Support Information for:

Azotic Bridge Enabled By-Standing Immobilization of Chiral Diene ligand

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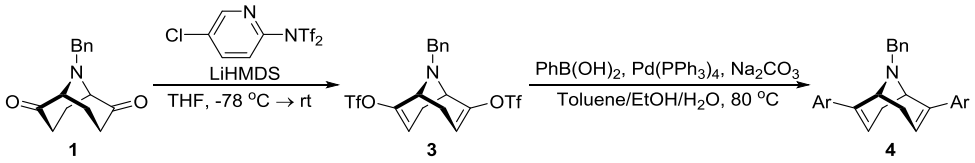
1. General information:

All reactions were carried out with standard Schlenk techniques under an argon atmosphere. All the solvents were dried using standard procedure and distilled before use. All commercially available chemical resources were used as received. Reactions were monitored by thin layer chromatography (TLC) supplied by Yantai Jiangyou Silicon Material Company (China). Visualization was accomplished with UV light or basic aqueous potassium permangante ($KMnO_4$). Chromatography was achieved using forced flow (flash chromatography) of the indicated solvent system on 300-400 mesh silica gel (Silicycle flash F60). Nuclear Magnetic Resonance (**NMR**) spectra were acquired on Agilent 400 or Bruker 400 instrument operating at 400, 100 and 376 MHz for ^{1}H, ^{13}C and ^{19}F, respectively. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard (TMS: δ 0.000 ppm) for **^{1}H NMR**, $CDCl_3$ (δ 77.16) for **^{13}C NMR**. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quintet = quint, heptet = hept, m = multiplet, br = broad resonance. High-resolution mass spectra (**HRMS**) and Low-resolution mass spectrometry (**LRMS**) were acquired through the National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry (CAS) and determined on a Waters Micromass GCT Premie spectrometer. X-ray photoelectron spectroscopy (**XPS**) was acquired through the large science instruments sharing platform of Shanghai University of Science and Technology and determined on ESCALAB 250Xi instrument for C, N.

The enantiomerically pure diketone **1** was prepared according to the literatures.[1] The N-tosylarylimines (**5a-f**) were prepared according to the literatures.[2]

2. Preparation of chiral diene ligand 4a-4f

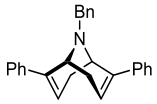


The diketone **1** (0.83 g, 3.4 mmol, 1 eq.) was dissolved in THF (50 mL), then a solution of LiHMDS in THF (1.0 M, 12 mL, 3.5 eq.) was added dropwisely at -78 ℃. After stirring at -78 ℃ for 0.5 h, a solution of Comins reagent (4.7 g, 12 mmol, 3.5 eq.) in THF (25mL) was added dropwisely. After stirring at -78 ℃ for 1 h, the temperature was allowed to reach room temperature. After stirring at rt for 0.5 h, the solvent was removed. The reside was diluted with water and extracted with ethyl acetate. The organic layer was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography (elute: hexane / EA = 50:1) to afford ditriflate **3** (1.4 g, 80% yield) as colorless oil. $[\alpha]_D^{25}$ +1.1 (c 1.15, $CHCl_3$) for 99% ee. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.25 (m, 5H), 5.87 (dd, *J* = 5.6, 2.2 Hz, 2H), 3.74 (d, *J* = 13.3 Hz, 1H), 3.70 (d, *J* = 13.3 Hz, 1H), 3.45 (d, *J* = 5.4 Hz, 2H), 2.67 (dd, *J* = 17.9, 4.8 Hz, 2H), 2.28 (dd, *J* = 18.0, 5.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.76, 136.85, 128.83, 128.66, 128.64, 127.88, 118.53 (q, *J* = 318.7 Hz), 114.80, 55.93, 52.18, 26.28. **^{19}F NMR** (376

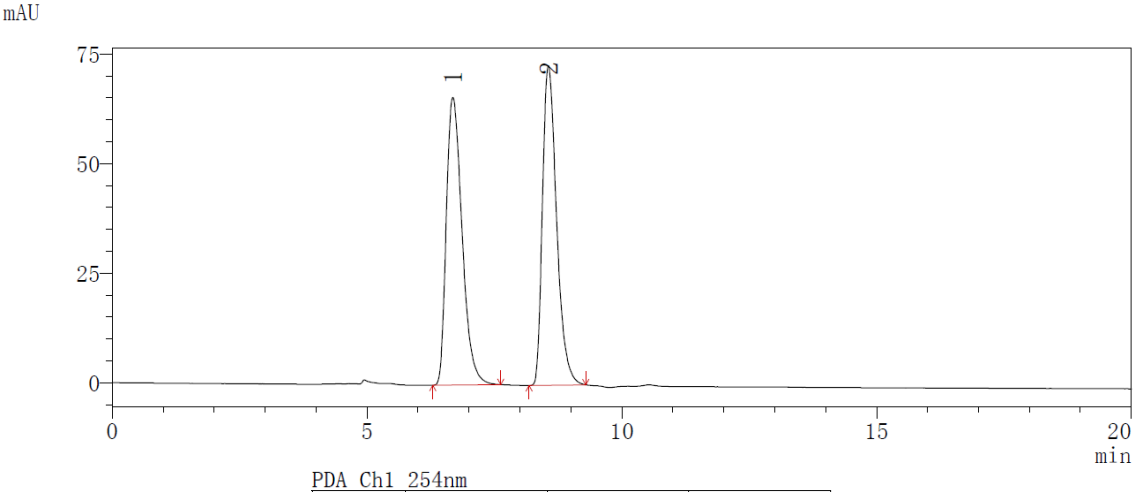
MHz, $CDCl_3$): δ 73.89. **ESI-MS**: 507.9 $[M+H]^+$. **HRMS**(ESI): m/z calcd for $C_{17}H_{16}O_6NF_6S_2$ $[M+H]^+$ 508.0318, found 508.0317.

Under nitrogen, a mixture of arylboronic acid (4.0 mmol, 4.0 eq.), $Pd(PPh_3)_4$ (116 mg, 10 mmol%), ditriflate **3** (0.51 mg, 1.0 mmol, 1.0 eq.), toluene (10 mL), EtOH (3.3 mL) and aqueous solution of Na_2CO_3 (1.2 M, 5.0 mL, 6 eq.) was heated at 80 ℃ overnight. The reaction was quenched with saturated NH_4Cl. The mixture is extracted with ethyl acetate, washed with brine. The organic layer was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford chiral dienes **4**.

(1*R*,5*R*)-9-Benzyl-2,6-diphenyl-9-azabicyclo[3.3.1]nona-2,6-diene (**4a**)

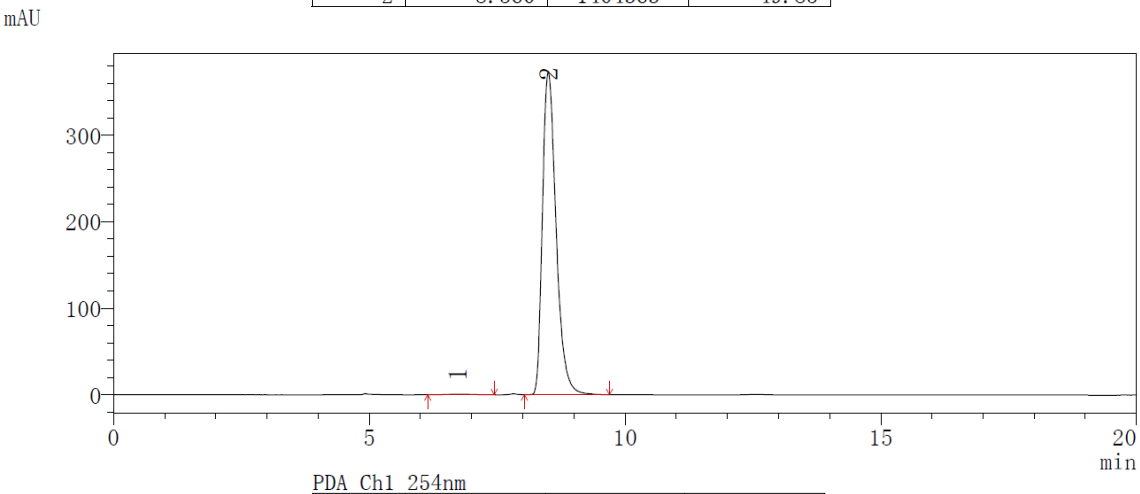


$[\alpha]_D^{25}$ +50.2 (c 1.00, $CHCl_3$) for 99% ee. Light yellow oil. **^{1}H NMR** (400 MHz, CDCl3): δ 7.52 – 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 (d, *J* = 4.2 Hz, 9H), 7.27 – 7.19 (m, 2H), 6.04 (dd, *J* = 5.4, 2.3 Hz, 2H), 3.94 (d, *J* = 6.4 Hz, 2H), 3.90 (d, *J* = 13.5 Hz, 1H), 3.81 (d, *J* = 13.1 Hz, 1H), 2.61 (dd, *J* = 18.1, 5.6 Hz, 2H), 1.91 (dd, *J* = 18.3, 5.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.33, 139.29, 138.61, 129.18, 128.53, 128.49, 127.23, 127.13, 126.15, 121.19, 57.01, 52.12, 28.12. **ESI-MS**: 364.2 $[M+H]^+$. **HRMS**(DART): m/z calcd for $C_{27}H_{26}N$ $[M+H]^+$ 364.2060, found 364.2053. **HPLC**: Chiralcel AD-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 98/2; flow = 0.7 mL/min; Retention time: 6.7 min [(*S*, *S*)-**4a**], 8.6 min [(*R*, *R*)-**4a**].



PDA Ch1 254nm

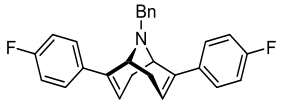
Number	Ret. Time	Area	Area%
1	6.685	1412828	50.15
2	8.560	1404363	49.85



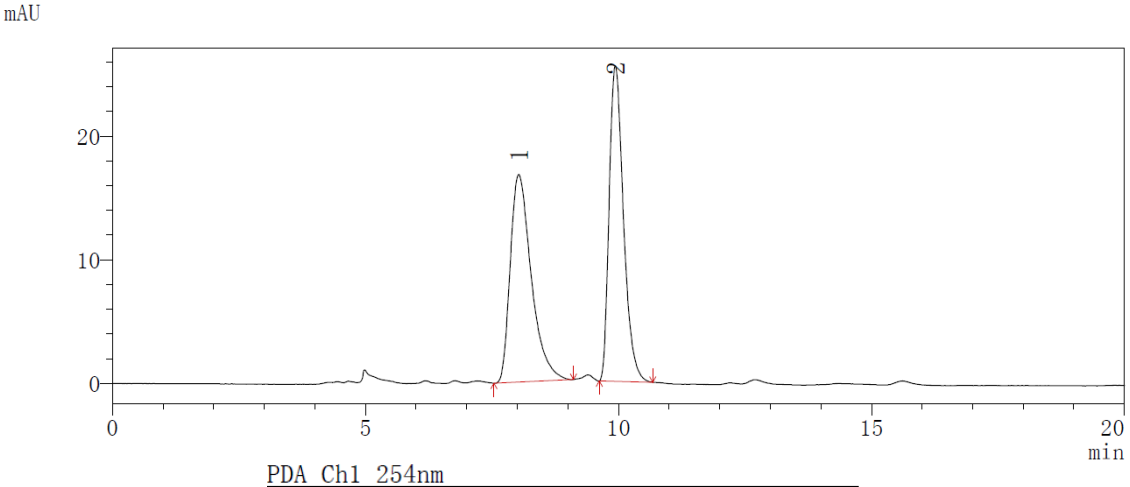
PDA Ch1 254nm

Number	Ret. Time	Area	Area%
1	6.720	30567	0.44
2	8.499	6935982	99.56

(1*R*,5*R*)-9-Benzyl-2,6-bis(4-fluorophenyl)-9-azabicyclo[3.3.1]nona-2,6-diene (**4b**)

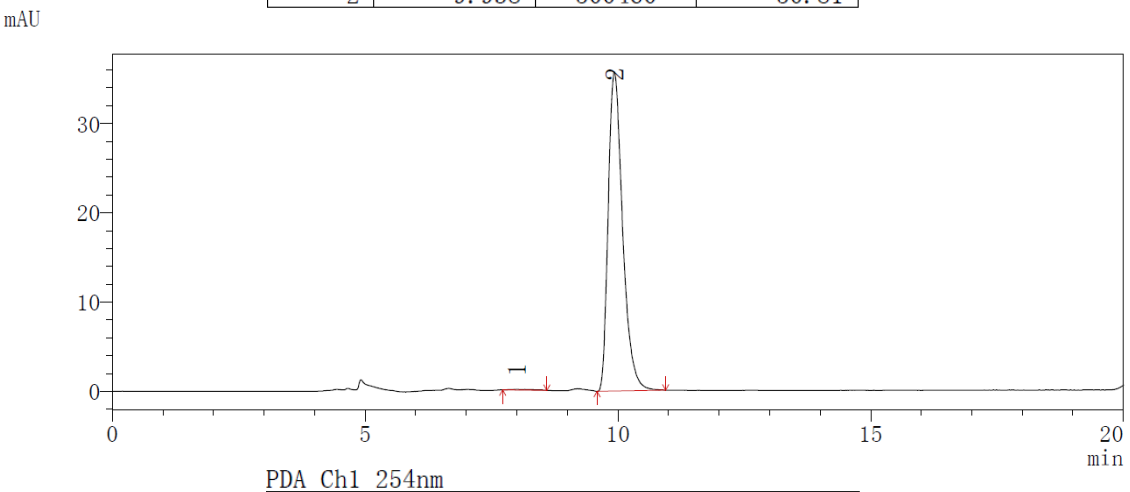


$[\alpha]_D^{25}$ +47.2 (c 1.07, $CHCl_3$) for 99% ee. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.27 – 7.19 (m, 4H), 7.05 – 6.92 (m, 4H), 6.01 – 5.92 (m, 2H), 3.92 – 3.83 (m, 3H), 3.78 (d, *J* = 13.1 Hz, 1H), 2.59 (dd, *J* = 18.4, 6.2 Hz, 2H), 1.86 (dd, *J* = 18.3, 5.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.18 (d, *J* = 246.0 Hz), 139.18, 137.83, 136.41 (d, *J* = 3.4 Hz), 129.10, 128.54, 127.70 (d, *J* = 7.7 Hz), 127.31, 121.06 (d, *J* = 1.4 Hz), 115.35 (d, *J* = 21.3 Hz), 56.99, 52.22, 27.99. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 115.71. **ESI-MS**: 400.2 $[M+H]^+$. **HRMS**(DART): m/z calcd for $C_{27}H_{24}NF_2$ $[M+H]^+$ 400.1871, found 400.1862. **HPLC**: Chiralcel AD-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 98/2; flow = 0.7 mL/min; Retention time: 8.0 min [(*S*, *S*)-**4b**], 9.9 min [(*R*, *R*)-**4b**].



PDA Ch1 254nm

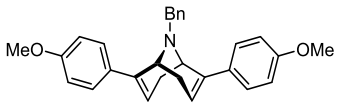
Number	Ret.Time	Area	Area%
1	8.030	484464	49.19
2	9.938	500460	50.81



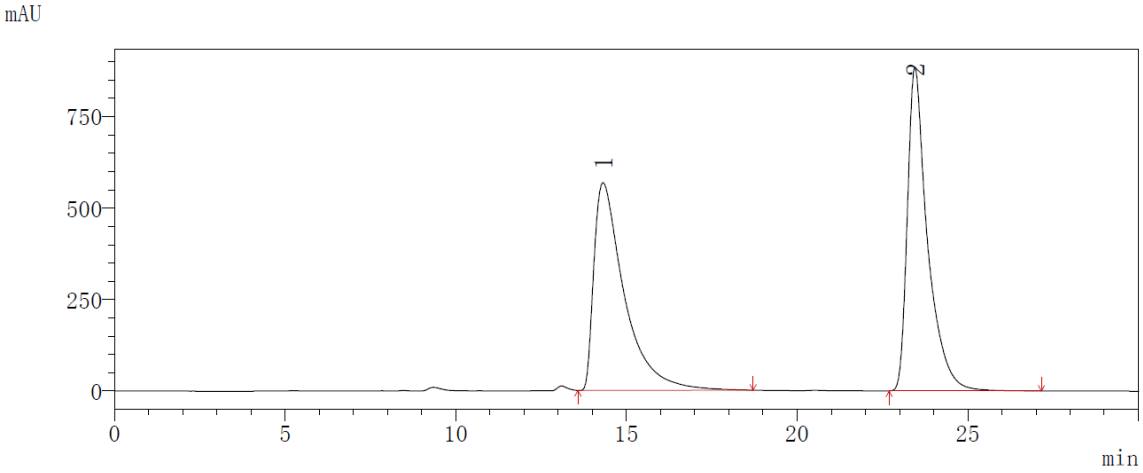
PDA Ch1 254nm

Number	Ret.Time	Area	Area%
1	7.994	2602	0.37
2	9.930	708605	99.63

(1*R*,5*R*)-9-Benzyl-2,6-bis(4-methoxyphenyl)-9-azabicyclo[3.3.1]nona-2,6-die (4c)

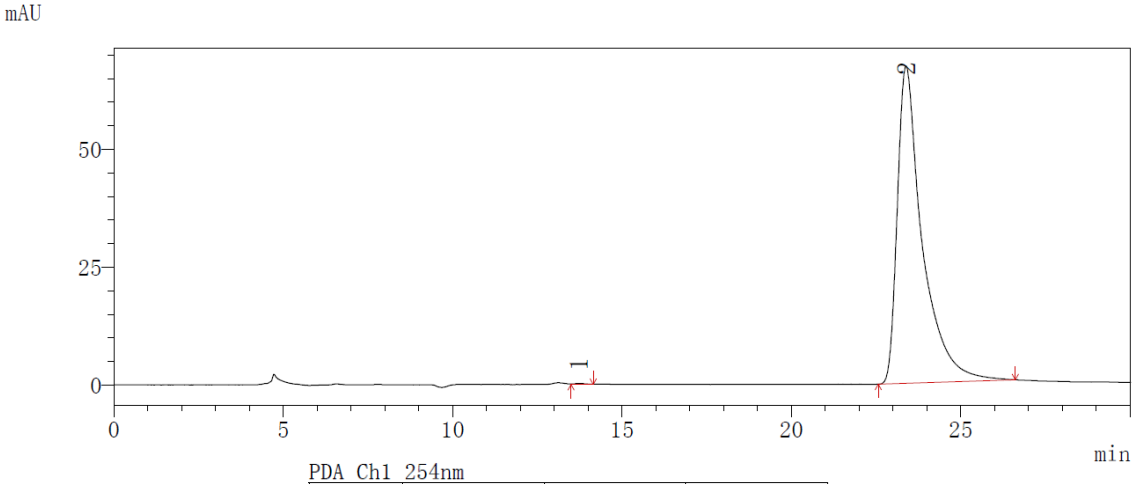


$[\alpha]_D^{25}$ +28.1 (c 1.20, $CHCl_3$) for 99% ee. Dark yellow solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.22 (d, *J* = 8.7 Hz, 4H), 6.83 (d, *J* = 8.7 Hz, 4H), 5.94 (dd, *J* = 5.3, 2.3 Hz, 2H), 3.91 – 3.79 (m, 4H), 3.77 (s, 6H), 2.59 (dd, *J* = 17.9, 5.7 Hz, 2H), 1.89 (dd, *J* = 18.2, 5.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.80, 139.40, 137.86, 132.90, 129.13, 128.42, 127.13, 127.08, 119.57, 113.84, 56.97, 55.32, 52.12, 28.10. **ESI-MS**: 424.2 $[M+H]^+$. **HRMS**(ESI): m/z calcd for $C_{29}H_{30}O_2N$ $[M+H]^+$ 424.2271, found 424.2271. **HPLC**: Chiralcel AD-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 98/2; flow = 0.7 mL/min; Retention time: 14.3 min [(*S*, *S*)-**4c**], 23.5 min [(*R*, *R*)- **4c**].



