1,3-Amino Group Migration Route to Acrylamidines

Dinesh Pratapsinh Chauhan, Sreejith Jayashree Varma, Arjun Vijeta, Pallavi Banerjee, and Pinaki Talukdar*

Department of Chemistry, Mendeleev Block, Indian Institute of Science Education and Research Pune, India.

E-mail: ptalukdar@iiserpune.ac.in

Supporting Information

I. General Methods:

All reactions were conducted under the nitrogen atmosphere. All the chemicals were purchased from commercial sources and used as received unless stated otherwise. Solvents: petroleum ether, ethyl acetate (EtOAc), dichloromethane (DCM), and methanol (MeOH) were distilled prior to thin layer and column chromatography. Column chromatography was performed on Merck silica gel (100–200 mesh). TLC was carried out with E. Merck silica gel 60-F-254 plates.

II. Physical Measurements:

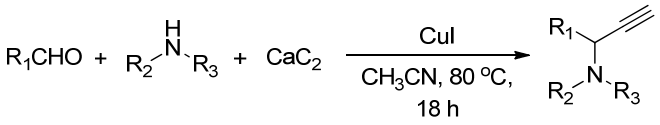
The ^{1}H and ^{13}C spectra were recorded on either 400 MHz Jeol ECS-400 (or 100 MHz for ^{13}C) or 400 MHz Bruker AV400 (or 100 MHz for ^{13}C) spectrometer using either residual solvent signals as an internal reference or from internal tetramethylsilane on the δ scale ($CDCl_3$ δ_H, 7.24 ppm, δ_C 77.0 ppm). The chemical shifts (δ) are reported in ppm and coupling constants

(*J*) in Hz. The following abbreviations are used: m (multiplet), s (singlet), br s (broad singlet), d (doublet), t (triplet) dd (doublet of doublet), dt (doublet of triplet), q (quartet), and sex (sextet). High-resolution mass spectra were obtained from MicroMass ESI-TOF MS spectrometer. Absorption spectra were recorded on a Thermo Scientific, Evolution 300 UV-VIS spectrophotometer. Steady State fluorescence experiments were carried out in a micro fluorescence cuvette (Hellma, path length 1.0 cm) on a Horiba JobinYvon, FluoroMax-4 instrument. (FT-IR) spectra were obtained using Bruker: α ALPHA spectrophotometer (neat) and reported in cm^{-1}. Melting points were measured using a VEEGO Melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Crystal structures were recorded on a Bruker single crystal X-Ray diffractometer.

III. Experimental Procedures:

Preparation of propargylamine derivatives:

One step protocol of three-component aldehyde-amine-calcium carbide reaction:[S1]

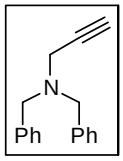


Scheme S1. Synthesis of propargylamine via one step protocol of three-component aldehyde-amine-calcium carbide reaction.

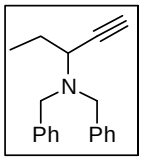
General Procedure A: To a two-neck round bottomed flask fitted with reflux condenser and placed under the N_2 atmosphere was added the aldehyde (1.0 mmol) followed by addition of acetonitrile (2 mL). To the solution were added amine (1.2 mmol), calcium carbide (1.5 mmol) and CuI catalyst (0.1 mmol). The reaction mixture was stirred at 80 °C for 18 h. After the completion of the reaction, the mixture was passed through celite pad and washed with Et_2O (2 × 10 mL). The combined filtrate was concentrated under reduced pressure to obtain liquid which was purified by column chromatography over silica gel to obtain the required propargylamine.

General Procedure B: To the round bottomed flask under N_2 atmosphere was added propargyl bromide (1.0 mmol) in acetonitrile (2 mL). To this solution were added amine (1.0 mmol), anhydrous K_2CO_3 (2.0 mmol) at 0 °C and the resultant reaction mixture was stirred at rt for 18 h. After completion of reaction, acetonitrile was evaporated and obtained residue was washed with water and extracted with EtOAc (2 × 5 mL) and dried over anhydrous

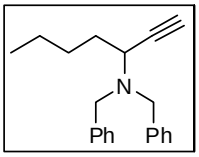
Na_2SO_4. The organic solvent was evaporated and resultant crude product was purified by column chromatography.



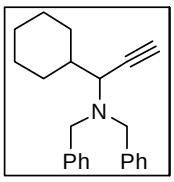
Synthesis of *N,N*-dibenzylprop–2-yn-1-amine (1) [$C_{17}H_{17}N$]:[S2] The compound **1** was prepared by following the *General Procedure B*. Starting from propargyl bromide (1.0 g, 8.40 mmol), dibenzylamine (1.6 mL, 8.40 mmol) and K_2CO_3 (2.30 g, 16.8 mmol) compound **1** was obtained (1.3 g, yield = 66%) as colorless solid. after column chromatographic purification. *Eluent*: 3% EtOAc in Petroleum ether (R_f = 0.7). Obtained data was matched with the reported literature data.



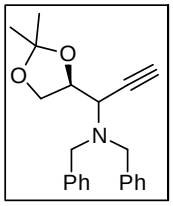
Synthesis of *N,N*-dibenzylpent–1-yn-3-amine (3a) [$C_{19}H_{21}N$]: The compound **3a** was prepared by following the *General Procedure A*. Starting from propionaldehyde (1.0 g, 17.21 mmol), dibenzylamine (3.92 mL, 20.65 mmol) and CaC_2 (1.65 g, 25.81 mmol) in the presence of CuI (326 mg, 1.72 mmol) compound **3a** was obtained (3.45 g, yield = 76%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). IR (neat): ν_{max}/cm^{-1} 3299, 2966, 2933, 1577, 1494, 1452, 1365, 1148, 1129, 1072, 1027; ^{1}H NMR (400 MHz, DCl_3): δ 7.41 (d, *J* = 7.56 Hz, 4H), 7.31 (t, *J* = 7.44 Hz, 4H), 7.24 (t, *J* = 7.24 Hz, 2H), 3.84 (d, *J* = 13.84 Hz, 2H), 3.42 (d, *J* = 13.84 Hz, 2H), 3.33 (td, *J* = 7.68 Hz, 1H), 2.32 (d, *J* = 2.16 Hz, 1H), 1.80 – 1.62 (m, 2H), 0.97 (t, *J* = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 139.8, 128.8, 128.3, 127.0, 82.1, 72.6, 54.8, 53.3, 26.9, 11.2; HRMS (ESI): Calc. for $C_{19}H_{22}N$ $[M+H]^+$: 264.1752; Found: 264.1753.



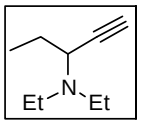
Synthesis of *N, N*-dibenzylhept–1-yn-3-amine (3b) [$C_{21}H_{25}N$]:[S3] The compound **3c** was prepared by following the *General Procedure A*. Starting from n-valeraldehyde (1.0 g, 11.62 mmol), dibenzylamine (2.7 mL, 13.95 mmol) and CaC_2 (1.1 g, 17.43 mmol) in the presence of CuI (220 mg, 1.16 mmol) compound **3b** was obtained (2.5 g, yield = 75%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). Obtained data was matched with the reported literature data.



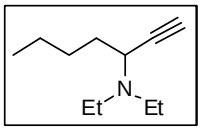
Synthesis of *N,N*-dibenzyl–1-cyclohexylprop-2-yn-1-amine (3c) [$C_{23}H_{27}N$]:[S4] The compound **3c** was prepared by following the *General Procedure A*. Starting from cyclohexaladehyde (1.0 g, 8.92 mmol), dibenzylamine (2.05 mL, 10.71 mmol) and CaC_2 (856 mg, 13.38 mmol) in the presence of CuI (169 mg, 0.89 mmol) compound **3c** was obtained (1.8 g, yield = 65%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). Obtained data was matched with the reported literature data.

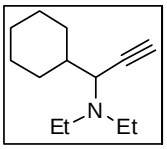


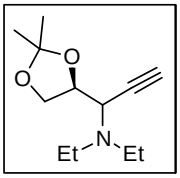
Synthesis of *N,N*-dibenzyl–1-((S)–2,2–dimethyl–1,3–dioxolan–4–yl)–prop–2–yn-1–amine (3d) [$C_{22}H_{25}NO_2$]:[S5] The compound **3d** was prepared by following the *General Procedure A*. Starting from D-glyceraldehyde (1.0 g, 7.68 mmol), dibenzylamine (1.76 mL, 9.21 mmol) and CaC_2 (737 mg, 11.52 mmol) in the presence of CuI (146 mg, 0.76 mmol) compound **3d** was obtained (1.80 g, yield = 70%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.90). Obtained data was matched with the reported literature data.



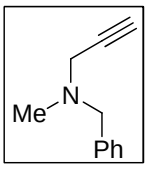
Synthesis of *N,N*-diethyl-1–pent–1-yn-3-amine (3e) [$C_9H_{17}N$]: The compound **3e** was prepared by following the *General Procedure A*. Starting from propionaldehyde (1.0 g, 17.21 mmol), diethylamine (1.04 mL, 20.65 mmol) and CaC_2 (1.60 g, 25.81 mmol) in the presence of CuI (326 mg, 1.72 mmol) compound **3e** was obtained (720 mg, yield = 30%) as colorless liquid. The compound **3b** was volatile, it was getting evaporated along with solvent while evaporating on rata evaporator causing poor yield so purification was avoided. The obtained data is recorded for crude compound. IR (neat): ν_{max}/cm^{-1} 3296, 3049, 2969, 2931, 2872, 2820, 1509, 1459, 1383, 1288, 1258, 1191, 1163, 1117, 1046; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.35 (td, *J* = 6.48, 2.16 Hz, 1H), 2.64 (sex, *J* = 7.40 Hz, 2H), 2.38 (sex, *J* = 7.00 Hz, 2H), 2.15 (d, *J* = 2.20 Hz, 1H), 1.64 (m, 2H), 1.03 (t, *J* = 7.20 Hz, 6H), 0.97 (t, *J* = 7.40 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 82.8, 72.0, 54.8, 44.8, 27.2, 13.8, 11.3; HRMS (ESI): Calc. for $C_9H_{18}N$ $[M+H]^+$: 140.1439; Found: 140.1436.

Synthesis of *N*,*N*-diethylhept-1-yn-3-amine (3f) [$C_{11}H_{21}N$]:  The compound **3f** was prepared by following the *General Procedure A*. Starting from n-valeraldehyde (1.0 g, 11.62 mmol), diethylamine (1.44 mL, 13.94 mmol) and CaC_2 (1.11 g, 17.43 mmol) in the presence of CuI (220 mg, 1.16 mmol) compound **3f** was obtained (970 mg, yield = 50%) as colourless liquid after column chromatographic purification. *Eluent*: 3% EtOAc in Petroleum ether (R_f = 0.65). IR (neat): ν_{max}/cm^{-1} 3306, 2958, 2927, 2864, 1685, 1610, 1562, 1459, 1378, 1278, 1193, 1075; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (td, *J* = 8.40, 2.16 Hz, 1H), 2.67 (sex, *J* = 7.40 Hz, 2H), 2.39 (sex, *J* = 7.40 Hz, 2H), 2.15 (d, *J* = 2.12 Hz, 1H), 1.63 (m, 2H), 1.45 – 1.26 (m, 4H), 1.05 (t, *J* = 7.24 Hz, 6H), 0.90 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 83.0, 72.0, 53.0, 44.8, 33.8, 29.0, 22.5, 14.1, 13.8; HRMS (ESI): Calc. for $C_{11}H_{22}N$ $[M+H]^+$: 168.1752; Found: 168.1759.

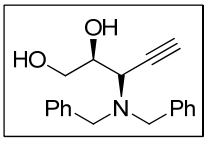
Synthesis of 1-cyclohexyl-*N, N*-diethylprop-2-yn-1-amine (3g) [$C_{13}H_{23}N$]:  The compound **3g** was prepared by following the *General Procedure A*. Starting from cyclohexaladehyde (1.0 g, 8.92 mmol), diethylamine (1.10 mL, 10.71 mmol) and CaC_2 (856 mg, 13.38 mmol) in the presence of CuI (169 mg, 0.89 mmol) compound **3g** was obtained (1.03 g, yield = 60%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). IR (neat): ν_{max}/cm^{-1} 3305, 2967, 2923, 2850, 2361, 1449, 1380, 1294, 1254, 1195; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (dd, *J* = 10.08, 2.20 Hz, 1H), 2.60 (sex, *J* = 7.44 Hz, 2H), 2.33 (sex, *J* = 6.90 Hz, 2H), 2.16 (d, *J* = 2.24 Hz, 1H), 2.04 (d, *J* = 12.80 Hz, 2H), 1.75 (m, 2H), 1.49 (m, 1H), 1.25 (m, 4H), 1.01 (t, *J* = 7.24 Hz, 6H), 0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.1, 72.4, 58.6, 44.7, 40.0, 31.2, 30.55, 26.8, 26.2, 26.0, 13.8; HRMS (ESI): Calc. for $C_{13}H_{24}N$ $[M+H]^+$: 194.1909; Found: 194.1900.

Synthesis of 1–((S)–2,2–dimethyl–1,3–dioxolan–4–yl)–*N, N*-diethylprop–2–yn-1–amine (3h) [$C_{12}H_{21}NO_2$]:  The compound **3h** was prepared by following the *General Procedure A*. Starting from D-glyceraldehyde (1.0 g, 7.68 mmol), diethylamine (961 mL, 9.21 mmol) and CaC_2 (737 mg, 11.52 mmol) in the presence of CuI (146 mg, 0.76 mmol) compound **3h** was obtained (1.05 g, yield = 65%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.90). M.p.: 56-57 ^{o}C; IR (neat): ν_{max}/cm^{-1} 3300, 2975, 2934, 2877,

2821, 2362, 1513, 1460, 1376, 1293, 1250, 1211,1157, 1119, 1064; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (q, *J* = 6.96 Hz, 1H), 4.10 (t, *J* = 7.40 Hz, 1H), 3.89 (t, *J* = 7.60 Hz, 1H), 3.63 (d, *J* = 7.84 Hz, 1H), 2.72 (sex, *J* = 6.44 Hz, 2H), 2.50 (sex, *J* = 6.73 Hz, 2H), 2.22 (s, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.09 (t, *J* = 7.16 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.0, 79.0, 76.0, 74.2, 67.7, 56.5, 45.3, 26.8, 25.7, 13.3; HRMS (ESI): Calc. for $C_{12}H_{22}NO_2$ $[M+H]^+$: 212.1651; Found: 212.1656.



Synthesis of *N*-benzyl-*N*-methylprop-2-yn-1-amine (3i) [$C_{11}H_{13}N$]: The compound **3i** was prepared by following the *General Procedure B*. Starting from propargyl bromide (1.0 g, 8.40mmol), dibenzylamine (1.60 mL, 8.40mmol) and K_2CO_3 (2.30 g, 16.8 mmol) compound **3i** was obtained (500 mg, yield = 50%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.70). IR (neat): ν_{max}/cm^{-1} 3294, 3029, 2940, 2837, 2793, 1494, 1451, 1365, 1328, 1192, 1075, 1027; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.34-7.29 (m, 5H), 3.56 (s, 2H), 3.3 (d, *J* = 2.36 Hz, 2H), 2.33 (s, 3H), 2.26 (t, *J* = 2.36, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ138.4, 129.2, 128.4, 127.3 78.5, 73.3, 59.9, 44.8, 41.7; HRMS(ESI): Calc. for $C_{11}H_{14}N$ $[M+H]^+$: 160.1126; Found: 160.1127.



Synthesis of (*2S*)-3-(dibenzylamino)pent-4-yne-1,2-diol (3j) [$C_{19}H_{21}NO_2$]: To a round bottom flask, compound **3j** (1g) was dissolved in methanol (10mL).The resultant solution was acidified using 1 mL of 2N HCl and was stirred for 3 hrs. Upon completion of the reaction as observed from TLC, the reaction mixture was reduced in vacuo and washed with water (10 mL) and extracted using ethyl acetate (3x10mL). The organic layer was dried over Na_2SO_4 and evaporated. The resulting residue was purified using flash chromatography (10% ethyl acetate in Petroleum ether) to afford compound **3j** as a colorless liquid (830 mg, yield = 95%). IR (neat): ν_{max}/cm^{-1} 3441, 3291, 3061, 3029, 2925, 2844, 1543, 1493, 1370, 1288, 1250, 1209, 1071; ^{1}H NMR (400 MHz, DMSO): δ 7.35 – 7.16 (m, 10H), 4.43 (s, 2H), 3.82 (d, *J* = 13.80 Hz, 2H), 3.58 (br. s, 1H), 3.53 (m, 1H), 3.38 (m, 4H), 2.45 (d, *J* = 1.56 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.2, 128.8, 128.7, 127.7, 76.0, 70.1, 62.9, 55.2, 53.4; HRMS(ESI): Calc. for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1650; Found: 296.1654.

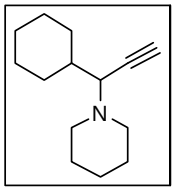
Synthesis of 1–(hept–1–yn–3–yl) pyrrolidine (3k) [$C_{11}H_{19}N$]: The compound **3k** was prepared by following the *General Procedure A*. Starting from n-valeraldehyde (1.0 g, 11.62 mmol), piperidine (1.14 mL, 13.94mmol) and CaC_2 (1.11 g, 17.43 mmol) in the presence of CuI (220 mg, 1.16mmol) compound **3k** was obtained (1.20 g, yield = 63%) as pale yellow liquid after column chromatographic purification. *Eluent*: 4% EtOAc in Petroleum ether (R_f = 0.60). IR (neat): ν_{max}/cm^{-1} 3304, 2956, 2932, 2868, 2813, 2361, 1731, 1691, 1646, 1459, 1349, 317, 1290, 1245, 1139, 1100, 1029; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.47 (m, 1H), 2.67 (m, 2H), 2.60 (m, 2H), 2.20 (d, *J* = 2.24 Hz, 1H), 1.77 (m, 4H), 1.62 (m, 2H), 1.35 (m, 4H), 0.88 (t, *J* =7.24 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.4, 72.7, 54.3, 49.4, 34.7, 28.8, 23.4, 22.5, 14.1; HRMS (ESI): Calc. for $C_{11}H_{20}N$ $[M+H]^+$: 166.1596; Found: 166.1605.

Synthesis of 1–(1–cyclohexylprop-2-yn–1–yl) pyrrolidine (3l) [$C_{13}H_{21}N$][S6]: The compound **3l** was prepared by following the *General Procedure A*. Starting from cyclohexaladehyde (1.0 g, 8.92 mmol), pyrrolidine (1.02 mL, 10.70 mmol) and CaC_2 (857 mg, 13.38 mmol) in the presence of CuI (170 mg, 0.89 mmol) compound **3l** was obtained (860 mg, yield = 50%) as pale yellow solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.90). Obtained data was matched with the reported literature data.

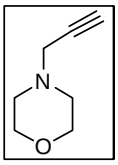
Synthesis of 1–(prop–2–yn–1–yl) piperidine (3m) [$C_8H_{13}N$]:[S7] The compound **3m** was prepared by following the *General Procedure B*. Starting from propargyl bromide (1.0 g, 8.40 mmol), piperidine (830 µL, 8.40mmol) and K_2CO_3 (2.30 g, 16.80mmol), compound **3m** was obtained (520 mg, yield = 50%) as pale yellow liquid after column chromatographic purification. The poor yield of compound is because of volatile nature of compound. *Eluent*: 2% dichloromethane in MeOH (R_f = 0.40). Obtained data was matched with the reported literature data.

Synthesis of 1–(hept–1–yn–3–yl) piperidine (3n) [$C_{12}H_{21}N$]: The compound **3n** was prepared by following the *General Procedure A*. Starting from n - valeraldehyde (1.0 g, 11.62 mmol), piperidine (1.90 mL, 13.95 mmol) and CaC_2 (1.11 g, 17.43 mmol) in the presence of CuI (220 mg, 1.16 mmol) compound **3n** was obtained (1.32 g, yield = 66%) as pale yellow liquid after

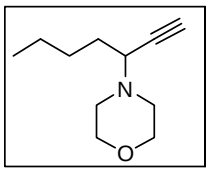
column chromatographic purification. *Eluent*: 2% EtOAc in Petroleum ether (R_f = 0.85). IR (neat): ν_{max}/cm^{-1} 3304, 2930, 2859, 2805, 2752, 2686, 2362, 1648, 1561, 1456, 1376, 1330, 1301, 1263, 1158, 1096, 1061, 1034; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.21 (td, *J* = 6.44, 1.92 Hz, 1H), 2.55 – 2.49 (m, 2H), 2.32 (m, 2H), 2.18 (d, *J* = 2.12 Hz, 1H), 1.58 – 1.25 (m, 13H), 0.85 (t, *J* = 14.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.2, 73.0, 58.0, 50.3, 33.2, 29.0, 26.2, 24.6, 22.5, 14.1; HRMS (ESI): Calc. for $C_{12}H_{22}N$ $[M+H]^+$: 180.1752; Found: 180.1755.

Synthesis of 1–(1–cyclohexylprop-2-yn–1–yl) piperidine (3o) [$C_{14}H_{23}N$]: 

The compound **3o** was prepared by following the *General Procedure A*. Starting from cyclohexaladehyde (1.0 g, 8.92 mmol), piperidine (1.14 mL, 10.71 mmol) and CaC_2 (856 mg, 13.38 mmol) in the presence of CuI (169 mg, 0.89 mmol) compound **3o** was obtained (1.28 g, yield = 70%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). M.p.: 118-119 ^oC; IR (neat): ν_{max}/cm^{-1} 3303, 2924, 2851, 2804, 2750, 2680, 2361, 1693, 1646, 1514, 1446, 1383, 1311, 1267, 1231, 1157, 1104, 1036; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 (m, 1H), 2.51 (m, 2H), 2.29 (m, 2H), 2.24 (d, *J* = 2.16 Hz, 1H), 2.03-1.94 (m, 2H), 1.74-1.48 (m, 9H), 1.42 (q, *J* = 5.76 Hz, 2H), 1.27-1.10 (m, 3H), 0.98-0.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 81.5, 73.3, 64.5, 63.7, 50.5, 39.4, 31.4, 31.2, 30.3, 26.8, 26.2, 26.1, 24.7; HRMS (ESI): Calc. for $C_{14}H_{24}N$ $[M+H]^+$: 206.1909; Found: 206.1919.

Synthesis of 4–(prop–2–yn–1–yl) morpholine (3p) [$C_7H_{11}NO$][S8]: 

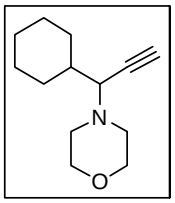
The compound **3p** was prepared by following the *General Procedure 2*. Starting from propargyl bromide (1.0 g, 8.40 mmol), morpholine (724 µL, 8.40 mmol) and K_2CO_3 (2.30 g, 16.80 mmol), compound **3p** was obtained (1.0 g, yield = 70%) as colorless solid after column chromatographic purification. *Eluent*: 1% dichloromethane in MeOH (R_f = 0.60). Obtained data was matched with the reported literature data.

Synthesis of 4–(hept–1–yn–3–yl) morpholine (3q) [$C_{11}H_{19}NO$]: 

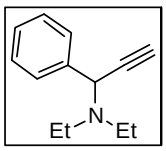
The compound **3q** was prepared by following the *General Procedure 1*. Starting from n-valeraldehyde (1.0 g, 11.62 mmol), morpholine (1.17 mL, 13.95 mmol) and CaC_2 (1.1 g, 17.43 mmol) in the presence of CuI (220 mg, 1.16 mmol) compound **3q** was obtained (1.4 g, yield = 70%) as colorless liquid after column chromatographic purification. *Eluent*: 2% EtOAc in Petroleum ether (R_f = 0.8). IR

(neat): ν_{max}/cm^{-1} 3301, 2955, 2929, 2859, 1728, 1656, 1456, 1378, 1328, 1286, 1256, 1177, 1114, 1071, 1034, 1001; ^1H NMR (400 MHz, $CDCl_3$): δ 3.75 – 3.65 (m, 4H), 3.27 (td, *J* = 7.60, 2.04 Hz, 1H), 2.66 (m, 2H), 2.48 (m, 2H), 2.28 (d, *J* = 2.04 Hz, 1H), 1.64 (q, *J* = 7.56 Hz, 2H), 1.49 – 1.27 (m, 5H), 0.89 (t, *J* = 7.16 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 81.3, 73.7, 67.1, 57.5, 49.5, 32.5, 28.7, 22.5, 14.1; HRMS (ESI): Calc. for $C_{11}H_{20}NO$ $[M+H]^+$: 182.1545; Found: 182.1546.

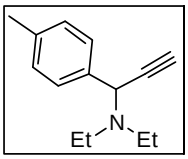
Synthesis of 4–(1–cyclohexylprop-2-yn–1–yl) morpholine (3r) [$C_{13}H_{21}NO$]: The compound **3r** was prepared by following the *General Procedure 1*. Starting from cyclohexaladehyde (1.0 g, 8.92 mmol), morpholine (914 µL, 10.71 mmol) and CaC_2 (856 mg, 13.38 mmol) in the presence of CuI (169 mg, 0.89 mmol) compound **3r** was obtained (1.38 g, yield = 75%) as colourless liquid after column chromatographic purification. *Eluent*: 2% EtOAc in Petroleum ether (R_f = 0.80). IR (KBr): ν_{max}/cm^{-1} 3299, 2922, 2850, 2753,2362, 1647, 1514, 1449, 1384, 1322, 1287, 1257, 1213, 1114, 1077, 1006; ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 - 3.64 (m, 4H), 2.91 (dd, *J* = 9.96, 2.16 Hz, 1H), 2.61 – 2.56 (m, 2H), 2.42 – 2.37 (m, 2H), 2.28 (d, *J* = 2.24 Hz, 1H), 2.03 (m, 2H), 1.75 – 1.64 (m, 3H), 1.54 – 1.44 (m, 1H), 1.27 – 1.11 (m, 3H), 1.00 – 0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 80.5, 74.1, 67.2, 63.3, 49.7, 38.9, 30.8, 30.2, 26.7, 26.1, 26.0; HRMS (ESI): Calc. for $C_{13}H_{21}NO$ $[M+H]^+$: 208.1701; Found: 208.1709.



Synthesis of *N, N*-diethyl-1–phenylprop-2-yn–1 amine (3s) [$C_{13}H_{17}N$]:[S1] The compound **3s** was prepared by following the *General Procedure A*. Starting from benzaldehyde (1.0 g, 9.42 mmol), diethylamine (1.18 mL, 11.30 mmol) and CaC_2 (798 mg, 14.13 mmol) in the presence of CuI (215 mg, 1.13 mmol) compound **3s** was obtained (1.14 g, yield = 65%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). Obtained data was matched with the reported literature data.

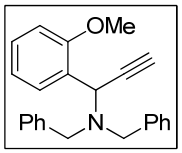


Synthesis of *N, N*-diethyl-1–(*p*-tolyl) prop-2-yn–1 amine (3t) [$C_{14}H_{19}N$]: The compound **3t** was prepared by following the *General Procedure A*. Starting from 4-methyl benzaldehyde (1.0 g, 8.32 mmol), diethylamine (1.04 mL, 9.98 mmol) and CaC_2 (798 mg, 12.48 mmol) in the presence of CuI (138 mg, 0.73

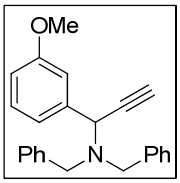


mmol) compound **3t** was obtained (1.09 g, yield = 65%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). IR (neat): ν_{max}/cm^{-1} 3300, 2968, 2927, 2823, 2361, 1646, 1510, 1459, 1381, 1291, 1264, 1190, 1168, 1115, 1050; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.00 Hz, 2H), 7.14 (d, *J* = 8.00 Hz, 2H), 4.79 (d, *J* = 1.36 Hz, 1H), 2.59 (m, 2H), 2.46 (m, 3H), 2.33 (s, 3H), 1.03 (t, *J* = 7.14 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 136.3, 128.8, 128.2, 80.3, 74.8, 56.1, 44.4, 21.2, 13.6; HRMS (ESI): Calc. for $C_{14}H_{20}N$ $[M+H]^+$: 202.1596; Found: 202.1603.

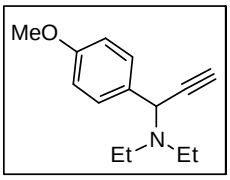
Synthesis of *N,N*-dibenzyl-1-(2-methoxyphenyl)prop-2-yn-1-amine (3u) [$C_{24}H_{23}NO$]: The compound **3u** was prepared by following the *General Procedure A*. Starting from 2-methoxybenzaldehyde (1.0 g, 7.34 mmol), dibenzylamine (1.70 mL, 8.81 mmol) and CaC_2 (705 mg, 11.01 mmol) in the presence of CuI (139 mg, 0.73 mmol) compound **3u** was obtained (1.70 g, yield = 70%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.82). M.p.: 104-105 ^{o}C; IR (neat): ν_{max}/cm^{-1} 3291, 3060, 3028, 2935, 2832, 1596, 1491, 1457, 1367, 1283, 1249, 1109, 1029; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.65 (d, *J* = 7.48 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 4H), 7.25 (t, *J* = 7.32 Hz, 4H), 7.18 (q, *J* = 7.00 Hz, 3H), 6.88 (t, *J* = 7.44 Hz, 1H), 6.81 (d, *J* = 8.16 Hz, 1H), 5.00 (s, 1H), 3.75 (d, *J* = 13.6 Hz, 2H), 3.66 (s, 3H), 3.44 (d, *J* = 13.6 Hz, 2H), 2.51 (d, *J* = 2.16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 139.8, 130.4, 129.1, 127.9, 126.8, 126.5, 119.7, 110.8, 79.9, 74.9, 55.0, 54.6, 50.7; HRMS (ESI): Calc. for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1858; Found: 342.1866.



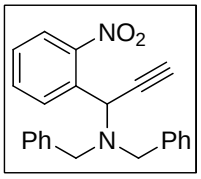
Synthesis of *N,N*-dibenzyl-1-(3-methoxyphenyl)prop-2-yn-1-amine (3v) [$C_{24}H_{23}NO$]: The compound **3v** was prepared by following the *General Procedure A*. Starting from 2-methoxybenzaldehyde (1.0 g, 7.34 mmol), dibenzylamine (1.70 mL, 8.81 mmol) and CaC_2 (705 mg, 11.01 mmol) in the presence of CuI (139 mg, 0.73 mmol) compound **3v** was obtained (1.60 g, yield = 65%) as yellow liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.82). IR (neat): ν_{max}/cm^{-1} 3290, 3061, 3028, 2937, 2834, 1598, 1488, 1454, 1310, 1276, 1251, 1110, 1048; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.40 Hz, 4H), 7.30 (t, *J* = 7.60 Hz, 4H), 7.24 (s, 2H), 7.22 (m, 3H), 6.78 (m, 1H), 4.67 (s, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 13.6, 2H), 3.43 (d, *J* = 13.52 Hz, 2H), 2.61(d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 140.3, 139.4, 129.1, 128.9, 128.4, 127.1, 120.6, 114.1, 112.8, 78.8, 76.1,



55.4, 55.4, 55.3, 54.5; HRMS(ESI): Calc. for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1858; Found: 342.1867.

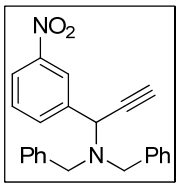


Synthesis of *N, N*-diethyl-1–(4-methoxyphenyl) prop-2-yn–1 amine (3w) [$C_{14}H_{19}NO$]: The compound **3w** was prepared by following the *General Procedure A*. Starting from 4-methoxy benzaldehyde (1.0 g, 7.34 mmol), diethylamine (802 µL, 8.81 mmol) and CaC_2 (704 mg, 11.01 mmol) in the presence of CuI (138 mg, 0.73 mmol) compound **3w** was obtained (798 mg, yield = 50%) as colorless liquid after column chromatographic purification. *Eluent*: 3% EtOAc in Petroleum ether (R_f = 0.70). IR (neat): ν_{max}/cm^{-1} 3295, 2968, 2933, 2829, 2362, 1610, 1584, 1508, 1461, 1381, 1299, 1244, 1171, 1114, 1038; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 8.68, 0.56 Hz, 2H), 6.86 (dd, *J* = 6.60, 2.16 Hz, 2H), 4.77 (d, *J* = 2.20 Hz, 1H), 3.79 (s, 3H), 2.58 (m, 2H), 2.44 (m, 3H), 1.03 (t, *J* = 7.20 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 131.4, 129.4, 113.4, 80.4, 74.8, 55.8, 55.3, 44.3, 13.6; HRMS (ESI): Calc. for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1545; Found: 218.1540.

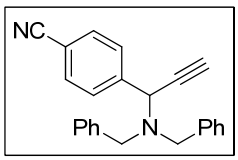


Synthesis of *N,N*-dibenzyl-1-(2-nitrophenyl)prop-2-yn-1-amine (3x) [$C_{23}H_{20}N_2O_2$]: The compound **3x** was prepared by following the *General Procedure A*. Starting from 2-nitrobenzaldehyde (1.0 g, 6.61 mmol), dibenzylamine (1.52 mL, 7.94 mmol) and CaC_2 (635 mg, 9.91 mmol) in the presence of CuI (125 mg, 0.66 mmol) compound **3x** was obtained (1.06 g, yield = 45%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). M.p.: 84-85 ^{o}C; IR (neat): ν_{max}/cm^{-1} 3289, 3030, 2837, 1604, 1528, 1493, 1450, 1361, 1308, 1103, 1072; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.76 Hz, 1H), 7.57 (d, *J* = 7.92 Hz, 1H), 7.40 (t, *J* = 7.60 Hz, 1H), 7.30 (t, *J* = 7.70 Hz, 1H), 7.25 – 7.16 (m, 10H), 5.44 (s, 1H), 3.50 (d, *J* = 13.12 Hz, 2H), 3.37 (d, *J* = 13.12 Hz, 2H), 2.76 (d, *J* = 1.20 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 149.8, 137.9, 132.0, 131.2, 130.7, 129.4, 128.8, 128.1, 121.2, 124.3, 78.4, 55.5, 53.3; HRMS (ESI): Calc. for $C_{23}H_{21}N_2O_2$ $[M+H]^+$: 357.1603; Found: 357.1602.

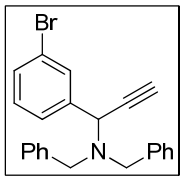
Synthesis of *N,N*-dibenzyl-1-(3-nitrophenyl)prop-2-yn-1-amine (3y) [$C_{23}H_{20}N_2O_2$]: The compound **3y** was prepared by following the *General Procedure A*. Starting from 3-nitrobenzaldehyde (1.0 g, 6.61 mmol), dibenzylamine (1.52 mL, 7.94 mmol) and CaC_2 (856 mg, 13.38 mmol) in the presence of CuI (125 mg, 0.66 mmol) compound **3y** was obtained (1.17 g, yield = 50%) as yellow semi- solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.85). IR (neat): ν_{max}/cm^{-1} 3292, 3062, 3029, 2925, 2837, 1529, 1493, 1452, 1350, 1253, 1109, 1073; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.10 (dd, *J* = 8.20, 2.20 Hz, 1H), 7.96 (dd, *J* = 8.00, 0.70 Hz, 1H), 7.50 (t, *J* = 8.00 Hz, 1H), 7.37 – 7.28 (m, 9H), 7.25 (m, 2H), 4.73 (d, *J* = 1.60 Hz, 1H), 3.70 (d, *J* = 13.44 Hz, 2H), 3.45 (d, *J* = 13.44 Hz, 2H), 2.73 (d, *J* = 2.32 Hz, 1H);. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 141.3, 138.7, 134.3, 129.1, 128.9, 128.6, 127.5, 123.2, 122.8, 77.6; HRMS (ESI): Calc. for $C_{23}H_{21}N_2O_2$ $[M+H]^+$: 357.1603; Found: 357.1602



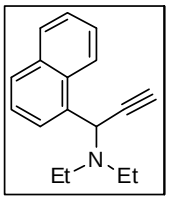
Synthesis of 4-(1-(dibenzylamino)prop-2-ynyl)benzonitrile (3z) [$C_{24}H_{20}N_2$]: The compound **3z** was prepared by following the *General Procedure A*. Starting from 4-cyanobenzaldehyde (1.0 g, 7.62 mmol), dibenzylamine (1.52 mL, 9.14 mmol) and CaC_2 (732 mg, 11.43 mmol) in the presence of CuI (144 mg, 0.76 mmol) compound **3z** was obtained (2.05 g, yield = 80%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.82). M.p.: 114-115 ^{o}C; IR (neat): ν_{max}/cm^{-1} 3291, 3061, 3029, 2887, 2836, 2228, 1605, 1496, 1451, 1405, 1368, 1108, 1072; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.58 (d, *J* = 8.20 Hz, 2H), 7.32 – 7.25 (m, 8H), 7.21 (m, 2H), 4.66 (s, 1H), 3.64 (d, *J* = 13.44 Hz, 2H), 3.41 (d, *J* = 13.44 Hz, 2H), 2.67 (d, *J* = 1.90 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 138.8, 132.1, 129.0, 128.9, 128.5, 127.5, 118.9, 111.6, 55.4, 54.7; HRMS (ESI): Calc. for $C_{24}H_{21}N_2$ $[M+H]^+$: 337.1704; Found: 337.1711.



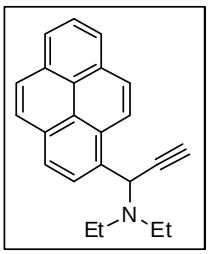
Synthesis of *N,N*-dibenzyl-1-(3-bromophenyl)prop-2-yn-1-amine (3a´) [$C_{23}H_{20}BrN$]: The compound **3a´** was prepared by following the *General Procedure A*. Starting from 3-bromobenzaldehyde (1.0 g, 5.40 mmol), dibenzylamine (1.24 mL, 6.48 mmol) and CaC_2 (520 mg, 8.10 mmol) in the presence of CuI (102 mg, 0.54 mmol) compound **3a´** was obtained (1.05 g, yield = 50%) as colorless solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum



ether (R_f = 0.84). M.p.: 104-105 ^oC; IR (neat): ν_{max}/cm^{-1} 3294, 3061, 3029, 2927, 2889, 2836, 1594, 1568, 1494, 1460, 1418, 1368, 1295, 1251, 1185, 1110, 1071, 1027; ^1H NMR (400 MHz, $CDCl_3$):δ 7.77 (s, 1H), 7.58 (d, *J* = 7.36 Hz, 5H), 7.30 (t, *J* = 7.50 Hz, 4H), 7.20 (m, 4H), 4.63 (s, 1H), 3.68 (d, *J* = 13.44 Hz, 2H), 3.40 (d, *J* = 13.44 Hz, 2H), 2.64 (d, *J* = 2.24 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 139.1, 131.2, 130.7, 129.7, 128.9, 128.4, 127.2, 126.9, 122.3, 78.0, 55.0, 54.5; HRMS (ESI): Calc. for $C_{23}H_{21}BrN$ $[M+H]^+$: 390.0857; Found: 390.0855.



Synthesis of *N*,*N*-diethyl-1-(naphthalen-1-yl) prop-2-yn-1-amine (3b´) [$C_{17}H_{19}N$]: The compound **3b´** was prepared by following the *General Procedure A*. Starting from α-naphthaldehyde (1.0 g, 6.40 mmol), diethylamine (802 µL, 7.68 mmol) and CaC_2 (614 mg, 9.60 mmol) in the presence of CuI (121 mg, 0.64 mmol) compound **3b´** was obtained (850 mg, yield = 56%) as colorless liquid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.90). IR (neat): ν_{max}/cm^{-1} 3295, 3049, 2969, 2931, 2872, 2820, 1509, 1459, 1383, 1288, 1256, 1191, 1163, 1117, 1046; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.00 Hz, 1H), 7.95 (d, *J* = 7.08 Hz, 1H), 7.84 (dd, *J* = 7.60, 1.88 Hz, 1H), 7.79 (d, *J* = 8.20 Hz, 1H), 7.51 (m, 3H), 5.52 (d, *J* = 2.16 Hz, 1H), 2.73 (m, 2H), 2.55 (d, *J* = 2.28 Hz, 1H), 2.53 (m, 2H), 1.03 (td, *J* = 7.24, 2.28 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.1, 134.0, 131.8, 128.7, 128.5, 127.2, 125.8, 125.6, 124.9, 80.2, 75.7, 55.2, 44.7, 13.5; HRMS (ESI): Calc. for $C_{17}H_{20}N$ $[M+H]^+$: 238.1596; Found: 238.1598.



Synthesis of *N*, *N*-diethyl-1-(pyren-1-yl) prop-2-yn-1-amine (3c´) [$C_{23}H_{21}N$]: The compound **3c´** was prepared by following the *General Procedure 1*. Starting from pyrene aldehyde (1.0 g, 4.34 mmol), diethylamine (544 µL, 5.21 mmol) and CaC_2 (416 mg, 6.51 mmol) in the presence of CuI (81 mg, 0.43 mmol) compound **3c´** was obtained (608 mg, yield = 45%) as yellow solid after column chromatographic purification. *Eluent*: 1% EtOAc in Petroleum ether (R_f = 0.90). M.p.: 83-84 ^oC; IR (neat): ν_{max}/cm^{-1} 3294, 3042, 2929, 2820, 2361, 1917, 1593, 1459, 1381, 1322, 1290, 1266, 1240, 1187, 1161, 1117, 1050 ; ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 9.32 Hz, 1H), 8.49 (d, *J* = 7.92 Hz, 1H), 8.18 – 8.09 (m, 4H), 8.04 (s, 2H), 8.00 (t, *J* = 7.60 Hz, 1H), 5.81 (d, *J* = 2.24 Hz, 1H), 2.76 – 2.68 (sex, *J* = 7.32 Hz, 2H), 2.65 (d, *J* = 2.28 Hz, 1H), 2.62 – 2.53 (sex, *J* = 6.96 Hz, 2H), 1.06 (t, *J* = 7.12

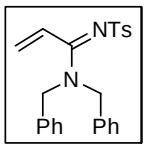
Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.9, 131.3, 131.2, 130.9, 129.4, 127.5, 127.4, 127.3, 127.1, 125.9, 125.3, 125.2, 124.8, 124.2, 124.1, 80.5, 76.0, 55.4, 44.8, 13.5; HRMS (ESI): Calc. for $C_{23}H_{22}N$ $[M+H]^+$: 312.1752; Found: 312.1752.

Synthesis of acrylamidine 2 in $CHCl_3$ under CuI catalytic conditions (Table 1, entry 1): To a round bottomed flask placed in a water bath at room temperature was added propargylamine **1** (300 mg, 1.27mmol) in $CHCl_3$ (3.0 mL). To the stirring solution were added sequentially triethylamine (207 µL, 1.52 mmol) and tosylazide (273 mg, 1.39mmol) followed by CuI (28 mg, 0.15mmol) when the evolution of N_2 gas was observed. The reaction mixture was stirred for thirty minutes under open atmospheric condition. After the completion, a saturated solution of NH_4Cl (10 mL) was added to the reaction mixture and stirred for additional 30 minutes. The crude product was extracted with $CHCl_3$ (2 × 10 mL), combined organic layer was washed with brine (5 mL) and concentrated under reduced pressure to give pale green residue which was purified by column chromatography over silica gel to provide the desired acrylamidine **2** (433 mg, yield 84%).

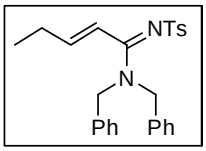
Synthesis of acrylamidines in $CHCl_3$ under CuCl catalytic conditions:

General Procedure C: To a round bottomed flask placed in water bath at room temperature was added propargylamine (1.0 mmol) in $CHCl_3$. To the stirring solution were added sequentially triethylamine (1.2 mmol) and tosylazide (1.1 mmol) followed by CuCl (0.1 mmol) when the evolution of N_2 gas was observed. The reaction mixture was stirred for either three minutes (for propargylamine with acyclic amino group) or 15-20 minutes (for propargylamine with cyclic amino group) under open atmospheric condition. After the completion, a saturated solution of NH_4Cl was added to the reaction mixture and stirred for additional 30 minutes. The crude product was extracted with $CHCl_3$ (three times) and combined organic layer was washed with brine and concentrated under reduced pressure to give pale green residue which was purified by column chromatography over silica gel to provide the desired acrylamidine.

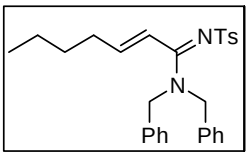
Synthesis of *N*, *N*-dibenzyl–*N′*-tosylacrylimidamide 2 [$C_{24}H_{24}N_2O_2S$]: The compound **2** was prepared by following the *General Procedure C*. Starting from propargylamine **1** (300 mg, 1.27 mmol) in $CHCl_3$ (3.0 mL), triethylamine (209 µL, 1.52 mmol), and tosylazide (273 mg, 1.39 mmol) in presence of CuCl (12 mg, 0.12 mmol) to obtain **2** (495 mg, yield = 96%) as a colorless solid after column chromatographic



purification. *Eluent*: Dichloromethane (R_f = 0.15). M.p.: 107-108 ^oC; IR (neat): ν_{max}/cm^{-1} 3029, 2923, 1629, 1596, 1516, 1444, 1431, 1359, 1281, 1144, 1086, 1023: ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.20 Hz, 2H), 7.28 (br. s, 6H), 7.20 (d, *J* = 8.40 Hz, 2H), 7.12 (br. s, 4H), 6.72 (dd, *J* = 18.00, 12.00 Hz, 1H), 5.72 (t, *J* = 17.40, 11.80 Hz, 2H), 4.63 (br. s, 2H), 4.56 (br. s,2H), 2.37 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$):δ 165.4, 142.0, 141.0, 135.6, 135.2, 129.1, 128.9, 128.6, 128.5, 128.2, 128.0, 127.0, 126.6, 125.0, 51.9, 49.9, 21.6; HRMS (ESI): Calc. for $C_{24}H_{25}N_2O_2S$ $[M+H]^+$: 405.1637; Found: 405.1632.

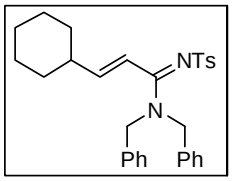


Synthesis of (2*E*)–*N*, *N*-dibenzyl-*N′*-tosylpent-2-enimidamide (4a) [$C_{26}H_{28}N_2O_2S$]: The compound **4a** was prepared by following the *General Procedure C*. Starting from propargylamine **3a** (300 mg, 1.15 mmol) in $CHCl_3$ (3.0 mL), triethylamine (188 µL, 1.36 mmol), and tosylazide (250 mg, 1.26 mmol) in presence of CuCl (11 mg, 0.11 mmol) to obtain **4a** (477 mg, yield = 96%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.25). M.p.: 94-95 ^oC; IR (neat): ν_{max}/cm^{-1}; 2967, 2927, 2362, 1653, 1596, 1516, 1452, 1430, 1359, 1284, 1145, 1089, 1024; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.24 Hz, 2H), 7.29 (br.s, 6H), 7.20 (d, *J* = 8.36, 2H), 7.12 (br.s, 4H), 6.29 (d, *J* = 16.48 Hz,1H), 6.20 (dt, *J* = 16.44, 5.84 Hz, 1H), 4.62 (br.s, 2H), 4.56 (br.s, 2H), 2.36 (s, 3H), 2.18 (qd, *J* = 6.08, 1.2 Hz, 2H), 0.98 (t, *J* = 7.40, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$):δ 166.0, 144.3, 141.8, 141.4, 135.8, 129.1, 128.0, 127.0, 126.5, 119.6, 52.0, 50.0, 26.0, 21.5, 21.1; HRMS (ESI): Calc. for $C_{26}H_{29}N_2O_2S$ $[M+H]^+$: 433.1950; Found: 433.1958.

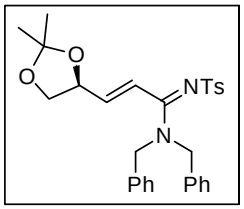


Synthesis of (2*E*)-*N*,*N*-dibenzyl–*N′*-tosylhept–2-enimidamide (4b) [$C_{28}H_{32}N_2O_2S$]: The compound **4b** was prepared by following the *General Procedure C*. Starting from propargylamine **3b** (300 mg, 1.02 mmol) in $CHCl_3$ (3.0 mL), triethylamine (170 µL, 1.23 mmol), and tosylazide (221 mg, 1.12 mmol) in presence of CuCl (10 mg, 0.10mmol) to obtain **4b** (431 mg, yield = 91%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.15). M.p.: 87-88 ^oC; IR (neat): ν_{max}/cm^{-1} 3030, 2955, 2926, 2864, 2363, 1740, 1651, 1597, 1515, 1455, 1430, 1360, 1283, 1145, 1089, 1026; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.28 Hz, 2H), 7.28 (br. s, 6H), 7.20 (d, *J* = 7.96 Hz, 2H), 7.12 (br. s, 4H), 6.31 (d, *J* = 16.44 Hz, 1H), 6.17 (dt, *J* = 16.44, 6.56 Hz, 1H), 4.61 (br. s, 2H), 4.56 (br. s,2H), 2.36 (s, 3H), 2.15(q, *J* = 6.80 Hz, 2H), 1.37 – 1.19 (m, 4H), 0.84 (t, *J* = 7.28 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 165.8, 143.3, 141.8, 141.4, 135.7, 129.1, 128.5, 128.0, 126.9, 126.5, 120.3, 77.5, 77.1, 76.8, 51.9, 50.1, 32.8,30.1, 22.3, 21.5, 13.9; HRMS(ESI): Calc. for $C_{28}H_{33}N_2O_2S$ $[M+H]^+$: 461.2263; Found: 461.2265.

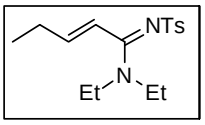


Synthesis of (2*E*)-*N*, *N*-dibenzyl–3–cyclohexyl-*N′*-tosylacrylimidamide (4c) [$C_{30}H_{34}N_2O_2S$]: The compound **4c** was prepared by following the *General Procedure C*. Starting from propargylamine **3c** (300 mg, 0.94 mmol) in $CHCl_3$ (3.0 mL), triethylamine (156 µL, 1.13 mmol), and tosylazide (204 mg, 1.03 mmol) in presence of CuCl (18 mg, 0.09mmol) to obtain **4c** (418 mg, yield = 91%) as a colorless semi-solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). IR (neat): ν_{max}/cm^{-1} 3017, 2925, 2852, 2361, 1649, 1596, 1513, 1445, 1359, 1280, 1142, 1086, 970; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.28 (br. s, 6H), 7.23 (d, *J* = 8.40 Hz, 2H), 7.12 (br. s, 4H), 6.27 (d, *J* = 16.50 Hz, 1H), 6.13 (dd, *J* = 16.56, 6.44 Hz, 1H), 4.63 (br. s, 2H), 4.56 (br. s, 2H), 2.37 (s, 3H), 2.08 (m, 1H), 1.71 (m, 5H), 1.31 - 1.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 147.9, 141.8, 141.4, 135.8, 135.6, 129.0, 128.0, 127.0, 126.5, 118.3, 52.0, 50.0, 41.0, 31.5, 29.8, 25.7, 21.5; HRMS (ESI): Calc. for $C_{30}H_{35}N_2O_2S$ $[M+H]^+$: 487.2419; Found: 487.2434.

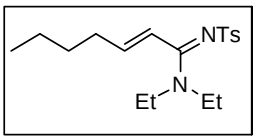


Synthesis of (2*E*)-*N*, *N*-dibenzyl–3–((S)–2,2–dimethyl–1, 3 dioxolan-4-yl)-*N′*-tosylacrylimidamide (4d) [$C_{29}H_{32}N_2O_4S$]: The compound **4d** was prepared by following the *General Procedure C*. Starting from propargylamine **3d** (300 mg, 0.89 mmol) in $CHCl_3$ (3.0 mL), triethylamine (148 µL, 1.07 mmol), and tosylazide (193 mg, 0.97 mmol) in presence of CuCl (8 mg, 0.08 mmol) to obtain **4d** (426 mg, yield = 95%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.20). M.p.: 100-101 ^{o}C; IR (neat): ν_{max}/cm^{-1} 3029, 2986, 2930, 2362, 1657, 1518, 1450, 1430, 1367, 1282, 1214, 1146, 1088, 1059; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.28 Hz, 2H), 7.27 (br.s, 6H), 7.20 (d, *J* = 8.04 Hz, 2H), 7.11 (br.s, 4H), 6.62 (dd, *J* = 16.44, 1.24 Hz, 1H), 6.20 (dd, *J* = 16.4, 5.72 Hz, 1H), 4.74 (br.d, *J* = 14.20 Hz, 1H), 4.60 (m, 4H), 4.15 (dd, *J* = 8.48, 6.64 Hz, 1H), 3.71 (dd, *J* = 8.32, 7.28 Hz, 1H), 2.36 (s, 3H), 1.35 (d, *J* = 1.64 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 164.8, 142.0, 141.1, 139.0, 135.6, 135.1, 129.1,

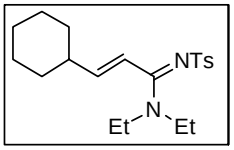
128.9, 128.5, 128.2, 128.0, 127.0, 126.5, 121.8, 110.1, 75.5, 68.6, 52.0, 50.0, 26.4, 25.9, 21.5; HRMS (ESI): Calc. for $C_{29}H_{32}N_2O_4S$ $[M+H]^+$: 505.2161; Found: 505.2162.



