *): δ = 13.99, 14.03*, 14.1*, 18.8, 20.4*, 20.6*, 20.9, 21.4, 27.5, 28.4*, 30.0*, 34.8*, 38.9*, 43.0, 54.5, 54.6*, 111.5, 111.6*, 111.9, 112.1*, 114.4, 120.5*, 121.0, 126.9*, 127.0, 129.35, 129.41*, 137.4, 140.3*, 142.8, 143.0*, 144.0*, 152.5, 153.8* ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{28}(^{79}Br)NNaO_3S$ $[M + Na]^+$ 488.0865, found 488.0863; **IR (ATR):** 2959, 2929, 2871, 1496, 1455, 1338, 1156, 1091, 1012 cm^{-1}.

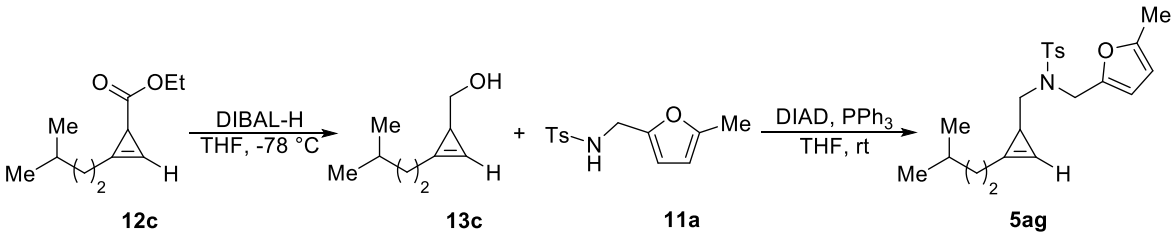
4-Bromo-*N*-((2,3-dipropylcycloprop-2-en-1-yl)methyl)-*N*-((5-methylfuran-2-yl)methyl) benzenesulfonamide **5af**



Following general procedure F, cyclopropenyl alcohol **13b** (70.6 mg, 0.458 mmol), 4-bromo-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide (152.3 mg, 0.461 mmol), PPh_3 (154.7 mg, 0.590 mmol) and THF (4.6 mL) were added to a flask. DIAD (0.12 mL, 0.609 mmol) was added with stirring at rt. Following purification the title compound **5af** was obtained as a colourless oil (82.3 mg, 0.176 mmol) in 39% yield with a purity of 83%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$) (contains cyclobutene by-product): δ = 0.84 (t, 3H, J = 7.5 Hz, CH_3, cyclobutene), 0.88 (t, 3H, J = 7.5 Hz, CH_3, cyclobutene), 0.93 (t, 6H, J = 7.5 Hz, 2CH_3, cyclopropene), 1.26-1.34 (m, 2H, CH_2, cyclobutene), 1.39 (appar. q, 2H, J = 7.5 Hz, CH_2, cyclobutene), 1.47 (t, 1H, J = 5.0 Hz, CH, cyclopropene), 1.51-1.58 (m, 4H, 2CH_2, cyclopropene), 1.66-1.74 (m, 1H, C$\underline{H_a}H_b$, cyclobutene), 1.86-2.04 (m, 3H, CH_2, C$H_a\underline{H_b}$, cyclobutene), 2.07 (d, 3H, J = 1.0 Hz, CH_3, cyclopropene), 2.11 (d, 3H, J = 1.0 Hz, CH_3, cyclobutene), 2.12-2.16 (m, 1H, C$\underline{H_a}H_b$, cyclobutene), 2.31-2.39 (m, 4H, 2CH_2, cyclopropene), 2.42-2.48 (m, 1H, C$H_a\underline{H_b}$, cyclobutene), 3.10 (d, 2H, J = 5.0 Hz, CH_2, cyclopropene), 4.12 (d, 1H, J = 16.0

Hz, C$\underline{H_a}H_b$, cyclobutene), 4.27 (d, 1H, J = 16.0 Hz, C$H_a\underline{H_b}$, cyclobutene), 4.45 (s, 2H, CH_2, cyclopropene), 4.77-4.80 (m, 1H, CH, cyclobutene), 5.78 (dq, 1H, J = 3.0, 1.0 Hz, CH_{Het}, cyclopropene), 5.81 (dq, 1H, J = 3.0, 1.0 Hz, CH_{Het}, cyclobutene), 5.98 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclopropene), 6.10 (d, 1H, J = 3.0 Hz, CH_{Het}, cyclobutene), 7.52-7.59 (m, 4H, 4CH_{Ar}, cyclopropene and cyclobutene) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (contains cyclobutene by-product indicated by asterisk): δ = 13.3, 14.02, 14.05*, 14.2*, 18.9, 20.4*, 20.6*, 20.9, 27.5, 28.5*, 30.0*, 35.0*, 39.1*, 42.9, 54.1, 54.7*, 106.0, 106.2*, 110.1, 110.3*, 114.4, 126.58, 126.65*, 128.5*, 128.7, 131.70, 131.73*, 139.9, 140.2*, 140.3*, 143.9*, 147.9, 148.9*, 151.5*, 151.9 ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{28}(^{79}Br)NNaO_3S$ $[M + Na]^+$ 488.0865, found 488.0873; **IR (ATR):** 2958, 2928, 2871, 1574, 1470, 1341, 1158, 1090, 1067, 1009 cm^{-1}.

N-((2-Isopentylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide **5ag**

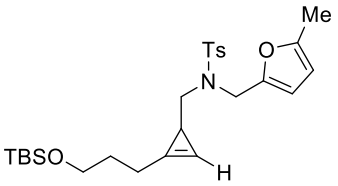


Following general procedure B, cyclopropenyl carboxylate **12c** (351.9 mg, 1.93 mmol) was dissolved in THF (10 mL) and to this was added DIBAL-H (1 M solution in cyclohexanes, 7.7 mL, 7.70 mmol) portionwise. After 1.5 h at –78 °C, the reaction was worked-up and purified to give cyclopropenyl alcohol **13c** as an oil (89.6 mg, 0.639 mmol) in 33% yield. Cyclopropenyl alcohol **13c** was used immediately in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.90 (d, 3H, J = 2.0 Hz, CH_3), 0.92 (d, 3H, J = 2.0 Hz, CH_3), 1.42-1.50 (m, 2H, CH_2), 1.57-1.66 (m, 1H, CH), 1.70 (td, 1H, J = 4.4, 1.6 Hz, CH), 2.45-2.53 (m, 2H, CH_2), 3.47 (dd, 1H, J = 10.7, 4.7 Hz, C$\underline{H_a}H_b$), 3.58 (dd, 1H, J = 10.6, 4.2 Hz, C$H_a\underline{H_b}$), 6.61-6.63 (m, 1H, CH) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 20.5, 22.3, 22.4, 24.3, 27.6, 36.1, 68.7, 101.5, 125.9 ppm.

Following general procedure F, cyclopropenyl alcohol **13c** (84.5 mg, 0.603 mmol), furyl sulfonamide **11a** (168.9 mg, 0.637 mmol), PPh_3 (209.3 mg, 0.798 mmol) and THF (6 mL) were added to a flask. DIAD (0.15 mL, 0.762 mmol) was added with stirring at rt. After 39 h the reaction was worked up and following purification the title compound **5ag** was obtained as an oil (145.2 mg, 0.375 mmol) in 62% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.88 (d, 3H, J = 6.5, CH_3), 0.89 (d, 3H, J = 6.5, CH_3), 1.39-1.44 (m, 2H, CH_2), 1.52 (ddd, 1H, J = 5.5, 4.5, 1.5 Hz, CH), 1.54-1.62 (m, overlapped with H_2O, 1H, CH), 2.11 (d, 3H, J = 1.0 Hz, CH_3), 2.36-2.48 (m, 2H, CH_2), 2.39 (s, 3H,

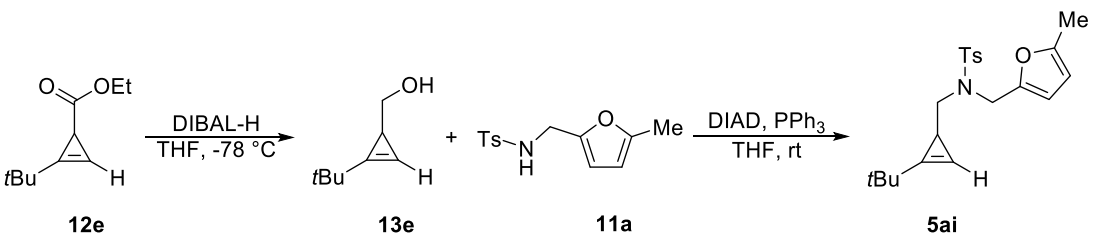
CH_3), 2.94 (dd, 1H, J = 14.0, 5.5 Hz, C$\underline{H_a}H_b$), 3.22 (dd, 1H, J = 14.0, 4.5 Hz, C$H_a\underline{H_b}$), 4.40 (d, 1H, J = 16.0 Hz, C$\underline{H_a}H_b$), 4.49 (d, 1H, J = 16.0 Hz, C$H_a\underline{H_b}$), 5.78-5.81 (m, 1H, CH_{Het}), 5.97 (d, 1H, J = 3.0 Hz, CH_{Het}), 6.50 (m, 1H, CH), 7.22 (d, 2H, J = 7.9 Hz, 2CH_{Ar}), 7.63-7.66 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.4, 17.0, 21.4, 22.2, 22.4, 23.9, 27.5, 36.0, 43.4, 54.0, 102.9, 106.0, 109.9, 125.2, 127.2, 129.2, 137.8, 142.5, 148.1, 151.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{30}NO_3S$ [M + H]$^+$ 388.1941, found 388.1937; **IR (ATR):** 2953, 2922, 2868, 1340, 1156, 1092, 1019 cm^{-1}.

<u>*N*-((2-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide **5ah**</u>



Following general procedure F, cycloropenyl alcohol **13d** (410.6 mg, 1.69 mmol), furyl sulfonamide **11a** (451.1 mg, 1.70 mmol), PPh_3 (586.7 mg, 2.24 mmol) and THF (17 mL) were added to a flask. DIAD (0.43 mL, 2.18 mmol) was added with stirring at rt. Following purification the title compound **5ah** was obtained as a colourless oil (545.4 mg, 1.11 mmol) in 66% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.03 (s, 6H, Si(CH_3)$_2$), 0.88 (s, 9H, C(CH_3)$_3$), 1.54 (ddd, 1H, J = 5.5, 4.5, 1.5 Hz, CH), 1.72-1.78 (m, 2H, CH_2), 2.11 (d, 3H, J = 1.0 Hz, CH_3), 2.39 (s, 3H, CH_3), 2.45-2.55 (m, 2H, CH_2), 2.92 (dd, 1H, J = 14.0, 5.5 Hz, C$\underline{H_a}H_b$), 3.23 (dd, 1H, J = 14.0, 4.5 Hz, C$H_a\underline{H_b}$), 3.60-3.66 (m, 2H, CH_2), 4.40 (d, 1H, J = 16.0 Hz, C$\underline{H_a}H_b$), 4.48 (d, 1H, J = 16.0 Hz, C$H_a\underline{H_b}$), 5.79 (dq, 1H, J = 3.0, 1.0 Hz, CH_{Het}), 5.97 (d, 1H, J = 3.0 Hz, CH_{Het}), 6.52-6.54 (m, 1H, CH), 7.22 (d, 2H, J = 7.9 Hz, 2CH_{Ar}), 7.62-7.66 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.3, 13.4, 17.0, 18.3, 21.4, 22.4, 25.9, 30.2, 43.5, 53.9, 62.2, 103.4, 106.0, 109.9, 124.7, 127.2, 129.2, 137.8, 142.5, 148.1, 151.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{26}H_{39}NNaO_4SSi$ [M + Na]$^+$ 512.2261, found 512.2257; **IR (ATR):** 2928, 2856, 1342, 1253, 1159, 1092, 1000, 834 cm^{-1}.

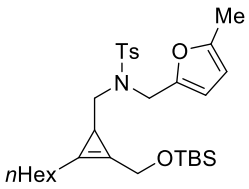
<u>*N*-((2-(*tert*-Butyl)cycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl) benzenesulfonamide **5ai**</u>



Following general procedure B, cyclopropenyl carboxylate **12e** (1.1870 g, 7.06 mmol) was dissolved in THF (35 mL) and to this was added DIBAL-H (1 M solution in THF, 21 mL, 21.0 mmol). After 1 h at –78 °C, the reaction was worked-up and purified to give cyclopropenyl alcohol **13e** as an oil (579.0 mg, 4.59 mmol) in 65% yield. Cyclopropenyl alcohol **13e** was used immediately in the next step. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.15-1.17 (m, 9H, C(CH_3)$_3$), 1.76-1.79 (m, 1H, CH), 3.40 (dd, 1H, J = 10.5, 5.0 Hz, C$\underline{H_a}H_b$), 3.63 (dd, 1H, J = 10.5, 4.0 Hz, C$H_a\underline{H_b}$), 6.52 (d, 1H, J = 1.5 Hz, CH) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 20.9, 28.0, 31.1, 69.1, 98.7, 133.9 ppm.

Following general procedure F, cyclopropenyl alcohol **13e** (536.2 mg, 4.25 mmol), furyl sulfonamide **11a** (1.1543 g, 4.35 mmol), PPh_3 (1.4505 g, 5.53 mmol) and THF (42 mL) were added to a flask. DIAD (1.09 mL, 5.54 mmol) was added with sitting at rt. Following purification the title compound **5ai** was obtained as a solid (400.2 mg, 1.07 mmol) in 25% yield. A second fraction of the title compound **5ai** (645.2 mg) was obtained with an estimated purity of 75% and was not included in the product yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.11 (s, 9H, C(CH_3)$_3$), 1.61 (ddd, 1H, J = 7.5, 3.0, 1.5 Hz, CH), 2.11 (d, 3H, J = 1.0 Hz, CH_3), 2.40 (s, 3H, CH_3), 2.52 (dd, 1H, J = 14.0, 7.5 Hz, C$\underline{H_a}H_b$), 3.65 (dd, 1H, J = 14.0, 3.0 Hz, C$H_a\underline{H_b}$), 4.48 (s, 2H, CH_2), 5.79 (dq, 1H, J = 3.0, 1.0 Hz, CH_{Het}), 5.98 (d, 1H, J = 3.0 Hz, CH_{Het}), 6.40 (d, 1H, J = 1.5 Hz, CH), 7.23 (d, 2H, J = 7.9 Hz, 2CH_{Ar}), 7.64-7.67 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.4, 17.4, 21.4, 28.1, 31.2, 43.3, 54.5, 100.9, 106.0, 109.9, 127.3, 129.2, 132.2, 137.7, 142.5, 148.1, 151.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{21}H_{27}NNaO_3S$ $[M + Na]^+$ 396.1604, found 396.1625; **IR (ATR):** 2964, 2917, 2868, 1340, 1323, 1157, 1092, 801 cm^{-1}; **MP:** 56.6–58.8 °C.

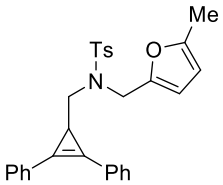
<u>*N*-((2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-3-hexylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl)benzenesulfonamide **5aj**</u>



Following general procedure F, cyclopropenyl alcohol **13h** (219.4 mg, 0.735 mmol), furyl sulfonamide **11a** (198.6 mg, 0.749 mmol), PPh_3 (256.9 mg, 0.979 mmol) and THF (7.5 mL) were added to a flask. DIAD (0.19 mL, 0.965 mmol) was added with stirring at rt. Following purification the title compound **5aj** was obtained as an oil (311.0 mg, 0.570 mmol) in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.06 (s, 6H, Si(CH_3)$_2$), 0.85-0.91 (m, 3H, CH_3), 0.89 (s, 9H, C(CH_3)$_3$), 1.23-1.35 (m, 6H, 3CH_2), 1.48-1.57 (m, 2H, CH_2), 1.60 (t, 1H, J = 4.8 Hz, CH), 2.09 (s, 3H, CH_3), 2.31-2.47 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 3.05 (dd, 1H, J = 14.1, 5.2 Hz, C$\underline{H_a}H_b$), 3.17 (dd, 1H, J = 14.1, 4.6 Hz, C$H_a\underline{H_b}$),

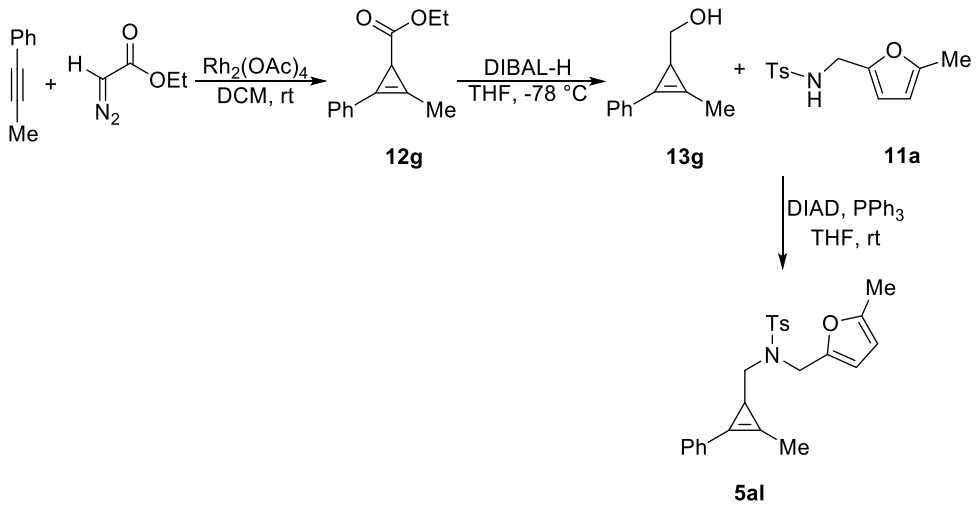
4.45 (d, 2H, J = 3.2 Hz, CH_2), 4.48-4.55 (m, 1H, C$\underline{H_a}H_b$), 4.58 (dt, 1H, J = 15.4, 1.7 Hz, C$H_a\underline{H_b}$), 5.78 (dq, 1H, J = 3.1, 1.2 Hz, CH_{Het}), 5.97 (d, 1H, J = 3.2 Hz, CH_{Het}), 7.20 (d, 2H, J = 8.2 Hz, 2CH_{Ar}), 7.59-7.63 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.43, -5.41, 13.3, 14.0, 18.3, 20.3, 21.4, 22.6, 25.4, 25.8, 27.5, 29.1, 31.5, 43.2, 53.7, 58.7, 106.0, 109.8, 113.8, 116.7, 127.2, 129.2, 137.8, 142.5, 148.4, 151.7 ppm; **HRMS (ESI):** *m/z* calcd for $C_{30}H_{47}NNaO_4SSi$ $[M + Na]^+$ 568.2887, found 568.2889; **IR (ATR):** 2927, 2855, 1343, 1253, 1157, 1093, 1021, 835, 776 cm^{-1}.

<u>*N*-((2,3-Diphenylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylfuran-2-yl)methyl) benzenesulfonamide **5ak**</u>



Following general procedure F, cyclopropenyl alcohol **13f** (249.1 mg, 1.12 mmol), furyl sulfonamide **11a** (297.0 mg, 1.12 mmol), PPh_3 (387.5 mg, 1.48 mmol) and THF (11 mL) were added to a flask. DIAD (0.29 mL, 1.47 mmol) was added with stirring at rt. Following purification title compound **5ak** was obtained as a yellow, viscous oil (422.3 mg, 0.899 mmol) in 80% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 2.02 (d, 3H, J = 1.0 Hz, CH_3), 2.36-2.39 (m, 4H, CH, CH_3), 3.37 (d, 2H, J = 5.0 Hz, CH_2), 4.47 (s, 2H, CH_2), 5.71 (dt, 1H, J = 3.0, 1.0 Hz, CH_{Het}), 5.84 (d, 1H, J = 3.0 Hz, CH_{Het}), 7.20 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.32-7.37 (m, 2H, 2CH_{Ar}), 7.43-7.48 (m, 4H, 4CH_{Ar}), 7.65-7.69 (m, 6H, 6CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.3, 19.4, 21.4, 44.5, 52.7, 106.0, 110.4, 116.0, 127.4, 128.6, 128.8, 129.2, 129.3, 129.6, 137.4, 142.7, 147.7, 152.0 ppm; **HRMS (ESI):** *m/z* calcd for $C_{29}H_{27}NNaO_3S$ $[M + Na]^+$ 492.1604, found 492.1603; **IR (ATR):** 2920, 1597, 1562, 1493, 1445, 1339, 1154, 1092, 1020, 754, 737 cm^{-1}.

4-Methyl-*N*-((2-methyl-3-phenylcycloprop-2-en-1-yl)methyl)-*N*-((5-methylfuran-2-yl) methyl)benzenesulfonamide **5al**



Following a variation of general procedure E, prop-1-yn-1-ylbenzene (136.0 mg, 1.17 mmol), $Rh_2(OAc)_4$ (5.6 mg, 12.7 μmol) and DCM (1.2 mL) were added to a round bottom flask. Ethyl diazoacetate (87% solution in DCM, 1.4 mL, 11.6 mmol) in DCM (1.6 mL) was added and following the complete addition of the ethyl diazoacetate, an additional portion of $Rh_2(OAc)_4$ (5.0 mg, 11.3 μmol) was added causing the reaction to fizz. Flash column chromatography (15:85 EtOAc:hex) have cyclopropenyl carboxylate **12g** (428.8 mg) with significant impurities from the dimerization of ethyl diazoacetate. The residue was subjected to the next step without further purification. In a separate case, to a mixture of prop-1-yn-1-ylbenzene (357.3 mg, 3.08 mmol), $Rh_2(OAc)_4$ (4.5 mg, 10.2 μmol) and DCM (1 mL) was added ethyl diazoacetate (87% solution in DCM, 0.25 mL, 2.07 mmol) in DCM (0.5 mL). Flash column chromatography, gave cyclopropenyl carboxylate **12g** as a colourless oil (53.8 mg, 0.266 mmol) in 13% yield. Characterisation data was consistent with that in the literature.[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.24 (t, 3H, J = 7.1 Hz, CH_3), 2.32 (s, 3H, CH_3), 2.43 (s, 1H, CH), 4.11-4.20 (m, 2H, CH_2), 7.27-7.33 (m, 1H, CH_{Ar}), 7.35-7.41 (m, 2H, 2CH_{Ar}), 7.44-7.48 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 10.6, 14.4, 22.5, 60.1, 105.2, 106.3, 127.1, 128.50, 128.54, 129.2, 175.7 ppm.

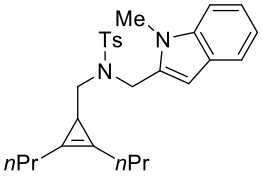
Following general procedure B, cyclopropenyl carboxylate **12g** (428.8 mg) was dissolved in THF (6 mL) and to this was added DIBAL-H (1 M solution in THF, 4.2 mL, 4.20 mmol). Following completion, the reaction was worked-up and purified to give cyclopropenyl alcohol **13g** as a yellow oil (30.8 mg). No yield was determined due to impurities and cyclopropenyl alcohol **13g** was used immediately in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.00 (t, 1H, J = 4.4 Hz, CH),

[12] Maestre, L.; Ozkal, E.; Ayats, C.; Beltran, A.; Diaz-Requejo, M. M.; Perez, P. J.; Pericas, M. A. *Chem. Sci.* **2015**, *6*, 1510.

2.34 (s, 3H, CH_3), 3.66-3.76 (m, 2H, CH_2), 7.26-7.30 (m, overlapped with $CHCl_3$, 1H, CH_{Ar}), 7.36-7.41 (m, 2H, 2CH_{Ar}), 7.47-7.51 (m, 2H, 2CH_{Ar}) ppm.

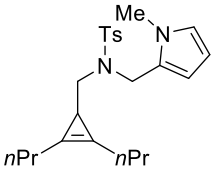
Following general procedure F, cyclopropenyl alcohol **13g** (30.8 mg, ~0.192 mmol), furyl sulfonamide **11a** (51.1 mg, 0.193 mmol), PPh_3 (68.9 mg, 0.263 mmol) and THF (2 mL) were added to a flask. DIAD (50 µL, 0.254 mmol) was added with stirring at rt. Following purification the title compound **5al** was obtained as an oil (13.2 mg, 32.4 µmol) in 3% yield over 3 steps. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.87 (dd, 1H, *J* = 6.0, 3.5 Hz, C*H*), 2.07 (d, 3H, *J* = 1.0 Hz, CH_3), 2.30 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.96 (dd, 1H, *J* = 14.0, 6.0 Hz, C$\underline{H_a}H_b$), 3.55 (ddd, 1H, *J* = 14.0, 3.5, 1.0 Hz, C$H_a\underline{H_b}$), 4.39 (d, 1H, *J* = 16.0 Hz, C$\underline{H_a}H_b$), 4.51 (d, 1H, *J* = 16.0 Hz, C$H_a\underline{H_b}$), 5.76 (dq, 1H, *J* = 3.0, 1.0 Hz, CH_{Het}), 5.92 (d, 1H, *J* = 3.0 Hz, CH_{Het}), 7.21 (d, 2H, *J* = 7.8 Hz, 2CH_{Ar}), 7.25-7.29 (m, overlapped with $CHCl_3$, 1H, CH_{Ar}), 7.35-7.39 (m, 2H, 2CH_{Ar}), 7.41-7.44 (m, 2H, 2CH_{Ar}), 7.63-7.66 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 11.5, 13.3, 19.7, 21.4, 43.7, 52.8, 106.0, 110.0, 112.7, 116.0, 127.3, 127.8, 128.5, 128.8, 129.2, 129.4, 137.7, 142.6, 148.0, 151.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{24}H_{26}NO_3S$ $[M + H]^+$ 408.1628, found 408.1628.

<u>*N*-((2,3-Dipropylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((1-methyl-1*H*-indol-2-yl)methyl)benzenesulfonamide **5ba**</u>



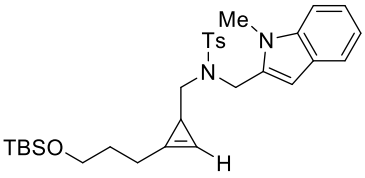
Following general procedure F, cyclopropenyl alcohol **13b** (99.5 mg, 0.645 mmol), 1*H*-indolyl sulfonamide **11g** (204.8 mg, 0.651 mmol), PPh_3 (221.9 mg, 0.846 mmol) and THF (6.5 mL) were added to a flask. DIAD (0.17 mL, 0.863 mmol) was added with stirring at rt. Following purification the title compound **5ba** was obtained as a yellow solid (185.5 mg, 0.412 mmol) in 64% yield with a purity of 94%.[11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.81 (t, 6H, *J* = 7.4 Hz, 2CH_3), 1.09 (t, 1H, *J* = 4.8 Hz, C*H*), 1.34-1.44 (m, 4H, 2CH_2), 2.10-2.17 (m, 4H, 2CH_2), 2.42 (s, 3H, CH_3), 2.99 (d, 2H, *J* = 4.8 Hz, CH_2), 3.84 (s, 3H, CH_3), 4.50 (s, 2H, CH_2), 6.27 (s, 1H, CH_{Het}), 7.07 (ddd, 1H, *J* = 8.0, 7.0, 1.2 Hz, CH_{Het}), 7.20 (ddd, 1H, *J* = 8.0, 7.0, 1.2 Hz, CH_{Het}), 7.27-7.32 (m, 3H, 2CH_{Ar}, CH_{Het}), 7.51 (d, 1H, *J* = 8.0 Hz, CH_{Het}), 7.71 (d, 2H, *J* = 8.3 Hz, 2CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.9, 19.0, 20.8, 21.5, 27.3, 30.0, 45.3, 55.0, 103.3, 109.2, 114.6, 119.4, 120.4, 121.7, 127.1, 127.3, 129.6, 133.7, 136.6, 138.2, 143.1 ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{35}N_2O_2S$ $[M + H]^+$ 451.2414, found 451.2434; **IR (ATR):** 2956, 2930, 2869, 1468, 1337, 1307, 1162, 1088, 878, 813, 733 cm^{-1}; **MP:** 63.4–65.1 °C.

N-((2,3-Dipropylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((1-methyl-1H-pyrrol-2-yl) methyl)benzenesulfonamide **5bb**



Following general procedure F, cyclopropenyl alcohol **13b** (118.7 mg, 0.770 mmol), 1*H*-pyrrolyl sulfonamide **11f** (200.4 mg, 0.758 mmol), PPh_3 (256.3 mg, 0.977 mmol) and THF (7.6 mL) were added to a flask. DIAD (0.19 mL, 0.965 mmol) was added with stirring at rt. Following purification the title compound **5bb** was obtained as an oil (166.0 mg, 0.414 mmol) in 54% yield with a purity of 95%.[11] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.87 (t, 6H, *J* = 7.4 Hz, 2CH_3), 1.04 (t, 1H, *J* = 4.9 Hz, C*H*), 1.40-1.51 (m, 4H, 2CH_2), 2.15-2.30 (m, 4H, 2CH_2), 2.42 (s, 3H, CH_3), 2.92 (d, 2H, *J* = 4.9 Hz, CH_2), 3.70 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 5.91 (dd, 1H, *J* = 3.6, 2.0 Hz, CH_{Het}), 5.98 (dd, 1H, J = 3.6, 2.8 Hz, CH_{Het}), 6.59 (dd, 1H, *J* = 2.8, 2.0 Hz, CH_{Het}), 7.28 (d, 2H, *J* = 8.0 Hz, 2CH_{Ar}), 7.64-7.68 (m, 2H, 2CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.0, 18.9, 20.8, 21.5, 27.4, 34.1, 44.6, 54.6, 106.6, 110.5, 114.7, 123.4, 126.0, 127.2, 129.5, 136.8, 142.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{32}N_2NaO_2S$ $[M + Na]^+$ 423.2077, found 423.2066; **IR (ATR):** 2958, 2871, 1453, 1336, 1302, 1156, 1091, 900, 814 cm^{-1}.

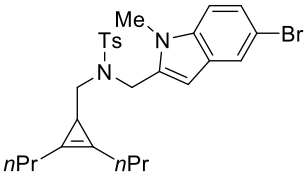
N-((2-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((1-methyl-1*H*-indol-2-yl)methyl)benzenesulfonamide **5bc**



Following general procedure F, cyclopropenyl alcohol **13d** (63.4 mg, 0.262 mmol), 1*H*-indolyl sulfonamide **11g** (75.5 mg, 0.240 mmol), PPh_3 (84.3 mg, 0.321 mmol) and THF (2.5 mL) were added to a flask. DIAD (60 µL, 0.305 mmol) was added with stirring at rt. After 7.5 h the reaction was worked up and following purification the title compound **5bc** was obtained as an oil (57.1 mg, 0.106 mmol) in 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.01 (s, overlapped with TMS, 6H, Si(CH_3)$_2$), 0.88 (s, 9H, C(CH_3)$_3$), 1.22-1.26 (m, 1H, C*H*), 1.57-1.66 (m, 2H, CH_2), 2.27-2.33 (m, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.70 (dd, 1H, *J* = 14.8, 6.0 Hz, C$\underline{H_a}H_b$), 3.28 (dd, 1H, *J* = 14.6, 3.6 Hz, C$H_a\underline{H_b}$), 3.48-3.54 (m, 2H, CH_2), 3.89 (s, 3H, CH_3), 4.43 (d, 1H, *J* = 14.2 Hz, C$\underline{H_a}H_b$), 4.62 (d, 1H, *J* = 14.2 Hz, C$H_a\underline{H_b}$), 6.02 (appar. q, 1H, *J* = 1.6 Hz, C*H*), 6.31 (s, 1H, CH_{Het}), 7.10 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz, CH_{Het}), 7.23 (ddd, 1H, *J* = 8.2, 7.0, 1.2 Hz, CH_{Het}), 7.30-7.36 (m, 3H, 2CH_{Ar}, CH_{Het}), 7.54 (dt, 1H, *J* = 8.0, 1.0 Hz, CH_{Het}), 7.73-7.77 (m, 2H, 2CH_{Ar}); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = -5.4, 17.2, 18.3, 21.5,

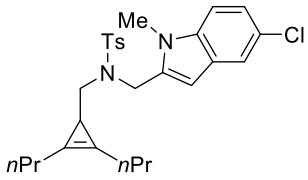
22.1, 25.9, 30.10, 30.12, 45.5, 54.8, 62.1, 103.4, 103.6, 109.2, 119.5, 120.4, 121.8, 124.1, 127.0, 127.3, 129.7, 133.4, 136.4, 138.2, 143.2 ppm; **HRMS (ESI):** *m/z* calcd for $C_{30}H_{43}N_2O_3SSi$ $[M + H]^+$ 539.2758, found 539.2758; **IR (ATR):** 2950, 2855, 1470, 1339, 1252, 1158, 1092, 834, 773, 747 cm^{-1}.

N-((5-Bromo-1-methyl-1*H*-indol-2-yl)methyl)-*N*-((2,3-dipropylcycloprop-2-en-1-yl)methyl)-4-methylbenzenesulfonamide **5bd**



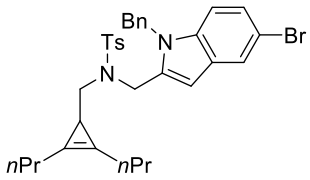
Following general procedure F, cyclopropenyl alcohol **13b** (32.1 mg, 0.208 mmol), 1*H*-indolyl sulfonamide **11h** (69.9 mg, 0.178 mmol), PPh_3 (62.3 mg, 0.238 mmol) and THF (1.8 mL) were added to a flask. DIAD (50 µL, 0.254 mmol) was added with stirring at rt. Following purification the title compound **5bd** was obtained as a white gum-like solid (59.6 mg, 0.113 mmol) in 63% yield with a purity of 89%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$) (contains cyclobutene by-product): δ = 0.63 (t, 3H, *J* = 7.0 Hz, C*H*$_3$, cyclobutene), 0.81 (t, 6H, *J* = 7.7 Hz, 2C*H*$_3$, cyclopropene, 3H, C*H*$_3$, cyclobutene), 1.05 (t, 1H, *J* = 5.0 Hz, C*H*, cyclopropene), 1.34-1.44 (m, 4H, 2C*H*$_2$, cyclopropene), 1.78-1.89 (m, 3H, C*H*$_2$, C*H*$_a$*H*$_b$, cyclobutene), 2.07-2.19 (m, 4H, 2C*H*$_2$,cyclopropene), 2.21-2.25 (m, 1H, C*H*$_a$*H*$_b$, cyclobutene), 2.41 (s, 3H, C*H*$_3$, cyclopropene), 2.42 (s, 3H, C*H*$_3$, cyclobutene), 2.98 (d, 2H, *J* = 5.0 Hz, C*H*$_2$, cyclopropene), 3.80 (s, 3H, C*H*$_3$, cyclobutene), 3.82 (s, 3H, C*H*$_3$, cyclopropene), 4.37 (d, 1H, *J* = 15.5 Hz, C*H*$_a$*H*$_b$, cyclobutene), 4.46 (s, 2H, C*H*$_2$, cyclopropene), 4.53 (d, 1H, *J* = 15.5 Hz, C*H*$_a$*H*$_b$, cyclobutene), 4.76-4.79 (m, 1H, C*H*, cyclobutene), 6.21 (s, 1H, C*H*$_{Het}$, cyclopropene), 6.25 (s, 1H, C*H*$_{Het}$, cyclobutene), 7.16 (d, 1H, *J* = 8.5 Hz, C*H*$_{Het}$, cyclopropene and cyclobutene), 7.25-7.30 (m, overlapped with $CHCl_3$, 3H, 2C*H*$_{Ar}$, C*H*$_{Het}$, cyclopropene and cyclobutene), 7.60 (d, 1H, *J* = 2.0 Hz, C*H*$_{Het}$, cyclobutene), 7.62 (d, 1H, *J* = 2.0 Hz, C*H*$_{Het}$, cyclopropene), 7.69 (d, 2H, *J* = 8.5 Hz, 2C*H*$_{Ar}$, cyclopropene), 7.72 (d, 2H, *J* = 8.5 Hz, 2C*H*$_{Ar}$, cyclobutene) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (contains cyclobutene by-product indicated by asterisk): δ = 13.88, 13.94*, 14.1*, 18.9, 20.2*, 20.5*, 20.8, 21.4, 21.5*, 27.3, 28.4*, 29.9*, 30.2, 33.5*, 40.2*, 45.2, 54.8*, 55.3, 102.5*, 102.6, 110.5*, 110.6, 112.7, 114.5, 122.6*, 122.8, 124.1*, 124.5, 127.15*, 127.23, 128.7, 128.9*, 129.59, 129.63*, 135.1, 136.3, 136.7, 137.0*, 140.6*, 142.9*, 143.2, 143.4* ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{33}(^{79}Br)N_2NaO_2S$ $[M + Na]^+$ 551.1338, found 551.1340; **IR (ATR):** 2956, 2927, 2870, 1470, 1338, 1160, 1089, 793, 773, 714 cm^{-1}; **MP:** 78.0–79.1 °C.

N-((5-Chloro-1-methyl-1*H*-indol-2-yl)methyl)-*N*-((2,3-dipropylcycloprop-2-en-1-yl)methyl)-4-methylbenzenesulfonamide **5be**



Following general procedure F, cyclopropenyl alcohol **13b** (39.6 mg, 0.257 mmol), 1*H*-indolyl sulfonamide **11i** (67.8 mg, 0.194 mmol), PPh_3 (66.1 mg, 0.252 mmol) and THF (2 mL) were added to a flask. DIAD (50 µL, 0.254 mmol) was added with stirring at rt. Following purification the title compound **5be** was obtained as a white gum-like solid (68.9 mg, 0.142 mmol) in 73% yield with a purity of 90%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.81 (t, 6H, J = 7.5 Hz, 2CH_3), 1.06 (t, 1H, J = 5.0 Hz, CH), 1.34-1.43 (m, 4H, 2CH_2), 2.07-2.19 (m, 4H, 2CH_2), 2.41 (s, 3H, CH_3), 2.98 (d, 2H, J = 5.0 Hz, CH_2), 3.82 (s, 3H, CH_3), 4.46 (s, 2H, CH_2), 6.22 (s, 1H, CH_{Het}), 7.14 (dd, 1H, J = 8.5, 2.0 Hz, CH_{Het}), 7.20 (d, 1H, J = 8.5 Hz, CH_{Het}), 7.28 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.46 (d, 1H, J = 2.0 Hz, CH_{Het}), 7.67-7.71 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.9, 18.9, 20.7, 21.4, 27.3, 30.2, 45.2, 55.2, 102.7, 110.1, 114.5, 119.7, 121.9, 125.1, 127.2, 128.0, 129.6, 135.2, 136.3, 136.5, 143.2 ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{34}(^{35}Cl)N_2O_2S$ $[M + H]^+$ 485.2024, found 485.2034; **IR (ATR):** 2957, 2926, 2871, 1475, 1336, 1159, 1089, 1061, 793, 772, 743, 716 cm^{-1}; **MP:** 65.4–67.8 °C.

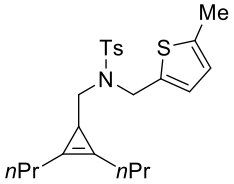
N-((1-Benzyl-5-bromo-1*H*-indol-2-yl)methyl)-*N*-((2,3-dipropylcycloprop-2-en-1-yl)methyl)-4-methylbenzenesulfonamide **5bf**



Following general procedure F, cyclopropenyl alcohol **13b** (26.3 mg, 0.171 mmol), 1*H*-indolyl sulfonamide **11j** (69.9 mg, 0.149 mmol), PPh_3 (51.3 mg, 0.196 mmol) and THF (1.5 mL) were added to a flask. DIAD (40 µL, 0.203 mmol) was added with stirring at rt. Following purification the title compound **5bf** was obtained as an oil (50.7 mg, 83.7 µmol) in 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.82 (t, 6H, J = 7.4 Hz, 2CH_3), 1.12 (t, 1H, J = 4.8 Hz, CH), 1.34-1.44 (m, 4H, 2CH_2), 2.07-2.19 (m, 4H, 2CH_2), 2.38 (s, 3H, CH_3), 3.02 (d, 2H, J = 5.0 Hz, CH_2), 4.38 (s, 2H, CH_2), 5.49 (s, 2H, CH_2), 6.30 (s, 1H, CH_{Het}), 6.94 (dd, 2H, J = 7.7, 1.8 Hz, 2CH_{Ar}), 7.10 (d, 1H, J = 8.8 Hz, CH_{Het}), 7.19-7.27 (m, overlapped with $CHCl_3$, 6H, 5CH_{Ar}, CH_{Het}), 7.61 (d, 2H, J = 8.3 Hz, 2CH_{Ar}), 7.67 (d, 1H, J = 1.9 Hz, CH_{Het}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.9, 18.8, 20.8, 21.4, 27.3, 44.6, 46.6, 55.1,

103.5, 111.3, 113.0, 114.5, 123.0, 124.9, 126.0, 127.3, 127.4, 128.7, 129.0, 129.5, 135.2, 136.5, 136.6, 137.4, 143.1 ppm; **HRMS (ESI):** *m/z* calcd for $C_{33}H_{38}(^{79}Br)N_2O_2S$ $[M + H]^+$ 605.1832, found 605.1833; **IR (ATR):** 2958, 2928, 2870, 1495, 1451, 1332, 1156, 1090, 899, 729 cm^{-1}.

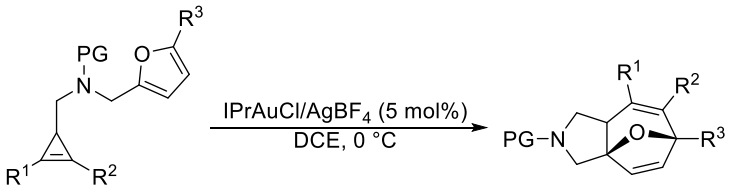
N-((2,3-Dipropylcycloprop-2-en-1-yl)methyl)-4-methyl-*N*-((5-methylthiophen-2-yl) methyl)benzenesulfonamide **5c**



Following general procedure F, cyclopropenyl alcohol **13b** (160.1 mg, 1.04 mmol), thiophenyl sulfonamide **11e** (306.9 mg, 1.09 mmol), PPh_3 (361.7 mg, 1.38 mmol) and THF (10 mL) were added to a flask. DIAD (0.27 mL, 1.37 mmol) was added with stirring at rt. Following purification the title compound **5c** was obtained as a colourless oil (344.8 mg, 0.826 mmol) in 80% yield with a purity of 93%.[11] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.5 Hz, 2CH_3), 1.39 (t, 1H, J = 5.0 Hz, CH), 1.45-1.55 (m, 4H, 2CH_2), 2.26-2.32 (m, 4H, 2CH_2), 2.39 (d, 3H, J = 1.0 Hz, CH_3), 2.40 (s, 3H, CH_3), 3.11 (d, 2H, J = 5.0 Hz, CH_2), 4.55 (s, 2H, CH_2), 6.52 (appar. dq, 1H, J = 3.5, 1.0 Hz, CH_{Het}), 6.65 (d, 1H, J = 3.5 Hz, CH_{Het}), 7.23 (d, 2H, J = 7.9 Hz, 2CH_{Ar}), 7.63-7.67 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.0, 15.3, 18.8, 20.9, 21.4, 27.5, 45.4, 54.0, 114.5, 124.5, 126.8, 127.2, 129.4, 137.2, 138.0, 140.0, 142.7 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{31}NNaO_2S_2$ $[M + Na]^+$ 440.1688, found 440.1687; **IR (ATR):** 2958, 2926, 2871, 1452, 1337, 1154, 1091, 902, 801, 761, 742 cm^{-1}.

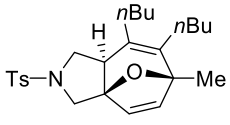
10. Au(I)-Catalysed Reactions of Cyclopropenyl Sulfonamides

10.1. Reactions of Cyclopropenyl Furyl Sulfonamides



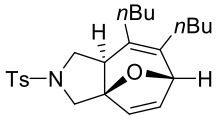
5a **6**

7,8-Dibutyl-6-methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6a**



Following general procedure G, cyclopropenyl furyl sulfonamide **5aa** (53.7 mg, 0.125 mmol) was dissolved in DCE (1.25 mL) and IPrAuCl (3.8 mg, 6.12 µmol) and $AgBF_4$ (1.2 mg, 6.16 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **6a** as a yellow oil (38.1 mg, 88.7 µmol) in 75% yield.[13] **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 0.84-0.93 (m, 6H, 2CH_3), 1.10-1.33 (m, 8H, 4CH_2), 1.34 (s, 3H, CH_3), 1.66-1.78 (m, 1H, C$\underline{H}_a H_b$), 1.90-2.18 (m, 4H, CH_2, C$H_a\underline{H}_b$, CH), 2.41 (s, 3H, CH_3), 2.97 (dd, 1H, J = 11.0, 9.0 Hz, C$\underline{H}_a H_b$), 3.33 (d, 1H, J = 12.0 Hz, C$\underline{H}_a H_b$), 3.80 (d, 1H, J = 12.0 Hz, C$H_a\underline{H}_b$), 3.92 (dd, 1H, J = 9.0, 7.7 Hz, C$H_a\underline{H}_b$), 5.70 (d, 1H, J = 5.7 Hz, CH), 6.18 (d, 1H, J = 5.7 Hz, CH), 7.30 (d, 2H, J = 8.1 Hz, 2CH_{Ar}), 7.72 (d, 2H, J = 8.1 Hz, 2CH_{Ar}) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 13.8, 13.9, 19.9, 21.5, 22.8, 22.9, 27.2, 30.6, 31.1, 32.4, 43.5, 51.8, 54.6, 85.1, 90.2, 126.9, 127.5, 128.0, 129.6, 134.3, 139.3, 143.1, 143.3 ppm; **HRMS (ESI):** *m/z* calcd for $C_{25}H_{35}NNaO_3S$ $[M + Na]^+$ 452.2230, found 452.2232; **IR (ATR):** 2957, 2931, 2871, 1458, 1346, 1164, 1117, 1092, 815, 716 cm^{-1}.

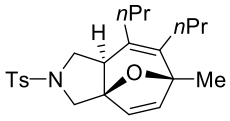
7,8-Dibutyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6b**



Following general procedure G, cyclopropenyl furyl sulfonamide **5ab** (300.4 mg, 0.723 mmol) was dissolved in DCE (7.09 mL) and IPrAuCl (22.1 mg, 35.6 µmol) and $AgBF_4$ (7.0 mg, 36.0 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification by column gave the title compound **6b** as a white solid (201.1 mg, 0.484 mmol) in 71% yield with minor impurities.[13] Recrystallization from pentane at 0 °C overnight gave the title compound **6b** as pure, white crystals (58.2 mg, 0.140 mmol) in 21% yield.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.85-0.91 (m, 6H, 2CH_3), 1.10-1.33 (m, 8H, 4CH_2), 1.64-1.74 (m, 1H, C$\underline{H}_a H_b$), 1.96-2.12 (m, 4H, CH_2, C$H_a\underline{H}_b$, CH), 2.42 (s, 3H, CH_3), 2.93 (dd, 1H, J = 11.0, 8.8 Hz, C$\underline{H}_a H_b$), 3.33 (d, 1H, J = 11.8 Hz, C$\underline{H}_a H_b$), 3.86 (d, 1H, J = 11.8 Hz, C$H_a\underline{H}_b$), 3.93 (dd, 1H, J = 8.8, 7.6 Hz, C$H_a\underline{H}_b$), 4.49 (d, 1H, J = 1.8 Hz, CH), 5.82 (d, 1H, J = 5.6 Hz, CH), 6.42 (dd, 1H, J = 5.6, 1.8 Hz, CH), 7.33 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.72 (d, 2H, J = 8.3 Hz, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.91, 13.94, 21.5, 22.60, 22.62, 29.2, 30.3, 30.4, 30.8, 42.0, 51.8, 54.3, 80.4, 90.3, 127.3, 127.5, 127.8, 129.7, 134.0, 136.9, 139.0, 143.4 ppm; **HRMS (DART):** *m/z* calcd for $C_{24}H_{34}NO_3S$ $[M + H]^+$ 416.2254, found 416.2260; **IR (ATR):** 2956, 2929, 2871, 2859, 1598, 1466, 1346, 1165, 1092, 1014, 816 cm^{-1}; **MP:** 76.3–78.4 °C.

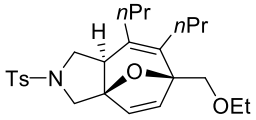
[13] The yield has been corrected after the gold(I)-catalysed reaction for the presence of cyclobutene in the starting material (see footnote 11).

6-Methyl-7,8-dipropyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6c**



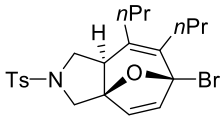
Following general procedure G, cyclopropenyl furyl sulfonamide **5ac** (20.0 mg, 49.8 µmol) was dissolved in DCE (0.5 mL) and IPrAuCl (1.6 mg, 2.50 µmol) and $AgBF_4$ (0.5 mg, 2.57 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **6c** as a yellow oil (12.0 mg, 29.9 µmol) in 65% yield.[13] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.83 (t, 3H, J = 7.5 Hz, CH_3), 0.89 (t, 3H, J = 7.5 Hz, CH_3), 1.16-1.24 (m, 2H, 2C$\underline{H_a}H_b$), 1.28-1.36 (m, 2H, 2C$\underline{H_a}H_b$), 1.35 (s, 3H, CH_3), 1.70-1.78 (m, 1H, C$\underline{H_a}H_b$), 1.95-2.05 (m, 2H, 2C$H_a\underline{H_b}$), 2.05-2.14 (m, 2H, C$\underline{H_a}H_b$, CH), 2.42 (s, 3H, CH_3), 2.97 (dd, 1H, J = 11.0, 9.0 Hz, C$\underline{H_a}H_b$), 3.33 (d, 1H, J = 11.5 Hz, C$\underline{H_a}H_b$), 3.81 (d, 1H, J = 11.5 Hz, C$H_a\underline{H_b}$), 3.92 (dd, 1H, J = 9.0, 7.5 Hz, C$H_a\underline{H_b}$), 5.72 (d, 1H, J = 5.5 Hz, CH), 6.18 (d, 1H, J = 5.5 Hz, CH), 7.31 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.71-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.1, 14.3, 19.9, 21.5, 21.7, 23.4, 29.6, 33.4, 43.5, 51.8, 54.6, 85.1, 90.2, 127.0, 127.5, 128.0, 129.7, 134.3, 139.4, 143.1, 143.3 ppm; **HRMS (ESI):** m/z calcd for $C_{23}H_{31}NNaO_3S$ $[M + Na]^+$ 424.1917, found 424.1916; **IR (ATR):** 2959, 2930, 2871, 1456, 1341, 1160, 1091, 813 cm^{-1}.

6-(Ethoxymethyl)-7,8-dipropyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6d**



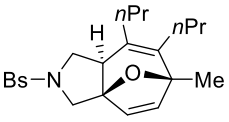
Following general procedure G, cyclopropenyl furyl sulfonamide **5ad** (44.8 mg, 0.101 mmol) was dissolved in DCE (1 mL) and IPrAuCl (3.2 mg, 5.15 µmol) and $AgBF_4$ (1.0 mg, 5.14 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **6d** as a yellow oil (23.5 mg, 52.7 µmol) in 55% yield.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.83 (t, 3H, J = 7.2 Hz, CH_3), 0.89 (t, 3H, J = 7.2 Hz, CH_3), 1.14 (t, 3H, J = 7.0 Hz, CH_3), 1.17-1.40 (m, 4H, 2CH_2), 1.69-1.78 (m, 1H, C$\underline{H_a}H_b$), 1.92-2.10 (m, 3H, 2C$H_a\underline{H_b}$, CH), 2.12-2.21 (m, 1H, C$\underline{H_a}H_b$), 2.42 (s, 3H, CH_3), 3.02 (dd, 1H, J = 11.0, 9.0 Hz, C$\underline{H_a}H_b$), 3.40 (d, 1H, J = 12.0 Hz, C$\underline{H_a}H_b$), 3.43-3.51 (m, 2H, CH_2), 3.60 (d, 1H, J = 11.0 Hz, C$\underline{H_a}H_b$), 3.66 (d, 1H, J = 11.0 Hz, C$H_a\underline{H_b}$), 3.83 (d, 1H, J = 12.0 Hz, C$H_a\underline{H_b}$), 3.93 (dd, 1H, J = 9.0, 7.7 Hz, C$H_a\underline{H_b}$), 5.76 (d, 1H, J = 5.6 Hz, CH), 6.23 (d, 1H, J = 5.6 Hz, CH), 7.30 (d, 2H, J = 7.7 Hz, 2CH_{Ar}), 7.70-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.1, 14.4, 14.9, 21.5, 21.6, 23.7, 29.4, 33.2, 43.3, 51.8, 54.5, 67.2, 70.7, 87.9, 90.6, 127.5, 127.6, 129.1, 129.6, 134.3, 138.0, 140.1, 143.3 ppm; **HRMS (ESI):** m/z calcd for $C_{25}H_{35}NNaO_4S$ $[M + Na]^+$ 468.2179, found 468.2181; **IR (ATR):** 2959, 2871, 1456, 1341, 1163, 1092, 908, 813 cm^{-1}.

6-Bromo-7,8-dipropyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6e**



Following general procedure G, cyclopropenyl furyl sulfonamide **5ae** (63.3 mg, 0.136 mmol) was dissolved in DCE (1.36 mL) and IPrAuCl (4.3 mg, 6.92 µmol) and $AgBF_4$ (1.3 mg, 6.68 µmol) were added at 0 °C with stirring. After 3 days at 0 °C, TLC and ^{1}H NMR indicated the reaction had only gone to ~50% completion so an additional portion of IPrAuCl (8.7 mg, 14.0 µmol) and $AgBF_4$ (2.5 mg, 12.8 µmol) were added. After another 18 h at 0 °C, the reaction was complete and purification gave the title compound **6e** as a pale yellow solid (7.9 mg, 16.9 µmol) in 14% yield.[13] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.85 (t, 3H, *J* = 7.5 Hz, C*H*$_3$), 0.91 (t, 3H, *J* = 7.5 Hz, C*H*$_3$), 1.20-1.36 (m, 3H, CH_2, C$\underline{H_a}H_b$), 1.44-1.51 (m, 1H, C$H_a\underline{H_b}$), 1.77-1.84 (m, 1H, C$\underline{H_a}H_b$), 2.00-2.08 (m, 1H, C$H_a\underline{H_b}$), 2.12 (dd, 1H, *J* = 11.0, 7.5 Hz, C*H*), 2.16-2.24 (m, 1H, C$\underline{H_a}H_b$), 2.28-2.35 (m, 1H, C$H_a\underline{H_b}$), 2.43 (s, 3H, C*H*$_3$), 2.98 (dd, 1H, *J* = 11.0, 9.0 Hz, C$\underline{H_a}H_b$), 3.40 (d, 1H, *J* = 12.0 Hz, C$\underline{H_a}H_b$), 3.89 (d, 1H, *J* = 12.0 Hz, C$H_a\underline{H_b}$), 3.96 (dd, 1H, *J* = 9.0, 7.5 Hz, C$H_a\underline{H_b}$), 5.82 (d, 1H, *J* = 5.5 Hz, C*H*), 6.52 (d, 1H, *J* = 5.5 Hz, C*H*), 7.32 (d, 2H, *J* = 8.0 Hz, 2C*H*$_{Ar}$), 7.71 (d, 2H, *J* = 8.0 Hz, 2C*H*$_{Ar}$) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.06, 14.13, 21.48, 21.55, 23.0, 32.2, 34.1, 44.4, 51.3, 53.8, 93.3, 97.5, 126.5, 127.5, 129.1, 129.8, 133.7, 138.3, 143.4, 143.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{29}(^{79}Br)NO_3S$ $[M + H]^+$ 466.1046, found 466.1062; **IR (ATR):** 2952, 2927, 2870, 1454, 1333, 1164, 1096, 1061, 975 cm^{-1}; **MP:** 119.7–121.8 °C.

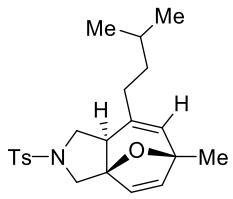
2-((4-Bromophenyl)sulfonyl)-6-methyl-7,8-dipropyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6f**



Following general procedure G, cyclopropenyl furyl sulfonamide **5af** (64.9 mg, 0.139 mmol) was dissolved in DCE (1.39 mL) and IPrAuCl (4.3 mg, 6.92 µmol) and $AgBF_4$ (1.4 mg, 7.19 µmol) were added at 0 °C and the reaction was stirred for 2.5 h. Purification gave the title compound **6f** as a white solid (32.9 mg, 70.5 µmol) in 61% yield.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.84 (t, 3H, *J* = 7.2 Hz, C*H*$_3$), 0.90 (t, 3H, *J* = 7.2 Hz, C*H*$_3$), 1.16-1.38 (m, 4H, 2C*H*$_2$), 1.34 (s, 3H, C*H*$_3$), 1.69-1.78 (m, 1H, C$\underline{H_a}H_b$), 1.92-2.16 (m, 4H, C*H*, C*H*$_2$, C$H_a\underline{H_b}$), 2.96 (dd, 1H, J = 11.0, 8.8 Hz, C$\underline{H_a}H_b$), 3.35 (d, 1H, *J* = 11.8 Hz, C$\underline{H_a}H_b$), 3.80 (d, 1H, *J* = 11.8 Hz, C$H_a\underline{H_b}$), 3.92 (dd, 1H, *J* = 8.8, 7.8 Hz, C$H_a\underline{H_b}$), 5.72 (d, 1H, *J* = 5.6 Hz, C*H*), 6.21 (d, 1H, *J* = 5.6 Hz, C*H*), 7.63-7.72 (m, 4H, 4C*H*$_{Ar}$) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.1, 14.3, 19.9, 21.6, 23.4, 29.6, 33.4, 43.4, 52.0, 54.7, 85.2, 90.1, 126.6, 127.6, 127.9,

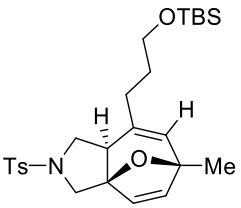
129.0, 132.3, 136.3, 139.6, 143.4 ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{29}(^{79}Br)NO_3S$ $[M + H]^+$ 466.1046, found 466.1064; **IR (ATR):** 2958, 2931, 2869, 1574, 1454, 1337, 1159, 1110, 1070, 1008, 814 cm^{-1}; **MP:** 136.6–138.5 °C.

