1,3-Dipolar Cycloaddition of Nitrones to Oxa(aza)bicyclic Alkenes

Yongqi Yao,[a] Wen Yang,[a] Qifu Lin,[a] Weitao Yang,[a] Huanyong Li,[b] Lin Wang,[b] Fenglong Gu,*[a] and Dingqiao Yang*[a]

[a]Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China
*E-mail: yangdq@scnu.edu.cn (D. Y.), gu@scnu.edu.cn (F. G.)

[b]Analytical and Testing Center, Jinan University, Guangzhou 510632, People's Republic of China

Supporting Information

1. Experimental procedures

General experimental. Unless otherwise noted, reactions were carried out in single-neck or two-neck flask round bottom flasks, with magnetic stirring. Air- or water-sensitive liquids and solutions were transferred *via* syringe. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 40 Torr (house vacuum). Analytical thin layer chromatography (TLC) was performed with Silicycle normal phase glass plates (0.25 mm, 60-A pore size, 230–400 mesh). Visualization was done under a 254 nm UV light source. Purification of reaction products was generally done by flash chromatography with Silicycle 230–400 mesh silica gel.

Materials. Unless otherwise indicated, all reagents and solvents were purchased for commercial suppliers and used without additional purification. Distilled water was used in the reactions. Oxa(aza)bicyclic alkenes **1a**–**1m**[1] and nitrone **2a–2t**[2] were prepared according to literature procedures.

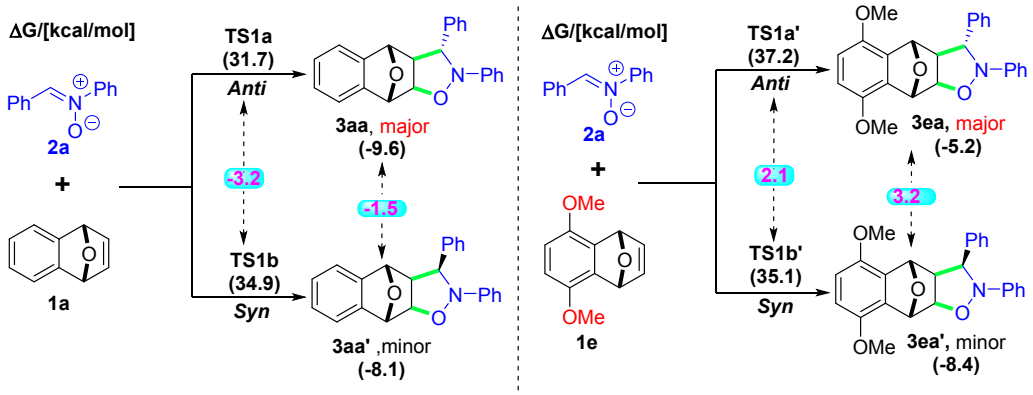
Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer (600 MHz for ^{1}H; 150 MHz for ^{13}C) at room temperature. All chemical shift values are quoted in ppm referenced to an internal tetramethylsilane at 0.00 ppm for ^{1}H NMR and relative to residual $CHCl_3$ at 77.00 ppm for ^{13}C unless otherwise noted. HRMS (ion trap) were obtained from mass spectrometer (ESI). Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected. All calculations were performed using the Gaussian 09 suite of the program. Geometry optimizations of all the intermediates and transition states were carried out at the B3LYP functional. The 6-311G** basis set for the main group elements of C, H, O and N. The optimization was carried out without imposing any symmetry constrains. The stationary points and transition states on the energy profiles were confirmed by the normal mode analysis. The intrinsic reaction coordinate (IRC) approach was used to confirm the transition state indeed connects two relevant minima. To obtain thermodynamic data, zero-point energies and relative free energies were obtained at the same level of theory. For modelling the solvent effects, the dielectric constant of the solution (toluene) was obtained by volume ratio and the PCM solvation model involved in all geometries optimization and frequency calculation. The free energies were employed to analyze the reaction mechanism and the energies are all in kcal/mol. The 3D model was presented by the Diamond 3.2 programe.

The general procedure for new compounds of 3aa–3gm: The substrate oxa(aza)bicyclic alkenes **1** (0.1 mmol) and nitrones **2** (0.1 mmol) were added to 5.0 mL round-bottomed flask, followed by addition of 2.0 mL toluene. The mixture was stirred at 60 ^{o}C for 6 h. The mixture was purified by column chromatography (Silica Gel: 200–300 mesh) to afford the desired product **3**.

Table S1. The electrical energies, zero-point vibrational energy (ZPE), free energies and the imaginary frequencies in solvent (water) for the optimized species

Lable	HF [Haretree]	ZPE [kcal/mol]	Free Energies [Haretree]	Imaginary Freq
1a	-461.1466396	94.9	-461.032023	-
2a	-632.0769501	130.0	-631.915267	-
TS1a	-1093.1984395	225.6	-1092.896735	-380.34
3aa	-1093.2695059	228.4	-1092.962575	-
TS1b	-1093.1937776	225.7	-1092.891673	-362.50
3aa'	-1093.267053	228.3	-1092.960002	-
TS2a	-1093.1796889	225.5	-1092.877919	-408.00
4	-1093.26332	228.4	-1092.95624	-
TS2b	-1093.1721307	225.8	-1092.869539	-406.78
4'	-1093.2581716	228.5	-1092.950488	-
TS3	-1093.1567599	223.5	-1092.862645	-473.38

Table S2. Energy barrier between two transition states of **3ea** and **3ea'.**



Lable	**TS1a**	**TS1b**	**TSEB**	**3ea** or **3aa**	**3ea' or 3aa'**	EB
3ea & 3ea'	**37.2**	**35.1**	**2.1**	**-5.2**	**-8.4**	**3.2**
3aa & 3aa' (model)	**31.7**	**34.9**	**-3.2**	**-9.6**	**-8.1**	**-1.5**

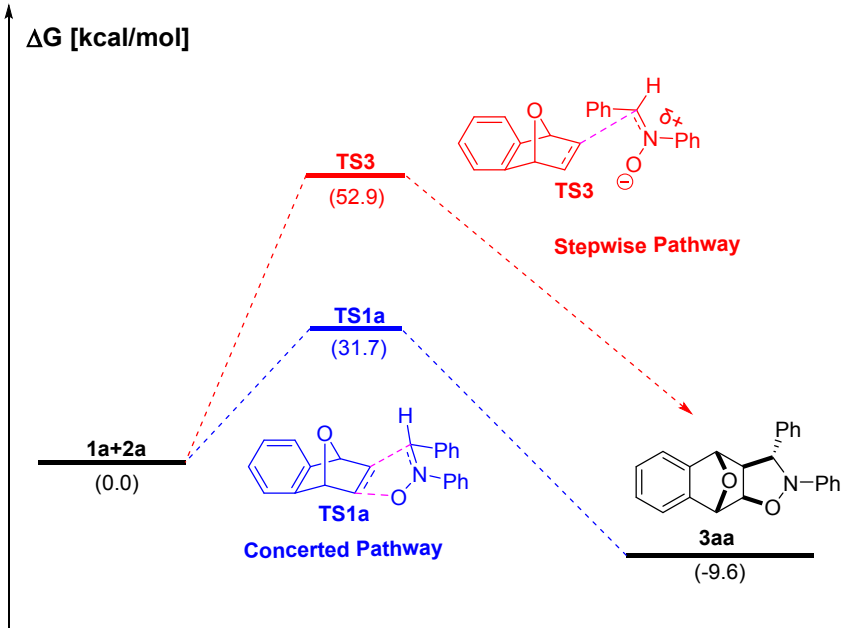
[a]TSEB = Energy barrier between the transition states of major and minor pathways. EB = Energy barrier between major and minor products.

[b]Energy barrier relationship (polarity) of **3ea** was opposite to **3aa**. The result indicated that the major product **3ea** goes a higher energy barrier than the minor product **3ea'**. Thus, the regioisomeric ratios of **3ea** (2:1 dr) was lower than the ones of other cycloaddition products (~6:1 dr) individually.

[c]So far the phenomenon can be attributed to the electronic effect and substituted position of the methoxy groups.

[d]The total energy of the oxabicyclic alkene **1a** or **1e** and nitrone **2a** was set as zero for reference (ΔG/[kcal/mol]).

Scheme S1. Comparisons between stepwise and concerted pathways [a,b,c]



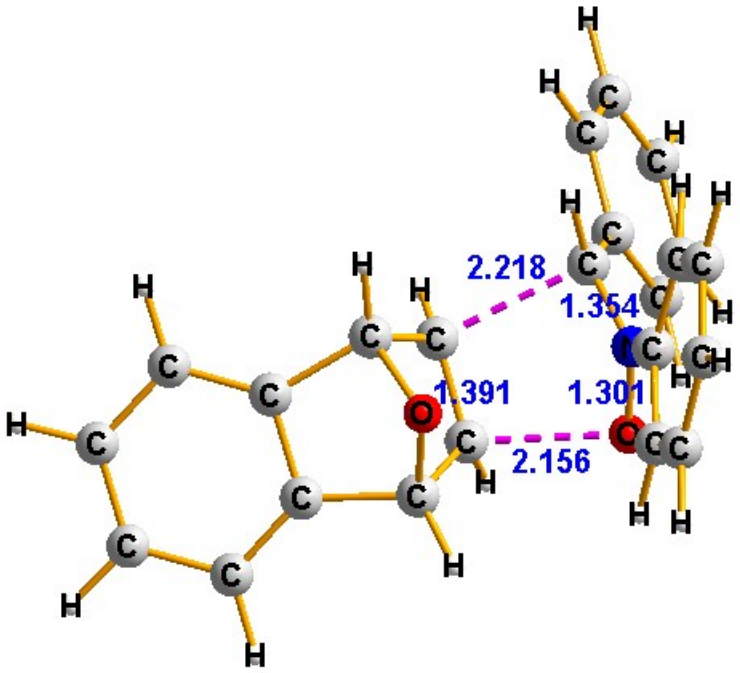
[a]The total energy of the reactants **1a** and **2a** was set as zero for reference (B3LYP / 6-311G**).

[b]Stepwise pathway is inexistent because of more energy requirement (~21.2 kcal/mol) and excessive activation energy (52.9 kcal/mol) for the **TS3**.

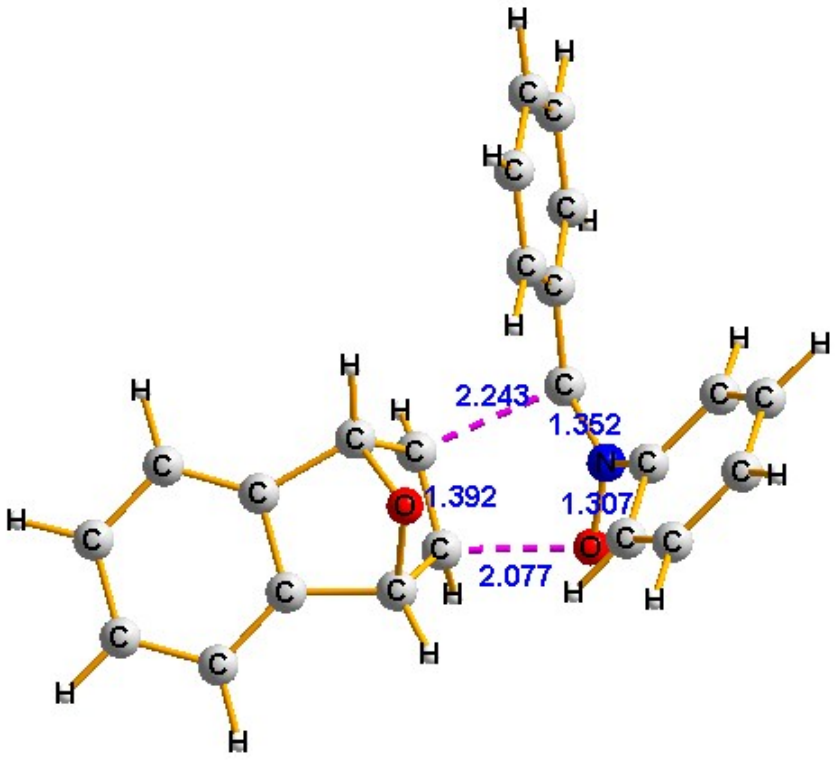
[c] scrf=(solvent=toluene, pcm), temperature=333.15 (under optimized conditions).

Scheme S2. 3D model of transition states.

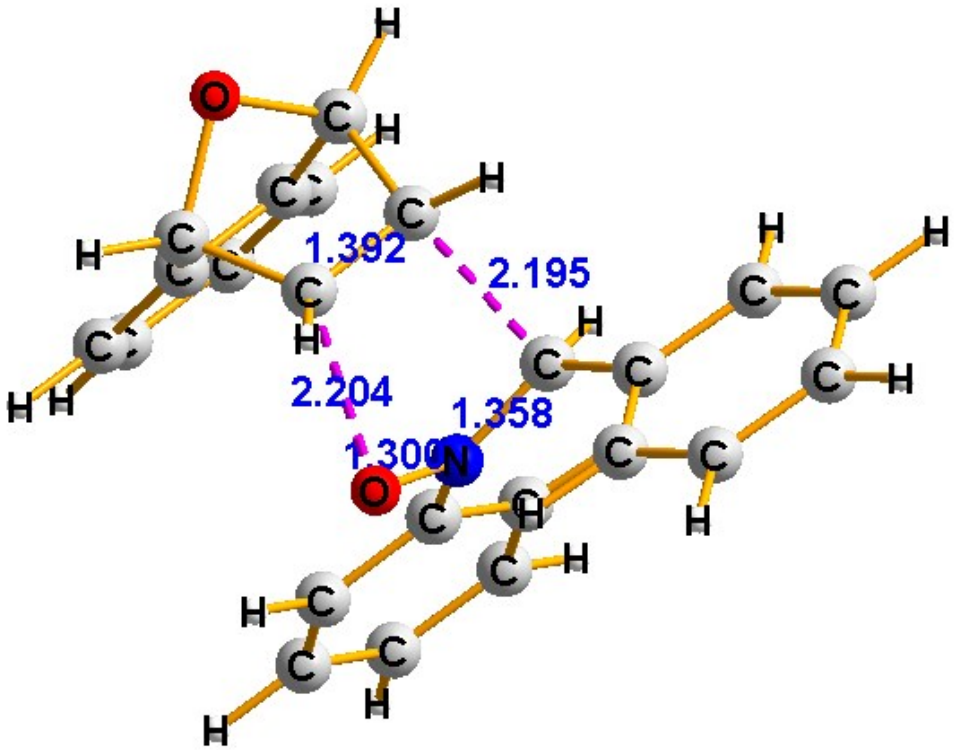
TS1a



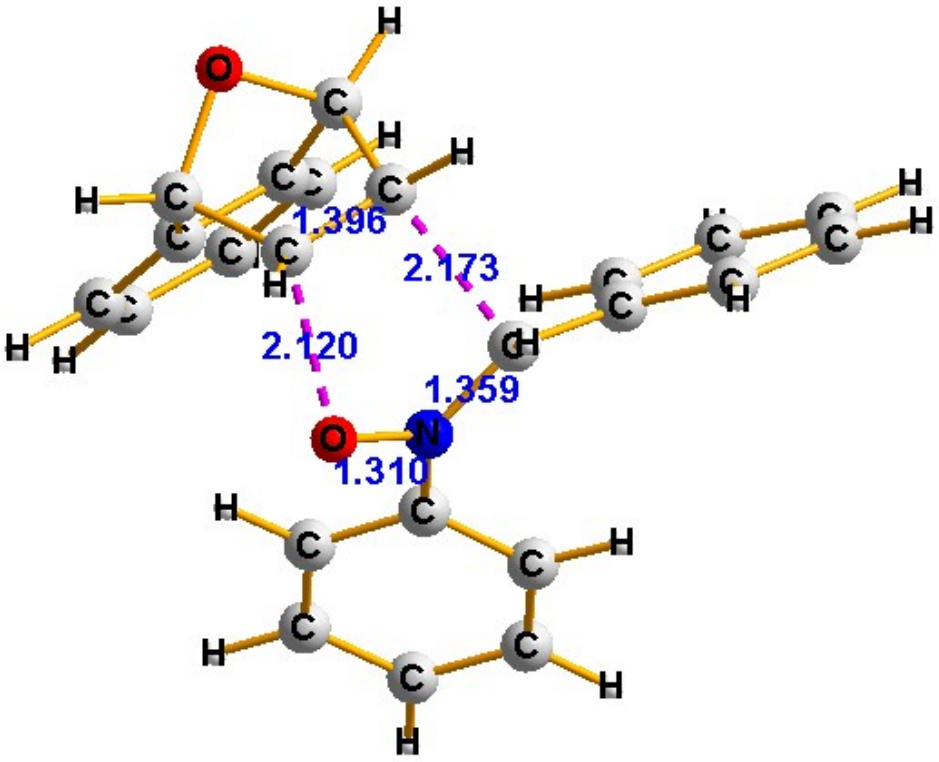
TS1b



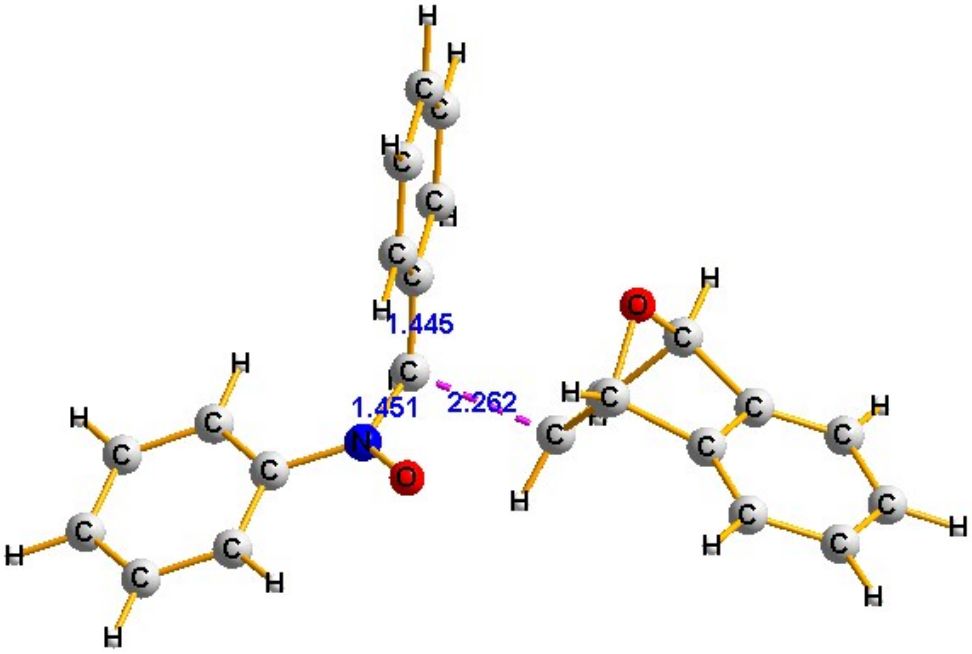
TS2a



TS2b

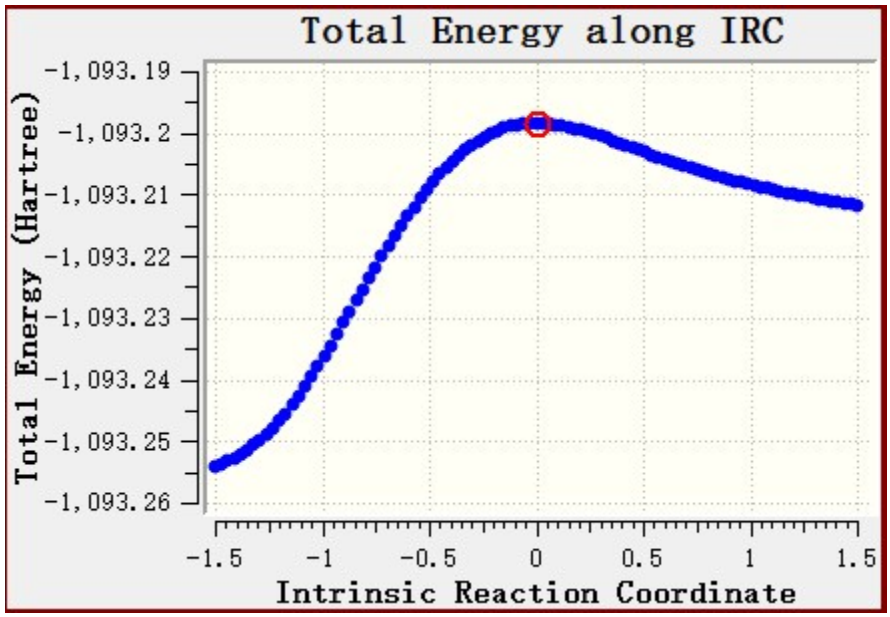


TS3



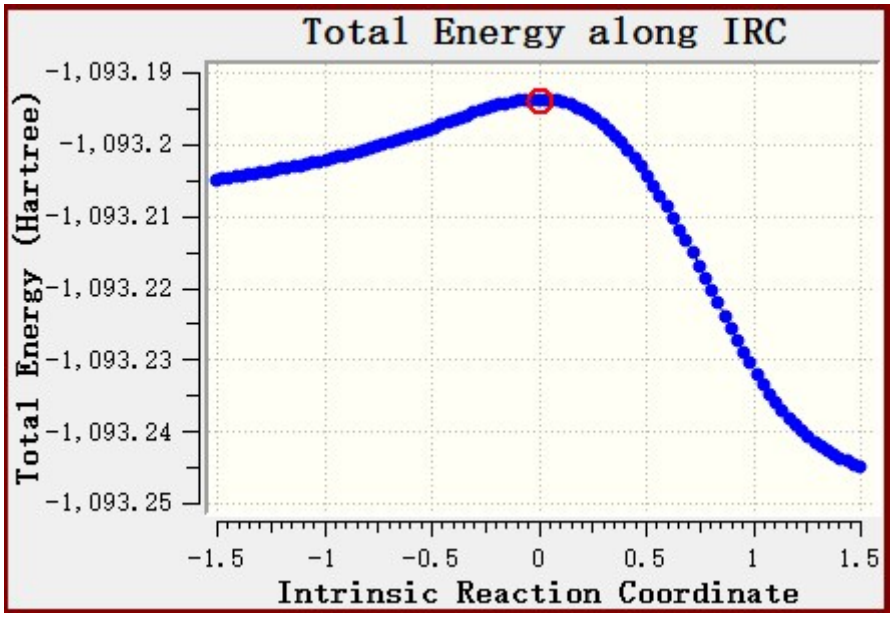
Scheme S3. Intrinsic reaction coordinate (IRC) of the transition states.

IRC for TS1a



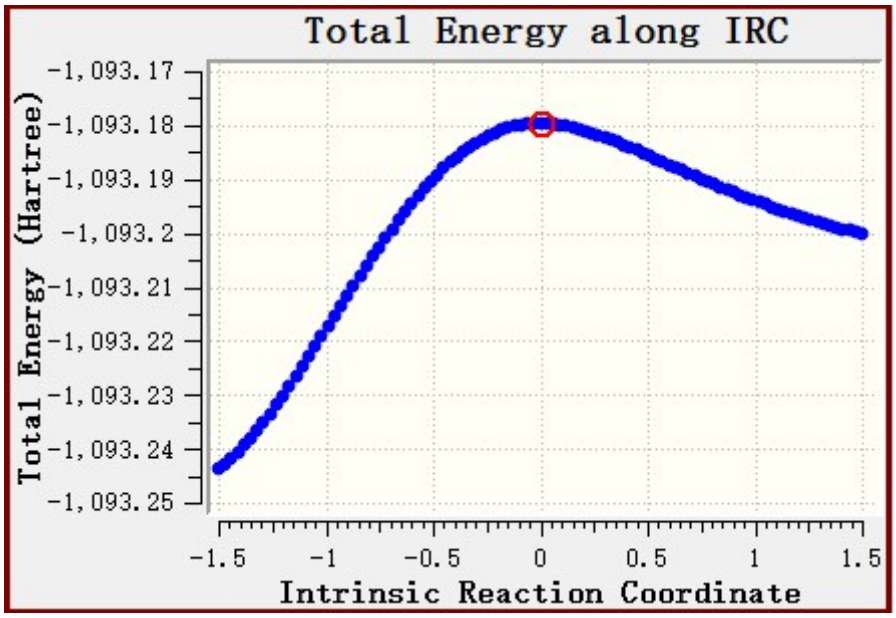
Intrinsic Reaction Coordinate = 0, Total Energy (Hartree) = -1093.198439

IRC for TS1b



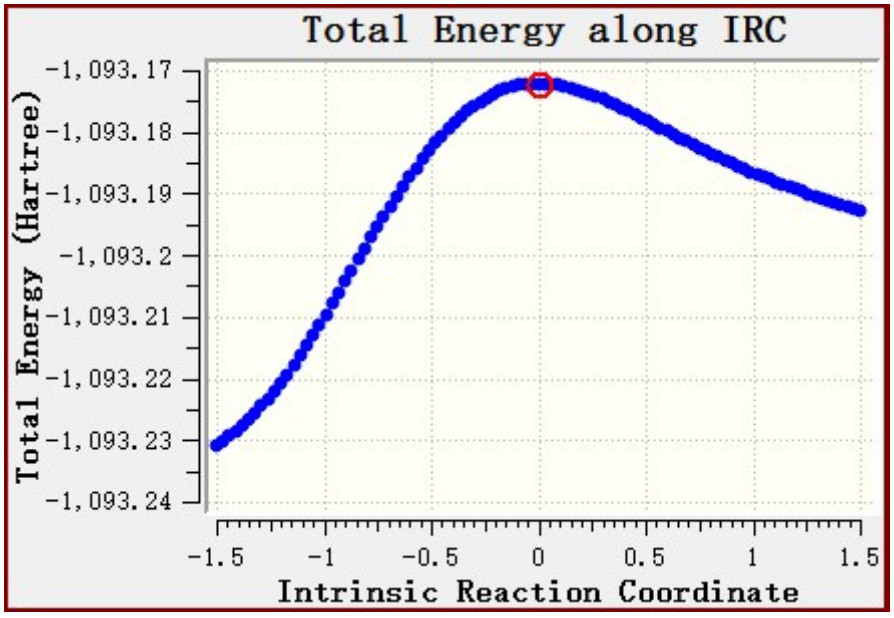
Intrinsic Reaction Coordinate = 0, Total Energy (Hartree) = -1093.193778

IRC for **TS2a**



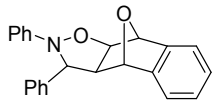
Intrinsic Reaction Coordinate = 0, Total Energy (Hartree) = -1093.179689

IRC for TS2b



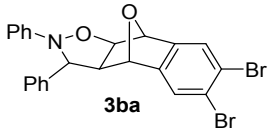
Intrinsic Reaction Coordinate = 0, Total Energy (Hartree) = -1093.172131

2. Characterization data of **3aa**–**3gh**



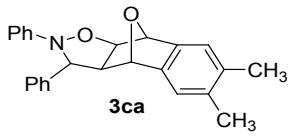
3aa

2,3-Diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3aa**). Following the general procedure, **3aa** was obtained as a colourless oil (33.8 mg, 99%, 6:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.40–7.32 (m, 4H), 7.20–7.14 (m, 5H), 7.04–6.98 (m, 3H), 5.42 (s, 1H), 5.33 (s, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.17 (d, *J* = 7.8 Hz, 1H), 3.00 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.0, 145.1, 141.4, 139.4, 129.0, 128.4, 128.1, 127.8, 127.5, 127.2, 124.1, 121.0, 119.8, 119.2, 82.7, 82.1, 80.4, 74.3, 62.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{19}NO_2$: 342.1494; found: 342.1488.



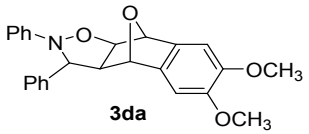
3ba

6,7-Dibromo-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ba**). Following the general procedure, **3ba** was obtained as a yellow solid (34.4 mg, 99%, 6:1 dr). m.p. 211.0–213.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.45 (s, 1H), 7.44–7.41 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.01–6.98 (m, 3H), 5.38 (s, 1H), 5.29 (s, 1H), 4.65 (d, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 7.2 Hz, 1H), 2.98 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.7, 146.1, 142.6, 138.9, 129.1, 128.44, 128.41, 128.3, 127.8, 126.4, 125.3, 124.4, 123.6, 123.2, 119.3, 82.1, 81.6, 79.9, 74.2, 62.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}Br_2NO_2$: 497.9704; found: 497.9700.



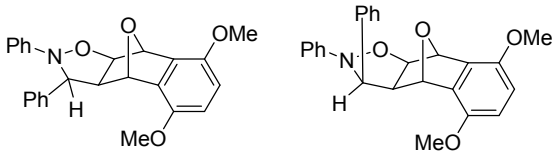
3ca

6,7-Dimethyl-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ca**). Following the general procedure, **3ca** was obtained as a white solid (35.1 mg, 96%, 6:1 dr). m.p. 188.0–190.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.39–7.34 (m, 2H), 7.34–7.30 (m, 1H), 7.18–6.12 (m, 3H), 7.03–6.95 (m, 4H), 5.36 (s, 1H), 5.27 (s, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 3.00 (t, *J* = 6.9 Hz, 1H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.1, 142.9, 139.6, 139.1, 135.6, 135.3, 129.0, 128.4, 128.0, 127.8, 124.1, 122.3, 121.1, 119.2, 83.0, 82.0, 80.3, 74.4, 63.4, 19.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{24}NO_2$: 370.1807; found: 370.1799.



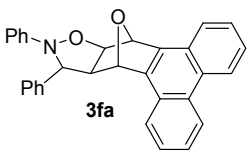
3da

6,7-Dimethoxy-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3da**). Following the general procedure, **3da** was obtained as a yellow solid (39.6 mg, 99%, 6:1 dr). m.p. 128.0–130.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.17–7.14 (m, 2H), 7.03–6.99 (m, 3H), 6.95 (s, 1H), 6.79 (m, 1H), 5.37 (s, 1H), 5.28 (s, 1H), 4.63 (d, *J* = 6.6 Hz, 1H), 4.14 (d, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.0, 148.4, 148.1, 139.5, 137.5, 133.4, 129.0, 128.3, 128.0, 127.8, 124.1, 119.2, 105.4, 104.4, 83.0, 82.2, 80.6, 74.2, 63.5, 56.3, 56.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{24}NO_4$: 402.1705; found: 402.1701.



3ea **3ea'**

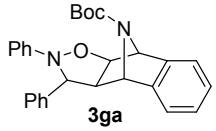
5,8-Dimethoxy-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ea** & **3ea'**). Following the general procedure, **3ea** and **3ea'** were obtained as a yellow oil (39.7 mg, 99%, 2:1 dr). **3ea**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.8 Hz, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 8.1 Hz, 2H), 7.03–6.95 (m, 3H), 6.65 (dd, *J* = 10.8, 8.0 Hz, 2H), 5.58 (s, 1H), 5.49 (s, 1H), 4.69 (d, *J* = 6.6 Hz, 1H), 4.18 (d, *J* = 6.6 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 3.01 (t, *J* = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.2, 147.9, 146.9, 139.7, 134.2, 130.4, 128.9, 128.3, 127.9, 127.8, 123.8, 118.9, 112.0, 111.8, 82.4, 80.2, 78.5, 74.0, 62.2, 56.1, 55.8. **3ea'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.35-7.29 (m, 3H), 7.18 (t, *J* = 8.1 Hz, 2H), 7.03–6.95 (m, 2H), 6.90 (t, *J* = 6.0 Hz, 1H), 6.60 (dd, *J* = 8.4, 7.8 Hz, 2H), 5.65 (s, 1H), 4.90 (s, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.73 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 3.17 (dd, *J* = 9.0, 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.8, 147.7, 146.7, 138.0, 134.7, 131.9, 128.6, 128.5, 128.2, 127.6, 122.3, 116.1, 112.0, 111.5, 84.1, 80.7, 77.6, 71.3, 56.9, 56.0, 55.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{24}NO_4$: 402.1705; found: 402.1701.



3fa

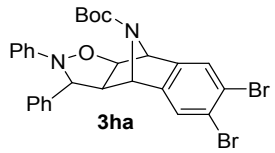
11,12-Diphenyl-9,9a,11,12,12a,13-hexahydro-9,13-epoxytriphenyleno[2,3-d]isoxazole (**3fa**). Following the general procedure, **3fa** was obtained as a yellow

solid (42.7 mg, 97%, 6:1 dr). m.p. 120.0–122.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77–8.69 (m, 2H), 8.00–7.97 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.71–7.69 (m, 2H), 7.67–7.64 (m, 1H), 7.59–7.57 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.36–7.32 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.06 (s, 1H), 5.96 (s, 1H), 4.75 (d, *J* = 6.6 Hz, 1H), 4.39 (d, *J* = 7.2 Hz, 1H), 3.09 (t, *J* = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.2, 141.4, 139.4, 137.2, 130.8, 130.1, 129.0, 128.4, 128.1, 127.6, 127.2, 126.71, 126.68, 126.2, 125.5, 124.1, 124.0, 123.9, 123.6, 119.0, 83.0, 81.7, 80.0, 74.0, 63.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{31}H_{24}NO_2$: 442.1807; found: 442.1805.



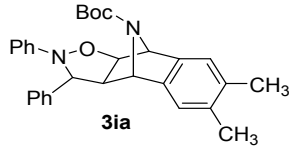
3ga

tert-Butyl-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epiminonaphtho[2,3-d]isoxazole-10-carboxylate (**3ga**). Following the general procedure, **3ga** was obtained as a white solid (43.5 mg, 99%, 6:1 dr). m.p. 167.0–168.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.40 (m, 2H), 7.40–7.29 (m, 4H), 7.20–7.10 (m, 5H), 6.99 (d, *J* = 8.4 Hz, 3H), 5.40–5.08 (m, 2H), 4.60 (d, *J* = 6.6 Hz, 1H), 4.33–4.03 (m, 1H), 2.89 (s, 1H), 1.38 (s, 3H), 1.32 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.0, 141.0, 128.9, 128.3, 128.1, 127.9, 127.7, 127.2, 126.9, 123.8, 121.9, 121.4, 120.5, 119.2, 118.9, 82.9, 80.4, 72.6, 64.6, 63.5, 61.8, 28.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{29}N_2O_3$: 441.2178; found: 441.2172.



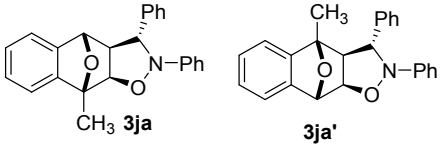
3ha

tert-Butyl-6,7-dibromo-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epiminonaphtho[2,3-d]isoxazole-10-carboxylate (**3ha**). Following the general procedure, **3ha** was obtained as a white solid (57.8 mg, 97%, 6:1 dr). m.p. 190.0–192.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.49–7.29 (m, 6H), 7.14 (t, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.35–5.03 (m, 2H), 4.56 (d, *J* = 6.0 Hz, 1H), 4.32–4.15 (m, 1H), 2.86 (t, *J* = 5.7 Hz, 1H), 1.34 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.8, 139.1, 129.0, 128.7, 128.40, 128.37, 127.7, 126.7, 125.9, 124.0, 123.4, 122.9, 119.0, 115.8, 120.0, 82.3, 81.0, 72.6, 64.2, 63.0, 61.4, 29.7, 28.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{27}Br_2N_2O_3$: 597.0388; found: 597.0387.

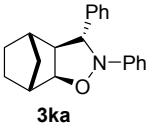


3ia

tert-Butyl-6,7-dimethyl-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epiminonaphtho[2,3-d]isoxazole-10-carboxylate (**3ia**). Following the general procedure, **3ia** was obtained as a white solid (45.8 mg, 98%, 6:1 dr). m.p. 215.0–217.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51–7.31 (m, 5H), 7.17–7.08 (m, 3H), 6.99 (d, *J* = 7.8 Hz, 4H), 5.34–5.02 (m, 2H), 4.58 (d, *J* = 6.0 Hz, 1H), 4.31–3.99 (m, 1H), 2.87 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H), 1.39 (s, 3H), 1.34 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 154.8, 149.1, 143.0, 139.7, 138.5, 135.3, 134.9, 128.9, 128.3, 128.1, 127.9, 127.7, 123.8, 122.7, 121.9, 118.9, 115.6, 82.2, 80.2, 72.8, 64.4, 63.9, 61.6, 28.4, 28.2, 19.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{30}H_{33}N_2O_3$: 469.2491; found: 469.2480.

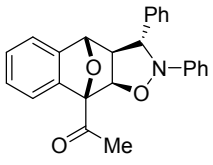


9-Methyl-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ja**) and *4-methyl-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole* (**3ja'**). Following the general procedure, **3ja** and **3ja'** was obtained as a yellow oil (28.8 mg, **3ja** : **3ja'** = 47% : 34%). **3ja**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, *J* = 6.3 Hz, 2H), 7.37 (q, *J* = 7.2 Hz, 4H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.18–7.15 (m, 4H), 7.05–6.99 (m, 3H), 5.24 (s, 1H), 4.47 (d, *J* = 6.0 Hz, 1H), 4.17 (d, *J* = 7.8 Hz, 1H), 3.08 (t, *J* = 7.3 Hz, 1H), 1.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.21, 146.0, 144.8, 139.2, 133.4, 128.9, 128.31, 128.10, 128.07, 127.3, 127.1, 124.23, 119.9, 119.4, 119.1, 88.0, 83.2, 79.4, 74.9, 64.6, 12.8. **3ja'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, *J* = 6.3 Hz, 2H), 7.34–7.30 (m, 3H), 7.24–7.18 (m, 5H), 7.10–7.08 (m, 1H), 7.05–6.99 (m, 3H), 5.36 (s, 1H), 4.74 (d, *J* = 6.6 Hz, 1H), 4.24 (d, *J* = 7.8 Hz, 1H), 2.96 (t, *J* = 6.9 Hz, 1H), 1.83 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.17, 148.4, 142.2, 139.5, 129.8, 128.87, 128.4, 128.33, 127.95, 127.5, 127.0, 124.16, 120.7, 119.6, 118.6, 86.3, 85.0, 81.0, 73.0, 64.3, 14.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO_2$: 356.1651; found: 356.1643.

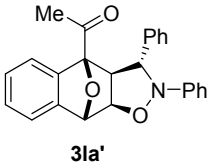


2,3-Diphenyloctahydro-4,7-methanobenzo[d]isoxazole (**3ka**). Following the general procedure, **3ka** was obtained as a colourless oil (23.9 mg, 82%, >20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.8 Hz, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.34 (d, *J* = 6.6 Hz, 1H), 2.69 (t, *J* = 8.1 Hz, 1H), 2.47 (d, *J* = 4.8 Hz, 1H), 1.78 (d, *J* = 3.6 Hz, 1H), 1.53 (d, *J* = 10.2 Hz, 1H), 1.51–1.46 (m, 1H), 1.36–1.32 (m, 1H), 1.05–0.94 (m, 2H), 0.80 (d, *J* = 10.2 Hz, 1H). ^{13}C{^{1}H} NMR (150

MHz, $CDCl_3$) δ 151.4, 139.4, 128.8, 128.0, 127.5, 126.8, 121.4, 114.9, 85.8, 72.0, 56.6, 39.3, 37.2, 33.2, 28.1, 23.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{22}NO$: 292.1701; found: 292.1696.

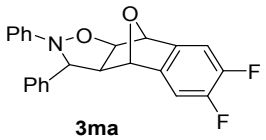


3la



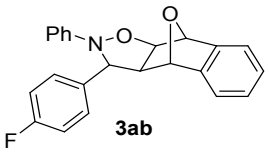
3la'

1-(2,3-Diphenyl-2,3,3a,9a-tetrahydro-4,9-epoxynaphtho[2,3-d]isoxazol-9(4H)-yl)ethan-1-one (**3la**) and *1-(2,3-diphenyl-3,3a,9,9a-tetrahydro-4,9-epoxynaphtho[2,3-d]isoxazol-4(2H)-yl)ethan-1-one* (**3la'**). Following the general procedure, **3la** and **3la'** was obtained as a colourless oil (36.9 mg, **3la** : **3la'** = 23% : 63%). **3la**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56–7.51 (m, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.36–7.32 (m, 2H), 7.22–7.14 (m, 6H), 6.99–6.96 (m, 2H), 5.41 (s, 1H), 4.89 (d, *J* = 6.6 Hz, 1H), 4.29 (d, *J* = 7.2 Hz, 1H), 3.06 (t, *J* = 6.9 Hz, 1H), 2.50 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 204.8, 148.8, 144.4, 140.0, 139.0, 129.1, 128.4, 128.3, 128.1, 127.84, 127.4, 124.0, 121.0, 119.9, 118.8, 94.1, 84.5, 80.1, 74.2, 64.0, 28.8. **3ja'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.36–7.32 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.22–7.14 (m, 4H), 6.99–6.96 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.53 (s, 1H), 4.71 (d, *J* = 6.0 Hz, 1H), 4.22 (d, *J* = 6.0 Hz, 1H), 3.33 (t, *J* = 5.7 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 205.1, 149.5, 144.2, 140.9, 139.5, 128.8, 128.5, 127.99, 127.97, 127.75, 127.5, 123.2, 121.2, 119.2, 117.3, 93.7, 84.3, 82.1, 72.2, 63.8, 28.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}NO_3$: 384.1600; found: 384.1588.