PDA Ch1 254nm

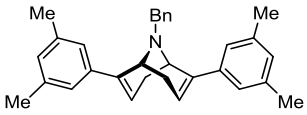
Number	Ret. Time	Area	Area%
1	14.314	35191080	49.19
2	23.450	36351641	50.81



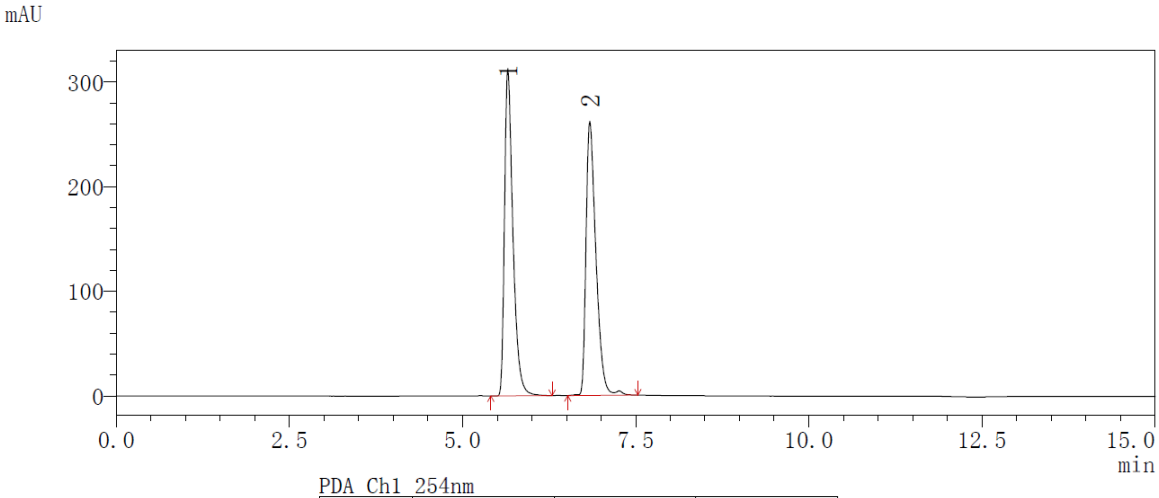
PDA Ch1 254nm

Number	Ret. Time	Area	Area%
1	13.721	5808	0.17
2	23.386	3458606	99.83

(1*R*,5*R*)-9-Benzyl-2,6-bis(3,5-dimethylphenyl)-9-azabicyclo[3.3.1]nona-2,6-diene (4d)

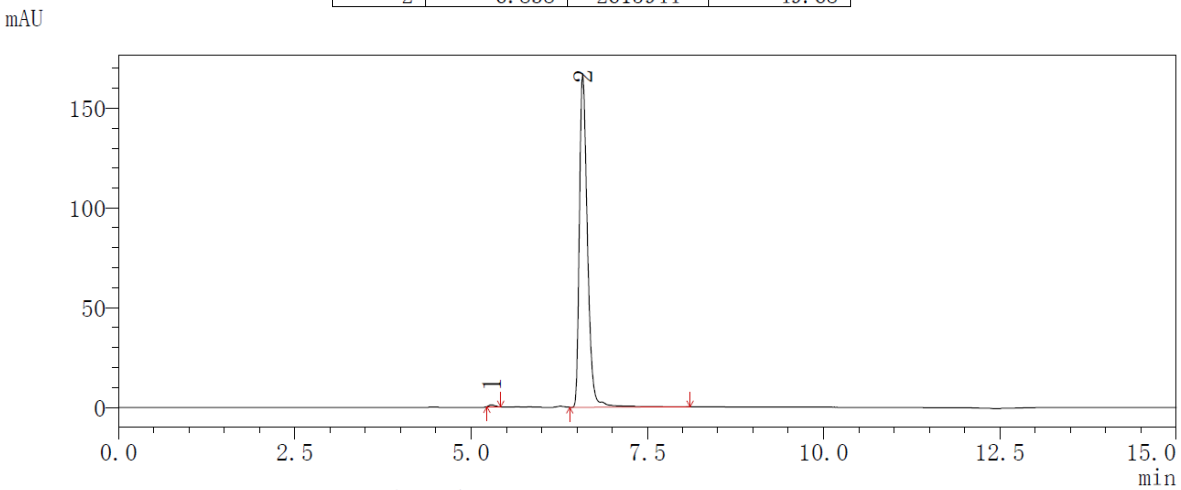


$[\alpha]_D^{25}$ +68.8 (c 1.00, $CHCl_3$) for 99% ee. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 1H), 6.91 (s, 4H), 6.88 (s, 2H), 5.98 (dd, *J* = 4.8, 1.8 Hz, 2H), 3.93 – 3.68 (m, 4H), 2.58 (dd, *J* = 18.0, 5.6 Hz, 2H), 2.29 (s, 12H), 1.89 (dd, *J* = 18.3, 5.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.56, 139.48, 138.84, 137.85, 129.25, 128.78, 128.41, 127.17, 124.15, 120.88, 56.98, 52.31, 28.15, 21.53. **ESI-MS**: 420.2 $[M+H]^+$. **HRMS**(ESI): m/z calcd for $C_{31}H_{34}N$ $[M+H]^+$ 420.2686, found 420.2685. **HPLC**: Chiralcel AD-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 5.7 min [(*S*, *S*)-**4d**], 6.8 min [(*R*, *R*)- **4d**].



PDA Ch1 254nm

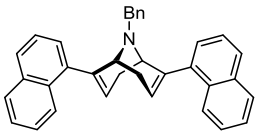
Number	Ret.Time	Area	Area%
1	5.653	2649280	50.32
2	6.838	2615944	49.68



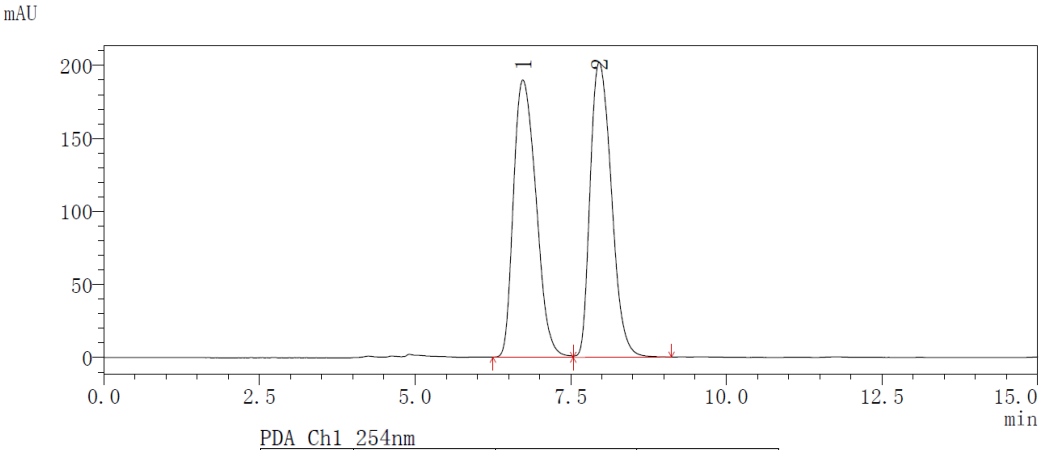
PDA Ch1 254nm

Number	Ret.Time	Area	Area%
1	5.288	5379	0.40
2	6.583	1330474	99.60

(1R,5R)-9-Benzyl-2,6-di(naphthalen-1-yl)-9-azabicyclo[3.3.1]nona-2,6-diene (4e)

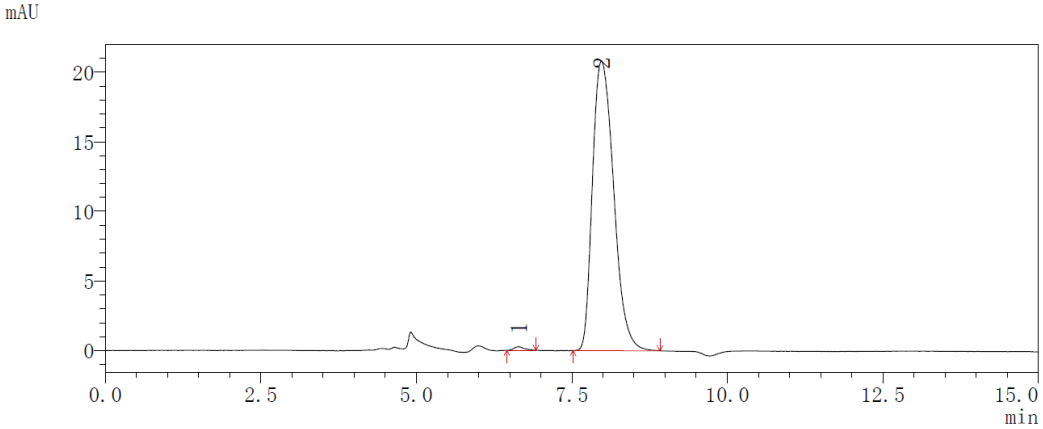


$[\alpha]_D^{25}$ +108.2 (c 1.13, $CHCl_3$) for 99% ee. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 8.18 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 7.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.42 (m, 6H), 7.42 – 7.35 (m, 2H), 7.35 – 7.24 (m, 3H), 5.89 (d, *J* = 3.6 Hz, 2H), 4.14 (d, *J* = 13.5 Hz, 1H), 4.05 (d, *J* = 13.5 Hz, 1H), 3.82 (d, *J* = 5.7 Hz, 2H), 2.51 (dd, *J* = 17.9, 4.8 Hz, 2H), 1.96 (dd, *J* = 18.1, 4.9 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.34, 139.17, 133.91, 132.41, 128.87, 128.50, 128.43, 127.46, 127.26, 126.42, 125.97, 125.88, 125.88, 125.84, 125.45, 124.18, 57.14, 55.42, 27.01. **DART-MS**: 464.2 $[M+H]^+$. **HRMS**(DART): m/z calcd for $C_{35}H_{30}N$ $[M+H]^+$ 464.2373, found 464.2374. **HPLC**: Chiralcel AD-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 98/2; flow = 0.7 mL/min; Retention time: 6.7 min [(*S*, *S*)-**4e**], 8.0 min [(*R*, *R*)- **4e**].



PDA Ch1 254nm

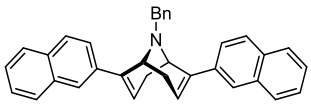
Number	Ret.Time	Area	Area%
1	6.732	4798028	50.10
2	7.958	4779027	49.90



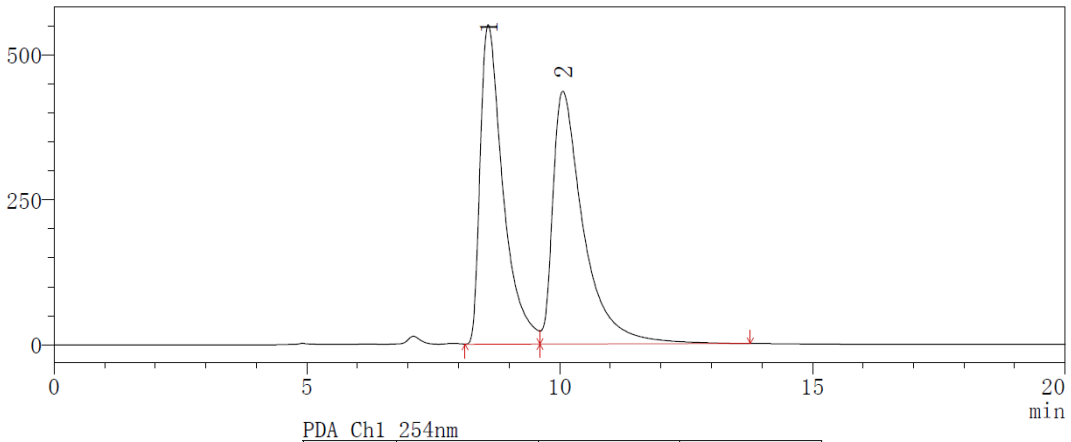
PDA Ch1 254nm

Number	Ret.Time	Area	Area%
1	6.641	3059	0.62
2	7.976	492183	99.38

(1*R*,5*R*)-9-Benzyl-2,6-di(naphthalen-2-yl)-9-azabicyclo[3.3.1]nona-2,6-diene (4f)

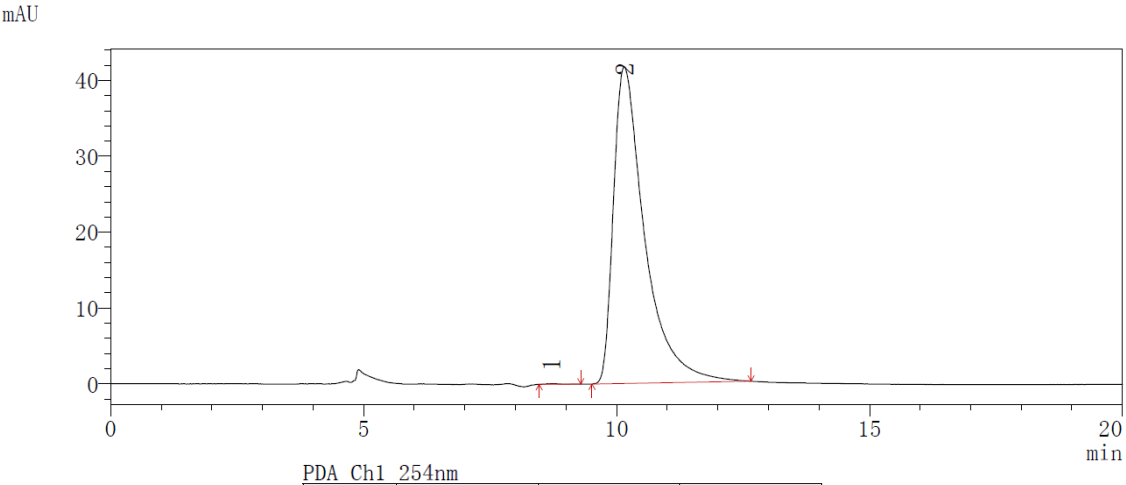


$[\alpha]_D^{25}$ -91.7 (c 1.00, $CHCl_3$) for 99% ee. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.84 – 7.74 (m, 6H), 7.71 (s, 2H), 7.58 – 7.50 (m, 4H), 7.49 – 7.38 (m, 6H), 7.38 – 7.31 (m, 1H), 6.22 (dd, *J* = 5.3, 2.3 Hz, 2H), 4.15 (d, *J* = 6.2 Hz, 2H), 4.01 (d, *J* = 13.1 Hz, 1H), 3.91 (d, *J* = 13.1 Hz, 1H), 2.74 (dd, *J* = 18.6, 6.3 Hz, 2H), 2.05 (dd, *J* = 18.4, 5.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.33, 137.39, 133.61, 132.73, 129.38, 128.59, 128.19, 128.11, 127.66, 127.43, 126.28, 125.83, 124.73, 124.46, 121.94, 57.07, 52.11, 28.44. (one carbon signal overlapped) **DART-MS**: 464.2 $[M+H]^+$. **HRMS**(DART): m/z calcd for $C_{35}H_{30}N$ $[M+H]^+$ 464.2373, found 464.2369. **HPLC**: Chiralcel AS-H Column; detected at 254 nm; *n*-hexane / *i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 8.6 min [(*S*, *S*)-**4f**], 10.1 min [(*R*, *R*)- **4f**].



PDA Ch1 254nm

Number	Ret. Time	Area	Area%
1	8.587	17311320	48.42
2	10.064	18440306	51.58



PDA Ch1 254nm

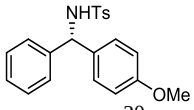
Number	Ret. Time	Area	Area%
1	8.706	1246	0.07
2	10.153	1790872	99.93

3. General procedure for asymmetric rhodium-catalyzed arylation of *N*-tosylarylimines

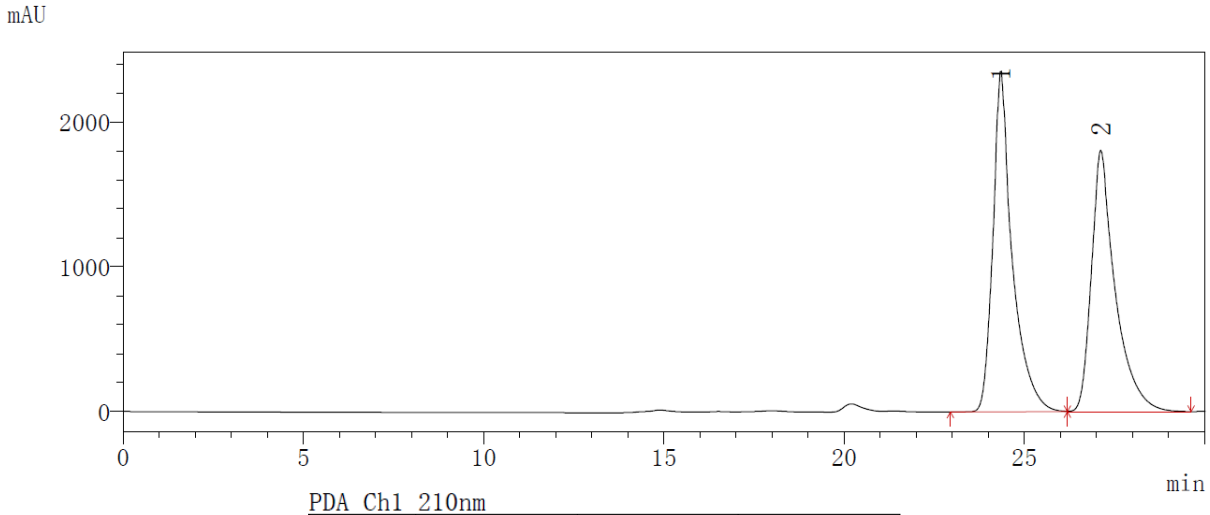
Under nitrogen, to a Schlenk flask charged with N-tosylarylimine **5** (0.20 mmol, 1.0 eq.), arylboronic acid (0.40 mmol, 2.0 eq.), $[RhCl(C_2H_4)_2]_2$ (2.0 mg, 0.0050 mmol, 2.5 mol%), chiral diene ligand **4f** (4.6 mg, 0.010 mmol, 5.0 mol%), KF (26 mg, 0.44 mmol, 2.2 eq.) was added 2.0 mL of toluene and 0.40 mL of water. The mixture was heated to 30 ℃ and stirred for 2 h. The solvent was removed and the residue was purified by silica gel column chromatography to afford the desired diarylmethylamine product **6**.

