Supporting Information

Copper-catalyzed aerobic asymmetric cross-dehydrogenative coupling of C(sp^3)−H bonds driven by visible light

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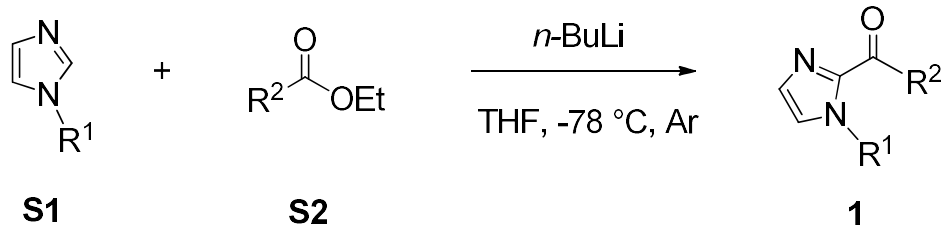
1. General Information

Synthesis of the substrates were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Visible-light-induced catalytic reactions were performed in 10 or 20 mL Schlenk tubes at the indicated temperature under an atmosphere of air and under irradiation with a 24 W blue LEDs lamp (λ_{max} = 455 nm; commercial supplier: Hong Chang Lighting Co. Ltd., website: http://hongchang-led.taobao.com). Solvents were distilled under argon from calcium hydride (CH_2Cl_2), calcium chloride ($CHCl_3$) or sodium/benzophenone (THF). Chiral BOX ligands **L1-L11** were purchased from Aldrich or J&K and used directly without further purification. All others reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa, Adamas-beta® and J&K) and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, pH = 6.7–7.0). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM (500 MHz) or Bruker AM (600 MHz) spectrometer at ambient temperature. NMR standards were used as follows: $CDCl_3$ = 7.26 ppm (^{1}H NMR), 77.0 ppm (^{13}C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. EPR spectra were recorded on a Bruker EMX-10/12. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 T FT-MS instrument using ESI technique. Optical rotations were measured on Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 in a 10.0 mm quartz cuvette. Cyclic voltammetry studies were carried out on a computer recorded on a CHI 760E potentiostat containing a glassy carbon disk working electrode (diameter, 1mm), scan range of ± 10 V and current range of ± 2 A. Enantiomeric excess of the products were determined by HPLC analysis on chiral stationary phases.

2. Synthesis of the Substrates and Racemic Reference Products

2.1 Synthesis of 2-acyl imidazoles

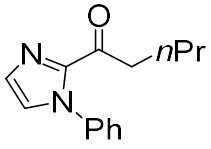
1f, **1g**, **1j**,[1] **1k**, **1p**, **1t**, **1s**,[2] **1r**[3] and **1u**[4] were prepared according to published procedures, **1h**, **1i**, **1l−1o**, **1q** and **1t** were prepared by a following method.



S1 **S2** **1**

Supplementary Scheme 1. Synthetic route to 2-acyl imidazoles.

General procedure A: To a solution of **S1** (1.0 eq) in dry tetrahydrofuran (THF, 0.60 M) under argon atmosphere at -78 ℃, *n*-BuLi in *n*-hexane (2.4 M, 1.1 eq) were added dropwise. The solution was warmed up and stirred at room temperature for 1 h. The reaction mixture was cooled to -78 ℃ and **S2** (2.5 eq) was added slowly. The mixture was warmed to room temperature again and stirred for additional 8 h, then quenched with a saturated solution of NH_4Cl. After removal of solvents by rotary evaporation, aqueous $NaHCO_3$ was added. The residue was extracted with dichloromethane (DCM) twice. The combined organic layers were dried by anhydrous Na_2SO_4, evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography (elution with petroleum ether: ethyl acetate = 20: 1 − 5: 1).



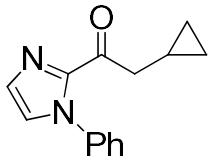
1h

According to **general procedure A**, 2-acyl imidazole **1h** was synthesized as a white solid (81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 3H), 7.26 (ddd, *J* = 8.1, 3.1, 1.7 Hz, 3H), 7.15 (d, *J* = 0.9 Hz, 1H), 3.17 – 3.12 (m, 2H), 1.69 – 1.59 (m, 2H), 1.37 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 142.9, 138.4, 129.3, 128.8, 128.6, 126.8, 125.8, 38.7, 25.9, 22.2, 13.7.

IR (film): ν (cm^{-1}) 3117, 3098, 2956, 1686, 1597, 1503, 1411, 1331, 1303, 1212, 1146, 951, 915, 789, 764, 694, 543.

HRMS (ESI, m/z) calcd for $C_{14}H_{16}N_2NaO$ $(M+Na)^+$: 251.1155, found: 251.1155.



1i

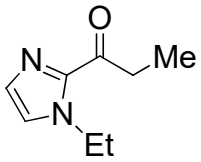
According to **general procedure A**, 2-acyl imidazole **1i** was synthesized as a white solid (73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 3H), 7.13 – 7.08 (m, 2H), 7.05 (d, J = 0.7 Hz, 1H), 6.98 (d, J = 0.8 Hz, 1H), 2.85 (d, J = 7.0 Hz, 2H), 0.97 – 0.86 (m, 1H), 0.37 – 0.30 (m, 2H), 0.01 (q, J = 4.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 142.9, 138.3, 129.4, 128.8, 128.5, 126.9, 125.8, 44.1, 6.2, 4.2.

IR (film): ν (cm^{-1}) 3135, 1718, 1685, 1579, 1498, 1409, 1396, 1210, 1142, 951, 793, 695, 542.

HRMS (ESI, m/z) calcd for $C_{14}H_{14}N_2NaO$ $(M+Na)^+$: 249.0998, found: 249.0999.



1l

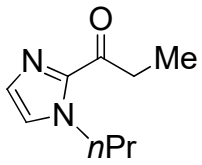
According to **general procedure A**, 2-acyl imidazole **1l** was synthesized as a yellow oil (79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.99 (s, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.02 (q, J = 7.4 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6, 141.6, 128.4, 124.4, 43.0, 31.8, 15.7, 7.5.

IR (film): ν (cm^{-1}) 3108, 2938, 2876, 1678, 1466, 1413, 1383, 1297, 1256, 1211, 1155, 1088, 1013, 943, 912, 768, 700, 667, 542.

HRMS (ESI, m/z) calcd for $C_8H_{12}N_2NaO$ $(M+Na)^+$: 175.0842, found: 175.0843.



1m

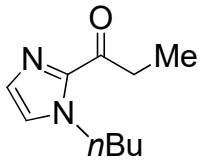
According to **general procedure A**, 2-acyl imidazole **1m** was synthesized as a yellow oil (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 2H), 4.27 – 4.20 (m, 2H), 3.03 (q, *J* = 7.4 Hz, 2H), 1.68 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 141.9, 128.3, 125.3, 49.7, 32.0, 23.9, 10.4, 7.6.

IR (film): ν (cm^{-1}) 3108, 2969, 2937, 1678, 1507, 1436, 1410, 1383, 1298, 1155, 1089, 1011, 950, 912, 769, 698, 608.

HRMS (ESI, m/z) calcd for $C_9H_{14}N_2NaO$ $(M+Na)^+$: 189.0998, found: 189.0998.



1n

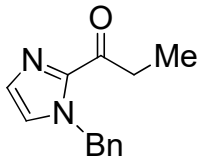
According to **general procedure A**, 2-acyl imidazole **1n** was synthesized as a yellow oil (76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 – 6.94 (m, 2H), 4.30 – 4.24 (m, 2H), 3.03 (q, *J* = 7.4 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.23 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 142.0, 128.4, 125.3, 48.0, 32.8, 32.1, 19.3, 13.2, 7.7.

IR (film): ν (cm^{-1}) 3107, 2961, 2936, 1678, 1464, 1411, 1383, 1301, 1235, 1155, 1089, 1012, 951, 911, 768, 698, 545.

HRMS (ESI, m/z) calcd for $C_{10}H_{16}N_2NaO$ $(M+Na)^+$: 203.1155, found: 203.1156.



1o

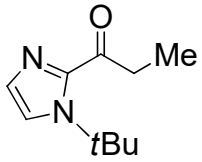
According to **general procedure A**, 2-acyl imidazole **1o** was synthesized as a light yellow oil (81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (ddd, *J* = 15.2, 7.8, 3.7 Hz, 3H), 7.13 (dd, *J* = 11.5, 3.8 Hz, 3H), 7.04 (s, 1H), 5.57 (s, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 142.0, 136.2, 128.8, 128.3, 127.5, 127.0, 125.3, 51.1, 32.1, 7.6.

IR (film): ν (cm^{-1}) 3065, 2937, 1678, 1460, 1411, 1380, 1292, 1148, 1011, 946, 911, 711, 582, 458.

HRMS (ESI, m/z) calcd for $C_{13}H_{14}N_2NaO$ $(M+Na)^+$: 237.0998, found: 237.0999.



1q

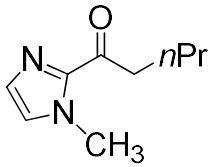
According to **general procedure A**, 2-acyl imidazole **1q** was synthesized as a white solid (73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.94 (s, 1H), 3.07 (q, *J* = 7.4 Hz, 2H), 1.55 (s, 9H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 143.8, 127.3, 122.9, 58.5, 33.7, 29.6, 8.3.

IR (film): ν (cm^{-1}) 3099, 2942, 2926, 1657, 1451, 1334, 1252, 1174, 1039, 955, 762, 676.

HRMS (ESI, m/z) calcd for $C_{10}H_{16}N_2NaO$ $(M+Na)^+$: 203.1155, found: 203.1157.



1t

According to **general procedure A**, 2-acyl imidazole **1t** was synthesized as a yellow oil (81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.93 (s, 1H), 3.88 (s, 3H), 3.06 – 2.93 (m, 2H), 1.57 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.28 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 142.6, 128.4, 126.4, 38.3, 35.7, 25.9, 22.0, 13.5.

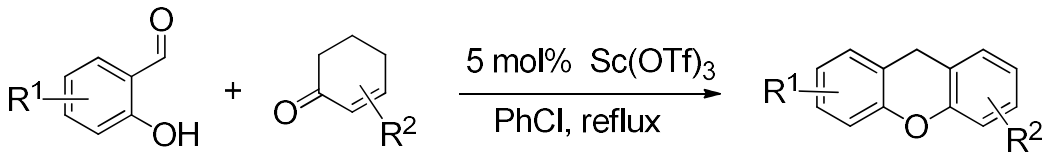
IR (film): ν (cm^{-1}) 3108, 2985, 2872, 1674, 1466, 1409, 1289, 1155, 1017, 968, 914, 768, 696, 610.

HRMS (ESI, m/z) calcd for $C_9H_{14}N_2NaO$ $(M+Na)^+$: 189.0998, found: 189.0996.

2.2 Synthesis of the xanthene derivatives

2e,[5] **2g**–**2j**, **2l**, **2n**,[6] **2o**,[7] and **2q**[8] were prepared by published procedures, **2b**–**2d**, **2f**, **2k, 2m, 2r-2w** were prepared by an analogous method,[6] **2p** was purchased from commercial supplier Sigma-Aldrich, **2x** was

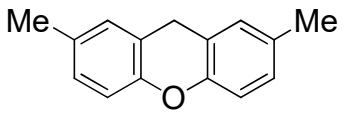
purchased from commercial supplier TCI.



S3 **S4** **2**

Supplementary Scheme 2. Synthetic route to the xanthene derivatives.

General procedure B: To a solution of scandium(III) triflate (5 mol%) and o-salicylaldehyde **S3** (1.1 eq) in PhCl (0.25 M) in a round bottom flask, α, β-unsaturated ketone **S4** (1.0 eq) was added. The reaction mixture was refluxed for 45 h (oil bath temperature: 165 °C), then cool to room temperature. DCM (20 mL) and saturated aqueous $NaHCO_3$ (20 mL) were added to the reaction mixture, and the two layers were separated. The aqueous phase was extracted with DCM (25 mL) and the combined organic layers were dried by anhydrous $MgSO_4$, filtered, and the solvent was removed by a rotary evaporator. Crude xanthene derivatives were purified by flash chromatography using *n*-hexane.



2b

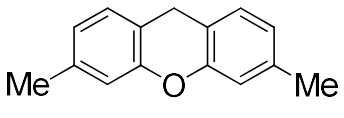
According to **general procedure B**, **2b** was synthesized as a white solid (37% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 – 6.93 (m, 4H), 6.91 (d, J = 8.2 Hz, 2H), 3.95 (s, 2H), 2.29 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 132.0, 129.2, 128.1, 120.1, 116.1, 27.8, 20.6.

IR (film): ν (cm^{-1}) 3029, 2921, 2871, 1685, 1654, 1579, 1491, 1388, 1260, 1209, 1125, 961, 879, 817.

HRMS (ESI, m/z) calcd for $C_{15}H_{14}NaO$ $(M+Na)^+$: 233.0937, found: 233.0941.



2c

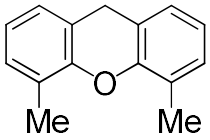
According to **general procedure B**, **2c** was synthesized as an off-white solid (41% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (t, J = 6.3 Hz, 2H), 6.90 – 6.75 (m, 4H), 3.95 (s, 2H), 2.32 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 137.5, 128.6, 123.6, 117.5, 116.8, 27.2, 21.0.

IR (film): ν (cm^{-1}) 2912, 2832, 1870, 1773, 1718, 1670, 1593, 1560, 1499, 1474, 1247, 1188, 879, 802.

HRMS (ESI, m/z) calcd for $C_{15}H_{14}NaO$ $(M+Na)^+$: 233.0937, found: 233.0941.



2d

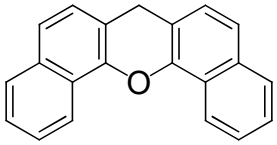
According to **general procedure B**, **2d** was synthesized as a white solid (36% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.3, 0.7 Hz, 2H), 7.03 (d, *J* = 6.9 Hz, 2H), 6.97 – 6.93 (m, 2H), 4.03 (s, 2H), 2.41 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 128.8, 126.2, 125.7, 122.3, 120.5, 28.3, 15.8.

IR (film): ν (cm^{-1}) 2916, 2854, 1772, 1677, 1641, 1561, 1494, 1389, 1274, 1151, 984, 886, 806.

HRMS (ESI, m/z) calcd for $C_{15}H_{14}NaO$ $(M+Na)^+$: 233.0937, found: 233.0939.



2f

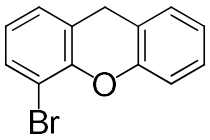
According to **general procedure B**, **2f** was synthesized as a white solid (39% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 133.4, 127.6, 126.7, 125.9, 125.9, 124.4, 122.6, 121.4, 114.2, 28.4.

IR (film): ν (cm^{-1}) 3072, 2923, 2898, 1670, 1629, 1569, 1541, 1508, 1396, 1304, 1258, 1205, 1101, 1025, 979, 798.

HRMS (ESI, m/z) calcd for $C_{21}H_{15}O$ $(M+H)^+$: 283.1117, found: 283.1120.



2k

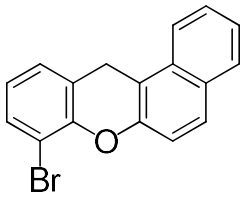
According to **general procedure B**, **2k** was synthesized as an off-white solid (42% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 1H), 7.23 – 7.17 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.05 (dtd, *J* = 8.5, 7.5, 1.1 Hz, 2H), 6.86 (t, *J* = 7.7 Hz, 1H), 4.02 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 148.8, 131.4, 128.6, 127.9, 127.8, 123.6, 123.5, 122.5, 120.3, 116.8, 110.7, 28.2.

IR (film): ν (cm^{-1}) 3021, 2924, 2876, 1654, 1629, 1577, 1489, 1451, 1272, 1247, 1177, 1100, 890, 751.

HRMS (ESI, m/z) calcd for $C_{13}H_9BrNaO$ $(M+Na)^+$: 282.9729, found: 282.9742.



2m

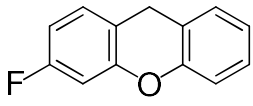
According to **general procedure B**, **2m** was synthesized as a white solid (33% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.2, 4.0 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.27 (s, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 4.41 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 148.0, 131.7, 131.6, 130.4, 128.54, 128.52, 128.4, 126.8, 124.4, 123.8, 122.3, 121.4, 117.9, 111.5, 110.8, 25.2.

IR (film): ν (cm^{-1}) 3095, 2924, 2863, 1647, 1629, 1574, 1541, 1400, 1253, 1218, 1176, 1135, 1095, 971, 891, 807.

HRMS (ESI, m/z) calcd for $C_{17}H_{11}BrNaO$ $(M+Na)^+$: 332.9885, found: 332.9890.



2n

According to **general procedure B**, **2n** was synthesized as a white solid (33% yield).