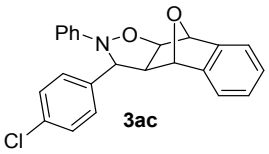
3ma

6,7-Difluoro-2,3-diphenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ma**). Following the general procedure, **3ma** was obtained as a colourless oil (37.2 mg, 99%, 6:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.36–7.32 (m, 1H), 7.20–7.15 (m, 3H), 7.04–6.99 (m, 4H), 5.40 (s, 1H), 5.31 (s, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 2.98 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.5 (dd, $J_{C\text{-}F}$ = 247.1, 29.3 Hz), 149.4 (dd, $J_{C\text{-}F}$ = 246.9, 30.0 Hz), 148.8, 141.1 (dd, $J_{C\text{-}F}$ = 6.4, 3.1 Hz), 139.0, 137.4 (dd, $J_{C\text{-}F}$ = 6.2, 3.0 Hz), 129.1, 128.4, 128.3, 127.8, 124.3, 119.2, 111.1 (d, $J_{C\text{-}F}$ = 19.7 Hz), 110.0 (d, $J_{C\text{-}F}$ = 20.0 Hz), 82.3, 81.7, 80.1, 74.1, 62.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -137.8 (d, *J* = 19.2 Hz), -138.3 (d, *J* = 19.2 Hz). HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}F_2NO_2$: 378.1306; found: 378.1301.



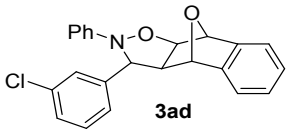
3ab

3-(4-Fluorophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ab**). Following the general procedure, **3ab** was obtained as a white solid (35.6 mg, 99%, 6:1 dr). m.p. 110–112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.37–7.34 (m, 1H), 7.22–7.15 (m, 5H), 7.06 (t, *J* = 8.7 Hz, 2H), 7.04–6.99 (m, 3H), 5.43 (s, 1H), 5.32 (s, 1H), 4.66 (d, *J* = 6.6 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 2.95 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 245.3 Hz), 148.8, 145.0, 141.3, 135.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.4, 127.5, 127.3, 124.4, 121.0, 119.8, 119.4, 115.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 82.7, 82.1, 80.3, 73.7, 62,8. ^{19}F NMR (564 MHz, $CDCl_3$) δ -113.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}FNO_2$: 360.1400; found: 360.1393.



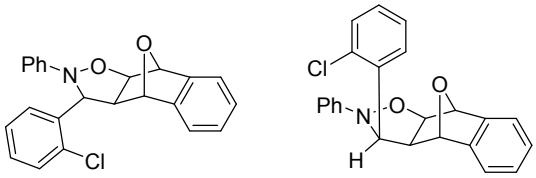
3ac

3-(4-Chlorophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ac**). Following the general procedure, **3ac** was obtained as a yellow solid (37.2 mg, 99%, 7:1 dr). m.p. 163.0–165.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.37–7.33 (m, 3H), 7.21–7.15 (m, 5H), 7.05–7.00 (m, 3H), 5.42 (s, 1H), 5.31 (s, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 2.93 (t, *J* = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.7, 144.9, 141.3, 137.9, 133.9, 129.2, 129.1, 128.5, 127.6, 127.3, 124.5, 121.1, 119.8, 119.4, 82.8, 82.1, 80.3, 73.6, 62.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_2$: 376.1104; found: 376.1097.



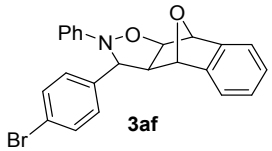
3ad

3-(3-Chlorophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ad**). Following the general procedure, **3ad** was obtained as a yellow solid (37.1 mg, 99%, 6:1 dr). m.p. 128.0–130.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37–7.33 (m, 2H), 7.32–7.29 (m, 2H), 7.22–7.17 (m, 5H), 7.05–7.00 (m, 3H), 5.42 (s, 1H), 5.34 (s, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.17 (d, *J* = 7.2 Hz, 1H), 2.95 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.8, 144.9, 141.8, 141.3, 134.9, 130.3, 128.5, 128.3, 127.7, 127.6, 127.3, 125.9, 124.3, 121.0, 119.8, 119.2, 82.8, 82.1, 80.4, 73.5, 63.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_2$: 376.1104; found: 376.1102.



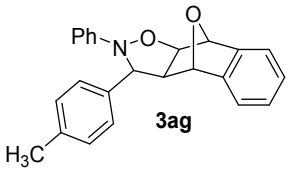
3ae **3ae'**

3-(2-Chlorophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ae** & **3ae'**). Following the general procedure, **3ae** and **3ae'** were obtained as a yellow solid (37.2 mg, 99%, 3:1 dr). m.p. 89.0–91.0 °C. **3ae**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.20–7.13 (m, 6H), 7.11–7.09 (m, 2H), 6.97–6.93 (m, 3H), 5.54 (s, 1H), 5.36 (s, 1H), 4.95 (d, *J* = 6.0 Hz, 1H), 4.60 (d, *J* = 6.6 Hz, 1H), 2.85 (t, *J* = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.3, 145.3, 141.5, 138.2, 132.6, 129.7, 128.8, 128.6, 127.6, 127.5, 127.2, 123.0, 120.9, 119.9, 117.2, 83.7, 82.3, 81.4, 68.7, 62.3. **3ae'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.32-7.22 (m, 6H), 7.08–7.05 (m, 2H), 6.92-6.86 (m, 3H), 5.35 (s, 1H), 5.19 (d, *J* = 9.0 Hz, 1H), 4.77 (d, *J* = 6.6 Hz, 1H), 4.60 (s, 1H), 3.26 (dd, *J* = 9.0, 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.8, 145.8, 142.5, 136.4, 132.0, 130.7, 128.9, 128.7, 127.5, 127.1, 126.9, 122.2, 120.7, 119.5, 115.0, 85.4, 81.8, 79.9, 68.4, 56.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_2$: 376.1104; found: 376.1103.



3af

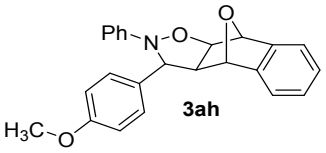
3-(4-Bromophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3af**). Following the general procedure, **3af** was obtained as a white solid (41.6 mg, 99%, 6:1 dr). m.p. 135.0–136.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.37–7.32 (m, 3H), 7.22–7.15 (m, 5H), 7.06–6.99 (m, 3H), 5.42 (s, 1H), 5.31 (s, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 2.93 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.7, 144.9, 141.3, 138.5, 132.2, 129.4, 128.5, 127.6, 127.3, 124.4, 122.0, 121.0, 119.8, 119.3, 82.8, 82.1, 80.3, 73.6, 62,9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}BrNO_2$: 420.0599; found: 420.0595.



3ag

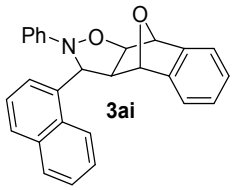
2-Phenyl-3-(p-tolyl)-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ag**). Following the general procedure, **3ag** was obtained as a white solid (35.2 mg, 99%, 6:1 dr). m.p. 155.0–157.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.33 (m, 3H), 7.21–7.15 (m, 7H), 7.05–6.98 (m, 3H), 5.42 (s, 1H), 5.32 (s, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.13 (d, *J* = 7.8 Hz, 1H), 2.99 (t, *J* = 7.2 Hz, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR

(150 MHz, $CDCl_3$) δ 149.0, 145.1, 141.4, 138.0, 136.2, 129.7, 128.4, 127.8, 127.5, 127.2, 124.2, 121.0, 119.8, 119.3, 82.7, 82.1, 80.4, 74.2, 62,8, 21.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO_2$: 356.1651; found: 356.1645.



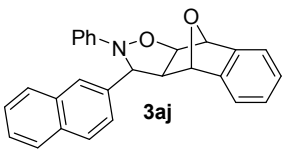
3ah

3-(4-Methoxyphenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ah**). Following the general procedure, **3ah** was obtained as a colorless oil (36.7 mg, 99%, 5:1 dr). ^1H NMR (600 MHz, $CDCl_3$) δ 7.38–7.34 (m, 3H), 7.20–7.15 (m, 5H), 7.02 (d, *J* = 7.8 Hz, 3H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 1H), 5.31 (s, 1H), 4.66 (d, *J* = 6.6 Hz, 1H), 4.10 (d, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 2.98 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 159.5, 149.0, 145.1, 141.4, 131.0, 129.1, 128.3, 127.5, 127.1, 124.2, 121.0, 119.8, 119.4, 114.3, 82.6, 82.1, 80.2, 74.1, 62.6, 55.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO_3$: 372.1600; found: 372.1593.



3ai

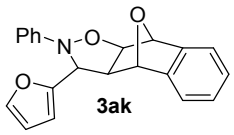
3-(Naphthalen-1-yl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ai**). Following the general procedure, **3ai** was obtained as a white solid (38.8 mg, 99%, 3:1 dr). m.p. 96.0–97.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.60–7.53 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.14–7.08 (m, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 5.50 (s, 1H), 5.41 (s, 1H), 4.91 (d, *J* = 7.2 Hz, 1H), 4.81 (d, *J* = 6.6 Hz, 1H), 3.20 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.3, 145.1, 141.4, 135.0, 134.2, 130.9, 129.1, 128.7, 128.4, 127.5, 127.2, 126.51, 126.47, 125.9, 125.8, 124.0, 123.7, 121.0, 119.9, 118.5, 83.1, 82.2, 80.9, 72.1, 62.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{22}NO_2$: 392.1651; found: 392.1646.



3aj

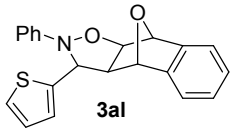
3-(Naphthalen-2-yl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3aj**). Following the general procedure, **3aj** was obtained as a yellow solid (38.7 mg, 99%, 6:1 dr). m.p. 164.0–166.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ

7.88 (d, *J* = 8.4 Hz, 1H), 7.87–7.84 (m, 2H), 7.84–7.80 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53–7.49 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.21–7.17 (m, 1H), 7.16–7.11 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 5.46 (s, 1H), 5.38 (s, 1H), 4.72 (d, *J* = 6.6 Hz, 1H), 4.33 (d, *J* = 7.2 Hz, 1H), 3.06 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 149.1, 145.0, 141.4, 136.9, 133.4, 133.2, 129.1, 128.4, 127.84, 127.77, 127.5, 127.2, 127.0, 126.4, 126.2, 125.1, 124.1, 121.0, 119.8, 119.1, 82.8, 82.1, 80.4, 74.8, 63.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{22}NO_2$: 392.1651; found: 392.1645.



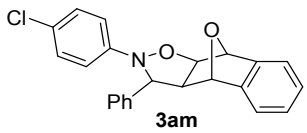
3ak

3-(Furan-2-yl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ak**). Following the general procedure, **3ak** was obtained as a yellow solid (32.5 mg, 98%, 6:1 dr). m.p. 115.0–117.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.37–7.24 (m, 1H), 7.25–7.19 (m, 5H), 7.09–7.05 (m, 1H), 7.03–7.00 (m, 2H), 6.36 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.25 (dd, *J* = 3.0, 0.6 Hz, 1H), 5.43 (s, 1H), 5.29 (s, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.26 (d, *J* = 7.8 Hz, 1H), 3.25 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 150.2, 148.7, 145.0, 143.0, 141.3, 128.4, 127.6, 127.3, 124.6, 121.0, 119.8, 119.2, 110.6, 109.7, 83.1, 82.1, 80.4, 68.3, 58.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}NO_3$: 332.1287; found: 332.1280.



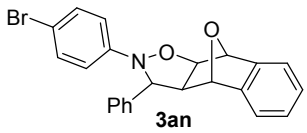
3al

2-Phenyl-3-(thiophen-2-yl)-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3al**). Following the general procedure, **3al** was obtained as a white solid (34.4 mg, 98%, 6:1 dr). m.p. 143.0–145.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.0 Hz, 1H), 7.32 (d, *J* = 5.4 Hz, 1H), 7.25–7.15 (m, 5H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.02 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.42 (s, 1H), 5.35 (s, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.48 (d, *J* = 7.2 Hz, 1H), 3.05 (t, *J* = 6.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 148.6, 144.9, 141.9, 141.3, 128.4, 127.6, 127.3, 126.8, 126.2, 126.1, 124.9, 121.1, 119.92, 119.88, 82.7, 82.1, 80.4, 70.3, 63.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{18}NO_2S$: 348.1058; found: 348.1055.



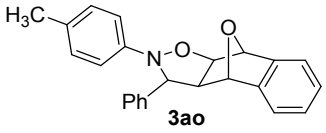
3am

2-(4-Chlorophenyl)-3-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3am**). Following the general procedure, **3am** was obtained as a yellow solid (37.2 mg, 99%, 7:1 dr). m.p. 157.0–159.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.36–7.33 (m, 2H), 7.21–7.16 (m, 3H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.42 (s, 1H), 5.33 (s, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 4.11 (d, *J* = 7.2 Hz, 1H), 3.00 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.7, 144.9, 141.3, 139.0, 129.1, 128.4, 128.3, 127.9, 127.6, 127.2, 121.0, 120.4, 119.8, 118.0, 82.9, 82.1, 80.4, 74.6, 62.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_2$: 376.1104; found: 376.1103.



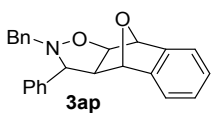
3an

2-(4-Bromophenyl)-3-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3an**). Following the general procedure, **3an** was obtained as a white solid (41.6 mg, 99%, 6:1 dr). m.p. 150.0–152.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.6 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.27–7.23 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.12–7.04 (m, 3H), 6.77 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 5.24 (s, 1H), 4.57 (d, *J* = 6.6 Hz, 1H), 4.02 (d, *J* = 7.2 Hz, 1H), 2.91 (t, *J* = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.2, 144.9, 141.2, 139.0, 131.3, 129.1, 128.3, 127.8, 127.6, 127.3, 121.0, 120.6, 119.8, 116.8, 82.9, 82.1, 80.4, 74.4, 62.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{19}BrNO_2$: 420.0599; found: 420.0591.



3ao

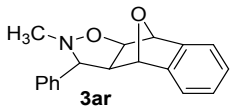
3-Phenyl-2-(p-tolyl)-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ao**). Following the general procedure, **3ao** was obtained as a white solid (35.1 mg, 99%, 6:1 dr). m.p. 174.0–176.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.6 Hz, 2H), 7.38–7.30 (m, 4H), 7.21–7.14 (m, 3H), 7.01–6.92 (m, 4H), 5.42 (s, 1H), 5.33 (s, 1H), 4.65 (d, *J* = 6.6 Hz, 1H), 4.12 (d, *J* = 7.2 Hz, 1H), 2.99 (t, *J* = 7.2 Hz, 1H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 146.4, 145.1, 141.5, 139.2, 134.2, 129.0, 128.9, 128.1, 128.0, 127.4, 127.1, 121.0, 119.9, 119.8, 82.7, 82.0, 80.3, 74.6, 62.8, 20.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO_2$: 356.1651; found: 356.1650.



3ap

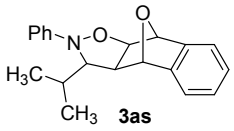
2-Benzyl-3-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ap**). Following the general procedure, **3ap** was obtained as a colourless oil (32.7 mg, 92%,

6:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.27–7.23 (m, 2H), 7.17–7.13 (m, 3H), 5.30 (s, 1H), 5.29 (s, 1H), 4.46 (d, *J* = 6.6 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.81 (d, *J* = 14.4 Hz, 1H), 3.71 (d, *J* = 7.8 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.1, 141.5, 138.4, 137.8, 128.9, 128.7, 128.5, 128.3, 128.22, 128.19, 128.1, 127.4, 127.12, 127.07, 120.9, 119.7, 83.1, 81.8, 80.0, 74.7, 61.5, 59.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}NO_2$: 356.1651; found: 356.1647.



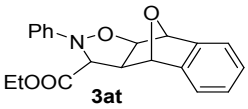
3ar

2-Methyl-3-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3ar**). Following the general procedure, **3ar** was obtained as a colourless oil (24.0 mg, 86%, >20:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.37 (m, 4H), 7.36–7.30 (m, 2H), 7.19–7.13 (m, 3H), 5.29 (s, 1H), 5.24 (s, 1H), 4.47 (d, *J* = 6.4 Hz, 1H), 3.43 (d, *J* = 8.4 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 1H), 2.60 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.2, 141.5, 138.1, 128.9, 128.3, 128.2, 127.4, 127.1, 121.0, 119.7, 83.0, 81.7, 80.0, 76.7, 62.1, 42.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}NO_2$: 280.1338; found: 280.1331.



3as

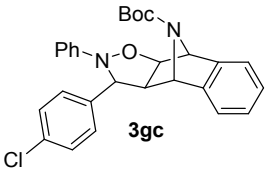
3-Isopropyl-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole (**3as**). Following the general procedure, **3as** was obtained as a colourless oil (28.2 mg, 96%, >20:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 7.25–7.22 (m, 1H), 7.19–7.15 (m, 4H), 7.03–6.98 (m, 1H), 5.37 (s, 1H), 5.12 (s, 1H), 4.45 (d, *J* = 6.4 Hz, 1H), 3.41 (t, *J* = 4.6 Hz, 1H), 2.77 (dd, *J* = 6.4, 4.4 Hz, 1H), 1.99–1.86 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3, 145.9, 142.1, 128.6, 127.4, 127.1, 122.7, 120.8, 119.5, 116.8, 84.5, 82.7, 82.4, 75.2, 54.3, 30.7, 19.5, 17.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{22}NO_2$: 308.1651; found: 308.1643.



3at

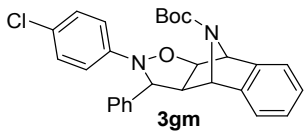
Ethyl-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epoxynaphtho[2,3-d]isoxazole-3-carboxylate (**3at**). Following the general procedure, **3at** was obtained as a yellow oil (25.6 mg, 76%, >20:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.26 (m, 4H), 7.22–7.18 (m, 2H), 7.17–7.14 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 5.38 (s, 2H), 4.63 (d, *J* =

6.6 Hz, 1H), 4.31–4.21 (m, 2H), 4.10 (d, *J* = 6.0 Hz, 1H), 3.22 (t, *J* = 6.0 Hz, 1H), 1.27 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 170.2, 149.1, 144.7, 141.3, 128.7, 127.7, 127.5, 123.7, 121.0, 119.3, 117.4, 83.6, 82.5, 81.2, 70.4, 61.8, 57.6, 14.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}NO_4$: 338.1392; found: 338.1386.



3gc

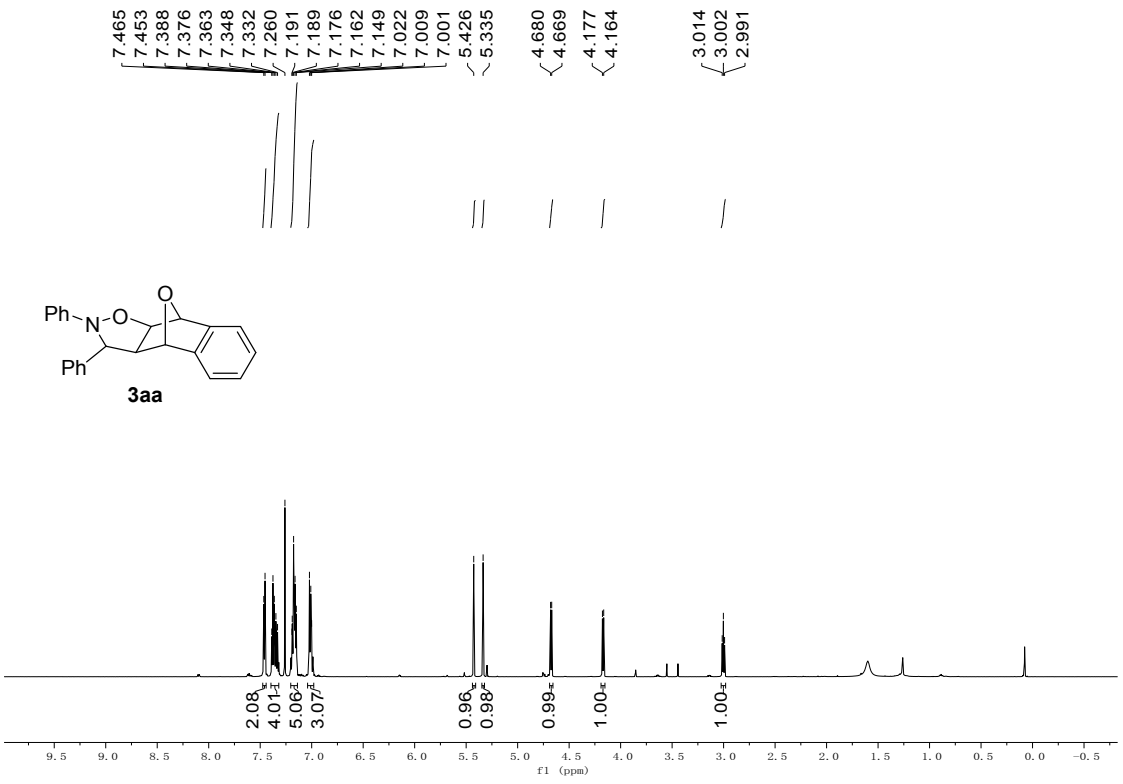
tert-Butyl-3-(4-chlorophenyl)-2-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epiminonaphtho[2,3-d]isoxazole-10-carboxylate (**3gc**). Following the general procedure, **3gc** was obtained as a white solid (46.9 mg, 99%, 7:1 dr). m.p. 177.0–179.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.44–7.30 (m, 5H), 7.22–7.11 (m, 5H), 7.04–7.00 (m, 3H), 5.41–5.02 (m, 2H), 4.58 (d, *J* = 6.6 Hz, 1H), 4.34–3.99 (m, 1H), 2.82 (s, 1H), 1.37 (s, 3H), 1.31 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 154.9, 148.6, 145.2, 145.1, 140.9, 138.1, 133.8, 129.2, 129.0, 128.4, 127.3, 127.0, 124.1, 121.4, 120.5, 119.1, 82.9, 80.5, 71.9, 64.6, 63.4, 61.7, 28.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{28}ClN_2O_3$: 475.1788; found: 475.1781.

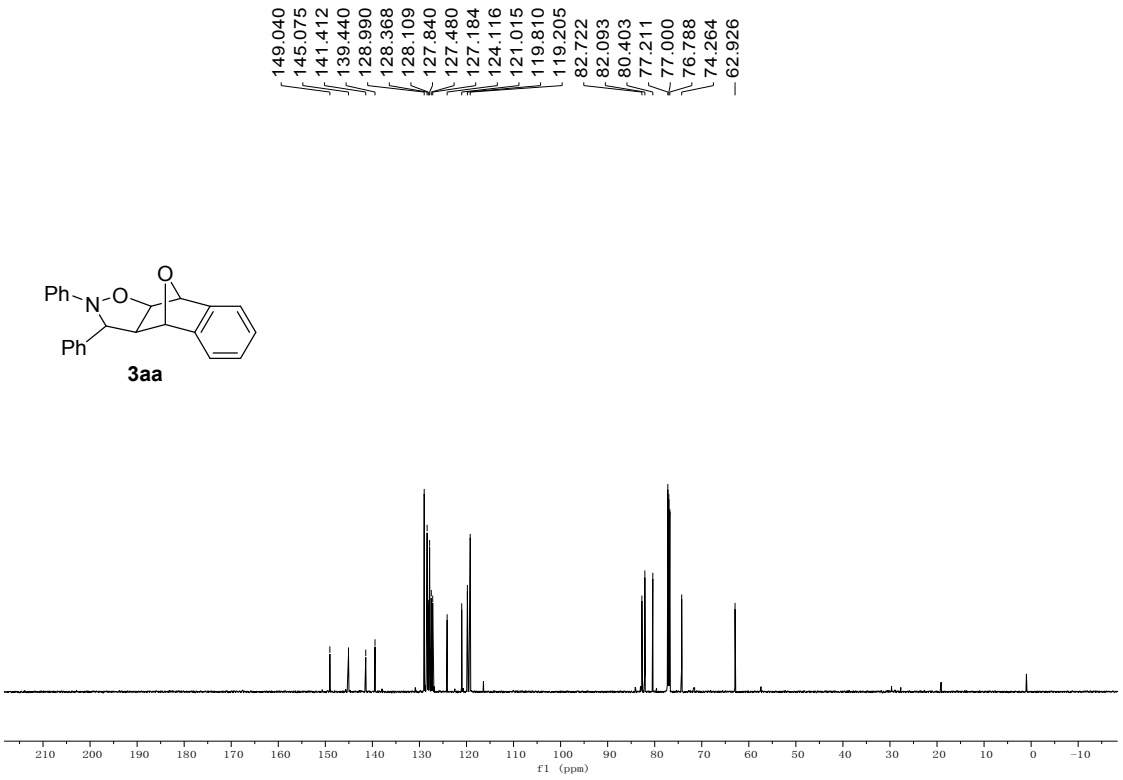


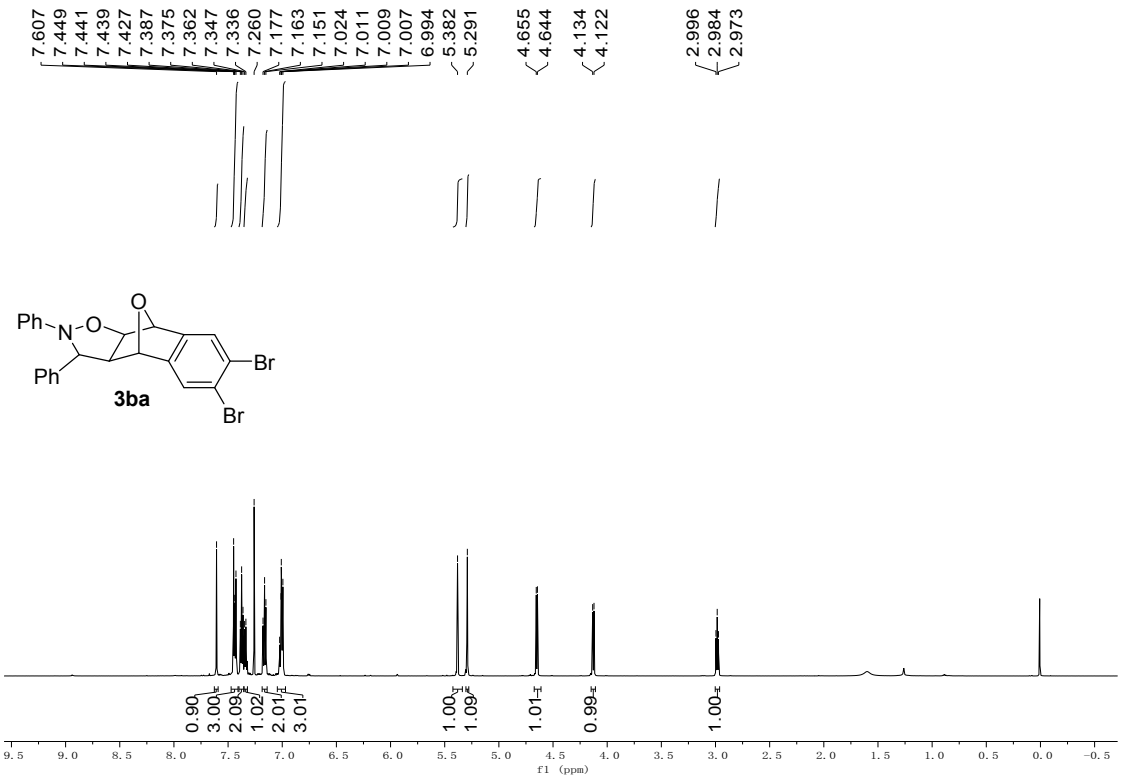
3gm

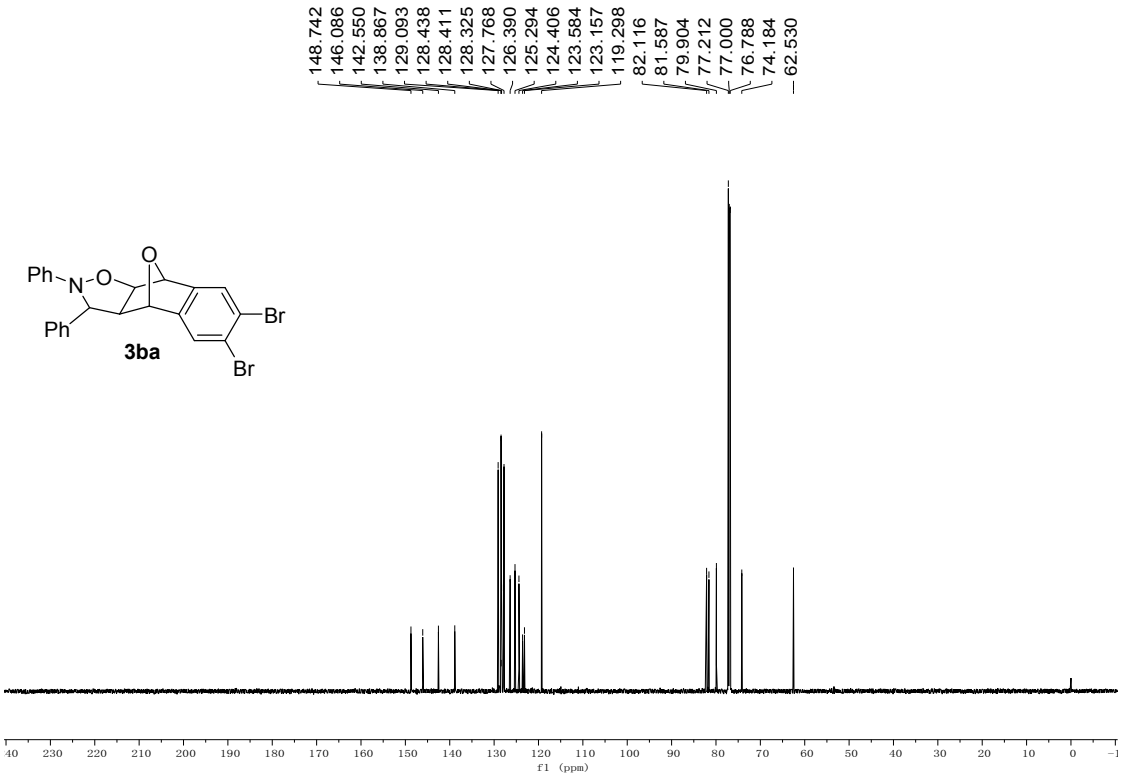
tert-Butyl-2-(4-chlorophenyl)-3-phenyl-2,3,3a,4,9,9a-hexahydro-4,9-epiminonaphtho[2,3-d]isoxazole-10-carboxylate (*3gm*). Following the general procedure, **3gm** was obtained as a yellow solid (47.0 mg, 99%, 7:1 dr). m.p. 194.0–196.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.49–7.30 (m, 6H), 7.22–7.12 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.42–5.06 (m, 2H), 4.59 (d, *J* = 6.6 Hz, 1H), 4.37–3.90 (m, 1H), 2.90 (s, 1H), 1.38 (s, 3H), 1.33 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 154.8, 147.7, 145.2, 140.9, 139.3, 129.0, 128.3, 128.1, 127.6, 127.3, 126.9, 121.4, 120.5, 120.4, 119.9, 83.1, 80.5, 72.7, 64.6, 63.4, 61.8, 28.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{28}ClN_2O_3$: 475.1788; found: 475.1790.

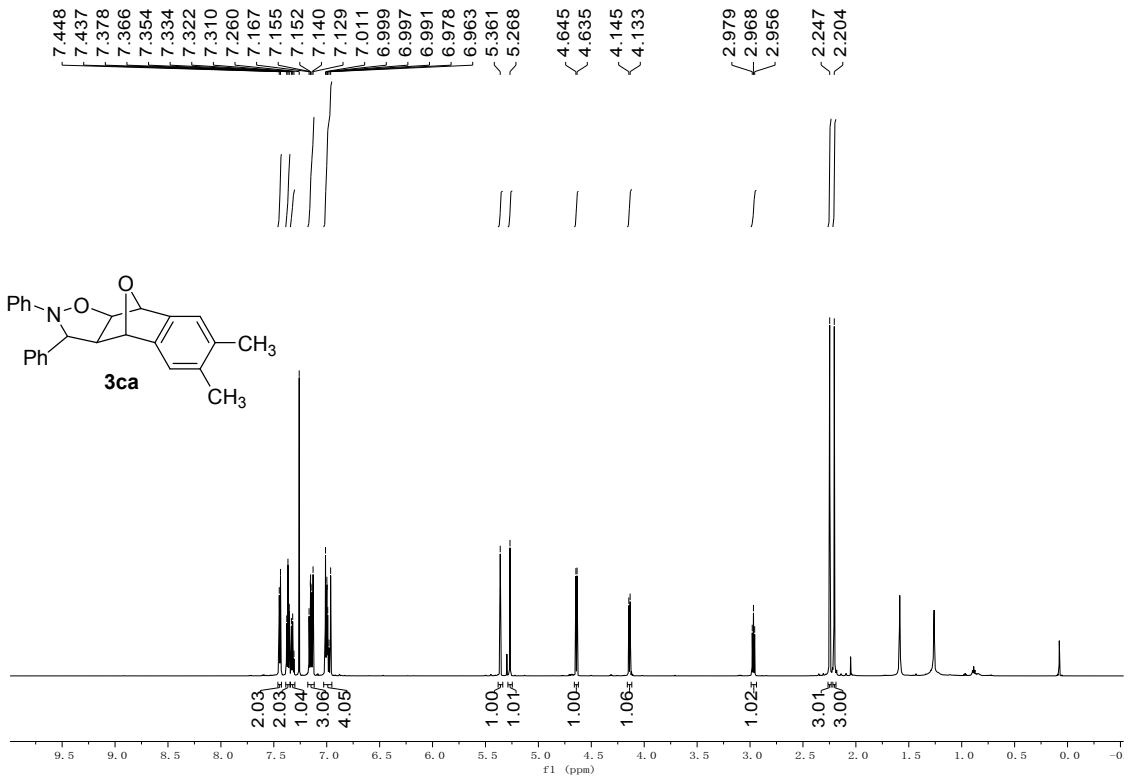
3. Copies of ^{1}H and ^{13}C NMR spectra of **3aa**–**3gh** and ^{19}F NMR spectra for **3ab**

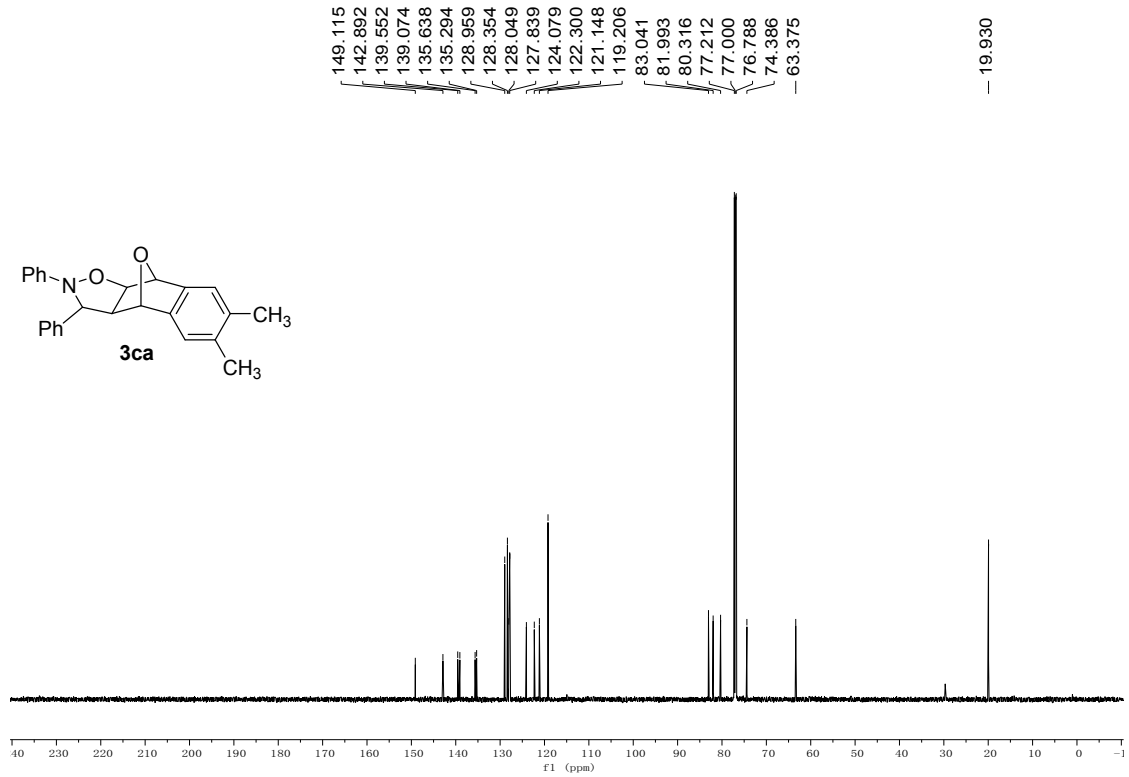


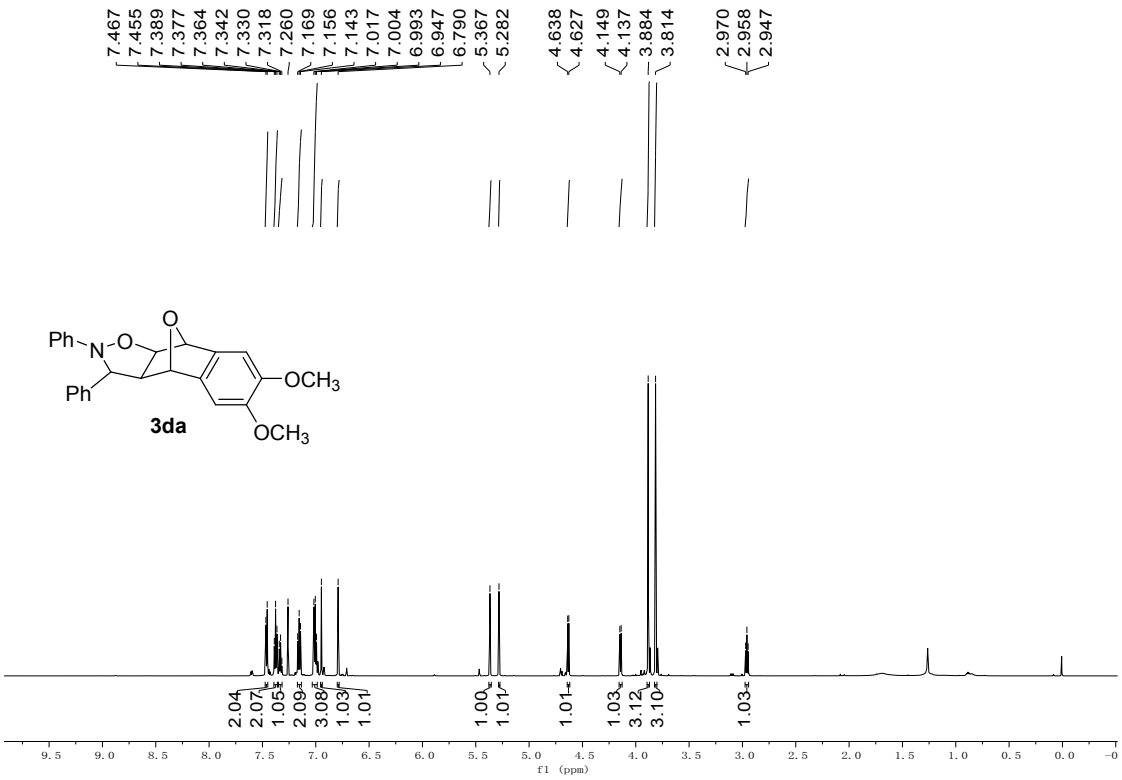


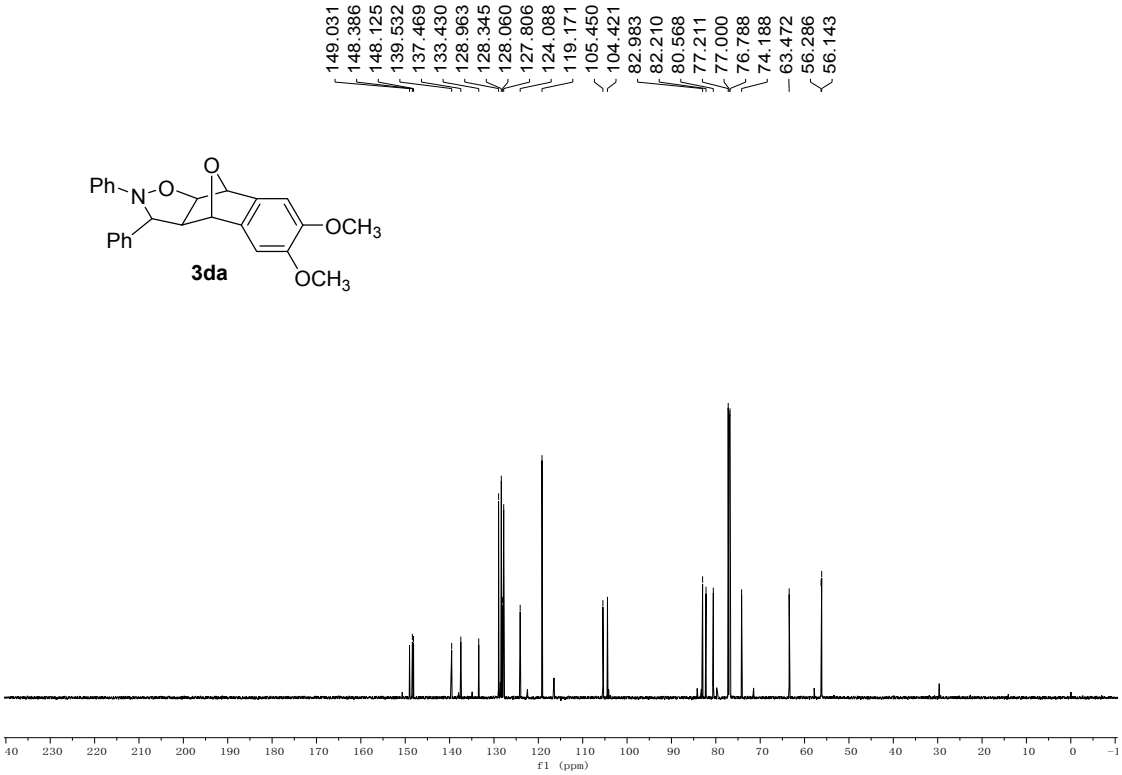

7.607
7.449
7.441
7.439
7.427
7.387
7.375
7.362
7.347
7.336
7.260
7.177
7.163
7.151
7.024
7.011
7.009
7.007
6.994
5.382
5.291
4.655
4.644
4.134
4.122
2.996
2.984
2.973
Ph
N
O
O
Ph
Br
Br
3ba
0.90
3.00
2.09
1.02
2.01
3.01
1.00
1.09
1.01
0.99
1.00
f1 (ppm)