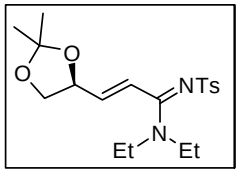
Synthesis of (2*E*)–*N*, *N*-diethyl-*N′*-tosylpent-2-enimidamide (4e) [$C_{16}H_{24}N_2O_2S$]: The compound **4e** was prepared by following the *General Procedure C*. Starting from propargylamine **3e** (300 mg, 2.15 mmol) in $CHCl_3$ (3.0 mL), triethylamine (356 µL, 2.58 mmol), and tosylazide (466 mg, 2.36 mmol) in presence of CuCl (21 mg, 0.21 mmol) to obtain **4e** (631 mg, yield = 95%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.20). M.p.: 72-73 ^oC; IR (neat): ν_{max}/cm^{-1} 2974, 2878, 2328, 1771, 1656, 1604, 1530, 1461, 1358, 1281, 1217, 1145, 1087, 1045, 1014, 979; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.24 Hz, 2H), 7.20 (d, *J* = 8.00 Hz, 2H), 6.15 (dt, *J* = 16.48, 1.56 Hz, 1H), 5.96 (dt, *J* = 16.48, 6.12 Hz, 1H), 3.45 (br. s, 2H), 3.37 (br. s, 2H), 2.36 (s, 3H), 2.17 (qd, *J* = 7.48, 1.60 Hz, 2H), 1.13 (m, 6H), 1.03 (t, *J* = 7.40, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 142.6, 141.8, 141.5, 128.9, 126.5, 119.9, 44.4, 42.6, 25.9, 21.5, 13.8, 12.2; HRMS (ESI): Calc. for $C_{16}H_{25}N_2O_2S$ $[M+H]^+$: 309.1637; Found: 309.1653.



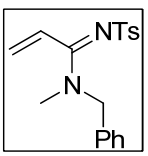
Synthesis of (2*E*)-*N*, *N*-diethyl-*N′*-tosylhept–2-enimidamide (4f) [$C_{18}H_{28}N_2O_2S$]: The compound **4f** was prepared by following the *General Procedure C*. Starting from propargylamine **3f** (300 mg, 1.79 mmol) in $CHCl_3$ (3.0 mL), triethylamine (295 µL, 1.97 mmol), and tosylazide (388 mg, 1.97 mmol) in presence of CuCl (17 mg, 0.17 mmol) to obtain **4f** (580 mg, yield = 96%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.20). M.p.: = 66-67 ^oC; IR (neat): ν_{max}/cm^{-1} 2961, 2929, 2868, 2362, 1654, 1599, 1526, 1460, 1439, 1359, 1279, 1217, 1144, 1086, 1043; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.20 (d, *J* = 7.92 Hz, 2H), 6.17 (d, *J* = 16.44 Hz, 1H), 5.95 – 5.88 (dt, *J* = 16.44, 6.60 Hz,1H), 3.45 (br. s, 2H), 3.37 (br. s, 2H), 2.36 (s, 3H), 2.15 (q, *J* = 6.60 Hz, 2H), 1.40 – 1.26 (m, 4H), 1.12 (t, *J* = 6.96 Hz, 6H), 0.90 (t, *J* = 7.20 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 141.8, 141.6, 141.5, 129.0, 126.4, 120.7, 44.4, 42.7, 32.6, 30.2, 29.8, 22.4, 21.5, 13.9, 12.1; HRMS (ESI): Calc. for $C_{18}H_{29}N_2O_2S$ $[M+H]^+$: 337.1950; Found: 337.1956.



Synthesis of (2*E*)–3-cyclohexyl–*N*,*N*-diethyl-*N*′-tosylacrylimidamide (4g) [$C_{20}H_{30}N_2O_2S$]: The compound **4g** was prepared by following the *General Procedure C*. Starting from propargylamine **3g** (300 mg, 1.55 mmol) in $CHCl_3$ (3.0 mL), triethylamine (255 µL, 1.86 mmol), and tosylazide (336 mg, 1.70 mmol) in presence of CuCl (15 mg, 0.15 mmol) to obtain **4g** (540 mg, yield = 96%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.25). M.p.: 93-94 ^oC; IR (neat): ν_{max}/cm^{-1} ; 2976, 2925, 2852, 2362, 1710, 1652, 1599, 1523, 1439, 1359, 1277, 1216, 1142, 1084, 1042, 978; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.20 (d, *J* = 8.00 Hz, 2H), 6.17(d, *J* = 16.56 Hz, 1H), 5.90(dd, *J* = 16.56, 6.48 Hz,1H), 3.45(br. s, 2H), 3.37 (br. s, 2H), 2.36(s, 3H), 2.07(m, 1H), 1.76 – 1.69(m, 5H), 1.28 – 1.07(m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 146.1, 141.8, 141.5, 129.0, 126.4, 118.7, 44.5, 42.7, 40.8, 31.7, 26.0, 21.5, 13.8, 12.1; HRMS (ESI): Calc. for $C_{20}H_{31}N_2O_2S$ $[M+H]^+$: 363.2106; Found: 363.2119.

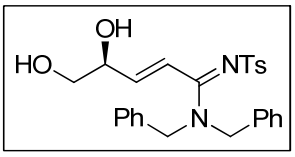


Synthesis of (2*E*)–3–((S)–2, 2–dimethyl–1, 3 dioxolan-4-yl)-*N*, *N* -diethyl–*N*'-tosylacrylimidamide (4h) [$C_{19}H_{28}N_2O_4S$]: The compound **4h** was prepared by following the *General Procedure C*. Starting from propargylamine **3h** (300 mg, 1.41mmol) in $CHCl_3$ (3.0 mL), triethylamine (234 µL, 1.70 mmol), and tosylazide (305 mg, 1.55mmol) in presence of CuCl (14 mg, 0.14mmol) to obtain **4h** (480 mg, yield = 89%) as a colorless solid after column chromatographic purification. *Eluent*: 1% MeOH/dichloromethane (R_f = 0.20). M.p.: 96-97 ^oC; IR (neat): ν_{max}/cm^{-1} 2983, 2931, 2362, 1709, 1659, 1603, 1529, 1458, 1368, 1277, 1215, 1144, 1084; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.20 (d, *J* = 7.84 Hz, 2H), 6.49(dd, *J* = 16.44, 1.24 Hz, 1H), 6.01(dd, *J* = 16.44, 6.00 Hz,1H), 4.62(q, *J* = 6.44 Hz,1H), 4.17(dd, *J* = 8.56, 6.48 Hz,1H), 3.73(dd, *J* = 8.56, 7.28 Hz,1H), 2.36(s, 3H), 1.42(s, 3H), 1.39(s, 3H), 1.14(t, *J* = 7.20 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 163.3, 141.7, 141.6, 137.6, 129.0, 126.3, 122.3, 110.0, 75.6, 68.7, 44.4, 42.7, 26.5, 25.9, 21.5, 13.8, 12.0; HRMS(ESI): Calc. for $C_{19}H_{28}N_2O_4S$ $[M+H]^+$: 381.1848; Found: 381.4848.

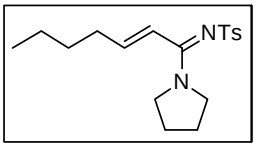


Synthesis of *(E)*-*N*-benzyl-*N*-methyl-*N*′-tosylacrylimidamide (4i) [$C_{18}H_{20}N_2O_2S$]: The compound **4i** was prepared by following the *General Procedure C*. Starting from propargylamine **3i** (300 mg, 1.88 mmol) in $CHCl_3$ (3.0 mL), triethylamine (310 µL, 2.26 mmol), and tosylazide (407 mg, 2.07 mmol) in presence of CuCl (17.82 mg, 0.18 mmol) to obtain **4i** (574 mg, yield = 88%) as a waxy liquid

after column chromatographic purification. *Eluent*: 25% EtOAc/Petroleum ether (R_f = 0.30). IR (neat): ν_{max}/cm^{-1} 3029, 1531, 1485, 1449, 1403, 1275, 1140, 1087, 1024; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.80(d, J=7.48 Hz, 1H), 7.73(d, J=7.52 Hz, 1H), 7.33(d, J=6.84, 1H), 7.27(br.s, 2H), 7.22(br.s, 3H), 7.10(d, J=6.84 Hz, 1H), 6.68(dd, J=18.08 Hz, 12.12 Hz, 1H), 5.74(dd, J=16 Hz, 12 Hz, 1H), 5.59(dd, J=17.92, 12.28 Hz, 1H), 4.69(s, 1H), 4.62(s, 1H), 2.97(s, 3H), 2.36(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 141.0, 135.3, 129.1, 128.8, 128.5, 128.3, 128.1, 128.0, 126.7, 126.5, 124.8, 55.3, 53.3, 37.6, 36.3, 21.5; HRMS(ESI): Calc. for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$: 329.1323; Found: 329.1324.

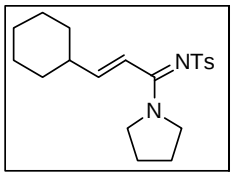


Synthesis of (*S,2E*)-*N,N*-dibenzyl-4,5-dihydroxy-*N′*-tosylpent-2-enimidamide (4j) [$C_{26}H_{28}N_2O_4S$]: The compound **4j** was prepared by following the *General Procedure C*. Starting from propargylamine **3j** (300 mg, 1.01 mmol) in $CHCl_3$ (3.0 mL), triethylamine (165 µL, 1.21 mmol) , and tosylazide (240 mg, 1.2 mmol) in presence of CuCl (19 mg, 0.10 mmol) to obtain **4j** (285 mg, yield = 60%) as a colorless semi-solid after column chromatographic purification. *Eluent*: 3% MeOH/Dichloromethane (R_f = 0.20 in EtOAc/Petroleum ether). IR (neat): ν_{max}/cm^{-1} 3030, 2924, 1602, 1522, 1352, 1280, 1144, 1088; ^{1}H NMR (400 MHz, DMSO): δ 7.47 (d, *J* = 8.24 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.22 (d, *J* = 7.28 Hz, 2H), 7.13 (d, *J* = 7.15 Hz, 4H), 6.43 (dd, *J* = 16.40, 1.80 Hz, 1H), 6.05 (dd, *J* = 16.40, 3.88 Hz, 1H), 5.11 (d, *J* = 5.16 Hz, 1H), 4.60 (m, 5H), 3.99 (t, *J* = 5.64 Hz, 1H), 3.20 (td, *J* = 5.90, 2.72 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 143.0, 141.9, 141.6, 136.3, 129.4, 129.2, 128.9, 128.1, 127.8, 127.5, 126.5, 119.8, 79.6, 71.6, 65.4, 52.8, 50.6, 21.4; HRMS (ESI): Calc. for $C_{26}H_{29}N_2O_4S$ $[M+H]^+$: 526.1800; Found: 526.1807.

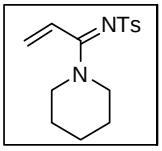


Synthesis of 4–methyl–*N*–((*E*)-1-(pyrrolidin–1-yl) hept–2-en–1–ylidene) benzenesulfonamide (4k) [$C_{18}H_{26}N_2O_2S$]: The compound **4k** was prepared by following the *General Procedure C*. Starting from propargylamine **3k** (300 mg, 1.81 mmol) in $CHCl_3$ (3.0 mL), triethylamine (300 µL, 2.17 mmol), and tosylazide (392 mg, 1.99 mmol) in presence of CuCl (18 mg, 0.18 mmol) to obtain **4k** (352 mg, yield = 58%) as a colorless solid after column chromatographic purification. *Eluent*: MeOH/Dichloromethane (R_f = 0.20). M.p.: 67-68 ^oC; IR (neat): ν_{max}/cm^{-1} 2958, 2926, 2873, 2362, 2654, 1600, 1519, 1457, 1337, 1275, 1141, 1089, 1023, 976; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.24 Hz, 2H), 7.19 (d, *J* = 8.00 Hz, 2H), 6.63 (d, *J* =

16.44 Hz, 1H), 6.09 (dt, *J* = 16.44, 6.80 Hz, 1H), 3.53 (t, *J* = 7.04 Hz, 2H), 3.44 (t, *J* = 6.60 Hz, 2H), 2.35 (s, 3H), 2.15 – 2.09 (qd, *J* = 6.50, 1.28 Hz, 2H), 1.89 (q, *J* = 3.12 Hz, 4H), 1.40 – 1.23 (m, 4H), 0.89 (t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 162.7, 143.1, 141.6, 129.0, 126.6, 121.7, 50.1, 48.6, 32.7, 30.2, 25.9, 24.4 22.3, 21.5, 14.0; HRMS (ESI): Calc. for $C_{18}H_{26}N_2O_2S$ $[M+H]^+$: 335.1793; Found: 335.1830.

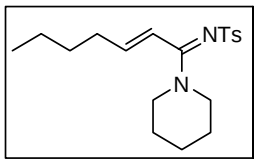


Synthesis of *N*–((*E*)–3-cyclohexyl–1–(pyrrolidin–1–yl) allylidene)–4-methylbenzenesulfonamide (4l) [$C_{20}H_{28}N_2O_2S$]: The compound **4l** was prepared by following the *General Procedure C*. Starting from propargylamine **3l** (300 mg, 1.56 mmol) in $CHCl_3$ (3.0 mL), triethylamine (260 µL, 1.88 mmol), and tosylazide (338 mg, 1.71 mmol) in presence of CuCl (15 mg, 0.15 mmol) to obtain **4l** (395 mg, yield = 70%) as a colorless solid after column chromatographic purification. *Eluent*: MeOH/Dichloromethane (R_f = 0.20). M.p.: 127-128 ^{o}C; IR (neat): ν_{max}/cm^{-1} 2924, 2852, 2361, 1651, 1600, 1518, 1453, 1337, 1275, 1192, 1141, 1089, 1022; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.20 Hz, 2H), 7.20 (d, *J* = 8.40 Hz, 2H), 6.29 (d, *J* = 16.56 Hz, 1H), 6.60 (dd, *J* = 16.60, 6.64 Hz,1H), 3.53 (t, *J* = 6.80 Hz, 2H), 3.44 (t, *J* = 6.44 Hz, 2H), 2.35 (s, 3H), 2.06 (m, 1H), 1.89 (m, 4H), 1.71 (br. s,2H), 1.69 (br. s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 147.7, 141.6, 141.5, 129.0, 126.6, 119.6, 50.2, 48.6, 40.9, 31.7, 29.8, 26.0, 25.9, 25.7, 24.4, 21.5; HRMS (ESI): Calc. for $C_{20}H_{28}N_2O_2S$ $[M+H]^+$: 361.1950; Found: 361.1955.

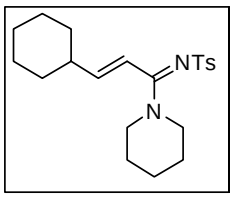


Synthesis of 4-methyl-*N*-(1-(piperidin-1-yl) allylidene) benzenesulfonamide (4m) [$C_{15}H_{20}N_2O_2S$]: The compound **4m** was prepared by following the *General Procedure C*. Starting from propargylamine **3m** (300 mg, 2.43 mmol) in $CHCl_3$ (3.0 mL), triethylamine (402 µL, 2.92 mmol), and tosylazide (526 mg, 2.67 mmol) in presence of CuCl (28 mg, 0.29 mmol) to obtain **4m** (341 mg, yield = 48%) as a colorless solid after column chromatographic purification. *Eluent*: 2% MeOH/Dichloromethane (R_f = 0.25). M.p.: 75-76 ^{o}C; IR (neat): ν_{max}/cm^{-1} 2937, 2860, 2362, 1707, 1601, 1526, 1449, 1399, 1362, 1274, 1144, 1086, 1015, 969; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.28 Hz, 2H), 7.21 (d, *J* = 8.00 Hz, 2H), 6.60 (dd, *J* = 18.16, 12.00 Hz, 1H), 5.65 (dd, *J* = 11.92, 0.80 Hz, 1H), 5.43 (dd, *J* = 17.68, 0.84 Hz, 1H), 3.67 (br. s, 2H), 3.51 (br. s, 2H), 2.36 (s, 3H), 1.66 (m, 2H), 1.62 (br. s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$):δ

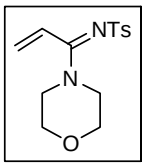
163.6, 141.8, 141.3, 129.0, 128.9, 126.6, 124.0, 49.2, 45.8, 26.5, 25.4, 24.2, 21.5; HRMS (ESI): Calc. for $C_{15}H_{20}N_2O_2S$ $[M+H]^+$: 293.1324; Found: 293.1332.



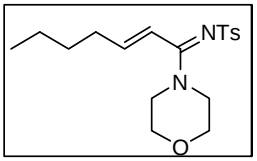
Synthesis of 4–methyl–*N*–((*E*)-1-(piperidin–1– yl) hept–2-en–1–ylidene) benzenesulfonamide (4n) [$C_{19}H_{28}N_2O_2S$]: The compound **4n** was prepared by following the *General Procedure C*. Starting from propargylamine **3n** (300 mg, 1.67 mmol) in $CHCl_3$ (3.0 mL), triethylamine (276 µL, 2.00 mmol), and tosylazide (362 mg, 1.83 mmol) in presence of CuCl (16 mg, 0.16 mmol) to obtain **4n** (297 mg, yield = 51%) as a colorless viscous liquid after column chromatographic purification. *Eluent*: 1% MeOH/dichloromethane (R_f = 0.20). IR (neat): ν_{max}/cm^{-1} 2929, 2860, 2361, 1651, 1601, 1516, 1442, 1366, 1273, 1142, 1085, 1020, 979; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.20 Hz, 2H), 7.20 (d, *J* = 8.24 Hz, 2H), 6.20 (d, *J* = 16.44 Hz, 1H), 5.87 (dt, *J* = 16.44, 6.72 Hz,1H), 3.64 (br. s, 2H), 3.51 (br. s, 2H), 2.36 (s, 3H), 2.12 (q, *J* = 6.72 Hz, 2H), 1.64m, 7H), 1.38 – 1.27 (m, 5H), 0.89 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 142.0, 141.6, 129.0, 126.6, 120.7, 32.5, 30.2, 24.3, 22.4, 21.5, 13.9; HRMS (ESI): Calc. for $C_{19}H_{29}N_2O_2S$ $[M+H]^+$: 349.1950; Found: 349.1949.



Synthesis of *N*–((*E*)–3-cyclohexyl–1–(piperidin-1-yl) allylidene)–4-methylbenzenesulfonamide (4o) [$C_{21}H_{30}N_2O_2S$]: The compound **4o** was prepared by following the *General Procedure C*. Starting from propargylamine **3o** (300 mg, 1.46 mmol) in $CHCl_3$ (3.0 mL), triethylamine (240 µL, 1.75 mmol), and tosylazide (316 mg, 1.60 mmol) in presence of CuCl (17 mg, 0.17 mmol) to obtain **4o** (344 mg, yield = 63%) as a colorless solid after column chromatographic purification. *Eluent*: 1% MeOH/Dichloromethane (R_f = 0.20). M.p.: 129-130 ^oC; IR (neat): ν_{max}/cm^{-1} 2925, 2853, 2362, 1649, 1598, 1519, 1446, 1365, 1276, 1145, 1088, 1022, 976; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.24 Hz, 2H), 7.20 (d, *J* = 8.12 Hz, 2H), 6.18 (dd, *J* = 16.70, 1.20 Hz, 1H), 5.83 (dd, *J* = 16.60, 6.48 Hz, 1H), 3.64 (br. s, 2H), 3.50 (br. s, 2H), 2.35 (s, 3H), 2.06 (m, 1H), 1.73 (m, 4H), 1.64 (m, 3H), 1.54 (br. s, 5H), 1.30 – 1.01 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 146.5, 141.5, 141.4, 128.8, 126.4, 118.4, 49.2, 45.8, 40.6, 31.5, 26.3, 25.9, 25.6, 24.2, 21.4; HRMS (ESI): Calc. for $C_{21}H_{30}N_2O_2S$ $[M+H]^+$: 375.2106; Found: 375.2112.

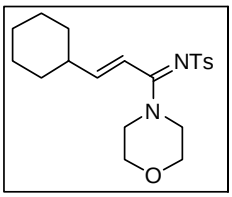


Synthesis of 4–methyl–*N*–(1–morpholinoallylidene) benzenesulfonamide (4p) [$C_{14}H_{18}N_2O_3S$]: The compound **4p** was prepared by following the *General Procedure B*. Starting from propargylamine **3p** (300 mg, 2.39 mmol) in $CHCl_3$ (3.0 mL), triethyl amine (396 µL, 2.87 mmol), and tosyl azide (517 mg, 2.63 mmol) in presence of CuCl (23 mg, 0.16 mmol) to obtain **4p** (585 mg, yield = 83%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). M.p.: 120-121 ^oC ; IR (neat): ν_{max}/cm^{-1} 2968, 2920, 2858, 2364, 1598, 1521, 1479, 1444, 1114, 1088, 1026; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.28 Hz, 2H), 7.22 (d, *J* = 7.76 Hz, 2H), 6.64 (dd, *J* = 18.20, 12.16 Hz, 1H), 5.74 (d, *J* = 11.9 Hz, 1H), 5.50 (d, *J* = 17.80 Hz, 1H), 3.65 (br. s, 8H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 142.2, 140.7, 129.1, 128.2, 126.6, 125.1, 66.4, 48.2, 44.9, 29.7, 21.5; HRMS (ESI): Calc. for $C_{14}H_{19}N_2O_3S$ $[M+H]^+$: 295.1117; Found: 295.1122.

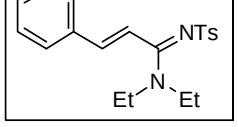


Synthesis of 4–methyl–*N*–((*E*)-1-morpholinohept–2–en–1-yl) hept–2-en–1–ylidene) benzenesulfonamide (4q) [$C_{18}H_{26}N_2O_3S$]: The compound **4q** was prepared by following the *General Procedure B*. Starting from propargylamine **3q** (300 mg, 1.65 mmol) in $CHCl_3$ (3.0 mL), triethyl amine (272 µL, 1.98 mmol), and tosyl azide (357 mg, 1.81 mmol) in presence of CuCl (16 mg, 0.16 mmol) to obtain **4q** (495 mg, yield = 85%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). M.p.: = 86-87 ^oC; IR (neat): ν_{max}/cm^{-1}; 3013, 2960, 2924, 2857, 2362, 1710, 1650, 1601, 1516, 1442, 1360, 1275, 1220, 1143, 1115, 1089; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.21 (d, *J* = 8.00 Hz, 2H), 6.26 (dt, *J* = 16.48, 1.44 Hz, 1H), 5.96 (dt, *J* = 16.44, 6.72 Hz, 1H), 3.64 (br. s, 6H), 2.37 (s, 3H), 2.18 (qd, *J* = 6.64, 1.52 Hz, 2H), 1.41 – 1.23 (m, 6H), 0.91 (t, *J* = 7.24 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 143.4, 142.0, 141.0, 129.1, 126.6, 120.0, 66.5, 32.6, 30.1, 29.8, 22.4 21.5, 14.00; HRMS (ESI): Calc. for $C_{18}H_{27}N_2O_3S$ $[M+H]^+$: 351.1748; Found: 351.1758.

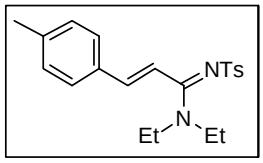
Synthesis of *N*–((*E*)–3-cyclohexyl–1–morpholinoallylidene)–4-methylbenzenesulfonamide (4r) [$C_{20}H_{28}N_2O_3S$]: The compound **4r** was prepared by following the *General Procedure B*. Starting from propargylamine **3r** (300 mg, 1.44 mmol) in $CHCl_3$ (3.0 mL), triethyl amine (238 µL, 1.73 mmol), and tosyl azide (312 mg, 1.58 mmol) in presence of CuCl (14 mg, 0.14 mmol) to obtain **4r** (450 mg, yield = 83%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.20). M.p.: = 138-139 ^oC; IR (neat): ν_{max}/cm^{-1} 2924, 2853, 2362, 1648, 1603, 1517, 1445, 1392, 1359, 1276, 1190, 1145, 1115, 1089, 973; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.24 Hz, 2H), 7.20 (d, *J* = 8.08 Hz, 2H), 6.22 (dd, *J* = 16.70, 1.33 Hz, 1H), 5.90 (dd, *J* = 16.64, 6.52 Hz, 1H), 3.65 (br. s, 8H), 2.36 (s, 3H), 2.11 (m, 1H), 1.75 – 1.63 (m, 5H), 1.31 – 1.04 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 148.1, 141.9, 141.1, 129.1, 126.5, 117.9, 66.5, 40.9, 31.6, 26.0, 25.7, 21.5; HRMS (ESI): Calc. for $C_{20}H_{29}N_2O_3S$ $[M+H]^+$: 377.1899; Found: 377.1907.



Synthesis of *N, N*-diethyl–*N′*-tosylcinnamimidamide (4s) [$C_{20}H_{24}N_2O_2S$]: The compound **4s** was prepared by following the *General Procedure C*. Starting from propargylamine **3s** (300 mg, 1.60 mmol) in $CHCl_3$ (3.0 mL), triethylamine (264 µL, 1.92 mmol), and tosylazide (346 mg, 1.76 mmol) in presence of CuCl (16 mg, 0.16 mmol) to obtain **4s** (548 mg, yield = 96%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). M.p.: 130-131 ^oC; IR (neat): ν_{max}/cm^{-1} 2977, 2361, 1693, 1642, 1531, 1467, 1438, 1360, 1276, 1216, 1143, 1085; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.24 Hz, 2H), 7.36 (m, 5H), 7.10 (d, *J* = 8.36 Hz, 2H), 6.81 (d, *J* = 16.90 Hz, 1H), 6.56 (d, *J* = 16.88 Hz, 1H), 3.52 (br.s, 2H), 3.45 (br.s, 2H), 2.32 (s, 3H), 1.17 (t, *J* = 6.20 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 141.6, 141.4, 137.4, 134.8, 129.4, 129.0, 128.8, 127.3, 126.7, 119.2, 44.7, 42.8, 21.5, 14.0, 12.2; HRMS (ESI): Calc. for $C_{20}H_{24}N_2O_2S$ $[M+H]^+$: 357.1636; Found: 357.1630.



Synthesis of (2*E*)–*N, N*-diethyl–3–(*p*-tolyl)-*N′*-tosylacrylimidamide (4t) [$C_{21}H_{26}N_2O_2S$]: The compound **4t** was prepared by following the *General Procedure C*. Starting from propargylamine **3t** (300 mg, 1.49 mmol) in $CHCl_3$ (3.0 mL), triethylamine (246 µL, 1.78 mmol), and tosylazide (323 mg, 1.63 mmol) in presence of CuCl (14 mg, 0.14 mmol) to obtain **4t** (513

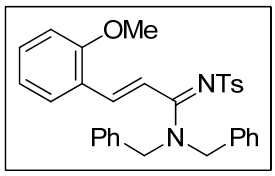


mg, yield = 93%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). M.p.: 130-131 ^oC; IR (neat): ν_{max}/cm^{-1} 2977, 2932, 2361, 1640, 1605, 1527, 1460, 1360, 1278, 1215, 1144, 1086, 1041; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.28 Hz, 2H), 7.26 (d, *J* = 8.20 Hz, 2H), 7.16 (d, *J* = 7.96 Hz, 2H), 7.10 (d, *J* = 8.56 Hz, 2H), 6.76 (d, *J* = 16.88 Hz, 1H), 6.53 (d, *J* = 16.88 Hz, 1H), 3.48 (br.s, 4H), 2.35 (s, 3H), 2.32 (s, 3H), 1.18 (t, *J* = 6.32 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 164.7, 141.5, 141.4, 139.7, 137.6, 132.0, 129.5, 129.0, 127.3, 126.7, 118.1, 44.7, 42.8, 21.5, 21.4, 14.0, 12.3; HRMS (ESI): Calc. for $C_{21}H_{26}N_2O_2S$ $[M+H]^+$: 371.1793; Found: 371.1800.

Variable temperature ^{1}H-NMR spectra for 4t: (Fig. S110 for spectra)

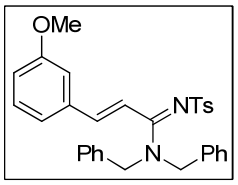
^{1}H-NMR (400 MHz, $CDCl_3$) at 323 K: δ 7.74 (d, *J* = 8.20 Hz, 2H), 7.32 (d, *J* = 8.04 Hz, 2H), 7.20 (d, *J* = 8.00 Hz, 2H), 7.15 (d, *J* = 8.12 Hz, 2H), 6.80 (d, *J* = 16.88 Hz, 1H), 6.64 (d, *J* = 16.88 Hz, 1H), 3.55 (q, *J* = 6.86 Hz, 4H), 2.39 (s, 3H), 2.36 (s, 3H), 1.23 (t, *J* = 7.10 Hz, 6H).

^{1}H-NMR (400 MHz, $CDCl_3$) at 273 K: δ 7.70 (d, *J* = 8.12 Hz, 2H), 7.29 (d, *J* = 7.90 Hz, 2H), 7.20 (d, *J* = 7.96 Hz, 2H), 7.13 (d, *J* = 8.08 Hz, 2H), 6.79 (d, *J* = 16.88 Hz, 1H), 6.50 (d, *J* = 16.88 Hz, 1H), 3.59 (q, *J* = 6.88 Hz, 2H), 3.46 (q, *J* = 6.88 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.24 (t, *J* = 6.84 Hz, 3H), 1.19 (t, *J* = 6.84 Hz, 3H).

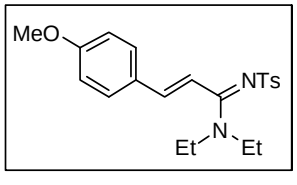


Synthesis of (*2E*)-*N*,*N*-dibenzyl-3-(2-methoxyphenyl)-*N′*-tosylacrylimidamide (4u) [$C_{31}H_{30}N_2O_3S$]: The compound **4u** was prepared by following the *General Procedure C*. Starting from propargylamine **3u** (300 mg, 0.88 mmol) in $CHCl_3$ (3.0 mL), triethylamine (144 µL, 1.05 mmol) , and tosylazide (190 mg, 0.97 mmol) in presence of CuCl (7.92 mg, 0.08 mmol) to obtain **4u** (400 mg, yield = 89%) as a colorless semi-solid after column chromatographic purification. *Eluent*: 25% EtOAc/Petroleum ether (R_f = 0.20). IR (neat): ν_{max}/cm^{-1} 3028, 2934, 2839, 1632, 1597, 1514, 1460, 1359, 1284, 1249, 1144, 1087, 1024; ^1H NMR (400 MHz, $CDCl_3$):δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.64 Hz, 1H), 7.28 (br.s, 6H), 7.24 (s, 1H), 7.16 (br.s, 4H), 7.11 (s, 1H), 7.09 (d, *J* = 4.8 Hz, 2H), 7.02 (d, *J* = 17.12 Hz, 1H), 6.90 (t, *J* = 7.5Hz, 1H), 6.80 (d, *J* = 8.32, 1H), 4.65 (br.s, 4H), 3.67 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 157.8, 141.7, 141.1, 135.7, 134.6, 130.8, 129.0, 128.9, 125.5, 127.9, 127.2, 126.7, 123.7, 120.8, 119.2, 111.0, 55.4, 52.3, 50.2, 21.5; HRMS (ESI): Calc. for $C_{31}H_{31}N_2O_3S$ $[M+H]^+$: 511.2055; Found: 511.2059.

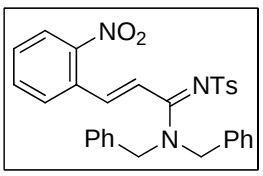
Synthesis of (*2E*)-*N*,*N*-dibenzyl-3-(3-methoxyphenyl)-*N′*-tosylacrylimidamide (4v) [$C_{31}H_{30}N_2O_3S$]: The compound **4v** was prepared by following the *General Procedure C*. Starting from propargylamine **3v** (300 mg, 0.88 mmol) in $CHCl_3$ (3.0 mL), triethylamine (144 µL, 1.05 mmol) , and tosylazide (190 mg, 0.97 mmol) in presence of CuCl (7.92 mg, 0.08 mmol) to obtain **4v** (430 mg, yield = 96%) as a viscous yellow liquid after column chromatographic purification. *Eluent*: 25% EtOAc/Petroleum ether (R_f = 0.20). IR (neat): ν_{max}/cm^{-1} 3028, 2927, 1638, 1588, 1514, 1458, 1429, 1359, 1277, 1144, 1087, 1042; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.20 Hz, 2H), 7.29 (br.s, 7H), 7.20 (d, *J* = 7.88 Hz, 1H), 7.15 (br.s, 4H), 7.12 (d, *J* = 8.16 Hz, 2H), 6.90 (d, *J* = 8.48 Hz, 1H), 6.84 (s, 1H), 6.81 (br.s, 1H), 6.73 (d, *J* = 16.8 Hz, 1H), 4.70 (br.s, 2H), 4.58 (br.s, 2H), 3.76 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 165.7, 159.9, 141.9, 141.0, 138.8, 136.0, 129.8, 129.1, 128.1, 127.0, 126.7, 120.1, 118.9, 115.6, 112.5, 55.4, 52.3, 50.3, 21.5; HRMS(ESI): Calc. for $C_{31}H_{31}N_2O_3S$ $[M+H]^+$: 511.2055; Found: 511.2059.



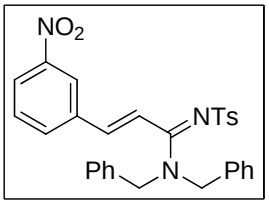
Synthesis of (2*E*)–*N*, *N*-diethyl–3–(4-methoxyphenyl)-*N′*-tosylacrylimidamide (4w) [$C_{21}H_{26}N_2O_3S$]: The compound **4w** was prepared by following the *General Procedure C*. Starting from propargylamine **3w** (300 mg, 1.38 mmol) in $CHCl_3$ (3.0 mL), triethylamine (227 µL, 1.65 mmol) , and tosylazide (300 mg, 1.51 mmol) in presence of CuCl (13 mg, 0.13 mmol) to obtain **4w** (506 mg, yield = 95%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.30). M.p.: 132-133 ^{o}C; IR (neat): ν_{max}/cm^{-1} 2976, 2936, 2839, 2361, 1637, 1604, 1518, 1458, 1359, 1250, 1216, 1174, 1142, 1084, 1029; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.20 Hz, 2H), 7.31 (d, *J* = 8.68 Hz, 2H), 7.09 (d, *J* = 8.00 Hz, 2H), 6.87 (d, *J* = 8.72 Hz, 2H), 6.66 (d, *J* = 16.84 Hz, 1H), 6.55 (d, *J* = 16.84 Hz, 1H), 3.81 (s, 3H), 3.47 (br.s, 4H), 2.31 (s, 3H), 1.17 (t, *J* = 7.00 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 160.7, 141.5, 142.4, 137.5, 128.9, 128.8, 127.5, 126.7, 116.7, 114.3, 55.5, 44.7, 42.9, 31.0, 21.5, 14.0, 12.3; HRMS (ESI): Calc. for $C_{21}H_{26}N_2O_3S$ $[M+H]^+$: 387.1742; Found: 387.1744.



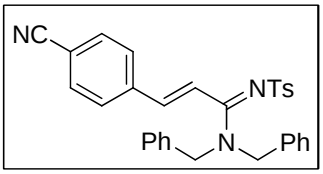
Synthesis of (*2E*)-*N*,*N*-dibenzyl-3-(2-nitrophenyl)-*N′*-tosylacrylimidamide (4x) [$C_{30}H_{27}N_3O_4S$]: The compound **4x** was prepared by following the *General Procedure C*. Starting from



propargylamine **3x** (300 mg, 0.84 mmol) in $CHCl_3$ (3.0 mL), triethylamine (138 µL, 1.01 mmol) , and tosylazide (181 mg, 0.92 mmol) in presence of CuCl (7.92 mg, 0.08 mmol) to obtain **4x** (353 mg, yield = 80%) as a pale yellow solid after column chromatographic purification. *Eluent*: EtOAc/Petroleum ether (R_f = 0.23). M.p.: 154-155 ^oC; IR (neat): ν_{max}/cm^{-1} 3033, 1603, 1570, 1521, 1455, 1346, 1281, 1144, 1088, 1024; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J=8.24 Hz, 1H), 7.9 (d, J=7.56, 1H), 7.71 (d, J=6.36 Hz, 2H), 7.69 (t, J=6 Hz, 1H), 7.50 (t, J=7.24 Hz, 1H), 7.28 (br. s, 6H), 7.17 (m, 7H), 6.95 (d, J=16.6 Hz, 1H), 4.79 (br. s, 2H), 4.70 (br. s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 147.3, 142.2, 140.7, 135.5, 135.2, 134.5, 133.5, 131.8, 130.5, 129.7, 129.2, 128.9, 128.4, 128.2, 128.0, 127.2, 126.4, 124.7, 124.0, 52.2, 21.5; HRMS (ESI): Calc. for $C_{30}H_{28}N_3O_4S$ $[M+H]^+$: 526.1800; Found: 526.1799.

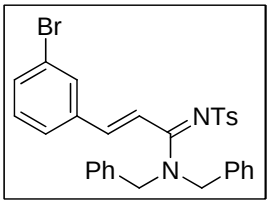


Synthesis of (*2E*)-*N,N*-dibenzyl-3-(3-nitrophenyl)-*N′*-tosylacrylimidamide (4y) [$C_{30}H_{27}N_3O_4S$]: The compound **4y** was prepared by following the *General Procedure C*. Starting from propargylamine **3y** (300 mg, 0.84 mmol) in $CHCl_3$ (3.0 mL), triethylamine (138 µL, 1.01 mmol), and tosylazide (181 mg, 0.92 mmol) in presence of CuCl (7.92 mg, 0.08 mmol) to obtain **4y** (330 mg, yield 75%) as a pale yellow solid after column chromatographic purification. *Eluent*: EtOAc/Petroleum ether (R_f = 0.23). M.p.: 112-113 ^oC; IR (neat): ν_{max}/cm^{-1} 3030, 2924, 1602, 1522, 1352, 1280, 1144, 1088; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (m, 2H), 7.76 (d, *J* = 8.20 Hz, 1H), 7.70 (d, *J* = 8.20 Hz, 2H), 7.53 (m, 1H), 7.13 (br. s, 6H), 7.20 (d, *J* = 8.20 Hz, 1H), 7.17 (d, *J* = 8.10 Hz, 1H), 7.13 (br. s, 4H), 7.00 (d, *J* = 16.90 Hz, 1H), 6.85 (d, *J* = 16.70 Hz, 1H), 4.72 (br. s, 2H), 4.58 (br. s, 2H), 2.36 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 148.5, 142.2, 140.8, 139.3, 136.3, 135.9, 133.0, 132.6, 129.9, 129.2, 128.5, 128.3, 128.1, 126.9, 126.5, 123.9, 123.3, 123.0, 122.0, 121.4, 52.3, 50.4, 21.5; HRMS (ESI): Calc. for $C_{30}H_{28}N_3O_4S$ $[M+H]^+$: 526.1800; Found: 526.1807.

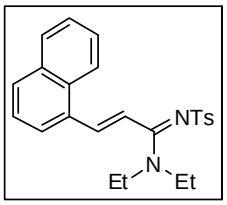


Synthesis of (*2E*)-*N,N*-dibenzyl-3-(4-cyanophenyl)-*N′*-tosylacrylimidamide (4z) [$C_{31}H_{27}N_3O_2S$]: The compound **4z** was prepared by following the *General Procedure C*. Starting from propargylamine **3z** (300 mg, 0.89 mmol) in $CHCl_3$ (3.0 mL), triethylamine (146 µL, 1.07 mmol) , and tosylazide (193 mg, 0.98 mmol) in presence of CuCl (7.92 mg, 0.08 mmol) to obtain **4z** (320 mg, yield =

71%) as a colorless solid after column chromatographic purification. *Eluent*: EtOAc/Petroleum ether (R_f = 0.25). M.p.: 75-76 ^oC; IR (neat): ν_{max}/cm^{-1} 3032, 2225, 1638, 1602, 1520, 1461, 1360, 1282, 1145, 1088; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.24 Hz, 2H), 7.60 (d, *J* = 8.24 Hz, 2H), 7.41 (d, *J* = 8.32 Hz, 2H), 7.30 (br. s, 6H), 7.15 (d, *J* = 8.32 Hz, 2H), 7.11 (br. s, 4H), 7.01 (d, *J* = 16.88 Hz, 1H), 6.81 (d, *J* = 16.88 Hz, 1H), 4.70 (br. s, 2H), 4.56 (br. s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 142.2, 140.7, 139.0, 136.4, 132.6, 129.2, 128.6, 127.9, 127.4, 126.9, 126.5, 122.6, 118.5, 112.7, 52.3, 50.5, 21.5; HRMS (ESI): Calc. for $C_{31}H_{28}N_3O_2S$ $[M+H]^+$: 506.1902; Found: 506.1909.

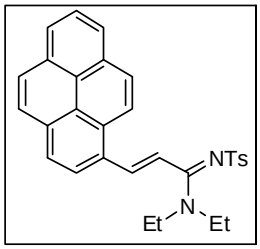


Synthesis of (2*E*)-*N*,*N*-dibenzyl-3-(3-bromophenyl)-*N*′-tosylacrylimidamide (4a´) [$C_{30}H_{27}BrN_2O_2S$]: The compound **4a´** was prepared by following the *General Procedure C*. Starting from propargylamine **3a´** (300 mg, 0.77 mmol) in $CHCl_3$ (3.0 mL), triethylamine (126 µL, 0.92 mmol) , and tosylazide (167 mg, 0.85 mmol) in presence of CuCl (6.93 mg, 0.07 mmol) to obtain **4a´** (412 mg, yield 96%) as a viscous yellow liquid after column chromatographic purification. *Eluent*: 25% EtOAc/Petroleum ether (R_f = 0.20). IR (neat): ν_{max}/cm^{-1} 3030, 2922, 1640, 1593, 1518, 1429, 1359, 1285, 1204, 1145, 1088; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.10 Hz, 2H), 7.42 (d, *J* = 9.00 Hz, 2H), 7.30 (br. s, 6H), 7.25 – 7.12 (m, 10H), 6.86 (d, *J* = 16.80 Hz, 1H), 6.67 (d, *J* = 16.80 Hz, 1H), 4.70 (br. s, 2H), 4.56 (br. s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 142.0, 140.8, 137.0, 136.6, 135.4, 132.4, 130.3, 130.2, 129.1, 128.1, 126.9, 126.6, 126.0, 122.9, 120.2, 52.3, 50.3, 21.5; HRMS (ESI): Calc. for $C_{30}H_{28}BrN_2O_2S$ $[M+H]^+$: 559.1055; Found: 559.1066.



Synthesis of (2*E*)–*N*, *N*-diethyl–3–(naphthalen-1-yl)-*N*′-tosylacrylimidamide (4b´) [$C_{24}H_{26}N_2O_2S$]: The compound **4b´** was prepared by following the *General Procedure C*. Starting from propargylamine **3b´** (300 mg, 1.26 mmol) in $CHCl_3$ (3.0 mL), triethylamine (208 µL, 1.51 mmol), and tosylazide (273 mg, 1.38 mmol) in presence of CuCl (12 mg, 0.12 mmol) to obtain **4b´** (494 mg, yield 96%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.35). M.p.: 137-138 ^oC; IR (neat): ν_{max}/cm^{-1} 2978, 2936, 2361, 1707, 1638, 1527, 1438, 1357, 1274, 1215, 1141, 1083,

1041; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (m, 1H), 7.86 (m, 2H), 7.74 (d, *J* = 8.16 Hz, 3H), 7.52 – 7.45 (m, 4H), 7.08 (d, *J* = 8.08 Hz, 2H), 6.90 (d, *J* = 16.64 Hz, 1H), 3.55 (br. s, 4H), 2.26 (s, 3H), 1.24 (t, *J* = 7.16 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 141.7, 135.2, 133.6, 132.7, 131.2, 129.7, 128.7, 126.7, 126.5, 126.1, 125.7, 124.8, 123.6, 122.1, 44.7, 43.0, 21.5, 14.1, 12.3; HRMS (ESI): Calc. for $C_{24}H_{26}N_2O_2S$ $[M+H]^+$: 407.1793; Found: 407.1799.



Synthesis of (2*E*)–*N*, *N*-diethyl–3–(pyren-1-yl)-*N*′-tosylacrylimidamide (4c′) [$C_{30}H_{28}N_2O_2S$]: The compound **4c′** was prepared by following the *General Procedure B*. Starting from propargylamine **3c′** (300 mg, 0.96 mmol) in $CHCl_3$ (3.0 mL), triethyl amine (160 µL, 1.15 mmol), and tosyl azide (208 mg, 1.05 mmol) in presence of CuCl (9 mg, 0.09 mmol) to obtain **4c′** (451 mg, yield 98%) as a colorless solid after column chromatographic purification. *Eluent*: Dichloromethane (R_f = 0.35). M.p.: = 193-194 ^{o}C; IR (neat): ν_{max}/cm^{-1} 2977, 2932, 2361, 1707, 1628, 1597, 1526, 1460, 1359, 1275, 1216, 1184, 1142, 1084, 1043; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.12 Hz, 1H), 8.20 (m, 4H), 8.10 (m, 4H), 7.78 (d, 3H), 7.07 (m, 3H), 3.59 (br. s, 4H), 2.24 (s, 3H), 1.28 (t, *J* = 7.08 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 141.7, 141.5, 135.3, 132.1, 131.4, 130.8, 129.1, 129.1, 128.4, 128.2, 127.5, 126.6, 126.3, 125.8, 125.6, 125.3, 124.9, 124.7, 124.1, 122.7, 121.7, 44.8, 43.0, 29.8, 21.4, 14.2, 12.5; HRMS (ESI): Calc. for $C_{30}H_{29}N_2O_2S$ $[M+H]^+$: 481.1950; Found: 481.1950.

IV. Crystal Structure Parameters.

CCDC 932113 (**2**), CCDC 932111 (**4d**), CCDC 932112 **(4p)** and CCDC 933156 (**4w**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure of compound 2 (CCDC 932113): $C_{24}H_{24}N_2O_2S$; Compound **2** was crystallized from DCM/Hexane at room temperature. A colorless rectangular shaped crystal with approximate dimensions 0.24 x 0.17 x 0.03 mm gave an Monoclinic with space group *C2/c*; a = 20.925(3) b = 11.0264(14)c = 18.650(2) Å, α = 90° β = 92.884(5)° γ = 90°; V = 4297.6(10) Å^3; T = 173 K; Z = 8; ρ_{calc}= 1.250Mgm^{-3}; $2\theta_{max}$= 57.06°; $MoK\alpha\lambda$ = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0506 (for 4242 reflection $I>2\sigma(I)$), wR= 0.1503 which was refined against |$F2$| and S = 1.026 for 264 parameters and 5425 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over the atoms to which they are bonded. μ = 0.173 mm^{-1}.

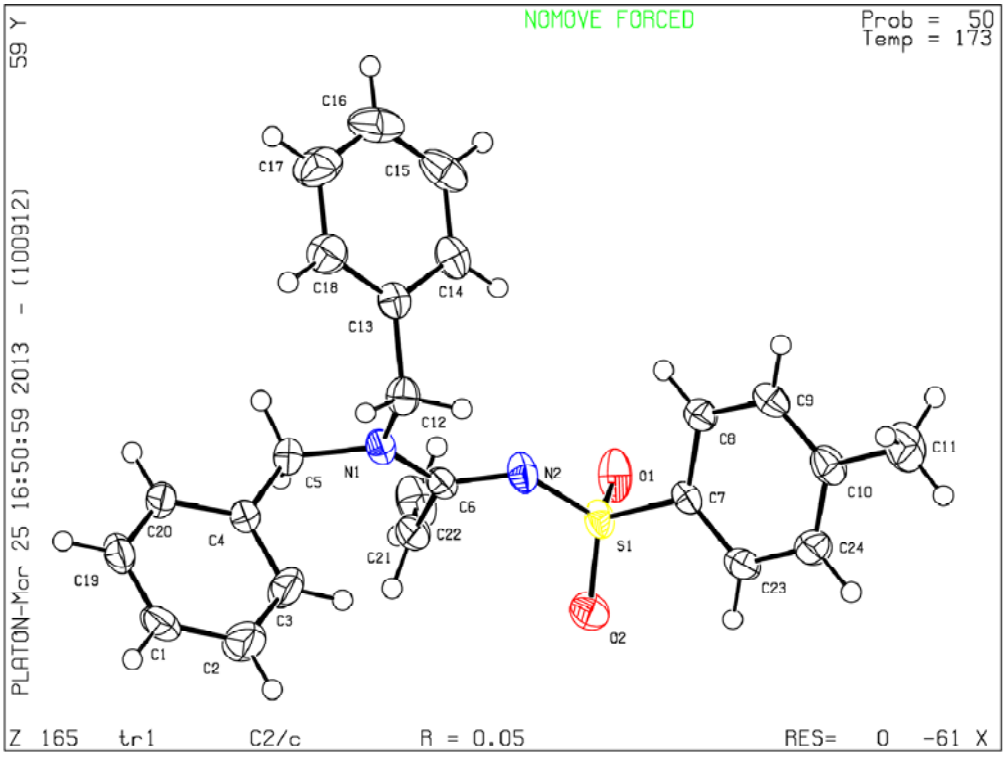


Fig. S1 ORTEP diagram of acrylamidine **2**.

Crystal structure of compound 4d (CCDC 932111): $C_{29}H_{32}N_2O_4S$; Compound **4d** was crystallized from DCM/Hexane at room temperature. A colorless rectangular shaped crystal with approximate dimensions 0.32 x 0.18 x 0.06 mm gave an Monoclinic with space group *P 21*; a = 9.7934(18) b = 11.215(2)c = 12.187(2) Å, α = 90° β = 96.377(4)° γ = 90°; V = 1330.2(4) Å^3; T = 100 K; Z = 2; ρ_{calc}= 1.260 Mgm^{-3}; $2\theta_{max}$= 56.66°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0496 (for 4223 reflection $I>2\sigma(I)$), wR= 0.1323 which was refined against |*F2*| and S = 1.052 for 329 parameters and 3466 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over the atoms to which they are bonded. μ = 0.159 mm^{-1}.

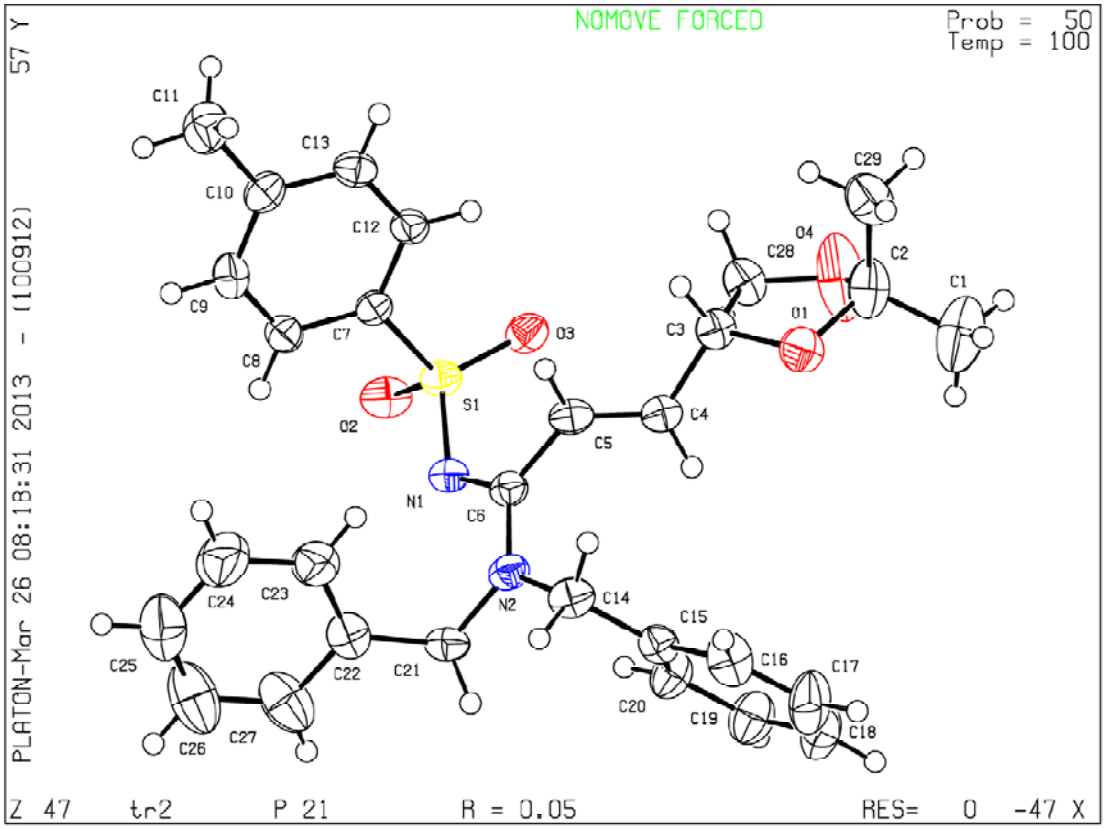


Fig. S2 ORTEP diagram of acrylamidine **4d**.

