Supporting Information

HKUST-1 Metal Organic Framework as an Efficient Dual Functional Catalyst: Aziridination and One-pot Ring-opening transformation for formation of *β*- aryl sulfonamides with C-C, C-N, C-S and C-O bonds.

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1. Methods and Experimental Section:

1.1 General Consideration: All the reactions were carried out in a glove box under a nitrogen atmosphere (O_2<0.1 ppm and H_2O< 0.1 ppm). Aziridination was carried under a nitrogen atmosphere using HPLC vials inside a glove box. Ring-opening reactions were carried out in a nitrogen atmosphere using the Schlenk technique. All the olefins were bought from Sigma except for 4-chloro styrene, 4-fluro styrene, 4- nitro styrene and 4-tert-buty styrene which was bought from TCI and was used without further purifying. $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, and $Ni(OAc)_2.4H_2O$ was brought from Rankem, India. Indole, phenol, acetophenone, and aniline were bought from Merck along with molecular sieves (5Å). 4-methoxy thiophenol, 2,4-dimethyl pyrrole was bought from TCI, India. The inhibitor 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), 2-bromo aniline was bought from Sigma while acetonitrile and DCM were bought from Merck and was properly dried before use. Dry DMSO, DMF, and THF were bought from Sigma and were used without further purifying. iodobenzene diacetate, *p*-toluenesulfonamide, chloroamine-T, 4-azidotoluene, and trimesic acid was brought from Sigma and was used as received.

1.2 General Methods: Powder X-ray diffraction (PXRD) analysis was performed on PANalytical high-resolution X-ray Diffractometer equipped with a Cu K_α radiation (λ = 1.5418 Å) at a scan rate of 5° min^{-1} over the angle (2θ) ranging from 5° to 90°. ^1H and ^{13}C-NMR were obtained in $CDCl_3$ and DMSO-d_6 using Bruker ASCEND^{TM} 400. Single-crystal X-ray diffraction (SCXRD) intensity data were collected using Super Nova Agilent Technology, Single Crystal Diffractometer. All the FTIR spectra were acquired using Bruker ALPHA E. The UV-visible spectra were collected using Perkin Elmer (Model: LS 55). The BET surface areas were obtained using Quanta chrome Nova Touch LX^2. TG analysis carried at a heating rate of 10 °C min^{-1} with a nitrogen gas flow rate of 60 mL min^{-1}in a TA Instruments, TGA Q-50 Analyzer. HRMS were obtained using a maXis impact (ESI) mass spectrometer (TOF). The thin-layer chromatography (TLC) was used for monitoring the reaction progress using silica gel 60 F_{254} coated plates under a UV lamp. Further I_2 stain was also used to monitor the formation of the product.

1.3 Synthesis of [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhINTs): PhINTs was synthesized according to the procedure as reported by Yamada *et al.* with few modifications.[1] In a typical synthesis, KOH (18.7 mmol) was dissolved in 30 mL methanol and *p*-toluene sulfonamide (7.2 mmol) was added to the mixture maintaining the temperature below 10 °C. The mixture was stirred till a clear solution was formed. To this solution, iodobenzene diacetate (2.4 g, 7.45 mmol) was slowly added with constant stirring for 10 min which turned the solution yellowish. The reaction mixture was further stirred for 3 h at room temperature. After the reaction time, the mixture and was poured into ice water resulted in the formation of a yellow precipitate which was allowed to stand overnight. The precipitate was filtered and washed using excess water followed by washing with diethyl ether and DCM.

1.4. Synthesis of Catalyst:

1.4.1 Synthesis of (HKUST-1), $[Cu_3(BTC)_2(H_2O)_3]_n$ (1):

HKUST-1 was synthesized as reported by Schlichte *et al.* with modification in temperature to avoid the formation of Cu_2O.[2] In a typical synthesis, about 0.42 g of trimesic acid (2 mmol) was dissolved in 6 mL EtOH and sonicated for 5 mins. To this mixture about 6 mL, an aqueous solution containing 0.875g $Cu(NO_3)_2.3H_2O$ (3.62 mmol) was added and further sonicated for 5 min. The reaction mixture was then transferred into a 25 mL PTFE lined autoclave and kept in a preheated (100 °C) hot air oven for 22 h. A turquoise blue crystalline material obtained was filtered, washed with ethanol and solvent exchanged with acetone thrice. The formation of HKUST-1 was confirmed following its well-matched PXRD pattern with that of the reported one. Further, the FT-IR spectra of the catalyst match well with the reported data. FT-IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3433 (b), 1646 (s), 1587 (w), 1448 (m), 1371 (m), 1112 (m), 727 (m).

1.4.2 Synthesis of $M_3(BTC)_2$ [M = Ni, Zn]

$Ni_3(BTC)_2$ MOF was synthesized following a reported procedure with slight modifications.[3] In a typical synthesis $Ni(OAc)_2.4H_2O$ (0.41 g, 2.3 mmol) was dissolved 7 mL water deionized. To this solution, 8 mL solution of trimesic acid (0.214 g, 1 mmol) in deionized water was poured slowly and sonicated for 5 min. The mixture was transferred into a 25 mL PTFE lined autoclave and heated in a muffle furnace at 5 ^oC/min to 140 ^oC and kept for 24 h.

The mixture was then cooled to 120 ^{o}C at 0.1 ^{o}C/min and held for 5 h. Further, it was cooled to 100 ^{o}C at the same rate and held for 5 h before cooling to room temperature. Light green crystals were obtained which was washed using DMF and ethanol. A similar procedure was followed for the synthesis of $Zn_3(BTC)_2$ using $Zn(NO_3)_2.6H_2O$ which resulted in the formation of white crystals.

1.4.3 Thermal activation of 1, generation of CUS in MOF ($\mathbf{1_{act}}$):

The synthesized material was then activated at 120 °C under a dynamic vacuum for 12 h to generate its coordinately unsaturated sites (CUS). Activation of the catalyst was indicated by a sharp color change from a turquoise blue to deep blue due to the removal of axially coordinated water molecules. The activated catalyst ($\mathbf{1_{act}}$) was stored in the glove box for future use.

1.4.4 Chemical activation of 1 using methylene chloride ($\mathbf{1_{CH2Cl2}}$):

Again, the synthesized catalyst (**1**) was chemically activated by a reported procedure[4] involving the exchange of co-coordinatively linked water with methylene chloride. The color of **1** changes when the H_2O molecules in its axial position are replaced by methylene chloride as shown.

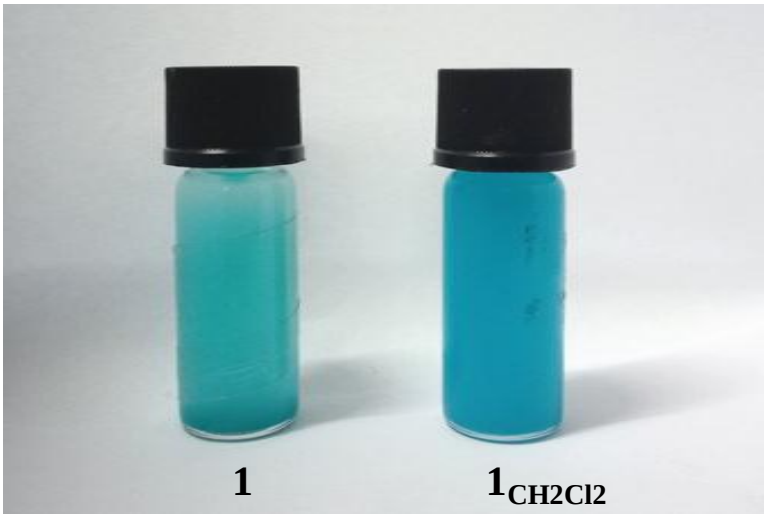


Figure S1: Color variation of **1**on exchange with methylene chloride.

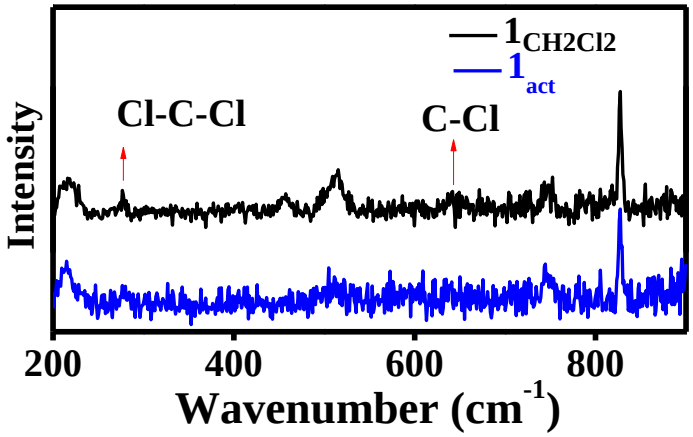


Figure S2: Raman spectra of $\mathbf{1}_{CH2Cl2}$ showing C-Cl stretching (643 cm^{-1}) and Cl-C-Cl scissor (275 cm^{-1}).

Table S1: Aziridination of styrene using different catalyst.

Sl.no.	Catalyst	Substrates	Solvent/time	Yield [a]
1.	**1**	Styrene / PhINTs	CH_3CN / 4 h	nr
2.	$\mathbf{1}_{act}$	Styrene / PhINTs	CH_3CN / 4 h	94 %
3.	$\mathbf{1}_{CH2Cl2}$	Styrene / PhINTs	CH_3CN / 4 h	<15 %
4.	$CuNO_3.6H_2O$	Styrene / PhINTs	CH_3CN / 4 h	trace
5.	$Cu(OAc)_2.H_2O$	Styrene / PhINTs	CH_3CN / 4 h	15 %
4.	Cu_2O	Styrene / PhINTs	CH_3CN / 4 h	nr
5.	CuO	Styrene / PhINTs	CH_3CN / 4 h	nr
6.	Cu(BDC)(DMF)	Styrene / PhINTs	CH_3CN / 4 h	nr
7.	Cu-BDC-Dabco	Styrene / PhINTs	CH_3CN / 4 h	11 %
8.	Cu-BDC(Bpy)	Styrene / PhINTs	CH_3CN / 4 h	33 %
9.	Cu-NENU	Styrene / PhINTs	CH_3CN / 4 h	15 %
10.	MOF-5 (Zn)	Styrene / PhINTs	CH_3CN / 4 h	nr
11.	UiO-66 (Zr)	Styrene / PhINTs	CH_3CN / 4 h	nr
12.	MIL-100 (Fe)	Styrene / PhINTs	CH_3CN / 4 h	nr

[a] based on ^{1}H-NMR analysis using acetophenone as internal standard. (nr= not recorded)

Table S2: Optimization study for aziridination of styrene

Sl. No.	Styrene	Catalyst (1_{act})	Nitrene Source	Solvent	Time	Yield
1.	0.15 mmol	5 mg	PhINTs (0.09 mmol)	CH_3CN (400 µL)	4h	75%
2.	0.15 mmol	10 mg	PhINTs (0.09) mmol	CH_3CN (200 µL)	4h	82%
3.	**0.15 mmol**	**10 mg**	**PhINTs (0.03 mmol)**	**CH_3CN (150 µL)**	**2h**	**94%**
4.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	CH_3CN (150 µL)	4h	94%
5.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	CH_3CN (150 µL)	1h	56%
6.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	DCM (150 µL)	2h	10%
7.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	DMF (150 µL)	2h	nr
8.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	DMSO (150 µL)	2h	nr
9.	0.15 mmol	10 mg	PhINTs (0.03 mmol)	Styrene (150 µL)	2h	14%
10.	0.15 mmol	15 mg	PhINTs (0.03 mmol)	CH_3CN (150 µL)	2h	88%
11.	0.15 mmol	8 mg	PhINTs (0.03 mmol)	CH_3CN (150 µL)	2h	83%
12.	0.06 mmol	10 mg	PhINTs (0.03 mmol)	CH_3CN (150 µL)	2h	86%
13.	0.15 mmol	10 mg	PhINNs (0.03 mmol)	CH_3CN (150 µL)	2h	31%
14.	0.15 mmol	10 mg	Chloramine-T (0.03 mmol)	CH_3CN (150 µL)	2h	nr
15.	0.15 mmol	Blank	PhINTs (0.03 mmol)	CH_3CN (150 µL)	2h	nr
16.	0.15 mmol	Blank	PhINTs (0.03 mmol)	CH_3CN (150 µL)	12h	nr

2. Procedure for Catalysis

2.1 General Procedure for Aziridination of Olefins: In a 2 mL screw-capped HPLC vial stored inside a glove box, PhINTs (11.5 mg, 0.03 mmol) was added followed by the addition of catalyst, **1_{act} (**10.5 mg**)**. Further, about 20 mg molecular sieves (5 Å) were added to the same vial and were tightly capped before removing out of the glove box. To this vial, a panel of olefins (0.150 mmol) was injected along with 150 µL dry solvent (CH_3CN). The reaction mixture was stirred at ambient temperature for 2h. From the final product, 40 µL was taken for calculation of yield using acetophenone (5.6 mg, 0.0472 mmol) as an internal standard. The yield of the reaction was monitored by ^{1}H-NMR where phenyl aziridines show a characteristic peak at δ 2.98 (d, 2H, J = 7.6 Hz, CH *cis*-aziridine) for its *cis*-hydrogen.

