Supporting Information

Au(I)/Ag(I) Co-operative Catalysis: Interception of Ag-Bound Carbocations with α-Gold(I) Enals in the Imino-Alkyne Cyclizations with *N*-allenamides

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General information:

Practical considerations: Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. The pyridino-alkyne cyclization reactions were performed in 2.5 mL glass vials with a PTFE-lined cap and all other reactions for the preparation of starting materials were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine, potassium permanganate solution and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for 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.

Materials: Unless otherwise noted, material obtained from commercial suppliers was used without further purification. Tetrahydrofuran was distilled from Na/benzophenone under an atmosphere of dry N_2. Anhydrous methanol, dichloromethane and petroleum ether were dried by using standard protocols under N_2. The catalyst CyJohnPhosAuCl was purchased from Sigma-Aldrich. All deuterated solvents were used as supplied by Sigma-Aldrich. The (pyridine-2-yl)alkynone[1] and *N*-tosylallenamides[2] were synthesized according to the literature known procedure.

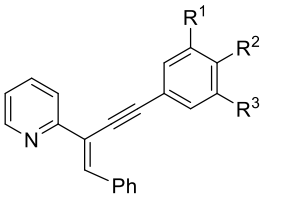
Instrumentation: Melting points are uncorrected and recorded using digital Büchi melting point apparatus B-540. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AV, 200/400/500, JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), quin (quintet), sep (septet), br.s. (broad singlet), m (multiplet) etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Single-crystal data was collected on a Bruker D8 Venture Kappa Duo Photon II CPAD diffractometer equipped with incoatech multilayer mirrors optics.

1 D. K. Friel, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc*. 2008, **130**, 9942.

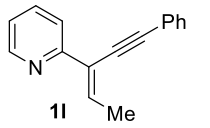
2 S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio and J. M. González, *Adv. Synth. Catal*., 2012, **354**, 1651.

Computational studies: The geometry optimizations were conducted employing density functional theory (DFT) with the Turbomole 6.4 suite of programs.[3] The Perdew, Burke, and Ernzerhof (PBE)[4] functional were used for the geometry optimization calculations. The triple-ζ basis set augmented by a polarization function (Turbomole basis set TZVP) was used for all the atoms. The resolution of identity (RI)[5] along with the multipole accelerated resolution of identity (marij)[6] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term. Solvent effects were accounted for as follows: we have done full geometry optimizations of all intermediates and transition states calculations using the COSMO model,[7] with solvent ethylene dichloride. Moreover, dispersion corrections (disp-3) were also included through these calculations[8] With regard to the transition states obtained during the investigations of these reactions, care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode.

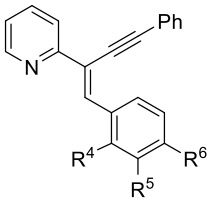
1. General procedure for the synthesis of 2-(2-enynyl) pyridine 1:



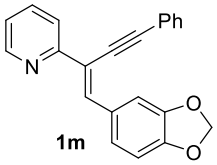
1a, R^2 = Me, R^1 = R^3 = H
1b, R^1 = R^2 = R^3 = H
1c, R^2 = ^{i}Pr, R^1 = R^3 = H
1d, R^2 = OMe, R^1 = R^3 = H
1e, R^1 = OMe, R^2 = R^3 = H
1f, R^2 = NMe_2, R^1 = R^3 = H
1g, R^1 = R^3 = OMe, R^2 = H
1h, R^2 = Br, R^1 = R^3 = H
1i, R^2 = F, R^1 = R^3 = H
1j, R^1 = Cl, R^2 = R^3 = H
1k, R^2 = ethynyl, R^1 = R^3 = H



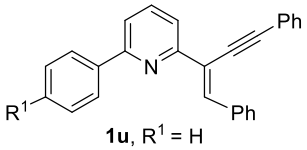
1l



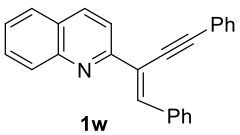
1n, R^4 = Me, R^5 = R^6 = H
1o, R^4 = R^5 = H, R^6 = OMe
1p, R^4 = R^5 = H, R^6 = NO_2
1q, R^4 = R^5 = H, R^6 = I
1r, R^4 = R^5 = H, R^6 = F
1s, R^4 = Br, R^5 = R^6 = H
1t, R^4 = R^5 = H, R^6 = Cl



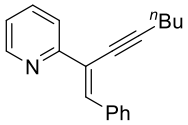
1m



1u, R^1 = H
1v, R^1 = OMe



1w



1x

3 R. Ahlrichs, M. Bar, M. Haser, H.Horn, C. Kolmel, *Chemical Physics Letters* 1989, **162**, 165.

4 J. P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters* 1996, **77**, 3865.

5 K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chemical Physics Letters* 1995, **240**, 283.

6 M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* 2003, **118**, 9136.

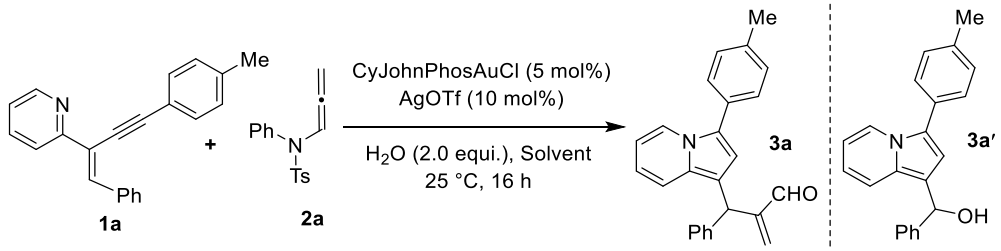
7 A. Klamt, G. Schuurmann, *Journal of the Chemical Society, Perkin Transactions* 1993, **2**, 799.

8 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of Chemical Physics* 2010, **132**, 154104-01.

The pyridine-2-yl alkynone **1a**, **1b**, **1d**, **1e**, **1j**, **1l**, **1o**, **1q**, **1r**, **1t, 1w** and **1x** were reported in the literature and prepared according to the known procedure.[9] On the other hand, compounds **1c**, **1f**, **1g**, **1h**, **1i**, **1k**, **1m**, **1n**, **1p**, **1s**, **1u** and **1v** are prepared by similar procedure.

Representative procedure: To a solution of the benzyl triphenylphosphonium bromide (1.2 equiv.) in dry THF (0.48 M) at 0 °C, *n*-butyllithium (1.6 M in Hexane, 1.2 equiv.) was added dropwise by syringe over 5 minutes. After 10 min, pyridine-2-yl alkynone (1.0 equiv.) was added to the solution. After completion of reaction (monitored by TLC), the mixture was poured into water and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The resultant residue was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether (05/95) as eluent to afford the 2-(2-enynyl)pyridine as *E*/*Z* mixture (*E*/*Z*:7/3) in 84% yield.

3. Solvent optimization for gold/silver catalyzed imino-alkyne cyclization reaction:



entry	Solvent	Yield[b] (%)	
		3a	**3a′**
1	DCM	45	30
2	Toluene	51	23
3	MeCN	00	42
4	$CHCl_3$	46	26

[a] Reaction conditions: 0.375 mmol **1a**, 0.250 mmol **2a**, 5 mol% Au catalyst and 10 mol% Ag catalyst, solvent (2 mL), 25 °C, 16 h. [b] Isolated yields (based on **2a**).

9 R.-R. Liu, Z.-Y. Cai, C.-J. Lu, S.-C. Ye, B. Xiang, J. Gao, Yi-X. Jia, *Org. Chem. Front*. 2015, **2**, 226.

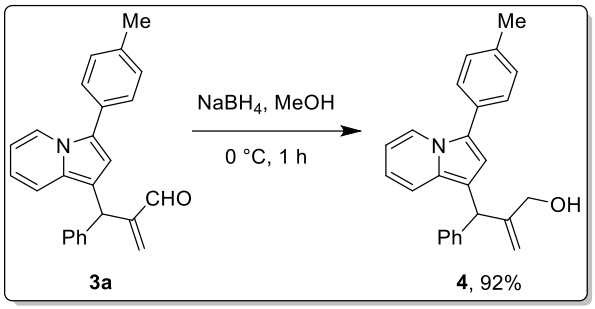
4. General procedure for gold/silver catalyzed imino-alkyne cyclization reactions:

To a oven dried screw cap vial, CyJohnPhosAuCl (5 mol%) and AgOTf (10 mol%) were dissolved in anhydrous DCE (0.12 M) under N_2 atmosphere. The reaction mixture was allowed to stir for 5-10 min and then pyridino-alkynes **1** (0.350 mmol) was added followed by the *N*-allenamides **2** (0.250 mmol) and H_2O (0.500 mmol). The reaction was stirred at 25 °C for specified time and after that the reaction mixture was loaded directly on silica gel column. After column chromatographic purification using ethyl acetate/petroleum ether as eluent, analytically pure products **3** were obtained.

Note: Both *E* and *Z* isomer gives the comparable yield under standard reaction condition. Geometry of the double bond in **1** does not affect yield of the reaction.

5. Modification of products:

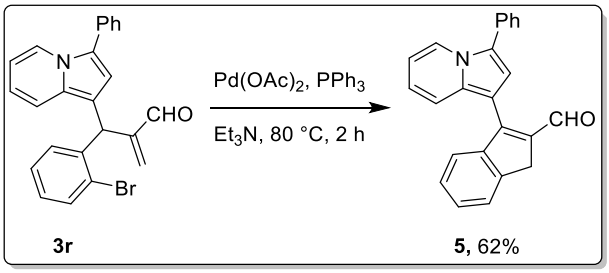
5.1 Reduction of 3a:



3a **4**, 92%

To a ice cooled (0 °C) solution of **3a** (50 mg, 0.142 mmol) in MeOH (1 mL), $NaBH_4$ (5.9 mg, 0.156 mmol) was added. After complete consumption of starting material (1 h), the reaction was quenched with cold water (3 mL). Then MeOH was removed under reduced pressure and the aqueous phase was extracted using DCM (3 x 5 mL). The organic layers were dried over Na_2SO_4, filtered and solvents were evaporated. The crude product thus obtained, was purified over silica gel chromatography using a mixture of ethyl acetate/petroleum ether (10:90) as eluent to afford analytically pure compound **4**.

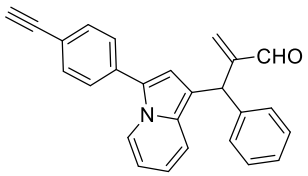
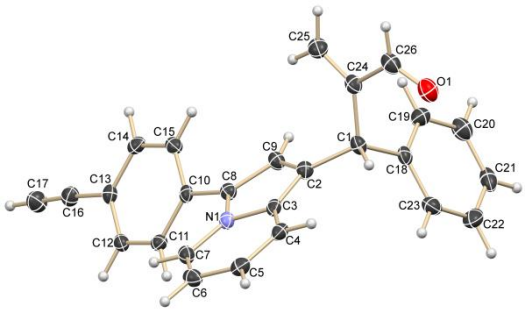
5.2 Heck reaction of 3r:



3r **5**, 62%

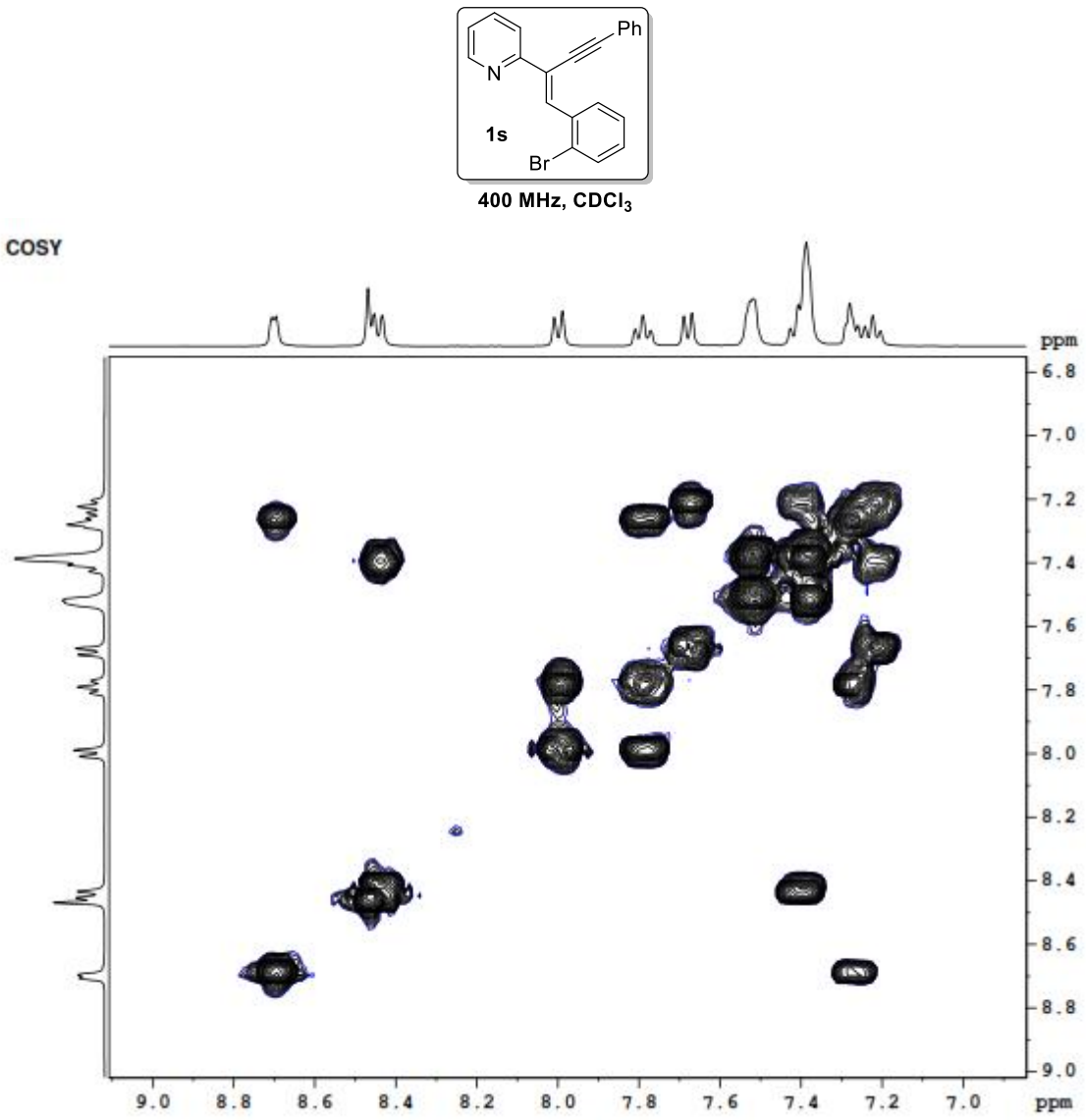
A stirred solution of **3r** (50 mg, 0.12 mmol), $Pd(OAc)_2$ (2.7 mg, 5 mol%), PPh_3 (3.4 mg, 10 mol%) in Et_3N (1 mL) was heated to 80 °C for 2 h under nitrogen atmosphere. The reaction mixture was allowed to cool at room temperature. The reaction was quenched with water (5 mL) and the reaction mixture was extracted with ethyl acetate (3 x 5 mL). The organic layer was washed with 5N HCl solution. Organics were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue thus obtained, was purified by column chromatography using ethyl acetate/petroleum ether (05:95) to afford analytically pure **5**.

6. ORTEP diagram:

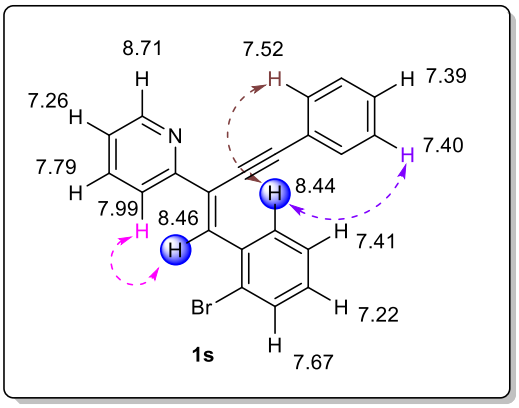
Compound Structure	ORTEP Diagram
 **3k** CCDC No. 1506109	

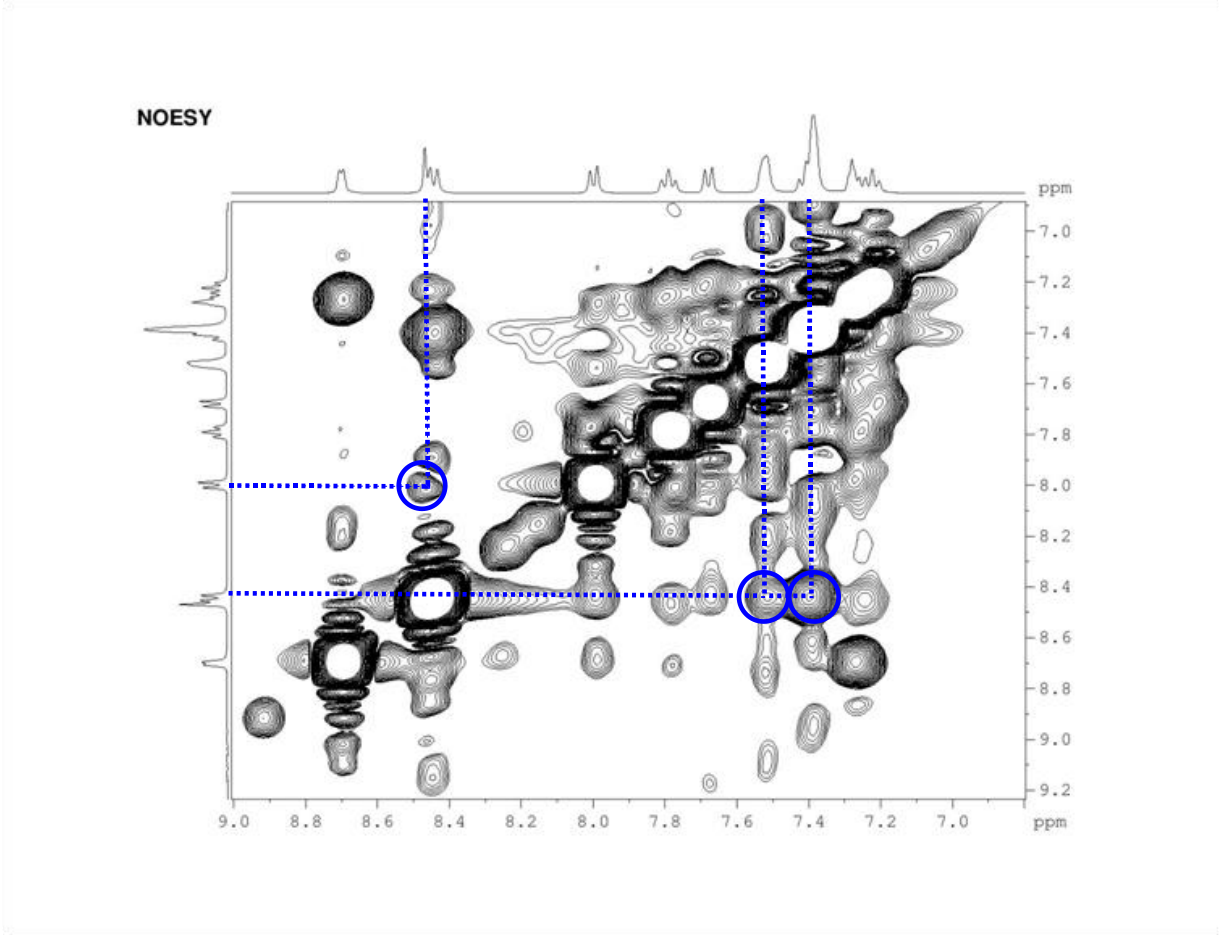
7. 2D NMR experiments:

7.1 2D NMR experiments for 1s:



Determination of geometry of double bond in 1s: NOESY Correlations





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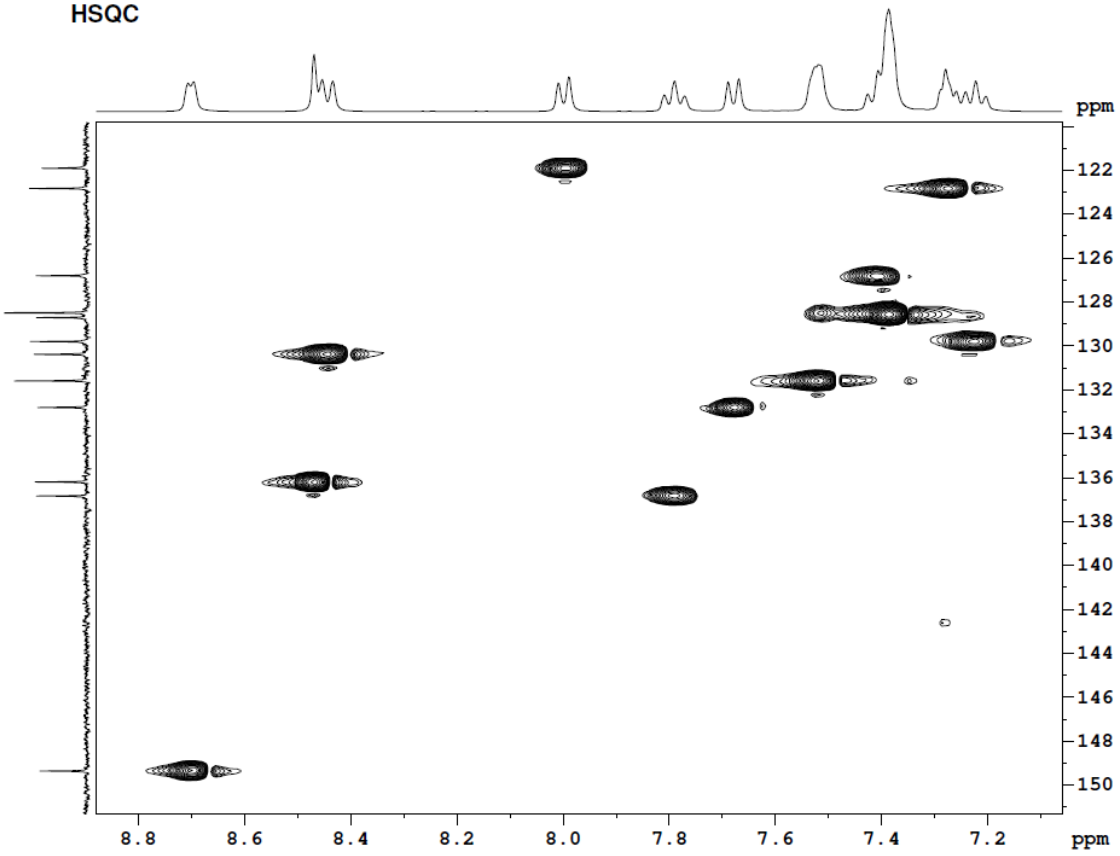
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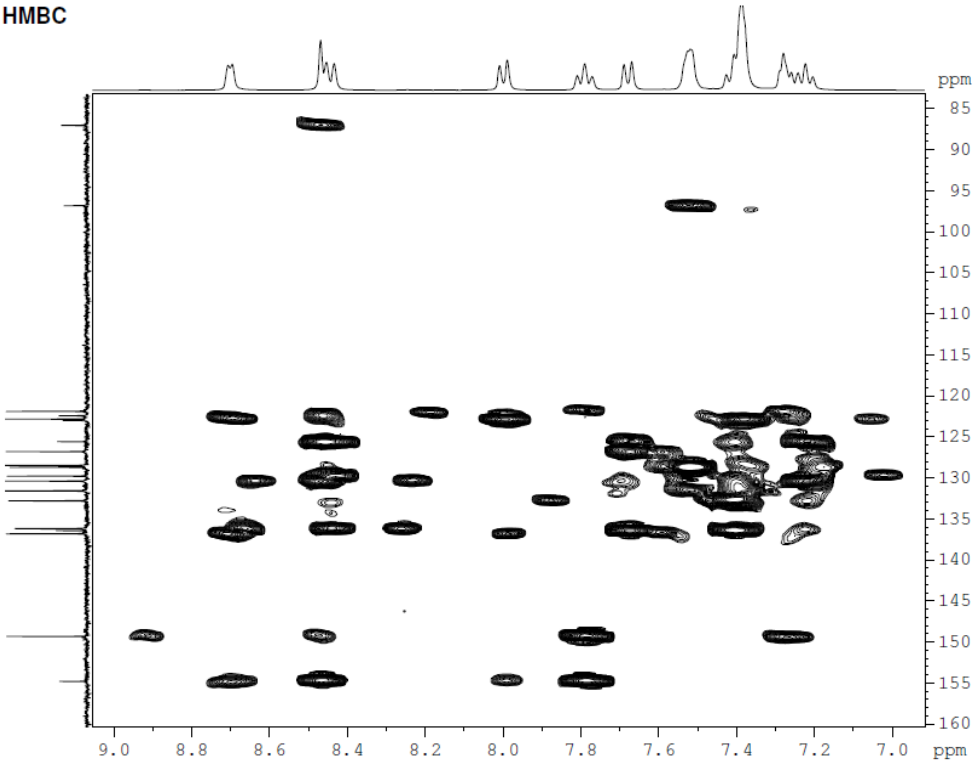
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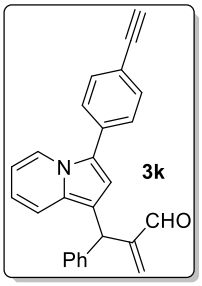
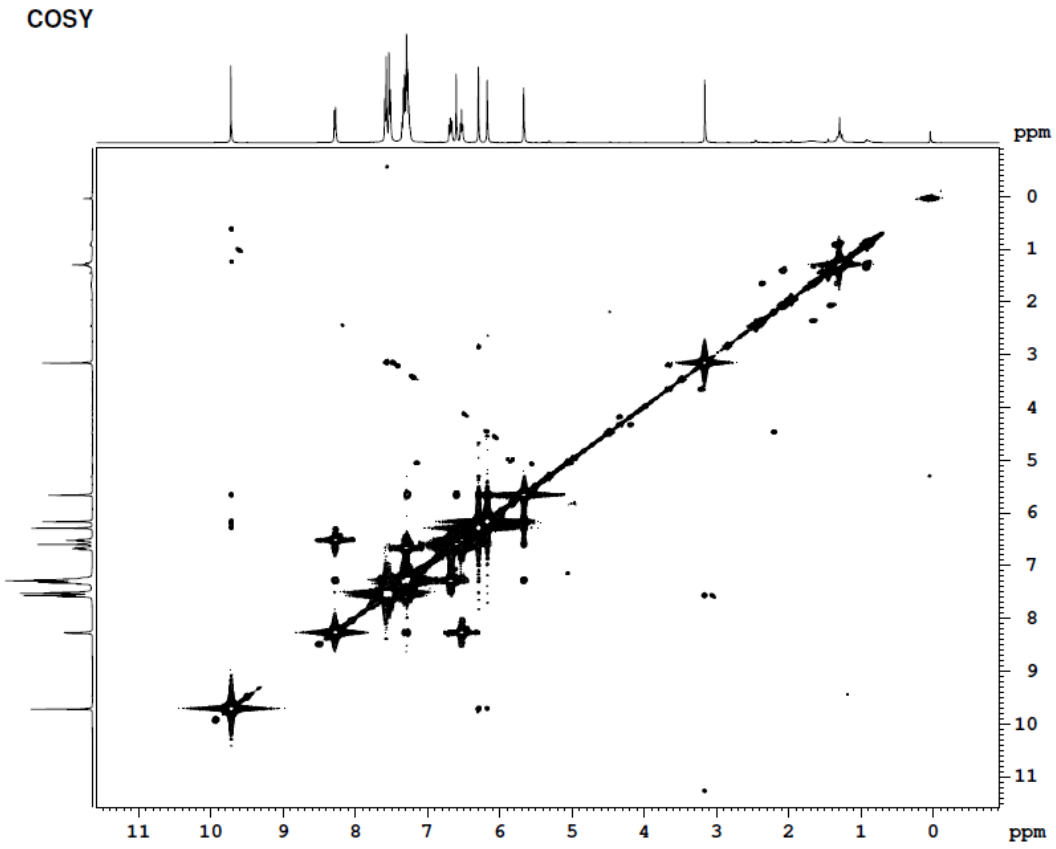
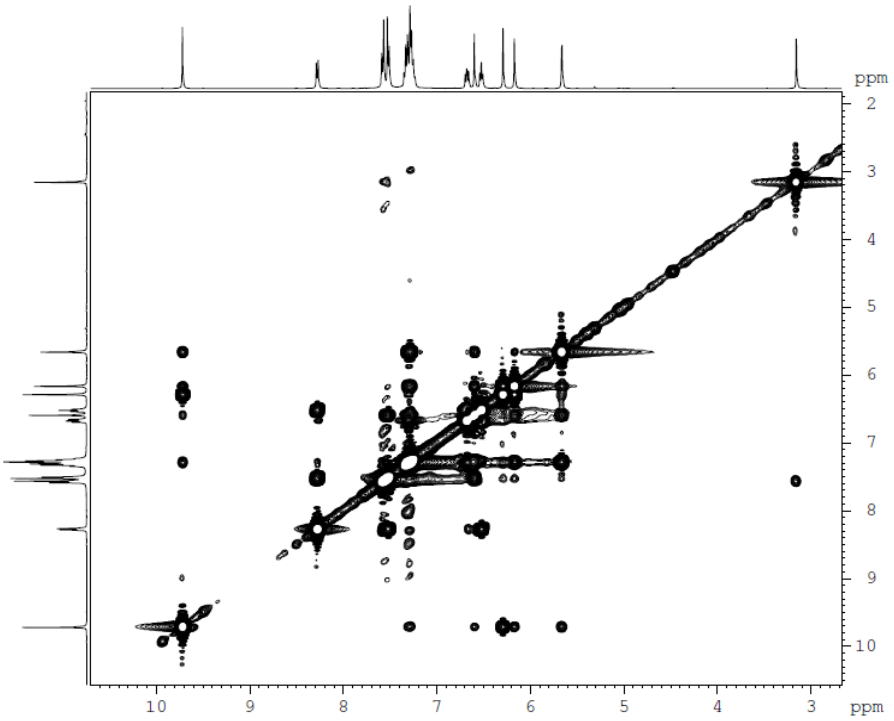
7.2 2D NMR experiments for 3k:



400 MHz, $CDCl_3$



NOESY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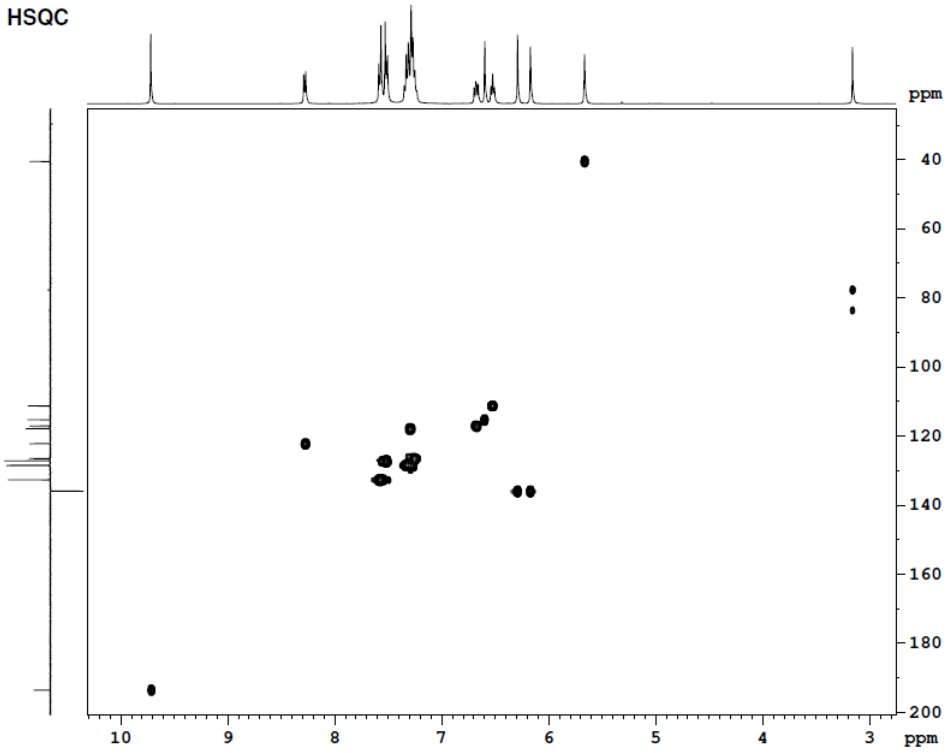
HSQC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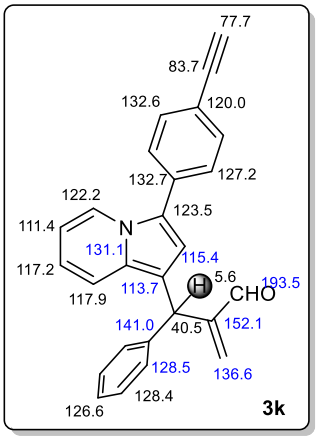
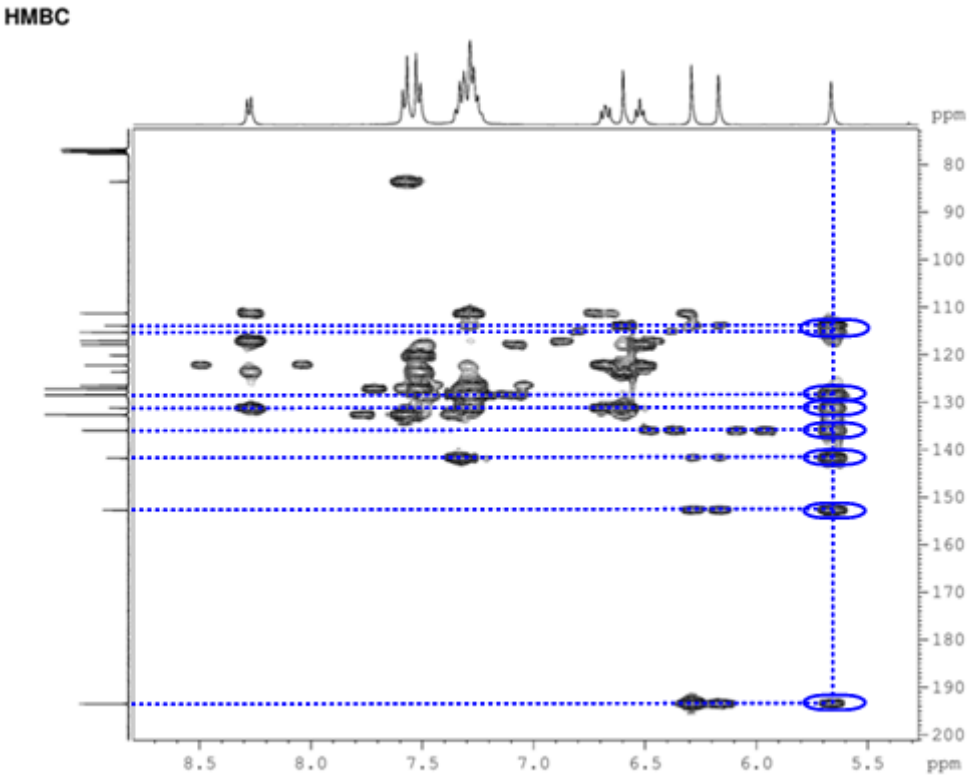
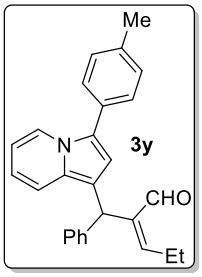
Correlations of 3k by HMBC spectrum:



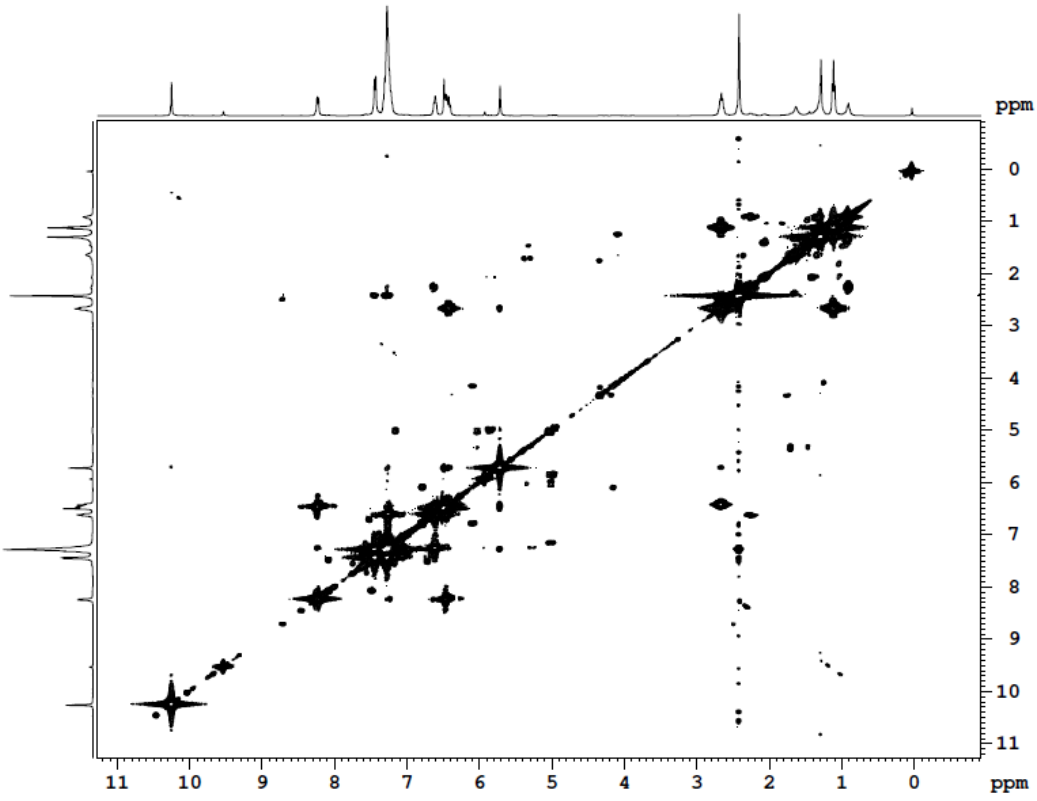


7.3 2D NMR experiments for 3y:

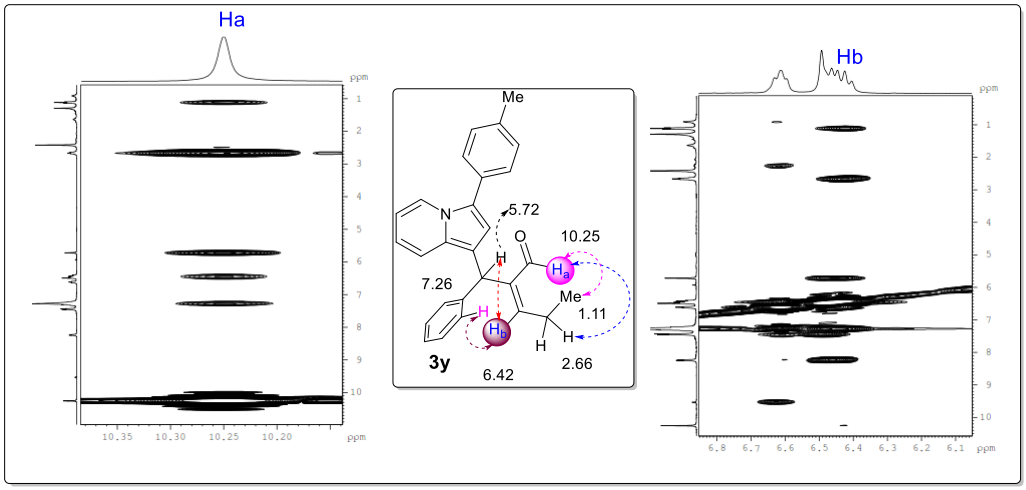


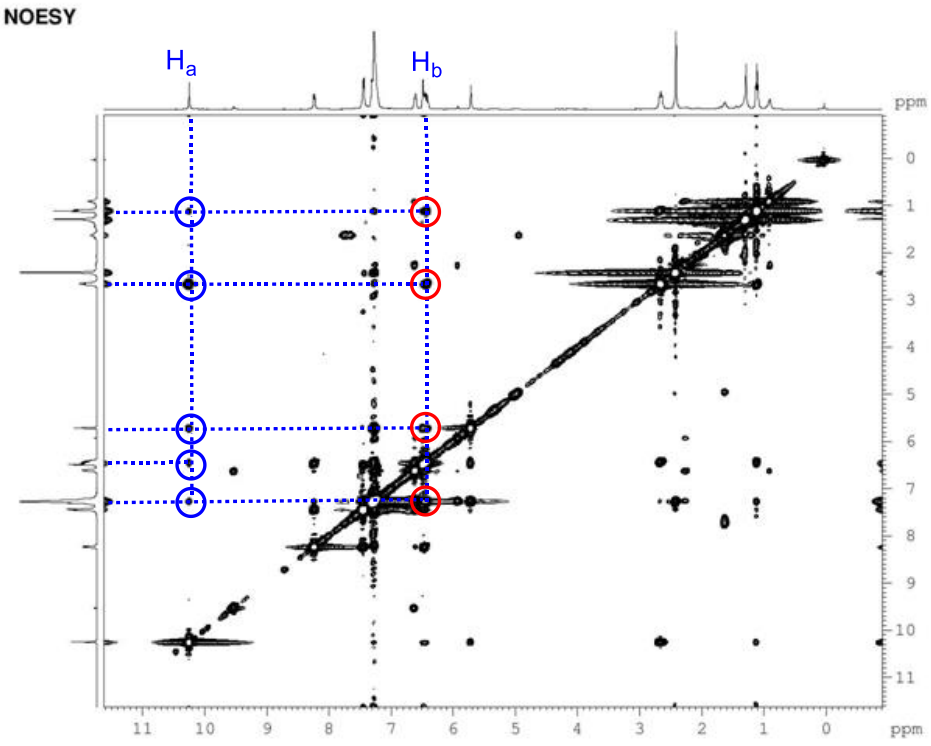
400 MHz, $CDCl_3$

COSY

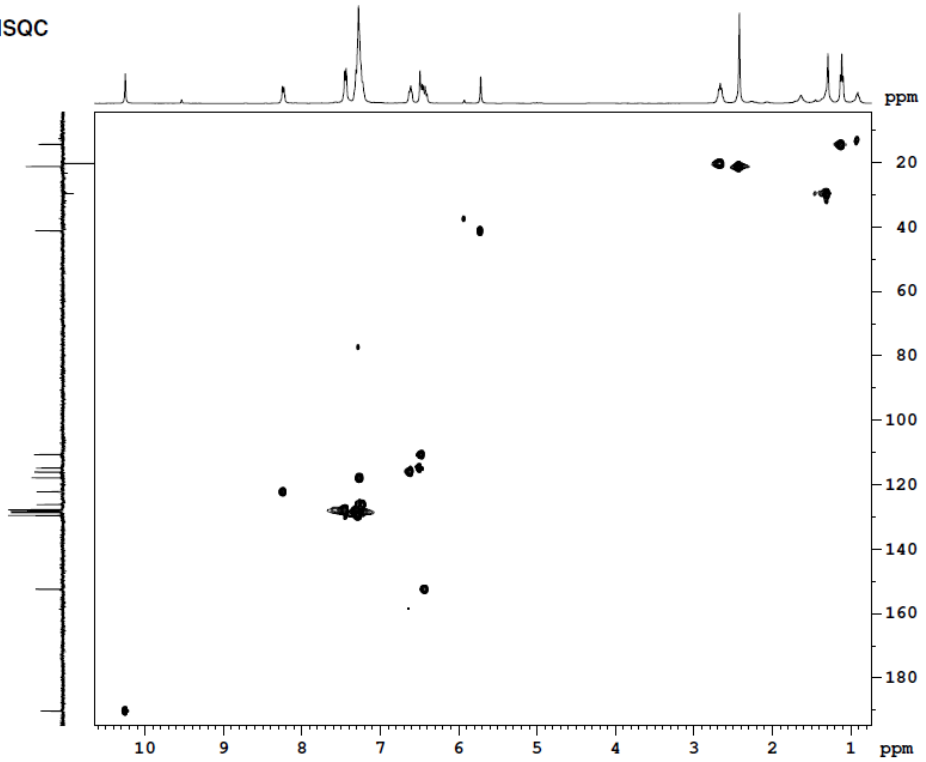


Correlations of 3y by NOESY spectrum:





HSQC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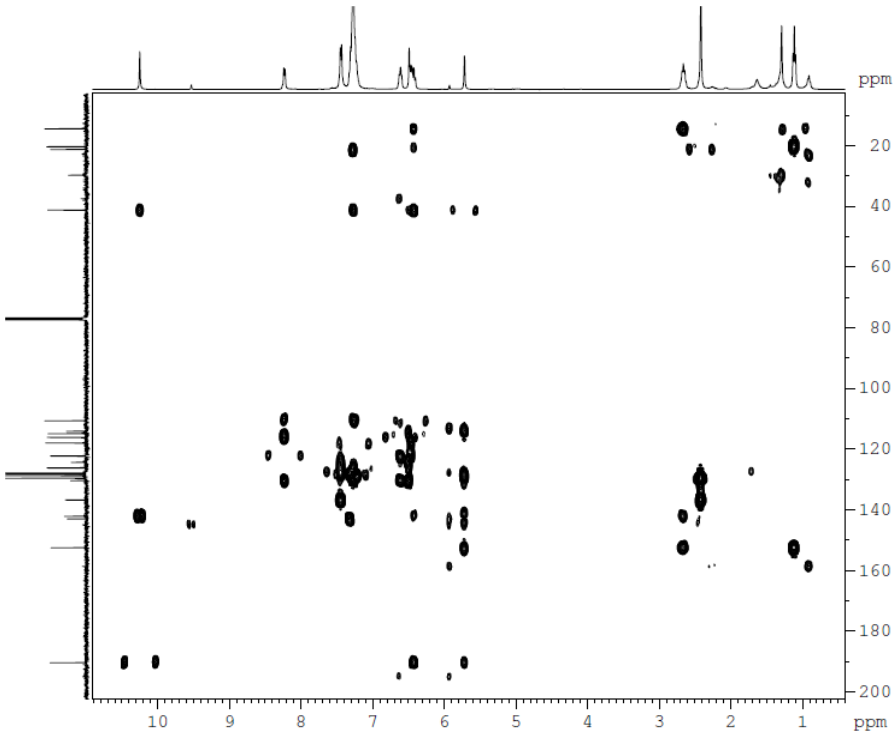
HMBC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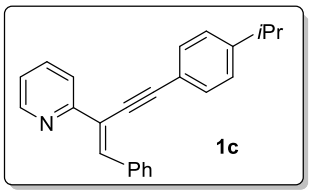
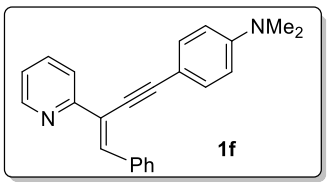
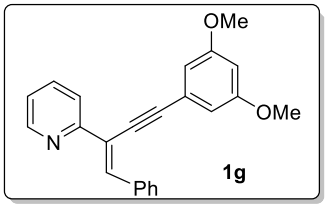
8. Characterization data for new compounds:



1c: Reaction performed on 2.00 mmol scale. Yield = 545 mg, 84% (*E*:*Z* = 7.0:3.0, *E*-isomer obtained in 60% yield as greenish thick liquid); R_f = 0.30 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) **δ** = 8.69 - 8.62 (m, 1 H), 8.24 (s, 1 H), 8.17 (d, *J* = 8.0 Hz, 2 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.81 - 7.73 (m, 1 H), 7.59 - 7.52 (m, *J* = 8.0 Hz, 2 H), 7.49 - 7.42 (m, 2 H), 7.40 - 7.33 (m, 1 H), 7.31 - 7.27 (m, *J* = 8.0 Hz, 2 H), 7.25 - 7.20 (m, 1 H), 2.97 (sep, *J* = 6.9 Hz, 1 H), 1.30 (d, *J* = 6.9 Hz, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 155.3, 149.7, 148.9, 136.8, 136.6, 136.4, 131.5, 129.8, 128.7, 128.3, 126.6, 122.4, 121.7, 120.5, 119.8, 97.9, 87.1, 34.1, 23.8; **HRMS** (**ESI**) calcd for $C_{24}H_{22}N$ $[M+H]^+$ 324.1747, found 324.1747.

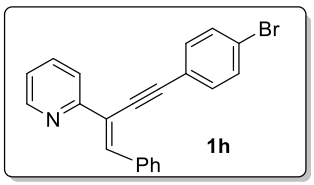


1f: Reaction performed on 1.99 mmol scale. Yield = 615 mg, 95% (*E*:*Z* = 6.8:3.2, *E*-isomer obtained in 65% yield as green solid); mp = 112-114 °C; R_f = 0.30 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.66 (d, *J* = 4.2 Hz, 1 H), 7.61 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.38 (d, *J* = 8.8 Hz, 2 H), 7.37 - 7.34 (m, 1 H), 7.24 - 7.19 (m, 2 H), 7.18 - 7.12 (m, 3 H), 7.01 (dd, *J* = 2.9, 6.3 Hz, 2 H), 6.63 (d, *J* = 9.2 Hz, 2 H), 2.98 (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 156.9, 150.0, 149.7, 137.0, 136.4, 136.0, 132.8, 129.2, 128.2, 128.0, 127.5, 124.7, 124.3, 122.5, 111.7, 110.0, 92.3, 89.2, 40.1; **HRMS** (**ESI**) calcd for $C_{23}H_{21}N_2$ $[M+H]^+$ 325.1699, found 325.1698.