Crystal structure of compound 4p (CCDC 932112): $C_{14}H_{18}N_2O_3S$; Compound **4p** was crystallized from DCM/Hexane at room temperature. A colorless rectangular shaped crystal with approximate dimensions 0.32 x 0.18 x 0.06 mm gave an Monoclinic with space group *P 21/n*; a = 8.2660(12) b = 25.831(4) c = 13.5551(19) Å, α = 90° β = 97.899(4)° γ = 90°; V = 2866.8(7) Å^3; T = 173 K; Z = 8; ρ_{calc} = 1.364 Mgm^{-3}; $2\theta_{max}$ = 57.04°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0395 (for 5766 reflection $I>2\sigma(I)$), wR = 0.1035 which was refined against |*F2*| and S = 1.019 for 364 parameters and 7267 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over the atoms to which they are bonded. μ = 0.235 mm^{-1}.

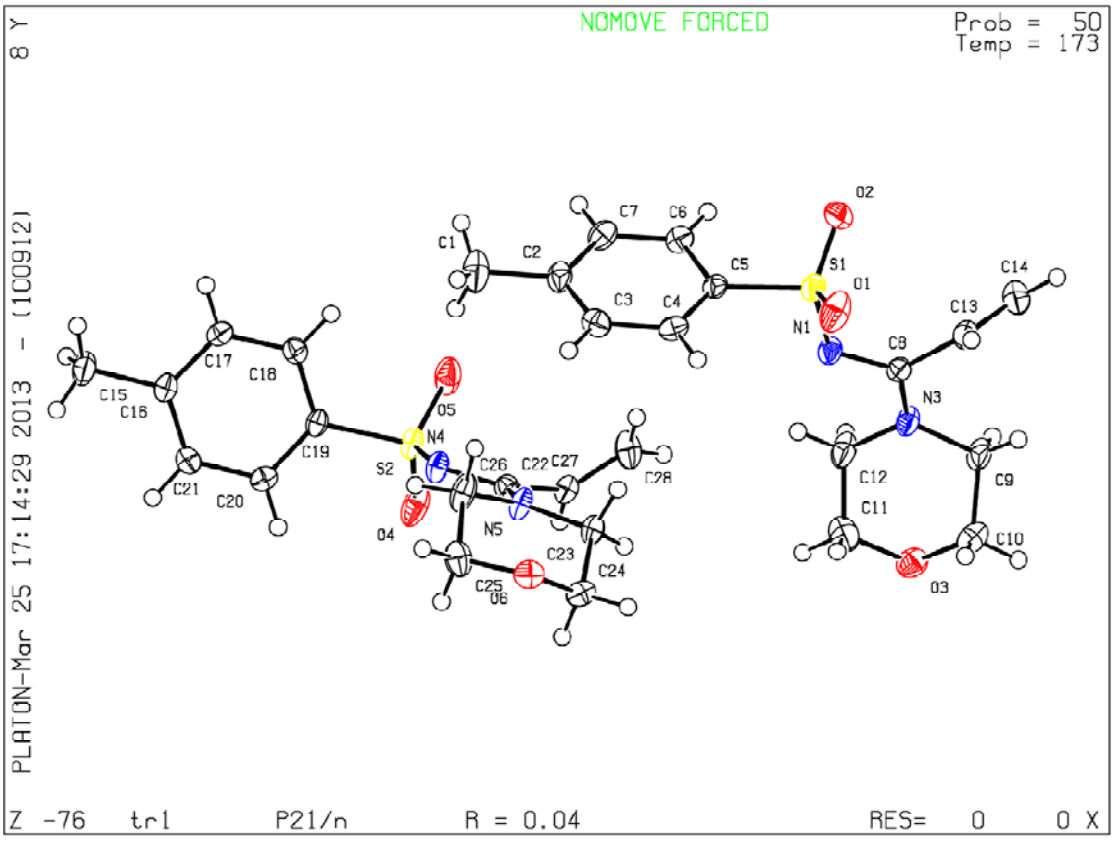


Fig. S3 ORTEP diagram of α,β-unsaturated sulfonylamidine **4p**.

Crystal structure of compound 4w (CCDC933156): $C_{21}H_{26}N_2O_3S$; Compound **4w** was crystallized from DCM/Hexane at room temperature. A colorless rectangular shaped crystal with approximate dimensions 0.263 x 0.206 x 0.048 mm gave an Triclinic with space group *P-1*; a = 9.0234(13) b = 9.3284(13)c = 12.4285(18) Å, α = 76.805(2)° β = 86.796(2)° γ = 74.132(2)°; V = 979.7(2) Å^3; T = 173 K; Z = 2; ρ_{calc}= 1.310Mgm^{-3}; $2\theta_{max}$= 56.86°; $MoK\alpha\lambda$ = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0346 (for 4400 reflection $I>2\sigma(I)$), wR= 0.1406 which was refined against $|F2|$ and S = 1.188 for 248 parameters and 4916 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over the atoms to which they are bonded. μ = 0.189 mm^{-1}.

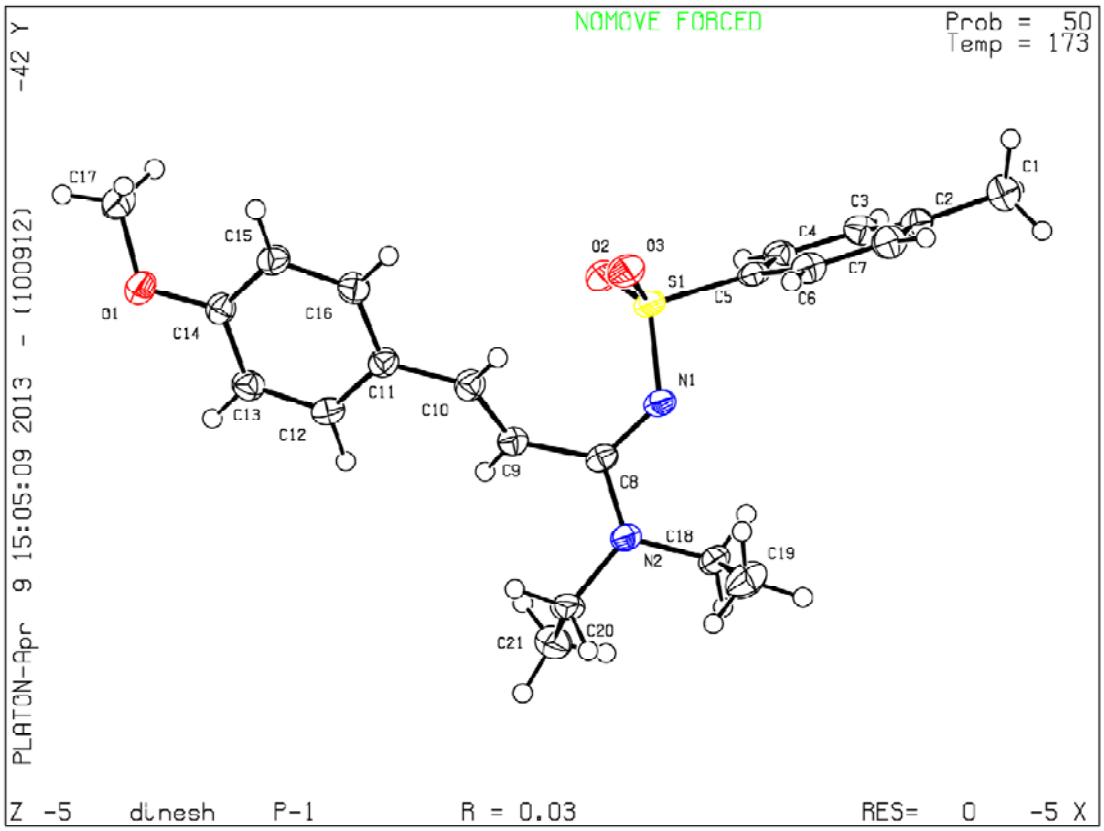


Fig. S4 ORTEP diagram of acrylamidine **4w**.

V. Photophysical Properties:

Procedures:

Medium of Photophysical studies: Deionized water was used throughout all experiments. All photophysical experiments were carried out in HEPES buffer (10 mM, pH 7.4).

Preparation of the primary stock solution of 3c′ (Solution A): Compound **3c′** (300 mg) was dissolved in 3.0 mL $CHCl_3$ to provide the stock solution of concentration = 320 mM.

Preparation of first diluted solution of 3c′ (Solution B): 10 µL of solution A (concentration = 320 mM) was added to 3190 µL HEPES buffer (10 mM, pH 7.4) to obtain the resulting concentration = 1000 µM.

Preparation of solution for Photophysical measurement of 3c′ (Solution C): 20 µL of solution B (concentration = 1000 µM) was added to 1960 µL HEPES buffer (10 mM, pH 7.4) to obtain the resulting concentration = 10 µM.

Preparation of the primary stock solution of 3c′ with TsN_3 (Solution D): Compound **3c′** (300 mg) was dissolved in 3.0 mL $CHCl_3$ followed by addition of TsN_3 (208 mg), Et_3N (160 µL), CuCl (9 mg) and the resulting solution was stirred for 3 minutes at room temperature for provide stock solution D.

Preparation of first diluted solution of 3c′ with TsN_3 (Solution E): 10 µL of solution D (concentration = 320 mM) was added to 3190 µL HEPES buffer (10 mM, pH 7.4) to obtain the resulting concentration = 1000 µM.

Preparation of solution for Photophysical measurement of 3c′ with TsN_3 (Solution F): 20 µL of solution E (concentration = 1000 µM) was added to 1960 µL HEPES buffer (10 mM, pH 7.4) to obtain the resulting concentration = 10 µM.

UV-visible studies: UV-visible studies for either **3c′** (10 µM) or for the mixture **3c′+TsN_3** was carried out in HEPES buffer (10 mM, pH = 7.4).

Fluorescence studies: Fluorescence spectrum for either **3c′** (10 µM) or for the mixture **3c′+TsN_3** was carried out in HEPES buffer (10 mM, pH = 7.4).

Fluorescence images under the hand-held UV lamp: Cuvette images were taken under hand-held UV lamp. Concentration of **3c′** was 50 µM and concentration of **4c′** was ~ 50 µM (considering 98% yield).

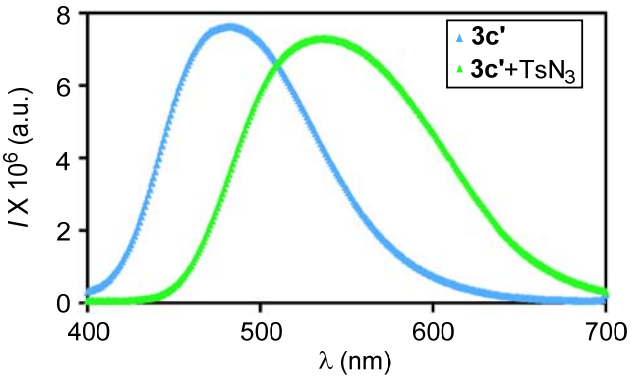


Fig. S5 Fluorescence spectra of **3c´** (10 μM) in absence and in presence of **TsN_3** (10 μM) recorded in HEPES buffer (concentration = 10 mM, pH = 7.4). Values of λ_{ex} were 353 nm and 375 nm, respectively.

VI. NMR Data.

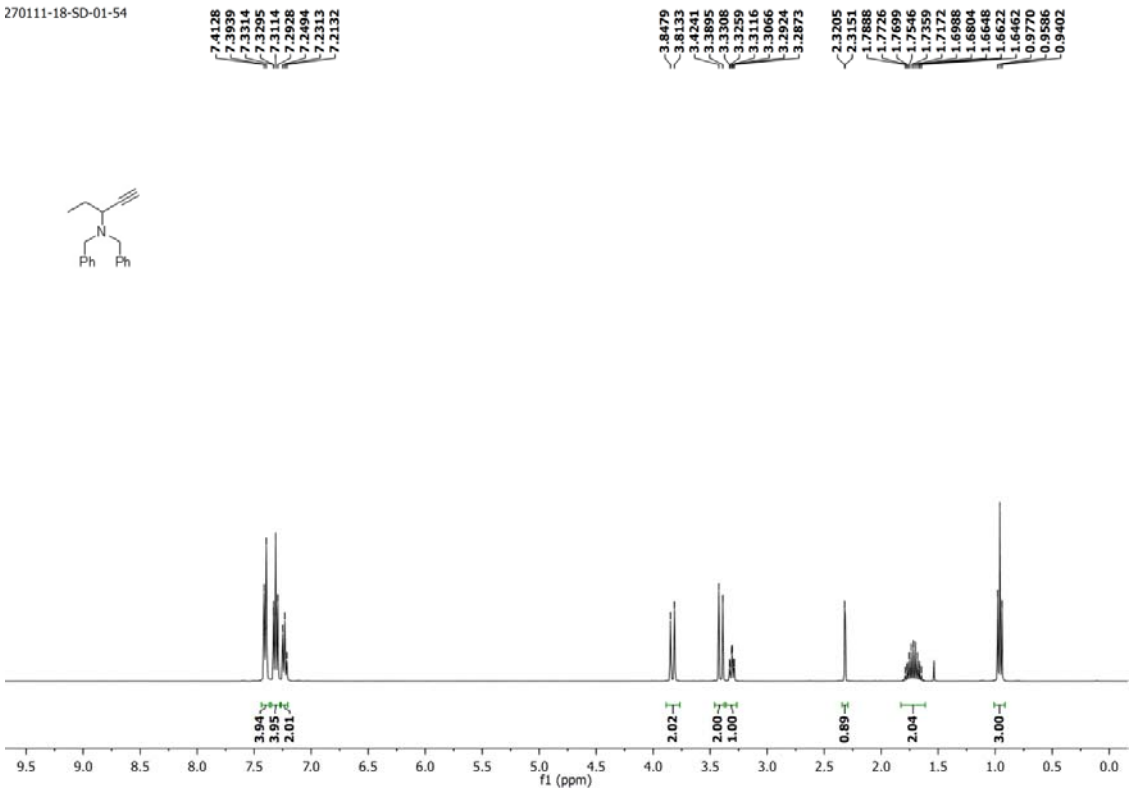


Fig. S6 ^{1}H NMR spectra of **3a** in $CDCl_3$.

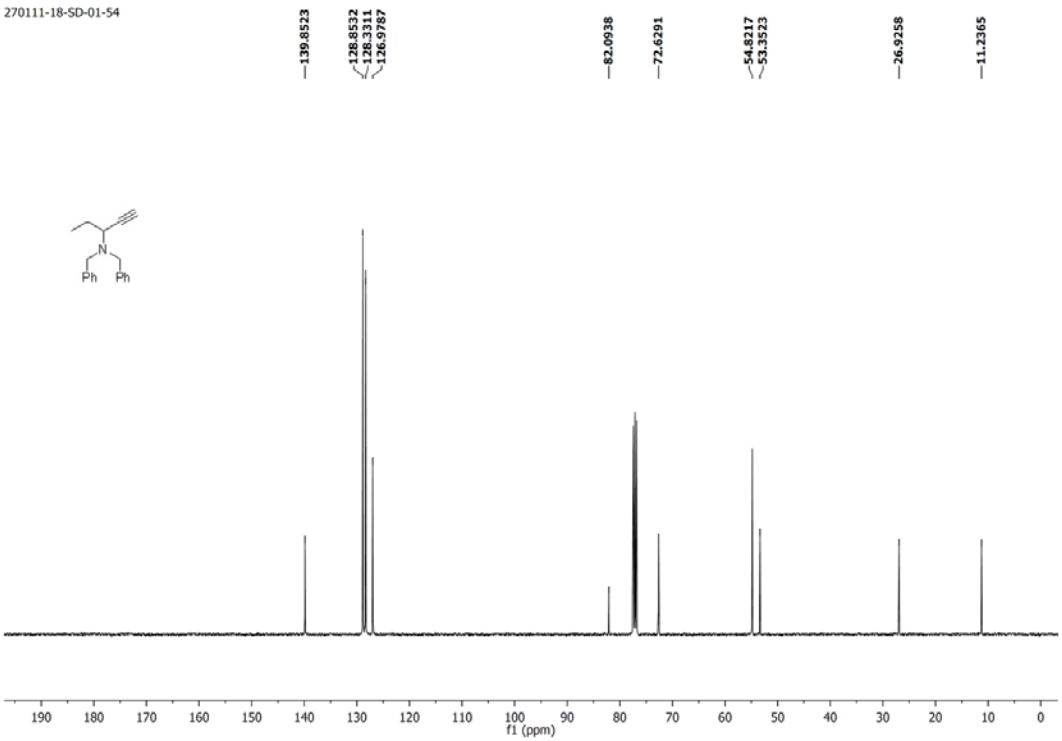


Fig. S7 ^{13}C NMR spectra of **3a** in $CDCl_3$.

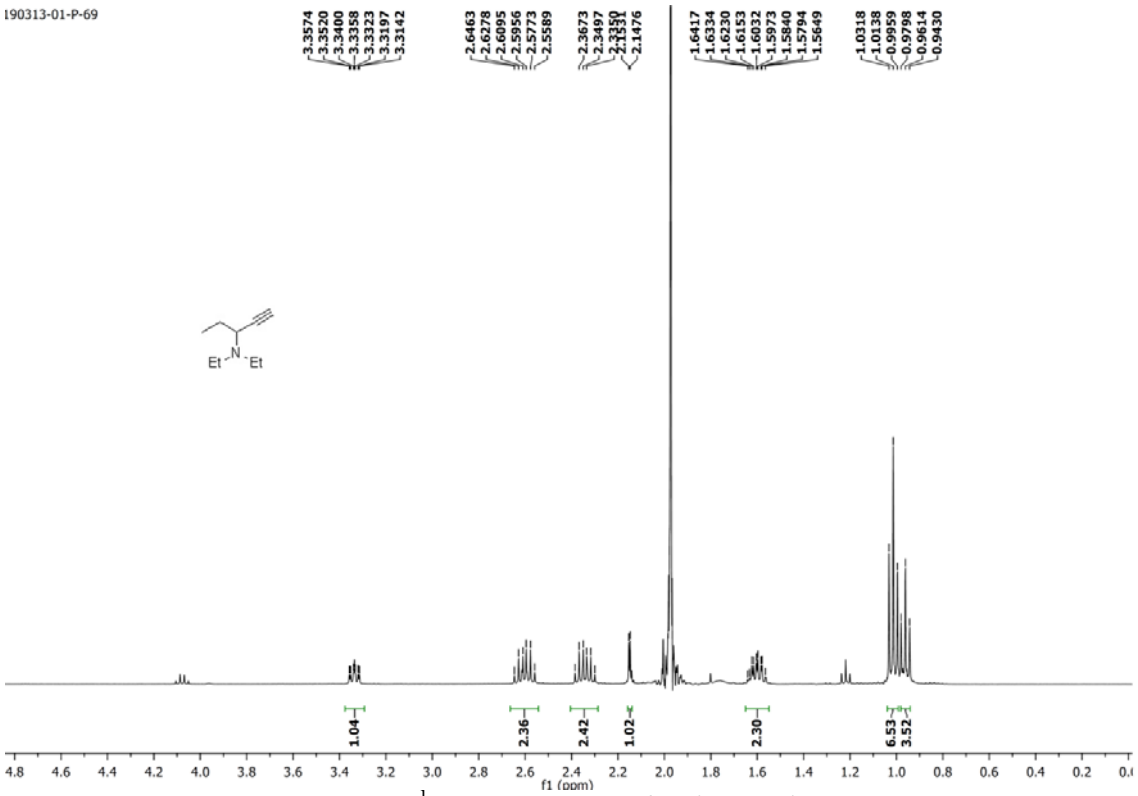


Fig. S8 ^{1}H NMR spectra of **3e** in $CDCl_3$.

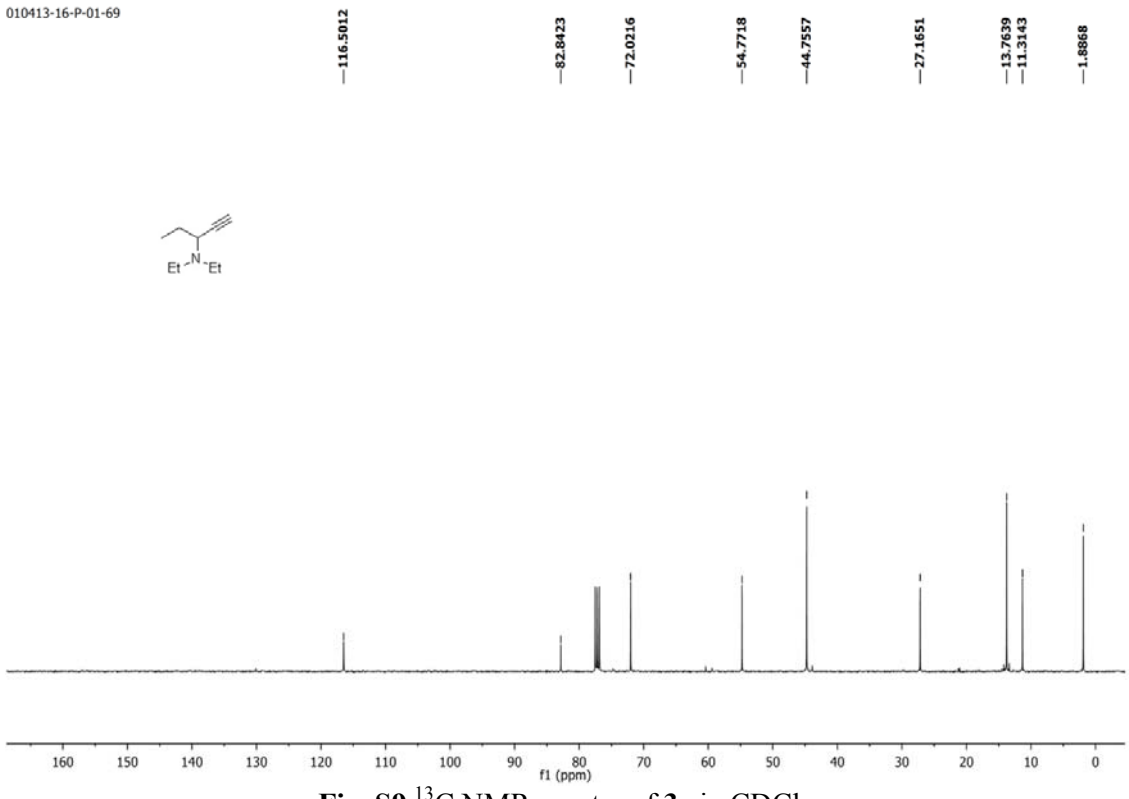


Fig. S9 ^{13}C NMR spectra of **3e** in $CDCl_3$.

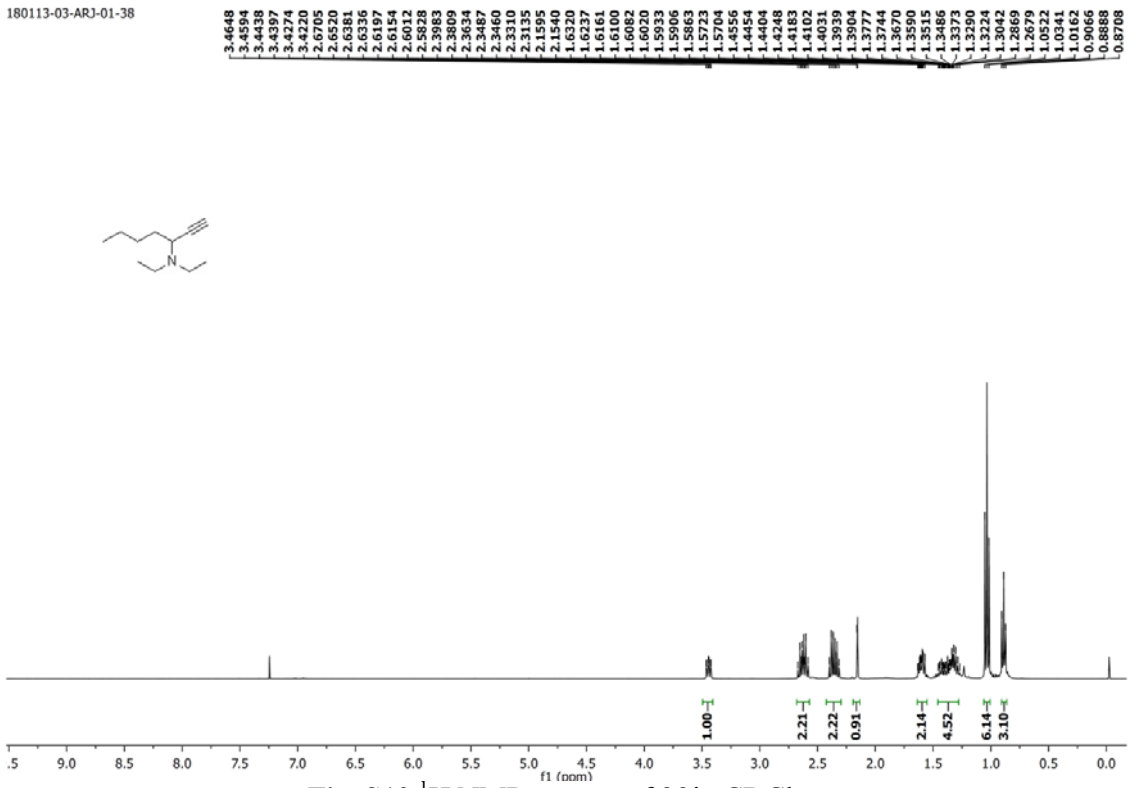


Fig. S10 ^{1}H NMR spectra of **3f** in $CDCl_3$.

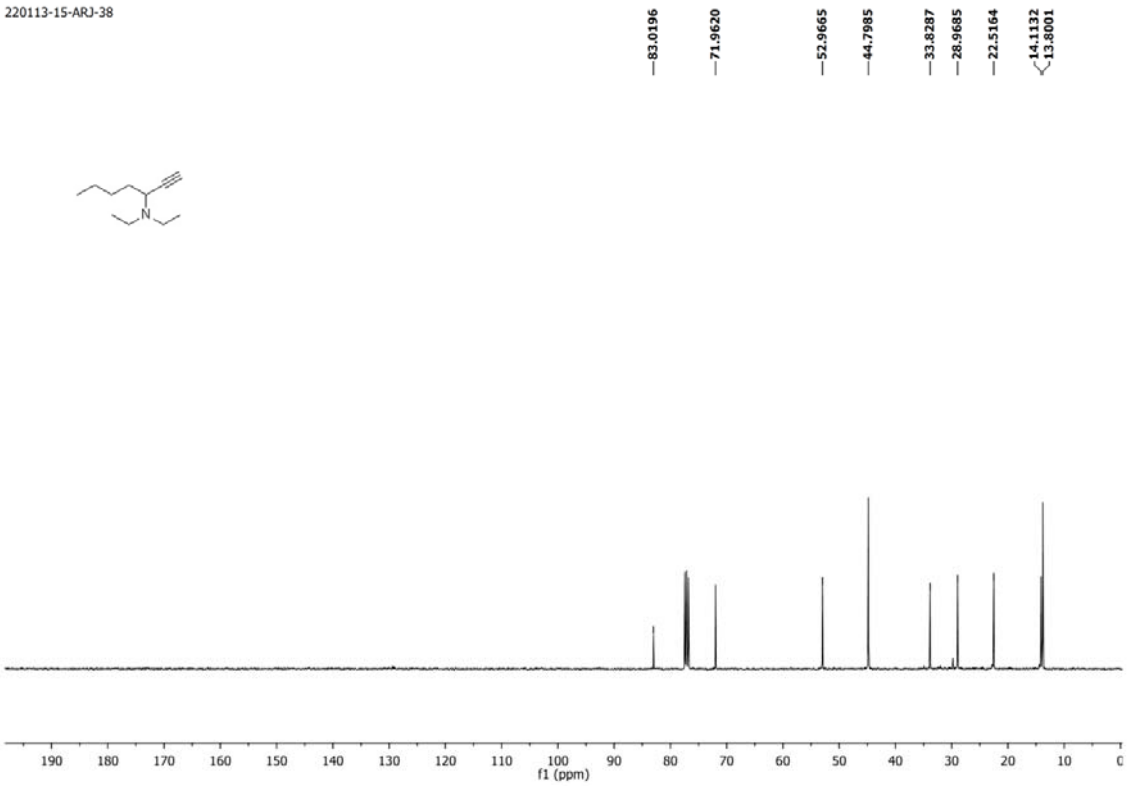


Fig. S11 ^{13}C NMR spectra of **3f** in $CDCl_3$.

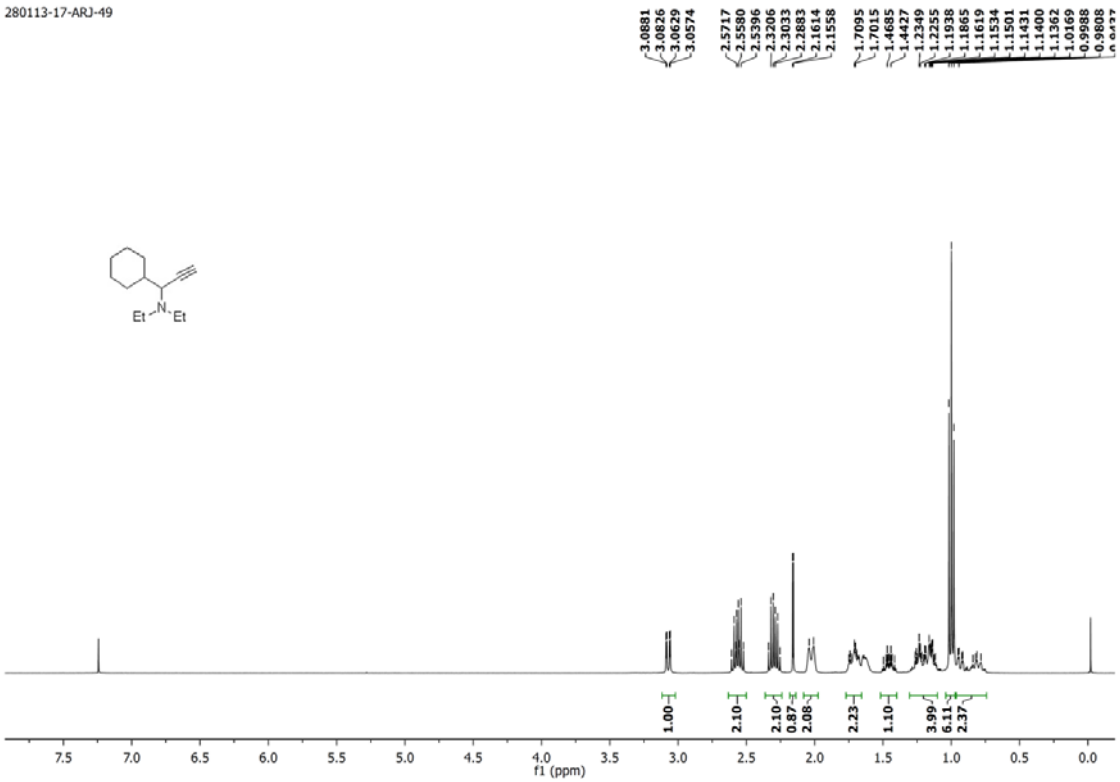


Fig. S12 ^{1}H NMR spectra of **3g** in $CDCl_3$.

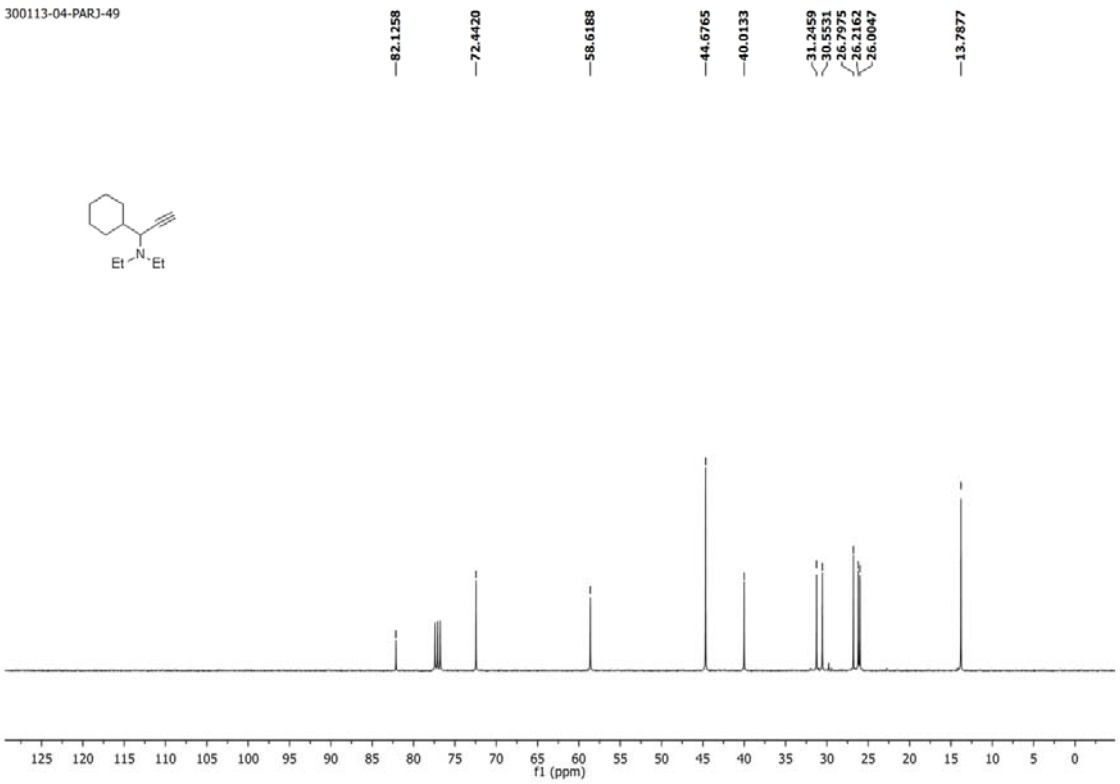


Fig. S13 ^{13}C NMR spectra of **3g** in $CDCl_3$.

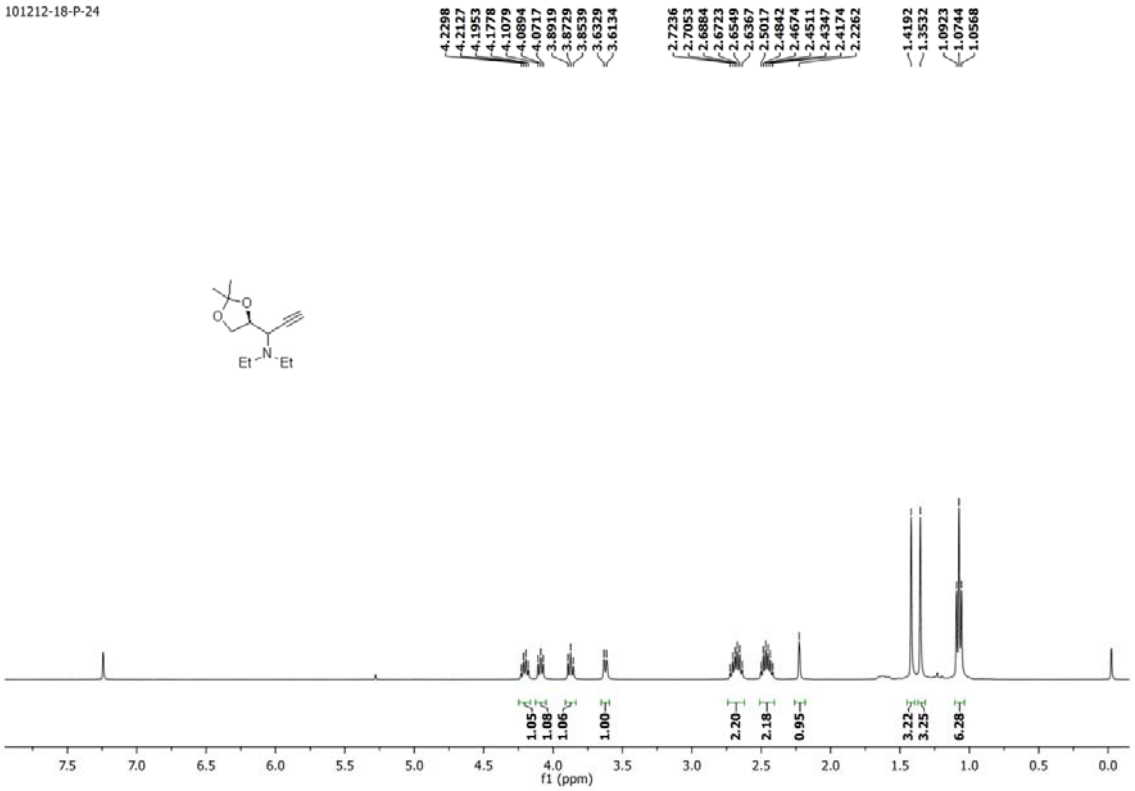


Fig. S14 ^{1}H NMR spectra of **3h** in $CDCl_3$.

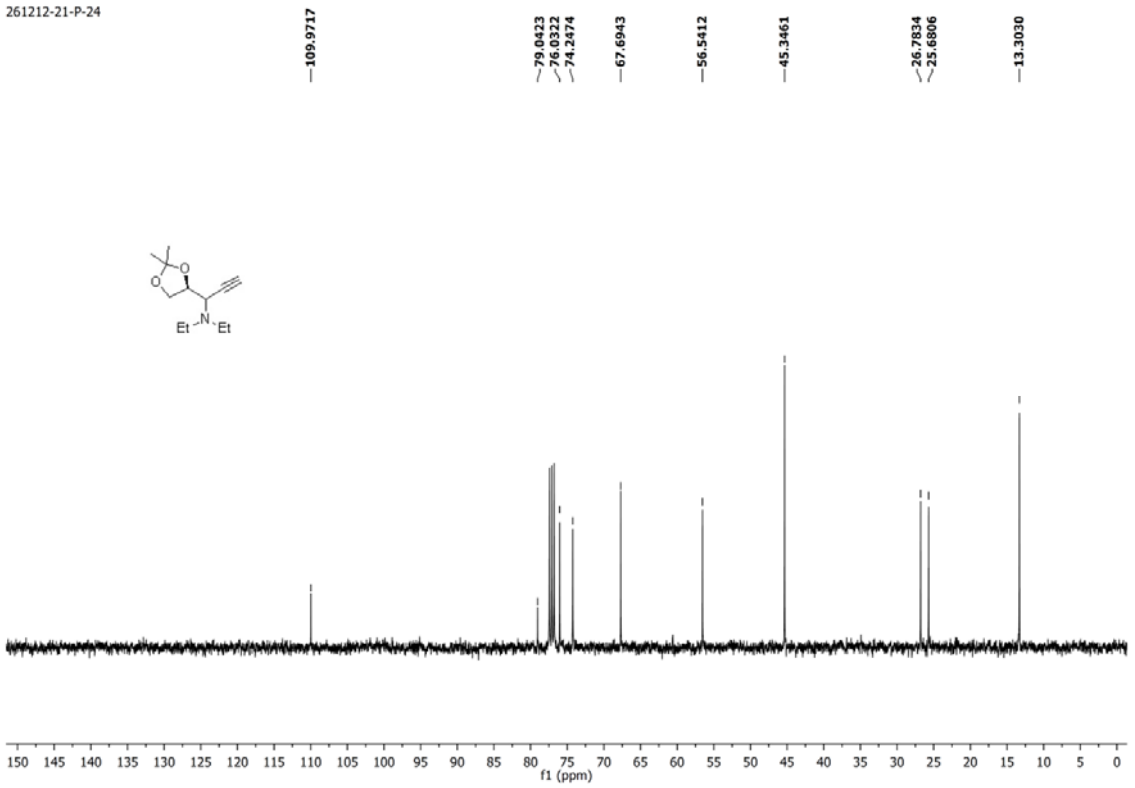


Fig. S15 ^{13}C NMR spectra of **3h** in $CDCl_3$.

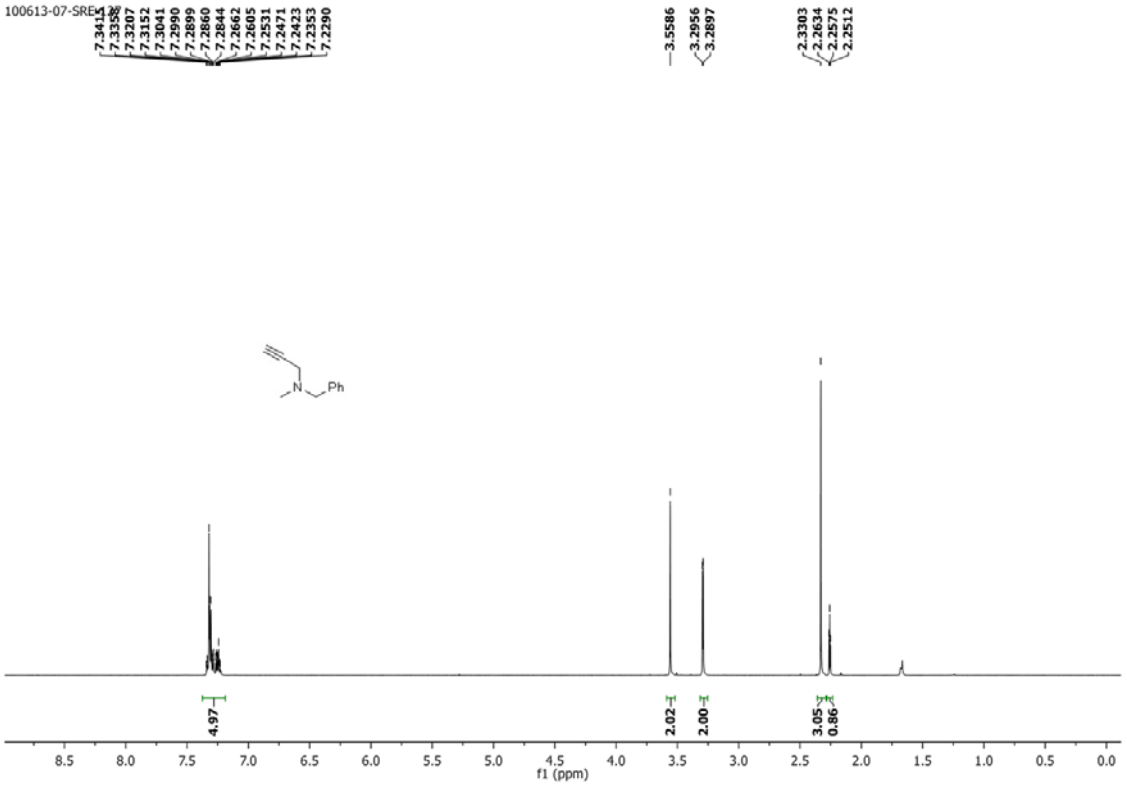


Fig. S16 ^{1}H NMR spectra of **3i** in $CDCl_3$.

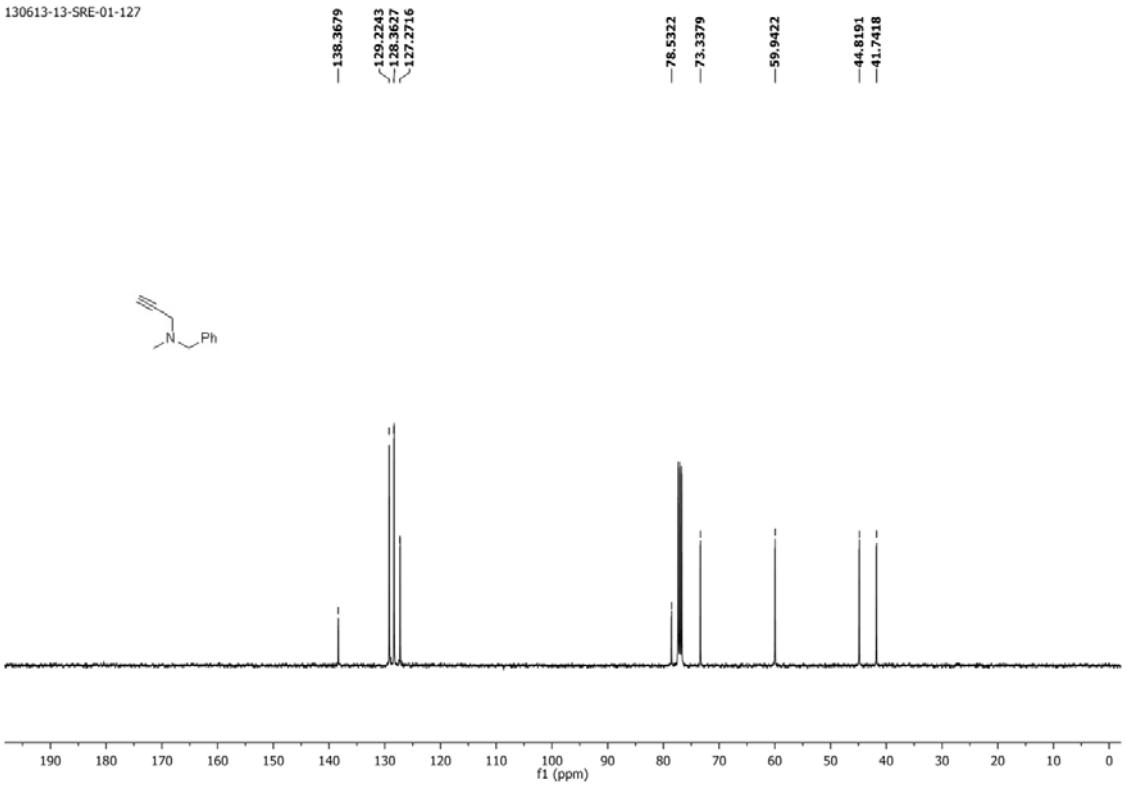


Fig. S17 ^{13}C NMR spectra of **3i** in $CDCl_3$.

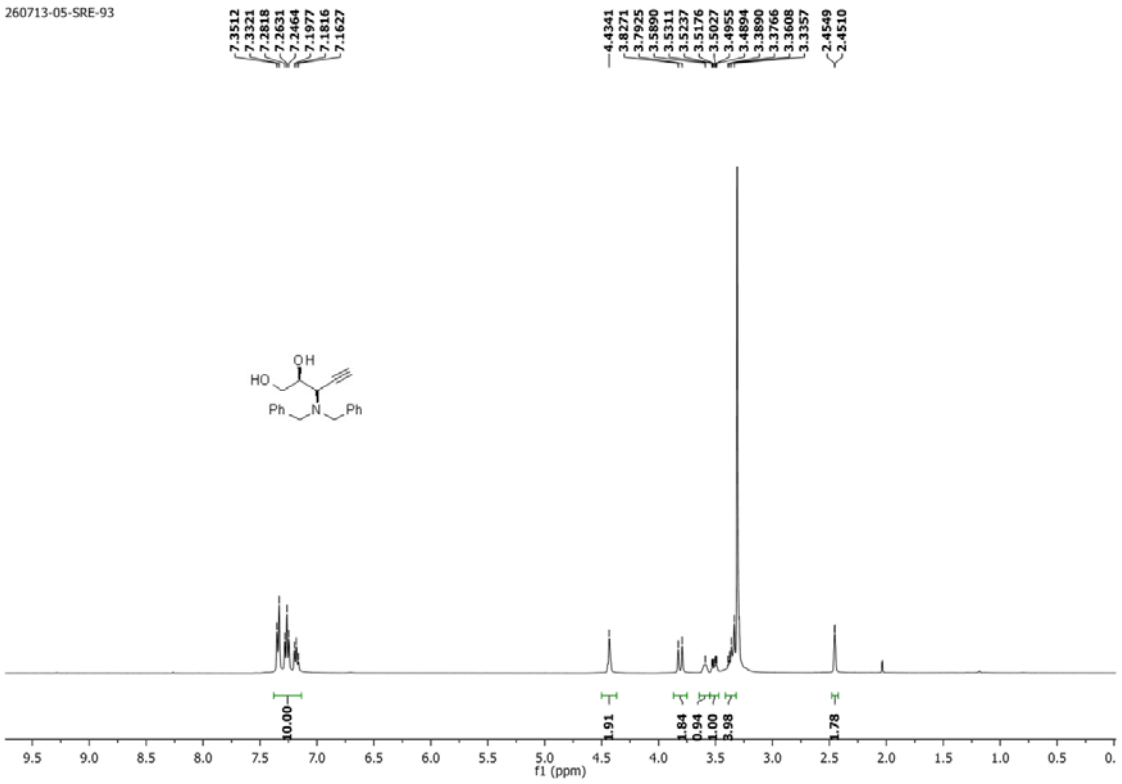


Fig. S18 ^{1}H NMR spectra of **3j** in $CDCl_3$.

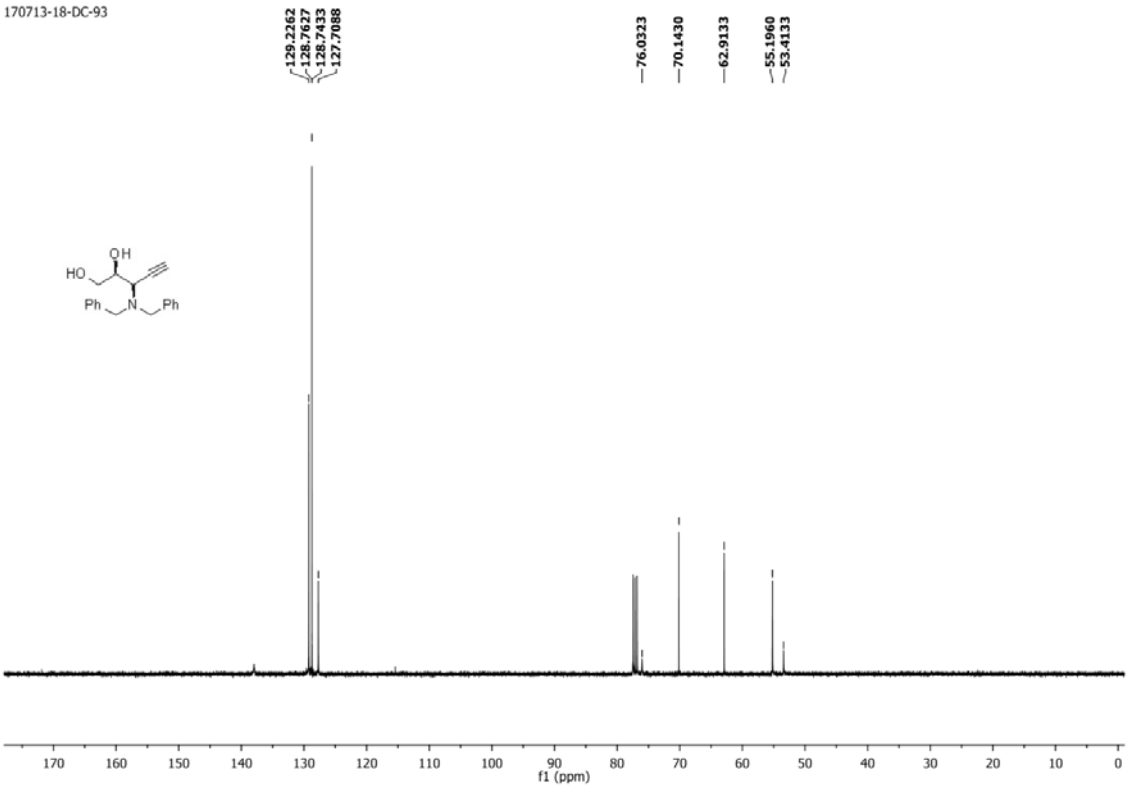


Fig. S19 ^{13}C NMR spectra of **3j** in $CDCl_3$.

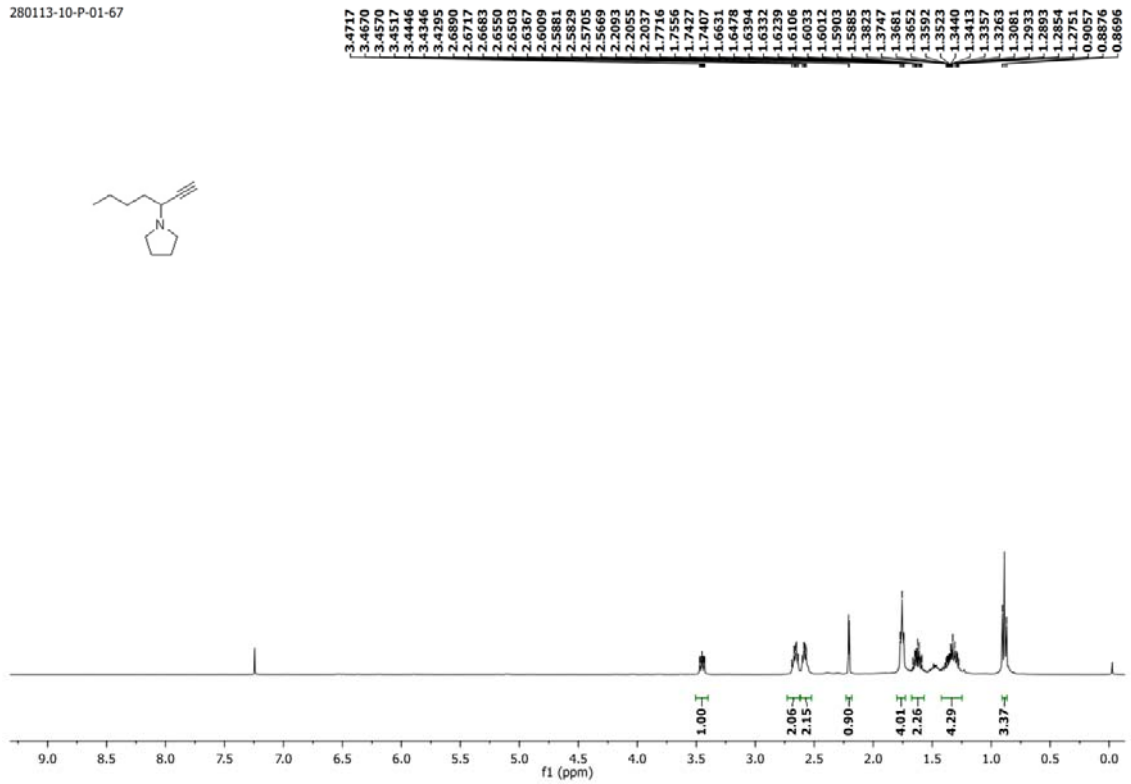


Fig. S20 ^{1}H NMR spectra of **3k** in $CDCl_3$.