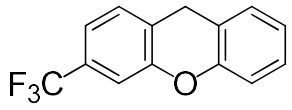
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (ddd, *J* = 8.2, 1.6, 0.8 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.08 (m,

1H), 7.07 – 7.02 (m, 2H), 6.76 (ddd, *J* = 10.9, 9.4, 2.6 Hz, 2H), 4.01 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 248.2 Hz), 152.6, 152.5, 151.4, 129.6 (d, *J* = 3.12 Hz), 128.3 (d, *J* = 148.1 Hz), 123.3, 120.2, 116.4, 116.2 (d, *J* = 3.2 Hz), 110.0 (d, *J* = 22.1 Hz), 103.9 (d, *J* = 24.9 Hz), 27.3.

IR (film): ν (cm^{-1}) 3102, 2965, 2844, 1722, 1665, 1578, 1501, 1394, 1327, 1213, 1184, 1165, 1075, 989, 813.

HRMS (ESI, m/z) calcd for $C_{13}H_9FNaO$ $(M+Na)^+$: 223.0530, found: 223.0527.



2o

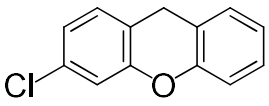
According to **general procedure B**, **2o** was synthesized as a white solid (15% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 7.12 (dd, *J* = 4.9, 3.1 Hz, 2H), 7.05 – 6.94 (m, 3H), 3.94 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 151.4, 130.2 (q, *J* = 58.2, 33.0 Hz), 130.1, 129.5, 129.4, 128.9, 128.0, 123.9(q, *J* = 271.6 Hz), 119.6, 119.5 (q, *J* = 3.8 Hz), 114.2 (q, *J* = 7.9 Hz), 113.8 (q, *J* = 4.2 Hz), 27.8.

IR (film): ν (cm^{-1}) 3149, 3042, 2768, 1788, 1623, 1567, 1510, 1477, 1242, 1196, 1156, 1078, 1034, 978, 846.

HRMS (ESI, m/z) calcd for $C_{14}H_9F_3NaO$ $(M+Na)^+$: 273.0498, found: 273.0497.



2p

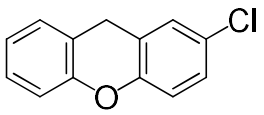
According to **general procedure B**, **2p** was synthesized as a white solid (40% yield).'

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 1H), 7.16 (dd, *J* = 4.9, 4.1 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.03 – 6.99 (m, 3H), 6.98 – 6.95 (m, 1H), 3.96 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 151.4, 132.6, 129.7, 128.9, 127.8, 123.3, 123.0, 120.0, 119.0, 116.7, 116.5, 27.3.

IR (film): ν (cm^{-1}) 3092, 2935, 2847, 1711, 1632, 1589, 1510, 1429, 1217, 1178, 1142, 1075, 946, 878, 739.

HRMS (ESI, m/z) calcd for $C_{13}H_9ClNaO$ $(M+Na)^+$: 239.0234, found: 239.0235.



2q

According to **general procedure B**, **2q** was synthesized as a white solid (37% yield).

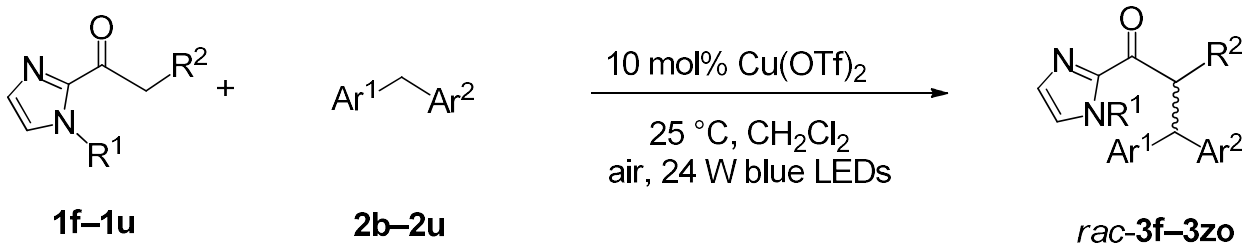
^1H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 7.18 – 7.12 (m, 3H), 7.06 – 7.01 (m, 2H), 6.99 – 6.95 (m, 1H), 4.02 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 150.5, 128.9, 128.5, 127.8, 127.6, 127.6, 123.2, 122.2, 119.6, 117.8, 116.5, 27.7.

IR (film): ν (cm^{-1}) 3087, 2946, 2871, 1639, 1603, 1538, 1489, 1422, 1235, 1181, 1159, 1057, 946, 879, 803.

HRMS (ESI, m/z) calcd for $C_{13}H_9ClNaO$ $(M+Na)^+$: 239.0234, found: 239.0235.

2.3 Synthesis of the racemic products as references



1f–1u **2b–2u** *rac*-**3f–3zo**

Supplementary Scheme 3. Synthesis of racemic reference compounds *rac*-**3f−3zo.**

General procedure C: A dried 10 mL Schlenk tube was charged with **1f–1u** (0.10 mmol), xanthene derivatives or other diaryl methane derivatives (0.20 mmol, **2b–2u**), $Cu(OTf)_2$ (3.62 mg, 0.010 mol), and freshly distilled CH_2Cl_2 (1.0 mL). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for the 15–30 h (monitored by TLC analysis), the

reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with petroleum ether (PE): ethyl acetate (EA) = 5: 1 or petroleum ether (PE): dichloromethane (DCM) = 1: 1) to afford racemic product *rac*-**3f–3zo** as the HPLC reference for determination of enantiomeric excess and diastereomeric ratio.

3. Copper-Catalyzed Aerobic Asymmetric Cross-dehydrogenation Coupling Reactions

3.1 Optimization of conditions for asymmetric cross-dehydrogenation coupling reactions

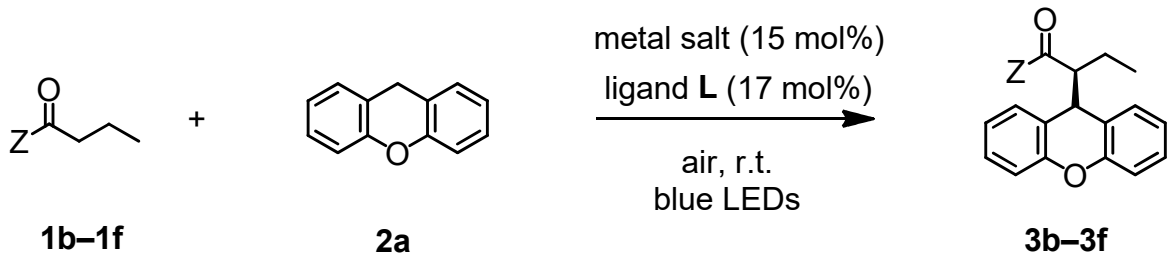
3.1.1 Preparation of 15 mM solutions of non-racemic metal catalyst [M-L1–L11] in CH_2Cl_2 and other solvents

A solution of metal salt (0.015 mmol) and chiral ligands **L1–L11** (0.017 mmol) in CH_2Cl_2 or others solvents (1.0 mL) was stirred at 35 °C for 1 h, which was used freshly for the catalytic reactions.

3.1.2 General procedure D

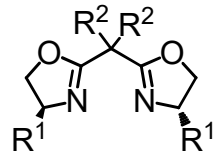
A dried 10 mL Schlenk tube was charged with 2-acyl imidazole **1b–1f** (0.10 mmol), xanthene **2a** (0.20 mmol), metal catalyst (0.015 mol, 1.0 mL taken from the 15 mM solution in the indicated solvent). The Schlenk tube was positioned approximately 5 cm away from the indicated light source in air. After being stirred at the indicated temperature for the indicated time, the reaction mixture was concentrated to dryness. The conversion was determined by ^{1}H NMR analysis of the crude product, and ee value was determined by chiral HPLC chromatography using a Daicel Chiralpak OD-H column or other chiral columns.

Supplementary Table 1. Optimization of conditions for the copper-catalyzed photocatalytic aerobic enantioselective cross-dehydrogenative coupling reaction.[a]

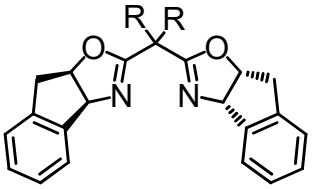


1b–1f **2a** **3b–3f**

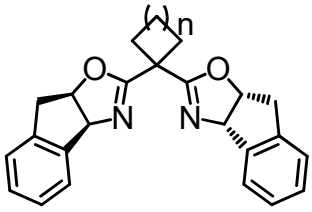
Z = **1b** **1c** **1d** **1e** **1f**



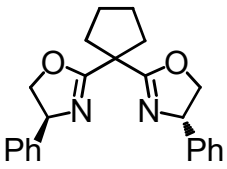
L1: R^1 = Ph, R^2 = Me
L2: R^1 = *i*Pr, R^2 = Me
L3: R^1 = Ph, R^2 = Bn
L4: R^1 = Ph, R^2 = CH_2Ph(4-*t*Bu)



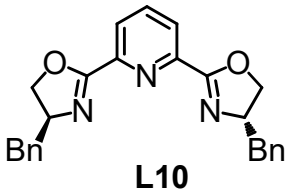
L5: R = Me
L6: R = CH_2Ph(3,5-*t*Bu)



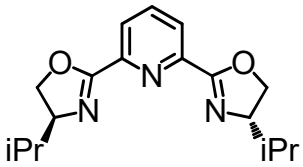
L7: n = 0
L8: n = 2



L9



L10



L11

Entry	Metal salt	Ligand	Subs.	Solvents	T (°C)	t (h)	Prod.	Conv. (%) [b]	Ee. (%) [c]
1	$Cu(OTf)_2$	**L1**	**1b**	DCM	25	24	**3b**	68	11
2	$Cu(OTf)_2$	**L1**	**1c**	DCM	25	24	**3c**	47	5
3	$Cu(OTf)_2$	**L1**	**1d**	DCM	25	24	**3d**	34	0
4	$Cu(OTf)_2$	**L1**	**1e**	DCM	25	24	**3e**	49	3
5	$Cu(OTf)_2$	**L1**	**1f**	DCM	25	24	**3f**	40	38
6 [d]	$Cu(OTf)_2$	**L1**	**1f**	DCM	25	24	**3f**	0	n.a
7	$Cu(OTf)_2$	none	**1f**	DCM	25	24	**3f**	57	0
8	none	**L1**	**1f**	DCM	25	24	**3f**	0	n.a

9	$Ni(OTf)_2$	**L1**	**1f**	DCM	25	24	**3f**	0	n.a
10	$Mg(OTf)_2$	**L1**	**1f**	DCM	25	24	**3f**	0	n.a
11	$Zn(OTf)_2$	**L1**	**1f**	DCM	25	24	**3f**	0	n.a
12	$Cu(OTf)_2$	**L1**	**1f**	DCM	25	48	**3f**	71	38
13	$Cu(OTf)_2$	**L2**	**1f**	DCM	25	48	**3f**	68	32
14	$Cu(OTf)_2$	**L3**	**1f**	DCM	25	48	**3f**	69	41
15	$Cu(OTf)_2$	**L4**	**1f**	DCM	25	48	**3f**	55	7
16	$Cu(OTf)_2$	**L5**	**1f**	DCM	25	48	**3f**	68	33
17	$Cu(OTf)_2$	**L6**	**1f**	DCM	25	48	**3f**	59	23
18	$Cu(OTf)_2$	**L7**	**1f**	DCM	25	48	**3f**	71	70
19	$Cu(OTf)_2$	**L8**	**1f**	DCM	25	48	**3f**	69	41
20	$Cu(OTf)_2$	**L9**	**1f**	DCM	25	48	**3f**	73	26
21	$Cu(OTf)_2$	**L10**	**1f**	DCM	25	48	**3f**	57	0
22	$Cu(OTf)_2$	**L11**	**1f**	DCM	25	48	**3f**	56	0
23	$Cu(OTf)_2$	**L7**	**1f**	DCE	25	48	**3f**	68	65
24	$Cu(OTf)_2$	**L7**	**1f**	$CHCl_3$	25	48	**3f**	73	70
25	$Cu(OTf)_2$	**L7**	**1f**	THF	25	48	**3f**	76	73
26	$Cu(OTf)_2$	**L7**	**1f**	1,4-dioaxne	25	48	**3f**	51	77
27	$Cu(OTf)_2$	**L7**	**1f**	acetone	25	48	**3f**	74	89
28	$Cu(OTf)_2$	**L7**	**1f**	CH_3CN	25	48	**3f**	77	84
29	$Cu(OTf)_2$	**L7**	**1f**	EtOH	25	48	**3f**	0	n.a
30	$Cu(OTf)_2$	**L7**	**1f**	$PhCF_3$	25	48	**3f**	53	65
31	$Cu(acac)_2$	**L7**	**1f**	acetone	25	48	**3f**	trace	n.a
32	$Cu(MeCN)_4BF_4$	**L7**	**1f**	acetone	25	48	**3f**	57	91
33	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	25	48	**3f**	76	92
34 [e]	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	25	48	**3f**	78	92
35 [e]	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	0	48	**3f**	32	93
36 [e]	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	-20	48	**3f**	6	92
37 [e, f]	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	25	24	**3f**	45	92
38 [e, g]	$Cu(BF_4)_2.H_2O$	**L7**	**1f**	acetone	25	24	**3f**	0	n.a

[a] Reaction conditions: **1b–f** (0.10 mmol), **2a** (0.20 mmol), metal salt (15 mol%), ligand (17 mol%), indicated solvents (1.0 mL), indicated temperature, indicated light source, under air. [b] Conversion and d.r. determined by ^{1}H-NMR. [c] Ee value determined by chiral HPLC. [d] In the dark. [e] **1f** (0.10 mmol), **2a** (0.30 mmol). [f] In the presence of 2.0 mol% $[Ru(bpy)_3](PF_6)_2$. [g] In the presence of 3 eq TEMPO. n.a. = not applicable.

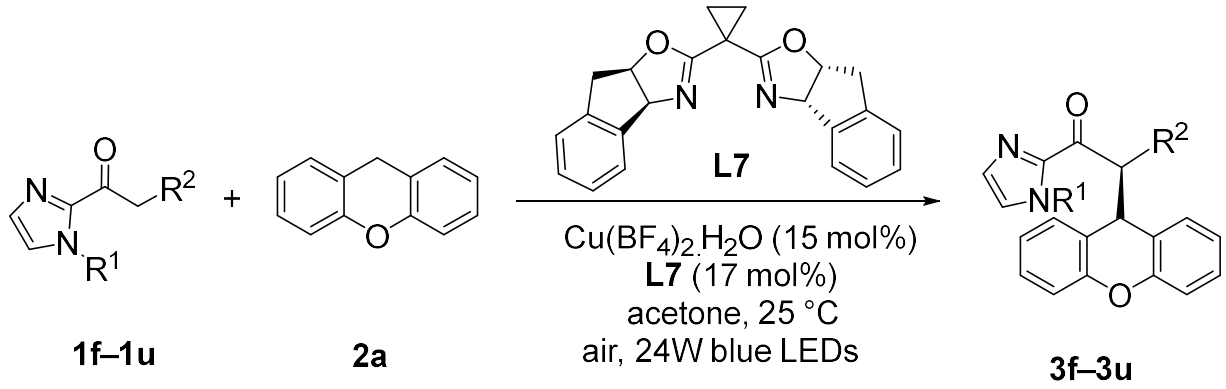
3.2 Substrate scope with regards to 2-acyl imidazoles

3.2.1 Preparation of 15 mM solution of non-racemic copper catalyst [Cu^{II}-L7] in acetone

A solution of $Cu(BF_4)_2 \cdot H_2O$ (38.2 mg, 0.15 mmol) and non-racemic BOX ligand **L7** (60.4 mg, 0.17 mmol) in acetone (10.0 mL) was stirred at 35 ℃ for 1 h, which was used freshly for the catalytic reactions.

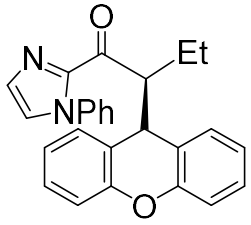
3.2.2 General procedure E

A dried 10 mL Schlenk tube was charged with **1f–1u** (0.20 mmol), xanthene (0.60 mmol), chiral copper catalyst [**Cu^{II}-L7**] (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for the indicated time, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1 or elution with PE: DCM = 1: 1) to afford non-racemic product **3f–3u**.



Supplementary Scheme 4. Copper-catalyzed asymmetric photoredox reaction to afford non-racemic products **3f–3u**.

