Intramolecular cascade rearrangements of enynamine derived ketenimines: Access to acyclic and cyclic amidines

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Supporting Information

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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.

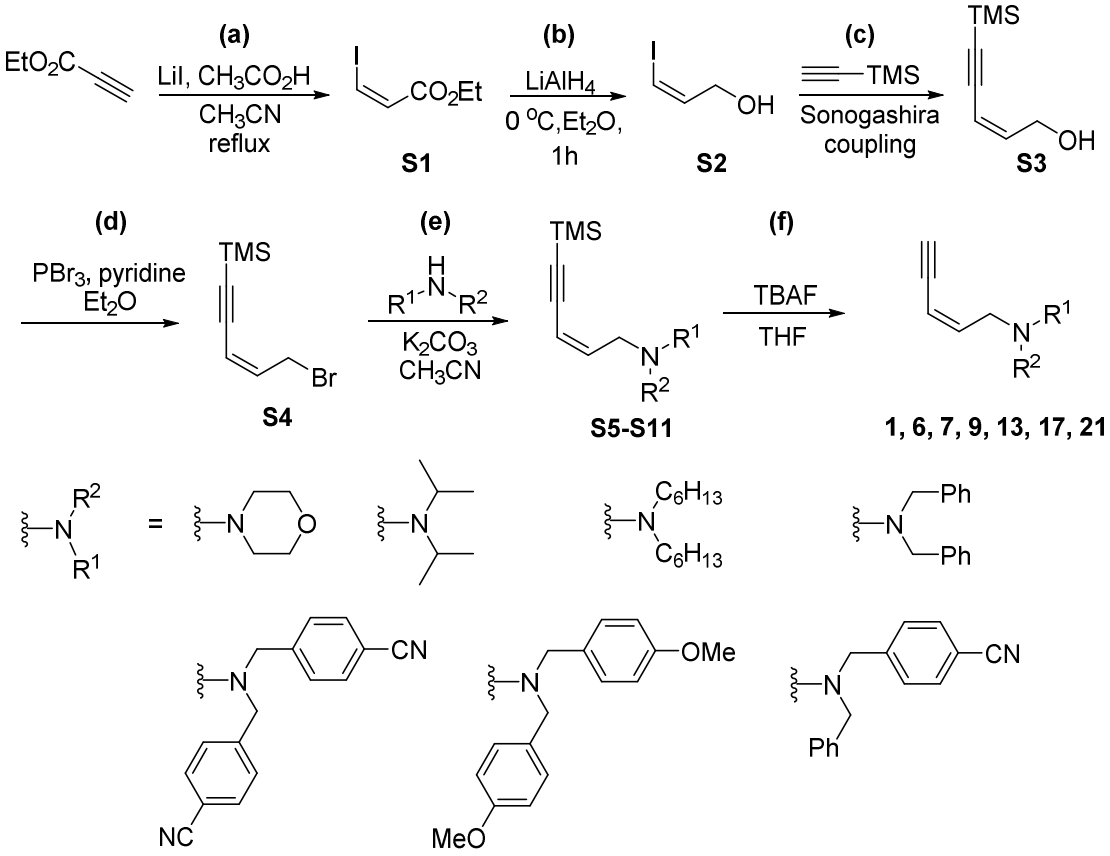
II. Physical Measurements.

The ^{1}H and ^{13}C spectra were recorded on 400 MHz Jeol ECS-400 (or 100 MHz for ^{13}C) spectrometers using either residual solvent signal 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), sex (sextet), and sept (septet). High-resolution mass spectra were obtained from Micro Mass ESTOF MS spectrometer. (FT-IR) spectra were obtained using Bruker: α ALPHA spectrophotometer (neat) and reported in cm^{-1}.Crystal structures were recorded on a Bruker single crystal X-Ray diffractometer.

III. Experimental Procedures.

General procedure for the synthesis of enynamines 1, 6, 7, 9, 13, 17, 21.



Scheme S1. Synthesis of enynamines **1**, **6**, **7**, **9**, **13**, **17**, **21**.

(a) Synthesis of (*Z*)-methyl-3-iodoacrylate S1:[S1] In a 100 mL flask ethyl propiolate (2.0 g, 20.38 mmol) was dissolved in 20 mL CH_3CN. Then lithium iodide (3.0 g, 22.43 mmol) was added followed by acetic acid (1.35 mL, 22.43 mmol). The resulting solution was heated to reflux under vigorous stirring. After 10 minutes white precipitate was formed, the stirring was continuous for 12 hours. After cooling, the reaction mixture was neutralized by pouring 50 mL 0.3 M K_2CO_3 solution. The resultant solution was extracted for four times with 120

mL of diethyl ether. The combined layers were washed with brine solution and dried over Na_2SO_4. Removal of the solvents under reduced pressure yielded the crude enoate, which was directly used without any further purification.

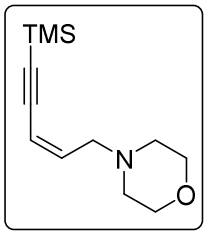
(b) Synthesis of (*Z*)-3-iodoprop-2-en-1-ol S2:[S1] A 250 mL flask was charged with $LiAlH_4$ (0.77 g, 20.38 mmol) in diethyl ether 60 mL. The resultant reaction mixture was cooled 0 ^oC and (*Z*)-3-iodopropenoate (4.6 g, 20.38 mmol) dissolved in diethyl ether 20 mL was added dropwise. The reaction was stirred for 30 minutes at 0 ^oC and allowed to warm at room temperature. The reaction was quenched at 0 ^oC by adding ethyl acetate 5 mL and saturated solution of Na_2SO_4 5 mL and resultant mixture was stirred vigorously for 30 minutes and filtered through celite pad. The obtained filtrate was washed with brine, extracted in etherand dried over Na_2SO_4. The solvent was evaporated and obtained compound was used for further reaction without purification.

(c) Synthesis of (*Z*)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol S3:[S2] The solution of 1.2 equivalents of TMS acetylene and 1 equivalents of (*Z*)-3-iodoprop-2-en-1-ol in degassed triethyl amine was further degassed for 10 minutes. To the resultant solution 2 mol% $PdCl_2(PPh_3)_2$ was added and stirred at room temperature for 15 minutes before 4 mol% CuI was added. The mixture was stirred for 12 hours. The reaction mixture was diluted with dichloromethane and filtered through celite pad. The solvent was evaporated and purified through column chromatography. The obtained yield was 79%.

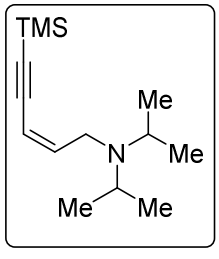
(d) Synthesis of (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane S4: (*Z*)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol was dissolved in diethyl ether and cooled to -15 ^oC. To this PBr_3 (0.4 equivalent) was added drop wisely followed by the addition of pyridine (0.03 equivalent). The resultant mixture was allowed to warm at room temperature and stirred for 2 hours. The reaction was quenched with ice cubes, extracted in ether and dried over Na_2SO_4. The obtained product was purified with column chromatography with 92% of yield. **IR (neat):** ν_{max}/cm^{-1} 2959, 2151, 1712, 1437, 1248, 1198, 1056, 972, 841; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.13 (dt, *J* = 11.0, 6.3 Hz, 2H), 5.62 (dt, *J* = 11.0, 1.5 Hz, 2H), 4.44 (d, *J* = 6.2 Hz, 4H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.99, 110.42, 62.94, 29.77, -0.05; **HRMS (ESI):** Calc. for $C_8H_{14}BrSi$ $[M+H]^+$: 217.0048; Found: 217.0064.

(e) Synthesis of TMS-protected enynamines S5-S11: To the solution of (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane in acetonitrile was added the amine (2 equivalent) drop wisely followed by K_2CO_3 (2 equivalent) at 0 ^oC. The resultant mixture was stirred for 12 hours. The solvent was evaporated and directly loaded on column for purification.

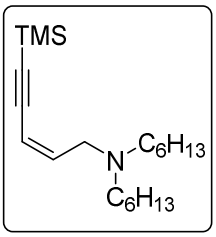
***(Z)*-4-(5-(trimethylsilyl)pent-2-en-4-yn-1-yl)morpholine S5:** The compound **S5** was prepared by using the above procedure **(e)**. (*Z*)-(5-Bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^oC and morpholine (160 µL, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S5** with 92% yield. **IR (neat):** ν_{max}/cm^{-1} 2959, 2856, 2811, 2148, 1707, 1516, 1453, 1369, 1328, 1292, 1249, 1249, 1213, 1118, 1074, 1002; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.04 (dt, *J* = 11.0 Hz, 7.0 Hz, 1H), 5.70 (dt, *J* = 11 Hz, 0.14 Hz, 1H), 4.29 (dd, *J* = 7.0 Hz, 1.4 Hz, 2H), 3.74 (t, *J* = 4.6 Hz, 4H), 2.51 (t, *J* = 4.5 Hz, 4H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.0, 112.6, 101.1, 100.4, 66.9, 57.7, 53.6, 0.1; **HRMS (ESI):** Calc. for $C_{12}H_{22}NOSi$ $[M+H]^+$: 224.1471; Found: 224.1474.



***(Z)*-*N*,*N*-diisopropyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S6:** The compound **S6** was prepared by using the above procedure **(e)**. (*Z*)-(5-Bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^oC and di isopropyl amine (190 mg, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S6** with 79% yield. **IR (neat):** ν_{max}/cm^{-1} 2962, 2147, 1461, 1385, 1368, 1327, 1250, 1204, 1173, 1079, 1038; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.02 (m, 1H), 5.5 (dt, *J* = 11.0 Hz, 1.7 Hz, 1H), 3.38 (dd, *J* = 7.0 Hz, 1.7 Hz, 2H), 3.05 (sept, *J* = 6.5 Hz, 2H), 1.06 (d, *J* = 6.6 Hz, 12H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 146.9, 108.9, 102.0, 99.3, 49.0, 44.8, 20.8, 0.03; **HRMS (ESI):** Calc. for $C_{14}H_{28}NSi$ $[M+H]^+$: 238.1991; Found: 238.1990.

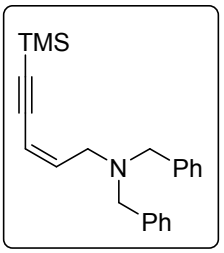


***(Z)*-*N*-hexyl-*N*-(5-(trimethylsilyl)pent-2-en-4-yn-1-yl)hexan-1-amine S7:** The compound **S7** was prepared by using the above procedure **(e).** (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^oC and dihexyl amine (316 µL, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol)to give **S7**

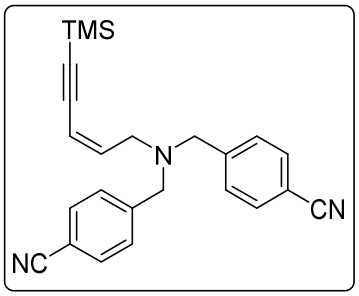


with 86% yield. **IR (neat):** ν_{max}/cm^{-1} 2954, 2927, 2859, 2149, 1625, 1461, 1375, 1250, 1152, 1082, 986; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.08 (dt, *J* = 11.0 Hz, 7.0 Hz, 1H), 5.63 (dt, *J* = 11.0 Hz, 1.4 Hz, 1H), 3.4 (dd, *J* = 7.0 Hz, 1.4 Hz, 2H), 2.44 (m, 4H), 1.47 (m, 4H), 1.29 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 6H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 142.3, 111.1, 101.6, 99.6, 54.2, 52.8, 31.8, 27.2, 27.0, 22.6, 14.0, 0.07; **HRMS (ESI):** Calc. for $C_{20}H_{40}NSi$ $[M+H]^+$: 322.2930; Found: 322.2933.

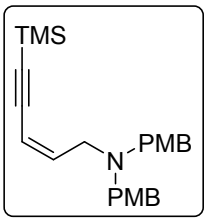
***(Z)*-*N*,*N*-dibenzyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S8:** The compound **S8** was prepared by using the above procedure**(e).** (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^oC and dibenzyl amine (355 µL, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S8** with 82% yield. **IR (neat):** ν_{max}/cm^{-1} 3028, 2958, 2798, 2147, 1742, 1599, 1493, 1448, 1363, 1326, 1248, 1119, 1071, 992; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.21 (m, 10H), 6.1 (dt, *J* = 11 Hz, 6.7 Hz, 1H), 5.64 (d, *J* = 11 Hz, 1H), 3.61 (s, 4H), 3.36 (d, *J* = 6.8 Hz, 2H), 0.17 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 142.0, 138.9, 128.9, 128.2, 126.9, 111.6, 101.4, 100.1, 58.0, 52.6, 0.03; **HRMS (ESI):** Calc. for $C_{22}H_{28}NSi$ $[M+H]^+$: 334.1991; Found: 334.1993.



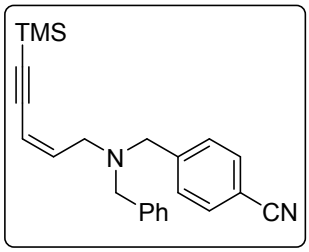
***(Z)*-4,4'-(((5-(trimethylsilyl)pent-2-en-4-yn-1-yl)azanediyl)bismethylene)) dibenzonitrile S9:** The compound **S9** was prepared by using the above procedure **(e).** (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^oC and 4,4'-(azanediylbis(methylene))dibenzonitrile (455 mg, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S9** with 83% yield. **IR (neat):** ν_{max}/cm^{-1} 3029, 2958, 2817, 2228, 2147, 1740, 1693, 1647, 1608, 1499, 1450, 1406, 1367, 1249, 1123, 1076, 1023; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.2 Hz, 4H), 6.01 (dt, *J* = 11.0, 6.9 Hz, 1H), 5.65 (d, *J* = 11.0 Hz, 1H), 3.63 (s, 4H), 3.30 (dd, *J* = 6.9, 1.1 Hz, 2H), 0.15 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.66, 140.11, 132.21, 129.23, 118.79, 112.88, 111.10, 100.91, 100.83, 57.94, 52.81, -0.11; **HRMS (ESI):** Calc. for $C_{23}H_{26}N_2Si$ $[M+H]^+$: 359.1944; Found: 359.1945.



***(Z)-N,N*-bis(4-methoxybenzyl)-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S10:** The compound **S10** was prepared by using the above procedure **(e).** (*Z*)-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^{o}C and bis(4-methoxybenzyl)amine (475 mg, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S10** with 95% yield. **IR (neat):** ν_{max}/cm^{-1} 3000, 2955, 2830, 2146, 1611, 1583, 1509, 1459, 1366, 1297, 1242, 1173, 1105, 1036; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 (d, *J* = 8.3 Hz, 4H), 6.88 (d, *J* = 8.3 Hz, 4H), 6.11 (dt, *J* = 11 Hz, 6.6 Hz, 1H), 5.64 (d, *J* = 11 Hz, 1H), 3.8 (s, 6H), 3.5 (s, 4H), 3.34 (d, *J* = 6.7 Hz, 2H), 0.2 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 158.6, 142.7, 131.4, 130.0, 113.6, 111.2, 101.5, 57.3, 55.2, 52.4, 0.05; **HRMS (ESI):** Calc. for $C_{24}H_{32}NO_2Si$ $[M+H]^+$: 394.2202; Found: 394.2202.

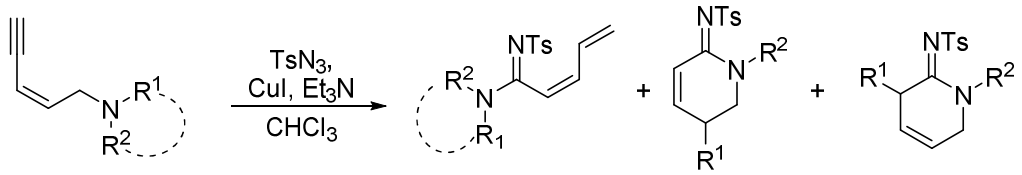


***(Z)*-4-((benzyl(5-(trimethylsilyl)pent-2-en-4-yn-1-yl)amino)methyl)benzonitrile S11:** The compound **S11** was prepared by using the above procedure **(e).** *(Z)*-(5-bromopent-3-en-1-yn-1-yl)trimethylsilane (200 mg, 0.92 mmol) in acetonitrile was cooled to 0 ^{o}C and 4-((benzylamino)methyl)benzonitrile (410 mg, 1.84 mmol) was added followed by K_2CO_3 (255 mg, 1.84 mmol) to give **S11** with 91% yield. **IR (neat):** ν_{max}/cm^{-1} 3029, 2958, 2817, 2228, 2147, 1740, 1693, 1647, 1608, 1499, 1450, 1406, 1367, 1249, 1123, 1076, 1023; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 (q, *J* = 7.6 Hz, 4H), 7.28 – 7.24 (m, 1H), 6.09 (dt, *J* = 11.1, 6.8 Hz, 1H), 5.66 (d, *J* = 11.0 Hz, 1H), 3.63 (d, *J* = 8.6 Hz, 4H), 3.35 (d, *J* = 6.8 Hz, 2H), 0.19 (s, 9H); **^{13}C NMR (100 MHz, CDCl3)**:δ 145.6, 141.4, 138.8, 132.2, 129.4, 128.9, 128.4, 127.3, 119.1, 112.2, 110.7, 101.2, 100.5, 58.5, 57.7, 52.9, 0.01; **HRMS (ESI):** Calc. for $C_{23}H_{27}N_2Si$ $[M+H]^+$: 359.1944; Found: 359.1943.



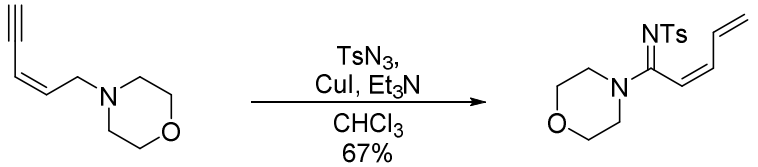
(f) Preparation of enynamines 1, 6, 7, 9, 13, 17, 21: To the ice cooled solution of (*Z*)-*N,N*-disubstituted-5-(trimethylsilyl)pent-2-en-4-yn-1-amine (1 equivalent) in THF was added TBAF (0.5 equivalent) and allowed to stir for two hours. The reaction was quenched by saturated NH_4Cl and extracted by ethyl acetate. The solvent was evaporated and obtained product was used further without any purification.

General procedure A: Cu(I)-catalyzed formation of conjugated amidines (acyclic and cyclic) and dihydro pyridines.



Scheme S2. Cu(I)-catalyzed reaction of enynamines **1**, **6**, **7**, **9**, **13**, **17**, **21**.

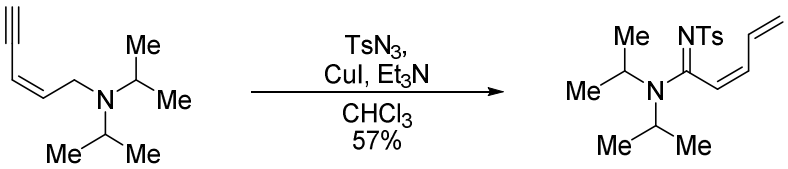
To the solution of eneynamine (1 equiv) in chloroform was added tosyl azide (1.2 equiv), Et_3N (1.5 equiv) followed by CuI (10 mol%) and stirred for 30 minutes at room temperature. The reaction was quenched by saturated NH_4Cl and compound was extracted in chloroform. Solvent was evaporated and obtained crude product was purified by column chromatography (20 - 30% EtOAc in Hexane) to afford desired compound and yields were calculated over two steps.



1 **1a**

Compound 1a: Compound **1a** (67%) was formed by following the general procedure **A.**

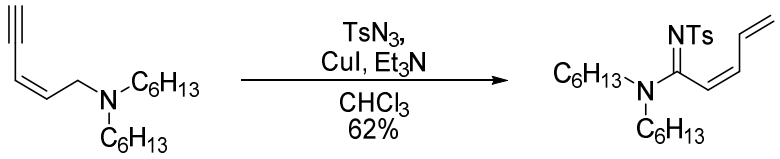
Physical state: Colorless semi-solid. **IR (neat):** ν_{max}/cm^{-1} 3743, 3678, 3648, 3619, 2967, 2921, 2861, 2319, 1740, 1693, 1643, 1595, 1519, 1476, 1444, 1346, 1273, 1190, 1141, 1114, 1087; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.30 (t, *J* = 11.4 Hz, 1H), 6.16 (d, *J* = 11.5 Hz, 1H), 5.96 (dt, *J* = 16.7 Hz, 10.7 Hz, 1H), 5.32 (d, *J* = 16.9 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 3.81 (t, *J* = 4.5 Hz, 2H), 3.68 (t, *J* = 5.0 Hz, 2H), 3.59 (t, *J* = 5.0 Hz, 2H), 3.46 (t, *J* = 5.0 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.1, 142.1, 140.2, 135.4, 131.3, 129.1, 126.9, 123.6, 120.3, 66.7, 66.3, 47.9, 44.7, 21.5; **HRMS (ESI):** Calc. for $C_{16}H_{21}N_2O_3S$ $[M+H]^+$: 321.1273; Found: 321.1281.



6 **6a**

Compound 6a: Compound **6a** (57%) was formed by following the general procedure **A.**

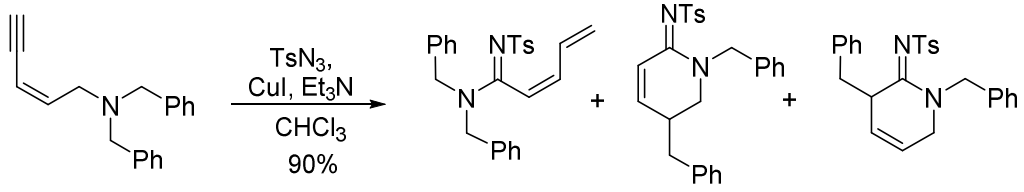
Physical state: Colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3740, 3672, 3642, 3615, 2950, 2922, 2860, 2314, 1733, 1705, 1691, 1641, 1602, 1524, 1461, 1370, 1280, 1141, 1082; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.26 – 6.01 (m, 3H), 5.25 (d, *J* = 16.4 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 4.23 (sept, *J* = 6.7 Hz, 1H), 3.64 (sept, *J* = 6.7 Hz, 1H), 2.34 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 162.1, 141.4, 141.1, 133.4, 131.8, 128.8, 126.5, 122.8, 121.6, 52.0, 47.9, 21.4, 20.4, 19.9; **HRMS (ESI):** Calc. for $C_{18}H_{27}N_2O_2S$ $[M+H]^+$: 335.1793; Found: 335.1793.



7 **7a**

Compound 7a: Compound **7a** (62%) was formed by following the general procedure **A.**

Physical state: Colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3744, 3678, 3648, 3619, 2954, 2927, 2861, 2318, 1739, 1707, 1693, 1645, 1606, 1529, 1463, 1372, 1282, 1145, 1088; **^{1}HNMR (400 MHz, $CDCl_3$)**: δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.28 (t, *J* = 11.2 Hz, 1H), 6.17 (d, *J* = 11.5 Hz, 1H), 6.0 (dt, *J* = 16.8 Hz, 10.2 Hz, 1H), 5.32 (d, *J* = 16.7 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 3.49 (br.s, 2H), 3.26 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.46 (m, 2H), 1.25 (m, 14H), 0.88 (td, *J* = 7.12 Hz, 2.45 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.2, 142.5, 141.0, 134.0, 131.7, 128.8, 126.6, 122.2, 121.6, 50.0, 48.1, 31.4, 31.3, 28.4, 26.9, 26.7, 26.3, 22.5, 22.4, 21.4, 13.9, 13.8; **HRMS (ESI):** Calc. for $C_{24}H_{39}N_2O_2S$ $[M+H]^+$: 419.2732; Found: 419.2732.



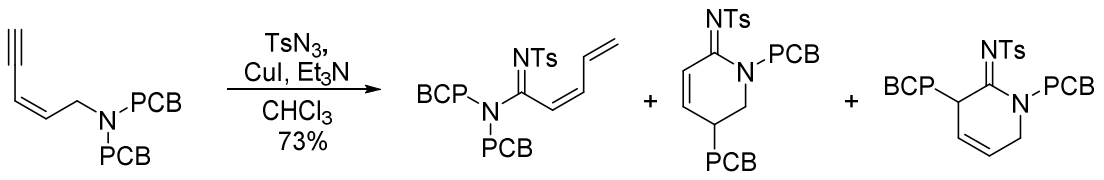
9 **9a** **9b** **9c**

Compounds **9a** (23%), **9b** (51%) and **9c** (16%) were formed by following the general procedure **A.**

Compound 9a: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3744, 3027, 2925, 2864, 1739, 1692, 1639, 1533, 1484, 1383, 1342, 1273, 1139, 1083, 1026; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.40-7.31 (m, 6H), 7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 6.5 Hz, 2H), 6.33 (m, 2H), 6.08 (m, 1H), 5.35 (dt, *J* = 16.7 Hz, 0.7 Hz, 1H), 5.22 (d, *J* = 10 Hz, 1H), 4.72 (br.s, 2H), 4.5 (s, 2H), 2.4 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 165.3, 141.8, 137.1, 135.2, 130.2, 129.1, 128.7, 128.1, 128.1, 126.5, 126.2, 121.9, 53.2, 48.2, 21.5; **HRMS (ESI):** Calc. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 431.1793; Found: 431.1785.

Compound 9b: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3742, 3029, 2924, 2863, 1740, 1691, 1638, 1531, 1481, 1382, 1340, 1270, 1137, 1081, 1025; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.33 (m, 3H), 7.24 – 7.20 (m, 9H), 6.84 (dd, *J* = 7.7 Hz, 2.3 Hz, 2H), 6.58 (dd, *J* = 9.8 Hz, 4.16 Hz,1H), 4.92 (d, *J* = 14.4 Hz, 1H), 4.51 (d, *J* = 14.4 Hz, 1H), 3.37 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 3.17 (dd, *J* = 12.7 Hz, 5.8 Hz, 1H), 2.67 (m, 2H), 2.41 (dd, *J* = 11.4, 4.6 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 157.9, 144.0, 142.1, 141.2, 137.7, 135.9, 129.2, 128.9, 128.9, 128.7, 128.6, 128.1, 126.8, 126.4, 119.9, 52.8, 48.9, 37.3, 35.7, 21.6; **HRMS (ESI):** Calc. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 431.1793; Found: 431.1790.

Compound 9c: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3743, 3030, 2925, 2859, 1708, 1647, 1597, 1552, 1516, 1495, 1450, 1341, 1270, 1141, 1084, 1029; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.21 (m, 10H), 7.09 (dd, *J* = 7.1 Hz, 1.6 Hz, 2H), 5.74 (m, 2H), 4.91 (d, *J* = 14.5 Hz, 1H), 4.74 (m, 1H), 4.26 (d, *J* = 14.6 Hz, 1H), 3.50 (m, 1H), 3.35 (dd, *J* = 13.0 Hz, 7.7 Hz, 1H), 3.06 (d, *J* = 17.5 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.3, 141.7, 141.6, 137.0, 135.2, 130.1, 129.1, 128.7, 128.0, 128.0, 127.8, 126.6, 126.4, 126.1, 121.7, 53.1, 48.1, 40.4, 40.2, 21.4; **HRMS (ESI):** Calc. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 431.1793; Found: 431.1792.



13 **13a** **13b** **13c**

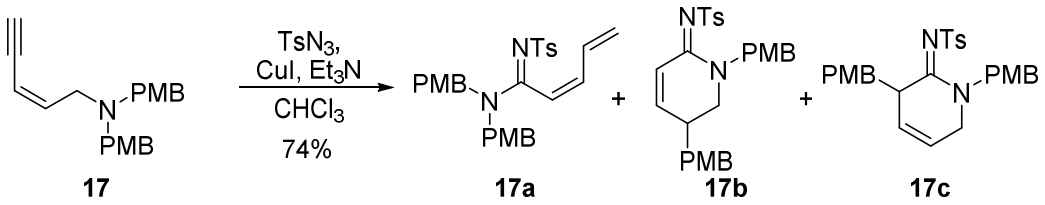
PCB = *4-cyano benzyl*

Compounds **13a** (13%), **13b** (37%) and **13c** (23%) were formed by following the general procedure **A.**

Compound 13a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3022, 2918, 2218, 1713, 1625, 1545, 1488, 1441, 1412, 1338, 1276, 1225, 1178, 1141, 1083, 1021;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 – 7.67 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 4H), 6.43 (t, *J* = 11.4 Hz, 1H), 6.24 (d, *J* = 11.6 Hz, 1H), 6.05 (dt, *J* = 16.8, 10.6 Hz, 1H), 5.42 (d, *J* = 16.7 Hz, 1H), 5.31 (d, *J* = 10.1 Hz, 1H), 4.77 – 4.66 (m, 2H), 4.61 (s, 2H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 164.6, 142.6, 140.8, 140.1, 139.7, 136.1, 133.0, 132.6, 130.9, 129.1, 129.0, 127.8, 126.7, 124.4, 119.9, 52.2, 50.3, 29.7, 21.5; **HRMS (ESI):** Calc. for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$: 481.1698; Found: 481.1702.

