## General experimental methods

All reactions were carried out in oven-dried glassware with magnetic stirring. Diphenylacetylene 98%, reagent grade *p*-toluenesulfonamide, ACS reagent copper(II) acetate monohydrate and 98% silver(I) hexafluoroantimonate were purchased from Sigma-Aldrich Co. and used without further purification. 1,4-dioxane was distilled from sodium–benzophenone. When necessary, organic solvents were routinely dried and/or distilled prior to use.

Column chromatography was performed on Silicycle® SilicaFlash® P60 (230-400 mesh). Thin layer chromatography was performed on Silicycle® 250µm silica gel 60A plates. Visualization was accomplished with UV light (254 nm), potassium permanganate or *p*-anisaldehyde stain.

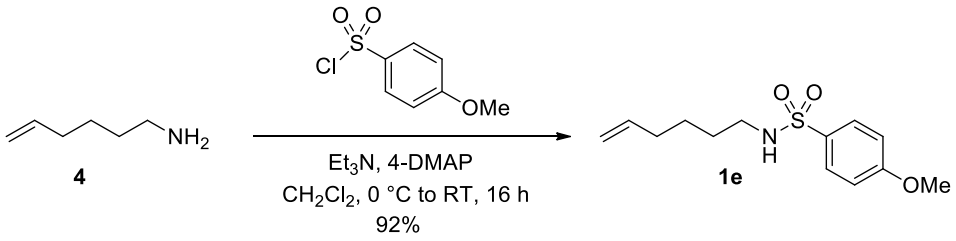
$^1$H NMR and $^{13}$C NMR spectra were collected at ambient temperature in $CDCl_3$ on a Varian 400 MHz. Chemical shifts are expressed as parts per million (δ, ppm) and are referenced to 7.26 ($CHCl_3$) for $^1$H NMR and 77.16 ($CDCl_3$) for $^{13}$C NMR. Proton signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and *J* = coupling constant. Mass spectra were obtained on a Agilent Technologies 6130 Quadropole Mass Spec (LRMS).

Infrared spectra were collected on a Bruker Tensor 27 FT-IR spectrometer.

### 1. Preparation of *N*-sulfonamides

*N*-sulfonamides **1a**,[1] **1b**,[1] **1c**,[2] and **1d**[3] were synthesized following described procedures and the NMR spectra matches with the data reported in the literature.

- Preparation of substrate **1e**




***N*-(Hex-5-en-1-yl)-4-methoxybenzene-1-sulfonamide (1e).** To a solution of amine **4**[4] (99.1 mg, 1.00 mmol) and 4-methoxybenzenesulfonamide (227.3 mg, 1.10 mmol, 1.1 equiv) in $CH_2Cl_2$ (10 mL) at 0 °C were added $Et_3N$ (181 µL, 1.30 mmol, 1.3 equiv) and 4-DMAP (12.2 mg, 0.100 mmol, 0.1 equiv). After 16 h stirring at RT, a saturated aqueous solution of $NH_4Cl$ was added. The layers were separated and the aqueous phase was extracted with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc: 90:10 to 60:40) to afford 248 mg (92%) of sulfonamide **1e** as a colorless oil.

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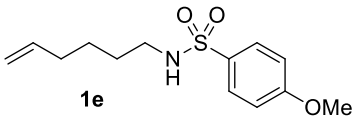
[1] M. Marhold, C. Stillig, R. Froelich, H. Guenter, *Eur. J. Org. Chem.* **2014**, 5777-5785.
[2] T. Cochet, V. Bellosta, D. Roche, J.-Y. Ortholand, A. Greiner, J. Cossy, *Chem. Commun.* **2012**, *48*, 10745-10747.
[3] T. H. Jespen, L. Mogens, M. B. Nielsen, *Tetrahedron*, **2010**, *66*, 6133-6137.
[4] F. E. Michael, B. M. Cochran, *J. Am. Chem. Soc.* **2006**, *128*, 4246-4247.

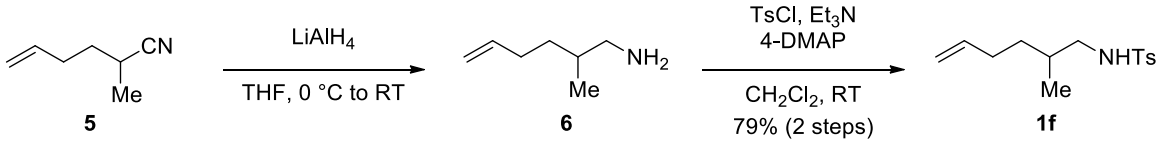



**1e**

$C_{13}H_{19}NO_3S$
M = 269.36 g/mol

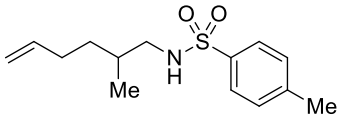
**Rf** (Hex/EA: 80:20) = 0.20. **IR** (neat, $cm^{-1}$) 3279, 1596, 1498, 1322, 1301, 1257, 1150, 1094, 1024, 910, 833, 667. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 8.9 Hz, 2H), 6.97 (d, $J$ = 8.9 Hz, 2H), 5.78 – 5.65 (m, 1H), 5.00 – 4.89 (m, 2H), 4.36 (br s, 1H), 3.87 (s, 3H), 2.98 – 2.89 (m, 2H), 1.99 (dd, app q, $J$ = 7.0 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.41 – 1.31 (m, 2H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 162.8, 138.0, 131.5, 129.2, 114.9, 114.2, 55.6, 43.0, 33.0, 28.9, 25.7. **LRMS** *m/z* (ESI+APCI) calcd for $C_{13}H_{20}NO_3S$ [M+H] 270.1. Found 270.1. **HRMS** calculated for $[C_{13}H_{19}NO_3S+H]^+$ 270.1158. Found 270.1166.

- Preparation of substrate **1f**




**4-Methyl-*N*-(2-methylhex-5-en-1-yl)benzene-1-sulfonamide (1f).** To a suspension of $LiAlH_4$ (228 mg, 6.00 mmol, 1.2 equiv) in THF (40 mL) at 0 °C was slowly added a solution of nitrile **5**[5] (546 mg, 5.00 mmol) in THF (10 mL). After 16 h stirring at RT, water (228 µL), NaOH 10% (228 µL) and water (684 µL) were successively added. After 1 h stirring at RT, the white suspension was filtered through Celite (EtOAc) and concentrated to afford crude amine **6**.

To a solution of crude amine **6** in $CH_2Cl_2$ (25 mL) was successively added TsCl (1.43 g, 7.50 mmol, 1.5 equiv), $Et_3N$ (976 µL, 7.00 mmol, 1.4 equiv) and 4-DMAP (611 mg, 0.50 mmol, 0.1 equiv). After 16 h stirring at RT, a saturated aqueous solution of $NH_4Cl$ was added. The layers were separated and the aqueous phase was extracted with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/$Et_2O$: 90:10 to 70:30) to afford 1.05 g (79%, 2 steps) of sulfonamide **1f** as a colorless oil.




**1f**

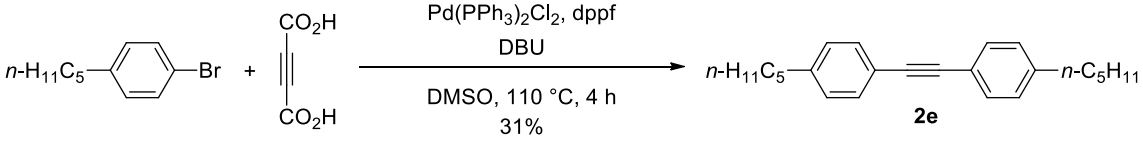
$C_{14}H_{21}NO_2S$
M = 267.39 g/mol

**Rf** (Hex/EA: 85:15) = 0.40. **IR** (neat, $cm^{-1}$) 3283, 1640, 1598, 1428, 1323, 1168, 1093, 1068, 909, 706, 661. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.74 (d, $J$ = 8.3 Hz, 2H), 7.30 (d, $J$ = 7.9 Hz, 2H), 5.78 – 5.63 (m, 1H), 5.01 – 4.87 (m, 2H), 4.51 (s, 1H), 2.79 (dd, $J$ = 41.2, 11.8 Hz, 2H), 2.43 (s, 3H), 2.11 – 1.88 (m, 2H), 1.58 (td, $J$ = 13.2, 6.6 Hz, 1H), 1.46 – 1.35 (m, 1H), 1.22 – 1.09 (m, 1H), 0.86 (d, $J$ = 6.7 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 143.3, 138.3, 137.0, 129.6, 127.0, 114.6, 48.9, 33.0, 32.6, 30.8, 21.5, 17.2. **LRMS** *m/z* (ESI+APCI) calcd for $C_{14}H_{22}NO_2S$ [M+H] 268.1. Found 268.1. **HRMS** calculated for $[C_{14}H_{21}NO_2S+H]^+$ 268.1366. Found 268.1373.

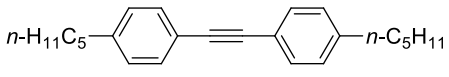
[5] G. A. Molander, S. K. Pack, *J. Org. Chem.* **2003**, *68*, 9214-6220.

## 2. Preparation of alkynes

Alkynes **2b**[6], **2c**,[7] **2d**,[6] **2f**,[6] **2g**,[8] **2h**,[9] **2i**[6] and **2j**[10] were synthesized following described procedures and the NMR spectra matches with the data reported in the literature.




**1-Pentyl-4-[2-(4-pentylphenyl)ethynyl]benzene (2e).** Following a described procedure.[6] $Pd(PPh_3)_2Cl_2$ (105 mg, 0.150 mmol, 0.05 equiv), 1,4-bis(diphenylphosphino)butane (128 mg, 0.300 mmol, 0.1 equiv), 4-pentylbromobenzene (1.36 g, 6.00 mmol, 2 equiv), and 2-butynedioic acid (342 mg, 3.00 mmol) were combined with DBU (913 mg, 6.0 mmol, 2 equiv) in a small round-bottomed flask. DMSO (15.0 mL) was added, and the flask was sealed with a septum. The resulting mixture was placed in an oil bath at 110 °C for 4 h. The reaction was warmed up to room temperature and poured into 25 mL of saturated aqueous ammonium chloride and extracted with $Et_2O$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes to hexanes/$Et_2O$: 98:2) to afford 296 mg (61%) of alkyne **2e** as a white solid.



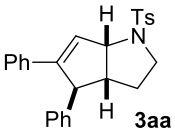

$C_{24}H_{30}$ **2e**
M = 318.50 g/mol

**Rf** (Hexanes) = 0.60. **Mp** = 54 °C. **IR** (neat, $cm^{-1}$) 1516, 1465, 1456, 1372, 1179, 1116, 1019, 828, 813, 784, 726. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 (d, $J$ = 8.1 Hz, 4H), 7.16 (d, $J$ = 8.1 Hz, 4H), 2.65 – 2.58 (m, 4H), 1.69 – 1.57 (m, 4H), 1.41 – 1.24 (m, 8H), 0.91 (t, $J$ = 6.9 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 143.2, 131.4, 128.4, 120.6, 88.9, 35.8, 31.4, 30.9, 22.5, 14.0. **LRMS** *m/z* (ESI+APCI) calcd for $C_{25}H_{35}O$ [M+MeOH+H] 351.3. Found 351.3. **HRMS** calculated for $[C_{24}H_{30}+H]^+$ 319.2420. Found 319.2430.

## 3. Reactions of *N*-sulfonamides with alkynes

[6] K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244-6251.
[7] R. J. Perner, Y.-G. Gu, C.-H. Lee, E. K. Bayburt, J. McKie, K. M. Alexander, K. L. Kohlhaas, C. T. Wismer, J. Mikusa, M. F. Jarvis, E. A. Kowaluk, S. S. Bhagwat, *J. Med. Chem.* **2003**, *46*, 5249-5257.
[8] M. Endou, Y. Ie, Y. Aso, *Heterocycles* **2008**, *76*, 1043-1048.
[9] M. J. Mayoral, M. Rest,V. Stepanenko, J. Schellheimer, R. Q. Albuquerque, G. Fernandez, *J. Am. Chem. Soc.* **2013**, *135*, 2148-2151.
[10] P. S. Pinkney, G. A. Nest, D. E. Pearson, C. S. Marvel, *J. Am. Chem. Soc.* **1937**, *59*, 2666-2668.

**General procedure: (3a*R**,4*S**,6a*R**)-1-(4-Methylbenzenesulfonyl)-4,5-diphenyl-1H,2H,3H,3aH,4H, 6aH-cyclopenta-[b]-pyrrole (3aa).** A 1.5 dram vial was charged with *N*-tosylamide **1a** (47.9 mg, 0.200 mmol), diphenylacetylene **2a** (44.6 mg, 0.250 mmol, 1.25 equiv), $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %). After addition of 1,4-dioxane (2 mL, 0.1M), the vial was sealed and heated at 120 °C for 16 h. The resulting blue mixture was filtrated through a short plug of silica and Celite (hexanes/EtOAc: 30:70) and concentrated under reduced pressure. Analysis of the crude material by $^1$H NMR and $^{13}$C NMR revealed the presence of a single diastereomer (d. r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 58.3 mg (70%) of **3aa** as a colorless oil. The residue was taken up in $Et_2O$ which have been slowly evaporated to afford suitable crystals for X-ray analysis.

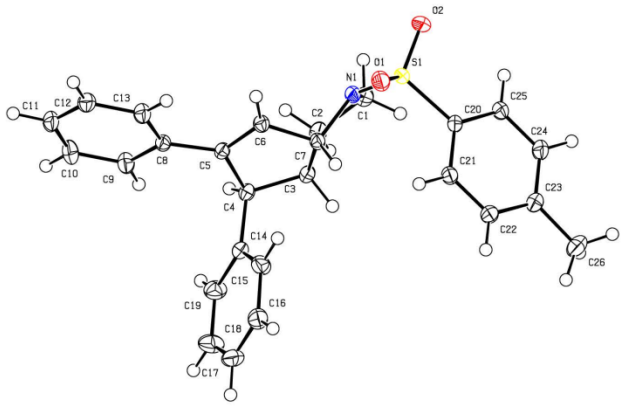



**3aa**

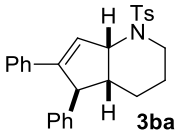
$C_{26}H_{25}NO_2S$
M = 415.55 g/mol

**Rf** (Hex/EA: 85:15) = 0.45. **Mp** = 140 °C. **IR** (neat, $cm^{-1}$) 1598, 1494, 1446, 1331, 1156, 1091, 1057, 756, 701, 661. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.76 (d, $J$ = 8.2 Hz, 2H), 7.38 – 7.09 (m, 12H), 6.54 (br s, 1H), 4.83 (br d, $J$ = 7.8 Hz, 1H), 4.06 (s, 1H), 3.56 – 3.49 (m, 1H), 3.06 (td, $J$ = 9.6 Hz and $J$ = 6.3 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.41 (s, 3H), 2.12 – 2.03 (m, 1H), 1.92 – 1.80 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 144.3, 143.5, 143.4, 134.6, 134.5, 129.7, 128.8, 128.3, 128.1, 127.8, 127.5, 127.0, 126.8, 126.6, 68.8, 57.3, 51.8, 48.2, 32.0, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{26}H_{26}NO_2S$ [M+H] 416.2. Found 416.2. **HRMS** calculated for $[C_{26}H_{25}NO_2S+H]^+$ 416.1679. Found 416.1691.

Single crystal X-ray analysis of this compound revealed that the phenyl group is located on the *exo* face of the molecule.



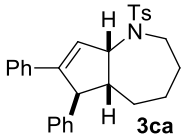

**(4a*R**,5*S**,7a*R**)-1-(4-Methylbenzenesulfonyl)-5,6-diphenyl-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta-[b]-pyridine (3ba).** This compound was prepared by treatment of *N*-tosylamide **1b** (50.7 mg, 0.200 mmol) and diphenylacetylene (44.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 61.0 mg (72%) of **3ba** as a colorless oil.




$C_{27}H_{27}NO_2S$
M = 429.57 g/mol

**Rf** (Hex/EA: 85:15) = 0.45. **IR** (neat, $cm^{-1}$) 1718, 1598, 1494, 1445, 1337, 1303, 1161, 1096, 1038, 969, 935, 815, 751, 700, 659. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.73 (d, $J$ = 8.2 Hz, 2H), 7.34 – 7.13 (m, 12H), 6.13 (s, 1H), 5.22 (d, $J$ = 6.4 Hz, 1H), 3.86 (s, 1H), 3.76 (br d, $J$ = 12.7 Hz, 1H), 2.92 (app td, $J$ = 12.1 Hz and $J$ = 2.4 Hz, 1H), 2.44 (s, 3H), 2.33 – 2.23 (m, 1H), 1.93 – 1.83 (m, 1H), 1.62 – 1.31 (m, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 145.3, 143.1, 141.0, 137.7, 134.7, 129.7, 128.8, 128.3, 127.9, 127.2, 127.1, 126.6, 126.4, 126.2, 60.0, 57.3, 46.4, 42.1, 27.6, 23.1, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{27}H_{28}NO_2S$ [M+H] 430.2. Found 430.2. **HRMS** calculated for $[C_{27}H_{27}NO_2S+H]^+$ 430.1835. Found 430.1841.

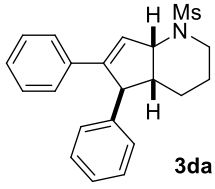
**(5a*R**,6*S**,8a*R**)-1-(4-Methylbenzenesulfonyl)-6,7-diphenyl-1H,2H,3H,4H,5H,5aH,6H,8aH-cyclopenta[b]azepine (3ca).** This compound was prepared by treatment of *N*-tosylamide **1c** (53.5 mg, 0.200 mmol) and diphenylacetylene (44.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 58.4 mg (66%) of **3ca** as a yellow oil.




$C_{28}H_{29}NO_2S$
M = 443.60 g/mol

**Rf** (Hex/EA: 90:10) = 0.20. **IR** (neat, $cm^{-1}$) 1598, 1494, 1445, 1331, 1157, 1111, 1090, 910, 815, 752, 700, 659. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.77 (d, $J$ = 8.1 Hz, 2H), 7.32 (d, $J$ = 8.1 Hz, 2H), 7.26 – 7.07 (m, 10H), 5.78 (br s, 1H), 5.36 (br d, $J$ = 9.5 Hz, 1H), 4.21 – 4.16 (m, 1H), 3.78 (br d, $J$ = 14.9 Hz, 1H), 2.82 – 2.71 (m, 2H), 2.45 (s, 3H), 1.94 – 1.51 (m, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 147.2, 144.5, 142.8, 138.7, 134.4, 129.7, 128.7, 128.2, 127.8, 127.1, 126.8, 126.7, 126.4, 126.3, 65.1, 55.1, 51.9, 44.9, 31.0, 29.0, 23.5, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{28}H_{30}NO_2S$ [M+H] 444.2. Found 444.2. **HRMS** calculated for $[C_{28}H_{29}NO_2S+H]^+$ 444.1992. Found 444.2007.

**(4a*R**,5*S**,7a*R**)-1-Methanesulfonyl-5,6-diphenyl-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta[b]pyridine (3da)**. This compound was prepared by treatment of *N*-methanesulfonylamide **1d** (32.6 mg, 0.200 mmol) and diphenylacetylene **2a** (44.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 65:35) gave 49.5 mg (70%) of **3da** as a yellow oil.

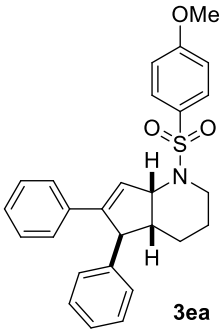



$C_{21}H_{23}NO_2S$
M = 353.48 g/mol

**Rf** (Hex/EA: 90:10) = 0.12. **IR** (neat, $cm^{-1}$) 1600, 1493, 1445, 1323, 1157, 1139, 1039, 936, 910, 891, 780, 726, 729, 700. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.35 (m, 2H), 7.31 – 7.15 (m, 8H), 6.41 (br s, 1H), 5.13 (d, $J$ = 6.3 Hz, 1H), 3.95 (s, 1H), 3.77 (br d, $J$ = 13.4 Hz, 1H), 3.06 – 2.97 (m, 1H), 2.91 (s, 3H), 2.41 – 2.33 (m, 1H), 2.07 – 1.98 (m, 1H), 1.72 – 1.63 (m, 1H), 1.62 – 1.47 (m, 2H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$

145.6, 140. 9, 134.6, 128.8, 128.4, 128.0, 127.2, 126.7, 126.7, 126.2, 59.8, 57.5, 46.5, 42.0, 39.9, 27.7, 23.7. **LRMS** *m/z* (ESI+APCI) calcd for $C_{21}H_{24}NO_2S$ [M+H] 354.2. Found 354.2. **HRMS** calculated for $[C_{21}H_{23}NO_2S+H]^+$ 354.1522. Found 354.1536.

**(4a*R**,5*S**,7a*R**)-1-(4-Methoxybenzenesulfonyl)-5,6-diphenyl-1H,2H,3H,4H,4aH,5H,7aH-cyclo-penta[b]-pyridine** (**3ea**). This compound was prepared by treatment of *N*-paramethoxy-benzenesulfonamide **1e** (53.9 mg, 0.200 mmol) and diphenylacetylene **2a** (44.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 90:10 to 60:40) gave 62.3 mg (70%) of **3ea** as a colorless oil.

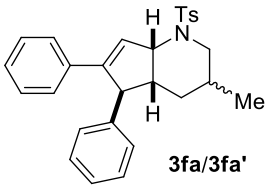



**3ea**

$C_{27}H_{27}NO_3S$
M = 445.57 g/mol

**Rf** (Hex/EA: 90:10) = 0.12. **IR** (neat, $cm^{-1}$) 1593, 1577, 1494, 1455, 1446, 1342, 1331, 1296, 1257, 1154, 1139, 1097, 1021, 935, 836, 826, 662. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, *J* = 8.9 Hz, 2H), 7.31 – 7.13 (m, 10H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.16 (s, 1H), 5.21 (d, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.87 (br s, 1H), 3.74 (br d, *J* = 12.6 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.33 – 2.24 (m, 1H), 1.94 – 1.84 (m, 1H), 1.60 – 1.31 (m, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 162.7, 145.3, 141.1, 134.8, 132.4, 129.2, 128.8, 128.6, 127.9, 127.2, 126.6, 126.4, 126.2, 114.2, 60.0, 57.3, 55.6, 46.4, 42.1, 27.6, 23.1. **LRMS** *m/z* (ESI+APCI) calcd for $C_{27}H_{28}NO_3S$ [M+H] 446.2. Found 446.2. **HRMS** calculated for $[C_{27}H_{27}NO_3S+H]^+$ 446.1784. Found 446.1788.

**(4a*R**,5*S**,7a*R**)-3-Methyl-1-(4-methylbenzenesulfonyl)-5,6-diphenyl-1H,2H,3H,4H,4aH,5H,7aH-cyclo-penta-[b]pyridine (3fa/3fa').** In a 1.5 dram vial were added *N*-tosylamide **1f** (53.5 mg, 0.200 mmol), diphenylacetylene **2a** (44.6 mg, 0.250 mmol, 1.25 equiv), $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %). After addition of 1,4-dioxane, the vial was sealed and heated at 120 °C for 16 h. The resulting blue mixture was filtrated through a short plug of silica and Celite (EtOAc) and concentrated under reduced pressure. $^1$H NMR spectra of the crude material showed a 1:1 mixture of diastereomers **3fa** and **3fa'** (determination with the vinylic proton signal). Purification by flash chromatography (hexanes/$Et_2O$: 95:5 to 80:20) gave 37.2 mg (42%) of a 1:1 mixture of regioisomers **3fa** and **3fa'** as a yellow solid.



