

Supplementary information

Organocatalytic Asymmetric Synthesis of Atropisomeric Tetraarylethenes: Design, Properties, and Applications

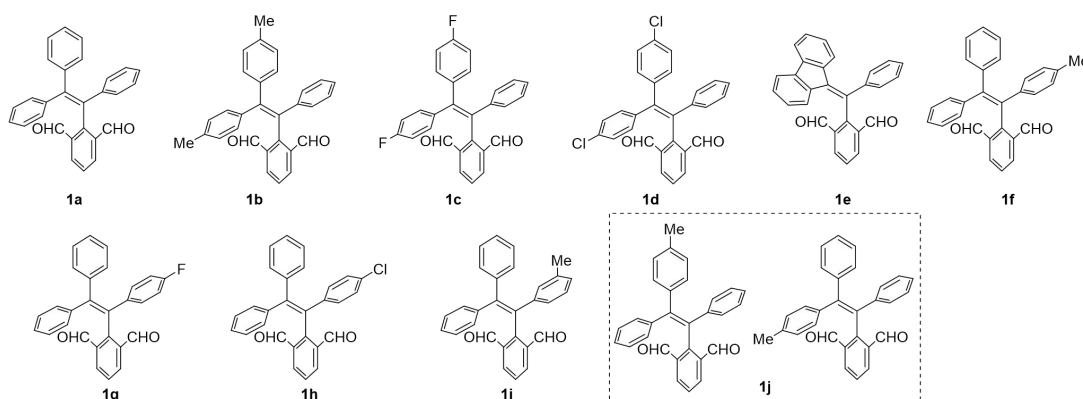
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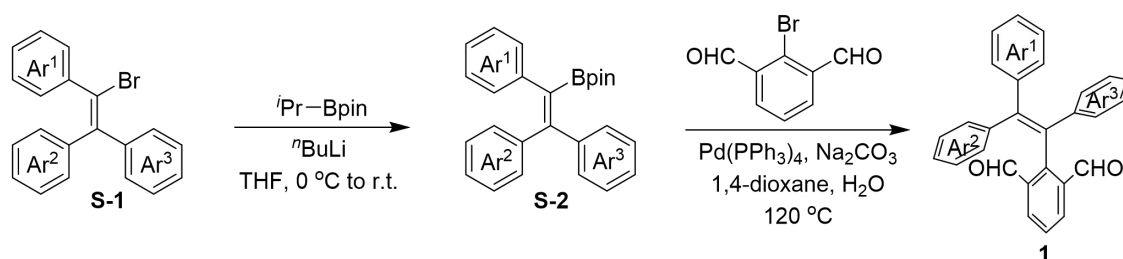
1. General Information

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. Solvents were dried and distilled before use by standard procedures. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (200-300 mesh). ^1H NMR spectra were recorded on a Bruker Avance operating at for ^1H NMR at 400 MHz and 600 MHz, ^{13}C NMR at 101 MHz and 151 MHz, ^{19}F NMR at 565 MHz and 367 MHz, and chemical shifts (δ) are reported in ppm relative to those of residual solvent signals: CDCl_3 (^1H NMR δ 7.26, ^{13}C NMR δ 77.00), DMSO- d_6 (^1H NMR δ 2.5, ^{13}C NMR δ 39.5). All coupling constants (J) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were recorded on Waters Xevo G2-XS QToF mass spectrometer. The enantiomeric excesses of the products were determined by HPLC analysis on Shimadzu LC-20AT using Chiralpak AD-H (4.6 mm Φ \times 250 mmL), OD-H (4.6 mm Φ \times 250 mmL), IA (4.6 mm Φ \times 250 mmL), IC (4.6 mm Φ \times 250 mmL), OX-H (4.6 mm Φ \times 250 mmL) columns purchased from Daicel Chemical Industries. Unless otherwise noted, materials were purchased from Energy Chemical Co., Bidepharm, Alfa Aesar, and other commercial suppliers and used as received. Solvents were dried over sodium (for THF, dioxane, toluene) and freshly distilled prior to use. Compound **S-1** were prepared following a literature procedure (28).

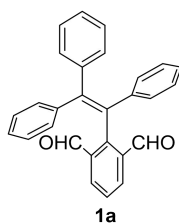
2. General Procedure for Synthesis of Starting Materials



Procedure A:



Under a nitrogen atmosphere, THF was added to a round-bottomed flask containing **S-1** (8 mmol). The mixture was cooled to $-78\text{ }^{\circ}\text{C}$, then $n\text{-BuLi}$ (1.1 equiv.) was added followed by 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 equiv.). The mixture was stirred for 20 minutes. The temperature was raised to room temperature and H_2O (40 mL) was added. The mixture was stirred for 15 minutes, the aqueous phase was extracted with ethyl acetate ($20\text{ mL} \times 3$) and the combined organic layer was washed with brine ($10\text{ mL} \times 3$), then dried over Na_2SO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography. Under a nitrogen atmosphere, 1,4-dioxane was added to a pressure-resistant bottle containing **S-2** (1.5 equiv.), 2-Bromoisophthalaldehyde (1 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.05 equiv.), followed by the addition of a sodium carbonate aqueous solution. The mixture was stirred at $120\text{ }^{\circ}\text{C}$ for 24 h, The aqueous phase was extracted with ethyl acetate ($20\text{ mL} \times 3$) and the combined organic layer was washed with brine ($10\text{ mL} \times 3$), then dried over Na_2SO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography to give the corresponding brominated product **1**.

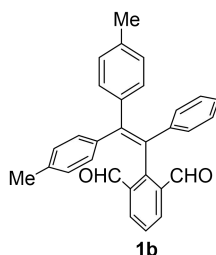


2-(1,2,2-triphenylvinyl)isophthalaldehyde (1a) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1a** as a yellow solid (338 mg, 87% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.47 (d, *J* = 0.7 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.23 – 7.17 (m, 3H), 7.15 – 7.09 (m, 5H), 7.06 – 7.02 (m, 3H), 7.01 – 6.98 (m, 2H), 6.93 – 6.87 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 190.4, 148.4, 141.1, 139.3, 137.4, 136.6, 134.2, 134.0, 129.8, 129.3, 128.9, 127.3, 126.9, 125.1, 124.4, 119.8, 119.7.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₁O₂⁺ 389.1536; Found 389.1529.

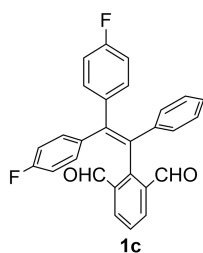


2-(1-phenyl-2,2-di-p-tolylvinyl)isophthalaldehyde (1b) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1b** as a yellow solid (291 mg, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.45 (d, *J* = 0.8 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.14 – 7.09 (m, 3H), 7.02 – 6.99 (m, 4H), 6.98 – 6.94 (m, 2H), 6.85 – 6.81 (m, 2H), 6.77 – 6.74 (m, 2H), 2.31 (s, 3H), 2.17 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 191.2, 149.4, 147.1, 142.2, 139.2, 138.7, 137.2, 134.9, 133.3, 130.8, 130.4, 129.9, 128.8, 128.3, 128.0, 127.2, 21.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₀H₂₅O₂⁺ 417.1849; Found 417.1841.



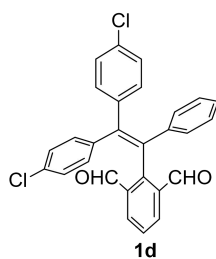
2-(2,2-bis(4-fluorophenyl)-1-phenylvinyl)isophthalaldehyde (1c) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1c** as a yellow solid (373 mg, 88% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.38 (d, *J* = 0.7 Hz, 2H), 8.05 (s, 1H), 8.03 (s, 1H), 7.51 – 7.48 (m, 1H), 7.16 – 7.11 (m, 3H), 7.10 – 7.06 (m, 2H), 6.98 – 6.95 (m, 2H), 6.92 – 6.87 (m, 2H), 6.86 – 6.83 (m, 2H), 6.76 – 6.71 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 192.3, 162.0, 161.9, 161.1 (dd, *J* = 245.3, 25.9 Hz), 160.4, 160.2, 150.8, 143.1, 142.4, 141.7, 140.6, 139.5, 138.6, 138.3, 134.4, 134.2, 132.8 (d, *J* = 8.0 Hz), 132.3, 131.4 (d, *J* = 8.0 Hz), 130.3, 128.1, 128.0, 127.2, 126.8, 115.2 (d, *J* = 21.5 Hz), 114.9 (d, *J* = 21.5 Hz), 114.5, 113.0, 55.2, 44.8.

¹⁹F NMR (565 MHz, CDCl₃) δ -112.8, -112.9.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₁₉F₂O₂⁺ 425.1348; Found 425.1338.

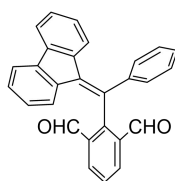


2-(2,2-bis(4-chlorophenyl)-1-phenylvinyl)isophthalaldehyde (1d) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1d** as a yellow solid (319 mg, 70% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.36 (s, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.14 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.04 – 7.00 (m, 4H), 6.98 – 6.94 (m, 2H), 6.81 – 6.77 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 190.7, 147.6, 143.7, 140.9, 140.2, 139.6, 134.9, 134.1, 133.8, 133.6, 133.1, 132.2, 131.2, 130.4.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₁₉Cl₂O₂⁺ 457.0757; Found 457.0749.



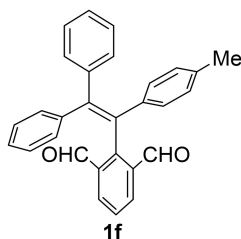
1e

2-((9H-fluoren-9-ylidene)(phenyl)methyl)isophthalaldehyde (1e) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1e** as a yellow solid (251 mg, 65% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.37 (d, *J* = 0.8 Hz, 2H), 8.35 (d, *J* = 7.8 Hz, 2H), 7.78 – 7.73 (m, 1H), 7.71 – 7.66 (m, 2H), 7.46 – 7.41 (m, 5H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 1H), 7.04 – 6.99 (m, 2H), 6.88 – 6.85 (m, 1H), 6.02 (dd, *J* = 7.9, 0.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 190.4, 148.4, 141.1, 139.3, 137.4, 136.6, 134.2, 134.0, 129.8, 129.3, 128.9, 127.3, 126.9, 125.1, 124.4, 119.8, 119.7.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₁₉O₂⁺ 387.1380; Found 387.1373.

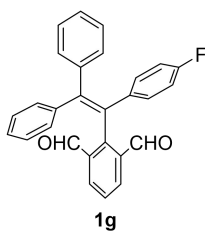


1f

2-(2,2-diphenyl-1-(p-tolyl)vinyl)isophthalaldehyde (1f) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1f** as a yellow solid (289 mg, 72% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.45 (d, *J* = 0.8 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.43 (m, 1H), 7.23 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 7.05 – 7.01 (m, 3H), 6.93 – 6.90 (m, 2H), 6.89 – 6.84 (m, 4H), 2.24 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 191.1, 149.1, 146.2, 142.1, 141.7, 137.4, 135.0, 133.2, 131.4, 130.8, 130.2, 129.9, 129.1, 128.2, 128.1, 128.1, 127.5, 127.3, 21.1.

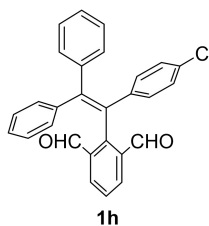


2-(1-(4-fluorophenyl)-2,2-diphenylvinyl)isophthalaldehyde (1g) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1g** as a yellow solid (333 mg, 82% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.42 (d, *J* = 0.8 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 2H), 51 – 7.43 (m, 1H), 7.24 – 7.19 (m, 3H), 7.13 – 7.11 (m, 2H), 7.05 – 7.02 (m, 3H), 6.97 – 6.94 (m, 2H), 6.90 – 6.85 (m, 2H), 6.83 – 6.79 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 190.8, 161.6 (d, *J* = 249.1 Hz), 148.2, 146.7, 141.9, 141.3, 137.7 (d, *J* = 3.5 Hz), 134.9, 133.8, 132.2 (d, *J* = 8.0 Hz), 130.8, 130.5, 129.8, 128.3 (d, *J* = 2.3 Hz), 128.2, 127.8, 127.5, 115.4 (d, *J* = 21.6 Hz).

¹⁹F NMR (565 MHz, CDCl₃) δ -113.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₀FO₂⁺ 407.1442; Found 407.1441.

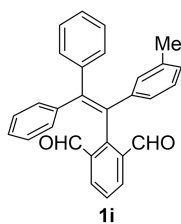


2-(1-(4-chlorophenyl)-2,2-diphenylvinyl)isophthalaldehyde (1h) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1h** as a yellow solid (308 mg, 73% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.51 – 10.34 (m, 2H), 8.04 (d, *J* = 2.3 Hz, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.25 – 7.19 (m, 3H), 7.13 – 7.11 (m, 3H), 7.09 – 7.08 (m, 1H), 7.06 – 7.03 (m, 3H), 7.02 – 6.93 (m, 1H), 6.92 – 6.86 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 190.7, 147.9, 147.1, 141.8, 141.2, 140.1, 135.0, 133.9, 133.4, 131.7, 130.8, 129.8, 128.5, 128.4, 128.2, 127.9, 127.6, 127.4.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₀ClO₂⁺ 423.1146; Found 423.1139.

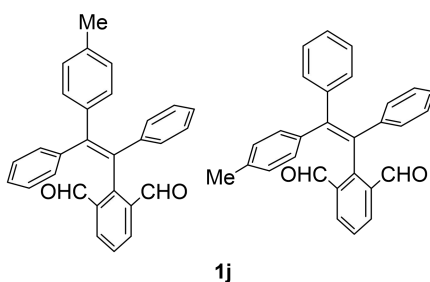


2-(2,2-diphenyl-1-(m-tolyl)vinyl)isophthalaldehyde (1i) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1i** as a yellow solid (225 mg, 56% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.47 (d, *J* = 0.8 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.22 – 7.18 (m, 3H), 7.13 – 7.10 (m, 2H), 7.05 – 7.02 (m, 3H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.93 – 6.91 (m, 1H), 6.90 – 6.86 (m, 2H), 6.80 – 6.77 (m, 1H), 6.75 – 6.73 (m, 1H), 2.12 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 191.1, 148.9, 146.7, 142.1, 141.6, 137.9, 135.0, 133.3, 131.5, 130.9, 130.8, 129.9, 128.3, 128.2, 128.1, 127.6, 127.6, 127.4, 21.3.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₂₃O₂⁺ 403.1693; Found 403.1686.



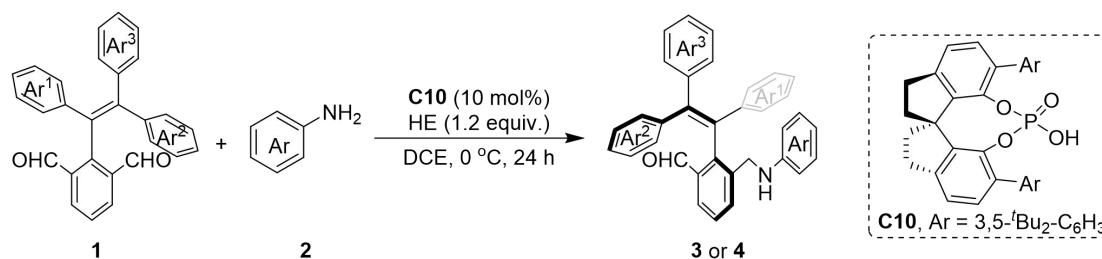
2-(1,2-diphenyl-2-(p-tolyl)vinyl)isophthalaldehyde (1j) was synthesized by following Procedure A. The crude material was purified by column chromatography to provide **1j** as a yellow solid (269 mg, 67% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.46 (d, *J* = 0.8 Hz, 2H), 8.06 – 8.00 (m, 2H), 7.51 – 7.39 (m, 1H), 7.21 – 7.19 (m, 1H), 7.13 – 7.10 (m, 4H), 7.04 – 7.02 (m, 1H), 7.01 – 6.98 (m, 3H), 6.98 – 6.96 (m, 1H), 6.90 – 6.87 (m, 1H), 6.85 – 6.82 (m, 1H), 6.78 – 6.75 (m, 1H), 2.43 – 2.05 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 191.1, 149.1, 149.0, 146.94, 146.9, 142.2, 141.9, 141.7, 139.0, 138.5, 137.6, 137.3, 135.0, 134.9, 133.4, 133.3, 130.9, 130.8, 130.39, 130.36, 129.93, 129.9, 128.9, 128.33, 128.29, 128.13, 128.12, 128.08, 128.07, 127.6, 127.4, 127.32, 127.30, 21.2, 21.1.

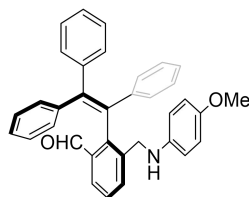
HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₂₃O₂⁺ 403.1693; Found 403.1686.

3. Experimental Procedures and Characterization of Products.



Procedure B:

Under air atmosphere, TAE dialdehyde **1** (0.1 mmol), aromatic amine **2** (0.1 mmol, 1.0 equiv.), **C10** (6.9 mg, 0.01 mmol, 10 mol%) and HE (30.4 mg, 0.12 mmol, 1.2 equiv.) were placed in a reaction tube and anhydrous DCE (1.0 mL) was added into this reaction mixture via syringe, and stirred at 0 °C for 24 h. After completion of the reaction, the crude mixture was purified by column chromatography on silica gel to afford the corresponding product **3** or **4**.



(*S*)-3-(((4-methoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde

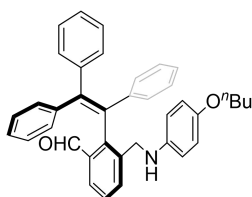
(**3a**) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3a** as a yellow solid (35.6 mg, 72% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.60 – 7.50 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.16 – 7.08 (m, 9H), 7.01 – 6.97 (m, 2H), 6.94 – 6.89 (m, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 6.11 – 6.06 (m, 2H), 5.80 (s, 1H), 4.32 – 4.20 (m, 1H), 4.12 – 4.05 (m, 1H), 3.58 (s, 3H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 150.8, 144.0, 143.6, 142.4, 142.3, 142.1, 140.7, 139.6, 134.1, 133.6, 132.2, 130.7, 130.3, 129.2, 128.2, 128.0, 127.9, 127.8, 127.3, 127.0, 126.3, 114.5, 113.0, 55.2, 44.9.

Optical [α]_D²⁵ = -3.22 (c = 0.12, CH₂Cl₂, 93% ee).

HPLC (IA, *i*PrOH/*n*-hexane = 30/70, flow rate = 0.8 mL/min, 254 nm) *t*_R = 7.9 min (major), 7.5 min (minor).



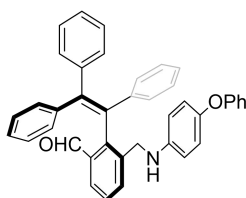
(S)-3-(((4-butoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3b) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, Toluene) to provide **3b** as a yellow solid (34.9 mg, 65% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.60 – 7.50 (m, 2H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.23 – 7.20 (m, 4H), 7.14 – 7.09 (m, 9H), 7.00 – 6.97 (m, 3H), 6.93 – 6.90 (m, 2H), 6.57 – 6.53 (m, 3H), 6.09 – 6.04 (m, 2H), 5.78 (q, *J* = 7.3, 6.7 Hz, 1H), 4.32 – 4.17 (m, 2H), 4.14 – 4.03 (m, 1H), 3.99 – 3.92 (m, 1H), 1.62 – 1.57 (m, 2H), 1.40 – 1.36 (m, 4H), 0.92 – 0.88 (m, 3H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 150.1, 143.9, 143.6, 142.4, 142.3, 142.1, 140.7, 139.6, 134.1, 133.6, 132.2, 130.6, 130.3, 129.2, 128.1, 128.0, 127.9, 127.2, 126.3, 122.2, 122.0, 115.3, 113.0, 67.5, 44.8, 31.0, 18.8, 13.7.

Optical [α]_D²⁵ = -0.09 (c = 0.04, CH₂Cl₂, 91% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 10.2 min (major), 11.4 min (minor).



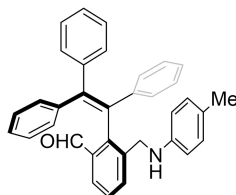
(S)-3-(((4-phenoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3c) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3c** as a yellow solid (38.2 mg, 69% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.59 (dd, *J* = 7.6, 4.5 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31 – 7.20 (m, 6H), 7.16 – 7.08 (m, 8H), 7.01 – 6.98 (m, 3H), 6.93 (d, *J* = 4.3 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 2H), 6.70 – 6.67 (m, 2H), 6.18 – 6.09 (m, 3H), 4.36 – 4.29 (m, 1H), 4.23 – 4.15 (m, 1H).

^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 158.8, 145.7, 145.2, 144.1, 143.7, 142.3, 142.1, 140.7, 139.2, 134.2, 133.6, 132.1, 130.7, 130.3, 129.7, 129.2, 128.2, 128.0, 127.9, 127.3, 127.0, 126.5, 121.9, 120.9, 116.5, 112.9, 79.2, 44.6.

Optical $[\alpha]_{\text{D}}^{25} = -6.80$ ($c = 0.18$, CH_2Cl_2 , 91% ee).

HPLC (IA, $i\text{PrOH/n-hexane} = 30/70$, flow rate = 0.8 mL/min, 254 nm) $t_{\text{R}} = 6.7$ min (major), 7.0 min (minor).



(S)-3-((p-tolylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3d) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 10:1) to provide **3d** as a yellow solid (32.3 mg, 67% yield).

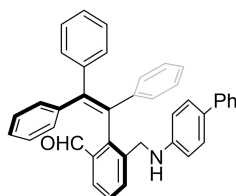
^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.36 (s, 1H), 7.60 – 7.54 (m, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 3.5$ Hz, 3H), 7.17 – 7.08 (m, 9H), 7.02 – 6.97 (m, 2H), 6.95 – 6.89 (m, 2H), 6.73 (d, $J = 8.0$ Hz, 2H), 6.05 – 5.97 (m, 2H), 4.36 – 4.20 (m, 1H), 4.16 – 4.06 (m, 1H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 145.9, 144.0, 143.6, 142.3, 142.1, 140.7, 139.5, 134.1, 133.6, 132.1, 130.7, 130.3, 129.3, 129.2, 128.2, 128.0, 127.9, 127.8, 127.3, 127.0, 126.3, 124.3, 112.1, 44.3, 20.0.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{30}\text{NO}^+$ 480.2322; Found 480.2316.

Optical $[\alpha]_{\text{D}}^{25} = -4.03$ ($c = 0.15$, CH_2Cl_2 , 91% ee).

HPLC (IA, $i\text{PrOH/n-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 12.5$ min (major), 11.9 min (minor).



(S)-3-(((1,1'-biphenyl)-4-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3e) was synthesized by following Procedure B. The crude material was purified by

column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3e** as a yellow solid (43.9 mg, 81% yield).

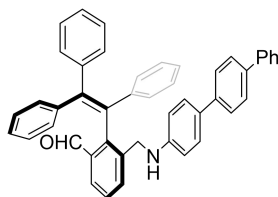
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.38 (s, 1H), 7.62 – 7.57 (m, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.25 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 4H), 7.18 – 7.11 (m, 8H), 7.05 – 7.00 (m, 2H), 6.98 – 6.92 (m, 2H), 6.43 (s, 1H), 6.30 – 6.09 (m, 2H), 4.49 – 4.34 (m, 1H), 4.27 – 4.13 (m, 1H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 147.8, 144.1, 143.6, 142.4, 142.1, 140.7, 140.4, 139.1, 134.2, 133.6, 132.0, 130.7, 130.3, 129.2, 128.7, 128.2, 128.05, 127.98, 127.8, 127.32, 127.28, 127.2, 127.1, 126.5, 125.8, 125.4, 112.4, 44.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₄₀H₃₂NO⁺ 542.2478; Found 542.2473.

Optical [α]_D²⁵ = -7.11 (c = 0.17, CH₂Cl₂, 91% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 17.0 min (major), 16.0 min (minor).



(S)-3-(((1,1':4',1''-terphenyl)-4-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3f) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3f** as a yellow solid (41.4 mg, 67% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.39 (s, 1H), 7.69 – 7.64 (m, 4H), 7.63 – 7.59 (m, 3H), 7.58 – 7.53 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.25 – 7.20 (m, 3H), 7.19 – 7.11 (m, 8H), 7.06 – 7.00 (m, 2H), 6.99 – 6.94 (m, 2H), 6.48 (s, 1H), 6.29 – 6.19 (m, 2H), 4.47 – 4.37 (m, 1H), 4.28 – 4.10 (m, 1H).

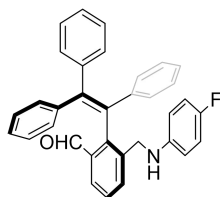
¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 148.0, 144.1, 143.6, 142.4, 142.1, 140.7, 139.8, 139.5, 139.1, 137.4, 134.2, 133.6, 132.0, 130.7, 130.3, 129.2, 128.9, 128.2, 128.1, 128.0, 127.32, 127.27, 127.27, 127.21, 127.1, 127.0, 126.5, 126.4, 125.8, 112.4, 79.2, 44.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₄₆H₃₆NO⁺ 618.2791; Found 618.2787.

Optical [α]_D²⁵ = -3.19 (c = 0.14, CH₂Cl₂, 90% ee).

HPLC (IA, ⁱPrOH/n-hexane = 30/70, flow rate = 0.8 mL/min, 254 nm) t_R = 9.4 min

(major), 9.0 min (minor).



(S)-3-(((4-fluorophenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3g) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3g** as a yellow solid (38.5 mg, 80% yield). The compound was reduced to the corresponding alcohol for NMR analysis.

¹H NMR (600 MHz, (CD₃)₂SO) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.13 – 7.04 (m, 9H), 6.97 – 6.92 (m, 4H), 6.76 – 6.67 (m, 2H), 6.06 – 5.98 (m, 3H), 5.22 – 5.17 (m, 1H), 4.49 – 4.41 (m, 1H), 4.39 – 4.32 (m, 1H), 4.19 – 4.12 (m, 2H).

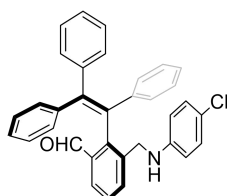
¹³C NMR (101 MHz, (CD₃)₂SO) δ 154.1 (d, *J* = 231.0 Hz), 145.2, 142.8, 142.6, 141.9, 140.7, 140.5, 138.0, 136.5, 135.7, 130.9, 130.2, 129.3, 128.2, 127.7 (d, *J* = 7.5 Hz), 127.0, 126.7, 124.6, 124.4, 115.1 (d, *J* = 21.9 Hz), 112.6 (d, *J* = 7.2 Hz), 61.0, 45.0.

¹⁹F NMR (565 MHz, (CD₃)₂SO) δ -129.9.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₄H₂₇FNO⁺ 484.2071; Found 484.2065.

Optical [α]_D²⁵ = -1.48 (c = 0.13, CH₂Cl₂, 93% ee).

HPLC (AD-H, ^{*i*}PrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 13.0 min (major), 12.2 min (minor).



(S)-3-(((4-chlorophenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3h) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3h** as a yellow solid (40.0 mg, 80% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.48 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 5.9, 1.6 Hz, 3H), 7.16

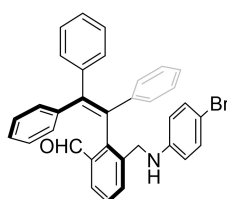
– 7.09 (m, 8H), 7.01 – 6.97 (m, 2H), 6.94 – 6.90 (m, 4H), 6.43 (t, $J = 6.0$ Hz, 1H), 6.09 – 5.95 (m, 2H), 4.36 – 4.28 (m, 1H), 4.19 – 4.10 (m, 1H).

^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 147.1, 144.1, 143.7, 142.3, 142.0, 140.7, 138.7, 134.3, 133.5, 131.9, 130.7, 130.3, 129.2, 128.5, 128.2, 128.03, 127.96, 127.30, 127.28, 127.1, 126.5, 119.2, 113.3, 44.0.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{27}\text{ClNO}^+$ 500.1776; Found 500.1770.

Optical $[\alpha]_{\text{D}}^{25} = -3.67$ ($c = 0.13$, CH_2Cl_2 , 90% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 13.0$ min (major), 12.0 min (minor).



(S)-3-(((4-bromophenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3i) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 10:1) to provide **3i** as a yellow solid (33.1 mg, 61% yield).

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.35 (s, 1H), 7.58 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.47 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 1H), 7.25 – 7.20 (m, 3H), 7.17 – 7.08 (m, 8H), 7.05 – 7.01 (m, 2H), 7.00 – 6.97 (m, 2H), 6.94 – 6.90 (m, 2H), 6.47 (t, $J = 6.0$ Hz, 1H), 6.05 – 5.91 (m, 2H), 4.37 – 4.27 (m, 1H), 4.18 – 4.09 (m, 1H).

^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 147.5, 144.1, 143.7, 142.3, 142.0, 140.7, 138.7, 134.3, 133.5, 131.9, 131.3, 130.7, 130.3, 129.2, 128.2, 128.04, 127.97, 127.31, 127.28, 127.1, 126.5, 113.9, 106.6, 43.9.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{27}\text{BrNO}^+$ 544.1271; Found 544.1265.

Optical $[\alpha]_{\text{D}}^{25} = -2.03$ ($c = 0.12$, CH_2Cl_2 , 90% ee).

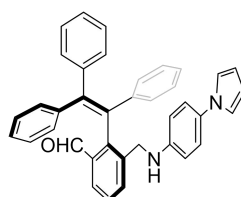
HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 13.3$ min (major), 12.4 min (minor).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 193.4, 192.1, 152.5, 144.2, 143.6, 142.3, 142.0, 140.6, 138.8, 138.2, 134.4, 133.4, 132.3, 131.8, 131.2, 130.7, 130.3, 129.2, 128.8, 128.20, 128.15, 128.1, 128.04, 128.96, 127.3, 127.1, 126.7, 124.3, 110.9, 43.5.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₄₁H₃₂NO₂⁺ 570.2428; Found 570.2422

Optical [α]_D²⁵ = -5.47 (c = 0.15, CH₂Cl₂, 89% ee).

HPLC (AD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 21.5 min (major), 18.8 min (minor).



(S)-3-(((4-(1H-pyrrol-1-yl)phenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (31) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **31** as a yellow solid (43.6 mg, 82% yield).

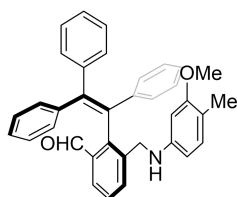
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.38 (s, 1H), 7.59 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 – 7.09 (m, 9H), 7.09 – 7.05 (m, 3H), 7.04 – 6.99 (m, 2H), 6.97 – 6.92 (m, 2H), 6.34 (t, *J* = 6.0 Hz, 1H), 6.24 – 6.09 (m, 4H), 4.43 – 4.30 (m, 1H), 4.26 – 4.09 (m, 1H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 146.3, 144.1, 143.7, 142.3, 142.0, 140.7, 139.0, 134.2, 133.6, 132.0, 130.7, 130.3, 130.2, 129.2, 128.2, 128.04, 127.97, 127.31, 127.26, 127.1, 126.4, 121.1, 119.0, 112.5, 109.2, 79.2, 44.3.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₈H₃₁N₂O⁺ 531.2431; Found 531.2427.

Optical [α]_D²⁵ = -3.22 (c = 0.13, CH₂Cl₂, 89% ee).

HPLC (OX-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 16.1 min (major), 18.5 min (minor).



(S)-3-(((3-methoxy-4-methylphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3m) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3m** as a yellow solid (35.2 mg, 69% yield).

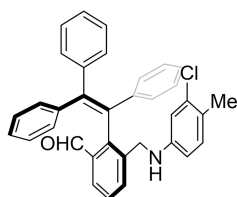
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.35 (s, 1H), 7.59 – 7.52 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 – 7.11 (m, 5H), 7.10 – 7.07 (m, 3H), 7.02 – 6.97 (m, 2H), 6.94 – 6.88 (m, 2H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.03 – 5.97 (m, 2H), 5.51 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.14 – 4.06 (m, 1H), 3.57 (s, 3H), 1.93 (s, 3H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 157.8, 147.9, 144.0, 143.5, 142.3, 142.1, 140.8, 139.5, 134.1, 133.6, 132.1, 130.7, 130.5, 130.2, 129.2, 128.2, 128.0, 127.9, 127.8, 127.3, 127.0, 126.3, 112.9, 103.2, 95.9, 54.8, 44.4, 15.2.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₂NO₂⁺ 510.2428; Found 510.2423.

Optical [α]_D²⁵ = -3.38 (c = 0.14, CH₂Cl₂, 91% ee).

HPLC (AD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 15.2 min (major), 13.9 min (minor).



(S)-3-(((3-chloro-4-methylphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3n) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, Toluene) to provide **3n** as a yellow solid (37.0 mg, 72% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.17 (m, 3H), 7.15 – 7.12 (m, 4H), 7.14 – 7.06 (m, 3H), 7.03 – 6.96 (m, 2H), 6.93 – 6.91 (m, 2H), 6.91 – 6.83 (m,

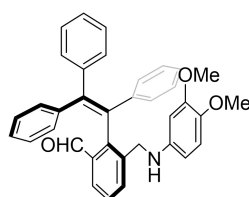
1H), 6.37 (s, 1H), 6.23 (d, $J = 2.4$ Hz, 1H), 5.99 (dd, $J = 8.3, 2.4$ Hz, 1H), 4.36 – 4.26 (m, 1H), 4.13 – 4.04 (m, 1H), 2.10 (s, 3H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 147.7, 144.2, 143.6, 142.3, 142.0, 140.6, 138.8, 134.2, 133.5, 133.5, 131.8, 131.3, 130.7, 130.3, 129.2, 128.2, 128.1, 127.9, 127.4, 127.3, 127.1, 126.4, 121.8, 111.7, 111.1, 44.1, 18.4.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{29}\text{ClNO}^+$ 514.1932; Found 514.1928.

Optical $[\alpha]_{\text{D}}^{25} = -7.37$ ($c = 0.17$, CH_2Cl_2 , 91% ee).

HPLC (IA, $i\text{PrOH/n-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 13.7$ min (major), 12.3 min (minor).



(S)-3-(((3,4-dimethoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3o) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 5:1) to provide **3o** as a yellow solid (36.8 mg, 70% yield).

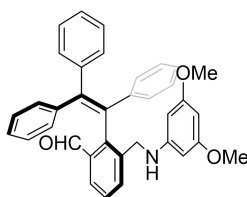
^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.35 (s, 1H), 7.58 – 7.54 (m, 2H), 7.38 – 7.32 (m, 1H), 7.25 – 7.19 (m, 3H), 7.16 – 7.11 (m, 5H), 7.10 – 7.07 (m, 3H), 7.02 – 6.98 (m, 2H), 6.94 – 6.86 (m, 2H), 6.58 – 6.49 (m, 1H), 6.18 – 6.02 (m, 1H), 5.57 – 5.46 (m, 1H), 4.34 – 4.24 (m, 1H), 4.13 – 4.04 (m, 1H), 3.60 – 3.52 (m, 6H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 149.9, 144.1, 143.6, 142.4, 142.1, 139.5, 134.1, 133.6, 132.2, 130.7, 130.3, 129.2, 128.2, 128.0, 127.91, 127.86, 127.3, 127.0, 126.3, 114.3, 102.5, 98.8, 56.5, 55.2, 44.9.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{32}\text{NO}_3^+$ 526.2377; Found 526.2373.

Optical $[\alpha]_{\text{D}}^{25} = -8.99$ ($c = 0.18$, CH_2Cl_2 , 92% ee).

HPLC (OX-H, $i\text{PrOH/n-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 36.6$ min (major), 34.0 min (minor).



(S)-3-(((3,5-dimethoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3p) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3p** as a yellow solid (42.1 mg, 80% yield).

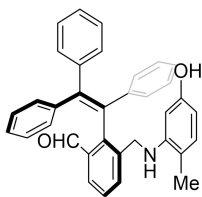
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.34 (s, 1H), 7.56 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.13 (dd, *J* = 5.0, 2.1 Hz, 5H), 7.08 (t, *J* = 3.3 Hz, 3H), 7.02 – 6.97 (m, 2H), 6.93 – 6.87 (m, 2H), 6.21 (t, *J* = 6.1 Hz, 1H), 5.72 (t, *J* = 2.1 Hz, 1H), 5.50 (d, *J* = 2.1 Hz, 2H), 4.36 – 4.21 (m, 1H), 4.04 – 3.96 (m, 1H), 3.57 (s, 6H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.0, 161.2, 150.3, 144.2, 143.5, 142.3, 142.1, 140.7, 139.3, 134.1, 133.6, 132.0, 130.7, 130.2, 129.1, 128.2, 128.0, 127.9, 127.33, 127.28, 127.1, 126.3, 90.9, 88.8, 54.7, 44.3.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₂NO₃⁺ 526.2377; Found 526.2372.

Optical [α]_D²⁵ = -5.36 (*c* = 0.14, CH₂Cl₂, 91% ee).

HPLC (IA, ⁱPrOH/n-hexane = 30/70, flow rate = 0.8 mL/min, 254 nm) *t*_R = 8.0 min (major), 8.8 min (minor).



(S)-3-(((5-hydroxy-2-methylphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3q) was synthesized by following Procedure B for 72 h. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 5:1) to provide **3q** as a yellow solid (33.2 mg, 67% yield).

¹H NMR (400 MHz, (CD₃)₂SO) δ 10.35 (s, 1H), 8.65 (s, 1H), 7.55 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.15 – 7.08 (m, 8H), 7.04 – 7.00 (m, 2H), 6.96 – 6.91 (m, 2H), 6.71 (dd, *J* = 7.8, 0.8

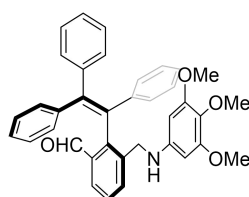
Hz, 1H), 5.92 (dd, $J = 7.9, 2.3$ Hz, 1H), 5.42 (d, $J = 2.3$ Hz, 1H), 5.32 (t, $J = 5.9$ Hz, 1H), 4.41 – 4.32 (m, 1H), 4.03 – 3.96 (m, 1H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.0, 156.4, 147.1, 144.2, 143.5, 142.3, 142.1, 140.6, 139.5, 134.1, 133.7, 132.2, 130.7, 130.3, 130.1, 129.2, 128.2, 128.0, 127.9, 127.8, 127.1, 126.1, 112.4, 102.7, 97.5, 44.7, 16.9.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{30}\text{NO}_2^+$ 496.2271; Found 496.2265.

Optical $[\alpha]_{\text{D}}^{25} = -2.61$ ($c = 0.14$, CH_2Cl_2 , 92% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 17.6$ min (major), 18.6 min (minor).



(S)-3-(((3,4,5-trimethoxyphenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3r) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 5:1) to provide **3r** as a yellow solid (38.9 mg, 70% yield).

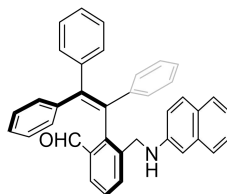
^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.34 (s, 1H), 7.60 – 7.52 (m, 2H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.26 – 7.17 (m, 3H), 7.14 – 7.10 (m, 5H), 7.08 – 7.04 (m, 3H), 7.05 – 6.97 (m, 2H), 6.93 – 6.85 (m, 2H), 6.04 (t, $J = 6.2$ Hz, 1H), 5.60 (s, 2H), 4.35 – 4.22 (m, 1H), 4.10 – 4.01 (m, 1H), 3.55 (s, 6H), 3.49 (s, 3H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 153.5, 145.2, 144.2, 143.5, 142.3, 142.1, 140.8, 139.4, 134.1, 133.6, 132.1, 130.7, 130.2, 129.2, 128.8, 128.2, 128.0, 127.90, 127.86, 127.3, 127.0, 126.3, 89.8, 60.2, 55.5, 44.6.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{34}\text{NO}_4^+$ 556.2482; Found 556.2479.

Optical $[\alpha]_{\text{D}}^{25} = -6.40$ ($c = 0.14$, CH_2Cl_2 , 93% ee).

HPLC (IC, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 30.3$ min (major), 23.3 min (minor).



(S)-3-((naphthalen-2-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3s) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3s** as a yellow solid (50.1 mg, 97% yield).

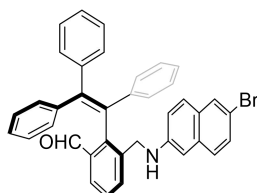
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.39 (s, 1H), 7.65 – 7.51 (m, 4H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.24 – 7.19 (m, 4H), 7.18 – 7.12 (m, 7H), 7.10 – 7.04 (m, 3H), 7.01 – 6.95 (m, 2H), 6.93 – 6.81 (m, 1H), 6.60 (t, *J* = 6.2 Hz, 1H), 5.98 (d, *J* = 2.4 Hz, 1H), 4.52 – 4.40 (m, 1H), 4.34 – 4.24 (m, 1H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 146.1, 144.2, 143.7, 142.4, 142.1, 140.8, 138.8, 134.8, 134.2, 133.6, 131.8, 130.7, 130.3, 129.2, 128.5, 128.2, 128.1, 127.9, 127.4, 127.4, 127.3, 127.1, 126.5, 126.4, 126.0, 125.2, 121.2, 118.0, 102.3, 79.2, 44.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₈H₃₀NO⁺ 516.2322; Found 516.2318.

Optical [α]_D²⁵ = -2.05 (c = 0.13, CH₂Cl₂, 89% ee).

HPLC (IA, ^{*i*}PrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 16.4 min (major), 14.9 min (minor).



(S)-3-(((6-bromonaphthalen-2-yl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3t) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3t** as a yellow solid (54.7 mg, 92% yield).

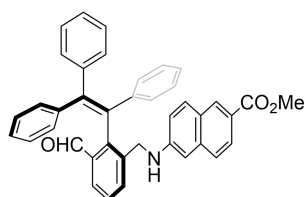
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.38 (s, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.36 – 7.33 (m, 2H), 7.25 – 7.17 (m, 7H), 7.17 – 7.12 (m, 6H), 7.07 – 7.04 (m, 2H), 6.98 – 6.95 (m, 2H), 6.92 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.74 (t, *J* = 6.1 Hz, 1H), 4.47 – 4.40 (m, 1H), 4.31 – 4.25 (m, 1H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.1, 146.6, 144.2, 143.7, 142.4, 142.0, 140.8, 138.5, 134.3, 133.5, 133.4, 131.8, 130.7, 130.3, 129.2, 129.2, 128.8, 128.2, 128.1, 128.0, 127.8, 127.6, 127.3, 127.3, 127.1, 126.5, 119.0, 113.4, 102.0, 43.9.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₈H₂₉BrNO⁺ 594.1427; Found 594.1420.

Optical [α]_D²⁵ = -6.78 (c = 0.18, CH₂Cl₂, 92% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 13.3 min (major), 14.8 min (minor).



(S)-methyl 6-((3-formyl-2-(1,2,2-triphenylvinyl)benzyl)amino)-2-naphthoate (3u) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 5:1) to provide **3u** as a yellow solid (47.7 mg, 83% yield).

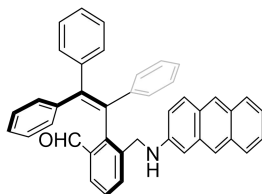
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.39 (s, 1H), 8.32 (d, *J* = 1.8 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.24 – 7.19 (m, 4H), 7.19 – 7.11 (m, 7H), 7.09 – 7.04 (m, 2H), 7.04 – 7.00 (m, 1H), 7.00 – 6.94 (m, 3H), 5.97 (d, *J* = 2.4 Hz, 1H), 4.55 – 4.43 (m, 1H), 4.40 – 4.28 (m, 1H), 3.83 (s, 1H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 166.6, 148.4, 144.3, 143.8, 142.4, 142.0, 140.8, 138.3, 137.5, 134.3, 133.5, 131.8, 130.7, 130.4, 130.3, 129.2, 128.2, 128.1, 128.04, 127.96, 127.4, 127.3, 127.2, 126.6, 125.3, 125.2, 121.8, 118.8, 101.8, 79.2, 51.8, 43.8.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₄₀H₃₂NO₃⁺ 574.2377; Found 574.2371.

Optical [α]_D²⁵ = -8.55 (c = 0.18, CH₂Cl₂, 87% ee).

HPLC (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 18.7 min (major), 20.3 min (minor).



(S)-3-((anthracen-2-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3v) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: DCM: EtOAc = 4:2:0.1) to provide **3v** as a yellow solid (36.2 mg, 64% yield).

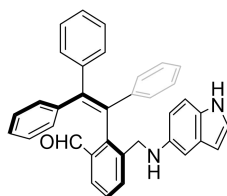
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.41 (s, 1H), 8.25 (s, 1H), 7.91 – 7.85 (m, 2H), 7.81 – 7.74 (m, 2H), 7.64 – 7.55 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.21 (m, 5H), 7.20 – 7.16 (m, 5H), 7.13 – 7.09 (m, 2H), 7.07 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.77 (t, *J* = 5.9 Hz, 1H), 5.94 (d, *J* = 2.2 Hz, 1H), 4.59 – 4.44 (m, 1H), 4.40 – 4.32 (m, 1H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 145.4, 144.2, 143.8, 142.4, 142.1, 140.8, 138.5, 134.3, 133.6, 133.3, 131.9, 131.9, 130.7, 130.4, 129.2, 128.9, 128.6, 128.2, 128.1, 128.0, 127.4, 127.3, 127.2, 127.1, 126.7, 126.5, 125.8, 125.3, 123.3, 121.4, 120.6, 99.3, 79.2, 44.1.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₄₂H₃₂NO⁺ 566.2478; Found 566.2472.

Optical [α]_D²⁵ = -3.68 (c = 0.14, CH₂Cl₂, 90% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 24.0 min (major), 26.3 min (minor).



(S)-3-(((1H-indol-5-yl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3w) was synthesized by following Procedure B for 72 h. The crude material was purified by column chromatography (SiO₂, petroleum ether: DCM: EtOAc = 2:2:0.1) to provide **3w** as a yellow solid (37.8 mg, 70% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.60 (s, 1H), 10.36 (s, 1H), 8.52 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 – 7.09 (m, 12H), 7.05 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.97 – 6.92 (m,

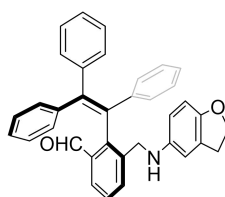
2H), 6.40 – 6.37 (m, 1H), 6.04 – 5.92 (m, 2H), 4.32 (d, $J = 7.1$ Hz, 2H), 4.19 – 4.12 (m, 1H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.2, 165.2, 161.3, 143.7, 142.4, 142.1, 140.8, 140.0, 134.1, 133.7, 132.4, 130.7, 130.3, 129.2, 128.3, 128.2, 128.0, 127.9, 127.8, 127.34, 127.27, 127.1, 122.8, 111.7, 100.0, 61.3.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{29}\text{N}_2\text{O}^+$ 505.2274; Found 505.2267.

Optical $[\alpha]_{\text{D}}^{25} = 0.01$ ($c = 0.01$, CH_2Cl_2 , 83% ee).

HPLC (IC, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 1.0 mL/min, 254 nm) $t_{\text{R}} = 13.0$ min (major), 11.8 min (minor).



(S)-3-(((2,3-dihydrobenzofuran-5-yl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3x) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 10:1) to provide **3x** as a yellow solid (20.8 mg, 41% yield).

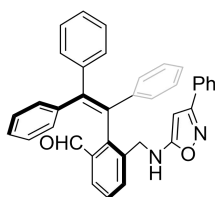
^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.35 (s, 1H), 7.58 – 7.53 (m, 2H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.24 – 7.20 (m, 3H), 7.16 – 7.12 (m, 5H), 7.11 – 7.08 (m, 3H), 7.00 – 6.97 (m, 2H), 6.93 – 6.90 (m, 2H), 6.37 (d, $J = 8.4$ Hz, 1H), 5.95 (d, $J = 2.4$ Hz, 1H), 5.91 – 5.88 (m, 1H), 5.77 (q, $J = 5.1, 4.1$ Hz, 1H), 4.31 (t, $J = 8.6$ Hz, 2H), 4.29 – 4.23 (m, 1H), 4.14 – 4.07 (m, 1H), 2.98 – 2.85 (m, 2H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.2, 151.1, 144.0, 143.6, 142.5, 142.4, 142.1, 140.8, 139.8, 134.1, 133.7, 132.2, 130.7, 130.3, 129.2, 128.2, 128.0, 127.9, 127.4, 127.32, 127.28, 127.0, 126.3, 111.3, 109.1, 108.8, 70.1, 45.0, 29.8.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{30}\text{NO}_2^+$ 508.2271; Found 508.2269.

Optical $[\alpha]_{\text{D}}^{25} = -3.56$ ($c = 0.15$, CH_2Cl_2 , 85% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 20.3$ min (major), 18.9 min (minor).



(S)-3-(((3-phenylisoxazol-5-yl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3y) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: DCM: EtOAc = 1:1:0.1) to provide **3y** as a yellow solid (20.8 mg, 39% yield).

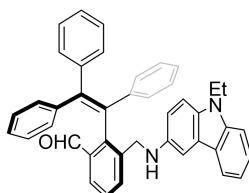
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.35 (s, 1H), 7.98 – 7.93 (m, 1H), 7.63 – 7.57 (m, 4H), 7.47 – 7.40 (m, 4H), 7.25 – 7.19 (m, 4H), 7.18 – 7.13 (m, 6H), 7.11 – 7.09 (m, 3H), 7.04 – 7.01 (m, 2H), 6.95 – 6.91 (m, 2H), 4.49 – 4.40 (m, 1H), 4.26 – 4.17 (m, 1H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.0, 170.5, 162.3, 144.5, 143.5, 142.3, 141.9, 140.7, 138.1, 134.1, 133.2, 131.7, 130.6, 130.3, 129.7, 129.5, 129.2, 128.8, 128.14, 128.07, 127.9, 127.3, 127.1, 126.8, 126.2, 74.0, 44.5.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₇H₂₉N₂O₂⁺ 533.2224; Found 533.2219.

Optical [α]_D²⁵ = -0.52 (c = 0.17, CH₂Cl₂, 88% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 33.8 min (major), 25.2 min (minor).



(S)-3-(((9-ethyl-9H-carbazol-3-yl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3z) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **3z** as a yellow solid (49 mg, 84% yield).

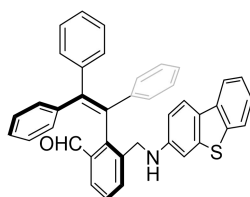
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.38 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.7, 6.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.14 (m, 9H), 7.14 – 7.10 (m, 3H), 7.10 – 7.05 (m, 3H), 7.01 – 6.94 (m, 2H), 6.80 (t, *J* = 2.4 Hz, 1H), 6.66 – 6.62 (m, 1H), 4.56 – 4.41 (m, 1H), 4.32 – 4.18 (m, 3H), 1.23 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 144.1, 143.7, 142.4, 142.1, 141.9, 140.9, 139.8, 139.7, 134.2, 133.7, 132.8, 132.3, 130.7, 130.3, 129.3, 128.2, 128.0, 127.9, 127.9, 127.3, 127.3, 127.1, 126.3, 125.1, 122.6, 121.7, 119.8, 117.6, 114.1, 109.7, 108.8, 101.3, 79.2, 45.3, 36.8, 13.7.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₄₂H₃₅N₂O⁺ 583.2744; Found 583.2737.

Optical [α]_D²⁵ = -4.12 (c = 0.17, CH₂Cl₂, 90% ee).

HPLC (OD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 38.0 min (major), 33.2 min (minor).



(S)-3-(((dibenzo[b,d]thiophen-3-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3aa) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, Toluene) to provide **3aa** as a yellow solid (36.0 mg, 63% yield).

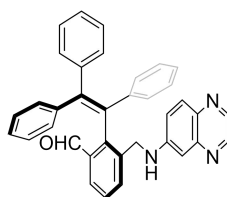
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.39 (s, 1H), 8.05 – 7.99 (m, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.18 (m, 6H), 7.18 – 7.14 (m, 5H), 7.06 – 7.03 (m, 2H), 6.99 – 6.97 (m, 2H), 6.77 (s, 1H), 6.60 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.10 (d, *J* = 2.1 Hz, 1H), 4.50 – 4.43 (m, 1H), 4.33 – 4.23 (m, 1H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.1, 148.0, 144.2, 143.8, 142.4, 142.0, 140.7, 140.5, 138.8, 136.6, 135.7, 134.3, 133.5, 131.8, 130.7, 130.4, 129.2, 128.2, 128.1, 128.02, 127.96, 127.5, 127.29, 127.25, 126.6, 124.7, 124.6, 124.5, 122.6, 122.4, 120.0, 112.4, 102.3, 44.0.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₄₀H₃₀NOS⁺ 572.2043; Found 572.2036.

Optical [α]_D²⁵ = -4.85 (c = 0.15, CH₂Cl₂, 91% ee).

HPLC (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 17.4 min (major), 16.0 min (minor).



(S)-3-((quinoxalin-6-ylamino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3ab) was synthesized by following Procedure B at -10 °C for 72 h. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 2:1) to provide **3ab** as a yellow solid (25.9 mg, 50% yield).

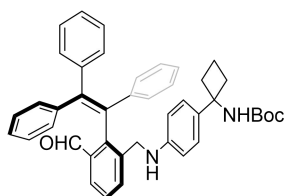
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.38 (s, 1H), 8.61 (d, *J* = 2.0 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.19 (m, 5H), 7.17 – 7.12 (m, 8H), 7.06 – 7.04 (m, 2H), 6.99 – 6.97 (m, 2H), 6.37 (d, *J* = 2.5 Hz, 1H), 4.58 – 4.43 (m, 1H), 4.21 – 4.13 (m, 1H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.0, 149.6, 145.2, 145.0, 144.5, 143.9, 142.4, 142.0, 140.7, 140.1, 137.9, 136.9, 134.4, 133.5, 131.9, 130.7, 130.3, 129.6, 129.2, 128.2, 128.1, 128.0, 127.4, 127.3, 127.2, 126.6, 122.2, 102.3, 44.2.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₂₈N₃O⁺ 518.2227; Found 518.2222.

Optical [α]_D²⁵ = -2.95 (*c* = 0.16, CH₂Cl₂, 82% ee).

HPLC (IA, *i*PrOH/*n*-hexane = 10/90, flow rate = 1.0 mL/min, 254 nm) *t*_R = 25.0 min (major), 27.7 min (minor).



(S)-tert-butyl(1-(4-((3-formyl-2-(1,2,2-triphenylvinyl)benzyl)amino)phenyl)cyclobutyl)carbamate (3ac) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 5:1) to provide **3ac** as a yellow solid (47.6 mg, 75% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.36 (s, 1H), 7.57 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 3H), 7.15 – 7.12 (m, 5H), 7.10 (s, 3H), 7.02 – 6.99 (m, 2H), 6.96 – 6.92 (m, 4H), 6.15 – 6.10 (m, 1H), 6.09 –

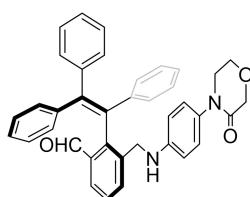
6.05 (m, 2H), 4.37 – 4.26 (m, 1H), 4.15 – 4.08 (m, 1H), 2.35 – 2.19 (m, 4H), 1.88 (s, 1H), 1.72 – 1.61 (m, 1H), 1.36 – 1.20 (m, 9H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.6, 146.9, 144.6, 144.1, 142.9, 142.6, 141.2, 140.0, 134.7, 134.2, 132.6, 131.2, 130.8, 129.7, 128.7, 128.5, 128.4, 127.8 (d, J = 4.6 Hz), 127.5, 126.8, 126.4, 111.9, 77.8, 58.4, 44.9, 34.4, 28.8, 14.6.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₄₃H₄₃N₂O₃⁺ 635.3268; Found 635.3261.

Optical [α]_D²⁵ = -5.06 (c = 0.17, CH₂Cl₂, 91% ee).

HPLC (IA, ⁱPrOH/n-hexane = 10/90, flow rate = 0.5 mL/min, 254 nm) t_R = 35.4 min (major), 37.6 min (minor).



(S)-3-(((4-(3-oxomorpholino)phenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3ad) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 1:1) to provide **3ad** as a yellow solid (40.7 mg, 72% yield).

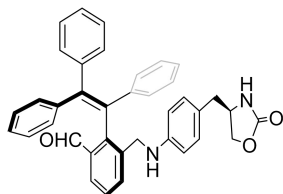
¹H NMR (400 MHz, (CD₃)₂SO) δ 10.37 (s, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.50 (m, 1H), 7.39 – 7.32 (m, 1H), 7.25 – 7.20 (m, 3H), 7.16 – 7.09 (m, 8H), 7.03 – 6.99 (m, 2H), 6.97 – 6.92 (m, 2H), 6.91 – 6.86 (m, 2H), 6.38 (t, J = 6.1 Hz, 1H), 6.13 – 6.02 (m, 2H), 4.39 – 4.31 (m, 1H), 4.20 – 4.09 (m, 3H), 3.92 – 3.86 (m, 2H), 3.60 – 3.50 (m, 2H).

¹³C NMR (101 MHz, (CD₃)₂SO) δ 192.1, 165.8, 146.8, 144.1, 143.6, 142.3, 142.0, 140.7, 139.1, 134.2, 133.6, 131.9, 130.7, 130.5, 130.3, 129.2, 128.2, 128.0, 127.9, 127.3, 127.1, 126.5, 126.4, 111.8, 67.7, 63.5, 49.6, 44.2.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₈H₃₃N₂O₃⁺ 565.2486; Found 565.2479.

Optical [α]_D²⁵ = -3.29 (c = 0.15, CH₂Cl₂, 86% ee).

HPLC (AD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 30.9 min (major), 34.5 min (minor).



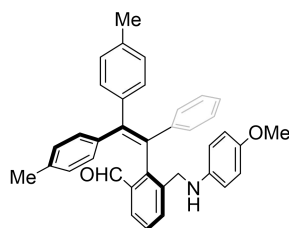
(S)-((R)-3-(((4-((2-oxooxazolidin-4-yl)methyl)phenyl)amino)methyl)-2-(1,2,2-triphenylvinyl)benzaldehyde (3ae) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 1:1) to provide **3ae** as a yellow solid (37.9 mg, 67% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.37 (s, 1H), 7.74 (s, 1H), 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.15 – 7.12 (m, 5H), 7.12 – 7.09 (m, 3H), 7.02 – 6.99 (m, 2H), 6.93 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.16 (t, *J* = 6.1 Hz, 1H), 6.08 (dd, *J* = 8.9, 2.7 Hz, 2H), 4.36 – 4.28 (m, 1H), 4.21 – 4.16 (m, 1H), 4.15 – 4.10 (m, 1H), 3.93 – 3.87 (m, 2H), 2.66 – 2.59 (m, 1H), 2.50 (q, *J* = 1.9 Hz, 1H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.1, 158.7, 147.0, 144.0, 143.6, 142.4, 142.1, 140.7, 139.3, 134.2, 133.6, 132.1, 130.7, 130.3, 129.9, 129.2, 128.2, 128.03, 127.95, 127.3, 127.1, 126.4, 123.6, 112.1, 68.1, 59.8, 52.8, 44.3.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₈H₃₃N₂O₃⁺ 565.2486; Found 565.2482.

Optical [α]_D²⁵ = -2.83 (c = 0.15, CH₂Cl₂, > 20/1 dr)



(S)-3-(((4-methoxyphenyl)amino)methyl)-2-(1-phenyl-2,2-di-p-tolylvinyl)benzaldehyde (4a) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4a** as a yellow solid (34.1 mg, 65% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.34 (s, 1H), 7.57 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.08 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 2H), 7.01 – 6.94 (m, 4H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.82 – 6.74 (m, 2H), 6.59

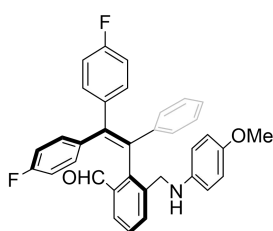
– 6.52 (m, 2H), 6.09 – 6.01 (m, 2H), 5.81 (t, $J = 6.1$ Hz, 1H), 4.29 – 4.19 (m, 1H), 4.12 – 4.03 (m, 1H), 3.58 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.2, 150.7, 144.1, 144.0, 142.4, 141.2, 139.7, 139.5, 139.3, 136.5, 136.4, 134.1, 132.6, 132.2, 130.7, 130.2, 129.3, 128.7, 128.5, 128.0, 127.7, 126.8, 126.1, 114.5, 113.0, 55.2, 44.8, 20.8, 20.7.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{34}\text{NO}_2^+$ 524.2584; Found 524.2578.

Optical $[\alpha]_{\text{D}}^{25} = -4.19$ ($c = 0.14$, CH_2Cl_2 , 87% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 17.4$ min (major), 16.5 min (minor).



(S)-2-(2,2-bis(4-fluorophenyl)-1-phenylvinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4b) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 10:1) to provide **4b** as a yellow solid (27.7 mg, 52% yield).

^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.31 (s, 1H), 7.61 – 7.58 (m, 1H), 7.57 – 7.55 (m, 1H), 7.39 – 7.35 (m, 1H), 7.19 – 7.14 (m, 5H), 7.09 – 7.05 (m, 2H), 7.00 – 6.98 (m, 2H), 6.97 – 6.94 (m, 4H), 6.58 – 6.55 (m, 2H), 6.09 – 6.06 (m, 2H), 5.81 (t, $J = 6.1$ Hz, 1H), 4.28 – 4.19 (m, 1H), 4.11 – 4.05 (m, 1H), 3.58 (s, 3H).

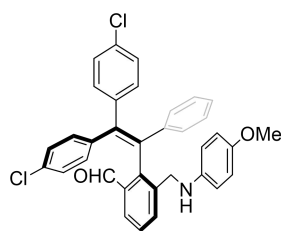
^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.3, 162.0, 161.9, 161.1 (dd, $J = 245.3, 25.9$ Hz), 160.4, 160.2, 150.8, 143.1, 142.4, 141.7, 140.6, 139.5, 138.6, 138.3, 134.4, 134.2, 132.8 (d, $J = 8.0$ Hz), 132.3, 131.4 (d, $J = 8.0$ Hz), 130.3, 128.1, 128.0, 127.2, 126.8, 115.2 (d, $J = 21.5$ Hz), 114.9 (d, $J = 21.5$ Hz), 114.5, 113.0, 55.2, 44.8.

^{19}F NMR (565 MHz, $(\text{CD}_3)_2\text{SO}$) δ -114.0, -114.2.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{28}\text{F}_2\text{NO}_2^+$ 532.2083; Found 532.2078.

Optical $[\alpha]_{\text{D}}^{25} = -0.94$ ($c = 0.07$, CH_2Cl_2 , 96% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 16.5$ min (major), 15.1 min (minor).



(S)-2-(2,2-bis(4-chlorophenyl)-1-phenylvinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4c) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4c** as a yellow solid (38.4 mg, 68% yield).

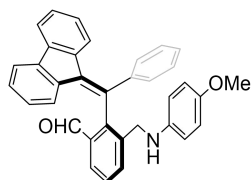
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.30 (s, 1H), 7.61 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.21 – 7.13 (m, 7H), 7.01 – 6.99 (m, 2H), 6.94 – 6.91 (m, 2H), 6.59 – 6.54 (m, 2H), 6.06 – 6.01 (m, 2H), 5.83 (t, *J* = 6.1 Hz, 1H), 4.25 – 4.18 (m, 1H), 4.14 – 4.08 (m, 1H), 3.59 (s, 3H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.3, 150.8, 142.7, 142.3, 141.1, 140.8, 140.6, 140.3, 139.3, 135.2, 134.3, 132.6, 132.4, 132.1, 131.2, 130.3, 128.3, 128.12, 128.09, 127.3, 127.1, 114.5, 113.0, 55.2, 44.8.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₂₈Cl₂NO₂⁺ 564.1492; Found 564.1487.

Optical [α]_D²⁵ = -3.14 (*c* = 0.12, CH₂Cl₂, 81% ee).

HPLC (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 18.7 min (major), 20.2 min (minor).



(S)-2-((9H-fluoren-9-ylidene)(phenyl)methyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4d) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4d** as a yellow solid (31.1 mg, 63% yield).

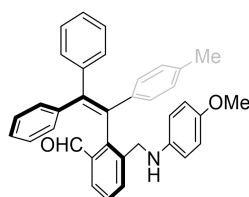
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.16 (s, 1H), 7.92 – 7.86 (m, 2H), 7.82 – 7.77 (m, 1H), 7.69 – 7.64 (m, 1H), 7.53 – 7.49 (m, 3H), 7.36 – 7.30 (m, 1H), 7.07 – 6.94 (m, 3H), 6.51 – 6.44 (m, 2H), 6.14 – 6.06 (m, 2H), 6.04 – 5.97 (m, 1H), 5.86 (t, *J* = 7.2 Hz, 1H), 4.12 – 3.99 (m, 1H), 3.60 – 3.47 (m, 4H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 191.7, 150.8, 143.0, 142.0, 140.3, 140.2, 139.2, 139.2, 138.0, 137.4, 136.6, 136.4, 133.9, 133.1, 129.19, 129.15, 128.8, 128.7, 127.2, 126.9, 124.4, 123.5, 120.1, 120.1, 114.5, 112.9, 55.2, 44.4.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₅H₂₈NO₂⁺ 494.2115; Found 494.2108.

Optical [α]_D²⁵ = -0.08 (c = 0.10, CH₂Cl₂, 90% ee).

HPLC (AD-H, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 24.0 min (major), 26.2 min (minor).



(S)-2-(2,2-diphenyl-1-(p-tolyl)vinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4e) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4e** as a yellow solid (36.2 mg, 71% yield).