Compound 13b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3013, 2927, 2238, 1711, 1609, 1552, 1491, 1452, 1422, 1345, 1273, 1218, 1171, 1141, 1086, 1021;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 8.4, 3.4 Hz, 4H), 7.29 (dd, *J* = 13.3, 8.4 Hz, 6H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.56 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.77 (d, *J* = 15.0 Hz, 1H), 4.64 (d, *J* = 15.0 Hz, 1H), 3.44 (dd, *J* = 12.9, 5.5 Hz, 1H), 3.18 (dd, *J* = 12.8, 6.6 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.63 (td, *J* = 10.6, 3.9 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.70, 143.30, 142.87, 141.22, 140.65, 138.71, 132.67, 132.63, 129.67, 129.34, 128.90, 128.67, 126.34, 120.38, 118.74, 111.20, 55.88, 52.91, 50.07, 37.67, 35.18, 21.59; **HRMS (ESI):** Calc. for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$: 481.1698;Found: 481.1699.

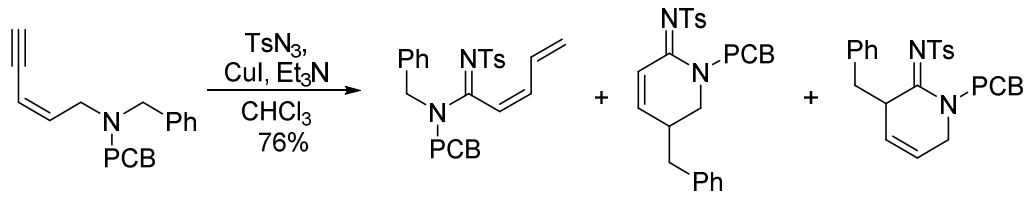
Compound 13c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3018, 2925, 2226, 1702, 1601, 1554, 1491, 1447, 1414, 1344, 1269, 1209, 1174, 1149, 1088, 1011; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.83 (dd, *J* = 10.0, 4.1 Hz, 1H), 5.77 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.94 (d, *J* = 15.1 Hz, 1H), 4.77 (s, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 3.64 (d, *J* = 15.7 Hz, 1H), 3.38 (m, 3H), 2.98 (s, 3H), 2.90 (s, 3H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 164.5, 142.7, 142.4, 140.8, 140.5, 132.5, 131.9, 130.7, 129.2, 128.2, 126.1, 126.0, 121.9, 118.8, 118.3, 111.7, 110.8, 53.1, 49.0, 40.5, 39.9, 21.5; **HRMS (ESI):** Calc. for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$: 481.1698; Found: 481.1697.



Compounds **17a** (0%), **17b** (62%) and **17c** (12%) were formed by following the general procedure **A.**

Compound 17b: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3743, 3007, 2927, 2839, 1638, 1610, 1533, 1510, 1479, 1382, 1350, 1274, 1244, 1173, 1139, 1083, 1030; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.20 (dd, *J* = 10.0 Hz, 4.2 Hz, 1H), 7.1 (d, *J* = 8.7 Hz, 2H), 6.8 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 4H), 6.51 (dd, *J* = 10.0 Hz, 4.2 Hz, 1H), 4.83 (d, *J* = 14.2 Hz, 1H), 4.41 (d, *J* = 14.3 Hz, 1H), 3.8 (s, 3H), 3.77 (s, 3H), 3.32 (dd, *J* = 13.0 Hz, 5.7 Hz, 1H), 3.12 (dd, *J* = 12.7 Hz, 5.84 Hz, 1H), 2.58 (m, 2H), 2.4 (s, 3H), 2.36 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.4, 158.4, 157.8, 144.0, 142.0, 141.3, 130.0, 129.9, 129.6, 129.2, 128.0, 126.4, 119.9, 114.2, 114.1, 55.4, 55.3, 52.1, 48.7, 36.5, 35.8, 21.5; **HRMS (ESI):** Calc. for $C_{28}H_{31}N_2O_4S$ $[M+H]^+$: 491.2005; Found: 491.2006.

Compound 17c: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3011, 2928, 2838, 1673, 1607, 1551, 1509, 1338, 1243, 1173, 1138, 1243, 1173, 1138, 1082, 1031; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 5.78 – 5.67 (m, 2H), 4.76 (d, *J* = 14.3 Hz, 1H), 4.69 (s, 1H), 4.25 (d, *J* = 14.3 Hz, 1H), 3.86 – 3.81 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.48 (m, 1H), 3.35 (dd, *J* = 13.3, 7.5 Hz, 1H), 3.15 (dd, *J* = 13.3, 3.4 Hz, 1H), 3.00 (d, *J* = 17.5 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.1, 159.2, 158.5, 141.8, 141.7, 131.1, 129.7, 129.1, 129.0, 127.2, 126.4, 126.1, 121.8, 114.0, 113.3, 55.2, 52.5, 47.9, 40.5, 39.3, 21.4; **HRMS (ESI):** Calc. for $C_{28}H_{31}N_2O_4S$ $[M+H]^+$: 491.2005; Found: 491.2004.



21 **21a** **21b** **21c**

PCB = *4-cyano benzyl*

Compounds **21a** (14%), **21b** (39%) and **21c** (23%) were formed by following the general procedure **A.**

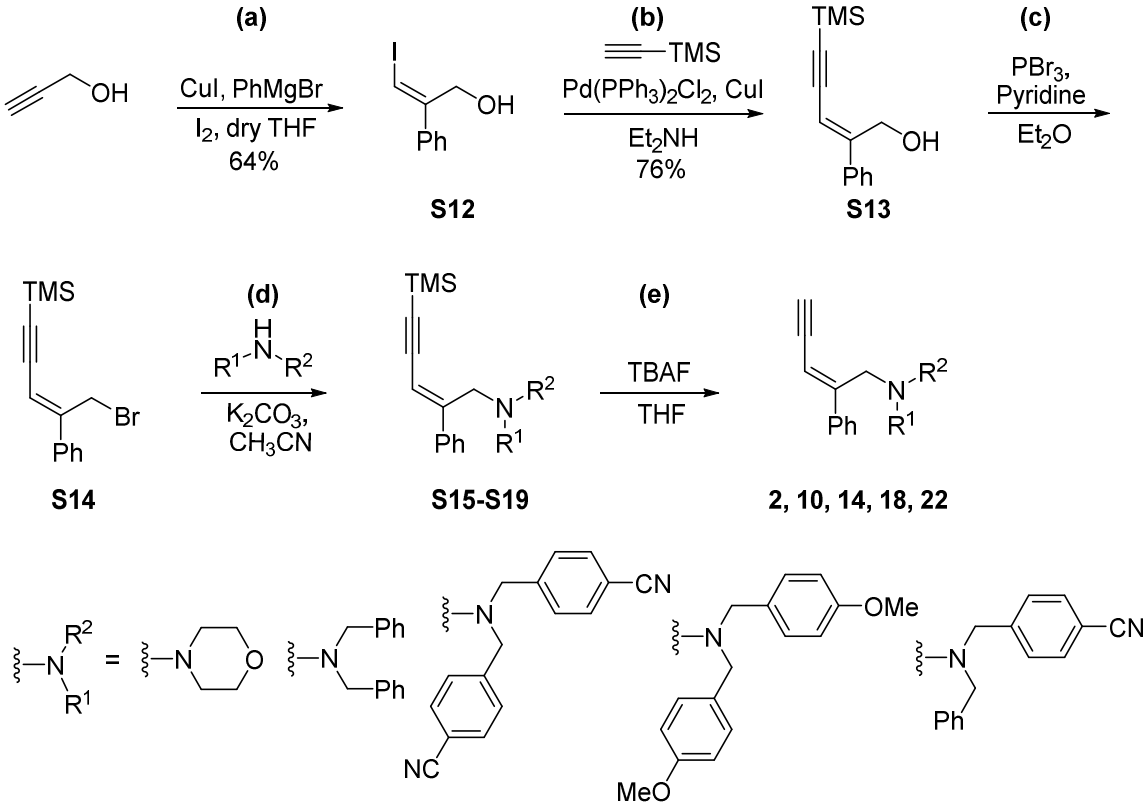
Compound 21a: Physical state: Compound **21a** could not be isolated in a pure form as it was inseparable from **21b** therefore it is characterized as mixture of **21a** and **21b**.**^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1.37H), 7.57 (d, *J* = 8.3 Hz, 1.24H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.36 (m, 4H), 7.31 – 7.19 (m, 13H), 7.11 (d, *J* = 8.4 Hz, 3H), 6.48 – 6.33 (m, 0.7H), 6.26 (dd, *J* = 23.8, 11.8 Hz, 0.7H), 6.07 (dq, *J* = 16.7, 10.6 Hz, 0.72H), 5.86 – 5.72 (m, 2H), 5.46 – 5.32 (m, 0.87H), 5.26 (t, *J* = 10.9 Hz, 0.7H), 4.90 (d, *J* = 15.2 Hz, 1H), 4.77 (m, 1H), 4.70 – 4.60 (m, 1H), 4.59 – 4.38 (m, 2H), 4.17 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.45 – 3.36 (m, 1H), 3.22 (dd, *J* = 13.1, 3.3 Hz, 1H), 3.10 (dd, *J* = 11.8, 10.2 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 2.6H); **HRMS (ESI):** Calc. for $C_{27}H_{26}N_3O_2S$ $[M+H]^+$: 456.1746; Found: 456.1753.

Compound 21b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3022, 2921, 2233, 1713, 1625, 1546, 1487, 1452, 1418, 1344, 1268, 1213, 1172, 1143, 1080, 1029; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.21 (m, 9H), 6.95 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.62 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.76 (d, *J* = 15.0 Hz, 1H), 4.64 (d, *J* = 15.0 Hz, 1H), 3.38 (dd, *J* = 12.8, 5.8 Hz, 1H), 3.19 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.83 – 2.70 (m, 2H), 2.59 – 2.49 (m, 1H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 157.94, 144.50, 142.29, 141.34, 140.74, 137.25, 132.49, 129.19, 128.83, 128.81, 128.73, 126.97, 126.27, 119.67, 118.46, 111.78, 52.84, 50.00, 37.44, 35.61, 21.49; **HRMS (ESI):** Calc. for $C_{27}H_{26}N_3O_2S$ $[M+H]^+$: 456.1746; Found: 456.1753.

Compound 21c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3038, 2930, 2231, 1713, 1612, 1548, 1492, 1451, 1416, 1345, 1272, 1214, 1171, 1146, 1085, 1022; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.17 (m, 6H), 7.05 (d, *J* = 6.4 Hz, 2H), 5.79 – 5.73 (m, 1H), 5.73 – 5.65 (m, 1H), 4.72 (s, 1H), 4.63 (d, *J* = 14.4 Hz, 1H), 4.45 (d, *J* = 14.4 Hz, 1H), 3.63 – 3.51 (m, 1H), 3.39

(dd, J = 13.0, 8.0 Hz, 1H), 3.32 (dd, J = 12.9, 3.5 Hz, 1H), 3.19 (d, J = 19.6 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.2, 142.8, 142.0, 141.3, 134.8, 131.8, 130.7, 129.2, 128.8, 128.3, 128.1, 126.1, 125.8, 122.2, 118.9, 110.6, 53.3, 48.3, 40.3, 40.1, 21.3; **HRMS (ESI):** Calc. for $C_{27}H_{26}N_3O_2S$ $[M+H]^+$: 456.1746; Found: 456.1753.

General procedure for the synthesis of enynamines 2, 10, 14, 18, 22:



Scheme S3. Synthesis of enynamines **2**, **10**, **14**, **18**, **22**.

(a) Synthesis of *(Z)*-3-iodo-2-phenylprop-2-en-1-ol S12:[S3] To a solution of propargyl alcohol (1.0 g, 17.8mmol) and CuI (338 mg, 1.7 mmol) in dry THF (20 mL) was added 3.0 M PhMgBr (15 mL, 44.5 mmol) at -10 ^{0}C. Upon complete addition of Grignard reagent, the reaction mixture was allowed to come at room temperature and stirred for overnight. The resultant mixture was then cooled to -78 ^{o}C and then added a solution of I_2 (9.0 g, 35.6 mmol) in THF (20 mL), the reaction mixture was allowed to cool at room temperature and stirred for 1 hour then cooling at 0 ^{o}C, the reaction mixture was quenched by saturated NH_4Cl. The reaction mixture was brought to room temperature and extracted with EtOAc, washed with

brine dried over Na_2SO_4 and concentrated under reduced pressure. The obtained compound was purified by column chromatography to give **S12** with 64% of yield.

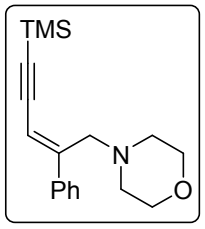
(b) Synthesis of *(Z)*-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol S13: To a solution of *(Z)*-3-iodo-2-phenylprop-2-en-1-ol **S12** in Et_2NH (0.5 M) was added $(Ph_3P)_2PdCl_2$ (2 mol %)and CuI (4 mol %) at 0 ºC. The system was degassed by N_2 and the resulting was added trimethyl silyl acetylene (1.3 equiv). Then it was warmed up to room temperature. The reaction was monitored by TLC. When the reaction completed, the reaction mixture was concentrated, and the residue was purified through silica gel flash column.

(c) Synthesis of *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane S14: To a solution of *(Z)*-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol **S13** (1 equiv.) in Et_2O was added pyridine (0.06 equiv.) and PBr_3 (0.45 equiv.) at 0 °C. The reaction was warmed to room temperature with additional stirring for 1 h. After completion of reaction, the mixture was quenched by ice cubes and extracted in EtOAc. Solvent was removed and obtained product was used for next reaction without purification.

IR (neat): ν/cm^{-1} 3060, 2959, 2852, 2148, 1644, 1597, 1492, 1447, 1339, 1250, 1197, 1077, 990; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.44 – 7.37 (m, 3H), 6.07 (s, 1H), 4.65 (s, 2H), 0.30 (s, 8H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.4, 137.3, 128.9, 128.7, 125.8, 110.8, 104.9, 101.6, 29.7, -0.13; **HRMS (ESI):** Calc. for $C_{14}H_{18}BrSi$ $[M+H]^+$: 293.0361, Found: 293.0370.

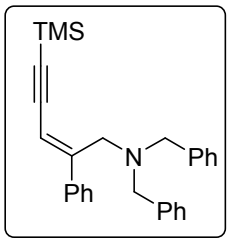
(d) Synthesis of TMS-protected enynamines S15-S19: To the solution of substituted *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** in acetonitrile was added the amine (1.2 equiv) at 0 ^{o}C drop wisely followed by the addition of K_2CO_3 (1.5 equiv) and allowed to warm at room temperature and stirred for 4 h. The reaction mixture was washed with water and extracted with EtOAc and purified by column chromatography.

***(Z)*-4-(2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)morpholine S15:** The compound **S15** was prepared by following the above procedure (**d**). *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added morpholine (115 µL, 1.36 mmol) followed by the addition of



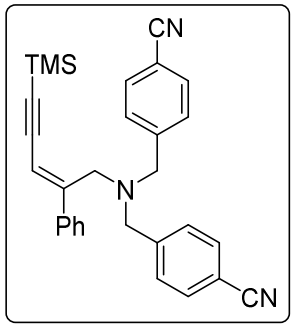
K_2CO_3 (190 mg, 1.36 mmol) to give **S15** as a yellow liquid with 90% of yield. **IR (neat):** ν/cm^{-1} 2955, 2853, 2809, 2144, 1705, 1512, 1450, 1364, 1325, 1290, 1245, 1242, 1211, 1115, 1071, 1000; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (m, 2H), 7.34 – 7.28 (m, 3H), 6.03 (s, 1H), 3.63 (t, *J* = 5.6 Hz, 6H), 2.5 (t, *J* = 4.5 Hz, 4H), 0.22 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 149.0, 139.8, 128.4, 126.3, 110.7, 103.1, 101.6, 67.1, 59.0, 53.5, 0.05; **HRMS (ESI):** Calc. for $C_{18}H_{26}NOSi$ $[M+H]^+$: 300.1784, Found: 300.1777.

***(Z)*-*N*,*N*-dibenzyl-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S16:** The compound **S16** was prepared by following the above procedure (d). *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 °C and to the reaction mixture was added dibenzylamine (260 µL, 1.36 mmol) followed by the addition of K_2CO_3 (190 mg, 1.36 mmol) to give **S16** as a yellow liquid with 92% of yield.

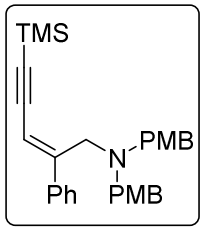


IR (neat): ν/cm^{-1} 3028, 2958, 2798, 2147, 1742, 1599, 1493, 1448, 1363, 1326, 1248, 1119, 1071, 992; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 – 7.18 (m, 11H), 7.11 (d, *J* = 7.2 Hz, 4H), 5.92 (s, 1H), 3.71 (s, 2H), 3.48 (s, 4H), 0.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 152.1, 139.5, 139.4, 129.3, 128.1, 128.0, 126.9, 110.1, 103.1, 101.2, 58.2, 54.4, 0.14; **HRMS (ESI):** Calc. for $C_{28}H_{32}NSi$ $[M+H]^+$: 410.2304, Found: 410.2305.

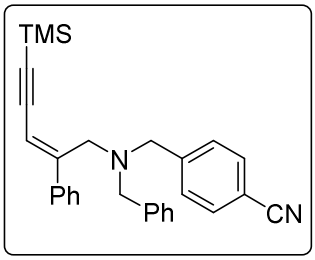
***(Z)*-4,4'-(((2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)azanediyl)bis(methylene))dibenzonitrile S17:** The compound **17a** was prepared by following the above procedure (d). *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 °C and to the reaction mixture was added dibenzylamine (338 mg, 1.36 mmol) followed by the addition of K_2CO_3 (190 mg, 1.36 mmol) to give **S17** as a yellow liquid with 93% of yield. **IR (neat):** ν/cm^{-1} 3021, 2959, 2826, 2228, 2137, 1706, 1500, 1448, 1411, 1367, 1248, 1099, 1017; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 8.3 Hz, 4H), 7.37 (t, *J* = 7.1 Hz,1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 4H), 7.14 (d, *J* = 7.0 Hz, 2H), 5.94 (s, 1H), 3.75 (s, 2H), 3.58 (s, 4H), 0.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 150.7, 144.6, 139.1, 132.0, 129.6, 128.5, 128.2, 126.6, 118.8, 111.2, 111.1, 102.5, 101.9, 58.0, 54.7, 0.0; **HRMS (ESI):** Calc. for $C_{30}H_{30}N_3Si$ $[M+H]^+$: 460.2209, Found: 460.2204.



***(Z)-N,N*-bis(4-methoxybenzyl)-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S18:** The compound **S18** was prepared by following the above procedure (d). *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added dibenzylamine (350 mg, 1.36 mmol) followed by the addition of K_2CO_3 (190 mg, 1.36 mmol) to give **S18** as a yellow liquid with 90% of yield. **IR (neat):** ν/cm^{-1} 3001, 2955, 2831, 2135, 1694, 1609, 1509, 1451, 1365, 1299, 1242, 1174, 1099, 1034; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.23 (m, 6H), 7.06 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 5.96 (s, 1H), 3.81 (s, 6H), 3.72 (s, 2H), 3.44 (s, 4H), 0.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 154.2, 148.0, 135.0, 127.2, 126.0, 123.7, 123.6, 122.6, 109.0, 105.5, 100.0, 98.8, 96.7, 52.9, 50.9, 49.7, -4.2, -4.3; **HRMS (ESI):** Calc. for $C_{30}H_{36}NO_2Si$ $[M+H]^+$: 470.2515, Found: 470.2514.



***(Z)*-4-((benzyl(2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)amino)methyl) benzonitrile S19:** The compound **S19** was prepared by following the above procedure (d). *(Z)*-(5-bromo-4-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S14** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added 4-((benzylamino)methyl)benzonitrile (302 mg, 1.36 mmol) followed by the addition of K_2CO_3 (190 mg, 1.36 mmol) to give **S19** as a yellow liquid with 84% of yield. **IR (neat):** ν/cm^{-1} 3021, 2959, 2826, 2228, 2137, 1706, 1500, 1448, 1411, 1367, 1248, 1099, 1017; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.26 (m, 7H), 7.19 (m, 3H), 7.16 (d, *J* = 6.3 Hz, 2H), 5.95 (s, 1H), 3.76 (s, 2H), 3.57 (s, 2H), 3.53 (s, 2H), 0.29 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.1, 141.2, 134.8, 134.3, 127.5, 125.2, 124.9, 124.0, 123.9, 123.8, 122.9, 122.4, 114.8, 106.2, 98.5, 97.2, 54.3, 53.3, 50.2, -4.3, -4.2; **HRMS (ESI):** Calc. for $C_{29}H_{31}N_2Si$ $[M+H]^+$: 435.2257, Found: 435.2259.

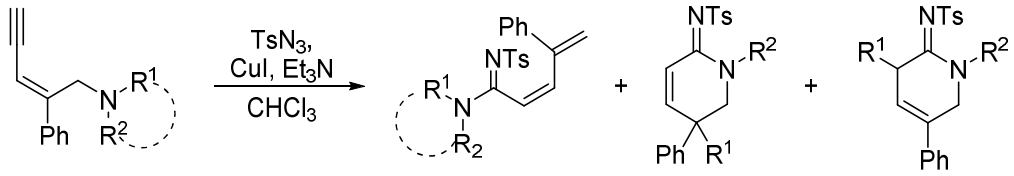


(e) Preparation of enynamines 2, 10, 14, 18, 22:

To the solution of (*Z*)-*N,N*-disubstituted-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine in THF was added TBAF (0.5 equiv) at 0 ^{o}C. Then reaction mixture allowed to warm at room temperature and reaction was monitored by TLC. When reaction was completed, the reaction

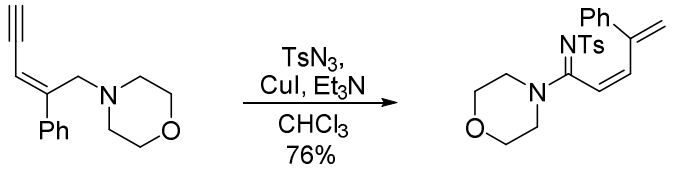
mixture was quenched by saturated NH_4Cl. The compound was extracted with ethyl acetate and used further for next reaction without any purification.

General procedure A: Cu(I)-catalyzed formation of conjugated amidines (acyclic and cyclic) and dihydro pyridines.



Scheme S4. Cu(I)-catalyzed reaction of enynamines **2**, **10**, **14**, **18**, **22**.

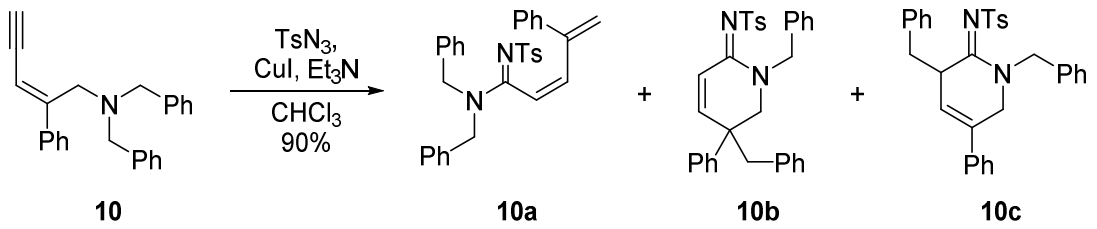
To the solution of enynamine (1 equiv) in chloroform was added tosyl azide (1.2 equiv), Et_3N (1.5 equiv) followed by CuI (10 mol%) and stirred for one hour at room temperature. The reaction was quenched by saturated NH_4Cl and compound was extracted in chloroform. Solvent was evaporated and obtained crude product was purified by column chromatography (20 – 30% EtOAc in Hexane) to afford desired compound.



2 **2a**

Compound **2a** (76%) was formed on by following the general procedure **A.**

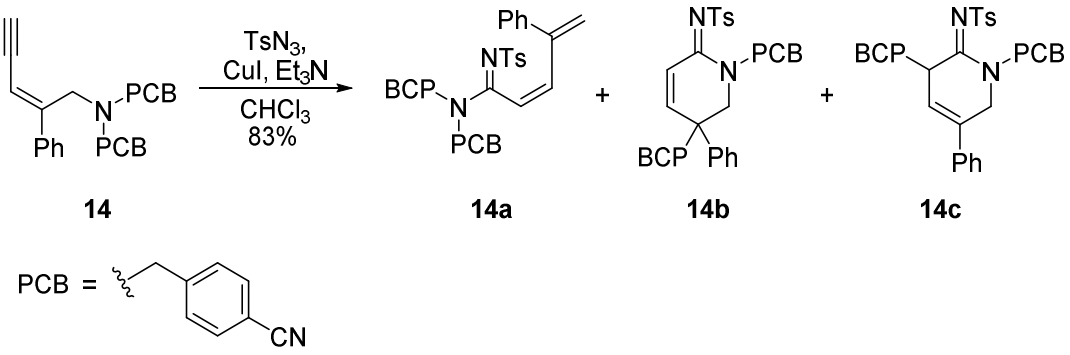
Compound 2a: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 2967, 2920, 2860, 1721, 1597, 1521, 1443, 1344, 1344, 1275, 1225, 1150, 1113, 1088, 1029; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 6.6, 3.3 Hz, 3H), 7.32 – 7.22 (m, 7H), 6.71 (dd, *J* = 12.4, 0.8 Hz, 1H), 6.48 (d, *J* = 12.5 Hz, 1H), 5.52 (s, 1H), 5.44 (s, 1H), 3.46 (dd, *J* = 11.3, 6.4 Hz, 4H), 3.34 (s, 2H), 2.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.2, 143.8, 142.2, 140.6, 138.2, 136.4, 129.2, 128.5, 128.4, 126.7, 126.7, 120.7, 120.4, 66.3, 65.7, 47.6, 44.1, 29.8, 21.6; **HRMS (ESI):** Calc. for $C_{22}H_{25}N_2O_3S$ $[M+H]^+$: 397.1586; Found: 397.1584.



Compounds **10a** (0%), **10b** (50%), and **10c** (40%) were formed by following the general procedure **A.**

Compound 10b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1}3008, 2931, 2838, 1621, 1577, 1534, 1514, 1467, 1441, 1381, 1275, 1246, 1174, 1140, 1113, 1084, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 10.2 Hz, 1H), 7.28 – 7.08 (m, 11H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.98 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.79 (d, *J* = 10.2 Hz, 1H), 6.65 (d, *J* = 6.8 Hz, 2H), 4.81 (d, *J* = 14.6 Hz, 1H), 4.54 (d, *J* = 14.6 Hz, 1H), 3.58 (s, 2H), 3.04 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 13.5 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.8, 146.6, 142.0, 141.2, 140.8, 135.3, 135.2, 130.4, 129.2, 128.7, 128.4, 128.1, 127.8, 127.4, 127.0, 126.5, 126.4, 120.1, 56.2, 52.9, 44.7, 44.0, 21.6; **HRMS (ESI):** Calc. for $C_{32}H_{31}N_2O_2S$ $[M+H]^+$: 507.2106; Found: 507.2115.

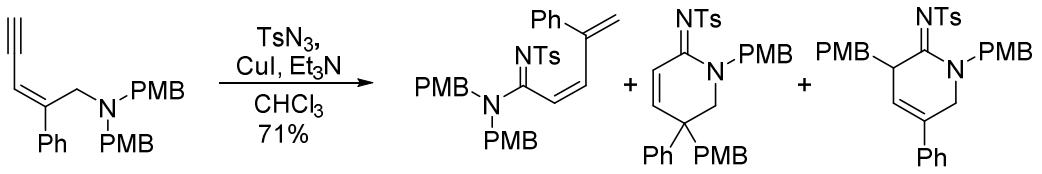
Compound 10c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3018, 2935, 2831, 1624, 1575, 1535, 1511, 1471, 1444, 1382, 1271, 1244, 1184, 1148, 1121, 1094, 1038; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.29 – 7.17 (m, 11H), 7.13 (m, 4H), 6.05 (dd, *J* = 5.6, 2.7 Hz, 1H), 4.94 (d, *J* = 14.5 Hz, 2H), 4.33 (d, *J* = 14.6 Hz, 1H), 3.77 (dd, *J* = 17.1, 1.7 Hz, 1H), 3.56 (dd, *J* = 13.1, 7.2 Hz, 1H), 3.29 (dd, *J* = 13.1, 3.5 Hz, 1H), 3.20 (dt, *J* = 17.1, 2.9 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.0, 141.8, 141.6, 136.9, 135.0, 133.4, 130.2, 129.1, 128.7, 128.7, 128.2, 128.1, 128.0, 127.8, 126.7, 126.2, 124.9, 122.3, 53.3, 49.9, 40.8, 40.4, 21.4; **HRMS (ESI):** Calc. for $C_{32}H_{31}N_2O_2S$ $[M+H]^+$: 507.2106; Found: 507.2115.



Compounds **14a** (0%), **14b** (51%), and **14c** (32%) were formed by following the general procedure **A.**

Compound 14b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3019, 2926, 2228, 1703, 1605, 1555, 1498, 1446, 1415, 1343, 1270, 1215, 1173, 1140, 1083, 1019; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 10.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.15 (m, 6H), 6.92 (t, *J* = 7.4 Hz, 4H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 10.3 Hz, 1H), 5.02 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 3.64 (d, *J* = 12.9 Hz, 1H), 3.56 (d, *J* = 12.9 Hz, 1H), 3.13 (d, *J* = 13.4 Hz, 1H), 2.96 (d, *J* = 13.4 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.5, 145.3, 142.4, 140.5, 140.5, 139.8, 132.3, 131.9, 130.9, 129.2, 128.9, 128.5, 127.9, 126.4, 126.3, 120.7, 118.4, 111.5, 111.2, 57.5, 52.7, 44.53, 44.1, 21.5; **HRMS (ESI):** Calc. for $C_{34}H_{29}N_4O_2S$ $[M+H]^+$: 557.2011; Found: 557.2012.