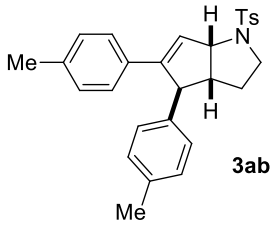

**3fa/3fa'**

$C_{28}H_{29}NO_2S$
M = 443.60 g/mol

**Rf** (Hex/EA: 85:15) = 0.40. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.77-7.70 (m, 2H), 7.34 – 7.11 (m, 12H), 6.11 (s, 0.5*1H), 6.06 (s,

0.5*1H), 5.22 (d, *J* = 6.2 Hz, 0.5*1H), 5.04 (d, *J* = 7.0 Hz, 0.5*1H), 3.87 (s, 0.5*1H), 3.82 (s, 0.5*1H), 3.71 (d, *J* = 12.6 Hz, 0.5*1H), 3.23 (dd, *J* = 12.2 Hz and *J* = 4.8 Hz, 0.5*1H), 3.18 (dd, *J* = 12.2 Hz and *J* = 4.1 Hz, 0.5*1H), 2.52 – 2.48 (m, 0.5*1H), 2.48 – 2.42 (m, 1H), 2.45 (s, 0.5*3H), 2.44 (s, 0.5*3H), 2.35 – 2.27 (m, 0.5*1H), 1.99 – 1.85 (m, 0.5*1H), 1.69 – 1.60 (m, 0.5*1H) 1.55 – 1.48 (m, 0.5*1H), 0.92 – 0.84 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 0.5*3H), 0.81 (d, *J* = 6.9 Hz, 0.5*3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 146.0, 145.0, 143.1, 143.1, 141.9, 140.7, 137.8, 137.1, 134.7, 134.7, 129.7, 129.6, 128.8, 128.8, 128.4, 128.3, 127.9, 127.8, 127.3, 127.2, 127.1, 126.6, 126.6, 126.5, 126.3, 126.1, 126.0, 60.1, 59.3, 57.4, 57.0, 48.5, 47.8, 46.9, 44.4, 37.1, 33.5, 29.3, 26.4, 21.5, 18.9, 17.6.

**(3a*R**,4*S**,6a*R**)-1-(4-Methylbenzenesulfonyl)-4,5-bis(4-methylphenyl)-1H,2H,3H,3aH,4H,6aH-cyclo-penta[b]pyrrole (3ab).** This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and 1,2-di-*p*-tolylethyne **2b**[6] (51.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 61.4 mg (69%) of **3ab** as a white solid.

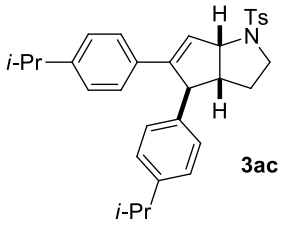


**3ab**

$C_{28}H_{29}NO_2S$
M = 443.60 g/mol

**Rf** (Hex/EA: 90:10) = 0.16. **Mp** = 150 °C. **IR** (neat, $cm^{-1}$) 1597, 1512, 1448, 1339, 1157, 1091, 1031, 885, 808, 729, 715, 663. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.95 (m, 6H), 6.46 (s, 1H), 4.81 (br d, *J* = 7.8 Hz, 1H), 4.00 (s, 1H), 3.55 – 3.46 (m, 1H), 3.04 (td, *J* = 9.6 Hz and *J* = 6.3 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.41 (s, 3H), 2.26 (s, 6H), 2.09 – 1.99 (m, 1H), 1.89 – 1.77 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) *δ* 144.2, 143.3, 140.6, 137.7, 136.1, 134.6, 131.8, 129.7, 129.5, 129.0, 127.5, 127.0, 126.9, 126.7, 68.8, 56.8, 51.9, 48.2, 32.0, 21.5, 21.1, 21.0. **LRMS** *m/z* (ESI+APCI) calcd for $C_{28}H_{30}NO_2S$ [M+H] 444.2. Found 444.2. **HRMS** calculated for $[C_{28}H_{29}NO_2S+H]^+$ 444.1992. Found 444.2008.

**(3a*R**,4*S**,6a*R**)-1-(4-Methylbenzenesulfonyl)-4,5-bis[4-(propan-2-yl)phenyl]-1H,2H,3H,3aH,4H, 6aH-cyclopenta[b]pyrrole (3ac).** This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and 1,2-bis(4-isopropylphenyl)ethyne **2c** (65.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 60.7 mg (61%) of **3ac** as a colorless oil.



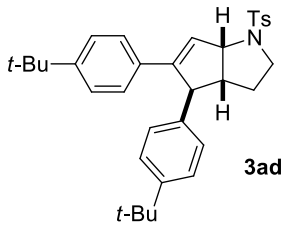
**3ac**

$C_{32}H_{37}NO_2S$
M = 499.71 g/mol

**Rf** (Hex/EA: 90:10) = 0.18. **IR** (neat, $cm^{-1}$) 1598, 1512, 1459, 1340, 1158, 1092, 1056, 908, 815, 729, 661. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.12 – 7.03 (m, 6H), 6.48 (s, 1H), 4.83 (br d, *J* = 7.7 Hz, 1H),

4.00 (s, 1H), 3.53 – 3.48 (m, 1H), 3.03 (td, *J* = 9.6 and *J* = 6.3 Hz, 1H), 2.90 –2.77 (m, 2H), 2.52 (app dd, *J* = 16.4 Hz and *J* = 8.2 Hz, 1H), 2.41 (s, 3H), 2.10 – 2.01 (m, 1H), 1.87 – 1.76 (m, 1H), 1.20 (br s, 6H), 1.19 (br s, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 148.6, 147.0, 144.2, 143.3, 140.9, 134.6, 132.3, 129.7, 127.6, 127.1, 126.9, 126.8, 126.8, 126.4, 68.8, 56.8, 51.9, 48.2, 33.8, 33.6, 32.0, 23.9, 23.9, 23.8, 23.8, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{32}H_{38}NO_2S$ [M+H] 500.2. Found 500.2. **HRMS** calculated for $[C_{32}H_{37}NO_2S+H]^+$ 500.2618. Found 500.2631.

**(3a*R**,4*S**,6a*R**)-4,5-bis(4-*tert*-Butylphenyl)-1-(4-methylbenzenesulfonyl)-1H,2H,3H,3aH,4H,6aH-cyclopenta[b]pyrrole (3ad).** This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and 1,2-bis(4-(*tert*-butyl)phenyl)ethyne **2d**[6] (72.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 63.2 mg (60%) of **3ad** as a white solid.

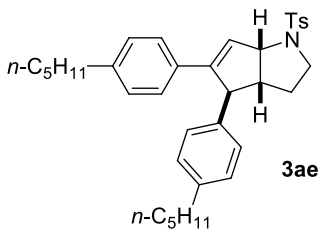



**3ad**

$C_{34}H_{41}NO_2S$
M = 527.76 g/mol

**Rf** (Hex/EA: 90:10) = 0.18. **Mp** = 98 °C. **IR** (neat, $cm^{-1}$) 1597, 1512, 1448, 1339, 1157, 1091, 1031, 885, 808, 729, 662. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.27 – 7.22 (m, 4H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.49 (s, 1H), 4.83 (d, *J* = 7.7 Hz, 1H), 4.00 (s, 1H), 3.53 – 3.46 (m, 1H), 3.02 (td, *J* = 9.6 Hz and *J* = 6.2 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.42 (s, 3H), 2.10 – 2.00 (m, 1H), 1.87 – 1.75 (m, 1H), 1.27 (s, 9H), 1.26 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 150.8, 149.3, 144.0, 143.3, 140.5, 134.6, 131.9, 129.7, 127.5, 127.2, 126.6, 126.5, 125.7, 125.2, 68. 8, 56.7, 51. 9, 48.2, 34.5, 34.3, 32.0, 31.3, 31.2, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{34}H_{42}NO_2S$ [M+H] 528.3. Found 528.3. **HRMS** calculated for $[C_{34}H_{41}NO_2S+H]^+$ 528.2931. Found 528.2942.

**(3a*R**,4*S**,6a*R**)-1-(4-Methylbenzenesulfonyl)-4,5-bis(4-pentylphenyl)-1H,2H,3H,3aH,4H,6aH-cyclopenta[b]pyrrole (3ae).** This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and 1,2-bis(4-pentylphenyl)ethyne **2e** (79.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 80:20) gave 65.9 mg (59%) of **3ae** as a white waxy solid.



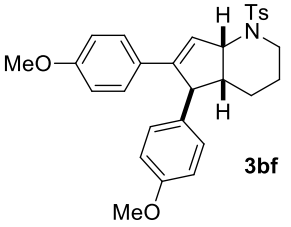

**3ae**

$C_{36}H_{45}NO_2S$
M = 555.81 g/mol

**Rf** (Hex/EA: 90:10) = 0.20. **IR** (neat, $cm^{-1}$) 1597, 1494, 1456, 1446, 1341, 1159, 1140, 1110, 1052, 934, 893, 816, 761, 751, 660. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.75 (d,

*J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.08 – 6.97 (m, 6H), 6.46 (br s, 1H), 4.83 (br d, *J* = 7.7 Hz, 1H), 4.00 (s, 1H), 3.54 – 3.45 (m, 1H), 3.04 (td, *J* = 9.5 Hz and *J* = 6.3 Hz, 1H), 2.57 – 2.47 (m, 5H), 2.41 (s, 3H), 2.11 – 1.99 (m, 1H), 1.91 – 1.77 (m, 1H), 1.61 – 1.49 (m, 4H), 1.37 – 1.22 (m, 8H), 0.92 – 0.83 (m, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 144.3, 143.3, 142.7, 141.2, 140.8, 134.7, 132.1, 129.7, 128.8, 128.3, 127.5, 127.0, 126.8, 126.7, 68.8, 56.9, 51.9, 48.2, 35.6, 35.5, 32.0, 31.6, 31.5, 31.1, 30.9, 22.5, 22.5, 21.5, 14.0, 14.0. **LRMS** *m/z* (ESI+APCI) calcd for $C_{36}H_{46}NO_2S$ [M+H] 556.3. Found 556.3. **HRMS** calculated for $[C_{36}H_{45}NO_2S+H]^+$ 556.3244. Found 556.3257.

**(4a*R**,5*S**,7a*R**)-5,6-bis(4-Methoxyphenyl)-1-(4-methylbenzenesulfonyl)-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta[b]pyridine (3bf).** This compound was prepared by treatment of *N*-tosylamide **1b** (50.7 mg, 0.200 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2f**[6] (59.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 90:10 to 70:30) gave 71.2 mg (73%) of **3bf** as an orange oil.

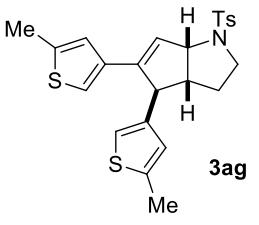



**3bf**

$C_{29}H_{31}NO_4S$
M = 489.63 g/mol

**Rf** (Hex/EA: 90:10) = 0.10. **IR** (neat, $cm^{-1}$) 1606, 1510, 1462, 1329, 1303, 1248, 1177, 1160, 1110, 1095, 1034, 908, 815, 727, 661. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.72 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 5.96 (br s, 1H), 5.18 (br d, *J* = 6.4 Hz, 1H), 3.77 – 3.72 (m, 1H) 3.77 (s, 3H), 3.74 (s, 3H), 2.96 – 2.87 (m, 1H), 2.44 (s, 3H), 2.25 – 2.17 (m, 1H), 1.90 – 1.79 (m, 1H), 1.57 – 1.24 (m, 4H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 159.3, 158.2, 145.0, 143.0, 137.8, 133.2, 129.7, 128.2, 127.6, 127.5, 127.1, 123.7, 114.1, 113.7, 60.0, 56.6, 55.2, 46.3, 42.0, 27.5, 23.1, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{29}H_{32}NO_4S$ [M+H] 490.2. Found 490.2. **HRMS** calculated for $[C_{29}H_{31}NO_4S+H]^+$ 490.2047. Found 490.2057.

**(3a*R**,4*R**,6a*R**)-1-(4-Methylbenzenesulfonyl)-4,5-bis(5-methylthiophen-3-yl)-1H,2H,3H,3aH,4H, 6aH-cyclopenta[b]pyrrole** (**3ag**). This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and 1,2-bis(5-methylthiophen-3-yl)ethyne **2g** (54.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2 \bullet H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/$Et_2O$: 95:5 to 70:30) gave 44.5 mg (49%) of **3ag** as a yellow oil.



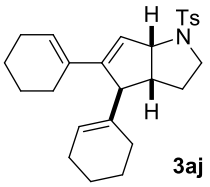

**3ag**

$C_{24}H_{25}NO_2S_3$
M = 455.66 g/mol

**IR** (neat, $cm^{-1}$) 1598, 1494, 1445, 1340, 1160, 1092, 816, 752, 700, 659. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.88 (br s, 1H), 6.72 (br s, 1H), 6.66

(br s, 1H), 6.47 (br s, 1H), 6.17 (br s, 1H), 4.79 (d, *J* = 7.7 Hz, 1H), 3.88 (s, 1H), 3.51 – 3.43 (m, 1H), 3.04 (td, *J* = 9.5 Hz and *J* = 6.3 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.42 (s, 6H), 2.39 (s, 3H), 2.04 – 1.96 (m, 1H), 1.81 – 1.70 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 144.2, 143.3, 140.6, 140.3, 139.7, 136.7, 134.7, 129.7, 127.5, 126.3, 124.8, 124.5, 120.9, 118.1, 68.8, 52.9, 50.8, 48.2, 31.7, 21.5, 15.4, 15.2. **LRMS** *m/z* (ESI+APCI) calcd for $C_{24}H_{26}NO_2S_3$ [M+H] 456.1. Found 456.1. **HRMS** calculated for $[C_{24}H_{25}NO_2S_3+H]^+$ 456.1120. Found 456.1128.

**(3a*R**,4*S**,6a*R**)-4,5-bis(Cyclohex-1-en-1-yl)-1-(4-methylbenzenesulfonyl)-1H,2H,3H,3aH,4H,6aH-cyclo-penta[b]pyrrole (3aj)**. This compound was prepared by treatment of *N*-tosylamide **1a** (47.9 mg, 0.200 mmol) and alkyne **2j** (44.6 mg, 0.250 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv) in 1,4-dioxane (2 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/$Et_2O$: 98:2 to 90:10) gave 48.3 mg (55%) of **3aj** as a colorless oil.

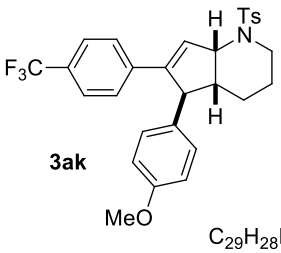



3aj

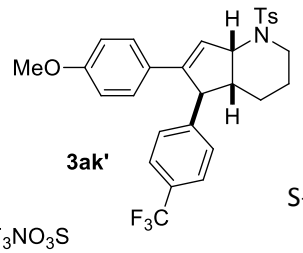
$C_{26}H_{33}NO_2S$
M = 423.61 g/mol

**Rf** (Hex/EA: 90:10) = 0.30. **IR** (neat, $cm^{-1}$) 1597, 1494, 1456, 1445, 1361, 1341, 1331, 1256, 1159, 1140, 1110, 1095, 1051, 934, 893, 837, 761, 751, 701, 659. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.77 (br s, 1H), 5.75 (s, 1H), 5.37 (br s, 1H), 4.57 (d, *J* = 7.8 Hz, 1H), 3.40 – 3.33 (m, 1H), 3.13 (s, 1H), 3.00 (td, *J* = 9.4 Hz and *J* = 6.3 Hz, 1H), 2.43 (s, 3H), 2.32 – 2.24 (m, 1H), 2.24 – 2.01 (m, 4H), 1.97 – 1.83 (m, 3H), 1.74 – 1.40 (m, 11H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 145.6, 143.1, 139.6, 135.0, 132.4, 129.6, 127.6, 127.3, 125.0, 121.8, 68.9, 58.7, 48.5, 48.0, 32.1, 26.3, 25.8, 25.4, 25.2, 22.9, 22.7, 22.5, 22.1, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{26}H_{34}NO_2S$ [M+H] 424.2. Found 424.2. **HRMS** calculated for $[C_{26}H_{33}NO_2S+H]^+$ 424.2305. Found 424.2309.

**(4a*R**,5*S**,7a*R**)-5-(4-Methoxyphenyl)-1-(4-methylbenzenesulfonyl)-6-[4-(trifluoromethyl)phenyl]-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta[b]pyridine (3ak) and (4a*R**,5*S**,7a*R**)-6-(4-Methoxyphenyl)-1-(4-methylbenzenesulfonyl)-5-[4-(trifluoromethyl)phenyl]-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta-[b]-pyridine (3ak').** In a 1.5 dram vial were added *N*-tosylamide **1b** (50.7 mg, 0.200 mmol), 1-methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene **2k** (69.1 mg, 0.250 mmol, 1.25 equiv), $Cu(OAc)_2•H_2O$ (83.9 mg, 0.420 mmol, 2.1 equiv), $AgSbF_6$ (17.2 mg, 0.050 mmol, 25 mol %) and $[RhCp^*Cl_2]_2$ (12.3 mg, 0.020 mmol, 10 mol %). After addition of 1,4-dioxane, the vial was sealed and heated at 120 °C for 16 h. The resulting blue mixture was filtrated through a short plug of silica and Celite (EtOAc) and concentrated under reduced pressure. $^1$H NMR spectra of the crude material showed a 1:1 mixture of regioisomers **3ak** and **3ak'** (determination with the vinylic proton signal). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 70:30) gave 61.0 mg (62%) of a 1:1 mixture of regioisomers **3ak** and **3ak'** as a yellow solid.




3ak




3ak'

$C_{29}H_{28}F_3NO_3S$
M = 527.60 g/mol

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.72 – 7.67 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 0.5*2H), 7.44 (d, *J* = 8.3 Hz, 0.5*2H), 7.37 – 7.21 (m, 4H), 7.14 (d, *J* = 8.8 Hz, 0.5*2H), 7.02 (d, *J* = 8.7 Hz, 0.5*2H), 6.79 (d,

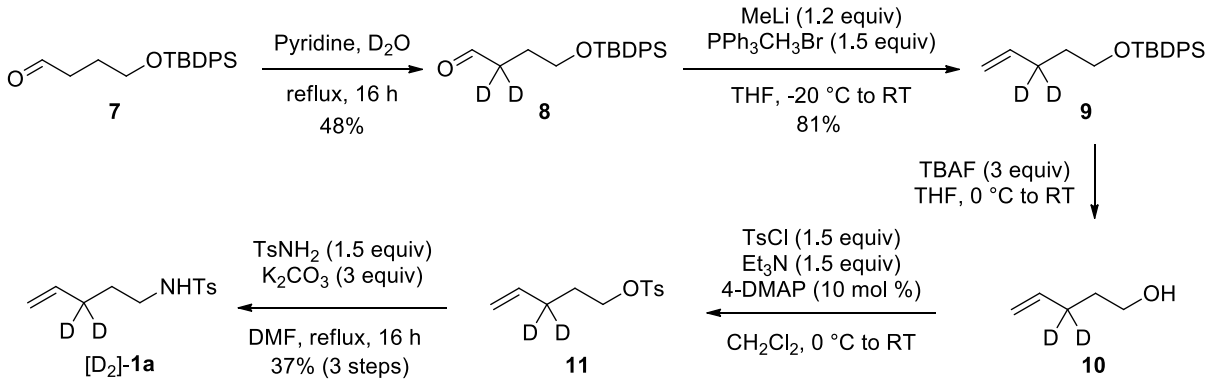
*J* = 8.7 Hz, 0.5*2H), 6.79 (d, *J* = 8.7 Hz, 0.5*2H), 6.73 (d, *J* = 8.9 Hz, 0.5*2H) 6.23 (s, 0.5*1H), 6.00 (s, 0.5*1H), 5.17 (d, *J* = 6.5 Hz, 0.5*1H), 5.13 (d, *J* = 6.5 Hz, 0.5*1H), 3.84 (s, 0.5*1H), 3.78 (s, 0.5*1H), 3.75 (s, 0.5*3H), 3.72 (s, 0.5*3H), 3.77 – 3.65 (m, 1H), 2.95 – 2.85 (m, 1H), 2.41 (s, 3H), 2.27 – 2.18 (m, 1H), 1.91 – 1.80 (m, 1H), 1.56 – 1.21 (m, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 159.5, 158.5, 145.4, 145.4, 144.5, 144.1, 143.3, 143.2, 138.2, 138.2, 137.7, 137.6, 132.4, 129.7, 129.7, 129.1, 128.1, 127.6, 127.4, 127.1, 127.1, 127.0, 126.4, 125.8 (q, *J* = 3.8 Hz), 125.3 (q, *J* = 3.8 Hz), 124.6, 114.3, 113.9, 60.0, 59.9, 57.1, 56.5, 55.2, 46.4, 46.2, 42.3, 42.0, 27.6, 27.4, 23.1, 23.0, 21.5.

## 4. Deuteration experiments

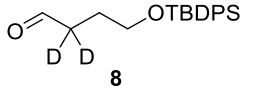
### a. Preparation of deuterated *N*-tosylamides

[$D_Z$]-**1a**[11] and [$D_E$]-**1a**[11] were synthesized following described procedures and the NMR spectra matches with the data reported in the literature.

- Preparation of sulfonamide **[$D_2$]-1a**




**4-[(*tert*-Butyldiphenylsilyl)oxy](2,2-$^2H_2$)butanal (8).** Aldehyde **7**[12] (3.92 g, 12.00 mmol) was dissolved in freshly distilled pyridine (6 mL) and $D_2O$ (6 mL) and the resulting solution was refluxed for 16 h. The reaction mixture was allowed to warm to RT and extracted with $CH_2Cl_2$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/$Et_2O$: 99:1 to 97:3) to afford 1.49 g (48%) of dideuterated aldehyde **8** as a colorless oil contaminated with an unknown impurity.




$C_{20}H_{24}D_2O_2Si$
M = 328.52 g/mol

**Rf** (Hex/EA: 90:10) = 0.40. **IR** (neat, $cm^{-1}$) 3071, 1724, 1472, 1427, 1390, 1361, 1108, 998, 822, 732, 699. **$^1$H NMR** (400

[11] G. Zhang, L. Cui, Y. Wang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 1474-1475.
[12] H. Zheng, S. Ghanbari, S. Nakamura, D. G. Hall, *Angew. Chem.* **2012**, *124*, 6291 –6294; *Angew. Chem. Int. Ed.* **2012**, *51*, 6187-6190.

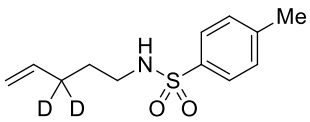
MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.70 – 7.64 (m, 4H), 7.47 – 7.36 (m, 6H), 3.71 (t, *J* = 6.0 Hz, 2H), 1.89 (t, *J* = 6.0 Hz, 2H), 1.07 (s, 9H). **LRMS** *m/z* (ESI+APCI) calcd for $C_{20}H_{25}D_2O_2Si$ [M+H] 329.2. Found 329.2.

**4-Methyl-*N*-[(3,3-$^2H_2$)pent-4-en-1-yl]benzene-1-sulfonamide ([$D_2$]-1a).** To a solution of $PPh_3CH_3Br$ (2.27 g, 6.34 mmol, 1.5 equiv) in THF (30 mmol) at -20 °C was added MeLi (3.17 mL, 1.6 M in $Et_2O$, 5.08 mmol, 1.2 equiv). After 1 h stirring at 0 °C, the reaction mixture was cooled to -20 °C and a solution of dideuterated aldehyde **8** (1.39 g, 4.23 mmol) in THF (5 mmol) at -20 °C was added. After 5 h stirring at RT, a saturated aqueous solution of $NH_4Cl$ was added. The layers were separated and the aqueous phase was extracted with $Et_2O$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/ $Et_2O$: 99:1 to 98:2) to afford 1.12 g (81%) of dideurated alkene **9** as a colorless oil.

