Supporting Information

(32 pages including the cover page)

A Bromo-Capped Diruthenium(I,I) N-Heterocyclic Carbene Compound for *in situ* Bromine Generation with NBS: Catalytic Olefin Aziridination Reactions[ξ]

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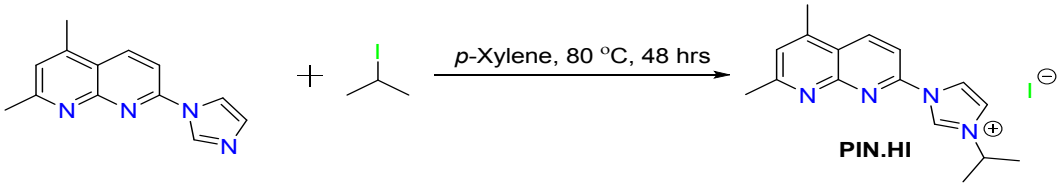
ξ Dedicated to Professor Kim R. Dunbar on the occasion of her 60th Birthday

‡ G.S. and P.P. contributed equally to this work

Contents

1. Synthesis and characterization

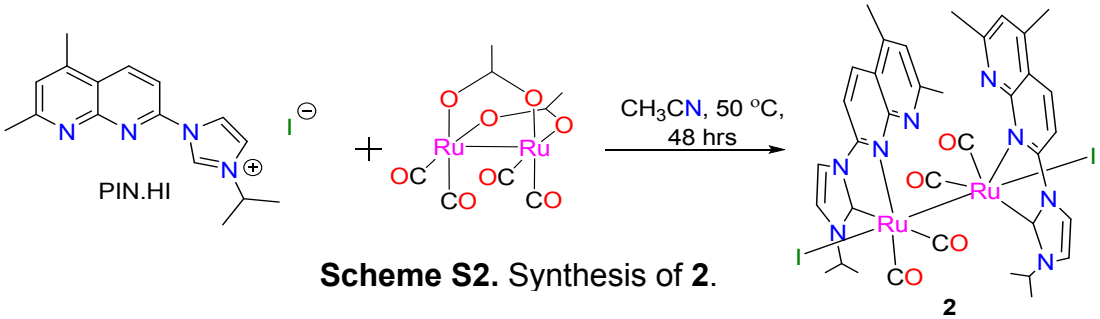
Synthesis of PIN HI



Scheme S1. Synthesis of **PIN.HI**.

^{1}H NMR (500 MHz, DMSO-D6, 294 K): δ 10.28 (s, 1H, Im), 8.95 (d, *J* = 9.1 Hz, 1H, NP), 8.69 (s, 1H, NP), 8.22 (d, *J* = 9.1 Hz, 1H, NP), 8.19 (s, 1H, Im), 7.52 (s, 1H, Im), 4.80 (m, 1H, CH-^{i}Pr), 2.73 (s, 3H, CH_3-NP), 2.68 (s, 3H, CH_3-NP),1.58 (d, 6H, J = 6.8 Hz, ^{i}Pr). ^{13}C NMR (125.8 MHz, DMSO-D6, 296.2 K): δ 164.7 (NCNNP), 153.5 (CCNNP), 147.8 (CCNNP), 139.9 (CCCNP), 135.3 (CCCNP), 124.9 (CCCNP), 122.4 (NCCIm), 121.5 (CCCNP), 120.1 (CCCNP), 112.7 (NImCC), 53.9 (CH^{i}Pr), 25.3 (CH_3 NP), 22.7 (CH_3 ^{i}Pr), 18.4 (CH_3 NP). ESI–MS, *m/z*: 267.1611, (z=1), $[M]^+$

Synthesis of 2



Scheme S2. Synthesis of **2**.

^{1}H NMR (500 MHz, CD_3CN, 294 K): δ 8.86 - 8.69 (m, 1H, NP), 8.14 (s, 1H, Im), 8.02 -7.88 (m, 1H, NP), 7.52 - 7.50 (m, 1H, NP), 7.40 (s, 1H, Im), 5.86 – 5.81 and 5.52 – 5.48 (m, 1H, CH-^{i}Pr), 2.83 – 2.74 (m, 6H, CH_3-NP), 1.68 – 1.47 (m, 6H, ^{i}Pr). ^{13}C NMR (125.8 MHz, CD_3CN, 296.2 K): δ 202.9 (CO), 191.3 (CO), 173.2 (NCNIm), 166.4 (NCNNP), 155.2 (NNPCNIm), 147.8 (CCNNP), 140.3 (CCCNP), 126.3 (CCCNP), 125.6 (CCCNP), 122.7 (NCCIm), 120.8 (CCCNP),112.5 (NImCC), 111.5 (NImCC), 55.4 (CH^{i}Pr), 25.7 (CH3 NP), 23.0 (CH3 ^{i}Pr), 22.8 (CH3 ^{i}Pr), 18.3 (CH3 NP). IR (KBr, cm^{-1}): ν(CO) 2009, 1991, 1968, 1924. Anal. Calcd for $C_{36}H_{36}N_8O_4I_2Ru_2.CH_3CN$: C, 39.89; H, 3.43; N, 11.03. Found: C, 39.34; H, 3.37; N, 11.08. ESI-MS, m/z 947.0106 corresponding to $[M–I–CO]^+$, where M is $Ru_2(CO)_4(PIN)_2I_2$.

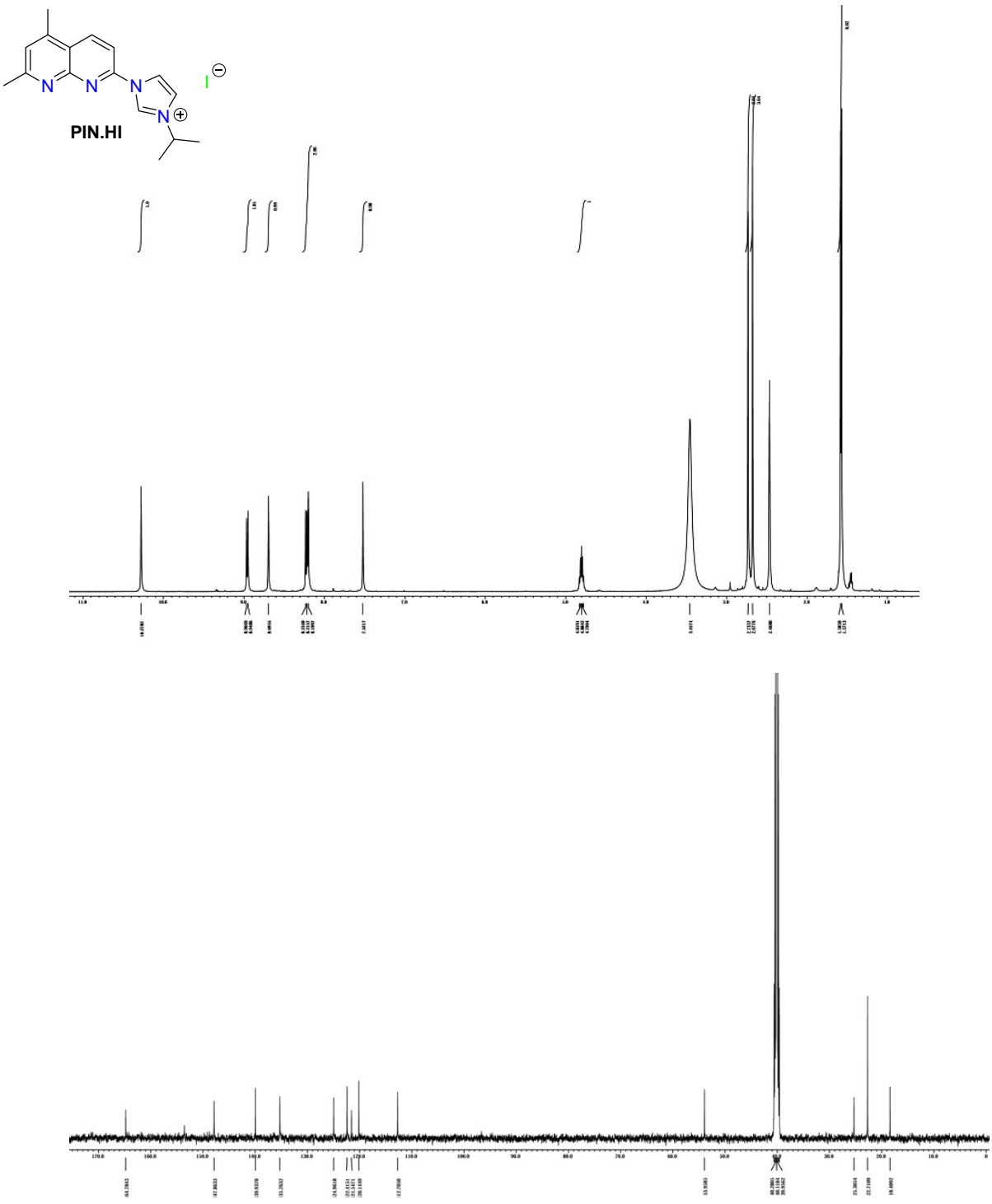


Figure S1. ^{1}H NMR (top) and ^{13}C NMR (below) of **PIN.HI**.

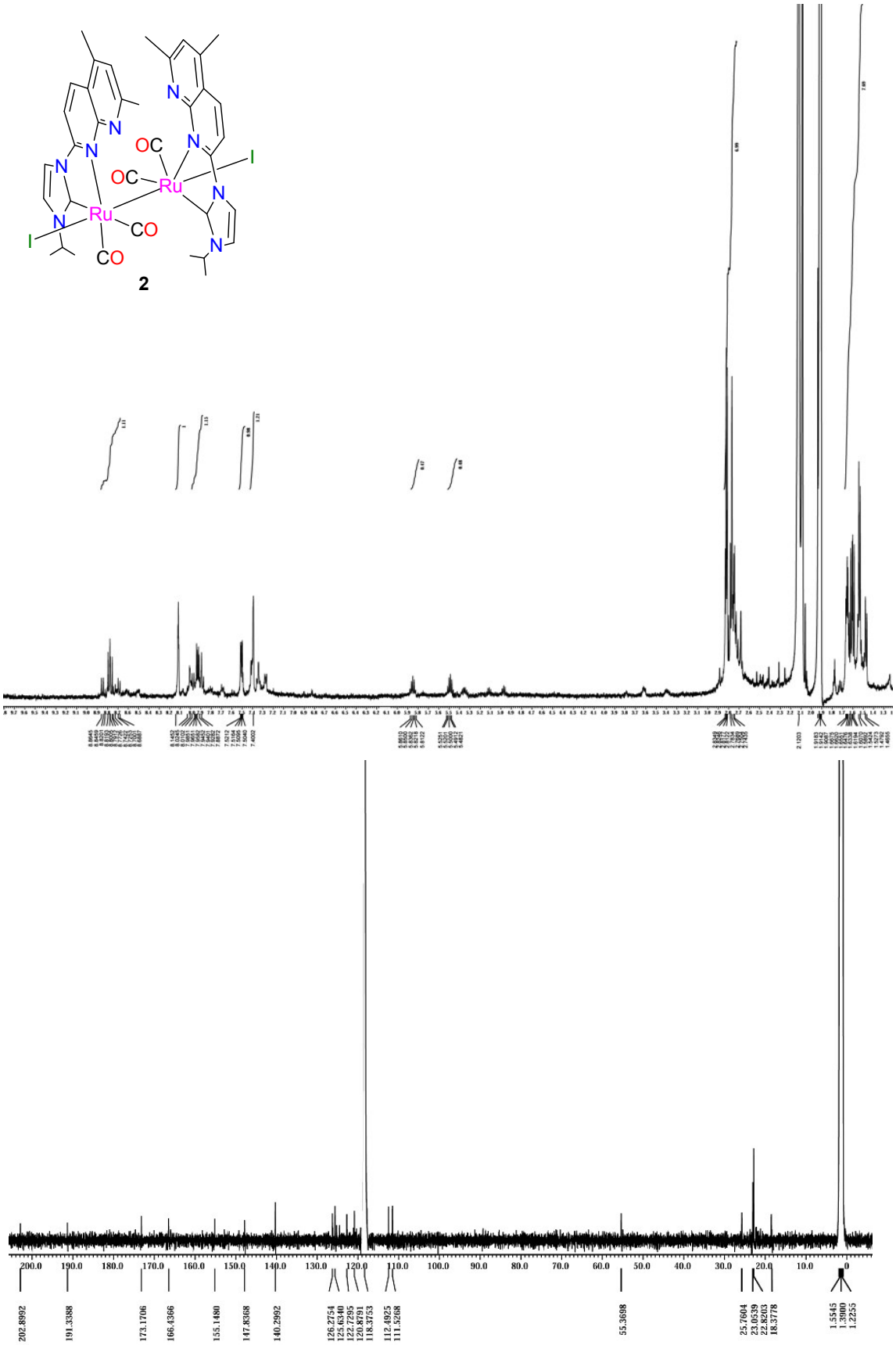


Figure S2. ^{1}H NMR (top) and ^{13}C NMR (below) of **2**.

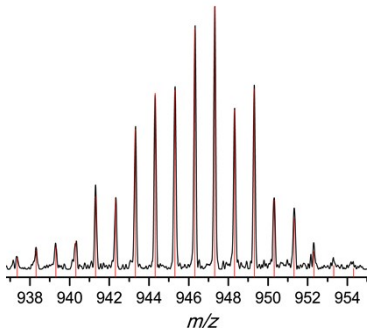


Figure S3. Simulated (red line) and experimental mass distributions (black line) for **2** $[M\text{-}I\text{-}CO]^+$ at *m/z* (z = 1) M = $Ru_2(CO)_4(PIN)_2I_2$.