Compound 14c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3024, 2922, 2222, 1706, 1603, 1551, 1495, 1444, 1411, 1347, 1277, 1214, 1173, 1142, 1085, 1012; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.10 (m, 4H), 6.02 (dd, *J* = 5.5, 2.6 Hz, 1H), 4.96 (d, *J* = 15.2 Hz, 2H), 4.24 (d, *J* = 15.1 Hz, 1H), 3.89 (dd, *J* = 17.1, 1.7 Hz, 1H), 3.55 (dt, *J* = 17.1, 2.8 Hz, 1H), 3.44 (qd, *J* = 13.0, 5.7 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: 164.31, 142.84, 142.55, 140.76, 140.42, 136.10, 133.27, 132.62, 132.00, 130.86, 129.30, 129.09, 128.87, 128.33, 126.11, 124.81, 121.66, 118.85, 118.41, 111.92, 111.03, 53.29, 50.71, 40.74, 40.40, 21.58; **HRMS (ESI):** Calc. for $C_{34}H_{29}N_4O_2S$ $[M+H]^+$: 557.2011; Found: 557.2012.

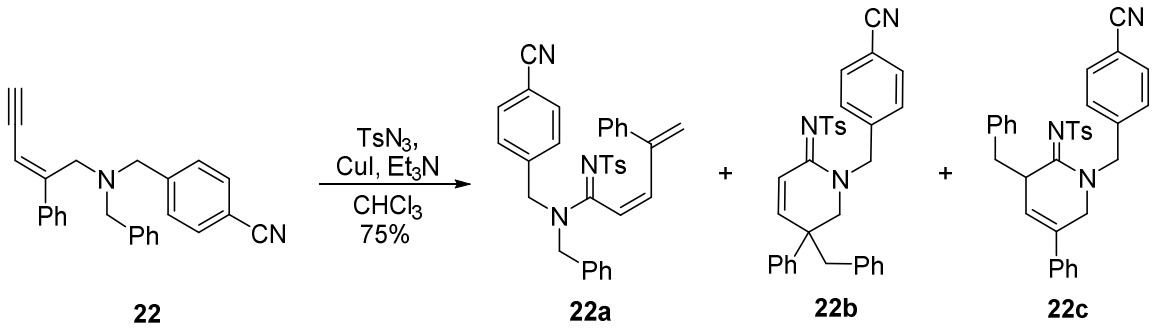


18 **18a** **18b** **18c**

Compounds**18a** (0%), **18b** (60%), and **18c** (11%) were formed by following the general procedure **A.**

Compound 18b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1}3011, 2924, 2840, 1638, 1609, 1535, 1510, 1477, 1379, 1351, 1276, 1244, 1173, 1138, 1113, 1082, 1030 ;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 10.2 Hz, 1H), 7.28 – 7.17 (m, 5H), 6.97 (m, 4H), 6.75 (d, *J* = 10.2 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.75 (d, *J* = 14.4 Hz, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.54 (s, 2H), 2.97 (d, *J* = 13.6 Hz, 1H), 2.85 (d, *J* = 13.7 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**:δ 159.24, 158.50, 157.68, 146.70, 141.98, 141.25, 140.97, 131.36, 129.85, 129.21, 128.63, 127.28, 127.23, 126.58, 126.42, 120.06, 114.06, 113.48, 55.85, 55.34, 55.22, 52.23, 44.02, 43.84, 21.57; **HRMS (ESI):** Calc. for $C_{34}H_{35}N_2O_4S$ $[M+H]^+$: 567.2317; Found:567.2314.

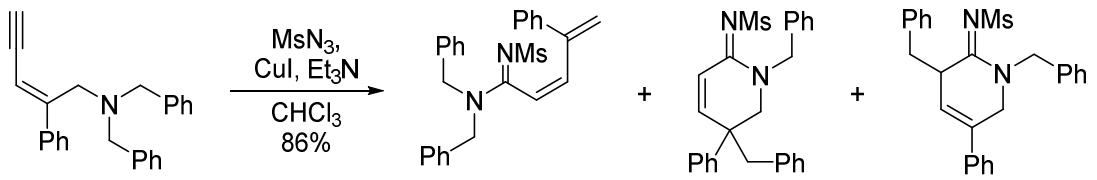
Compound 18c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3007, 2926, 2840, 1693, 1609, 1555, 1507, 1449, 1341, 1246, 1173, 1139, 1111, 1084, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.31 (dt, *J* = 7.9, 5.1 Hz, 7H), 7.13 (dd, *J* = 12.5, 8.0 Hz, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.03 (dd, *J* = 5.4, 2.3 Hz, 1H), 4.88 (s, 1H), 4.79 (d, *J* = 14.3 Hz, 1H), 4.35 (d, *J* = 14.3 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.75 (s, 1H), 3.52 (dd, *J* = 13.3, 7.0 Hz, 1H), 3.20 (dd, *J* = 10.6, 7.0 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.8, 159.3, 158.6, 141.7, 137.0, 133.2, 131.2, 129.7, 129.1, 128.9, 128.7, 128.1, 127.1, 126.2, 124.9, 122.4, 114.1, 113.4, 55.2, 55.2, 52.7, 49.7, 41.0, 39.5, 21.4; **HRMS (ESI):** Calc. for $C_{34}H_{35}N_2O_4S$ $[M+H]^+$: 567.2319; Found: 567.2314.



Compounds **22a** (0%), **22b** (50%), and **22c** (25%) were formed by following the general procedure **A.**

Compound 22b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1}3017, 2928, 2230, 1701, 1600, 1550, 1496, 1440, 1412, 1341, 1272, 1211, 1172, 1142, 1081, 1020; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 10.2 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.15 (m, 8H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 10.2 Hz, 1H), 6.74 (d, *J* = 6.5 Hz, 2H) 5.1 (d, *J* = 15.1 Hz, 1H), 4.21 (d, *J* = 15.1 Hz, 1H), 3.73 (d, *J* = 15.1 Hz,1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.58 (d, *J* = 12.8 Hz, 1H), 3.14 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 13.5 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.9, 146.7, 142.2, 140.7, 140.7, 135.0, 132.2, 130.3, 129.1, 128.7, 128.4, 128.2, 127.5, 127.1, 126.6, 126.3, 120.2, 118.5, 111.3, 57.4, 52.7, 44.8, 44.2, 29.7, 21.5; **HRMS (ESI):** Calc. for $C_{33}H_{30}N_3O_2S$ $[M+H]^+$: 532.2058; Found: 532.2057.

Compound 22c:Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1}3025, 2921, 2227, 1708, 1605, 1557, 1491, 1441, 1415, 1341, 1274, 1218, 1176, 1144, 1082, 1017; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz,2H), 7.36 (m, 3H), 7.22 (m, 7H), 7.16 (d, *J* = 7.6 Hz, 4H), 6.09 (dd, *J* = 5.6 Hz, 2.6 Hz, 1H), 4.97 (d, *J* = 15.1 Hz, 2H), 4.26 (d, *J* = 15.2 Hz, 1H), 3.75 (dd, *J* = 16.8 Hz, 1.6 Hz, 1H), 3.60 (dd, *J* = 13.1 Hz, 7.0 Hz, 1H), 3.27 – 3.20 (m, 2H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.1, 142.2, 141.2, 140.7, 136.8, 136.7, 133.2, 132.5, 130.3, 129.2, 128.9, 128.5, 128.4, 128.1, 127.0, 126.1, 124.9, 122.4, 118.5, 111.7, 53.2, 50.7, 40.7, 40.5, 21.6; **HRMS (ESI):** Calc. for $C_{33}H_{30}N_3O_2S$ $[M+H]^+$: 532.2059; Found: 532.2057.

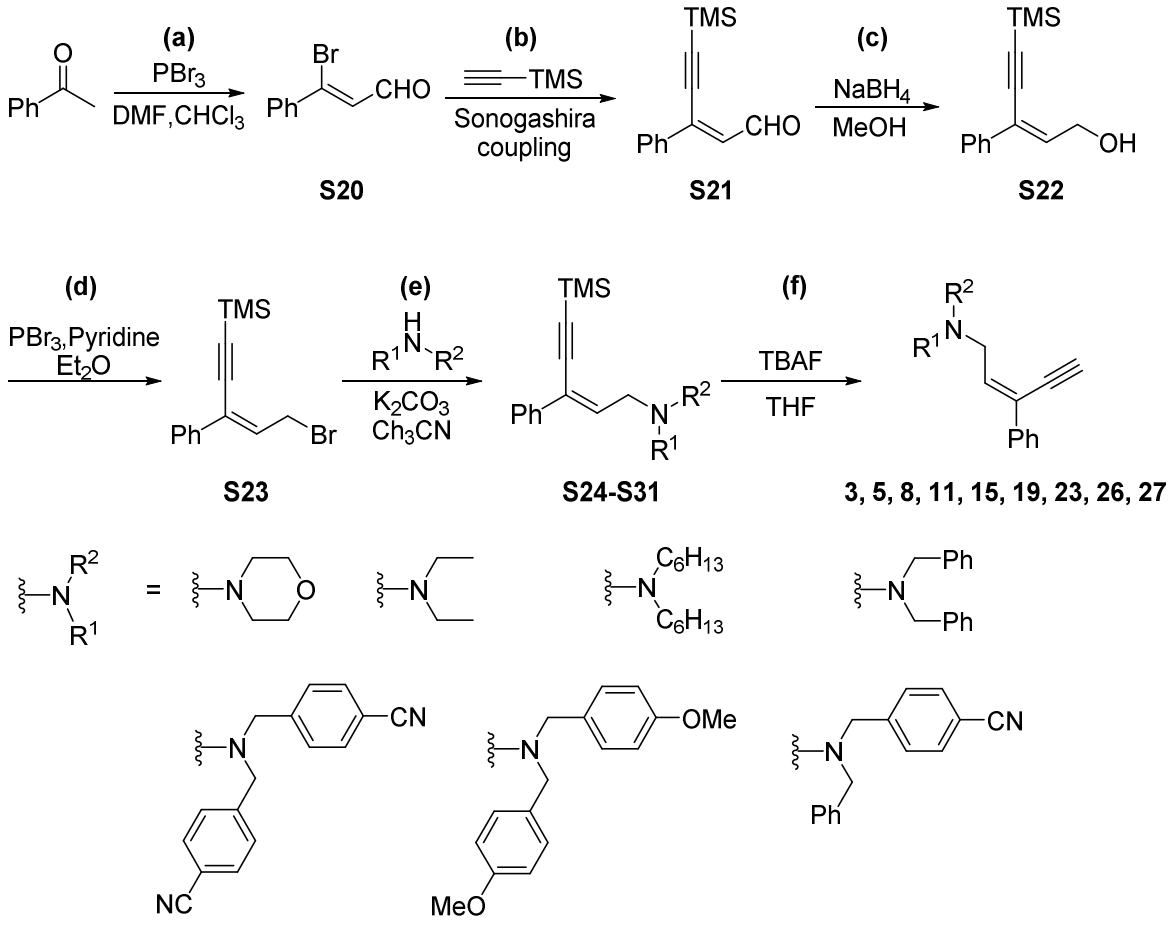


Compounds **25a** (0%), **25b** (52%), and **25c** (34%) were formed by following the general procedure **A.**

Compound 25b:Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3008, 2931, 2838, 1621, 1577, 1534, 1514, 1467, 1441, 1381, 1275, 1246, 1174, 1140, 1113, 1084, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26 (d, *J* = 10.3 Hz, 1H), 7.25 – 7.21 (m, 6H), 7.15 – 7.06 (m, 5H), 7.06 – 7.00 (m, 2H), 6.81 (d, *J* = 10.1 Hz, 1H), 6.67 (dd, *J* = 7.9, 1.4 Hz, 2H), 4.76 (d, *J* = 14.7 Hz, 1H), 4.49 (d, *J* = 14.7 Hz, 1H), 3.55 (s, 2H), 3.03 (d, *J* = 13.5 Hz, 1H), 3.00 (s, 3H), 2.95 (d, *J* = 13.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.6, 146.5, 140.9, 135.3, 135.2, 130.3, 128.7, 128.7, 128.2, 128.1, 127.8, 127.3, 126.9, 126.5, 120.2, 55.8, 52.7, 44.9, 44.0, 43.5; **HRMS (ESI):** Calc. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 431.1793; Found: 431.1791.

Compound 25c: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3018, 2933, 2833, 1618, 1574, 1544, 1524, 1471, 1446, 1382, 1277, 1252, 1175, 1143, 1133, 1082, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.26 (m, 7H), 7.21 – 7.16 (m, 6H), 7.09 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.00 (dd, *J* = 5.6, 2.7 Hz, 1H), 4.92 (d, *J* = 14.7 Hz, 1H), 4.83 – 4.73 (m, 1H), 4.32 (d, *J* = 14.7 Hz, 1H), 3.72 (d, *J* = 17.0 Hz, 1H), 3.50 (dd, *J* = 13.1, 7.2 Hz, 1H), 3.20 (dd, *J* = 13.1, 3.4 Hz, 1H), 3.15 (dt, *J* = 17.1, 2.8 Hz, 1H), 3.07 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.3, 137.0, 137.0, 135.2, 133.5, 130.3, 129.9, 129.1, 128.9, 128.8, 128.7, 128.3, 128.1, 128.0, 128.0, 127.4, 126.8, 125.2, 125.0, 122.3, 53.1, 49.8, 44.1, 41.0, 40.3; **HRMS (ESI):** Calc. for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$: 431.1793; Found: 431.1793.

General procedure for the synthesis of enynamines 3, 5, 8, 11, 15, 19, 23, 26, 27.



Scheme S5. Synthesis of enynamines **3**, **5**, **8**, **11**, **15**, **19**, **23**, **26**, **27**.

(a) Synthesis of (*Z*)-3-bromo-3-phenylacrylaldehyde S20:[S4] To a solution of DMF (167.9 mmol, 12.9 mL) in chloroform (80 mL), PBr_3 (152.8 mmol, 15.4 mL) was added dropwise at 0 ^oC. The mixture was stirred for 60 min, and then a solution of acetophenone (50.9 mmol) was added. The solution was stirred for 48 h at room temperature, and the content was poured to water (300 mL), neutralized with saturated $NaHCO_3$ and extracted with dichloromethane (3×150 mL). The extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by passing through short silica gel column to afford (*Z*)-3-bromo-3-phenylacrylaldehyde as yellow oil.

(b) Synthesis of (*Z*)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-ynal S21:The solution of (*Z*)-3-bromo-3-phenylacrylaldehyde in THF and triethyl amine (1.5 equiv) was degassed by N_2 for 10 minutes and trimethyl silyl acetylene (1.3 equiv) was added followed by PPh_3 (2

mol%) and degassed further for 5 minutes and $Pd(PPh_3)_2Cl_2$ (4 mol%) was added. CuI (4 mol%) was added after 10 minutes of degassing further at 0 ^oC and resulting reaction mixture was stirred for 24 h. After completion, reaction mixture was filtered through celite pad and washed with sat $NaHCO_3$ and extracted in ethyl acetate. The obtained crude product was carried forward for reduction without any purification.

(c) Synthesis of (*Z*)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol S22: The crude product **S21** was dissolved in MeOH and cooled to 0 ^oC and then was added $NaBH_4$ (1 equiv) and stirred for 30 minutes. Reaction was quenched with saturated NH_4Cl and compound was extracted with EtOAc and purified by column chromatography. The two step yield was 79%.

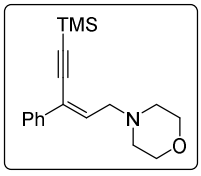
(d) Synthesis of (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane S23: (*Z*)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol was dissolved in diethyl ether and cooled to -15 ^oC and PBr_3 (0.4 equiv) was added drop wisely followed by the addition of pyridine (0.03equiv) and allowed to warm at room temperature and stirred for 4 h. The reaction was quenched by ice cubes and extracted by ether. The obtained product was purified by column chromatography with 90% of yield.

IR (neat): ν/cm^{-1} 3060, 2960, 2897, 2136, 1689, 1596, 1494, 1445, 1249, 1206, 1098, 989; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 4H), 7.33 – 7.20 (m, 10H), 6.54 (t, *J* = 6.8 Hz, 1H), 3.64 (s, 4H), 3.52 (d, *J* = 6.7 Hz, 2H), 0.22 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.3, 131.6, 128.7, 128.5, 127.6, 126.4, 104.7, 99.9, 30.4, -0.1; **HRMS (ESI):** Calc. for $C_{14}H_{18}BrSi$ $[M+H]^+$: 293.0361, Found: 293.0365.

(e) Synthesis of TMS protected enynamines S24-S31

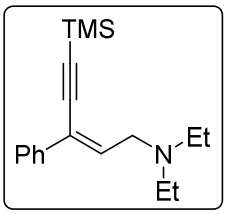
To the solution of substituted (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilanein acetonitrile was added the amine (1.2 equiv) at 0 ^oC drop wisely followed by the addition of K_2CO_3 (1.5 equiv) and allowed to warm at room temperature and stirred for 4 h. The reaction mixture was washed with water and extracted with EtOAc and purified by column chromatography.

***(Z)*-4-(3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)morpholine S24:** The compound **S24** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-

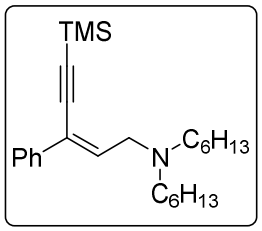


yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added morpholine (115 µL, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S24** as a yellow liquid with 85% of yield. **IR (neat):** ν/cm^{-1} 2960, 2858, 2815, 2150, 1710, 1518, 1455, 1370, 1330, 1295, 1250, 1247, 1211, 1115, 1078, 1001; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.6 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.25 (m, 3H), 6.5 (t, *J* = 7.0 Hz, 1H), 3.73 (t, *J* = 4.6 Hz, 4H), 3.46 (d, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 4.3 Hz, 4H), 0.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.1, 134.0, 128.5, 128.1, 126.7, 126.1, 102.1, 101.6, 67.0, 59.0, 53.8, 0.07; **HRMS (ESI):** Calc. for $C_{18}H_{26}NOSi$ $[M+H]^+$: 300.1784, Found: 300.1780.

***(Z)-N,N*-diethyl-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S25:** The compound **S25** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added diethylamine (145 µL, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S25** as a yellow liquid with 61% of yield. **IR (neat):** ν/cm^{-1} 3060, 2955, 2928, 2860, 2150, 1678, 1550, 1498, 1458, 1370, 1250, 1158, 1081; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.6 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 2H), 7.25 (t, *J* = 7.1 Hz, 1H), 6.54 (t, *J* = 7.1 Hz, 1H), 3.58 (d, *J* = 7.0 Hz, 2H), 2.61 (q, *J* = 7.0 Hz, 4H), 1.09 (t, *J* = 7.0 Hz, 6H), 0.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.4, 135.8, 128.4, 127.9, 126.1, 125.6, 101.8, 101.6, 53.1, 47.2, 29.8, 11.8, 0.1; **HRMS (ESI):** Calc. for $C_{18}H_{28}NSi$ $[M+H]^+$: 286.1991, Found: 286.1993.

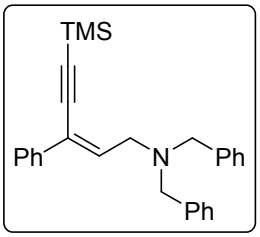


***(Z)-N*-hexyl-*N*-(3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)hexan-1-amine S26:** The compound **S26** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added dihexylamine (252 mg, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S26** as a yellow liquid with 70% of yield. **IR (neat):** ν/cm^{-1} 2954, 2926, 2858, 2148, 1676, 1549, 1495, 1457, 1368, 1249, 1155, 1079; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.58 (t, *J* = 6.9 Hz, 1H), 3.58 (d, *J* = 6.9 Hz, 2H), 2.53 (d, *J* = 7.5 Hz, 2H), 2.50 (d, *J* = 7.5 Hz, 2H), 1.52 (m, 4H), 1.31 (br.s, 14H), 0.90 (t, *J* = 6.9 Hz, 6H), 0.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.5, 136.7, 128.3, 127.7, 126.0, 125.0,

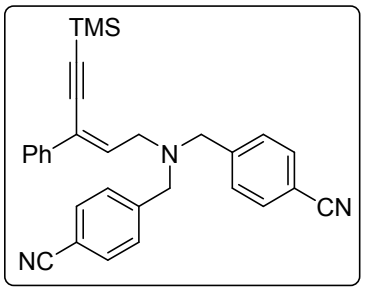


101.9, 101.2, 54.4, 54.3, 31.8, 27.3, 27.2, 22.7, 14.0, 0.01; **HRMS (ESI):** Calc. for $C_{26}H_{44}NSi$ $[M+H]^+$: 398.3243, Found: 398.3236.

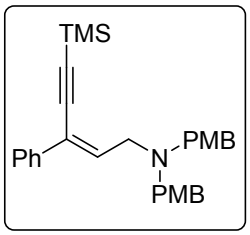
***(Z)*-*N*,*N*-dibenzyl-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S27:** The compound **S27** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^oC and to the reaction mixture was added dibenzylamine (260 µL, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S27** as a yellow liquid with 92% of yield. **IR (neat):** ν/cm^{-1} 3028, 2958, 2798, 2147, 1742, 1599, 1493, 1448, 1363, 1326, 1248, 1119, 1071, 992; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 6.8 Hz, 6H), 7.42 – 7.33 (m, 10H), 6.62 (t, *J* = 8.3 Hz, 3H), 4.44 (d, *J* = 8.3 Hz, 6H), 0.31 (s, 27H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ139.5, 137.5, 136.9, 129.0, 128.4, 128.3, 127.8, 127.0, 126.1, 125.4, 101.9, 101.7, 58.5, 54.2, 0.1; **HRMS (ESI):** Calc. for $C_{28}H_{32}NSi$ $[M+H]^+$: 410.2304, Found: 410.2305.



***(Z)*-4,4'-(((3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)azanediyl)bis(methylene))dibenzonitrile S28:** The compound **S28** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^oC and to the reaction mixture was added 4,4'-(azanediylbis(methylene))dibenzonitrile (335 mg, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S28** as a yellow liquid with 79% of yield. **IR (neat):** ν/cm^{-1} 3026, 2959, 2826, 2228, 2147, 1675, 1607, 1499, 1447, 1410, 1365, 1249, 1104, 994; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 8.4 Hz, 4H), 7.53 – 7.50 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 4H), 7.36 – 7.26 (m, 3H), 6.43 (t, *J* = 7.0 Hz, 1H), 3.69 (s, 4H), 3.49 (d, *J* = 7.0 Hz, 2H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.9, 137.1, 134.5, 132.3, 129.3, 128.5, 128.3, 126.7, 126.1, 118.91, 111.1, 102.4, 101.4, 58.4, 54.5, 0.06; **HRMS (ESI):** Calc. for $C_{30}H_{30}N_3Si$ $[M+H]^+$: 460.2209, Found: 460.2204.

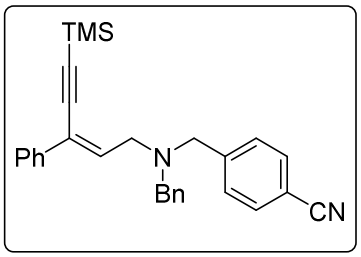


***(Z)*-*N*,*N*-bis(4-methoxybenzyl)-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S29**



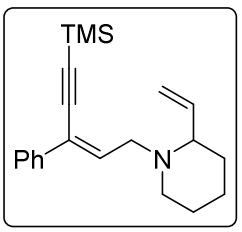
The compound **S29** was prepared by following the above procedure **(e)**. (*Z*)-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added bis(4-methoxybenzyl)amine (350 mg, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S29** as a yellow liquid with 95% of yield; **IR (neat):** ν/cm^{-1} 3000, 2955, 2830, 2147, 1610, 1509, 1451, 1363, 1298, 1244, 1174, 1101, 1036; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.30 (m, 8H), 6.89 (d, *J* = 8.4 Hz, 4H), 6.56 (t, *J* = 6.6 Hz, 1H), 3.82 (s, 6H), 3.6 (s, 4H), 3.54 (d, *J* = 6.7 Hz, 2H), 0.26 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 158.6, 137.5, 137.2, 131.5, 130.0, 128.3, 127.7, 126.0, 125.0, 113.6, 101.9, 101.5, 57.7, 55.2, 53.9, 0.03; **HRMS (ESI):** Calc. for $C_{30}H_{36}NO_2Si$ $[M+H]^+$: 470.2515, Found: 470.2513.

***(Z)*-4-((benzyl(3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)amino)methyl) benzonitrile S30**



The compound **S30** was prepared by following the above procedure **(e)**. *(Z)*-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added 4-((benzylamino)methyl)benzonitrile (302 mg, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S30** as a yellow liquid with 86% of yield. **IR (neat):** ν/cm^{-1} 3026, 2959, 2826, 2228, 2147, 1675, 1607, 1499, 1447, 1410, 1365, 1249, 1104, 994; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.41-7.26 m, 9H), 6.52 (t, *J* = 6.9 Hz, 1H), 3.71 (s, 2H), 3.69 (s, 2H), 3.55 (d, *J* = 6.9 Hz, 2H), 0.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.6, 138.8, 137.2, 135.6, 132.1, 129.3, 128.8, 128.4, 128.0, 127.2, 126.0, 119.0, 110.7, 102.0, 101.6, 58.9, 58.0, 54.4, 0.00; **HRMS (ESI):** Calc. for $C_{29}H_{31}N_2Si$ $[M+H]^+$: 435.2256, Found: 435.2256.

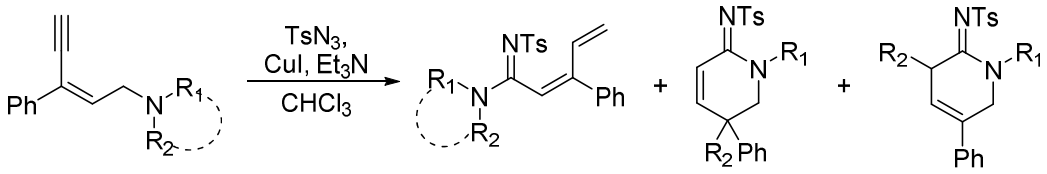
***(Z)*-1-(3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)-2-vinylpiperidine S31:** The compound **S31** was prepared by following the above procedure **(e)**. *(Z)*-(5-bromo-3-phenylpent-3-en-1-yn-1-yl)trimethylsilane **S23** (200 mg, 0.68 mmol) in acetonitrile was cooled



to 0 ^{o}C and to the reaction mixture was added 2-vinylpiperidine (150 mg, 1.36 mmol) followed by K_2CO_3 (190 mg, 1.36 mmol) to give **S31** as a yellow liquid with 78% of yield. **IR (neat):** ν/cm^{-1}2962, 2856, 2811, 2155, 1713, 1512, 1450, 1376, 1338, 1291, 1254, 1241, 1213, 1116, 1078, 1009; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.21 – 7.08 (m, 3H), 6.37 (dd, *J* = 7.9, 6.1 Hz, 1H), 5.65 (m, 1H), 5.02 (dd, *J* = 17.2, 1.4 Hz, 1H), 4.92 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.59 (dd, *J* = 15.0, 6.1 Hz, 1H), 3.13 (dd, *J* = 15.0, 7.9 Hz, 1H), 2.84 (d, *J* = 12.1 Hz, 1H), 2.51 (t, *J* = 7.6 Hz, 1H), 1.91 (dd, *J* = 11.2, 3.1 Hz, 1H), 1.47 (s, 6H), 0.07 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.9, 137.3, 135.1, 128.4, 127.9, 126.1, 116.8, 110.1, 101.8, 66.8, 55.8, 52.8, 33.2, 25.6, 23.8, 0.1; **HRMS (ESI):** Calc. for $C_{21}H_{30}NSi$ $[M+H]^+$: 324.2148, Found: 324.2154.

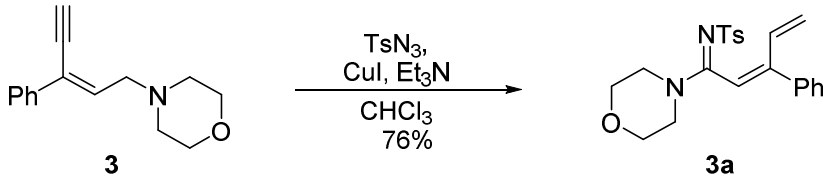
(f) Preparation of enynamines 3, 5, 8, 11, 15, 19, 23, 26, 27: To the solution of (*Z*)-*N,N*-disubstituted-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine in THF was added TBAF (0.5 equiv) at 0 ^{o}C. Then reaction mixture was allowed to warm at room temperature and reaction was monitored by TLC. When reaction was completed, the reaction mixture was quenched by saturated NH_4Cl. The compound was extracted with ethyl acetate and used further for next reaction without any purification.

General procedure A: Cu(I)-catalyzed formation of conjugated amidines (acyclic and cyclic) and dihydro pyridines.



Scheme S6. Cu(I)-catalyzed reaction of enynamines **3, 5, 8, 11, 15, 19, 23, 26, 27**.