To a solution of dideurated alkene **9** (1.02 g, 3.12 mmol) in THF (15 mmol) at 0 °C was added TBAF (9.36 mL, 1M in THF, 9.36 mmol, 3 equiv). After 16 h stirring at RT, a saturated aqueous solution of $NH_4Cl$ was added. The layers were separated and the aqueous phase was extracted with $Et_2O$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated at 0 °C under moderate reduced pressure to afford alcool **10** along with $Et_2O$.

The residue was taken up in $CH_2Cl_2$ (30 mL). To the resulting mixture were successively added at 0 °C TsCl (892 mg, 4.68 mmol, 1.5 equiv), $Et_3N$ (652 µL, 4.68 mmol, 1.5 equiv) and 4-DMAP (37.9 mg, 0.31 mmol, 0.1 equiv). After stirring 16 h at RT, a saturated aqueous solution of $NH_4Cl$ was added. The layers were separated and the aqueous phase was extracted with $Et_2O$. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to afford the crude tosylate **11** which was used without further purification.

To a solution of crude **11** in DMF (30 mL) were added $TsNH_2$ (801 mg, 4.68 mmol, 1.5 equiv) and $K_2CO_3$ (1.29 g, 9.36 mmol, 3 equiv) and the reaction mixture was refluxed for 16 h. The resulting suspension was cooled to RT, filtrated over Celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/AcOEt: 95:5 to 85:15) to afford 279 mg (37%, 3 steps) of dideurated *N*-tosylamide **[$D_2$]-1a** as a colorless oil contaminated with DMF.




[$D_2$]-1a

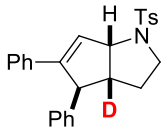
$C_{12}H_{15}D_2NO_2S$
M = 241.35 g/mol

**Rf** (Hex/EA: 90:10) = 0.15. **IR** (neat, $cm^{-1}$) 3279, 1663, 1416, 1322, 1155, 1092, 913, 814, 659. **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 7.72 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.67 (dd, *J* = 17.1 and *J* = 10.2 Hz, 1H), 4.98 – 4.89 (m, 2H), 4.51 (s, 1H), 2.94 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.52 (t, *J* = 7.0 Hz, 2H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) *δ* 143.3, 137.1, 137.0, 129.7, 127.1, 115.6, 42.6, 28.5, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{12}H_{16}D_2NO_2S$ [M+H] 242.1. Found 242.1. **HRMS** calculated for $[C_{12}H_{15}D_2NO_2S + H]^+$ 242.1178. Found 242.1179.

## b. Reactions of deuterated *N*-tosylamides

- *Reactivity of sulfonamide [$D_2$]-**1a***

**1-(4-Methylbenzenesulfonyl)-4,5-diphenyl(3a-$^2$H)-1H,2H,3H,3aH,4H,6aH-cyclopenta[b]pyrrole ([$D_2$]-3aa).** This compound was prepared by treatment of *N*-tosylamide [$D_2$]-**1a** (24.1 mg, 0.100 mmol) and diphenylacetylene **2a** (17.8 mg, 0.125 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (6.2 mg, 0.005 mmol, 10 mol %), $AgSbF_6$ (8.6 mg, 0.025 mmol, 25 mol %) and $Cu(OAc)_2$ (38.1 mg, 0.240 mmol, 2.1 equiv) in 1,4-dioxane (1 mL) (120 °C, 16 h, d.r. > 96:4). Purification by flash chromatography (hexanes/EtOAc: 95:5 to 85:15) gave 16.2 mg (38%) of [$D_2$]-**3aa** as a yellow oil.



[$D_2$]-**3aa**

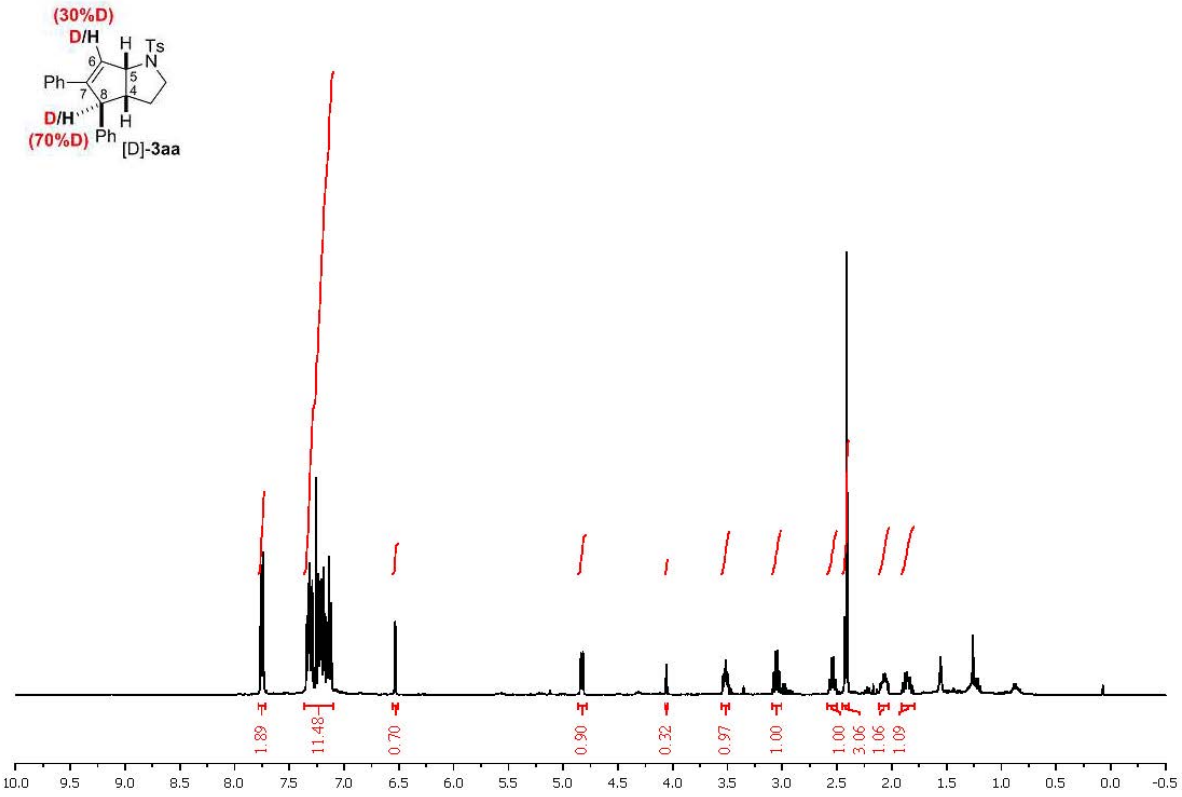
$C_{26}H_{24}DNO_2S$
M = 416.55 g/mol

**Rf** (Hex/EA: 90:10) = 0.15. **IR** (neat, $cm^{-1}$) 1598, 1494, 1446, 1640, 1160, 1092, 815, 756, 700, 662. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.73 (d, $J$ = 8.1 Hz, 2H), 7.34 – 7.07 (m, 10H), 6.51 (s, 1H), 4.80 (s, 1H), 4.03 (s, 1H), 3.53 – 3.44 (m, 1H), 3.02 (dd, $J$ = 15.9 Hz and $J$ = 9.5 Hz, 1H), 2.38 (s, 3H), 2.08 – 1.98 (m, 1H), 1.88 – 1.78 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 144.3, 143.4, 143.4, 142.8, 134.5, 134.5, 129.7, 128.8, 128.3, 128.1, 127.8, 127.5, 127.0, 126.8, 126.6, 68.7, 57.1, 48.2, 31.9, 21.5. **LRMS** *m/z* (ESI+APCI) calcd for $C_{26}H_{25}DNO_2S$ [M+H] 417.2. Found 417.2. **HRMS** calculated for $[C_{26}H_{24}DNO_2S+H]^+$ 417.1742. Found 417.1753.

- *Reactivity of sulfonamide* (*E*)-[D]-**1a**

Treatment of *N*-tosylamide (*E*)-[D]-**1a** (24.0 mg, 0.100 mmol) and diphenylacetylene **2a** (17.8 mg, 0.125 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (6.2 mg, 0.005 mmol, 10 mol %), $AgSbF_6$ (8.6 mg, 0.025 mmol, 25 mol %) and $Cu(OAc)_2$ (38.1 mg, 0.240 mmol, 2.1 equiv) in 1,4-dioxane (1 mL) (120 °C, 16 h, d.r. > 96:4) followed by purification by flash chromatography (hexanes/EtOAc: 95:5 to 85:15) gave 13.5 mg (32%) of [D]-**3aa** as a yellow oil.

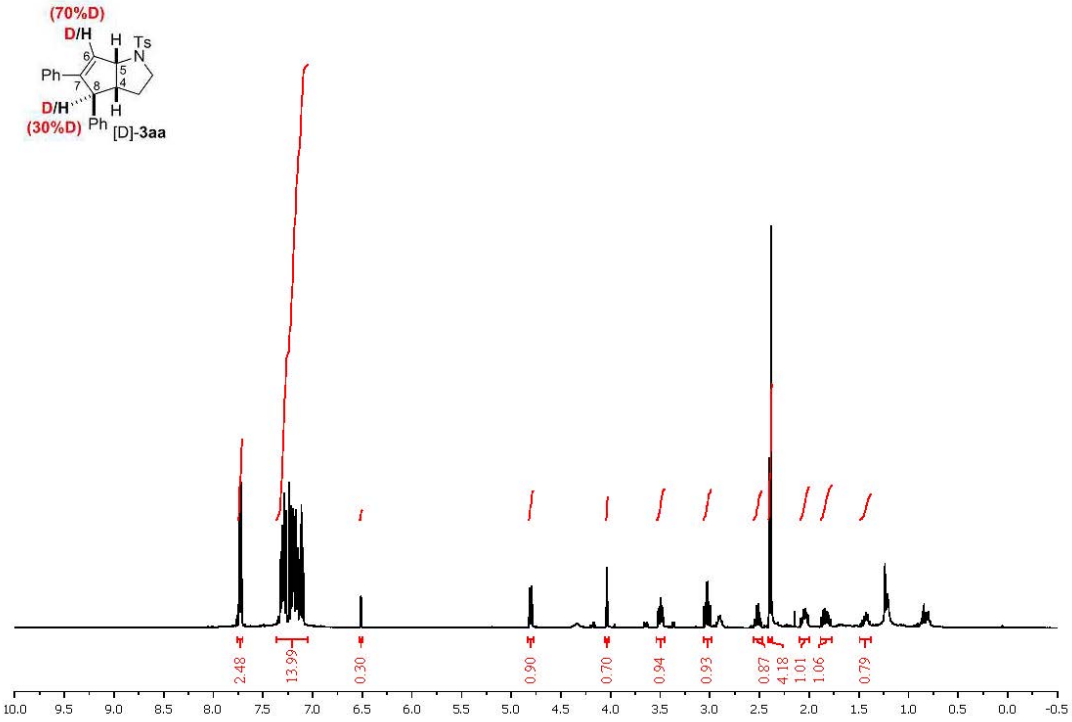
Analysis of the $^1$H NMR spectra showed 30% deuteration at position 6 and 70% deuteration at position 8.




- *Reactivity of sulfonamide* (*Z*)-[D]-**1a**

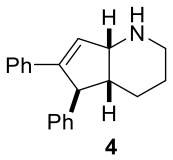
Treatment of *N*-tosylamide (*Z*)-[D]-**1a** (24.0 mg, 0.100 mmol) and diphenylacetylene **2a** (17.8 mg, 0.125 mmol, 1.25 equiv) by $[RhCp^*Cl_2]_2$ (6.2 mg, 0.005 mmol, 10 mol %), $AgSbF_6$ (8.6 mg, 0.025 mmol, 25 mol %) and $Cu(OAc)_2$ (38.1 mg, 0.240 mmol, 2.1 equiv) in 1,4-dioxane (1 mL) (120 °C, 16 h, d.r. > 96:4) followed by purification by flash chromatography (hexanes/EtOAc: 95:5 to 85:15) gave 16.6 mg (40%) of [D]-**3aa** as a yellow oil.

Analysis of the $^1H$ NMR spectra showed 70% deuteration at position 6 and 30% deuteration at position 8.




### c. Deprotection of the tosyl group

**5,6-Diphenyl-1H,2H,3H,4H,4aH,5H,7aH-cyclopenta[b]pyridine (4)**. To a solution of *N*-tosylamide (161 mg, 375 µmol) **3ba** in THF at -78 °C was added a freshly prepared solution of sodium naphthalenide in THF (2.50 mL, 0.2M, 500 µmol, 1.33 equiv) until the green color persisted. After 30 min stirring at -78 °C, more sodium naphthalenide was added (2.50 mL, 0.2M, 500 µmol, 1.33 equiv). After 1 h stirring at -78 °C, the cold reaction mixture was poured into a saturated aqueous solution of $NH_4Cl$, extracted with EtOAc and the combined organic extracts were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes to EtOAc/$Et_3N$: 90:10) to afford 71 mg (69%) of bicyclic amine **4** as a yellow oil.

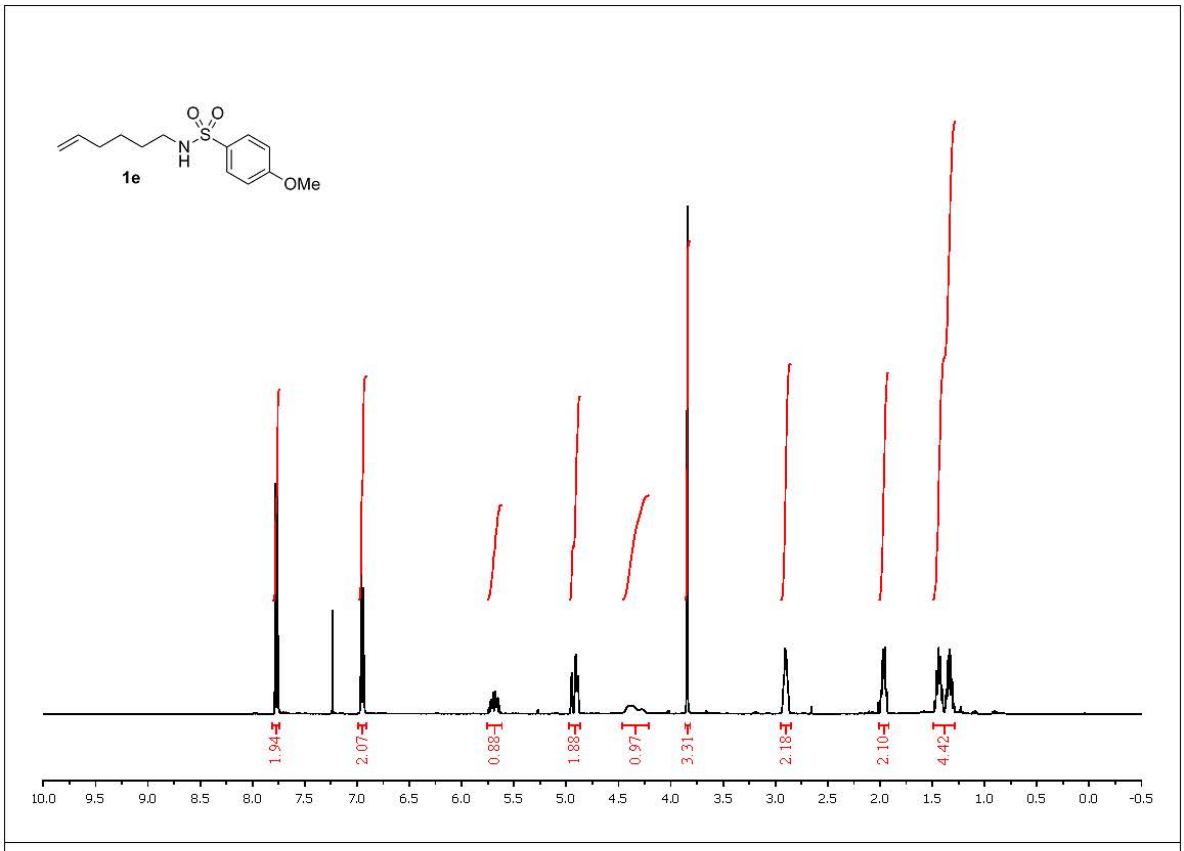


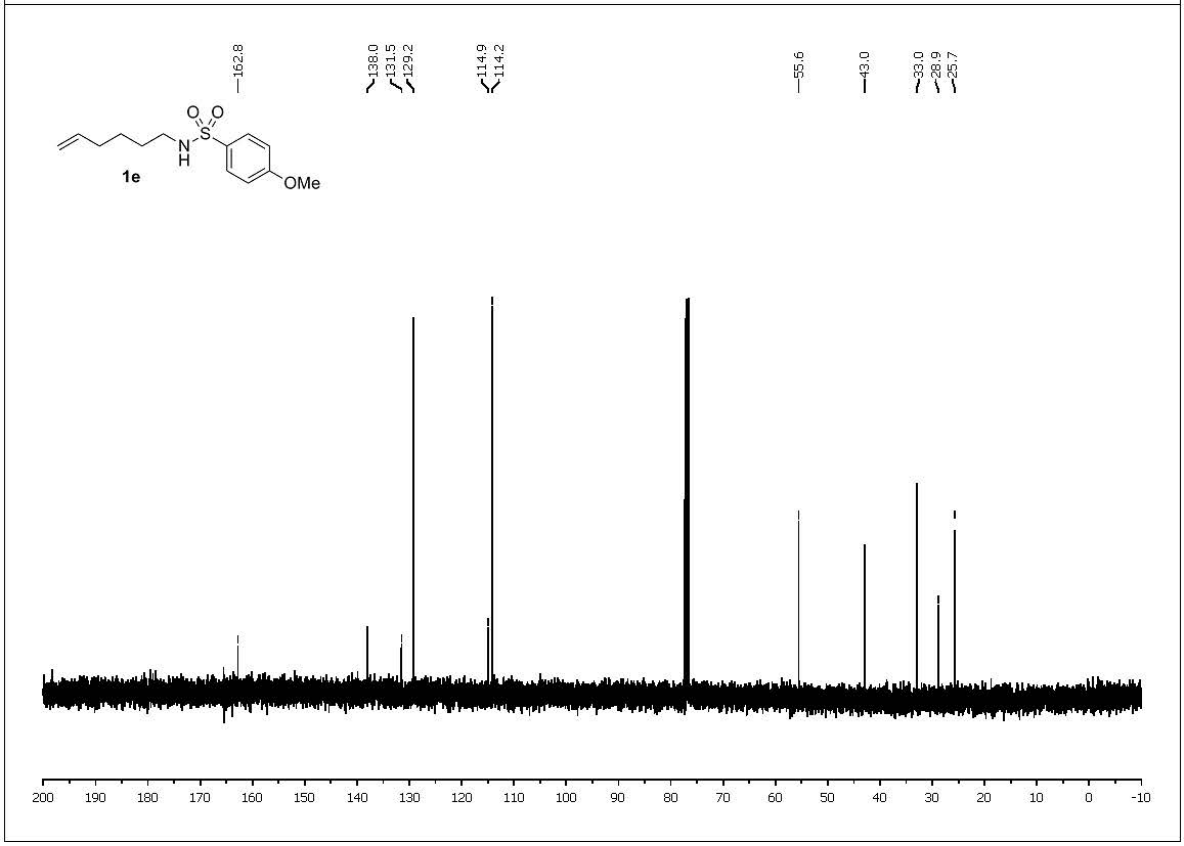

**4**

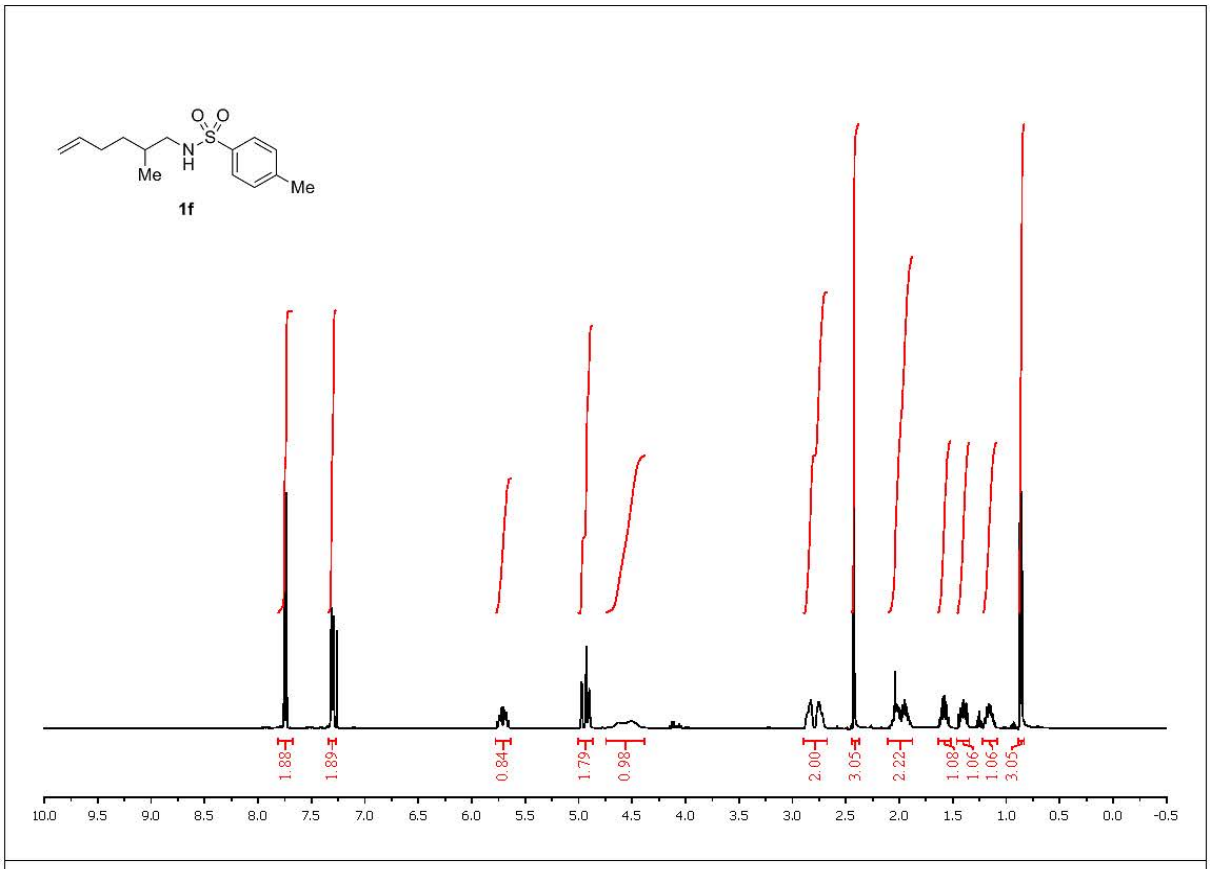
$C_{20}H_{21}N$
M = 275.40 g/mol

**Rf** (EA/$Et_3N$: 90:10) = 0.25. **IR** (neat, $cm^{-1}$) 1737, 1600, 1492, 1445, 1331, 1242, 1169, 1132, 1074, 1030, 908, 878, 754, 728, 697. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31 – 7.08 (m, 9H), 6.41 (br s, 1H), 4.06 (br d, $J$ = 5.8 Hz, 1H), 4.01 (br d, $J$ = 5.3 Hz, 1H), 2.88 (ddd, $J$ = 12.9 Hz, $J$ = 6.8 Hz and $J$ = 3.6 Hz, 1H), 2.69 (ddd, $J$ = 12.9 Hz, $J$ = 7.5 Hz and $J$ = 3.4 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.84 (br s, 1H), 1.82 – 1.66 (m, 2H), 1.62 – 1.51 (m, 1H), 1.50 – 1.40 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 146.5, 142.8, 135.7, 131.4, 128.4, 128.1, 127.8, 127.2, 126.4, 126.1, 60.3, 55.4, 47.8, 43.2, 25.5, 24.2. **LRMS** *m/z* (ESI+APCI) calcd for $C_{20}H_{22}N$ [M+H] 276.2. Found 276.2. **HRMS** calculated for $[C_{20}H_{21}N+H]^+$ 276.1747. Found 276.1753.