8-Isopentyl-6-methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6g**



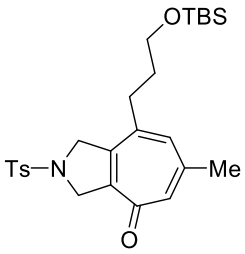
Following general procedure G, cyclopropenyl furyl sulfonamide **5ag** (64.8 mg, 0.167 mmol) was dissolved in DCE (1.67 mL) and IPrAuCl (5.2 mg, 8.37 µmol) and $AgBF_4$ (1.6 mg, 8.22 µmol) were added at 0 °C and the reaction was complete after 45 min. Purification gave the title compound **6g** as an off-white crystal (21.5 mg, 55.5 µmol) in 33% yield. Small impurities (≤6%) were observed that were attributed to ring-opening of **6g**, to the corresponding tropone on the silica gel column (see **6h** for explanation of the tropone formation). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.85 (d, 6H, *J* = 6.6 Hz, 2CH_3), 1.14-1.21 (m, 2H, CH_2), 1.31 (s, 3H, CH_3), 1.38-1.49 (m, 1H, C*H*), 1.74-1.92 (m, 2H, CH_2), 2.03 (dd, 1H, *J* = 10.6, 8.3 Hz, C*H*), 2.42 (s, 3H, CH_3), 2.96 (dd, 1H, *J* = 11.0, 9.0 Hz, C$\underline{H}_a H_b$), 3.37 (d, 1H, *J* = 11.8 Hz, C$\underline{H}_a H_b$), 3.84 (d, 1H, *J* = 11.8 Hz, C$H_a\underline{H}_b$), 3.93 (dd, 1H, *J* = 9.0, 7.8 Hz, C$H_a\underline{H}_b$), 5.65 (q, 1H, *J* = 1.6 Hz, C*H*), 5.74 (d, 1H, *J* = 5.6 Hz, C*H*), 6.22 (d, 1H, *J* = 5.6 Hz, CH), 7.31 (d, 2H, *J* = 7.9 Hz, 2CH_{Ar}), 7.71-7.75 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.50, 21.55, 22.2, 22.6, 27.7, 32.9, 35.9, 43.4, 51.2, 54.5, 82.4, 90.5, 127.2, 127.5, 128.7, 129.7, 134.2, 136.0, 142.8, 143.4 ppm; **HRMS (ESI):** *m/z* calcd for $C_{22}H_{29}NNaO_3S$ $[M + Na]^+$ 410.1760, found 410.1781; **IR (ATR):** 2956, 2928, 2872, 2860, 1465, 1338, 1162, 1111, 1096, 816, 807, 731, 724 cm^{-1}; **MP:** 93.5–96.5 °C.

8-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)-6-methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6h**



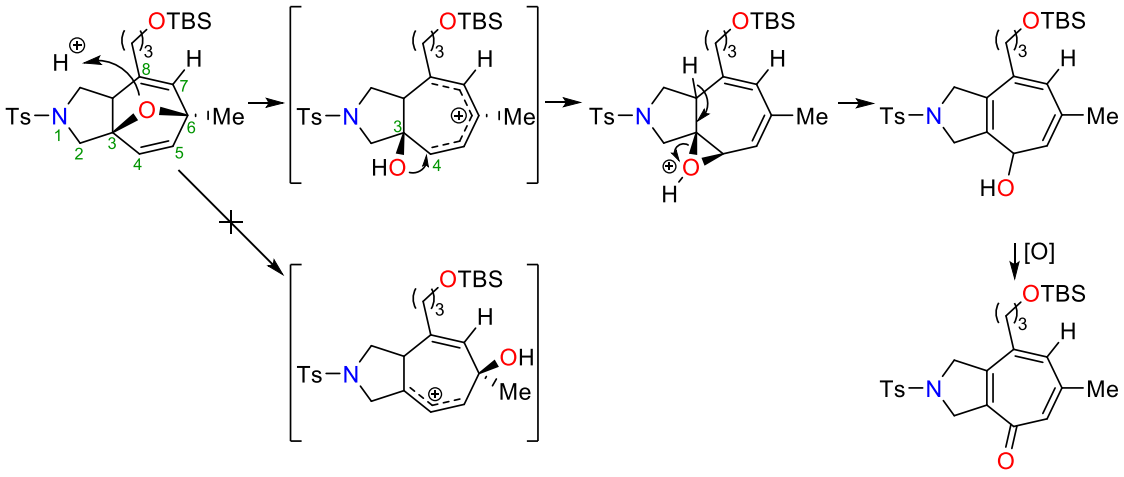
Following general procedure G, cyclopropenyl furyl sulfonamide **5ah** (133.0 mg, 0.272 mmol) was dissolved in DCE (2.90 mL) and IPrAuCl (8.5 mg, 13.7 µmol) and $AgBF_4$ (2.6 mg, 13.4 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound

6h as an off-white crystal (31.3 mg, 63.9 µmol) in 24% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.03 (s, 6H, Si(CH_3)$_2$), 0.89 (m, 9H, C(CH_3)$_3$), 1.31 (s, 3H, CH_3), 1.46-1.58 (m, overlapped with H_2O, 2H, CH_2), 1.82-1.96 (m, 2H, CH_2), 2.03 (dd, 1H, J = 10.5, 8.5 Hz, CH), 2.42 (s, 3H, CH_3), 2.96 (dd, 1H, J = 11.0, 9.0 Hz, CH_aH_b), 3.38 (d, 1H, J = 12.0 Hz, CH_aH_b), 3.48-3.56 (m, 2H, CH_2), 3.83 (d, 1H, J = 12.0 Hz, CH_aH_b), 3.93 (dd, 1H, J = 9.0, 8.0 Hz, CH_aH_b), 5.66 (q, 1H, J = 1.5 Hz, CH), 5.75 (d, 1H, J = 5.5 Hz, CH), 6.22 (d, 1H, J = 5.5 Hz, CH), 7.31 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.71-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.3, 18.3, 21.51, 21.53, 25.9, 29.9, 31.2, 43.4, 51.2, 54.4, 62.3, 82.3, 90.5, 127.3, 127.5, 129.1, 129.7, 134.1, 135.3, 142.8, 143.4 ppm; **HRMS (ESI):** *m/z* calcd for $C_{26}H_{39}NNaO_4SSi$ $[M + Na]^+$ 512.2261, found 512.2254; **IR (ATR):** 2927, 2855, 1338, 1252, 1164, 1115, 1084, 832, 815 cm^{-1}; **MP:** 104.4–105.4 °C.

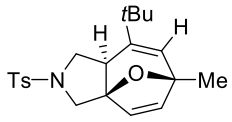


In addition to the 5,7-fused heterocycle above, tropone **14** was isolated as an oil (12.2 mg, 25.0 µmol) in 9% yield. Formation of this product is believed to have occurred during purification on silica gel. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.09 (s, 6H, Si(CH_3)$_2$), 0.94 (s, 9H, C(CH_3)$_3$), 1.74-1.81 (m, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.66-2.71 (m, 2H, CH_2), 3.66 (t, 2H, J = 6.0 Hz, CH_2), 3.99 (s, 2H, CH_2), 4.48 (s, 2H, CH_2), 7.21-7.24 (m, 3H, 3CH_{Ar}), 7.56 (bs, 1H, CH_{Ar}), 7.59-7.62 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.3, 18.3, 20.9, 21.5, 26.0, 28.6, 33.0, 44.9, 53.8, 62.0, 125.2, 127.6, 129.8, 130.2, 133.3, 133.7, 136.1, 137.3, 138.6, 144.1, 191.5 ppm; **HRMS (ESI):** *m/z* calcd for $C_{26}H_{37}NNaO_4SSi$ $[M + Na]^+$ 510.2105, found 510.2111; **IR (ATR):** 2928, 2856, 1694, 1351, 1160, 1091, 834 cm^{-1}.

This compound likely forms via a rearrangement of **6h** in the presence of silica gel according to the following mechanism. The small impurities observed in **6i** and **6g** also appear to correspond to this rearrangement product, but could not be isolated in these cases.

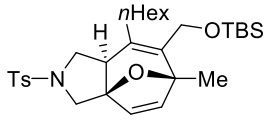


8-(*tert*-Butyl)-6-methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6i**



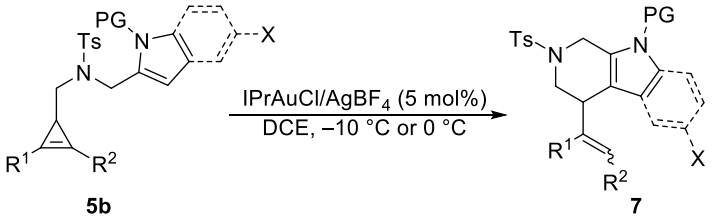
Following general procedure G, cyclopropenyl furyl sulfonamide **5ai** (115.2 mg, 0.308 mmol) was dissolved in DCE (3.00 mL) and IPrAuCl (9.8 mg, 15.8 µmol) and $AgBF_4$ (3.0 mg, 15.4 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **6i** as a white crystal (19.8 mg, 53.0 µmol) in 17% yield. Other complex side products were also obtained which could not be isolated or identified. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.94 (s, 9H, C(CH_3)$_3$), 1.32 (s, 3H, CH_3), 2.10 (ddd, 1H, *J* = 11.0, 7.5, 1.0 Hz, C*H*), 2.42 (s, 3H, CH_3), 3.07 (dd, 1H, *J* = 11.0, 9.5 Hz, C$\underline{H_a}H_b$), 3.39 (d, 1H, *J* = 12.0 Hz, C$\underline{H_a}H_b$), 3.78 (d, 1H, *J* = 12.0 Hz, C$H_a\underline{H_b}$), 4.07 (dd, 1H, *J* = 9.5, 7.5 Hz, C$H_a\underline{H_b}$), 5.66 (d, 1H, *J* = 5.5 Hz, C*H*), 5.74 (d, 1H, *J* = 1.0 Hz, C*H*), 6.26 (d, 1H, *J* = 5.5 Hz, C*H*), 7.31 (d, 2H, *J* = 8.0 Hz, 2CH_{Ar}), 7.72-7.76 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 21.46, 21.50, 29.4, 34.9, 41.2, 52.8, 53.9, 82.4, 91.3, 126.6, 127.48, 127.55, 129.7, 134.4, 142.9, 143.4, 143.6 ppm; **HRMS (ESI):** *m/z* calcd for $C_{21}H_{27}NNaO_3S$ $[M + Na]^+$ 396.1604, found 396.1623; **IR (ATR):** 2955, 2863, 1340, 1159, 1108, 1026, 1016 cm^{-1}; **MP:** 173.2–174.9 °C.

7-(((*tert*-Butyldimethylsilyl)oxy)methyl)-8-hexyl-6-methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrole **6j**

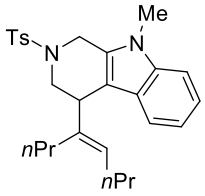


Following general procedure G, cyclopropenyl furyl sulfonamide **5aj** (111.4 mg, 0.204 mmol) was dissolved in DCE (2.04 mL) and IPrAuCl (6.3 mg, 10.1 µmol) and $AgBF_4$ (2.0 mg, 10.3 µmol) were added at 0 °C and the reaction was stirred for 2 h. Purification gave the title compound **6j** as an off-white crystal (3.0 mg, 5.50 µmol) in 3% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.03 (s, 3H, SiCH_3), 0.05 (s, 3H, SiCH_3), 0.87-0.89 (m, 12H, C(CH_3)$_3$, CH_3), 1.18-1.32 (m, 8H, 4CH_2), 1.43 (s, 3H, CH_3), 1.74-1.82 (m, 1H, C$\underline{H_a}H_b$), 1.99-2.07 (m, 2H, C$H_a\underline{H_b}$, C*H*), 2.42 (s, 3H, CH_3), 2.98 (dd, 1H, *J* = 11.0, 9.0 Hz, C$\underline{H_a}H_b$), 3.36 (d, 1H, *J* = 12.0 Hz, C$\underline{H_a}H_b$), 3.82 (d, 1H, *J* = 12.0 Hz, C$H_a\underline{H_b}$), 3.92 (dd, 1H, *J* = 9.0, 8.0 Hz, C$H_a\underline{H_b}$), 4.03 (d, 1H, *J* = 11.5 Hz, C$\underline{H_a}H_b$), 4.23 (d, 1H, *J* = 11.5 Hz, C$H_a\underline{H_b}$), 5.67 (d, 1H, *J* = 5.5 Hz, C*H*), 6.22 (d, 1H, *J* = 5.5 Hz, C*H*), 7.30 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.71-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = -5.6, -5.4, 14.0, 18.1, 19.3, 21.5, 22.5, 25.8, 28.9, 29.2, 31.4, 31.6, 43.2, 51.6, 54.6, 57.3, 84.8, 90.2, 126.0, 127.5, 129.7, 130.7, 134.3, 138.6, 143.4, 144.3 ppm; **HRMS (ESI):** *m/z* calcd for $C_{30}H_{47}NNaO_4SSi$ $[M + Na]^+$ 568.2887, found 568.2885; **IR (ATR):** 2927, 2857, 1470, 1338, 1250, 1164, 1123, 1058, 834, 773 cm^{-1}.

10.2. Reactions of Cyclopropenyl Pyrrolyl- and Indolyl Sulfonamides



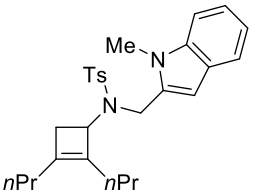
(*E*)-9-Methyl-4-(oct-4-en-4-yl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7a**



Following general procedure G, cyclopropenyl indolyl sulfonamide **5ba** (98.1 mg, 0.218 mmol) was dissolved in DCE (2.20 mL) and IPrAuCl (6.8 mg, 10.9 μmol) and $AgBF_4$ (2.1 mg, 10.8 μmol) were added at 0 °C and the reaction was complete after 17 h. Purification gave the title compound **7a** as a yellow solid (88.4 mg, 0.196 mmol) in 96% yield.[13] The *E*-isomer was the major product and the ratio of *E*:*Z* isomers was estimated to be 8:1. **^{1}H NMR** (500 MHz, $CDCl_3$) (mixture of isomers): δ = 0.72 (t, 3H, *J* = 7.5 Hz, C*H*$_3$, minor isomer), 0.83 (t, 3H, *J* = 7.5 Hz, C*H*$_3$, major isomer), 0.88 (t, 3H, *J* = 6.9 Hz, C*H*$_3$, minor isomer), 0.94 (t, 3H, *J* = 7.5 Hz, C*H*$_3$, major isomer), 1.24-1.30 (m, 2H, C*H*$_2$, for each isomer), 1.42-1.56 (m, 2H, C*H*$_2$, for each isomer), 1.86-1.92 (m, 1H, C*H*$_a$*H*$_b$, major isomer), 1.98 (appar. q, 2H, *J* = 7.5 Hz, C*H*$_2$, major isomer), 2.20-2.28 (m, 1H, C*H*$_a$*H*$_b$, major isomer), 2.39 (s, 3H, C*H*$_3$, minor isomer), 2.41 (s, 3H, C*H*$_3$, major isomer), 2.91 (dd, 1H, *J* = 12.0, 9.0 Hz, C*H*$_a$*H*$_b$, minor isomer), 3.13 (dd, 1H, *J* = 12.0, 6.5 Hz, C*H*$_a$*H*$_b$, major isomer), 3.54 (dd, 1H, *J* = 12.0, 5.0 Hz, C*H*$_a$*H*$_b$, major isomer), 3.59 (s, 3H, C*H*$_3$, major isomer), 3.61 (s, 3H, C*H*$_3$, minor isomer), 3.66 (t, 1H, *J* = 6.0 Hz, C*H*, major isomer), 3.70 (dd, 1H, *J* = 12.0, 5.5 Hz, C*H*$_a$*H*$_b$, minor isomer), 4.11-4.15 (m, 1H, C*H*$_2$ C*H*$_a$*H*$_b$, minor isomer), 4.15-4.20 (m, 1H, C*H*, minor isomer), 4.27 (dd, 1H, *J* = 14.5, 1.5 Hz, C*H*$_a$*H*$_b$, major isomer), 4.36 (d, 1H, *J* = 14.5 Hz, C*H*$_a$*H*$_b$, major isomer), 4.64 (d, 1H, *J* = 14.5 Hz, C*H*$_a$*H*$_b$, minor isomer), 5.09 (t, 1H, *J* = 7.5 Hz, C*H*, major isomer), 5.44 (t, 1H, *J* = 7.5 Hz, C*H*, minor isomer), 6.98-7.03 (m, 1H, C*H*$_{Ar}$, for each isomer), 7.13-7.17 (m, 1H, C*H*$_{Ar}$, for each isomer), 7.24 (d, 1H, *J* = 8.0 Hz, C*H*$_{Ar}$, for each isomer), 7.31 (d, 2H, *J* = 8.0 Hz, 2C*H*$_{Ar}$, for each isomer), 7.35 (d, 1H, *J* = 8.0 Hz, C*H*$_{Ar}$, major isomer), 7.37 (d, 1H, *J* = 8.0 Hz, C*H*$_{Ar}$, minor isomer), 7.71-7.76 (m, 2H, 2C*H*$_{Ar}$, for each isomer) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (mixture of stereoisomers, minor stereoisomer indicated by asterisk): δ = 13.9, 14.0*, 14.1*, 14.5, 21.48, 21.54*, 22.6*, 22.7, 22.9, 23.2*, 29.41, 29.45*, 29.8*, 30.1, 31.6*, 32.1, 35.4*, 40.7, 42.6*, 42.7, 48.3*, 49.7, 108.6, 109.3*, 109.8, 118.9, 119.12*, 119.15*, 119.7, 121.2, 121.3 *, 126.0, 126.2*, 127.5*, 127.6, 129.2, 129.68,

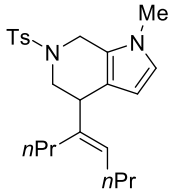
129.70*, 131.0, 133.9, 134.1*, 137.1*, 137.3, 137.7, 143.6, 143.7* ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{35}N_2O_2S$ $[M + H]^+$ 451.2414, found 451.2439; **IR (ATR):** 2958, 2926, 2857, 1471, 1457, 1387, 1377, 1164, 1089, 948, 811, 743 cm^{-1}; **MP:** 113.3–114.3 °C.

N-(2,3-Dipropylcyclobut-2-en-1-yl)-4-methyl-*N*-((1-methyl-1*H*-indol-2-yl)methyl)benzenesulfonamide **5ba'**



In addition to the desired tetrahydro-β-carboline **7a**, the cyclobutene **5ba'** (4.7 mg, 10.4 µmol) was also isolated. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.62 (t, 3H, *J* = 7.0 Hz, CH_3), 0.81 (t, 3H, *J* = 7.5 Hz, CH_3), 1.03-1.10 (m, 2H, 2C$\underline{H_a}H_b$), 1.12-1.19 (m, 1H, C$H_a\underline{H_b}$), 1.25-1.30 (m, 2H, overlapped with grease, CH_2), 1.45-1.50 (m, 1H, C$H_a\underline{H_b}$), 1.79-1.89 (m, 3H, CH_2, C$\underline{H_a}H_b$), 2.21-2.26 (m, 1H, C$H_a\underline{H_b}$), 2.43 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 4.45 (d, 1H, *J* = 15.5 Hz, C$\underline{H_a}H_b$), 4.54 (d, 1H, *J* = 15.5 Hz, C$H_a\underline{H_b}$), 4.75-4.78 (m, 1H, C*H*), 6.31 (d, 1H, *J* = 1.0 Hz, CH_{Het}), 7.06 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz, CH_{Het}), 7.19 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz, CH_{Ar}), 7.29 (appar. d, 3H, *J* = 8.0 Hz, 2CH_{Ar}, CH_{Het}), 7.49 (dt, 1H, *J* = 8.0, 1.0 Hz, CH_{Het}), 7.72-7.75 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.0, 14.2, 20.3, 20.5, 21.5, 28.6, 30.0, 30.1, 33.7, 40.5, 54.9, 103.1, 109.0, 119.3, 120.3, 121.4, 127.2, 127.3, 129.6, 135.6, 137.1, 137.7, 140.6, 142.7, 143.3 ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{34}N_2NaO_2S$ $[M + Na]^+$ 473.2233, found 473.2247; **IR (ATR):** 2957, 2871, 1466, 1335, 1265, 1159, 1090, 814 cm^{-1}.

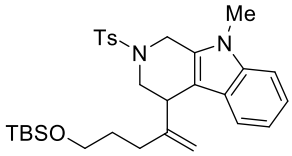
(*E*)-1-Methyl-4-(oct-4-en-4-yl)-6-tosyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridine **7b**



Following general procedure G, cyclopropenyl pyrrolyl sulfonamide **5bb** (112.7 mg, 0.281 mmol) was dissolved in DCE (2.77 mL) and IPrAuCl (8.6 mg, 13.8 µmol) and $AgBF_4$ (2.7 mg, 13.9 µmol) were added at 0 °C and the reaction was complete after 17.5 h. Purification gave the title compound **7b** as a colourless oil (79.0 mg, 0.197 mmol) in 74% yield.[13] The *E*-isomer was the major product and the ratio of *E*:*Z* isomers was estimated to be 6:1. **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture of isomers): δ = 0.80 (t, 3H, *J* = 7.2 Hz, CH_3, minor isomer), 0.85-0.92 (m, 6H, 2CH_3, major

isomer, 3H, CH_3, minor isomer) 1.29-1.44 (m, 4H, 2CH_2, for each isomer), 1.79-1.88 (m, 1H, C$\underline{H_a}H_b$, for each isomer), 1.94-2.01 (m, 2H, CH_2, for each isomer), 2.08-2.17 (m, 1H, C$H_a\underline{H_b}$, for each isomer), 2.42 (s, 3H, CH_3, for each isomer), 2.67-2.72 (m, 1H, C$\underline{H_a}H_b$, minor isomer), 2.75 (dd, 1H, J = 11.6, 8.2 Hz, C$\underline{H_a}H_b$, major isomer), 3.39 (dd, 1H, J = 8.0, 5.0 Hz, CH, major isomer), 3.45 (s, 3H, CH_3, major isomer), 3.46 (s, 3H, CH_3, minor isomer), 3.61 (dd, 1H, J = 11.6, 4.8 Hz, C$H_a\underline{H_b}$, major isomer), 3.66 (dd, 1H, J = 12.4, 5.2 Hz, C$H_a\underline{H_b}$, minor isomer), 3.84-3.89 (m, 2H, CH, C$\underline{H_a}H_b$, minor isomer), 3.93 (dd, 1H, J = 13.6, 1.6 Hz, C$\underline{H_a}H_b$, major isomer), 4.31 (d, 1H, J = 13.5 Hz, C$H_a\underline{H_b}$, major isomer), 4.50 (d, 1H, J = 13.4 Hz, C$H_a\underline{H_b}$, minor isomer), 5.17 (t, 1H, J = 7.2 Hz, CH, major isomer), 5.32 (t, 1H, J = 7.4 Hz, CH, minor isomer), 5.72 (d, 1H, J = 2.8 Hz, CH_{Het}, minor isomer), 5.77 (d, 1H, J = 2.8 Hz, CH_{Het}, major isomer), 6.44 (d, 1H, J = 2.8 Hz, CH_{Het}, minor isomer), 6.46 (d, 1H, J = 2.8 Hz, CH_{Het}, major isomer), 7.31 (d, 2H, J = 8.0 Hz, 2CH_{Ar}, for each isomer), 7.69-7.73 (m, 2H, 2CH_{Ar}, for each isomer) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) (mixture of stereoisomers, minor indicated by asterisk): δ = 13.8, 14.0*, 14.3, 21.5, 21.8*, 22.6, 23.0, 23.3*, 29.6*, 29.9, 32.1, 33.2, 34.7*, 36.2*, 41.7, 42.65*, 42.70, 48.0*, 49.8, 105.6*, 106.0, 118.4*, 119.0, 120.96*, 120.99, 123.2, 127.57*, 127.60, 128.5, 129.59, 129.62, 134.0, 137.8*, 139.0, 143.4 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{33}N_2O_2S$ $[M + H]^+$ 401.2257, found 401.2267; **IR (ATR):** 2955, 2928, 2869, 1499, 1456, 1345, 1314, 1162, 1090, 941, 814 cm^{-1}.

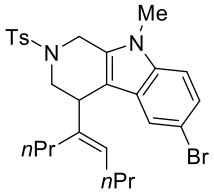
4-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-en-2-yl)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7c**



Following general procedure G, cyclopropenyl indolyl sulfonamide **5bc** (42.0 mg, 77.9 µmol) was dissolved in DCE (0.78 mL) and IPrAuCl (2.5 mg, 4.03 µmol) and $AgBF_4$ (0.8 mg, 4.11 µmol) were added at –10 °C and the reaction was complete after 15 mins. Purification gave the title compound **7c** as a yellow solid (28.5 mg, 52.9 µmol) in 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.01 (s, 3H, Si(CH_3)$_2$), 0.02 (s, 3H, Si(CH_3)$_2$), 0.86 (s, 9H, C(CH_3)$_3$), 1.63-1.82 (m, 2H, CH_2), 2.09 (t, 2H, J = 8.0 Hz, CH_2), 2.41 (s, 3H, CH_3), 3.27 (dd, 1H, J = 12.0, 6.2 Hz, C$\underline{H_a}H_b$), 3.48 (dd, 1H, J = 12.0, 5.0 Hz, C$H_a\underline{H_b}$), 3.54-3.66 (m, 2H, CH_2), 3.60 (s, 3H, CH_3), 3.75 (t, 1H, J = 5.6 Hz, CH), 4.32 (d, 2H, J = 1.5 Hz, CH_2), 4.81 (bs, 1H, C$\underline{H_a}H_b$), 4.95 (appar. q, 1H, J = 1.6 Hz, C$H_a\underline{H_b}$), 7.02 (ddd, 1H, J = 8.0, 7.0, 1.2 Hz, CH_{Ar}), 7.16 (ddd, 1H, J = 8.0, 7.0, 1.2 Hz, CH_{Ar}), 7.22-7.26 (m, overlapped with $CHCl_3$, 1H, CH_{Ar}), 7.32 (d, 2H, J = 8.0 Hz, 2CH_{Ar}), 7.37 (dt, 1H, J = 7.8, 1.0 Hz, CH_{Ar}), 7.72-7.76 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = -5.3, 18.3, 21.5, 25.9, 29.4, 29.8, 31.3, 40.7, 42.7, 49.0, 62.8, 108.7, 109.1, 112.9, 119.20, 119.22, 121.4, 126.0, 127.6, 129.7, 130.8, 133.8, 137.3, 143.7, 148.0 ppm; **HRMS**

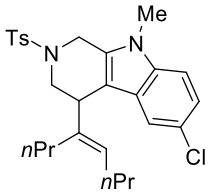
(ESI): *m/z* calcd for $C_{30}H_{42}N_2NaO_3SSi$ $[M + Na]^+$ 561.2578, found 561.2576; **IR (ATR):** 2926, 2893, 2853, 1461, 1348, 1251, 1164, 1100, 1073, 938, 835, 774, 735 cm^{-1}; **MP:** 125.9–127.0 °C.

(*E*)-6-Bromo-9-methyl-4-(oct-4-en-4-yl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7d**



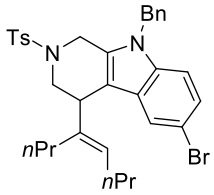
Following general procedure G, cyclopropenyl indolyl sulfonamide **5bd** (45.4 mg, 85.7 µmol) was dissolved in DCE (0.86 mL) and IPrAuCl (2.5 mg, 4.03 µmol) and $AgBF_4$ (0.8 mg, 4.11 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **7d** as a yellow solid (35.4 mg, 66.9 µmol) in 88% yield.[13] The *E*-isomer was the major product and the ratio of *E*:*Z* isomers was estimated to be 6:1. **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture of isomers): δ = 0.74 (t, 3H, *J* = 7.2 Hz, CH_3, minor isomer), 0.86 (t, 3H, *J*= 7.3 Hz, CH_3, major isomer), 0.94 (t, 3H, *J* = 7.3 Hz, CH_3, major isomer), 1.30 (appar. q, 2H, *J* = 7.4 Hz, CH_2, for each isomer), 1.40-1.52 (m, 2H, CH_2, for each isomer), 1.82-1.91 (m, 1H, C$\underline{H_a}H_b$, major isomer), 1.99 (appar. qd, 2H, *J* = 7.2, 3.2 Hz, CH_2, major isomer), 2.17-2.27 (m, 1H, C$H_a\underline{H_b}$, major isomer), 2.41 (s, 3H, CH_3, minor isomer), 2.42 (s, 3H, CH_3, major isomer), 2.88 (dd, 1H, *J* = 12.0, 9.2 Hz, C$\underline{H_a}H_b$, minor isomer), 3.06 (dd, 1H, *J* = 11.2, 6.3 Hz, C$\underline{H_a}H_b$, major isomer), 3.54-3.64 (m, 5H, CH_3, CH, C$H_a\underline{H_b}$, major isomer, 3H, CH_3, minor isomer), 3.70 (dd, 1H, *J* = 11.6, 5.5 Hz, C$H_a\underline{H_b}$, minor isomer), 4.08-4.14 (m, 2H, CH, C$\underline{H_a}H_b$, minor isomer), 4.22 (dd, 1H, *J* = 14.8, 1.6 Hz, C$\underline{H_a}H_b$, major isomer), 4.38 (d, 1H, *J* = 14.8 Hz, C$H_a\underline{H_b}$, major isomer), 4.64 (d, 1H, *J* = 14.8 Hz, C$H_a\underline{H_b}$, minor isomer), 5.08 (t, 1H, *J* = 7.2 Hz, CH, major isomer), 5.46 (t, 1H, *J* = 7.2 Hz, CH, minor isomer), 7.10 (d, 1H, *J* = 8.7 Hz, CH_{Ar}, for each isomer), 7.22 (dd, 1H, *J* = 8.8, 2.0 Hz, CH_{Ar}, for each isomer), 7.28-7.34 (m, 2H, 2CH_{Ar}, for each isomer), 7.45 (d, 1H, *J* = 2.0 Hz, CH_{Ar}, major isomer), 7.47 (d, 1H, *J* = 2.0 Hz, CH_{Ar}, minor isomer), 7.73 (m, 2H, 2CH_{Ar}, for each isomer) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.9, 14.5, 21.5, 22.8, 22.9, 29.6, 30.1, 32.2, 40.7, 42.7, 49.7, 109.6, 110.1, 112.4, 122.3, 124.0, 127.5, 127.6, 129.6, 129.7, 132.3, 133.9, 136.0, 137.4, 143.8 ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{34}(^{79}Br)N_2O_2S$ $[M + H]^+$ 529.1519, found 529.1522; **IR (ATR):** 2952, 2923, 2858, 1473, 1341, 1161, 953, 814, 798, 712 cm^{-1}; **MP:** 153.9–155.2 °C.

(*E*)-6-Chloro-9-methyl-4-(oct-4-en-4-yl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7e**



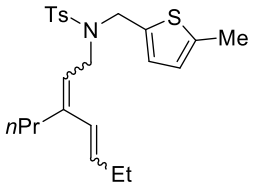
Following general procedure G, cyclopropenyl indolyl sulfonamide **5be** (60.3 mg, 0.124 mmol) was dissolved in DCE (1.24 mL) and IPrAuCl (4.2 mg, 6.76 µmol) and $AgBF_4$ (1.2 mg, 6.16 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **7e** as a yellow solid (49.1 mg, 0.101 mmol) in 90% yield.[13] The *E*-isomer was the major product and the ratio of *E*:*Z* isomers was estimated to be 7:1. **^{1}H NMR** (400 MHz, $CDCl_3$) (mixture of stereoisomers): δ = 0.74 (t, 3H, *J* = 7.3 Hz, CH_3, minor isomer), 0.85 (t, 3H, *J* = 7.4 Hz, CH_3, major isomer), 0.87-0.91 (m, 3H, CH_3, minor isomer), 0.94 (t, 3H, *J* = 7.3 Hz, CH_3, major isomer), 1.26-1.33 (m, 2H, CH_2, major isomer), 1.41-1.52 (m, 2H, CH_2, for each isomer), 1.82-1.92 (m, 1H, C$\underline{H_a}H_b$, major isomer), 1.99 (qd, 2H, *J* = 7.2, 2.0 Hz, CH_2, major isomer), 2.18-2.27 (m, 1H, C$H_a\underline{H_b}$, major isomer), 2.41 (s, 3H, CH_3, minor isomer), 2.42 (s, 3H, CH_3, major isomer), 2.88 (dd, 1H, *J* = 12.0, 9.2 Hz, C$\underline{H_a}H_b$, minor isomer), 3.07 (dd, 1H, *J* = 11.5, 6.5 Hz, C$\underline{H_a}H_b$, major isomer), 3.54-3.63 (m, 5H, CH_3, CH, C$H_a\underline{H_b}$, major isomer, 3H, CH_3, minor isomer), 3.70 (dd, 1H, *J* = 12.0, 5.6 Hz, C$H_a\underline{H_b}$, minor isomer), 4.08-4.14 (m, 2H, CH, C$\underline{H_a}H_b$, minor isomer), 4.23 (dd, 1H, *J* = 14.6, 1.5 Hz, C$\underline{H_a}H_b$, major isomer), 4.37 (d, 1H, *J* = 14.6 Hz, C$H_a\underline{H_b}$, major isomer), 4.64 (d, 1H, *J* = 14.8 Hz, C$H_a\underline{H_b}$, minor isomer), 5.07 (t, 1H, *J* = 7.3 Hz, CH, major isomer), 5.46 (t, 1H, *J* = 7.2 Hz, CH, minor isomer),7.09 (dd, 1H, J = 8.7, 2.0 Hz, CH_{Ar}, for each isomer), 7.15 (d, 1H, *J* = 8.6 Hz, CH_{Ar}, for each isomer), 7.29 (d, 1H, *J* = 1.7 Hz, CH_{Ar}, for each isomer), 7.32 (d, 2H, *J* = 8.0 Hz, 2CH_{Ar}, for each isomer), 7.71-7.75 (m, 2H, 2CH_{Ar}, for each isomer) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) (mixture of isomers, minor stereoisomer indicated by asterisk): δ = 13.9, 13.97*, 14.03*, 14.5, 21.5, 22.8, 22.9, 29.6, 29.8*, 30.1, 32.2, 40.6, 42.6*, 42.7, 48.2*, 49.7, 109.61, 109.65, 119.2, 121.5, 124.8, 127.5*, 126.9, 127.6, 129.5, 129.7, 132.5, 133.9, 135.7, 137.4, 143.7 ppm; **HRMS (ESI):** *m/z* calcd for $C_{27}H_{33}(^{35}Cl)N_2NaO_2S$ $[M + Na]^+$ 507.1843, found 507.1846; **IR (ATR):** 2951, 2923, 2859, 1475, 1341, 1305, 1161, 1139, 954, 814, 799, 714 cm^{-1}; **MP:** 152.5–153.9 °C.

(*E*)-9-Benzyl-6-bromo-4-(oct-4-en-4-yl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7f**



Following general procedure G, cyclopropenyl indolyl sulfonamide **5bf** (44.2 mg, 73.0 µmol) was dissolved in DCE (0.73 mL) and IPrAuCl (2.5 mg, 4.03 µmol) and $AgBF_4$ (0.7 mg, 3.60 µmol) were added at 0 °C and the reaction was complete after 1 h. Purification gave the title compound **7f** as a white solid (38.5 mg, 63.6 µmol) in 87% yield. The *E*-isomer was the major product and the ratio of *E*:*Z* isomers was estimated to be 6:1. **^{1}H NMR** (500 MHz, $CDCl_3$) (mixture of stereoisomers): δ = 0.77 (t, 3H, *J* = 7.3 Hz, CH_3, minor isomer), 0.87 (t, 3H, *J* = 7.4 Hz, CH_3, major isomer), 0.95 (t, 3H, *J* = 7.3 Hz, CH_3, major isomer), 1.29-1.35 (m, 2H, CH_2, for each isomer), 1.39-1.53 (m, 2H, CH_2, for each isomer), 1.84-1.92 (m, 1H, C$\underline{H_a}H_b$, major isomer), 2.00 (qd, 2H, *J* = 7.2, 3.5 Hz, CH_2, major isomer), 2.19-2.27 (m, 1H, C$H_a\underline{H_b}$, major isomer), 2.39 (s, 3H, CH_3, minor isomer), 2.40 (s, 3H, CH_3, major isomer), 2.91 (dd, 1H, *J* = 12.4, 9.2 Hz, C$\underline{H_a}H_b$, minor isomer), 3.09 (dd, 1H, *J* = 12.0, 6.7 Hz, C$\underline{H_a}H_b$, major isomer), 3.56 (dd, 1H, *J* = 12.0, 4.9 Hz, C$H_a\underline{H_b}$, major isomer), 3.62 (t, 1H, *J* = 5.8 Hz, C*H*, major isomer), 3.72 (dd, 1H, *J* = 12.4, 5.4 Hz, C$H_a\underline{H_b}$, minor isomer), 4.03 (dd, 1H, *J* = 15.2, 2.0 Hz, C$\underline{H_a}H_b$, minor isomer), 4.06-4.12 (m, 1H, C*H*, minor isomer), 4.15 (dd, 1H, *J* = 14.8, 1.6 Hz, C$\underline{H_a}H_b$, major isomer), 4.26 (d, 1H, *J* = 14.8 Hz, C$H_a\underline{H_b}$, major isomer), 4.55 (d, 1H, *J* = 15.2 Hz, C$H_a\underline{H_b}$, minor isomer), 5.09 (t, 1H, *J* = 7.3 Hz, C*H*, major isomer), 5.19 (s, 2H, CH_2, major isomer), 5.20 (s, 2H, CH_2, minor isomer), 5.46 (t, 1H, *J* = 7.3 Hz, C*H*, minor isomer), 6.89-6.94 (m, 2H, 2CH_{Ar}, for each isomer), 7.06 (d, 1H, *J* = 8.7 Hz, CH_{Ar}, for each isomer), 7.16-7.19 (m, 1H, CH_{Ar}, for each isomer), 7.24-7.29 (m, overlapped with $CHCl_3$, 5H, 5CH_{Ar}, for each isomer), 7.49 (d, 1H, *J* = 2.0 Hz, CH_{Ar}, major isomer), 7.50 (d, 1H, *J* = 2.0 Hz, CH_{Ar}, minor isomer), 7.60 (d, 2H, *J* = 8.6 Hz, 2C$H_{Ar,}$ minor isomer), 7.62 (m, 2H, *J* = 8.3 Hz, 2CH_{Ar}, major isomer) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (mixture of isomers, minor stereoisomer indicated by asterisk): δ = 13.9, 14.0*, 14.1*, 14.6, 21.5, 21.6*, 22.8, 22.9, 23.2*, 29.8*, 30.0, 32.1, 40.4, 42.5*, 42.6, 46.78*, 46.81, 48.0*, 49.5, 110.2, 110.7, 112.5, 112.7*, 121.8*, 122.4, 124.3, 124.4*, 125.88*, 125.93, 127.3*, 127.5, 127.7, 127.8, 128.9, 129.5, 129.66, 129.69*, 132.3, 133.7, 134.1*, 135.5*, 135.7, 136.5, 137.3, 143.67, 143.73* ppm; **HRMS (ESI):** *m/z* calcd for $C_{33}H_{38}(^{79}Br)N_2O_2S$ $[M + H]^+$ 605.1832, found 605.1830; **IR (ATR):** 2954, 2928, 2868, 1598, 1453, 1340, 1158, 1094, 937, 810, 783 cm^{-1}; **MP:** 147.7–149.8 °C.

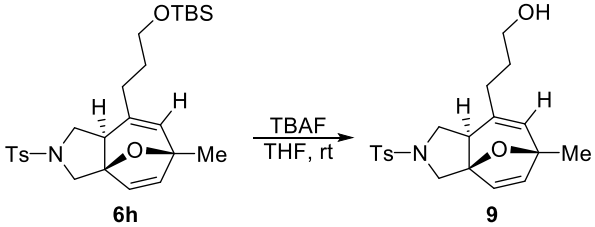
4-Methyl-*N*-((5-methylthiophen-2-yl)methyl)-*N*-((2*Z*,4*E*)-3-propylhepta-2,4-dien-1-yl) benzenesulfonamide **8**



Following general procedure M, cyclopropenyl thiophenyl sulfonamide **5c** (206.7 mg, 0.495 mmol) was dissolved in DCE (5.02 mL) and IPrAuCl (15.2 mg, 24.5 µmol) and $AgBF_4$ (4.8 mg, 24.7 µmol) were added at 0 °C for 1 h and then was warmed to rt. After 24 h, the reaction was complete and purification gave the title compound **8** as a yellow oil (175.9 mg, 0.421 mmol) in 85% yield with a purity of 93%.[13] The 2*Z*,4*E* -diene was identified as the major isomer; however, two other diene isomers could also be seen which could not be conclusively identified. The ratio of diene isomers was estimated to be 16:3:1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.84 (t, 3H, *J*= 7.4 Hz, CH_3), 0.98 (t, 3H, *J* = 7.4 Hz, CH_3), 1.29-1.39 (m, 2H, CH_2), 2.03-2.10 (m, 4H, 2CH_2), 2.41 (d, 3H, *J* = 1.2 Hz, CH_3), 2.42 (s, 3H, CH_3), 3.95 (d, 2H, *J* = 7.2 Hz, CH_2), 4.43 (s, 2H, CH_2), 4.98 (t, 1H, *J* = 7.2 Hz, C*H*), 5.75 (dt, 1H, *J* = 15.6, 6.4 Hz, C*H*), 6.03 (dq, 1H, *J* = 15.8, 1.4 Hz, C*H*), 6.50-6.52 (m, 1H, CH_{Het}), 6.63 (d, 1H, *J* = 3.4 Hz, CH_{Het}), 7.26-7.29 (m, overlapped with $CHCl_3$, 2H, 2CH_{Ar}), 7.68-7.72 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 13.5, 13.9, 15.3, 21.4, 21.6, 26.2, 36.1, 43.1, 44.8, 120.3, 124.2, 124.4, 127.2, 127.3, 129.5, 134.0, 136.6, 137.7, 140.5, 140.9, 143.0 ppm; **HRMS (ESI):** *m/z* calcd for $C_{23}H_{31}NNaO_2S_2$ $[M + Na]^+$ 440.1688, found 440.1686; **IR (ATR):** 2958, 2927, 2870, 1598, 1493, 1453, 1339, 1155, 1091, 906, 799 cm^{-1}.

11. Chemical Transformations on Heterocycles

3-(6-Methyl-2-tosyl-2,3,6,8a-tetrahydro-1*H*-3a,6-epoxycyclohepta[*c*]pyrrol-8-yl)propan-1-ol **9**



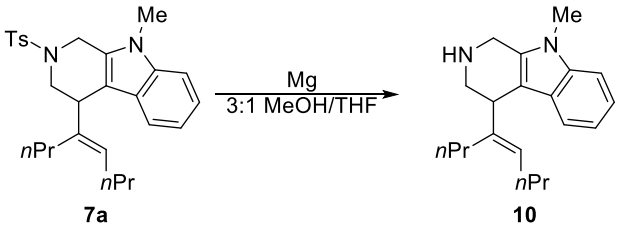
6h **9**

In accordance with the literature procedure,[14] heterocycle **6h** (21.5 mg, 43.9 µmol) was dissolved in dry THF (1.10 mL) under a nitrogen atmosphere and to this was added tetrabutylammonium fluoride (TBAF, 1 M solution in THF, 0.10 mL, 0.100 mmol) with stirring. The reaction was left at

[14] Marcé, P.; Díaz, Y.; Matheu, M. I.; Castillón, S. *Org. Lett.* **2008**, *10*, 4735.

rt for 1.5 h until TLC analysis indicated the reaction had gone to completion. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography (50:50 EtOAc:hex) to obtained the title compound **9** as a colourless oil (solid in fridge) (14.4 mg, 38.4 μmol) in 87% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) = δ 1.32 (s, 3H, CH_3), 1.55-1.64 (m, 2H, CH_2), 1.88-2.01 (m, 2H, CH_2), 2.04-2.09 (m, 1H, CH), 2.43 (s, 3H, CH_3), 2.97 (dd, 1H, J = 11.1, 9.0 Hz, C$\underline{H_a}H_b$), 3.39 (d, 1H, J = 11.8 Hz, C$\underline{H_a}H_b$), 3.58 (td, 2H, J = 6.4, 1.3 Hz, CH_2), 3.83 (d, 1H, J = 11.8 Hz, C$H_a\underline{H_b}$), 3.94 (dd, 1H, J = 9.0, 7.9 Hz, C$H_a\underline{H_b}$), 5.70 (q, 1H, J = 1.5 Hz, CH), 5.76 (d, 1H, J = 5.6 Hz, CH), 6.23 (d, 1H, J = 5.6 Hz, CH), 7.31 (d, 2H, J = 7.7 Hz, 2CH_{Ar}), 7.71-7.74 (m, 2H, 2CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 21.50, 21.52, 29.7, 31.4, 43.3, 51.1, 54.4, 62.2, 82.3, 90.5, 127.3, 127.5, 129.4, 129.7, 134.1, 135.1, 142.7, 143.5 ppm; **HRMS (ESI):** *m/z* calcd for $C_{20}H_{25}NNaO_4S$ $[M + Na]^+$ 398.1397, found 398.1396; **IR (ATR):** 3361 (br), 2929, 2860, 1334, 1161, 1111, 1026, 808 cm^{-1}.

(*E*)-9-Methyl-4-(oct-4-en-4-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **10**

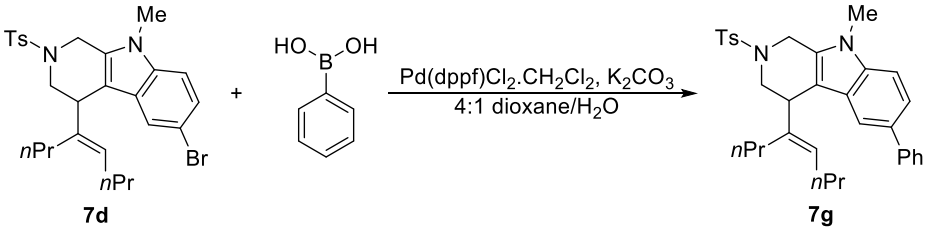


7a **10**

To an oven dried round bottom flask was added tetrahydro-β-carboline **7a** (20.0 mg, 44.4 μmol) and powdered Mg solid (54.4 mg, 2.24 mmol) and the reaction was sealed with a new rubber septum. The flask was evacuated under vacuum and was refilled with argon. To the reaction flask was added dry THF (0.36 mL) and the reaction was swirled until the starting material appeared to be dissolved. Dry MeOH (1.10 mL) was subsequently added and the reaction was shaken vigouously before been sonicated for 45 mins (sonication was paused roughly every 2 mins for the first 10 mins to shake the reaction flask). Once finished, the reaction was diluted with EtOAc and filtered over celite and the crude residue was concentrated under reduced pressure. Flash column chromatography (95:4:1 DCM:MeOH:Et_3N) gave the title compound **10** as a yellow solid (10.0 mg, 33.7 μmol) in 76% yield with minor impurities. A second column was performed first using 100% EtOAc to remove impurities and then 10:90 MeOH:DCM to obtain title compound **10** (7.2 mg, 24.3 μmol) in 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.80 (t, 3H, J = 7.4 Hz, CH_3), 1.00 (t, 3H, J = 7.3 Hz, CH_3), 1.19-1.28 (m, 2H, CH_2), 1.48-1.57 (m, 1H, C$\underline{H_a}H_b$), 1.58-1.69 (m, 1H, C$H_a\underline{H_b}$), 1.85-1.94 (m, 1H, C$\underline{H_a}H_b$), 1.93-2.02 (m, 2H, CH_2), 2.24-2.34 (m, 1H C$H_a\underline{H_b}$), 3.07 (dd, 1H, J = 13.0, 3.7 Hz, C$\underline{H_a}H_b$), 3.19 (dd, 1H, J = 13.0, 4.9 Hz, C$H_a\underline{H_b}$), 3.61 (s, 3H, CH_3), 3.64-3.69 (m, 1H, CH), 4.14 (s, 2H, CH_2), 4.99 (t, 1H, J = 7.2 Hz, CH), 7.03 (ddd, 1H, J = 7.9, 7.0, 1.0 Hz, CH_{Ar}), 7.17 (ddd, 1H, J =

8.2, 7.0, 1.2 Hz, CH_{Ar}), 7.25-7.29 (m, overlapped with $CHCl_3$, 2H, CH_{Ar}), 7.35 (dt, 1H, *J* = 7.9, 1.0 Hz, CH_{Ar}) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 13.9, 14.5, 22.7, 23.0, 29.4, 30.0, 32.3, 39.1, 41.8, 48.0, 108.6, 109.5, 119.0, 119.1, 121.2, 126.4, 129.0, 132.9, 137.1, 138.9 ppm; **HRMS (ESI):** *m/z* calcd for $C_{20}H_{29}N_2$ $[M + H]^+$ 297.2325, found 297.2332; **IR (ATR):** 3381, 2955, 2928, 2869, 1467, 1013 cm^{-1} **MP:** decomp > 150 °C.

9-Methyl-4-(oct-4-en-4-yl)-6-phenyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **7g**

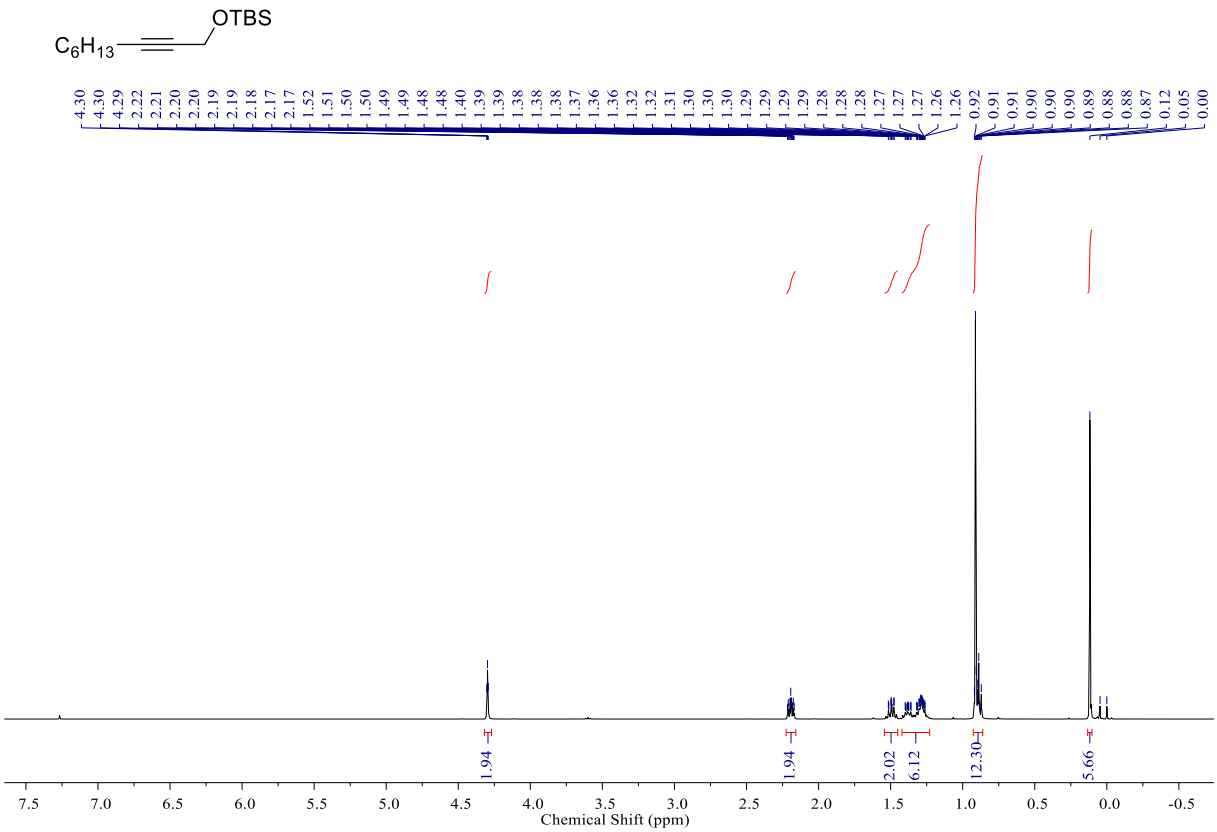


To a Schlenk flask was added heterocycle **7d** (20.5 mg, 38.7 μmol), K_2CO_3 (10.8 mg, 78.1 μmol) and phenylboronic acid (7.9 mg, 64.8 μmol). A mixture of dioxane:H_2O (4:1, 0.5 mL) was added and the mixture was thrice subjected to a freeze-pump-thaw process before the reaction was put under a nitrogen atmosphere. Once at rt, Pd(dppf)Cl_2.CH_2Cl_2 (3.4 mg, 4.16 μmol) was added and the reaction was heated to 85-90 °C for 21 h. Following a short column (30:70 Et_2O:hex) and analysis by ^{1}H NMR, title compound **7g** (17.8 mg) was obtained but ~5% starting material remained. The residue was resubjected to the reaction conditions using K_2CO_3 (1.6 mg, 11.6 μmol), phenylboronic acid (1.4 mg, 11.5 μmol), Pd(dppf)Cl_2·CH_2Cl_2 (0.3 mg, 0.367 μmol) and a mixture of dioxane:H_2O (4:1, 0.5 mL) and was heated for 6 h at 90-95 °C. Flash column chromatography (30:70 Et_2O:hex) gave the title compound **7g** as a pale yellow solid (16.4 mg, 31.1 μmol) in 80% yield (5.7:1 *E*:*Z* ratio). **^{1}H NMR** (500 MHz, $CDCl_3$) (mixture of double bond isomers): δ = 0.73 (t, 3H, *J* = 7.3 Hz, CH_3, minor isomer), 0.83 (t, 3H, *J* = 7.4 Hz, CH_3, major isomer), 0.94 (t, 3H, *J* = 7.3 Hz, CH_3, major isomer), 1.26-1.33 (m, 2H, CH_2, for each isomer), 1.44-1.54 (m, 2H, CH_2, for each isomer), 1.86-1.94 (m, 1H, C$\underline{H}_a H_b$, major isomer), 2.00 (qd, 2H, *J* = 7.2, 2.5 Hz, CH_2, major isomer), 2.21-2.29 (m, 1H, C$H_a\underline{H}_b$, major isomer), 2.40 (s, 3H, CH_3, minor isomer), 2.42 (s, 3H, CH_3, major isomer), 2.94 (dd, 1H, *J* = 12.1, 9.1 Hz, C$\underline{H}_a H_b$, minor isomer), 3.14 (dd, 1H, *J* = 11.9, 6.7 Hz, C$\underline{H}_a H_b$, major isomer), 3.57 (dd, 1H, *J* = 12.0, 5.0 Hz, C$H_a\underline{H}_b$, major isomer), 3.63 (s, 3H, CH_3, major isomer), 3.65 (s, 3H, CH_3, minor isomer), 3.70 (t, *J* = 5.8 Hz, 1H, C*H*, major isomer), 3.71-3.74 (m, 1H, C$H_a\underline{H}_b$, minor isomer), 4.15 (dd, 1H, *J* = 14.7, 2.1 Hz, C$\underline{H}_a H_b$, minor isomer), 4.18-4.24 (m, 1H, C*H*, minor isomer), 4.28 (dd, 1H, *J* = 14.5, 1.6 Hz, C$\underline{H}_a H_b$, major isomer), 4.38 (d, 1H, *J* = 14.4 Hz, C$H_a\underline{H}_b$, major isomer), 4.65 (d, 1H, *J* = 14.9 Hz, C$H_a\underline{H}_b$, minor isomer), 5.17 (t, 6H, *J* = 7.3 Hz, C*H*, major isomer), 5.46 (t, 1H, *J* = 7.3 Hz, C*H*, minor isomer), 7.26-7.34 (m, 4H, 4CH_{Ar}, for each isomer),

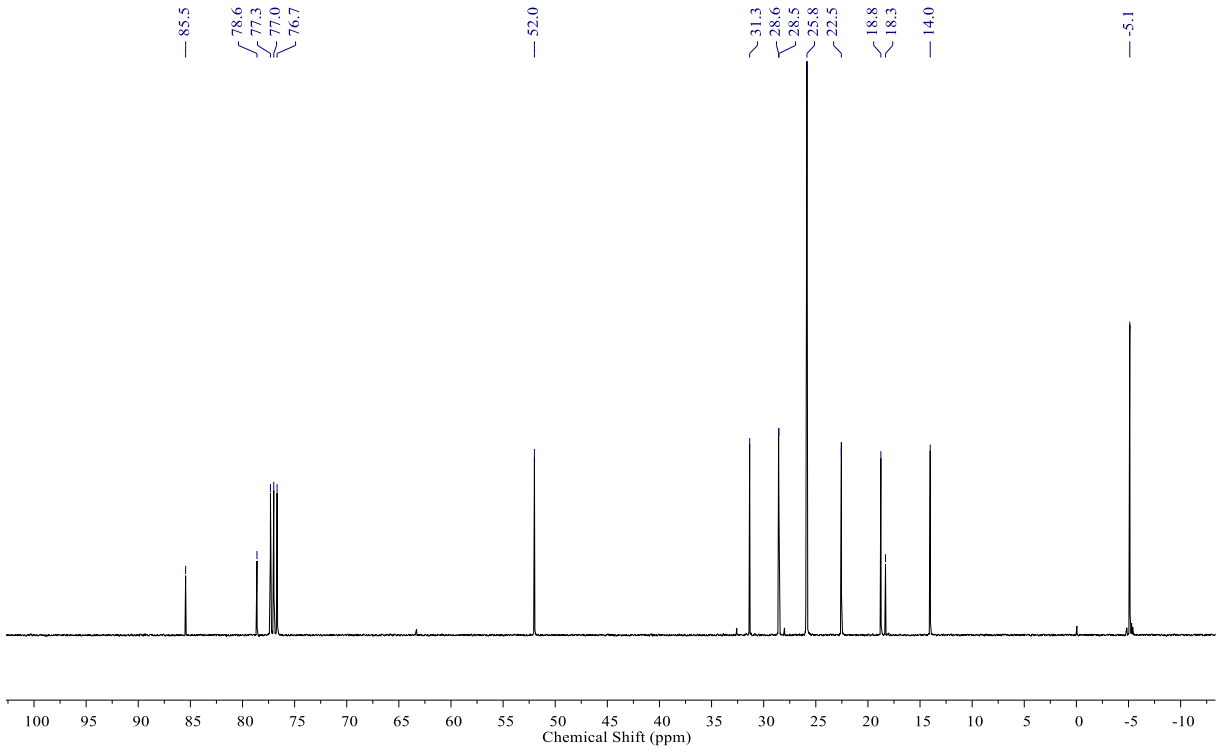
7.38-7.44 (m, 3H, 3CH_{Ar}, for each isomer), 7.54-7.59 (m, 3H, 3CH_{Ar}, major isomer, 2H, 2CH_{Ar}, minor isomer), 7.60 (d, 1H, J = 1.4 Hz, CH_{Ar}, minor isomer), 7.72-7.77 (m, 2H, 2CH_{Ar}, for each isomer) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) (mixture of diastereoisomer, minor isomer indicated by asterisk): δ = 13.9, 14.0*, 14.1*, 14.5, 21.5, 22.8, 23.0, 23.2*, 29.59, 29.62*, 30.1, 32.1, 35.4*, 40.8, 42.6*, 42.8, 48.3*, 49.7, 108.9, 110.2, 117.6*, 118.2, 121.0, 121.1*, 126.2, 126.5, 126.7*, 127.2, 127.5*, 127.6, 128.59, 128.62*, 129.4, 129.71, 129.73*, 131.7, 132.5, 132.6*, 134.0, 134.1*, 136.7*, 136.9, 137.7*, 137.8, 142.5, 143.67, 143.74* ppm; **HRMS (ESI):** *m/z* calcd for $C_{33}H_{39}N_2O_2S$ $[M + H]^+$ 527.2727, found 527.2738; **IR (ATR):** 2952, 2925, 2866, 1599, 1473, 1455, 1341, 1314, 1157, 1095, 938, 807, 752 cm^{-1}; **MP:** 142.0–143.7 °C.