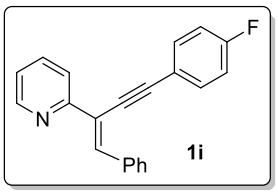


1g: Reaction performed on 1.87 mmol scale. Yield = 568 mg, 89% (*E*:*Z* = 6.5:3.5, *E*-isomer obtained in 58% yield as greenish thick liquid); R_f = 0.20 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.68 - 8.63 (m, 1 H), 8.24 (s, 1 H), 8.13 (d, *J* = 7.6 Hz, 2 H), 7.98 (d, *J* = 8.0

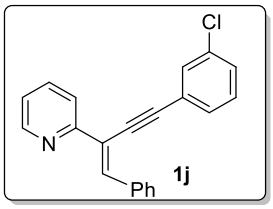
Hz, 1 H), 7.77 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.47 - 7.41 (m, 2 H), 7.39 - 7.34 (m, 1 H), 7.26 - 7.21 (m, 1 H), 6.76 (d, *J* = 2.3 Hz, 2 H), 6.53 (t, *J* = 2.3 Hz, 1 H), 3.84 (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 160.6, 155.1, 149.0, 137.3, 136.8, 136.3, 129.8, 128.9, 128.3, 124.4, 122.5, 121.7, 119.6, 109.4, 101.9, 97.4, 87.3, 55.4; **HRMS** (ESI) calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1489, found 342.1488.



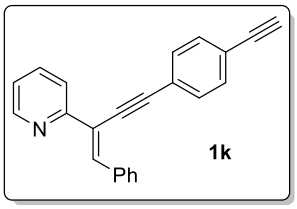
1h: Reaction performed on 1.75 mmol scale. Yield = 553 mg, 88% (*E*:*Z* = 6.4:3.6, *E*-isomer obtained in 57% yield as off white solid); mp = 99-101 °C; R_f = 0.60 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.69 - 8.63 (m, 1 H), 8.24 (s, 1 H), 8.10 (d, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.44 (dd, *J* = 6.5, 8.0 Hz, 4 H), 7.39 - 7.35 (m, 1 H), 7.26 - 7.22 (m, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 154.9, 149.0, 137.6, 136.8, 136.2, 132.9, 131.8, 131.5, 129.8, 129.8, 129.0, 128.3, 122.9, 122.6, 122.1, 121.6, 119.5, 96.2, 88.9; **HRMS** (ESI) calcd for $C_{21}H_{14}BrN$ $[M+H]^+$ 362.0362, found 362.0352.



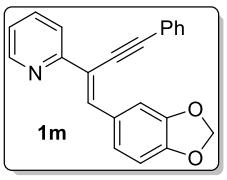
1i: Reaction performed on 2.22 mmol scale. Yield = 611 mg, 92% (*E*:*Z* = 6.8:3.2, *E*-isomer obtained in 57% yield as off white solid); mp = 61-63 °C; R_f = 0.50 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 8.65 (td, *J* = 0.9, 5.0 Hz, 1 H), 8.23 (s, 1 H), 8.11 (d, *J* = 7.8 Hz, 2 H), 7.96 (d, *J* = 7.8 Hz, 1 H), 7.77 (dt, *J* = 1.4, 7.8 Hz, 1 H), 7.62 - 7.53 (m, 2 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.3 Hz, 1 H), 7.24 (dd, *J* = 4.8, 7.6 Hz, 1 H), 7.11 (t, *J* = 8.5 Hz, 2 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 164.0 (d, *J* = 250.16 Hz), 155.1, 149.0, 137.2, 136.8, 136.3, 133.4, 133.4, 129.8, 128.9, 128.3, 122.5, 121.7, 119.6, 119.3 (d, *J* = 2.83 Hz), 116.0, 115.7, 96.3, 87.5; **HRMS** (ESI) calcd for $C_{21}H_{15}FN$ $[M+H]^+$ 300.1183, found 300.1183.



1j: Reaction performed on 2.07 mmol scale. Yield = 540 mg, 83% (*E*:*Z* = 6.6:3.4, *E*-isomer obtained in 55% yield as gray solid); mp = 71-73 °C; R_f = 0.5 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.66 (d, *J* = 3.8 Hz, 1 H), 8.26 (br. s., 1 H), 8.10 (d, *J* = 7.6 Hz, 2 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.77 (t, *J* = 7.6 Hz, 1 H), 7.58 (s, 1 H), 7.49 - 7.42 (m, 3 H), 7.41 - 7.30 (m, 3 H), 7.26 - 7.21 (m, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 154.9, 149.1, 137.9, 136.9, 136.2, 134.4, 131.3, 129.8, 129.7, 129.6, 129.1, 128.8, 128.4, 124.9, 122.6, 121.6, 119.4, 95.8, 89.0; **HRMS** (ESI) calcd for $C_{21}H_{15}ClN$ $[M+H]^+$ 316.0888, found 316.0889.

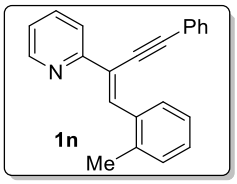


1t: Reaction performed on 2.16 mmol scale. Yield = 495 mg, 75% (*E*:*Z* = 7.0:3.0, *E*-isomer obtained in 53% yield as yellow solid); mp = 108-110°C; R_f = 0.30 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.66 (br. s., 1 H), 8.26 (br. s., 1 H), 8.12 (d, *J* = 6.5 Hz, 2 H), 7.96 (d, *J* = 7.2 Hz, 1 H), 7.81 - 7.71 (m, 1 H), 7.54 (br. s., 4 H), 7.49 - 7.42 (m, 2 H), 7.38 (d, *J* = 6.9 Hz, 1 H), 7.24 (br. s., 1 H), 3.22 (br. s., 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 155.0, 149.0, 137.7, 136.8, 136.2, 132.2, 131.3, 129.8, 129.0, 128.3, 123.6, 122.5, 122.3, 121.6, 119.5, 96.7, 89.8, 83.2, 79.2; **HRMS** (ESI) calcd for $C_{23}H_{16}N$ $[M+H]^+$ 306.1277, found 306.1277.

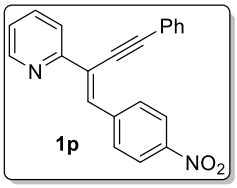


1m: Reaction performed on 2.41 mmol scale. Yield = 722 mg, 92% (*E*:*Z* = 5.9:4.1, *E*-isomer obtained in 55% yield as greenish solid); mp = 78-80 °C; R_f = 0.20 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.66 - 8.59 (m, 1 H), 8.15 (s, 1 H), 8.01 - 7.98 (m, 1 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.75 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.62 (dd, *J* = 1.7, 7.8 Hz, 2 H), 7.48 (dd, *J* = 1.3, 8.2 Hz, 1 H), 7.45 - 7.35 (m, 3 H), 7.21 (ddd, *J* = 1.1, 4.8, 7.4 Hz, 1 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 6.02 (s, 2 H);

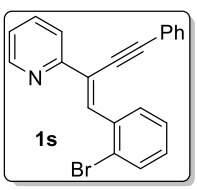
^{13}C NMR (**125 MHz**, **$CDCl_3$**) δ = 155.3, 148.9, 148.2, 147.6, 136.8, 136.6, 131.4, 130.8, 128.5, 128.5, 125.9, 123.2, 122.2, 121.5, 117.6, 108.7, 108.2, 101.3, 97.8, 88.0; **HRMS** (ESI) calcd for $C_{22}H_{16}NO_2$ $[M+H]^+$ 326.1176, found 326.1176.



1n: reaction performed on 2.41 mmol scale. Yield = 663 mg, 93% (*E*:*Z* = 6.4:3.6, *E*-isomer obtained in 60% yield as off white solid); mp = 86-88°C; R_f = 0.60 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.69 - 8.64 (m, 1 H), 8.45 (s, 1 H), 8.36 (d, *J* = 6.9 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 1 H), 7.78 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.56 - 7.50 (m, 2 H), 7.41 - 7.34 (m, 3 H), 7.33 - 7.26 (m, 3 H), 7.26 - 7.22 (m, 1 H), 2.51 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 155.1, 149.1, 137.9, 136.8, 135.7, 135.4, 131.5, 130.1, 128.7, 128.6, 128.4, 128.4, 125.4, 123.3, 122.5, 121.7, 120.9, 96.1, 87.7, 20.2; **HRMS** (ESI) calcd for $C_{22}H_{18}N$ $[M+H]^+$ 296.1434, found 296.1434.

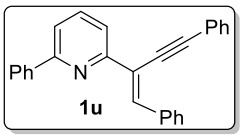


1p: Reaction performed on 2.41 mmol scale. Yield = 677 mg, 86% (*E*:*Z* = 7.5:3.5, *E*-isomer obtained in 65% yield as yellow solid); mp = 132-134 °C; R_f = 0.10 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.66 (d, *J* = 4.2 Hz, 1 H), 8.30 - 8.25 (m, 3 H), 8.25 - 8.22 (m, 2 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.83 - 7.77 (m, 1 H), 7.60 (dd, *J* = 2.7, 6.5 Hz, 2 H), 7.47 - 7.40 (m, 3 H), 7.29 (dd, *J* = 4.8, 7.1 Hz, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 154.1, 149.1, 147.0, 142.7, 137.0, 133.9, 131.6, 130.1, 129.6, 129.3, 128.7, 127.4, 123.8, 123.6, 123.3, 122.4, 122.2, 99.4, 86.9; **HRMS** (ESI) calcd for $C_{21}H_{15}N\,O_2$ $[M+H]^+$ 327.1128, found 327.1128.

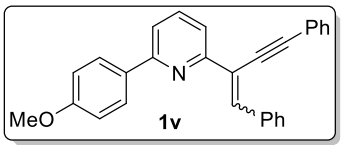


1s: Reaction performed on 2.41 mmol scale. Yield = 738 mg, 85% (*E*:*Z* = 6.3:3.7, *E*-isomer obtained in 54% yield as yellow solid); mp = 103-105°C; R_f = 0.10 (ethyl acetate/petroleum ether = 10/90); **^{1}H**

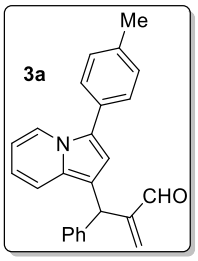
NMR (**500 MHz**, **$CDCl_3$**) δ = 8.71 (d, *J* = 4.3 Hz, 1 H), 8.55 - 8.38 (m, 2 H), 8.01 (d, *J* = 7.9 Hz, 1 H), 7.80 (t, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.9 Hz, 1 H), 7.57 - 7.49 (m, 2 H), 7.46 - 7.36 (m, 4 H), 7.31 - 7.28 (m, 1 H), 7.26 - 7.19 (m, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 154.8, 149.3, 136.8, 136.4, 136.2, 132.8, 131.6, 130.4, 129.8, 128.7, 128.5, 126.8, 125.6, 123.0, 122.8, 122.4, 121.9, 96.8, 87.0; **HRMS** (ESI) calcd for $C_{21}H_{15}{}^{81}BrNO_2$ $[M+H]^+$ 362.0362, found 362.0352.



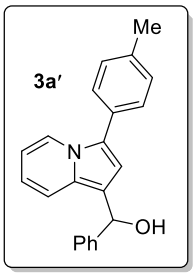
1u: Reaction performed on 1.77 mmol scale. Yield = 498 mg, 79% (*E*:*Z* = 7.3:2.7, *E*-isomer obtained in 55% yield as white solid); mp = 124-126 °C; R_f = 0.20 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) 7.86 - 7.78 (m, 2 H), 7.77 - 7.70 (m, 1 H), 7.70 - 7.64 (m, 1 H), 7.57 - 7.52 (m, 2 H), 7.45 - 7.31 (m, 8 H), 7.25 - 7.20 (m, 3 H), 7.20 - 7.14 (m, 2 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 156.9, 155.9, 139.0, 137.3, 136.3, 131.6, 129.4, 129.3, 128.9, 128.5, 128.3, 128.2, 128.1, 127.7, 127.0, 124.2, 123.4, 122.5, 119.3, 91.3, 90.6; **HRMS** (ESI) calcd for $C_{27}H_{20}N$ $[M+H]^+$ 358.1590, found 358.1590.



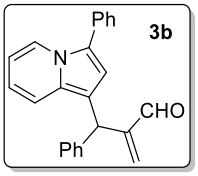
1v: Reaction performed on 1.60 mmol scale. Yield = 457 mg, 74% (mixture of *E*:*Z* = 7:3 isolated as greenish solid;); mp = 93-99 °C; R_f = 0.20 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.22 - 8.04 (m, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.72 - 7.66 (m, 1 H), 7.66 - 7.57 (m, 2 H), 7.57 - 7.50 (m, 1 H), 7.50 - 7.44 (m, 1 H), 7.44 - 7.39 (m, 1 H), 7.39 - 7.30 (m, 4 H), 7.24 - 7.14 (m, 4 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 6.91 (d, *J* = 8.4 Hz, 1 H), 3.85 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 160.5, 160.4, 156.5, 155.9, 155.6, 154.4, 138.9, 137.4, 137.2, 137.0, 136.5, 136.4, 132.0, 131.8, 131.6, 131.5, 129.8, 129.3, 128.7, 128.5, 128.5, 128.3, 128.2, 128.1, 127.7, 124.3, 123.4, 123.3, 121.7, 120.0, 119.4, 118.5, 118.5, 114.1, 113.9, 97.3, 91.3, 90.5, 88.1, 55.4, 55.3; **HRMS** (ESI) calcd for $C_{28}H_{22}ON$ $[M+H]^+$ 388.1696, found 388.1696.



3a: Yellow thick liquid; yield = 75 mg, 86% with *E* isomer of **1a** and 71 mg, 81% with *Z* isomer of **1a**; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.71 (s, 1 H), 8.23 (d, *J* = 7.3 Hz, 1 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.36 - 7.29 (m, 3 H), 7.28 - 7.20 (m, 5 H), 6.66 - 6.59 (m, 1 H), 6.53 (s, 1 H), 6.50 - 6.44 (m, 1 H), 6.28 (s, 1 H), 6.18 (s, 1 H), 5.66 (s, 1 H), 2.42 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 152.9, 142.0, 136.8, 135.8, 130.3, 129.6, 129.4, 128.5, 128.4, 127.8, 126.4, 124.5, 122.3, 117.7, 116.3, 114.5, 113.2, 110.7, 40.6, 21.2; **HRMS** (ESI) calcd for $C_{25}H_{21}NO$ $[M]^+$ 351.1618, found 351.1617.

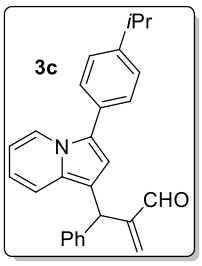


3a': Bluish thick liquid; R_f = 0.7 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) = 8.21 (d, *J* = 7.2 Hz, 1 H), 7.55 - 7.31 (m, 4 H), 7.31 - 7.11 (m, 6 H), 6.64 (s, 1 H), 6.55 - 6.48 (m, 1 H), 6.43 - 6.35 (m, 1 H), 5.99 (s, 1 H) , 2.39 (s, 3H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 145.5, 136.5, 130.3, 129.7, 129.5, 129.5, 128.5, 128.2, 127.8, 125.8, 124.2, 122.2, 118.1, 117.0, 115.7, 114.9, 110.3, 40.1, 21.2; **HRMS** (ESI) calcd for $C_{22}H_{20}NO$ $[M+H]^+$ 314.1539, found 314.1541.

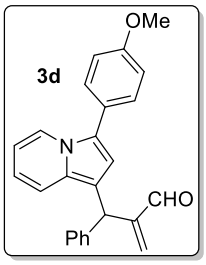


3b: Yellow thick liquid; yield = 58 mg, 69%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.68 (s, 1 H), 8.23 (d, *J* = 7.2 Hz, 1 H), 7.52 (d, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.32 - 7.23 (m, 6 H), 7.21 (t, *J* = 7.1 Hz, 1 H), 6.61 (dd, *J* = 6.7, 8.6 Hz, 1 H), 6.54 (s, 1 H), 6.45 (t, *J* = 6.7 Hz, 1 H), 6.25 (s, 1 H), 6.15 (s, 1 H), 5.64 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 152.8, 141.9, 135.8, 132.3, 130.6, 128.9, 128.5, 128.4, 127.8, 127.0, 126.4, 124.4,

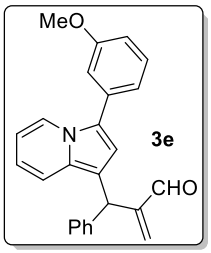
122.2, 117.7, 116.5, 114.8, 113.3, 110.8, 40.6; **HRMS** (ESI) calcd for $C_{24}H_{20}NO$ $[M+H]^+$ 338.1539, found 338.1530.



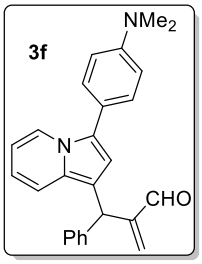
3c: Yellow thick liquid; yield = 79 mg, 84%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.68 (s, 1 H), 8.23 (d, *J* = 6.5 Hz, 1 H), 7.44 (d, *J* = 6.9 Hz, 2 H), 7.33 - 7.24 (m, 7 H), 7.21 (d, *J* = 6.1 Hz, 1 H), 6.60 (t, *J* = 6.9 Hz, 1 H), 6.50 (br. s., 1 H), 6.47 - 6.39 (m, 1 H), 6.24 (br. s., 1 H), 6.14 (br. s., 1 H), 5.63 (br. s., 1 H), 3.00 - 2.87 (m, 1 H), 1.28 (d, *J* = 6.5 Hz, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 152.9, 147.8, 142.0, 135.8, 130.3, 129.8, 128.5, 128.4, 127.8, 126.9, 126.4, 124.5, 122.3, 117.7, 116.3, 114.6, 113.2, 110.6, 40.6, 33.9, 24.0; **HRMS** (ESI) calcd for $C_{27}H_{26}NO$ $[M+H]^+$ 380.2009, found 380.2004.



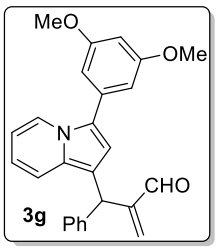
3d: Yellow thick liquid; yield = 72 mg, 79%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.15 (d, *J* = 7.3 Hz, 1 H), 7.47 - 7.41 (m, 2 H), 7.33 - 7.27 (m, 3 H), 7.26 (br. s., 1 H), 7.25 - 7.20 (m, 2 H), 7.03 - 6.96 (m, 2 H), 6.63 - 6.58 (m, 1 H), 6.48 (s, 1 H), 6.47 - 6.41 (m, 1 H), 6.27 (s, 1 H), 6.17 (s, 1 H), 5.65 (s, 1 H), 3.86 (s, 3 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 158.7, 152.9, 142.0, 135.9, 130.0, 129.4, 128.5, 128.4, 126.4, 124.8, 124.2, 122.1, 117.7, 116.1, 114.3, 114.3, 113.0, 110.6, 55.3, 40.6; **HRMS** (ESI) calcd for $C_{25}H_{22}NO_2$ $[M+H]^+$ 368.1645, found 368.1633.



3e: Yellow thick liquid; yield = 63 mg, 69%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.28 (d, *J* = 7.0 Hz, 1 H), 7.37 (t, *J* = 7.9 Hz, 1 H), 7.33 - 7.29 (m, 2 H), 7.29 - 7.25 (m, 3 H), 7.24 (d, *J* = 7.0 Hz, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 7.08 - 7.04 (m, 1 H), 6.90 - 6.85 (m, 1 H), 6.67 - 6.60 (m, 1 H), 6.56 (s, 1 H), 6.51 - 6.44 (m, 1 H), 6.27 (s, 1 H), 6.17 (s, 1 H), 5.65 (s, 1 H), 3.85 (s, 3 H);); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 160.0, 152.8, 141.9, 135.9, 133.6, 130.7, 129.9, 128.5, 128.4, 126.5, 124.3, 122.4, 120.2, 117.7, 116.6, 114.9, 113.5, 113.3, 112.4, 110.9, 55.3, 40.5; **HRMS** (ESI) calcd for $C_{25}H_{22}NO$ $[M+H]^+$ 368.1645, found 368.1645.

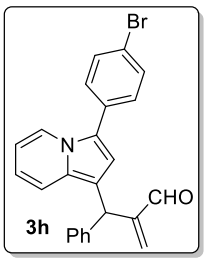


3f: Yellow thick liquid; yield = 78 mg, 82%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.17 (d, *J* = 7.3 Hz, 1 H), 7.42 - 7.37 (m, *J* = 8.9 Hz, 2 H), 7.33 - 7.27 (m, 4 H), 7.25 - 7.21 (m, 2 H), 6.84 - 6.78 (m, *J* = 8.9 Hz, 2 H), 6.57 (dd, *J* = 6.6, 8.4 Hz, 1 H), 6.46 (s, 1 H), 6.44 - 6.40 (m, 1 H), 6.26 (s, 1 H), 6.18 (s, 1 H), 5.65 (s, 1 H), 3.01 (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.6, 152.9, 149.6, 142.1, 135.9, 129.7, 129.3, 129.1, 128.5, 128.3, 127.2, 126.3, 124.9, 122.3, 120.3, 117.6, 115.7, 113.9, 112.8, 112.6, 110.3, 40.6, 40.5; **HRMS** (ESI) calcd for $C_{26}H_{24}ON$ $[M]^+$ 380.1883, found 380.1882.

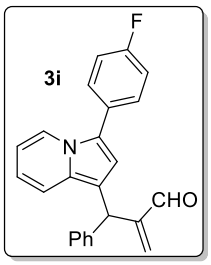


3g: Yellow thick liquid; yield = 87 mg, 88%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.30 (d, *J* = 7.2 Hz, 1 H), 7.34 - 7.28 (m, 2 H), 7.27 - 7.21 (m, 4 H), 6.68 (d, *J* = 1.9 Hz, 2 H), 6.66 - 6.60 (m, 1 H), 6.56 (s, 1 H), 6.48 (t, *J* = 6.5 Hz, 1 H), 6.44

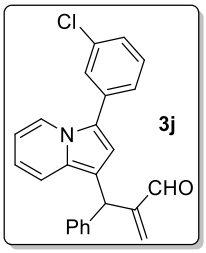
(s, 1 H), 6.27 (s, 1 H), 6.16 (s, 1 H), 5.65 (s, 1 H), 3.83 (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 161.2, 152.8, 141.9, 135.8, 134.1, 130.7, 128.5, 128.4, 126.5, 124.3, 122.6, 117.8, 116.6, 114.9, 113.3, 110.9, 105.9, 99.1, 55.5, 40.6; **HRMS** (ESI) calcd for $C_{26}H_{24}NO_3$ $[M+H]^+$ 398.1751, found 398.1750.



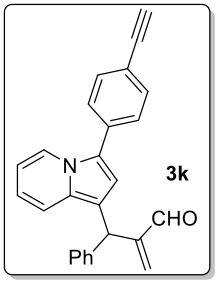
3h: Yellow solid; yield = 74 mg, 71%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); mp = 115-117 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.71 (s, 1 H), 8.19 (d, *J* = 7.0 Hz, 1 H), 7.59 - 7.55 (m, *J* = 8.2 Hz, 2 H), 7.43 - 7.38 (m, *J* = 8.2 Hz, 2 H), 7.34 - 7.28 (m, 3 H), 7.27 - 7.20 (m, 3 H), 6.66 (dd, *J* = 6.7, 8.9 Hz, 1 H), 6.55 (s, 1 H), 6.50 (t, *J* = 6.4 Hz, 1 H), 6.28 (s, 1 H), 6.16 (s, 1 H), 5.65 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.4, 152.8, 141.8, 135.9, 132.0, 131.2, 130.9, 129.2, 128.9, 128.5, 128.4, 127.8, 126.5, 123.2, 122.0, 120.6, 117.9, 116.9, 115.0, 113.7, 111.2, 40.5; **HRMS** (ESI) calcd for $C_{24}H_{19}NOBr$ $[M+H]^+$ 416.0645, found 416.0630.



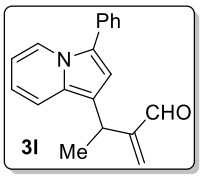
3i: Yellow thick liquid; yield = 65 mg, 73%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (d, *J* = 1.8 Hz, 1 H), 8.13 (d, *J* = 7.3 Hz, 1 H), 7.48 (ddd, *J* = 2.1, 5.7, 8.2 Hz, 2 H), 7.33 - 7.27 (m, 3 H), 7.27 - 7.18 (m, 3 H), 7.14 (dt, *J* = 1.8, 8.7 Hz, 2 H), 6.66 - 6.59 (m, 1 H), 6.51 (s, 1 H), 6.50 - 6.43 (m, 1 H), 6.26 (s, 1 H), 6.15 (s, 1 H), 5.65 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 163.0 (d, *J* = 246.33 MHz), 152.8, 141.9, 135.9, 130.4, 129.7 (d, *J* = 7.67 Hz), 128.5, 128.4, 126.5, 123.3, 121.9, 117.8, 116.5, 116.0, 115.8, 114.7, 113.3, 111.0, 40.5; **HRMS** (ESI) calcd for $C_{24}H_{19}ONF$ $[M+H]^+$ 356.1445, found 356.1449.



3j: Yellow thick liquid; yield = 64 mg, 69%; R_f = 0.30 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.71 (s, 1 H), 8.24 (d, *J* = 6.8 Hz, 1 H), 7.52 (s, 1 H), 7.46 - 7.41 (m, 1 H), 7.40 - 7.36 (m, 1 H), 7.35 - 7.28 (m, 4 H), 7.27 - 7.20 (m, 3 H), 6.67 (dd, *J* = 7.1, 8.1 Hz, 1 H), 6.57 (s, 1 H), 6.52 (t, *J* = 6.6 Hz, 1 H), 6.28 (s, 1 H), 6.16 (s, 1 H), 5.65 (s, 1 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 193.4, 152.7, 141.8, 135.9, 134.8, 134.1, 131.1, 130.1, 129.6, 128.5, 128.4, 127.6, 126.8, 126.5, 125.6, 122.9, 122.1, 117.9, 117.1, 115.3, 113.7, 111.3, 40.5; **HRMS** (ESI) calcd for $C_{24}H_{19}NOCl$ $[M+H]^+$ 372.1150, found 372.1154.

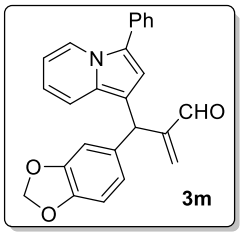


3k: Yellow solid; yield = 74 mg, 82%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95; mp = 131-133 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.68 (s, 1 H), 8.24 (d, *J* = 7.3 Hz, 1 H), 7.56 - 7.52 (m, 2 H), 7.50 - 7.46 (m, 2 H), 7.32 - 7.27 (m, 2 H), 7.26 - 7.18 (m, 4 H), 6.64 (dd, *J* = 6.0, 9.2 Hz, 1 H), 6.57 (s, 1 H), 6.51 - 6.46 (m, 1 H), 6.25 (s, 1 H), 6.13 (s, 1 H), 5.63 (s, 1 H), 3.12 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.4, 152.7, 141.7, 135.9, 132.7, 132.6, 131.2, 128.5, 128.4, 127.2, 126.5, 123.6, 122.2, 120.1, 117.9, 117.1, 115.3, 113.9, 111.2, 83.6, 77.7, 40.5; **HRMS** (ESI) calcd for $C_{26}H_{20}NO$ $[M+H]^+$ 362.1539, found 362.1541.

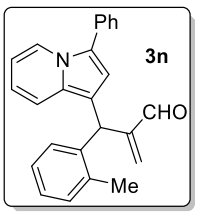


3l: Yellow thick liquid; yield = 38 mg, 56%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **DMSO-d_6**) δ = 9.57 (s, 1 H), 8.30 (d, *J* = 7.3 Hz, 1 H), 7.59 - 7.53 (m, 2 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 7.46 - 7.42 (m, 1 H), 7.37 - 7.25 (m, 1 H), 6.84 (s, 1 H), 6.69 (dd, *J* = 6.1, 9.0 Hz, 1 H), 6.59 - 6.50 (m, 1 H), 6.42 (s, 1 H), 6.22 (s, 1 H), 4.25 (q, *J* = 7.0 Hz, 1 H), 1.46 (d, *J* = 7.3 Hz, 3

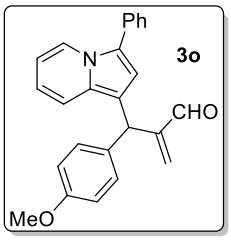
H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 194.9, 153.9, 134.3, 131.8, 129.7, 129.1, 127.3, 126.9, 123.7, 122.1, 117.7, 116.4, 116.2, 113.0, 111.0, 27.7, 20.3; **HRMS** (ESI) calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1383.



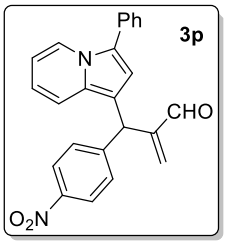
3m: Yellow thick liquid; yield = 60 mg, 63%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.27 (d, *J* = 7.3 Hz, 1 H), 7.57 - 7.53 (m, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.35 - 7.31 (m, 1 H), 7.28 - 7.23 (m, 1 H), 6.78 - 6.72 (m, 3 H), 6.65 (dd, *J* = 6.1, 9.2 Hz, 1 H), 6.56 (s, 1 H), 6.49 (t, *J* = 7.0 Hz, 1 H), 6.27 (s, 1 H), 6.18 (s, 1 H), 5.94 (s, 2 H), 5.57 (s, 1 H); **^{13}CNMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 152.9, 147.7, 146.1, 135.9, 135.8, 132.3, 130.5, 128.9, 127.8, 127.0, 124.4, 122.3, 121.5, 117.7, 116.6, 114.7, 113.4, 110.9, 109.1, 108.1, 100.9, 92.6, 40.2, 29.7; **HRMS** (ESI) calcd for $C_{25}H_{20}NO_3$ $[M+H]^+$ 382.1438, found 382.1436.



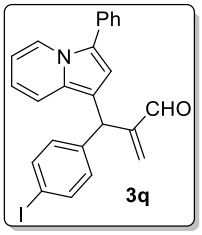
3n: Yellow thick liquid; yield = 73 mg, 83%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.72 (s, 1 H), 8.27 (d, *J* = 7.3 Hz, 1 H), 7.54 (d, *J* = 7.9 Hz, 2 H), 7.48 - 7.39 (m, 2 H), 7.34 - 7.29 (m, 1 H), 7.26 - 7.21 (m, 1 H), 7.21 - 7.06 (m, 4 H), 6.63 (dd, *J* = 6.7, 9.2 Hz, 1 H), 6.54 - 6.40 (m, 2 H), 6.27 (s, 1 H), 6.09 (s, 1 H), 5.76 (s, 1 H), 2.34 (s, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 193.4, 152.6, 140.1, 136.2, 135.8, 132.3, 130.6, 130.5, 128.9, 127.8, 127.6, 126.9, 126.4, 125.7, 124.4, 122.3, 117.7, 116.5, 115.3, 112.6, 110.8, 37.0, 19.6; **HRMS** (ESI) calcd for $C_{25}H_{22}NO$ $[M+H]^+$ 352.1696, found 352.1696.



3o: Yellow thick liquid; yield = 59 mg, 65%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.61 (s, 1 H), 8.16 (d, *J* = 6.9 Hz, 1 H), 7.48 - 7.40 (m, 2 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.25 - 7.19 (m, 1 H), 7.16 (d, *J* = 10.1 Hz, 1 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H), 6.54 (dd, *J* = 6.6, 8.9 Hz, 1 H), 6.45 (s, 1 H), 6.38 (t, *J* = 6.6 Hz, 1 H), 6.16 (s, 1 H), 6.06 (s, 1 H), 5.51 (s, 1 H), 3.70 (s, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 193.6, 158.1, 153.1, 135.6, 134.0, 132.3, 130.5, 129.5, 128.9, 127.8, 126.9, 124.4, 122.2, 117.8, 116.5, 114.8, 113.8, 110.8, 55.2, 39.8; **HRMS** (ESI) calcd for $C_{25}H_{22}NO_2$ $[M+H]^+$ 368.1645, found 368.1636.

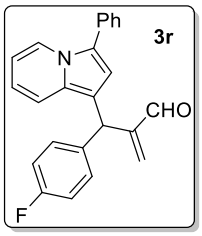


3p: Yellow thick liquid; yield = 73 mg, 77%; R_f = 0.20 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**200 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.26 (d, *J* = 7.2 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 2 H), 7.56 - 7.48 (m, 2 H), 7.48 - 7.37 (m, 4 H), 7.37 - 7.29 (m, 1 H), 7.27 - 7.18 (m, 1 H), 6.68 (dd, *J* = 6.5, 8.9 Hz, 1 H), 6.58 - 6.48 (m, 1 H), 6.47 (s, 1 H), 6.35 (s, 1 H), 6.20 (s, 1 H), 5.71 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.0, 151.6, 149.8, 146.6, 136.7, 131.9, 130.5, 129.2, 128.9, 127.8, 127.2, 125.0, 123.7, 122.4, 117.2, 114.4, 111.4, 111.1, 40.6; **HRMS** (ESI) calcd for $C_{24}H_{18}N_2O_3$ $[M^+]$ 382.1312, found 382.1308.

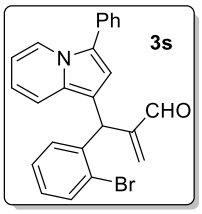


3q: Yellow thick liquid; yield = 76 mg, 66%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.69 (s, 1 H), 8.26 (d, *J* = 7.2 Hz, 1 H), 7.66 - 7.58 (m, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 6.9 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.32 (t, *J* = 7.4 Hz, 1 H), 7.24 (d, *J* = 8.8 Hz, 1 H), 7.05 - 6.98 (m, *J* = 8.4 Hz, 2 H), 6.65 (dd, *J* = 6.5, 9.2 Hz, 1 H), 6.51 (s, 1 H), 6.50 - 6.46 (m, 1 H),

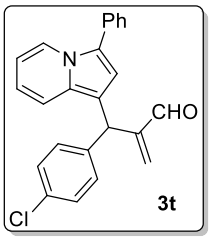
6.28 (s, 1 H), 6.16 (s, 1 H), 5.59 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.3, 152.3, 141.8, 137.5, 136.2, 132.1, 131.5, 130.6, 130.5, 130.3, 128.9, 127.8, 127.1, 124.6, 122.3, 117.6, 116.8, 114.6, 112.6, 110.9, 91.9, 40.2; **HRMS** (ESI) calcd for $C_{24}H_{19}NOI$ $[M+H]^+$ 464.0506, found 464.0497.



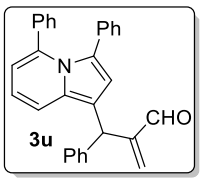
3r: Yellow thick liquid; yield = 70 mg, 79%; R_f = 0.40 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.70 (s, 1 H), 8.26 (d, *J* = 7.2 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.26 - 7.19 (m, 3 H), 7.00 (t, *J* = 8.8 Hz, 2 H), 6.65 (dd, *J* = 6.7, 8.6 Hz, 1 H), 6.52 (s, 1 H), 6.49 (t, *J* = 6.5 Hz, 1 H), 6.28 (s, 1 H), 6.15 (s, 1 H), 5.63 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.4, 162.5 (d, *J* = 244.14 Hz) 152.8, 137.6 (d, *J* = 2.86 Hz), 135.9, 132.2, 130.5, 129.9 (d, *J* = 7.63 Hz), 128.9, 127.8, 127.0, 124.6, 122.3, 117.6, 116.7, 115.3, 115.1 (d, *J* = 54.36 Hz), 113.1, 110.9, 39.9; **HRMS** (ESI) calcd for $C_{24}H_{19}ONF$ $[M+H]^+$ 356.1445, found 356.1443.



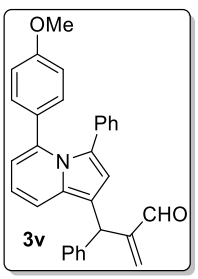
3s: Yellow thick liquid; yield = 70 mg, 68%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.71 (s, 1 H), 8.27 (d, *J* = 6.9 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 7.6 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.35 - 7.31 (m, 2 H), 7.22 (t, *J* = 7.2 Hz, 1 H), 7.17 (d, *J* = 6.5 Hz, 1 H), 7.10 (t, *J* = 7.2 Hz, 1 H), 6.69 - 6.62 (m, 1 H), 6.57 (s, 1 H), 6.49 (t, *J* = 6.7 Hz, 1 H), 6.28 (s, 1 H), 6.00 (s, 1 H), 6.03 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 192.9, 151.7, 141.5, 135.4, 133.1, 132.2, 130.9, 129.9, 129.4, 128.9, 128.1, 127.8, 127.2, 127.0, 126.2, 124.7, 124.5, 122.2, 117.8, 116.8, 114.8, 111.5, 111.0, 40.4; **HRMS** (ESI) calcd for $C_{24}H_{19}NOBr$ $[M+H]^+$ 418.0624, found 418.0622.



3t: Yellow thick liquid; yield = 57 mg, 62%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.71 (br. s., 1 H), 8.28 (d, *J* = 6.1 Hz, 1 H), 7.55 (d, *J* = 6.9 Hz, 2 H), 7.50 - 7.43 (m, 2 H), 7.38 - 7.32 (m, 1 H), 7.32 - 7.24 (m, 3 H), 7.22 (d, *J* = 6.9 Hz, 2 H), 6.66 (t, *J* = 6.5 Hz, 1 H), 6.54 (br. s., 1 H), 6.50 (br. s., 1 H), 6.29 (br. s., 1 H), 6.17 (br. s., 1 H), 5.64 (br. s., 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.3, 152.5, 140.5, 136.0, 132.2, 132.2, 130.5, 129.8, 128.9, 128.5, 127.8, 127.1, 124.6, 122.3, 117.6, 116.8, 114.6, 112.7, 110.9, 40.0; **HRMS** (ESI) calcd for $C_{24}H_{19}NOCl$ $[M+H]^+$ 372.1150, found 372.1152.

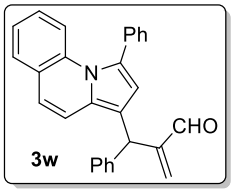


3u: Yellow thick liquid; yield = 63 mg, 61%; R_f = 0.30 (ethyl acetate/petroleum ether = 20/80; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.73 (s, 1 H), 7.37 (d, *J* = 9.2 Hz, 1 H), 7.35 - 7.29 (m, 4 H), 7.26 - 7.21 (m, 1 H), 7.12 - 7.06 (m, 2 H), 7.03 (d, *J* = 7.2 Hz, 1 H), 7.00 - 6.95 (m, 2 H), 6.94 - 6.88 (m, 3 H), 6.88 - 6.83 (m, 2 H), 6.82 - 6.77 (m, 1 H), 6.56 (s, 1 H), 6.52 (d, *J* = 6.5 Hz, 1 H), 6.29 (s, 1 H), 6.19 (s, 1 H), 5.75 (s, 1 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**) δ = 193.5, 152.8, 141.9, 137.2, 136.2, 135.9, 134.2, 132.6, 128.6, 128.4, 128.2, 128.1, 127.8, 127.5, 127.4, 126.9, 126.5, 126.0, 125.4, 117.8, 116.6, 115.0, 113.8, 40.6; **HRMS** (ESI) calcd for $C_{30}H_{24}NO$ $[M+H]^+$ 414.1852, found 414.1852.

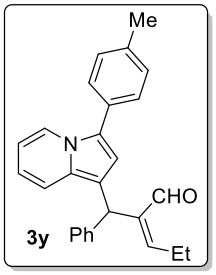


3v: Yellow thick liquid; yield = 83 mg, 75%; R_f = 0.30 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 9.73 (s, 1 H), 7.38 - 7.32 (m, 3 H), 7.32 - 7.30 (m, 2 H), 7.27 - 7.21 (m, 1 H), 7.03 - 6.99 (m, *J* = 8.8 Hz, 2 H), 6.96 - 6.91 (m, 3 H), 6.88 - 6.84 (m, 2 H), 6.78 (dd, *J* = 6.7, 9.0 Hz, 1 H), 6.57 (s, 1 H), 6.53 - 6.50 (m, *J* = 8.8 Hz, 2 H), 6.49 - 6.46 (m, 1 H), 6.29 (s, 1 H), 6.20 (s, 1

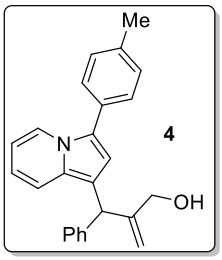
H), 5.76 (s, 1 H), 3.71 (s, 3 H); **^{13}C NMR** (**500 MHz**, **$CDCl_3$**) δ = 193.5, 159.1, 152.8, 141.9, 137.1, 135.9, 134.3, 132.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.4, 128.0, 126.8, 126.7, 126.4, 126.0, 125.5, 125.3, 117.7, 116.6, 116.2, 114.3, 113.5, 112.8, 55.3, 40.6; **HRMS** (ESI) calcd for $C_{31}H_{26}NO$ $[M+H]^+$ 444.1958, found 444.1956.



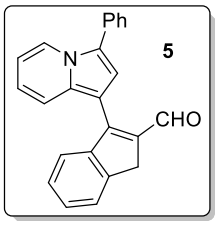
3w: Yellow thick liquid; yield = 78 mg, 82%; R_f = 0.20 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 9.67 (br. s., 1 H), 7.63 - 7.33 (m, 8 H), 7.33 - 7.12 (m, 7 H), 7.07 (d, *J* = 8.5 Hz, 1 H), 6.37 (br. s., 1 H), 6.28 - 6.21 (m, 1 H), 6.20 - 6.11 (m, 1 H), 5.65 (br. s., 1 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 193.4, 152.8, 141.8, 136.0, 135.4, 134.2, 129.5, 129.2, 128.5, 128.4, 127.5, 126.5, 126.3, 125.4, 123.3, 118.8, 117.6, 117.1, 116.2, 40.4; **HRMS** (ESI) calcd for $C_{28}H_{22}NO$ $[M+H]^+$ 388.1696, found 388.1688.



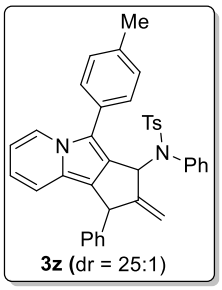
3y: Brownish thick liquid; yield = 55 mg, 61%; R_f = 0.50 (ethyl acetate/petroleum ether = 05/95; **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 10.23 (s, 1 H), 8.22 (d, *J* = 7.3 Hz, 1 H), 7.43 (d, *J* = 7.3 Hz, 2 H), 7.31 - 7.20 (m, 8 H), 6.61 - 6.55 (m, 1 H), 6.47 (s, 1 H), 6.45 - 6.40 (m, 2 H), 5.70 (s, 1 H), 2.68 - 2.60 (m, 2 H), 2.39 (s, 3 H), 1.09 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 190.2, 152.4, 143.0, 142.1, 136.7, 130.3, 129.5, 128.6, 128.2, 128.2, 128.1, 127.8, 126.2, 124.3, 122.2, 117.9, 116.1, 114.8, 114.0, 110.6, 110.6, 41.2, 21.2, 20.3, 14.4; **HRMS** (ESI) calcd for $C_{27}H_{26}NO$ $[M+H]^+$ 380.2009, found 380.2004.



4: Yellow thick liquid; yield = 46 mg, 92%; R_f = 0.30 (ethyl acetate/petroleum ether = 10/90); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 8.21 (d, *J* = 6.7 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 2 H), 7.33 - 7.26 (m, 5 H), 7.25 - 7.14 (m, 3 H), 6.61 (s, 1 H), 6.59 - 6.54 (m, 1 H), 6.42 (t, *J* = 6.7 Hz, 1 H), 5.32 (s, 1 H), 5.14 (s, 1 H), 4.82 (s, 1 H), 4.17 (s, 2 H), 2.39 (s, 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 151.5, 142.6, 136.7, 130.6, 129.5, 129.5, 128.8, 128.3, 127.8, 126.3, 124.5, 122.3, 117.8, 116.1, 114.6, 113.8, 112.8, 110.5, 65.9, 45.8, 21.2; **HRMS** (ESI) calcd for $C_{25}H_{24}NO$ $[M+H]^+$ 354.1852, found 354.1850.



5: Brownish thick liquid; yield = 25 mg, 62%; R_f = 0.30 (ethyl acetate/petroleum ether = 05/95); **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ = 10.08 (s, 1 H), 8.47 - 8.28 (m, 1 H), 7.74 (d, *J* = 7.6 Hz, 1 H), 7.71 - 7.61 (m, 3 H), 7.61 - 7.50 (m, 3 H), 7.49 - 7.37 (m, 3 H), 7.16 (s, 1 H), 6.94 - 6.77 (m, 1 H), 6.73 - 6.54 (m, 1 H), 3.89 (br. s., 2 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 189.7, 153.3, 145.0, 144.2, 138.2, 133.3, 131.4, 129.2, 128.9, 128.4, 128.1, 127.9, 126.9, 126.8, 124.9, 124.0, 122.9, 119.6, 118.7, 115.8, 111.9, 105.5, 36.0; **HRMS** (ESI) calcd for $C_{24}H_{18}NO$ $[M+H]^+$ 336.1383, found 336.1377.

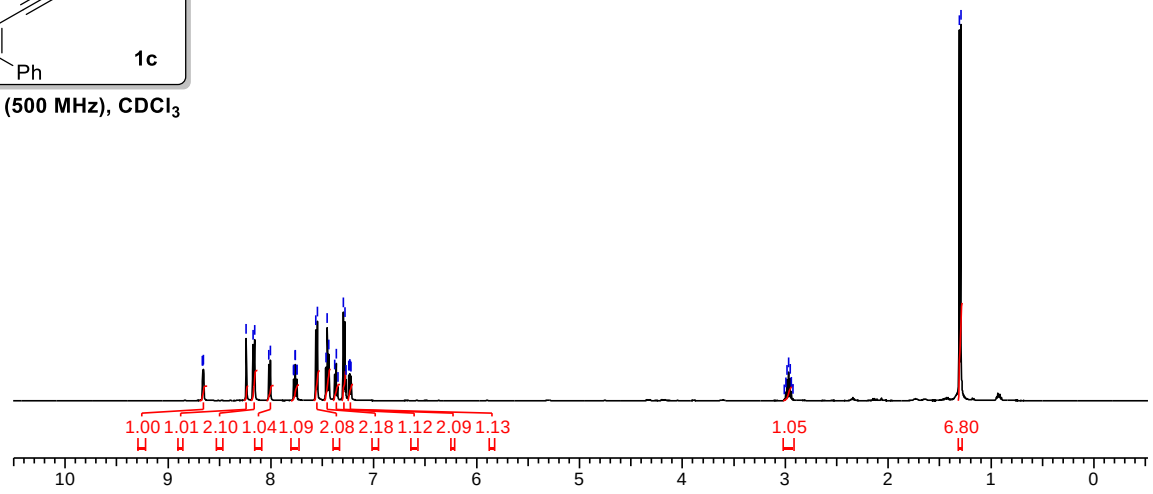


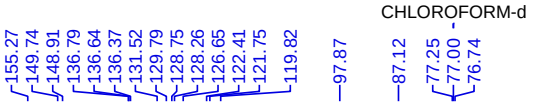
3z: Yellow solid; yield = 30 mg, 30%; R_f = 0.30 (ethyl acetate/petroleum ether = 05/95); mp = 173-175 °C; dr = 25:1, exact stereoselectivity was not determined ; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 8.19 (d, *J* = 7.2 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.54 - 7.39 (m, 3 H), 7.30 - 7.26 (m, 2 H), 7.26 - 7.21 (m, 1 H), 7.20 - 7.08 (m, 6 H), 7.07 - 6.88 (m, 6 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 6.60 (d, *J* = 8.8 Hz, 1

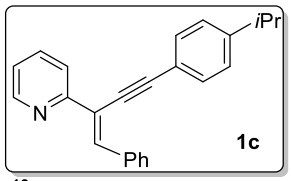
H), 6.47 - 6.26 (m, 2 H), 5.88 (br. s., 1 H), 5.11 (br. s., 1 H), 4.37 (br. s., 1 H), 2.56 (br. s., 3 H), 2.34 (br. s., 3 H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ = 159.9, 143.4, 142.6, 137.4, 137.2, 136.3, 132.2, 130.1, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 126.4, 125.3, 122.8, 122.3, 118.2, 118.2, 116.1, 116.0, 110.7, 62.5, 49.0, 21.5; **HRMS** (ESI) calcd for $C_{24}H_{18}NO$ $[M+H]^+$ 336.1383, found 336.1377.