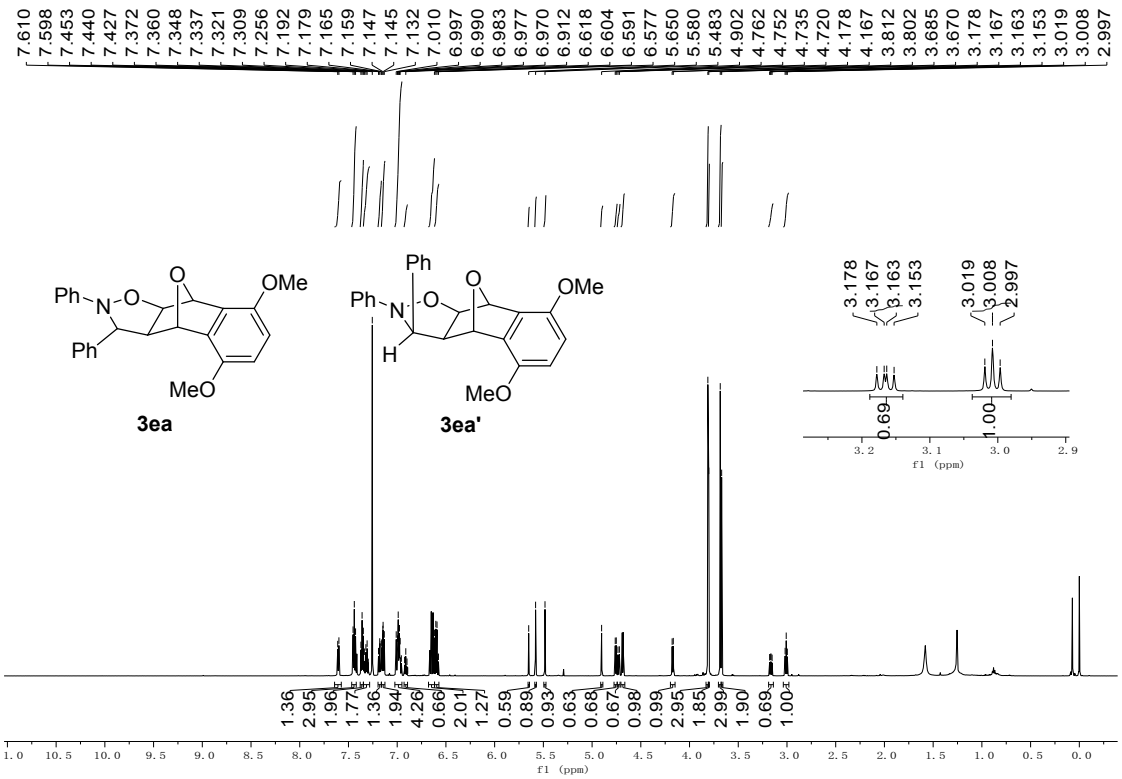

148.742
146.086
142.550
138.867
129.093
128.438
128.411
128.325
127.768
126.390
125.294
124.406
123.584
123.157
119.298
82.116
81.587
79.904
77.212
77.000
76.788
74.184
62.530
Ph
N
O
O
Ph
Br
Br
3ba
f1 (ppm)

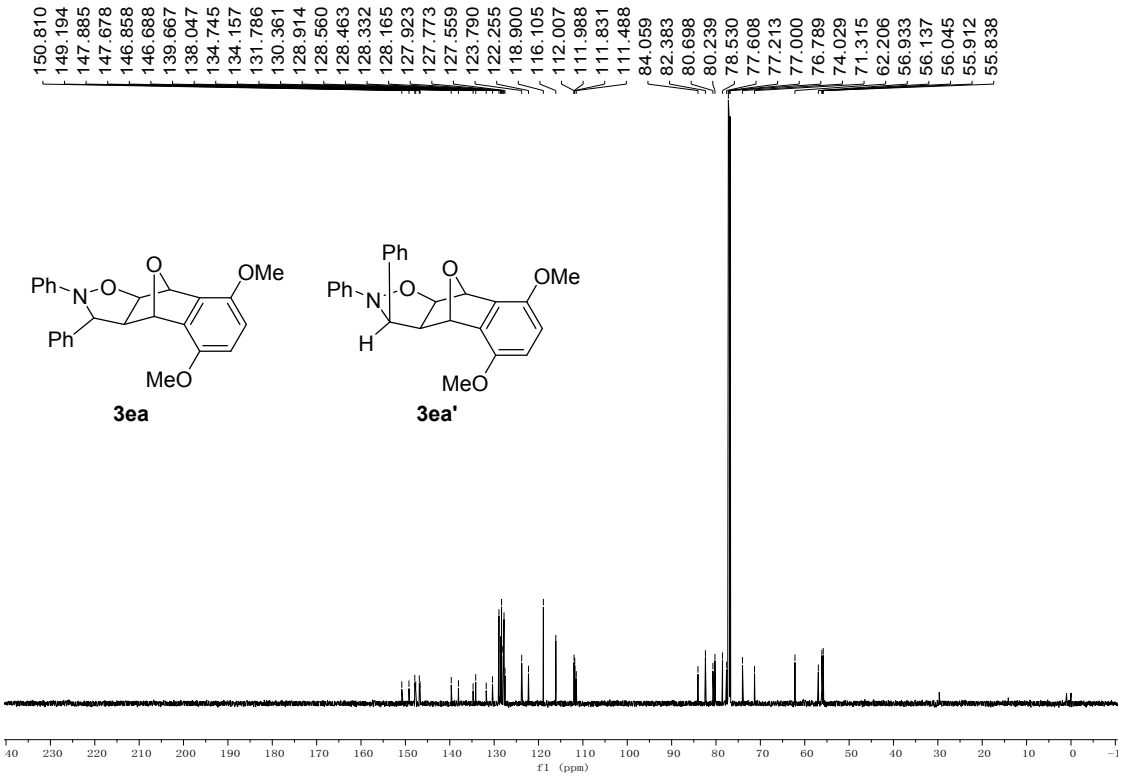

7.448
7.437
7.378
7.366
7.354
7.334
7.322
7.310
7.260
7.167
7.155
7.152
7.140
7.129
7.011
6.999
6.997
6.991
6.978
6.963
5.361
5.268
4.645
4.635
4.145
4.133
2.979
2.968
2.956
2.247
2.204
Ph
N
O
O
Ph
CH3
CH3
3ca
2.03
2.03
1.04
3.06
4.05
1.00
1.01
1.00
1.06
1.02
3.01
3.00
f1 (ppm)

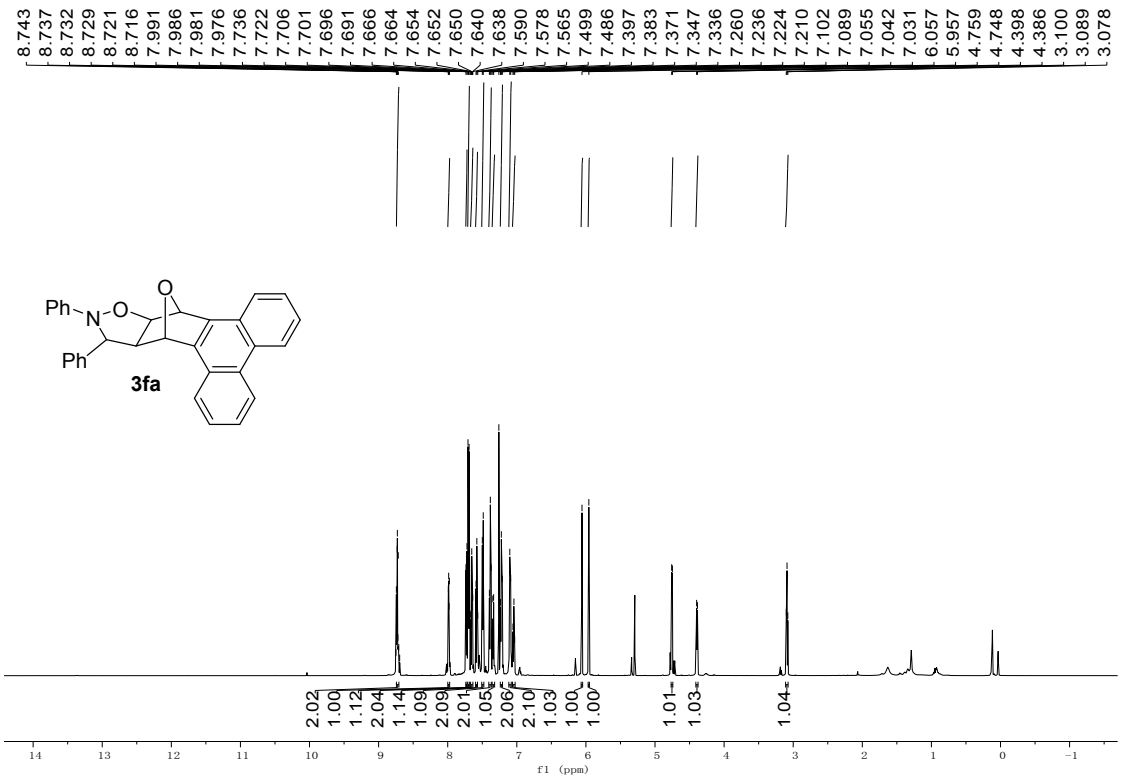

149.115
142.892
139.552
139.074
135.638
135.294
128.959
128.354
128.049
127.839
124.079
122.300
121.148
119.206
83.041
81.993
80.316
77.212
77.000
76.788
74.386
63.375
19.930
Ph
N
O
O
Ph
CH3
CH3
3ca
f1 (ppm)

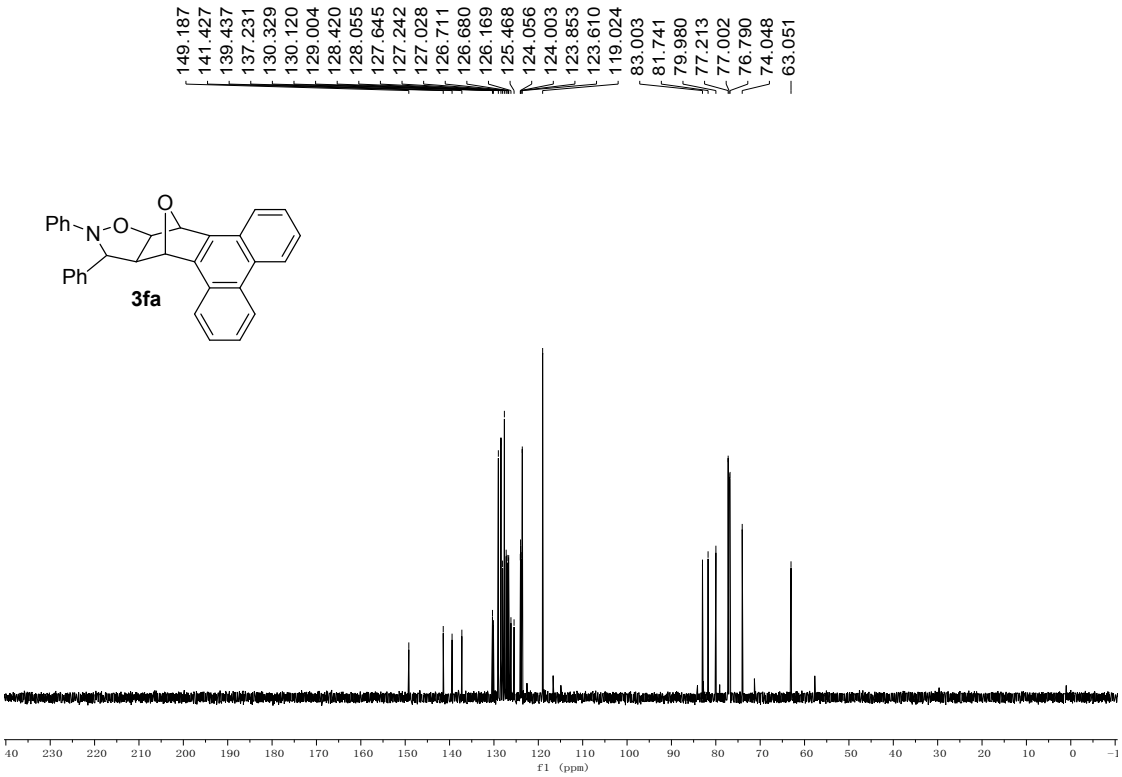

7.467
7.455
7.389
7.377
7.364
7.342
7.330
7.318
7.260
7.169
7.156
7.143
7.017
7.004
6.993
6.947
6.790
5.367
5.282
4.638
4.627
4.149
4.137
3.884
3.814
2.970
2.958
2.947
Ph
N
O
O
Ph
OCH3
OCH3
3da
2.04
2.07
1.05
2.09
3.08
1.03
1.01
1.00
1.01
1.01
1.03
3.12
3.10
1.03
f1 (ppm)

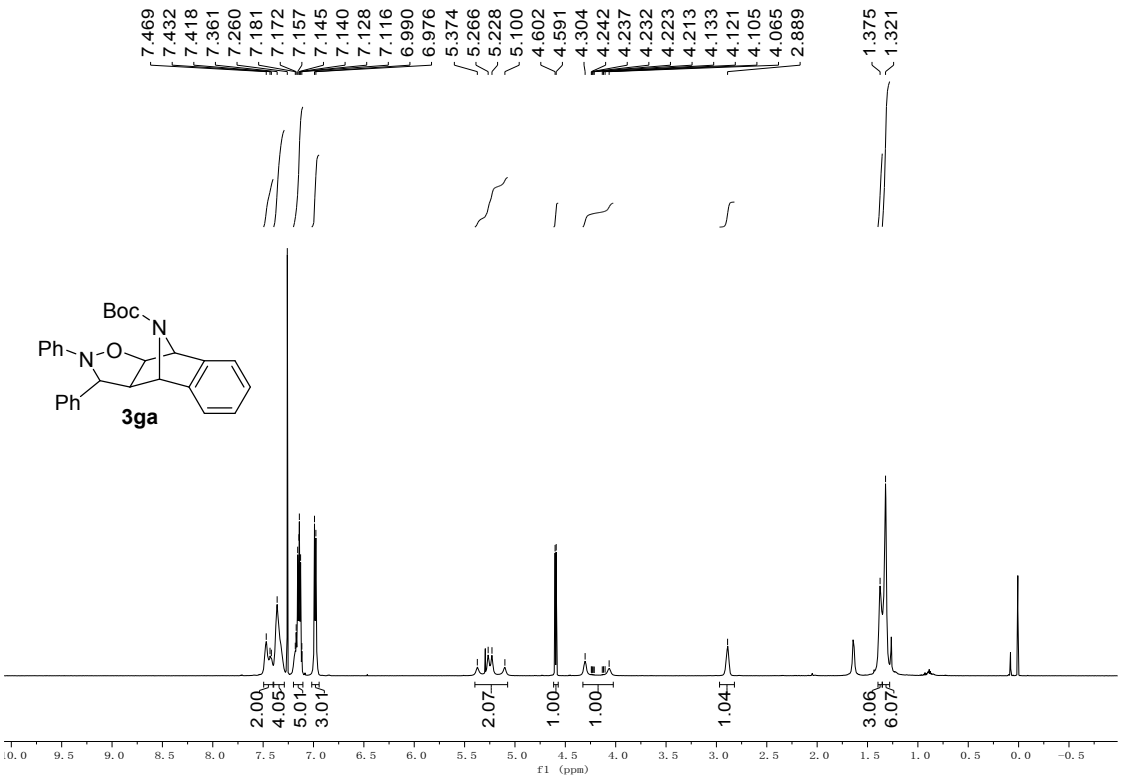

149.031
148.386
148.125
139.532
137.469
133.430
128.963
128.345
128.060
127.806
124.088
119.171
105.450
104.421
82.983
82.210
80.568
77.211
77.000
76.788
74.188
63.472
56.286
56.143
Ph
N
O
O
Ph
OCH3
OCH3
3da
f1 (ppm)

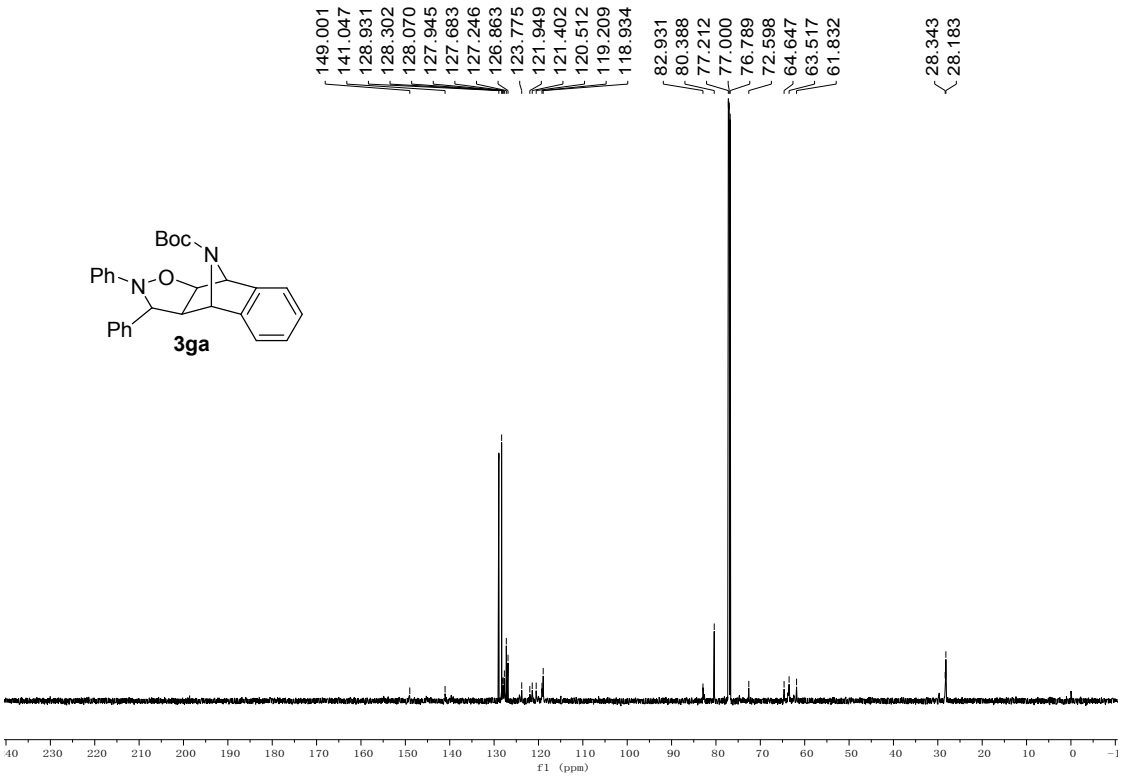

7.610 7.598 7.453 7.440 7.427 7.372 7.360 7.348 7.337 7.321 7.309 7.256 7.192 7.179 7.165 7.159 7.147 7.145 7.132 7.010 6.997 6.990 6.983 6.977 6.970 6.912 6.618 6.604 6.591 6.577 5.650 5.580 5.483 4.902 4.762 4.752 4.735 4.720 4.178 4.167 3.812 3.802 3.685 3.670 3.178 3.167 3.163 3.153 3.019 3.008 2.997
Ph
N
O
OMe
MeO
H
3ea
3ea'
0.69
1.00
f1 (ppm)
1.36 2.95 1.96 1.77 1.36 1.94 4.26 0.66 2.01 1.27 0.59 0.89 0.93 0.63 0.68 0.67 0.98 0.99 2.95 1.85 2.99 1.90 0.69 1.00

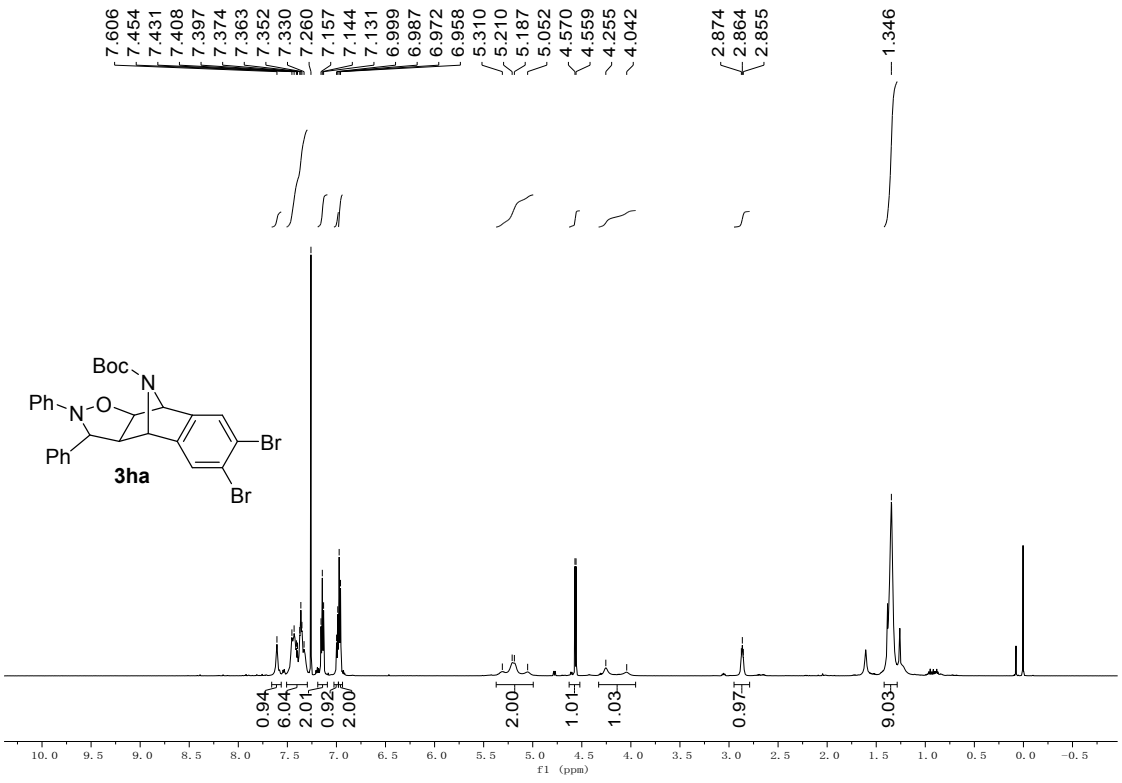

150.810 149.194 147.885 147.678 146.858 146.688 139.667 138.047 134.745 134.157 131.786 130.361 128.914 128.560 128.463 128.332 128.165 127.923 127.773 127.559 123.790 122.255 118.900 116.105 112.007 111.988 111.831 111.488 84.059 82.383 80.698 80.239 78.530 77.608 77.213 77.000 76.789 74.029 71.315 62.206 56.933 56.137 56.045 55.912 55.838
Ph
N
O
OMe
MeO
H
3ea
3ea'
f1 (ppm)

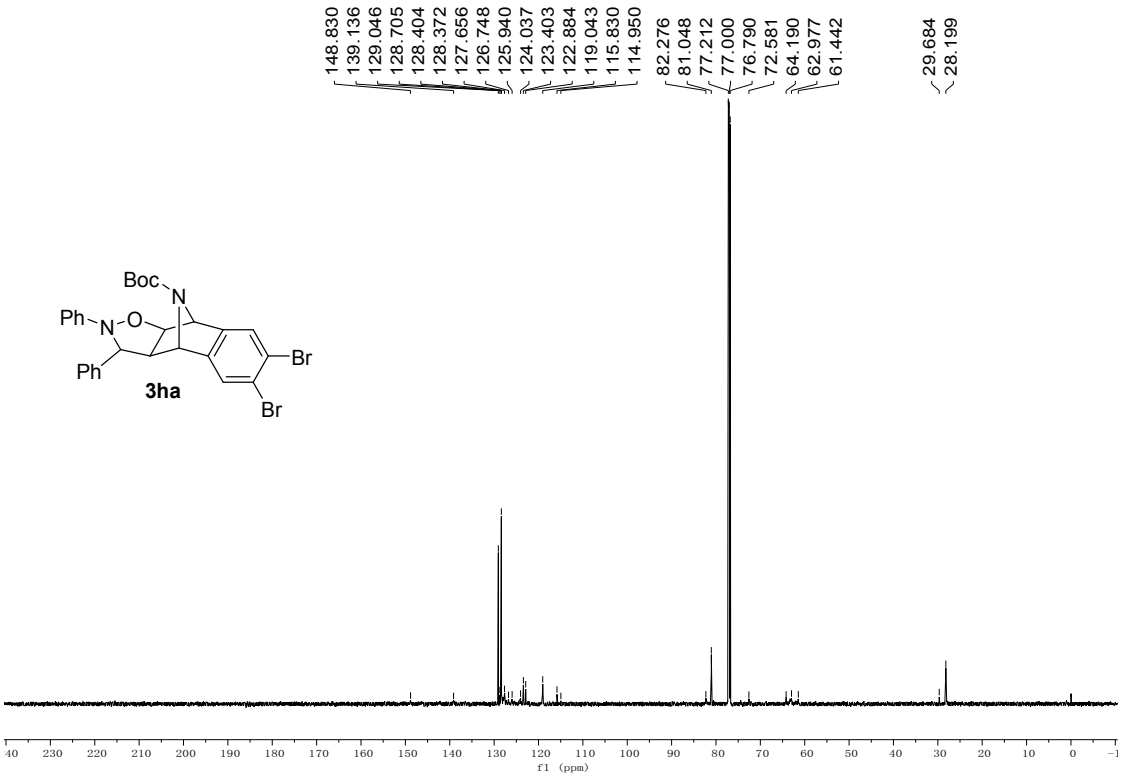

8.743
8.737
8.732
8.729
8.721
8.716
7.991
7.986
7.981
7.976
7.736
7.722
7.706
7.701
7.696
7.691
7.666
7.664
7.654
7.652
7.650
7.640
7.638
7.590
7.578
7.565
7.499
7.486
7.397
7.383
7.371
7.347
7.336
7.260
7.236
7.224
7.210
7.102
7.089
7.055
7.042
7.031
6.057
5.957
4.759
4.748
4.398
4.386
3.100
3.089
3.078
Ph
N
O
O
Ph
3fa
2.02
1.00
1.12
2.04
1.14
1.09
2.09
2.01
1.05
2.06
2.10
1.03
1.00
1.00
1.01
1.03
1.04
f1 (ppm)

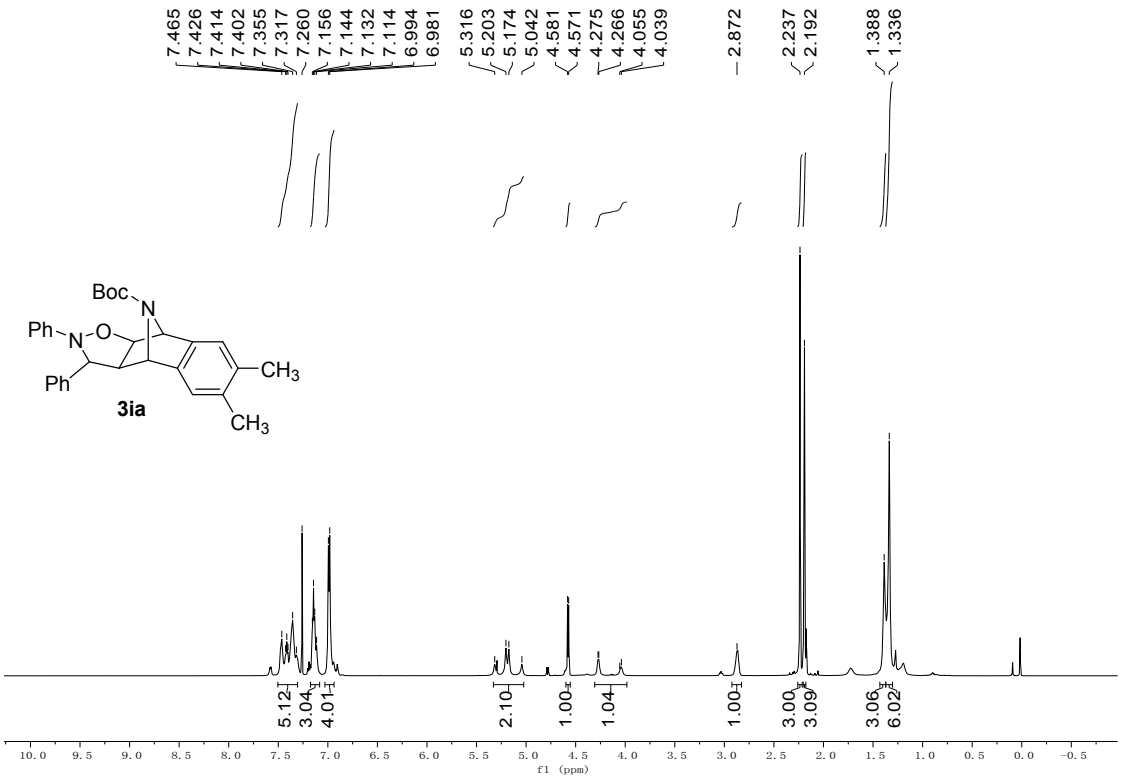

149.187
141.427
139.437
137.231
130.329
130.120
129.004
128.420
128.055
127.645
127.242
127.028
126.711
126.680
126.169
125.468
124.056
124.003
123.853
123.610
119.024
83.003
81.741
79.980
77.213
77.002
76.790
74.048
63.051
Ph
N
O
O
Ph
3fa
f1 (ppm)

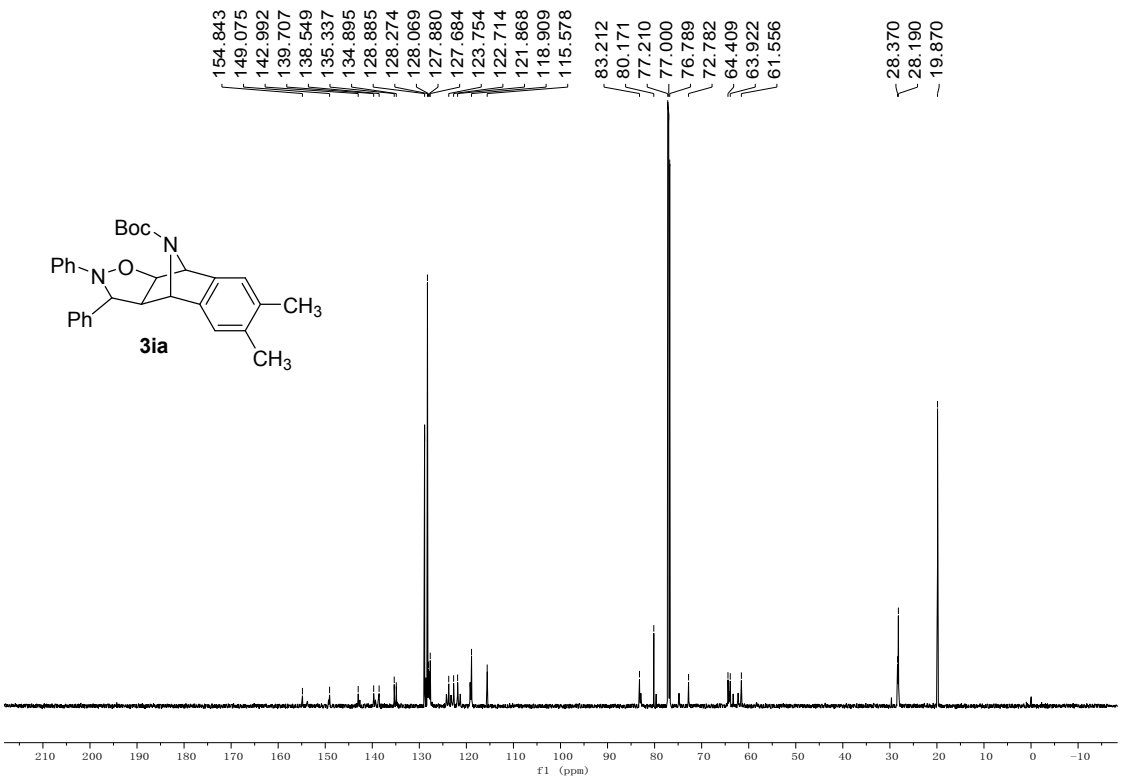

7.469
7.432
7.418
7.361
7.260
7.181
7.172
7.157
7.145
7.140
7.128
7.116
6.990
6.976
5.374
5.266
5.228
5.100
4.602
4.591
4.304
4.242
4.237
4.232
4.223
4.213
4.133
4.121
4.105
4.065
2.889
1.375
1.321
Boc
N
Ph
N
O
Ph
3ga
2.00
4.05
5.01
3.01
2.07
1.00
1.00
1.04
3.06
6.07
f1 (ppm)

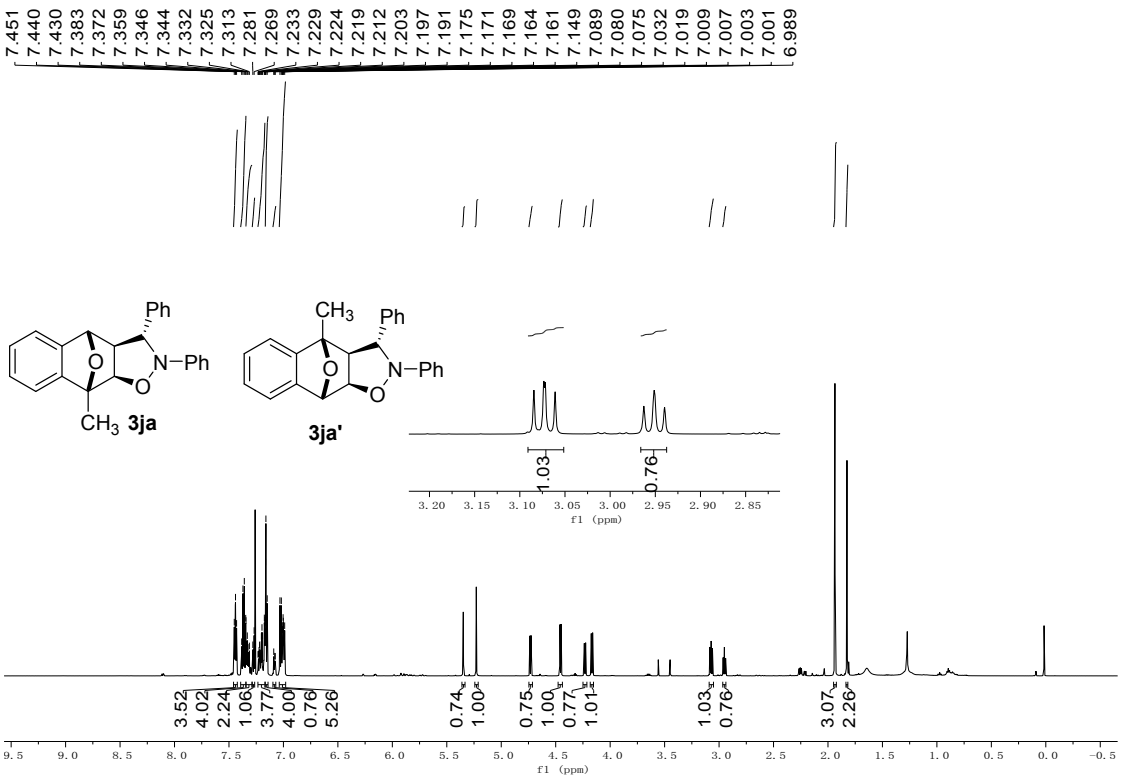

149.001
141.047
128.931
128.302
128.070
127.945
127.683
127.246
126.863
123.775
121.949
121.402
120.512
119.209
118.934
82.931
80.388
77.212
77.000
76.789
72.598
64.647
63.517
61.832
28.343
28.183
Boc
N
Ph
N
O
Ph
3ga
f1 (ppm)

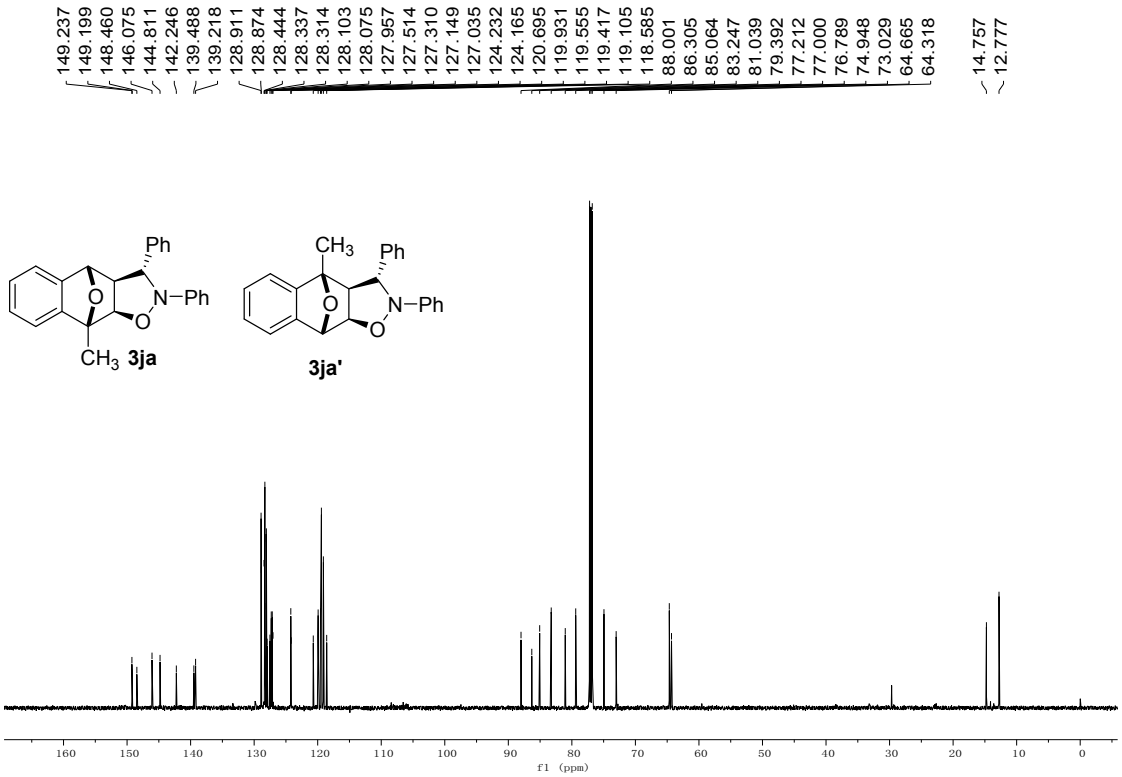

7.606
7.454
7.431
7.408
7.397
7.374
7.363
7.352
7.330
7.260
7.157
7.144
7.131
6.999
6.987
6.972
6.958
5.310
5.210
5.187
5.052
4.570
4.559
4.255
4.042
2.874
2.864
2.855
1.346
Boc
N
Ph
N
O
Ph
Br
Br
3ha
0.94
6.04
2.01
0.92
2.00
2.00
1.01
1.03
0.97
9.03
f1 (ppm)