2. X–Ray Data Collection and Refinements

Single–crystal X–ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low–temperature attachment. All the data were collected at 100(2) K using graphite–monochromated Mo–Kα radiation (λα = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[1] and the data were corrected for absorption using the SADABS program.[2] The structure was solved and refined with the SHELX suite of programs as implemented in X–seed.[3] All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. The crystal was brittle and poorly diffracting. Number of datasets was collected on single crystals from different batches, whereof one of the best data is reported herein. Despite our best efforts, the Rint value is on the higher side, which generated a B level alert. Some of the lattice solvent molecules in the crystal lattice of **2** cannot be modelled satisfactorily due to the presence of severe disorders. Therefore, the Olex–2 mask program has been used to discard those disordered solvents molecules. A total electron densities of 254 were removed which can be tentatively ascribed for four CH_3CN, one Et_2O and one H_2O molecules. Pertinent crystallographic data for compound **2** is summarized in Table S1. The crystallographic figure used in this manuscript has been generated using Diamond 3.1e software.[4] CCDC number 1841806 contains the supplementary crystallographic data for compound **2**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

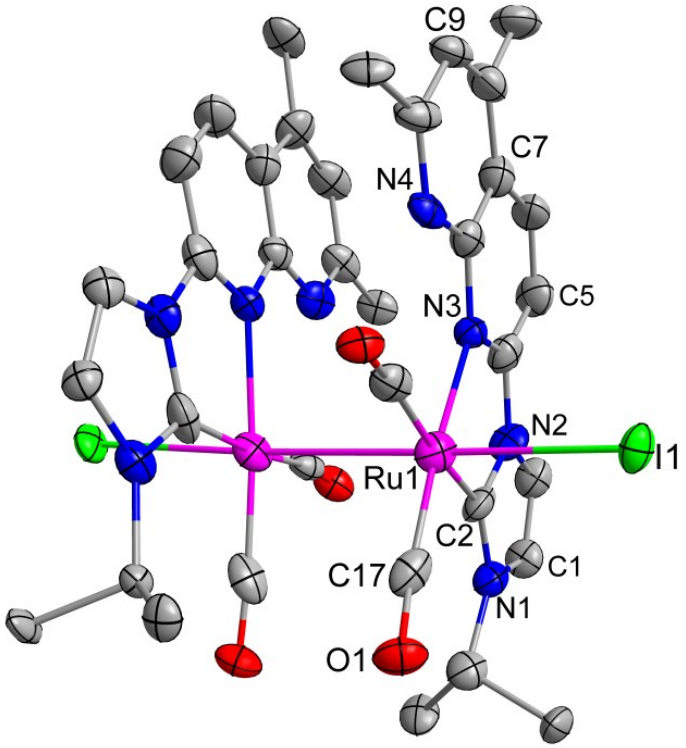


Figure S4. Molecular structure of **2** with important atoms labelled. All hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ru1–Ru1' 2.8448(16), Ru1–C2 2.049(10), Ru1–N3 2.172(7), Ru1–I1 2.7560(11), Ru1–C17 1.829(14), C17–O1 1.174(13). Ru1'–Ru1–I1 177.00(4), Ru1'–Ru1–C2 89.5(3), Ru1'–Ru1–N3 91.96(17), Ru1'–Ru1–C17 89.9(3), C2–Ru1–C17 98.4(4). Dihedral angles (deg): N3–Ru1–Ru1'–N3' 37.1(6), C2–Ru1–Ru1'–C2' 170.3(6).

Table S1. Crystallographic data and refinement parameters for **2**.

	2
Empirical Formula	$C_{36}H_{36}N_8O_4I_2Ru_2$
Formula Weight	1100.67
Crystal System	Trigonal
Space Group	P -3c1
a (Å)	21.118(2)
b (Å)	21.118(2)
c (Å)	17.870(3)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	6901.7(18)
Z	6
ρ_{calcd} (g cm^{-3})	1.589
μ (mm^{-1})	2.040
F(000)	3204
Reflections Collected	57918
Independent	4063
Observed [I >2σ (I)]	2358
No. of parameters	239
GooF	1.027
R_{int}	0.2467
Final R indices [I > 2σ(I)][a]	R1 = 0.0720 wR2 = 0.1506
R indices (all data)[a]	R1 = 0.1292 wR2 = 0.1733

[a] $R_1 = \Sigma\, ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

3. HPLC method for the separation of *d,l* (rac) and meso-1,2-dibromo1,2-diphenylethane compound

The *d,l* and meso-1,2-dibromo1,2-diphenylethane compounds were dissolved in ^{i}PrOH and subjected to normal phase chiral HPLC analysis (Chiral AD-H column, 5:95 ^{i}PrOH:Hexane, flow rate 0.5 ml/min, detection at 254 nm).

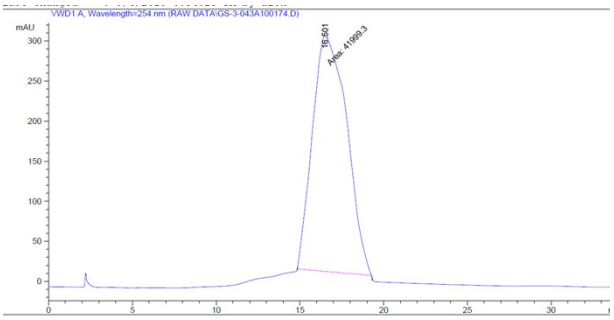


Figure S5. HPLC chromatogram of meso-1,2-dibromo1,2-diphenylethane.

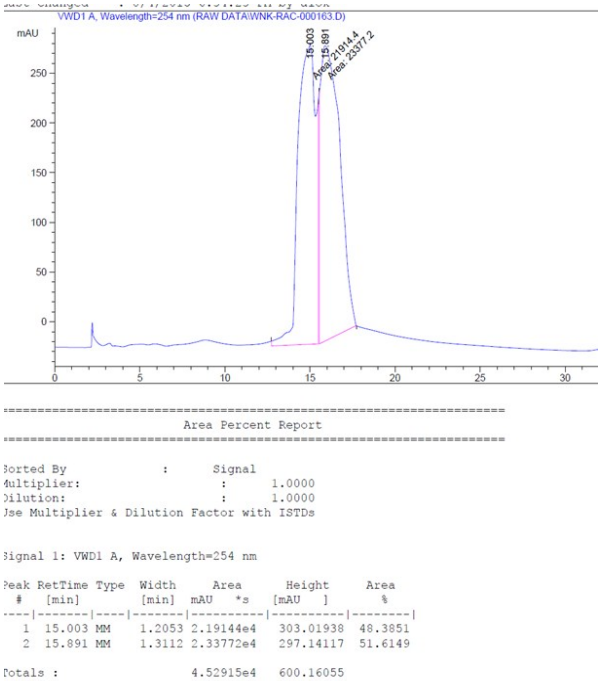


Figure S6. HPLC chromatogram of *d,l*-1,2-dibromo1,2-diphenylethane.

4. *In situ* generation of Iodine from an Iodide analogue of 1

A mixture of complex **2** (20 mg) and NIS (3.5 mg) was dissolved in 2 mL of acetonitrile solution and stirred for 20 minutes. After that freshly prepared starch solution was added to the reaction mixture. Immediately the color of solution changed from brownish yellow to dark blue. Similar reaction was repeated with tetrabutylammonium iodide and NIS, however, with addition of starch solution no color change was observed.

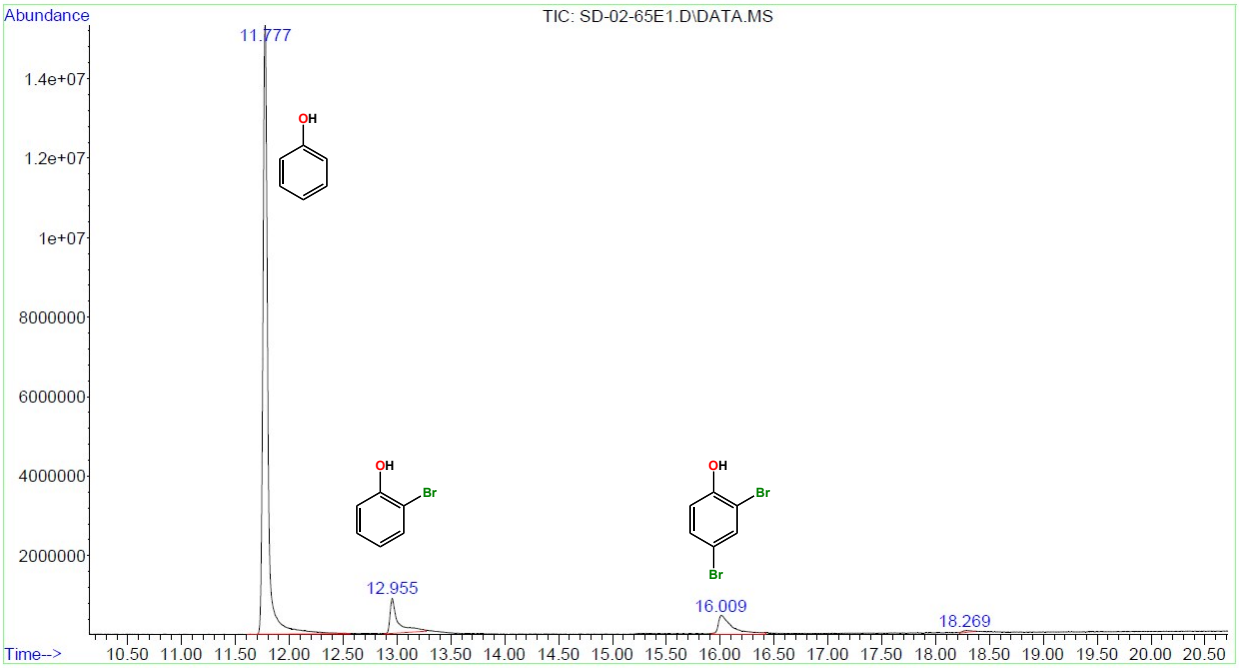


Figure S7a. Bromination of phenol in NBS and K_2CO_3 (GC-MS conversion).

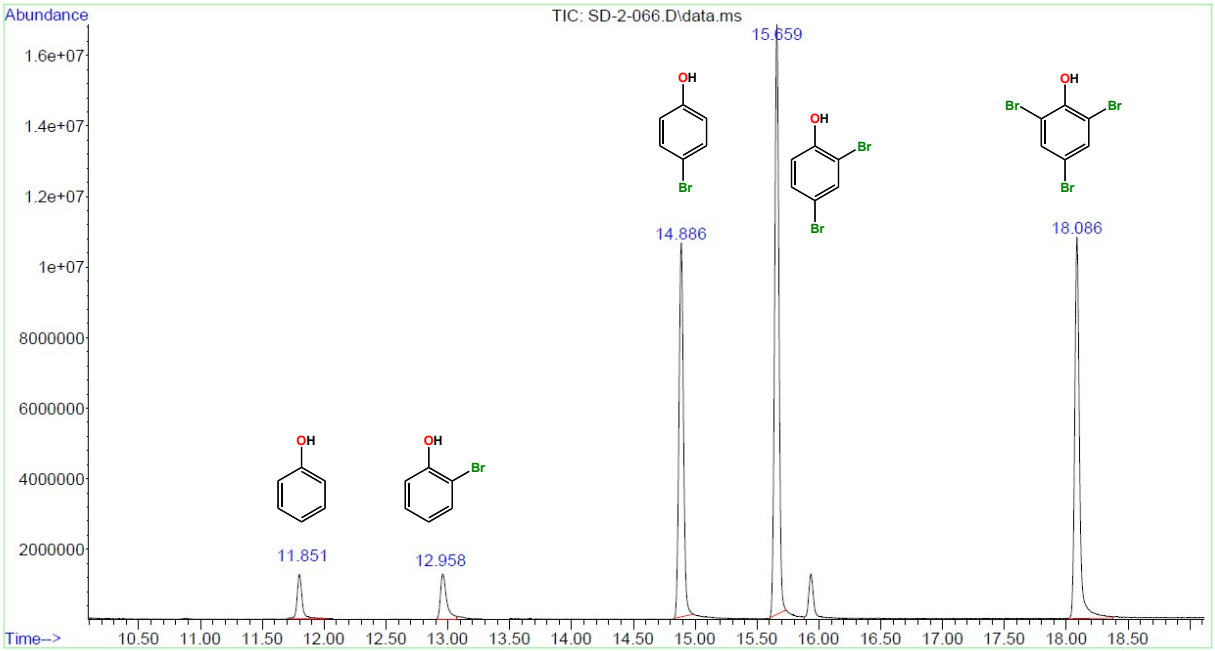


Figure S7b. Bromination of phenol in liquid Br_2 (GC-MS conversion).

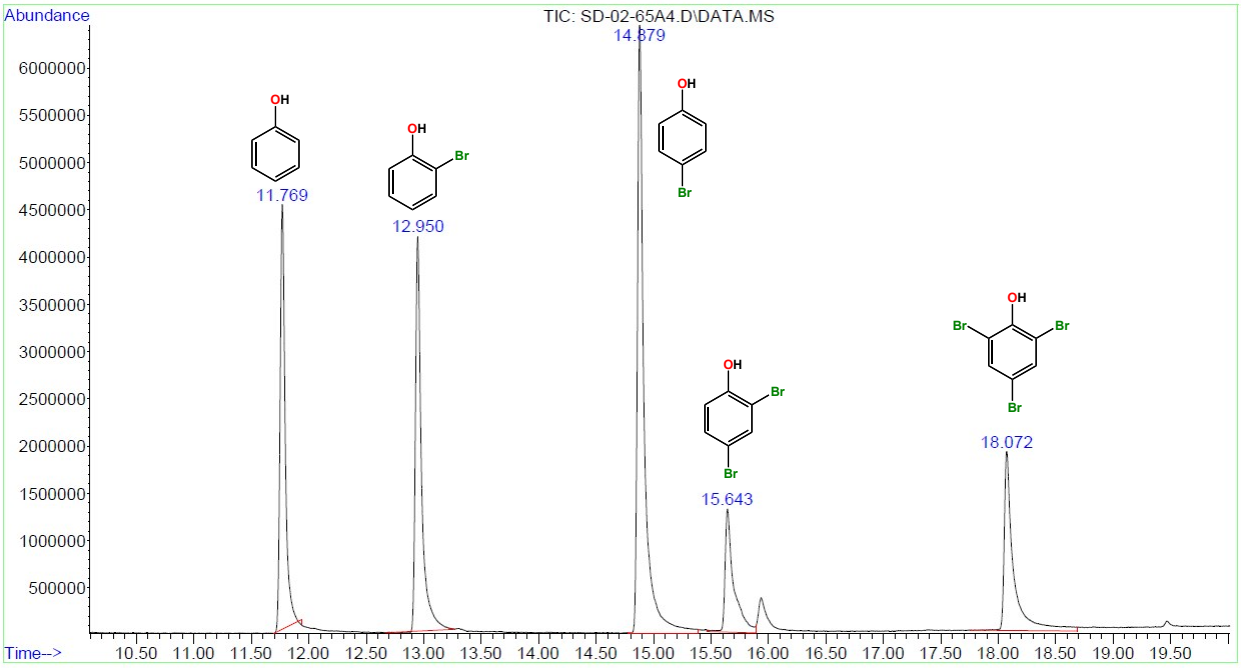


Figure S7c. Bromination of phenol in catalyst **1**, NBS, K_2CO_3 (GC-MS conversion).