4. Characterization of the obtained products 6a-6f

(*S*)-*N*-((4-methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (6a)[3]

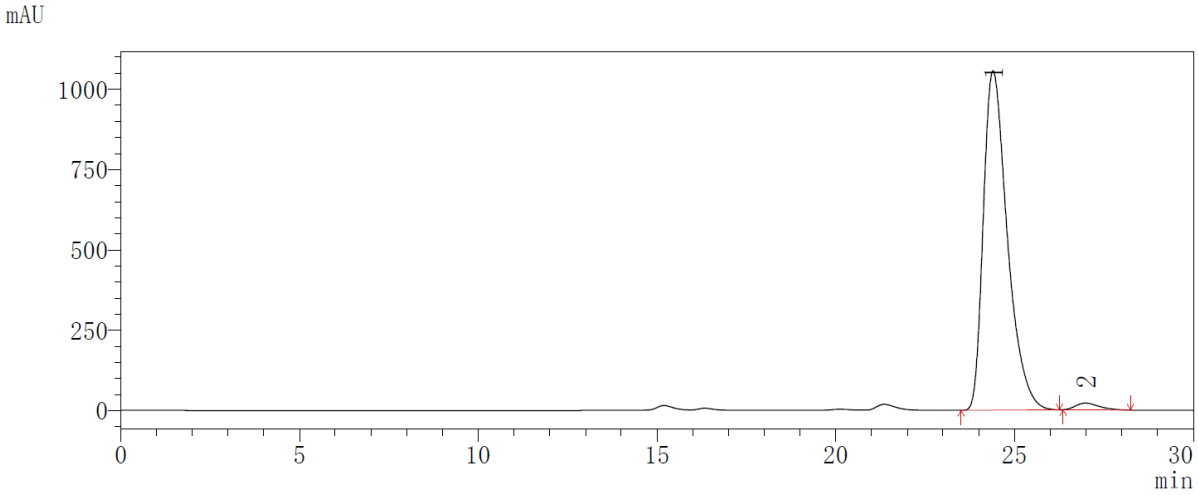


$[\alpha]_D^{25}$ -24.6 (*c* 1.07, $CHCl_3$) for 96% ee [lit. $[\alpha]_D^{20}$ -19.7 (*c* 1.03, $CHCl_3$) for 99% ee in the *S*-isomer; *J. Am. Chem. Soc.* **2004**, *126*, 13584.]. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.14 – 7.05 (m, 4H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.51 (d, *J* = 7.3 Hz, 1H), 5.44 (d, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 3H). **ESI-MS**: 197.1 $[M+H-TsNH_2]^+$, 390.0 $[M+Na]^+$, 406.1 $[M+K]^+$. **HPLC**: Chiralcel PC-H Column; detected at 200 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 24.3 min [(*S*)-**6a**], 27.1 min [(*R*)- **6a**].



PDA Ch1 210nm

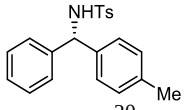
Number	Ret.Time	Area	Area%
1	24.335	87806799	51.48
2	27.117	82763657	48.52



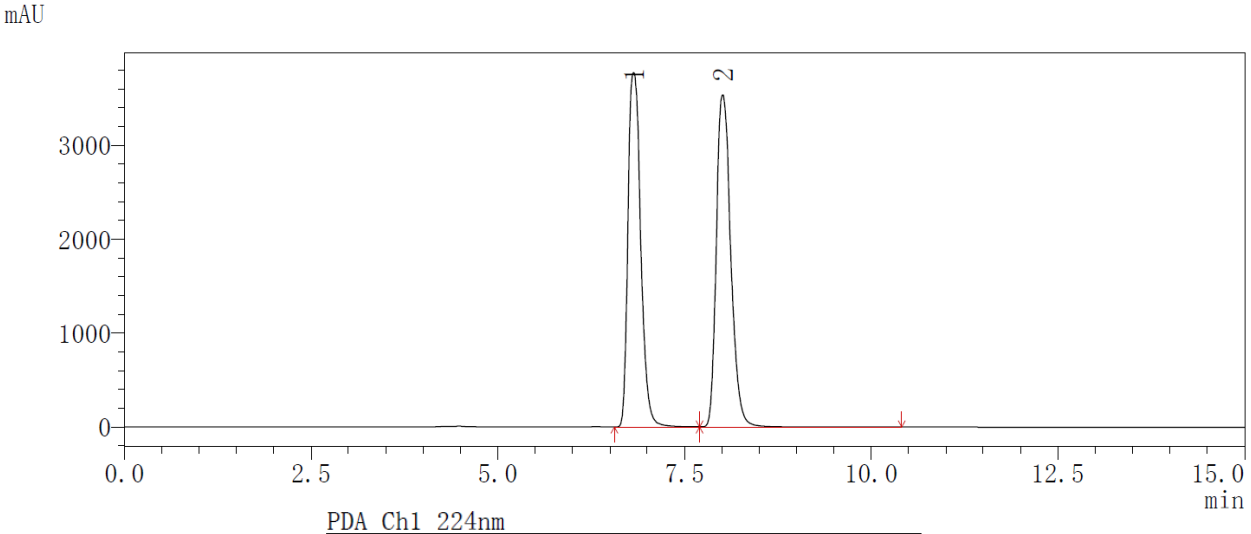
PDA Ch1 234nm

Number	Ret.Time	Area	Area%
1	24.399	49308623	98.10
2	26.987	955757	1.90

(*S*)-4-methyl-*N*-(phenyl(p-tolyl)methyl)benzenesulfonamide (6b)[4]

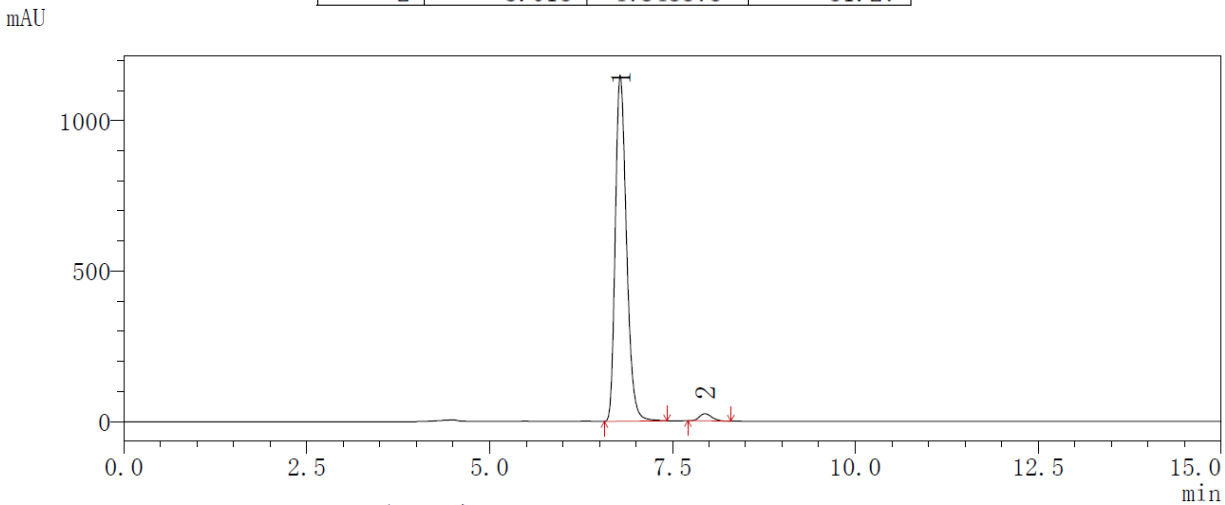


$[\alpha]_D^{25}$ -10.6 (c 1.27, $CHCl_3$) for 96% ee [lit. $[\alpha]_D^{20}$ +12.7 (*c* 0.97, $CHCl_3$) for 99% ee in the *R*-isomer; *J. Am. Chem. Soc.* **2007**, *129*, 5336.]. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.14 – 7.06 (m, 4H), 7.02 – 6.93 (m, 4H), 5.51 (d, *J* = 7.2 Hz, 1H), 5.28 (d, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.22, 140.81, 137.77, 137.48, 137.41, 129.43, 129.31, 128.59, 127.55, 127.41, 127.39, 127.32, 61.22, 21.59, 21.14. **ESI-MS**: 181.1 $[M+H-TsNH_2]^+$, 374.0 $[M+Na]^+$. **HPLC**: Chiralcel OD-H Column; detected at 224 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 6.8 min [(*S*)-**6b**], 8.0 min [(*R*)-**6b**].



PDA Ch1 224nm

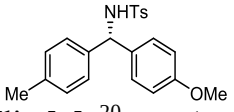
Number	Ret.Time	Area	Area%
1	6.821	45007714	48.73
2	8.015	47348875	51.27



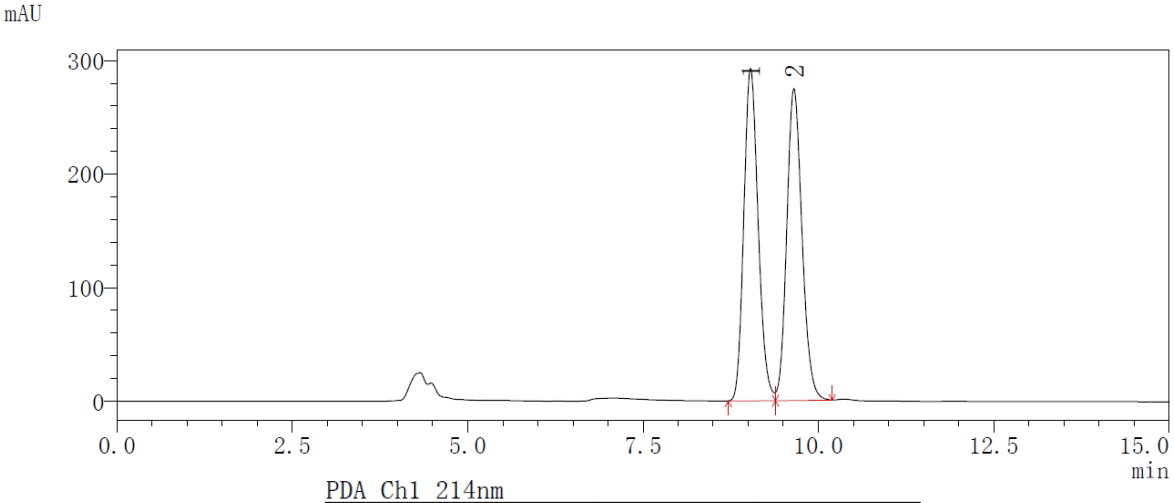
PDA Ch1 224nm

Number	Ret.Time	Area	Area%
1	6.786	12242127	97.77
2	7.947	278620	2.23

(*S*)-*N*-((4-methoxyphenyl)(p-tolyl)methyl)-4-methylbenzenesulfonamide (6c)[4]

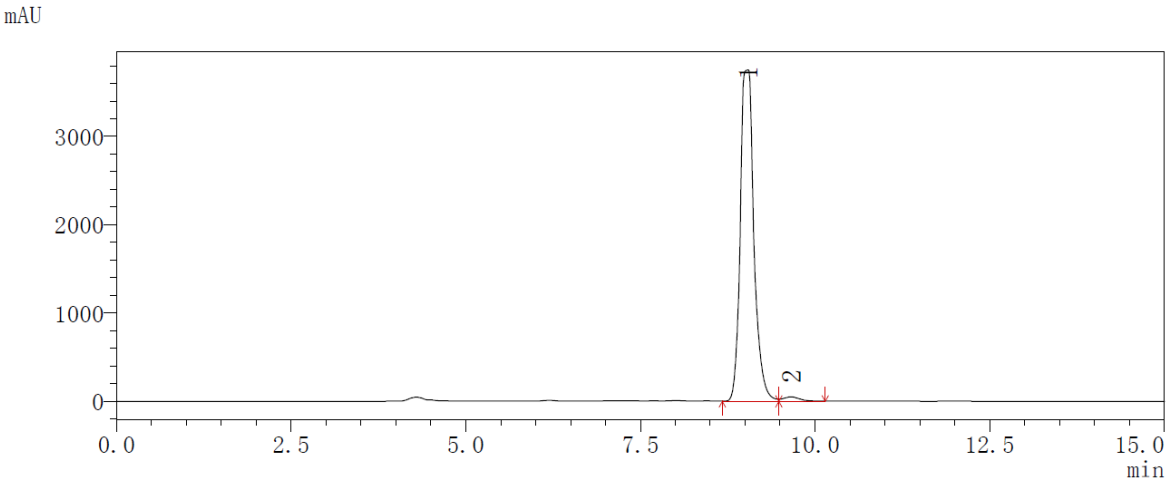


$[\alpha]_D^{25}$ -6.8 (c 1.07, $CHCl_3$) for 96% ee [lit. $[\alpha]_D^{20}$ -7.5 (*c* 1.03, $CHCl_3$) for 98% ee in the *S*-isomer; *J. Am. Chem. Soc.* **2007**, *129*, 5336.]. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.93 (m, 6H), 6.69 (d, *J* = 8.7 Hz, 2H), 5.50 – 5.40 (m, 2H), 3.72 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.92, 143.05, 137.98, 137.58, 137.16, 133.06, 129.35, 129.20, 128.62, 127.27, 113.88, 60.69, 55.30, 21.53, 21.08. **ESI-MS**: 211.1 $[M+H-TsNH_2]^+$, 404.0 $[M+Na]^+$. **HPLC**: Chiralcel OD-H Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 9.0 min [(*S*)-**6c**], 9.7 min [(*R*)- **6c**].



PDA Ch1 214nm

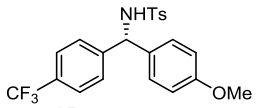
Number	Ret.Time	Area	Area%
1	9.031	4149569	49.90
2	9.651	4166568	50.10



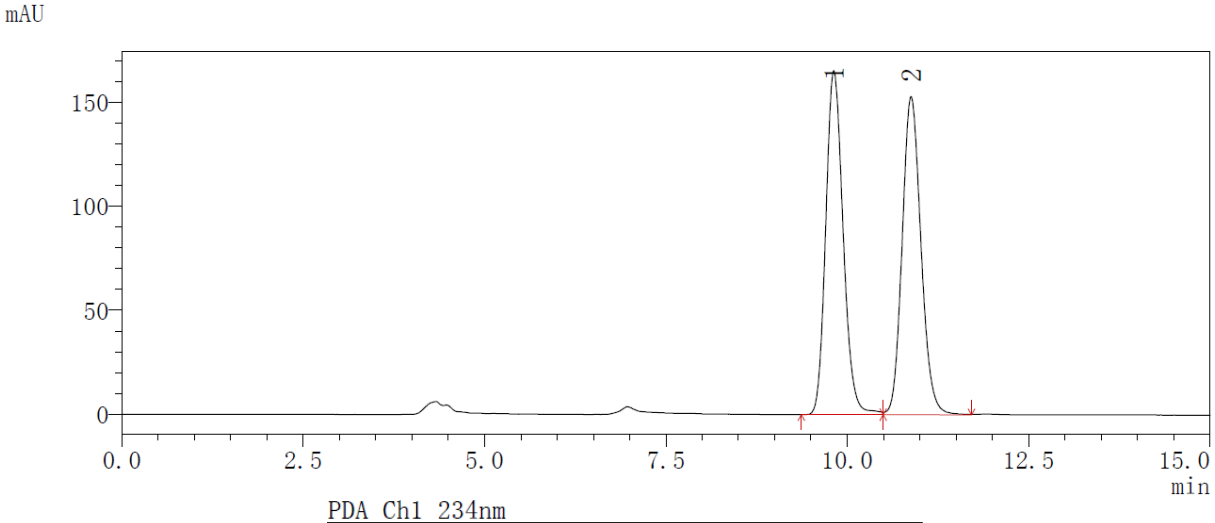
PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	9.040	50804397	98.37
2	9.654	842626	1.63

(*S*)-*N*-((4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-4-methylbenzenesulfonamide (6d)[5]

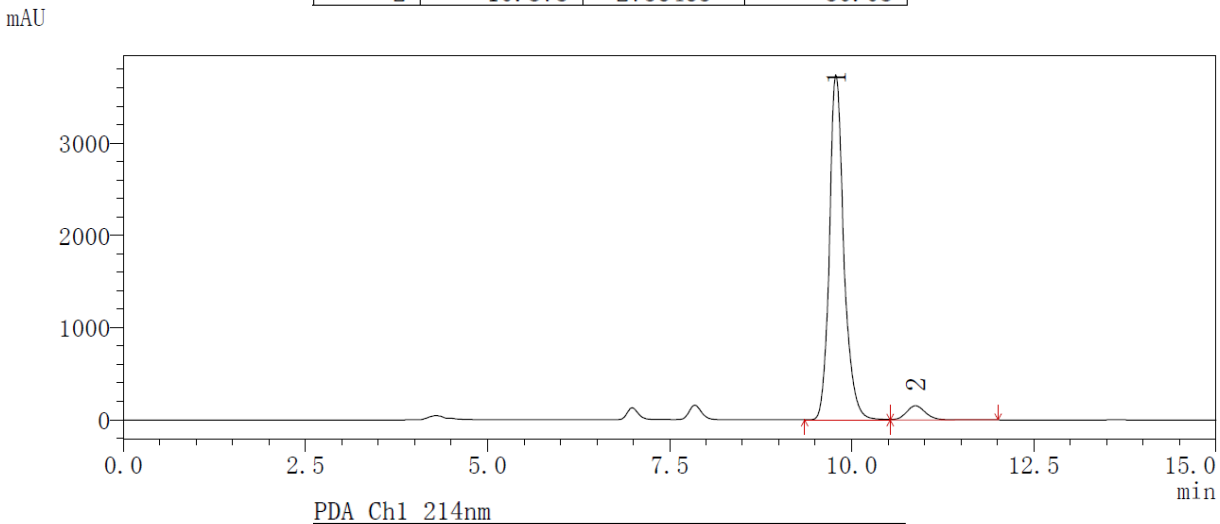


$[\alpha]_D^{25}$ -20.6 (c 1.00, $CHCl_3$) for 90% ee [lit. $[\alpha]_D^{27}$ -26.6 (*c* 1.03, $CHCl_3$) for 94% ee in the *S*-isomer; *Org. Lett.* **2010**, *17*, 3820.]. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.56 (d, *J* = 6.9 Hz, 1H), 5.31 – 5.17 (m, 1H), 3.75 (s, 3H), 2.37 (s, 3H). **ESI-MS**: 265.0 $[M+H-TsNH_2]^+$, 458.0 $[M+Na]^+$. **HPLC**: Chiralcel OD-H Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 9.8 min [(*S*)-**6d**], 10.9 min [(*R*)- **6d**].