3.2.3 Experimental details and characterization data



3f

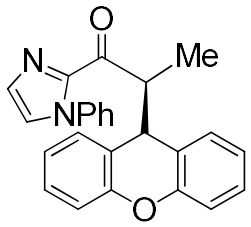
A dried 10 mL Schlenk tube was charged with **1f** (42.8 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3f** (56.0 mg, 0.142 mmol, yield: 71%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 92% (HPLC: IA, 220 nm, *n*-hexane/isopropanol = 98:2, flow rate: 0.4 mL/min, 30 °C, t_r(major) = 16.7 min, t_r(minor) = 17.5 min. $[\alpha]_D^{23}$ = +40.4° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.27 (dd, *J* = 7.2, 2.3 Hz, 3H), 7.21 – 7.13 (m, 3H), 7.07 (dd, *J* = 7.6, 4.3 Hz, 3H), 6.99 (q, *J* = 7.2 Hz, 3H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.09 (ddd, *J* = 10.5, 6.7, 3.6 Hz, 1H), 1.56 (ddd, *J* = 14.5, 9.0, 5.0 Hz, 1H), 1.40 (ddd, *J* = 13.5, 7.5, 3.7 Hz, 1H), 0.69 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 156.2, 153.2, 143.7, 138.6, 134.9, 129.6, 128.9, 128.7, 127.9, 127.7, 127.0, 126.8, 126.1, 124.8, 123.9, 122.9, 122.7, 118.0, 116.5, 56.5, 42.4, 21.2, 11.9.

IR (film): ν (cm^{-1}) 2967, 2871, 2813, 1958, 1734, 1653, 1640, 1560, 1458, 1406, 1255, 1097, 953, 754, 475.

HRMS (ESI, m/z) calcd for $C_{26}H_{22}N_2NaO_2$ $(M+Na)^+$: 417.1573, found: 417.1578.



3g

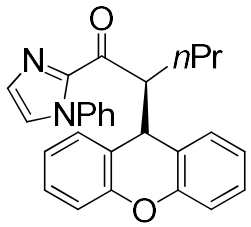
A dried 10 mL Schlenk tube was charged with **1g** (40.0 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE : EA = 5 : 1) to afford product **3g** (56.3 mg, 0.148 mmol, yield: 74%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 92% (HPLC: IC, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 30 °C, t_r(major) = 10.6 min, t_r(minor) = 21.8 min. $[\alpha]_D^{23}$ = +74.9° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 3H), 7.37 – 7.31 (m, 1H), 7.29 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 7.13 (s, 1H), 7.09 (dd, *J* = 7.8, 4.2 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.94 (m, 2H), 4.59 (d, *J* = 6.6 Hz, 1H), 4.14 (p, *J* = 6.9 Hz, 1H), 0.92 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.9, 153.3, 153.1, 142.8, 138.5, 129.6, 129.5, 129.0, 128.9, 128.7, 127.9, 127.7, 127.0, 126.0, 124.9, 123.0, 122.7, 122.6, 116.4, 116.4, 49.9, 42.3, 12.8.

IR (film): ν (cm^{-1}) 2917, 2840, 1773, 1718, 1685, 1617, 1576, 1478, 1401, 1254, 1097, 950, 754, 691.

HRMS (ESI, m/z) calcd for $C_{25}H_{20}N_2NaO_2$ $(M+Na)^+$: 403.1417, found: 403.1423.



3h

A dried 10 mL Schlenk tube was charged with **1h** (45.6 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for

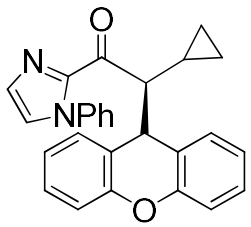
48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3h** (55.5 mg, 0.136 mmol, yield: 68%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 87% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.45 mL/min, 30 °C, t_r(major) = 11.0 min, t_r(minor) = 11.9 min. $[\alpha]_D^{23}$ = +37.9° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 3H), 7.28 – 7.25 (m, 3H), 7.21 – 7.13 (m, 3H), 7.07 (t, *J* = 6.7 Hz, 3H), 7.02 – 6.96 (m, 3H), 4.40 (d, *J* = 6.6 Hz, 1H), 4.17 (ddd, *J* = 10.4, 6.6, 3.4 Hz, 1H), 1.29 (ddd, *J* = 13.9, 8.0, 4.9 Hz, 2H), 1.16 – 1.05 (m, 1H), 1.01 (ddd, *J* = 16.5, 10.0, 5.0 Hz, 1H), 0.70 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 153.2, 153.1, 143.6, 138.6, 129.6, 129.5, 128.9, 128.8, 128.7, 127.8, 127.6, 127.0, 126.0, 124.6, 123.3, 122.9, 122.6, 116.42, 116.36, 54.7, 42.6, 30.2, 20.7, 14.2.

IR (film): ν (cm^{-1}) 2918, 2850, 1734, 1675, 1617, 1576, 1478, 1401, 1302, 1254, 1095, 891, 755, 695.

HRMS (ESI, m/z) calcd for $C_{27}H_{24}N_2NaO_2$ $(M+Na)^+$: 431.1730, found: 431.1733.



3i

A dried 10 mL Schlenk tube was charged with **1i** (45.2 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3i** (50.3 mg, 0.124 mmol, yield: 62%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 90% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, t_r(major) = 11.4 min, t_r(minor) = 12.0 min. $[\alpha]_D^{23}$ = +32.9° (*c* = 1.0, CH_2Cl_2).

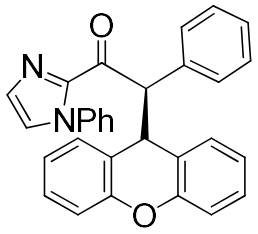
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.28 (dd, *J* = 6.4, 3.7 Hz, 2H), 7.22 – 7.12 (m, 5H), 7.09 – 7.05 (m, 3H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.94 (m, 1H), 4.58 (d, *J* = 7.6 Hz, 1H), 3.34 (dd, *J* =

10.4, 7.6 Hz, 1H), 0.91 – 0.82 (m, 1H), 0.31 – 0.24 (m, 2H), 0.07 (ddd, *J* = 9.5, 4.9, 3.0 Hz, 1H), -0.35 – -0.45 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 153.3, 153.2, 143.4, 138.5, 130.0, 129.6, 128.9, 128.8, 128.7, 127.8, 127.6, 127.1, 126.0, 124.9, 123.7, 122.8, 122.7, 116.4, 116.1, 59.4, 42.6, 10.9, 5.4, 2.6.

IR (film): ν (cm^{-1}) 2941, 2833, 1759, 1673, 1561, 1449, 1403, 1323, 1254, 1094, 903, 781, 711.

HRMS (ESI, m/z) calcd for $C_{27}H_{22}N_2NaO_2$ $(M+Na)^+$: 429.1573, found: 429.1575.



3j

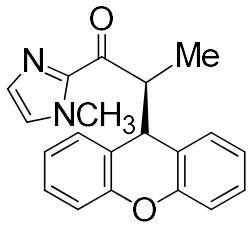
A dried 10 mL Schlenk tube was charged with **1j** (52.5 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3j** (43.3 mg, 0.098 mmol, yield: 49%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 58% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 30 °C, t_r(major) = 15.0 min, t_r(minor) = 26.0 min. $[\alpha]_D^{23}$ = +19.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 3H), 7.24 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.20 – 7.14 (m, 6H), 7.13 – 7.04 (m, 6H), 7.01 – 6.96 (m, 2H), 6.65 – 6.59 (m, 1H), 6.35 (d, *J* = 7.4 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.65 (d, *J* = 10.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 153.6, 153.3, 143.0, 138.4, 136.4, 129.9, 129.8, 129.5, 129.3, 128.9, 128.7, 128.2, 127.7, 127.5, 127.2, 127.1, 125.8, 125.0, 123.8, 122.6, 122.2, 116.7, 116.1, 60.2, 43.8.

IR (film): ν (cm^{-1}) 2921, 2842, 1730, 1677, 1654, 1571, 1463, 1403, 1371, 1266, 1077, 898, 751, 692.

HRMS (ESI, m/z) calcd for $C_{30}H_{22}N_2NaO_2$ $(M+Na)^+$: 465.1573, found: 465.1576.



3k

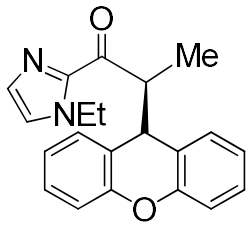
A dried 10 mL Schlenk tube was charged with **1k** (27.6 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3k** (46.5 mg, 0.146 mmol, yield: 73%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.7 mL/min, 30 °C, t_r(major) = 11.3 min, t_r(minor) = 13.3 min. $[\alpha]_D^{23}$ = +21.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.7 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.08 (dd, *J* = 15.8, 6.4 Hz, 3H), 7.04 – 6.98 (m, 3H), 6.92 (d, *J* = 7.4 Hz, 1H), 4.64 (d, *J* = 5.8 Hz, 1H), 4.15 (p, *J* = 6.8 Hz, 1H), 3.99 (s, 3H), 0.94 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.4, 153.3, 153.0, 142.9, 129.4, 129.2, 128.9, 128.0, 127.7, 126.8, 124.7, 123.1, 122.7, 122.4, 116.4, 116.3, 50.2, 42.4, 36.2, 12.1.

IR (film): ν (cm^{-1}) 2918, 2850, 1752, 1701, 1653, 1576, 1478, 1406, 1256, 1096, 964, 755, 610.

HRMS (ESI, m/z) calcd for $C_{20}H_{18}N_2NaO_2$ $(M+Na)^+$: 341.1260, found: 341.1275.



3l

A dried 10 mL Schlenk tube was charged with **1l** (30.4 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h

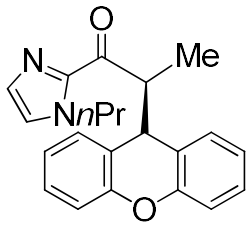
under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3l** (41.9 mg, 0.126 mmol, yield: 63%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 88% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 8.7 min, t_r(minor) = 9.7 min. $[\alpha]_D^{23}$ = +18.9° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.13 (s, 1H), 7.10 – 7.05 (m, 3H), 7.01 (dtd, *J* = 8.7, 7.4, 1.2 Hz, 2H), 6.91 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 4.49 (d, *J* = 7.2 Hz, 2H), 4.22 – 4.13 (m, 1H), 1.44 (t, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.1, 153.3, 153.0, 142.2, 129.44, 129.36, 128.9, 127.9, 127.6, 125.2, 124.7, 123.1, 122.6, 122.4, 116.4, 116.3, 50.3, 43.8, 42.4, 16.4, 12.1.

IR (film): ν (cm^{-1}) 2919, 2850, 1773, 1719, 1654, 1617, 1576, 1530, 1458, 1406, 1256, 1097, 951, 914, 755.

HRMS (ESI, m/z) calcd for $C_{21}H_{20}N_2NaO_2$ $(M+Na)^+$: 355.1417, found: 355.1421.



3m

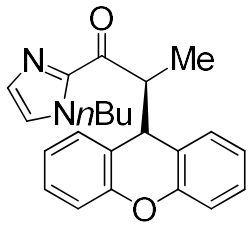
A dried 10 mL Schlenk tube was charged with **1m** (33.4 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3m** (42.2 mg, 0.122 mmol, yield: 61%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 84% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, t_r(major) = 9.4 min, t_r(minor) = 10.5 min. $[\alpha]_D^{23}$ = +29.9° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.09 (dd, *J* = 18.9, 9.6 Hz, 3H), 7.05 – 6.97 (m, 3H), 6.93 – 6.88 (m, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.38 (dt, *J* = 14.3, 7.2 Hz, 1H), 4.33 – 4.26 (m, 1H), 4.18 (p, *J* = 6.9 Hz, 1H), 1.88 – 1.78 (m, 2H), 0.94 (dd, *J* = 15.6, 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.2, 153.3, 153.0, 142.3, 129.5, 129.2, 128.9, 128.0, 127.7, 126.0, 124.8, 123.1, 122.6, 122.4, 116.4, 116.3, 50.4, 50.3, 42.4, 24.3, 12.2, 11.0.

IR (film): ν (cm^{-1}) 2898, 2812, 1719, 1654, 1641, 1494, 1458, 1384, 1255, 1098, 964, 916, 754.

HRMS (ESI, m/z) calcd for $C_{22}H_{22}N_2NaO_2$ $(M+Na)^+$: 369.1573, found: 369.1587.



3n

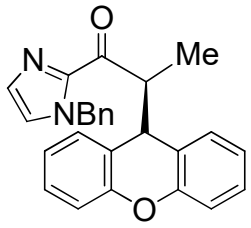
A dried 10 mL Schlenk tube was charged with **1n** (36.0 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3n** (43.0 mg, 0.120 mmol, yield: 58%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 85% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.4 mL/min, 30 °C, t_r(major) = 12.4 min, t_r(minor) = 13.1 min. $[\alpha]_D^{23}$ = +23.0° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dt, *J* = 7.9, 4.0 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.09 (dd, *J* = 18.1, 9.0 Hz, 3H), 7.04 – 6.97 (m, 3H), 6.93 – 6.88 (m, 1H), 4.68 (d, *J* = 6.0 Hz, 1H), 4.43 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.35 – 4.28 (m, 1H), 4.20 – 4.14 (m, 1H), 1.81 – 1.73 (m, 2H), 1.37 (dd, *J* = 15.2, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.1, 153.3, 153.0, 142.2, 134.8, 129.4, 129.2, 128.9, 127.9, 127.6, 125.9, 123.1, 122.5, 122.4, 116.4, 116.2, 50.3, 48.6, 42.4, 33.1, 19.7, 13.7, 12.1.

IR (film): ν (cm^{-1}) 2920, 2856, 1735, 1719, 1685, 1577, 1458, 1406, 1256, 1098, 966, 914, 755.

HRMS (ESI, m/z) calcd for $C_{22}H_{22}N_2NaO_2$ $(M+Na)^+$: 383.1730, found: 383.1735.



3o

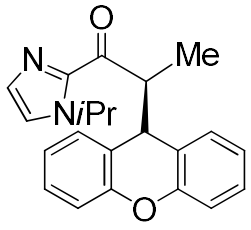
A dried 10 mL Schlenk tube was charged with **1o** (42.8 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: DCM = 1: 1) to afford product **3o** (52.7 mg, 0.134 mmol, yield: 67%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 88% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(minor) = 11.5 min, t_r(major) = 14.2 min. $[\alpha]_D^{23}$ = +29.7° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 4H), 7.18 (ddd, *J* = 15.5, 9.6, 4.2 Hz, 5H), 7.11 (s, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (td, *J* = 7.5, 0.9 Hz, 1H), 6.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.77 (d, *J* = 14.9 Hz, 1H), 5.50 (d, *J* = 14.9 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 1H), 4.19 (dd, *J* = 6.8, 5.6 Hz, 1H), 0.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.1, 153.2, 152.9, 142.2, 136.5, 134.8, 129.5, 129.4, 128.9, 128.8, 128.0, 127.8, 127.6, 127.5, 126.2, 123.2, 122.6, 121.8, 116.3, 116.2, 51.9, 50.4, 42.1, 11.5.

IR (film): ν (cm^{-1}) 2918, 2850, 1734, 1701, 1664, 1617, 1577, 1495, 1457, 1256, 1098, 965, 913, 755, 713.

HRMS (ESI, m/z) calcd for $C_{26}H_{22}N_2NaO_2$ $(M+Na)^+$: 417.1573, found: 417.1586.



3p

A dried 10 mL Schlenk tube was charged with **1p** (33.4 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for

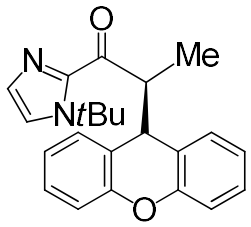
48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3p** (44.3 mg, 0.128 mmol, yield: 64%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 87% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(minor) = 8.2 min, t_r(major) = 9.1 min. $[\alpha]_D^{23}$ = +24.3° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.24 – 7.12 (m, 4H), 7.08 (t, *J* = 8.7 Hz, 2H), 7.00 (tdd, *J* = 7.4, 2.9, 1.1 Hz, 2H), 6.94 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.52 (hept, *J* = 6.7 Hz, 1H), 4.63 (d, *J* = 6.0 Hz, 1H), 4.20 (p, *J* = 6.9 Hz, 1H), 1.46 (dd, *J* = 9.2, 6.7 Hz, 6H), 0.95 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 153.3, 153.0, 142.2, 129.6, 129.4, 128.9, 127.9, 127.6, 124.8, 123.1, 122.59, 122.57, 121.0, 116.4, 116.2, 50.5, 49.1, 42.5, 23.7, 23.6, 12.3.

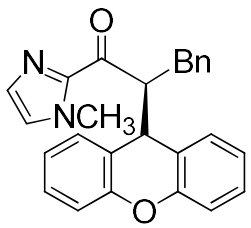
IR (film): ν (cm^{-1}) 2918, 2847, 1751, 1654, 1630, 1577, 1478, 1401, 1255, 1092, 959, 915, 756.

HRMS (ESI, m/z) calcd for $C_{23}H_{24}N_2NaO_2$ $(M+Na)^+$: 369.1573, found: 369.1588.