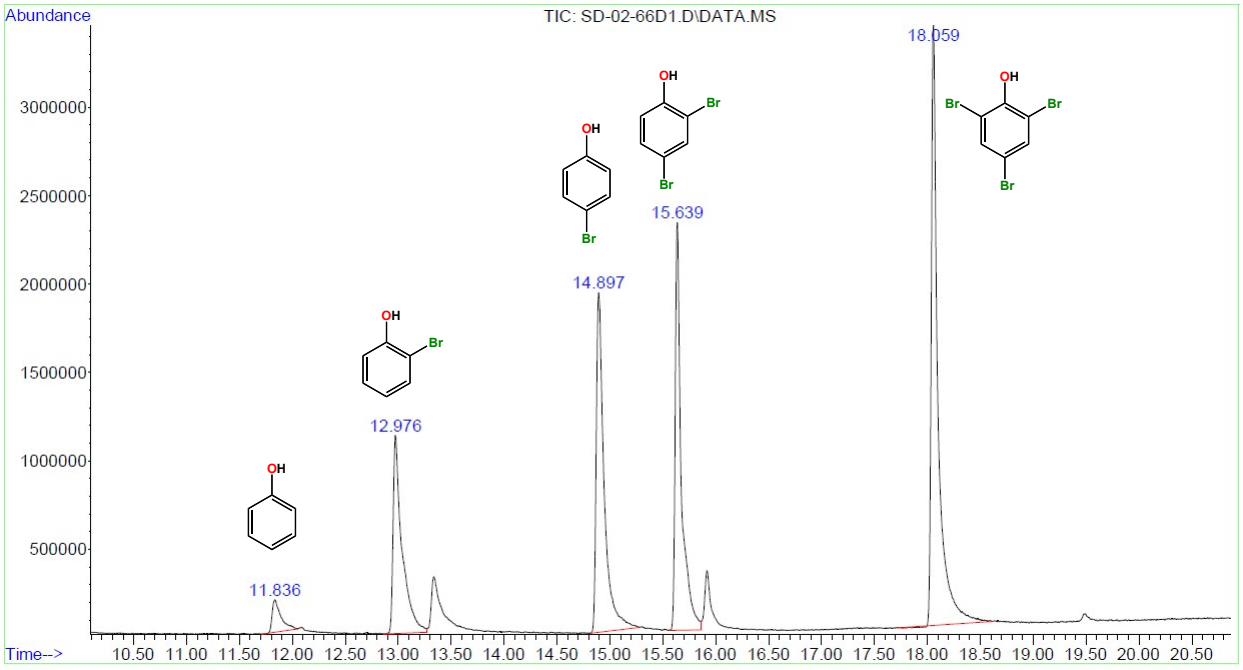
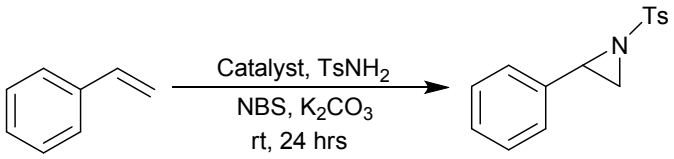


Figure S7d. Bromination of phenol in catalyst **1**, NBS (GC-MS conversion).

5. Control experiment for olefin aziridination reaction

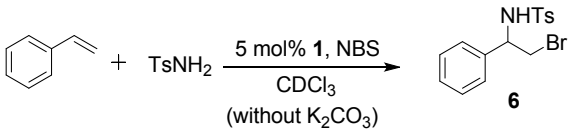
Table S2. Catalyst screening for aziridination recation.



Entry	Catalyst (mol%)	Yield [a](%)
1.	**1** (5)	90
2.	No catalyst	17
3.[b]	**1** and $TlBF_4$ (5)	18
4.	**3** (5)	20
5.	**4** (5)	76
6.[c]	**5** (1.0, 0.1)	77, 62

[a] Isolated yields, [b] catalyst **1** and $TlBF_4$ was stirred in acetonitrile solution and the residue obtained after workup was used as a catalyst, [c] A. J. Catino, J. M. Nichols, R. E. Forslund and M. P. Doyle, *Org. Lett.,* 2005, **7**, 2787.

6. ^{1}H NMR study



Scheme. S3. Formation of β–bromoamide product.

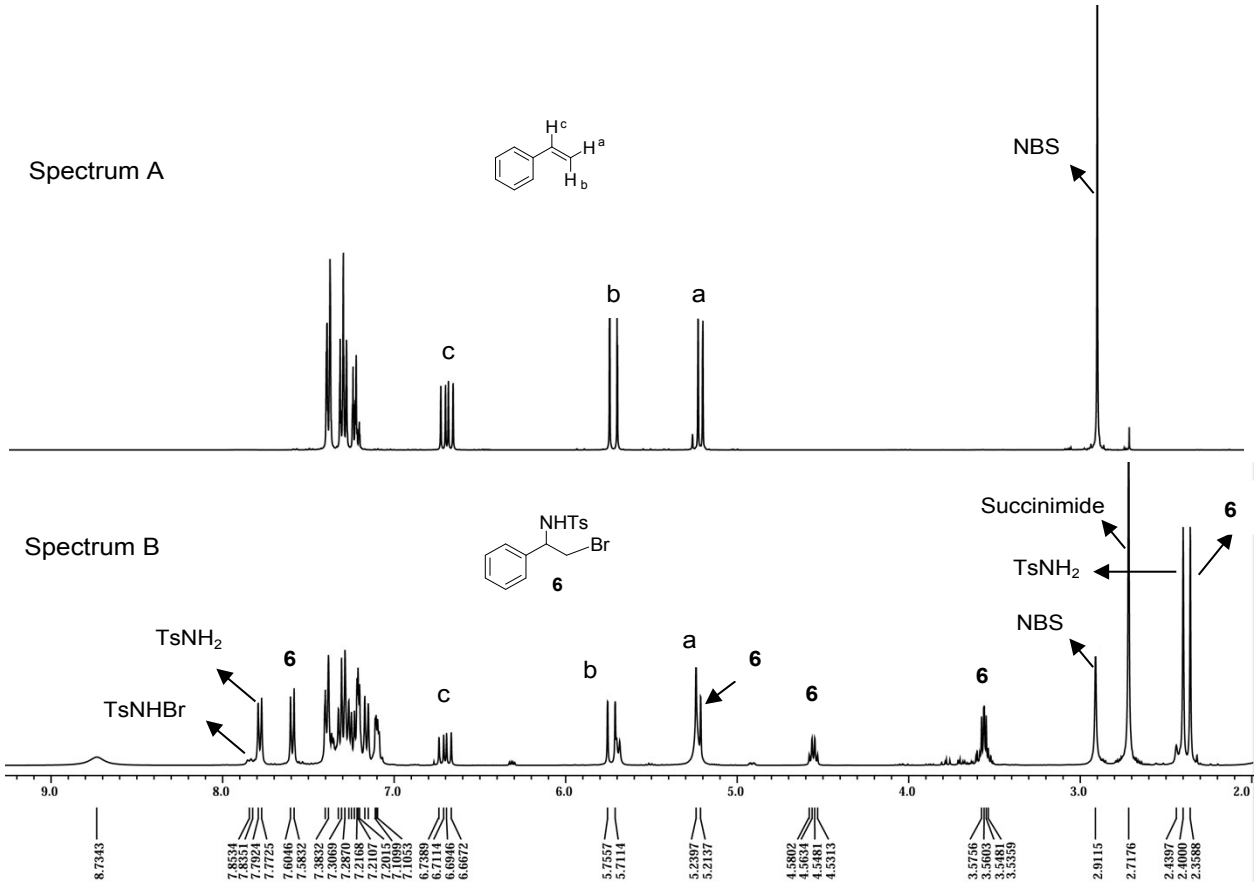


Figure S8. Spectrum A: ^{1}H NMR study for reaction mixture of styrene and NBS. Spectrum B: ^{1}H NMR study on the reaction mixture of styrene and NBS with $TsNH_2$, 5 mol% **1**.

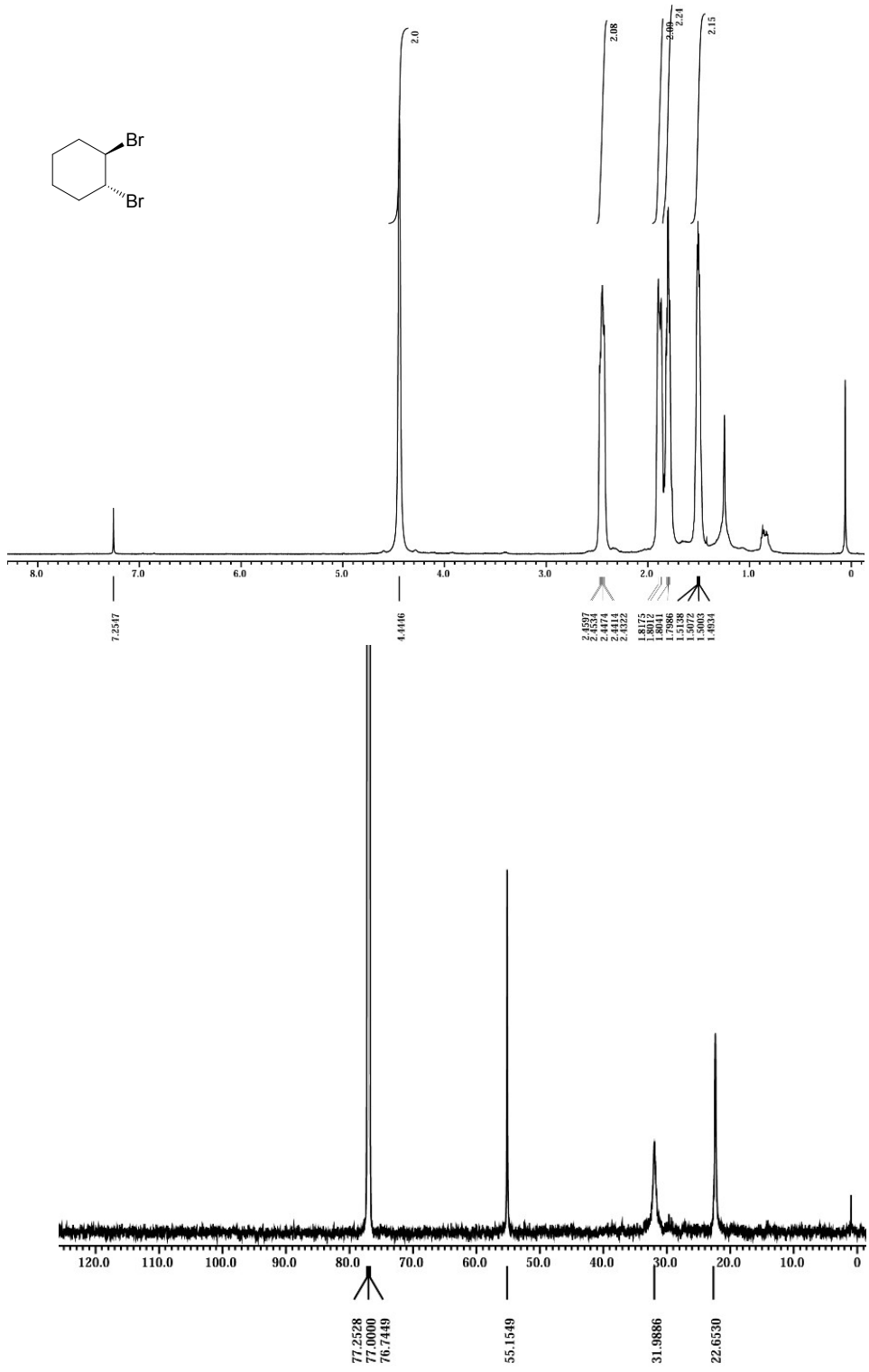
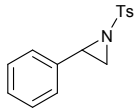
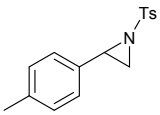


Figure S9. ^{1}H NMR (top) and ^{13}C NMR (below) of *trans*1,2-dibromocyclohexane.

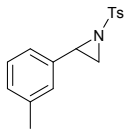
7. Spectral data of the aziridines



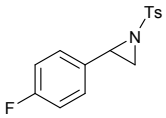
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.28-7.19 (m, 5H), 3.76 (dd, *J* = 4.6 Hz, 7.3 Hz, 1H), 2.97 (d, *J* = 7.3 Hz, 1H), 2.42 (s, 3H) 2.37 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.8, 135.1, 135.0, 129.9, 128.7, 128.4, 128.0, 126.6, 41.1, 36.0, 21.8.



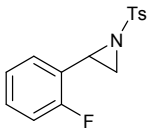
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.04 (s, 4H), 3.68 (q, *J* = 4.3 Hz, 1H), 2.92 (d, *J* = 7.3 Hz, 1H), 2.37 (s, 3H), 2.32 (d, *J* = 4.9 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.7, 138.3, 135.2, 132.1, 129.8, 129.3, 128.0, 126.6, 41.1, 35.8, 21.7, 21.2.



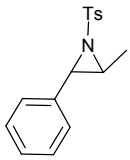
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.25-7.01 (m, 4H), 3.72 (br, 1H), 2.95 (d, *J* = 7.3 Hz, 1H), 2.43 (s, 3H), 2.36 (m, 1H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.6, 138.4, 134.9, 134.6, 129.8, 129.1, 128.5, 128.0, 127.2, 123.7, 41.1, 35.9, 29.7, 21.7, 21.3.



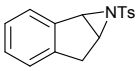
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (q, *J* = 8.6 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H) 3.75 (dd, *J* = 4.0 Hz, 7.4 Hz, 1H), 2.96 (d, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 2.34 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.9, 134.9, 129.9, 128.4, 128.3, 128.0, 115.7, 115.5, 40.4, 36.1, 21.3.