2.2 Recyclability Experiment: To a 2 mL screw-capped HPLC vial stored inside a glove box, PhINTs (11.5 mg, 0.03 mmol) was added followed by the addition of the catalyst, $\mathbf{1}_{act}$ (10.5 mg). To this vial styrene (18 μL, 0.150 mmol) was injected along with 150 μL dry solvent (MeCN). The reaction mixture was stirred at ambient temperature for 2 h. The product yield was calculated by ^{1}H NMR using acetophenone (5.6 mg, 0.0472 mmol) as an internal standard. The yield of the corresponding aziridine product **12a** for the 1st cycle was 94%. For the 2nd cycle, PhINTs (11.5 mg, 0.03 mmol) and styrene (18 μL, 0.150 mmol) was added into the same reaction vial and stirred at ambient temperature for another 2 h. The overall yield for the 2nd cycle was 90%. The above step was repeated for the 3rd and 4th cycle thereby delivering overall yields of **12a** in 86% and 80% respectively as depicted in Figure S3c. The catalyst ($\mathbf{1}_{act}$) was found to be very efficient till four catalytic cycles with a minimum decrease in the overall yield. The PXRD shows a characteristic pattern for HKUST-1 even after the fourth cycle. The Full width at half maximum (FWHM) of a peak at 11.57 degree is respectively 0.1899 and 0.4524 for the pristine catalyst and after the 4th cycle. The slight broadening is attributed to a decrease in grain/crystallite size during the catalysis process, consistent with Debye Scherrer equation[4] (Figure S3a).

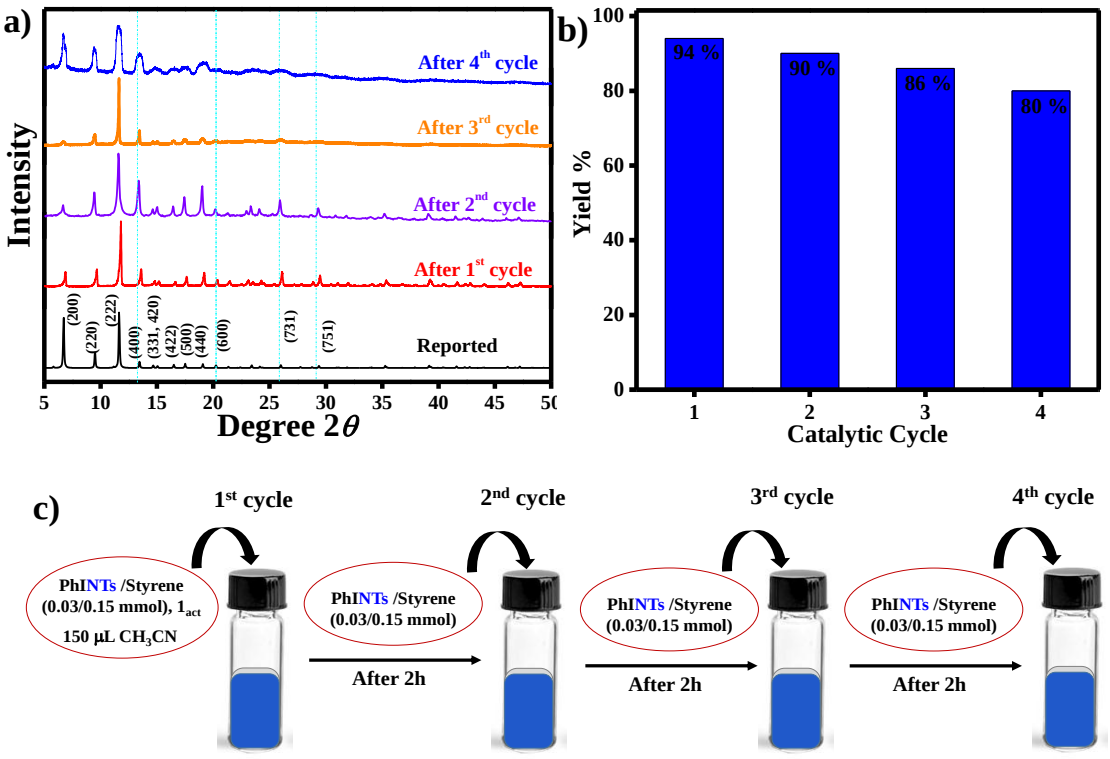


Figure S3: (a) PXRD of the catalyst after each catalytic cycle indicative of framework robustness. The diffraction patterns are indexed for each cycle in a cubic crystal system (*Fm-3m*). (b) Recycling experiment of $\mathbf{1}_{act}$ for up to four catalytic cycles (c) Representation of the recyclability test of $\mathbf{1}_{act}$ for the aziridination reaction for four cycles.

2.3 Heterogeneity test: Catalyst leaching experiment

To confirm the heterogeneity of the $\mathbf{1}_{act}$ catalyst, a control aziridination reaction of **2a** with PhINTs in CH_3CN as solvent was conducted with a simple filtration in between the progress of the reaction. After 20 min, a conversion of 15% was observed and the catalyst was separated from the reaction mixture using centrifugation technique. The remaining liquid mixture (free of catalyst) was then transferred into a new vessel and was magnetically stirred for an additional 100 min. On calculating the ^{1}H NMR yield of the liquid mixture after 1 h 40 min, no further conversion was observed indicating the method to be a true heterogeneous catalytic system**.**

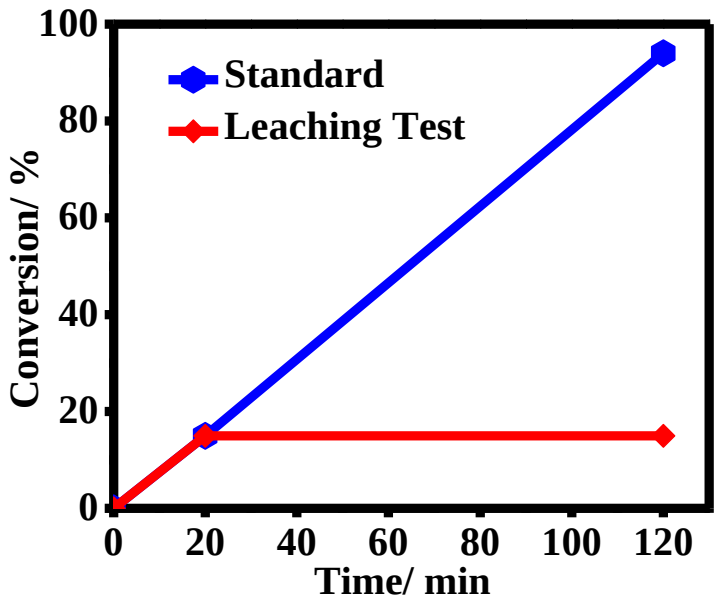


Figure S4: Catalyst leaching experiment for $\mathbf{1}_{act}$ catalyzed aziridination of styrene (**2a**)

3. General Procedure for ring-opening reaction

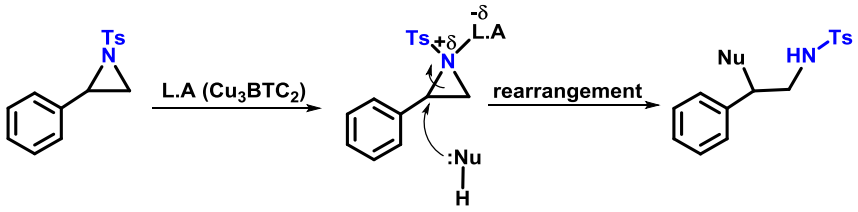
3.1 General Procedure for ring-opening of aziridination.

Method A (Starting with pure aziridine): About 30 mg of $\mathbf{1_{act}}$ was taken in a two-neck round bottom under the nitrogen atmosphere inside a glove box. To this, about 400 μL of dry acetonitrile containing 100 mg aziridine was added quickly under constant nitrogen flow. Finally, about 1.5 eq nucleophile was added similarly. When indole and phenol were used as the nucleophile, the reaction temperature was maintained at 80 °C, however, opening using aniline and thiol were carried out at room temperature. The progress of the reaction was monitored using TLC. For the reaction involving **1,** the only difference was that the catalyst and the substrate were all loaded outside the glove box, however, the reaction was kept under a nitrogen atmosphere. The NMR spectra of the isolated compound matches well with the previously reported data.[6a]

3.2 General procedure for one pot ring opening reaction

Method B: In a two-neck round bottom kept inside a glove box, PhINTs (1 eq) was added along with $\mathbf{1_{act}}$ (0.5 eq), and the container was sealed. Outside the glove box, styrene (5 eq) along with the solvent (dry acetonitrile, 400 μL) was injected using a 1 mL syringe. The reaction mixture was then allowed under a nitrogen atmosphere for 2 h. After 2 h, on a constant flow of nitrogen in a Schlenk line, nucleophile was added and the reaction was treated according to the nucleophile as mentioned in method A. After completion of the reaction as monitored by TLC, the opening product was separated by simply centrifuging the reaction mixture. The pure product was separated by column chromatography using hexane and ethyl acetate as the eluent. The NMR spectra of the isolated compound matches well with the previously reported data.[6b]

Scheme S1: Plausible mechanism for Ring-opening transformation of aziridination catalyzed by **1**$_{act}$.



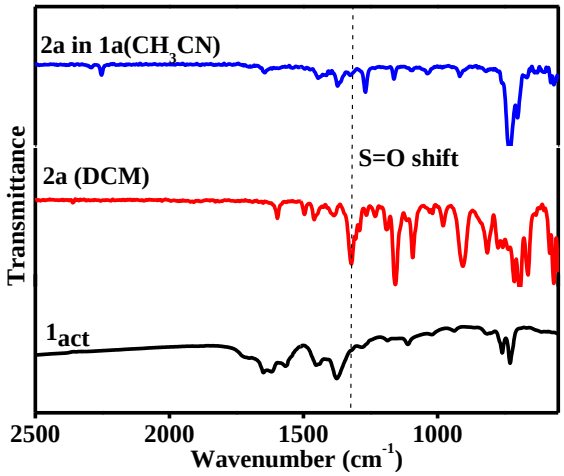


Figure S5: FT-IR studies for the polarization effect of L.A. on interaction with the tosyl group.

3.3. Thiol Recyclability:

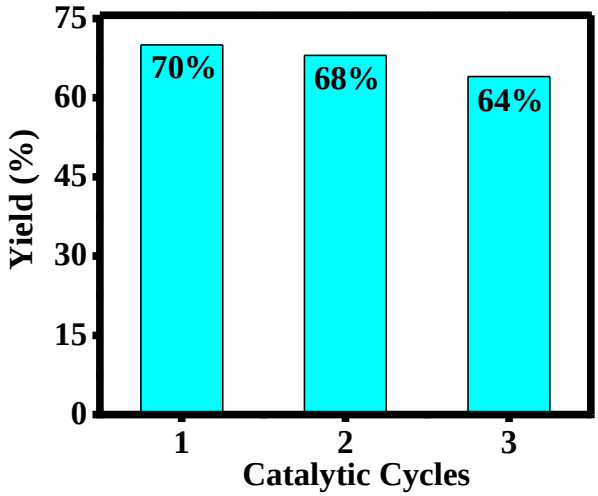
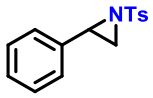


Figure S6: Recycling experiment yield graph of **11a/b** on ring opening reaction of **3a** by **1act** for up to three cycles.

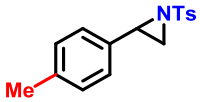
3.4 NMR data of isolated products:

3.4.1 Synthesis of 2-phenyl-*N*-tosylaziridine (3a):



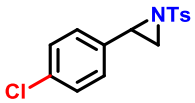
Separation of the product (3a, white solid) was performed using column chromatography in 9:1 (Hexane/ EtOAc). Isolated Yield: 89 %. FTIR ($\tilde{\nu}_{max}$,cm^{-1}); 1597 (w), 1499 (w), 1388 (w), 1321 (s), 1236 (w),1160 (s), 1088 (s), 980 (m),905 (s), 811 (s), 688 (s), 659 (m), 561 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.16 Hz, 2H), 7.29-7.16 (m, 8H), 3.74 (dd, *J*= 4.44 Hz, 2.72 Hz, 1H), 2.94 (d, *J* = 7.21 Hz, 1H), 2.38 (s, 3H), 2.35 (d, *J*= 4.44 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 135.1, 135.0, 129.8, 128.6, 128.3, 127.9, 126.6, 41.1, 35.9, 21.6 ; HRMS (ESI-TOF) calculated for $C_{15}H_{16}NO_2S$ (M+H)+ 274.0902, found 274.0890.