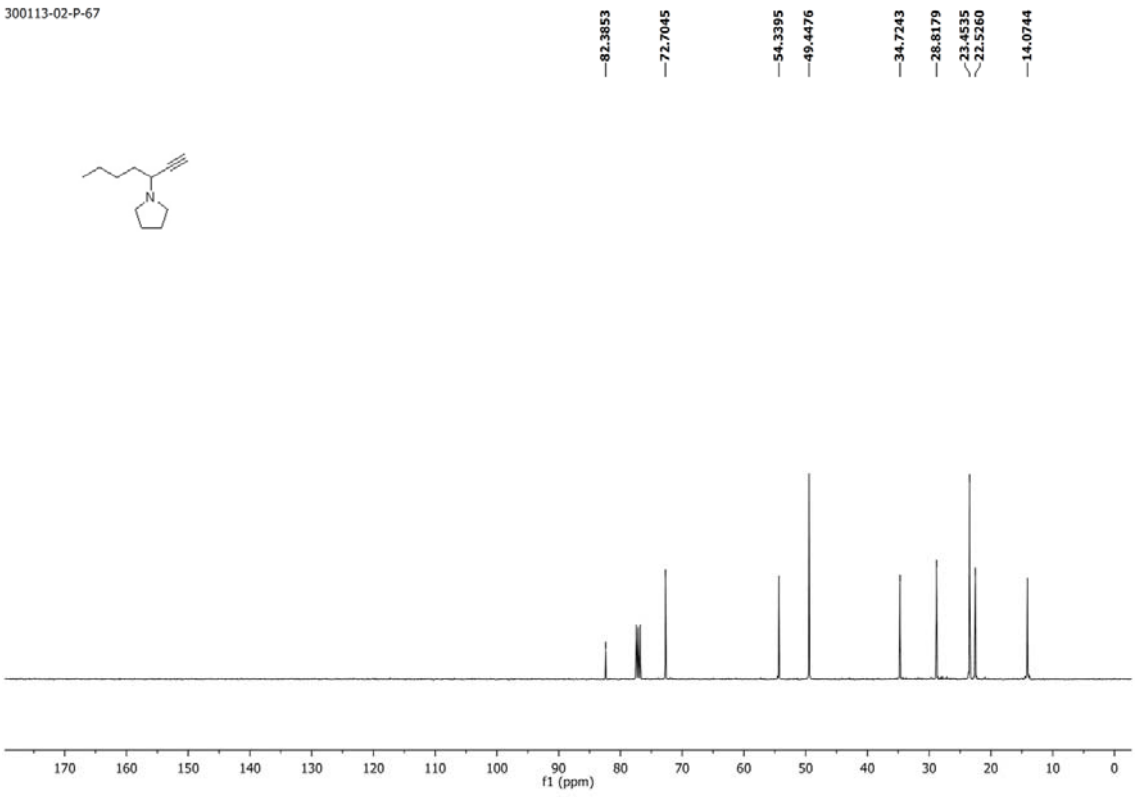


Fig. S21 ^{13}C NMR spectra of **3k** in $CDCl_3$.

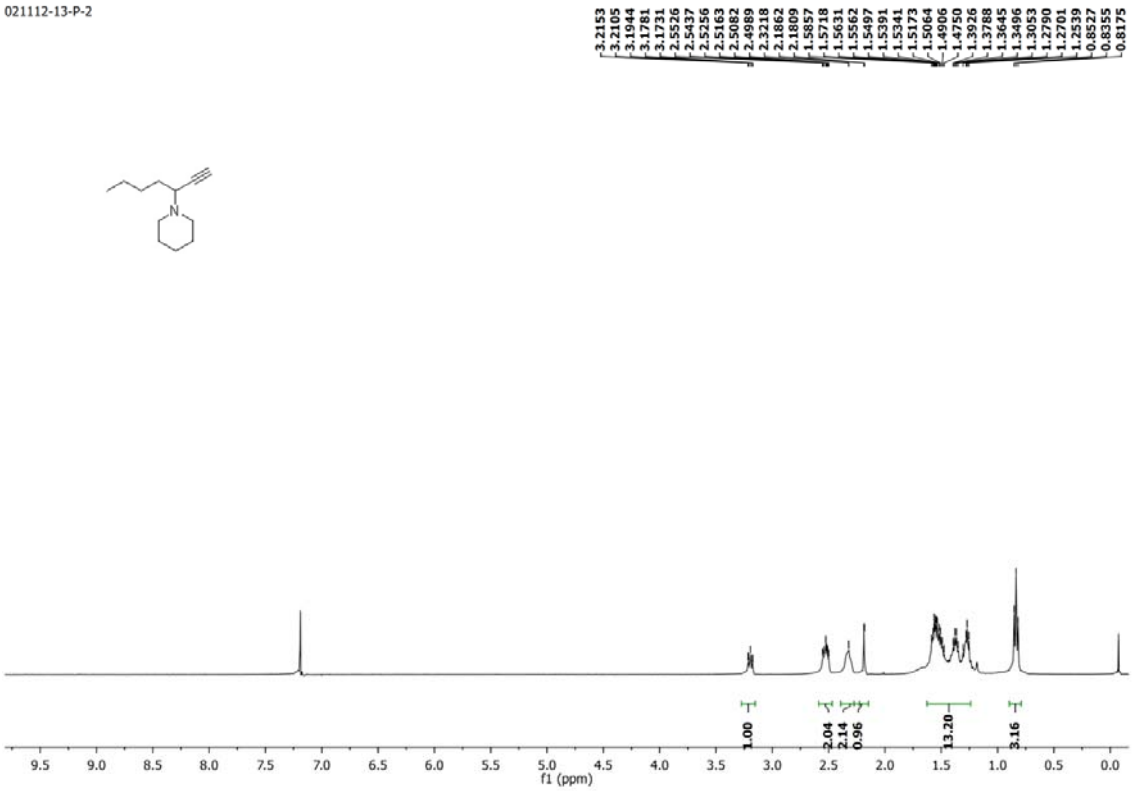


Fig. S22 ^{1}H NMR spectra of **3n** in $CDCl_3$.

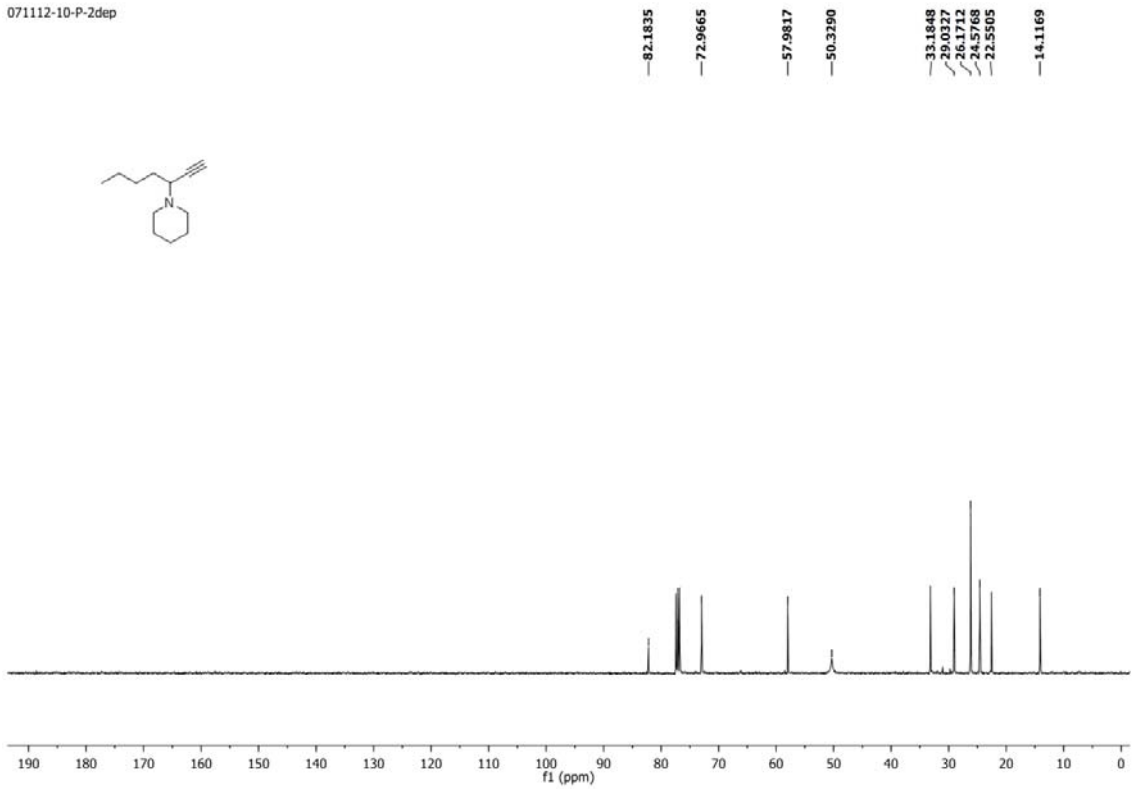


Fig. S23 ^{13}C NMR spectra of **3n** in $CDCl_3$.

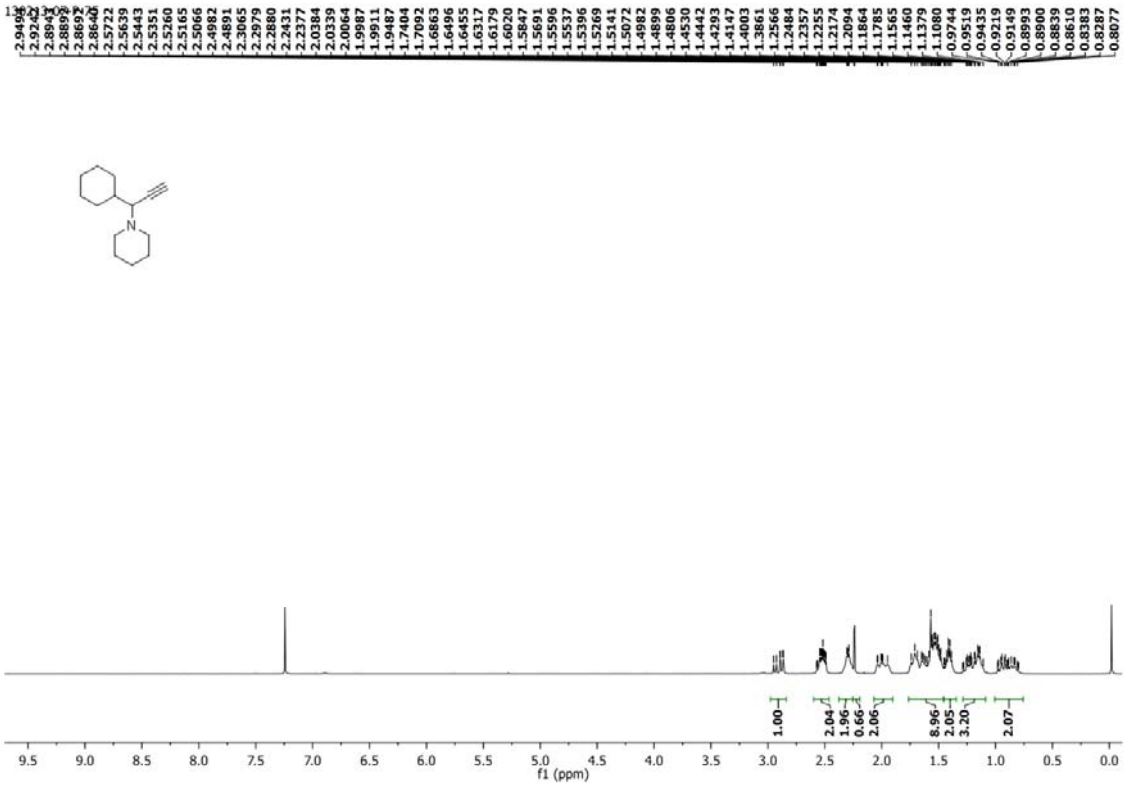


Fig. S24 ^{1}H NMR spectra of **3o** in $CDCl_3$.

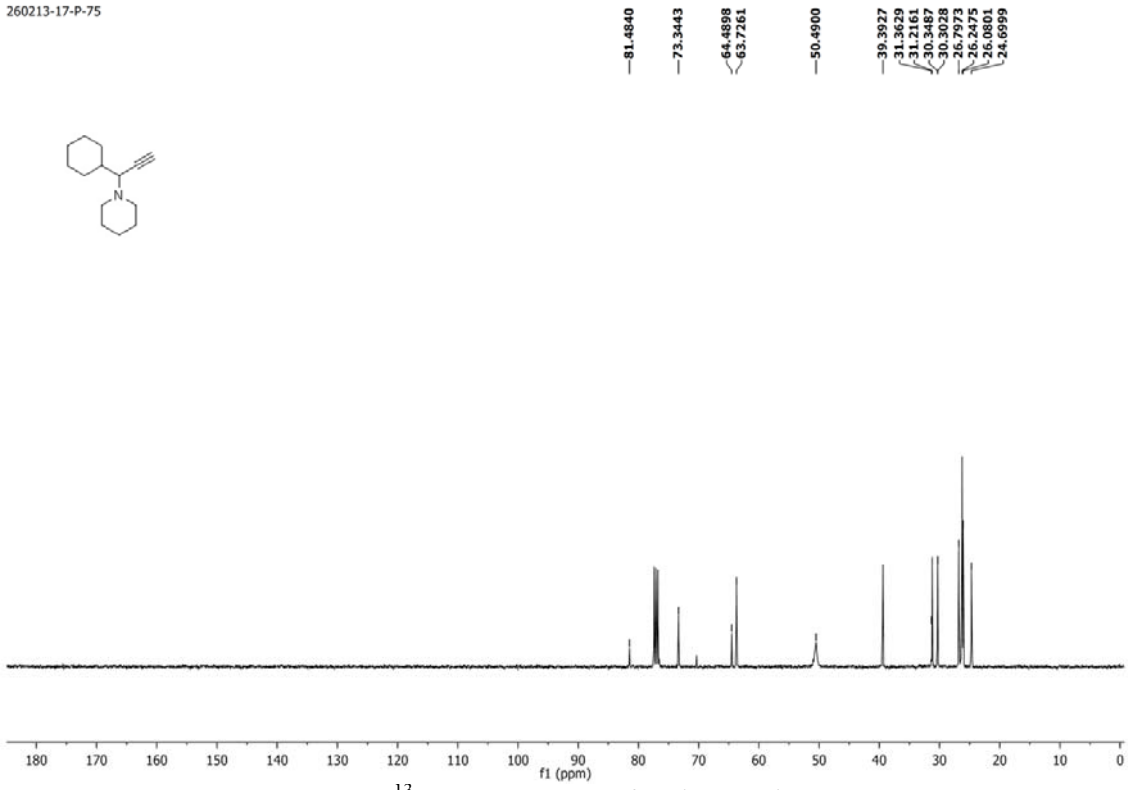


Fig. S25 ^{13}C NMR spectra of **3o** in $CDCl_3$.

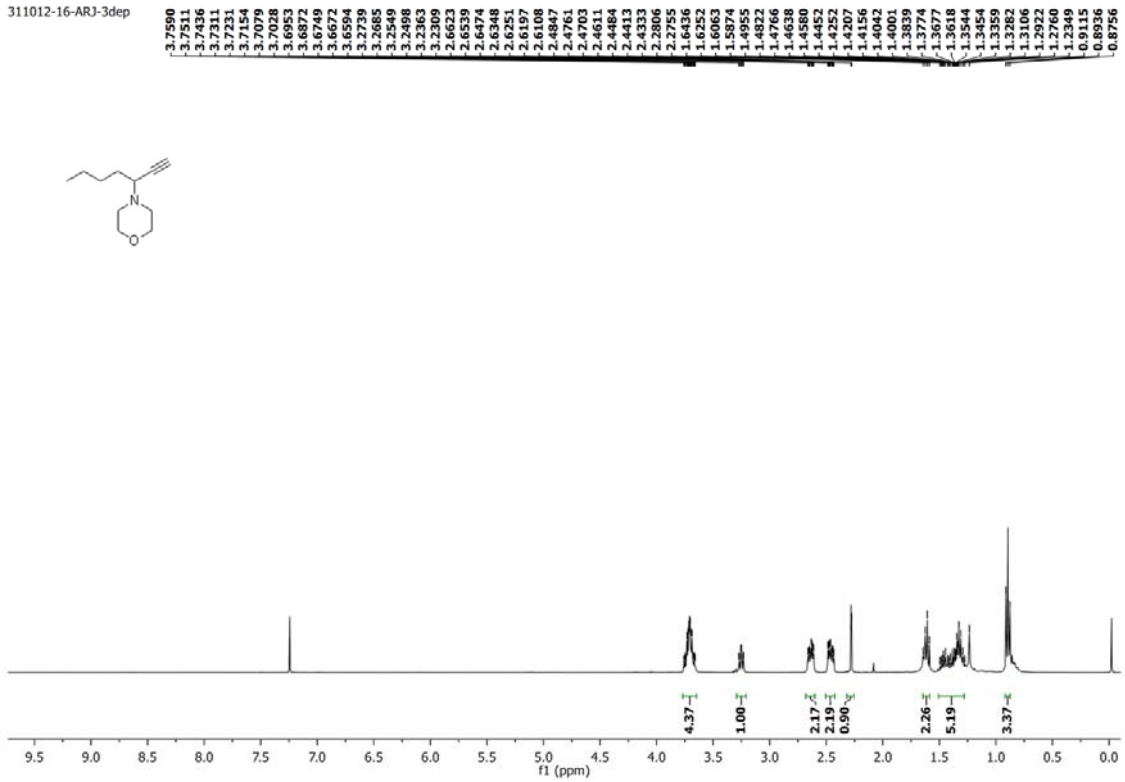


Fig. S26 ^{1}H NMR spectra of **3q** in $CDCl_3$.

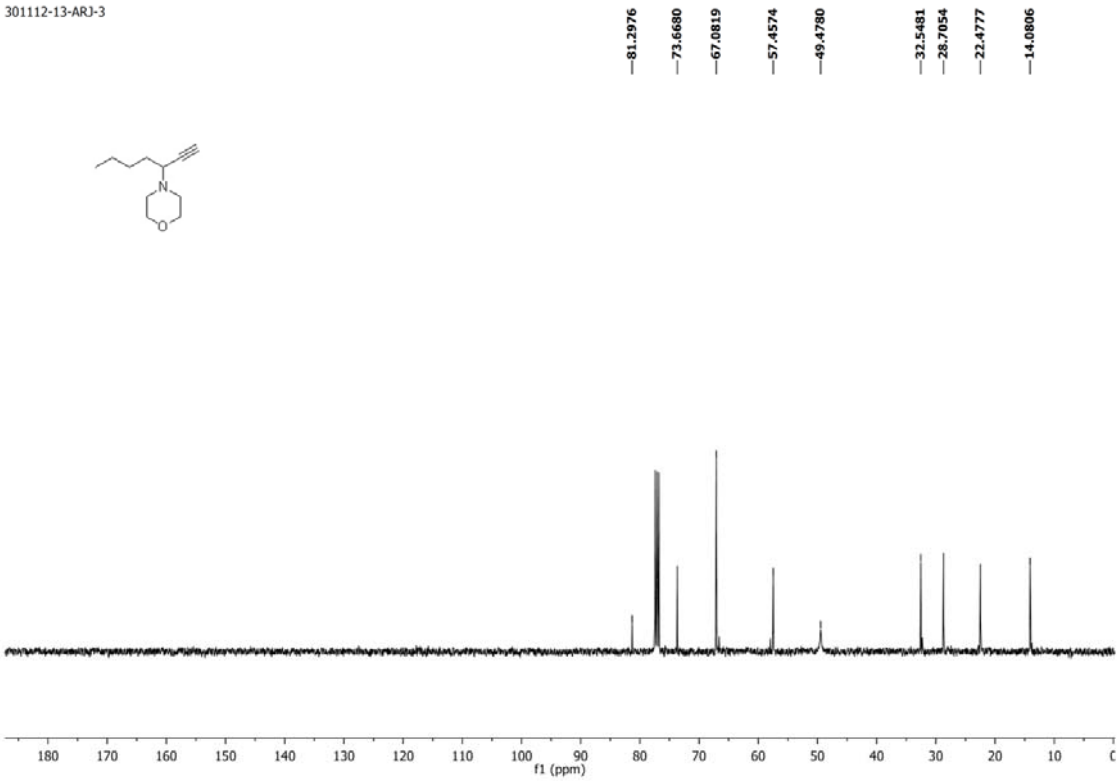


Fig. S27 ^{13}C NMR spectra of **3q** in $CDCl_3$.

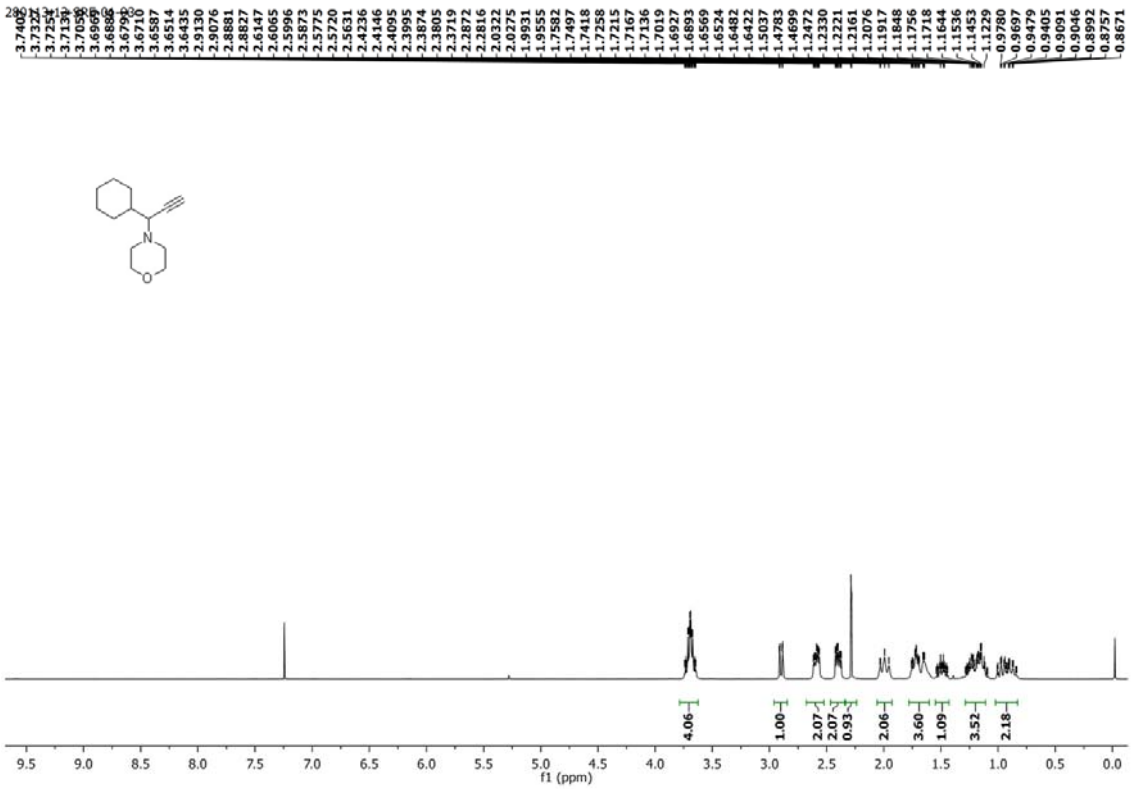


Fig. S28 ^{1}H NMR spectra of **3r** in $CDCl_3$.

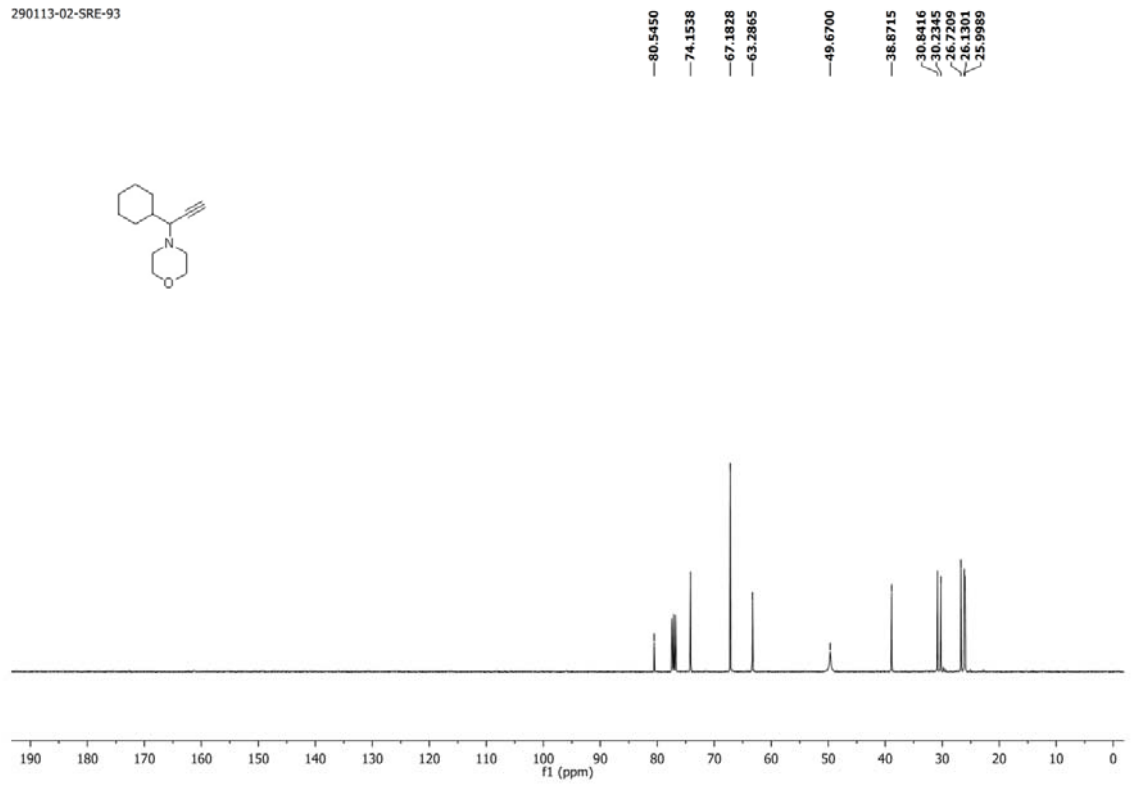


Fig. S29 ^{13}C NMR spectra of **3r** in $CDCl_3$.

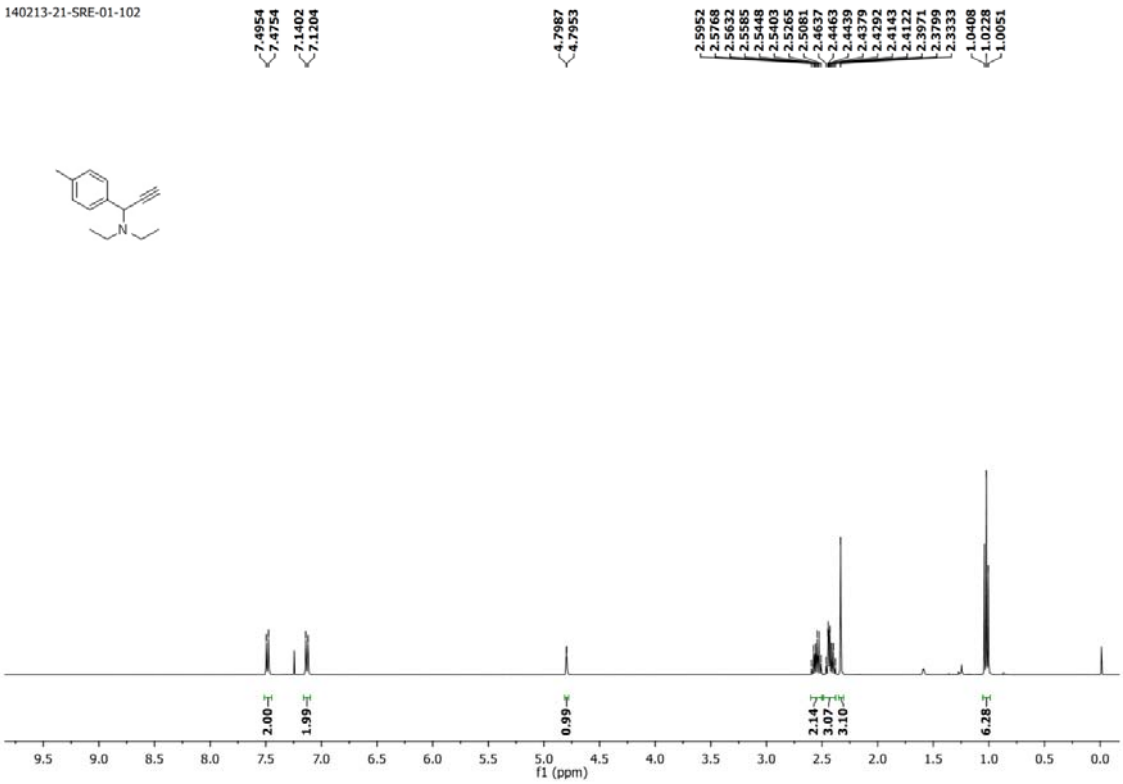


Fig. S30 ^{1}H NMR spectra of **3t** in $CDCl_3$.

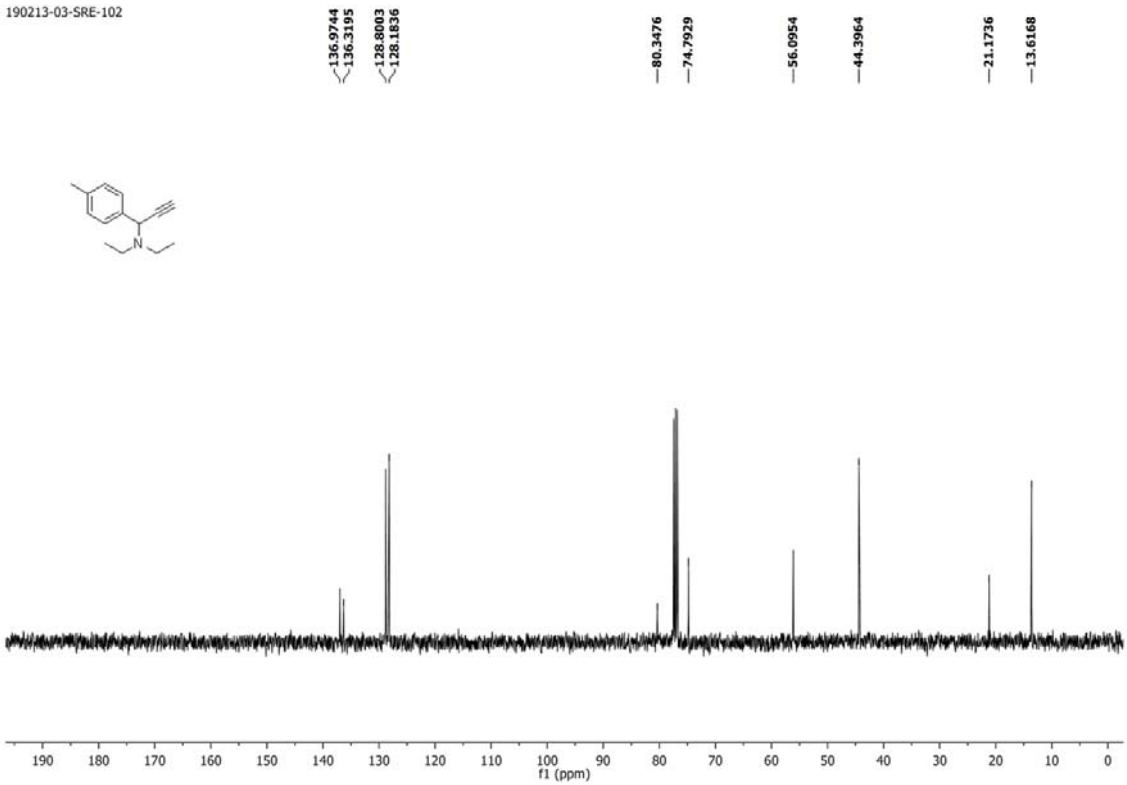


Fig. S31 ^{13}C NMR spectra of **3t** in $CDCl_3$.

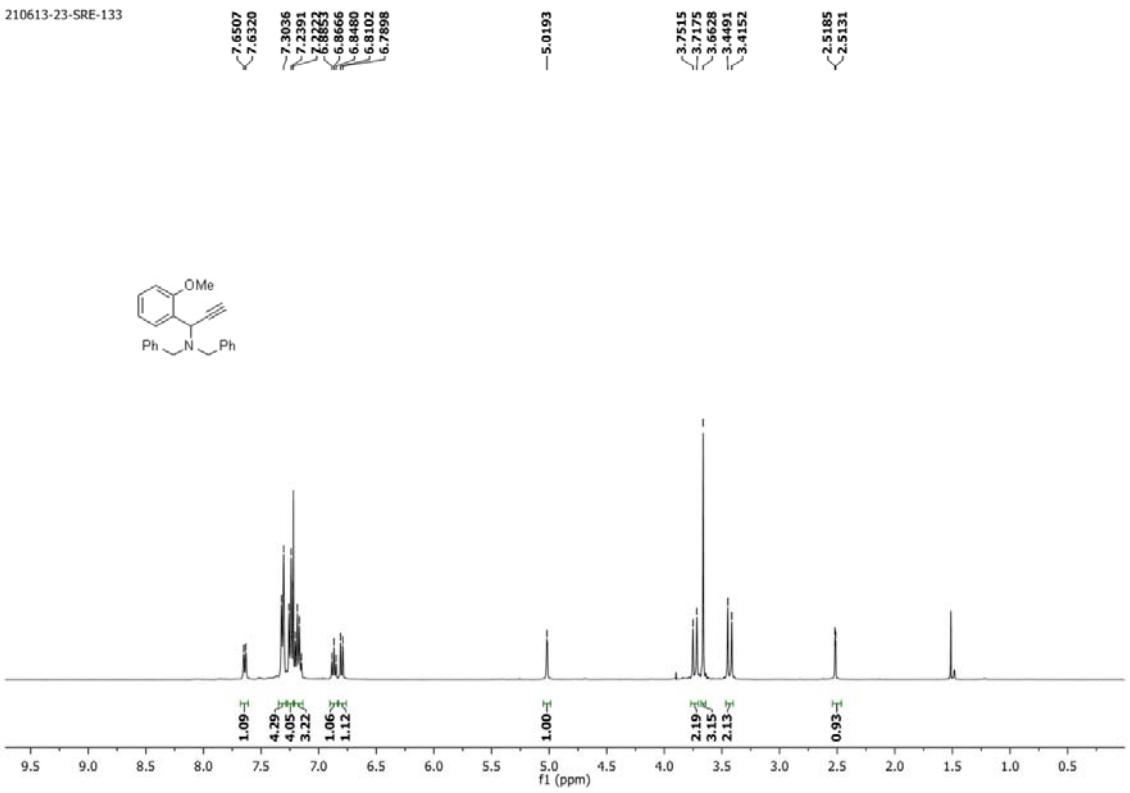


Fig. S32 ^{1}H NMR spectra of **3u** in $CDCl_3$.

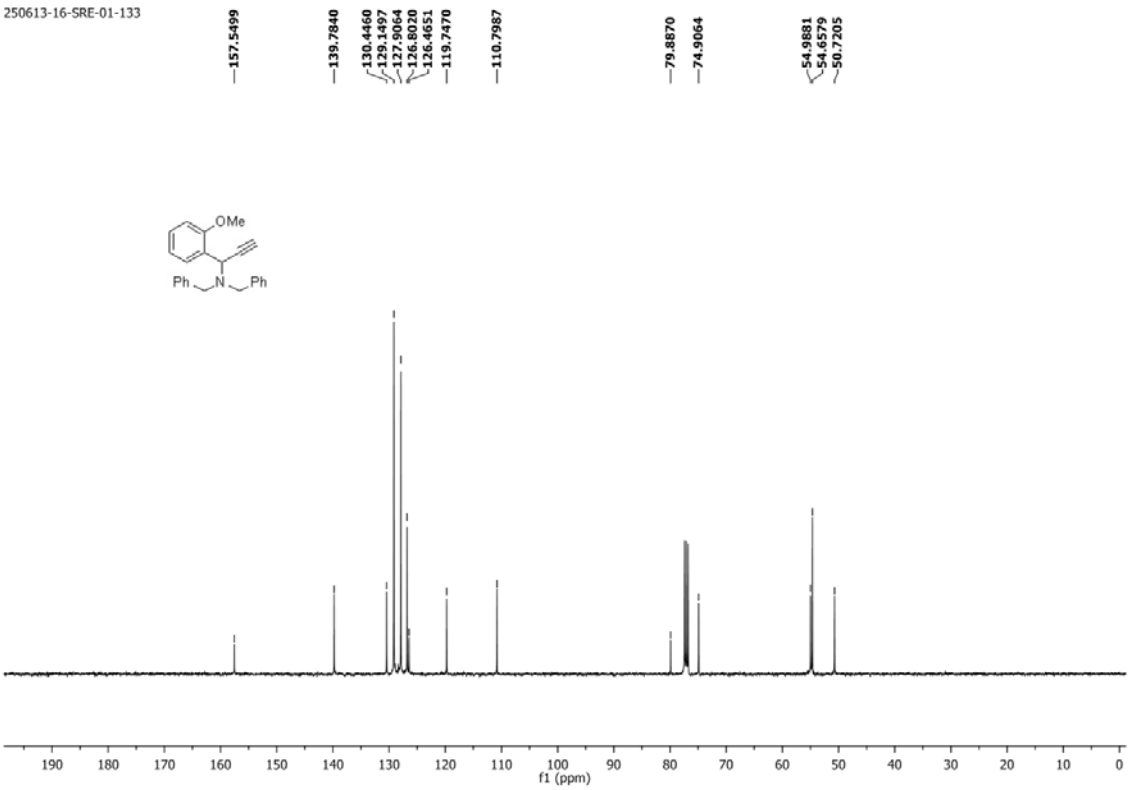


Fig. S33 ^{13}C NMR spectra of **3u** in $CDCl_3$.

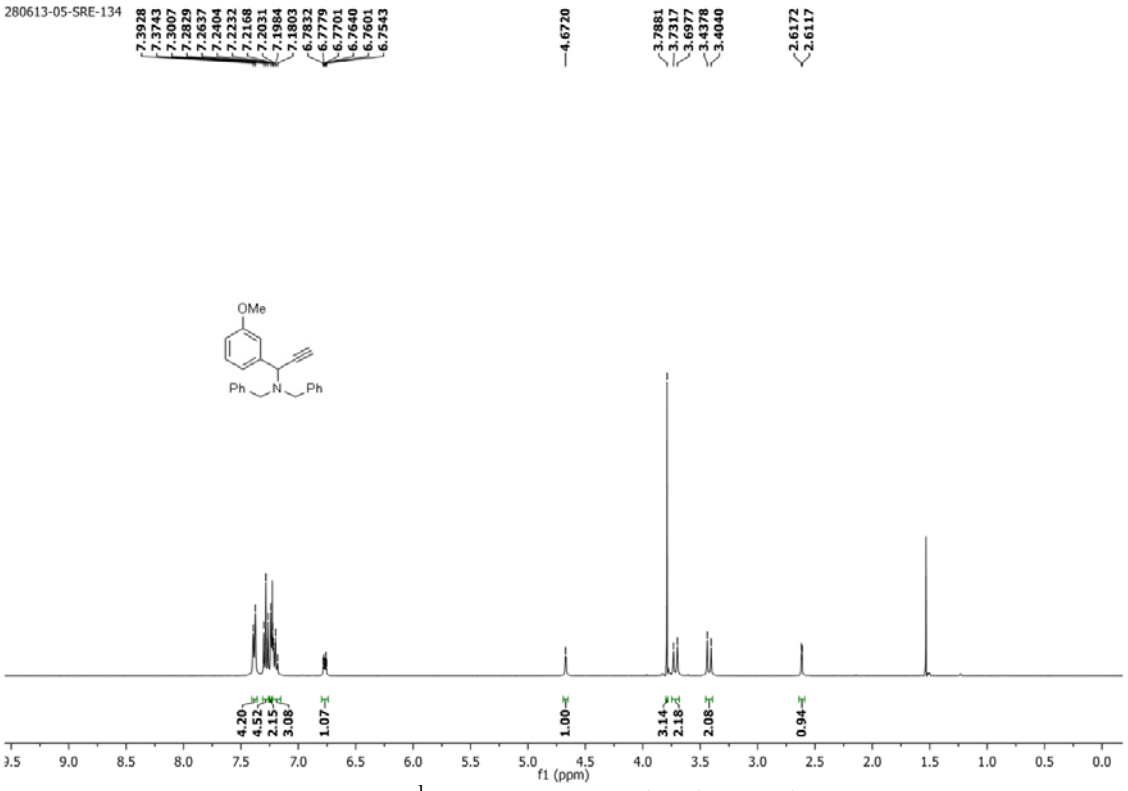


Fig. S34 ^{1}H NMR spectra of **3v** in $CDCl_3$.

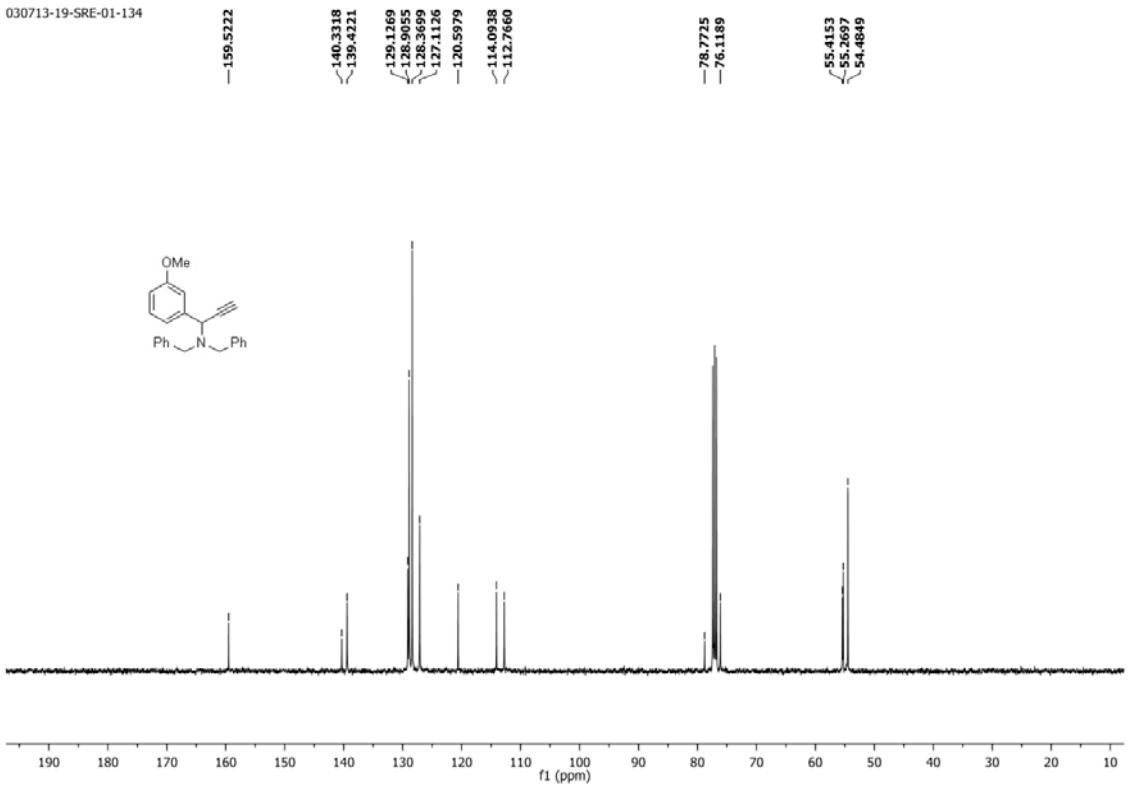


Fig. S35 ^{13}C NMR spectra of **3v** in $CDCl_3$.

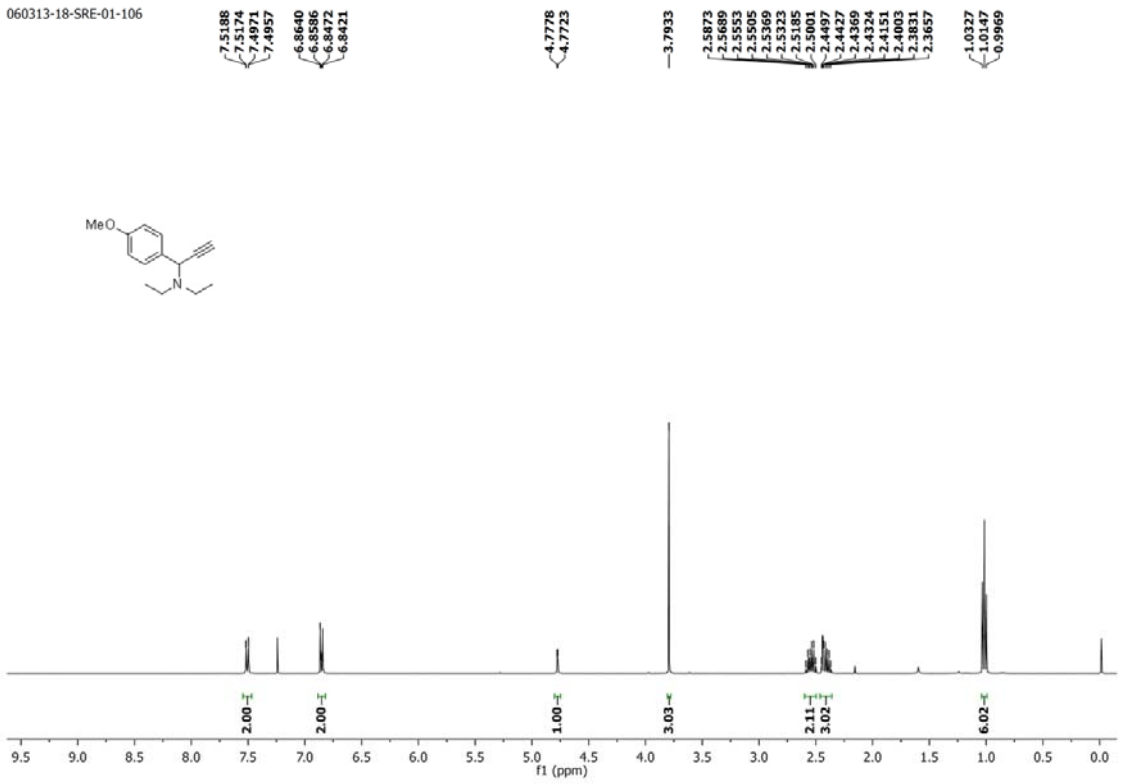


Fig. S36 ^{1}H NMR spectra of **3w** in $CDCl_3$.

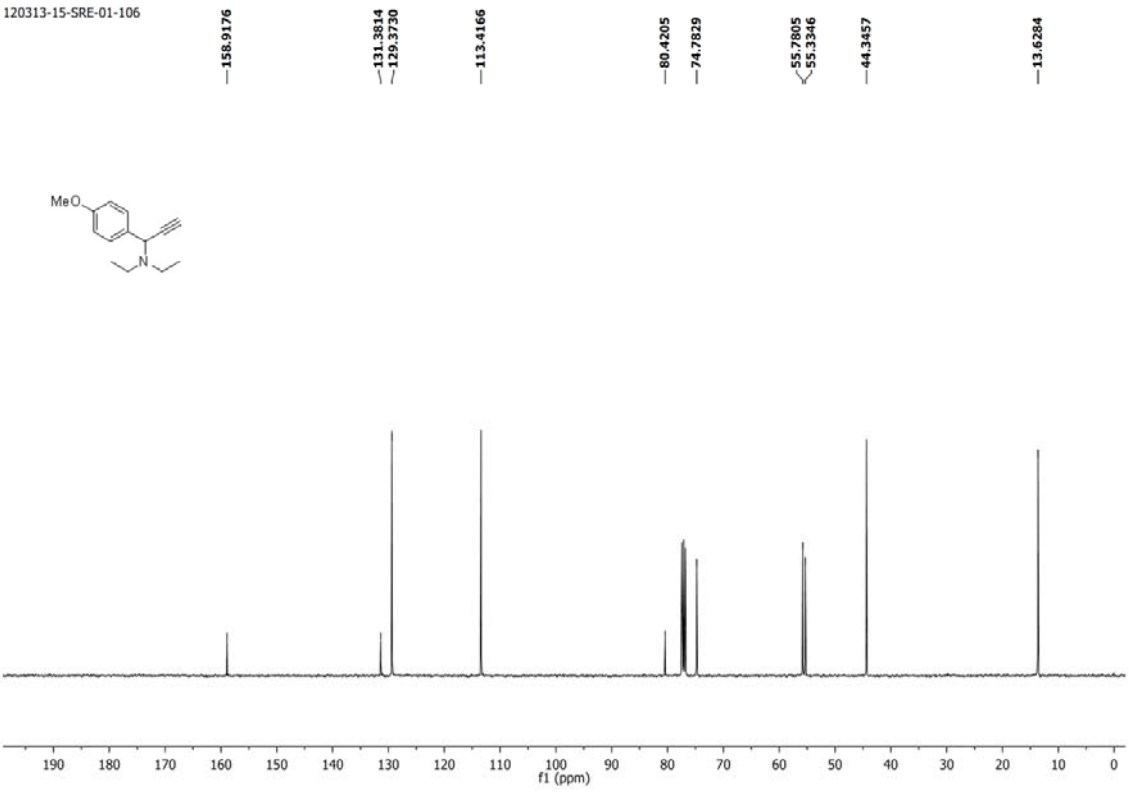


Fig. S37 ^{13}C NMR spectra of **3w** in $CDCl_3$.

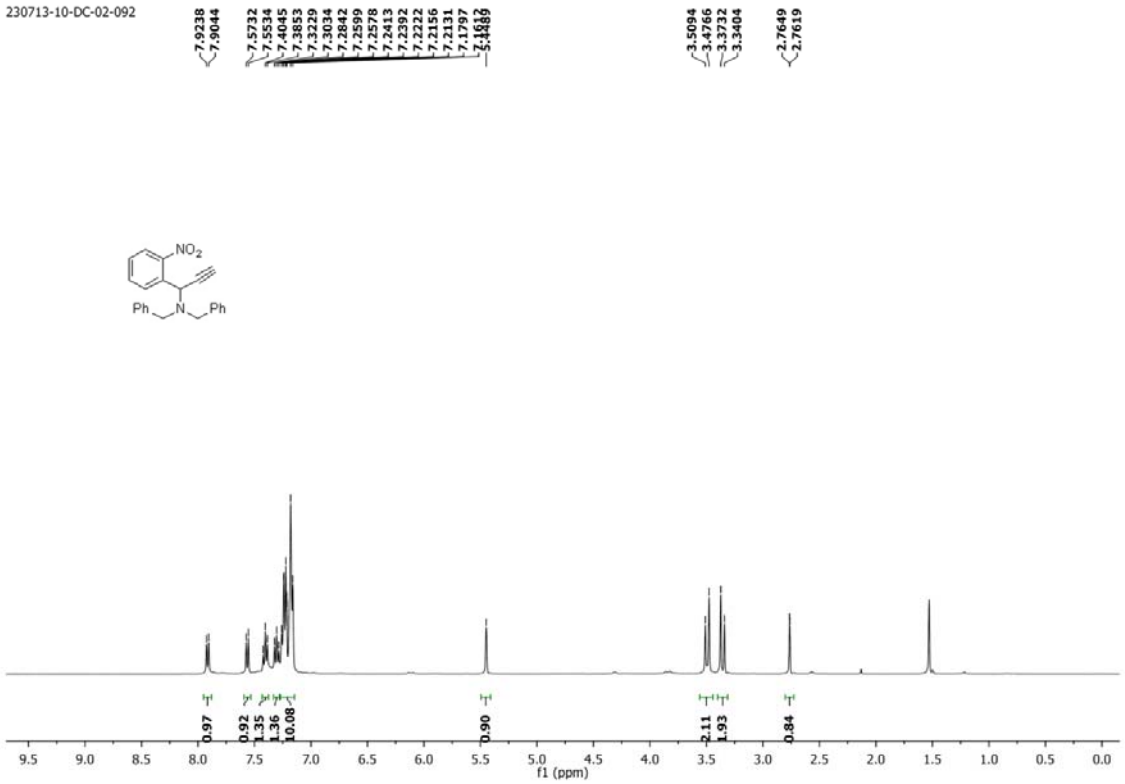


Fig. S38 ^{1}H NMR spectra of **3x** in $CDCl_3$.