## 5. NMR Spectra




1f
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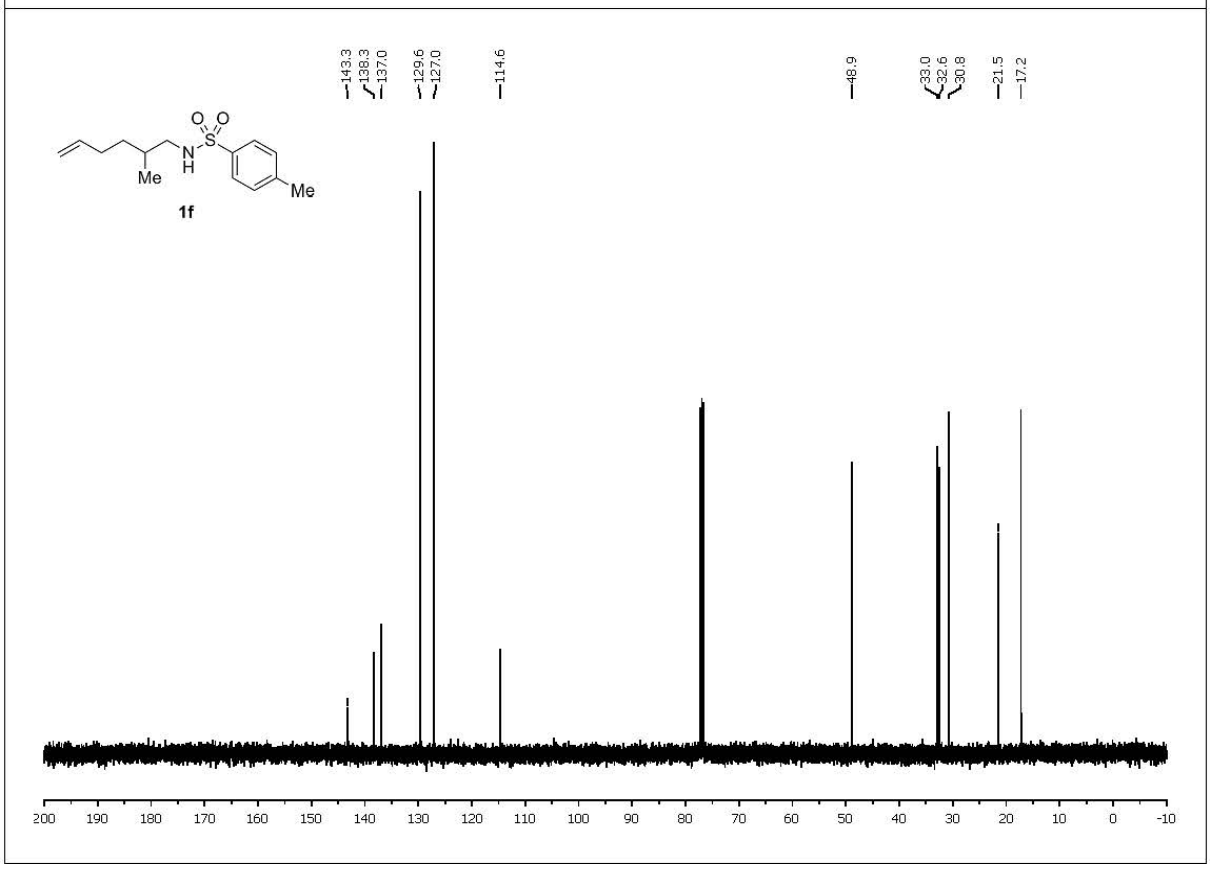
1.79
0.98
2.00
3.05
2.22
1.08
1.06
1.06
3.05


143.3
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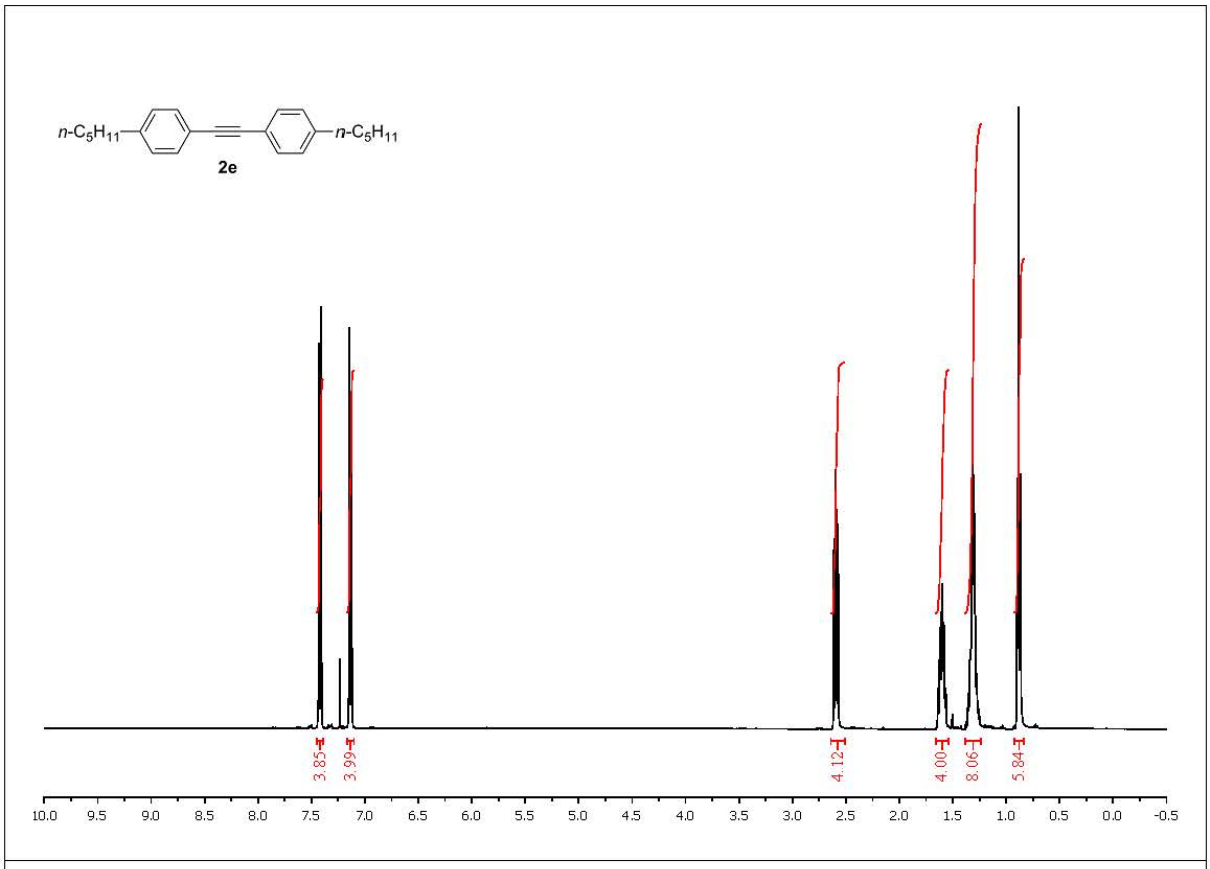
129.6
127.0
114.6
48.9
33.0
32.6
30.8
21.5
17.2
1f


n-C5H11
n-C5H11
2e
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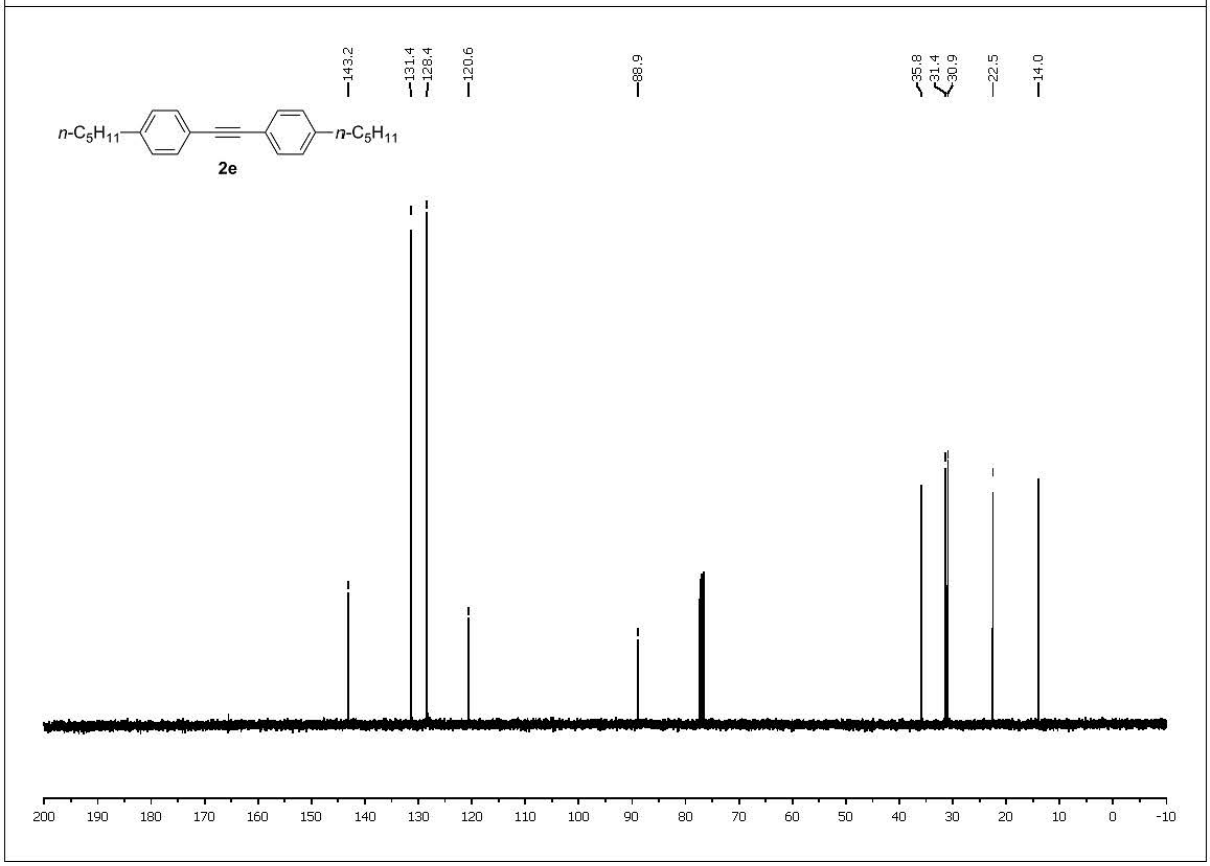
3.99
4.12
4.00
8.06
5.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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120.6
88.9
35.8
31.4
30.9
22.5
14.0
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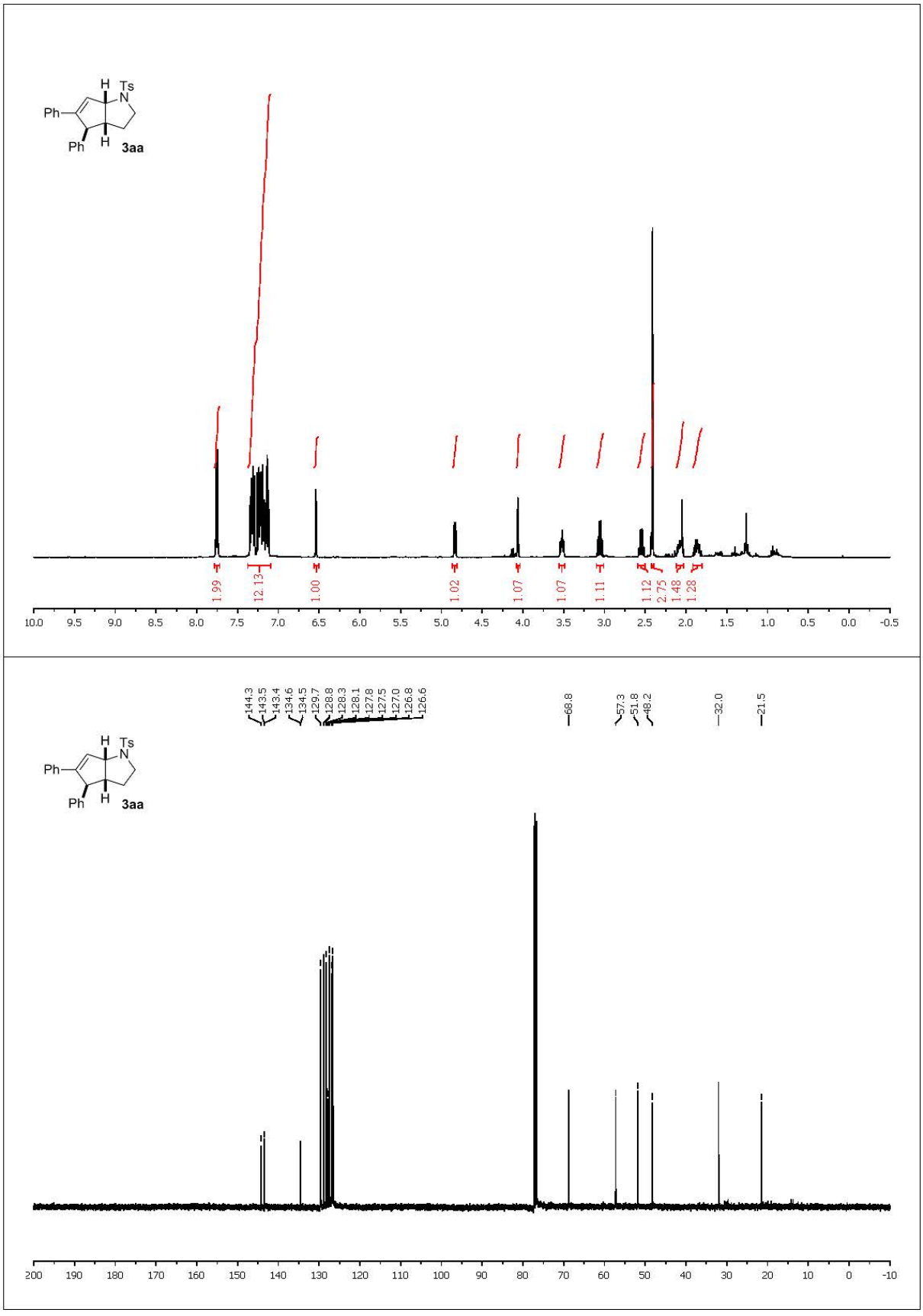
n-C5H11
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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Ts
N
Ph
Ph
H
3aa
1.99
12.13
1.00
1.02
1.07
1.07
1.11
1.12
2.75
1.48
1.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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144.3
143.5
143.4
134.6
134.5
129.7
128.8
128.3
128.1
127.8
127.5
127.0
126.8
126.6
68.8
57.3
51.8
48.2
32.0
21.5
200
190
180
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120
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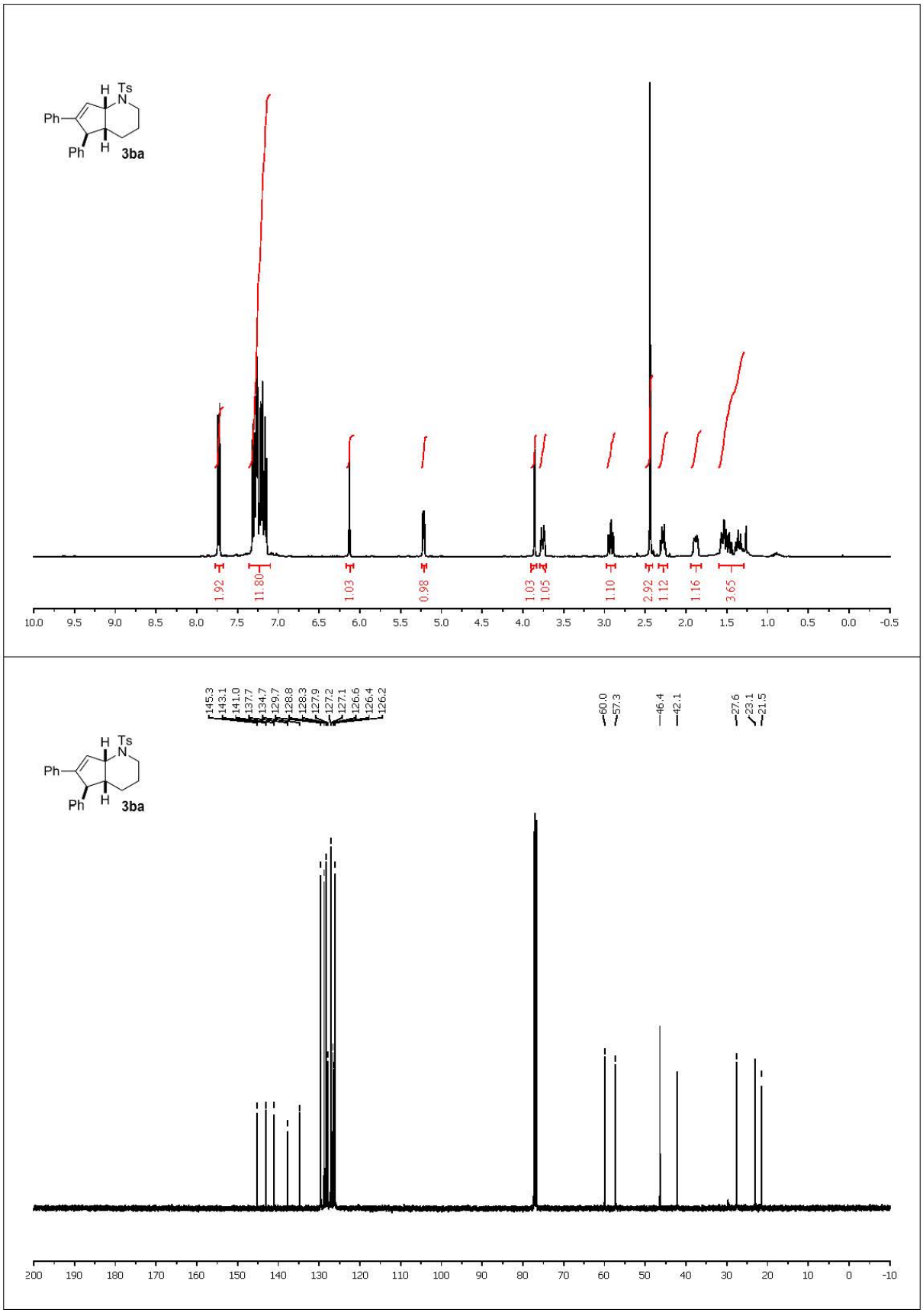
100
90
80
70
60
50
40
30
20
10
0
-10