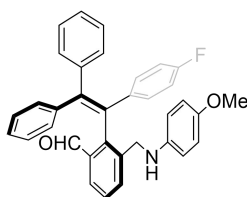
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.35 (s, 1H), 7.59 – 7.47 (m, 2H), 7.36 – 7.30 (m, 1H), 7.24 – 7.20 (m, 3H), 7.15 – 7.12 (m, 2H), 7.11 – 7.08 (m, 3H), 6.97 – 6.95 (m, 2H), 6.92 – 6.90 (m, 2H), 6.88 – 6.85 (m, 2H), 6.61 – 6.53 (m, 2H), 6.11 – 6.02 (m, 2H), 5.80 (t, *J* = 6.1 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.12 – 4.06 (m, 1H), 3.59 (s, 3H), 2.20 (s, 3H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.1, 150.8, 143.9, 143.4, 142.5, 142.4, 142.2, 139.5, 137.9, 136.3, 134.1, 133.5, 132.2, 130.6, 130.2, 129.2, 128.6, 128.2, 127.9, 127.7, 127.2, 126.1, 114.5, 113.0, 55.2, 44.8, 20.7.

HRMS: (ESI) m/z: [M+H]⁺ Calcd for C₃₆H₃₂NO₂⁺ 510.2428; Found 510.2425.

Optical [α]_D²⁵ = -5.84 (c = 0.15, CH₂Cl₂, 91% ee).

HPLC (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 15.5 min (major), 13.0 min (minor).



(S)-2-(1-(4-fluorophenyl)-2,2-diphenylvinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4f) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4f** as a yellow solid (45.3 mg, 88% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.32 (s, 1H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.15 – 7.12 (m, 2H), 7.12 – 7.10 (m, 3H), 7.00 (dd, *J* = 7.1, 4.1 Hz, 4H), 6.93 – 6.90 (m, 2H), 6.59 – 6.56 (m, 2H), 6.11 – 6.08 (m, 2H), 5.82 (t, *J* = 6.1 Hz, 1H), 4.26 (s, 1H), 4.10 – 4.04 (m, 1H), 3.59 (s, 3H).

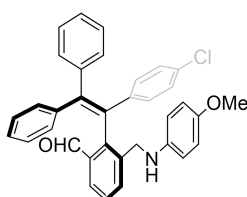
¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.1, 160.7 (d, *J* = 245.4 Hz), 150.8, 144.0, 143.2, 142.4, 142.2, 141.9, 139.5, 137.2, 134.2, 132.7, 132.4, 130.7, 129.2, 128.2, 127.9, 127.3 (d, *J* = 4.2 Hz), 126.7, 114.9 (d, *J* = 21.5 Hz), 114.5, 113.0, 55.2, 44.9.

¹⁹F NMR (565 MHz, (CD₃)₂SO-d₆) δ -114.4.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₂₉FNO₂⁺ 514.2177; Found 514.2173.

Optical [α]_D²⁵ = -5.47 (c = 0.18, CH₂Cl₂, 90% ee).

HPLC (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 16.0 min (major), 13.8 min (minor).



(S)-2-(1-(4-chlorophenyl)-2,2-diphenylvinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4g) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4g** as a yellow solid (32.9 mg, 62% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 10.37 – 10.29 (m, 1H), 7.60 – 7.52 (m, 2H), 7.37 – 7.32 (m, 1H), 7.26 – 7.21 (m, 3H), 7.15 – 7.12 (m, 2H), 7.12 – 7.09 (m, 3H), 7.00 – 6.97 (m, 2H), 6.93 – 6.90 (m, 2H), 6.59 – 6.53 (m, 2H), 6.08 (dd, *J* = 8.2, 1.5 Hz, 2H),

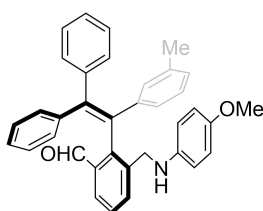
5.84 – 5.78 (m, 1H), 4.31 – 4.20 (m, 1H), 4.12 – 4.04 (m, 1H), 3.59 (d, $J = 3.6$ Hz, 3H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 150.8, 144.5, 142.9, 142.4, 142.1, 141.8, 139.7, 139.5, 134.2, 132.6, 132.3, 132.1, 131.5, 130.7, 130.3, 129.1, 128.3, 128.0, 127.9, 127.5, 127.4, 127.2, 126.9, 114.53, 114.51, 113.0, 55.2, 44.9.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{29}\text{ClNO}_2^+$ 530.1881; Found 530.1875.

Optical $[\alpha]_{\text{D}}^{25} = -3.64$ ($c = 0.14$, CH_2Cl_2 , 90% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 16.5$ min (major), 14.4 min (minor).



(S)-2-(2,2-diphenyl-1-(m-tolyl)vinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4h) was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO_2 , petroleum ether: EtOAc = 10:1) to provide **4h** as a yellow solid (39.8 mg, 78% yield).

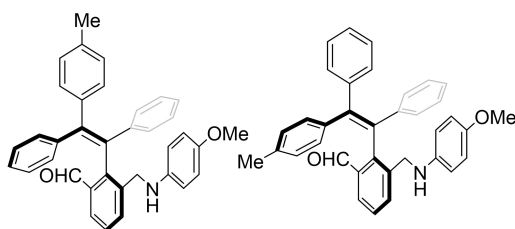
^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.35 (s, 1H), 7.57 – 7.52 (m, 2H), 7.36 – 7.30 (m, 1H), 7.24 – 7.21 (m, 3H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.97 – 6.93 (m, 1H), 6.93 – 6.89 (m, 2H), 6.81 – 6.77 (m, 2H), 6.58 – 6.54 (m, 2H), 6.13 – 6.03 (m, 2H), 5.80 (t, $J = 6.1$ Hz, 1H), 4.28 – 4.21 (m, 1H), 4.13 – 4.06 (m, 1H), 3.59 (s, 3H), 2.07 (d, $J = 0.8$ Hz, 3H).

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 192.1, 150.8, 143.9, 143.7, 142.4, 142.2, 140.7, 139.6, 137.0, 134.1, 133.7, 132.2, 130.6, 129.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.2, 126.1, 114.5, 113.0, 55.2, 44.8.

HRMS: (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{32}\text{NO}_2^+$ 510.2428; Found 510.2421.

Optical $[\alpha]_{\text{D}}^{25} = -3.81$ ($c = 0.15$, CH_2Cl_2 , 91% ee).

HPLC (IA, $i\text{PrOH}/n\text{-hexane} = 20/80$, flow rate = 0.5 mL/min, 254 nm) $t_{\text{R}} = 14.8$ min (major), 13.3 min (minor).



(*S,E*)-2-(1,2-diphenyl-2-(*p*-tolyl)vinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde/(*S,Z*)-2-(1,2-diphenyl-2-(*p*-tolyl)vinyl)-3-(((4-methoxyphenyl)amino)methyl)benzaldehyde (4i**)** was synthesized by following Procedure B. The crude material was purified by column chromatography (SiO₂, petroleum ether: EtOAc = 10:1) to provide **4i** as a yellow solid (36.2 mg, 71% yield).

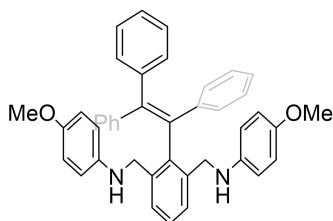
¹H NMR (600 MHz, (CD₃)₂SO) δ 10.35 (dd, *J* = 4.1, 0.8 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.38 – 7.30 (m, 1H), 7.22 – 7.20 (m, 1H), 7.17 – 7.13 (m, 2H), 7.13 – 7.08 (m, 4H), 7.03 (s, 1H), 7.01 – 6.98 (m, 2H), 6.98 – 6.96 (m, 1H), 6.93 – 6.89 (m, 2H), 6.82 – 6.77 (m, 1H), 6.58 – 6.51 (m, 2H), 6.09 – 6.03 (m, 2H), 5.84 – 5.79 (m, 1H), 4.29 – 4.21 (m, 1H), 4.13 – 4.04 (m, 1H), 3.58 (d, *J* = 1.1 Hz, 3H), 2.29 – 2.16 (m, 3H).

¹³C NMR (151 MHz, (CD₃)₂SO) δ 192.2, 192.1, 150.7, 144.00, 143.95, 143.9, 143.8, 142.5, 142.4, 142.4, 142.3, 141.0, 140.9, 139.6, 139.5, 139.1, 136.6, 136.5, 134.1, 133.2, 133.1, 132.2, 130.7, 130.6, 130.3, 129.2, 129.2, 128.8, 128.5, 128.1, 128.03, 127.97, 127.9, 127.8, 127.2, 127.0, 126.9, 126.2, 126.1, 114.5, 114.5, 113.0, 55.2, 44.8, 20.8.

HRMS: (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₂NO₂⁺ 510.2428; Found 510.2422.

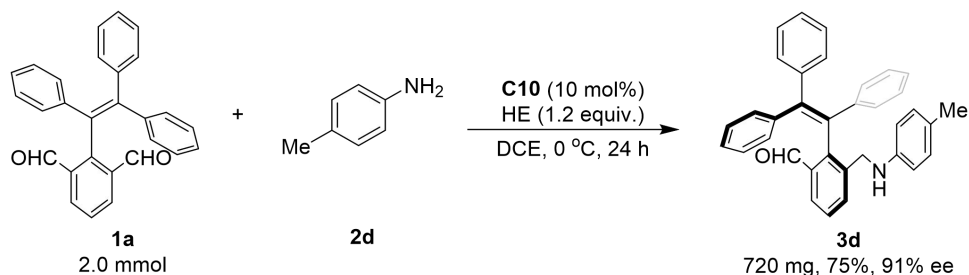
Optical [α]_D²⁵ = -3.64 (*c* = 0.14, CH₂Cl₂, 85% ee, 80% ee).

HPLC (AD-H, ⁱPrOH/*n*-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 30.2 min (major), 33.2 min (minor). *t*_R = 46.2 min (major), 43.4 min (minor).



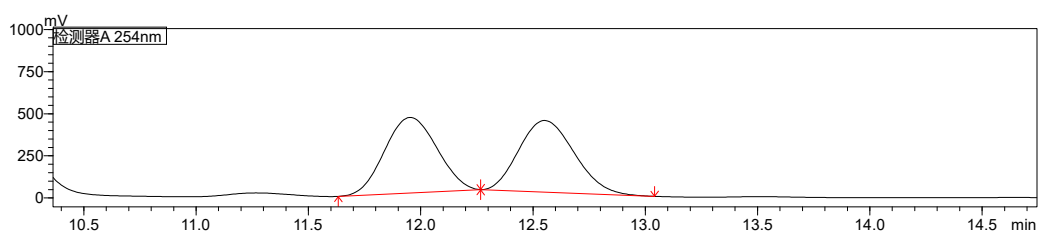
¹H NMR (400 MHz, (CD₃)₂SO) δ 7.22 (d, *J* = 6.3 Hz, 4H), 7.17 – 7.07 (m, 11H), 7.02 – 6.92 (m, 5H), 6.60 – 6.51 (m, 4H), 6.13 – 6.05 (m, 4H), 4.27 – 4.10 (m, 4H), 3.59 (s, 6H).

4. Synthetic Applications

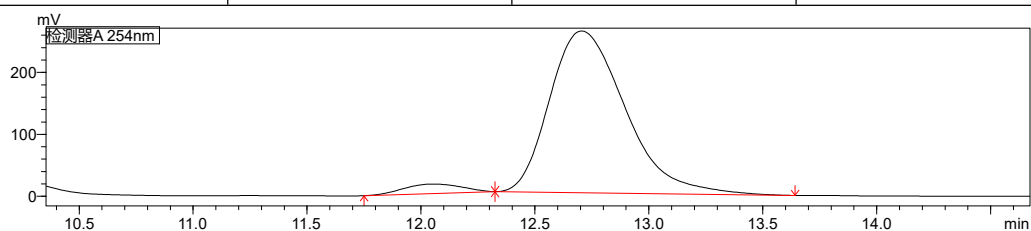


Under air atmosphere, TAE dialdehyde **1a** (2.0 mmol, 796.3 mg), aromatic amine **2d** (214.3 mg, 2.0 mmol, 1.0 equiv.), **C10** (138.2 mg, 0.2 mmol, 10 mol%) and HE (729.8 mg, 2.4 mmol, 1.2 equiv.) were placed in a reaction tube and anhydrous DCE (20.0 mL) was added into this reaction mixture via syringe, and stirred at 0 °C for 24 h. After completion of the reaction, the crude mixture was purified by column chromatography on silica gel to afford the corresponding product **3d** (720 mg, 75% yield, 91% ee).

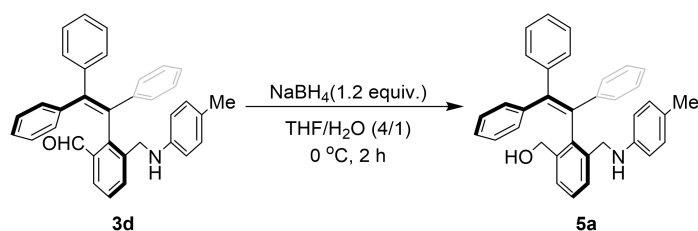
HPLC conditions: Chiralpak IA, 20% ⁱPrOH/Hx eluent, 0.5 mL/min, 254 nm



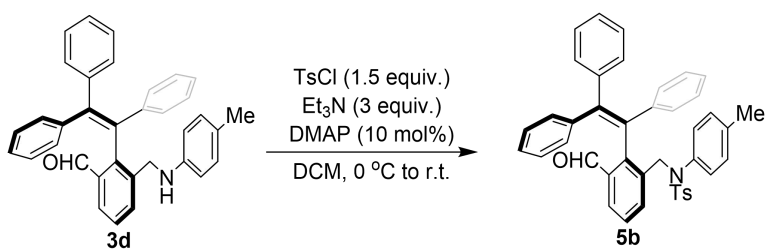
Peak#	Ret. Time	Height	Area%
1	11.953	448209	49.934
2	12.551	425045	50.066



Peak#	Ret. Time	Height	Area%
1	12.054	15346	4.333
2	12.704	261134	95.667

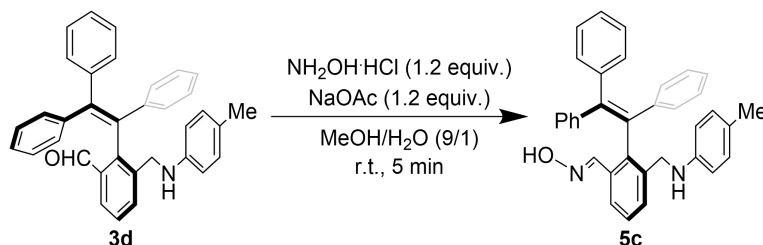


To a solution of **3d** (47.9 mg, 0.10 mmol, 1.0 equiv.) in THF/H₂O (4:1 v/v, 10.0 mL) was added NaBH₄ (4.5 mg, 0.12 mmol, 1.2 equiv.) under air. The mixture was stirred for another 2 h and quenched with saturated aqueous NH₄Cl and extracted with ethyl acetate. The organic layer was combined, dried over anhydrous Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 5:1) to afford **5a** as colorless solid (29.4 mg, 61% yield, 91% ee). ¹H NMR (600 MHz, (CD₃)₂SO) δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.06 (m, 9H), 6.98 – 6.94 (m, 4H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.04 – 5.98 (m, 2H), 5.86 (t, *J* = 6.1 Hz, 1H), 5.18 (t, *J* = 5.5 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.41 – 4.35 (m, 1H), 4.16 (d, *J* = 6.1 Hz, 2H), 2.08 (s, 3H). ¹³C NMR (151 MHz, (CD₃)₂SO) δ 146.3, 142.8, 142.6, 141.8, 140.7, 140.3, 137.9, 137.0, 135.7, 130.9, 130.1, 129.22, 129.19, 128.1, 127.7, 127.6, 127.1, 126.9, 126.6, 124.5, 124.4, 123.9, 112.1, 61.0, 44.8, 20.0. **HRMS:** (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₃₂NO⁺ 482.2478; Found 482.2472. **Optical** [α]_D²⁵ = 0.75 (*c* = 0.13, CH₂Cl₂, 91% ee). **HPLC** (IA, ^tPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) *t*_R = 17.4 min (major), 14.5 min (minor).

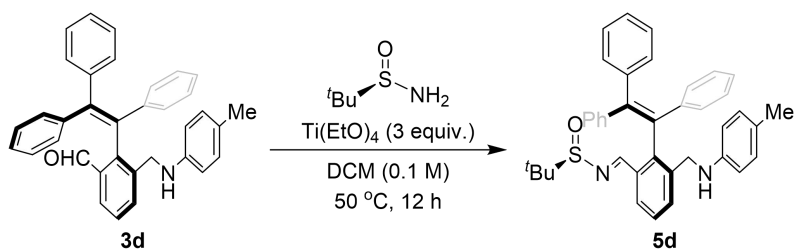


To a solution of **3d** (47.9 mg, 0.10 mmol, 91% ee) and 4-toluene sulfonyl chloride (47.5 mg, 0.25 mmol) in DCM (2.0 mL) was added Et₃N (30.5 mg, 0.30 mmol) and DMAP (1.2 mg, 0.010 mmol) at 0 °C, then the mixture was allowed to warm to room temperature and stirred for 12 h, after which the mixture was filtered and the solvent was removed in vacuo. The residue was purified with flash chromatography (PE/EA = 10:1) to afford the product **5b** (32.3 mg, 51% yield, 89%

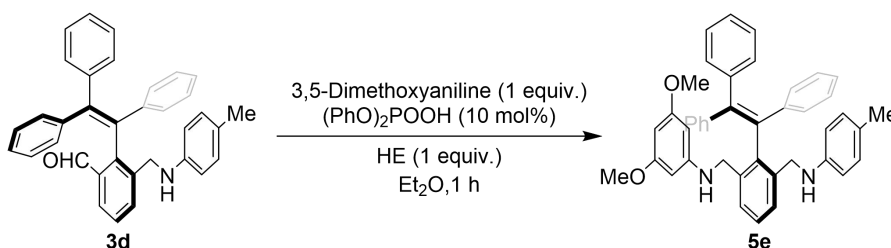
ee). **¹H NMR** (600 MHz, (CD₃)₂SO) δ 10.19 (s, 1H), 7.86 – 7.74 (m, 1H), 7.64 – 7.51 (m, 1H), 7.43 – 7.40 (m, 2H), 7.34 – 7.31 (m, 2H), 7.23 – 7.21 (m, 3H), 7.15 – 7.08 (m, 2H), 7.08 – 7.03 (m, 4H), 7.02 – 6.99 (m, 4H), 6.97 – 6.94 (m, 2H), 6.76 – 6.72 (m, 2H), 6.66 – 6.63 (m, 2H), 6.63 – 6.60 (m, 1H), 4.61 – 4.37 (m, 2H), 2.41 (s, 3H), 2.26 – 2.23 (m, 3H). **¹³C NMR** (151 MHz, (CD₃)₂SO) δ 191.7, 145.0, 143.9, 143.4, 141.9, 141.8, 140.7, 137.7, 136.2, 135.5, 134.2, 134.0, 133.0, 132.9, 130.6, 130.2, 129.8, 129.7, 129.6, 129.3, 128.1, 128.0, 127.8, 127.7, 127.3, 120.5, 51.4, 21.0. **HRMS:** (ESI) m/z: [M+H]⁺ Calcd for C₄₂H₃₆NO₃S⁺ 634.2410; Found 634.2403. **Optical** [α]_D²⁵ = -0.90 (c = 0.08, CH₂Cl₂, 89% ee). **HPLC** (AD-H, *i*PrOH/n-hexane = 10/90, flow rate = 0.5 mL/min, 254 nm) t_R = 28.3 min (major), 31.5 min (minor).



3a (47.9 mg, 0.10 mmol, 1.0 equiv.), NH₂OH·HCl (0.12 mmol) and NaOAc (0.12 mmol) were stirred at 25 °C for 5 min in a 9:1 mixture of MeOH/ H₂O (1.5 mL) under air. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and treated with saturated aqueous NH₄Cl (1 mL). The organic layer was combined, dried over anhydrous Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 1:1) to afford the desired product **5c** as colorless oil (27.8 mg, 56% yield, 91% ee). **¹H NMR** (600 MHz, (CD₃)₂SO) δ 11.26 (s, 1H), 8.34 (s, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.23 – 7.20 (m, 4H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.14 – 7.10 (m, 6H), 7.10 – 7.07 (m, 2H), 6.95 – 6.92 (m, 4H), 6.74 – 6.69 (m, 2H), 6.03 – 5.99 (m, 2H), 5.94 (t, *J* = 6.1 Hz, 1H), 4.26 – 4.14 (m, 2H), 2.08 (s, 3H). **¹³C NMR** (151 MHz, (CD₃)₂SO) δ 146.7, 146.1, 143.0, 142.5, 142.4, 140.7, 139.8, 138.3, 134.9, 131.4, 130.7, 130.0, 129.2, 129.1, 128.2, 128.0, 127.7, 127.4, 127.2, 126.9, 124.1, 123.3, 112.1, 44.7, 20.0, 14.1. **HRMS:** (ESI) m/z: [M+H]⁺ Calcd for C₃₅H₃₁N₂O⁺ 495.2431; Found 495.2425. **Optical** [α]_D²⁵ = -0.14 (c = 0.06, CH₂Cl₂, 91% ee). **HPLC** (IA, *i*PrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 13.2 min (major), 14.8 min (minor).



The **3d** (47.9 mg, 0.1 mmol), (*R*)-(+)-2-Methyl-2-propanesulfonamide (36.5 mg, 0.3 mmol), and $\text{Ti}(\text{OEt})_4$ (0.78 mL, 3.5 mmol) were mixed and stirred at 2 mL DCM at 50 °C. After reflux overnight, add 10 mL of water to the solution and filter through sand core funnel. The filtrate was extracted with DCM for three times and the organic phase was collected. The organic phase was dried with anhydrous sodium sulfate and concentrated in vacuo to give a residue, which was purified by flash chromatography (PE/EA = 10:1) to afford the products **5d** as white solid. (42.0 mg, 72% yield, > 20/1 dr). $^1\text{H NMR}$ (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 7.23 – 7.20 (m, 3H), 7.17 (d, $J = 7.1$ Hz, 1H), 7.13 (d, $J = 7.5$ Hz, 2H), 7.10 (dd, $J = 7.6, 4.0$ Hz, 8H), 7.02 – 6.98 (m, 4H), 6.72 (d, $J = 8.1$ Hz, 2H), 6.10 (t, $J = 6.1$ Hz, 1H), 6.02 (d, $J = 8.0$ Hz, 2H), 5.87 (t, $J = 6.1$ Hz, 1H), 5.70 (t, $J = 2.1$ Hz, 1H), 5.54 (d, $J = 2.1$ Hz, 2H), 4.19 – 4.13 (m, 3H), 4.11 – 4.06 (m, 1H), 3.58 (s, 6H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, $(\text{CD}_3)_2\text{SO}$) δ 165.2, 161.8, 161.3, 146.0, 143.8, 142.9, 142.1, 140.3, 139.9, 139.4, 134.0, 130.5, 130.1, 129.2, 128.9, 128.2, 128.0, 127.7, 127.2, 125.3, 124.2, 122.7, 112.1, 61.2, 57.5, 44.6, 22.1, 20.0. **HRMS:** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{39}\text{H}_{39}\text{N}_2\text{OS}^+$ 583.2778; Found 583.2772. **Optical** $[\alpha]_{\text{D}}^{25} = -14.83$ ($c = 0.18, \text{CH}_2\text{Cl}_2$).



A 25 mL vial containing a magnetic stir bar, was added **5a** (47.9 mg, 0.1 mmol, 1.0 equiv.), diphenyl phosphate (2.5 mg, 0.01 mmol, 0.1 equiv.), HE (25.0 mg, 0.1 mmol, 1.0 equiv.), 3,4,5-trimethoxyaniline (18.0 mg, 0.1 mmol, 1.0 equiv.) and 7.5 mL dry Et_2O . After stirring at the 25 °C for 1 h, the reaction mixture concentrated in vacuo to give a residue, which was purified by flash chromatography (PE/EA = 10:1) to afford the products **5e** as Black green oil (28.4 mg, 46% yield, 87% ee). $^1\text{H NMR}$

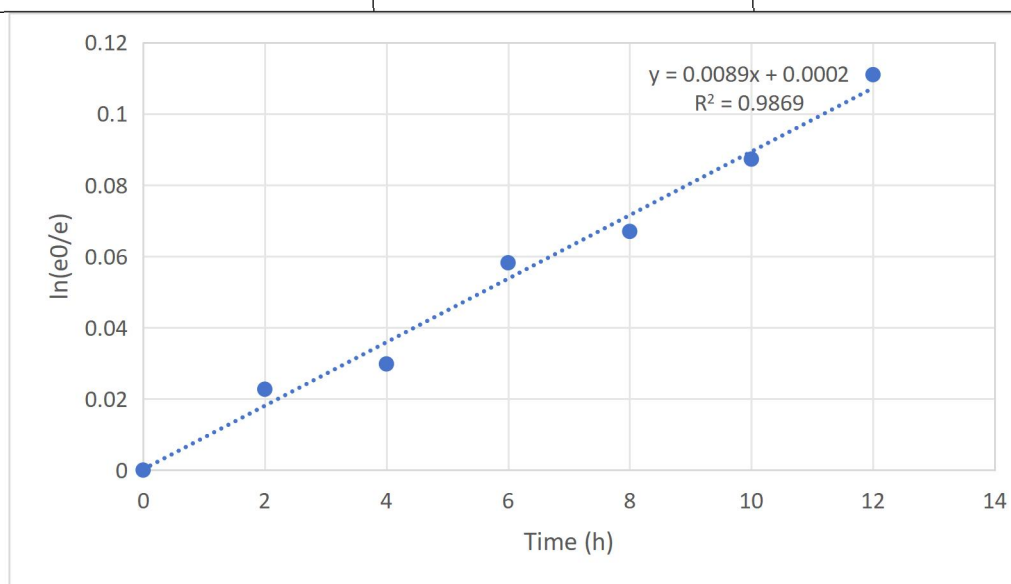
(600 MHz, (CD₃)₂SO) δ 7.23 – 7.20 (m, 3H), 7.17 (d, J = 7.1 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 7.10 (dd, J = 7.6, 4.0 Hz, 8H), 7.02 – 6.98 (m, 4H), 6.72 (d, J = 8.1 Hz, 2H), 6.10 (t, J = 6.1 Hz, 1H), 6.02 (d, J = 8.0 Hz, 2H), 5.87 (t, J = 6.1 Hz, 1H), 5.70 (t, J = 2.1 Hz, 1H), 5.54 (d, J = 2.1 Hz, 2H), 4.19 – 4.13 (m, 3H), 4.11 – 4.06 (m, 1H), 3.58 (s, 6H), 2.08 (s, 3H). **¹³C NMR** (151 MHz, (CD₃)₂SO) δ 161.1, 150.6, 146.3, 142.8, 142.6, 142.2, 140.6, 138.9, 137.6, 137.5, 135.7, 130.9, 130.2, 129.2, 128.2, 127.8, 127.7, 127.3, 127.2, 127.0, 126.8, 124.7, 124.6, 123.9, 112.0, 90.8, 54.7, 44.9, 20.0. **HRMS:** (ESI) m/z : [M+H]⁺ Calcd for C₄₃H₄₁N₂O₂⁺ 617.3163; Found 617.3154. **Optical** [α]_D²⁵ = -1.73 (c = 0.16, CH₂Cl₂, 87% ee). **HPLC** (IA, ⁱPrOH/n-hexane = 20/80, flow rate = 0.5 mL/min, 254 nm) t_R = 33.0 min (major), 25.4 min (minor).

5. Mechanistic Experiments

Racemization experiments.

Racemization of **3p** in toluene at 120 °C

Time (h)	ee (%)	ln(e0/e)
0	91.474	0
2	89.412	0.0227
4	88.786	0.0298
6	86.298	0.0582
8	85.542	0.067
10	83.828	0.0873
12	81.868	0.111



$$k_{\text{racemisation}} = 0.0089 \text{ h}^{-1}$$

$$k_{\text{enantiomerisation}} = 0.00445 \text{ h}^{-1}$$

$$\Delta G_{\ddagger}^{\text{enantiomerization}} = RT \times \ln \frac{k_B \times T}{h \times k_{\text{enantiomerisation}}}$$

$$\Delta G_{\ddagger}^{\text{enantiomerization}} = 141.66 \text{ KJ/mol} = 33.8 \text{ Kcal/mol}$$

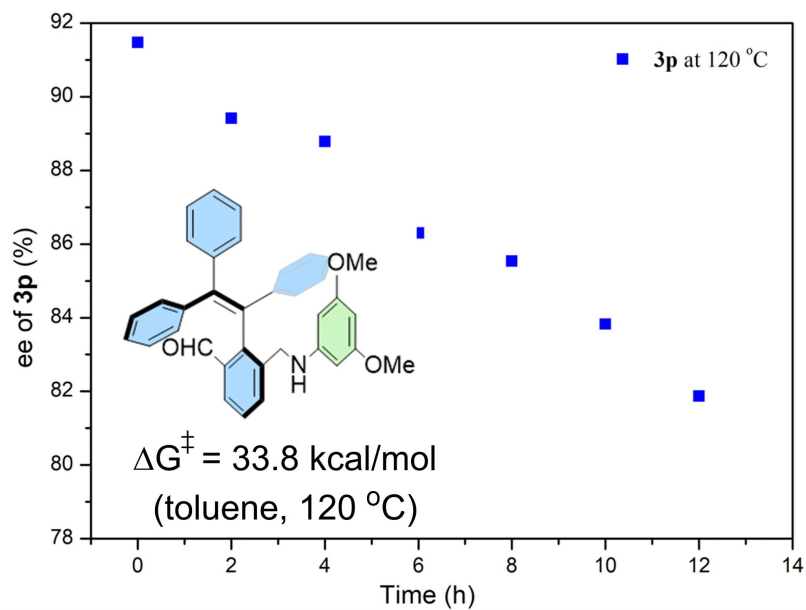
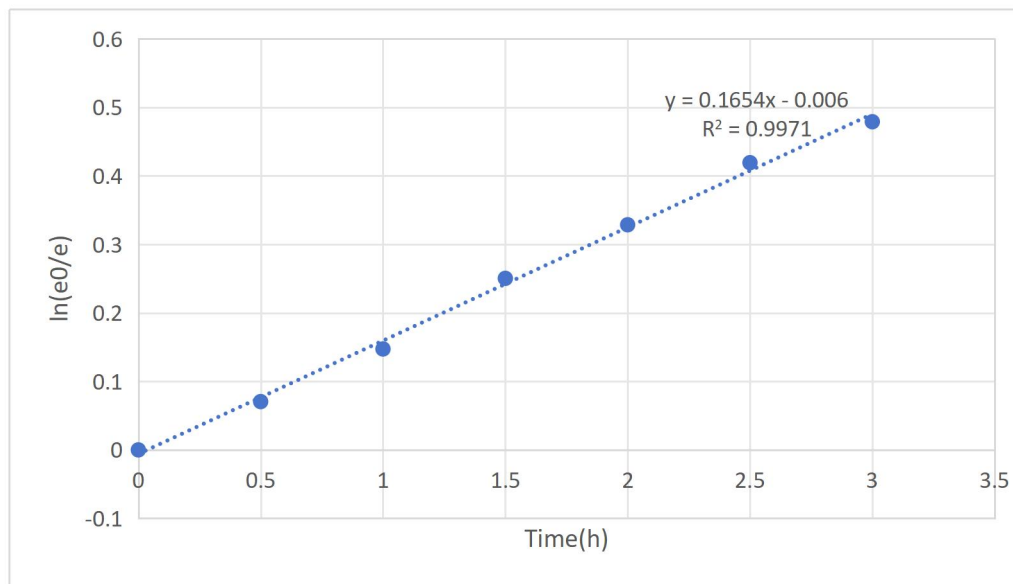


Figure S1. Racemization of **3p** in toluene

Racemization of **3ab** in Mesitylene at 140 °C

Time (h)	ee (%)	$\ln(e_0/e)$
0	81.156	0
0.5	75.630	0.0705
1	70.042	0.1473
1.5	63.178	0.2504
2	58.428	0.3286
2.5	53.364	0.4192
3	50.268	0.4790



$$k_{\text{racemisation}} = 0.1654 \text{ h}^{-1}$$

$$k_{\text{enantiomerisation}} = 0.0827 \text{ h}^{-1}$$

$$\Delta G_{\ddagger}^{\text{enantiomerization}} = RT \times \ln \frac{k_B \times T}{h \times k_{\text{enantiomerisation}}}$$

$$\Delta G_{\ddagger}^{\text{enantiomerization}} = 139.00 \text{ KJ/mol} = 33.2 \text{ Kcal/mol}$$

Non-linear effect.

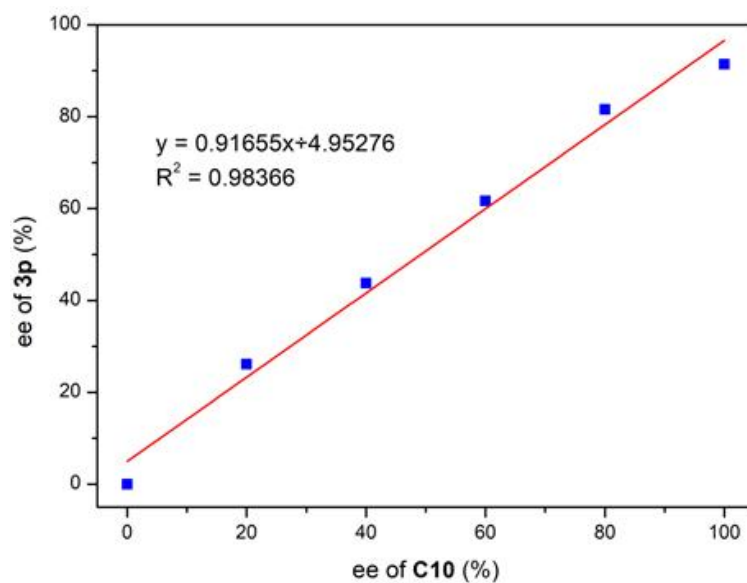
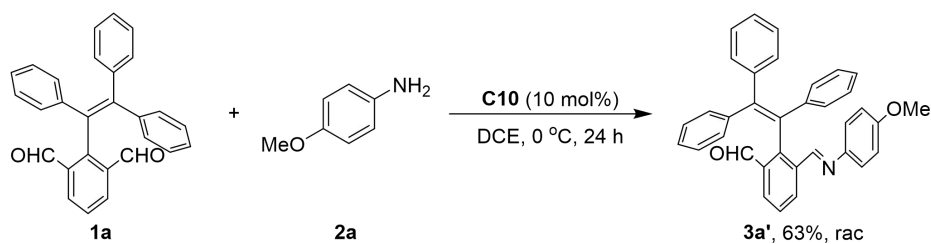


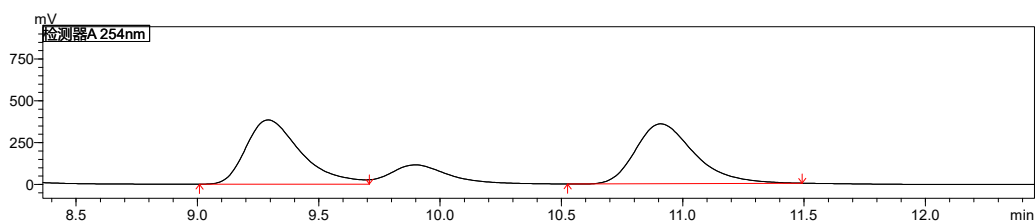
Figure S2. Non-linear effect of the C10

Control experiment.

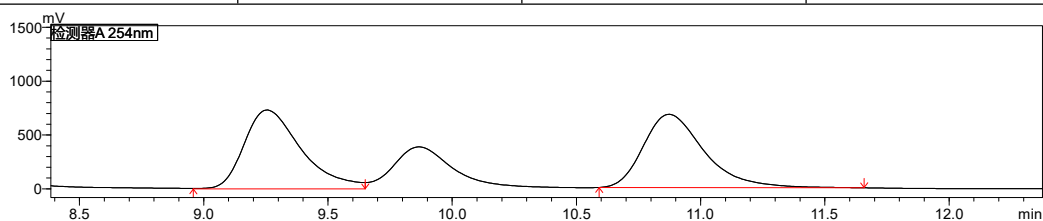


Under air atmosphere, TAE dialdehyde **1a** (0.1 mmol), aromatic amine **2a** (0.1 mmol, 1.0 equiv.) and **C10** (6.9 mg, 0.01 mmol, 10 mol%) were placed in a reaction tube and anhydrous DCE (1.0 mL) was added into this reaction mixture via syringe, and stirred at 0 °C for 24 h. After completion of the reaction, the crude mixture was purified by column chromatography on silica gel to afford the corresponding product **3a'** (31.2 mg, 63% yield).

HPLC conditions: Chiralpak AD, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

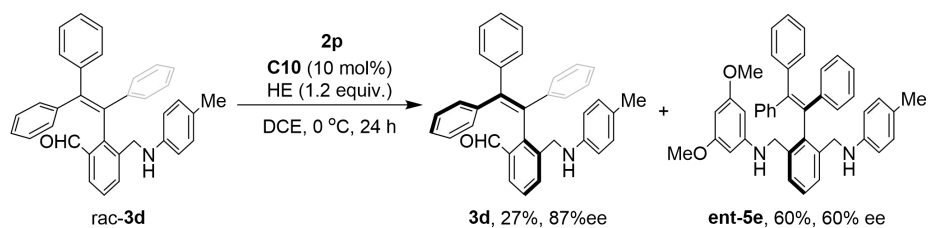


Peak#	Ret. Time	Height	Area%
1	9.291	6113345	50.325
2	10.909	6034368	49.675



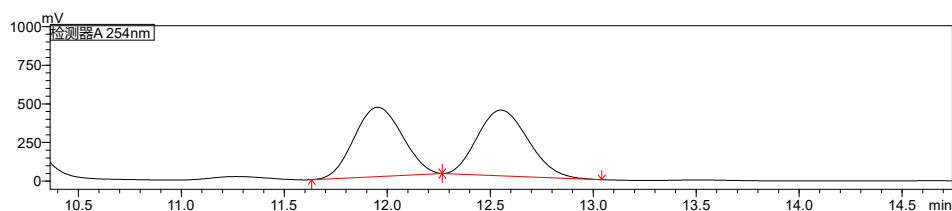
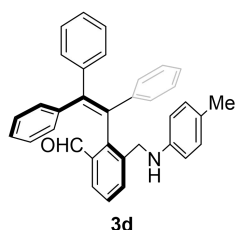
Peak#	Ret. Time	Height	Area%
1	9.255	11806152	50.472
2	10.873	11585454	49.528

Kinetic resolution.

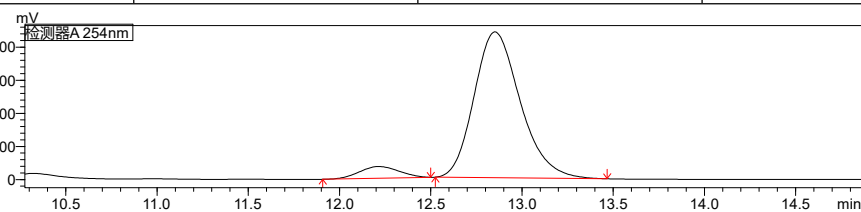


Under air atmosphere, *rac*-**3d** (0.1 mmol), **2p** (0.1 mmol, 1.0 equiv.), **C10** (6.9 mg, 0.01 mmol, 10 mol%) and **HE** (30.4 mg, 0.12 mmol, 1.2 equiv.) were placed in a reaction tube and anhydrous DCE (1.0 mL) was added into this reaction mixture via syringe, and stirred at 0 °C for 24 h. After completion of the reaction, the crude mixture was purified by column chromatography on silica gel to afford the corresponding product **ent-5e** (28.4 mg, 60% yield, 60% ee) and **3d** (12.9 mg, 27% yield, 87% ee).

HPLC conditions: Chiralpak IA, 20% ⁱPrOH/Hx eluent, 0.5 mL/min, 254 nm

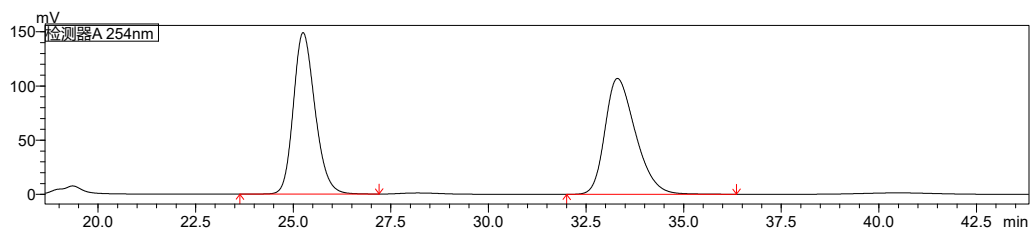
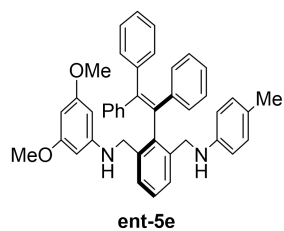


Peak#	Ret. Time	Height	Area%
1	11.953	448209	49.934
2	12.551	425045	50.066

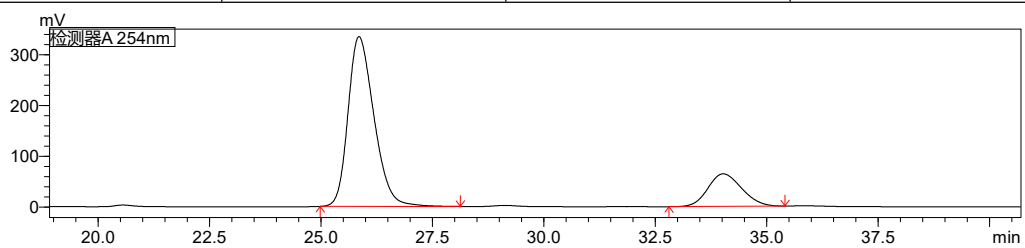


Peak#	Ret. Time	Height	Area%
1	12.215	35522	6.509
2	12.852	440575	93.491

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm



Peak#	Ret. Time	Height	Area%
1	25.250	149114	49.738
2	33.303	106910	50.262



Peak#	Ret. Time	Height	Area%
1	25.852	334598	79.999
2	34.024	64186	20.001

6. Copies of Optical spectras

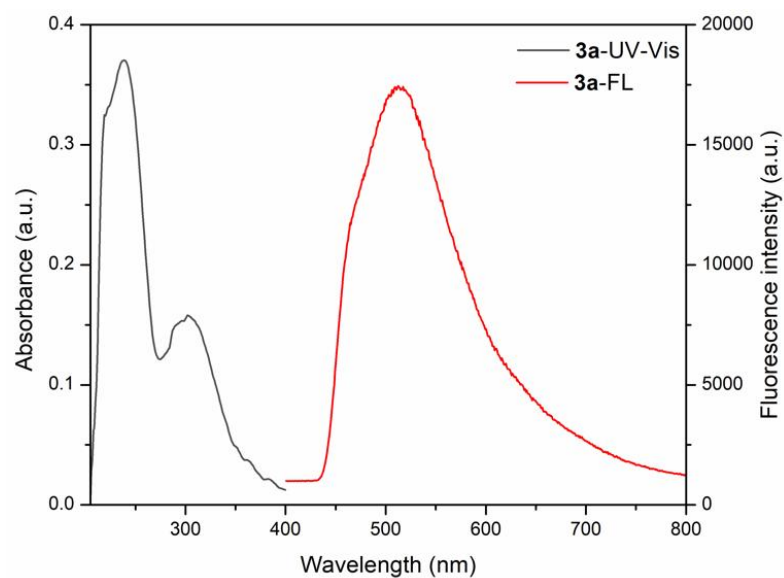


Figure S3. Absorption spectra and emission spectra of **3a** in THF at 25 °C (ca. 1×10^{-5} M).

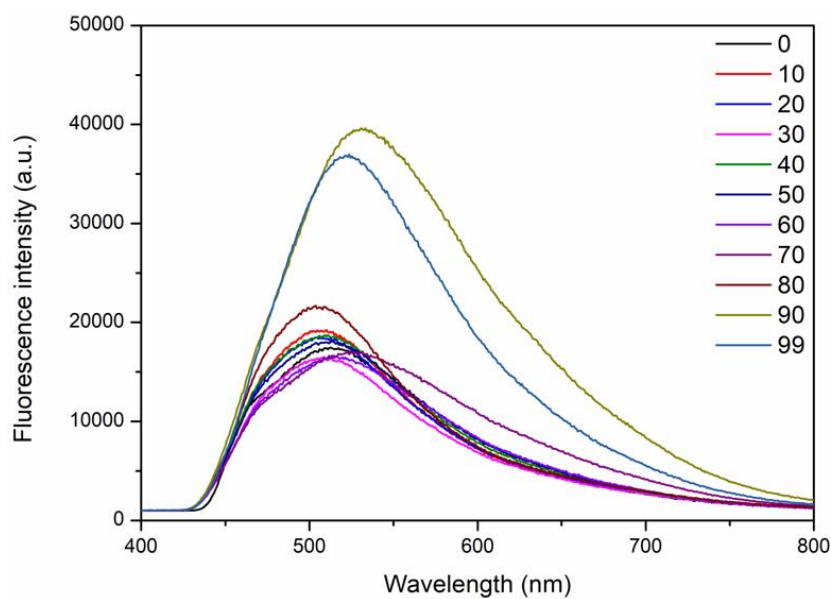


Figure S4. The PL intensity of **3a** in THF/H₂O mixed solvents at 25 °C (ca. 1×10^{-5} M).

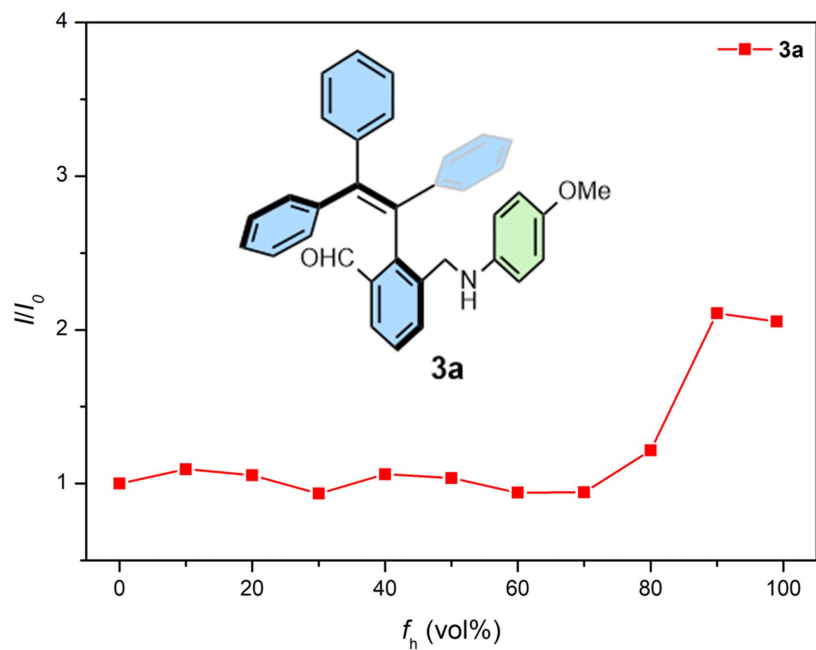


Figure S5. Relative PL intensity of **3a**.

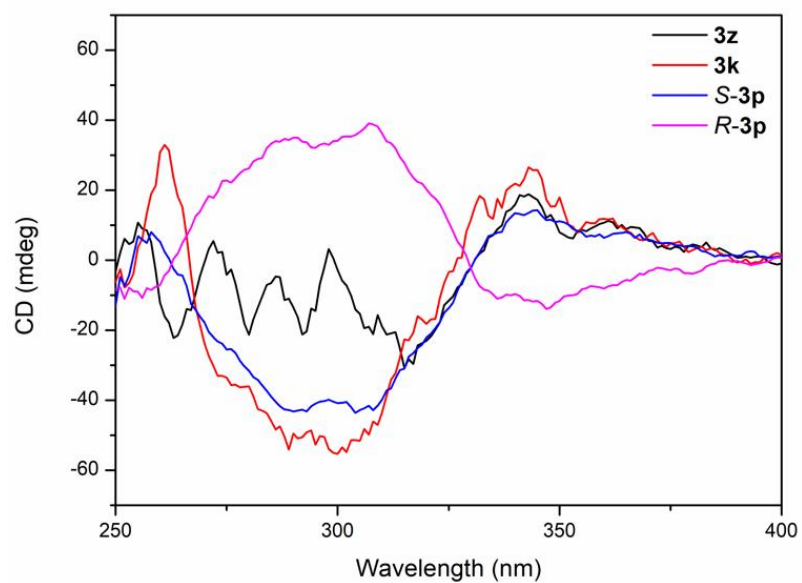


Figure S6. CD spectra of **3z**, **3k**, **S-3p** and **R-3p** in THF at 25 °C (ca. 1×10^{-3} M).

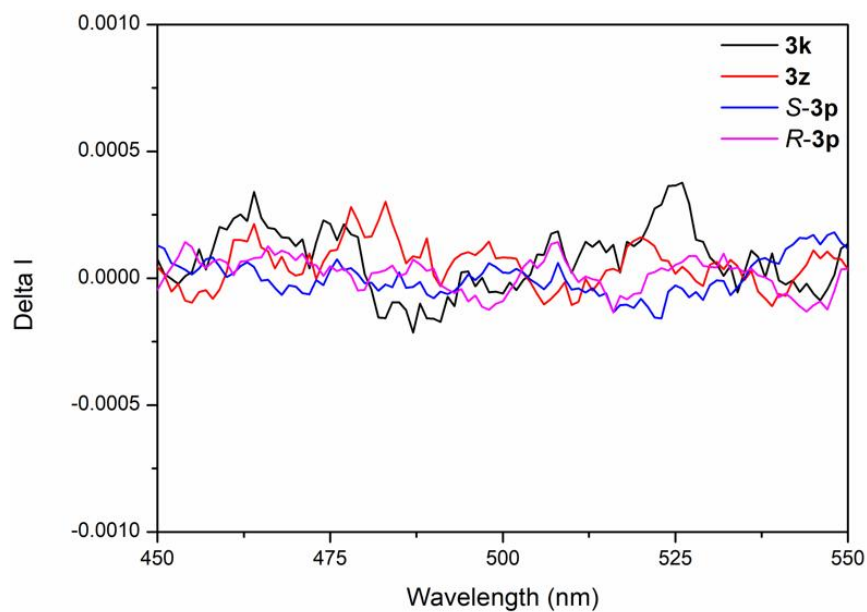


Figure S7. CPL spectra of **3z**, **3k**, **S-3p** and **R-3p** in THF at 25 °C (ca. 1×10^{-5} M).

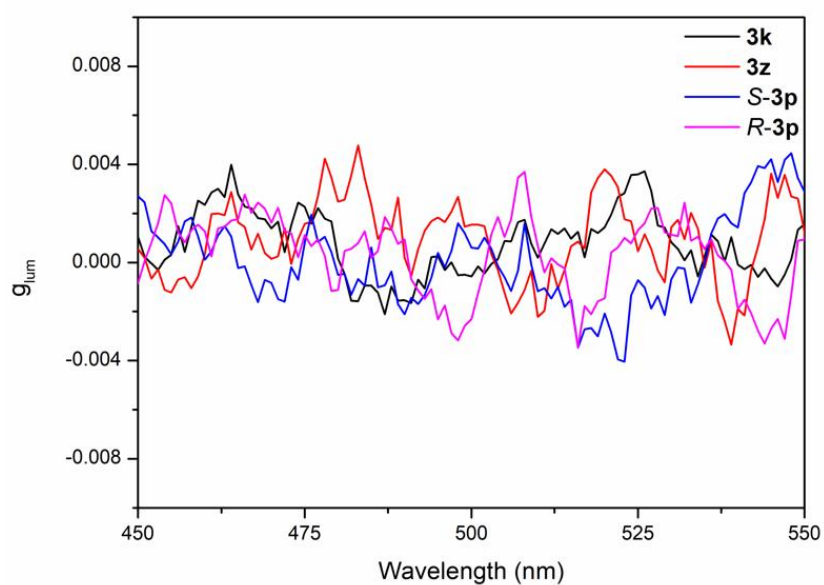
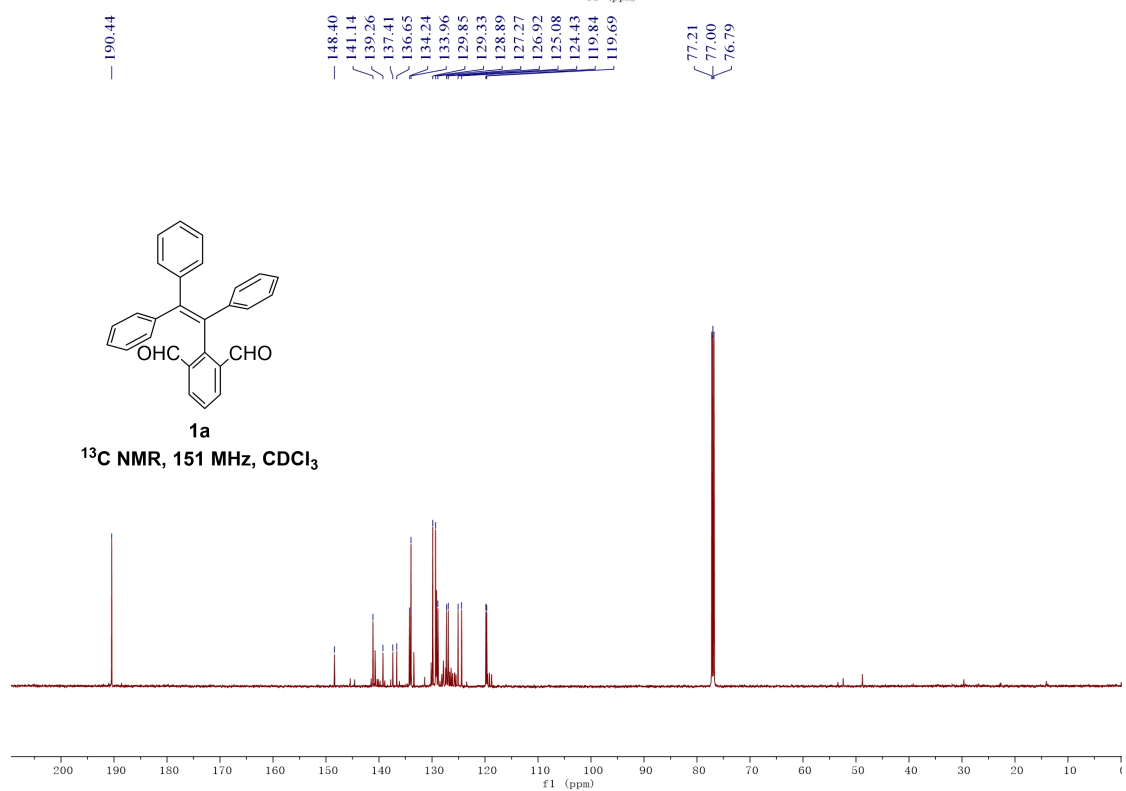
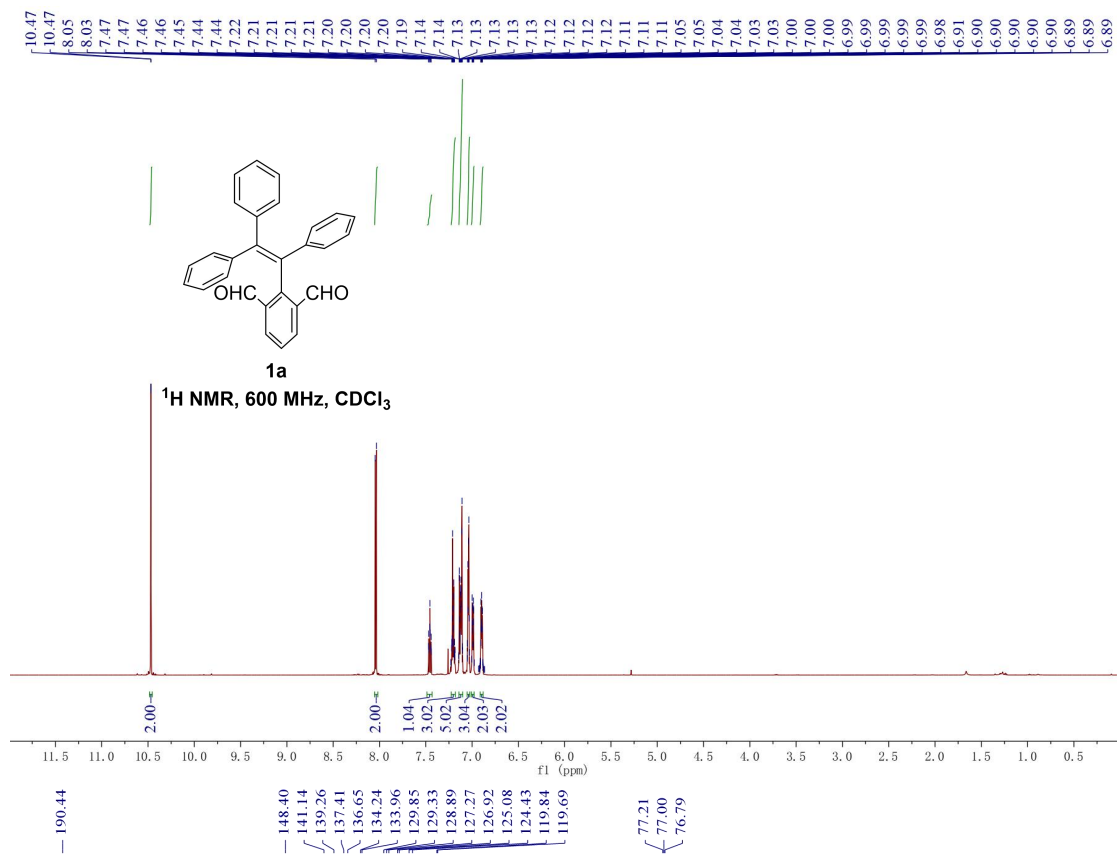
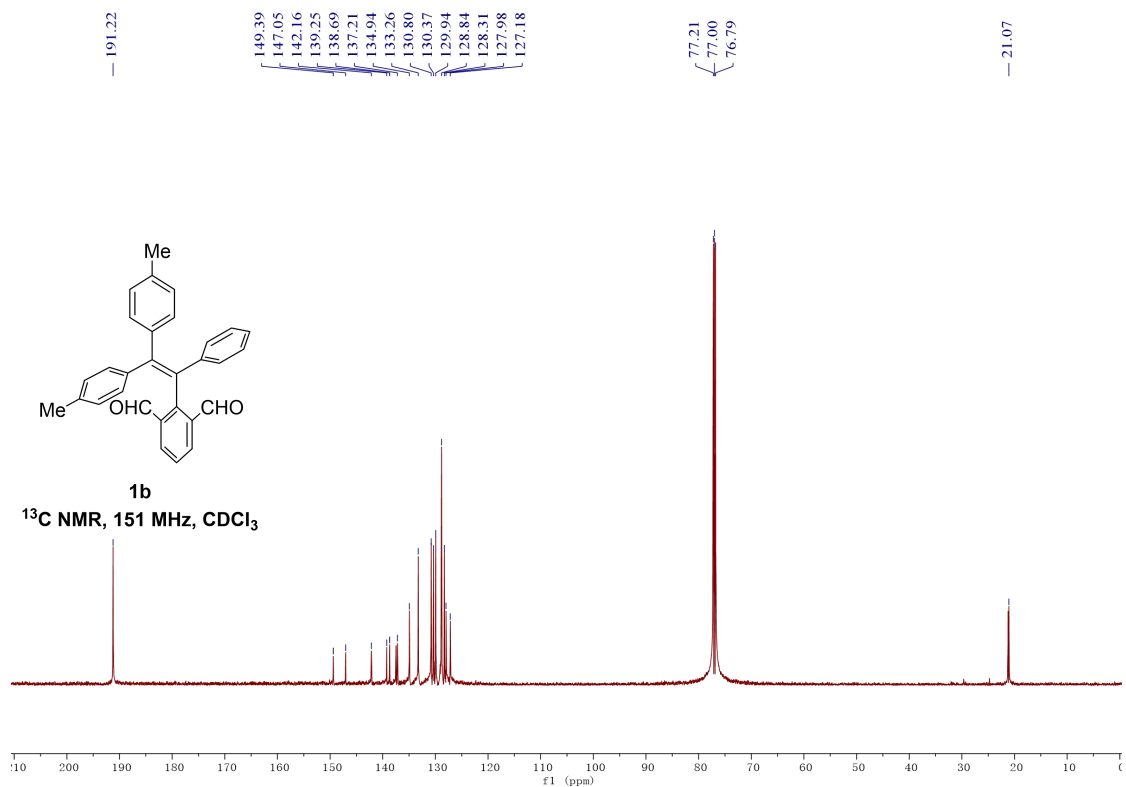
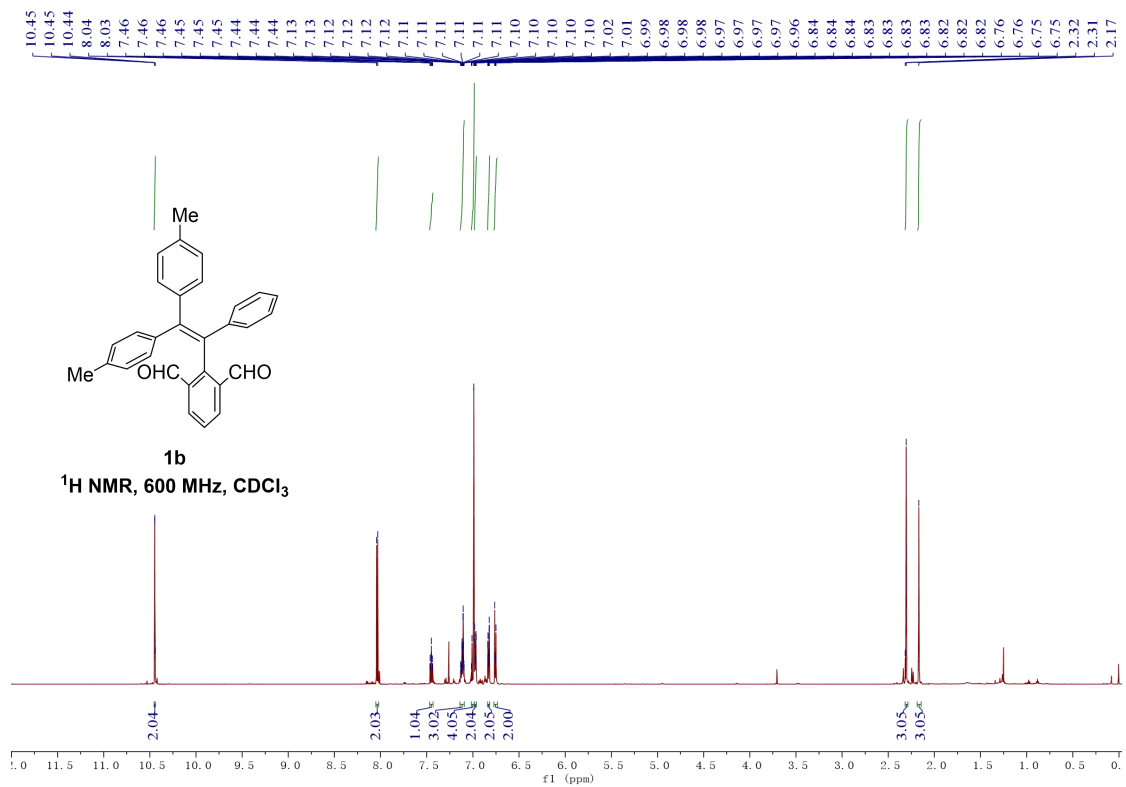
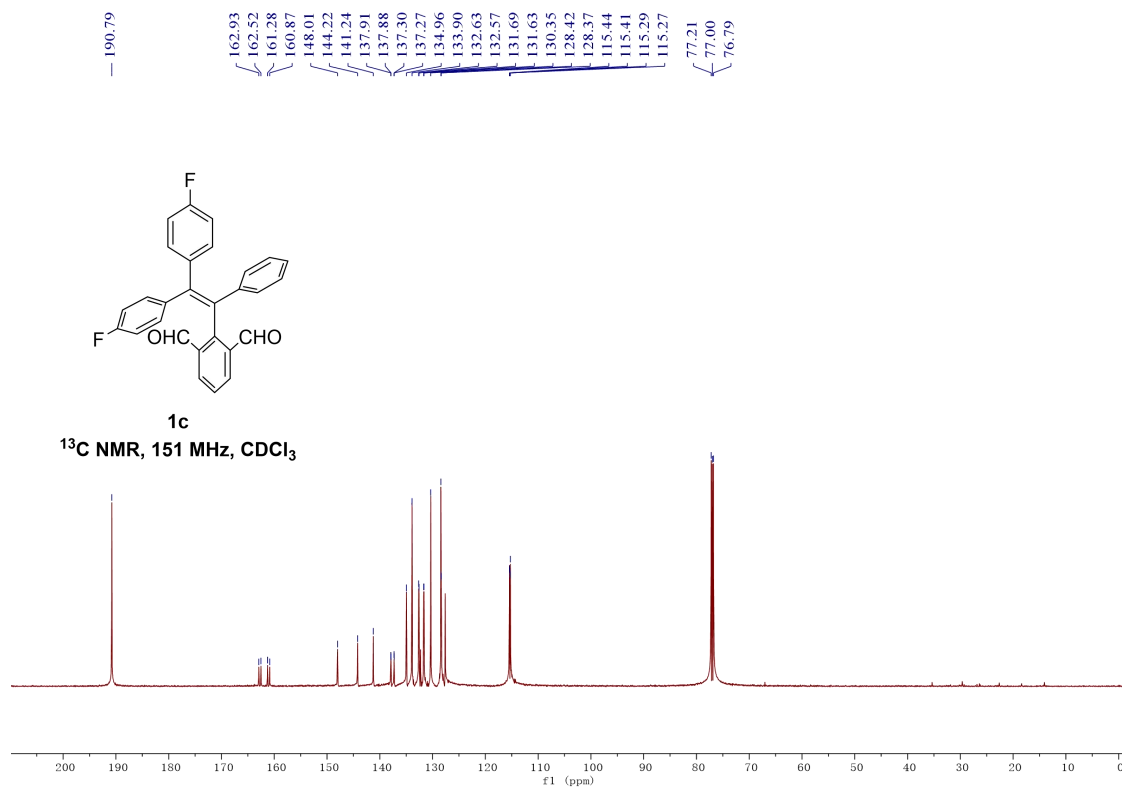
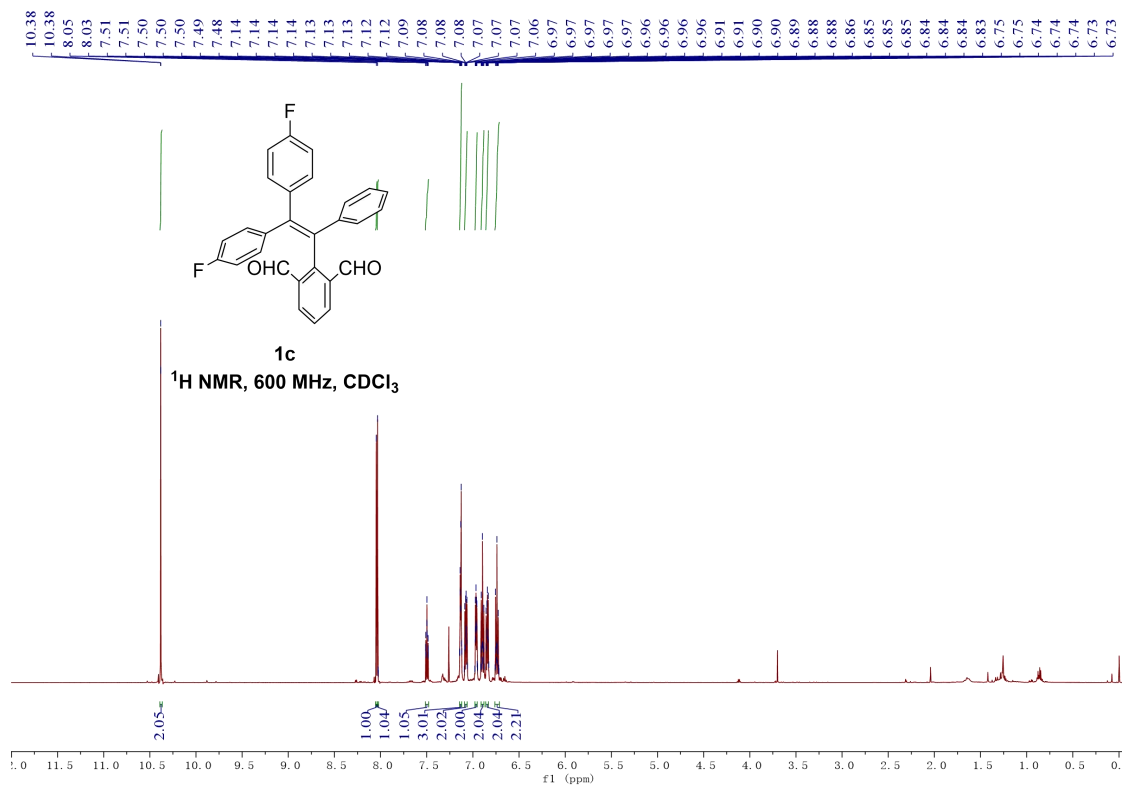


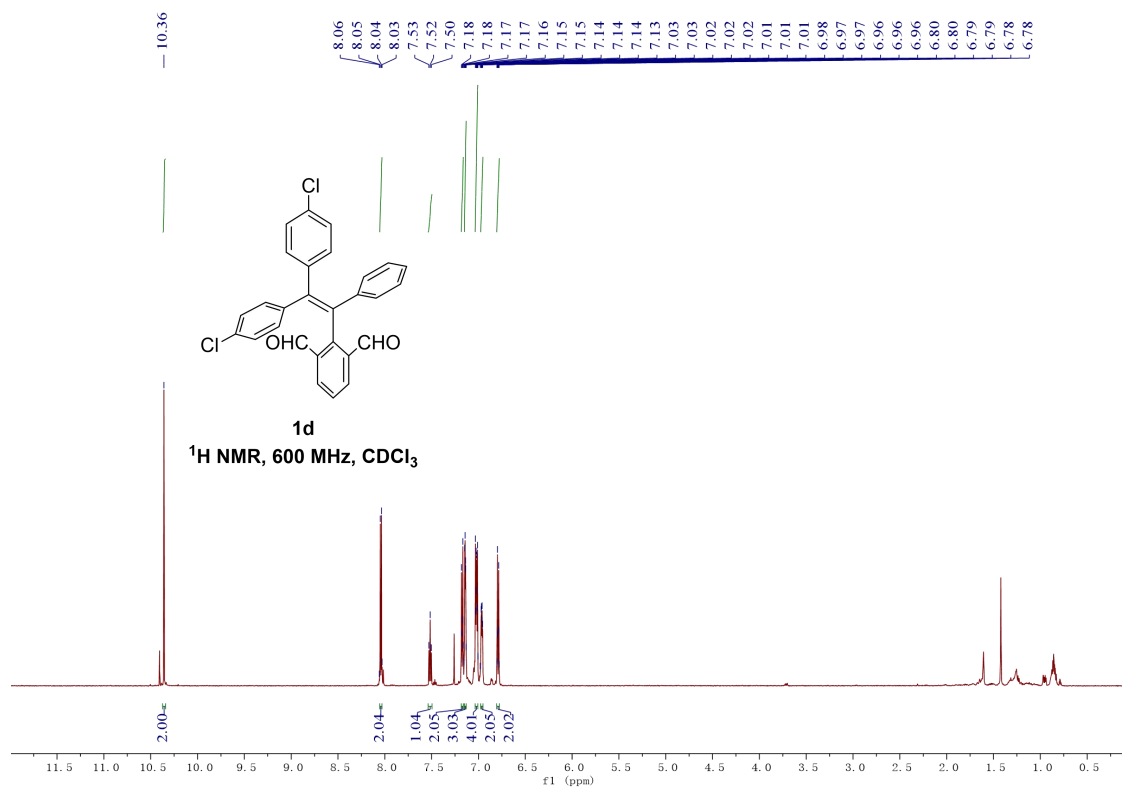
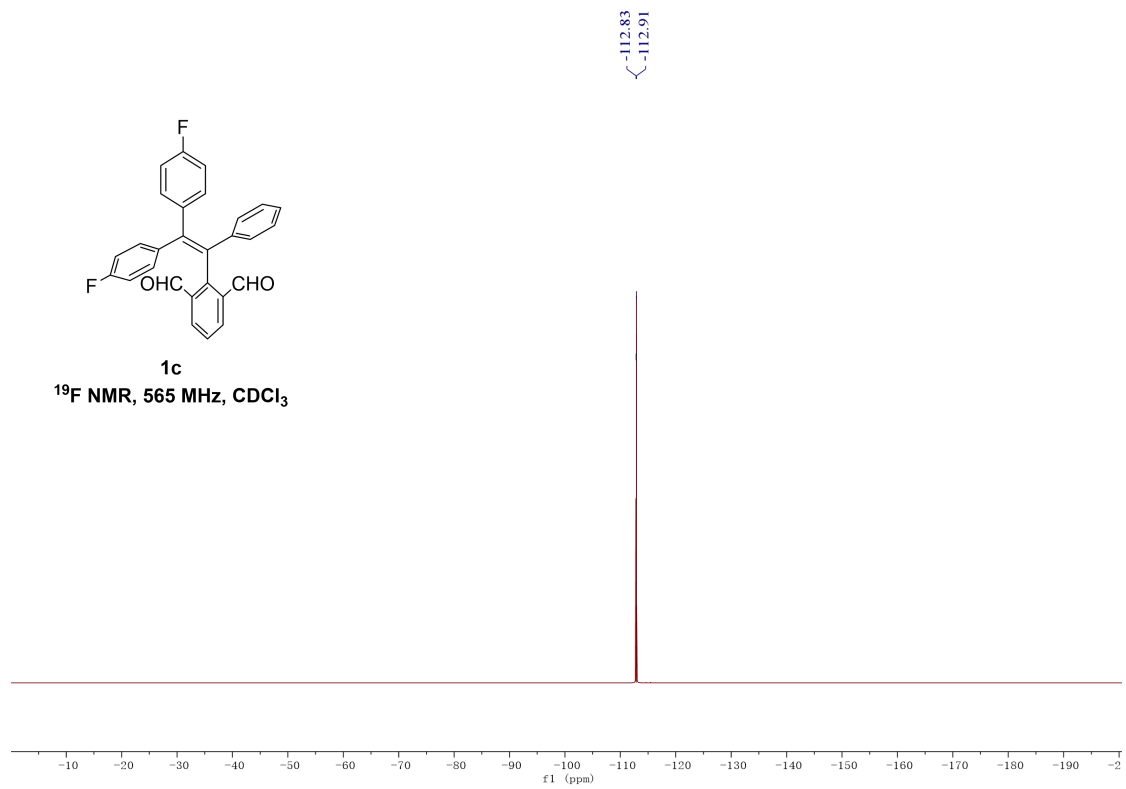
Figure S8. CPL (g_{lum}) spectra of **3z**, **3k**, **S-3p** and **R-3p** in THF at 25 °C (ca. 1×10^{-5} M).