3q

A dried 10 mL Schlenk tube was charged with **1q** (36.0 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, compound **3q** was not formed (detected by TLC and ^{1}H NMR analysis).



3r

A dried 10 mL Schlenk tube was charged with **1r** (43.0 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube

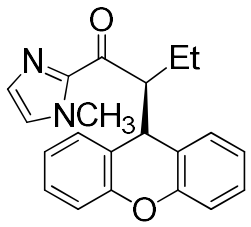
was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3r** (52.0 mg, 0.132 mmol, yield: 66%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 87% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 10.9 min, t_r(minor) = 13.2 min. $[\alpha]_D^{23}$ = +20.5° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 1H), 7.26 – 7.18 (m, 3H), 7.08 (dq, *J* = 11.4, 3.8 Hz, 5H), 7.05 – 7.02 (m, 2H), 6.99 (dd, *J* = 8.9, 1.7 Hz, 2H), 6.94 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.90 (s, 1H), 4.69 (d, *J* = 4.9 Hz, 1H), 4.56 (ddd, *J* = 11.3, 4.8, 3.6 Hz, 1H), 3.90 (s, 3H), 2.90 (dd, *J* = 13.9, 11.4 Hz, 1H), 2.68 (dd, *J* = 13.9, 3.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 153.0, 152.9, 143.4, 139.8, 129.4, 129.1, 128.9, 128.8, 128.1, 128.0, 127.9, 126.6, 125.7, 123.9, 123.3, 122.8, 122.1, 116.4, 116.3, 57.4, 42.4, 36.0, 32.2.

IR (film): ν (cm^{-1}) 2918, 2849, 1734, 1683, 1654, 1577, 1478, 1406, 1255, 1096, 757, 703, 611.

HRMS (ESI, m/z) calcd for $C_{26}H_{22}N_2NaO_2$ $(M+Na)^+$: 417.1573, found: 417.1586.



3s

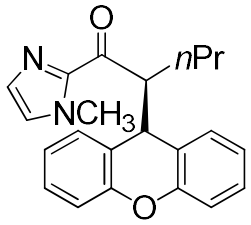
A dried 10 mL Schlenk tube was charged with **1s** (30.4 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3s** (46.4 mg, 0.140 mmol, yield: 70%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 9.0 min, t_r(minor) = 11.1 min. $[\alpha]_D^{23}$ = +18.5° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.19 (ddd, *J* = 8.7, 7.0, 2.0 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.08 – 7.03 (m, 3H), 7.03 – 6.96 (m, 3H), 6.95 (s, 1H), 4.46 (d, *J* = 6.0 Hz, 1H), 4.08 (ddd, *J* = 10.8, 6.0, 3.6 Hz, 1H), 3.98 (s, 3H), 1.69 – 1.61 (m, 1H), 1.46 – 1.38 (m, 1H), 0.71 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.2, 153.1, 153.1, 143.8, 129.4, 129.1, 128.8, 127.9, 127.7, 126.7, 124.5, 123.0, 122.9, 122.7, 116.3, 116.3, 56.8, 42.5, 36.2, 20.5, 12.0.

IR (film): ν (cm^{-1}) 2919, 2849, 1734, 1654, 1576, 1512, 1478, 1407, 1257, 1098, 757, 652.

HRMS (ESI, m/z) calcd for $C_{21}H_{20}N_2NaO_2$ $(M+Na)^+$: 355.1417, found: 355.1407.



3t

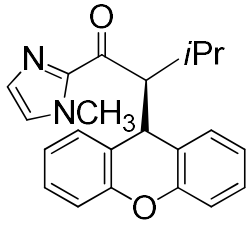
A dried 10 mL Schlenk tube was charged with **1t** (33.4 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3t** (42.3 mg, 0.122 mmol, yield: 61%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 86% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 8.5 min, t_r(minor) = 10.0 min. $[\alpha]_D^{23}$ = +21.5° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.16 – 7.12 (m, 1H), 7.05 (dd, *J* = 8.4, 3.8 Hz, 3H), 7.03 – 6.96 (m, 3H), 6.94 (s, 1H), 4.44 (d, *J* = 6.0 Hz, 1H), 4.20 – 4.13 (m, 1H), 3.97 (s, 3H), 1.69 – 1.62 (m, 1H), 1.33 – 1.29 (m, 1H), 1.18 – 1.09 (m, 1H), 1.08 – 0.97 (m, 1H), 0.73 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 153.1, 143.7, 129.4, 129.1, 128.8, 127.9, 127.7, 126.7, 124.4, 123.1, 122.9, 122.7, 116.34, 116.26, 55.0, 42.6, 36.1, 29.6, 20.7, 14.2.

IR (film): ν (cm^{-1}) 2919, 2847, 1734, 1654, 1650, 1477, 1458, 1406, 1255, 1096, 754, 600, 476.

HRMS (ESI, m/z) calcd for $C_{22}H_{22}N_2NaO_2$ $(M+Na)^+$: 369.1573, found: 369.1582.



3u

A dried 10 mL Schlenk tube was charged with **1u** (33.2 mg, 0.20 mmol), **2a** (109.3 mg, 0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3u** (35.9 mg, 0.104 mmol, yield: 52%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 57% (HPLC: IA, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 10.4 min, t_r(minor) = 11.4 min. $[\alpha]_D^{23}$ = +25.5° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.18 – 7.13 (m, 1H), 7.10 – 6.97 (m, 4H), 6.87 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.78 (d, *J* = 4.5 Hz, 2H), 4.48 (d, *J* = 6.4 Hz, 1H), 4.12 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.83 (s, 3H), 2.07 – 2.00 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 153.4, 152.8, 144.6, 129.0, 128.9, 128.6, 127.8, 127.6, 126.3, 124.6, 123.7, 123.2, 122.6, 116.3, 115.8, 60.0, 40.2, 35.9, 27.5, 21.4, 19.7.

IR (film): ν (cm^{-1}) 2923, 2851, 1742, 1656, 1571, 1451, 1387, 1241, 1087, 953, 759, 607, 495.

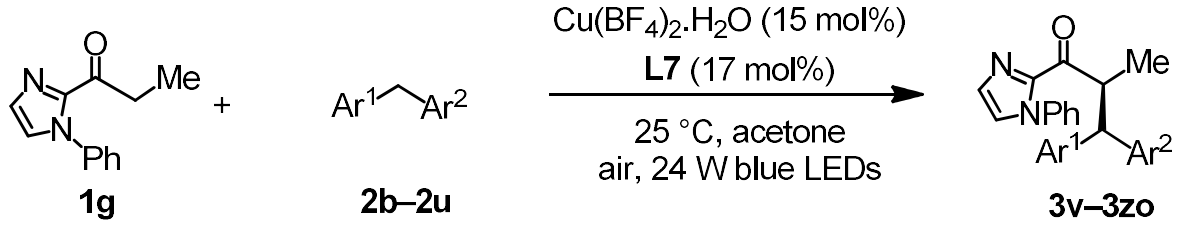
HRMS (ESI, m/z) calcd for $C_{22}H_{22}N_2NaO_2$ $(M+Na)^+$: 369.1573, found: 369.1577.

3.3 Substrate scope regarding xanthene derivatives or other diaryl methane derivatives

3.3.1 General procedure F

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), xanthene derivatives or other diaryl methane derivatives **2b−2x** (0.60 mmol), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for the indicated time, the reaction mixture was concentrated

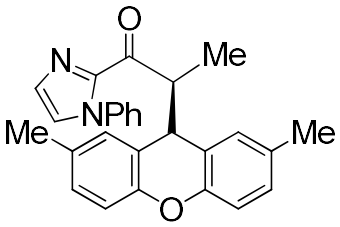
to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1 or PE: DCM = 3: 2) to afford non-racemic product **3v−3zr.**



1g **2b–2u** **3v–3zo**

Supplementary Scheme S5. Copper-catalyzed asymmetric photoredox reaction to afford non-racemic products **3v–3zr**.

3.3.2 Experimental details and characterization data



3v

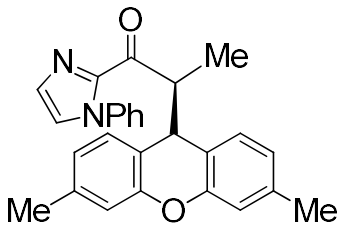
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2b** (0.60 mmol, 126 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3v** (56.8 mg, 0.140 mmol, yield: 70%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 91% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(minor) = 12.3 min, t_r(major) = 13.7 min. $[\alpha]_D^{23}$ = +23.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.33 – 7.27 (m, 3H), 7.19 (d, *J* = 1.3 Hz, 1H), 7.17 (d, *J* = 0.9 Hz, 1H), 7.00 – 6.92 (m, 4H), 6.64 (s, 1H), 4.59 (d, *J* = 5.9 Hz, 1H), 4.17 – 4.10 (m, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 0.86 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 151.4, 151.2, 142.7, 138.5, 132.2, 131.5, 129.7, 129.6, 129.1, 128.9, 128.7, 128.5, 128.3, 127.0, 126.0, 124.4, 121.8, 116.0, 115.9, 50.4, 42.2, 20.7, 20.6, 11.9.

IR (film): ν (cm^{-1}) 2922, 2850, 1958, 1719, 1676, 1654, 1560, 1487, 1443, 1401, 1302, 1259, 1221, 1110, 949, 911, 813, 759.

HRMS (ESI, m/z) calcd for $C_{27}H_{24}N_2NaO_2$ $(M+Na)^+$: 431.1730, found: 431.1732.



3w

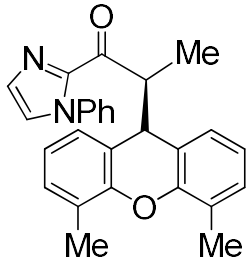
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2c** (0.60 mmol, 126 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3w** (57.1 mg, 0.140 mmol, yield: 70%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 77% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 30 °C, t_r(minor) = 12.0 min, t_r(major) = 14.2 min. $[\alpha]_D^{23}$ = +11.3° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.2, 1.8 Hz, 3H), 7.28 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.24 (s, 2H), 7.14 (s, 1H), 6.88 (s, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 4.59 (d, *J* = 5.9 Hz, 1H), 4.10 (p, *J* = 6.7 Hz, 1H), 2.31 (d, *J* = 7.8 Hz, 6H), 0.86 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 153.2, 152.9, 142.8, 138.5, 137.9, 137.6, 129.6, 129.1, 128.9, 128.7, 128.6, 126.9, 126.0, 123.8, 123.6, 123.3, 119.3, 116.8, 116.7, 50.5, 41.5, 38.7, 21.1, 12.2.

IR (film): ν (cm^{-1}) 2921, 2851, 1959, 1719, 1685, 1654, 1618, 1494, 1401, 1264, 1117, 911, 754, 691.

HRMS (ESI, m/z) calcd for $C_{27}H_{24}N_2NaO_2$ $(M+Na)^+$: 431.1730, found: 431.1734.



3x

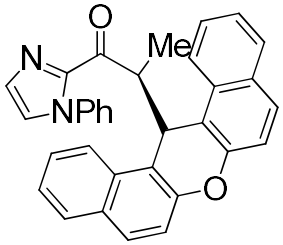
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2d** (0.60 mmol, 126 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3x** (49.7 mg, 0.122 mmol, yield: 61%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 91% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 30 °C, t_r(minor) = 13.0 min, t_r(major) = 15.5 min. $[\alpha]_D^{23}$ = +20.7° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 3H), 7.25 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.17 (t, *J* = 3.1 Hz, 1H), 7.09 (t, *J* = 3.7 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.89 (td, *J* = 7.4, 5.8 Hz, 2H), 6.83 (d, *J* = 6.8 Hz, 1H), 4.47 (d, *J* = 7.3 Hz, 1H), 4.08 (s, 1H), 2.40 (s, 6H), 0.94 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 151.7, 151.6, 142.9, 138.5, 129.53, 129.49, 129.1, 128.8, 128.7, 127.0, 126.9, 126.5, 126.0, 125.7, 125.6, 124.8, 122.9, 122.3, 122.1, 49.5, 42.9, 15.9, 15.8, 13.6.

IR (film): ν (cm^{-1}) 2922, 2849, 1958, 1719, 1679, 1654, 1607, 1494, 1278, 1123, 937, 826, 698.

HRMS (ESI, m/z) calcd for $C_{27}H_{24}N_2NaO_2$ $(M+Na)^+$: 431.1730, found: 431.1732.



3y

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2e** (0.60 mmol, 168 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h

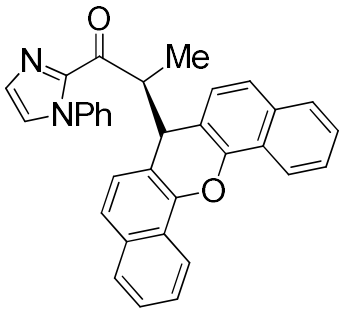
under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 3: 2) to afford product **3y** (59.4 mg, 0.124 mmol, yield: 62%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 83% (HPLC: IA, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 30 °C, t_r(minor) = 11.8 min, t_r(major) = 13.0 min. $[\alpha]_D^{23}$ = +87.6° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.75 (ddd, *J* = 20.9, 11.7, 5.3 Hz, 4H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.34 (dt, *J* = 15.0, 7.2 Hz, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.16 (s, 1H), 6.72 (d, *J* = 7.7 Hz, 2H), 6.39 (d, *J* = 5.7 Hz, 1H), 4.42 (p, *J* = 6.7 Hz, 1H), 0.83 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.6, 151.8, 151.3, 142.9, 138.2, 132.2, 131.2, 131.0, 130.9, 129.8, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 126.9, 125.8, 125.7, 124.2, 123.9, 123.7, 122.5, 117.7, 117.6, 117.5, 114.7, 49.0, 34.7, 11.7.

IR (film): ν (cm^{-1}) 2918, 2847, 1959, 1676, 1630, 1560, 1492, 1402, 1240, 1077, 946, 913, 814, 750, 693.

HRMS (ESI, m/z) calcd for $C_{33}H_{24}N_2NaO_2$ $(M+Na)^+$: 503.1730, found: 503.1738.



3z

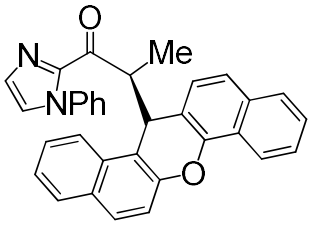
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2f** (0.60 mmol, 168 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3z** (66.2 mg, 0.138 mmol, yield: 69%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 82% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 12.1 min, t_r(minor) = 13.5 min. $[\alpha]_D^{23}$ = +144.3° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (t, *J* = 9.2 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.56 (m, 4H), 7.52 – 7.43 (m, 6H), 7.30 – 7.26 (m, 2H), 7.20 (d, *J* = 0.8 Hz, 1H), 7.10 (d, *J* = 0.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.01 (d, *J* = 5.2 Hz, 1H), 4.34 – 4.27 (m, 1H), 0.91 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.6, 148.0, 147.7, 142.7, 138.4, 133.4, 133.3, 129.6, 128.9, 128.7, 127.54, 127.53, 127.0, 126.9, 126.6, 126.1, 126.0, 125.9, 125.8, 124.3, 124.2, 123.0, 122.3, 121.5, 121.4, 118.6, 116.1, 50.8, 42.3, 11.9.

IR (film): ν (cm^{-1}) 2929, 2848, 1959, 1682, 1617, 1567, 1503, 1397, 1301, 1258, 1198, 1101, 945, 912, 811, 753, 692.

HRMS (ESI, m/z) calcd for $C_{33}H_{24}N_2NaO_2$ $(M+Na)^+$: 503.1730, found: 503.1747.



3za

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2g** (0.60 mmol, 168 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. Diastereomeric ratio was determined by ^{1}H-NMR of the crude product as 2.3:1 dr. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 3: 2) to afford product **3za**. The less polar diastereomer was collected as a white solid (39.3 mg, 0.082 mmol, yield: 41%), and the more polar diastereomer was collected as a white solid (21.0 mg, 0.044 mmol, yield: 22%).

Analytic data of the less polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 92% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 1 mL/min, 30 °C, t_r(major) = 6.7 min, t_r(minor) = 12.1 min. $[\alpha]_D^{23}$ = +86.4° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.69 (m, 4H), 7.59 – 7.55 (m, 1H), 7.53 – 7.46 (m, 7H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.28 (m,

2H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.99 (d, *J* = 4.1 Hz, 1H), 4.43 (qd, *J* = 6.8, 4.3 Hz, 1H), 0.80 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.3, 151.0, 148.2, 142.9, 138.5, 133.4, 131.5, 131.1, 129.8, 128.9, 128.7, 128.6, 128.5, 127.5, 127.0, 126.7, 126.2, 126.1, 125.8, 124.3, 124.2, 124.0, 122.2, 121.4, 117.6, 116.3, 115.1, 49.2, 39.5, 9.9.