12. NMR Spectra

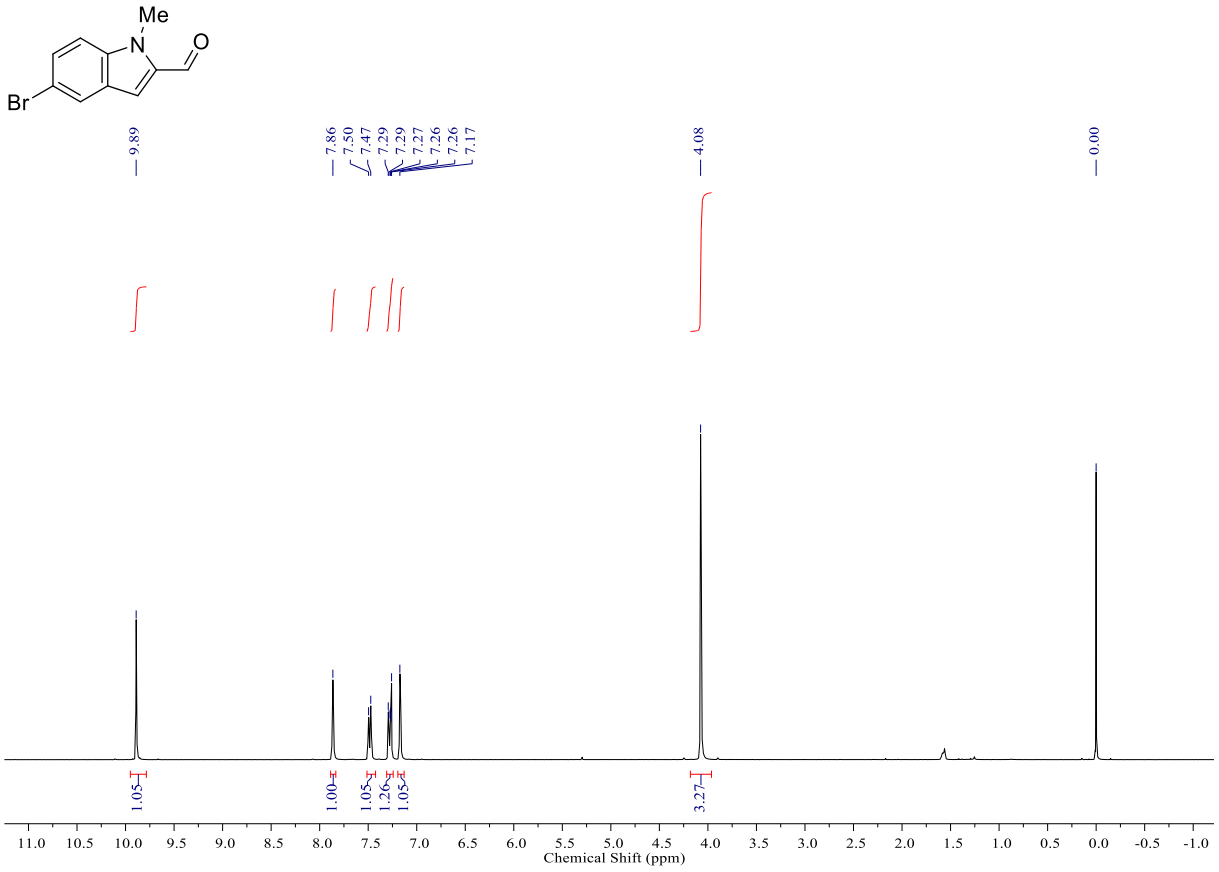
^{1}H NMR S3



^{13}C NMR S3



^{1}H NMR S8



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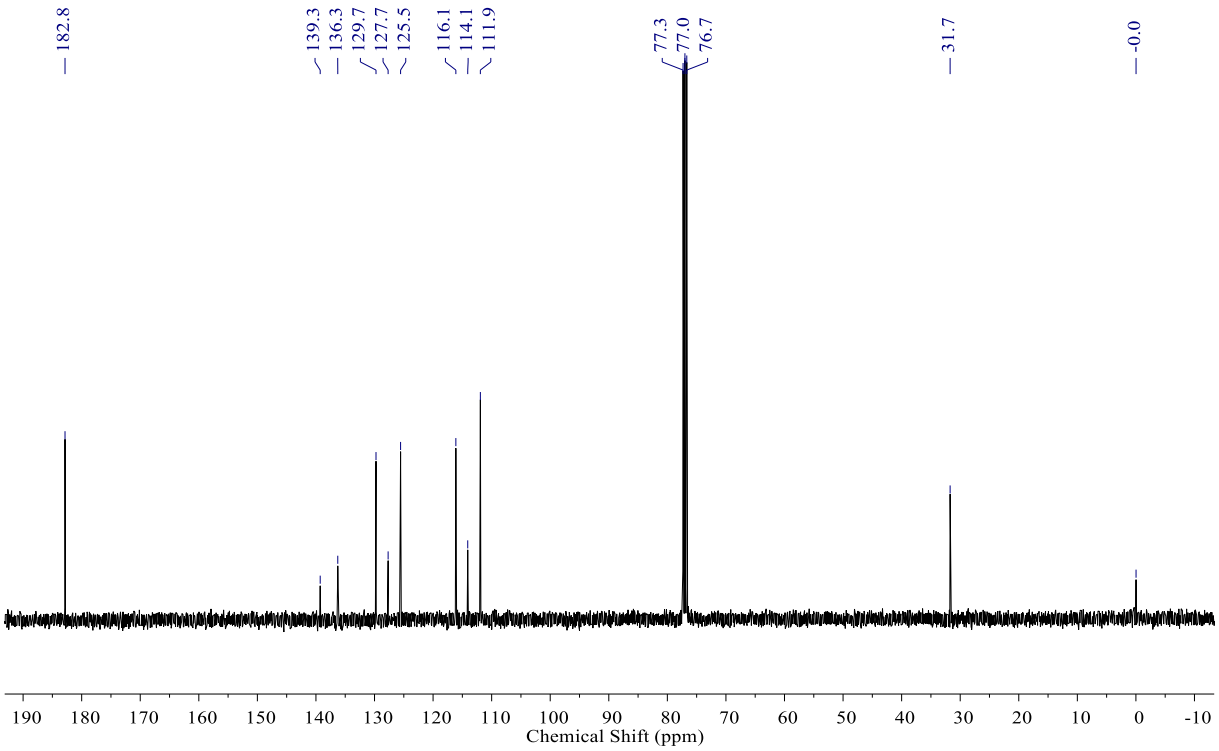

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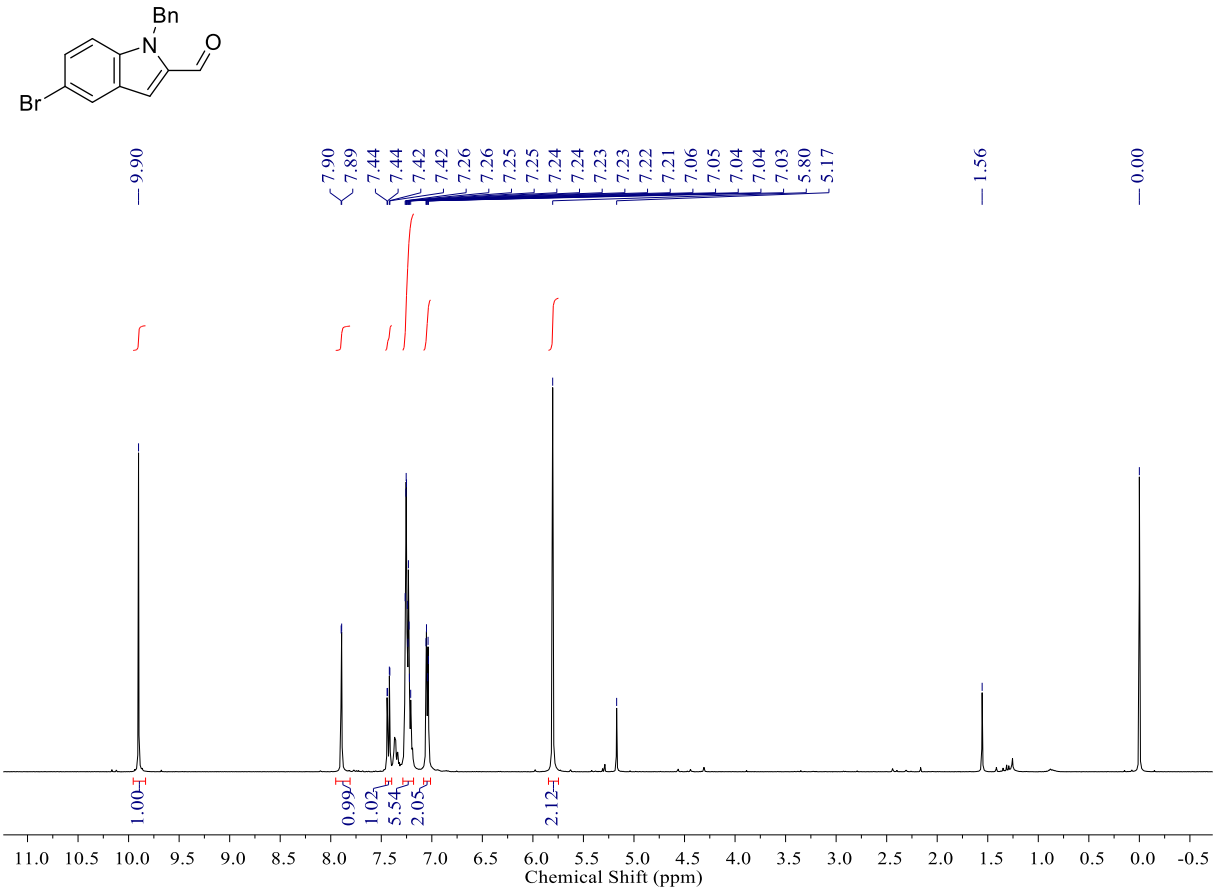
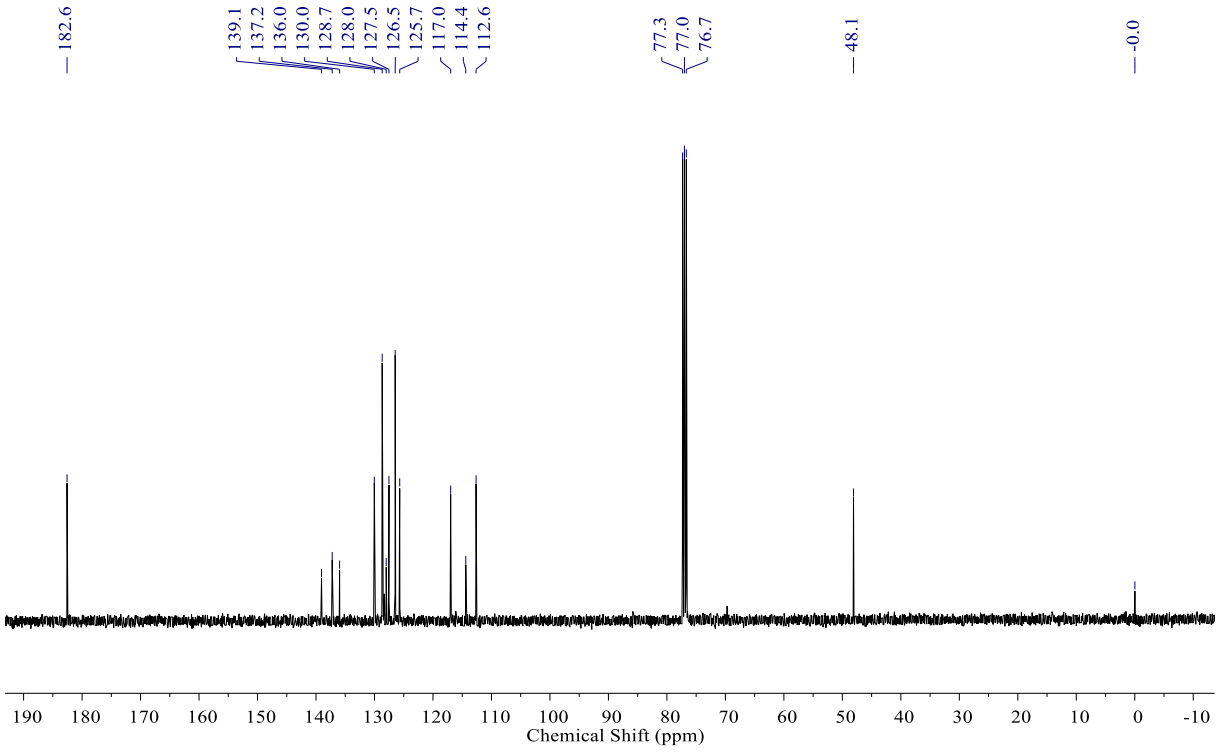
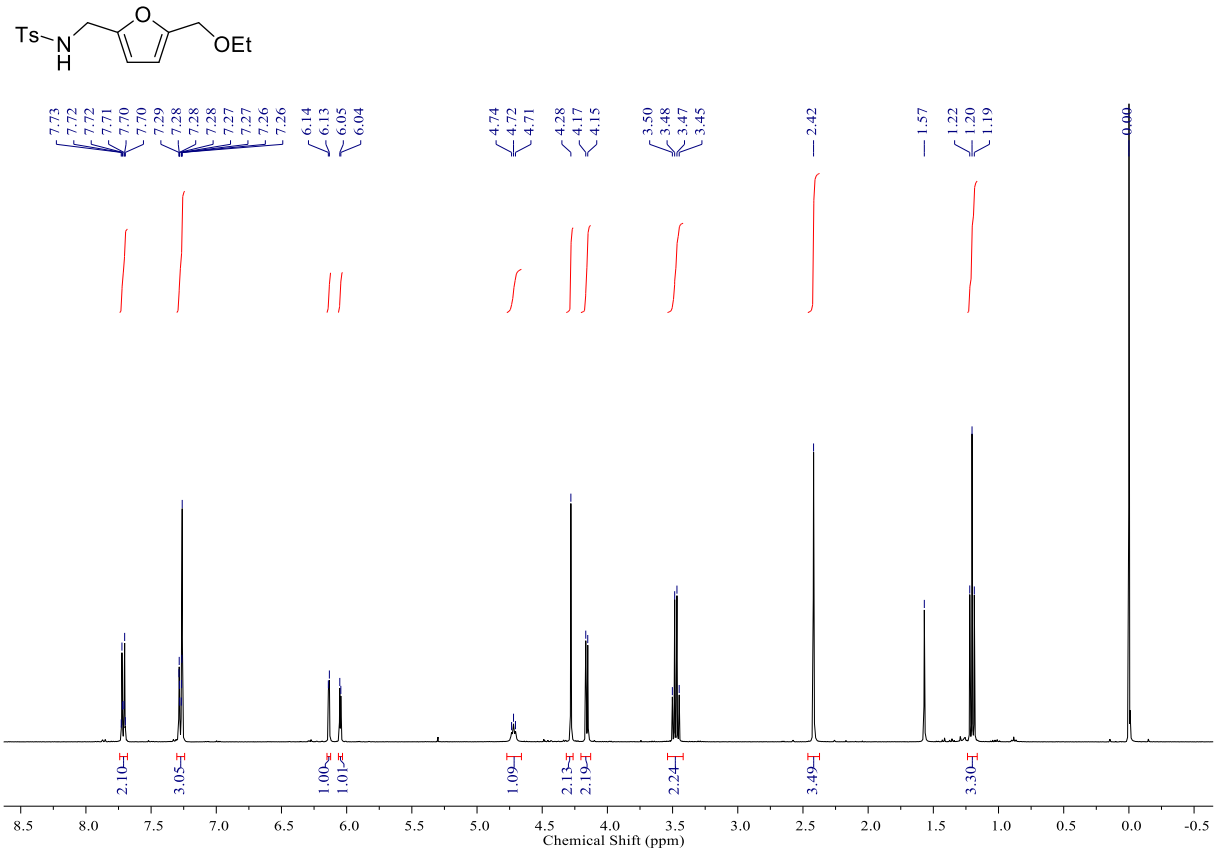


^{13}C NMR S12



^{1}H NMR 11c



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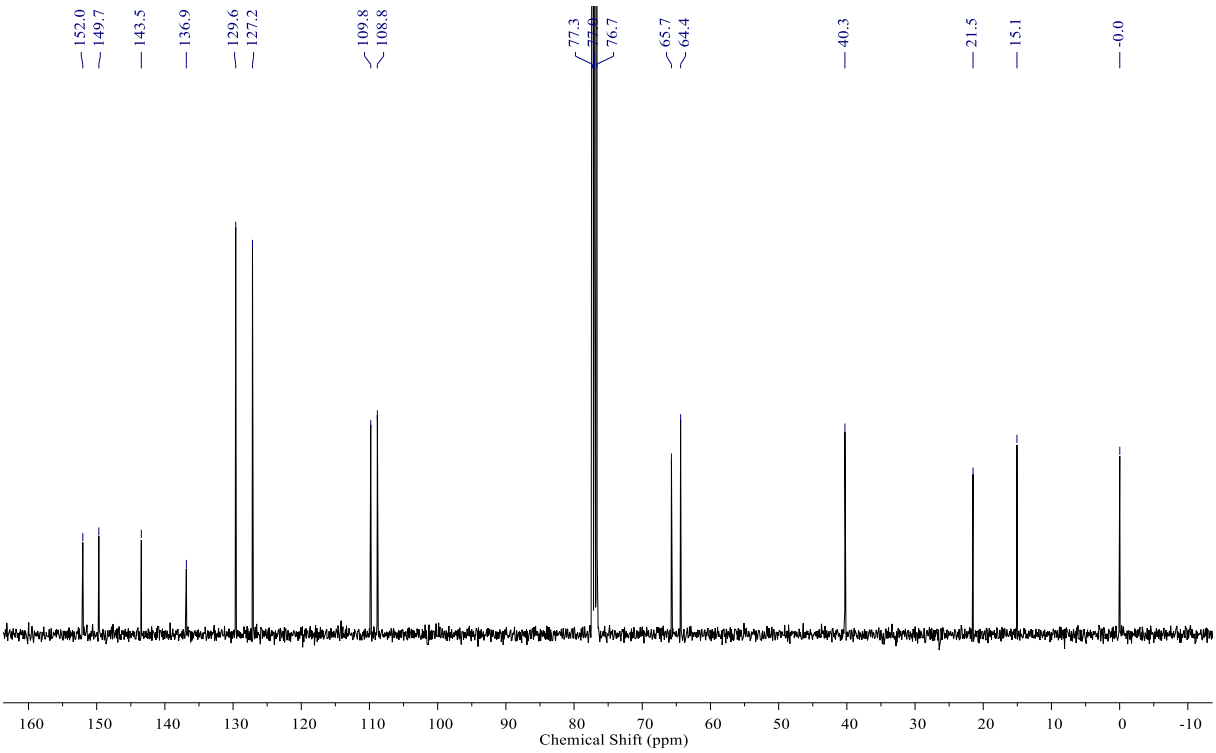
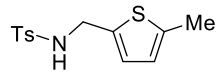
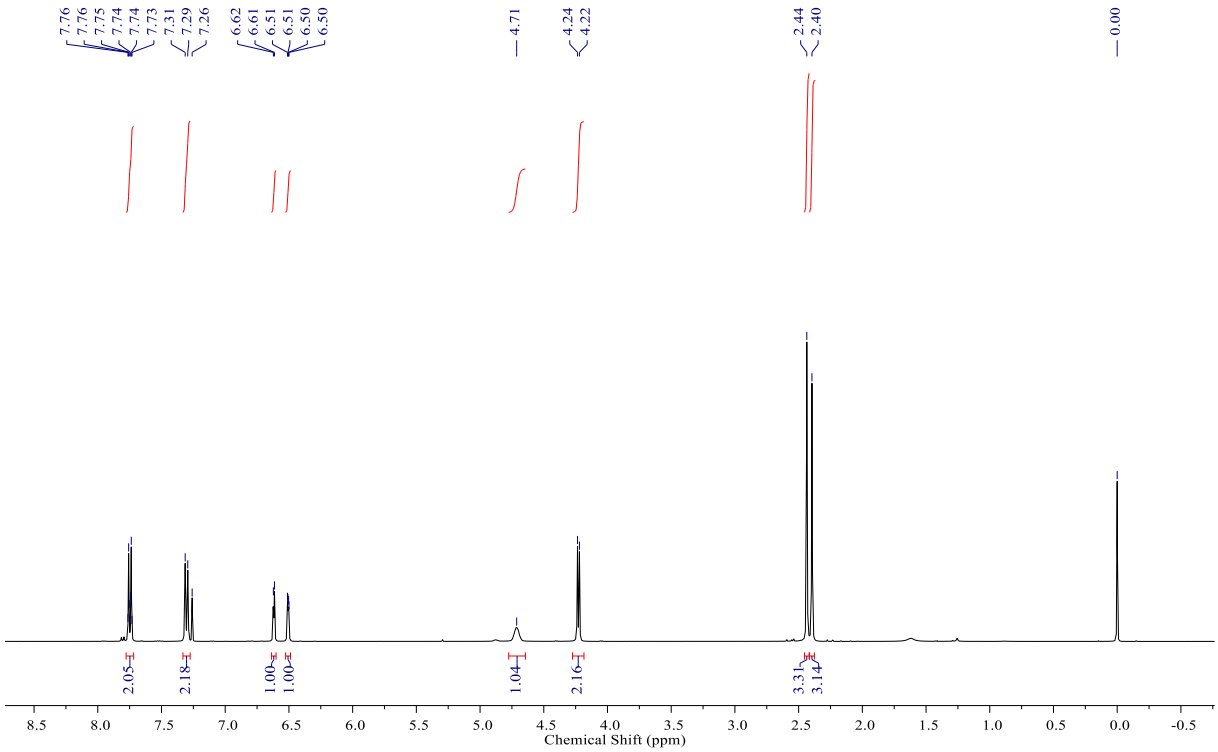


^{1}H NMR 11e





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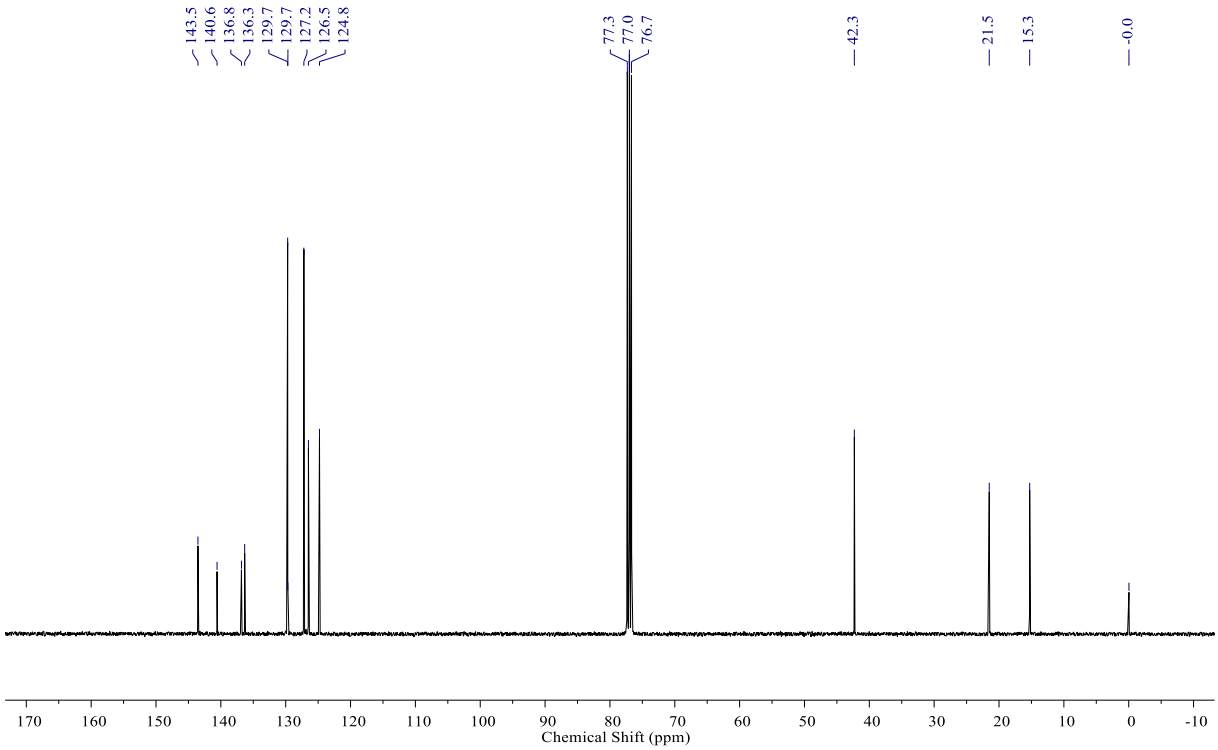
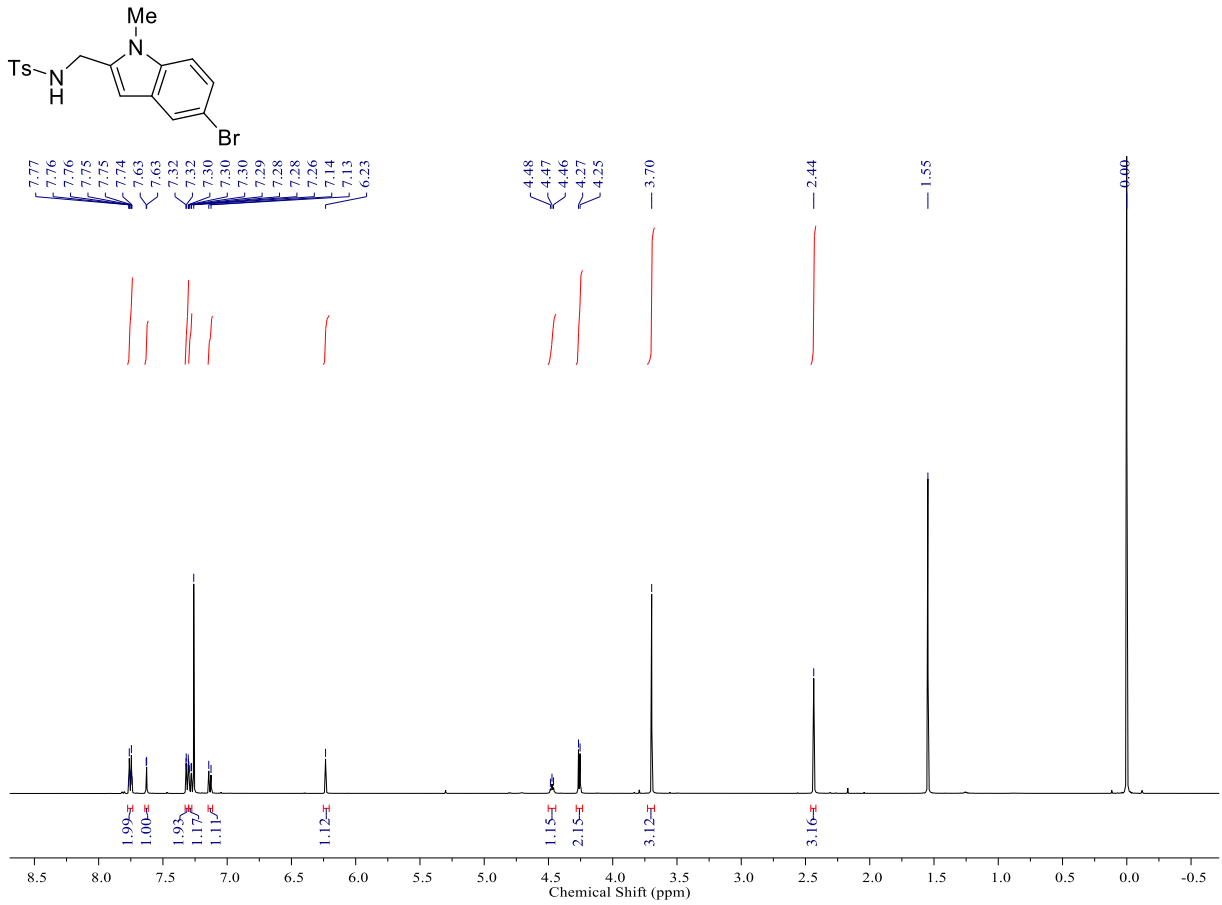
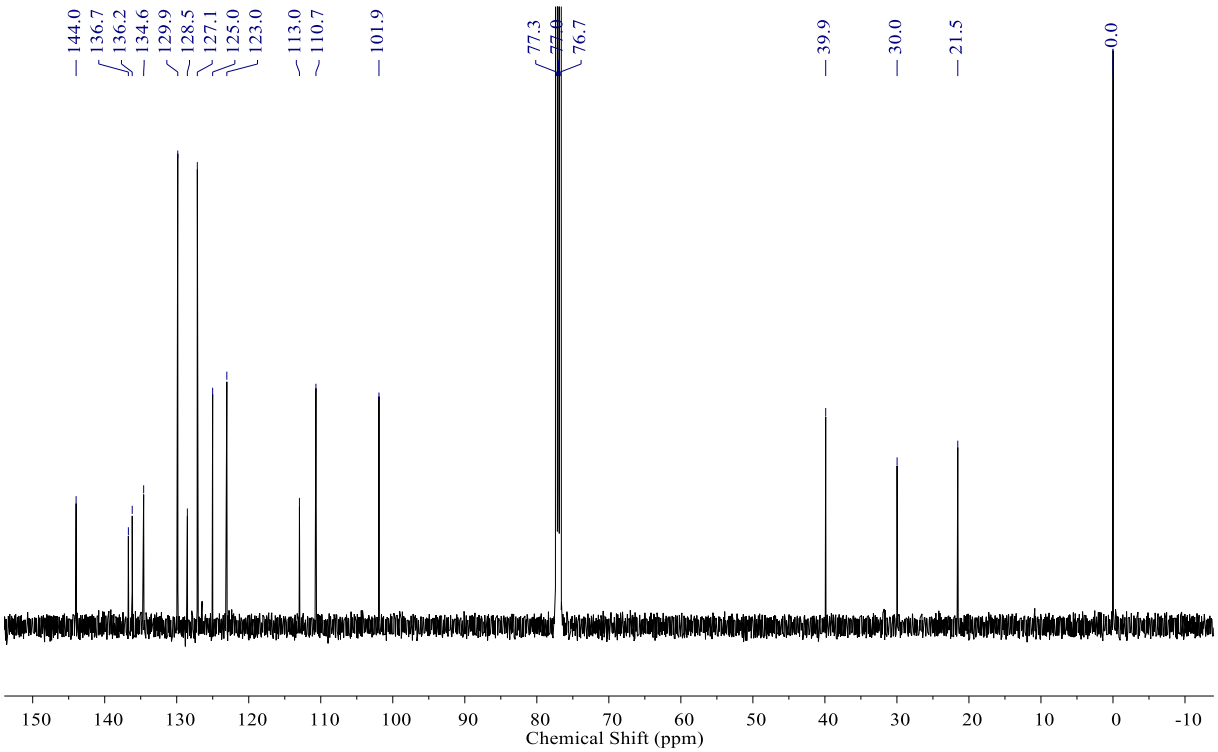


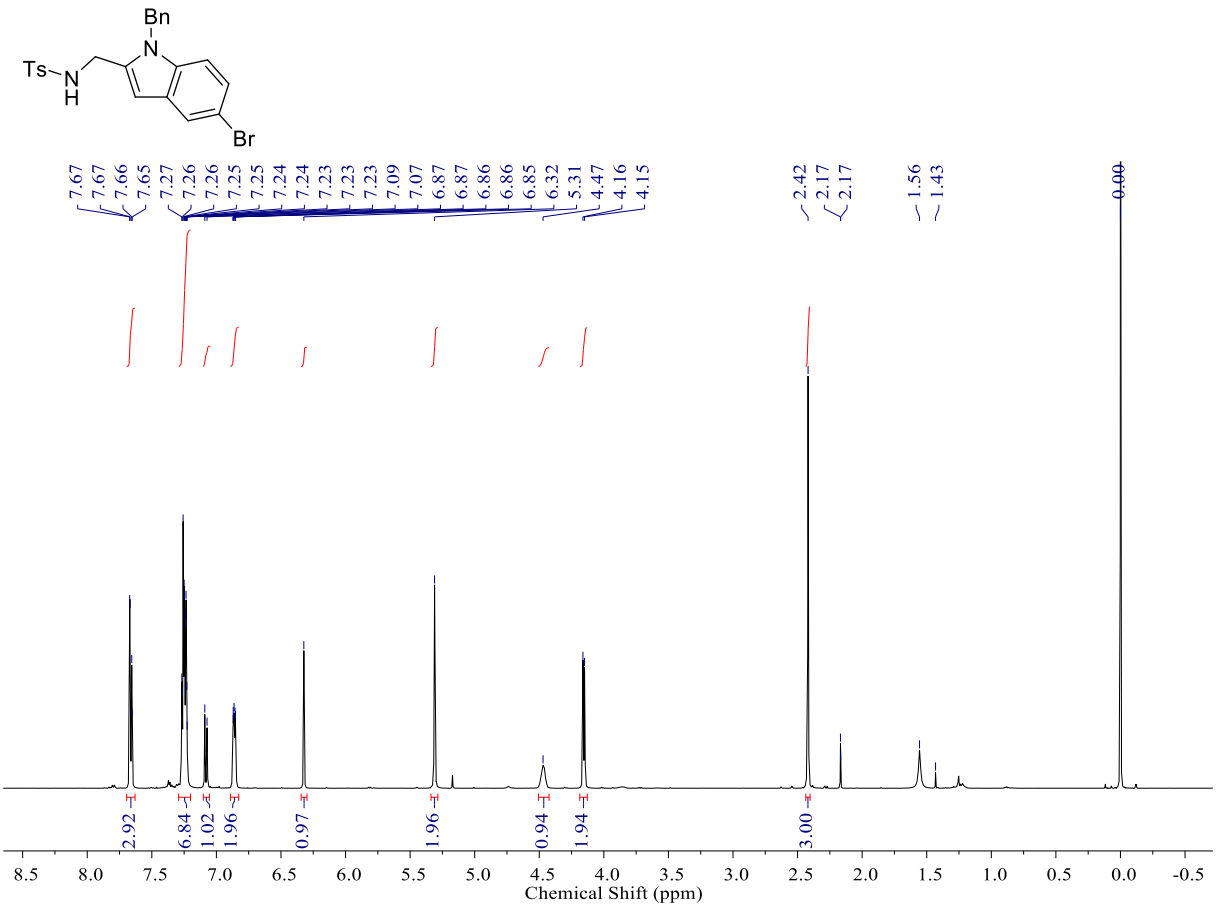
^{1}H NMR 11h



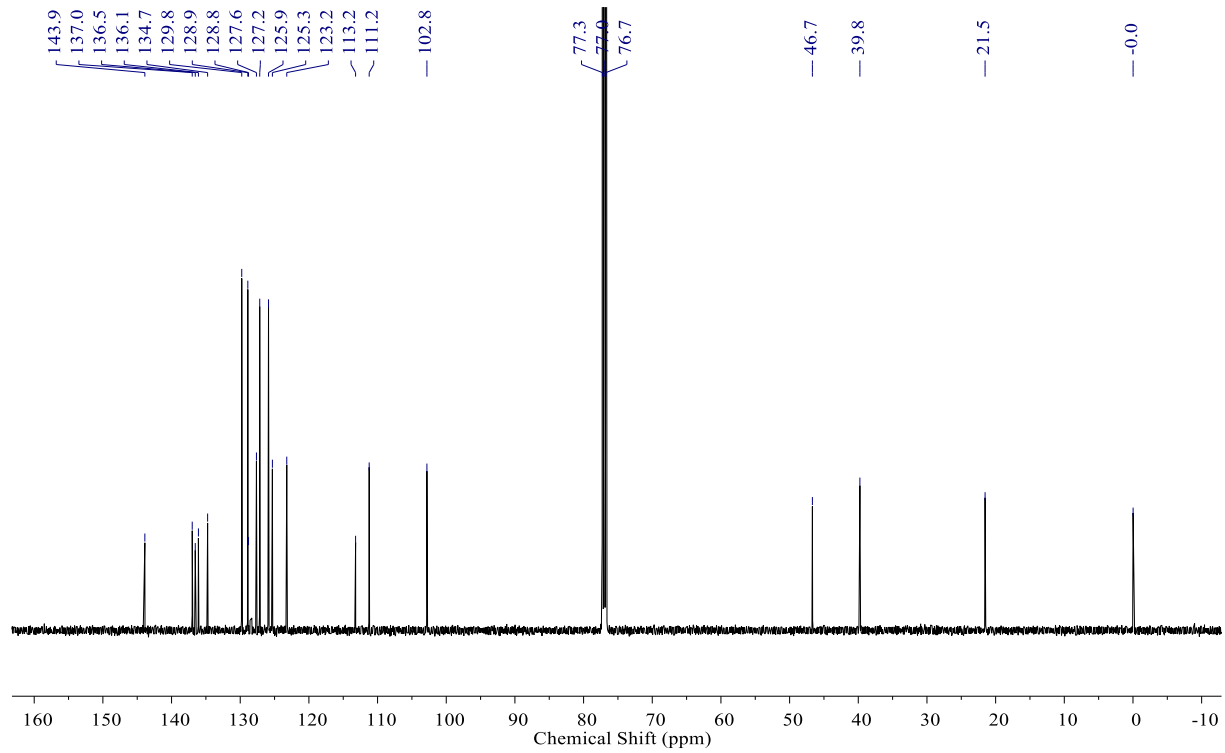
^{13}C NMR 11h



^{1}H NMR 11j



^{13}C NMR 11j



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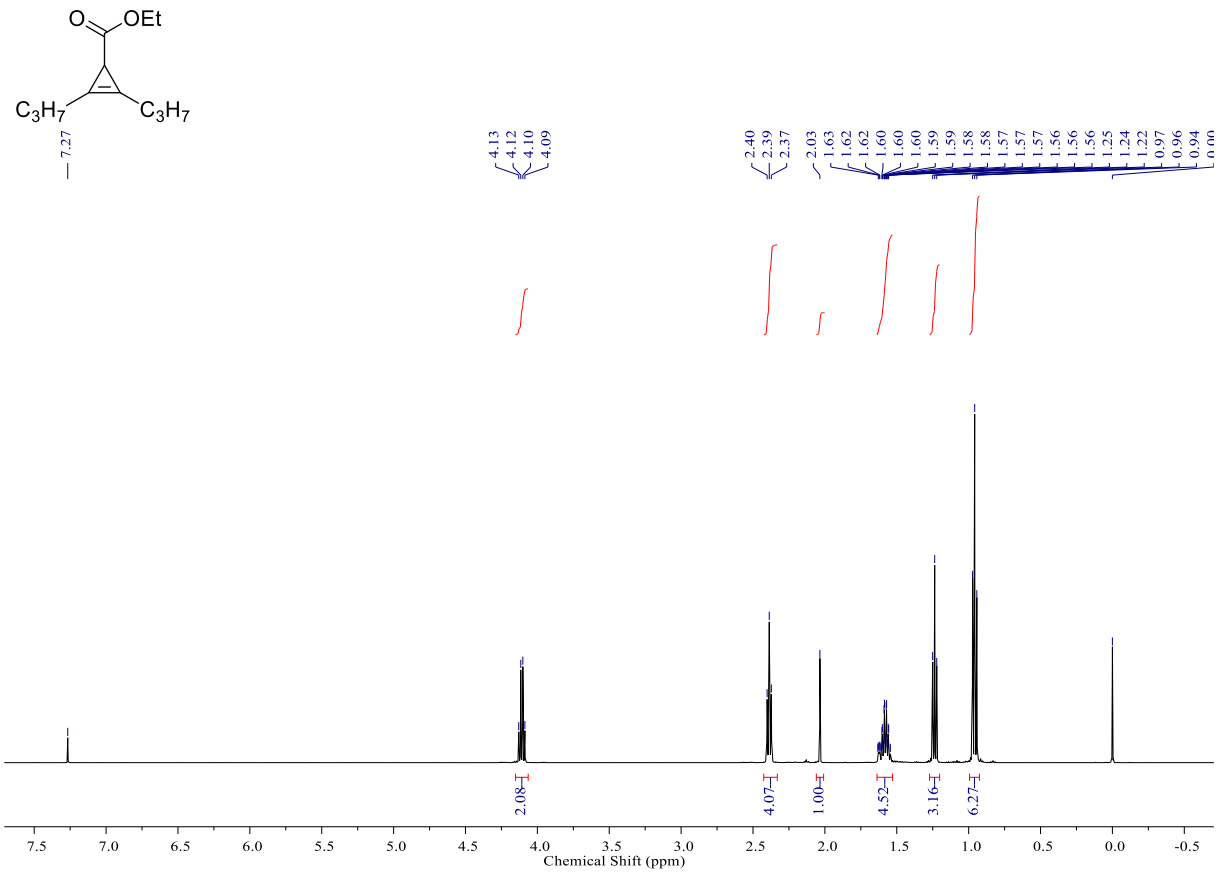

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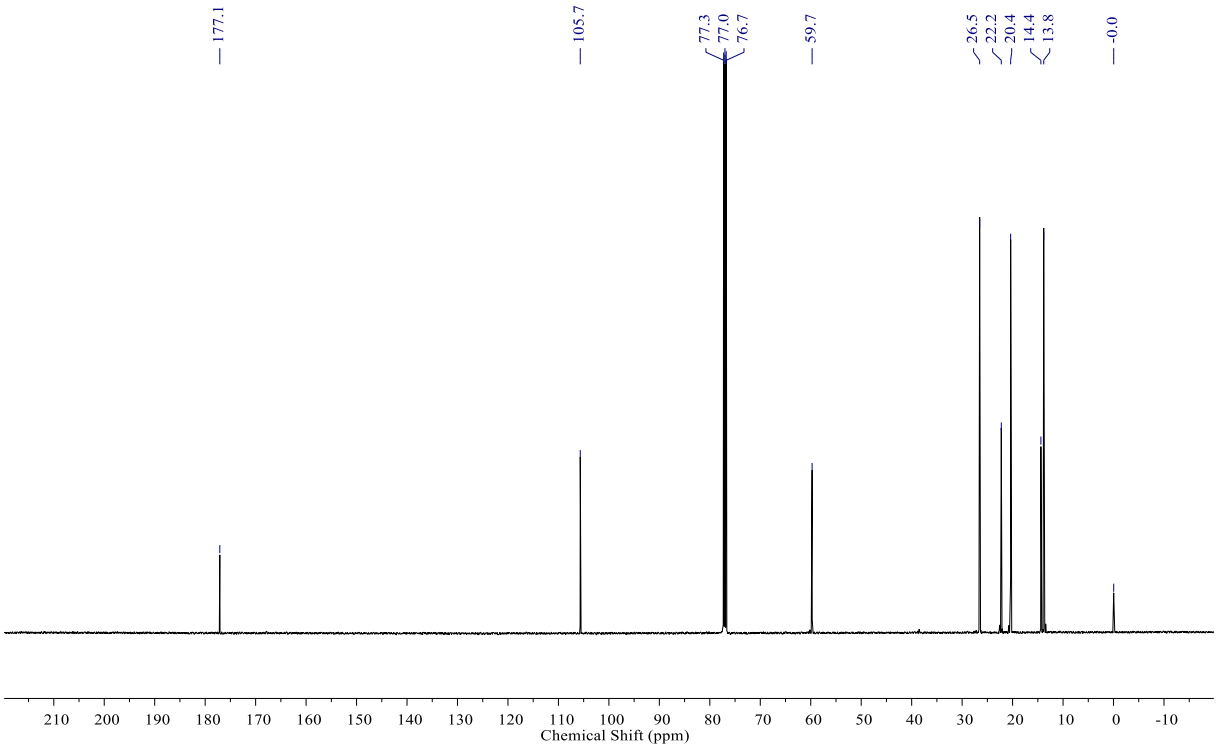

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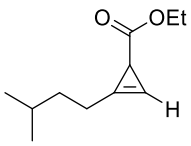

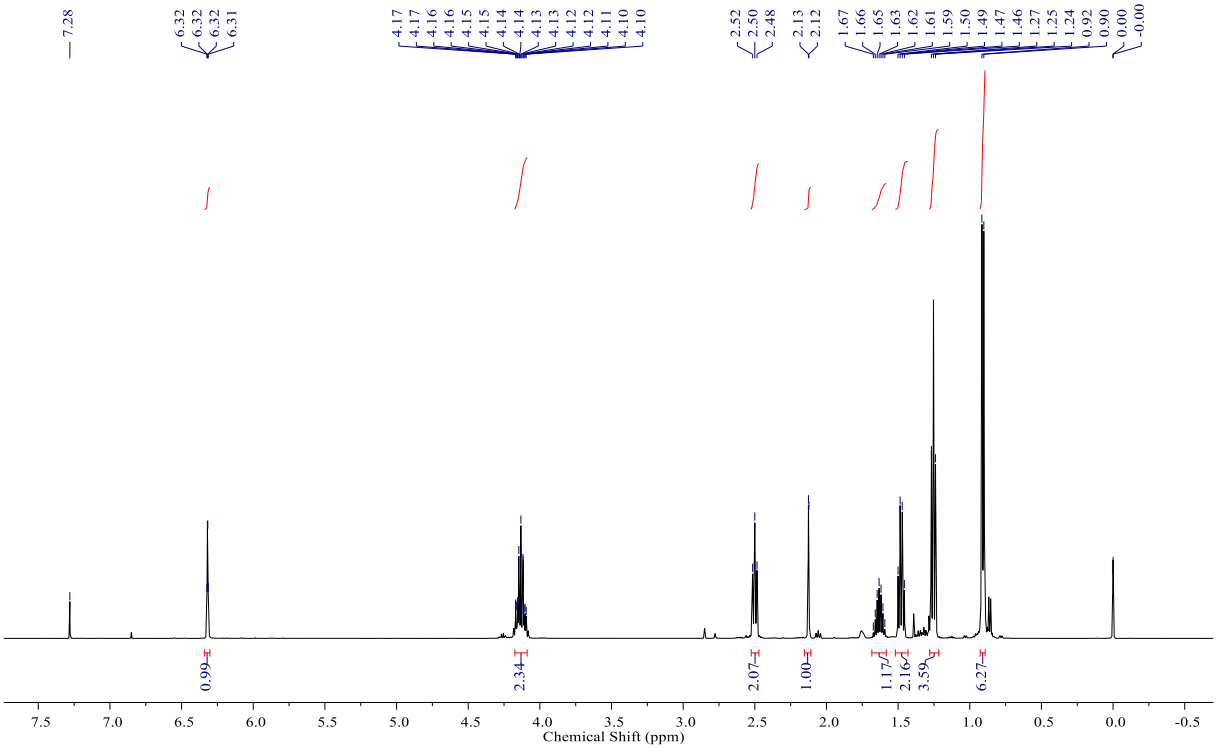

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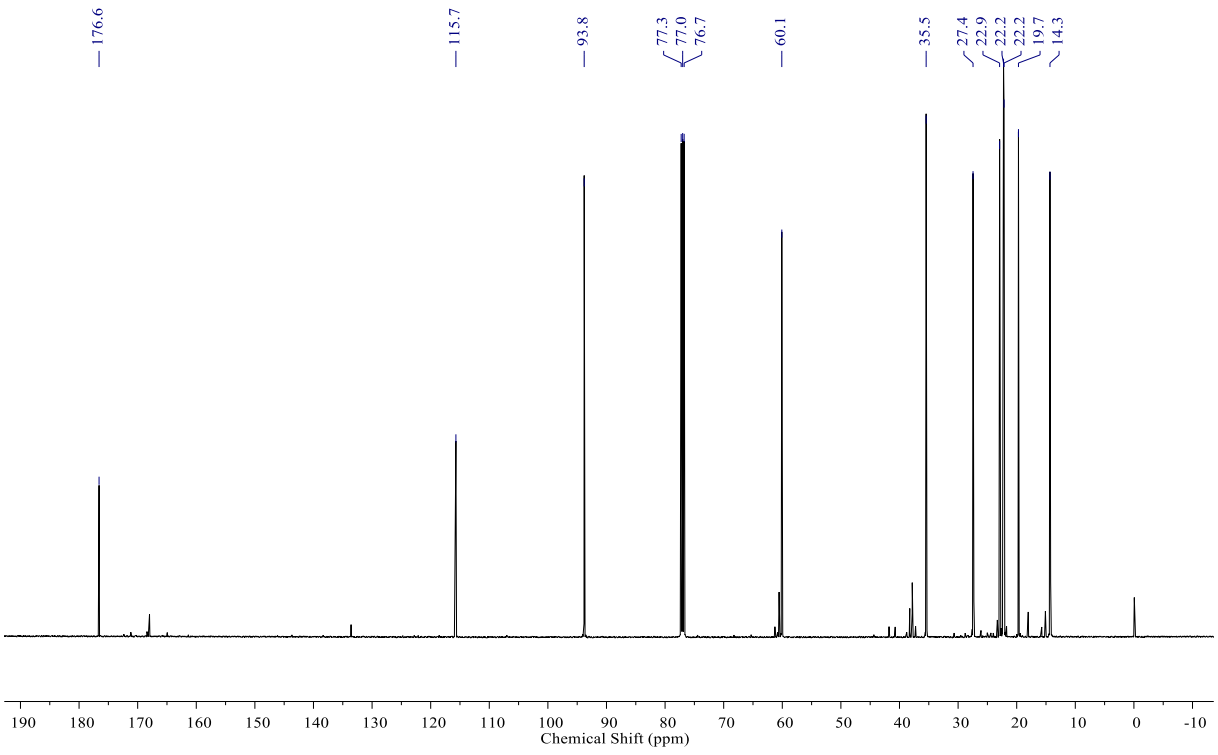

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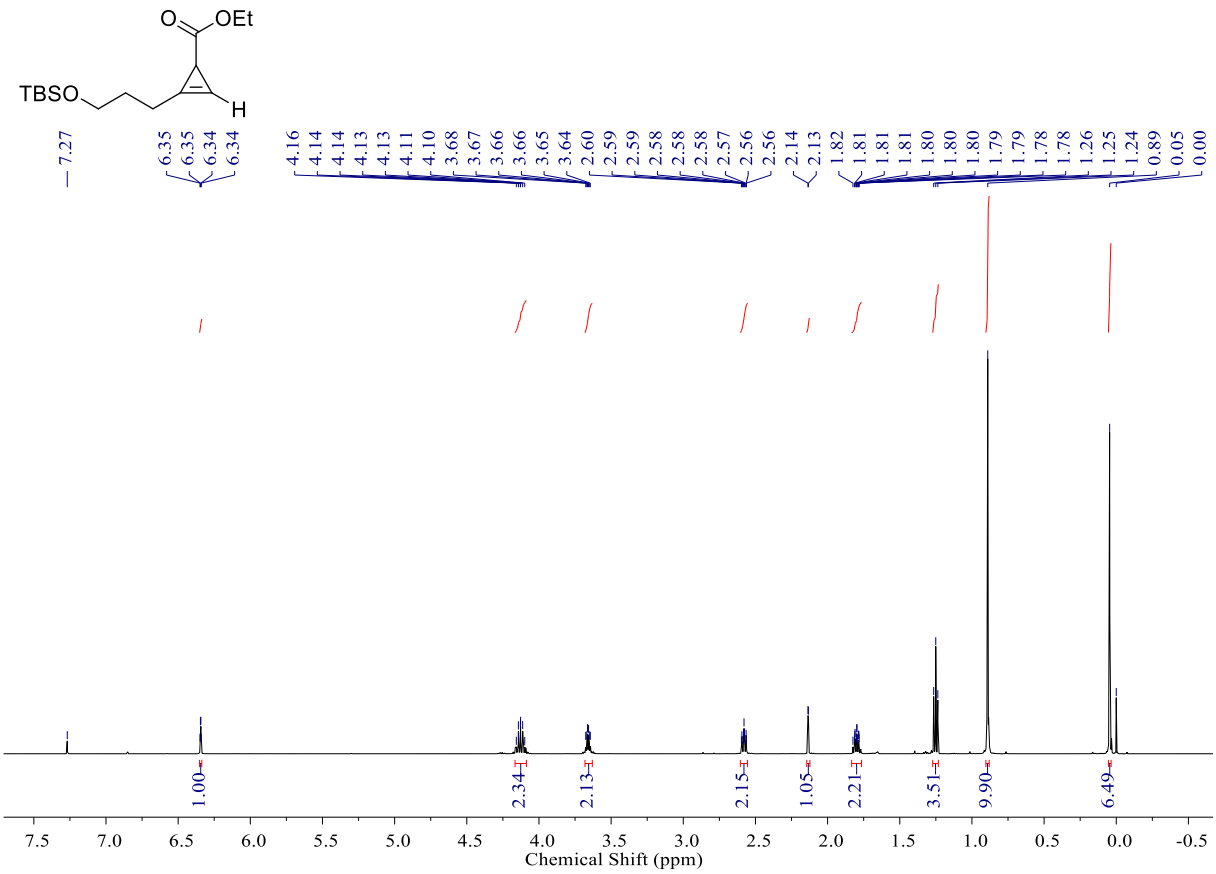

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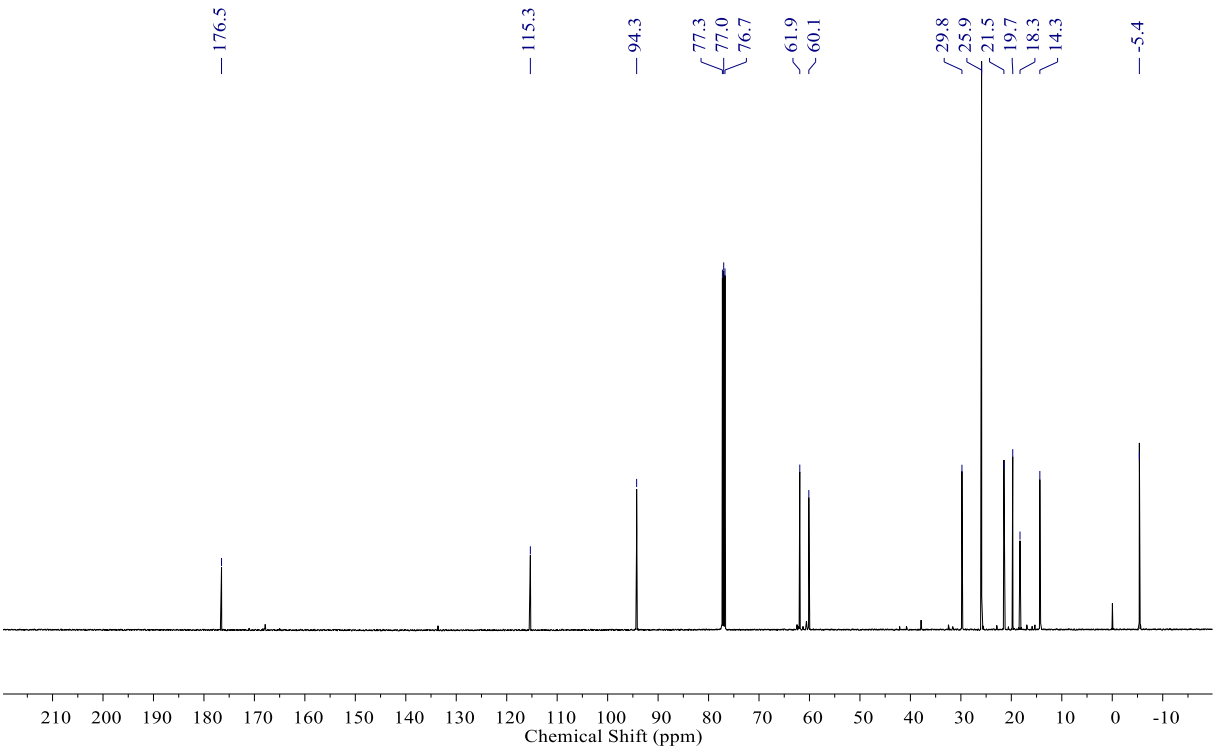

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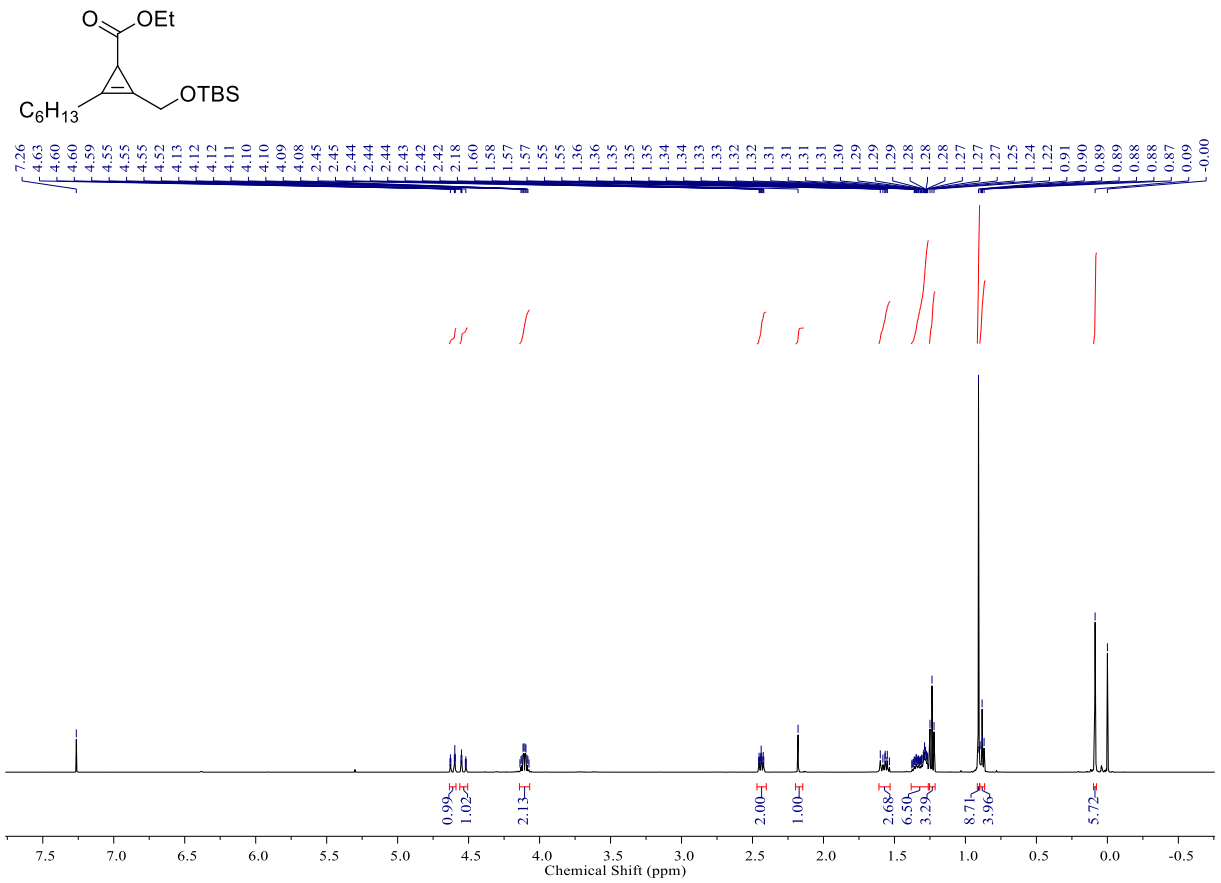

