Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

[3+2]-Annulation of Platinum-Bound AzomethineYlides with Distal C=C bonds of *N*-Allenamides

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1 Experimental section:

1.1 General information:

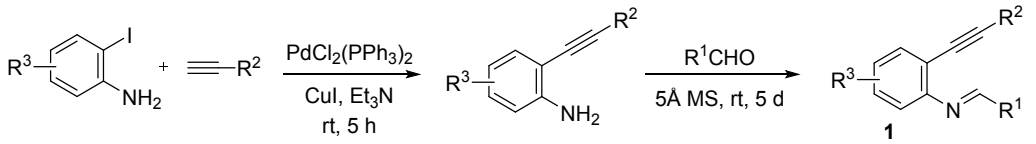
Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringes cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ or anisaldehyde and charring on a hot plate. Solvents were removed in vacuum and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Melting points are uncorrected and recorded using digital Büchi Melting Point Apparatus B-540. The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AV, 200/400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), br (broad signal), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet) etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Single-crystal data was collected on a Super Nova Dual source X-ray diffractometer system (Agilent Technologies) equipped with CCD area detector and graphite-monochromatized (MoK_α= 0.71073Å, CuK_α= 1.54184Å) radiation. The catalysts used in this study were procured from Sigma-Aldrich.

1.2 General procedure for the synthesis of imino-alkynes (1):

The imino-alkynes were prepared by literature known procedure.[1] The representative procedure is given below.

General Procedure: To a stirred solution of *o*-ethynylanilines[2] (2.6 mmol) in toluene (5.0 mL) were added 5Å MS (5.0 g) and corresponding aldehydes (2.7 mmol) at room temperature. After 5 days, the reaction mixture was filtered through short pad of celite and the filtrate was concentrated under reduced pressure to afford imnoalkynes **1a-1l** which were used as such without further purification.



R^3 = H
R^3 = 4,5-Me_2
R^3 = 3-F

R^2 = Ph, R^3 = H
R^2 = *p*-MeC_6H_4, R^3 = H
R^2 = *p*-$OMeC_6H_4$, R^3 = H
R^2 = *p*-$COCH_3C_6H_4$, R^3 = H
R^2 = Ph, R^3 = 4,5-Me_2
R^2 = Ph, R^3 = 3-F

1a R^1, R^2 = Ph, R^3 = H
1b R^1 = 3,5-$(OMe)_2C_6H_3$, R^2 = Ph, R^3 = H
1c R^1 = 3,4,5-$(OMe)_3C_6H_2$, R^2 = Ph, R^3 = H
1d R^1 = 2-Br, 5-FC_6H_3, R^2 = Ph, R^3 = H
1e R^1 = *p*-$NO_2C_6H_4$, R^2 = Ph, R^3 = H
1f R^1 = 2-thienyl, R^2 = Ph, R^3 = H
1g R^1 = N-Me 2-pyrrolyl, R^2 = Ph, R^3 = H
1h R^1 = Ph, R^2 = *p*-MeC_6H_4, R^3 = H
1i R^1 = Ph, R^2 = *p*-$OMeC_6H_4$, R^3 = H
1j R^1 = Ph, R^2 = *p*-$COCH_3C_6H_4$, R^3 = H
1k R^1, R^2 = Ph, R^3 = 4,5-Me_2
1l R^1, R^2 = Ph, R^3 = 3-F

1.3 Preparation of *N*-tosylallenamides (2):

a) Preparation of *N*-tosyl propargylamines:

N-tosyl propargylamines (**S1**,[3] **S3**,[4] **S4**,[3] **S5**,[3] **S11**[5] and **S12**[6]) were prepared by literature known procedures. Whereas, other *N*-tosyl propargylamines (**S2**, **S6-10**), which were not known were synthesized using a slightly modified procedure reported by Shi *et al*.[3]

Synthesis of *N*-tosyl propargylamines (S2, S6-10): To a solution of *N*-tosyl anilines (2 mmol) in acetone (15 mL) was added K_2CO_3 (6 mmol). The suspension was stirred for 10 min and

(1) Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 11592.

(2) Takeda, A.; Kamijo, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5662.

(3) Tang, X.-Y.; Zhang, Y.-S.; He, L.; Wei, Y.; Shi, M. *Chem. Commun.* **2015**, *51*, 133.

(4) Roy, B.; Ansary, I.; Samanta, S.; Majumdar, K. C. *Tetrahedron Letters* **2012**, *53*, 5119.

(5) Ballesteros, A.; Morán-Poladura, P.; González, J. M. *Chem. Commun.* **2016**, *52*, 2905.

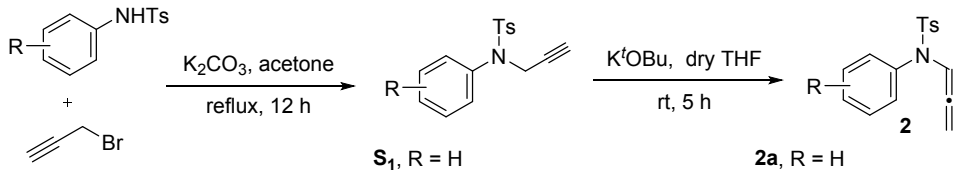
(6) Zhou, W.; Li, X.-X.; Li, G.-H.; Wu, Y.; Chen, Z. *Chem. Commun.* **2013**, *49*, 3552.

then propargyl bromide (3 mmol) was added via syringe at room temperature. The reaction mixture was stirred for 10 h at reflux condition. The residue was filtered through a celite pad and washed with ethyl acetate. The collected filtrate was concentrated in vacuum and the resultant residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford *N*-tosyl propargylamines **S_2**, **$S_{6\text{-}10}$**.

b) Preparation of *N*-tosylallenamides:

N-tosylallenamides **2a**,[7] **2c**,[5] **2e**,[7] **2k**,[7] and **2l**[6] were prepared by literature known procedures. Other *N*-tosylallenamides **2b**, **2d**, **2f-j** were prepared through base promoted isomerization reaction of *N*-tosyl propargylamines as described below.

Synthesis of 2b, 2d, 2f-j: To a THF (10 mL) solution of *N*-tosyl propargylamine (1 mmol), KO^{t}Bu (0.3 mmol) was added portion wise 0 °C under N_2 atmosphere. The reaction was allowed to stir at room temperature for 5 h. The progress of reaction was monitored by TLC. After completion of the reaction; the residue was filtered through a celite pad and washed with ethyl acetate. The filtrate was concentrated in vacuum and the resultant residue purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford the *N*-tosylallenamides **2b**, **2d**, **2f-j**.



S_1, R = H	**2a**, R = H
S_2, R = 4-EtC_6H_4	**2b**, R = 4-EtC_6H_4
S_3, R = 4-MeOC_6H_4	**2c**, R = 4-MeOC_6H_4
S_4, R = 4-ClC_6H_4	**2d**, R = 4-ClC_6H_4
S_5, R = 4-BrC_6H_4	**2e**, R = 4-BrC_6H_4
S_6, R = 4-$NO_2C_6H_4$	**2f**, R = 4-$NO_2C_6H_4$
S_7, R = 2-OPhC_6H_4	**2g**, R = 2-OPhC_6H_4
S_8, R = 3-$CF_3C_6H_4$	**2h**, R = 3-$CF_3C_6H_4$
S_9, R = 3-Br, 4-MeC_6H_3	**2i**, R = 3-Br, 4-MeC_6H_3
S_{10}, R = 3,4-methylenedioxyphenyl	**2j**, R = 3,4-methylenedioxyphenyl
S_{11}, R = benzyl	**2k**, R = benzyl
S_{12}, R = 2,4,6-$Me_3C_6H_2$	**2l**, R = 2,4,6-$Me_3C_6H_2$

1.4 General procedure for the platinum catalyzed [3+2]-annulation reaction:

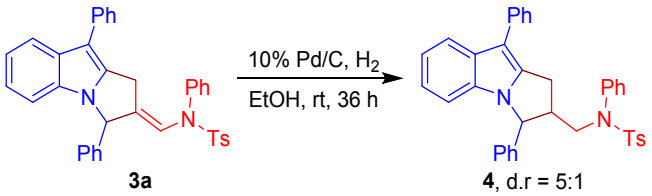
To a oven-dried screw-capped vial equipped with magnetic stir bar, were added iminoalkynes **1** (0.2 mmol), *N*-allenamides **2** (0.4 mmol), 5Å MS (50 mg), $PtCl_2$ (10 mol%) and freshly dried toluene (2 mL) under nitrogen atmosphere. The reaction mixture was heated

(7) Suárez-Pantiga, S.; Hernández-Diaz, C.; Rubio, E.; González, J. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 11552.

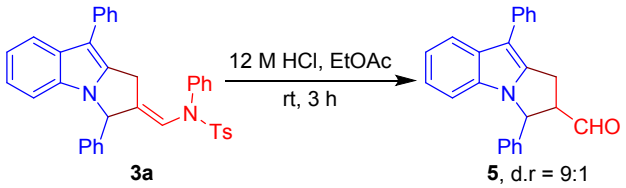
to 85 °C (for specified time) and the progress of reaction was monitored by TLC. After completion of the reaction, the mixture was filtered through a celite pad and washed with ethyl acetate. The filtrate was concentrated in vacuum and the resultant residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to afford substituted pyrrolo[1,2-*a*]indoles **3**.

2 Transformation of product:

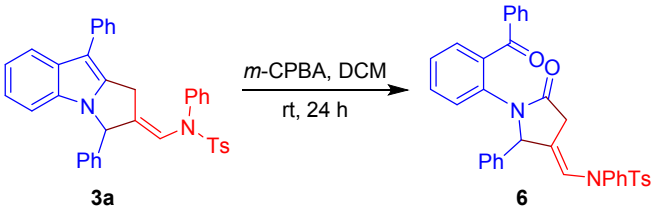
Catalytic hydrogenation of 3a: To a solution of **3a** (0.1 mmol) in ethanol 10 mL, 10% Pd/C (11 mg, 20% w/w) was added and the mixture was stirred vigorously under hydrogen atmosphere (balloon pressure) at room temperature for 36 h. The reaction mixture was filtered through the celite pad and further purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **4** as a white solid (83% yield, dr = 5:1).



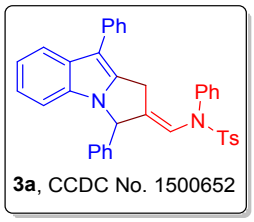
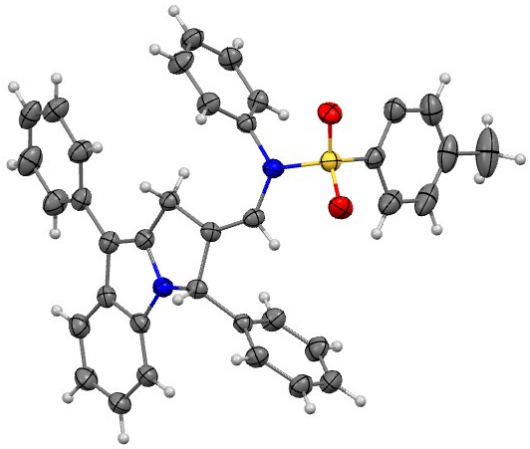
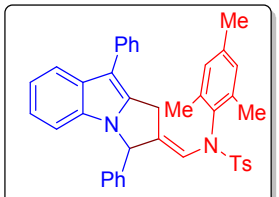
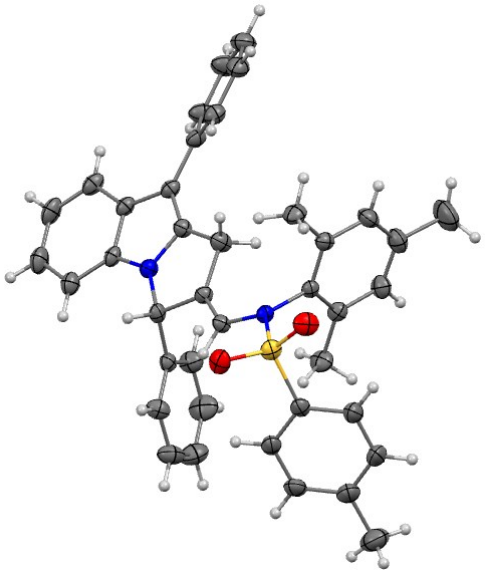
Hydrolysis of 3a: To a solution of **3a** (0.1 mmol) in ethyl acetate 5 mL, 12 M HCl (2 mL) and H_2O (0.2 mmol) were added and the mixture was stirred vigorously at room temperature for 3 h. The reaction mixture was neutralized by $NaHCO_3$ solution and extracted with ethyl acetate. The collected residue was concentrated under vacuo to the obtain residue which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford 5 as a greenish thick liquid (41% yield, dr = 9:1).

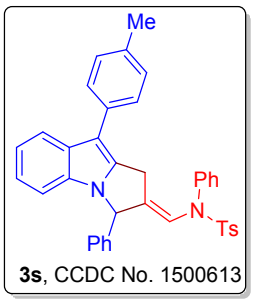
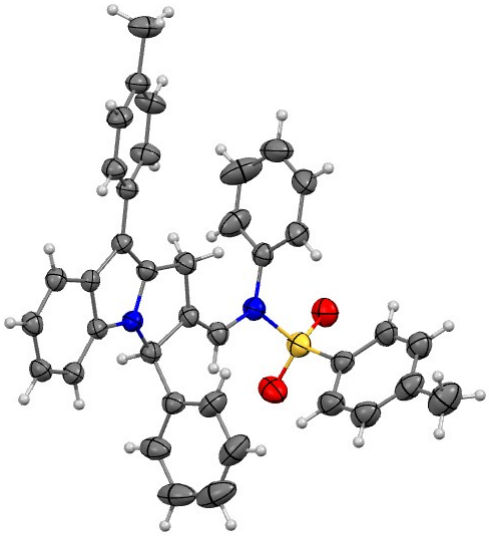


Oxidation of 3a: To a solution of **3a** (0.1 mmol) in DCM (5 mL), *m*-CPBA (0.2 mmol) was added and the mixture was stirred vigorously under nitrogen atmosphere at room temperature for 24 h. The reaction mixture was neutralized by aq. $NaHCO_3$ solution and extracted with DCM. After evaporation of solvent, the resultant residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **6** as a brown thick liquid (68% yield).



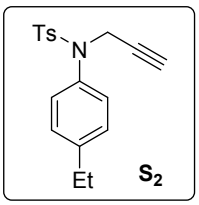
3 ORTEP diagram:

Sr. No.	Compound Structure	ORTEP Diagram
1	 **3a**, CCDC No. 1500652	
2	 **3l**, CCDC No. 1500621	

3	 **3s**, CCDC No. 1500613	

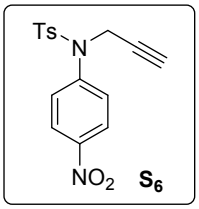
4 Characterization data:

S_2: brown solid; 495 mg, 79% yield; mp = 79 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (200 MHz, $CDCl_3$)** δ = 7.82 - 7.61 (m, 2 H), 7.46 - 7.33 (m, 2 H), 4.56 (d, *J* = 2.5 Hz, 2 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 2.56 (s, 3 H), 2.30 (t, *J* = 2.5 Hz, 1 H), 1.37 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ = 144.4, 143.5, 136.7, 135.7, 129.2, 128.4, 128.0, 41.1, 28.4, 21.5, 15.2; **HRMS (ESI)** calcd 314.1209 for $C_{18}H_{20}O_2NS$ $[M+H]^+$, found 314.1201.



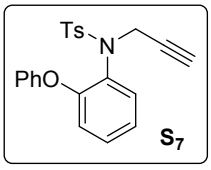
S_2

S_6: brown viscous liquid; 535 mg, 81% yield; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (200 MHz, $CDCl_3$)** δ = 8.29 - 8.04 (m, 2 H), 7.61 - 7.41 (m, 4 H), 7.23 (s, 2 H), 4.51 (d, *J* = 2.4 Hz, 2 H), 2.41 (s, 3 H), 2.25 (t, *J* = 2.5 Hz, 1 H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ = 146.1, 145.2, 144.6, 134.5, 129.6, 127.8, 126.9, 124.3, 74.8, 40.2, 21.5; **HRMS (ESI)** calcd 331.0747 for $C_{16}H_{15}O_4N_2S$ $[M+H]^+$, found 331.0735.



S_6

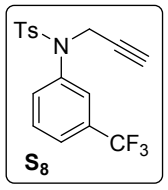
S_7: yellow solid; 641 mg, 85% yield; mp = 102 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR (200 MHz, $CDCl_3$)** δ = 7.70 - 7.59 (m, 2 H), 7.46 (dd, *J* = 1.8, 7.8 Hz, 1 H), 7.34 - 7.28 (m, 1 H), 7.26 - 7.17 (m, 3 H), 7.16 - 7.01 (m, 2 H), 6.84 - 6.60 (m, 3 H), 4.53 (d, *J* = 2.5 Hz, 2 H), 2.40 (s, 3 H), 2.19



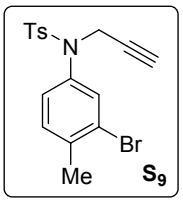
S_7

(t, *J* = 2.5 Hz, 1 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 155.6, 154.9, 143.3, 136.9, 133.3, 129.8, 129.6, 129.3, 128.0, 127.7, 123.9, 122.8, 119.4, 117.9, 73.4, 40.1, 21.5; **HRMS** (**ESI**) calcd 378.1158 for $C_{22}H_{20}O_3NS$ $[M+H]^+$, found 378.1151.

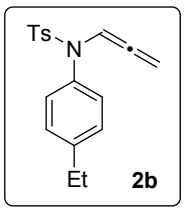
S_8: brown liquid; 583 mg, 87% yield; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 7.68 - 7.42 (m, 6 H), 7.35 - 7.20 (m, 2 H), 4.54 - 4.41 (m, 2 H), 2.45 (s, 3 H), 2.22 (br. s, 1 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 144.3, 139.9, 134.9, 131.8, 129.6, 129.4, 128.0, 125.2-125.1 (q, *J* = 3.1 Hz), 124.9-124.8 (q, *J* = 3.1 Hz), 40.8, 21.5; **HRMS** (**ESI**) calcd 376.0590 for $C_{17}H_{14}O_2NF_3NaS$ $[M+Na]^+$, found 376.0576.



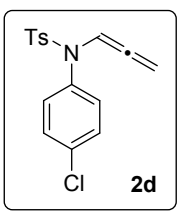
S_9: yellow solid; 620 mg, 82% yield; mp = 105 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 2.3 Hz, 1 H), 7.29 (s, 2 H), 7.19 (d, *J* = 8.4 Hz, 1 H), 7.10 (dd, *J* = 1.9, 8.0 Hz, 1 H), 4.41 (d, *J* = 2.3 Hz, 2 H), 2.45 (s, 3 H), 2.40 (s, 3 H), 2.20 (t, *J* = 2.5 Hz, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 143.9, 138.1, 137.9, 135.2, 132.0, 130.7, 129.3, 128.9, 127.2, 124.4, 74.0, 40.9, 22.5, 21.5; **HRMS** (**ESI**) calcd 378.0150 for $C_{17}H_{17}O_2NBrS$ $[M+H]^+$, found 378.0147.



2b: brown solid; 238 mg, 76% yield; mp = 78 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.66 - 7.50 (m, 2 H), 7.35 - 7.26 (m, 2 H), 7.15 - 7.06 (m, 3 H), 6.98 - 6.85 (m, 2 H), 5.03 (d, *J* = 6.3 Hz, 2 H), 2.64 (q, *J* = 7.6 Hz, 2 H), 2.45 (s, 3 H), 1.23 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 201.0, 144.7, 143.7, 135.3, 134.6, 129.4, 129.2, 128.1, 127.7, 102.4, 87.4, 28.4, 21.6, 15.1; **HRMS** (**ESI**) calcd 314.1209 for $C_{18}H_{20}O_2NS$ $[M+H]^+$, found 314.1201.

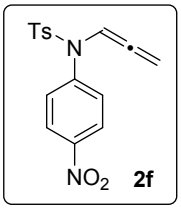


2d: white solid; 209 mg, 65% yield; mp = 96 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 7.59 - 7.51 (m, *J* = 7.9 Hz, 2 H), 7.31 - 7.23 (m, 4 H), 7.09 (t, *J* = 6.1 Hz, 1 H), 7.00 - 6.88 (m, *J* = 8.5 Hz, 2

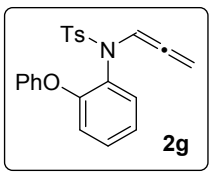


H), 5.06 (d, *J* = 6.1 Hz, 2 H), 2.45 (s, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 200.8, 144.1, 135.6, 134.9, 134.5, 130.9, 129.6, 129.0, 127.6, 102.2, 87.9, 21.6; **HRMS** (**ESI**) calcd 320.0507 for $C_{16}H_{15}O_2NClS$ $[M+H]^+$, found 320.0498.

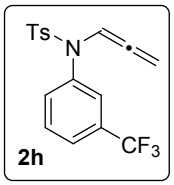
2f: yellow solid; 228 mg, 69% yield; mp = 87 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 8.27 - 8.09 (m, 2 H), 7.63 - 7.49 (m, 2 H), 7.35 - 7.22 (m, 4 H), 7.07 (t, *J* = 6.3 Hz, 1 H), 5.12 (d, *J* = 6.2 Hz, 2 H), 2.46 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 201.1, 147.0, 144.7, 143.3, 134.6, 129.8, 127.5, 124.1, 101.5, 88.1, 21.6; **HRMS** (**ESI**) calcd 331.0747 for $C_{16}H_{15}O_4N_2S$ $[M+H]^+$, found 331.0736.



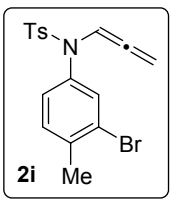
2g: yellow solid; 272 mg, 72% yield; mp = 119 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.64 (d, *J* = 8.2 Hz, 2 H), 7.24 - 7.14 (m, 5 H), 7.14 - 6.92 (m, 4 H), 6.81 - 6.66 (m, 3 H), 5.04 (d, *J* = 6.2 Hz, 2 H), 2.37 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 201.3, 155.9, 154.9, 143.6, 136.5, 132.3, 130.1, 129.4, 127.7, 127.1, 123.6, 122.8, 119.3, 118.2, 102.1, 87.5, 21.5; **HRMS** (**ESI**) calcd 378.1158 for $C_{22}H_{20}O_3NS$ $[M+H]^+$, found 378.1150.



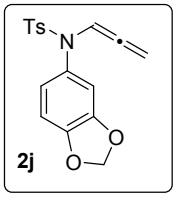
2h: brown liquid; 233 mg, 66% yield; R_f = 0.8 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.62 - 7.39 (m, 4 H), 7.26 (s, 1 H), 7.31 (s, 2 H), 7.19 - 7.02 (m, 2 H), 5.05 (d, *J* = 6.3 Hz, 2 H), 2.45 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 200.8, 144.5, 137.8, 134.7, 133.2, 131.5, 130.8, 129.7, 129.4, 127.7, 126.6-126.4 (q, *J* = 3.6 Hz), 125.4-125.2 (q, *J* = 3.3 Hz), 102.0, 88.0, 21.6; **HRMS** (**ESI**) calcd 354.0697 for $C_{17}H_{15}O_2NF_3S$ $[M+H]^+$, found 354.0689.



2i: yellow solid; 287 mg, 76% yield; mp = 108 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.62 - 7.52 (m, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.19 - 7.12 (m, 2 H), 7.06 (t, *J* = 6.3 Hz, 1 H), 6.86 (dd, *J* = 2.1, 8.1 Hz, 1 H), 5.07 (d, *J* = 6.2 Hz, 2 H), 2.46 (s, 3 H), 2.38 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 200.9, 144.1, 138.6, 135.7, 134.9, 133.1, 130.5, 129.6,

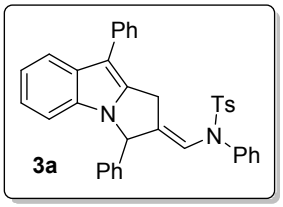


128.3, 127.7, 124.1, 102.2, 87.8, 22.6, 21.6; **HRMS** (**ESI**) calcd 378.0158 for $C_{17}H_{17}O_2NBrS$ $[M+H]^+$, found 378.0147.

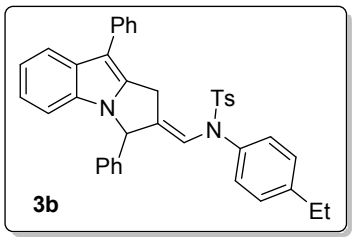


2j: Compound **2j** was found to be unstable hence carry forwarded for the next step without further purification.

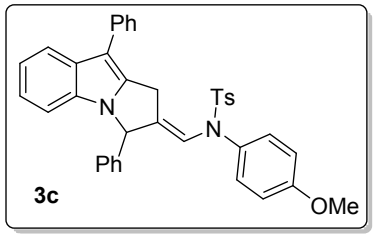
3a: white solid; 68 mg, 60% yield; mp = 157 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.85 (d, *J* = 8.2 Hz, 1 H), 7.48 (d, *J* = 7.3 Hz, 2 H), 7.43 - 7.39 (m, 5 H), 7.37 - 7.29 (m, 5 H), 7.27 - 7.17 (m, 5 H), 7.14 - 7.04 (m, 3 H), 6.99 (t, *J* = 7.6 Hz, 1 H), 6.83 (d, *J* = 7.9 Hz, 1 H), 6.54 - 6.45 (m, 1 H), 5.94 (s, 1 H), 3.47 (dd, *J* = 21.7 Hz, 38.8 Hz, 2 H), 2.41 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.0, 138.9, 136.5, 129.5, 129.2, 129.1, 128.7, 128.3, 127.5, 127.1, 126.9, 125.1, 119.6, 110.4, 108.0, 64.2, 28.4, 21.6; **HRMS** (**ESI**) calcd 589.1920 for $C_{37}H_{30}O_2N_2NaS$ $[M+Na]^+$, found 589.1922.



3b: white solid; 77 mg, 65% yield; mp = 197 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.87 (d, *J* = 8.0 Hz, 1 H), 7.51 - 7.33 (m, 8 H), 7.25 - 7.14 (m, 6 H), 7.12 - 6.91 (m, 4 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 6.49 (d, *J* = 1.8 Hz, 1 H), 5.92 (s, 1 H), 3.40 (dd, *J* = 11.1 Hz, 21.73 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 2.42 (s, 3 H), 1.27 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 143.9, 140.6, 134.3, 129.5, 129.0, 128.6, 128.5, 128.3, 127.5, 127.1, 126.9, 125.1, 120.9, 110.4, 107.9, 64.4, 28.5, 28.2, 21.5, 15.5; **HRMS** (**ESI**) calcd 595.2414 for $C_{39}H_{35}O_2N_2S$ $[M+H]^+$, found 595.2418.

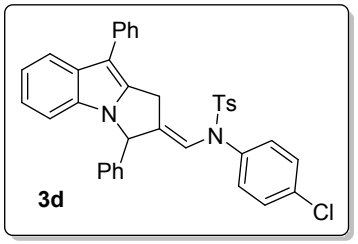


3c: yellow solid; 80 mg, 67% yield; mp = 179 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.86 (d, *J* = 8.0 Hz, 1 H), 7.61 - 7.44 (m, 4 H), 7.42 - 7.30 (m, 6 H), 7.25 - 7.15



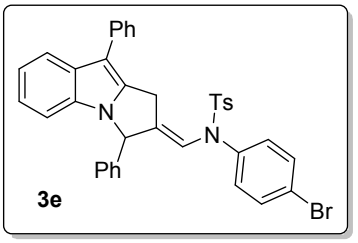
(m, 5 H), 7.11 - 7.01 (m, 1 H), 7.00 - 6.92 (m, 3 H), 6.85 - 6.73 (m, 3 H), 6.48 (d, *J* = 1.8 Hz, 1 H), 5.93 (s, 1 H), 3.83 (s, 3 H), 3.44 (dd, *J* = 9.0 Hz, 21.7 Hz, 2 H), 2.41 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 159.3, 144.0, 140.6, 134.2, 130.1, 129.5, 129.0, 128.6, 127.6, 127.3, 127.1, 126.9, 125.5, 114.4, 114.3, 110.4, 107.9, 64.3, 55.5, 28.3, 21.6; **HRMS** (**ESI**) calcd 596.2128 for $C_{38}H_{32}O_3N_2S$ $[M+H]^+$, found 596.2133.

3d: white solid; 78 mg, 65% yield; mp = 201 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.87 (d, *J* = 7.8 Hz, 1 H), 7.55 - 7.48 (m, 2 H), 7.45 (s, 1 H), 7.43 - 7.37 (m, 3 H), 7.36 - 7.24 (m, 6 H), 7.23 - 7.16 (m, 4 H), 7.09 (d, *J* = 6.9 Hz, 1 H), 7.04 - 6.95 (m, 3 H), 6.82 (d, *J* = 8.1 Hz, 1 H), 6.36 (d, *J* = 1.8 Hz, 1 H), 5.93 (s, 1 H), 3.55 (dd, *J* = 7.7 Hz, 22.4 Hz, 2 H), 2.41 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 144.3, 140.3, 138.4, 133.8, 129.6, 129.3, 129.2, 129.1, 128.7, 128.4, 127.5, 127.2, 121.1, 119.7, 110.4, 64.1, 28.5, 21.6; **HRMS** (**ESI**) calcd 601.1711 for $C_{37}H_{30}O_2N_2ClS$ $[M+H]^+$, found 601.1716.



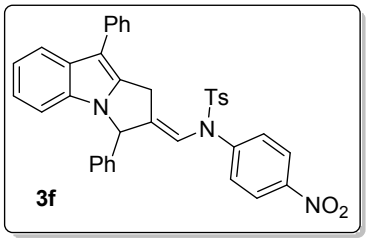
3d

3e: white solid; 90 mg, 70% yield; mp = 198 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.89 (d, *J* = 7.6 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.51 - 7.45 (m, 4 H), 7.45 - 7.40 (m, 3 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.30 - 7.28 (m, 1 H), 7.24 - 7.19 (m, 4 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 7.06 - 6.94 (m, 3 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.37 (br. s., 1 H), 5.96 (s, 1 H), 3.57 (dd, *J* = 21.4 Hz, 31.7 Hz, 2 H), 2.43 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.4, 140.3, 138.6, 132.4, 129.7, 129.5, 129.1, 128.8, 127.5, 127.2, 126.9, 125.3, 121.1, 119.7, 110.4, 108.3, 64.2, 28.5, 21.6; **HRMS** (**ESI**) calcd 645.1206 for $C_{37}H_{30}O_2N_2BrS$ $[M+H]^+$, found 645.1206.



3e

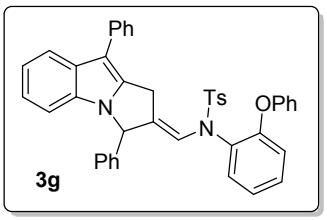
3f: yellow solid; 75 mg, 61% yield; mp = 170 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 8.13 (d, *J* = 9.1 Hz, 2 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.55 - 7.45 (m, 3 H), 7.43 - 7.37 (m, 4 H), 7.30 (d, *J* = 8.3 Hz, 3 H), 7.26 - 7.19 (m, 5 H),



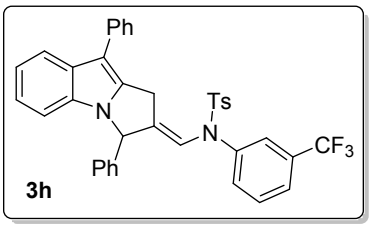
3f

7.11 - 6.95 (m, 2 H), 6.82 (d, *J* = 7.7 Hz, 1 H), 6.23 (d, *J* = 1.9 Hz, 1 H), 6.00 (s, 1 H), 3.73 - 3.60 (m, 2 H), 2.39 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 145.6, 137.5, 130.9, 129.3, 128.8, 128.7, 127.4, 126.8, 125.7, 124.7, 123.8, 119.8, 110.3, 63.9, 28.7, 21.6; **HRMS** (**ESI**) calcd 611.1873 for $C_{37}H_{29}O_4N_3S$ $[M]^+$, found 611.1873.

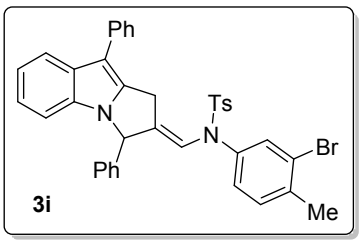
3g: white solid; 87 mg, 66% yield; mp = 95 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.87 (d, *J* = 8.0 Hz, 1 H), 7.56 - 7.49 (m, 2 H), 7.42 (d, *J* = 8.3 Hz, 5 H), 7.34 - 7.28 (m, 3 H), 7.19 (d, *J* = 8.3 Hz, 3 H), 7.13 - 7.03 (m, 7 H), 7.01 - 6.90 (m, 2 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.58 - 6.42 (m, 3 H), 5.79 (s, 1 H), 3.58 (d, *J* = 10.1 Hz, 2 H), 2.36 - 2.23 (m, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 155.1, 154.0, 143.7, 136.1, 131.9, 129.6, 129.7, 129.3, 128.9, 128.6, 127.5, 127.1, 126.8, 123.8, 119.0, 110.4, 107.9, 64.1, 28.0, 21.4; **HRMS** (**ESI**) calcd 659.2363 for $C_{43}H_{35}O_3N_2S$ (M^++ H), found 659.2366.



3h: yellow solid; 79 mg, 62% yield; mp = 153 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.84 (d, *J* = 8.0 Hz, 1 H), 7.58 - 7.50 (m, 2 H), 7.46 (d, *J* = 6.7 Hz, 3 H), 7.42 - 7.34 (m, 5 H), 7.31 (s, 3 H), 7.24 - 7.12 (m, 6 H), 7.10 - 6.92 (m, 2 H), 6.85 - 6.76 (m, 1 H), 6.31 (d, *J* = 1.8 Hz, 1 H), 5.93 (s, 1 H), 3.55 (d, *J* = 6.9 Hz, 20.7 Hz, 2 H), 2.38 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.6, 140.6, 140.3, 140.2, 138.2, 135.4, 134.1, 132.5, 131.1, 130.7, 129.9, 129.7, 129.2, 128.7, 128.6, 127.5, 127.2, 126.9, 125.3, 124.7, 124.40 - 124.2 (m, CF_3), 121.2, 120.3, 119.8, 110.4, 108.4, 64.1, 28.7, 21.6; **HRMS** (**ESI**) calcd 635.1975 for $C_{38}H_{30}O_2N_2F_3S$ (M^++ H), found 635.1972.

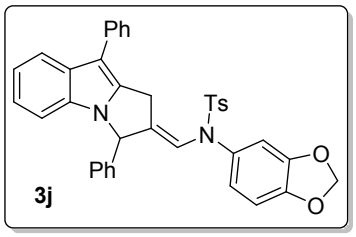


3i: white solid; 94 mg, 71% yield; mp = 159 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.86 (d, *J* = 7.6 Hz, 1 H), 7.54 (d, *J* = 7.2 Hz, 2 H), 7.48 - 7.38 (m, 5 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.27 - 7.23 (m, 1 H), 7.23 - 7.15 (m, 6 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 7.02 - 6.95 (m, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 6.41 - 6.24 (m, 1 H), 5.94 (s, 1 H), 3.58 (dd, *J* = 21.4 Hz, 42.7 Hz, 2 H), 2.41 (s, 3 H), 2.40 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.3, 139.0,

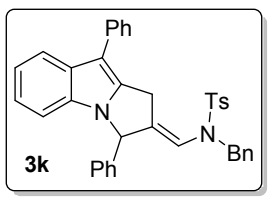


134.4, 131.4, 130.9, 129.6, 129.1, 128.7, 127.6, 127.2, 127.0, 125.2, 119.7, 110.4, 108.2, 64.2, 28.6, 22.5, 21.6; **HRMS** (**ESI**) calcd 659.1362 for $C_{38}H_{32}O_2N_2BrS$ $[M+H]^+$, found 659.1362.

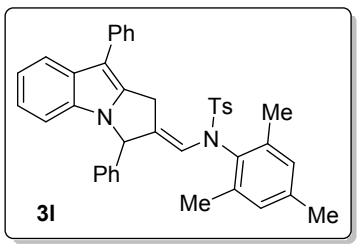
3j: white solid; 89 mg, 73% yield; mp = 136 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.87 (d, *J* = 7.8 Hz, 1 H), 7.59 - 7.49 (m, 2 H), 7.49 - 7.31 (m, 7 H), 7.26 - 7.13 (m, 5 H), 7.12 - 6.94 (m, 2 H), 6.89 - 6.66 (m, 2 H), 6.61 - 6.35 (m, 3 H), 6.00 (s, 2 H), 5.93 (s, 1 H), 3.56 (dd, *J* = 11.9 Hz, 21.1 Hz, 2 H), 2.41 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 147.5, 144.1, 139.0, 135.6, 129.6, 129.1, 128.7, 127.6, 127.2, 126.9, 125.4, 122.5, 121.0, 120.2, 110.4, 109.7, 108.0, 101.8, 64.3, 28.3, 21.6; **HRMS** (**ESI**) calcd 611.1999 for $C_{38}H_{31}O_4N_2S$ $[M+H]^+$, found 611.2018.



3k: white solid; 81 mg, 70% yield; mp = 160 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.86 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.40 - 7.28 (m, 5 H), 7.25 - 7.15 (m, 7 H), 7.11 - 7.04 (m, 3 H), 6.96 (t, *J* = 7.6 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.83 (s, 1 H), 5.23 - 5.09 (m, 1 H), 4.24 (d, *J* = 13.4 Hz, 1 H), 4.17 - 4.08 (m, 2 H), 3.93 (s, 1 H), 2.42 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 150.7, 143.8, 140.2, 135.5, 135.3, 134.1, 130.7, 129.7, 129.0, 128.7, 128.7, 128.6, 128.3, 128.1, 127.5, 127.4, 127.1, 125.3, 123.8, 121.0, 120.2, 119.7, 110.2, 108.2, 63.8, 54.6, 29.4, 21.5; **HRMS** (**ESI**) calcd 581.2184 for $C_{38}H_{33}O_2N_2S$ $[M+H]^+$, found 581.2187.

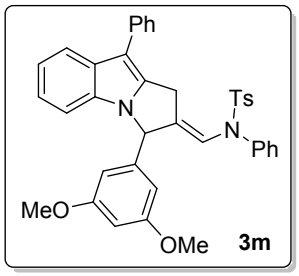


3l: white solid; 83 mg, 68% yield; mp = 215 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.94 (d, *J* = 7.8 Hz, 1 H), 7.53 (d, *J* = 8.2 Hz, 2 H), 7.47 - 7.41 (m, 6 H), 7.24 (d, *J* = 3.8 Hz, 4 H), 7.19 - 7.00 (m, 3 H), 6.95 - 6.74 (m, 3 H), 5.98 (s, 1 H), 2.97 (s, 2 H), 2.46 (s, 3 H), 2.42 (s, 3 H), 2.24 (s, 3 H), 1.67 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 143.9, 140.6,

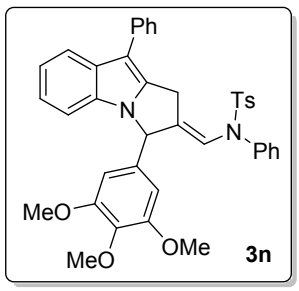


134.3, 129.5, 129.0, 128.6, 128.5, 128.3, 127.5, 127.1, 126.9, 125.1, 120.9, 110.4, 107.9, 64.4, 28.5, 28.2, 21.5, 15.5; **HRMS** (**ESI**) calcd 609.2570 for $C_{40}H_{37}O_2N_2S$ $[M+H]^+$, found 609.2581.

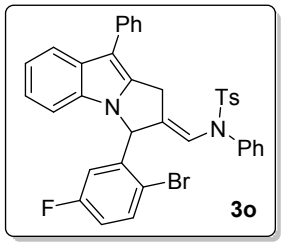
3m: white solid; 94 mg, 75% yield; mp = 151 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.77 (d, *J* = 7.7 Hz, 1 H), 7.46 - 7.35 (m, 3 H), 7.32 (d, *J* = 3.8 Hz, 2 H), 7.25 - 7.11 (m, 6 H), 7.11 - 6.96 (m, 4 H), 6.96 - 6.80 (m, 2 H), 6.47 - 6.34 (m, 2 H), 6.34 - 6.21 (m, 2 H), 5.75 (s, 1 H), 3.69 (s, 6 H), 3.40 (dd, *J* = 9.7 Hz, 21.8 Hz, 2 H), 2.33 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 161.3, 144.0, 142.8, 138.8, 136.6, 129.6, 129.1, 128.7, 128.23, 127.6, 127.2, 125.1, 121.1, 120.2, 119.6, 110.5, 105.1, 100.0, 64.3, 55.4, 28.4, 21.6; **HRMS** (**ESI**) calcd 627.2312 for $C_{39}H_{35}O_4N_2S$ $[M+H]^+$, found 627.2319.