IR (film): ν (cm^{-1}) 2920, 2850, 1959, 1774, 1719, 1654, 1560, 1438, 1401, 1235, 1084, 945, 814, 689.

HRMS (ESI, m/z) calcd for $C_{33}H_{24}N_2NaO_2$ $(M+Na)^+$: 503.1730, found: 503.1741.

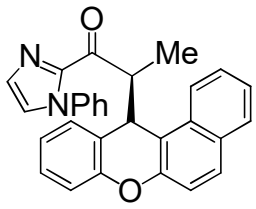
Analytic data of the more polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 81% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 30 °C, t_r(minor) = 10.5 min, t_r(major) = 12.5 min. $[\alpha]_D^{23}$ = +2.6° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 14.3, 8.0 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 7.44 – 7.36 (m, 4H), 7.15 (d, *J* = 6.2 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.45 (d, *J* = 7.2 Hz, 1H), 4.35 (p, *J* = 7.0 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 151.5, 148.1, 142.8, 138.4, 133.2, 132.4, 130.8, 129.6, 128.9, 128.7, 128.6, 128.3, 127.5, 126.9, 126.8, 126.3, 126.0, 125.84, 125.77, 124.2, 124.1, 122.9, 122.7, 121.5, 119.5, 117.8, 116.5, 50.1, 38.3, 14.7.

IR (film): ν (cm^{-1}) 2920, 2850, 1958, 1719, 1685, 1654, 1560, 1493, 1401, 1235, 1084, 945, 910, 814, 689.

HRMS (ESI, m/z) calcd for $C_{33}H_{24}N_2NaO_2$ $(M+Na)^+$: 503.1730, found: 503.1738.



3zb

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2h** (0.60 mmol, 139.2 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 48 h under air, the reaction mixture was concentrated to dryness. Diastereomeric ratio was determined by

^{1}H-NMR of the crude product as 1.5:1 dr. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 3: 2) to afford product **3zb**. The less polar diastereomer was collected as a white solid (27.3 mg, 0.068 mmol, yield: 34%), and the more polar diastereomer was collected as a white solid (26.7 mg, 0.062 mmol, yield: 31%).

Analytic data of the less polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 11.3 min, t_r(minor) = 14.0 min. $[\alpha]_D^{23}$ = +51.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 18.6, 6.4 Hz, 5H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 4.2 Hz, 1H), 4.40 – 4.24 (m, 1H), 0.77 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.3, 153.1, 151.0, 142.9, 138.5, 131.5, 130.8, 129.7, 129.1, 128.8, 128.7, 128.6, 128.5, 128.0, 127.0, 126.9, 126.0, 124.2, 124.1, 122.7, 121.3, 117.6, 116.2, 48.9, 39.1, 10.0.

IR (film): ν (cm^{-1}) 2920, 2863, 1735, 1701, 1653, 1629, 1553, 1492, 1438, 1401, 1244, 1074, 947, 913, 754, 694.

HRMS (ESI, m/z) calcd for $C_{29}H_{22}N_2NaO_2$ $(M+Na)^+$: 453.1573, found: 453.1582.

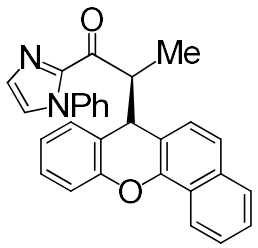
Analytic data of the more polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 87% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(minor) = 11.0 min, t_r(major) = 11.9 min. $[\alpha]_D^{23}$ = +7.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.46 (dd, *J* = 8.6, 6.3 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.18 (dt, *J* = 8.9, 5.4 Hz, 4H), 7.11 (s, 1H), 7.08 (s, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.26 (d, *J* = 8.1 Hz, 1H), 4.27 (p, *J* = 7.2 Hz, 1H), 0.95 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0, 153.2, 151.5, 142.8, 138.5, 132.4, 130.6, 129.6, 128.80, 128.78, 128.64, 128.58, 128.4, 127.6, 127.0, 126.2, 125.9, 125.6, 123.9, 123.1, 122.9, 117.8, 116.7, 116.4, 49.6, 38.0, 15.0.

IR (film): ν (cm^{-1}) 2919, 2841, 1958, 1723, 1654, 1401, 1245, 1101, 948, 911, 764, 693.

HRMS (ESI, m/z) calcd for $C_{29}H_{22}N_2NaO_2$ $(M+Na)^+$: 453.1573, found: 453.1582.



3zc

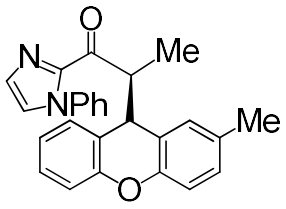
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2i** (0.60 mmol, 139.2 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE : EA = 5 : 1) to afford product **3zc** as a diastereomeric mixture (56.0 mg, 0.13 mmol, yield: 65%). Diastereomeric ratio was determined by ^{1}H NMR as 1.3:1 dr. Enantiomeric excess was established by HPLC analysis using a Chiralpak IA column, ee = 93%, 89%. (HPLC: IA, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 30 °C, t_r(diastereoisomer 1, major) = 20.6 min, t_r(diastereoisomer 1, minor) = 22.1 min, t_r(diastereoisomer 2, major) = 38.8 min, t_r(diastereoisomer 2, minor) = 46.1 min; $[\alpha]_D^{23}$ = +33.1° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.3 Hz, 2H), 7.80 (dd, *J* = 11.2, 8.1 Hz, 2H), 7.58 – 7.52 (m, 4H), 7.48 (dd, *J* = 7.0, 4.9 Hz, 8H), 7.43 (dd, *J* = 15.0, 7.7 Hz, 2H), 7.31 – 7.28 (m, 4H), 7.24 (s, 4H), 7.22 (d, *J* = 3.8 Hz, 2H), 7.14 (s, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 4.85 (d, *J* = 5.6 Hz, 1H), 4.78 (d, *J* = 6.3 Hz, 1H), 4.24 (dd, *J* = 13.2, 6.7 Hz, 2H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.9, 192.6, 153.2, 153.0, 148.2, 147.9, 142.8, 142.7, 138.5, 133.4, 133.3, 129.65, 129.64, 129.4, 129.0, 128.9, 128.7, 127.9, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.7, 126.2, 126.1, 126.0, 125.9, 125.7, 124.9, 124.1, 123.3, 122.9, 122.6, 122.2, 122.0, 121.6, 121.5, 118.6, 116.5, 116.5, 50.5, 50.4, 42.4, 42.2, 12.7, 12.0.

IR (film): ν (cm^{-1}) 2918, 2850, 1958, 1676, 1654, 1576, 1492, 1437, 1400, 1256, 1240, 1086, 947, 912, 873, 813, 761, 594.

HRMS (ESI, m/z) calcd for $C_{29}H_{22}N_2NaO_2$ $(M+Na)^+$: 453.1573, found: 453.1591.



3zd

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2j** (0.60 mmol, 117.6 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3zd** as a diastereomeric mixture (51.9 mg, 0.132 mmol, yield: 66%). Diastereomeric ratio was determined by ^{1}H-NMR as 1.3:1 dr.

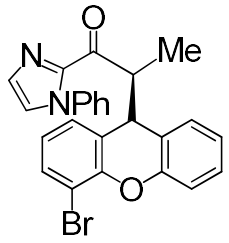
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 86%, 89% (HPLC: IG, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, t_r(diastereoisomer 1, minor) = 14.0 min, t_r(diastereoisomer 2, minor) = 15.3 min, t_r(diastereoisomer 1, major) = 18.5 min, t_r(diastereoisomer 2, major) = 31.6 min; $[\alpha]_D^{23}$ = +53.9° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.8, 4.1 Hz, 6H), 7.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.33 – 7.23 (m, 7H), 7.20 – 7.14 (m, 4H), 7.08 – 7.02 (m, 3H), 6.98 – 6.90 (m, 6H), 6.68 (s, 1H), 4.59 (d, *J* = 3.9 Hz, 1H), 4.58 (d, *J* = 4.3 Hz, 1H), 4.14 (dt, *J* = 12.3, 6.7 Hz, 2H), 2.32 (s, 3H), 2.24 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 192.8, 153.5, 153.3, 151.2, 151.1, 142.9, 142.8, 138.6, 132.4, 131.8, 129.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 127.8, 127.0, 126.1, 126.0, 124.8, 124.6, 122.9, 122.7, 122.4, 122.0, 116.4, 116.3, 116.2, 116.1, 116.0, 50.3, 50.2, 42.3, 42.2, 20.8, 20.7, 12.7, 12.1.

IR (film): ν (cm^{-1}) 2921, 2850, 1956, 1749, 1723, 1654, 1560, 1486, 1437, 1351, 1153, 947, 913, 835.

HRMS (ESI, m/z) calcd for $C_{26}H_{22}N_2NaO_2$ $(M+Na)^+$: 417.1573, found: 417.1575.



3ze

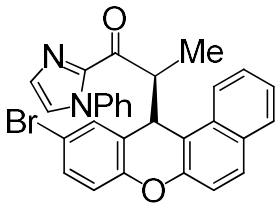
A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2k** (0.60 mmol, 156 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3ze** as a diastereomeric mixture (60.1 mg, 0.132 mmol, yield: 66%). Diastereomeric ratio was determined by ^{1}H NMR as 1.2:1 dr. Enantiomeric excess was established by HPLC analysis using a Chiralpak OJH column, ee = 90%, 95%. (HPLC: OJH, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 30 °C, t_r(diastereoisomer 1, minor) = 42.2 min, t_r(diastereoisomer 1, major) = 61.1 min, t_r(diastereoisomer 2, major) = 75.5 min, t_r(diastereoisomer 2, minor) = 99.0 min; $[\alpha]_D^{23}$ = +17.8° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 6H), 7.46 – 7.41 (m, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.22 (m, 4H), 7.22 – 7.18 (m, 5H), 7.13 (s, 2H), 7.08 – 6.97 (m, 3H), 6.97 – 6.84 (m, 3H), 4.59 (d, *J* = 6.5 Hz, 1H), 4.56 (d, *J* = 6.7 Hz, 1H), 4.18 – 4.12 (m, 2H), 0.94 (d, *J* = 1.6 Hz, 3H), 0.93 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 192.4, 152.9, 152.8, 150.0, 149.8, 142.7, 138.4, 132.3, 131.70, 131.5, 130.9, 129.7, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.9, 127.1, 127.0, 126.8, 126.7, 126.0, 125.9, 124.8, 124.6, 123.7, 123.6, 123.4, 123.3, 122.6, 116.8, 110.7, 110.6, 49.8, 49.6, 42.8, 42.7, 13.2, 13.0.

IR (film): ν (cm^{-1}) 2921, 2850, 1958, 1752, 1719, 1654, 1560, 1492, 1448, 1401, 1245, 1104, 950, 909, 756.

HRMS (ESI, m/z) calcd for $C_{25}H_{19}BrN_2NaO_2$ $(M+Na)^+$: 481.0522, found: 481.0521.



3zf

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2l** (0.60 mmol, 187.5 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. Diastereomeric ratios was determined by ^{1}H-NMR of the crude product as 1.3:1 dr. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 1: 1) to afford product **3zf**. The less polar diastereomer was collected as a white solid (33.5 mg, 0.066 mmol, yield: 33%), and the more polar diastereomer was collected as a white solid (21.4 mg, 0.042 mmol, yield: 21%).

Analytic data of the less polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 92% (HPLC: OJ, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 30 °C, t_r(minor) = 18.7 min, t_r(major) = 28.1 min. $[\alpha]_D^{23}$ = +47.2° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.53 – 7.47 (m, 5H), 7.35 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.31 (dd, *J* = 13.4, 5.5 Hz, 3H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 5.85 (d, *J* = 3.8 Hz, 1H), 4.34 (tt, *J* = 10.8, 5.3 Hz, 1H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 152.3, 150.6, 142.6, 138.4, 131.62, 131.57, 131.4, 131.0, 129.9, 129.8, 129.1, 128.9, 128.8, 128.5, 127.2, 126.2, 124.5, 124.1, 123.3, 118.0, 117.4, 115.5, 115.0, 48.9, 39.1, 9.4.

IR (film): ν (cm^{-1}) 2921, 2853, 1955, 1654, 1487, 1451, 1277, 1174, 963, 905, 784.

HRMS (ESI, m/z) calcd for $C_{29}H_{21}BrN_2NaO_2$ $(M+Na)^+$: 531.0679, found: 531.0683.

Analytic data of the more polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 90% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.8 mL/min, 30 °C, t_r(minor) = 11.5 min, t_r(major) = 26.2 min. $[\alpha]_D^{23}$ = +16.0° (*c* = 1.0, CH_2Cl_2).

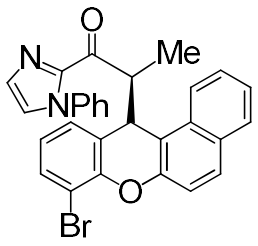
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.42 – 7.38 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.29 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.24 –

7.21 (m, 2H), 7.12 (d, *J* = 12.1 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 5.18 (d, *J* = 8.9 Hz, 1H), 4.23 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.93 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 152.5, 151.3, 142.6, 138.4, 132.4, 131.3, 131.2, 130.7, 129.8, 129.7, 129.0, 128.9, 128.6, 128.5, 128.1, 127.3, 126.4, 126.0, 124.2, 122.9, 117.7, 116.4, 115.4, 49.4, 37.7, 15.5.

IR (film): ν (cm^{-1}) 2921, 2850, 1957, 1654, 1489, 1451, 1401, 1257, 1073, 973, 825, 697.

HRMS (ESI, m/z) calcd for$C_{29}H_{21}BrN_2NaO_2$ $(M+Na)^+$: 531.0679, found: 531.0683.



3zg

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2m** (0.60 mmol, 186 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. Diasteromeric ratio was determined by ^{1}H-NMR of the crude product as 1.3:1 dr. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 3: 2) to afford product **3zg**. The less polar diastereomer was collected as a white solid (34.5 mg, 0.068 mmol, yield: 34%), and the more polar diastereomer was collected as a white solid (30.5 mg, 0.060 mmol, yield: 30%).

Analytic data of the less polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 11.6 min, t_r(minor) = 13.6 min. $[\alpha]_D^{23}$ = +62.8° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 11.8, 7.6 Hz, 6H), 7.24 – 7.19 (m, 3H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 4.3 Hz, 1H), 4.38 – 4.29 (m, 1H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.0, 150.8, 149.9, 142.7, 138.4, 131.8, 131.2, 131.1, 129.8, 128.9, 128.8, 128.7, 128.5, 128.3, 127.1, 126.0, 124.5, 124.1, 123.4, 123.3, 117.7, 116.3, 110.6, 48.9, 39.6, 10.2.

IR (film): ν (cm^{-1}) 2920, 2850, 1957, 1654, 1492, 1450, 1401, 1249, 1043, 947, 899, 761.

HRMS (ESI, m/z) calcd for $C_{29}H_{21}BrN_2NaO_2$ $(M+Na)^+$: 531.0679, found: 531.0690.

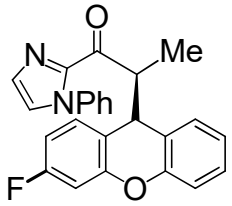
Analytic data of the more polar diastereomer: Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(minor) = 11.4 min, t_r(major) = 12.2 min. $[\alpha]_D^{23}$ = +4.0° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 6.9 Hz, 1H), 7.53 – 7.39 (m, 8H), 7.18 (dd, *J* = 6.5, 2.7 Hz, 2H), 7.07 (s, 2H), 6.91 (t, *J* = 7.7 Hz, 1H), 5.24 (d, *J* = 7.7 Hz, 1H), 4.30 (p, *J* = 7.1 Hz, 1H), 0.98 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 151.1, 150.0, 142.7, 138.4, 132.1, 131.4, 130.9, 129.6, 128.8, 128.7, 128.6, 128.1, 127.2, 127.1, 126.5, 125.9, 124.3, 123.9, 122.8, 117.8, 116.7, 110.6, 49.1, 38.6, 15.0.

IR (film): ν (cm^{-1}) 2923, 2850, 1959, 1685, 1654, 1630, 1492, 1449, 1420, 1401, 1245, 1070, 949, 905, 761, 692.

HRMS (ESI, m/z) calcd for $C_{29}H_{21}BrN_2NaO_2$ $(M+Na)^+$: 531.0679, found: 531.0690.



3zh

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2n** (0.60 mmol, 133.7 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3zh** as a diastereomeric mixture (24.5 mg, 0.062 mmol, yield: 31%). Diastereomeric ratio was determined by ^{1}H NMR as 1.3:1 dr. Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 92%, 89%. (HPLC: IG, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.35 mL/min, 30 °C, t_r(diastereoisomer 1, minor) = 19.1 min, t_r(diastereoisomer 2, minor) = 20.5 min, t_r(diastereoisomer 2, major) = 26.0 min, t_r(diastereoisomer 1, major) = 31.2 min; $[\alpha]_D^{23}$ = +74.6° (*c* = 1.0, CH_2Cl_2).