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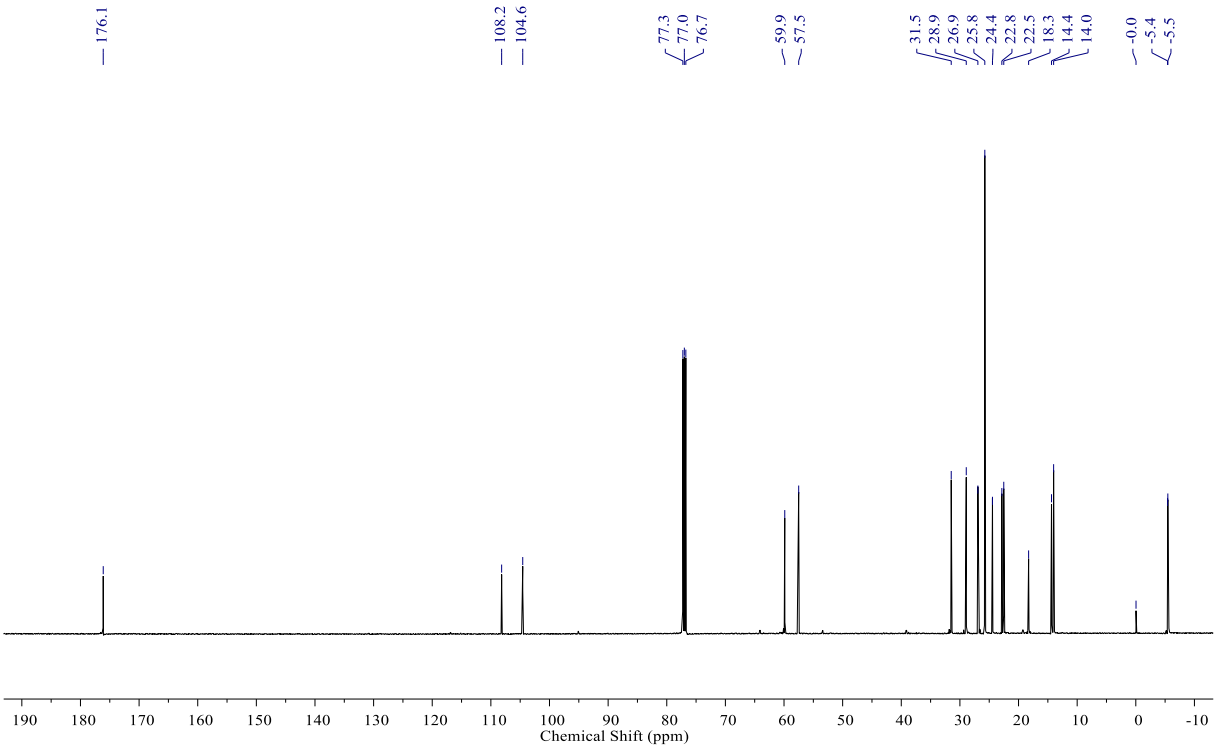

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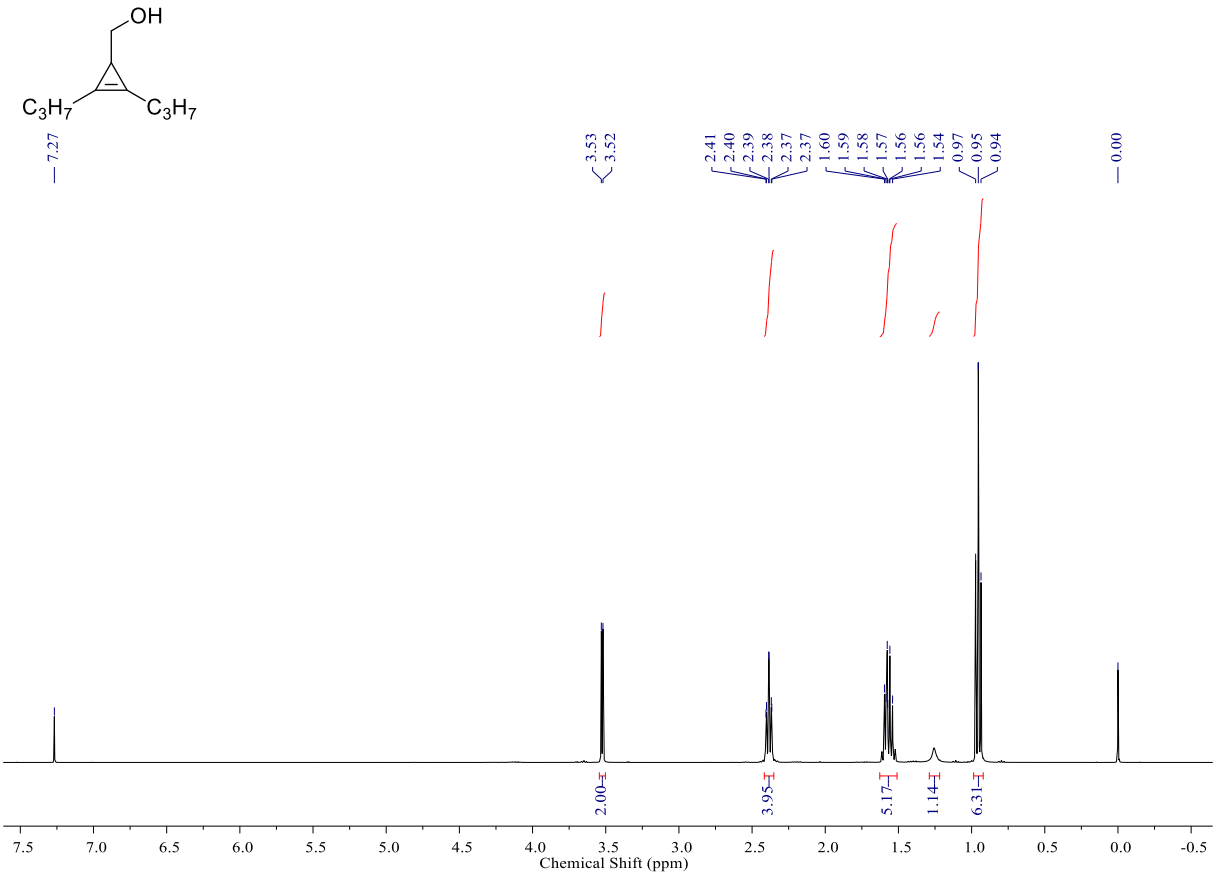

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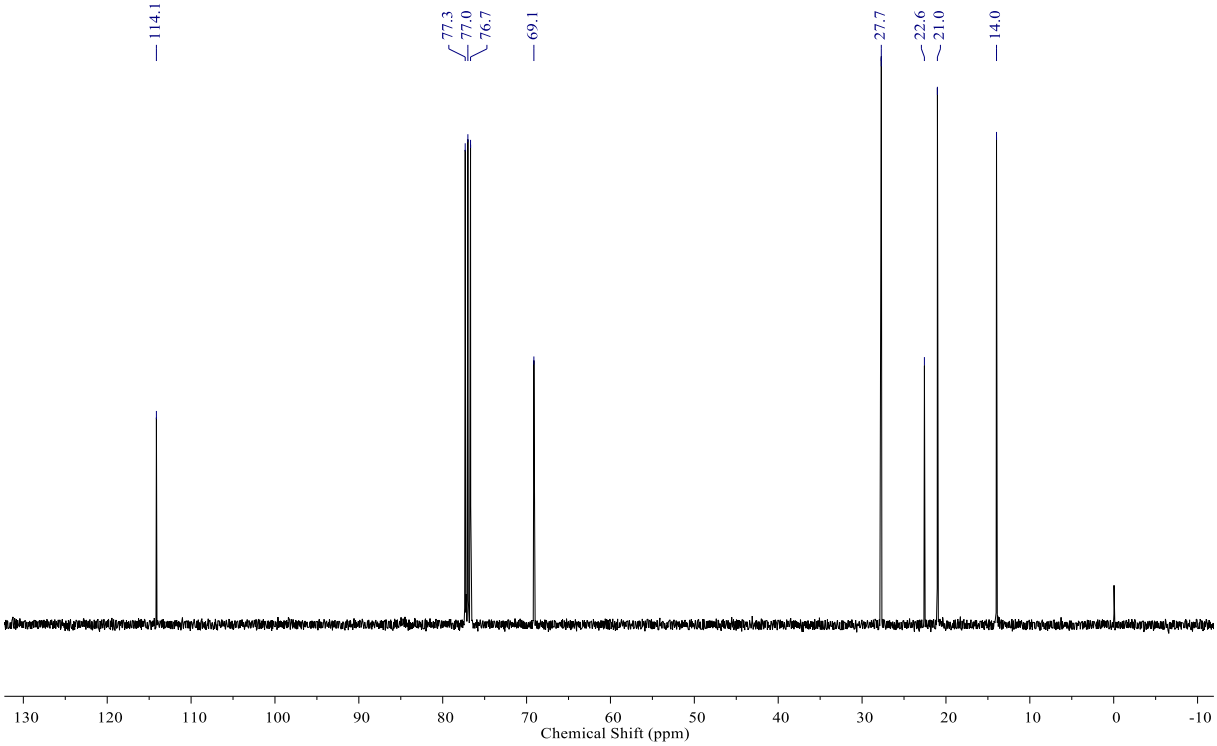

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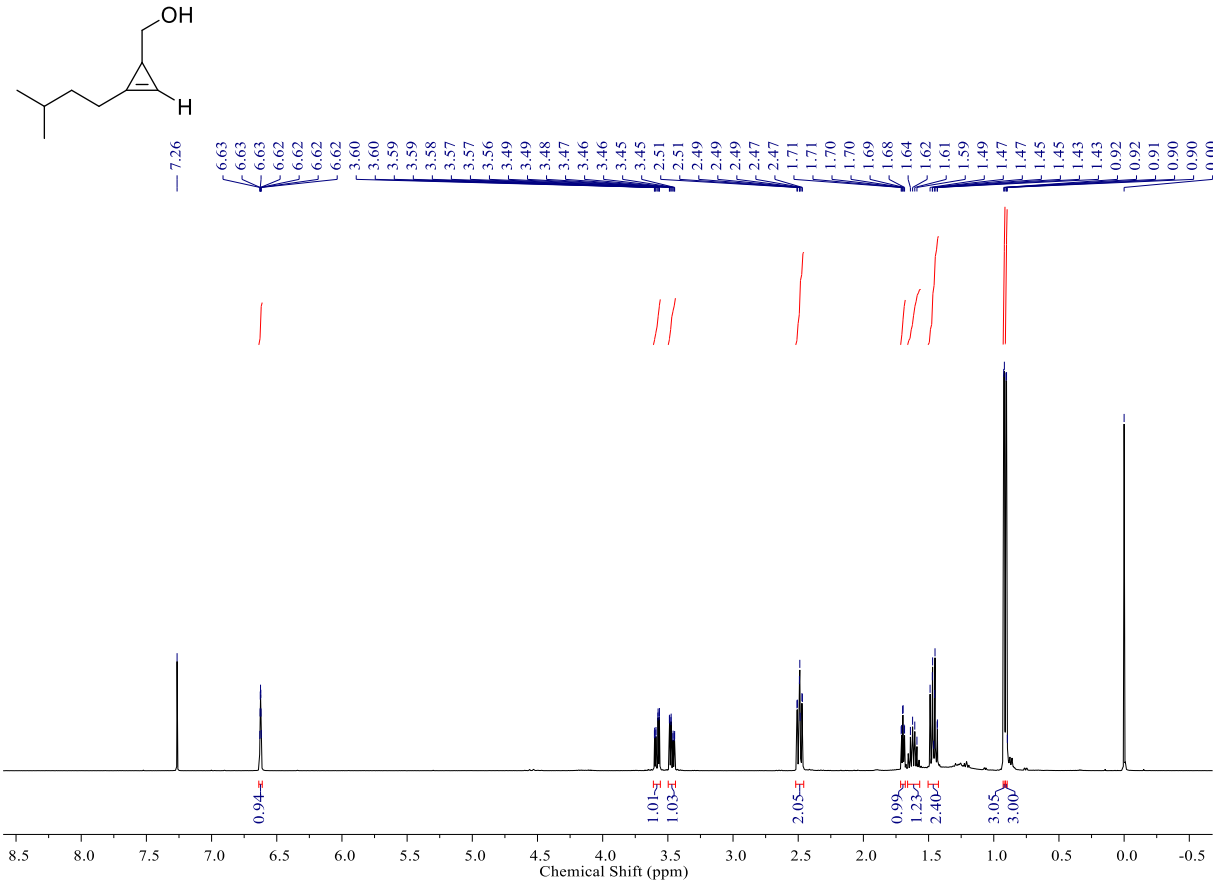

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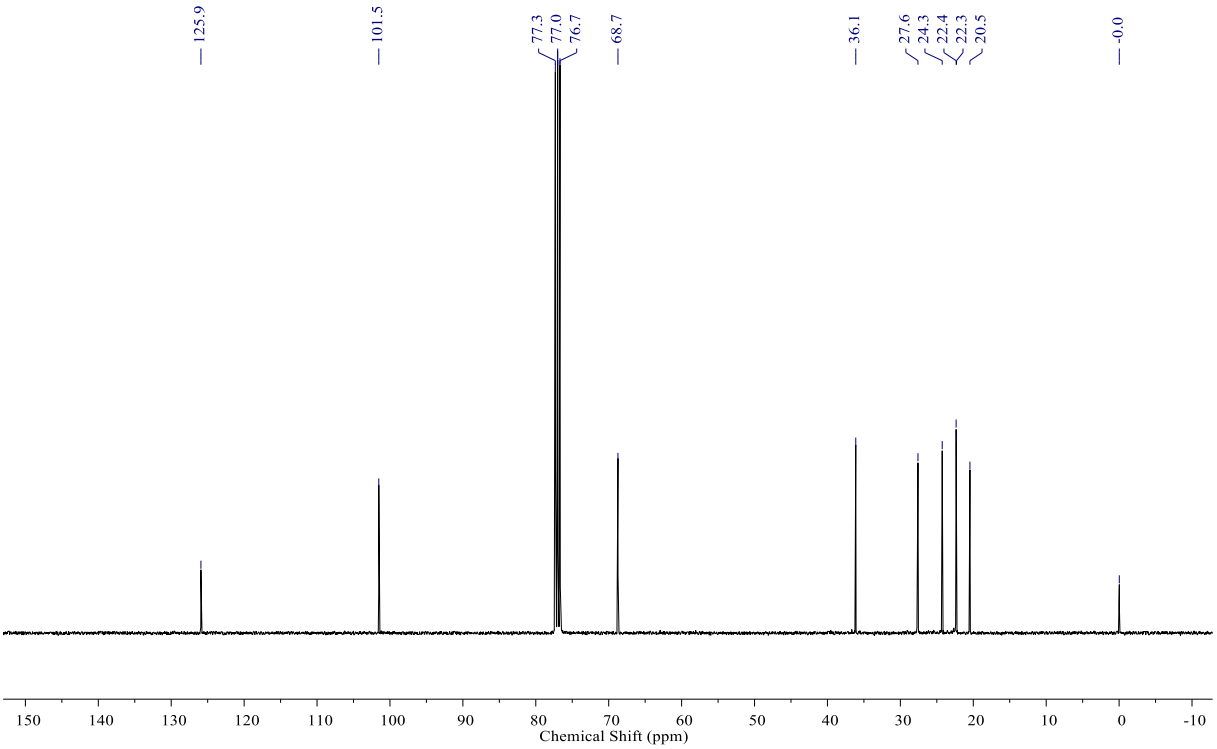

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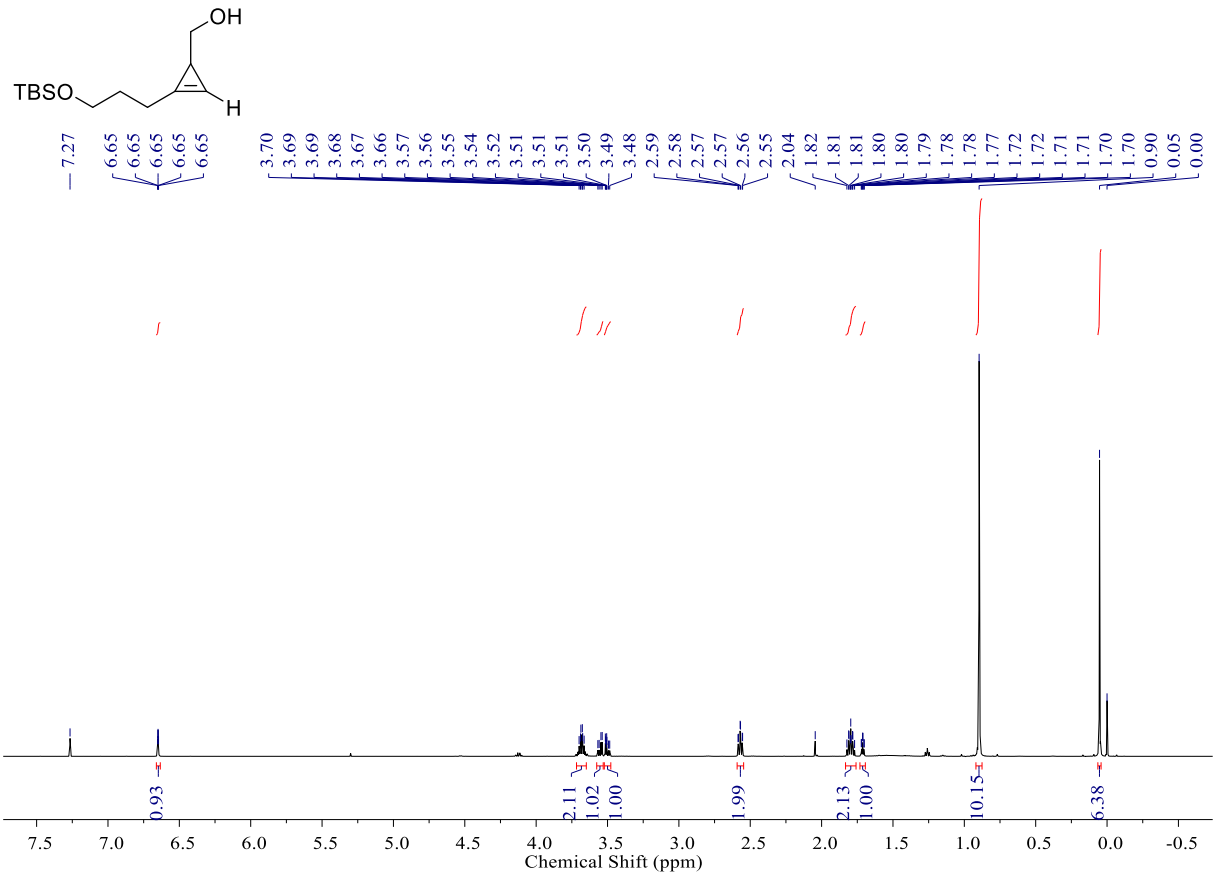

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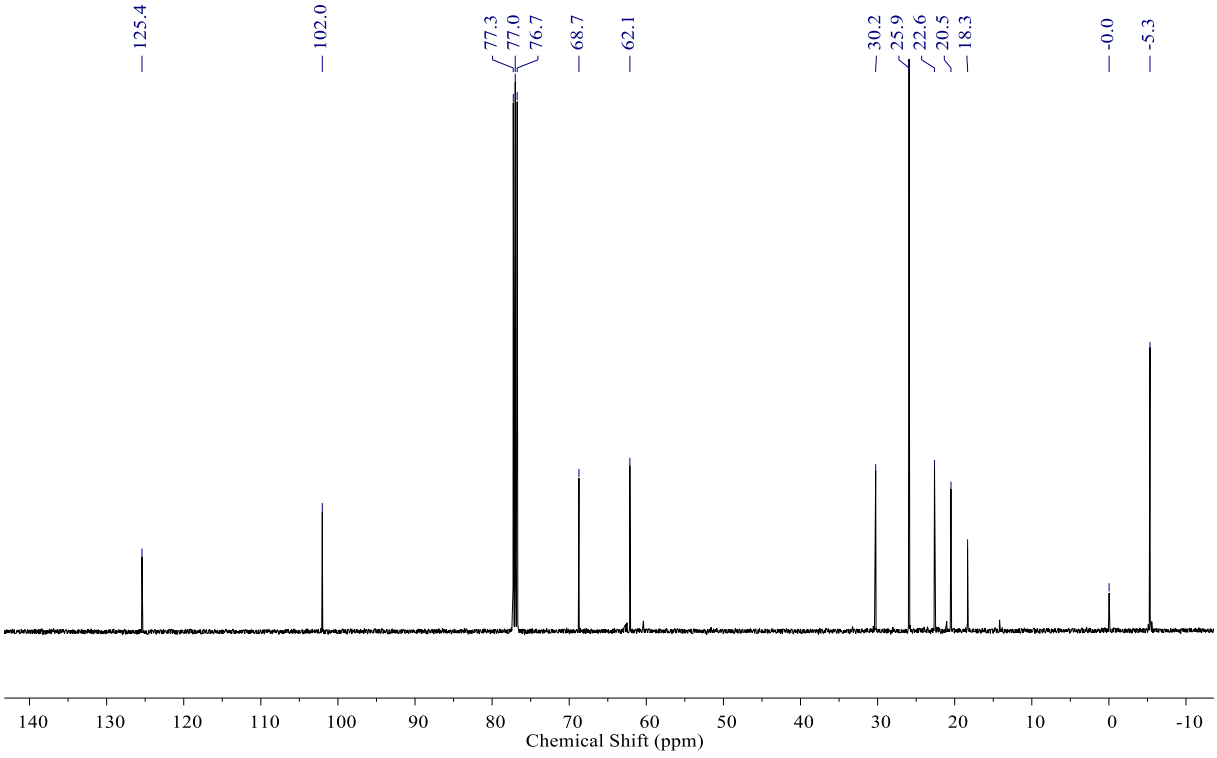

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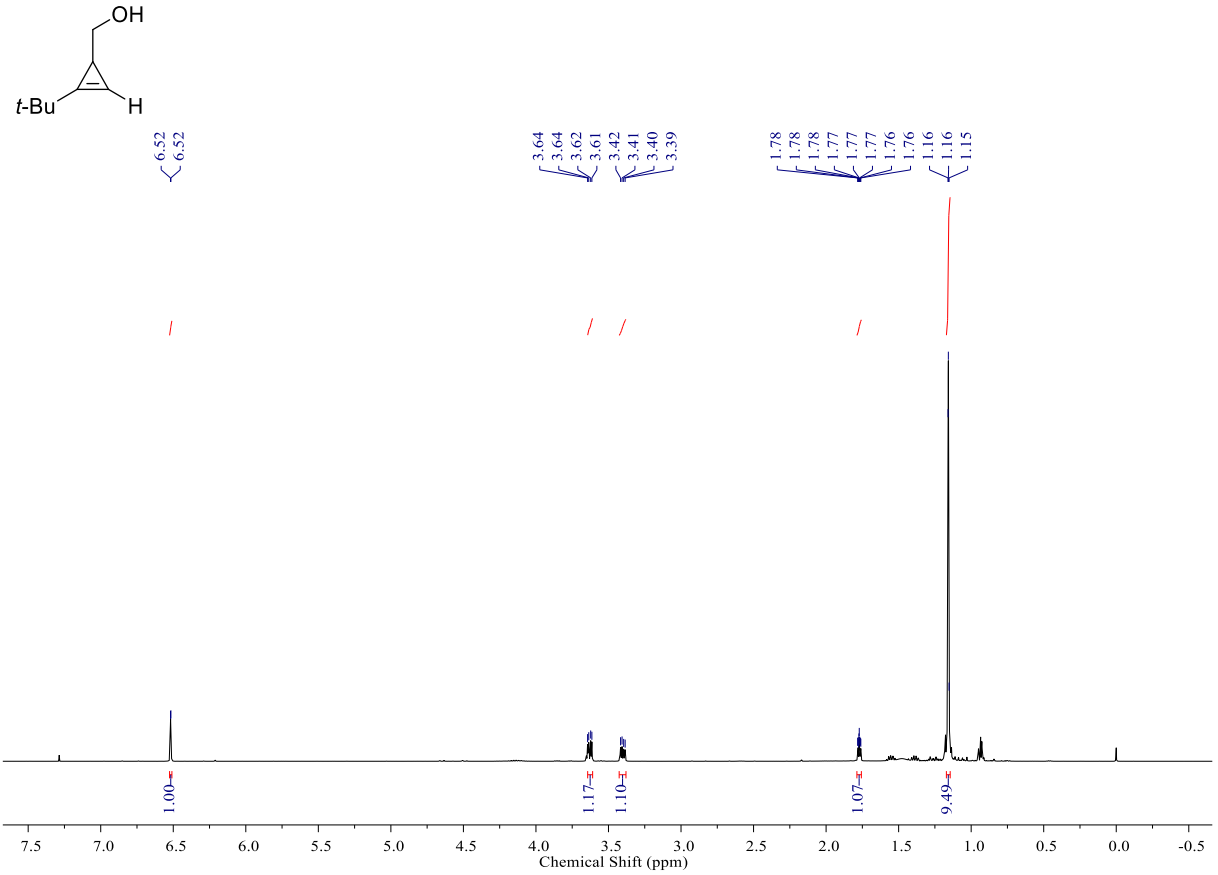

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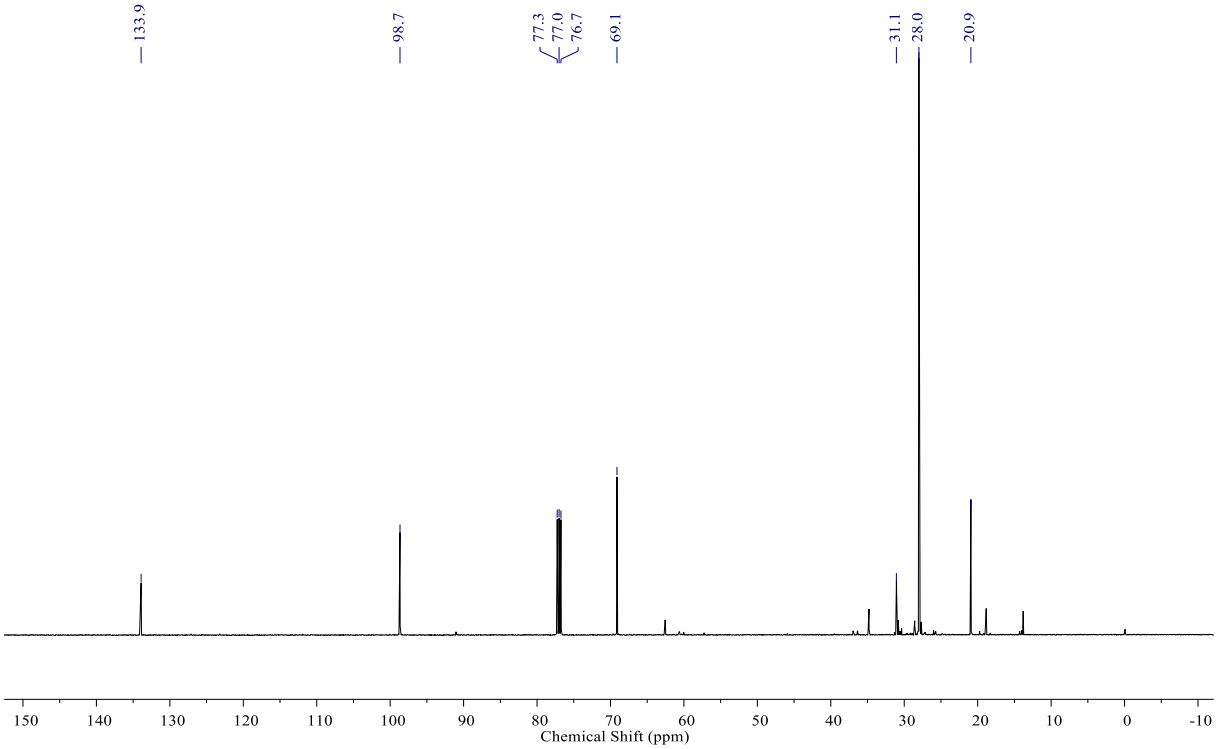

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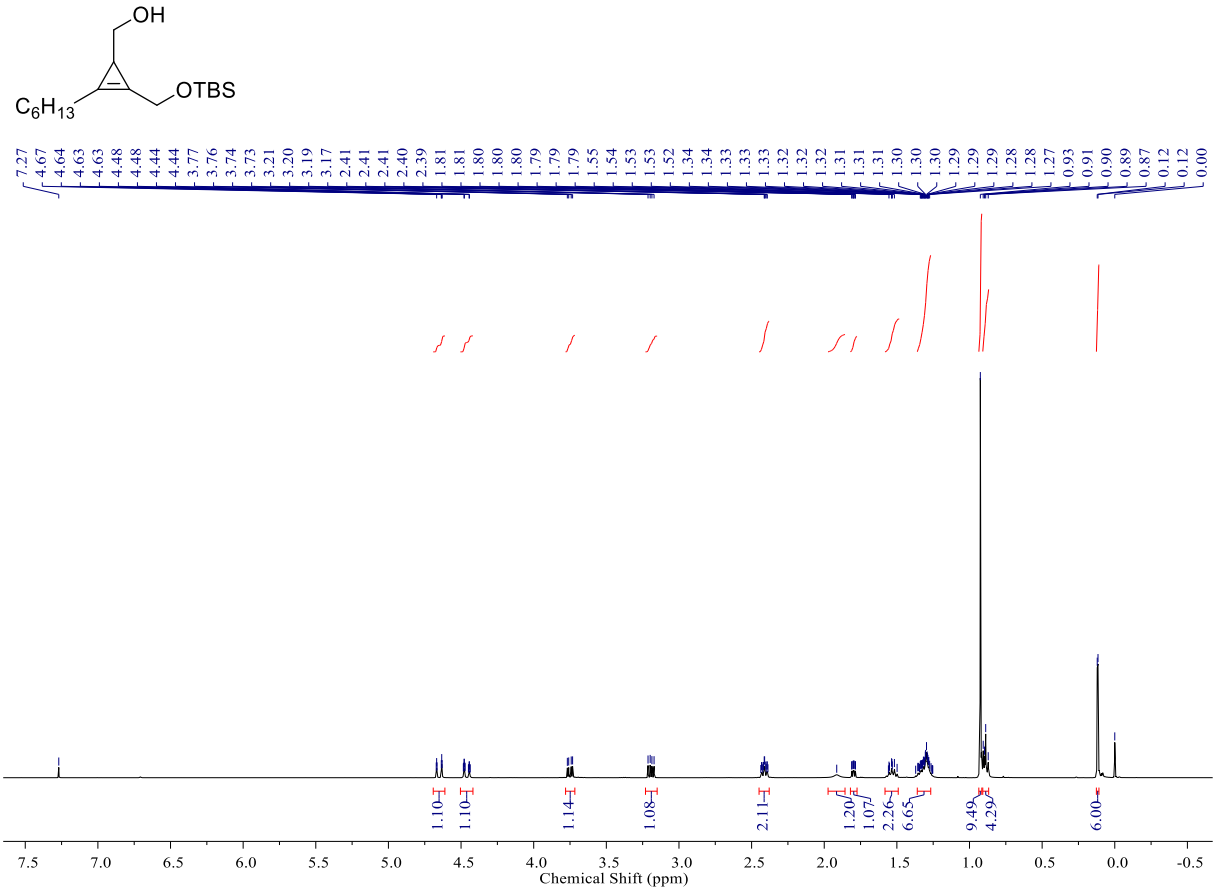

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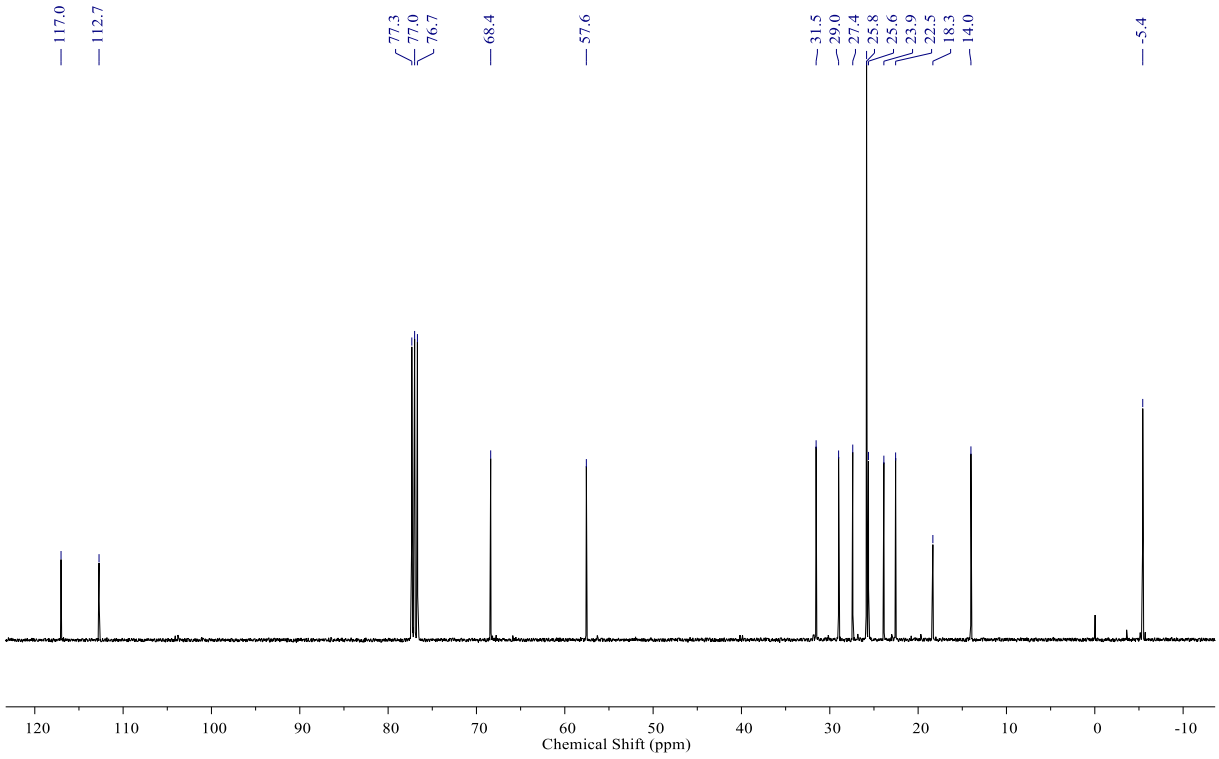

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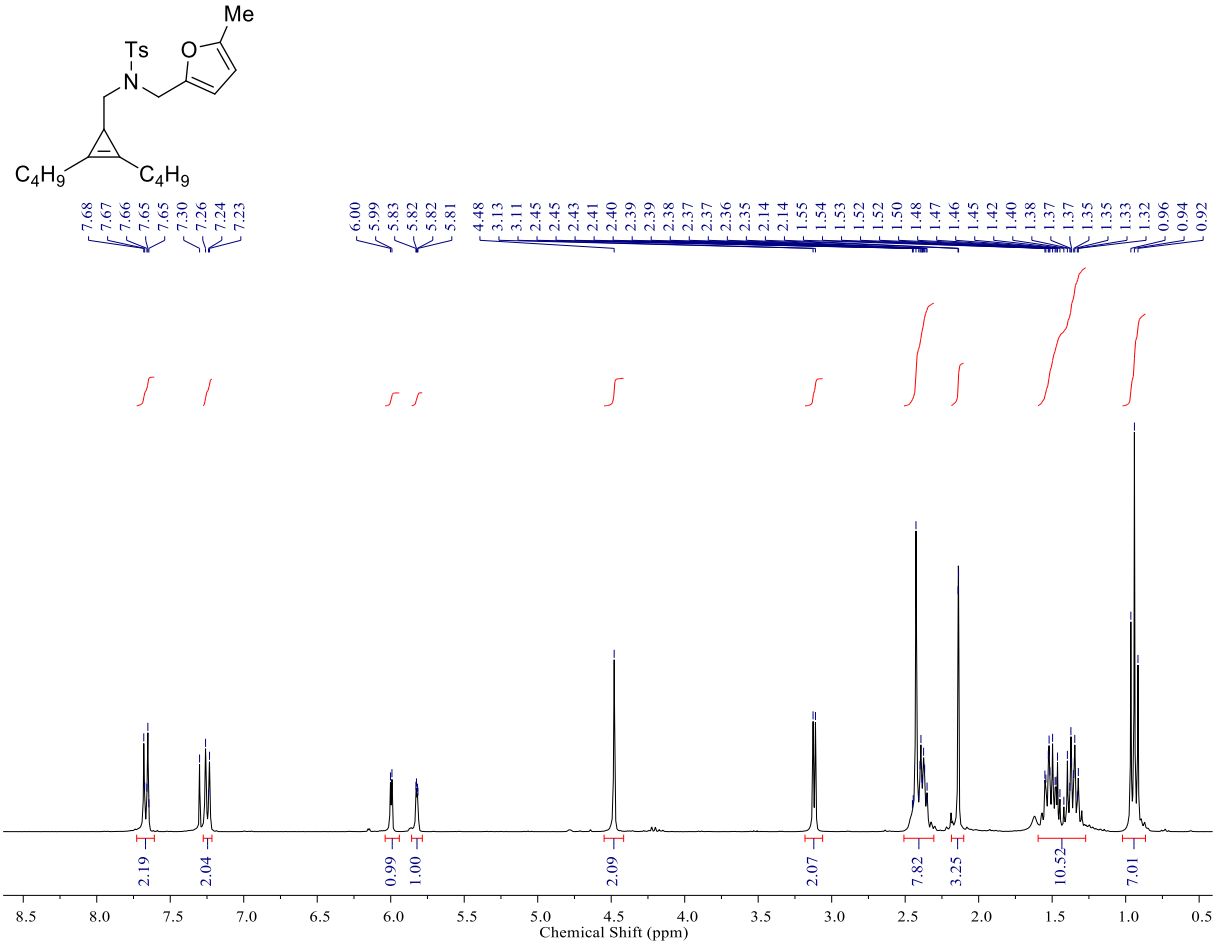

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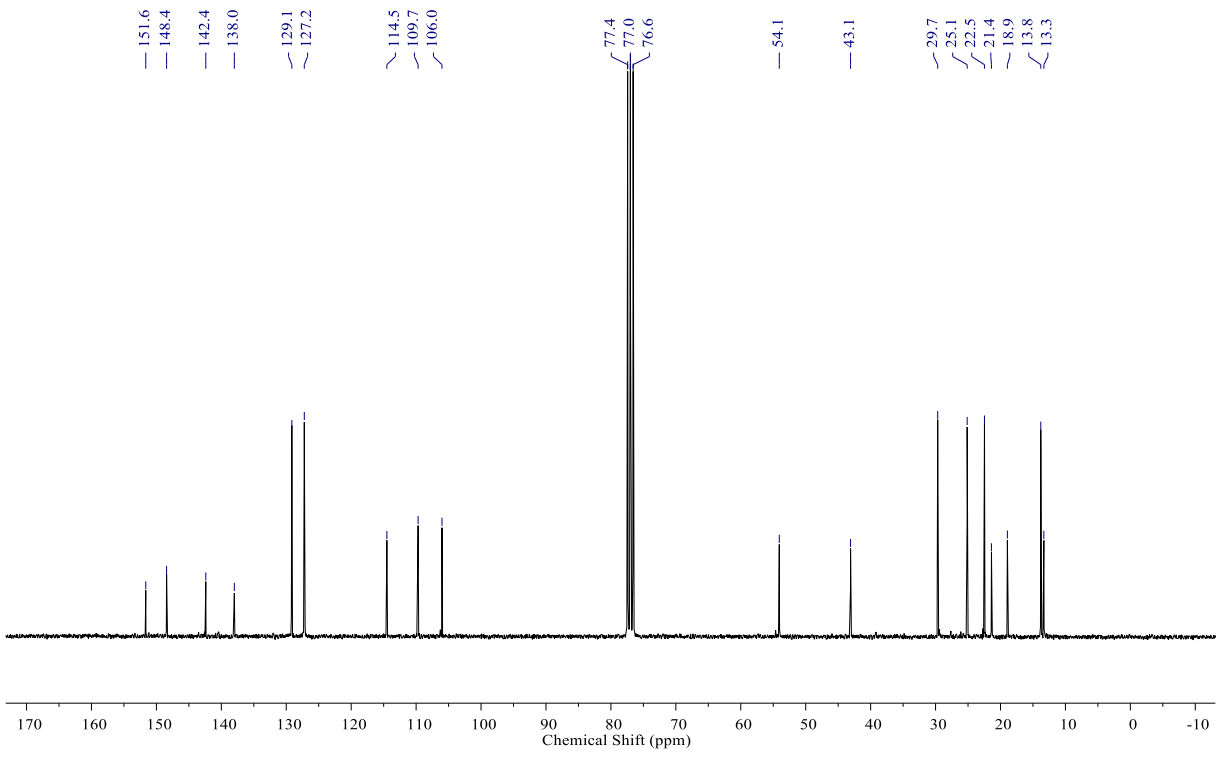

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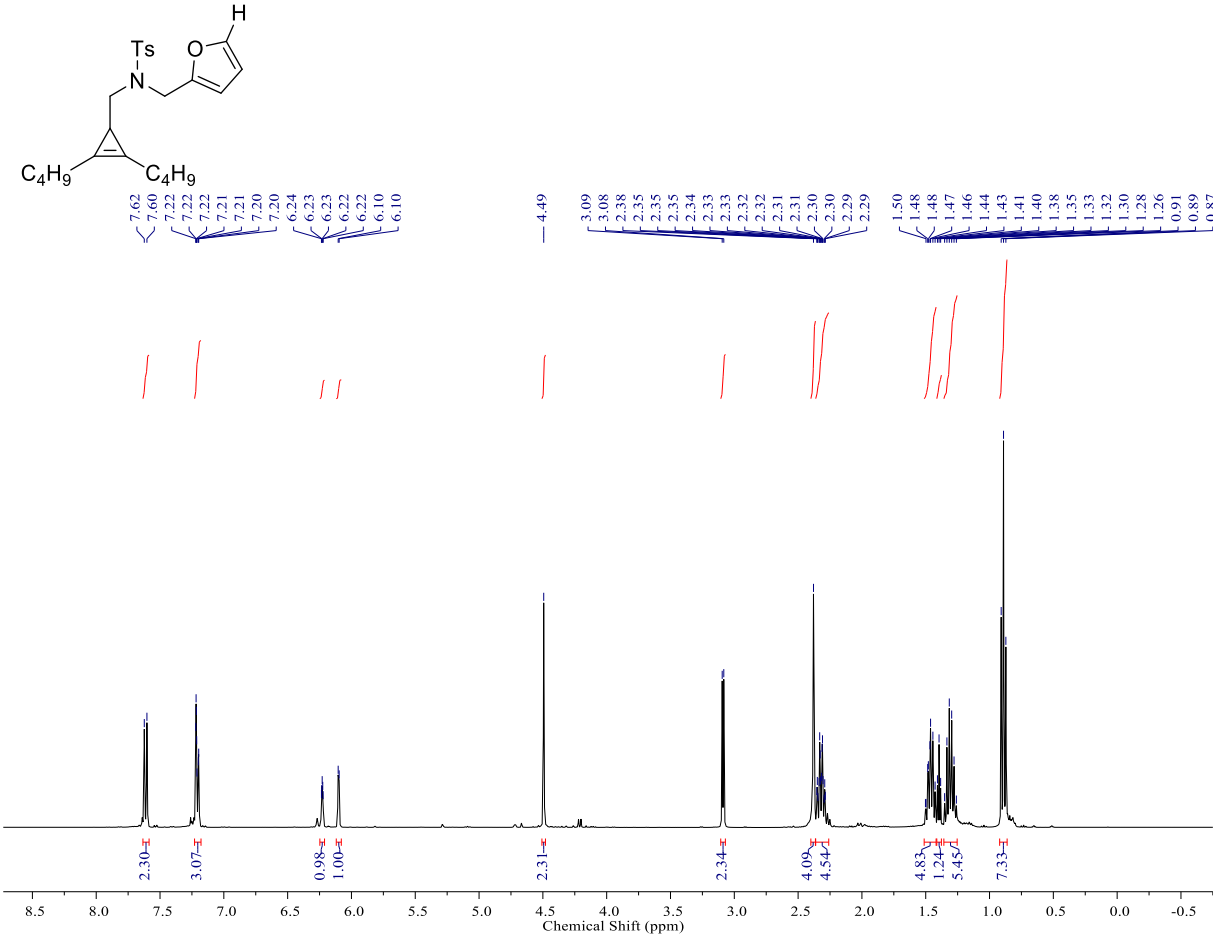

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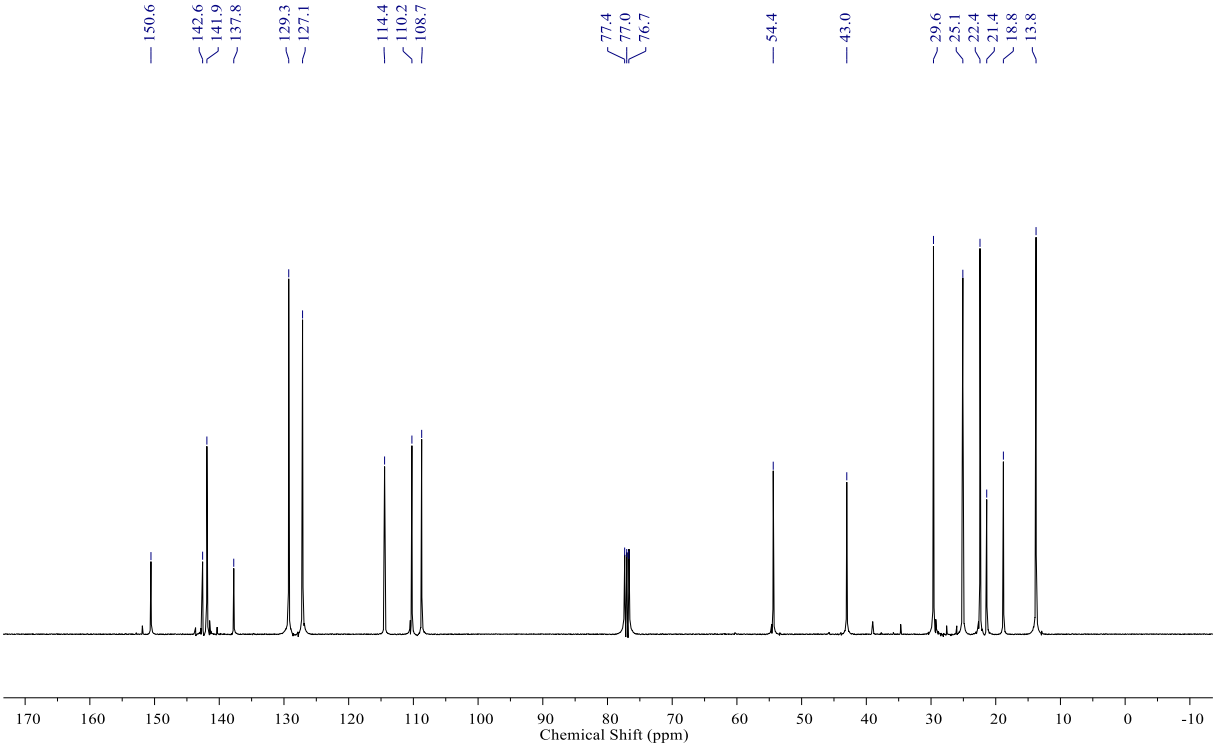

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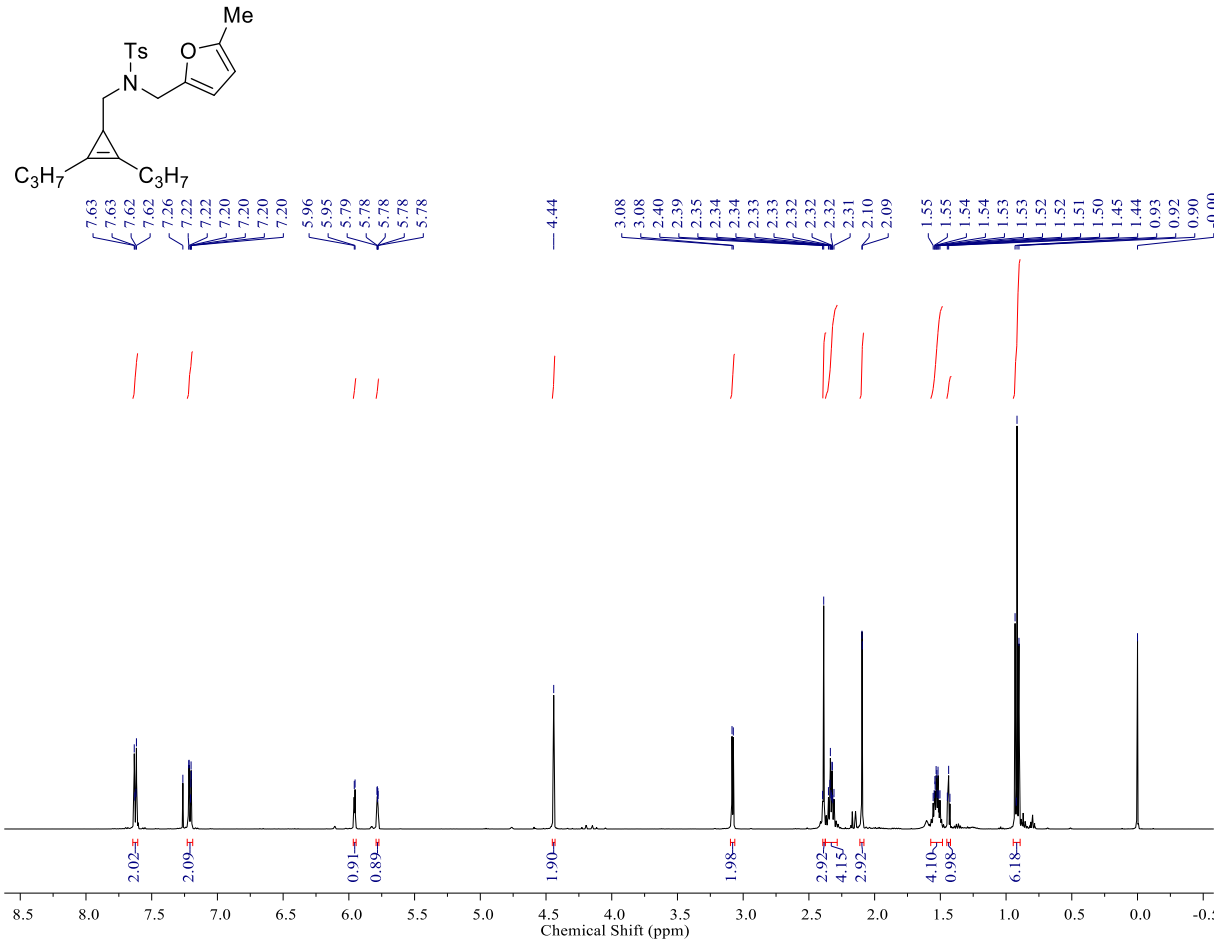

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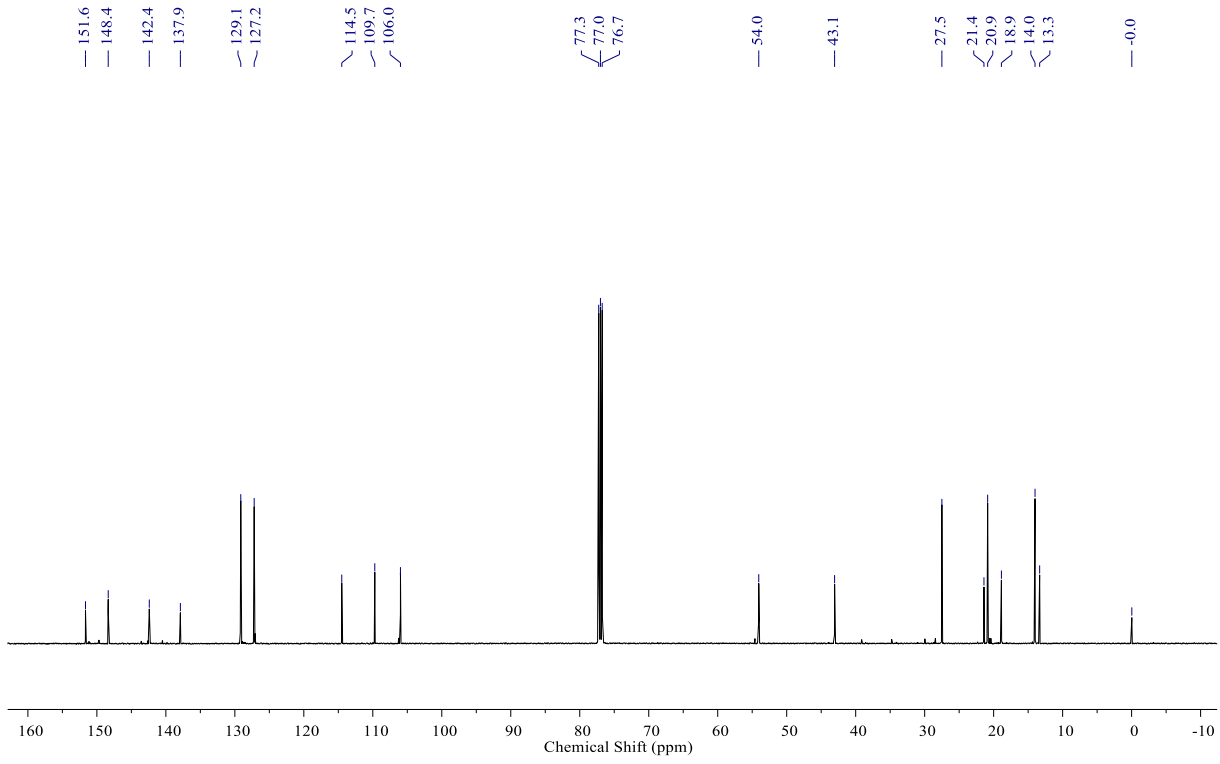

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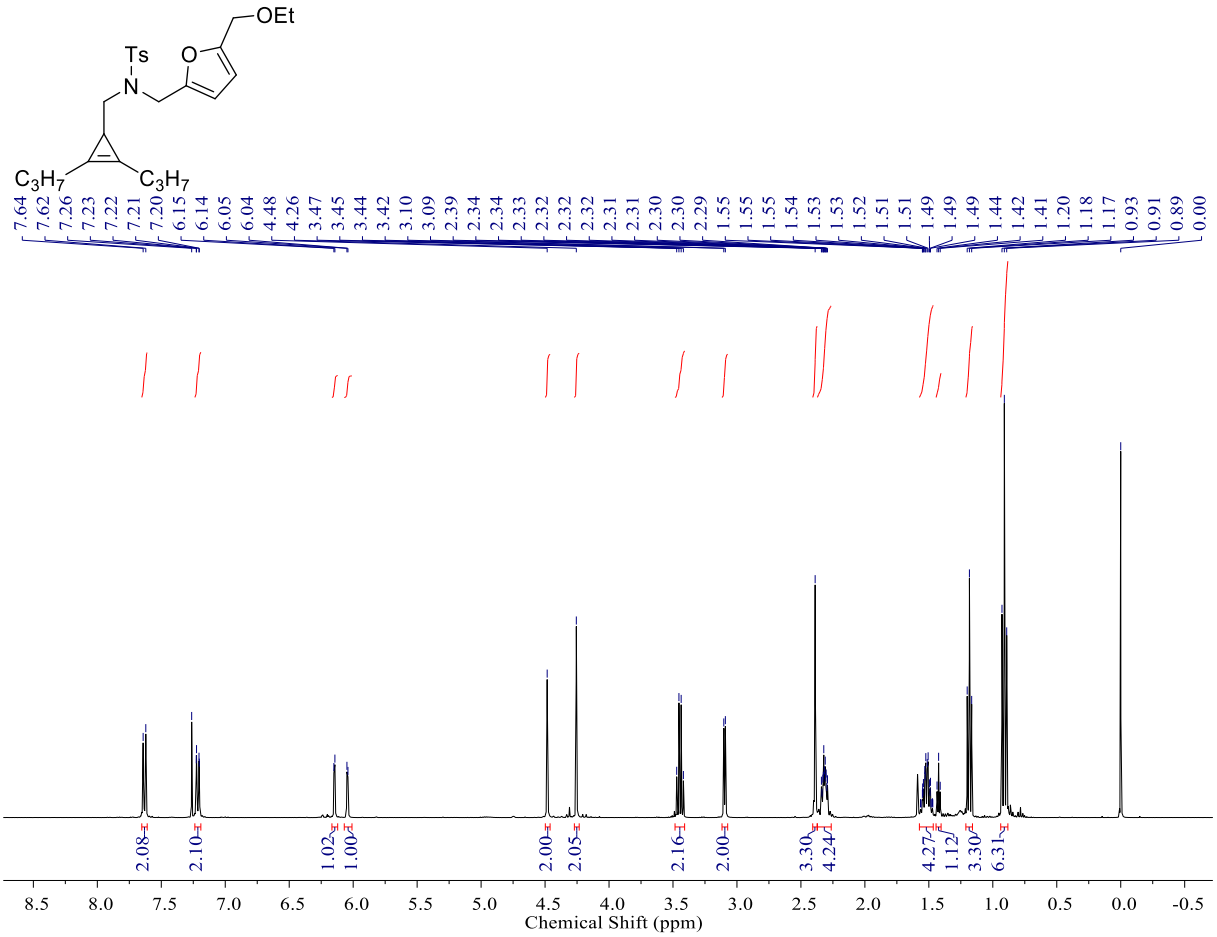