9. NMR spectra:

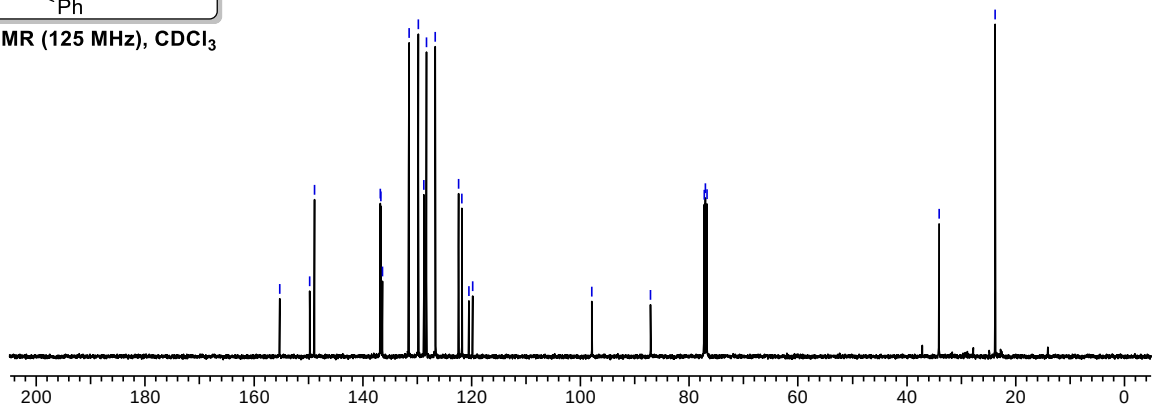
^{1}H NMR (500 MHz), $CDCl_3$

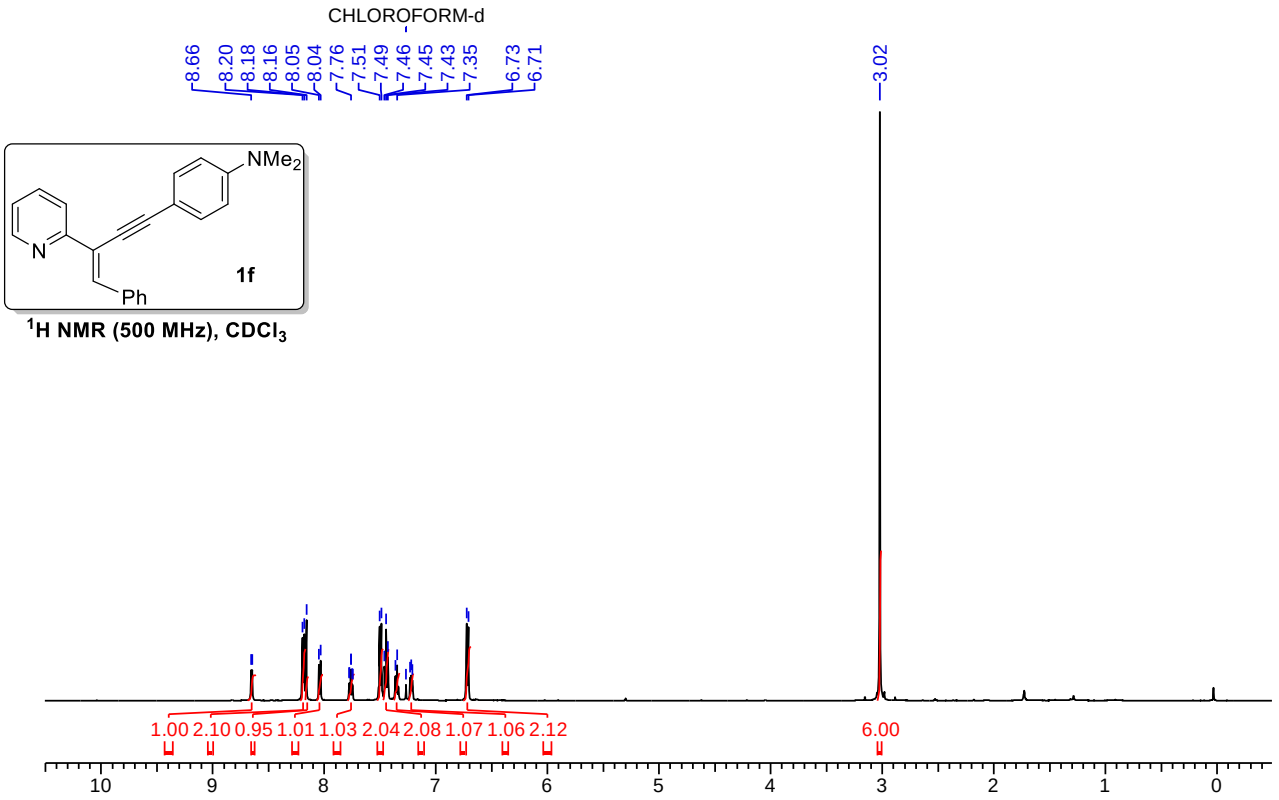




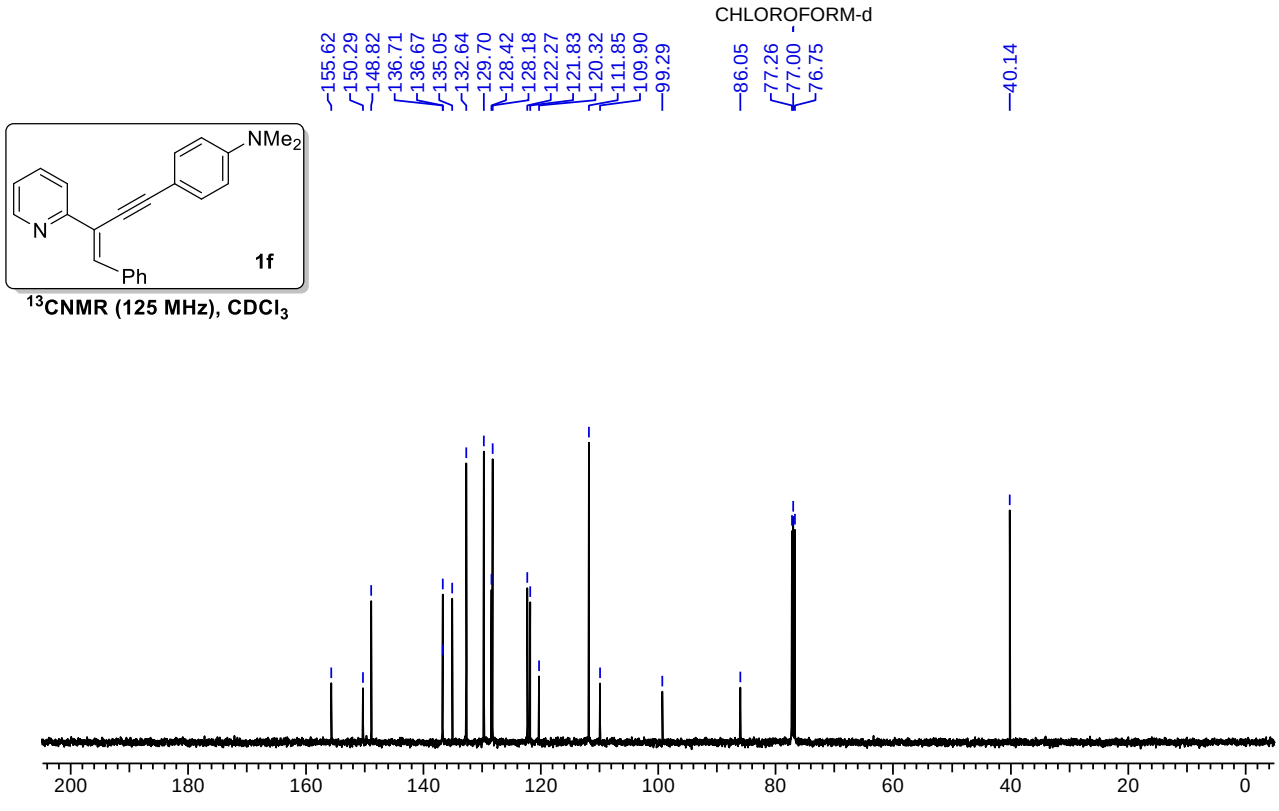


^{13}C NMR (125 MHz), $CDCl_3$

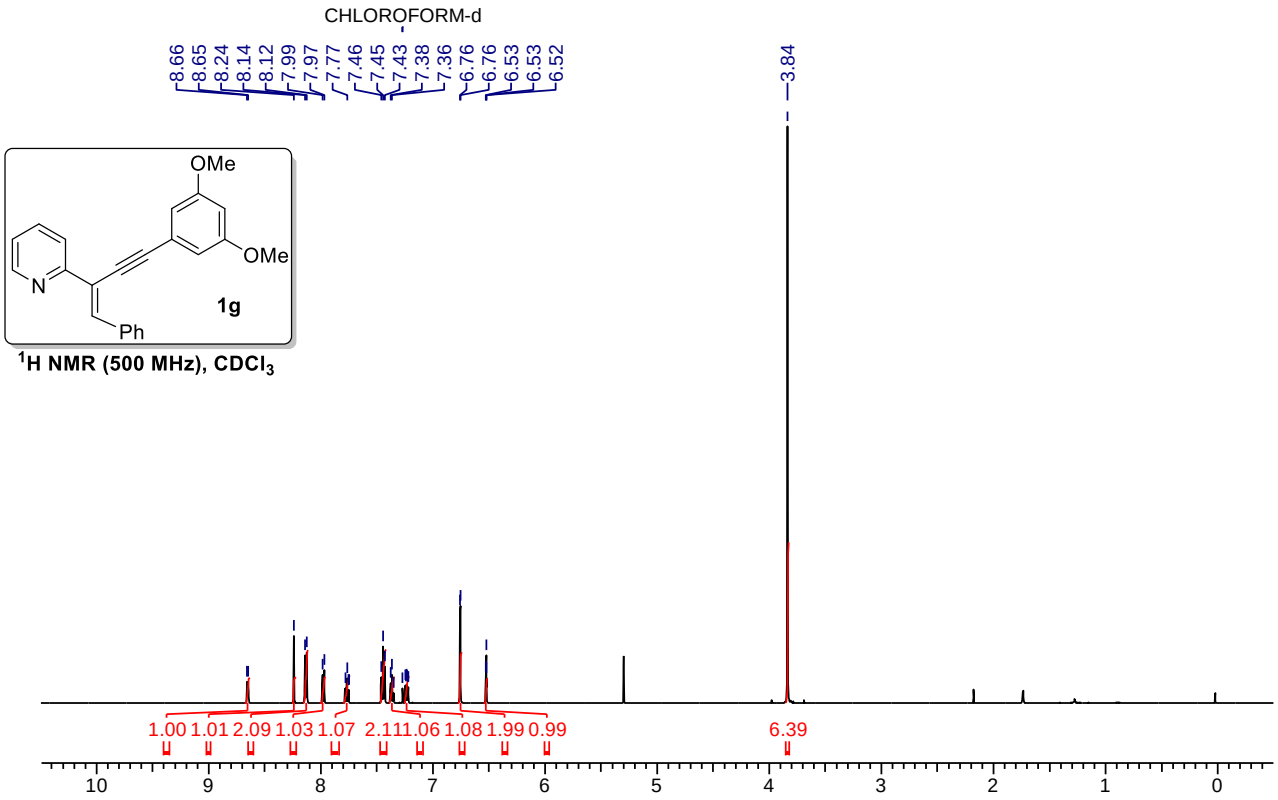




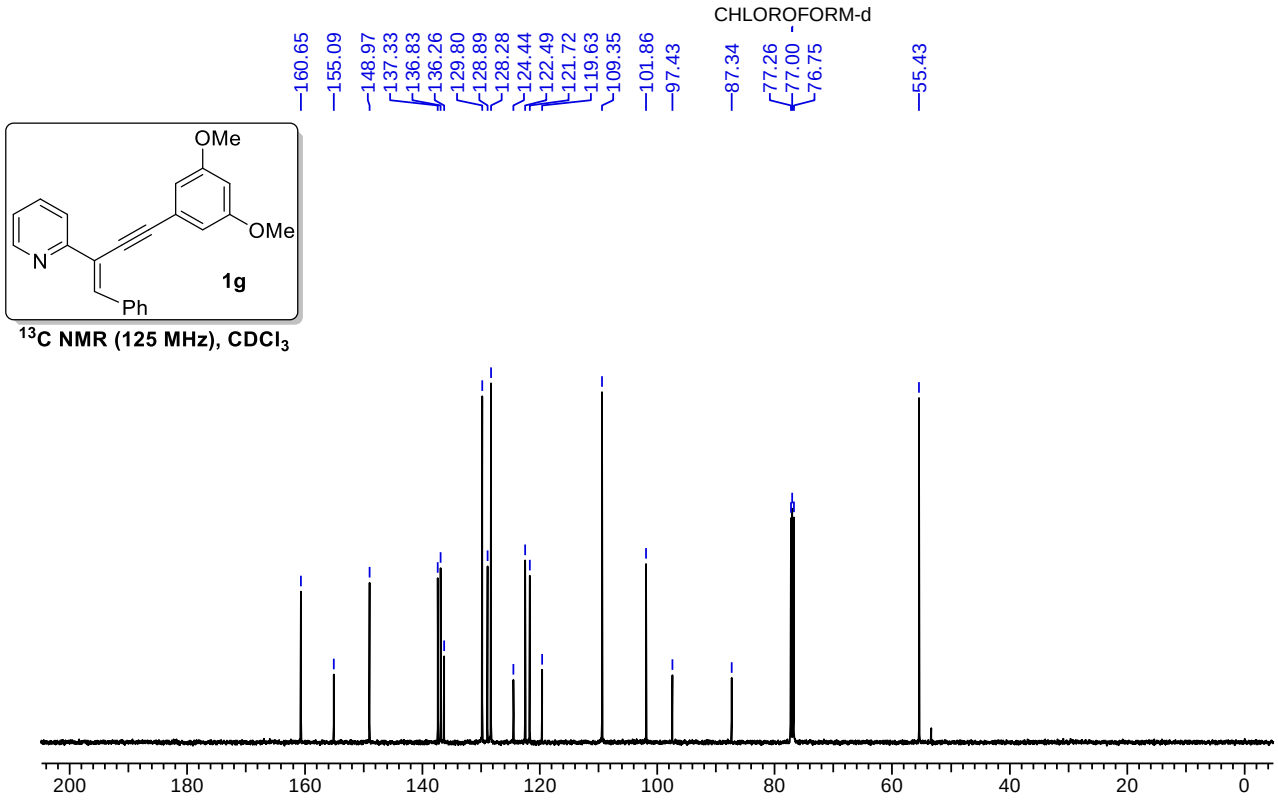
^{1}H NMR (500 MHz), $CDCl_3$



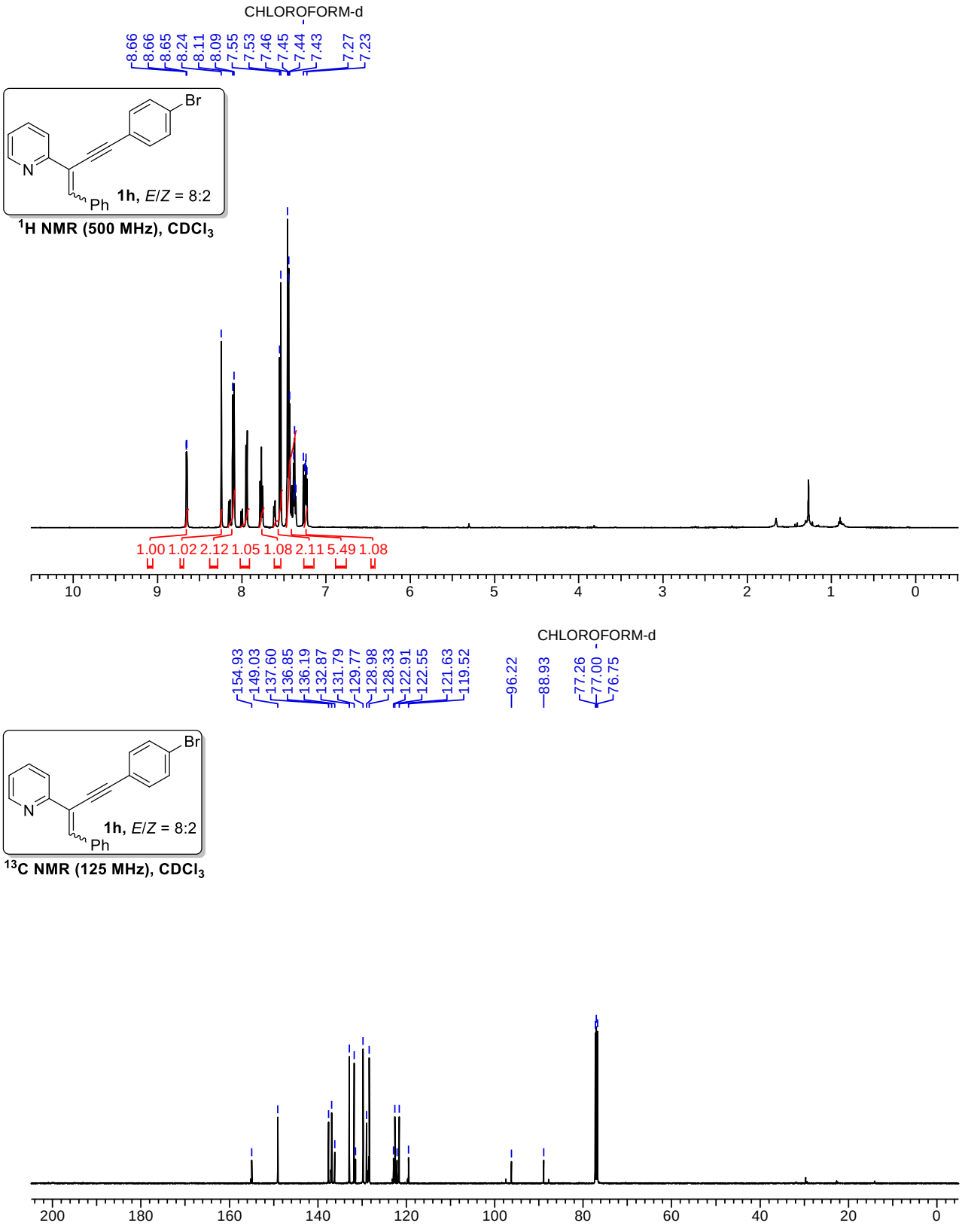
^{13}CNMR (125 MHz), $CDCl_3$

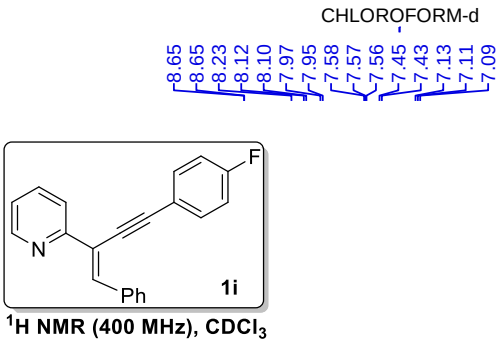


^{1}H NMR (500 MHz), $CDCl_3$

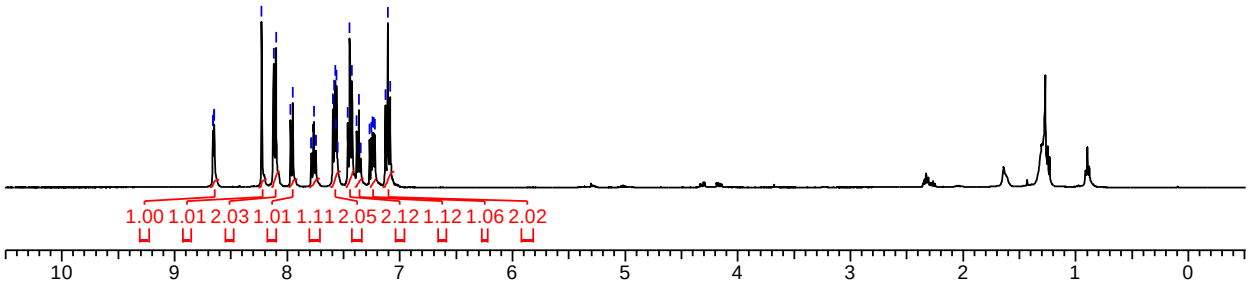


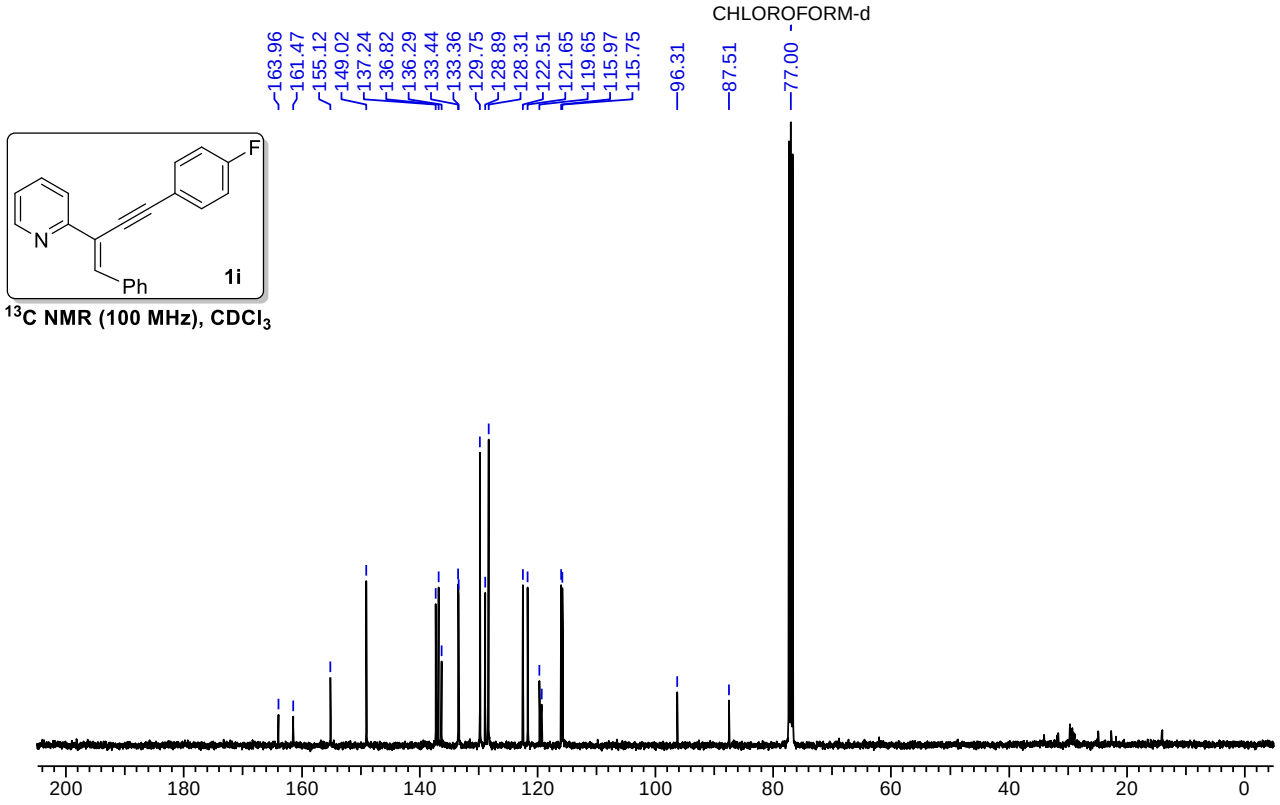
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
8.66
8.66
8.65
8.24
8.11
8.09
7.55
7.53
7.46
7.45
7.44
7.43
7.27
7.23
Br
N
Ph
1h, E/Z = 8:2
1H NMR (500 MHz), CDCl3
1.00 1.02 2.12 1.05 1.08 2.11 5.49 1.08
10 9 8 7 6 5 4 3 2 1 0
CHLOROFORM-d
154.93
149.03
137.60
136.85
136.19
132.87
131.79
129.77
128.98
128.33
122.91
122.55
121.63
119.52
96.22
88.93
77.26
77.00
76.75
Br
N
Ph
1h, E/Z = 8:2
13C NMR (125 MHz), CDCl3
200 180 160 140 120 100 80 60 40 20 0