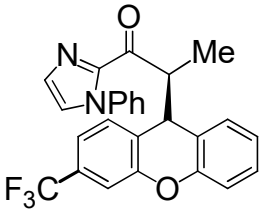
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 6H), 7.35 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.26 (m, 4H), 7.25 (d, *J* = 3.9 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.14 (s, 2H), 7.06 (ddd, *J* = 11.5, 8.5, 4.1 Hz, 3H), 7.00 (td,

J = 7.4, 1.1 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.89 (dd, *J* = 8.4, 6.3 Hz, 1H), 6.81 (dt, *J* = 9.6, 2.7 Hz, 2H), 6.76 – 6.67 (m, 2H), 4.58 (d, *J* = 6.3 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 4.15 – 4.09 (m, 2H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 192.7, 161.2 (d, *J* = 2.8 Hz), 154.0, 153.9, 153.8, 153.7, 152.9, 152.8, 152.6, 138.7, 138.5 (d, *J* = 2.4 Hz), 138.4, 130.4, 130.3, 129.9, 129.8, 129.7 (d, *J* = 2.5 Hz), 129.6, 129.5, 129.1, 128.9, 128.8, 128.7, 128.1, 127.8, 127.1 (d, *J* = 4.5 Hz), 126.0, 123.4, 123.0, 116.4, 116.3, 110.2, 110.0, 109.9, 109.7, 104.1, 104.0, 103.9, 103.8, 50.1, 50.0, 41.7, 41.7, 12.9, 12.6.

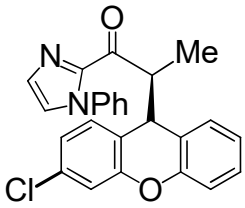
IR (film): ν (cm^{-1}) 2996, 2879, 2013, 1947, 1669, 1581, 1514, 1468, 1421, 1374, 1253, 1211, 1077, 978, 934, 872, 724, 596.

HRMS (ESI, m/z) calcd for $C_{25}H_{19}FN_2NaO_2$ $(M+Na)^+$: 421.1323, found: 421.1325.



3zi

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2o** (0.60 mmol, 163.7 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, products **3zi** was not formed (detected by TLC and ^{1}H NMR analysis).



3zj

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2p** (0.60 mmol, 143.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3zj** as a diastereomeric mixture (42.2 mg, 0.102 mmol, yield: 51%). Diastereomeric ratio was determined by ^{1}H NMR as 1.2:1 dr.

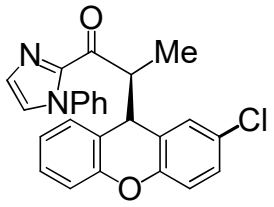
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 89%, 88%. (HPLC: IG, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, t_r(diastereoisomer 1, minor) = 13.9 min, t_r(diastereoisomer 2, minor) = 16.3 min, t_r(diastereoisomer 2, major) = 18.6 min, t_r(diastereoisomer 1, major) = 21.4 min; $[\alpha]_D^{23}$ = +81.4° (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 6H), 7.35 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 (d, *J* = 1.1 Hz, 2H), 7.25 (d, *J* = 2.5 Hz, 3H), 7.24 – 7.17 (m, 4H), 7.14 (dd, *J* = 3.6, 0.8 Hz, 2H), 7.08 (ddd, *J* = 16.4, 6.6, 1.7 Hz, 5H), 6.99 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.95 (dd, *J* = 8.1, 2.0 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.58 (d, *J* = 6.3 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 4.15 – 4.08 (m, 2H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.6, 192.5, 153.7, 153.6, 152.8, 142.7, 142.6, 140.8, 138.4, 133.1, 132.4, 132.0, 131.5, 130.8, 130.4, 130.0, 129.8, 129.7, 129.5, 129.0, 128.9, 128.8, 128.7, 128.1, 127.9, 127.2, 127.1, 126.0, 124.4, 123.6, 123.5, 123.2, 123.1, 122.9, 122.3, 121.2, 116.8, 116.8, 116.5, 116.4, 50.0, 49.9, 41.9, 41.6, 12.9, 12.6.

IR (film): ν (cm^{-1}) 2967, 2871, 1973, 1749, 1683, 1629, 1527, 1433, 1359, 1287, 1158, 963, 872, 748.

HRMS (ESI, m/z) calcd for $C_{25}H_{19}ClN_2NaO_2$ $(M+Na)^+$: 437.1027, found: 437.1028.



3zk

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2q** (0.60 mmol, 143.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3zk** as a diastereomeric mixture (38.2 mg, 0.092 mmol, yield: 49%). Diastereomeric ratio was determined by ^{1}H NMR as 1.3:1 dr. Enantiomeric excess was established by HPLC analysis using a Chiralpak ADH column, ee = 90%, 90%. (HPLC: ADH, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 0.35 mL/min, 30 °C, t_r(diastereoisomer 1, major) = 24.4 min, t_r(diastereoisomer 1, minor) = 26.6 min, t_r(diastereoisomer 2, minor) = 27.9 min, t_r(diastereoisomer 2, major) = 37.6 min; $[\alpha]_D^{23}$ = +31.7° (*c* = 1.0, CH_2Cl_2).

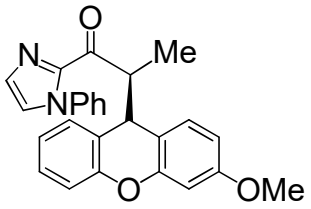
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 9.6, 6.0 Hz, 6H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.29 (s, 4H), 7.28 (s, 2H), 7.23 (dd, *J* = 17.2, 8.9 Hz, 5H), 7.19 – 7.15 (m, 3H), 7.10 (dt, *J* = 14.6, 8.1 Hz, 4H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 4.59 (d, *J* = 6.3 Hz, 1H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.14 (dp, *J* = 20.7, 6.9 Hz, 2H), 0.94 (d, *J* = 8.2 Hz, 3H), 0.92 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.6, 192.5, 153.9, 153.7, 152.8, 152.5, 142.7, 142.6, 138.4, 130.7, 130.3, 129.8, 129.7, 129.5, 129.0, 128.9, 128.9, 128.8, 128.1, 127.9, 127.2, 127.2, 126.1, 126.0, 125.8, 124.8, 124.4, 124.1, 123.9, 123.5, 123.1, 122.3, 121.7, 120.8, 120.5, 119.7, 119.7, 116.5, 116.4, 99.9, 49.9, 49.8, 41.9, 41.8, 12.9, 12.6.

IR (film): ν (cm^{-1}) 2979, 2831, 1948, 1760, 1672, 1634, 1568, 1478, 1349, 1245, 1169, 968, 849, 767.

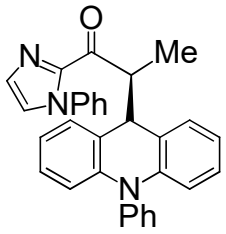
HRMS (ESI, m/z) calcd for $C_{25}H_{19}ClN_2NaO_2$ $(M+Na)^+$: 437.1027, found: 437.1028.

Inapplicable substrates:



3zl

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2r** (0.60 mmol, 127.4 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, product **3zl** was not formed (detected by TLC and ^{1}H NMR analysis).



3zm

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), 10-phenyl-9,10-dihydroacridine (**2s**, 0.60 mmol, 154.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After

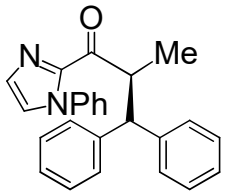
being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford the product **3zm** (67.3 mg, 0.148 mmol, yield: 74 %). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 0 % (HPLC: ADH, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.6 mL/min, 30 °C, t_r(major) = 8.3 min, t_r(minor) = 10.1 min.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 5H), 7.23 – 7.17 (m, 4H), 7.07 (s, 1H), 7.00 (dd, *J* = 12.3, 7.5 Hz, 2H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 2H), 6.39 (d, *J* = 8.2 Hz, 1H), 6.25 (d, *J* = 8.2 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.31 (p, *J* = 7.1 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 143.1, 142.7, 142.5, 140.7, 138.6, 132.5, 131.3, 130.5, 129.49, 129.45, 129.40, 129.39, 129.0, 128.9, 128.8, 128.6, 128.1, 126.92, 126.87, 126.8, 126.0, 123.7, 121.9, 48.6, 46.0, 13.7.

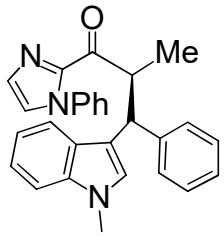
IR (film): ν (cm^{-1}) 2933, 2847, 1956, 1735, 1684, 1568, 1463, 1421, 1245, 1083, 839, 695.

HRMS (ESI, m/z) calcd for $C_{31}H_{25}N_3NaO$ $(M+Na)^+$: 478.1890, found: 478.1892.



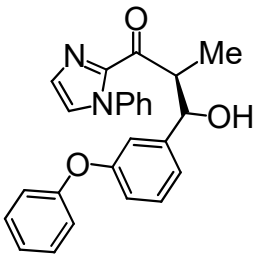
3zn

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), diphenylmethane (**2t**, 0.60 mmol, 101 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, product **3zn** was not formed (detected by TLC and ^{1}H NMR analysis).



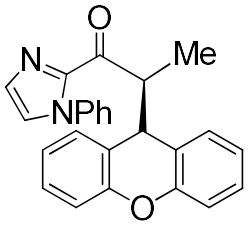
3zo

A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), 3-benzyl-1-methyl-1H-indole (**2u**, 0.60 mmol, 132.7 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, product **3zo** was not formed (detected by TLC and ^{1}H NMR analysis).



A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), 3-phenoxybenzyl alcohol (0.60 mmol, 120.1 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the desired product was not formed (detected by TLC and ^{1}H NMR analysis).

3.4 A Scale-up Catalytic Reaction

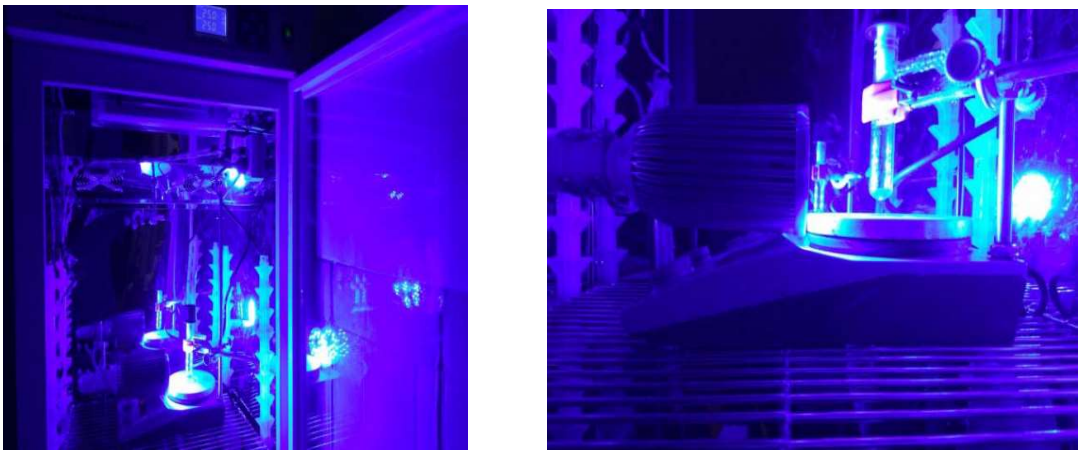


3g

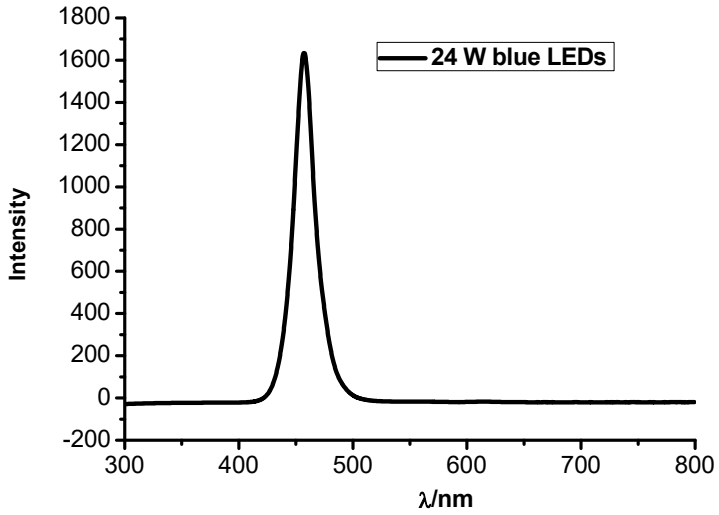
A dried 50 mL Schlenk tube was charged with **1g** (200.0 mg, 1.00 mmol), **2a** (546.5 mg, 3.00 mmol), chiral copper catalyst **[Cu^{II}-L7]** (10.0 mL taken from the 15 mM solution in acetone). The Schlenk tube

was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE : EA = 5 : 1) to afford product **3g** (269.9 mg, 0.71 mmol, yield: 71%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 92% (HPLC: IC, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate: 0.7 mL/min, 30 °C, t_r(major) = 9.6 min, t_r(minor) = 17.5 min. $[\alpha]_D^{23}$ = +84.6° (*c* = 1.0, CH_2Cl_2).

3.5 Set-up of the photoreactions and emission spectra of the light source



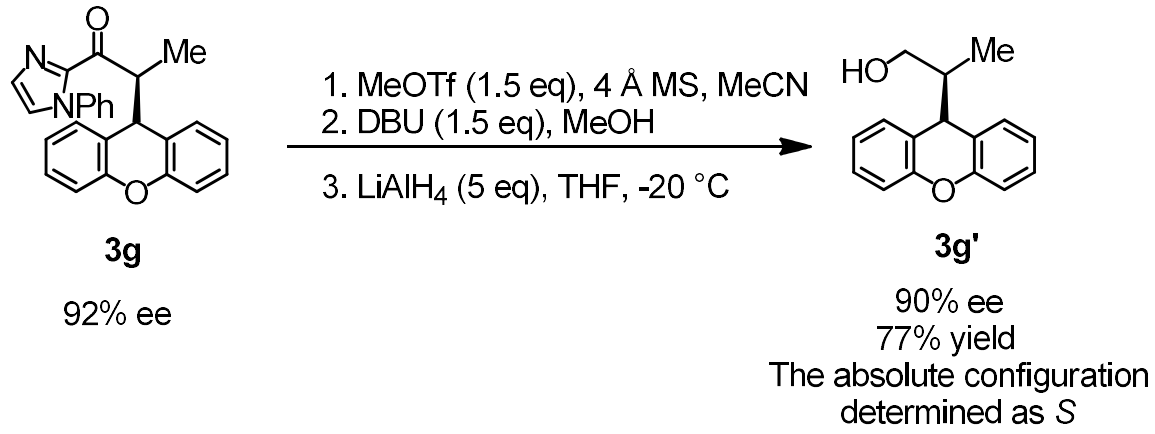
Supplementary Fig. 1 Reaction set-up of the photochemical catalysis in a constant temperature cabinet.[9]



Supplementary Fig. 2 Emission spectra of the light source (maxium emission at λ = 455 nm).

4. Synthetic Transformation and Absolute Configuration Assignment of the Products

4.1 Transformation of product 3g to its alcohol derivative (*S*)-3g'



Supplementary Scheme 6. Transformation of **3g** to alcohol derivative (*S*)-**3g'**.