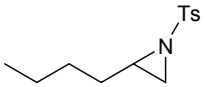
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25-6.97 (m, 4H), 3.96 (dd, *J* = 4.3 Hz, 7.3 Hz, 1H), 2.99 (d, *J* = 7.1 Hz, 1H), 2.42 (s, 3H), 2.38 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.5, 144.9, 134.7, 129.9, 129.8, 128.2, 127.5, 124.4, 115.3, 35.6, 35.2, 21.8.



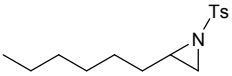
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.26-7.24 (m, 5H), 7.14 (d, *J* = 6.1 Hz, 2H), 3.79 (d, *J* = 4.3 Hz, 1H), 2.90 (dq, *J* = 6.1, 4.6 Hz, 1H), 2.38 (s, 3H), 1.83 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.0, 137.9, 135.6, 129.8, 128.3, 128.1, 127.3, 126.3, 49.3, 49.2, 21.7, 14.2.



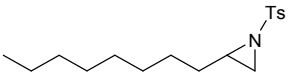
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.23-7.22 (m, 1H), 7.19-7.15 (m, 2H), 4.30 (d, *J* = 5.2 Hz, 1H), 3.95 (m, 1H), 3.02 (d, *J* = 3.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.6, 138.4, 129.8, 129.0, 128.0, 126.9, 125.7, 125.2, 50.3, 45.1, 34.9, 21.8.



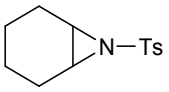
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.74-2.69 (m, 1H), 2.62 (d, *J* = 7.3 Hz, 1H,) 2.43 (s, 3H), 2.04 (d, *J* = 4.8 Hz, 1H,) 1.55-1.49 (m, 1H), 1.27-1.20 (m, 5H), 0.80 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.4, 135.3, 129.7, 128.0, 40.5, 33.9, 31.0, 29.8, 22.2, 21.7, 13.9.



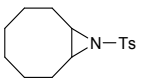
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.66-2.63 (m, 1H), 2.59 (d, *J* = 6.7 Hz, 1H,) 2.39 (s, 3H), 2.02 (d, *J* = 4.6 Hz, 1H,) 1.53-1.45 (m, 1H), 1.20-1.10 (m, 9H), 0.80 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 135.2, 129.6, 128.0, 40.5, 33.8, 31.6, 31.4, 28.7, 26.7, 22.5, 21.6, 14.0.



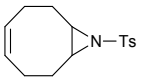
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.73-2.67 (m, 1H), 2.62 (d, *J* = 7.0 Hz, 1H,) 2.42 (s, 3H), 2.04 (d, *J* = 4.6 Hz, 1H,) 1.25-1.19 (br, m, 14H), 0.86 (t, *J* = 7.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.3, 135.2, 129.5, 127.9, 40.5, 33.7, 31.7, 31.2, 29.3, 29.1, 29.0, 22.5, 21.5, 14.0.



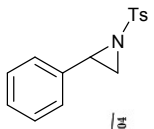
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.85 (s, 2H), 2.55 (s, 3H), 1.68 – 1.66 (m, 4H,) 1.30-1.26 (m, 2H), 1.14-1.10 (m, 2H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.8, 135.3, 129.2, 127.3, 39.6, 29.3, 22.4, 21.2, 21.1, 19.1.



^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2 77 (br, 2H), 2.43 (s, 3H), 2.02 -1.99 (m, 2H), 1.57-1.50 (m, 6H), 1.43-1.24 (m, 4H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 144.1, 135.9, 129.7, 127.6, 44.0, 26.5, 26.2, 25.3, 21.7.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.68 - 5.64 (m, 1H), 5.54 -5.47 (m, 1H), 4.33 (t, *J* = 6.7 Hz, 1H), 3.65 – 3.59 (m, 1H), 2.42 (s, 3H), 2.07 – 1.94 (m, 2H), 1.88 – 1.80 (m, 2H), 1.54 – 1.47 (m, 2H), 1.23 (s, 2H,); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 137.8, 130.6, 129.9, 126.9, 35.6, 29.7, 25.7, 21.6.