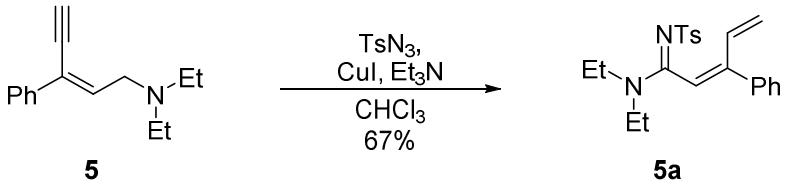
To the solution of enynamine (1 equiv) in chloroform was added tosyl azide (1.2 equiv), Et_3N (1.5 equiv) followed by CuI (10 mol%) and stirred for one hour at room temperature. The reaction was quenched by saturated NH_4Cl and compound was extracted in chloroform. Solvent was evaporated and obtained crude product was purified by column chromatography (20 – 30% EtOAc in Hexane) to afford desired compound.



3 3a

Compound **3a** (76%) was formed by following the general procedure **A.**

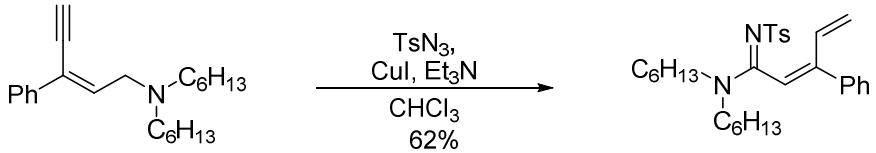
Compound 3a: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 2967, 2920, 2860, 1721, 1597, 1521, 1443, 1344, 1344, 1275, 1225, 1150, 1113, 1088, 1029; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.35 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.25 (s, 1H), 6.20 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.30 (dt, *J* = 10.8, 1.2 Hz, 1H), 5.20 (d, *J* = 17.3 Hz, 1H), 3.96 – 3.89 (m, 2H), 3.80 – 3.75 (m, 2H), 3.72 – 3.67 (m, 2H), 3.62 – 3.56 (m, 2H), 2.38 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3, 145.2, 142.1, 140.4, 137.7, 132.1, 129.1, 128.7, 128.6, 128.5, 126.9, 122.8, 119.7, 66.7, 66.3, 47.8, 44.8, 29.8, 21.5; **HRMS (ESI):** Calc. for $C_{22}H_{25}N_2O_3S$ $[M+H]^+$: 397.1586; Found: 397.1584.



5 5a

Compound **5a** (67%) was formed by following the general procedure **A.**

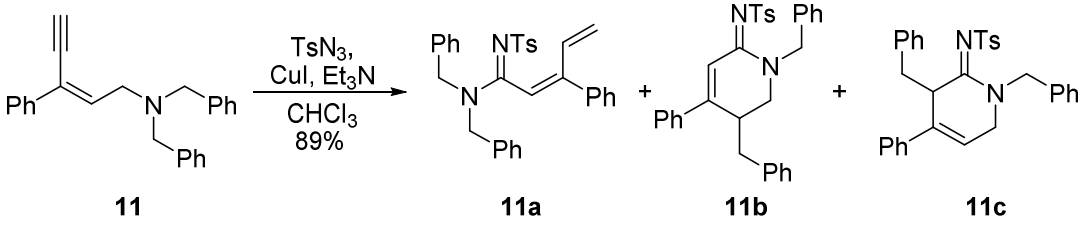
Compound 5a: Physical state: colorless semi-solid : **IR (neat):** ν_{max}/cm^{-1} 3740, 3675, 3641, 3611, 2955, 2927, 2868, 2315, 1735, 1705, 1694, 1645, 1605, 1522, 1461, 1375, 1287, 1145, 1088; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.40 (m, 5H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.21 (s, 1H), 6.14 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.17 (d, *J* = 10.8, 1H) 5.12 (d, *J* = 17.2 Hz, 1H), 3.67 (d, *J* = 6.3 Hz, 2H), 3.44 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.35, 143.50, 141.60, 140.96, 137.99, 132.10, 128.99, 128.94, 128.67, 128.33, 126.74, 121.58, 121.15, 44.51, 42.63, 21.41, 13.81, 12.17; **HRMS (ESI):** Calc. for $C_{22}H_{27}N_2O_2S$ $[M+H]^+$: 383.1793; Found: 383.1794.



8 **8a**

Compound **8** (62%) was formed by following the general procedure **A.**

Compound 8a: Physical state: colorless semi-solid : **IR (neat):** ν_{max}/cm^{-1} 3742, 3677, 3645, 3614, 2951, 2924, 2865, 2313, 1734, 1703, 1691, 1642, 1603, 1524, 1462, 1372, 1284, 1141, 1085; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (m, 5H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.13 (dd, *J* = 15.9, 9.5 Hz, 2H), 5.13 (dd, *J* = 25.1, 14.2 Hz, 2H), 3.52 (s, 2H), 3.30 (s, 2H), 2.33 (s, 3H), 1.62 (m, 3H), 1.57 – 1.45 (m, 3H), 1.26 (t, *J* = 8.2 Hz, 13H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.42, 143.44, 141.52, 141.11, 138.11, 132.32, 128.88, 128.66, 128.32, 128.25, 126.65, 121.61, 121.40, 50.12, 48.22, 31.49, 31.34, 28.49, 26.85, 26.74, 26.40, 22.54, 22.46, 21.40, 14.01, 13.93; **HRMS (ESI):** Calc. for $C_{30}H_{43}N_2O_2S$ $[M+H]^+$: 495.3045; Found: 495.3042.

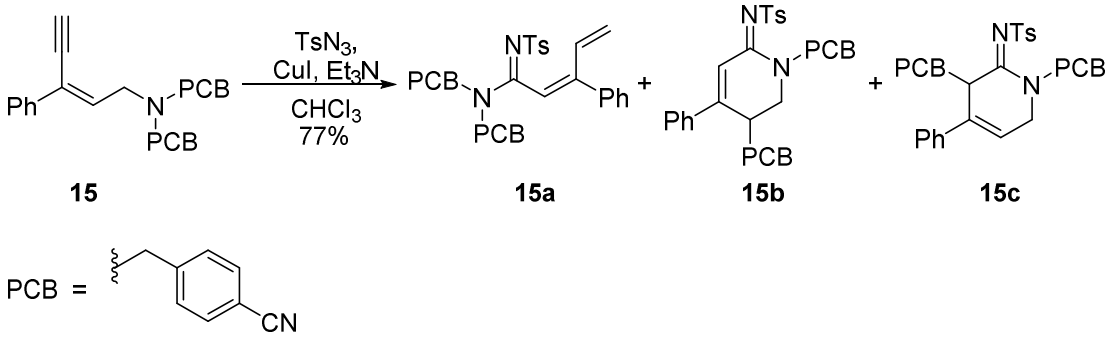


11 **11a** **11b** **11c**

Compound **11a** (84%), **11b** (5%), and **11c** (0%) were formed by following the general procedure **A.**

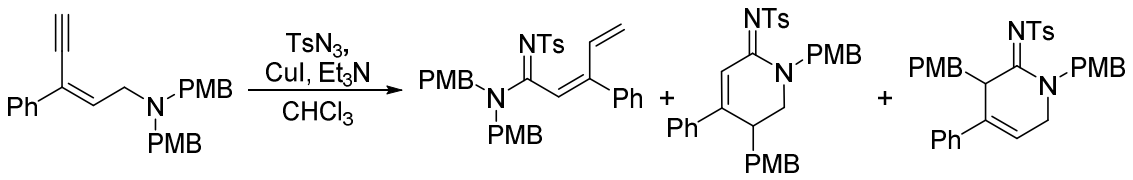
Compound 11a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3740, 3025, 2922, 2862, 1733, 1690, 1635, 1530, 1480, 1381, 1341, 1271, 1135, 1081, 1022; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.39-7.28 (m, 13H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 8.1 Hz, 1.7 Hz, 2H), 6.33 (s, 1H), 6.22 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 5.21 (dt, *J* = 10.8 Hz, 1.2 Hz, 1H), 5.13 (dd, *J* = 17.2 Hz, 0.84 Hz, 1H), 4.59 (br.s, 2H), 2.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 164.8, 144.8, 142.0, 140.7, 137.9, 135.8, 135.2, 132.1, 129.2, 129.1, 128.9, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.4, 126.9, 122.5, 120.5, 51.9, 50.0, 21.5; **HRMS (ESI):** Calc. for $C_{32}H_{31}N_2O_2S$ $[M+H]^+$: 507.2106; Found: 507.2106.

Compound 11b: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3740, 3025, 2921, 2861, 1743, 1693, 1635, 1535, 1485, 1384, 1342, 1273, 1135, 1085, 1021; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.60 (m, 3H), 7.43 (m, 3H), 7.32 (m, 3H), 7.26 (m, 5H), 7.11 (m, 3H), 6.53 (dd, *J* = 7.2 Hz, 3.7 Hz, 2H), 5.09 (d, *J* = 14.3 Hz, 1H), 4.39 (d, *J* = 14.3 Hz, 1H), 3.47 (dd, *J* = 13.2 Hz, 5.0 Hz, 1H), 3.23 (d, *J* = 13.2 Hz, 1H), 3.02 (m, 1H), 2.59 (dd, *J* = 14.0 Hz, 3.2 Hz, 1H), 2.39 (s, 3H), 2.31 (dd, *J* = 14.0 Hz, 11.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.5, 153.7, 142.0, 141.5, 138.3, 136.1, 135.9, 130.5, 129.3, 129.2, 129.1, 129.0, 128.9, 128.7, 128.2, 127.0, 126.7, 126.4, 114.7, 52.6, 47.2, 38.0, 36.1, 21.5 **HRMS (ESI):** Calc. for $C_{32}H_{31}N_2O_2S$ $[M+H]^+$: 507.2106; Found: 507.2110.



Compound **15a** (77%), **15b** (0%), and **15c** (0%) were formed by following the general procedure **A.**

Compound 15a: **Physical state:** colorless semi-solid, **IR (neat):** ν/cm^{-1} 3022, 2924, 2226, 1703, 1605, 1555, 1498, 1444, 1414, 1343, 1275, 1210, 1170, 1145, 1085, 1018; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.1 Hz, 4H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.35 (s, 1H), 7.31 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.27 (s, 1H), 6.20 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 17.3 Hz, 1H), 4.68 (s, 3H), 2.42 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.86, 145.69, 142.59, 140.78, 140.31, 139.84, 137.36, 133.01, 132.56, 131.82, 129.16, 128.85, 128.51, 128.45, 127.83, 126.75, 123.41, 119.20, 118.31, 118.07, 112.54, 112.08, 52.41, 50.57, 21.50; **HRMS (ESI):** Calc. for $C_{34}H_{29}N_4O_2S$ $[M+H]^+$: 557.2011; Found: 557.2018.

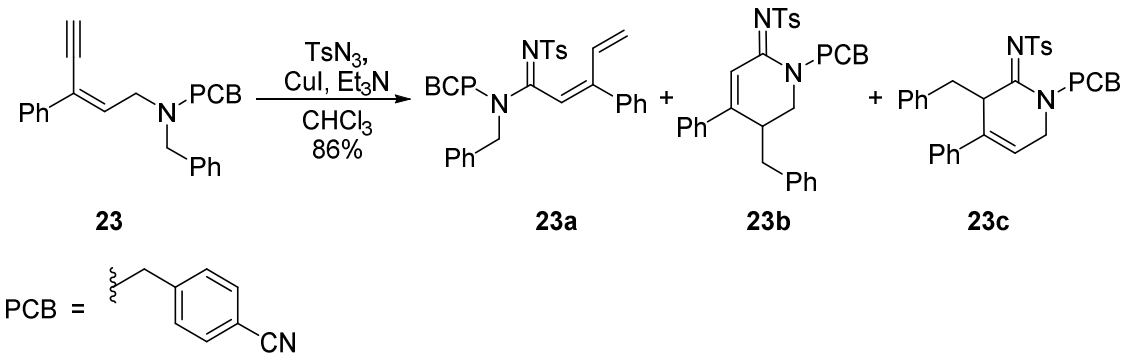


19 **19a** **19b** **19c**

Compound **19a** (8%), **19b** (70%), and **19c** (6%) were formed by following the general procedure **A.** The mixture of **19a** and **19c** could not be separated hence the mixture was charecterized.

Compound 19a and **19c: Physical state:** colorless semi-solid, **IR (neat):** ν/cm^{-1} 3014, 2925, 2844, 1633, 1601, 1534, 1515, 1474, 1375, 1352, 1274, 1242, 1171, 1133, 1118, 1088, 1034; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.3 Hz, 1.5H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.45 (m, 1.5H), 7.44 – 7.34 (m, 7H), 7.30 (d, *J* = 8.1 Hz, 1.4H), 7.28 (s, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (dd, *J* = 8.6, 5.6 Hz, 3.5H), 6.97 (d, *J* = 8.6 Hz, 1.4H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 1.4H), 6.64 (d, *J* = 8.6 Hz, 1.47H), 6.33 (s, 1H), 6.19 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.93 (dd, *J* = 5.4, 1.7 Hz, 0.7H), 5.40 (s, 0.8H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 17.3 Hz, 1H), 4.85 (d, *J* = 14.2 Hz, 1H), 4.49 (s, 2H), 4.13 (d, *J* = 14.3 Hz, 0.7H), 3.85 (s, 3H), 3.83 (s, 3H), 3.80 (s, 2H), 3.77 (s, 2H), 3.71 (dd, *J* = 13.8, 5.3 Hz, 1H), 3.48 (m, 1H), 2.87 (dd, *J* = 13.7, 3.6 Hz, 0.77H), 2.56 (d, *J*= 18.0 Hz, 0.76H), 2.44 (s, 2H), 2.39 (s, 3H); **HRMS (ESI):** Calc. for $C_{34}H_{35}N_2O_4S$ $[M+H]^+$: 567.2318; Found: 567.2325.

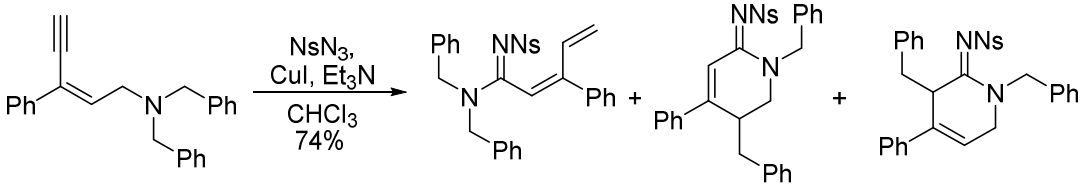
Compound 19b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1}3008, 2931, 2838, 1621, 1577, 1534, 1514, 1467, 1441, 1381, 1275, 1246, 1174, 1140, 1113, 1084, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.58 (m, 2H), 7.55 (s, 1H), 7.42 (t, *J* = 3.5 Hz, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 5.02 (d, *J* = 14.2 Hz, 1H), 4.33 (d, *J* = 14.2 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.42 (dd, *J* = 13.2 Hz, 5.0 Hz, 1H), 3.24 (d, *J* = 13.0 Hz, 1H), 2.95 (m, 1H), 2.53 (dd, *J* = 14.0 Hz, 3.0 Hz, 1H), 2.39 (s, 3H), 2.24 (dd, *J* = 14.0 Hz, 11.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.6, 158.4, 158.3, 153.7, 142.0, 141.6, 135.9, 130.5, 130.3, 129.9, 129.3, 129.1, 128.2, 127.0, 126.4, 114.7, 114.2, 114.0, 55.4, 55.3, 51.9, 46.9, 38.1, 35.2, 21.6.; **HRMS (ESI):** Calc. for $C_{34}H_{35}N_2O_4S$ $[M+H]^+$: 567.2318; Found: 567.2325.



23 23a 23b 23c

Compound **23a** (86%), **23b** (0%), and **23c** (0%) were formed by following the general procedure **A.**

Compound 23a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3021, 2922, 2224, 1701, 1602, 1552, 1495, 1442, 1412, 1341, 1274, 1211, 1171, 1143, 1080, 1015; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 6.3 Hz, 8H), 7.33 – 7.10 (m, 6H), 6.37 – 6.13 (m, 2H), 5.22 (m, 2H), 4.63 (s, 3H), 2.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.8, 164.7, 145.2, 142.3, 142.2, 141.4, 140.9, 140.3, 140.2, 137.7, 137.6, 135.2, 134.6, 132.8, 132.4, 132.1, 131.9, 129.2, 129.2, 129.1, 129.1, 128.9, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 127.8, 127.5, 126.8, 126.7, 122.96, 122.8, 119.9, 119.8, 118.5, 118.2, 112.2, 111.7, 52.9, 51.6, 50.6, 50.1, 21.4; **HRMS (ESI):** Calc. for $C_{33}H_{30}N_3O_2S$ $[M+H]^+$: 532.2059; Found: 532.2063.



11 26a 26b 26c

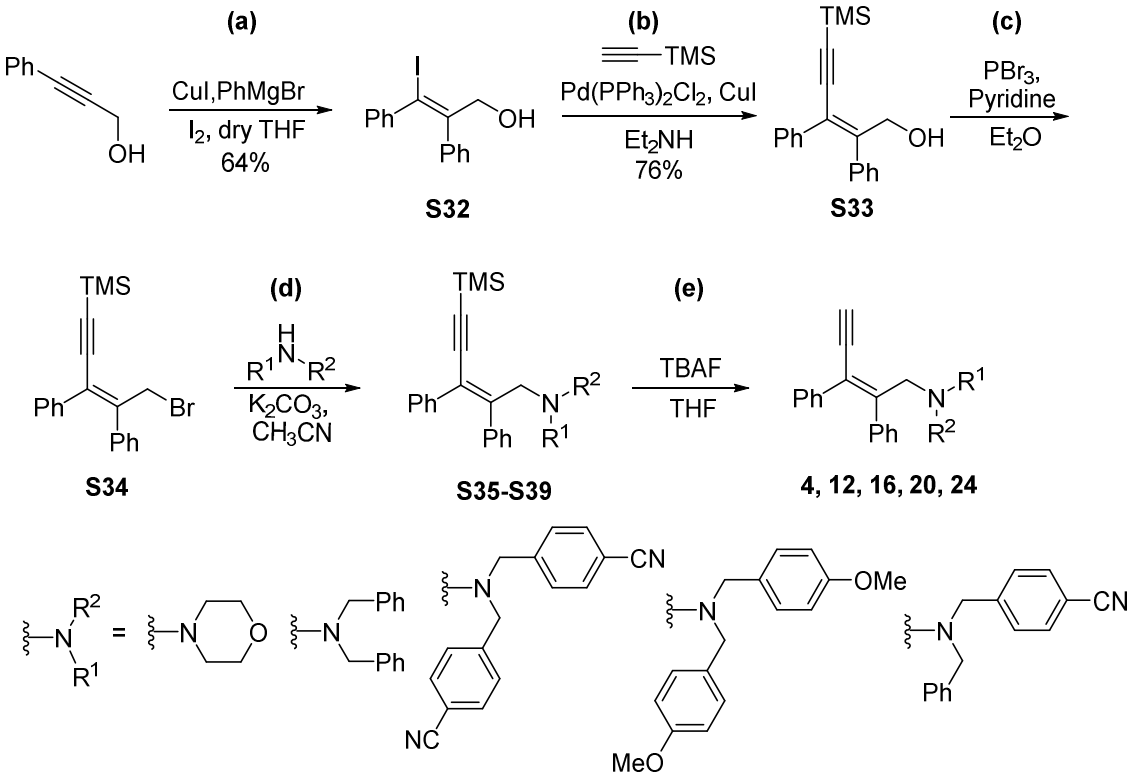
Compound **26a** (49%), **26b** (25%), and **26c** (0%) were formed by following the general procedure **A.**

Compound 26a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3740, 3025, 2922, 2862, 1733, 1690, 1635, 1530, 1480, 1381, 1341, 1271, 1135, 1081, 1022; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 8.9 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.44 – 7.33 (m, 11H), 7.28 (dd, *J* = 5.9, 3.6 Hz, 3H), 7.17 (d, *J* = 6.4 Hz, 2H), 6.36 (s, 1H), 6.24 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.24 (dd, *J* = 20.1, 14.0 Hz, 2H), 4.66 (s, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.2, 149.3, 149.1, 145.3, 137.5, 135.4, 134.7, 131.9, 129.3, 129.0, 128.9, 128.6, 128.3,

128.1, 127.5, 123.8, 120.2, 52.7, 50.6; **HRMS (ESI):** Calc. for $C_{31}H_{28}N_3O_4S$ $[M+H]^+$: 538.1801; Found: 538.1806.

Compound 26b: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 3740, 3025, 2921, 2861, 1743, 1693, 1635, 1535, 1485, 1384, 1342, 1273, 1135, 1085, 1021; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.34 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 7.70 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.59 (s, 1H), 7.56 – 7.48 (m, 3H), 7.38 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.28 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.62 (dd, *J* = 6.5, 2.8 Hz, 2H), 5.04 (d, *J* = 14.4 Hz, 1H), 4.44 (d, *J* = 14.4 Hz, 1H), 3.58 (dd, *J* = 13.4, 5.1 Hz, 1H), 3.31 (d, *J* = 13.4 Hz, 1H), 3.19 – 3.08 (m, 1H), 2.70 (dd, *J* = 14.0, 3.0 Hz, 1H), 2.39 (dd, *J* = 13.9, 11.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.66, 154.86, 149.77, 137.93, 135.53, 135.47, 130.81, 129.26, 129.03, 128.77, 128.69, 128.66, 128.31, 127.55, 126.93, 126.75, 123.93, 114.38, 52.96, 47.57, 37.90, 36.11; **HRMS (ESI):** Calc. for $C_{31}H_{28}N_3O_4S$ $[M+H]^+$: 538.1801; Found: 538.1801.

General procedure for the synthesis of enynamines 4, 12, 16, 20, 24.



Scheme S7. Synthesis of enynamines **4, 12, 16, 20, 24**.

(a) Synthesis of *(Z)*-3-iodo-2-methyl-3-phenylprop-2-en-1-ol S32:[S3] To a solution of propargyl alcohol (1.0 g, 17.8 mmol) and CuI (338 mg, 1.7 mmol) in dry THF (20 mL) was added 3.0 M PhMgBr (15 mL, 44.5 mmol) at -10 ^{o}C. Upon complete addition of Grignard reagent, the reaction mixture was allowed to come at room temperature and stirred for overnight. The resultant mixture was then cooled to -78 ^{o}C and then added a solution of I_2 (9.0 g, 35.6 mmol) in THF (20 mL), the reaction mixture was allowed to cool at room temperature and stirred for 1 hour then cooling at 0^{o}C, the reaction mixture was quenched by saturated NH_4Cl. The reaction mixture was brought to room temperature and extracted with EtOAc, washed with brine dried over Na_2SO_4 and concentrated under reduced pressure. The obtained compound was purified by column chromatography to give **S32** with 64% of yield.

(b) Synthesis of *(Z)*-2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol S33. To a solution of *(Z)*-3-iodo-2-phenylprop-2-en-1-ol **S31** in Et_2NH (0.5 M) was added $(Ph_3P)_2PdCl_2$ (2 mol %)and CuI (4 mol %) at 0 ºC. The system was degassed by N_2 and the resulting was added trimethyl silyl acetylene (1.3 equiv). Then it was warmed up to room temperature. The reaction was monitored by TLC. When the reaction completed, the reaction mixture was concentrated, and the residue was purified through silica gel flash column.

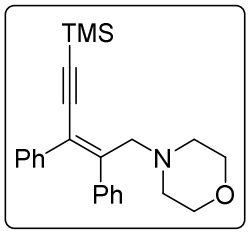
(c) Synthesis of *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane S34. To a solution of *(Z)*-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol **S32** (1 equiv.) in Et_2O was added pyridine (0.06 equiv.) and PBr_3 (0.45 equiv.) at 0°C. The reaction was warmed to room temperature with additional stirring for 1 h. After completion of reaction, the mixture was quenched by ice cubes and extracted in EtOAc. Solvent was removed and obtained product was purified by column chromatography.

IR (neat): ν_{max}/cm^{-1} 2960, 2138, 1756, 1682, 1598, 1490, 1442, 1249, 1210, 1148, 1069, 1000; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25 – 7.21 (m, 3H), 7.18 – 7.12 (m, 7H), 4.76 (s, 2H), 0.31 (s, 9H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.47, 138.29, 137.26, 129.92, 129.72, 129.12, 128.25, 127.75, 125.62, 103.83, 103.60, 36.88, -0.14; **HRMS (ESI):** Calc. for $C_{20}H_{22}BrSi$ $[M+H]^+$: 369.0674; Found: 369.0680.

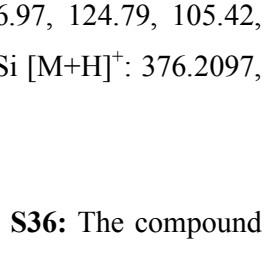
(d) Synthesis of TMS protected enynamines S35-39: To the solution of substituted *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane **S34** in acetonitrile was added the amine (1.2 equiv) at 0 ^{o}C drop wisely followed by the addition of K_2CO_3 (1.5 equiv) and

allowed to warm at room temperature and stirred for 4h. The reaction mixture was washed with water and extracted with EtOAc and purified by column chromatography.

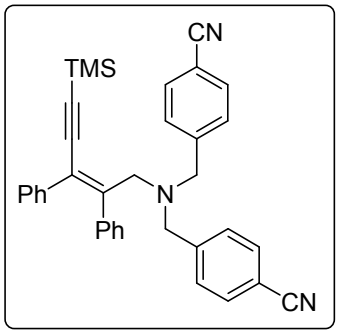
***(Z)*-4-(2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)morpholine S35:** The compound **S35** was prepared by following the above procedure **(d)**. *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane **S34** (200 mg, 0.41 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added morpholine (72 mg, 0.82 mmol) followed by K_2CO_3 (113 mg, 0.82 mmol) to give **S35** as a yellow liquid with 86% of yield. **IR (neat):** ν/cm^{-1} 2960, 2858, 2815, 2150, 1710, 1518, 1455, 1370, 1330, 1295, 1250, 1247, 1211, 1115, 1078, 1001; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21 – 7.07 (m, 10H), 3.79 (s, 2H), 3.73 – 3.61 (m, 4H), 2.67 – 2.54 (m, 4H), 0.27 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.65, 140.39, 138.30, 129.86, 129.20, 127.79, 127.66, 127.04, 126.97, 124.79, 105.42, 100.41, 67.10, 63.67, 53.59, 0.02; **HRMS (ESI):** Calc. for $C_{24}H_{30}NOSi$ $[M+H]^+$: 376.2097, Found: 376.2095.



***(Z)*-*N*,*N*-dibenzyl-3-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S36:** The compound **S36** was prepared by following the above procedure **(d)**. *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane **S34** (200 mg, 0.41 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added dibenzylamine (160 μL, 0.82 mmol) followed by K_2CO_3 (113 mg, 0.82 mmol) to give **S36** as a yellow liquid with 92% of yield. **IR (neat):** ν/cm^{-1} 3333, 3060, 2927,1748, 1600, 1491, 1445, 1350, 1263, 1190, 1077, 1000, 949; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25 – 7.19 (m, 7H), 7.17 – 7.06 (m, 11H), 6.86 (d, *J* = 6.9 Hz, 2H), 3.89 (s, 2H), 3.60 (s, 4H), 0.30 (s, 9H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.5, 139.7, 139.3, 138.4, 129.9, 129.7, 128.9, 127.9, 127.6, 127.5, 126.9, 126.8, 126.7, 126.0, 123.6, 106.9, 105.6, 102.7, 100.0, 98.2, 59.0, 58.1, 0.1; **HRMS (ESI):** Calc. for $C_{34}H_{36}NSi$ $[M+H]^+$: 486.2617, Found: 486.2618.

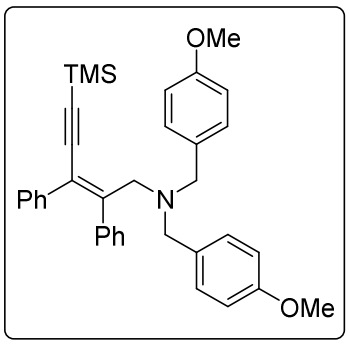


***(Z)*-4,4'-(((2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)azanediyl)bis (methylene))dibenzonitrile S37:** The compound **S37** was prepared by following the above procedure **(d)**. *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-



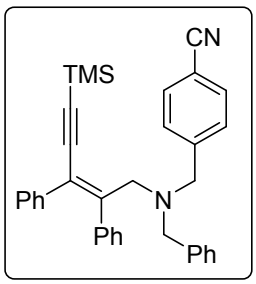
yl)trimethylsilane **S34** (200 mg, 0.41 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added 4,4'-(azanediylbis(methylene))dibenzonitrile (202 mg, 0.82 mmol) followed by K_2CO_3 (113 mg, 0.82 mmol) to give **S37** as a yellow liquid with 89% of yield. **IR (neat):** ν/cm^{-1} 3027, 2955, 2822, 2221, 2143, 1673, 1601, 1489, 1442, 1418, 1361, 1244, 1107, 998; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 8.4 Hz, 13H), 7.25 (d, *J* = 7.4 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 7H), 7.13 (d, *J* = 8.3 Hz, 13H), 7.11 (s, 15H), 6.81 (d, *J* = 7.0 Hz, 6H), 3.88 (s, 6H), 3.64 (s, 13H), 0.30 (s, 28H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 146.82, 144.89, 139.10, 137.81, 132.00, 129.78, 129.37, 129.31, 127.88, 127.73, 127.36, 127.19, 124.59, 118.87, 110.89, 105.12, 100.68, 59.32, 57.93, 0.05; **HRMS (ESI):** Calc. for $C_{36}H_{34}N_3Si$ $[M+H]^+$: 536.2522, Found: 536.2527.