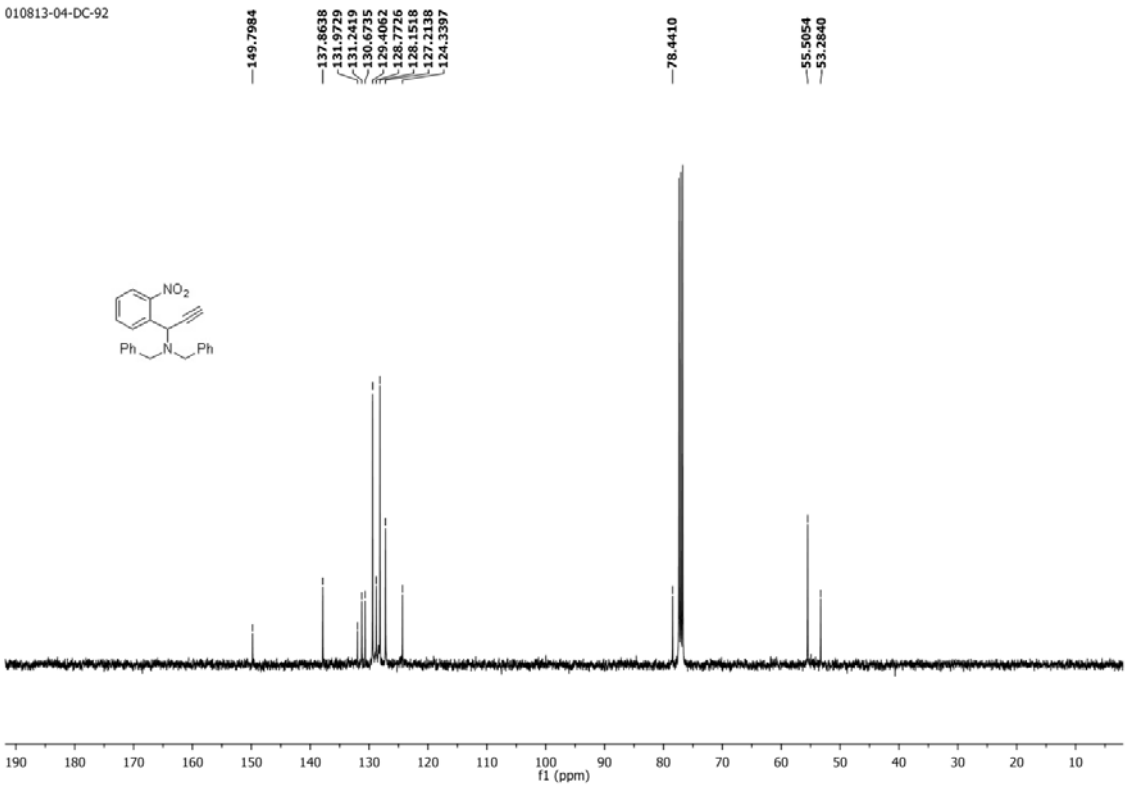


Fig. S39 ^{13}C NMR spectra of **3x** in $CDCl_3$.

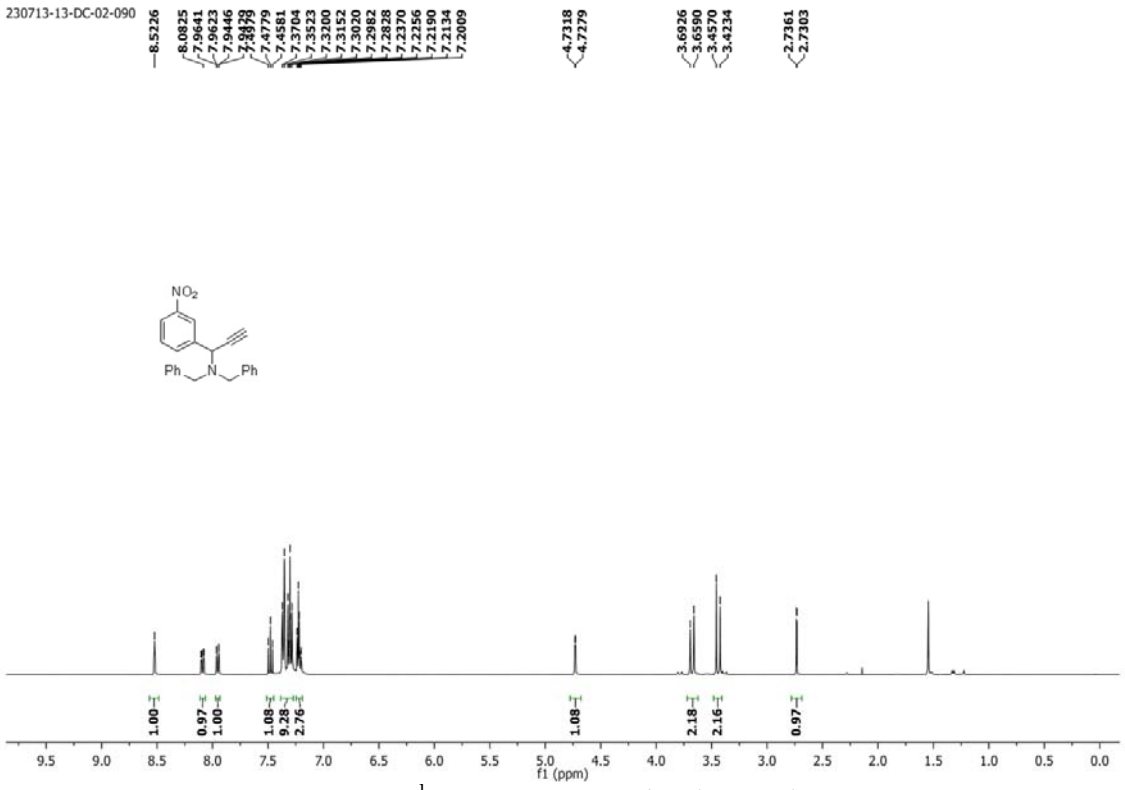


Fig. S40 ^{1}H NMR spectra of **3y** in $CDCl_3$.

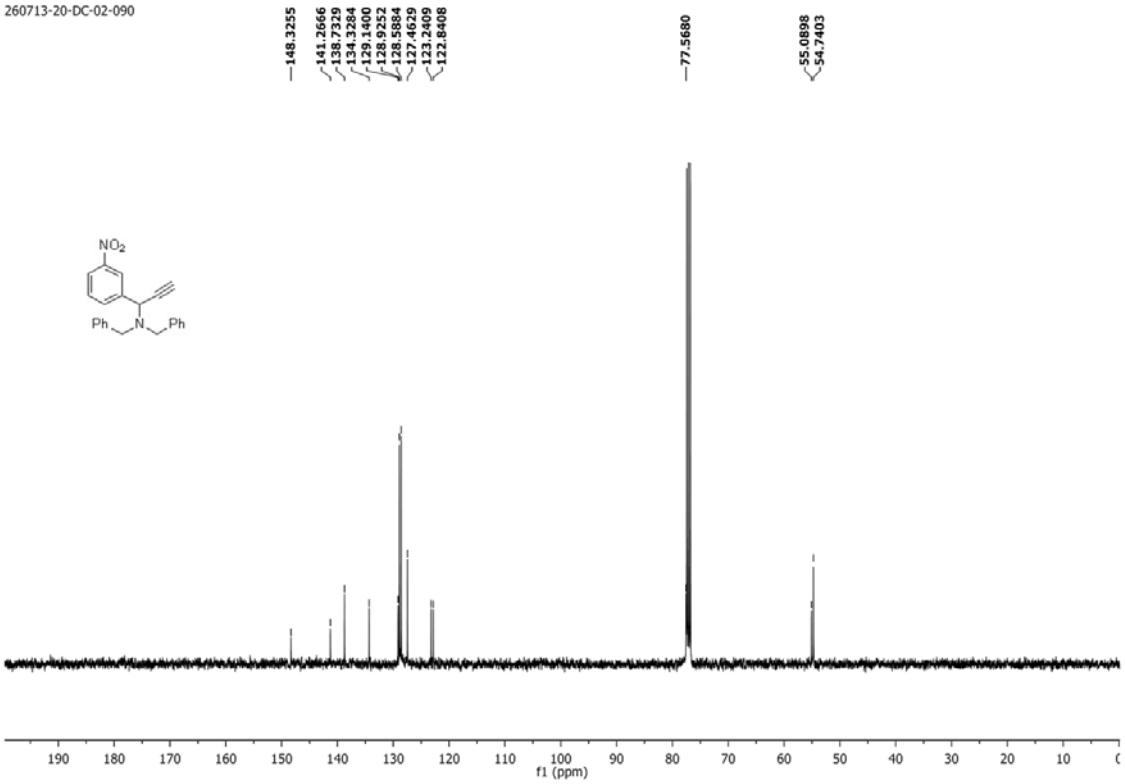


Fig. S41 ^{13}C NMR spectra of **3y** in $CDCl_3$.

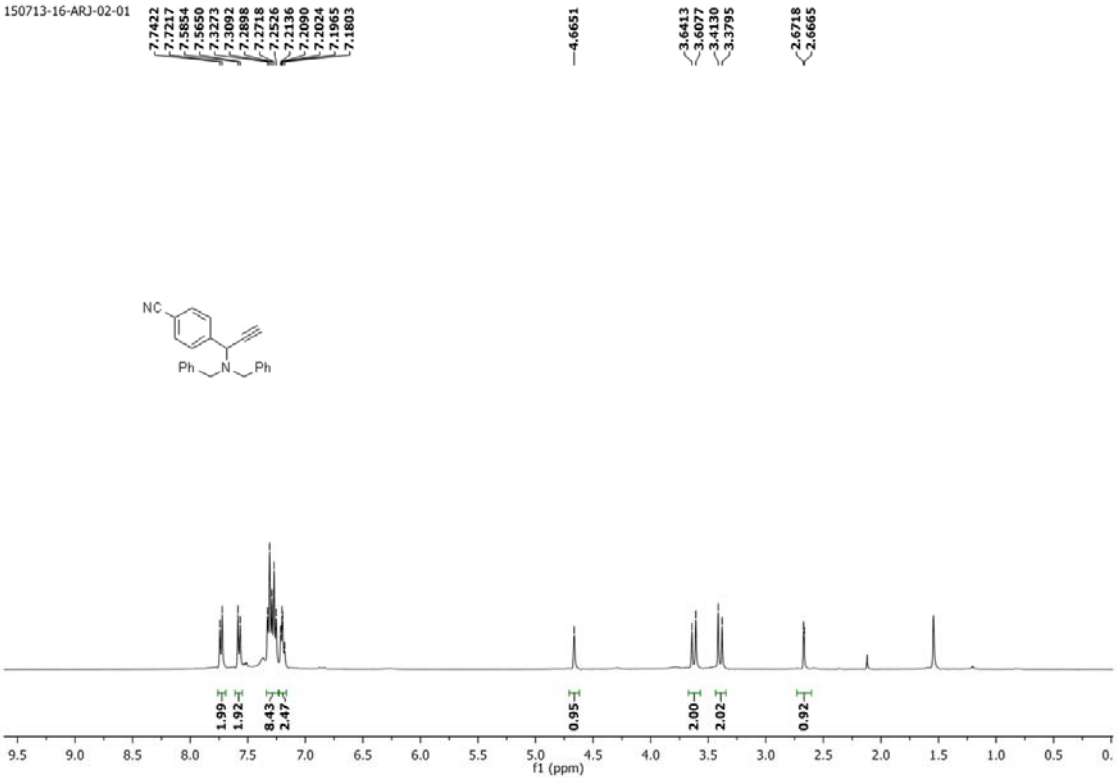


Fig. S42 ^{1}H NMR spectra of **3z** in $CDCl_3$.

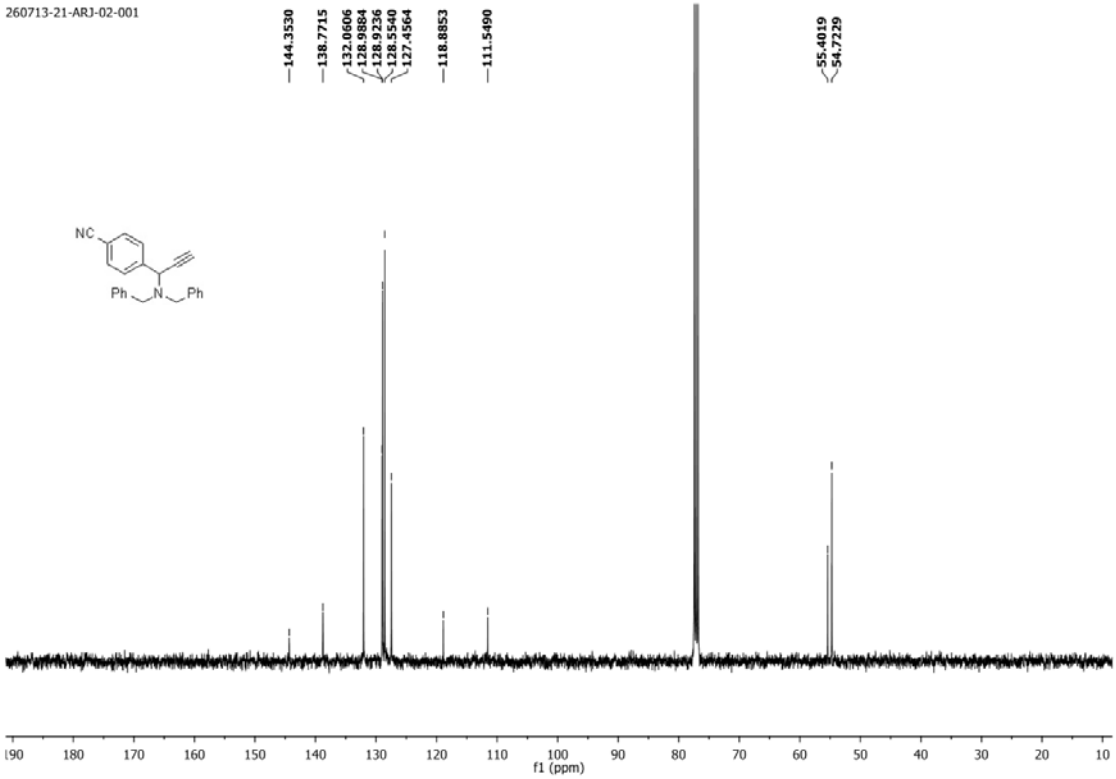


Fig. S43 ^{13}C NMR spectra of **3z** in $CDCl_3$.

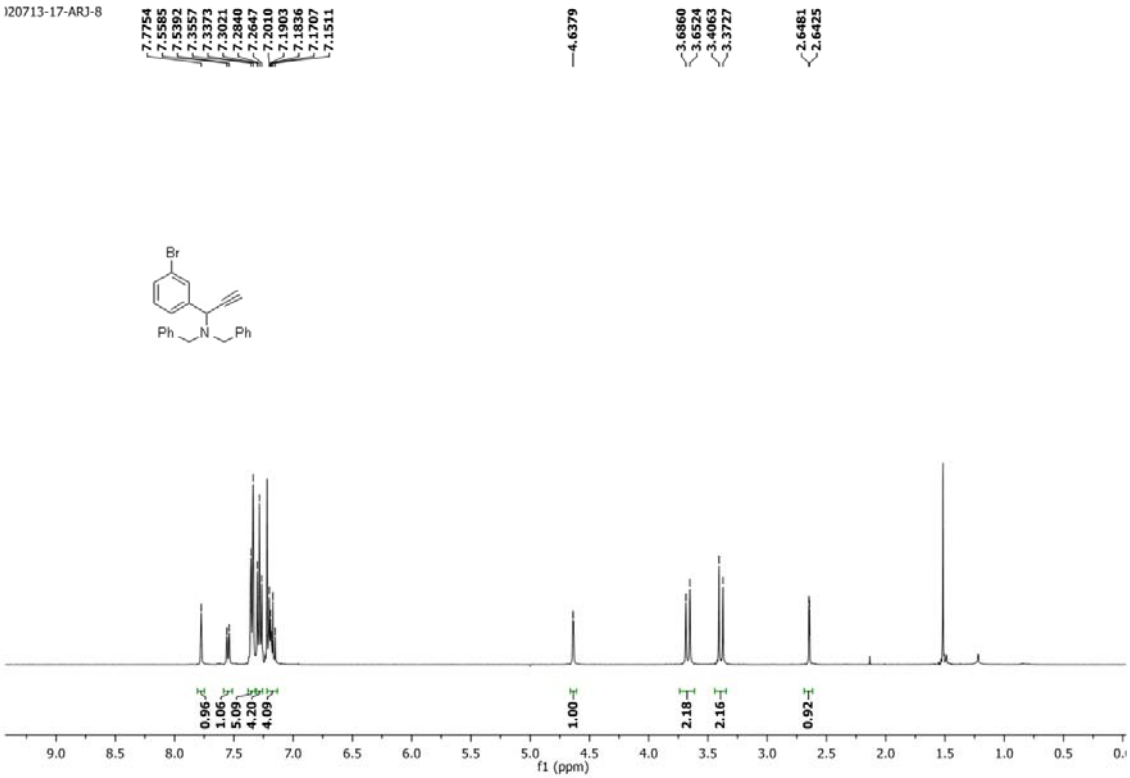


Fig. S44 ^{1}H NMR spectra of **3a´** in $CDCl_3$.

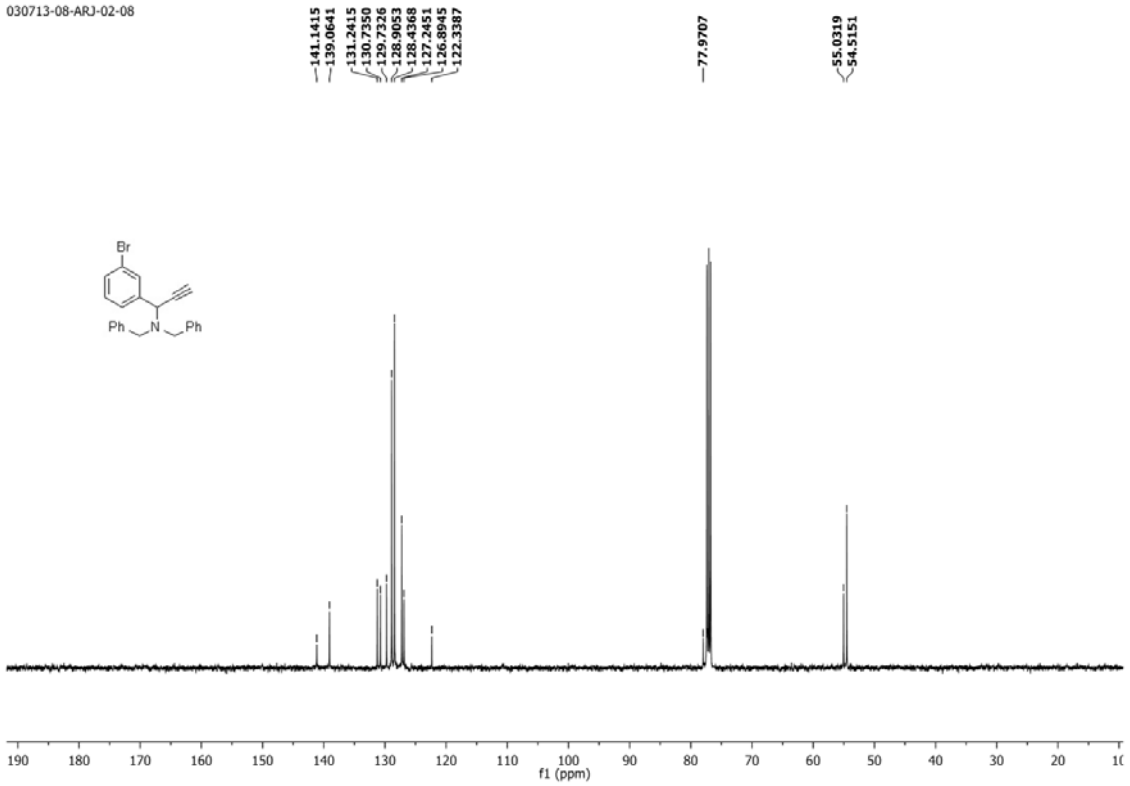


Fig. S45 ^{13}C NMR spectra of **3a´** in $CDCl_3$.

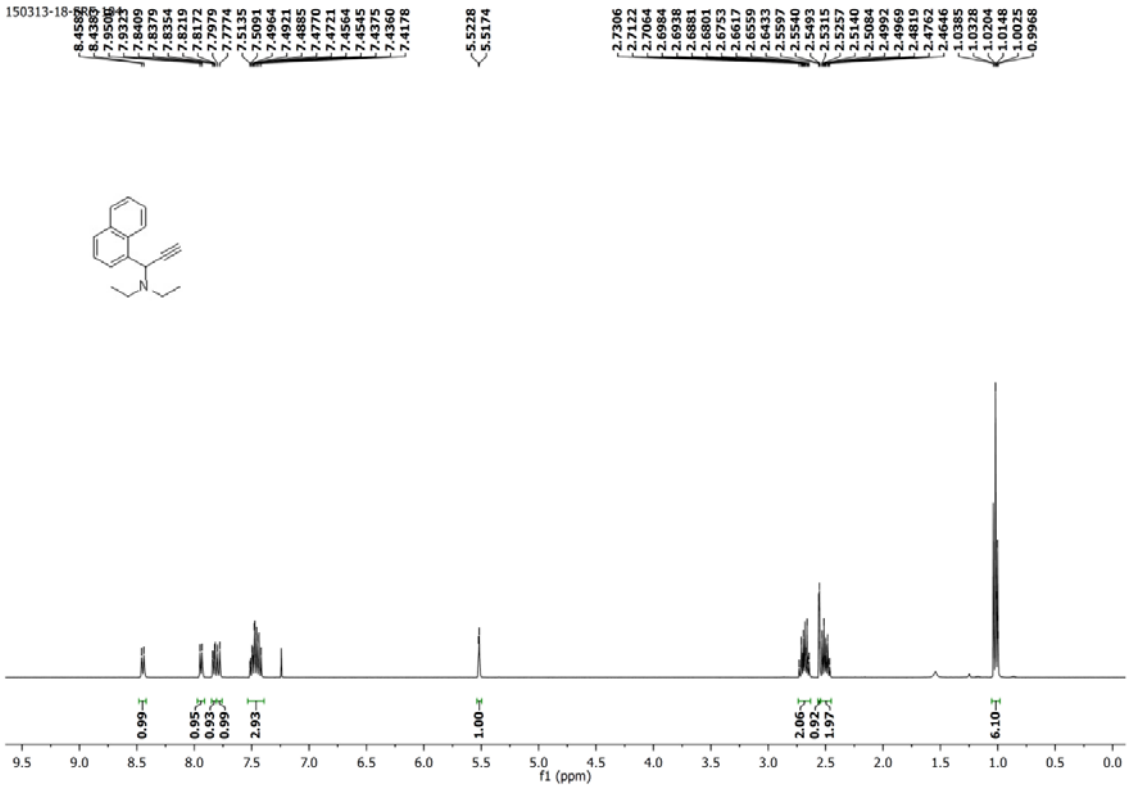


Fig. S46 ^{1}H NMR spectra of **3b´** in $CDCl_3$.

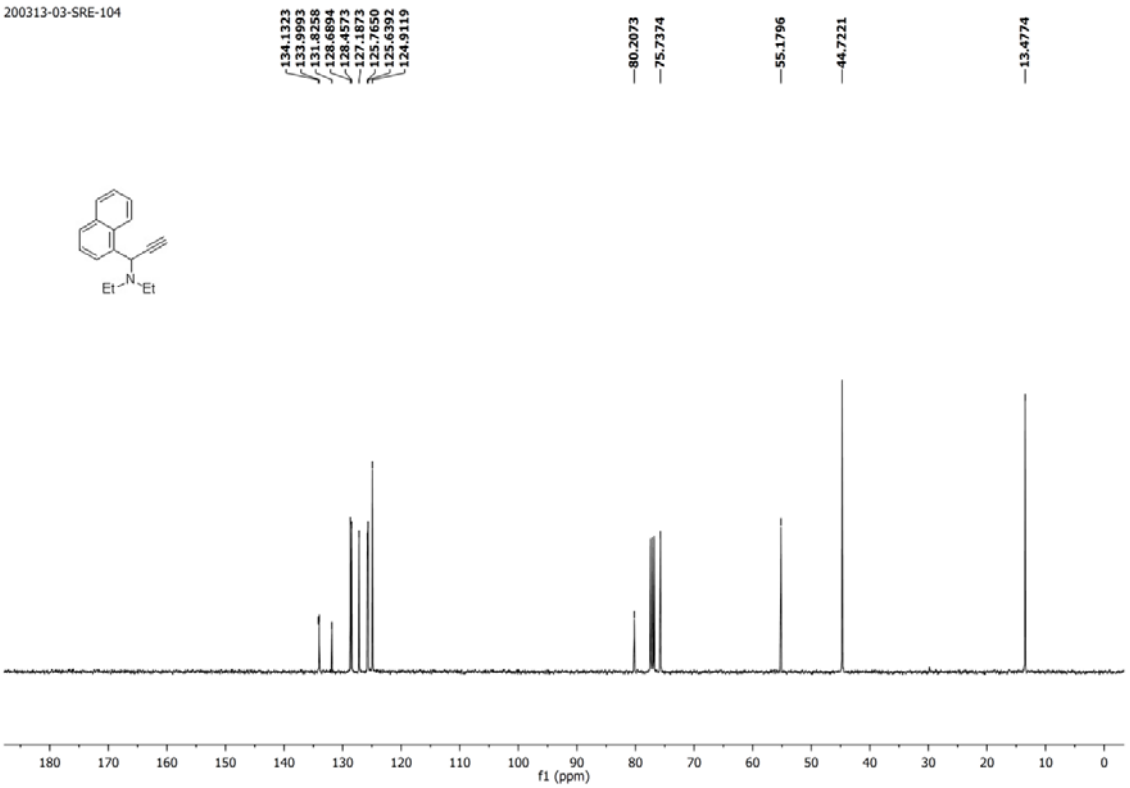


Fig. S47 ^{13}C NMR spectra of **3b´** in $CDCl_3$.

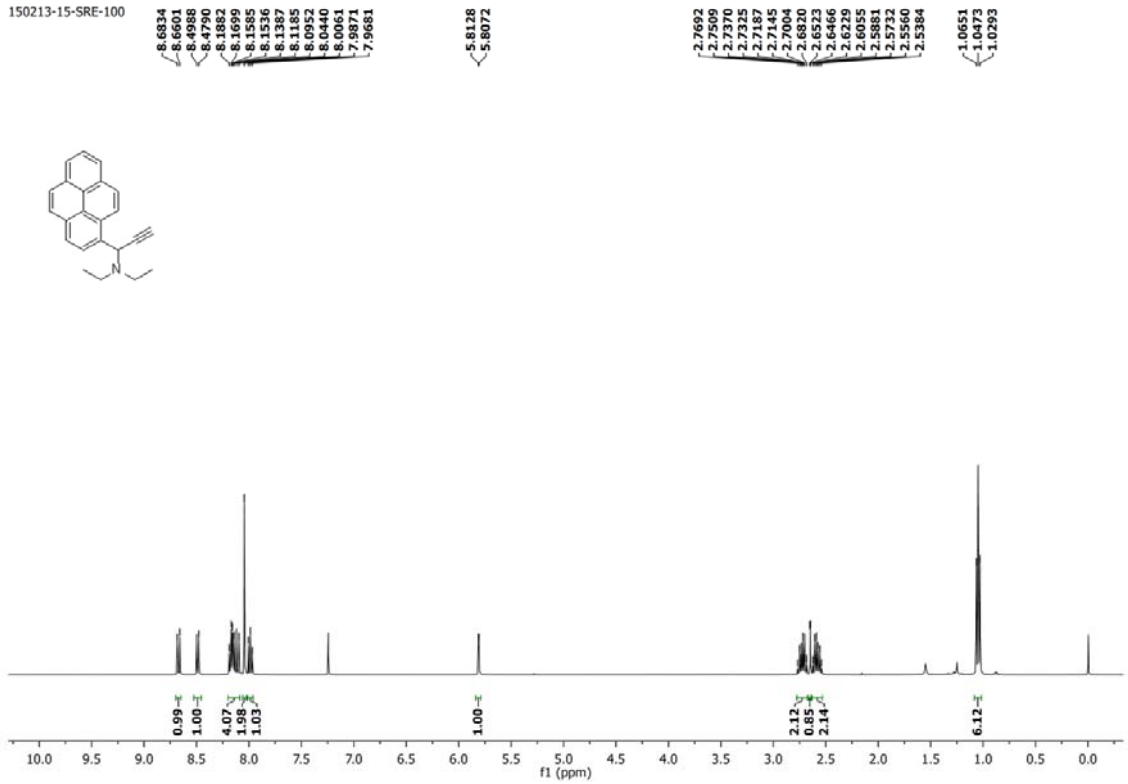


Fig. S48 ^{1}H NMR spectra of **3c´** in $CDCl_3$.

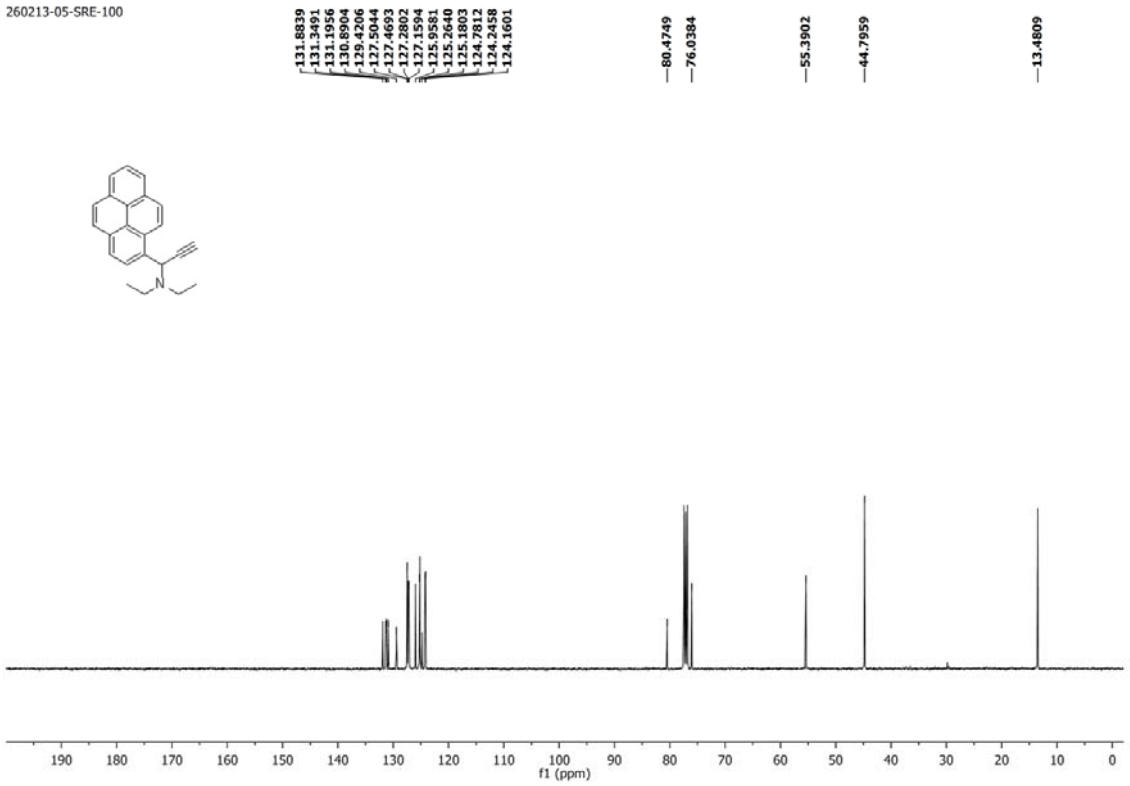


Fig. S49 ^{13}C NMR spectra of **3c´** in $CDCl_3$.

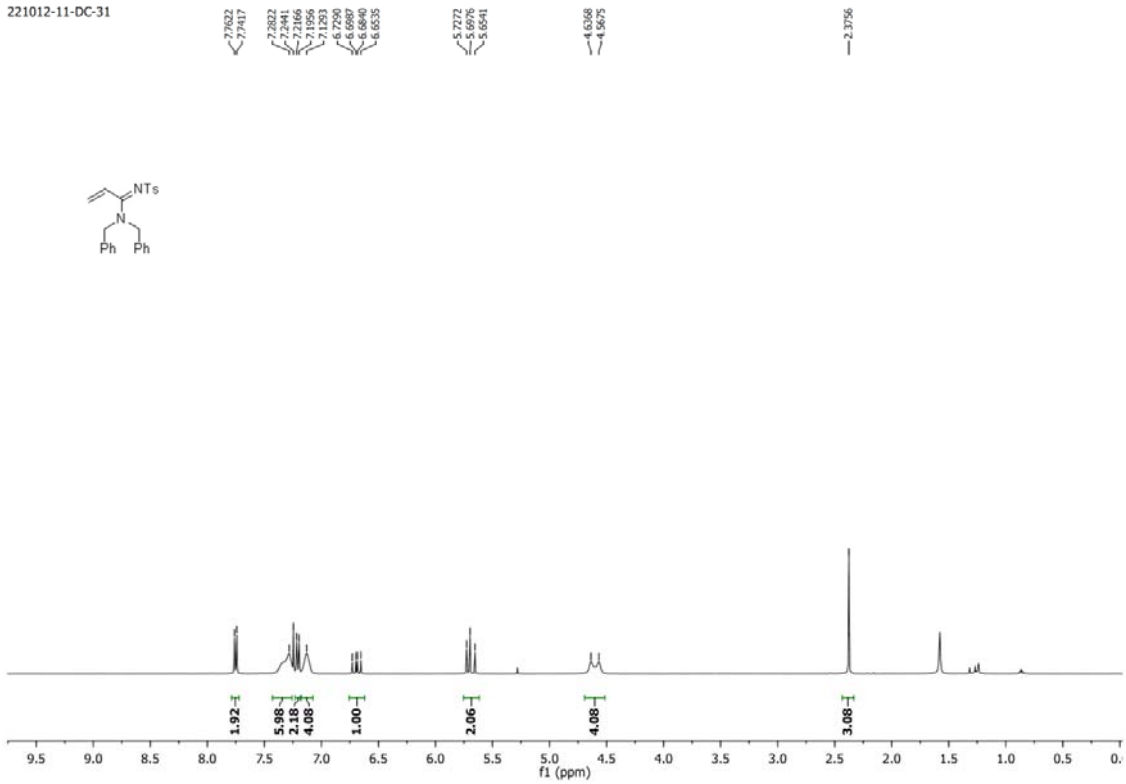


Fig. 50 ^{1}H NMR spectra of **2** in $CDCl_3$.

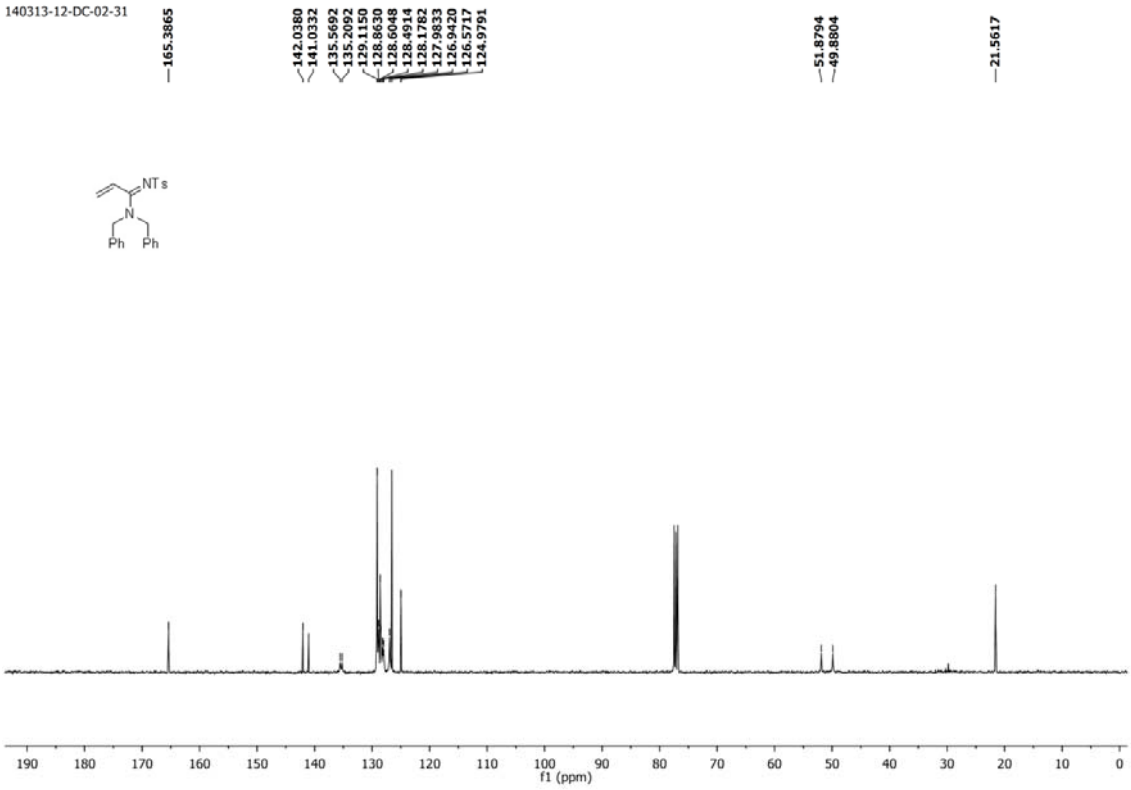


Fig. S51 ^{13}C NMR spectra of **2** in $CDCl_3$.

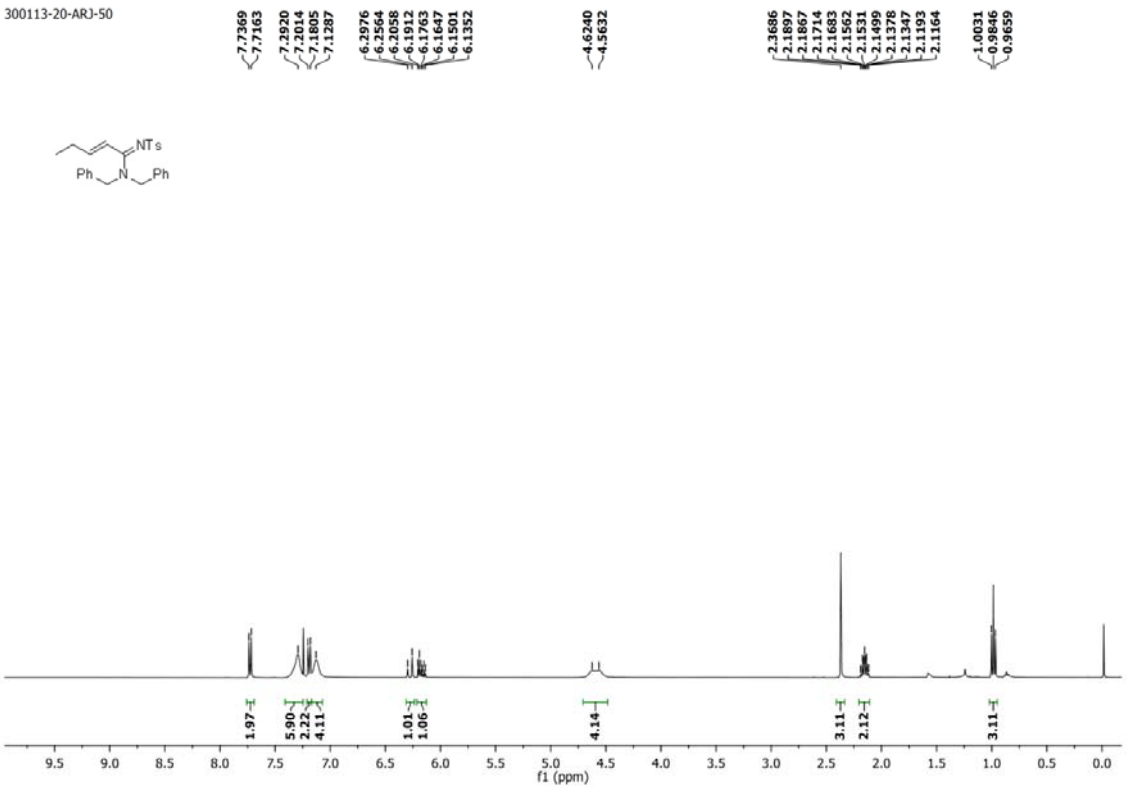


Fig. S52 ^{1}H NMR spectra of **4a** in $CDCl_3$.

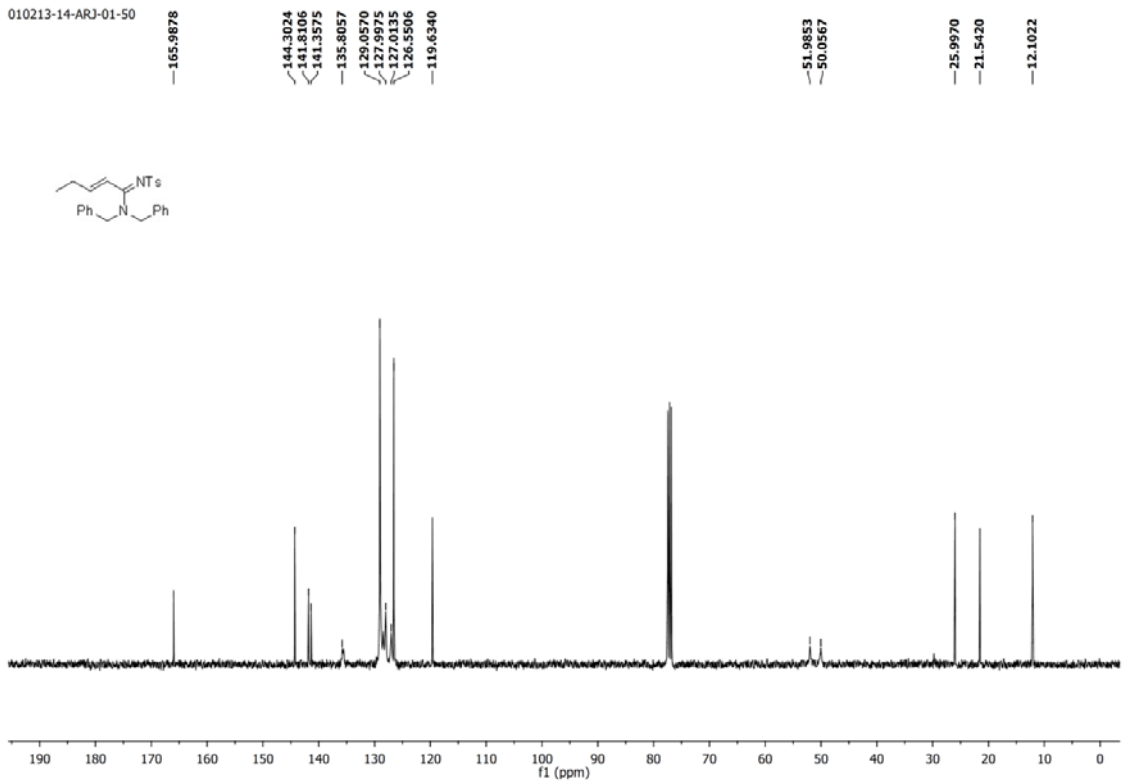


Fig. S53 ^{13}C NMR spectra of **4a** in $CDCl_3$.

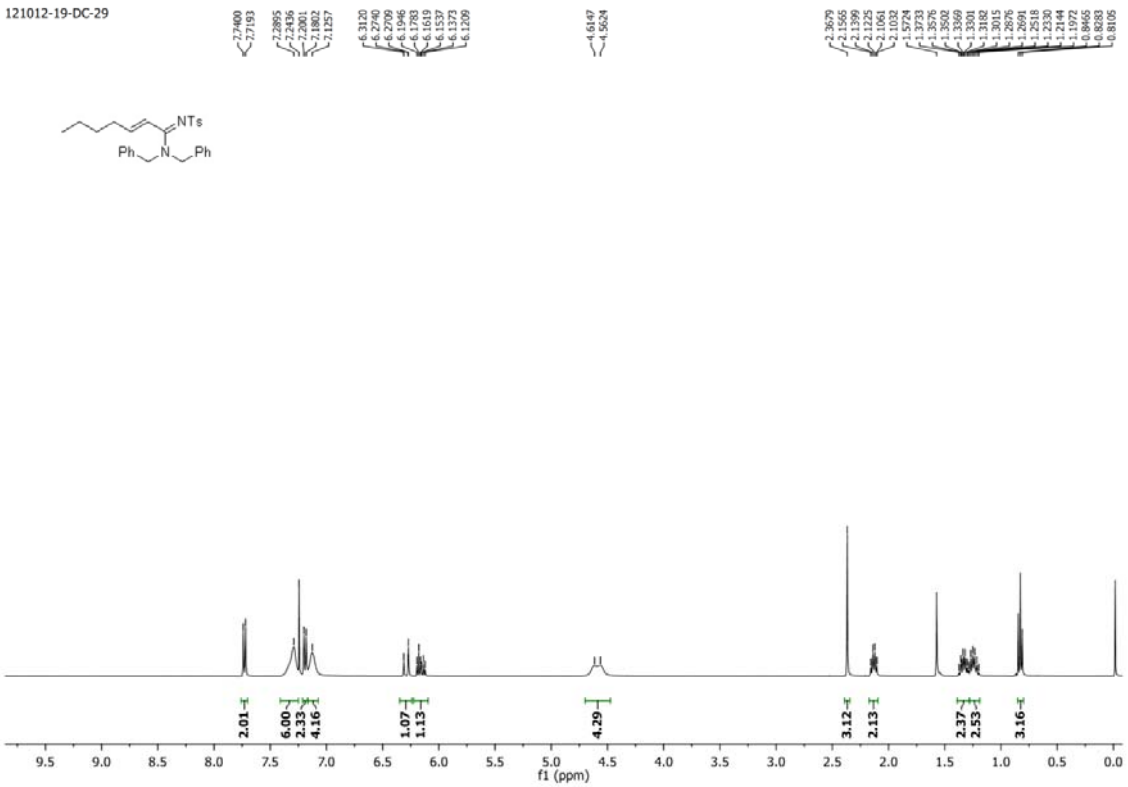


Fig. S54 ^{1}H NMR spectra of **4b** in $CDCl_3$.

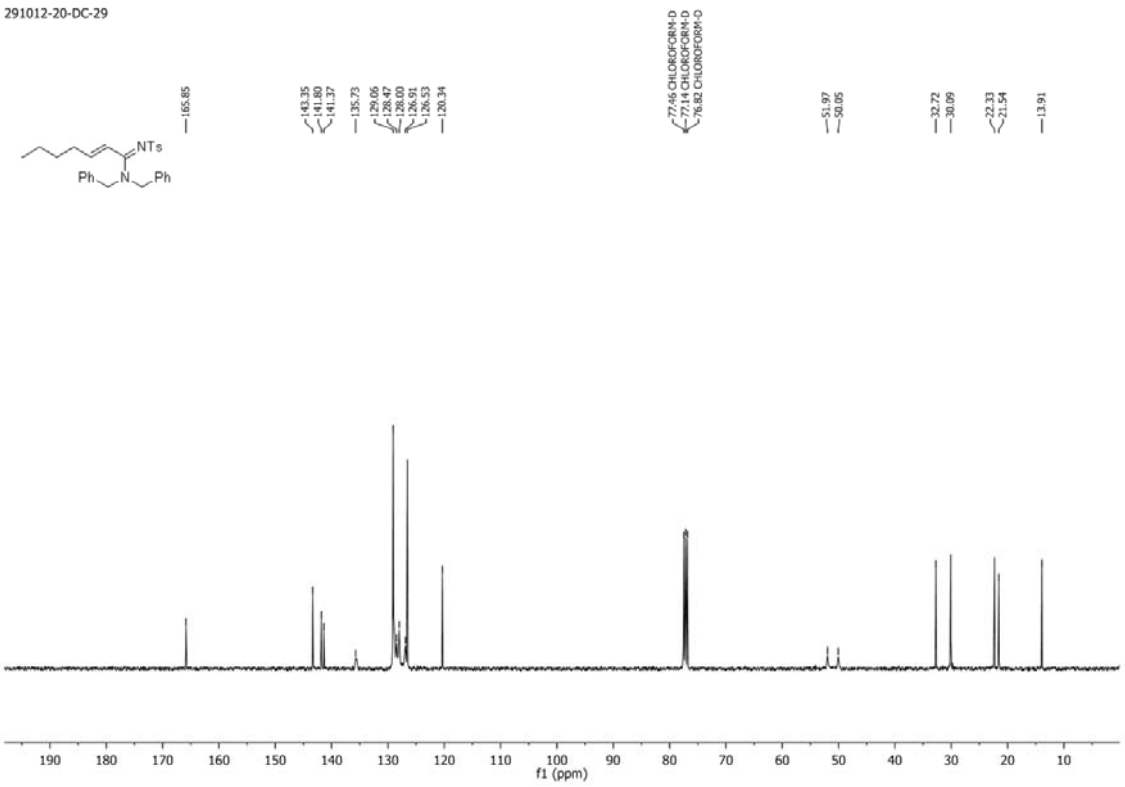


Fig. S55 ^{13}C NMR spectra of **4b** in $CDCl_3$.

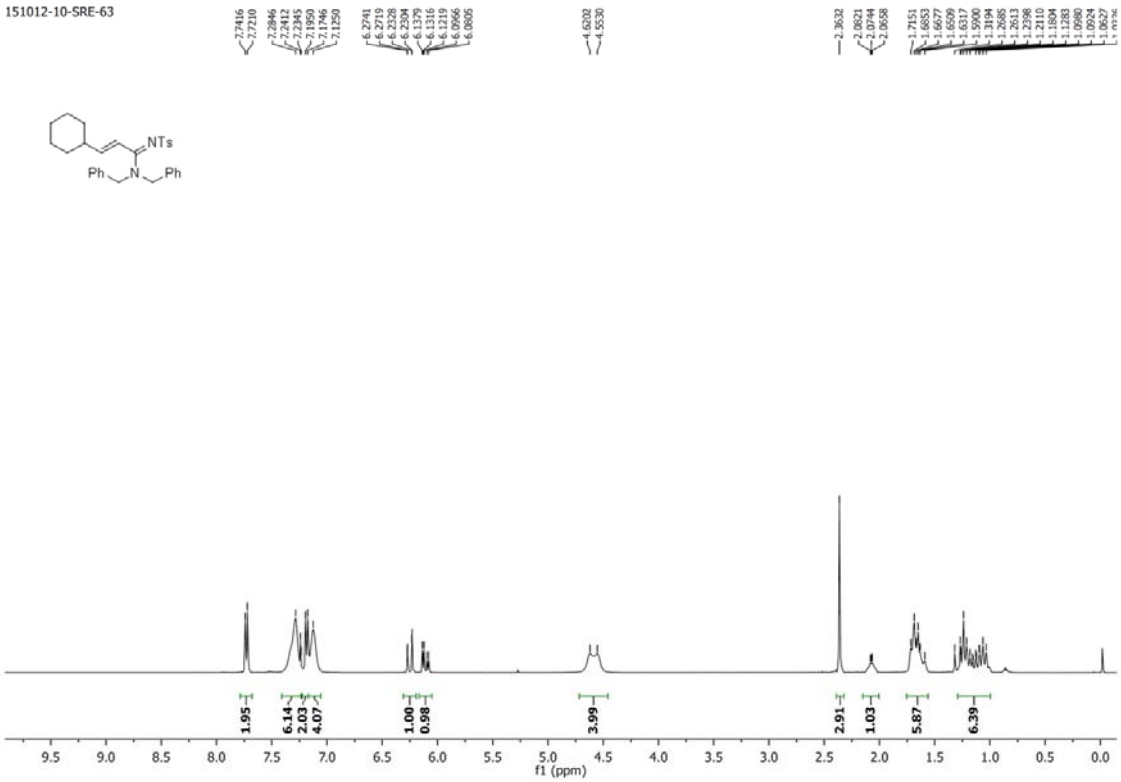


Fig. S56 ^{1}H NMR spectra of **4c** in $CDCl_3$.