Ts
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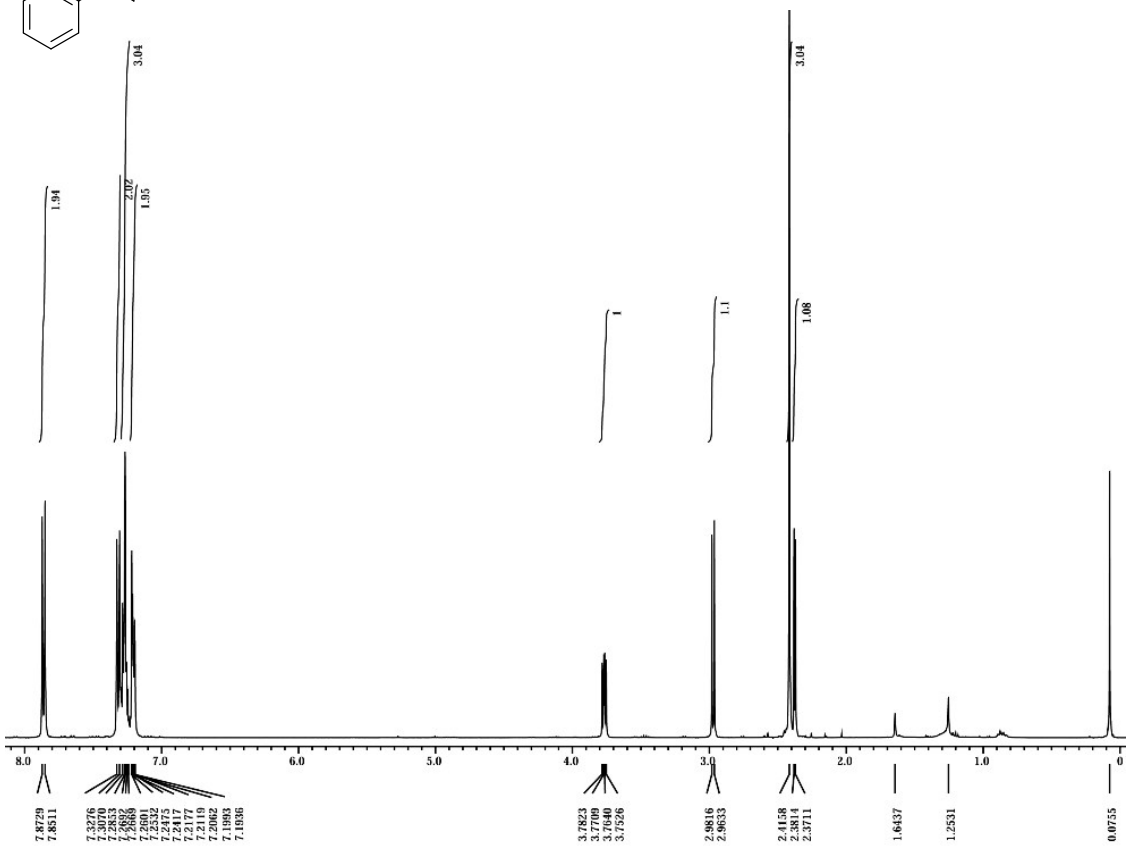
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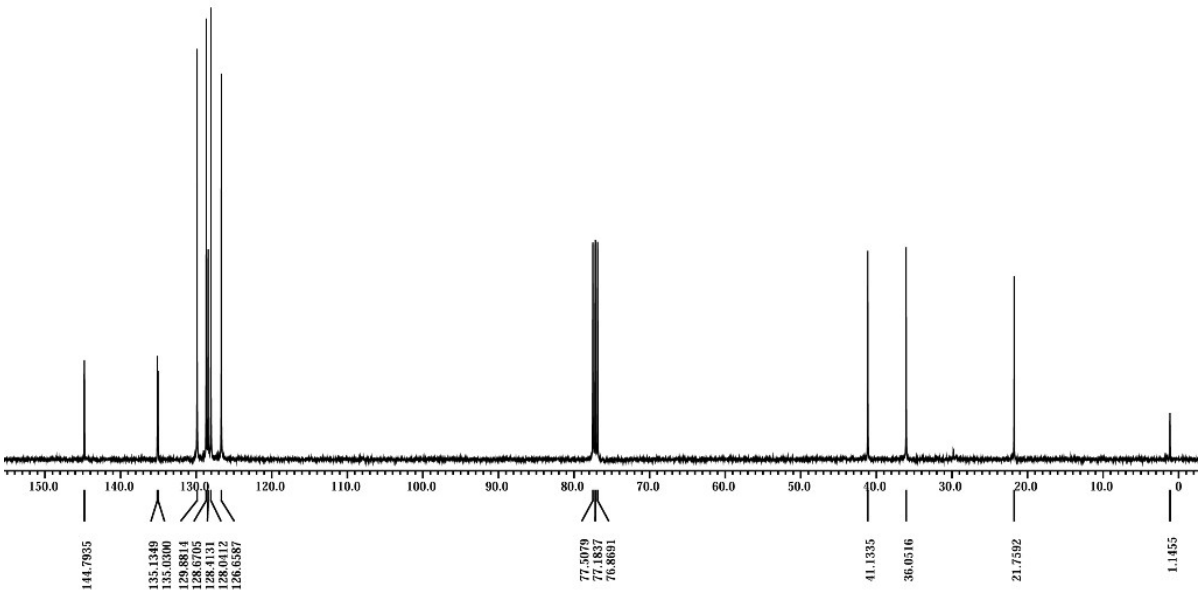
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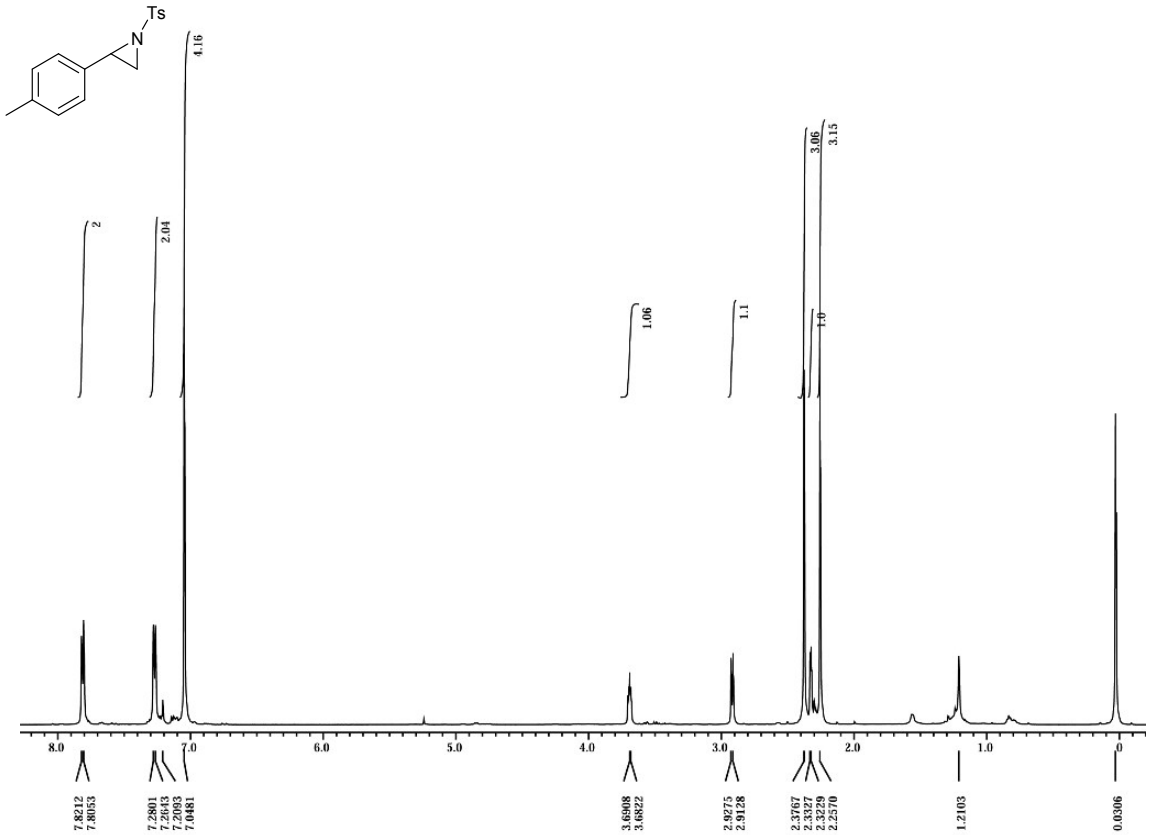
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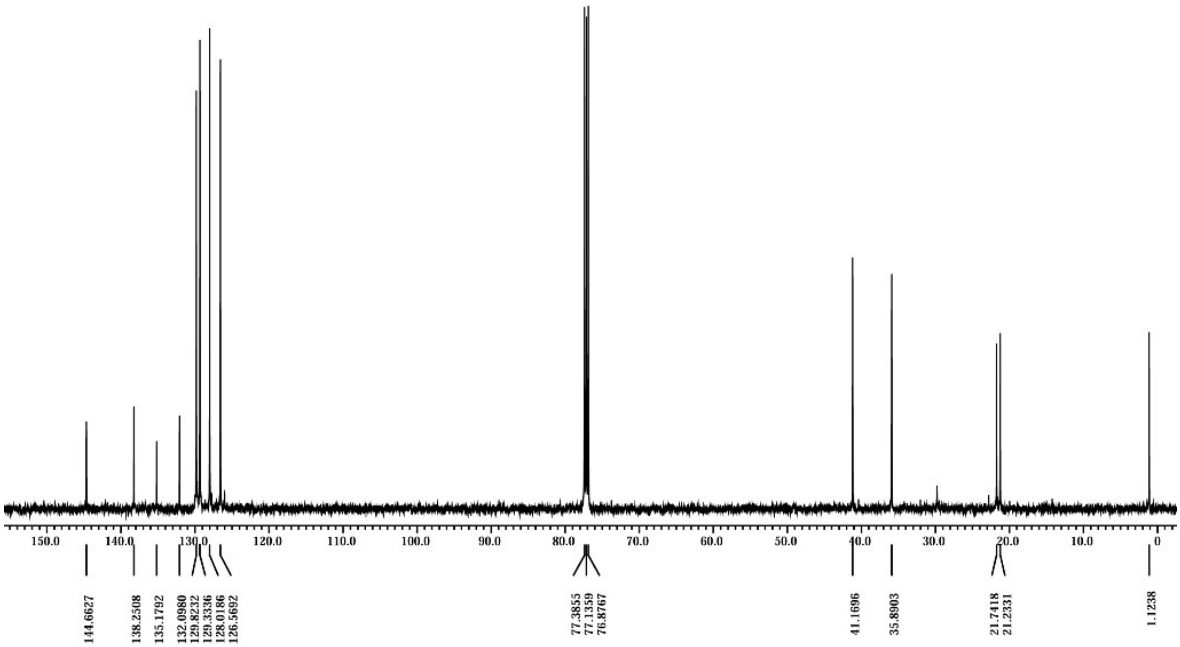
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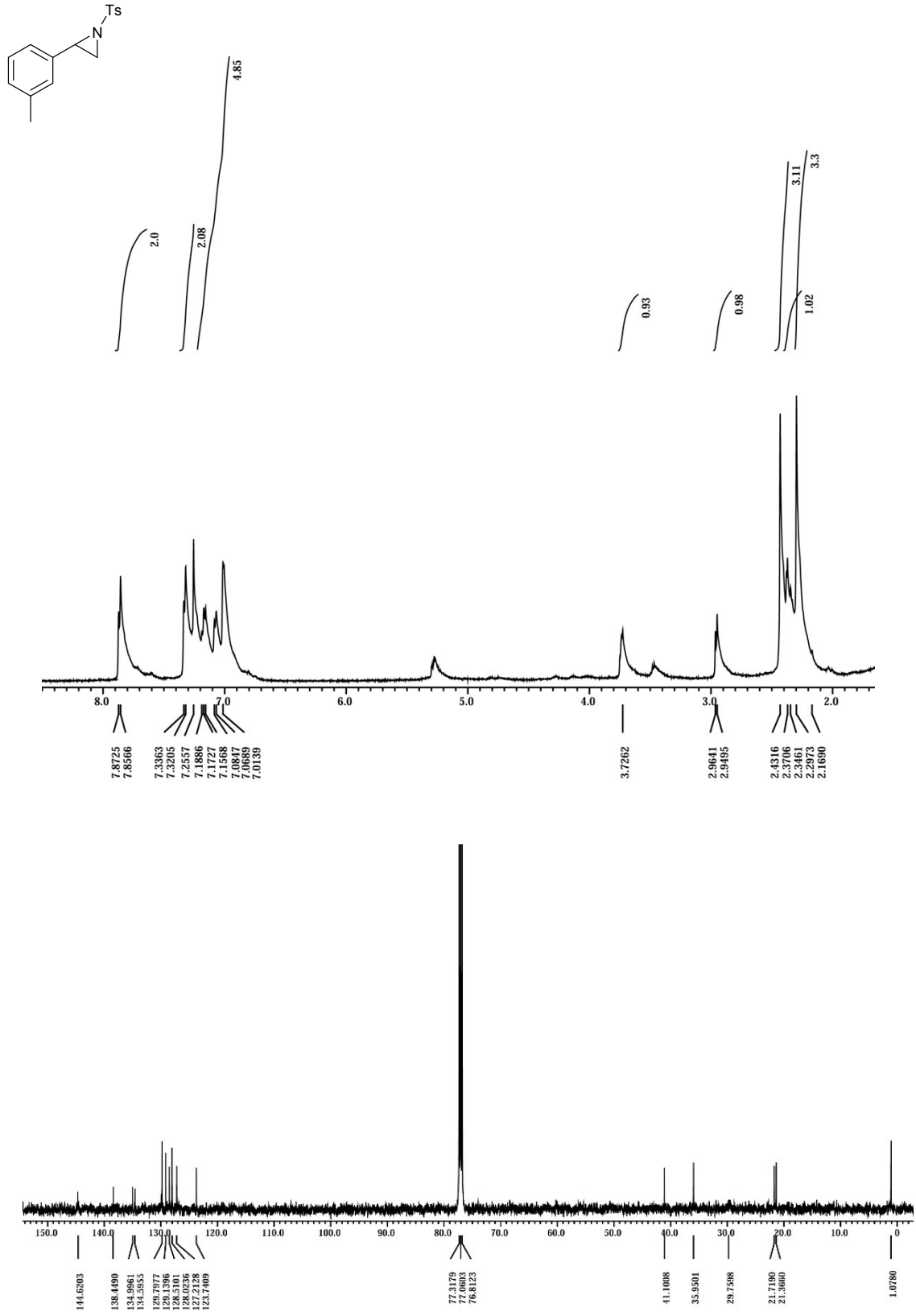