3.4.2 Synthesis of 2-(*p*-tolyl)-*N*-tosylaziridine (3b):



Separation of the product (3b, white solid) was performed using column chromatography in 9:1 (Hexane/ EtOAc). Isolated Yield: 77 %. FTIR ($\tilde{\nu}_{max}$,cm^{-1}); 1323 (m), 1290 (w), 1186 (w), 1160 (s), 1092 (w), 978 (w), 911 (m), 814 (m), 731 (w), 659 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.36 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 4H), 3.74 (dd, *J*= 4.40 Hz, 2.72 Hz, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.38 (d, *J*= 4.48 Hz, 1H), 2.30(s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.6, 138.1, 135.1, 132.0, 129.7, 129.2, 127.9, 126.5, 41.1, 35.8, 21.7, 21.1

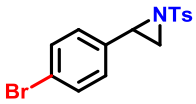
3.4.3 Synthesis of 2-(4-chlorophenyl)-*N*-tosylaziridine (3f):



Separation of the product (3f, white solid) was performed using column chromatography in 9:1 (Hexane/ EtOAc). Isolated Yield: 92 % . FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 1597 (w), 1558 (w), 1541 (w), 1507 (m), 1456 (w), 1417 (w), 1376 (w), 1324 (s), 1160 (s), 1091 (s), 1015 (w), 981 (w), 909 (s), 815 (s), 776 (w), 570 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.12 Hz, 2H), 7.33 (d, *J* = 7.76 Hz, 2H), 7.26 (d, *J*= 8.44, 2H), 7.15 (d, *J*= 8.44, 2H), 3.73 (dd, *J*= 4.4, 2.76 Hz, 1H), 2.98 (d, *J* =

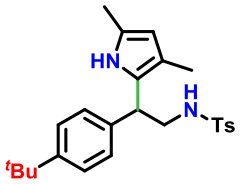
7.16 Hz, 1H), 2.44 (s, 3H), 2.34 (d, *J*= 4.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 134.8, 134.2, 133.6, 129.8, 128.8, 127.9, 127.9, 40.3, 36.1, 21.7

3.4.4 Synthesis of 2-(4-bromophenyl)-*N*-tosylaziridine (3g):



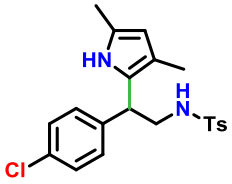
Separation of the product (3g, white solid) was performed using column chromatography in 9:1 (Hexane/ EtOAc). Isolated Yield: 81 % . FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 1596 (w), 1490 (m), 1404 (w), 1376 (w), 1323 (s), 1159 (s), 1092 (m), 1071 (w), 1011(w), 980 (w), 908 (s), 815 (s), 706 (s), 692 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.24 Hz, 2H), 7.41 (d, *J* = 8.36 Hz, 2H), 7.33 (d, *J*= 8.0, 2H), 7.08 (d, *J*= 8.32, 2H), 3.72 (dd, *J*= 4.32 Hz, 2.8 Hz, 1H), 2.98 (d, *J* = 7.16 Hz, 1H), 2.43 (s, 3H), 2.34 (d, *J*= 4.36 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 134.8, 134.2, 131.7, 129.8, 128.2, 127.9, 122.3, 40.3, 21.7

3.4.5 *N*-(2-(4-chlorophenyl)-2-(3,5-dimethylpyrrol-2-yl)ethyl)-4-methylbenzenesulfonamide (10a):



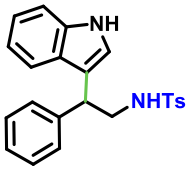
The compound was synthesized using Method B, where 4-^{t}Bu-styrene was the substrate used and 2,4-dimethyl pyrrole was used as a nucleophile. The reaction was performed at 80℃. The compound was isolated as sticky reddish black solid in 6:1 (Hexane/EtOA) and characterized using FT-IR, NMR (^{1}H and ^{13}C), mass spectroscopy. FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 3448-3168 (b), 2959 (m), 1695 (w), 1606 (w), 1511 (w), 1459 (w), 1470 (w), 1326 (m), 1157 (s), 1090 (m), 1009 (w), 818 (m), 759 (m), 663 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.24 Hz, 2H), 7.30 (d, *J* = 8.32 Hz, 4H), 7.01 (d, *J*= 8.28 Hz, 2H), 5.64 (s, 1H), 4.43–4.40 (m, 1H), 4.11 (t, *J* = 7.4 Hz, 1H), 3.70 (s, 1H), 3.54–3.32 (m, 2H), 2.43 (s, 3H) 2.12 (s, 3H), 1.89 (s, 3H), 1.29 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.1, 143.6, 136.7, 129.8, 127.2, 126.5, 125.9, 124.1, 116.0, 108.4, 67.1, 46.5, 41.3, 34.5, 31.3, 21.6, 13.0, 11.0 HRMS (ESI-TOF) calculated for $C_{25}H_{33}N_2O_2S$ $(M+H)^+$ 425.2263, found 425.2269.

3.4.6 *N*-(2-(4-chlorophenyl)-2-(3,5-dimethylpyrrol-2-yl)ethyl)-4-methylbenzenesulfonamide (**10b**):



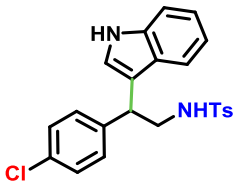
The compound was synthesized using Method B, where 4-Cl-styrene was the substrate used and 2,4-dimethyl pyrrole was used as a nucleophile. The reaction was performed at 80℃. The compound was isolated as greyish black solid in 6:1 (Hexane/EtOA) and characterized using FT-IR, NMR (^{1}H and ^{13}C), mass spectroscopy. FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 3472-3161 (b), 2930 (m), 1689 (w), 1485 (m), 1408 (w), 1320 (m), 1158 (s), 1326 (m), 1158 (s), 1087 (m), 1018 (w), 818 (m), 664 (m), 605 (m), 554 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.08 Hz, 2H), 7.21 (d, J= 8.28 Hz, 2H), 7.02 (d, J = 8.4, 2H) 5.64 (s, 1H), 4.68 (dd, J = 5.52 Hz, 2.28 Hz, 1H), 4.13 (t, J = 7.32 Hz, 1H), 3.69 (s, 1H), 3.69–3.46 (m, 1H), 3.37–3.30 (m, 1H), 2.44 (s, 3H) 2.13 (s, 3H), 1.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 138.8, 136.4, 132.8, 129.8, 129.0, 127.1, 126.9, 123.5, 116.2, 108.5, 67.1, 46.4, 41.5, 21.6, 12.9, 11.0. HRMS (ESI-TOF) calculated for $C_{21}H_{24}ClN_2O_2S$ (M+H)+ 403.1247, found 403.1249.

3.4.7 Synthesis of *N*-(2-(1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide (4a):



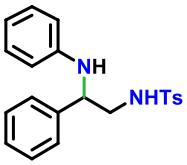
The compound was synthesized using Method B, where styrene was the substrate used and the nucleophile used was indole. The reaction was performed at 80 °C. A white solid compound was obtained which was characterized by FTIR, mass spectroscopy, and NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 2856-2926 (b), 2367 (b), 1418 (w), 1290 (m), 1185 (w), 1092 (s), 1073 (w), 813 (w), 745 (m), 700 (w), 665 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (bs, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.33–6.96 (m, 12H), 4.44 (t, J = 7.54 Hz, 1H), 3.69–3.52 (m, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.4, 143.0, 138.1, 130.0, 128.6, 128.5, 127.0, 126.6, 121.5, 118.8, 115.9, 111.8, 48.0, 43.1, 21.4

3.4.8 Synthesis of *N*-(2-(4-chlorophenyl)-2-(indol-3-yl)ethyl)-4-methylbenzenesulfonamide (4b):



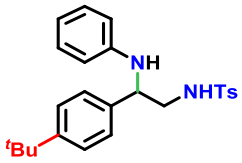
The compound was synthesized using Method B, where 4-chloro styrene was the substrate used and the nucleophile used was indole. The reaction was performed at 80 °C. A white solid compound was obtained which was characterized by NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 2855-2924 (b), 2410 (b), 1338 (b), 1158 (s), 1091 (w), 1014 (w), 813 (w), 745 (m), 702 (w), 664 (w); ^{1}H NMR (400 MHz, DMSO-d_6) δ10.29 (bs, 1H), 7.59-7.54 (m, 2H), 7.26–6.96 (m, 11H), 6.83 (t, J = 7.4 Hz, 1H), 4.28 (t, J = 7.45 Hz, 1H), 3.49–3.39 (m, 1H), 3.27–3.21 (m, 1H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ143.0, 141.5, 137.8, 136.8, 130.0, 129.7, 128.5, 126.7, 122.4, 121.71, 119.0, 115.2, 111.8, 47.8, 42.6, 21.6

3.4.9 Synthesis of 4-methyl-*N*-(2-phenyl-2-(phenylamino)ethyl)benzenesulfonamide (5a):



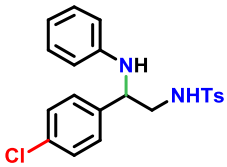
The compound was synthesized using Method B, where styrene was the substrate used and aniline was used as a nucleophile. The reaction was performed at room temperature. The compound obtained was characterized by NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 3274 (w), 2924 (b),2359 (m), 1599 (m), 1560 (m), 1510 (s), 1458 (m), 1315 (s),1153 (s),1091 (s),953 (w), 875(w), 814(m), 745(s), 697(s), 632 (s), 592 (w) 545 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.33–7.23 (m, 7H), 7.08 (t, J = 7.84 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 4.9 (bs,1H), 4.48 (bs,1H), 4.40 (dd, J = 4.4Hz, 3Hz, 1H), 3.35–3.32 (m, 1H), 3.21–3.14 (m, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ146.8, 144.0, 140.2, 136.9, 130.1, 129.3, 128.5, 128.3, 127.3, 126.6, 118.8, 112.9, 110.5, 57.5, 49.2, 21.7

3.4.10 Synthesis of *N*-(2-(4-(tert-butyl)phenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (5b):



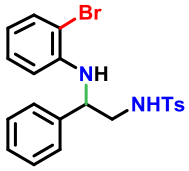
The compound was synthesized using Method B, where 4-^{t}Bu-styrene was the substrate used and aniline was used as a nucleophile. The reaction was performed at room temperature. The compound obtained was characterized by NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 2963 (w), 2362 (b), 2323 (b), 1489 (m), 1270 (m), 1152 (s), 1092 (w), 745 (w), 664 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.24 Hz, 2H), 7.35–7.28 (m, 4H), 7.21 (d, J = 8.28 Hz, 2H), 7.11 (t, J = 7.9, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 7.88 Hz, 1H), 4.89 (bs,1H), 4.41 (dd, J = 4.88 Hz, 1.96 Hz, 1H), 3.36–3.189 (m, 2H), 2.4 (s, 3H), 1.3 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ151.0, 147.0, 143.9, 137.0, 130.0, 129.3, 127.3, 126.4, 126.0, 118.1, 113.8, 57.1, 49.1, 34.7, 31.5, 21.7

3.4.11 Synthesis of *N*-(2-(4-chlorophenyl)-2-(phenylamino)ethyl)-4-methylbenzenesulfonamide (5c):



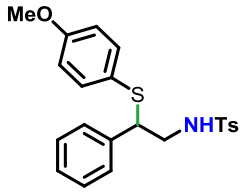
The compound was synthesized using Method B, where 4-chloro-styrene was the substrate used and aniline was used as a nucleophile. The reaction was performed at room temperature. The compound obtained was characterized by NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 3391 (b), 3278 (b), 2927 (w),1601 (s), 1497 (m), 1433 (w), 1408 (w), 1319 (s), 1156 (s),1090 (s), 872 (w); 814 (m), 750 (s), 692 (m), 661 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 (d, J = 8.2 Hz, 2H), 7.23–7.28 (m, 6H), 7.07 (t, J = 7.9, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.43 (d, J = 7.88 Hz, 2H), 5.12 (t, J = 6.52 Hz, 1H), 4.55 (s, 1H), 4.37 (dd, J = 4.24 Hz, 3.52 Hz, 1H), 3.32–3.11 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ146.7, 144.1, 138.9, 136.8, 133.7, 130.1, 129.3, 128.1, 127.2, 118.4, 113.9, 57.2, 49.2, 22.5, 21.7

3.4.12 Synthesis of *N*-(2-((2-bromophenyl)amino)-2-phenylethyl)-4-methylbenzenesulfonamide (5d):



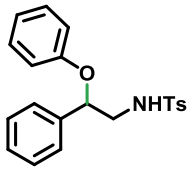
The compound was synthesized using Method B, where styrene was the substrate used and 2-bromo aniline was used as a nucleophile. The reaction was performed at room temperature. The compound obtained was characterized by NMR (^{1}H and ^{13}C). FTIR ($\tilde{\nu}_{max}$,cm^{-1}) 3373-3282 (b), 2923 (w), 1597 (m), 1452 (m), 1429 (w), 1411 (w), 1323 (s),1092 (m), 1019 (w); 813 (w), 744 (m), 702 (m), 662 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.84 Hz, 2H), 7.4 (d, J = 7.88, 1H), 7.33–7.25 (m, 7H), 6.97 (t, J = 7.7, 1H), 6.54 (t, J = 7.58 Hz, 1H), 6.3 (d, J = 8.12 Hz, 1H), 4.97 (d, J = 6.16 Hz, 1H), 4.88 (bs, 1H), 4.47 (dd, J = 6.36 Hz, 5.52 Hz, 1H), 3.41–3.21 (m, 2H), 2.4 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ143.9, 143.6, 139.5, 137.0, 132.6, 130.0, 129.3, 128.5, 128.3, 127.3, 126.6, 118.8, 112.9, 110.5, 57.5, 49.2, 21.7

3.4.13 4-methyl-*N*-(2-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (11a):



The compound was synthesized using Method B, where styrene was the substrate used and 4-methoxy thiophenol was used as the nucleophile. The reaction was performed at room temperature. The opening resulted in formation of non-separable regio-isomer, ^{1}H-NMR of major product (11a) has been depicted below. ^{1}H NMR (400 MHz, $CDCl_3$) 7.64 (d, J = 8.16 Hz, 2H), 7.28 –7.23 (m, 5H), 7.19–7.17 (m, 2H), 7.13–7.09 (m, 3H), 6.74 (d, J= 8.68 Hz, 2H), 4.84 (t, J = 6.64 Hz, 1H), 4.24 – 4.20 (m, 1H), 3.95 (t, J = 7.52 Hz, 1H), 3.77 (s, 3H), 3.34 (t, J = 6.84Hz, 2H), 2.44 (s, 3H).