Ph
Ph
H
Ts
N
H
3ba
1.92
11.80
1.03
0.98
1.03
1.05
1.10
2.92
1.12
1.16
3.65
145.3
143.1
141.0
137.7
134.7
129.7
128.8
128.3
127.9
127.2
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126.6
126.4
126.2
60.0
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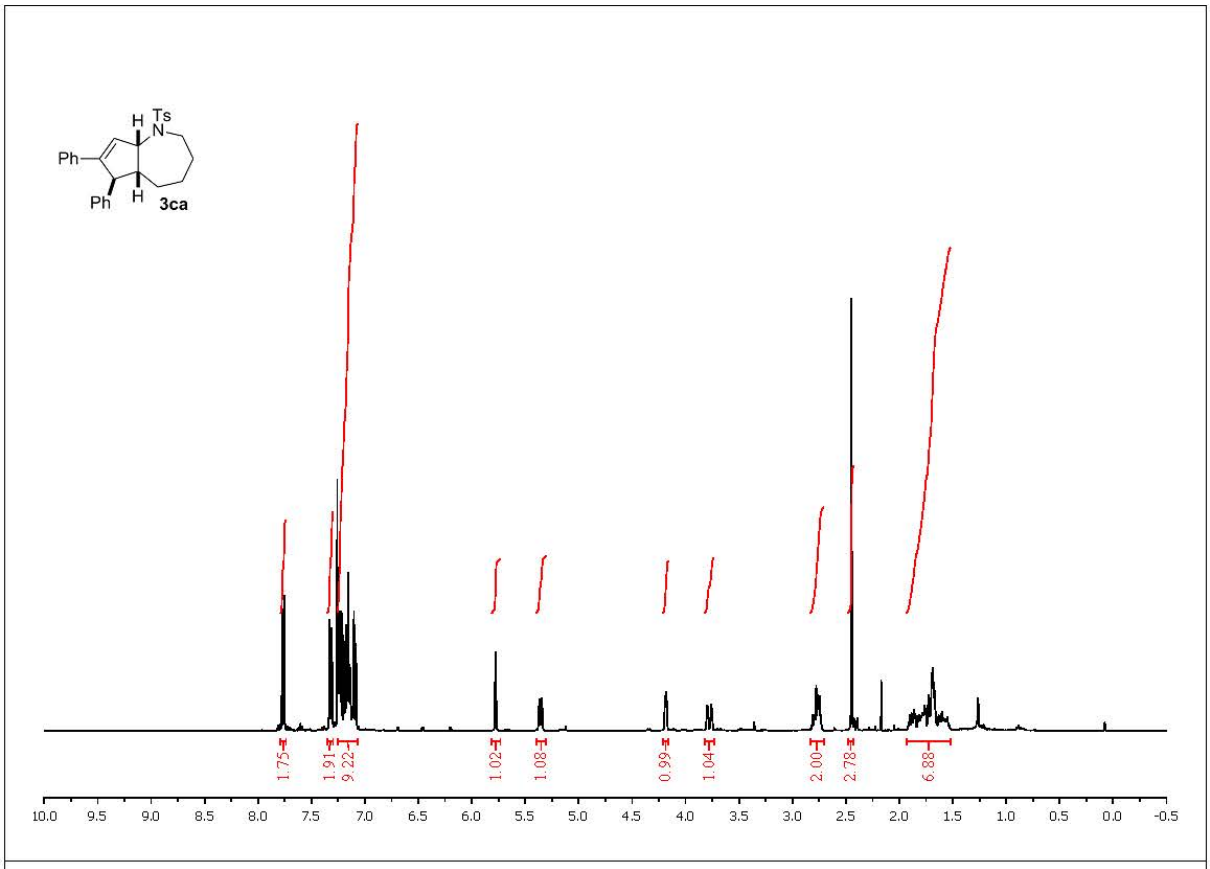
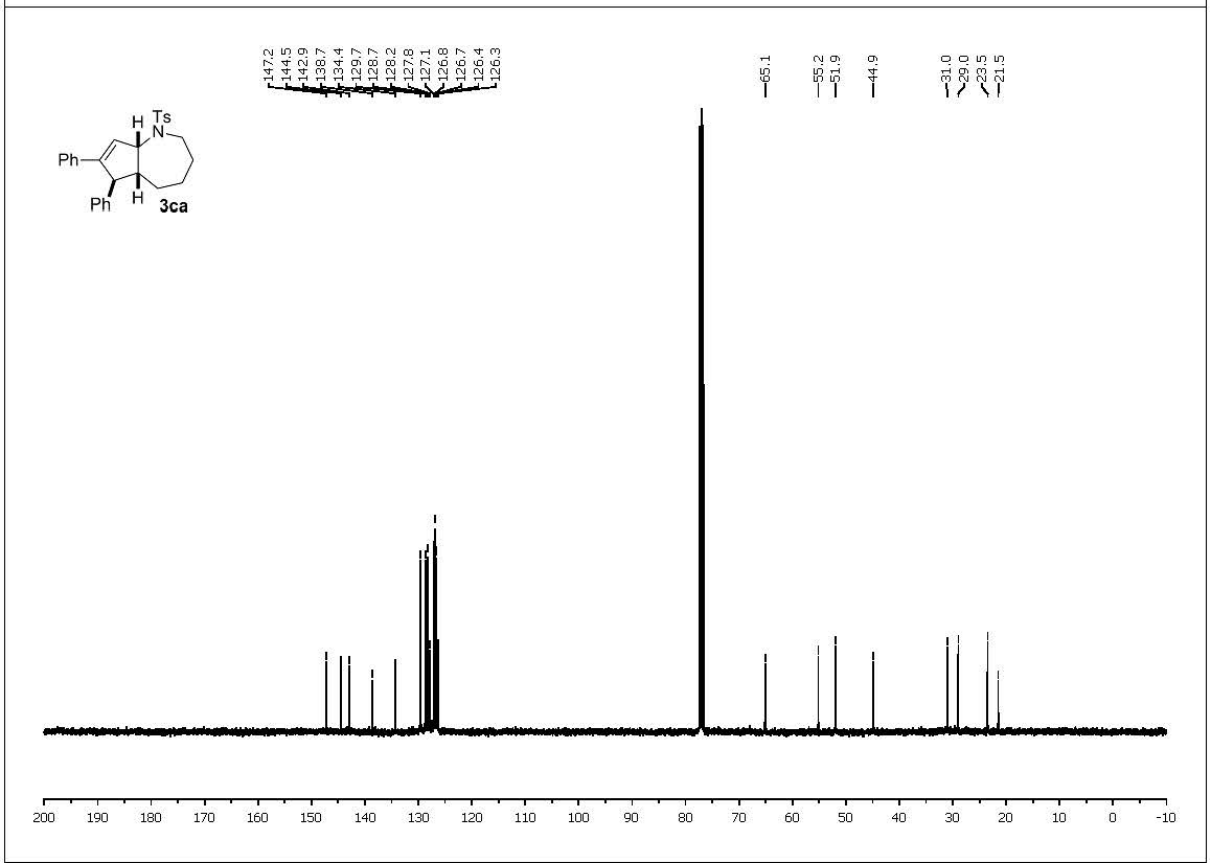
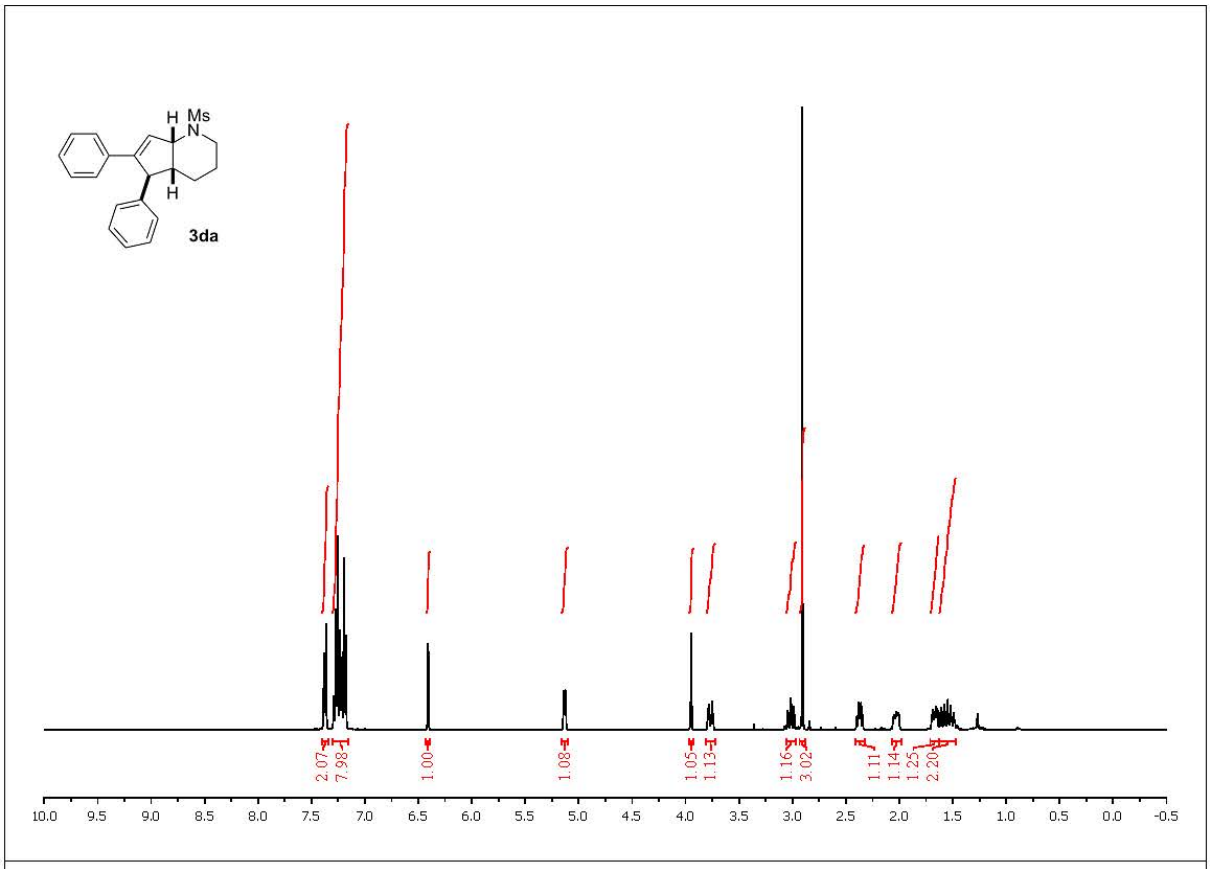
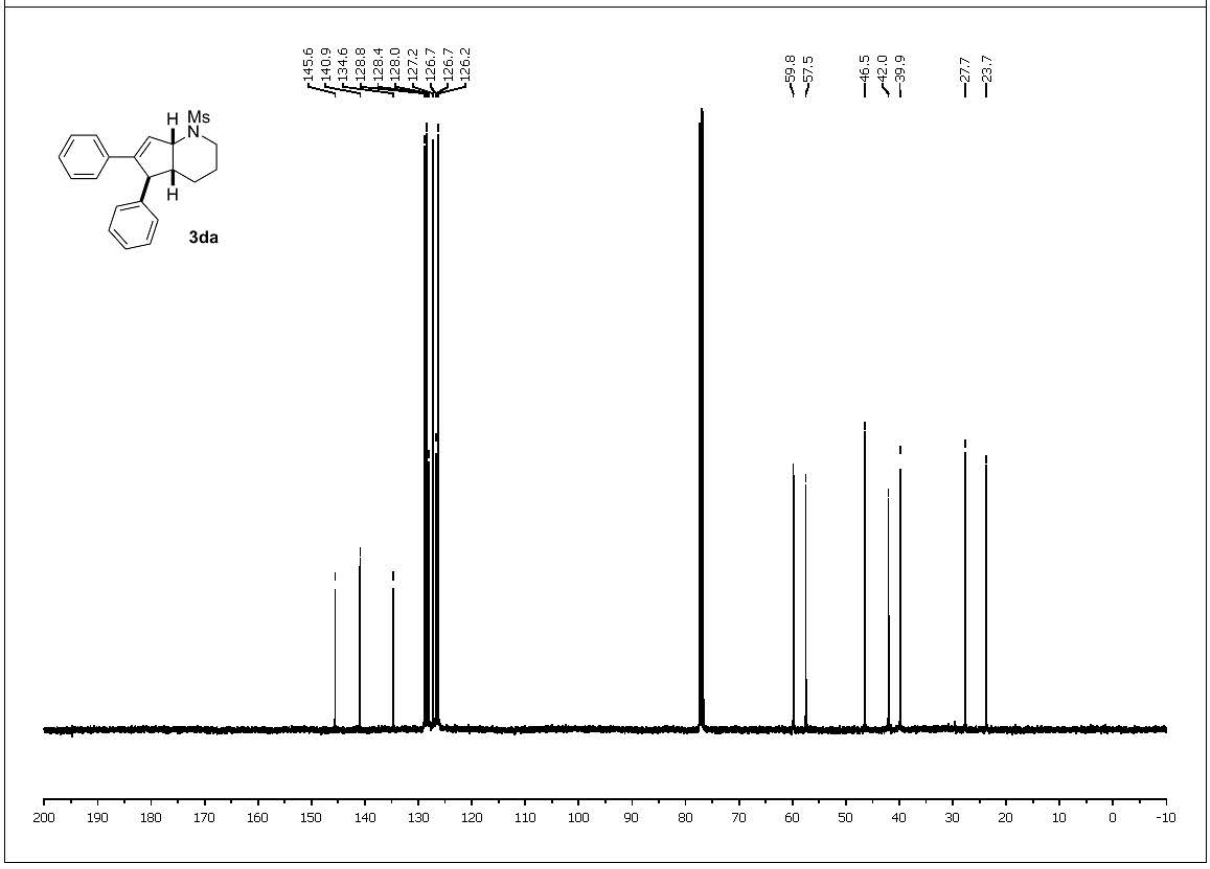
46.4
42.1
27.6
23.1
21.5


Ts
N
H
Ph
Ph
H
3ca
1.75
1.91
9.22
1.02
1.08
0.99
1.04
2.00
2.78
6.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


147.2
144.5
142.9
138.7
134.4
129.7
128.7
128.2
127.8
127.1
126.8
126.7
126.4
126.3
65.1
55.2
51.9
44.9
31.0
29.0
23.5
21.5
Ts
N
H
Ph
Ph
H
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


H
Ms
N
H
3da
2.07
7.98
1.00
1.08
1.05
1.13
1.16
3.02
1.11
1.14
1.25
2.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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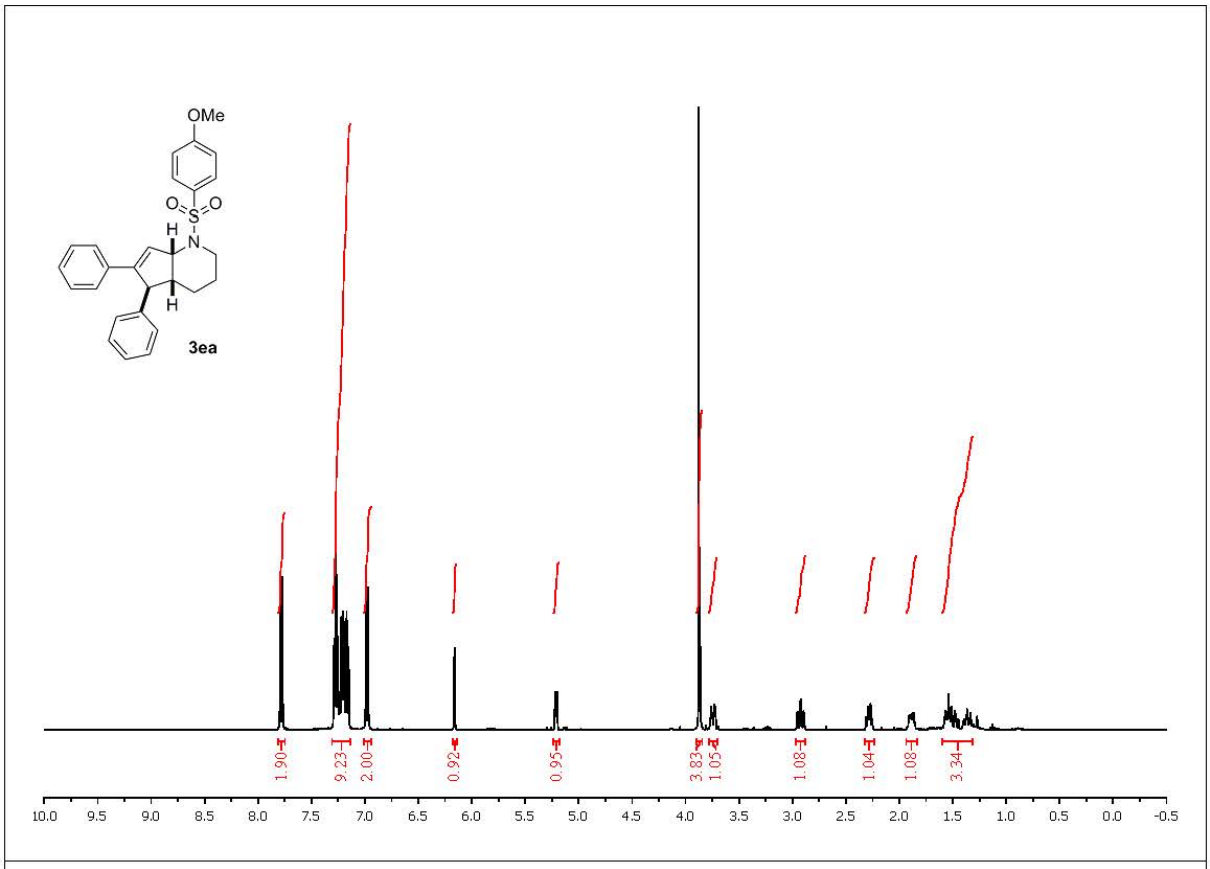
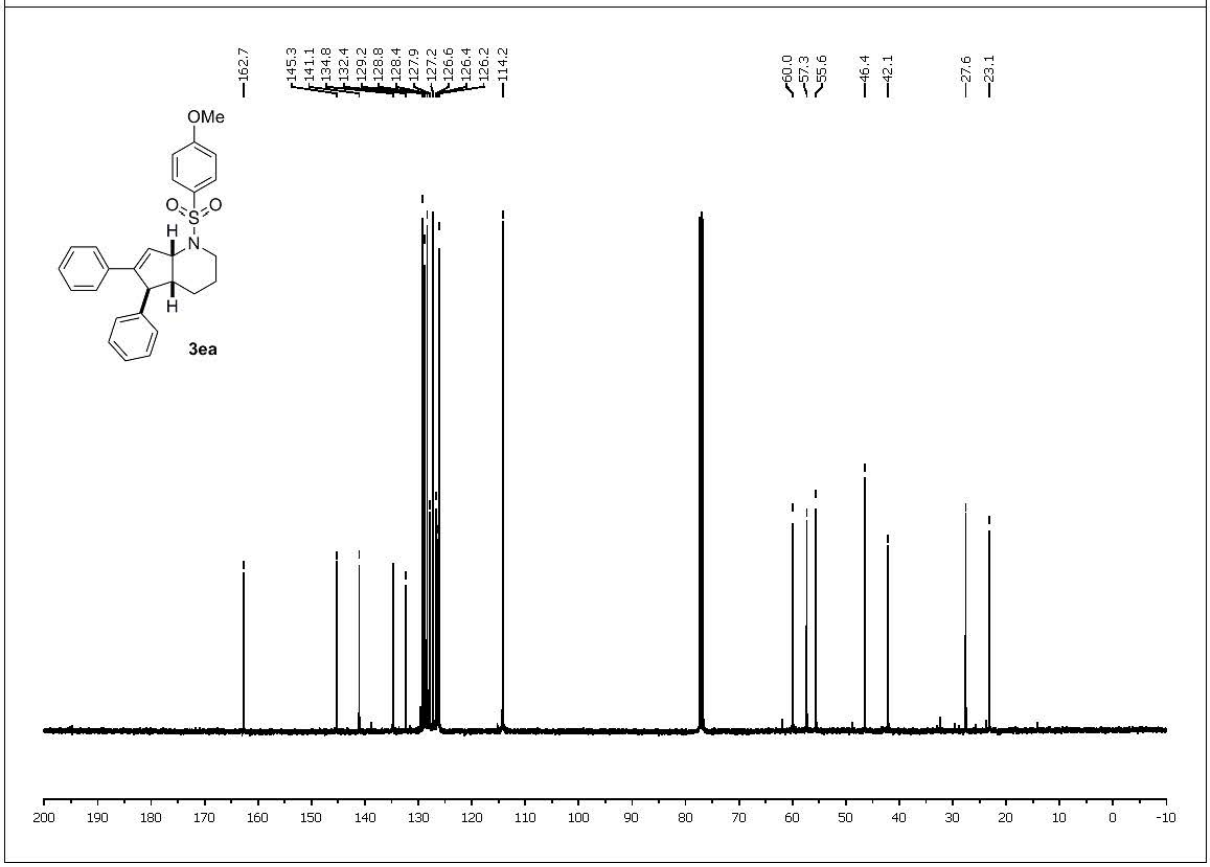
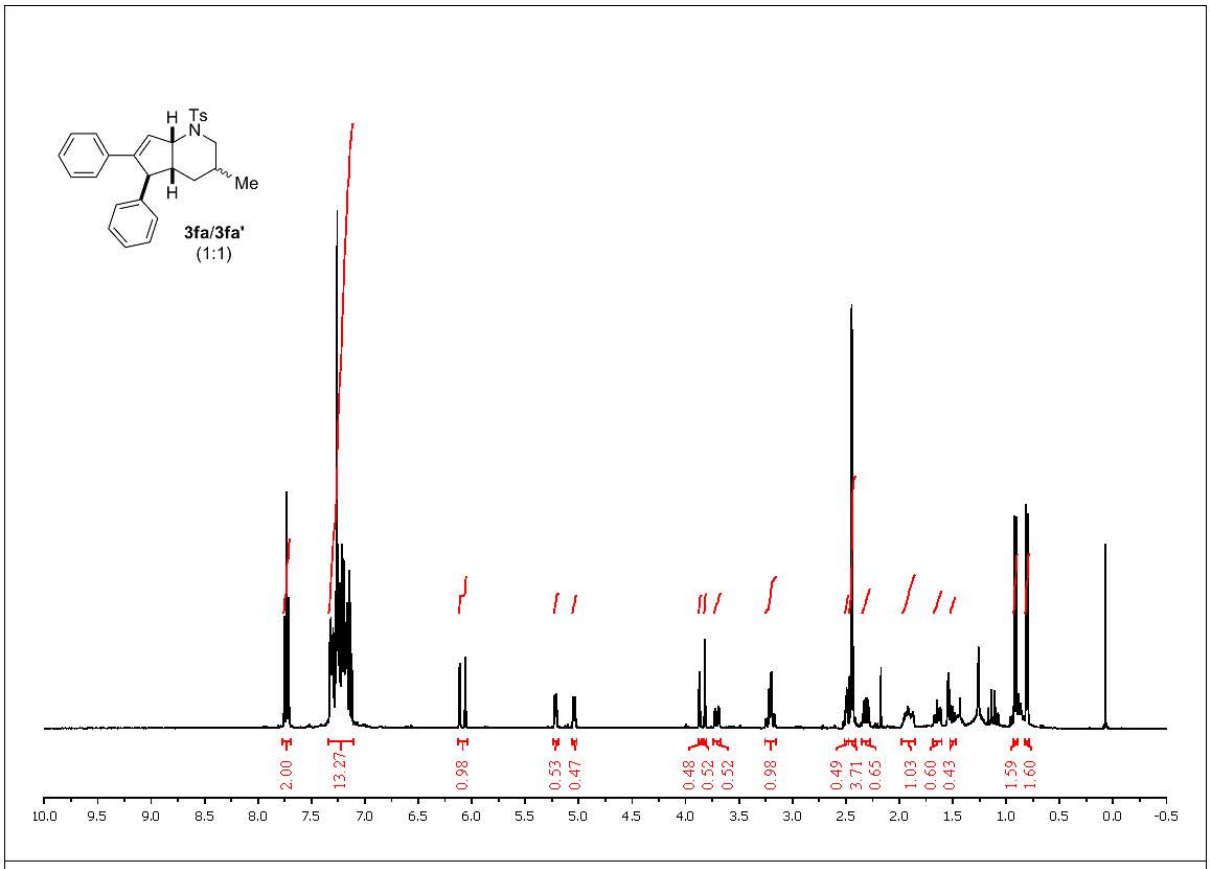
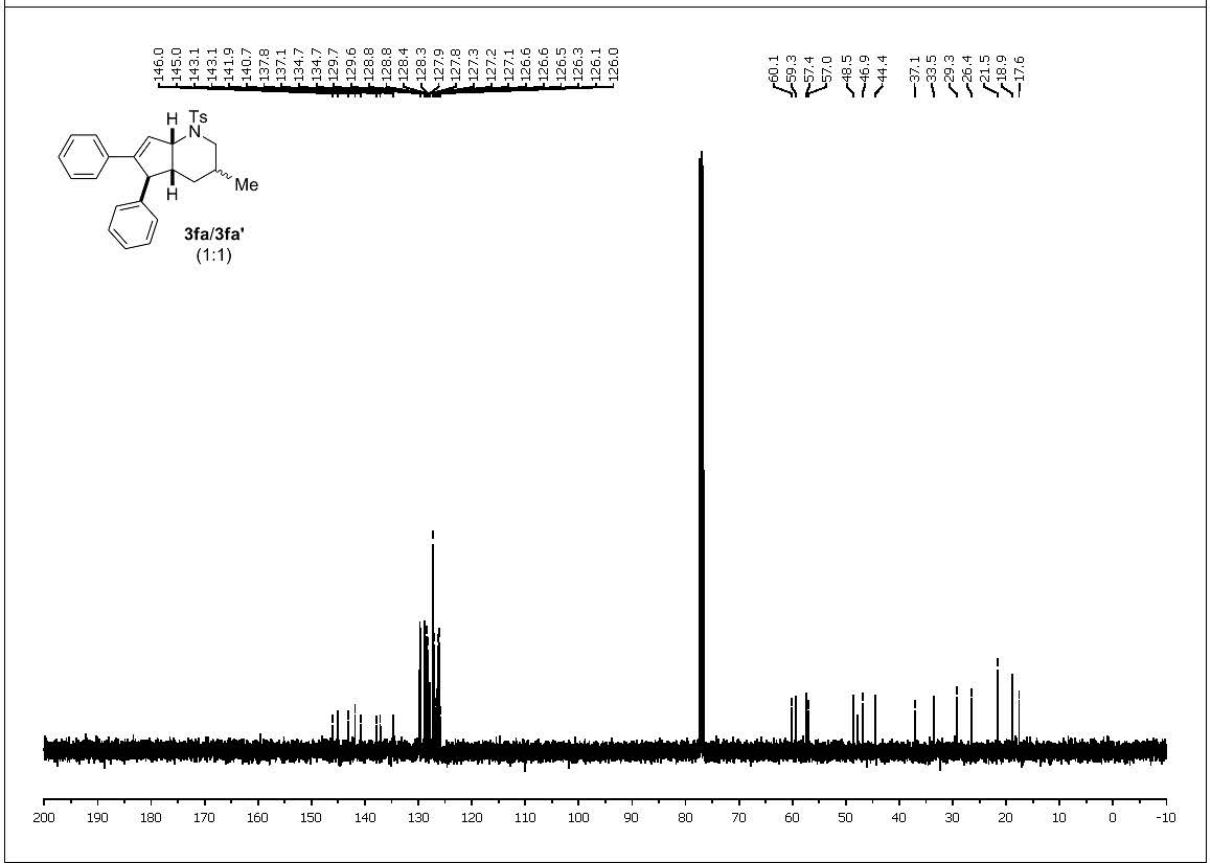
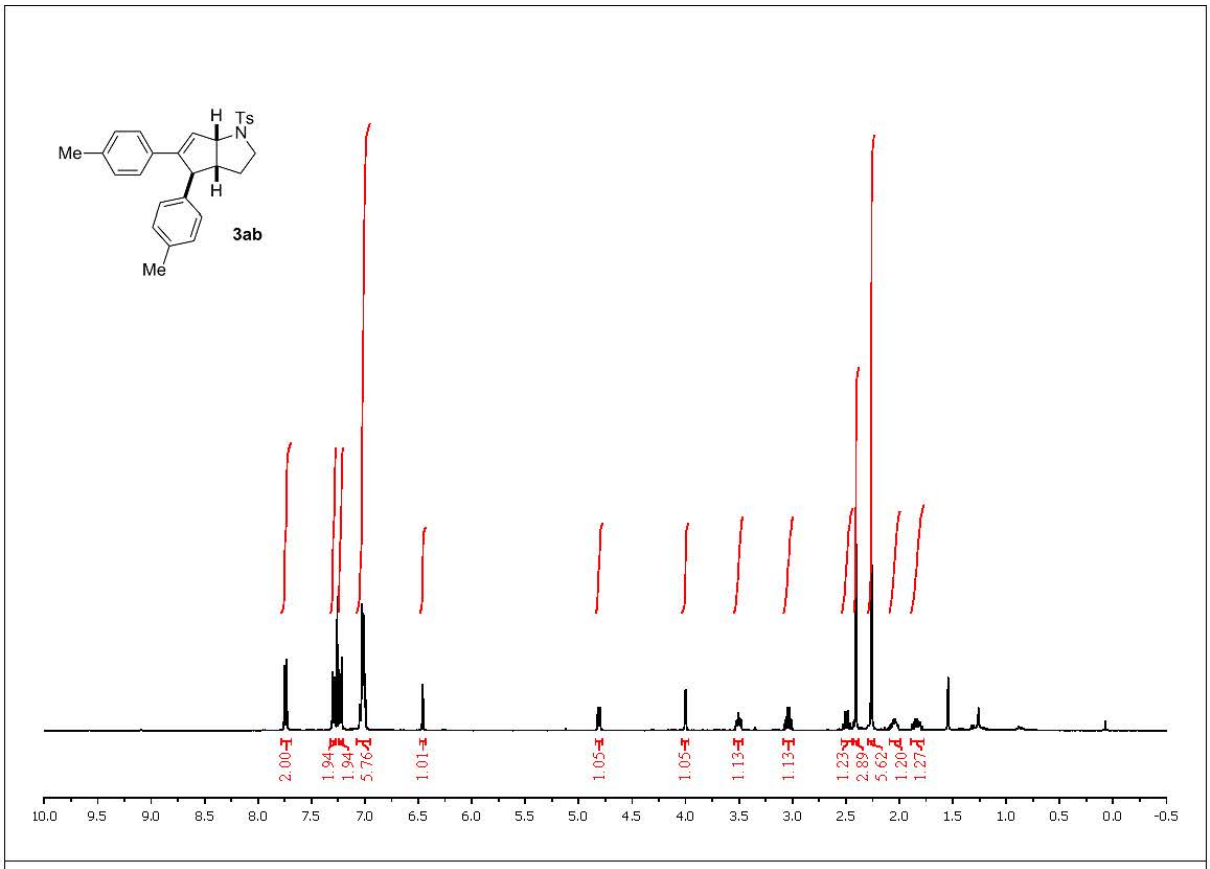
140.9
134.6
128.8
128.4
128.0
127.2
126.7
126.7
126.2
59.8
57.5
46.5
42.0
39.9
27.7
23.7
H
Ms
N
H
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