PDA Ch1 234nm

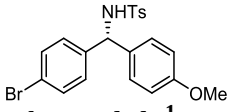
Number	Ret.Time	Area	Area%
1	9.814	2747907	49.92
2	10.878	2756465	50.08



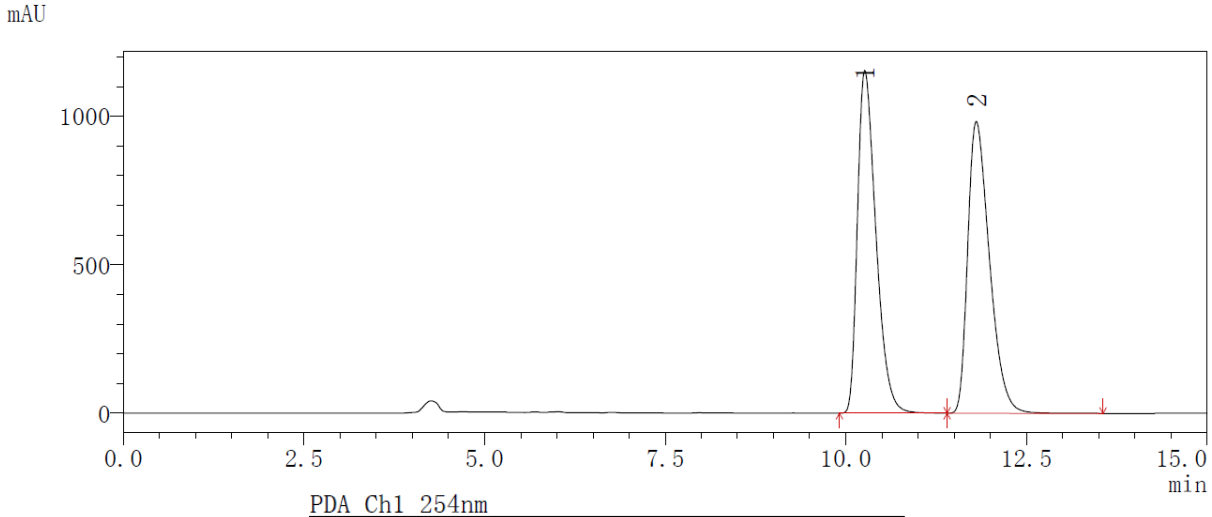
PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	9.783	51473517	94.86
2	10.874	2786575	5.14

(*R*)-*N*-((4-bromophenyl)(4-methoxyphenyl)methyl)-4-methylbenzenesulfonamide (6e)

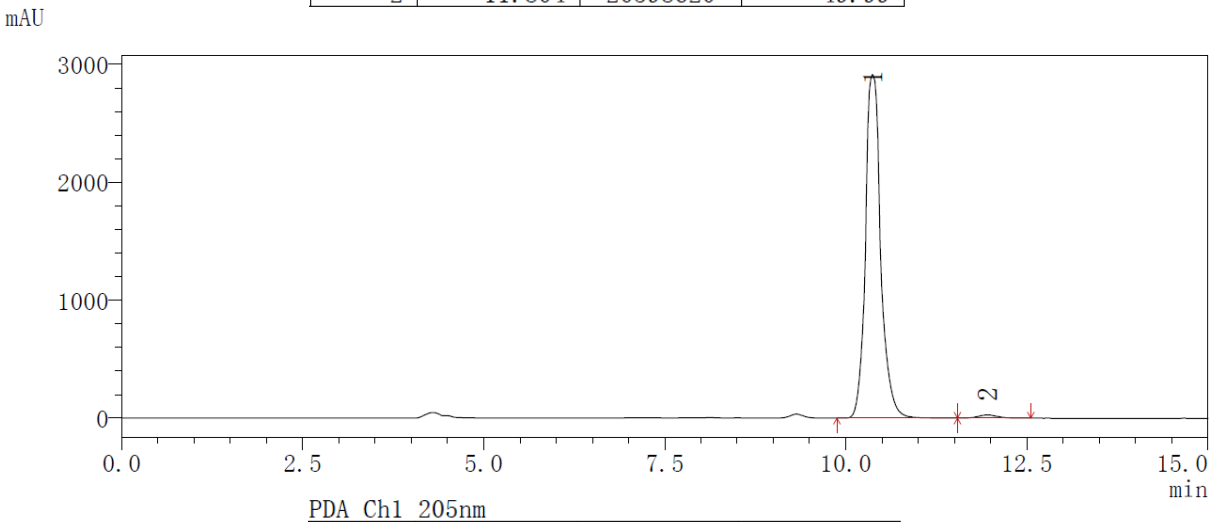


$[\alpha]_D^{25}$ -9.9 (c 1.27, $CHCl_3$) for 97%ee. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.65 (d, *J* = 7.5 Hz, 1H), 5.45 (d, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.17, 143.41, 139.90, 137.33, 132.29, 131.55, 129.47, 129.16, 128.62, 127.23, 121.45, 114.10, 60.39, 55.34, 21.58. **ESI-MS**: 468.0 $[M+Na]^+$. **HRMS**(ESI): m/z calcd for $C_{22}H_{20}O_3NBrNaS$ $[M+Na]^+$ 468.0239, found 468.0246. **HPLC**: Chiralcel OD-H Column; detected at 205 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 10.3 min [(*R*)-**6e**], 11.8 min [(*S*)- **6e**].



PDA Ch1 254nm

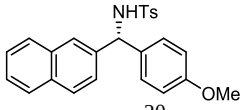
Number	Ret.Time	Area	Area%
1	10.262	20609051	50.01
2	11.804	20598620	49.99



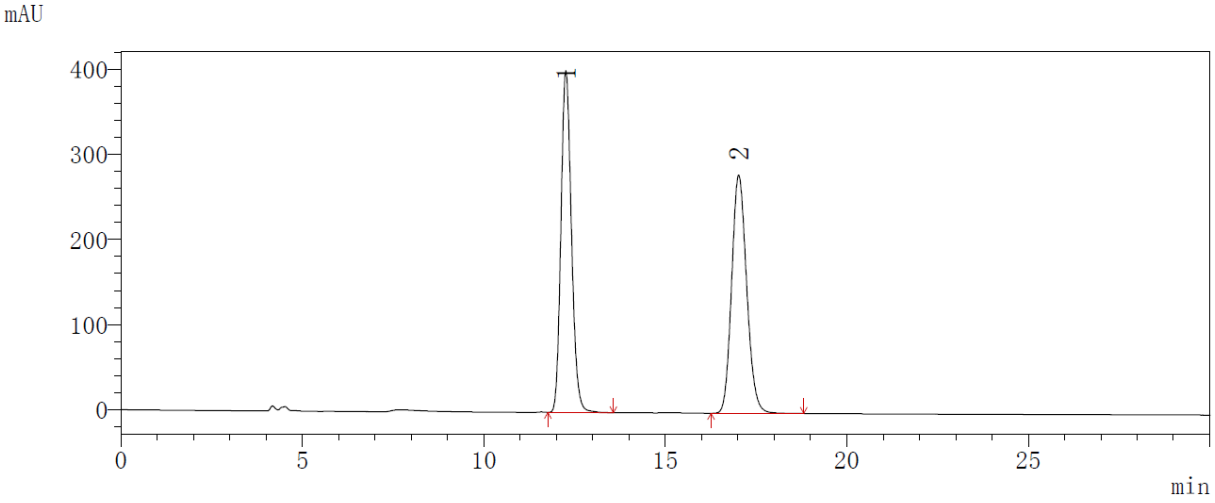
PDA Ch1 205nm

Number	Ret.Time	Area	Area%
1	10.368	42914677	98.75
2	11.951	543687	1.25

(*R*)-*N*-((4-methoxyphenyl)(naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide (6f)[6]

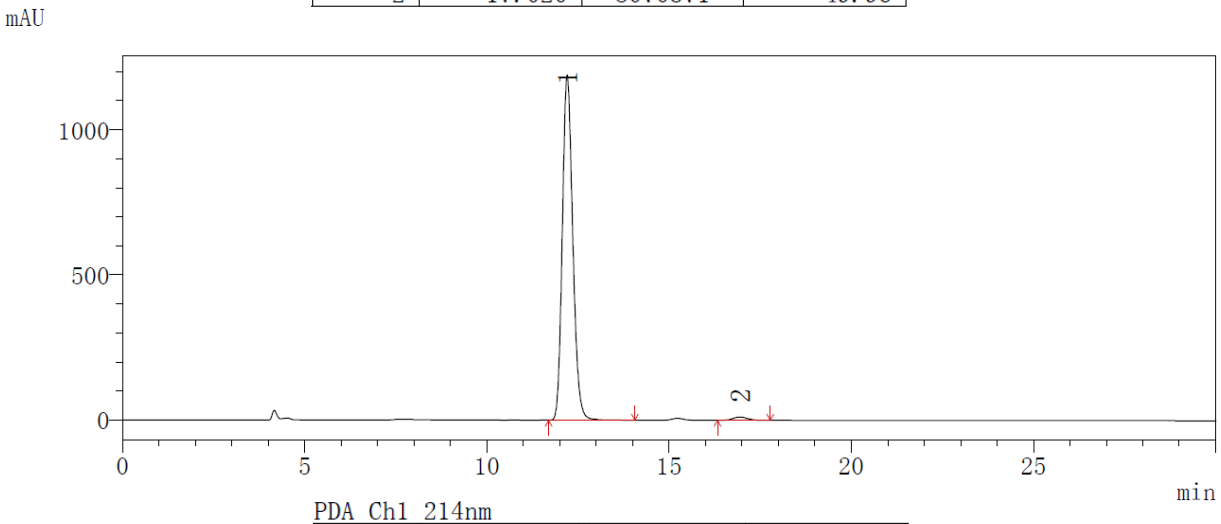


$[\alpha]_D^{25}$ -2.5 (c 1.27, $CHCl_3$) for 97% ee [lit. $[\alpha]_D^{20}$ +8.1 (*c* 0.55, $CHCl_3$) for 98% ee in the *S*-isomer; *RSC Adv.* **2019**, *9*, 25377.]. White solid. **^{1}H NMR** (400 MHz, CDCl3): δ 7.76 – 7.68 (m, 1H), 7.66 – 7.57 (m, 2H), 7.55 – 7.46 (m, 3H), 7.45 – 7.37 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 5.68 (d, *J* = 7.6 Hz, 1H), 5.60 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 2.22 (s, 3H). **ESI-MS**: 247.1 $[M+H-TsNH_2]^+$, 440.0 $[M+Na]^+$. **HPLC**: Chiralcel OD-H Column; detected at 214 nm; *n*-hexane / *i*-propanol = 75/25; flow = 0.7 mL/min; Retention time: 12.3 min [(*R*)-**6f**], 17.0 min [(*S*)- **6f**].



PDA Ch1 214nm

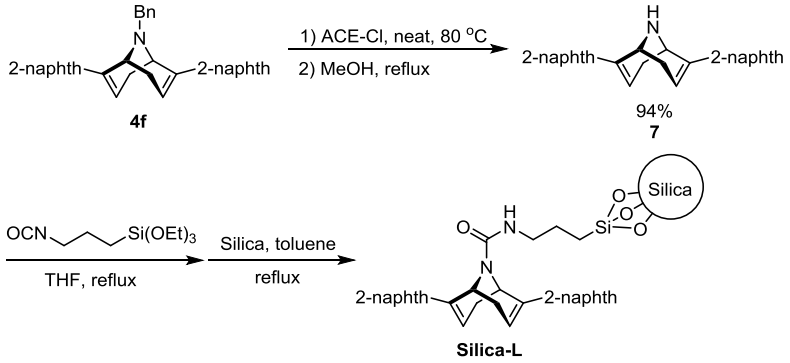
Number	Ret.Time	Area	Area%
1	12.258	8083917	50.04
2	17.020	8070371	49.96



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	12.202	23726641	98.64
2	16.944	326098	1.36

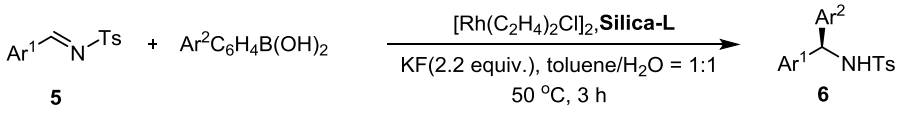
5. General procedure for the immobilization of ligand with silica



Under nitrogen, a mixture of **4f** (107 mg, 0.23 mmol, 1.0 eq.) and ACE-Cl (0.50 mL, 4.6 mmol 20 eq.) was heated at 80 ℃ overnight. After 4 mL MeOH was added, the mixture was heated at 70 ℃ for 4 h. The solvent was dried and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford 81 mg amine **7** (94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 – 7.67 (m, 8H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.39 (m, 4H), 6.20 (dd, *J* = 5.5, 2.3 Hz, 2H), 4.60 (d, *J* = 6.3 Hz, 2H), 2.81 (dd, *J* = 18.6, 6.4 Hz, 2H), 2.20 (dd, *J* = 18.5, 5.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.88, 136.45, 133.59, 132.84, 128.26, 128.25, 127.66, 126.38, 126.01, 124.49, 124.45, 121.86, 47.27, 30.65. **ESI-MS**: 374.1 $[M+H]^+$. **HRMS**(ESI): m/z calcd for $C_{35}H_{30}N$ $[M+H]^+$ 374.1903, found 374.1902.

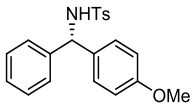
Under nitrogen, a solution of 3-Isocyanatopropyltriethoxysilane (52 mL, 0.21 mmol, 1.05 eq.) in THF was added dropwise to a solution of **7** (75 mg, 0.20 mmol, 1.0 eq.) in THF. The mixture was stirred at rt for 0.5 h, and then it was heated at 70 ℃ for 2 h. The solvent was dried and concentrated under vacuum to get the crude siloxane. And then it was added to a suspension of 1g silica (100-200 mesh) in 10 mL of toluene and the resulting mixture was refluxed for 2 h. The resulting **silica-L** was washed with toluene, dried under reduced pressure, and stored under an inert atmosphere. **Elemental Analysis**: C 4.90%, N 0.32%. **FT-IR**(KBr): *ν*(C=O) 1632 cm^{-1}, *ν*(N-H) 1538 cm^{-1}.

6. The rhodium-catalyzed arylation of *N*-tosylarylimines with silica-L

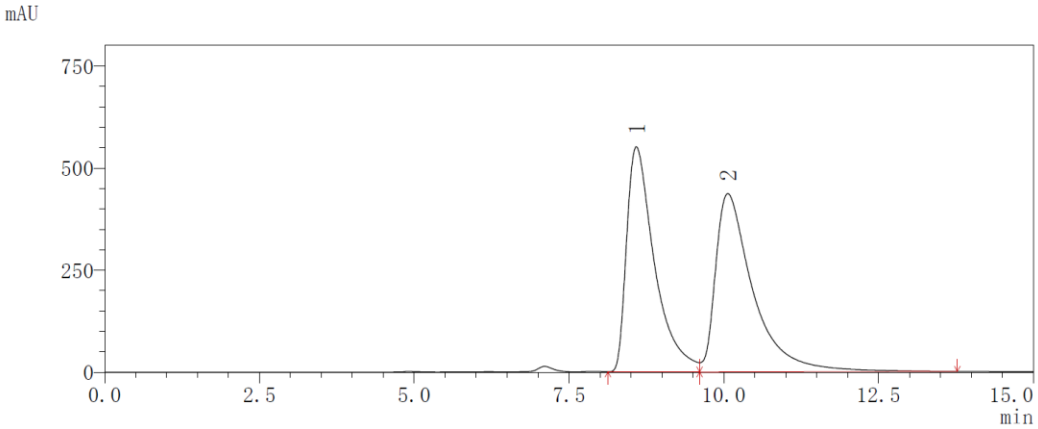


Under nitrogen, to a Schlenk flask charged with N-tosylarylimine **5** (0.20 mmol, 1.0 eq.), arylboronic acid (0.40 mmol, 2.0 eq.), $[RhCl(C_2H_4)_2]_2$ (3.9 mg, 0.010 mmol, 5 mol%), immobilized ligand **Silica-L** (102 mg, 0.012 mmol, 6 mol%, 0.114 mmol/g), KF (26 mg, 0.44 mmol, 2.2 eq.) was added 1.0 mL of toluene and 1.0 mL of water. The mixture was heated to 50 ℃ and stirred for 3 h. The mixture was filtered under vacuum and washed with ethanol. The solvent of filtrate was removed and the residue was purified by silica gel column chromatography to afford the desired diarylmethylamine product **6**. The filter cake was dried under vacuum and used as recovered catalyst for the next run reaction.