3.4.14 4-methyl-*N*-(2-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (12a):



The compound was synthesized using Method B, where styrene was the substrate used and 4-methoxy thiophenol was used as the nucleophile. The opening resulted in formation of non-separable regio-isomers, ^{1}H-NMR of major product (12a) has been shown below. ^{1}H NMR (400 MHz, $CDCl_3$) 7.75 (d, *J* = 8.16 Hz, 2H), 7.29 –7.13 (m, 15H), 7.14 (d, *J*= 7.88 Hz, 2H), 6.89 (t, *J*= 7.60 Hz, 1H), 6.72 (d, *J*= 7.88 Hz, 2H), 5.34 (dd, *J*= 5.28 Hz, 3.64 Hz, 1H), 5.12 (dd, *J*= 5.4 Hz, 3.56 Hz, 1H), 3.47 – 3.40 (m, 1H), 3.29– 3.26 (m, 1H), 2.44 (s, 3H). (note: the multiplet at 7.19-7.17 has higher integration (15H instead of 7H) due to proton interference of regio-isomer **12b**

4. Mechanistic Consideration (Aziridination):

4.1 Aziridination with isostructural Zn and Ni MOFs.

To establish the involvement of Cu in aziridination *via* metal nitrene interaction, we performed the aziridination of styrene using isostructural MOFs $Ni_3(BTC)_2$ and $Zn_3(BTC)_2$ obtained *via* reported solvothermal procedure thereby eliminating Cu from the system keeping other parameters intact. Both isostructural MOFs failed to furnish the aziridine 12a which may be attributed to the inability of Ni and Zn centers to form metal nitrene species (Table S3)

Table S3. **Aziridination of styrene using iso-structural HKUST-1 MOFs**

Sl. No.	Catalyst	Substrates	Solvent/time	Product (12a)
1.	$Zn_3(BTC)_2$	Styrene / PhINTs	CH_3CN / 2 h	Non
2.	$Ni_3(BTC)_2$	Styrene / PhINTs	CH_3CN / 2 h	Non
3.	HKUST-1	Styrene / PhINTs	CH_3CN / 2 h	94 %

4.2 Substitution effect (Hammett plot) *via* competitive reaction:

A series of para-substituted styrene was competitively reacted with styrene using $\mathbf{1_{act}}$ as the catalyst and with the help of ^{1}H-NMR the ratio of the aziridines (X/H, X = para substitution) was obtained for the construction of Hammett plot. The positive $\log(k_X/k_H)$ experimental values for an electron-donating substituent in styrene suggest the reaction being more favored by an electron-donating substituent, whereas para-substitution of styrene with electron-withdrawing group retards the rate. A non-linear correlation was obtained when the polar substitution constant (σ^+) was plotted against the reaction rate using eq. 1. We performed a multiple co-efficient linear regression for the Jackson Dual parameter (equation 2) to obtain the values of reaction constants (ρ^+= -0.515, $\rho^{\bullet}$= 0.498).

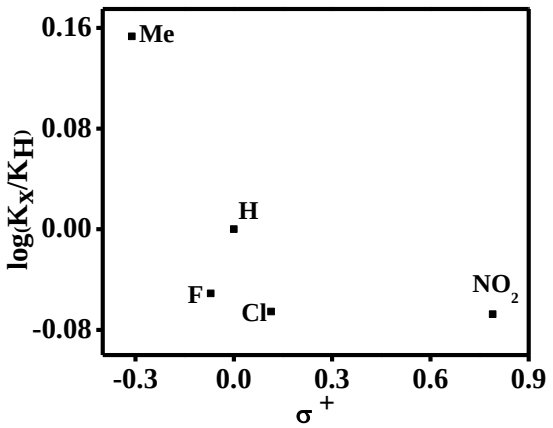


Figure S7: A non-linear correlation considering only the polar substitution constant.

Substitution	K_X/K_H	$\log(k_X/k_H)$ experimental	σ_+	$\sigma^{\cdot}$
NO_2	0.8	-0.096	0.79	0.76
Cl	0.833	-0.079	0.11	0.18
F	0.86	-0.051	-0.07	0.12
H	1	0	0	0
Me	1.75	0.301	-0.13	0.39

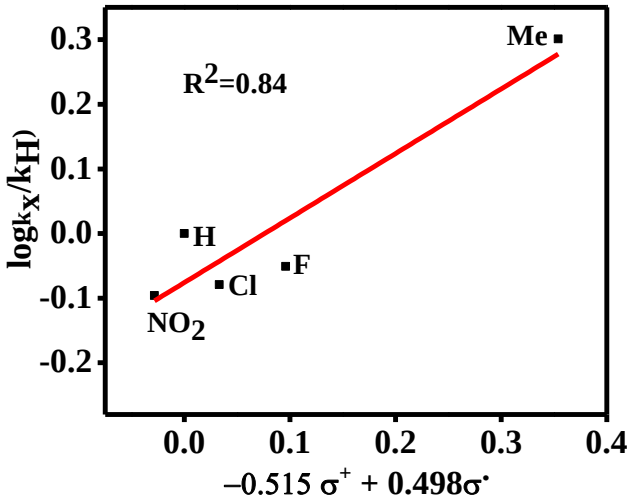


Figure S8: Linear free energy relation for aziridination of styrene catalyzed by HKUST-1.

$$log\frac{k_X}{k_H} = \rho^+\sigma^+ \quad (1)$$

$$log\frac{k_X}{k_H} = \rho^+\sigma^+ + \rho^\bullet\sigma^\bullet \quad (2)$$

The negative value of polar reaction constant (ρ^+) suggests a modest positive charge being developed during the transition state and the attack on alkenes being electrophilic in nature, whereas a positive $\rho^\bullet$ value suggests that the para substituents are involved in delocalization of spin during the transition state. Furthermore, the ratio of the constants $\rho^+/\rho^\bullet$ was found to be 1.03 (where ρ^+ and $/\rho^\bullet$ are polar and radical contribution of reaction constant) suggested that of both polar and spin delocalization effects where involved during the reaction.[7] This could be possible only if the reaction proceeds *via* a stepwise fashion with generation of an intermediate benzyl radical stabilized by the delocalization effect.

4.3 Effect of radical inhibition:

The existence of a metal nitrene species during aziridination has been well documented in the literature but its spin multiplicity (singlet or triplet) being uncertain and often fluctuating with the change in metal catalyst mostly aspire for a proper study. We performed a couple of aziridination reactions with styrene, one in the presence and the other in absence of a radical inhibitor 2,2',6,6'-tetramethylpiperidinyloxy (TEMPO). The ratio of styrene (substrate), PhINTs (nitrene source), and TEMPO (inhibitor) were 100:20:5.

Table S4: Radical inhibition reaction in presence of TEMPO

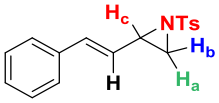
Catalyst	Inhibitor	Reaction Time	Yield %
$\mathbf{1}_{act}$	Absent	2h	94
$\mathbf{1}_{act}$	TEMPO	2h	40

Note: Reaction Condition: Catalyst (10.5 mg), PhINTs (0.03 mmol), olefins (0.15 mmol), molecular sieves (5 Å, 25 mg), and inhibitor (0.075 mmol) was stirred for 2 h at room temperature. Yield determined by ^{1}H- NMR using an internal standard.

Table S5. The diastereoselective reaction of *trans-β*-methyl styrene:

Conf.	H_a(Reported)	H_a(Found)	H_b(Reported)	H_b(Found)
cis	δ3.72 (d, 1H, J= 7.30 Hz)	δ3.67(d, 1H, J=7.0 Hz)	δ3.18 (dq, 1H, J= 7.3, 5.8 Hz)	δ3.01(dq, 1H, J=5.08, 1.92 Hz)
trans	δ3.79 (d, 1H, J= 4.30 Hz)	δ3.76(d, 1H, J=4.3 Hz)	δ2.90 (dq, 1H, J= 6.0, 4.4 Hz)	δ2.88(dq, 1H, J=4.06, 1.36 Hz)

Table S6. Regio-selective reaction of *trans*-1-phenyl-1,3-butadiene:

Compound (3p)	H_a	H_b	H_c	H
	δ2.29 (d 1H, J= 4.44Hz, *trans*- CH)	δ2.83(d 1H, J=7.04, *cis*- CHPh)	δ3.42 (td 1H, J= 7.5, 4.56 Hz, azi CH)	δ5.81(dd 1H, J=7.9, 15.8 Hz, PhCH=CH)

NMR Spectra:

5.1 NMR spectra of aziridine:

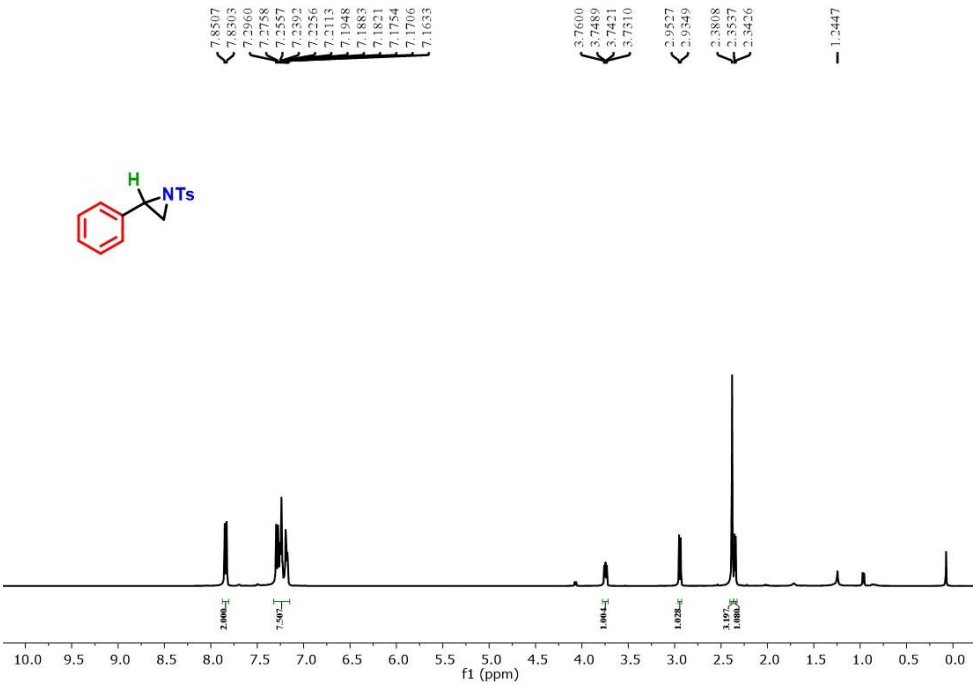


Figure S9: ^{1}H-NMR of **3a** in $CDCl_3$

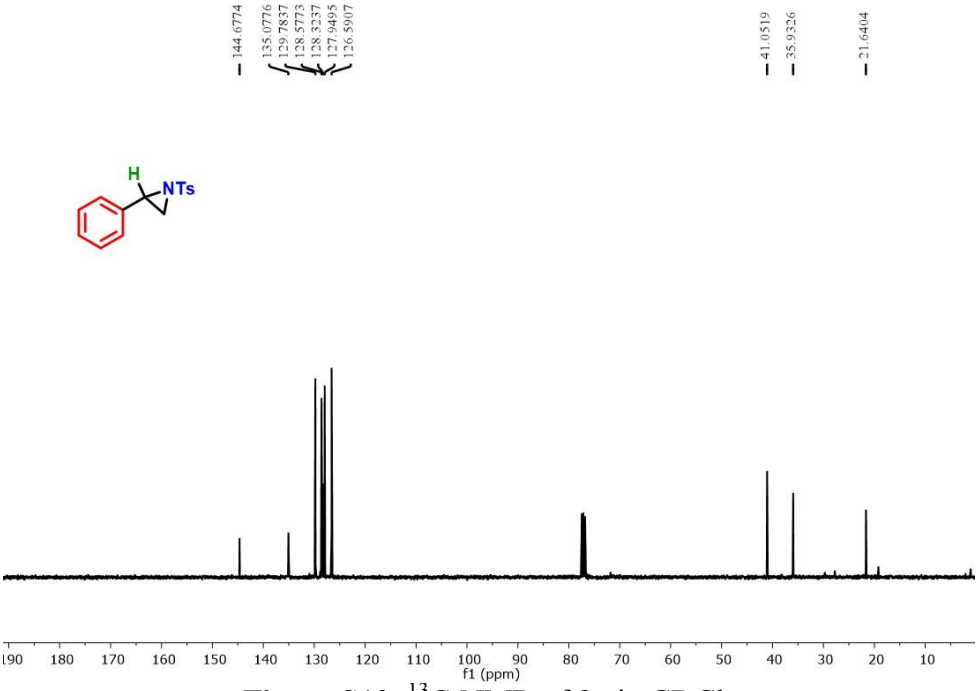


Figure S10: ^{13}C-NMR of **3a** in $CDCl_3$

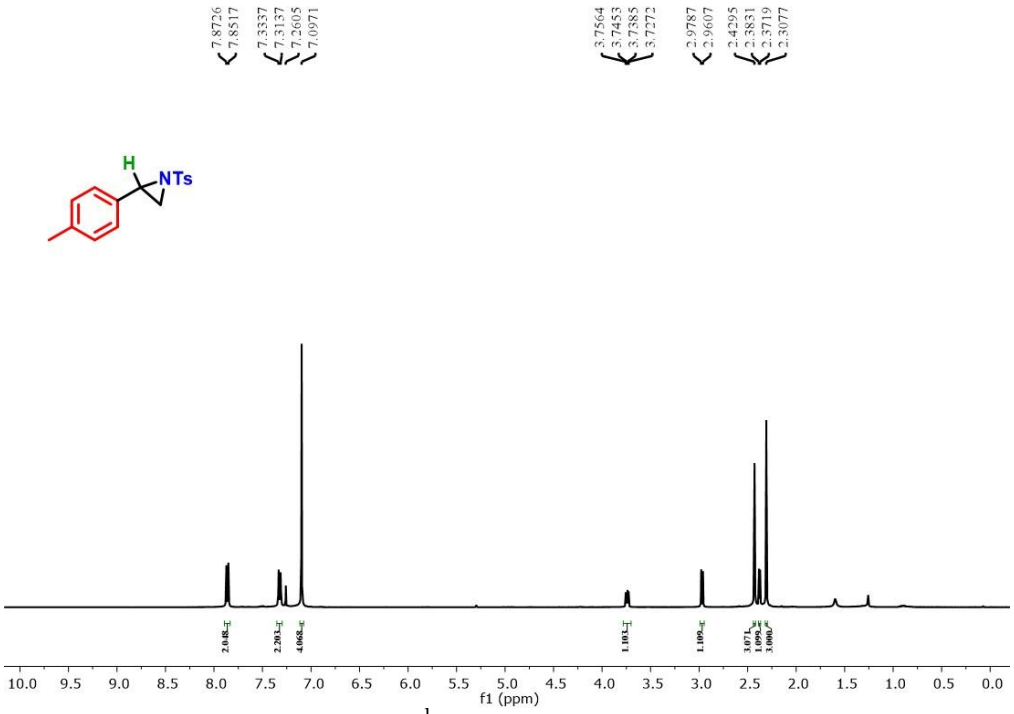


Figure S11: ^{1}H-NMR of **3b** in $CDCl_3$

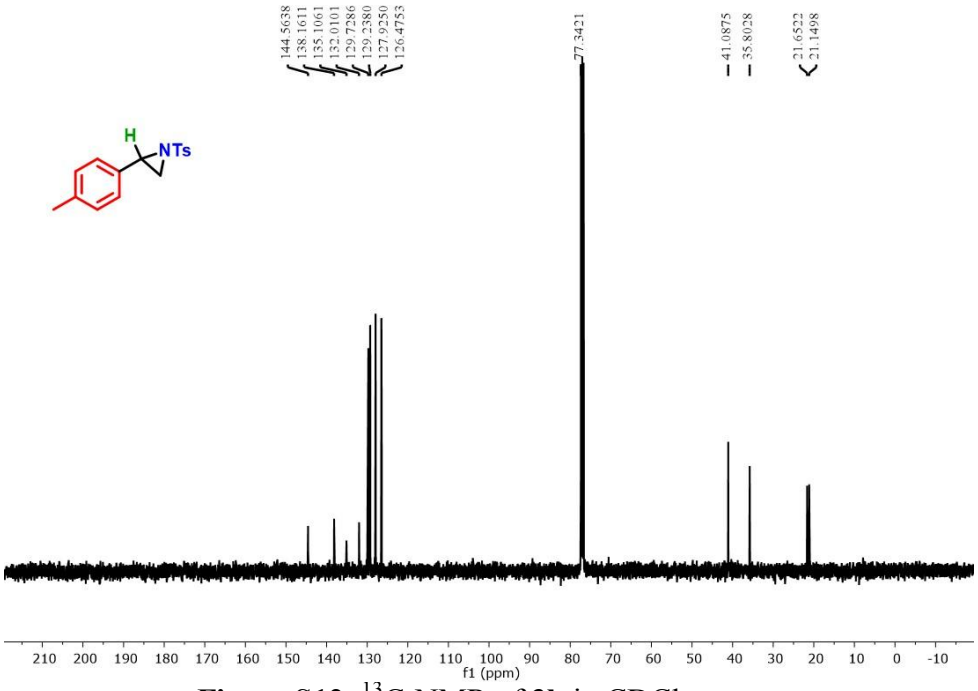


Figure S12: ^{13}C-NMR of **3b** in $CDCl_3$

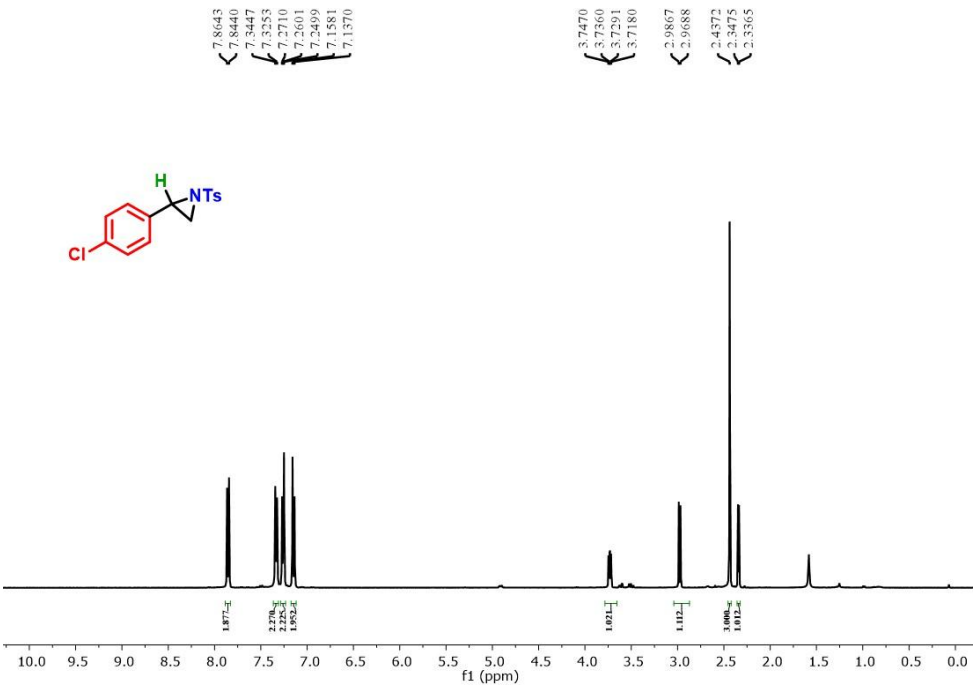


Figure S13: ^{1}H-NMR of **3f** in $CDCl_3$

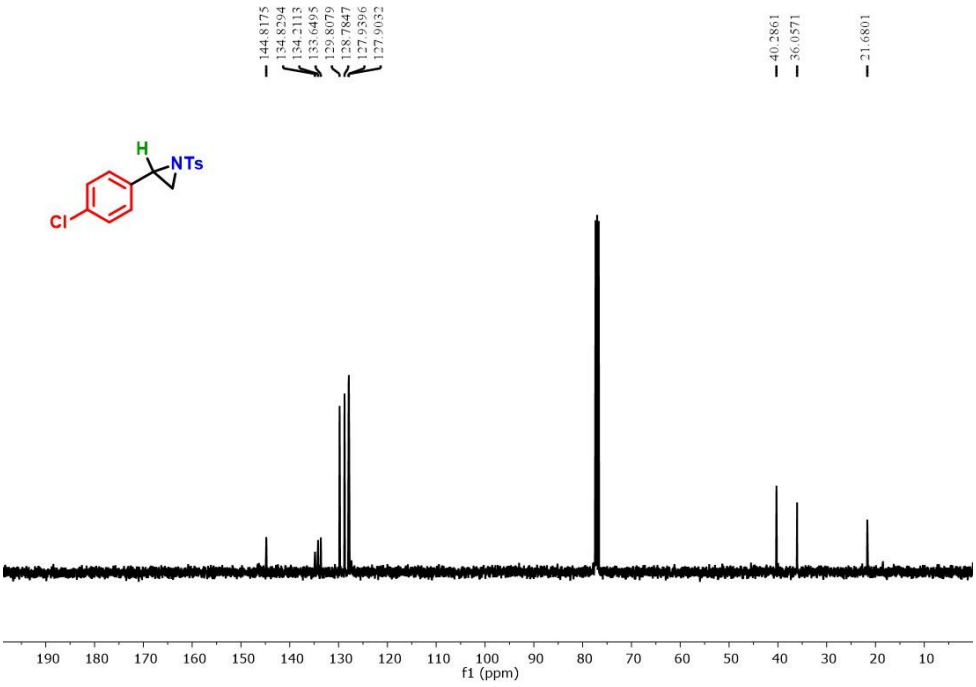


Figure S14: ^{13}C-NMR of **3f** in $CDCl_3$

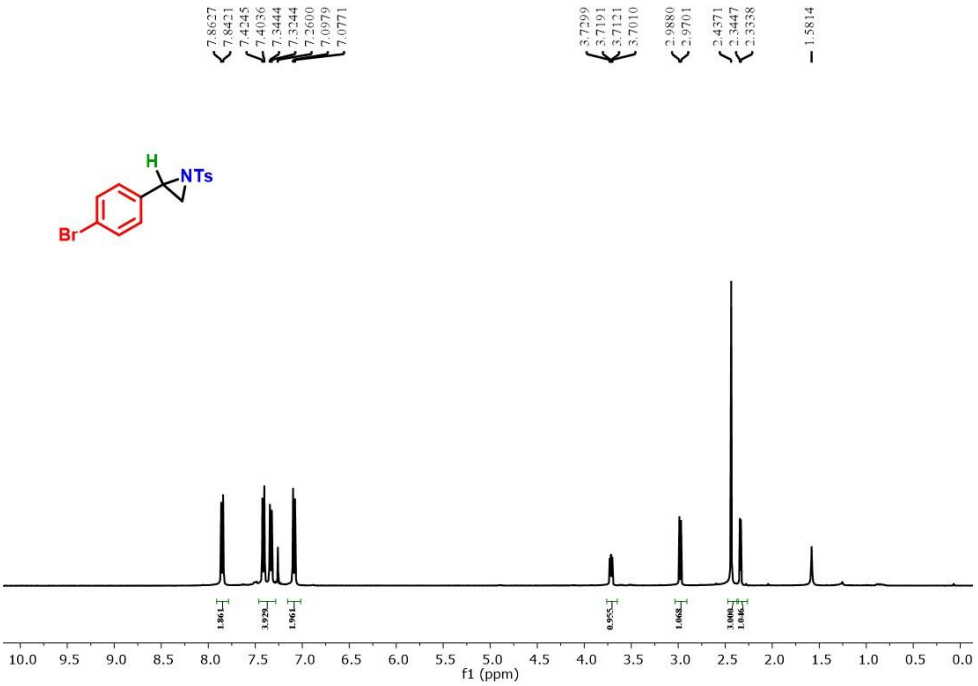


Figure S15: ^{1}H-NMR of **3f** in $CDCl_3$

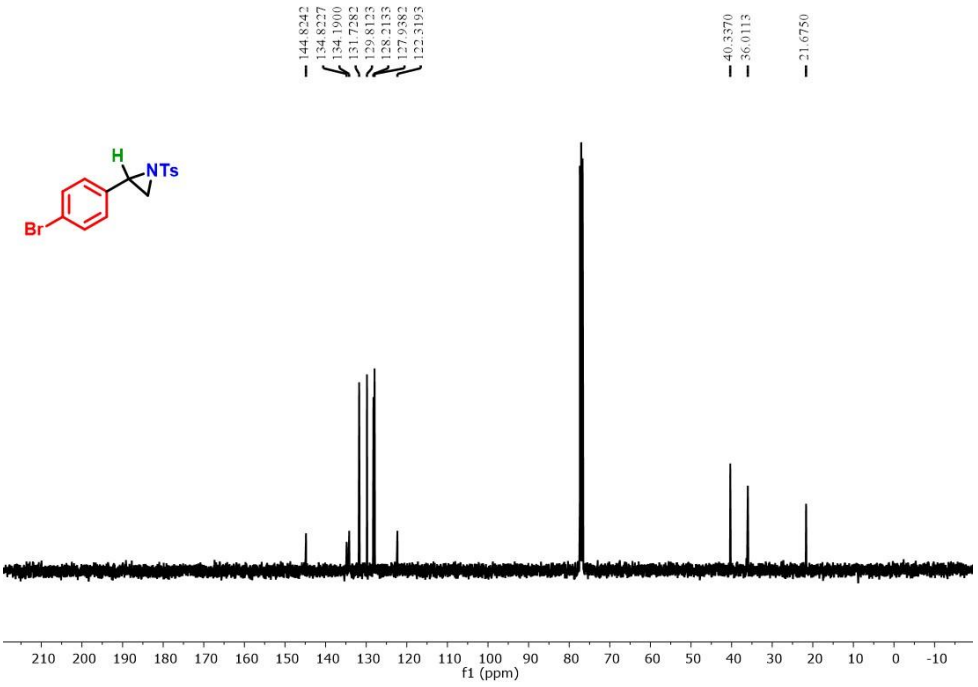