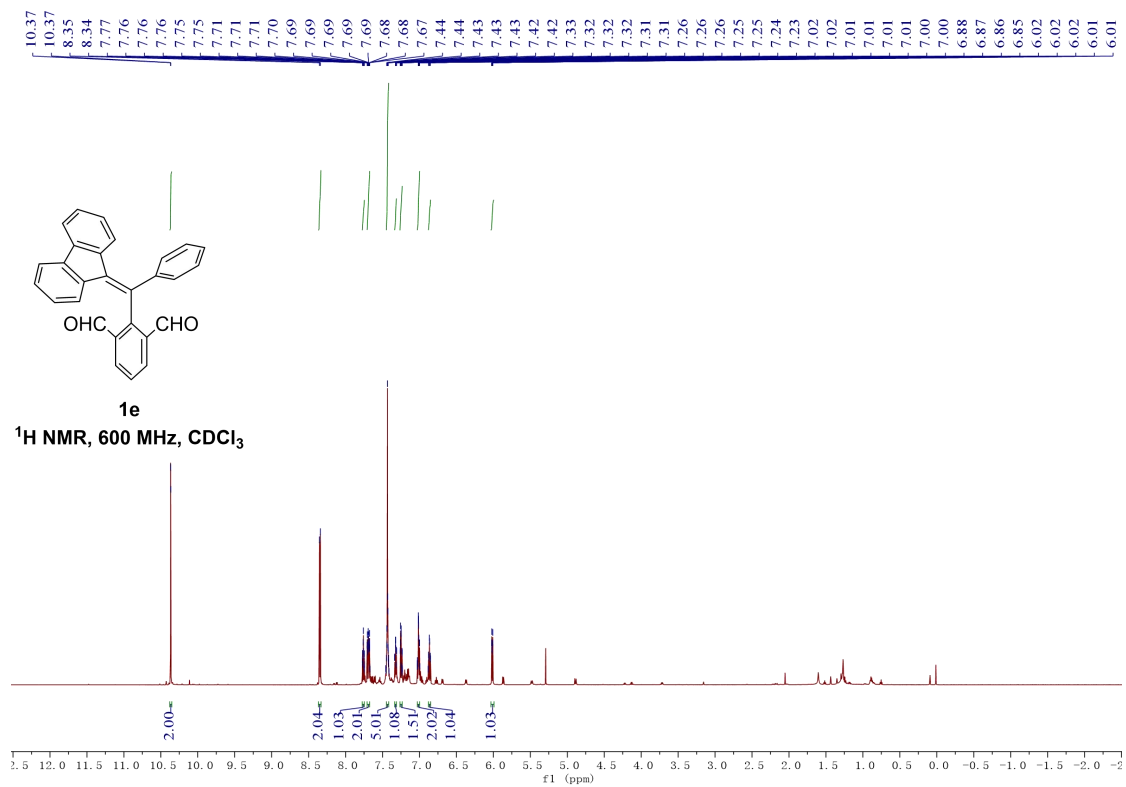
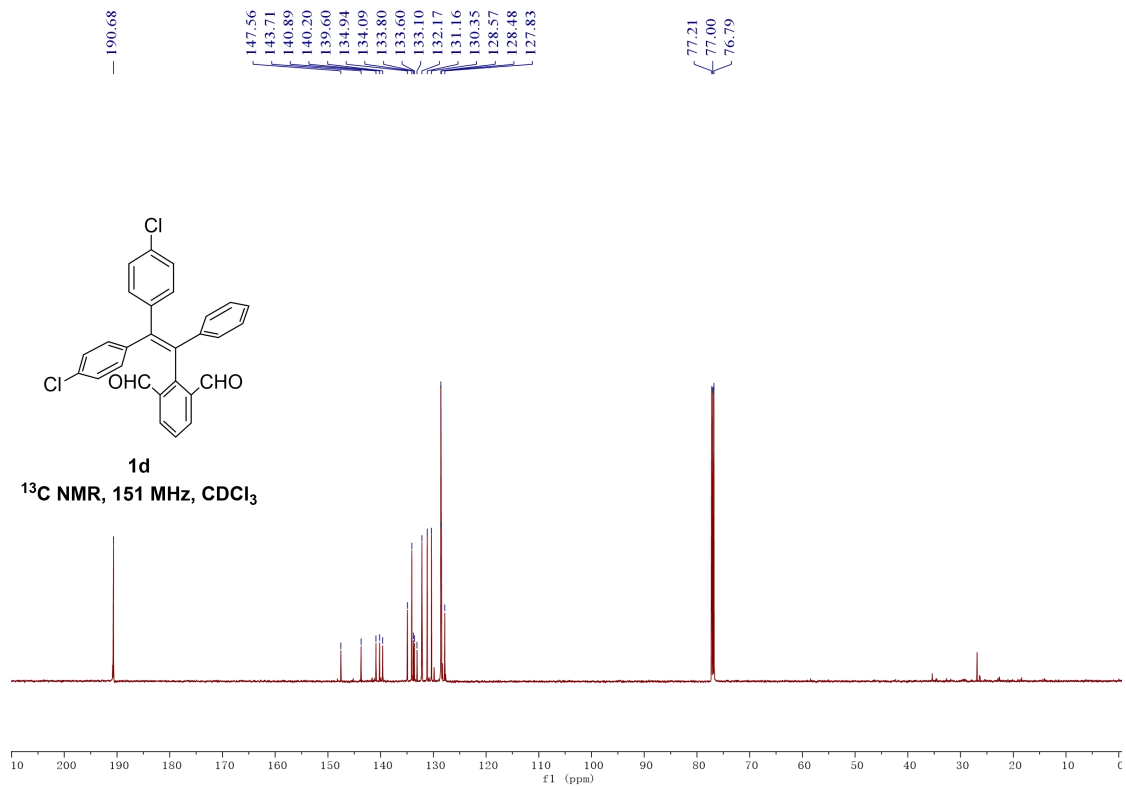
7. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectras

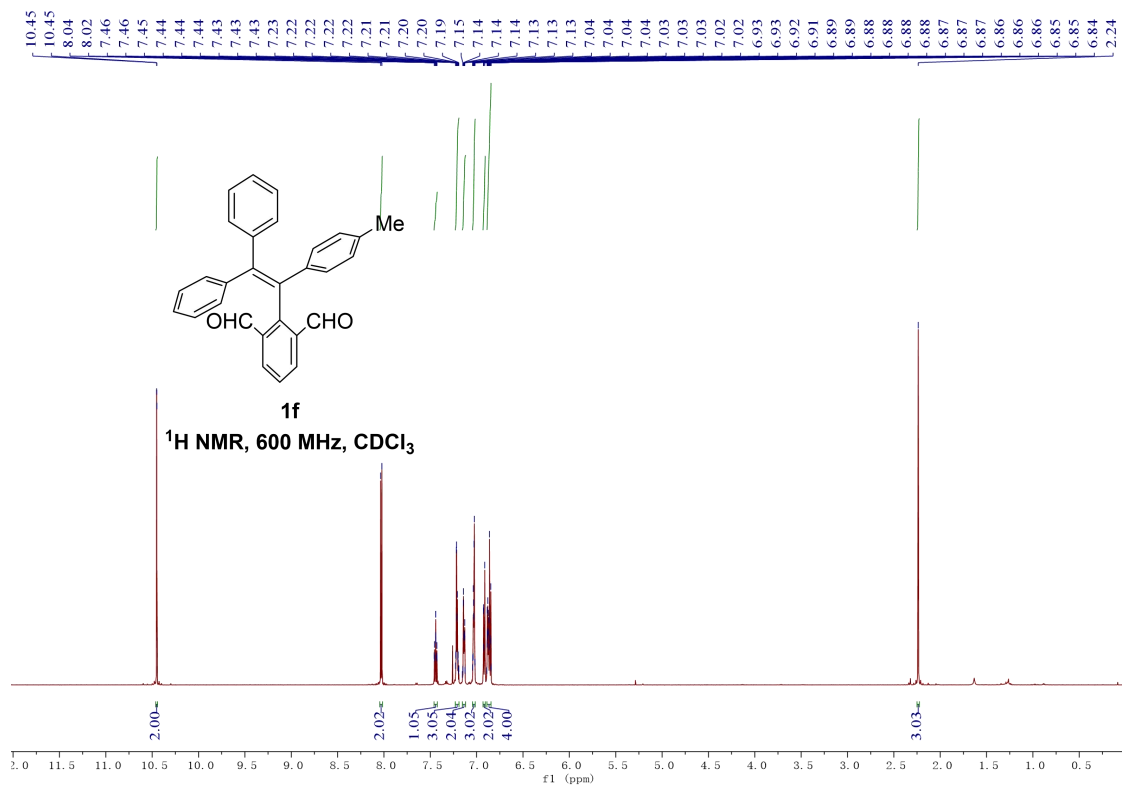
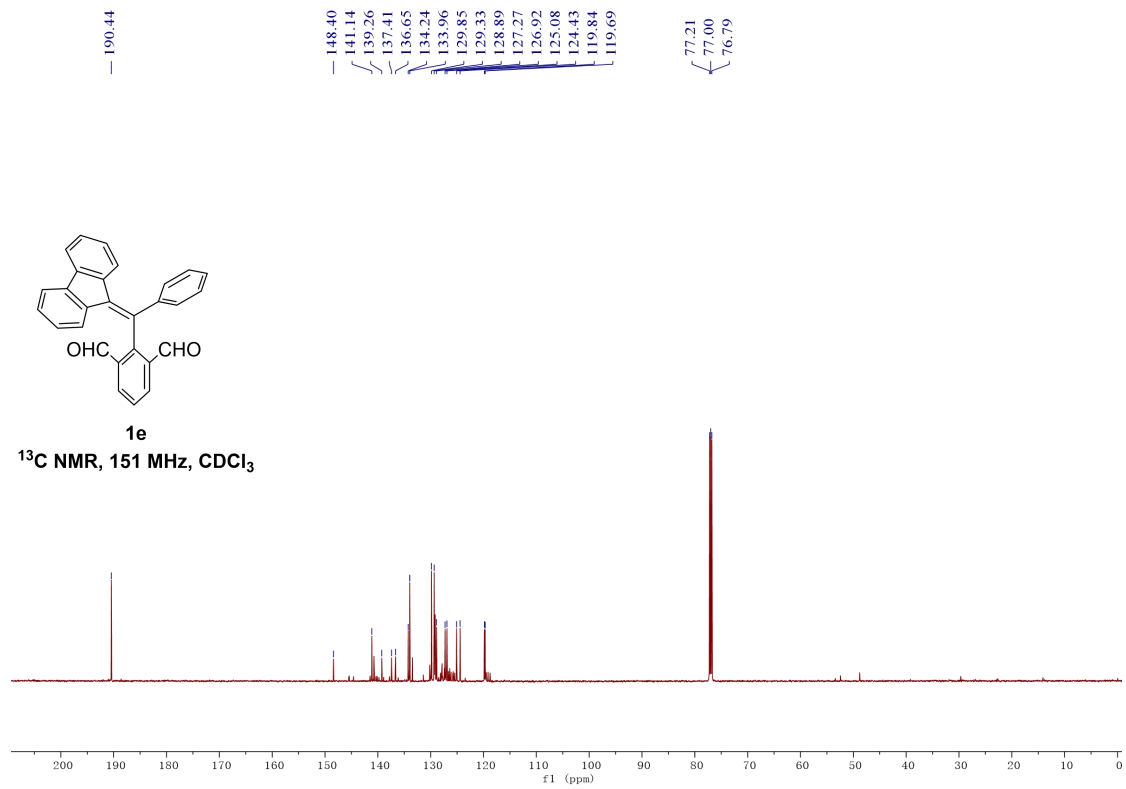


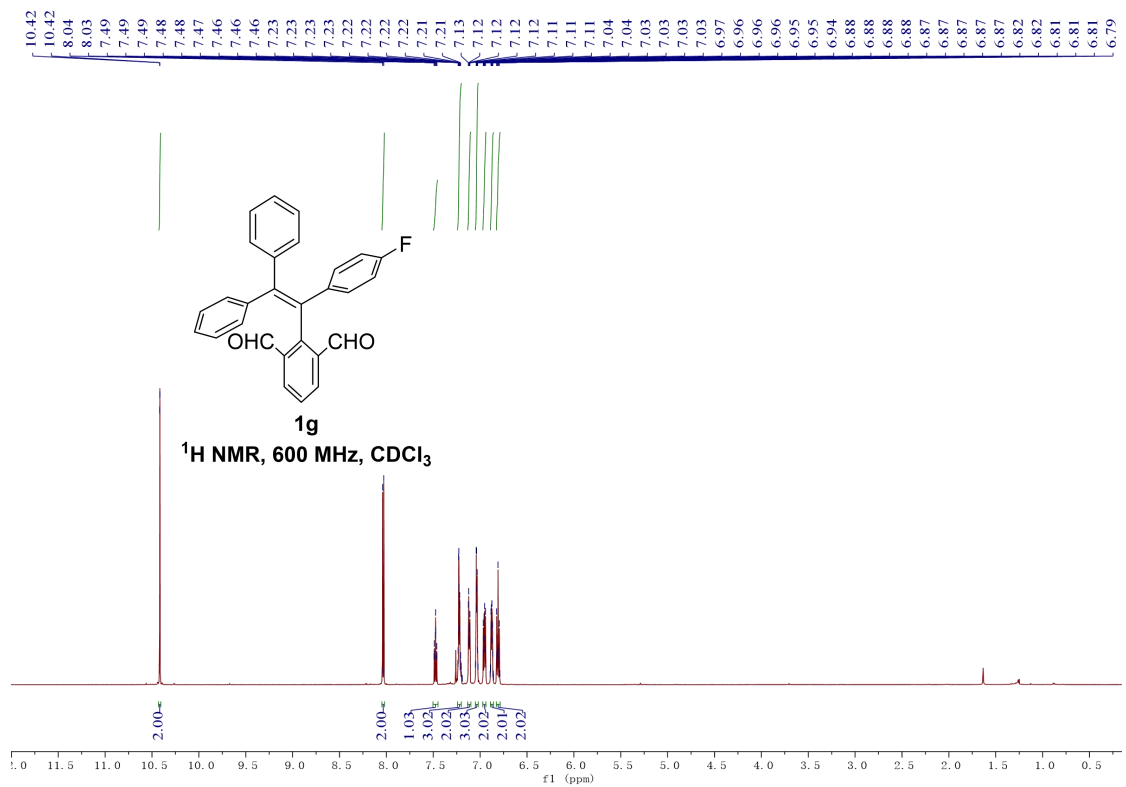
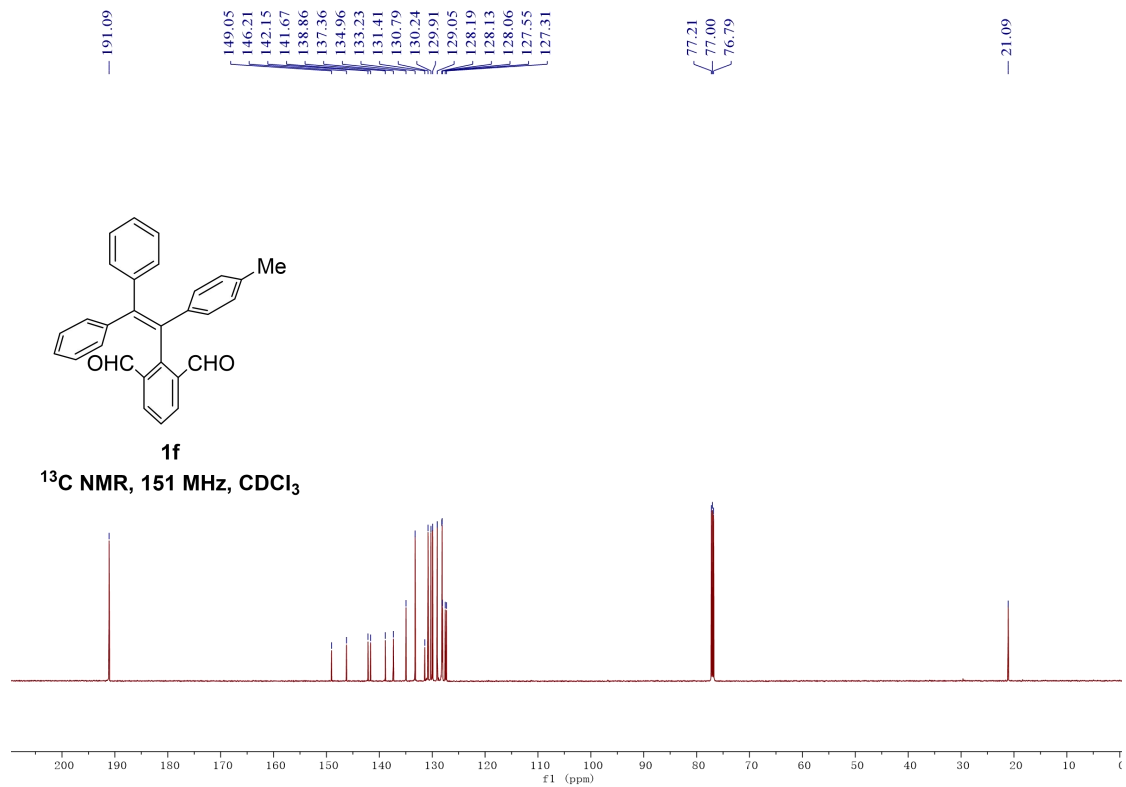


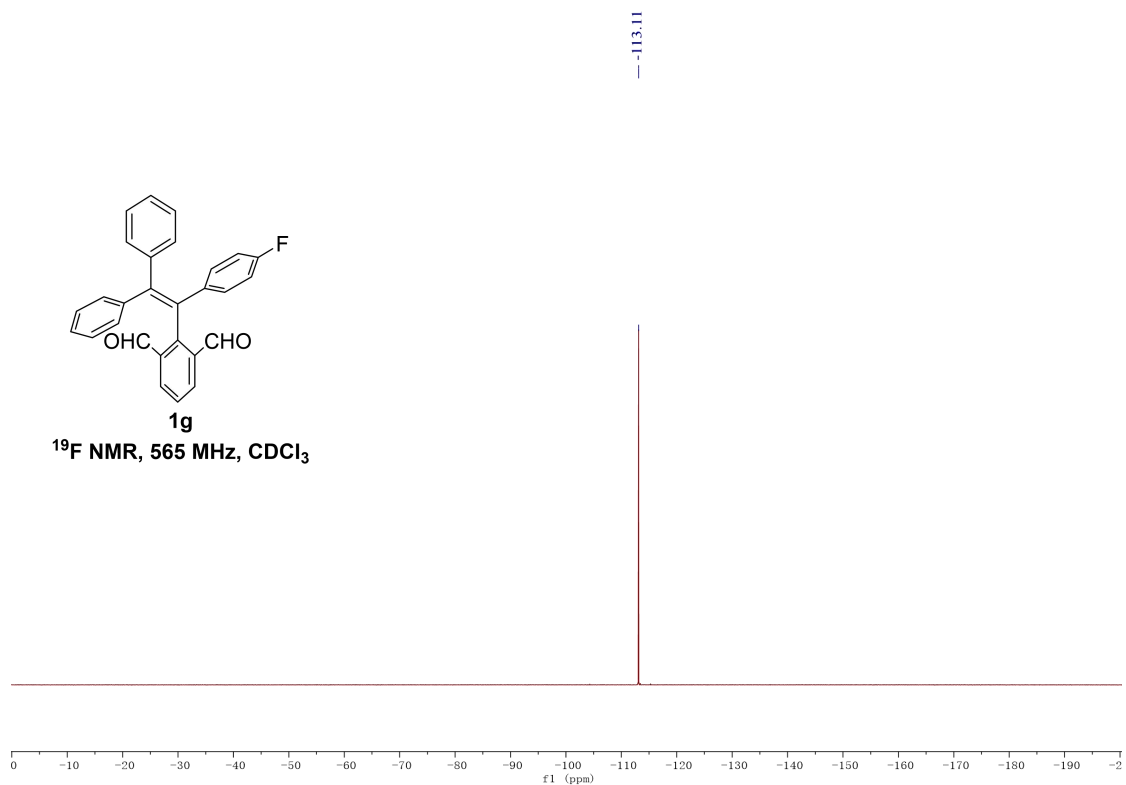
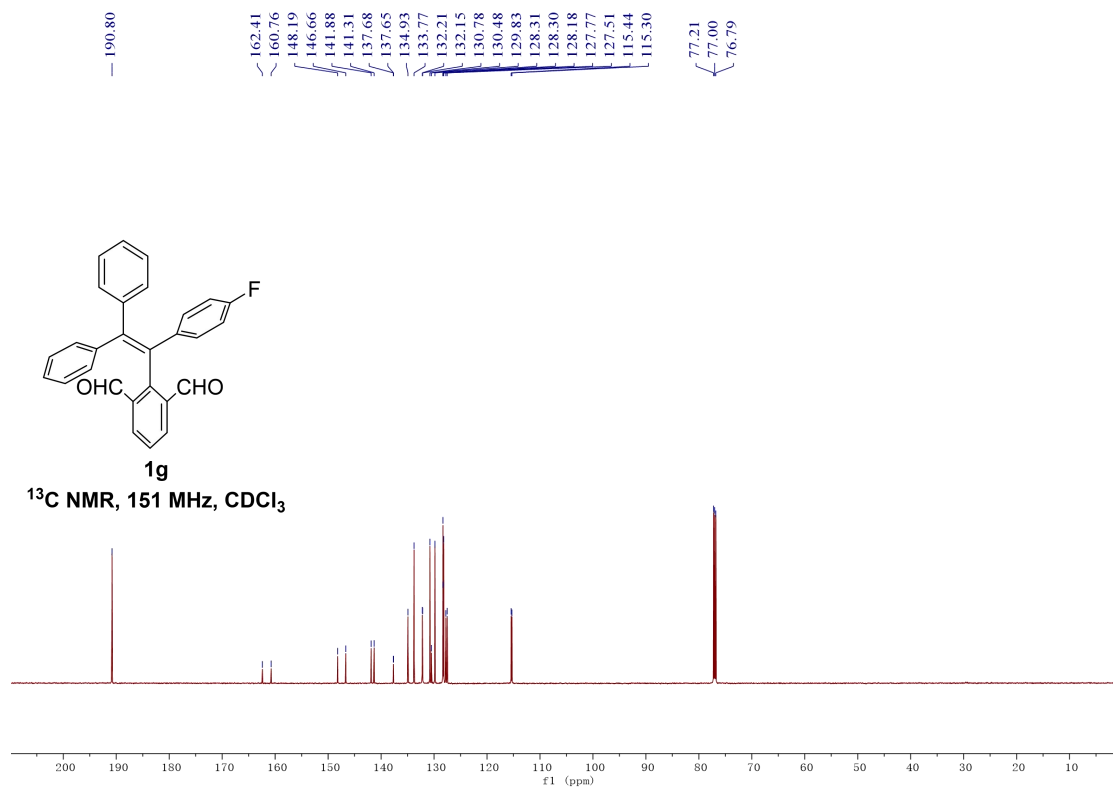


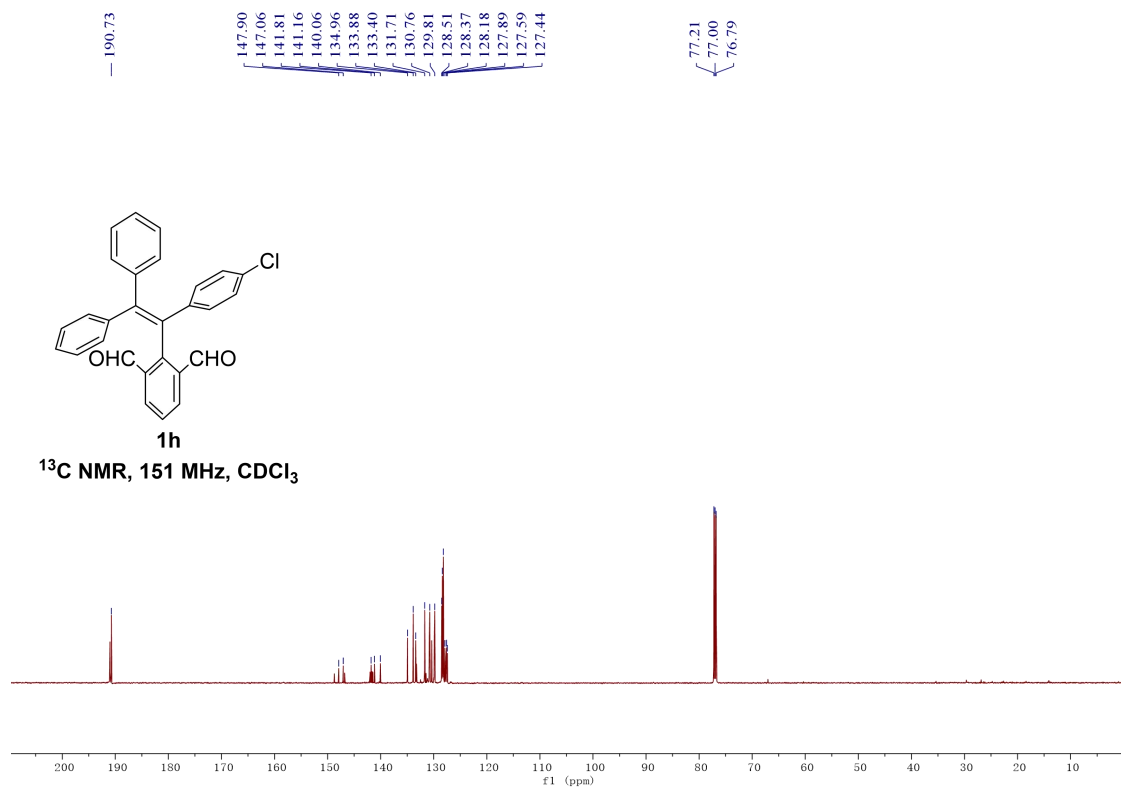
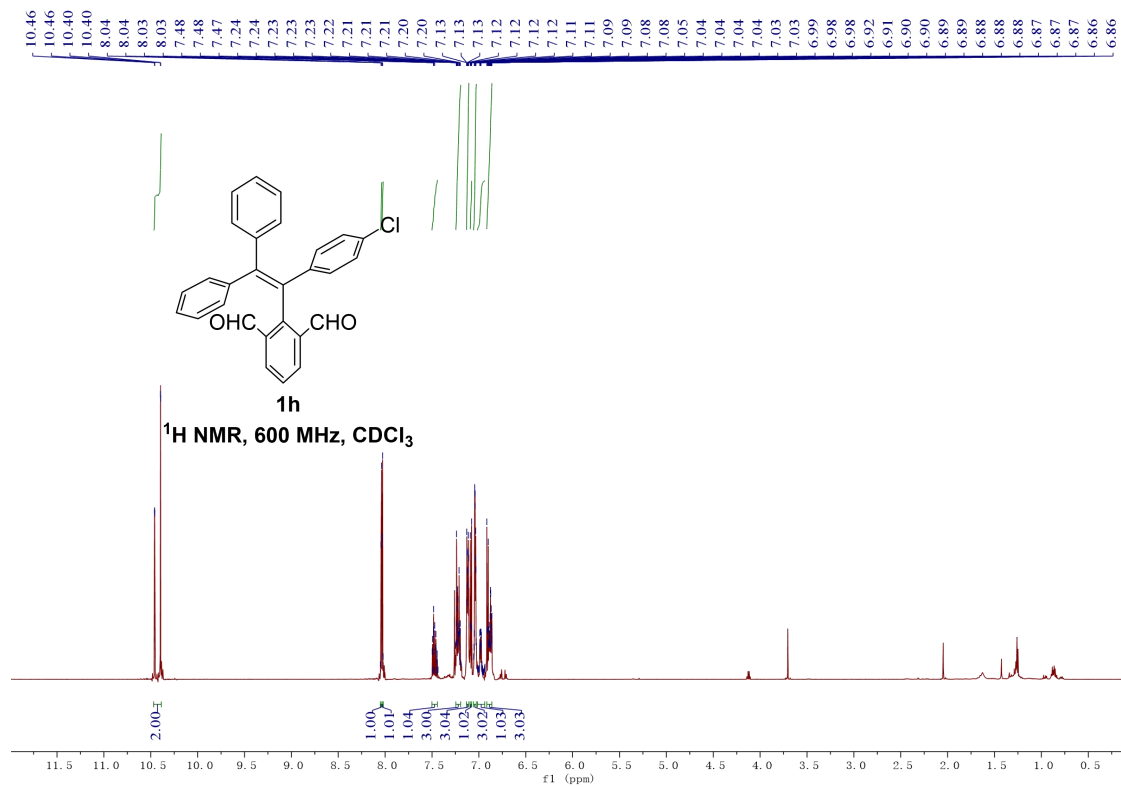


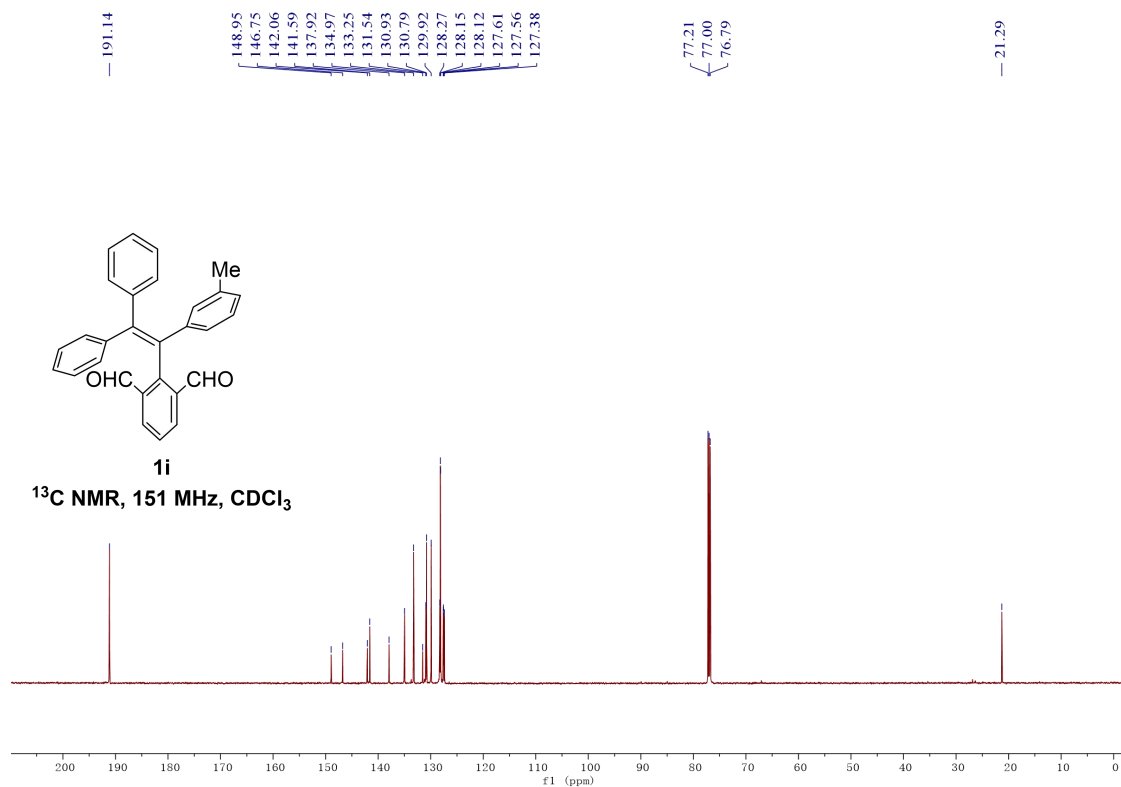
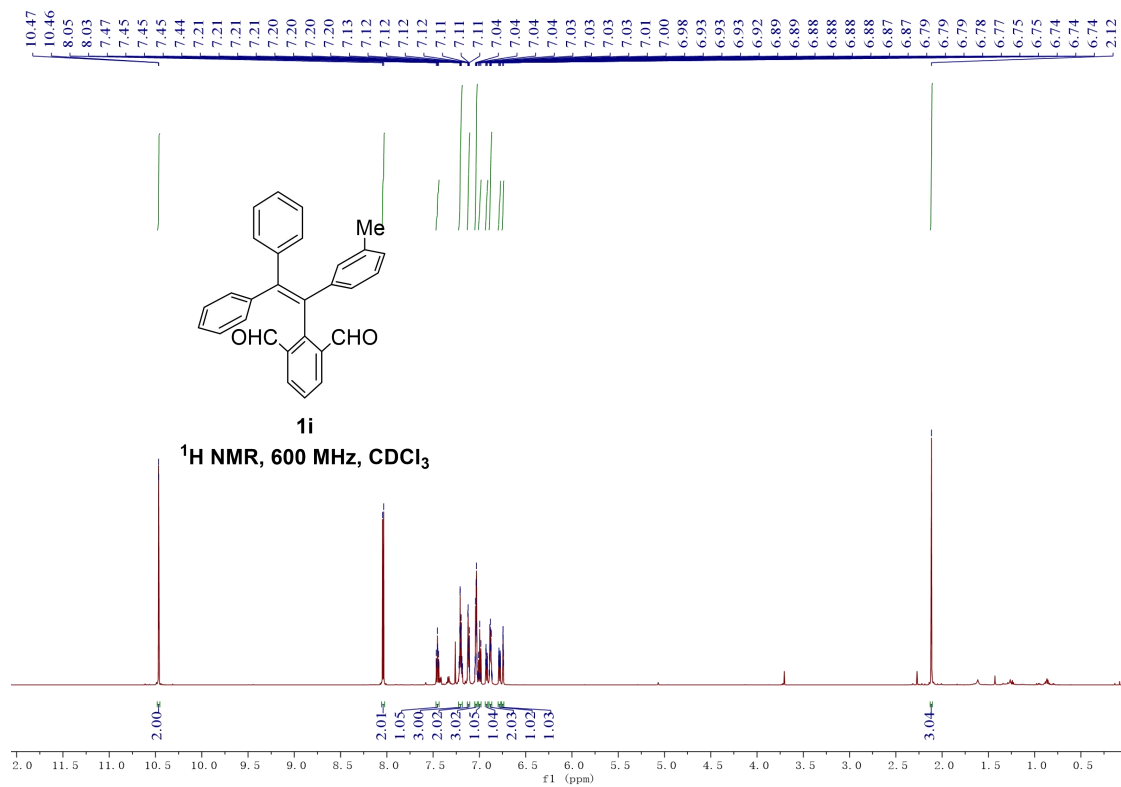


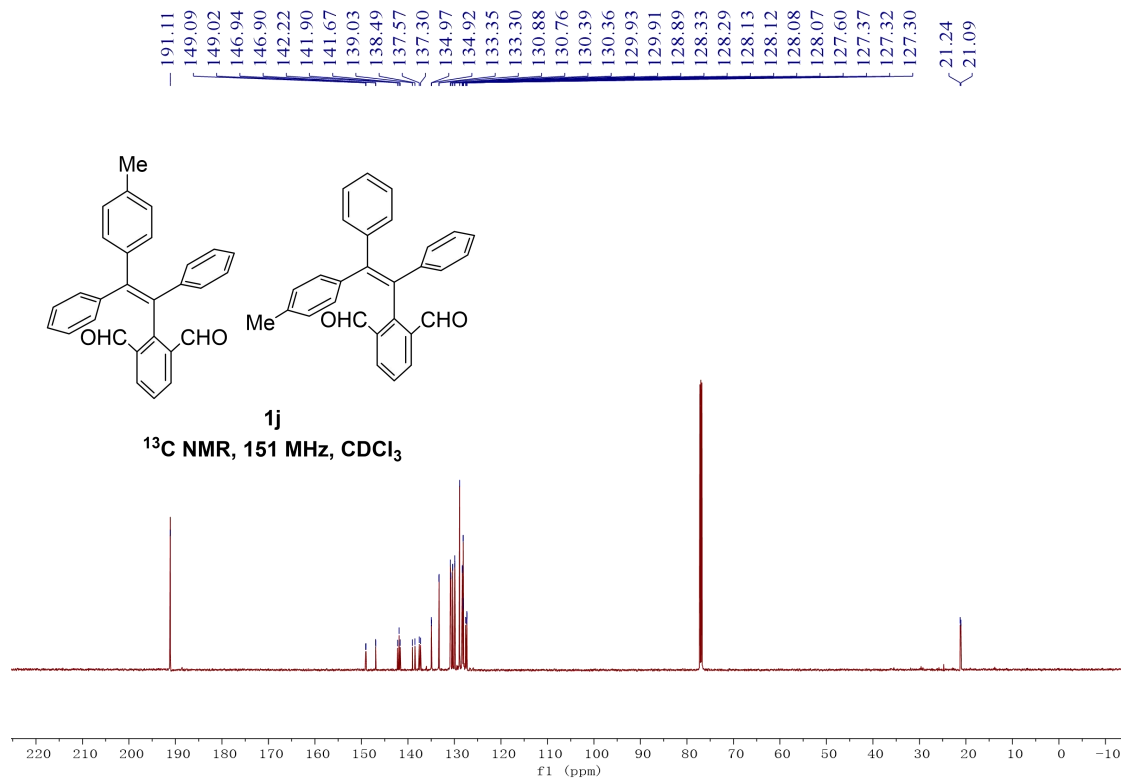
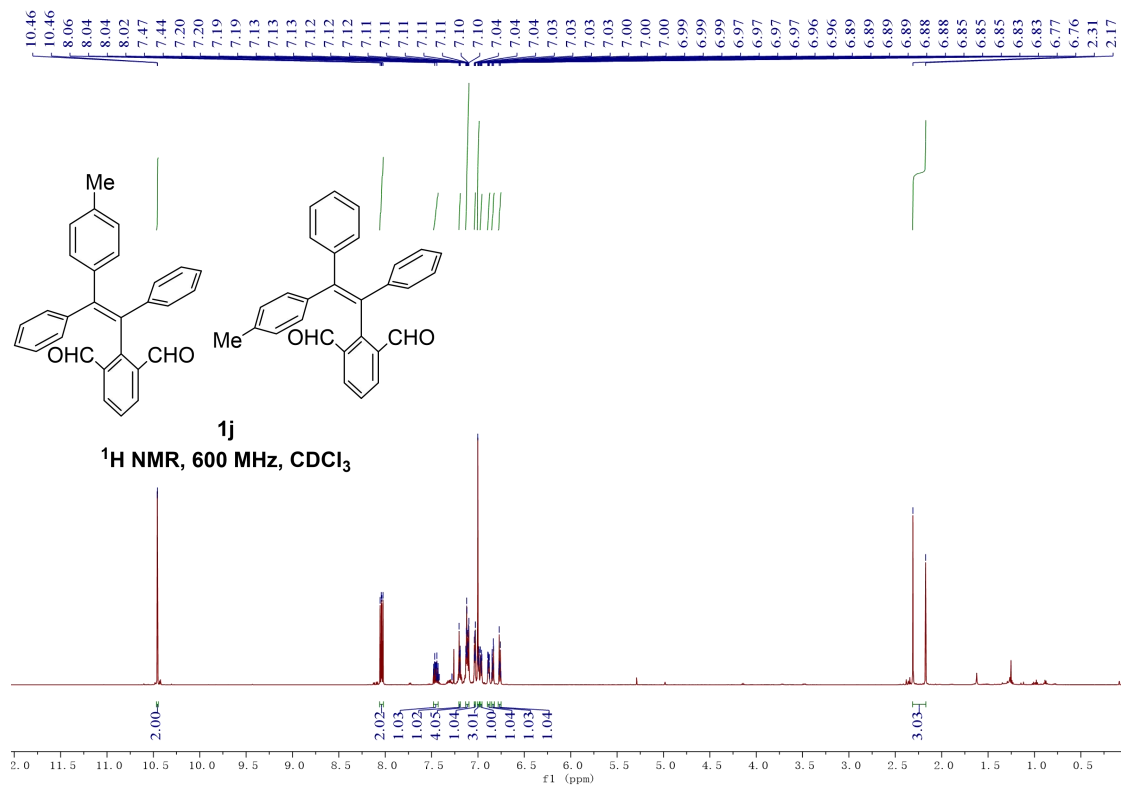


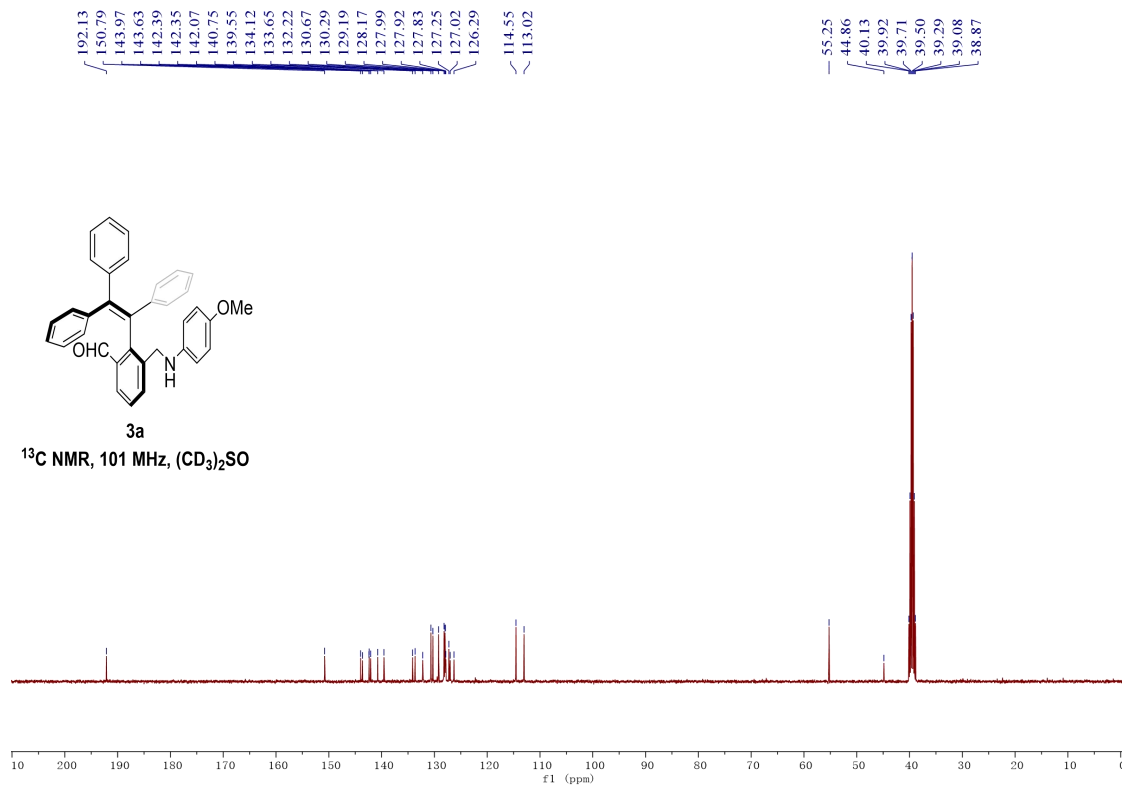
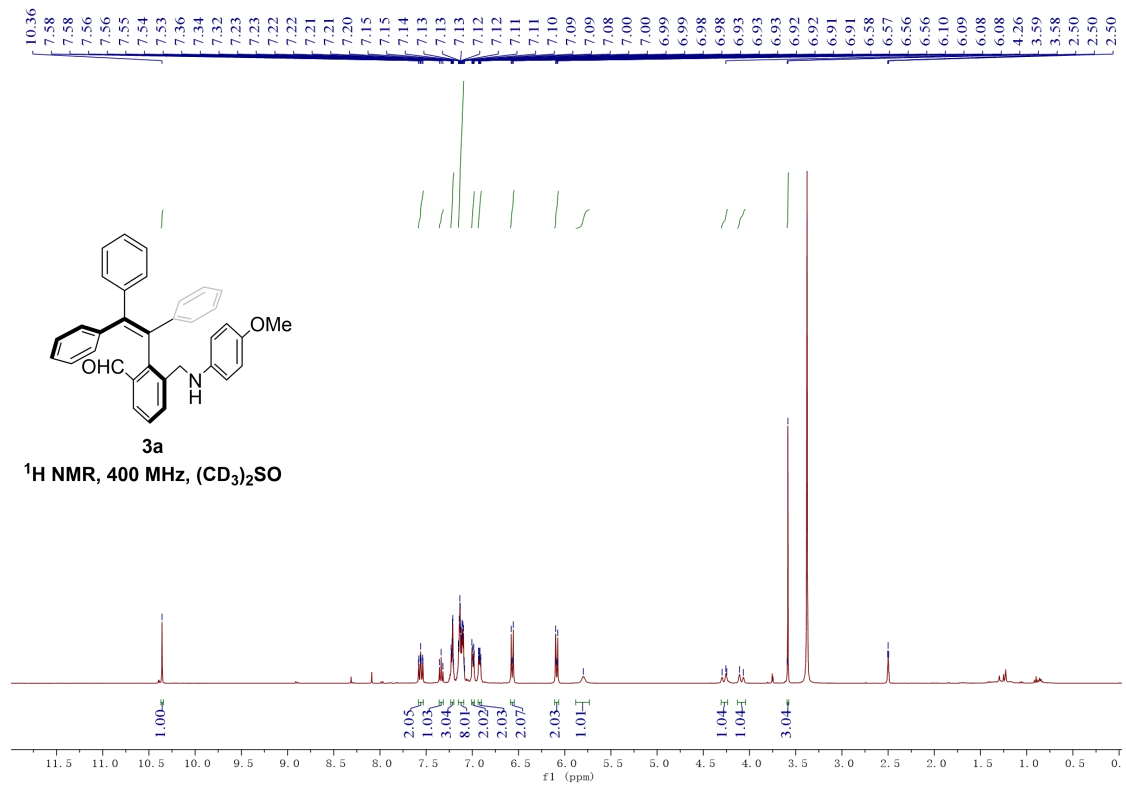


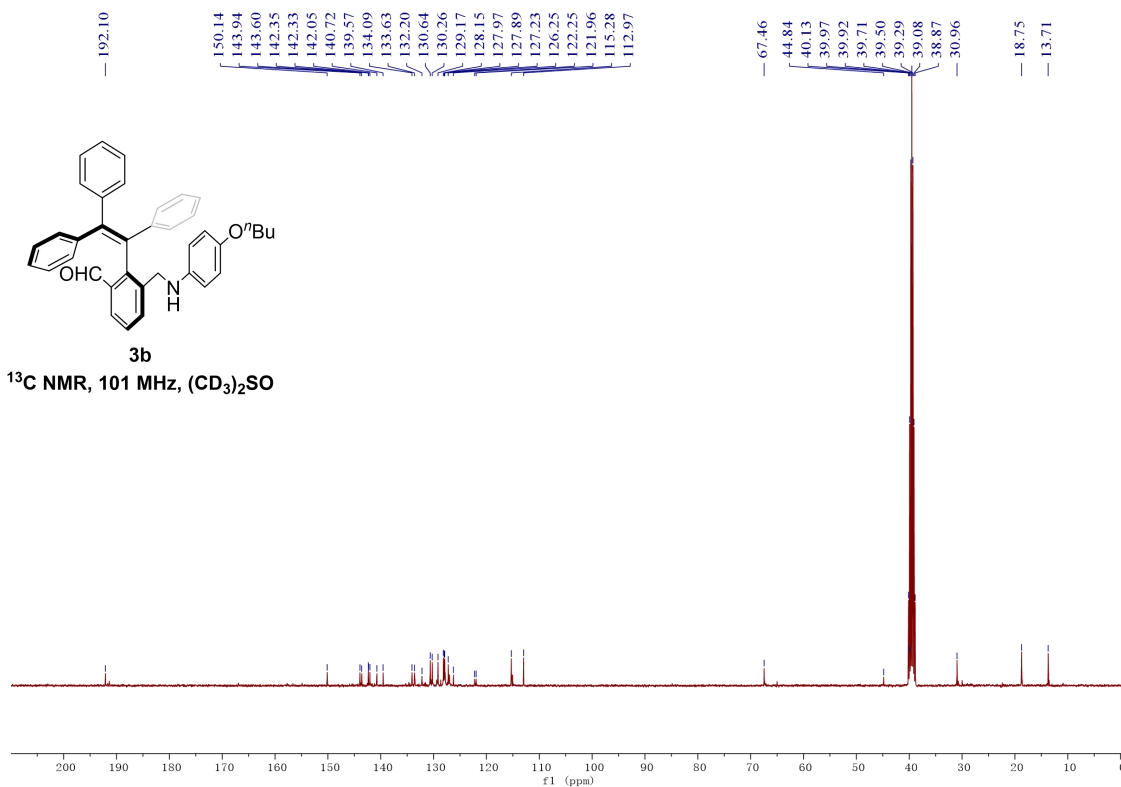
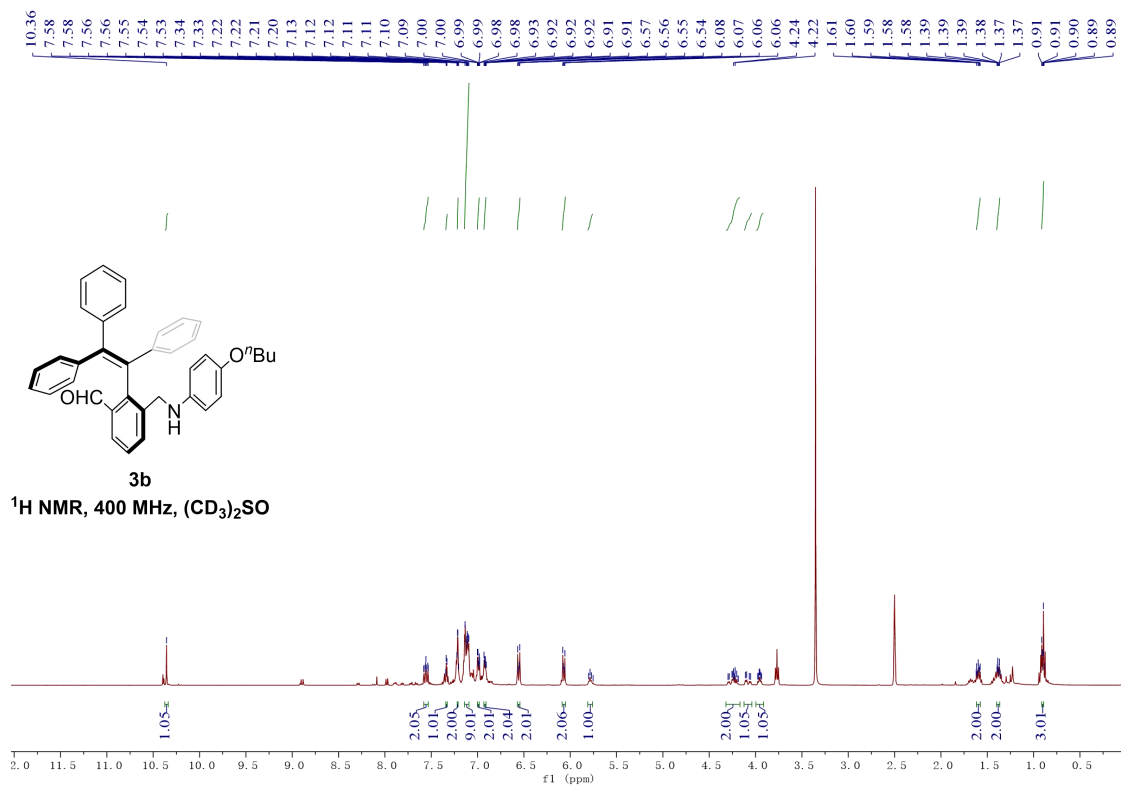


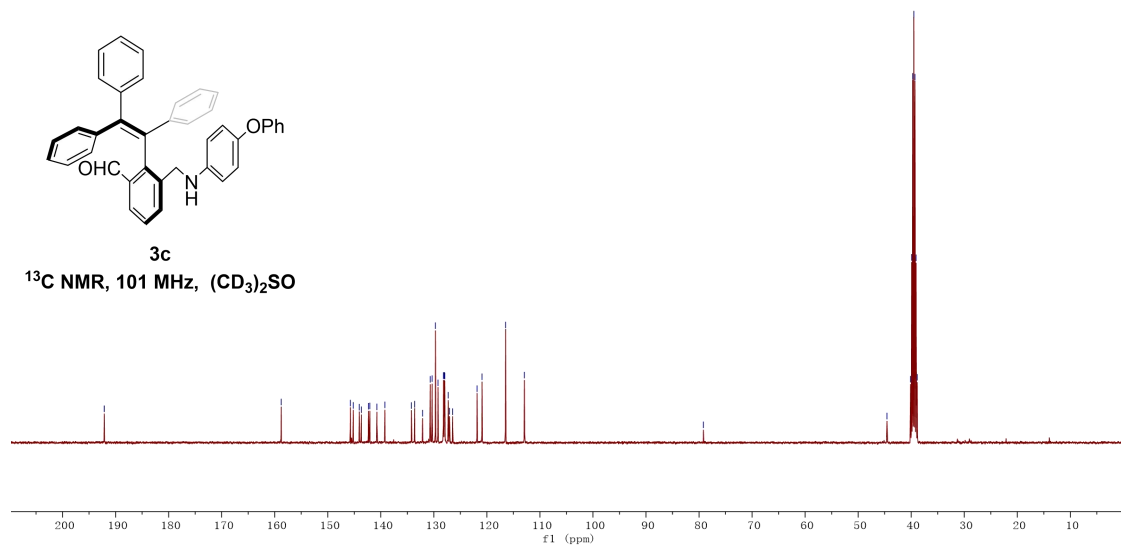
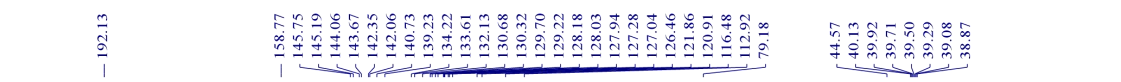
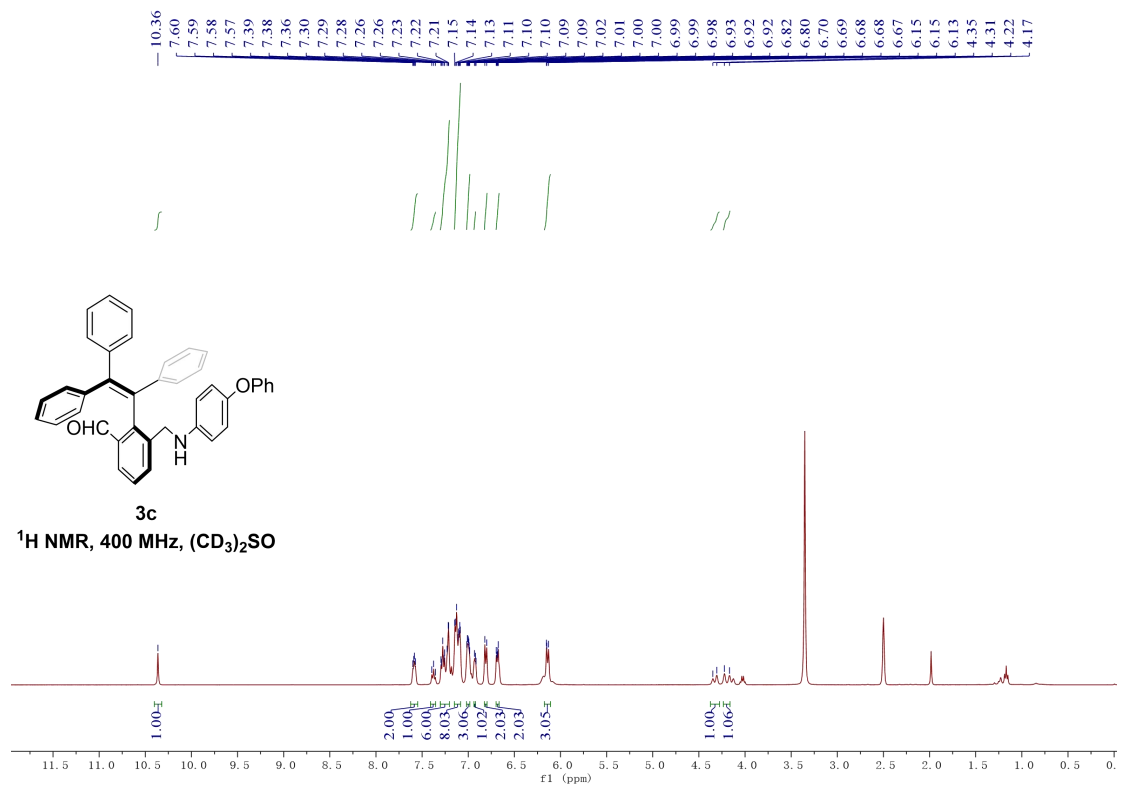