3n: white solid; 100 mg, 76% yield; mp = 139 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.86 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.8 Hz, 3 H), 7.37 - 7.32 (m, 5 H), 7.27 - 7.19 (m, 5 H), 7.14 - 7.01 (m, 5 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 6.45 (s, 2 H), 5.81 (s, 1 H), 3.92 (s, 3 H), 3.81 (s, 6 H), 3.52 (dd, *J* = 21.36 Hz, 45.01 Hz, 2 H), 2.41 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 153.7, 144.2, 138.7, 137.2, 129.5, 129.1, 128.7, 128.2, 128.0, 127.5, 127.1, 125.2, 120.2, 119.7, 110.4, 108.2, 104.2, 64.5, 60.9, 56.2, 28.5, 21.5; **HRMS** (**ESI**) calcd 657.2418 for $C_{40}H_{37}O_5N_2S$ $[M+H]^+$, found 657.2415.

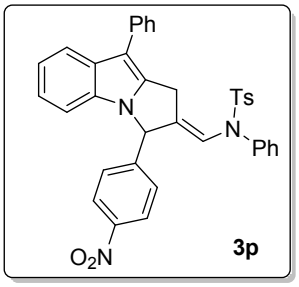


3o: white solid; 80 mg, 60% yield; mp = 179 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.88 (d, *J* = 7.63 Hz, 1 H), 7.71 (dd, *J* = 5.0 Hz, 8.41 Hz, 1 H), 7.49 - 7.46 (m, 2 H), 7.46 - 7.40 (m, 4 H), 7.36 (dd, *J* = 1.53 Hz, 5.0 Hz, 3 H), 7.29 (s, 1 H), 7.25 (d, *J* = 7.62 Hz, 3 H), 7.17 - 7.12 (m, 1 H), 7.11 - 7.03 (m, 3 H), 7.02 - 6.95 (m, 1 H), 6.86 - 6.77 (m, 2 H), 6.50 (br. s., 1 H), 3.37 (dd, *J* = 21.74 Hz, 24.41 Hz, 2 H) 2.44 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.3, 138.6,

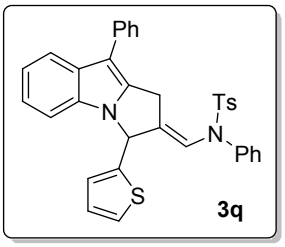


135.2, 134.6, 132.5, 132.0, 130.8, 129.6, 129.2, 128.7, 128.7, 128.3, 127.6, 127.2, 125.3-125.1 (d, *J* = 34.3 Hz), 121.4, 120.5, 119.9, 117.5-117.3 (d, *J* = 22.8 Hz), 116.3 (d, *J* = 2.9 Hz), 110.2, 108.6, 28.2, 21.6; **HRMS** (**ESI**) calcd 663.1112 for $C_{37}H_{29}O_2N_2BrFS$ $[M+H]^+$, found 663.1113.

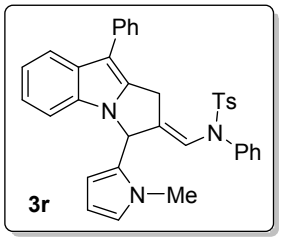
3p: white solid; 77 mg, 63% yield; mp = 95 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 8.19 (d, *J* = 7.3 Hz, 2 H), 7.80 (d, *J* = 8.2 Hz, 1 H), 7.59 (d, *J* = 7.3 Hz, 1 H), 7.43 - 7.27 (m, 9 H), 7.22 - 7.11 (m, 4 H), 7.10 - 6.91 (m, 4 H), 6.79 - 6.63 (m, 2 H), 6.56 - 6.42 (m, 1 H), 6.01 - 5.98 (m, 1 H), 3.37 - 3.25 (m, 1 H), 2.35 (s, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 147.9, 147.8, 144.5, 138.5, 129.6, 129.3, 128.8, 128.73, 128.42, 127.6, 127.5, 126.00, 124.5, 121.5, 110.0, 108.7, 63.3, 61.8, 30.4, 28.2, 21.6; **HRMS** (**ESI**) calcd 612.1952 for $C_{37}H_{30}O_4N_3S$ $[M+H]^+$, found 612.1949.



3q: brown solid; 82 mg, 72% yield; mp = 60 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.78 (d, *J* = 6.7 Hz, 1 H), 7.43 - 7.32 (m, 6 H), 7.29 (d, *J* = 3.2 Hz, 3 H), 7.22 - 7.09 (m, 5 H), 7.09 - 6.94 (m, 6 H), 6.66 (d, *J* = 1.8 Hz, 1 H), 6.20 (s, 1 H), 3.40 - 3.17 (m, 2 H), 2.36 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 144.2, 134.8, 129.6, 129.2, 128.7, 128.6, 128.1, 127.5, 127.2, 126.7, 125.2, 119.7, 110.2, 108.3, 59.7, 27.8, 21.6; **HRMS** (**ESI**) calcd 573.1665 for $C_{35}H_{29}O_2N_2S$ $[M+H]^+$, found 573.1668.

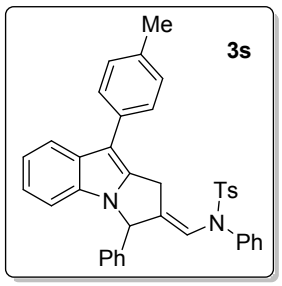


3r: yellow solid; 80mg, 70% yield; mp = 197 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.85 (d, *J* = 7.7 Hz, 1 H), 7.55 - 7.40 (m, 4 H), 7.40 - 7.30 (m, 5 H), 7.27 - 7.18 (m, 3 H), 7.17 - 6.91 (m, 6 H), 6.62 (s, 1 H), 6.50 (dd, *J* = 1.8, 3.4 Hz, 1 H), 6.33 (d, *J* = 2.1 Hz, 1 H), 6.23 - 6.04 (m, 2 H), 3.59 (dd, *J* = 21.9 Hz, 39.1 Hz, 1 H), 2.96 (s, 3 H), 2.42 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 144.2, 135.9, 135.5, 129.6, 129.2, 128.7, 128.4, 127.71, 127.43, 127.20, 125.3, 121.3, 119.6,

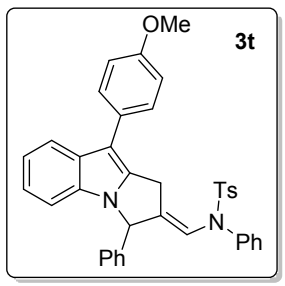


112.2, 110.2, 106.7, 58.3, 34.0, 28.6, 21.6; **HRMS** (**ESI**) calcd 570.2210 for $C_{36}H_{32}O_2N_3S$ $[M+H]^+$, found 570.2211.

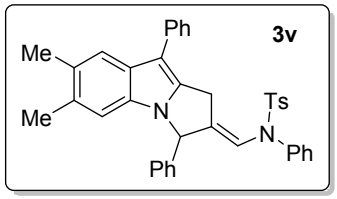
3s: yellow solid; 75 mg, 65% yield; mp = 156 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.83 (d, *J* = 8.0 Hz, 1 H), 7.43 - 7.36 (m, 5 H), 7.35 - 7.30 (m, 5 H), 7.24 - 7.19 (m, 4 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.10 - 7.04 (m, 3 H), 6.98 (t, *J* = 7.4 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 6.45 (br. s., 1 H), 5.93 (s, 1 H), 3.45 (dd, *J* = 21.7 Hz, 37.4 Hz, 2 H), 2.40 (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.0, 140.5, 139.2, 138.6, 136.7, 134.8, 134.7, 132.5, 132.4, 130.8, 129.5, 129.4, 129.2, 129.1, 128.3, 128.0, 127.5, 127.1, 127.0, 125.2, 120.9, 120.0, 119.7, 110.3, 108.0, 64.3, 28.3, 21.6, 21.1; **HRMS** (**ESI**) calcd 581.2257 for $C_{38}H_{33}O_2N_2S$ $[M+H]^+$, found 581.2247.



3t: white solid; 81 mg, 68% yield; mp = 154 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.48 - 7.44 (m, 1 H), 7.35 - 7.32 (m, 4 H), 7.32 - 7.31 (m, 3 H), 7.30 - 7.28 (m, 3 H), 7.25 (d, *J* = 7.6 Hz, 3 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.09 - 7.02 (m, 3 H), 6.95 (d, *J* = 7.6 Hz, 4 H), 6.85 (d, *J* = 13.7 Hz, 1 H), 6.33 (s, 1 H), 3.86 (s, 3 H), 3.38 (dd, *J* = 6.6 Hz, 7.3 Hz, 2 H), 2.43 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 159.7, 143.5, 139.5, 138.8, 137.1, 135.7, 135.0, 131.7, 130.0, 129.7, 129.5, 129.3, 128.7, 128.3, 127.9, 127.4, 126.1, 123.7, 121.6, 119.8, 118.9, 114.0, 113.8, 112.0, 111.4, 85.4, 63.4, 55.3, 25.0, 21.6, 14.8; **HRMS** (**ESI**) calcd 597.2206 for $C_{38}H_{33}O_3N_2S$ $[M+H]^+$, found 597.2208.

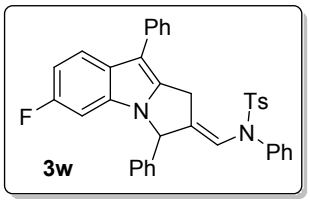


3v: white solid; 80 mg, 67% yield; mp = 154 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.65 (s, 1 H), 7.55 - 7.46 (m, 3 H), 7.45 - 7.39 (m, 4 H), 7.32 (d, *J* = 6.6 Hz, 6 H), 7.25 - 7.16 (m, 4 H), 7.11 (br. s., 2 H), 6.63 (s, 1 H), 6.47 (br. s., 1 H), 5.91 (s, 1 H), 3.46 (d, *J* = 6.6 Hz, 2 H), 2.43 (s, 3 H), 2.34 (s, 3 H), 2.24 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 144.0, 138.1, 137.1, 129.5, 129.1,

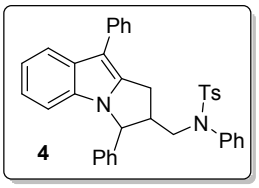


129.0, 128.6, 128.3, 127.5, 127.1, 126.8, 124.9, 119.9,110.8, 107.4, 84.1, 30.9, 28.3, 21.5, 20.3, 20.2; **HRMS** (**ESI**) calcd 595.2414 for $C_{39}H_{35}O_2N_2S$ $[M+H]^+$, found 595.2414.

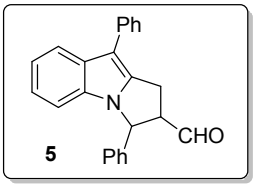
3w: white solid; 82 mg, 70% yield; mp = 175 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 90/10); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 7.74 (dd, *J* = 5.2, 8.8 Hz, 1 H), 7.43 (d, *J* = 5.4 Hz, 7 H), 7.36 - 7.28 (m, 5 H), 7.26 - 7.13 (m, 5 H), 7.12 - 7.01 (m, 2 H), 6.91 - 6.76 (m, 1 H), 6.56 - 6.36 (m, 2 H), 5.88 (s, 1 H), 3.45 (dd, *J* = 10.0 Hz, 21.38 Hz, 2 H), 2.40 (s, 3 H); **^{13}C NMR** (**50 MHz**, **$CDCl_3$**) δ = 161.3-156.5 (d, *J* = 237.9 Hz), 144.1, 139.9, 139.1, 139.0, 136.2, 135.1, 134.6, 132.2, 129.5, 129.2, 128.7, 128.6, 128.6, 128.4, 128.0, 127.5, 127.1, 127.0, 125.4 (d, *J* = 2.6 Hz), 120.4, 120.2, 108.8-108.2 (d, *J* = 30.7 Hz), 108.3, 97.1, 96.6, 64.3, 28.3, 21.5; **HRMS** (**ESI**) calcd 585.2007 for $C_{37}H_{30}O_2N_2FS$ $[M+H]^+$, found 585.2004.



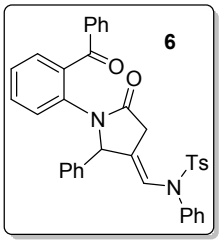
4: brown solid; 37 mg, 65% yield in total (5:1 d.r.); mp = 158 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 90/10); Major diastereomer: **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.89 (d, *J* = 8.0 Hz, 1 H), 7.76 - 7.58 (m, 2 H), 7.55 - 7.37 (m, 3 H), 7.35 - 7.25 (m, 8 H), 7.25 - 7.14 (m, 3 H), 7.12 - 7.08 (m, 1 H), 7.08 - 7.02 (m, 2 H), 7.02 - 6.88 (m, 3 H), 5.34 (d, *J* = 4.3 Hz, 1 H), 3.42 - 3.18 (m, 4 H), 2.42 (s, 3 H), 0.93 - 0.84 (m, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 143.6, 140.0, 138.9, 136.7, 135.8, 134.4, 132.3, 130.5, 129.3, 129.3, 128.9, 128.8, 128.5, 128.3, 128.3, 127.7, 127.5, 126.8, 125.2, 121.1, 120.0, 119.6, 110.1, 61.6, 51.9, 45.3, 28.7, 21.5; **HRMS** (**ESI**) calcd 569.2184 for $C_{37}H_{33}O_2N_2S$ $[M+H]^+$, found 569.2180.



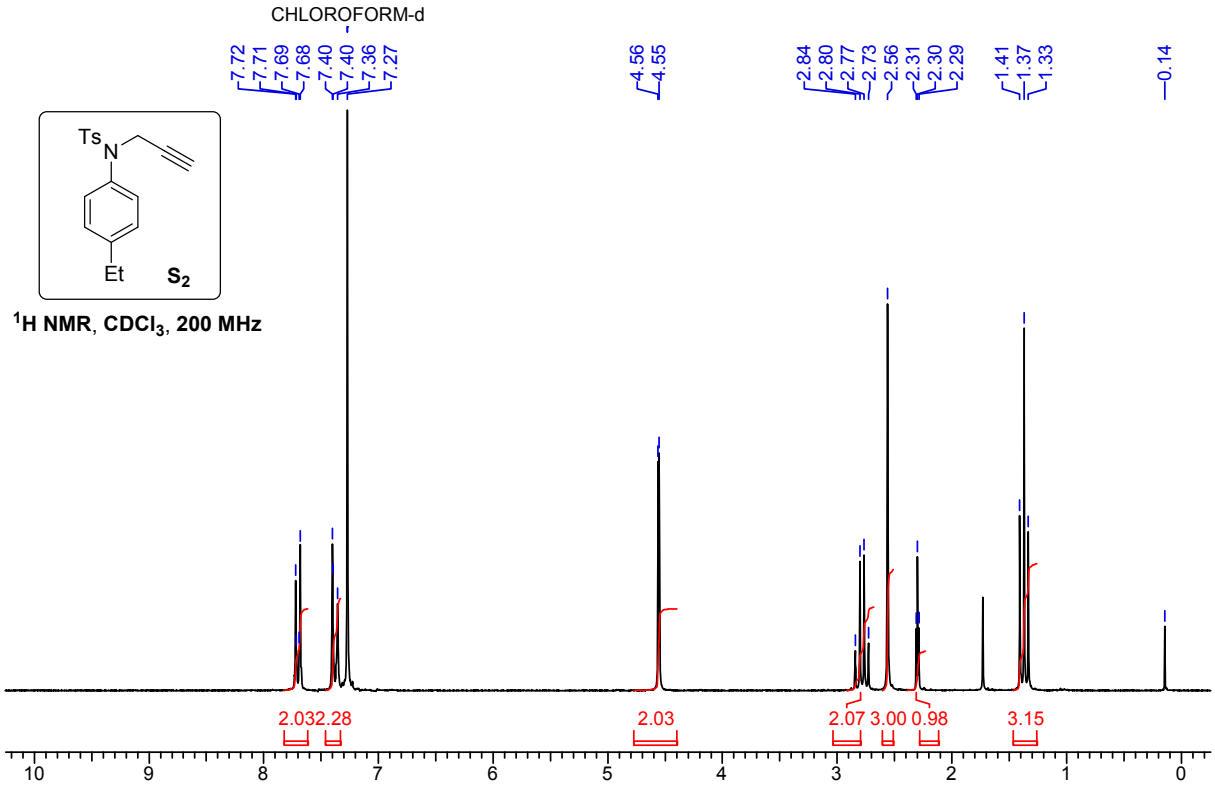
5: greenish thick liquid; 14 mg, 41% yield in total (9:1 d.r.); R_f = 0.3 (petroleum ether/ethyl acetate = 90/10); Major diastereomer: **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.91 (s, 1 H), 7.90 (d, *J* = 7.9 Hz, 1 H), 7.68 (d, *J* = 7.3 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.40 - 7.33 (m, 4 H), 7.19 - 7.13 (m, 3 H), 7.07 - 7.03 (m, 1 H), 6.87 (d, *J* = 7.9 Hz, 1 H), 5.91 (d, *J* = 4.3 Hz, 1 H), 3.73 - 3.69 (m, 1 H), 3.66 - 3.62 (m, 1 H), 3.61 - 3.54 (m, 1 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 198.7, 139.4, 138.6, 135.4, 132.6, 129.2, 128.8, 128.4, 127.5, 126.2, 125.5, 121.4, 120.3, 119.8, 110.5, 77.3, 76.7, 63.4, 60.0, 24.7; **HRMS** (**ESI**) calcd 337.1467 for $C_{24}H_{19}NO$ $[M+H]^+$, found 337.1465.



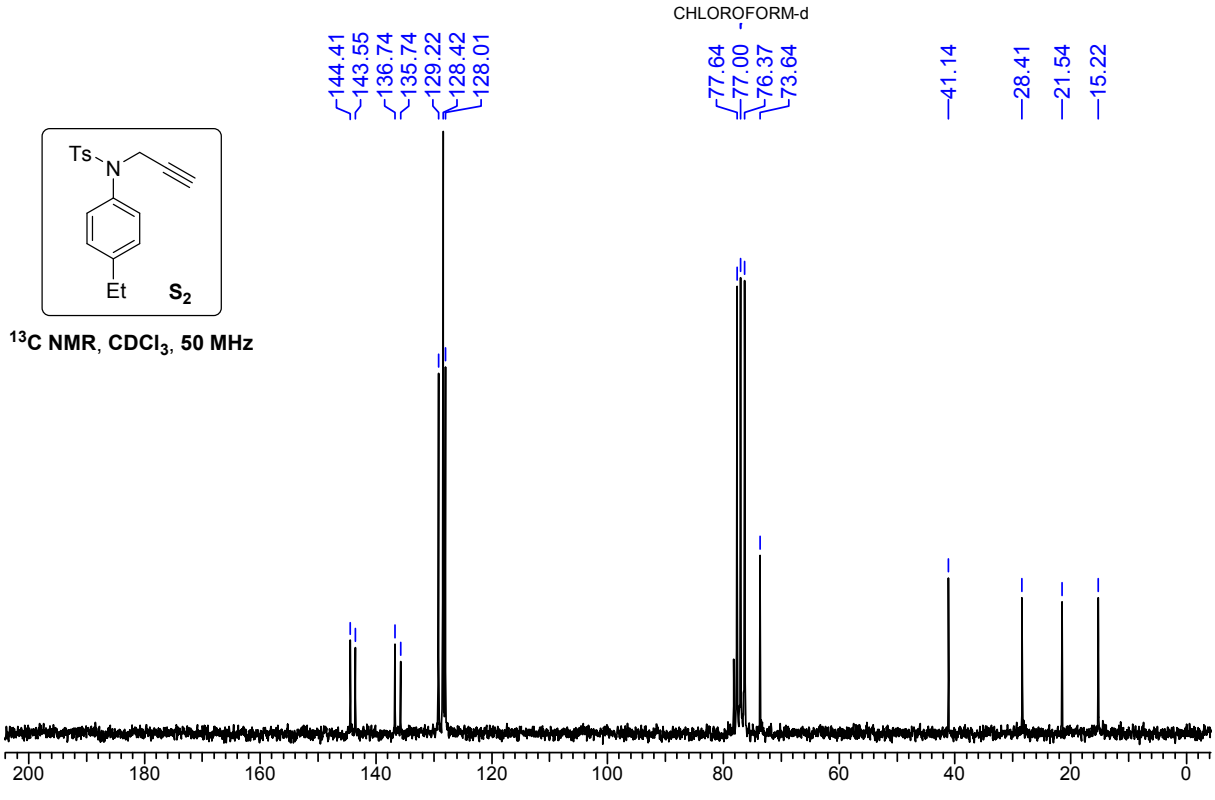
6: brown thick liquid; 41 mg, 68% yield; R_f = 0.3 (petroleum ether/ethyl acetate = 80/20); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.77 (d, *J* = 7.2 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 3 H), 7.37 - 7.31 (m, 5 H), 7.30 - 7.27 (m, 6 H), 7.25 - 7.19 (m, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.94 (dd, *J* = 2.7, 6.5 Hz, 2 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 6.37 - 6.32 (m, 1 H), 5.55 (s, 1 H), 2.53 (d , *J* = 22.23 Hz, 1 H), 2.41 (s, 3 H), 2.24 (d, *J* = 22.13 Hz, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 196.1, 172.1, 144.0, 139.9, 138.1, 137.0, 136.1, 135.3, 135.0, 133.0, 131.2, 130.1, 130.0, 129.5, 129.2, 128.9, 128.8, 128.5, 128.4, 128.2, 128.2, 127.7, 127.4, 126.6, 125.4, 122.6, 77.3, 76.7, 69.5, 34.3, 21.6; **HRMS** (**ESI**) calcd 599.1999 for $C_{37}H_{30}N_2O_4S$ $[M+H]^+$, found 599.2000.



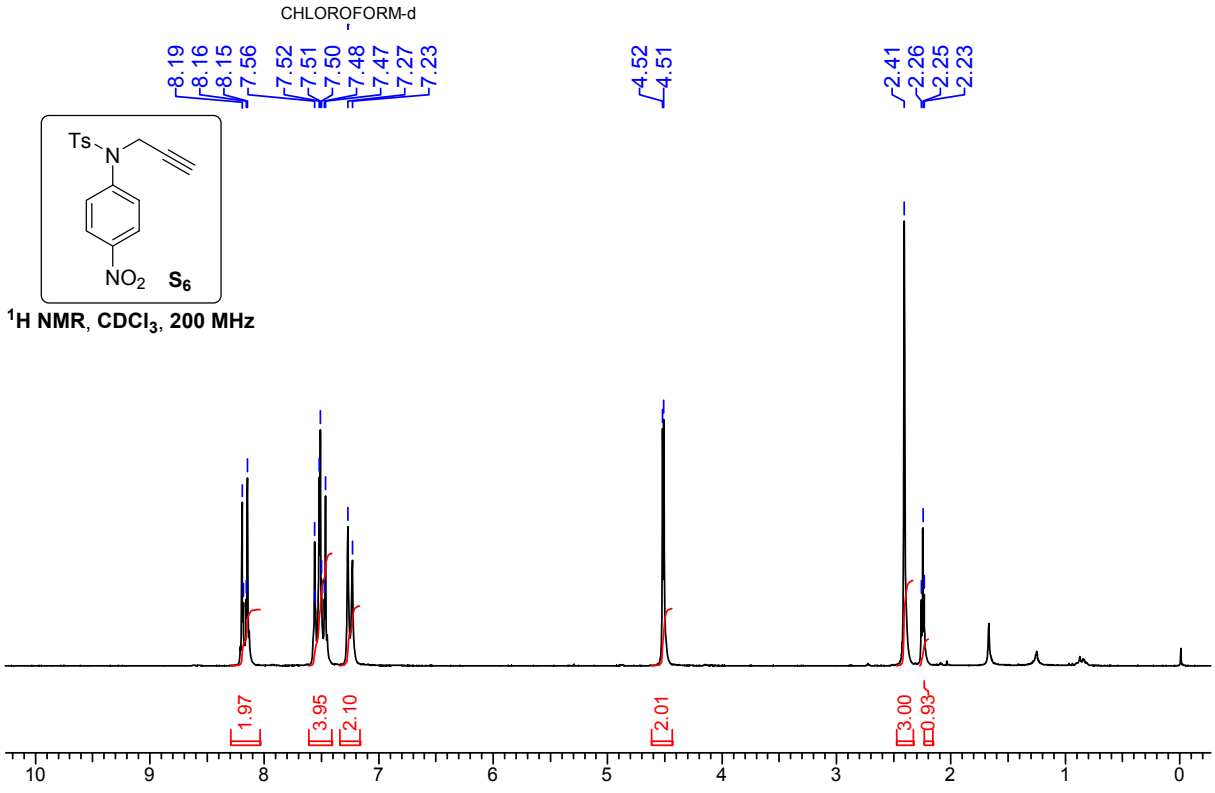
5 Spectral data:



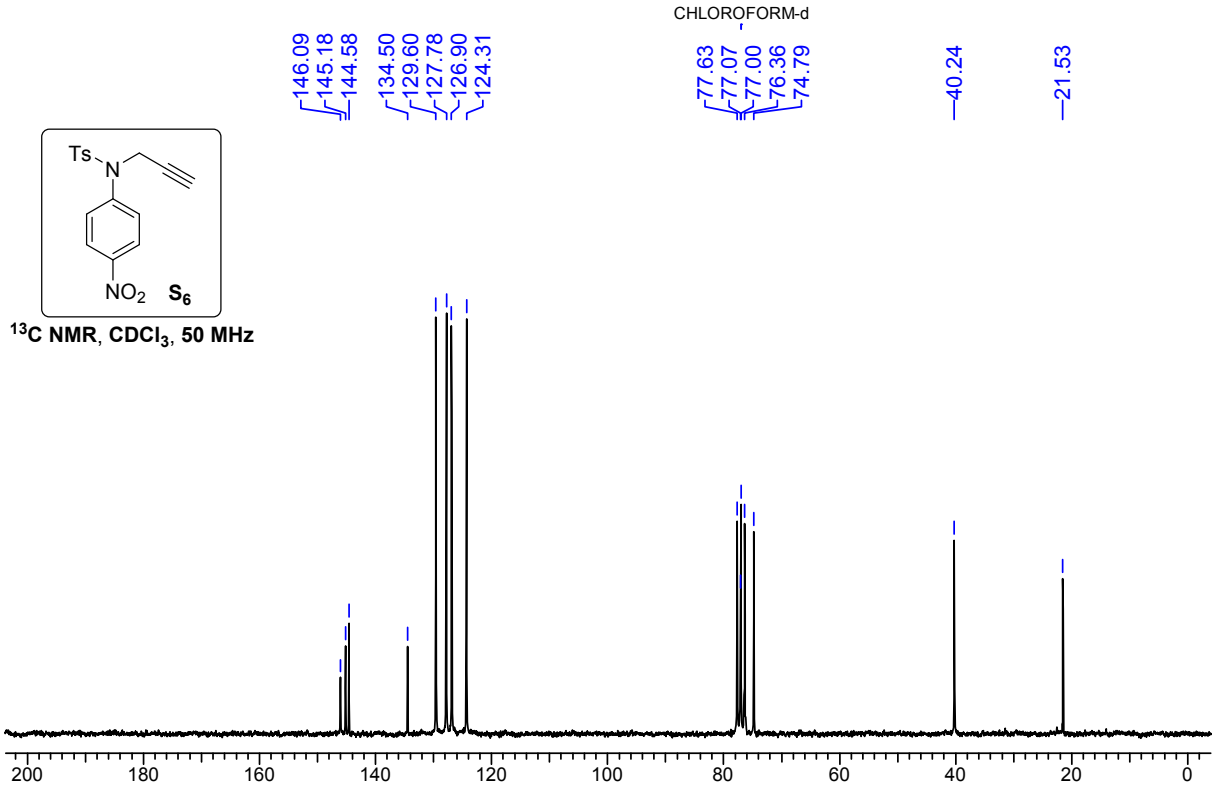
^{1}H NMR, $CDCl_3$, 200 MHz



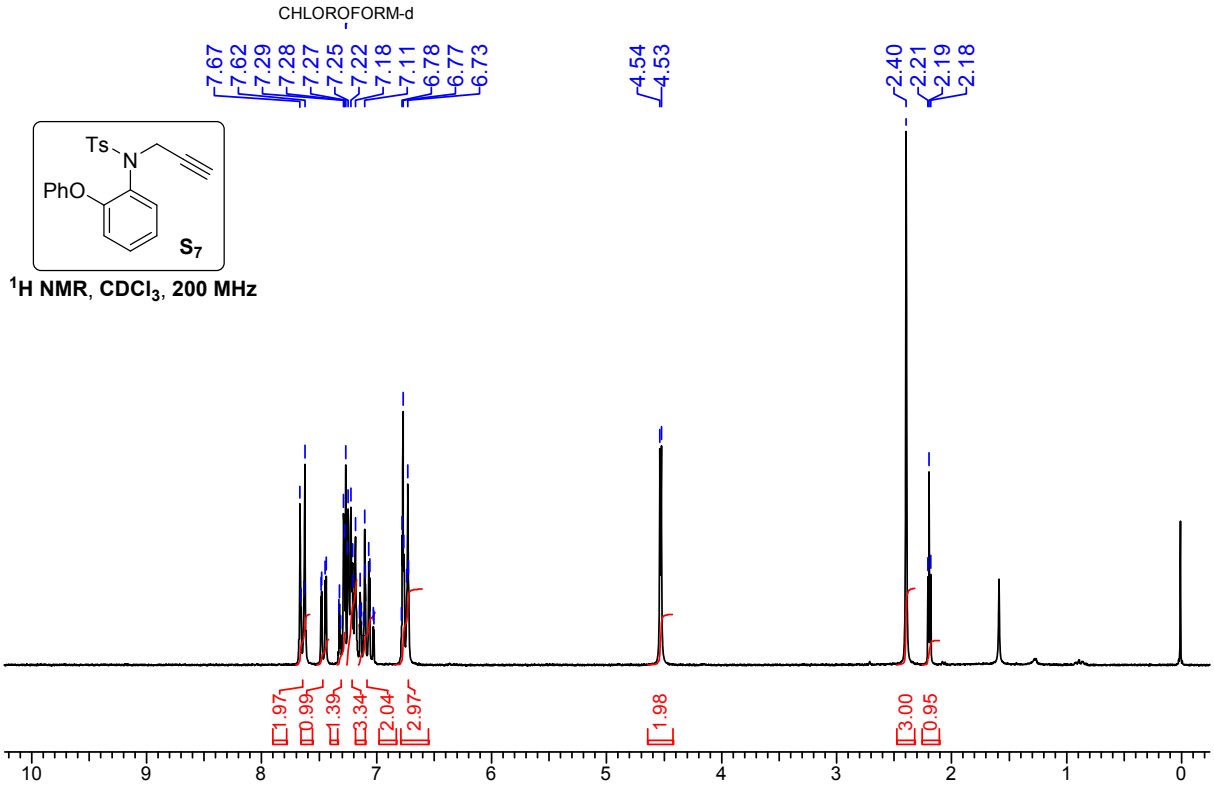
^{13}C NMR, $CDCl_3$, 50 MHz



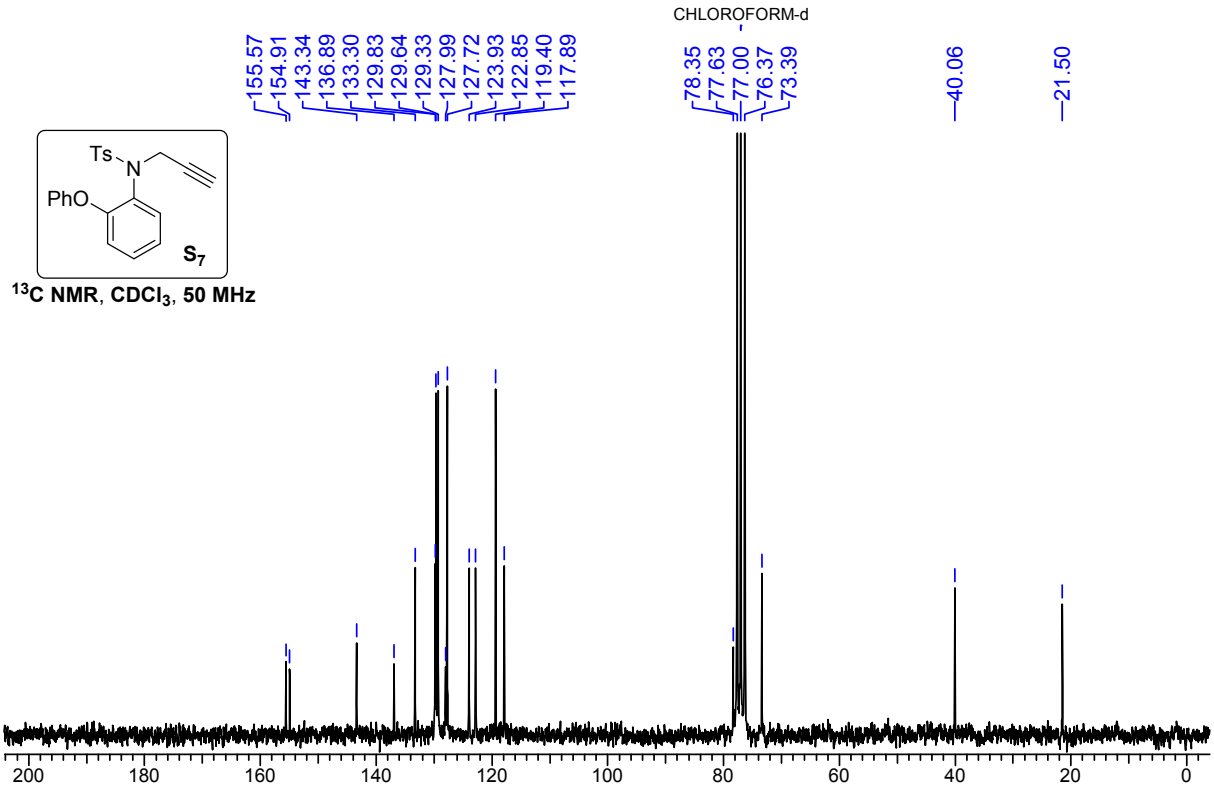
^{1}H NMR, $CDCl_3$, 200 MHz



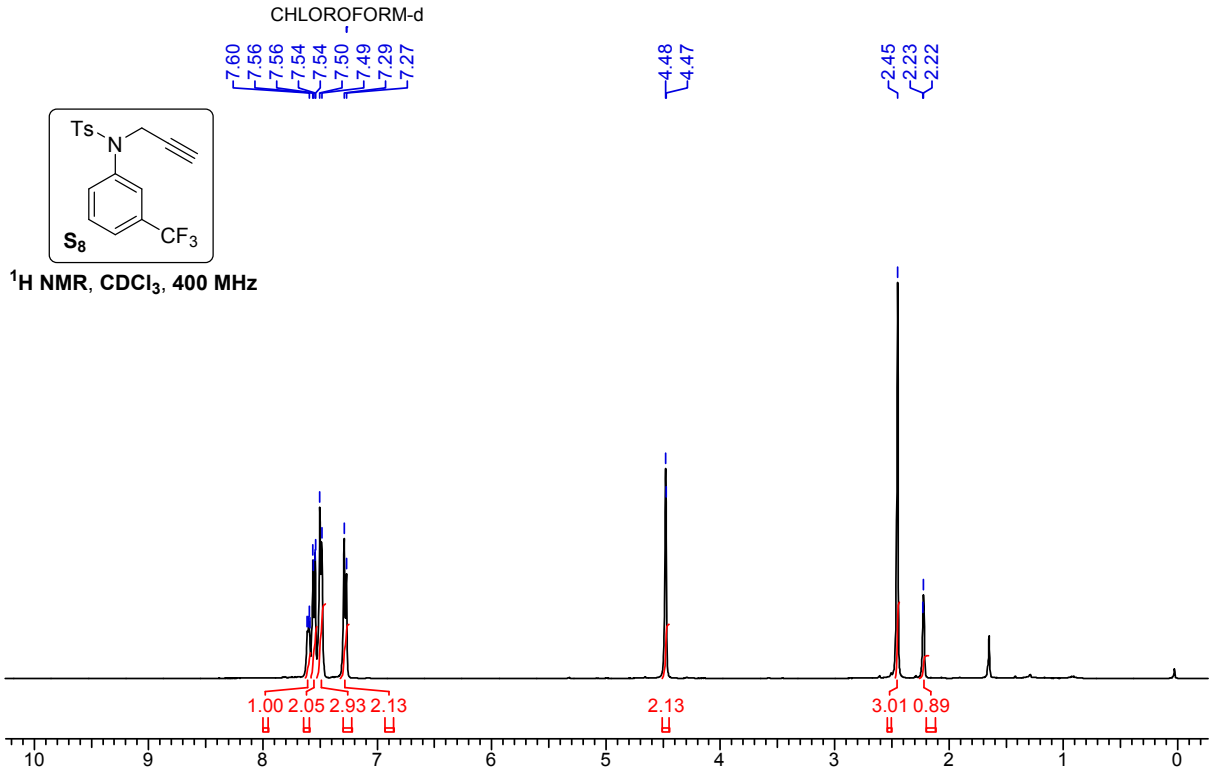
^{13}C NMR, $CDCl_3$, 50 MHz



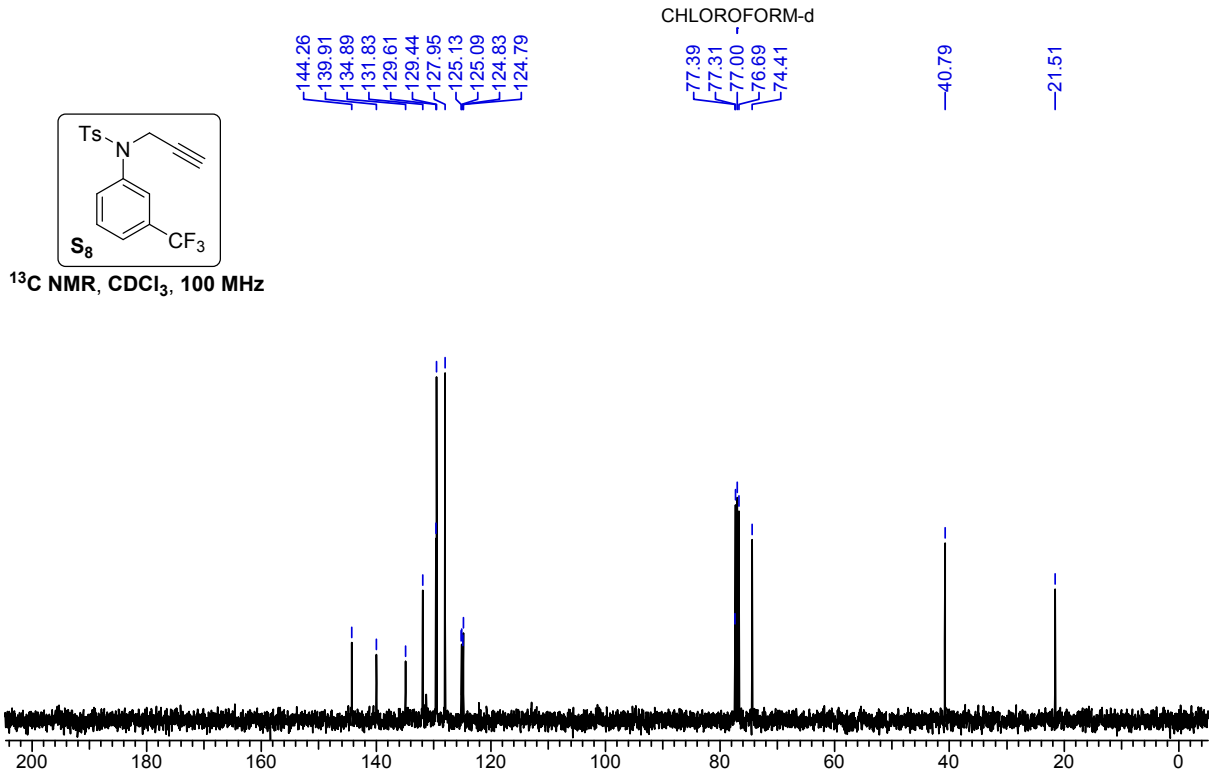
^{1}H NMR, $CDCl_3$, 200 MHz



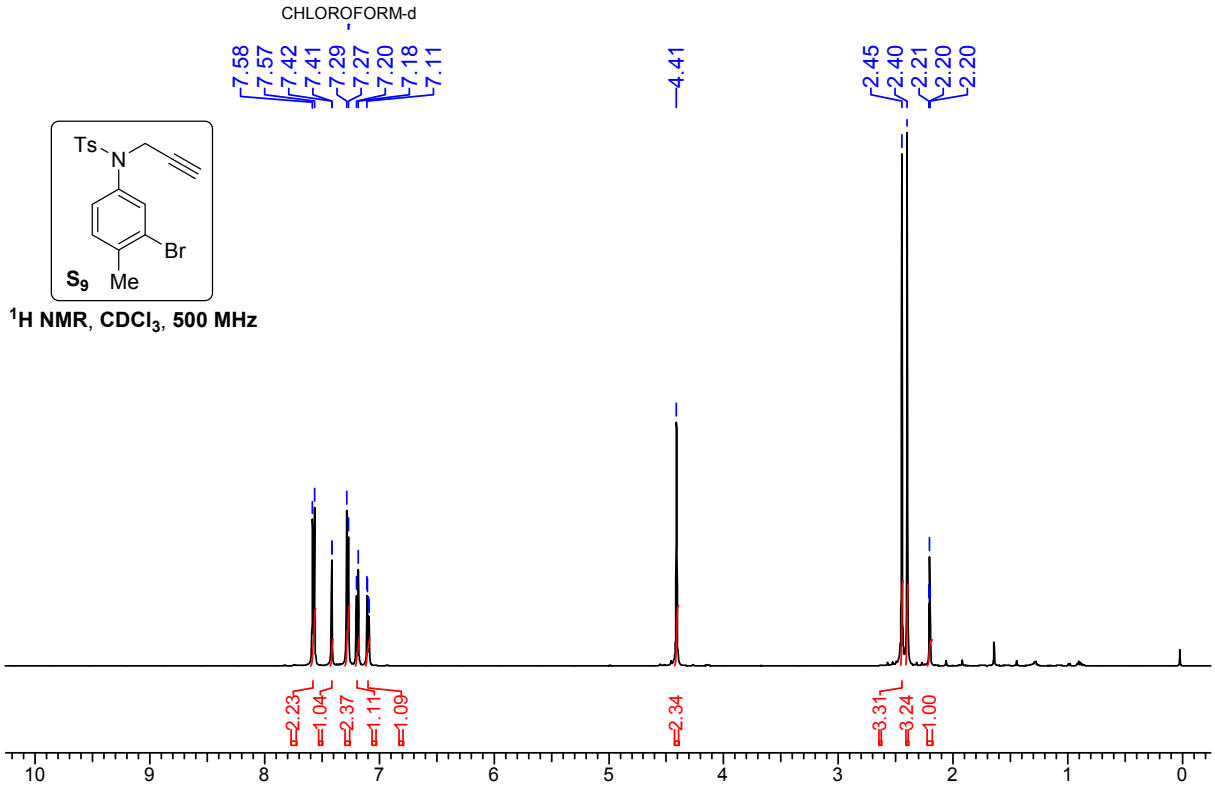
^{13}C NMR, $CDCl_3$, 50 MHz



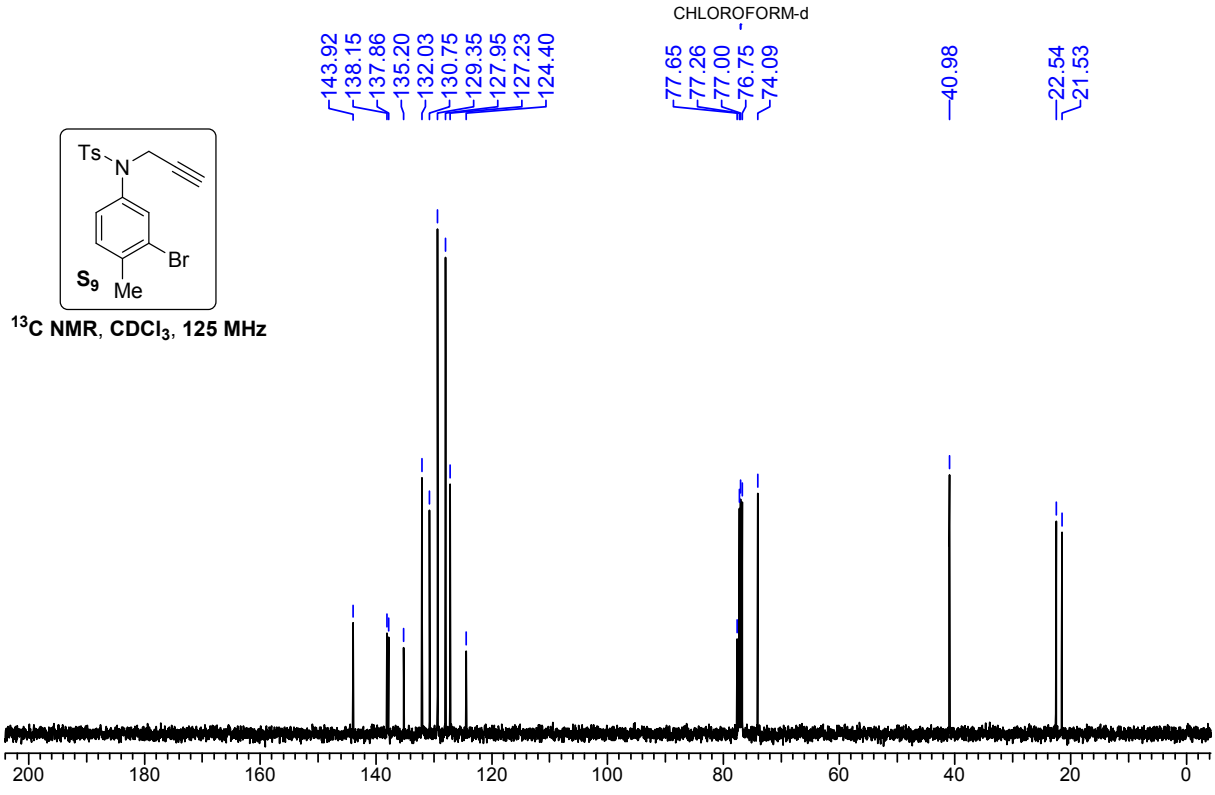
^{1}H NMR, $CDCl_3$, 400 MHz



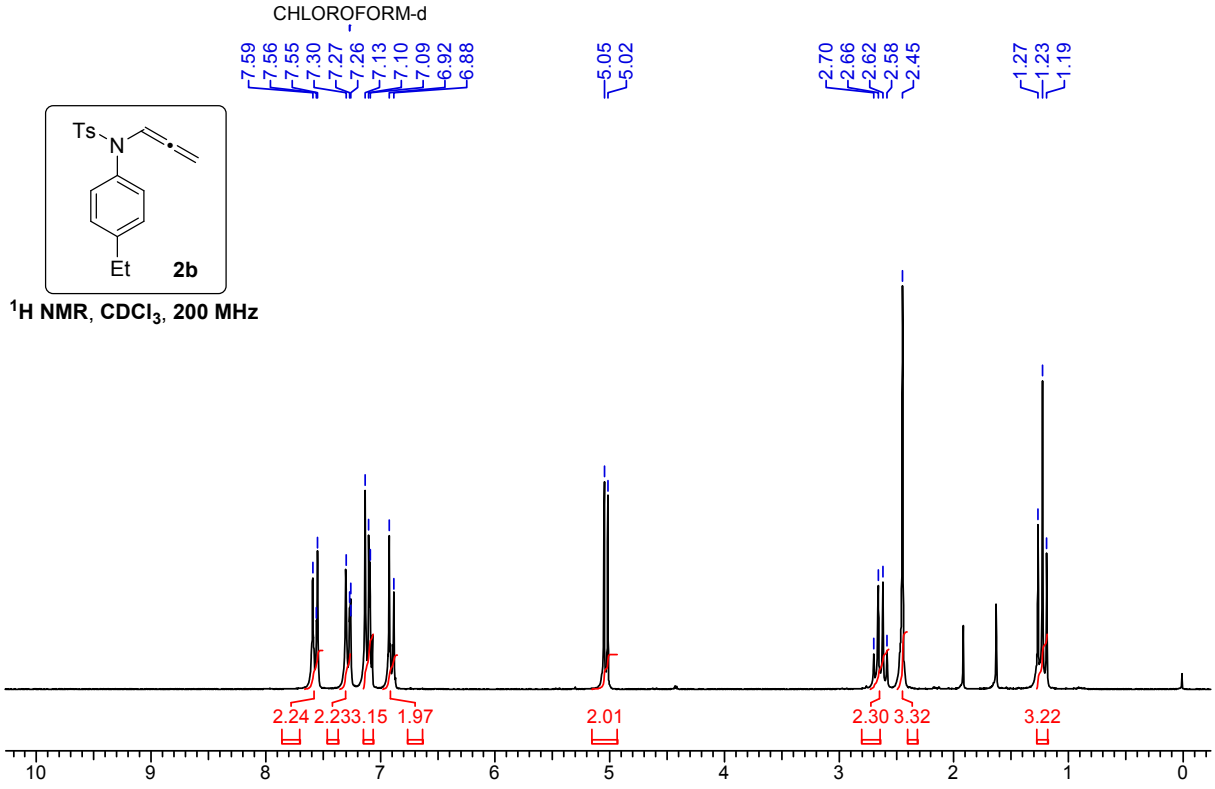
^{13}C NMR, $CDCl_3$, 100 MHz



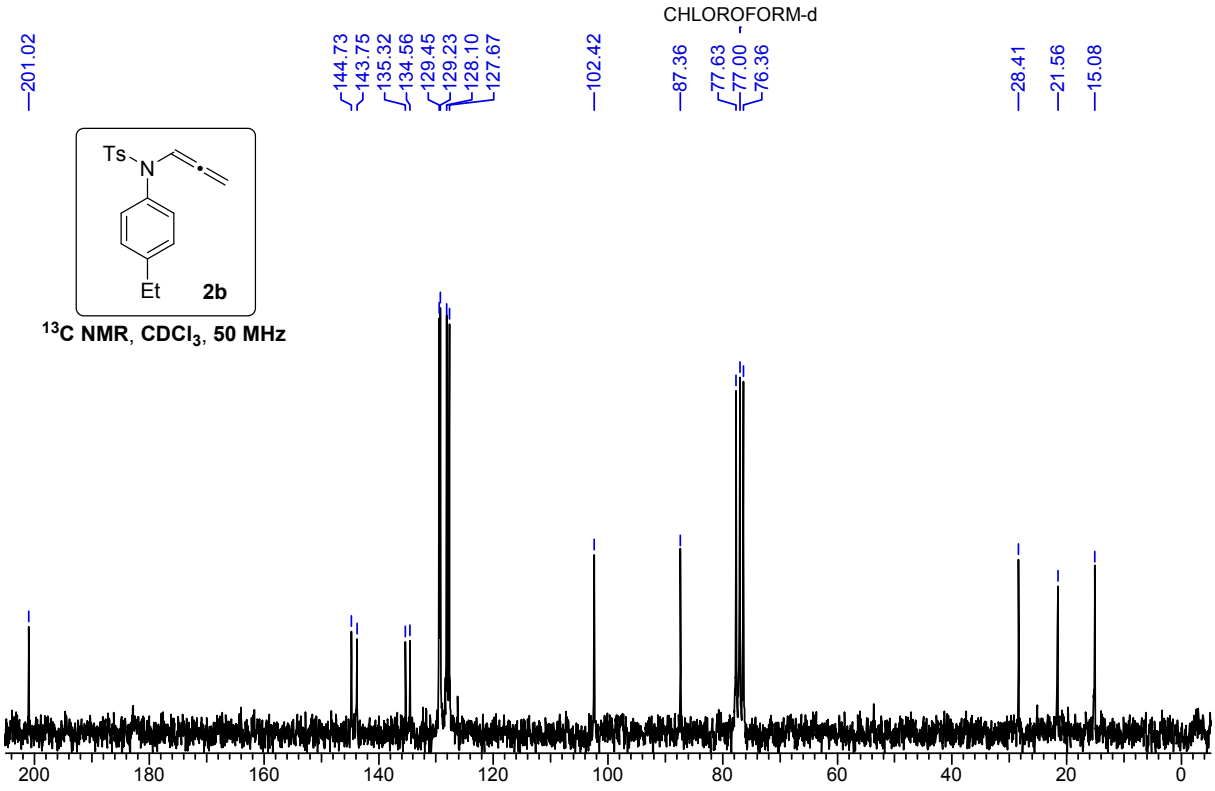
^{1}H NMR, $CDCl_3$, 500 MHz



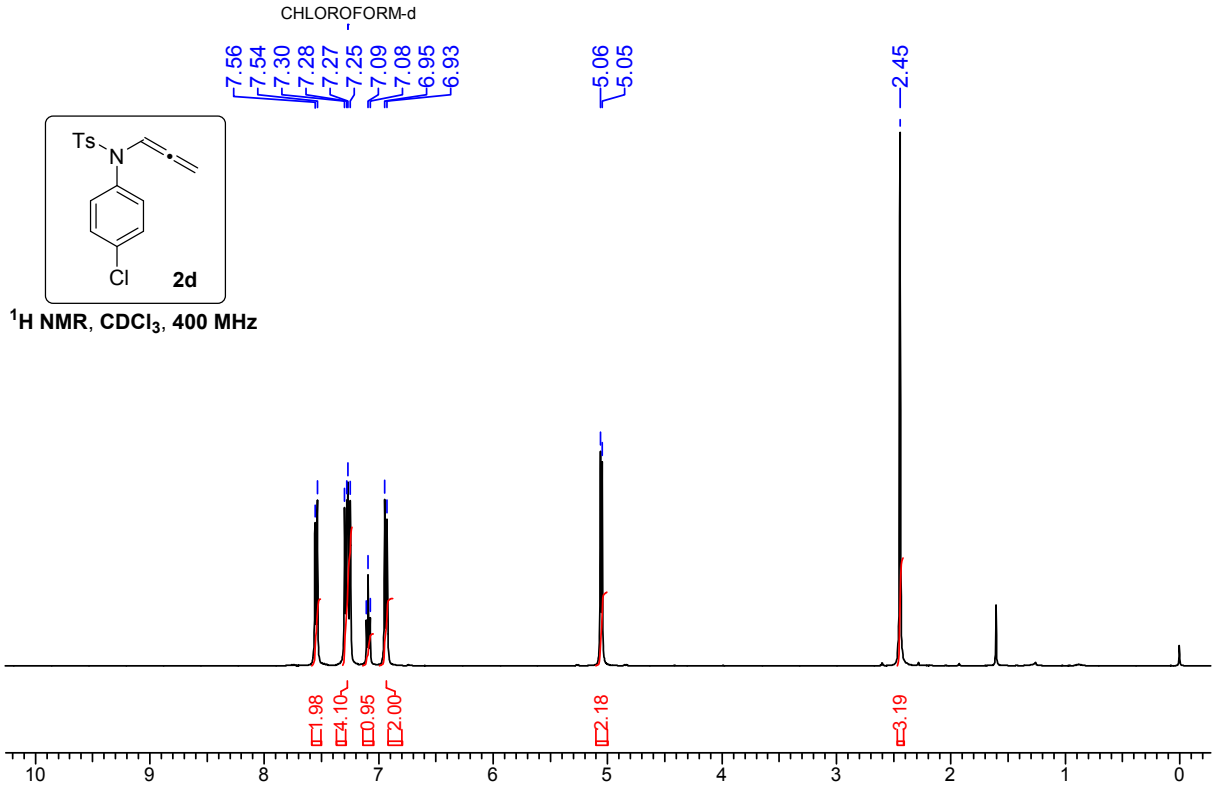
^{13}C NMR, $CDCl_3$, 125 MHz



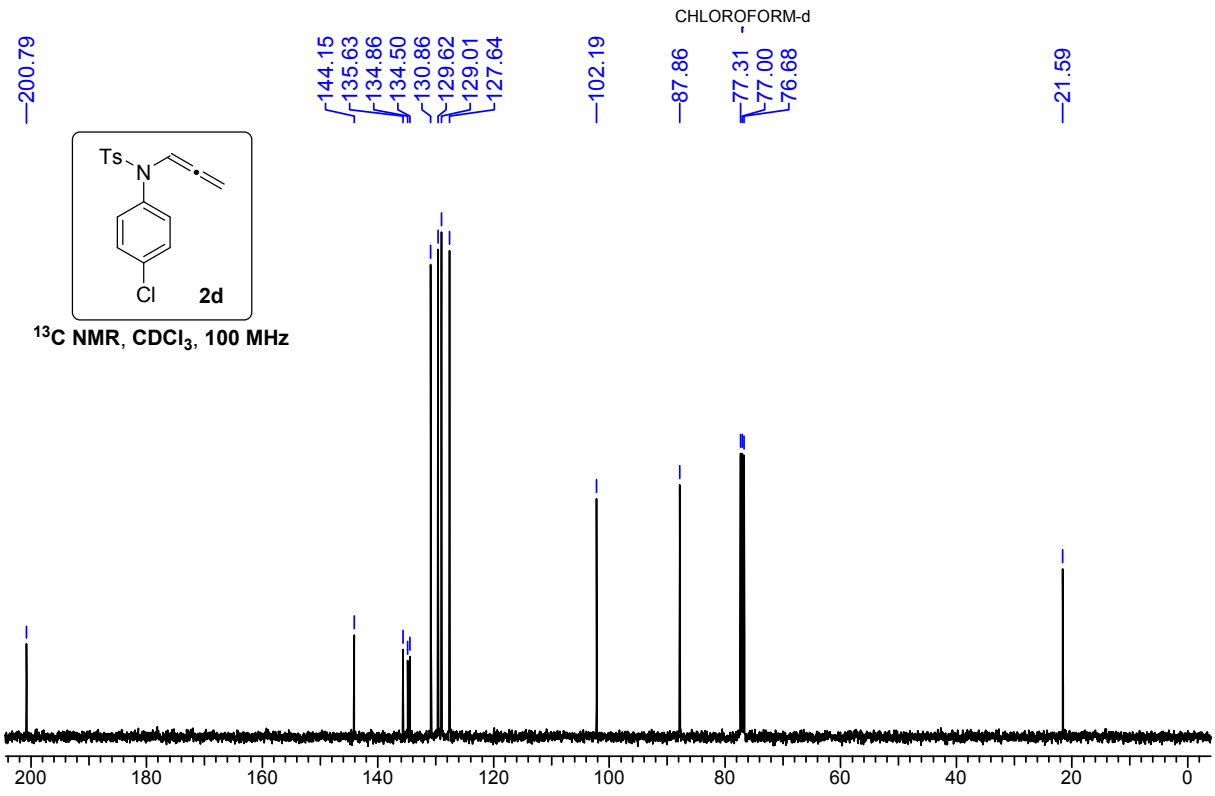
^{1}H NMR, $CDCl_3$, 200 MHz



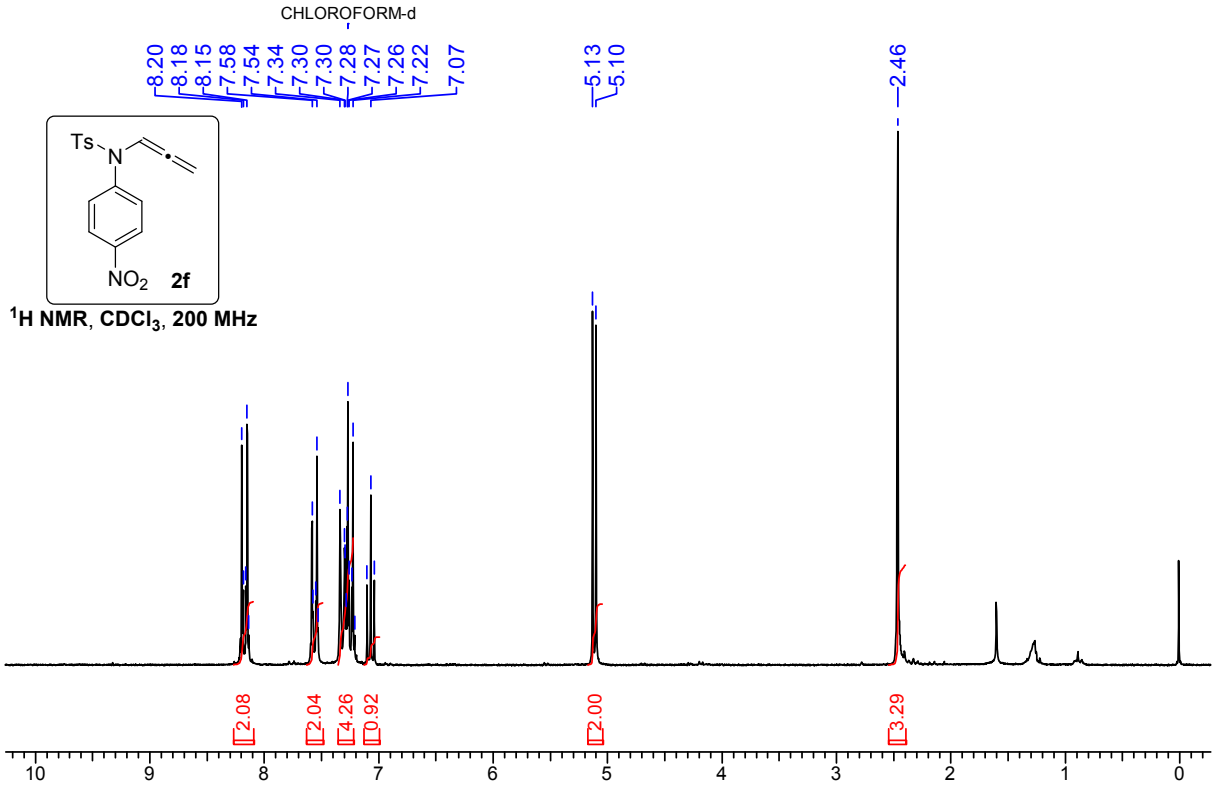
^{13}C NMR, $CDCl_3$, 50 MHz

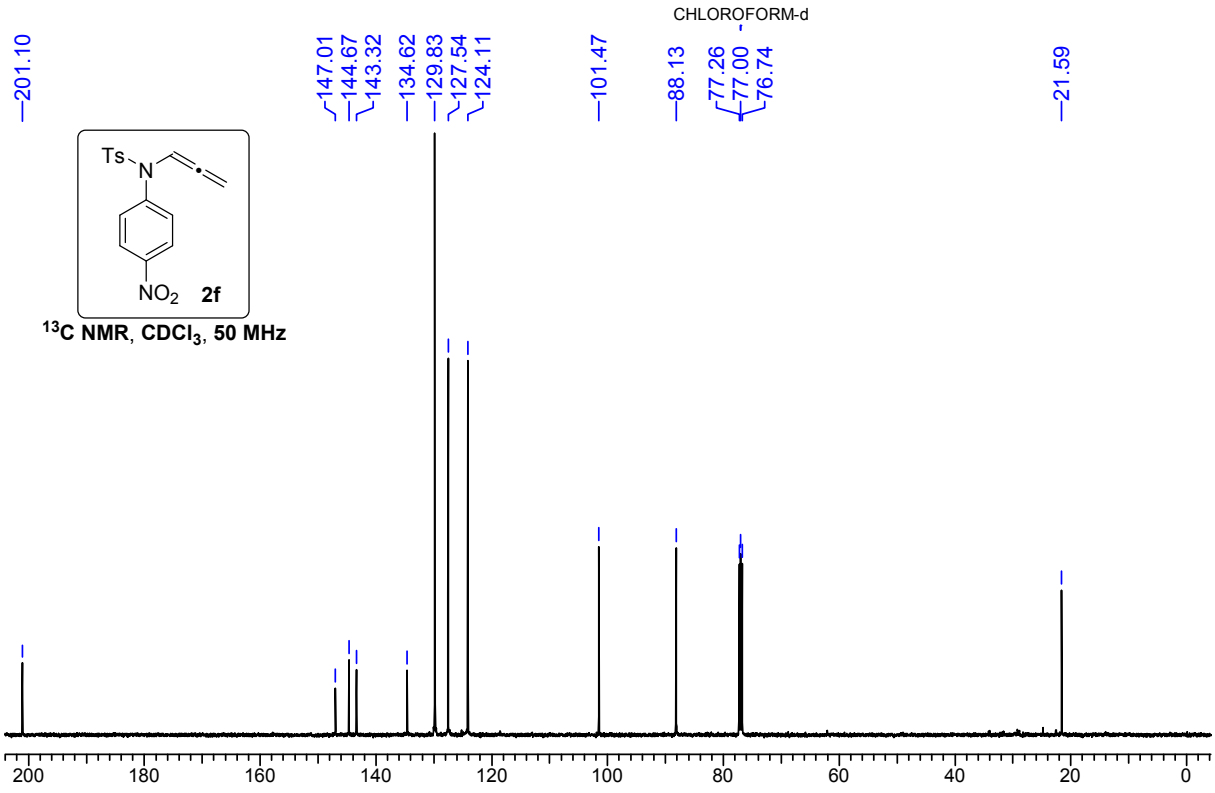


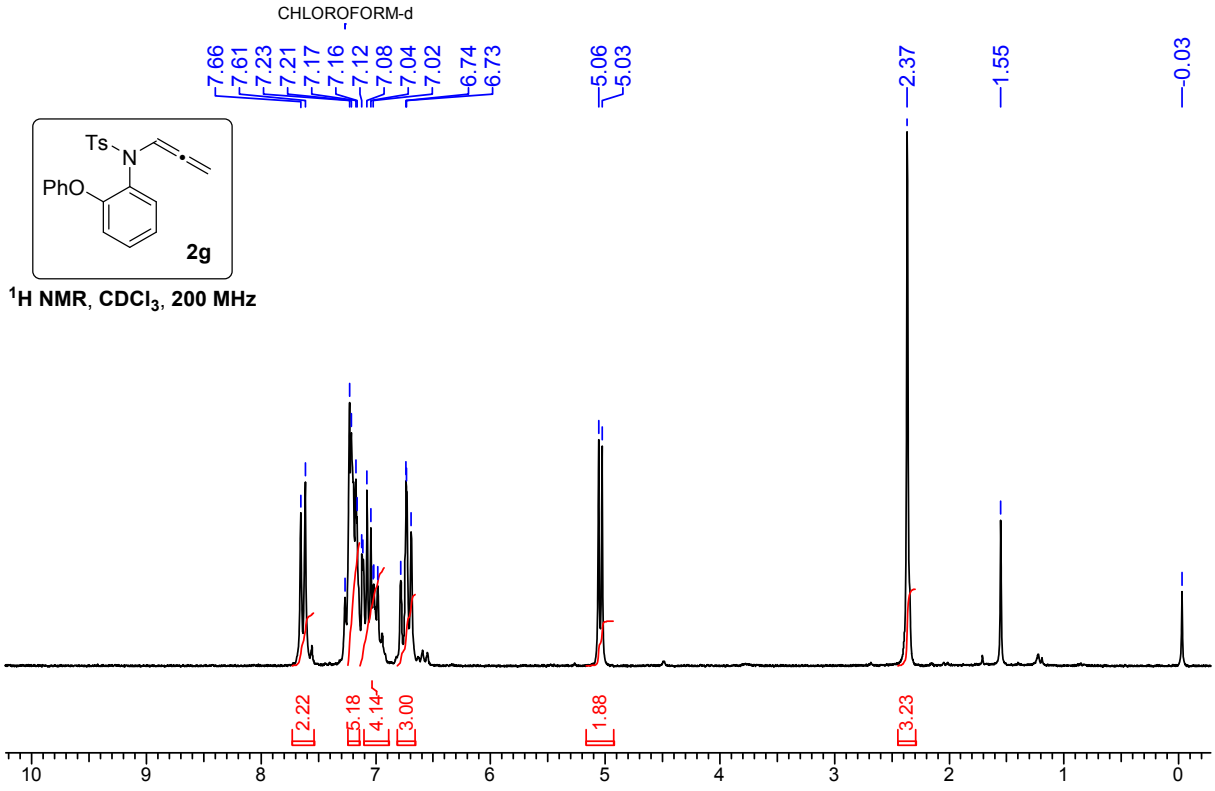
^{1}H NMR, $CDCl_3$, 400 MHz



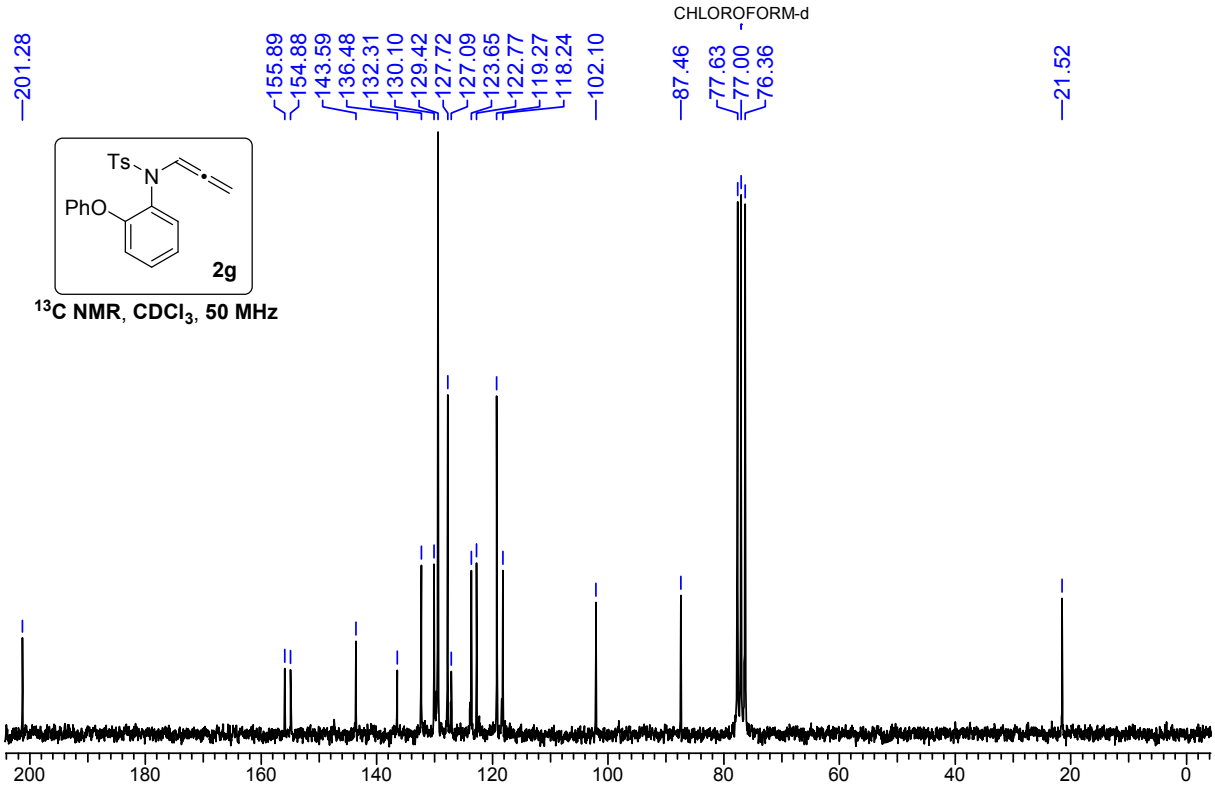
^{13}C NMR, $CDCl_3$, 100 MHz


CHLOROFORM-d
8.20
8.18
8.15
7.58
7.54
7.34
7.30
7.30
7.28
7.27
7.26
7.22
7.07
5.13
5.10
2.46
Ts
N
NO2
2f
1H NMR, CDCl3, 200 MHz
2.08
2.04
4.26
0.92
2.00
3.29
10
9
8
7
6
5
4
3
2
1
0

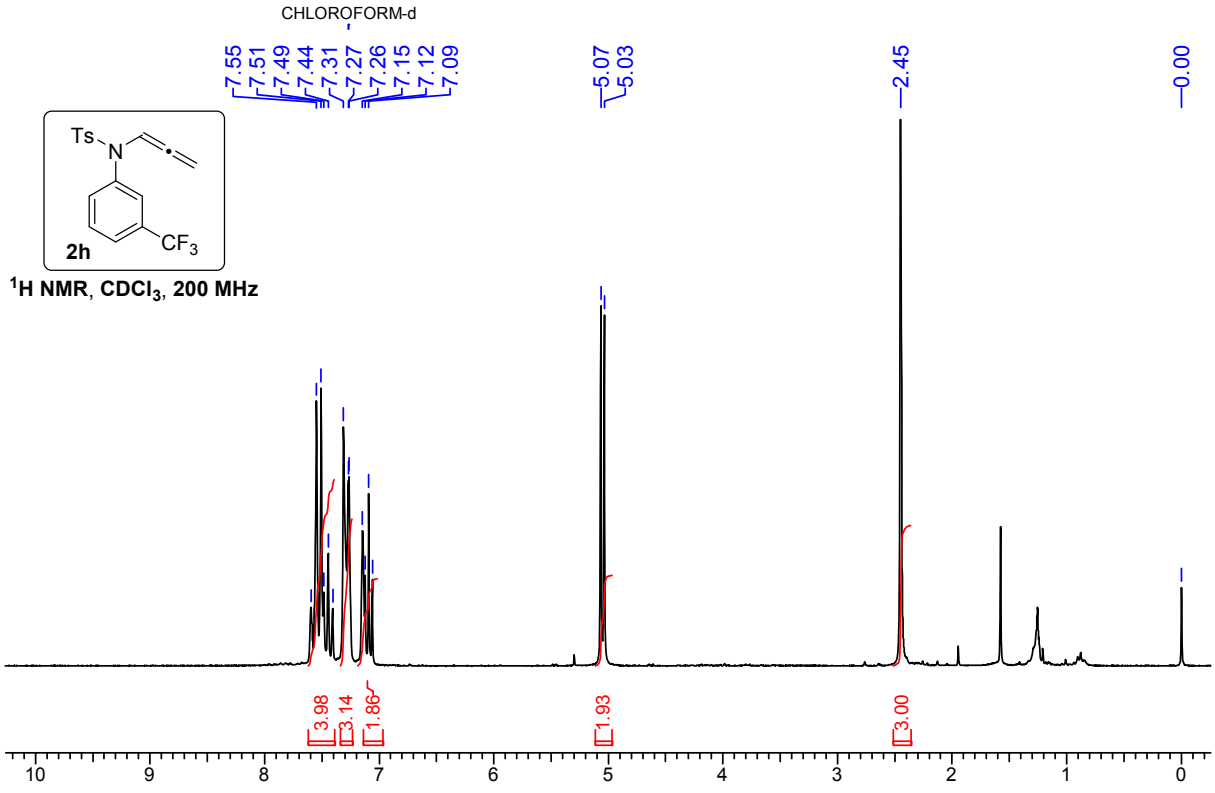

CHLOROFORM-d
201.10
147.01
144.67
143.32
134.62
129.83
127.54
124.11
101.47
88.13
77.26
77.00
76.74
21.59
Ts
N
NO2
2f
13C NMR, CDCl3, 50 MHz
200
180
160
140
120
100
80
60
40
20
0