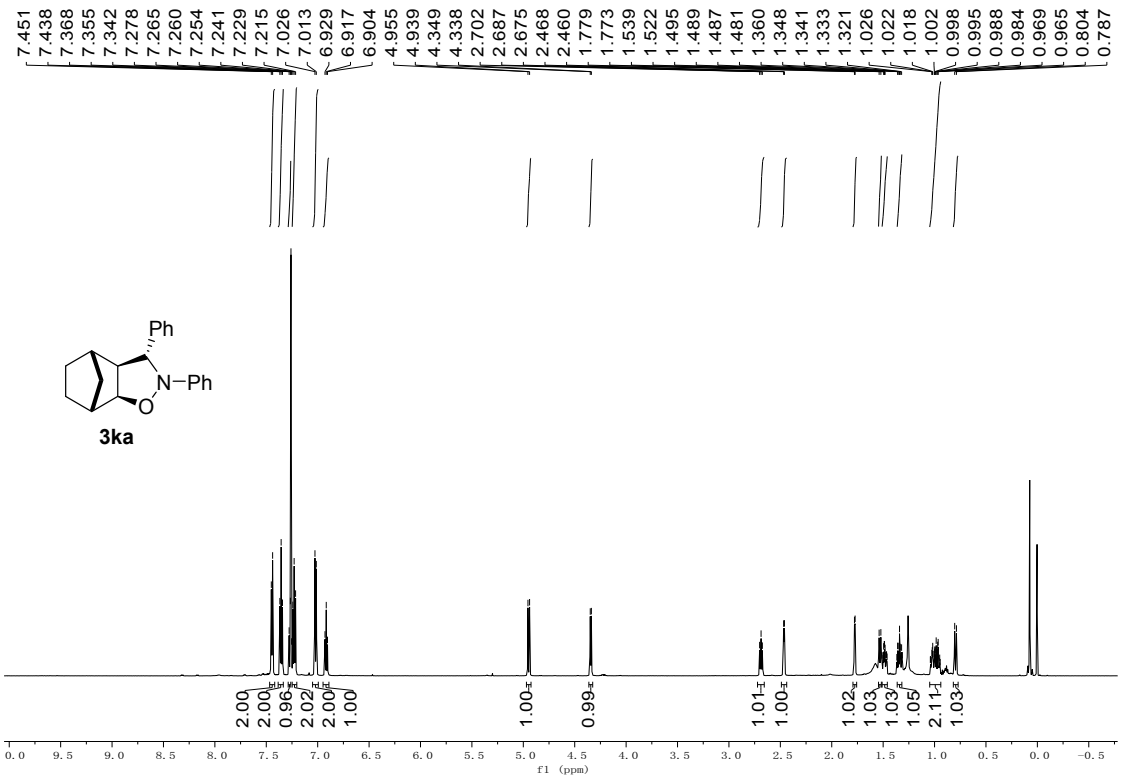

148.830
139.136
129.046
128.705
128.404
128.372
127.656
126.748
125.940
124.037
123.403
122.884
119.043
115.830
114.950
82.276
81.048
77.212
77.000
76.790
72.581
64.190
62.977
61.442
29.684
28.199
Boc
N
Ph
N
O
Ph
Br
Br
3ha
f1 (ppm)

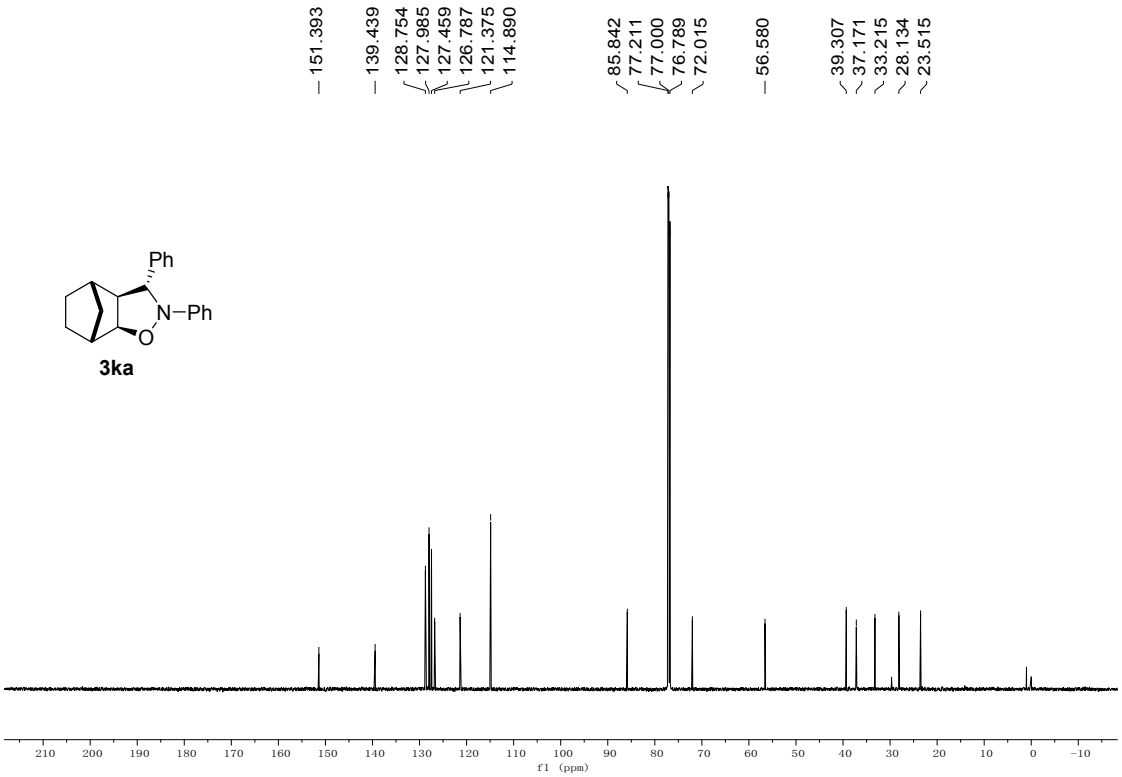

7.465
7.426
7.414
7.402
7.355
7.317
7.260
7.156
7.144
7.132
7.114
6.994
6.981
5.316
5.203
5.174
5.042
4.581
4.571
4.275
4.266
4.055
4.039
2.872
2.237
2.192
1.388
1.336
Boc
N
Ph
N
O
Ph
CH3
CH3
3ia
5.12
3.04
4.01
2.10
1.00
1.04
1.00
3.00
3.09
3.06
6.02
f1 (ppm)

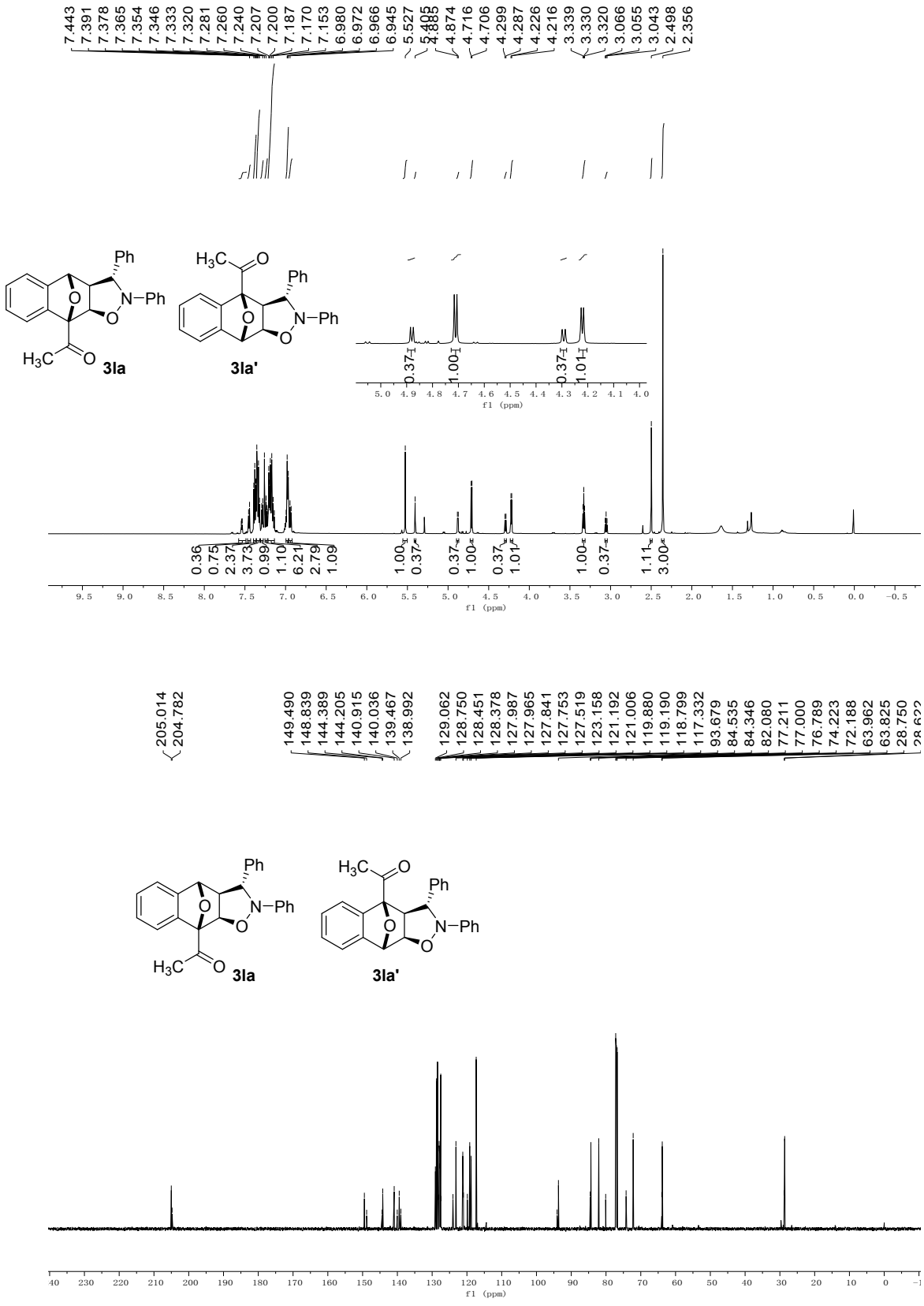

154.843
149.075
142.992
139.707
138.549
135.337
134.895
128.885
128.274
128.069
127.880
127.684
123.754
122.714
121.868
118.909
115.578
83.212
80.171
77.210
77.000
76.789
72.782
64.409
63.922
61.556
28.370
28.190
19.870
Boc
N
Ph
N
O
Ph
CH3
CH3
3ia
f1 (ppm)

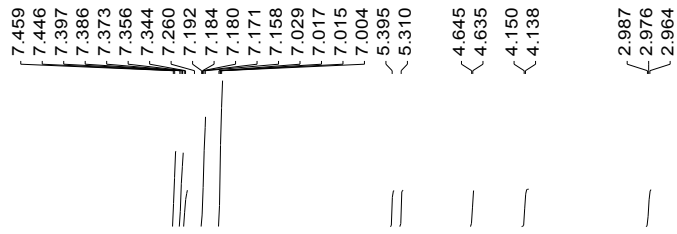

7.451
7.440
7.430
7.383
7.372
7.359
7.346
7.344
7.332
7.325
7.313
7.281
7.269
7.233
7.229
7.224
7.219
7.212
7.203
7.197
7.191
7.175
7.171
7.169
7.164
7.161
7.149
7.089
7.080
7.075
7.032
7.019
7.009
7.007
7.003
7.001
6.989
Ph
N−Ph
O
O
CH3 3ja
CH3
Ph
N−Ph
O
O
3ja'
1.03
0.76
3.20 3.15 3.10 3.05 3.00 2.95 2.90 2.85
f1 (ppm)
3.52
4.02
2.24
1.06
3.77
4.00
0.76
5.26
0.74
1.00
0.75
1.00
0.77
1.01
1.03
0.76
3.07
2.26
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
f1 (ppm)

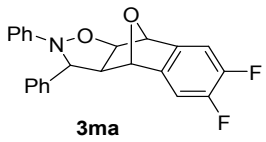

149.237
149.199
148.460
146.075
144.811
142.246
139.488
139.218
128.911
128.874
128.444
128.337
128.314
128.103
128.075
127.957
127.514
127.310
127.149
127.035
124.232
124.165
120.695
119.931
119.555
119.417
119.105
118.585
88.001
86.305
85.064
83.247
81.039
79.392
77.212
77.000
76.789
74.948
73.029
64.665
64.318
14.757
12.777
Ph
N−Ph
O
O
CH3 3ja
CH3
Ph
N−Ph
O
O
3ja'
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.451
7.438
7.368
7.355
7.342
7.278
7.265
7.260
7.254
7.241
7.229
7.215
7.026
7.013
6.929
6.917
6.904
4.955
4.939
4.349
4.338
2.702
2.687
2.675
2.468
2.460
1.779
1.773
1.539
1.522
1.495
1.489
1.487
1.481
1.360
1.348
1.341
1.333
1.321
1.026
1.022
1.018
1.002
0.998
0.995
0.988
0.984
0.969
0.965
0.804
0.787
Ph
N–Ph
O
3ka
2.00
2.00
0.96
2.02
2.00
1.00
1.00
0.99
1.01
1.00
1.02
1.03
1.03
1.05
2.11
1.03
f1 (ppm)

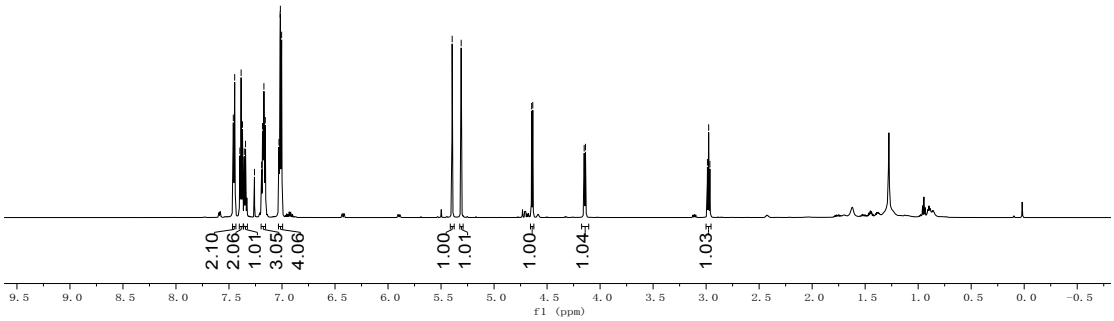

151.393
139.439
128.754
127.985
127.459
126.787
121.375
114.890
85.842
77.211
77.000
76.789
72.015
56.580
39.307
37.171
33.215
28.134
23.515
Ph
N–Ph
O
3ka
f1 (ppm)

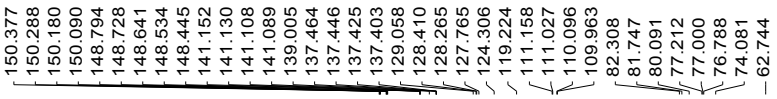

7.443
7.391
7.378
7.365
7.354
7.346
7.333
7.320
7.281
7.260
7.240
7.207
7.200
7.187
7.170
7.153
6.980
6.972
6.966
6.945
5.527
4.874
4.716
4.706
4.299
4.287
4.226
4.216
3.339
3.330
3.320
3.066
3.055
3.043
2.498
2.356
Ph
N−Ph
O
O
H3C
O
3la
H3C
O
Ph
N−Ph
O
O
3la'
0.37
1.00
0.37
1.01
f1 (ppm)
0.36
0.75
2.37
3.73
0.99
1.10
6.21
2.79
1.09
1.00
0.37
0.37
1.00
0.37
1.01
1.00
0.37
1.11
3.00
f1 (ppm)
205.014
204.782
149.490
148.839
144.389
144.205
140.915
140.036
139.467
138.992
129.062
128.750
128.451
128.378
127.987
127.965
127.841
127.753
127.519
123.158
121.192
121.006
119.880
119.190
118.799
117.332
93.679
84.535
84.346
82.080
77.211
77.000
76.789
74.223
72.188
63.962
63.825
28.750
Ph
N−Ph
O
O
H3C
O
3la
H3C
O
Ph
N−Ph
O
O
3la'
f1 (ppm)

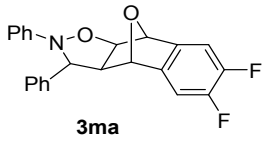

7.459
7.446
7.397
7.386
7.373
7.356
7.344
7.260
7.192
7.184
7.180
7.171
7.158
7.029
7.017
7.015
7.004
5.395
5.310
4.645
4.635
4.150
4.138
2.987
2.976
2.964


Ph
N
O
O
Ph
F
F

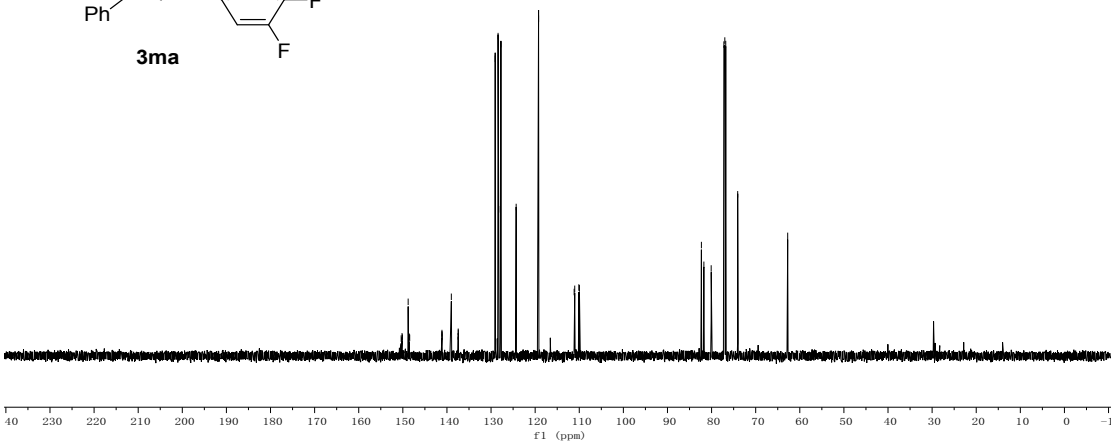
3ma

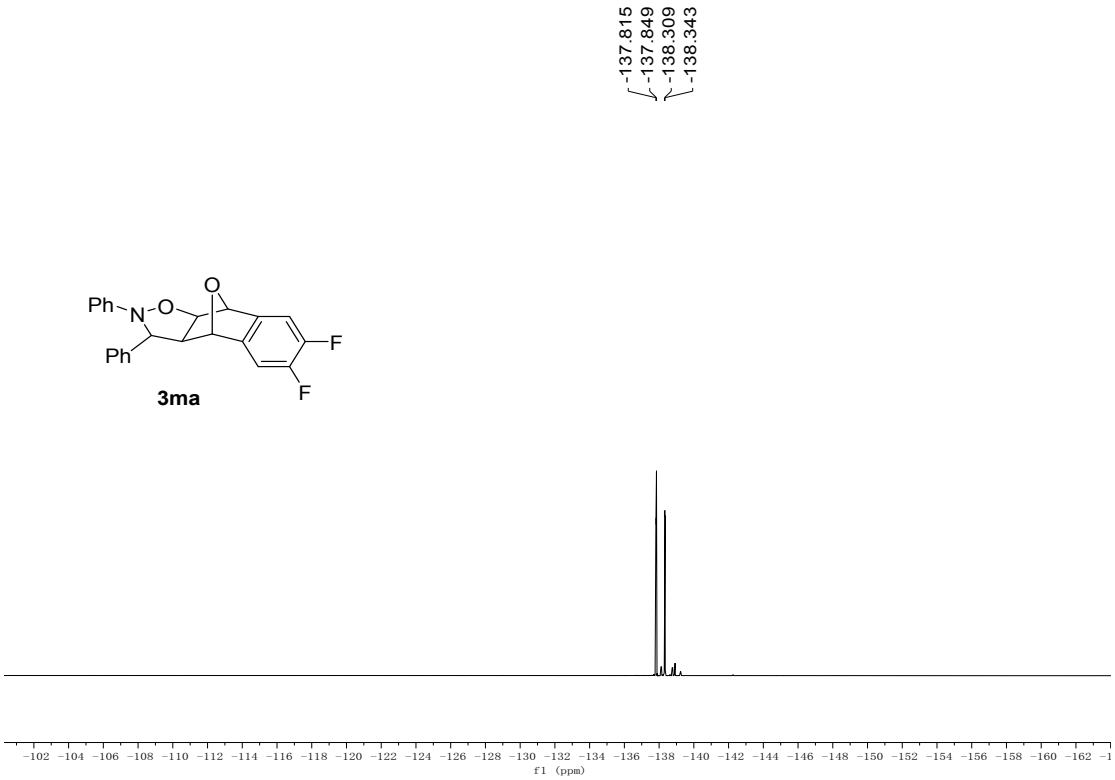

2.10
2.06
1.01
3.05
4.06
1.00
1.01
1.00
1.04
1.03
f1 (ppm)

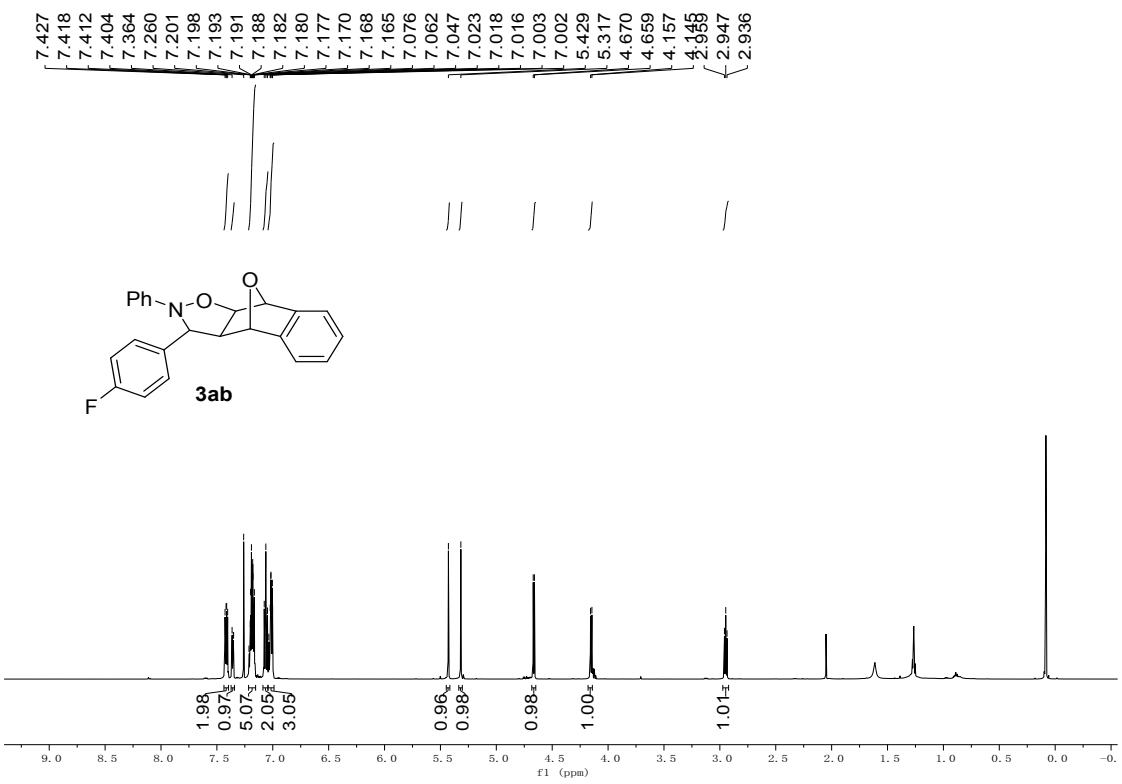

150.377
150.288
150.180
150.090
148.794
148.728
148.641
148.534
148.445
141.152
141.130
141.108
141.089
139.005
137.464
137.446
137.425
137.403
129.058
128.410
128.265
127.765
124.306
119.224
111.158
111.027
110.096
109.963
82.308
81.747
80.091
77.212
77.000
76.788
74.081
62.744

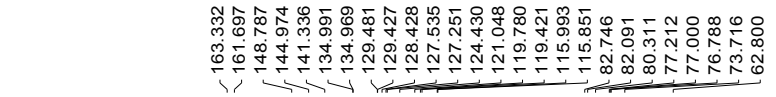

Ph
N
O
O
Ph
F
F

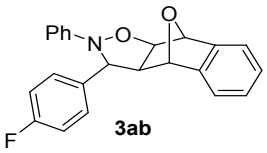
3ma


f1 (ppm)

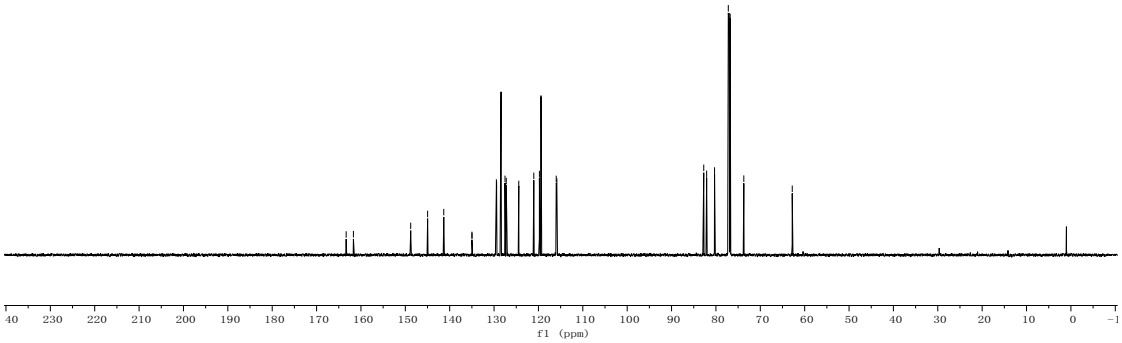

-137.815
-137.849
-138.309
-138.343
Ph
N
O
O
Ph
F
F
3ma
f1 (ppm)

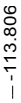

7.427
7.418
7.412
7.404
7.364
7.260
7.201
7.198
7.193
7.191
7.188
7.182
7.180
7.177
7.170
7.168
7.165
7.076
7.062
7.047
7.023
7.018
7.016
7.003
7.002
5.429
5.317
4.670
4.659
4.157
2.959
2.947
2.936
Ph
N
O
O
F
3ab
1.98
0.97
5.07
2.05
3.05
0.96
0.98
0.98
1.00
1.01
f1 (ppm)

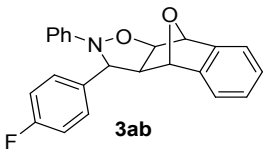

163.332
161.697
148.787
144.974
141.336
134.991
134.969
129.481
129.427
128.428
127.535
127.251
124.430
121.048
119.780
119.421
115.993
115.851
82.746
82.091
80.311
77.212
77.000
76.788
73.716
62.800


Ph
N
O
O
F

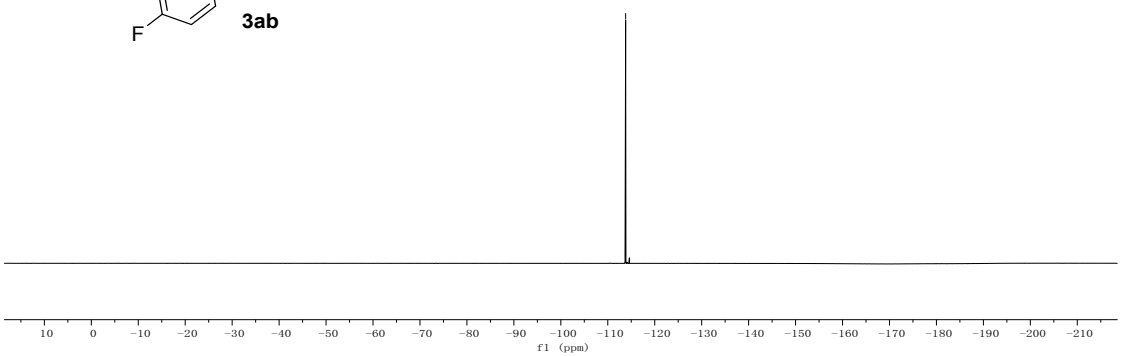
3ab

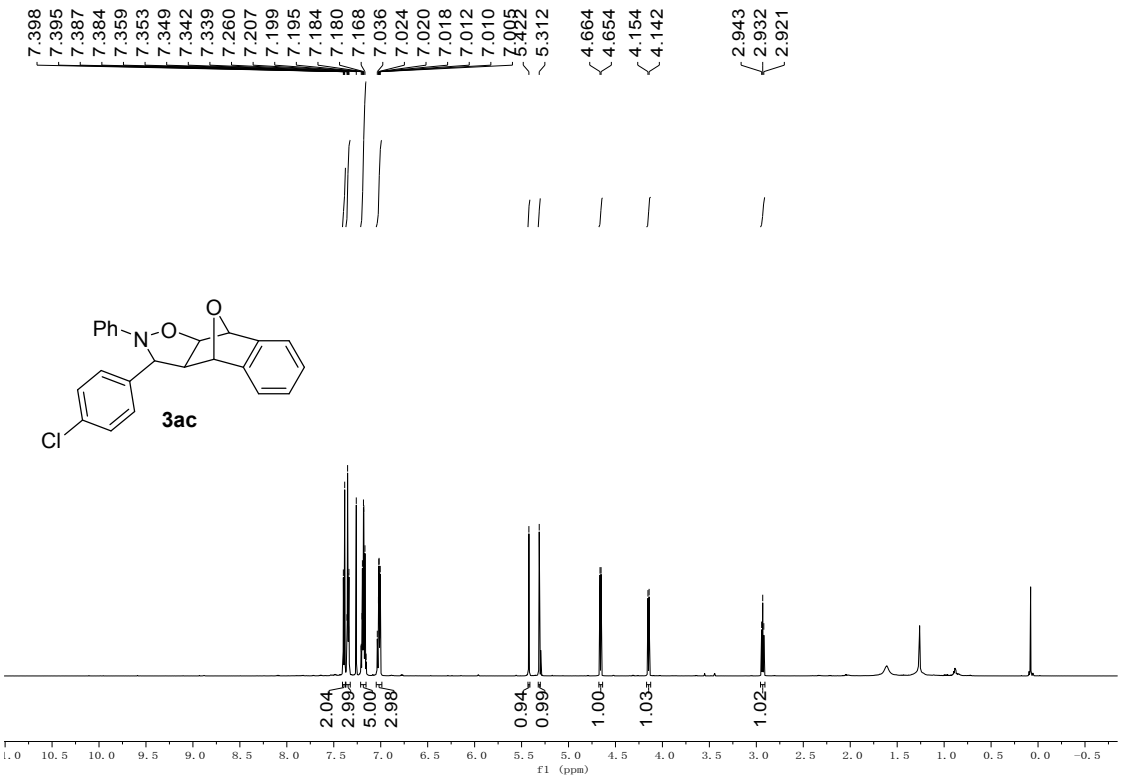

40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

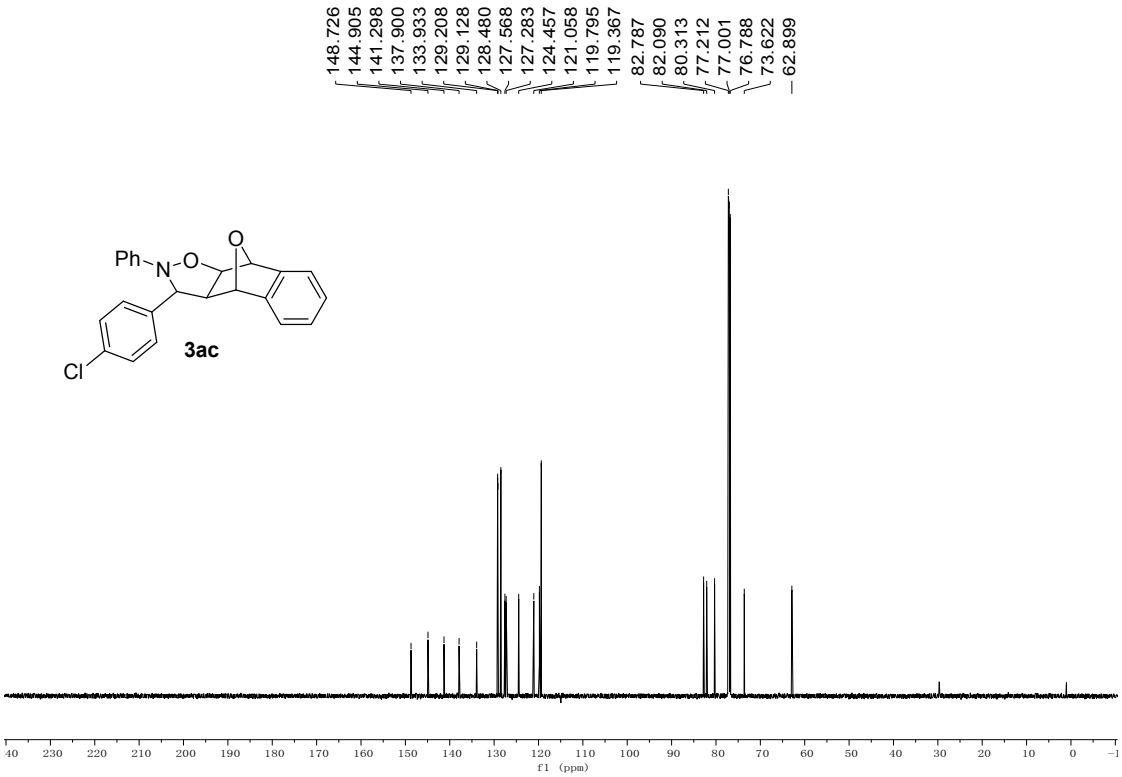

-113.806

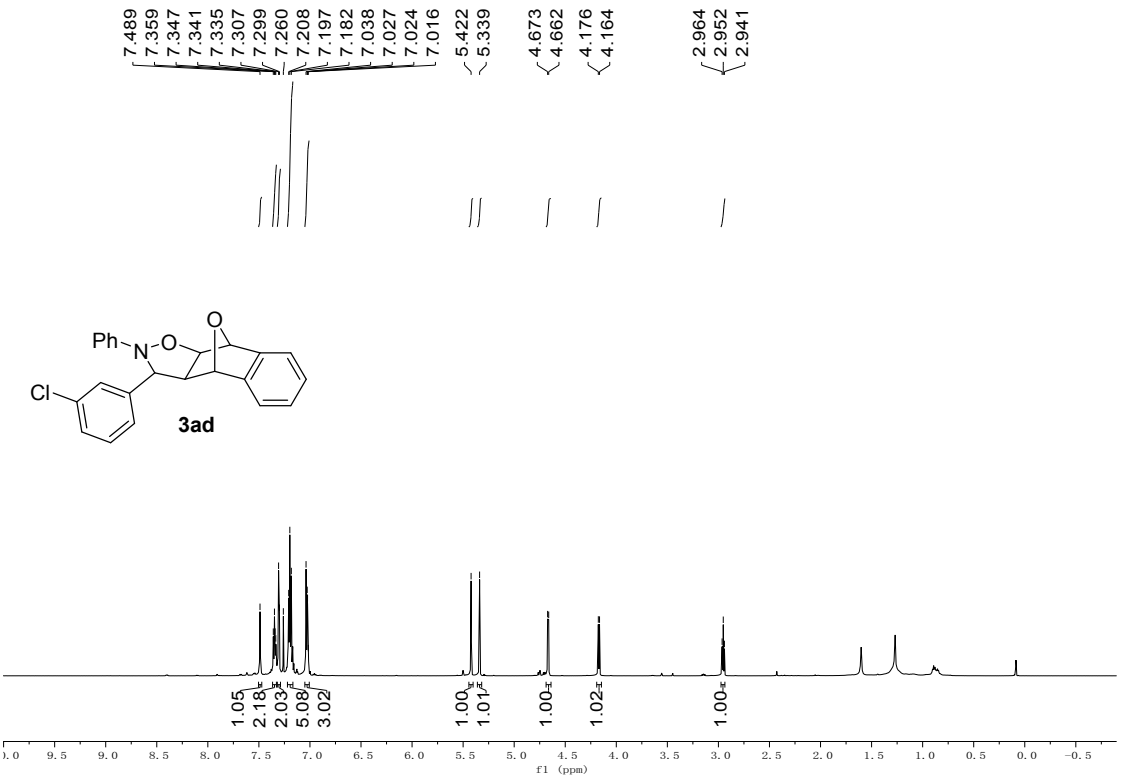

Ph
N
O
O
F

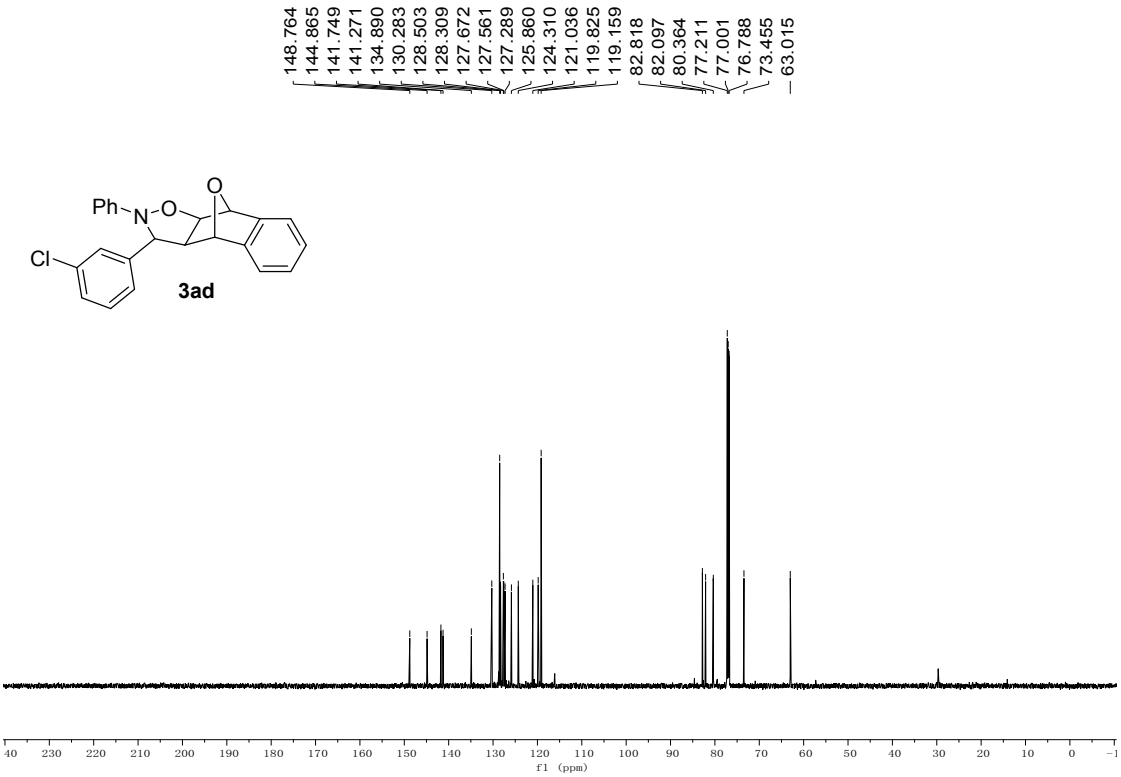
3ab

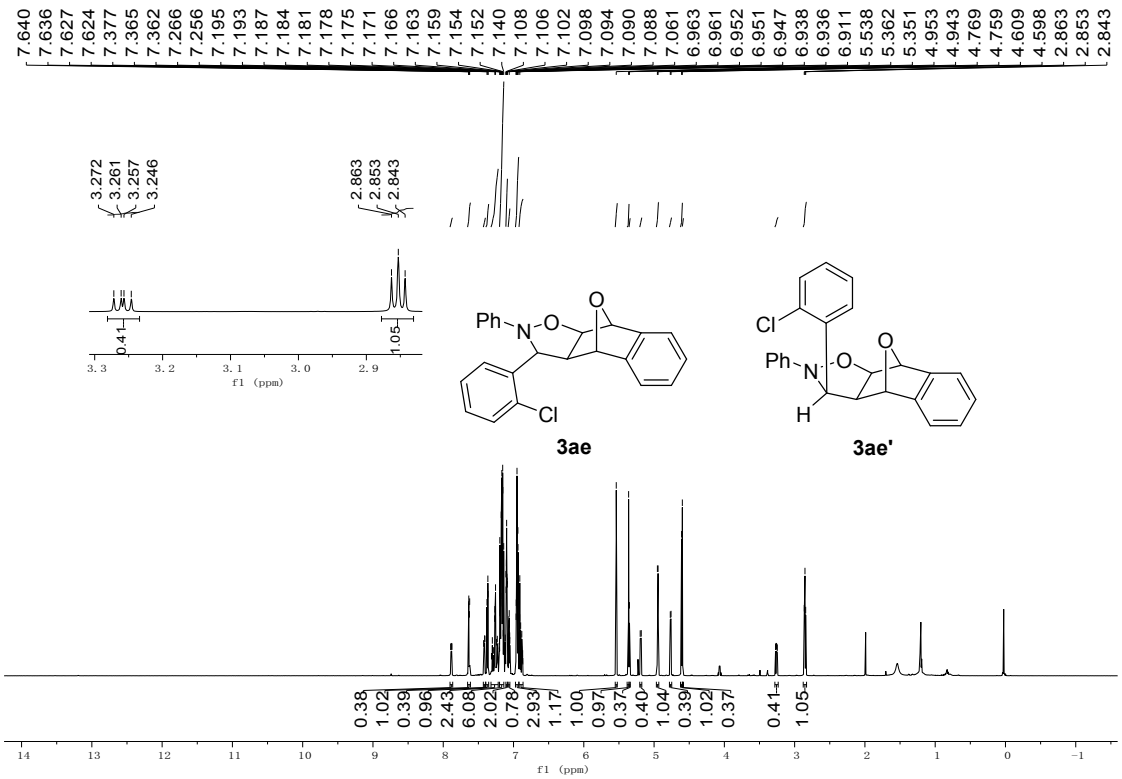

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

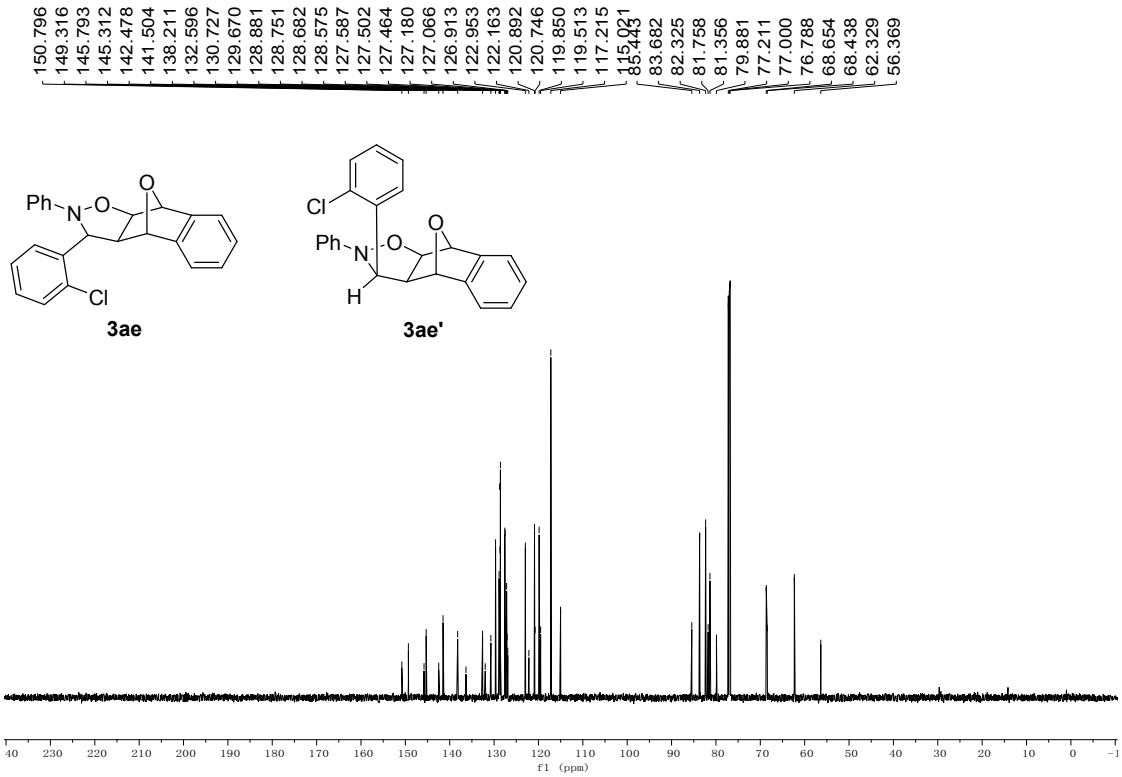

7.398
7.395
7.387
7.384
7.359
7.353
7.349
7.342
7.339
7.260
7.207
7.199
7.195
7.184
7.180
7.168
7.036
7.024
7.020
7.018
7.012
7.010
7.005
5.422
5.312
4.664
4.654
4.154
4.142
2.943
2.932
2.921
Ph
N
O
O
Cl
3ac
2.04
2.99
5.00
2.98
0.94
0.99
1.00
1.03
1.02
f1 (ppm)