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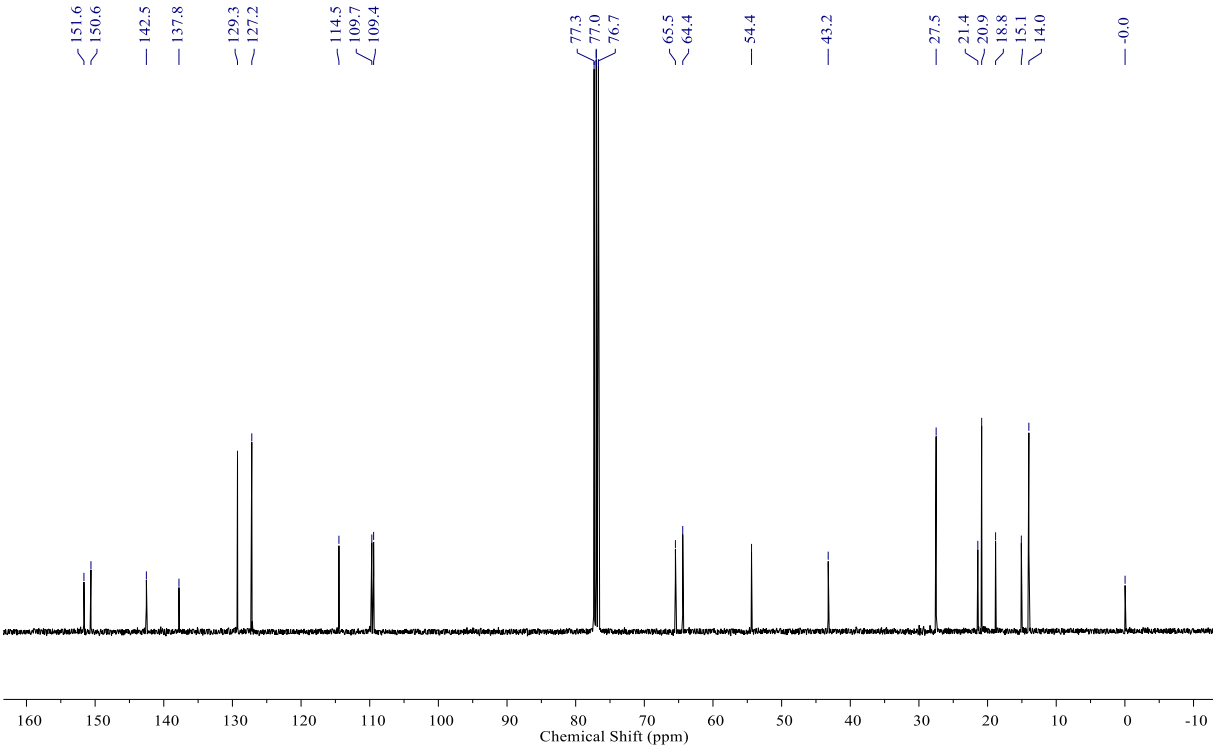

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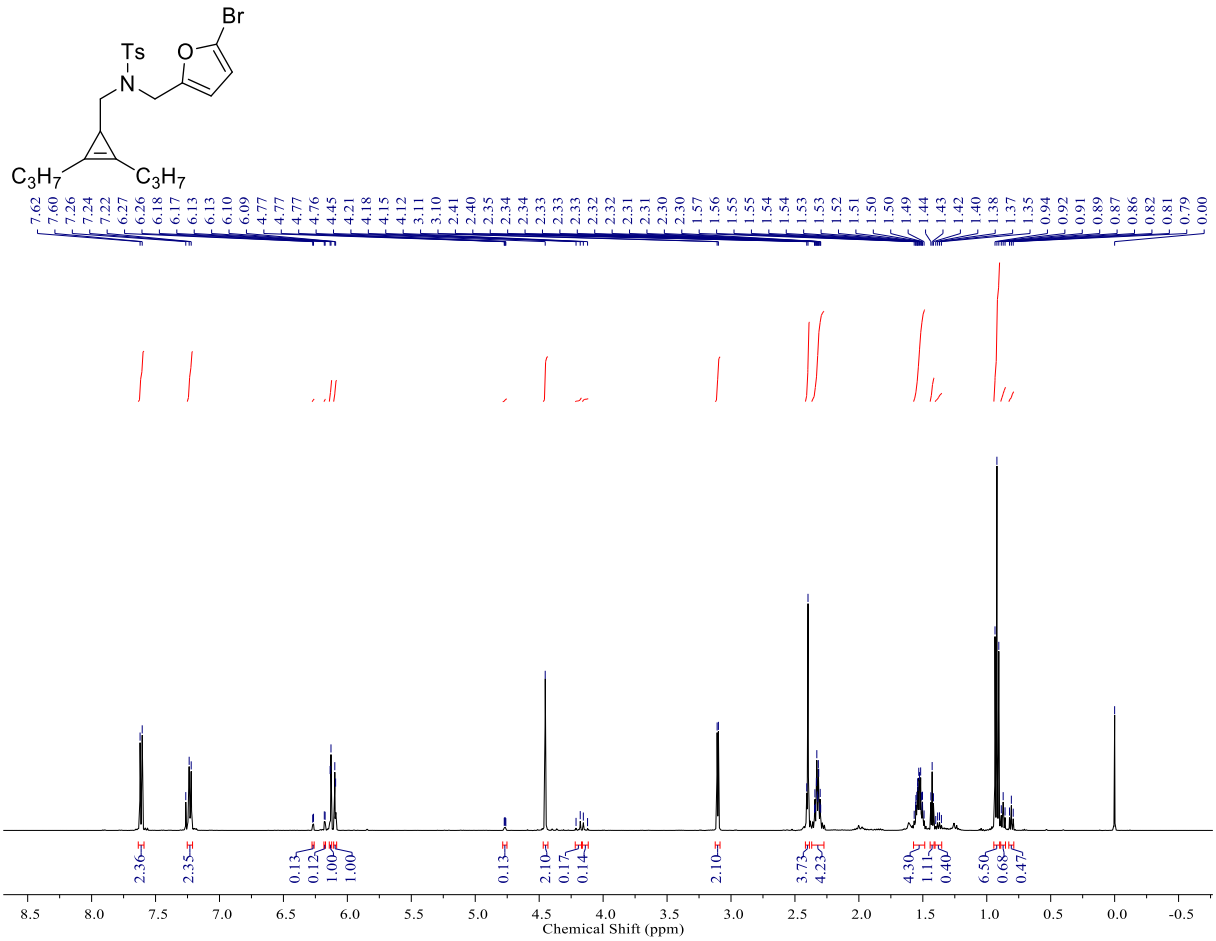

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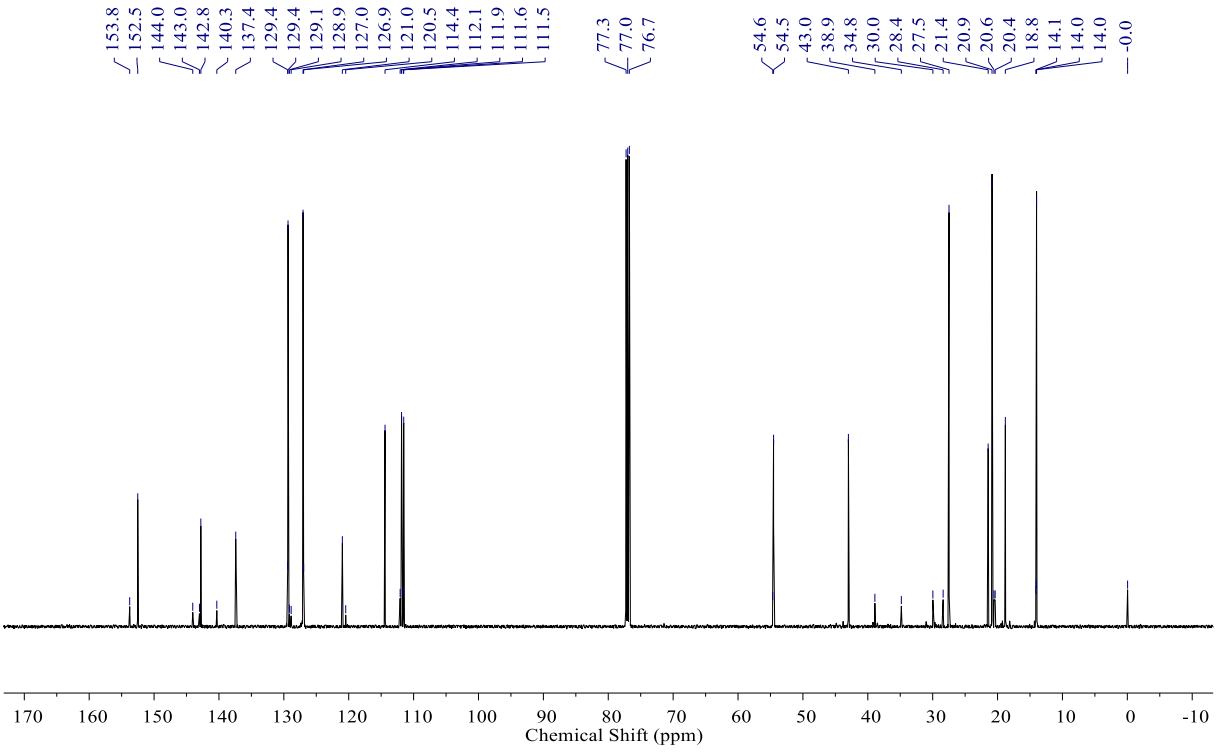

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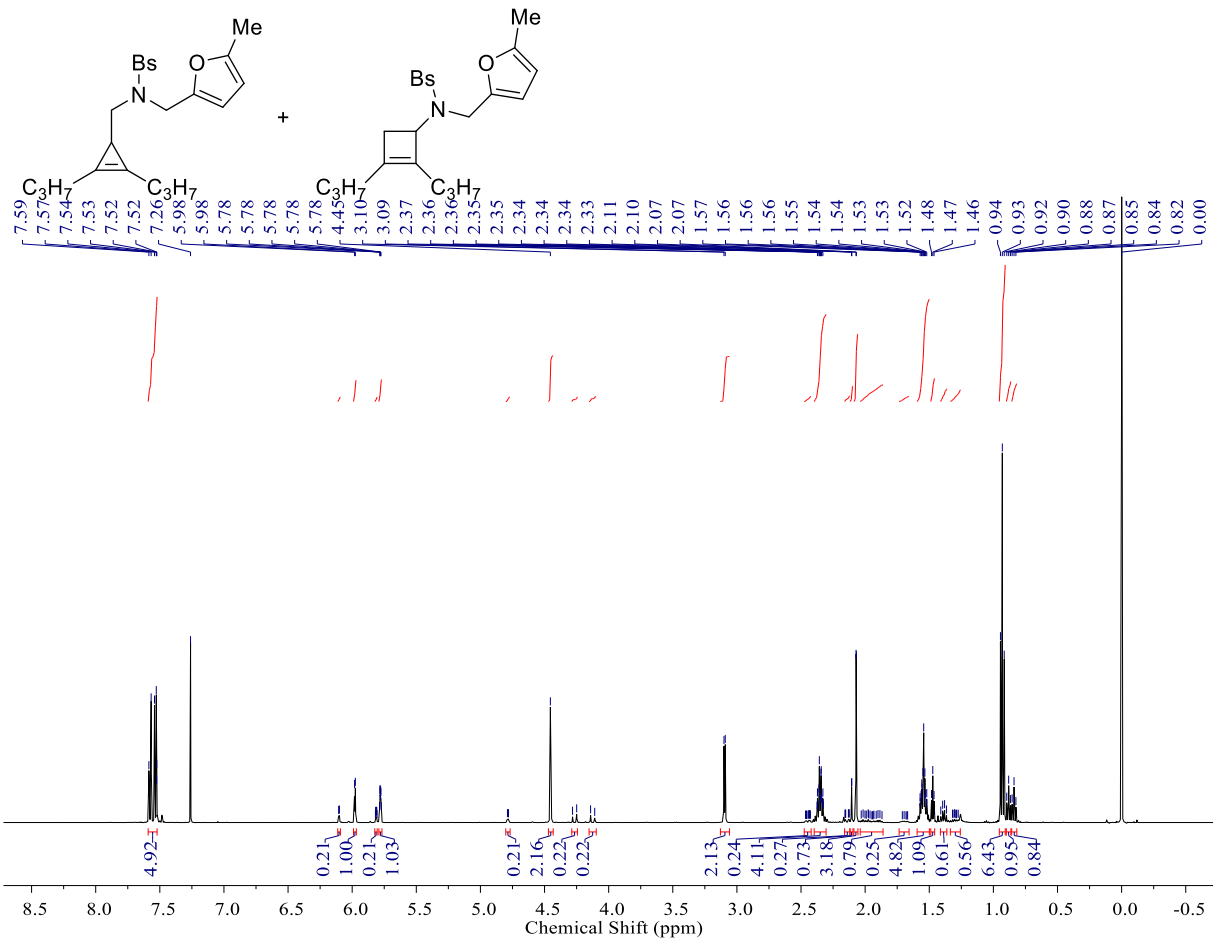

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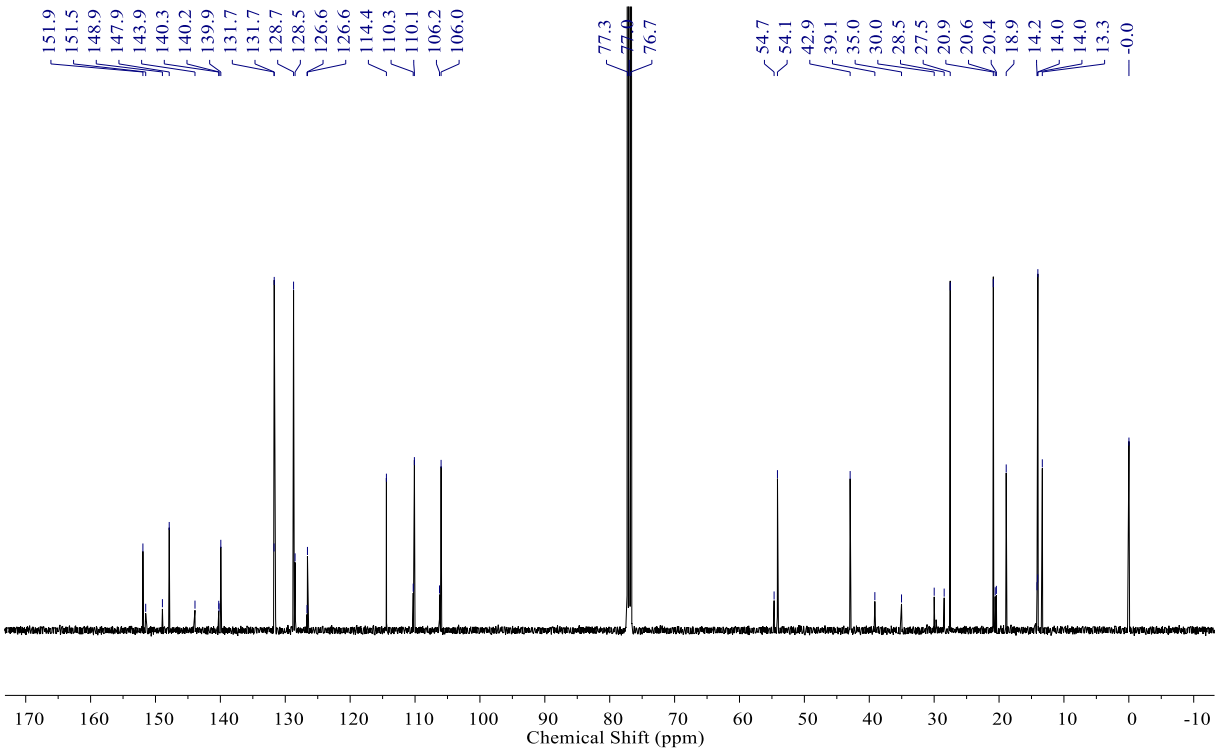

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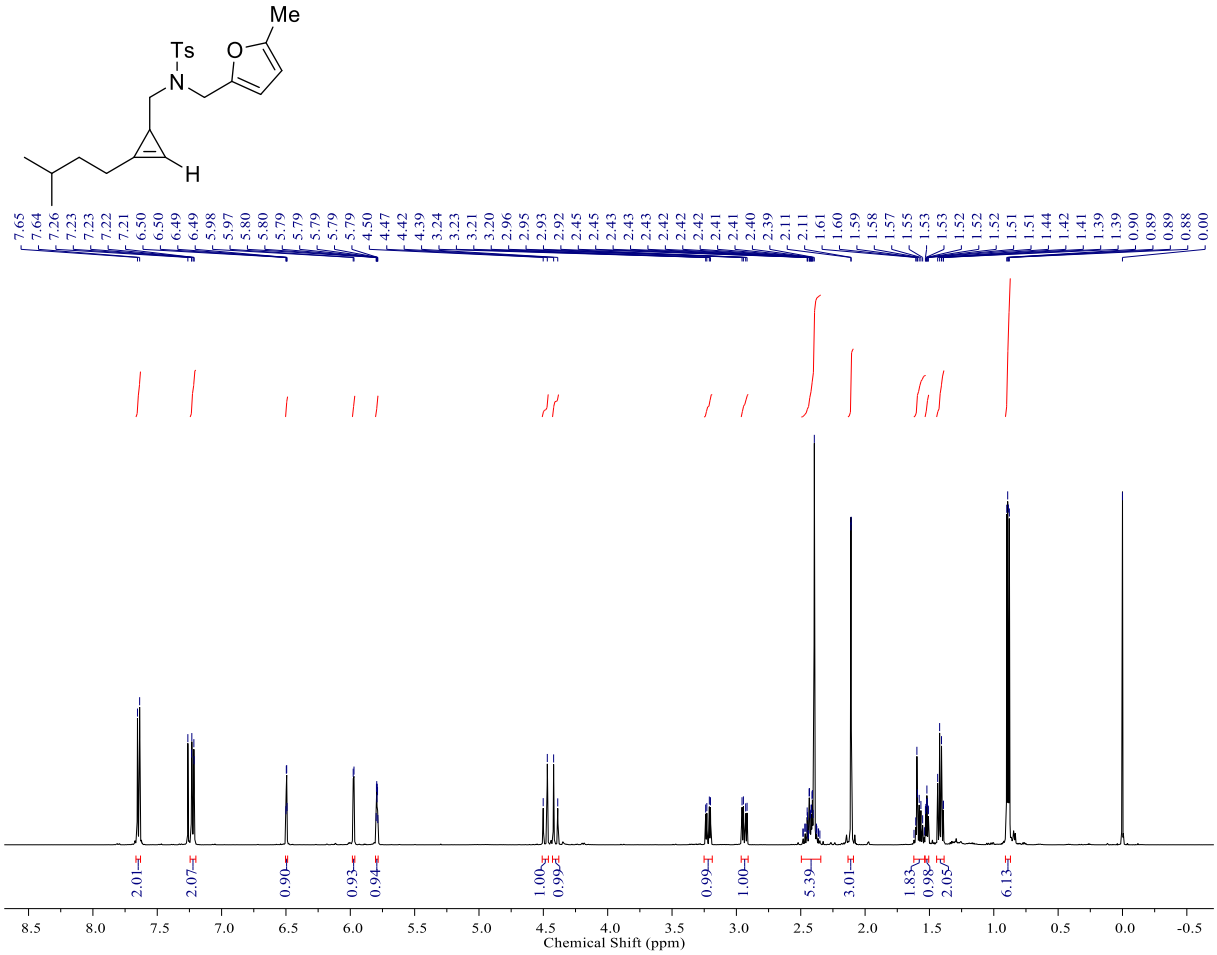

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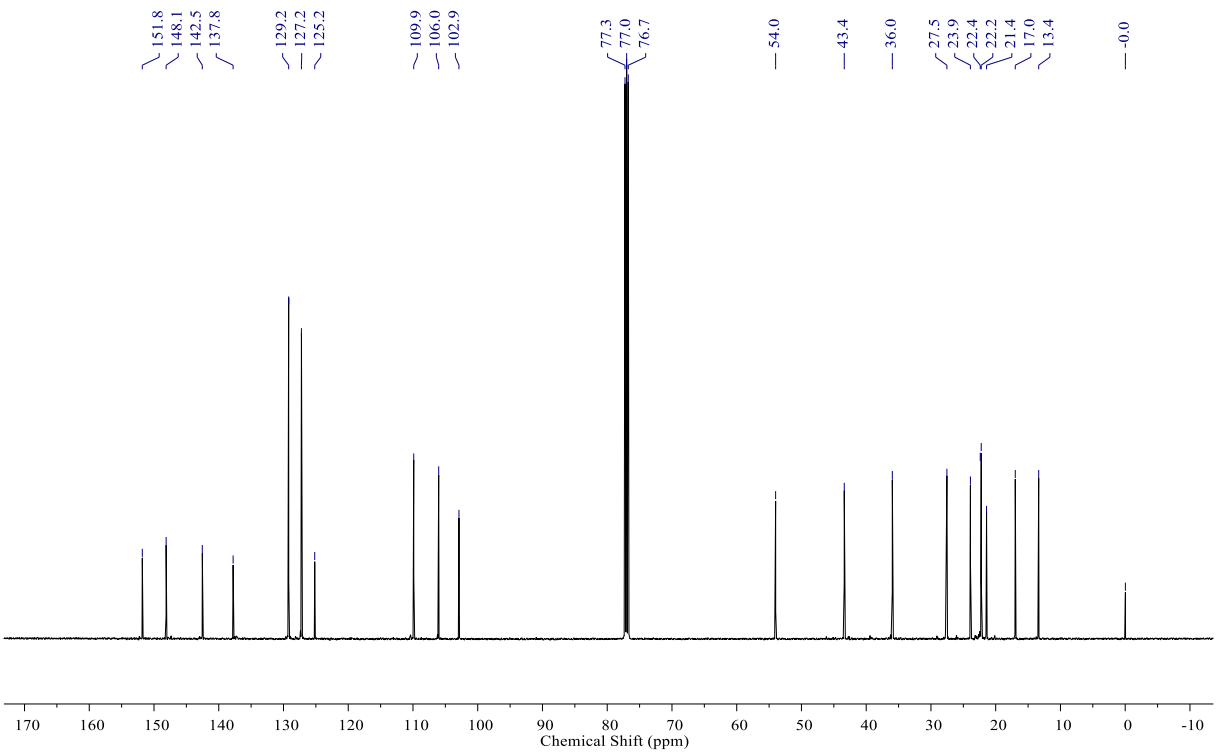

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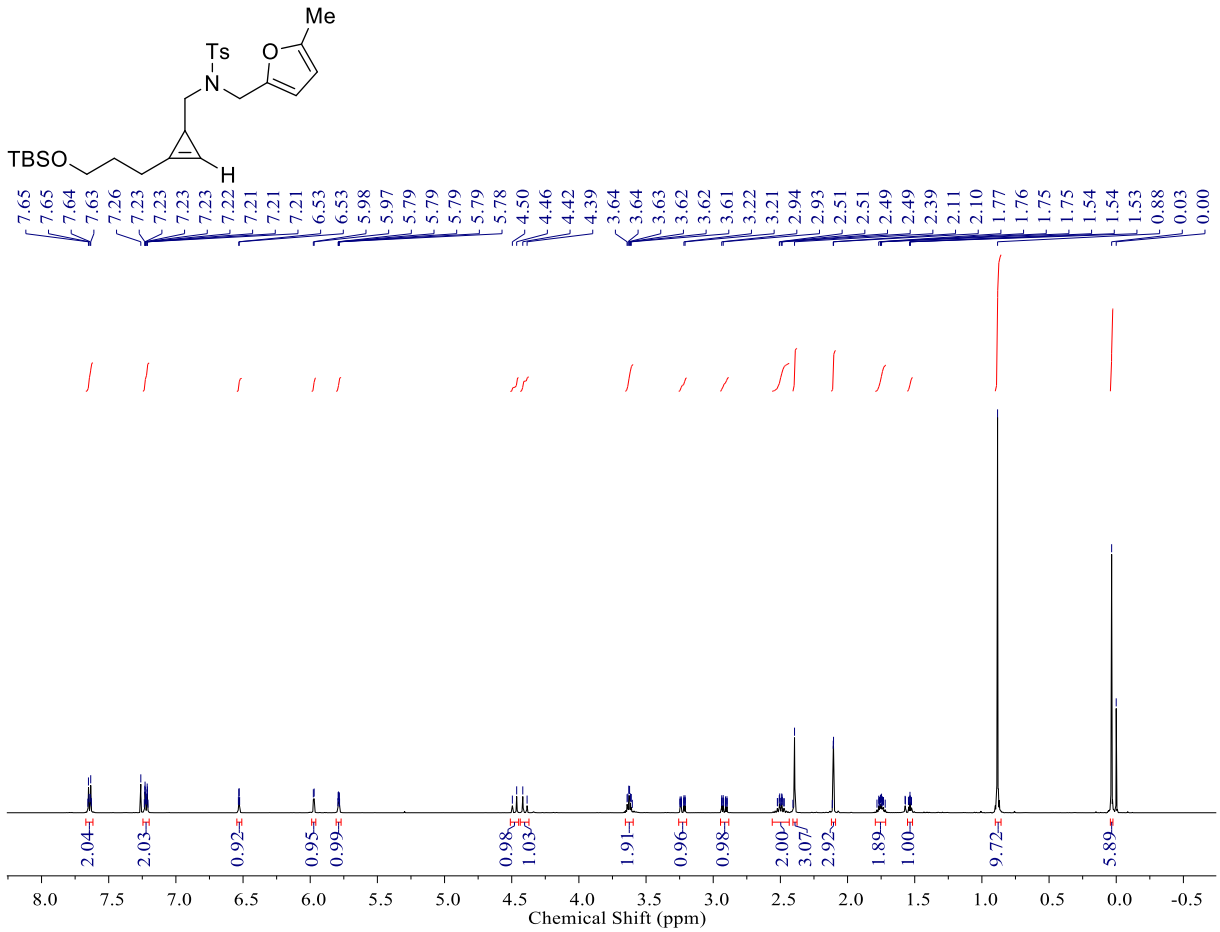

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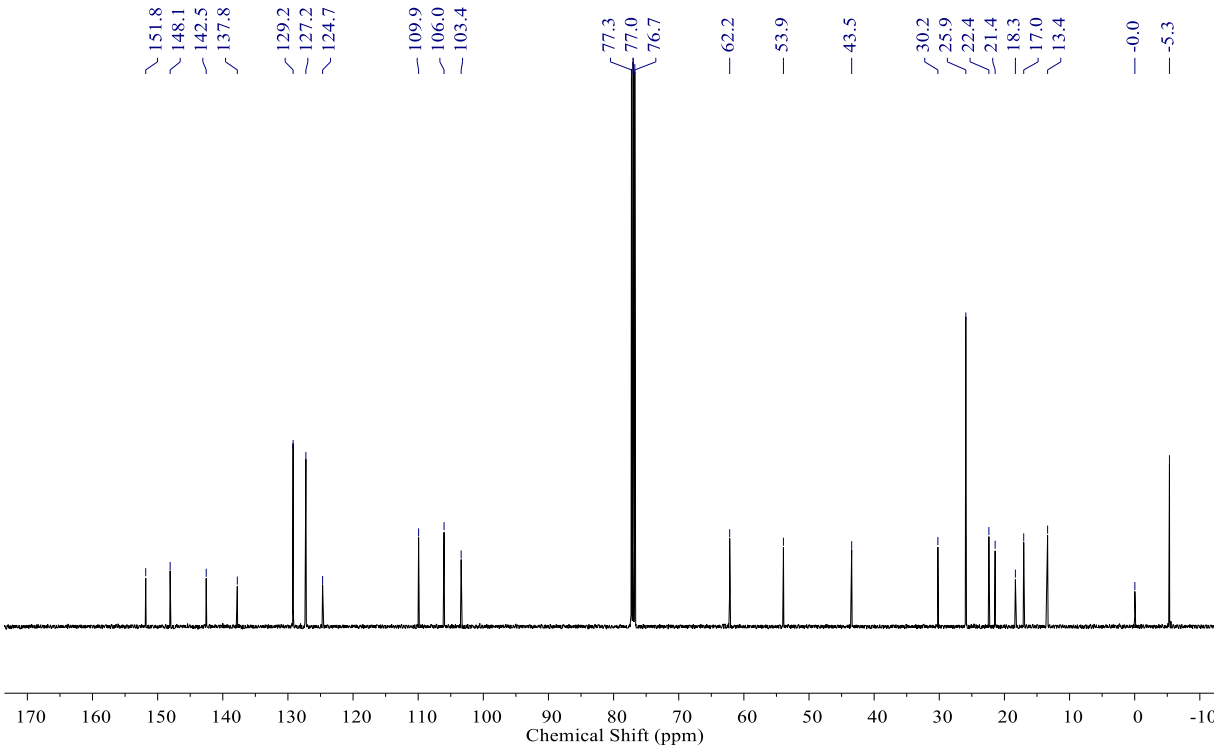

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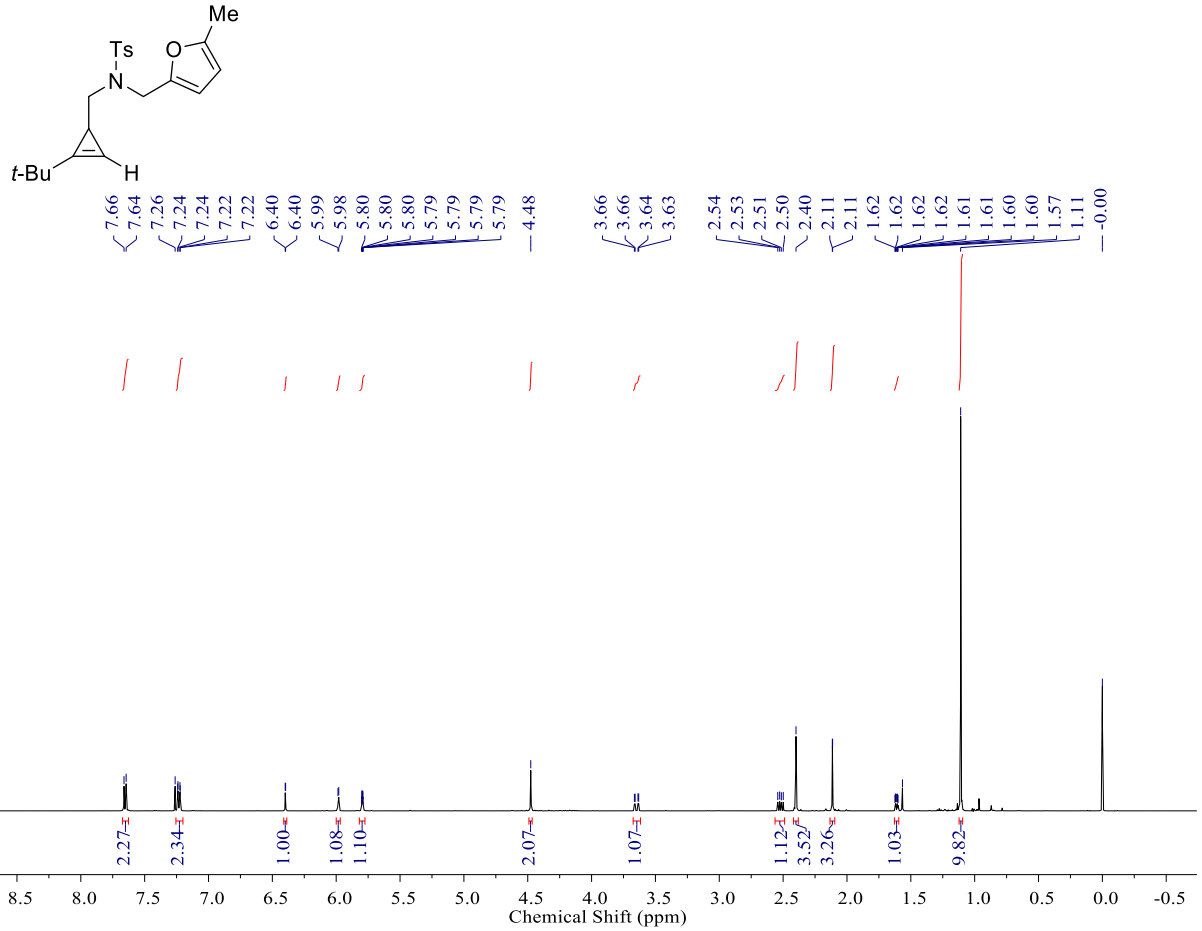

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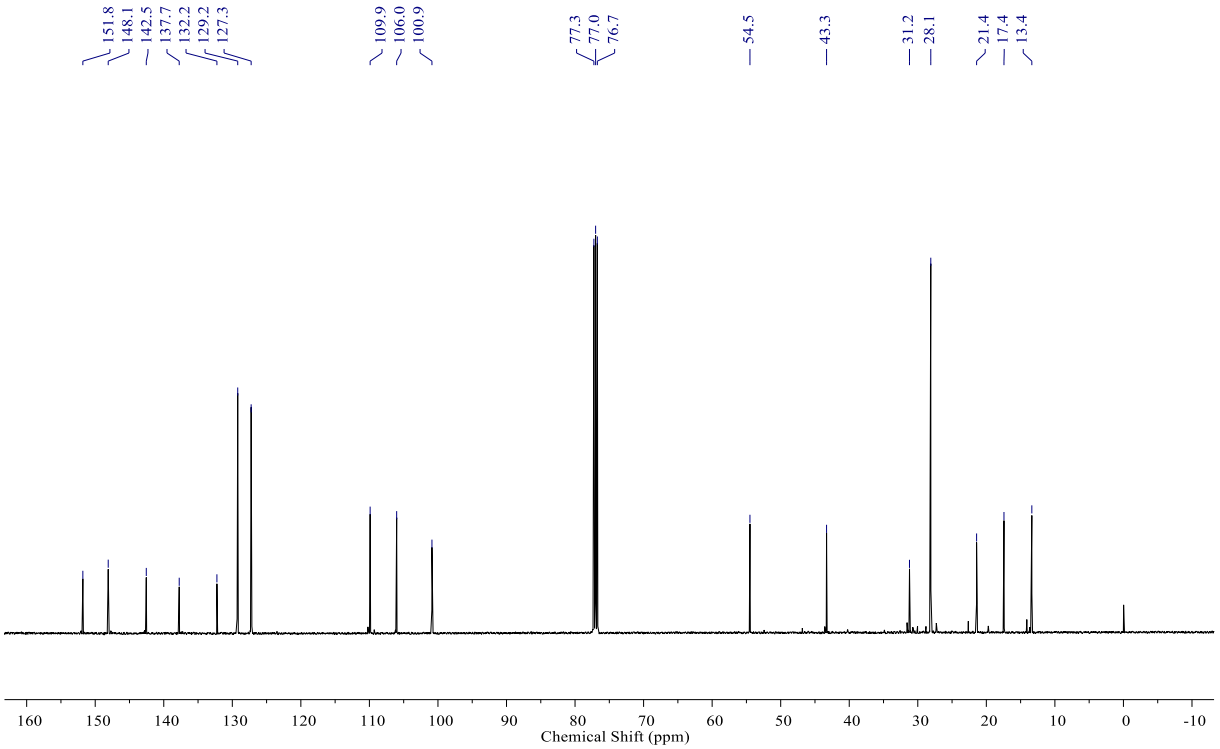

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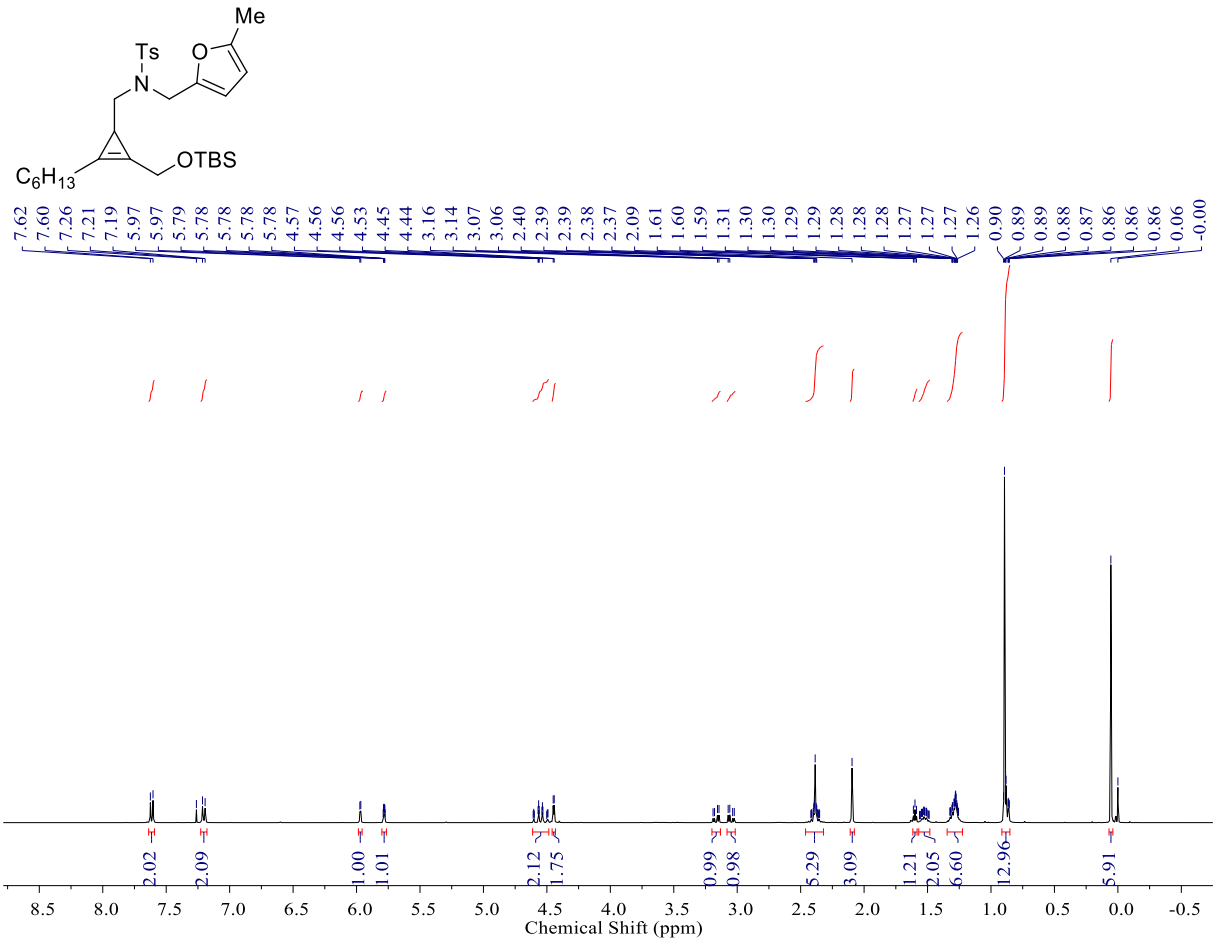

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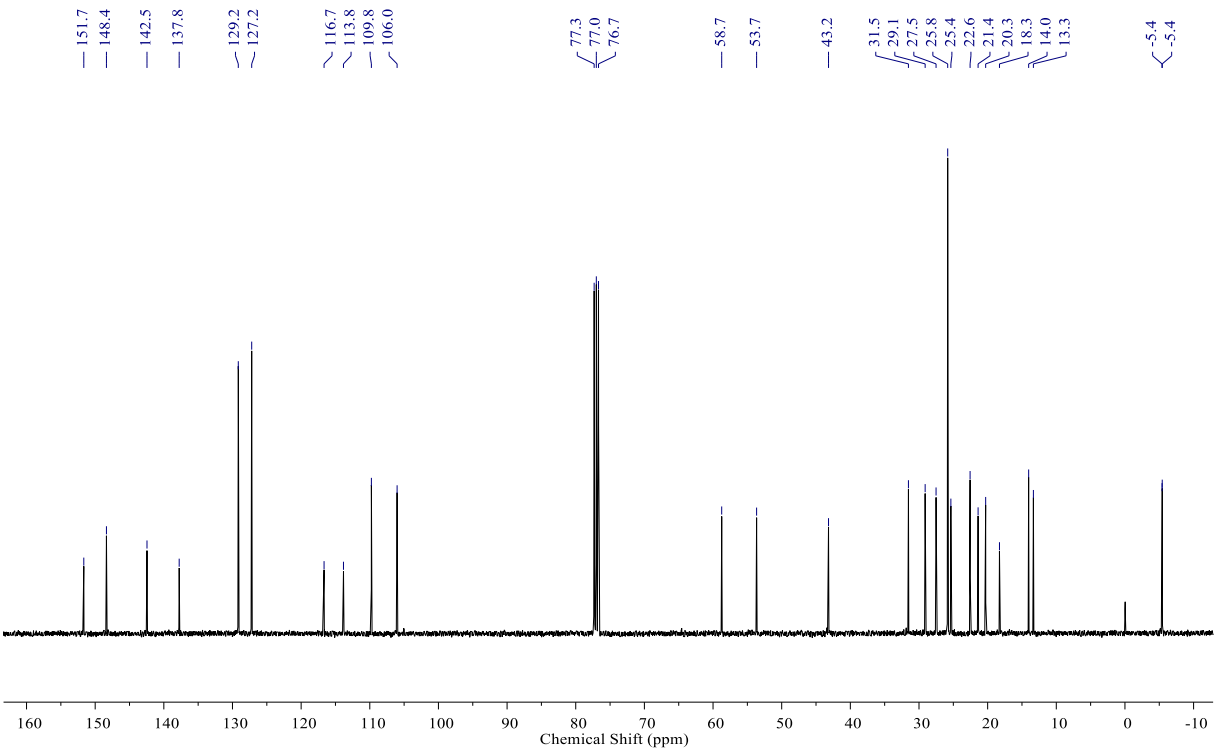

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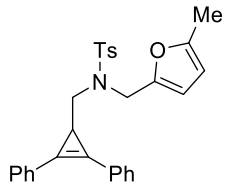

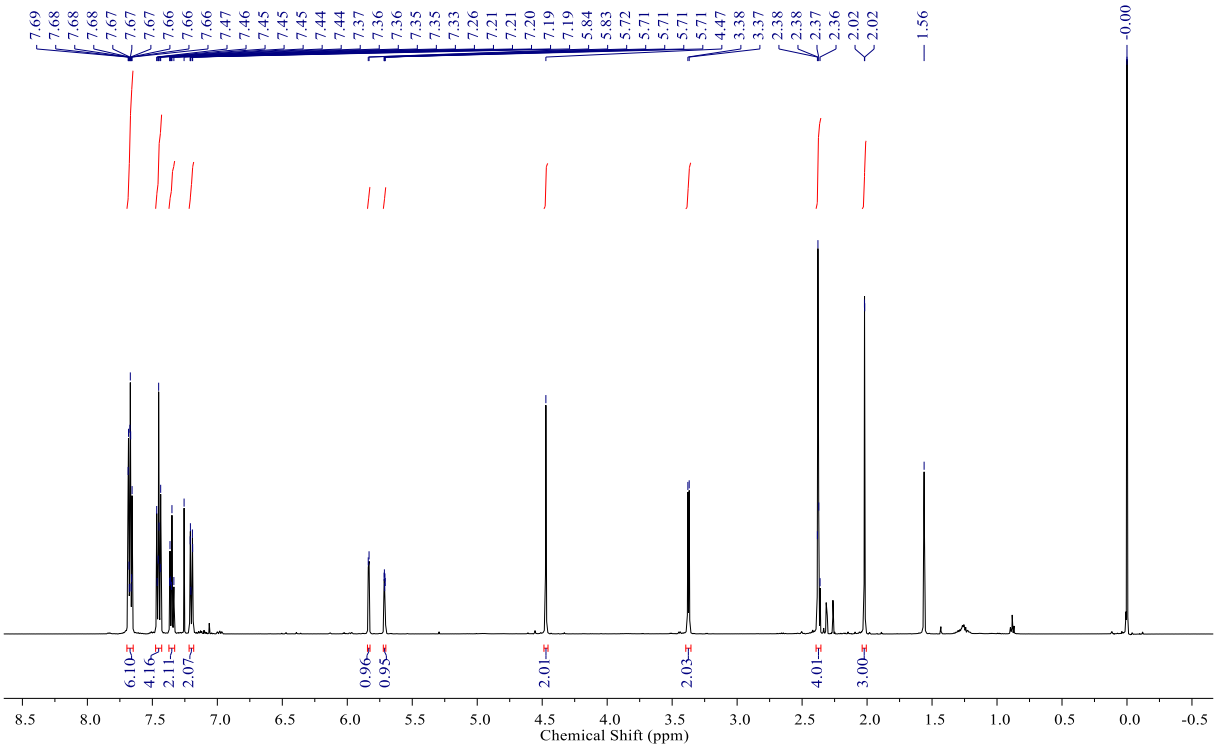

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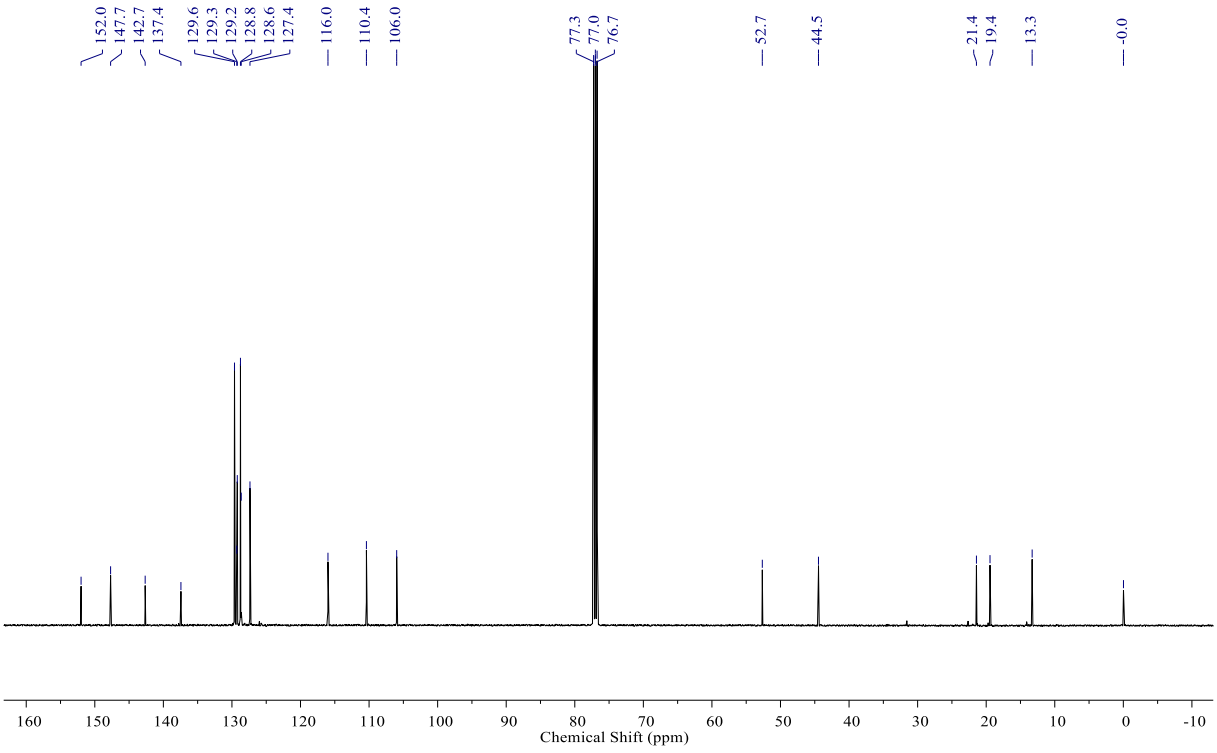

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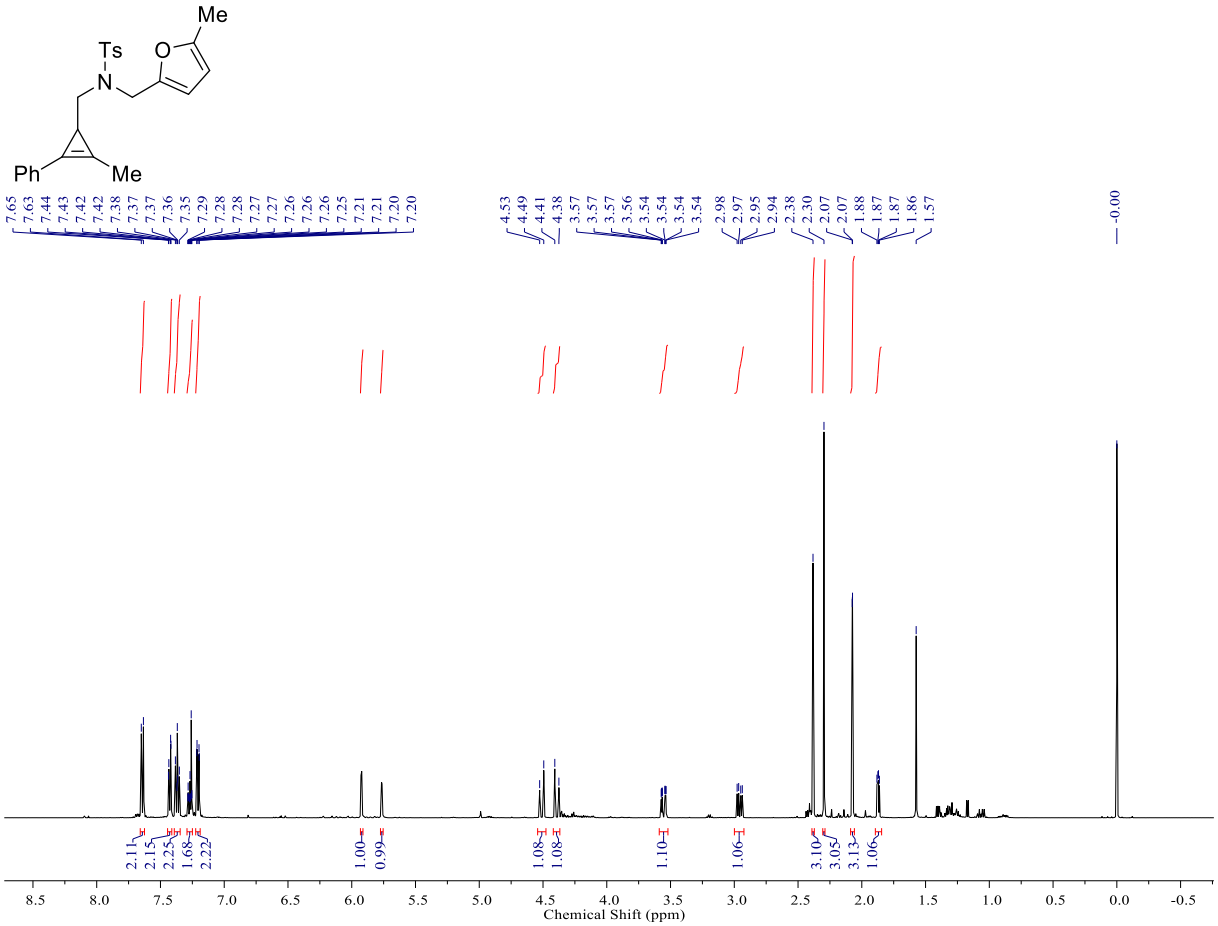

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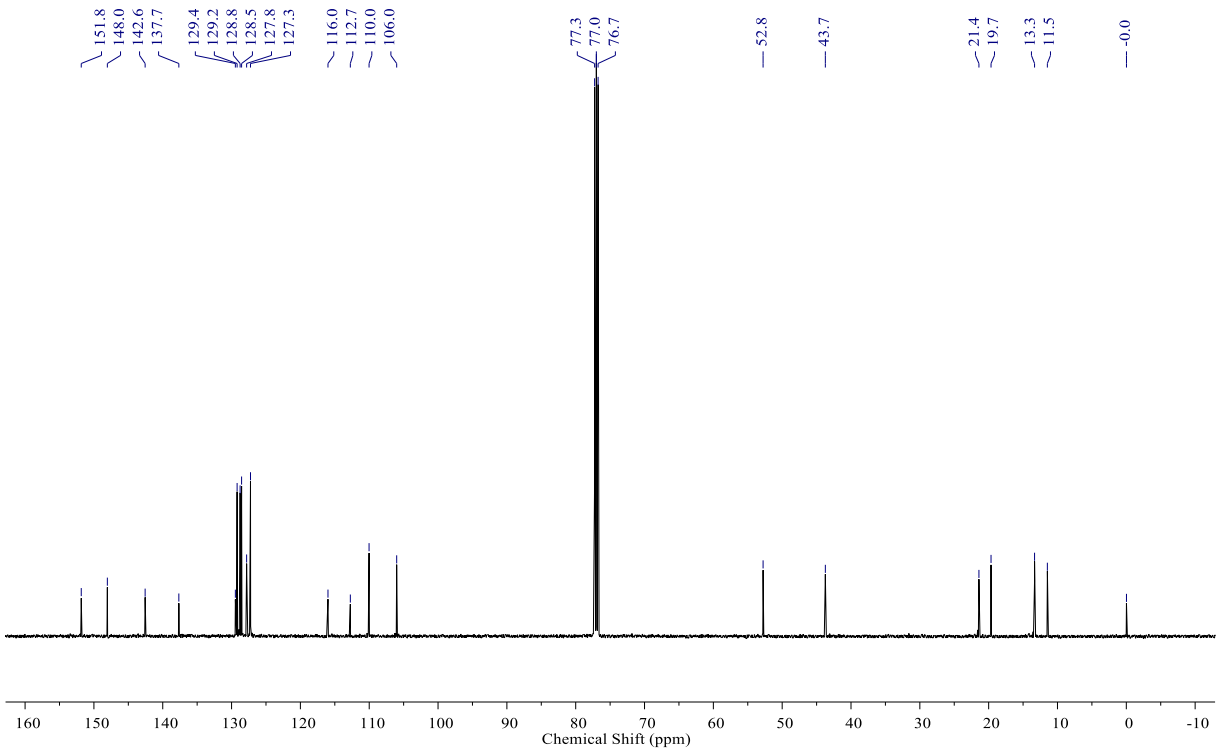

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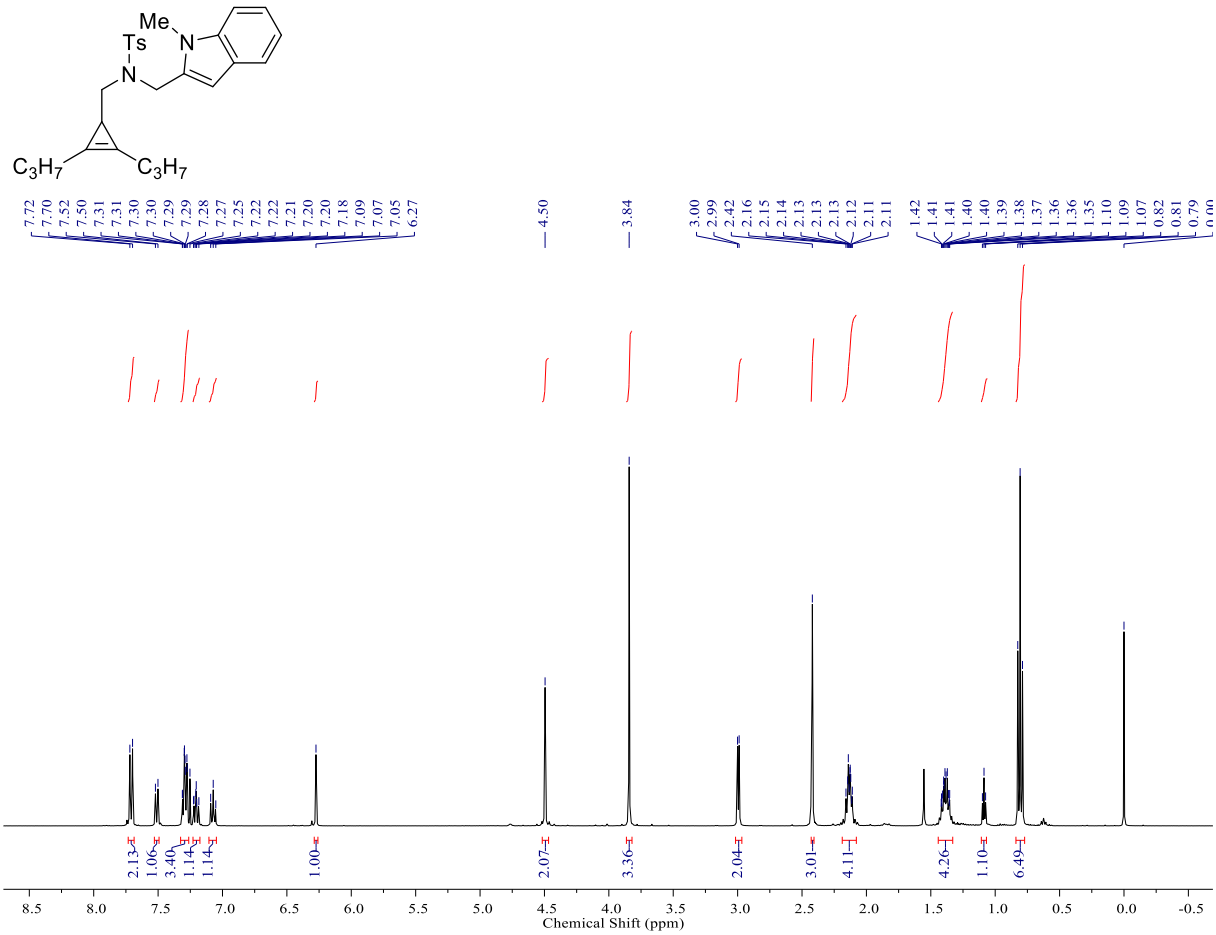