***(Z)*-*N,N*-bis(4-methoxybenzyl)-2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine S38**



The compound **S38** was prepared by following the above procedure **(d)**. *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane **S34** (200 mg, 0.41 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added bis(4-methoxybenzyl)amine (210 mg, 0.82 mmol) followed by K_2CO_3 (113 mg, 0.82 mmol) to give **S38** as a yellow liquid with 90% of yield. **IR (neat):** ν/cm^{-1} 3003, 2958, 2835, 2138, 1698, 1612, 1512, 1455, 1368, 1301, 1245, 1176, 1103, 1036; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22 – 7.07 (m, 8H), 6.97 (d, *J* = 8.3 Hz, 4H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 4H), 3.87 (s, 2H), 3.80 (s, 6H), 3.50 (s, 4H), 0.29 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.43, 148.80, 139.35, 138.50, 131.78, 129.98, 129.92, 129.72, 127.60, 127.46, 126.82, 126.79, 123.32, 113.33, 105.68, 99.91, 58.74, 57.22, 55.24, 0.08; **HRMS (ESI):** Calc. for $C_{36}H_{40}NO_2Si$ $[M+H]^+$: 546.2828, Found: 546.2832.

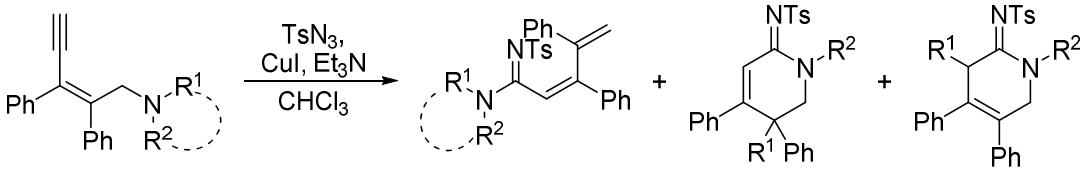
***(Z)*-4-((benzyl(2,3-diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)amino)methyl) benzonitrile S39:** The compound **S39** was prepared by following the above procedure **(d)**. *(Z)*-(5-bromo-3,4-diphenylpent-3-en-1-yn-1-yl)trimethylsilane **S34** (200 mg, 0.41 mmol) in acetonitrile was cooled to 0 ^{o}C and to the reaction mixture was added 4-((benzylamino)methyl)benzonitrile (182 mg, 0.82 mmol) followed by K_2CO_3 (113 mg, 0.82 mmol) to give **S39** as a yellow liquid with 90% of



yield. **IR (neat):** ν/cm^{-1} 3021, 2960, 2821, 2225, 2149, 1678, 1610, 1500, 1450, 1412, 1368, 1250, 1105, 1000; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.10 (dt, *J* = 5.2, 3.6 Hz, 9H), 6.84 (d, *J* = 7.0 Hz, 2H), 3.89 (s, 2H), 3.62 (s, 4H), 0.30 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.7, 145.8, 139.3, 139.1, 138.2, 131.9, 129.9, 129.6, 129.4, 129.0, 128.2, 127.8, 127.7, 127.2, 127.1, 127.1, 124.1, 119.2, 110.5, 105.4, 100.4, 59.3, 58.5, 57.7, 0.1; **HRMS (ESI):** Calc. for $C_{35}H_{35}N_2Si$ $[M+H]^+$: 511.2570, Found: 511.2579.

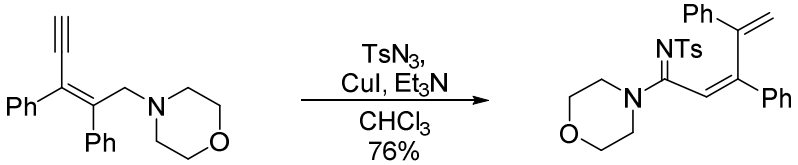
(e) Preperation of enynamines 4, 12, 16, 20, 24: To the solution of (*Z*)-*N,N*-disubstituted-2-phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-amine in THF was added TBAF (0.5 equiv) at 0 ^oC. Then reaction mixture was allowed to warm at room temperature and reaction was monitored by TLC. When reaction was completed, the reaction mixture was quenched by saturated NH_4Cl. The compound was extracted with ethyl acetate and used further for next reaction without any purification.

General procedure A: Cu(I)-catalyzed formation of conjugated amidines (acyclic and cyclic) and dihydro pyridines



Scheme S8. Cu(I)-catalyzed reaction of enynamines **4, 12, 16, 20, 24**.

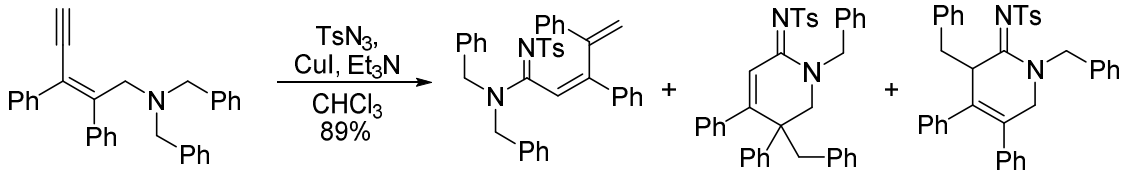
To the solution of enynamine (1 equiv) in chloroform was added tosyl azide (1.2 equiv), Et_3N (1.5 equiv) followed by CuI (10 mol%) and stirred for one hour at room temperature. The reaction was quenched by saturated NH_4Cl and compound was extracted in chloroform. Solvent was evaporated and obtained crude product was purified by column chromatography (20 - 30 EtOAc in Hexane) to afford desired compound.



4 **4a**

Compound **4a** (65%) was formed by following the general procedure **A.**

Compound 4a: Physical state: colorless semi-solid, **IR (neat):** ν_{max}/cm^{-1} 2967, 2920, 2860, 1721, 1597, 1521, 1443, 1344, 1344, 1275, 1225, 1150, 1113, 1088, 1029; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.34 (m, 3H), 7.26 (dd, *J* = 6.7, 3.3 Hz, 2H), 7.23 – 7.19 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 5.86 (d, *J* = 0.6 Hz, 1H), 5.34 (s, 1H), 3.58 (s, 4H), 3.40 (s, 2H), 3.25 (s, 2H), 2.40 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 162.49, 148.81, 143.98, 142.01, 140.37, 139.06, 137.34, 129.04, 128.76, 128.65, 128.54, 128.18, 128.06, 127.96, 127.41, 126.88, 126.56, 119.30, 119.03, 66.11, 65.68, 48.12, 44.53, 21.49; **HRMS (ESI):** Calc. for $C_{28}H_{29}N_2O_3S$ $[M+H]^+$: 473.1899; Found: 473.1894.

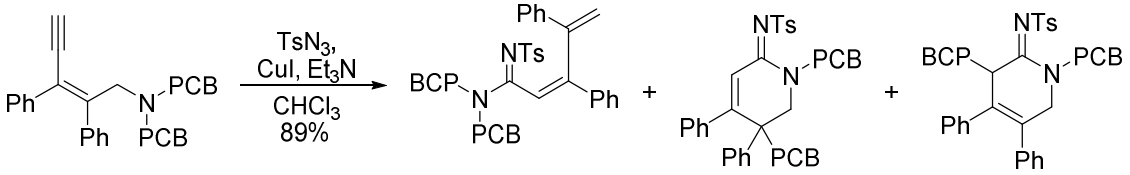


Compound **12a** (48%), **12b** (30%), and **12c** (0%) were formed by following the general procedure **A.**

Compound 12a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3744, 3035, 2933, 2866, 1723, 1688, 1645, 1538, 1481, 1382, 1342, 1275, 1138, 1088, 1021; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 6H), 7.31 (m, 6H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.01 (m, 10H), 6.90 (s, 1H), 5.69 (d, *J* = 0.6 Hz, 1H), 5.37 (d, *J* = 0.5 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.9, 148.0, 142.7, 141.9, 140.6, 138.8, 137.1, 135.5, 135.3, 129.1, 129.1, 129.0, 128.9, 128.6, 128.4, 128.3, 128.1, 127.8, 127.7, 127.2, 127.1, 126.8, 126.7, 119.6, 119.3, 52.2, 49.6, 21.5; **HRMS (ESI):** Calc. for $C_{38}H_{35}N_2O_2S$ $[M+H]^+$: 583.2419; Found: 583.2430.

Compound 12b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3738, 3032, 2925, 2867, 1722, 1687, 1638, 1531, 1483, 1382, 1344, 1277, 1133, 1077, 1032; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.0 Hz, 4H), 7.63 (s, 2H), 7.42 – 7.31 (m, 7H), 7.28 – 7.13 (m, 23H), 7.13 – 7.02 (m, 8H), 6.76 (d, *J* = 7.5 Hz, 4H), 6.61 (d, *J* = 7.4 Hz, 4H), 4.92 (d, *J* = 14.7 Hz, 2H), 4.06 (d, *J* = 14.7 Hz, 2H), 3.91 (d, *J* = 13.0 Hz, 2H), 3.46 (d, *J* = 14.3 Hz, 2H), 3.39 (d, *J* = 13.0 Hz, 2H), 3.26 (d, *J* = 14.3 Hz, 2H), 2.41 (s, 6H); **^{13}C NMR (101 MHz,**

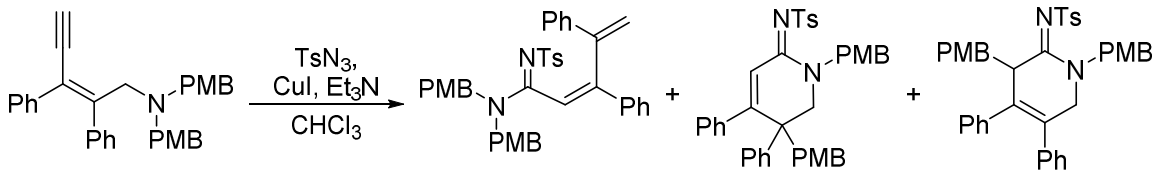
$CDCl_3$): δ 157.52, 156.04, 141.74, 141.46, 141.31, 137.96, 135.91, 134.88, 130.55, 129.29, 129.01, 128.73, 128.49, 128.46, 128.37, 128.02, 128.01, 127.45, 127.33, 127.14, 126.90, 126.37, 121.50, 57.74, 52.28, 47.61, 42.00, 21.46; **HRMS (ESI):** Calc. for $C_{38}H_{35}N_2O_2S$ $[M+H]^+$: 583.2419; Found: 583.2420.



Compound **16a** (73%), **16b** (18%), and **16c** (0%) were formed by following the general procedure **A.**

Compound 16a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3025, 2921, 2227, 1708, 1601, 1554, 1496, 1432, 1411, 1348, 1275, 1213, 1173, 1141, 1088, 1011; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.34 (m, 6H), 7.23 – 7.13 (m, 10H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.86 (s, 1H), 5.79 (d, *J* = 0.5 Hz, 1H), 5.40 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.2, 149.1, 143.1, 142.6, 140.5, 140.4, 139.8, 138.3, 136.6, 132.9, 132.2, 129.2, 129.2, 128.8, 128.6, 127.5, 127.1, 126.7, 126.4, 119.1, 118.5, 112.4, 111.8, 52.7, 50.2, 21.5; **HRMS (ESI):** Calc. for $C_{40}H_{34}N_4O_2S$ $[M+H]^+$: 633.2324; Found: 633.2317.

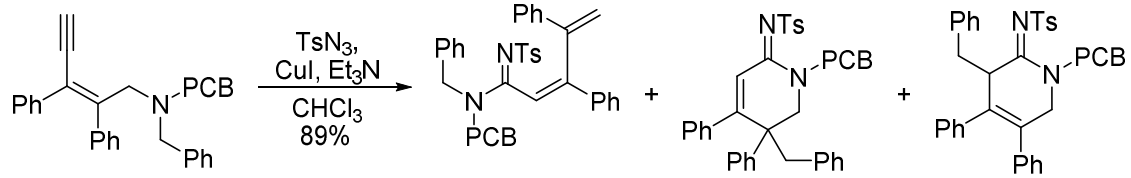
Compound 16b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3018, 2920, 2216, 1711, 1612, 1542, 1491, 1438, 1410, 1339, 1268, 1251, 1179, 1133, 1085, 1013; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 5.8 Hz, 6H), 7.62 (s, 3H), 7.38 – 7.29 (m, 17H), 7.23 (d, *J* = 8.2 Hz, 8H), 7.22 – 7.16 (m, 19H), 7.14 (d, *J* = 7.9 Hz, 6H), 6.69 (dd, *J* = 8.1, 5.8 Hz, 12H), 5.13 (d, *J* = 15.1 Hz, 3H), 3.95 (d, *J* = 12.7 Hz, 3H), 3.81 (d, *J* = 15.1 Hz, 3H), 3.51 (d, *J* = 14.3 Hz, 3H), 3.37 (d, *J* = 12.8 Hz, 3H), 3.30 (d, *J* = 14.4 Hz, 3H), 2.40 (s, 10H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 142.30, 141.37, 140.92, 140.71, 140.43, 137.43, 132.12, 131.72, 131.22, 129.88, 129.14, 129.03, 128.86, 128.26, 128.13, 127.99, 127.01, 126.30, 121.59, 118.53, 118.43, 111.12, 111.00, 58.58, 52.07, 47.83, 42.07, 21.49; **HRMS (ESI):** Calc. for $C_{40}H_{34}N_4O_2S$ $[M+H]^+$: 633.2324; Found: 633.2321.



20 **20a** **20b** **20c**

Compound **20a** (0%), **20b** (68%), and **20c** (0%) were formed by following the general procedure **A.**

Compound 20b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3017, 2926, 2840, 1632, 1606, 1532, 1518, 1473, 1377, 1353, 1277, 1248, 1179, 1133, 1112, 1083, 1031; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.42 – 7.30 (m, 4H), 7.27 – 7.10 (m, 10H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.61 (dd, *J* = 15.6, 8.7 Hz, 4H), 6.49 (d, *J* = 8.7 Hz, 2H), 4.86 (d, *J* = 14.5 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 3.87 (d, *J* = 13.0 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.18 (d, *J* = 14.4 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.85, 158.43, 157.32, 155.99, 141.68, 141.54, 138.02, 131.57, 129.43, 129.00, 128.63, 128.45, 128.35, 127.14, 126.36, 121.58, 113.85, 113.40, 55.24, 55.20, 47.66, 41.15, 29.70, 27.43, 21.45; **HRMS (ESI):** Calc. for $C_{40}H_{39}N_2O_4S$ $[M+H]^+$: 643.2631; Found: 643.2626.



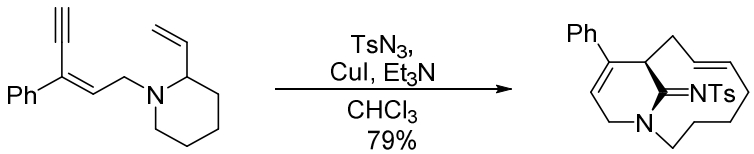
24 **24a** **24b** **24c**

Compound **24a** (46%), **24b** (29%), and **24c** (0%) were formed by following the general procedure **A.**

Compound 24a: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3020, 2940, 2226, 1722, 1618, 1532, 1481, 1441, 1417, 1344, 1262, 1254, 1174, 1131, 1081, 1011; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.33 (m, 8H), 7.18 (m, 9H), 6.88 (s, 2H), 5.78 (s, 1H), 5.46 (s, 1H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 164.7, 149.0, 143.5, 143.0, 141.1, 140.2, 140.1, 138.5, 137.1, 133.1, 132.6, 129.3, 129.7, 129.1, 128.5, 127.1, 127.1, 127.4, 126.4, 119.5, 118.1, 112.8,

112.2, 52.3, 50.2, 21.6; **HRMS (ESI):** Calc. for $C_{39}H_{34}N_3O_2S$ $[M+H]^+$: 608.2372; Found: 608.2371.

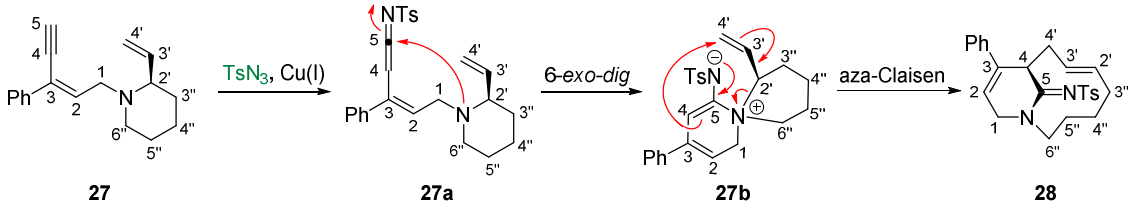
Compound 24b: Physical state: colorless semi-solid, **IR (neat):** ν/cm^{-1} 3017, 2921, 2214, 1716, 1611, 1548, 1499, 1433, 1411, 1344, 1265, 1256, 1172, 1135, 1088, 1011; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.66 (s, 1H), 7.36 (dd, *J* = 12.8, 8.1 Hz, 5H), 7.26 – 7.15 (m, 10H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.71 (d, *J* = 8.3 Hz, 2H), 4.85 (d, *J* = 14.6 Hz, 1H), 4.08 (d, *J* = 14.7 Hz, 1H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.48 (dd, *J* = 28.6, 13.6 Hz, 2H), 3.33 (d, *J* = 14.3 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 157.58, 156.55, 142.10, 141.54, 140.90, 140.68, 137.80, 135.70, 132.06, 130.57, 129.57, 129.06, 128.85, 128.65, 128.34, 128.21, 128.12, 127.68, 127.19, 127.05, 126.31, 121.30, 118.63, 110.96, 58.66, 52.11, 47.78, 41.95, 21.47; **HRMS (ESI):** Calc. for $C_{39}H_{34}N_3O_2S$ $[M+H]^+$: 608.2372; Found: 608.2371.



27 **28**

Compound **28** (79%) was formed by following the general procedure **A**.

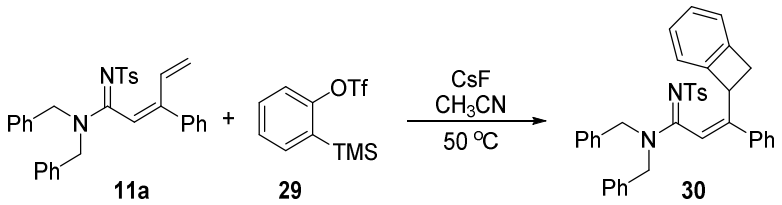
Compound 28: Physical state: colorless semi-solid. **IR (neat):** ν_{max}/cm^{-1} 3741, 3679, 3648, 3613, 2951, 2929, 2863, 2312, 1731, 1708, 1697, 1647, 1604, 1529, 1465, 1378, 1288, 1144, 1089; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 6.9 Hz, 2H), 7.41 – 7.30 (m, 5H), 6.05 (d, *J* = 2.8 Hz, 1H), 5.56 (dd, *J* = 26.8, 15.4 Hz, 1H), 5.50 – 5.35 (m, 1H), 5.17 (d, *J* = 5.1 Hz, 1H), 4.76 (s, 1H), 4.24 (d, *J* = 18.8 Hz, 1H), 3.71 (d, *J* = 18.7 Hz, 1H), 3.16 – 3.00 (m, 1H), 2.82 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.32 (dd, *J* = 12.5, 4.5 Hz, 2H), 1.77 – 1.60 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ165.6, 143.5, 139.3, 137.1, 136.8, 129.7, 129.2, 128.8, 128.3, 127.2, 126.5, 126.3, 125.9, 116.2, 56.5, 53.2, 49.9, 43.6, 37.7, 29.8, 26.5, 21.6; **HRMS (ESI):** Calc. for $C_{25}H_{29}N_2O_2S$ $[M+H]^+$: 421.1950; Found: 421.1951.



27 **27a** **27b** **28**

Scheme S9. Mechanism for the formation of bridged bicyclic amidine **28**.

Synthesis of (1Z,2Z)-*N*,*N*-dibenzyl-3-(bicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)-*N*'-tosylacrylimidamide 30.



Scheme S9. [2+2] Cycloaddition of amidine **11a** with benzyne **29**.

To the solution of **11a** (50 mg, 0.09 mmol) in acetonitrile (2 mL) was added benzyne precursor **29** (60 mg, 0.19 mmol) followed by CsF (40 mg, 0.24 mmol) and resultant mixture was heated at 50 ^{o}C for overnight to obtain the product **30** with 86% yield. **IR (neat):** ν_{max}/cm^{-1} 3748, 3671, 3644, 3610, 2958, 2936, 2871, 2315, 1739, 1701, 1693, 1653, 1614, 1532, 1468, 1375, 1282, 1141, 1085; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.81 (d, *J* = 8.2 Hz, 8H), 7.37 – 7.29 (m, 14H), 7.25 – 7.15 (m, 56H), 7.14 – 7.08 (m, 14H), 6.91 (d, *J* = 6.9 Hz, 8H), 6.36 (s, 4H), 5.00 (s, 9H), 4.56 (s, 7H), 3.12 (dd, *J* = 14.4, 5.5 Hz, 4H), 2.84 (s, 4H), 2.36 (s, 13H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ 165.0, 142.1, 141.0, 139.2, 135.6, 135.1, 129.3, 129.2, 128.9, 128.7, 128.3, 128.1, 128.0, 127.6, 127.4, 126.6, 122.9, 120.5, 49.8, 45.7, 35.8, 29.8, 21.6; **HRMS (ESI):** Calc. for $C_{38}H_{35}N_2O_2S$ $[M+H]^+$: 583.2419; Found: 583.2417.

IV. Crystal Structure Data:[S5]

Crystal structure of compound 11a (CCDC 1525177) : $C_{26}H_{26}N_2O_2S$; Compound **11a** was crystallized from slow evaporation of CH_2Cl_2/hexane at room temperature. A colorless cubic shaped crystal with approximate dimensions 0.185 x 0.161 x 0.058 mm gave an Orthorhombic with space group *C2/c*; *a* = 27.148(6) *b* = 6.2305(14) *c* = 27.401(6) Å, α = 90^{o} β = 92.154^{o} γ = 90^{o}; *V* = 4631.5(18) Å^3; *T* = 296 (2) K; *Z* = 8; ρ_{calc}= 1.235 Mgm^{-3}; θ_{max}= 26.37^{o}; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. *R* = 0.0514 (for 2576 reflection $I>2\sigma(I)$), *wR* = 0.1764 which was refined against |*F2*| and S = 0.941 for 281 parameters and 4739 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S5] All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the fil cycle of refinement as riding over atoms to which they are bonded. μ = 0.164 mm^{-1}.

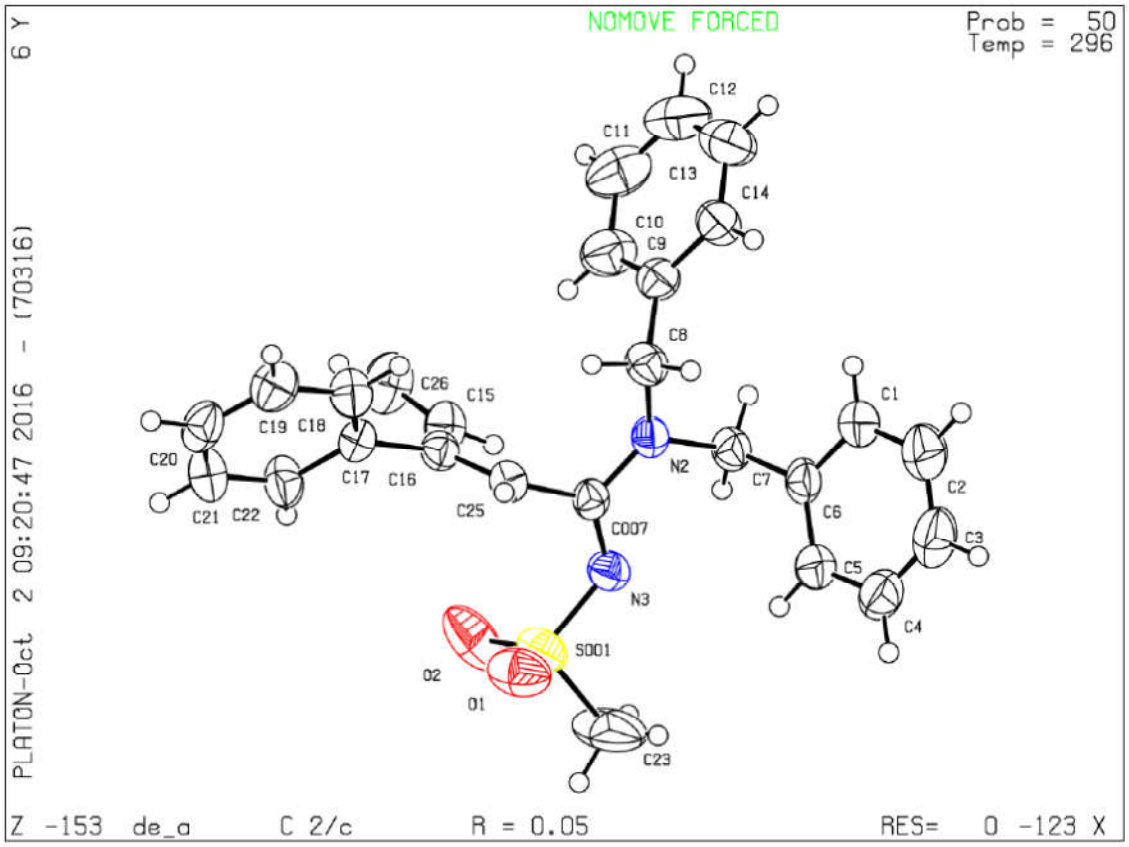


Fig. S1 ORTEP diagram of **11a**.

Crystal structure of compound 10b (CCDC 1525176): $C_{32}H_{30}N_2O_2S$; Compound **10b** was crystallized from slow evaporation of CH_2Cl_2/hexane at room temperature. A colorless cubic shaped crystal with approximate dimensions 0.185 x 0.161 x 0.058 mm gave an Orthorhombic with space group *P21/c*; *a* = 8.0697(3) *b* = 32.4621(12) *c* = 9.8721(4) Å, α = 90° β = 90.5490° γ = 90°; *V* = 2585.97(17) Å^3; *T* = 296 (2) K; *Z* = 4; ρ_{calc}= 1.301 Mgm^{-3}; θ_{max}= 68.384°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. *R* = 0.0434 (for 4143 reflection $I>2\sigma(I)$), *wR* = 0.1365 which was refined against |*F2*| and S = 1.101 for 335 parameters and 4726 unique reflections. The structure was obtained by direct methods using SHELXS-97. All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over atoms to which they are bonded. μ = 1.364 mm^{-1}.

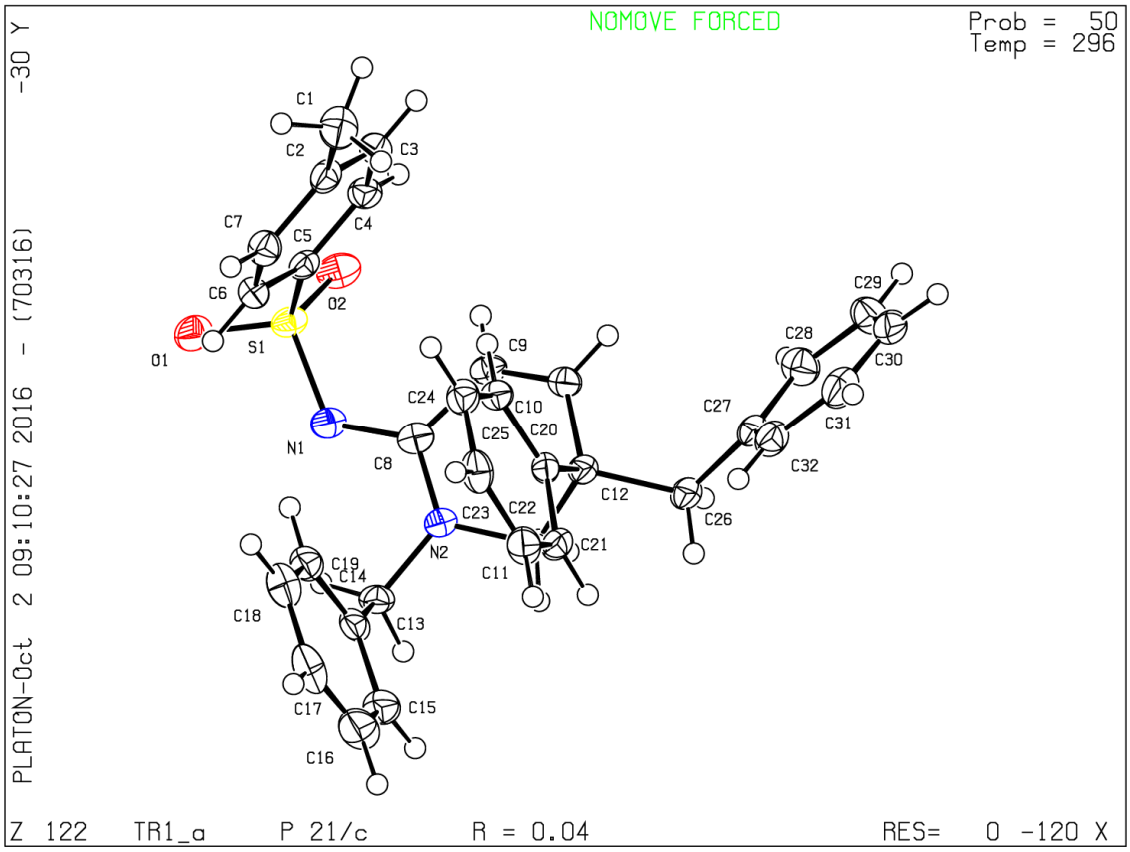


Fig. S2 ORTEP diagram of **10b.**

Crystal structure of compound 28 (CCDC 1525520): $C_{25}H_{28}N_2O_2S$; Compound **28** was crystallized from slow evaporation of CH_2Cl_2/hexane at room temperature. A colorless cubic shaped crystal with approximate dimensions 0.185 x 0.161 x 0.058 mm gave an Orthorhombic with space group P^{-1}; a = 9.0423(4) b = 10.9846(5) c = 11.4374(5) Å, α = 91.995° β = 100.164° γ = 103.818°; V = 2128.3(8) Å^3; T = 0 (2) K; Z = 2; ρ_{calc}= 1.291 Mgm^{-3}; θ_{max}= 54.76°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0361 (for 4159 reflection $I>2\sigma(I)$), wR = 0.0820 which was refined against |*F2*| and S = 0.935 for 258 parameters and 4839 unique reflections. The structure was obtained by direct methods using SHELXS-97. All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over atoms to which they are bonded. μ = 0.174 mm^{-1}.