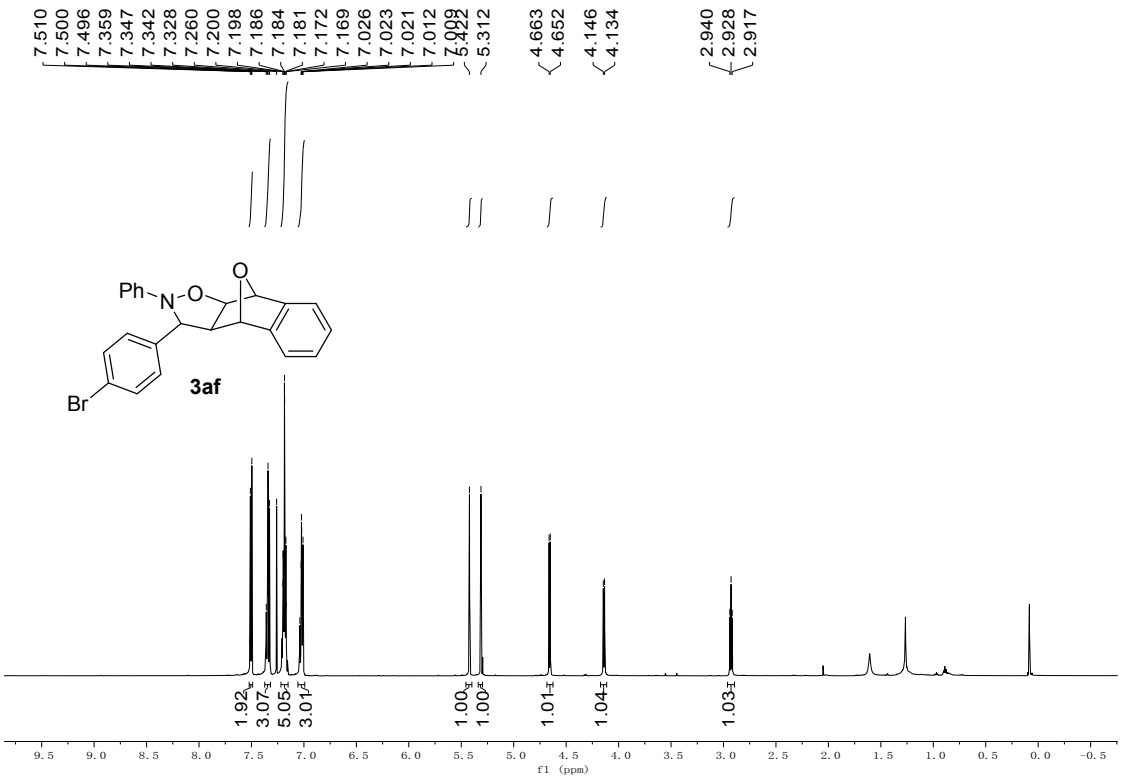

148.726
144.905
141.298
137.900
133.933
129.208
129.128
128.480
127.568
127.283
124.457
121.058
119.795
119.367
82.787
82.090
80.313
77.212
77.001
76.788
73.622
62.899
Ph
N
O
O
Cl
3ac
f1 (ppm)

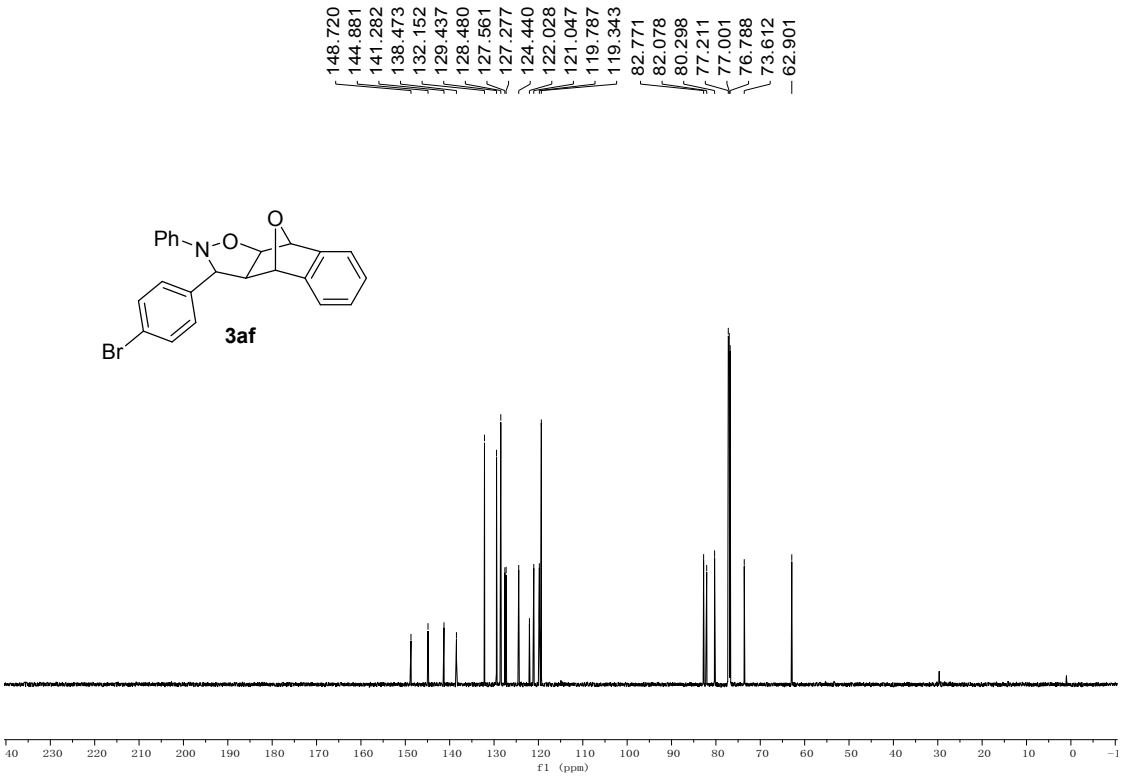

7.489
7.359
7.347
7.341
7.335
7.307
7.299
7.260
7.208
7.197
7.182
7.038
7.027
7.024
7.016
5.422
5.339
4.673
4.662
4.176
4.164
2.964
2.952
2.941
Ph
N
O
O
Cl
3ad
1.05
2.18
2.03
5.08
3.02
1.00
1.01
1.00
1.02
1.00
f1 (ppm)

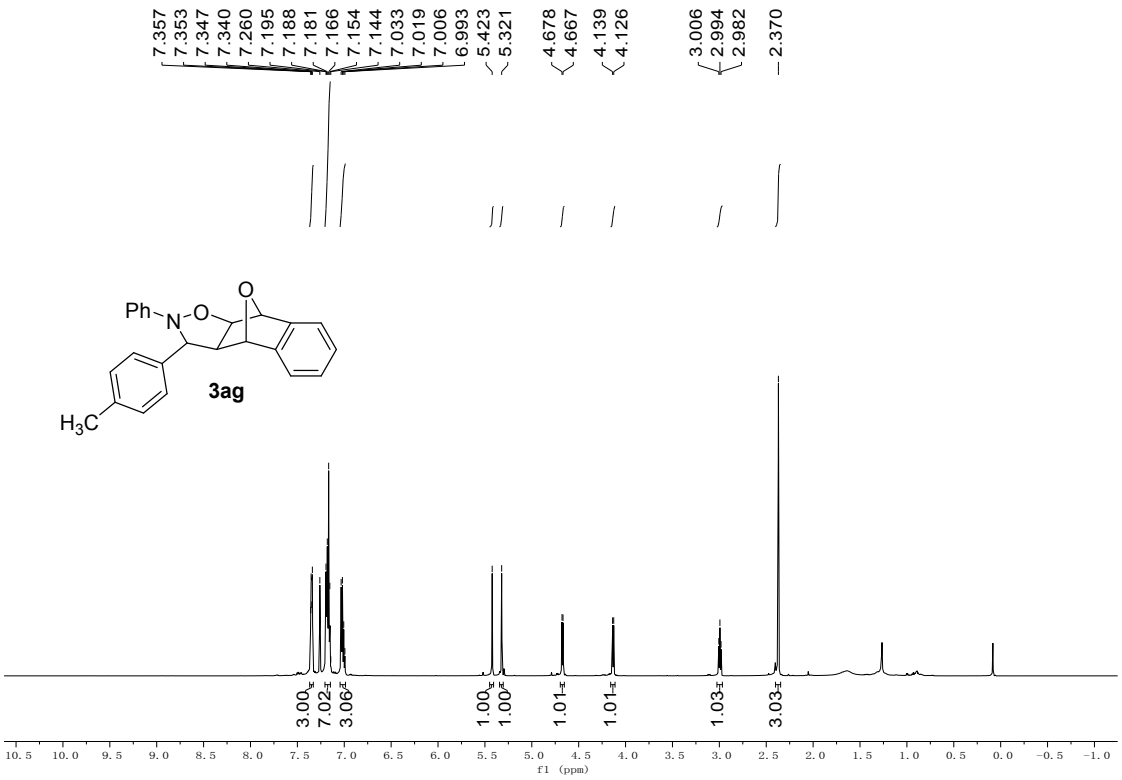

148.764
144.865
141.749
141.271
134.890
130.283
128.503
128.309
127.672
127.561
127.289
125.860
124.310
121.036
119.825
119.159
82.818
82.097
80.364
77.211
77.001
76.788
73.455
63.015
Ph
N
O
O
Cl
3ad
f1 (ppm)

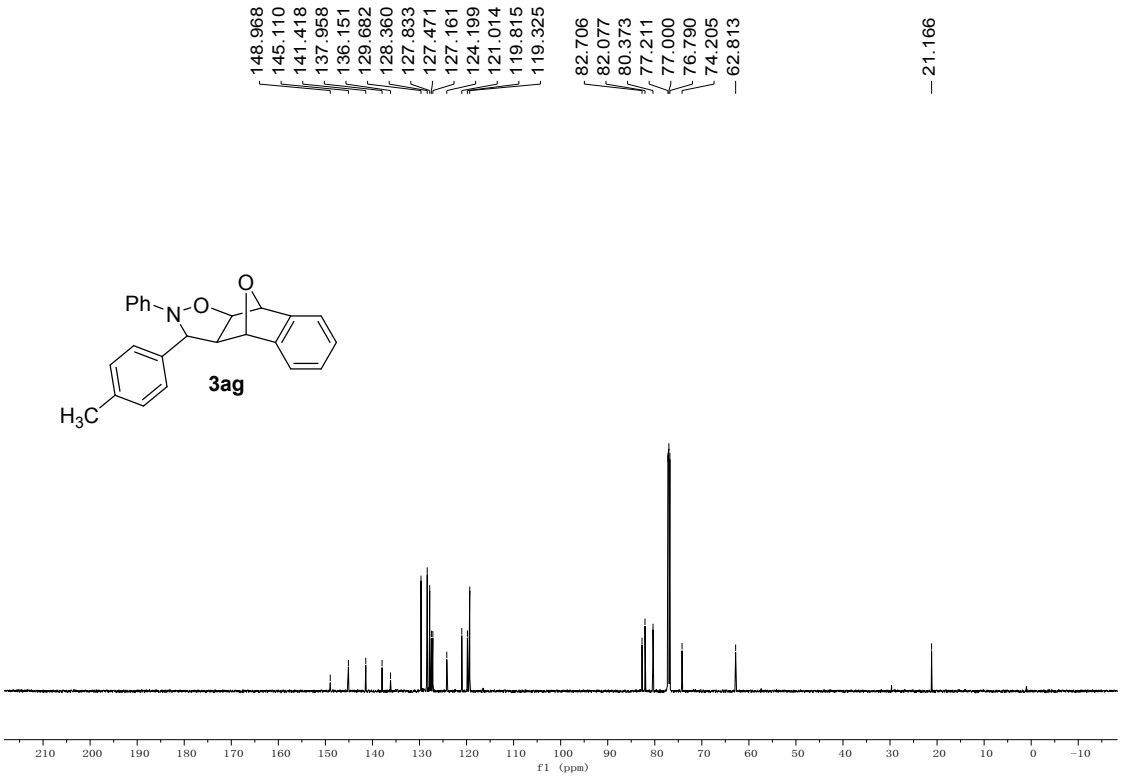

7.640
7.636
7.627
7.624
7.377
7.365
7.362
7.266
7.256
7.195
7.193
7.187
7.184
7.181
7.178
7.175
7.171
7.166
7.163
7.159
7.154
7.152
7.140
7.108
7.106
7.102
7.098
7.094
7.090
7.088
7.061
6.963
6.961
6.952
6.951
6.947
6.938
6.936
6.911
5.538
5.362
5.351
4.953
4.943
4.769
4.759
4.609
4.598
2.863
2.853
2.843
3.272
3.261
3.257
3.246
0.41
1.05
f1 (ppm)
Ph
N
O
Cl
H
3ae
3ae'
0.38
1.02
0.39
0.96
2.43
6.08
2.02
0.78
2.93
1.17
1.00
0.97
0.37
0.40
1.04
0.39
1.02
0.37
0.41
1.05
f1 (ppm)

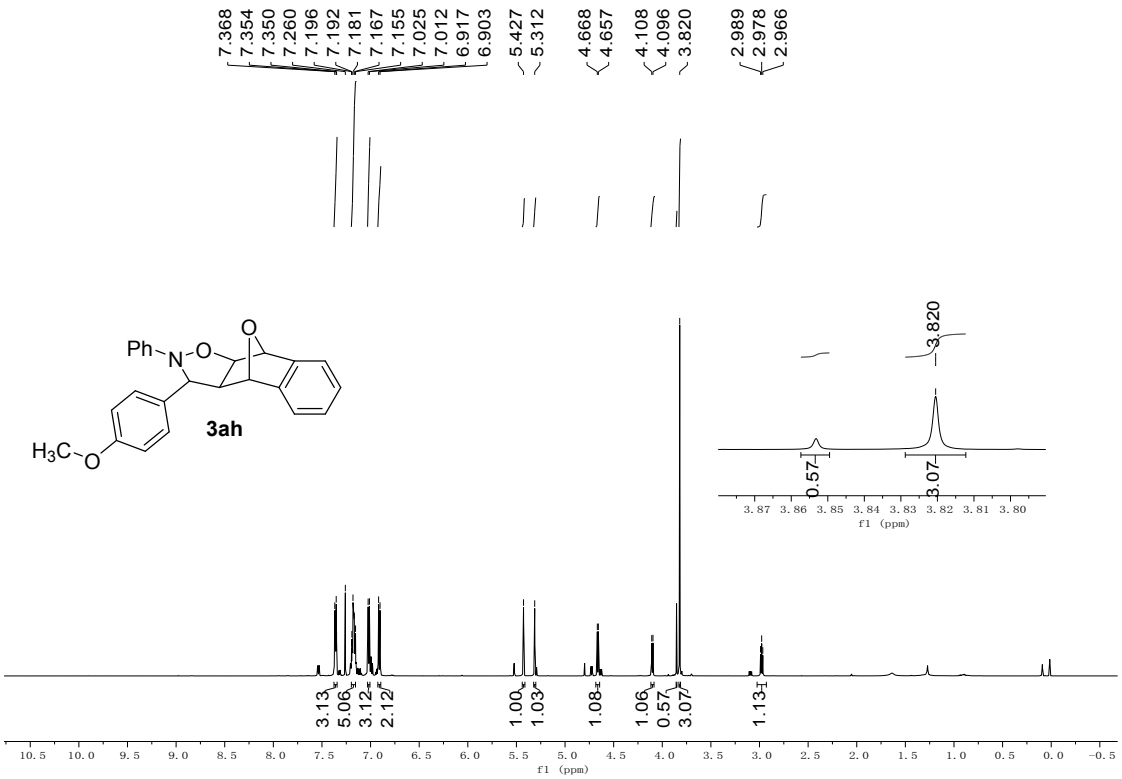

150.796
149.316
145.793
145.312
142.478
141.504
138.211
132.596
130.727
129.670
128.881
128.751
128.682
128.575
127.587
127.502
127.464
127.180
127.066
126.913
122.953
122.163
120.892
120.746
119.850
119.513
117.215
115.021
85.443
83.682
82.325
81.758
81.356
79.881
77.211
77.000
76.788
68.654
68.438
62.329
56.369
Ph
N
O
Cl
H
3ae
3ae'
f1 (ppm)

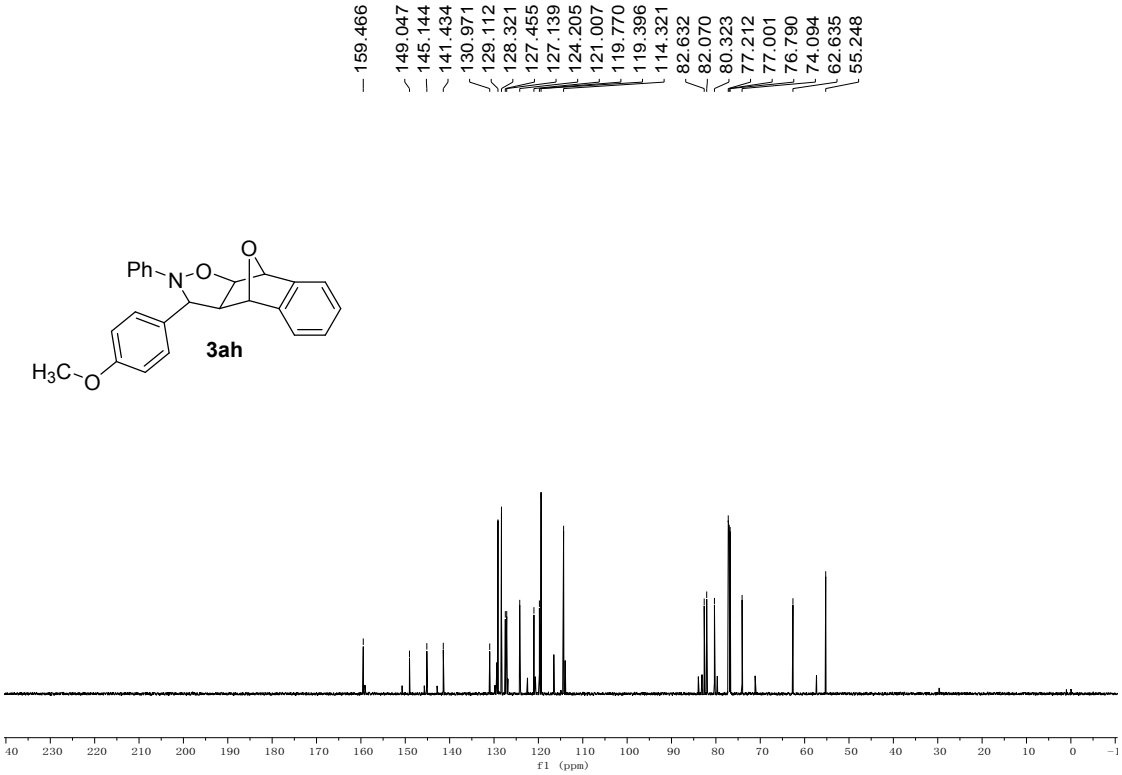

7.510
7.500
7.496
7.359
7.347
7.342
7.328
7.260
7.200
7.198
7.186
7.184
7.181
7.172
7.169
7.026
7.023
7.021
7.012
5.322
5.312
4.663
4.652
4.146
4.134
2.940
2.928
2.917
Ph
N
O
O
Br
3af
1.92
3.07
5.05
3.01
1.00
1.00
1.01
1.04
1.03
f1 (ppm)

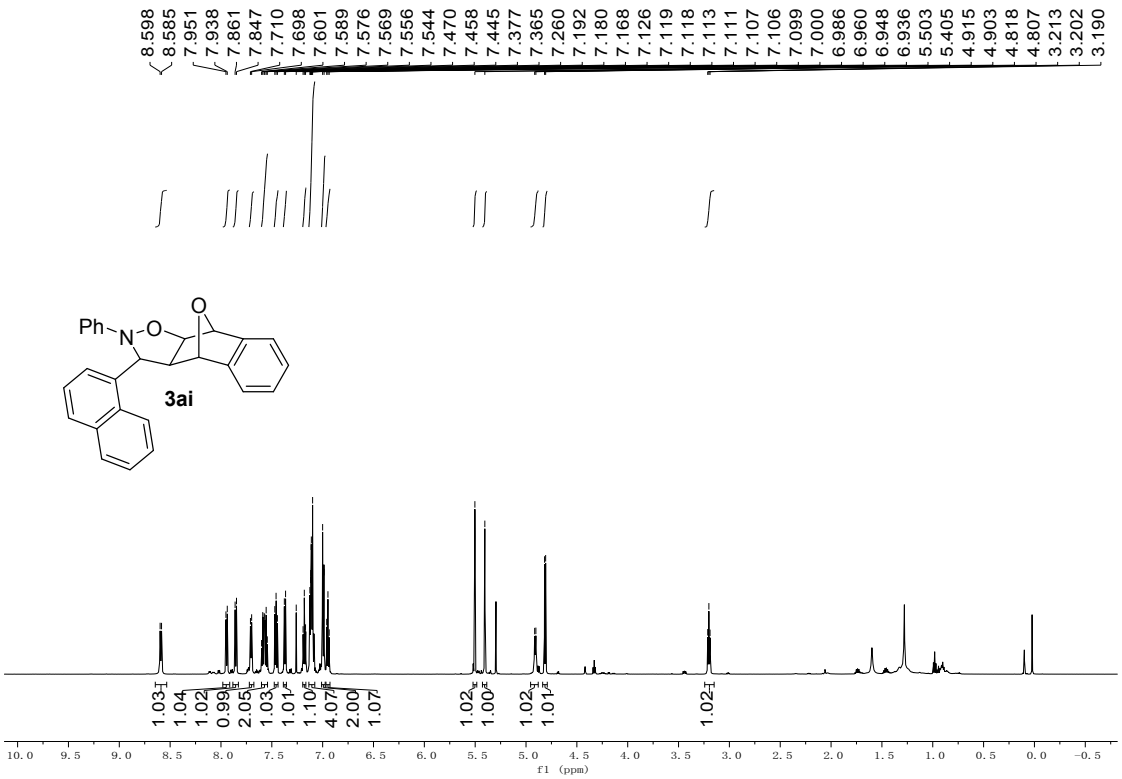

148.720
144.881
141.282
138.473
132.152
129.437
128.480
127.561
127.277
124.440
122.028
121.047
119.787
119.343
82.771
82.078
80.298
77.211
77.001
76.788
73.612
62.901
Ph
N
O
O
Br
3af
f1 (ppm)

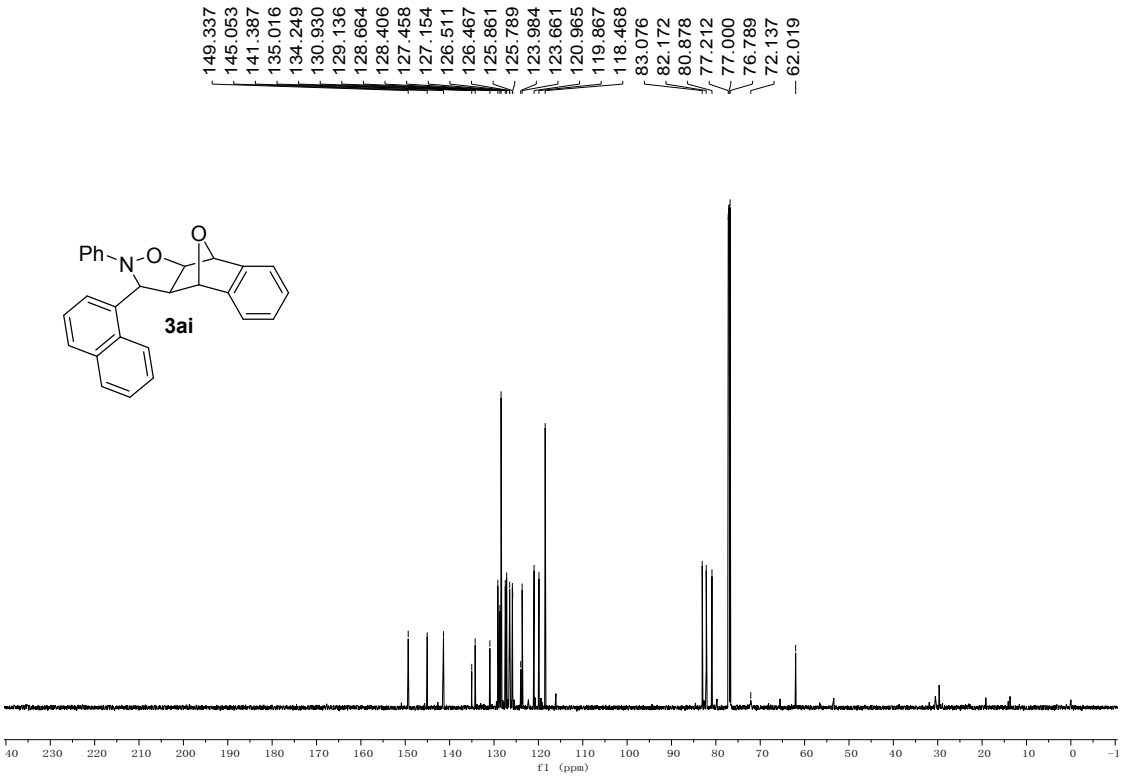

7.357
7.353
7.347
7.340
7.260
7.195
7.188
7.181
7.166
7.154
7.144
7.033
7.019
7.006
6.993
5.423
5.321
4.678
4.667
4.139
4.126
3.006
2.994
2.982
2.370
Ph
N
O
O
3ag
H3C
3.00
7.02
3.06
1.00
1.00
1.01
1.01
1.03
3.03
f1 (ppm)

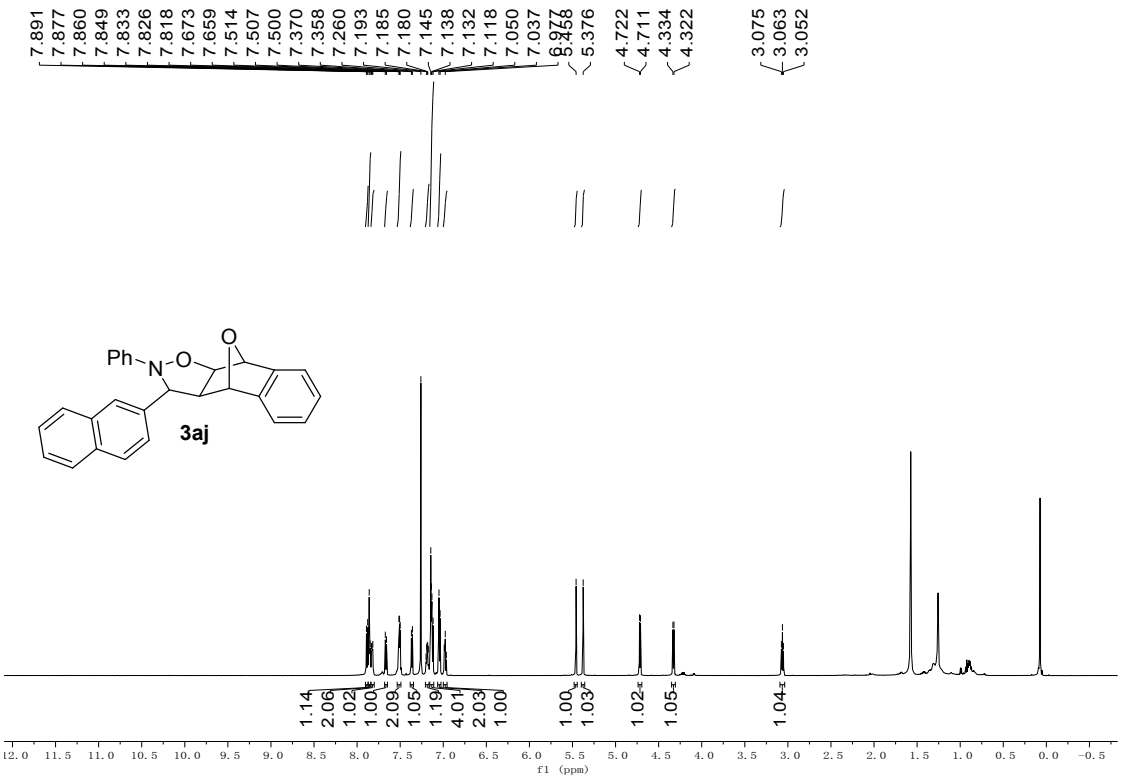

148.968
145.110
141.418
137.958
136.151
129.682
128.360
127.833
127.471
127.161
124.199
121.014
119.815
119.325
82.706
82.077
80.373
77.211
77.000
76.790
74.205
62.813
21.166
Ph
N
O
O
3ag
H3C
f1 (ppm)

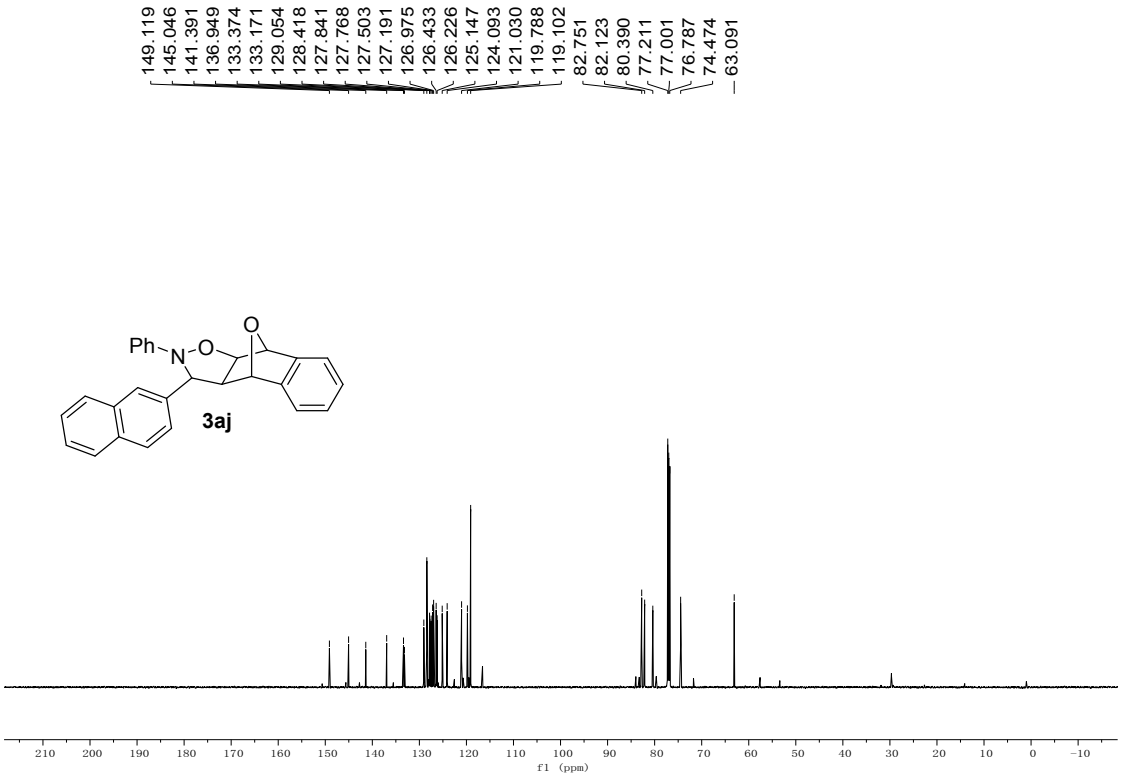

7.368
7.354
7.350
7.260
7.196
7.192
7.181
7.167
7.155
7.025
7.012
6.917
6.903
5.427
5.312
4.668
4.657
4.108
4.096
3.820
2.989
2.978
2.966
Ph
N
O
O
H3C
O
3ah
3.820
0.57
3.07
3.87 3.86 3.85 3.84 3.83 3.82 3.81 3.80
f1 (ppm)
3.13
5.06
3.12
2.12
1.00
1.03
1.08
1.06
0.57
3.07
1.13
10.5 10.0 9.5 9.0 8.5 8.0 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
f1 (ppm)

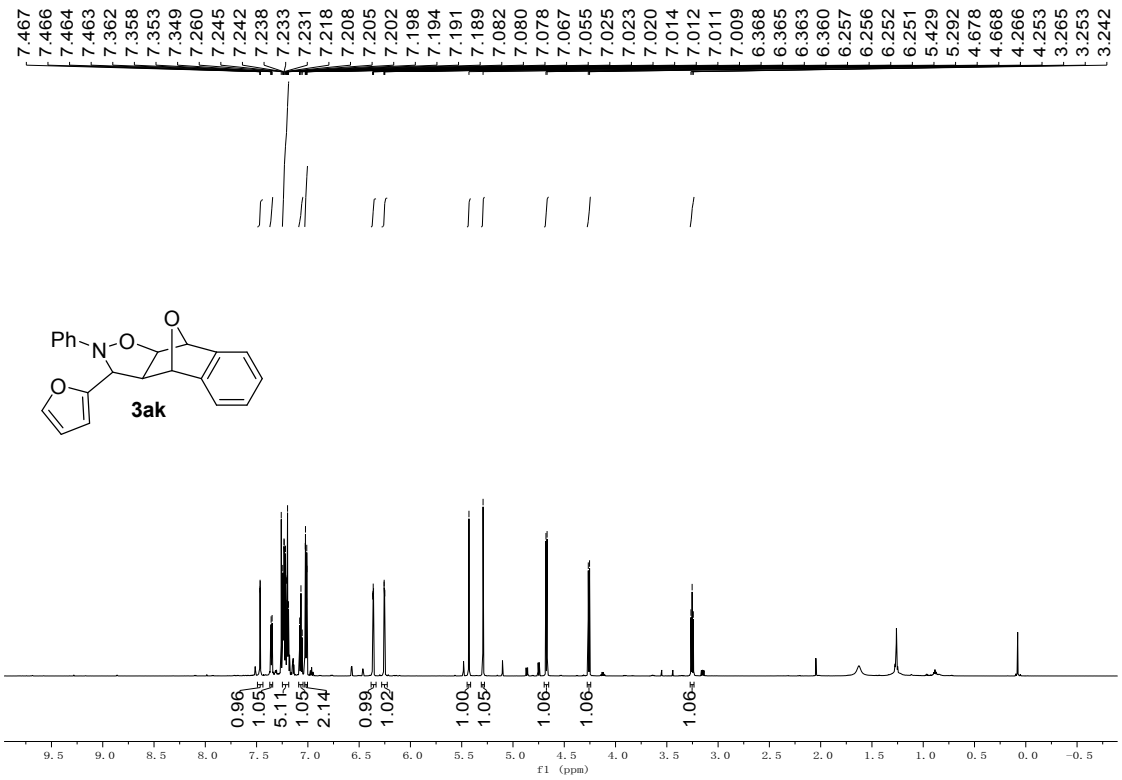

159.466
149.047
145.144
141.434
130.971
129.112
128.321
127.455
127.139
124.205
121.007
119.770
119.396
114.321
82.632
82.070
80.323
77.212
77.001
76.790
74.094
62.635
55.248
Ph
N
O
O
H3C
O
3ah
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