(*S*)-*N*-((4-methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (6a)

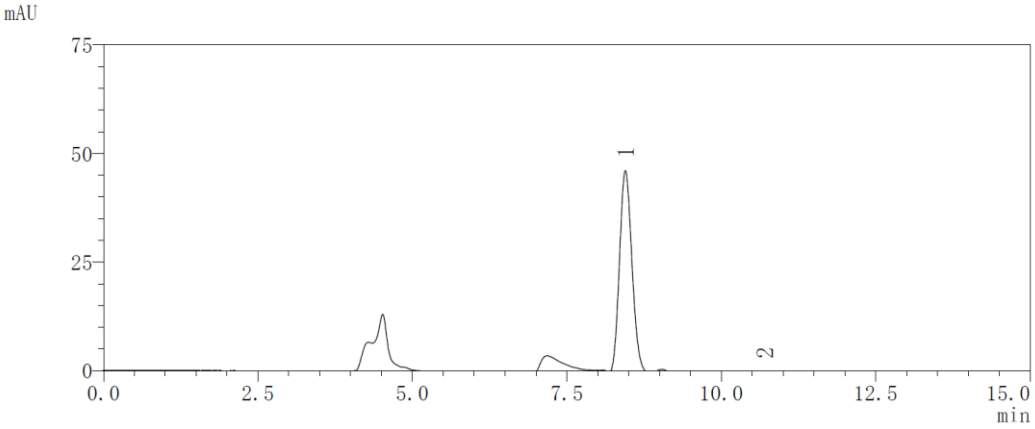


HPLC: Chiralcel OD-H Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 8.45 min [(*S*)-**6a**], 10.70 min [(*R*)- **6a**].



PDA Ch1 254nm

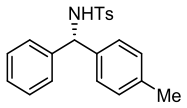
Number	Ret. Time	Area	Area%
1	8.587	17311320	48.42
2	10.064	18440306	51.58



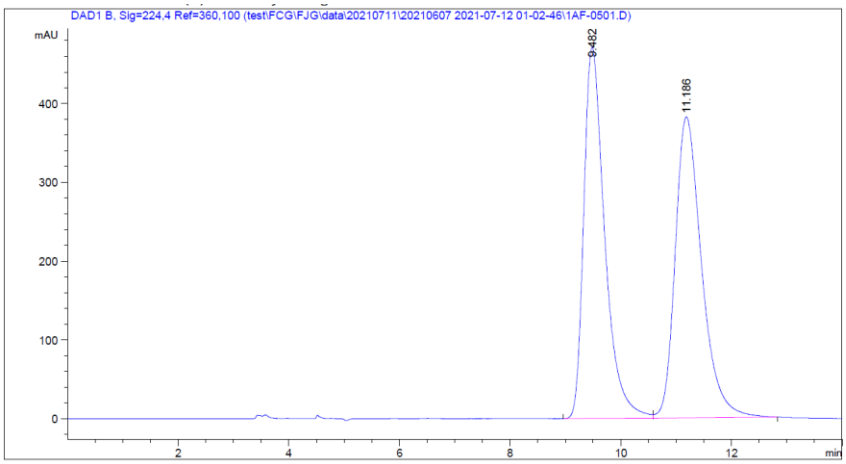
PDA Ch1 214nm

Number	Ret. Time	Area	Area%
1	8.447	678045	99.35
2	10.701	4442	0.65

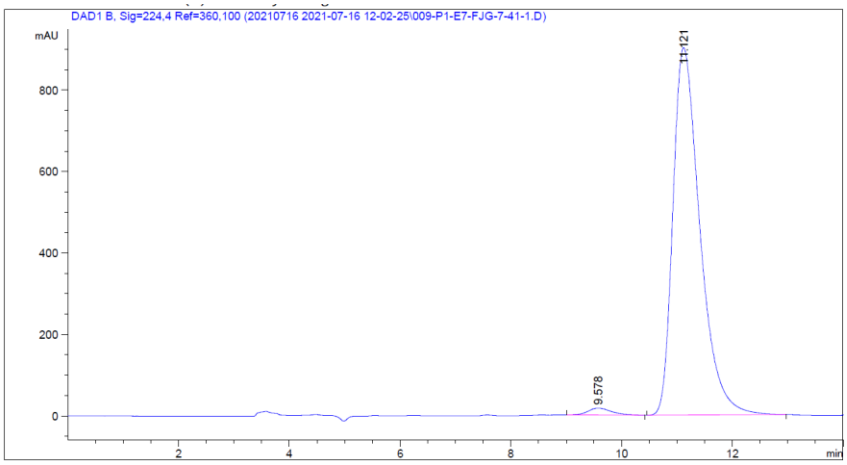
(*S*)-4-methyl-*N*-(phenyl(p-tolyl)methyl)benzenesulfonamide (6b)



HPLC: Chiralpak OJ-3 Column; detected at 224 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.5 mL/min; Retention time: 9.5 min [(*R*)-**6b**], 11.2 min [(*S*)-**6b**].

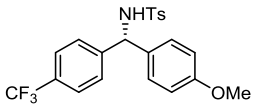


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.482	BV	0.3890	1.23749e4	471.11304	49.4502
2	11.186	VB	0.4845	1.26501e4	381.82816	50.5498

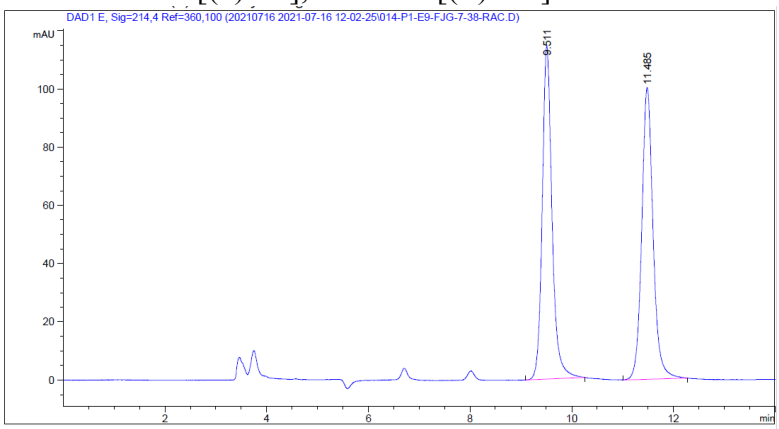


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.578	BB	0.3451	499.93915	16.99772	1.6095
2	11.121	BB	0.4970	3.05624e4	901.52655	98.3905

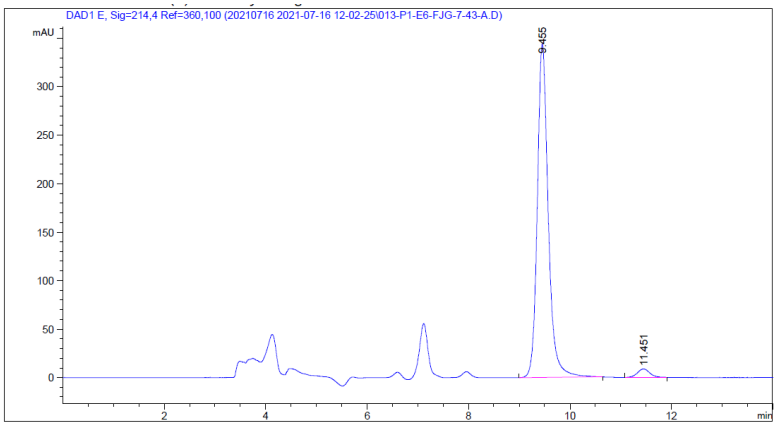
(*S*)-*N*-((4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-4-methylbenzenesulfonamide (6d)



HPLC: Chiralpak IB-3 Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow = 0.5 mL/min; Retention time: 9.5 min [(*S*)-**6d**], 11.5 min [(*R*)- **6d**].



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.511	BB	0.2019	1535.12573	114.48547	49.7276
2	11.485	BB	0.2281	1551.94385	100.24756	50.2724



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.455	BB	0.2252	5150.80957	344.02362	97.2670
2	11.451	BB	0.2023	144.72511	8.75809	2.7330

7. References

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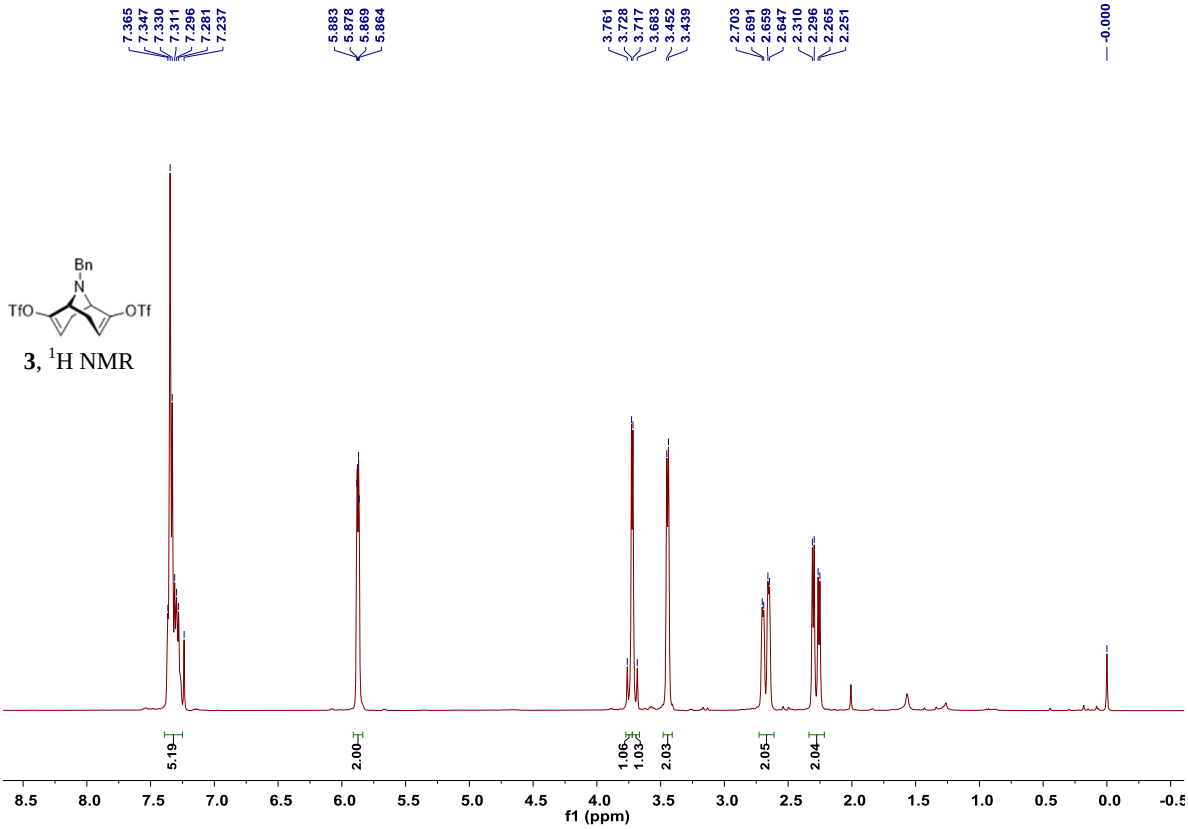
(3) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani R.; Hayashi, T. C_2-Symmetric Bicyclo[2.2.2]Octadienes as Chiral Ligands: Their High Performance in Rhodium-Catalyzed Asymmetric Arylation of N-Tosylarylimines. *J. Am. Chem. Soc.* 2004, **126**, 13584-13585.

(4) Z.-Q. Wang, C.-G. Feng, M.-H. Xu, and G.-Q. Lin, Design of C_2-Symmetric Tetrahydropentalenes as New Chiral Diene Ligands for Highly Enantioselective Rh-Catalyzed Arylation of N-Tosylarylimines with Arylboronic Acids. *J. Am. Chem. Soc.* 2007, **129**, 5336-5337.

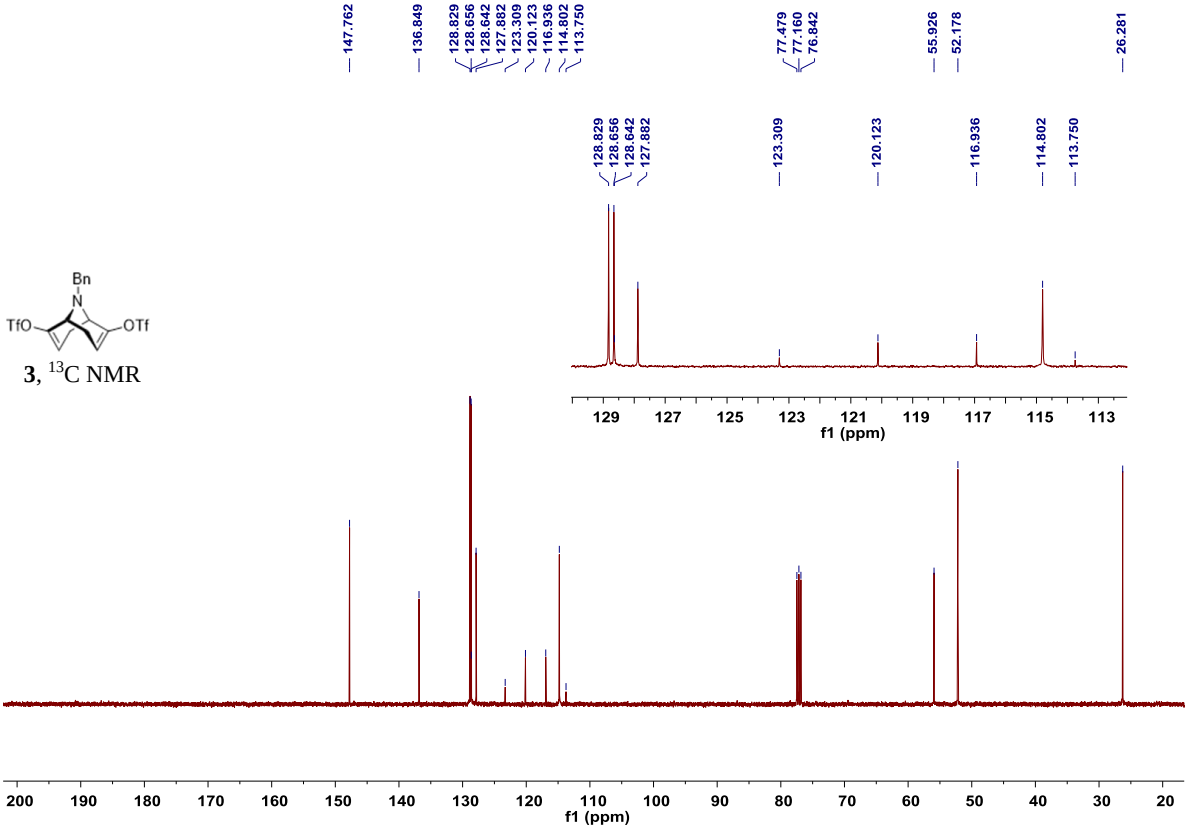
(5) C. Shao, H.-J. Yu, N.-Y. Wu, C.-G. Feng and G.-Q. Lin, C_1-Symmetric Dicyclopentadienes as New Chiral Diene Ligands for Asymmetric Rhodium-Catalyzed Arylation of N-Tosylarylimines. *Org. Lett.* 2010, **17**, 3820-3823.

(6) F. Xue, Q. Liu, Y. Zhu, Y. Qing and B. Wan, Chiral Benzene Backbone-Based Sulfoxide-Olefin Ligands for Highly Enantioselective Rh-Catalyzed Addition of Arylboronic Acids to N-Tosylarylimines. *RSC Adv.* 2019, **9**, 25377-25381.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds 3, 4, 6 and 7