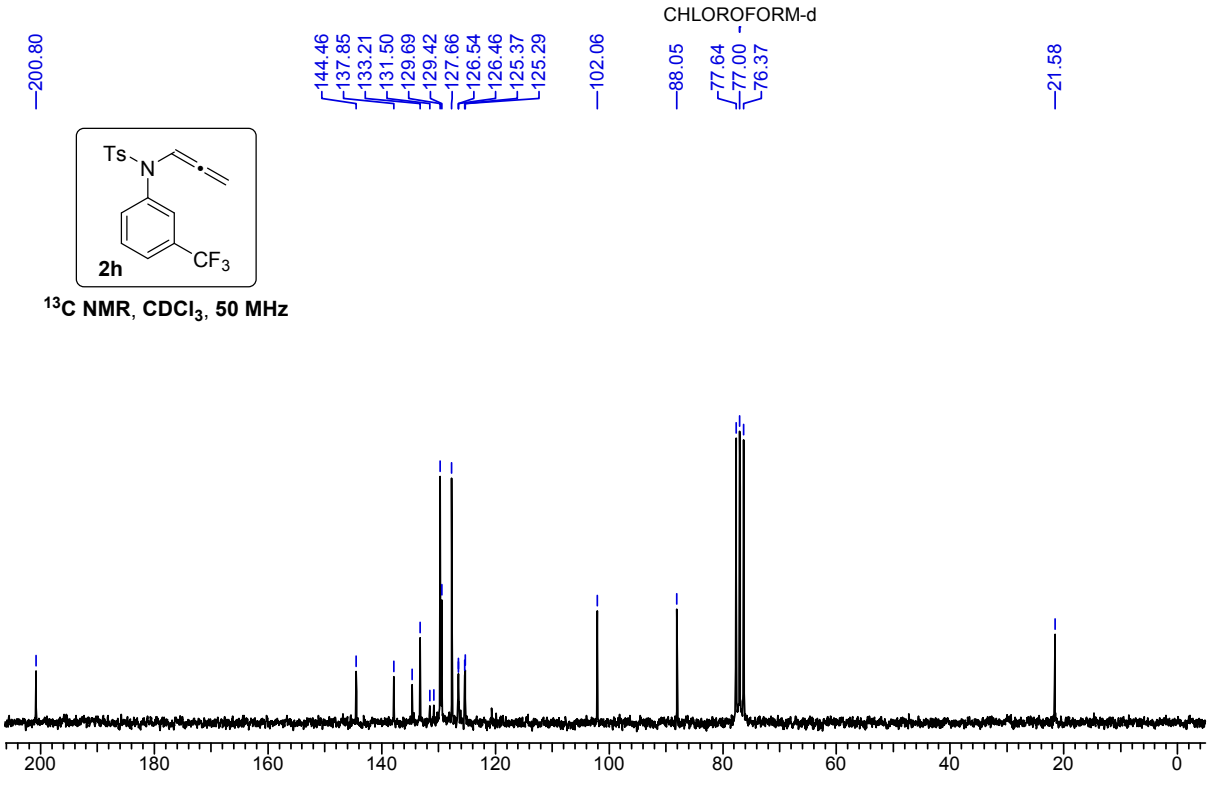
^{1}H NMR, $CDCl_3$, 200 MHz



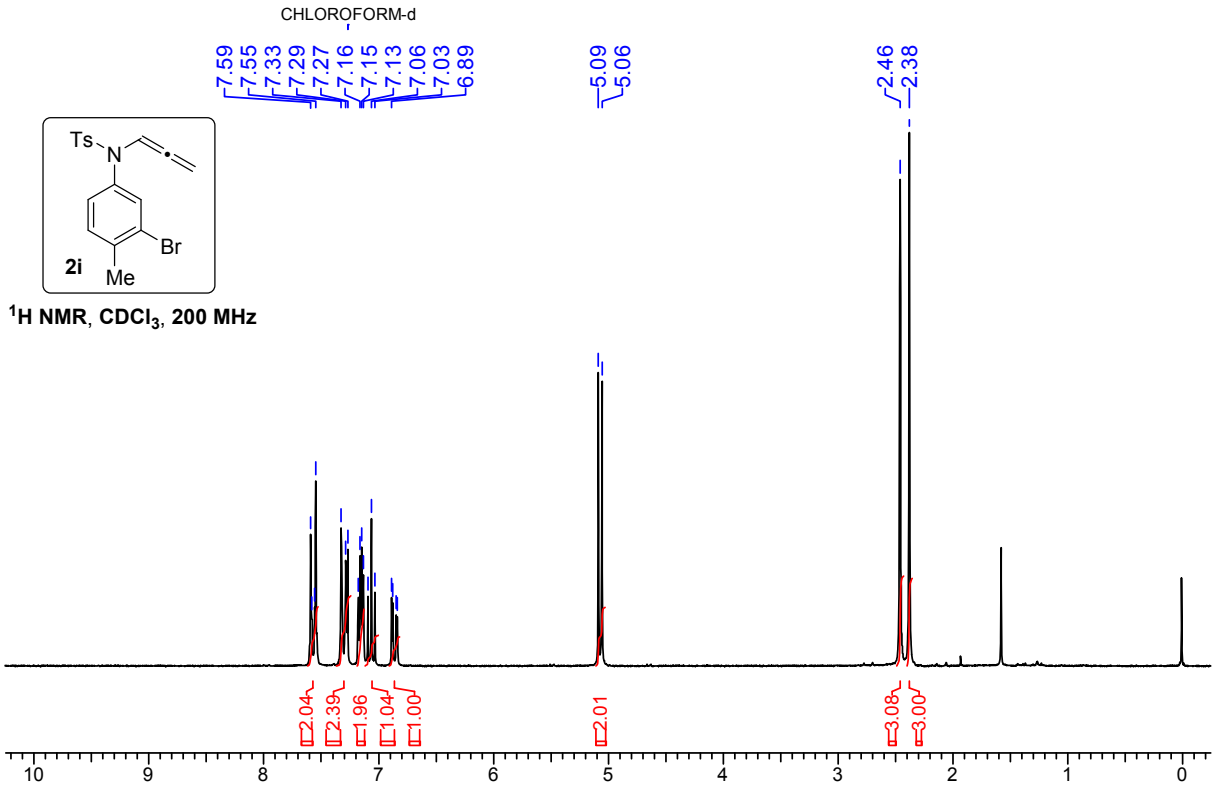
^{13}C NMR, $CDCl_3$, 50 MHz



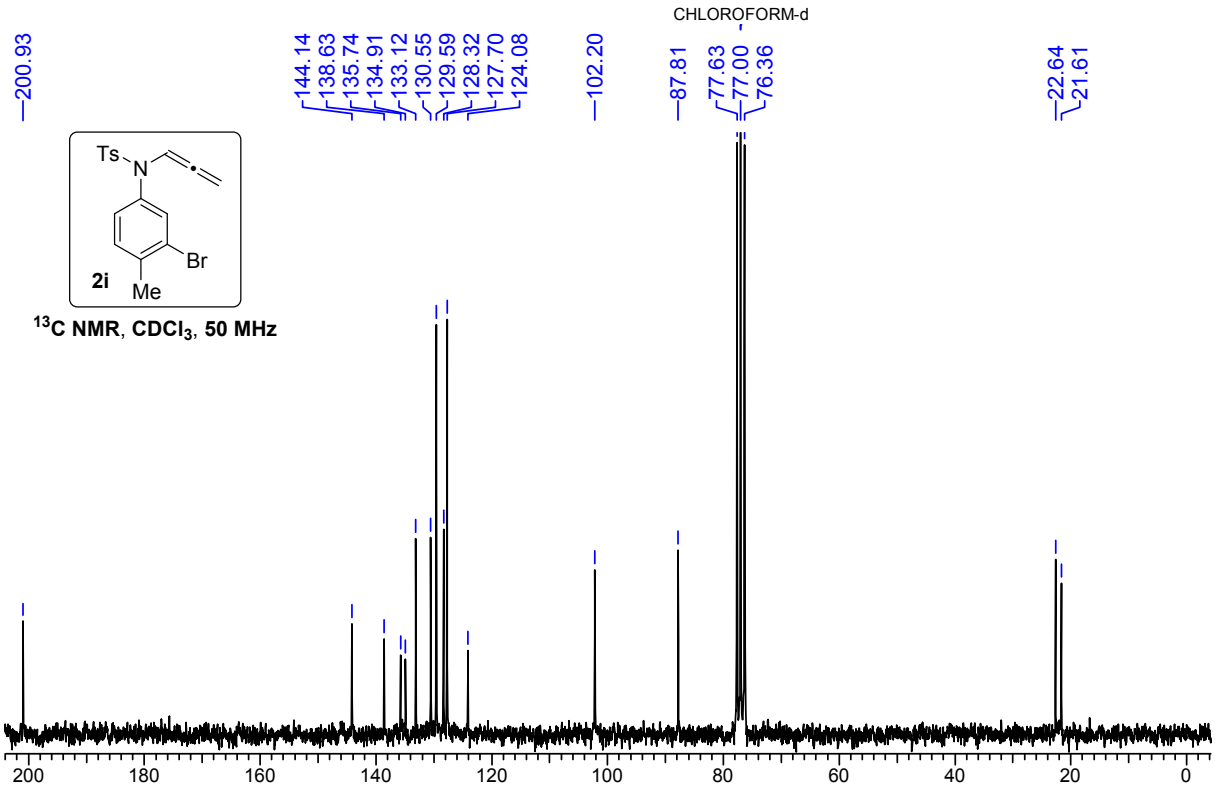
^{1}H NMR, $CDCl_3$, 200 MHz



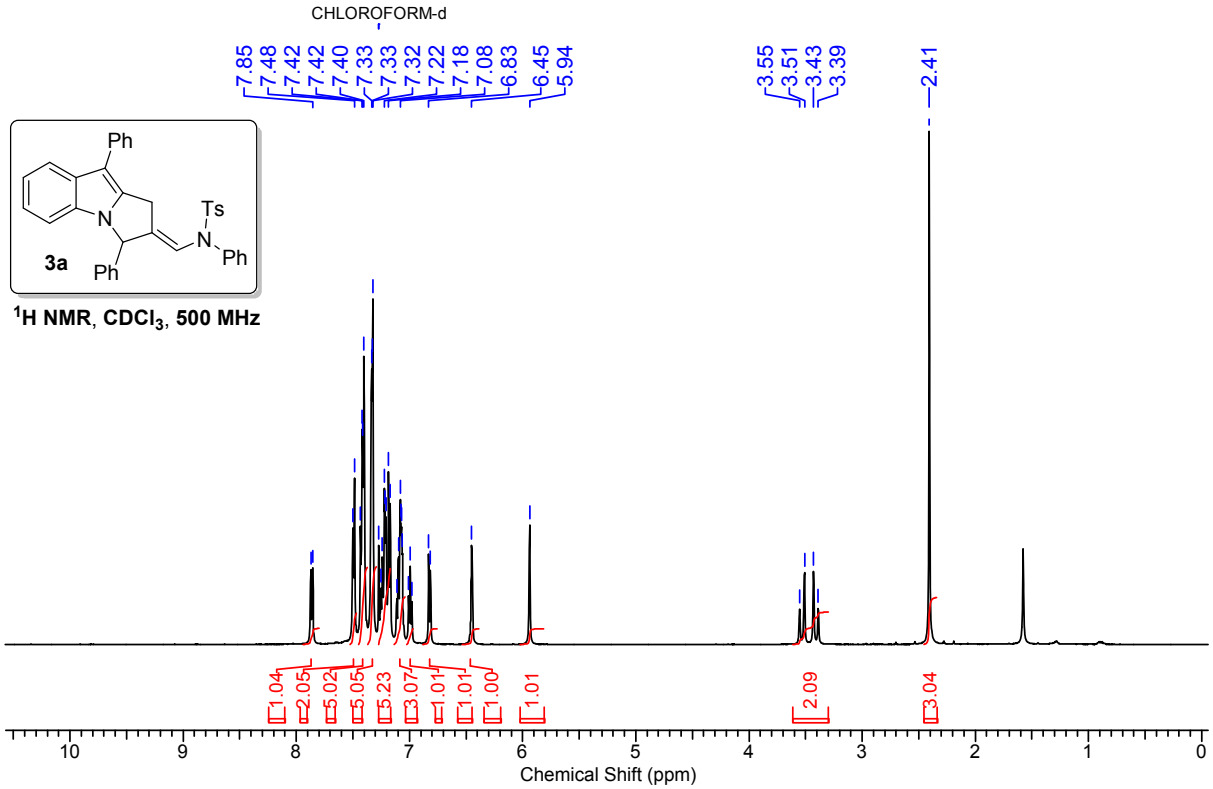
^{13}C NMR, $CDCl_3$, 50 MHz

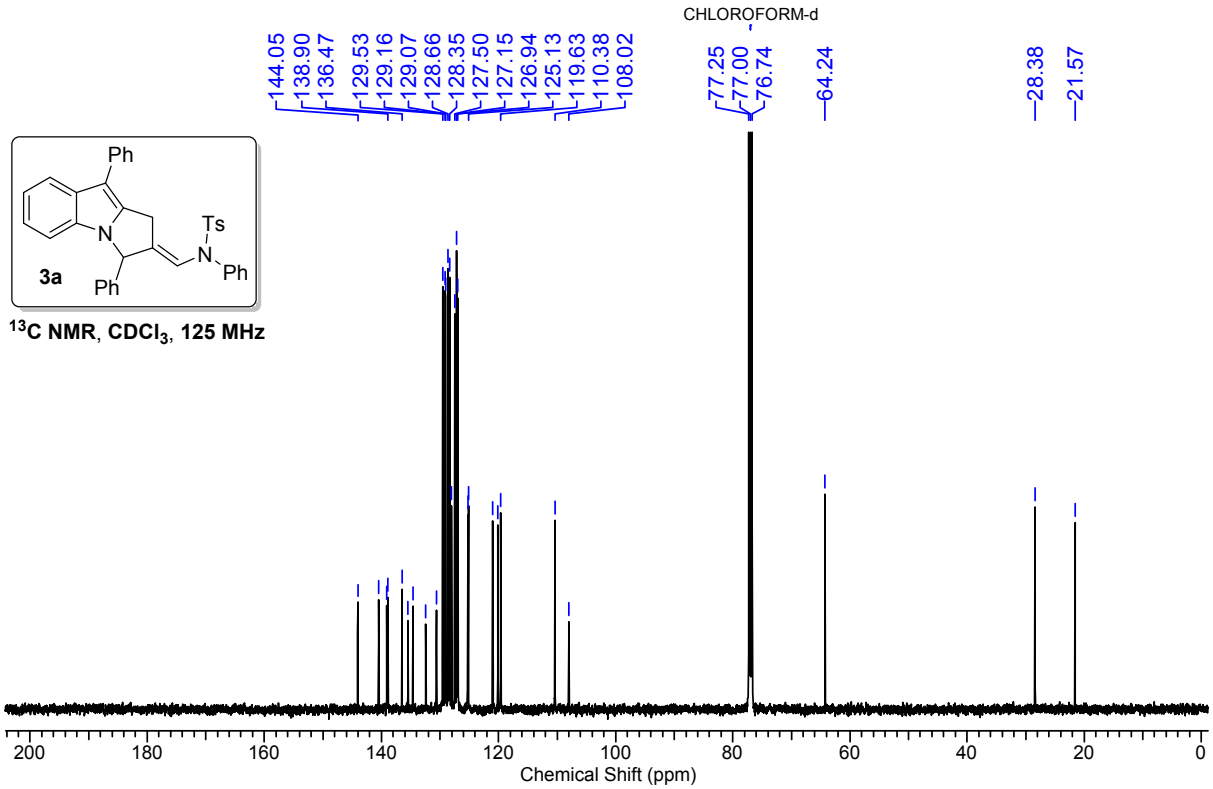


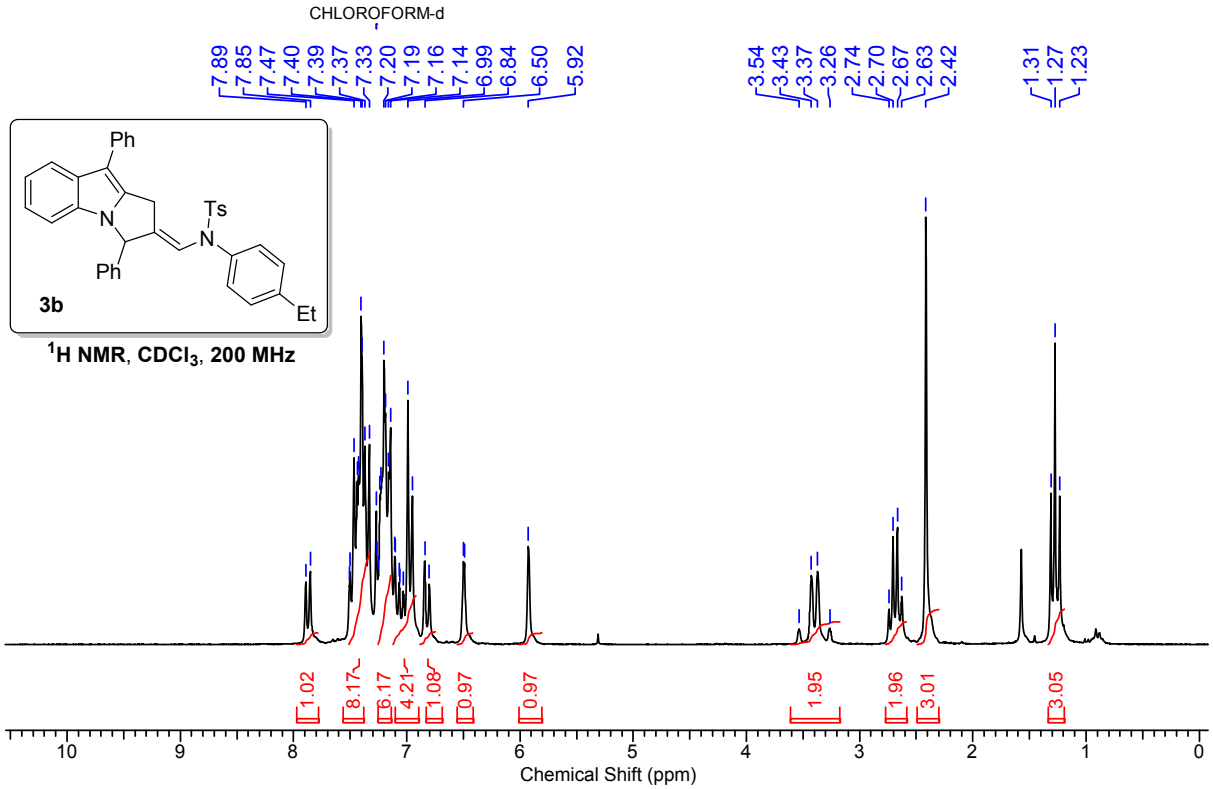
^{1}H NMR, $CDCl_3$, 200 MHz

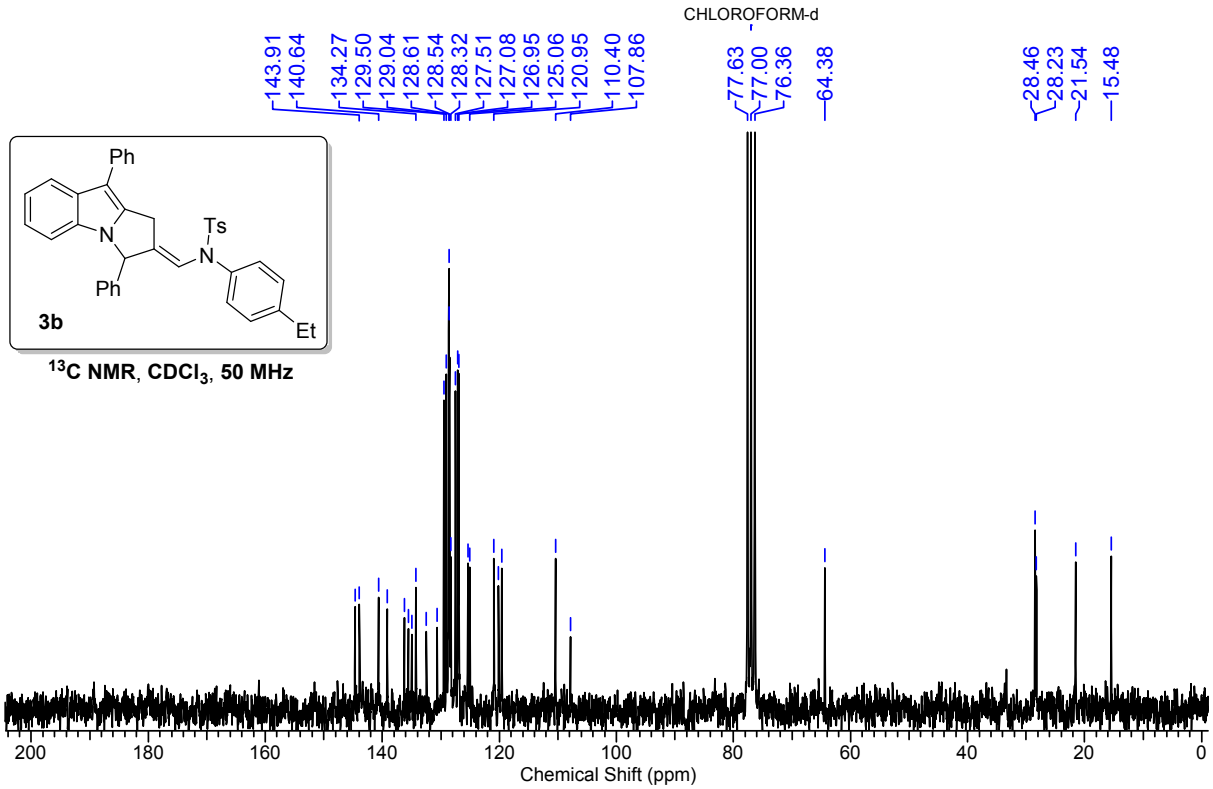


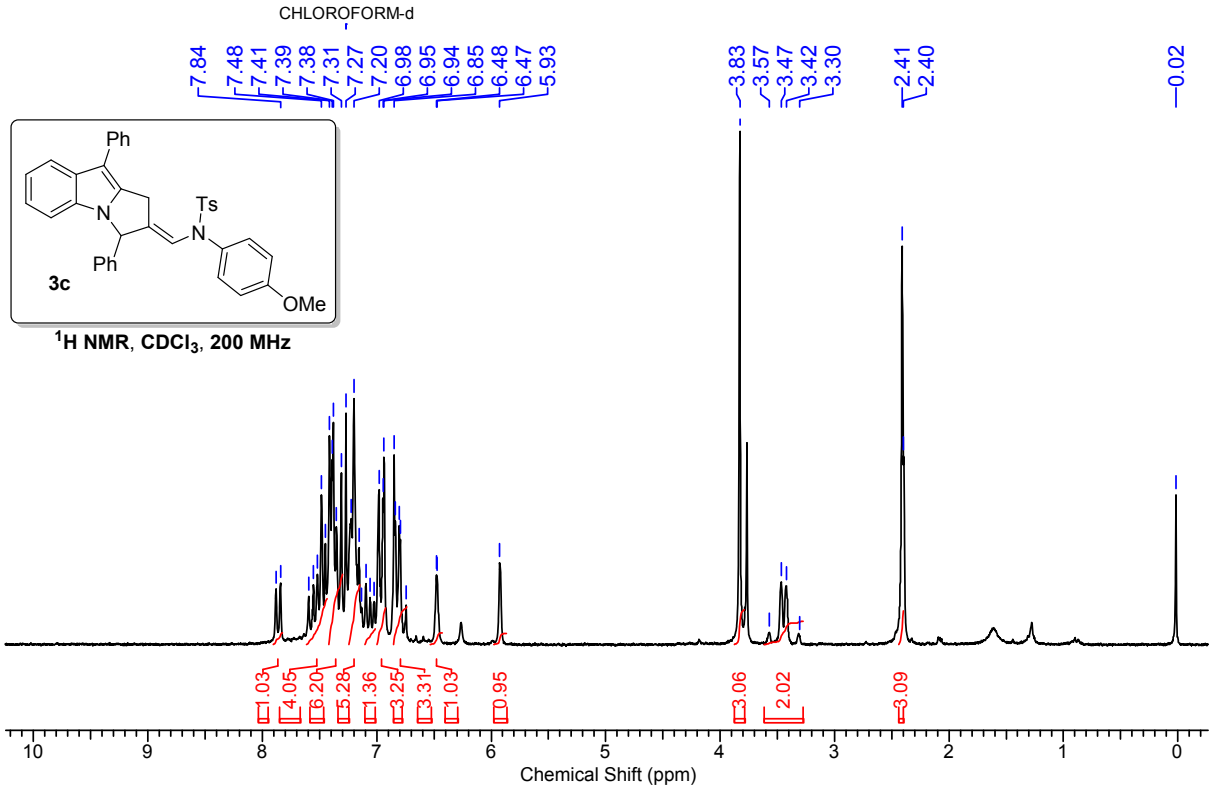
^{13}C NMR, $CDCl_3$, 50 MHz


CHLOROFORM-d
7.85
7.48
7.42
7.42
7.40
7.33
7.33
7.32
7.22
7.18
7.08
6.83
6.45
5.94
3.55
3.51
3.43
3.39
2.41
Ph
Ts
N
Ph
3a
Ph
1H NMR, CDCl3, 500 MHz
1.04
2.05
5.02
5.05
5.23
3.07
1.01
1.01
1.00
1.01
2.09
3.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

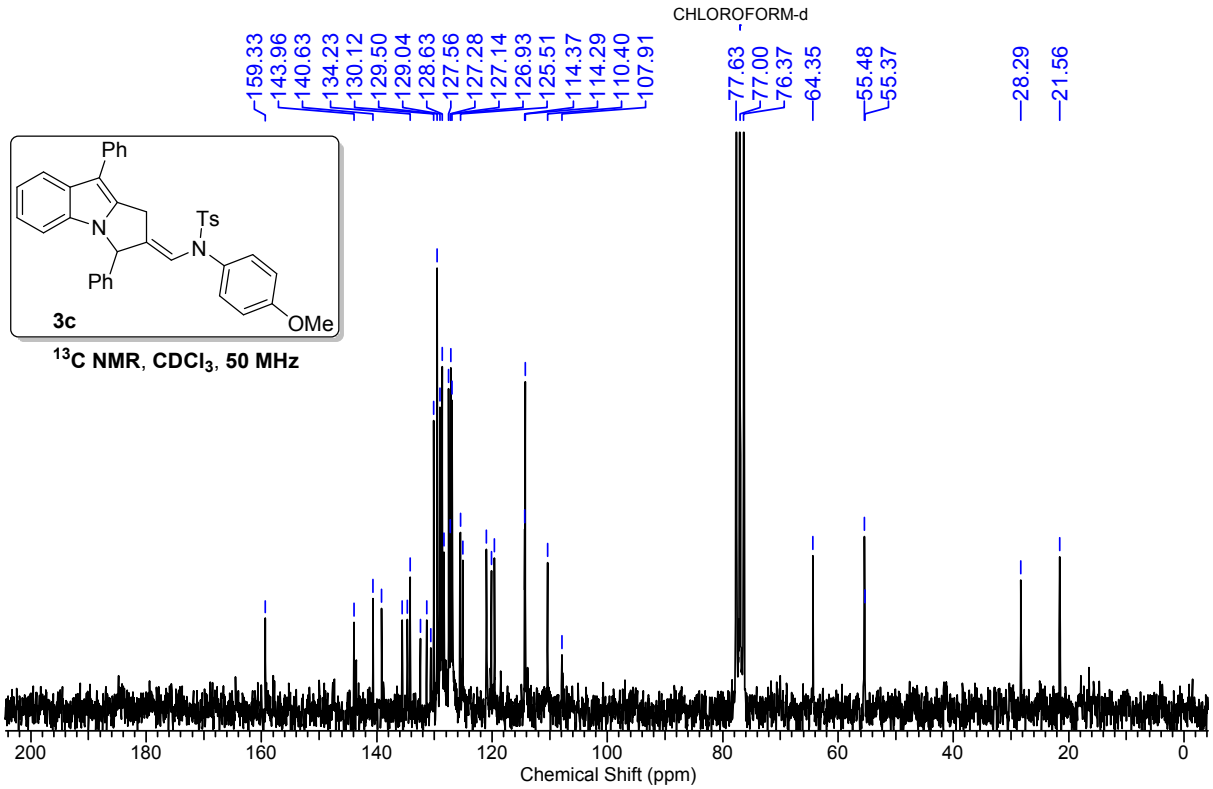

CHLOROFORM-d
144.05
138.90
136.47
129.53
129.16
129.07
128.66
128.35
127.50
127.15
126.94
125.13
119.63
110.38
108.02
77.25
77.00
76.74
64.24
28.38
21.57
Ph
Ts
N
Ph
3a
Ph
13C NMR, CDCl3, 125 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
7.89
7.85
7.47
7.40
7.39
7.37
7.33
7.20
7.19
7.16
7.14
6.99
6.84
6.50
5.92
3.54
3.43
3.37
3.26
2.74
2.70
2.67
2.63
2.42
1.31
1.27
1.23
Ph
N
Ts
N
Ph
Et
3b
1H NMR, CDCl3, 200 MHz
1.02
8.17
6.17
4.21
1.08
0.97
0.97
1.95
1.96
3.01
3.05
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

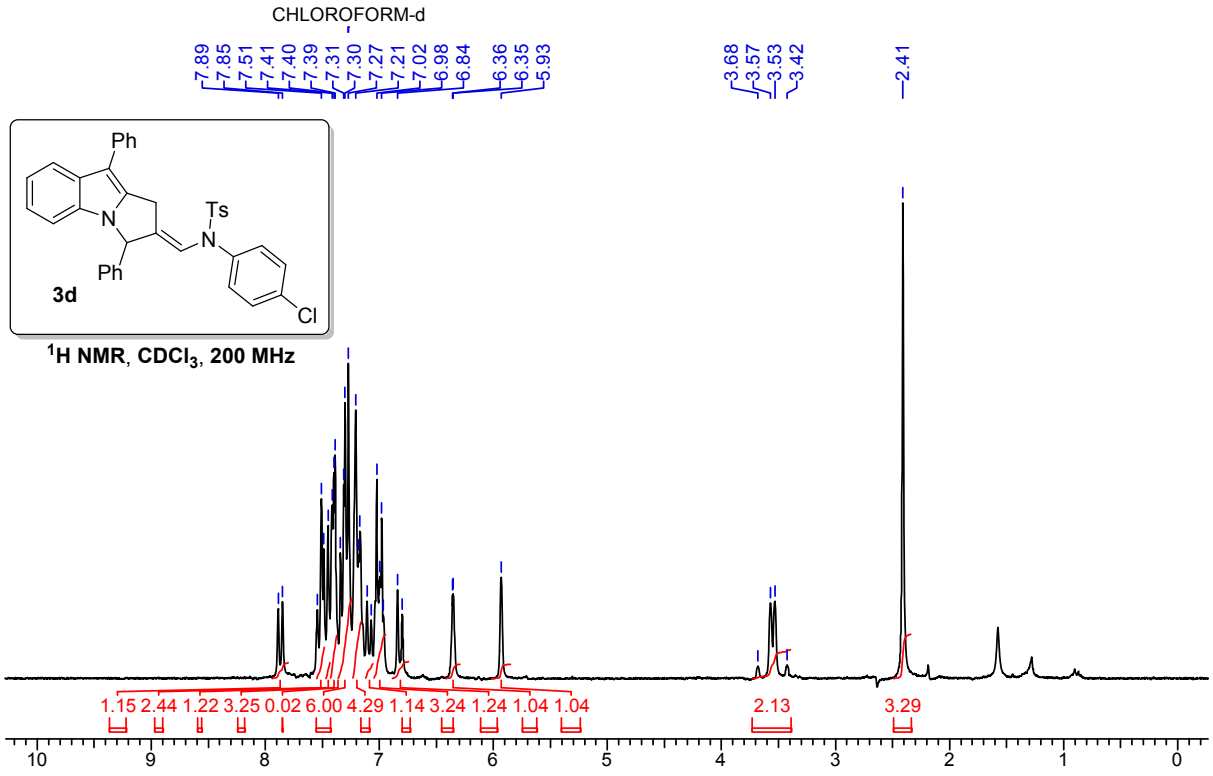

CHLOROFORM-d
143.91
140.64
134.27
129.50
129.04
128.61
128.54
128.32
127.51
127.08
126.95
125.06
120.95
110.40
107.86
77.63
77.00
76.36
64.38
28.46
28.23
21.54
15.48
Ph
N
Ts
N
Ph
Et
3b
13C NMR, CDCl3, 50 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