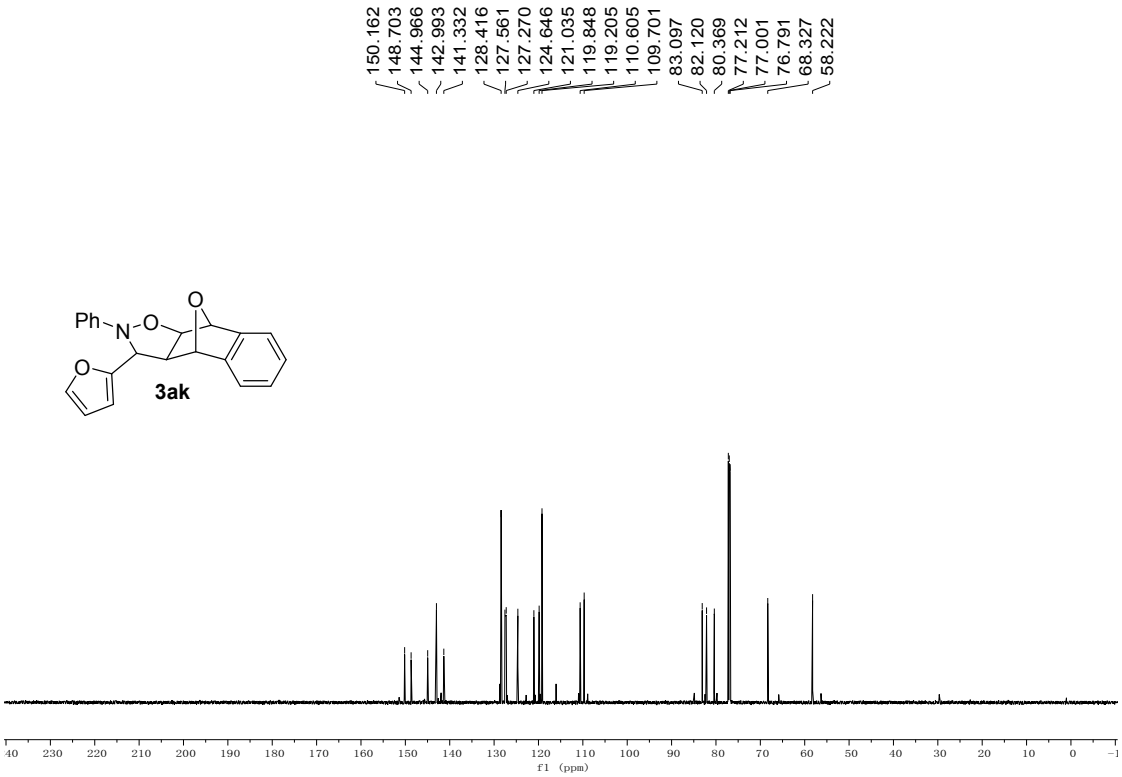

8.598
8.585
7.951
7.938
7.861
7.847
7.710
7.698
7.601
7.589
7.576
7.569
7.556
7.544
7.470
7.458
7.445
7.377
7.365
7.260
7.192
7.180
7.168
7.126
7.119
7.118
7.113
7.111
7.107
7.106
7.099
7.000
6.986
6.960
6.948
6.936
5.503
5.405
4.915
4.903
4.818
4.807
3.213
3.202
3.190
Ph
N
O
O
3ai
1.03
1.04
1.02
0.99
2.05
1.03
1.01
1.10
4.07
2.00
1.07
1.02
1.00
1.02
1.01
1.02
f1 (ppm)

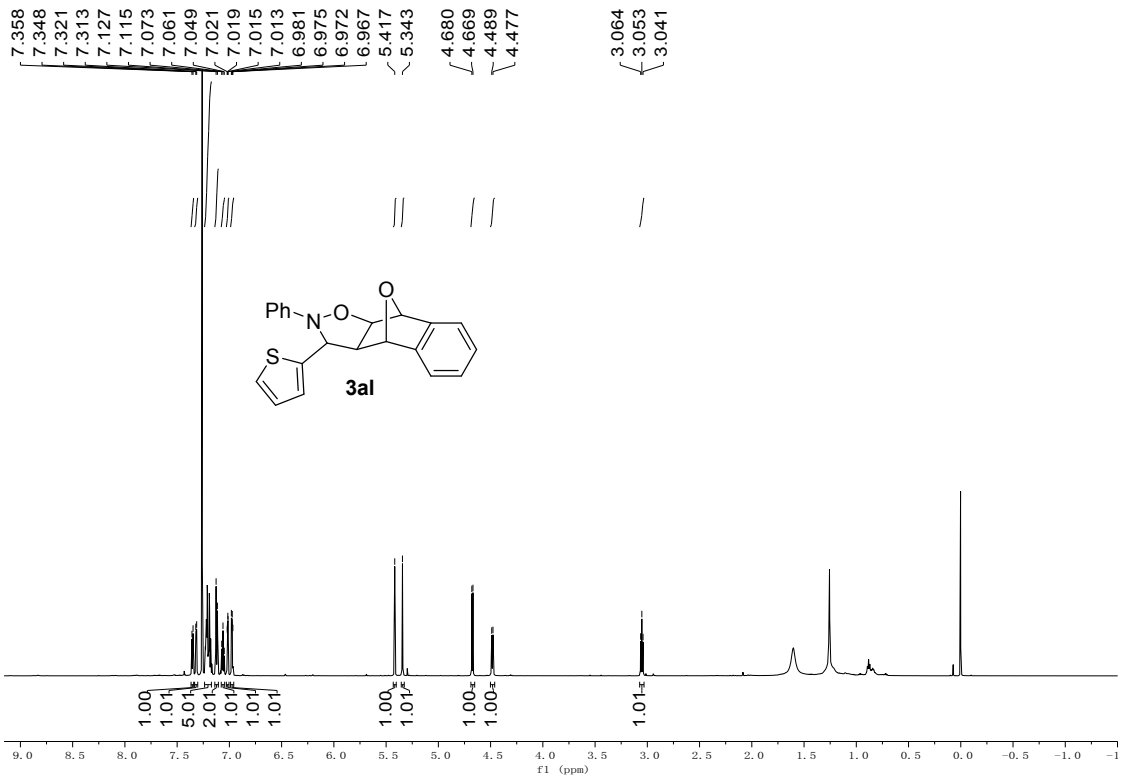

149.337
145.053
141.387
135.016
134.249
130.930
129.136
128.664
128.406
127.458
127.154
126.511
126.467
125.861
125.789
123.984
123.661
120.965
119.867
118.468
83.076
82.172
80.878
77.212
77.000
76.789
72.137
62.019
Ph
N
O
O
3ai
f1 (ppm)

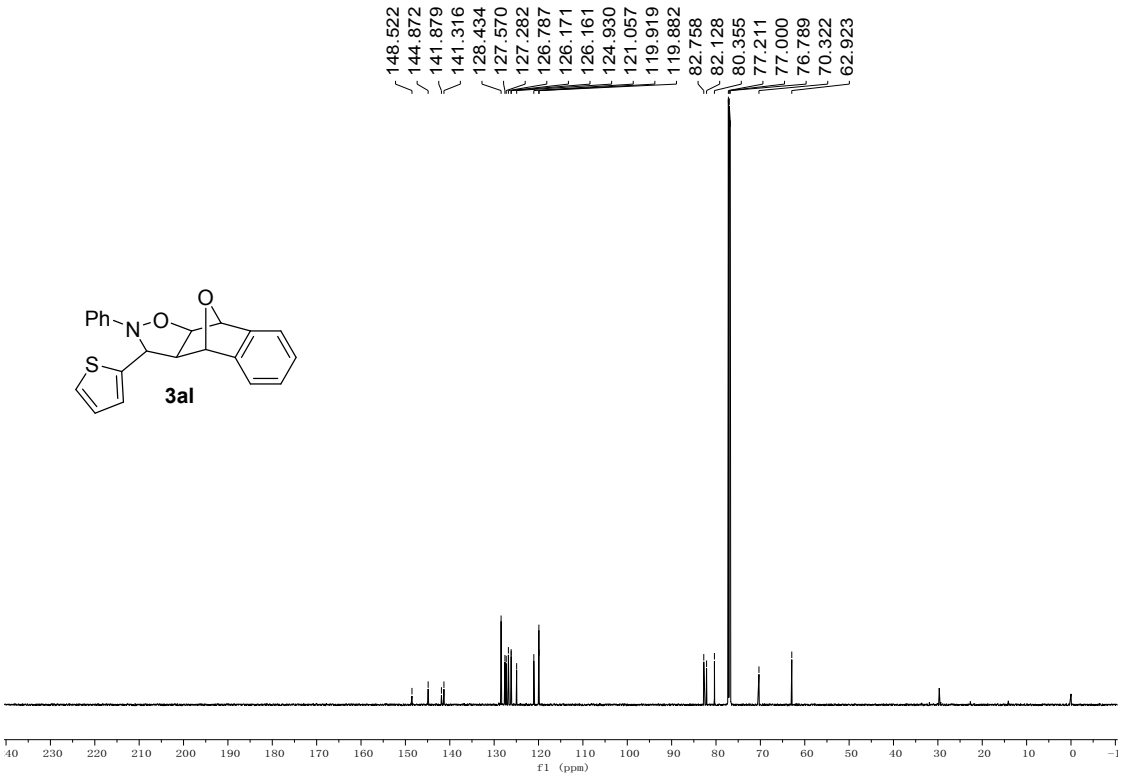

7.891
7.877
7.860
7.849
7.833
7.826
7.818
7.673
7.659
7.514
7.507
7.500
7.370
7.358
7.260
7.193
7.185
7.180
7.145
7.138
7.132
7.118
7.050
7.037
6.977
5.458
5.376
4.722
4.711
4.334
4.322
3.075
3.063
3.052
Ph
N
O
O
3aj
1.14
2.06
1.02
1.00
2.09
1.05
1.19
4.01
2.03
1.00
1.00
1.03
1.02
1.05
1.04
f1 (ppm)

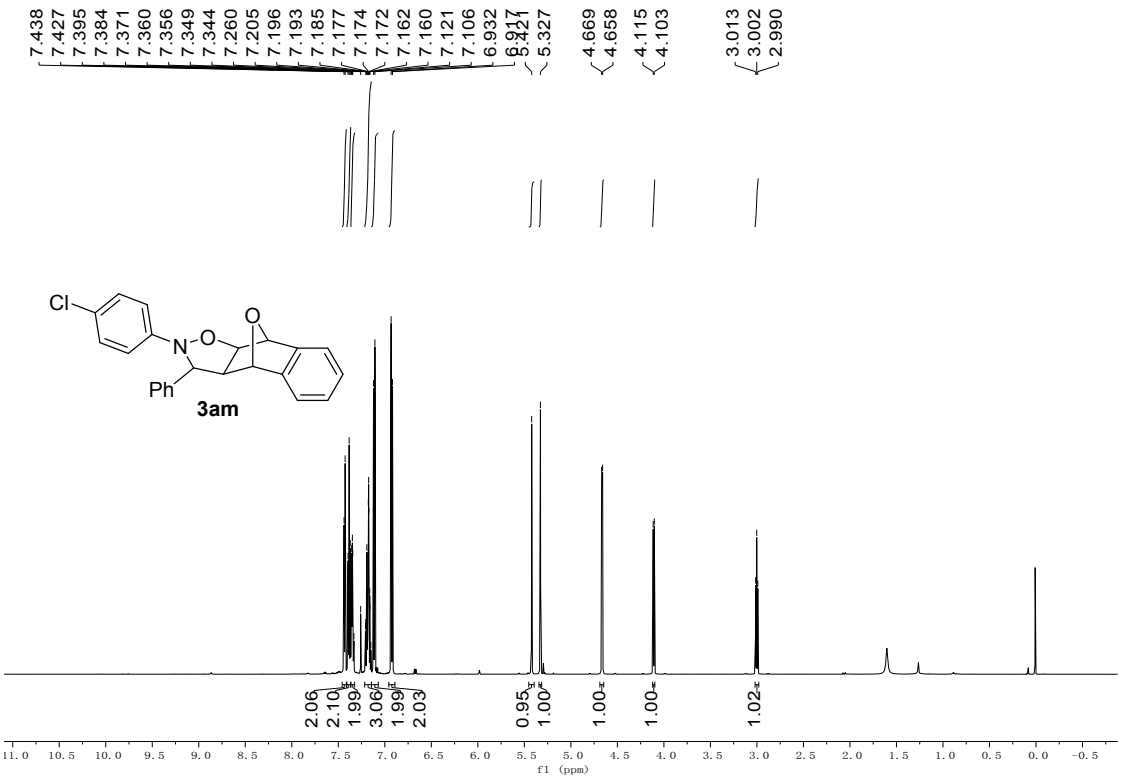

149.119
145.046
141.391
136.949
133.374
133.171
129.054
128.418
127.841
127.768
127.503
127.191
126.975
126.433
126.226
125.147
124.093
121.030
119.788
119.102
82.751
82.123
80.390
77.211
77.001
76.787
74.474
63.091
Ph
N
O
O
3aj
f1 (ppm)

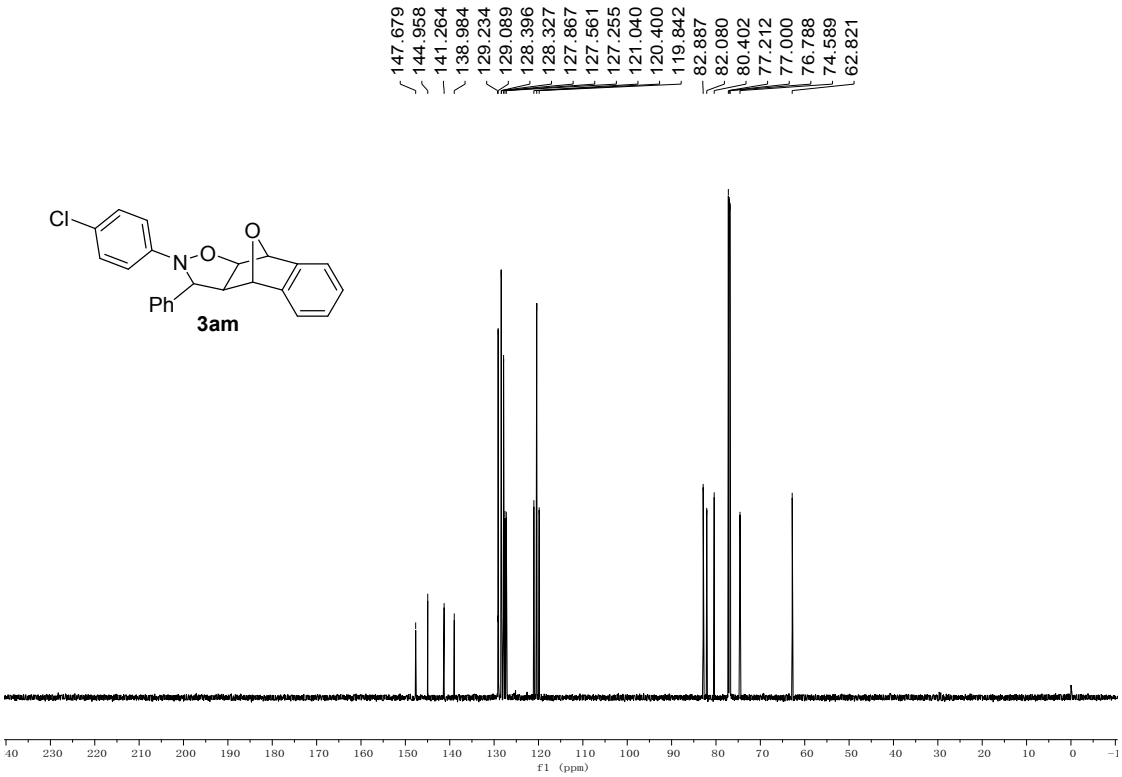

7.467
7.466
7.464
7.463
7.362
7.358
7.353
7.349
7.260
7.245
7.242
7.238
7.233
7.231
7.218
7.208
7.205
7.202
7.198
7.194
7.191
7.189
7.082
7.080
7.078
7.067
7.055
7.025
7.023
7.020
7.014
7.012
7.011
7.009
6.368
6.365
6.363
6.360
6.257
6.256
6.252
6.251
5.429
5.292
4.678
4.668
4.266
4.253
3.265
3.253
3.242
Ph
N
O
O
O
3ak
0.96
1.05
5.11
1.05
2.14
0.99
1.02
1.00
1.05
1.06
1.06
1.06
f1 (ppm)

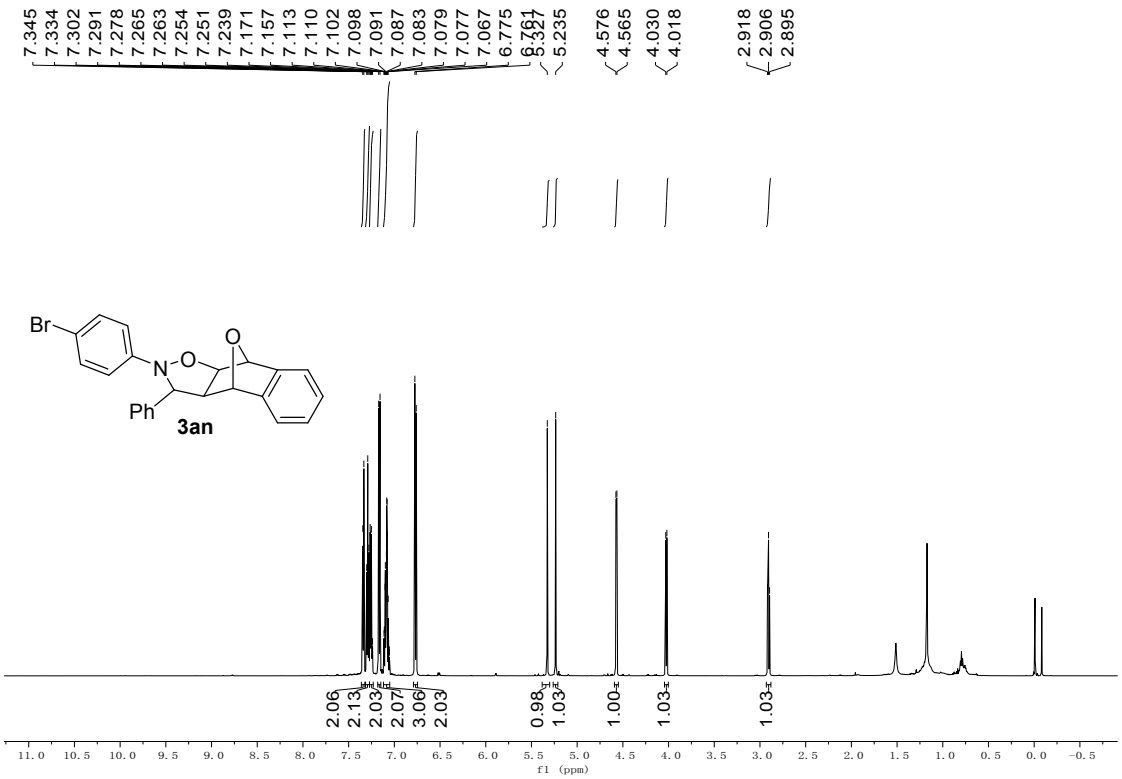

150.162
148.703
144.966
142.993
141.332
128.416
127.561
127.270
124.646
121.035
119.848
119.205
110.605
109.701
83.097
82.120
80.369
77.212
77.001
76.791
68.327
58.222
Ph
N
O
O
O
3ak
f1 (ppm)

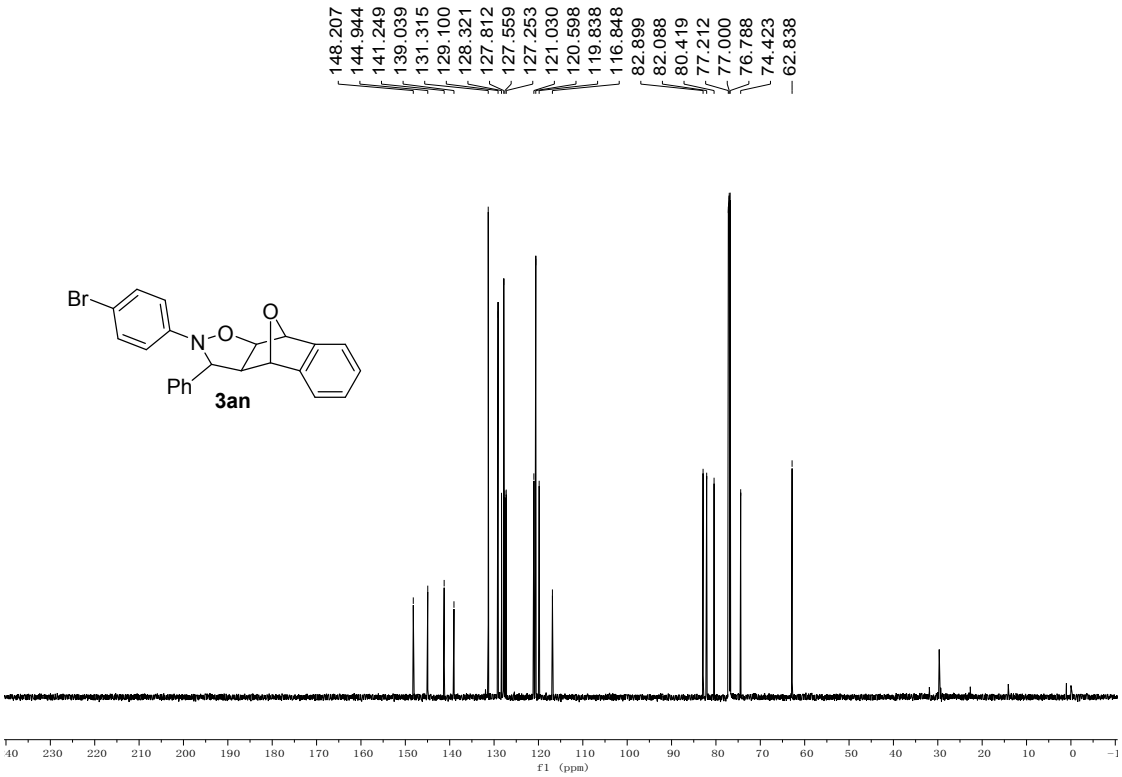

7.358
7.348
7.321
7.313
7.127
7.115
7.073
7.061
7.049
7.021
7.019
7.015
7.013
6.981
6.975
6.972
6.967
5.417
5.343
4.680
4.669
4.489
4.477
3.064
3.053
3.041
Ph
N
O
O
S
3al
1.00
1.01
5.01
2.01
1.01
1.01
1.01
1.00
1.01
1.00
1.00
1.01
f1 (ppm)

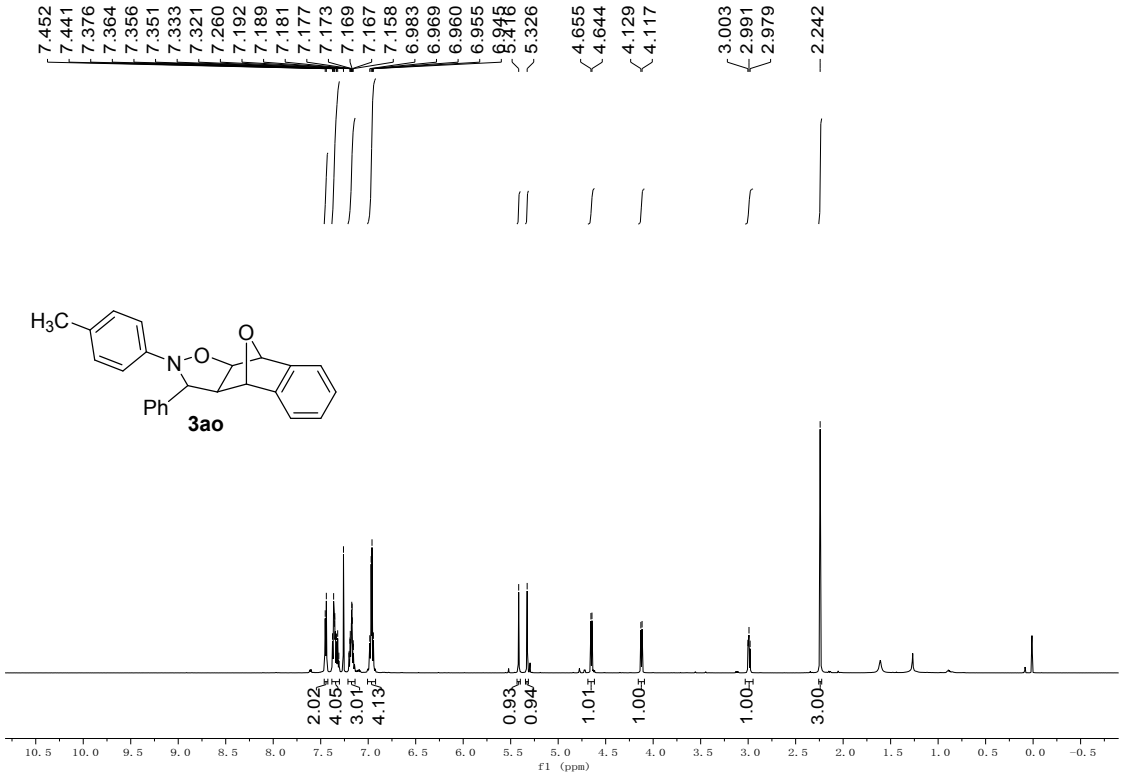

148.522
144.872
141.879
141.316
128.434
127.570
127.282
126.787
126.171
126.161
124.930
121.057
119.919
119.882
82.758
82.128
80.355
77.211
77.000
76.789
70.322
62.923
Ph
N
O
O
S
3al
f1 (ppm)

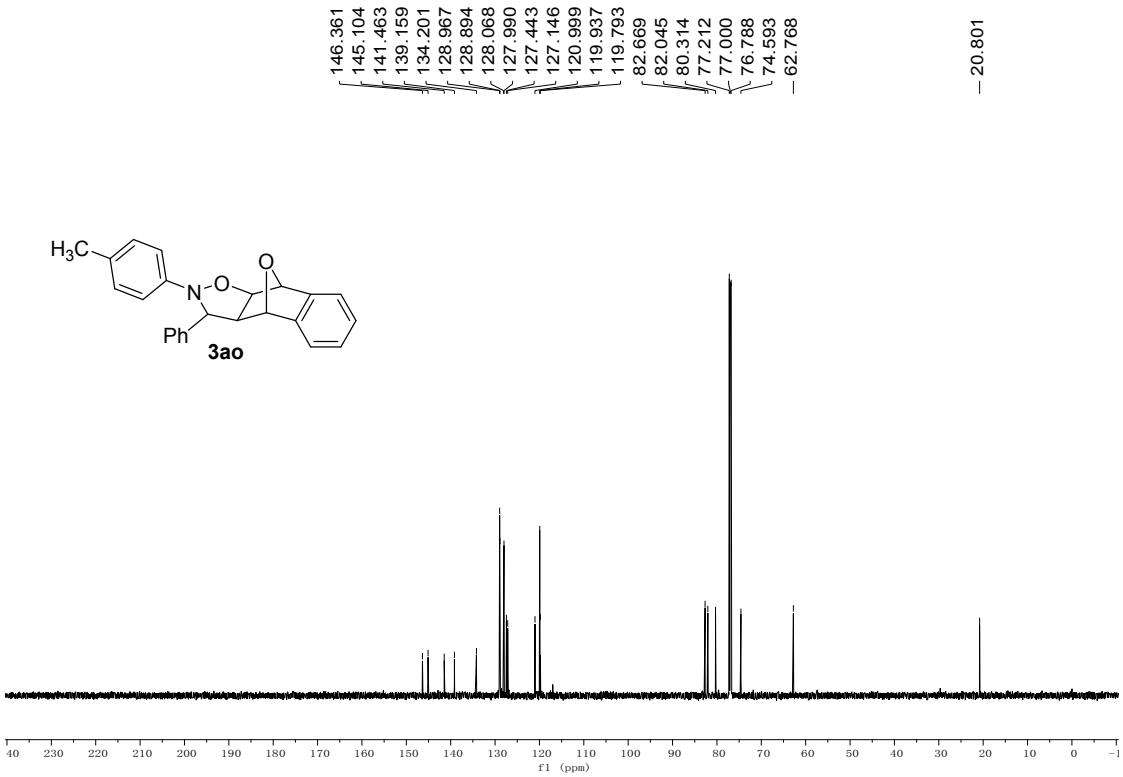

7.438
7.427
7.395
7.384
7.371
7.360
7.356
7.349
7.344
7.260
7.205
7.196
7.193
7.185
7.177
7.174
7.172
7.162
7.160
7.121
7.106
6.932
6.917
5.421
5.327
4.669
4.658
4.115
4.103
3.013
3.002
2.990
Cl
N
O
O
Ph
3am
2.06
2.10
1.99
3.06
1.99
2.03
0.95
1.00
1.00
1.00
1.02
f1 (ppm)

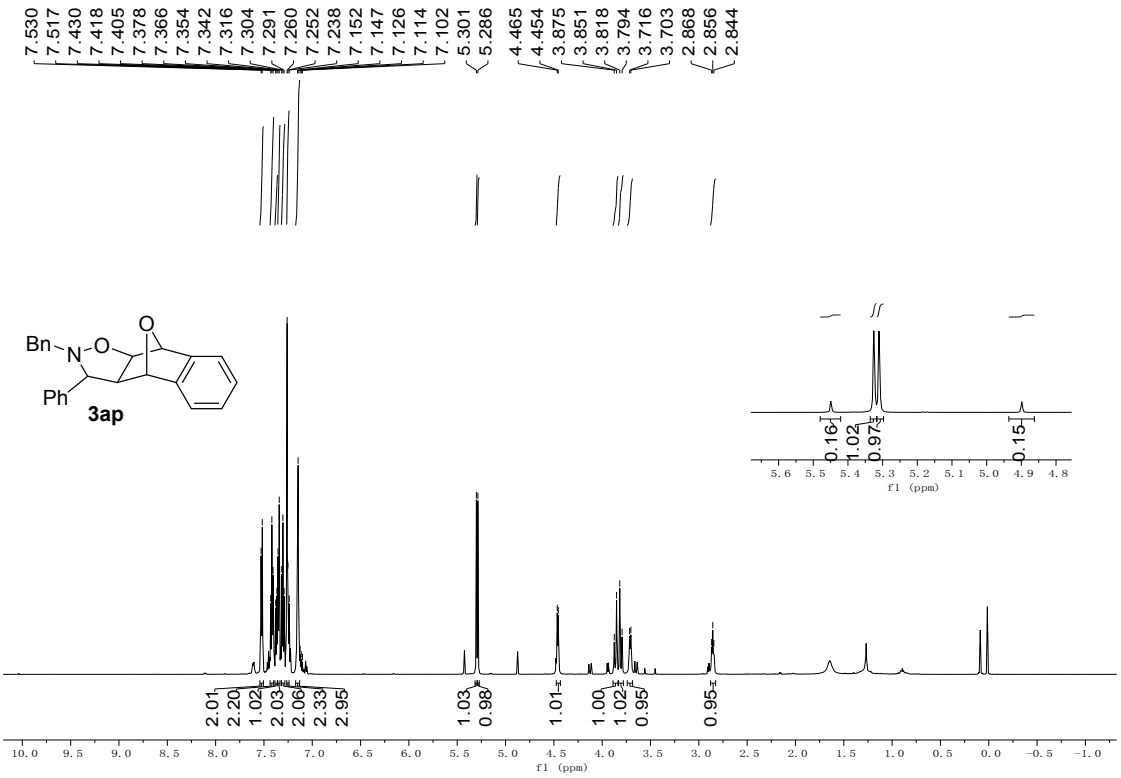

147.679
144.958
141.264
138.984
129.234
129.089
128.396
128.327
127.867
127.561
127.255
121.040
120.400
119.842
82.887
82.080
80.402
77.212
77.000
76.788
74.589
62.821
Cl
N
O
O
Ph
3am
f1 (ppm)

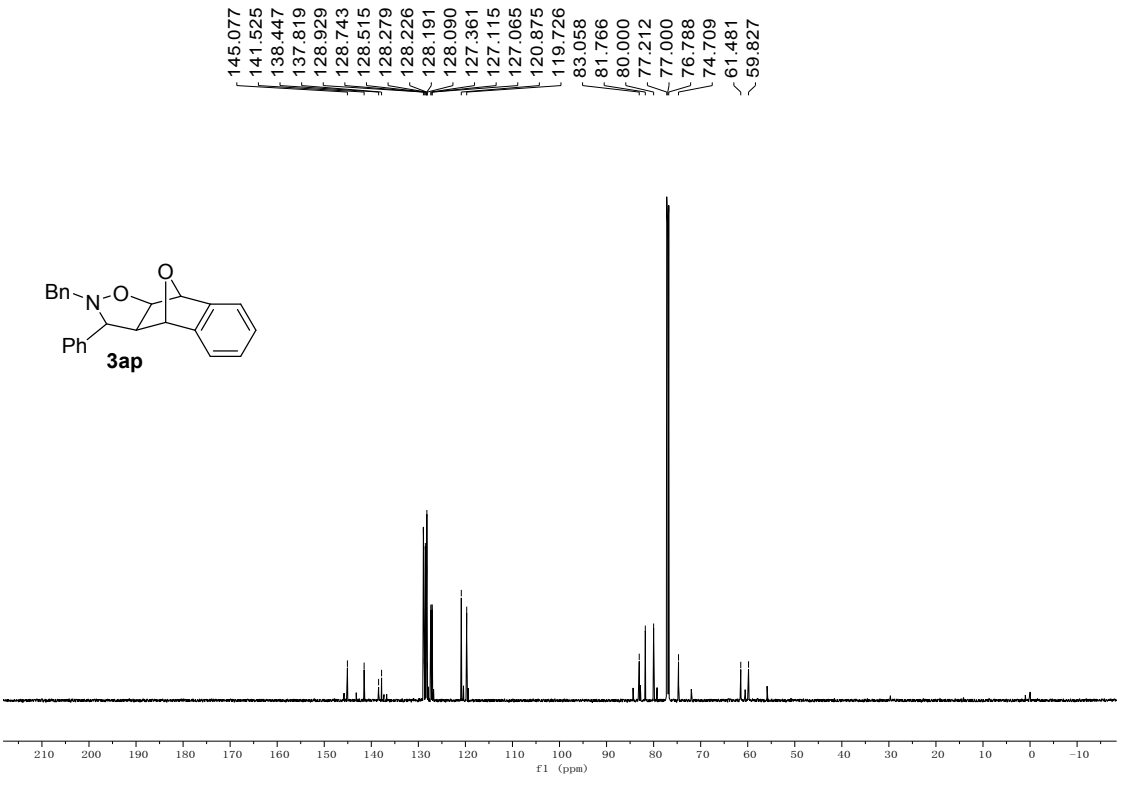

7.345
7.334
7.302
7.291
7.278
7.265
7.263
7.254
7.251
7.239
7.171
7.157
7.113
7.110
7.102
7.098
7.091
7.087
7.083
7.079
7.077
7.067
6.775
6.761
5.327
5.235
4.576
4.565
4.030
4.018
2.918
2.906
2.895
Br
O
N
O
Ph
3an
2.06
2.13
2.03
2.07
3.06
2.03
0.98
1.03
1.00
1.03
1.03
f1 (ppm)

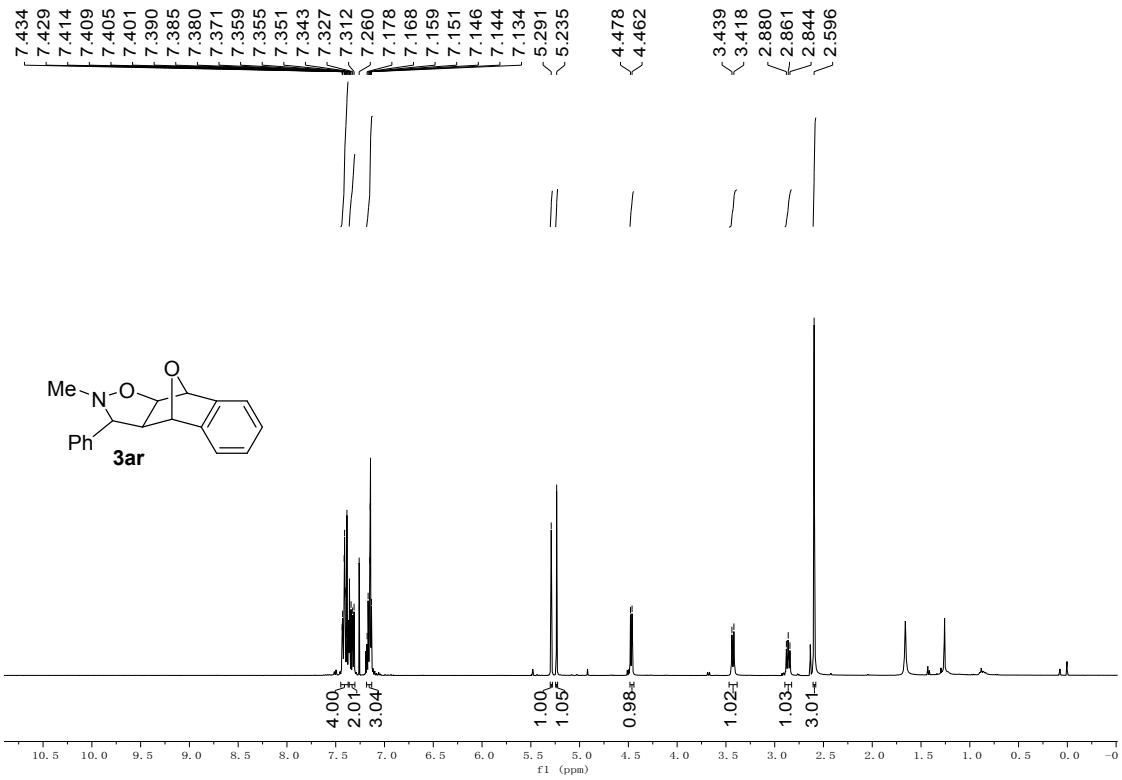

148.207
144.944
141.249
139.039
131.315
129.100
128.321
127.812
127.559
127.253
121.030
120.598
119.838
116.848
82.899
82.088
80.419
77.212
77.000
76.788
74.423
62.838
Br
O
N
O
Ph
3an
f1 (ppm)

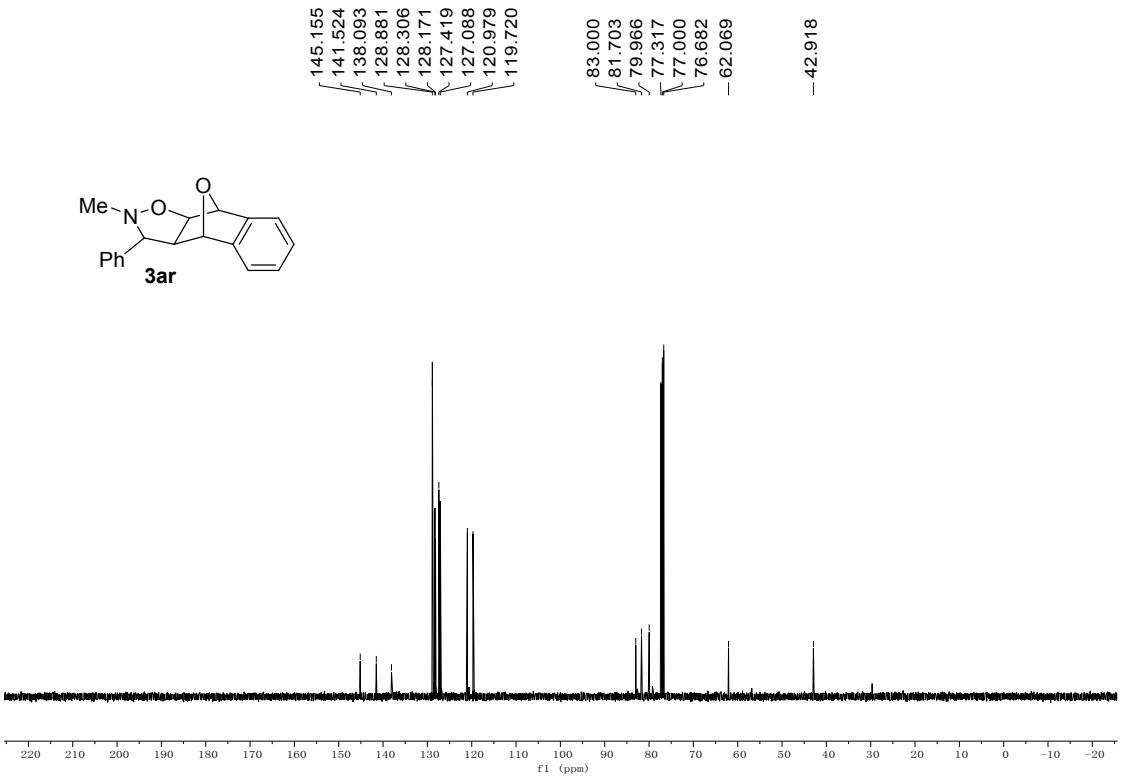

7.452
7.441
7.376
7.364
7.356
7.351
7.333
7.321
7.260
7.192
7.189
7.181
7.177
7.173
7.169
7.167
7.158
6.983
6.969
6.960
6.955
6.945
5.416
5.326
4.655
4.644
4.129
4.117
3.003
2.991
2.979
2.242
H3C
N
O
O
Ph
3ao
2.02
4.05
3.01
4.13
0.93
0.94
1.01
1.00
1.00
3.00
f1 (ppm)