3, ^{1}H NMR

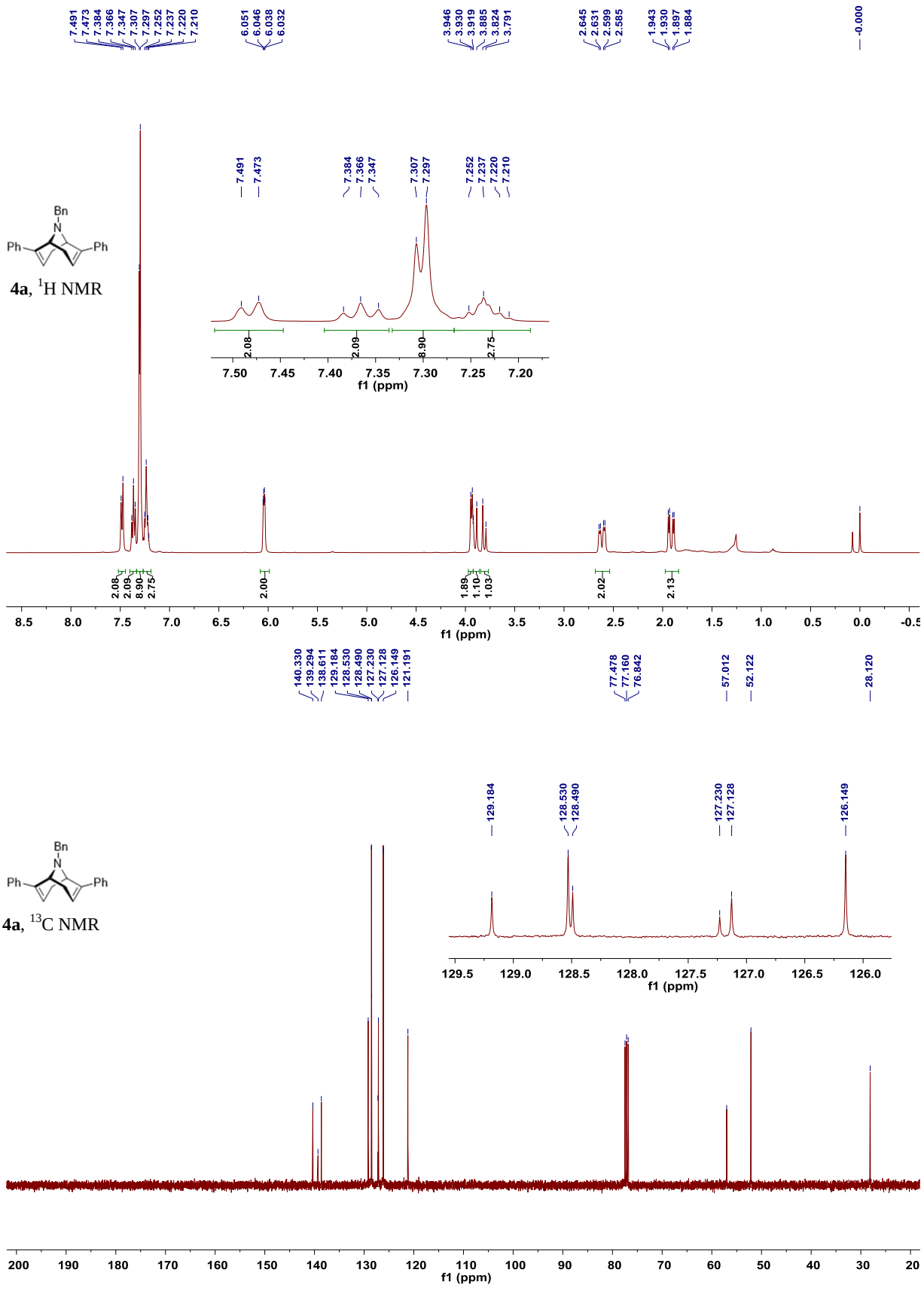


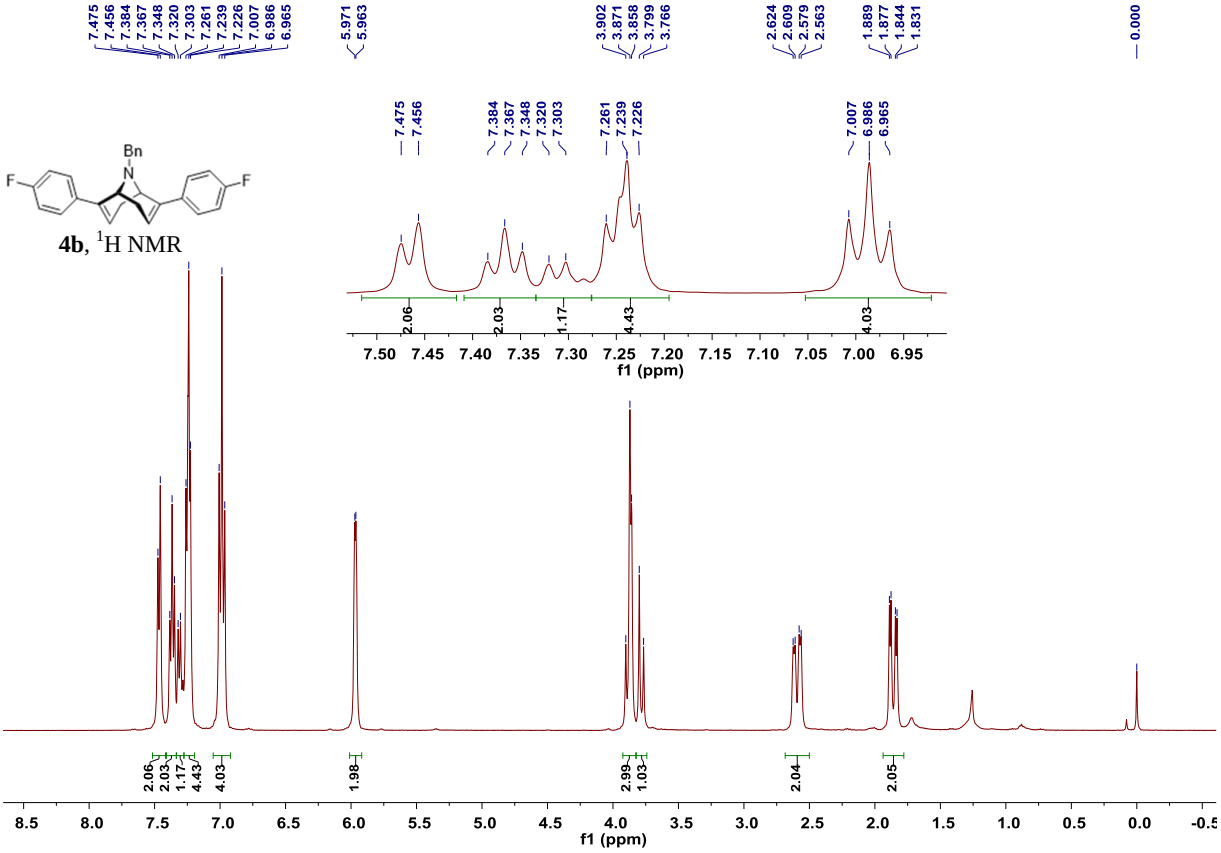
3, ^{13}C NMR


Bn
N
TfO
OTf

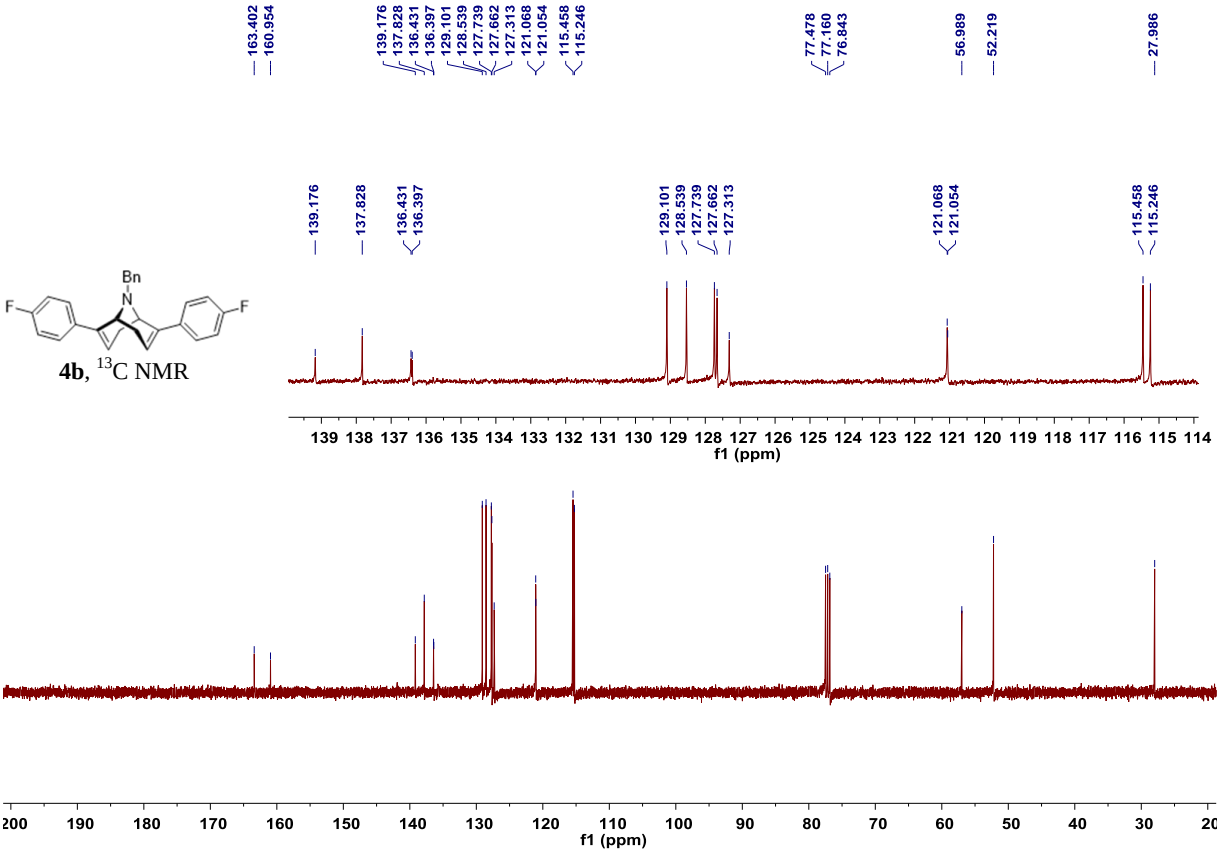
3, ^{19}F NMR

-73.888
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

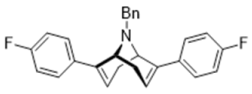

7.491
7.473
7.384
7.366
7.347
7.307
7.297
7.252
7.237
7.220
7.210
6.051
6.046
6.038
6.032
3.946
3.930
3.919
3.885
3.824
3.791
2.645
2.631
2.599
2.585
1.943
1.930
1.897
1.884
-0.000
Bn
N
Ph
Ph
4a, 1H NMR
2.08
2.09
8.90
2.75
2.00
1.89
1.10
1.03
2.02
2.13
f1 (ppm)
140.330
139.294
138.611
129.184
128.530
128.490
127.230
127.128
126.149
121.191
77.478
77.160
76.842
57.012
52.122
28.120
4a, 13C NMR
f1 (ppm)



4b, ^{1}H NMR

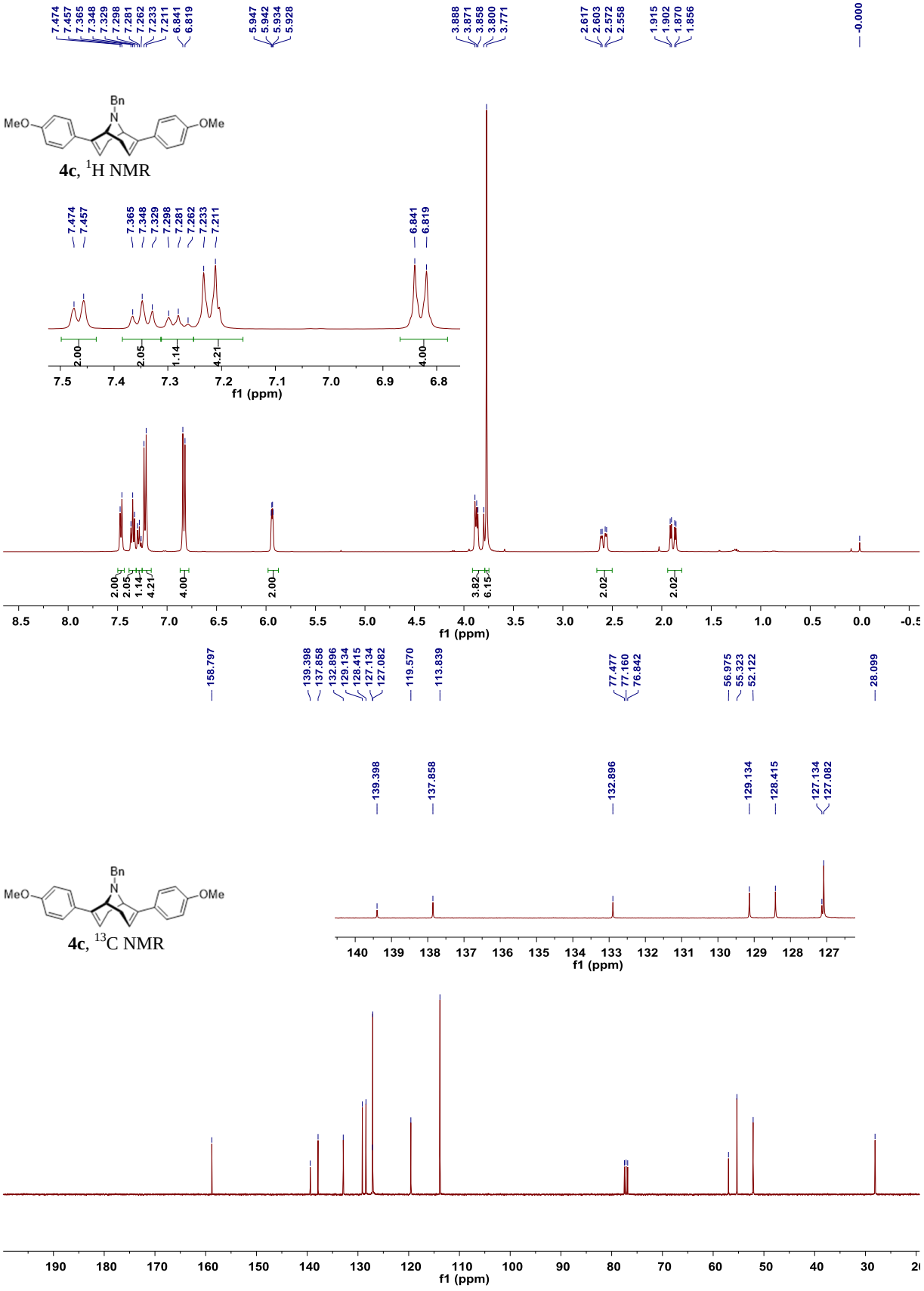


4b, ^{13}C NMR


Bn
N
F
F

4b, ^{19}F NMR

-115.714
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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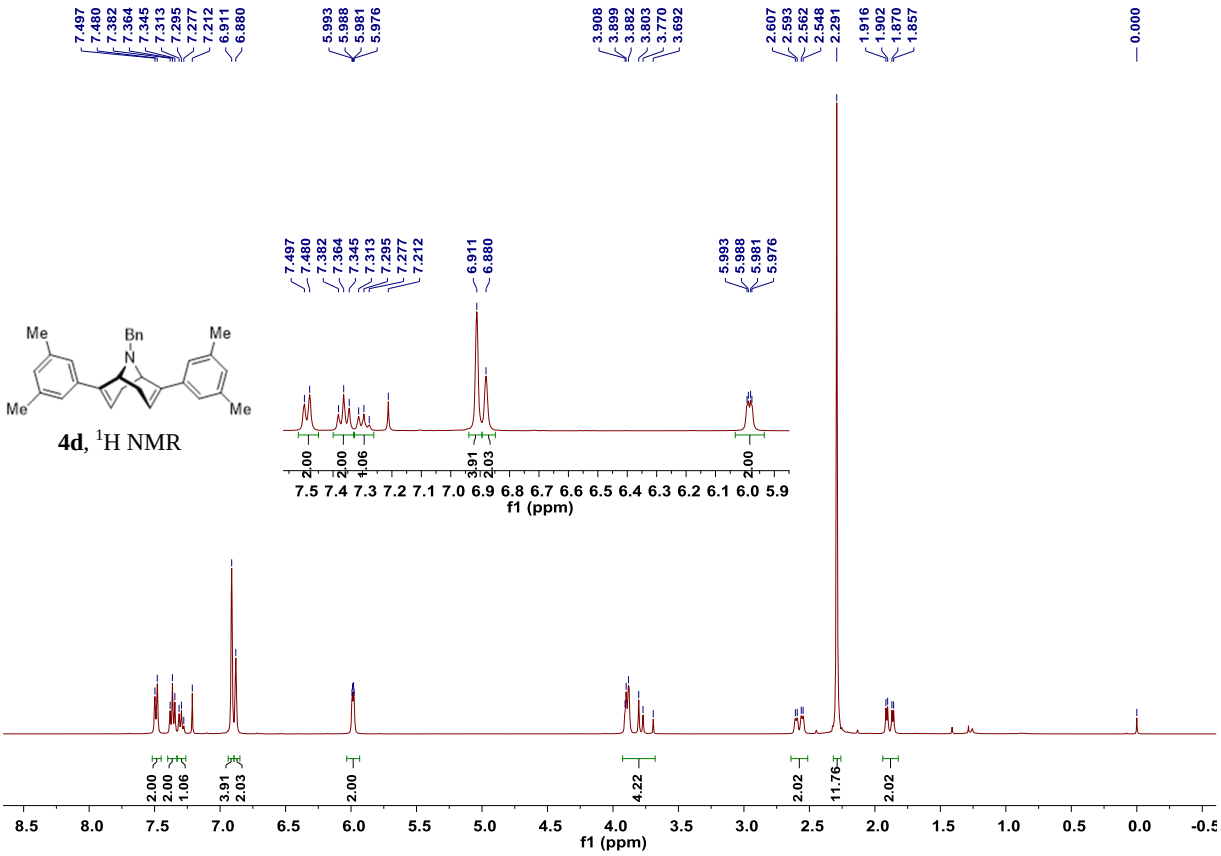
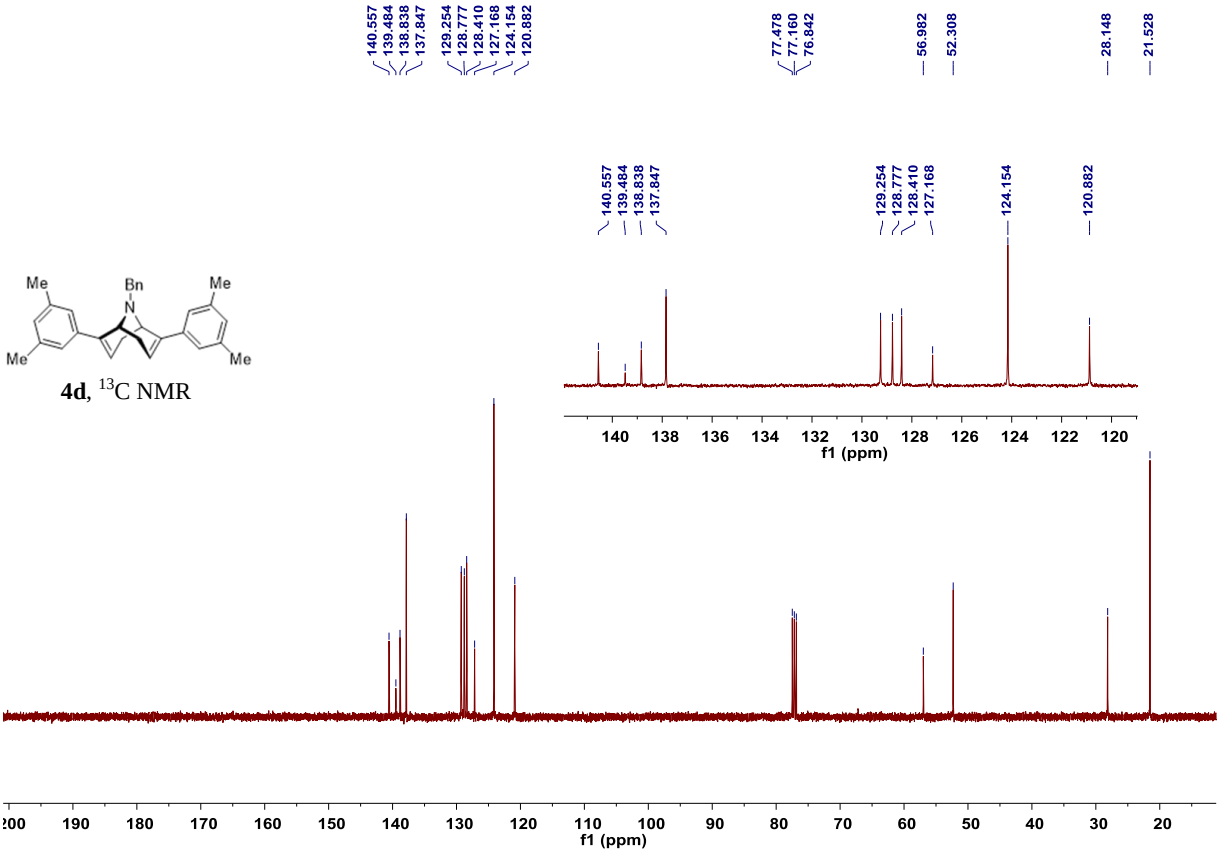
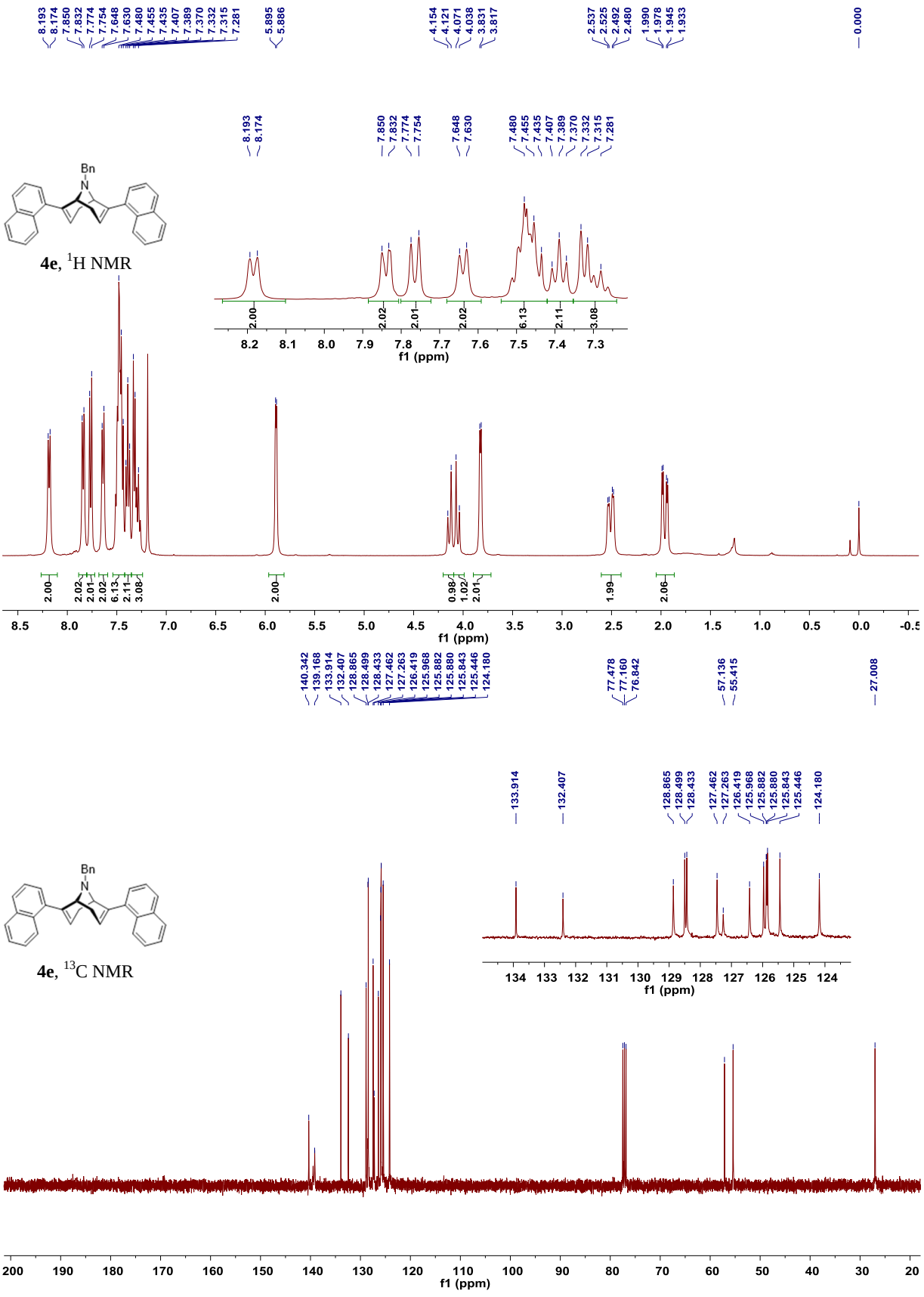
7.457
7.365
7.348
7.329
7.298
7.281
7.262
7.233
7.211
6.841
6.819
5.947
5.942
5.934
5.928
3.888
3.871
3.858
3.800
3.771
2.617
2.603
2.572
2.558
1.915
1.902
1.870
1.856
-0.000
Bn
N
MeO
OMe
4c, 1H NMR
2.00
2.05
1.14
4.21
4.00
2.00
3.82
6.15
2.02
2.02
f1 (ppm)
158.797
139.398
137.858
132.896
129.134
128.415
127.134
127.082
119.570
113.839
77.477
77.160
76.842
56.975
55.323
52.122
28.099
4c, 13C NMR
f1 (ppm)