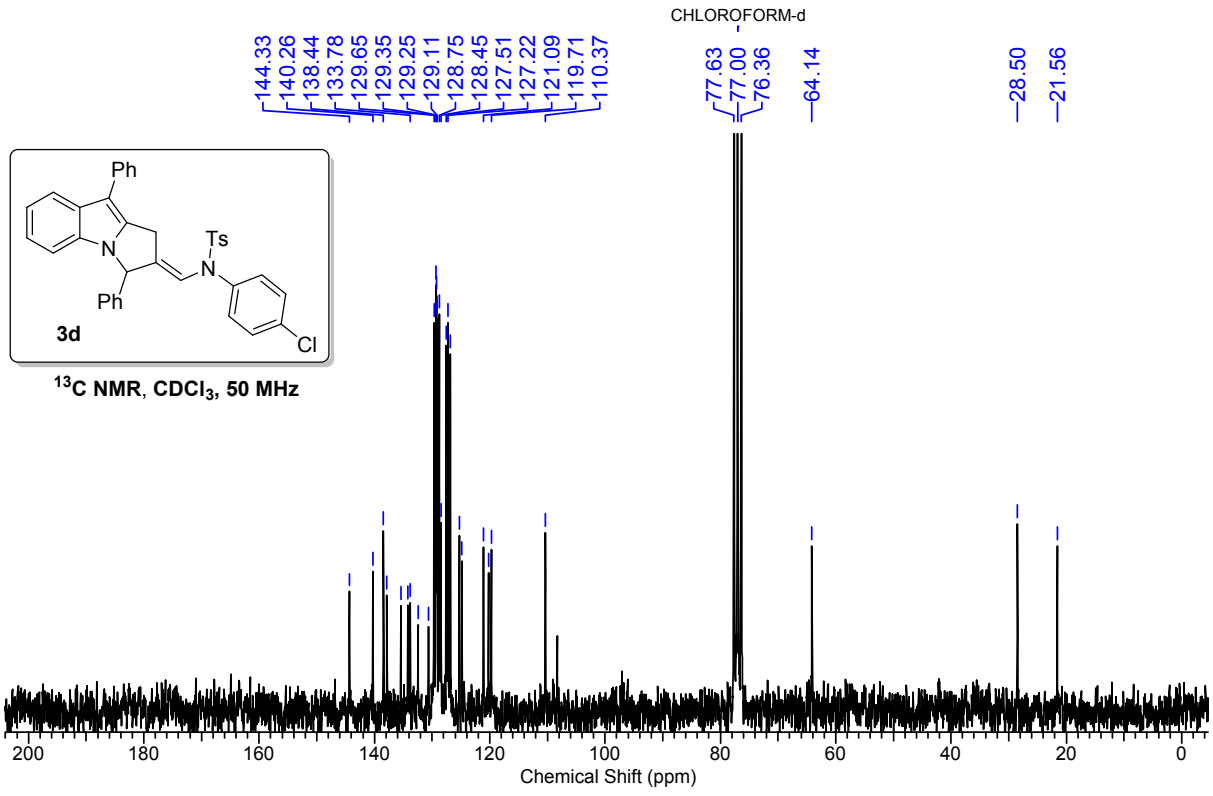
^{1}H NMR, $CDCl_3$, 200 MHz



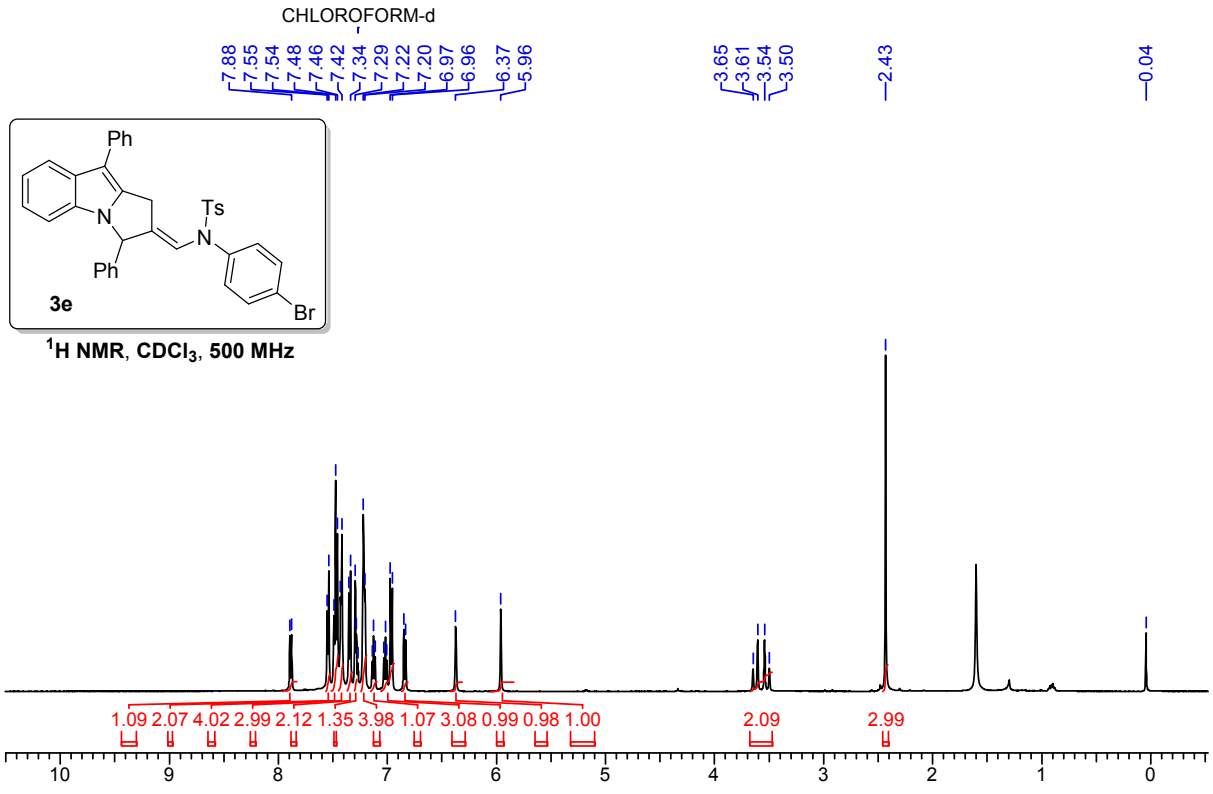
^{13}C NMR, $CDCl_3$, 50 MHz



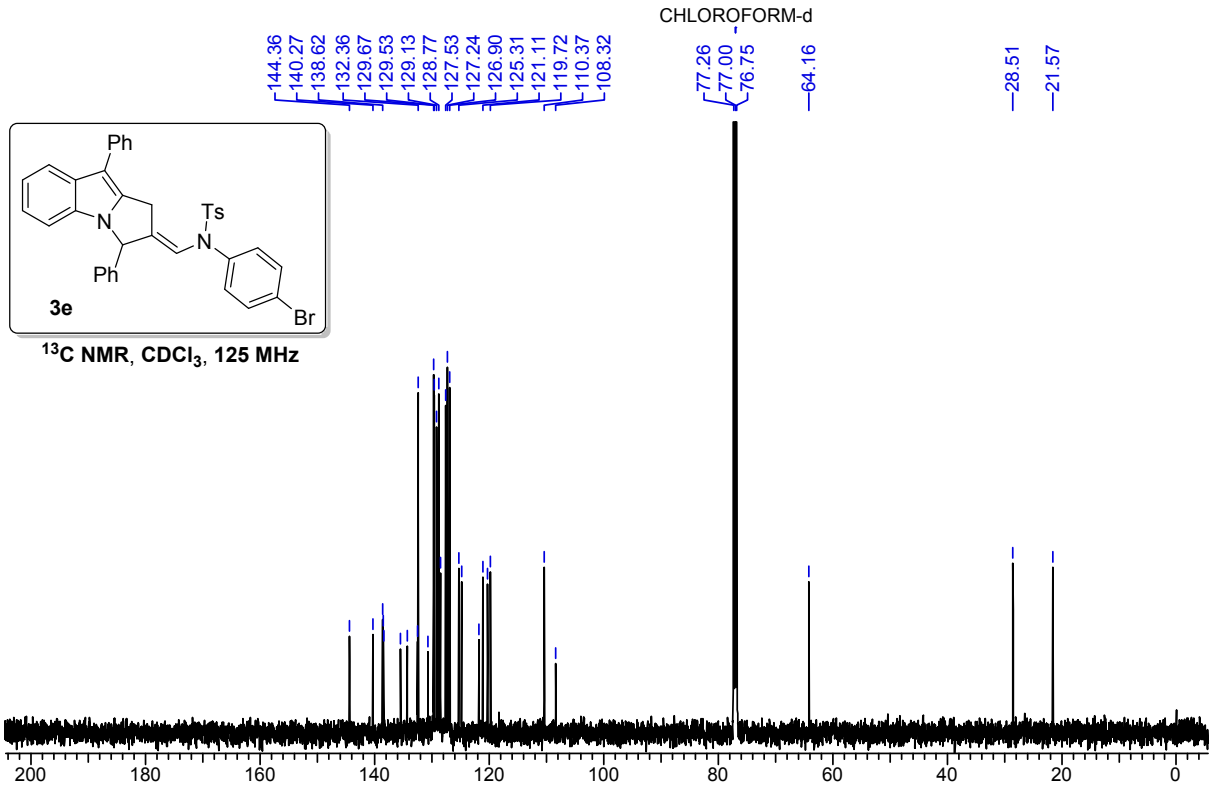
^{1}H NMR, $CDCl_3$, 200 MHz



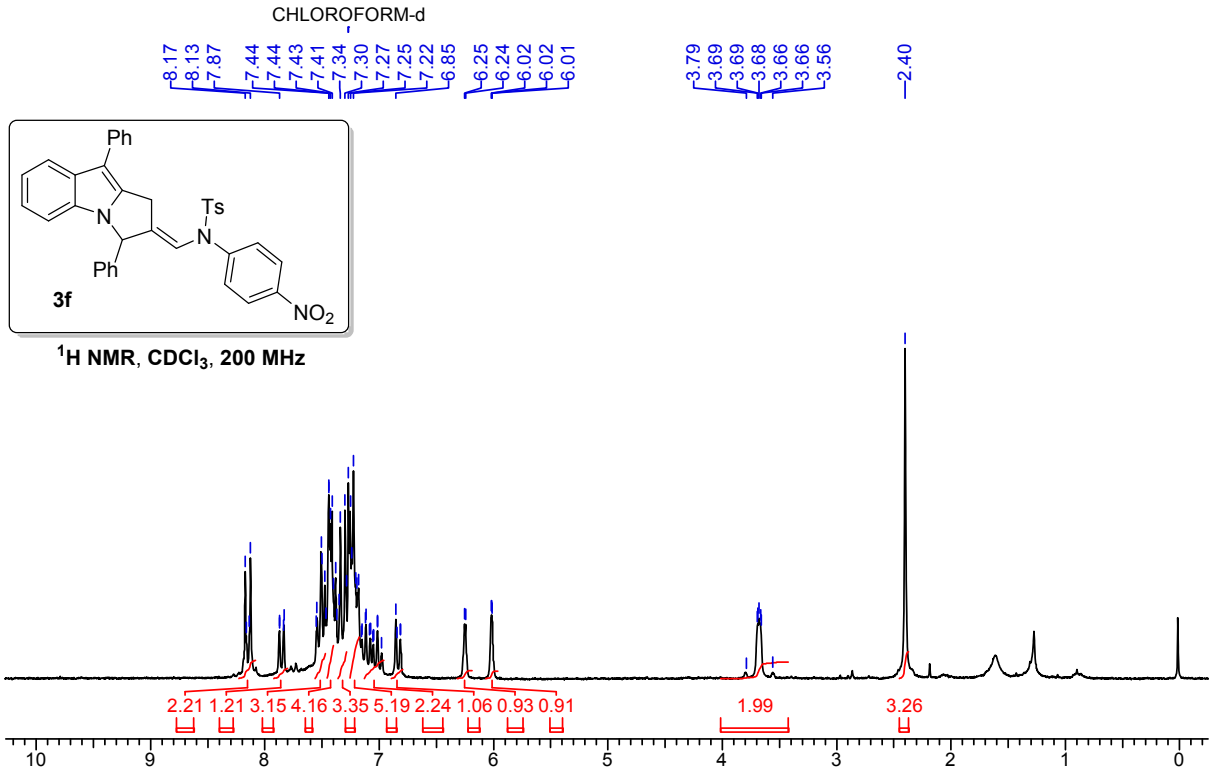
^{13}C NMR, $CDCl_3$, 50 MHz



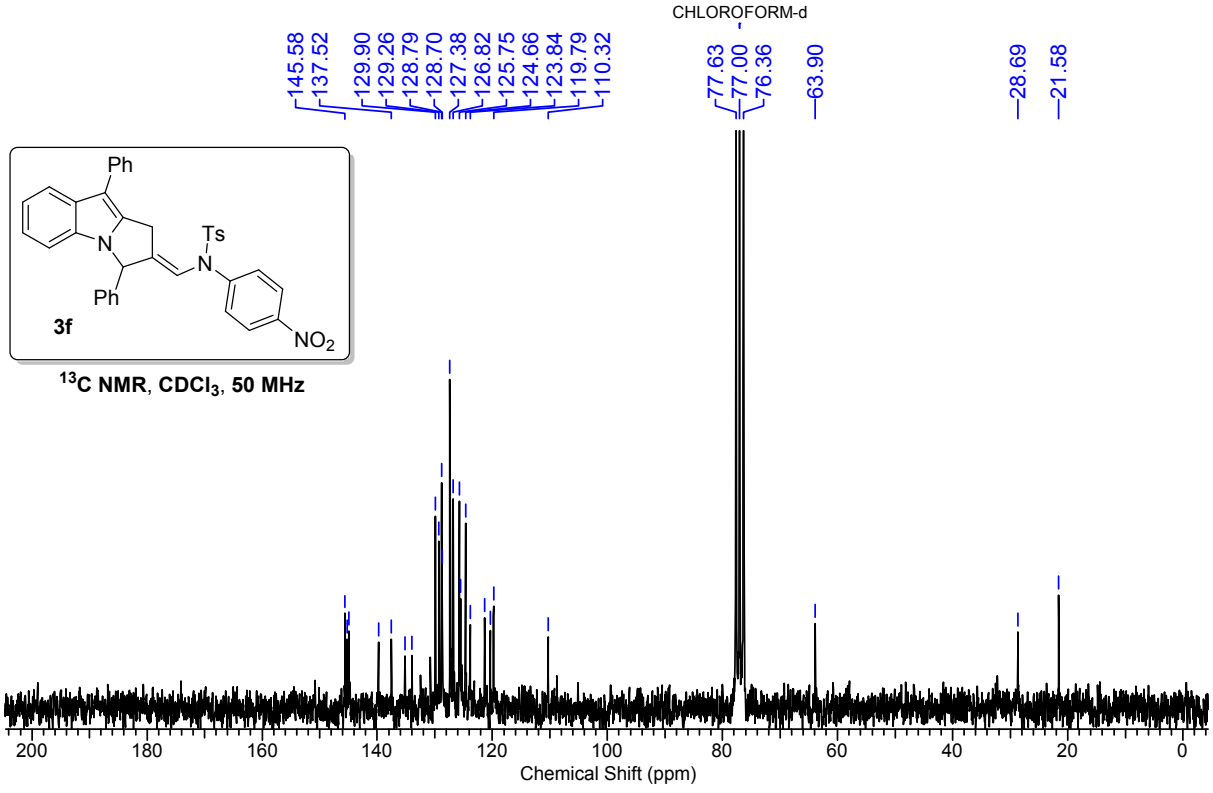
^{1}H NMR, $CDCl_3$, 500 MHz



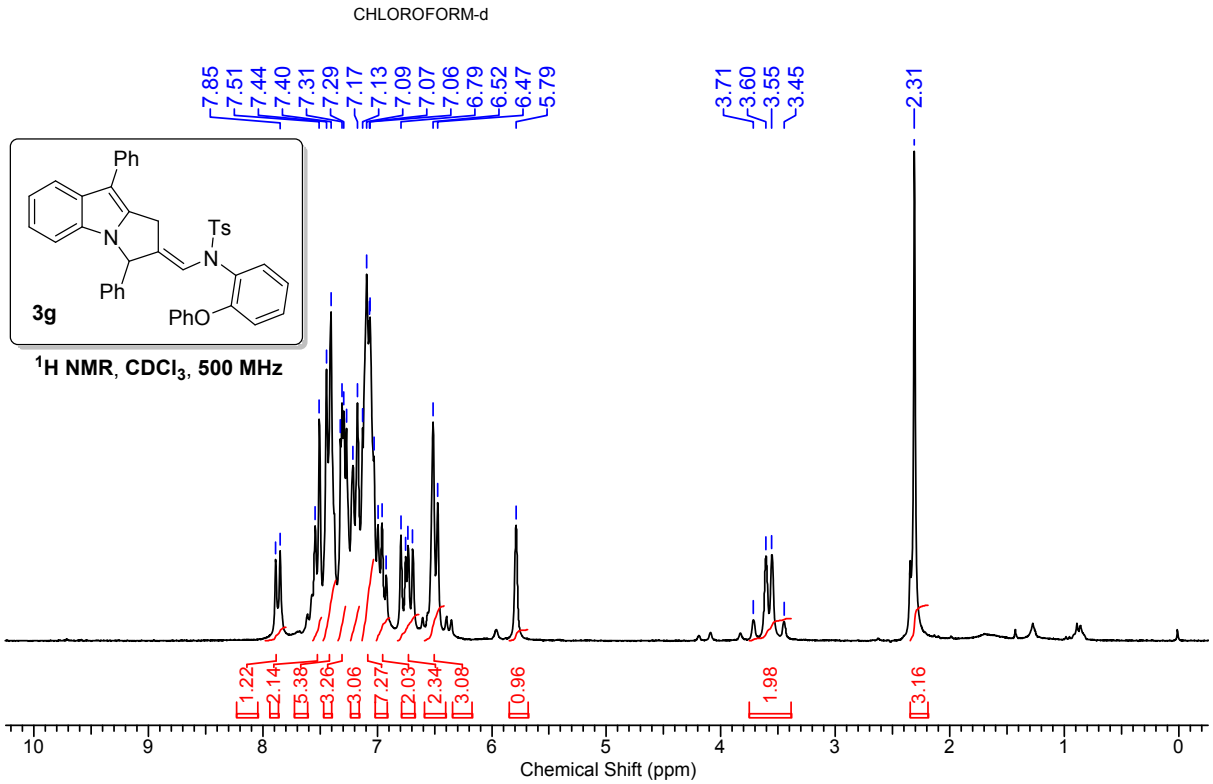
^{13}C NMR, $CDCl_3$, 125 MHz

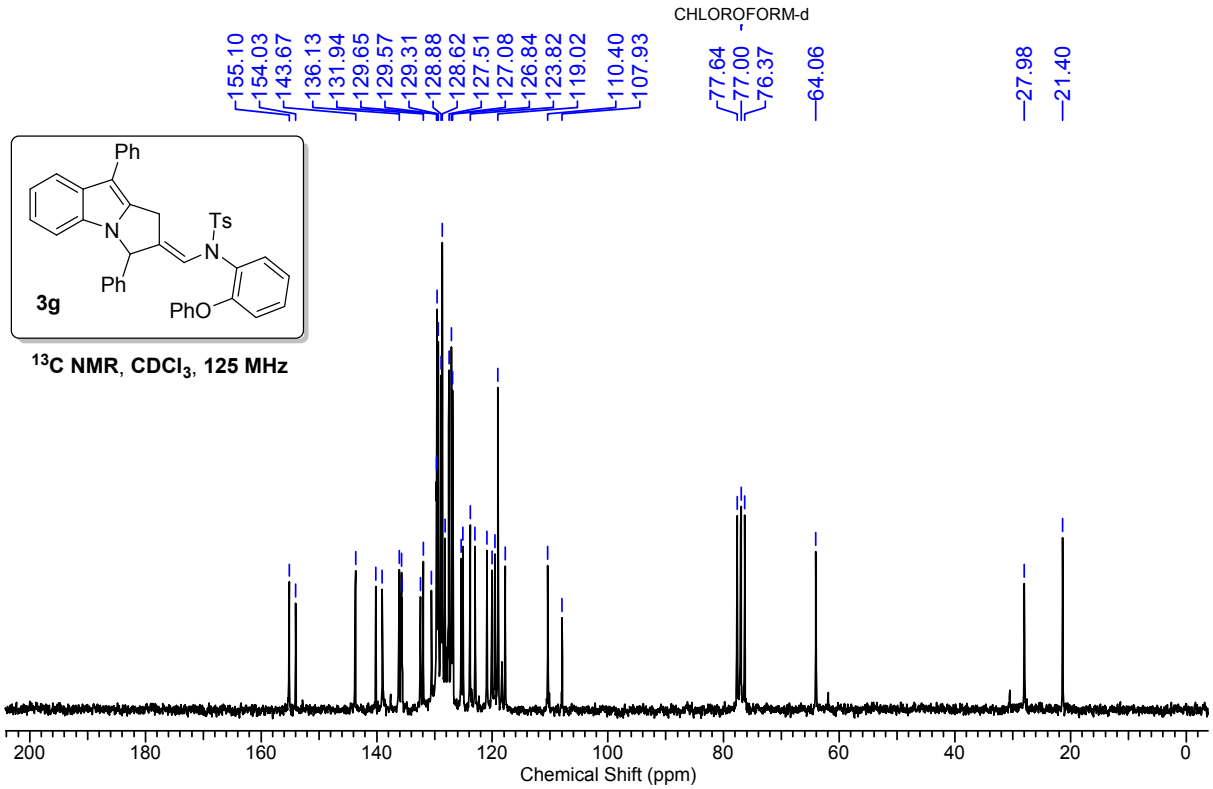


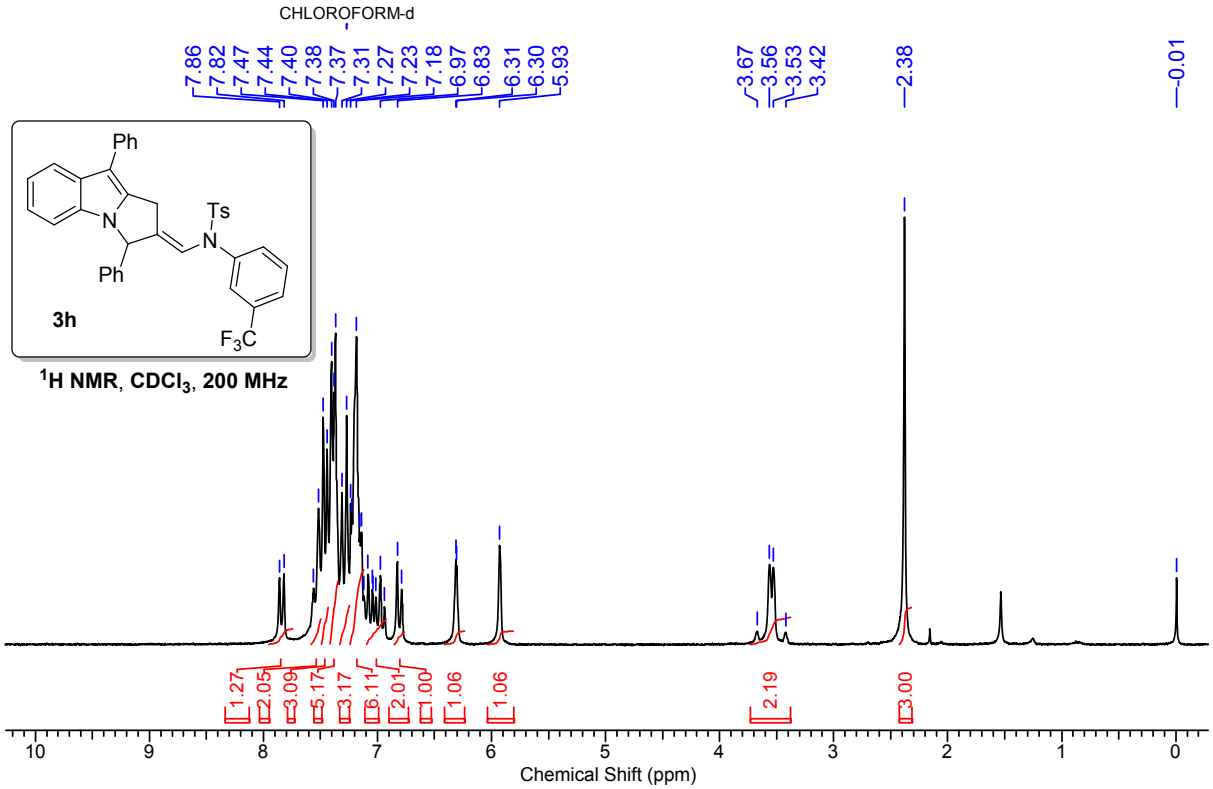
^{1}**H NMR, $CDCl_3$, 200 MHz**

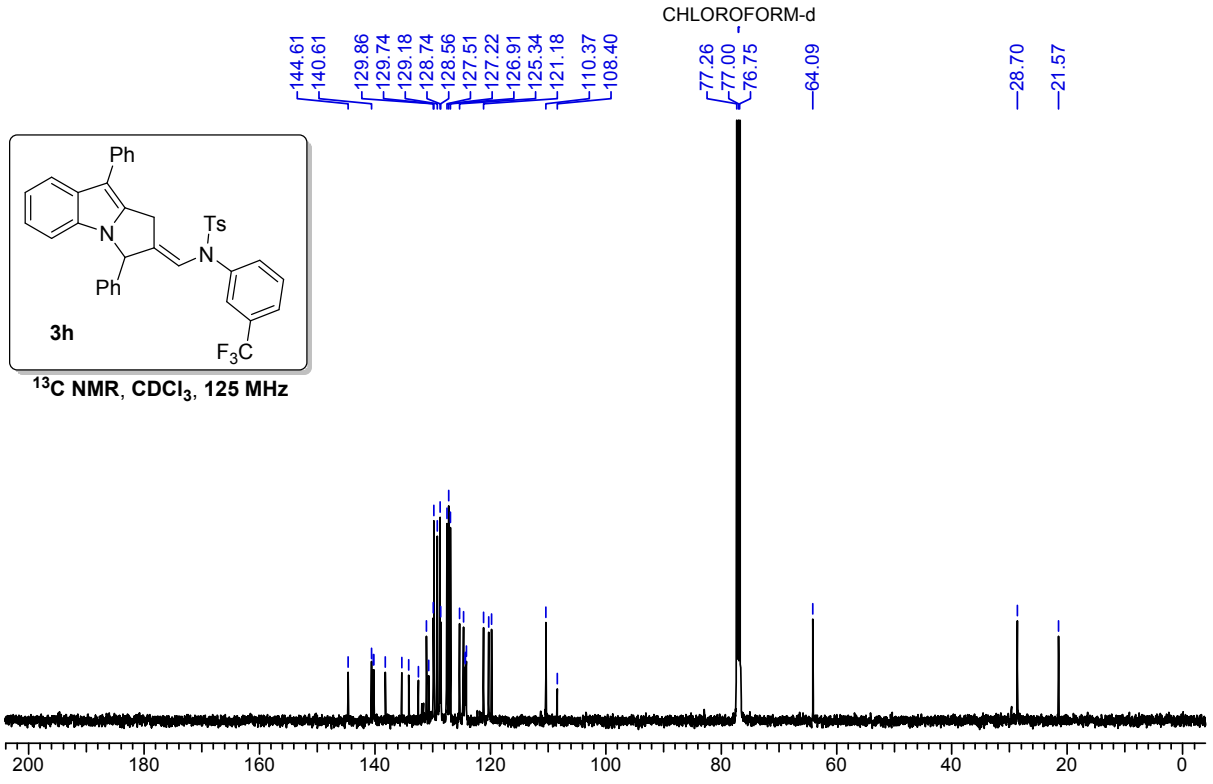


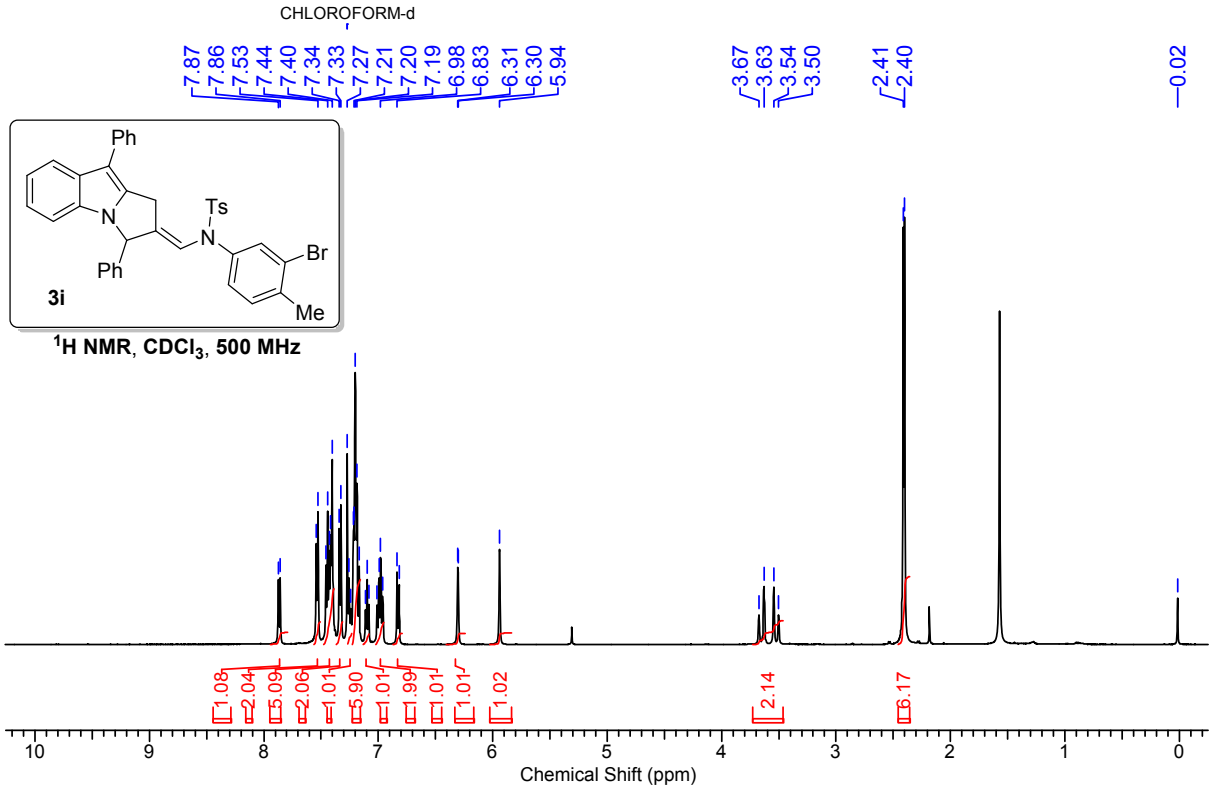
^{13}**C NMR, $CDCl_3$, 50 MHz**


CHLOROFORM-d
7.85
7.51
7.44
7.40
7.31
7.29
7.17
7.13
7.09
7.07
7.06
6.79
6.52
6.47
5.79
3.71
3.60
3.55
3.45
2.31
Ph
N
Ts
N
Ph
PhO
3g
1H NMR, CDCl3, 500 MHz
1.22
2.14
5.38
3.26
3.06
7.27
2.03
2.34
3.08
0.96
1.98
3.16
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

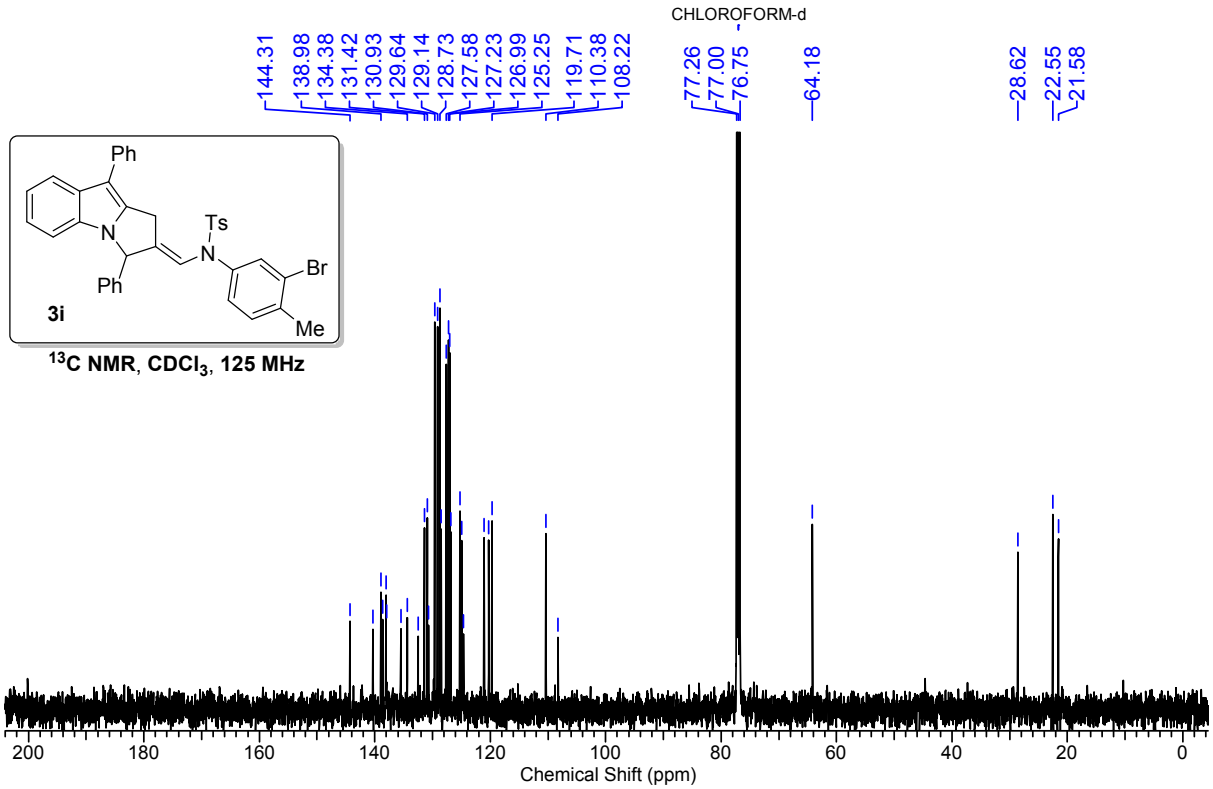

CHLOROFORM-d
155.10
154.03
143.67
136.13
131.94
129.65
129.57
129.31
128.88
128.62
127.51
127.08
126.84
123.82
119.02
110.40
107.93
77.64
77.00
76.37
64.06
27.98
21.40
Ph
N
Ts
N
Ph
PhO
3g
13C NMR, CDCl3, 125 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
7.86
7.82
7.47
7.44
7.40
7.38
7.37
7.31
7.27
7.23
7.18
6.97
6.83
6.31
6.30
5.93
3.67
3.56
3.53
3.42
2.38
0.01
Ph
N
Ts
N
Ph
3h
F3C
1H NMR, CDCl3, 200 MHz
1.27
2.05
3.09
5.17
3.17
6.11
2.01
1.00
1.06
1.06
2.19
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

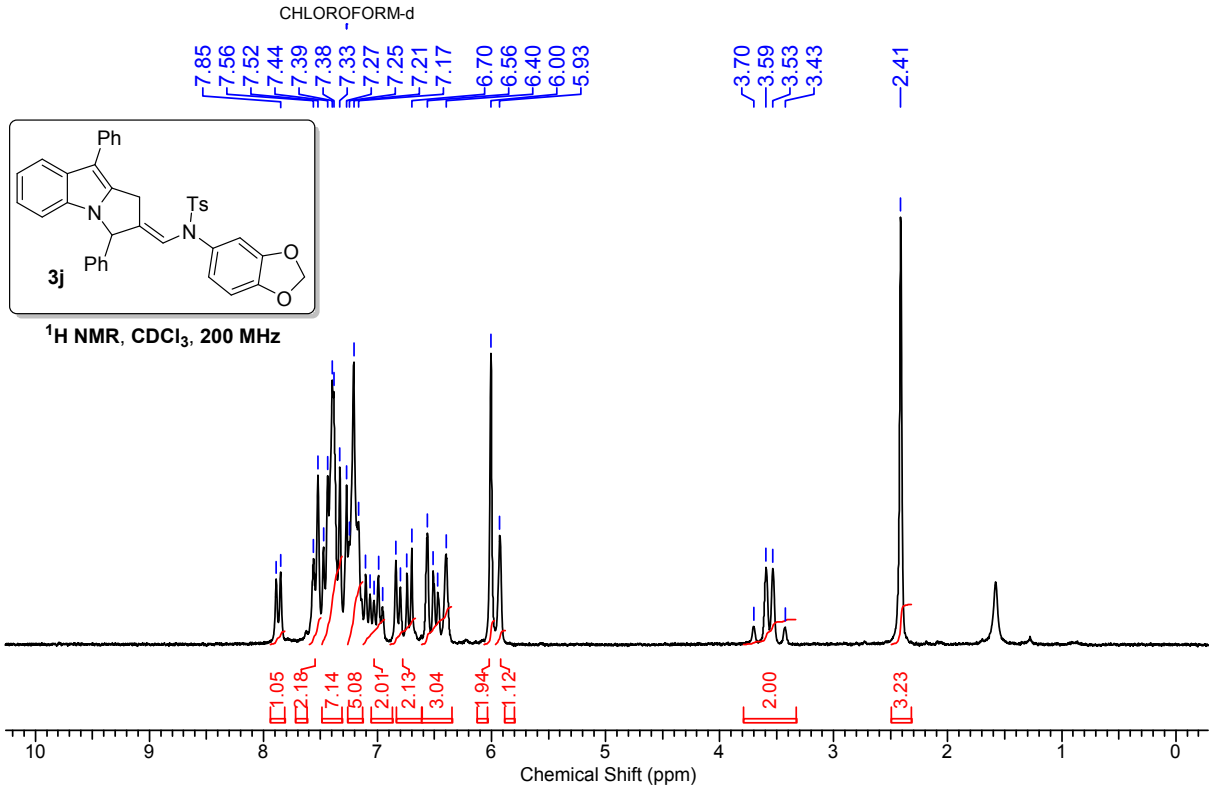

CHLOROFORM-d
144.61
140.61
129.86
129.74
129.18
128.74
128.56
127.51
127.22
126.91
125.34
121.18
110.37
108.40
77.26
77.00
76.75
64.09
28.70
21.57
Ph
N
Ts
N
Ph
3h
F3C
13C NMR, CDCl3, 125 MHz
200
180
160
140
120
100
80
60
40
20
0