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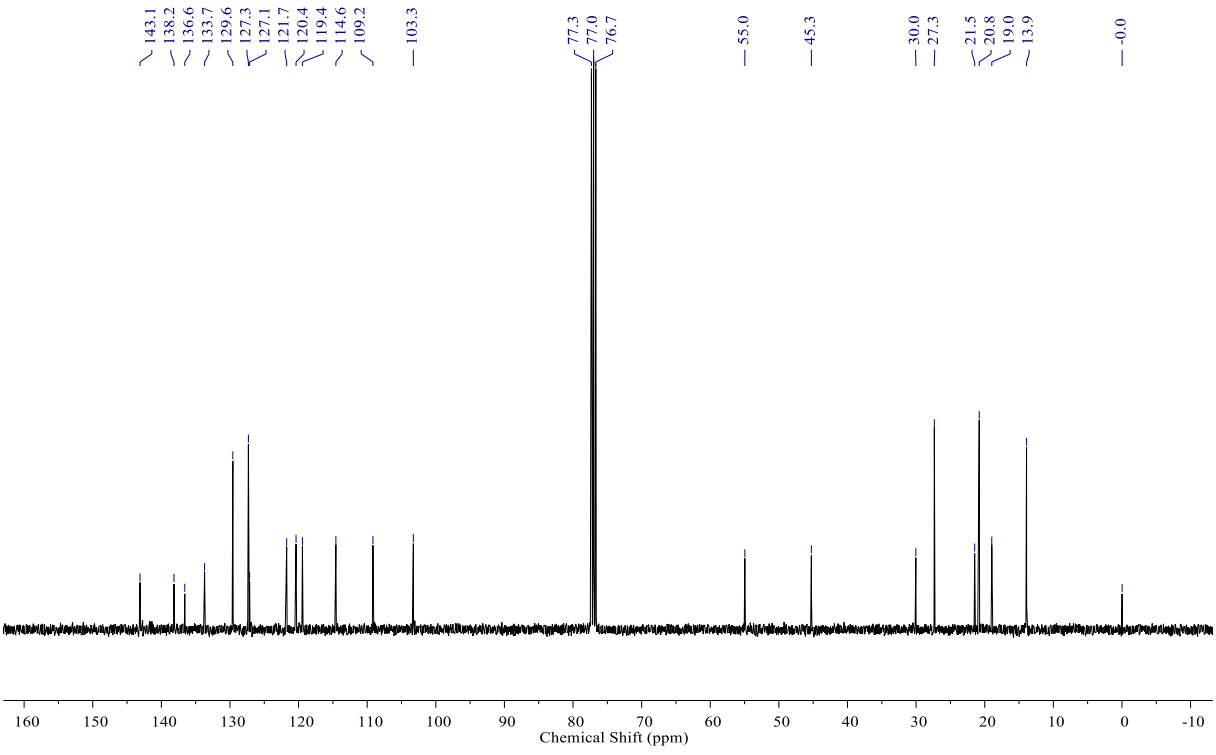

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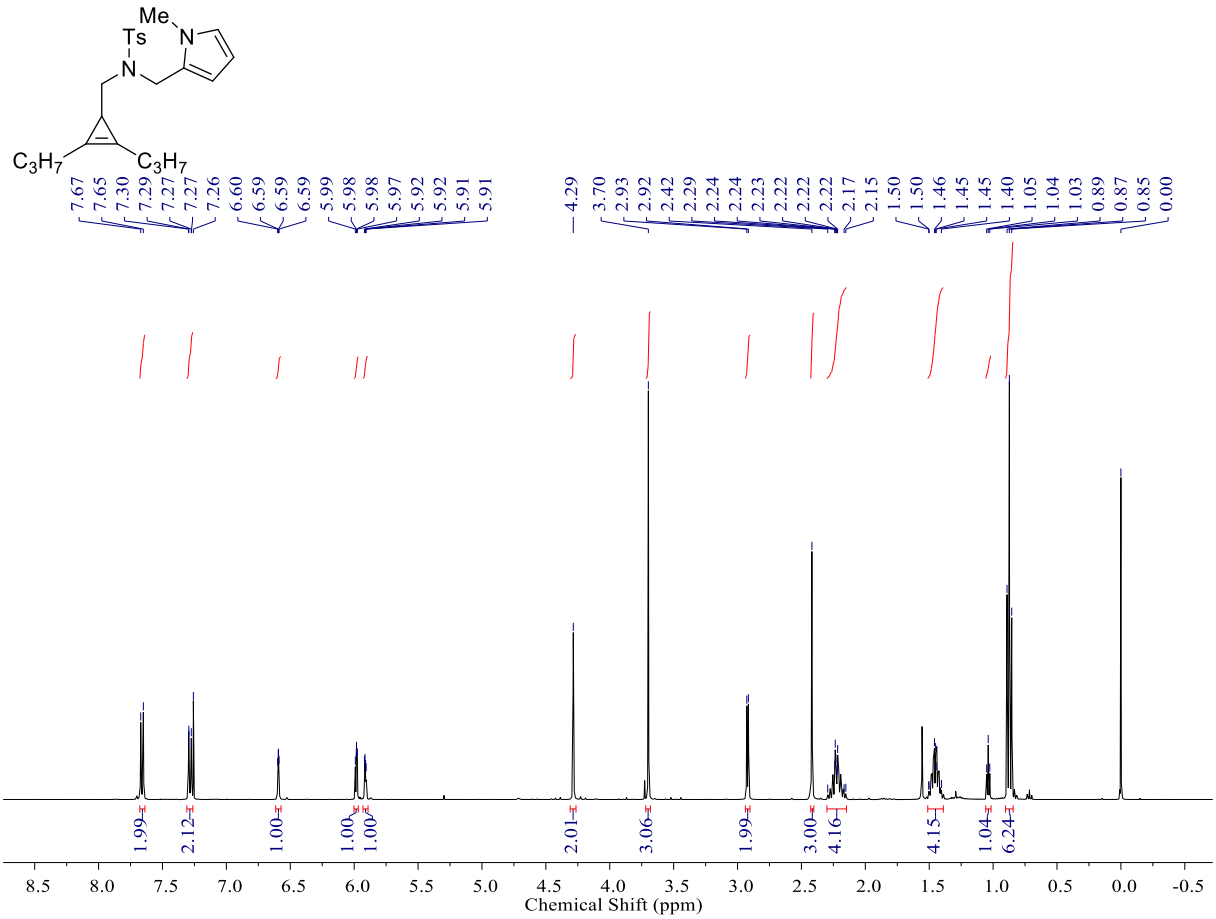

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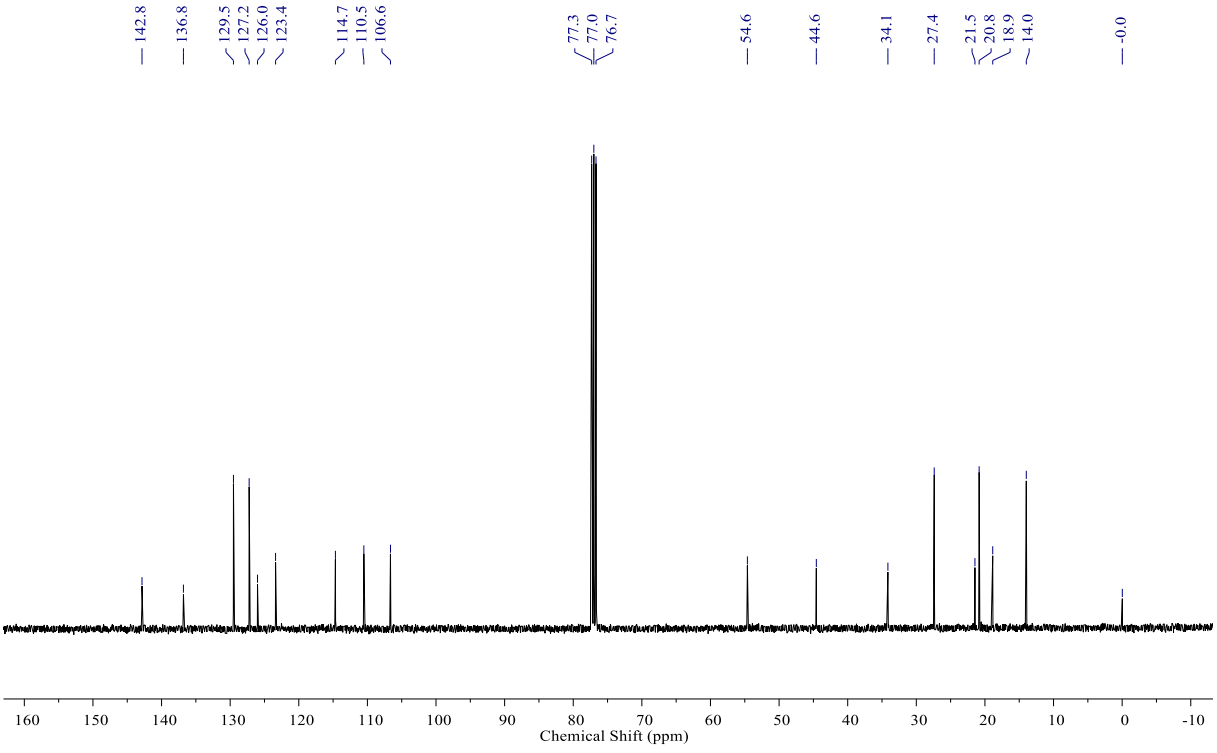

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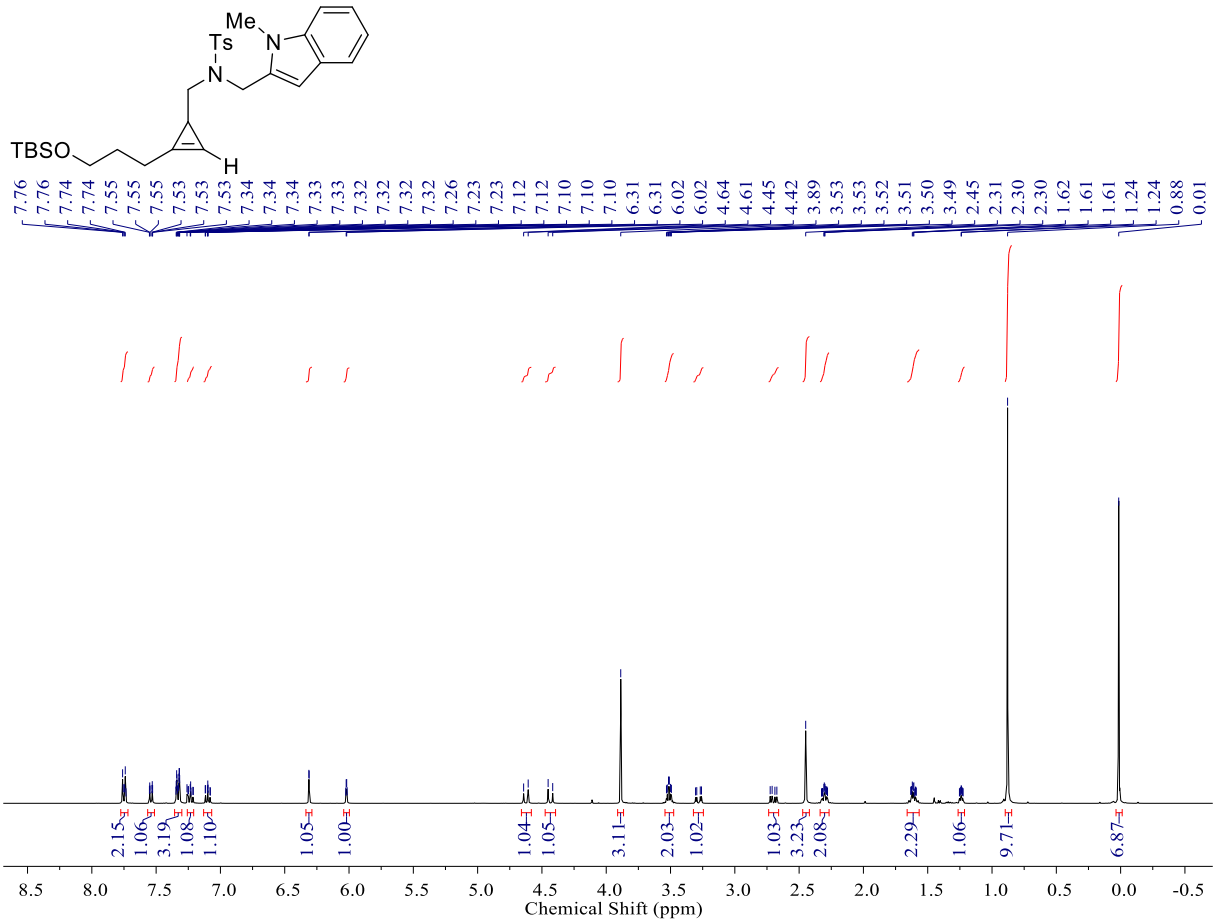

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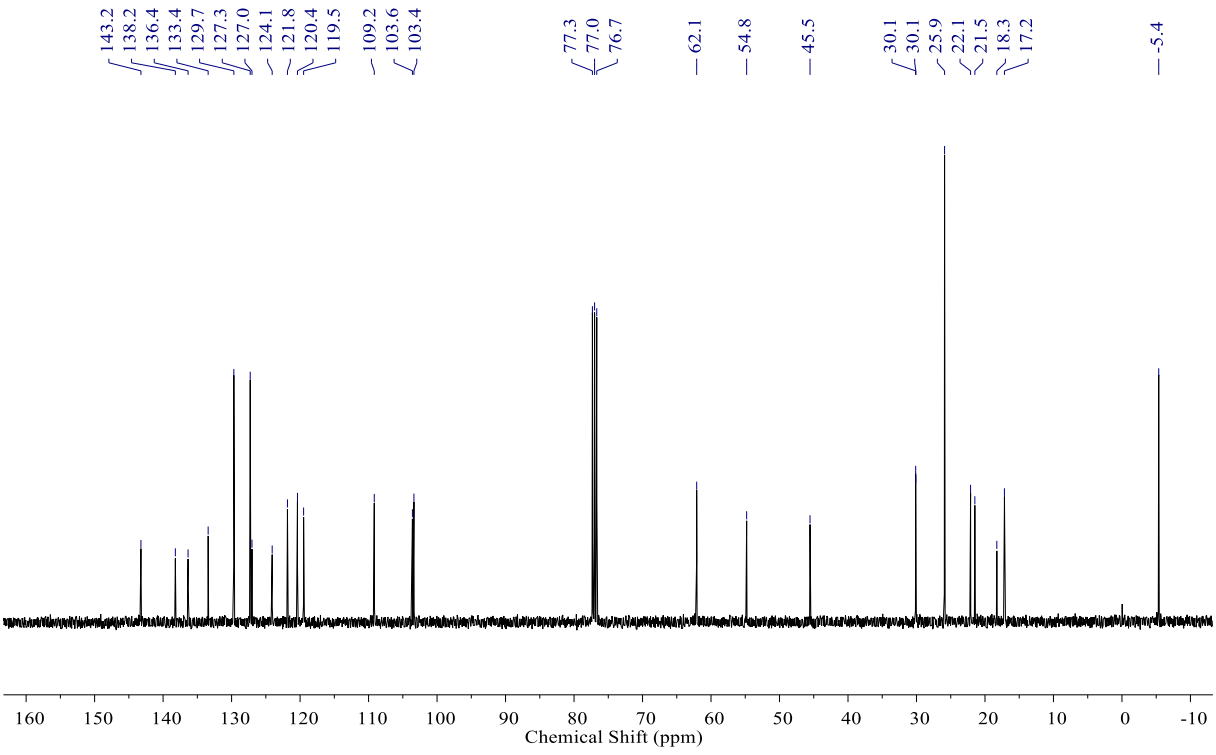

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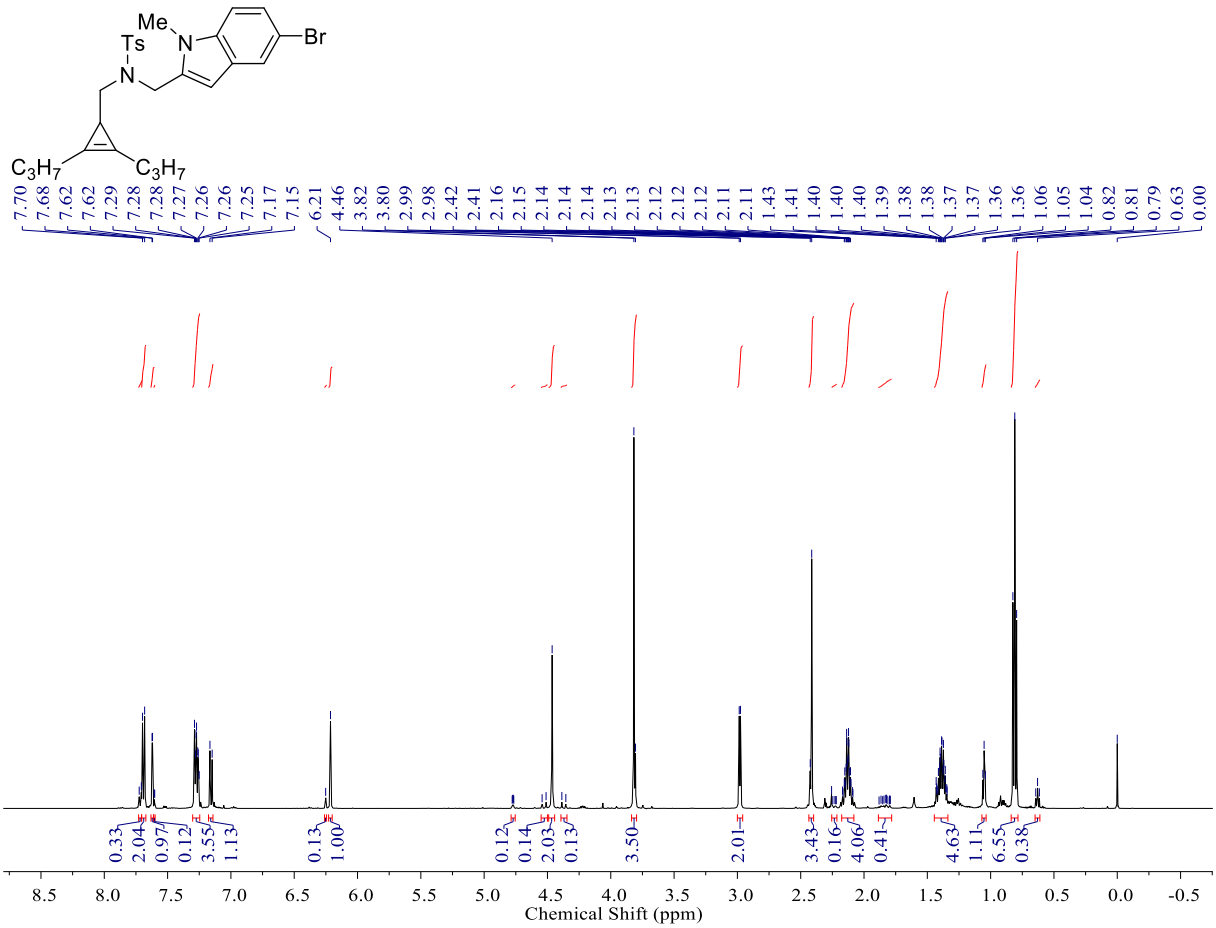

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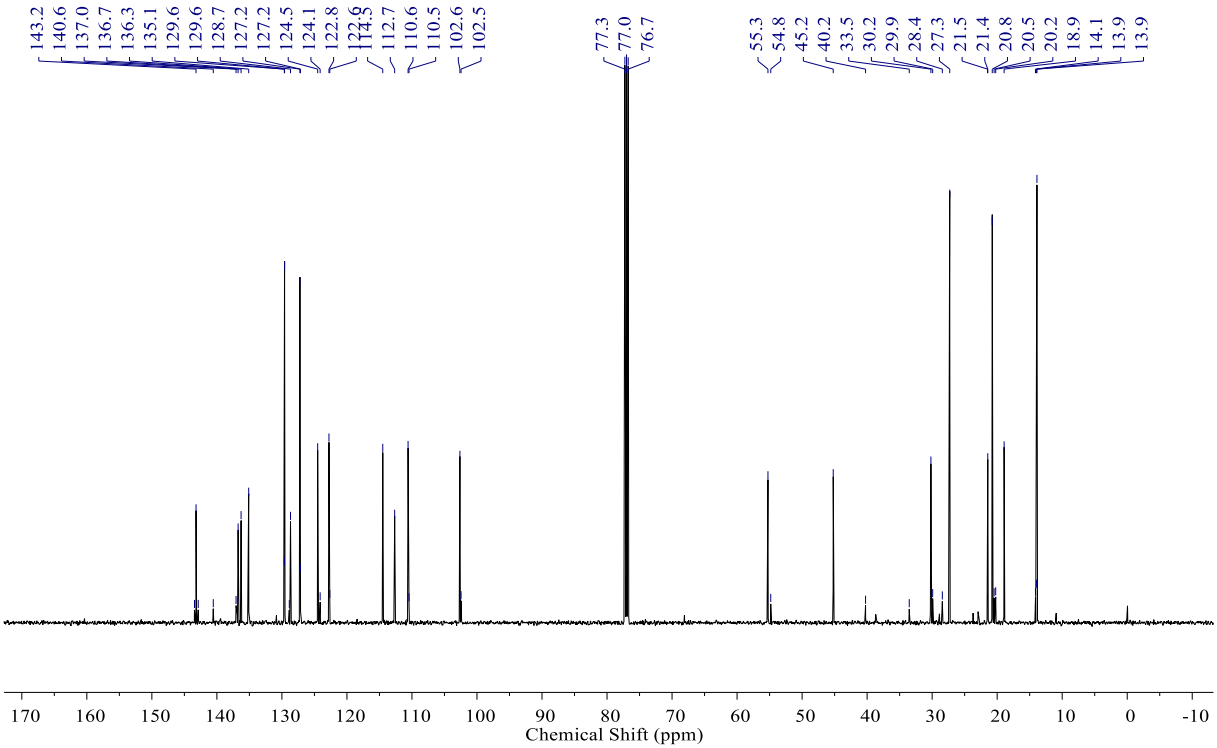

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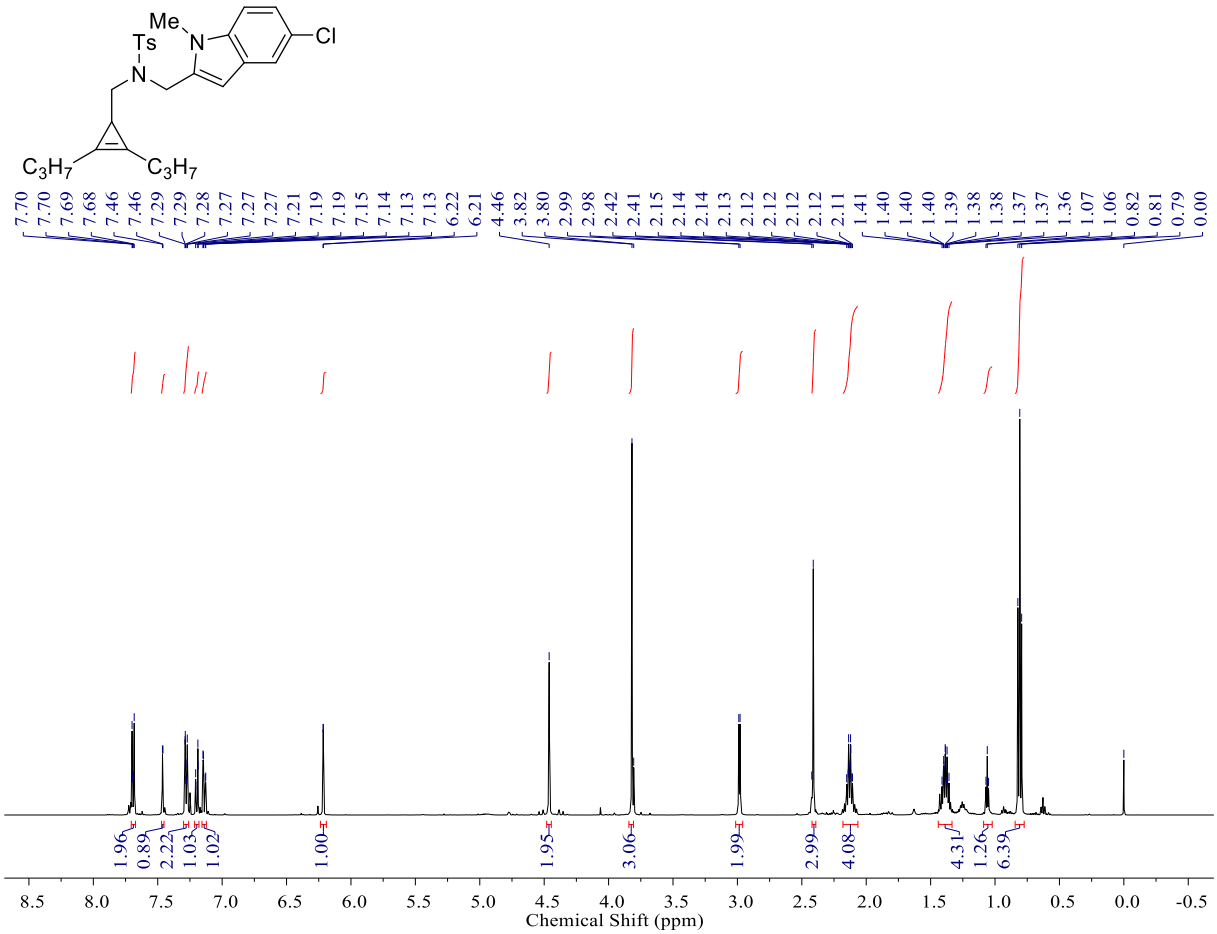

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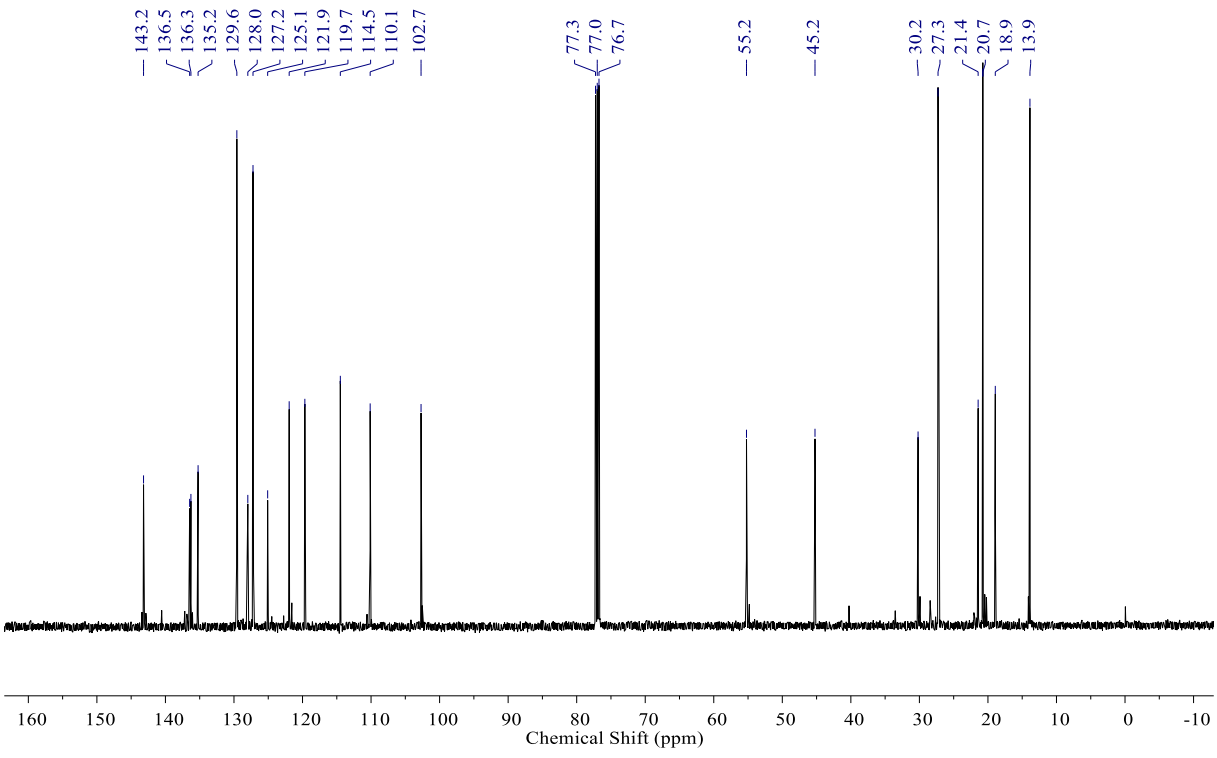

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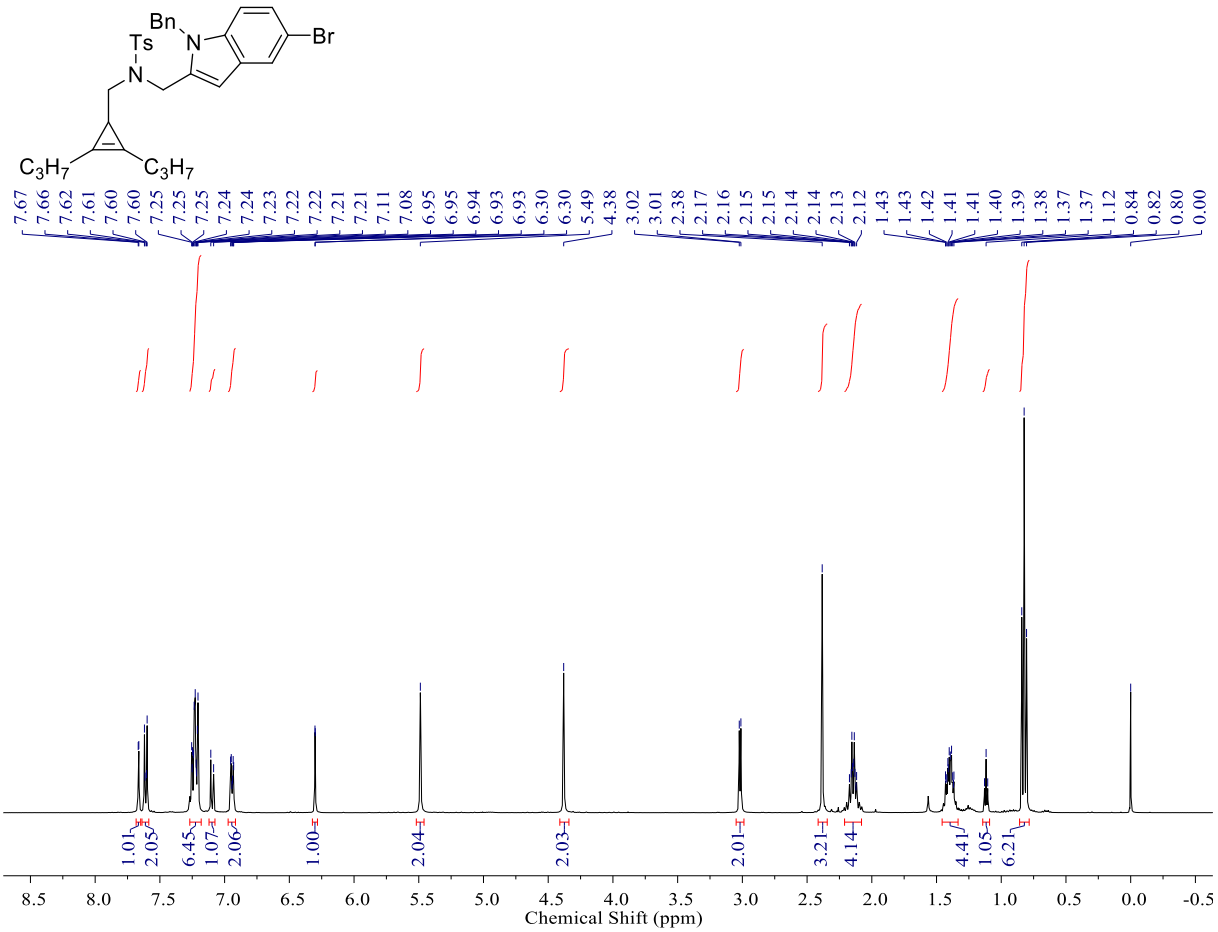

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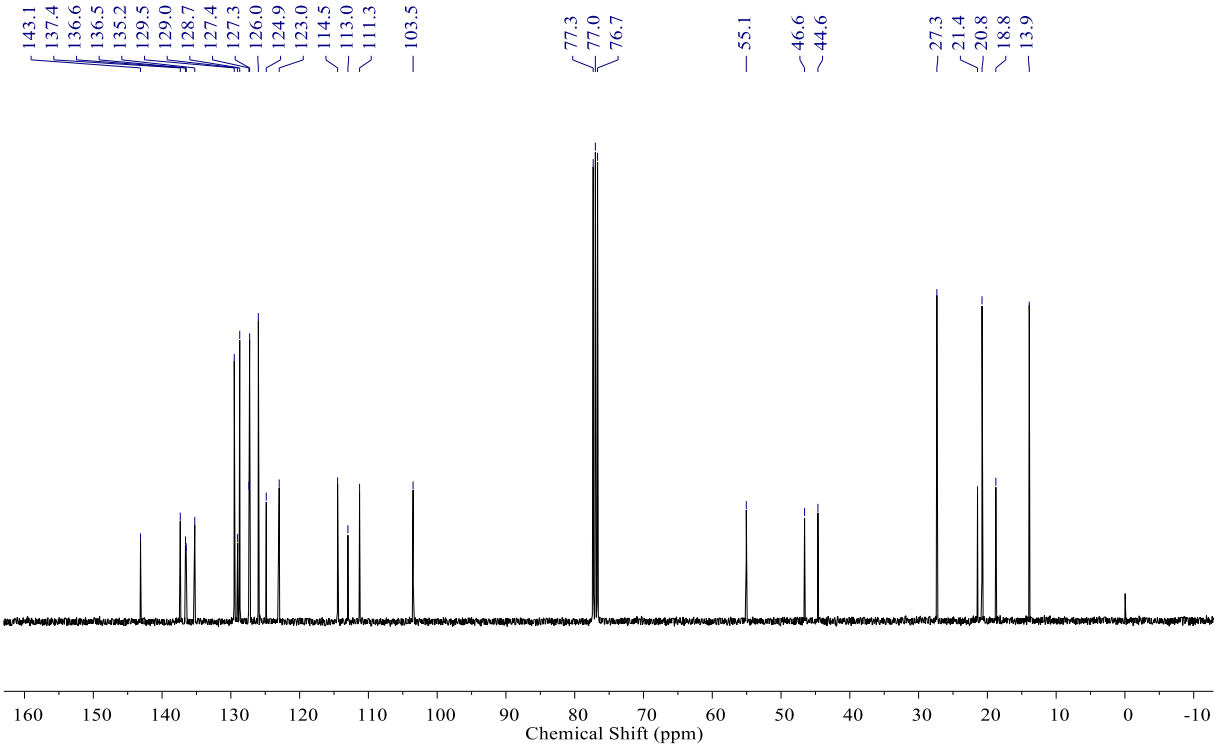

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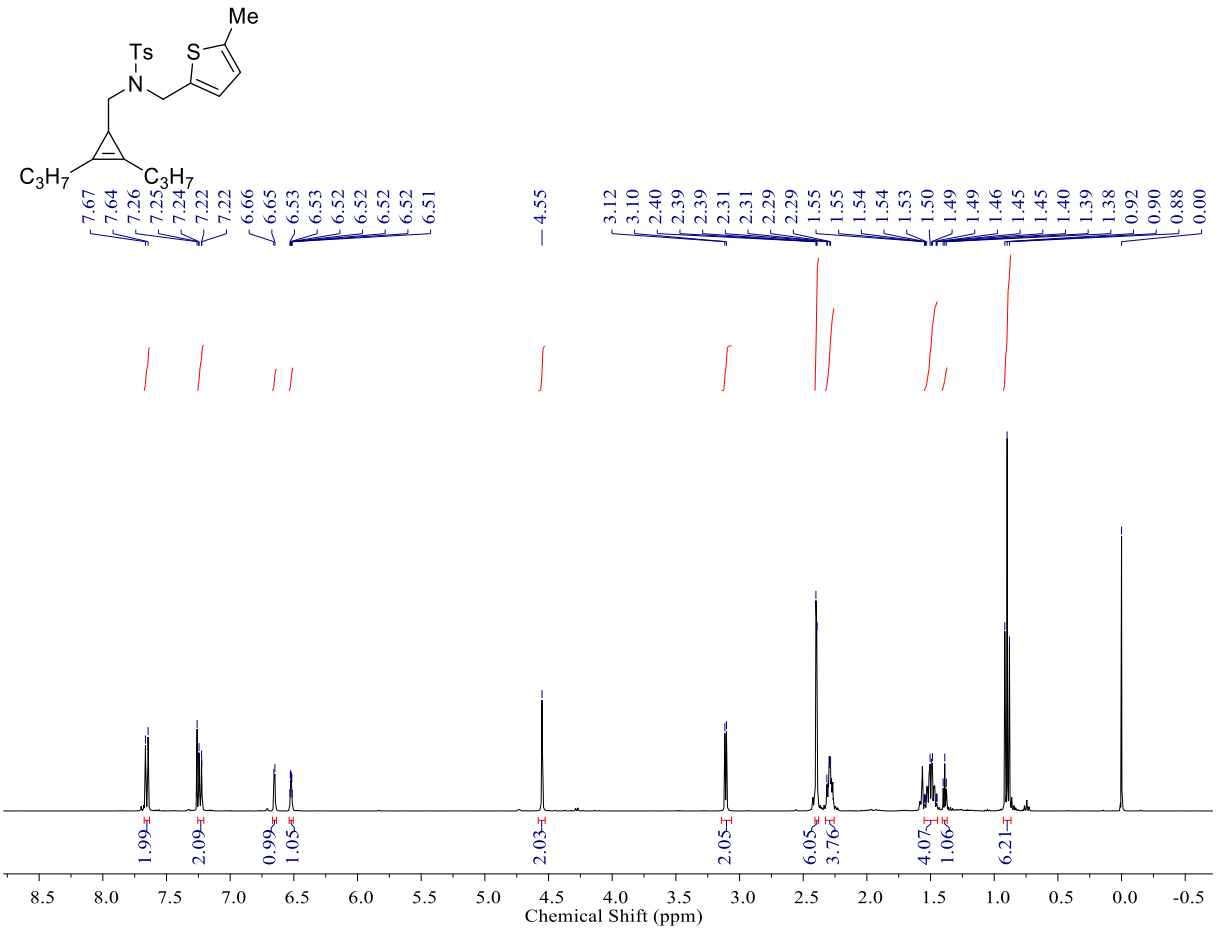

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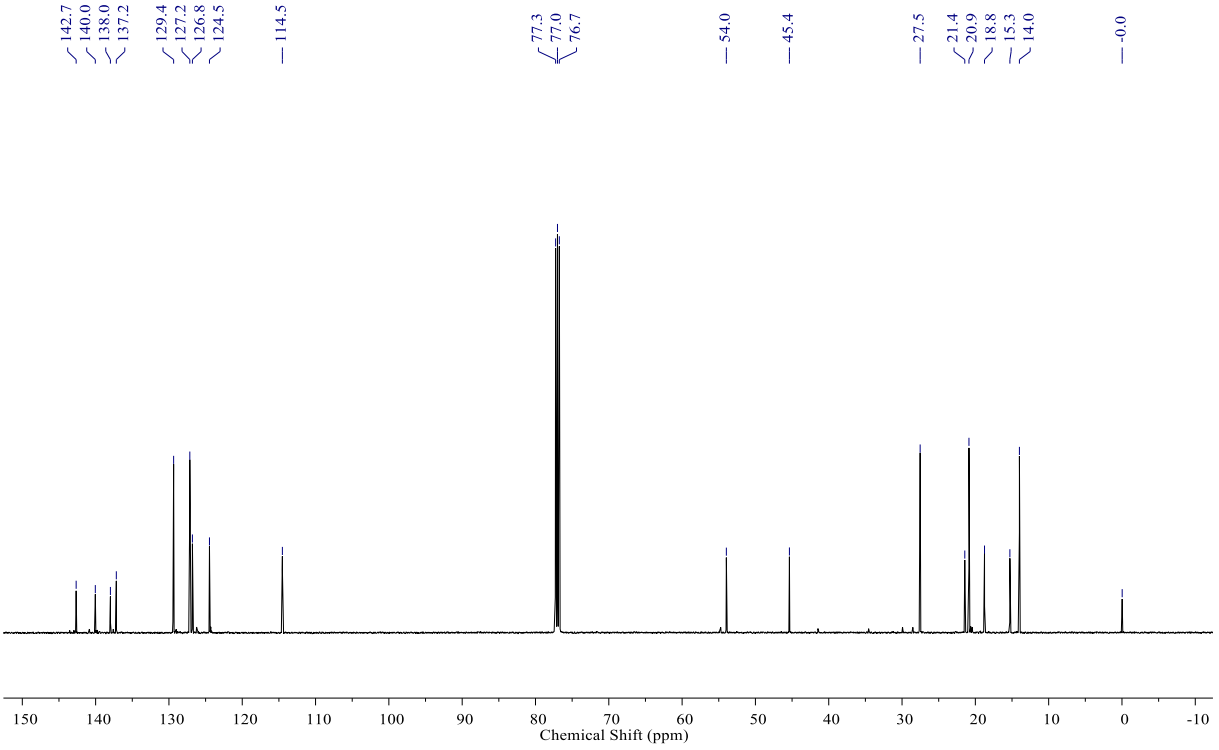

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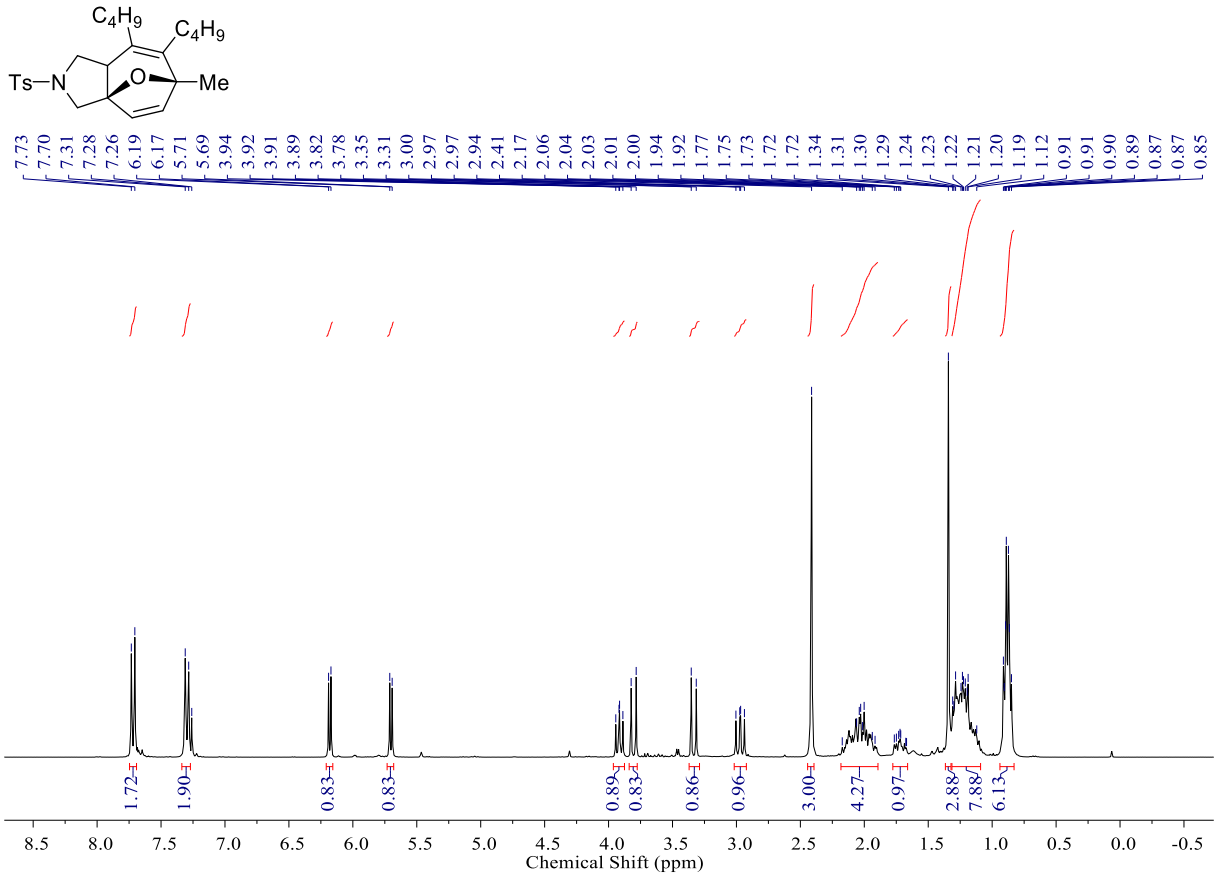

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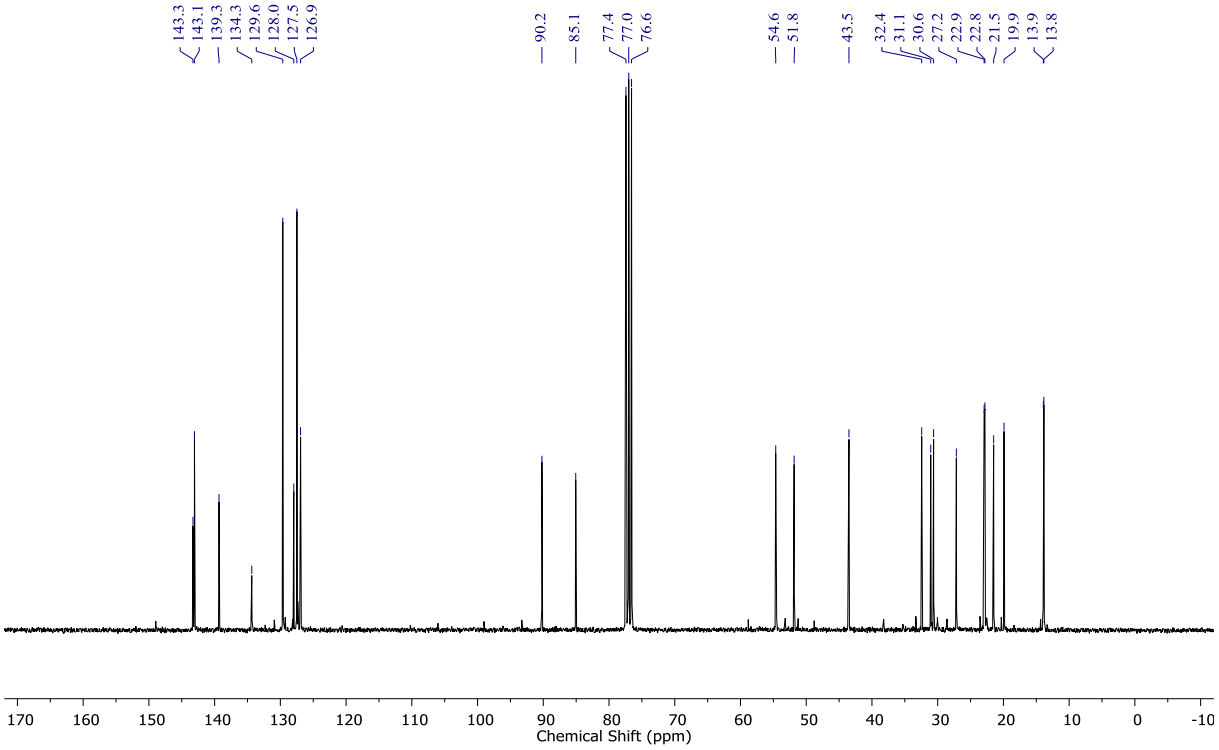

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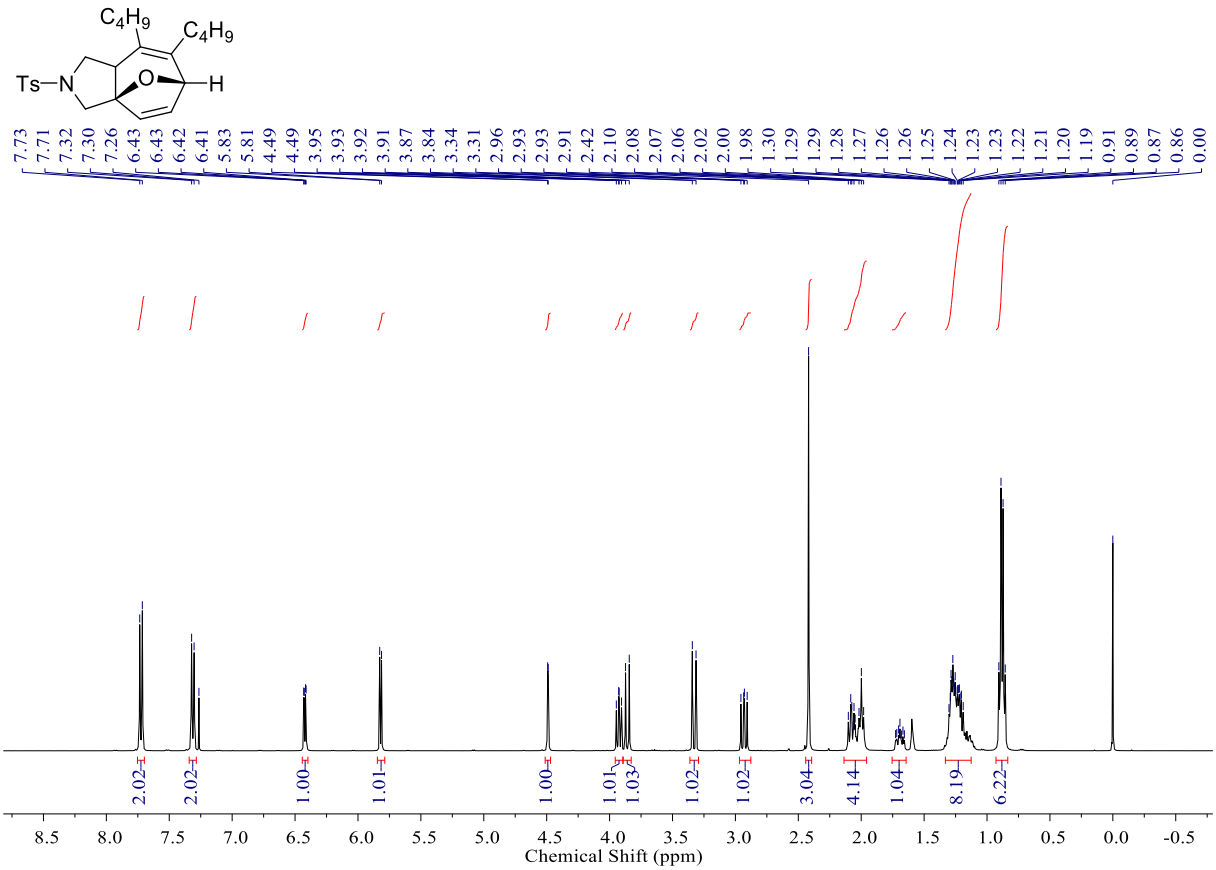

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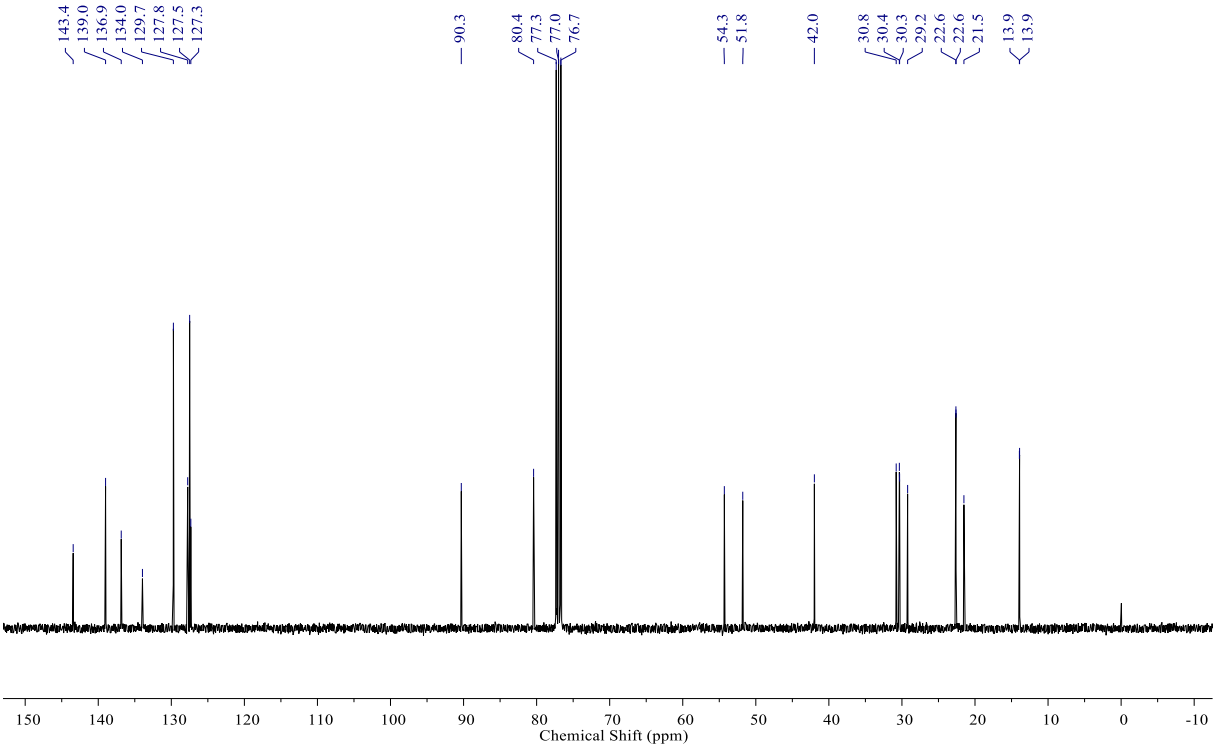

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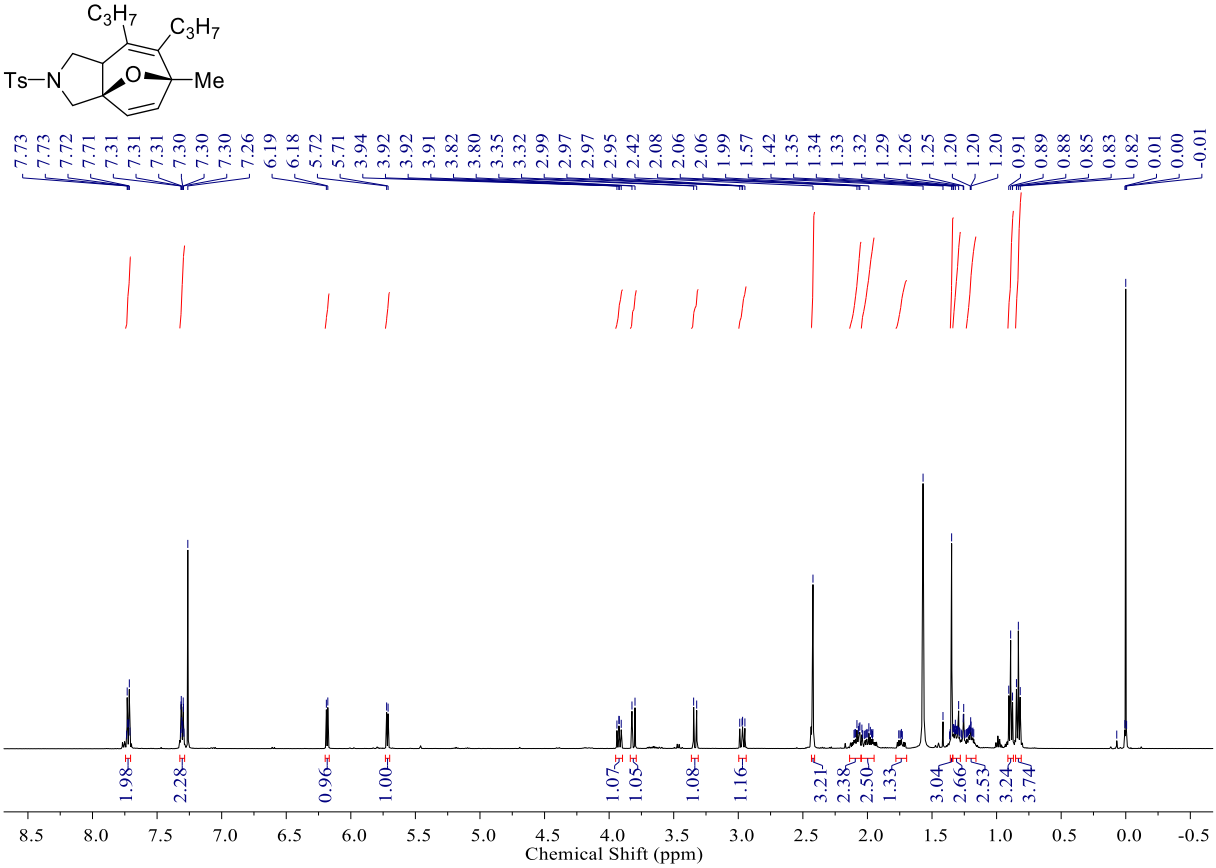

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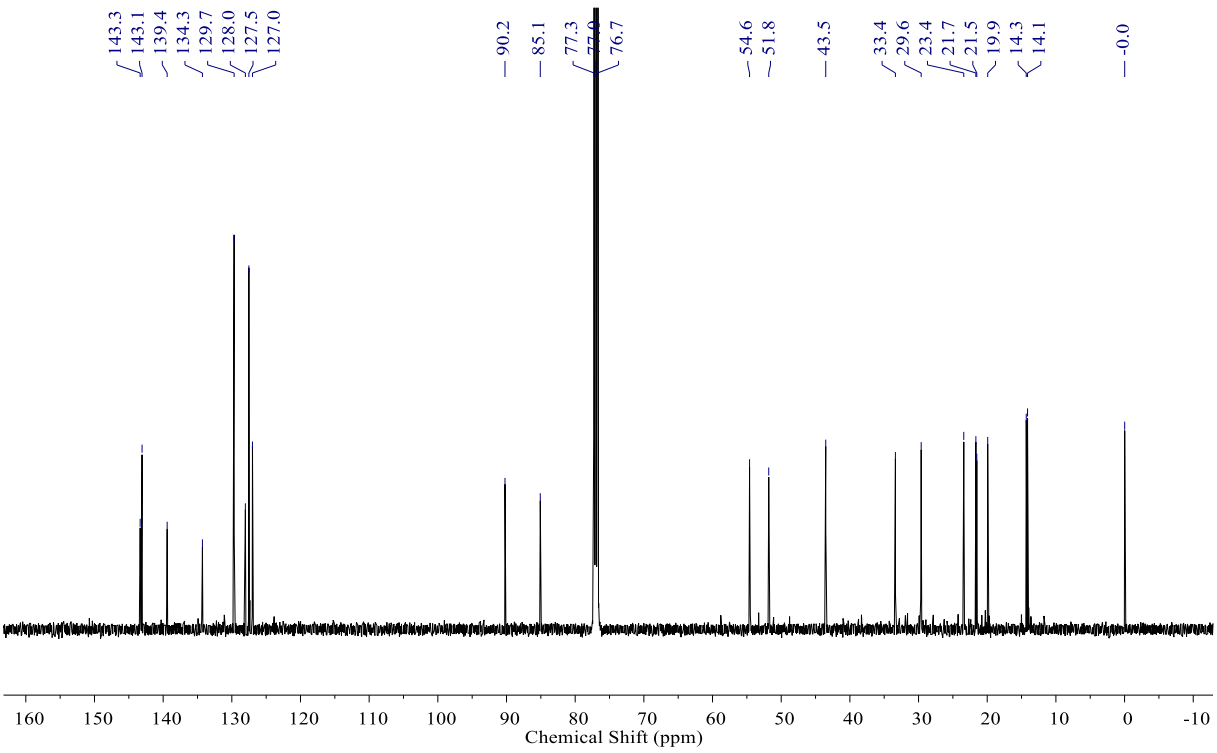