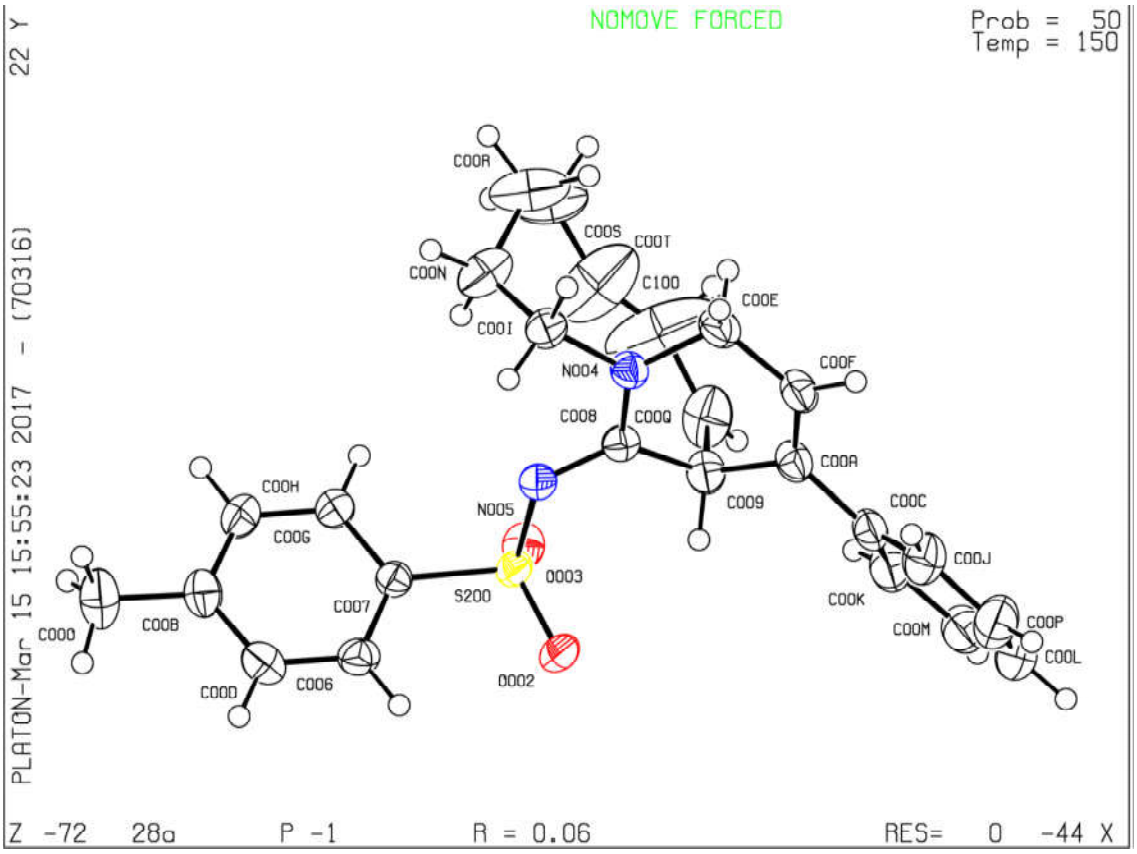


Fig. S3 ORTEP diagram of **28**.

Crystal structure of compound 30 (CCDC 1525179): $C_{38}H_{34}N_2O_2S$; Compound **30** was crystallized from slow evaporation of CH_2Cl_2/hexane at room temperature. A colorless cubic shaped crystal with approximate dimensions 0.185 x 0.161 x 0.058 mm gave an Orthorhombic with space group *P21/c*; a = 12.375(4) b = 17.958(7) c = 14.179(6) Å, α = 90° β = 91.594° γ = 90°; V = 3150(2) Å^3; T = 296 (2) K; Z = 4; ρ_{calc}= 1.229 Mgm^{-3}; θ_{max}= 28.282°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0805 (for 2133 reflection $I>2\sigma(I)$), wR = 0.2471 which was refined against |*F2*| and S = 0.912 for 389 parameters and 5734 unique reflections. The structure was obtained by direct methods using SHELXS-97. All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in thefinal cycle of refinement as riding over atoms to which they are bonded. μ = 0.139 mm^{-1}.

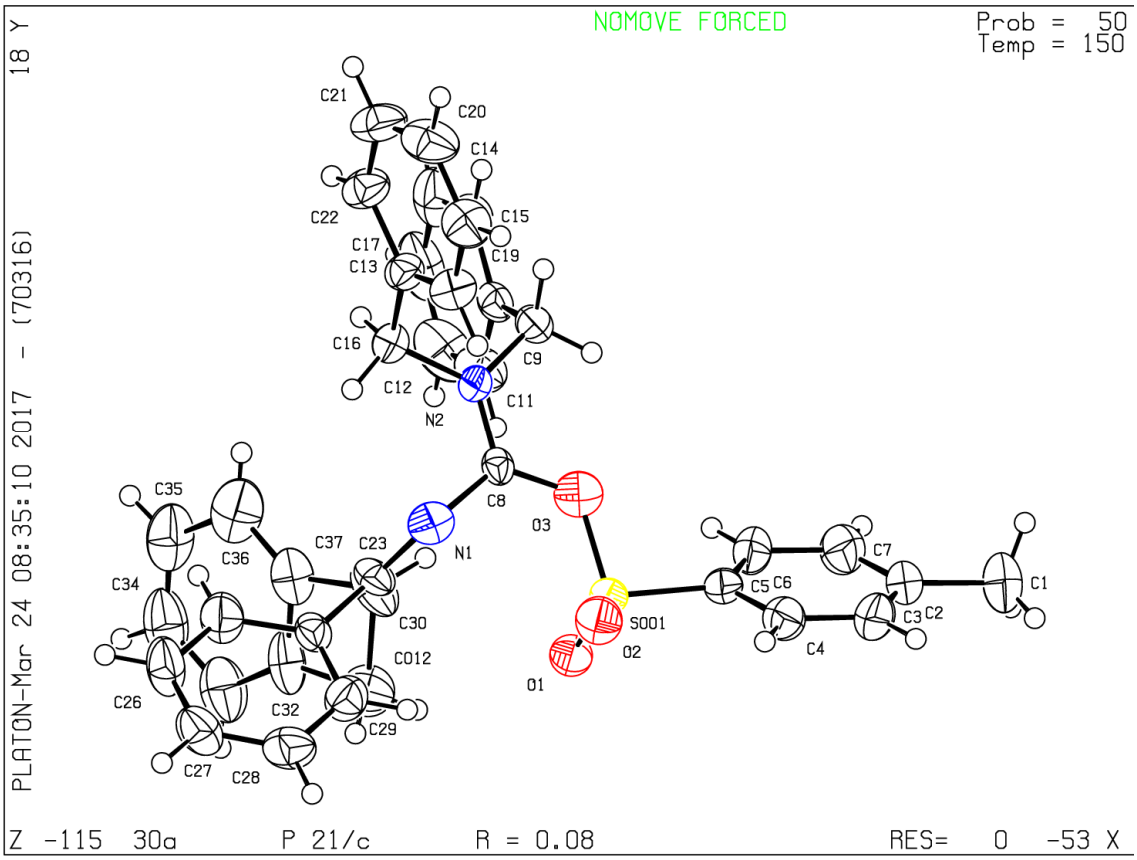


Fig. S4 ORTEP diagram of **30**.

Crystal structure of compound 22b (CCDC 1525178): $C_{33}H_{29}N_3O_2S$; Compound **22b** was crystallized from slow evaporation of CH_2Cl_2/hexane at room temperature. A colorless cubic shaped crystal with approximate dimensions 0.185 x 0.161 x 0.058 mm gave an Orthorhombic with space group P^{-1}; a = 8.7353(11) b = 10.2521(13) c = 15.765(2) Å, α = 101.925° β = 98.258° γ = 93.270°; V = 1361.6(3) Å^3; T = 296 (2) K; Z = 2; ρ_{calc}= 1.334 Mgm^{-3}; θ_{max}= 77.283°; *MoKαλ* = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. R = 0.0948 (for 4453 reflection $I>2\sigma(I)$), wR = 0.2636 which was refined against |*F2*| and S = 1.782 for 353 parameters and 5550 unique reflections. The structure was obtained by direct methods using SHELXS-97. All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in thefinal cycle of refinement as riding over atoms to which they are bonded. μ = 1.334 mm^{-1}.

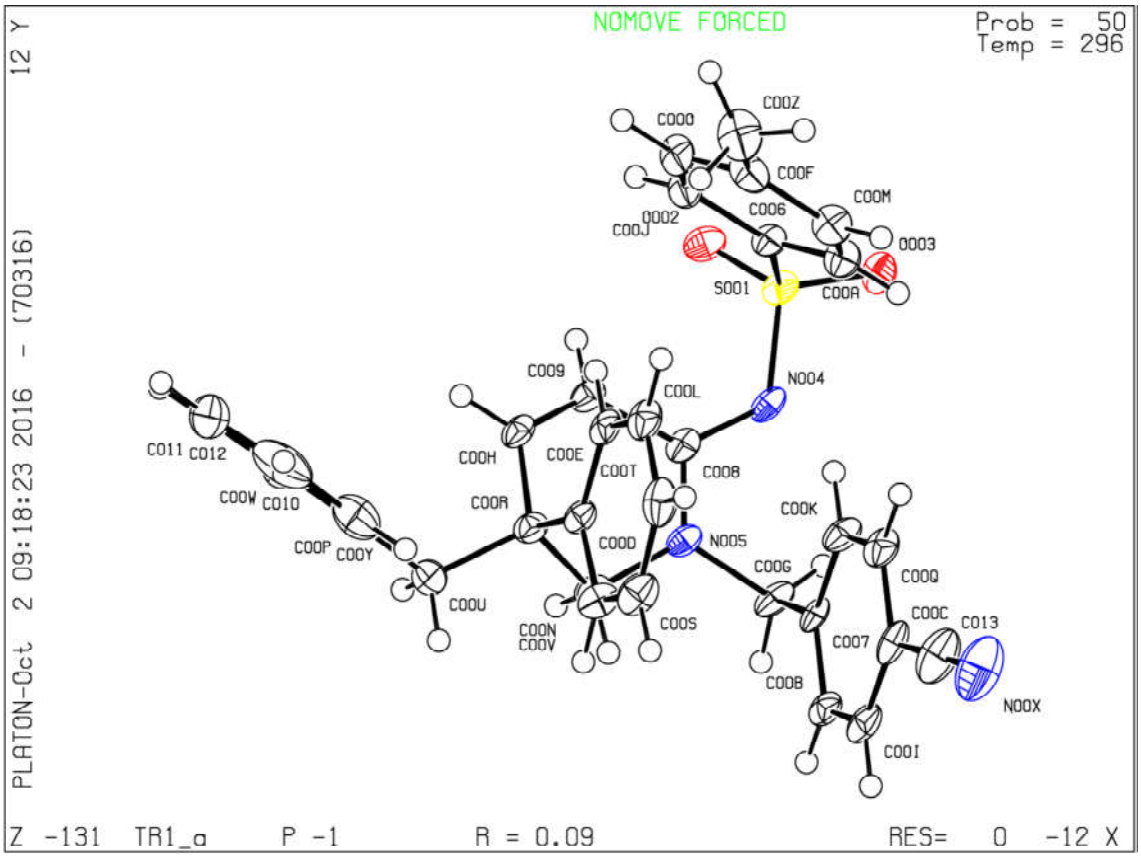


Fig. S5 ORTEP diagram of **22b**.

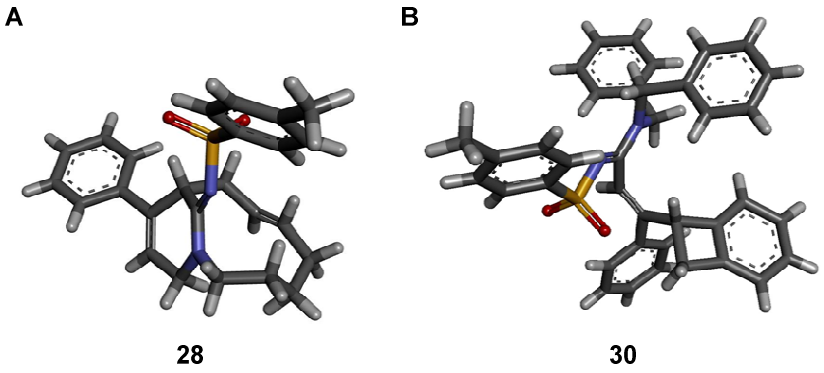


Fig. S6 Single crystal X-raydiffraction structures of **28** (**A**) and **30** (**B**) represented in the stick model.

V. Theoretical Calculations.

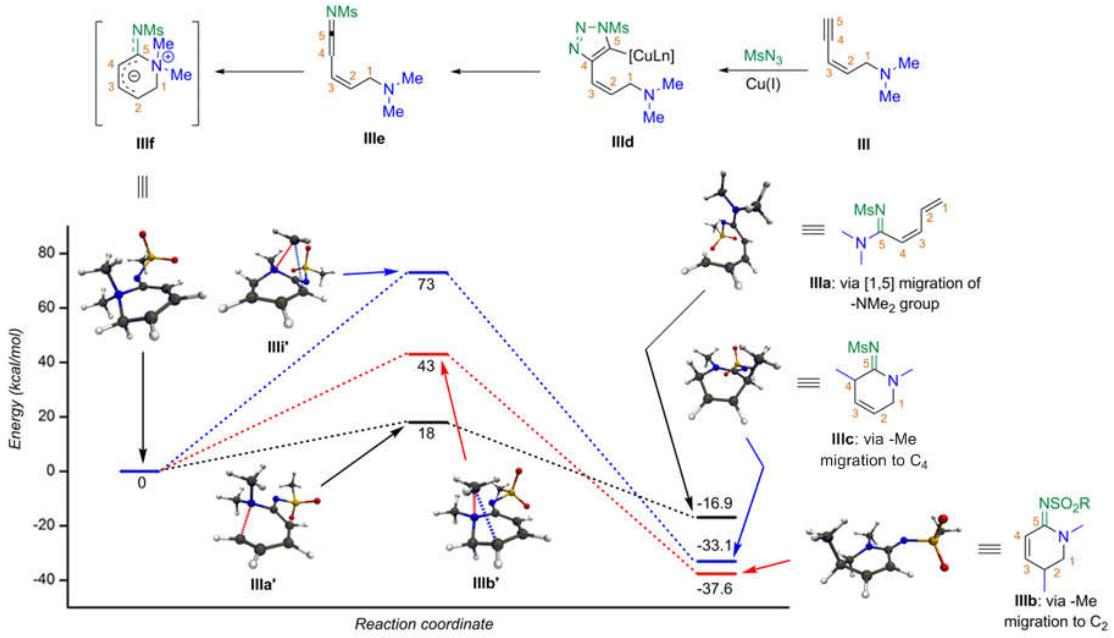


Fig. S7 Representation of the enynamine **III** (a simplified version of **II** with $R^1 = R^2 = Me$, $R^3 = R^4 = H$), corresponding intermediates and products along with the energy profile diagram. All energies were calculated at the MP2/6-31G level.

Table S1. Calculated energy barriers to products **IIIa**, **IIIb**, and **IIIc**.

Quantity calculated	Barrier height for product formation (kcal/mol)		
	For **IIIa**	For **IIIb**	for **IIIc**
E_{MP2} (energy using MP2 (6-31G))	18.4	43.1	73.1
E_{DFT} (energy using DFT(6-31G))	13.3	44.3	63.6
$\Delta E_{MP2-DFT} = E_{MP2} - E_{DFT}$	**5.1**	**-1.2**	**9.5**

Table S2. Calculated energy barriers for formation of product types **a** (1,5-amino migration product) and **b** (cyclic amidine via migration of $-R_1$ group to C_2) from corresponding substrates **9-12**.

Substrate	Barrier height for product formation (kcal/mol)				Prediction
	a		**b**		
	E_a (energy using DFT (6-31G))	E_a + **5.1** (estimated energy with correction)	E_b (energy using DFT (6-31G))	E_a–**1.2** (estimated energy with correction)	
9	16.4	**21.5**	22.7	**21.5**	Both

					products
10	16.5	**21.6**	19.6	**18.4**	Cyclic product
11	11.6	**16.7**	21.3	**20.1**	1,5-amino migration product
12	9.2	**14.3**	16.1	**14.9**	Both products

Cartesian coordinates of stationary points for simplified system ($R^1 = R^2 = Me$, $R^3 = R^4 = H$) and four sets of reactions (Substrates 9, 10, 11 and 12) considered in theoretical study:

Simplified system-Intermediate IIIf(DFT)

N	-1.713315	-0.867378	0.078846
C	-0.497149	0.091433	0.392301
C	-0.766865	1.433667	0.292211
C	-2.046230	1.952871	-0.123357
C	-3.159659	1.176656	-0.120984
C	-3.037315	-0.185043	0.480001
N	0.619323	-0.640442	0.576312
S	2.106309	0.073302	-0.203133
O	2.439851	1.628563	0.231192
O	2.089374	-0.269872	-1.817159
C	3.371818	-1.027687	0.634637
H	3.287033	-0.838684	1.702800
H	3.117960	-2.053664	0.376540
H	4.342319	-0.730837	0.239992
H	-3.848258	-0.863580	0.199438
H	-2.978190	-0.136314	1.578534
H	-4.128974	1.519156	-0.462047
H	-2.091564	2.985584	-0.457703
H	0.071356	2.104856	0.442072
C	-1.580553	-2.161780	0.849302
H	-0.601626	-2.584852	0.638133
H	-2.388601	-2.826942	0.537717
C	-1.656578	-1.149124	-1.415446
H	-0.633878	-1.440259	-1.660054
H	-1.922653	-0.232685	-1.941789
H	-2.365707	-1.945531	-1.654123
H	-1.655005	-1.939239	1.914601

Simplified system-Product IIIa (DFT)

C	1.659244	1.761265	-1.706516
N	1.731294	-1.369376	0.087223
C	0.646623	-0.582180	0.332635
C	0.792681	0.664557	1.133425
C	1.481071	1.768424	0.776712
C	2.179171	2.017437	-0.493379

C	1.575254	-2.563226	-0.757868
C	3.055959	-1.163935	0.683765
N	-0.520180	-1.048718	-0.119400
S	-1.932769	0.111198	0.012233
O	-2.292690	0.529166	1.564644
C	-3.238121	-1.102156	-0.564774
O	-1.816301	1.315267	-1.105942
H	0.649247	1.376857	-1.824069
H	2.211517	1.991208	-2.613480
H	3.150293	2.508607	-0.415868
H	1.509082	2.585189	1.498782
H	0.210521	0.671202	2.050638
H	-4.180145	-0.556272	-0.562417
H	-2.949492	-1.423711	-1.563283
H	-3.235906	-1.924009	0.148279
H	1.188493	-3.412370	-0.180729
H	2.550040	-2.825694	-1.176830
H	3.388883	-2.089002	1.168977
H	3.015182	-0.371279	1.428072
H	0.868444	-2.351220	-1.561584
H	3.784601	-0.887145	-0.087579

Simplified system-Product IIIb (DFT)

C	3.317433	-0.650376	-1.564304
C	3.033873	-0.851262	-0.072376
C	1.845955	-1.744374	0.134000
C	0.611025	-1.236763	0.292620
C	0.371772	0.219639	0.241361
N	1.477036	1.016439	0.225081
C	1.291552	2.458529	0.277886
N	-0.795840	0.819476	0.173865
S	-2.171030	-0.109951	-0.026414
C	-3.373241	1.179325	0.178926
C	2.759999	0.460586	0.649466
O	-2.349216	-1.061668	1.083962
O	-2.249440	-0.605904	-1.407976
H	3.911250	-1.307111	0.395018
H	1.984992	-2.819289	0.110055
H	-0.245762	-1.874017	0.447594
H	-4.349862	0.715922	0.064472
H	-3.265832	1.602397	1.172605
H	-3.215982	1.934259	-0.584666
H	2.767072	0.297971	1.734401
H	3.530456	1.195491	0.413922
H	0.526776	2.742413	-0.438519
H	2.235795	2.932916	0.022326
H	2.471933	-0.158562	-2.042404
H	3.479474	-1.607929	-2.057432
H	4.208191	-0.037528	-1.707601
H	0.972199	2.788861	1.269277

Simplified system-Product IIIc (DFT)

C	1.568697	2.394019	0.728199
C	1.688219	1.317082	-0.362526
C	3.098769	0.840501	-0.464715
C	3.446100	-0.435090	-0.290570

C	2.452656	-1.491716	0.040045
N	1.094279	-0.996121	0.287035
C	0.659693	0.227703	-0.102856
N	-0.560168	0.699977	-0.200357
S	-2.029931	-0.051233	-0.063975
C	-3.040201	1.331236	-0.531701
C	0.165272	-2.078750	0.630658
O	-2.196108	-1.095022	-1.091549
O	-2.352803	-0.375174	1.336892
H	-0.503798	-1.753658	1.421478
H	-0.426273	-2.383390	-0.230112
H	0.755845	-2.918293	0.986438
H	3.852571	1.590568	-0.676414
H	4.478641	-0.752916	-0.362718
H	2.774606	-2.021371	0.941401
H	2.404417	-2.240912	-0.760114
H	1.394261	1.773325	-1.312197
H	0.563925	2.806457	0.740376
H	2.288377	3.193008	0.549849
H	1.780581	1.952073	1.702201
H	-4.070700	0.985944	-0.504547
H	-2.888349	2.136375	0.179722
H	-2.768622	1.642190	-1.535273

Simplified system-Transition state IIIa′ (DFT)

N	-1.695074	-1.020044	-0.034781
C	-3.288217	0.218989	0.595063
C	-3.149898	1.383018	-0.152524
C	-1.881268	1.994129	-0.153111
C	-0.709694	1.312932	0.182374
C	-0.532933	-0.101012	0.169350
N	0.591480	-0.800731	0.167802
S	2.192199	0.130084	-0.079240
O	2.417065	0.425784	-1.679887
C	-1.719370	-2.167736	0.903799
C	-1.835144	-1.404133	-1.466977
C	3.320792	-1.274807	0.441158
O	2.429921	1.372485	0.974786
H	-2.777087	0.155173	1.554086
H	-4.160330	-0.423269	0.492523
H	-3.949712	1.748259	-0.789226
H	-1.779277	3.025883	-0.486407
H	0.205309	1.886676	0.284352
H	4.337694	-0.918059	0.284381
H	3.112348	-1.469780	1.491356
H	3.079025	-2.124920	-0.193138
H	-0.828000	-2.793246	0.790886
H	-2.618653	-2.757087	0.705804
H	-0.937225	-1.908614	-1.837768
H	-2.014113	-0.497160	-2.050880
H	-1.752570	-1.791082	1.930335
H	-2.699581	-2.066575	-1.562703

Simplified system-Transition state IIIb' (DFT)

C	1.652188	-1.515102	0.709814
C	1.922639	0.303643	-2.120380

N	1.094047	0.698153	-0.062588
C	2.447460	1.084520	0.434250
C	3.383030	0.008429	0.003895
C	2.981523	-1.280391	0.355345
C	0.628109	-0.569656	0.395045
N	-0.619527	-1.079602	0.360450
S	-2.140477	-0.094858	0.252036
C	-3.298409	-1.534248	0.533003
C	0.159324	1.832669	-0.273864
O	-2.346755	0.982609	1.489931
O	-2.433266	0.472268	-1.277497
H	-0.588381	1.569095	-1.027157
H	-0.370260	2.082229	0.651513
H	0.740684	2.687527	-0.621059
H	3.683348	-2.109832	0.331055
H	4.411017	0.247672	-0.244713
H	2.695331	2.060020	0.016653
H	2.397207	1.176184	1.534407
H	1.313405	-2.486139	1.044354
H	0.863085	0.209270	-2.330525
H	2.520846	-0.570196	-2.338892
H	2.373079	1.262963	-2.354842
H	-4.306337	-1.136866	0.425847
H	-3.060356	-2.274371	-0.227546
H	-3.102139	-1.901546	1.538016

Simplified system-Transition state IIIc′ (DFT)

C	0.005269	0.016295	-0.002378
C	0.003474	-0.006336	1.438122
C	1.212159	-0.008385	2.168795
N	2.370925	0.477864	1.397816
C	2.485651	-0.084983	0.014151
C	1.159909	-0.022053	-0.707095
C	3.679029	0.718259	2.033014
N	1.177996	-0.506485	3.411756
S	2.311685	0.106963	4.734108
O	3.766685	-0.649847	4.883758
O	2.322845	1.773812	4.751096
C	1.149628	2.430249	1.752813
C	1.249153	-0.473338	6.160733
H	3.581387	1.425532	2.857525
H	4.133808	-0.204081	2.414457
H	4.337673	1.155311	1.276933
H	-0.951451	0.048251	-0.516374
H	1.173756	-0.030370	-1.792266
H	3.235774	0.530369	-0.497211
H	2.897169	-1.115711	0.048130
H	-0.903546	-0.217008	1.989618
H	1.410184	2.443319	2.810702
H	0.108189	2.492902	1.474800
H	1.877442	2.805565	1.046483
H	1.785209	-0.203192	7.069089
H	0.294559	0.039957	6.071044
H	1.146156	-1.550650	6.046502

Simplified system-Intermediate IIIf(MP2)

C	-3.038071	-0.278442	0.384235
N	-1.681407	-0.870193	-0.058485
C	-0.509838	0.043199	0.467521
C	-0.801125	1.393055	0.561845
C	-2.074386	1.957310	0.134283
C	-3.170157	1.157487	-0.044309
C	-1.545074	-2.273259	0.515868
C	-1.540710	-0.911903	-1.580028
N	0.629259	-0.697234	0.594533
S	2.082450	0.132650	-0.060885
O	2.044537	0.079244	-1.701668
C	3.365187	-1.076278	0.546911
O	2.420137	1.587492	0.611947
H	-3.016693	-0.372724	1.483857
H	-3.821564	-0.932381	-0.022297
H	-4.134440	1.526717	-0.387573
H	-2.123671	3.026825	-0.074830
H	0.012779	2.042300	0.883805
H	4.326437	-0.721073	0.168716
H	3.319313	-1.055485	1.636780
H	3.096737	-2.052222	0.139921
H	-0.562566	-2.655194	0.239432
H	-2.359193	-2.880428	0.103873
H	-0.486572	-1.110060	-1.801281
H	-1.832151	0.067512	-1.969333
H	-1.620623	-2.201772	1.604893
H	-2.197494	-1.697104	-1.971860

Simplified system-Product IIIa (MP2)

C	1.573996	1.724222	-1.709983
N	1.738116	-1.385755	0.149235
C	0.655819	-0.582735	0.361097
C	0.790828	0.666289	1.178716
C	1.486521	1.769677	0.790776
C	2.177920	1.942581	-0.513178
C	1.559690	-2.570322	-0.725865
C	3.097007	-1.098625	0.658206
N	-0.505069	-1.035893	-0.152341
S	-1.922206	0.092759	0.037953
O	-2.285534	0.419704	1.598624
C	-3.212152	-1.085364	-0.609682
O	-1.815966	1.355189	-0.997559
H	0.521118	1.446300	-1.770354
H	2.108889	1.880795	-2.646679
H	3.206806	2.314397	-0.479850
H	1.513343	2.619608	1.478566
H	0.223426	0.675605	2.109816
H	-4.155918	-0.535115	-0.606061
H	-2.902571	-1.368193	-1.616823
H	-3.229423	-1.936124	0.073279
H	0.832409	-3.263465	-0.285545
H	2.531593	-3.062436	-0.833087
H	3.542263	-2.034062	1.018292
H	3.036520	-0.389228	1.486512
H	1.184991	-2.257581	-1.708990
H	3.729580	-0.672144	-0.133409

Simplified system-Product IIIb (MP2)