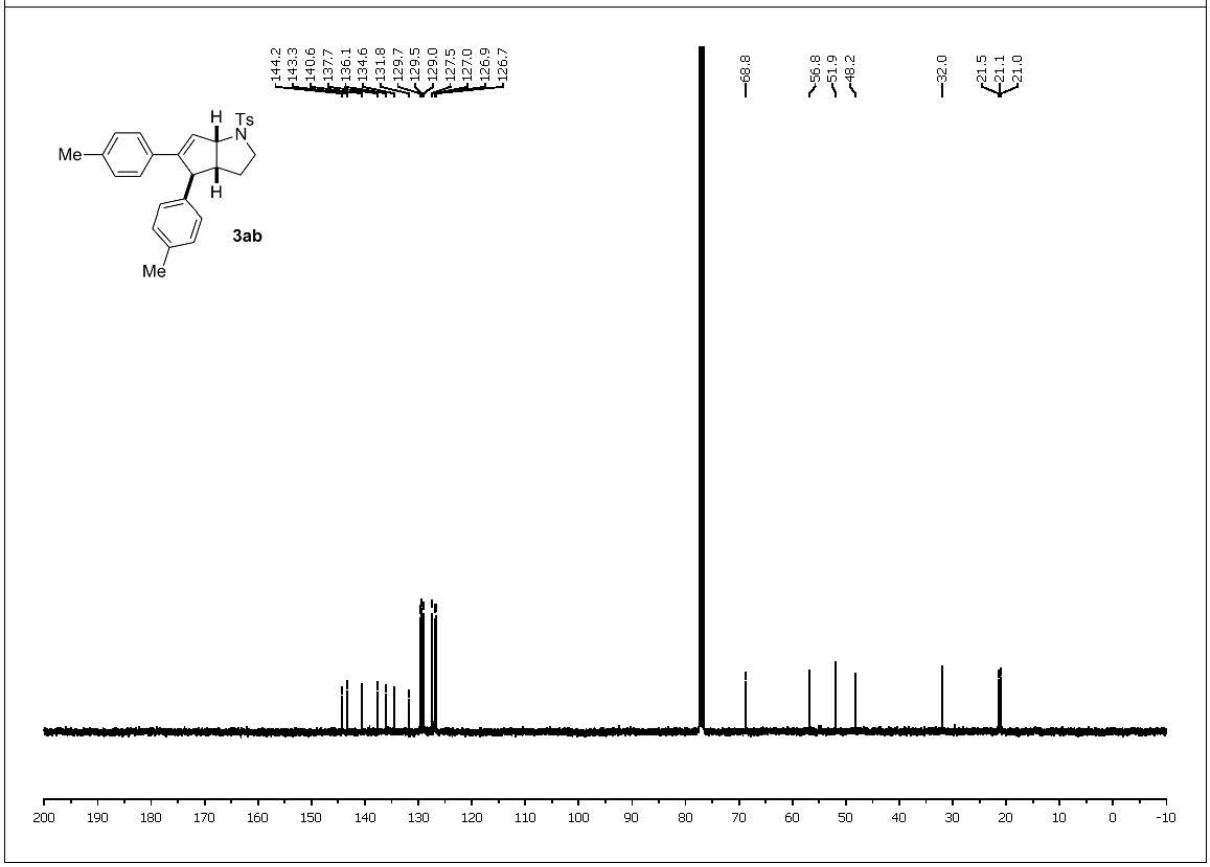

OMe
O
S
O
H
N
H
3ea
1.90
9.23
2.00
0.92
0.95
3.83
1.05
1.08
1.04
1.08
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


162.7
145.3
141.1
134.8
132.4
129.2
128.8
128.4
127.9
127.2
126.6
126.4
126.2
114.2
60.0
57.3
55.6
46.4
42.1
27.6
23.1
OMe
O
S
O
H
N
H
3ea
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


H
Ts
N
Me
H
3fa/3fa'
(1:1)
2.00
13.27
0.98
0.53
0.47
0.48
0.52
0.52
0.98
0.49
3.71
0.65
1.03
0.60
0.43
1.59
1.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


146.0
145.0
143.1
143.1
141.9
140.7
137.8
137.1
134.7
134.7
129.7
129.6
128.8
128.8
128.4
128.3
127.9
127.8
127.3
127.2
127.1
126.6
126.6
126.5
126.3
126.1
126.0
60.1
59.3
57.4
57.0
48.5
46.9
44.4
37.1
33.5
29.3
26.4
21.5
18.9
17.6
H
Ts
N
Me
H
3fa/3fa'
(1:1)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


H
Ts
N
H
Me
Me
3ab
2.00
1.94
1.94
5.76
1.01
1.05
1.05
1.13
1.13
1.23
2.89
5.62
1.20
1.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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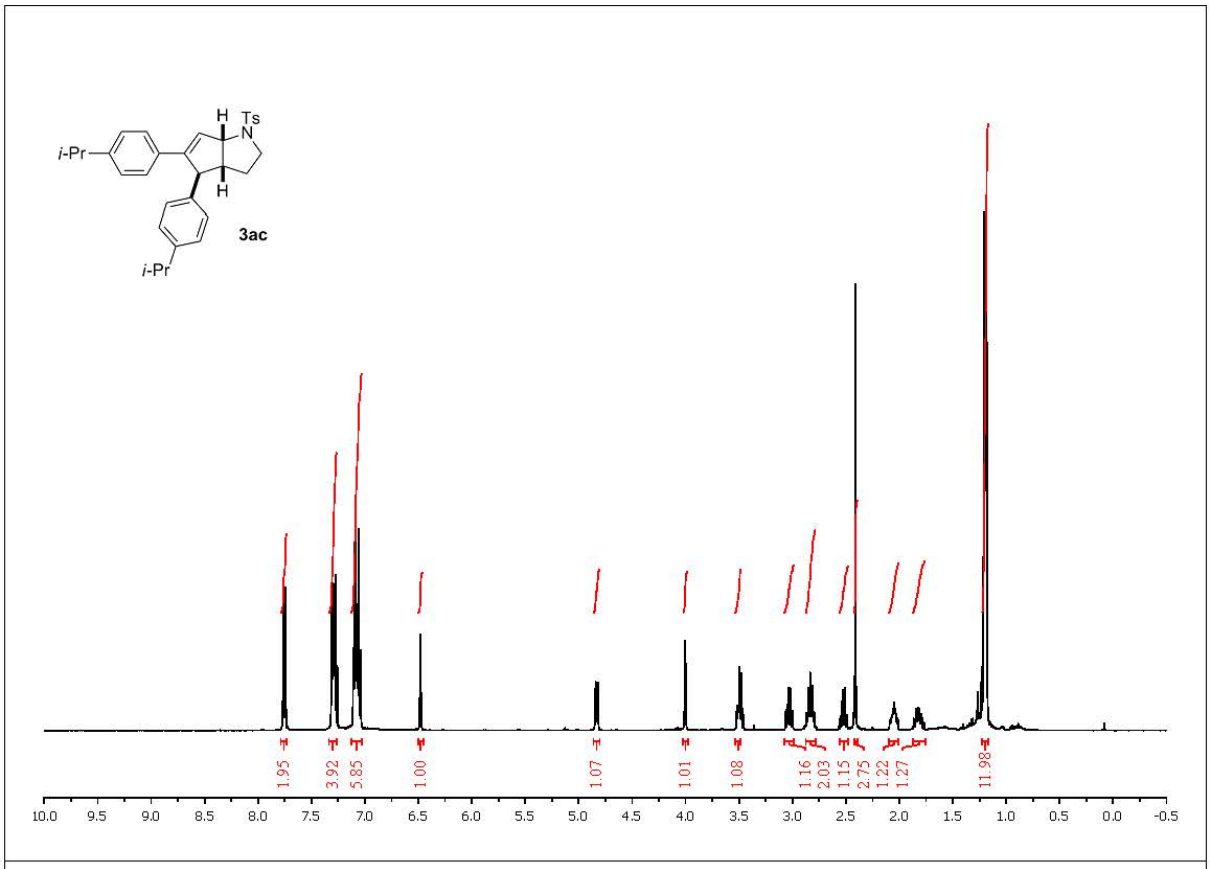
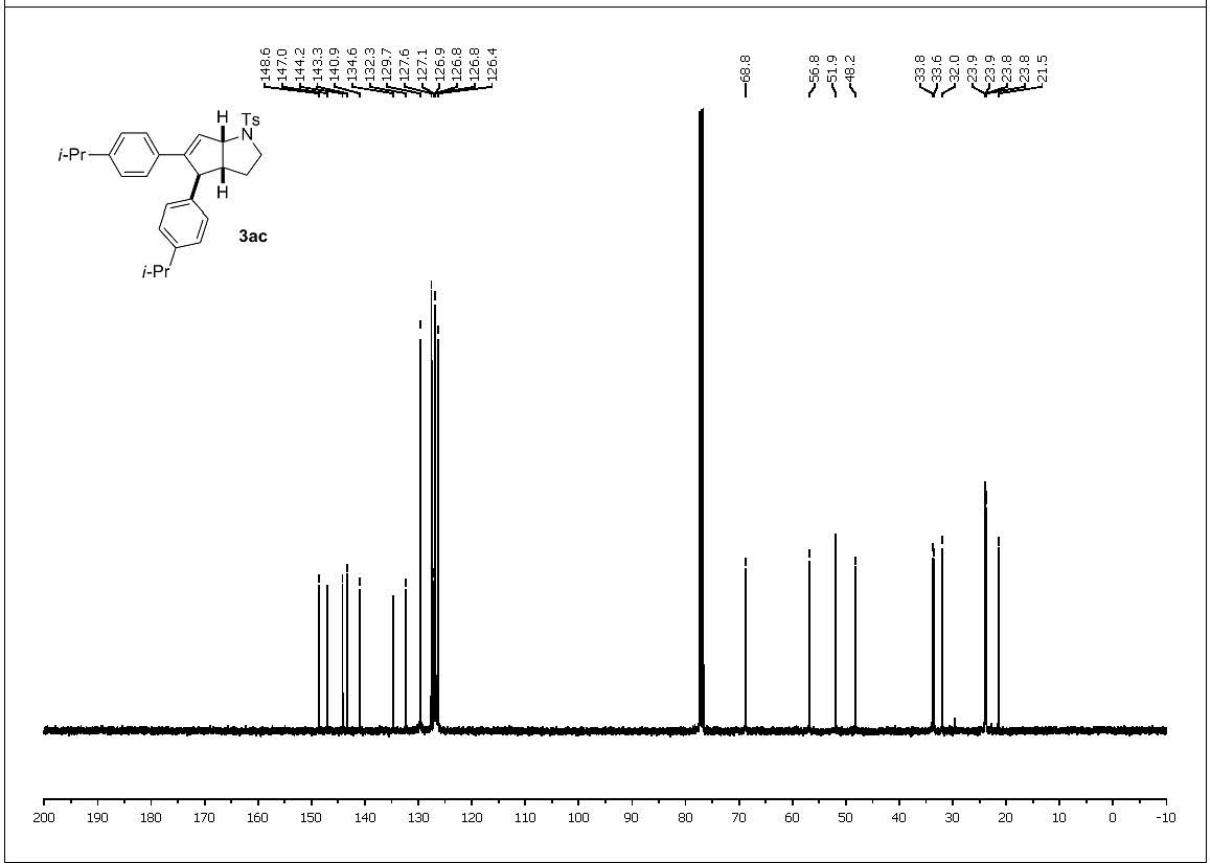
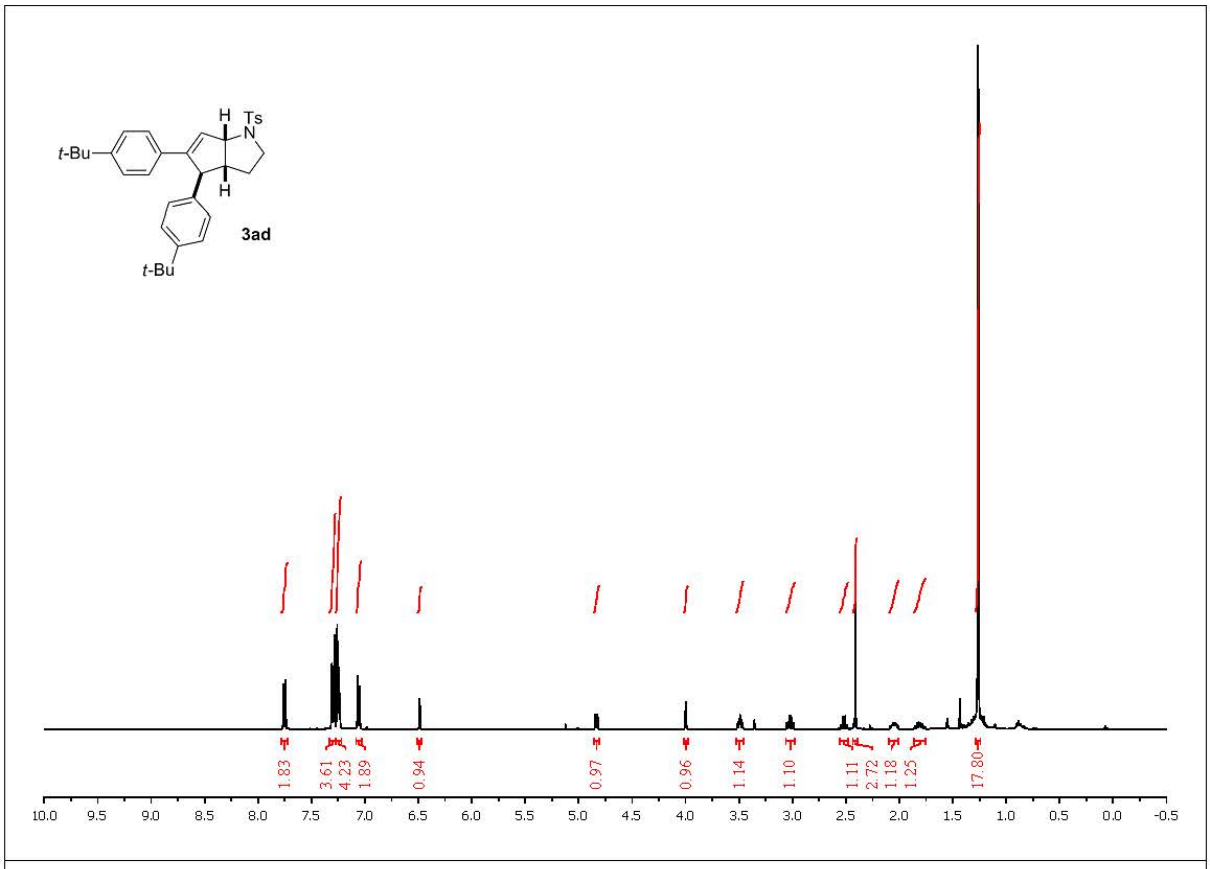
143.3
140.6
137.7
136.1
134.6
131.8
129.7
129.5
129.0
127.5
127.0
126.9
126.7
68.8
56.8
51.9
48.2
32.0
21.5
21.1
21.0
H
Ts
N
H
Me
Me
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


H
Ts
N
H
i-Pr
i-Pr
3ac
1.95
3.92
5.85
1.00
1.07
1.01
1.08
1.16
2.03
1.15
2.75
1.22
1.27
11.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


148.6
147.0
144.2
143.3
140.9
134.6
132.3
129.7
127.6
127.1
126.9
126.8
126.8
126.4
68.8
56.8
51.9
48.2
33.8
33.6
32.0
23.9
23.9
23.8
23.8
21.5
H
Ts
N
H
i-Pr
i-Pr
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