Figure S16: ^{13}C-NMR of **3f** in $CDCl_3$

5.2 NMR spectra of ring-opening products:

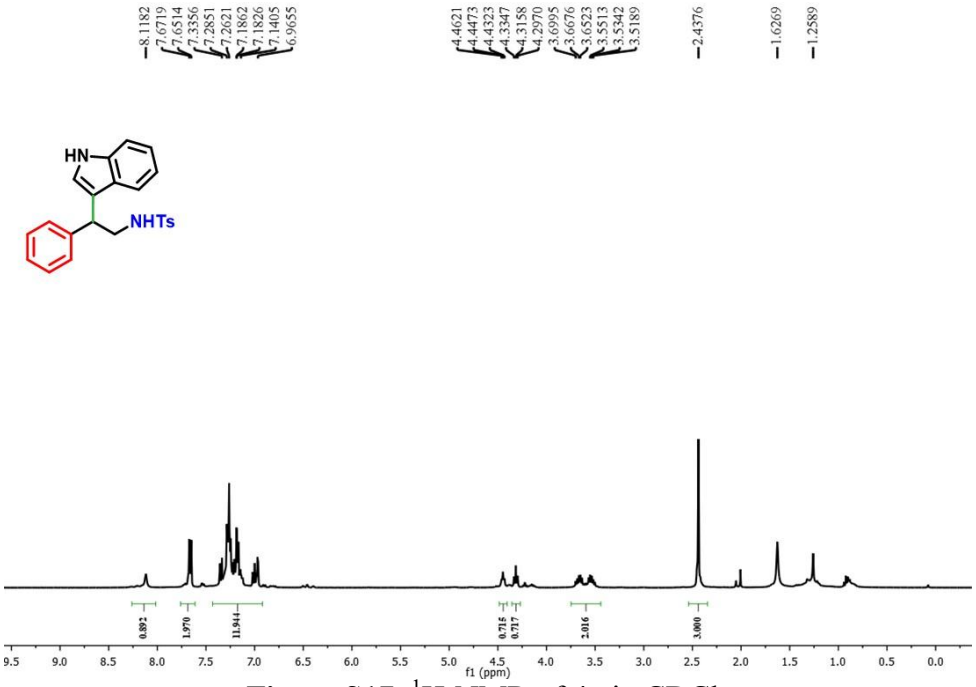


Figure S17: ^{1}H-NMR of **4a** in $CDCl_3$

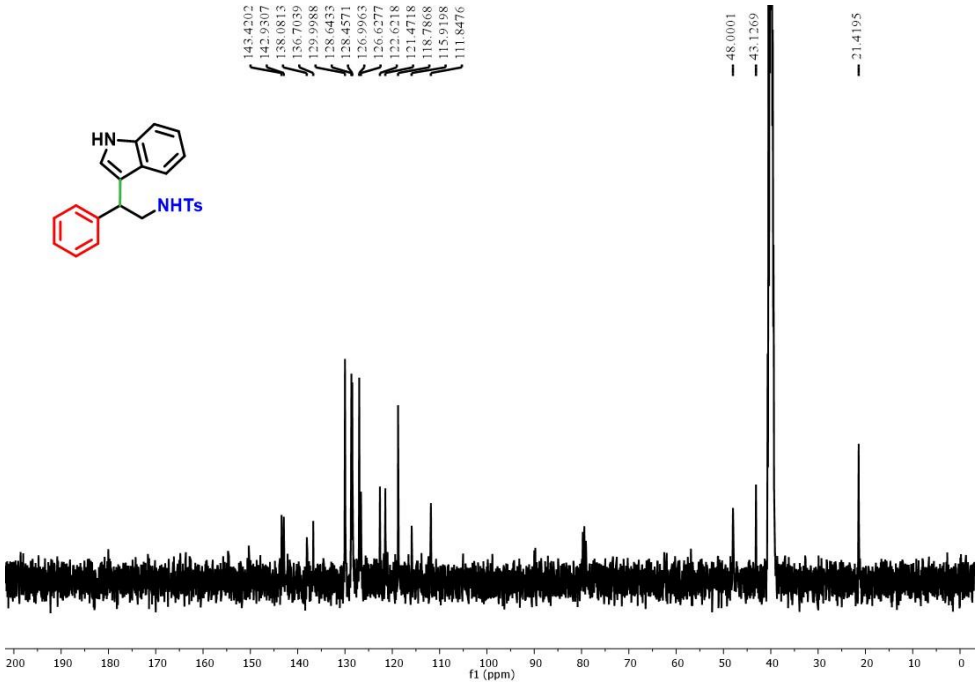


Figure S18: ^{13}C-NMR of **4a** in $CDCl_3$

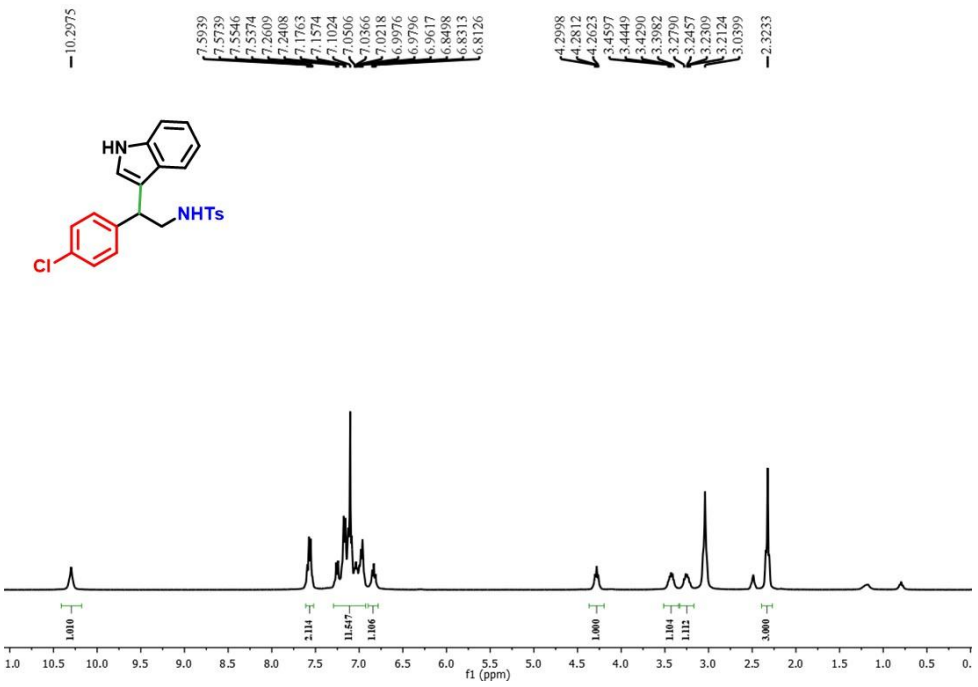


Figure S19: ^{1}H-NMR of compound **4b** in DMSO-d6

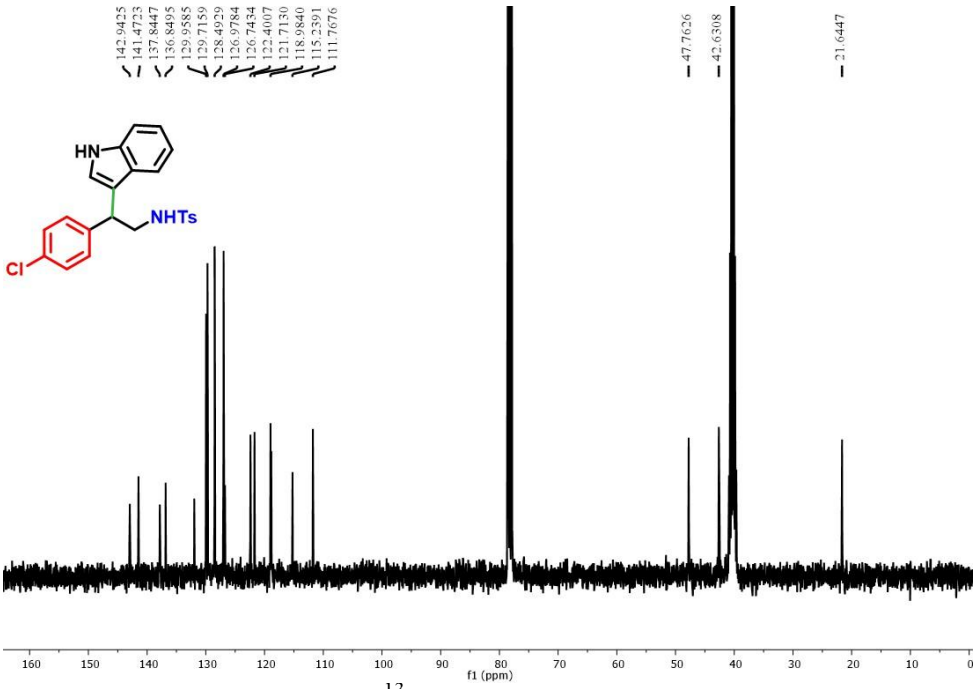


Figure S20: ^{13}C-NMR of **4b** in DMSO-d_6

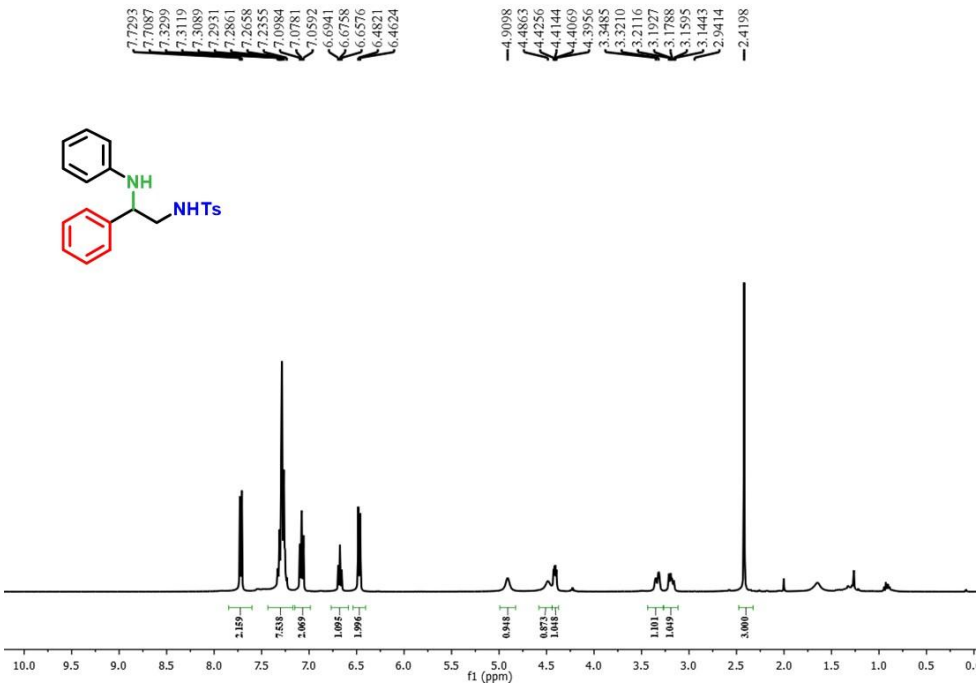


Figure S21: ^{1}H-NMR of compound **5a** in $CDCl_3$

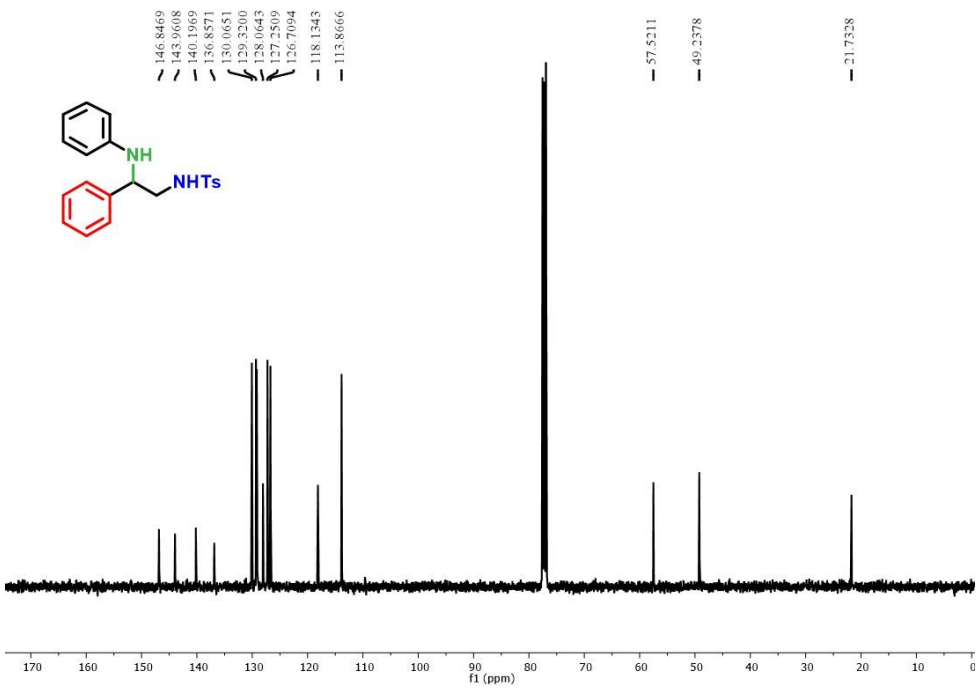


Figure S22: ^{13}C-NMR of **5a** in $CDCl_3$

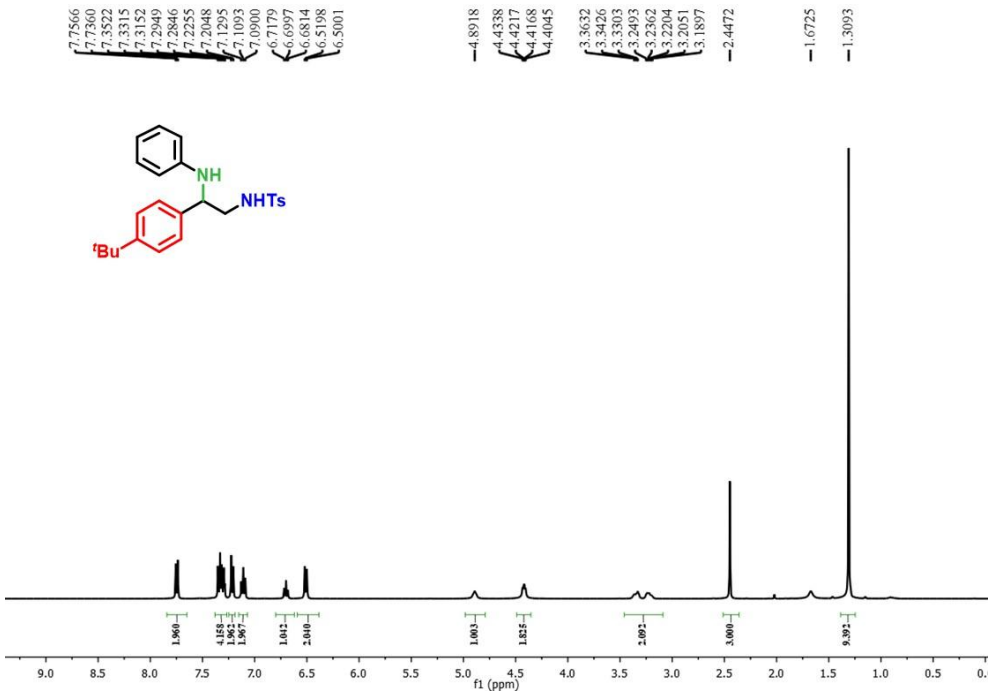


Figure S23: ^{1}H-NMR of **5b** in $CDCl_3$.