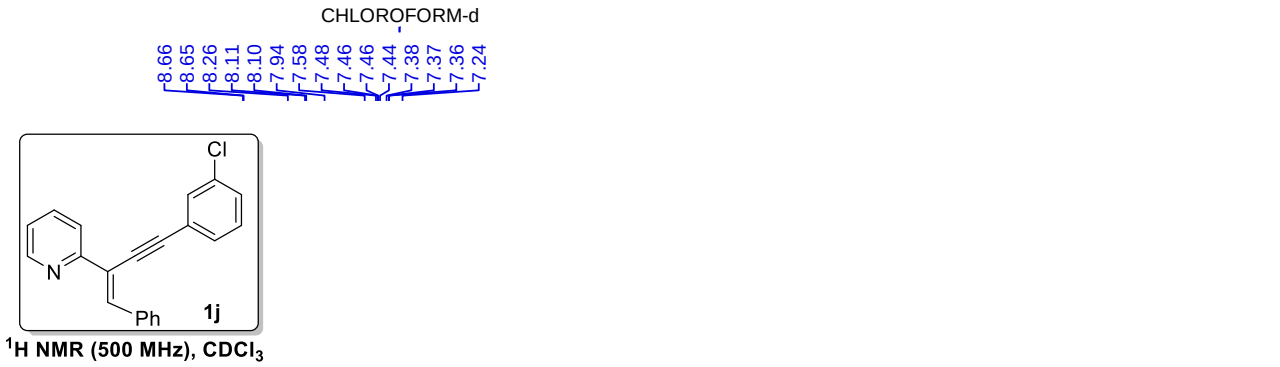


^{1}H NMR (400 MHz), $CDCl_3$

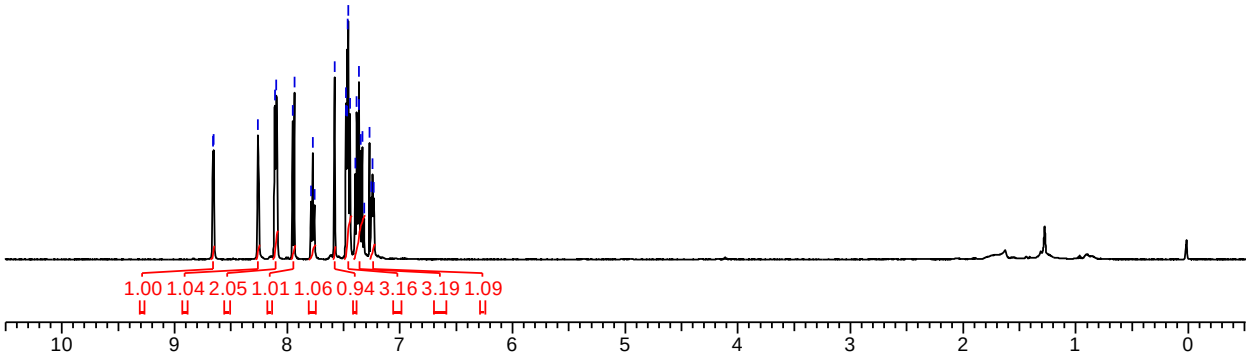


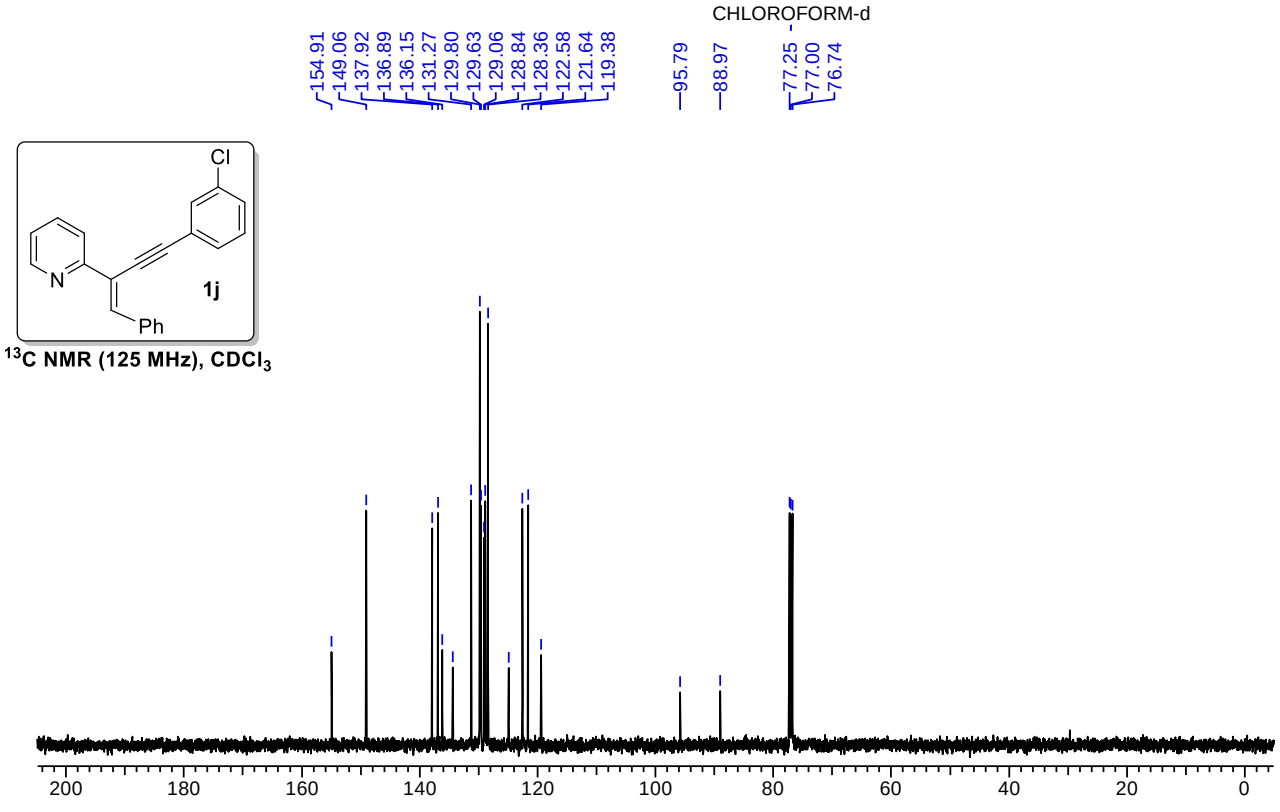


^{13}C NMR (100 MHz), $CDCl_3$

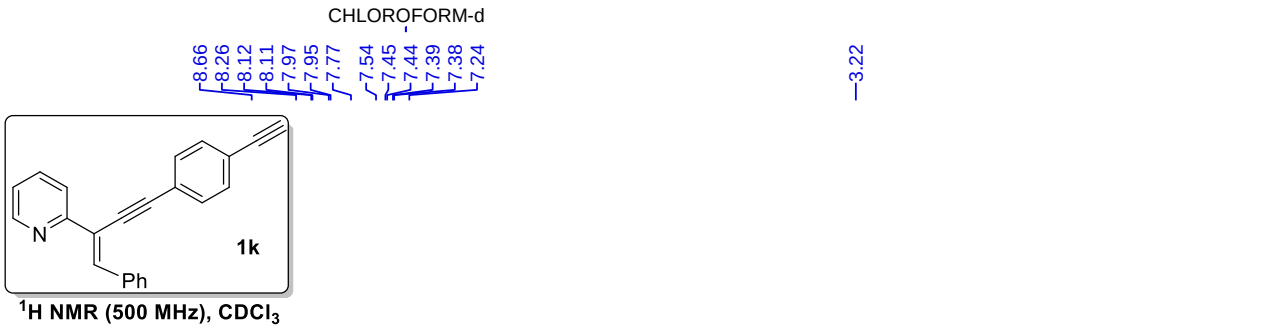


^{1}H NMR (500 MHz), $CDCl_3$

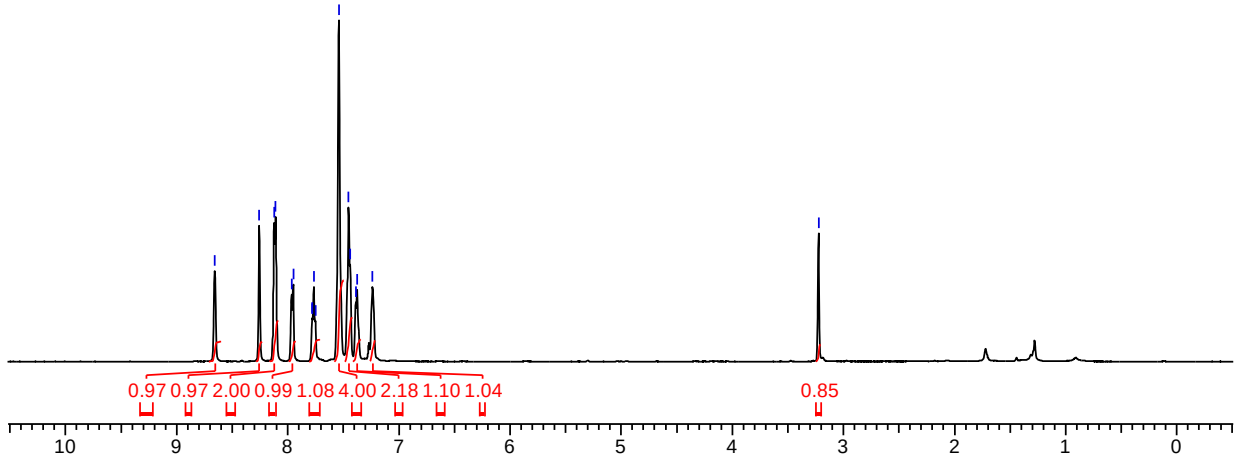


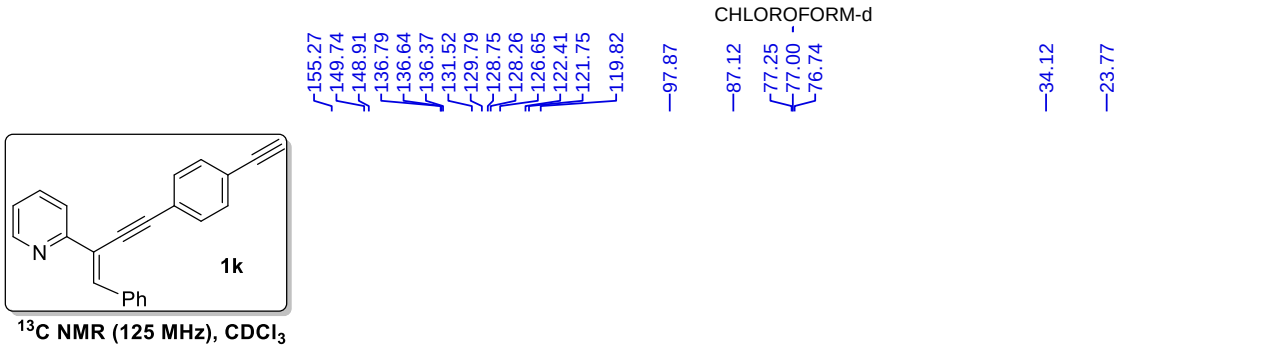


^{13}C NMR (125 MHz), $CDCl_3$

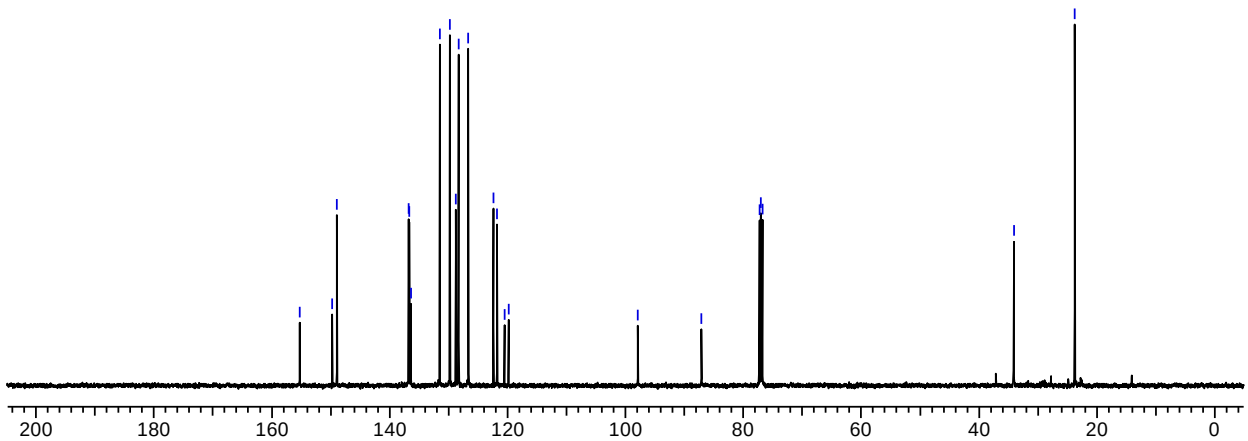


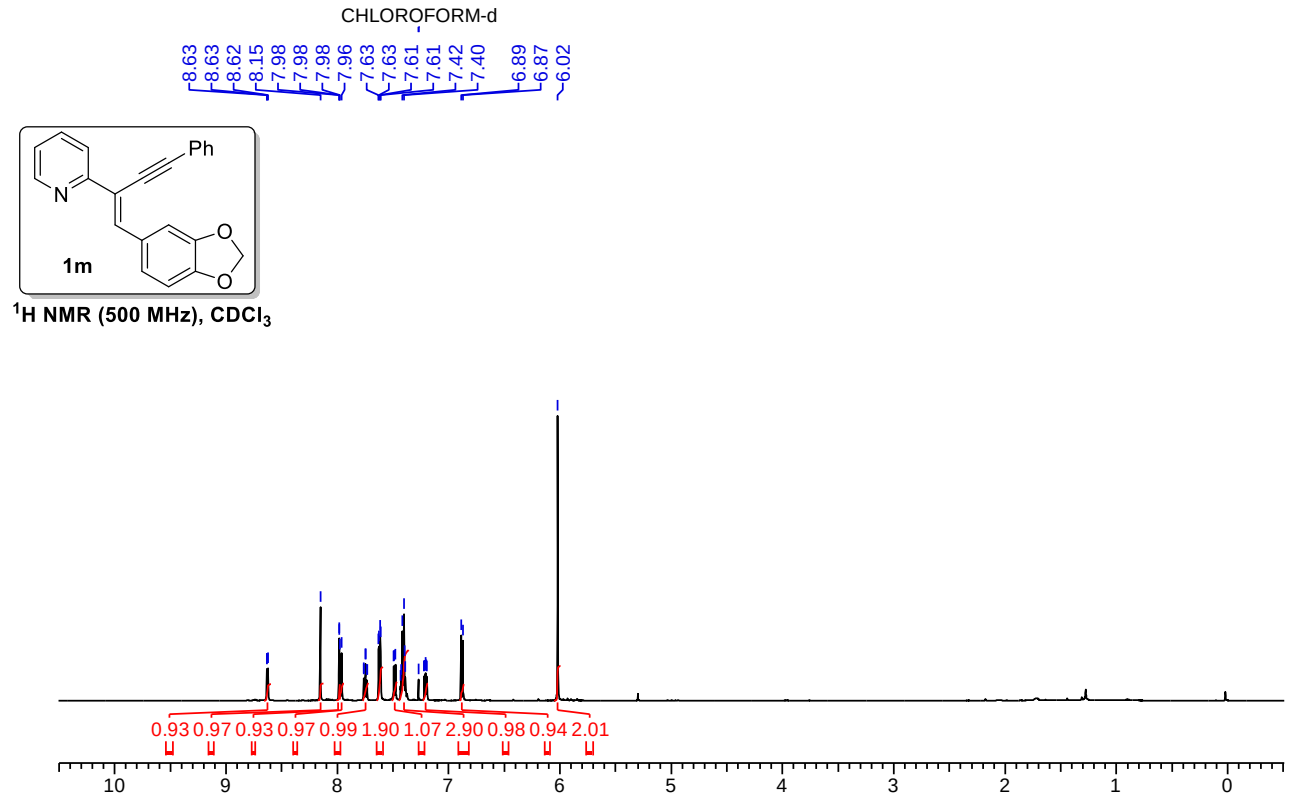
^{1}H NMR (500 MHz), $CDCl_3$



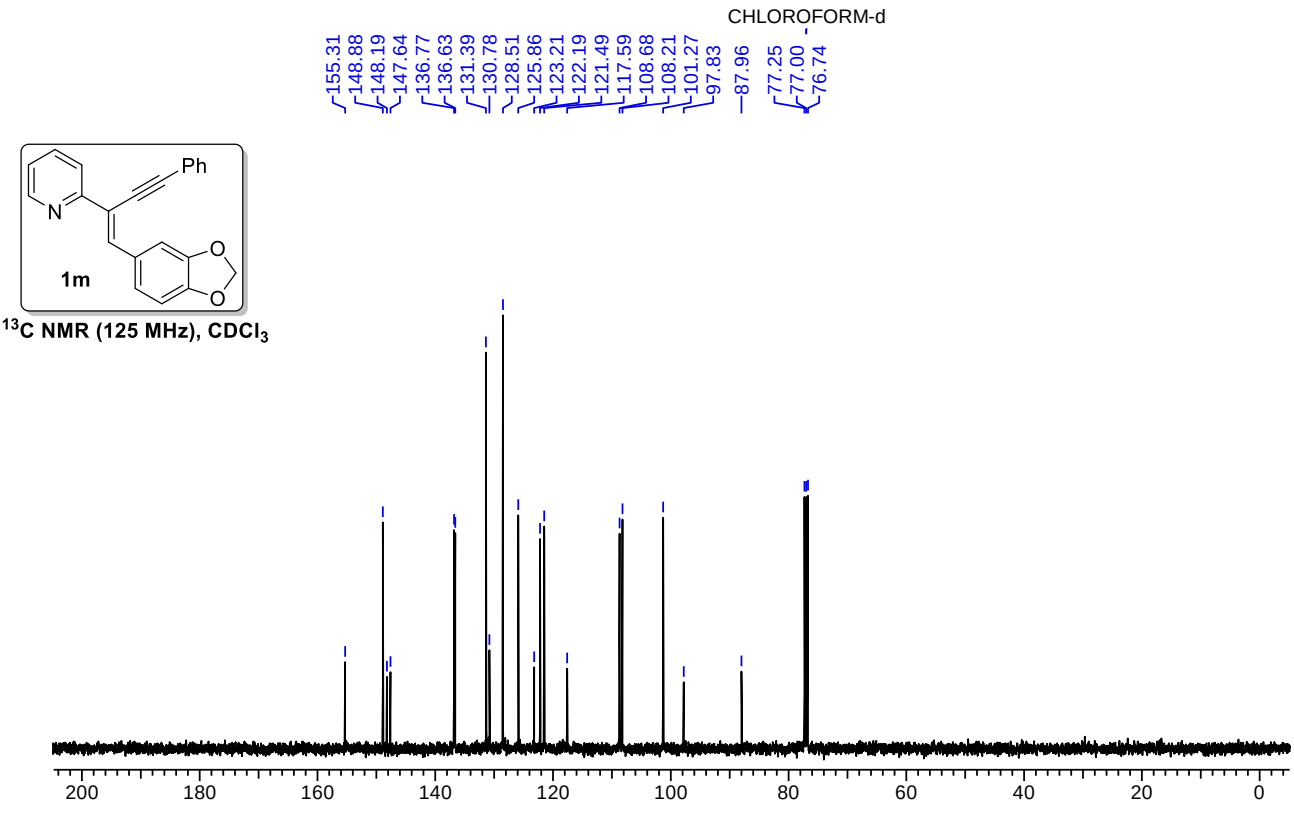


^{13}C NMR (125 MHz), $CDCl_3$

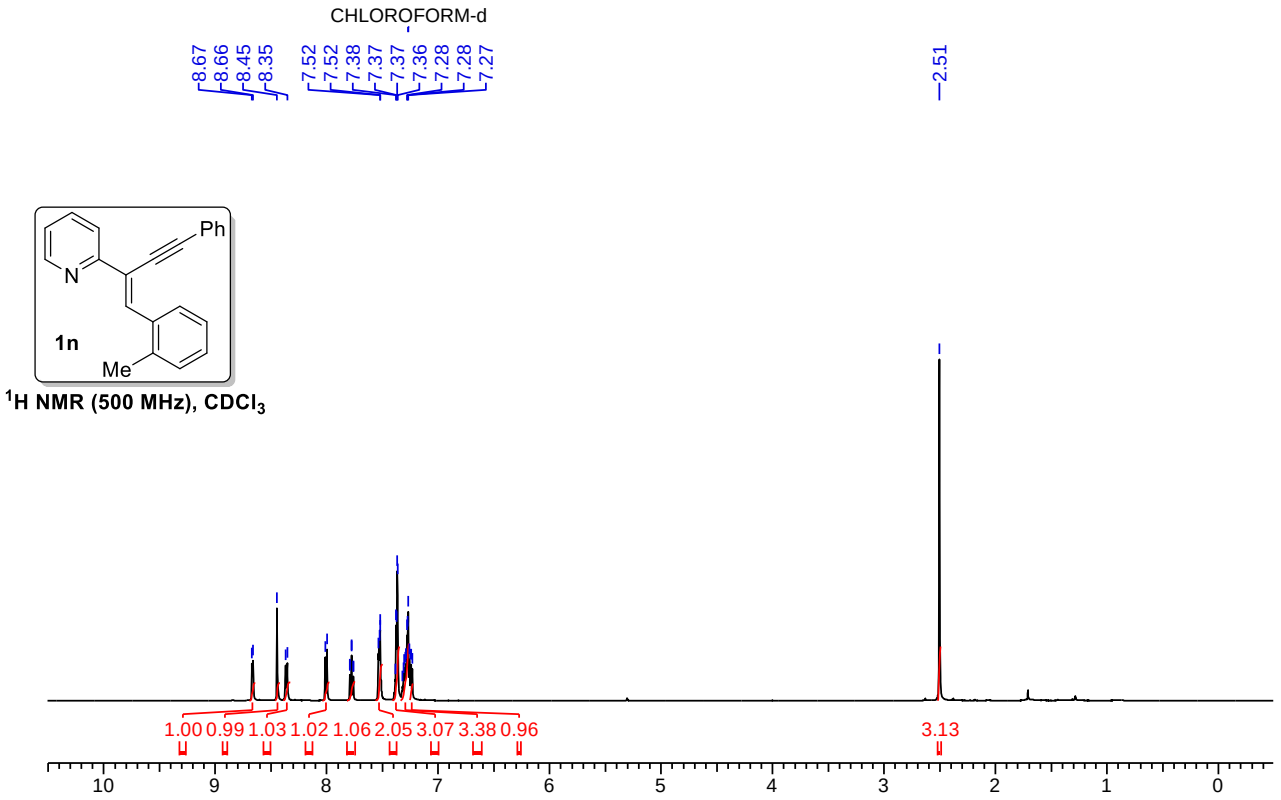




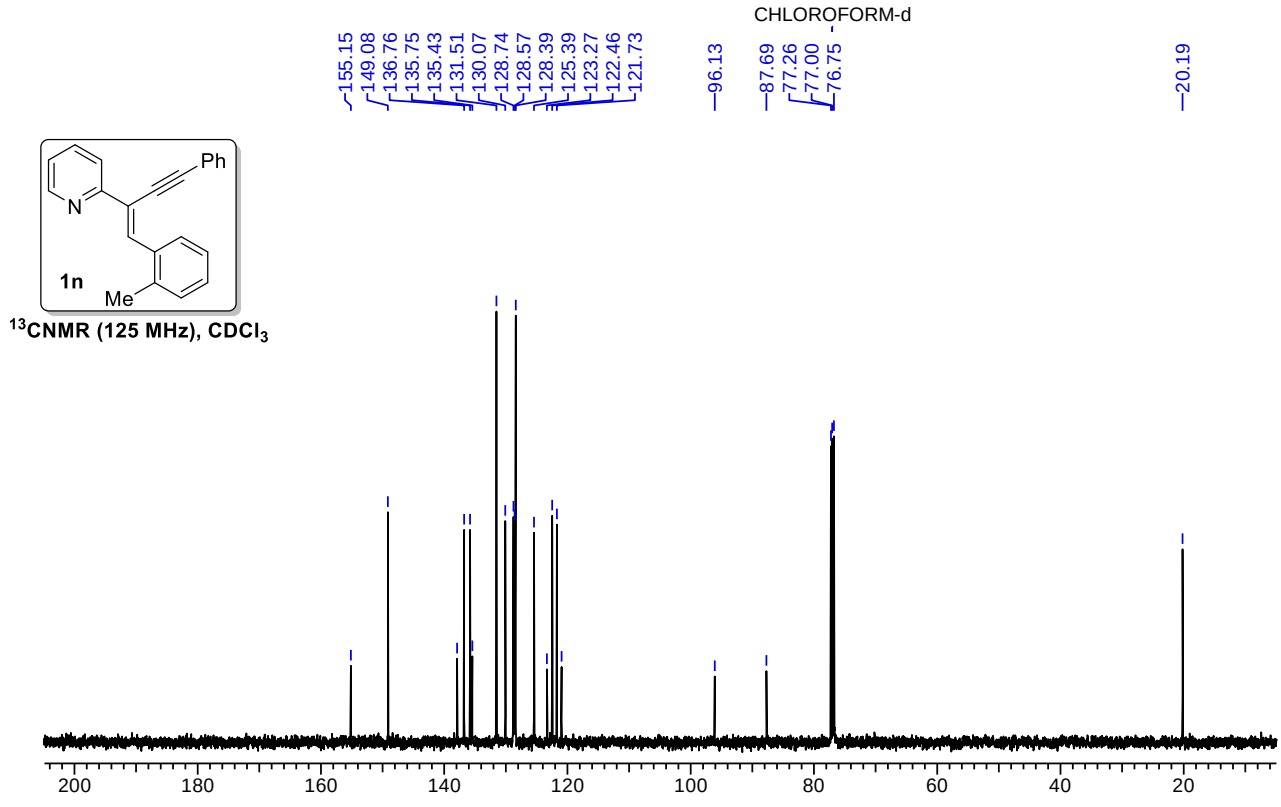
^{1}H NMR (500 MHz), $CDCl_3$



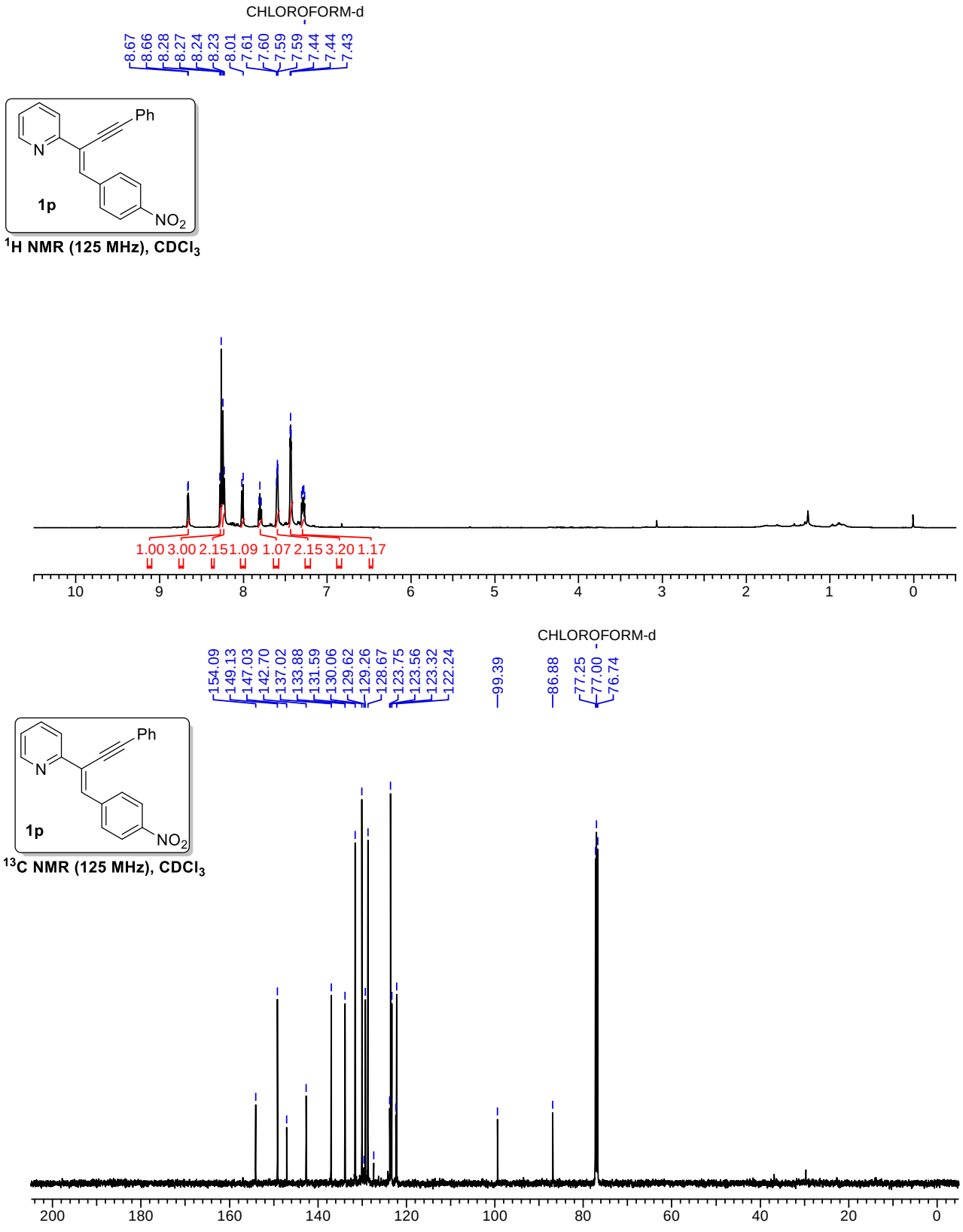
^{13}C NMR (125 MHz), $CDCl_3$



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

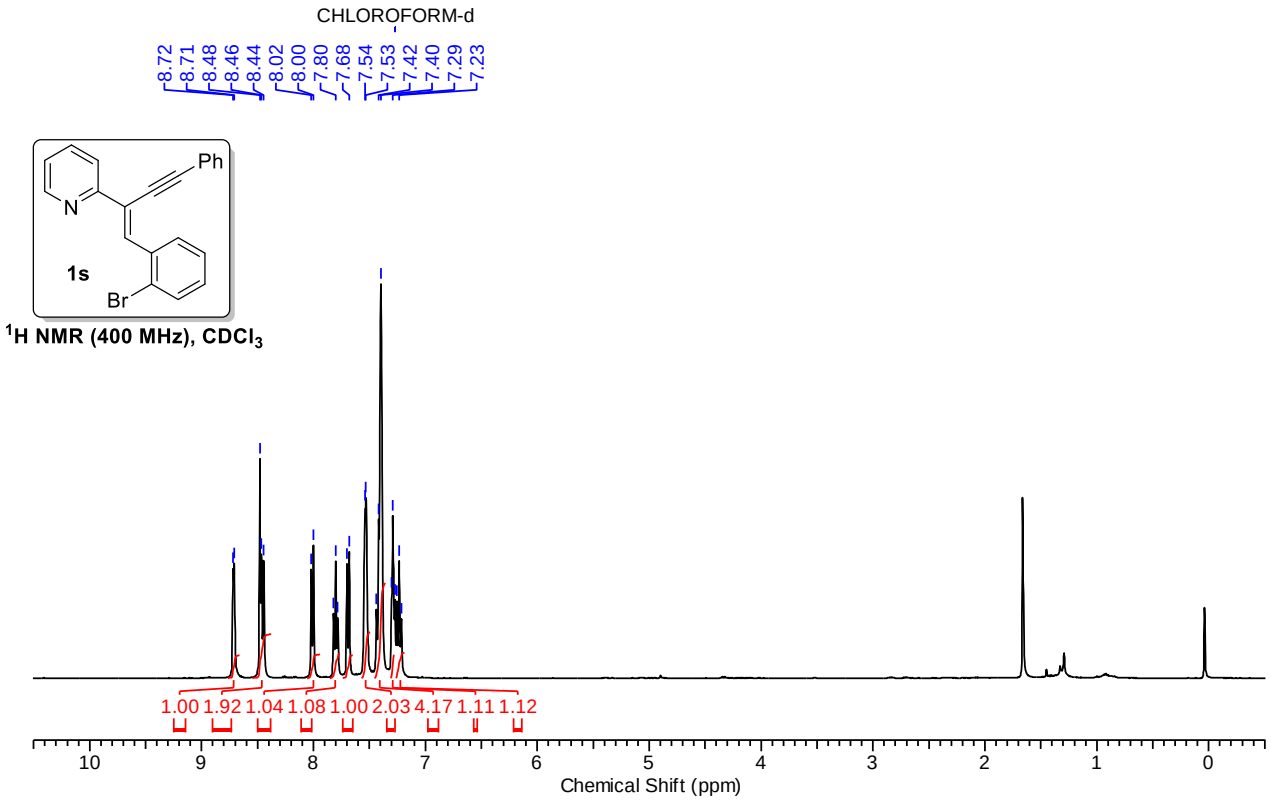


^{13}CNMR (125 MHz), $CDCl_3$

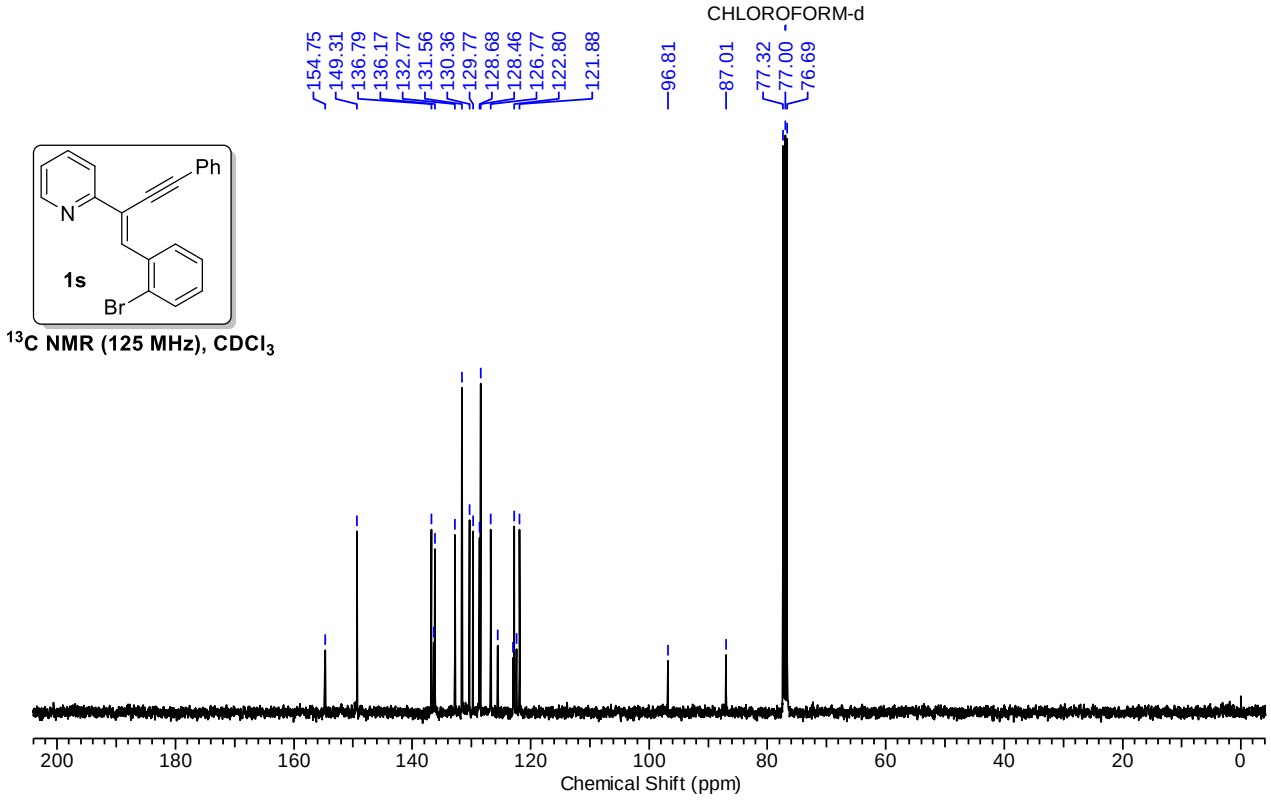


^{1}H NMR (125 MHz), $CDCl_3$

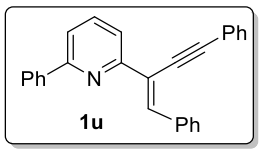
^{13}C NMR (125 MHz), $CDCl_3$



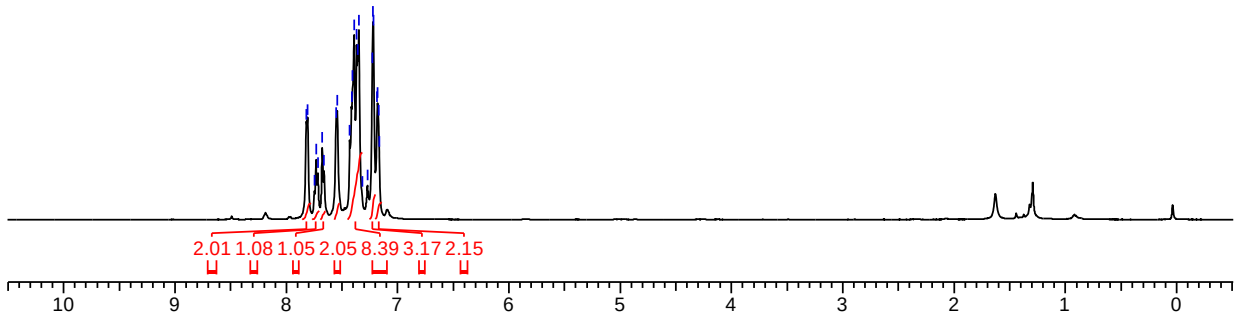
^{1}H NMR (400 MHz), $CDCl_3$

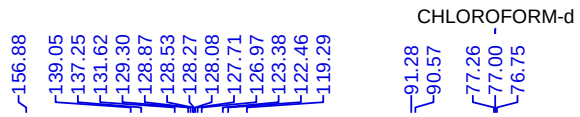


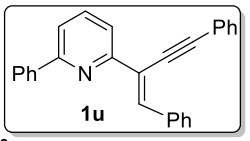
^{13}C NMR (125 MHz), $CDCl_3$



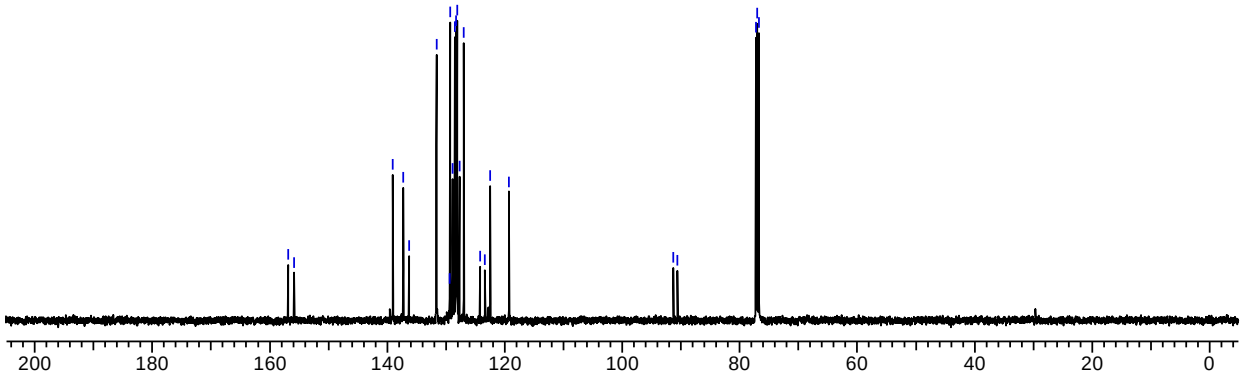
^{1}H NMR (500 MHz), $CDCl_3$

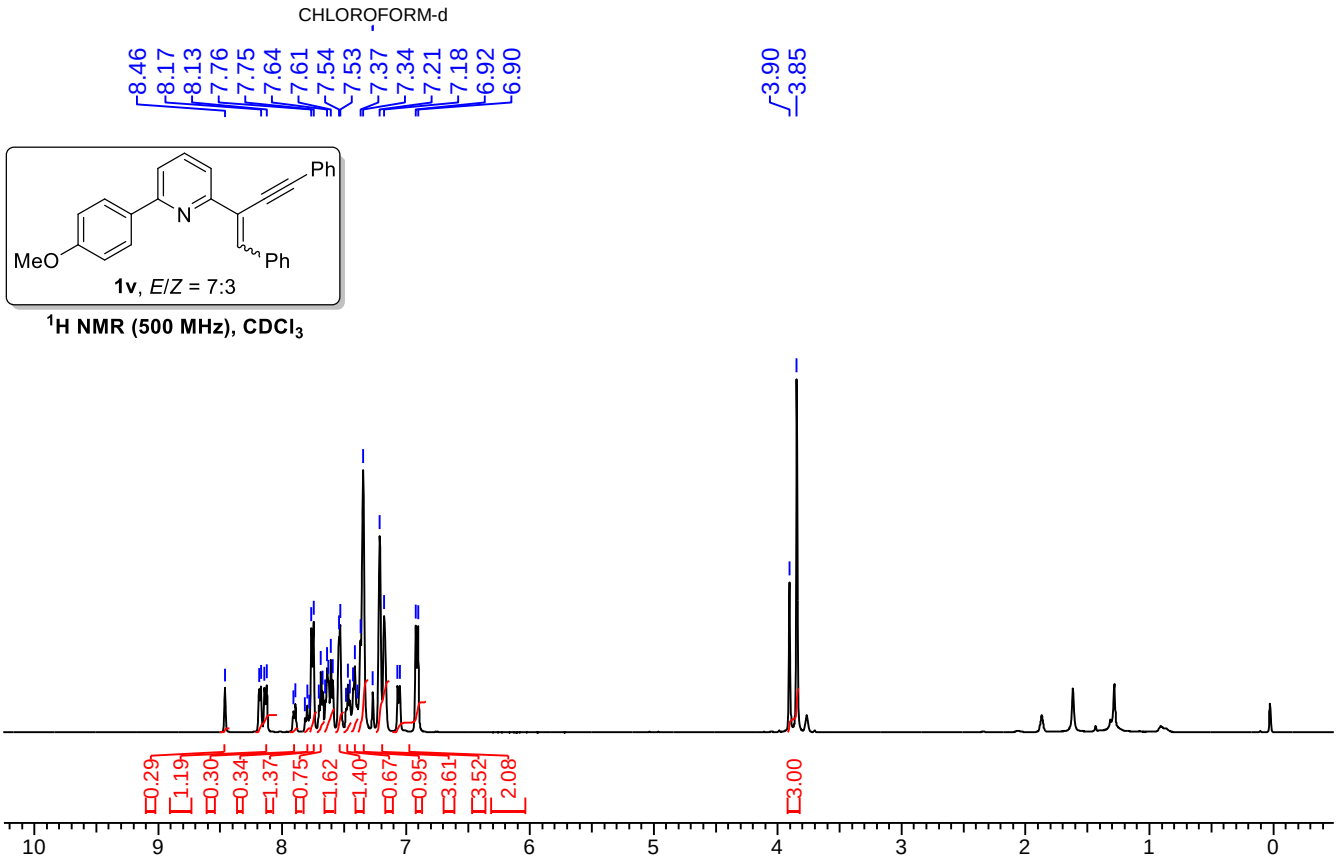




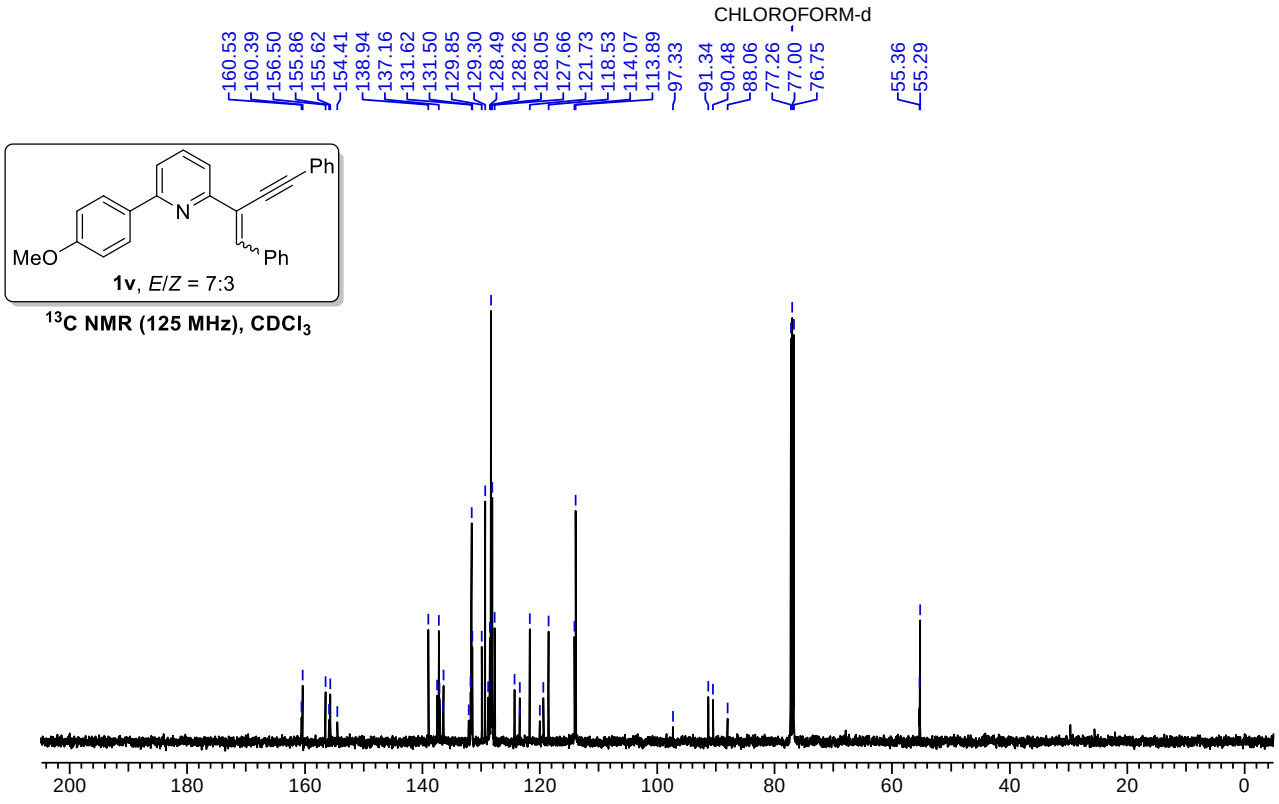


^{13}C NMR (125 MHz), $CDCl_3$

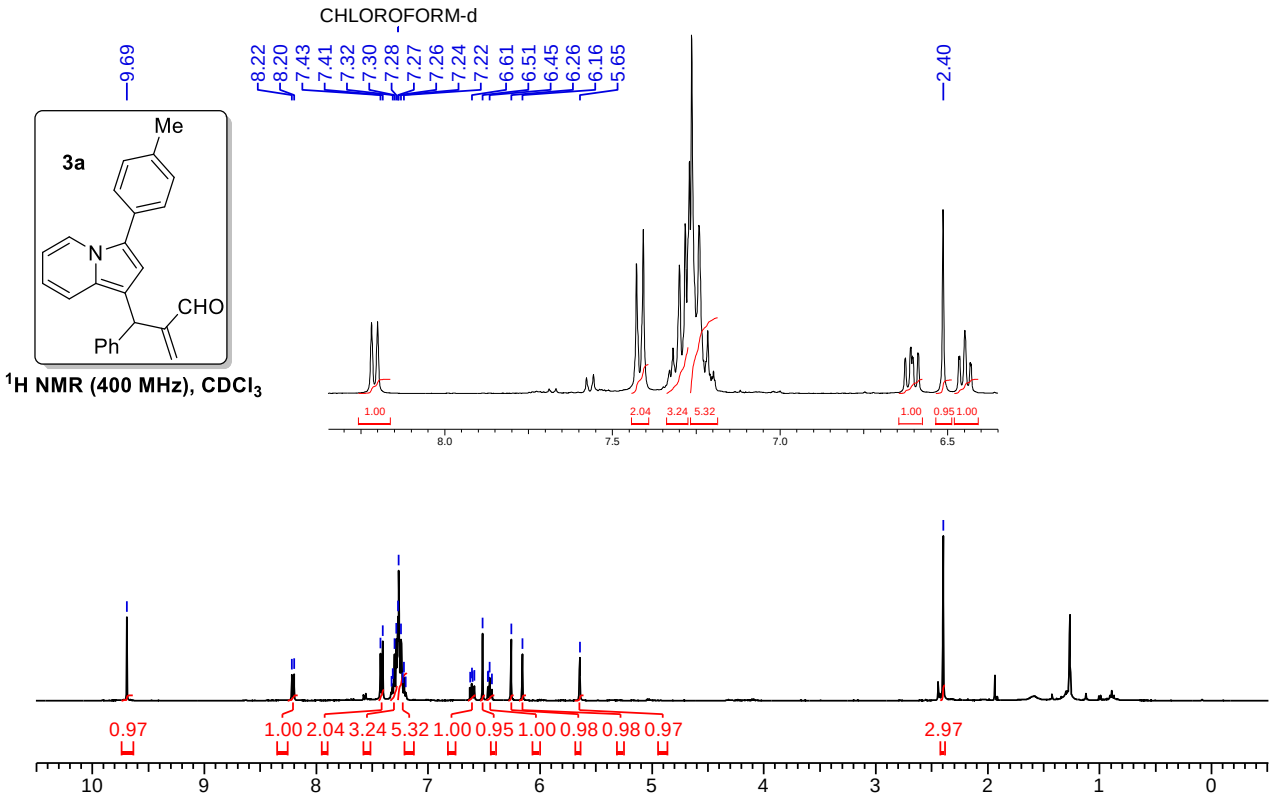




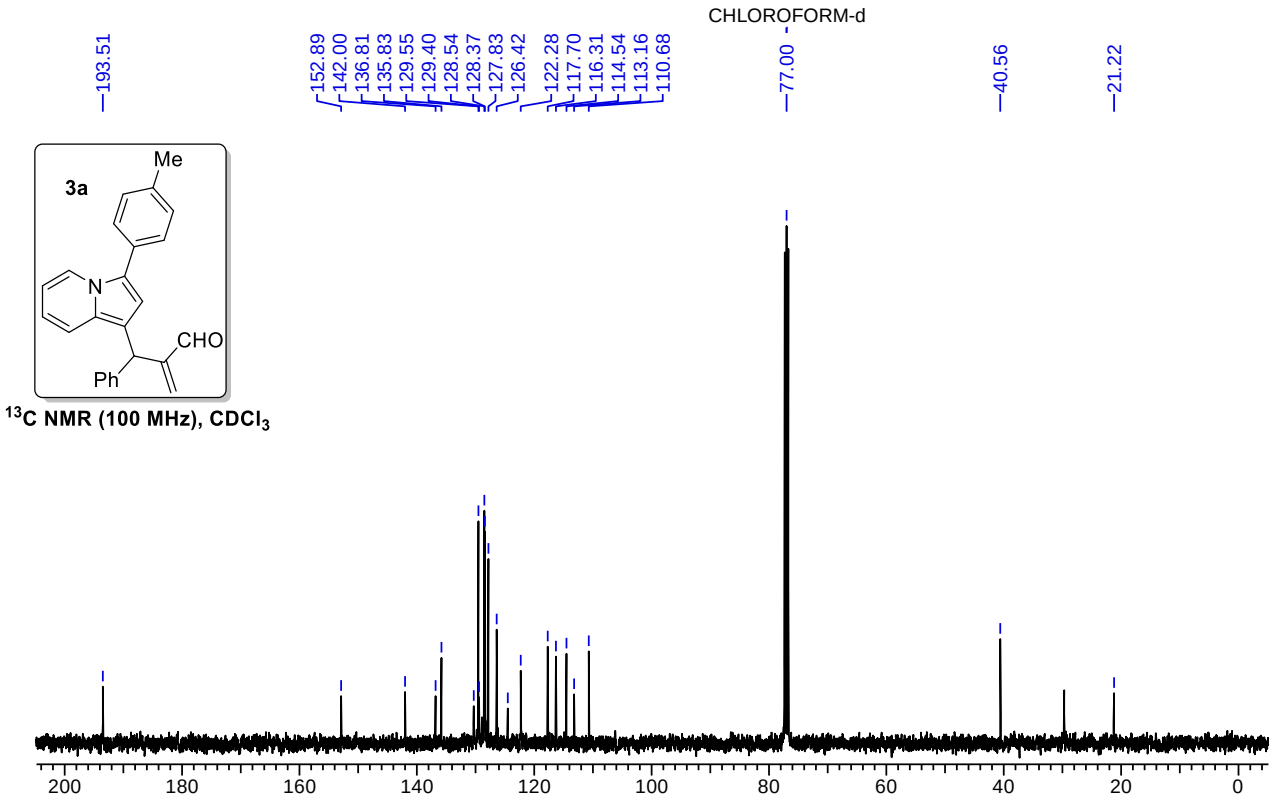
^{1}H NMR (500 MHz), $CDCl_3$



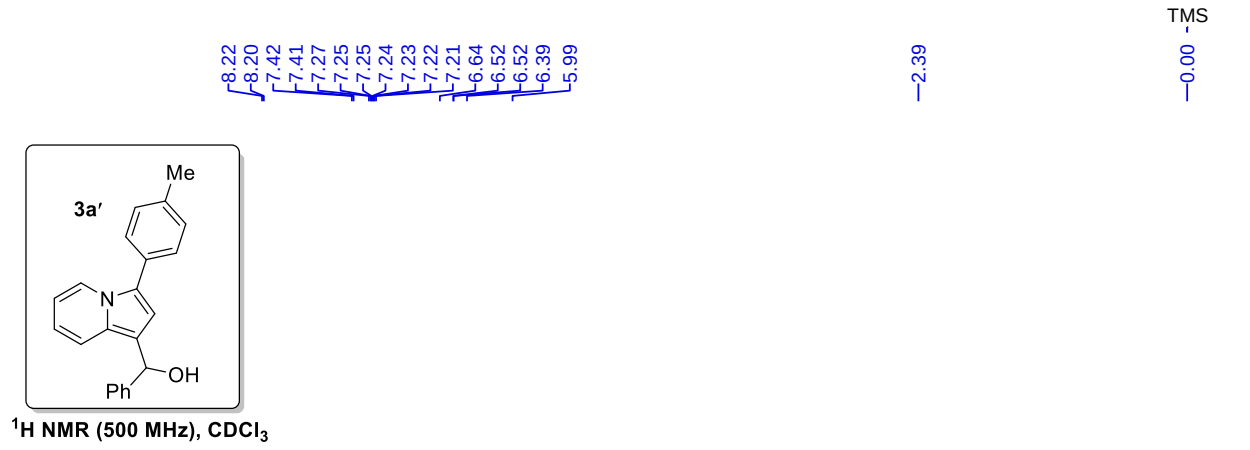
^{13}C NMR (125 MHz), $CDCl_3$



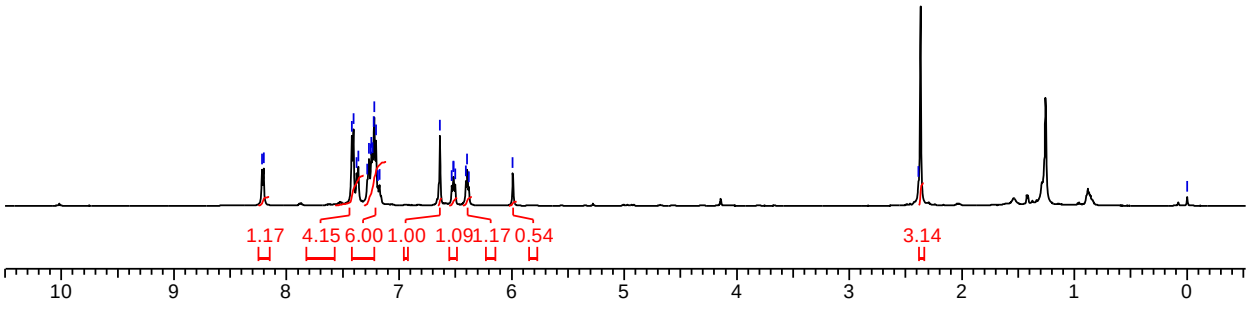
^{1}H NMR (400 MHz), $CDCl_3$

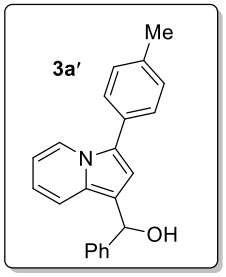


^{13}C NMR (100 MHz), $CDCl_3$

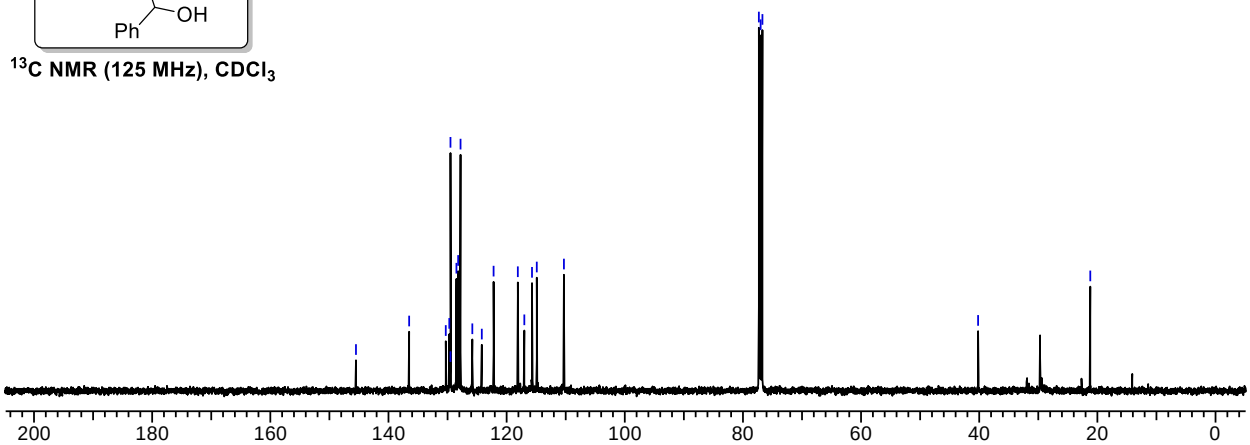


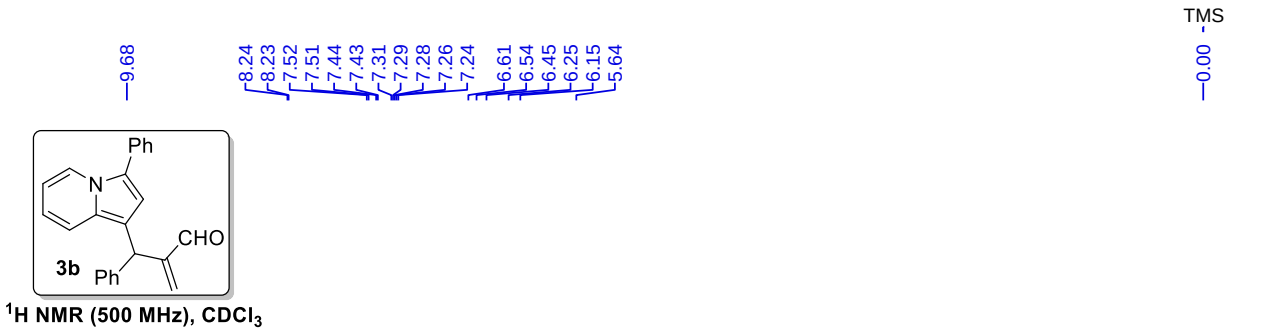
^{1}H NMR (500 MHz), $CDCl_3$



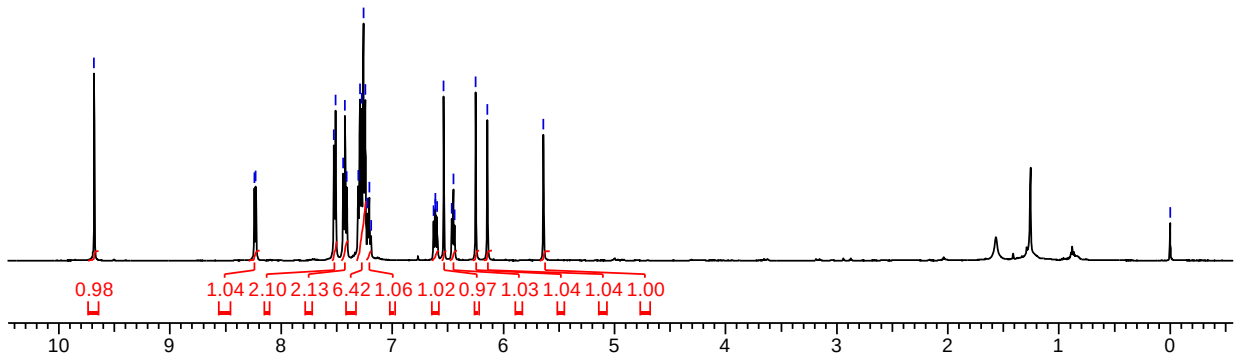


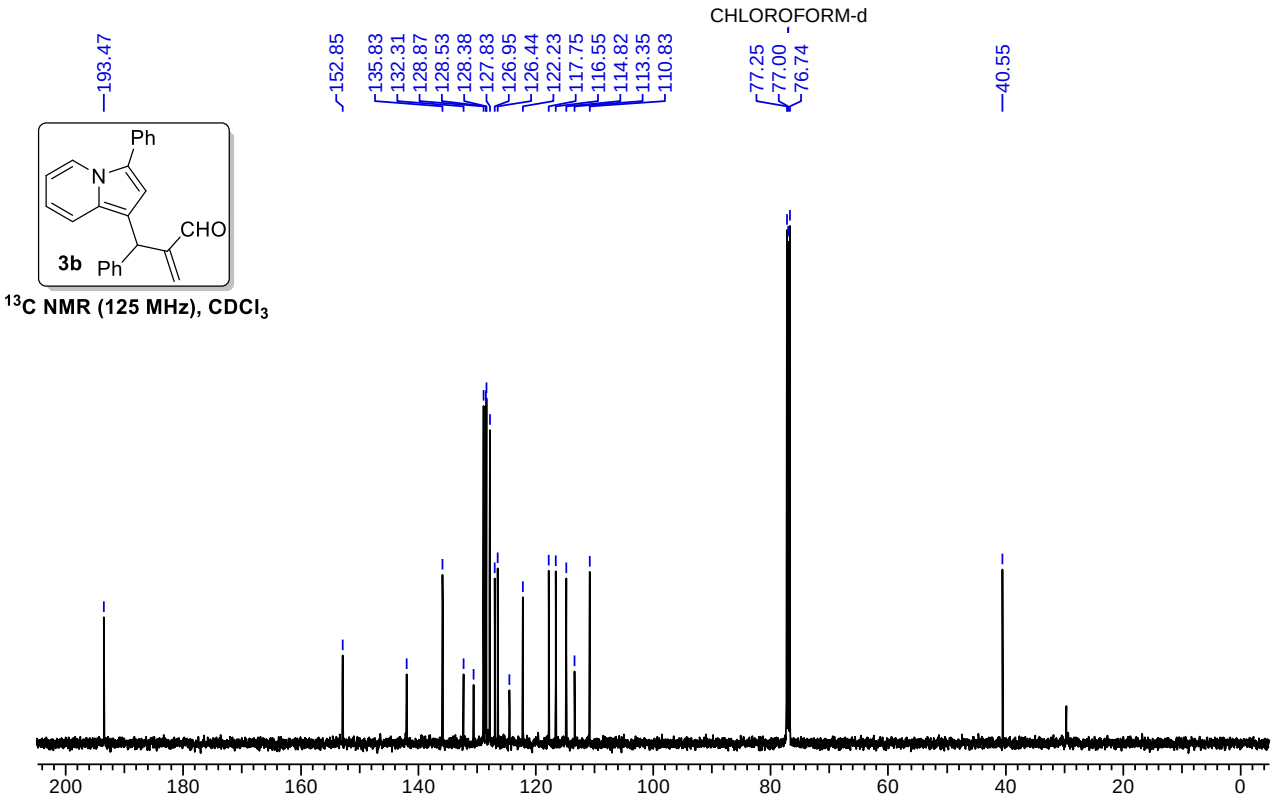
^{13}C NMR (125 MHz), $CDCl_3$



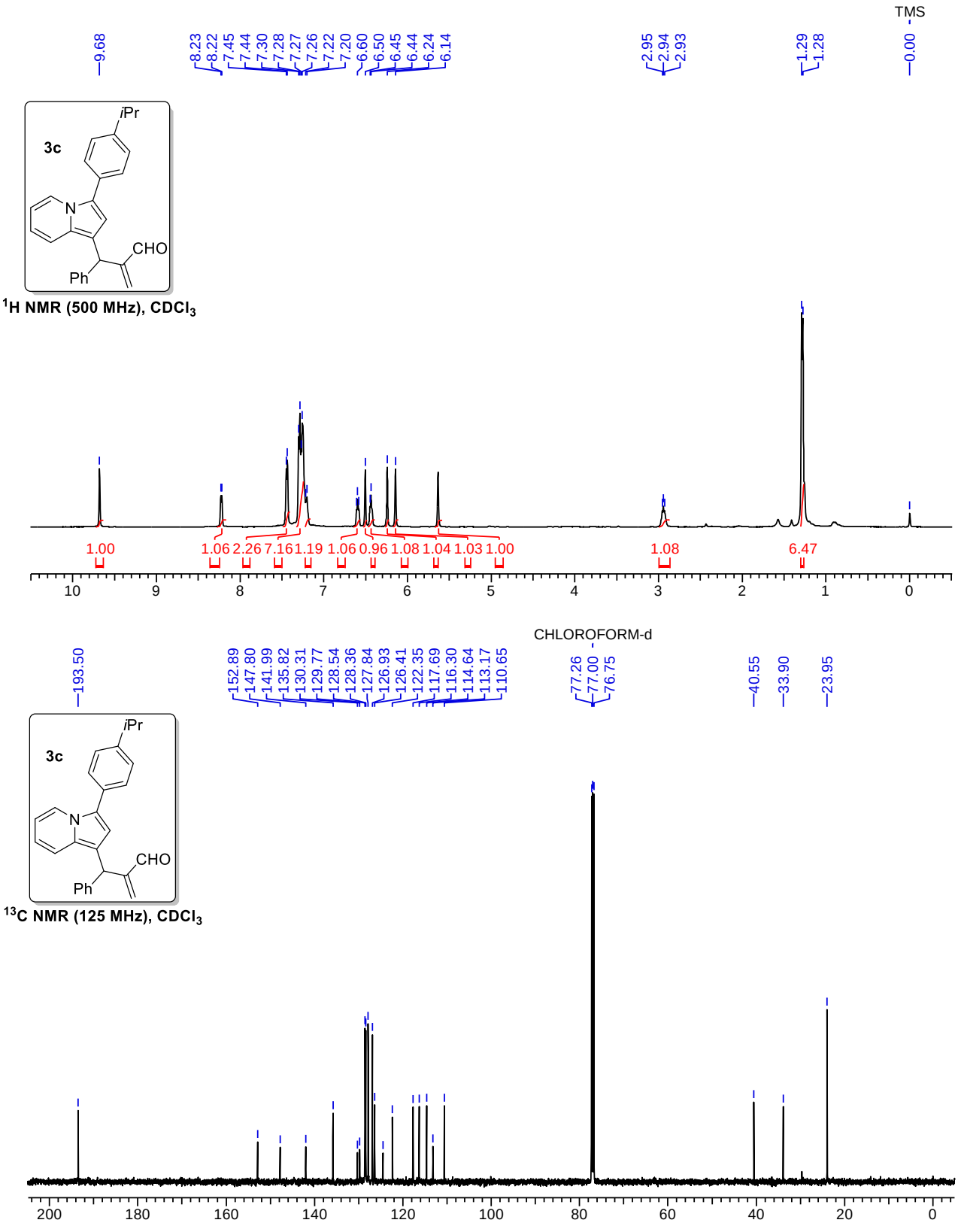


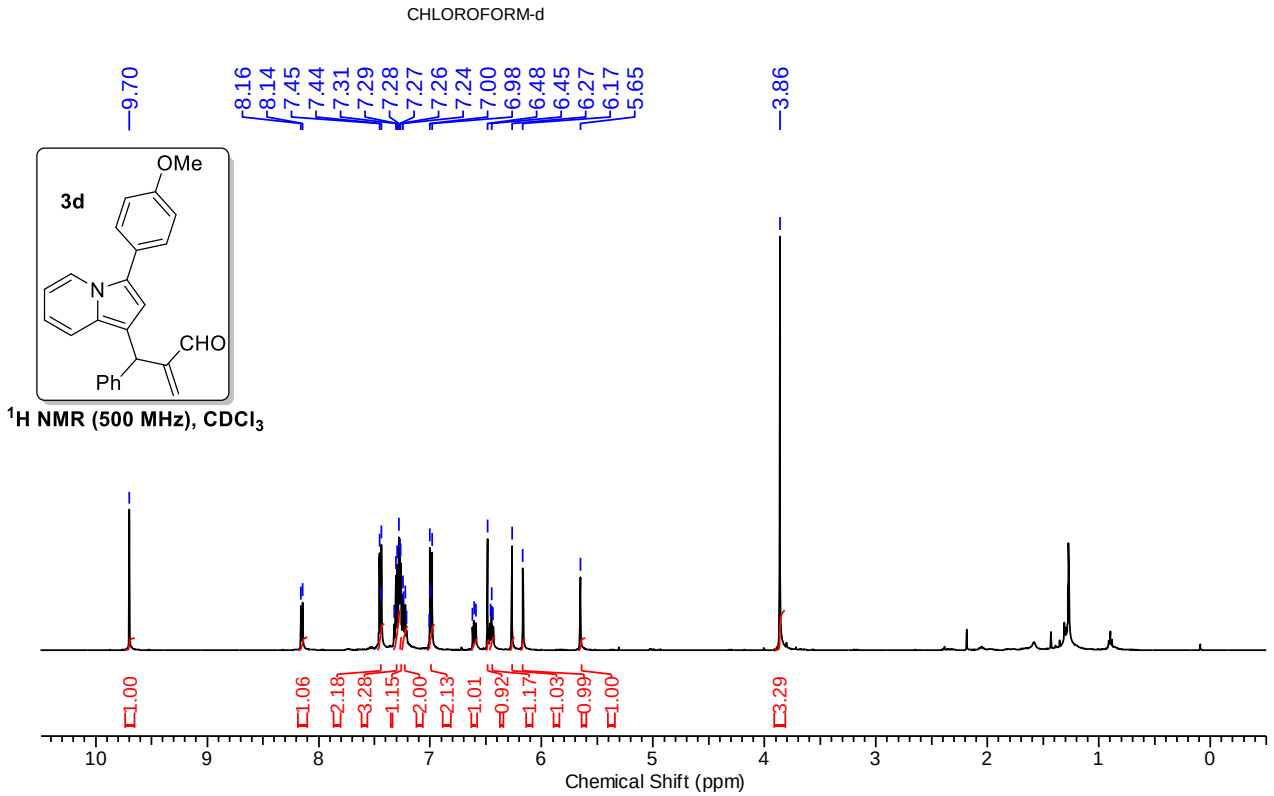
^{1}H NMR (500 MHz), $CDCl_3$



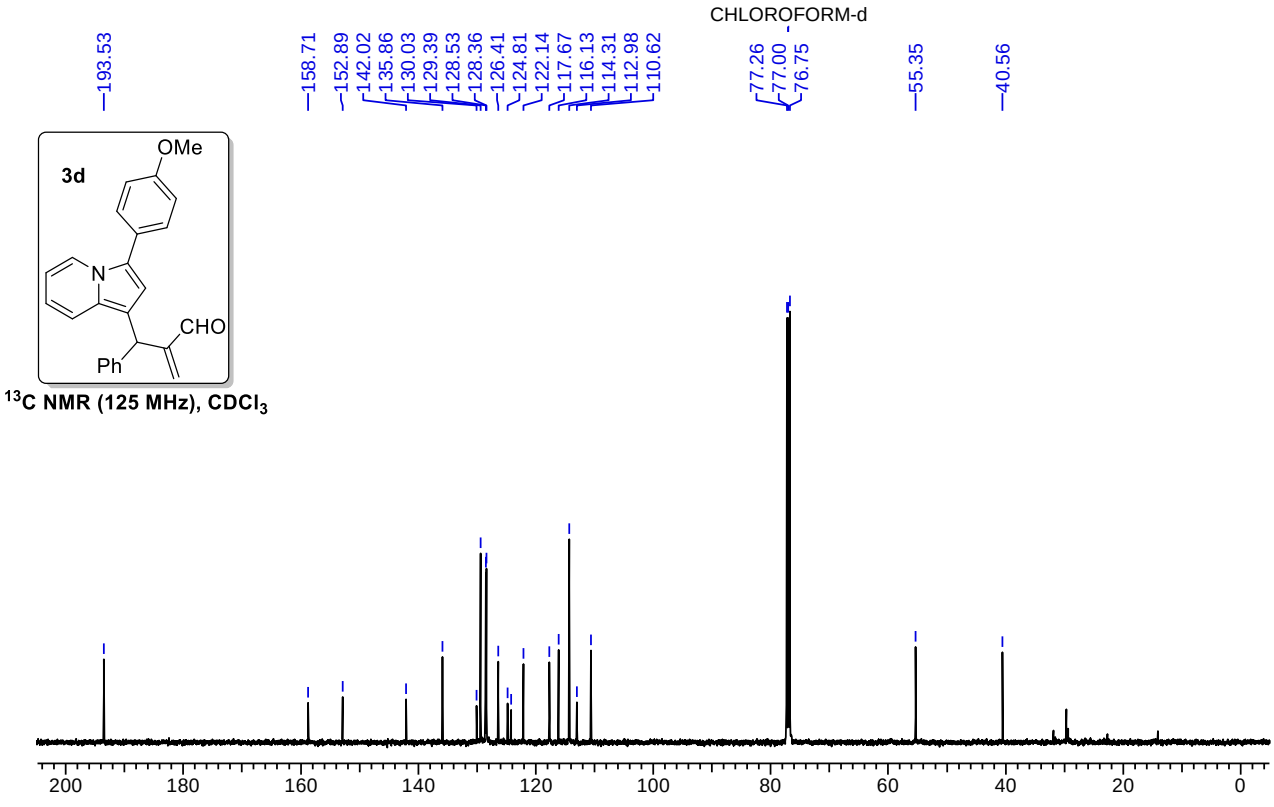


^{13}C NMR (125 MHz), $CDCl_3$

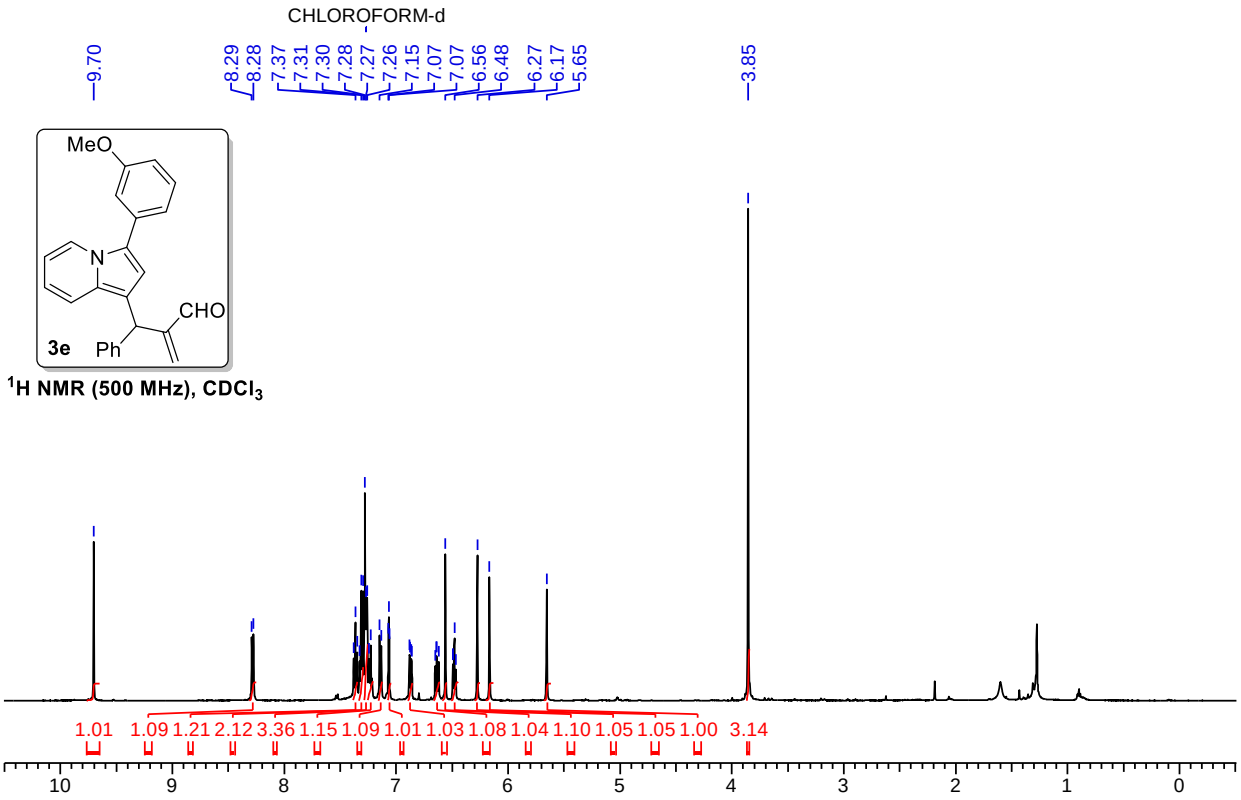

TMS
9.68
8.23
8.22
7.45
7.44
7.30
7.28
7.27
7.26
7.22
7.20
6.60
6.50
6.45
6.44
6.24
6.14
2.95
2.94
2.93
1.29
1.28
0.00
iPr
3c
N
CHO
Ph
1H NMR (500 MHz), CDCl3
1.00
1.06
2.26
7.16
1.19
1.06
0.96
1.08
1.04
1.03
1.00
1.08
6.47
CHLOROFORM-d
193.50
152.89
147.80
141.99
135.82
130.31
129.77
128.54
128.36
127.84
126.93
126.41
122.35
117.69
116.30
114.64
113.17
110.65
77.26
77.00
76.75
40.55
33.90
23.95
13C NMR (125 MHz), CDCl3