C	3.404679	-0.764486	-1.375844
C	3.104700	-0.726286	0.147150
C	1.914445	-1.604343	0.508940
C	0.657382	-1.095588	0.569036
C	0.400003	0.339333	0.260191
N	1.487222	1.172586	0.177988
C	1.269259	2.608222	-0.105159
N	-0.796305	0.903719	0.030725
S	-2.215660	-0.243616	-0.096566
C	-3.532978	1.072503	-0.143440
C	2.815379	0.702561	0.658998
O	-2.449599	-1.129488	1.260154
O	-2.205800	-1.047250	-1.515764
H	3.994516	-1.089209	0.688242
H	2.083666	-2.667917	0.685701
H	-0.194509	-1.708235	0.859177
H	-4.485482	0.545858	-0.237899
H	-3.457342	1.620563	0.796970
H	-3.320977	1.702572	-1.008465
H	2.847991	0.720094	1.762801
H	3.566847	1.409682	0.281172
H	0.577390	2.703804	-0.948824
H	2.237052	3.054841	-0.357038
H	2.548608	-0.369616	-1.939239
H	3.588276	-1.796438	-1.705025
H	4.294883	-0.161564	-1.608130
H	0.833368	3.128052	0.760732

Simplified system-Product IIIc (MP2)

C	2.272974	1.842357	1.320977
C	1.835535	1.343916	-0.088356
C	2.994021	0.748028	-0.868032
C	3.265263	-0.572190	-0.791228
C	2.399161	-1.503846	0.026022
N	1.025593	-0.969505	0.286817
C	0.689131	0.327762	0.040043
N	-0.499707	0.941203	-0.038278
S	-2.099166	0.039980	-0.108921
C	-3.083661	1.498747	-0.718220
C	0.068553	-2.006631	0.763117
O	-2.115674	-1.113952	-1.269367
O	-2.687347	-0.371716	1.363236
H	-0.682974	-1.552320	1.417087
H	-0.436226	-2.497015	-0.077167
H	0.644789	-2.734058	1.347416
H	3.614449	1.421245	-1.461117
H	4.108958	-1.019644	-1.317345
H	2.874062	-1.742926	0.994465
H	2.265524	-2.454704	-0.513418
H	1.412264	2.192047	-0.641910
H	1.414215	2.286200	1.841528
H	3.064419	2.598437	1.221902
H	2.662520	1.005075	1.917457
H	-4.120282	1.160147	-0.783699
H	-2.952595	2.292189	0.018749

H	-2.673902	1.767514	-1.692892

Simplified system-Transition state IIIa′ (MP2)

N	-1.705524	-1.030896	-0.013007
C	-3.300392	0.231437	0.524406
C	-3.139017	1.388758	-0.237274
C	-1.865329	2.018312	-0.151233
C	-0.719540	1.321393	0.254697
C	-0.548392	-0.110164	0.205555
N	0.590792	-0.803016	0.175327
S	2.176727	0.153138	-0.034576
O	2.341238	0.608682	-1.590708
C	-1.745184	-2.147093	0.978092
C	-1.789887	-1.472247	-1.441880
C	3.318267	-1.282886	0.314721
O	2.429659	1.280492	1.119084
H	-2.823197	0.202539	1.508420
H	-4.178333	-0.408749	0.412564
H	-3.893594	1.719519	-0.950706
H	-1.743464	3.062758	-0.450766
H	0.195992	1.890750	0.420559
H	4.334315	-0.902241	0.185931
H	3.122524	-1.590860	1.343238
H	3.073632	-2.064004	-0.406565
H	-0.841598	-2.767827	0.907426
H	-2.641383	-2.747957	0.781099
H	-0.881115	-1.999482	-1.760502
H	-1.938487	-0.574806	-2.056590
H	-1.806193	-1.714031	1.984366
H	-2.664828	-2.126362	-1.540263

Simplified system-Transition state IIIb′ (MP2)

N	1.649151	-0.882499	-0.288401
C	2.319241	-0.508973	1.684027
C	3.067304	0.984237	-0.114266
C	1.948436	1.840339	-0.120869
C	0.681574	1.329407	-0.464459
C	0.466126	-0.083117	-0.448206
N	-0.691496	-0.801987	-0.410445
S	-2.102557	0.163363	0.165542
O	-1.938308	0.537562	1.753231
O	-2.520079	1.398601	-0.827982
C	-3.395069	-1.164655	-0.019358
H	-3.088425	-1.996896	0.616019
H	-4.338449	-0.721055	0.307573
H	-3.413034	-1.435218	-1.076322
H	-0.182314	1.979057	-0.600318
H	2.046603	2.886003	0.174606
H	4.069596	1.350919	0.105308
C	2.886078	-0.286159	-0.890994
H	2.701960	-0.110165	-1.967785
H	3.707264	-0.999288	-0.764726
H	1.479546	0.106820	2.015455
H	2.165307	-1.578482	1.857814
H	3.291809	-0.176030	2.054591
C	1.465013	-2.362055	-0.429428

H	2.428587	-2.836788	-0.218360
H	0.698525	-2.679361	0.280067
H	1.124967	-2.597309	-1.445583

Simplified system-Transition state IIIc′ (MP2)

C	-3.123523	-1.060169	-0.432273
C	-1.767461	-1.481351	-0.074901
C	-0.690151	-0.552237	-0.156692
N	-1.195254	0.832936	0.134785
C	-2.287648	1.264586	-0.806383
C	-3.397234	0.223756	-0.804601
C	-0.291055	1.946429	0.534462
N	0.523349	-0.966353	-0.526974
S	2.043061	-0.060446	-0.079118
O	2.374638	1.246380	-1.007610
O	2.151283	0.134012	1.556737
C	-1.623317	-0.170840	2.003570
C	3.223374	-1.410049	-0.577077
H	0.422658	1.598996	1.286630
H	0.263348	2.350691	-0.323355
H	-0.929492	2.726244	0.972026
H	-3.918364	-1.807003	-0.401913
H	-4.396655	0.538666	-1.104985
H	-2.650232	2.224540	-0.408792
H	-1.879922	1.460244	-1.821348
H	-1.499875	-2.537896	-0.111680
H	-0.571800	-0.260951	2.284005
H	-2.229498	-1.042670	2.233145
H	-2.093264	0.776610	2.264866
H	4.226690	-1.023121	-0.383834
H	2.985821	-2.277202	0.040490
H	3.050377	-1.598367	-1.637914

Substrate 9-Intermediate

C	1.238301	2.771430	0.581610
C	-0.115427	2.388787	0.525310
C	-1.097095	3.382349	0.352910
C	-0.737984	4.728635	0.226584
C	0.611278	5.098276	0.272821
C	1.595319	4.117402	0.451157
C	-0.532369	0.949831	0.727957
N	-0.343154	0.014399	-0.490187
C	-0.968682	0.642212	-1.742802
C	-0.691277	-0.172622	-2.968215
C	0.551641	-0.697239	-3.101321
C	1.516043	-0.608220	-2.031211
C	1.175623	-0.300005	-0.739779
N	1.854507	-0.338055	0.432641
S	2.996882	-1.754695	0.574297
C	3.897420	-1.183299	2.116196
C	-0.959660	-1.394077	-0.170145
C	-2.415447	-1.397903	0.219249
C	-2.794511	-1.408403	1.575140
C	-4.144427	-1.449194	1.939440
C	-5.136757	-1.488264	0.952127
C	-4.772802	-1.497944	-0.400026

C	-3.422393	-1.457014	-0.762963
O	2.139602	-3.118096	0.938864
O	4.116200	-1.873826	-0.630890
H	-0.495015	1.629282	-1.815129
H	-1.447735	-0.232729	-3.742352
H	2.548081	-0.892392	-2.203690
H	-2.033282	0.780465	-1.540471
H	-0.315736	-1.798570	0.614391
H	-0.794686	-1.967858	-1.083162
H	0.055633	0.478549	1.515931
H	-1.594955	0.893534	0.967517
H	-2.027407	-1.401285	2.344364
H	-4.419345	-1.460895	2.989358
H	-6.184393	-1.523697	1.233809
H	-5.537310	-1.548126	-1.169072
H	-3.142552	-1.492420	-1.812277
H	-2.147160	3.101368	0.326896
H	-1.507172	5.483801	0.097317
H	0.892769	6.142354	0.176258
H	2.642487	4.400283	0.494434
H	1.993658	2.005920	0.727282
H	4.616364	-1.964856	2.356955
H	4.384226	-0.244379	1.860600
H	3.147005	-1.060386	2.894176
H	0.846207	-1.209606	-4.012799

Substrate 9-Product a

C	-2.274937	2.341171	0.390827
C	-2.457800	1.242186	-0.466759
C	-3.764754	0.829315	-0.772294
C	-4.870646	1.506743	-0.244042
C	-4.680129	2.600762	0.607102
C	-3.379185	3.013054	0.925466
C	-1.277501	0.521851	-1.096622
N	-0.245313	0.088876	-0.125315
C	-0.718207	-0.798158	0.970986
C	-1.201726	-2.159214	0.496118
C	-0.334214	-3.050172	-0.163187
C	-0.790783	-4.304766	-0.579486
C	-2.116488	-4.690678	-0.337971
C	-2.984549	-3.812813	0.319825
C	-2.529362	-2.553151	0.729378
C	1.094280	0.255232	-0.339606
C	1.565275	1.151968	-1.436441
C	1.585929	2.500265	-1.440773
C	1.197208	3.430787	-0.370142
C	1.575163	3.330847	0.916883
N	1.915040	-0.491895	0.400591
S	3.710976	-0.153122	0.209934
C	4.288397	-1.596228	1.256139
O	4.153033	1.234158	0.979723
O	4.253962	-0.397313	-1.324708
H	3.817327	-1.486608	2.230528
H	3.970762	-2.502246	0.744072
H	5.372805	-1.512986	1.309385
H	0.114823	-0.905299	1.668746
H	-1.533485	-0.274291	1.478038

H	0.696962	-2.758606	-0.335014
H	-0.111987	-4.983804	-1.086960
H	-2.466824	-5.666967	-0.658903
H	-4.013039	-4.103485	0.511822
H	-3.208159	-1.870858	1.234205
H	-1.642525	-0.368156	-1.626546
H	-0.786728	1.162335	-1.832380
H	-3.916220	-0.026947	-1.424211
H	-5.874903	1.176975	-0.492334
H	-5.535544	3.125713	1.021054
H	-3.225021	3.859313	1.588286
H	-1.268385	2.663399	0.638020
H	2.000129	0.617599	-2.277243
H	0.620824	4.299230	-0.693295
H	2.244730	2.546790	1.259837
H	1.274094	4.081410	1.643101
H	1.950850	2.972974	-2.353671

Substrate 9-Product b

C	1.508162	-0.750551	0.166910
C	1.272476	-1.956654	-0.653934
C	0.037710	-2.458972	-0.821222
C	-1.188827	-1.803642	-0.233350
C	-0.916628	-0.304651	-0.043668
N	0.403166	-0.050724	0.572857
C	-2.449740	-2.046515	-1.111026
C	-3.724707	-1.462091	-0.529822
C	-4.317321	-0.319559	-1.094301
C	-5.481217	0.231668	-0.544524
C	-6.071273	-0.354371	0.580791
C	-5.493632	-1.496857	1.150058
C	-4.331596	-2.045598	0.597897
C	0.533130	1.161383	1.412296
C	0.273527	2.454850	0.656125
C	-0.806148	3.276253	1.016108
C	-1.058199	4.469641	0.328049
C	-0.232204	4.849815	-0.734822
C	0.848678	4.035657	-1.101986
C	1.103725	2.847214	-0.410405
N	2.691924	-0.303628	0.581537
S	4.189124	-1.205149	0.025838
C	5.347615	-0.460498	1.294661
O	4.643483	-0.697057	-1.468816
O	4.133022	-2.831039	0.285620
H	-6.975010	0.069827	1.006975
H	-5.925836	1.113259	-0.996023
H	-3.866894	0.135444	-1.972354
H	-5.951061	-1.962190	2.017890
H	-3.896201	-2.938900	1.038817
H	-2.562360	-3.131678	-1.243200
H	-2.269742	-1.625499	-2.109066
H	-1.376964	-2.257158	0.755400
H	2.138747	-2.478168	-1.038254
H	-1.674053	0.143630	0.603297
H	-0.973579	0.207012	-1.017014
H	-0.181817	1.069948	2.238864
H	1.543281	1.146798	1.826418

H	-1.450570	2.979942	1.840093
H	-1.896587	5.095029	0.619441
H	-0.426386	5.772576	-1.272924
H	1.494188	4.329452	-1.924028
H	1.947844	2.223689	-0.689866
H	6.343749	-0.818073	1.038123
H	5.260591	0.620133	1.204315
H	5.019361	-0.821453	2.267256
H	-0.094769	-3.390077	-1.368362

Substrate 9-Transition state for Product a

C	-1.208694	2.469893	-0.661267
C	0.150058	2.106612	-0.596664
C	1.104089	3.103715	-0.321597
C	0.715744	4.429626	-0.101694
C	-0.638983	4.778003	-0.155464
C	-1.597007	3.795740	-0.435844
C	0.614500	0.687608	-0.868892
N	0.450581	-0.279672	0.283421
C	1.273741	-1.553321	0.167097
C	2.723407	-1.347264	-0.211072
C	3.679833	-0.987962	0.755690
C	5.023469	-0.821335	0.402312
C	5.431571	-1.017522	-0.923038
C	4.491085	-1.387533	-1.891781
C	3.147982	-1.552762	-1.536027
C	-0.976639	-0.673687	0.555595
C	-1.409595	-0.970128	1.879021
C	-0.602671	-0.959204	3.020410
C	0.624593	-0.278135	3.078352
C	0.842211	0.700891	2.107602
N	-1.613531	-0.858772	-0.590316
S	-3.393832	-1.398898	-0.547888
O	-3.740789	-2.609315	0.513479
C	-3.418426	-2.145836	-2.270881
O	-4.340228	-0.055544	-0.548664
H	-3.105533	-1.360720	-2.955968
H	-4.444827	-2.464084	-2.447502
H	-2.725319	-2.984622	-2.257625
H	-2.378546	-1.451314	1.947433
H	1.398912	-0.565478	3.782960
H	0.011432	1.336381	1.816992
H	1.825746	1.131751	1.943056
H	1.207288	-2.019237	1.156728
H	3.370050	-0.854673	1.787657
H	5.751209	-0.547865	1.160172
H	6.474453	-0.890555	-1.196113
H	4.801472	-1.551842	-2.918908
H	2.421368	-1.846528	-2.288808
H	1.681873	0.698174	-1.091810
H	0.080834	0.274909	-1.731514
H	2.158206	2.838866	-0.286864
H	1.466597	5.186059	0.106241
H	-0.944714	5.805777	0.014847
H	-2.649127	4.058157	-0.484152
H	-1.962298	1.720931	-0.881054
H	0.782845	-2.213321	-0.557208

H	-0.929145	-1.559466	3.868347

Substrate 9-Transition state for Product b

C	0.792775	0.379466	1.878572
C	0.569404	-0.736095	2.845538
C	-0.668464	-1.342779	2.876630
C	-1.626372	-1.093750	1.876131
C	-1.267115	-0.390681	0.697526
N	0.019807	0.165213	0.640989
C	0.407502	1.006555	-0.518578
C	0.211994	2.497016	-0.286950
C	1.322657	3.344971	-0.149636
C	1.151360	4.717980	0.066860
C	-0.137283	5.255892	0.153137
C	-1.251864	4.416915	0.015054
C	-1.081488	3.046837	-0.206669
N	-1.999167	-0.246506	-0.438874
S	-3.189228	-1.583025	-0.728341
C	-3.983304	-0.855896	-2.260734
O	-2.371264	-2.953656	-1.153113
O	-4.382894	-1.746490	0.401100
C	1.295274	-2.165286	0.214323
C	2.560012	-1.754719	-0.260419
C	3.696970	-1.709244	0.605573
C	4.945402	-1.327703	0.127119
C	5.107849	-0.972625	-1.223446
C	4.004925	-0.998427	-2.093921
C	2.749400	-1.372638	-1.625741
H	3.569924	-1.986681	1.648026
H	5.798702	-1.305652	0.797631
H	6.084346	-0.676730	-1.593090
H	4.133651	-0.726747	-3.136826
H	1.898727	-1.405807	-2.299519
H	0.434470	-2.228346	-0.441874
H	1.196388	-2.612186	1.193942
H	1.462216	0.797318	-0.727098
H	-0.200896	0.662218	-1.356611
H	2.325358	2.929800	-0.218532
H	2.019798	5.361992	0.168295
H	-0.273408	6.319518	0.323480
H	-2.253608	4.831623	0.075670
H	-1.941491	2.394242	-0.323445
H	-3.177886	-0.634967	-2.957796
H	-4.510434	0.041608	-1.943185
H	-4.662348	-1.617375	-2.640575
H	-2.627303	-1.502558	1.938120
H	1.310585	-0.903925	3.619910
H	1.849005	0.471236	1.596833
H	0.503800	1.351739	2.325141
H	-0.913849	-2.039235	3.673936

Substrate 10-Intermediate

C	5.307519	-1.142392	0.714781
H	6.013629	-1.924439	0.989227
H	5.137606	-0.436530	1.524901

H	5.586340	-0.646884	-0.212917
S	3.673307	-2.002832	0.391934
O	3.886673	-2.998716	-0.904798
O	3.162101	-2.702629	1.796982
N	2.683125	-0.505287	0.059365
C	1.463101	-0.752930	-0.468298
N	0.374950	0.153029	0.194285
C	-0.046492	-0.647860	1.483651
H	-0.483306	-1.566972	1.091144
H	0.902996	-0.889440	1.967252
C	-0.997206	0.063314	2.410905
C	-2.388272	0.020672	2.195473
H	-2.786026	-0.526951	1.346383
C	-3.264906	0.662170	3.077859
H	-4.334615	0.618513	2.899068
C	-2.765794	1.345976	4.192946
H	-3.447058	1.839318	4.879147
C	-1.385793	1.377632	4.429654
H	-0.993586	1.889971	5.302456
C	-0.509523	0.738470	3.546647
H	0.558909	0.748729	3.744017
C	0.965291	1.523875	0.612254
H	0.257686	1.931045	1.334249
H	1.901345	1.264452	1.107679
C	1.184864	2.510010	-0.510867
C	0.302348	3.597012	-0.650144
H	-0.536030	3.695250	0.035108
C	0.497344	4.553870	-1.651253
H	-0.191025	5.388145	-1.743498
C	1.581440	4.433220	-2.528323
H	1.735387	5.173296	-3.307493
C	2.470940	3.359072	-2.392760
H	3.316399	3.268161	-3.067508
C	2.280795	2.403799	-1.388134
H	2.971917	1.575127	-1.271684
C	-0.800919	0.353514	-0.766126
H	-0.384888	0.953897	-1.583368
H	-1.543285	0.951743	-0.234726
C	-1.349516	-0.953242	-1.282566
C	-2.793833	-1.099197	-1.527101
C	0.986787	-1.699503	-1.341720
H	1.717800	-2.380856	-1.762059
C	-0.407213	-1.886299	-1.620301
H	-0.697851	-2.796981	-2.135296
C	-3.394311	-2.379071	-1.603928
C	-4.756699	-2.523074	-1.868096
C	-5.569103	-1.395082	-2.049231
C	-4.997554	-0.120727	-1.964119
C	-3.631200	0.026817	-1.707573
H	-2.788341	-3.262808	-1.432447
H	-5.189287	-3.517823	-1.919079
H	-6.629603	-1.508986	-2.249925
H	-5.613100	0.762520	-2.107484
H	-3.208998	1.026797	-1.681780

Substrate 10-Product a

C	-3.901598	-3.387633	1.160583

H	-4.618255	-2.778929	0.613142
H	-3.723407	-3.010213	2.165287
H	-4.170267	-4.442840	1.157164
S	-2.273689	-3.266157	0.241645
O	-2.542707	-3.703026	-1.322669
O	-1.146278	-4.108019	1.097761
N	-2.077646	-1.451940	0.447028
C	-1.045268	-0.894247	-0.190063
N	-0.849751	0.441960	0.016846
C	-0.014182	1.283557	-0.870603
H	-0.680904	1.866166	-1.520223
H	0.563602	0.614271	-1.510870
C	0.908175	2.238063	-0.130295
C	0.944671	3.590924	-0.505508
C	1.820178	4.484176	0.123179
C	2.663368	4.034061	1.145332
C	2.626984	2.687756	1.531915
C	1.757995	1.793884	0.897630
H	1.735249	0.751056	1.197114
H	3.280675	2.332059	2.322476
H	3.341157	4.724946	1.637139
H	1.838183	5.526616	-0.180108
H	0.282282	3.945472	-1.291001
C	-1.706832	1.174441	0.988933
H	-2.149372	0.421066	1.643126
H	-1.046916	1.810440	1.585752
C	-2.785911	2.021769	0.335425
C	-2.766259	3.419085	0.475935
C	-3.764538	4.210838	-0.105344
C	-4.792358	3.612036	-0.841729
C	-4.818956	2.218432	-0.990200
C	-3.825480	1.427553	-0.404601
H	-3.853583	0.347366	-0.507463
H	-5.616831	1.748544	-1.557592
H	-5.566867	4.223600	-1.294436
H	-3.736918	5.289666	0.015357
H	-1.965556	3.887521	1.041869
C	-0.207074	-1.635746	-1.179145
H	-0.762624	-1.940337	-2.063078
C	1.982635	-1.905858	0.109363
C	1.553830	-2.187450	1.360893
H	0.562264	-2.587303	1.545070
H	2.211994	-2.085184	2.218897
C	1.070247	-2.047260	-1.050632
C	3.394007	-1.526558	-0.194864
H	1.492693	-2.578243	-1.903724
C	4.461075	-1.947990	0.625546
C	5.776078	-1.572764	0.341388
C	6.058971	-0.778682	-0.777997
C	5.013875	-0.366241	-1.611406
C	3.697034	-0.738235	-1.323412
H	4.259403	-2.595264	1.472614
H	6.582826	-1.912154	0.984076
H	7.082252	-0.493108	-1.001306
H	5.221759	0.247906	-2.482334
H	2.894188	-0.403502	-1.973124

Substrate 10-Product b

C	1.423820	2.785167	0.123997
C	0.534281	3.869505	0.060362
H	-0.356764	3.867817	0.683451
C	0.788317	4.953226	-0.790191
H	0.092786	5.786137	-0.828357
C	1.936056	4.960292	-1.590009
H	2.134965	5.798092	-2.251266
C	2.830972	3.882870	-1.531654
H	3.725348	3.886807	-2.147371
C	2.579245	2.803843	-0.679753
H	3.273836	1.971654	-0.625867
C	1.141497	1.605300	1.040252
H	2.016648	1.368282	1.649067
H	0.303576	1.841597	1.705059
N	0.788106	0.362294	0.313477
C	1.718799	-0.616593	0.096810
N	2.944592	-0.415643	0.581126
S	4.096661	-1.848356	0.545015
O	3.769918	-2.904548	1.759530
O	4.328416	-2.473955	-0.964297
C	5.631033	-0.869607	0.987026
H	5.420941	-0.361142	1.925569
H	6.435668	-1.597174	1.080721
H	5.801802	-0.172204	0.169391
C	1.274484	-1.796748	-0.666074
H	2.046153	-2.475403	-1.010479
C	-0.024515	-2.014980	-0.930607
C	-1.124817	-1.066468	-0.470263
H	-0.341466	0.717352	-1.436462
C	-0.497320	0.344114	-0.415074
H	-1.165597	1.037860	0.100267
C	-1.583203	-1.540577	0.978647
H	-1.991365	-2.552398	0.872851
H	-0.679396	-1.626916	1.590851
C	-2.585636	-0.646081	1.682568
C	-2.158121	0.241199	2.688729
C	-3.068774	1.069404	3.355973
C	-4.428746	1.021925	3.029367
C	-4.870255	0.135228	2.039168
C	-3.958643	-0.691901	1.374688
H	-4.314313	-1.381458	0.616285
H	-5.925579	0.082212	1.788714
H	-5.138505	1.659725	3.547160
H	-2.718129	1.740374	4.134663
H	-1.107317	0.262532	2.966008
C	-2.317575	-1.112476	-1.445832
H	-0.311420	-2.908633	-1.475951
C	-2.895357	0.045076	-1.994791
C	-3.994410	-0.037311	-2.860275
C	-4.541621	-1.278827	-3.193623
C	-3.982157	-2.441653	-2.649490
C	-2.885564	-2.356361	-1.787283
H	-2.504781	1.026437	-1.753299
H	-4.420226	0.873558	-3.269947
H	-5.391749	-1.342147	-3.865452
H	-4.396773	-3.414153	-2.896820
H	-2.476081	-3.272744	-1.372083

Substrate 10-Transition state for Product a

C	0.135911	-0.012403	0.062472
N	0.049757	-0.069650	2.181074
C	1.524909	-0.109901	2.450246
N	1.773412	0.325200	3.672715
S	3.538964	0.377582	4.272057
O	4.461387	-0.943091	3.928435
O	4.140970	1.866610	3.923826
C	3.129856	0.308063	6.103660
H	2.696670	-0.673089	6.288824
H	2.426094	1.114826	6.296863
H	4.073383	0.445797	6.629745
C	-0.629552	1.183879	2.692729
H	-1.699160	0.990366	2.608192
H	-0.375325	1.291261	3.752937
C	-0.293526	2.462330	1.946652
C	-1.217114	2.986926	1.023510
H	-2.147740	2.455752	0.838687
C	-0.957628	4.184408	0.348056
C	0.234115	4.878051	0.589495
C	1.156754	4.370653	1.512546
C	0.895539	3.175491	2.192598
H	1.619872	2.798870	2.906804
H	2.081018	4.904010	1.710694
H	0.438976	5.807584	0.067222
H	-1.683448	4.575275	-0.358747
H	-0.270072	-1.499119	3.733869
C	-0.569092	-1.366839	2.687596
H	-0.096240	-2.155286	2.092742
C	-2.074015	-1.448799	2.558293
C	-2.674348	-1.827742	1.343974
C	-4.066431	-1.923312	1.238133
C	-4.878286	-1.648937	2.345755
C	-4.291075	-1.285185	3.563569
C	-2.899093	-1.188868	3.668017
H	-2.446992	-0.914644	4.617629
H	-4.913015	-1.082949	4.430157
H	-5.957928	-1.727117	2.263209
H	-4.514246	-2.221933	0.295325
H	-2.052470	-2.064586	0.486567
H	-0.907788	0.142295	-0.194728
H	0.709306	0.893725	0.221072
C	2.419793	-0.720816	1.521842
H	3.428879	-0.867318	1.890693
C	2.061037	-1.365584	0.342154
C	0.810621	-1.187827	-0.301787
C	0.229253	-2.202504	-1.207240
H	2.775232	-2.075653	-0.071700
C	-0.719083	-1.842830	-2.192968
C	-1.276745	-2.799936	-3.044529
C	-0.885373	-4.141752	-2.954655
C	0.065642	-4.514590	-1.997025
C	0.607797	-3.562555	-1.129155
H	-0.995426	-0.799439	-2.312308
H	-2.002660	-2.493865	-3.792246

H	-1.311813	-4.883524	-3.622646
H	0.375239	-5.552323	-1.914283
H	1.313596	-3.878067	-0.366992

Substrate 10-Transition state for Product b

C	-0.083451	0.128492	-0.204314
H	-0.152957	0.345994	0.859199
H	0.945367	0.134543	-0.560635
H	-0.725951	0.773456	-0.799998
S	-0.702986	-1.621188	-0.451082
O	0.164783	-2.632300	0.518210
O	-0.656270	-1.917779	-2.075144
N	-2.367224	-1.362845	0.234167
C	-3.217755	-2.403414	0.071100
N	-4.288761	-2.440195	0.972154
C	-4.548395	-1.271327	1.853240
H	-4.947813	-1.666341	2.793233
H	-3.576308	-0.810029	2.036579
C	-5.521177	-0.256431	1.272076
C	-6.808456	-0.117948	1.816187
H	-7.105400	-0.742336	2.655615
C	-7.707518	0.822044	1.297143
H	-8.698060	0.920773	1.730993
C	-7.327251	1.632236	0.221752
H	-8.022141	2.361696	-0.183015
C	-6.044363	1.501557	-0.327412
H	-5.743254	2.131421	-1.159055
C	-5.144359	0.567147	0.194196
H	-4.146234	0.469111	-0.220880
C	-3.240312	-4.133525	2.659013
H	-2.537065	-3.309856	2.660483
H	-3.090563	-4.900306	1.911078
C	-4.145723	-4.326906	3.723534
C	-4.241290	-3.386137	4.799214
H	-3.588041	-2.518682	4.795772
C	-5.130637	-3.590522	5.848043
H	-5.183114	-2.873115	6.660880
C	-5.958993	-4.727322	5.865132
H	-6.650099	-4.882692	6.687321
C	-5.888846	-5.663150	4.819696
H	-6.528514	-6.539658	4.832471
C	-5.004756	-5.471614	3.763652
H	-4.950017	-6.194385	2.957537
C	-3.112167	-3.488673	-0.843284
H	-2.321777	-3.454222	-1.582548
C	-5.457061	-3.299567	0.697121
H	-5.986053	-3.418328	1.647569
H	-6.142191	-2.764918	0.012417
C	-3.946871	-4.600657	-0.736551
C	-5.055541	-4.629127	0.114066
C	-5.911474	-5.794905	0.291816
C	-5.476885	-7.095134	-0.086673
H	-4.483259	-7.230094	-0.499927
C	-7.203862	-5.689046	0.870669
H	-7.591431	-4.718935	1.161086
C	-8.017002	-6.812440	1.041742
H	-9.005340	-6.694419	1.476143