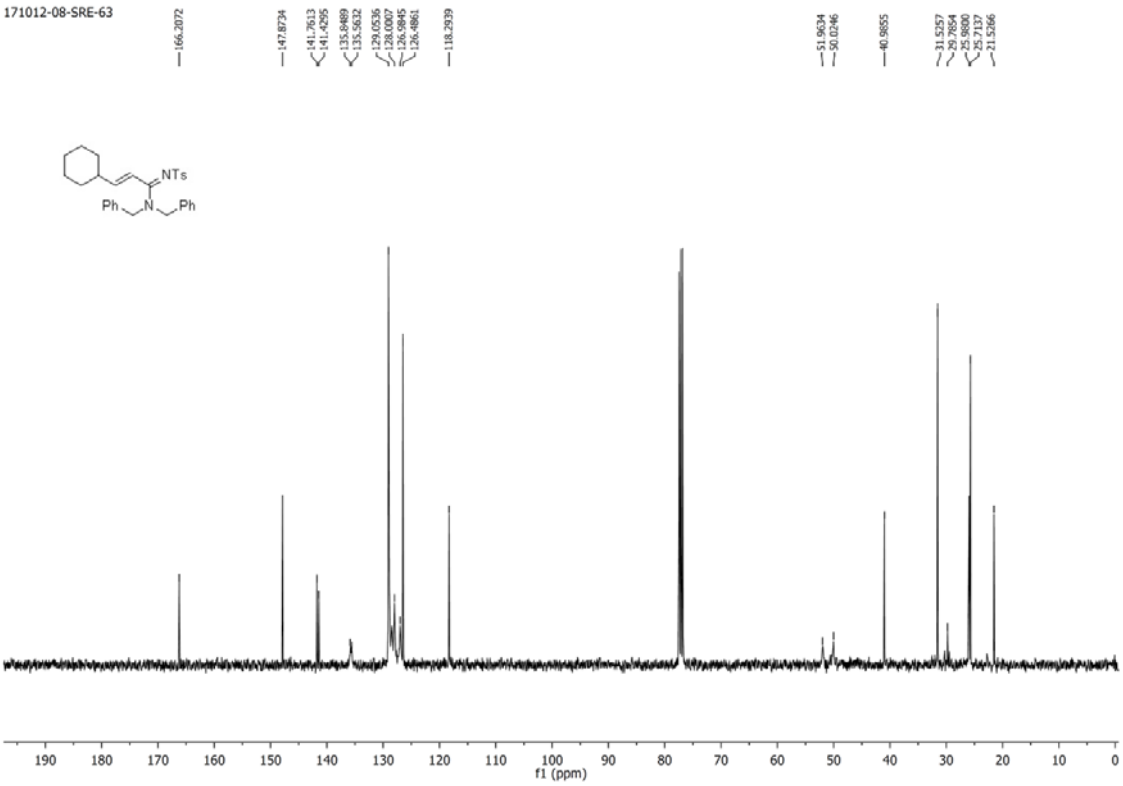


Fig. S57 ^{13}C NMR spectra of **4c** in $CDCl_3$.

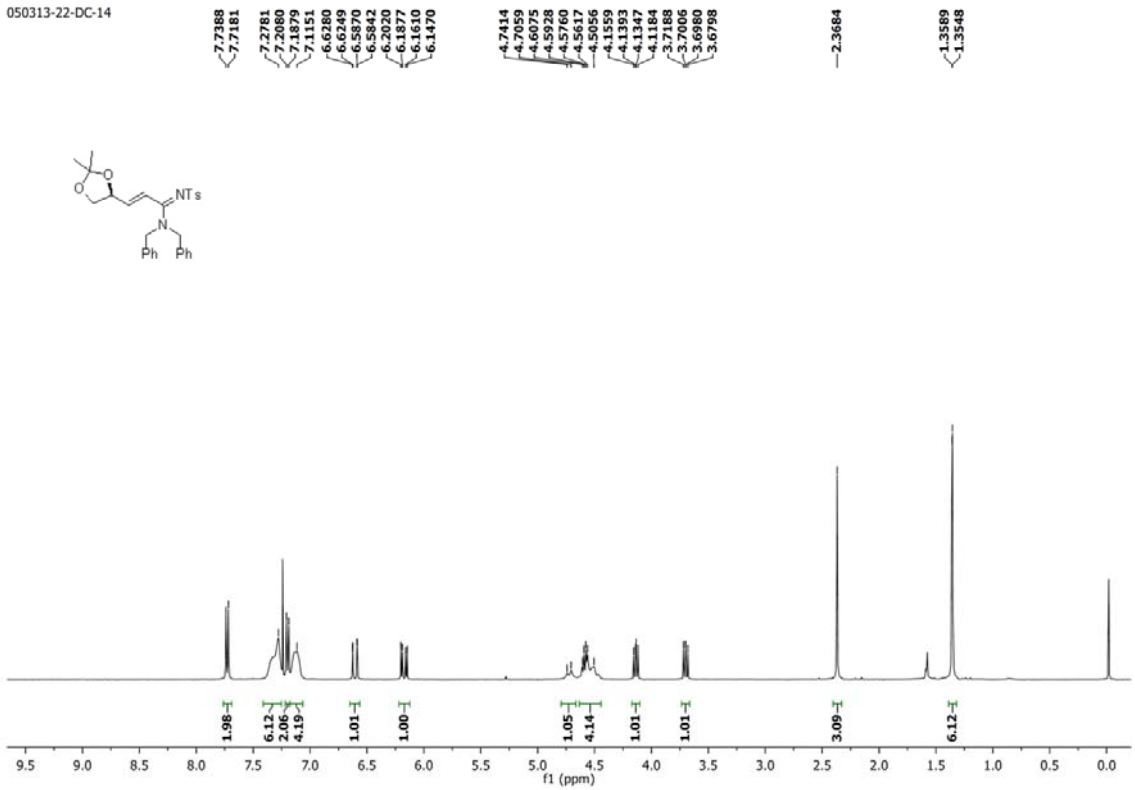


Fig. S58 ^{1}H NMR spectra of **4d** in $CDCl_3$.

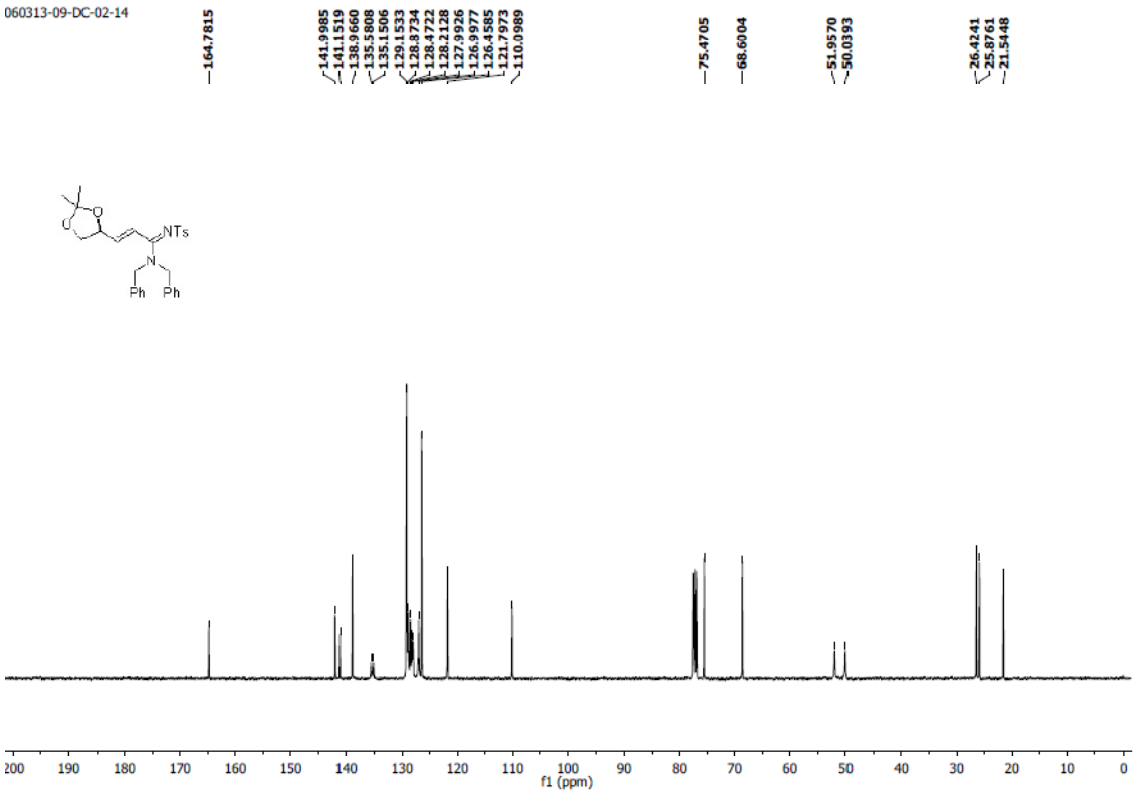


Fig. S59 ^{13}C NMR spectra of **4d** in $CDCl_3$.

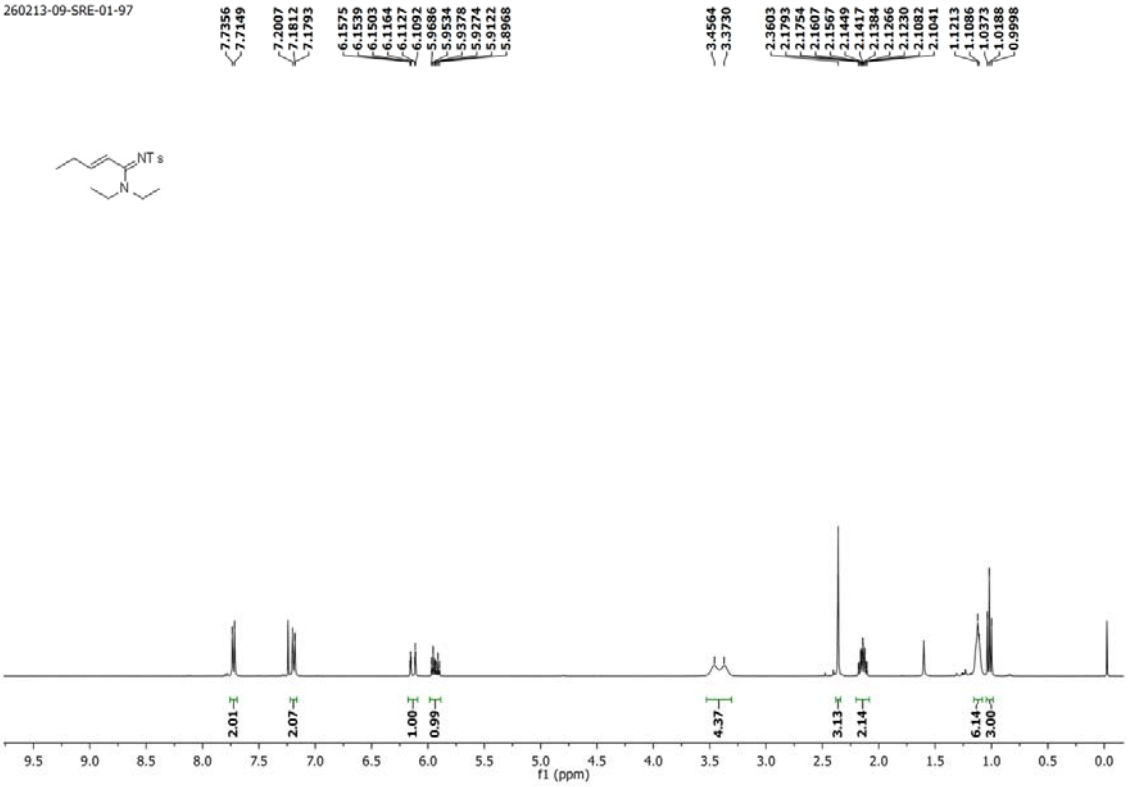


Fig. S60 ^{1}H NMR spectra of **4e** in $CDCl_3$.

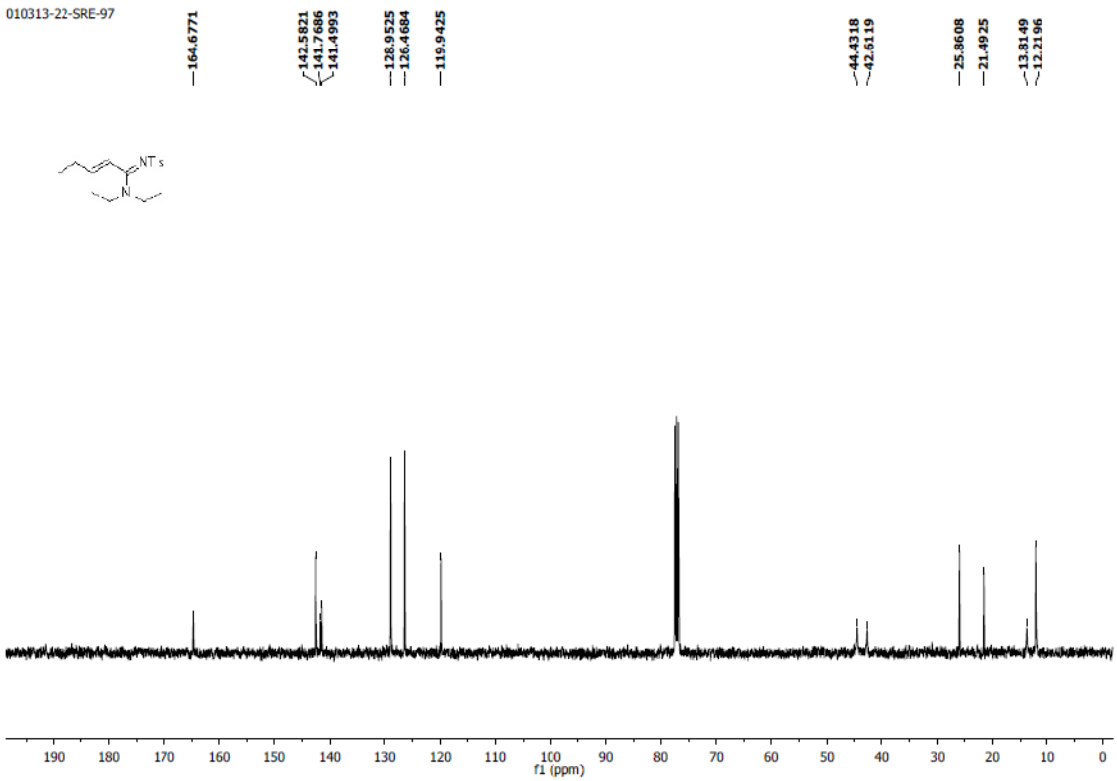


Fig. S61 ^{13}C NMR spectra of **4e** in $CDCl_3$.

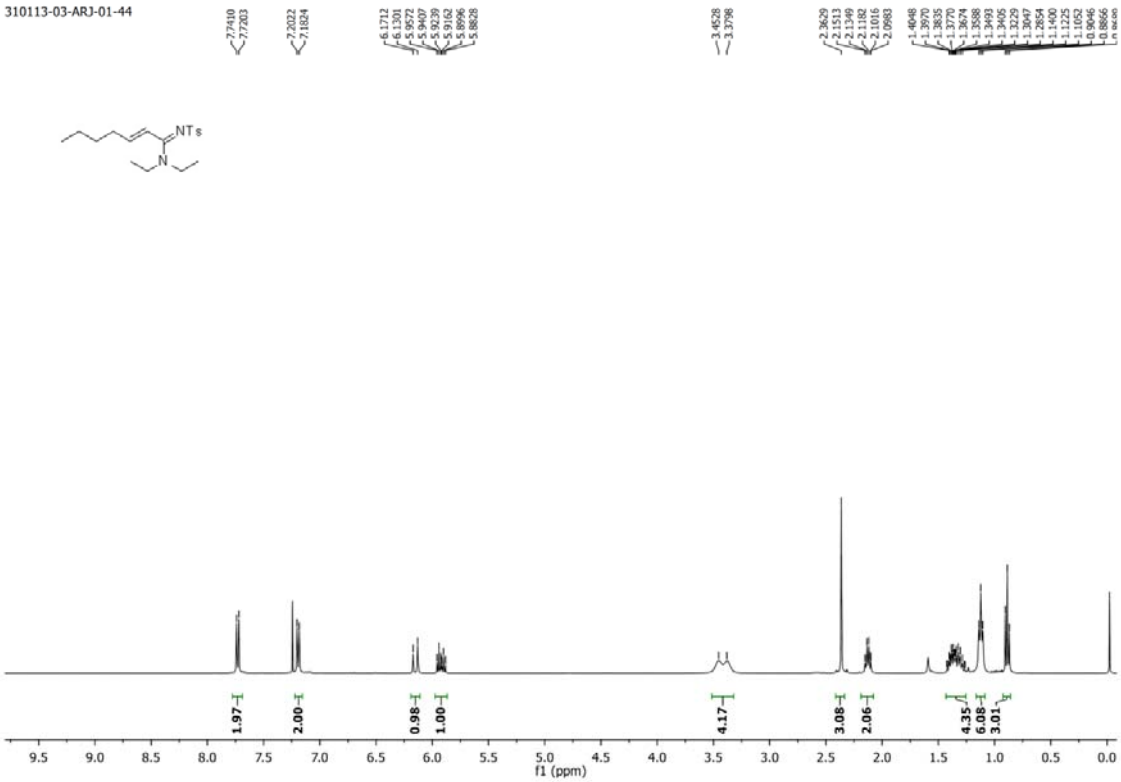


Fig. S62 ^{1}H NMR spectra of **4f** in $CDCl_3$.

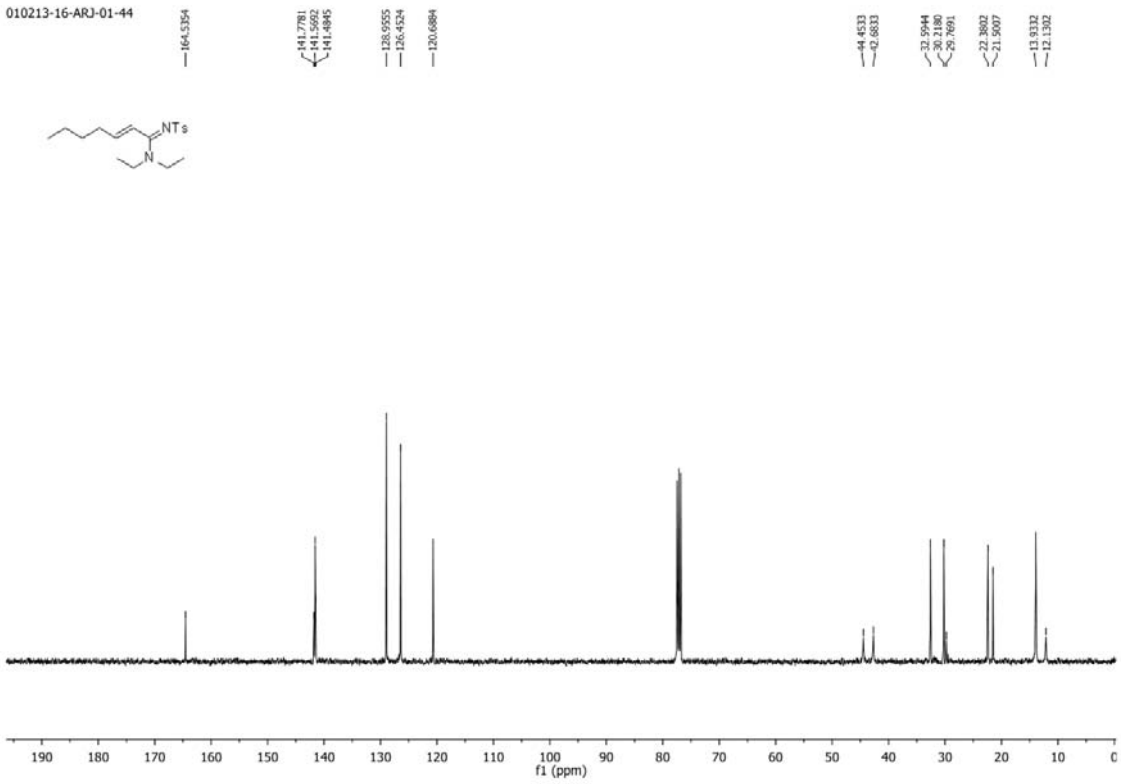


Fig. S63 ^{13}C NMR spectra of **4f** in $CDCl_3$.

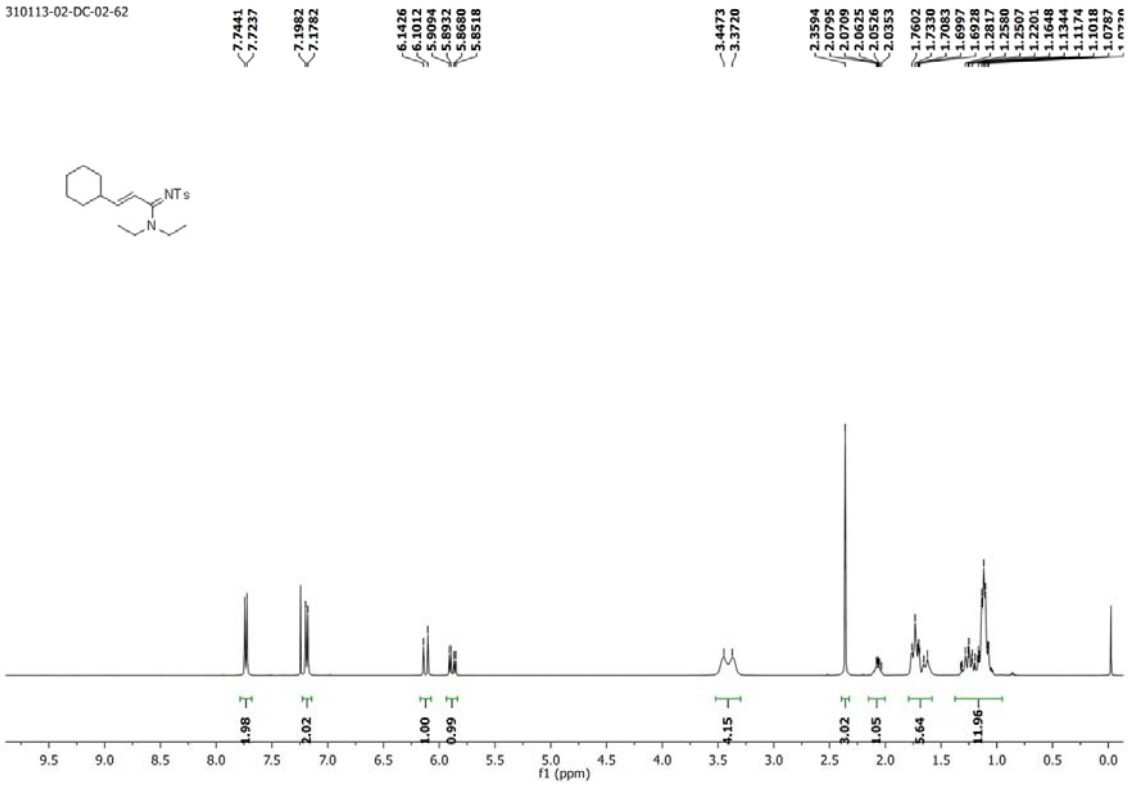


Fig. S64 ^{1}H NMR spectra of **4g** in $CDCl_3$.

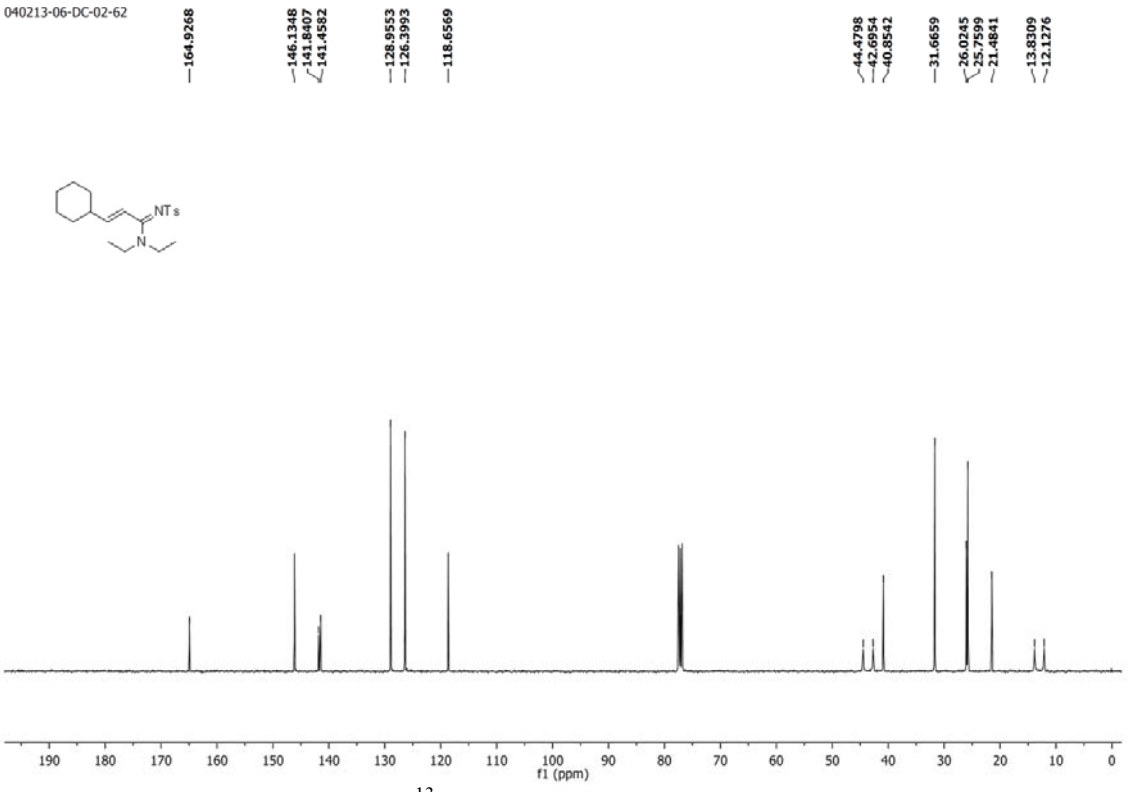


Fig. S65 ^{13}C NMR spectra of **4g** in $CDCl_3$.

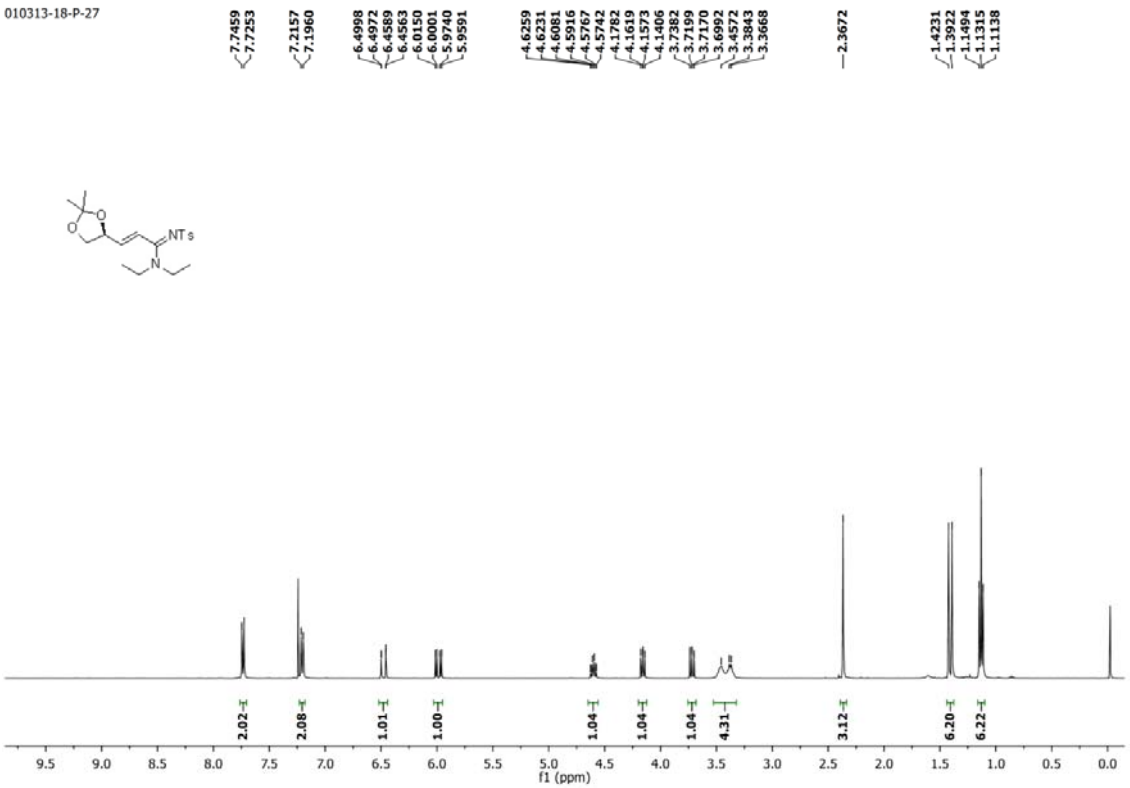


Fig. S66 ^{1}H NMR spectra of **4h** in $CDCl_3$.

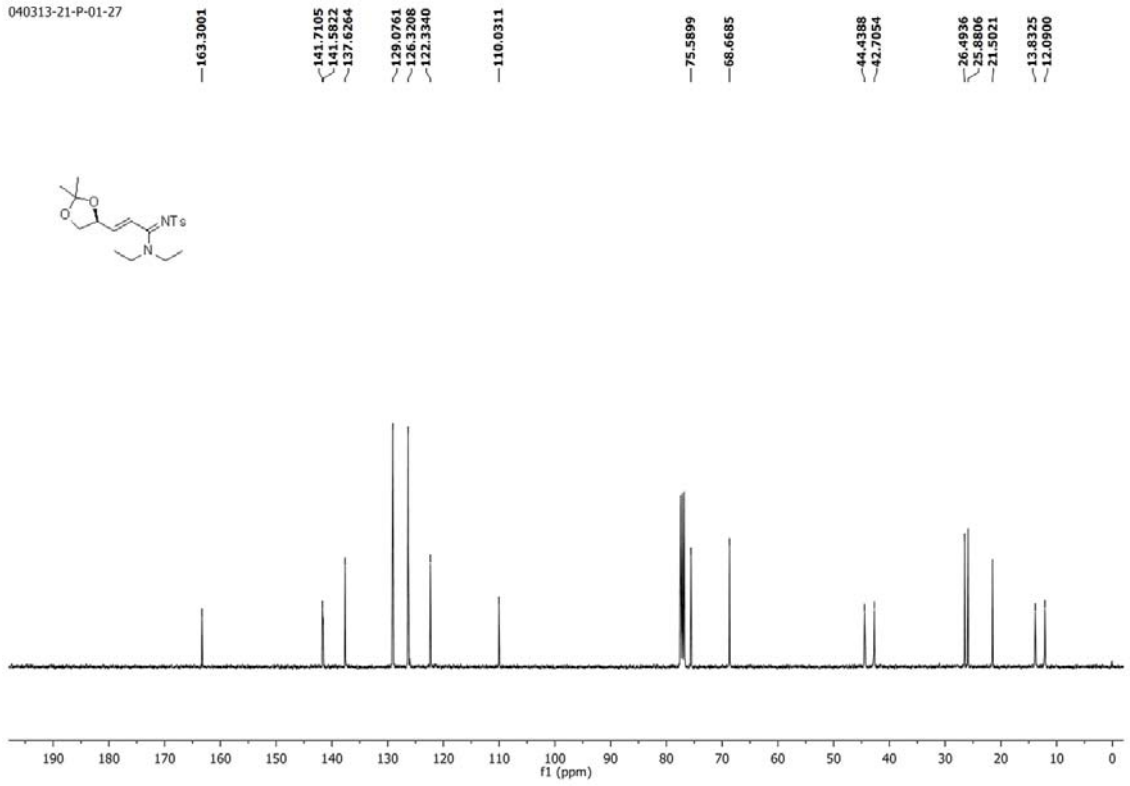


Fig. S67 ^{13}C NMR spectra of **4h** in $CDCl_3$.

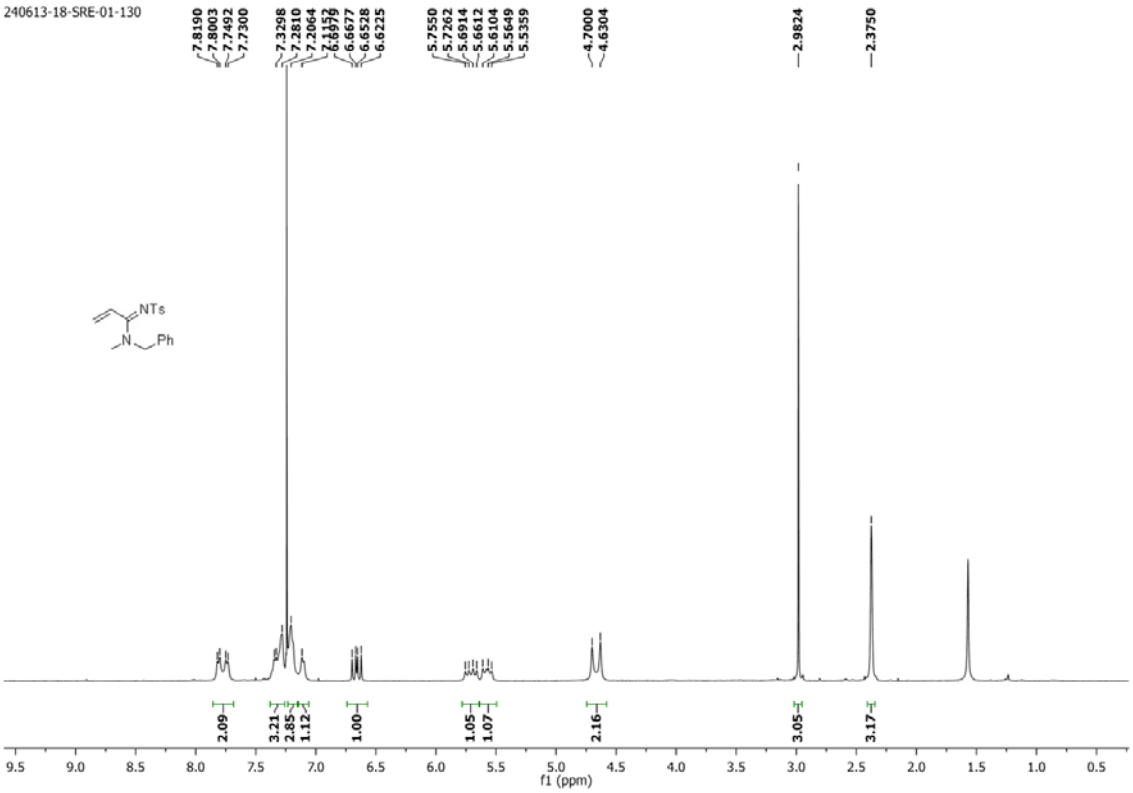


Fig. S68 ^{1}H NMR spectra of **4i** in $CDCl_3$.

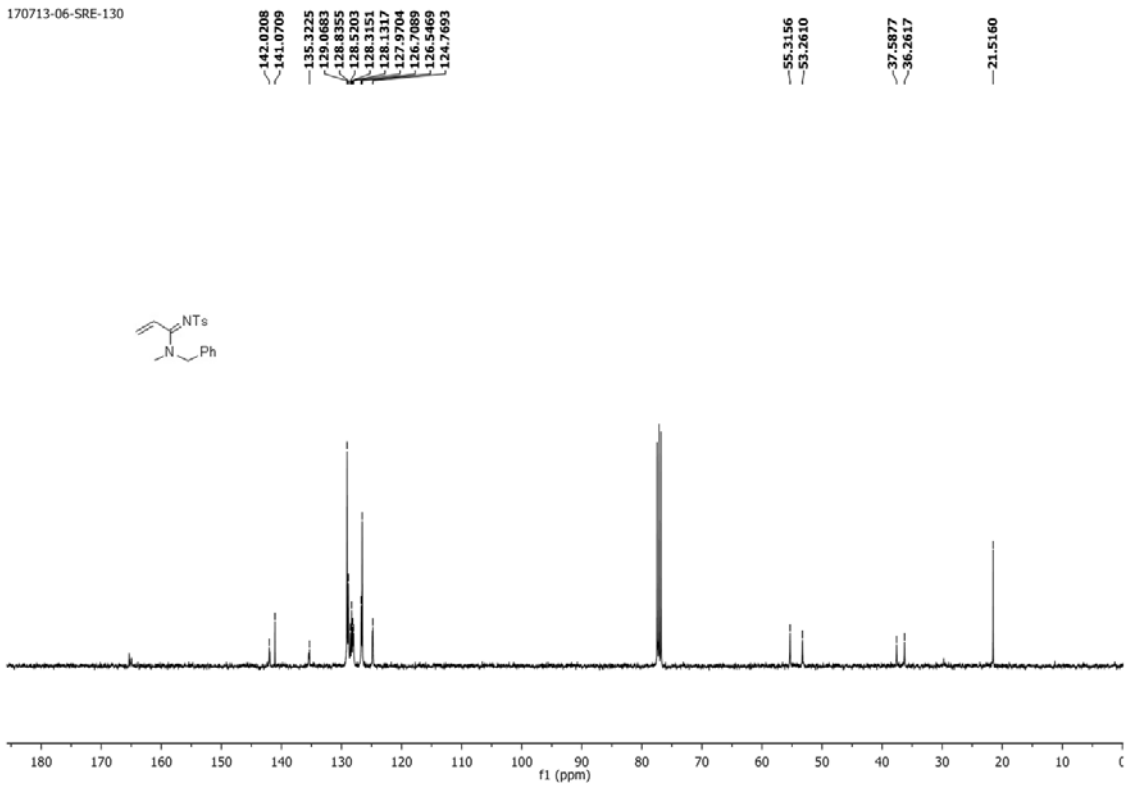


Fig. S69 ^{13}C NMR spectra of **4i** in $CDCl_3$.

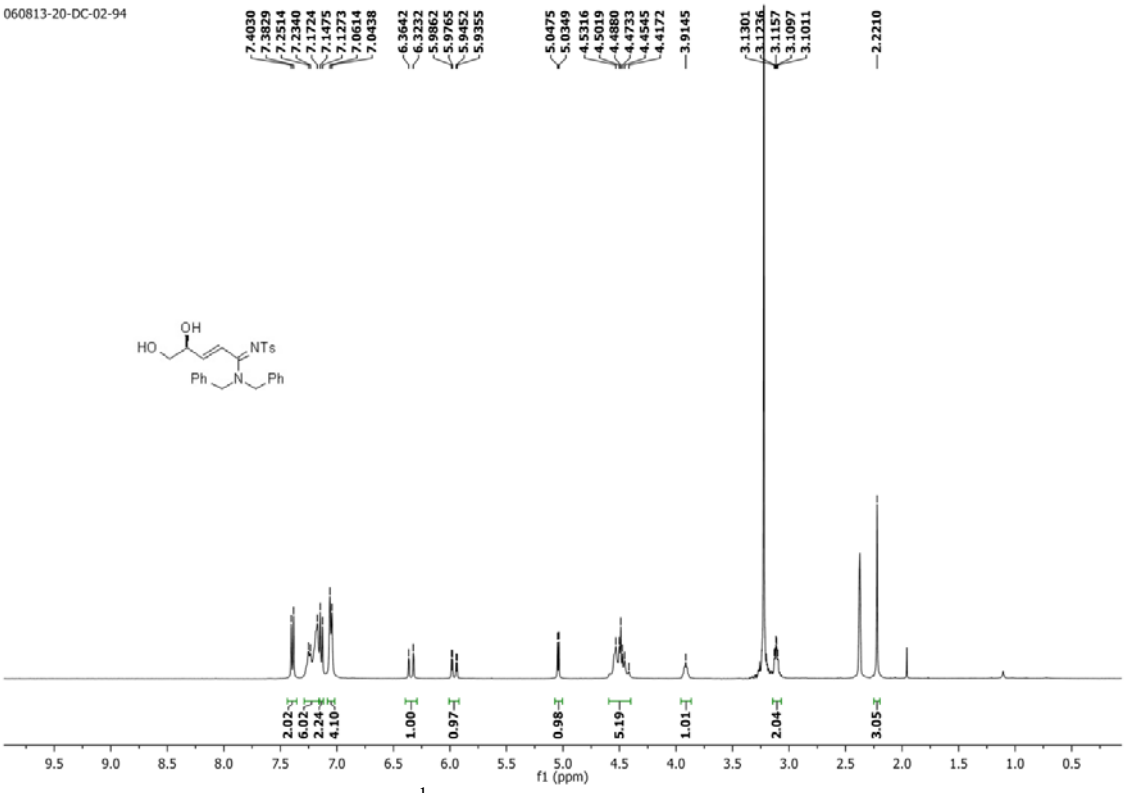


Fig. S70 ^{1}H NMR spectra of **4j** in DMSO.

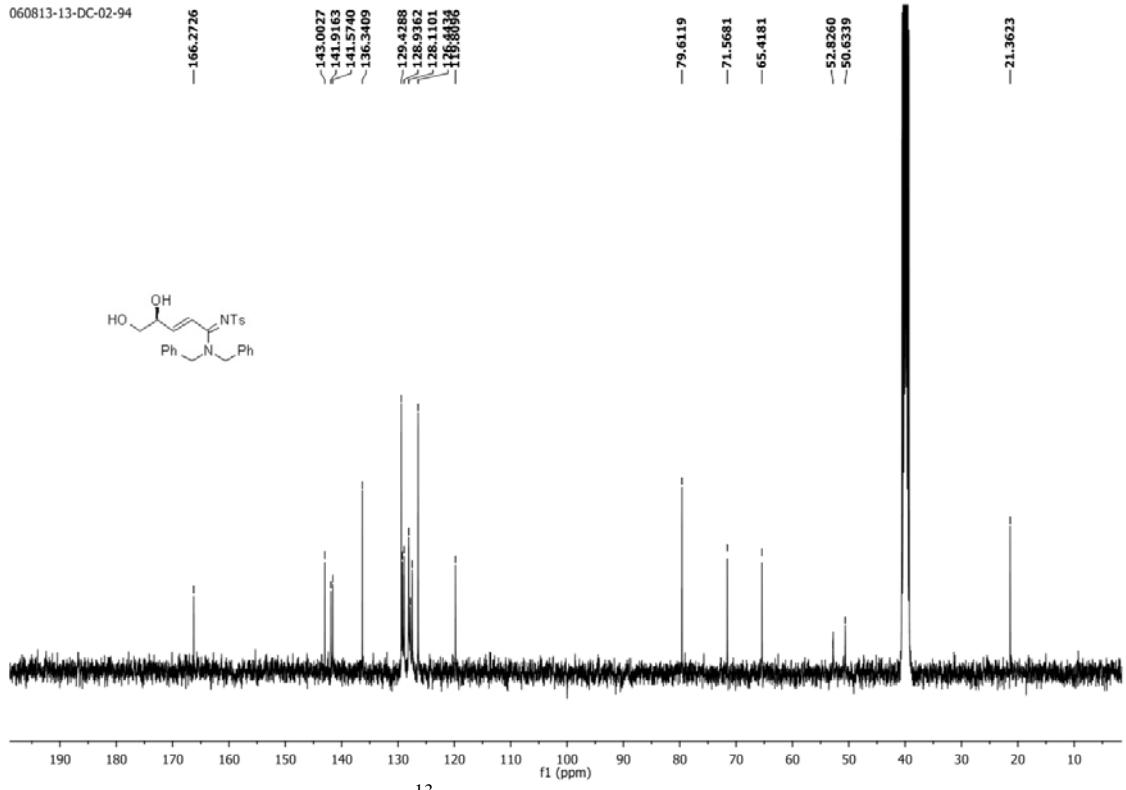


Fig. S71 ^{13}C NMR spectra of **4j** in DMSO.

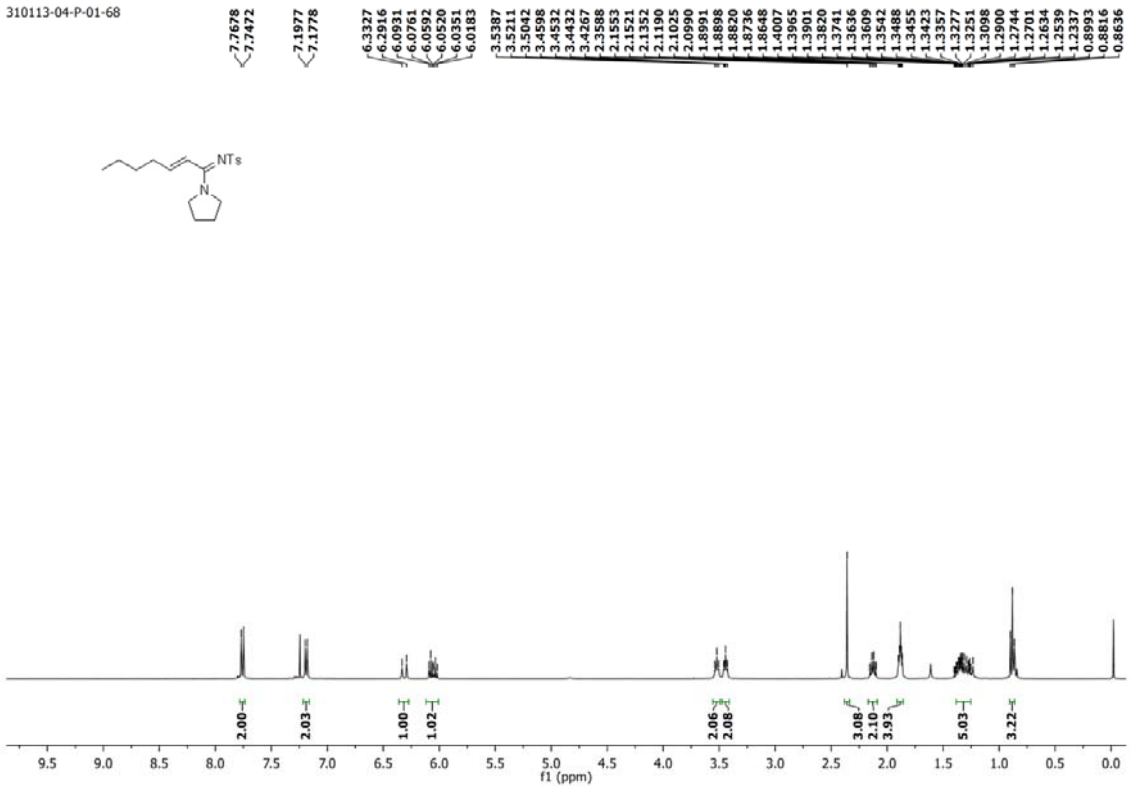


Fig. S72 ^{1}H NMR spectra of **4k** in $CDCl_3$.

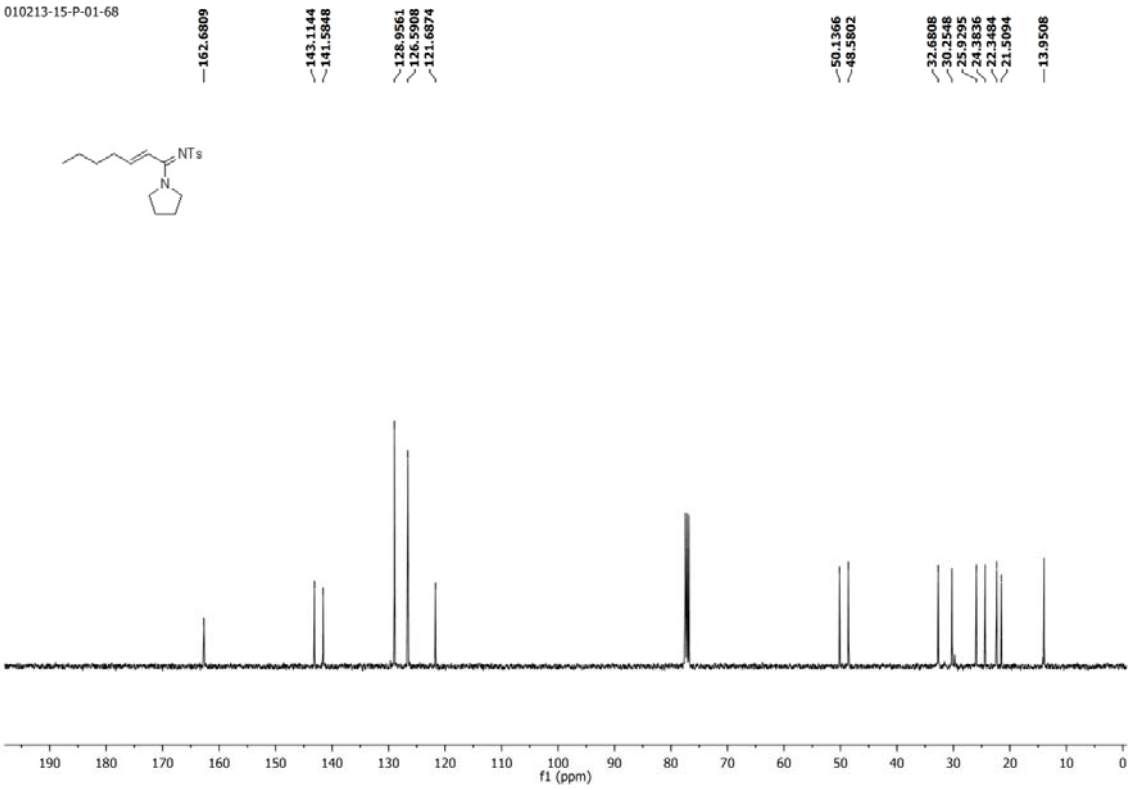


Fig. S73 ^{13}C NMR spectra of **4k** in $CDCl_3$.

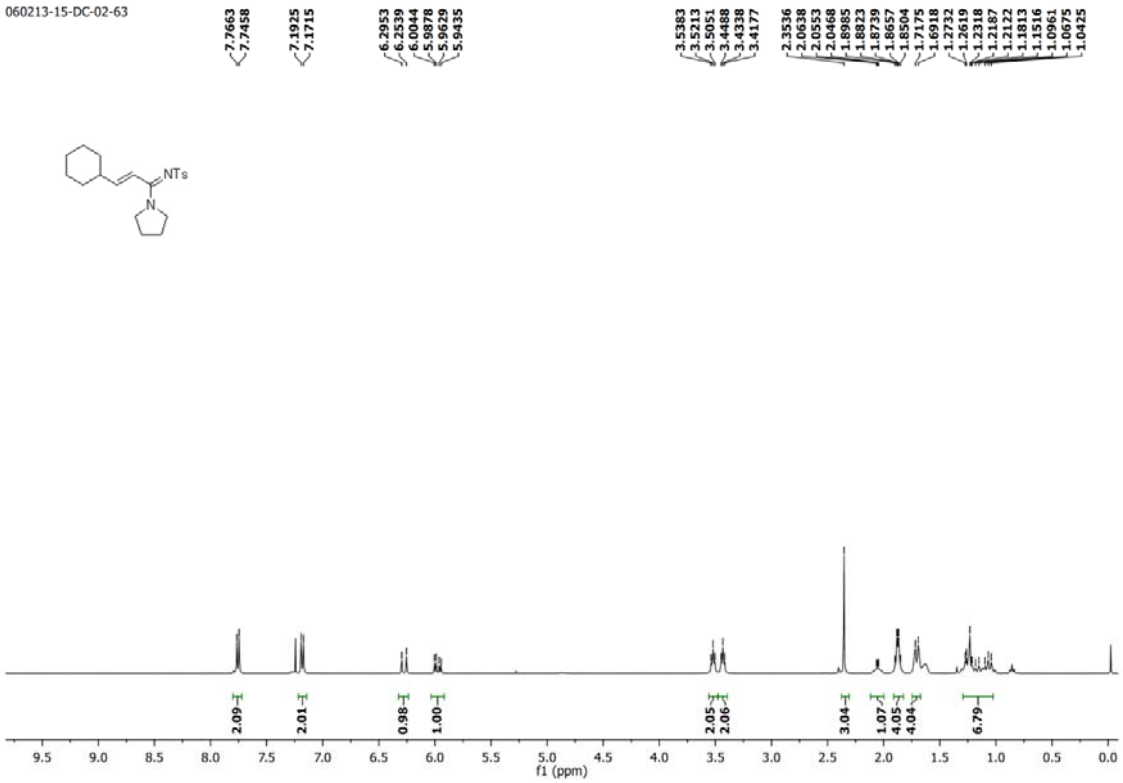


Fig. S74 ^{1}H NMR spectra of **4l** in $CDCl_3$.