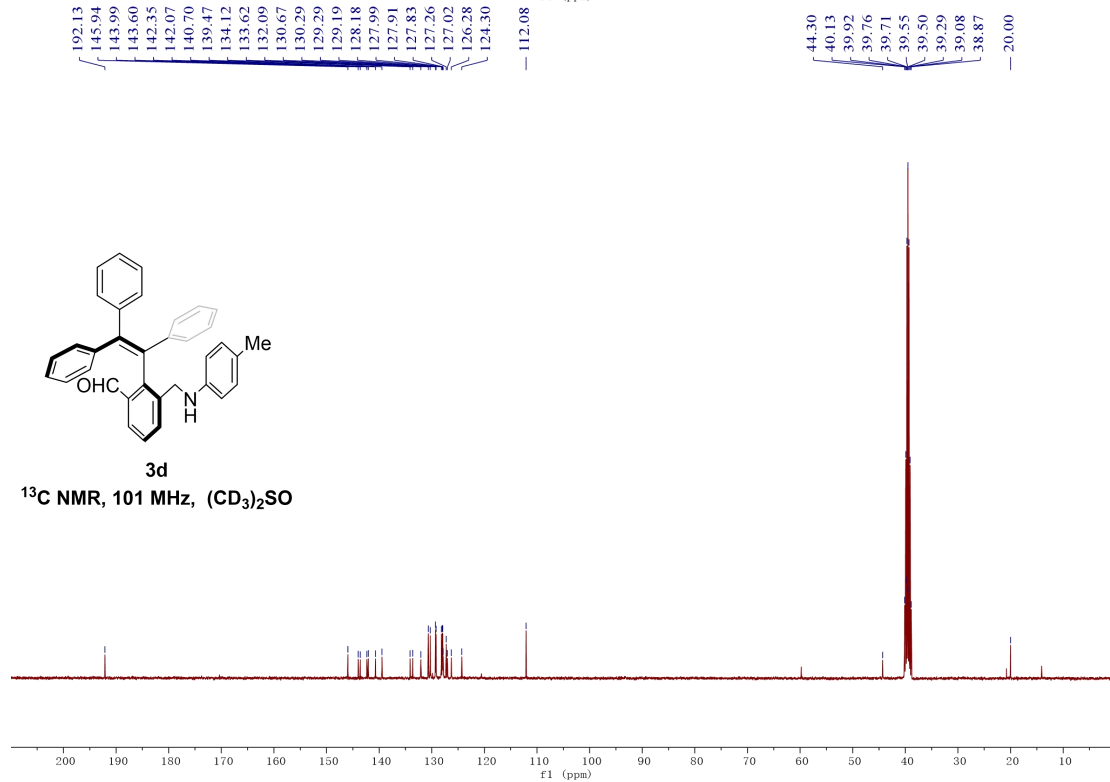
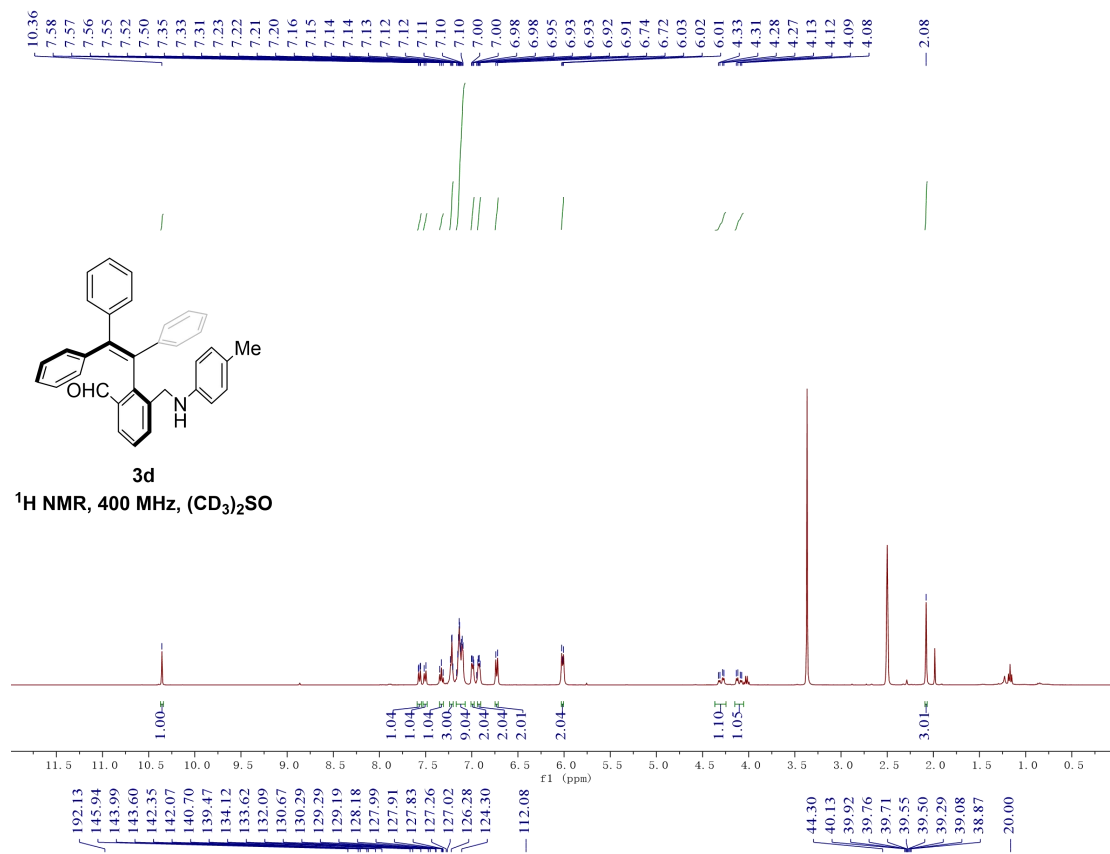


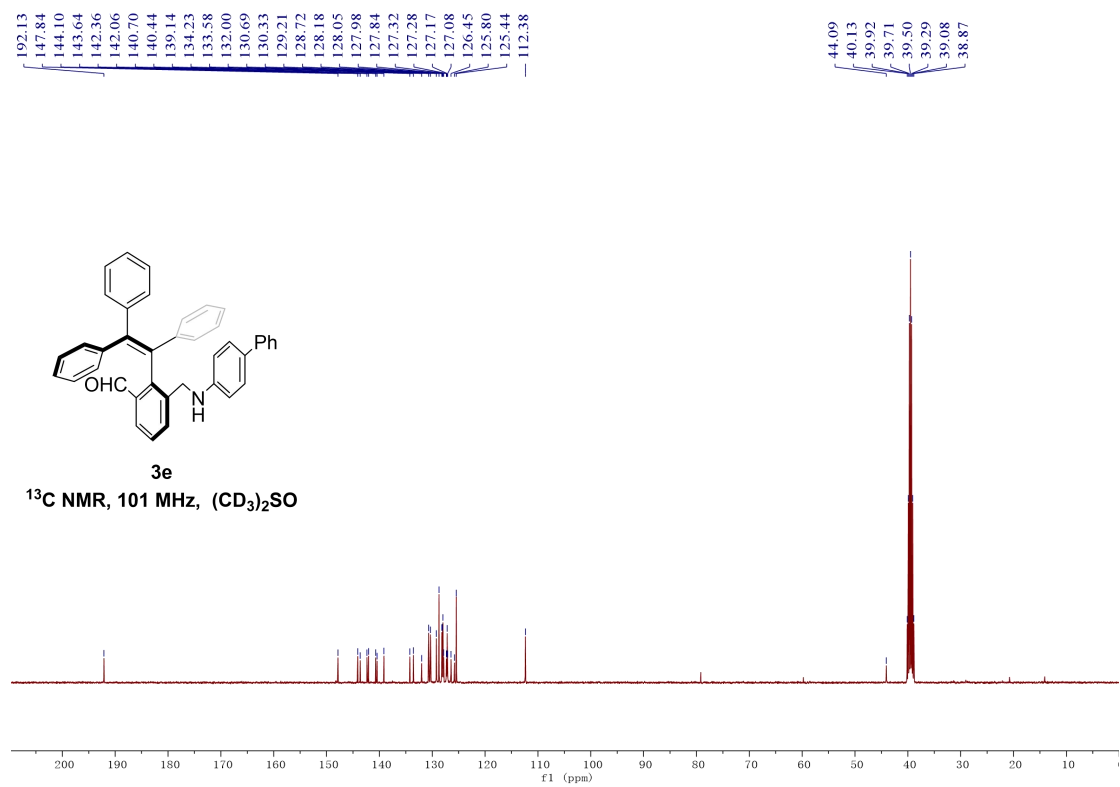
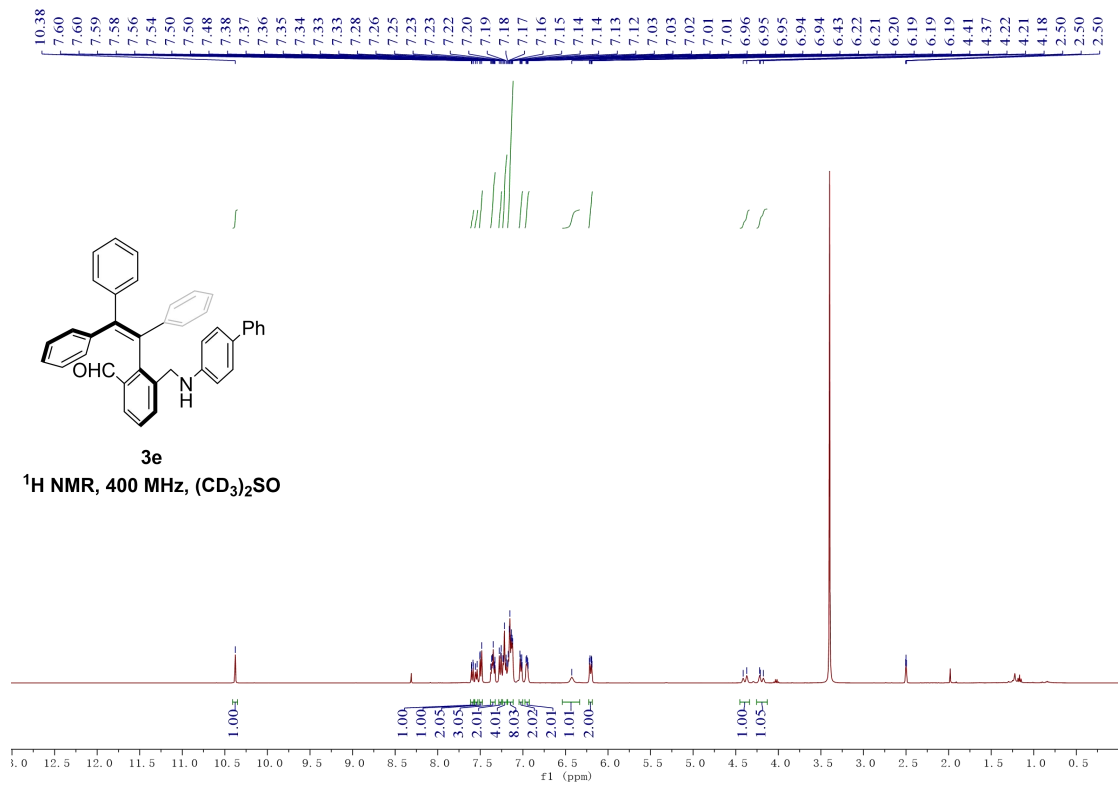


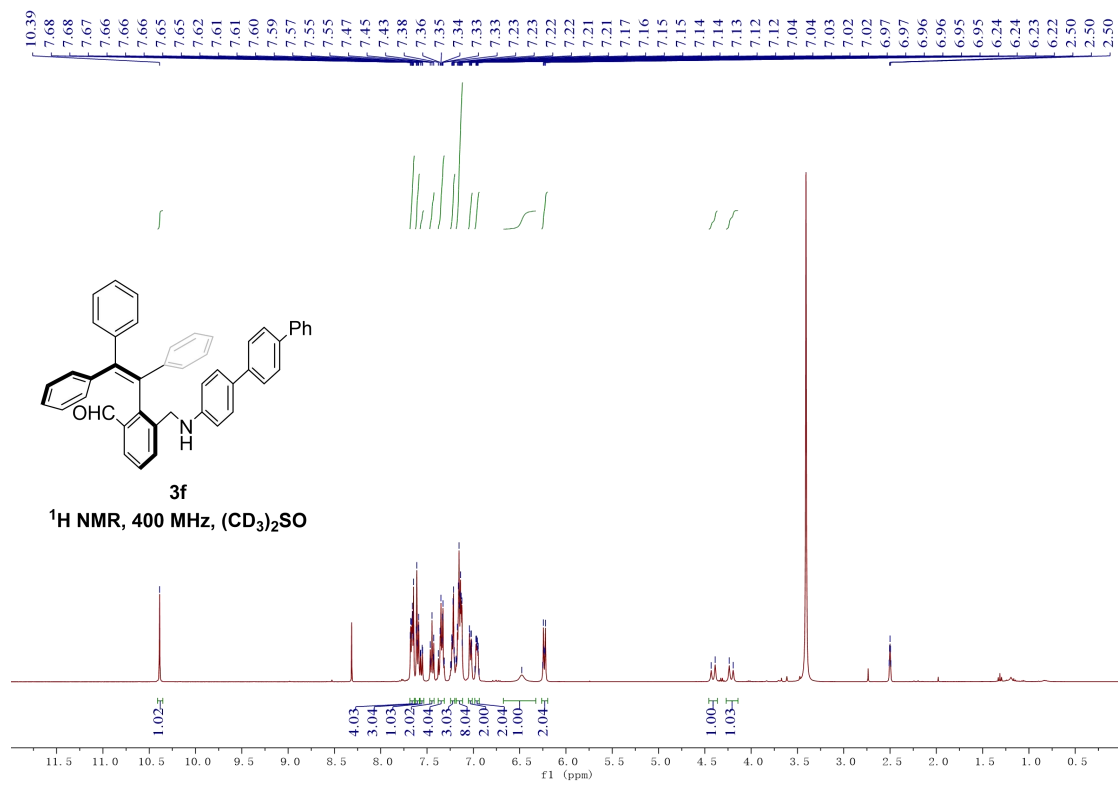


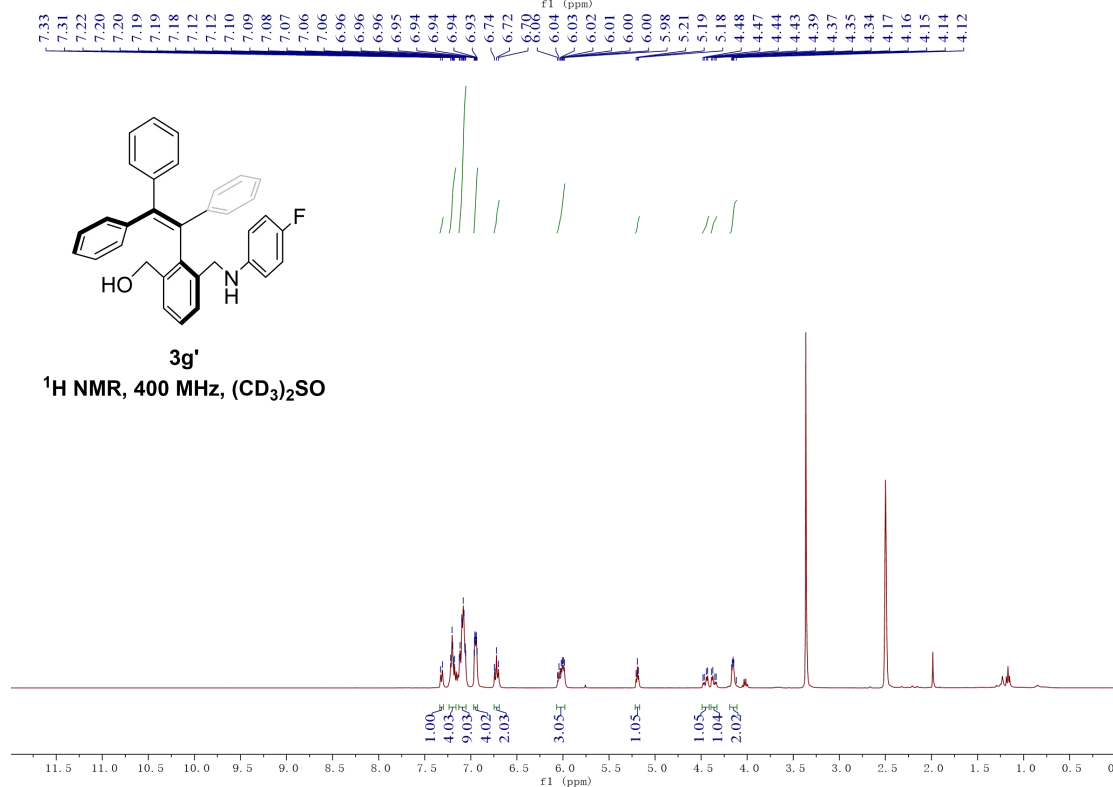
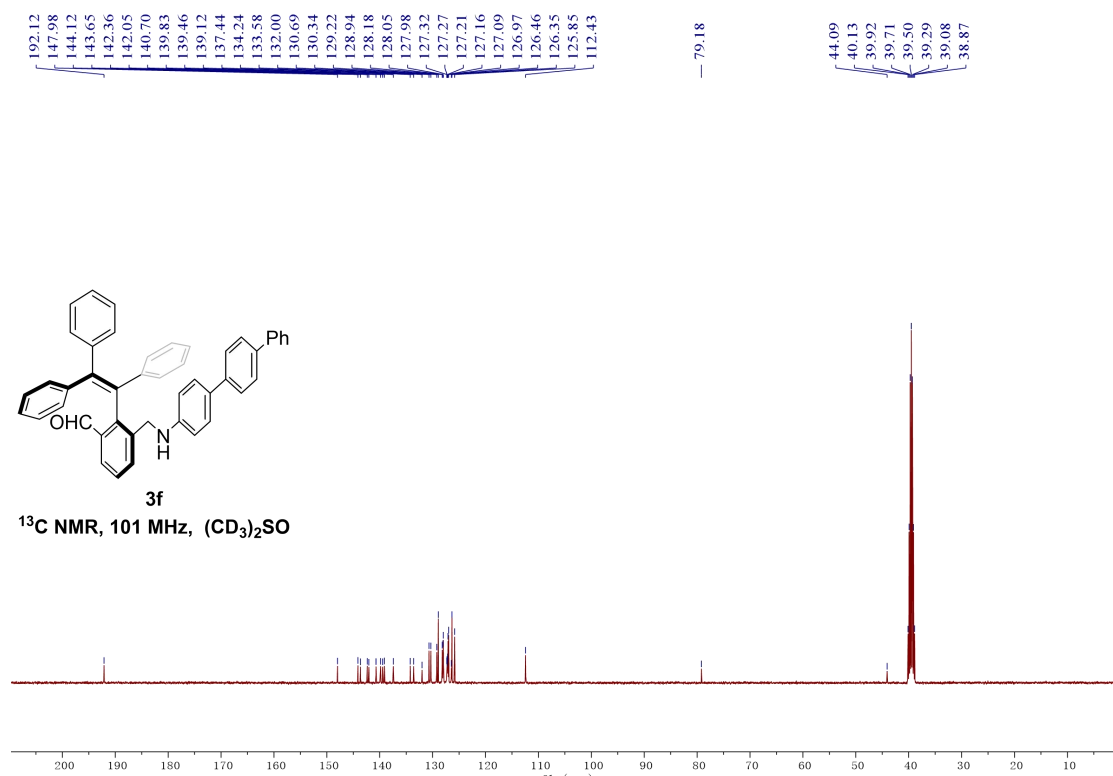


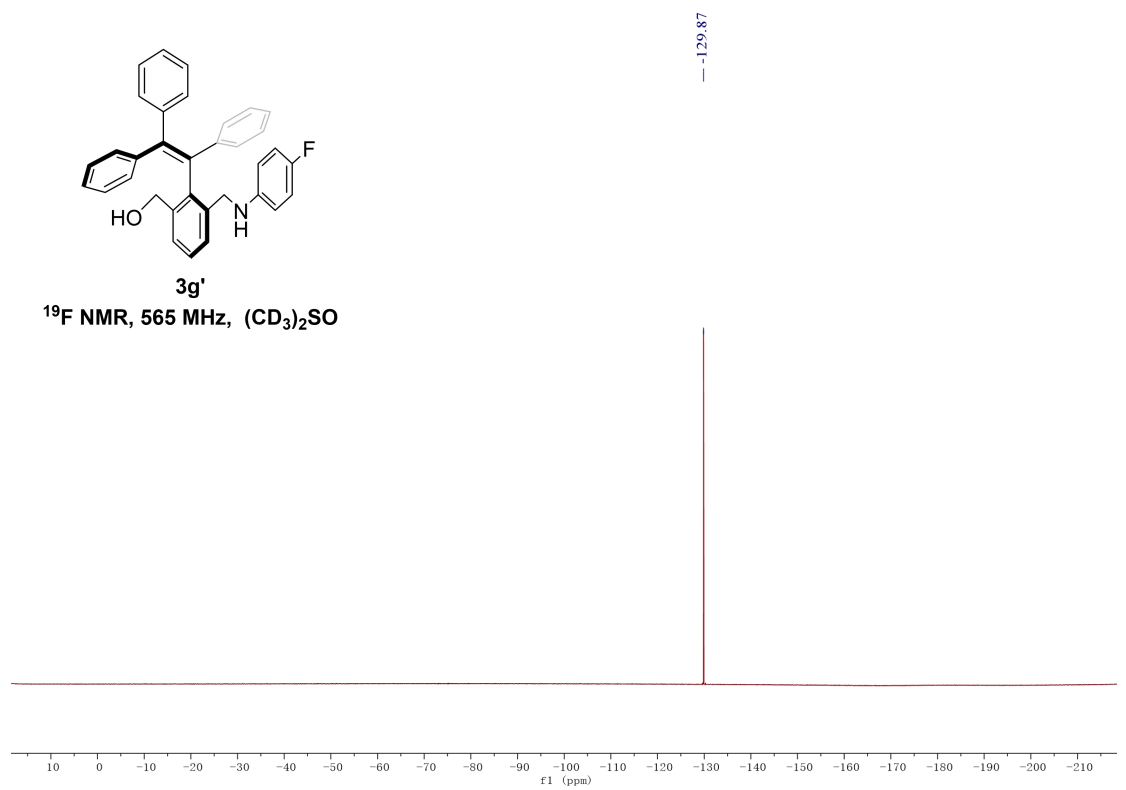
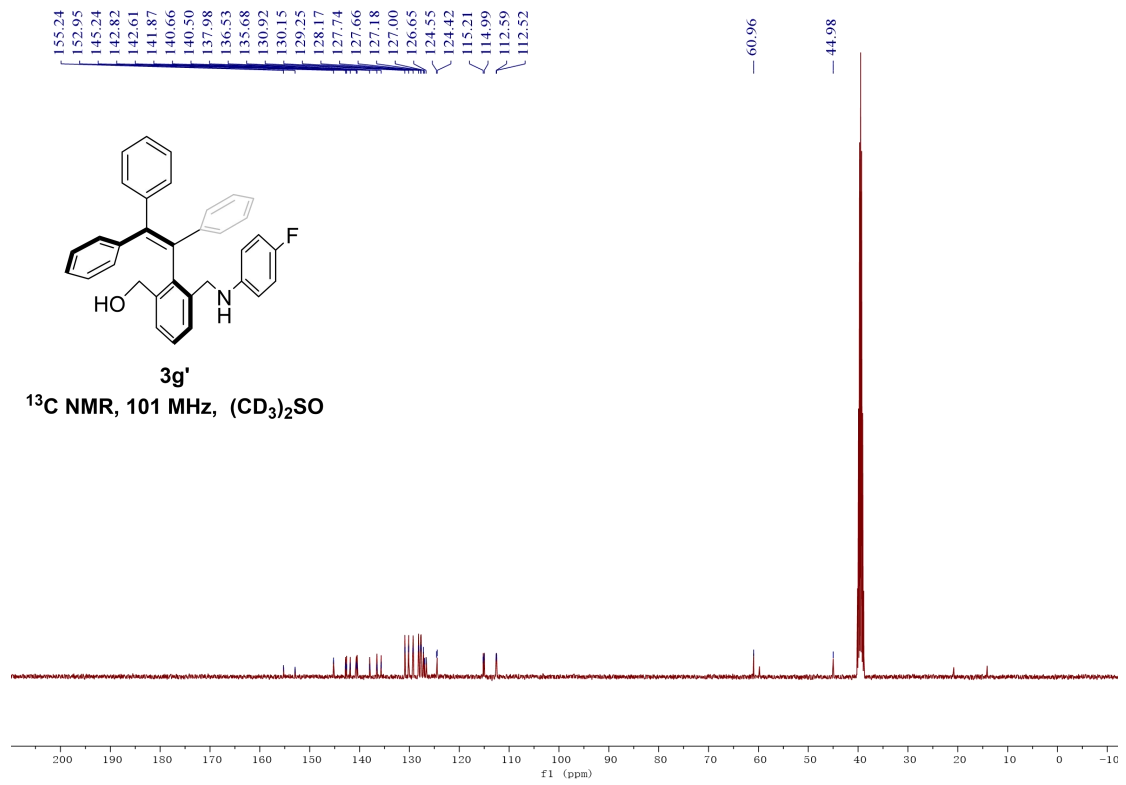


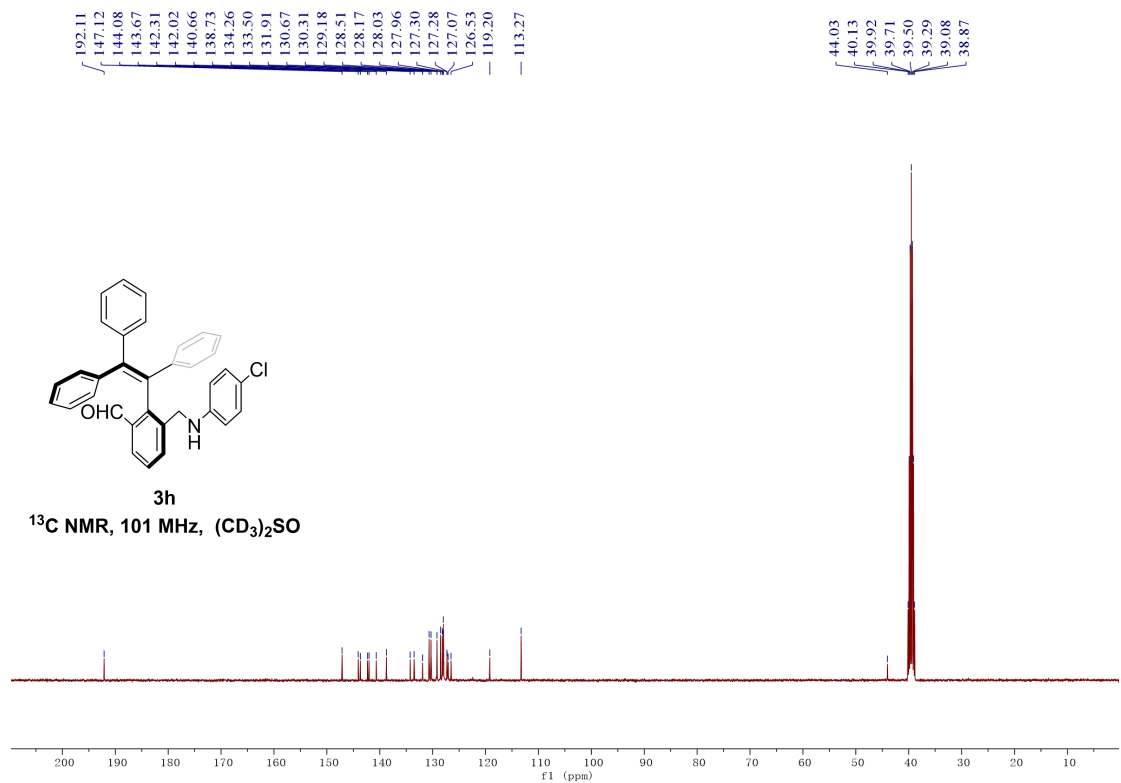
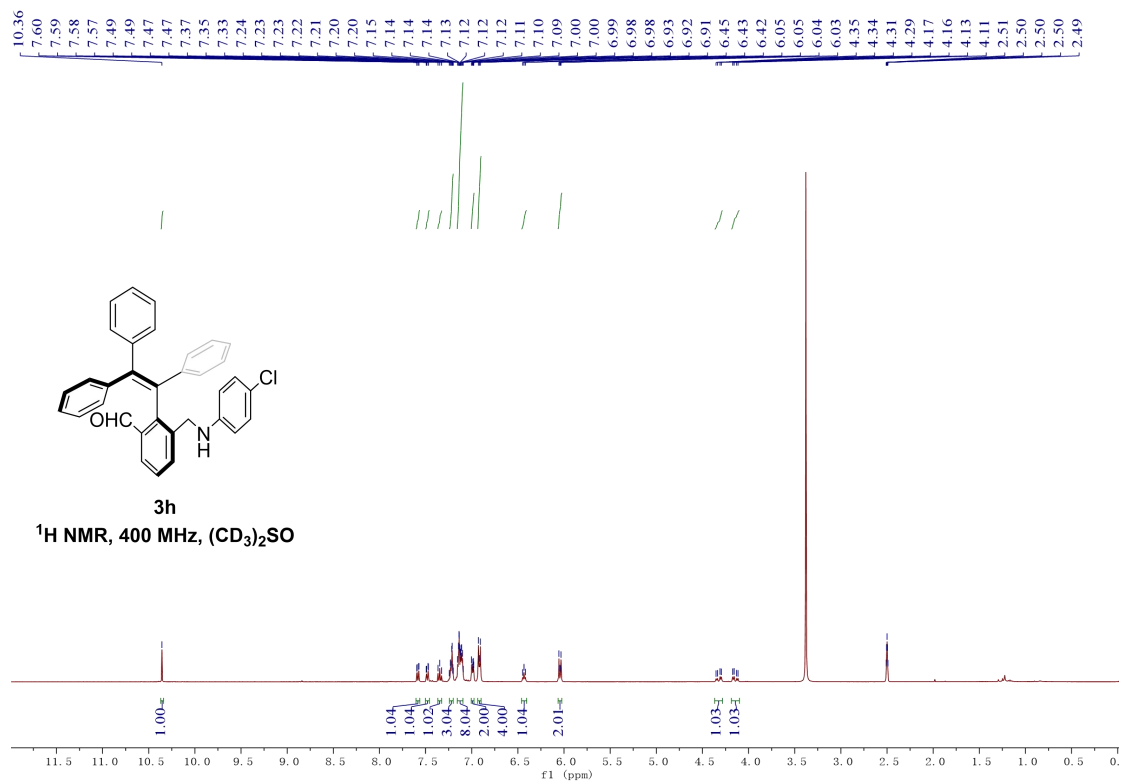


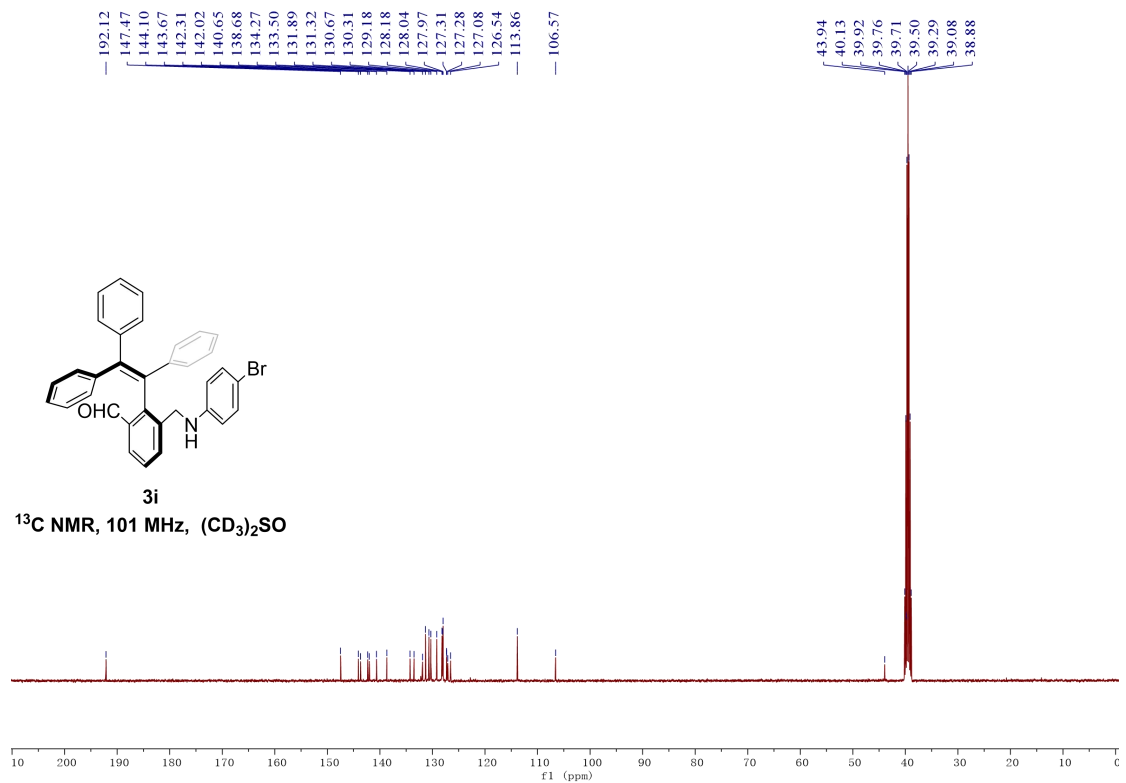
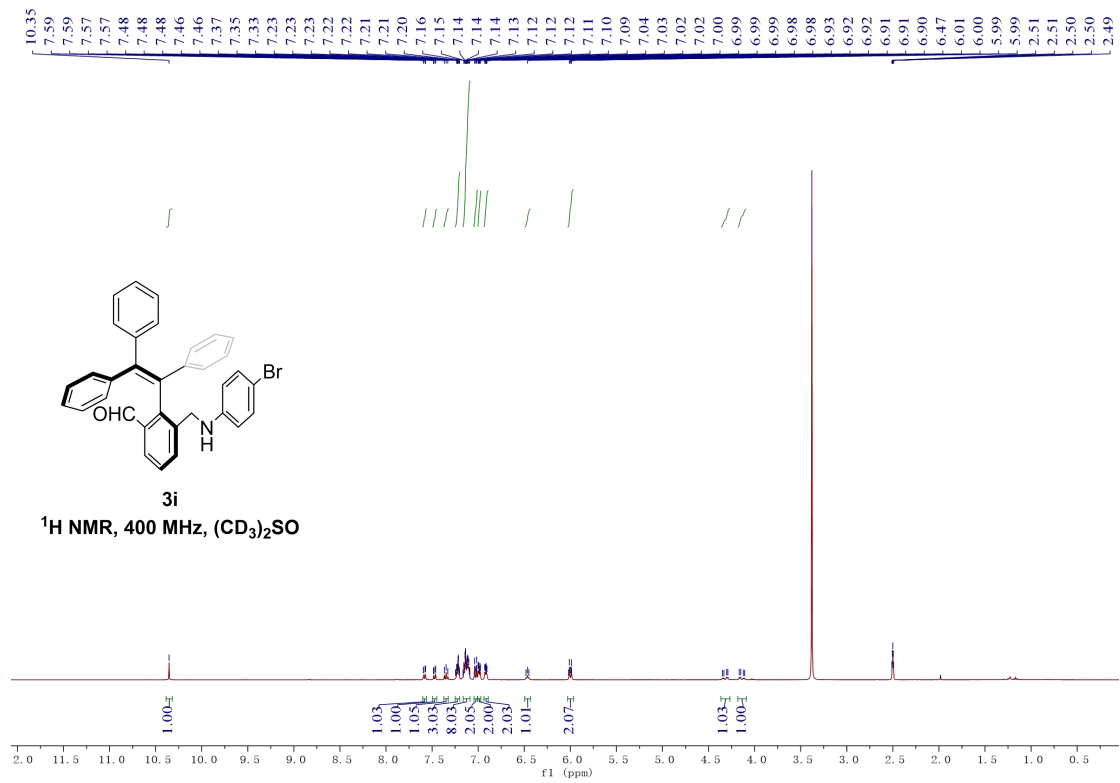


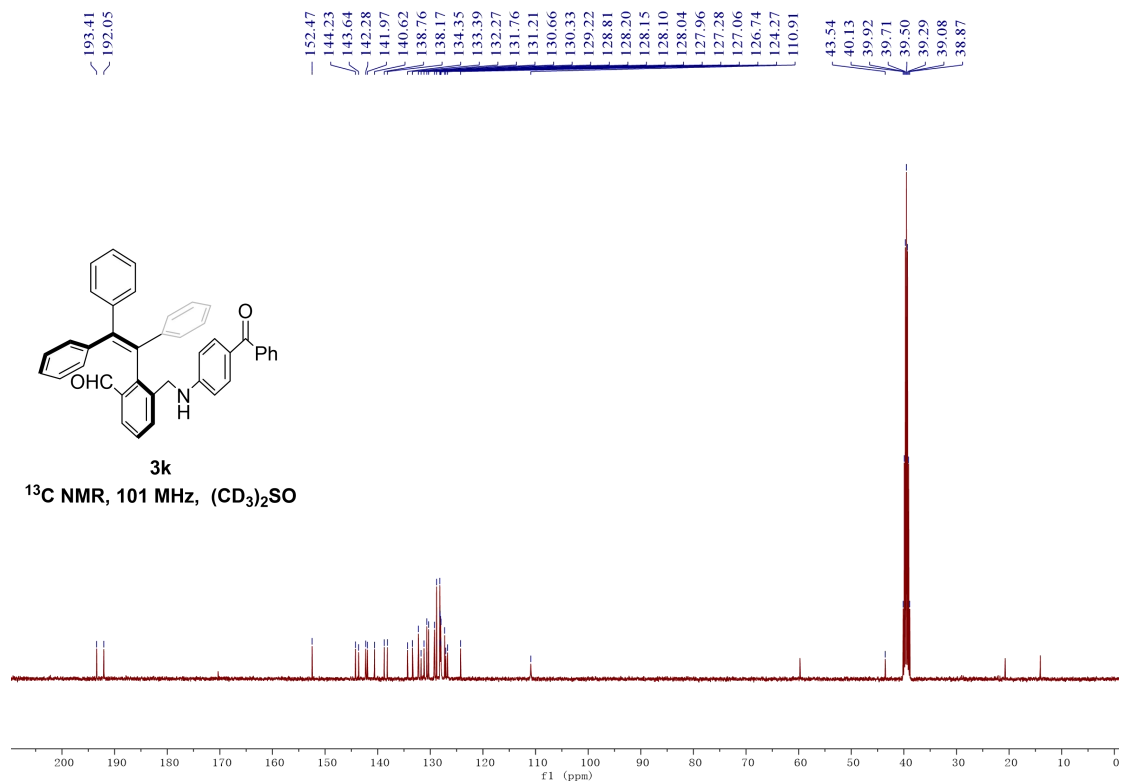
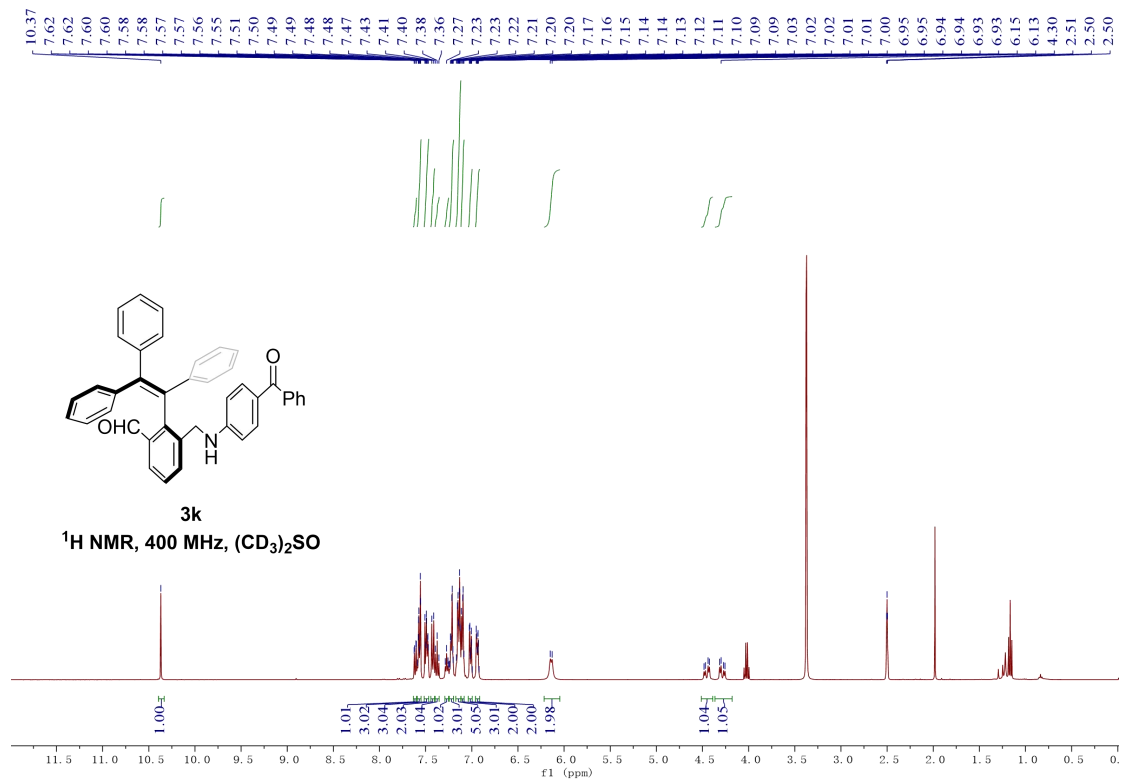


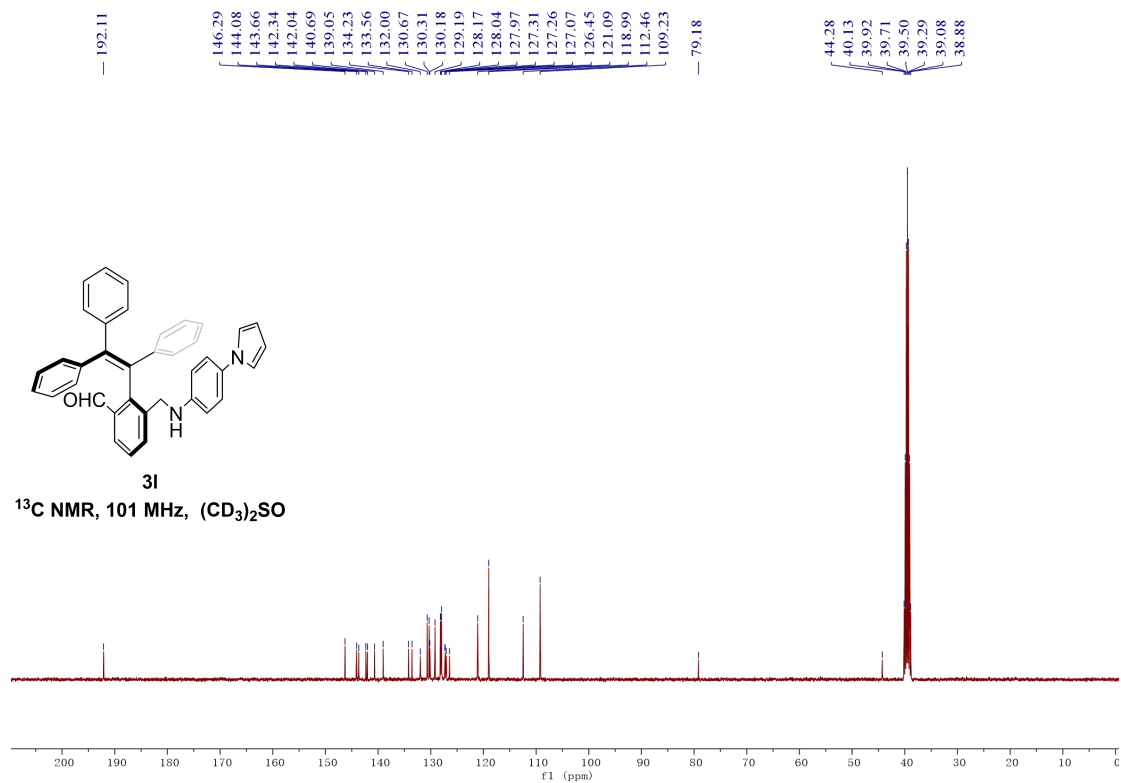
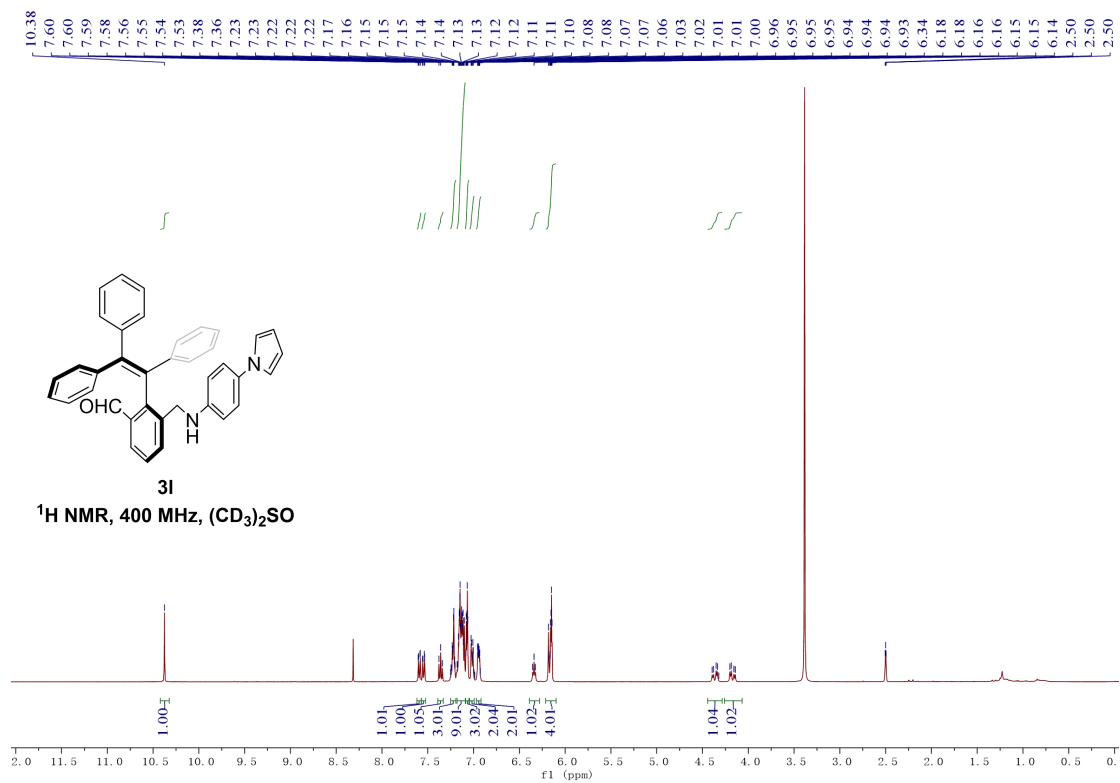


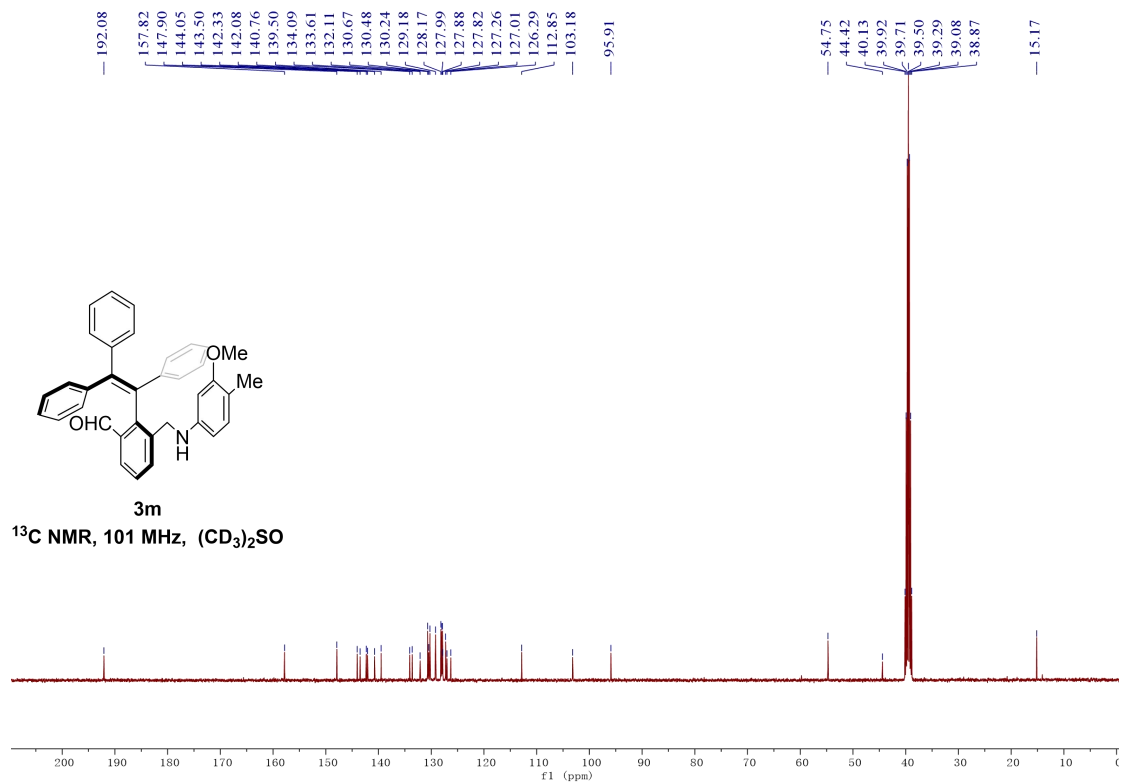
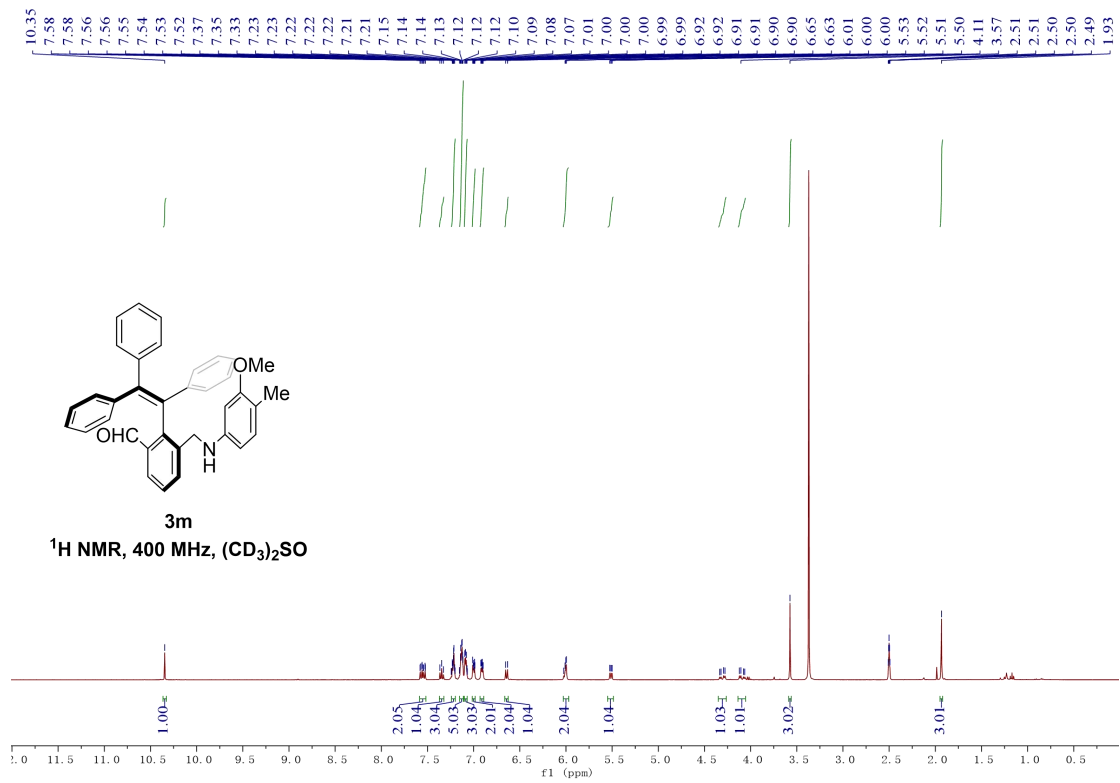


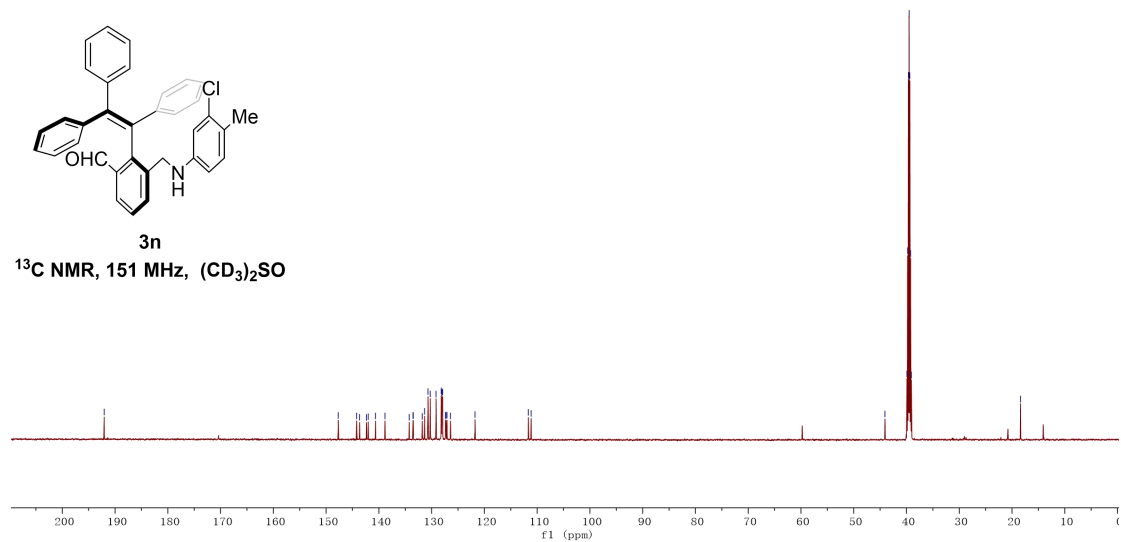
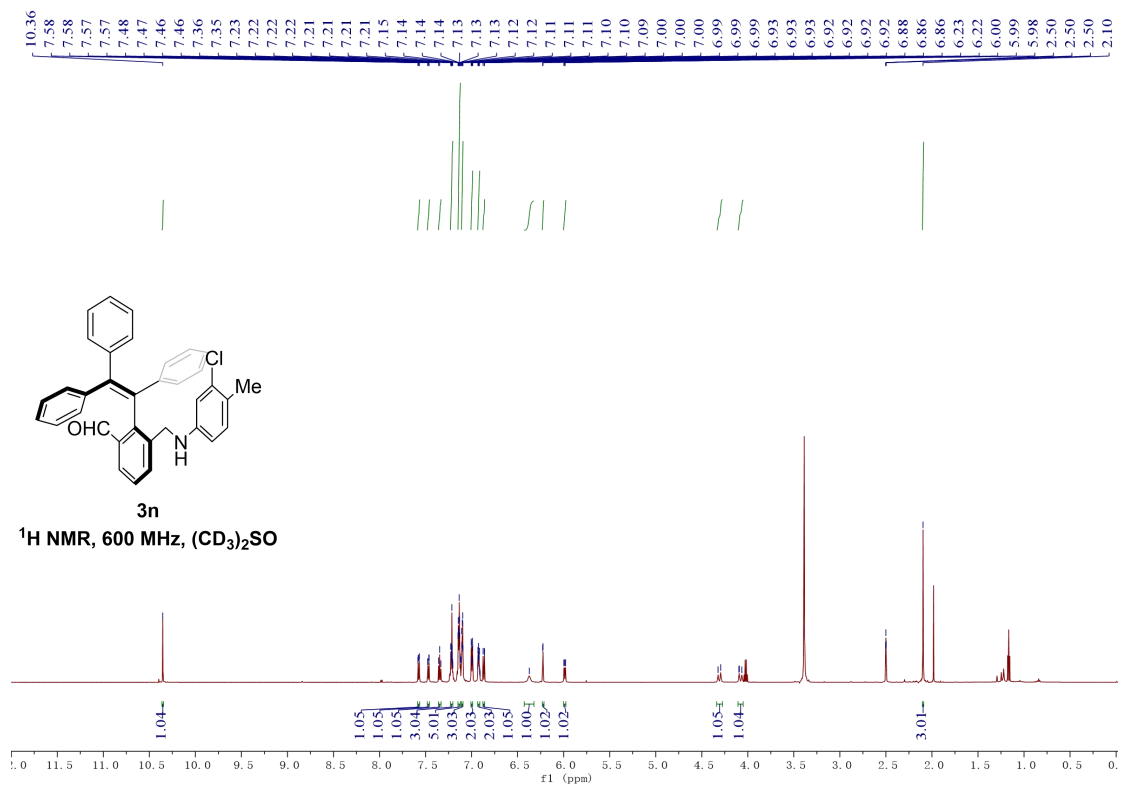


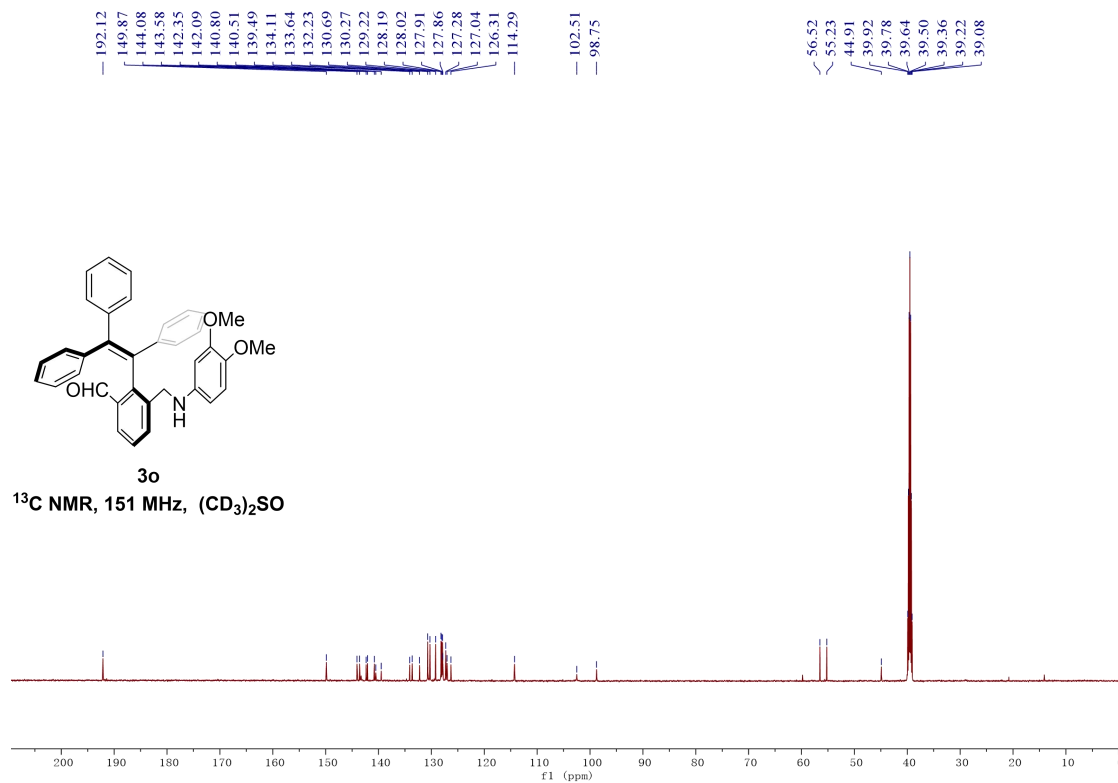
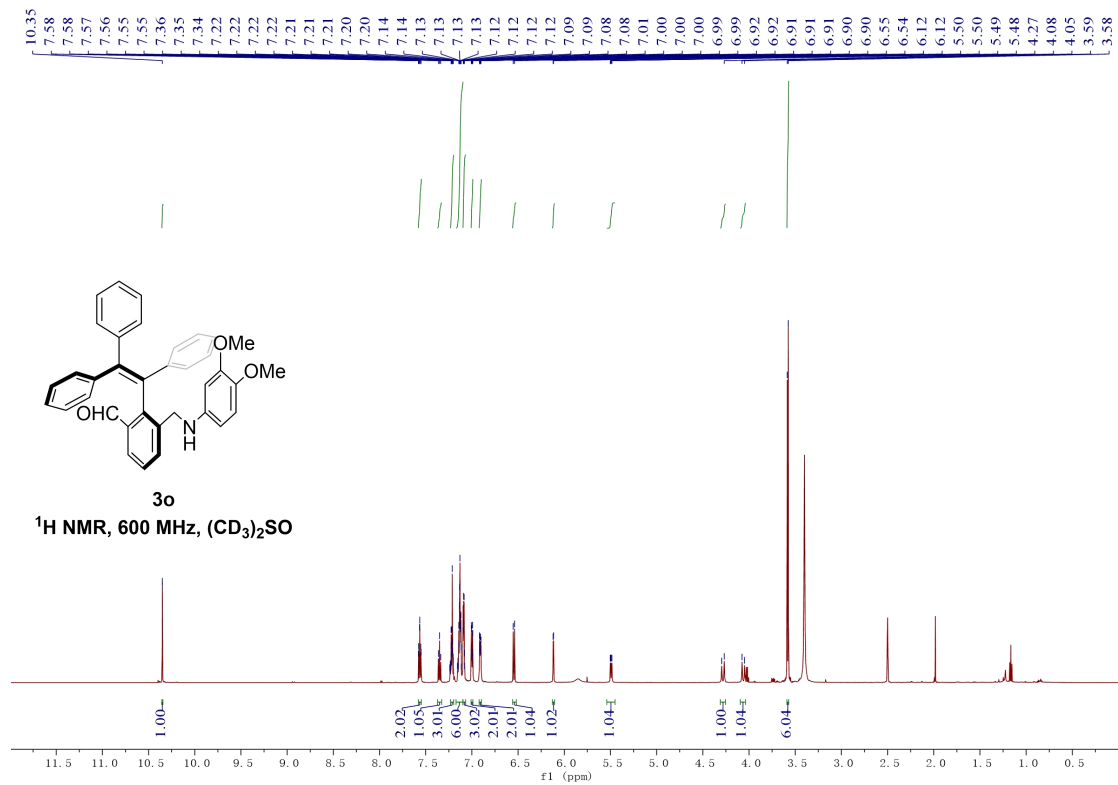


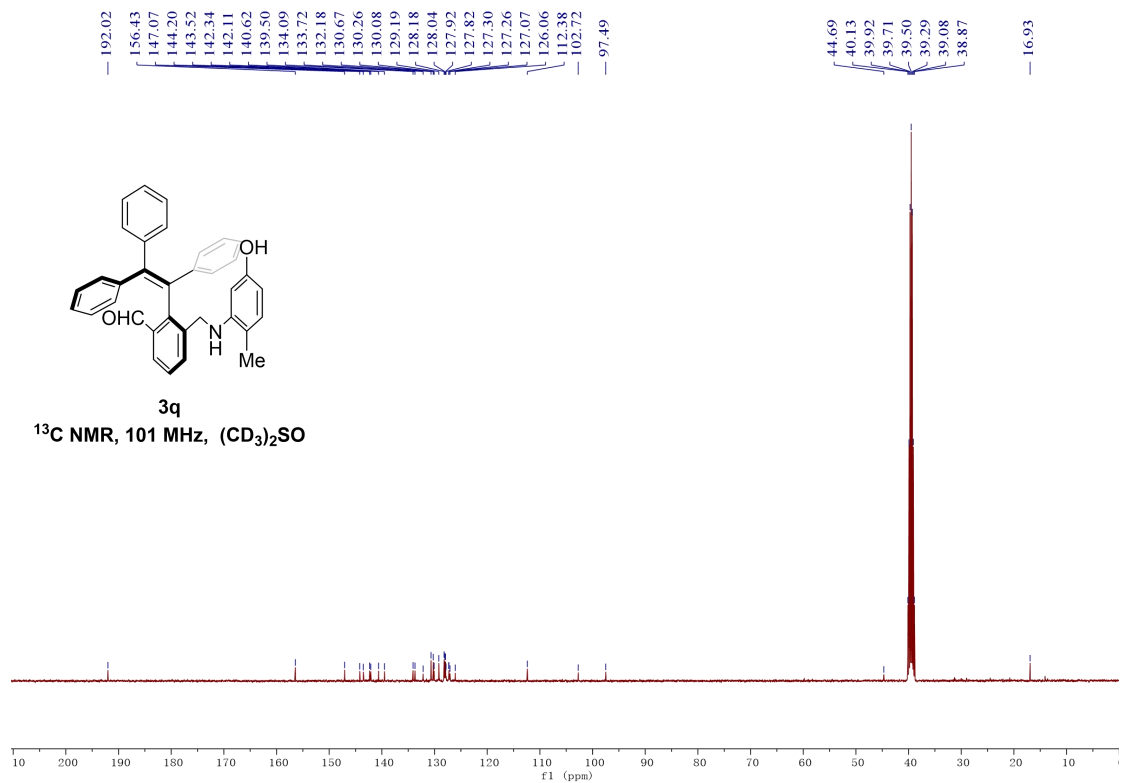
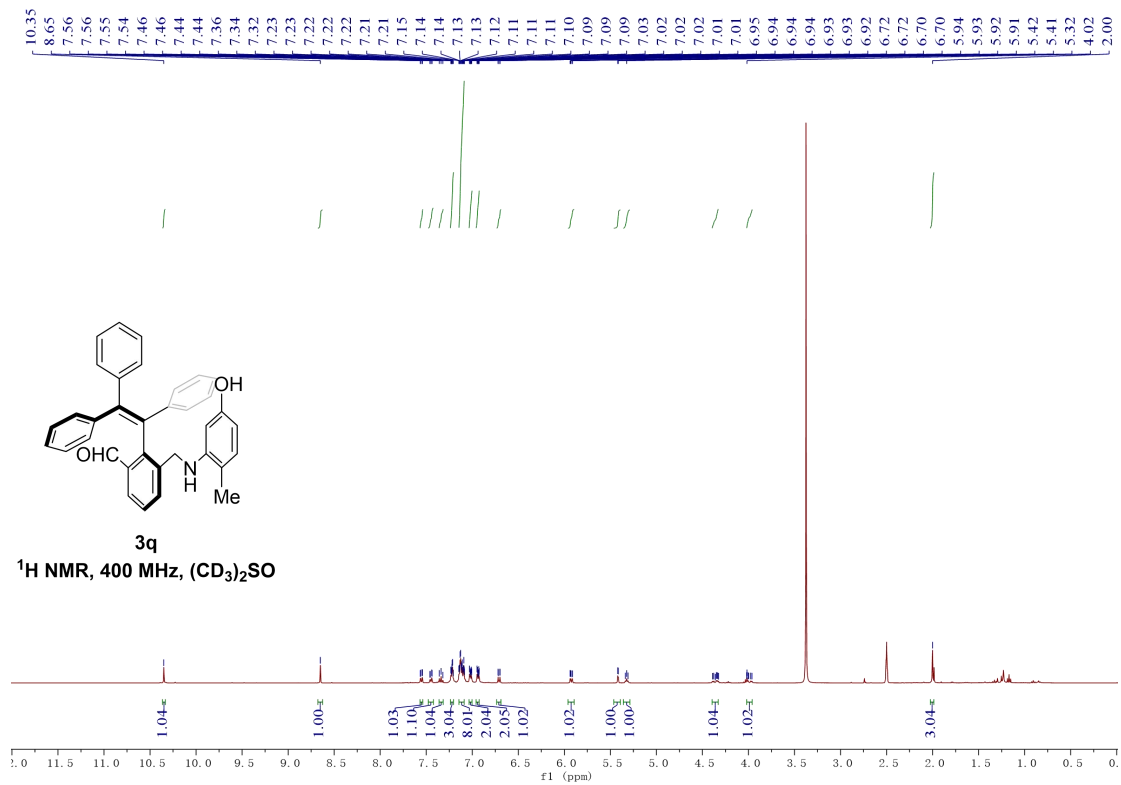