H
Ts
N
H
t-Bu
t-Bu
3ad
1.83
3.61
4.23
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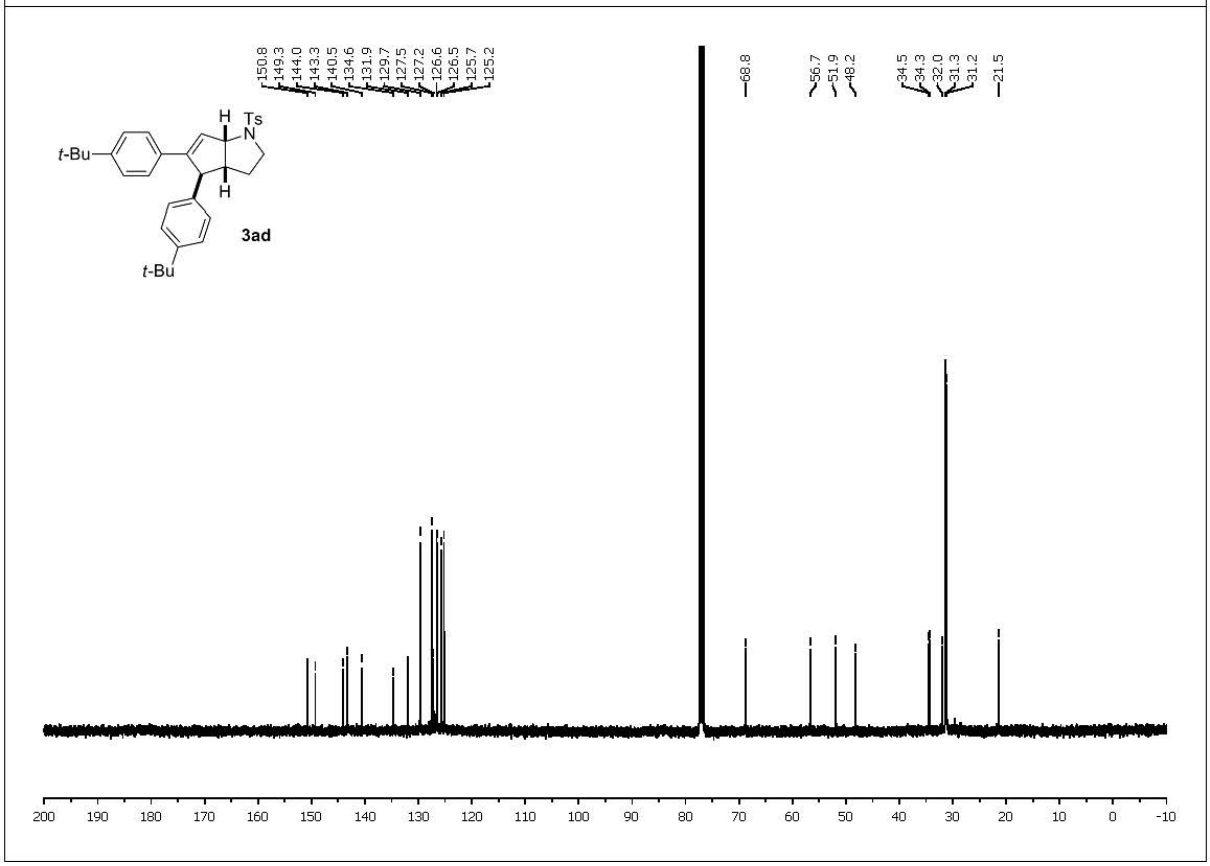
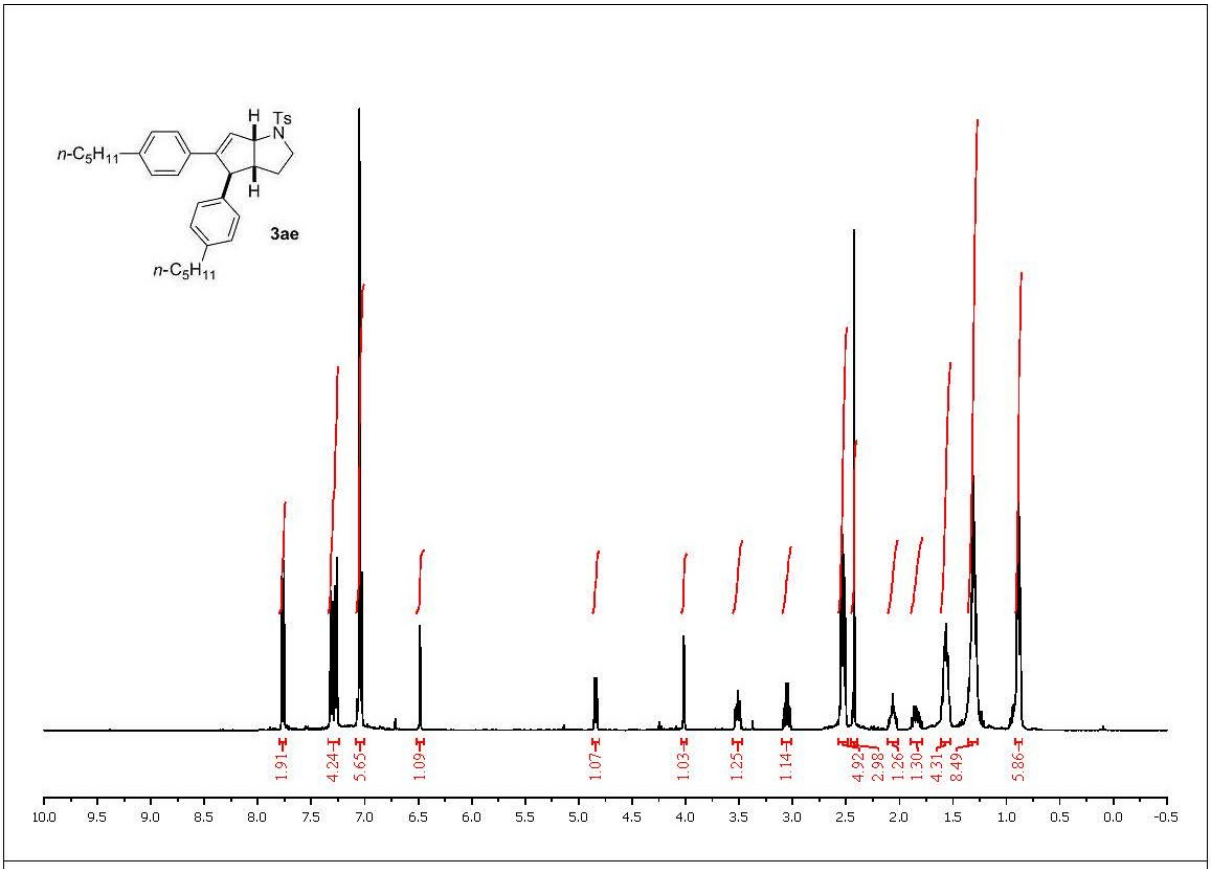
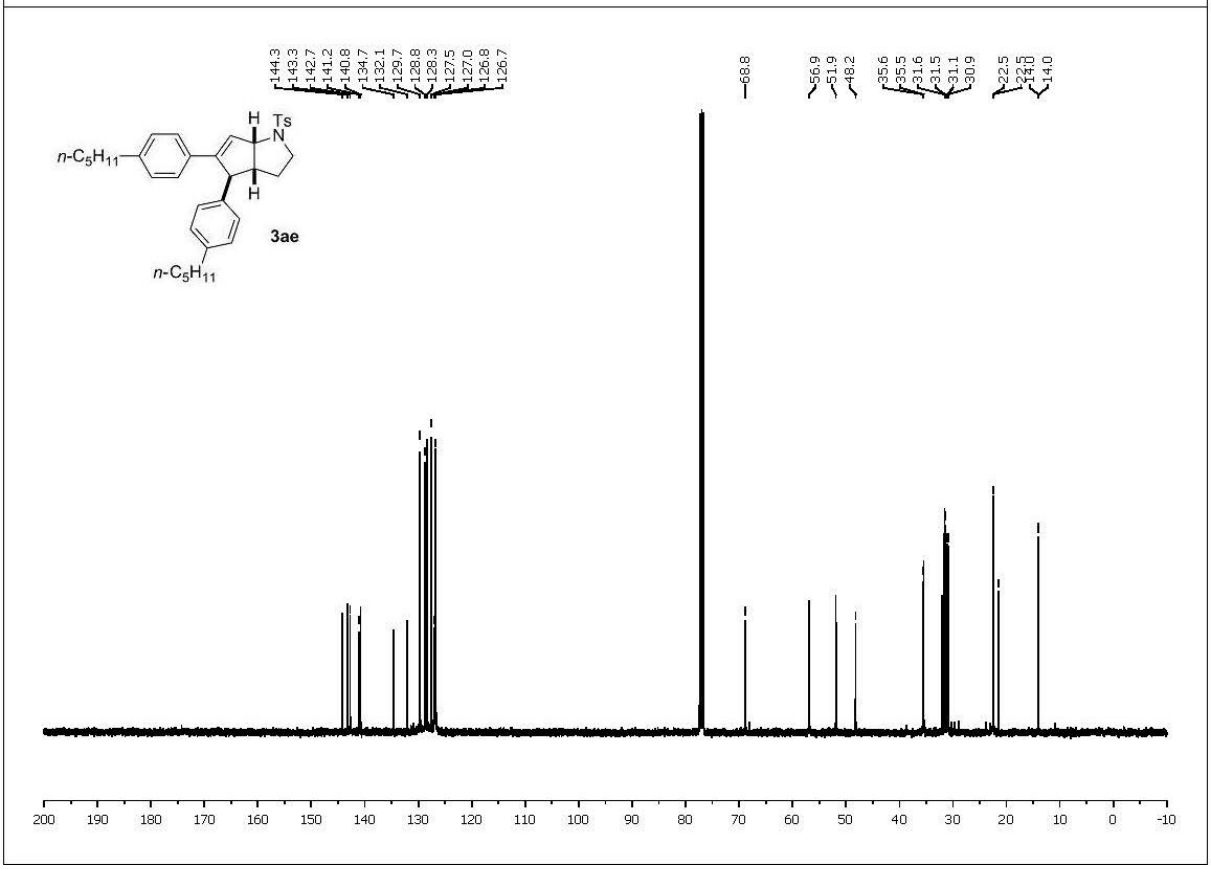
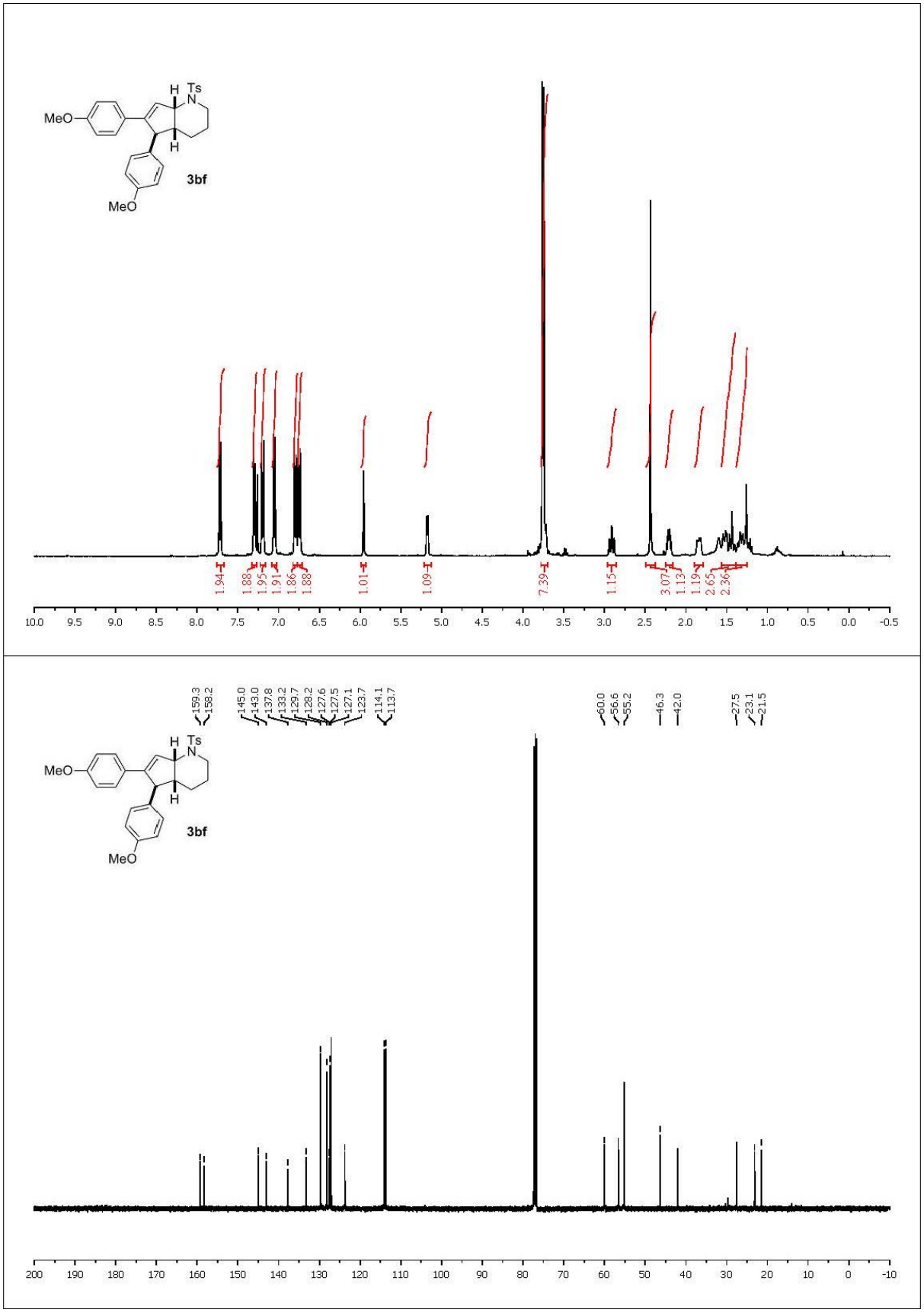
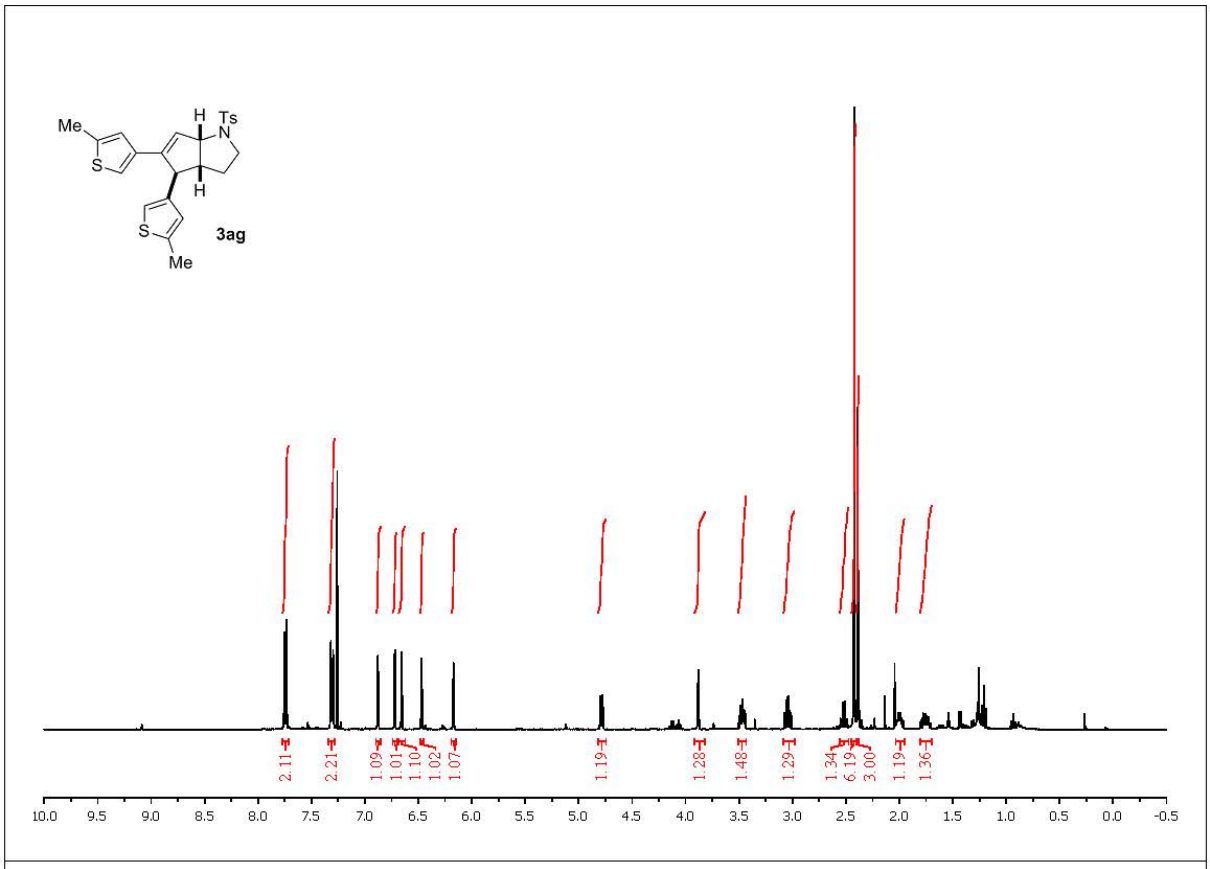
0.94
0.97
0.96
1.14
1.10
1.11
2.72
1.18
1.25
17.80

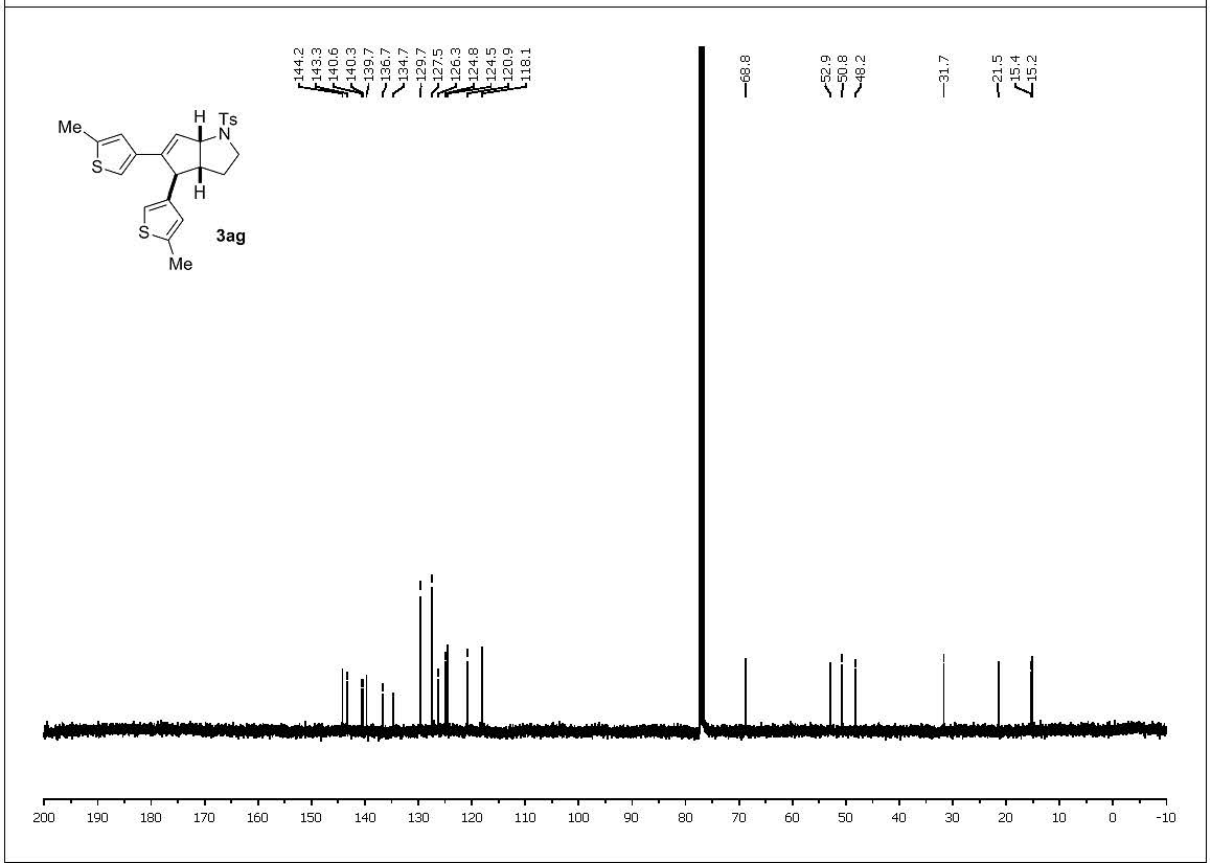

150.8
149.3
144.0
143.3
140.5
134.6
131.9
129.7
127.5
127.2
126.6
126.5
125.7
125.2
68.8
56.7
51.9
48.2
34.5
34.3
32.0
31.3
31.2
21.5
H
Ts
N
H
t-Bu
t-Bu
3ad

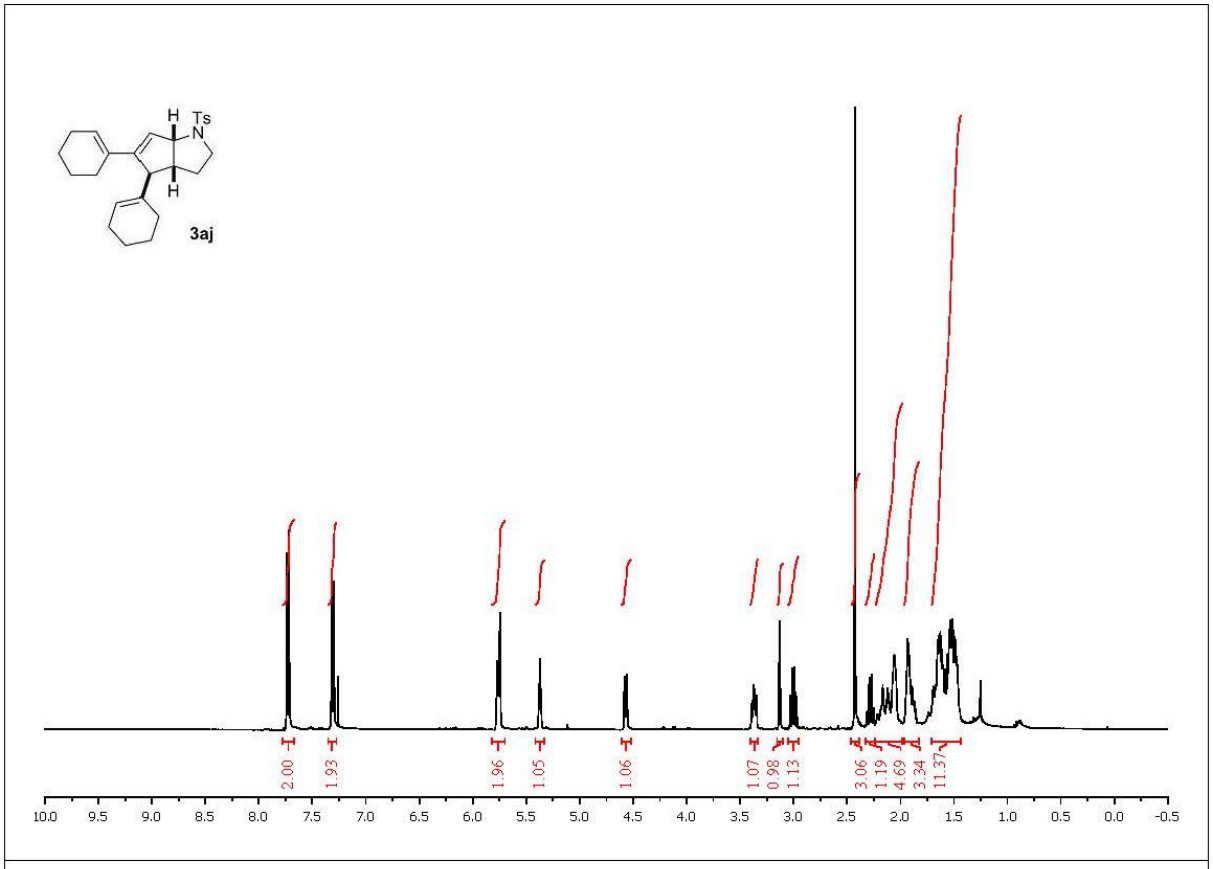

H
Ts
N
H
n-C5H11
3ae
n-C5H11
1.91
4.24
5.65
1.09
1.07
1.03
1.25
1.14
4.92
2.98
1.26
1.30
4.31
8.49
5.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

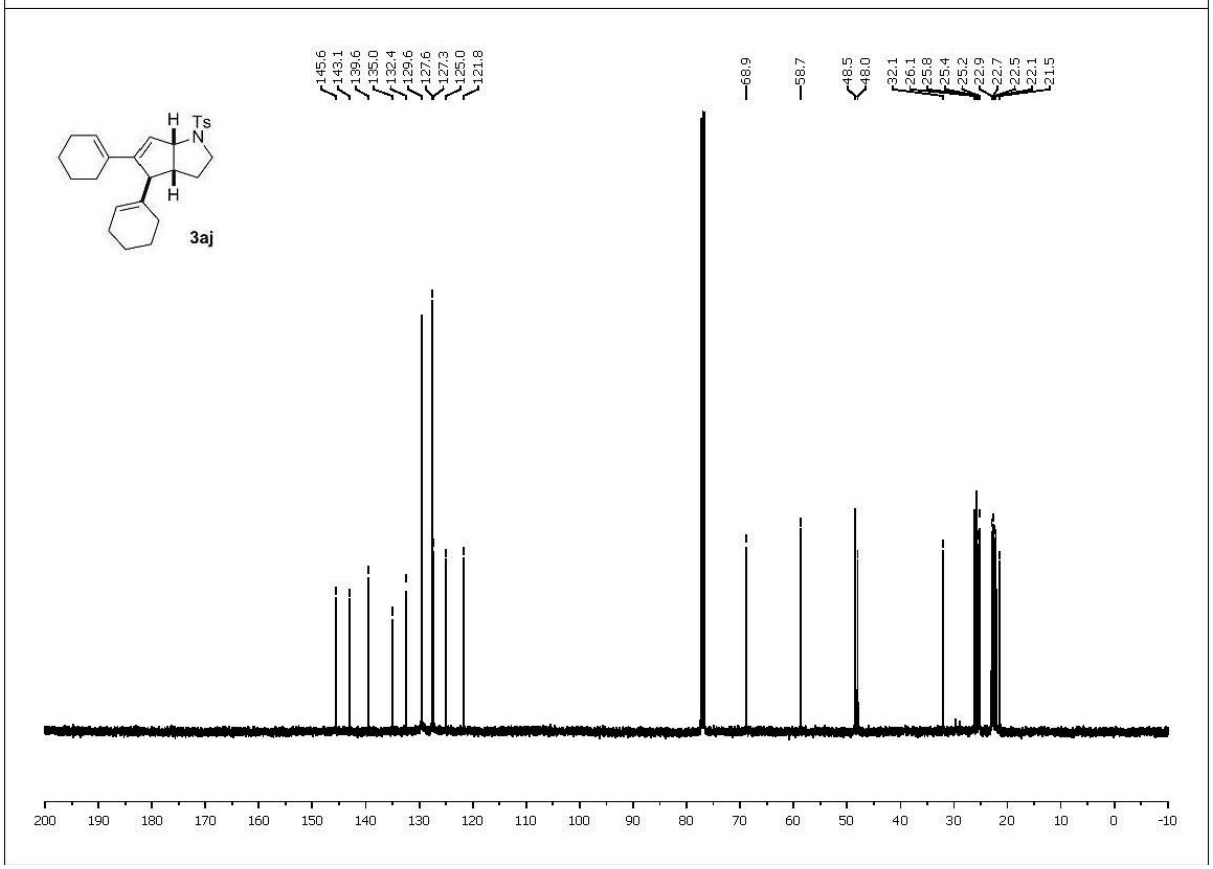

144.3
143.3
142.7
141.2
140.8
134.7
132.1
129.7
128.8
128.3
127.5
127.0
126.8
126.7
68.8
56.9
51.9
48.2
35.6
35.5
31.6
31.5
31.1
30.9
22.5
22.5
14.0
14.0
H
Ts
N
H
n-C5H11
3ae
n-C5H11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