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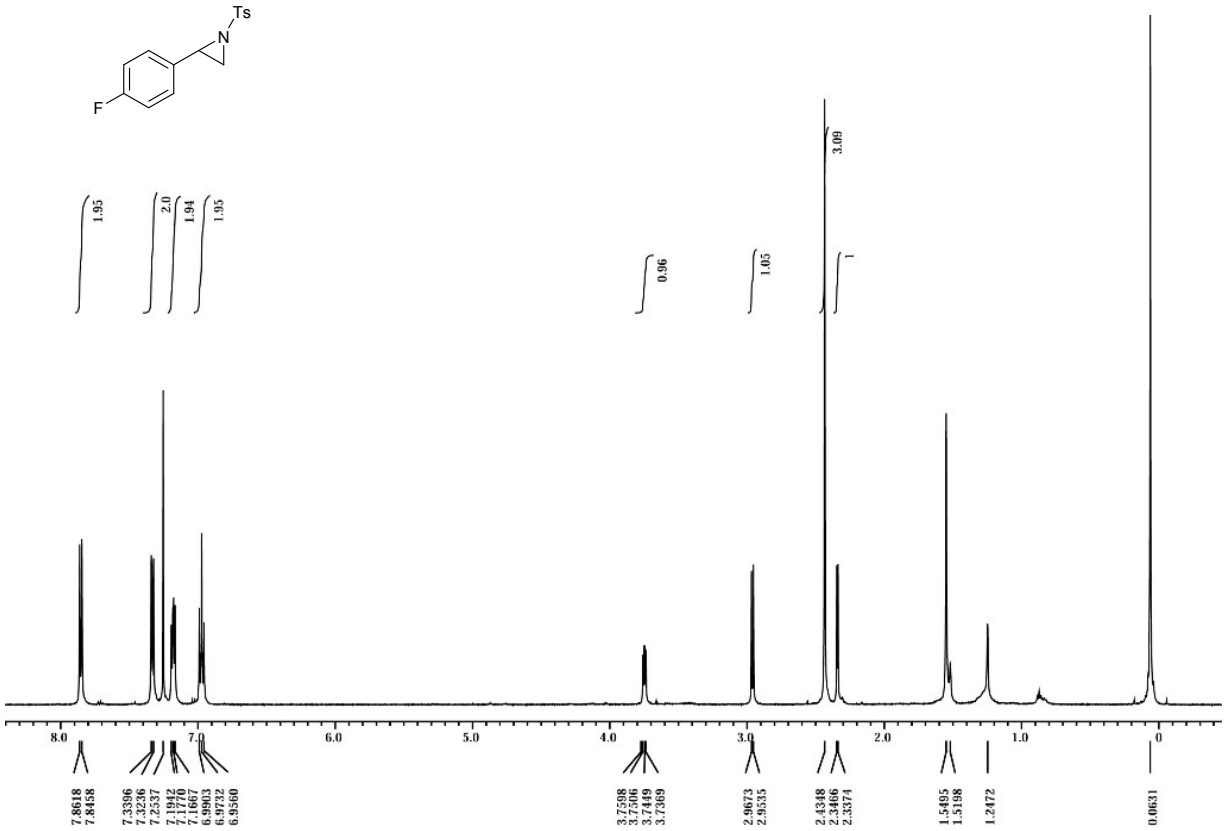
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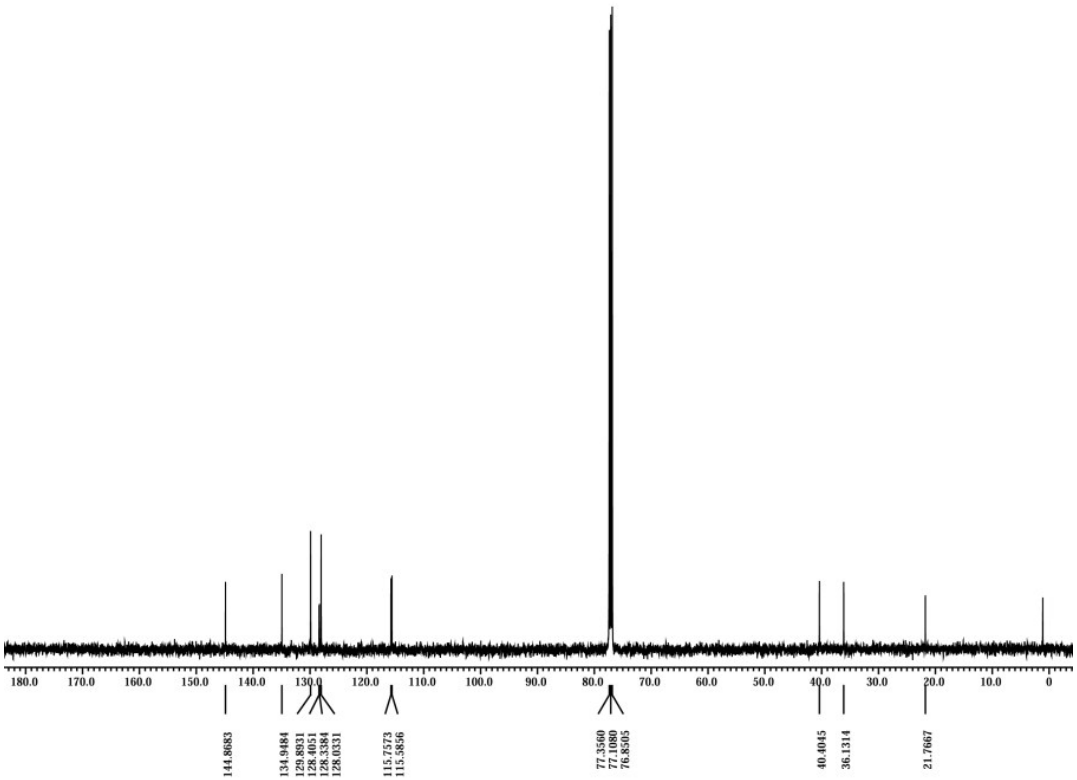
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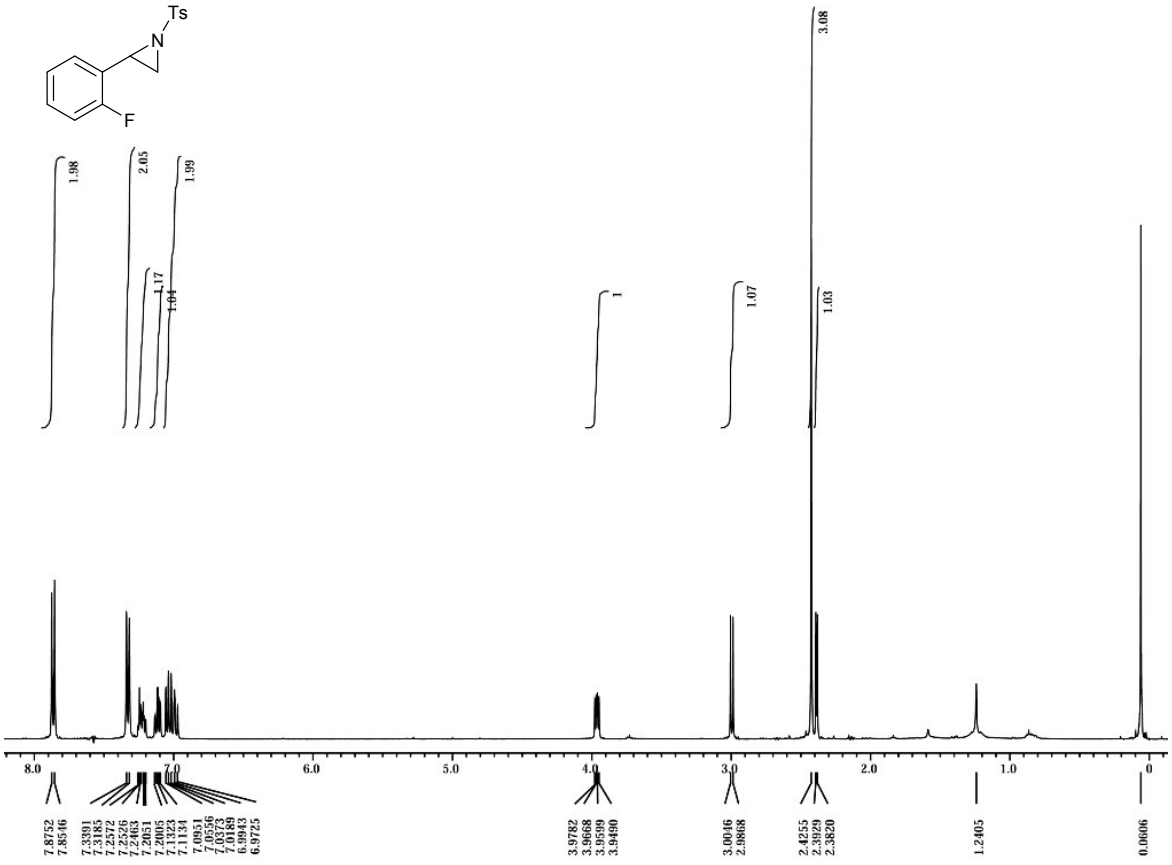
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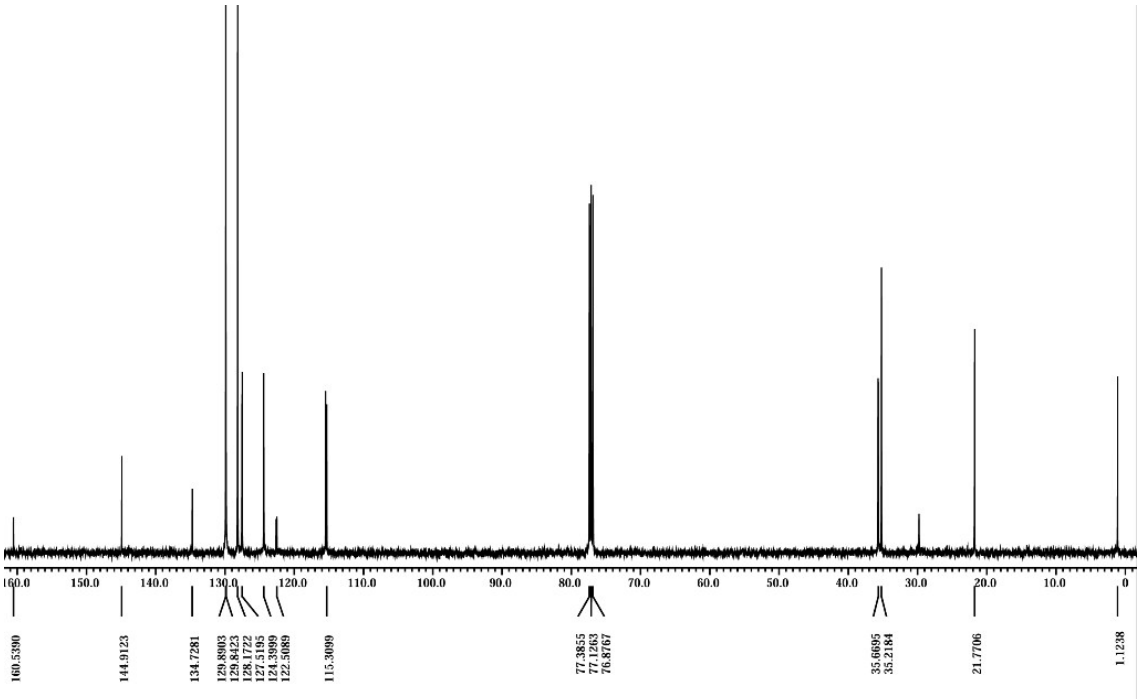
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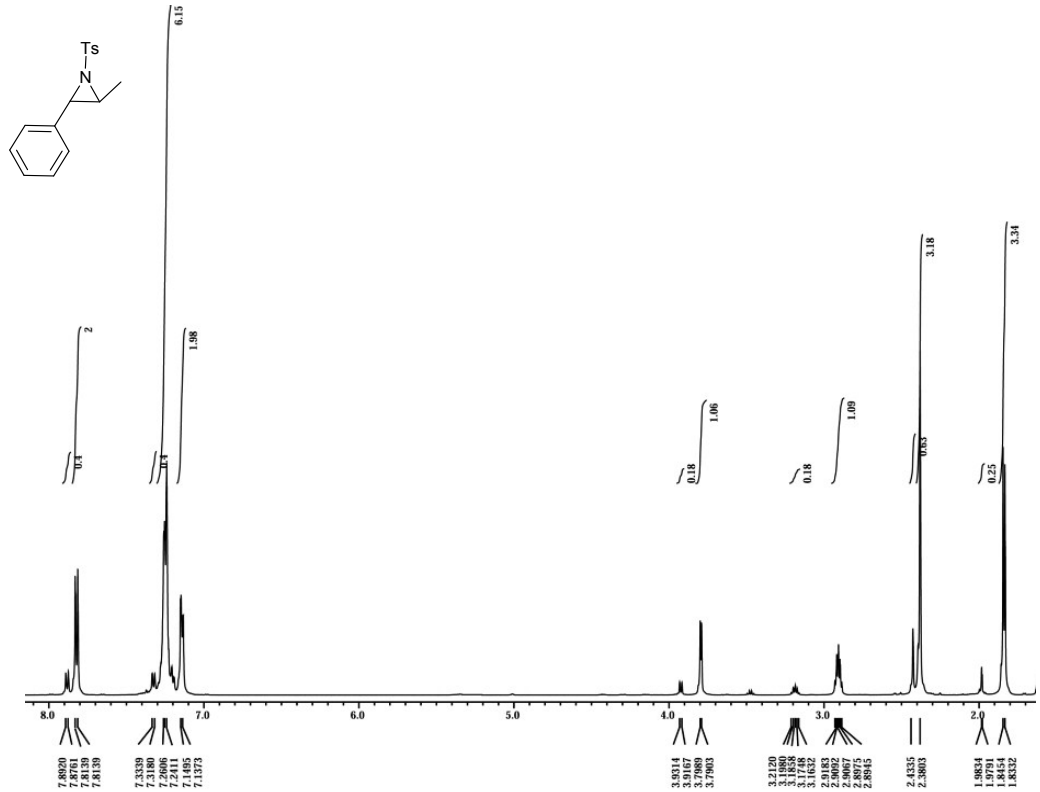
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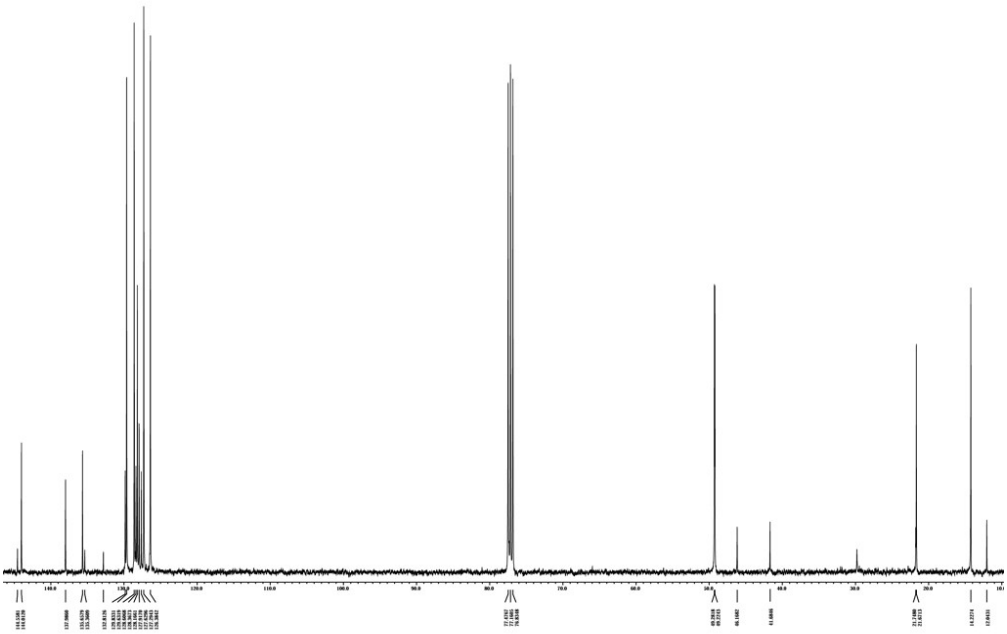