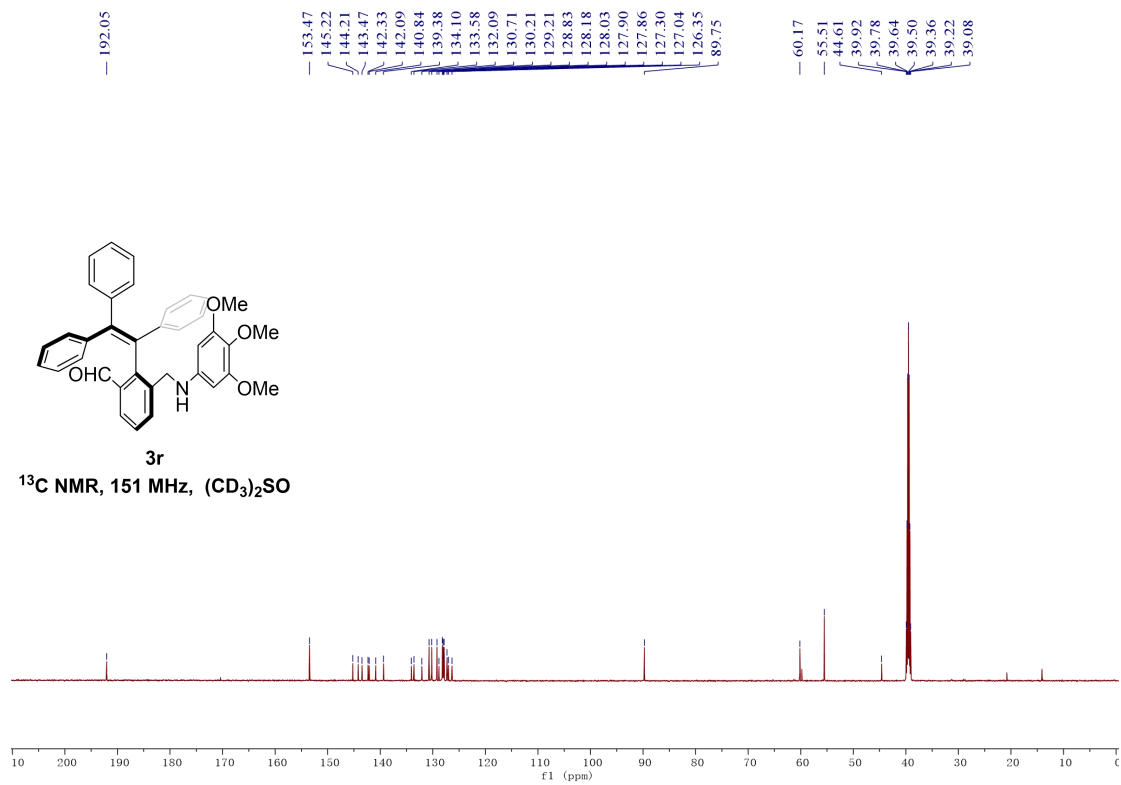
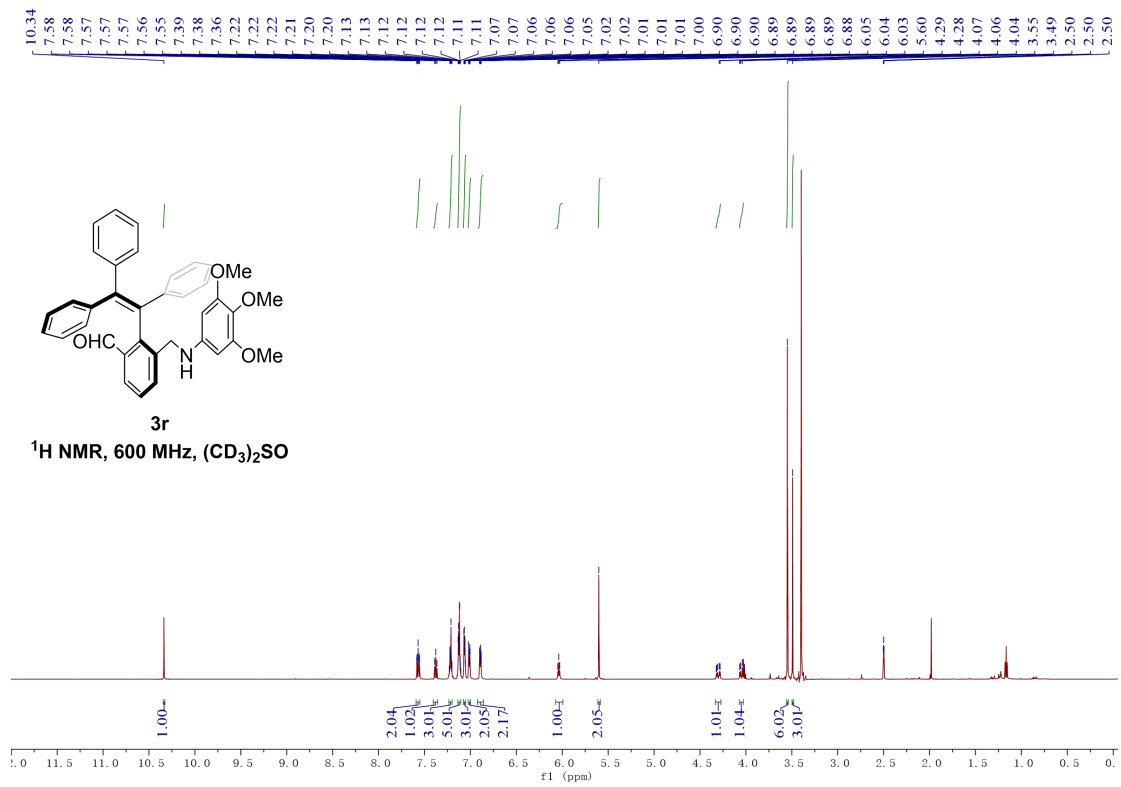


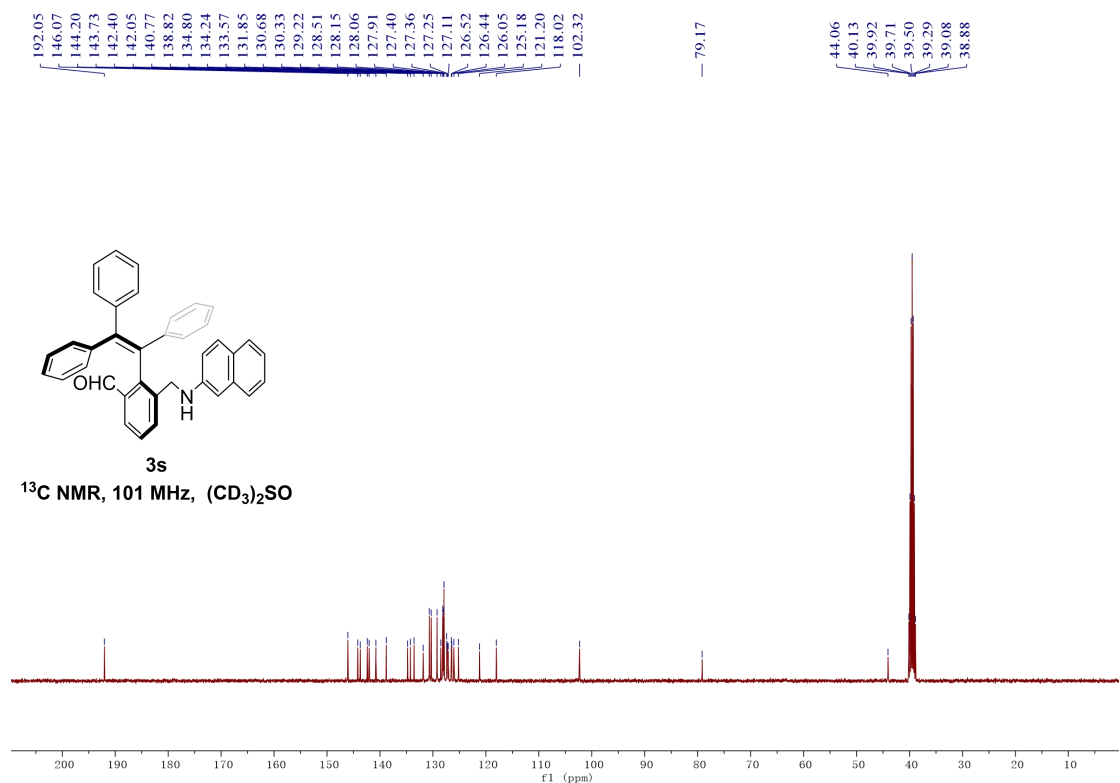
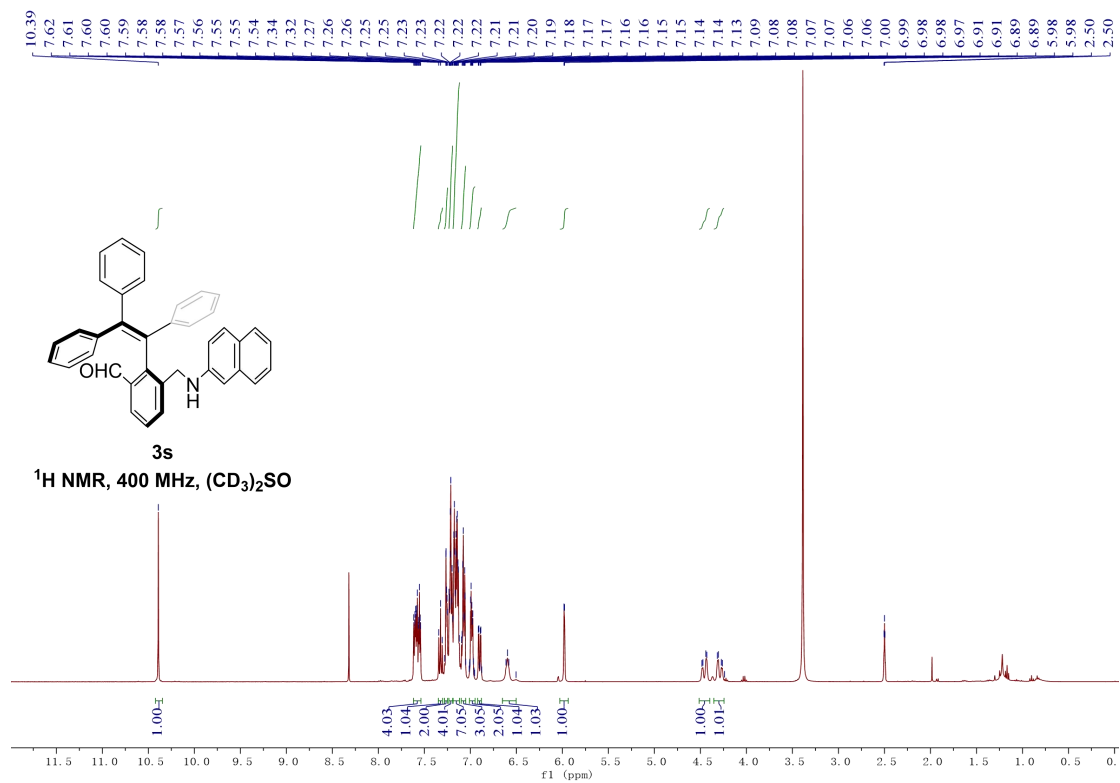


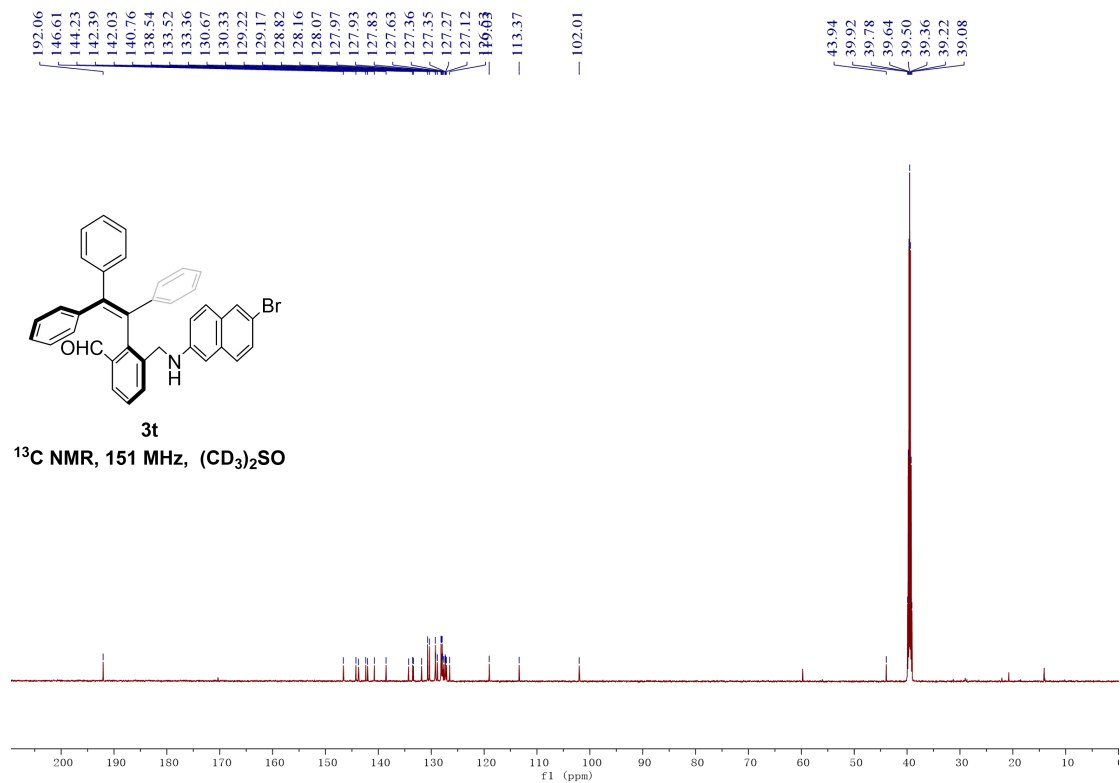
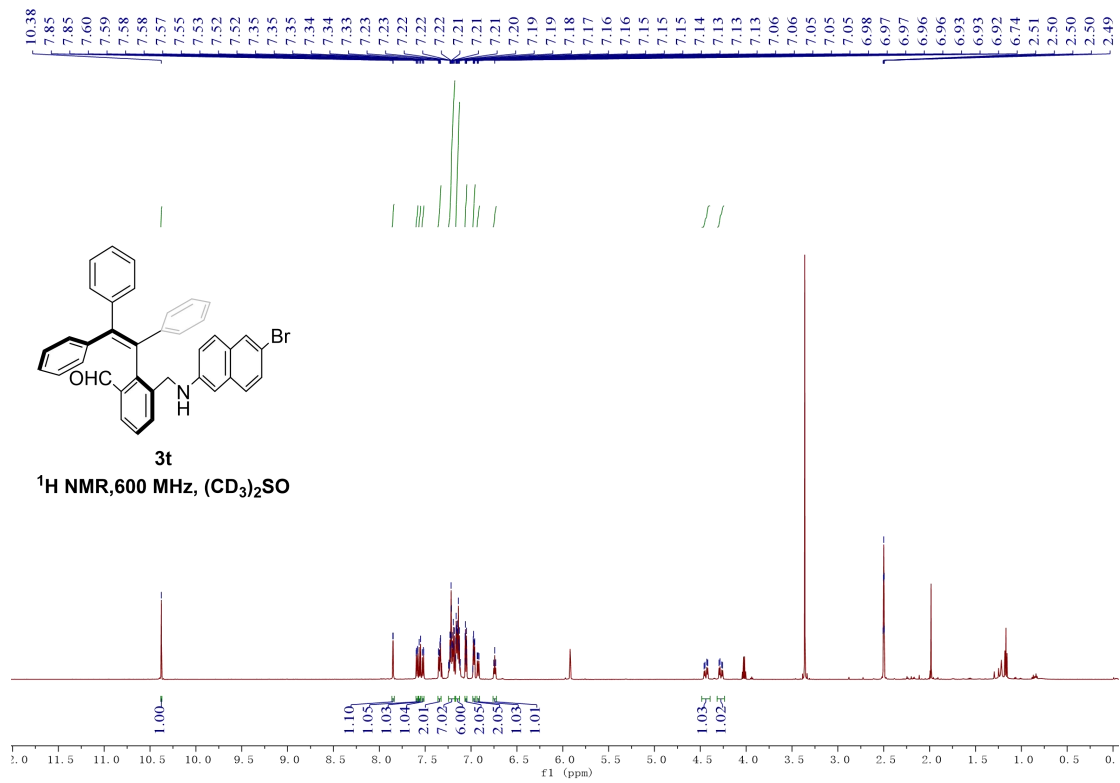


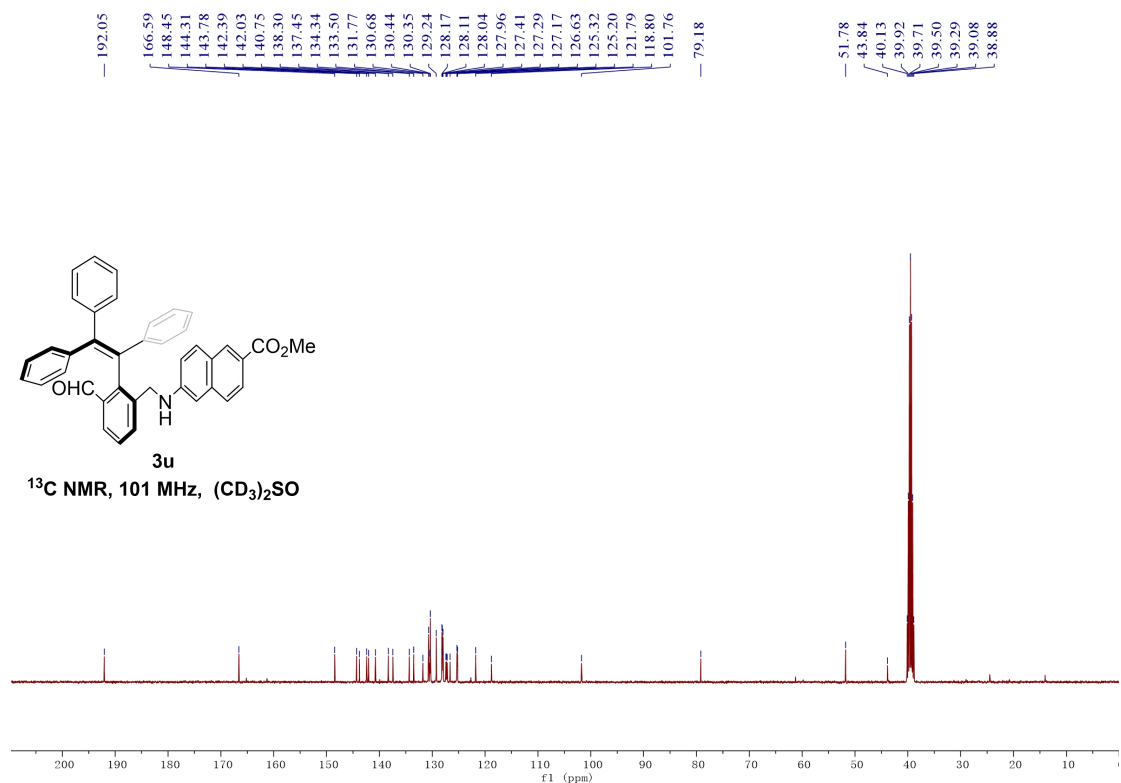
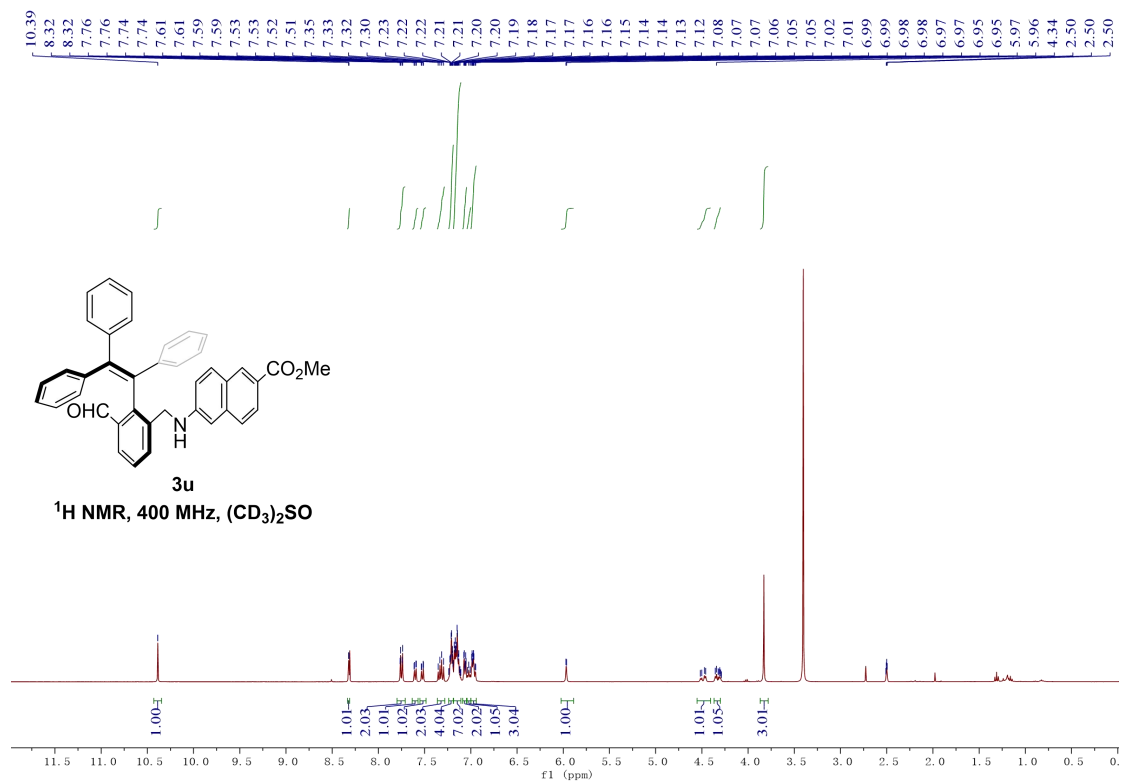


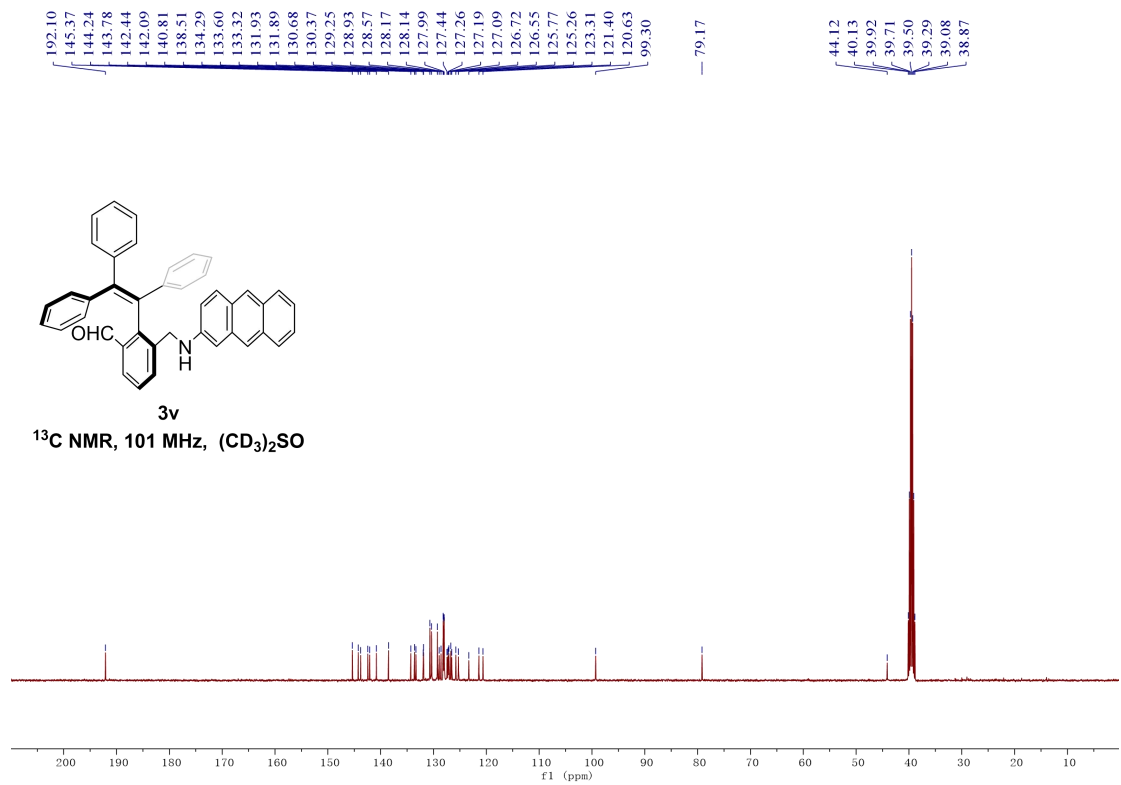
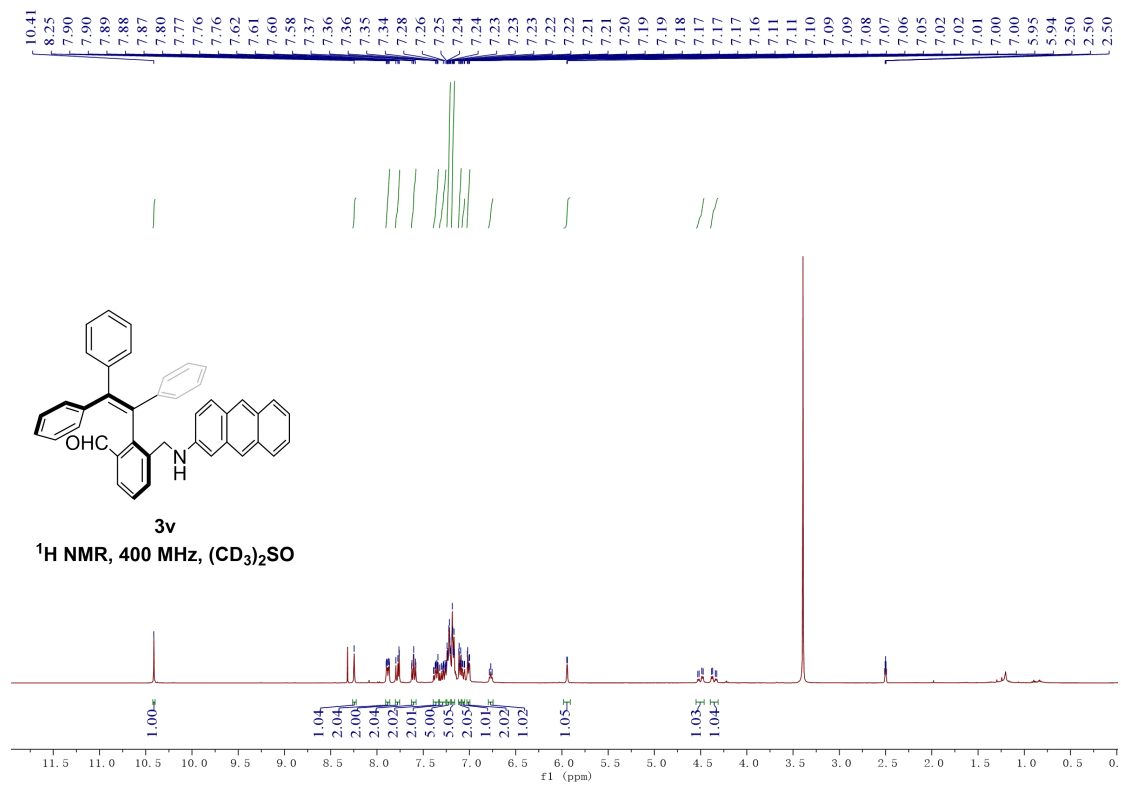


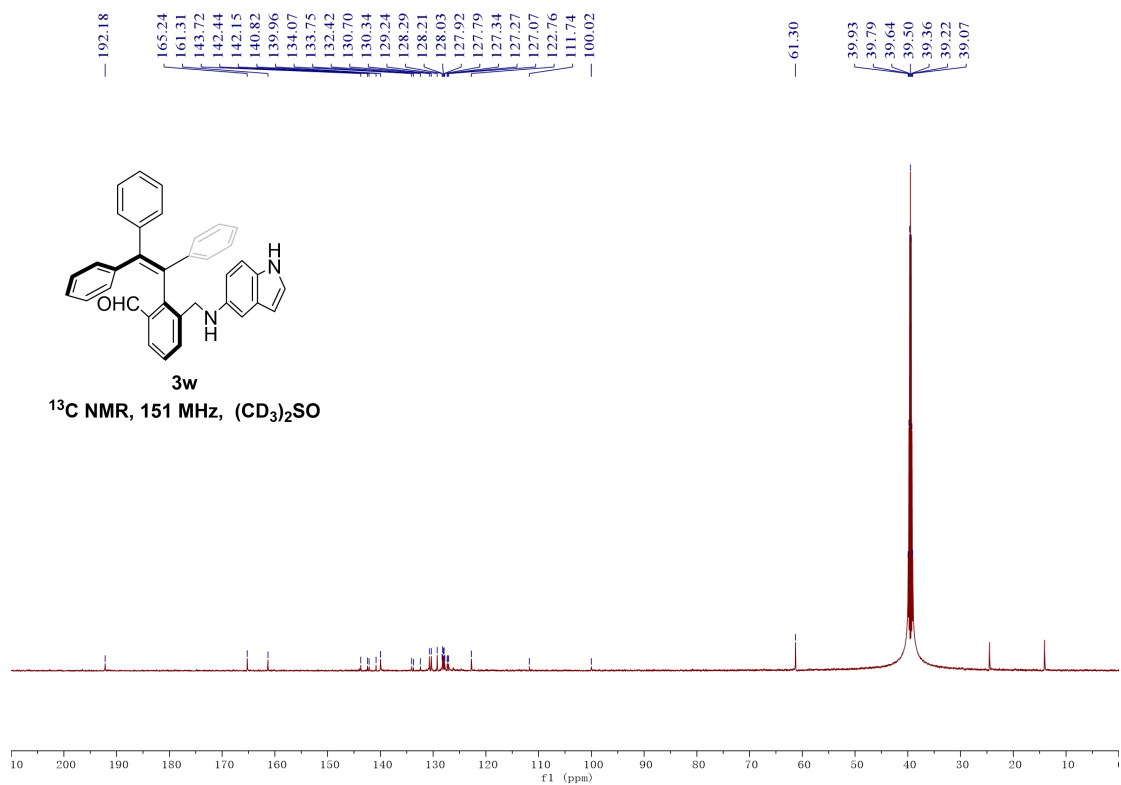
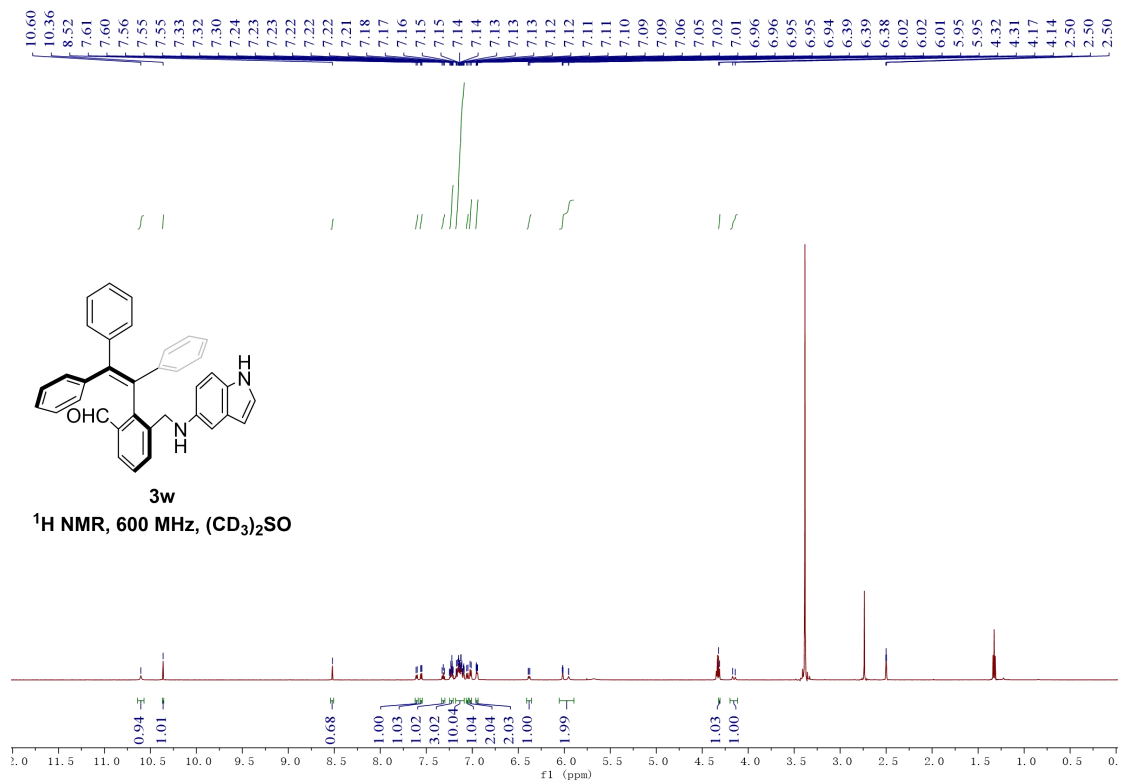


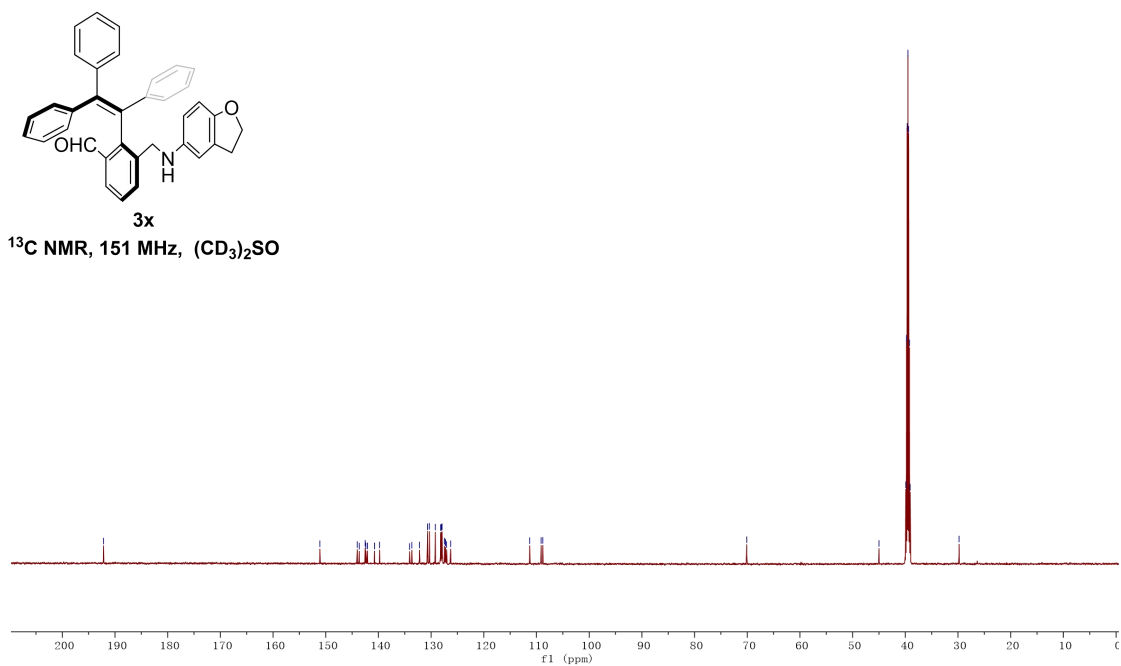
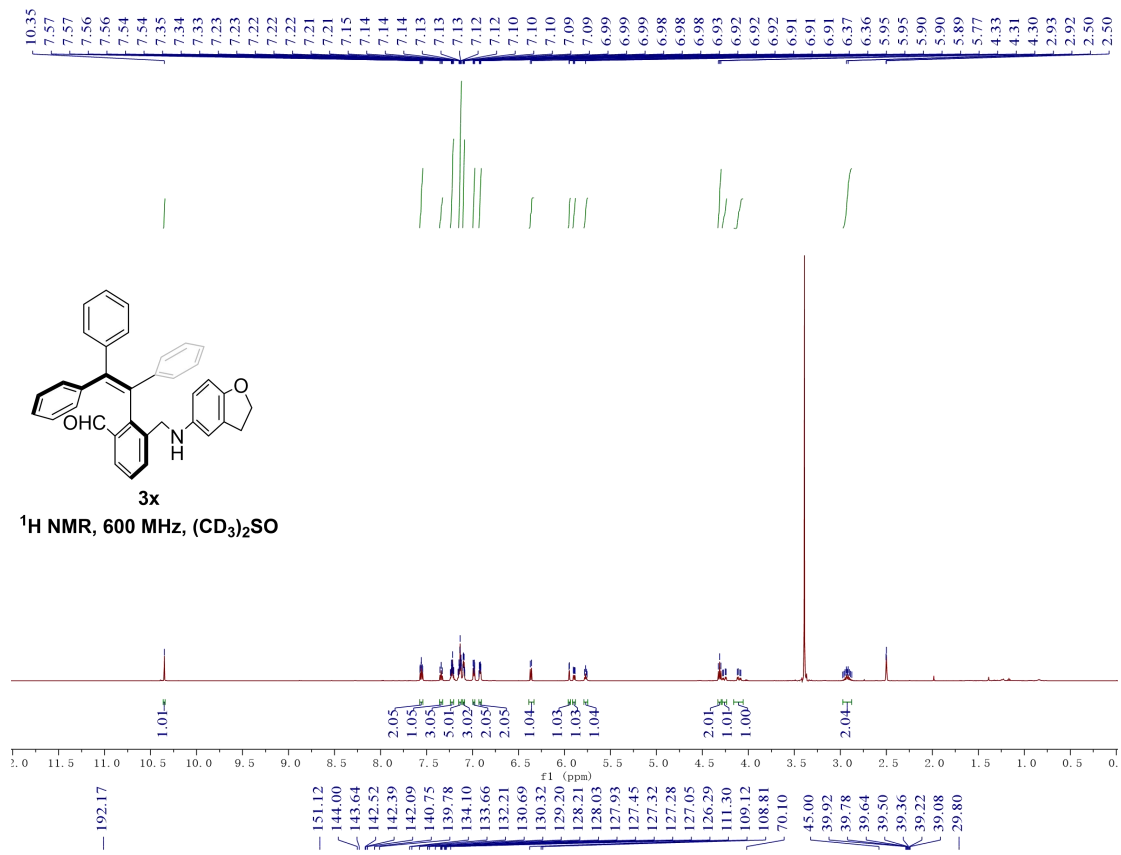


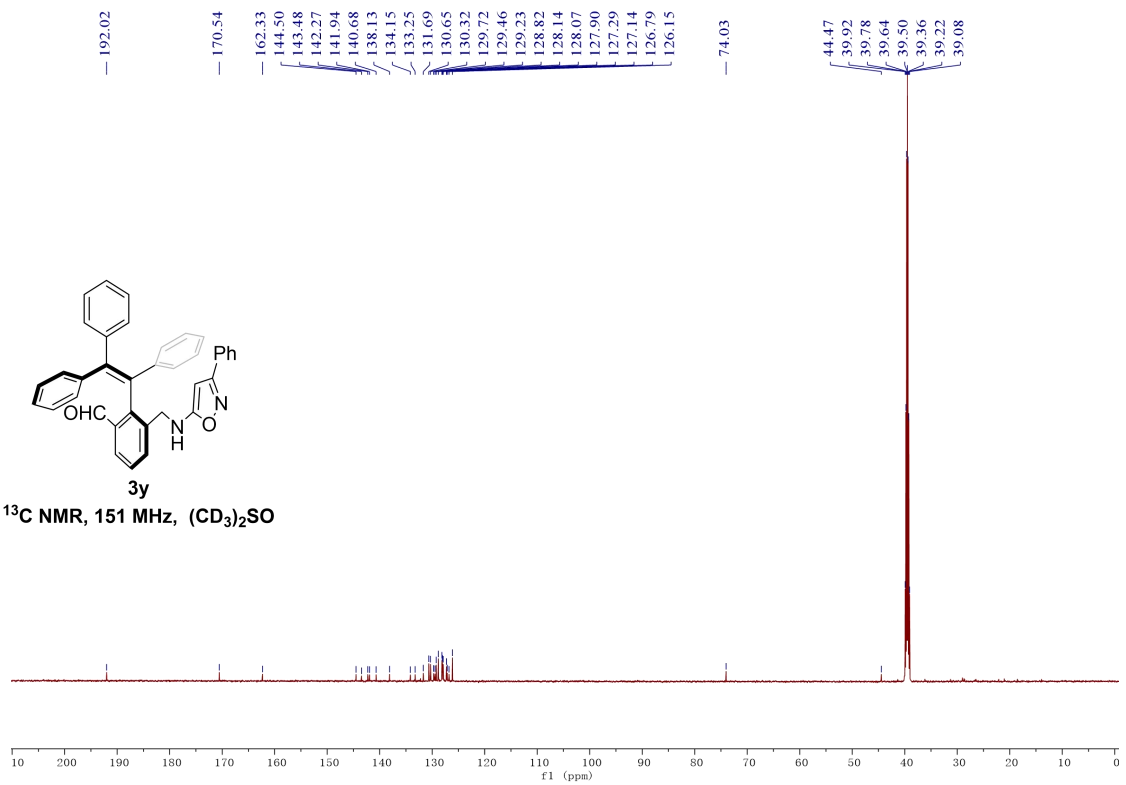
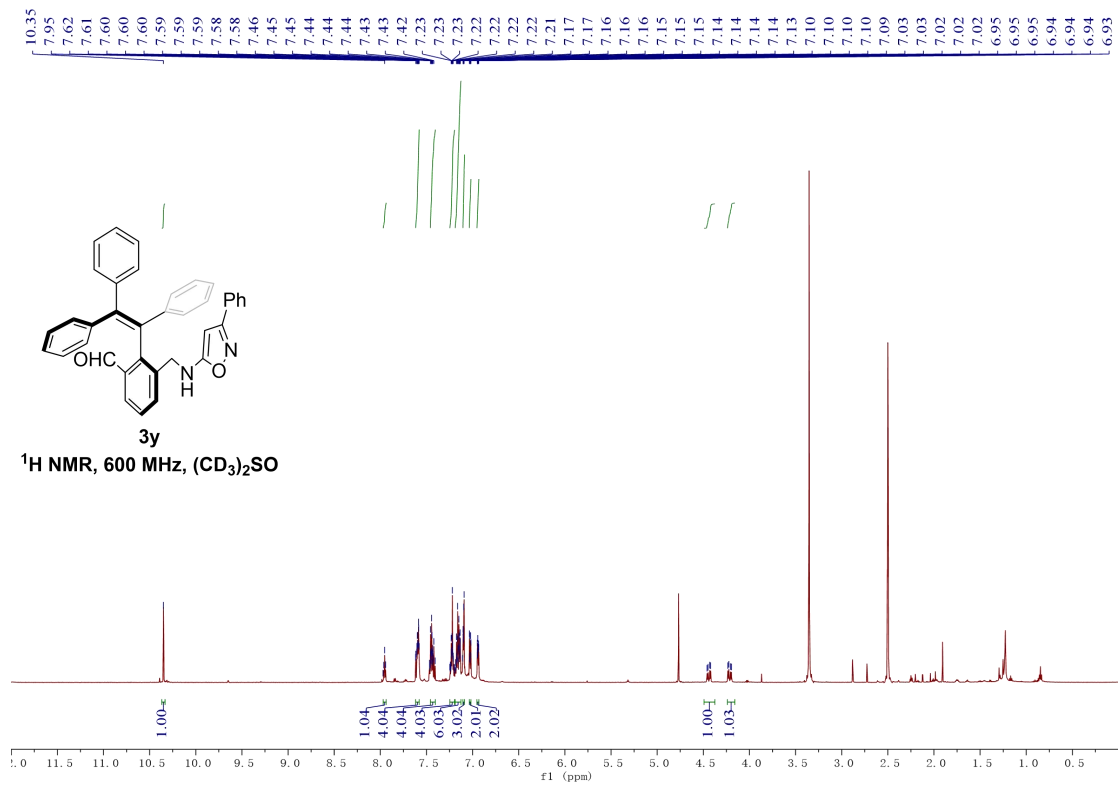


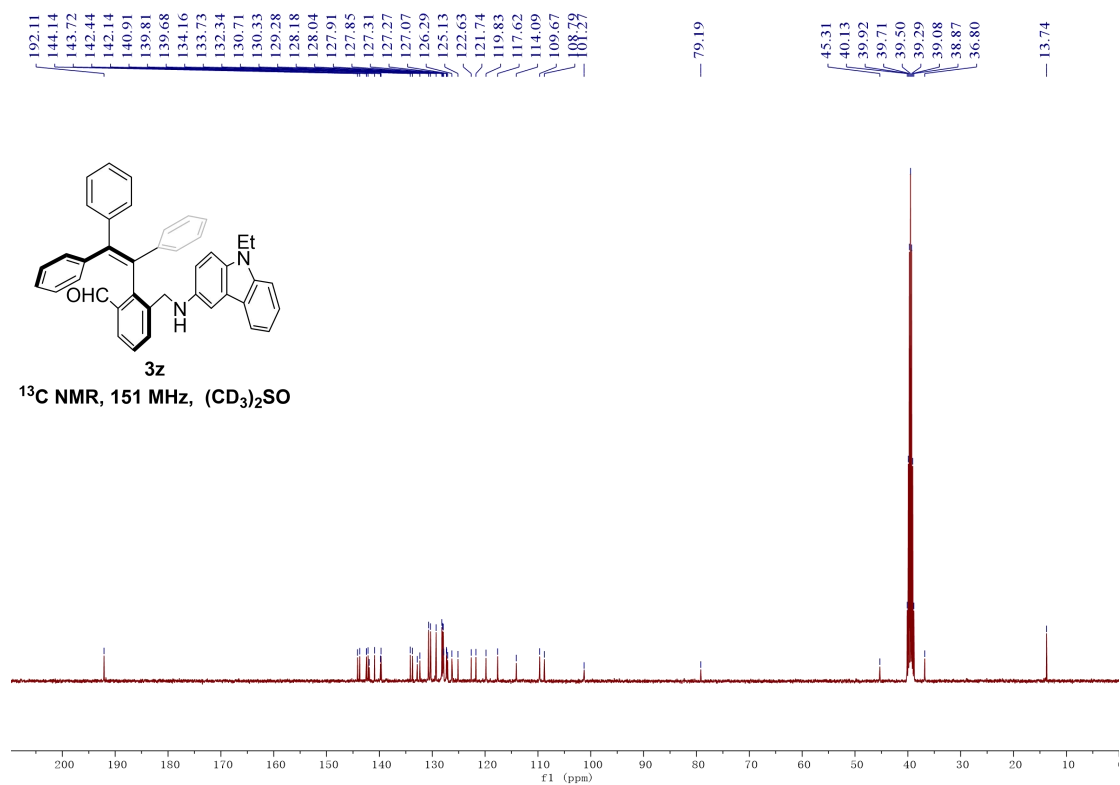
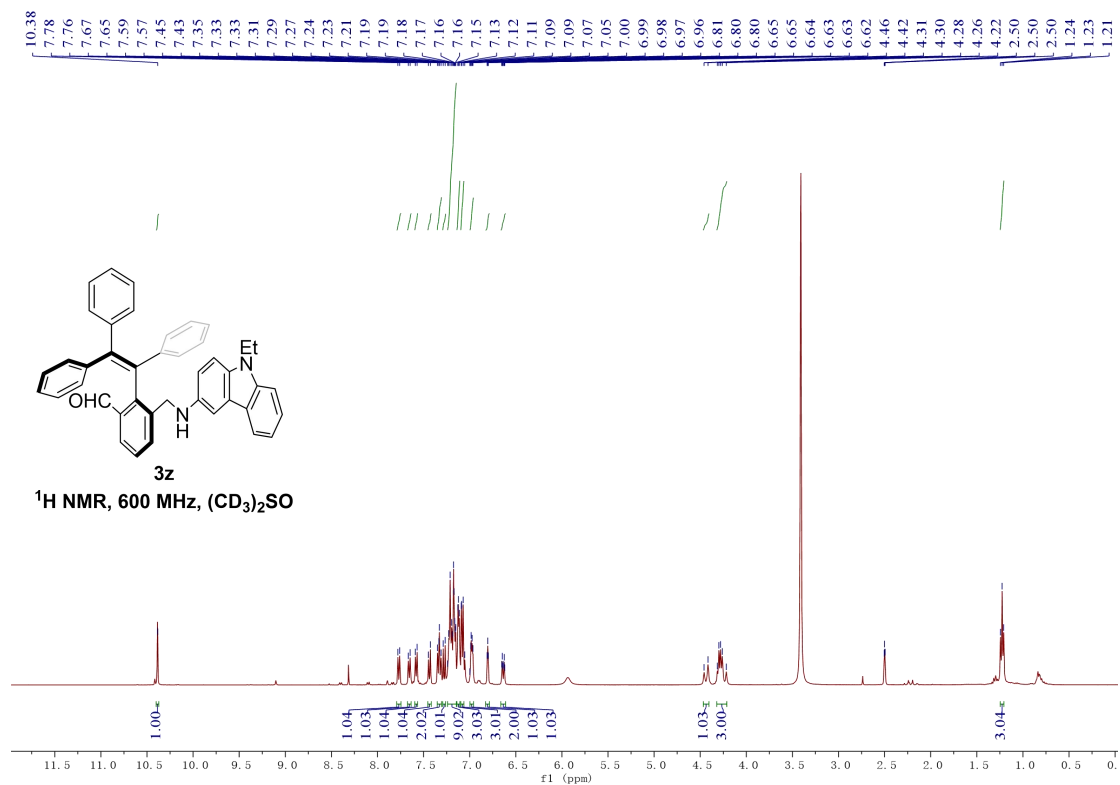


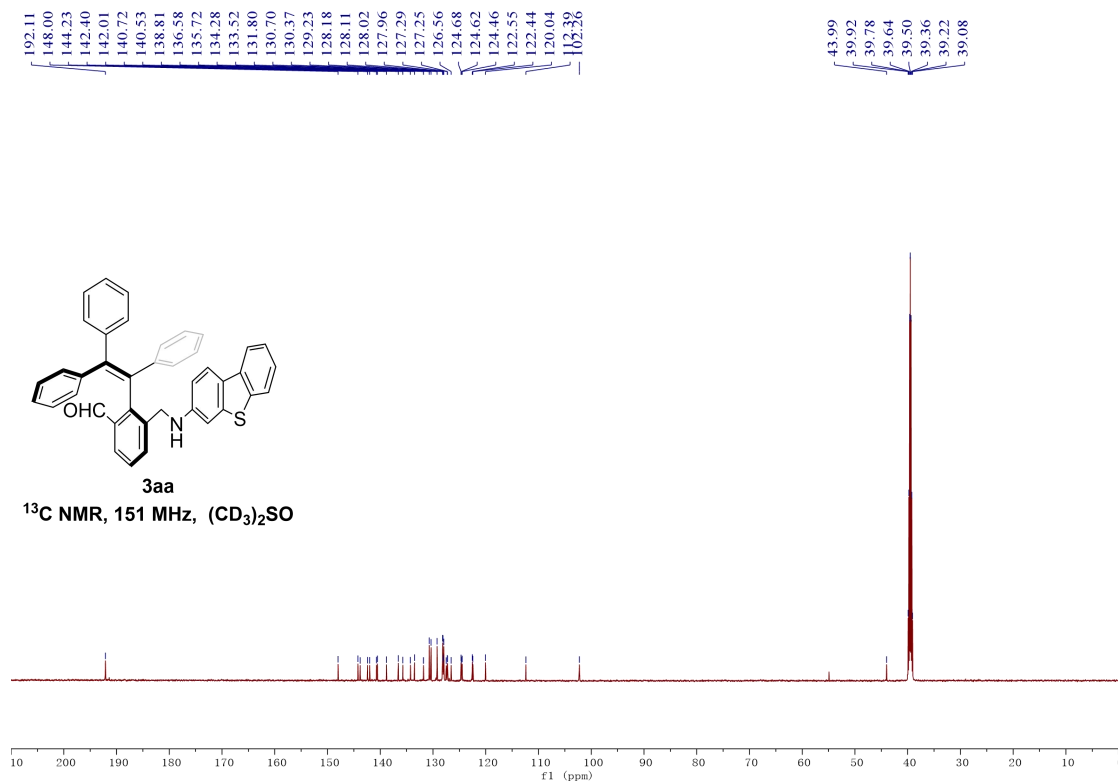
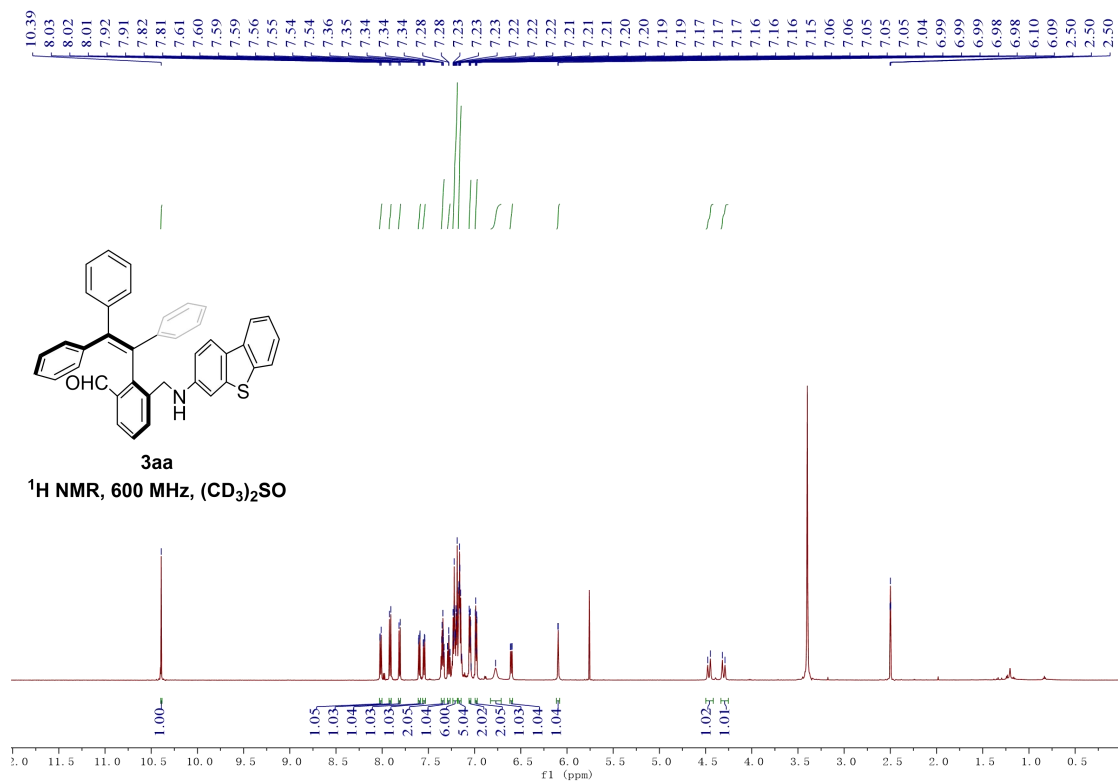


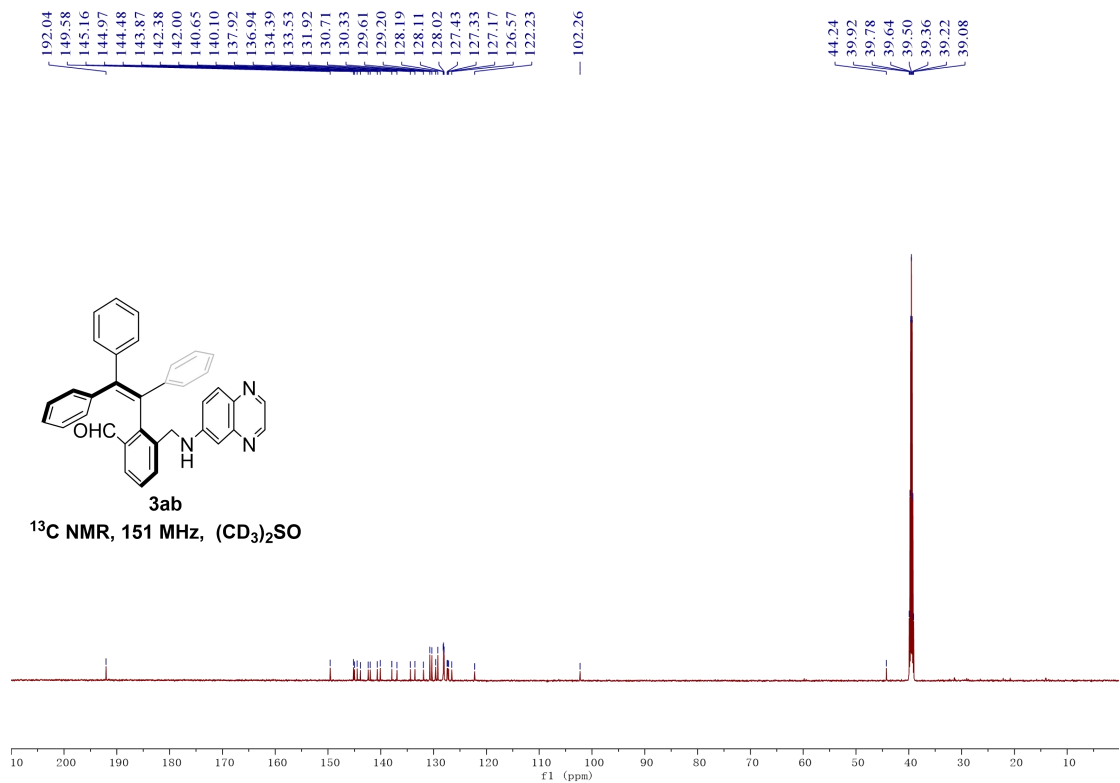
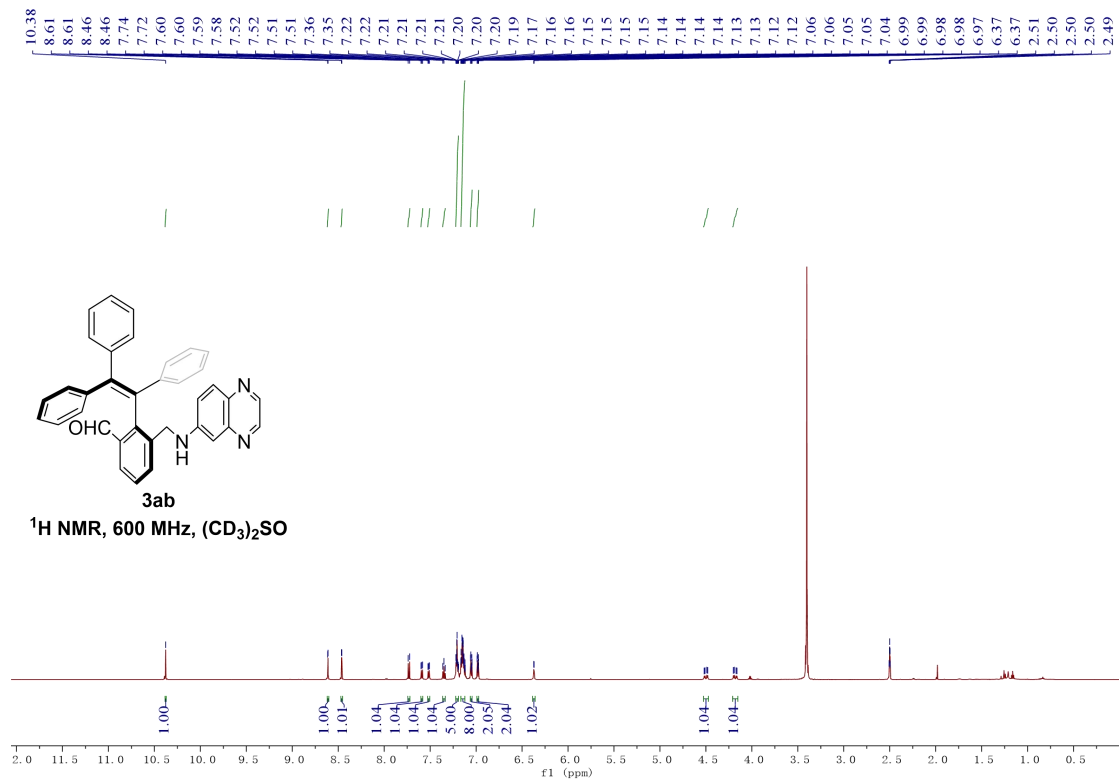


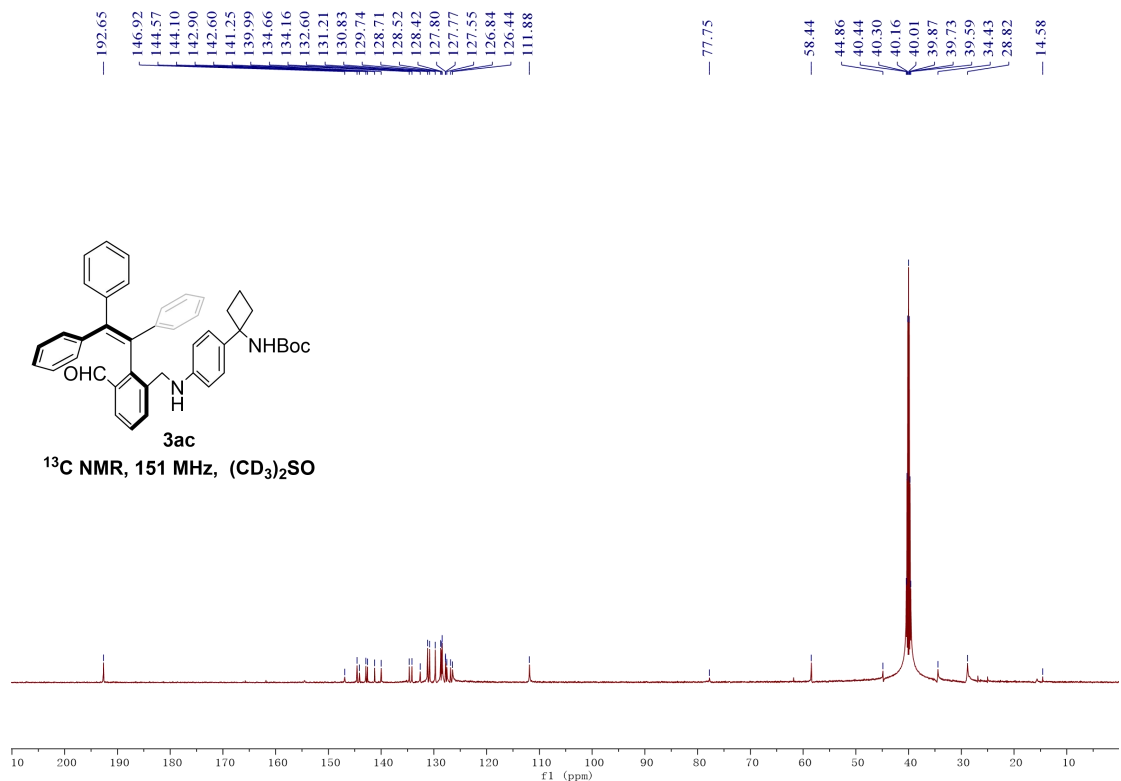
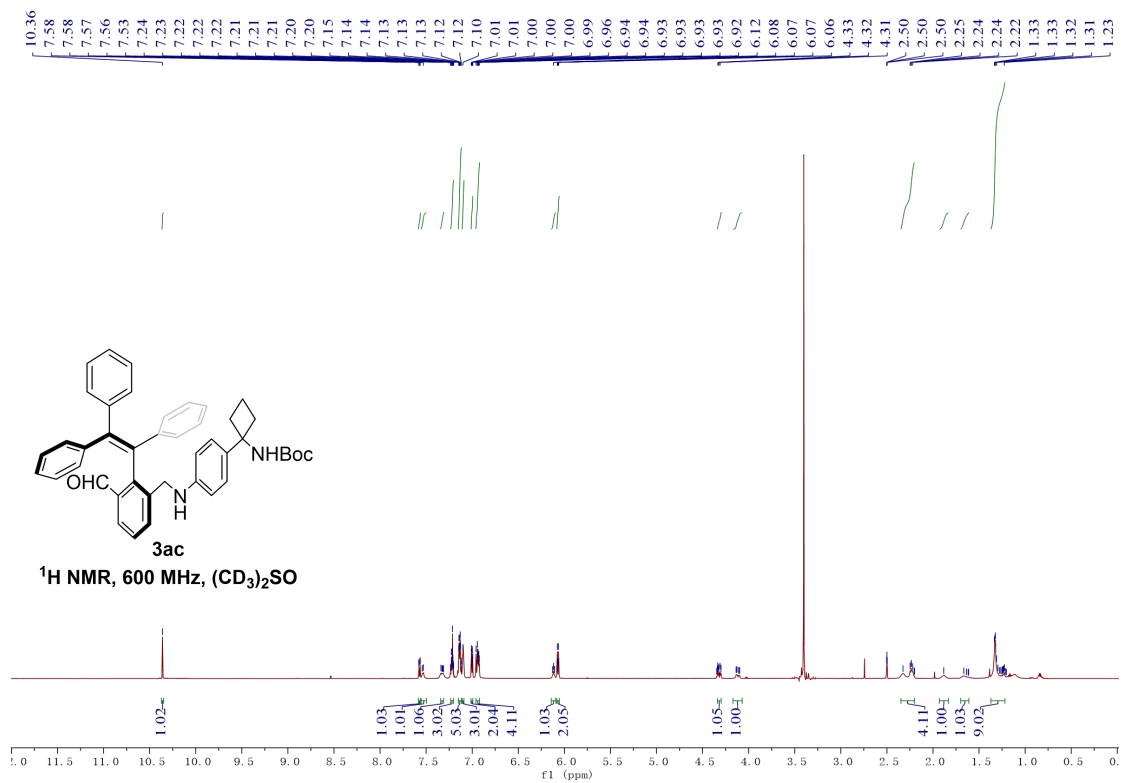