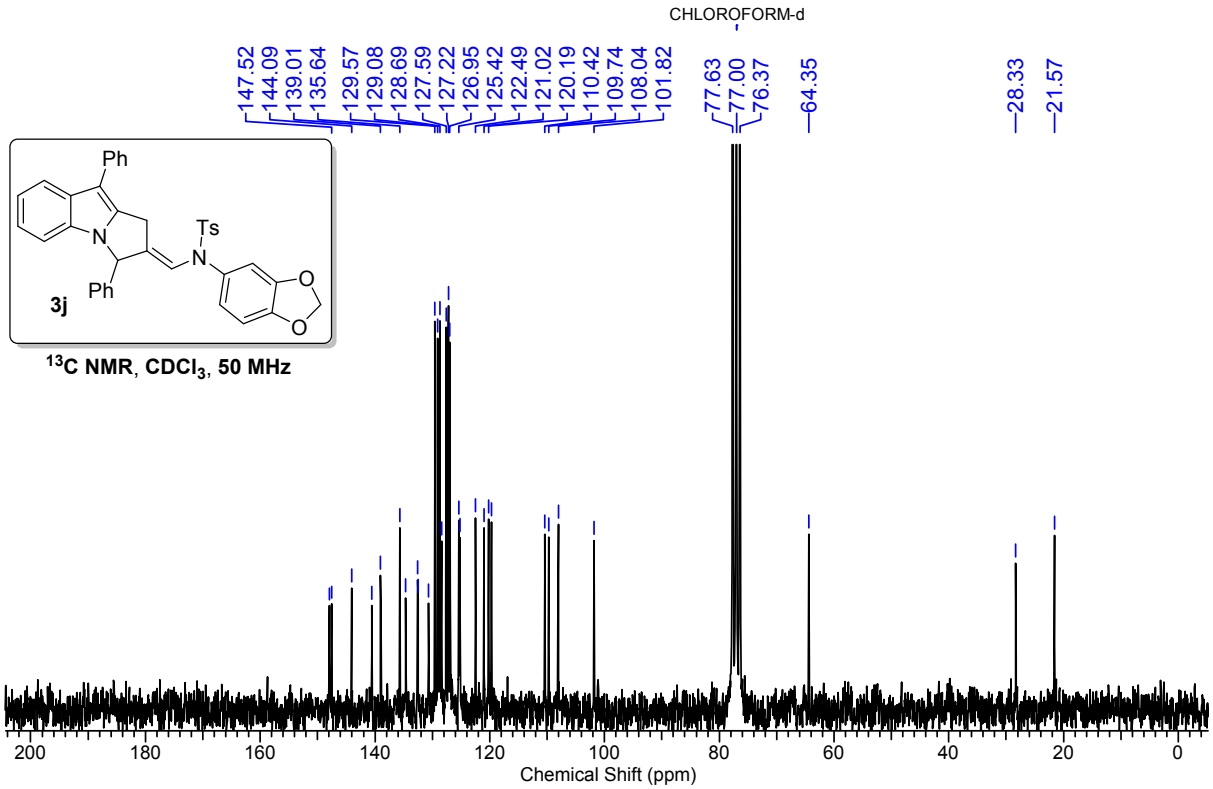
^{1}H NMR, $CDCl_3$, 500 MHz



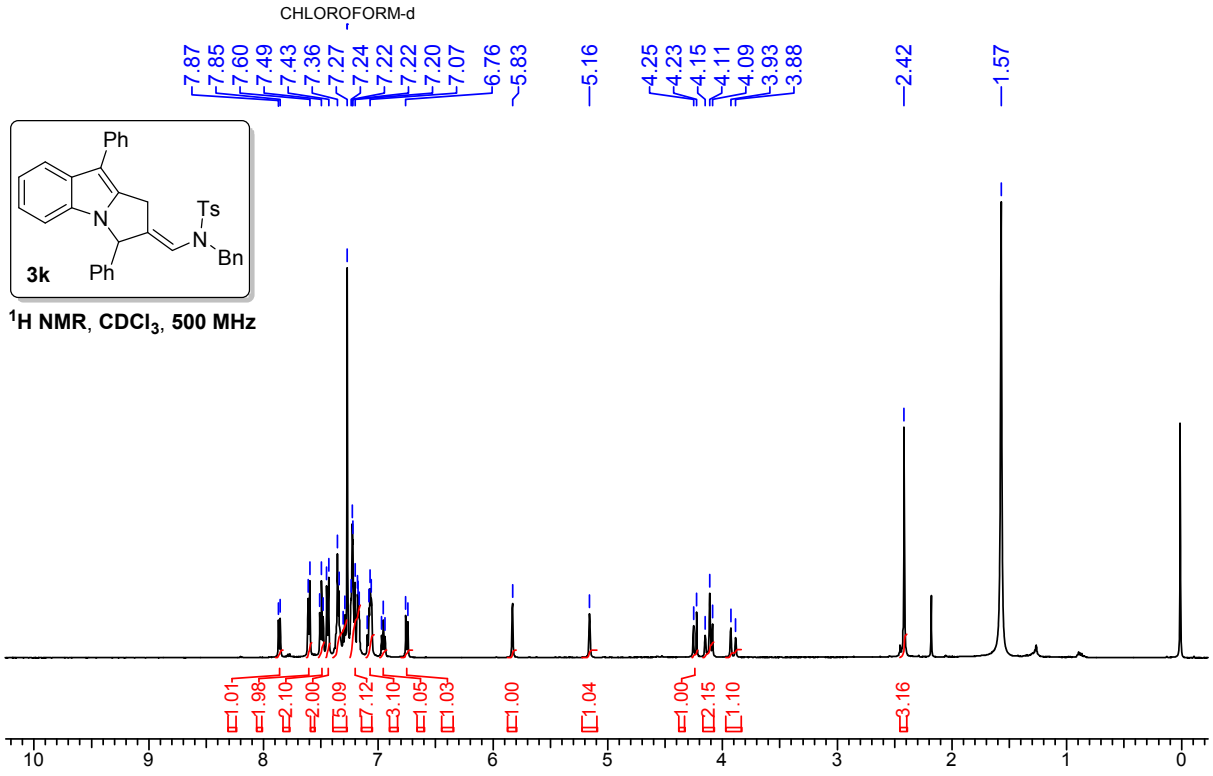
^{13}C NMR, $CDCl_3$, 125 MHz



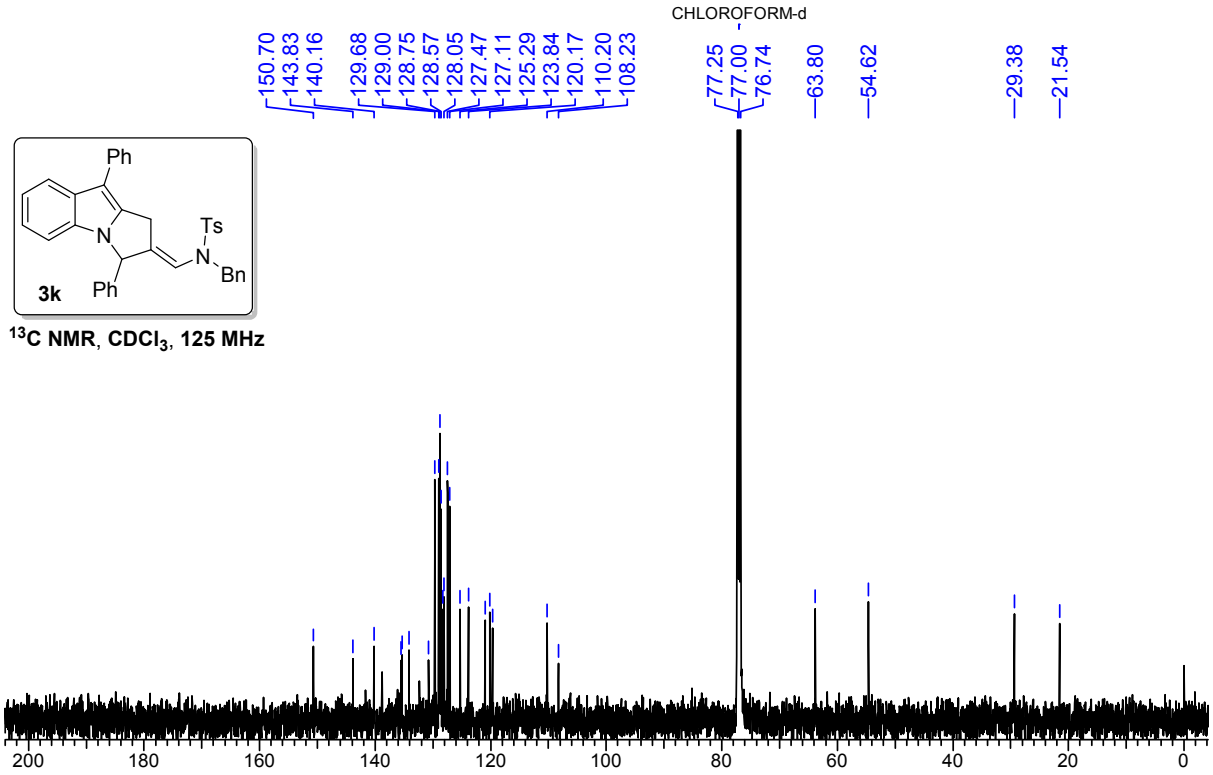
^{1}**H NMR, $CDCl_3$, 200 MHz**



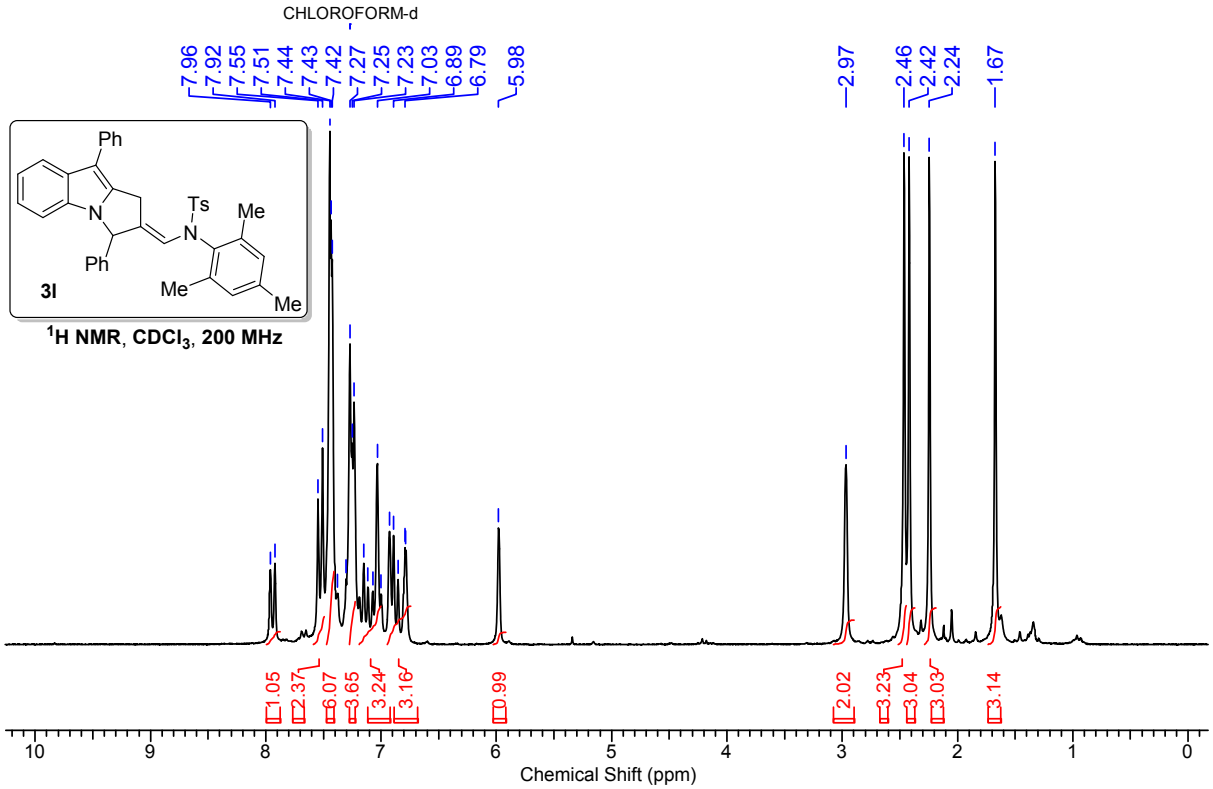
^{13}**C NMR, $CDCl_3$, 50 MHz**

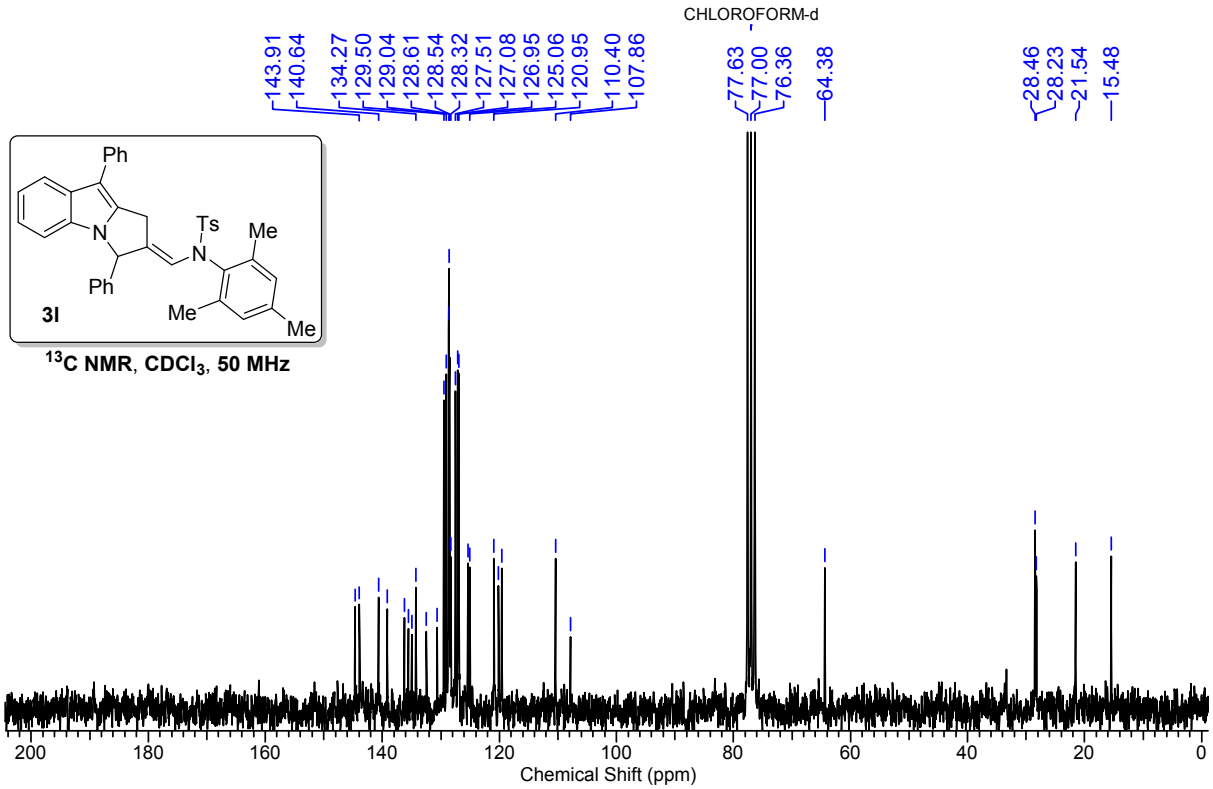


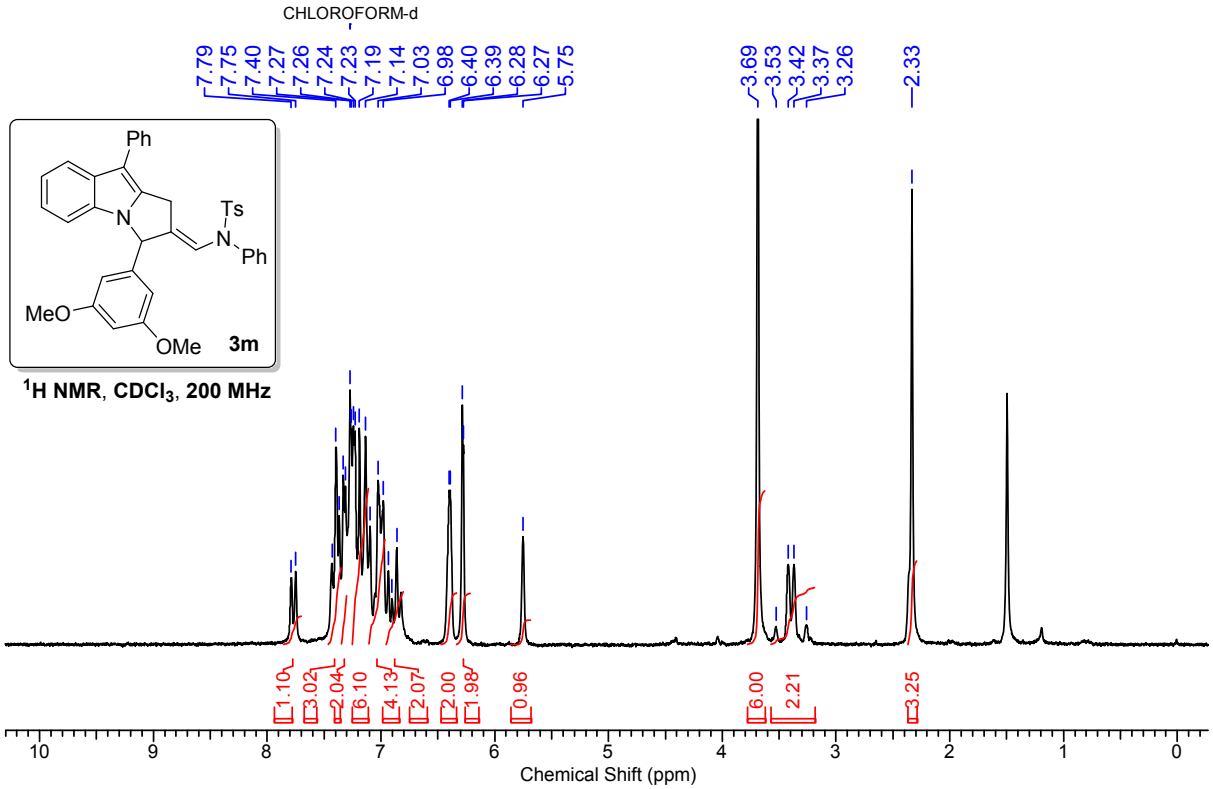
^{1}H NMR, $CDCl_3$, 500 MHz



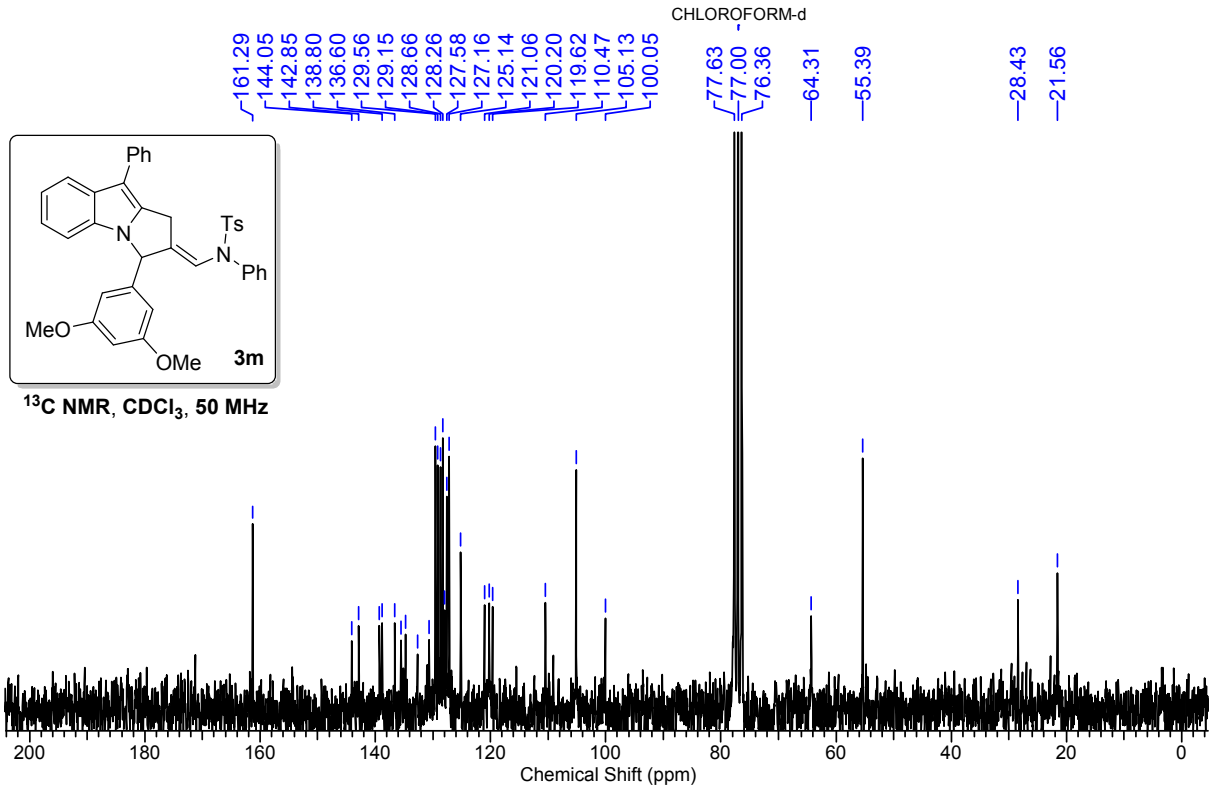
^{13}C NMR, $CDCl_3$, 125 MHz


CHLOROFORM-d
7.96
7.92
7.55
7.51
7.44
7.43
7.42
7.27
7.25
7.23
7.03
6.89
6.79
5.98
2.97
2.46
2.42
2.24
1.67
Ph
N
Ts
N
Me
Ph
Me
Me
3l
1H NMR, CDCl3, 200 MHz
1.05
2.37
6.07
3.65
3.24
3.16
0.99
2.02
3.23
3.04
3.03
3.14
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

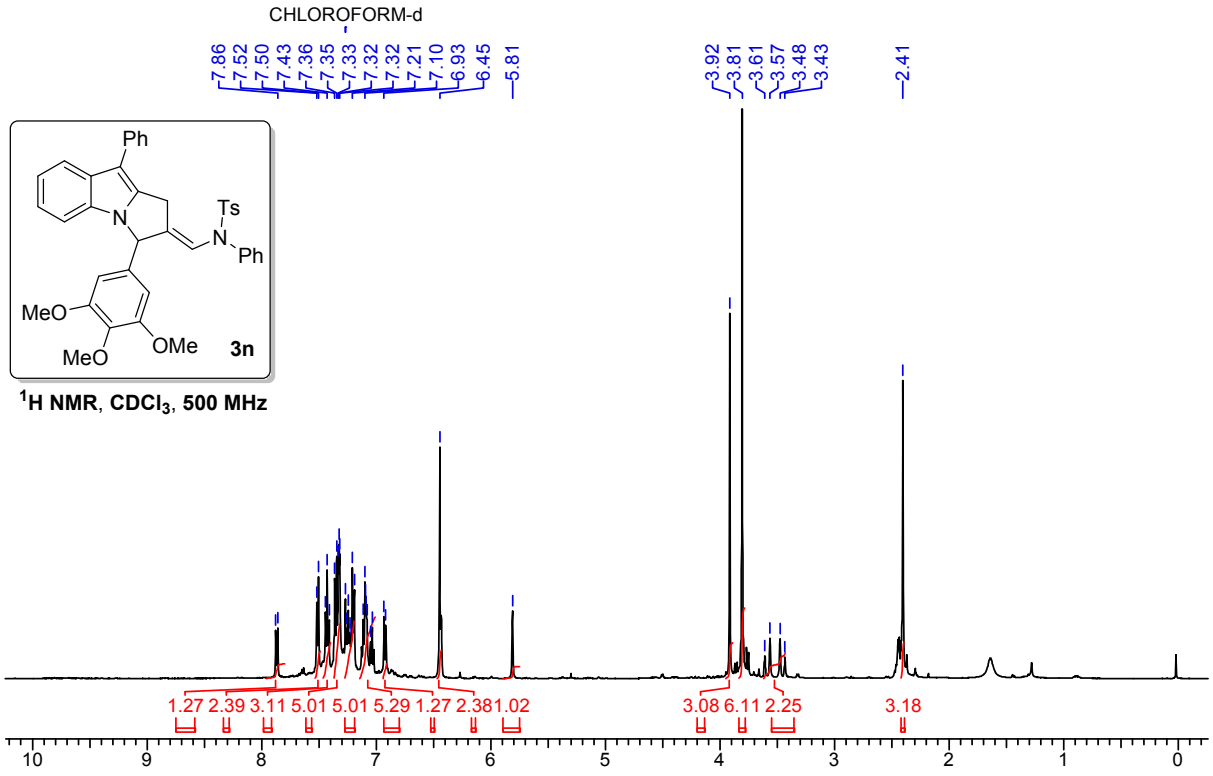

CHLOROFORM-d
143.91
140.64
134.27
129.50
129.04
128.61
128.54
128.32
127.51
127.08
126.95
125.06
120.95
110.40
107.86
77.63
77.00
76.36
64.38
28.46
28.23
21.54
15.48
Ph
N
Ts
N
Me
Ph
Me
Me
3l
13C NMR, CDCl3, 50 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