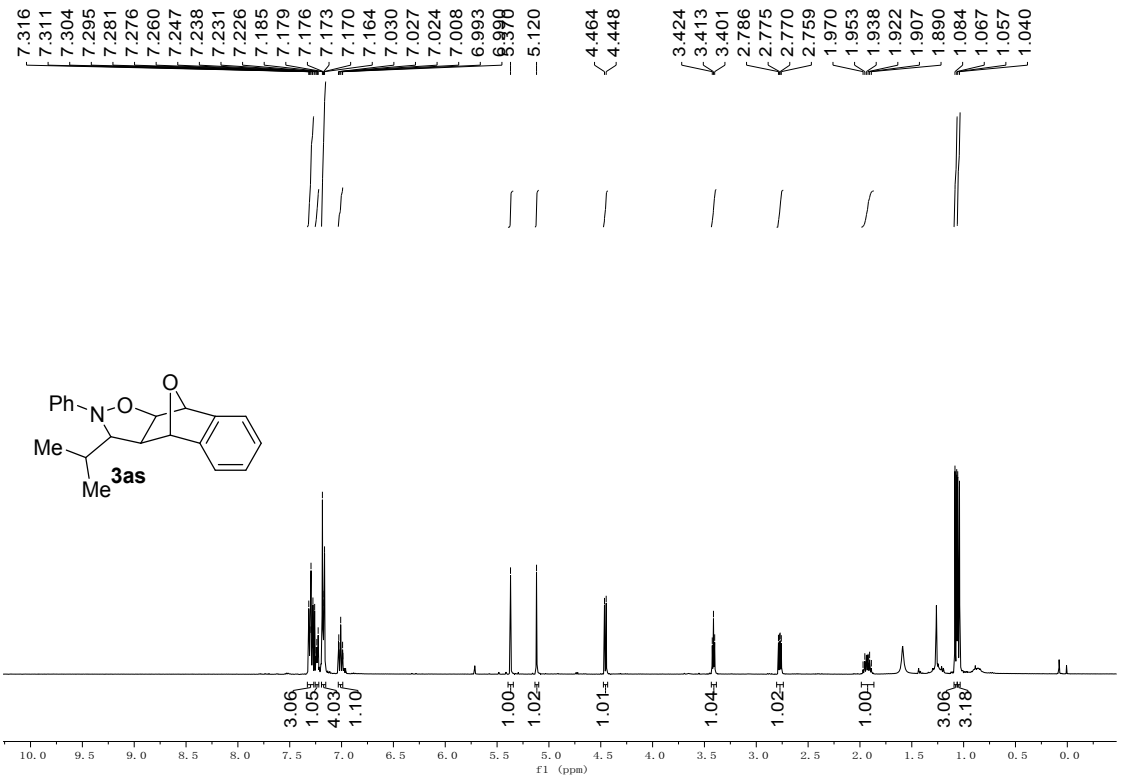

146.361
145.104
141.463
139.159
134.201
128.967
128.894
128.068
127.990
127.443
127.146
120.999
119.937
119.793
82.669
82.045
80.314
77.212
77.000
76.788
74.593
62.768
20.801
H3C
N
O
O
Ph
3ao
f1 (ppm)

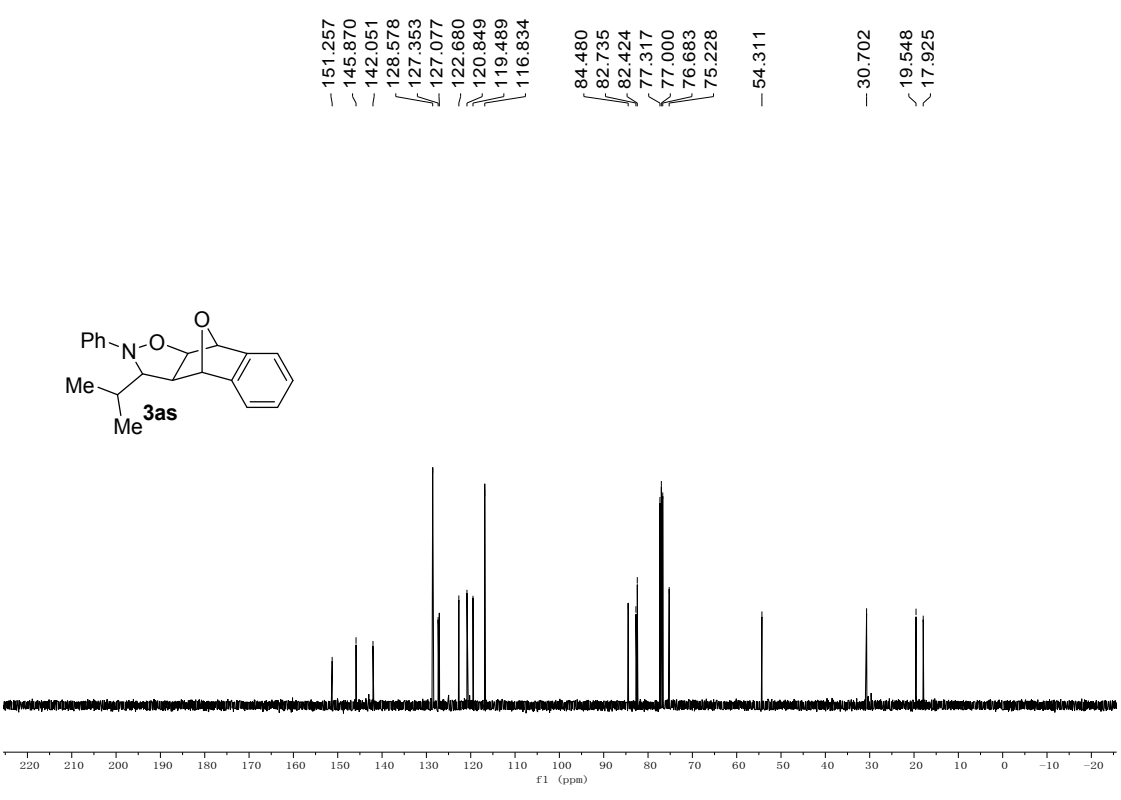

7.530
7.517
7.430
7.418
7.405
7.378
7.366
7.354
7.342
7.316
7.304
7.291
7.260
7.252
7.238
7.152
7.147
7.126
7.114
7.102
5.301
5.286
4.465
4.454
3.875
3.851
3.818
3.794
3.716
3.703
2.868
2.856
2.844
Bn
N
O
O
Ph
3ap
2.01
2.20
1.02
2.03
2.06
2.33
2.95
1.03
0.98
1.01
1.00
1.02
0.95
0.95
0.16
1.02
0.97
0.15
f1 (ppm)

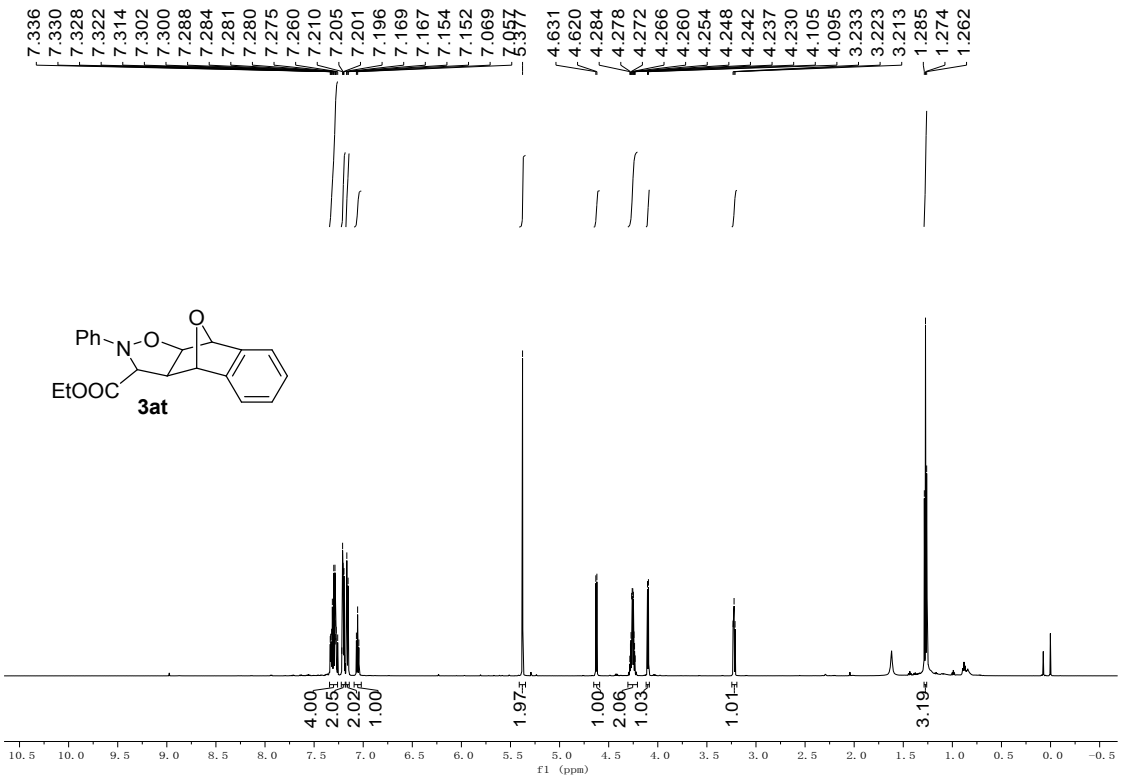

145.077
141.525
138.447
137.819
128.929
128.743
128.515
128.279
128.226
128.191
128.090
127.361
127.115
127.065
120.875
119.726
83.058
81.766
80.000
77.212
77.000
76.788
74.709
61.481
59.827
Bn
N
O
O
Ph
3ap
f1 (ppm)

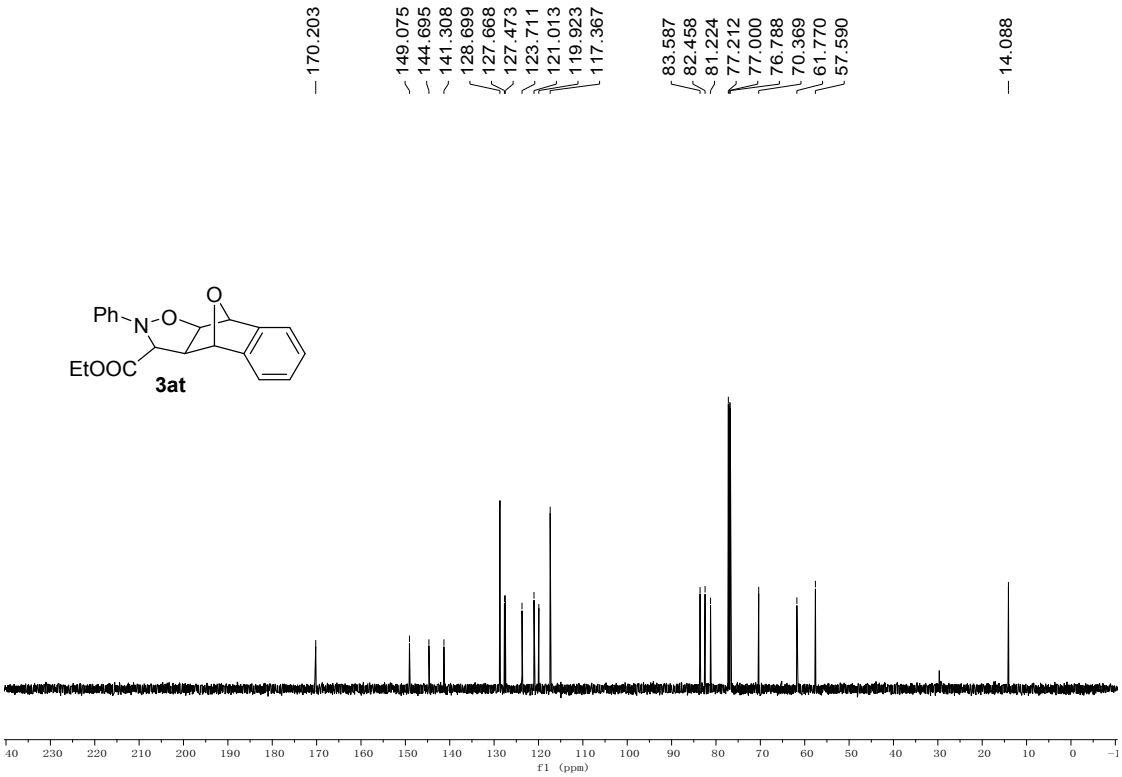

7.434
7.429
7.414
7.409
7.405
7.401
7.390
7.385
7.380
7.371
7.359
7.355
7.351
7.343
7.327
7.312
7.260
7.178
7.168
7.159
7.151
7.146
7.144
7.134
5.291
5.235
4.478
4.462
3.439
3.418
2.880
2.861
2.844
2.596
Me
N
O
O
Ph
3ar
4.00
2.01
3.04
1.00
1.05
0.98
1.02
1.03
3.01
f1 (ppm)

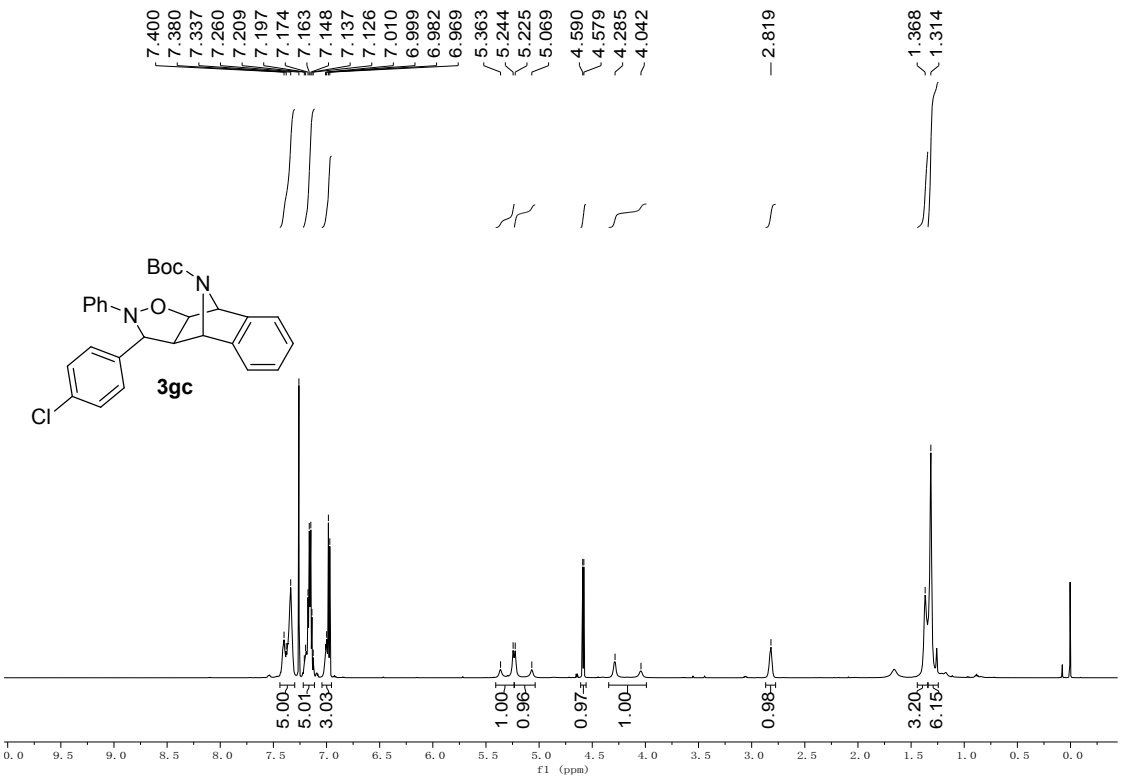

145.155
141.524
138.093
128.881
128.306
128.171
127.419
127.088
120.979
119.720
83.000
81.703
79.966
77.317
77.000
76.682
62.069
42.918
Me
N
O
O
Ph
3ar
f1 (ppm)

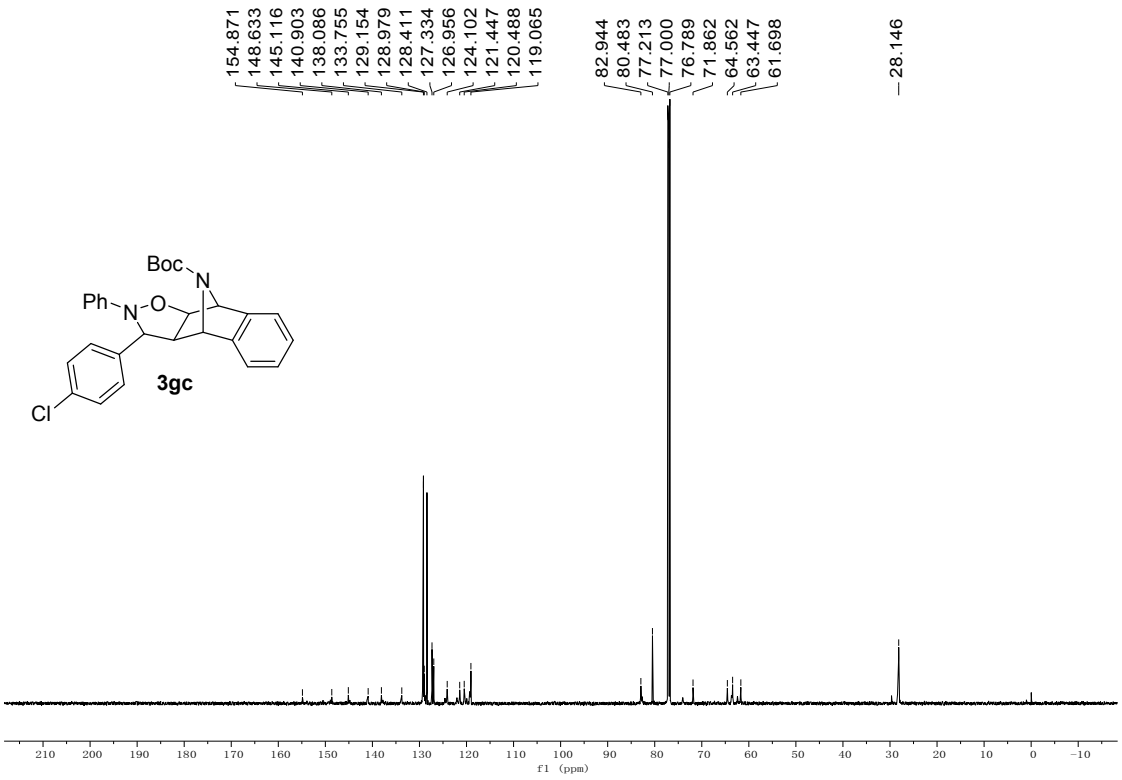

7.316
7.311
7.304
7.295
7.281
7.276
7.260
7.247
7.238
7.231
7.226
7.185
7.179
7.176
7.173
7.170
7.164
7.030
7.027
7.024
7.008
6.993
5.120
4.464
4.448
3.424
3.413
3.401
2.786
2.775
2.770
2.759
1.970
1.953
1.938
1.922
1.907
1.890
1.084
1.067
1.057
1.040
Ph
N
O
O
Me
Me
3as
3.06
1.05
4.03
1.10
1.00
1.02
1.01
1.04
1.02
1.00
3.06
3.18
f1 (ppm)

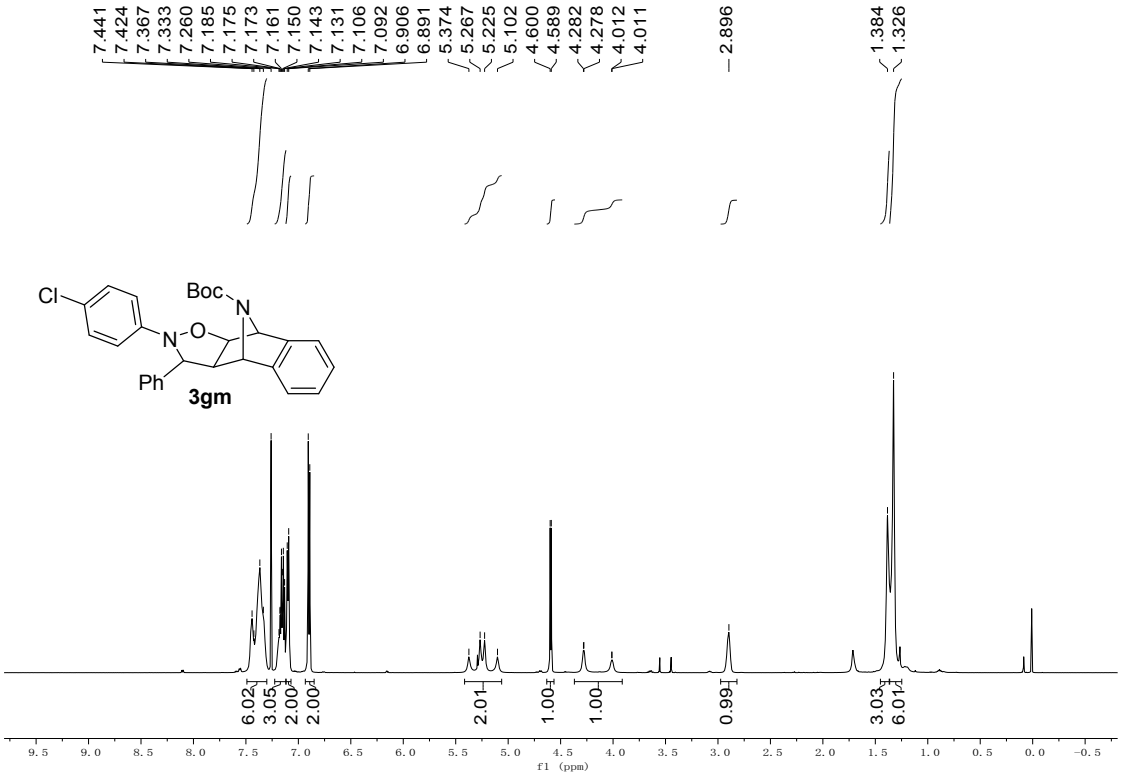

151.257
145.870
142.051
128.578
127.353
127.077
122.680
120.849
119.489
116.834
84.480
82.735
82.424
77.317
77.000
76.683
75.228
54.311
30.702
19.548
17.925
Ph
N
O
O
Me
Me
3as
f1 (ppm)

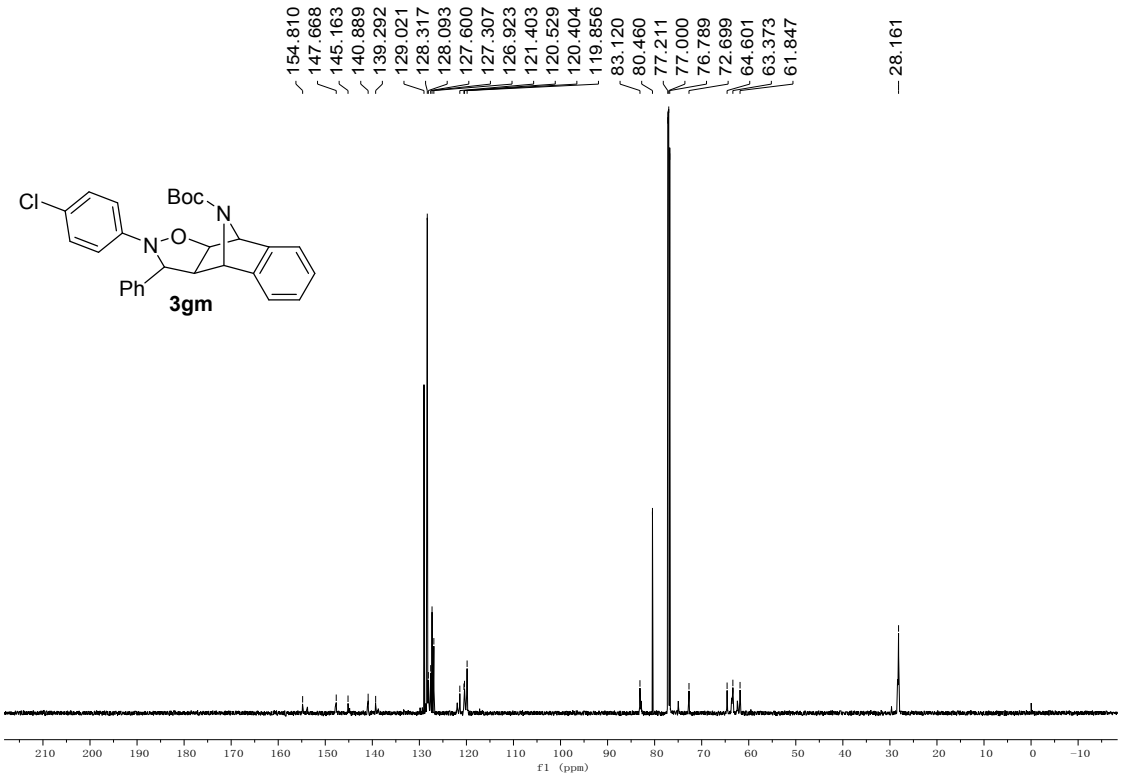

7.336
7.330
7.328
7.322
7.314
7.302
7.300
7.288
7.284
7.281
7.280
7.275
7.260
7.210
7.205
7.201
7.196
7.169
7.167
7.154
7.152
7.069
7.057
5.377
4.631
4.620
4.284
4.278
4.272
4.266
4.260
4.254
4.248
4.242
4.237
4.230
4.105
4.095
3.233
3.223
3.213
1.285
1.274
1.262
Ph
N
O
O
EtOOC
3at
4.00
2.05
2.02
1.00
1.97
1.00
2.06
1.03
1.01
3.19
f1 (ppm)


170.203
149.075
144.695
141.308
128.699
127.668
127.473
123.711
121.013
119.923
117.367
83.587
82.458
81.224
77.212
77.000
76.788
70.369
61.770
57.590
14.088
Ph
N
O
O
EtOOC
3at
f1 (ppm)

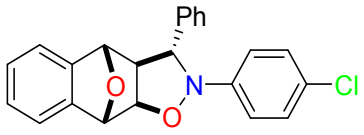

7.400
7.380
7.337
7.260
7.209
7.197
7.174
7.163
7.148
7.137
7.126
7.010
6.999
6.982
6.969
5.363
5.244
5.225
5.069
4.590
4.579
4.285
4.042
2.819
1.368
1.314
Boc
N
Ph
N
O
Cl
3gc
5.00
5.01
3.03
1.00
0.96
0.97
1.00
0.98
3.20
6.15
f1 (ppm)


154.871
148.633
145.116
140.903
138.086
133.755
129.154
128.979
128.411
127.334
126.956
124.102
121.447
120.488
119.065
82.944
80.483
77.213
77.000
76.789
71.862
64.562
63.447
61.698
28.146
Boc
N
Ph
N
O
Cl
3gc
f1 (ppm)

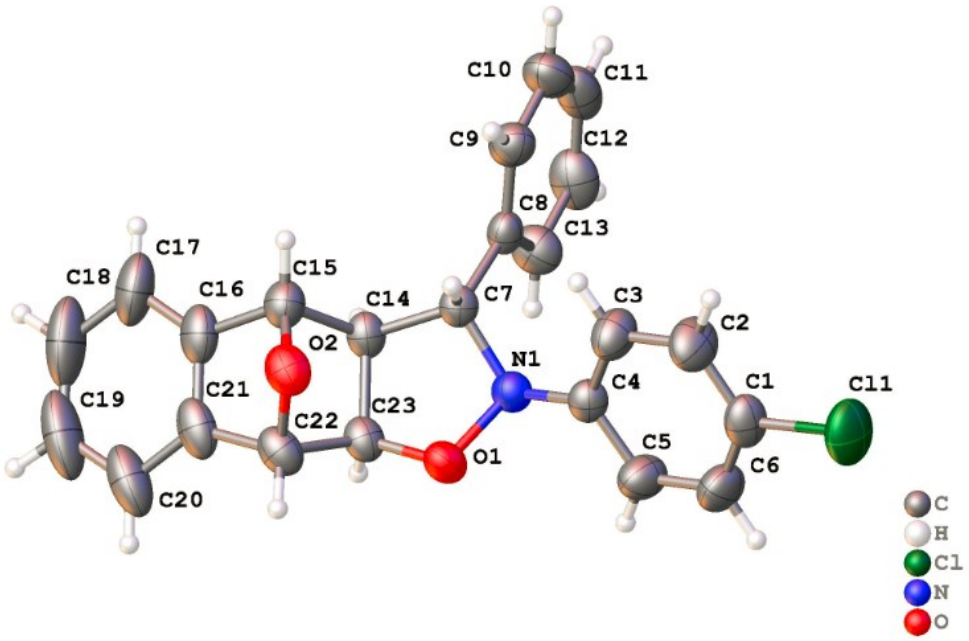

7.441
7.424
7.367
7.333
7.260
7.185
7.175
7.173
7.161
7.150
7.143
7.131
7.106
7.092
6.906
6.891
5.374
5.267
5.225
5.102
4.600
4.589
4.282
4.278
4.012
4.011
2.896
1.384
1.326
Cl
Boc
N
O
Ph
3gm
6.02
3.05
2.00
2.00
2.01
1.00
1.00
0.99
3.03
6.01
f1 (ppm)

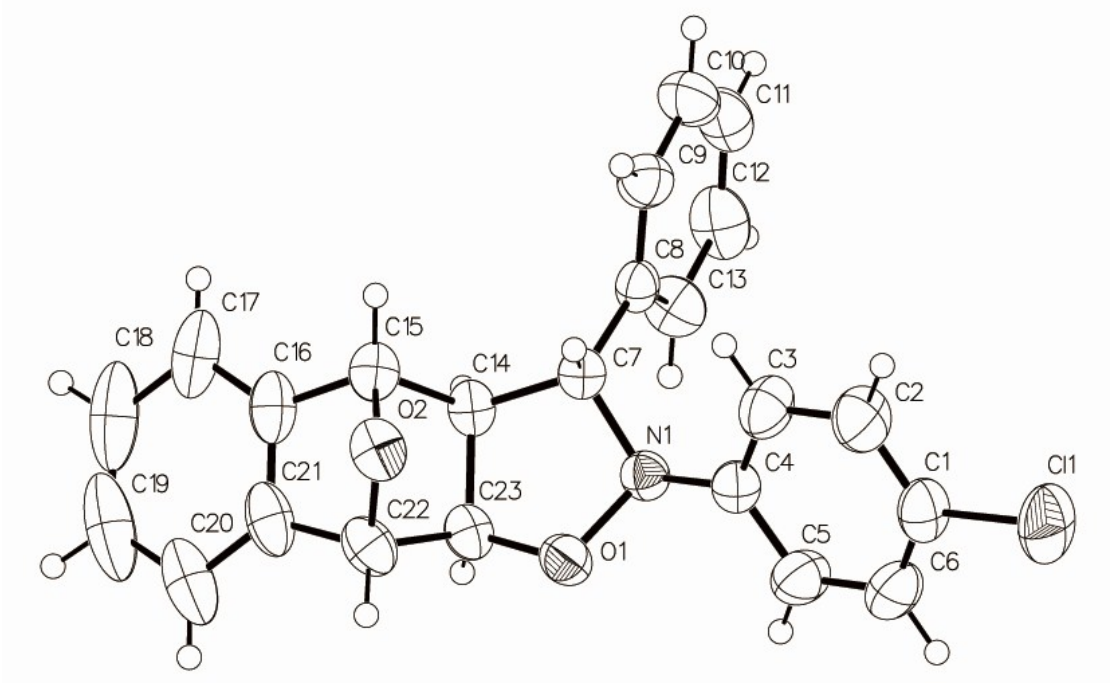

154.810
147.668
145.163
140.889
139.292
129.021
128.317
128.093
127.600
127.307
126.923
121.403
120.529
120.404
119.856
83.120
80.460
77.211
77.000
76.789
72.699
64.601
63.373
61.847
28.161
Cl
Boc
N
O
Ph
3gm
f1 (ppm)

4. X-Ray single crystal data for compound **3am** (**CCDC 1901847**)



3am





Identification code	exp_6478
Empirical formula	$C_{23}H_{18}ClNO_2$
Formula weight	375.83
Temperature	173(13) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.2832(7) A alpha = 87.027(6) deg. b = 10.0044(7) A beta = 65.546(8) deg. c = 11.1070(9) A gamma = 82.335(6) deg.
Volume	930.61(13) A^3
Z, Calculated density	2, 1.341 Mg/m^3
Absorption coefficient	0.223 mm^-1
F(000)	392
Crystal size	0.25 x 0.2 x 0.16 mm
Theta range for data collection	3.369 to 26.997 deg.
Limiting indices	-10<=h<=11, -12<=k<=12, -13<=l<=14
Reflections collected / unique	7976 / 3900 [R(int) = 0.0219]
Completeness to theta = 25.242	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.81504
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3900 / 0 / 244
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1265
R indices (all data)	R1 = 0.0775, wR2 = 0.1381
Extinction coefficient	n/a
Largest diff. peak and hole	0.218 and -0.371 e.A^-3

Table S3-1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3)

	x	y	z	U(eq)
Cl(1)	8145(1)	2701(1)	-2381(1)	76(1)
O(1)	4546(2)	3426(2)	4084(2)	45(1)
O(2)	3669(2)	1187(2)	5841(2)	48(1)
N(1)	6304(2)	3254(2)	3384(2)	39(1)
C(4)	6667(3)	3026(2)	2020(2)	39(1)
C(7)	6815(3)	2154(2)	4115(2)	36(1)
C(8)	8551(3)	2158(2)	3845(2)	38(1)
C(14)	5675(3)	2481(2)	5557(2)	40(1)
C(23)	4247(3)	3377(2)	5453(2)	41(1)
C(22)	2868(3)	2545(3)	6213(2)	48(1)
C(15)	4876(3)	1262(3)	6331(2)	47(1)
C(9)	9563(3)	961(3)	3611(3)	50(1)
C(1)	7520(3)	2795(3)	-666(2)	52(1)
C(13)	9148(3)	3341(3)	3912(3)	54(1)
C(11)	11694(3)	2106(4)	3523(3)	62(1)
C(12)	10733(3)	3309(3)	3736(3)	63(1)
C(21)	2581(3)	2573(3)	7658(3)	56(1)
C(5)	6316(3)	4092(3)	1311(3)	56(1)
C(16)	3861(3)	1743(3)	7735(2)	55(1)
C(3)	7449(3)	1829(3)	1362(2)	56(1)
C(2)	7882(4)	1712(3)	7(3)	63(1)
C(10)	11124(3)	940(3)	3455(3)	63(1)
C(6)	6735(4)	3981(3)	-30(3)	61(1)
C(20)	1420(4)	3250(3)	8760(3)	78(1)
C(17)	4033(5)	1565(4)	8909(3)	78(1)
C(19)	1565(6)	3029(5)	9946(4)	102(2)
C(18)	2850(6)	2228(5)	10017(3)	103(2)

Table S3-2. Bond lengths [A] and angles [deg]

C1(1)-C(1)	1.751(3)
O(1)-N(1)	1.478(2)
O(1)-C(23)	1.427(3)
O(2)-C(22)	1.450(3)
O(2)-C(15)	1.446(3)
N(1)-C(4)	1.432(3)
N(1)-C(7)	1.477(3)
C(4)-C(5)	1.377(3)
C(4)-C(3)	1.384(3)
C(7)-H(7)	0.9800
C(7)-C(8)	1.513(3)
C(7)-C(14)	1.533(3)
C(8)-C(9)	1.383(3)
C(8)-C(13)	1.390(3)
C(14)-H(14)	0.9800
C(14)-C(23)	1.540(3)
C(14)-C(15)	1.543(3)
C(23)-H(23)	0.9800
C(23)-C(22)	1.537(3)
C(22)-H(22)	0.9800
C(22)-C(21)	1.516(4)
C(15)-H(15)	0.9800
C(15)-C(16)	1.514(3)
C(9)-H(9)	0.9300
C(9)-C(10)	1.384(4)
C(1)-C(2)	1.369(4)
C(1)-C(6)	1.367(4)
C(13)-H(13)	0.9300
C(13)-C(12)	1.398(4)
C(11)-H(11)	0.9300
C(11)-C(12)	1.367(4)
C(11)-C(10)	1.361(4)
C(12)-H(12)	0.9300
C(21)-C(16)	1.385(4)
C(21)-C(20)	1.384(4)
C(5)-H(5)	0.9300
C(5)-C(6)	1.381(4)
C(16)-C(17)	1.377(4)
C(3)-H(3)	0.9300
C(3)-C(2)	1.394(4)
C(2)-H(2)	0.9300
C(10)-H(10)	0.9300
C(6)-H(6)	0.9300
C(20)-H(20)	0.9300
C(20)-C(19)	1.383(6)
C(17)-H(17)	0.9300
C(17)-C(18)	1.390(5)
C(19)-H(19)	0.9300
C(19)-C(18)	1.374(6)
C(18)-H(18)	0.9300

C(23)-O(1)-N(1)	104.46(16)
C(15)-O(2)-C(22)	96.75(17)
C(4)-N(1)-O(1)	106.53(16)
C(4)-N(1)-C(7)	117.91(18)
C(7)-N(1)-O(1)	103.62(15)
C(5)-C(4)-N(1)	117.7(2)
C(5)-C(4)-C(3)	118.6(2)
C(3)-C(4)-N(1)	123.6(2)
N(1)-C(7)-H(7)	110.1
N(1)-C(7)-C(8)	110.46(17)
N(1)-C(7)-C(14)	102.65(17)
C(8)-C(7)-H(7)	110.1
C(8)-C(7)-C(14)	113.36(18)
C(14)-C(7)-H(7)	110.1
C(9)-C(8)-C(7)	120.4(2)
C(9)-C(8)-C(13)	118.2(2)
C(13)-C(8)-C(7)	121.3(2)
C(7)-C(14)-H(14)	112.3
C(7)-C(14)-C(23)	104.01(18)
C(7)-C(14)-C(15)	113.63(19)
C(23)-C(14)-H(14)	112.3
C(23)-C(14)-C(15)	101.46(18)
C(15)-C(14)-H(14)	112.3
O(1)-C(23)-C(14)	106.54(17)
O(1)-C(23)-H(23)	112.6
O(1)-C(23)-C(22)	109.94(19)
C(14)-C(23)-H(23)	112.6
C(22)-C(23)-C(14)	101.92(19)
C(22)-C(23)-H(23)	112.6
O(2)-C(22)-C(23)	100.79(18)
O(2)-C(22)-H(22)	115.3
O(2)-C(22)-C(21)	101.1(2)
C(23)-C(22)-H(22)	115.3
C(21)-C(22)-C(23)	107.1(2)
C(21)-C(22)-H(22)	115.3
O(2)-C(15)-C(14)	101.43(19)
O(2)-C(15)-H(15)	115.3
O(2)-C(15)-C(16)	101.1(2)
C(14)-C(15)-H(15)	115.3
O(2)-C(22)-C(21)	101.1(2)
C(23)-C(22)-H(22)	115.3
C(21)-C(22)-C(23)	107.1(2)
C(21)-C(22)-H(22)	115.3
O(2)-C(15)-C(14)	101.43(19)
O(2)-C(15)-H(15)	115.3
O(2)-C(15)-C(16)	101.1(2)
C(14)-C(15)-H(15)	115.3
C(16)-C(15)-C(14)	106.6(2)
C(16)-C(15)-H(15)	115.3
C(8)-C(9)-H(9)	119.5
C(8)-C(9)-C(10)	121.0(3)
C(10)-C(9)-H(9)	119.5
C(2)-C(1)-C1(1)	120.0(2)
C(6)-C(1)-C1(1)	118.9(2)
C(6)-C(1)-C(2)	121.1(2)