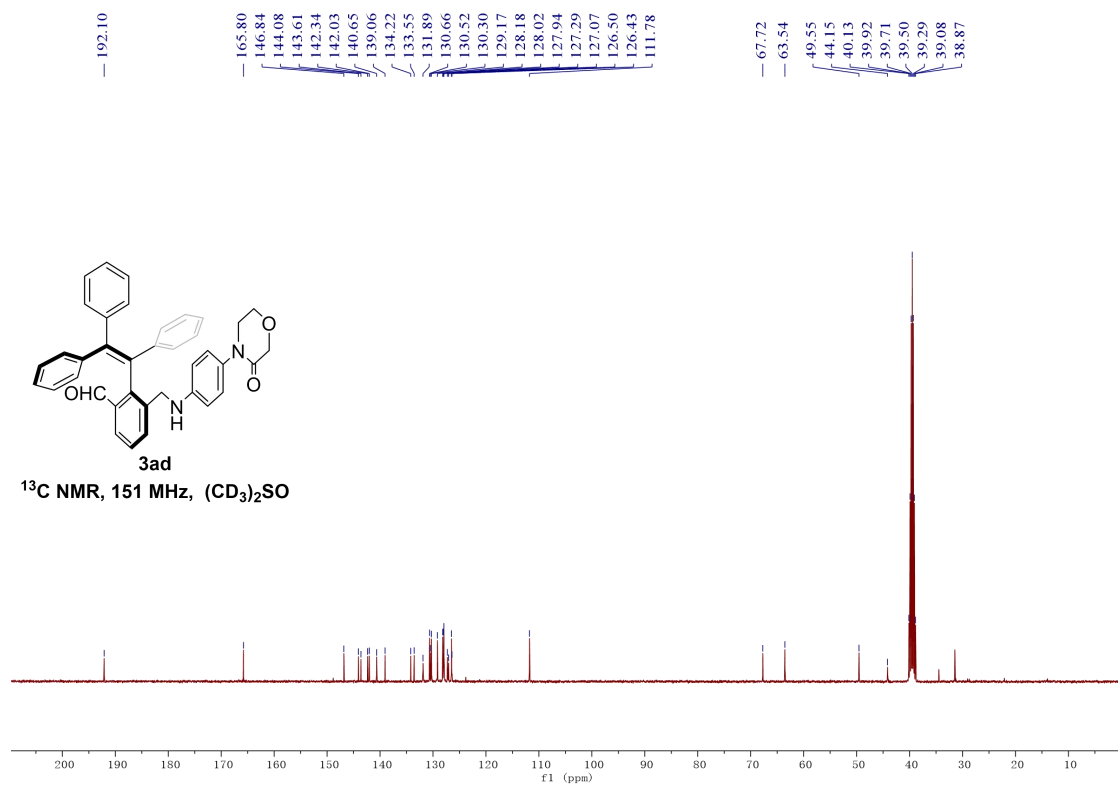
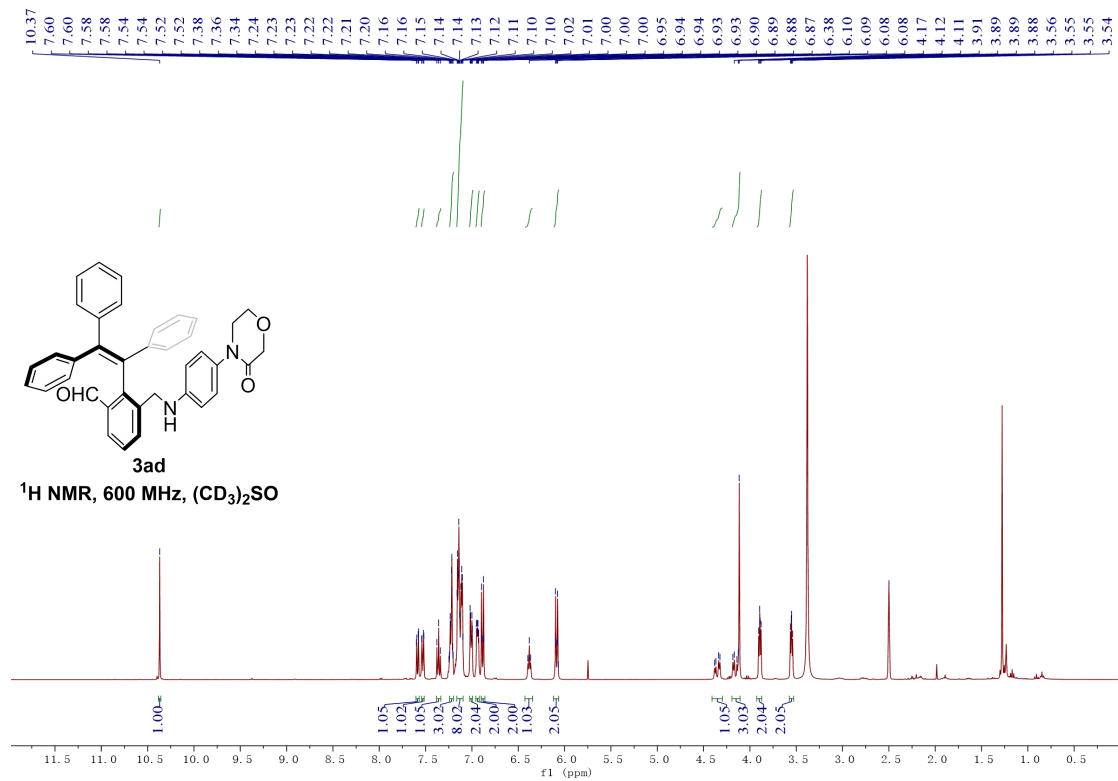


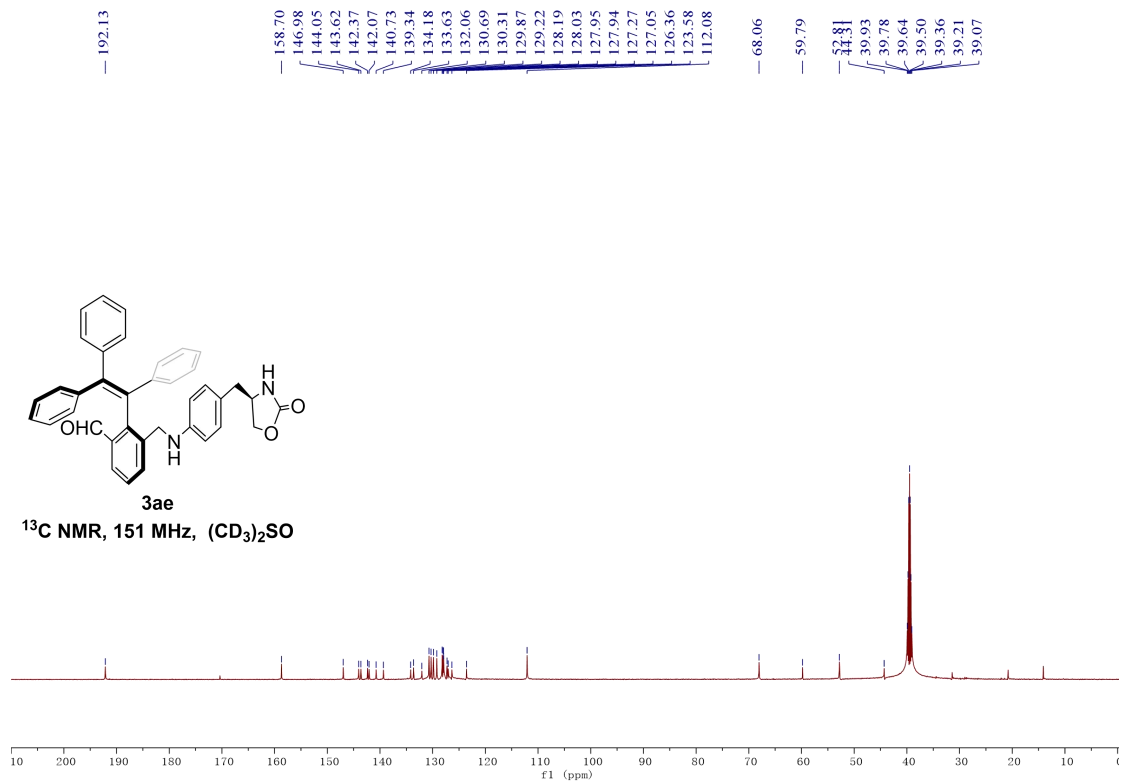
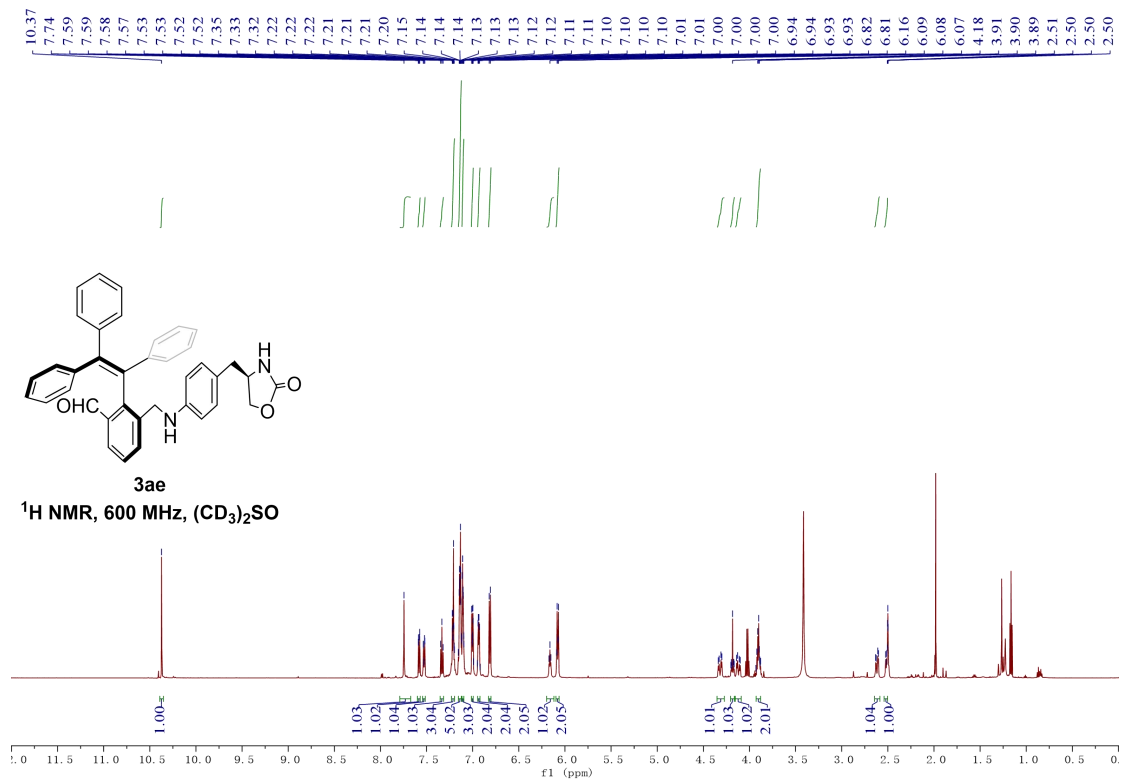


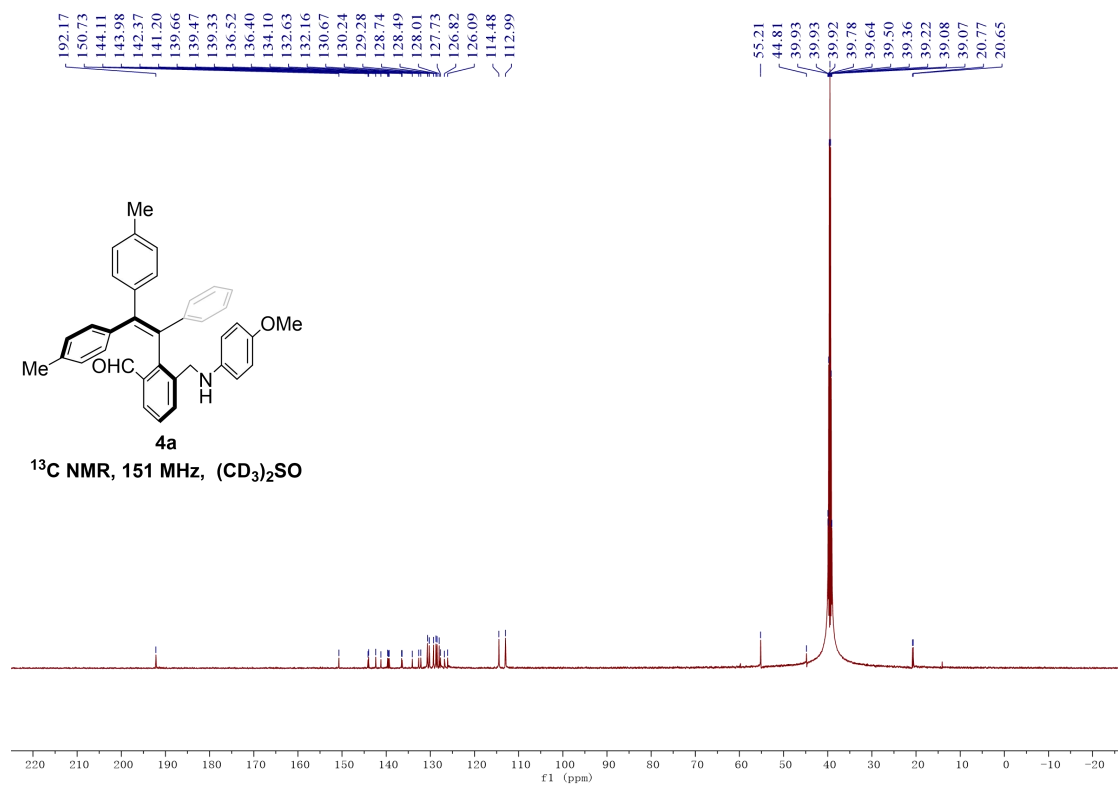
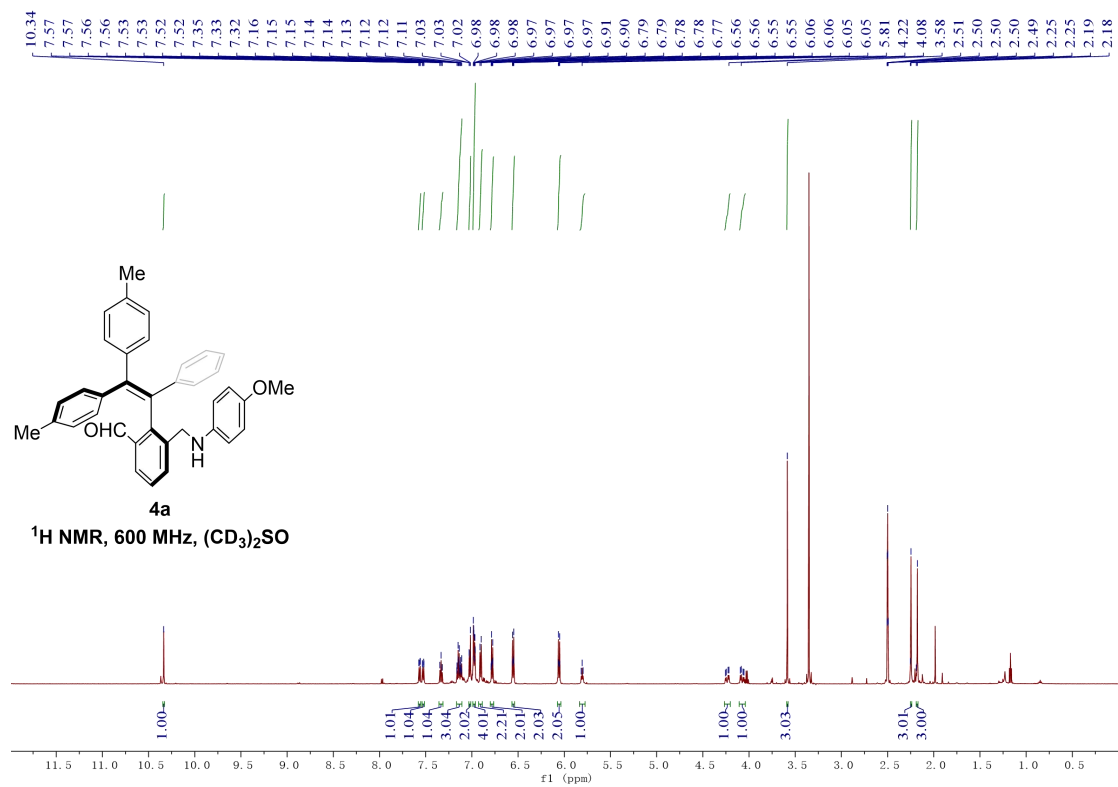


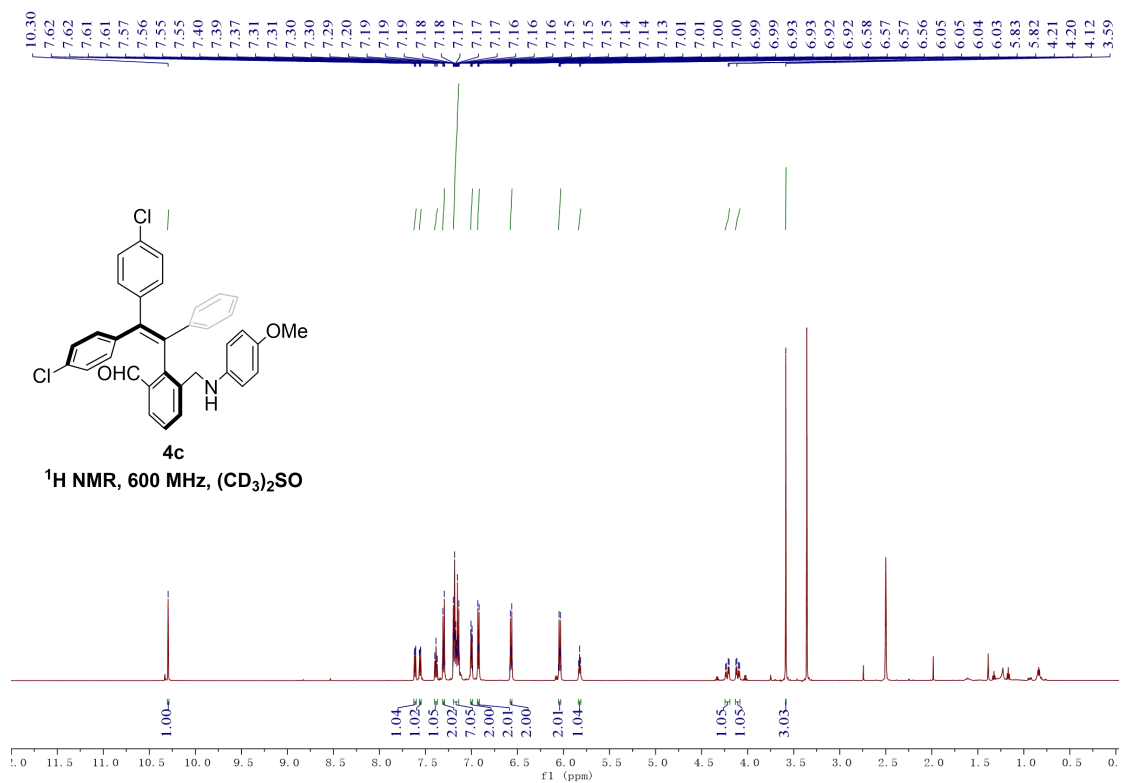
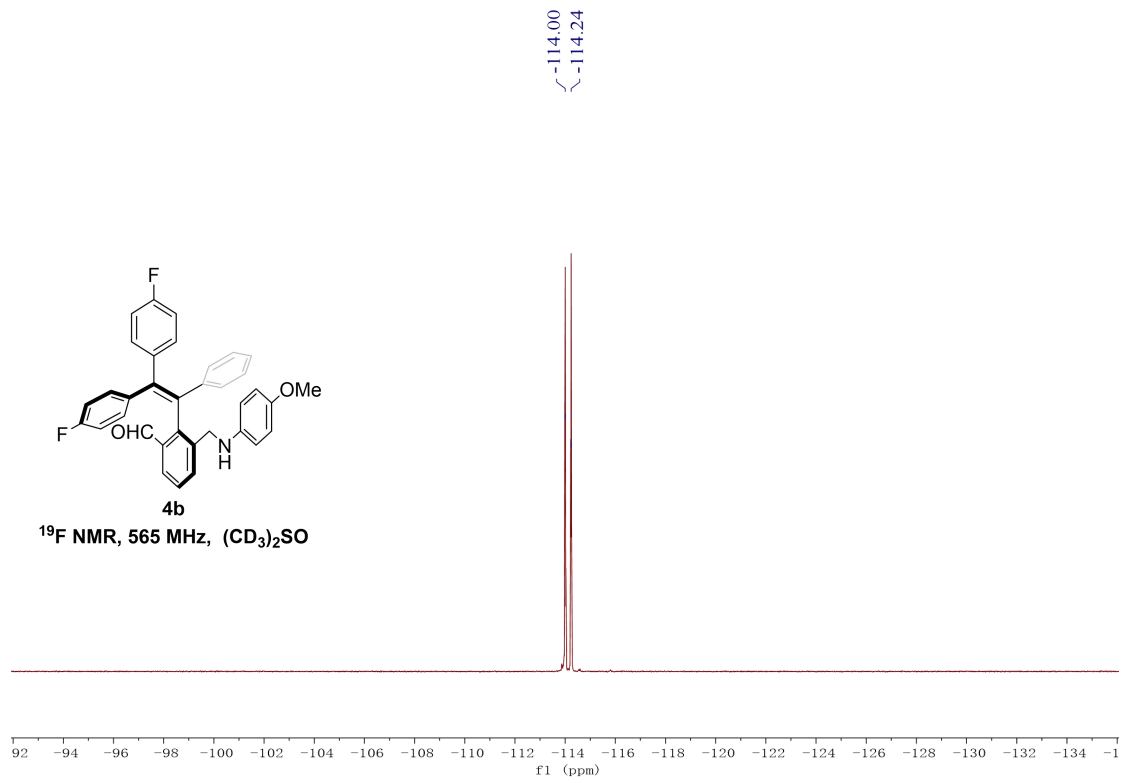


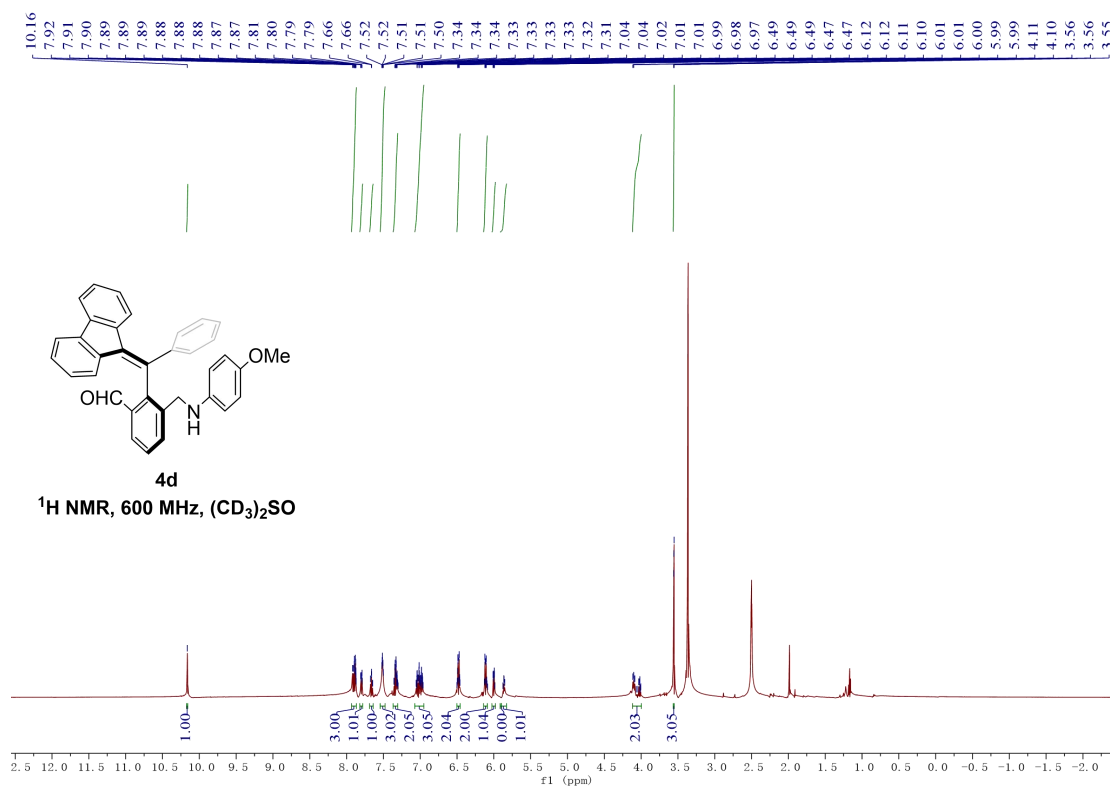
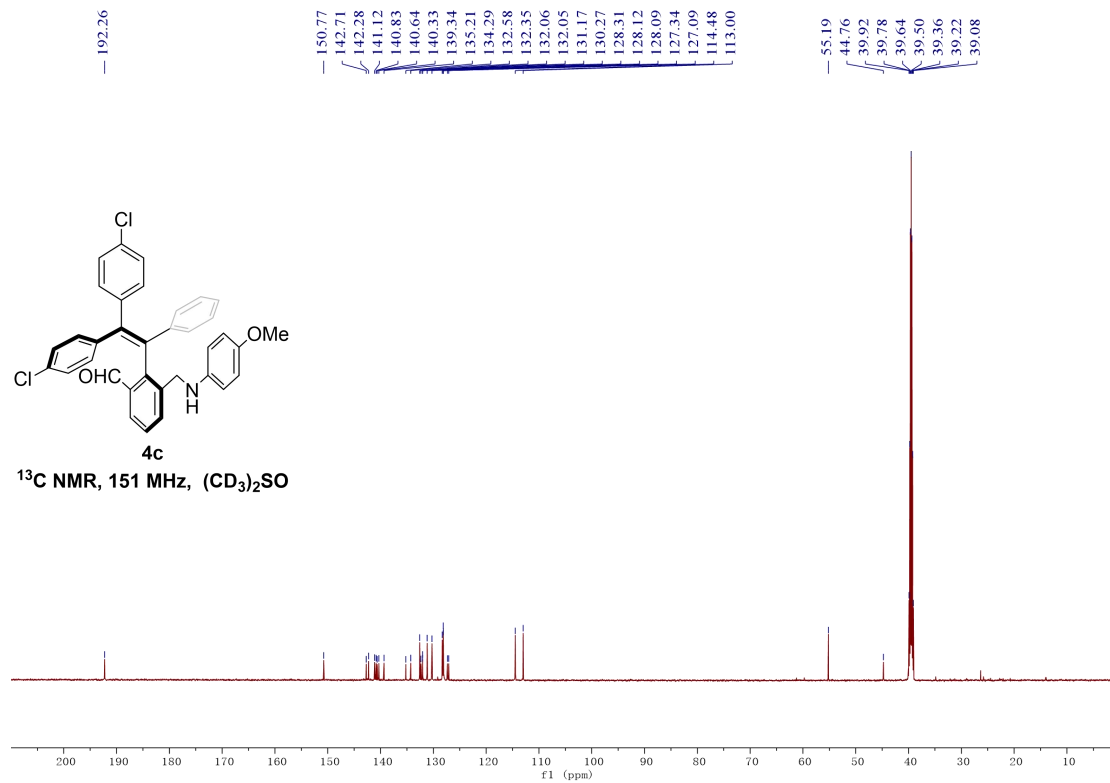


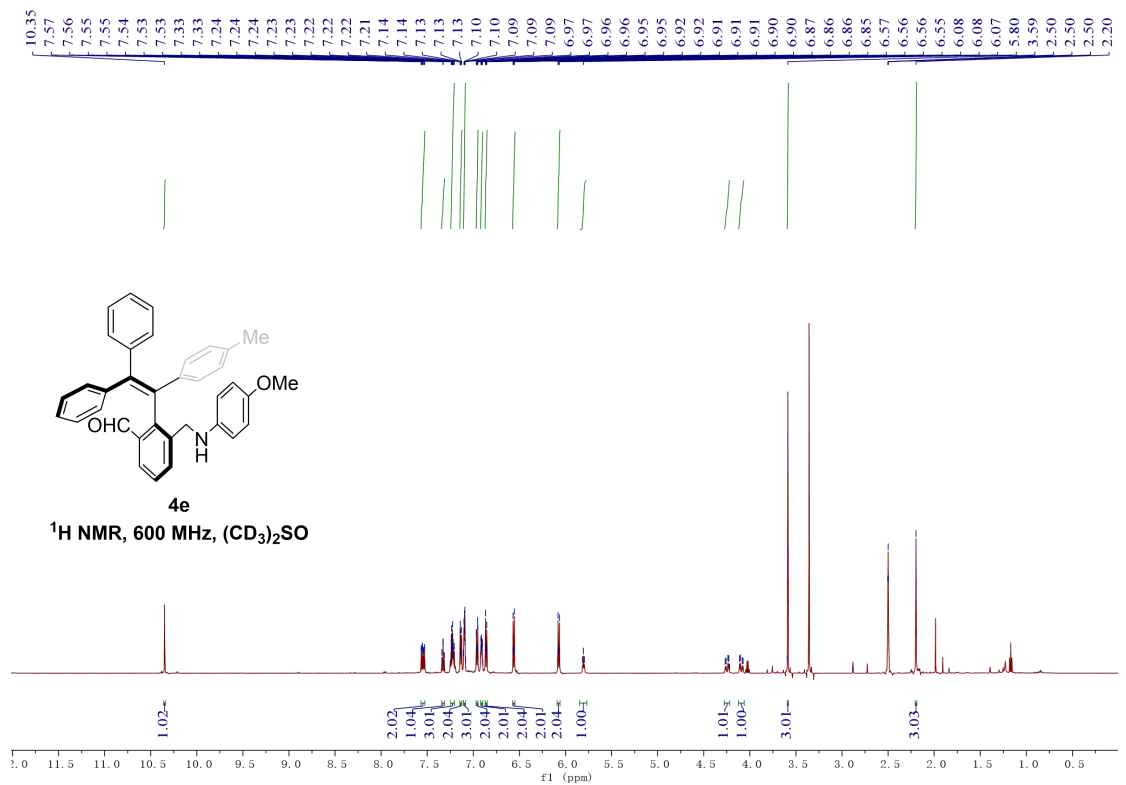
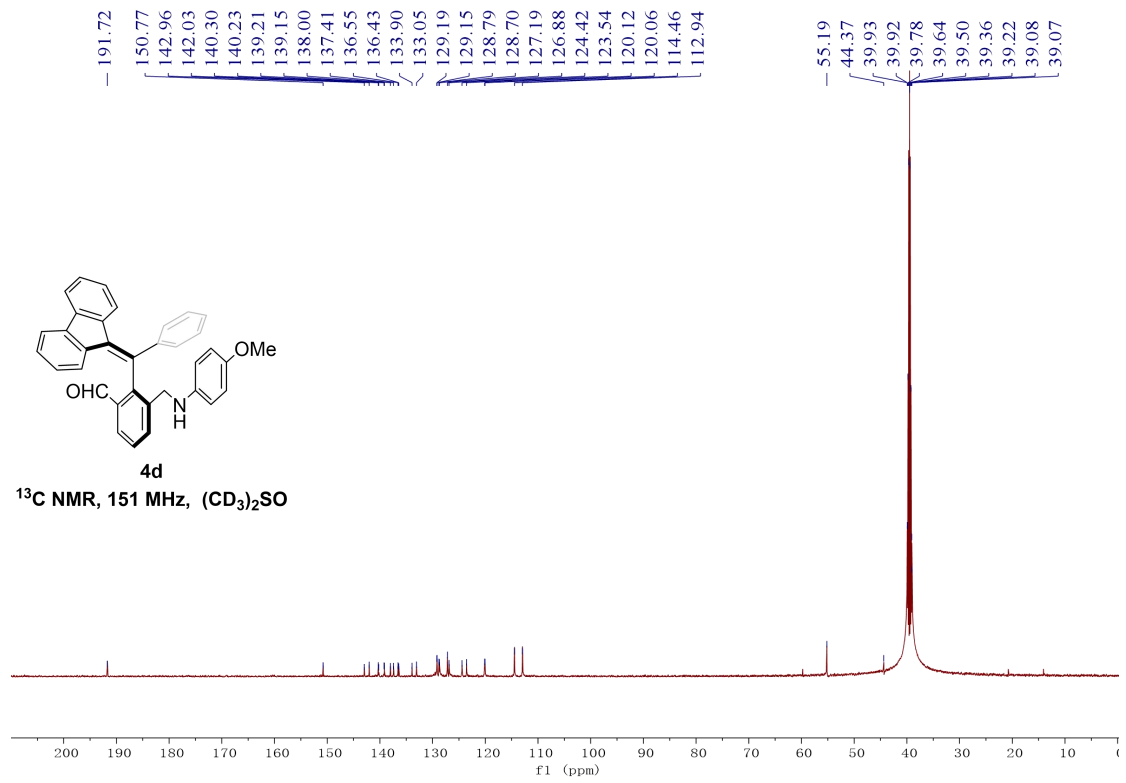


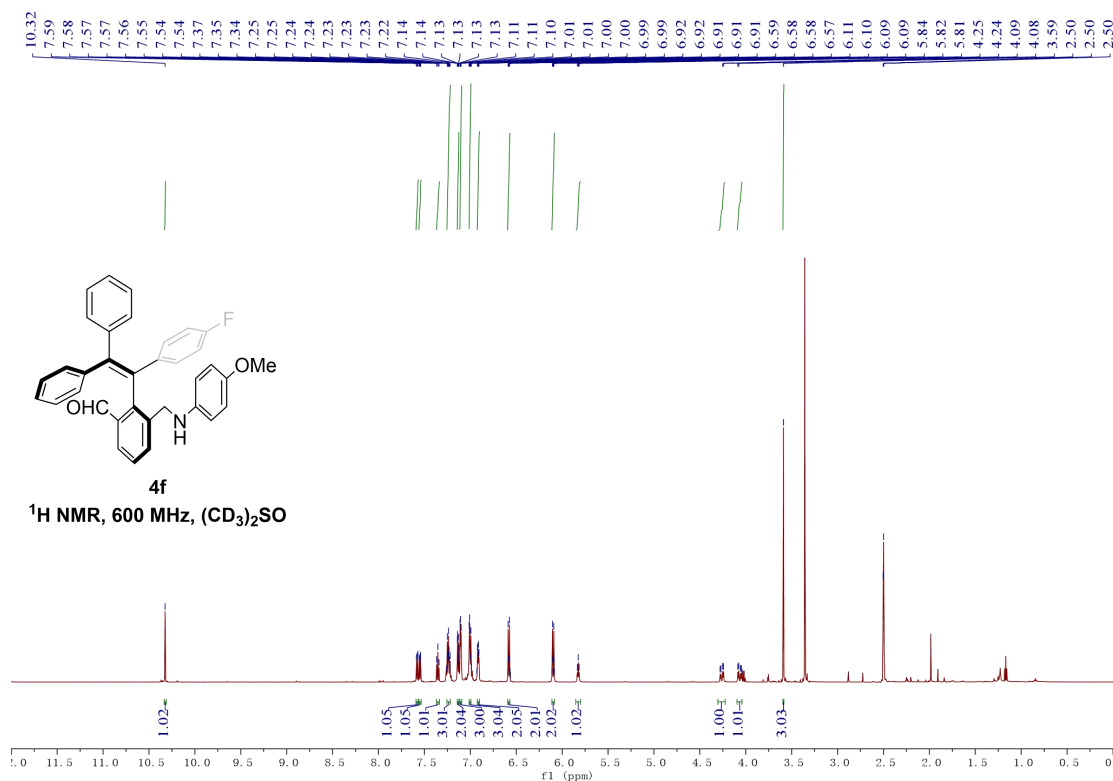
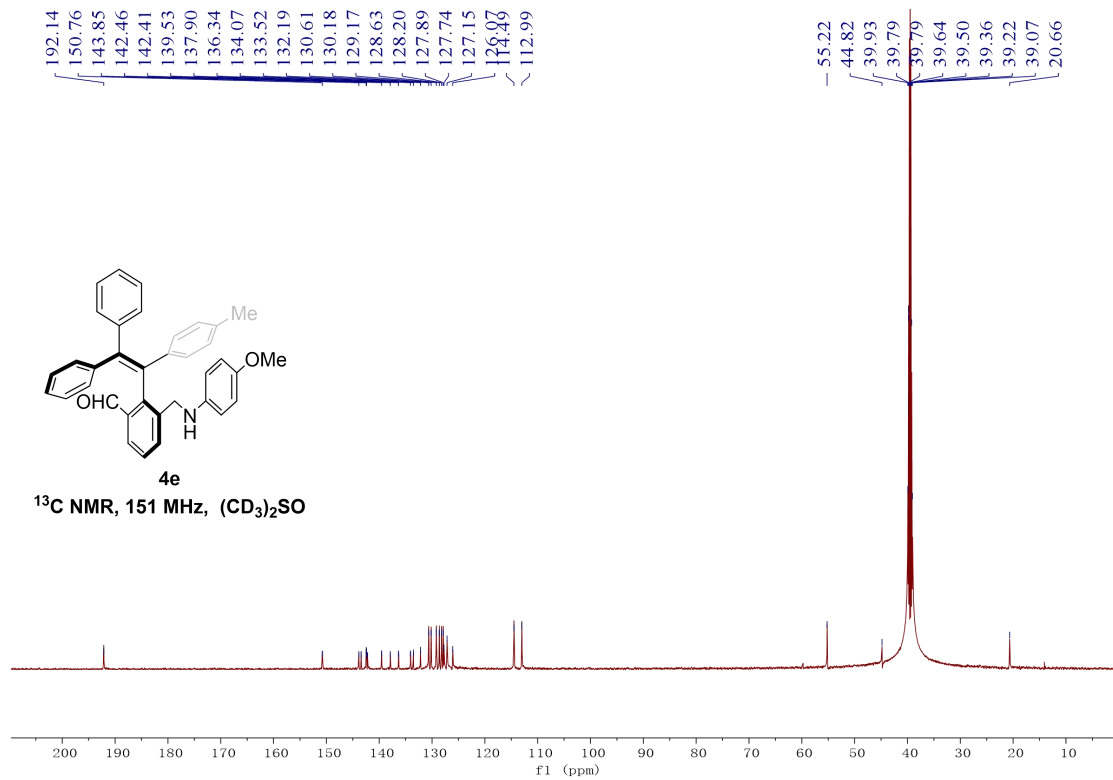


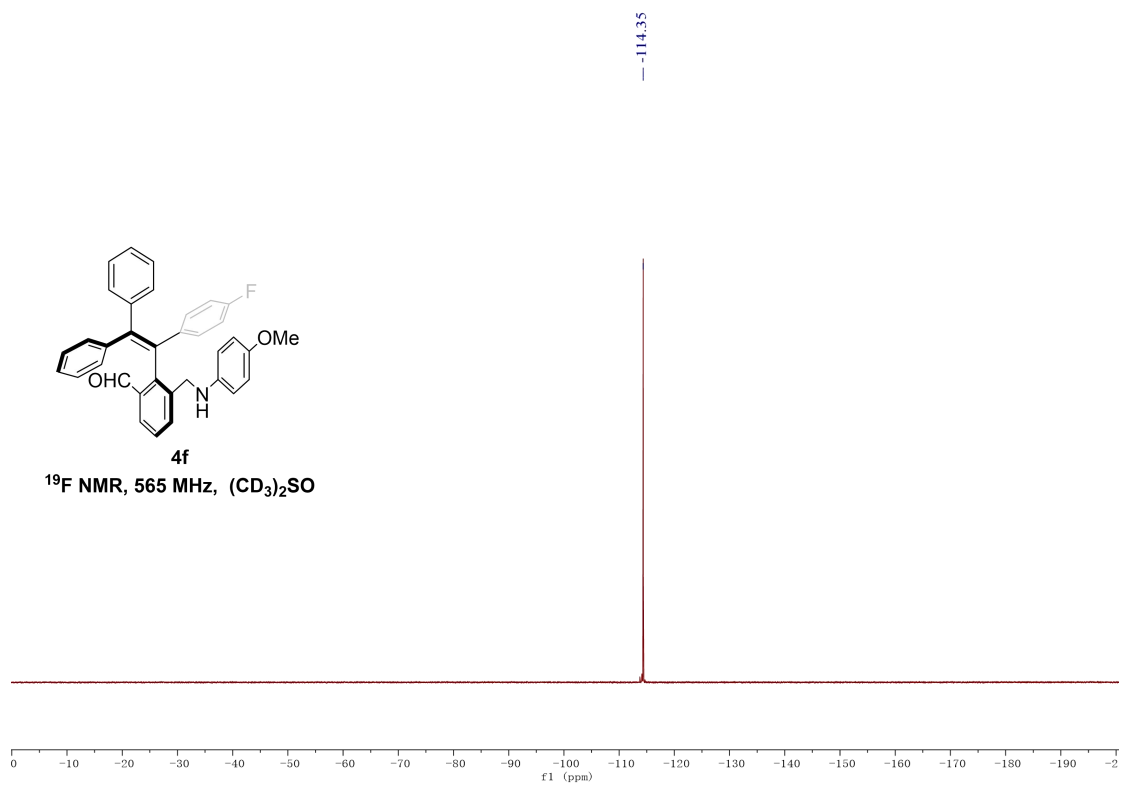
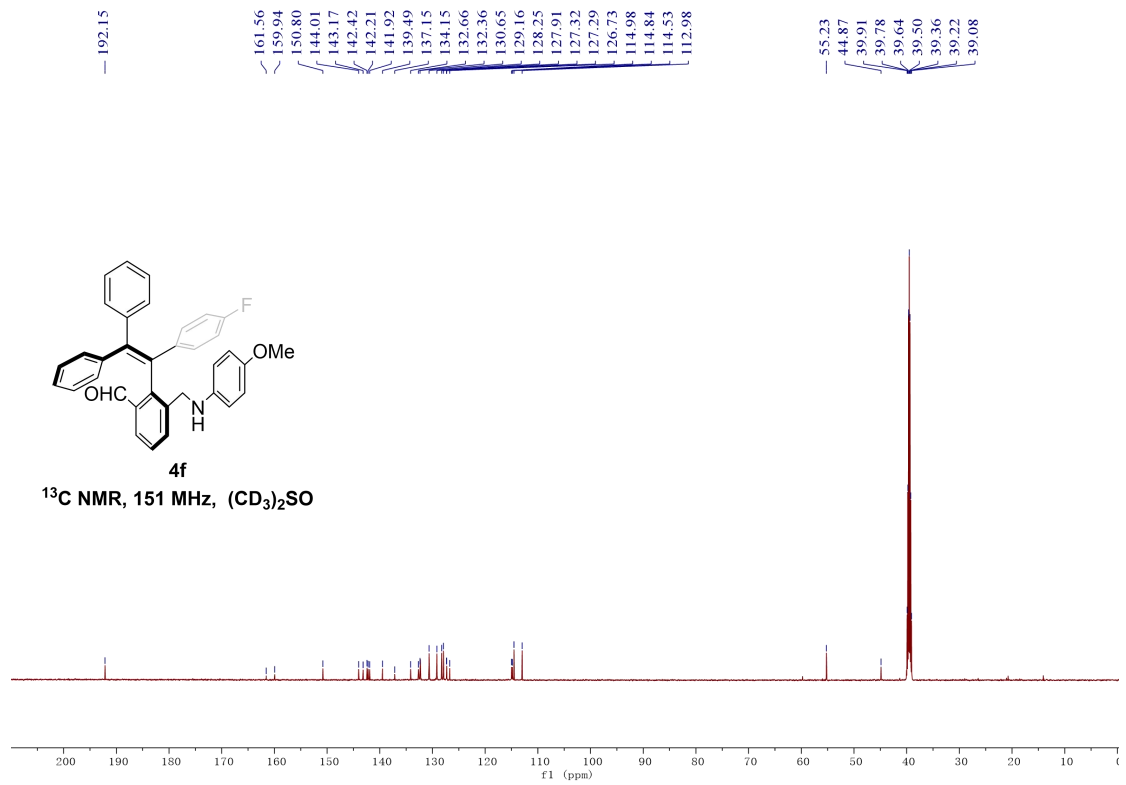


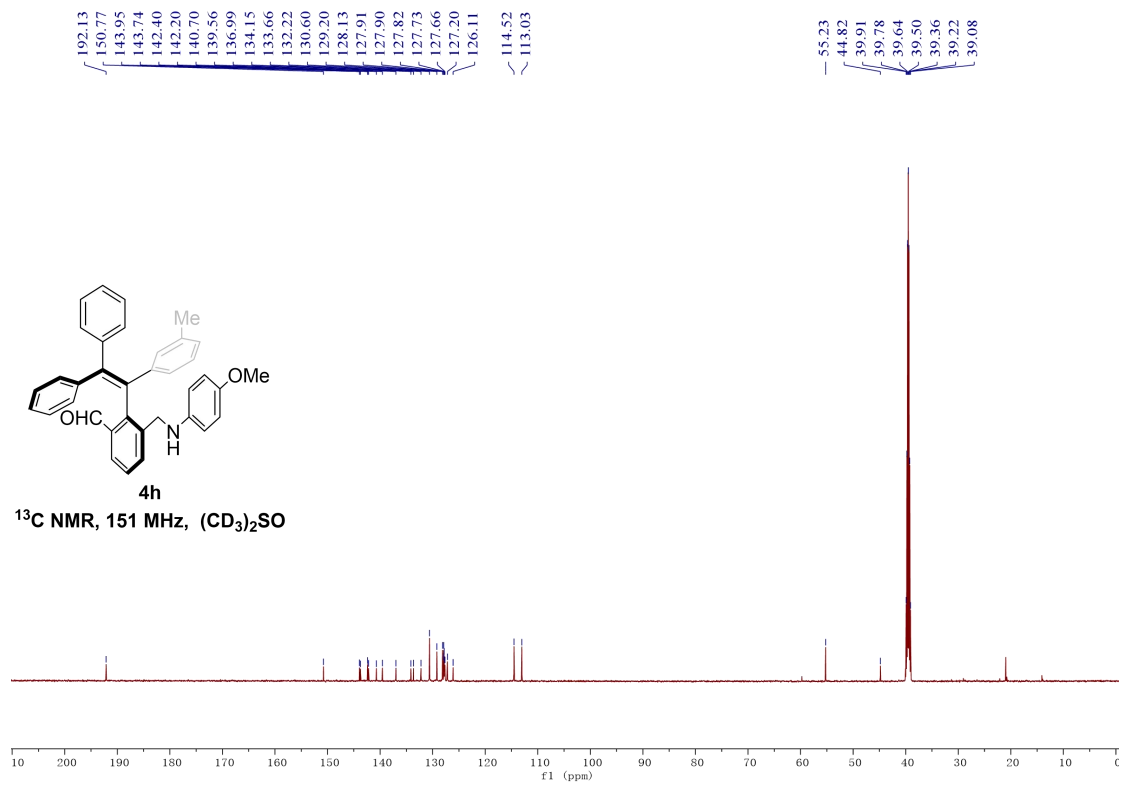
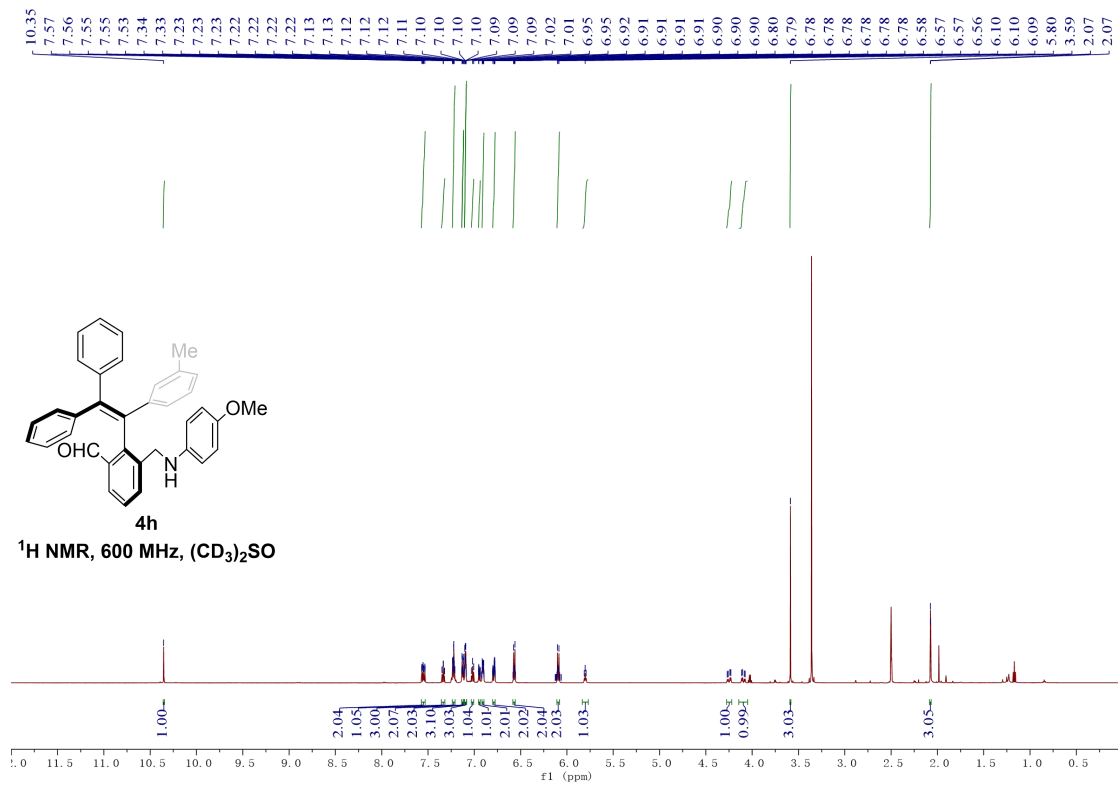


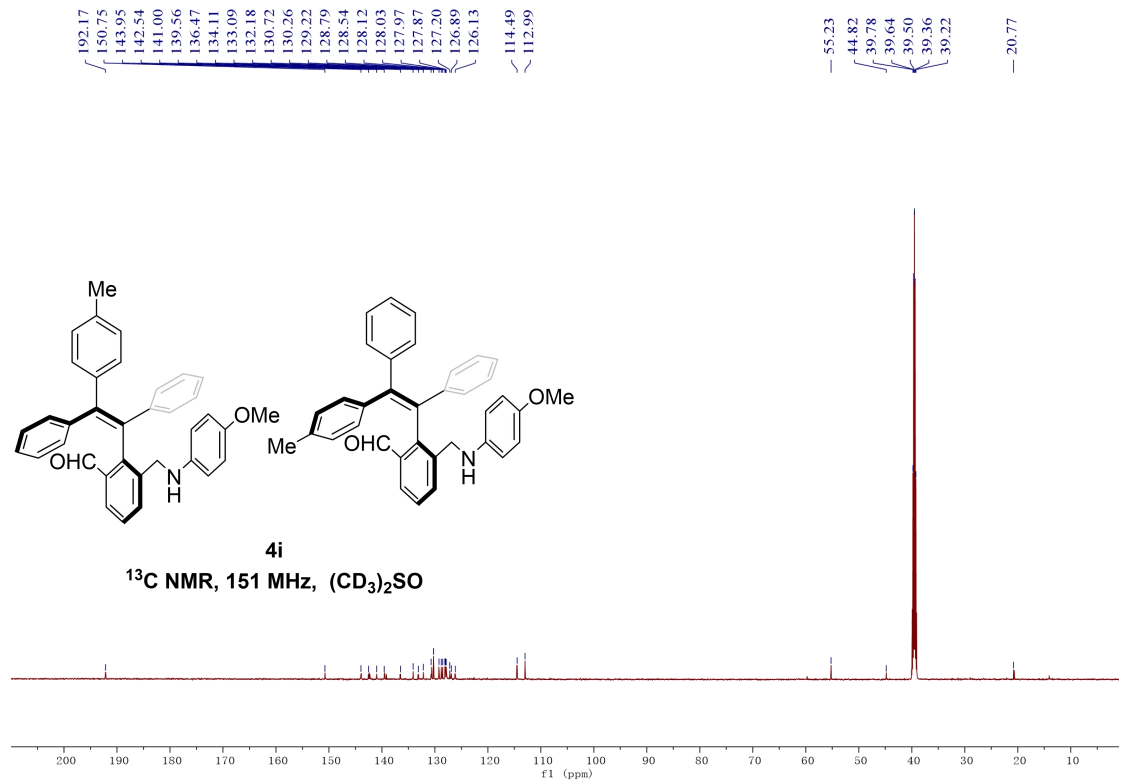
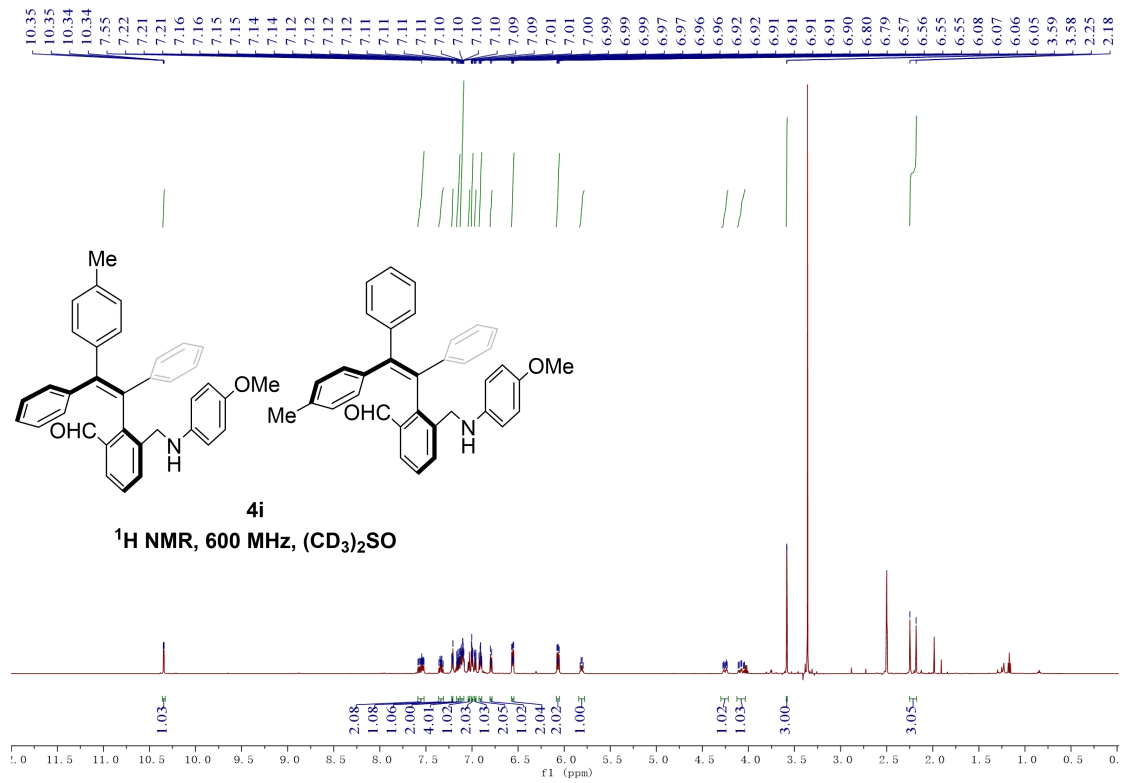


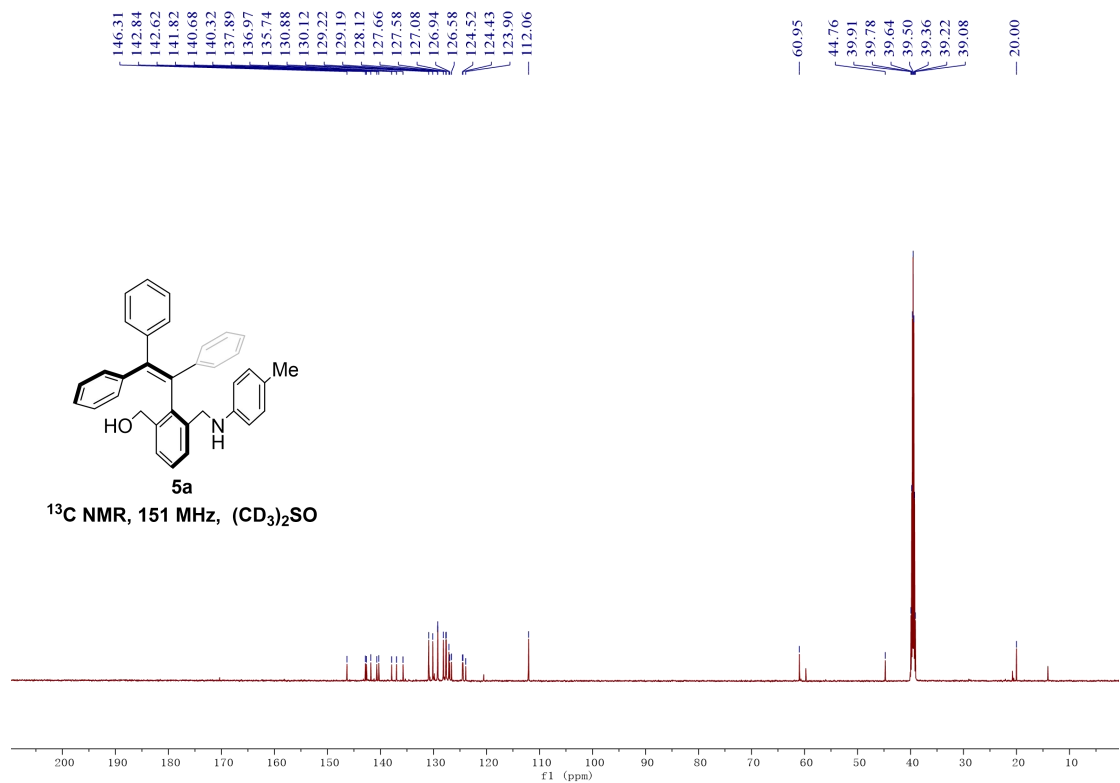
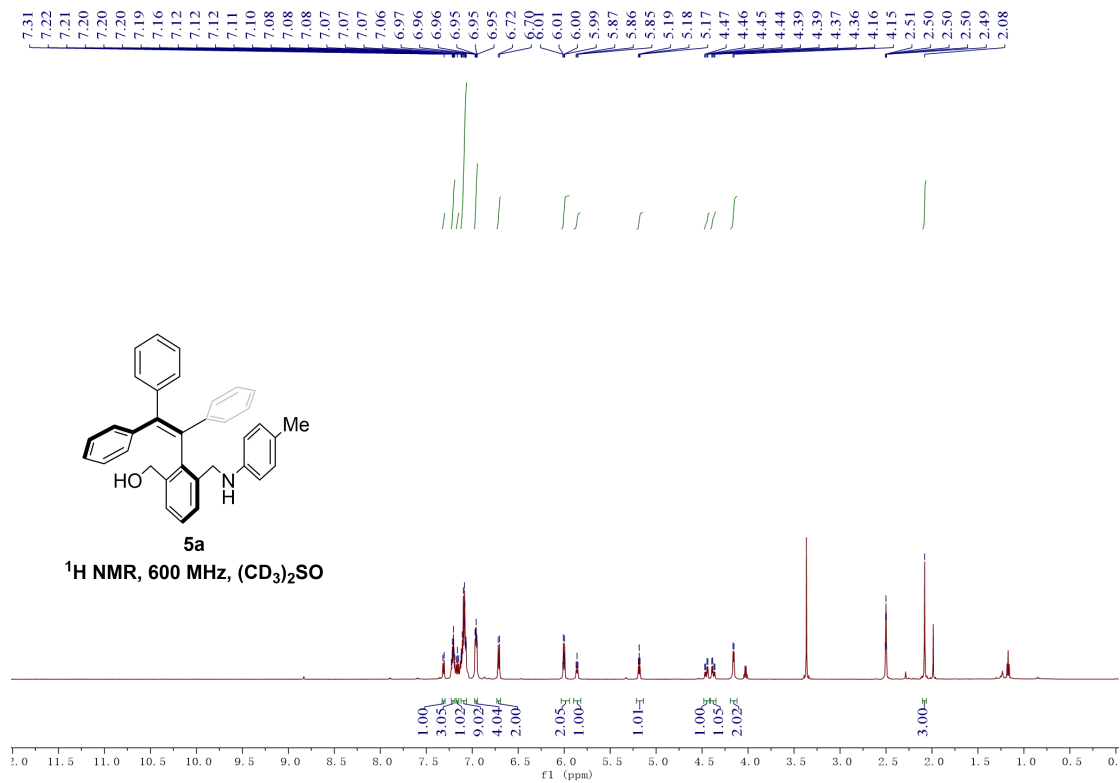


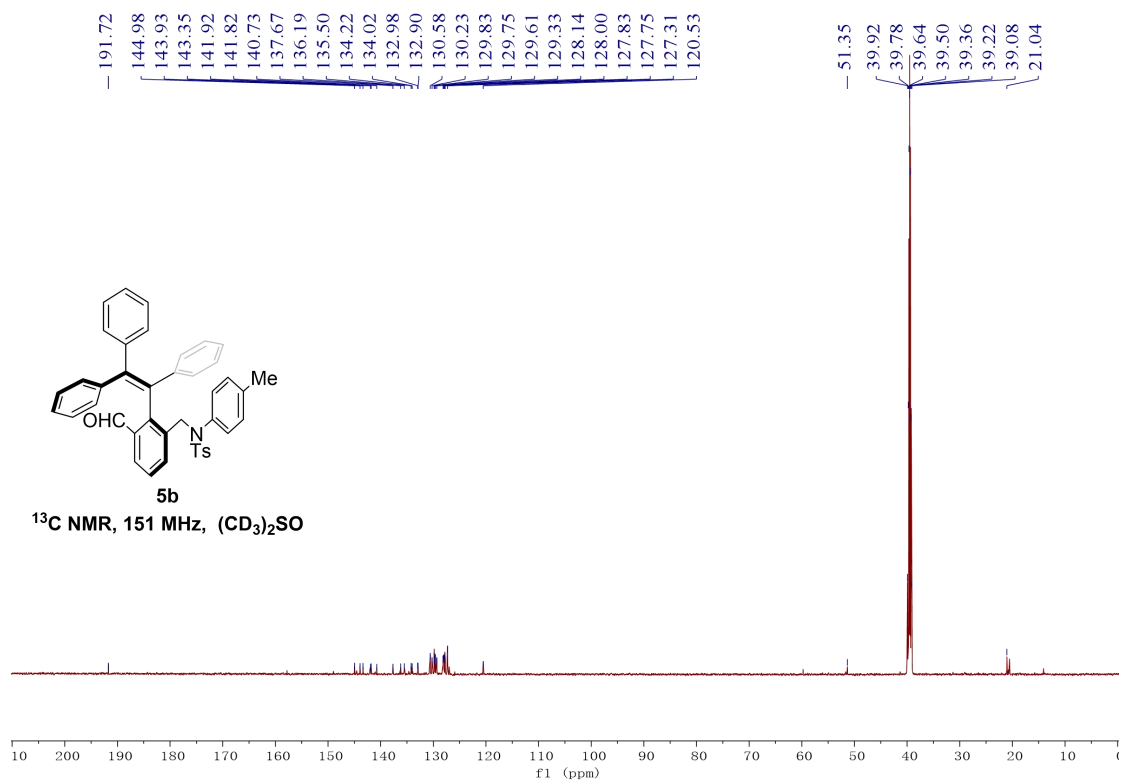
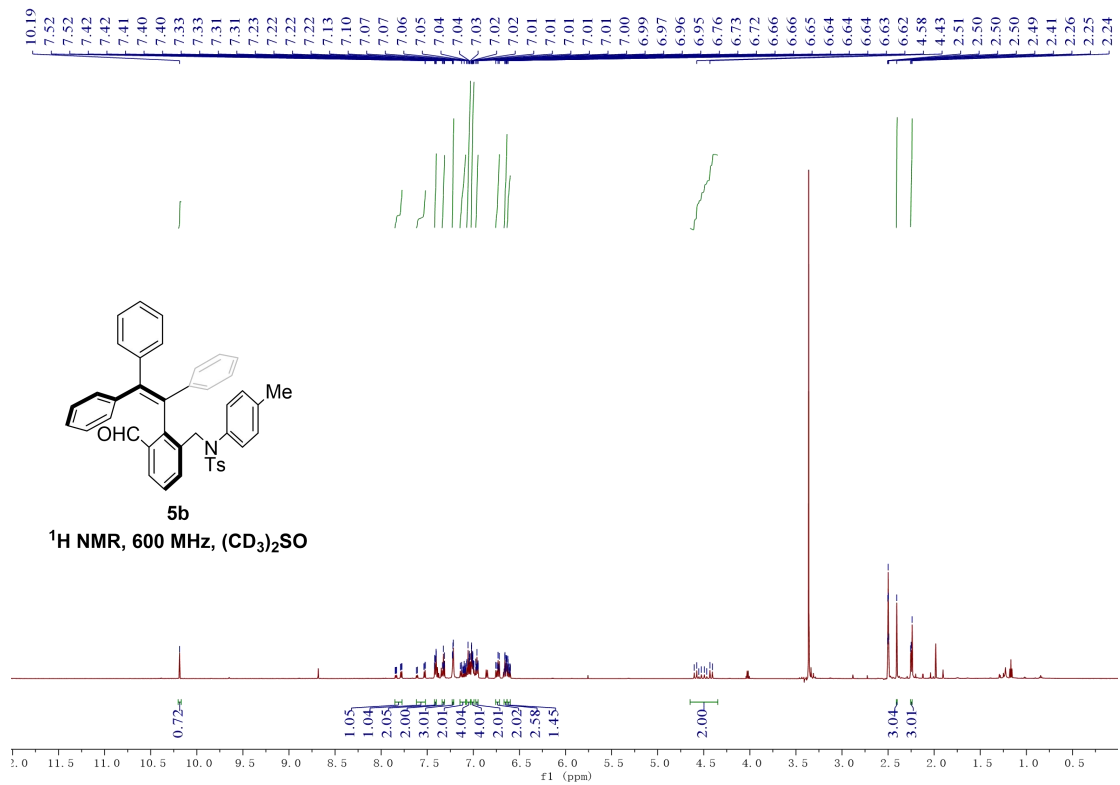