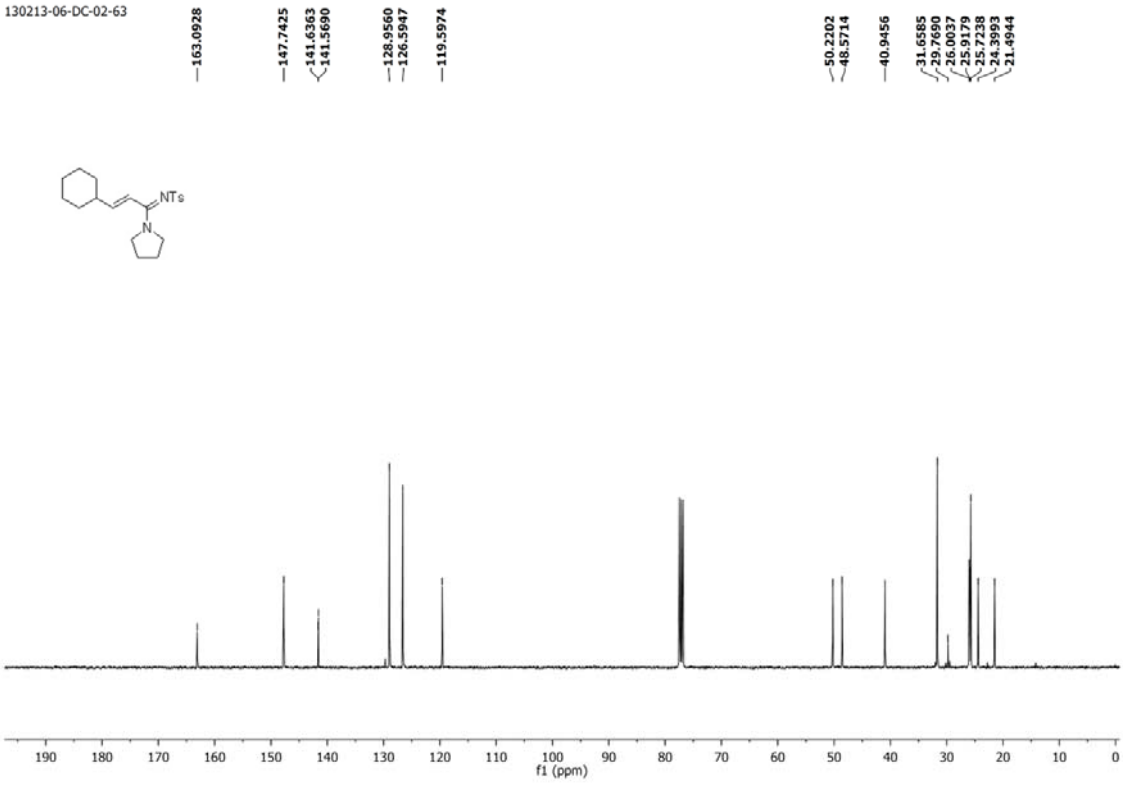


Fig. S75 ^{13}C NMR spectra of **4l** in $CDCl_3$.

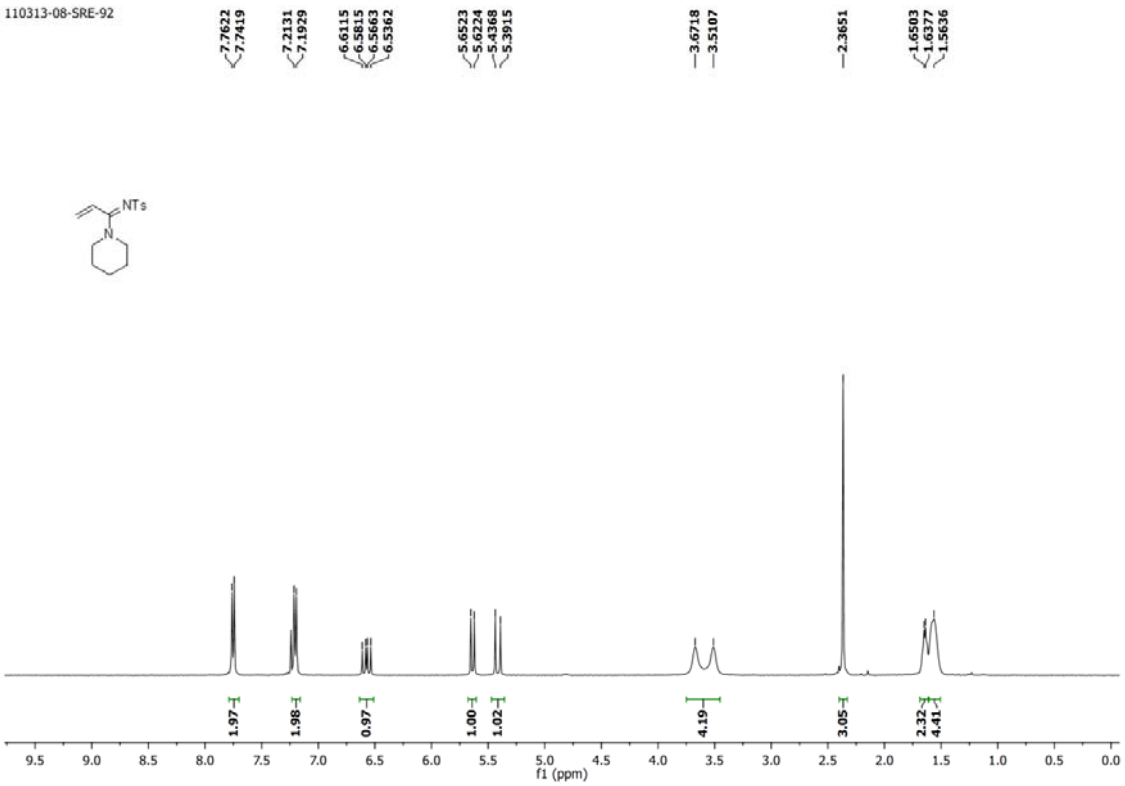


Fig. S76 ^{1}H NMR spectra of **4m** in $CDCl_3$.

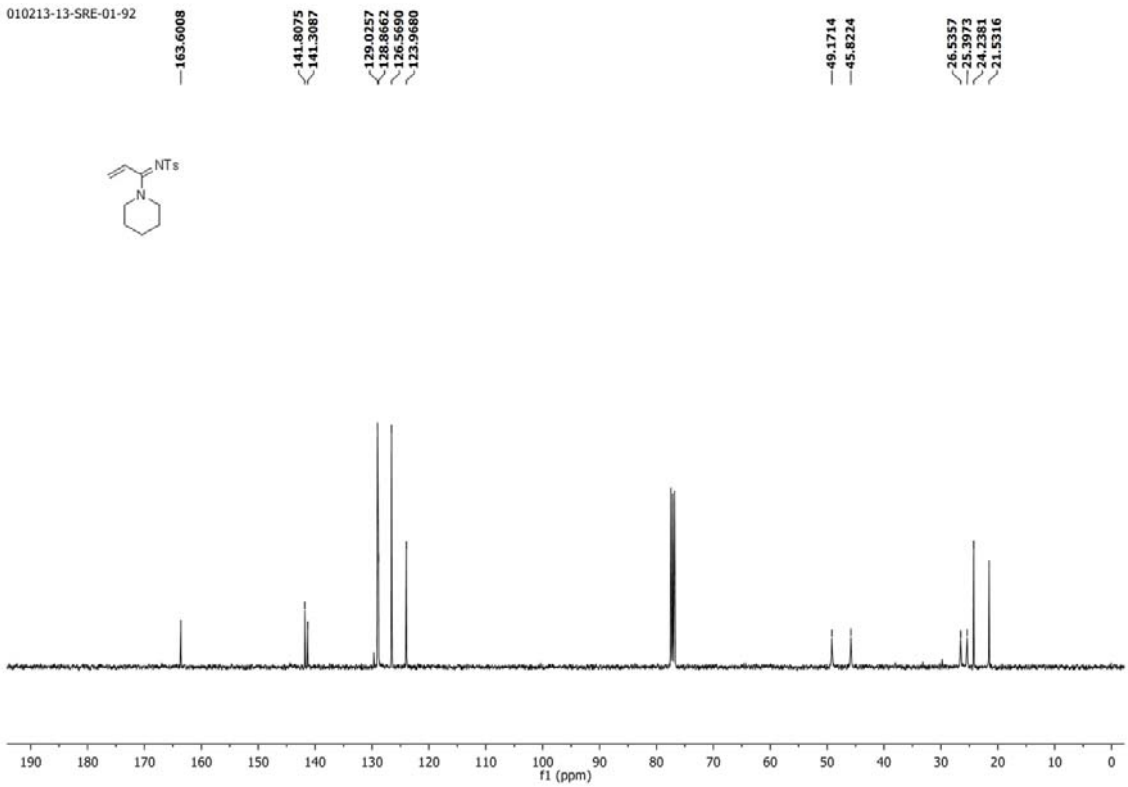


Fig. S77 ^{13}C NMR spectra of **4m** in $CDCl_3$.

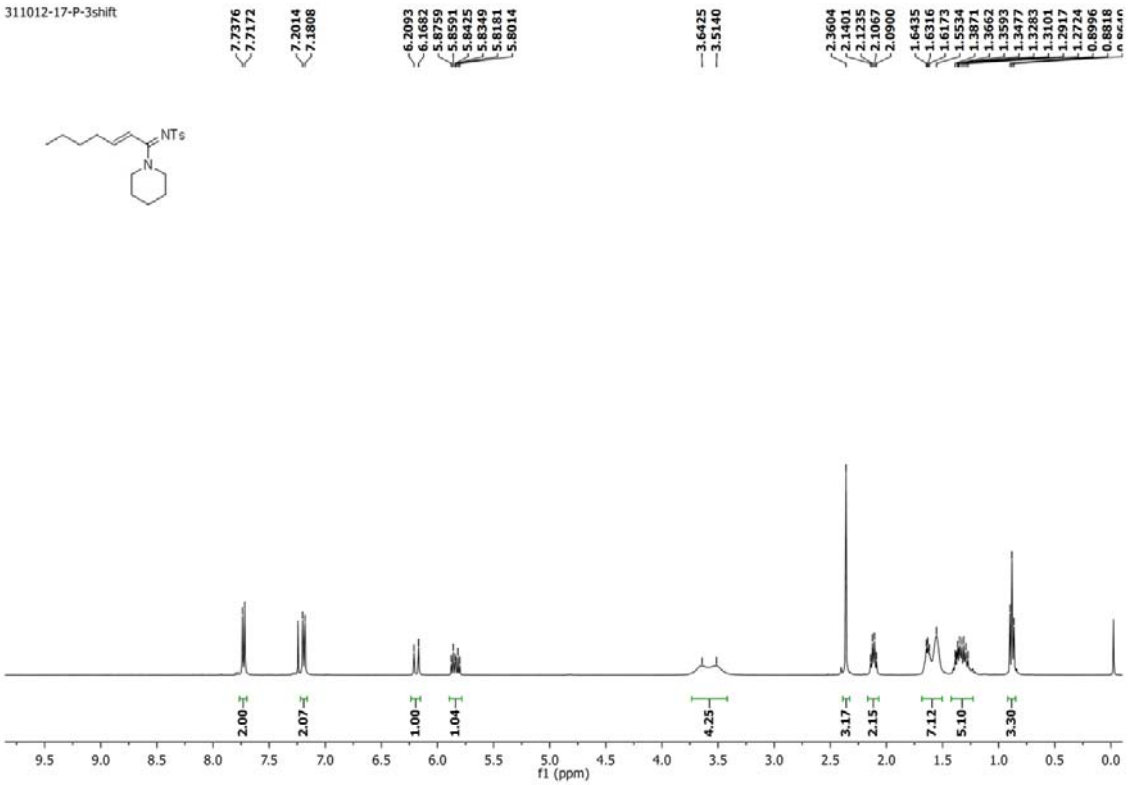


Fig. S78 ^{1}H NMR spectra of **4n** in $CDCl_3$.

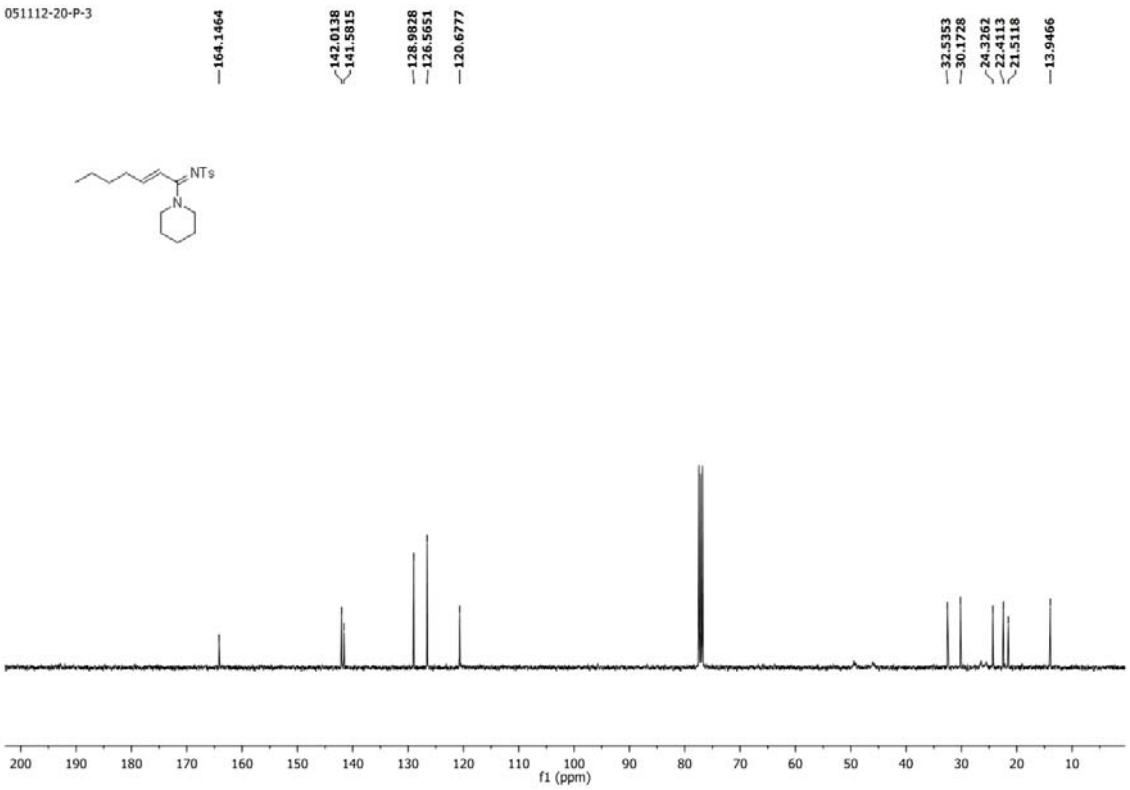


Fig. S79 ^{13}C NMR spectra of **4n** in $CDCl_3$.

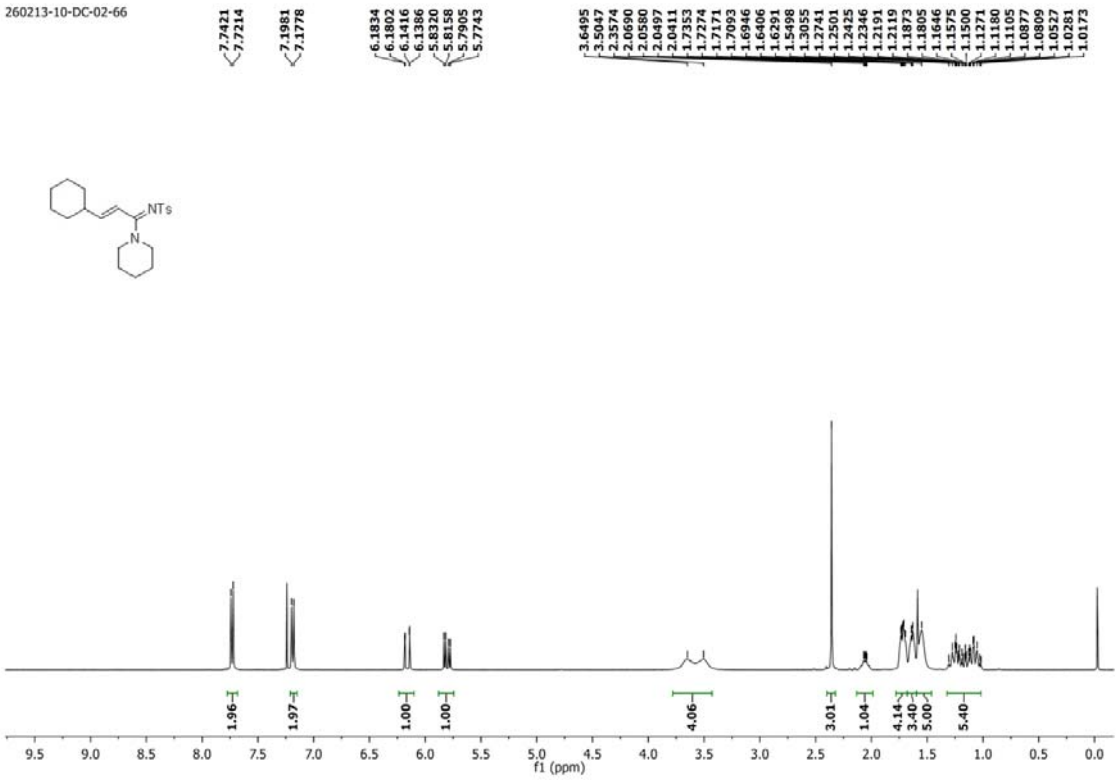


Fig. S80 ^{1}H NMR spectra of **4o** in $CDCl_3$.

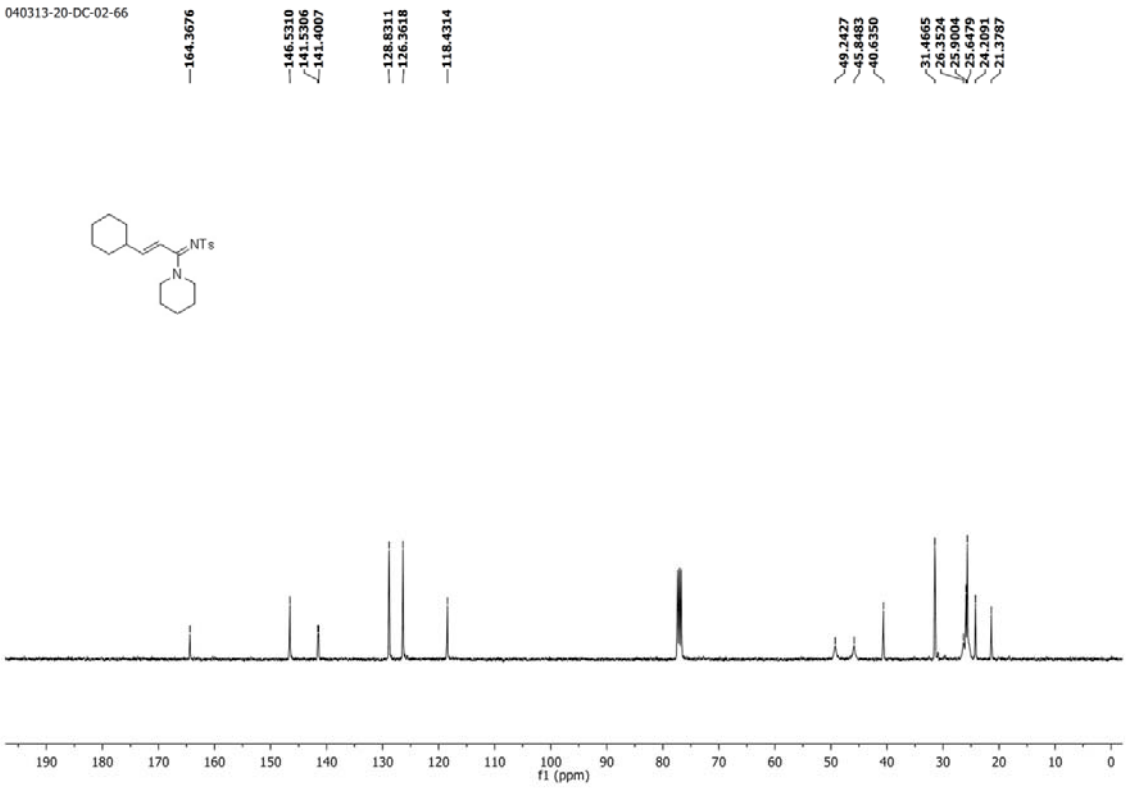


Fig. S81 ^{13}C NMR spectra of **4o** in $CDCl_3$.

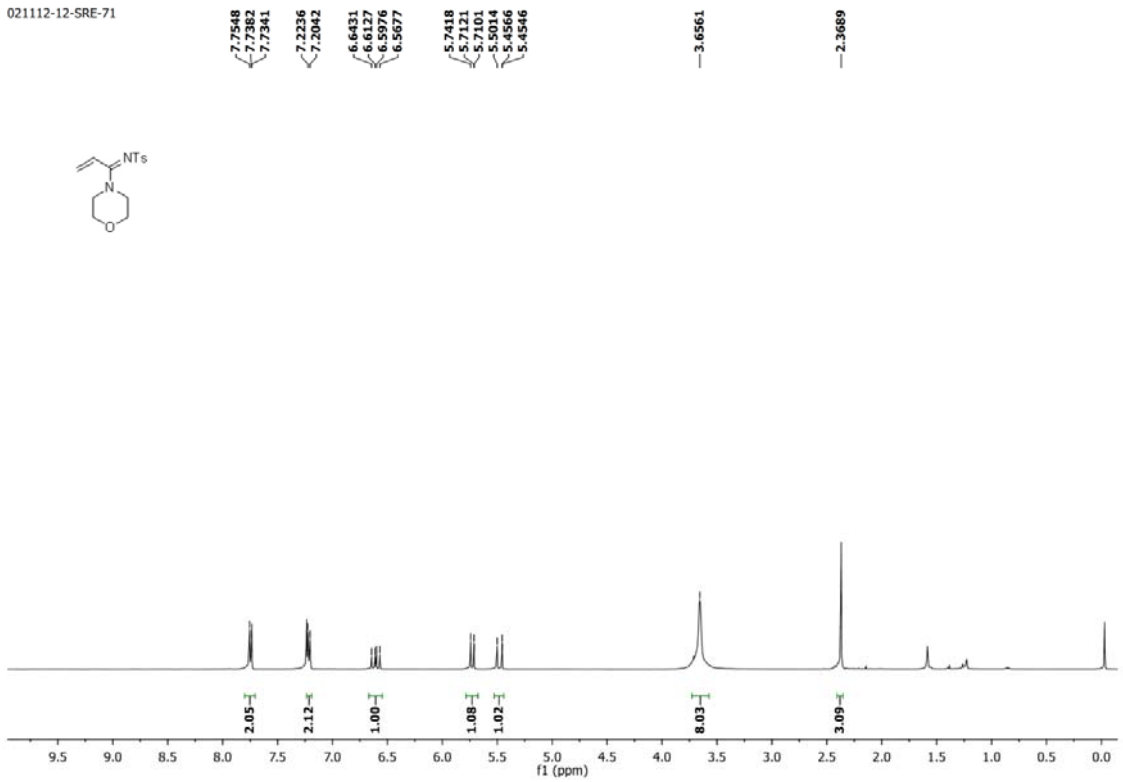


Fig. S82 ^{1}H NMR spectra of **4p** in $CDCl_3$.

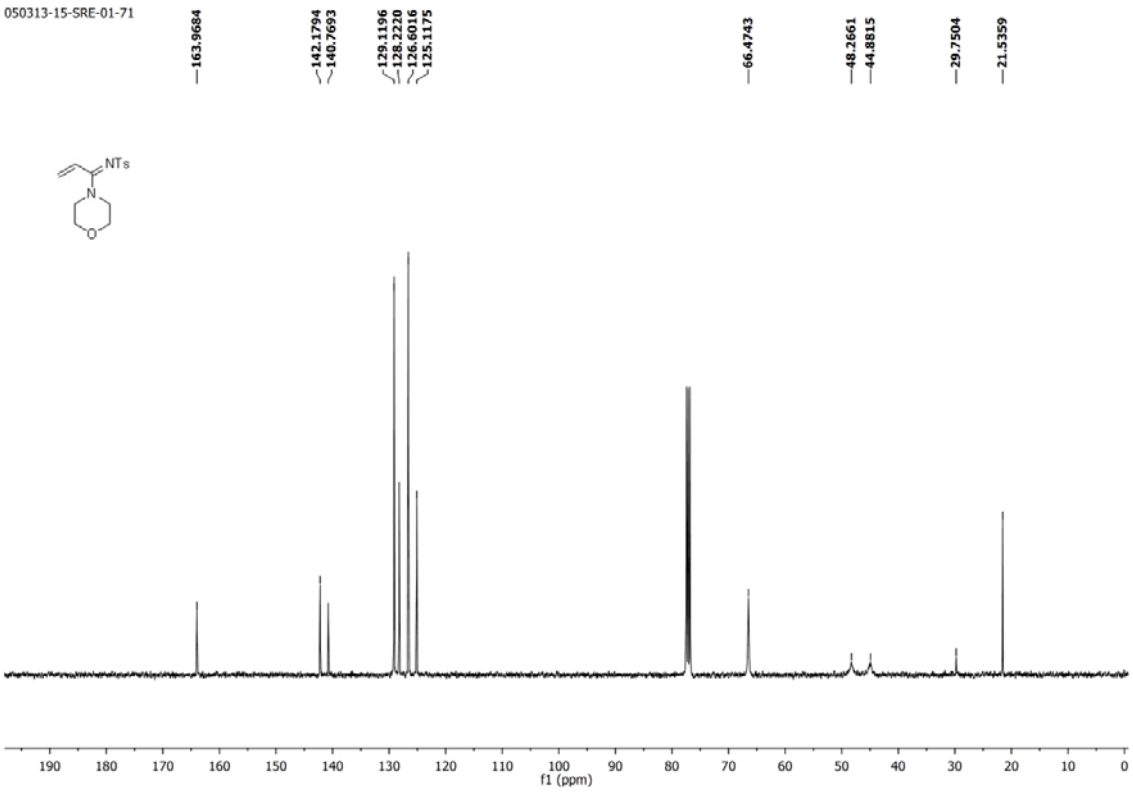


Fig. S83 ^{13}C NMR spectra of **4p** in $CDCl_3$.

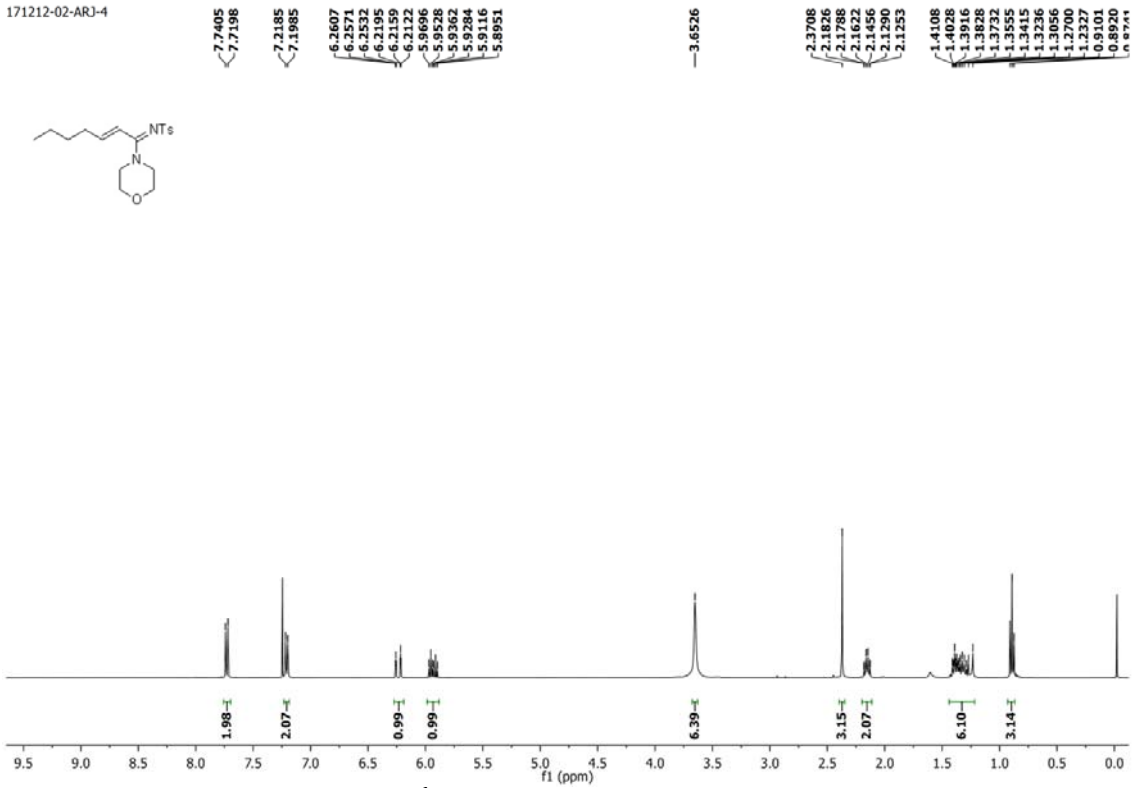


Fig. S84 ^{1}H NMR spectra of **4q** in $CDCl_3$.

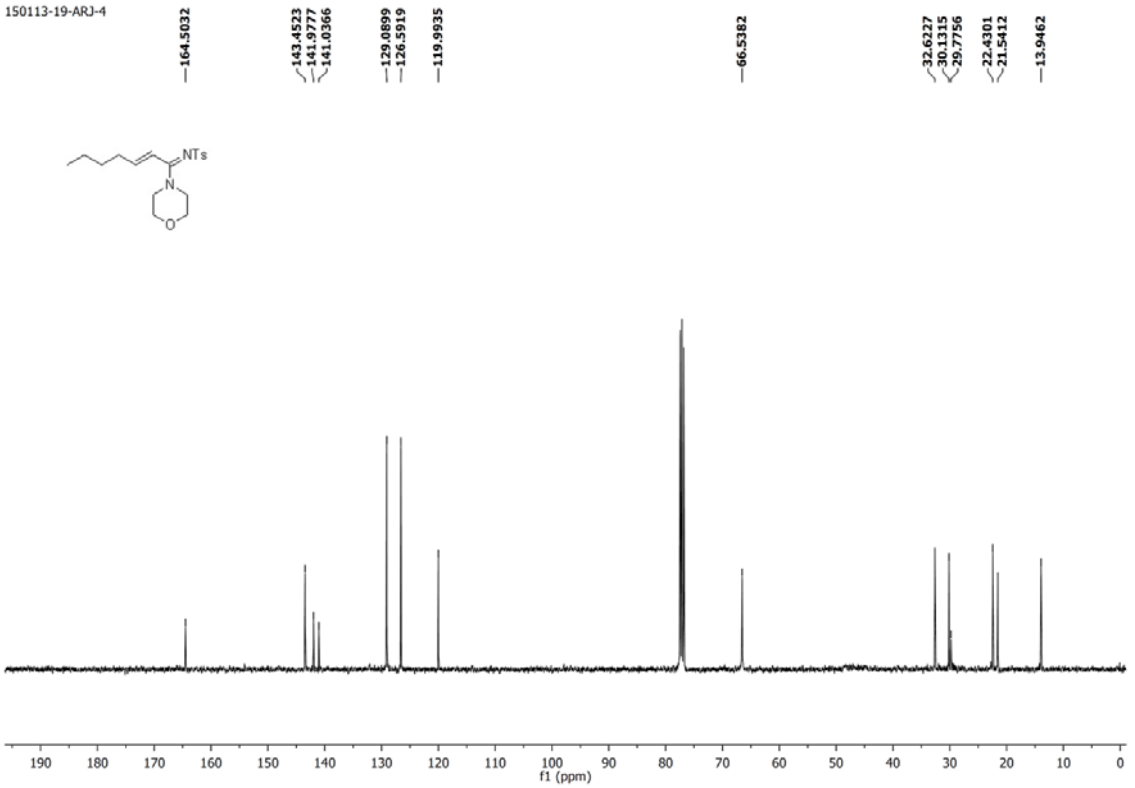


Fig. S85 ^{13}C NMR spectra of **4q** in $CDCl_3$.

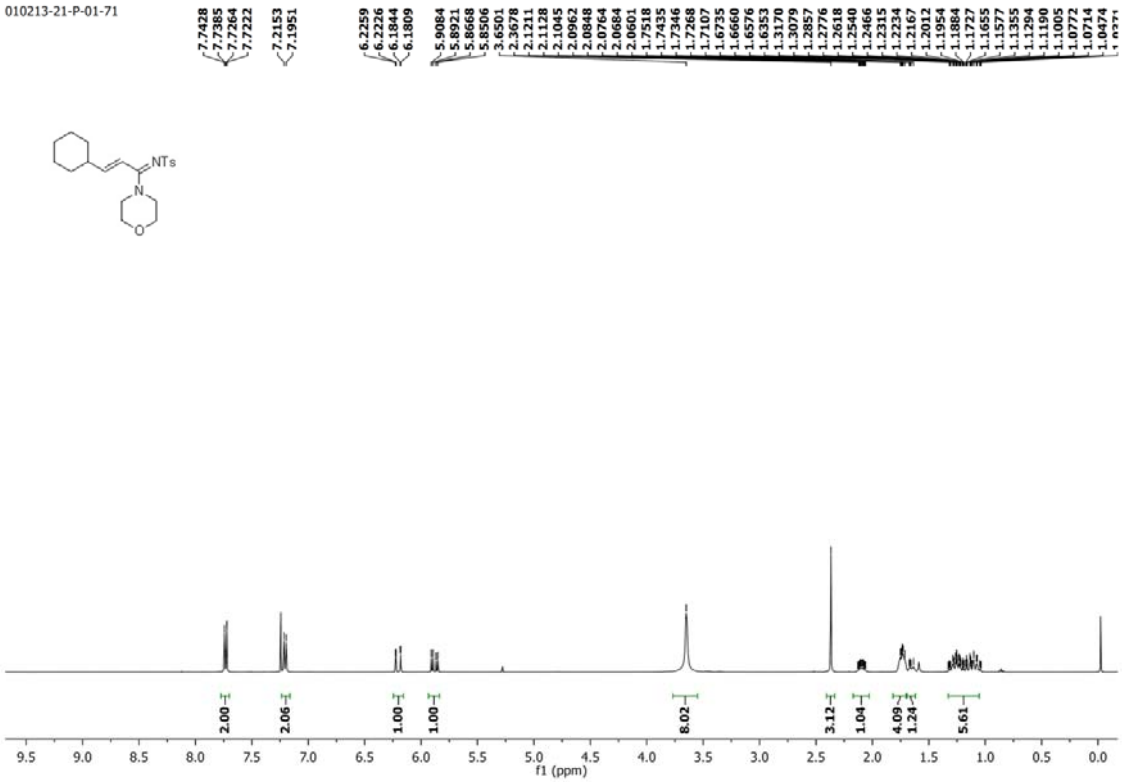


Fig. S86 ^{1}H NMR spectra of **4r** in $CDCl_3$.

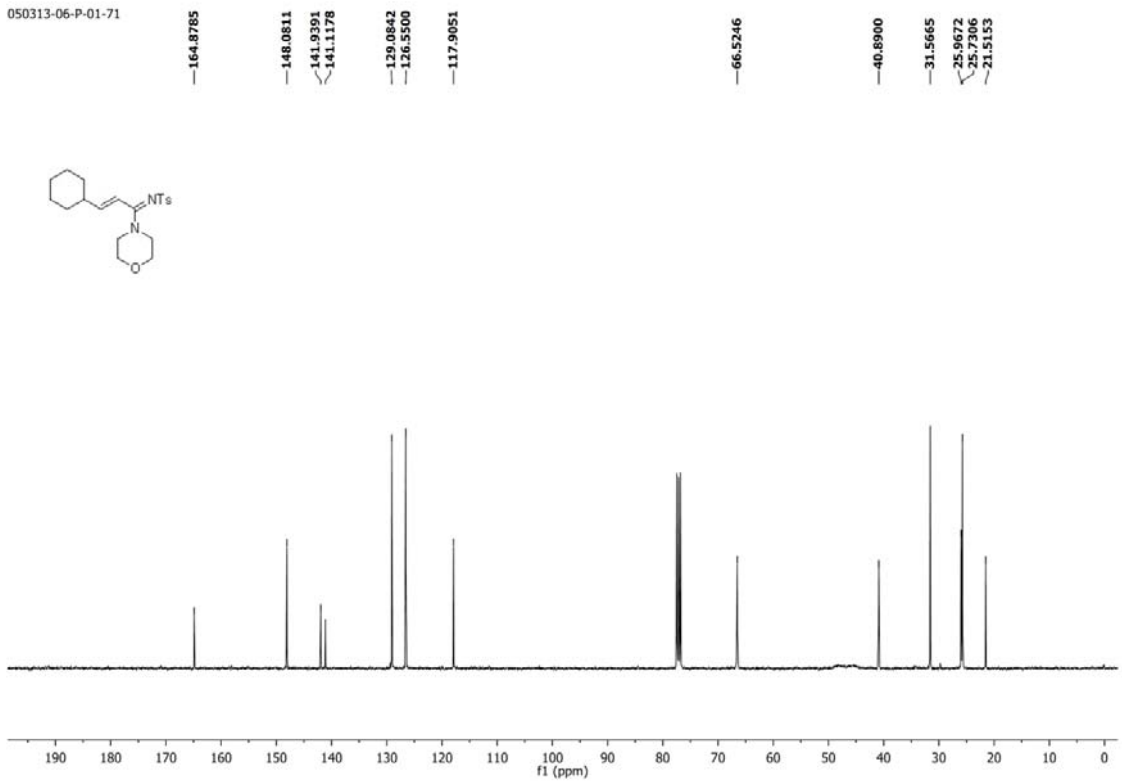


Fig. S87 ^{13}C NMR spectra of **4r** in $CDCl_3$.

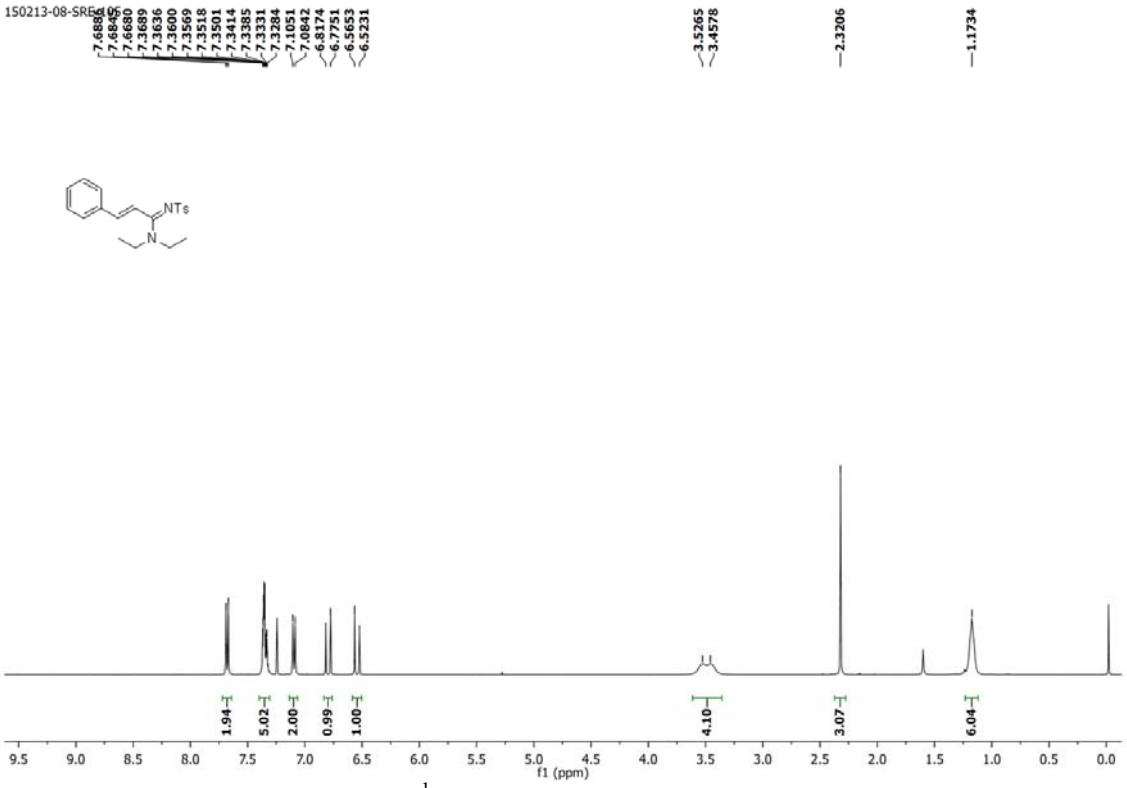


Fig. S88 ^{1}H NMR spectra of **4s** in $CDCl_3$.

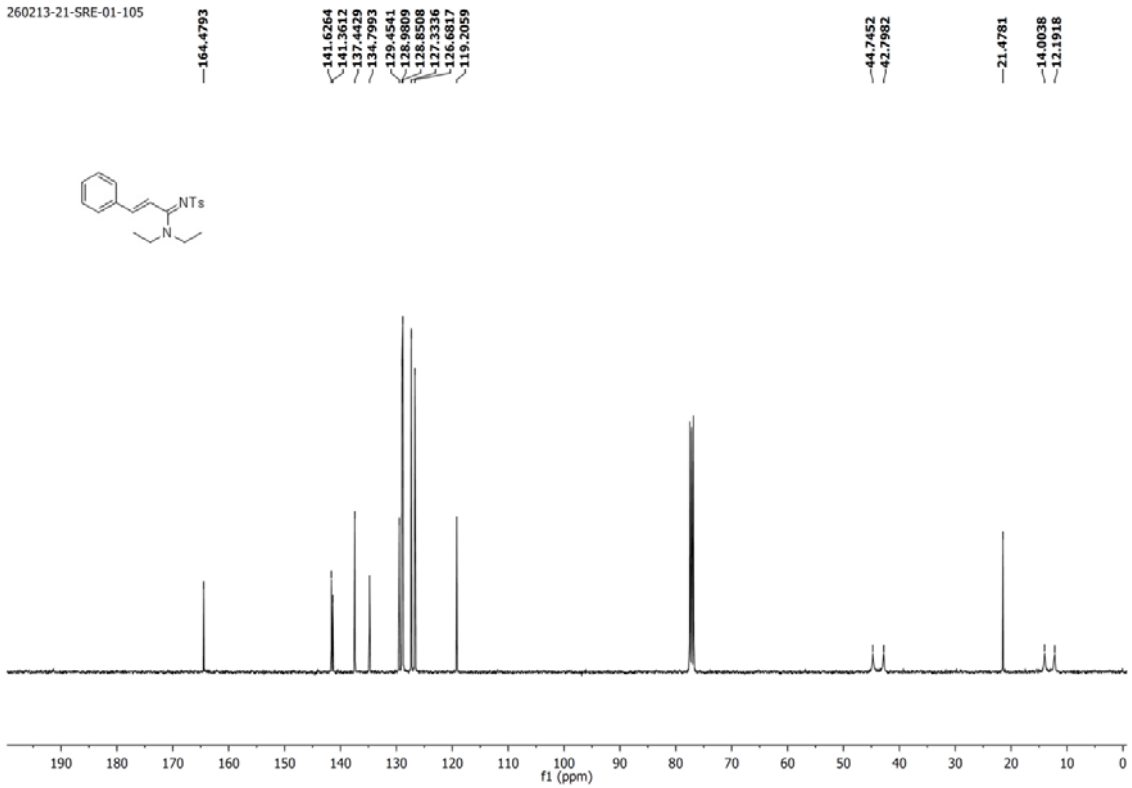


Fig. S89 ^{13}C NMR spectra of **4s** in $CDCl_3$.

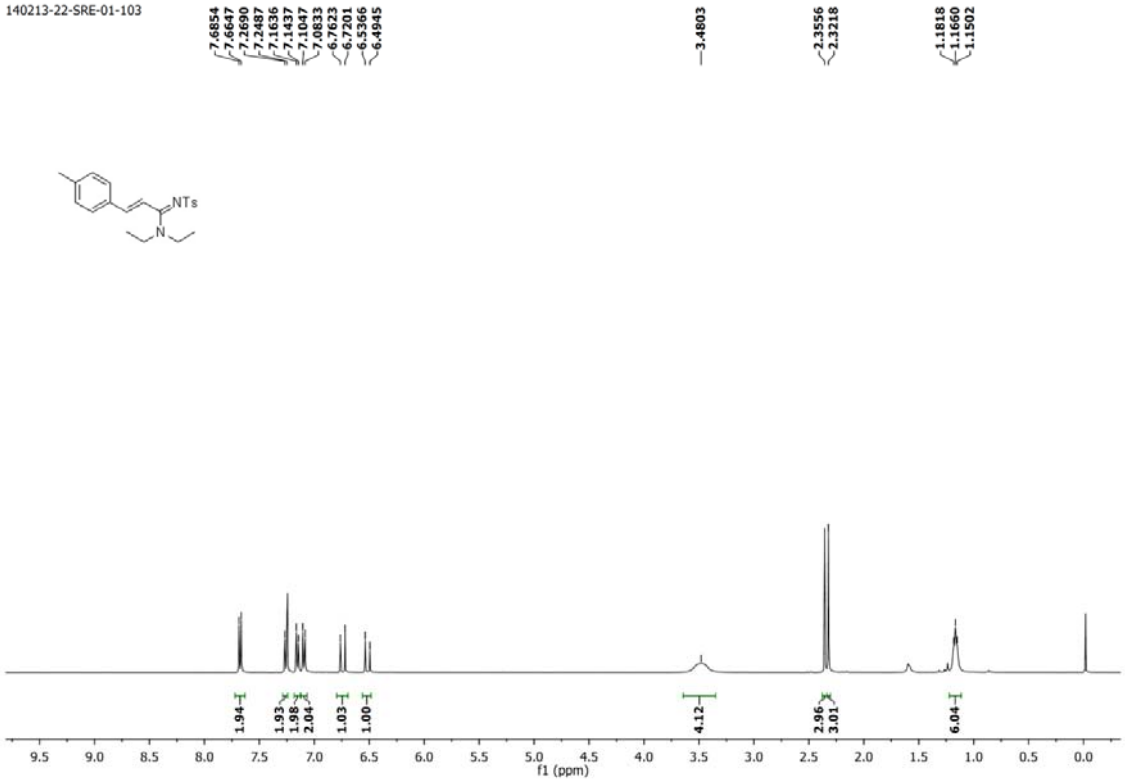


Fig. S90 ^{1}H NMR spectra of **4t** in $CDCl_3$.

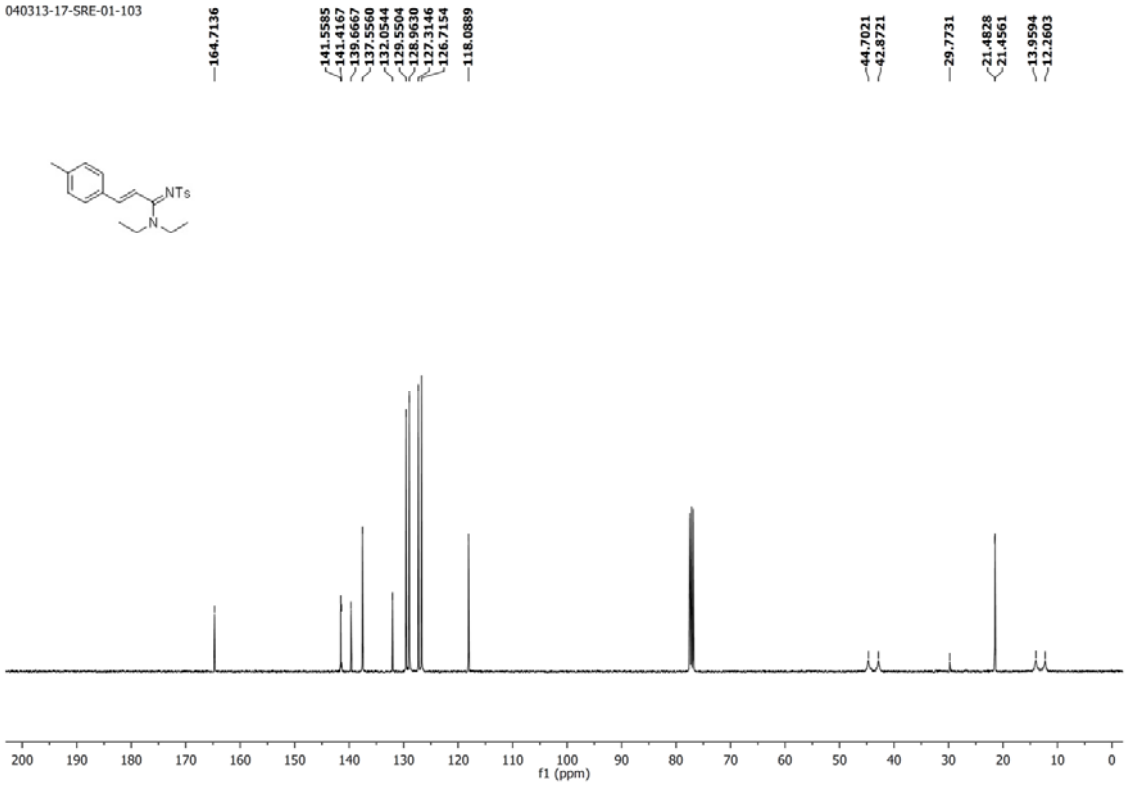


Fig. S91 ^{13}C NMR spectra of **4t** in $CDCl_3$.

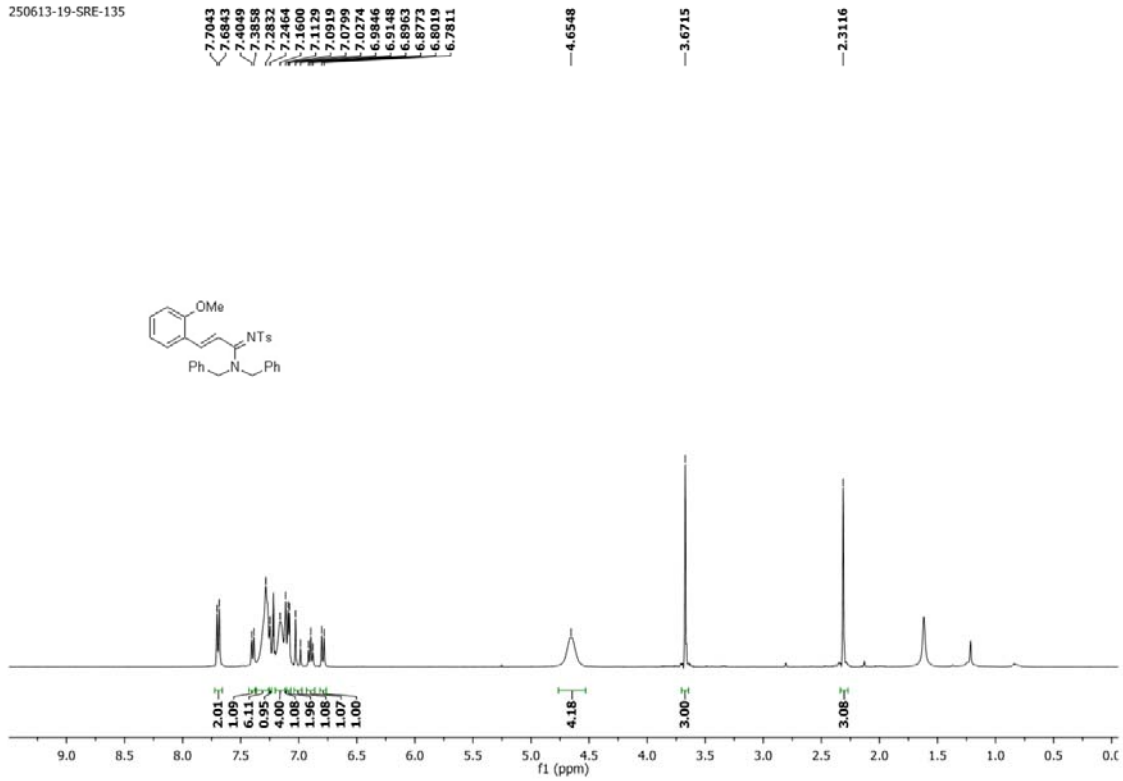


Fig. S92 ^{1}H NMR spectra of **4u** in $CDCl_3$.

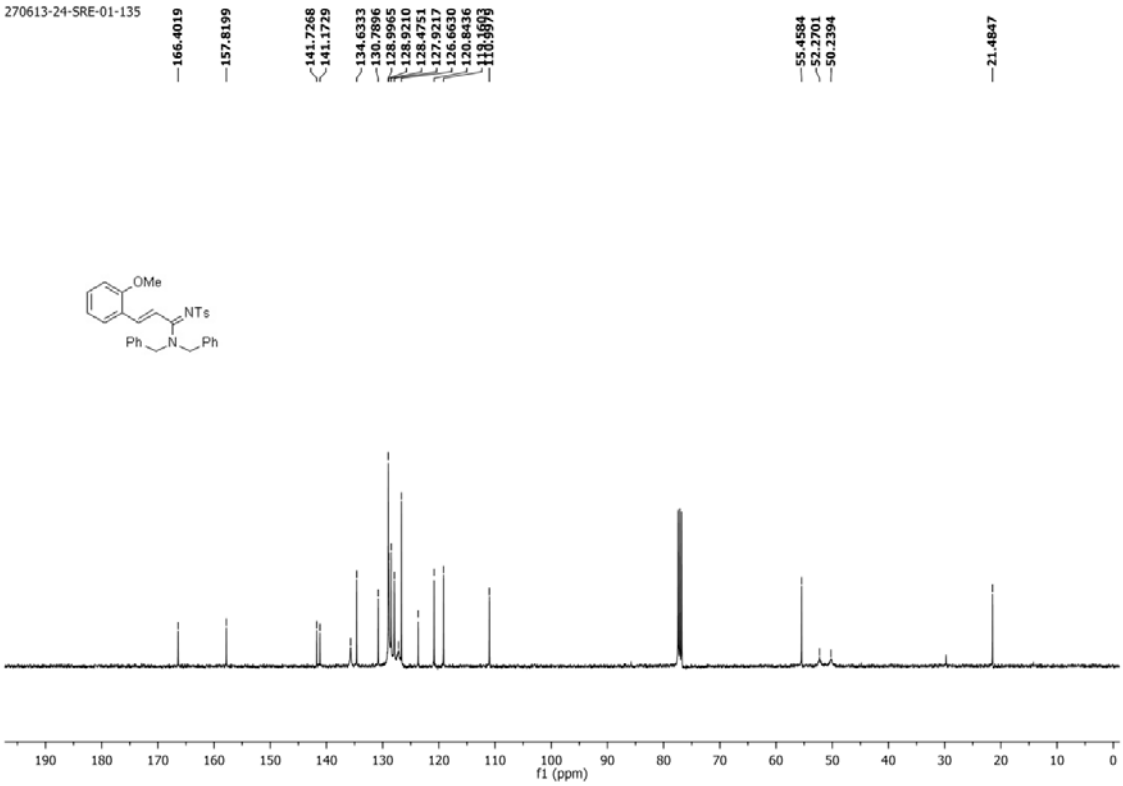


Fig. S93 ^{13}C NMR spectra of **4u** in $CDCl_3$.