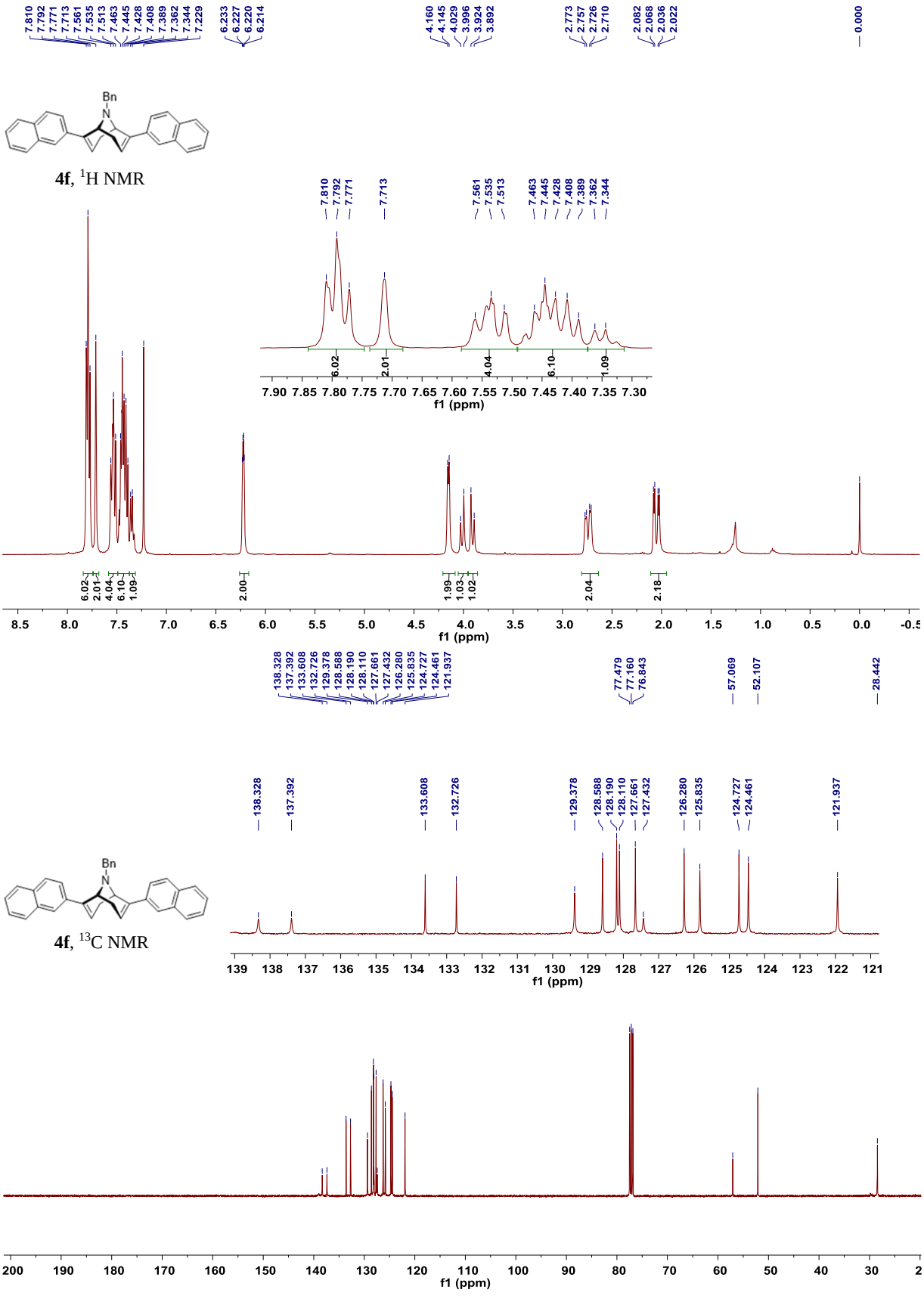


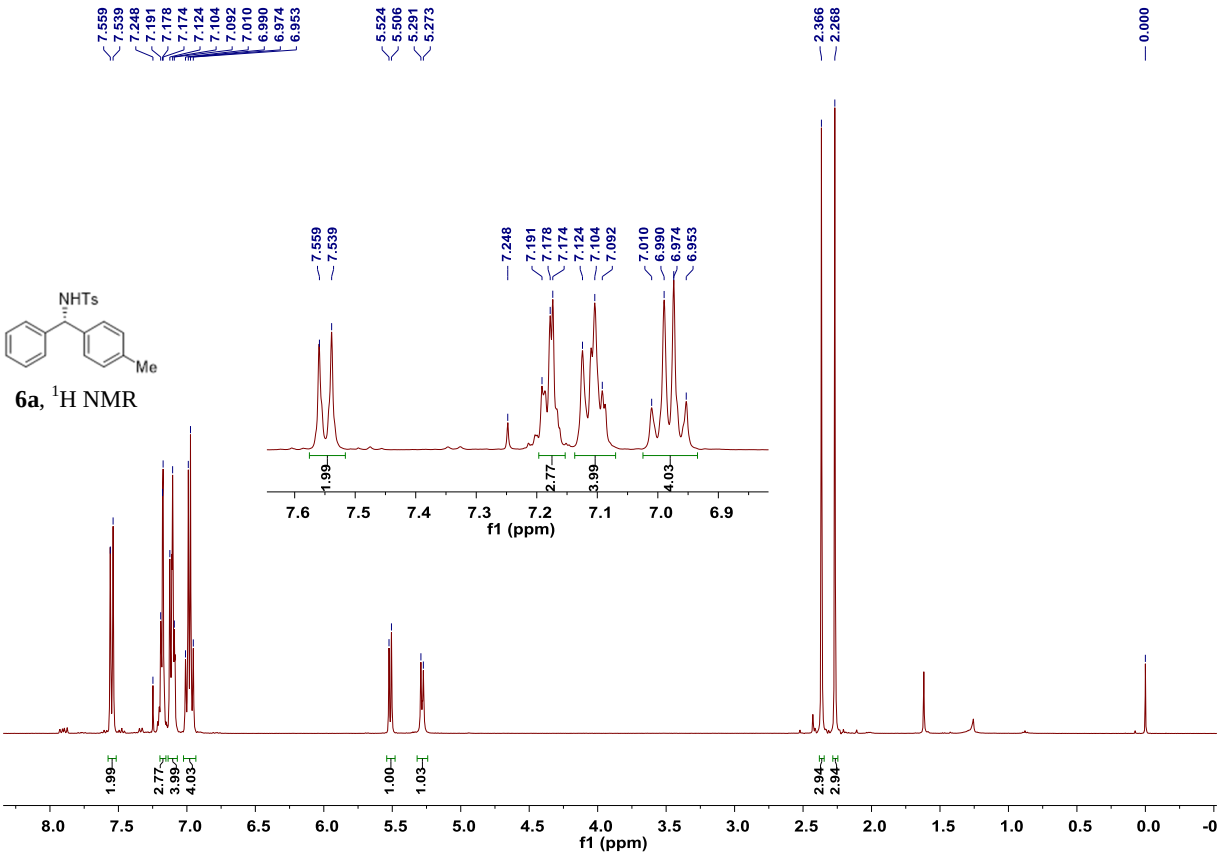
4d, ^{1}H NMR



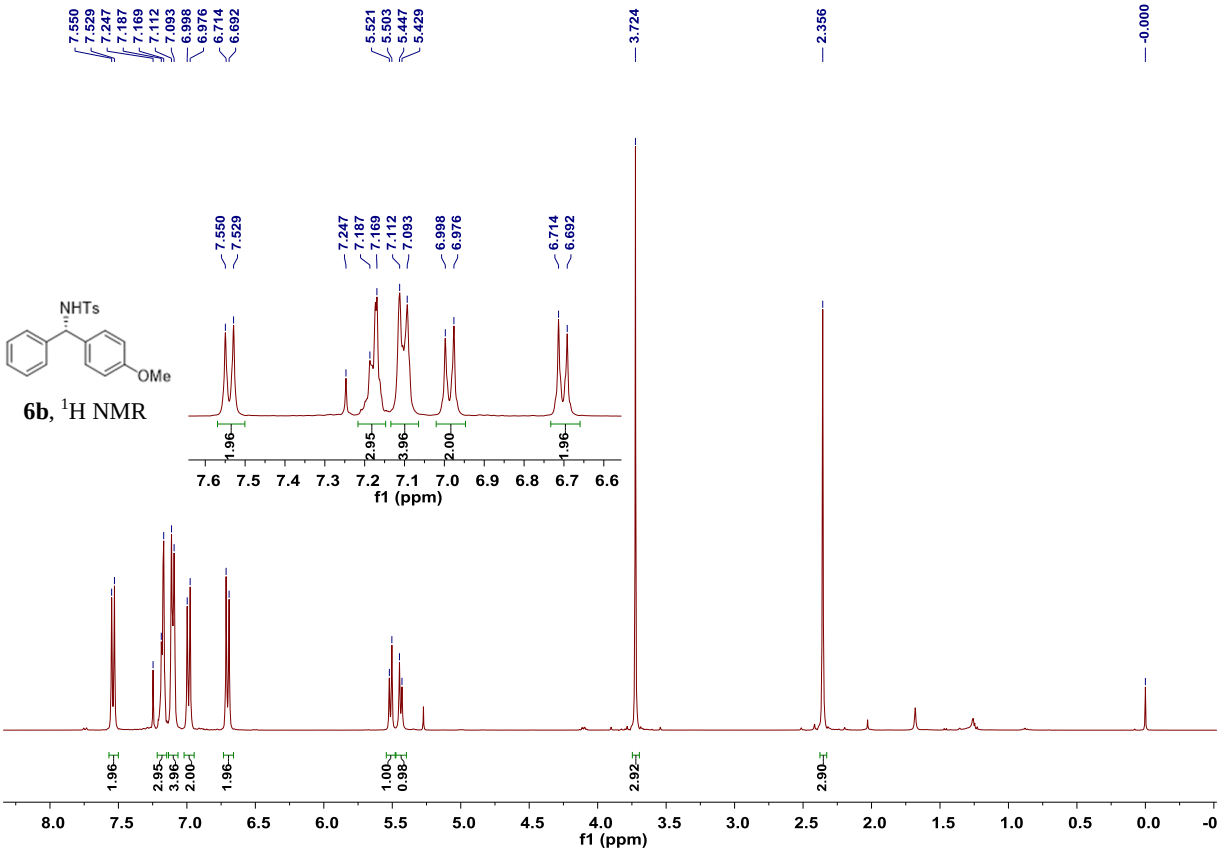
4d, ^{13}C NMR


8.193
8.174
7.850
7.832
7.774
7.754
7.648
7.630
7.480
7.455
7.435
7.407
7.389
7.370
7.332
7.315
7.281
5.895
5.886
4.154
4.121
4.071
4.038
3.831
3.817
2.537
2.525
2.492
2.480
1.990
1.978
1.945
1.933
0.000
Bn
N
4e, 1H NMR
f1 (ppm)
140.342
139.168
133.914
132.407
128.865
128.499
128.433
127.462
127.263
126.419
125.968
125.882
125.880
125.843
125.446
124.180
77.478
77.160
76.842
57.136
55.415
27.008
4e, 13C NMR
f1 (ppm)

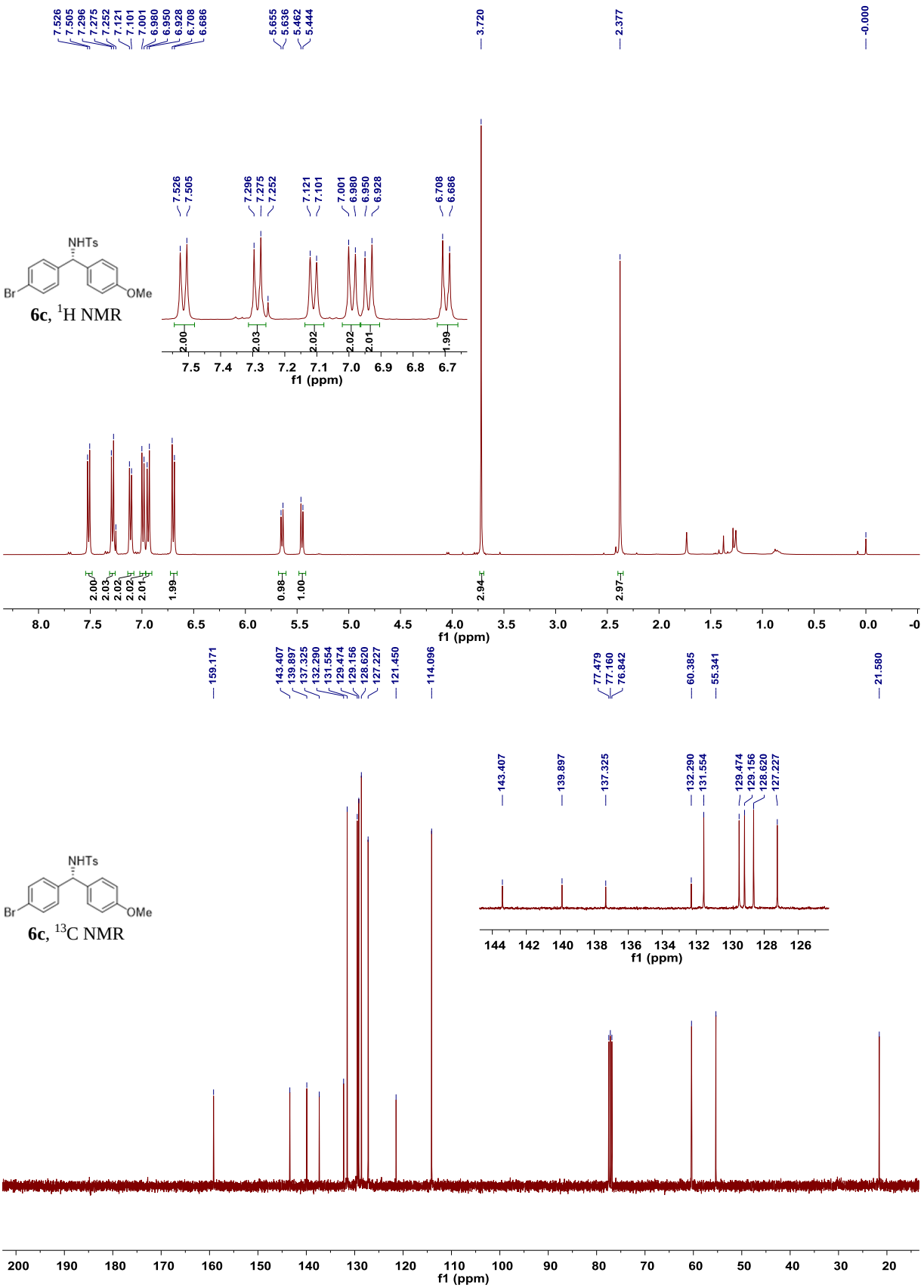

7.810
7.792
7.771
7.713
7.561
7.535
7.513
7.463
7.445
7.428
7.408
7.389
7.362
7.344
7.229
6.233
6.227
6.220
6.214
4.160
4.145
4.029
3.996
3.924
3.892
2.773
2.757
2.726
2.710
2.082
2.068
2.036
2.022
0.000
Bn
N
4f, 1H NMR
6.02
2.01
4.04
6.10
1.09
2.00
1.99
1.03
1.02
2.04
2.18
f1 (ppm)
138.328
137.392
133.608
132.726
129.378
128.588
128.190
128.110
127.661
127.432
126.280
125.835
124.727
124.461
121.937
77.479
77.160
76.843
57.069
52.107
28.442
4f, 13C NMR
f1 (ppm)