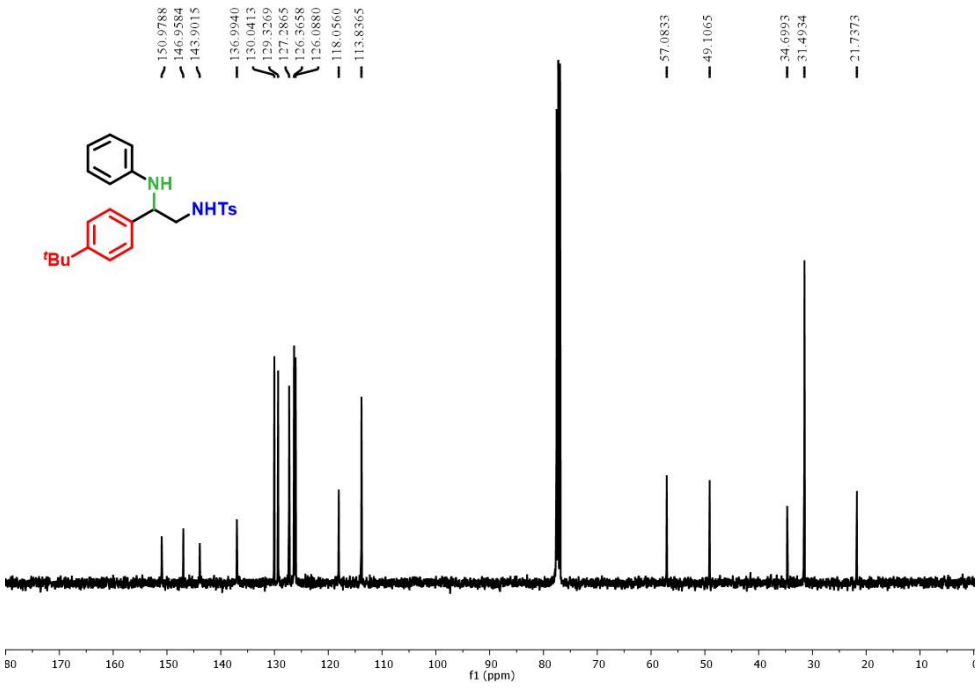


Figure S24: ^{13}C-NMR of **5b** in $CDCl_3$

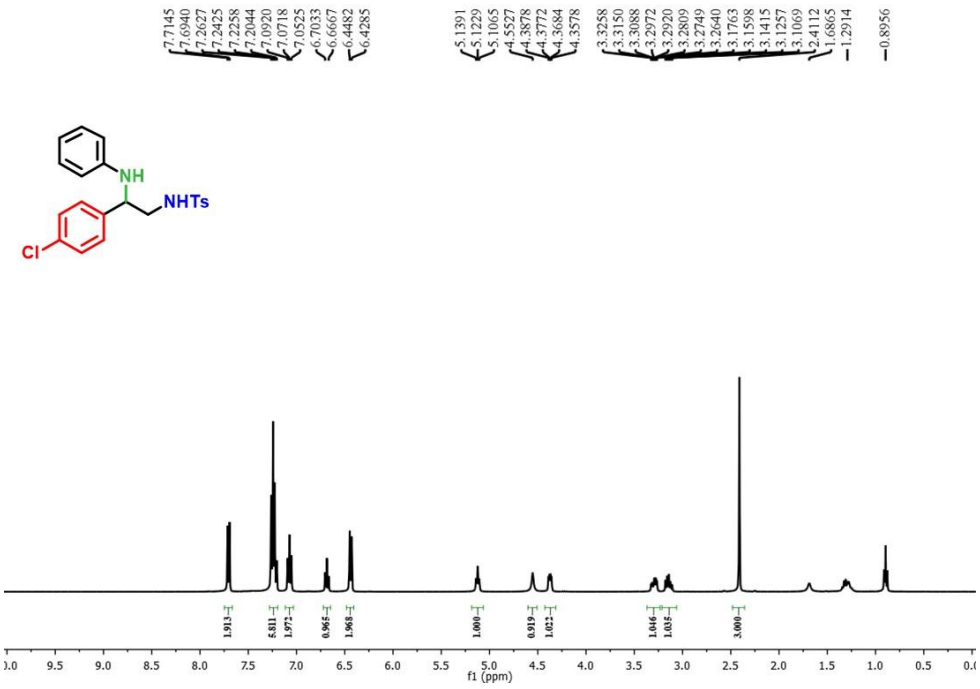


Figure S25: ^{1}H-NMR of **5c** in $CDCl_3$

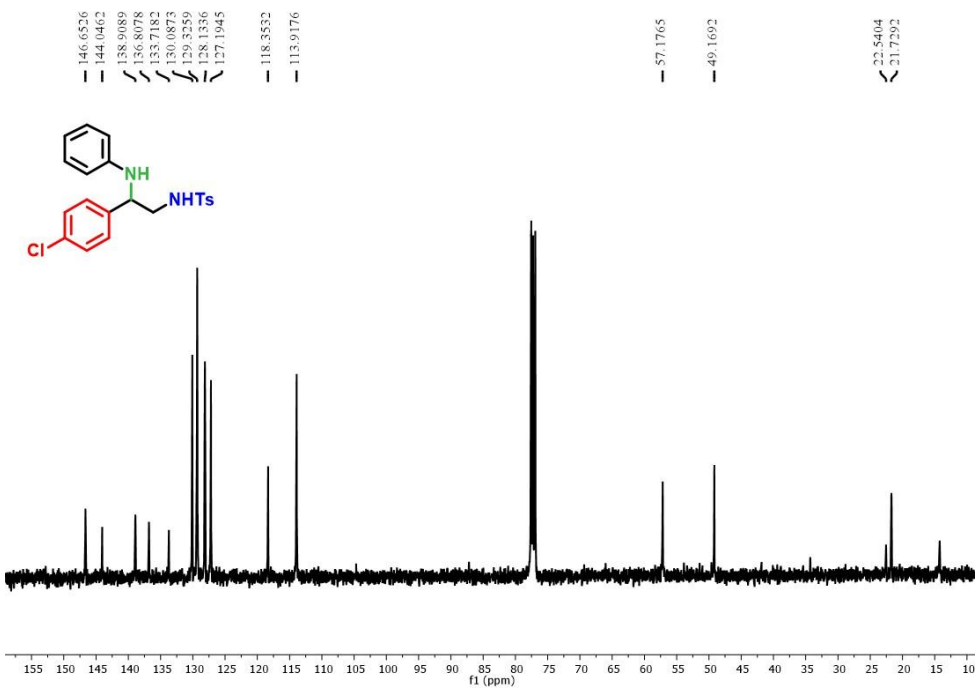


Figure S26: ^{13}C-NMR of **5c** in $CDCl_3$

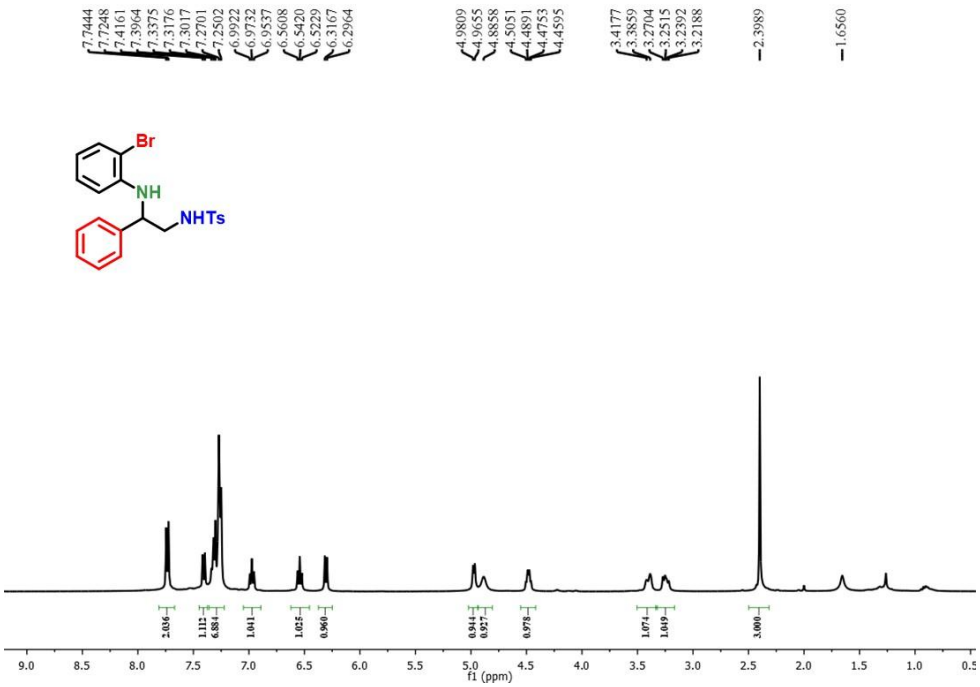


Figure S27: ^{1}H-NMR of **5d** in $CDCl_3$.