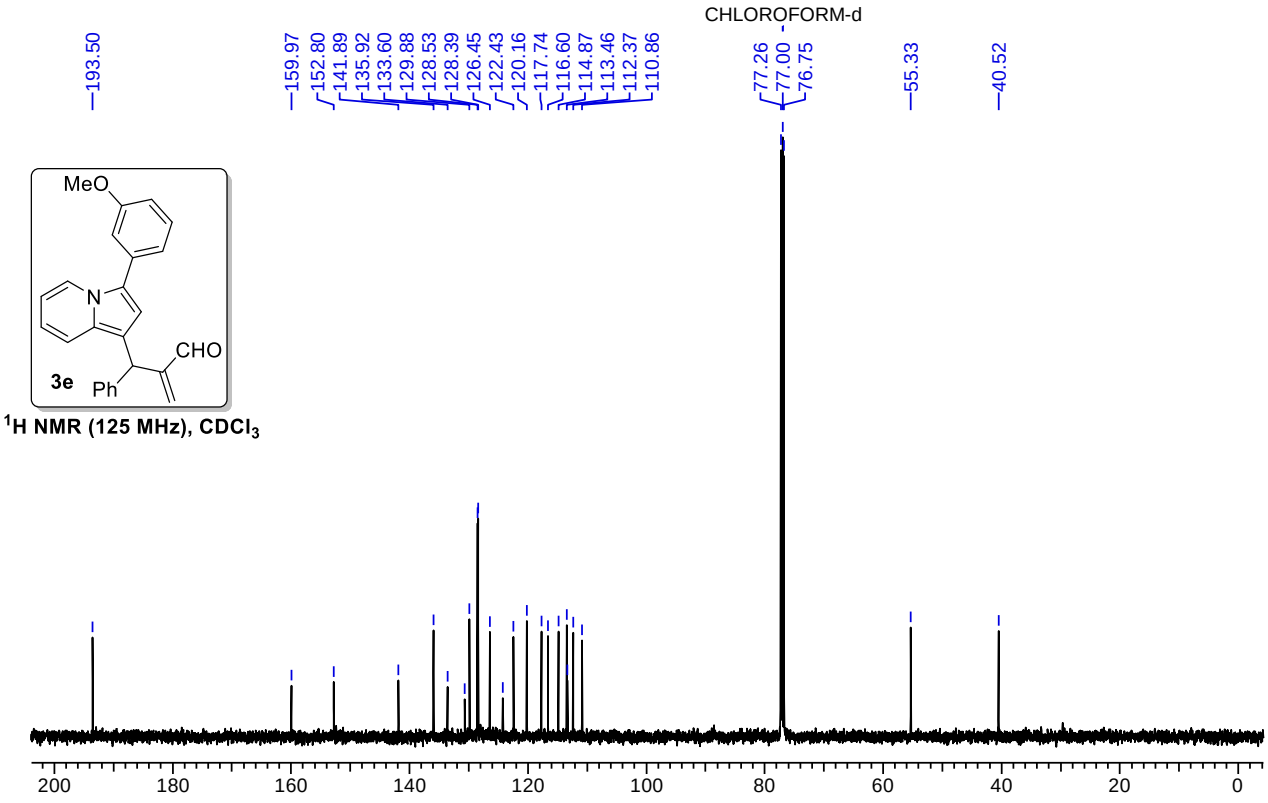
^{1}H NMR (500 MHz), $CDCl_3$



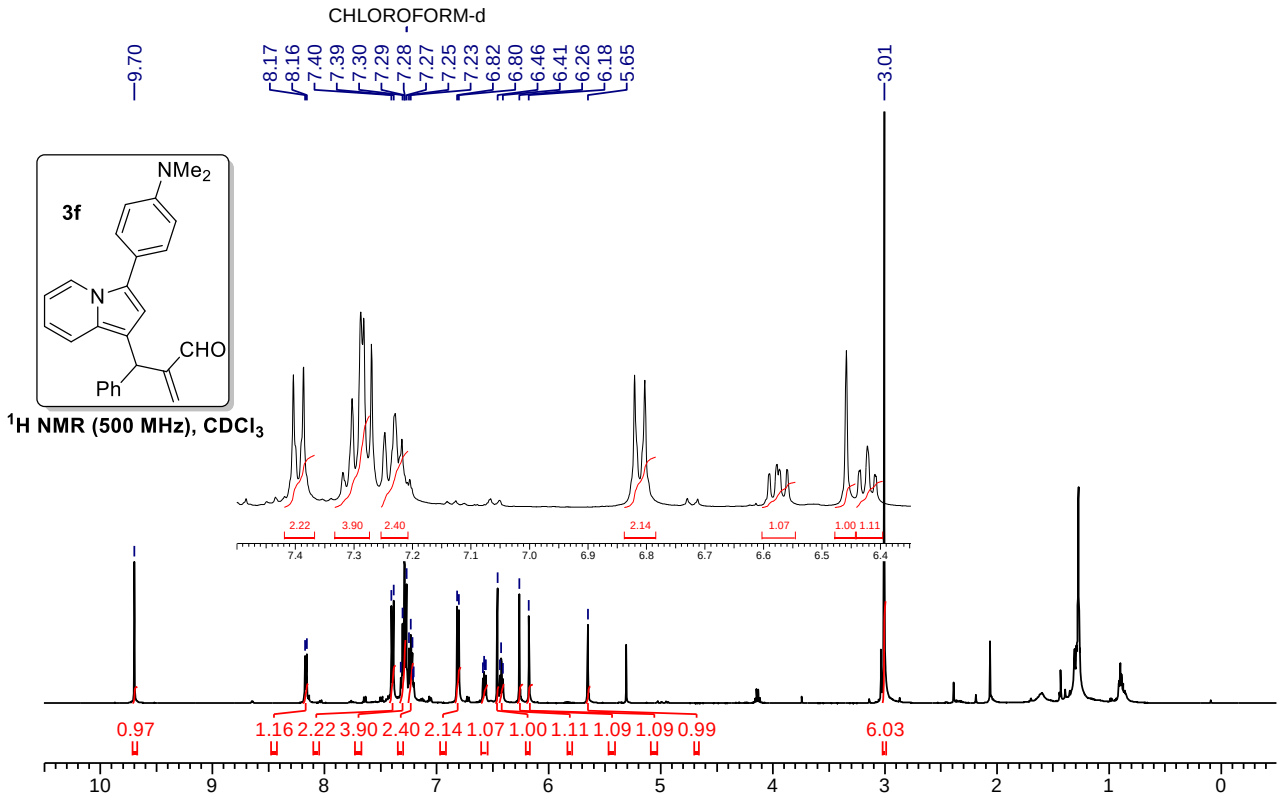
^{13}C NMR (125 MHz), $CDCl_3$



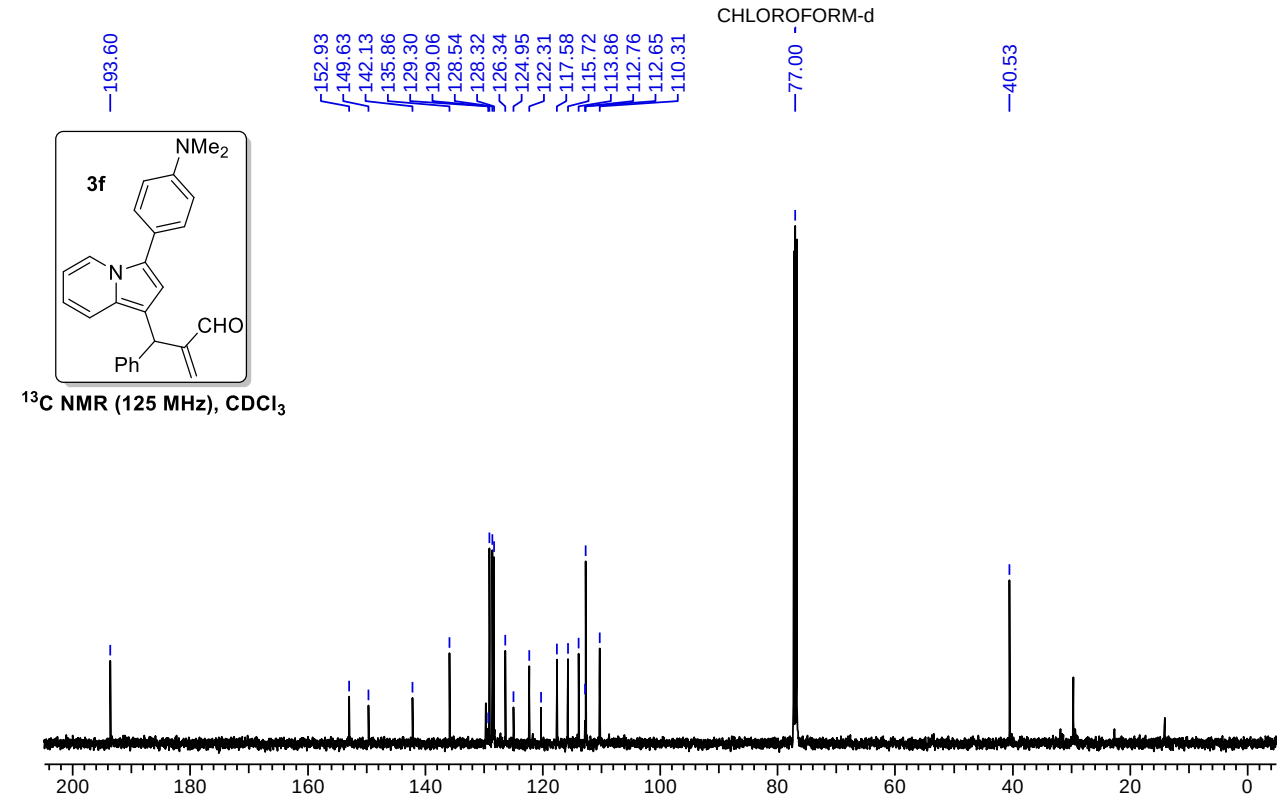
^{1}H NMR (500 MHz), $CDCl_3$



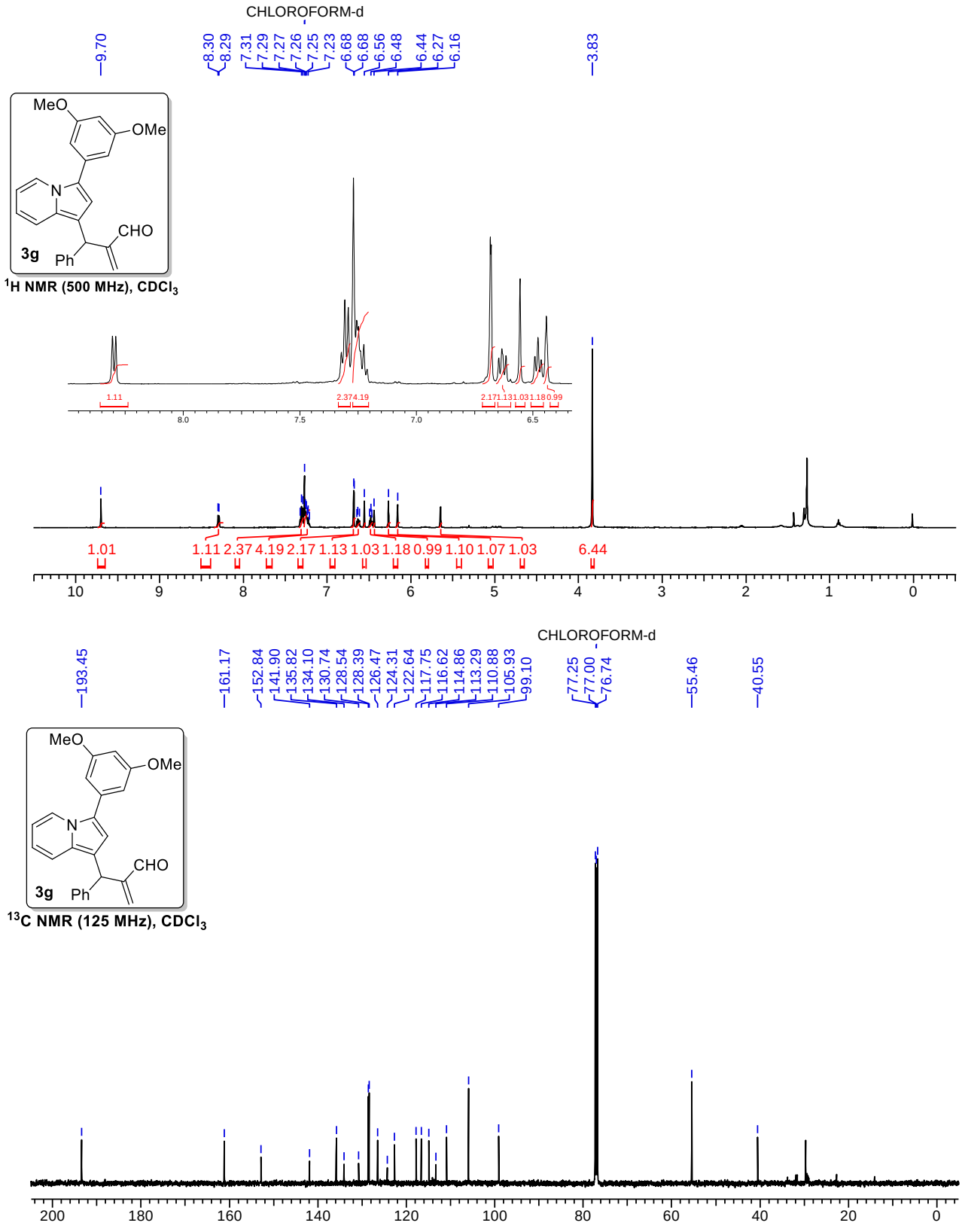
^{1}H NMR (125 MHz), $CDCl_3$

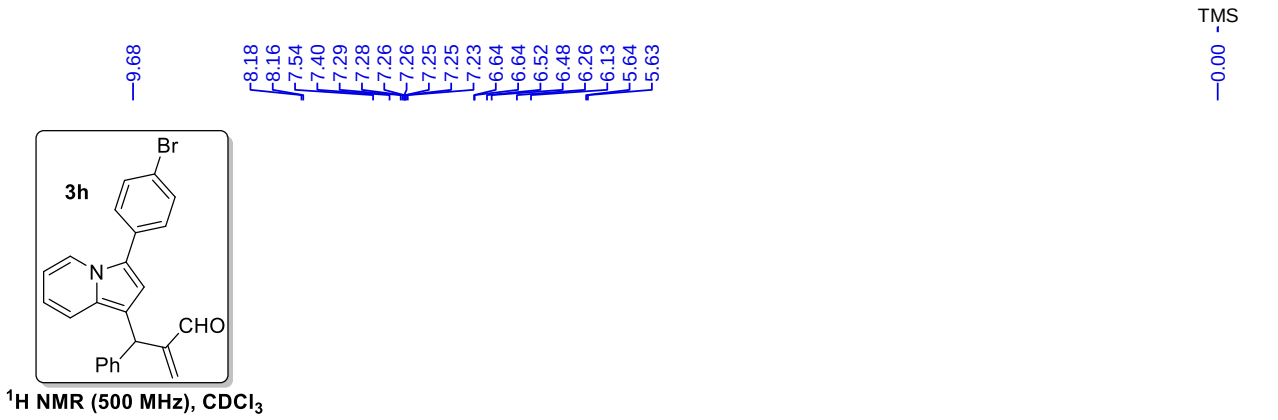


^{1}H NMR (500 MHz), $CDCl_3$

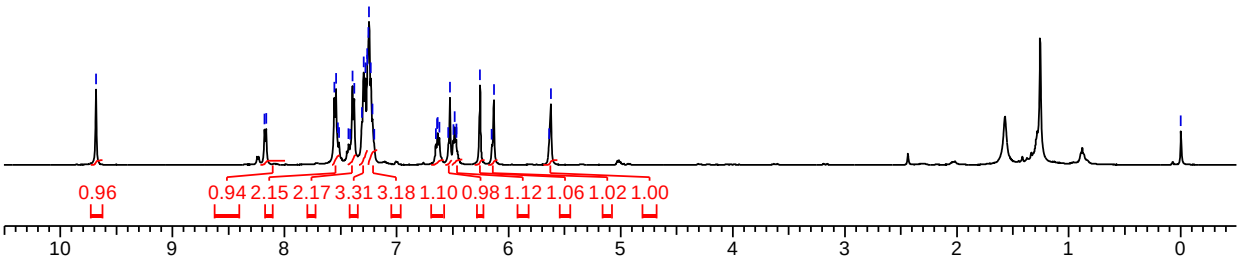


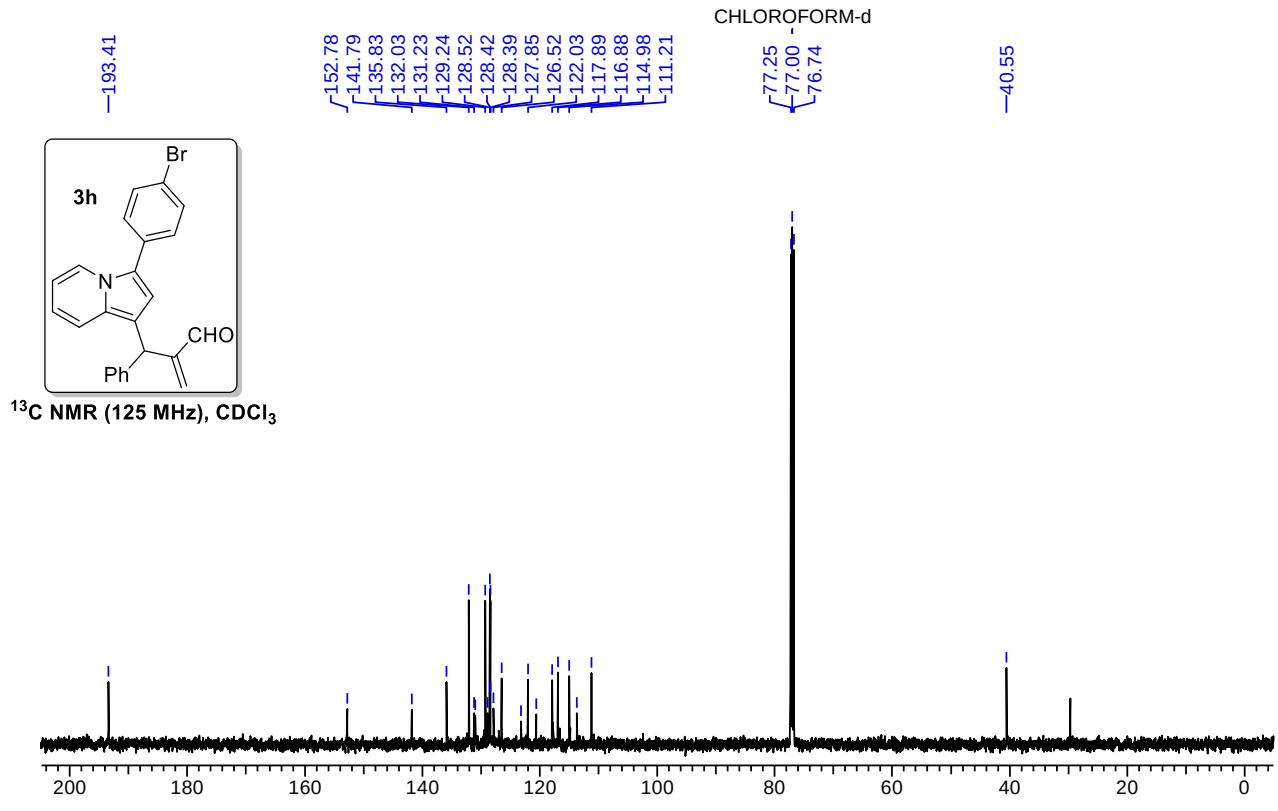
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
9.70
8.30
8.29
7.31
7.29
7.27
7.26
7.25
7.23
6.68
6.68
6.56
6.48
6.44
6.27
6.16
3.83
MeO
OMe
N
CHO
3g
Ph
1H NMR (500 MHz), CDCl3
1.01
1.11
2.37
4.19
2.17
1.13
1.03
1.18
0.99
1.10
1.07
1.03
6.44
CHLOROFORM-d
193.45
161.17
152.84
141.90
135.82
134.10
130.74
128.54
128.39
126.47
124.31
122.64
117.75
116.62
114.86
113.29
110.88
105.93
99.10
77.25
77.00
76.74
55.46
40.55
13C NMR (125 MHz), CDCl3

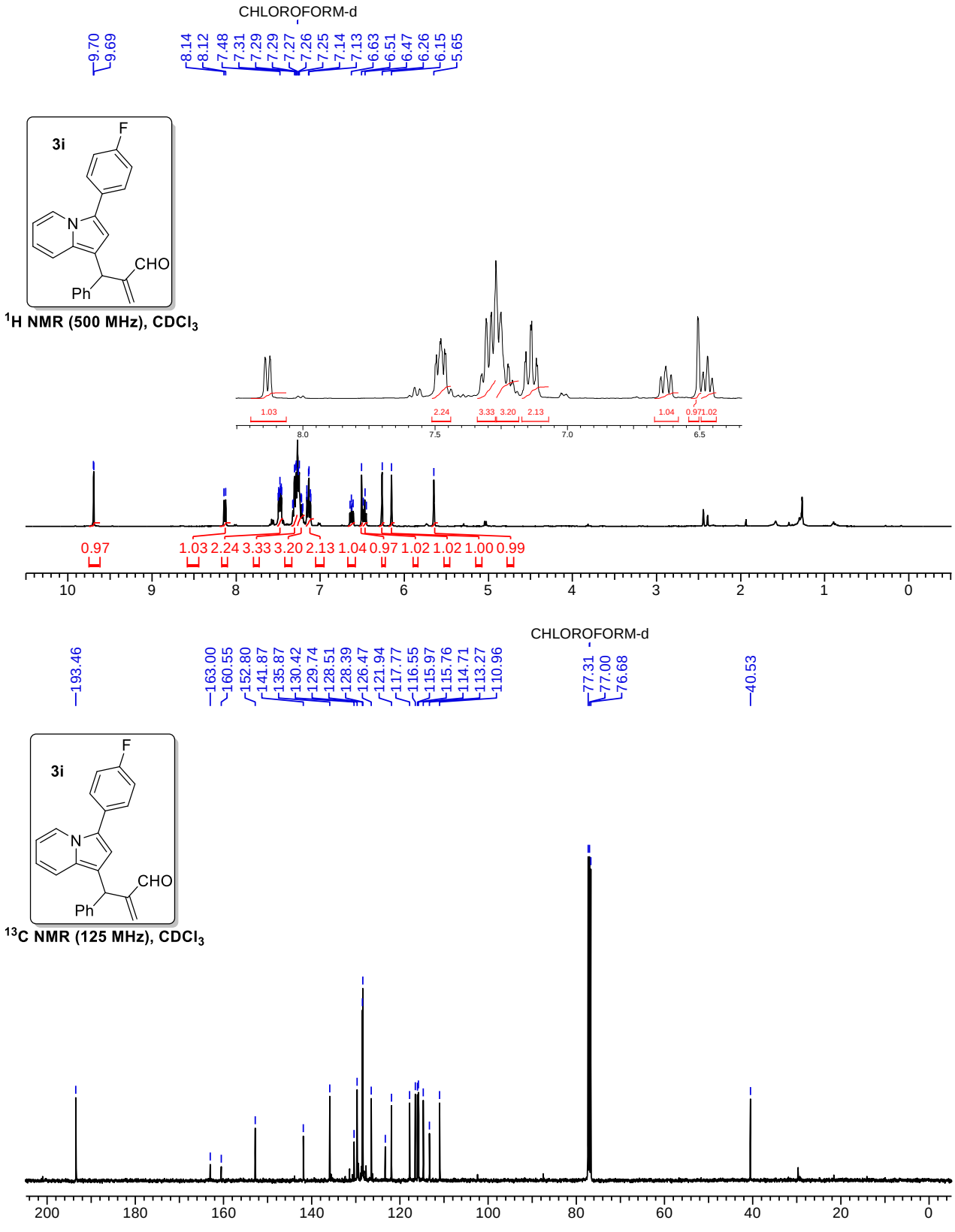


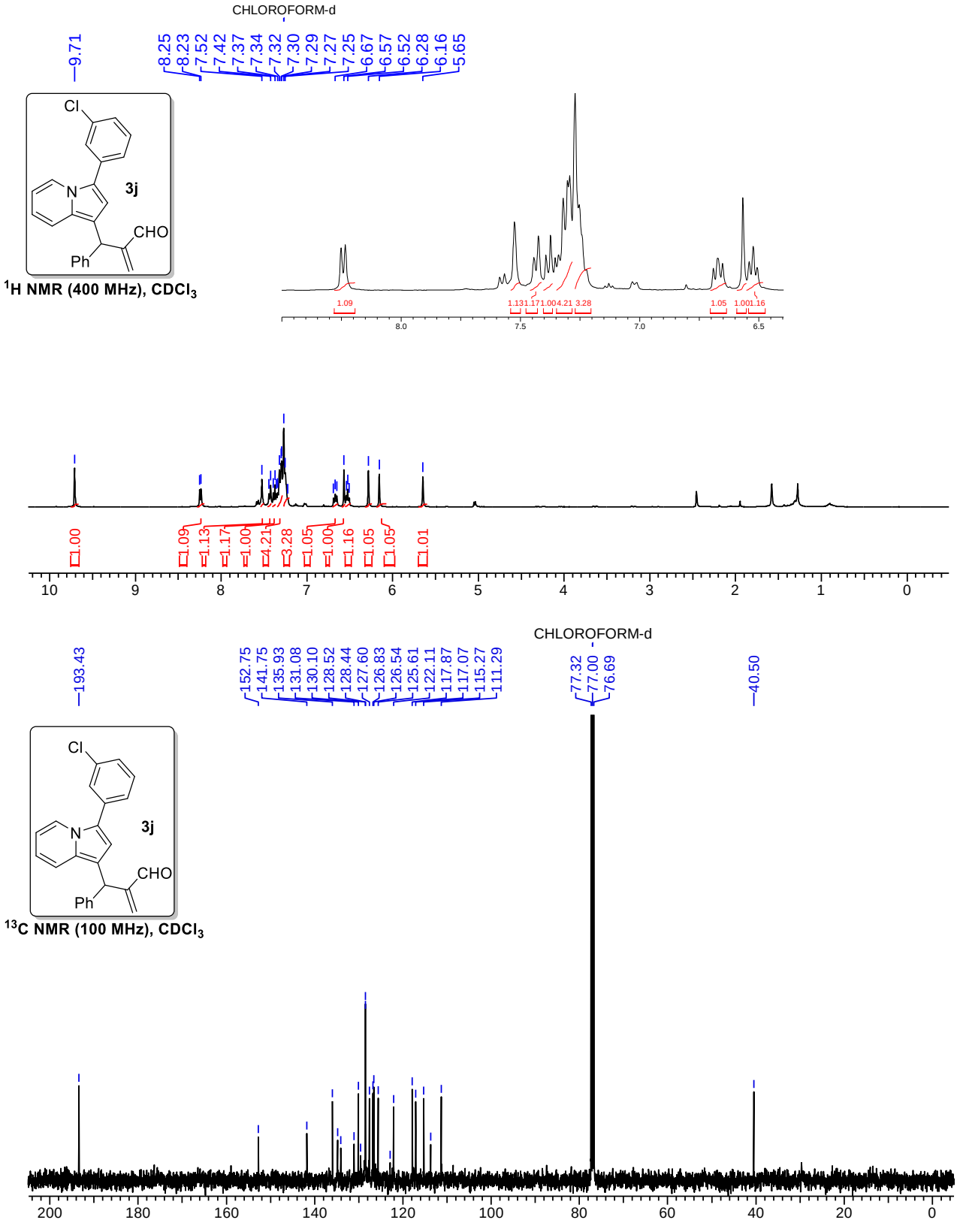
^{1}H NMR (500 MHz), $CDCl_3$





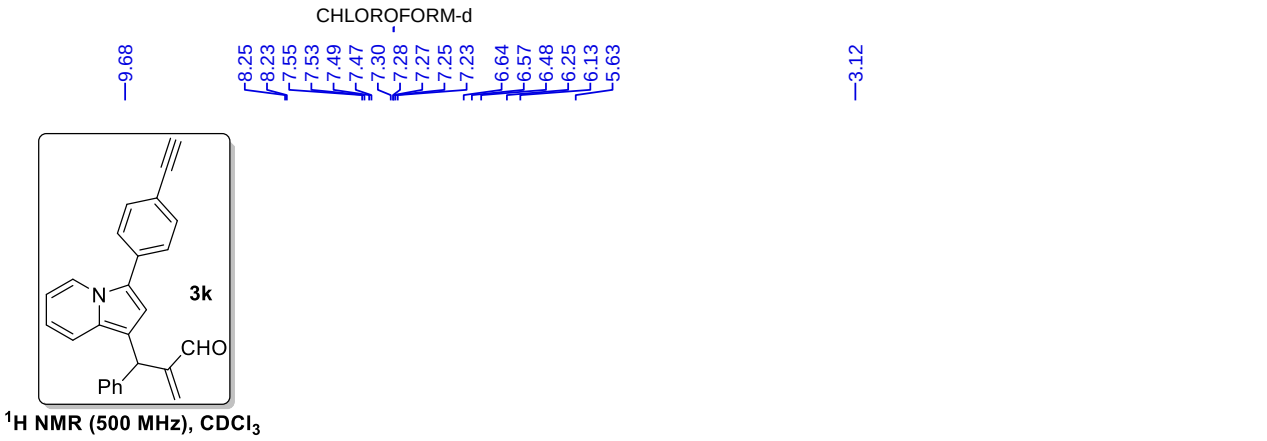
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
9.70
9.69
8.14
8.12
7.48
7.31
7.29
7.29
7.27
7.26
7.25
7.14
7.13
6.63
6.51
6.47
6.26
6.15
5.65
3i
F
N
CHO
Ph
1H NMR (500 MHz), CDCl3
1.03
2.24
3.33
3.20
2.13
1.04
0.97
1.02
0.97
1.03 2.24 3.33 3.20 2.13 1.04 0.97 1.02 1.02 1.00 0.99
CHLOROFORM-d
193.46
163.00
160.55
152.80
141.87
135.87
130.42
129.74
128.51
128.39
126.47
121.94
117.77
116.55
115.97
115.76
114.71
113.27
110.96
77.31
77.00
76.68
40.53
3i
13C NMR (125 MHz), CDCl3