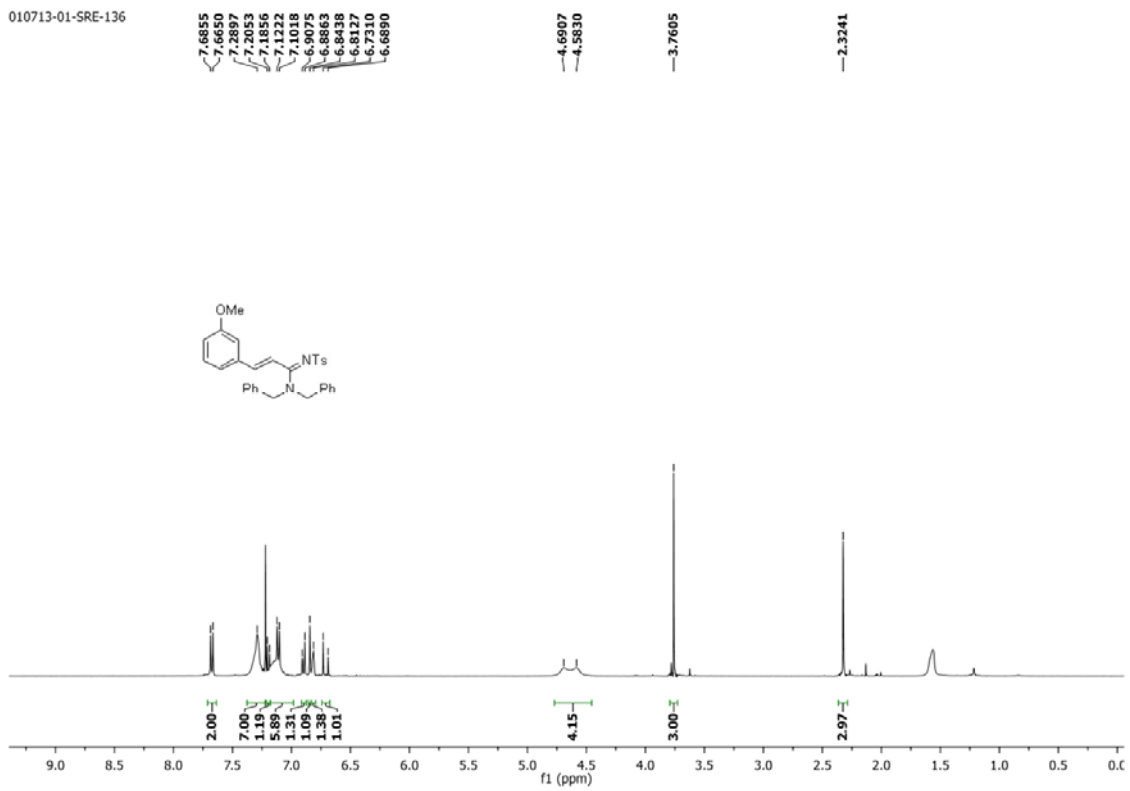


Fig. S94 ^{1}H NMR spectra of **4v** in $CDCl_3$.

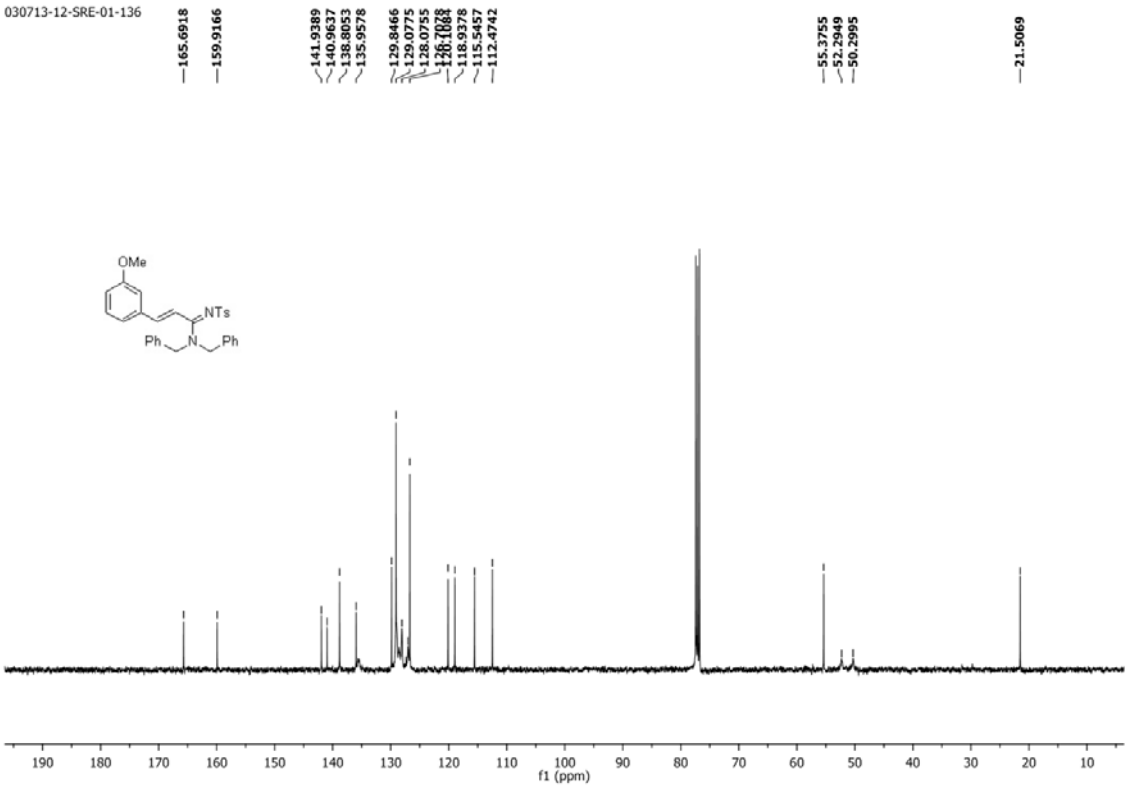


Fig. S95 ^{13}C NMR spectra of **4v** in $CDCl_3$.

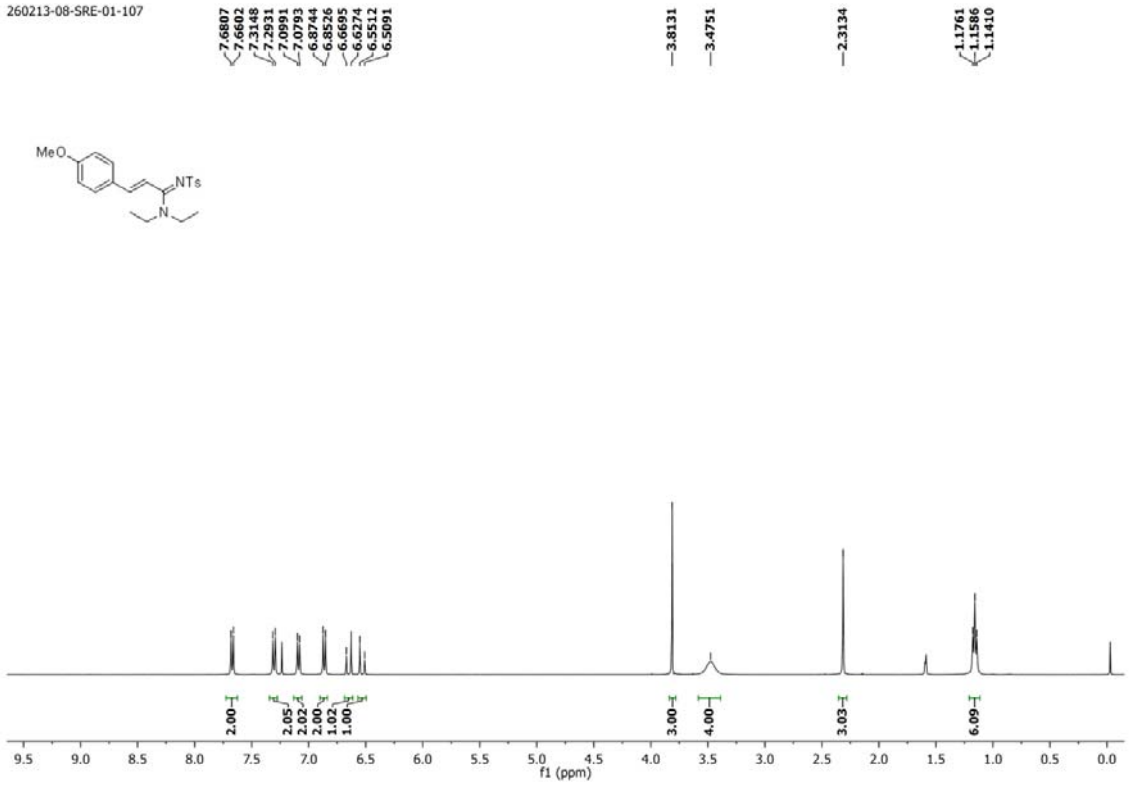


Fig. S96 ^{1}H NMR spectra of **4w** in $CDCl_3$.

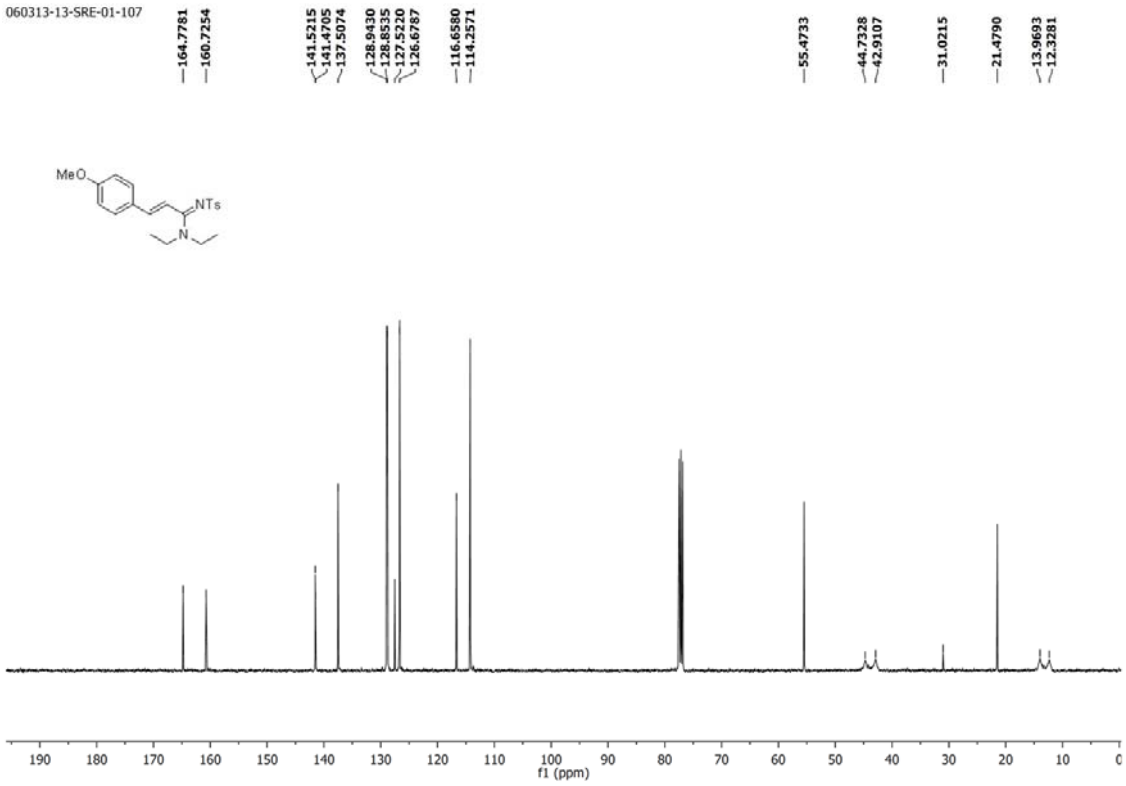


Fig. S97 ^{13}C NMR spectra of **4w** in $CDCl_3$.

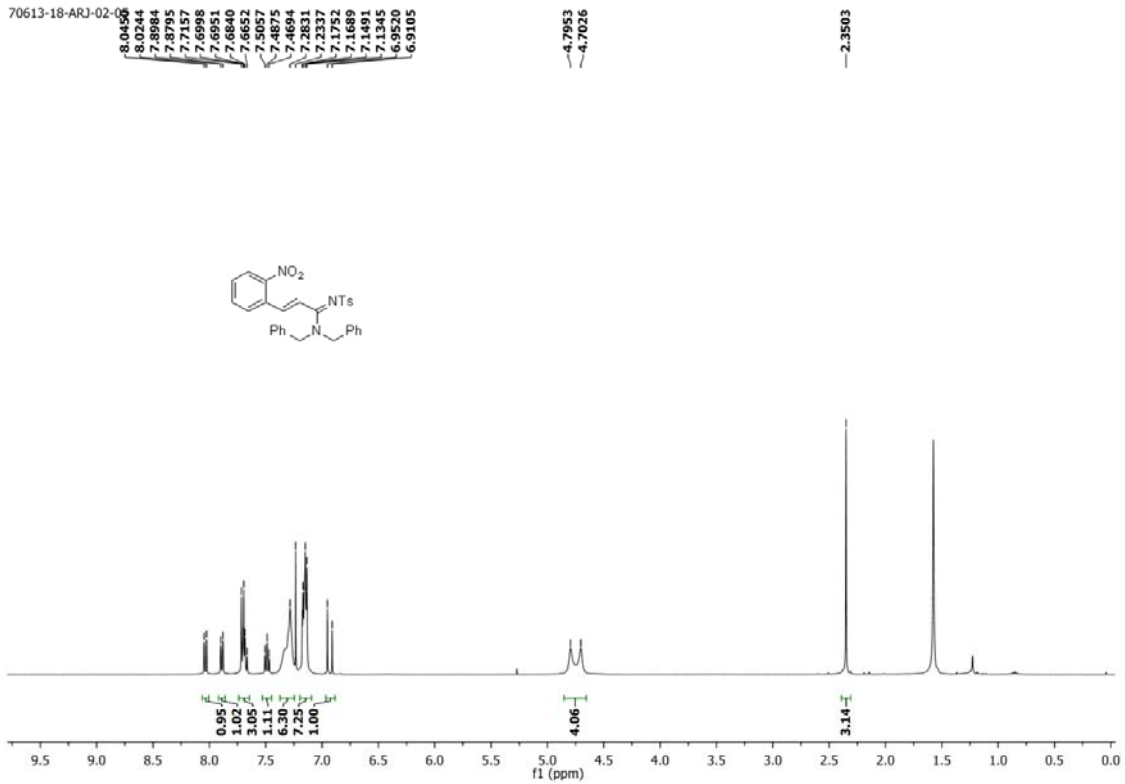


Fig. S98 ^{1}H NMR spectra of **4x** in $CDCl_3$.

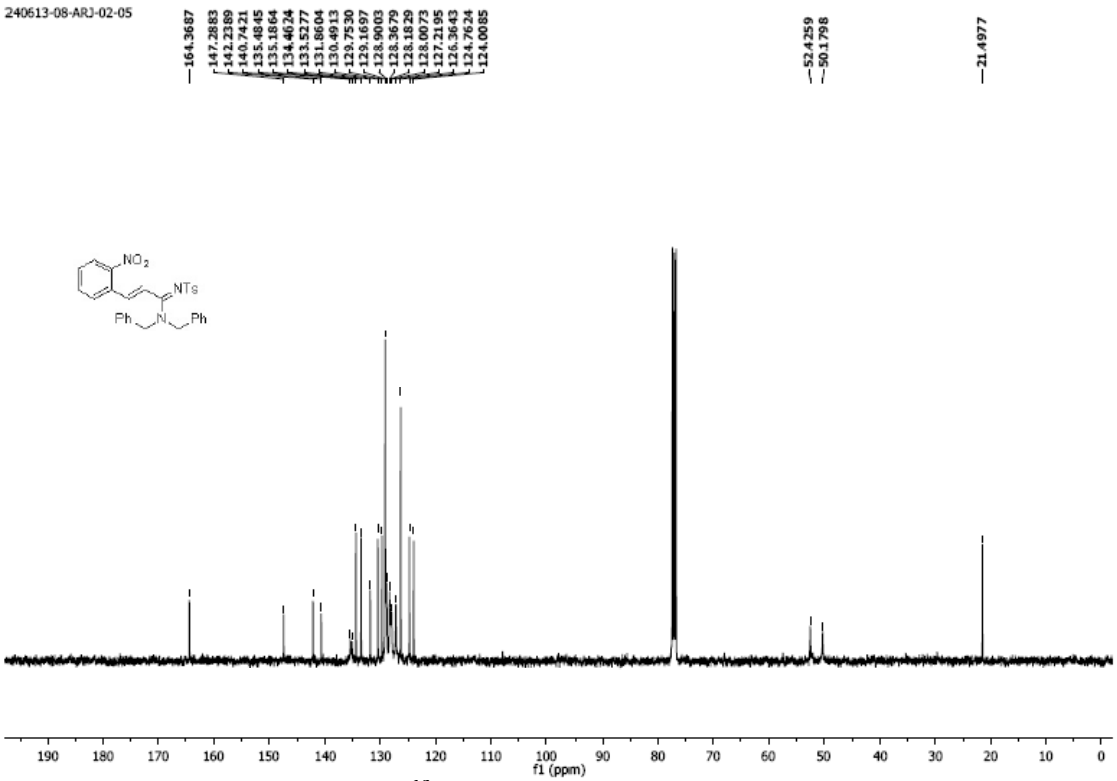


Fig. S99 ^{13}C NMR spectra of **4x** in $CDCl_3$.

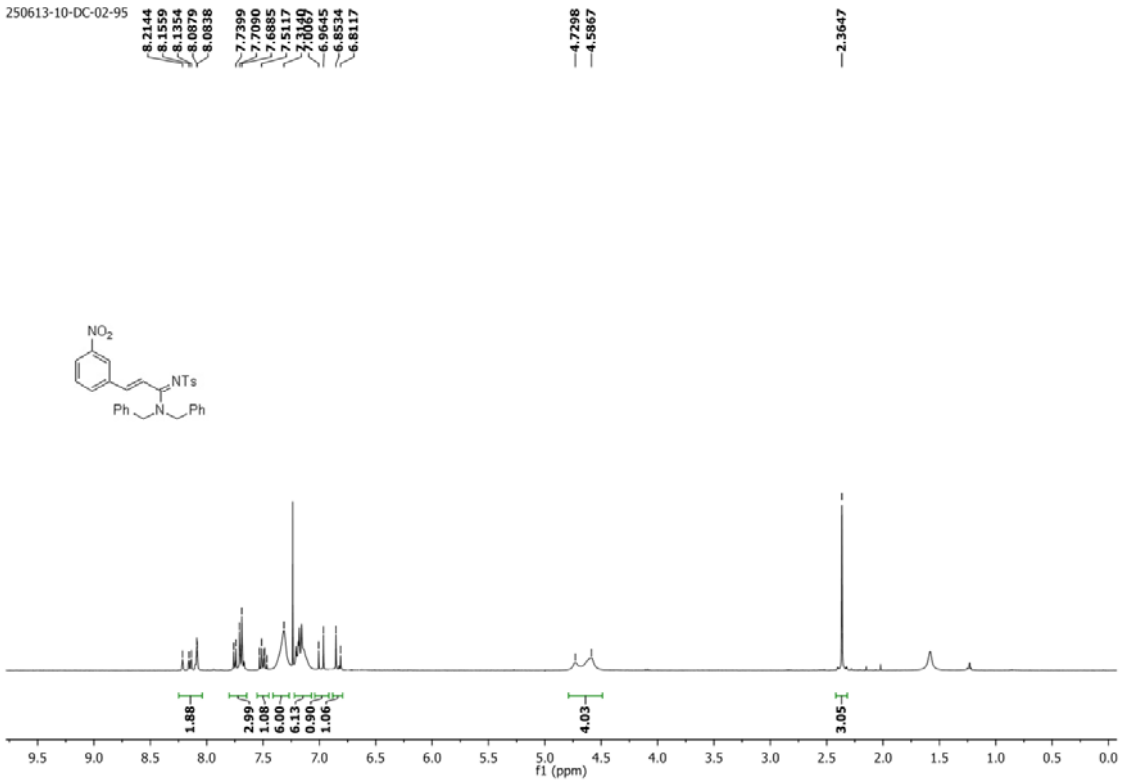


Fig. S100 ^{1}H NMR spectra of **4y** in $CDCl_3$.

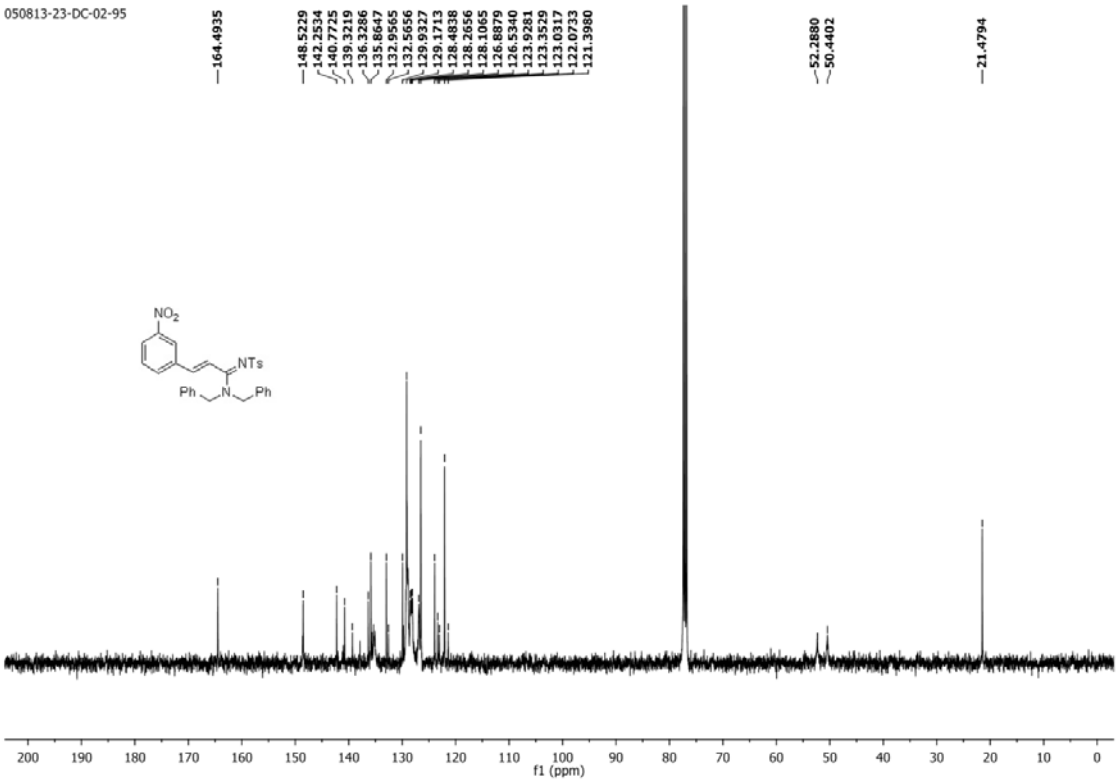


Fig. S101 ^{13}C NMR spectra of **4y** in $CDCl_3$.

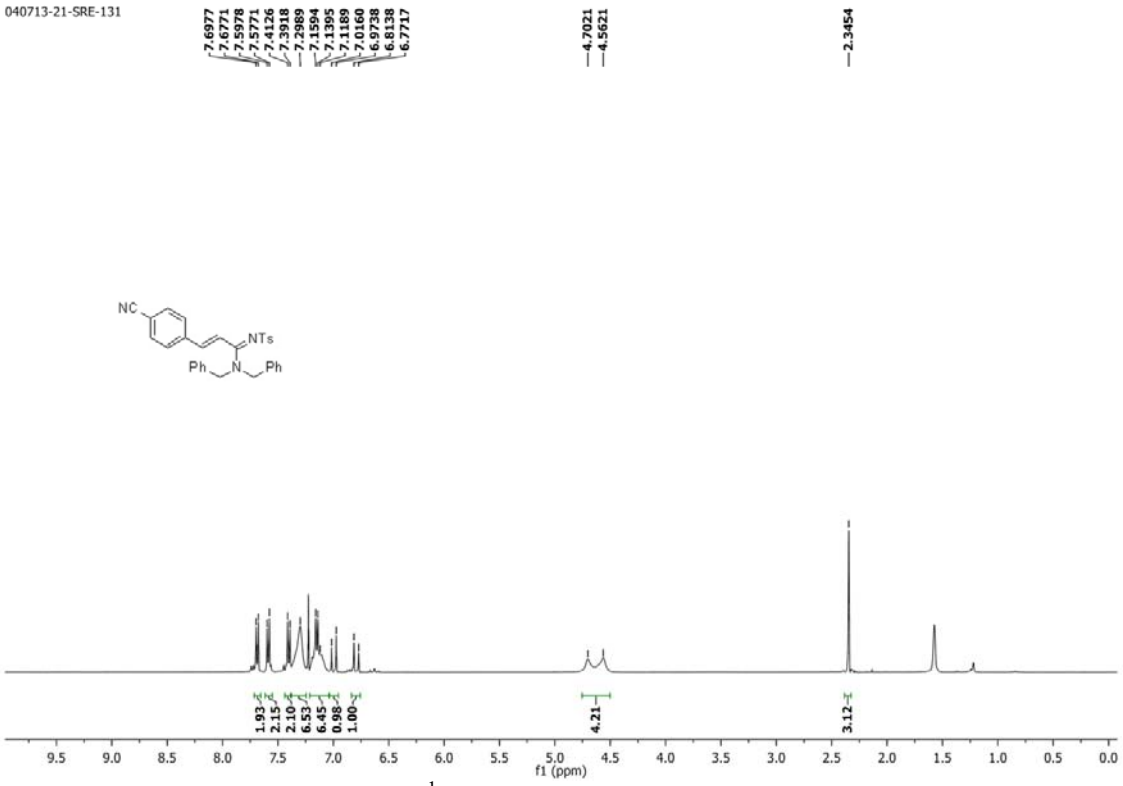


Fig. S102 ^{1}H NMR spectra of **4z** in $CDCl_3$.

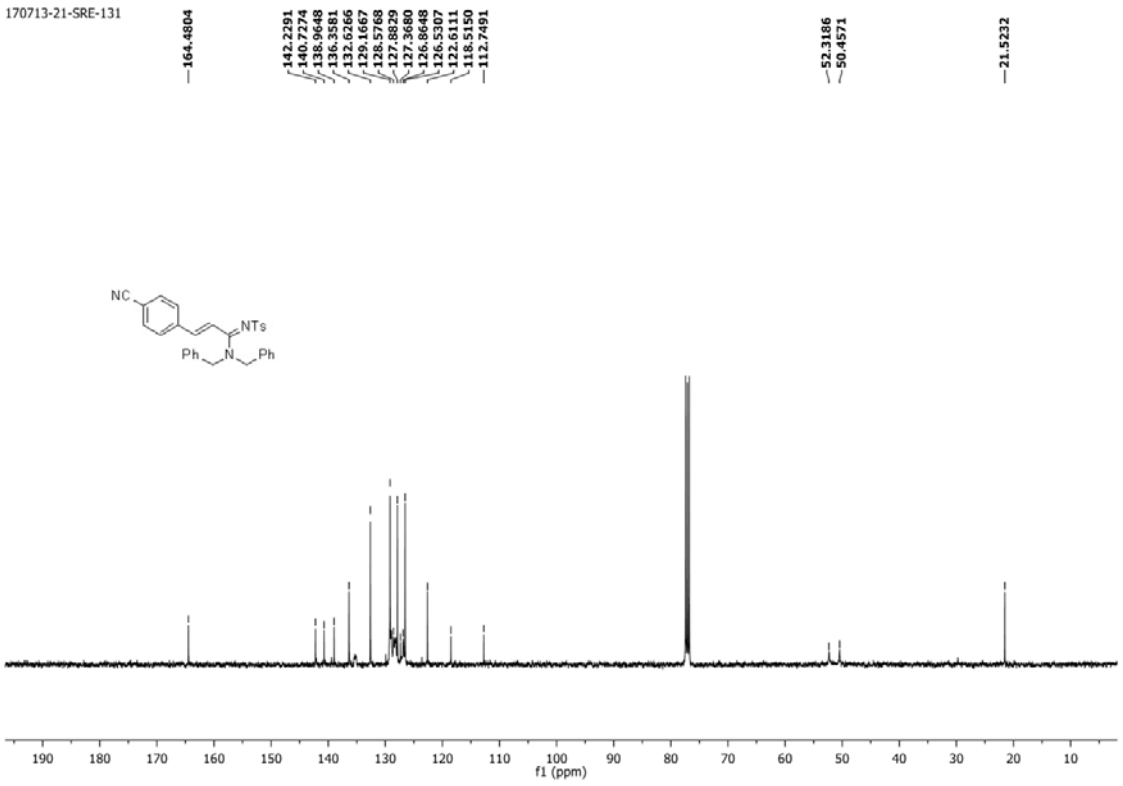


Fig. S103 ^{13}C NMR spectra of **4z** in $CDCl_3$.

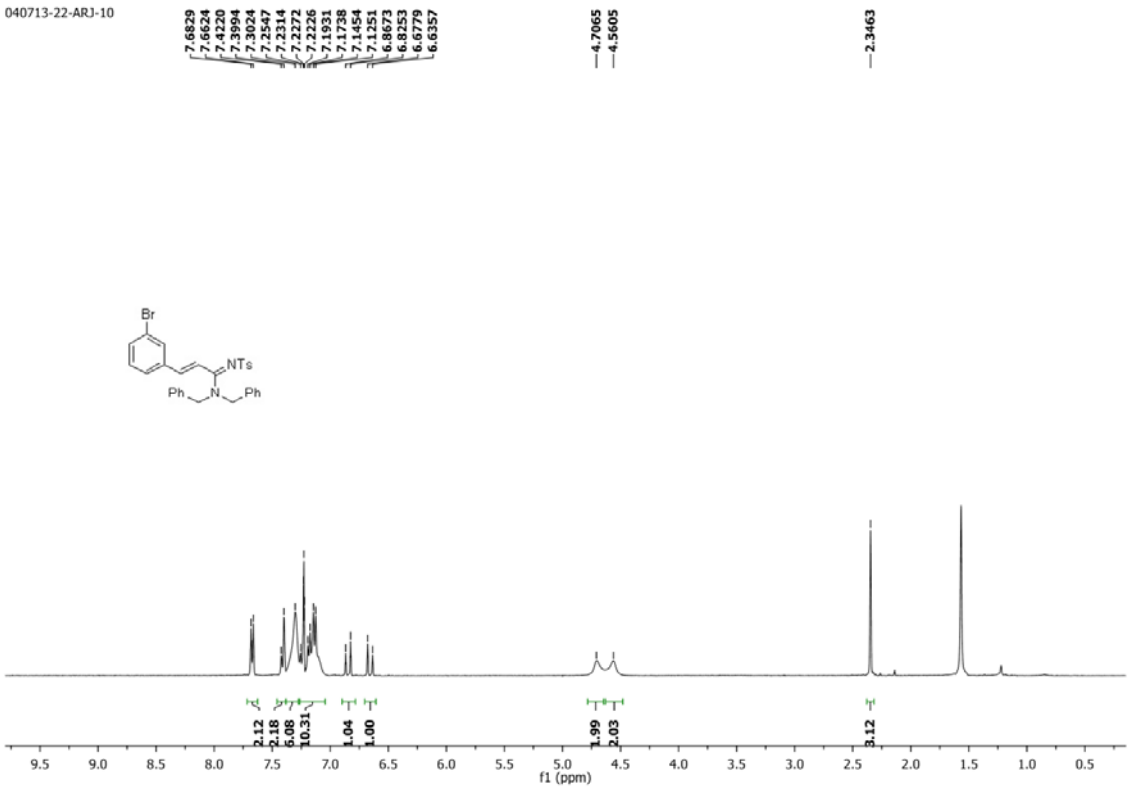


Fig. S104 ^{1}H NMR spectra of **4a´** in $CDCl_3$.

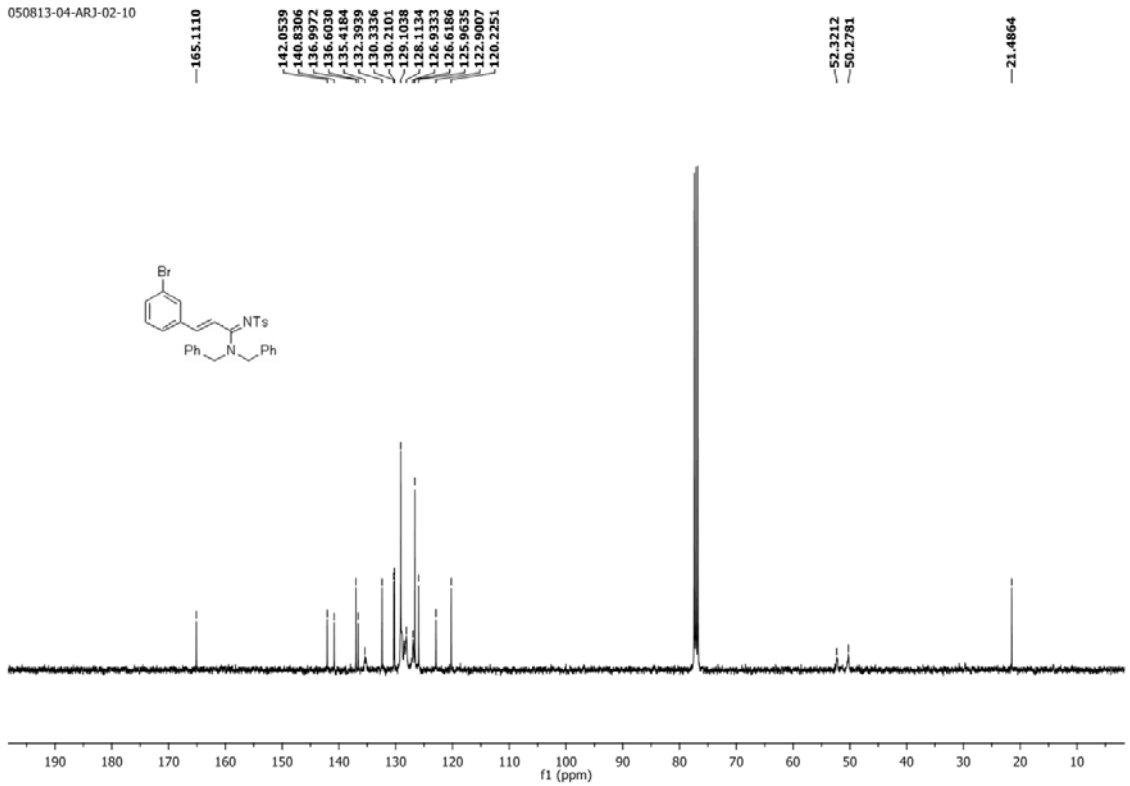


Fig. S105 ^{13}C NMR spectra of **4a´** in $CDCl_3$.

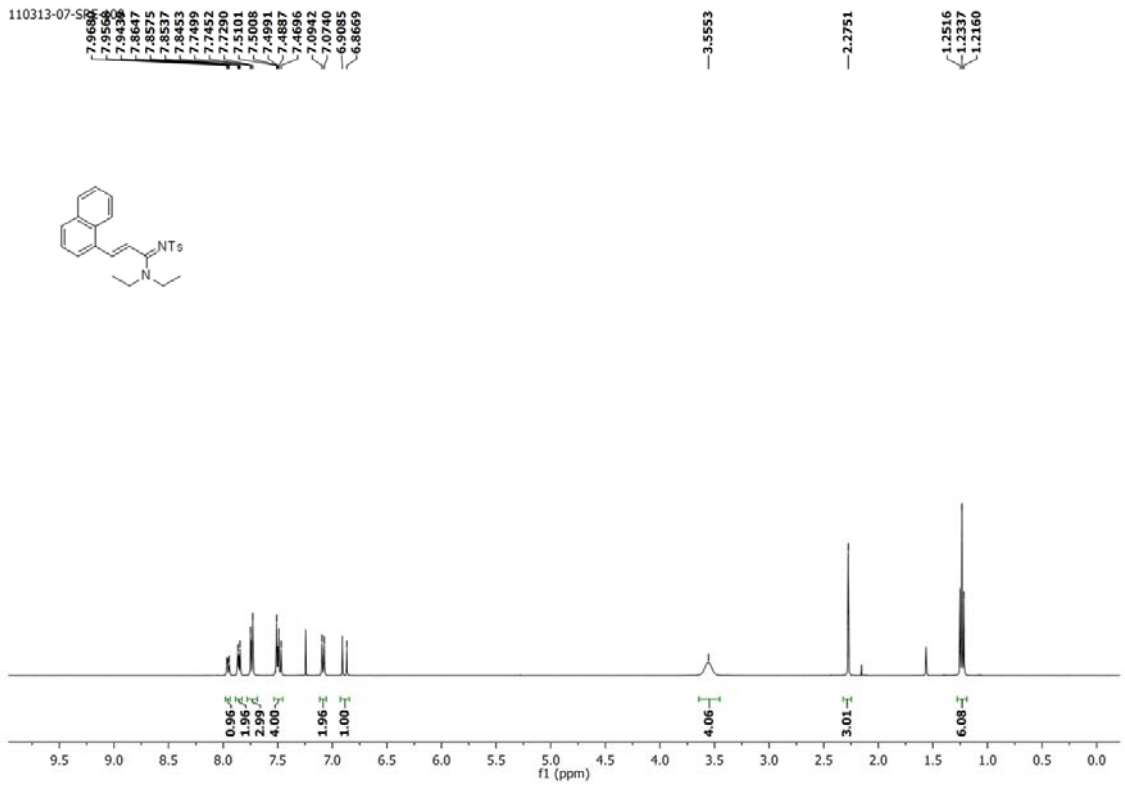


Fig. S106 ^{1}H NMR spectra of **4b´** in $CDCl_3$.

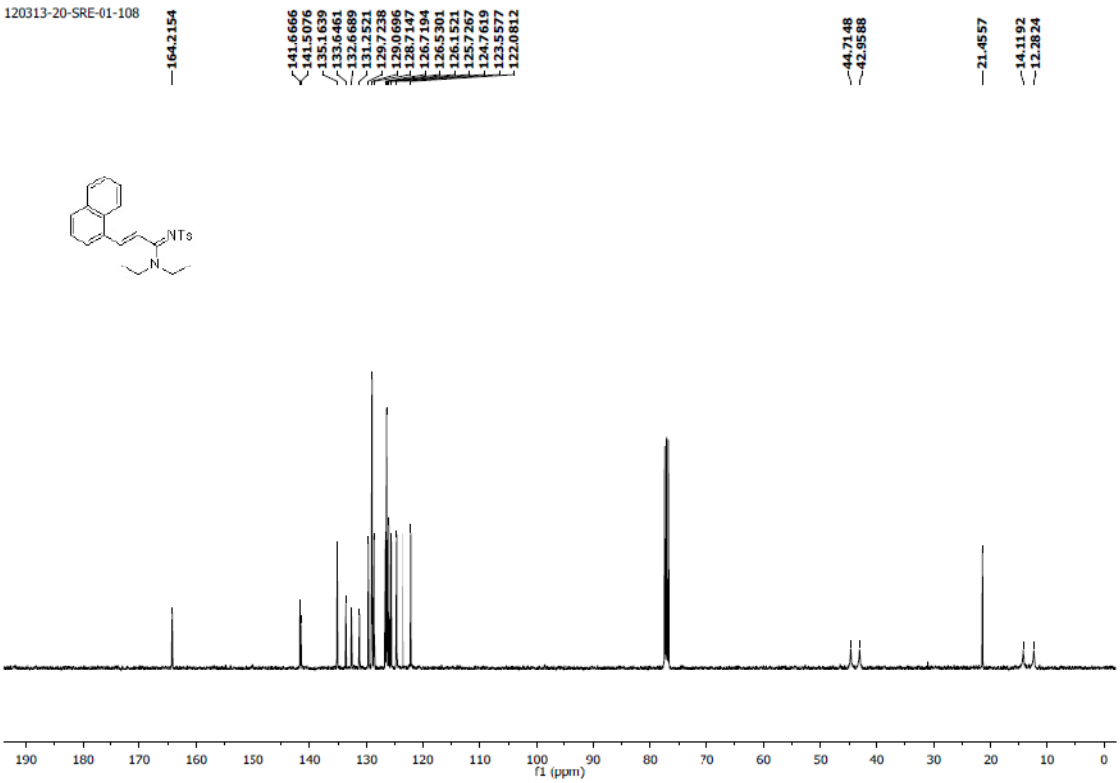


Fig. S107 ^{13}C NMR spectra of **4b´** in $CDCl_3$.

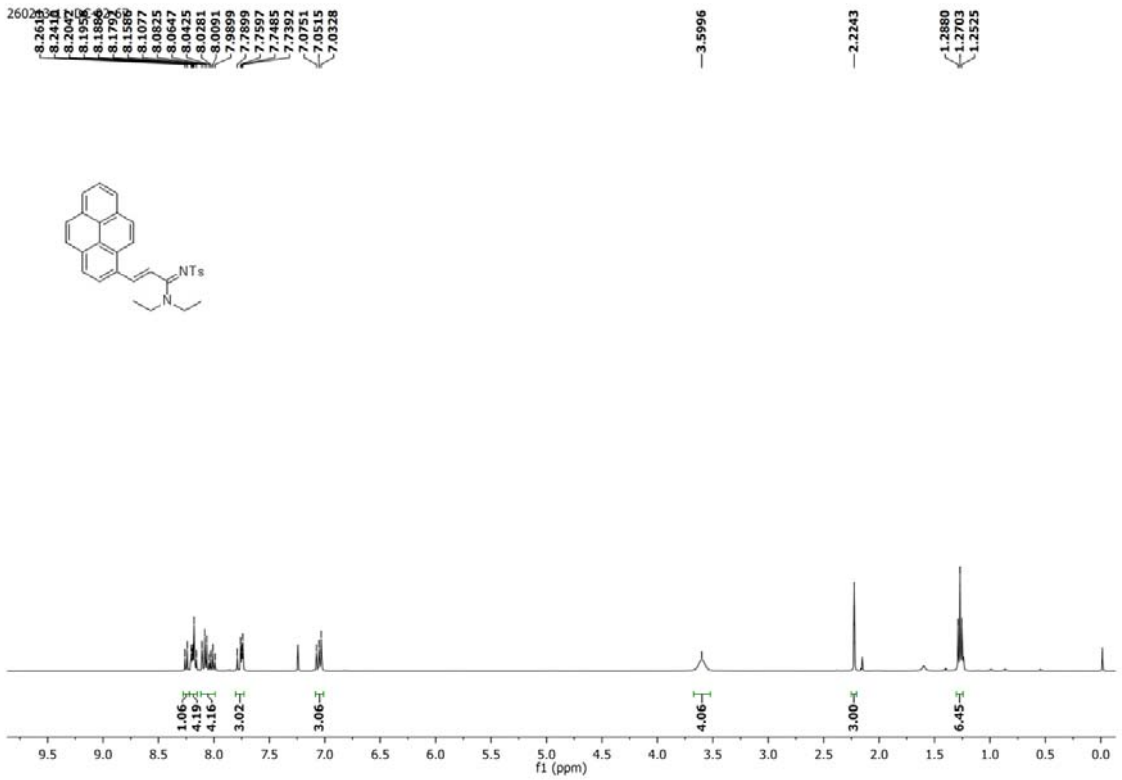


Fig. S108 ^{1}H NMR spectra of **4c´** in $CDCl_3$.

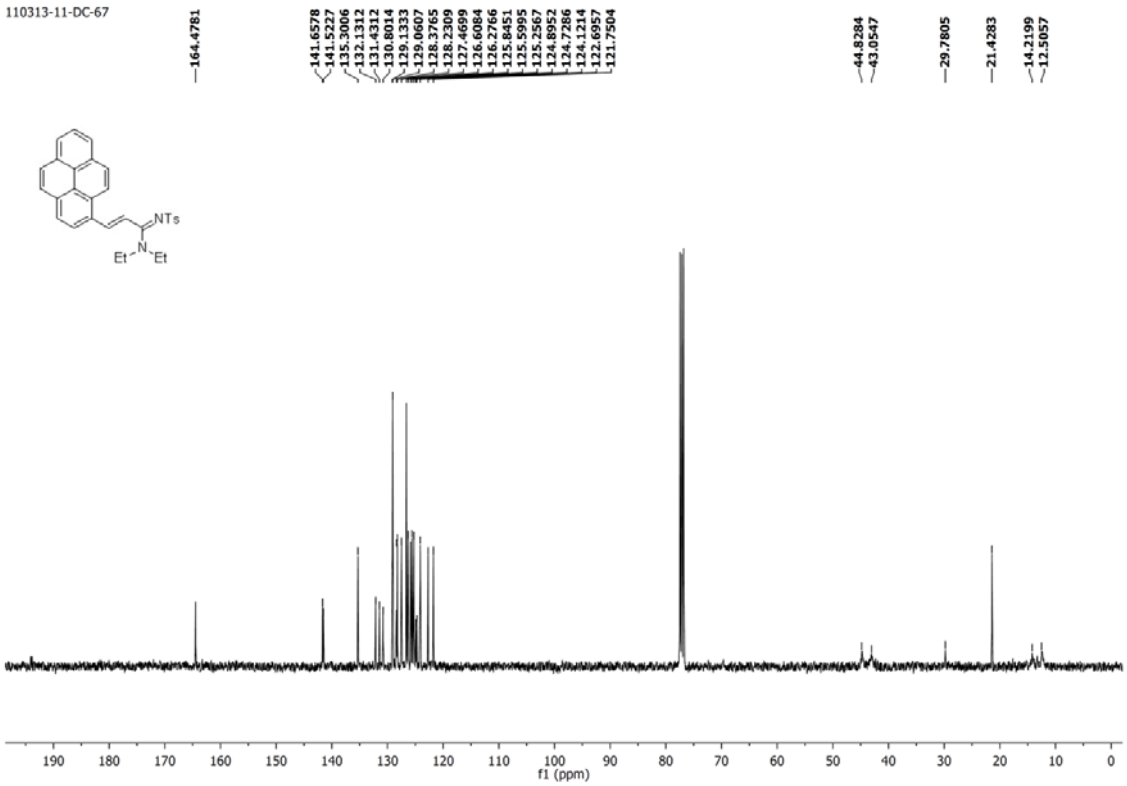


Fig. S109 ^{13}C NMR spectra of **4c´** in $CDCl_3$.

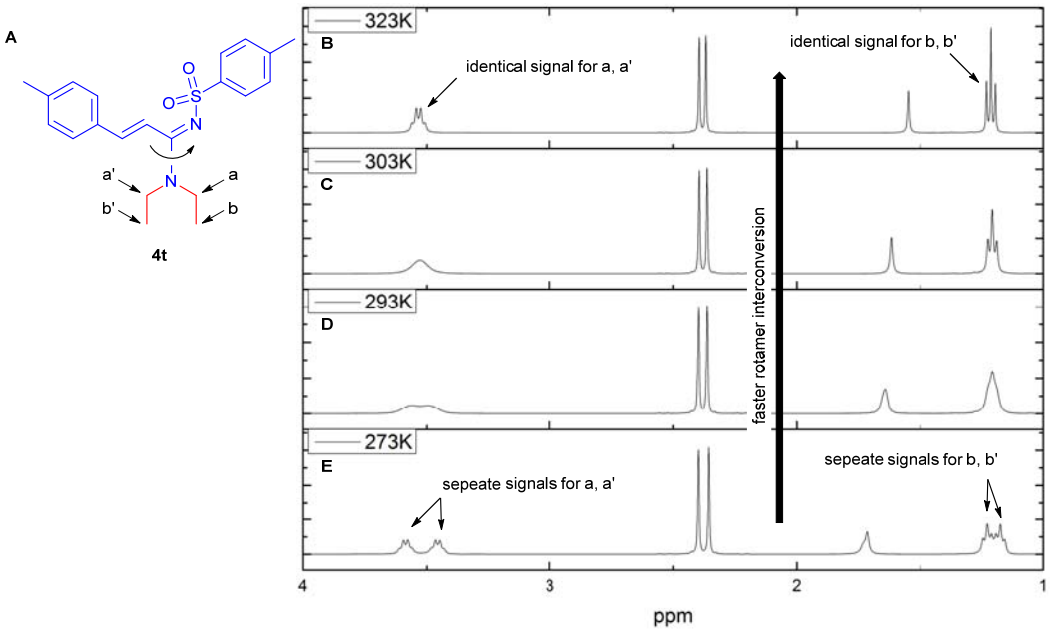


Fig. S110 Variable temperature ^{1}H NMR (400 MHz) spectra of **4t** in $CDCl_3$. Only the range 1.0 - 4.0 ppm is shown for clarity.

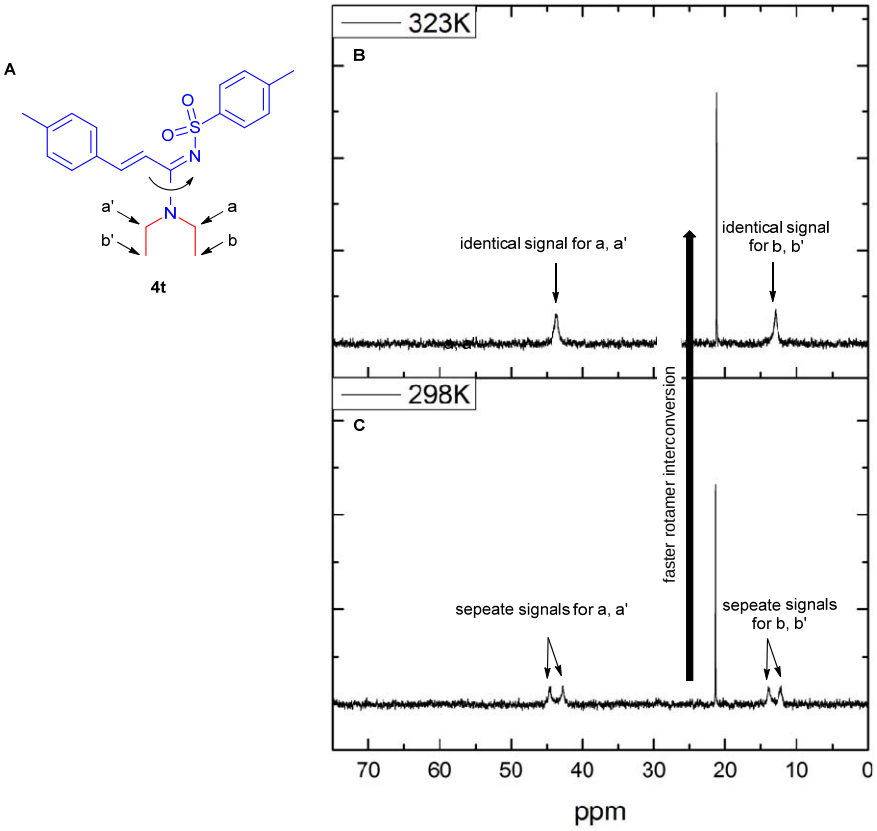


Fig. S111 Variable temperature ^{13}C NMR (100 MHz) spectra of **4t** in $CDCl_3$. Only the range 0-75 ppm is shown for clarity.

VII. References.

S1. Z. Lin, D. Yu, Y. N. Sum and Y. Zhang, *ChemSusChem* 2012, **5**, 625.

S2. M. D'Hooghe, W. Van Brabandt and N. De Kimpe, *J. Org. Chem.* 2004, **69**, 2703.

S3. C. Koradin, N. Gommermann and K. Polborn, *Chem. Eur. J.* 2003, **9**, 2797.

S4. N. Gommermann, C. Koradin, K. Polborn and P. Knochel, *Angew.Chem. Int. Ed.*2003, **42**, 5763.

S5. S. C. Deshmukh, A. Roy and P. Talukdar, *Org. Biomol. Chem.* 2012, **10**, 7536.

S6 A. S. Y. Lee, G. A. Chen, Y. T. Chang and S. F. Chu, *Synlett.* 2009, **3**, 341.

S7. A. Viola, J. J. Collins, N. Filipp and J. S. Locke, *J. Org. Chem.* 1993, **58**, 5067.

S8. J. Verron, P. Malherbe, E. Prinssen, A. W. Thomas, N. Nock and R. Masciadri, *Tetrahedron Lett.* 2007, **48**, 377.

S9. SHELXS-97: (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467; (b) G. M. Sheldrick *SHELXL-97*, *Universität Göttingen (Germany)*, 1997.