C(8)-C(13)-H(13)	119.8
C(8)-C(13)-C(12)	120.3(3)
C(12)-C(13)-H(13)	119.8
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(10)-C(11)-C(12)	120.3(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-C(13)	119.9(3)
C(11)-C(12)-H(12)	120.0
C(16)-C(21)-C(22)	104.9(2)
C(20)-C(21)-C(22)	133.7(3)
C(20)-C(21)-C(16)	121.4(3)
C(4)-C(5)-H(5)	119.4
C(4)-C(5)-C(6)	121.2(3)
C(6)-C(5)-H(5)	119.4
C(21)-C(16)-C(15)	104.9(2)
C(17)-C(16)-C(15)	133.7(3)
C(17)-C(16)-C(21)	121.3(3)
C(4)-C(3)-H(3)	119.7
C(4)-C(3)-C(2)	120.6(3)
C(2)-C(3)-H(3)	119.7
C(1)-C(2)-C(3)	119.2(3)
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-H(2)	120.4
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-C(9)	120.3(3)
C(11)-C(10)-H(10)	119.9
C(1)-C(6)-C(5)	119.4(3)
C(1)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(21)-C(20)-H(20)	121.4
C(19)-C(20)-C(21)	117.1(4)
C(19)-C(20)-H(20)	121.4
C(16)-C(17)-H(17)	121.4
C(16)-C(17)-C(18)	117.2(4)
C(18)-C(17)-H(17)	121.4
C(20)-C(19)-H(19)	119.3
C(18)-C(19)-C(20)	121.5(3)
C(18)-C(19)-H(19)	119.3
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-C(17)	121.5(4)
C(19)-C(18)-H(18)	119.3

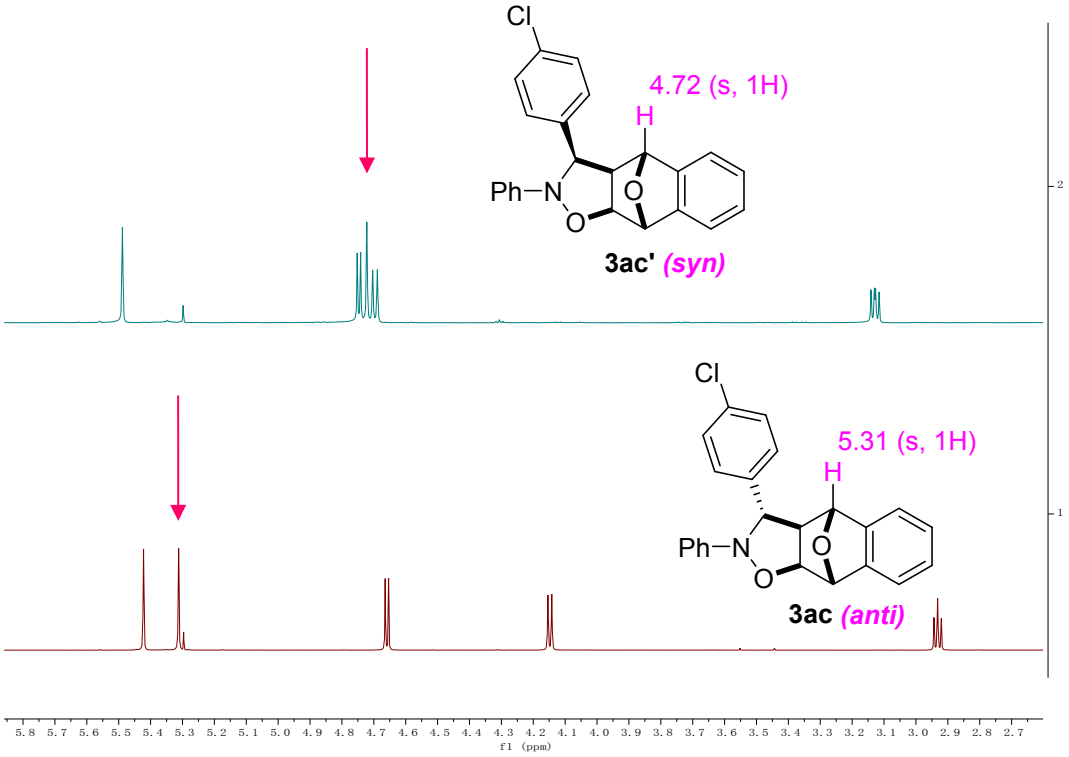
Table S3-3. Anisotropic displacement parameters (A^2 x 10^3)

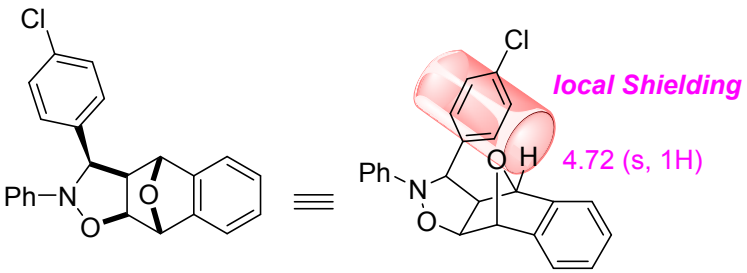
	U11	U22	U33	U23	U13	U12
C1(1)	88(1)	107(1)	39(1)	-1(1)	-28(1)	-22(1)
O(1)	37(1)	54(1)	42(1)	-4(1)	-15(1)	-1(1)
O(2)	50(1)	43(1)	51(1)	-8(1)	-16(1)	-15(1)
N(1)	37(1)	41(1)	39(1)	0(1)	-16(1)	-6(1)
C(4)	38(1)	46(1)	37(1)	0(1)	-18(1)	-10(1)
C(7)	38(1)	38(1)	35(1)	-1(1)	-16(1)	-9(1)
C(8)	38(1)	47(1)	31(1)	4(1)	-15(1)	-11(1)
C(14)	41(1)	45(1)	35(1)	-2(1)	-14(1)	-13(1)
C(23)	42(1)	40(1)	39(1)	-5(1)	-12(1)	-9(1)
C(22)	40(1)	51(1)	51(1)	-10(1)	-12(1)	-10(1)
C(15)	51(1)	48(1)	41(1)	2(1)	-16(1)	-11(1)
C(9)	48(1)	53(2)	53(2)	5(1)	-23(1)	-7(1)
C(1)	52(2)	72(2)	38(1)	0(1)	-22(1)	-17(1)
C(13)	50(2)	54(2)	64(2)	-6(1)	-25(1)	-12(1)
C(11)	42(2)	100(2)	46(2)	-1(2)	-21(1)	-13(2)
C(12)	56(2)	81(2)	59(2)	-4(2)	-24(1)	-29(2)
C(21)	52(2)	59(2)	46(1)	-8(1)	-2(1)	-27(1)
C(5)	66(2)	54(2)	49(1)	-2(1)	-28(1)	4(1)
C(16)	62(2)	59(2)	40(1)	5(1)	-11(1)	-28(1)
C(3)	75(2)	49(2)	42(1)	0(1)	-24(1)	-7(1)
C(2)	81(2)	57(2)	45(1)	-11(1)	-21(1)	0(2)
C(10)	46(2)	80(2)	62(2)	0(2)	-23(1)	2(1)
C(6)	70(2)	69(2)	47(2)	8(1)	-30(1)	0(2)
C(20)	67(2)	83(2)	58(2)	-19(2)	8(2)	-28(2)
C(17)	98(3)	94(2)	41(2)	19(2)	-20(2)	-44(2)
C(19)	106(3)	116(3)	49(2)	-24(2)	17(2)	-54(3)
C(18)	138(4)	127(4)	36(2)	6(2)	-13(2)	-70(3)

Table S3-4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3)

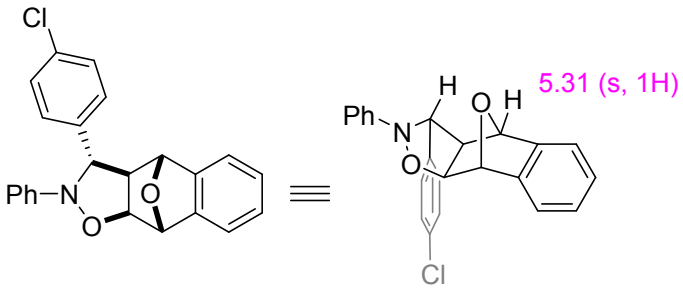
	x	y	z	U(eq)
H(7)	6650	1283	3860	43
H(14)	6170	2933	6023	48
H(23)	4073	4275	5838	49
H(22)	1916	2777	6034	58
H(15)	5600	430	6246	57
H(9)	9189	159	3557	61
H(13)	8490	4158	4074	65
H(11)	12741	2084	3425	74
H(12)	11133	4105	3763	76
H(5)	5789	4901	1742	67
H(3)	7687	1096	1827	67
H(2)	8411	907	-434	76
H(10)	11787	126	3303	76
H(6)	6485	4707	-496	73
H(20)	579	3828	8704	93
H(17)	4903	1025	8957	94
H(19)	775	3431	10713	123
H(18)	2930	2126	10825	123

5. Local shielding effect of **3ac** and **3ac'** [a,b,c]



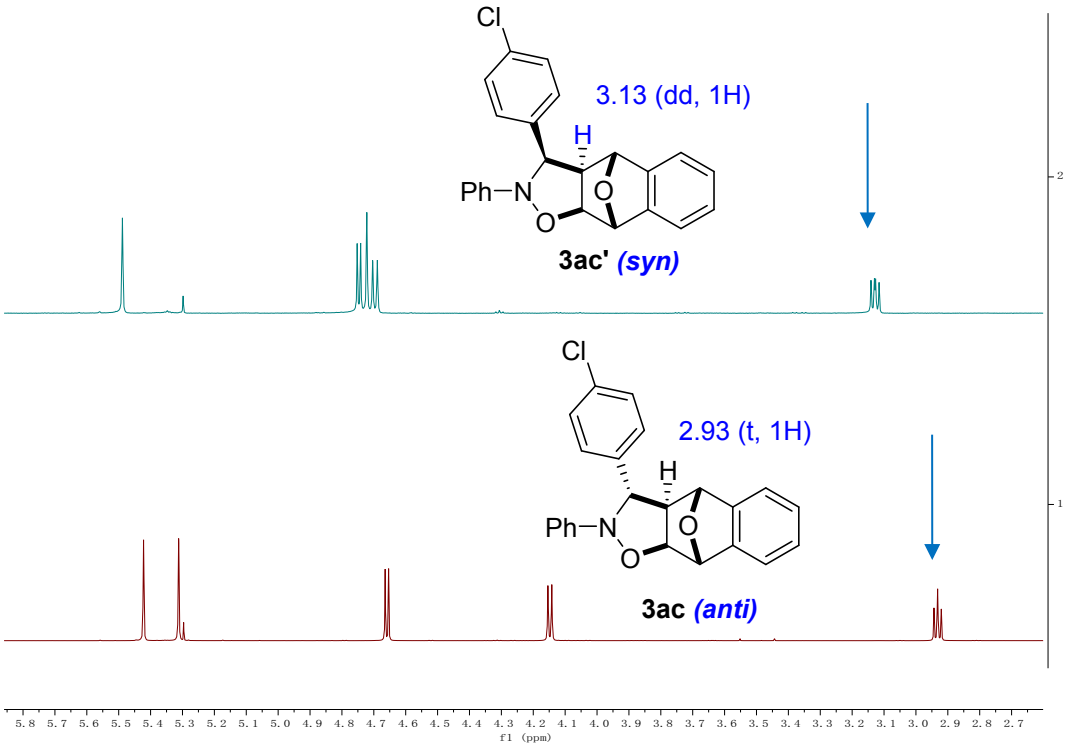


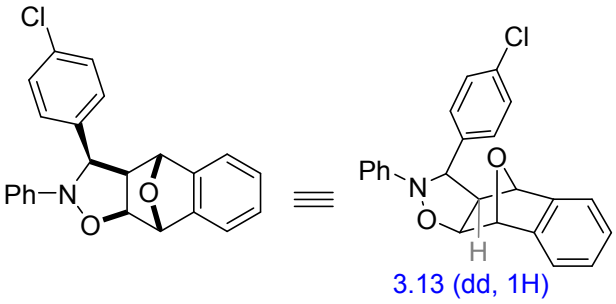
minor product *(syn)*



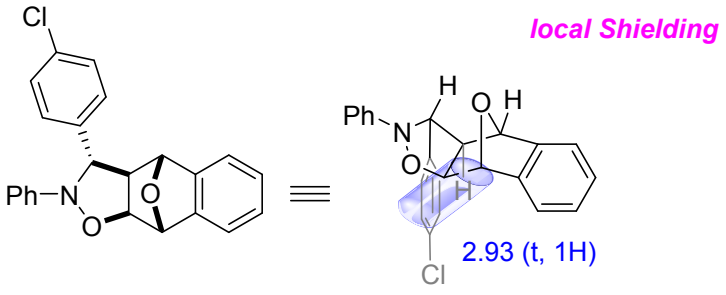
major product *(anti)*

[a]The chemical shift of the bridgehead hydrogen decreased from δ 5.31 (*anti*) to δ 4.72 (*syn*) by the local shielding effects of chlorophenyl group.





minor product *(syn)*



major product *(anti)*

[b]The chemical shift of the *endo*-hydrogen decreased from δ 3.31 (*syn*) to δ 2.93 (*anti*) by the local shielding effects of chlorophenyl group.

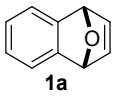
[c]*anti*-Adduct **3ac** was the major cycloaddition product.

6. References

1 (a) R. R. Burton, W. Tam, *J. Org. Chem.,* 2007, **72**, 7333; (b) D.-Q. Yang, Y.-H. Long, H. Wang, Z.-M. Zhang, *Org. Lett.,* 2008, **10**, 4723; (c) H.-C. Cheng, D.-Q. Yang, *J. Org. Chem.,* 2012, **77**, 9756; (d) L. Meng, W. Yang, X.-J. Pan, M. Tao, G. Cheng, S.-Y. Wang, H.-P. Zeng, Y.-H. Long, D.-Q. Yang, *J. Org. Chem.,* 2015, **80**, 2503; (e) Y. Li, W. Yang, G. Cheng, D.-Q. Yang, *J. Org. Chem.,* 2016, **81**, 4744; (f) R.-H. Wu, W. Yang, W.-K. Chen, D.-Q. Yang, *Org. Chem. Front.,* 2017, **4**, 1921; (g) X. Yang, W. Yang, Y, -Q. Yao, Y.-Y. Deng, X.-J. Zuo, D.-Q. Yang, *J. Org. Chem.,* 2018, **83**, 10097; (h) Y.-Q. Yao, W. Yang, C.-Y. Wang, F.-L. Gu, W.-T. Yang, D.-Q. Yang, *Asian J. Org. Chem.,* 2019, **8**, 506.

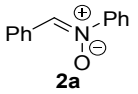
2 (a) D. A. Evans, H.-J. Song, K. R. Fandrick, *Org. Lett.,* 2006, **8**, 3351; (b) B. M. Dooley, S.-E. Bowles, T. Storr, N. Frank, *Org. Lett.,* 2007, **9**, 4781; (c) C.-X. Wang, D.-P. Wang, H. Yan, H.-L. Wang, B. Pan, X.-Y. Xin, X.-C. Li, F. Wu, B.-S. Wan, *Angew. Chem., Int. Ed.,* 2014, **53**, 11940; (d) L.-W. Zheng, F. Gao, C. Yang, G.-L. Gao, Y.-T. Zhao, Y. Gao, W.-J. Xia, *Org. Lett.,* 2017, **19**, 5086; (e) M. Choi, M. Viji, D. Kim, Y.-H. Lee, J. Sim, Y.-S. Kwak, K. Lee, H. Lee, J.-K. Jung, *Tetrahedron,* 2018, **74**, 4182; (f) L. Ke, G.-R. Zhu, H. Qian, G.-Y. Xiang, Q. Chen, Z.-L. Chen, *Org. Lett.,* 2019, **21**, 4008; (g) X. Li, T. Feng, D.-J. Li, H.-H. Chang, W.-C. Gao, W.-L. Wei, *J. Org. Chem.,* 2019, **84**, 4402.

7. Coordinates of DFT-computed stationary points



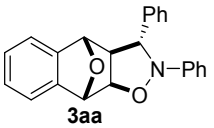
1a

C	-2.58246500	-0.69483300	0.16296100
C	-2.58252500	0.69469200	0.16293800
C	-1.38418600	1.41702200	0.00476600
C	-0.21717700	0.70197400	-0.15600000
C	-0.21711200	-0.70193600	-0.15598700
C	-1.38406600	-1.41706900	0.00480600
C	1.26190300	1.07463400	-0.34695800
C	1.98967000	0.66535900	0.94988300
C	1.98993100	-0.66549400	0.94962500
C	1.26197700	-1.07451100	-0.34717800
O	1.67008200	0.00016300	-1.22738900
H	-3.51741300	-1.23105200	0.28105400
H	-3.51751600	1.23083600	0.28103600
H	-1.39287500	2.50174000	0.00386700
H	-1.39267800	-2.50178800	0.00386200
H	1.48879400	2.04687100	-0.77539000
H	2.33299600	1.34788800	1.71393900
H	2.33347200	-1.34818900	1.71343500
H	1.48886900	-2.04664300	-0.77584700



2a

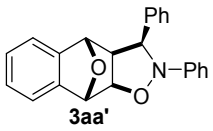
C	3.91871300	-1.05437900	-0.25688700
C	4.69114900	0.07203100	0.02048000
C	4.06281100	1.28046800	0.32754400
C	2.67831200	1.35543700	0.35398100
C	1.88208200	0.22345800	0.07431600
C	2.52911700	-0.99207800	-0.23114400
C	0.44871900	0.40810400	0.12400600
N	-0.47559800	-0.50644400	-0.10382500
C	-1.88584500	-0.12698900	-0.04568700
O	-0.24542800	-1.74101500	-0.34949700
C	-2.77825500	-1.06670800	0.46415900
C	-4.13055200	-0.75105400	0.53441900
C	-4.58991400	0.48605300	0.08181200
C	-3.69036400	1.40751500	-0.44946300
C	-2.33193800	1.10500700	-0.51903400
H	4.40227400	-1.99532700	-0.49470000
H	5.77330000	0.01106400	-0.00059500
H	4.65450100	2.16228000	0.54556800
H	2.19637700	2.29807100	0.59209200
H	1.92670800	-1.86184400	-0.44054000
H	0.07069500	1.38543500	0.38435600
H	-2.39754400	-2.02592600	0.78636000
H	-4.82759300	-1.47471700	0.94042900
H	-5.64577800	0.72502200	0.13135400
H	-4.04384600	2.36001800	-0.82641200
H	-1.64070100	1.80796500	-0.96616500



3aa

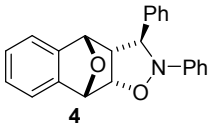
C	5.50878100	0.72617100	0.21590000
C	5.64442100	-0.57022500	0.70903300
C	4.59797600	-1.49670800	0.59493100
C	3.43982700	-1.09051700	-0.04339100
C	3.30312800	0.21332900	-0.53782300
C	4.32243800	1.13936800	-0.40739800
C	2.10457500	-1.75168200	-0.34084600
C	1.07844100	-1.15181500	0.65716200
C	0.90711200	0.28960500	0.09733800
C	1.89283600	0.26115400	-1.10530700
O	1.72690000	-1.09555000	-1.57187100
O	-0.17632900	-1.79455400	0.48790800
N	-1.17490000	-0.73168100	0.51964100
C	-0.59000100	0.35203300	-0.29723500
C	-2.43104800	-1.29012400	0.18320600
C	-1.20221200	1.70919900	-0.00832600
C	-1.35401900	2.63356800	-1.04573900
C	-1.85209900	3.91100500	-0.79298100
C	-2.21153500	4.27601300	0.50215600
C	-2.06826100	3.35695100	1.54143700
C	-1.56377300	2.08397100	1.28997500
C	-3.38074800	-0.58162700	-0.56533400
C	-4.63861300	-1.13435800	-0.80188700
C	-4.96629100	-2.39742800	-0.31971900
C	-4.01583600	-3.10804200	0.41442900
C	-2.76383000	-2.56478100	0.67154700
H	6.33361800	1.42325900	0.31131100
H	6.57305800	-0.86770600	1.18277100
H	4.70763200	-2.50184700	0.98705500

H	4.22147700	2.15222500	-0.78172300
H	2.07176300	-2.83195600	-0.45183000
H	1.40043200	-1.19329000	1.70071200
H	1.15363300	1.06226500	0.82315500
H	1.69596500	0.96946600	-1.90659400
H	-0.69122800	0.11437300	-1.36450500
H	-1.08890200	2.35022900	-2.05945800
H	-1.96486400	4.61606600	-1.60895700
H	-2.60528700	5.26644200	0.70033300
H	-2.35301900	3.63155200	2.55105600
H	-1.46189400	1.36675900	2.09563800
H	-3.15483600	0.40136700	-0.95274700
H	-5.36097400	-0.56764300	-1.37907900
H	-5.94347300	-2.82405400	-0.51337200
H	-4.25095100	-4.09631600	0.79431400
H	-2.03003600	-3.11895400	1.23936700



3aa'

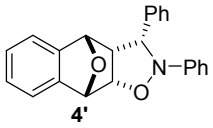
C	-5.51110600	0.21089900	-0.62478300
C	-5.58431400	-1.12370600	-0.22937200
C	-4.45913100	-1.78509700	0.28324500
C	-3.28459300	-1.06423000	0.40817500
C	-3.21052100	0.27676300	0.00856900
C	-4.31050500	0.92799700	-0.52083100
C	-1.87414900	-1.39691900	0.86454700
C	-1.01461200	-1.49542900	-0.43191400
C	-0.89637600	0.00281900	-0.84145100
C	-1.76407600	0.67512400	0.26332200
O	-1.44764500	-0.13374800	1.41689500
O	0.30329800	-1.98058200	-0.24030200
N	1.15460300	-0.83044100	0.04668700
C	0.63666500	0.26610400	-0.79183000
C	2.50184000	-1.23931900	-0.07121300
C	1.19143100	2.69127800	-1.16514100
C	1.49869100	3.97249400	-0.71140600
C	1.64558600	4.21194300	0.65346700
C	1.48026900	3.16387200	1.55781800
C	1.16613000	1.88412700	1.10568000
C	1.01923800	1.63661900	-0.26293400
C	3.49682400	-0.37884900	-0.55791400
C	4.82833700	-0.79107300	-0.58175100
C	5.19213500	-2.06050600	-0.14410700
C	4.20071200	-2.92100700	0.32909800
C	2.87165600	-2.52051700	0.37331900
H	-6.39609300	0.70250500	-1.01285700
H	-6.52517000	-1.65563200	-0.31448100
H	-4.52133700	-2.82576300	0.58222700
H	-4.25947700	1.96433900	-0.83671400
H	-1.73038700	-2.20485800	1.57678300
H	-1.46772600	-2.14660100	-1.17947100
H	-1.27697200	0.21652400	-1.83893800
H	-1.56019600	1.72269100	0.46160000
H	1.01866700	0.16598100	-1.81866300
H	1.09210800	2.50779900	-2.23058600
H	1.63081200	4.77927200	-1.42372500
H	1.89175300	5.20609000	1.00913700
H	1.59690100	3.34187400	2.62107100
H	1.02938100	1.06942300	1.80493700
H	3.24636600	0.61441300	-0.90188200
H	5.58242400	-0.10758700	-0.95651200
H	6.22842700	-2.37635000	-0.17094200
H	4.46374900	-3.91583600	0.67189900
H	2.10853900	-3.19086700	0.74200100



4

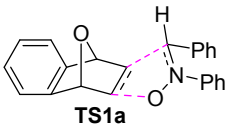
C	-3.49301300	0.87261900	1.94929500
C	-3.86610500	1.44909300	0.73693800
C	-3.56936000	0.82169000	-0.48097900
C	-2.91162700	-0.39328200	-0.43900900
C	-2.53297100	-0.97248200	0.77978700
C	-2.80758400	-0.35042300	1.98405500
C	-2.41976700	-1.36193900	-1.49170600
C	-0.85874000	-1.29211100	-1.59924400
C	-0.42052400	-1.91365200	-0.24345300
C	-1.81342900	-2.24716000	0.39081000
O	-2.54134200	-2.63085000	-0.80442500
O	-0.25609500	-0.00836200	-1.68871100
N	0.00482200	0.38357300	-0.31976900
C	0.45939200	-0.81871300	0.40013000
C	1.94777000	-1.13649900	0.32896800
C	2.59513800	-1.63931400	1.46095200
C	3.94641200	-1.97860400	1.41965500

C	4.67077700	-1.80961900	0.24209600
C	4.03556000	-1.29971400	-0.88959400
C	2.68392200	-0.96669900	-0.84897400
C	0.62318800	1.63185000	-0.23240000
C	0.55900700	2.54753700	-1.29580700
C	1.10115100	3.82107400	-1.15246700
C	1.71234400	4.21323400	0.03647000
C	1.77780800	3.30250000	1.09045500
C	1.24686500	2.02422000	0.96575100
H	-3.74088100	1.37396800	2.87806100
H	-4.39762200	2.39397300	0.73634800
H	-3.85406400	1.28034500	-1.42121800
H	-2.51698600	-0.79164100	2.93151200
H	-2.94780100	-1.38762100	-2.44136600
H	-0.51910000	-1.85027100	-2.47073500
H	0.13836300	-2.83796300	-0.37335700
H	-1.81085700	-3.06212700	1.11028700
H	0.17656400	-0.68249500	1.44755300
H	2.03896400	-1.76449300	2.38530000
H	4.43288000	-2.36621600	2.30788700
H	5.72325900	-2.06717800	0.20737600
H	4.59505900	-1.15773300	-1.80750500
H	2.19889800	-0.56397900	-1.72990500
H	0.08486800	2.25274500	-2.22037900
H	1.04303200	4.51270000	-1.98616600
H	2.13312000	5.20634800	0.13981200
H	2.25440200	3.58426400	2.02312600
H	1.31637700	1.33442700	1.79646200



4'

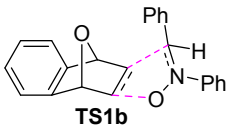
C	2.37251400	-0.30314600	2.73565300
C	2.37897800	-1.68893900	2.58385100
C	2.38257000	-2.27103300	1.30922000
C	2.38816800	-1.42772600	0.21341100
C	2.34856300	-0.03613300	0.36346300
C	2.34890800	0.54408500	1.61960200
C	2.44937200	-1.64556700	-1.28015400
C	1.05732300	-1.31372200	-1.91236200
C	1.02776500	0.22954700	-1.82460000
C	2.36480100	0.50909000	-1.05264500
O	3.19756200	-0.48255400	-1.71456800
O	-0.08920900	-1.80114400	-1.22833400
N	-0.66863000	-0.68354300	-0.46086600
C	-0.36617900	0.52833100	-1.23902500
C	-0.45816600	1.82258600	-0.44502400
C	-0.57728100	1.85869400	0.94554600
C	-0.65671200	3.07920800	1.61569300
C	-0.61261000	4.27778500	0.90797000
C	-0.49640200	4.25046600	-0.48131900
C	-0.42630000	3.03187800	-1.15075800
C	-2.01516700	-1.02537500	-0.18175400
C	-2.29689500	-2.32179800	0.28046100
C	-3.59531200	-2.67797800	0.61783800
C	-4.63690000	-1.75305000	0.51973500
C	-4.35938300	-0.46820700	0.06626000
C	-3.06243100	-0.10202800	-0.29495900
H	2.39150100	0.12526300	3.73159000
H	2.39813200	-2.32336900	3.46292000
H	2.39907800	-3.34907900	1.19423100
H	2.33335000	1.61999500	1.74605600
H	2.91856600	-2.55796300	-1.63901700
H	1.00132800	-1.69745300	-2.93202400
H	1.12434200	0.69358100	-2.80528500
H	2.77642400	1.50462200	-1.19444300
H	-1.05789400	0.60414700	-2.09338900
H	-0.60835000	0.93078900	1.50046100
H	-0.75579600	3.08951900	2.69548800
H	-0.67541700	5.22490300	1.43174600
H	-0.46812900	5.17657300	-1.04445700
H	-0.35239100	3.02050000	-2.23387600
H	-1.49000800	-3.03679900	0.36110500
H	-3.79493000	-3.68511600	0.96709300
H	-5.64768800	-2.03325000	0.79233800
H	-5.15588200	0.26256900	-0.02077900
H	-2.87799900	0.90314100	-0.64711400



TS1a

C	5.16458700	-1.21635700	0.95069500
C	5.39000000	-0.87570100	-0.37842500
C	4.37901700	-0.27431500	-1.15013000
C	3.16462500	-0.02701800	-0.54416300
C	2.93613300	-0.37248900	0.79775400

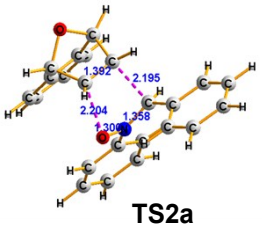
C	3.92000200	-0.96889100	1.55862700
C	1.83290000	0.57701300	-1.00971500
C	0.83960500	-0.58583900	-1.07883300
C	0.59342300	-0.93057100	0.24604900
C	1.48124200	0.04149800	1.05001500
O	1.40437900	1.21829600	0.21442800
O	-1.02098100	0.34398900	-1.64685000
N	-1.50077000	0.64419700	-0.47570400
C	-1.53860600	-0.35225100	0.44073100
C	-1.59491600	2.02955000	-0.11640600
C	-2.13752800	-1.67385400	0.17394200
C	-2.46562900	-2.46918400	1.28521900
C	-3.05814400	-3.71686800	1.12431800
C	-3.34529400	-4.19394800	-0.15362500
C	-3.03056700	-3.41064200	-1.26336000
C	-2.42329800	-2.16791000	-1.10933900
C	-2.33770700	2.43250000	0.99781800
C	-2.44632500	3.78694100	1.30290600
C	-1.84466000	4.74521900	0.49112300
C	-1.13607900	4.33661600	-0.63911300
C	-1.01162700	2.98801600	-0.94788400
H	5.95982900	-1.67402200	1.52849800
H	6.35868100	-1.07071100	-0.82479200
H	4.56278800	-0.00939900	-2.18588600
H	3.75351100	-1.23640600	2.59669400
H	1.85875800	1.27897000	-1.83762600
H	0.75523400	-1.23475400	-1.93594500
H	0.41271300	-1.94210700	0.57981100
H	1.19578200	0.27102400	2.07339200
H	-1.65023000	-0.00582200	1.46110800
H	-2.26014000	-2.09995800	2.28511900
H	-3.30275300	-4.31252600	1.99666200
H	-3.80905100	-5.16517000	-0.28300200
H	-3.25310600	-3.77274900	-2.26106400
H	-2.16745600	-1.56821100	-1.97117400
H	-2.85637100	1.70554300	1.60925200
H	-3.02157100	4.09029100	2.17018100
H	-1.93862000	5.79864000	0.72732000
H	-0.67306800	5.07397200	-1.28503800
H	-0.47365300	2.65663100	-1.82342800



TS1b

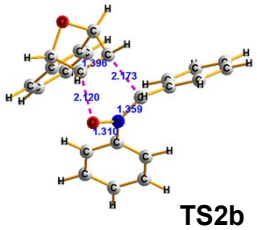
C	5.32434000	1.03708600	-0.87633400
C	5.65052500	-0.23528400	-0.42030000
C	4.64877100	-1.12803900	0.00303500
C	3.33788300	-0.70283100	-0.05629300
C	3.00795100	0.58260900	-0.51525000
C	3.98488600	1.46539000	-0.92653000
C	1.98715100	-1.32945200	0.31097000
C	1.49525900	-0.59398000	1.56061300
C	1.15015200	0.67806200	1.11169300
C	1.48106300	0.64851200	-0.38877100
O	1.14364600	-0.72571000	-0.70077200
O	-0.33652200	-1.44278500	2.04754400
N	-1.19159400	-0.75920500	1.33358300
C	-1.06821000	0.58442500	1.42626200
C	-1.98014700	-1.49280100	0.38168600
C	-2.19004300	2.76319100	1.15293600
C	-2.76783100	3.76921700	0.38407800
C	-2.88284700	3.61397300	-0.99565800
C	-2.40728800	2.44921100	-1.59947000
C	-1.82870700	1.44306500	-0.83410600
C	-1.72451300	1.57801600	0.56132400
C	-3.33324400	-1.18040900	0.22906000
C	-4.12281200	-1.93536900	-0.63317400
C	-3.57563800	-3.01378400	-1.32598900
C	-2.23199600	-3.33937400	-1.14198100
C	-1.43334400	-2.58826200	-0.28614500
H	6.11195900	1.70705000	-1.20286300
H	6.68900500	-0.54604800	-0.39541100
H	4.91012700	-2.12010800	0.35561700
H	3.73938200	2.45925300	-1.28540400
H	1.91551300	-2.41341900	0.29536800
H	1.84101200	-0.84829600	2.55051000
H	1.26325700	1.57973300	1.69809600
H	0.95398600	1.33886900	-1.04175500
H	-0.84493900	0.90444000	2.43477900
H	-2.10190600	2.89031100	2.22675700
H	-3.12747000	4.67293300	0.86289400
H	-3.33188400	4.39575800	-1.59748900
H	-2.48175200	2.32625000	-2.67403700
H	-1.45342300	0.55055900	-1.31745100
H	-3.76402000	-0.35936400	0.78718900
H	-5.17171300	-1.68775500	-0.74916800
H	-4.19371200	-3.60407100	-1.99250600
H	-1.80098600	-4.18388000	-1.66758500

H	-0.39643600	-2.83885100	-0.12674800



TS2a

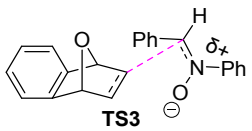
C	-3.47781700	-0.56436200	1.35897900
C	-3.86086300	-0.70659700	0.02846700
C	-3.02506900	-1.34891500	-0.89779100
C	-1.82171100	-1.84926900	-0.44318100
C	-1.44202300	-1.72174300	0.90021100
C	-2.24972500	-1.07120100	1.81242400
C	-0.71453000	-2.68620300	-1.06995200
C	0.60910200	-1.89950500	-1.10607900
C	0.98799500	-1.76653900	0.22645000
C	-0.13570900	-2.49822100	0.99909900
O	-0.43075300	-3.57763500	0.05477400
O	0.46114000	0.22275500	-1.68216300
N	0.34147700	0.79223200	-0.52018900
C	1.21721300	0.40613400	0.44352600
C	2.68202300	0.46054200	0.24596000
C	3.49060600	0.45894200	1.39463600
C	4.87563800	0.54108800	1.29628400
C	5.48256500	0.63553400	0.04516700
C	4.68921500	0.64377500	-1.10143000
C	3.30384700	0.54668100	-1.00967100
C	-0.80151400	1.62420000	-0.28084300
C	-1.74674800	1.76263500	-1.30091200
C	-2.80525000	2.65042100	-1.14999100
C	-2.93788400	3.40878500	0.01179900
C	-1.98710400	3.27763400	1.02183200
C	-0.91408000	2.40361400	0.87735800
H	-4.14220200	-0.06772300	2.05694700
H	-4.82028200	-0.31969500	-0.29549100
H	-3.33008500	-1.45719200	-1.93294600
H	-1.96603100	-0.97321000	2.85496400
H	-0.96060200	-3.25076000	-1.96501000
H	1.26607000	-1.93110700	-1.95845000
H	2.00776300	-1.88142500	0.56065000
H	0.13231500	-2.90011100	1.97251300
H	0.89903500	0.65750600	1.44833700
H	3.02690300	0.40096400	2.37446900
H	5.47950000	0.53953600	2.19682100
H	6.56154200	0.70135900	-0.03534700
H	5.15261000	0.71943900	-2.07894100
H	2.69193800	0.54003200	-1.90086400
H	-1.62447300	1.17762900	-2.19994900
H	-3.53021300	2.75040500	-1.94993200
H	-3.76179700	4.10387500	0.12295200
H	-2.06396000	3.87446300	1.92353700
H	-0.16053500	2.36485600	1.65213300



TS2b

C	-2.12075500	0.70280200	2.49461600
C	-3.15956100	1.06821200	1.64344000
C	-3.42212200	0.33684800	0.47441900
C	-2.62261400	-0.75558300	0.20136500
C	-1.58263300	-1.13374300	1.06269200
C	-1.31549000	-0.41247600	2.21139900
C	-2.66601600	-1.86078800	-0.84152400
C	-1.39953600	-1.84434400	-1.71865800
C	-0.36474500	-2.24631000	-0.87164700
C	-1.07356600	-2.45252000	0.48951300
O	-2.34990200	-3.00237500	0.01824400
O	-0.69732600	0.04254100	-2.38332800
N	0.29181500	0.32884600	-1.57320200
C	1.11716500	-0.71876600	-1.31246200
C	2.20623000	-0.76645900	-0.31666800
C	2.09354800	-0.27659100	0.99436300
C	3.14234800	-0.41946800	1.89497100
C	4.32126900	-1.06270900	1.51424900
C	4.44069700	-1.56739500	0.22195300
C	3.39132500	-1.42362700	-0.68201200
C	0.30231000	1.63644800	-0.98295200
C	-0.90121400	2.31762300	-0.80130300
C	-0.89047900	3.62637700	-0.33092800
C	0.31365800	4.27261300	-0.05647400
C	1.51504800	3.60065500	-0.27671000
C	1.51661100	2.29311800	-0.75163300

H	-1.94459600	1.27307100	3.39971200
H	-3.78297200	1.91906200	1.89428300
H	-4.24324000	0.61511800	-0.17751200
H	-0.53217400	-0.71172400	2.89901100
H	-3.60522700	-2.01423000	-1.36576300
H	-1.46152000	-2.04010600	-2.77647100
H	0.37593700	-2.97958600	-1.15810600
H	-0.59236400	-3.13700600	1.18226500
H	1.30041800	-1.29973100	-2.20686900
H	1.18415800	0.21842100	1.30583200
H	3.03851200	-0.03086700	2.90185600
H	5.13520100	-1.17341200	2.22151500
H	5.34902800	-2.07349600	-0.08463300
H	3.48999300	-1.82124800	-1.68661000
H	-1.82454100	1.81545000	-1.04221000
H	-1.83145700	4.14398300	-0.18284800
H	0.31718200	5.29413800	0.30562100
H	2.46034200	4.10073000	-0.09909500
H	2.45357900	1.79468500	-0.95694100



TS3

C	5.04043100	-2.18839700	0.95666800
C	5.71001300	-1.63742900	-0.13064600
C	5.09853400	-0.65805200	-0.93409100
C	3.82142300	-0.25588900	-0.60070900
C	3.14407500	-0.81316000	0.49646400
C	3.73372700	-1.78086000	1.28249900
C	2.81016100	0.73786100	-1.19360500
C	1.70289400	-0.12711400	-1.79718400
C	1.00681400	-0.64415200	-0.72851800
C	1.77847900	-0.11528200	0.49805600
O	2.16573000	1.19283000	0.01678000
C	-1.06169300	0.24965000	-0.53215400
N	-1.73378800	-0.75189700	0.27397400
C	-1.01133200	1.60318800	-0.02914400
C	-1.23277700	1.91182100	1.32995500
O	-1.10662300	-1.25872800	1.27362300
C	-1.15806500	3.22558800	1.77503300
C	-0.85879000	4.25935000	0.88694300
C	-0.63316900	3.96750600	-0.46139700
C	-0.70572700	2.66002700	-0.91441700
C	-3.05985900	-1.15961600	0.00219700
C	-3.84994300	-0.49043800	-0.94619300
C	-5.14756100	-0.92742800	-1.19095200
C	-5.67103500	-2.02326100	-0.50645700
C	-4.88227300	-2.68148300	0.43982200
C	-3.58664000	-2.25865200	0.70026300
H	5.53297200	-2.93913400	1.56448800
H	6.71871000	-1.96280200	-0.35955100
H	5.62730500	-0.23303400	-1.78054800
H	3.21696000	-2.21556800	2.13114000
H	3.19755900	1.57016300	-1.77529500
H	1.61705700	-0.39214600	-2.84152900
H	0.49412000	-1.59487600	-0.72591900
H	1.23307700	-0.05456500	1.43253000
H	-1.22965800	0.11418600	-1.59202800
H	-1.46314500	1.11585400	2.02681800
H	-1.33541800	3.44598500	2.82175800
H	-0.80138800	5.28251700	1.23995700
H	-0.39976700	4.76620300	-1.15663800
H	-0.52185100	2.43740300	-1.95986200
H	-3.46687700	0.37508800	-1.46943800
H	-5.75403500	-0.40123800	-1.91917900
H	-6.68222500	-2.35856600	-0.70405700
H	-5.28073600	-3.53289800	0.97990100
H	-2.96512800	-2.75479600	1.43180100