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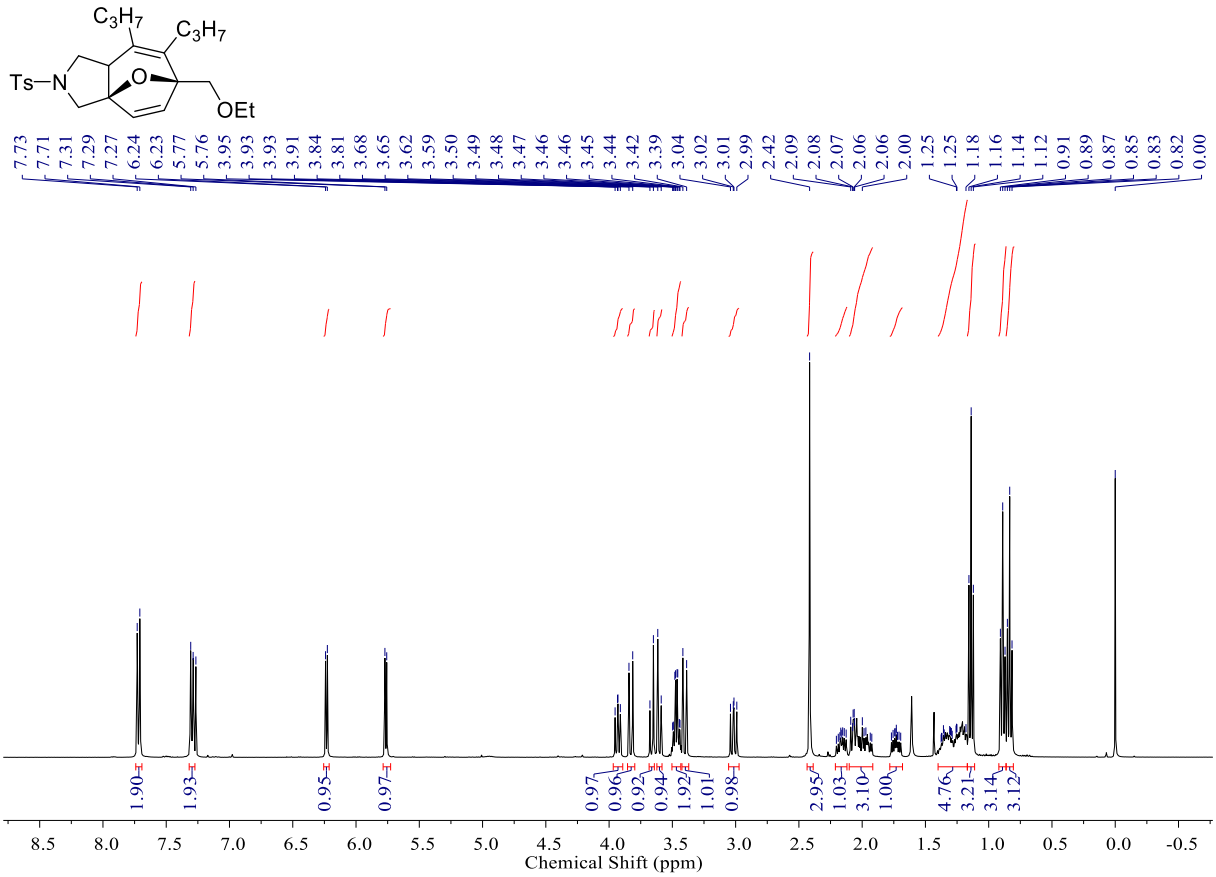

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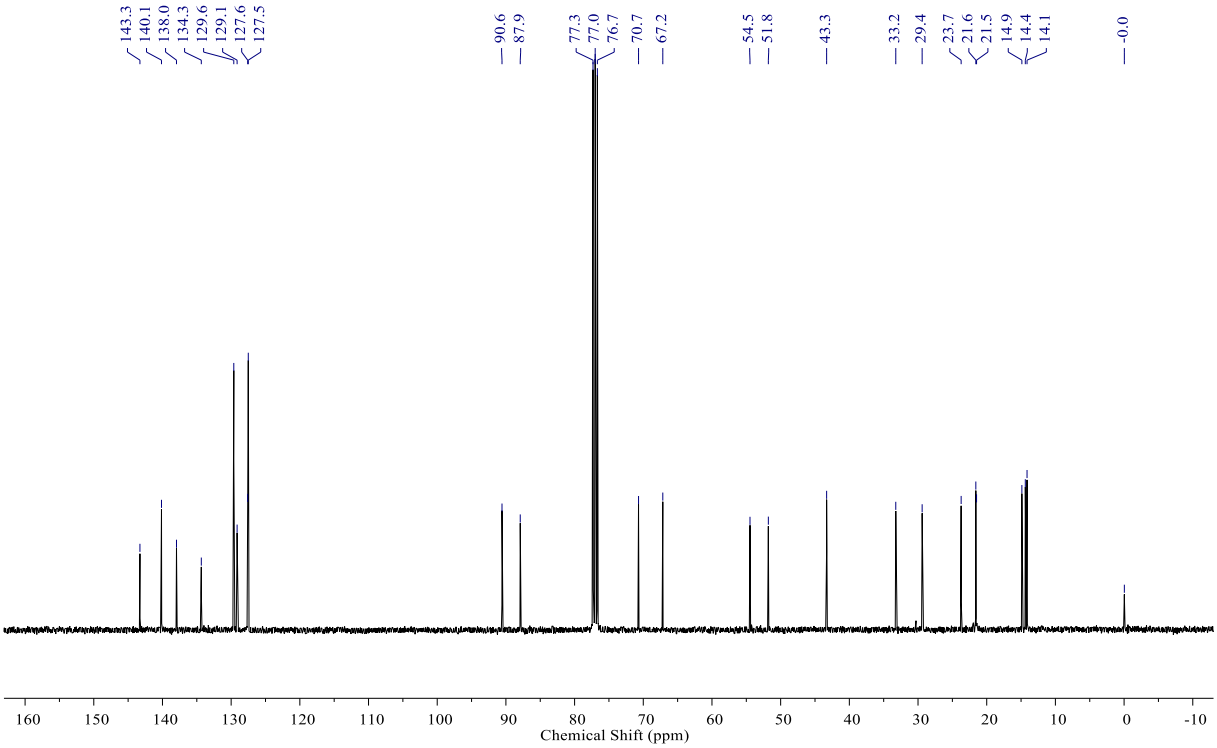

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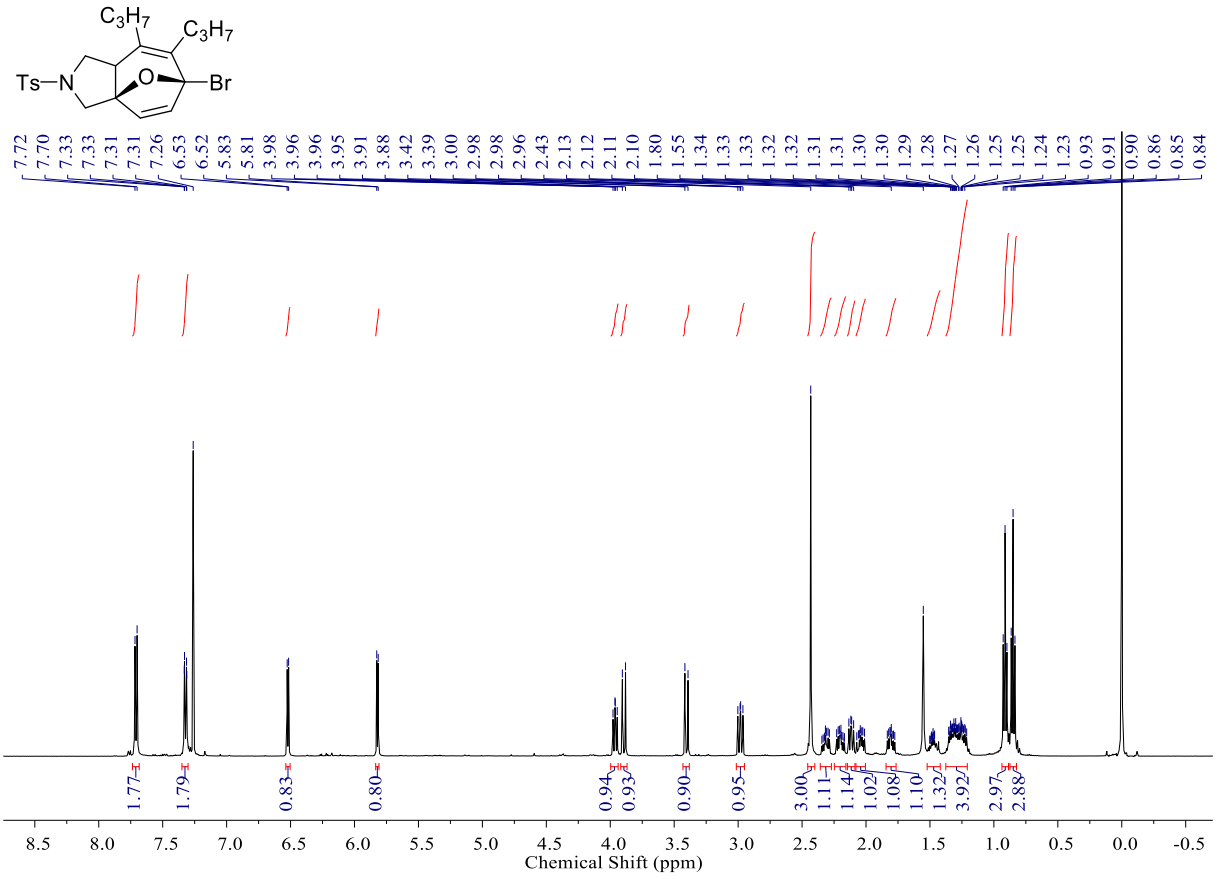

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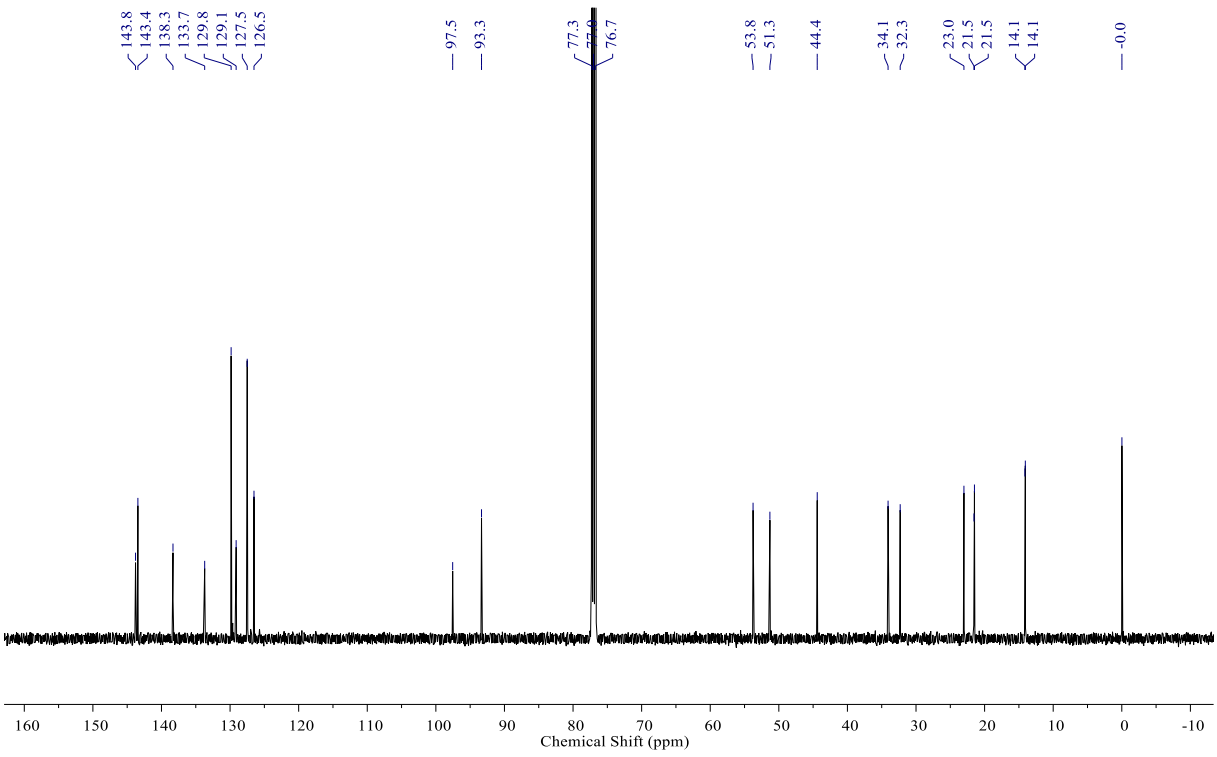

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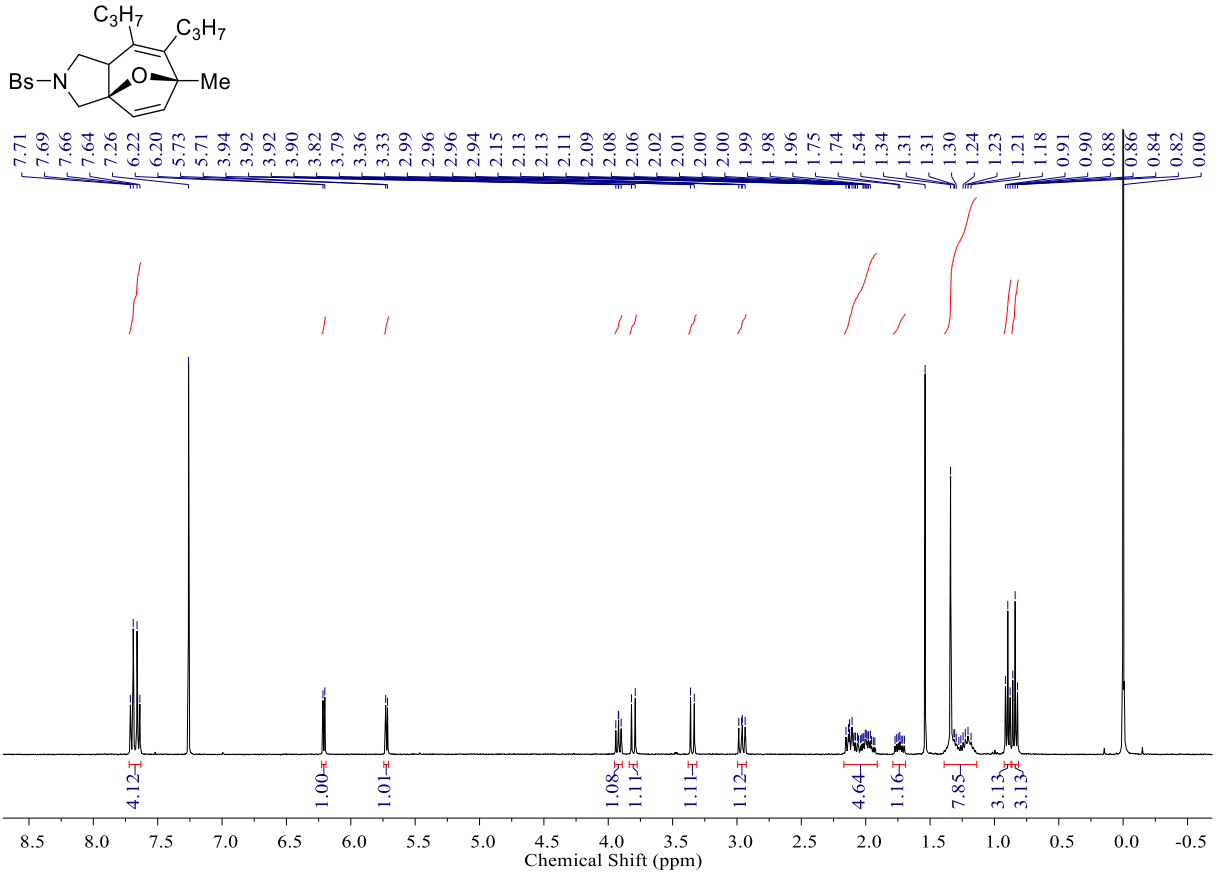

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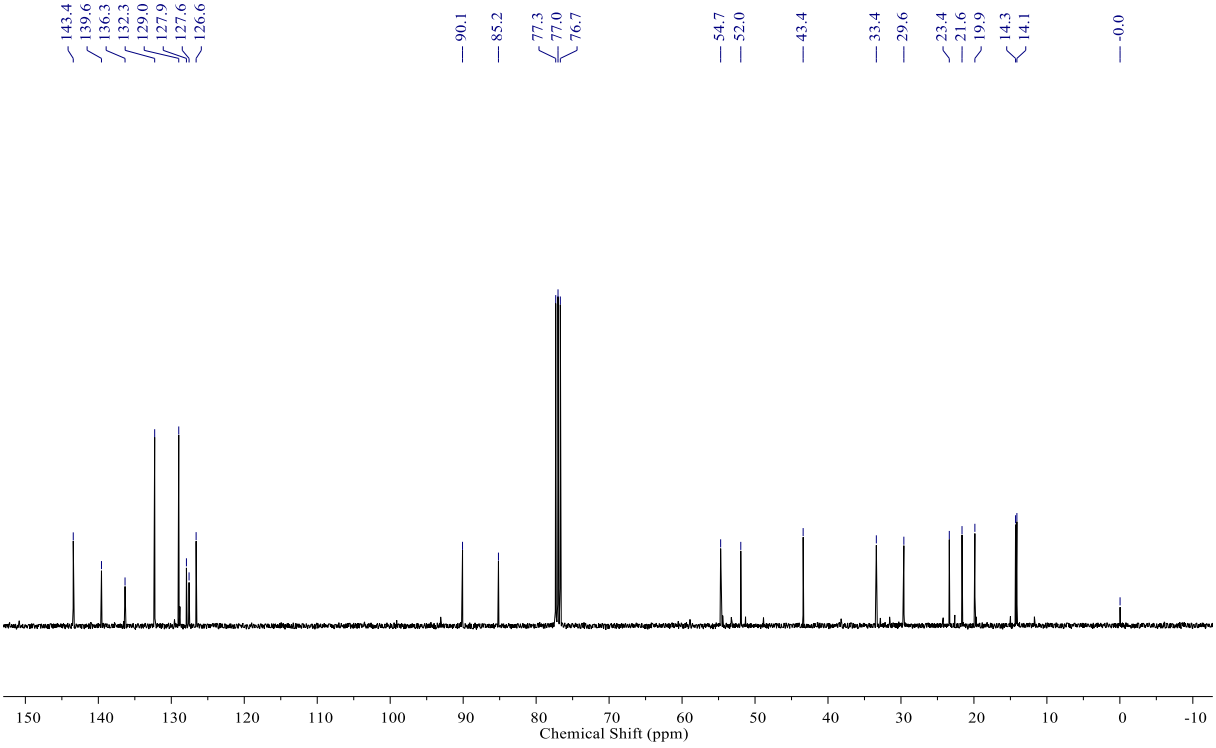

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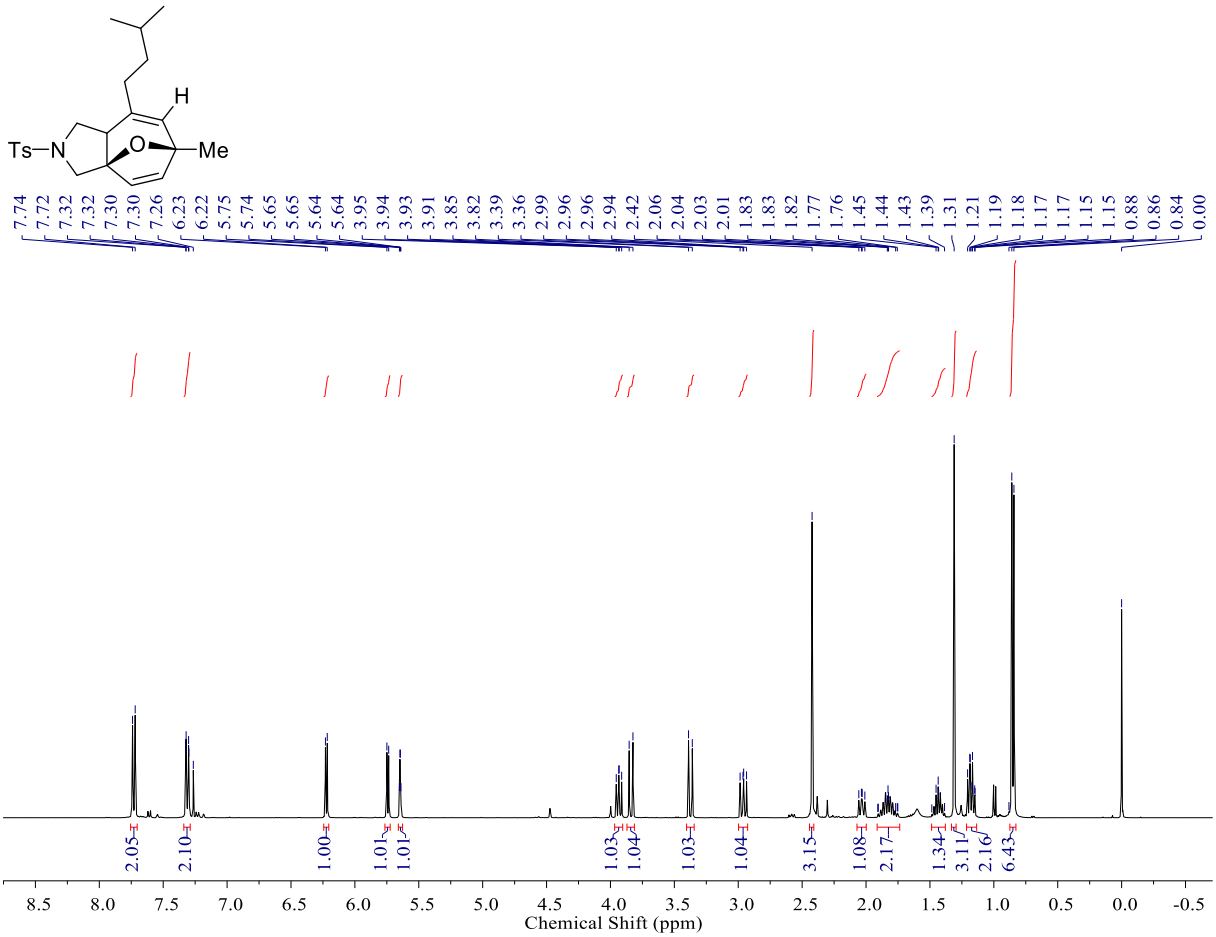

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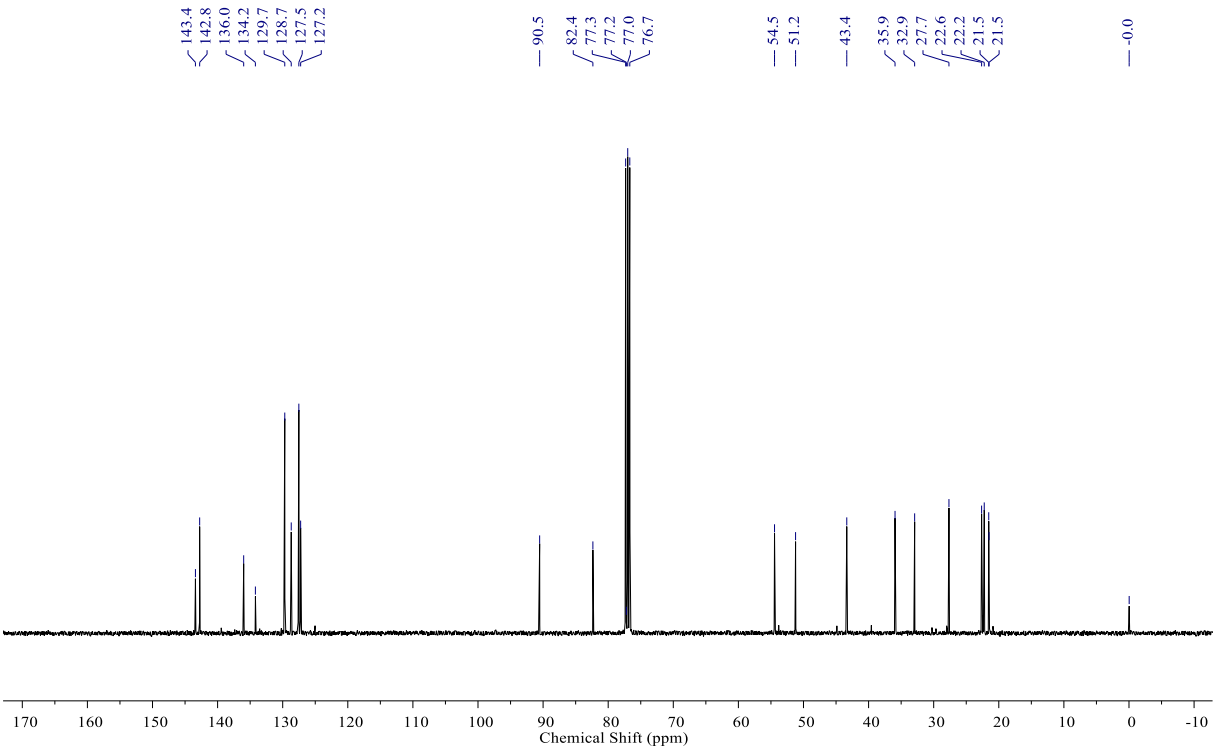

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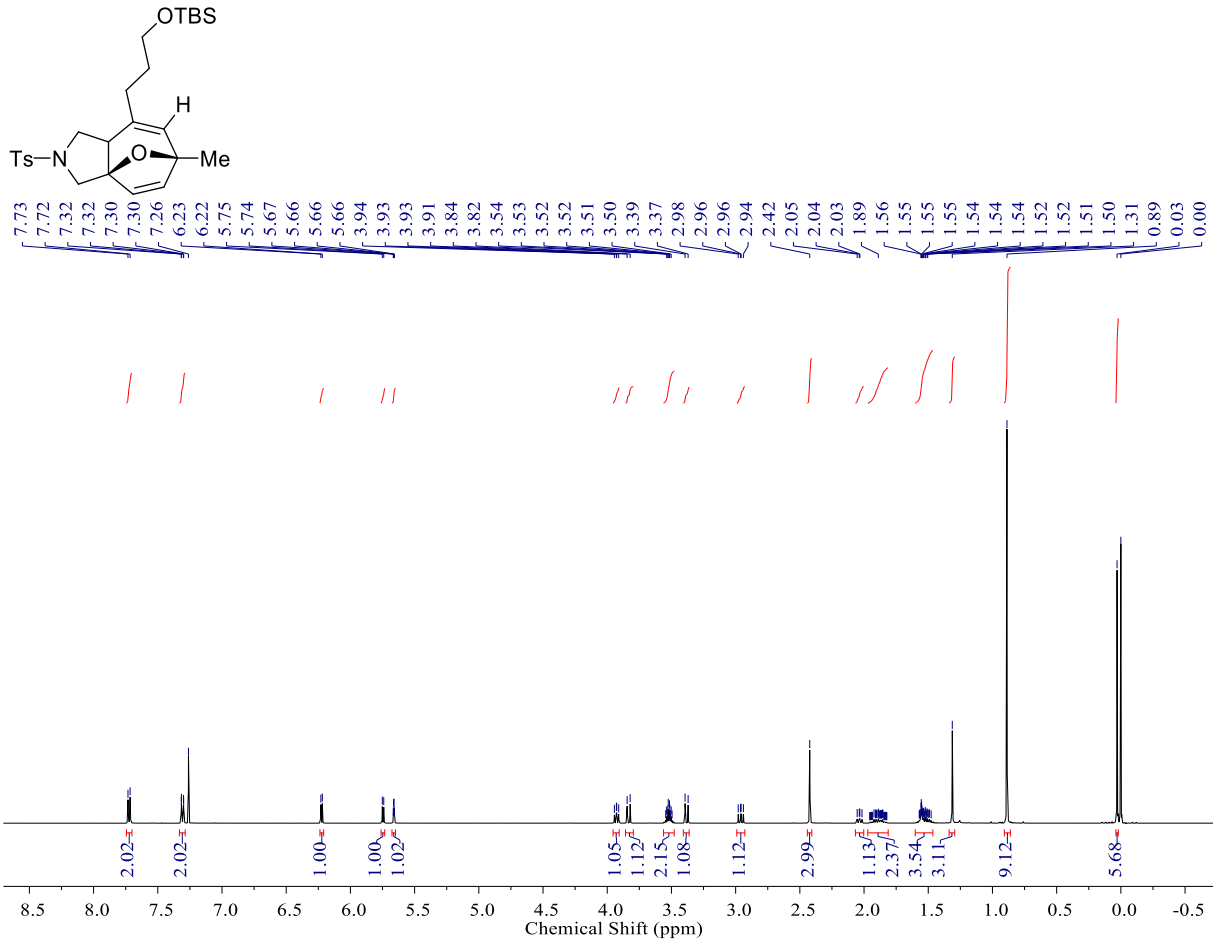

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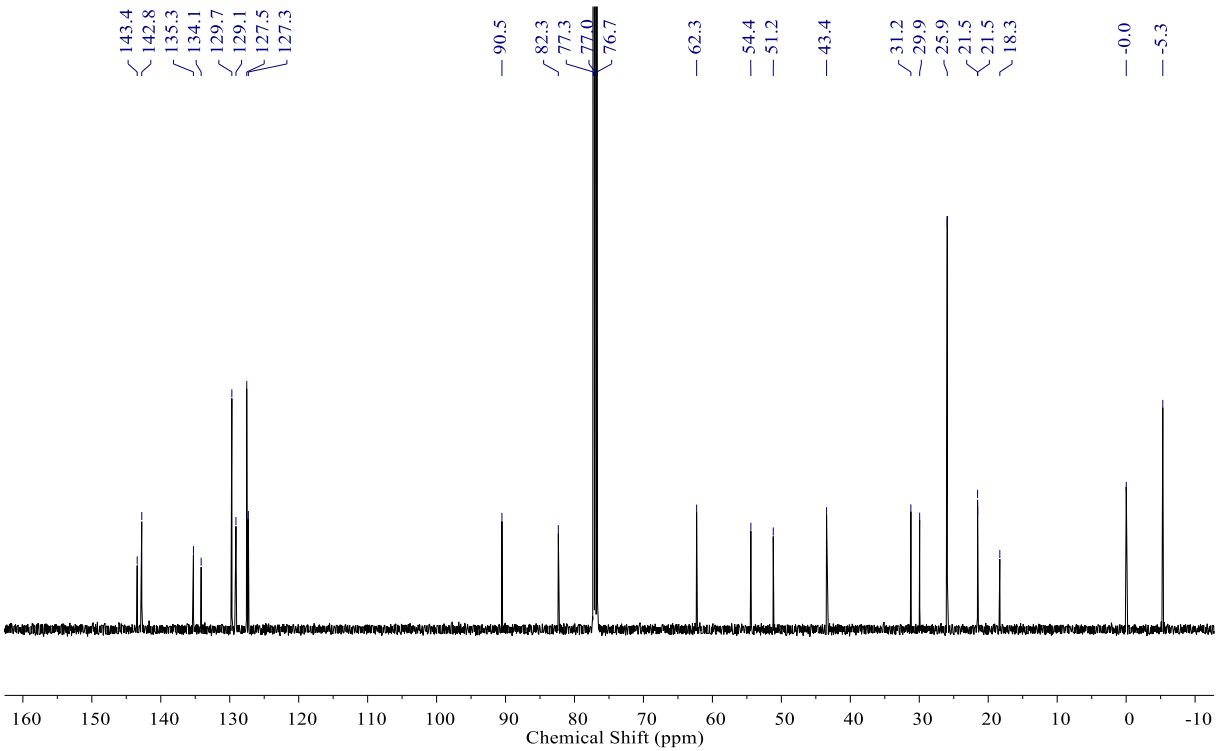

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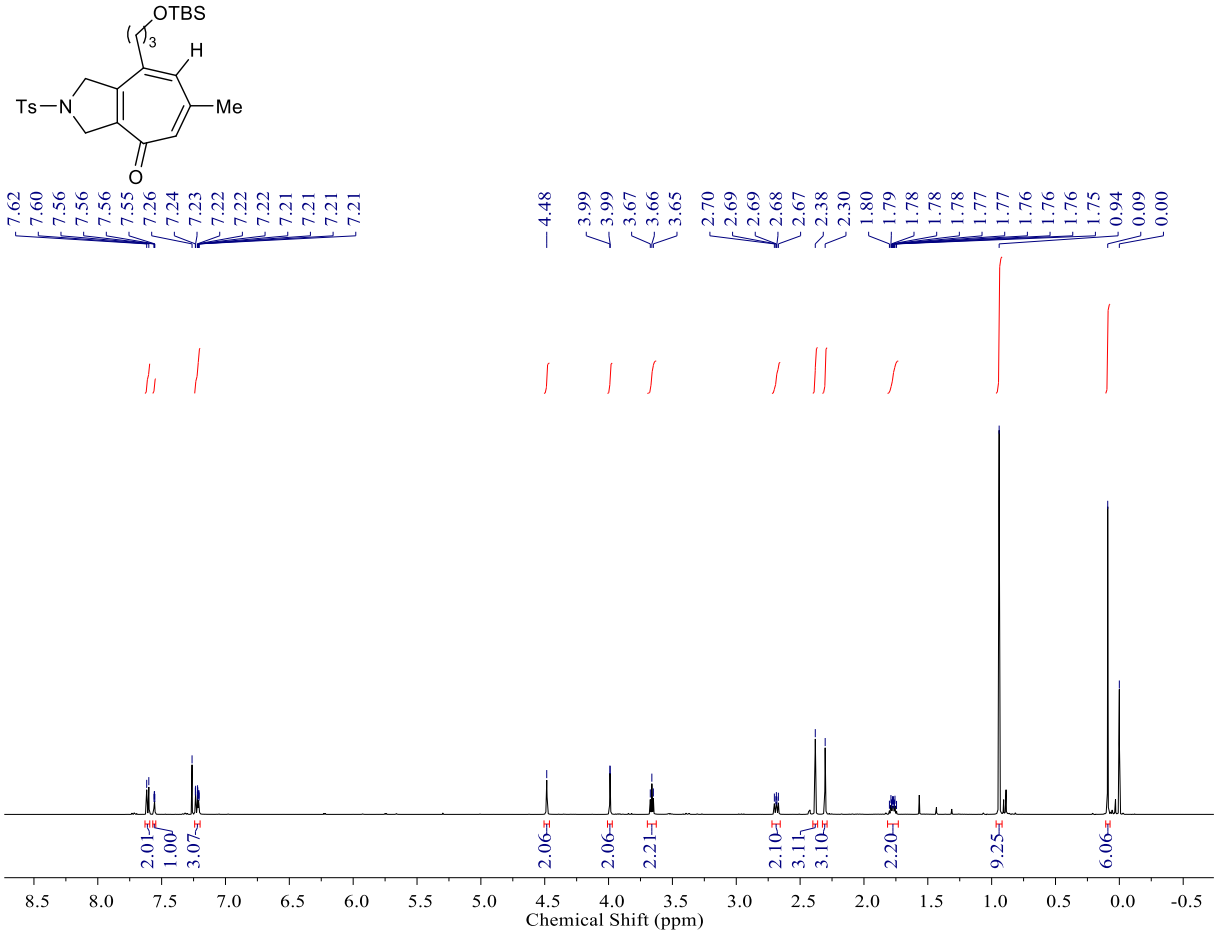

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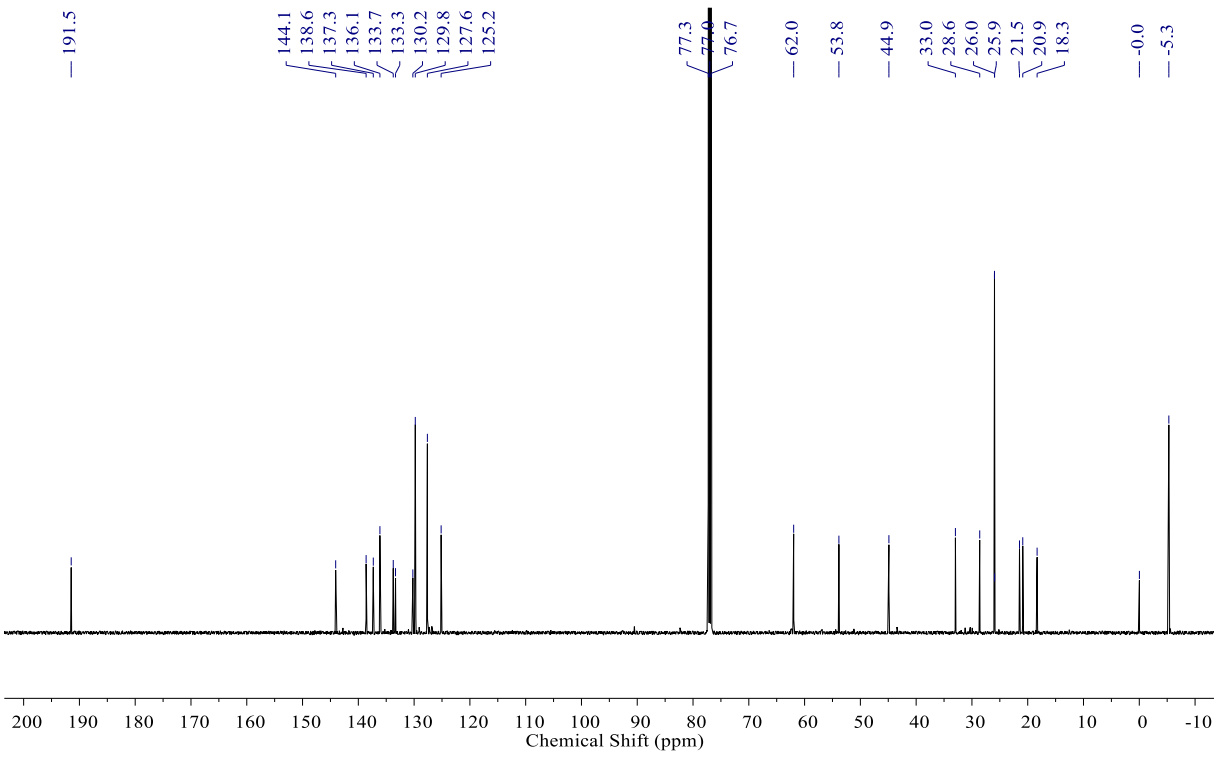

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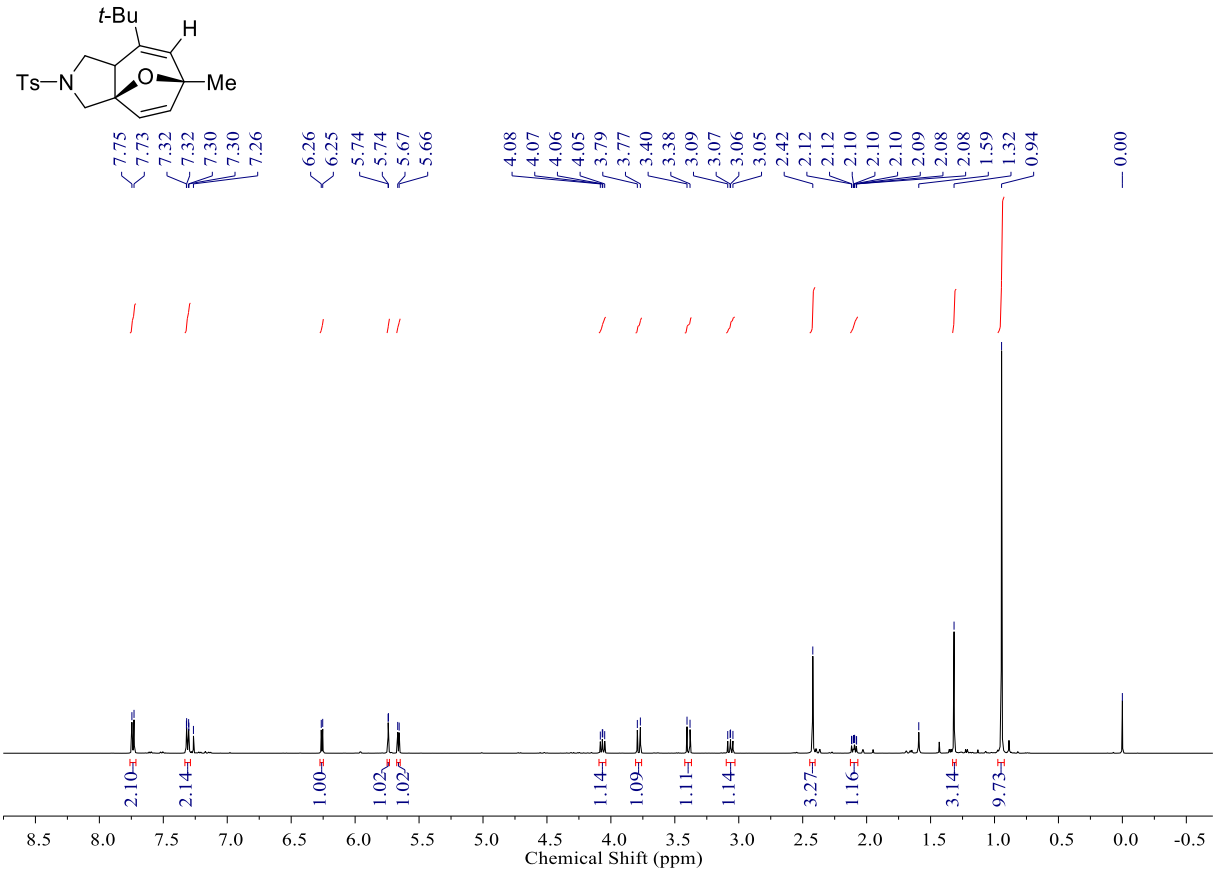

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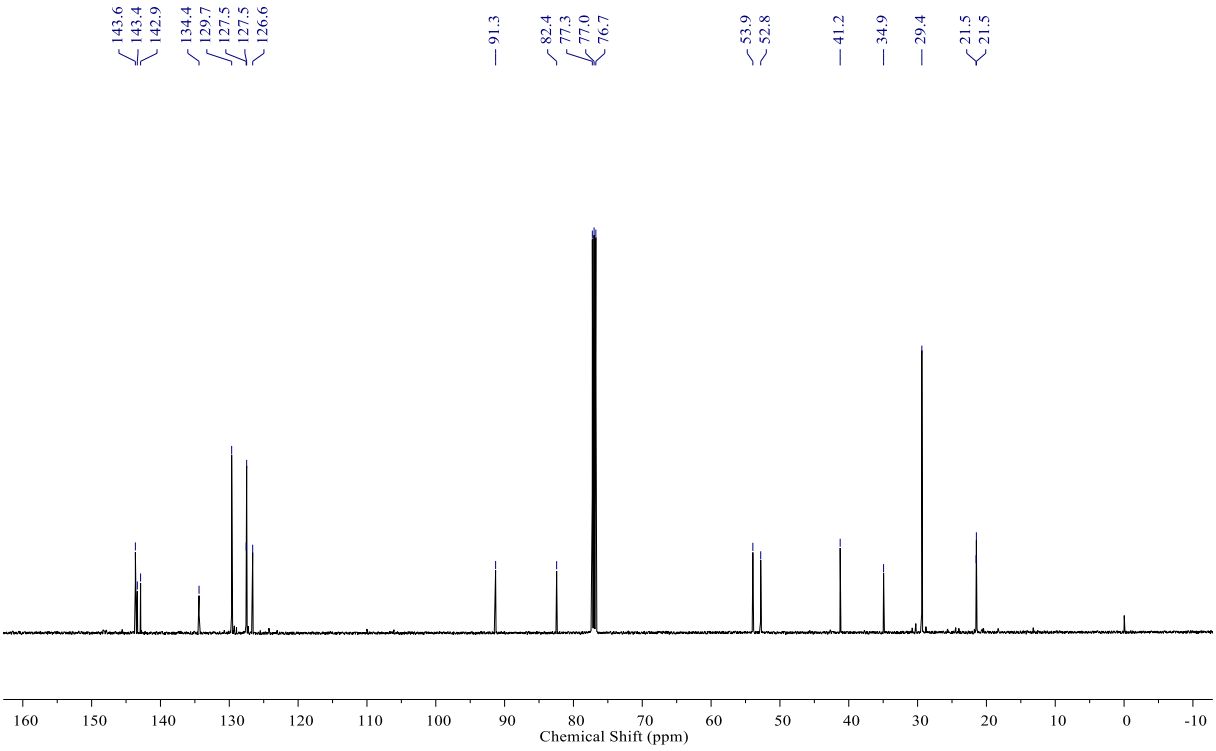

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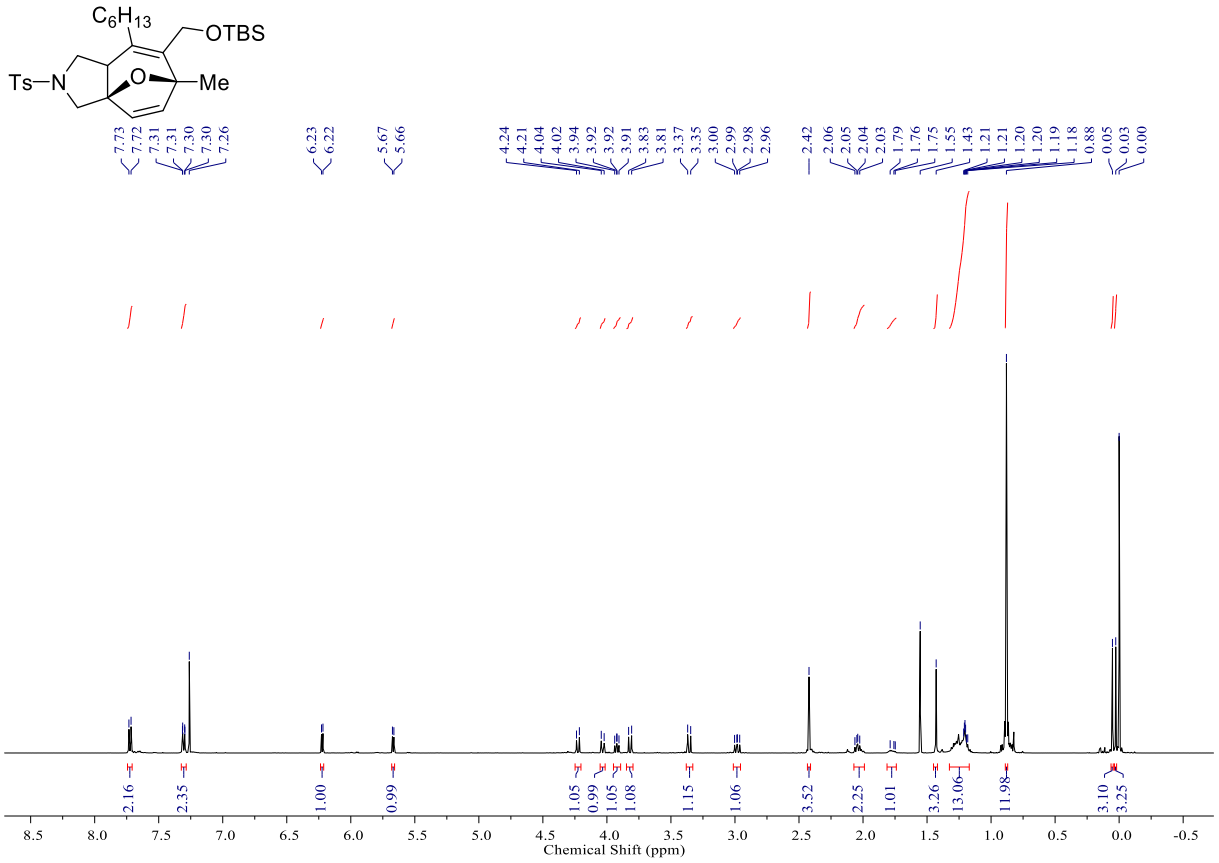

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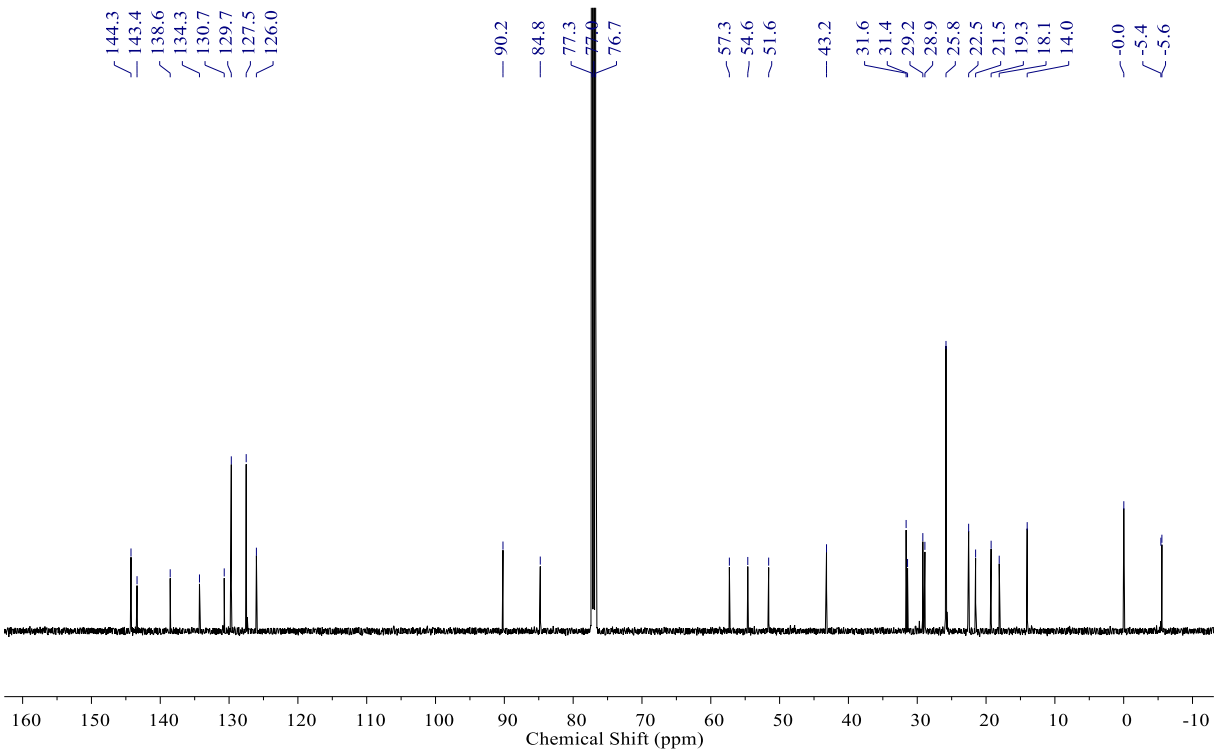

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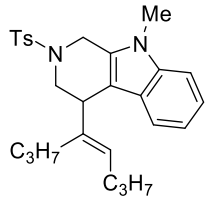

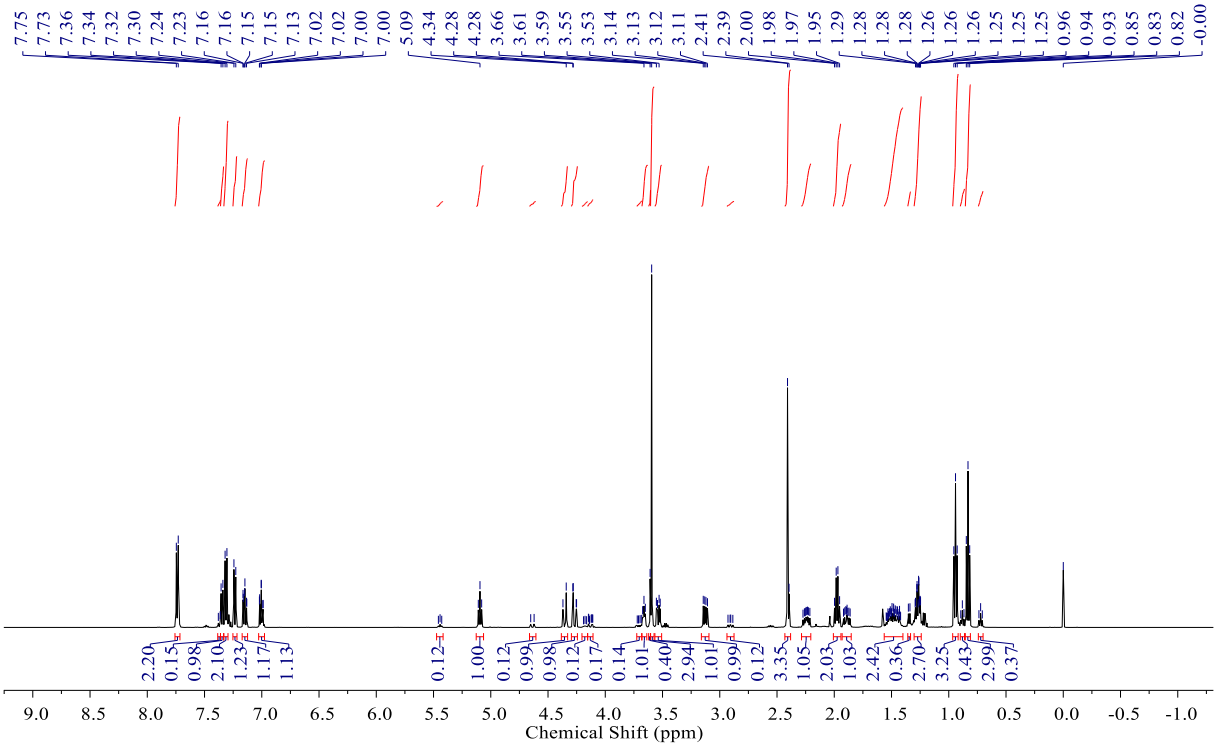

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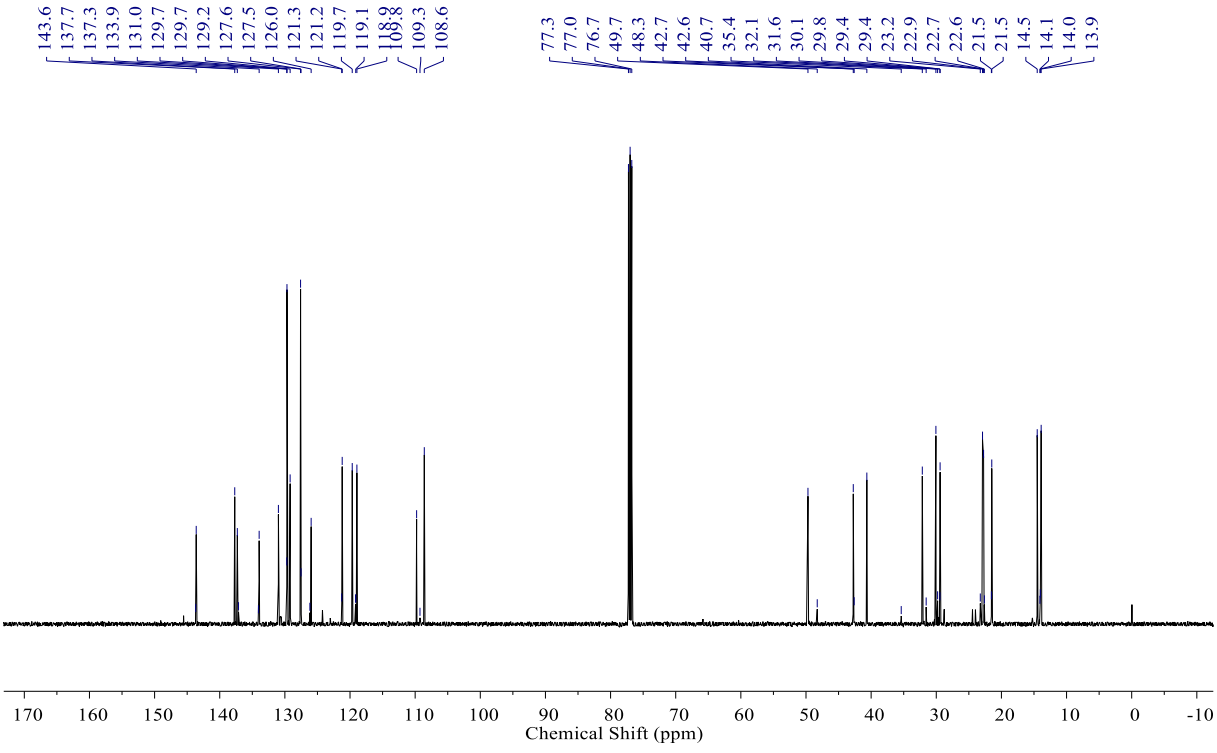