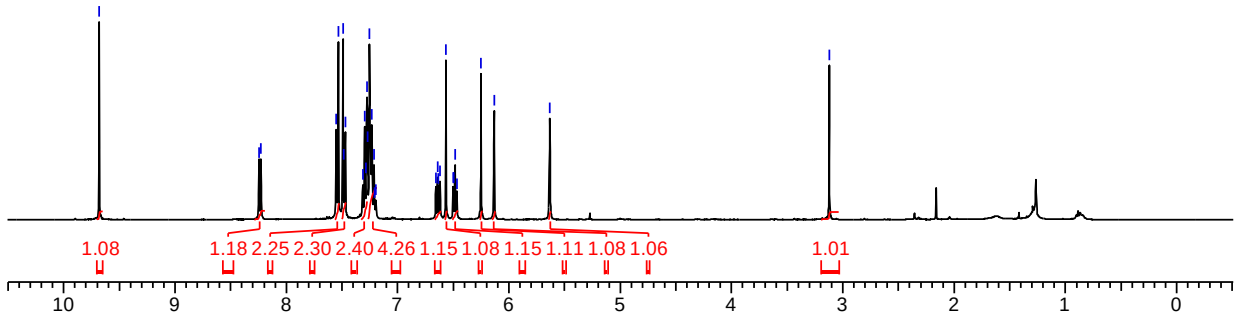


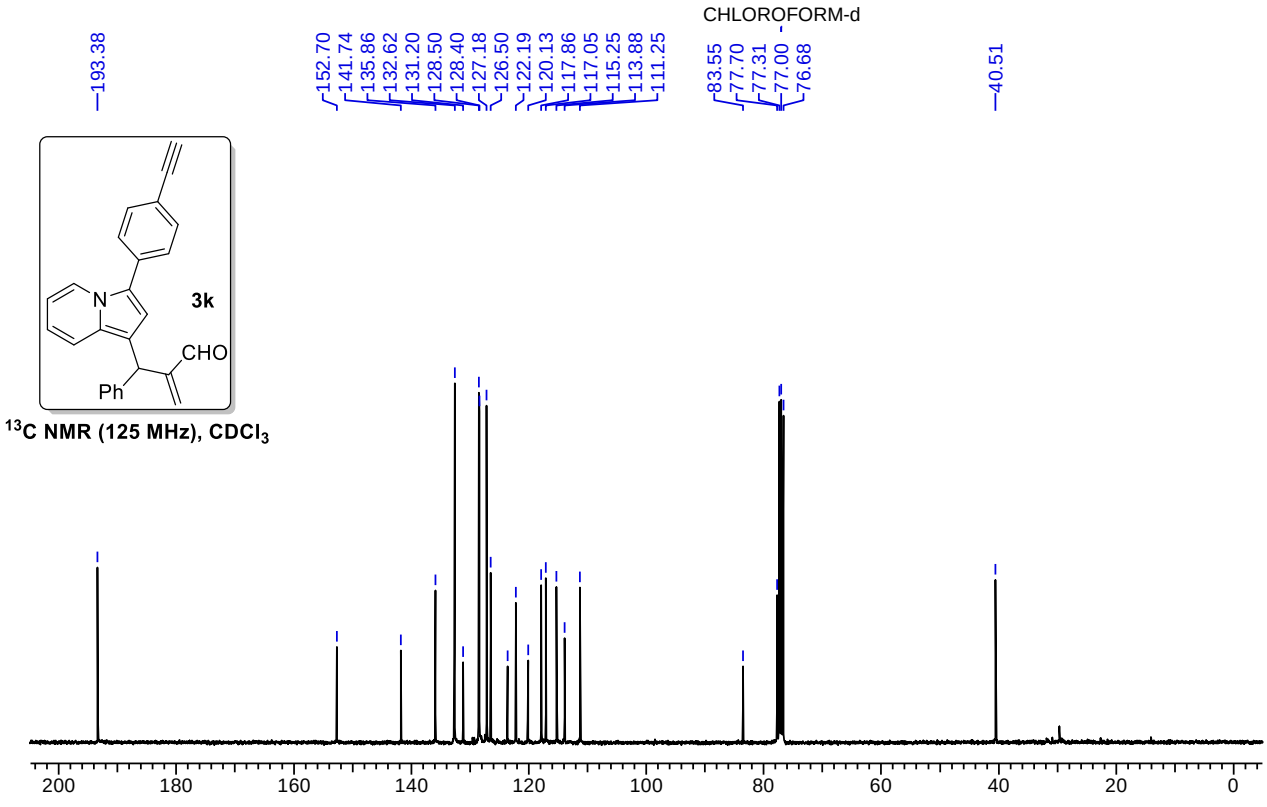
^{1}H NMR (400 MHz), $CDCl_3$

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

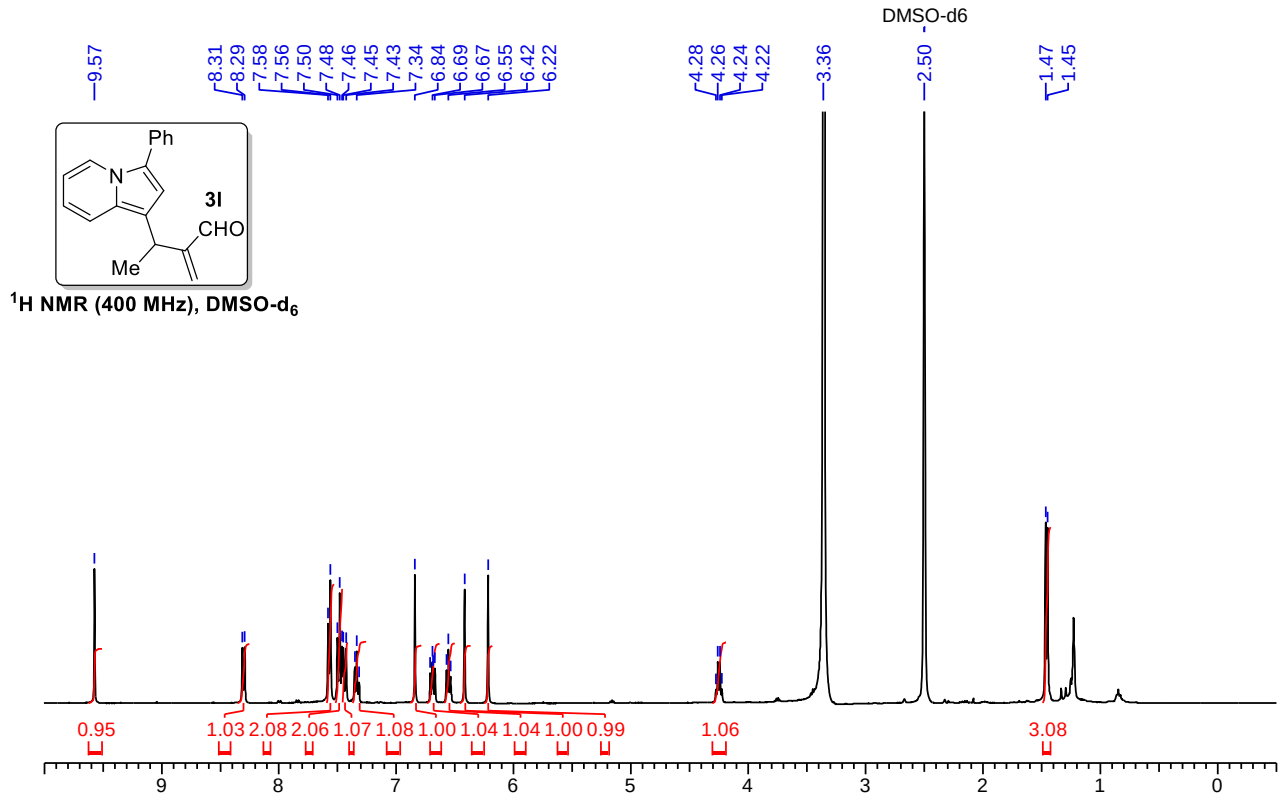


^{1}H NMR (500 MHz), $CDCl_3$

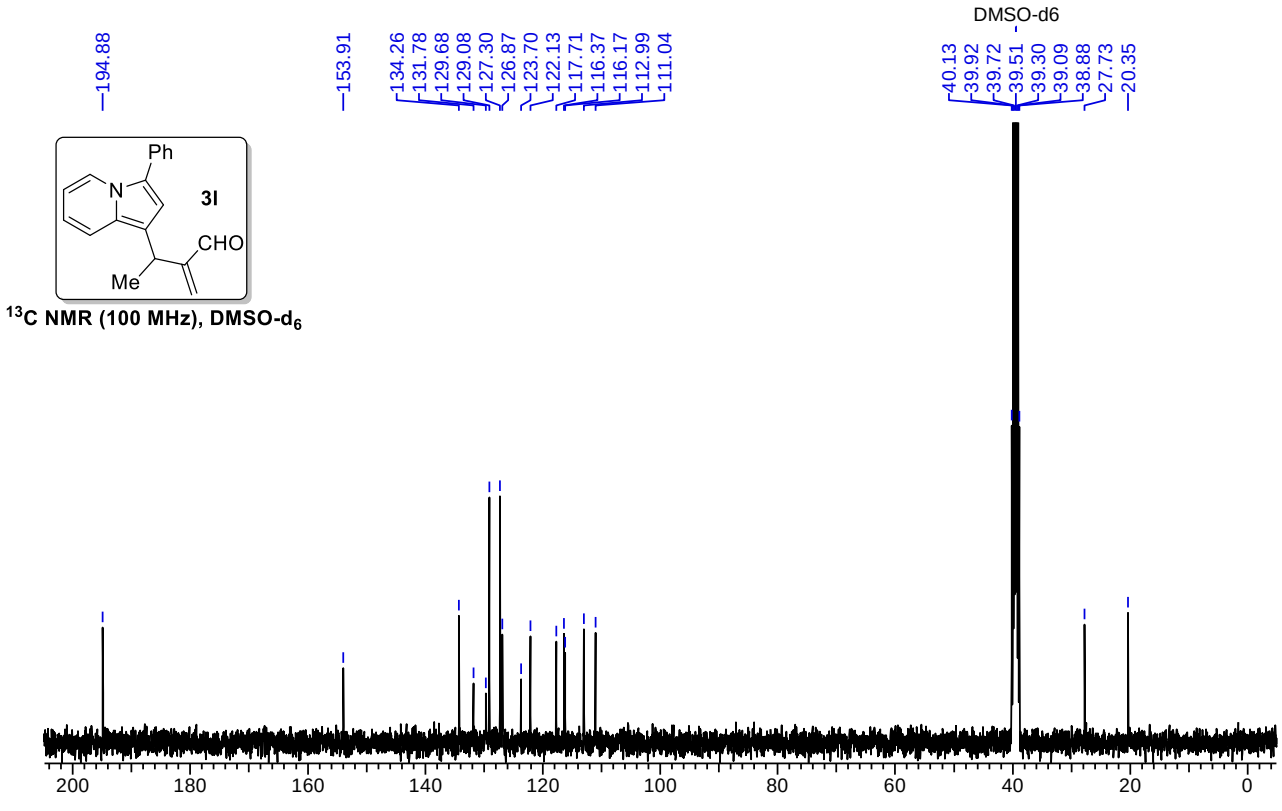




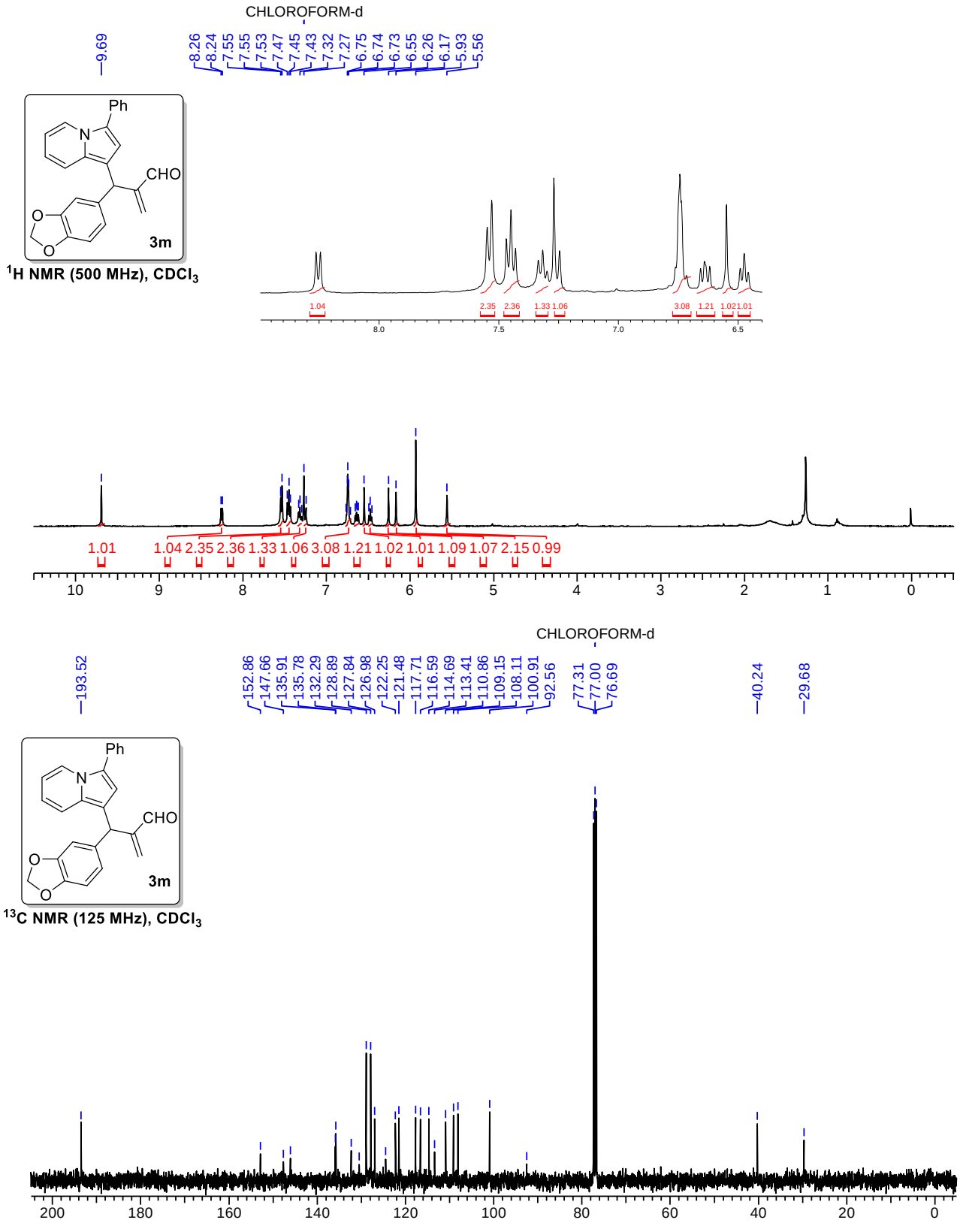
^{13}C NMR (125 MHz), $CDCl_3$



^{1}H NMR (400 MHz), DMSO-d_6

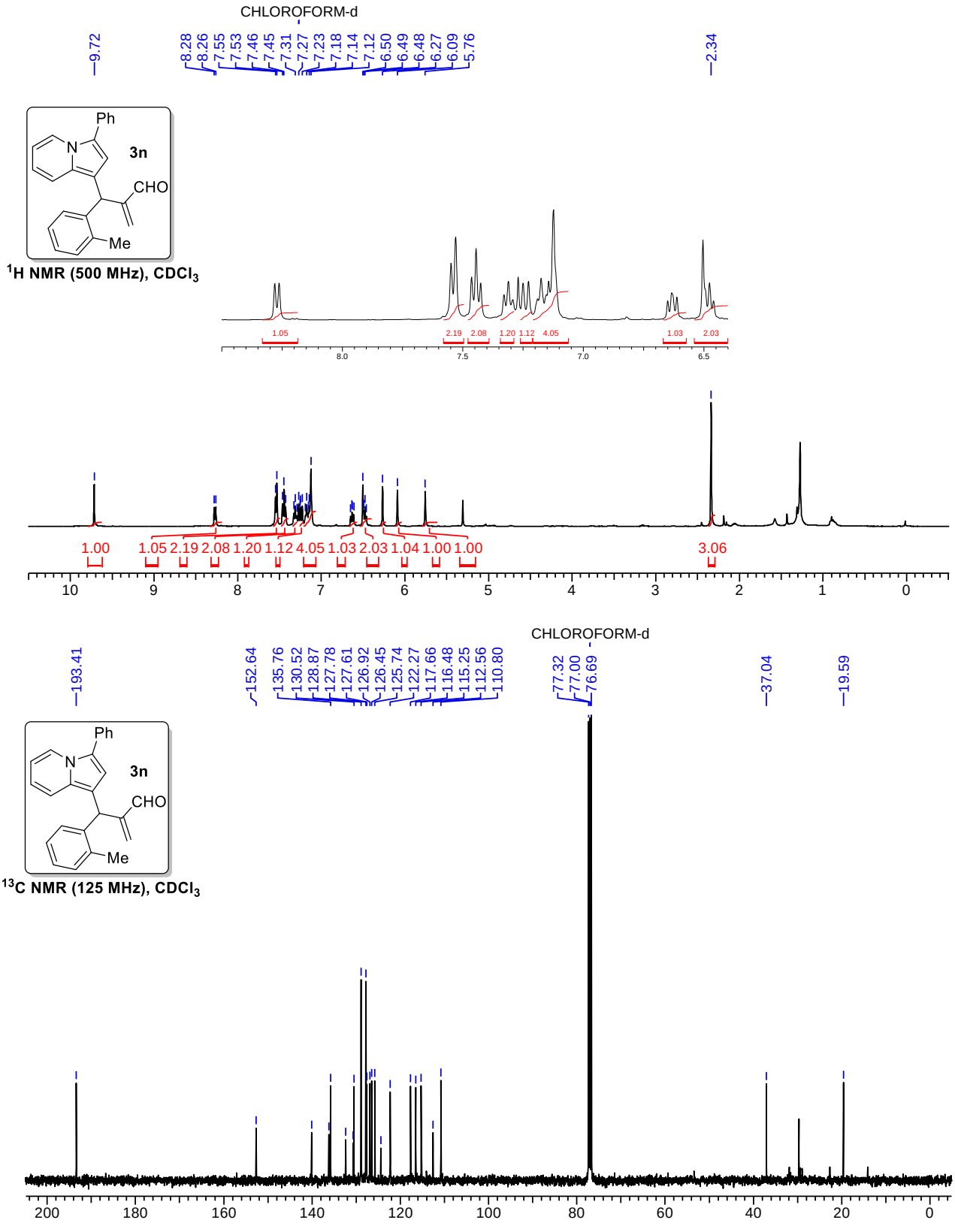


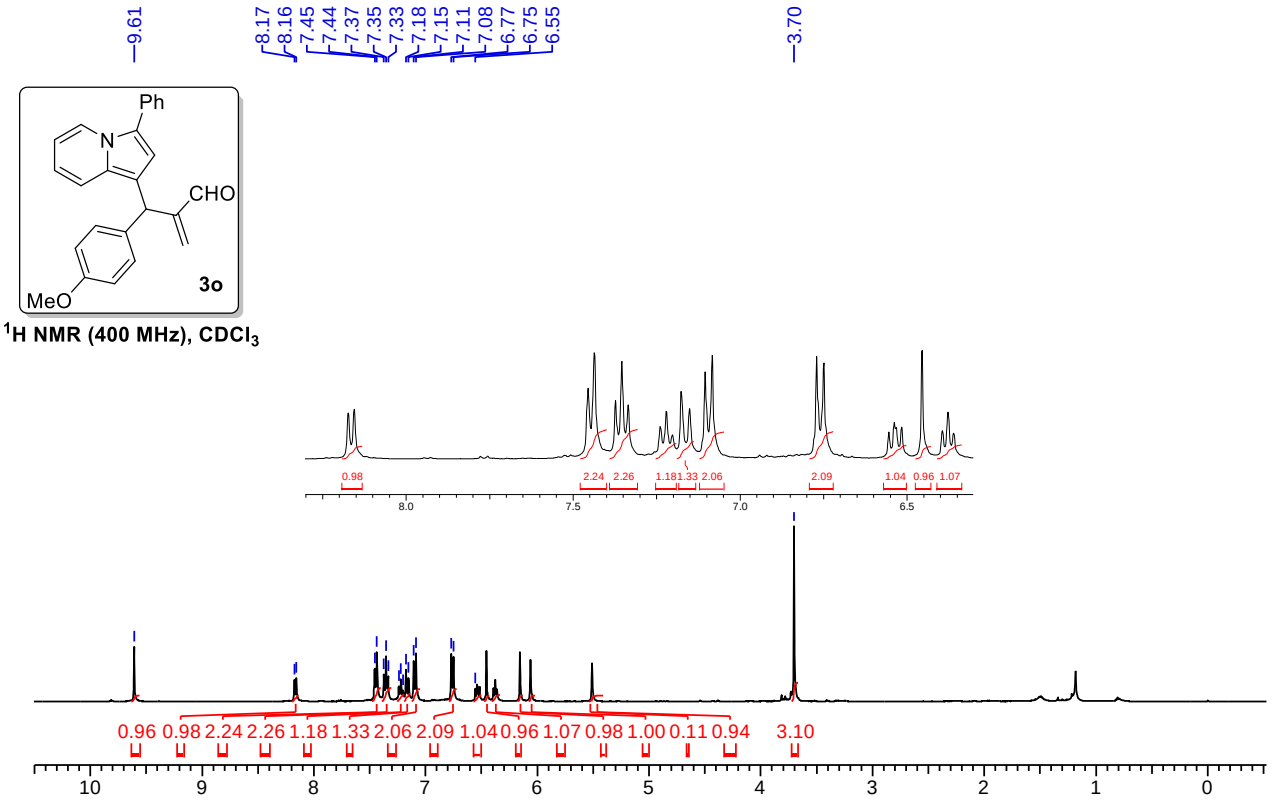
^{13}C NMR (100 MHz), DMSO-d_6



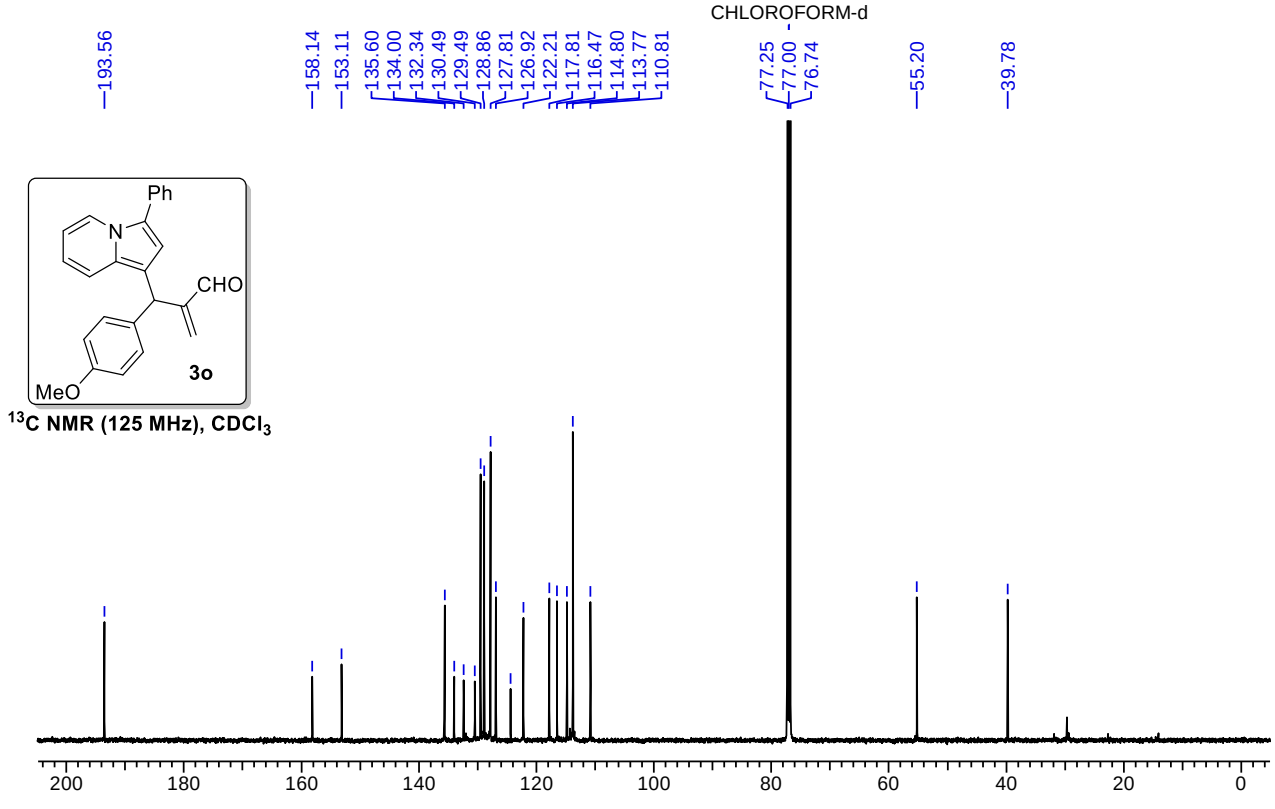
^{1}H NMR (500 MHz), $CDCl_3$

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

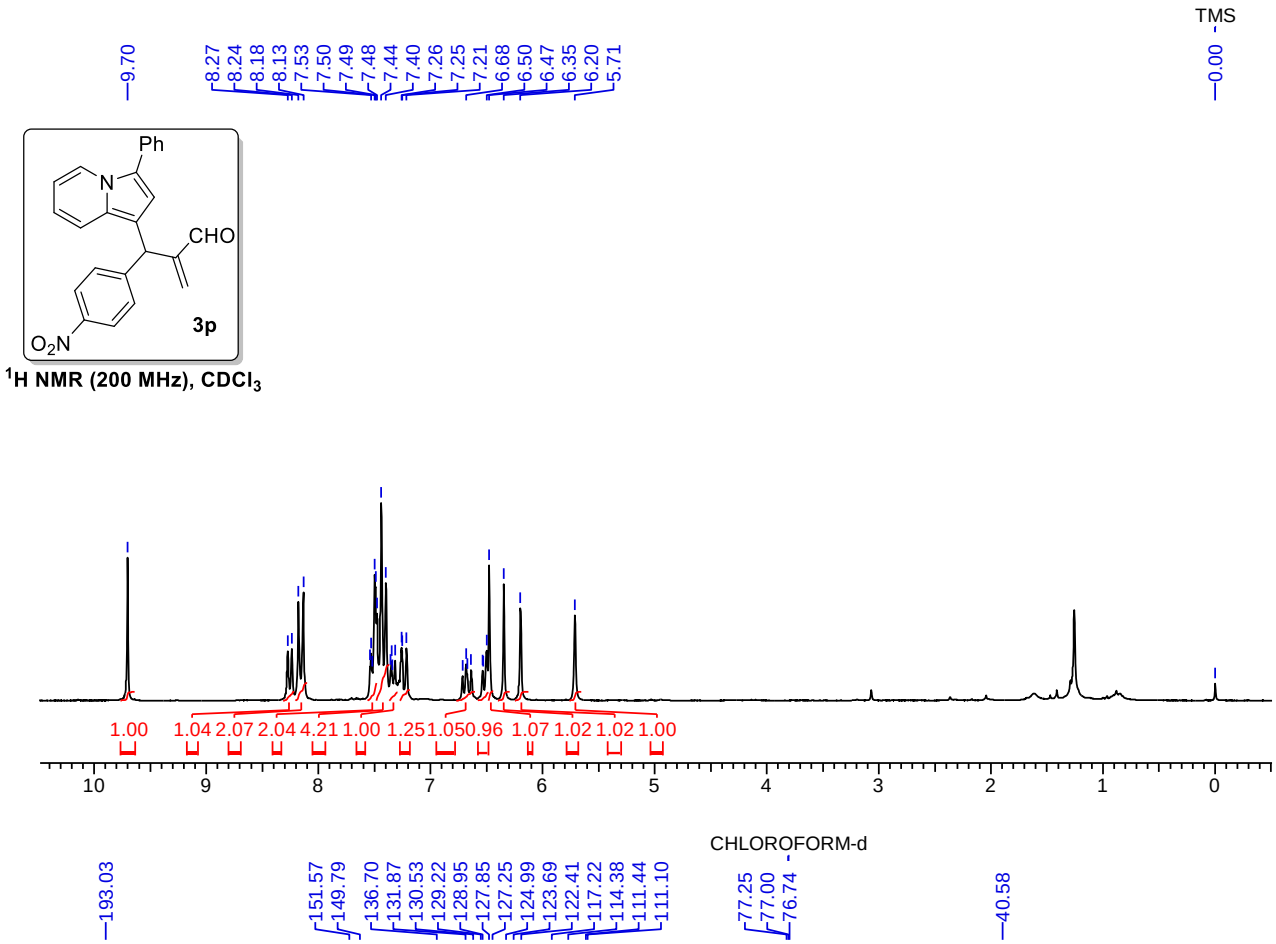

CHLOROFORM-d
9.72
8.28
8.26
7.55
7.53
7.46
7.45
7.31
7.27
7.23
7.18
7.14
7.12
6.50
6.49
6.48
6.27
6.09
5.76
2.34
Ph
N
3n
CHO
Me
1H NMR (500 MHz), CDCl3
1.05
2.19
2.08
1.20
1.12
4.05
1.03
2.03
1.00
1.05 2.19 2.08 1.20 1.12 4.05 1.03 2.03 1.04 1.00 1.00
3.06
CHLOROFORM-d
193.41
152.64
135.76
130.52
128.87
127.78
127.61
126.92
126.45
125.74
122.27
117.66
116.48
115.25
112.56
110.80
77.32
77.00
76.69
37.04
19.59
13C NMR (125 MHz), CDCl3



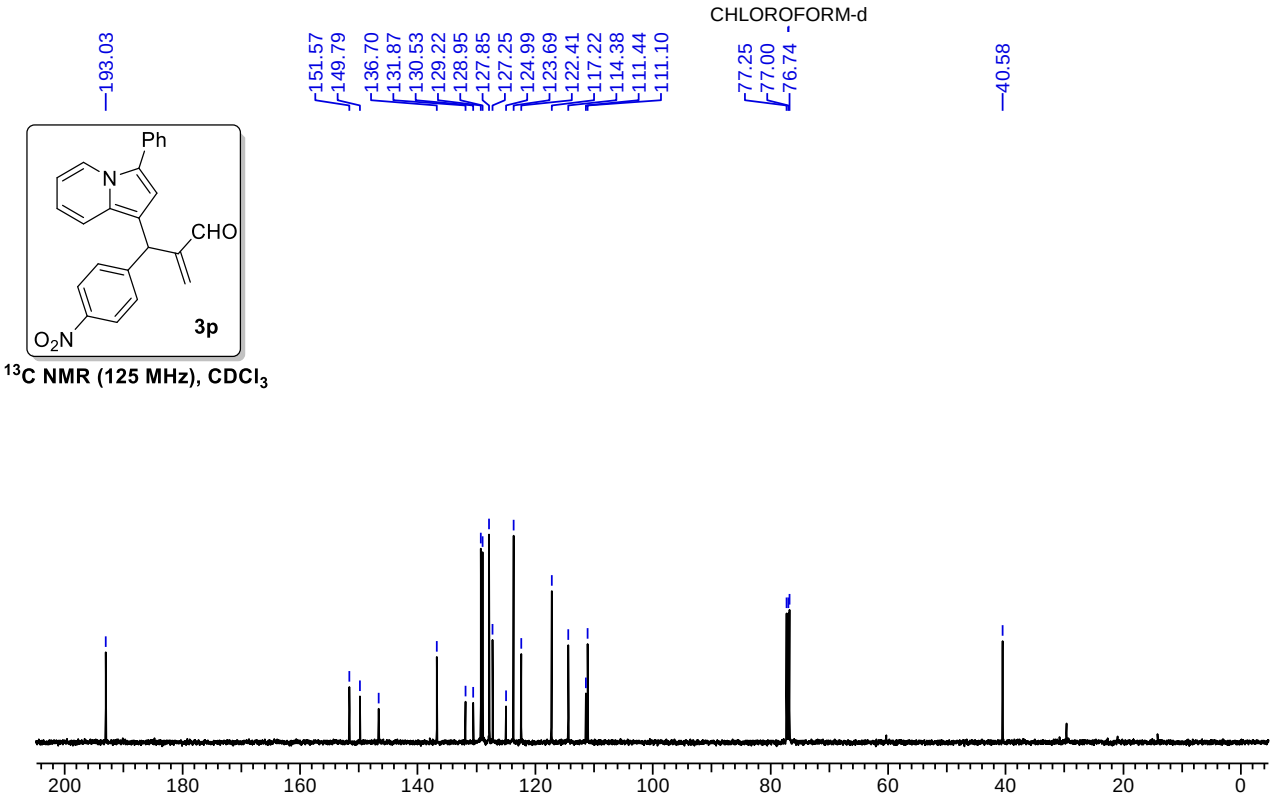
^{1}H NMR (400 MHz), $CDCl_3$



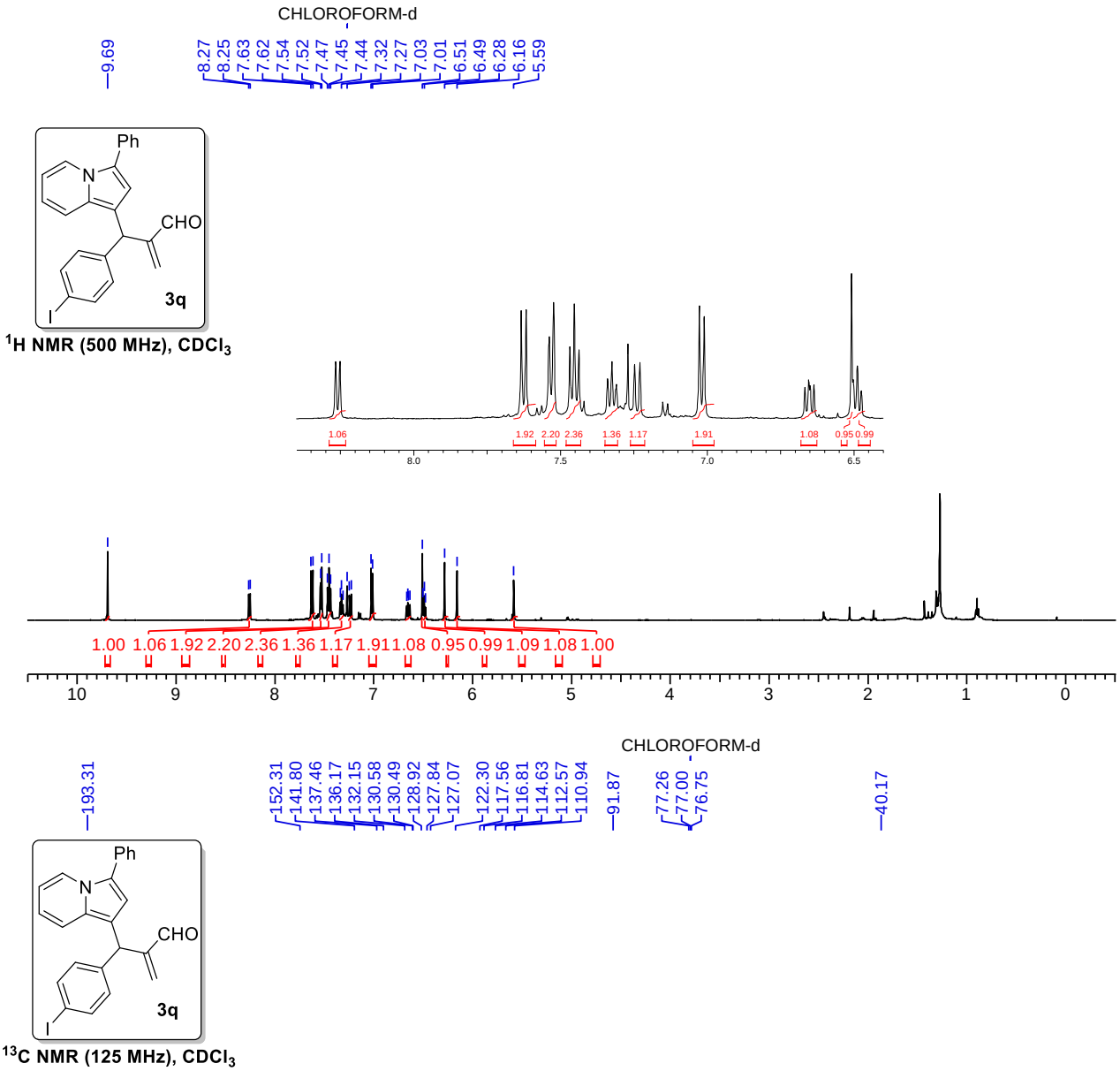
^{13}C NMR (125 MHz), $CDCl_3$

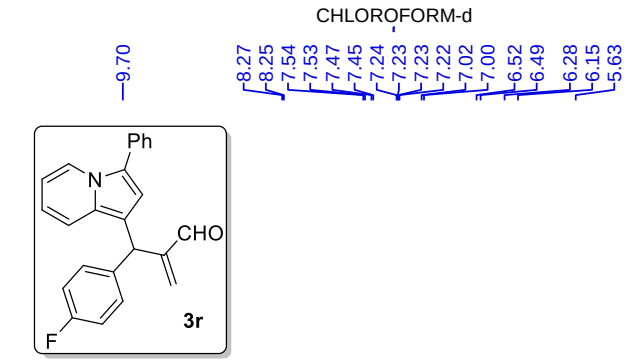


^{1}H NMR (200 MHz), $CDCl_3$

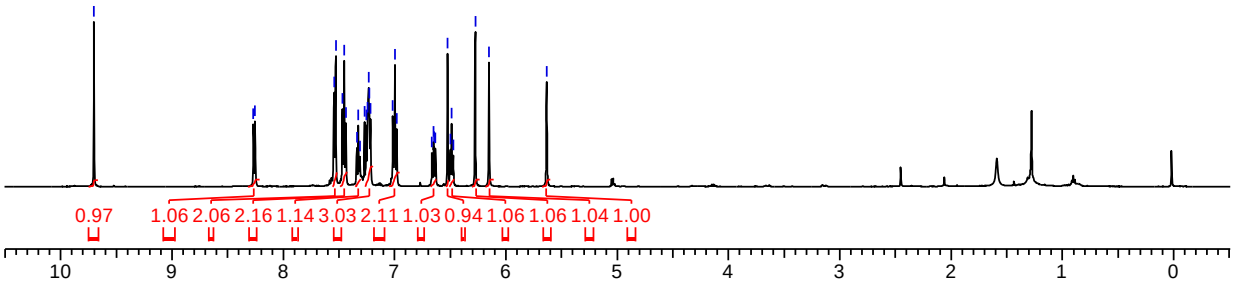


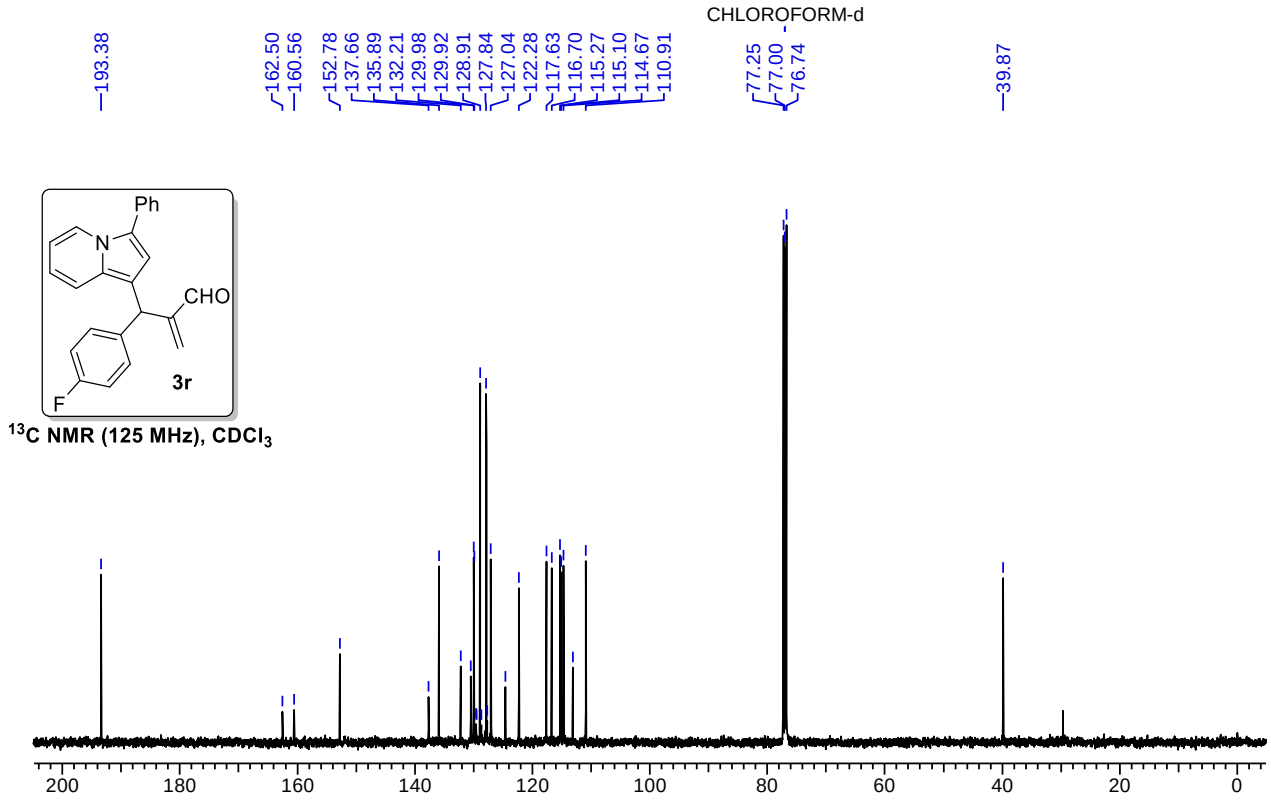
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
9.69
8.27
8.25
7.63
7.62
7.54
7.52
7.47
7.45
7.44
7.32
7.27
7.03
7.01
6.51
6.49
6.28
6.16
5.59
Ph
N
CHO
I
3q
1H NMR (500 MHz), CDCl3
1.06
1.92
2.20
2.36
1.36
1.17
1.91
1.08
0.95
0.99
1.09
1.08
1.00
10
9
8
7
6
5
4
3
2
1
0
CHLOROFORM-d
193.31
152.31
141.80
137.46
136.17
132.15
130.58
130.49
128.92
127.84
127.07
122.30
117.56
116.81
114.63
112.57
110.94
91.87
77.26
77.00
76.75
40.17
Ph
N
CHO
I
3q
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0

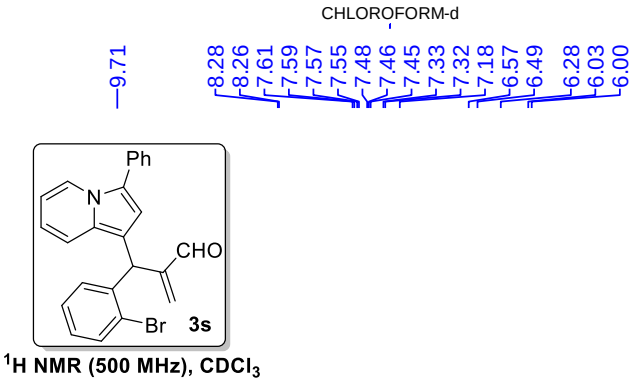


^{1}H NMR (500 MHz), $CDCl_3$

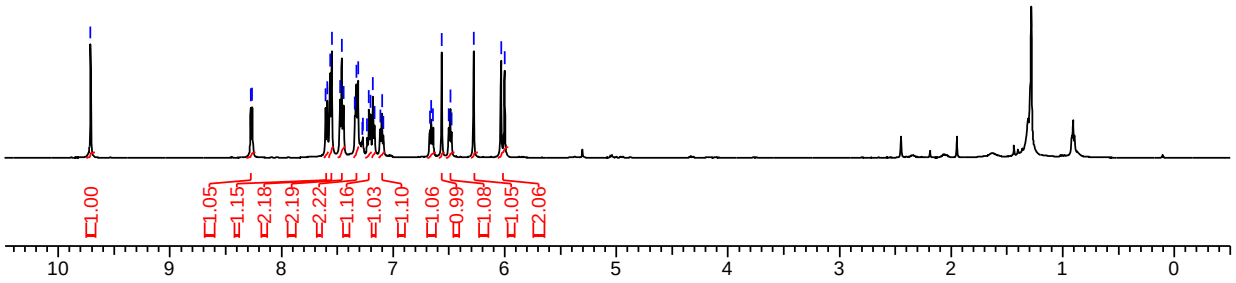


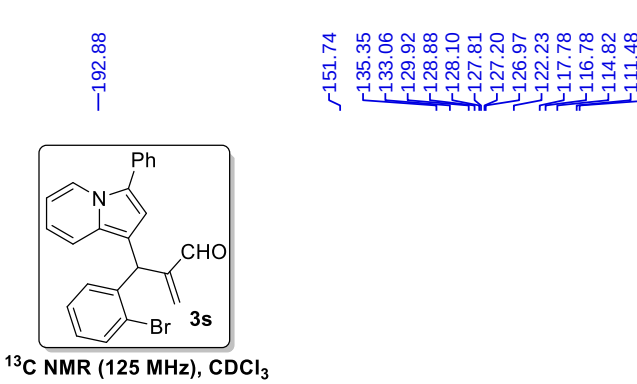


^{13}C NMR (125 MHz), $CDCl_3$

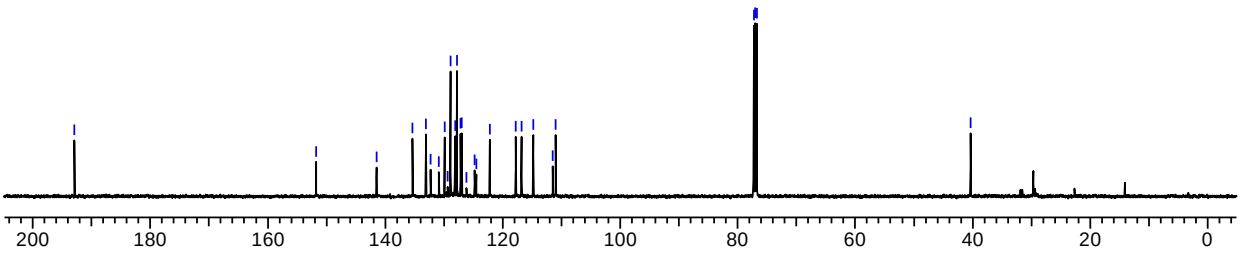


^{1}H NMR (500 MHz), $CDCl_3$

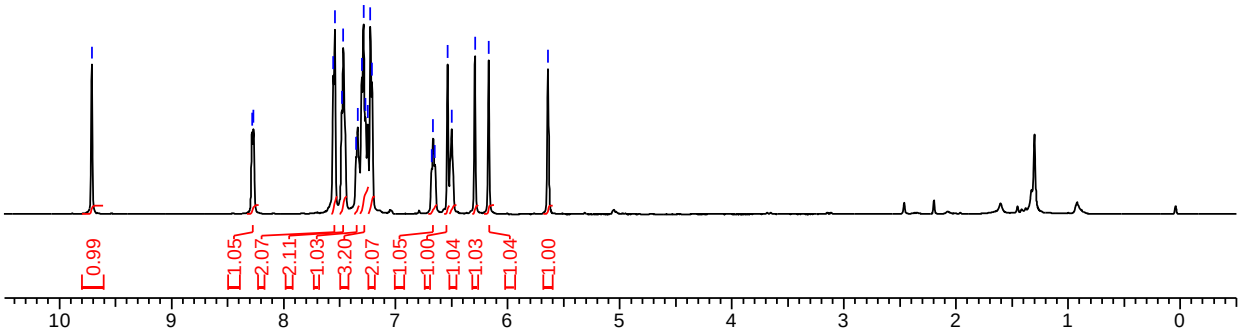


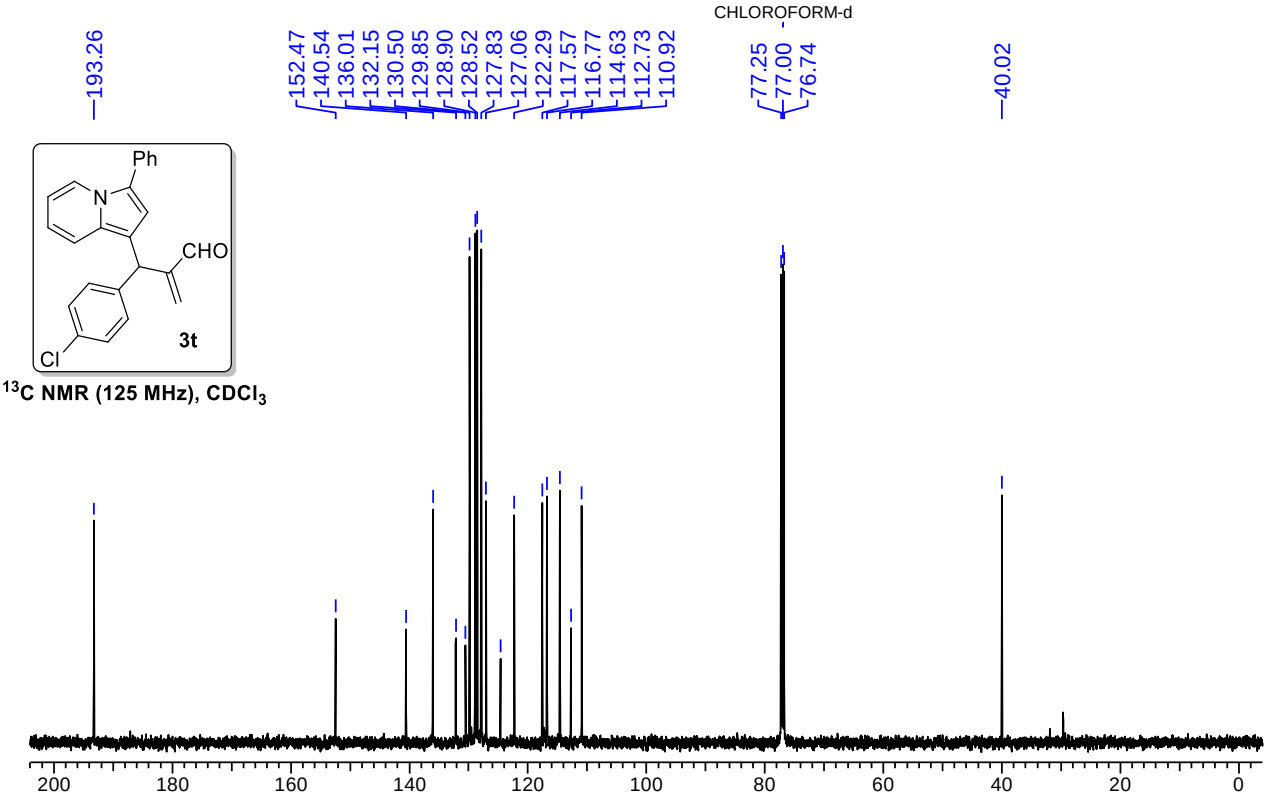


^{13}C NMR (125 MHz), $CDCl_3$

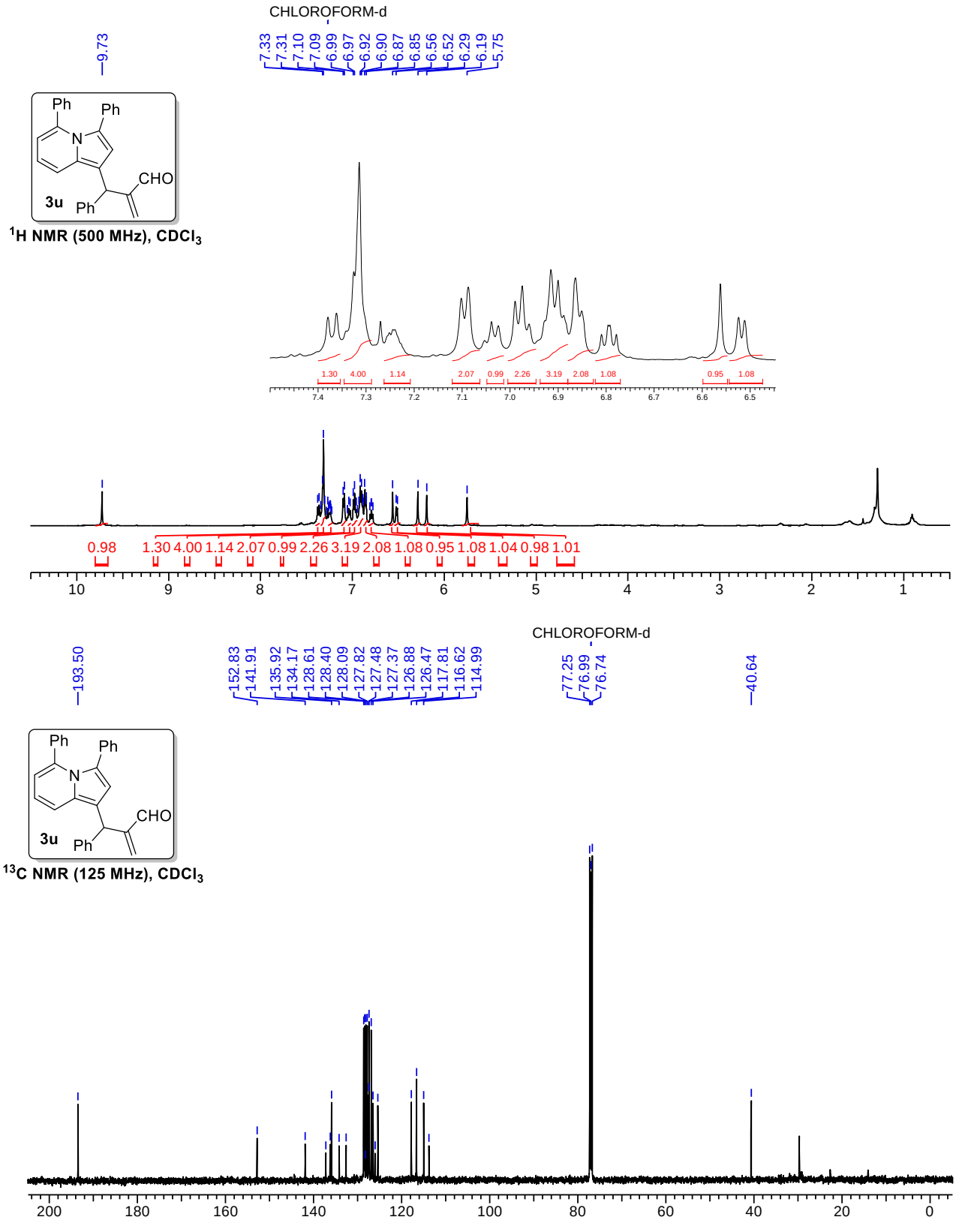


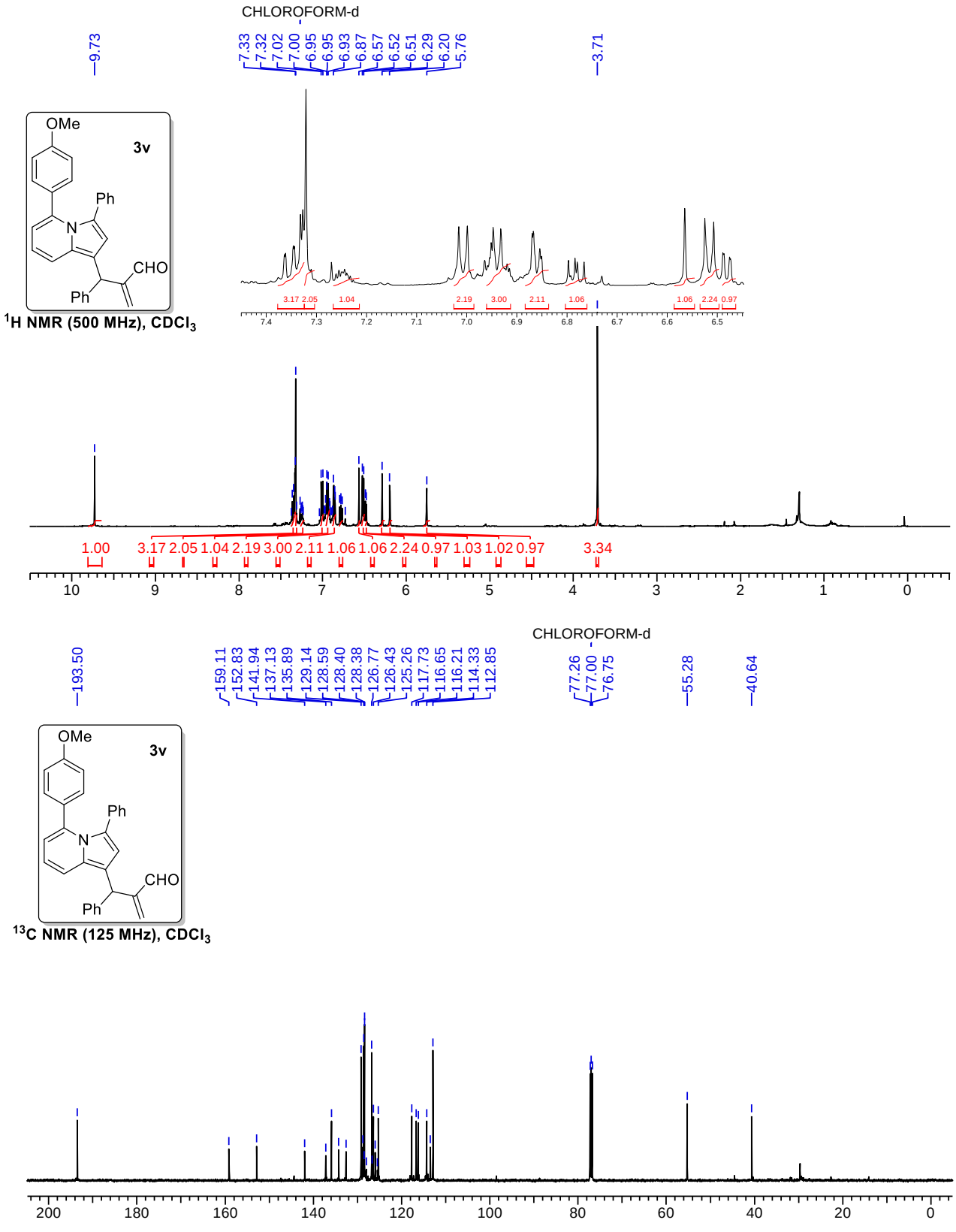
^{1}H NMR (500 MHz), $CDCl_3$

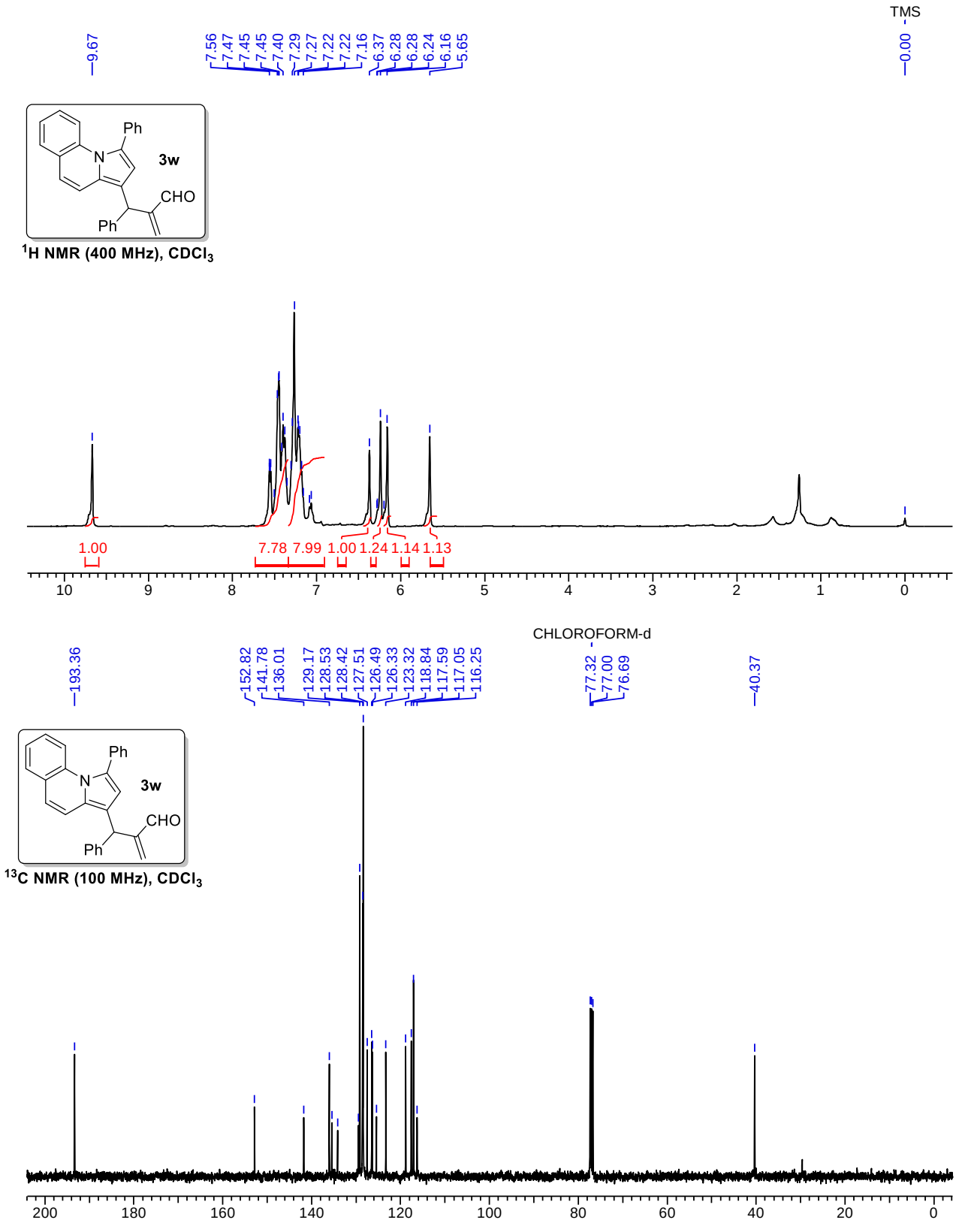


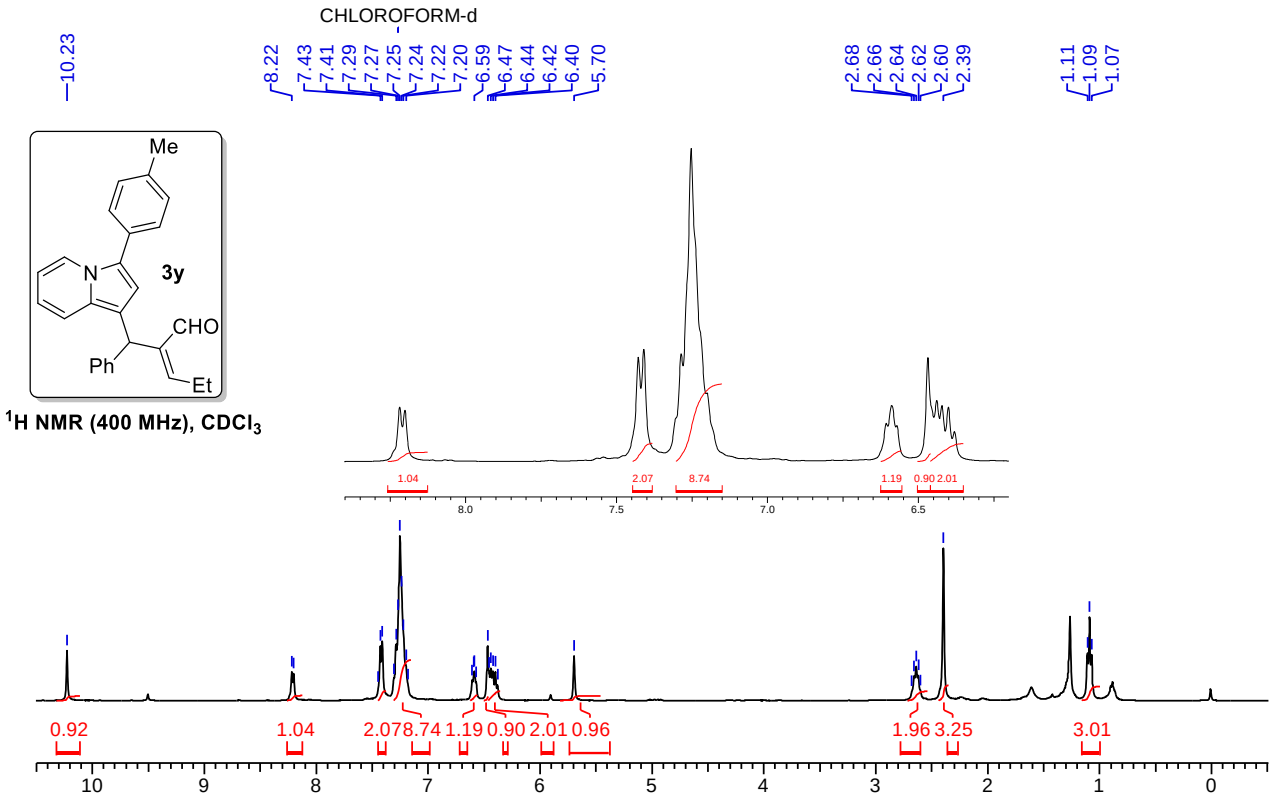


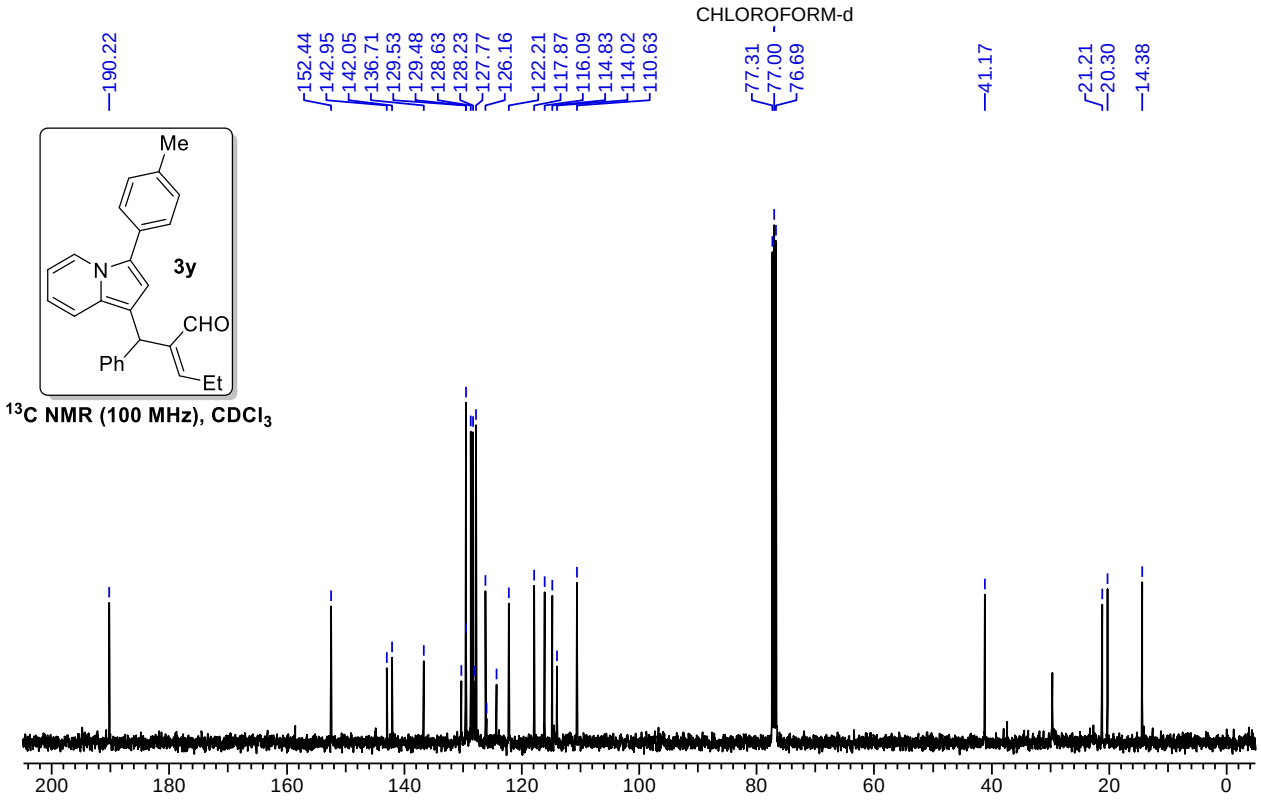
^{13}C NMR (125 MHz), $CDCl_3$

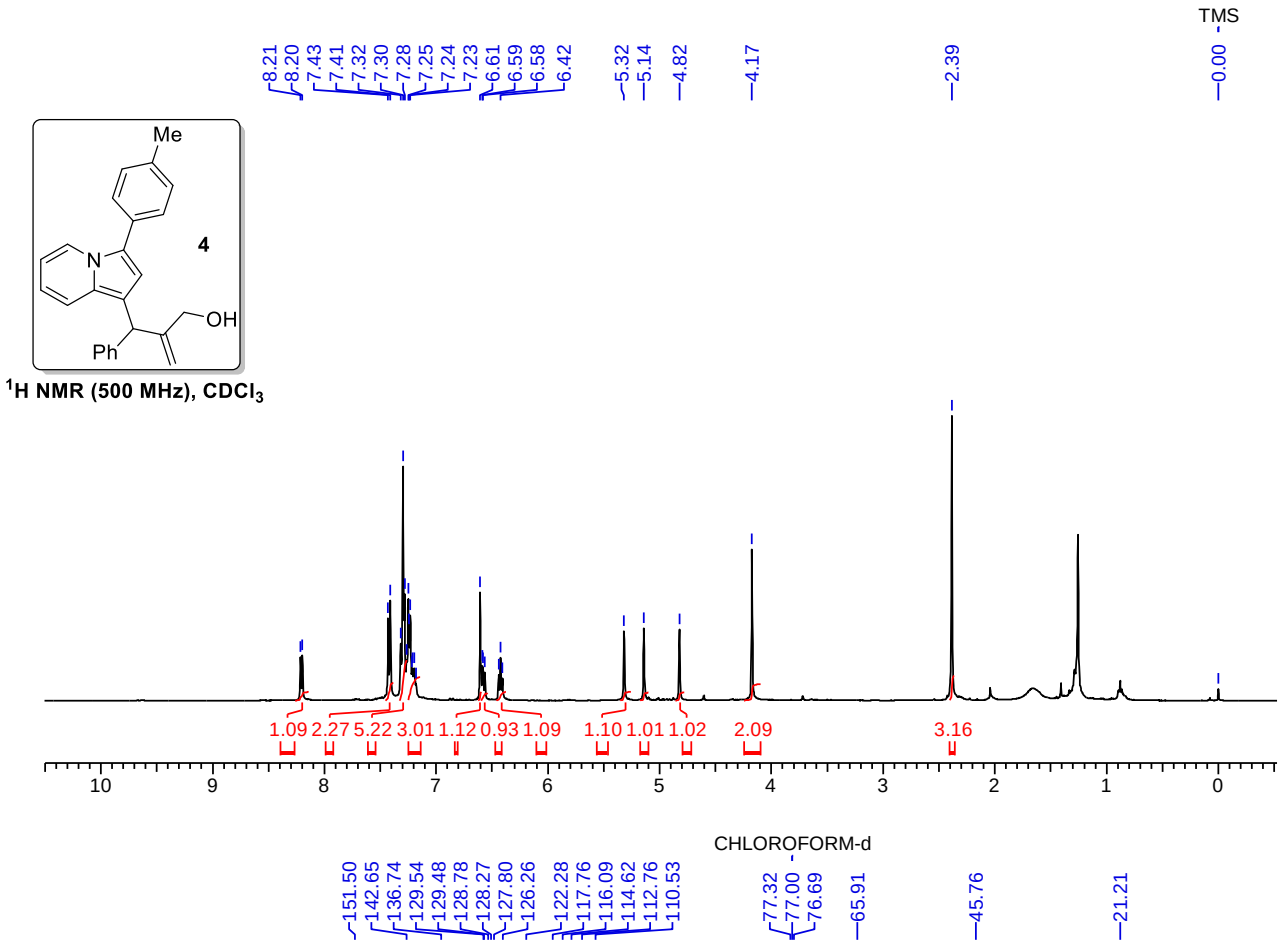

CHLOROFORM-d
9.73
7.33
7.31
7.10
7.09
6.99
6.97
6.92
6.90
6.87
6.85
6.56
6.52
6.29
6.19
5.75
Ph
Ph
N
CHO
3u
Ph
1H NMR (500 MHz), CDCl3
1.30 4.00 1.14 2.07 0.99 2.26 3.19 2.08 1.08 0.95 1.08
0.98 1.30 4.00 1.14 2.07 0.99 2.26 3.19 2.08 1.08 0.95 1.08 1.04 0.98 1.01
CHLOROFORM-d
193.50
152.83
141.91
135.92
134.17
128.61
128.40
128.09
127.82
127.48
127.37
126.88
126.47
117.81
116.62
114.99
77.25
76.99
76.74
40.64
13C NMR (125 MHz), CDCl3