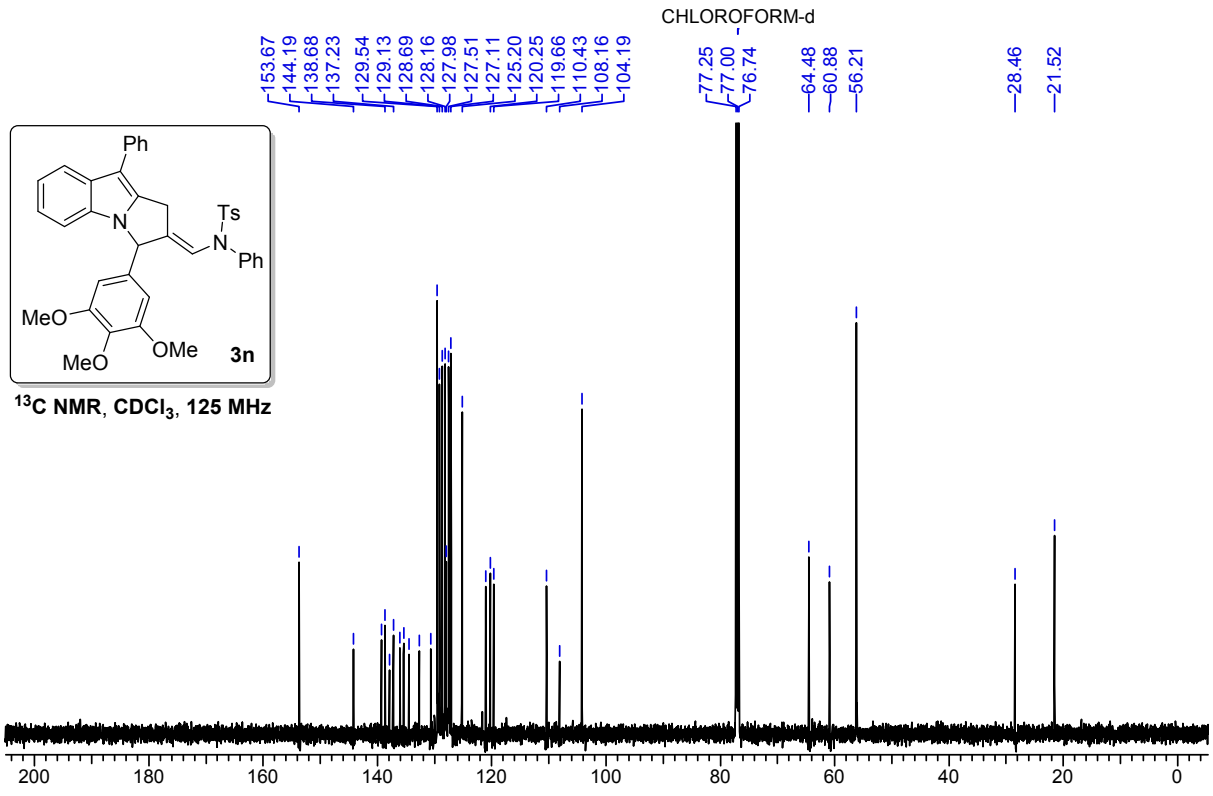
^{1}**H NMR, $CDCl_3$, 200 MHz**



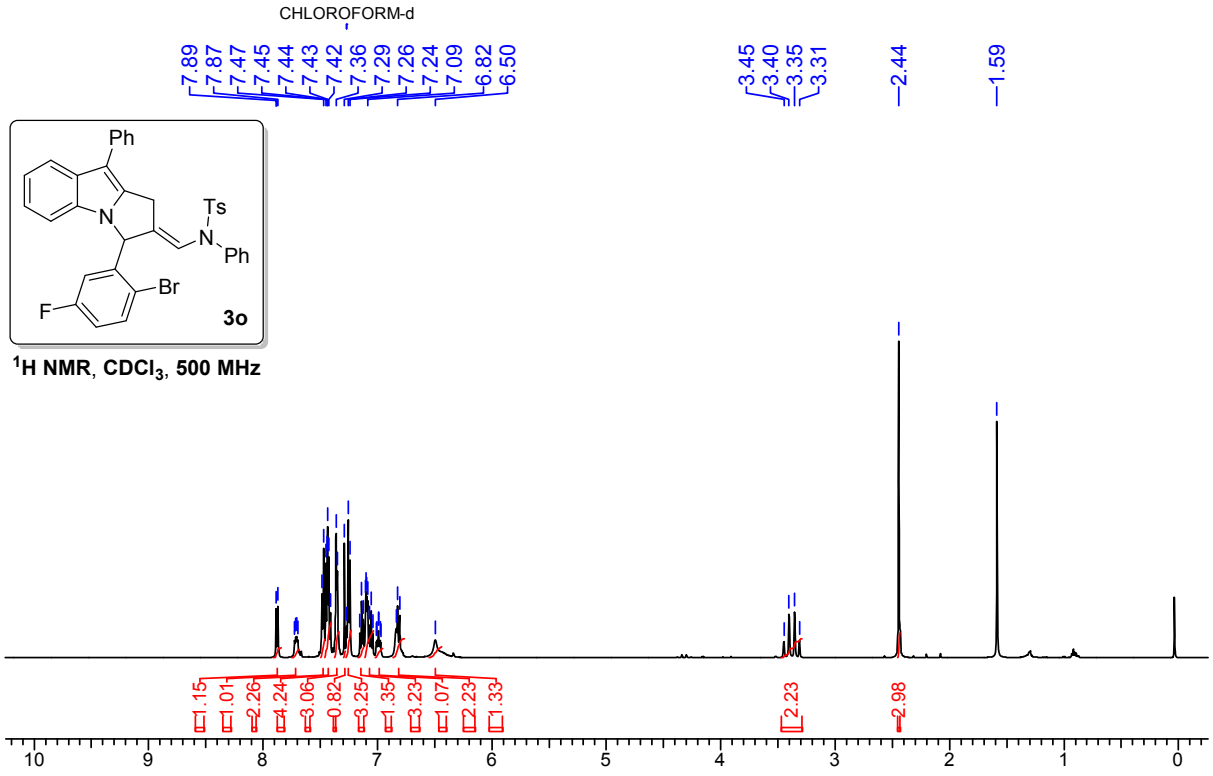
^{13}**C NMR, $CDCl_3$, 50 MHz**



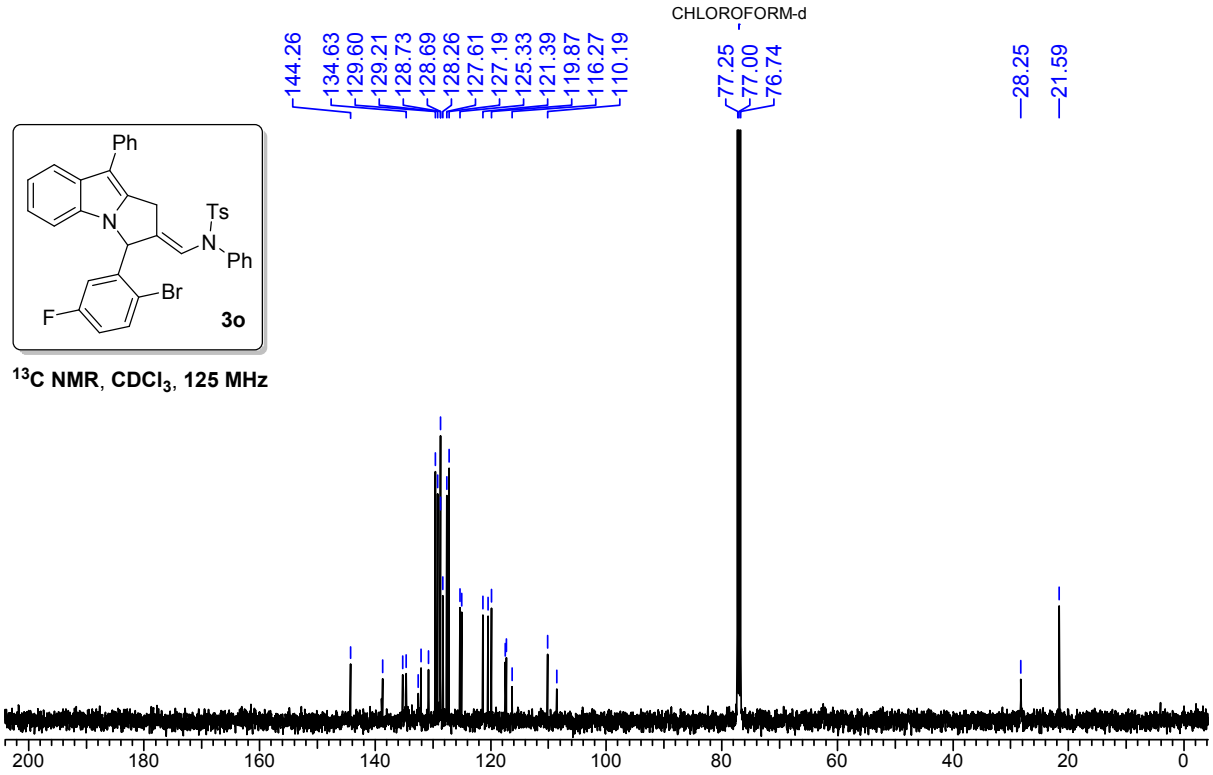
^{1}H NMR, $CDCl_3$, 500 MHz



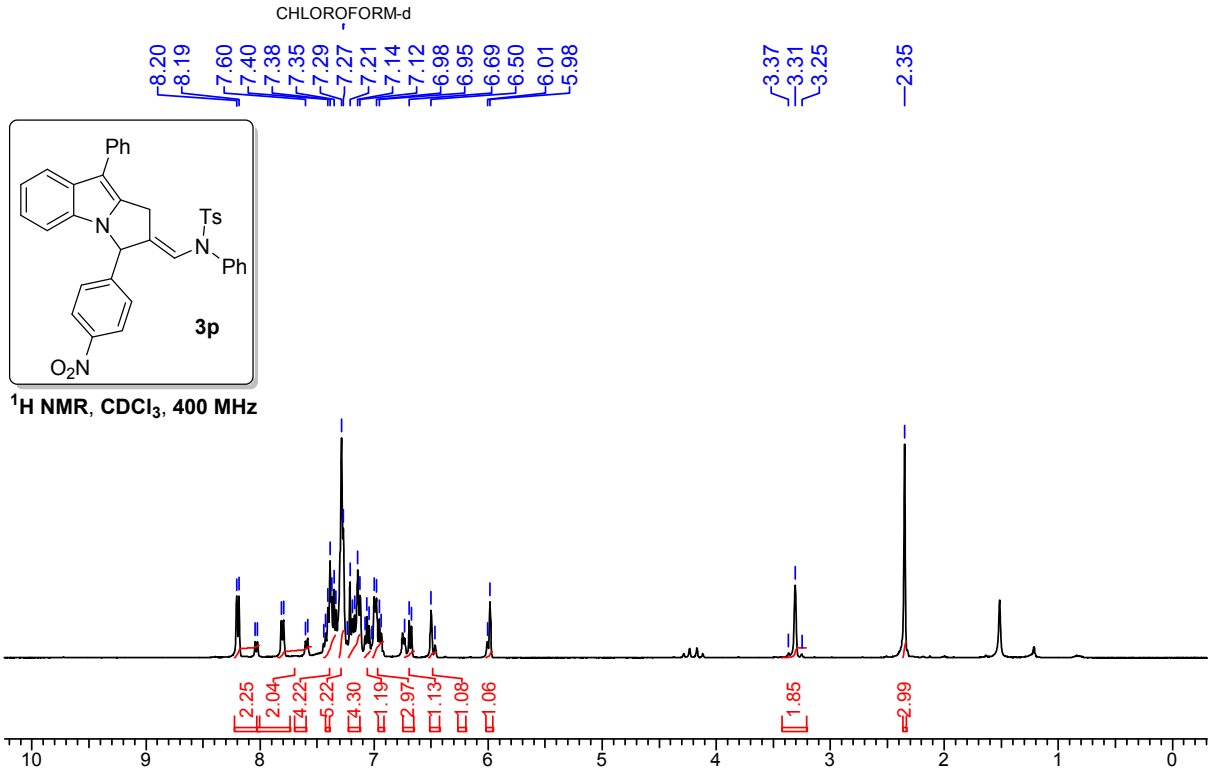
^{13}C NMR, $CDCl_3$, 125 MHz



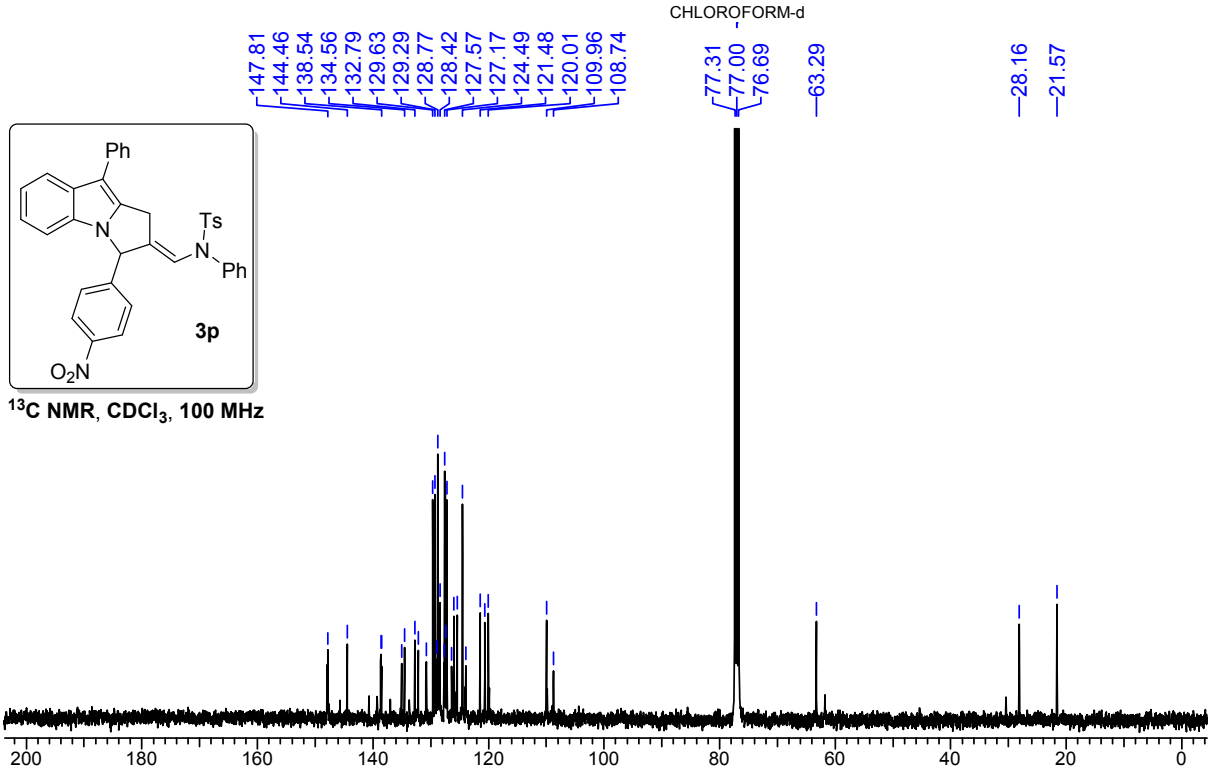
^{1}H NMR, $CDCl_3$, 500 MHz



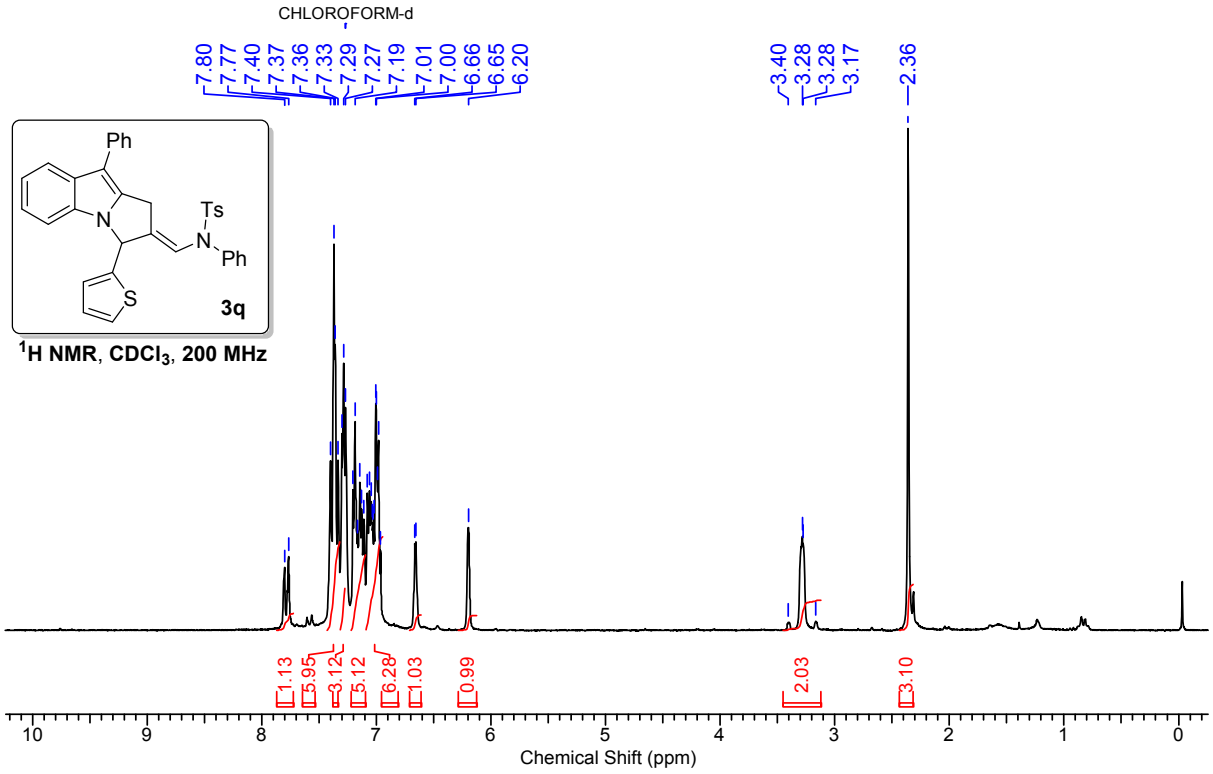
^{13}C NMR, $CDCl_3$, 125 MHz



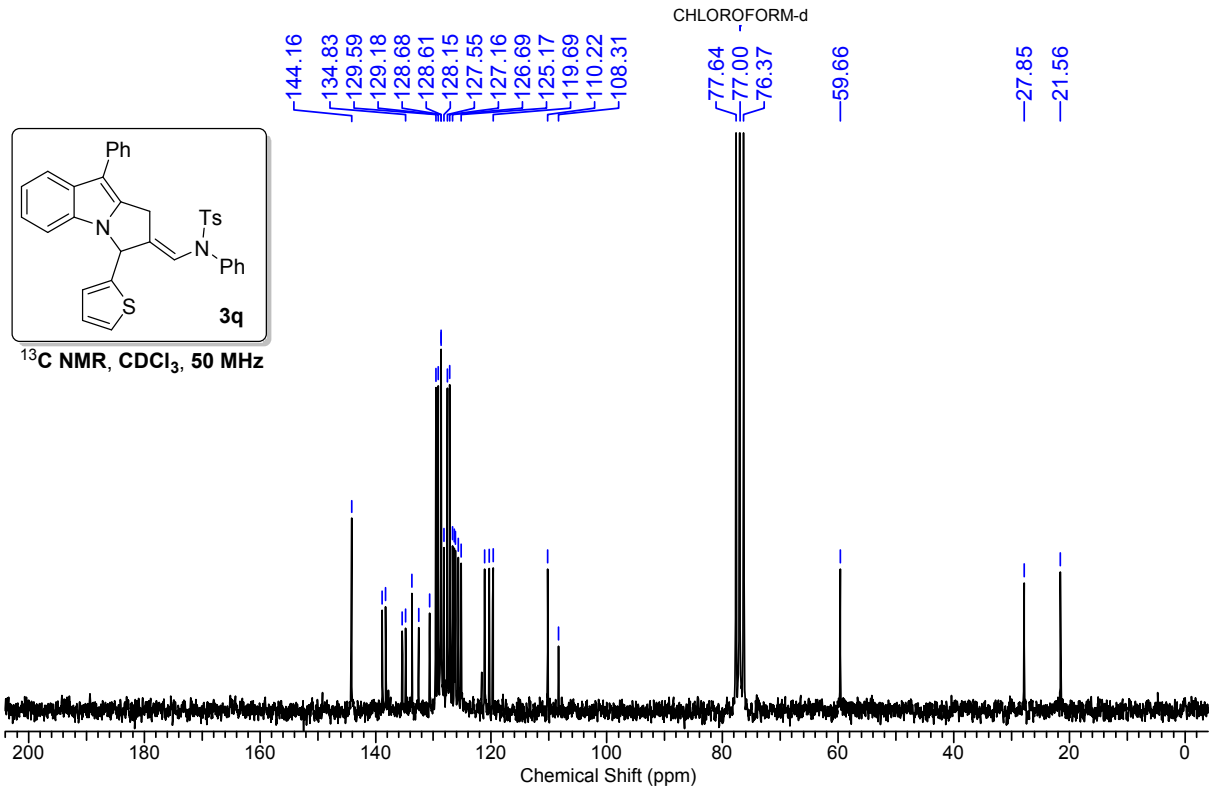
^{1}H NMR, $CDCl_3$, 400 MHz



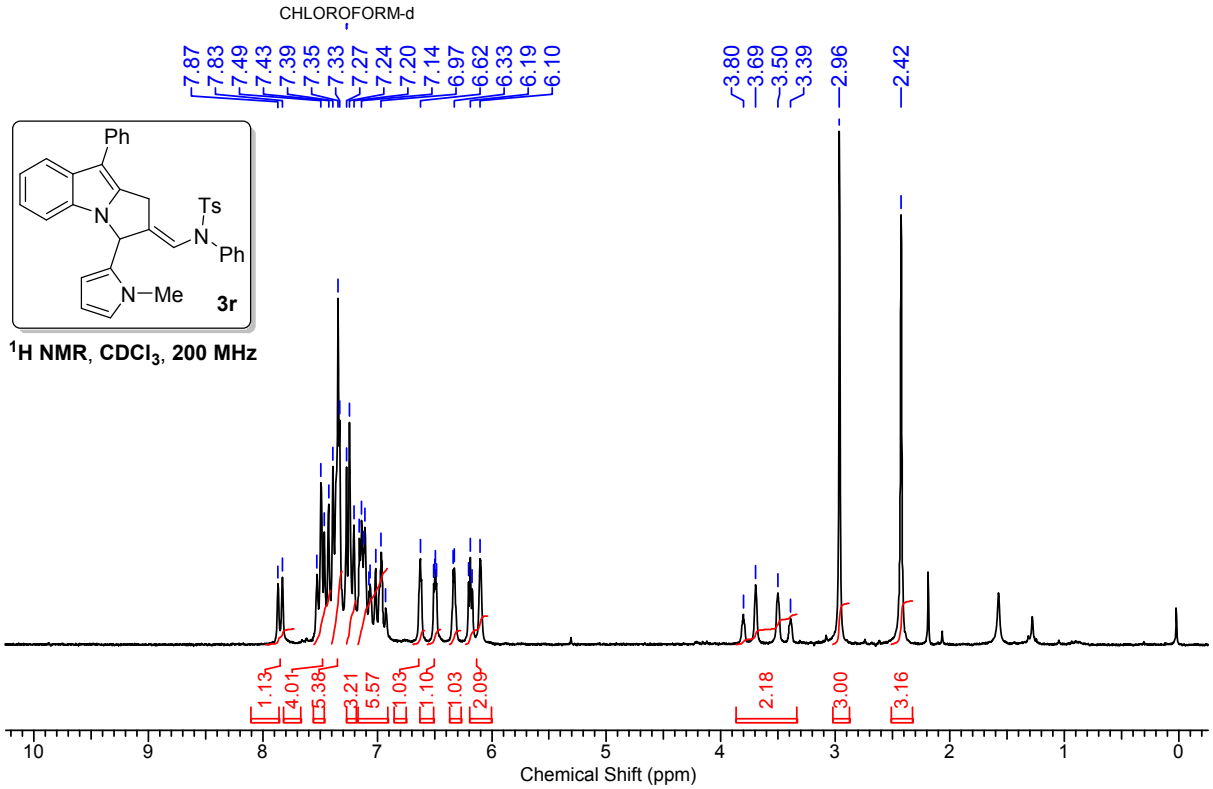
^{13}C NMR, $CDCl_3$, 100 MHz



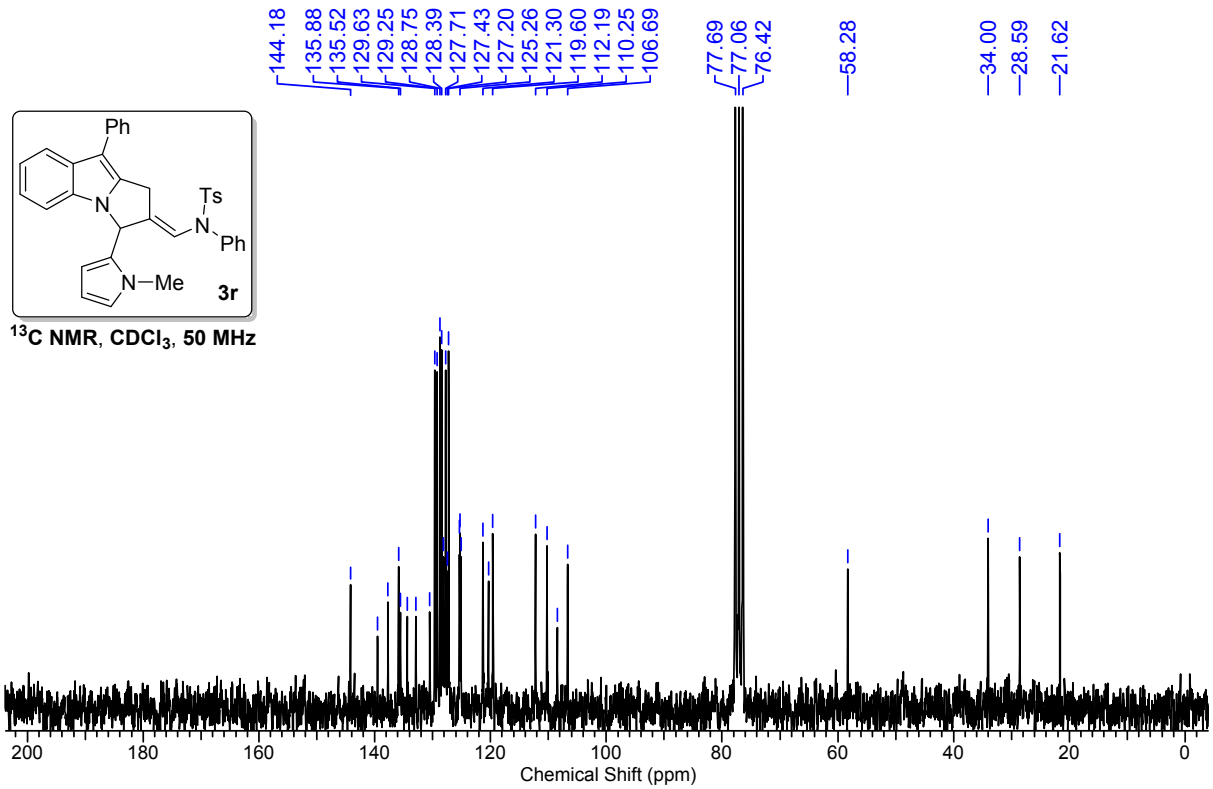
^{1}**H NMR, $CDCl_3$, 200 MHz**



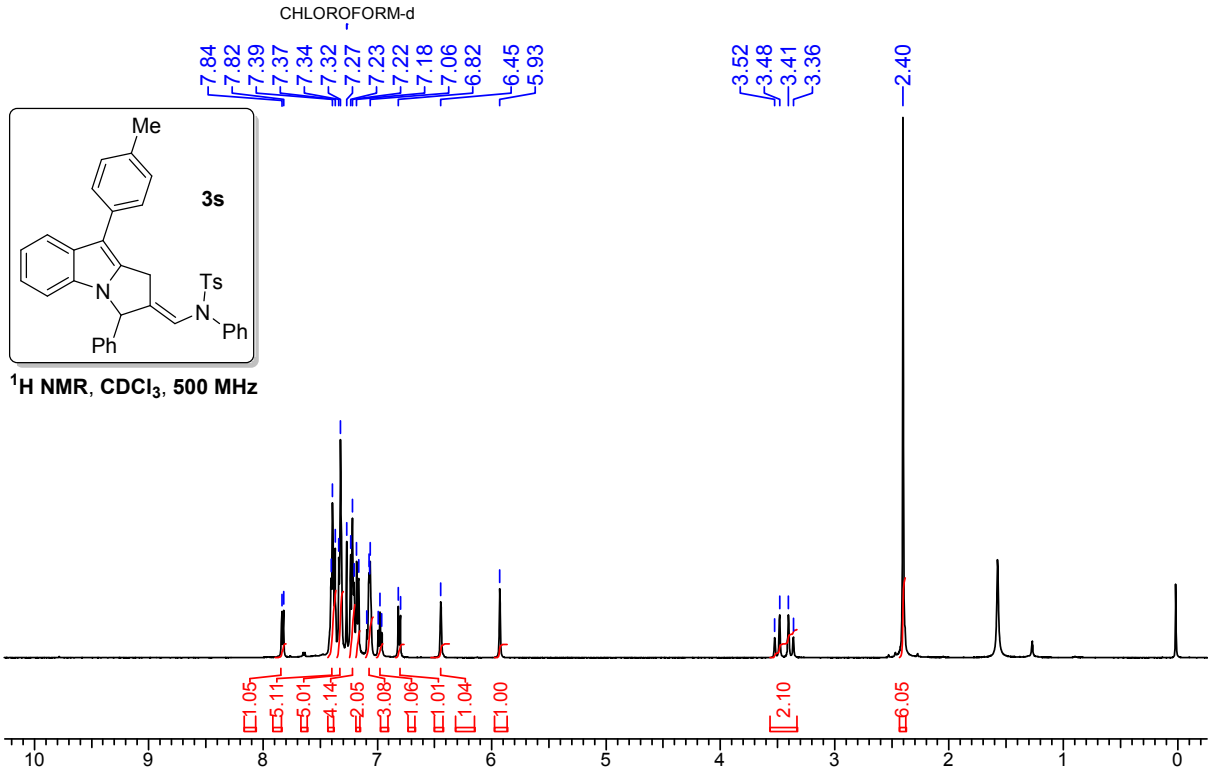
^{13}**C NMR, $CDCl_3$, 50 MHz**



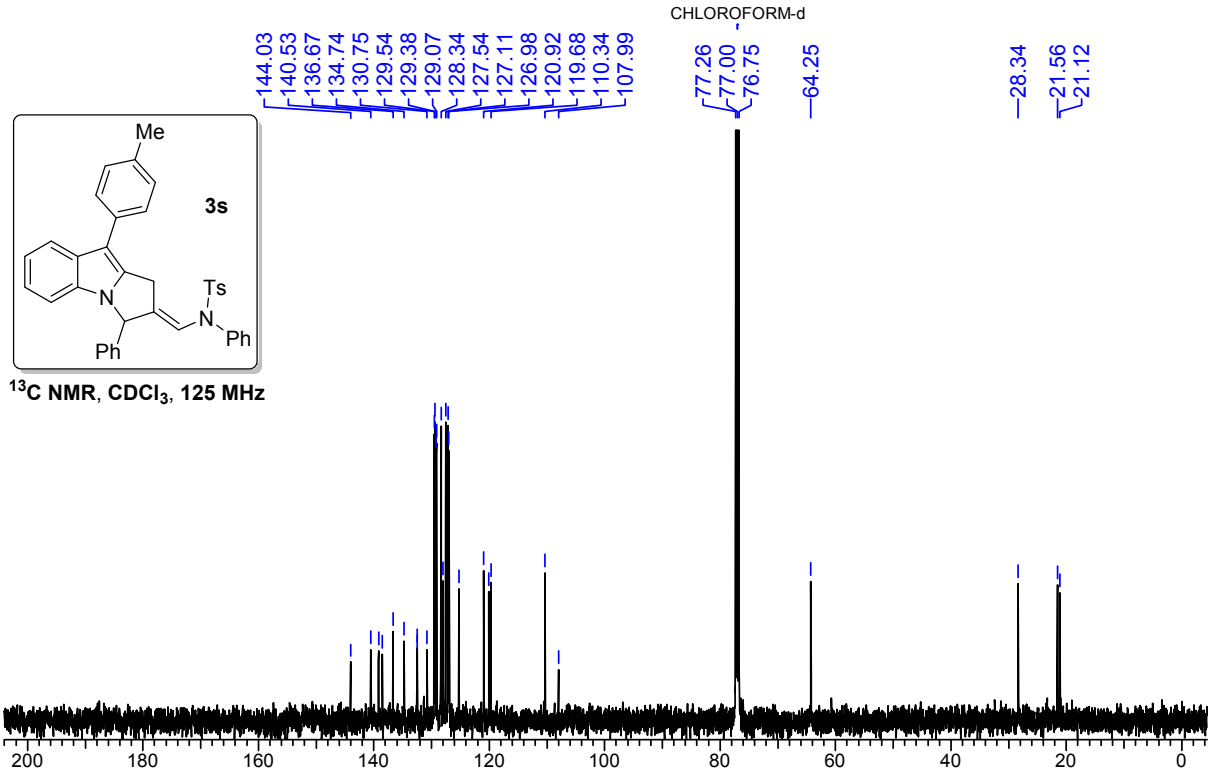
^{1}H NMR, $CDCl_3$, 200 MHz



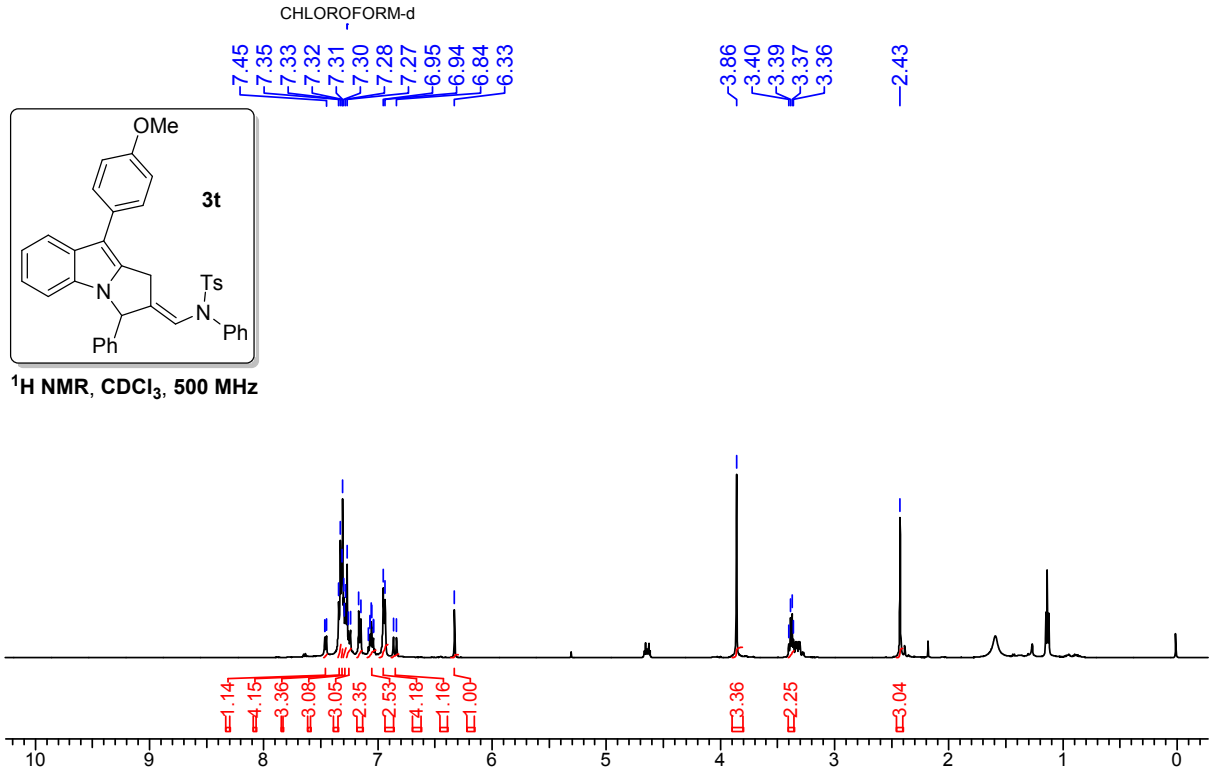
^{13}C NMR, $CDCl_3$, 50 MHz



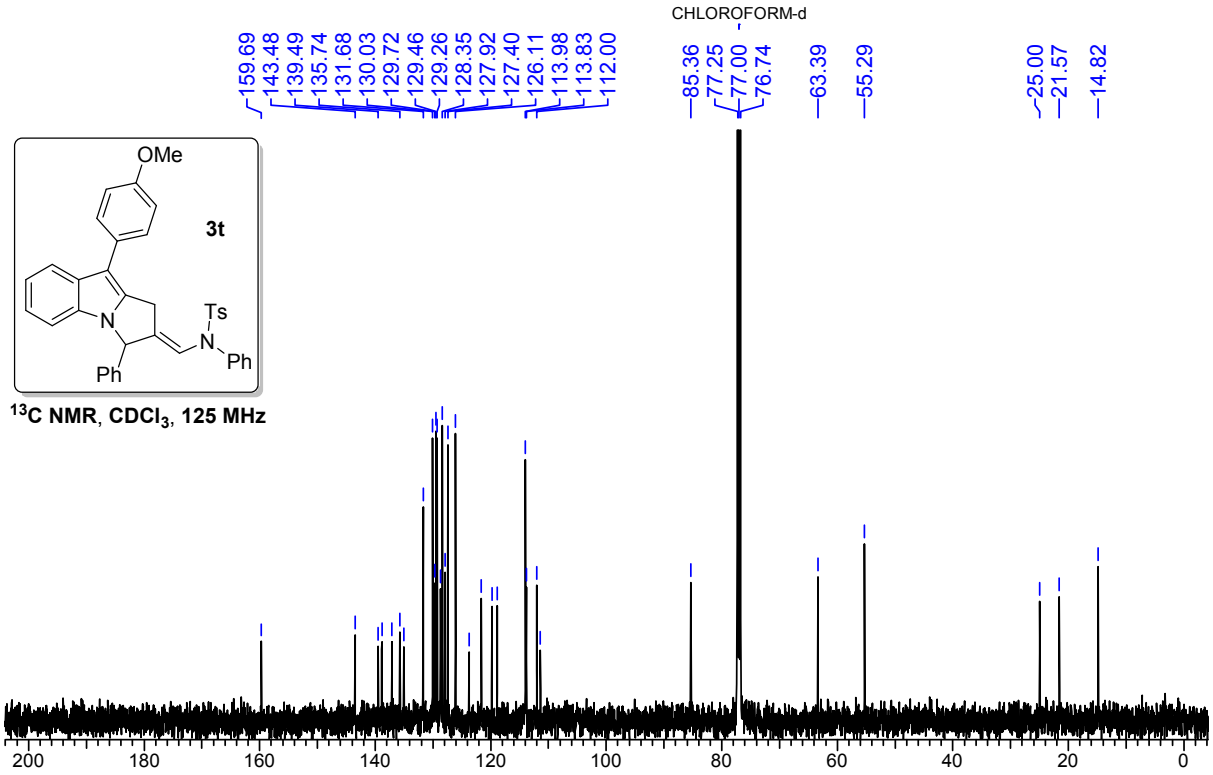
^{1}H NMR, $CDCl_3$, 500 MHz



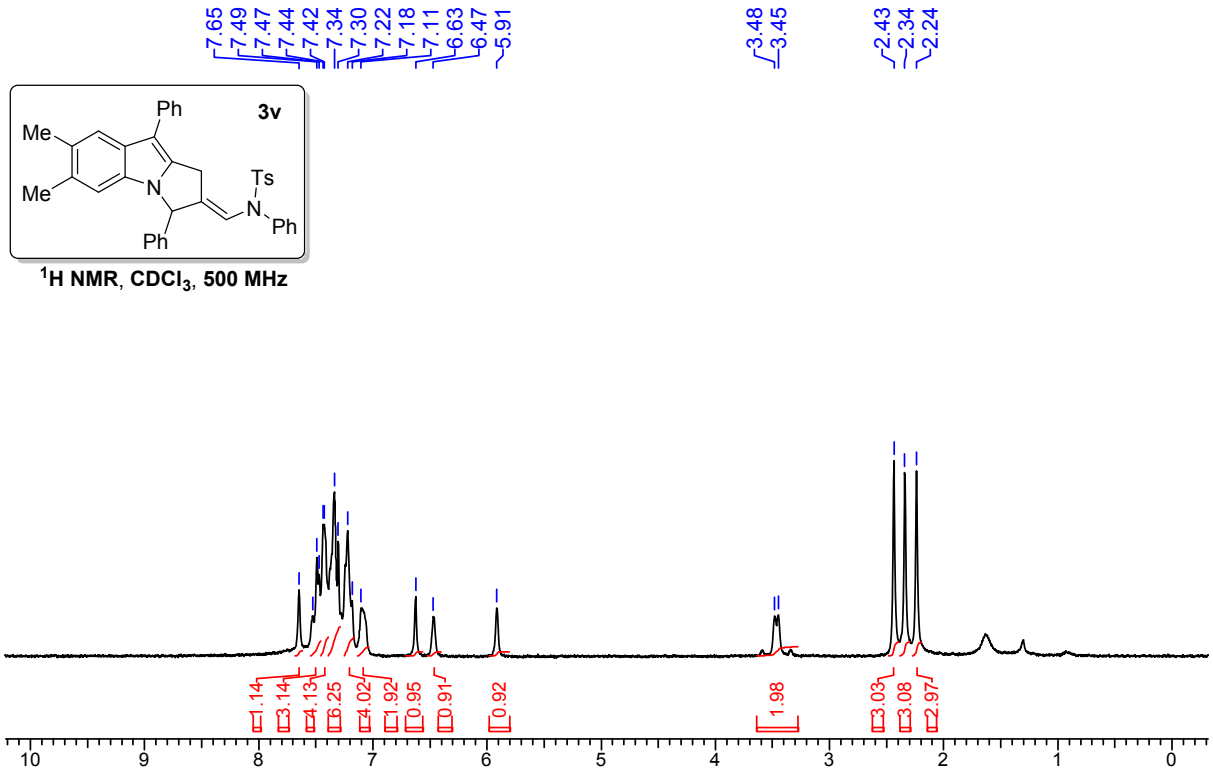
^{13}C NMR, $CDCl_3$, 125 MHz



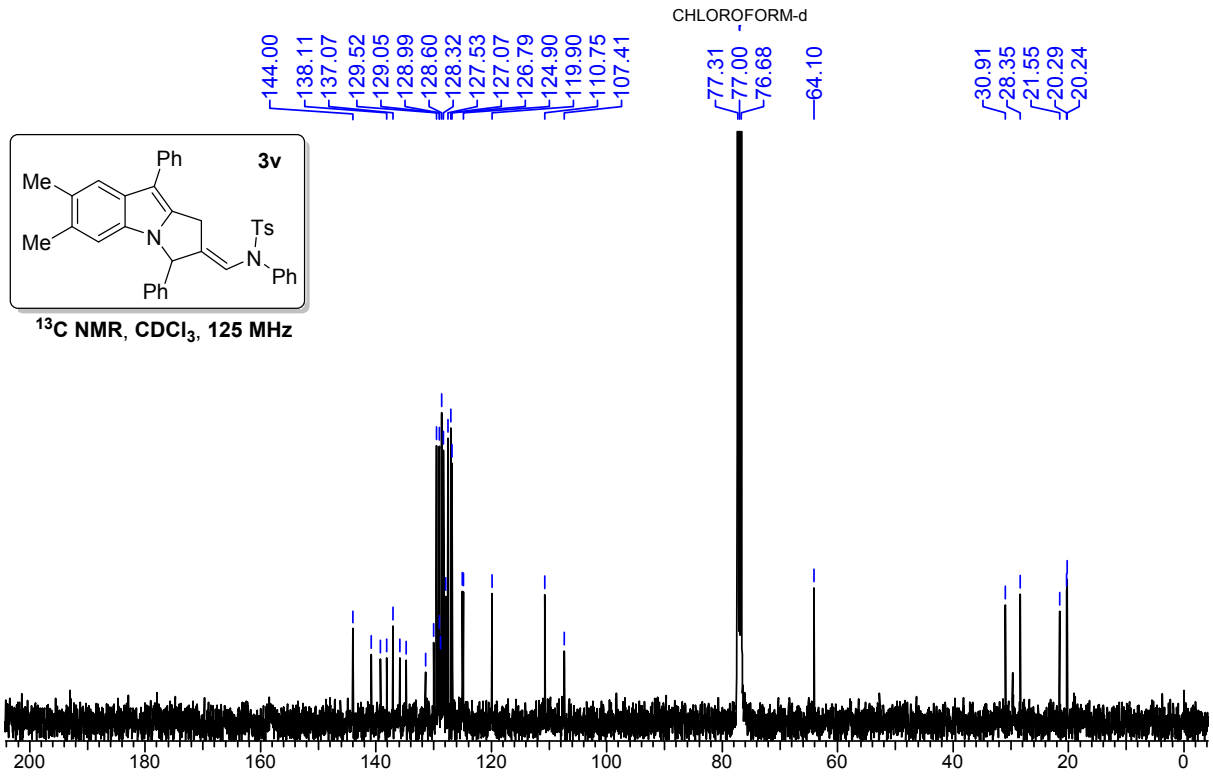
^{1}H NMR, $CDCl_3$, 500 MHz



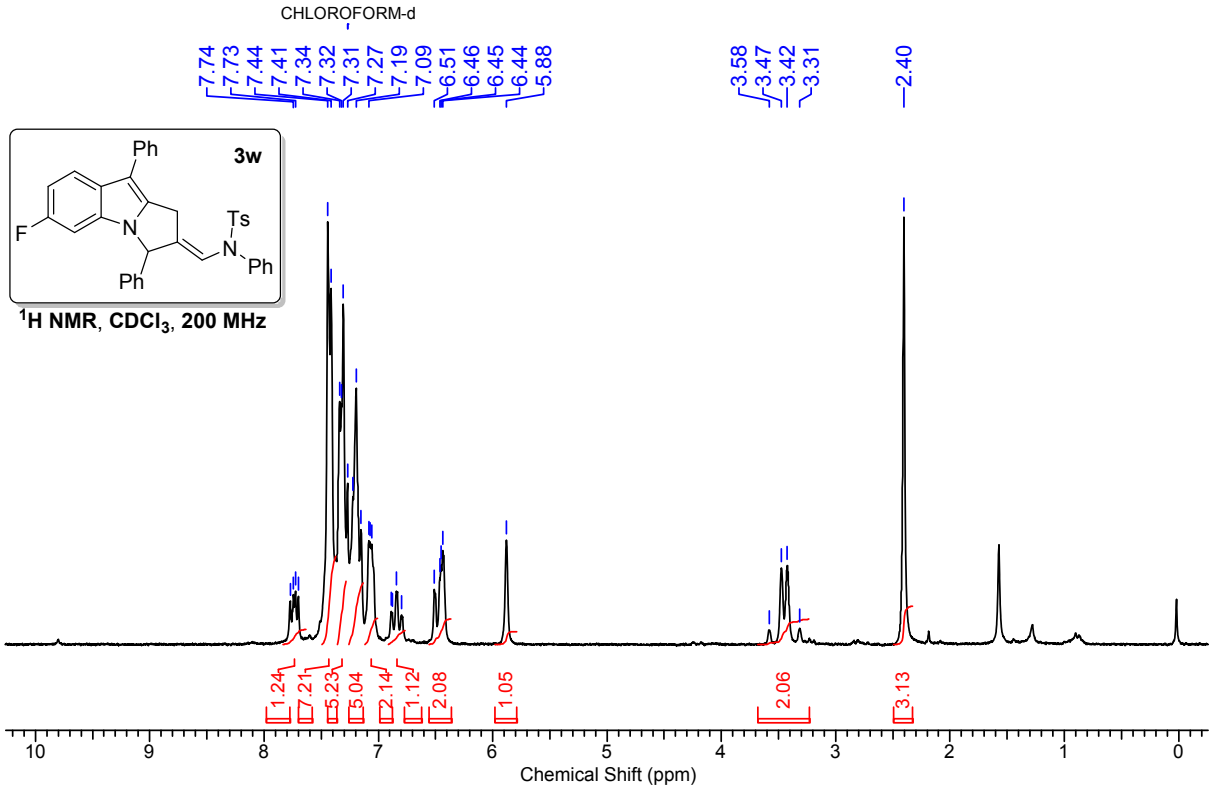
^{13}C NMR, $CDCl_3$, 125 MHz

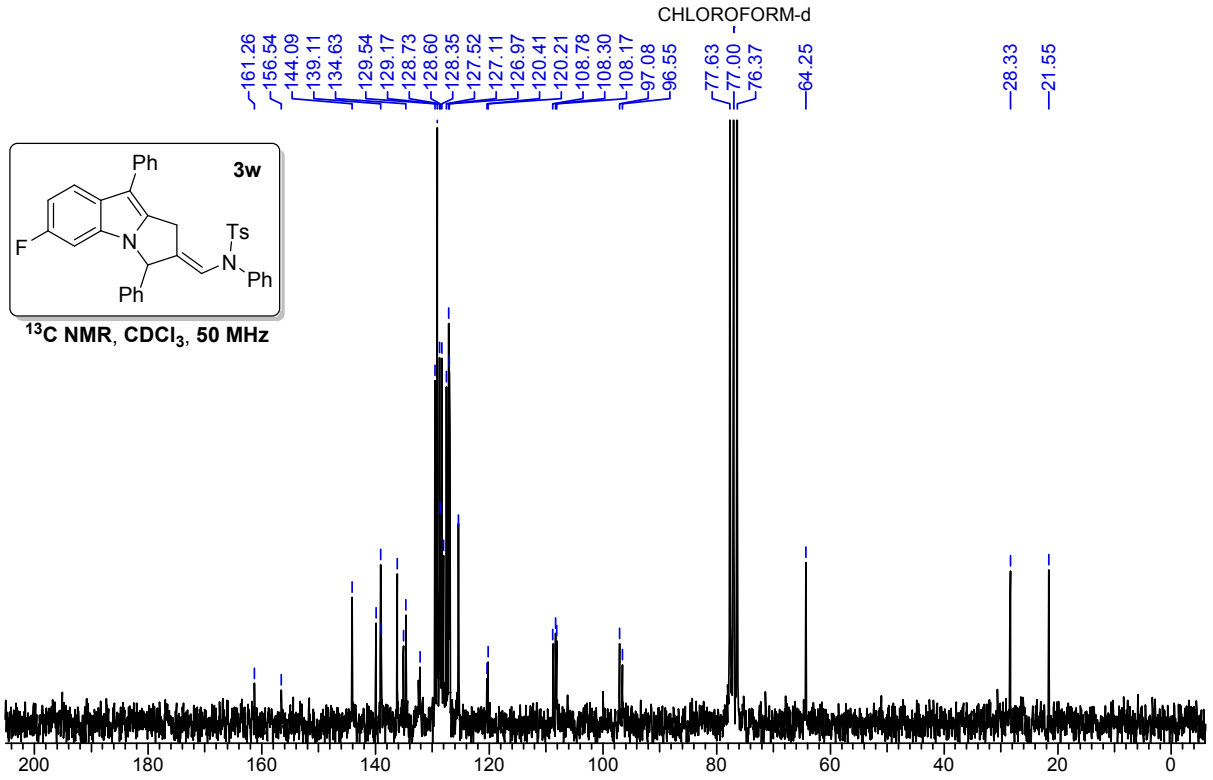


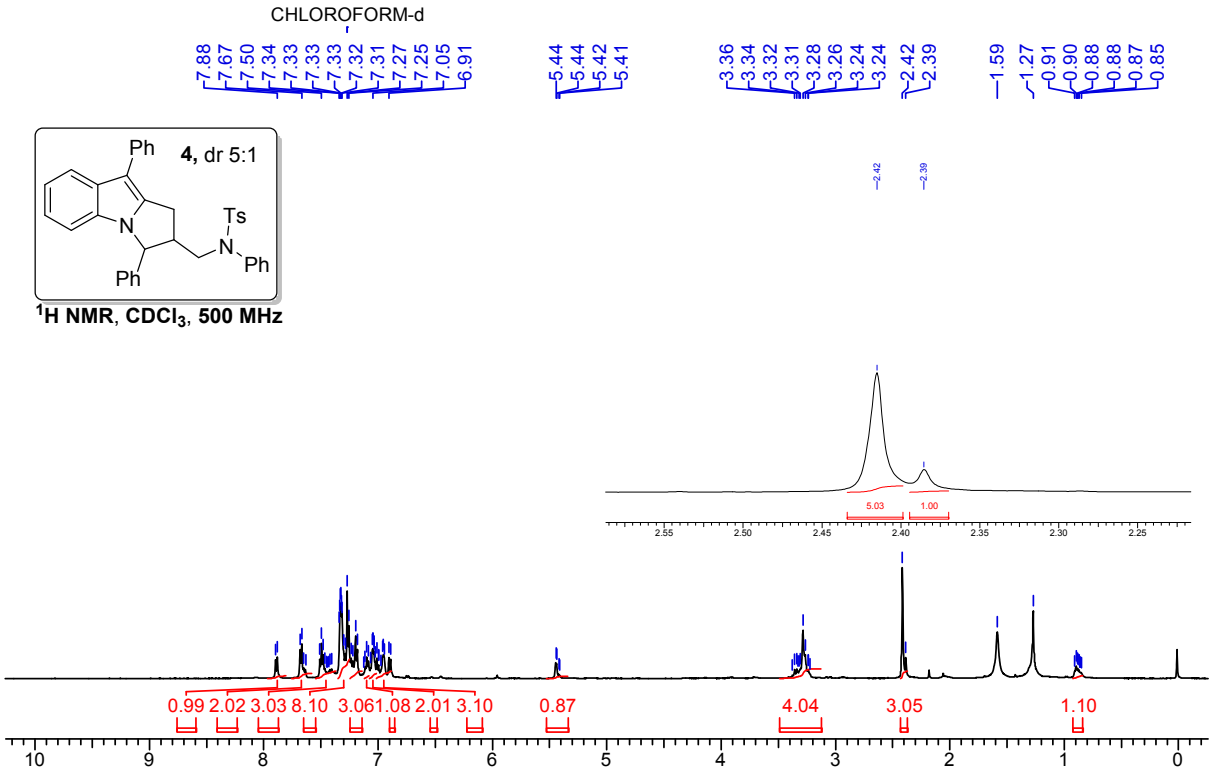
^{1}H NMR, $CDCl_3$, 500 MHz



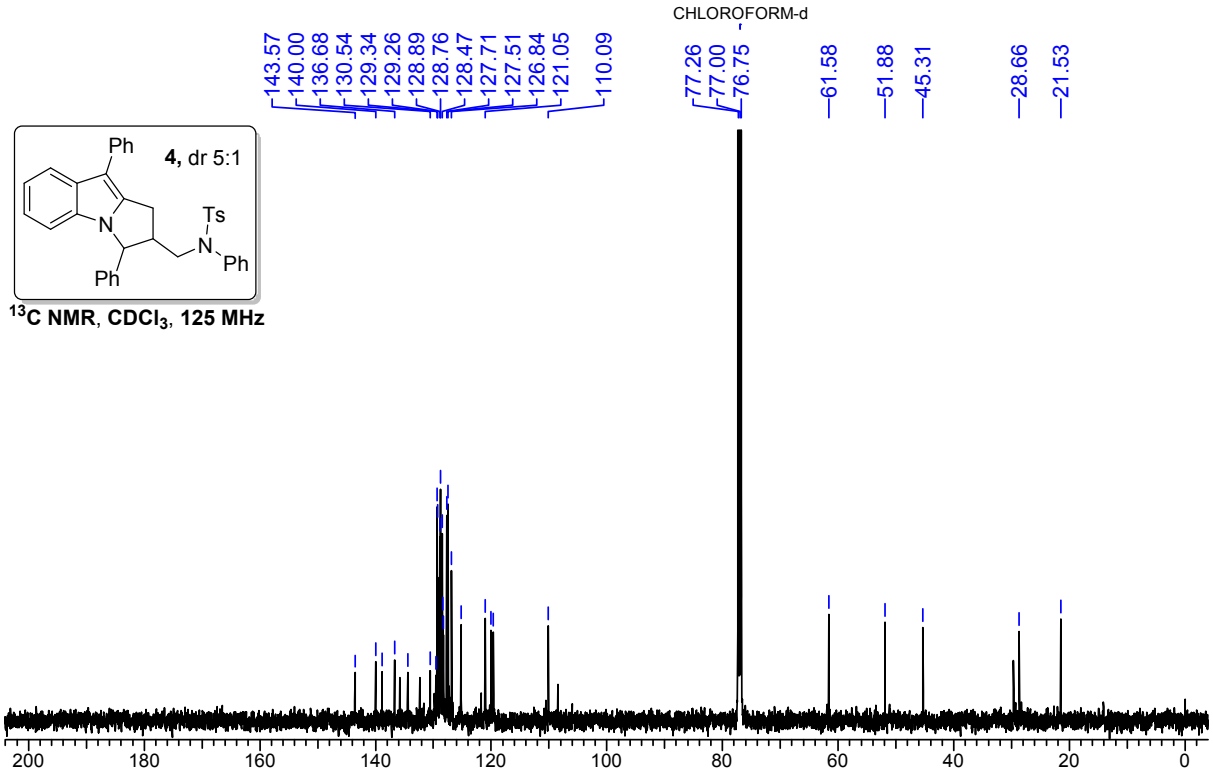
^{13}C NMR, $CDCl_3$, 125 MHz


CHLOROFORM-d
7.74
7.73
7.44
7.41
7.34
7.32
7.31
7.27
7.19
7.09
6.51
6.46
6.45
6.44
5.88
3.58
3.47
3.42
3.31
2.40
3w
Ph
F
N
Ts
N
Ph
Ph
1H NMR, CDCl3, 200 MHz
1.24
7.21
5.23
5.04
2.14
1.12
2.08
1.05
2.06
3.13
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

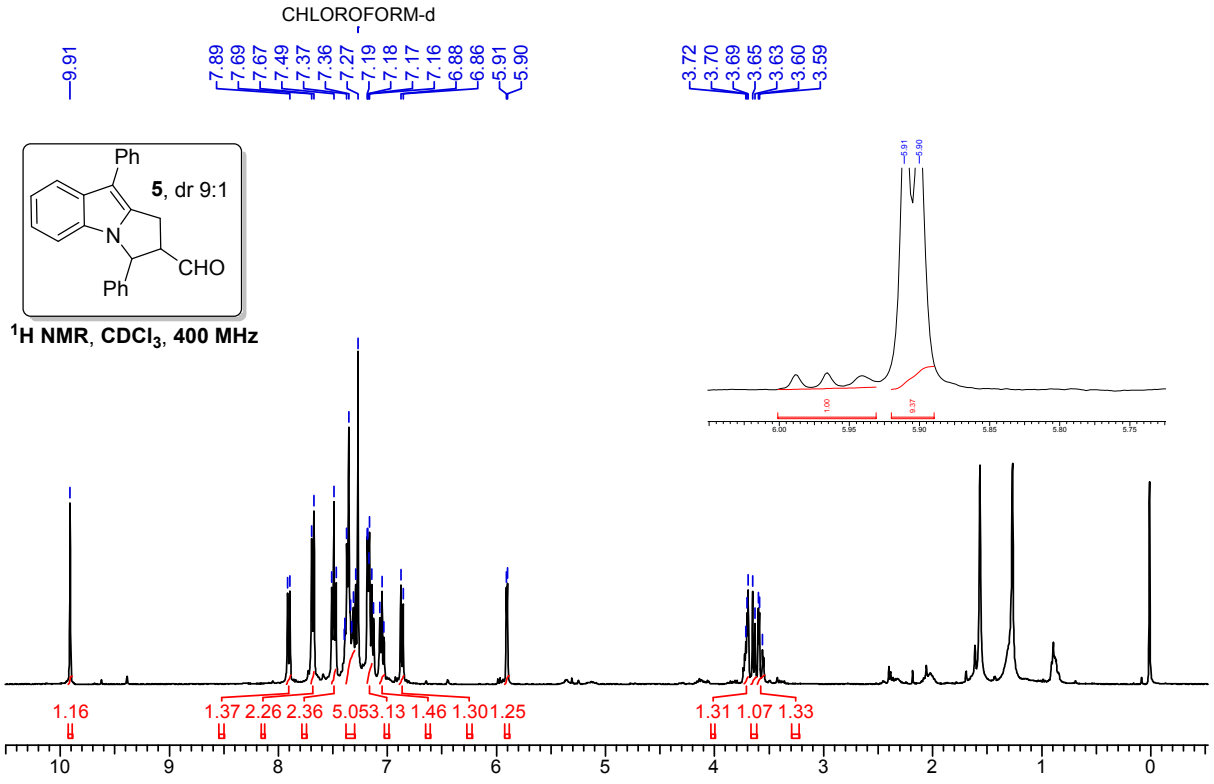

CHLOROFORM-d
161.26
156.54
144.09
139.11
134.63
129.54
129.17
128.73
128.60
128.35
127.52
127.11
126.97
120.41
120.21
108.78
108.30
108.17
97.08
96.55
77.63
77.00
76.37
64.25
28.33
21.55
3w
Ph
F
N
Ts
N
Ph
Ph
13C NMR, CDCl3, 50 MHz
200
180
160
140
120
100
80
60
40
20
0

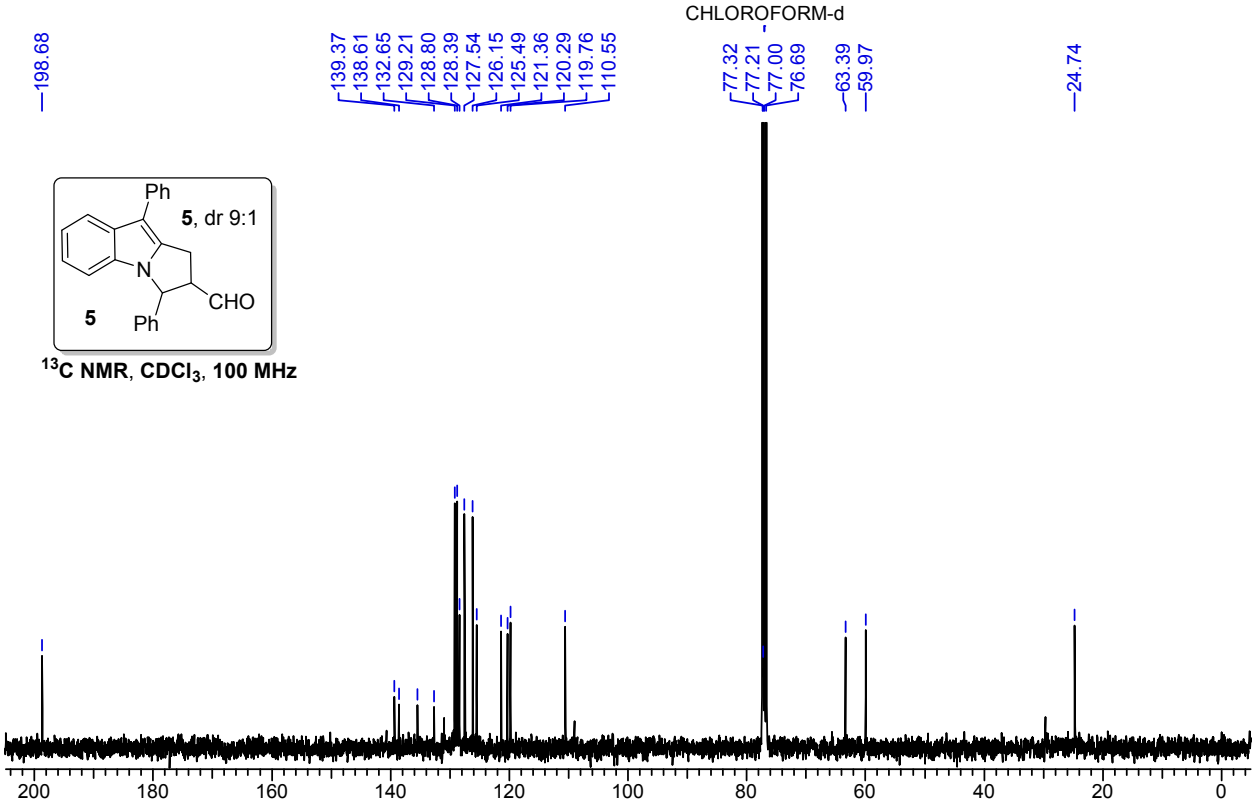


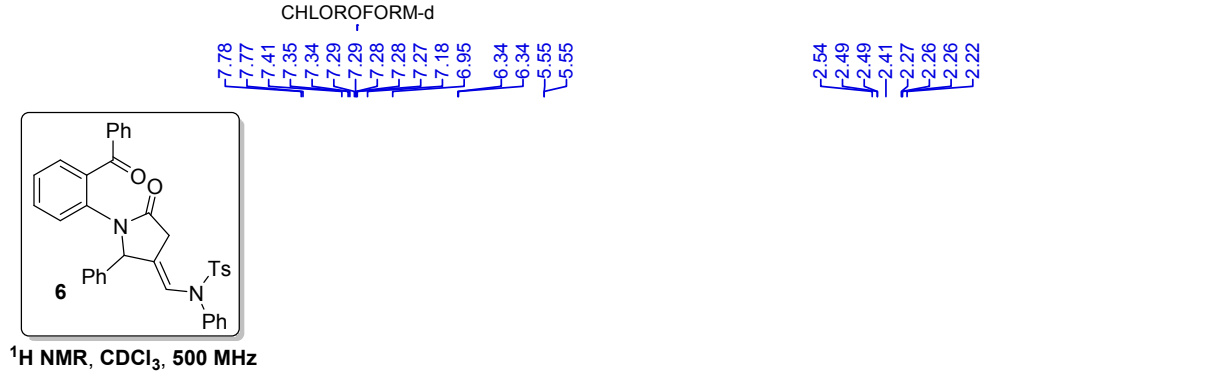
^{1}H NMR, $CDCl_3$, 500 MHz



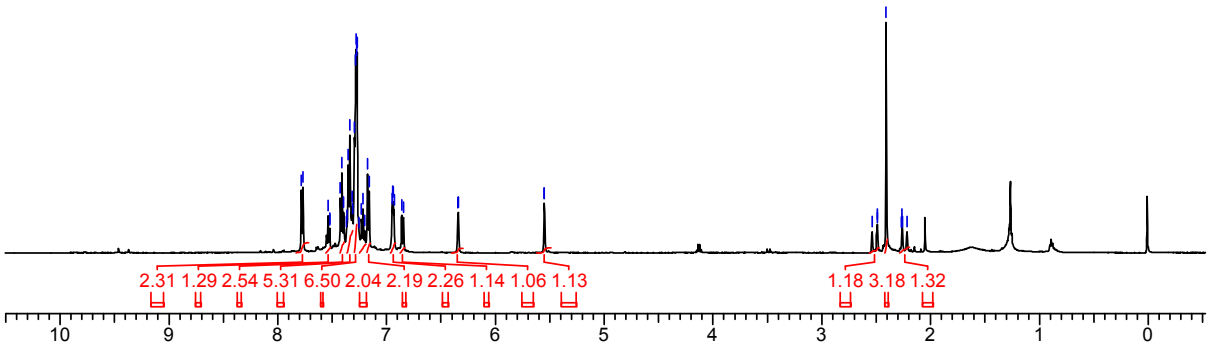
^{13}C NMR, $CDCl_3$, 125 MHz

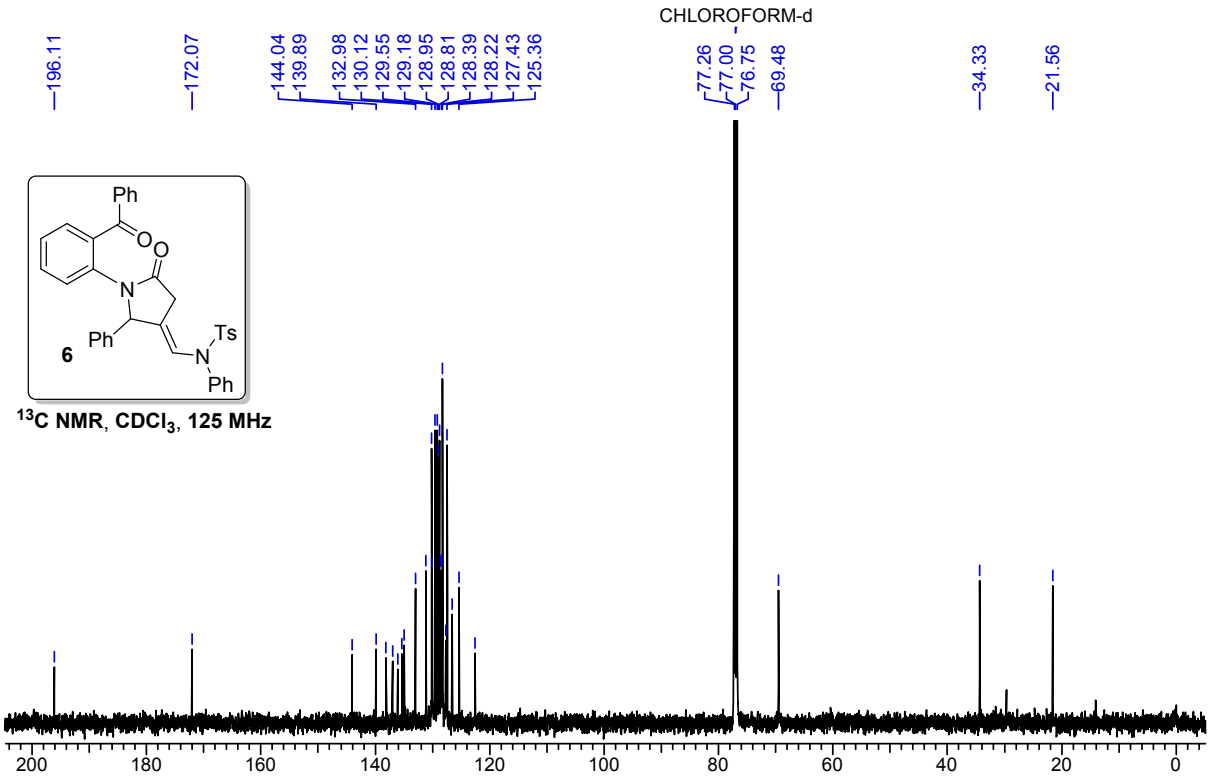

CHLOROFORM-d
9.91
7.89
7.69
7.67
7.49
7.37
7.36
7.27
7.19
7.18
7.17
7.16
6.88
6.86
5.91
5.90
3.72
3.70
3.69
3.65
3.63
3.60
3.59
Ph
5, dr 9:1
N
CHO
Ph
1H NMR, CDCl3, 400 MHz
1.16
1.37 2.26 2.36 5.05 3.13 1.46 1.30 1.25
1.31 1.07 1.33
10
9
8
7
6
5
4
3
2
1
0