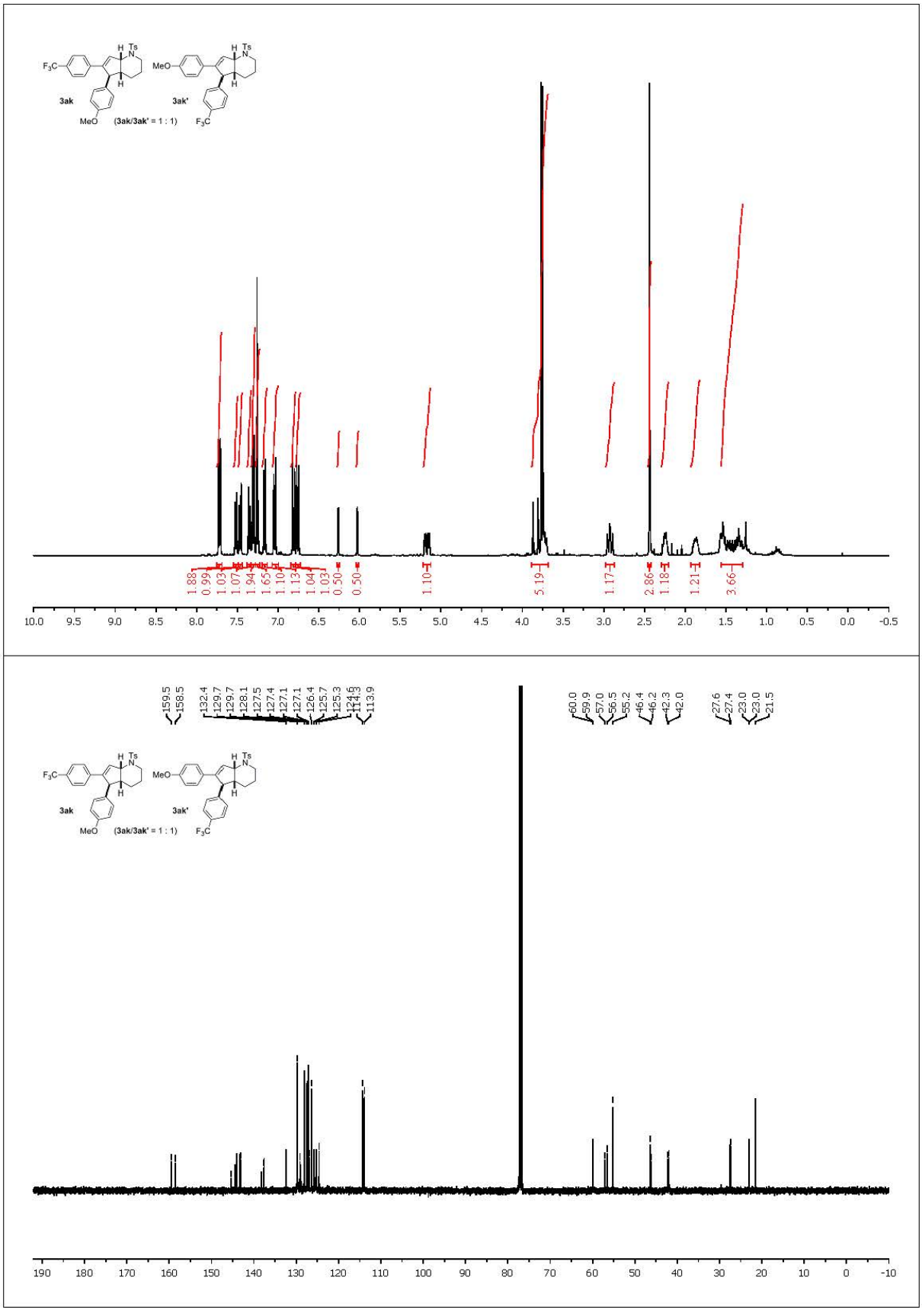

H
Ts
N
MeO
H
MeO
3bf
1.94
1.88
1.95
1.91
1.86
1.88
1.01
1.09
7.39
1.15
3.07
1.13
1.19
2.65
2.36
159.3
158.2
145.0
143.0
137.8
133.2
129.7
128.2
127.6
127.5
127.1
123.7
114.1
113.7
60.0
56.6
55.2
46.3
42.0
27.5
23.1
21.5

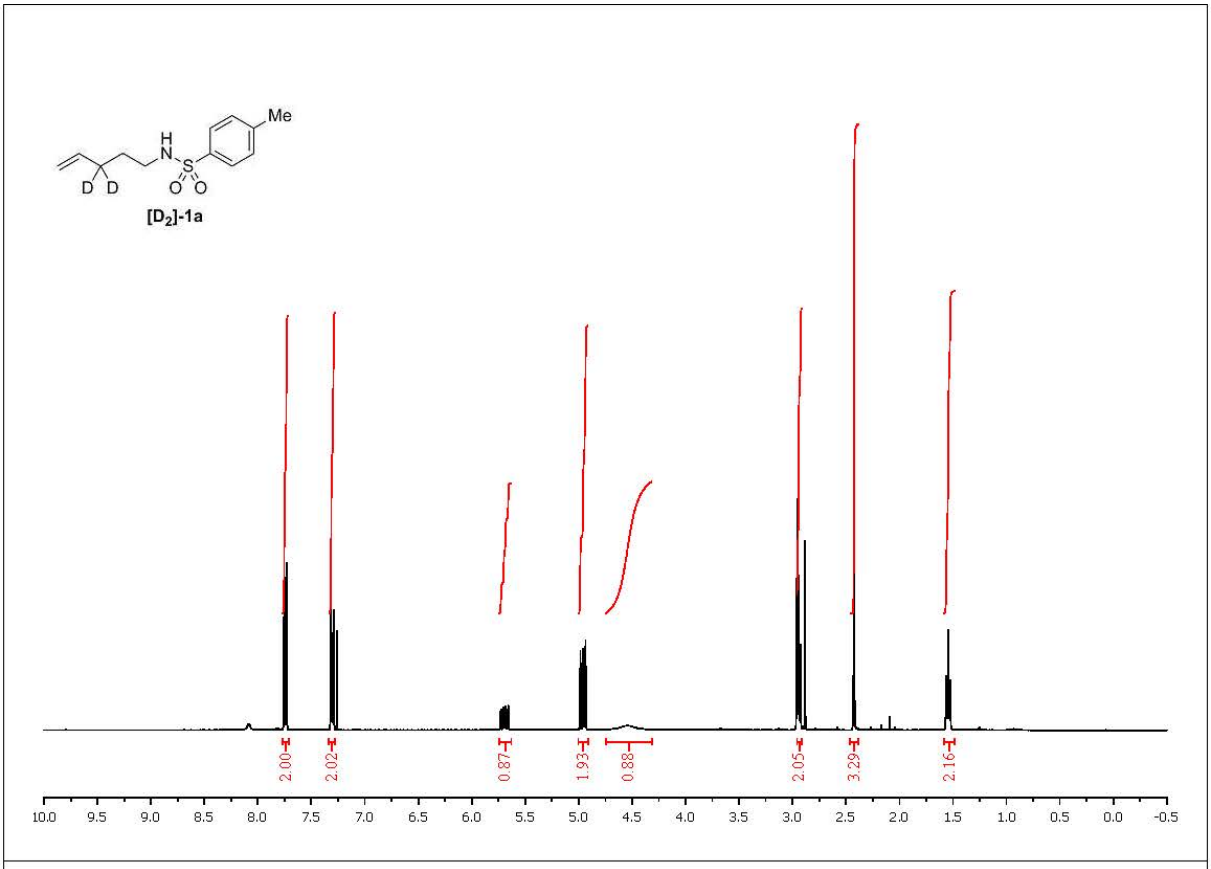

Me
S
H
Ts
N
H
S
Me
3ag
2.11
2.21
1.09
1.01
1.10
1.02
1.07
1.19
1.28
1.48
1.29
1.34
6.19
3.00
1.19
1.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

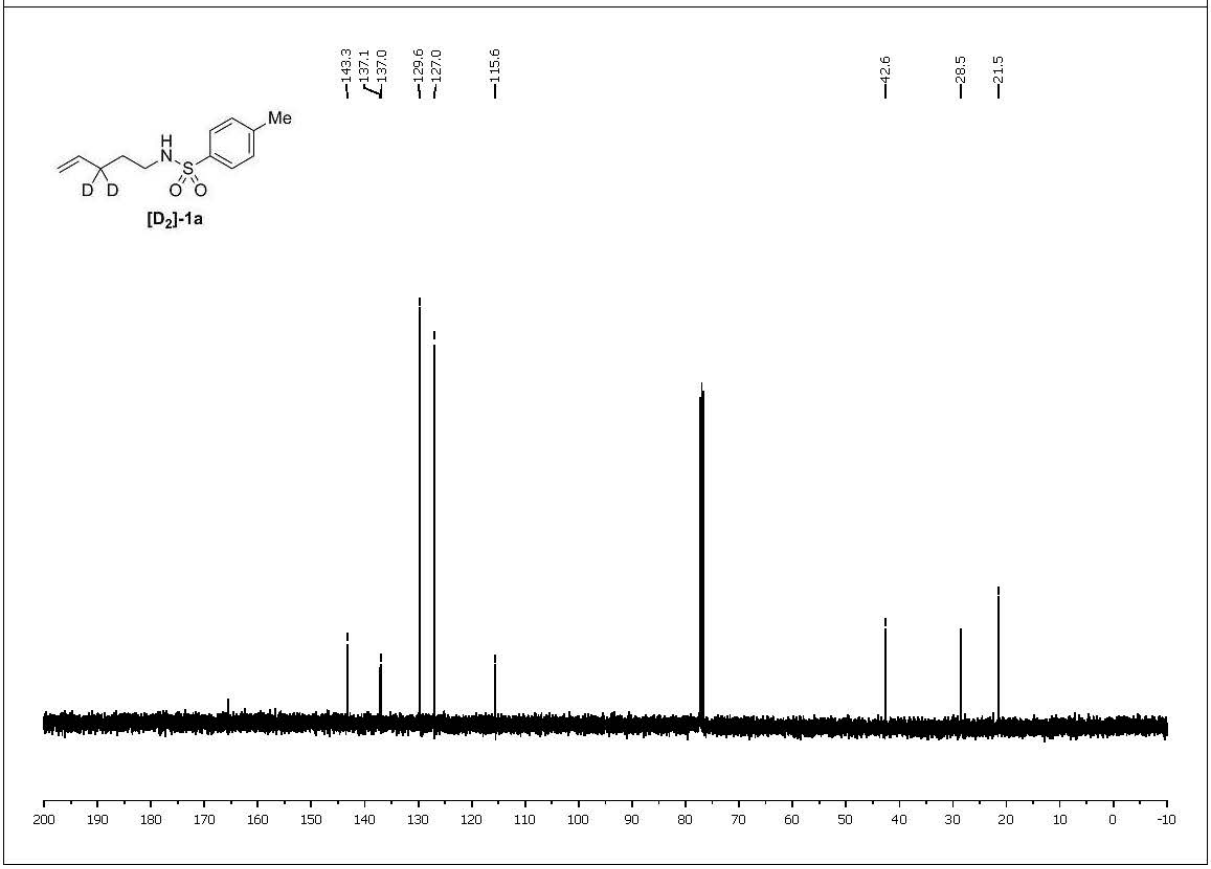

144.2
143.3
140.6
140.3
139.7
136.7
134.7
129.7
127.5
126.3
124.8
124.5
120.9
118.1
68.8
52.9
50.8
48.2
31.7
21.5
15.4
15.2
Me
S
H
Ts
N
H
S
Me
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

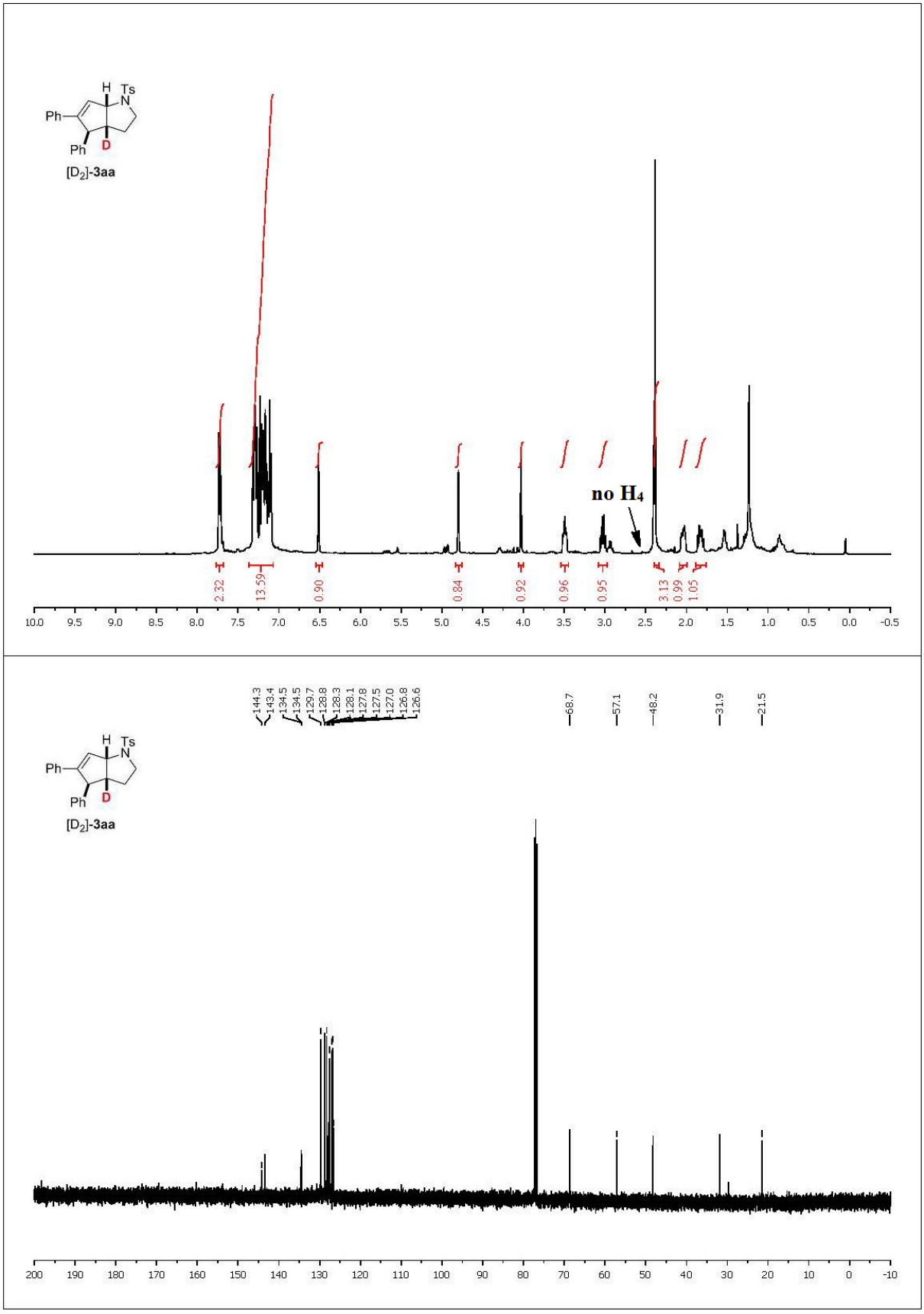

H
Ts
N
H
3aj
2.00
1.93
1.96
1.05
1.06
1.07
0.98
1.13
3.06
1.19
4.69
3.34
11.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

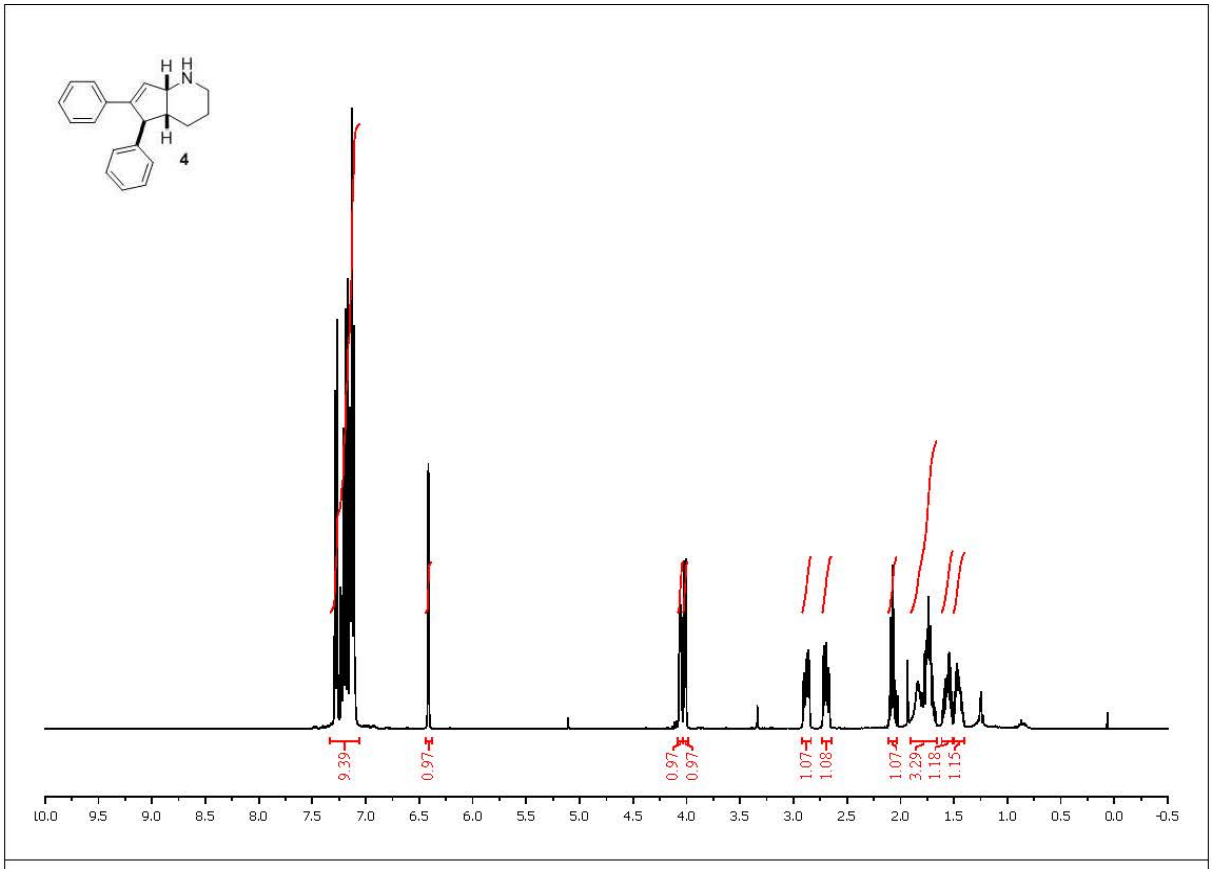

145.6
143.1
139.6
135.0
132.4
129.6
127.6
127.3
125.0
121.8
68.9
58.7
48.5
48.0
32.1
26.1
25.8
25.4
25.2
22.9
22.7
22.5
22.1
21.5
H
Ts
N
H
3aj
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

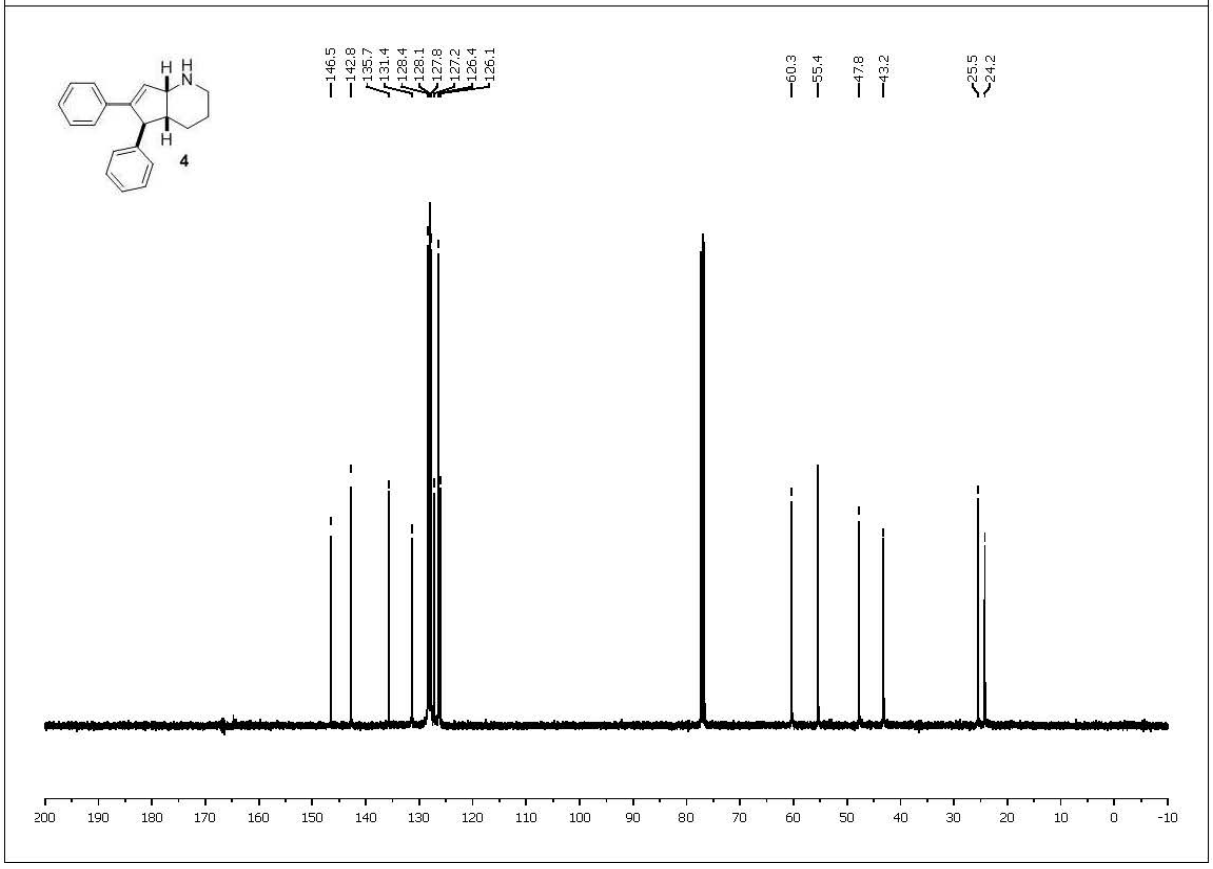

3ak
3ak'
(3ak/3ak' = 1 : 1)
1.88
0.99
1.03
1.07
1.94
1.65
1.10
1.13
1.04
1.03
0.50
0.50
1.10
5.19
1.17
2.86
1.18
1.21
3.66
159.5
158.5
132.4
129.7
129.7
128.1
127.5
127.4
127.1
127.1
126.4
125.7
125.3
114.5
113.9
60.0
59.9
57.0
56.5
55.2
46.4
46.2
42.3
42.0
27.6
27.4
23.0
23.0
21.5


Me
H
N
S
O O
D D
[D2]-1a
2.00
2.02
0.87
1.93
0.88
2.05
3.29
2.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


143.3
137.1
137.0
129.6
127.0
115.6
42.6
28.5
21.5
Me
H
N
S
O O
D D
[D2]-1a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


H
Ts
N
Ph
Ph
D
[D2]-3aa
no H4
2.32
13.59
0.90
0.84
0.92
0.96
0.95
3.13
0.99
1.05
144.3
143.4
134.5
134.5
129.7
128.8
128.3
128.1
127.8
127.5
127.0
126.8
126.6
68.7
57.1
48.2
31.9
21.5


4
9.39
0.97
0.97
0.97
1.07
1.08
1.07
3.29
1.18
1.15


4
146.5
142.8
135.7
131.4
128.4
128.1
127.8
127.2
126.4
126.1
60.3
55.4
47.8
43.2
25.5
24.2