CHLOROFORM-d
9.73
7.33
7.32
7.02
7.00
6.95
6.95
6.93
6.87
6.57
6.52
6.51
6.29
6.20
5.76
3.71
OMe
3v
Ph
N
CHO
Ph
1H NMR (500 MHz), CDCl3
1.00 3.17 2.05 1.04 2.19 3.00 2.11 1.06 1.06 2.24 0.97 1.03 1.02 0.97 3.34
CHLOROFORM-d
193.50
159.11
152.83
141.94
137.13
135.89
129.14
128.59
128.40
128.38
126.77
126.43
125.26
117.73
116.65
116.21
114.33
112.85
77.26
77.00
76.75
55.28
40.64
OMe
3v
Ph
N
CHO
Ph
13C NMR (125 MHz), CDCl3

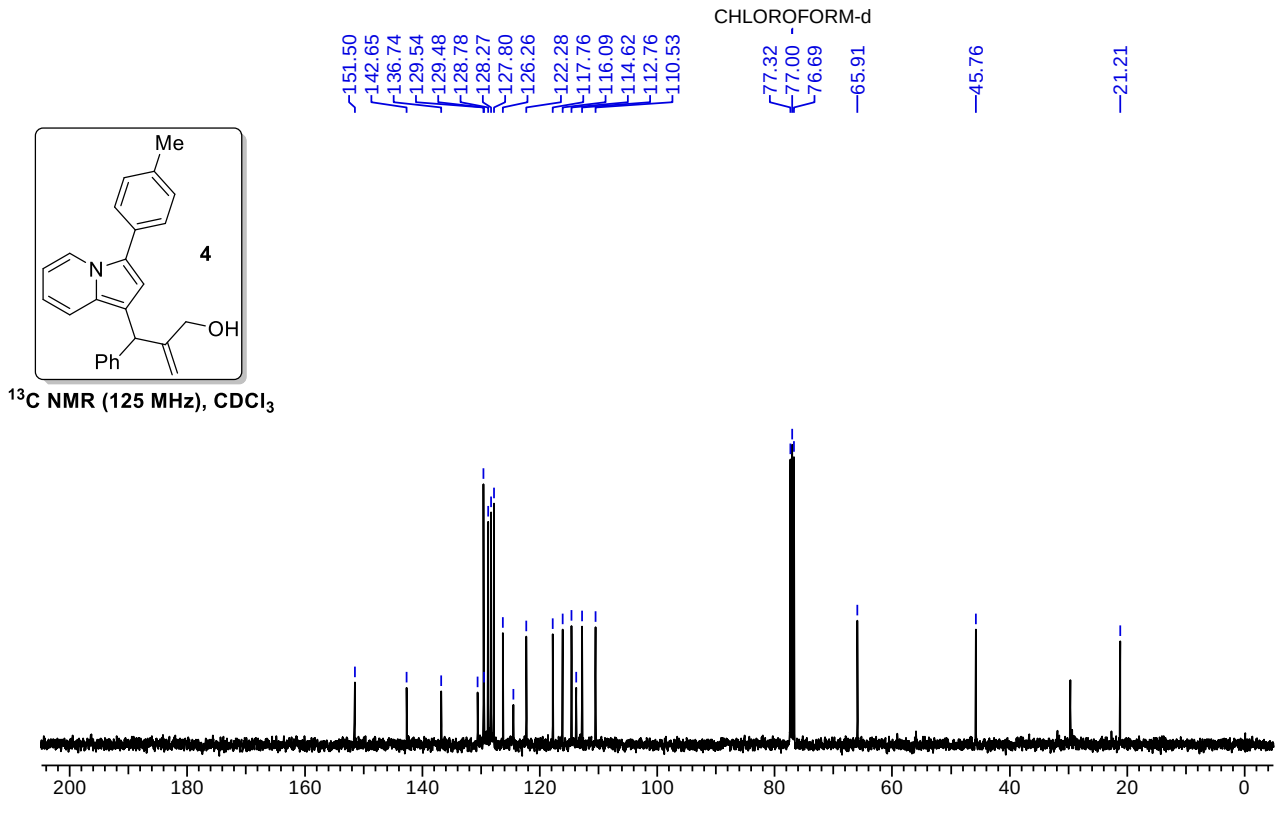

TMS
9.67
7.56
7.47
7.45
7.45
7.40
7.29
7.27
7.22
7.22
7.16
6.37
6.28
6.28
6.24
6.16
5.65
0.00
Ph
N
3w
CHO
Ph
1H NMR (400 MHz), CDCl3
1.00
7.78
7.99
1.00
1.24
1.14
1.13
10
9
8
7
6
5
4
3
2
1
0
CHLOROFORM-d
193.36
152.82
141.78
136.01
129.17
128.53
128.42
127.51
126.49
126.33
123.32
118.84
117.59
117.05
116.25
77.32
77.00
76.69
40.37
Ph
N
3w
CHO
Ph
13C NMR (100 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0


CHLOROFORM-d
10.23
8.22
7.43
7.41
7.29
7.27
7.25
7.24
7.22
7.20
6.59
6.47
6.44
6.42
6.40
5.70
2.68
2.66
2.64
2.62
2.60
2.39
1.11
1.09
1.07
Me
N
3y
CHO
Ph
Et
1H NMR (400 MHz), CDCl3
1.04
2.07
8.74
1.19
0.90
2.01
0.92
1.04
2.07
8.74
1.19
0.90
2.01
0.96
1.96
3.25
3.01

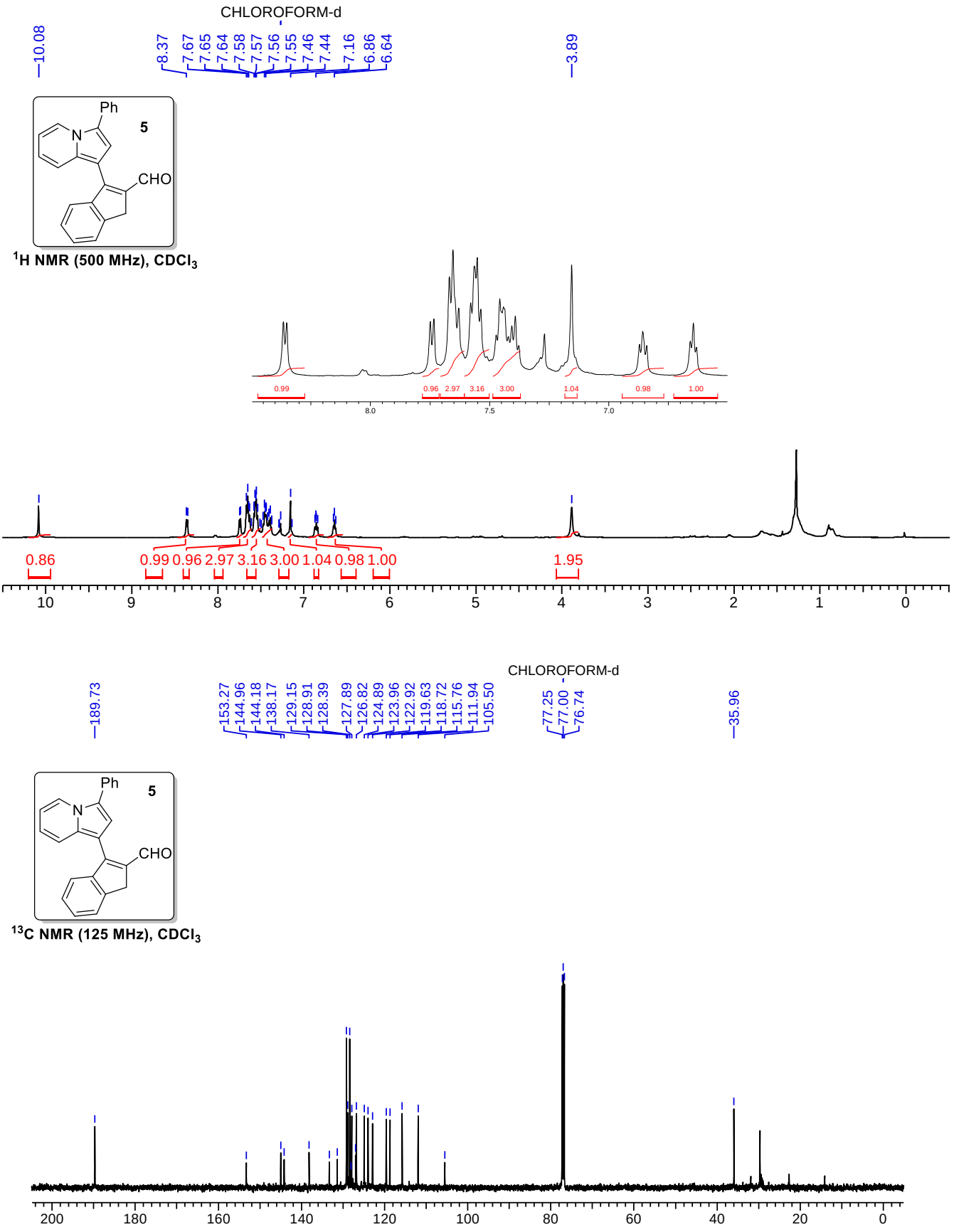

CHLOROFORM-d
190.22
152.44
142.95
142.05
136.71
129.53
129.48
128.63
128.23
127.77
126.16
122.21
117.87
116.09
114.83
114.02
110.63
77.31
77.00
76.69
41.17
21.21
20.30
14.38
Me
N
3y
CHO
Ph
Et
13C NMR (100 MHz), CDCl3



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

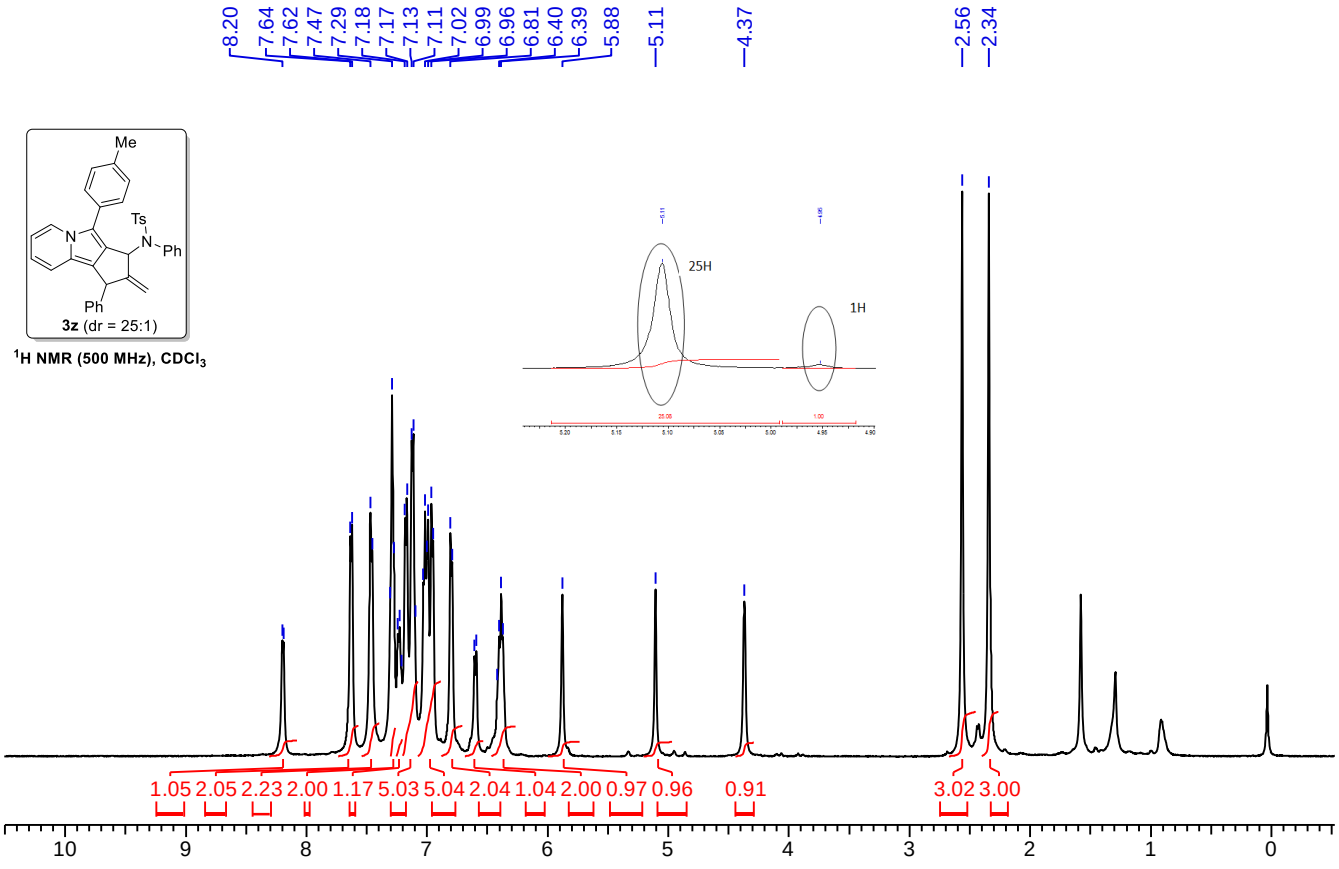


^{13}C NMR (125 MHz), $CDCl_3$

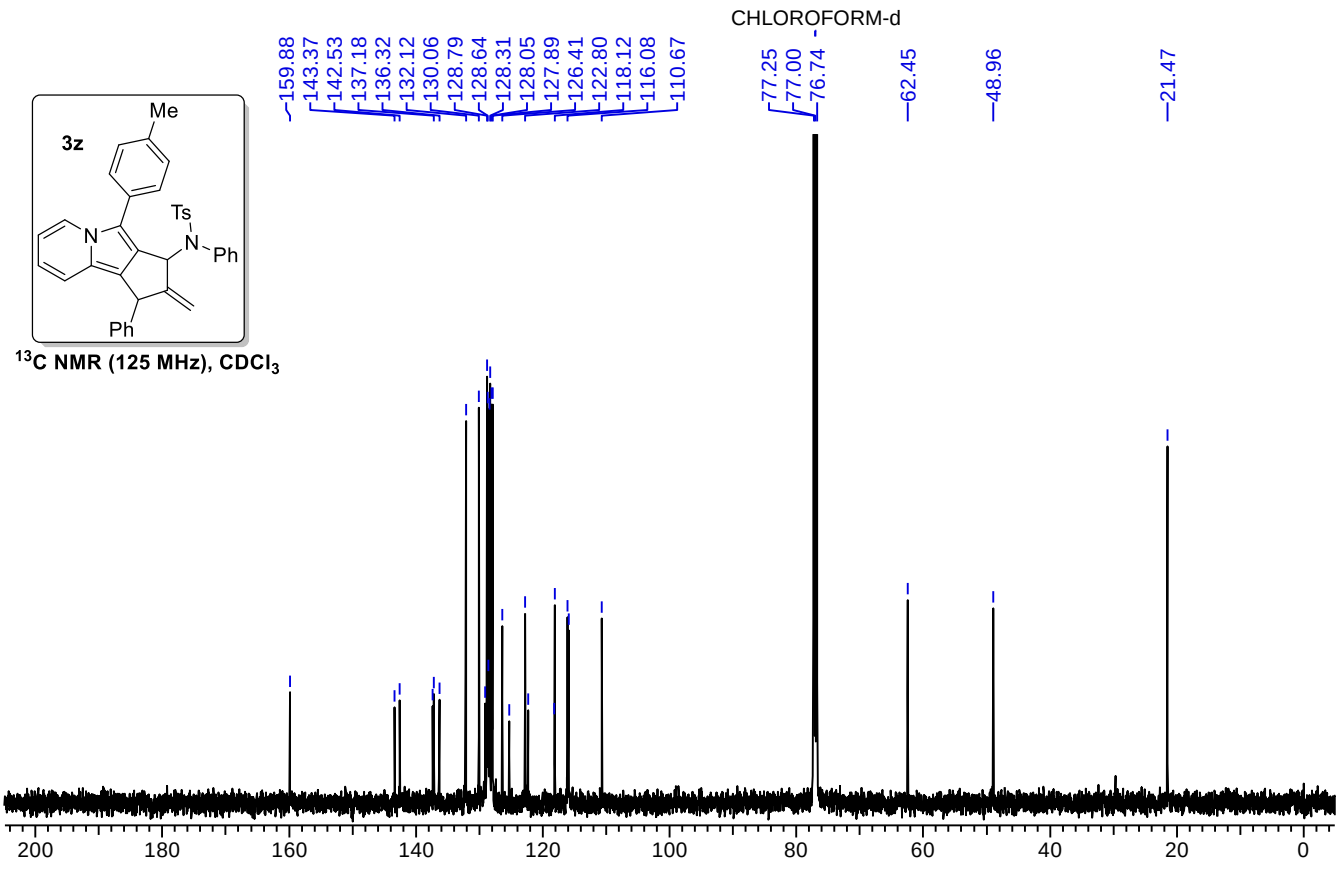


^{1}H NMR (500 MHz), $CDCl_3$

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



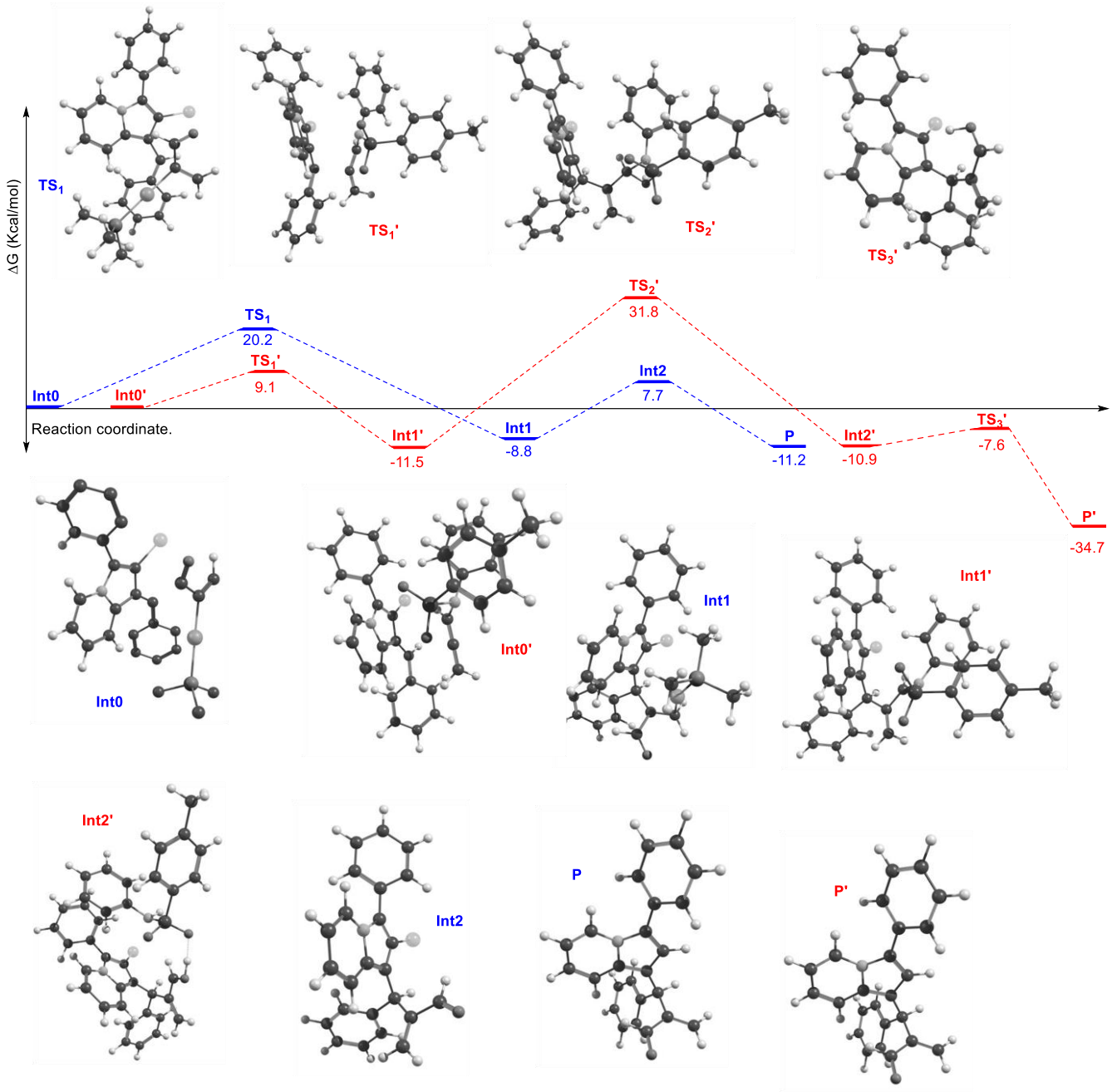
^{1}H NMR (500 MHz), $CDCl_3$



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

10. DFT study:

Figure S1. Interception of Ag-bound carbocation with α-gold enal vs. *N*-allenamide - computational investigation [possibility (i) vs (ii)]



To reveal the formation of product either by direct attack of *N*-allenamide under the Ag-catalysis [possibility (ii)] or attack of α-gold(I) enal intermediate under the Au/Ag co-operative catalysis [possibility (i)], detail quantum chemical calculations were performed with $AuP(Me)_3$ as a model catalyst. Initially, the C-C bond forming step was investigated by the union of silver bound carbocation **E** with the α-gold(I) enal **C** [possibility (i), marked in blue]. In this step, the α-gold(I) enal species approaches the silver bound carbocation, resulting in the formation of Au- and Ag-bound

intermediate **Int1** with generation of new C-C bond *via* transition state **TS$_1$** [20.2 kcal/mol above **Int0**]. Simultaneously, the C-C bond forming step was investigated by quenching the Ag-bound carbocation **E** with **2a** [possibility (ii), marked in red). This results in the formation of Ag-bound intermediate **Int1′** *via* transition state **TS$_1$′** [14.0 kcal/mol above **Int0′**]. Although there is higher exergonicity of transformation **Int0′→Int1′** [-11.5 kcal/mol above **Int0′**] than **Int0→Int1** [-8.8 kcal/mol above **Int0′**], it is compensated in the subsequent step where the transition state for hydrolysis **TS$_2$′** is high energy demanding (31.8 kcal/mol) as compared to **Int2** (7.7 kcal/mol above **Int0**). The intermediate **Int2** after protonation forms product **P**. Similarly, **Int2′** undergoes protodeauration to form product **P′** (transition state **TS$_3$′**, -7.6 kcal/mol above **Int0′**). The computational results, therefore, support the proposed Au/Ag co-operative catalysis and rule out alternative mononuclear mechanistic pathways.

Figure S2. Interception of Ag-bound carbocation with α-gold enal vs α-gold en-imine - computational investigation [possibility (i) vs (iii)]

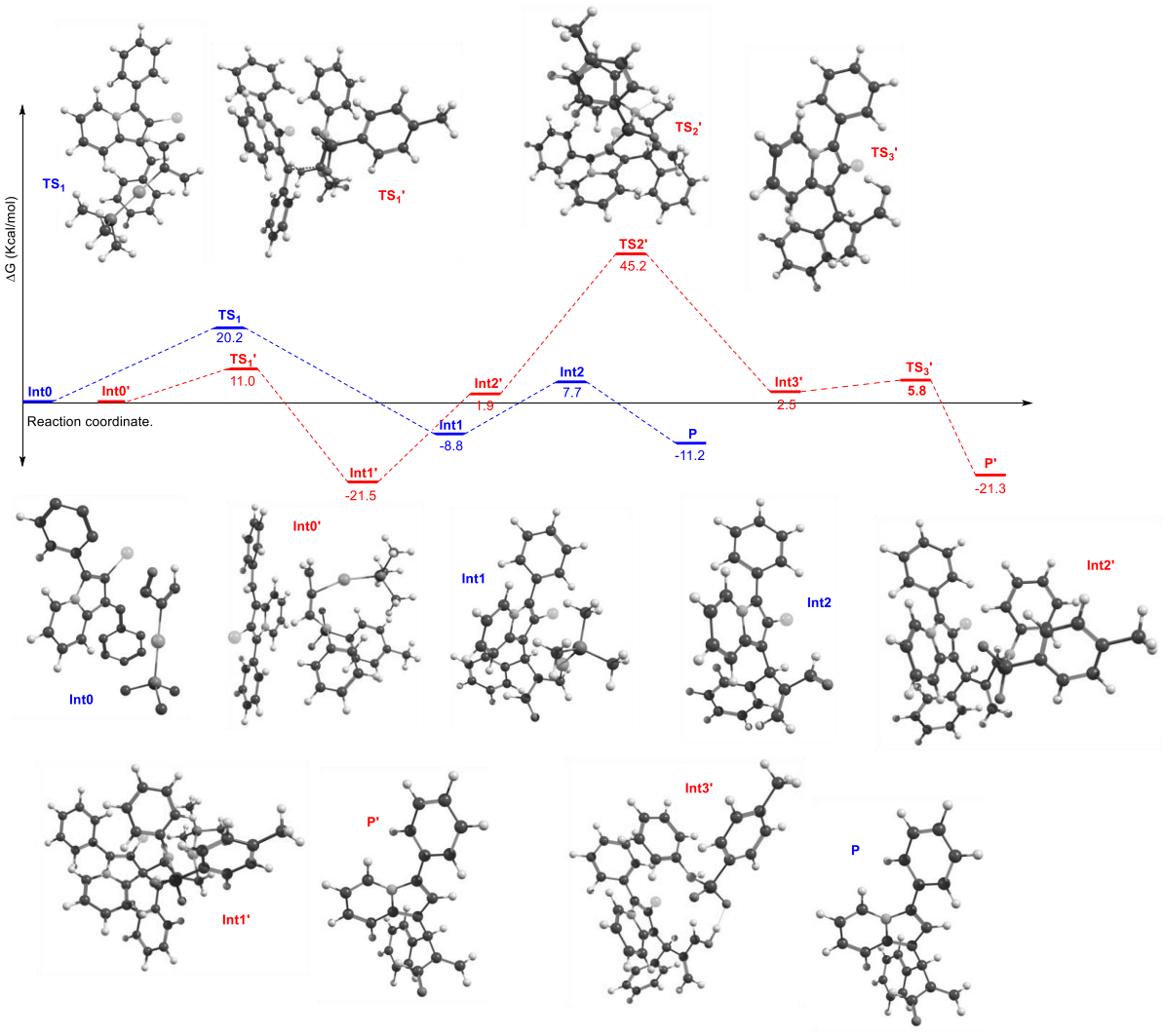
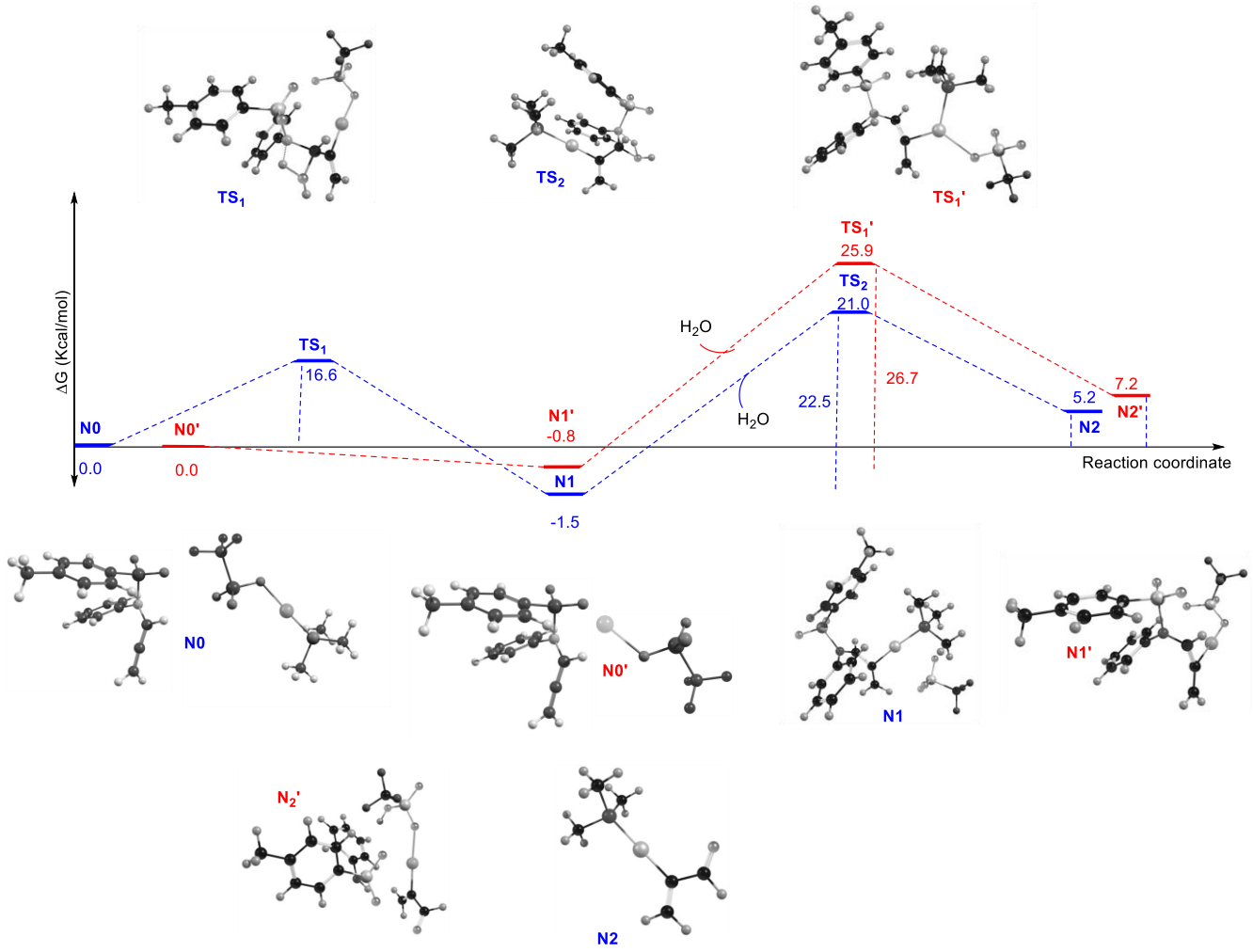


Figure S3. Computational mechanistic investigation: the formation of α-gold enal species vs α-silver enal.



Computed Cartesian coordinates of all the molecules reported in this study

Figure S1

Int0

59

C	-1.305	2.613	3.654
C	-1.344	1.219	3.853
C	-1.528	0.716	5.156
C	-1.662	1.592	6.235
C	-1.619	2.976	6.029
C	-1.442	3.483	4.737
C	-1.159	0.284	2.735
N	-2.007	0.353	1.571
C	-1.635	-0.627	0.661
C	-0.509	-1.340	1.257
C	-0.290	-0.759	2.579
C	-3.104	1.137	1.392
C	-3.891	0.966	0.267
C	-3.564	-0.031	-0.662
C	-2.437	-0.827	-0.460
C	0.196	-2.415	0.776
C	0.271	-2.993	-0.548
C	0.168	-2.224	-1.729
C	0.293	-2.826	-2.980
C	0.519	-4.206	-3.077
C	0.651	-4.977	-1.915
C	0.548	-4.375	-0.663
Ag	1.042	-1.439	4.006
C	-1.796	-4.051	3.278
C	-0.697	-4.545	3.889
C	-2.478	-2.898	3.899
O	-2.627	-2.720	5.110
Au	-2.551	-4.709	1.461
P	-3.436	-5.477	-0.588
C	-3.307	-4.284	-1.987
C	-2.644	-7.010	-1.229
C	-5.231	-5.883	-0.518
H	-0.312	-4.092	4.814
H	-2.179	-1.611	-1.167
H	-4.192	-0.190	-1.539
H	-4.767	1.599	0.135
H	-3.322	1.857	2.179
H	-1.141	3.016	2.652
H	-1.399	4.561	4.571

TS_1

59

C	0.229	-2.401	-1.022
C	0.715	-2.945	0.180
C	1.638	-4.009	0.099
C	1.981	-4.574	-1.127
C	1.429	-4.070	-2.310
C	0.572	-2.966	-2.252
C	0.379	-2.406	1.525
C	-0.361	-1.214	1.812
C	-1.594	-0.748	1.256
N	-1.927	0.437	1.931
C	-0.947	0.707	2.917
C	-0.009	-0.306	2.878
C	-2.519	-1.265	0.336
C	-3.709	-0.598	0.087
C	-3.988	0.609	0.760
C	-3.095	1.104	1.684
C	-1.049	1.878	3.800
C	-0.992	1.703	5.195
C	-1.063	2.802	6.053
C	-1.199	4.094	5.532
C	-1.257	4.280	4.146
C	-1.180	3.183	3.285
Ag	1.623	-0.436	4.134
C	-0.629	-3.854	2.625
C	-1.474	-3.122	3.626
Au	-1.812	-4.627	1.003
P	-3.091	-5.491	-0.738
C	-2.120	-6.621	-1.811
C	0.225	-4.810	3.100
H	0.322	-4.997	4.177
C	-4.579	-6.430	-0.217
C	-3.721	-4.186	-1.870
H	-2.289	-2.203	-0.165
H	-4.428	-1.002	-0.626
H	-4.911	1.157	0.575
H	-3.268	2.007	2.264
H	-1.197	3.342	2.204
H	-1.353	5.285	3.732
H	-1.261	4.952	6.203
H	-1.024	2.649	7.134
H	-0.911	0.692	5.602
H	-0.402	-1.514	-1.006
H	0.178	-2.531	-3.173
H	1.691	-4.514	-3.272
H	2.689	-5.404	-1.161
H	2.092	-4.396	1.013
H	1.236	-2.479	2.201
H	0.847	-5.413	2.437
H	-2.160	-2.356	3.199
O	-1.495	-3.360	4.828
H	-4.281	-4.645	-2.696
H	-4.385	-3.510	-1.314
H	-2.876	-3.614	-2.275
H	-2.740	-6.970	-2.648
H	-1.244	-6.083	-2.196
H	-1.779	-7.480	-1.218
H	-5.118	-6.798	-1.102
H	-4.274	-7.277	0.410
H	-5.234	-5.771	0.366

Int1

59

C	1.653	-1.618	0.355
C	1.396	-2.881	0.903
C	2.351	-3.901	0.731
C	3.524	-3.666	0.009
C	3.766	-2.404	-0.542
C	2.830	-1.381	-0.361
C	0.143	-3.175	1.725
C	-0.894	-2.081	1.835
C	-1.636	-1.455	0.807
N	-2.521	-0.535	1.434
C	-2.327	-0.582	2.816
C	-1.337	-1.541	3.073
C	-1.668	-1.544	-0.604
C	-2.576	-0.808	-1.336
C	-3.497	0.041	-0.663
C	-3.455	0.166	0.699
C	-3.041	0.293	3.753
C	-3.555	-0.231	4.958
C	-4.184	0.595	5.891
C	-4.325	1.964	5.638
C	-3.822	2.499	4.446
C	-3.184	1.676	3.516
Ag	-0.632	-2.044	4.945
C	-0.484	-4.511	1.306
C	-0.816	-5.500	2.213
Au	-2.800	-4.391	1.819
P	-5.070	-3.910	1.811
C	-6.125	-5.383	2.077
C	-0.531	-4.850	-0.170
O	-0.923	-5.920	-0.607
C	-5.551	-2.690	3.090
C	-5.577	-3.192	0.202
H	-0.956	-2.197	-1.106
H	-2.593	-0.881	-2.423
H	-4.243	0.610	-1.218
H	-4.134	0.800	1.264
H	-2.762	2.119	2.612
H	-3.912	3.569	4.246
H	-4.820	2.610	6.365

H	-4.577	0.165	6.814
H	-3.466	-1.301	5.152
H	0.930	-0.813	0.496
H	3.014	-0.390	-0.781
H	4.682	-2.217	-1.106
H	4.253	-4.469	-0.115
H	2.183	-4.887	1.172
H	0.481	-3.328	2.766
H	-0.155	-4.058	-0.850
H	-0.609	-5.376	3.278
H	-1.078	-6.500	1.857
H	-6.652	-2.964	0.228
H	-5.009	-2.270	0.016
H	-5.368	-3.911	-0.598
H	-7.182	-5.084	2.039
H	-5.918	-6.123	1.294
H	-5.898	-5.821	3.057
H	-6.627	-2.481	3.010
H	-5.326	-3.097	4.083
H	-4.981	-1.764	2.947

Int2

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C	-5.425	-5.576	1.779
C	-4.418	-4.625	2.019
C	-4.690	-3.279	1.741
C	-5.941	-2.889	1.247
C	-6.938	-3.842	1.021
C	-6.674	-5.191	1.286
C	-3.080	-5.096	2.573
C	-3.135	-5.527	4.035
C	-1.889	-6.194	4.501
C	-1.908	-4.162	2.383
C	-1.622	-3.002	3.134
N	-0.418	-2.453	2.615
C	0.035	-3.259	1.569
C	-0.872	-4.318	1.427
C	-2.254	-2.329	4.205
C	-1.688	-1.195	4.751
C	-0.454	-0.705	4.237
C	0.159	-1.339	3.189
C	1.258	-2.967	0.813
C	1.525	-1.685	0.289
C	2.680	-1.441	-0.455
C	3.592	-2.473	-0.703
C	3.337	-3.753	-0.198
C	2.188	-3.996	0.557
Ag	-0.743	-5.813	0.016
C	-4.160	-5.342	4.885
H	-4.072	-5.663	5.925
H	-3.187	-2.734	4.592
H	-2.176	-0.681	5.580
H	0.021	0.174	4.668
H	1.108	-1.016	2.766
H	0.804	-0.878	0.440
H	2.863	-0.442	-0.856
H	4.495	-2.282	-1.286
H	4.045	-4.565	-0.380
H	2.007	-4.989	0.973
H	-3.913	-2.530	1.903
H	-6.133	-1.835	1.035
H	-7.913	-3.538	0.634
H	-7.442	-5.946	1.103
H	-5.225	-6.632	1.983
H	-2.810	-6.007	2.000
H	-5.095	-4.879	4.566
H	-1.170	-6.454	3.688
O	-1.626	-6.472	5.668

P

45

C	1.815	-1.650	0.567
C	1.428	-2.891	1.116
C	2.371	-3.941	1.119
C	3.652	-3.755	0.598
C	4.028	-2.513	0.071
C	3.102	-1.464	0.057
C	0.078	-3.146	1.620
N	-0.667	-2.257	2.391
C	-1.937	-2.833	2.678
C	-1.965	-4.103	2.067
C	-0.716	-4.278	1.435
C	-0.301	-1.040	2.929
C	-1.184	-0.335	3.703
C	-2.483	-0.852	3.968
C	-2.842	-2.086	3.467
C	-3.058	-5.154	2.092
C	-2.757	-6.158	3.197
C	-2.626	-5.629	4.582
O	-2.365	-6.307	5.572
C	-4.480	-4.592	2.123
C	-4.842	-3.588	1.208
C	-6.138	-3.072	1.188
C	-7.102	-3.550	2.085
C	-6.757	-4.555	2.991
C	-5.456	-5.075	3.005
C	-2.556	-7.467	2.961
H	-3.826	-2.508	3.670
H	-3.185	-0.279	4.574
H	-0.868	0.623	4.114
H	0.709	-0.702	2.716
H	1.095	-0.832	0.504
H	3.378	-0.497	-0.365
H	5.033	-2.366	-0.327
H	4.366	-4.581	0.615
H	2.093	-4.905	1.550
H	-4.091	-3.199	0.517
H	-6.398	-2.290	0.471
H	-8.115	-3.142	2.074
H	-7.500	-4.942	3.691
H	-5.211	-5.872	3.710
H	-2.970	-5.711	1.144
H	-2.789	-4.533	4.692
H	-2.644	-7.887	1.957
H	-2.290	-8.143	3.777
H	-0.418	-5.147	0.853

Figure S1

Int0′

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C	-7.020	-0.247	2.076
C	-6.057	-0.526	1.101
C	-6.401	-1.044	-0.146
C	-7.749	-1.290	-0.418
C	-8.745	-1.019	0.533
C	-8.358	-0.500	1.783
S	-4.336	-0.158	1.464
O	-3.475	-0.782	0.409
C	-10.198	-1.256	0.223
N	-4.375	1.608	1.334
C	-3.234	2.265	1.905
C	-3.130	2.481	3.199
C	-4.785	2.083	0.031
C	-4.011	1.865	-1.116
C	-4.454	2.345	-2.350
C	-5.663	3.044	-2.439
C	-6.433	3.259	-1.290
C	-5.997	2.778	-0.053
C	-2.990	2.683	4.480
O	-4.026	-0.445	2.892
C	-0.619	-1.448	1.286
N	-0.182	-0.167	1.398

C	-0.068	0.472	2.624
C	-0.434	-0.221	3.773
C	-0.864	-1.544	3.677
C	-0.941	-2.163	2.424
C	0.103	0.764	0.333
C	0.345	1.992	0.885
C	0.300	1.859	2.339
C	0.519	2.904	3.203
C	0.711	2.930	4.639
C	1.383	1.906	5.344
C	1.555	1.994	6.724
C	1.057	3.099	7.427
C	0.416	4.136	6.738
C	0.265	4.065	5.355
C	0.120	0.336	-1.070
C	0.809	-0.820	-1.484
C	0.849	-1.175	-2.834
C	0.207	-0.384	-3.792
C	-0.468	0.774	-3.393
C	-0.512	1.130	-2.045
Ag	0.826	3.703	-0.169
H	-3.324	3.611	4.956
H	-0.391	0.276	4.739
H	-1.155	-2.086	4.576
H	-1.288	-3.190	2.319
H	-0.727	-1.843	0.280
H	1.347	-1.429	-0.755
H	1.395	-2.070	-3.139
H	0.237	-0.666	-4.846
H	-0.970	1.399	-4.135
H	-1.047	2.030	-1.737
H	-0.223	4.878	4.814
H	0.045	5.008	7.280
H	1.188	3.162	8.509
H	2.090	1.204	7.254
H	1.810	1.064	4.798
H	0.551	3.886	2.716
H	-2.436	2.576	1.219
H	-2.537	1.927	5.128
H	-3.087	1.292	-1.040
H	-3.856	2.168	-3.247
H	-6.009	3.416	-3.405
H	-7.379	3.800	-1.357
H	-6.586	2.928	0.852
H	-5.630	-1.250	-0.888
H	-8.030	-1.699	-1.391
H	-9.118	-0.291	2.539
H	-6.727	0.157	3.046
H	-10.713	-0.300	0.035
H	-10.323	-1.885	-0.667
H	-10.712	-1.738	1.068