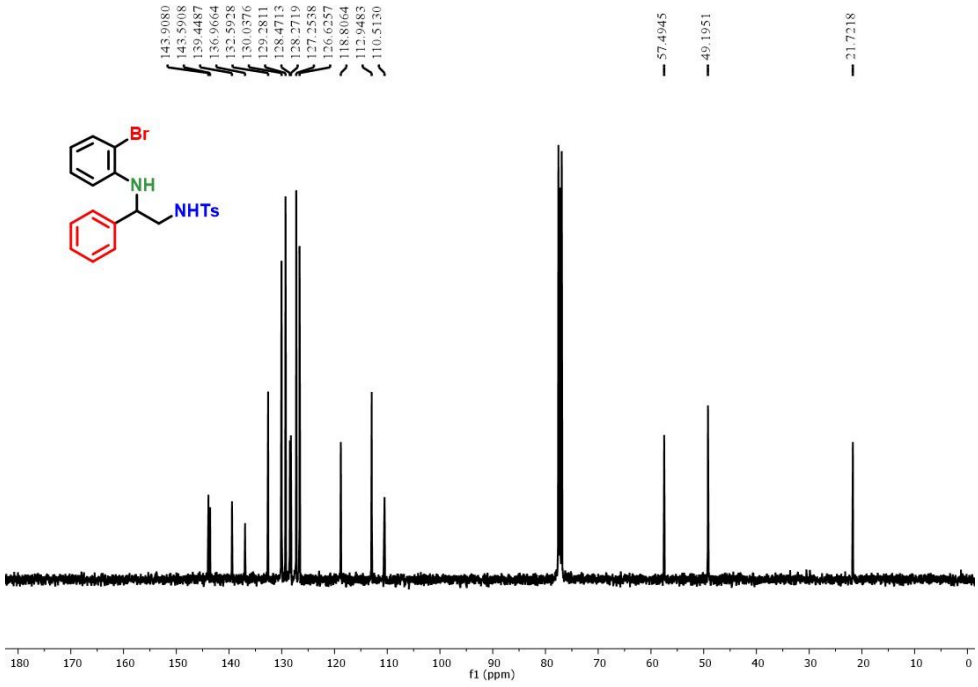


Figure S28: ^{13}C-NMR of **5d** in $CDCl_3$

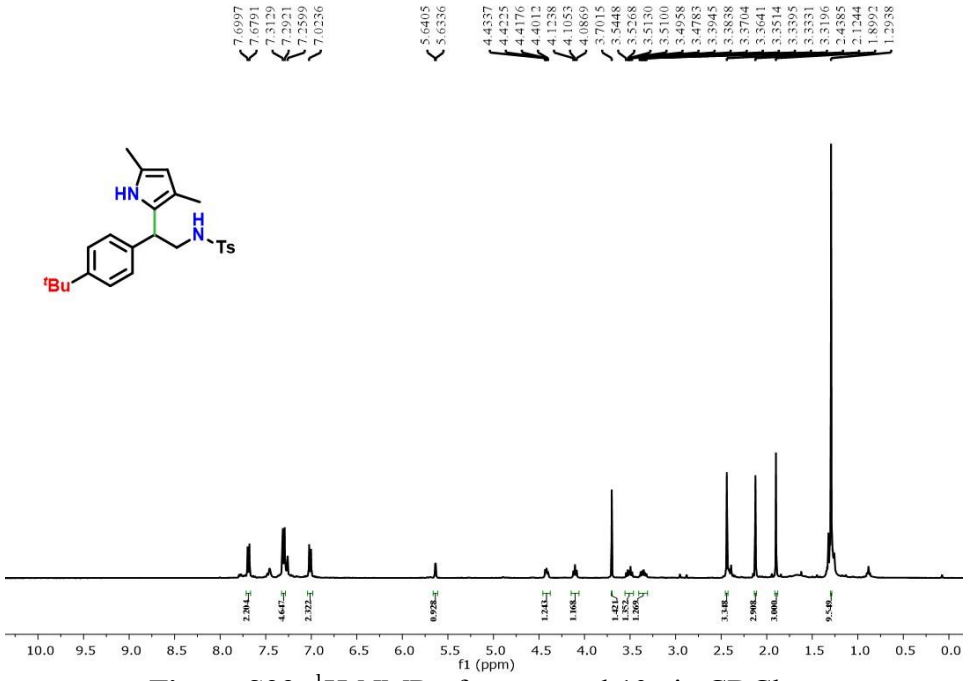


Figure S29: ^{1}H-NMR of compound **10a** in $CDCl_3$

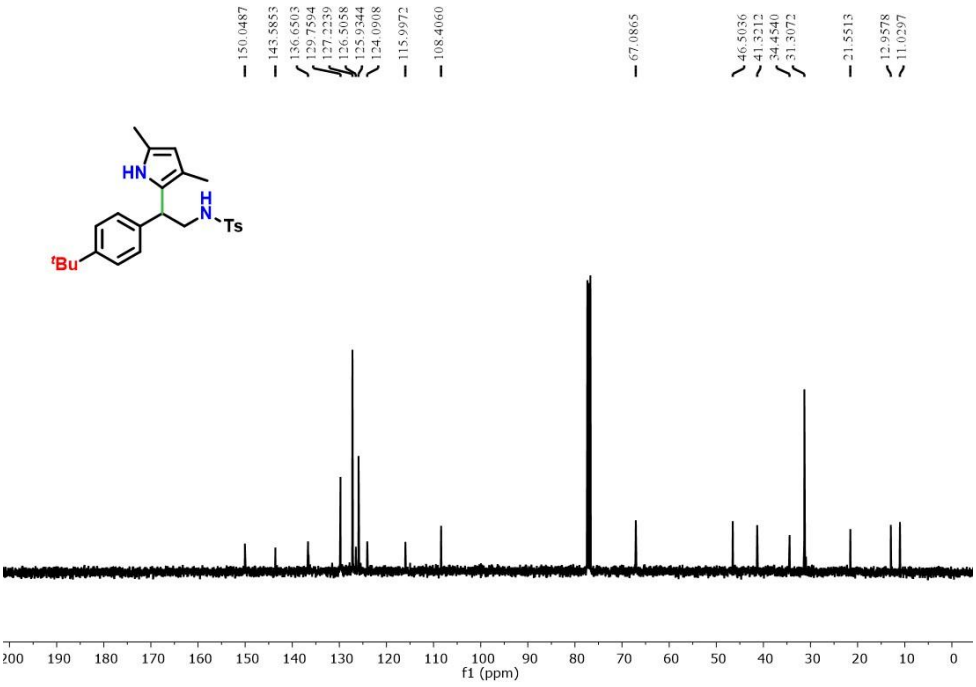


Figure S30: ^{13}C-NMR of compound **10a** in $CDCl_3$

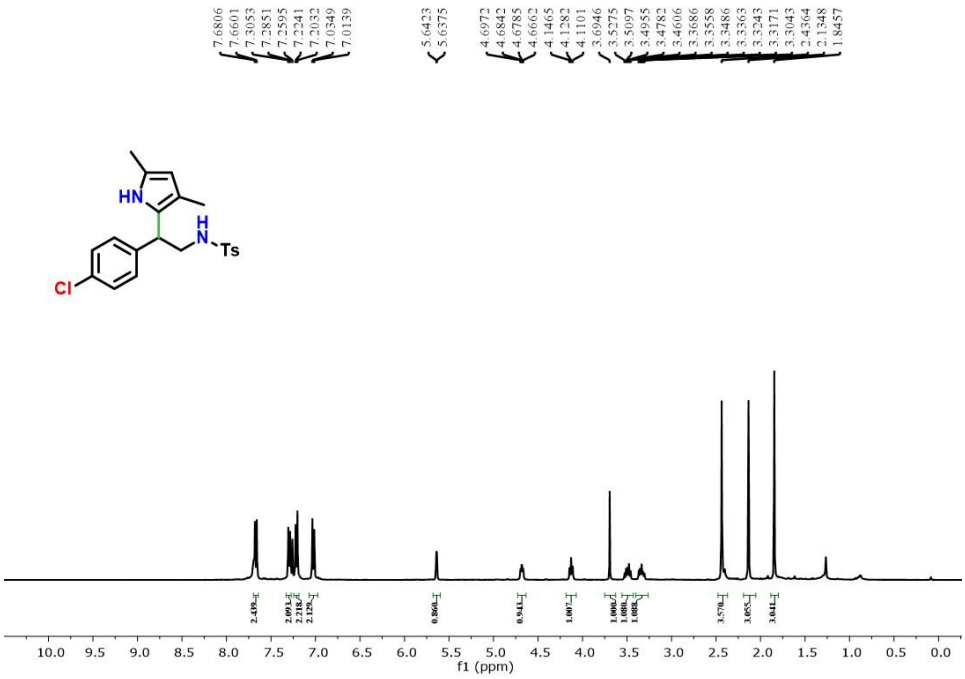


Figure S31: ^{1}H-NMR of compound **10b** in $CDCl_3$

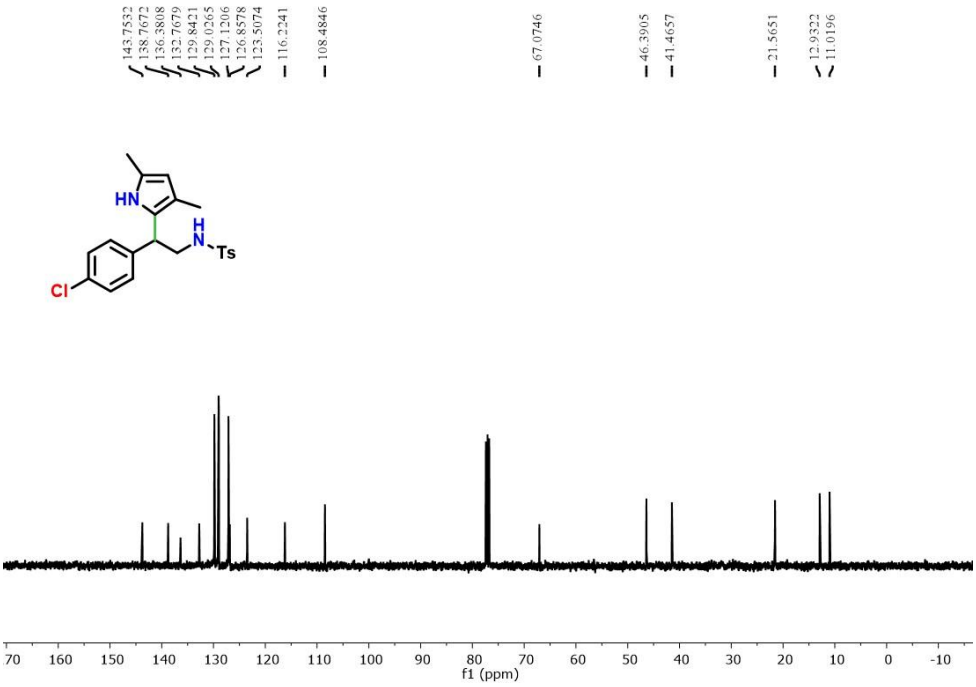


Figure S32: ^{13}C-NMR of compound **10b** in $CDCl_3$

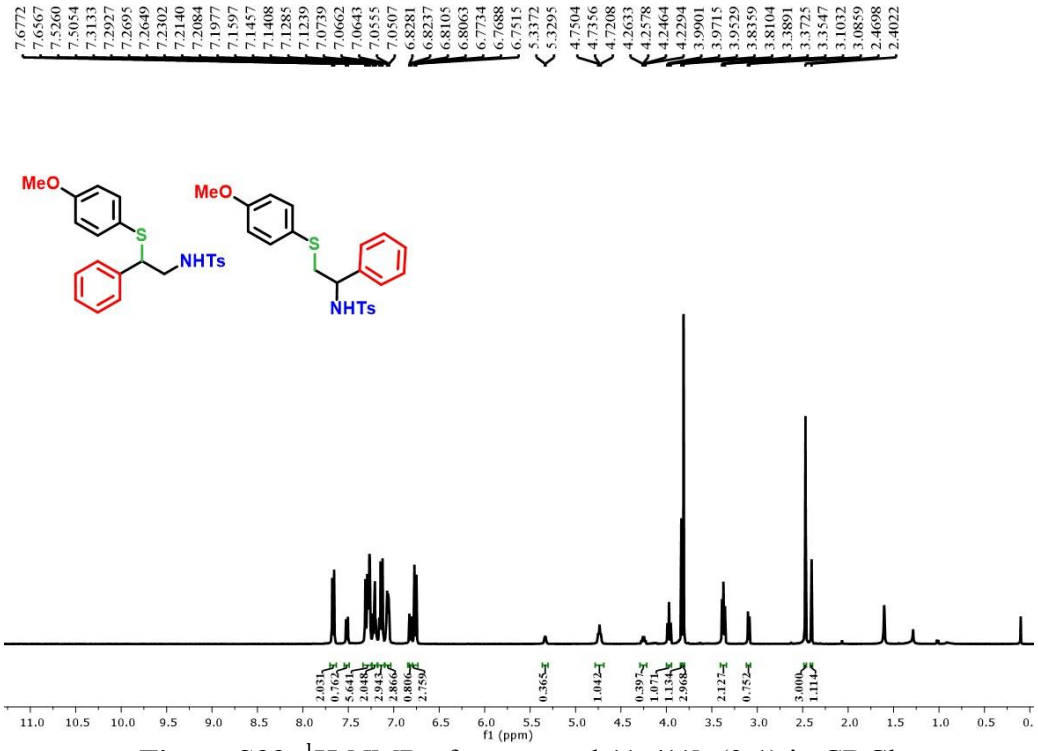


Figure S33: ^{1}H-NMR of compound **11a/11b** (3:1) in $CDCl_3$

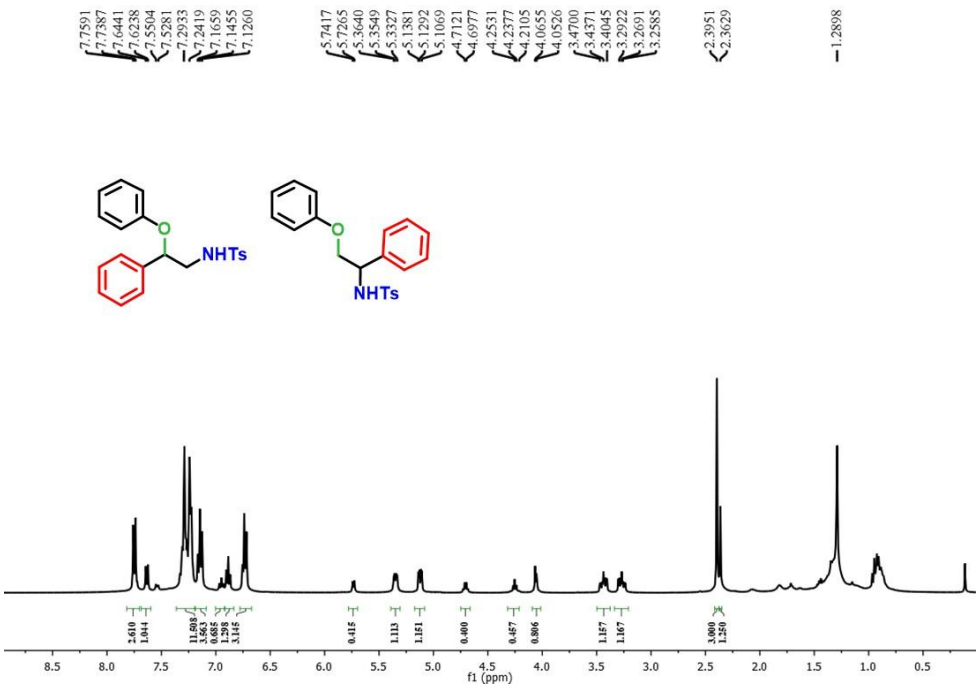


Figure S34: ^{1}H-NMR of compound **12a/12b** (3:1) in $CDCl_3$

6. Reference

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