To a solution of cross dehydrogenation coupling product **3g** (50 mg, 0.13 mmol, 92% ee) in freshly distilled MeCN (2.6 mL, 0.05 M) in a brown Schlenk tube, 4 Å MS (13.0 mg, 100 mg/mmol) was added. The resulting mixture was stirred at room temperature for 90 min under argon. MeOTf (32.0 mg, 0.20 mmol) was added. The suspension was stirred at room temperature for additional 3 h (monitored by TLC). After cooling to 0 ℃, DBU (29.7 mg, 0.19 mmol) in MeOH (2.0 mL) was added dropwise. The resulting mixture was stirred at 0 °C for 30 min, then stirred at room temperature for another 1h (monitored by TLC). Organic solvent was removed in vacuo. The residue was dissolved in dry tetrahydrofuran (4.5 mL), which was added dropwise to a suspension of lithium aluminium hydride (24.7 mg, 0.65 mmol, 5 eq) in 10 mL dry tetrahydrofuran at -20 ℃ under argon. The mixture was stirred at room temperature overnight, quenched with H_2O (8 mL), filtered with silica gel, and extracted with DCM (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (elution with PE: DCM = 8: 1 to 1: 1) to afford the alcohol product **3g'** as a white solid (24.0 mg, 0.10 mmol, yield: 77%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 90% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate: 1.0 mL/min, 30 °C, t_r(major) = 12.3 min, t_r(minor) = 13.1 min). $[\alpha]_D^{23}$ = -63.1° (*c* = 1.0, CH_2Cl_2). The absolute configuration was assigned as *S* by comparing the optical rotation.[6]

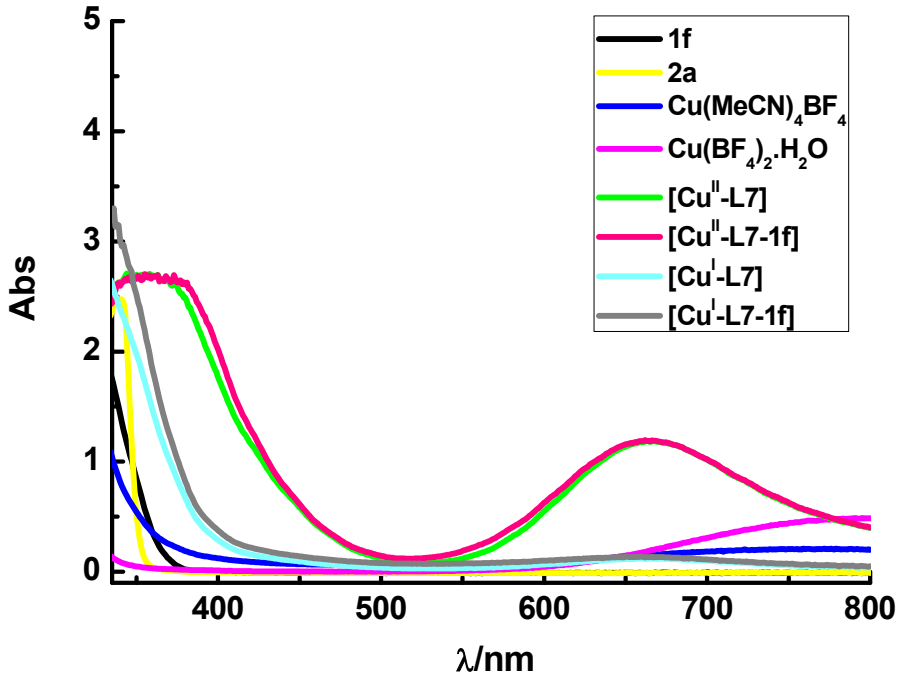
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 4H), 7.14 – 7.03 (m, 4H), 4.23 (d, *J* = 4.2 Hz, 1H), 3.54 (dd, *J* = 10.7, 7.9 Hz, 1H), 3.45 (dd, *J* = 10.7, 6.0 Hz, 1H), 2.02 – 1.97 (m, 1H), 0.65 (d, *J* = 6.9 Hz, 3H). Other analytic data of **3g '** are consistent with the literature.[6]

4.2 Absolute configuration assignment of the products

The absolute configuration of the alcohol derivative **3g'** (90% ee, synthesized from product **3g** of the copper-catalyzed asymmetric photocatalysis) was assigned as *S* by comparison of its optical rotation with the published literature.[6] In addition, the absolute configuration of the product can also be determined as *S* by comparing its HPLC peak shape with the reported data.[6] Accordingly, **3g** and all other products were assigned as *S* in analogy.

5. Mechanistic Investigations

5.1 UV/Vis-Absorption Spectra of the Reaction Components



Supplementary Fig. 3 UV-Vis spectra of the individual substrates **1f**, **2a**, copper salts $Cu(BF_4)_2{\cdot}H_2O$, $Cu(MeCN)_4BF_4$, copper complexes **[Cu^{I}-L7]**, **[Cu^{I}-L7-1f]**, **[Cu^{II}-L7]** and **[Cu^{II}-L7-1f]**. All the samples were prepared as a 30 mM solution in acetone and used freshly for the measurement.

Preparation of the samples for UV-Vis spectra measurement.

1e in acetone (30 mM): 1f (12.9 mg, 0.060 mmol) was dissolved in distilled acetone (2.0 mL).

2a in acetone (30 mM): 2a (10.9 mg, 0.060 mmol) was dissolved in distilled acetone (2.0 mL).

$Cu(MeCN)_4BF_4$ in acetone (30 mM): A solution of $Cu(MeCN)_4BF_4$ (18.9 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 °C in argon for 1 h, then used freshly for the measurement.

$Cu(BF_4)_2{\cdot}H_2O$ in acetone (30 mM): A solution of $Cu(BF_4)_2{\cdot}H_2O$ (15.3 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 °C for 1 h, then used freshly for the measurement.

[Cu^{I}-L7] in acetone (30 mM): A solution of $Cu(MeCN)_4BF_4$ (18.9 mg, 0.060 mmol) and ligand **L7** (21.4 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 ℃ in argon for 1 h. The solution was used freshly for the measurement.

[Cu^{I}-L7-1f] in acetone (30 mM): A solution of $Cu(MeCN)_4BF_4$ (18.9 mg, 0.060 mmol) and ligand **L7** (21.4 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 ℃ in argon for 1 h, then **1f** (12.9 mg, 0.060 mmol) was added. The resulting mixure was heated at 35 ℃ in argon for additional 1 h. The solution was used freshly for the measurement.

[Cu^{II}-L7] in acetone (30 mM): A solution of $Cu(BF_4)_2{\cdot}H_2O$ (15.3 mg, 0.060 mmol) and ligand **L7** (21.4 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 ℃ for 1 h. The solution was used freshly for the measurement.

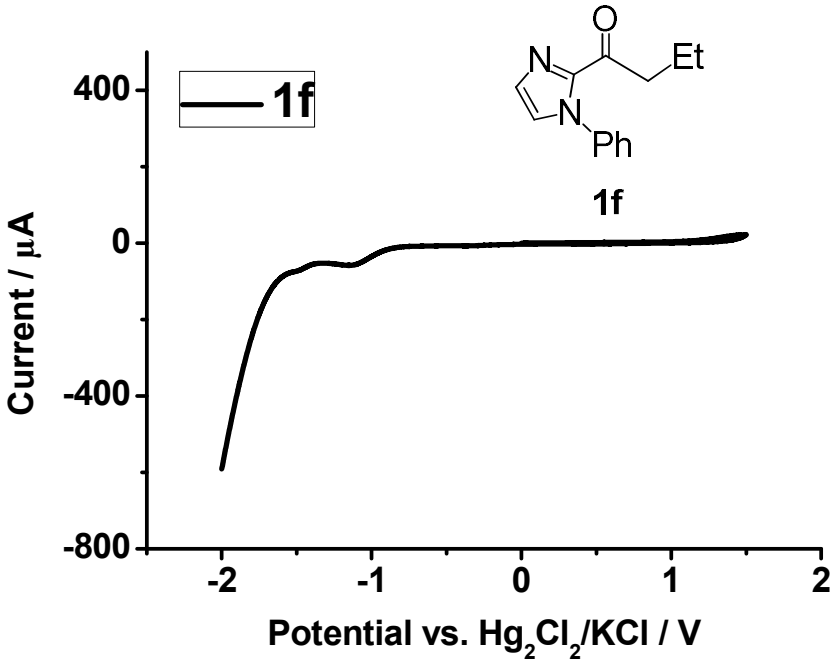
[Cu^{II}-L7-1f] in acetone (30 mM): A solution of $Cu(BF_4)_2{\cdot}H_2O$ (15.3 mg, 0.060 mmol) and ligand **L7** (21.4 mg, 0.060 mmol) in distilled acetone (2.0 mL) was stirred at 35 ℃ for 1 h, then **1f** (12.9 mg, 0.060 mmol) was added. The resulting mixure was heated at 35 ℃ for additional 1 h. The solution was used freshly for the measurement.

Remarks: All of the individual substrates **1f, 2a** and copper salts $Cu(BF_4){\cdot}H_2O$, $Cu(MeCN)_4BF_4$ had no obvious absorption in the visible light region. However, the chiral copper complexes **[Cu^{I}-L7]**, **[Cu^{II}-L7]**, and potential intermediates **[Cu^{I}-L7-1f]**, **[Cu^{II}-L7-1f]** exhibited significant absorption enhancement in the range of 400–550 nm.

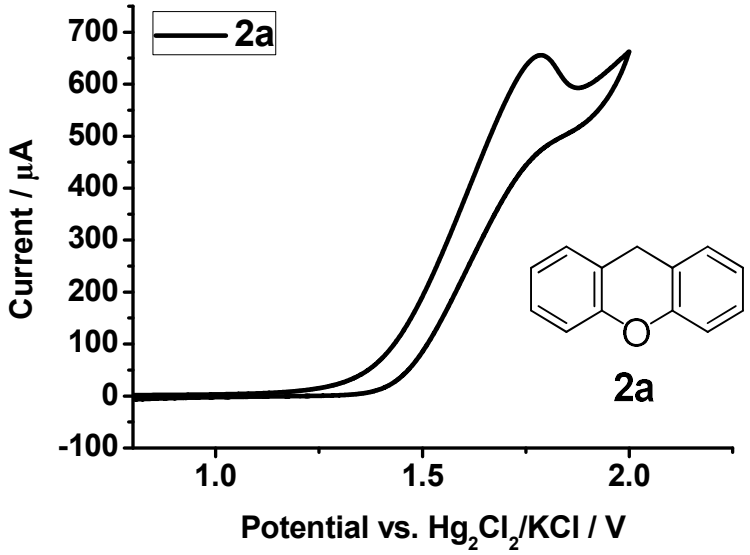
5.2 Cyclic Voltammetry Analysis

Voltammetric experiments were conducted with a computer recorded on a CHI 760E potentiostat containing a glassy carbon disk working electrode (diameter, 1mm), a Pt wire auxiliary electrode and a SCE (Hg_2Cl_2 / KCl) reference electrode. The scan rate is 100 mV/s.

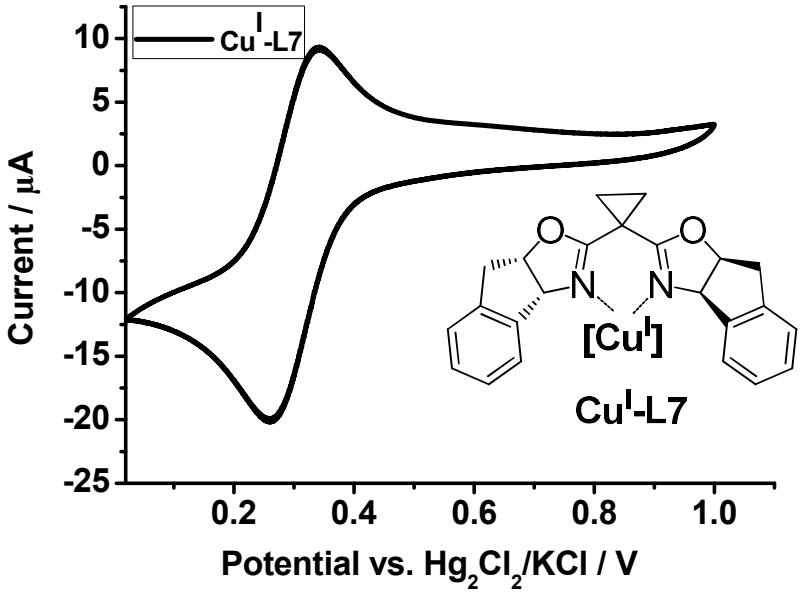
All solutions used for the voltammetric experiments were deoxygenated by purging with high purity argon gas and measurements were performed in a Faraday cage at room temperature (25 ± 2 ℃). HPLC purity acetone was purchased from OCEANPAK. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$), was purchased from commercial suppliers Aldrich.



Supplementary Fig. 4 Cyclic voltammogram of **1f** in acetone (0.030 M) containing 0.1 M nBu$_4$NPF$_6$. Scan rate: 100 mV/s. Substrate **1f** does not show any obvious signals.



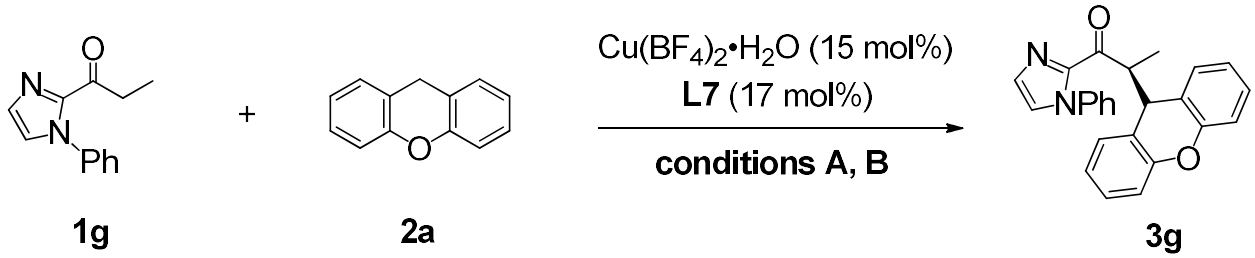
Supplementary Fig. 5 Cyclic voltammogram of **2a** in acetone (0.030 M) containing 0.1 M nBu$_4$NPF$_6$. Scan rate: 100 mV/s. E_p = +1.78 V.



Supplementary Fig. 6 Cyclic voltammogram of **[Cu^I-L7]** in acetone (0.030 M) containing 0.1 M nBu$_4$NPF$_6$. Scan rate: 100 mV/s. $E_{1/2}$ = +0.30 V.

5.3 Control Experiments

5.3.1 Air and light were all essential for the transformation

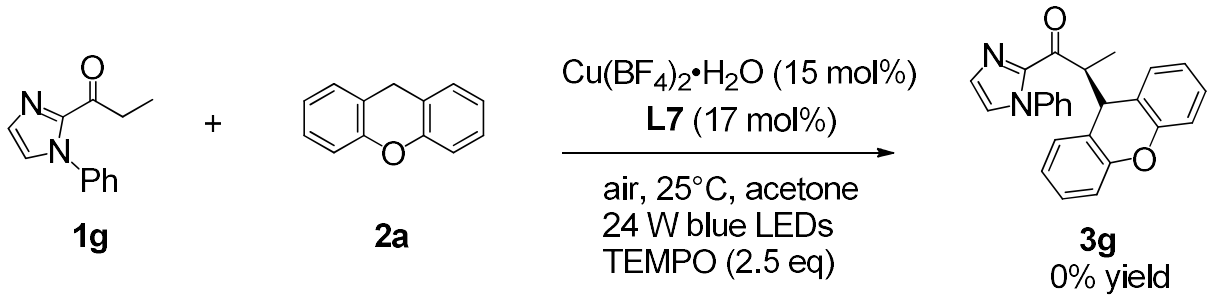


Supplementary Scheme 7. Reaction **1g**+**2a**→**3g** in the dark or argon.

Conditions A: A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2a** (0.60 mmol, 109.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned **in the dark**. After being stirred at 25 ℃ for 48 h under air, target product **3g** was not formed (detected by TLC and ^{1}H NMR analysis).

Conditions B: A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2a** (0.60 mmol, 109.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The mixture was degassed via three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h **under argon**, target product **3g** was not formed (detected by TLC and ^{1}H NMR analysis).

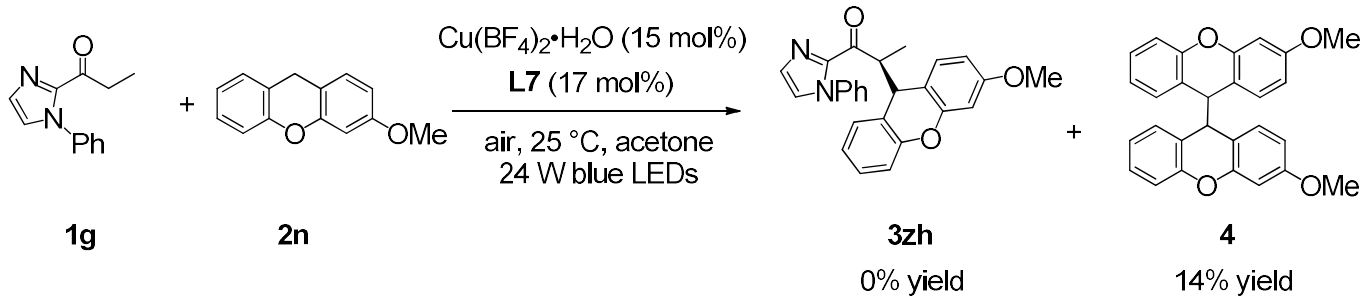
5.3.2 Evidence for a radical pathway



Supplementary Scheme 8. Reaction **1g** + **2a** → **3g** in the presence of TEMPO.

Catalytic reaction interfered with a radical quencher: A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2a** (0.60 mmol, 109.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 0.5 mmol, 78.1 mg). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, target product **3g** was not formed (detected by TLC and ^{1}H NMR analysis).

5.3.3 Evidence for formation of the benzylic radical



1g **2n** **3zh** 0% yield **4** 14% yield

Supplementary Scheme 9. Reaction **1g** + **2n**→ **4** under standard conditions.