TS₁′

73

C	-1.204	1.074	1.835
C	-0.719	1.152	0.517
C	0.248	2.132	0.215
C	0.766	2.959	1.214
C	0.298	2.848	2.527
C	-0.698	1.912	2.829
C	-1.162	0.291	-0.603
C	-0.957	-1.105	-0.726
C	-0.677	-2.114	0.262
N	-0.401	-3.300	-0.436
C	-0.492	-3.062	-1.834
C	-0.863	-1.747	-2.018
C	-0.185	-4.488	0.206
C	-0.153	-4.528	1.581
C	-0.341	-3.342	2.319
C	-0.609	-2.150	1.662
C	-0.174	-4.102	-2.823
C	1.008	-4.863	-2.737
C	1.323	-5.801	-3.722
C	0.468	-5.995	-4.813
C	-0.706	-5.240	-4.913
C	-1.026	-4.306	-3.927
Ag	-1.136	-0.863	-3.864
C	-3.301	0.750	-0.721
C	-3.539	1.979	-0.302
C	-3.842	-0.320	-1.378
N	-3.954	-1.609	-0.947
C	-4.464	-2.608	-1.848
C	-3.871	-3.876	-1.874
C	-4.379	-4.854	-2.730
C	-5.466	-4.568	-3.563
C	-6.057	-3.300	-3.530
C	-5.568	-2.321	-2.665
S	-4.348	-1.970	0.815
O	-3.859	-0.803	1.585
C	-6.134	-1.989	0.776
C	-6.818	-0.772	0.866
C	-8.207	-0.786	0.765
C	-8.913	-1.987	0.567
C	-8.188	-3.189	0.486
C	-6.798	-3.204	0.579
C	-10.409	-1.983	0.422
O	-3.823	-3.335	1.051
H	-4.565	2.345	-0.195
H	-0.787	-1.239	2.224
H	-0.295	-3.362	3.408
H	0.023	-5.482	2.077
H	-0.044	-5.362	-0.424
H	1.705	-4.698	-1.912
H	2.248	-6.375	-3.644
H	0.716	-6.729	-5.582
H	-1.382	-5.388	-5.757
H	-1.956	-3.739	-3.992
H	-2.025	0.395	2.062
H	-1.093	1.842	3.844
H	0.693	3.500	3.308
H	1.529	3.698	0.963
H	0.609	2.230	-0.810
H	-1.043	0.787	-1.573
H	-3.982	-0.221	-2.461
H	-2.737	2.655	0.000
H	-3.023	-4.088	-1.225
H	-3.913	-5.840	-2.755
H	-5.857	-5.335	-4.233
H	-6.915	-3.076	-4.166
H	-6.052	-1.344	-2.606
H	-6.240	-4.138	0.512
H	-8.721	-4.132	0.344
H	-8.756	0.154	0.847
H	-6.278	0.162	1.027
H	-10.688	-1.918	-0.641
H	-10.853	-2.906	0.820
H	-10.861	-1.122	0.933

Int1′

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C	-0.440	-6.908	0.977
C	-1.650	-6.658	0.305
C	-1.865	-7.266	-0.938
C	-0.901	-8.117	-1.492
C	0.289	-8.372	-0.808
C	0.519	-7.761	0.429
C	-2.652	-5.709	0.933
C	-3.832	-5.251	0.103
C	-4.918	-6.070	-0.311
N	-5.814	-5.243	-1.018
C	-5.299	-3.932	-1.056
C	-4.082	-3.931	-0.376

C	-7.004	-5.735	-1.498
C	-7.308	-7.065	-1.348
C	-6.409	-7.935	-0.684
C	-5.228	-7.436	-0.167
C	-6.010	-2.824	-1.705
C	-6.530	-2.932	-3.011
C	-7.171	-1.848	-3.615
C	-7.299	-0.633	-2.933
C	-6.778	-0.508	-1.641
C	-6.145	-1.593	-1.031
Ag	-2.858	-2.292	-0.120
C	-3.306	-6.177	2.239
C	-3.063	-7.306	2.928
C	-4.251	-5.124	2.587
N	-5.418	-5.123	3.209
C	-6.054	-3.853	3.472
C	-5.971	-3.313	4.758
C	-6.594	-2.091	5.018
C	-7.294	-1.429	4.004
C	-7.364	-1.980	2.719
C	-6.744	-3.200	2.444
S	-6.680	-6.562	3.215
O	-5.913	-7.821	3.321
C	-7.543	-6.198	4.730
C	-8.719	-5.444	4.670
C	-9.361	-5.131	5.864
C	-8.842	-5.550	7.103
C	-7.656	-6.308	7.119
C	-6.995	-6.640	5.939
C	-9.556	-5.216	8.382
O	-7.529	-6.249	2.045
H	-3.611	-7.561	3.832
H	-4.526	-8.079	0.362
H	-6.654	-8.992	-0.572
H	-8.255	-7.433	-1.743
H	-7.663	-5.019	-1.984
H	-6.404	-3.861	-3.572
H	-7.560	-1.950	-4.630
H	-7.799	0.212	-3.409
H	-6.874	0.434	-1.100
H	-5.759	-1.500	-0.014
H	-2.785	-7.066	-1.488
H	-1.085	-8.577	-2.465
H	1.039	-9.038	-1.240
H	1.453	-7.942	0.965
H	-0.245	-6.421	1.936
H	-2.096	-4.782	1.184
H	-3.891	-4.109	2.377
H	-2.280	-7.989	2.596
H	-5.428	-3.847	5.539
H	-6.532	-1.656	6.017
H	-7.783	-0.476	4.213
H	-7.903	-1.460	1.926
H	-6.792	-3.649	1.452
H	-9.117	-5.108	3.712
H	-10.279	-4.541	5.835
H	-7.243	-6.644	8.072
H	-6.076	-7.227	5.960
H	-8.864	-5.184	9.234
H	-10.077	-4.252	8.310
H	-10.315	-5.984	8.602

TS$_2$′

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C	-7.113	-0.718	1.074
C	-6.345	-1.320	2.087
C	-6.909	-1.455	3.361
C	-8.217	-1.022	3.613
C	-8.976	-0.440	2.596
C	-8.416	-0.284	1.322
C	-4.916	-1.756	1.763
C	-4.037	-2.090	2.939
C	-4.140	-3.222	3.773
N	-3.115	-3.118	4.749
C	-2.399	-1.934	4.538
C	-2.961	-1.300	3.418
C	-2.909	-4.133	5.663
C	-3.752	-5.212	5.696
C	-4.840	-5.308	4.785
C	-5.017	-4.328	3.833
C	-1.299	-1.496	5.401
C	-1.364	-1.590	6.809
C	-0.316	-1.128	7.608
C	0.818	-0.550	7.027
C	0.891	-0.434	5.634
C	-0.149	-0.907	4.833
Ag	-2.354	0.504	2.631
C	-4.847	-2.859	0.700
C	-5.881	-3.628	0.333
C	-3.527	-2.893	-0.016
O	-3.742	-2.977	-1.531
N	-2.534	-4.046	-0.061
C	-1.164	-3.699	0.275
C	-0.216	-3.725	-0.753
C	1.115	-3.422	-0.465
C	1.492	-3.113	0.845
C	0.537	-3.097	1.867
C	-0.800	-3.385	1.589
S	-2.990	-5.749	0.593
O	-4.239	-6.093	-0.129
C	-1.628	-6.694	-0.069
C	-0.515	-6.953	0.737
C	0.516	-7.724	0.209
C	0.449	-8.235	-1.100
C	-0.683	-7.945	-1.881
C	-1.730	-7.176	-1.378
C	1.549	-9.105	-1.640
O	-2.915	-5.696	2.069
H	-5.802	-4.377	-0.450
H	-5.820	-4.394	3.101
H	-5.514	-6.164	4.829
H	-3.569	-5.993	6.433
H	-2.057	-4.018	6.328
H	-2.257	-1.994	7.287
H	-0.393	-1.207	8.694
H	1.635	-0.189	7.654
H	1.770	0.015	5.167
H	-0.076	-0.830	3.746
H	-6.320	-1.894	4.167
H	-8.639	-1.139	4.614
H	-9.996	-0.103	2.794
H	-8.995	0.181	0.522
H	-6.684	-0.594	0.076
H	-4.438	-0.869	1.300
H	-2.936	-1.996	0.204
H	-6.853	-3.505	0.813
H	-0.520	-3.995	-1.766
H	1.857	-3.437	-1.264
H	2.536	-2.886	1.072
H	0.835	-2.864	2.890
H	-1.551	-3.372	2.379
H	-0.462	-6.564	1.754
H	1.391	-7.935	0.826
H	-0.752	-8.335	-2.899
H	-2.612	-6.968	-1.984
H	1.555	-9.113	-2.737
H	2.534	-8.777	-1.279
H	1.408	-10.144	-1.301
H	-2.911	-3.803	-1.392
H	-3.449	-2.160	-1.992

NHTsPh

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C	0.041	-0.204	-0.165
C	-0.429	-0.451	1.133
C	0.474	-0.523	2.194
C	1.848	-0.379	1.967
C	2.316	-0.148	0.669
C	1.417	-0.048	-0.394
H	-1.498	-0.585	1.299
H	0.103	-0.713	3.203
H	2.552	-0.450	2.799
H	3.386	-0.036	0.483
H	1.777	0.151	-1.406
N	-0.885	-0.182	-1.256
S	-1.881	1.247	-1.411
H	-0.409	-0.294	-2.158
C	-3.095	0.658	-2.602
C	-4.084	-0.230	-2.172
C	-5.023	-0.682	-3.098
C	-4.988	-0.258	-4.438
C	-3.980	0.637	-4.833
C	-3.029	1.103	-3.924
H	-4.120	-0.563	-1.134
H	-5.798	-1.380	-2.774
C	-6.022	-0.732	-5.423
H	-3.935	0.977	-5.870
H	-2.251	1.801	-4.233
H	-5.588	-0.875	-6.422
H	-6.482	-1.676	-5.100
H	-6.828	0.012	-5.522
O	-2.524	1.452	-0.083
O	-1.117	2.377	-2.025

Int2′

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C	-3.199	-4.622	-6.816
C	-4.104	-3.577	-6.597
C	-4.504	-2.715	-7.622
C	-3.992	-2.927	-8.902
C	-3.085	-3.969	-9.164
C	-2.700	-4.807	-8.103
S	-4.644	-3.269	-4.920
O	-4.582	-4.518	-4.125
C	-2.559	-4.202	-10.553
N	-3.551	-2.146	-4.200
C	-2.157	-2.477	-4.214
C	-1.689	-3.549	-3.444
C	-0.326	-3.849	-3.443
C	0.570	-3.075	-4.186
C	0.097	-2.003	-4.949
C	-1.266	-1.708	-4.975
O	-5.940	-2.485	-4.979
C	-0.650	-0.527	-1.564
C	-1.148	-1.370	-0.552
C	-0.225	-2.018	0.294
C	1.147	-1.833	0.123
C	1.627	-0.994	-0.888
C	0.721	-0.339	-1.728
C	-2.595	-1.505	-0.367
N	-3.221	-2.741	-0.128
C	-4.603	-2.529	0.073
C	-4.828	-1.127	-0.056
C	-3.580	-0.514	-0.341
C	-2.681	-4.005	-0.127
C	-3.477	-5.093	0.130
C	-4.858	-4.917	0.394
C	-5.408	-3.649	0.371
C	-6.136	-0.392	0.102
C	-7.168	-1.164	-0.707
C	-8.364	-1.629	-0.269
Ag	-3.241	1.507	-0.566
C	-6.570	-0.069	1.522
C	-7.395	1.044	1.746
C	-7.842	1.356	3.032
C	-7.466	0.555	4.117
C	-6.640	-0.551	3.906
C	-6.195	-0.862	2.616
C	-6.676	-1.461	-2.020
O	-7.236	-2.354	-2.768
H	-9.001	-2.241	-0.910
H	-6.468	-3.497	0.570
H	-5.486	-5.781	0.611
H	-3.026	-6.085	0.128
H	-1.618	-4.075	-0.340
H	-0.581	-2.641	1.116
H	1.846	-2.337	0.794
H	2.702	-0.853	-1.021
H	1.085	0.305	-2.530
H	-1.352	-0.046	-2.247
H	-7.687	1.675	0.901
H	-8.480	2.228	3.189
H	-7.812	0.799	5.124
H	-6.335	-1.176	4.747
H	-5.543	-1.723	2.463
H	-5.989	0.576	-0.412
H	-5.821	-0.905	-2.425
H	-8.719	-1.392	0.733
H	-2.394	-4.135	-2.856
H	0.039	-4.682	-2.839
H	1.637	-3.303	-4.165
H	0.790	-1.394	-5.531
H	-1.643	-0.882	-5.583
H	-2.900	-5.281	-6.000
H	-1.994	-5.620	-8.286
H	-4.304	-2.266	-9.714
H	-5.207	-1.904	-7.429
H	-2.624	-3.294	-11.166
H	-1.514	-4.542	-10.532
H	-3.147	-4.986	-11.057
H	-6.765	-2.415	-3.686
H	-3.741	-1.229	-4.619

TS$_3$′

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C	-4.318	-7.180	-1.592
C	-3.200	-6.990	-0.760
C	-2.226	-7.995	-0.705
C	-2.352	-9.154	-1.480
C	-3.455	-9.324	-2.320
C	-4.442	-8.332	-2.370
C	-3.126	-5.750	0.117
C	-3.283	-4.415	-0.610
C	-3.178	-4.213	-1.949
C	-1.917	-5.582	1.004
C	-0.583	-5.401	0.616
N	0.131	-4.957	1.763
C	-0.743	-4.813	2.828
C	-2.039	-5.161	2.368
C	0.113	-5.524	-0.608
C	1.456	-5.229	-0.671
C	2.140	-4.788	0.498
C	1.479	-4.654	1.687
C	-0.333	-4.399	4.173
C	-1.110	-3.450	4.869
C	-0.783	-3.086	6.176
C	0.325	-3.657	6.810
C	1.103	-4.599	6.129
C	0.777	-4.971	4.823
C	-3.498	-3.223	0.181
O	-3.461	-3.132	1.446
Ag	-3.493	-5.850	3.718
H	-3.254	-3.209	-2.373
H	-0.433	-5.860	-1.489

H	1.998	-5.325	-1.612
H	3.201	-4.540	0.460
H	1.947	-4.294	2.600
H	1.368	-5.740	4.321
H	1.962	-5.059	6.621
H	0.581	-3.370	7.832
H	-1.392	-2.345	6.698
H	-1.966	-2.989	4.372
H	-1.368	-7.882	-0.042
H	-1.583	-9.927	-1.421
H	-3.551	-10.227	-2.926
H	-5.316	-8.461	-3.011
H	-5.105	-6.422	-1.627
H	-3.988	-5.815	0.810
H	-3.738	-2.290	-0.350
H	-3.005	-5.039	-2.639
H	-2.942	-4.049	2.002

Figure S2

2a

35

C	-0.441	0.388	-0.201
C	-0.183	-0.762	0.383
N	0.511	1.217	-0.854
H	-1.441	0.826	-0.148
C	1.853	0.736	-1.061
C	2.097	-0.480	-1.713
C	3.413	-0.905	-1.906
C	4.479	-0.120	-1.452
C	4.229	1.093	-0.802
C	2.915	1.524	-0.603
H	1.262	-1.083	-2.070
H	3.607	-1.849	-2.417
H	5.507	-0.454	-1.605
H	5.059	1.707	-0.446
H	2.699	2.468	-0.102
C	0.035	-1.881	1.026
S	-0.127	2.196	-2.172
O	-1.467	2.652	-1.707
O	0.946	3.175	-2.486
C	-0.330	1.080	-3.566
C	0.696	0.970	-4.507
C	0.564	0.036	-5.535
C	-0.564	-0.793	-5.626
C	-1.578	-0.656	-4.660
C	-1.471	0.271	-3.626
H	1.577	1.609	-4.440
H	1.357	-0.049	-6.281
C	-0.693	-1.811	-6.726
H	-2.469	-1.285	-4.718
H	-2.268	0.377	-2.889
H	-0.680	-2.833	-6.315
H	-1.646	-1.694	-7.264
H	0.125	-1.726	-7.452
H	-0.093	-2.855	0.542
H	0.366	-1.891	2.070

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C	-1.653	-0.160	-3.745
C	-0.646	0.757	-3.424
C	0.476	0.948	-4.236
C	0.579	0.198	-5.405
C	-0.412	-0.729	-5.769
C	-1.524	-0.894	-4.921
S	-0.783	1.695	-1.915
O	0.053	2.908	-1.976
C	-0.311	-1.498	-7.055
N	0.158	0.582	-0.695
C	1.508	0.249	-1.045
C	1.770	-0.998	-1.623
C	3.076	-1.308	-2.000
C	4.100	-0.374	-1.815
C	3.823	0.872	-1.245
C	2.521	1.194	-0.856
C	-0.491	0.150	0.364
C	0.009	-0.774	1.322
C	0.994	-0.600	2.214
O	-2.168	1.666	-1.392
H	-1.531	0.496	0.429
H	0.955	-1.709	-1.768
H	3.294	-2.280	-2.445
H	5.120	-0.619	-2.115
H	4.623	1.600	-1.101
H	2.283	2.166	-0.422
H	1.240	1.676	-3.962
H	1.447	0.339	-6.052
H	-2.308	-1.602	-5.196
H	-2.524	-0.273	-3.098
H	-0.762	-2.496	-6.968
H	-0.849	-0.968	-7.858
H	0.731	-1.611	-7.380
H	1.315	-1.403	2.879
H	1.489	0.366	2.341
Au	-1.166	-2.511	1.187
P	-2.451	-4.473	1.203
C	-2.905	-5.113	-0.463
C	-1.612	-5.883	2.038
C	-4.052	-4.279	2.088
H	-4.612	-5.224	2.082
H	-3.862	-3.972	3.124
H	-4.648	-3.498	1.599
H	-2.255	-6.774	2.028
H	-0.669	-6.108	1.524
H	-1.386	-5.608	3.077
H	-3.507	-6.028	-0.371
H	-3.482	-4.350	-1.002
H	-1.993	-5.332	-1.032

Int0′

87

C	-6.877	-0.736	2.282
C	-6.058	-0.473	1.160
C	-6.627	-0.581	-0.131
C	-7.939	-1.021	-0.296
C	-8.725	-1.312	0.824
C	-8.196	-1.148	2.112
C	-4.682	-0.034	1.261
C	-3.704	-0.296	2.190
C	-3.660	-1.296	3.258
N	-2.444	-1.129	3.908
C	-1.703	-0.056	3.288
C	-2.429	0.416	2.227
C	-4.463	-2.372	3.621
C	-4.063	-3.222	4.652
C	-2.845	-3.003	5.303
C	-2.030	-1.962	4.897
C	-0.404	0.381	3.814
C	-0.195	0.602	5.190
C	1.037	1.066	5.654
C	2.079	1.322	4.756
C	1.878	1.122	3.386
C	0.649	0.655	2.920
Ag	-1.870	1.988	1.005
C	2.382	-1.845	0.221
C	1.113	-2.218	0.668
C	0.432	-3.259	0.024
C	1.012	-3.923	-1.062
C	2.281	-3.544	-1.507
C	2.967	-2.507	-0.864

N	-0.877	-3.700	0.450
C	-1.929	-2.751	0.305
C	-3.126	-3.114	-0.113
C	-4.422	-3.243	-0.448
S	-0.902	-4.479	2.070
O	-2.327	-4.857	2.286
C	0.082	-5.949	1.783
C	1.478	-5.862	1.781
C	2.215	-7.021	1.545
C	1.582	-8.260	1.328
C	0.178	-8.311	1.365
C	-0.580	-7.161	1.586
C	2.395	-9.495	1.060
O	-0.209	-3.610	3.068
Au	-3.408	-5.259	-0.883
P	-2.948	-7.369	-1.757
C	-1.164	-7.561	-2.136
C	-3.412	-8.763	-0.663
C	-3.833	-7.652	-3.336
H	-4.779	-2.975	-1.448
H	-5.398	-2.549	3.094
H	-4.695	-4.064	4.935
H	-2.502	-3.658	6.101
H	-1.041	-1.781	5.308
H	-1.008	0.448	5.901
H	1.179	1.239	6.722
H	3.042	1.683	5.123
H	2.683	1.325	2.678
H	0.499	0.497	1.850
H	-6.020	-0.331	-1.004
H	-8.356	-1.121	-1.299
H	-9.757	-1.642	0.697
H	-8.822	-1.332	2.987
H	-6.490	-0.564	3.287
H	-4.354	0.625	0.449
H	-1.750	-1.697	0.559
H	-5.179	-3.430	0.321
H	0.664	-1.732	1.534
H	2.921	-1.042	0.728
H	3.960	-2.215	-1.209
H	2.736	-4.062	-2.353
H	0.463	-4.733	-1.544
H	1.980	-4.912	1.964
H	3.305	-6.964	1.538
H	-0.328	-9.269	1.226
H	-1.669	-7.200	1.632
H	2.847	-9.448	0.057
H	3.220	-9.591	1.780
H	1.779	-10.403	1.111
H	-0.987	-8.562	-2.553
H	-0.869	-6.801	-2.871
H	-0.574	-7.433	-1.221
H	-3.562	-8.641	-3.730
H	-4.915	-7.606	-3.161
H	-3.549	-6.875	-4.057
H	-3.141	-9.711	-1.147
H	-2.891	-8.678	0.297
H	-4.494	-8.734	-0.483

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C	-6.970	-0.675	0.696
C	-6.221	-1.865	0.809
C	-6.899	-3.095	0.716
C	-8.286	-3.130	0.567
C	-9.023	-1.941	0.505
C	-8.359	-0.711	0.564
C	-4.761	-1.707	0.992
C	-3.961	-2.154	2.079
C	-4.186	-3.136	3.105
N	-3.112	-3.032	4.003
C	-2.219	-2.014	3.566
C	-2.716	-1.498	2.388
C	-2.966	-3.889	5.060
C	-3.934	-4.834	5.316
C	-5.074	-4.908	4.490
C	-5.192	-4.070	3.391
C	-1.031	-1.635	4.340
C	-1.113	-1.363	5.721
C	0.015	-0.944	6.428
C	1.240	-0.785	5.771
C	1.330	-1.047	4.399
C	0.206	-1.471	3.690
Ag	-1.837	0.026	1.294
C	-3.896	-2.452	-0.771
Au	-3.660	-0.423	-1.984
P	-2.933	1.665	-2.689
C	-3.640	3.030	-1.694
C	-2.602	-2.920	-0.530
N	-2.238	-3.938	0.267
C	-0.849	-4.142	0.575
C	-0.486	-4.475	1.885
C	0.861	-4.675	2.188
C	1.836	-4.541	1.194
C	1.463	-4.217	-0.114
C	0.118	-4.028	-0.433
S	-3.254	-5.515	0.317
O	-4.586	-5.094	-0.174
C	-2.398	-6.490	-0.899
C	-1.361	-7.333	-0.485
C	-0.662	-8.043	-1.459
C	-0.973	-7.910	-2.824
C	-2.025	-7.052	-3.198
C	-2.740	-6.330	-2.247
C	-0.183	-8.651	-3.864
O	-3.046	-6.059	1.674
C	-4.773	-2.430	-1.816
C	-1.110	1.832	-2.595
C	-3.398	1.980	-4.430
H	-4.582	-3.009	-2.725
H	-6.053	-4.143	2.734
H	-5.856	-5.636	4.704
H	-3.804	-5.505	6.163
H	-2.067	-3.769	5.661
H	-2.071	-1.446	6.239
H	-0.066	-0.729	7.495
H	2.120	-0.457	6.326
H	2.284	-0.931	3.881
H	0.285	-1.703	2.626
H	-6.332	-4.024	0.701
H	-8.794	-4.093	0.491
H	-10.108	-1.974	0.393
H	-8.922	0.220	0.500
H	-6.456	0.288	0.737
H	-4.443	-0.697	0.707
H	-1.772	-2.251	-0.781
H	-5.788	-2.046	-1.678
H	-1.252	-4.576	2.652
H	1.149	-4.925	3.210
H	2.888	-4.696	1.438
H	2.218	-4.130	-0.896
H	-0.182	-3.817	-1.461
H	-1.115	-7.440	0.570
H	0.141	-8.714	-1.151
H	-2.291	-6.951	-4.252
H	-3.560	-5.675	-2.544
H	0.701	-8.063	-4.158
H	0.177	-9.615	-3.482
H	-0.777	-8.826	-4.772
H	-0.817	2.821	-2.973
H	-0.778	1.728	-1.554
H	-0.640	1.049	-3.202
H	-3.271	3.990	-2.080

H	-4.735	3.001	-1.763
H	-3.342	2.918	-0.644
H	-3.032	2.973	-4.726
H	-2.948	1.211	-5.071
H	-4.490	1.942	-4.529

Int1′

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C	-6.945	-1.297	1.419
C	-6.321	-2.219	0.561
C	-7.101	-3.180	-0.093
C	-8.485	-3.222	0.109
C	-9.099	-2.308	0.969
C	-8.324	-1.344	1.626
C	-4.819	-2.138	0.426
C	-3.915	-2.774	1.567
C	-4.541	-3.575	2.654
N	-3.952	-3.203	3.845
C	-2.994	-2.132	3.616
C	-2.991	-1.840	2.296
C	-4.244	-3.805	5.023
C	-5.206	-4.803	5.053
C	-5.859	-5.170	3.874
C	-5.517	-4.556	2.663
C	-2.190	-1.592	4.722
C	-2.791	-0.990	5.844
C	-1.996	-0.450	6.857
C	-0.601	-0.504	6.762
C	0.001	-1.100	5.649
C	-0.787	-1.644	4.634
Ag	-1.838	-0.392	1.366
C	-4.089	-2.963	-0.626
C	-4.284	-3.171	-1.964
Au	-2.770	-1.436	-1.972
P	-1.281	0.226	-2.606
C	0.395	-0.052	-1.921
C	-3.103	-3.548	0.376
N	-2.663	-4.905	0.392
C	-1.376	-5.150	1.002
C	-1.259	-5.351	2.383
C	0.008	-5.511	2.947
C	1.148	-5.470	2.137
C	1.024	-5.278	0.756
C	-0.240	-5.120	0.184
S	-3.733	-6.269	0.234
O	-4.996	-5.698	-0.316
C	-2.897	-7.251	-1.010
C	-3.213	-7.054	-2.356
C	-2.533	-7.803	-3.317
C	-1.545	-8.734	-2.950
C	-1.262	-8.911	-1.584
C	-1.932	-8.178	-0.605
C	-0.801	-9.523	-3.992
O	-3.747	-7.035	1.509
C	-1.096	0.318	-4.423
C	-1.808	1.887	-2.042
H	-3.742	-3.966	-2.482
H	-5.997	-4.848	1.732
H	-6.627	-5.944	3.890
H	-5.440	-5.280	6.003
H	-3.697	-3.461	5.899
H	-3.879	-0.920	5.912
H	-2.469	0.022	7.720
H	0.016	-0.081	7.556
H	1.089	-1.147	5.574
H	-0.324	-2.128	3.771
H	-6.345	-0.537	1.927
H	-8.797	-0.621	2.294
H	-10.179	-2.342	1.126
H	-9.082	-3.976	-0.406
H	-6.632	-3.914	-0.749
H	-4.543	-1.073	0.353
H	-2.167	-2.968	0.313
H	-5.151	-2.742	-2.471
H	-2.155	-5.401	3.002
H	0.105	-5.668	4.023
H	2.137	-5.594	2.582
H	1.912	-5.255	0.123
H	-0.359	-4.976	-0.890
H	-1.715	-8.331	0.451
H	-0.508	-9.639	-1.278
H	-2.781	-7.667	-4.371
H	-3.992	-6.350	-2.649
H	0.242	-9.179	-4.064
H	-0.769	-10.591	-3.730
H	-1.262	-9.419	-4.982
H	1.070	0.739	-2.274
H	0.364	-0.033	-0.822
H	0.768	-1.030	-2.250
H	-1.085	2.636	-2.393
H	-2.804	2.110	-2.444
H	-1.854	1.914	-0.944
H	-0.378	1.113	-4.669
H	-0.730	-0.643	-4.801
H	-2.069	0.541	-4.877

Int2′

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C	-0.440	-6.908	0.977
C	-1.650	-6.658	0.305
C	-1.865	-7.266	-0.938
C	-0.901	-8.117	-1.492
C	0.289	-8.372	-0.808
C	0.519	-7.761	0.429
C	-2.652	-5.709	0.933
C	-3.832	-5.251	0.103
C	-4.918	-6.070	-0.311
N	-5.814	-5.243	-1.018
C	-5.299	-3.932	-1.056
C	-4.082	-3.931	-0.376
C	-7.004	-5.735	-1.498
C	-7.308	-7.065	-1.348
C	-6.409	-7.935	-0.684
C	-5.228	-7.436	-0.167
C	-6.010	-2.824	-1.705
C	-6.530	-2.932	-3.011
C	-7.171	-1.848	-3.615
C	-7.299	-0.633	-2.933
C	-6.778	-0.508	-1.641
C	-6.145	-1.593	-1.031
Ag	-2.858	-2.292	-0.120
C	-3.306	-6.177	2.239
C	-3.063	-7.306	2.928
C	-4.251	-5.124	2.587
N	-5.418	-5.123	3.209
C	-6.054	-3.853	3.472
C	-5.971	-3.313	4.758
C	-6.594	-2.091	5.018
C	-7.294	-1.429	4.004
C	-7.364	-1.980	2.719
C	-6.744	-3.200	2.444
S	-6.680	-6.562	3.215
O	-5.913	-7.821	3.321
C	-7.543	-6.198	4.730
C	-8.719	-5.444	4.670
C	-9.361	-5.131	5.864
C	-8.842	-5.550	7.103
C	-7.656	-6.308	7.119
C	-6.995	-6.640	5.939
C	-9.556	-5.216	8.382
O	-7.529	-6.249	2.045
H	-3.611	-7.561	3.832

H	-4.526	-8.079	0.362
H	-6.654	-8.992	-0.572
H	-8.255	-7.433	-1.743
H	-7.663	-5.019	-1.984
H	-6.404	-3.861	-3.572
H	-7.560	-1.950	-4.630
H	-7.799	0.212	-3.409
H	-6.874	0.434	-1.100
H	-5.759	-1.500	-0.014
H	-2.785	-7.066	-1.488
H	-1.085	-8.577	-2.465
H	1.039	-9.038	-1.240
H	1.453	-7.942	0.965
H	-0.245	-6.421	1.936
H	-2.096	-4.782	1.184
H	-3.891	-4.109	2.377
H	-2.280	-7.989	2.596
H	-5.428	-3.847	5.539
H	-6.532	-1.656	6.017
H	-7.783	-0.476	4.213
H	-7.903	-1.460	1.926
H	-6.792	-3.649	1.452
H	-9.117	-5.108	3.712
H	-10.279	-4.541	5.835
H	-7.243	-6.644	8.072
H	-6.076	-7.227	5.960
H	-8.864	-5.184	9.234
H	-10.077	-4.252	8.310
H	-10.315	-5.984	8.602

TS$_2$′

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C	-7.113	-0.718	1.074
C	-6.345	-1.320	2.087
C	-6.909	-1.455	3.361
C	-8.217	-1.022	3.613
C	-8.976	-0.440	2.596
C	-8.416	-0.284	1.322
C	-4.916	-1.756	1.763
C	-4.037	-2.090	2.939
C	-4.140	-3.222	3.773
N	-3.115	-3.118	4.749
C	-2.399	-1.934	4.538
C	-2.961	-1.300	3.418
C	-2.909	-4.133	5.663
C	-3.752	-5.212	5.696
C	-4.840	-5.308	4.785
C	-5.017	-4.328	3.833
C	-1.299	-1.496	5.401
C	-1.364	-1.590	6.809
C	-0.316	-1.128	7.608
C	0.818	-0.550	7.027
C	0.891	-0.434	5.634
C	-0.149	-0.907	4.833
Ag	-2.354	0.504	2.631
C	-4.847	-2.859	0.700
C	-5.881	-3.628	0.333
C	-3.527	-2.893	-0.016
O	-3.742	-2.977	-1.531
N	-2.534	-4.046	-0.061
C	-1.164	-3.699	0.275
C	-0.216	-3.725	-0.753
C	1.115	-3.422	-0.465
C	1.492	-3.113	0.845
C	0.537	-3.097	1.867
C	-0.800	-3.385	1.589
S	-2.990	-5.749	0.593
O	-4.239	-6.093	-0.129
C	-1.628	-6.694	-0.069
C	-0.515	-6.953	0.737
C	0.516	-7.724	0.209
C	0.449	-8.235	-1.100
C	-0.683	-7.945	-1.881
C	-1.730	-7.176	-1.378
C	1.549	-9.105	-1.640
O	-2.915	-5.696	2.069
H	-5.802	-4.377	-0.450
H	-5.820	-4.394	3.101
H	-5.514	-6.164	4.829
H	-3.569	-5.993	6.433
H	-2.057	-4.018	6.328
H	-2.257	-1.994	7.287
H	-0.393	-1.207	8.694
H	1.635	-0.189	7.654
H	1.770	0.015	5.167
H	-0.076	-0.830	3.746
H	-6.320	-1.894	4.167
H	-8.639	-1.139	4.614
H	-9.996	-0.103	2.794
H	-8.995	0.181	0.522
H	-6.684	-0.594	0.076
H	-4.438	-0.869	1.300
H	-2.936	-1.996	0.204
H	-6.853	-3.505	0.813
H	-0.520	-3.995	-1.766
H	1.857	-3.437	-1.264
H	2.536	-2.886	1.072
H	0.835	-2.864	2.890
H	-1.551	-3.372	2.379
H	-0.462	-6.564	1.754
H	1.391	-7.935	0.826
H	-0.752	-8.335	-2.899
H	-2.612	-6.968	-1.984
H	1.555	-9.113	-2.737
H	2.534	-8.777	-1.279
H	1.408	-10.144	-1.301
H	-2.911	-3.803	-1.392
H	-3.449	-2.160	-1.992

NHTsPh

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C	0.041	-0.204	-0.165
C	-0.429	-0.451	1.133
C	0.474	-0.523	2.194
C	1.848	-0.379	1.967
C	2.316	-0.148	0.669
C	1.417	-0.048	-0.394
H	-1.498	-0.585	1.299
H	0.103	-0.713	3.203
H	2.552	-0.450	2.799
H	3.386	-0.036	0.483
H	1.777	0.151	-1.406
N	-0.885	-0.182	-1.256
S	-1.881	1.247	-1.411
H	-0.409	-0.294	-2.158
C	-3.095	0.658	-2.602
C	-4.084	-0.230	-2.172
C	-5.023	-0.682	-3.098
C	-4.988	-0.258	-4.438
C	-3.980	0.637	-4.833
C	-3.029	1.103	-3.924
H	-4.120	-0.563	-1.134
H	-5.798	-1.380	-2.774
C	-6.022	-0.732	-5.423
H	-3.935	0.977	-5.870
H	-2.251	1.801	-4.233
H	-5.588	-0.875	-6.422
H	-6.482	-1.676	-5.100
H	-6.828	0.012	-5.522
O	-2.524	1.452	-0.083
O	-1.117	2.377	-2.025

Int3′

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C	-3.199	-4.622	-6.816
C	-4.104	-3.577	-6.597
C	-4.504	-2.715	-7.622
C	-3.992	-2.927	-8.902
C	-3.085	-3.969	-9.164
C	-2.700	-4.807	-8.103
S	-4.644	-3.269	-4.920
O	-4.582	-4.518	-4.125
C	-2.559	-4.202	-10.553
N	-3.551	-2.146	-4.200
C	-2.157	-2.477	-4.214
C	-1.689	-3.549	-3.444
C	-0.326	-3.849	-3.443
C	0.570	-3.075	-4.186
C	0.097	-2.003	-4.949
C	-1.266	-1.708	-4.975
O	-5.940	-2.485	-4.979
C	-0.650	-0.527	-1.564
C	-1.148	-1.370	-0.552
C	-0.225	-2.018	0.294
C	1.147	-1.833	0.123
C	1.627	-0.994	-0.888
C	0.721	-0.339	-1.728
C	-2.595	-1.505	-0.367
N	-3.221	-2.741	-0.128
C	-4.603	-2.529	0.073
C	-4.828	-1.127	-0.056
C	-3.580	-0.514	-0.341
C	-2.681	-4.005	-0.127
C	-3.477	-5.093	0.130
C	-4.858	-4.917	0.394
C	-5.408	-3.649	0.371
C	-6.136	-0.392	0.102
C	-7.168	-1.164	-0.707
C	-8.364	-1.629	-0.269
Ag	-3.241	1.507	-0.566
C	-6.570	-0.069	1.522
C	-7.395	1.044	1.746
C	-7.842	1.356	3.032
C	-7.466	0.555	4.117
C	-6.640	-0.551	3.906
C	-6.195	-0.862	2.616
C	-6.676	-1.461	-2.020
O	-7.236	-2.354	-2.768
H	-9.001	-2.241	-0.910
H	-6.468	-3.497	0.570
H	-5.486	-5.781	0.611
H	-3.026	-6.085	0.128
H	-1.618	-4.075	-0.340
H	-0.581	-2.641	1.116
H	1.846	-2.337	0.794
H	2.702	-0.853	-1.021
H	1.085	0.305	-2.530
H	-1.352	-0.046	-2.247
H	-7.687	1.675	0.901
H	-8.480	2.228	3.189
H	-7.812	0.799	5.124
H	-6.335	-1.176	4.747
H	-5.543	-1.723	2.463
H	-5.989	0.576	-0.412
H	-5.821	-0.905	-2.425
H	-8.719	-1.392	0.733
H	-2.394	-4.135	-2.856
H	0.039	-4.682	-2.839
H	1.637	-3.303	-4.165
H	0.790	-1.394	-5.531
H	-1.643	-0.882	-5.583
H	-2.900	-5.281	-6.000
H	-1.994	-5.620	-8.286
H	-4.304	-2.266	-9.714
H	-5.207	-1.904	-7.429
H	-2.624	-3.294	-11.166
H	-1.514	-4.542	-10.532
H	-3.147	-4.986	-11.057
H	-6.765	-2.415	-3.686
H	-3.741	-1.229	-4.619

TS3′

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C	-4.318	-7.180	-1.592
C	-3.200	-6.990	-0.760
C	-2.226	-7.995	-0.705
C	-2.352	-9.154	-1.480
C	-3.455	-9.324	-2.320
C	-4.442	-8.332	-2.370
C	-3.126	-5.750	0.117
C	-3.283	-4.415	-0.610
C	-3.178	-4.213	-1.949
C	-1.917	-5.582	1.004
C	-0.583	-5.401	0.616
N	0.131	-4.957	1.763
C	-0.743	-4.813	2.828
C	-2.039	-5.161	2.368
C	0.113	-5.524	-0.608
C	1.456	-5.229	-0.671
C	2.140	-4.788	0.498
C	1.479	-4.654	1.687
C	-0.333	-4.399	4.173
C	-1.110	-3.450	4.869
C	-0.783	-3.086	6.176
C	0.325	-3.657	6.810
C	1.103	-4.599	6.129
C	0.777	-4.971	4.823
C	-3.498	-3.223	0.181
O	-3.461	-3.132	1.446
Ag	-3.493	-5.850	3.718
H	-3.254	-3.209	-2.373
H	-0.433	-5.860	-1.489
H	1.998	-5.325	-1.612
H	3.201	-4.540	0.460
H	1.947	-4.294	2.600
H	1.368	-5.740	4.321
H	1.962	-5.059	6.621
H	0.581	-3.370	7.832
H	-1.392	-2.345	6.698
H	-1.966	-2.989	4.372
H	-1.368	-7.882	-0.042
H	-1.583	-9.927	-1.421
H	-3.551	-10.227	-2.926
H	-5.316	-8.461	-3.011
H	-5.105	-6.422	-1.627
H	-3.988	-5.815	0.810
H	-3.738	-2.290	-0.350
H	-3.005	-5.039	-2.639
H	-2.942	-4.049	2.002

Figure S3

TS1

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C	2.606	0.948	-0.929
C	1.532	0.060	-1.027
C	1.724	-1.275	-1.402
C	3.015	-1.724	-1.683
C	4.098	-0.841	-1.596
C	3.894	0.490	-1.221
N	0.200	0.523	-0.750
C	-0.491	0.150	0.364
C	0.009	-0.774	1.322
Au	-1.445	-2.923	1.155
P	-3.318	-3.038	-0.496
C	-2.821	-3.616	-2.166
S	-0.655	1.384	-2.071
O	-2.058	1.516	-1.592
C	-0.586	0.275	-3.475
C	-1.720	-0.467	-3.811
C	-1.650	-1.334	-4.901
C	-0.468	-1.473	-5.648
C	0.650	-0.701	-5.285
C	0.603	0.178	-4.207
C	-0.404	-2.402	-6.828
O	0.187	2.570	-2.358
C	0.859	-1.071	2.315
C	-4.676	-4.153	0.034
C	-4.105	-1.395	-0.726
H	-1.511	0.528	0.446
H	0.869	-1.949	-1.466
H	3.174	-2.763	-1.976
H	5.106	-1.194	-1.821
H	4.739	1.176	-1.149
H	2.426	1.982	-0.634
H	1.471	0.782	-3.944
H	1.576	-0.789	-5.857
H	-2.534	-1.911	-5.180
H	-2.647	-0.351	-3.249
H	-1.237	-3.118	-6.824
H	-0.458	-1.831	-7.769
H	0.541	-2.961	-6.843
H	1.019	-2.086	2.682
H	1.421	-0.277	2.825
H	-3.679	-3.571	-2.853
H	-2.008	-2.987	-2.549
H	-2.462	-4.650	-2.091
H	-4.887	-1.455	-1.497
H	-4.554	-1.083	0.225
H	-3.354	-0.648	-1.015
H	-5.510	-4.104	-0.679
H	-4.293	-5.180	0.093
H	-5.009	-3.849	1.034
O	-1.596	-4.887	2.740
S	-2.926	-5.016	3.472
O	-3.610	-6.329	3.246
C	-2.378	-5.083	5.308
O	-3.791	-3.794	3.405
F	-3.460	-5.127	6.115
F	-1.623	-6.178	5.546
F	-1.653	-3.988	5.626

N1

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C	0.192	0.327	-3.957
C	-0.742	0.682	-2.980
C	-2.029	0.135	-2.944
C	-2.383	-0.781	-3.931
C	-1.469	-1.173	-4.927
C	-0.184	-0.605	-4.923
S	-0.261	1.825	-1.696
O	0.892	2.641	-2.136
C	-1.875	-2.159	-5.986
N	0.448	0.735	-0.408
C	-0.354	0.303	0.574
C	-0.039	-0.727	1.468
C	0.644	-0.865	2.602
C	1.747	0.179	-0.673
C	2.885	0.886	-0.275
C	4.144	0.342	-0.536
C	4.257	-0.888	-1.192
C	3.110	-1.584	-1.591
C	1.846	-1.050	-1.335
Au	-1.078	-2.294	0.470
O	0.107	-4.242	2.677
S	-1.038	-4.263	3.654
O	-0.891	-3.340	4.830
P	-2.080	-4.172	-0.516
C	-3.797	-4.486	0.050
C	-2.185	-4.102	-2.352
C	-1.151	-5.714	-0.157
O	-1.462	2.416	-1.054
O	-2.405	-4.284	3.024
C	-0.899	-6.011	4.425
F	0.311	-6.191	4.999
F	-1.848	-6.199	5.371
F	-1.059	-6.961	3.472
H	-1.332	0.793	0.624
H	0.941	-1.582	-1.632
H	3.198	-2.544	-2.102
H	5.244	-1.309	-1.393
H	5.040	0.882	-0.226
H	2.776	1.845	0.232
H	1.187	0.772	-3.966
H	0.536	-0.894	-5.690
H	-3.392	-1.199	-3.929
H	-2.744	0.433	-2.176
H	-2.489	-2.968	-5.565
H	-2.482	-1.661	-6.760
H	-1.000	-2.601	-6.481
H	0.732	-1.831	3.098
H	1.121	0.000	3.073
H	-2.614	-5.038	-2.737
H	-2.821	-3.258	-2.645
H	-1.183	-3.954	-2.775
H	-4.187	-5.394	-0.429
H	-3.773	-4.608	1.140
H	-4.430	-3.627	-0.206
H	-1.677	-6.575	-0.592
H	-0.144	-5.638	-0.587
H	-1.062	-5.826	0.929

N2

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P	-0.064	-0.000	0.354
Au	-0.244	-0.000	2.706
C	1.663	-0.000	-0.283
C	-0.853	1.449	-0.465
C	-0.853	-1.449	-0.465
H	1.668	0.000	-1.382
H	2.185	0.891	0.087
H	2.184	-0.892	0.086

H	-0.757	1.368	-1.557
H	-1.915	1.483	-0.190
H	-0.370	2.372	-0.118
H	-0.757	-1.368	-1.557
H	-0.370	-2.372	-0.119
H	-1.915	-1.483	-0.191
C	-0.413	0.000	4.771
C	0.618	0.000	5.649
C	-1.748	-0.000	5.396
H	0.444	0.000	6.736
H	1.663	0.000	5.333
O	-2.826	-0.000	4.801
H	-1.744	-0.000	6.519

N1'

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C	-1.593	-0.437	-4.037
C	-1.112	0.638	-3.281
C	-0.067	1.452	-3.722
C	0.505	1.176	-4.964
C	0.058	0.102	-5.750
C	-1.002	-0.690	-5.271
S	-1.800	0.927	-1.659
O	-1.425	2.277	-1.176
C	0.705	-0.211	-7.070
N	-0.822	-0.274	-0.686
C	0.605	-0.119	-0.705
C	1.369	-1.003	-1.472
C	2.757	-0.855	-1.495
C	3.364	0.170	-0.761
C	2.586	1.047	0.003
C	1.196	0.910	0.035
C	-1.467	-1.054	0.199
C	-0.848	-1.776	1.224
C	-0.259	-2.954	1.407
O	-3.193	0.423	-1.560
H	-2.558	-1.068	0.098
H	0.875	-1.792	-2.042
H	3.364	-1.538	-2.091
H	4.449	0.285	-0.783
H	3.061	1.844	0.577
H	0.581	1.587	0.631
H	0.286	2.284	-3.114
H	1.320	1.807	-5.323
H	-1.371	-1.521	-5.876
H	-2.414	-1.055	-3.672
H	1.368	-1.085	-6.971
H	-0.045	-0.460	-7.833
H	1.311	0.629	-7.432

H	-0.170	-3.669	0.582
H	0.148	-3.259	2.371
Ag	-1.150	-0.281	2.680
O	-1.375	1.283	4.160
S	-1.000	2.722	3.732
O	-0.724	3.595	4.905
O	-0.049	2.764	2.578
C	-2.657	3.358	3.001
F	-2.477	4.572	2.450
F	-3.095	2.507	2.048
F	-3.593	3.450	3.964

TS$_1$'

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C	1.035	0.960	0.523
C	0.598	0.070	-0.464
C	1.507	-0.539	-1.335
C	2.872	-0.276	-1.197
C	3.318	0.603	-0.205
C	2.400	1.222	0.648
N	-0.807	-0.215	-0.665
C	-1.550	-1.176	0.253
Ag	-0.640	-0.312	2.960
O	-0.425	1.036	4.647
S	0.066	2.487	4.482
C	-1.570	3.427	4.146
F	-2.371	3.381	5.229
S	-1.845	1.277	-1.093
O	-3.090	0.667	-1.629
C	-0.844	1.978	-2.391
C	-0.907	1.411	-3.668
C	-0.082	1.933	-4.661
C	0.797	2.999	-4.393
C	0.822	3.546	-3.098
C	0.010	3.041	-2.085
C	1.706	3.525	-5.468
O	-1.877	2.159	0.097
C	-0.838	-1.693	1.424
C	-0.434	-2.970	1.508
O	0.576	3.048	5.765
O	0.880	2.713	3.248
F	-1.305	4.718	3.858
F	-2.218	2.873	3.102
H	-2.560	-0.805	0.460
H	1.147	-1.208	-2.118
H	3.584	-0.753	-1.872
H	4.385	0.813	-0.104
H	2.734	1.914	1.422
H	0.326	1.473	1.173

H	0.035	3.465	-1.081
H	1.490	4.380	-2.877
H	-0.125	1.507	-5.666
H	-1.590	0.589	-3.885
H	2.602	2.888	-5.553
H	1.210	3.521	-6.449
H	2.045	4.545	-5.245
H	-0.589	-3.722	0.718
H	0.073	-3.357	2.392
O	-1.792	-2.164	-0.962
H	-1.275	-2.988	-0.819
H	-1.134	-1.268	-1.445

N2'

47

C	-0.899	-0.983	-3.613
C	-1.347	-0.140	-2.591
C	-1.534	1.227	-2.793
C	-1.256	1.760	-4.052
C	-0.800	0.946	-5.103
C	-0.626	-0.429	-4.861
S	-1.711	-0.842	-0.976
O	-2.091	0.284	-0.066
C	-0.528	1.528	-6.463
N	-0.187	-1.544	-0.499
C	0.822	-0.698	0.034
C	1.425	0.284	-0.768
C	2.431	1.097	-0.246
C	2.878	0.923	1.068
C	2.301	-0.076	1.863
C	1.269	-0.875	1.355
O	-2.612	-2.018	-1.111
Ag	-1.854	-0.918	2.623
O	-1.767	1.335	2.927
S	-0.942	2.574	2.954
C	-1.114	3.394	1.200
F	-2.395	3.342	0.840
C	-1.879	-2.998	2.508
C	-0.837	-3.819	2.742
C	-3.204	-3.542	2.186
O	-3.445	-4.338	1.275
O	-1.171	3.607	3.970
O	0.648	2.228	2.995
F	-0.704	4.660	1.288
F	-0.354	2.722	0.332
H	-4.042	-3.155	2.819
H	1.107	0.410	-1.803
H	2.883	1.863	-0.878
H	3.673	1.553	1.470

H	2.662	-0.250	2.879
H	0.830	-1.660	1.974
H	-1.877	1.862	-1.976
H	-1.390	2.831	-4.219
H	-0.267	-1.076	-5.664
H	-0.753	-2.049	-3.433
H	0.236	0.952	-7.001
H	-1.444	1.511	-7.076
H	-0.200	2.574	-6.394
H	-0.962	-4.910	2.735
H	0.167	-3.462	2.982
H	-0.435	-2.327	0.119
H	0.884	1.399	2.489