CHLOROFORM-d
198.68
139.37
138.61
132.65
129.21
128.80
128.39
127.54
126.15
125.49
121.36
120.29
119.76
110.55
77.32
77.21
77.00
76.69
63.39
59.97
24.74
Ph
5, dr 9:1
N
CHO
5
Ph
13C NMR, CDCl3, 100 MHz
200
180
160
140
120
100
80
60
40
20
0



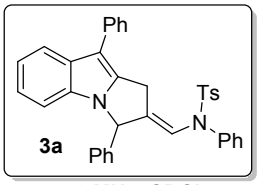
^{1}H NMR, $CDCl_3$, 500 MHz





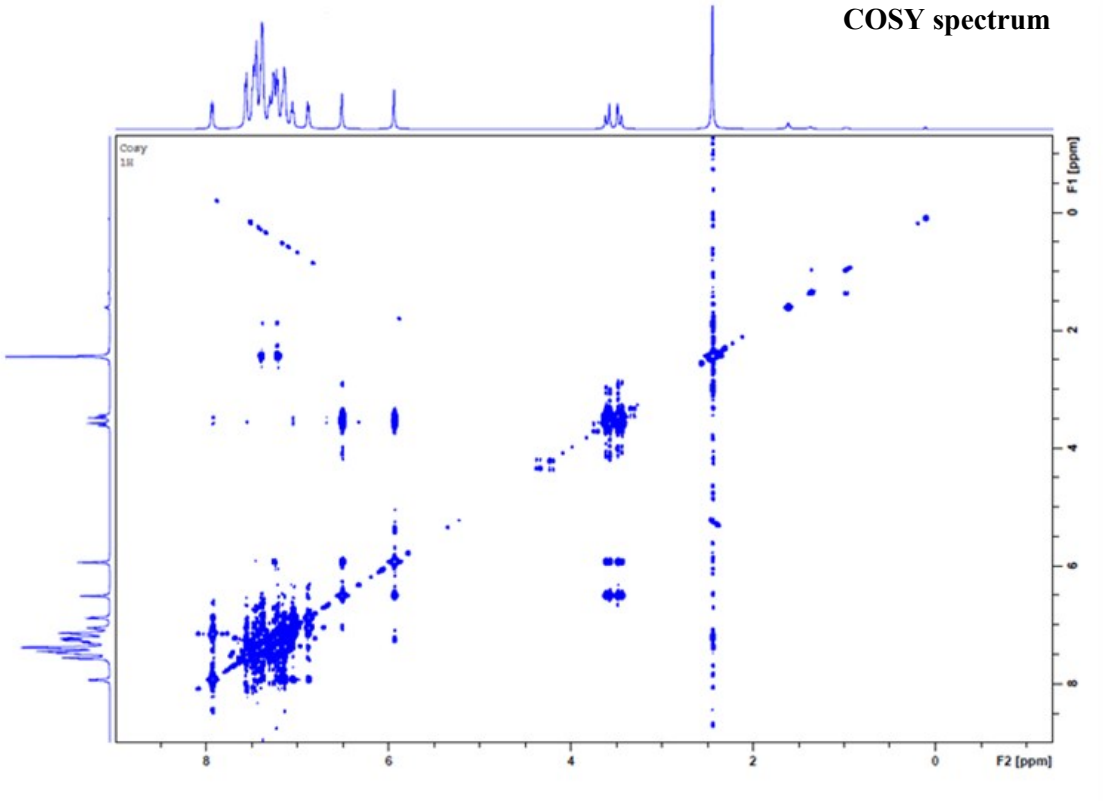
^{13}C NMR, $CDCl_3$, 125 MHz

6 2D NMR spectrum for 3a:

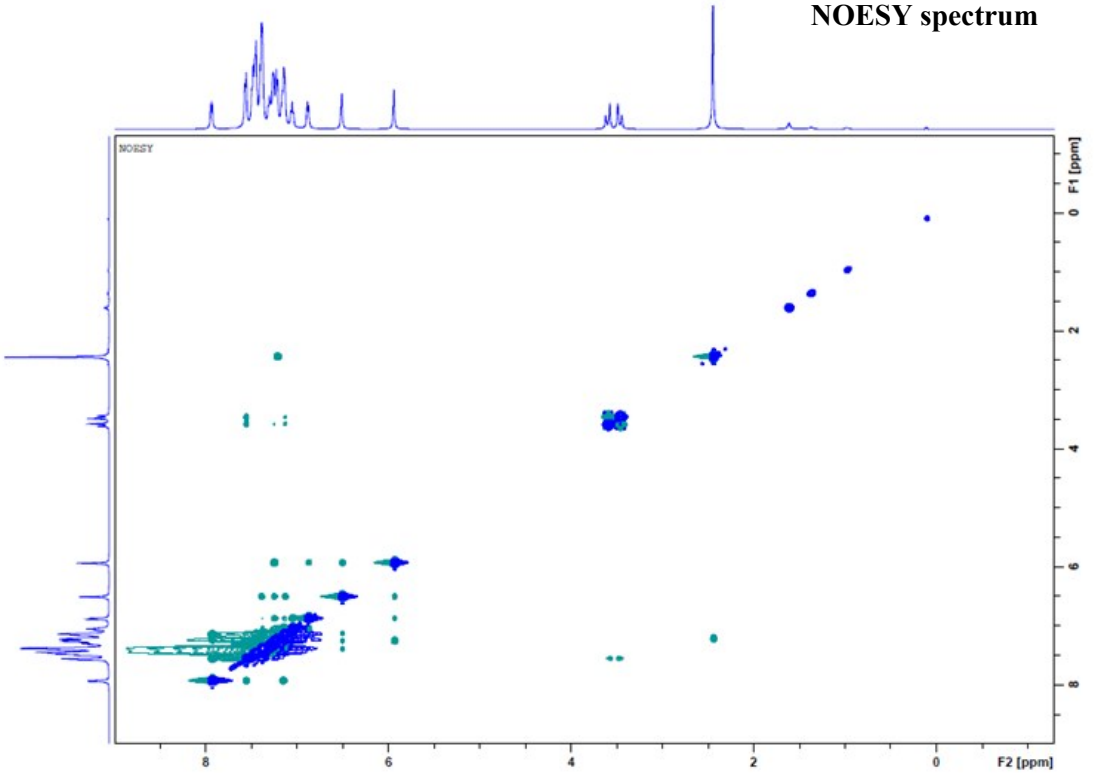


500 MHz, $CDCl_3$

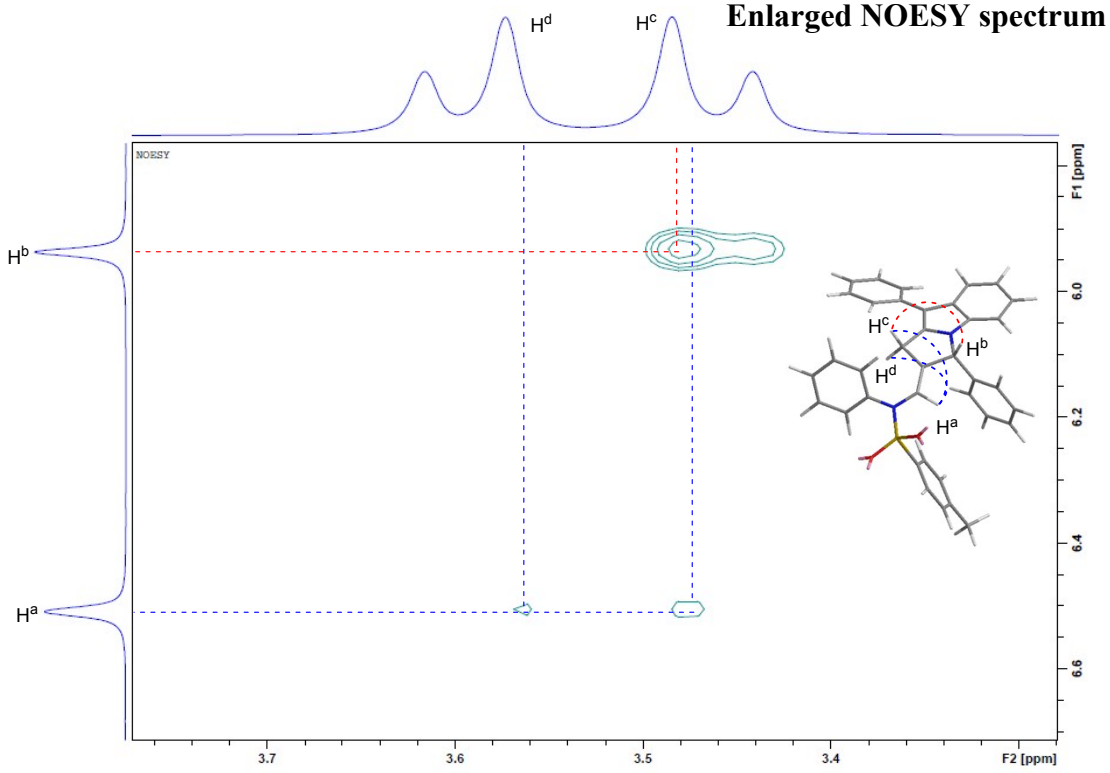
COSY spectrum



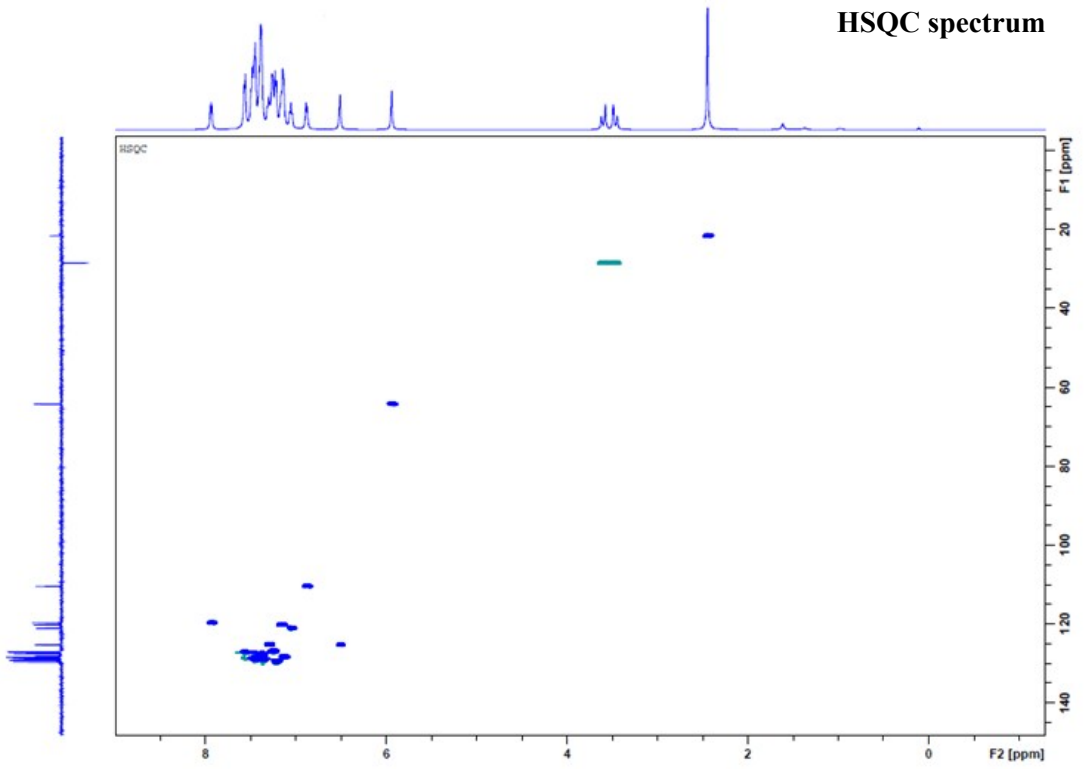
NOESY spectrum



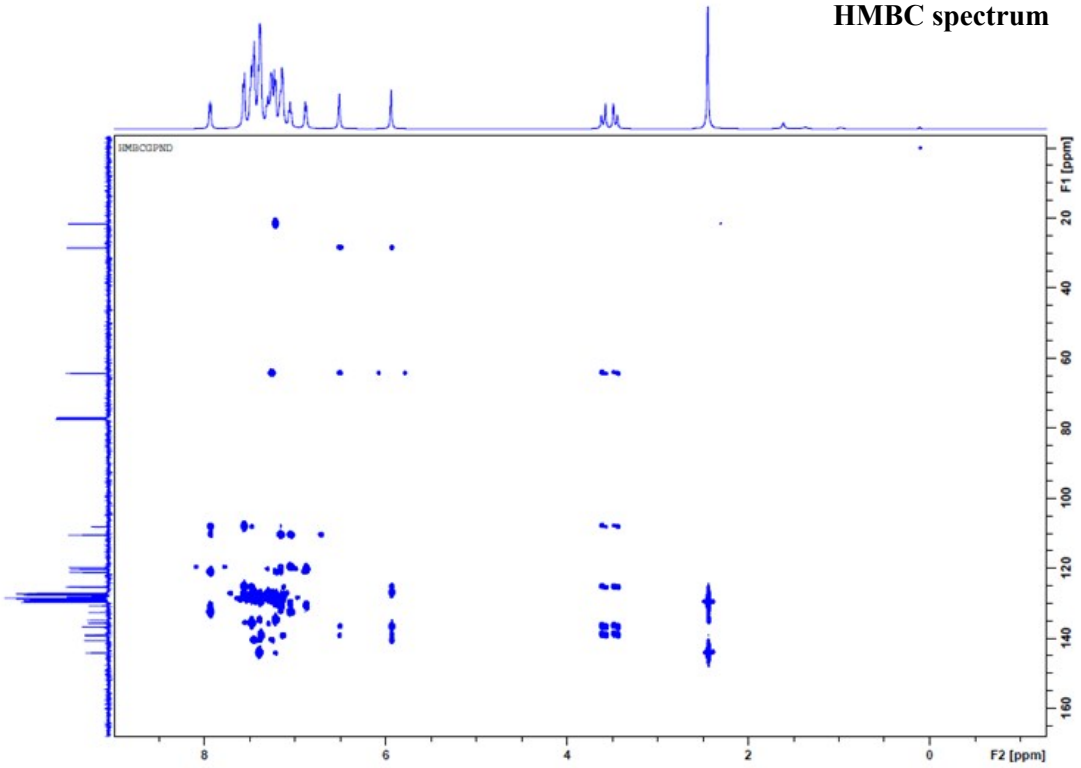
Enlarged NOESY spectrum



HSQC spectrum

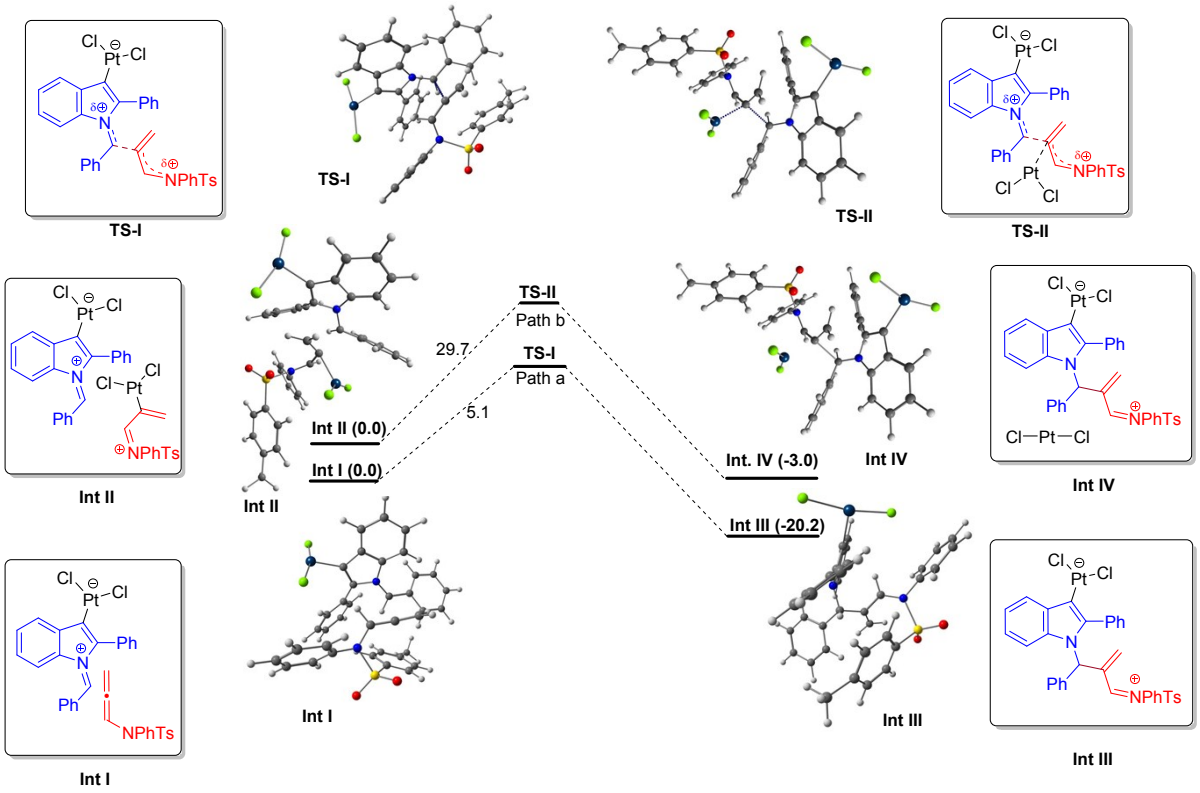


HMBC spectrum



7 Computational studies:

7.1 Determination of plausible reaction pathway by DFT studies:



To shed light on the plausible reaction pathway, we performed DFT studies (PBE/TZVP level of theory) for the $PtCl_2$-catalyzed reaction between **1a** and **2a**. The calculations have been carried out with Turbomole 7.0[8,9] using the TZVP basis set.[10] Geometry optimizations were performed using the Perdew, Burke and Ernzerhof functional (PBE).[11] Dispersion corrections[12] have been included in all the calculations. The resolution of identity (RI)[13] along with the multipole accelerated RI (marij)[14] approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT

(8) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(9)TURBOMOLE GmbH, "TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007," 2011.

(10) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(12) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(13) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283.

(14) Sierka, M.; Hogekamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *118*, 9136.

calculations. Solvent corrections have also been included in all the calculations using the cosmo model,[15] with epsilon (∈) = 2.38 employed, to model for the toluene solvent. With regard to the transition state, care was taken to make sure that the structures possessed only one imaginary frequency corresponding to correct normal mode.

The study revealed endergonic coordination between the Pt-bound azomethine ylide **I** and *N*-allenamide **2a** (**Int I**) to form the **Int III** via TS I (path a, ΔE = 5.1 Kcal/mol). Whereas, ΔE is found to be 29.7 Kcal/mol in the case of path b where Pt-bound azomethine ylide **I** coordinates with alkenyl-Pt intermediates (**Int II**) through TS II to furnish **Int IV**. These results revealed that path a is energetically favourable and hence the reaction would be following the same path.

(15) Klamt, A.; Schüürmann, G. *J. Chem. Soc. Perkin Trans*. **1993**, *2*, 799.

7.2 Cartesian coordinates:

1. **Int I**

N	2.323805	-0.811032	1.694199
C	1.143927	-1.499820	1.311138
C	0.290766	-2.158045	2.071065
C	-2.059289	0.271776	1.704599
N	-1.979714	0.013560	0.401276
C	-1.061313	0.674636	-0.466340
C	-1.074937	0.033850	-1.692240
C	-2.008651	-1.083881	-1.615816
C	-2.572424	-1.092739	-0.324083
C	-3.388799	-2.127843	0.113149
H	-3.777809	-2.179108	1.126986
H	-4.360722	-3.948085	-0.500001
C	-3.706874	-3.133071	-0.813206
H	-3.469684	-3.899951	-2.816986
C	-3.200352	-3.106605	-2.118088
C	-2.331848	-2.088084	-2.527567
H	-1.886459	-2.075356	-3.522800
Pt	-0.072390	0.492537	-3.248227
Cl	-1.574459	2.004788	-4.149120
H	-2.091242	2.911474	0.716094
C	-1.012835	2.964588	0.549744
C	-0.338593	1.880870	-0.046958
C	1.041144	1.990879	-0.297123
H	1.571459	1.160422	-0.764742
C	1.726897	3.156701	0.047288
H	2.796499	3.229683	-0.157859
C	1.053443	4.224311	0.648818
H	1.593914	5.134540	0.915127
C	-0.320541	4.124949	0.896032
H	-0.859230	4.962132	1.344468
Cl	1.739340	-0.878058	-2.739024
C	-0.566615	-2.884919	2.741072
C	-3.133915	-0.050779	2.603667
C	-4.491252	-0.075074	2.202474
H	-4.752551	0.114333	1.160599
H	-1.430474	-2.453355	3.257550
H	-1.779144	-0.166746	4.292799
C	-2.820742	-0.217658	3.972820
C	-3.827354	-0.460924	4.901955
H	-3.570555	-0.608356	5.952415
C	-5.164955	-0.502714	4.490600
H	-5.956141	-0.678443	5.221530
C	-5.491644	-0.295957	3.142572
H	-6.536370	-0.295830	2.827903
H	0.950158	-1.397913	0.236400
H	-1.226663	0.861957	2.095566
H	3.915731	1.237922	1.101038
C	4.155697	0.338115	0.535815
C	5.186132	0.334060	-0.403292

S	2.766020	-0.805655	3.398986
C	3.420863	-0.832506	0.760754
C	3.721569	-2.003780	0.054710
H	3.144784	-2.910805	0.243313
C	4.744341	-1.994701	-0.895032
H	4.964960	-2.902861	-1.458371
H	6.275968	-0.822380	-1.870324
C	5.478674	-0.828486	-1.124965
O	4.048669	-0.059185	3.468315
H	5.756265	1.247625	-0.581664
C	1.461024	0.224112	4.109722
C	1.143302	1.448452	3.517607
H	1.591790	1.742670	2.567080
C	0.231480	2.286679	4.159650
H	-0.026987	3.240176	3.693793
C	-0.347204	1.929895	5.390632
C	0.008323	0.697564	5.963711
H	-0.425805	0.403009	6.922046
C	0.904406	-0.164854	5.328326
H	1.171401	-1.126585	5.768110
C	-1.358821	2.825945	6.051781
H	-2.368009	2.623285	5.655614
H	-1.141547	3.886343	5.863327
H	-1.392777	2.663456	7.137595
O	2.671428	-2.169159	3.988441
H	-0.437327	-3.968854	2.831872

2. TS-I

N	6.730109	-2.065231	-0.255628
C	5.384401	-2.060882	0.002837
C	4.777841	-2.109164	1.216478
C	3.981322	0.139582	1.290961
N	3.172254	0.182778	0.201233
C	3.632205	0.667419	-1.060902
C	2.796890	0.175610	-2.052561
C	1.781273	-0.645746	-1.417845
C	2.018339	-0.632582	-0.024191
C	1.283828	-1.425365	0.852693
H	1.493618	-1.458189	1.919772
H	-0.361962	-2.805984	0.982408
C	0.240767	-2.189563	0.313504
H	-0.858248	-2.781176	-1.450201
C	-0.036809	-2.176817	-1.061795
C	0.736659	-1.414010	-1.940025
H	0.561069	-1.420094	-3.016447
Pt	2.880349	0.501662	-3.941172
Cl	1.580533	2.418484	-3.945965
H	4.104982	2.800555	0.581415
C	4.842798	2.694115	-0.217090
C	4.729317	1.636363	-1.145180
C	5.662605	1.560131	-2.195926
H	5.586149	0.745422	-2.916925
C	6.674588	2.513727	-2.313243
H	7.384849	2.440522	-3.139509

C	6.785424	3.551983	-1.383171
H	7.577741	4.296699	-1.480633
C	5.863690	3.637493	-0.333560
H	5.926324	4.455945	0.386455
Cl	4.230990	-1.348382	-4.398784
C	4.284732	-2.801766	2.221261
C	3.526631	0.289664	2.664829
C	2.232947	0.747751	2.995523
H	1.510242	0.956171	2.205953
H	3.852968	-2.324177	3.105352
H	5.476129	-0.220831	3.448229
C	4.468294	0.109511	3.700173
C	4.119259	0.341159	5.027266
H	4.858596	0.187473	5.815717
C	2.826436	0.772254	5.346668
H	2.551925	0.959666	6.386239
C	1.892126	0.984416	4.325544
H	0.892993	1.351393	4.566749
H	4.781959	-1.856525	-0.892792
H	4.992555	0.496286	1.091191
H	8.127948	-0.102287	-1.394394
C	7.936068	-0.938589	-2.066209
C	8.384272	-0.910515	-3.386381
S	7.884736	-2.730283	0.964907
C	7.206873	-2.041330	-1.615227
C	6.937515	-3.122776	-2.460449
H	6.375470	-3.978556	-2.082605
C	7.389676	-3.085872	-3.780187
H	7.168811	-3.917656	-4.450183
H	8.456162	-1.952239	-5.277583
C	8.111634	-1.982183	-4.242688
O	9.196312	-2.651140	0.280884
H	8.939105	-0.043900	-3.749614
C	7.835877	-1.509452	2.287839
C	8.104022	-0.169355	1.994683
H	8.257234	0.158523	0.965696
C	8.181765	0.741229	3.045728
H	8.383161	1.791880	2.826000
C	8.018019	0.327508	4.381405
H	8.257234	0.158523	0.965696
C	8.181765	0.741229	3.045728
H	8.383161	1.791880	2.826000
C	8.018019	0.327508	4.381405
C	7.758142	-1.028446	4.636109
H	7.625739	-1.368270	5.665452
C	7.656932	-1.955489	3.596812
H	7.442113	-3.006019	3.794405
C	8.093177	1.326987	5.502385
H	7.220430	1.999404	5.480178
H	8.988845	1.958596	5.411536
H	8.115558	0.833226	6.482527
O	7.346575	-4.019035	1.466171
H	4.300307	-3.896491	2.202269

3. **Int III**

N	1.921968	-1.254652	1.606955
C	0.654570	-1.159960	1.268806
C	-0.500183	-1.256084	2.150520
C	-1.571105	-0.179926	1.885833
N	-1.767615	-0.084232	0.433172
C	-0.943461	0.797469	-0.309627
C	-0.703902	0.243250	-1.575330
C	-1.357126	-1.039121	-1.612993
C	-1.981263	-1.233055	-0.349601
C	-2.646803	-2.423061	-0.034619
H	-3.103327	-2.583097	0.941898
H	-3.235545	-4.339087	-0.809337
C	-2.714513	-3.404335	-1.025040
H	-2.205824	-4.003871	-3.042848
C	-2.127611	-3.214134	-2.293534
C	-1.446687	-2.039776	-2.596696
H	-0.970190	-1.884688	-3.565508
Pt	0.232689	1.049932	-3.054346
Cl	-1.250628	2.812065	-3.353645
H	-2.513332	2.505689	1.104056
C	-1.504480	2.889926	0.938070
C	-0.578485	2.116080	0.209057
C	0.703436	2.648277	-0.033984
H	1.418059	2.058531	-0.612160
C	1.042412	3.918854	0.429774
H	2.037060	4.319657	0.224147
C	0.113692	4.682253	1.148656
H	0.379295	5.680947	1.500998
C	-1.160235	4.161650	1.399807
H	-1.897076	4.754390	1.945895
Cl	1.930940	-0.550356	-3.092740
C	-0.636198	-2.306142	2.987160
C	-2.860217	-0.266734	2.684969
C	-4.113740	-0.261120	2.058994
H	-4.174570	-0.246315	0.970543
H	-1.546474	-2.435210	3.572076
H	-1.841091	-0.196417	4.593285
C	-2.807635	-0.233511	4.088426
C	-3.979364	-0.227079	4.847268
H	-3.917141	-0.201831	5.937187
C	-5.226684	-0.243284	4.214487
H	-6.144274	-0.235322	4.805629
C	-5.287689	-0.252728	2.819163
H	-6.254619	-0.247571	2.312326
H	0.494929	-1.000339	0.190808
H	-1.104107	0.776946	2.174253
H	3.595593	0.645395	0.695961
C	3.747362	-0.332991	0.240647
C	4.725879	-0.525321	-0.731362
S	2.598169	-1.086124	3.406544
C	2.943799	-1.416292	0.612416
C	3.103543	-2.680958	0.034083
H	2.459787	-3.505143	0.344293

C	4.090580	-2.858040	-0.935289
H	4.216631	-3.835242	-1.403056
H	5.668916	-1.926815	-2.076042
C	4.903700	-1.785304	-1.311459
O	3.954355	-0.552799	3.154507
H	5.342789	0.316531	-1.047334
C	1.546894	0.176072	4.113667
C	1.441728	1.412857	3.473343
H	1.954376	1.617397	2.532439
C	0.637307	2.390313	4.055000
H	0.522709	3.347676	3.544022
C	-0.033509	2.154284	5.267779
C	0.134777	0.909901	5.900426
H	-0.364561	0.716340	6.852352
C	0.908026	-0.096891	5.325234
H	1.011773	-1.072550	5.800397
C	-0.953437	3.191104	5.846406
H	-1.977233	3.035788	5.466278
H	-0.648180	4.206164	5.560307
H	-0.997632	3.128227	6.942114
O	2.388496	-2.394956	4.064925
H	0.135750	-3.070051	3.072627

4. **Int II**

C	7.443401	1.863229	3.596009
H	8.579252	-2.813175	4.560209
C	8.570051	-1.981241	5.263143
C	9.745318	-1.334847	5.648139
H	10.701381	-1.678067	5.250149
C	9.698809	-0.249557	6.530657
H	10.623448	0.250449	6.825032
C	7.353354	-1.511842	5.766855
N	6.123120	-2.141539	5.363290
C	7.286864	-0.424568	6.645923
H	6.317477	-0.070639	6.998867
H	8.433822	1.060348	7.703358
C	8.472738	0.205689	7.026172
C	6.128219	-2.826135	8.798492
H	7.184356	-3.030851	8.622707
C	5.171513	-3.120696	7.820515
C	3.807386	-2.878303	8.007583
H	3.080337	-3.122250	7.232491
C	3.400701	-2.323918	9.219391
H	2.338042	-2.127994	9.377871
C	4.327816	-2.011994	10.228929
C	3.866525	-1.439375	11.540710
H	4.672224	-0.891453	12.047409
H	3.539357	-2.246523	12.216232
H	3.011716	-0.762940	11.403413
S	5.720837	-3.767456	6.254173
O	7.058775	-4.380281	6.393396
O	4.615483	-4.384462	5.499616
C	5.325744	-1.534846	4.513728
C	3.967384	-1.850156	4.104964

C	3.520430	-2.582768	3.088206
Pt	2.961654	-0.660129	5.328370
Cl	1.232248	-2.180532	5.582304
Cl	4.284394	1.272722	5.377507
C	2.133733	2.411843	2.851099
C	1.581554	3.678926	3.150276
H	2.206838	4.570313	3.065256
N	4.227309	1.483562	1.838115
C	3.545489	2.364677	2.558449
C	0.249980	3.794334	3.538978
H	-0.172314	4.778842	3.745794
C	1.335009	1.258286	3.024990
H	1.766257	0.269060	2.878640
C	-0.535118	2.644649	3.690531
H	-1.572762	2.732373	4.017633
C	0.017195	1.379294	3.451538
H	-0.575502	0.478413	3.617735
C	3.726234	0.460515	0.951066
C	2.485079	0.332289	0.340716
H	1.668843	1.026535	0.528377
C	2.312826	-0.739418	-0.546888
H	1.345338	-0.871162	-1.033139
C	3.359672	-1.629033	-0.820153
H	3.194434	-2.458765	-1.509313
C	4.623400	-1.447979	-0.247409
H	5.458857	-2.108550	-0.479301
C	4.807269	-0.381790	0.632145
C	6.000425	0.150483	1.287251
C	5.659584	1.317624	1.940809
C	6.503728	2.290856	2.642780
C	6.437718	3.661791	2.326156
H	5.758032	4.006450	1.542877
Pt	7.728715	-0.681460	1.182363
Cl	8.826302	1.093222	0.190902
Cl	7.039667	-2.734634	2.079372
C	7.274423	4.579336	2.962411
H	7.218281	5.636676	2.696676
C	8.197770	4.142107	3.917071
H	8.856067	4.859053	4.411528
C	8.283634	2.780880	4.223919
H	9.006909	2.427395	4.960826
H	7.525457	0.802012	3.833725
H	6.423217	-2.039208	10.775026
C	5.690692	-2.274253	10.000108
H	4.240036	-3.123419	2.468582
H	2.460526	-2.658084	2.853893
H	5.744672	-0.610978	4.098014
H	4.168879	3.132750	3.017460

5. TS -II

C	1.458188	1.734728	2.275165
C	2.402813	0.705021	2.479779
C	2.804652	0.405951	3.793970
C	2.245650	1.081983	4.876543

C	1.302608	2.092488	4.664992	C	7.702077	-1.467188	3.502294
C	0.920251	2.423256	3.360251	C	8.795548	-0.793450	4.049480
C	3.026918	0.073950	1.309139	C	9.649996	-0.054735	3.223949
N	2.343446	-0.176122	0.171583	C	9.408431	0.016760	1.847765
C	0.951011	-0.559833	0.065085	C	8.312103	-0.643344	1.291045
C	0.695376	-0.824059	-1.296325	S	6.710475	-3.649040	0.731683
C	1.944347	-0.637528	-2.018951	O	5.496427	-4.008181	-0.032864
C	2.931666	-0.275857	-1.101572	C	6.888910	-4.677650	2.180035
C	-0.565426	-1.260733	-1.698671	C	5.755376	-5.301431	2.717817
C	-1.547498	-1.450028	-0.716370	C	5.872062	-5.945036	3.947187
C	-1.260265	-1.233391	0.634977	C	7.092305	-5.968843	4.645214
C	0.004731	-0.786395	1.054257	C	8.214777	-5.358282	4.060172
Pt	2.169701	-0.798519	-3.899032	C	8.125428	-4.699568	2.834581
Cl	2.096090	-3.105465	-4.036638	C	7.182972	-6.635881	5.989726
C	4.353326	-0.010411	-1.349957	O	8.021177	-3.422147	0.087639
C	5.130640	-1.006690	-1.967609	C	2.944758	-3.107391	1.201052
C	6.467996	-0.759061	-2.278496	Cl	3.640033	-3.480057	5.614387
C	7.040166	0.481836	-1.981425	H	0.218276	-0.657664	2.112716
C	6.275407	1.473902	-1.357315	H	-2.023807	-1.421555	1.390691
C	4.938239	1.231923	-1.041668	H	-2.541591	-1.792003	-1.007828
Cl	2.308183	1.448633	-4.414809	H	-0.757243	-1.469757	-2.751618
C	3.823187	-2.157392	1.725028	H	3.509023	-0.403070	3.986935
Pt	3.101192	-3.040834	3.364623	H	2.542795	0.807643	5.889796
Cl	0.800346	-3.039944	3.796989	H	0.869329	2.623619	5.514142
C	5.110510	-1.826800	2.127521	H	0.198744	3.222836	3.184171
N	6.323755	-2.034537	1.534714	H	1.163251	2.005549	1.260401
C	7.463104	-1.378575	2.123725	H	4.332242	2.024148	-0.596256

H	6.716479	2.446599	-1.132779
H	8.082810	0.678701	-2.239686
H	7.063543	-1.539714	-2.754585
H	7.039857	-2.059778	4.137778
H	8.982713	-0.852577	5.122896
H	10.504288	0.469991	3.655174
H	10.070833	0.597654	1.203760
H	8.095981	-0.588062	0.224618
H	4.808738	-5.304526	2.178554
H	4.989006	-6.413700	4.384595
H	9.173975	-5.381553	4.581505
H	8.994096	-4.211304	2.392599
H	7.030249	-7.722616	5.899527
H	6.401476	-6.254831	6.664087
H	8.160573	-6.467725	6.460280
H	4.679779	-1.972674	-2.198696
H	3.300558	-4.068120	0.822057
H	1.983101	-2.774579	0.804198
H	5.173138	-1.131037	2.970288
H	4.086411	0.254382	1.136506

6. **Int IV**

C	1.605068	1.967775	2.167657
C	2.191654	0.693750	2.275889
C	2.197610	0.051649	3.520840
C	1.624648	0.663381	4.641484
C	1.044453	1.927783	4.524562
C	1.030298	2.575824	3.283569
C	2.890303	0.108333	1.053853
N	2.020220	-0.032313	-0.130549
C	0.689970	-0.486621	-0.177569
C	0.359394	-0.701845	-1.547192
C	1.526855	-0.392531	-2.320219
C	2.542263	-0.018052	-1.409022
C	-0.899283	-1.207362	-1.891568
C	-1.815381	-1.492647	-0.870102
C	-1.475816	-1.281246	0.469567
C	-0.211271	-0.786202	0.841709
Pt	1.714939	-0.353030	-4.218779
Cl	1.636362	-2.615219	-4.613507
C	3.951662	0.261960	-1.697142
C	4.712018	-0.731095	-2.343564
C	6.067445	-0.520370	-2.594480
C	6.673711	0.682451	-2.217249
C	5.919124	1.684044	-1.595790
C	4.562496	1.479263	-1.341967
Cl	1.821334	1.939033	-4.496871
C	3.689038	-1.181220	1.290438
Pt	-0.830927	-4.873385	-1.154938
Cl	-1.949968	-6.033868	-2.715611
C	5.087272	-0.922512	1.386571
N	6.183093	-1.686938	1.491440
C	7.390823	-1.035042	1.940891
C	7.649094	-1.014329	3.316235

C	8.792374	-0.366013	3.785947
C	9.660569	0.263449	2.888792
C	9.385514	0.244488	1.516003
C	8.251453	-0.411292	1.031855
S	6.454805	-3.408404	0.778990
O	5.208575	-3.760426	0.071960
C	6.651965	-4.374436	2.269899
C	5.561546	-5.106494	2.755536
C	5.698467	-5.774046	3.969313
C	6.899007	-5.716458	4.703186
C	7.985863	-5.006999	4.161815
C	7.877184	-4.335044	2.944046
C	7.004977	-6.420531	6.028172
O	7.758781	-3.254004	0.098274
C	3.043105	-2.361624	1.511664
Cl	0.352750	-4.011965	0.557463
H	0.033752	-0.644488	1.893639
H	-2.192222	-1.533432	1.253115
H	-2.790662	-1.905724	-1.125850
H	-1.140576	-1.387906	-2.939860
H	2.647405	-0.937411	3.614751
H	1.639962	0.154584	5.608821
H	0.604276	2.411688	5.397970
H	0.574328	3.564661	3.193252
H	1.591996	2.482456	1.203117
H	3.957792	2.279083	-0.908726
H	6.383712	2.635121	-1.328443
H	7.736014	0.843320	-2.410761
H	6.650514	-1.298688	-3.090504
H	6.954527	-1.496499	4.004508
H	8.993726	-0.348824	4.857571
H	10.548321	0.776902	3.263683
H	10.054023	0.748722	0.816821
H	8.015314	-0.431522	-0.032434
H	4.633960	-5.171889	2.187146
H	4.854002	-6.350114	4.356266
H	8.936706	-4.975713	4.698745
H	8.725239	-3.789479	2.529949
H	6.880761	-7.507381	5.902734
H	6.209949	-6.085386	6.711368
H	7.971513	-6.238786	6.515152
H	4.234585	-1.668189	-2.632440
H	3.626323	0.866638	0.753529
H	1.955581	-2.402119	1.509537
H	3.560873	-3.296009	1.707800
H	5.341454	0.141363	1.472562