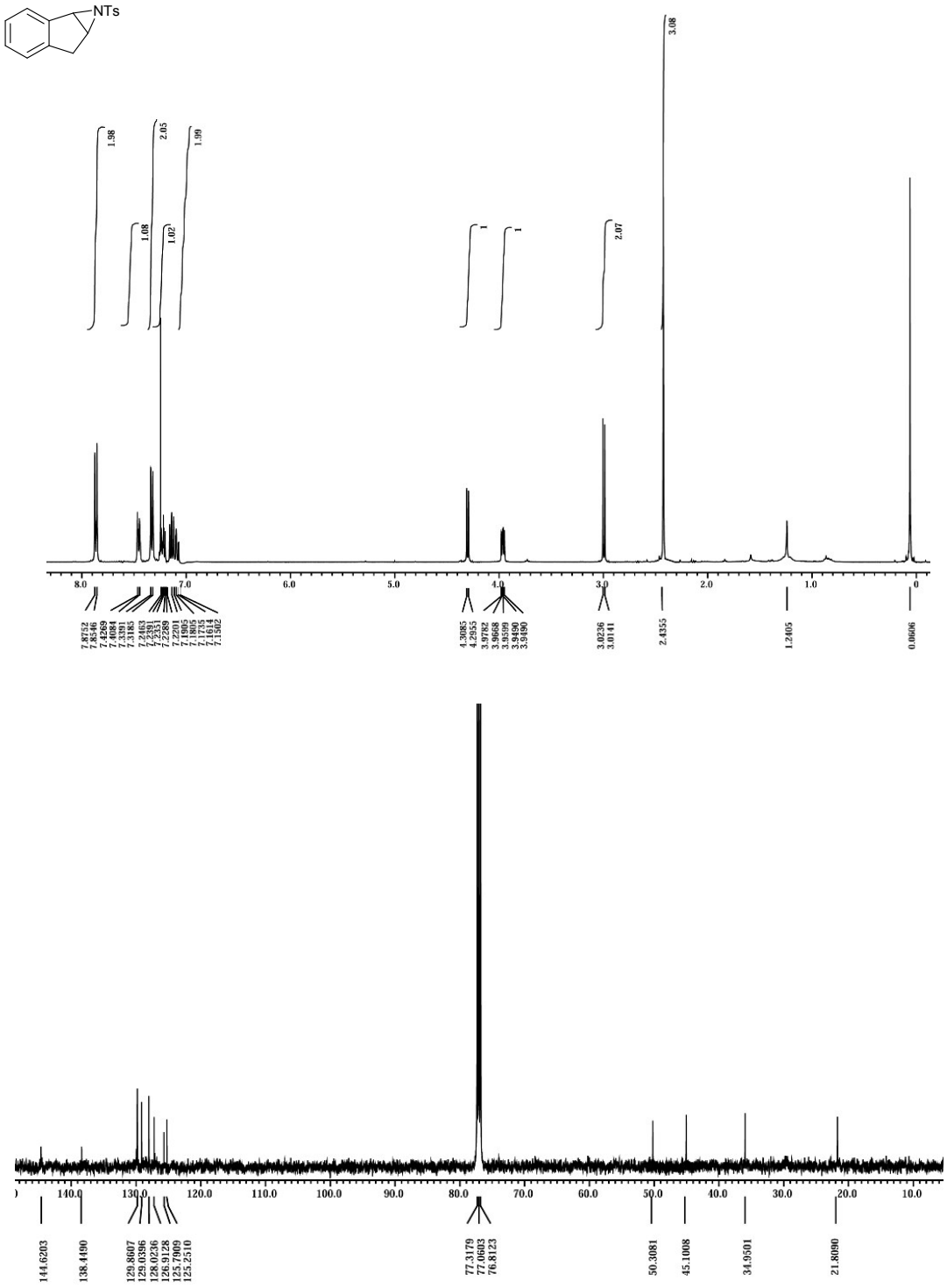
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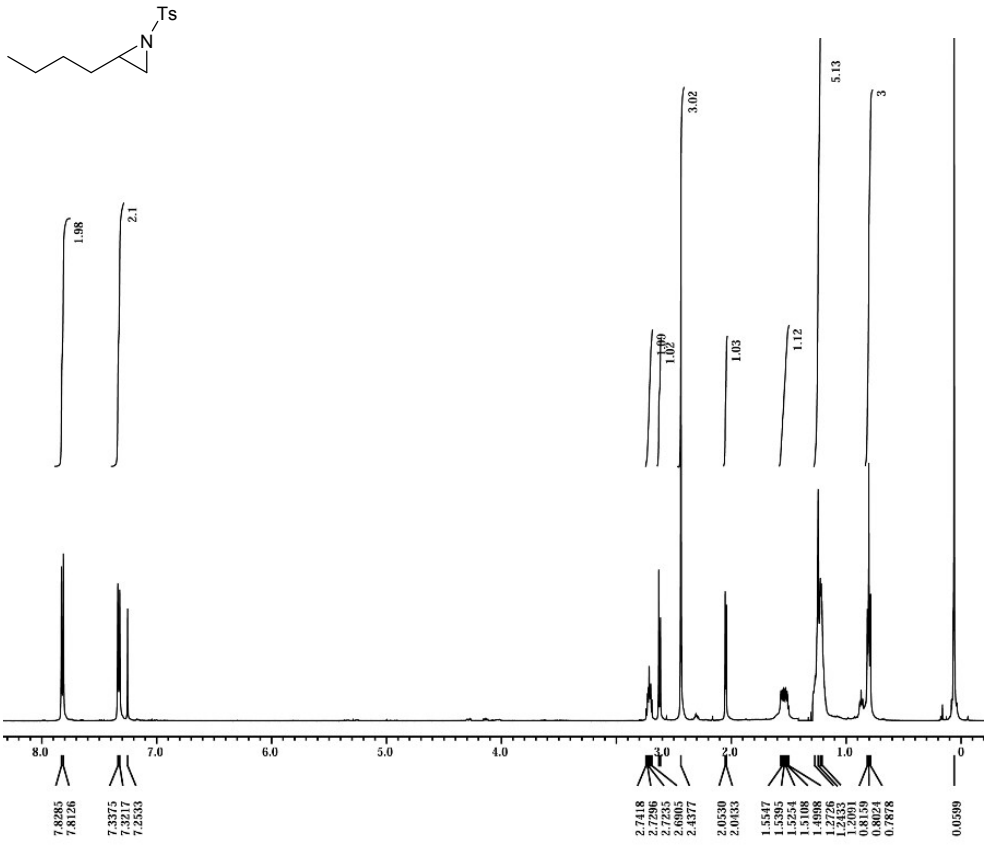
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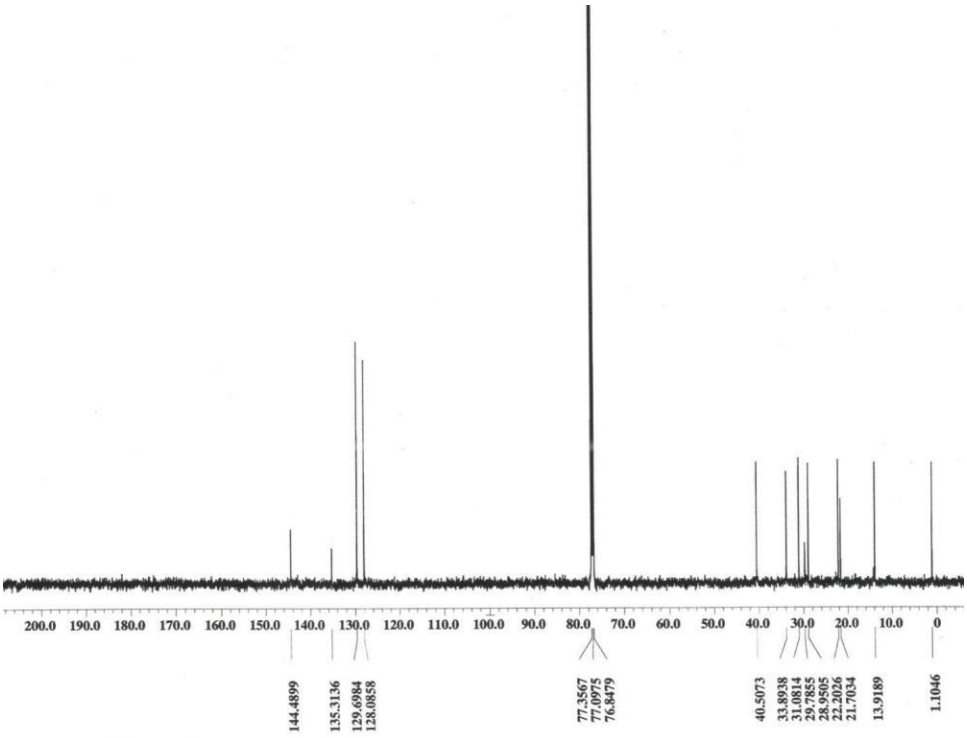
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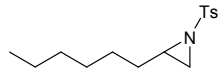
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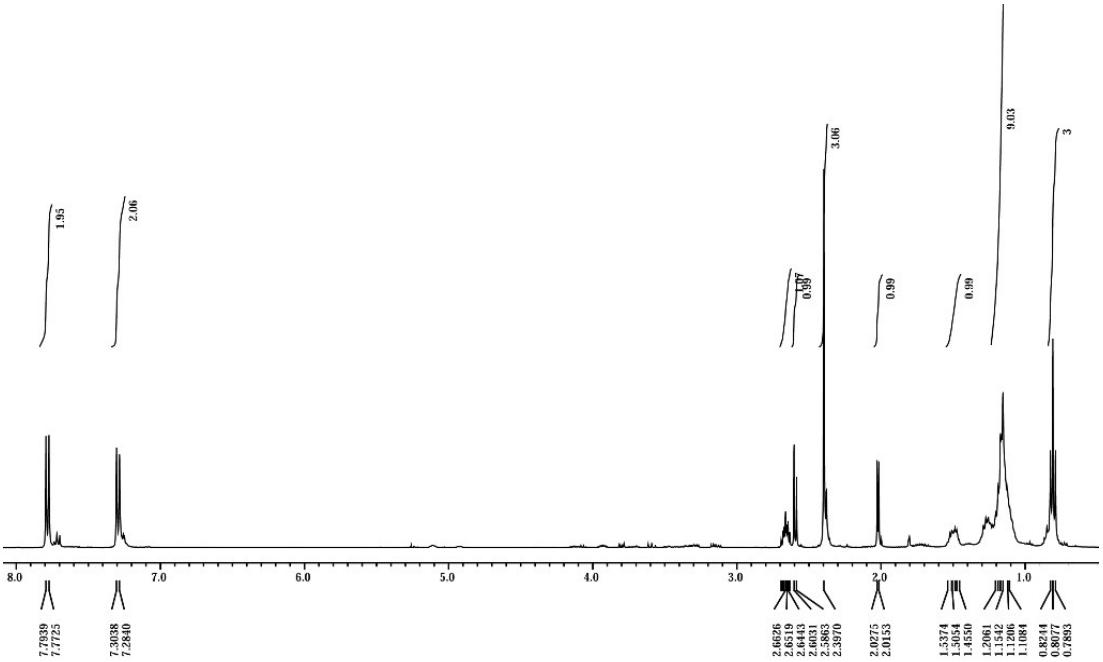
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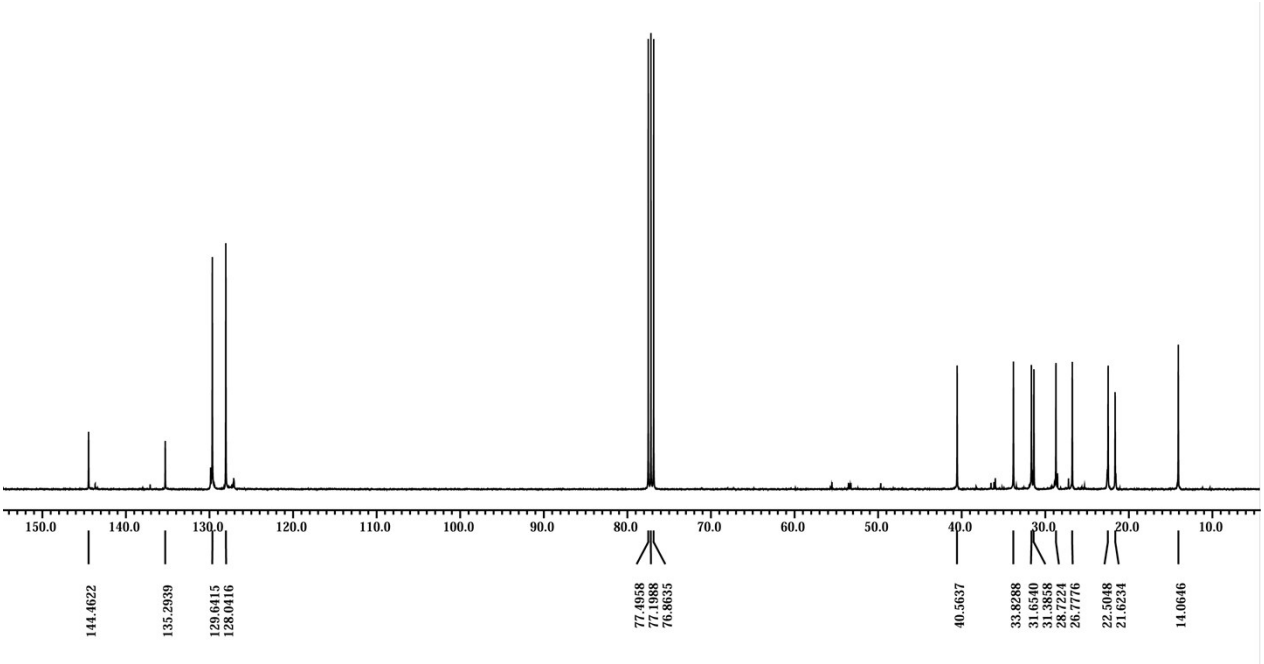
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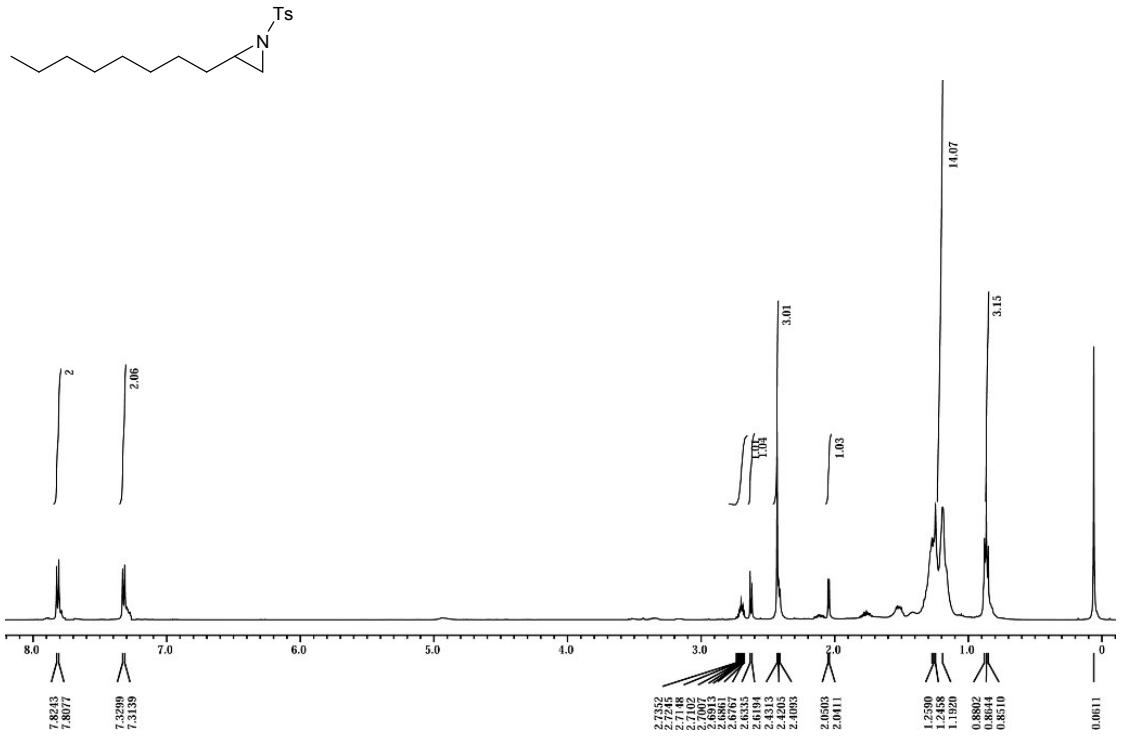
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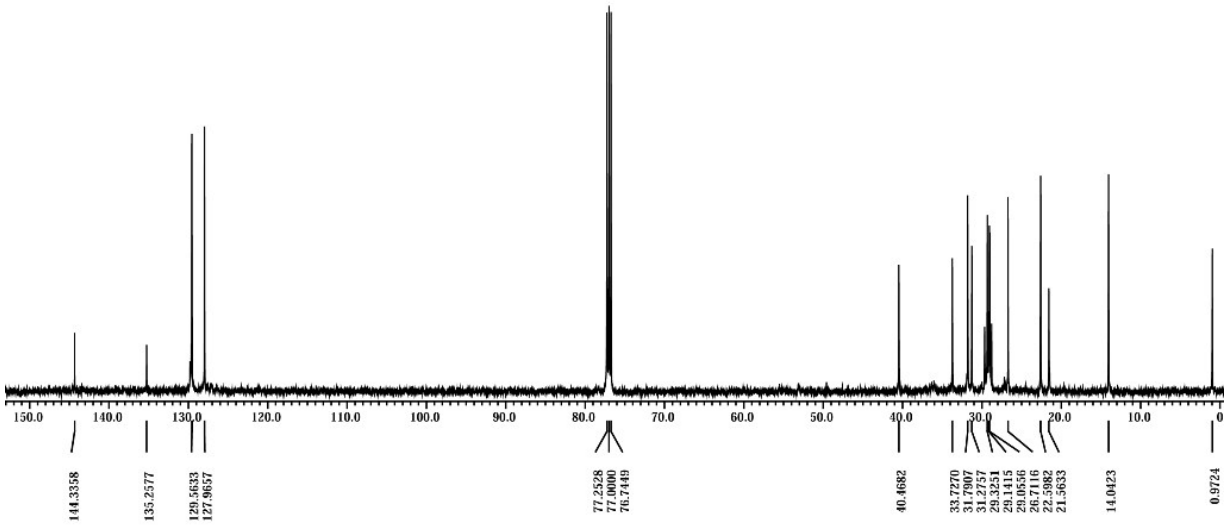
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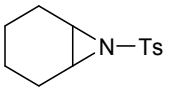
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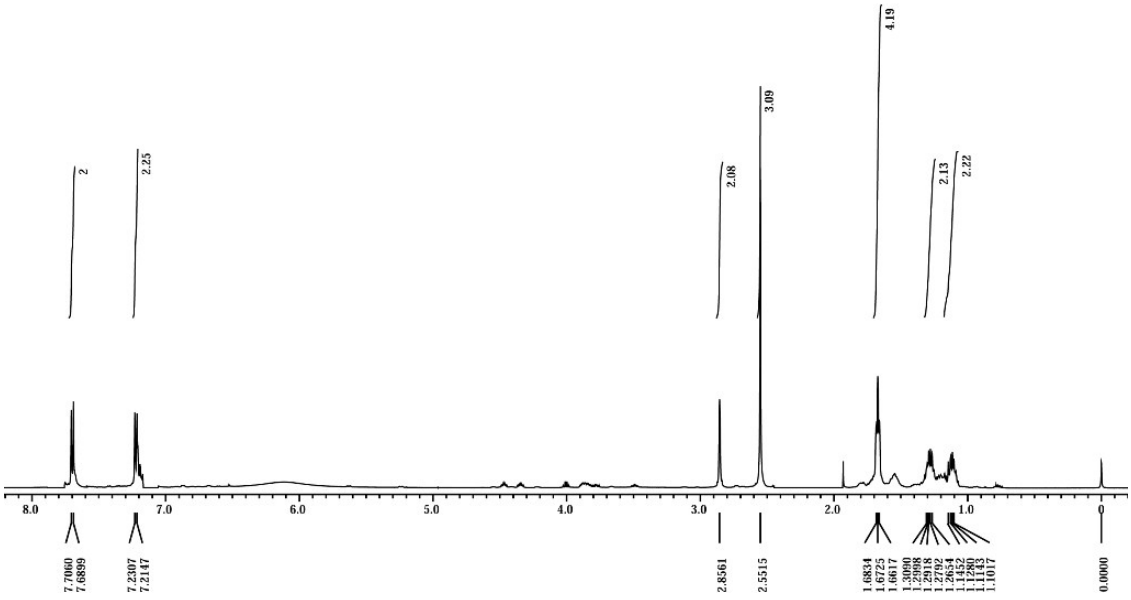
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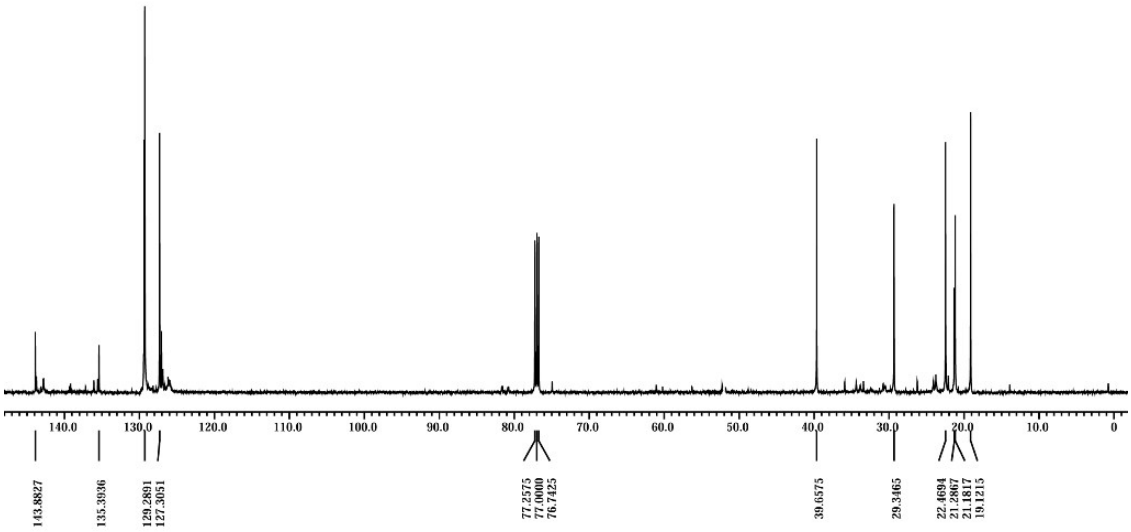