C	-7.570323	-8.079580	0.652064
H	-8.202591	-8.951420	0.785381
C	-6.291278	-8.210627	0.087836
H	-5.927947	-9.189672	-0.209639
H	-3.720337	-5.462078	-1.357070

Substrate 11- Intermediate

C	-0.098153	1.041919	1.371579
C	1.377315	0.836136	1.468597
H	-0.633966	0.425538	2.104794
C	1.899802	-0.331314	0.991815
H	1.959162	1.547635	2.042244
C	1.028708	-1.240426	0.266791
C	3.332651	-0.688994	1.180147
C	-0.183241	-0.879070	-0.260549
H	1.376724	-2.232609	0.004409
N	-0.653476	0.577289	0.019488
H	-0.401029	2.082976	1.504871
C	3.732144	-2.031769	1.329009
C	5.076289	-2.360295	1.528414
C	6.050636	-1.356761	1.576055
C	5.668827	-0.018471	1.420909
C	4.325641	0.310784	1.223366
H	2.991122	-2.823118	1.302377
H	5.361241	-3.401556	1.643425
H	7.094962	-1.614654	1.722761
H	6.418219	0.767295	1.440584
H	4.044550	1.348228	1.071509
C	-2.197960	0.694334	0.006650
C	-0.051354	1.400026	-1.175326
H	-0.366995	0.847606	-2.062947
C	-0.441838	2.854158	-1.232911
H	1.026880	1.284515	-1.055095
H	-2.495156	0.204332	-0.920741
C	-2.911411	0.092792	1.195907
H	-2.399286	1.764635	-0.052812
C	-1.492093	3.279491	-2.068519
C	-1.830367	4.633712	-2.157796
C	-1.119588	5.584523	-1.414887
C	-0.062975	5.176396	-0.591445
C	0.276205	3.822032	-0.505047
H	-2.033174	2.545974	-2.659692
H	-2.638442	4.946621	-2.811398
H	-1.379295	6.636047	-1.486092
H	0.502677	5.911862	-0.027998
H	1.114752	3.510881	0.111988
C	-3.455285	0.937704	2.181404
C	-4.169804	0.409144	3.261884
C	-4.349290	-0.974829	3.370098
C	-3.817777	-1.823580	2.390519
C	-3.108092	-1.296956	1.306752
H	-3.325502	2.014007	2.097102
H	-4.585972	1.074364	4.012133
H	-4.903136	-1.388536	4.207185
H	-3.960463	-2.897036	2.467260
H	-2.700098	-1.946897	0.539658

N	-1.041905	-1.487551	-1.117355
S	-0.245873	-2.622123	-2.293614
O	0.477244	-1.769643	-3.506548
O	0.635563	-3.831094	-1.596897
C	-1.812798	-3.398510	-2.968513
H	-1.493950	-4.113387	-3.725509
H	-2.309074	-3.882932	-2.130318
H	-2.408599	-2.591866	-3.390826

Substrate 11- Product a

S	1.474573	-3.029532	0.974546
O	2.377943	-2.490570	2.243559
O	2.241875	-3.340175	-0.448378
C	0.626786	-4.607816	1.522281
H	0.025112	-4.355108	2.392710
H	0.019743	-4.948236	0.685948
H	1.425302	-5.308303	1.761994
N	-0.064233	-2.051531	0.766965
C	0.084458	-0.821001	0.268066
N	-1.042216	-0.044263	0.229190
C	-2.314336	-0.556579	0.813359
H	-2.037032	-1.332263	1.528657
H	-2.775270	0.273023	1.356676
C	-3.285260	-1.097197	-0.224089
C	-2.999461	-2.278997	-0.933584
H	-2.076340	-2.809381	-0.724135
C	-3.896646	-2.765331	-1.889391
H	-3.665906	-3.678197	-2.430361
C	-5.092986	-2.082210	-2.148066
H	-5.788628	-2.463029	-2.889688
C	-5.387972	-0.909869	-1.443990
H	-6.313938	-0.376581	-1.637297
C	-4.487291	-0.420366	-0.489410
H	-4.715812	0.492711	0.053633
C	-1.162623	1.163640	-0.619302
H	-1.763762	0.906931	-1.501920
H	-0.161581	1.421167	-0.969570
C	-1.803964	2.352575	0.078927
C	-2.826282	3.061780	-0.572426
H	-3.171044	2.726703	-1.547166
C	-3.406054	4.189451	0.021414
H	-4.194147	4.727079	-0.496937
C	-2.975549	4.615105	1.282840
H	-3.426048	5.486406	1.748041
C	-1.962616	3.907998	1.944107
H	-1.625961	4.232234	2.924310
H	-0.594969	2.239635	1.861321
C	-1.378659	2.785643	1.346775
C	1.352957	-0.339911	-0.342959
H	1.660319	-0.928968	-1.202915
C	2.175022	0.644634	0.104288
C	3.355928	1.054777	-0.708381
C	3.327724	1.010002	-2.117237
H	2.423248	0.691528	-2.625781
C	4.441070	1.394813	-2.867631
H	4.398488	1.356475	-3.951808
C	5.603657	1.839505	-2.225378

H	6.468043	2.140827	-2.809007
C	5.643190	1.896335	-0.827307
H	6.542553	2.234150	-0.321609
C	4.529254	1.511927	-0.075533
H	4.572347	1.539110	1.008190
C	1.985827	1.353547	1.393862
C	1.826615	0.741075	2.579702
H	2.055774	2.440867	1.348411
H	1.851929	-0.342204	2.674677
H	1.720677	1.321088	3.493263

Substrate 11- Product b

H	-6.288547	-3.301271	-1.289890
C	-5.572805	-2.574756	-0.917881
H	-5.079346	-3.714912	0.846943
C	-4.891980	-2.806381	0.282569
H	-3.448922	-2.049822	1.697269
C	-3.970425	-1.866451	0.761614
C	-3.715131	-0.680447	0.052136
C	-4.411180	-0.458620	-1.151485
C	-5.329585	-1.395708	-1.634262
H	-5.859076	-1.204352	-2.562839
H	-4.238274	0.459338	-1.708037
C	-2.716182	0.346859	0.558095
H	-3.189096	1.333403	0.581208
H	-2.431577	0.115637	1.592908
C	-1.421523	0.420013	-0.307081
H	-1.726317	0.548682	-1.359665
C	-0.488265	1.577171	0.048495
C	-1.029754	2.908512	0.426969
C	-0.423329	3.645825	1.464577
H	0.406827	3.210383	2.011124
C	-0.887956	4.919434	1.802518
H	-0.407869	5.468609	2.606294
C	-1.965664	5.483219	1.110142
H	-2.325453	6.473153	1.372284
C	-2.576499	4.763749	0.075175
H	-3.405572	5.199322	-0.473950
C	-2.117355	3.487077	-0.260851
H	-2.584373	2.952453	-1.082633
C	0.854161	1.417724	-0.058566
H	1.503254	2.271016	0.087536
C	-0.669051	-0.915631	-0.174224
H	-1.234193	-1.709397	-0.668260
H	-0.594590	-1.183707	0.891394
N	0.678782	-0.891753	-0.766911
H	0.527364	-2.563753	-2.008916
C	1.227090	-2.175683	-1.259285
H	2.171362	-1.941783	-1.754771
C	1.429814	-3.210718	-0.162559
C	0.635835	-4.367752	-0.126337
H	-0.116726	-4.524712	-0.895337
C	0.806098	-5.321527	0.885134
H	0.184811	-6.211989	0.898552
C	1.773757	-5.123269	1.875654
H	1.906984	-5.859570	2.662352
C	2.572745	-3.971656	1.846891

H	3.328496	-3.815669	2.610658
C	2.405436	-3.021380	0.834748
H	3.029700	-2.133535	0.810524
C	1.489133	0.189781	-0.553446
N	2.779429	0.043832	-0.859656
S	3.901430	1.462594	-0.568794
O	4.429865	1.469721	0.987303
O	3.370309	2.891629	-1.195092
C	5.284891	0.845119	-1.670102
H	6.090364	1.572063	-1.577789
H	5.569603	-0.137039	-1.298890
H	4.882730	0.803204	-2.680282

Substrate 11- Transition state for Product a

C	0.011092	0.003971	-0.103054
H	-0.007045	-0.083082	0.981502
H	1.026264	0.029245	-0.496388
H	-0.598301	-0.756423	-0.587264
S	-0.750637	1.662611	-0.525299
O	0.090246	2.832357	0.266596
O	-0.849327	1.767435	-2.168793
N	-2.404058	1.338486	0.255554
C	-3.346622	2.256181	0.041645
C	-3.206220	3.514224	-0.587878
H	-2.184758	3.822593	-0.773373
C	-4.228245	4.249268	-1.227816
C	-3.878617	5.112869	-2.379972
C	-2.755047	4.818255	-3.183461
H	-2.153337	3.939488	-2.970433
C	-2.431926	5.632325	-4.271732
H	-1.567188	5.390144	-4.881282
C	-3.221273	6.747208	-4.580543
H	-2.966265	7.377601	-5.427137
C	-4.341766	7.046426	-3.793601
H	-4.951671	7.914566	-4.024925
C	-4.669188	6.236005	-2.703880
H	-5.522368	6.482967	-2.079547
C	-5.572547	4.069502	-0.820264
H	-6.389382	4.232469	-1.516498
C	-5.788860	3.517724	0.438649
H	-5.117617	3.783579	1.248311
H	-6.775286	3.182216	0.746111
N	-4.689440	1.706994	0.410387
C	-5.152166	0.788114	-0.715064
H	-5.203810	1.432915	-1.599223
C	-6.486874	0.118277	-0.477128
C	-7.692266	0.783113	-0.766300
H	-7.660164	1.791920	-1.166751
C	-8.923813	0.150702	-0.562969
H	-9.845403	0.675934	-0.794442
C	-8.968597	-1.160049	-0.071946
H	-9.923775	-1.651753	0.084331
C	-7.775605	-1.838432	0.205294
H	-7.802487	-2.859295	0.573700
C	-6.545602	-1.203813	0.000165
H	-5.621502	-1.737958	0.204503
C	-4.715203	1.049604	1.773430

H	-5.703286	0.595714	1.862835
H	-3.964258	0.249708	1.770455
C	-4.478959	1.975401	2.951912
C	-5.567311	2.392250	3.740043
H	-6.571871	2.070390	3.476416
C	-5.371928	3.206754	4.860953
H	-6.223412	3.515553	5.459881
C	-4.079913	3.616340	5.210784
H	-3.924169	4.248661	6.079434
C	-2.987856	3.201188	4.438497
H	-1.982343	3.510800	4.705928
C	-3.183109	2.381688	3.321751
H	-2.332324	2.058864	2.731962
H	-4.369862	0.040693	-0.881829

Substrate 11- Transition state for Product b

C	-1.354944	0.820974	-1.244769
C	-0.816255	1.337939	1.669112
N	0.770866	0.372367	-0.144599
C	-0.549966	2.726904	1.768742
C	-1.404223	3.689154	1.148516
H	-2.252779	3.336006	0.569955
C	-1.161224	5.051303	1.278980
H	-1.827083	5.766971	0.806722
C	-0.054396	5.506083	2.017881
H	0.133753	6.570613	2.114111
C	0.807900	4.581387	2.628512
H	1.658995	4.933250	3.202990
C	0.572350	3.213952	2.505455
H	1.227442	2.500463	2.996570
H	-0.202115	0.615508	2.192137
H	-1.762934	0.983516	1.287202
C	2.116810	0.845619	0.272027
H	1.996671	1.878043	0.617272
H	2.409225	0.213040	1.112320
C	3.164229	0.790716	-0.829646
C	3.643797	1.975613	-1.411460
H	3.261754	2.934351	-1.068635
C	4.614636	1.934589	-2.420051
H	4.978992	2.858993	-2.858188
C	5.112978	0.703626	-2.860248
H	5.865488	0.668136	-3.642159
C	4.640061	-0.483909	-2.284946
H	5.027062	-1.441255	-2.620774
C	3.674624	-0.443751	-1.274348
H	3.311067	-1.359702	-0.819121
C	0.436037	-0.983144	0.009053
N	1.305522	-1.707014	0.761716
S	0.577895	-3.223422	1.445615
O	-0.630368	-2.875538	2.517826
O	0.245528	-4.386460	0.324213
C	2.083078	-3.787029	2.403728
H	2.302662	-3.015389	3.138702
H	2.887284	-3.905842	1.680547
H	1.807366	-4.731844	2.869344
C	-0.791742	-1.415296	-0.545422
H	-1.019138	-2.472787	-0.515566

C	-1.751066	-0.489622	-1.023951
C	-3.163204	-0.923367	-1.197941
C	-3.727701	-1.850437	-0.297363
C	-5.060360	-2.249467	-0.434676
C	-5.849383	-1.732956	-1.469632
H	-3.123395	-2.240662	0.516490
H	-5.481428	-2.960730	0.269009
H	-6.883552	-2.046210	-1.575939
C	-5.297561	-0.813696	-2.371210
H	-5.901141	-0.419366	-3.183236
C	-3.965533	-0.411911	-2.236337
H	-3.535002	0.279454	-2.954843
H	-2.052088	1.577904	-1.587004
H	0.274756	2.207016	-1.009941
H	0.586922	0.915712	-2.178363
C	0.101168	1.144704	-1.209843

Substrate 12- Intermediate

C	-0.363299	-0.909788	-2.878182
C	0.279332	-1.685173	-1.886575
C	0.244944	-3.091876	-2.025293
C	-0.394592	-3.690971	-3.112803
C	-1.021506	-2.905614	-4.089916
C	-1.002860	-1.511953	-3.966655
C	0.907816	-1.033744	-0.713257
C	0.188039	0.156674	-0.116667
N	0.128323	0.099893	1.410383
C	1.588161	-0.065291	1.969774
C	2.455851	-0.716290	1.139439
C	2.098349	-1.369209	-0.110697
C	-0.633704	-1.165259	1.938957
C	-2.128188	-1.164246	1.739218
C	-2.706531	-1.582234	0.525515
C	-4.097467	-1.610739	0.373399
C	-4.929907	-1.234519	1.434457
C	-4.366431	-0.836770	2.653253
C	-2.976498	-0.804530	2.804301
C	-0.531357	1.378234	1.978084
C	0.020415	2.683407	1.452864
C	-0.705358	3.416652	0.496046
C	-0.235174	4.650819	0.033831
C	0.968535	5.168063	0.526842
C	1.693579	4.449588	1.486180
C	1.223731	3.217321	1.952198
N	1.714703	0.366259	3.247575
S	2.289854	-0.965586	4.385147
C	2.840598	0.123426	5.807262
O	3.599205	-1.819491	3.851374
O	0.993152	-1.857177	4.896449
H	0.721104	1.089835	-0.330935
H	-0.838282	0.244090	-0.477566
C	3.083601	-2.360965	-0.631131
H	3.461466	-0.847659	1.517612
H	3.041274	-0.540283	6.646604
H	3.734435	0.646334	5.472768
H	2.016533	0.805200	6.007797

H	-0.379646	1.292858	3.054920
H	-1.591700	1.285796	1.741650
H	-0.366984	-1.230661	2.998492
H	-0.161434	-1.997276	1.413200
H	-1.646182	3.023218	0.118837
H	-0.807486	5.206709	-0.702487
H	1.335132	6.125739	0.170266
H	2.623357	4.851103	1.877020
H	1.777614	2.656165	2.698531
H	-2.541058	-0.518296	3.757545
H	-5.006136	-0.562941	3.486375
H	-6.008769	-1.263783	1.317361
H	-4.528475	-1.939188	-0.567160
H	-2.070931	-1.907671	-0.292396
H	0.716588	-3.710810	-1.270431
H	-0.410764	-4.773708	-3.193331
H	-1.519026	-3.374565	-4.933102
H	-1.480516	-0.891324	-4.719056
H	-0.341623	0.174308	-2.810115
C	3.443330	-2.399873	-1.993314
C	4.398076	-3.311083	-2.452159
C	5.011040	-4.200145	-1.559490
C	4.671475	-4.162267	-0.202146
C	3.721967	-3.246020	0.262758
H	2.980439	-1.707595	-2.688116
H	4.668982	-3.322263	-3.503776
H	5.752984	-4.907475	-1.917824
H	5.147923	-4.840024	0.499357
H	3.480908	-3.209028	1.321475

Substrate 12-Product a

C	-1.520734	-3.291632	0.759946
C	-1.163783	-2.180890	-0.031223
C	-1.932510	-1.921919	-1.186159
C	-3.031382	-2.716952	-1.515775
C	-3.384634	-3.804407	-0.706794
C	-2.619541	-4.091352	0.428750
C	-0.015933	-1.298828	0.336708
C	0.105793	-0.033043	-0.123106
C	1.083124	-1.849070	1.201510
C	1.489830	-1.236846	2.344740
C	0.891132	-0.028708	2.974790
N	1.536319	1.134487	3.088123
S	3.155351	1.244388	2.230613
C	3.585285	2.957134	2.853343
N	-0.352345	-0.088623	3.544809
C	-0.987861	1.150257	4.062470
C	-2.457532	1.250319	3.698811
C	-3.422985	1.484981	4.690507
C	-4.775369	1.622192	4.351466
C	-5.177405	1.515068	3.015766
C	-4.220984	1.273924	2.019975
C	-2.870429	1.146676	2.358366
C	-0.985126	-1.363756	3.949578
C	-0.924329	-1.608585	5.451795
C	0.294354	-1.519252	6.147621
C	0.350823	-1.783965	7.519556

C	-0.810639	-2.145659	8.215138
C	-2.028106	-2.235133	7.531490
C	-2.084195	-1.963004	6.158515
O	3.005216	1.332390	0.591289
O	4.259801	0.188592	2.846201
H	0.990820	0.563377	0.079377
H	-0.661151	0.421437	-0.743779
C	1.811765	-3.053624	0.709148
H	2.419226	-1.554207	2.810860
H	4.568363	3.188049	2.446291
H	2.815532	3.628554	2.478293
H	3.590673	2.903422	3.939923
H	-0.862151	1.193809	5.151599
H	-0.472512	-2.166214	3.418176
H	-0.420866	1.983430	3.640171
H	-2.024542	-1.355955	3.610255
H	-3.115668	1.558174	5.730240
H	-5.510842	1.806012	5.128869
H	-6.225786	1.616331	2.752082
H	-4.526371	1.186135	0.981820
H	-2.130913	0.955982	1.586402
H	-3.033563	-2.023314	5.633181
H	-2.933615	-2.508893	8.064532
H	-0.765409	-2.352780	9.279865
H	1.298884	-1.709597	8.043542
H	1.200022	-1.235347	5.618974
H	-1.652308	-1.106738	-1.844374
H	-3.603157	-2.496523	-2.412130
H	-4.236136	-4.425610	-0.966237
H	-2.875150	-4.939920	1.056009
H	-0.931207	-3.537070	1.636362
C	1.941520	-3.288348	-0.674376
C	2.653299	-4.392810	-1.148098
C	3.243896	-5.289699	-0.249703
C	3.115137	-5.074129	1.128115
C	2.403597	-3.969866	1.602985
H	1.500144	-2.589137	-1.375703
H	2.750577	-4.550605	-2.217841
H	3.795501	-6.148882	-0.618643
H	3.563198	-5.768794	1.832052
H	2.292731	-3.824088	2.673006

Substrate 12-Product b

C	-0.312129	1.426900	4.061518
C	-0.514323	1.199395	2.682417
C	-1.521722	1.936569	2.039993
C	-2.276685	2.890883	2.737497
C	-2.049687	3.117936	4.096839
C	-1.062365	2.376092	4.758587
C	0.264469	0.051827	1.995497
C	1.763045	-0.019978	2.387184
C	2.280252	-1.247110	2.678850
C	1.598697	-2.516582	2.424479
N	0.250245	-2.472263	2.237675
C	-0.442706	-1.224901	2.574731
C	0.122939	-0.025920	0.423574
C	0.984327	0.863410	-0.458441

C	2.227208	0.391698	-0.922183
C	3.019308	1.171987	-1.770457
C	2.579110	2.436033	-2.180385
C	1.340830	2.912614	-1.735867
C	0.551158	2.131300	-0.885004
N	2.198971	-3.707715	2.309977
S	4.026468	-3.653134	2.238045
O	4.560039	-2.862675	0.891069
C	-0.536547	-3.674118	1.891119
C	-1.273348	-4.289789	3.070173
C	-2.676334	-4.316209	3.097527
C	-3.359938	-4.887606	4.178621
C	-2.643139	-5.434289	5.248101
C	-1.241431	-5.412314	5.229119
C	-0.559676	-4.847583	4.147275
C	4.284422	-5.490453	2.000682
O	4.714967	-3.215121	3.668716
C	2.699638	1.143661	2.345240
H	3.292469	-1.333383	3.048151
H	5.360679	-5.636851	1.924147
H	3.863833	-5.980209	2.876596
H	3.764300	-5.766740	1.085860
H	-0.525940	-1.127685	3.663819
H	-1.457500	-1.280417	2.170986
H	0.167629	-4.389429	1.458618
H	-1.255505	-3.382848	1.116098
H	0.352908	-1.066586	0.167279
H	-0.935798	0.117421	0.177677
H	-3.236991	-3.892881	2.267589
H	-4.445696	-4.903313	4.184623
H	-3.169666	-5.876126	6.088553
H	-0.680855	-5.840216	6.054740
H	0.525723	-4.841321	4.125717
H	2.581702	-0.587015	-0.609576
H	3.976662	0.790836	-2.111817
H	3.192351	3.041186	-2.841269
H	0.987291	3.889118	-2.053758
H	-0.408450	2.513846	-0.553565
H	-1.734657	1.780304	0.990634
H	-3.043094	3.451313	2.210787
H	-2.632636	3.858069	4.635769
H	-0.875328	2.536857	5.815904
H	0.457983	0.870605	4.587516
C	4.079676	0.893126	2.124084
C	5.011813	1.929815	2.101813
C	4.600497	3.256756	2.274527
C	3.241121	3.529655	2.448911
C	2.303389	2.493087	2.478947
H	4.422620	-0.113447	1.913733
H	6.058184	1.698991	1.928317
H	5.325941	4.064390	2.253929
H	2.901079	4.554383	2.563208
H	1.265080	2.750304	2.613394

Substrate 12-Transition state for Product a

C	-0.005647	-0.933859	-1.264010
N	-1.268824	-0.399699	0.336594

C	-0.970496	1.064161	0.368794
C	0.198565	1.596563	-0.227512
C	1.362056	0.896618	-0.601453
C	1.277508	-0.501623	-0.896354
C	2.378257	-1.481230	-0.704173
C	2.491620	-2.594525	-1.567361
C	3.488937	-3.557013	-1.382448
C	4.410693	-3.424125	-0.337446
C	4.320435	-2.321247	0.522454
C	3.316623	-1.365355	0.346306
C	-2.713272	-0.704435	-0.006622
C	-3.125203	-0.386394	-1.430507
C	-3.454173	0.923800	-1.824619
C	-3.858418	1.189202	-3.137567
C	-3.952589	0.150036	-4.071792
C	-3.642403	-1.159515	-3.686495
C	-3.232651	-1.423309	-2.374910
C	-0.824341	-1.010742	1.665281
C	-1.094604	-2.492207	1.809172
C	-0.206617	-3.447230	1.281499
C	-0.451718	-4.815106	1.446819
C	-1.583217	-5.249697	2.147842
C	-2.466377	-4.308563	2.690792
C	-2.220525	-2.941262	2.524400
N	-1.861695	1.704682	1.121944
S	-1.381843	3.420864	1.662708
O	-1.435359	4.512340	0.434403
C	2.634083	1.663320	-0.636516
C	2.861145	2.701142	0.294242
C	4.039074	3.451829	0.244218
C	5.004380	3.186169	-0.734003
C	4.788473	2.159648	-1.664082
C	3.617339	1.400791	-1.613729
O	-0.022476	3.382161	2.594161
C	-2.861138	3.719785	2.773148
H	-3.745057	3.608663	2.148119
H	-2.753564	4.733818	3.155204
H	-2.820266	2.974421	3.564687
H	0.262251	2.678082	-0.213019
H	2.121133	2.908035	1.062379
H	4.199593	4.242528	0.970378
H	5.916964	3.773417	-0.773086
H	5.531038	1.955355	-2.429444
H	3.450354	0.612264	-2.339729
H	-0.632435	-0.275221	-1.853286
H	-0.231396	-1.992359	-1.349799
H	0.250944	-0.812804	1.718838
H	0.686789	-3.122231	0.758174
H	0.246929	-5.538051	1.036906
H	-1.769611	-6.311141	2.279101
H	-3.339070	-4.636434	3.247299
H	-2.902305	-2.214668	2.959014
H	-2.842064	-1.771152	0.179518
H	-3.340155	-0.146191	0.699514
H	-2.997668	-2.442383	-2.077753
H	-3.721823	-1.972226	-4.402187
H	-4.270239	0.358018	-5.088916
H	-4.102646	2.206103	-3.428396

H	-3.389553	1.731652	-1.103335
H	-1.314138	-0.453956	2.470935
H	1.805354	-2.686326	-2.404015
H	3.555168	-4.400096	-2.063953
H	5.191150	-4.165541	-0.197499
H	5.029051	-2.209709	1.337694
H	3.252667	-0.522917	1.026543

Substrate 12-Transition state for Product b

C	1.223697	0.165274	0.763330
C	0.183747	0.732408	-2.098740
N	-1.149986	0.304618	0.086161
C	-1.236639	-1.084157	-0.040298
C	-0.102882	-1.832104	0.360415
C	1.147028	-1.234872	0.621357
C	-0.100967	0.862985	0.963306
C	2.443837	0.974028	0.849419
C	2.460023	2.181855	1.593421
C	3.596061	2.994354	1.637172
C	4.749639	2.638084	0.929512
C	4.752743	1.453876	0.177101
C	3.624740	0.634757	0.136887
C	0.123693	2.125823	-2.327304
C	1.216730	2.982333	-1.983883
C	1.147868	4.351745	-2.219911
C	0.001896	4.915554	-2.805141
C	-1.085392	4.095120	-3.153725
C	-1.034133	2.726233	-2.915335
C	-2.371750	1.135037	-0.084712
C	-3.124199	1.393656	1.211341
C	-3.121297	2.673537	1.789144
C	-3.807908	2.919441	2.984885
C	-4.502654	1.882625	3.617067
C	-4.513826	0.602739	3.045548
C	-3.832797	0.357810	1.848915
N	-2.377052	-1.546218	-0.611064
S	-2.194188	-3.194500	-1.354063
C	-3.928849	-3.328376	-2.043599
C	2.309581	-2.166020	0.737430
C	2.472770	-3.192934	-0.214218
C	3.524300	-4.108240	-0.096856
C	4.419745	-4.018190	0.975111
C	4.257685	-3.008387	1.933320
C	3.212627	-2.088585	1.815752
O	-1.123430	-3.141477	-2.611632
O	-2.004523	-4.425026	-0.272654
H	2.108344	2.546841	-1.545829
H	1.988058	4.985785	-1.955346
H	-0.042714	5.983540	-2.993249
H	-1.966777	4.531865	-3.612523
H	-1.869156	2.090280	-3.193784
H	-0.607007	0.072199	-2.434105
H	1.105103	0.265869	-1.779698
H	-2.055217	2.084471	-0.528354
H	-3.000836	0.596897	-0.796490
H	-2.584302	3.481865	1.298442

H	-3.798745	3.914837	3.418874
H	-5.033931	2.069652	4.545369
H	-5.056380	-0.203439	3.530011
H	-3.845882	-0.630041	1.398677
H	-4.071171	-2.485778	-2.716814
H	-4.606180	-3.293692	-1.192679
H	-3.973711	-4.283952	-2.563672
H	-0.194901	-2.910308	0.382446
H	1.770791	-3.269807	-1.039502
H	3.637966	-4.892514	-0.838576
H	5.232421	-4.732113	1.068397
H	4.940722	-2.942864	2.774800
H	3.085477	-1.313714	2.564207
H	-0.024689	1.926446	0.724131
H	-0.440538	0.782890	2.012963
H	1.586997	2.471652	2.169334
H	3.579571	3.904491	2.229423
H	5.631468	3.270061	0.960453
H	5.637329	1.170674	-0.385396
H	3.646059	-0.268871	-0.460163

VI. References.

S1 S.Ma, X. Lu and Z. Li,*J. Org. Chem.*,1992, **57**, 709.

S2 J.Waser, J. C.Gonzalez-Gomez, H.Nambu, P. Huber and E. M. Carreira,*Org. Lett.*,2005, **7**, 4249.

S3 J. G.Duboudin, B. Jousseaume and A. Bonakdar,*J. Organomet. Chem.*,1979, **168**, 227.

S4 J.-J.Lian, A.Odedra, C.-J. Wu and R.-S. Liu,*J. Am. Chem. Soc.*,2005, **127**, 4186.

S5 (a) *SAINTPlus*, (Version 7.03); Bruker AXS Inc.: Madison, WI, **2004**; (b) G. M. Sheldrick, *SHELXTL*, *Reference Manual*: version 5.1: Bruker AXS; Madison, WI, **1997**; (c) G. M. Sheldrick, *Acta Crystallogr. Sect. A,***2008**, 112; (d) WINGX version 1.80.05 Louis Farrugia, University of Glasgow; (e) A. L. Spek, *A* PLATON, *Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2005**.