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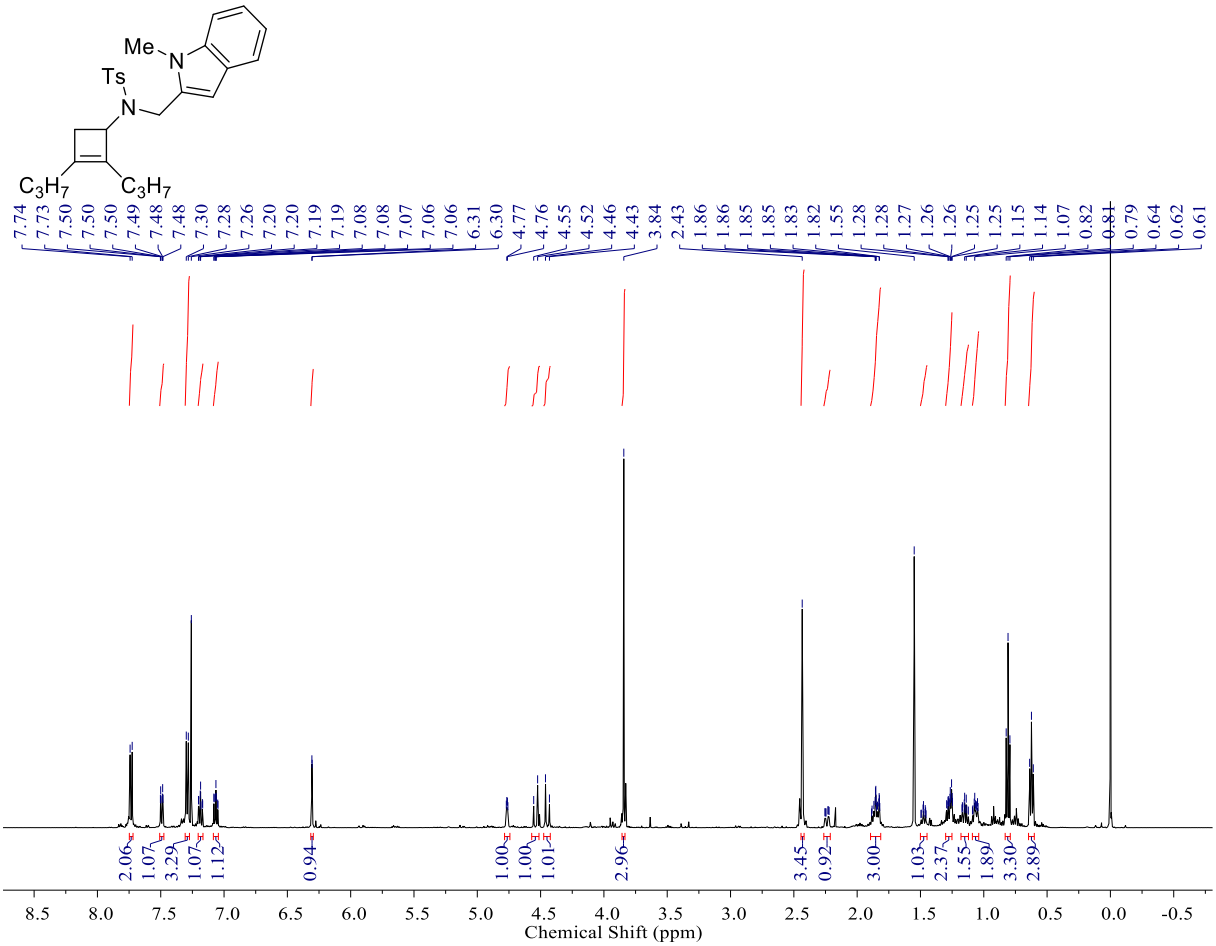

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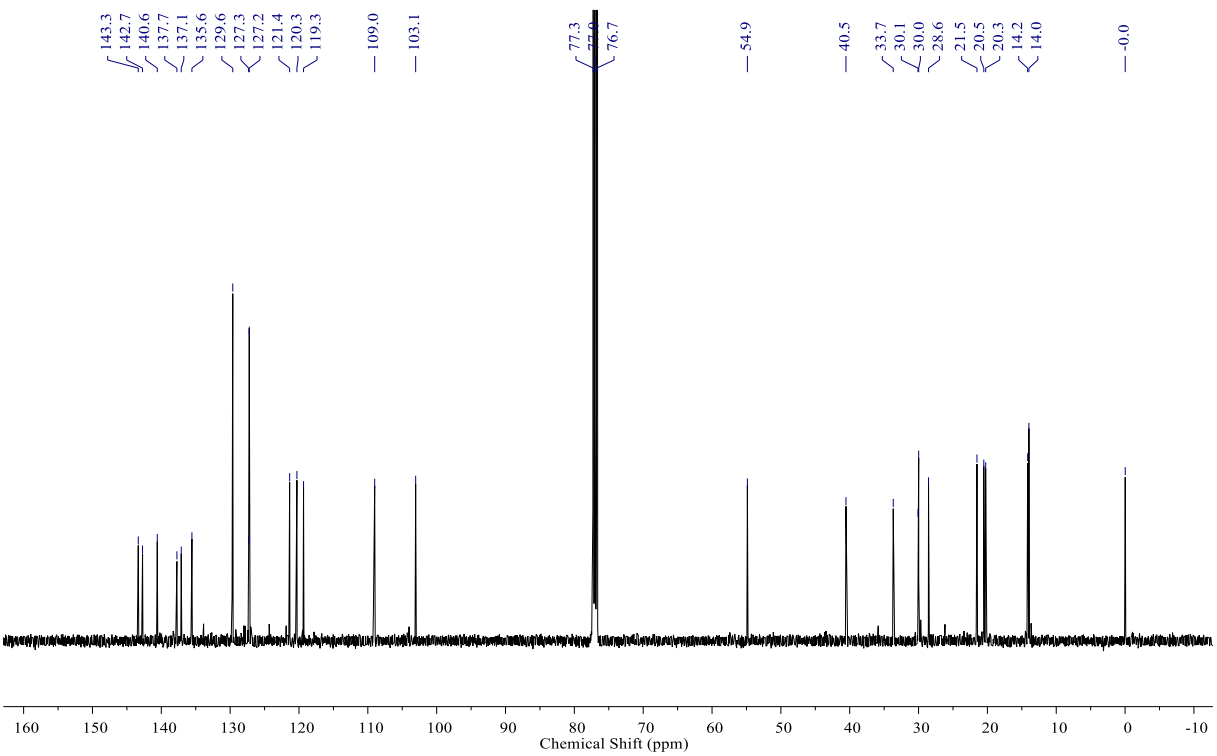

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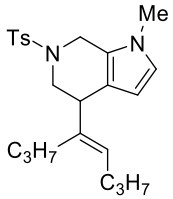

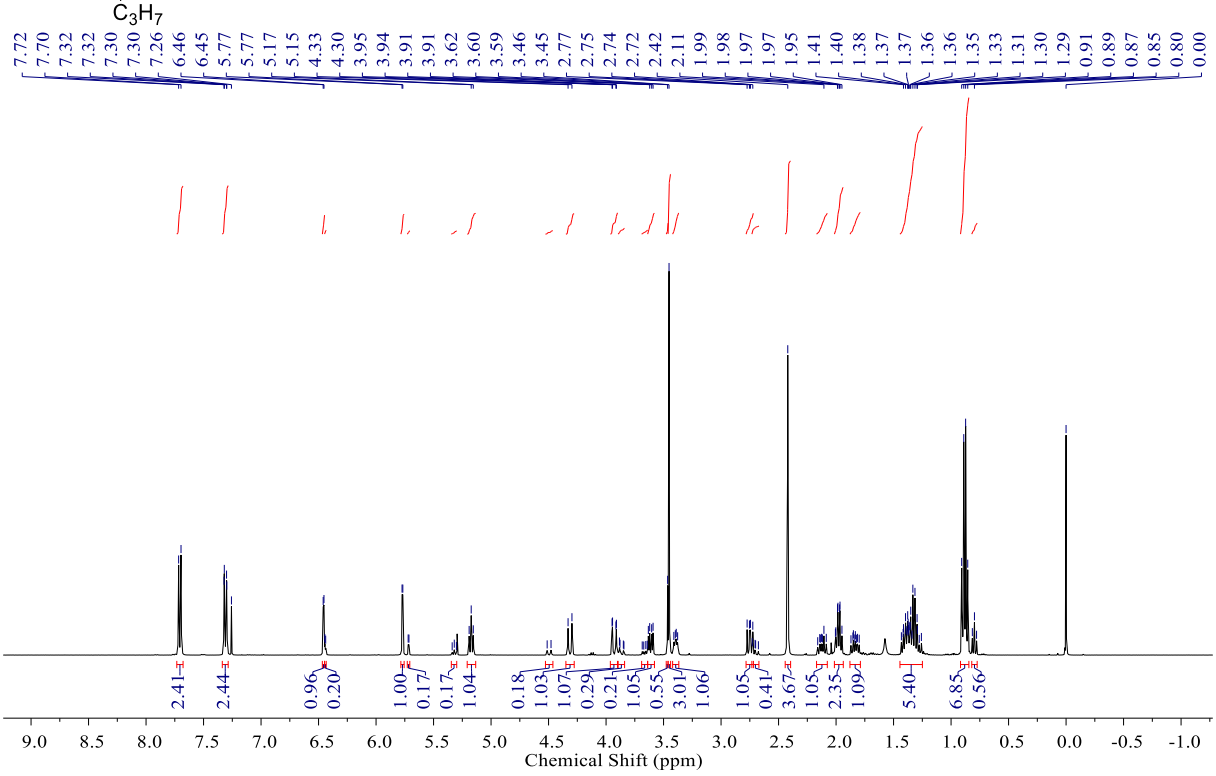

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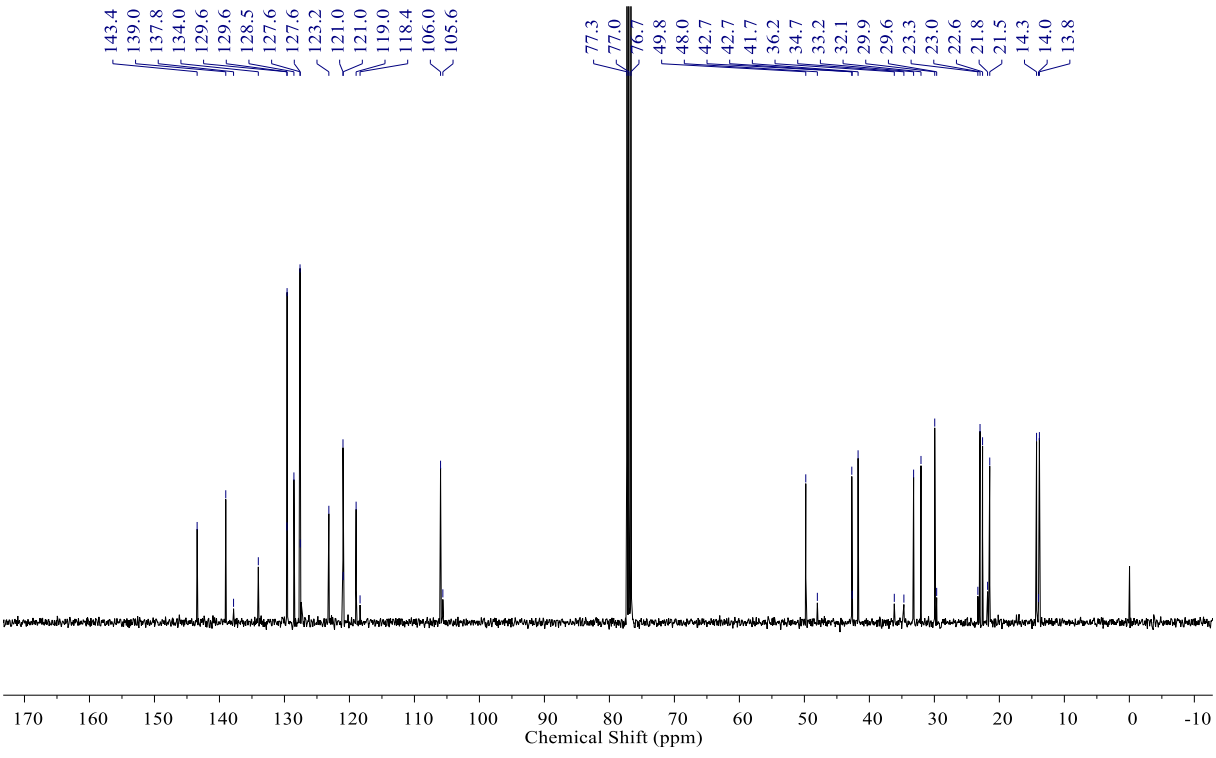

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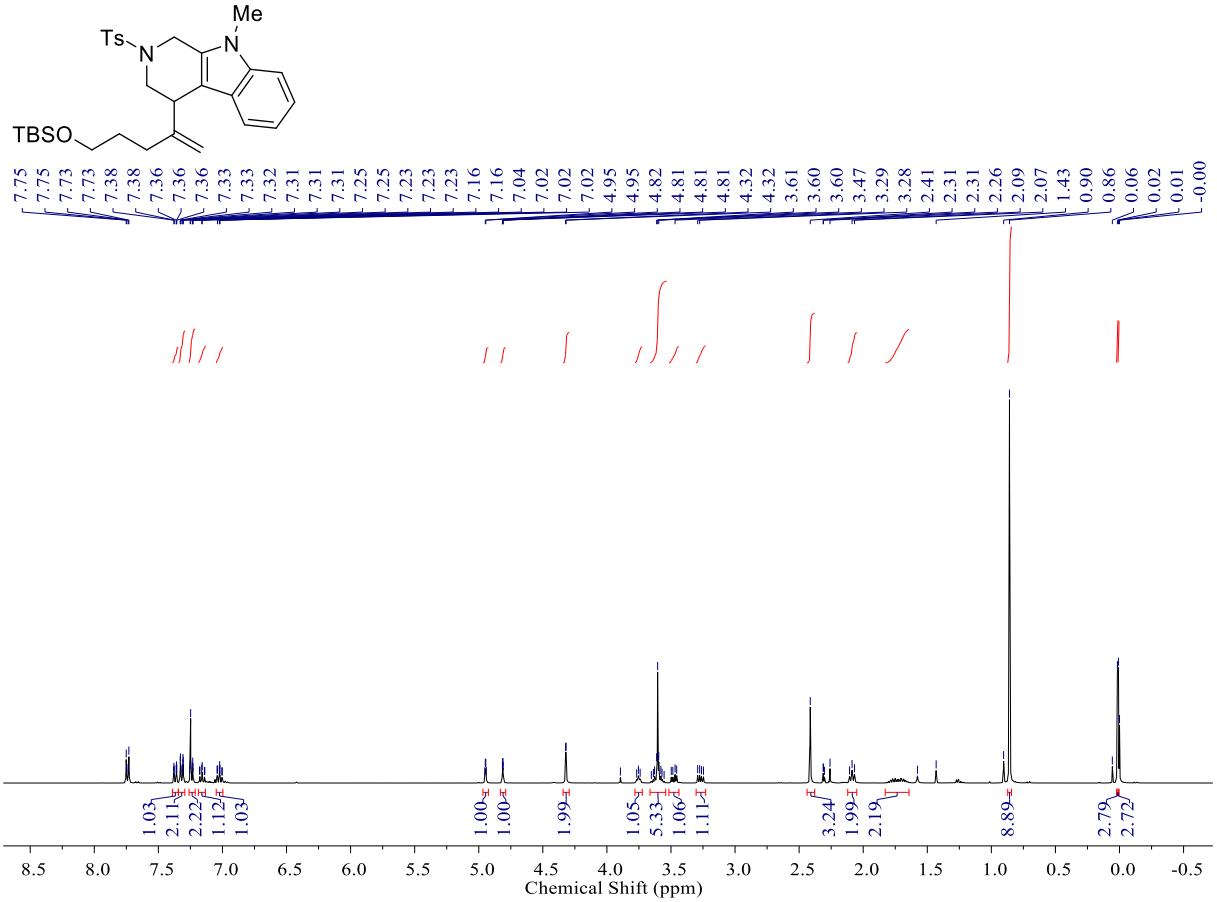

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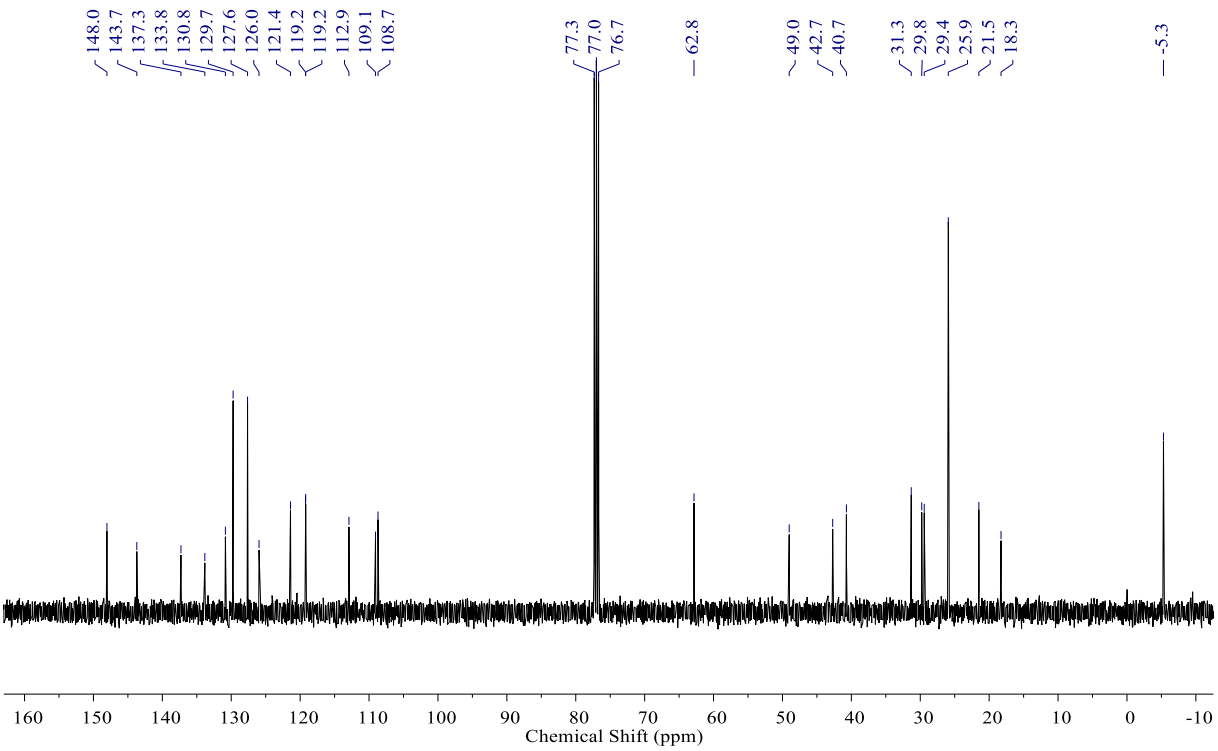

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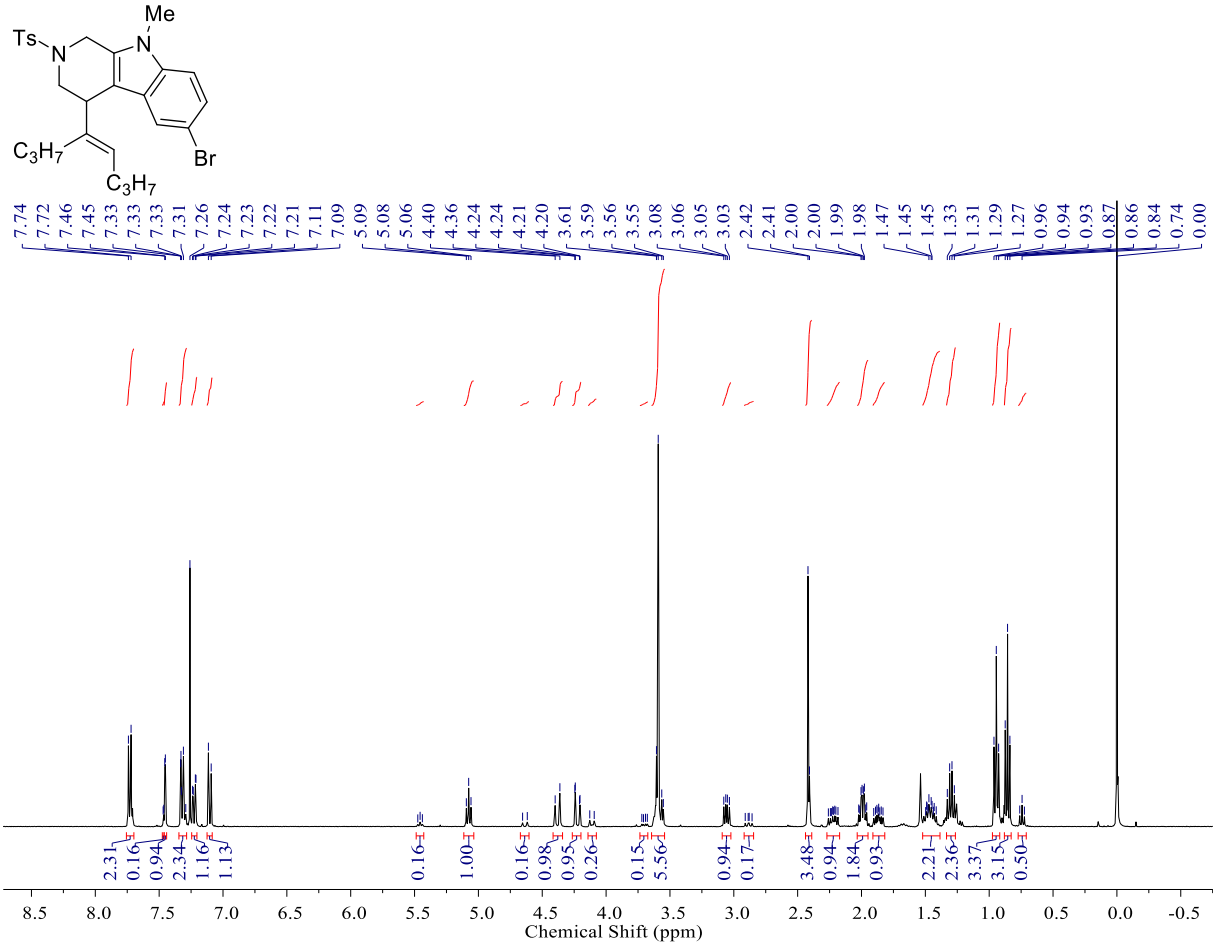

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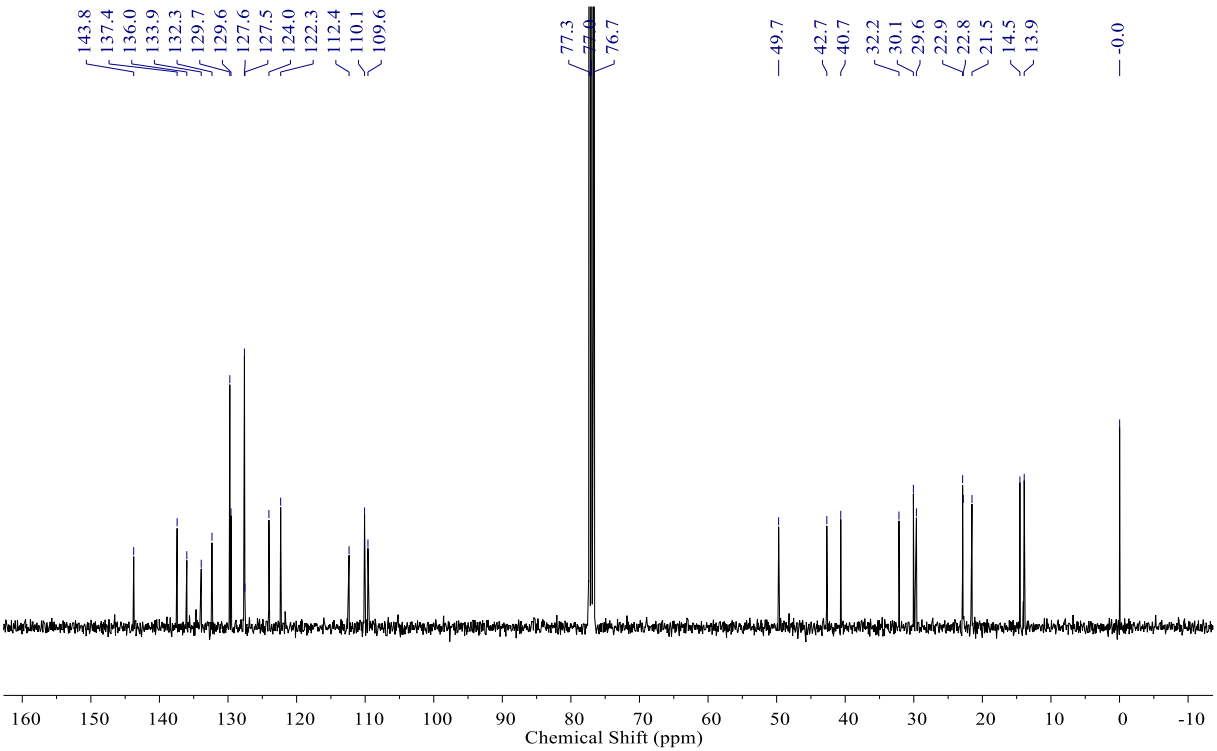

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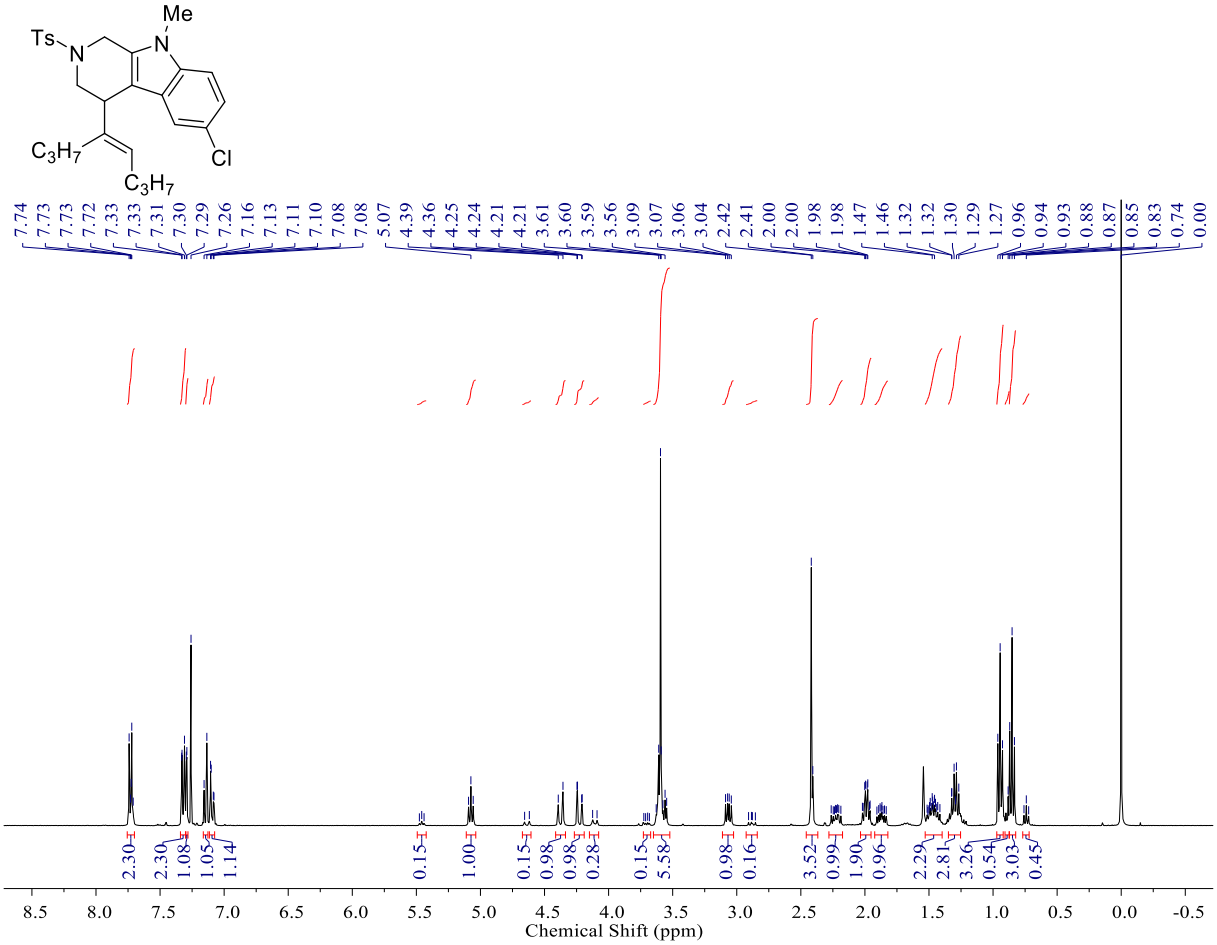

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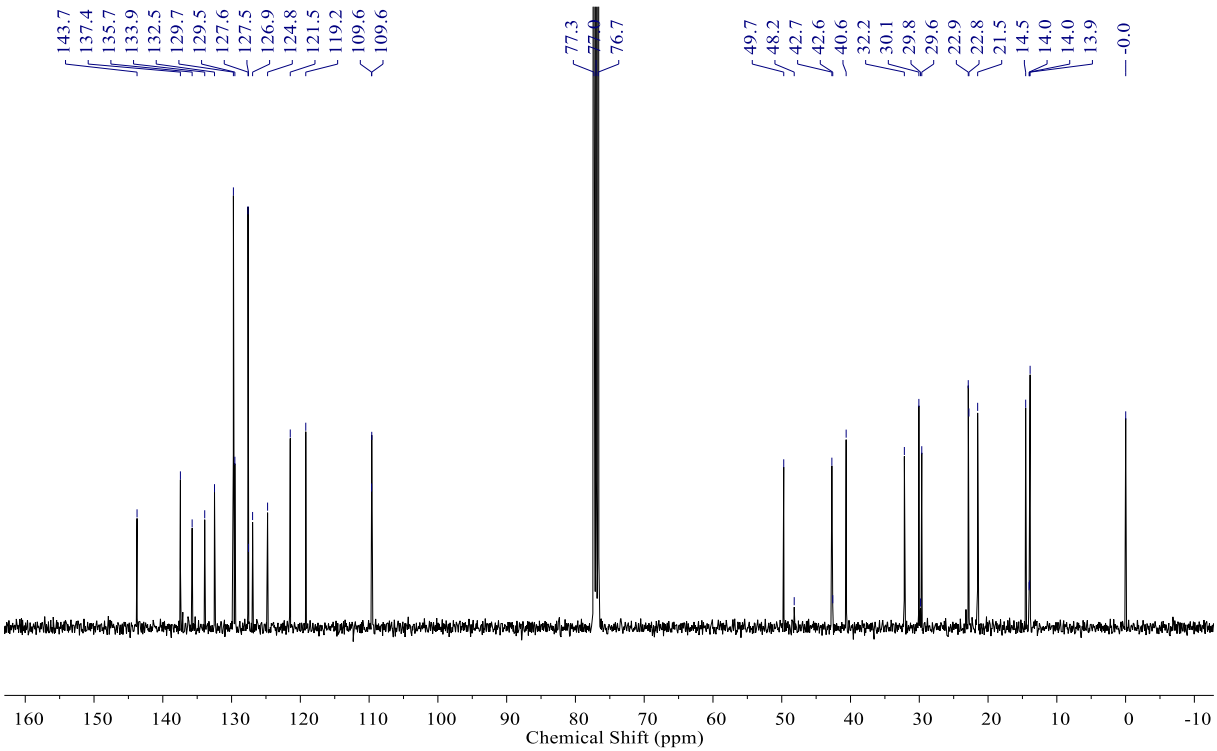

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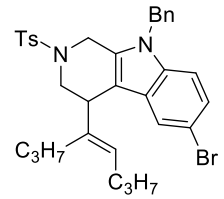

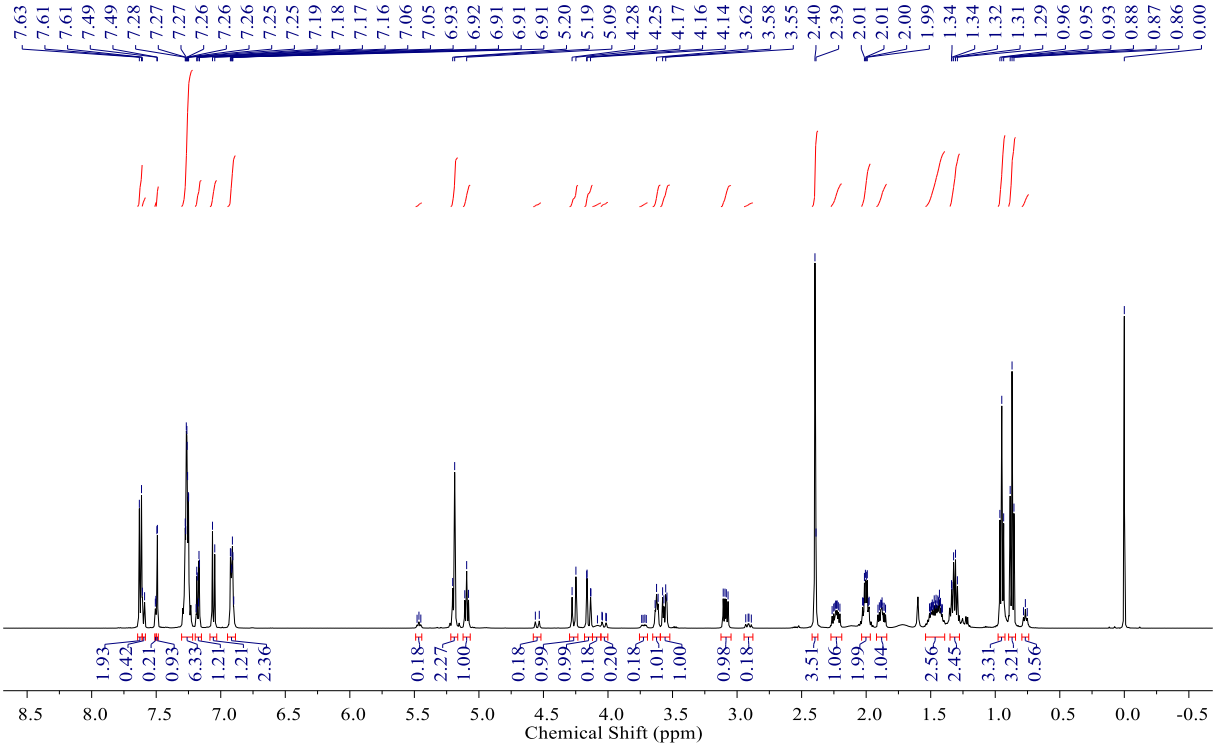

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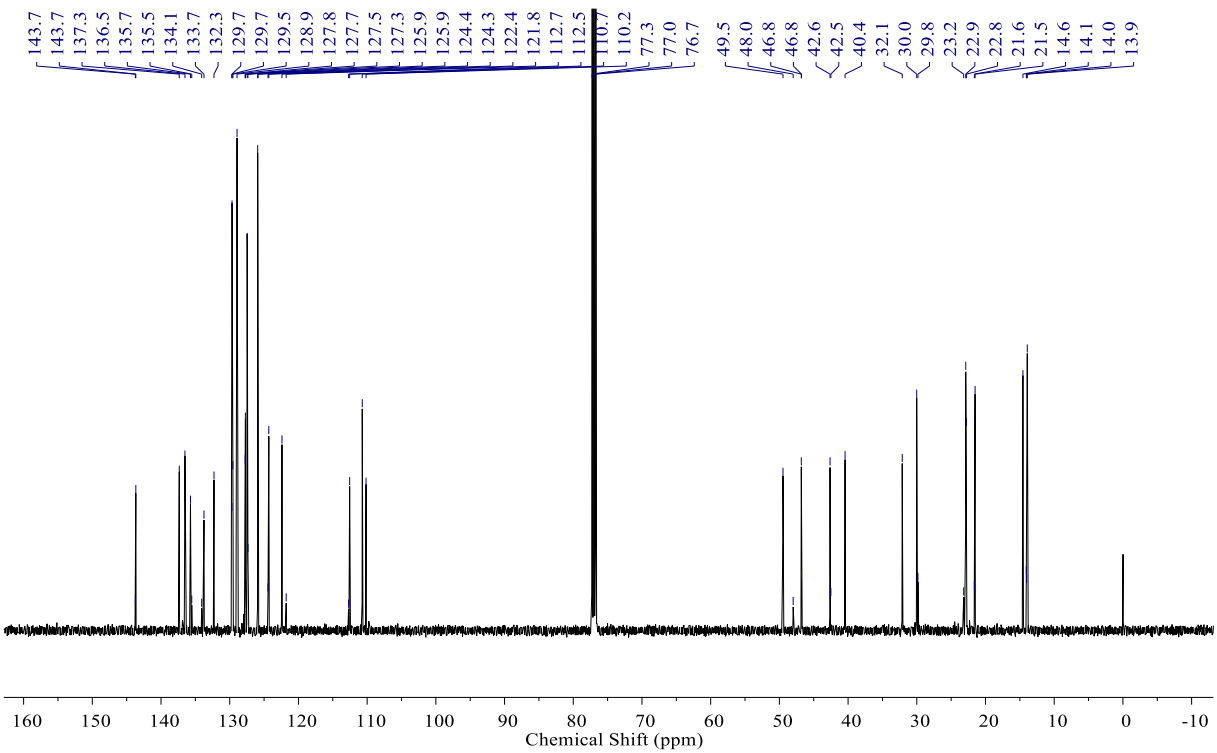

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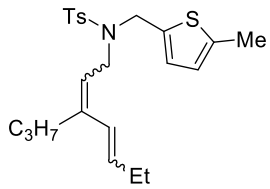

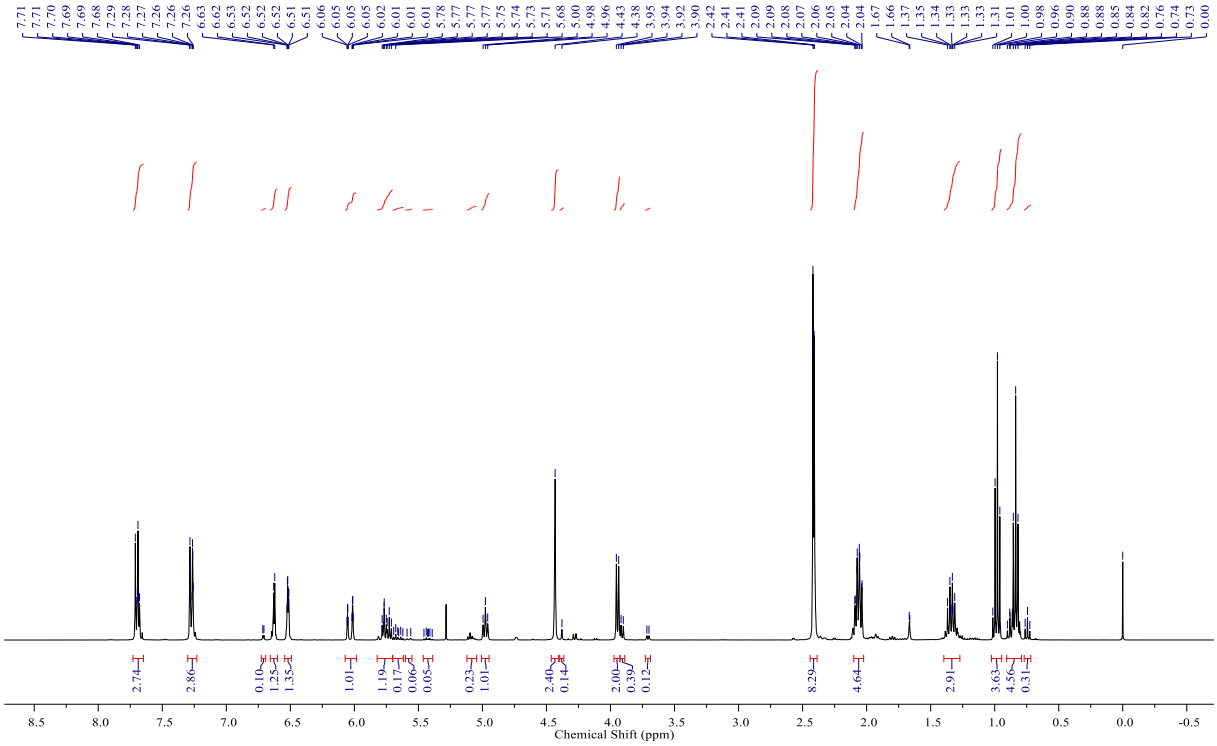

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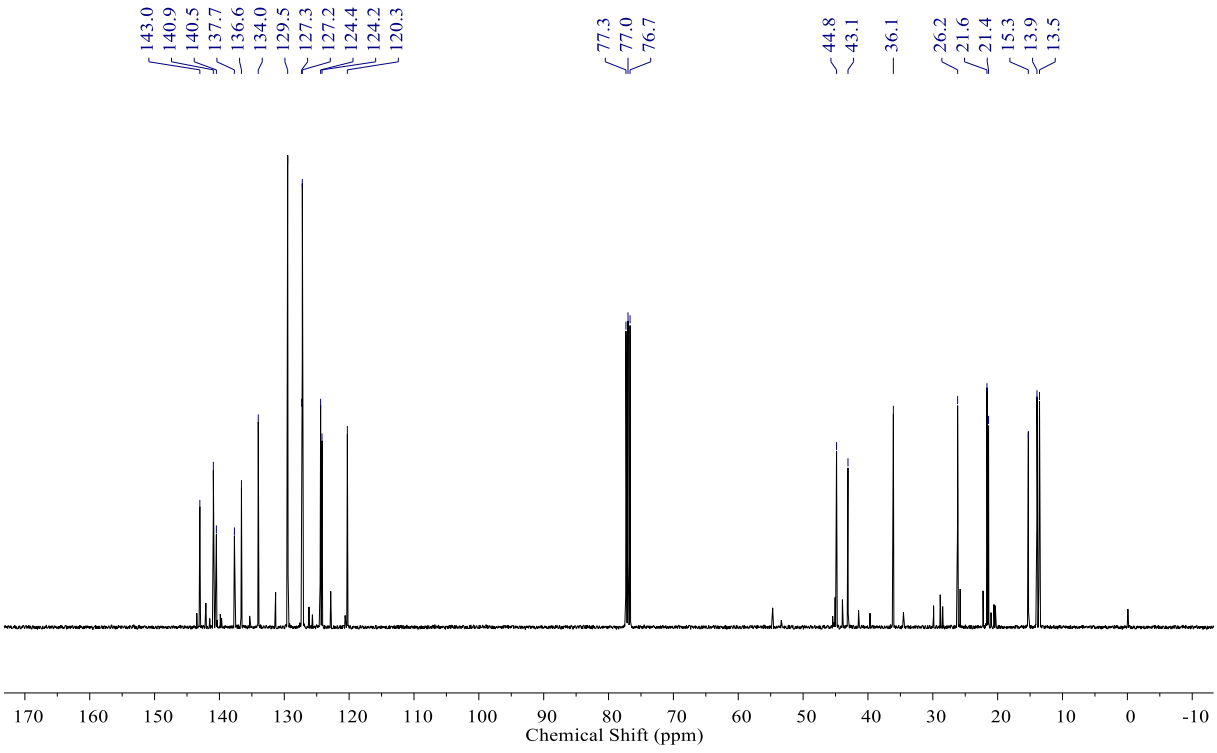

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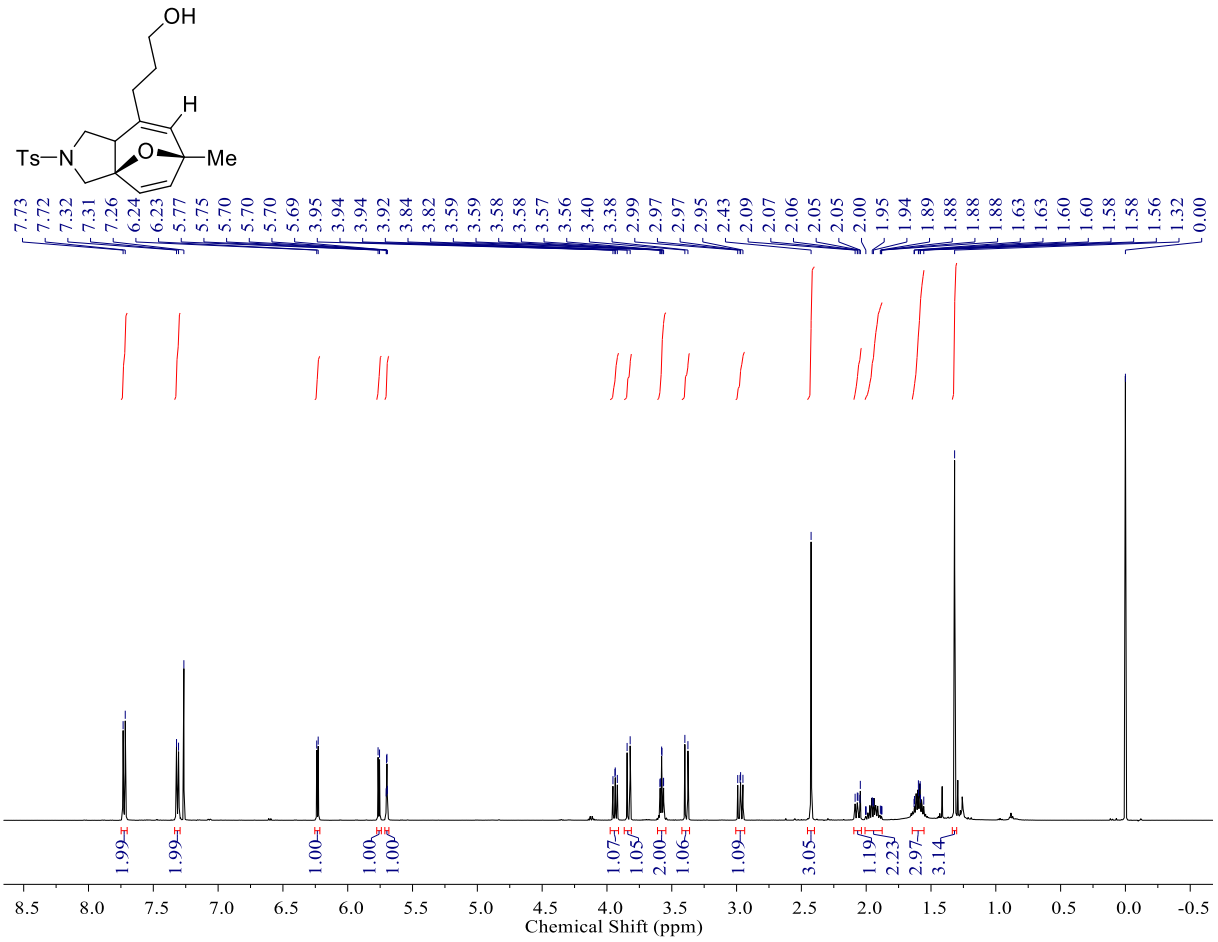

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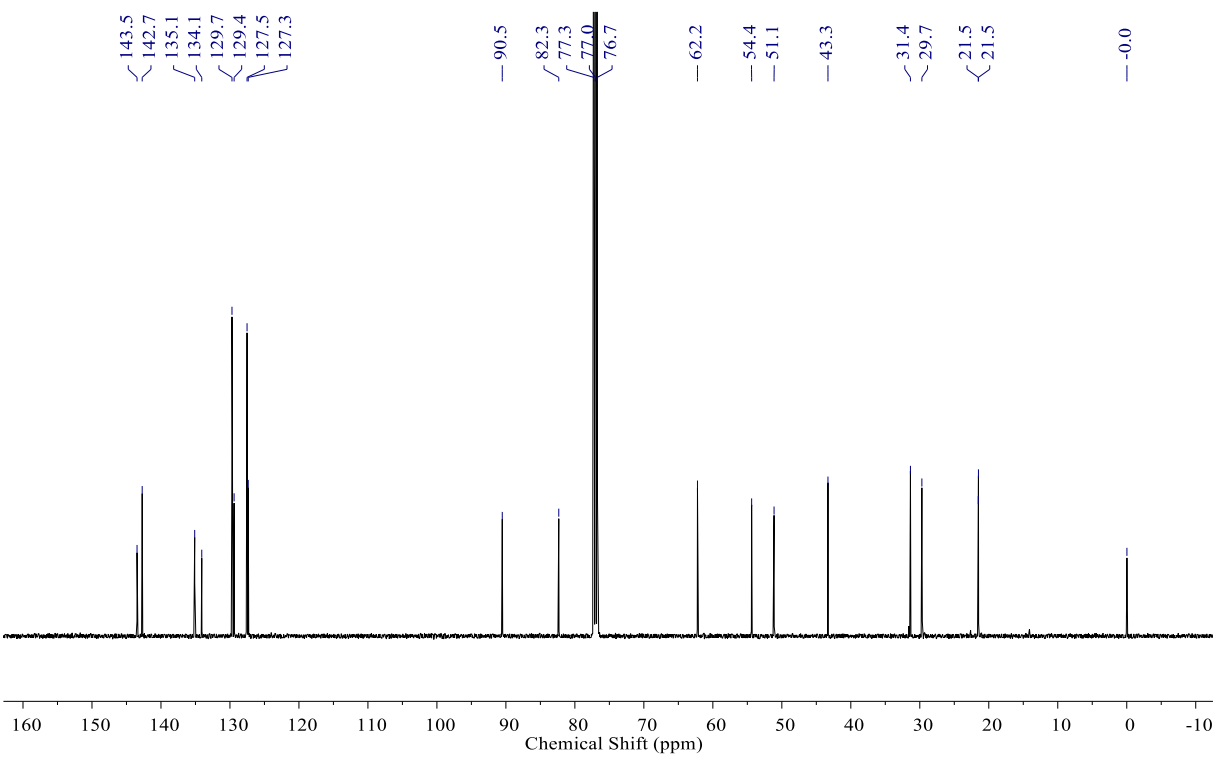

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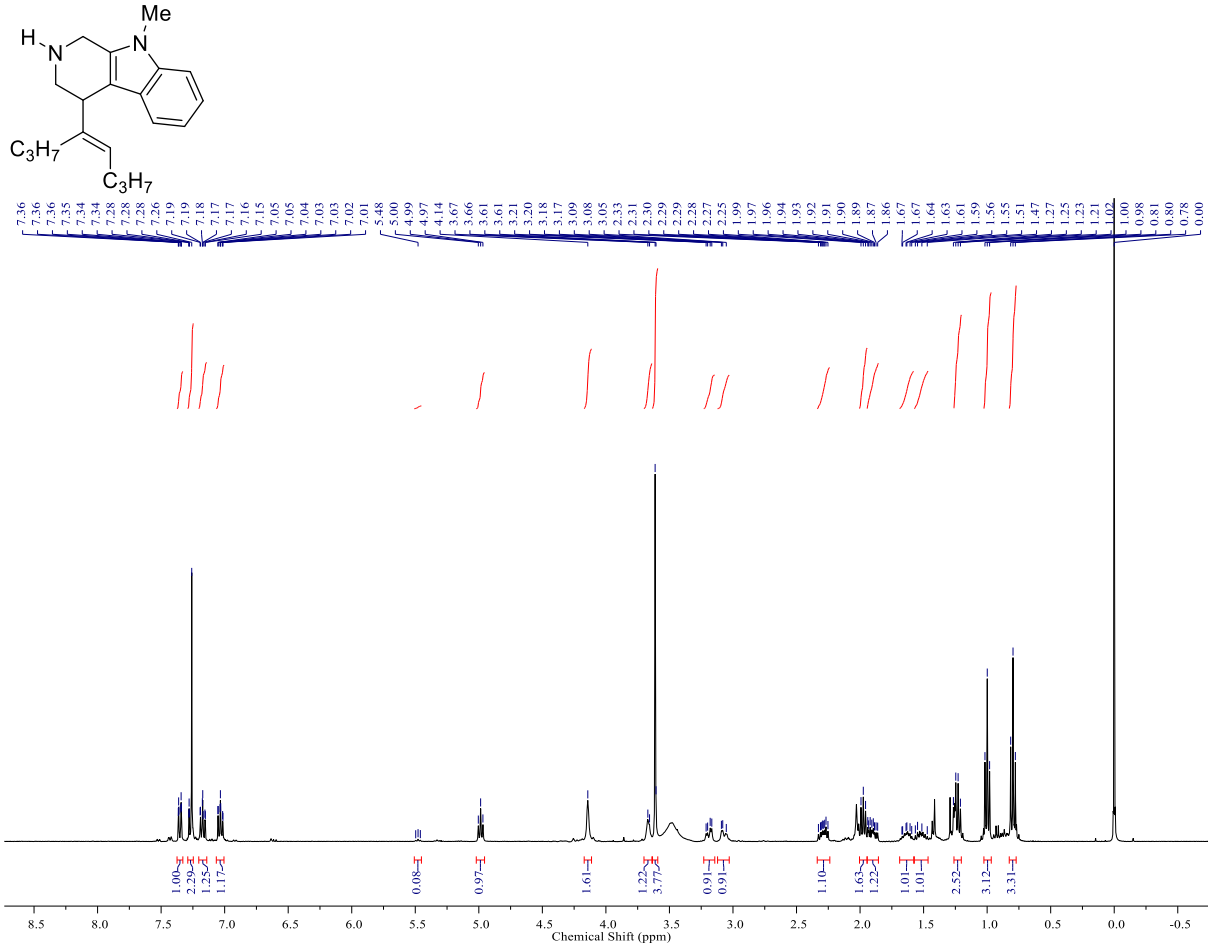

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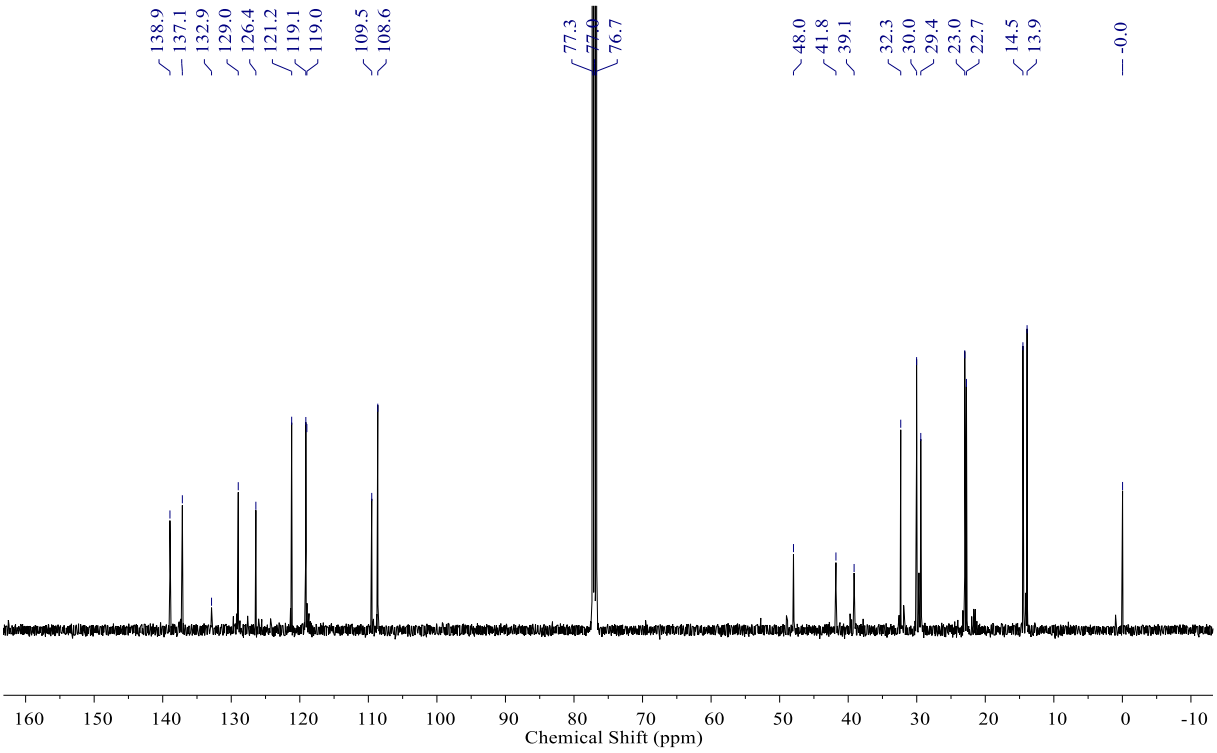

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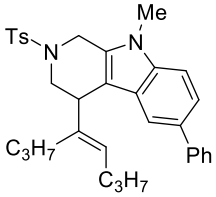

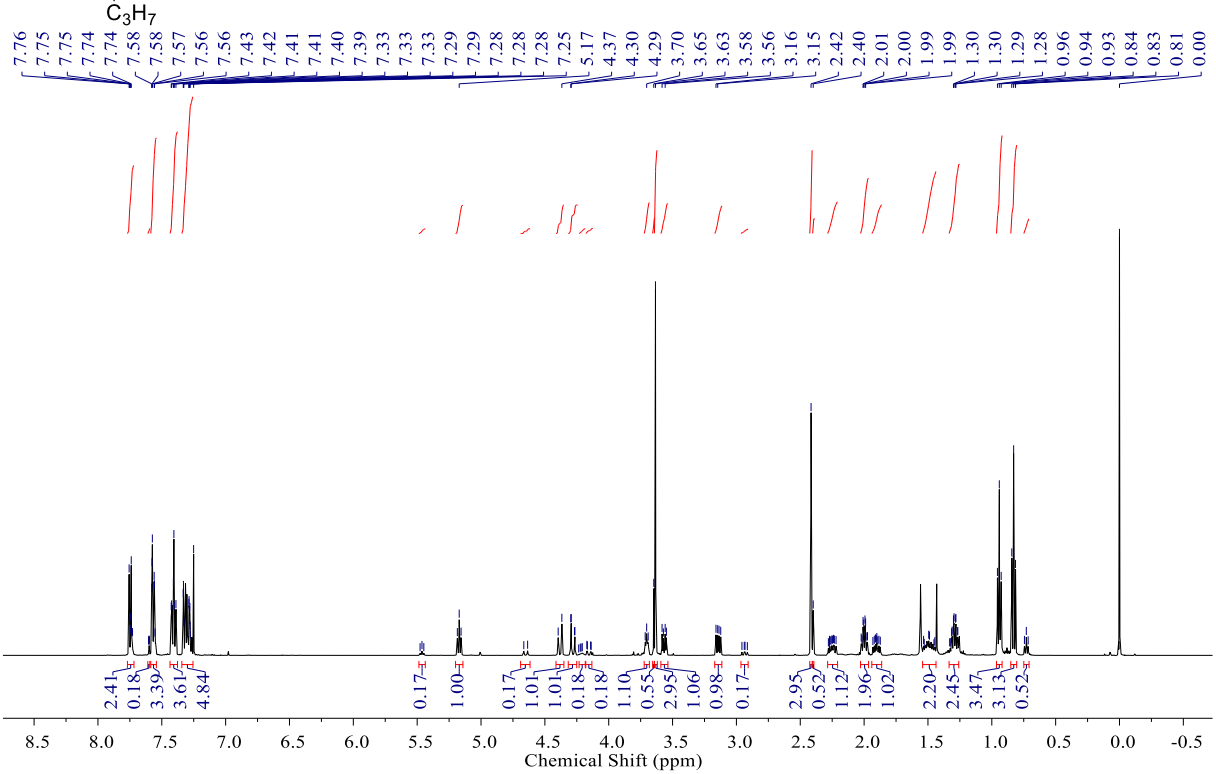

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