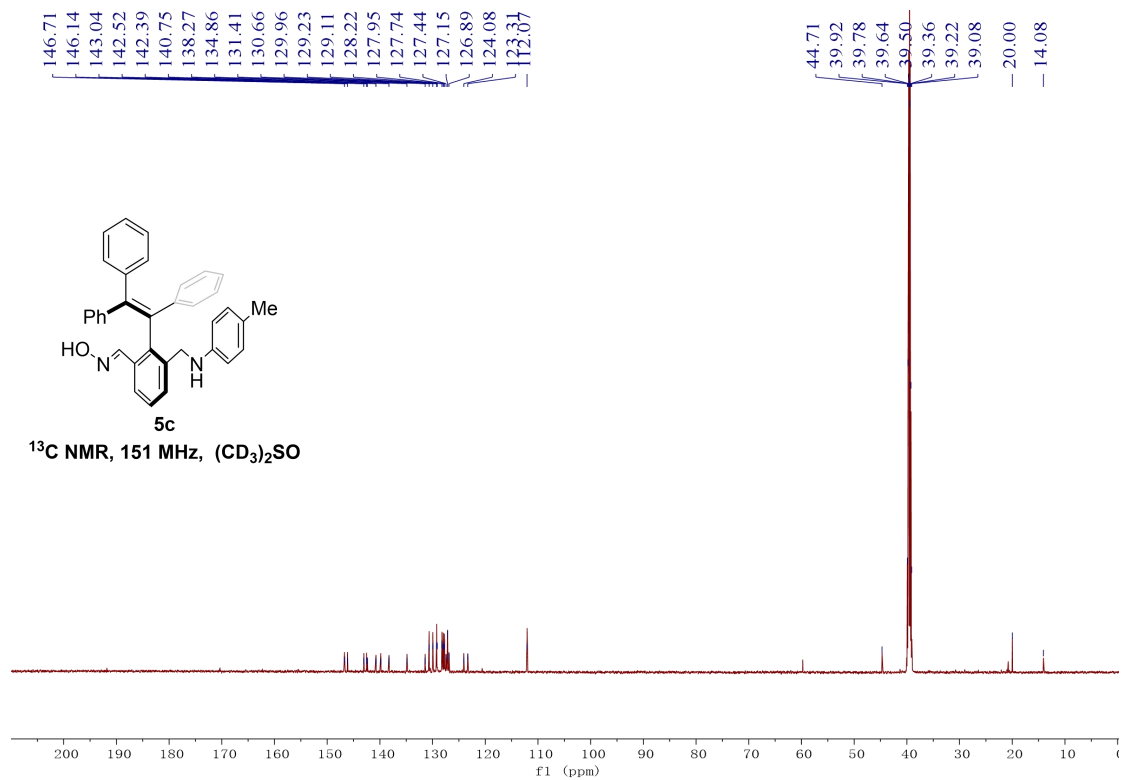
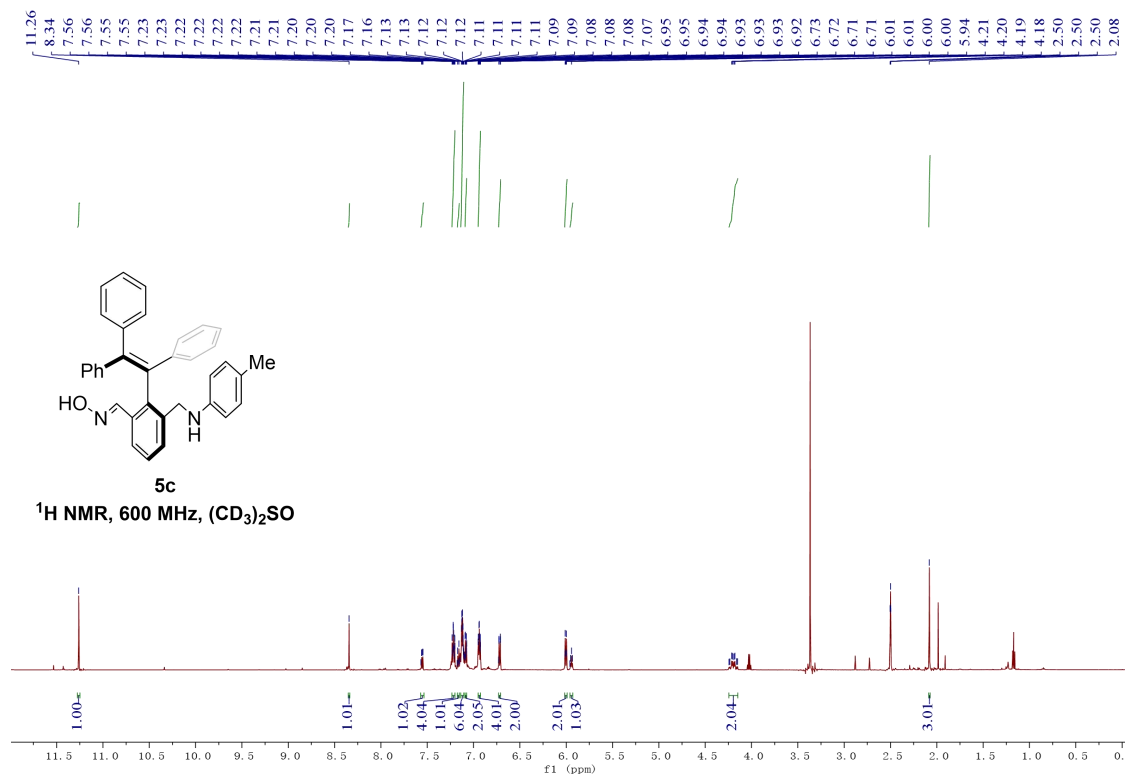


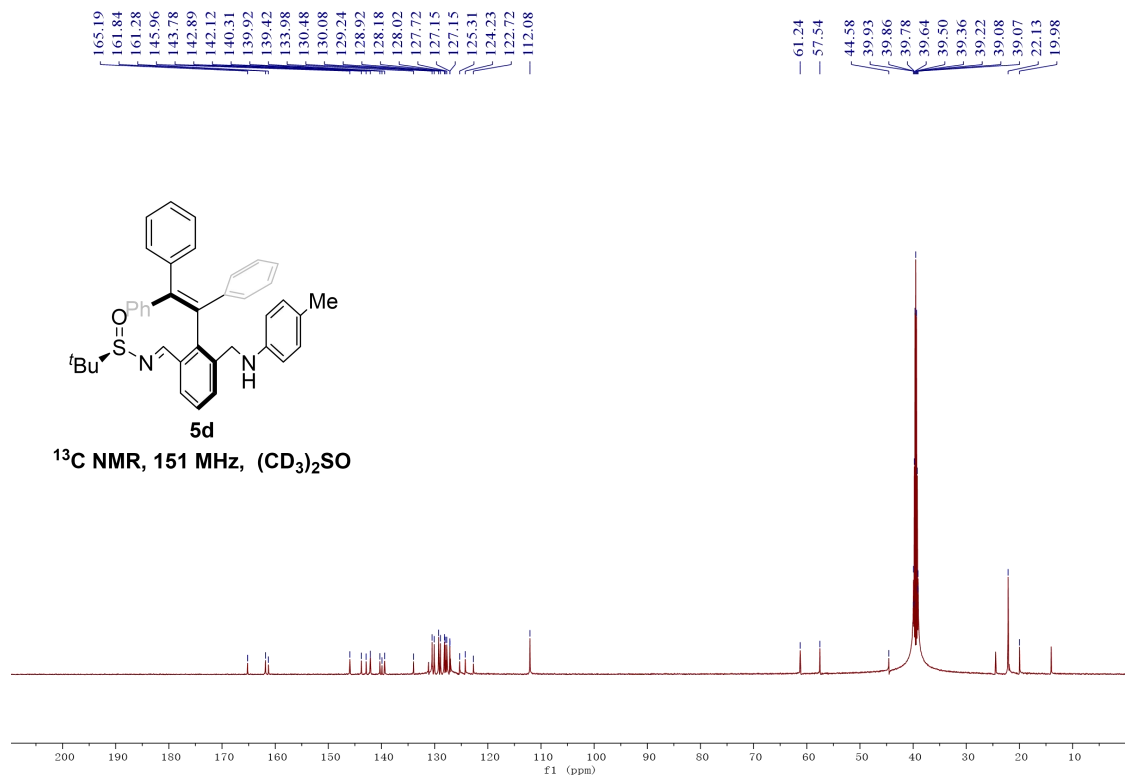
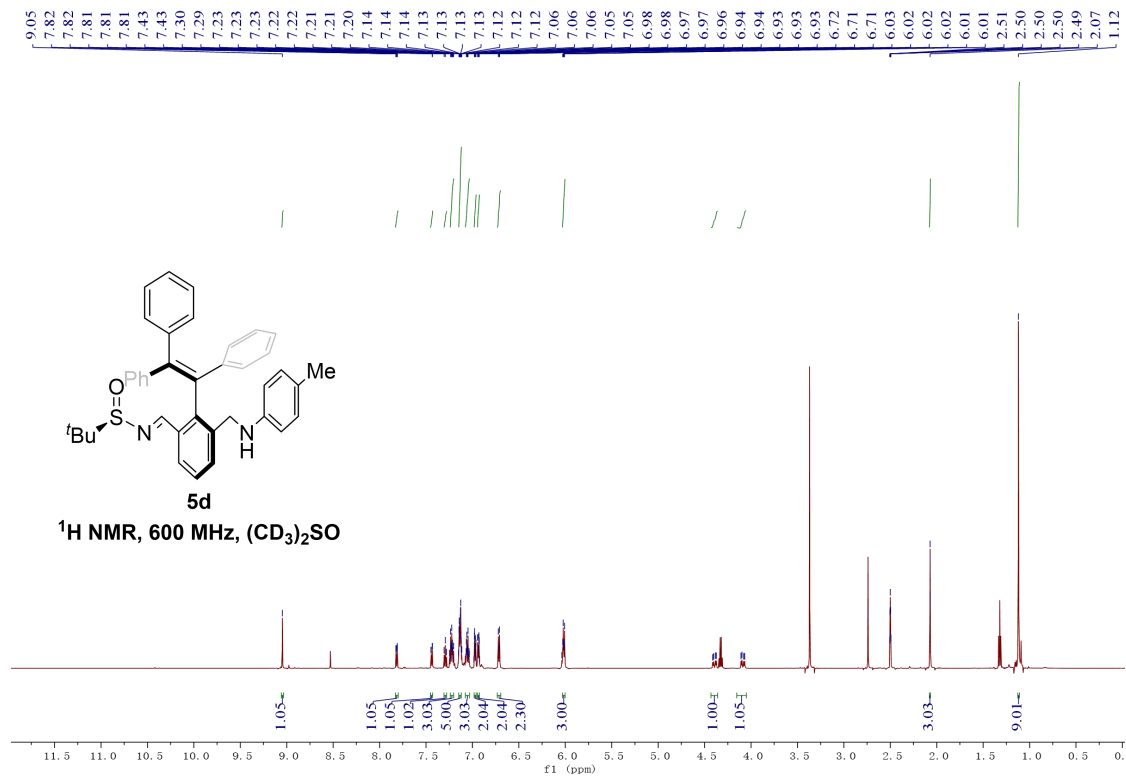


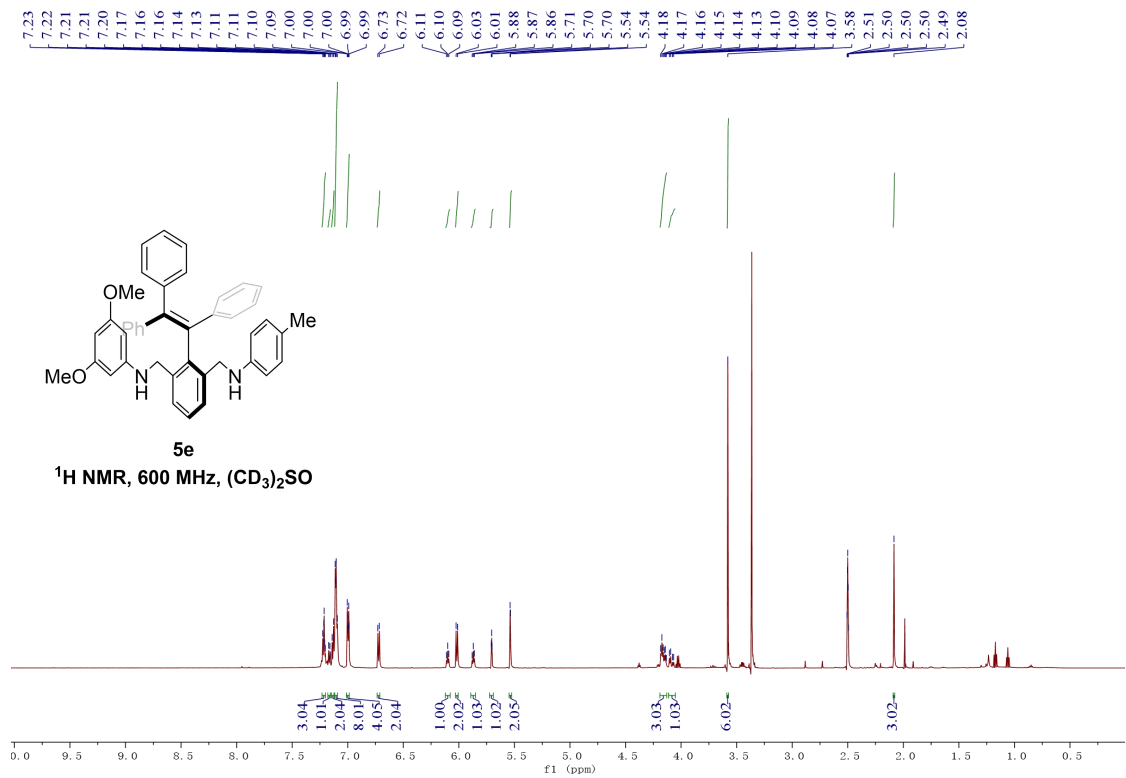


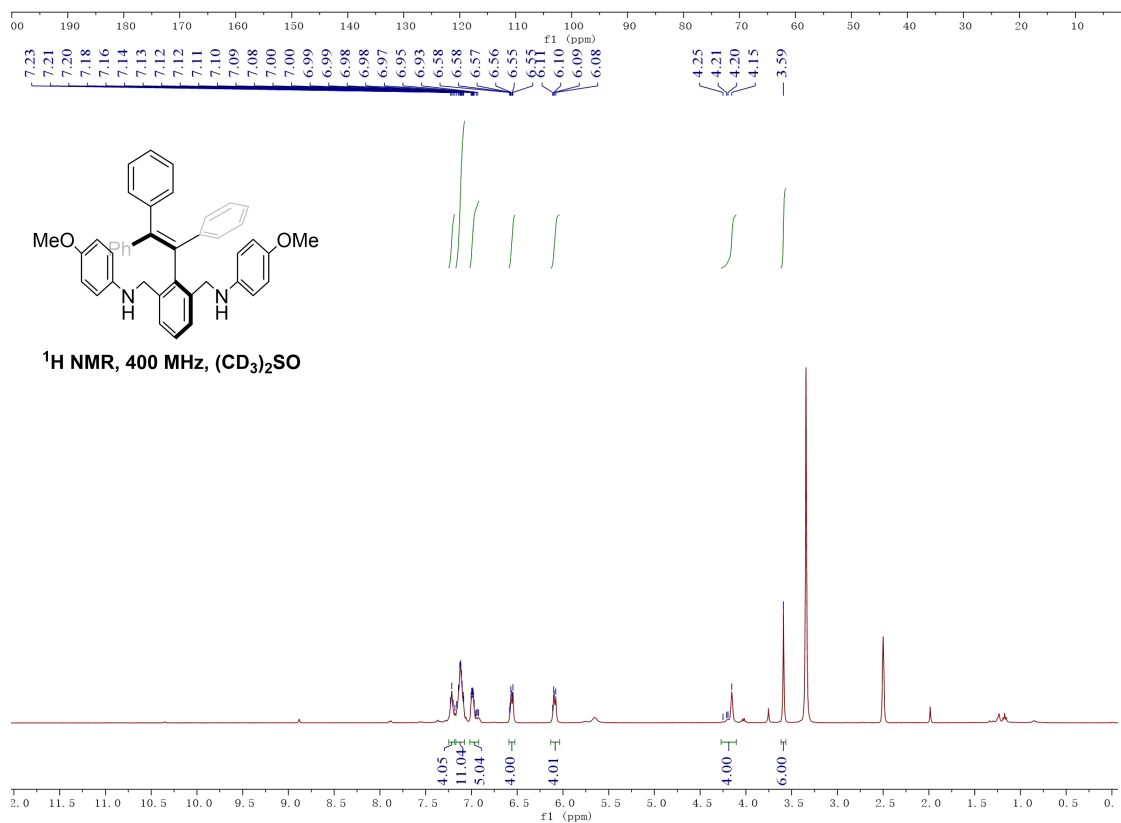
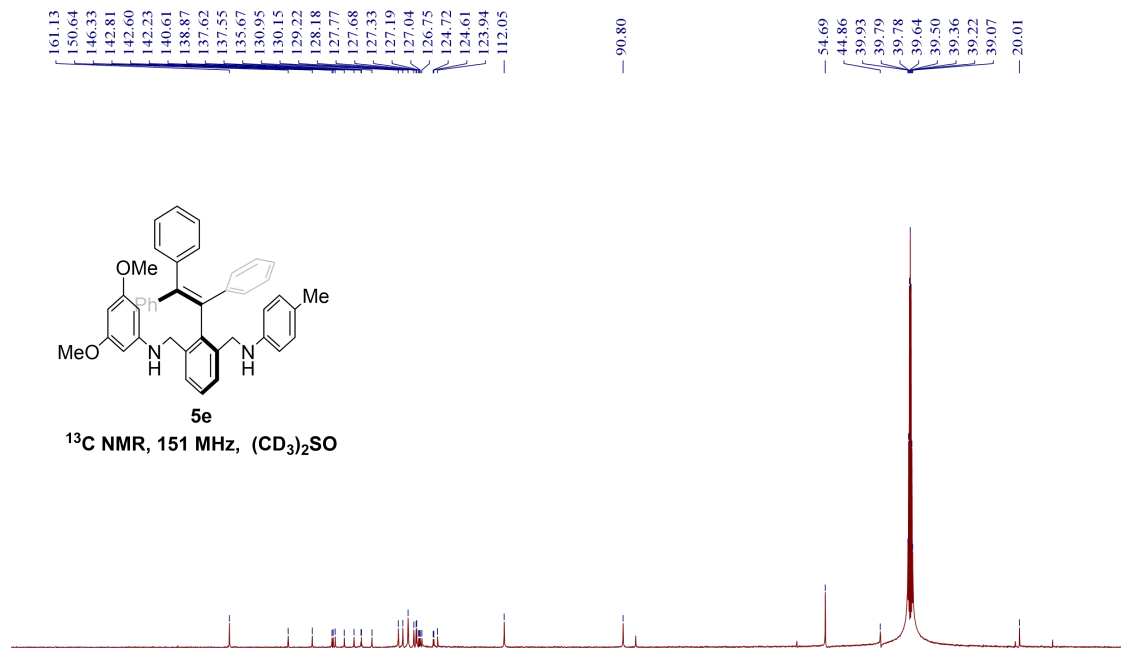






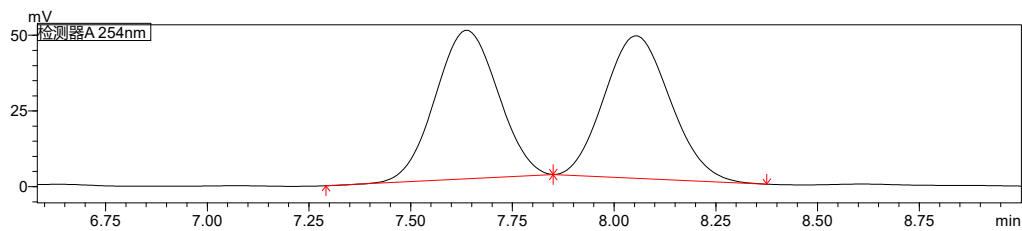
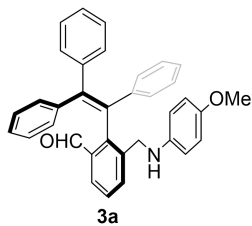




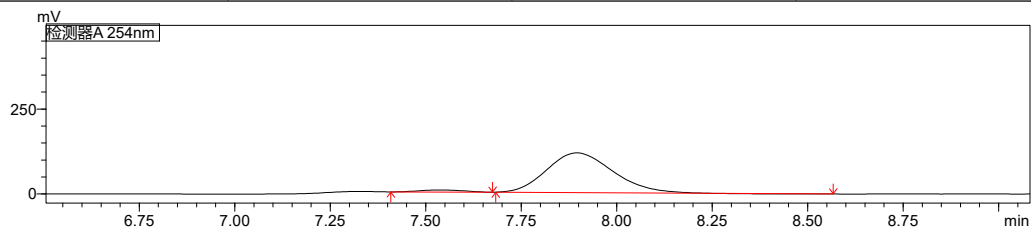


8. Copies of HPLC Spectras.

HPLC conditions: Chiralpak IA, 30% ⁱPrOH/Hx eluent, 0.8 mL/min, 254 nm

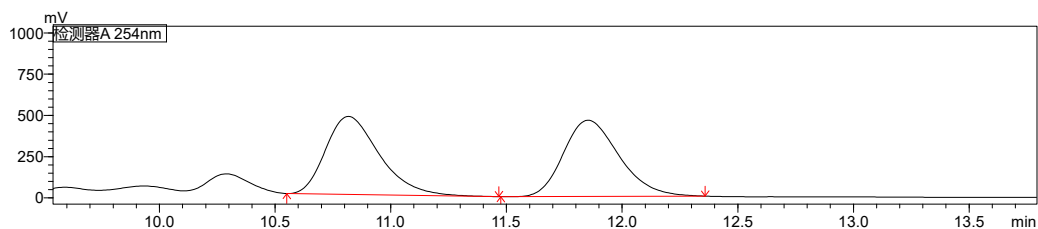
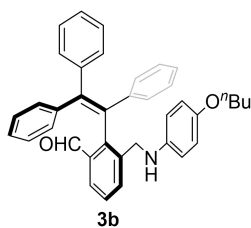


Peak#	Ret. Time	Height	Area%
1	7.637	49004	49.774
2	8.053	47049	50.226

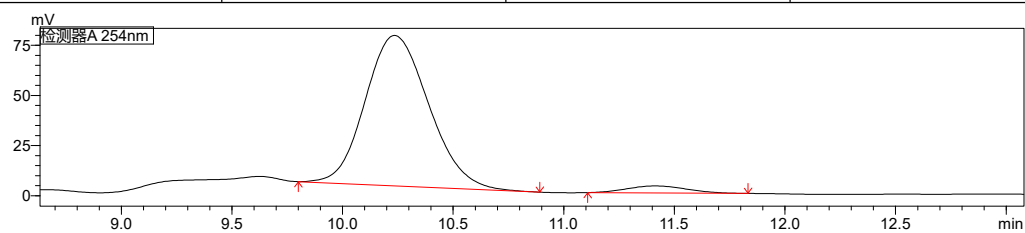


Peak#	Ret. Time	Height	Area%
1	7.539	6166	3.370
2	7.896	116886	96.630

HPLC conditions: Chiralpak OD-H, 20% ⁱPrOH/Hx eluent, 0.5 mL/min, 254 nm

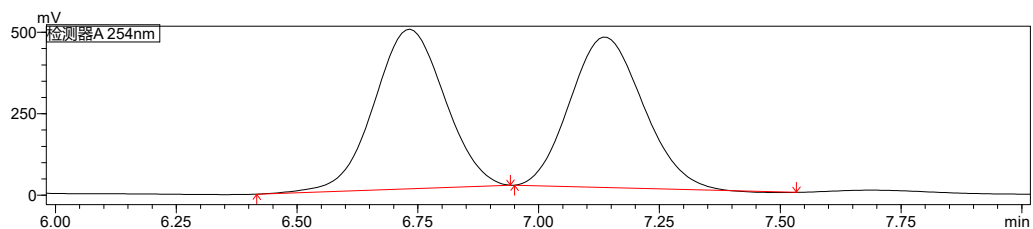
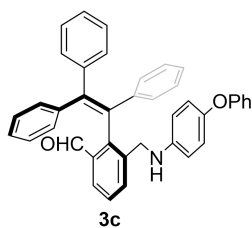


Peak#	Ret. Time	Height	Area%
1	10.817	473502	49.689
2	11.853	462368	50.311

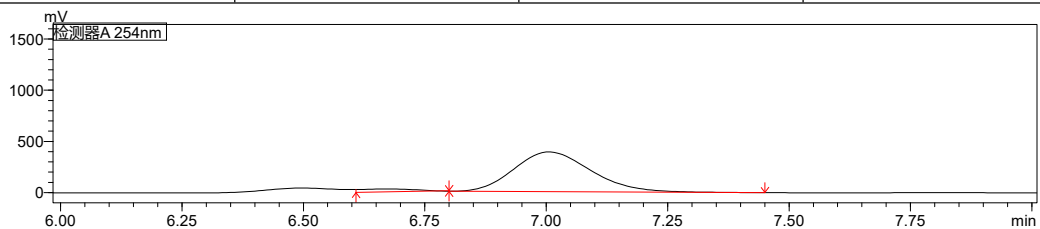


Peak#	Ret. Time	Height	Area%
1	10.235	75075	95.828
2	11.412	3500	4.172

HPLC conditions: Chiralpak IA, 30% *i*PrOH/Hx eluent, 0.8 mL/min, 254 nm

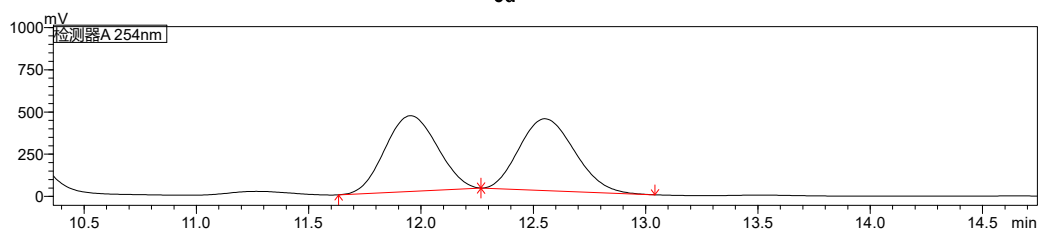
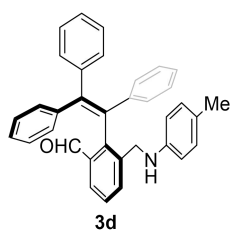


Peak#	Ret. Time	Height	Area%
1	6.732	489813	50.668
2	7.136	461398	49.332

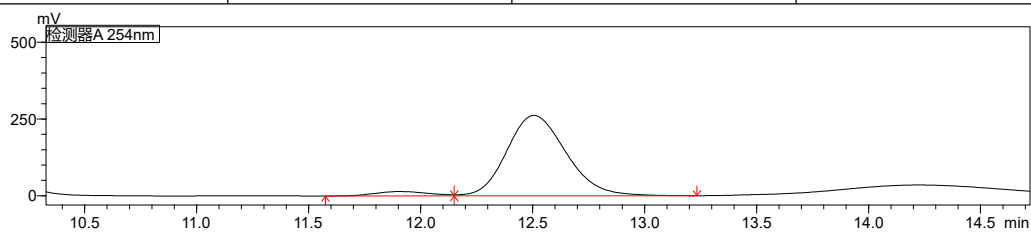


Peak#	Ret. Time	Height	Area%
1	6.674	28146	4.549
2	7.006	387927	95.451

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

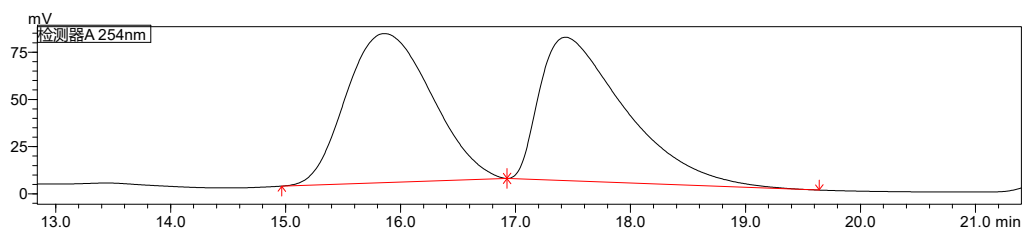
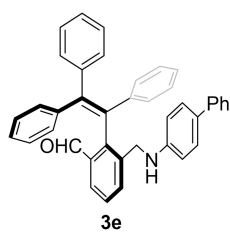


Peak#	Ret. Time	Height	Area%
1	11.953	448209	49.934
2	12.551	425045	50.066

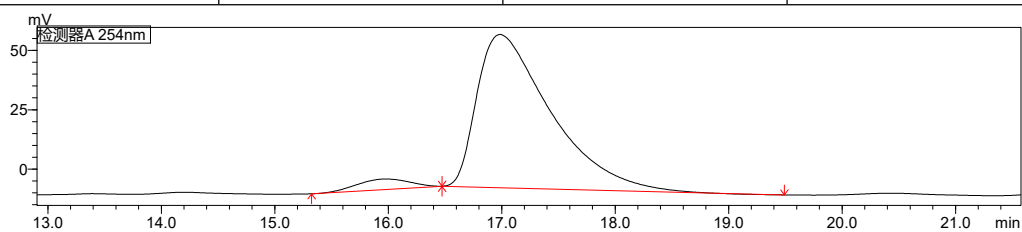


Peak#	Ret. Time	Height	Area%
1	11.908	14328	4.756
2	12.505	261912	95.244

HPLC conditions: Chiralpak OD-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

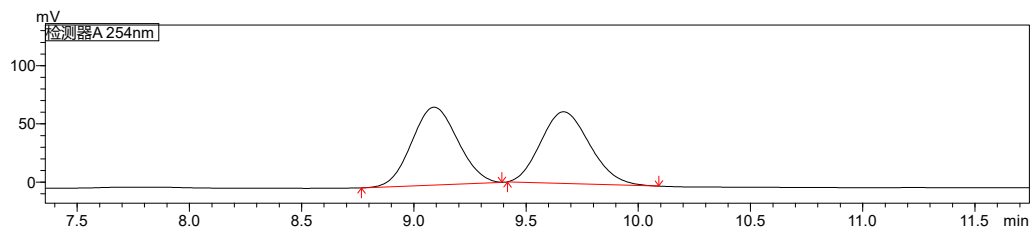
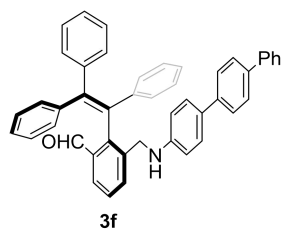


Peak#	Ret. Time	Height	Area%
1	15.861	78899	50.811
2	17.434	75926	49.189

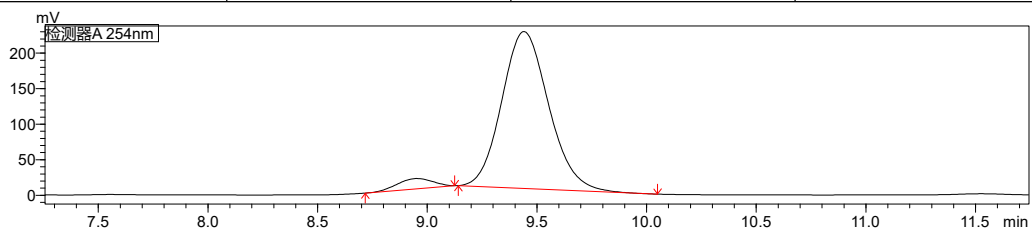


Peak#	Ret. Time	Height	Area%
1	15.982	4399	4.704
2	16.985	64558	95.296

HPLC conditions: Chiralpak IA, 30% *i*PrOH/Hx eluent, 0.8 mL/min, 254 nm

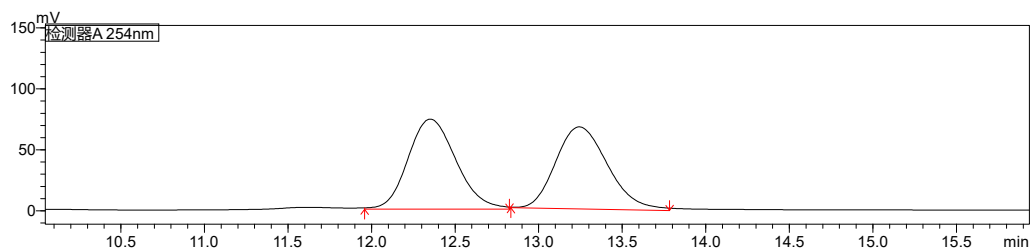
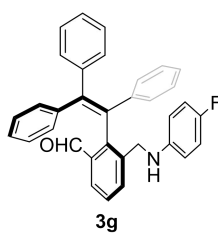


Peak#	Ret. Time	Height	Area%
1	9.090	66833	50.499
2	9.667	61550	49.501

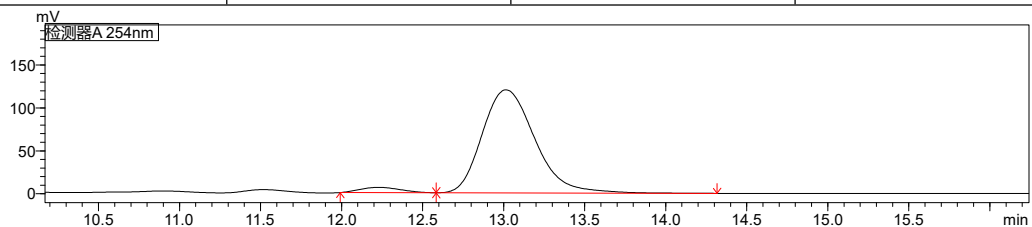


Peak#	Ret. Time	Height	Area%
1	8.952	14595	4.884
2	9.440	220973	95.116

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

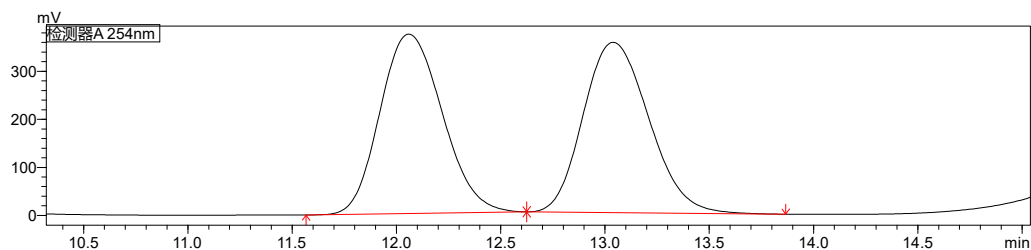
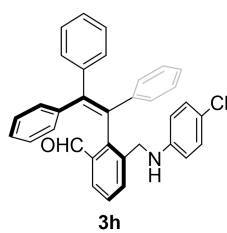


Peak#	Ret. Time	Height	Area%
1	12.351	72296	49.825
2	13.242	66400	50.175

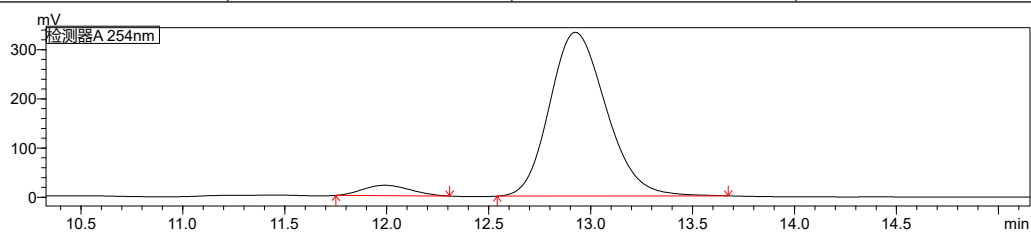


Peak#	Ret. Time	Height	Area%
1	12.227	6074	3.722
2	13.014	120030	96.278

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

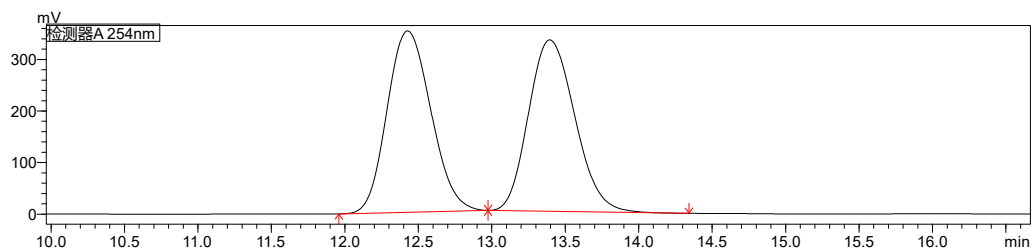
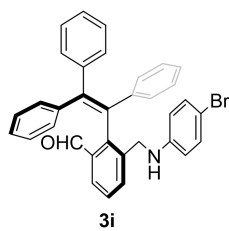


Peak#	Ret. Time	Height	Area%
1	12.059	373552	49.946
2	13.038	354652	50.054

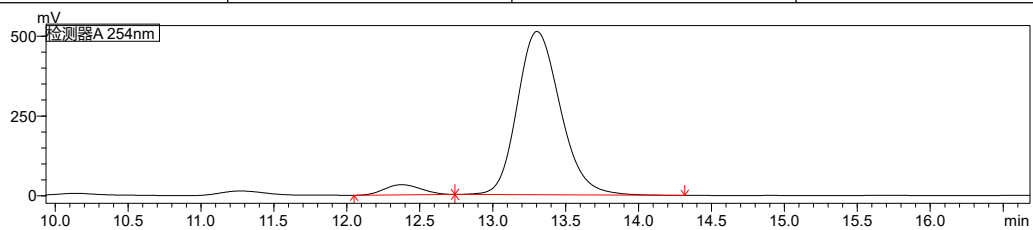


Peak#	Ret. Time	Height	Area%
1	11.988	21163	5.088
2	12.925	333062	94.912

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

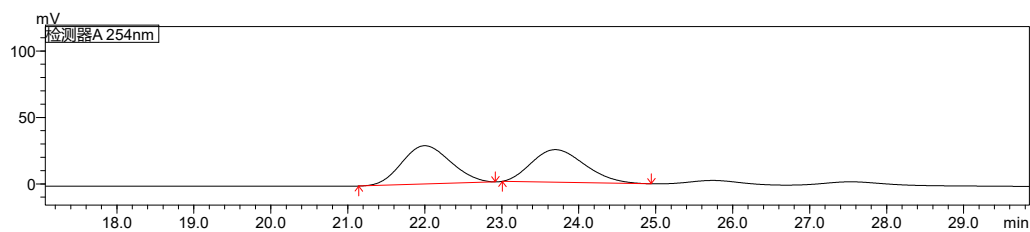
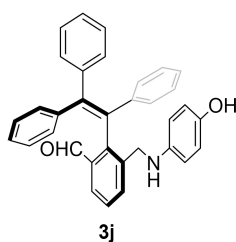


Peak#	Ret. Time	Height	Area%
1	12.426	352135	49.979
2	13.394	332663	50.021

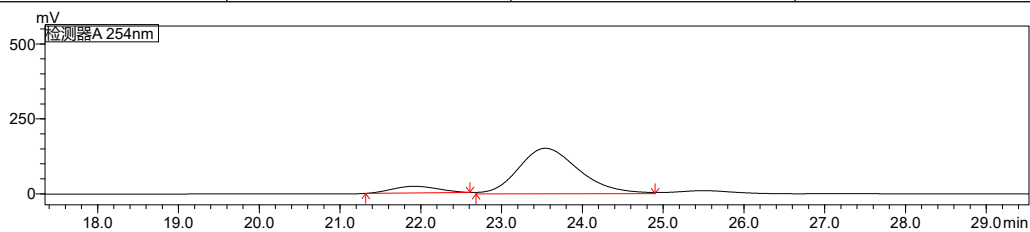


Peak#	Ret. Time	Height	Area%
1	12.376	31968	5.064
2	13.303	511511	94.936

HPLC conditions: Chiralpak OX-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

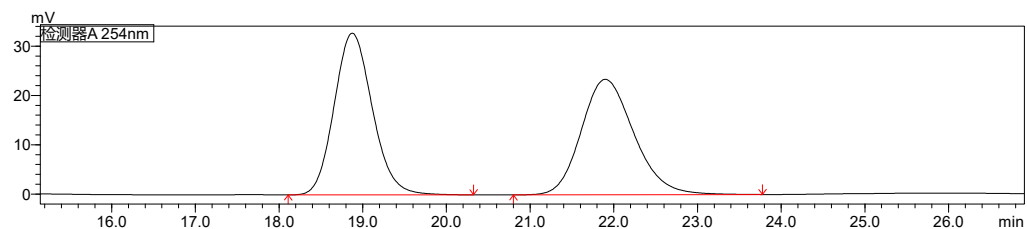
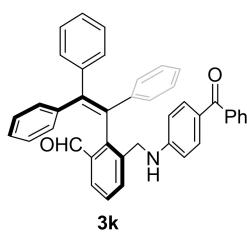


Peak#	Ret. Time	Height	Area%
1	22.000	28845	51.936
2	23.695	24483	48.064

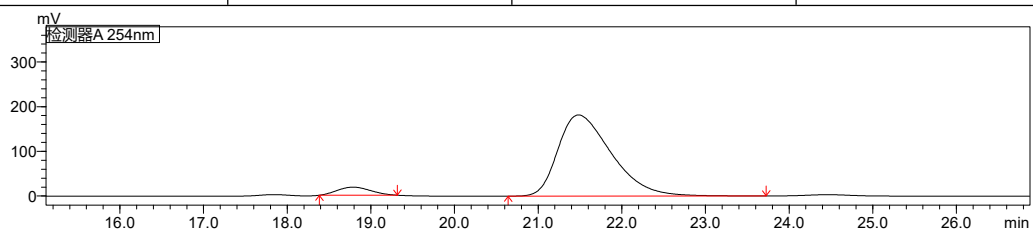


Peak#	Ret. Time	Height	Area%
1	21.920	22193	9.873
2	23.540	151910	90.127

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

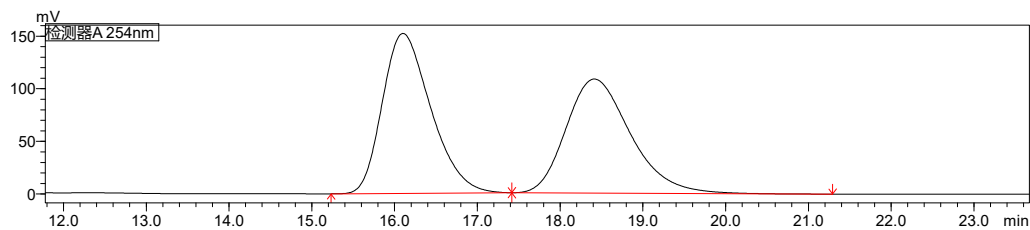
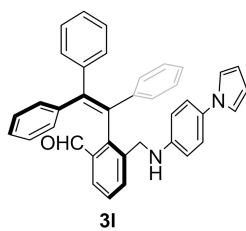


Peak#	Ret. Time	Height	Area%
1	18.875	32787	50.340
2	21.896	23411	49.660

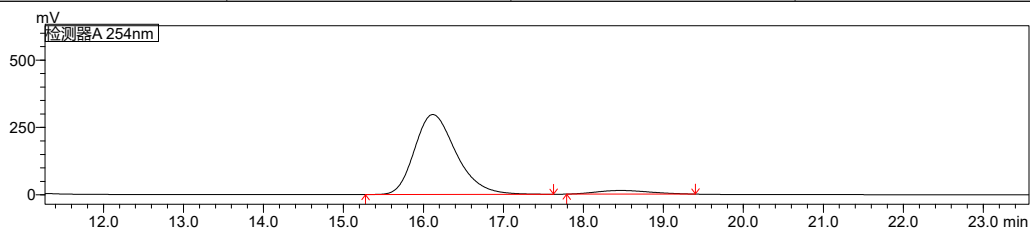


Peak#	Ret. Time	Height	Area%
1	18.785	18066	5.841
2	21.483	181517	94.159

HPLC conditions: Chiralpak OX-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

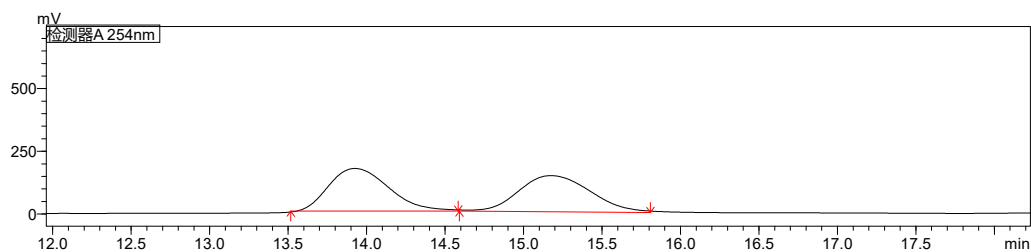
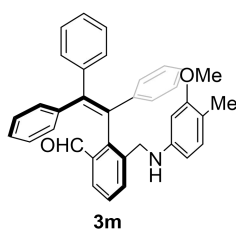


Peak#	Ret. Time	Height	Area%
1	16.101	151957	51.317
2	18.413	108359	48.683

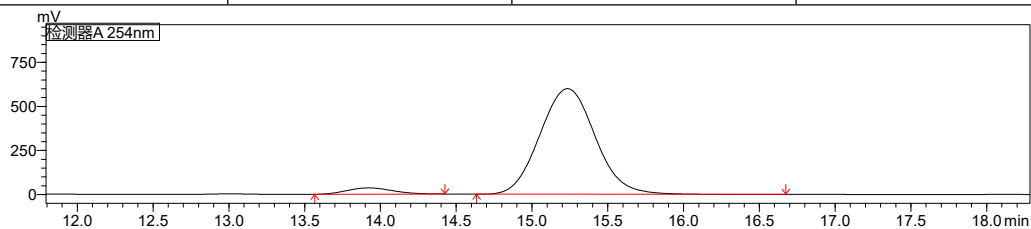


Peak#	Ret. Time	Height	Area%
1	16.117	296711	94.445
2	18.464	13489	5.555

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

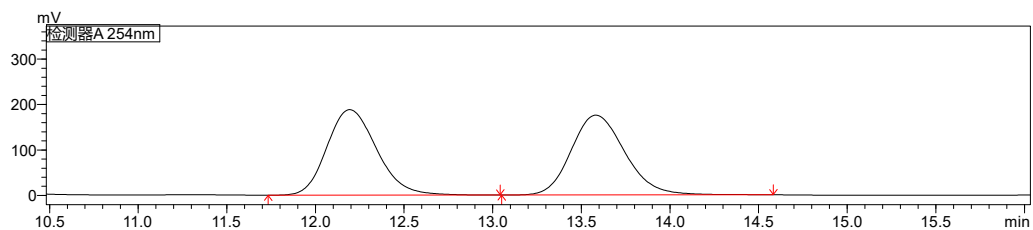
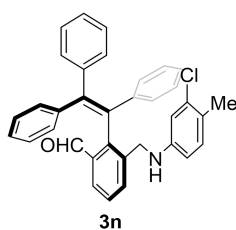


Peak#	Ret. Time	Height	Area%
1	13.924	169549	49.635
2	15.174	143871	50.365

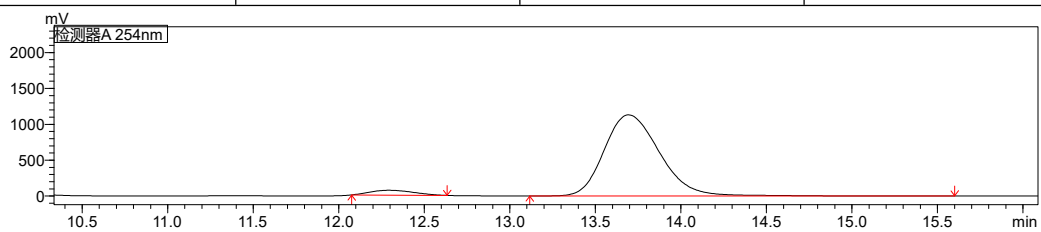


Peak#	Ret. Time	Height	Area%
1	13.921	35526	4.649
2	15.235	599132	95.351

HPLC conditions: Chiralpak IA-H, 20% ⁱPrOH/Hx eluent, 0.5 mL/min, 254 nm

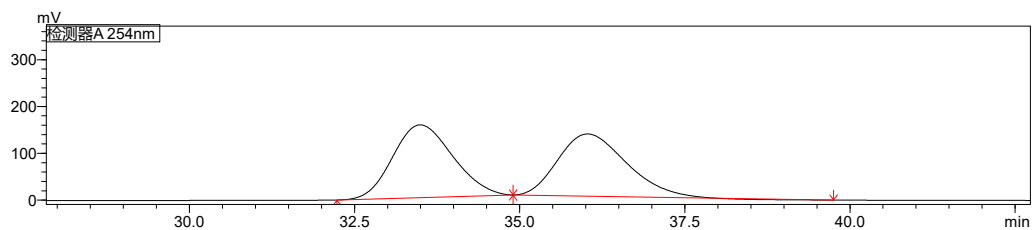
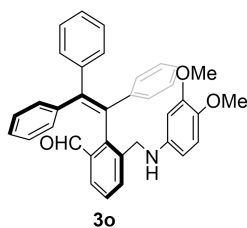


Peak#	Ret. Time	Height	Area%
1	12.193	188167	49.824
2	13.582	175682	50.176

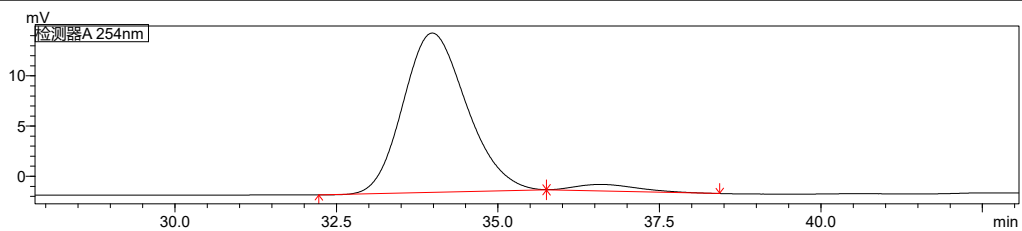


Peak#	Ret. Time	Height	Area%
1	12.293	67341	4.470
2	13.694	1130061	95.530

HPLC conditions: Chiralpak OX-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

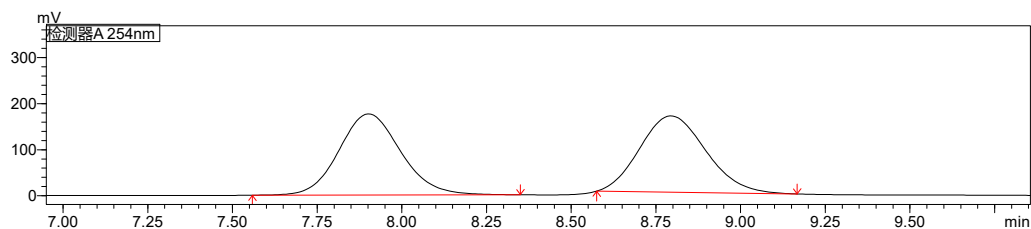
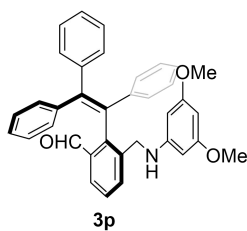


Peak#	Ret. Time	Height	Area%
1	33.492	155488	50.768
2	36.028	132800	49.232

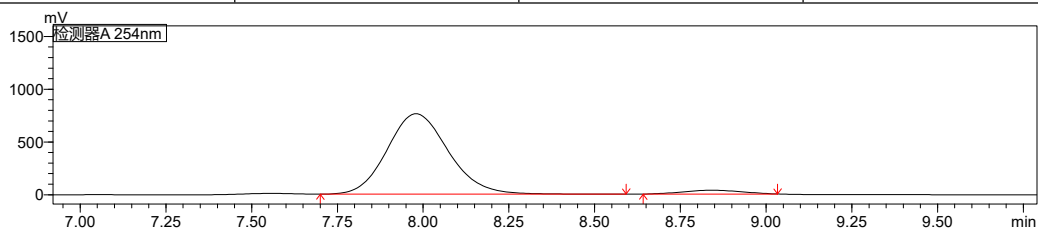


Peak#	Ret. Time	Height	Area%
1	33.981	15860	96.163
2	36.595	646	3.837

HPLC conditions: Chiralpak IA, 30% *i*PrOH/Hx eluent, 0.8 mL/min, 254 nm

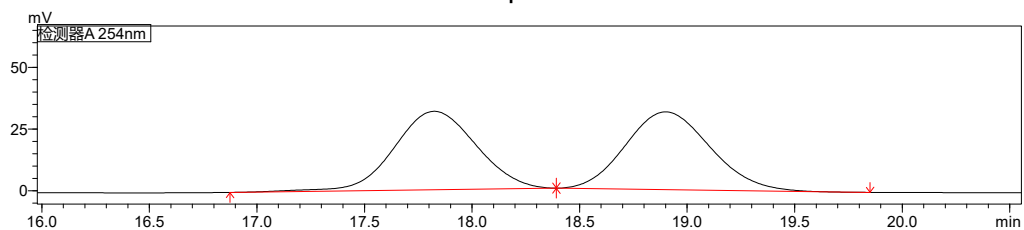
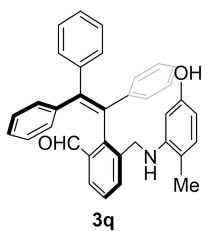


Peak#	Ret. Time	Height	Area%
1	7.901	176370	49.948
2	8.794	165760	50.052

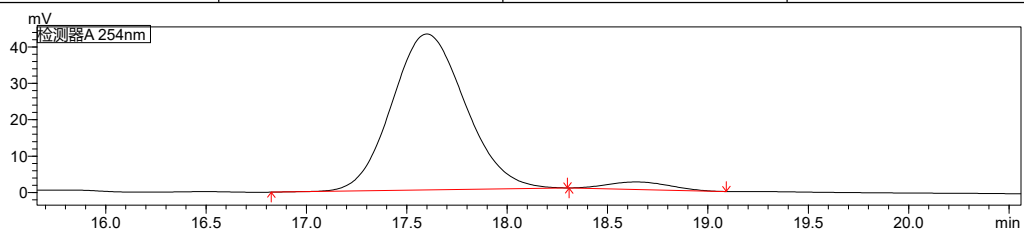


Peak#	Ret. Time	Height	Area%
1	7.979	762140	95.721
2	8.843	35669	4.279

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

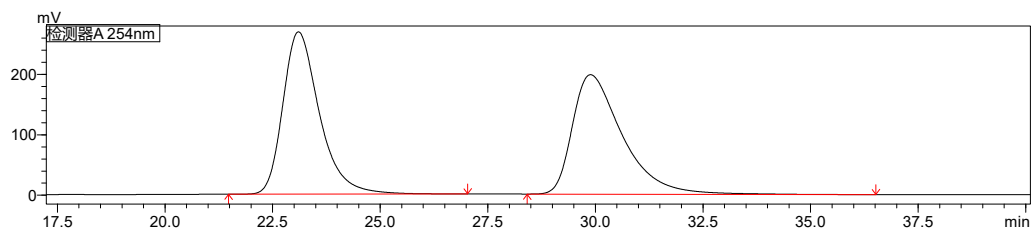
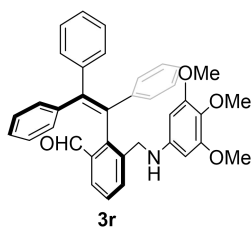


Peak#	Ret. Time	Height	Area%
1	17.824	31825	49.459
2	18.899	31536	50.541

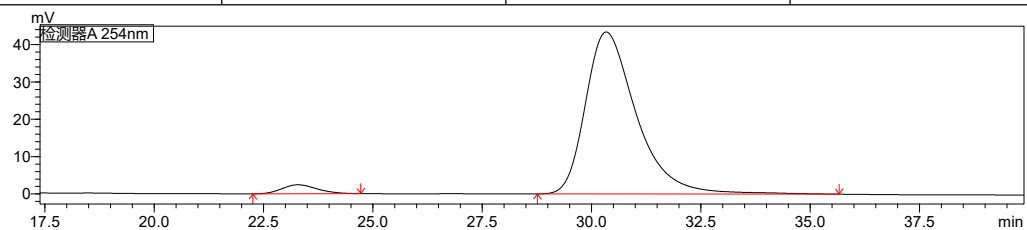


Peak#	Ret. Time	Height	Area%
1	17.600	42883	96.141
2	18.642	2055	3.859

HPLC conditions: Chiralpak IC, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

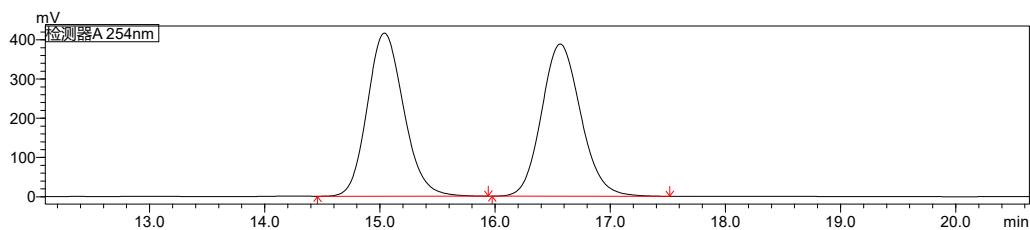
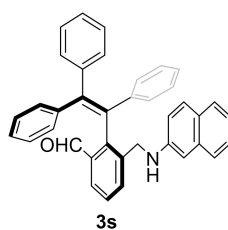


Peak#	Ret. Time	Height	Area%
1	23.100	268641	49.831
2	29.888	197728	50.169

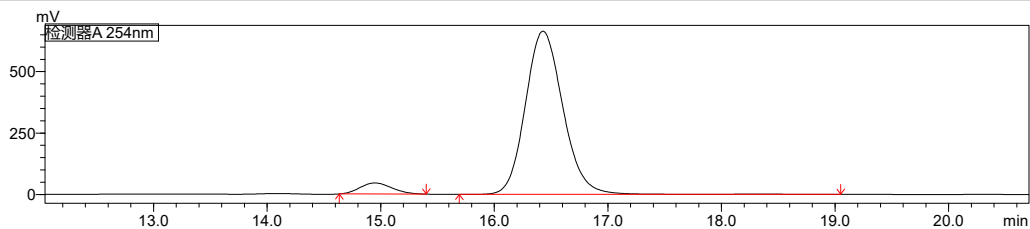


Peak#	Ret. Time	Height	Area%
1	23.286	2404	3.700
2	30.333	43387	96.300

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

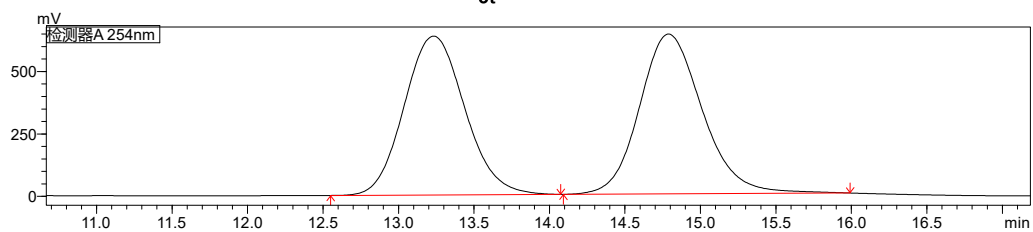
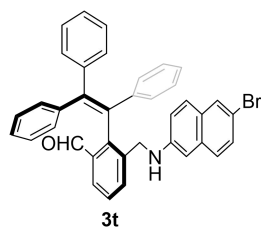


Peak#	Ret. Time	Height	Area%
1	15.038	415859	49.879
2	16.565	388222	50.121

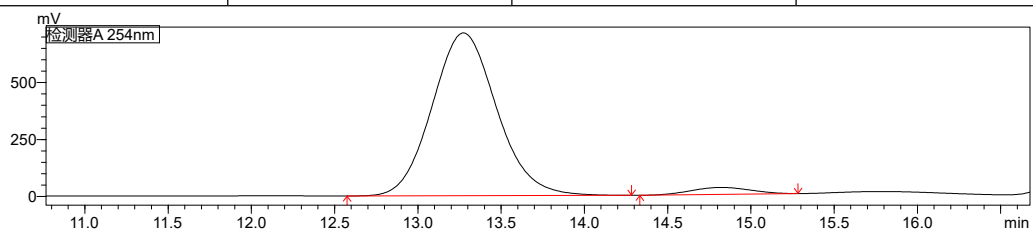


Peak#	Ret. Time	Height	Area%
1	14.948	44859	5.430
2	16.428	664316	94.570

HPLC conditions: Chiralpak OD-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

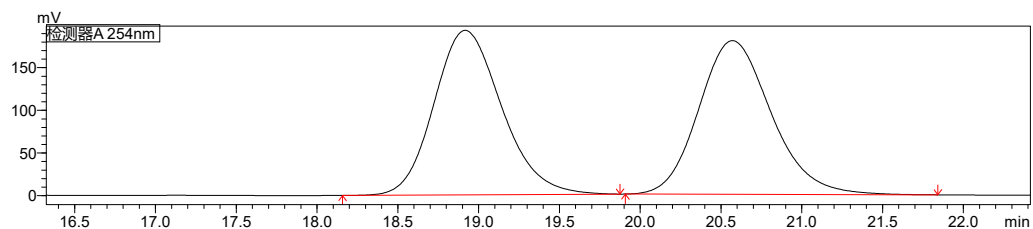
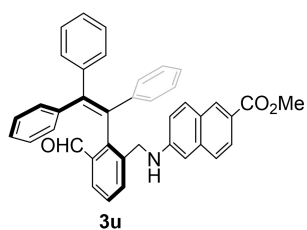


Peak#	Ret. Time	Height	Area%
1	13.232	636174	48.985
2	14.788	639820	51.015

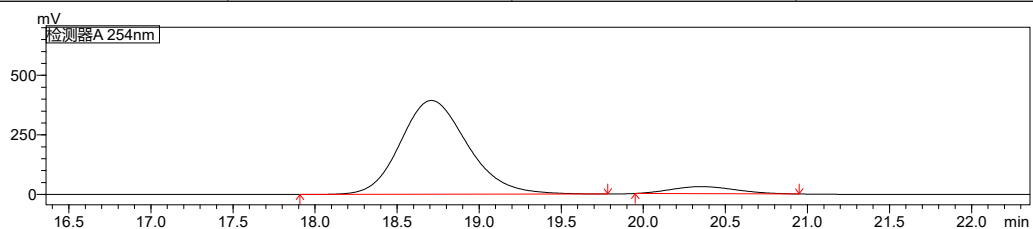


Peak#	Ret. Time	Height	Area%
1	13.274	714431	96.194
2	14.821	30563	3.806

HPLC conditions: Chiralpak IA, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

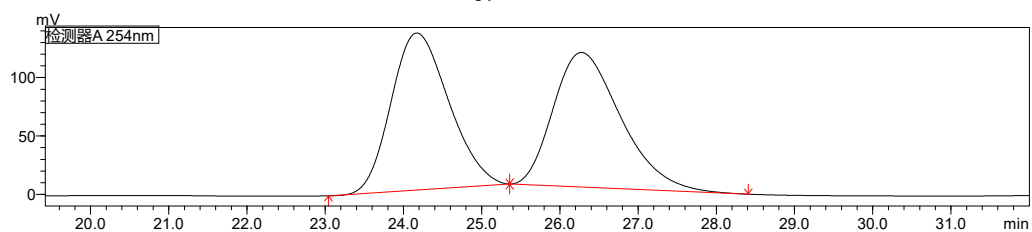
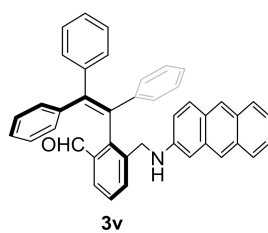