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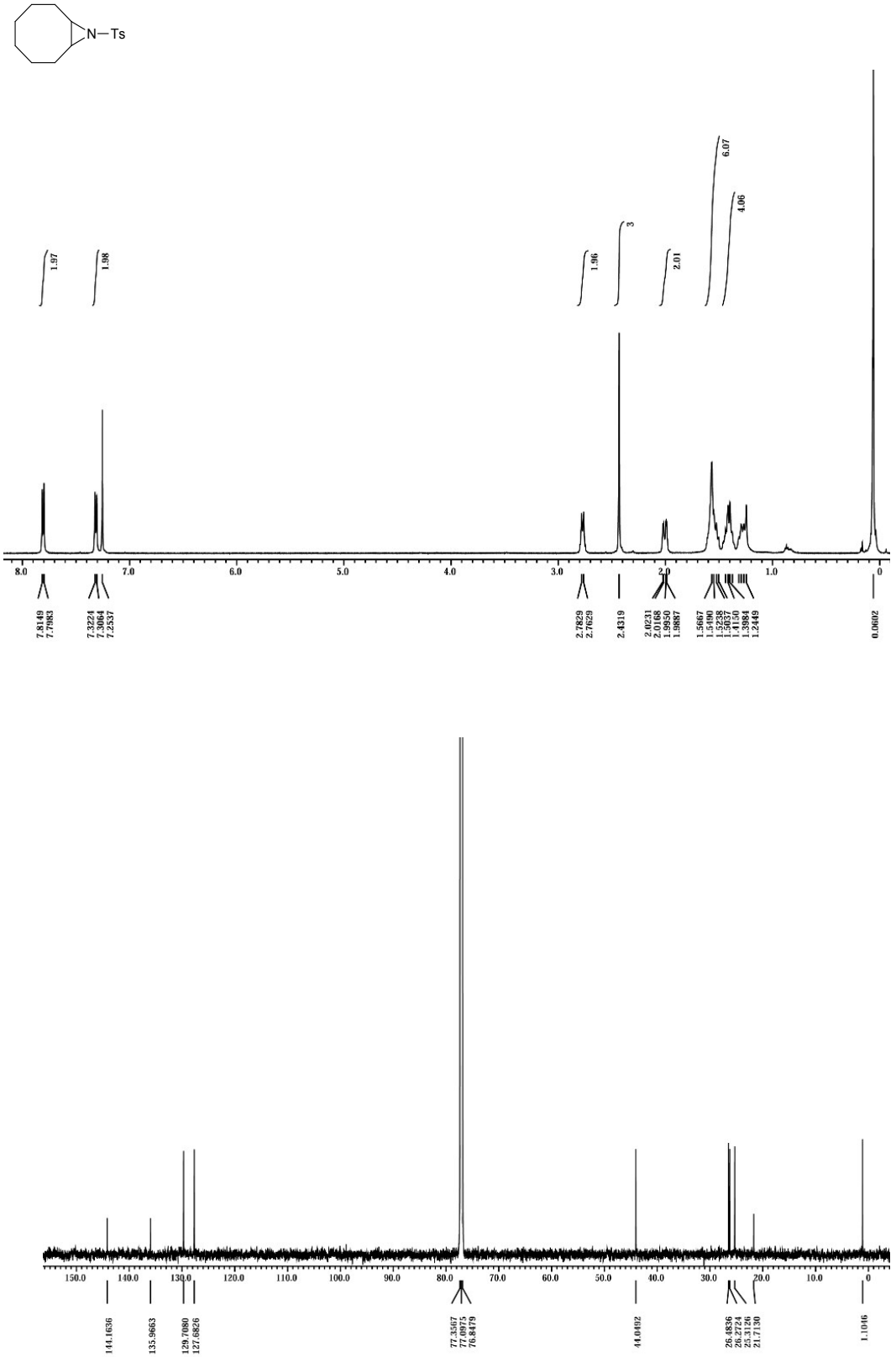
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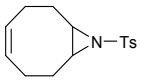
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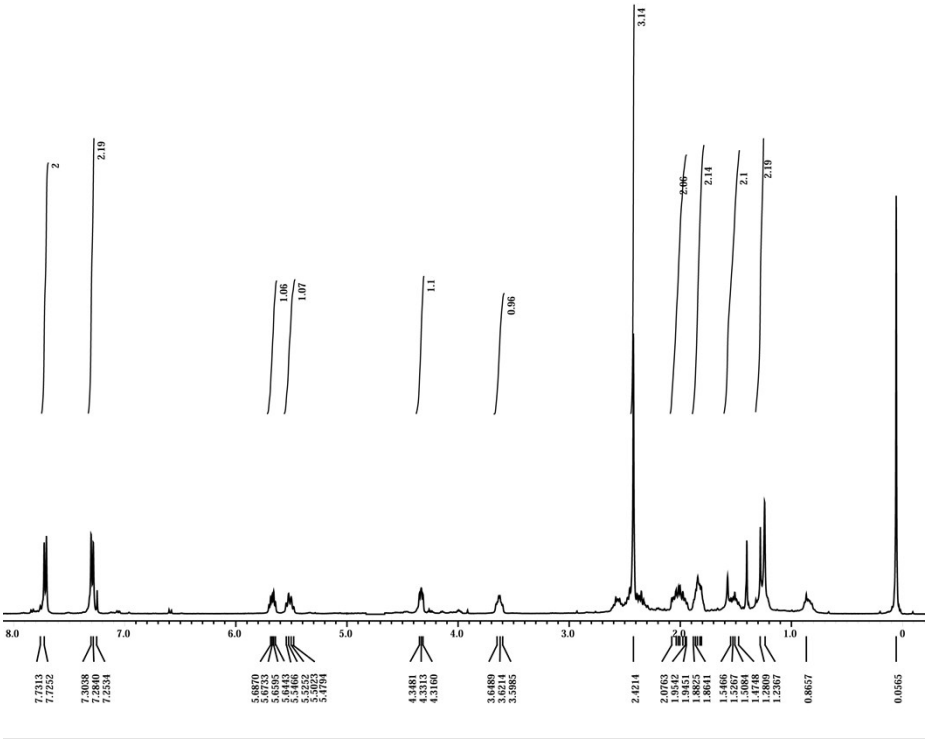
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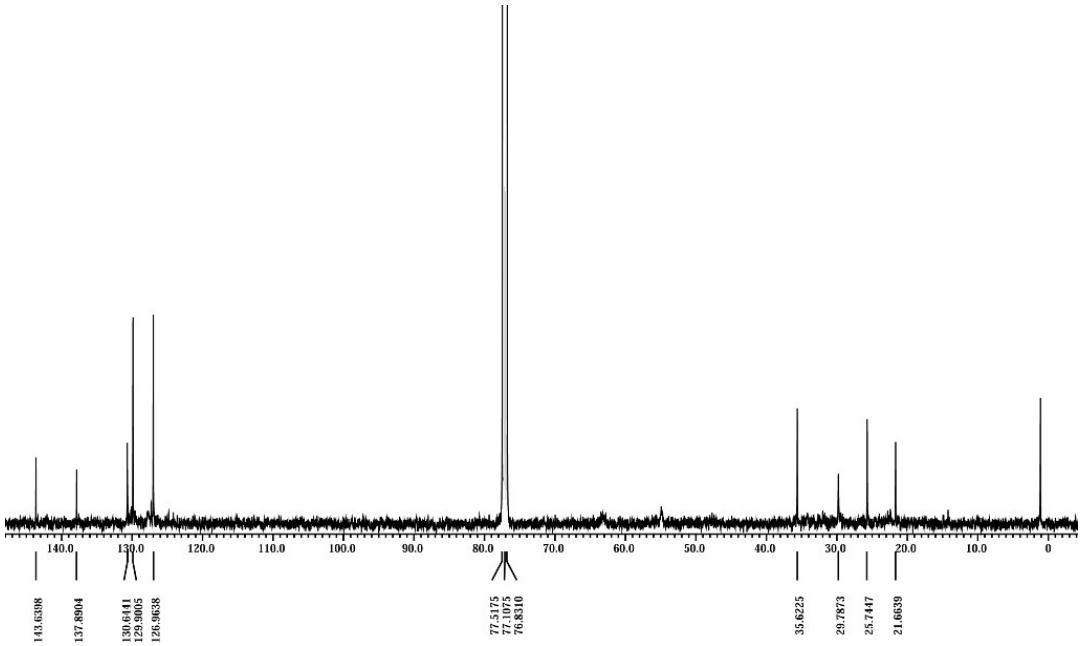
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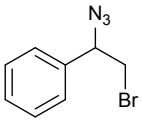
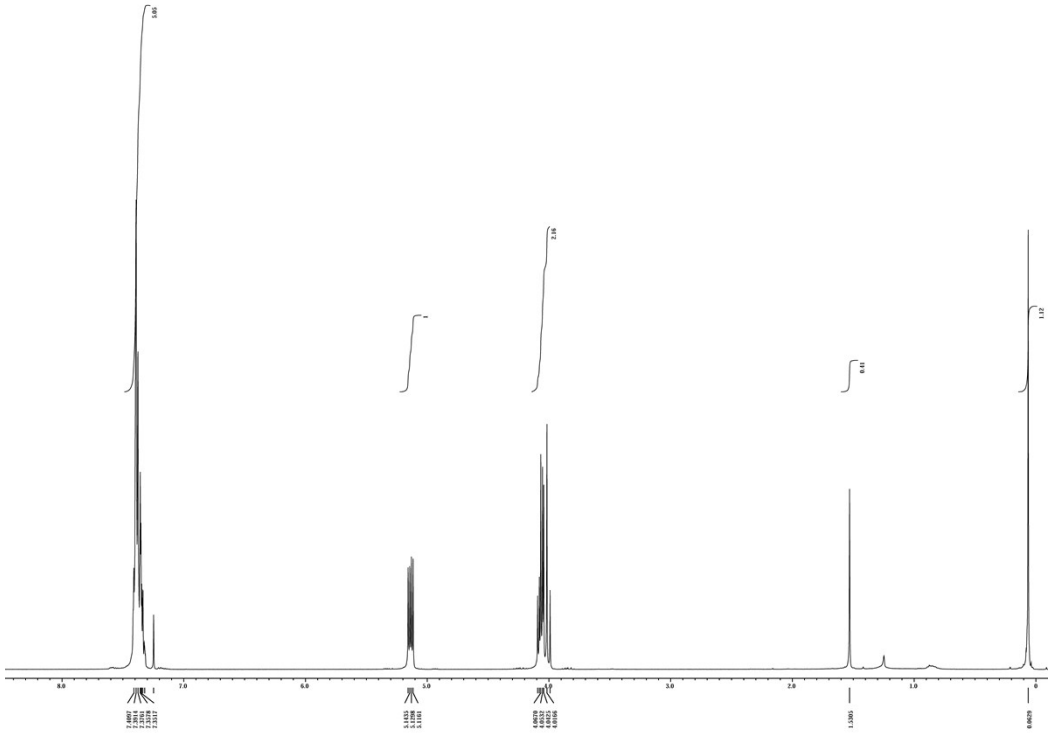
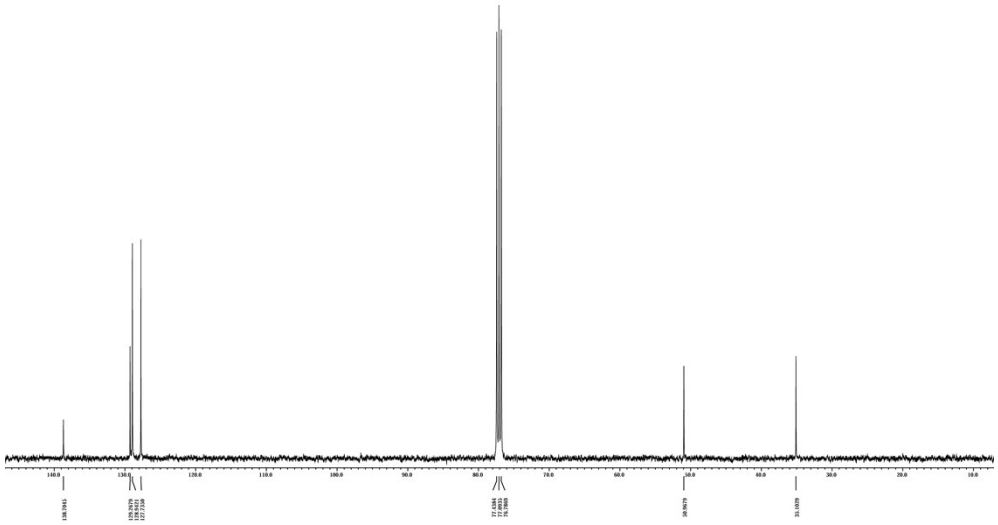

N3
Br





8. References

1. *SAINT*+ Software for CCD difractometers; Bruker AXS: Madison, WI, 2000.

2. a) *SHELXTL* Package v. 6.10*;* Bruker AXS, Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXS-86 and SHELXL-97;* University of Göttingen, Göttingen, Germany, 1997.

3. a) J. L. Atwood and L. J. Barbour, *Cryst. Growth Des*., 2003, **3**, 3; (b) L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

4. Bradenburg, K. *Diamond, version 3.1e;* Crystal Impact GbR, Bonn, Germany, 2005.