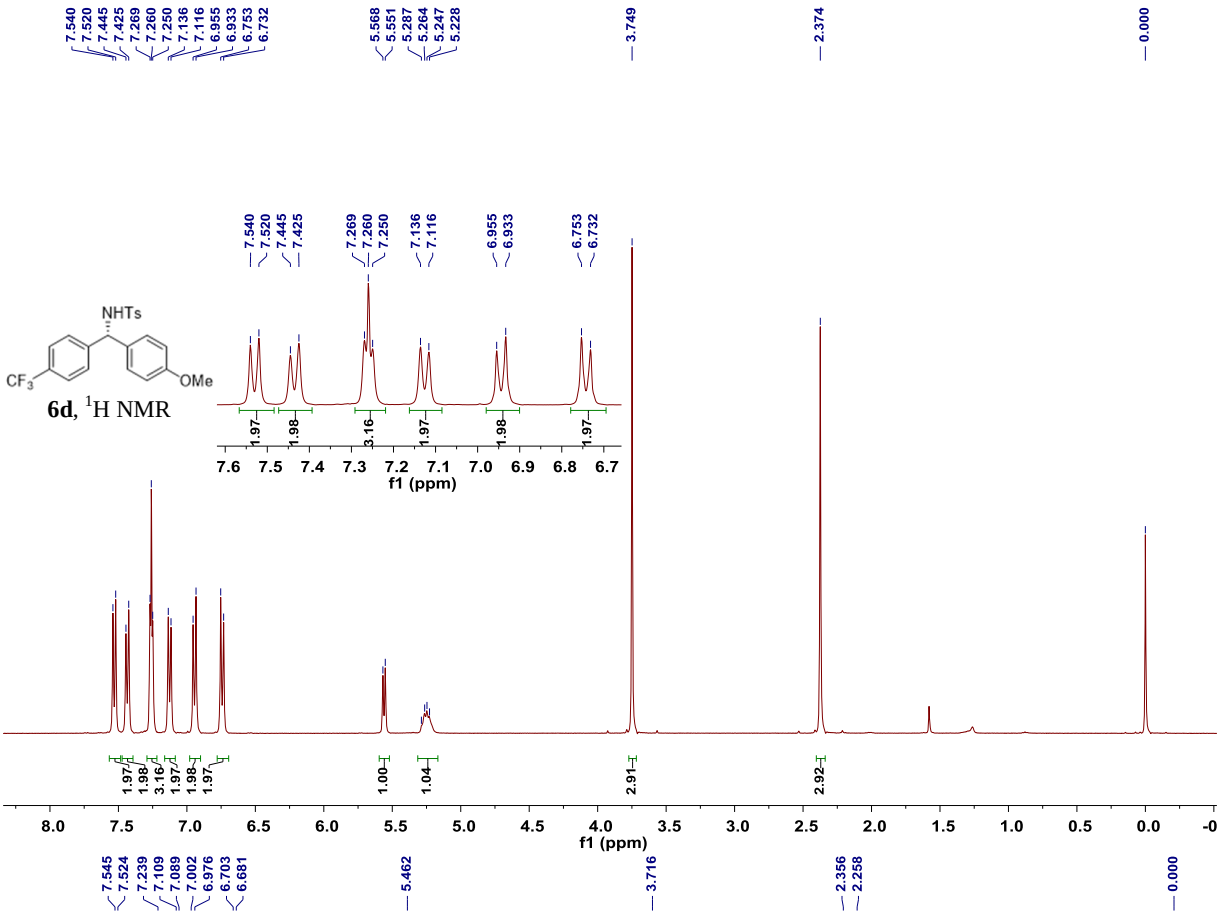


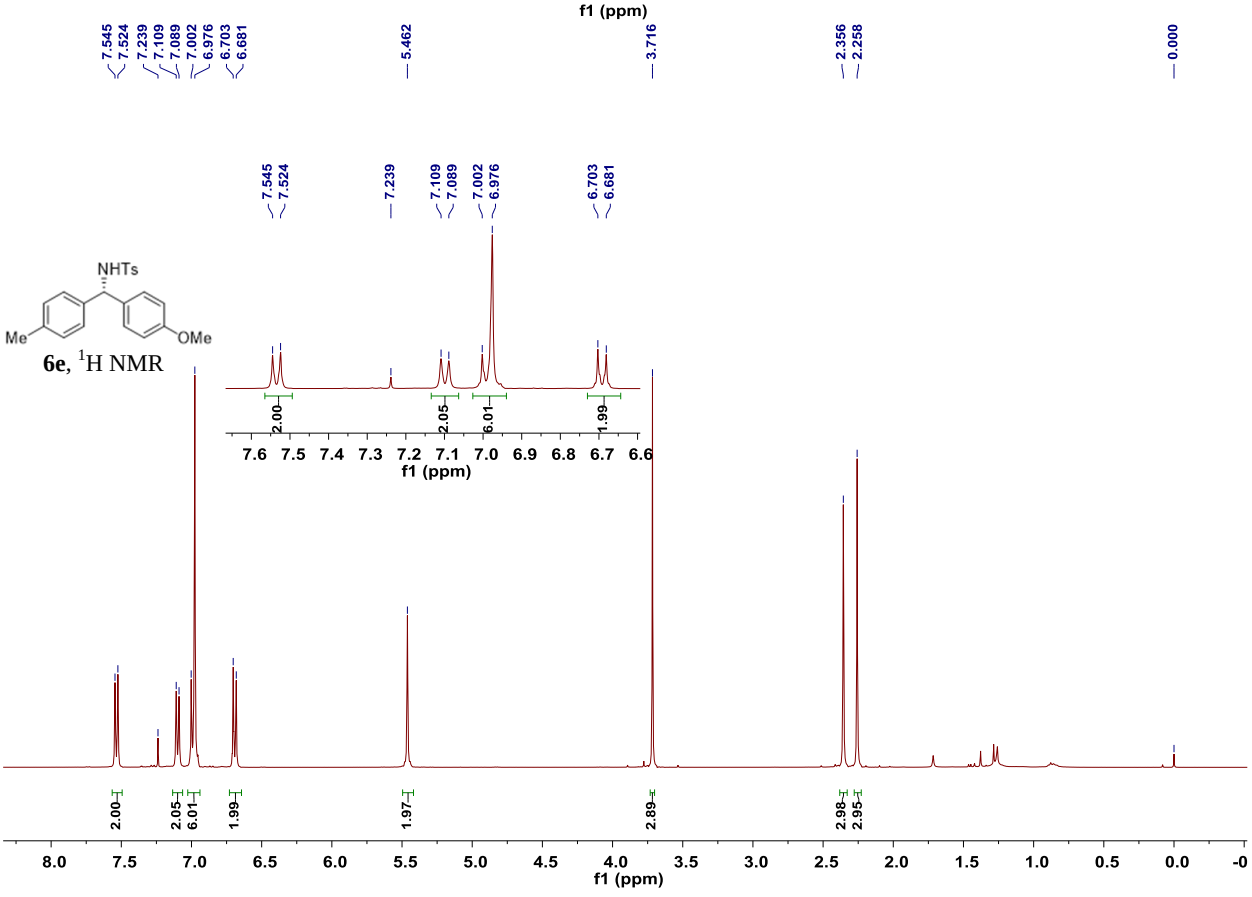
6a, ^{1}H NMR



6b, ^{1}H NMR


7.526
7.505
7.296
7.275
7.252
7.121
7.101
7.001
6.980
6.950
6.928
6.708
6.686
5.655
5.636
5.462
5.444
3.720
2.377
-0.000
NHTs
Br
OMe
6c, 1H NMR
2.00
2.03
2.02
2.02
2.01
1.99
0.98
1.00
2.94
2.97
f1 (ppm)
159.171
143.407
139.897
137.325
132.290
131.554
129.474
129.156
128.620
127.227
121.450
114.096
77.479
77.160
76.842
60.385
55.341
21.580
6c, 13C NMR


7.540
7.520
7.445
7.425
7.269
7.260
7.250
7.136
7.116
6.955
6.933
6.753
6.732
5.568
5.551
5.287
5.264
5.247
5.228
3.749
2.374
0.000
NHTs
CF3
OMe
6d, 1H NMR
1.97
1.98
3.16
1.97
1.98
1.97
1.00
1.04
2.91
2.92
f1 (ppm)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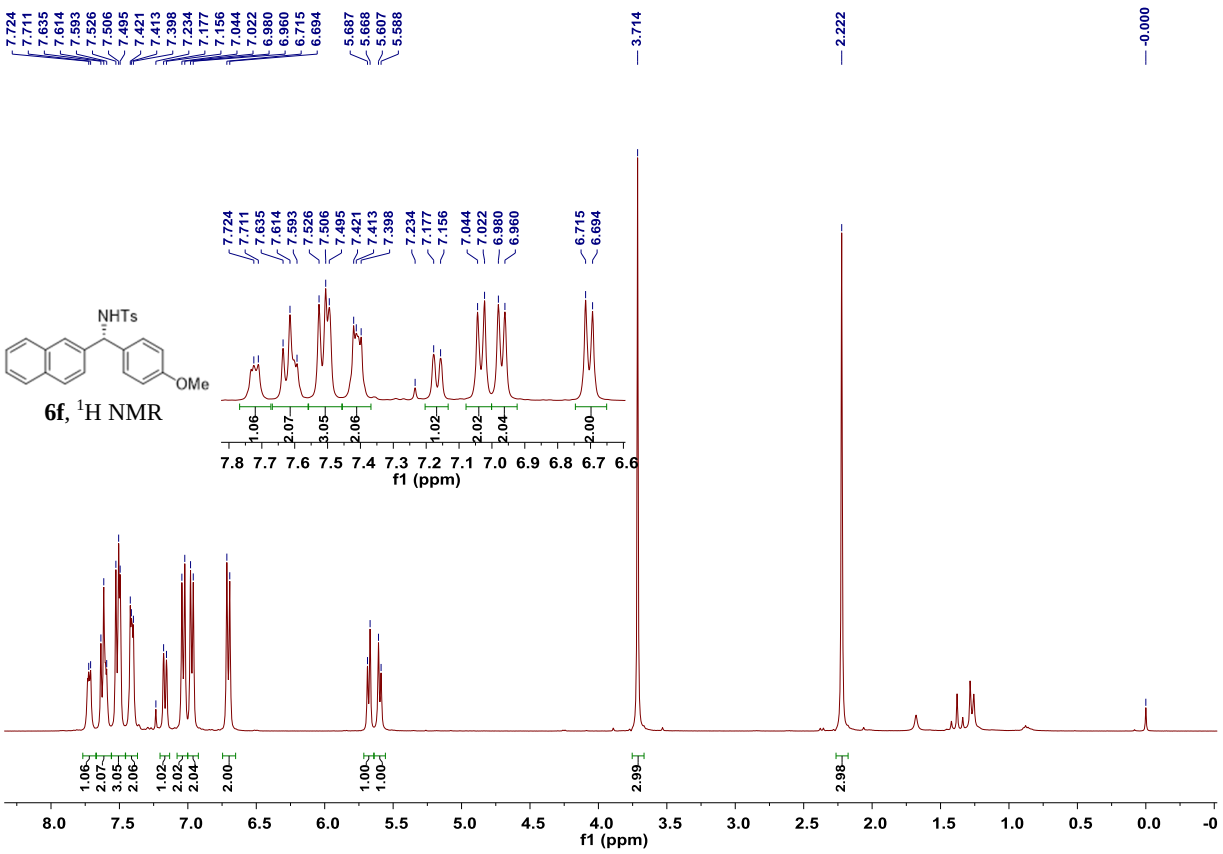
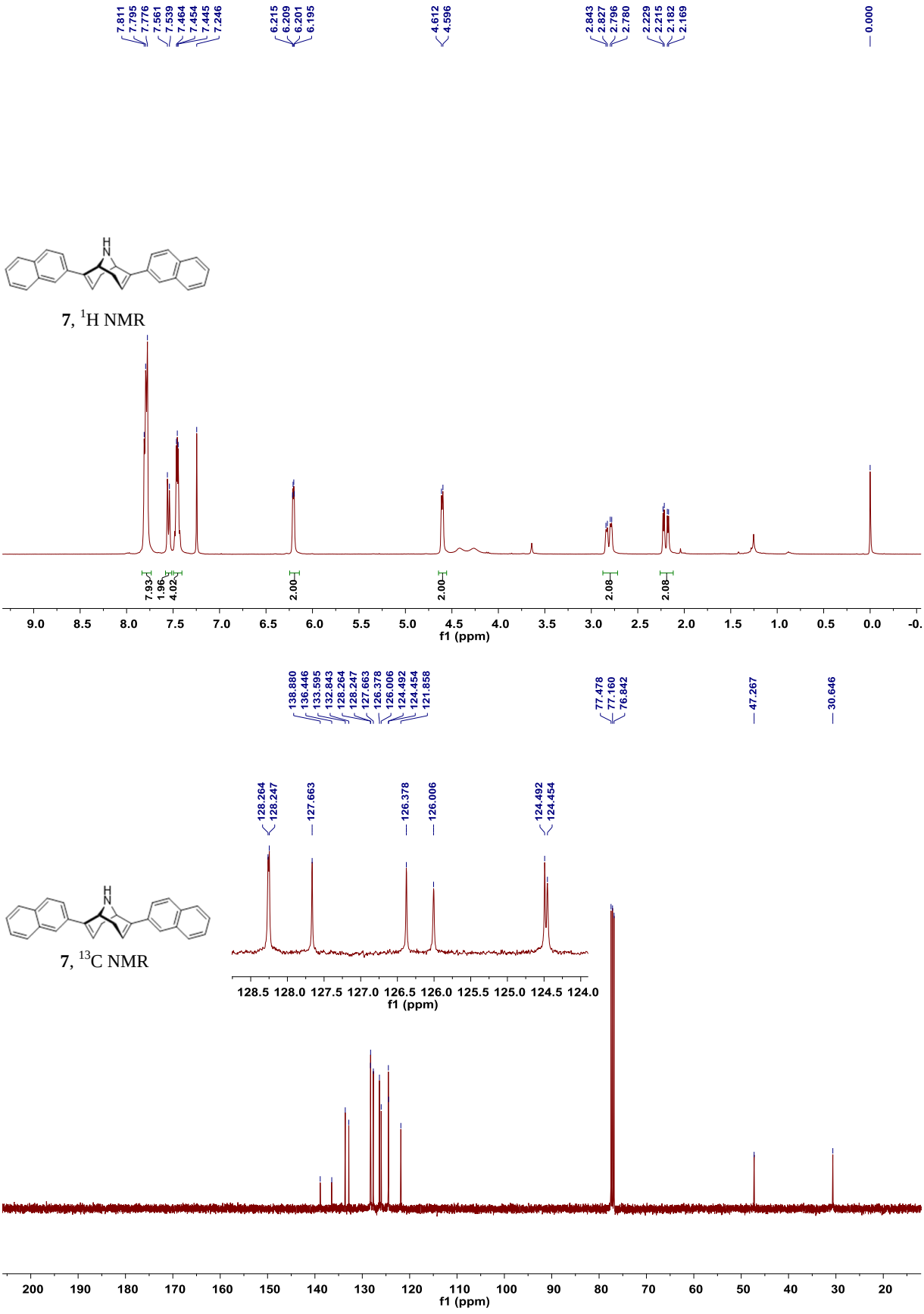
7.239
7.109
7.089
7.002
6.976
6.703
6.681
5.462
3.716
2.356
2.258
0.000
NHTs
Me
OMe
6e, 1H NMR
2.00
2.05
6.01
1.99
1.97
2.89
2.98
2.95
f1 (ppm)


7.724
7.711
7.635
7.614
7.593
7.526
7.506
7.495
7.421
7.413
7.398
7.234
7.177
7.156
7.044
7.022
6.980
6.960
6.715
6.694
5.687
5.668
5.607
5.588
3.714
2.222
-0.000
NHTs
OMe
1.06
2.07
3.05
2.06
1.02
2.02
2.04
2.00
1.00
1.00
2.99
2.98
f1 (ppm)

6f, ^{1}H NMR


7.811
7.795
7.776
7.561
7.539
7.464
7.454
7.445
7.246
6.215
6.209
6.201
6.195
4.612
4.596
2.843
2.827
2.796
2.780
2.229
2.215
2.182
2.169
0.000
7, 1H NMR
7.93
1.96
4.02
2.00
2.00
2.08
2.08
f1 (ppm)
138.880
136.446
133.595
132.843
128.264
128.247
127.663
126.378
126.006
124.492
124.454
121.858
77.478
77.160
76.842
47.267
30.646
128.264
128.247
127.663
126.378
126.006
124.492
124.454
7, 13C NMR
f1 (ppm)
f1 (ppm)