Peak#	Ret. Time	Height	Area%
1	18.917	192830	50.006
2	20.571	180099	49.994

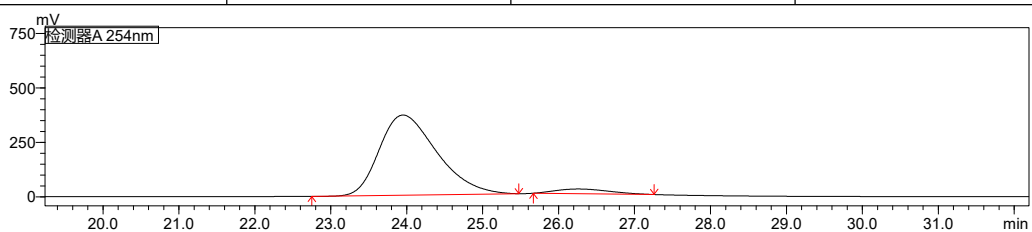


Peak#	Ret. Time	Height	Area%
1	18.709	394322	93.253
2	20.352	29634	6.747

HPLC conditions: Chiralpak OD-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

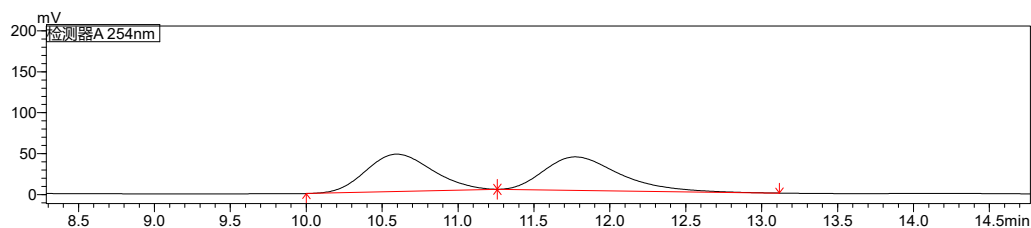
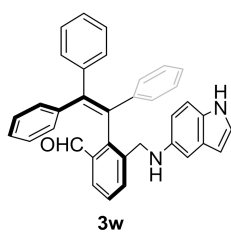


Peak#	Ret. Time	Height	Area%
1	24.170	134481	49.908
2	26.274	115257	50.092

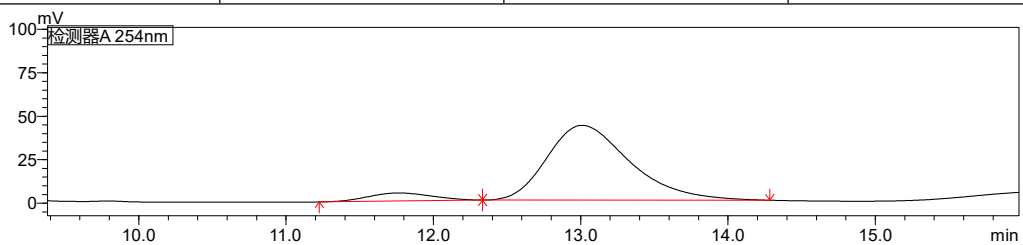


Peak#	Ret. Time	Height	Area%
1	23.950	367746	94.805
2	26.257	21627	5.195

HPLC conditions: Chiralpak IC, 20% *i*PrOH/Hx eluent, 1.0 mL/min, 254 nm

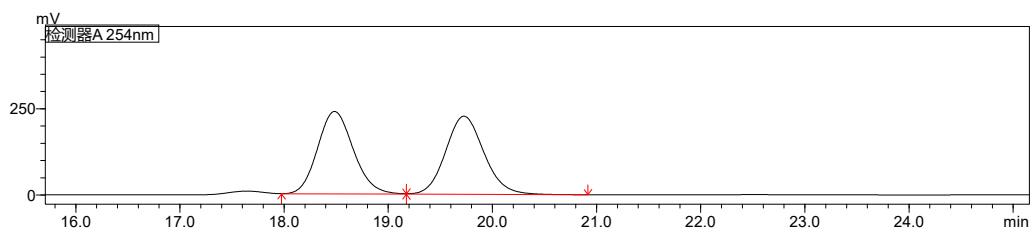
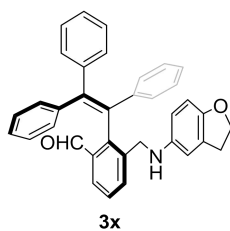


Peak#	Ret. Time	Height	Area%
1	10.596	45665	49.455
2	11.772	40883	50.545

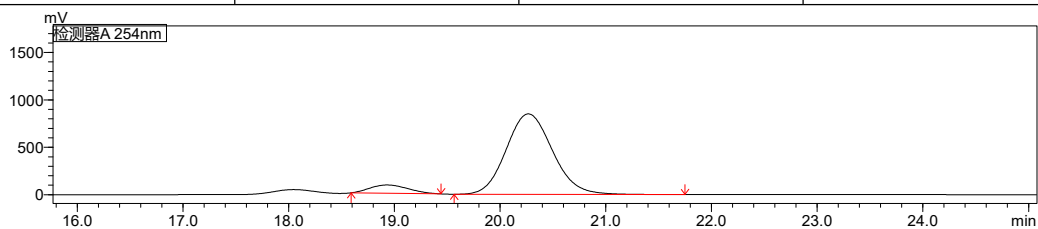


Peak#	Ret. Time	Height	Area%
1	11.766	4620	7.628
2	13.010	43013	92.372

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

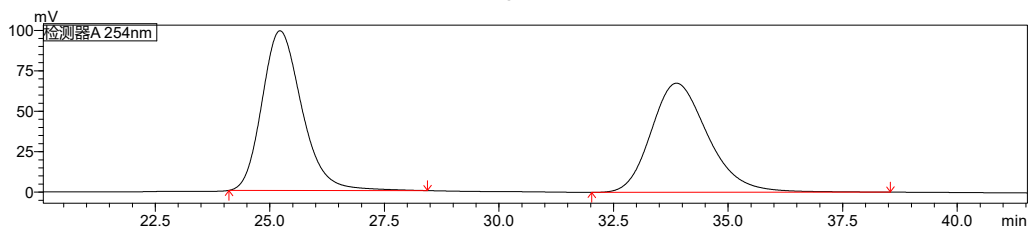
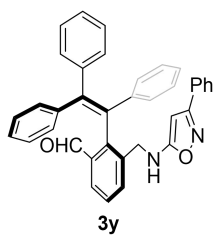


Peak#	Ret. Time	Height	Area%
1	18.484	239140	49.548
2	19.726	226621	50.452

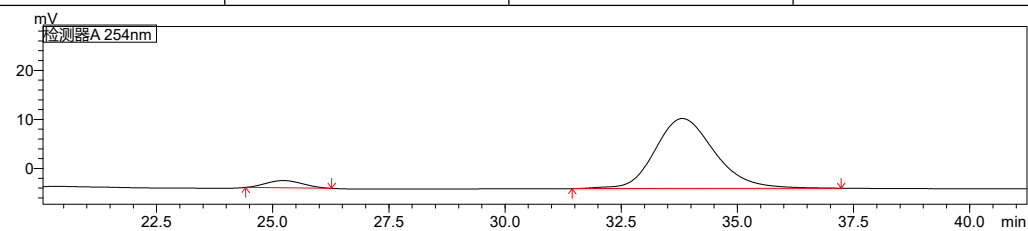


Peak#	Ret. Time	Height	Area%
1	18.931	87118	7.784
2	20.267	849054	92.216

HPLC conditions: Chiralpak OD-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

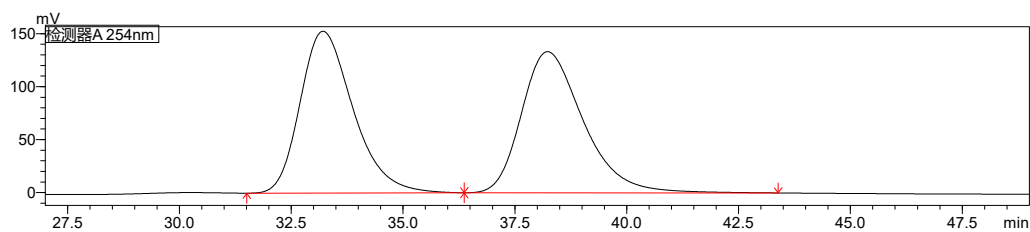
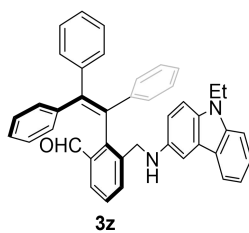


Peak#	Ret. Time	Height	Area%
1	25.220	98673	50.640
2	33.874	67458	49.360

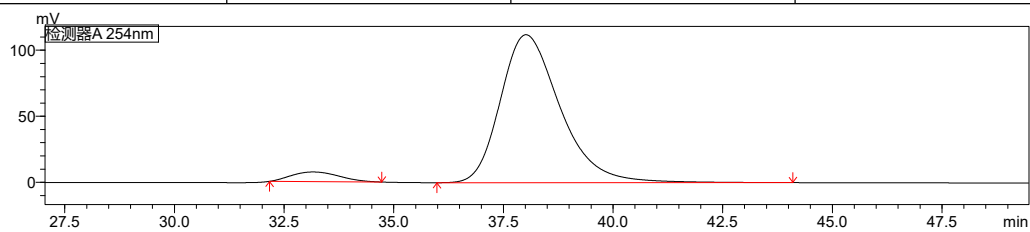


Peak#	Ret. Time	Height	Area%
1	25.236	1478	5.984
2	33.814	14251	94.016

HPLC conditions: Chiralpak OD-H, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

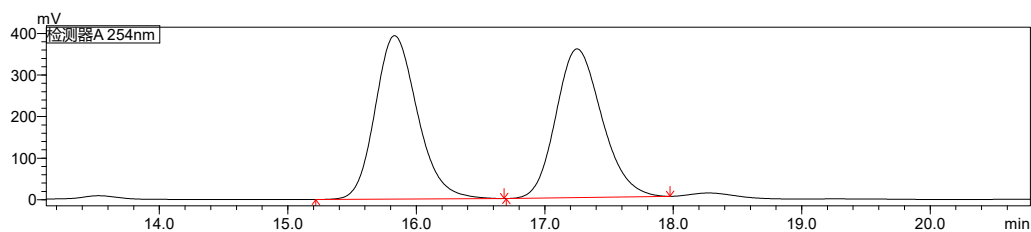
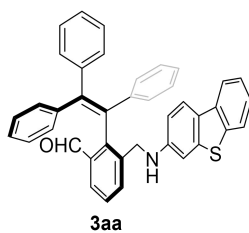


Peak#	Ret. Time	Height	Area%
1	33.211	152690	49.532
2	38.229	133170	50.468

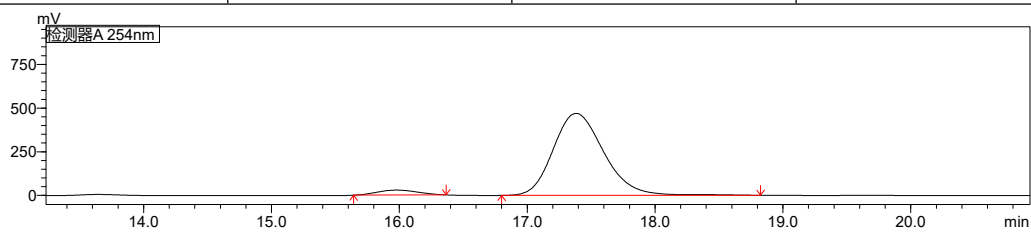


Peak#	Ret. Time	Height	Area%
1	33.164	7300	4.952
2	38.013	112001	95.048

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

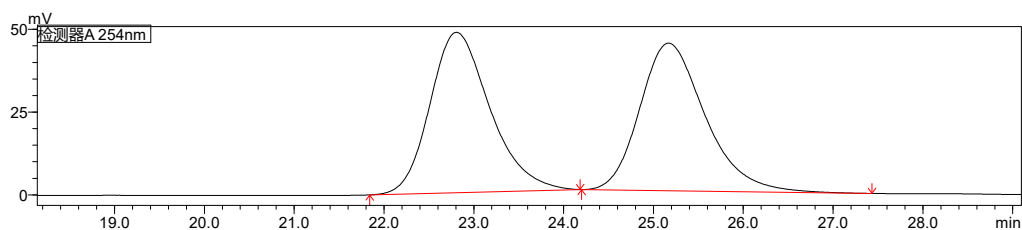
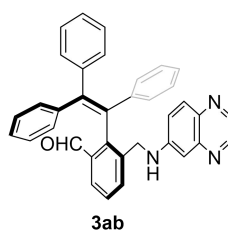


Peak#	Ret. Time	Height	Area%
1	15.830	393270	50.282
2	17.251	357918	49.718

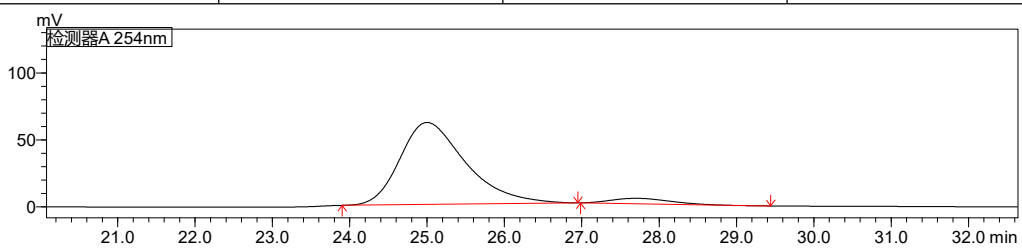


Peak#	Ret. Time	Height	Area%
1	15.978	28423	4.614
2	17.382	469530	95.386

HPLC conditions: Chiralpak IA, 10% *i*PrOH/Hx eluent, 1.0 mL/min, 254 nm

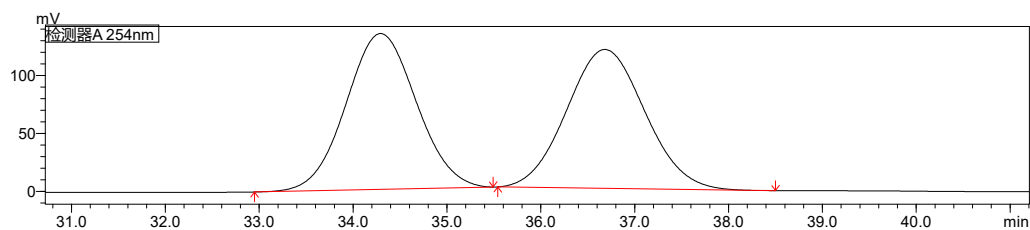
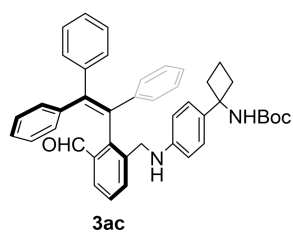


Peak#	Ret. Time	Height	Area%
1	22.807	48465	49.968
2	25.167	44588	50.032

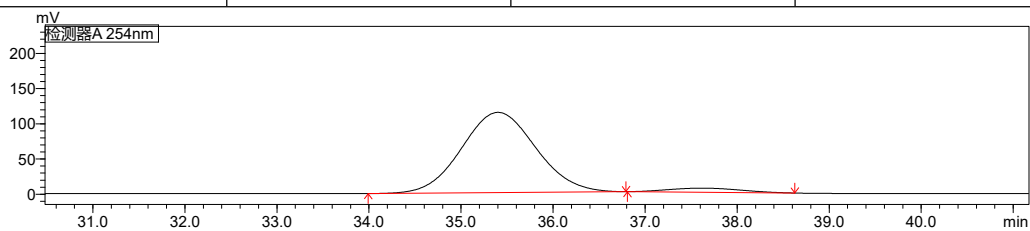


Peak#	Ret. Time	Height	Area%
1	24.999	61229	94.505
2	27.696	4064	5.495

HPLC conditions: Chiralpak IA, 10% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

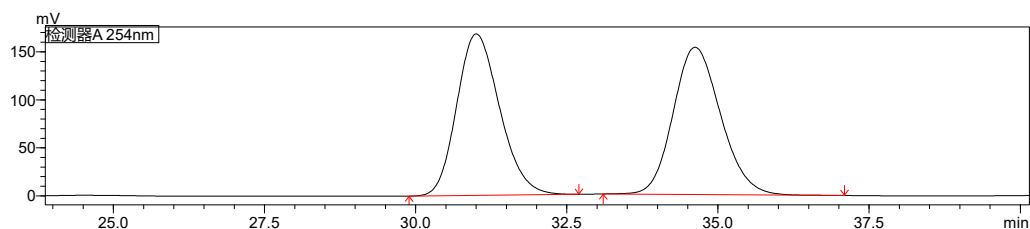
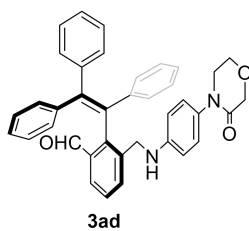


Peak#	Ret. Time	Height	Area%
1	34.293	134442	50.201
2	36.682	119773	49.799

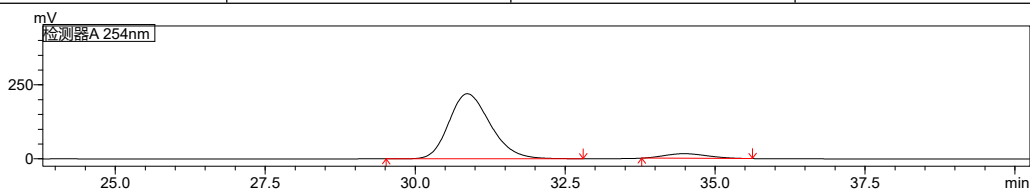


Peak#	Ret. Time	Height	Area%
1	35.401	113993	95.266
2	37.616	5897	4.734

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

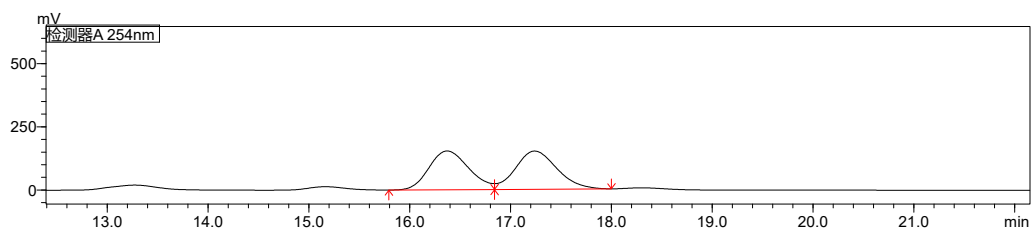
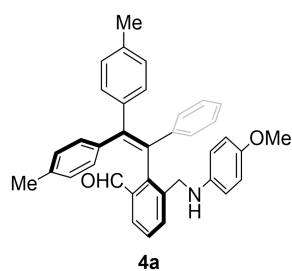


Peak#	Ret. Time	Height	Area%
1	30.999	168166	49.748
2	34.622	153402	50.252

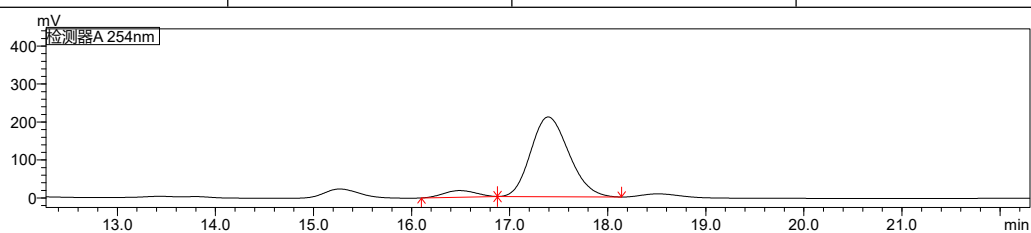


Peak#	Ret. Time	Height	Area%
1	30.870	219603	93.093
2	34.485	15654	6.907

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

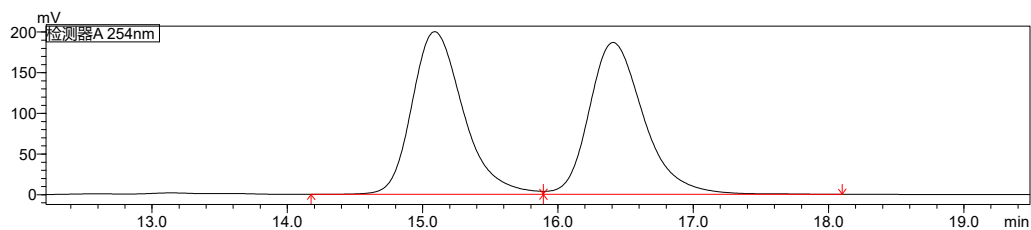
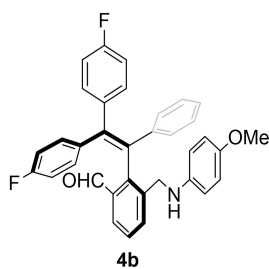


Peak#	Ret. Time	Height	Area%
1	16.370	153612	49.431
2	17.238	151140	50.569

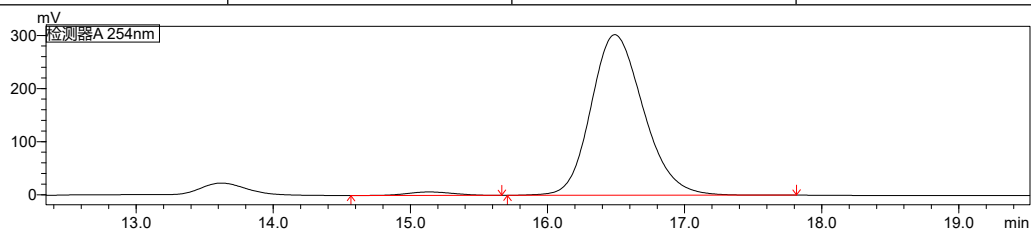


Peak#	Ret. Time	Height	Area%
1	16.491	17505	6.586
2	17.392	210031	93.414

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

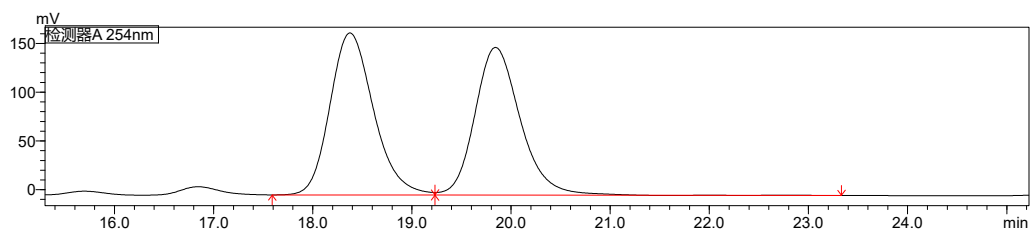
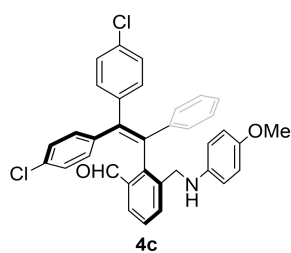


Peak#	Ret. Time	Height	Area%
1	15.089	200056	50.230
2	16.407	186752	49.770

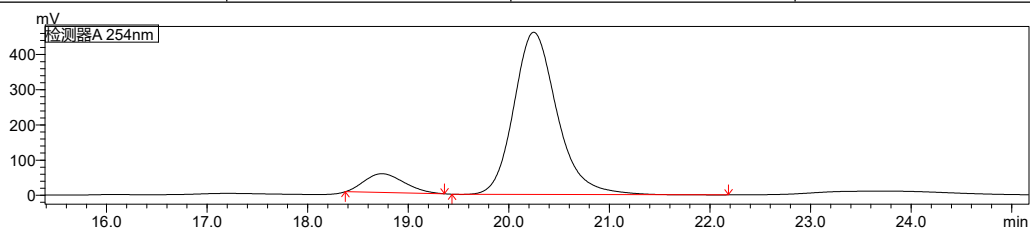


Peak#	Ret. Time	Height	Area%
1	15.137	6561	1.900
2	16.491	302575	98.100

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

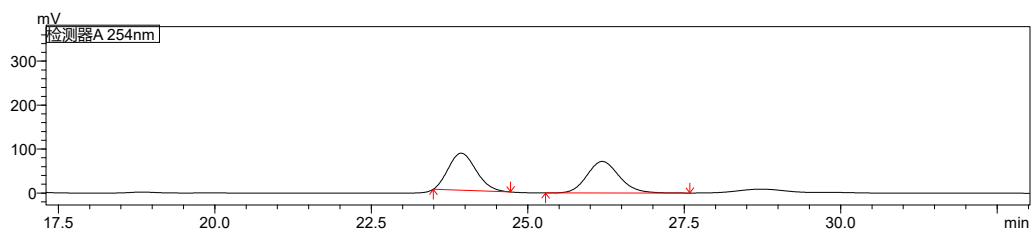
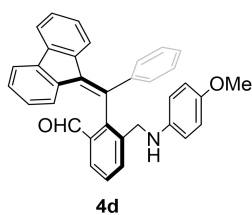


Peak#	Ret. Time	Height	Area%
1	18.375	166199	51.279
2	19.843	151468	48.721

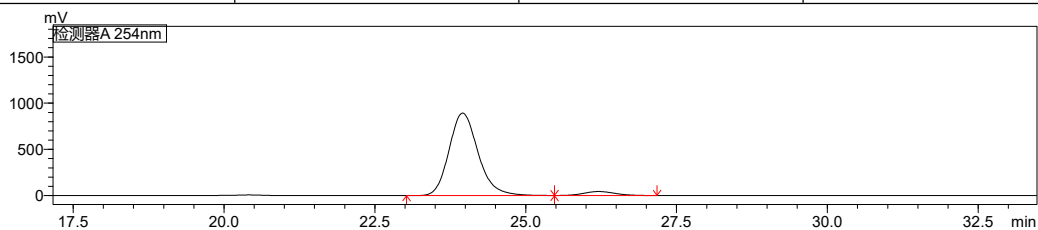


Peak#	Ret. Time	Height	Area%
1	18.736	53401	9.632
2	20.247	460939	90.368

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

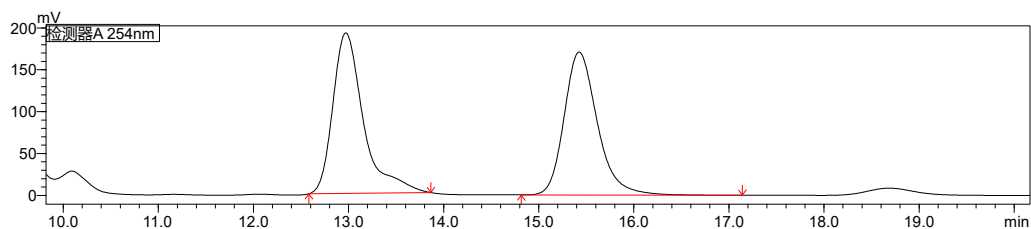
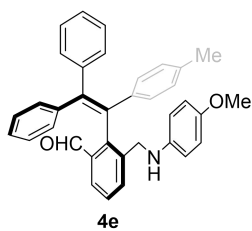


Peak#	Ret. Time	Height	Area%
1	23.935	84150	50.095
2	26.189	71717	49.905

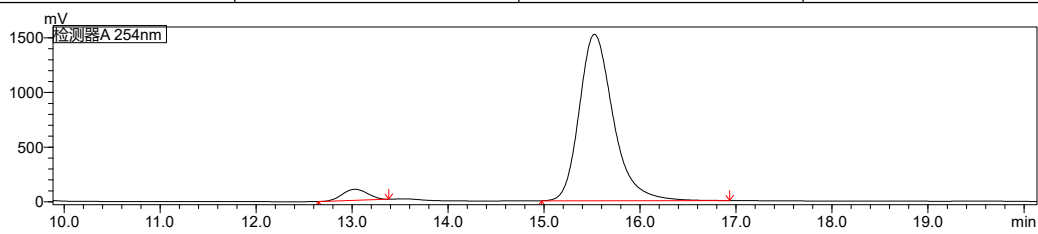


Peak#	Ret. Time	Height	Area%
1	23.954	892877	95.113
2	26.208	43101	4.887

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

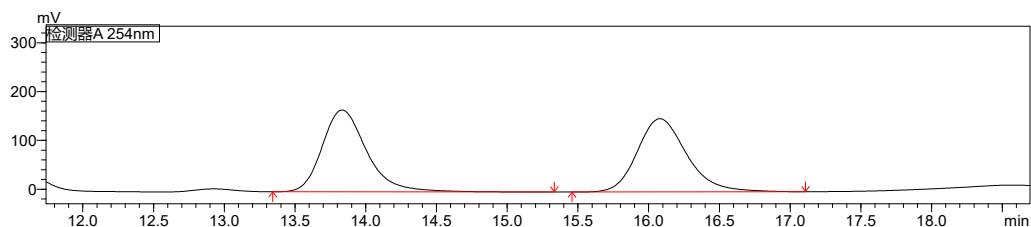
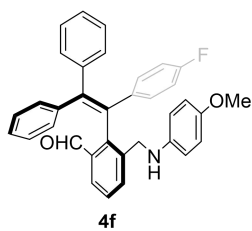


Peak#	Ret. Time	Height	Area%
1	12.971	191727	50.821
2	15.425	170761	49.179

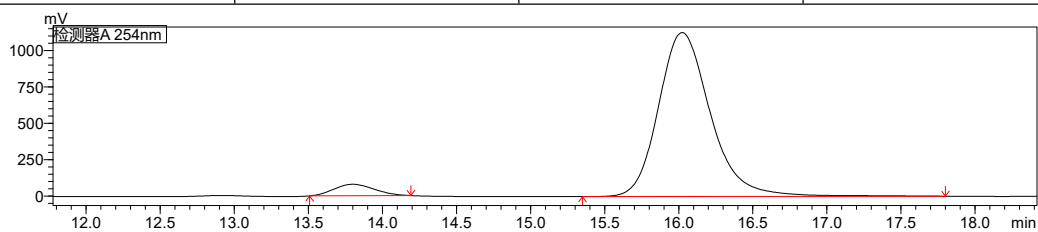


Peak#	Ret. Time	Height	Area%
1	13.030	101665	4.754
2	15.525	1523180	95.246

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

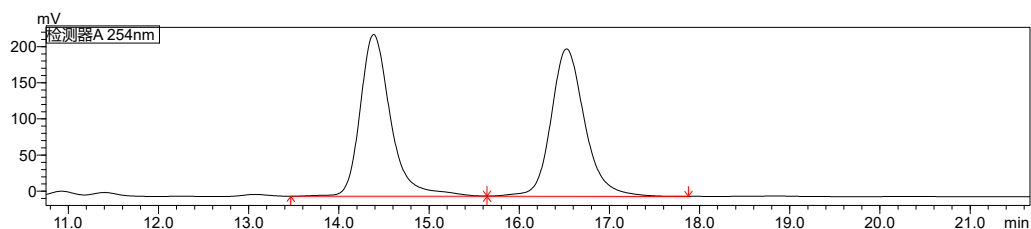
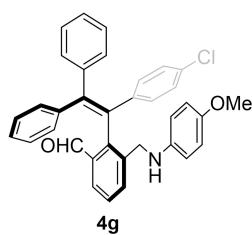


Peak#	Ret. Time	Height	Area%
1	13.832	167576	50.155
2	16.079	149871	49.845

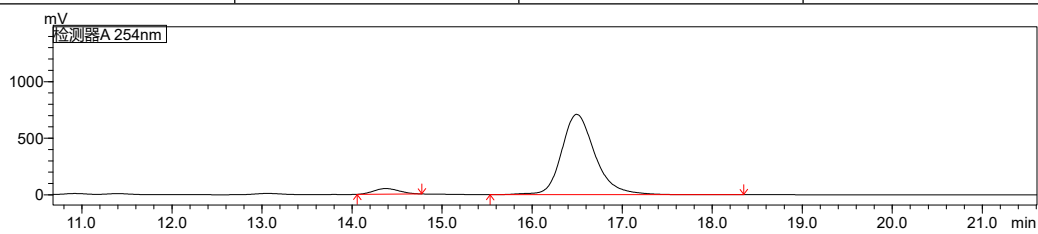


Peak#	Ret. Time	Height	Area%
1	13.800	78986	5.166
2	16.023	1125570	94.834

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

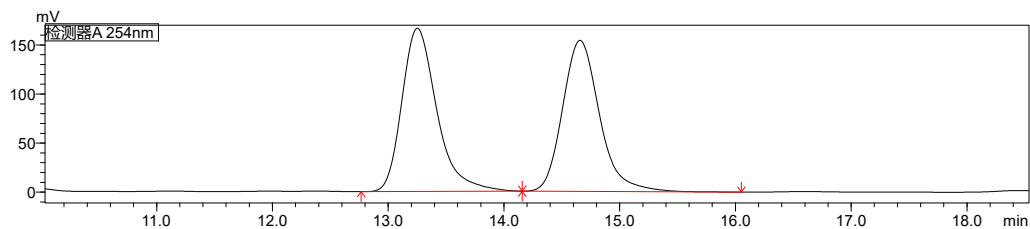
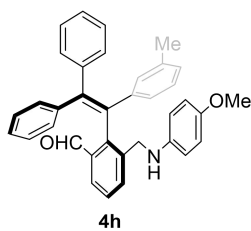


Peak#	Ret. Time	Height	Area%
1	14.385	223916	49.898
2	16.525	203963	50.102

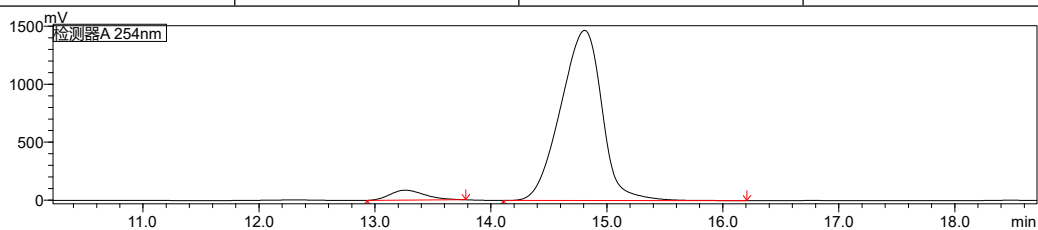


Peak#	Ret. Time	Height	Area%
1	14.375	49301	5.032
2	16.495	710815	94.968

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

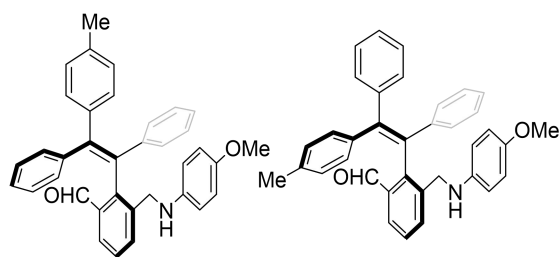


Peak#	Ret. Time	Height	Area%
1	13.252	166494	50.659
2	14.657	154040	49.341

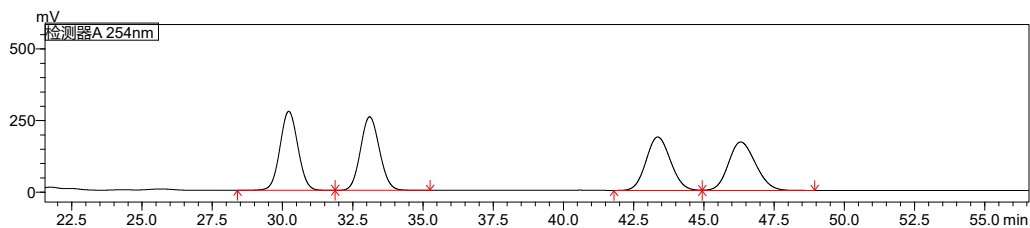


Peak#	Ret. Time	Height	Area%
1	13.263	85725	4.702
2	14.808	1468375	95.298

HPLC conditions: Chiralpak AD-H, 20% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

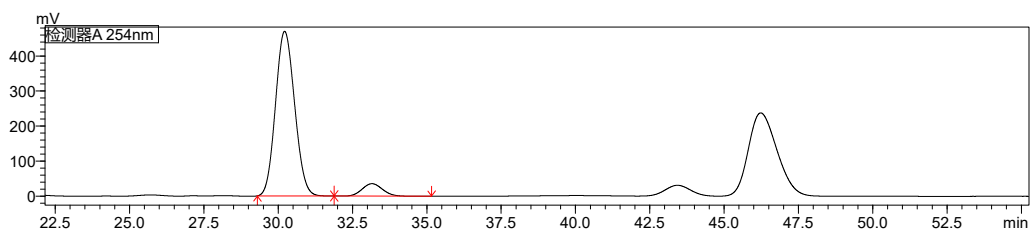


4i



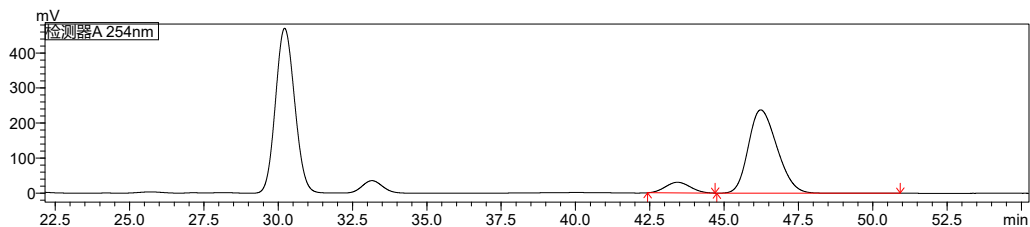
Peak#	Ret. Time	Height	Area%
1	30.222	276144	26.105
2	33.101	256810	25.731
3	43.357	186684	24.020
4	46.310	169193	24.144

数据文件名:AM-2-146-9-AD9010-254-0.5.lcd
样品名:AM-2-146-9-AD9010-254-0.5



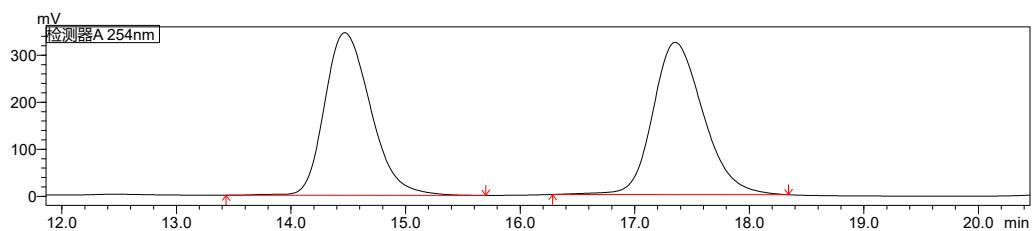
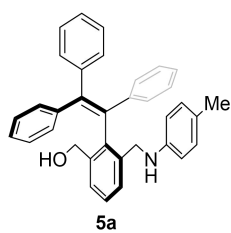
Peak#	Ret. Time	Height	Area%
1	30.215	469948	92.567
2	33.152	35563	7.433

数据文件名:AM-2-146-9-AD9010-254-0.5.lcd
样品名:AM-2-146-9-AD9010-254-0.5

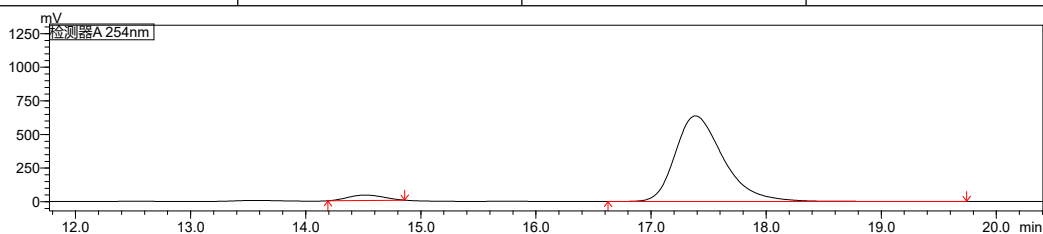


Peak#	Ret. Time	Height	Area%
1	43.431	30422	10.012
2	46.232	237862	89.988

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

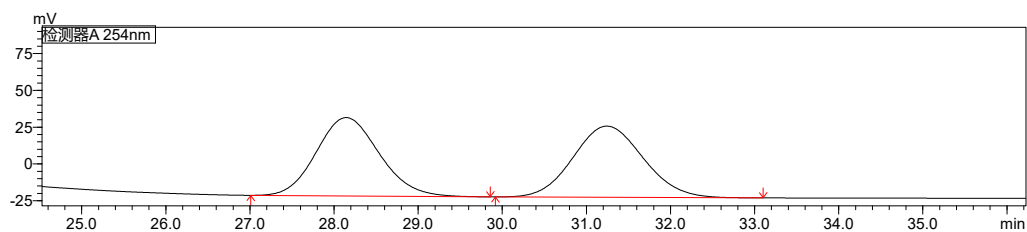
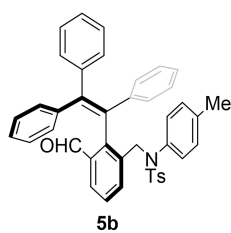


Peak#	Ret. Time	Height	Area%
1	14.468	345600	49.374
2	17.353	323398	50.626

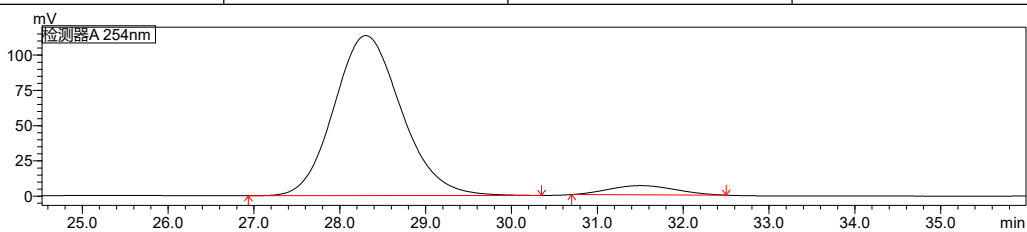


Peak#	Ret. Time	Height	Area%
1	14.517	40220	4.421
2	17.385	636788	95.579

HPLC conditions: Chiralpak AD-H, 10% iPrOH/Hx eluent, 0.5 mL/min, 254 nm

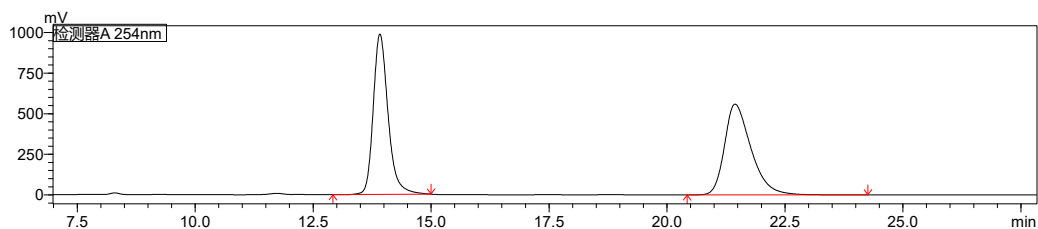
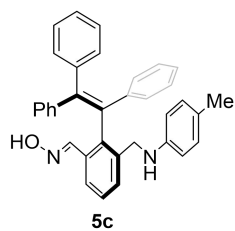


Peak#	Ret. Time	Height	Area%
1	28.143	53293	49.693
2	31.243	48416	50.307

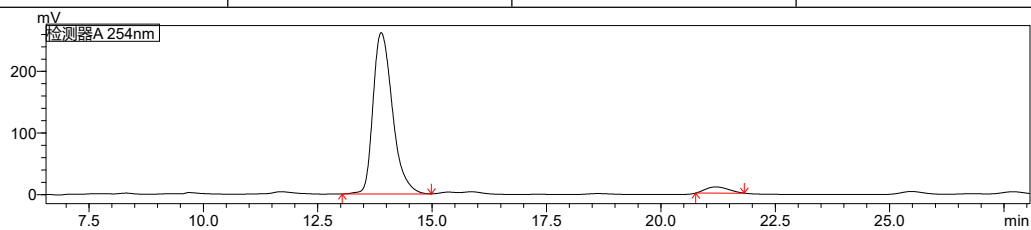


Peak#	Ret. Time	Height	Area%
1	28.302	113513	94.618
2	31.504	6543	5.382

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm

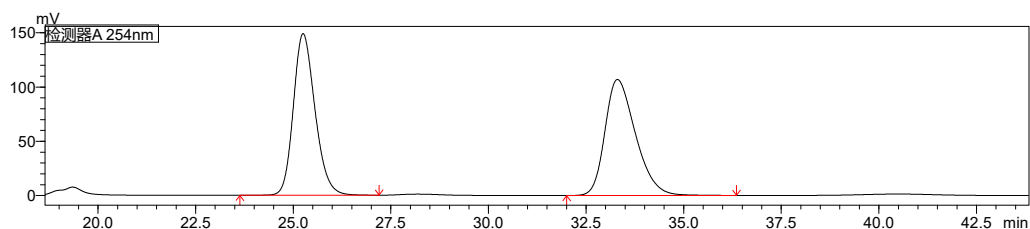
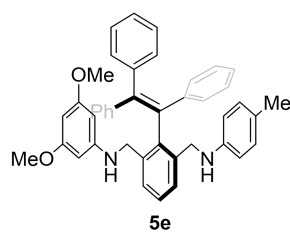


Peak#	Ret. Time	Height	Area%
1	13.915	987442	49.764
2	21.442	559099	50.236

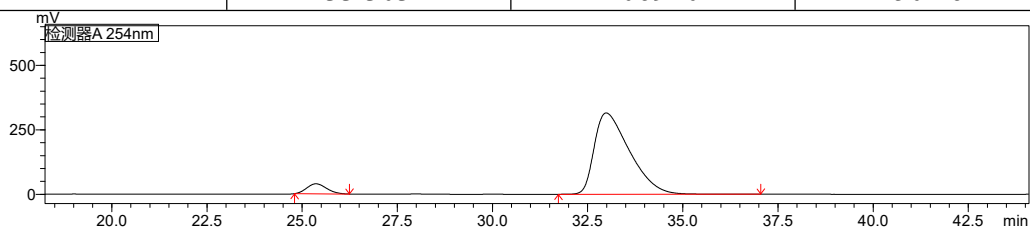


Peak#	Ret. Time	Height	Area%
1	13.263	85725	4.702
2	14.808	1468375	95.298

HPLC conditions: Chiralpak IA, 20% *i*PrOH/Hx eluent, 0.5 mL/min, 254 nm



Peak#	Ret. Time	Height	Area%
1	25.250	149114	49.738
2	33.303	106910	50.262



Peak#	Ret. Time	Height	Area%
1	25.363	38773	6.450
2	32.988	315539	93.550

9. Crystallographic Data

Datablock 71_1 - ellipsoid plot

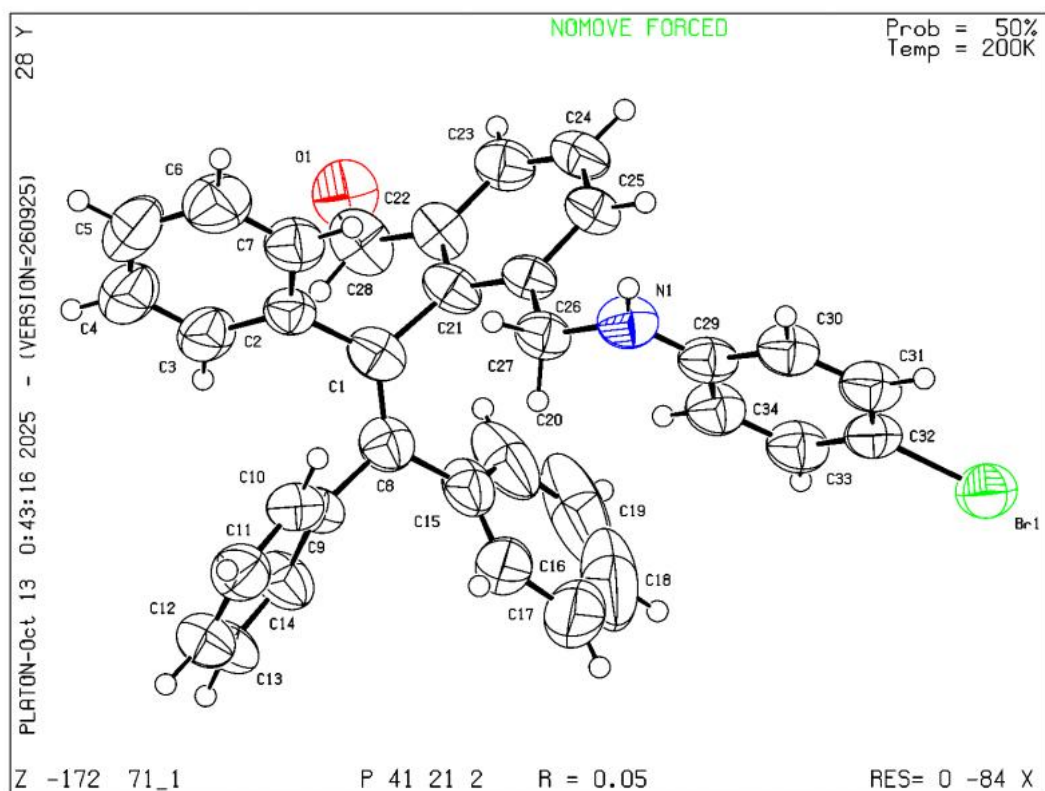


Table S1 Crystal data and structure refinement for 3i.

Identification code	3i
Empirical formula	C ₃₄ H ₂₆ BrNO
Formula weight	544.47
Temperature/K	199.99(10)
Crystal system	tetragonal
Space group	P4 ₁ 2 ₁ 2
a/Å	10.01780(10)
b/Å	10.01780(10)
c/Å	53.4159(16)
α/°	90

$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	5360.62(19)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.349
μ/mm^{-1}	2.291
F(000)	2240.0
Crystal size/ mm^3	$0.14 \times 0.12 \times 0.1$
Radiation	Cu K α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	6.62 to 146.22
Index ranges	$-10 \leq h \leq 11, -12 \leq k \leq 12, -65 \leq l \leq 60$
Reflections collected	27123
Independent reflections	5255 [$R_{\text{int}} = 0.0495, R_{\text{sigma}} = 0.0255$]
Data/restraints/parameters	5255/0/334
Goodness-of-fit on F^2	1.082
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0504, wR_2 = 0.1350$
Final R indexes [all data]	$R_1 = 0.0543, wR_2 = 0.1378$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.45/-0.33
Flack/Hooft parameter	0.039(12)/0.054(7)

Crystal structure determination of **[3i]**

Crystal Data for $\text{C}_{34}\text{H}_{26}\text{BrNO}$ ($M = 544.47 \text{ g/mol}$): tetragonal, space group $P4_12_12$ (no. 92), $a = 10.01780(10) \text{ \AA}$, $c = 53.4159(16) \text{ \AA}$, $V = 5360.62(19) \text{ \AA}^3$, $Z = 8$, $T = 199.99(10) \text{ K}$, $\mu(\text{Cu K}\alpha) = 2.291 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.349 \text{ g/cm}^3$, 27123 reflections measured ($6.62^\circ \leq 2\Theta \leq 146.22^\circ$), 5255 unique ($R_{\text{int}} = 0.0495, R_{\text{sigma}} = 0.0255$) which were used in all calculations. The final R_1 was 0.0504 ($I > 2\sigma(I)$) and wR_2 was 0.1378 (all data).

Refinement model description

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Br1	-515.4(7)	6052.9(6)	6816.9(2)	78.9(2)
O1	6372(4)	-2262(4)	7236.0(9)	85.7(11)
N1	5206(5)	4889(4)	7122.9(8)	65.6(10)
C1	7262(5)	1252(4)	6876.4(9)	63.0(12)
C2	8695(5)	1058(5)	6956.5(8)	55.7(10)
C3	9477(6)	103(5)	6846.4(11)	75.3(14)
C4	10745(7)	-119(7)	6924.6(13)	93(2)
C5	11267(8)	628(9)	7116.7(15)	106(2)
C6	10497(7)	1606(9)	7234.1(13)	97(2)
C7	9213(6)	1793(6)	7153.8(10)	74.0(13)
C8	6927(5)	1439(5)	6638.0(9)	64.7(11)
C9	7975(5)	1664(5)	6437.8(8)	59.0(10)
C10	8893(5)	2676(5)	6456.4(9)	61.8(11)
C11	9738(6)	2962(6)	6263.2(11)	77.4(14)
C12	9707(7)	2218(7)	6051.1(11)	82.0(16)
C13	8792(7)	1217(8)	6024.4(10)	88.8(18)
C14	7918(6)	912(6)	6219.4(10)	76.3(15)
C15	5523(5)	1536(6)	6551.9(10)	76.2(15)
C16	5226(8)	2501(10)	6369.2(12)	110(3)
C17	3962(15)	2563(19)	6265.6(19)	191(8)
C18	2992(16)	1610(30)	6354(4)	240(14)
C19	3288(10)	790(20)	6515(3)	208(10)
C20	4530(6)	667(9)	6622.9(15)	117(3)

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C21	6230(5)	1258(5)	7082.7(8)	59.9(11)
C22	5961(5)	60(5)	7211.7(10)	64.2(12)
C23	5102(5)	72(5)	7416.5(9)	66.7(12)
C24	4526(5)	1236(5)	7493.0(9)	67.7(12)
C25	4792(5)	2422(5)	7368.8(8)	61.5(11)
C26	5637(5)	2448(4)	7163.4(7)	53.5(10)
C27	5951(5)	3772(5)	7035.0(8)	58.7(10)
C28	6523(6)	-1220(5)	7130.0(12)	79.5(15)
C29	3912(6)	5126(5)	7053.3(8)	60.2(11)
C30	3256(6)	6288(5)	7132.3(9)	66.1(12)
C31	1954(6)	6565(5)	7067.7(9)	69.5(13)
C32	1280(5)	5658(5)	6917.7(8)	62.0(11)
C33	1871(6)	4513(5)	6838.6(9)	68.6(12)
C34	3172(6)	4237(5)	6906.9(9)	67.1(12)

Table S3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	92.0(4)	77.6(4)	67.2(3)	-0.4(3)	-6.2(3)	6.1(3)
O1	95(3)	56(2)	106(3)	2(2)	4(2)	-13.6(18)
N1	83(3)	52(2)	61(2)	-10.1(17)	-9(2)	-9.4(18)
C1	81(3)	48(2)	60(3)	-8.4(19)	9(2)	-10(2)
C2	66(3)	52(2)	49(2)	2.8(18)	2.1(19)	0.4(19)

Table S3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	96(4)	60(3)	70(3)	6(2)	-6(3)	18(3)
C4	105(5)	85(4)	90(4)	9(3)	-10(4)	29(4)
C5	91(5)	120(6)	108(5)	9(5)	-28(4)	31(4)
C6	88(4)	125(6)	78(4)	-12(4)	-20(3)	-10(4)
C7	79(4)	80(3)	63(3)	-11(3)	-7(2)	-3(3)
C8	68(3)	62(3)	64(3)	-13(2)	-2(2)	-5(2)
C9	68(3)	63(3)	45(2)	-4.7(19)	4(2)	0(2)
C10	74(3)	59(2)	52(2)	2.3(19)	-5(2)	-3(2)
C11	72(3)	84(4)	76(3)	12(3)	3(3)	-5(3)
C12	83(4)	98(4)	65(3)	10(3)	16(3)	6(3)
C13	103(4)	111(5)	53(3)	-28(3)	9(3)	14(4)
C14	79(3)	84(4)	66(3)	-26(3)	7(3)	-10(3)
C15	58(3)	107(4)	64(3)	-35(3)	-2(2)	1(3)
C16	104(5)	157(7)	70(4)	-24(4)	-14(4)	53(5)
C17	168(11)	320(20)	89(6)	-74(9)	-46(7)	145(13)
C18	100(9)	430(30)	187(15)	-197(19)	-56(9)	104(14)
C19	62(5)	340(20)	223(15)	-206(17)	21(7)	-37(9)
C20	70(4)	179(8)	103(5)	-82(5)	21(3)	-40(4)
C21	71(3)	59(3)	50(2)	-11.8(19)	11(2)	-18(2)
C22	68(3)	54(2)	70(3)	-7(2)	10(2)	-12.3(19)
C23	73(3)	68(3)	59(2)	7(2)	6(2)	-14(2)
C24	73(3)	82(3)	48(2)	1(2)	11(2)	-11(2)
C25	74(3)	65(3)	46(2)	-7.5(19)	8(2)	-1(2)
C26	64(2)	55(2)	41.4(19)	-7.0(17)	0.9(18)	-8.9(19)

Table S3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	71(3)	55(2)	50(2)	-5.5(19)	1(2)	-4(2)
C28	94(4)	52(3)	93(4)	-3(3)	26(3)	-19(2)
C29	84(3)	51(2)	46(2)	-3.8(18)	-5(2)	-6(2)
C30	90(3)	50(2)	58(2)	-7(2)	-3(2)	-8(2)
C31	101(4)	52(2)	56(2)	-2(2)	2(3)	1(2)
C32	81(3)	59(3)	46(2)	2.9(19)	-4(2)	2(2)
C33	90(3)	59(2)	57(2)	-13(2)	-6(2)	-7(2)
C34	86(3)	55(3)	60(3)	-14(2)	-6(2)	-4(2)

Table S4 Bond Lengths for 3i.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Br1	C32	1.918(5)	C15	C16	1.406(10)
O1	C28	1.197(7)	C15	C20	1.375(10)
N1	C27	1.425(6)	C16	C17	1.384(15)
N1	C29	1.369(7)	C17	C18	1.44(3)
C1	C2	1.511(7)	C18	C19	1.22(3)
C1	C8	1.330(7)	C19	C20	1.378(16)
C1	C21	1.511(7)	C21	C22	1.410(7)
C2	C3	1.369(7)	C21	C26	1.399(7)
C2	C7	1.386(7)	C22	C23	1.392(7)
C3	C4	1.355(9)	C22	C28	1.467(8)
C4	C5	1.373(11)	C23	C24	1.364(8)
C5	C6	1.396(11)	C24	C25	1.387(7)

Table S4 Bond Lengths for 3i.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C6	C7	1.369(9)	C25	C26	1.387(6)
C8	C9	1.515(7)	C26	C27	1.526(6)
C8	C15	1.483(8)	C29	C30	1.402(7)
C9	C10	1.372(7)	C29	C34	1.398(7)
C9	C14	1.390(7)	C30	C31	1.377(8)
C10	C11	1.365(8)	C31	C32	1.387(7)
C11	C12	1.356(9)	C32	C33	1.358(7)
C12	C13	1.365(10)	C33	C34	1.382(8)
C13	C14	1.394(9)			

Table S5 Bond Angles for 3i.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C29	N1	C27	122.9(4)	C19	C18	C17	120.7(13)
C2	C1	C21	116.3(4)	C18	C19	C20	125.1(19)
C8	C1	C2	121.9(5)	C15	C20	C19	118.7(12)
C8	C1	C21	121.7(5)	C22	C21	C1	118.9(4)
C3	C2	C1	120.8(5)	C26	C21	C1	121.3(4)
C3	C2	C7	118.9(5)	C26	C21	C22	119.5(4)
C7	C2	C1	120.2(5)	C21	C22	C28	121.7(4)
C4	C3	C2	121.2(6)	C23	C22	C21	119.7(5)
C3	C4	C5	119.9(6)	C23	C22	C28	118.6(5)
C4	C5	C6	120.5(6)	C24	C23	C22	120.3(5)
C7	C6	C5	118.4(6)	C23	C24	C25	120.5(4)
C6	C7	C2	121.1(6)	C26	C25	C24	120.8(5)

Table S5 Bond Angles for 3i.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C8	C9	121.5(5)	C21	C26	C27	121.0(4)
C1	C8	C15	123.0(5)	C25	C26	C21	119.2(4)
C15	C8	C9	115.4(4)	C25	C26	C27	119.8(4)
C10	C9	C8	121.5(4)	N1	C27	C26	115.3(4)
C10	C9	C14	119.3(5)	O1	C28	C22	124.9(5)
C14	C9	C8	118.9(5)	N1	C29	C30	120.4(4)
C11	C10	C9	121.0(5)	N1	C29	C34	122.9(5)
C12	C11	C10	120.1(6)	C34	C29	C30	116.7(5)
C11	C12	C13	120.4(5)	C31	C30	C29	122.4(5)
C12	C13	C14	120.3(5)	C30	C31	C32	118.3(5)
C9	C14	C13	118.8(6)	C31	C32	Br1	118.9(4)
C16	C15	C8	117.5(6)	C33	C32	Br1	119.7(4)
C20	C15	C8	124.0(7)	C33	C32	C31	121.4(5)
C20	C15	C16	118.3(7)	C32	C33	C34	119.9(5)
C17	C16	C15	120.2(13)	C33	C34	C29	121.4(5)
C16	C17	C18	117.1(15)				

Table S6 Torsion Angles for 3i.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C32	C33	C34	178.8(4)	C14	C9	C10	C11	0.7(8)
N1	C29	C30	C31	-179.8(5)	C15	C8	C9	C10	120.0(6)
N1	C29	C34	C33	-179.5(5)	C15	C8	C9	C14	-53.5(7)
C1	C2	C3	C4	-177.0(5)	C15	C16	C17	C18	0.1(15)
C1	C2	C7	C6	178.1(6)	C16	C15	C20	C19	-0.8(9)

Table S6 Torsion Angles for 3i.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C8	C9	C10	-55.9(7)	C16	C17	C18	C19	1(2)
C1	C8	C9	C14	130.6(6)	C17	C18	C19	C20	-1(3)
C1	C8	C15	C16	139.2(6)	C18	C19	C20	C15	1.5(19)
C1	C8	C15	C20	-46.8(8)	C20	C15	C16	C17	0.1(10)
C1	C21	C22	C23	174.4(5)	C21	C1	C2	C3	128.6(5)
C1	C21	C22	C28	-8.1(8)	C21	C1	C2	C7	-47.4(6)
C1	C21	C26	C25	-173.9(4)	C21	C1	C8	C9	169.5(4)
C1	C21	C26	C27	3.7(7)	C21	C1	C8	C15	-6.1(8)
C2	C1	C8	C9	-8.8(7)	C21	C22	C23	C24	-0.3(8)
C2	C1	C8	C15	175.6(5)	C21	C22	C28	O1	177.3(6)
C2	C1	C21	C22	-69.0(6)	C21	C26	C27	N1	175.5(4)
C2	C1	C21	C26	104.7(5)	C22	C21	C26	C25	-0.2(7)
C2	C3	C4	C5	-0.4(10)	C22	C21	C26	C27	177.4(4)
C3	C2	C7	C6	2.0(9)	C22	C23	C24	C25	-0.3(8)
C3	C4	C5	C6	0.7(12)	C23	C22	C28	O1	-5.2(9)
C4	C5	C6	C7	0.4(12)	C23	C24	C25	C26	0.6(8)
C5	C6	C7	C2	-1.7(11)	C24	C25	C26	C21	-0.4(7)
C7	C2	C3	C4	-0.9(8)	C24	C25	C26	C27	-178.0(4)
C8	C1	C2	C3	-53.0(7)	C25	C26	C27	N1	-6.9(6)
C8	C1	C2	C7	131.0(5)	C26	C21	C22	C23	0.5(7)
C8	C1	C21	C22	112.6(6)	C26	C21	C22	C28	178.0(5)
C8	C1	C21	C26	-73.7(6)	C27	N1	C29	C30	-175.8(5)
C8	C9	C10	C11	-172.8(5)	C27	N1	C29	C34	5.5(7)
C8	C9	C14	C13	173.2(6)	C28	C22	C23	C24	-177.9(5)

Table S6 Torsion Angles for 3i.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C8	C15	C16	C17	174.4(7)	C29	N1	C27	C26	-78.3(6)
C8	C15	C20	C19	-174.7(6)	C29	C30	C31	C32	-0.4(7)
C9	C8	C15	C16	-36.7(7)	C30	C29	C34	C33	1.7(8)
C9	C8	C15	C20	137.3(5)	C30	C31	C32	Br1	-178.0(4)
C9	C10	C11	C12	-1.9(9)	C30	C31	C32	C33	0.9(7)
C10	C9	C14	C13	-0.5(9)	C31	C32	C33	C34	-0.2(8)
C10	C11	C12	C13	3.0(10)	C32	C33	C34	C29	-1.2(8)
C11	C12	C13	C14	-2.8(11)	C34	C29	C30	C31	-0.9(7)
C12	C13	C14	C9	1.5(10)					

Table S7 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3i.

Atom	x	y	z	U(eq)
H1	5594.03	5451.63	7226.38	79
H3	9124.5	-413.35	6712.75	90
H4	11270.81	-789.63	6846.74	112
H5	12158.98	477.44	7170.05	127
H6	10855.33	2128.48	7366.4	117
H7	8667.55	2438.07	7234.73	89
H10	8941.49	3185.19	6606.1	74
H11	10348.5	3682.98	6277.26	93
H12	10324.82	2393.98	5920.32	98
H13	8750.69	727.18	5872.35	107
H14	7294.47	203.14	6203.15	92

Table S7 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for 3i.

Atom	x	y	z	U(eq)
H16	5895.01	3112.5	6316.84	132
H17	3741.14	3206.87	6141.72	230
H18	2115.31	1610.27	6286.31	288
H19	2609.42	195.56	6568.99	250
H20	4697.13	-5.5	6744.26	141
H23	4915.79	-734.46	7503.28	80
H24	3937.1	1233.86	7632.43	81
H25	4389.81	3226.73	7425.13	74
H27A	6912.46	3965.36	7057.29	70
H27B	5785.56	3669.89	6853.32	70
H28	7047.63	-1221.99	6981.82	95
H30	3726.65	6906.97	7234.13	79
H31	1529.35	7356.98	7124.31	83
H33	1390.69	3903.58	6736.37	82
H34	3572.19	3426.18	6853.3	81

10. Reference

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