The photocatalytic reaction of an electronically more rich xanthenes derivatives led to the formation of homocoupling product 4: A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2n** (0.60 mmol, 101.9 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone), The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, product **3zh** was not formed (detected by TLC and ^{1}H NMR analysis). The reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: DCM = 10: 1 to 2: 1) to afford product **4** as a white solid (11.8 mg, 0.028 mmol, yield: 14% based on **1g**).

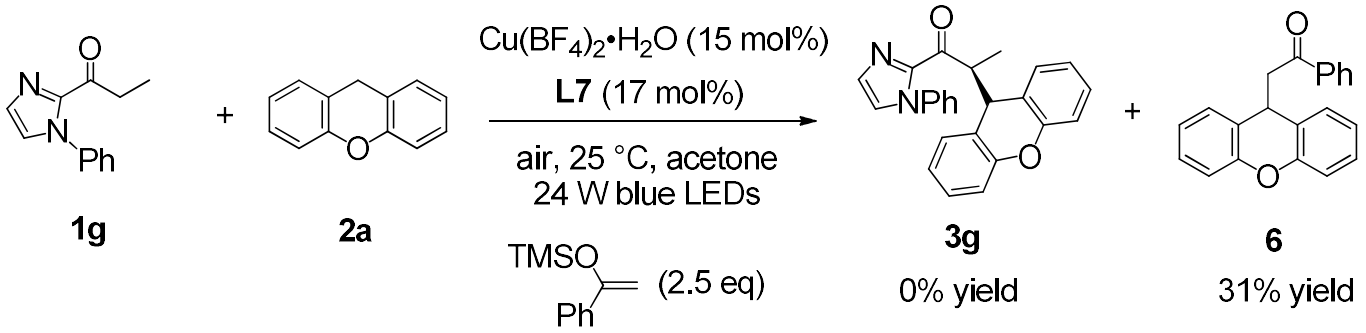
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 6.93 (tt, *J* = 7.4, 3.8 Hz, 2H), 6.84 (dd, *J* = 7.8, 2.9 Hz, 2H), 6.72 – 6.67 (m, 1H), 6.66 – 6.63 (m, 1H), 6.53 (ddt, *J* = 10.7, 8.6, 5.3 Hz, 4H), 6.42 (dd, *J* = 4.0, 2.4 Hz, 2H), 4.13 (s, 2H), 3.78 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 153.73, 153.72, 152.93, 152.91, 129.64, 129.60, 129.18, 129.14, 127.9, 122.58, 122.55, 122.11, 122.10, 115.75, 115.73, 113.97, 113.96, 109.5, 109.4, 100.72, 100.65, 55.4, 48.9.

IR (film): ν (cm^{-1}) 3029, 2881, 1564, 1479, 1401, 1251, 1095, 913, 899, 767, 583.

HRMS (ESI, m/z) calcd for $C_{28}H_{22}NaO_4$ $(M+Na)^+$: 445.1410, found: 445.1412.

5.3.4 Evidence for possible pathway via benzylic cation



Supplementary Scheme 10. Reaction **1g** + **2a** → **3g** in the presence of 1-phenyl-1-trimethylsiloxyethene.

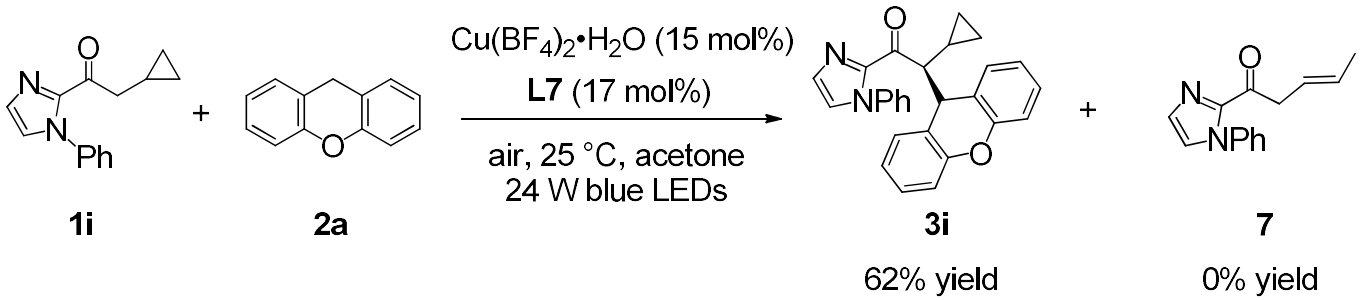
Photocatalytic reaction interfered with a nucleophilic reagent: A dried 10 mL Schlenk tube was charged with **1g** (0.20 mmol, 40.0 mg), **2a** (0.60 mmol, 109.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone), 1-phenyl-1-trimethylsiloxyethene (0.50 mmol, 96.2 mg). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 48 h under air, compound **3g** was not formed (detected by TLC and ^{1}H NMR analysis). The reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 30: 1 to 10: 1) to afford product **6** as a white solid (18.5 mg, 0.062 mmol, yield: 31% based on **1g**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.52 – 7.47 (m, 1H), 7.39 – 7.35 (m, 2H), 7.32 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.11 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.02 (td, *J* = 7.5, 1.2 Hz, 2H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.35 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 152.3, 137.0, 133.1, 128.8, 128.5, 128.1, 127.9, 125.5, 123.5, 116.5, 49.7, 34.7.

Other analytic data of **6** are consistent with the literature.[11]

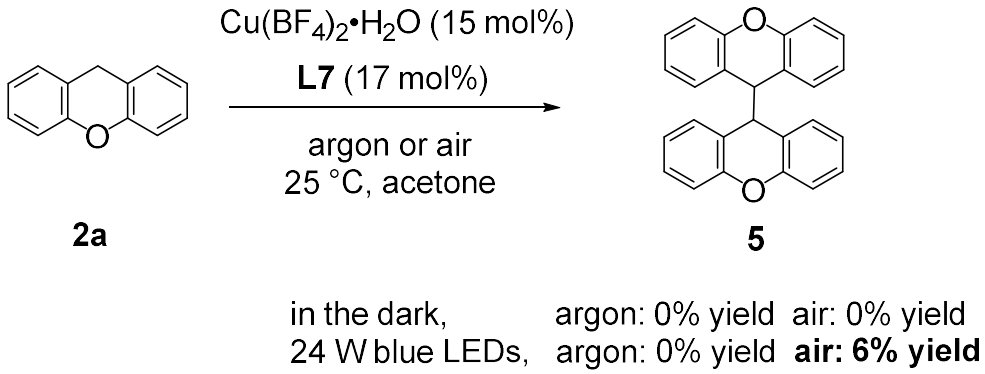
5.3.5 Evidence for the absence of the α-keto radical



Supplementary Scheme 11. Reaction **1i** + **2a** → **3i** under standard conditions.

Radical clock experiment: A dried 10 mL Schlenk tube was charged with **1i** (0.20 mmol, 45.2 mg), **2a** (0.60 mmol, 109.3 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (elution with PE: EA = 5: 1) to afford product **3i** (50.3 mg, 0.124 mmol, yield: 62%). Compound **7** was not formed (detected by TLC and ^{1}H NMR analysis).

5.3.6 Evidences for light-induced oxidation of xanthene by the copper(II) catalyst



Supplementary Scheme 12. Oxidation of xanthene **2a** by copper(II) under different conditions.

In argon atmosphere:

A dried 10 mL Schlenk tube was charged with **2a** (0.20 mmol, 36.4 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone), The mixture was degassed via three

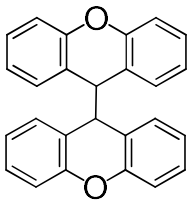
freeze-pump-thaw cycles. The Schlenk tube was positioned in the dark. After being stirred at 25 ℃ for 48 h under argon, compound **5** was not formed (detected by TLC and ^{1}H NMR analysis).

The same Schlenk tube was degassed via three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under argon, compound **5** was not formed (detected by TLC and ^{1}H NMR analysis).

In air atmosphere:

A dried 10 mL Schlenk tube was charged with **2a** (0.20 mmol, 36.4 mg), chiral copper catalyst **[Cu^{II}-L7]** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned in the dark. After being stirred at 25 ℃ for 48 h under air, compound **5** was not formed (detected by TLC and ^{1}H NMR analysis).

The same Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 48 h under air, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (eluted with PE: DCM = 12 : 1 to PE: DCM = 3 : 2) to afford product **5** as a white solid (4.4 mg, 0.012 mmol, yield: 6 % based on **2a**).



5

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 4H), 6.92 (td, *J* = 7.5, 1.0 Hz, 4H), 6.87 (d, *J* = 8.1 Hz, 4H), 6.66 (dd, *J* = 7.5, 1.4 Hz, 4H), 4.20 (s, 2H).

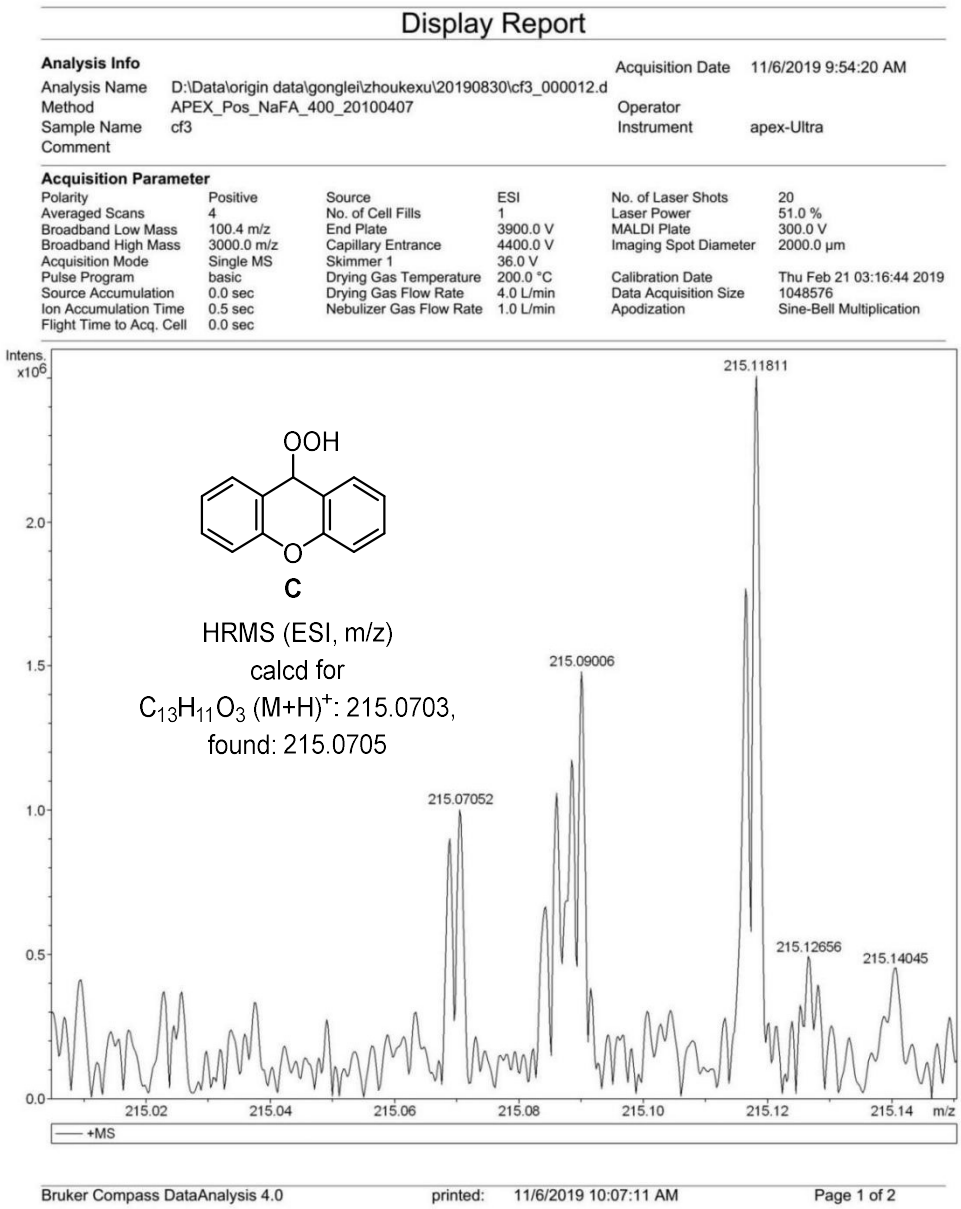
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 129.1, 128.1, 122.6, 115.8, 100.0, 29.7.

Other analytic data of **5** are consistent with the literature.[10]

Note: The visible light, chiral ligand, copper(II) salt and air were all essential for the transformation to compound **5**.

5.3.7 Detection of Intermediate C

Preparation of the samples for HRMS analysis. A dried 10 mL Schlenk tube was charged with **2a** (0.20 mmol, 36.4 mg), chiral copper catalyst **Cu^{II}-L7** (2.0 mL taken from the 15 mM solution in acetone). The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 ℃ for 72 h, the solution was used directly for HRMS analysis.

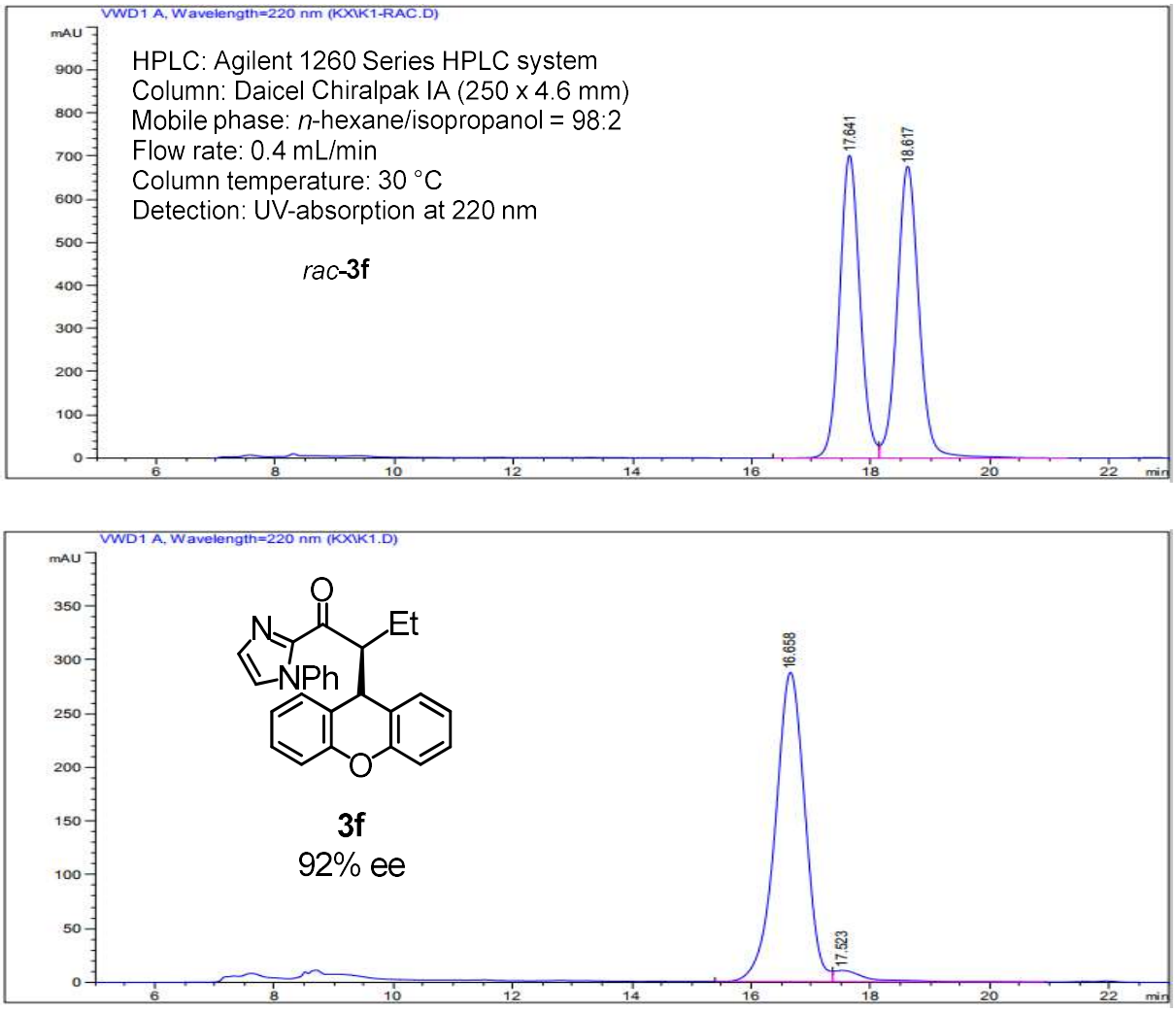


Supplementary Fig. 7 HRMS spectra.

6. Chiral Chromatography

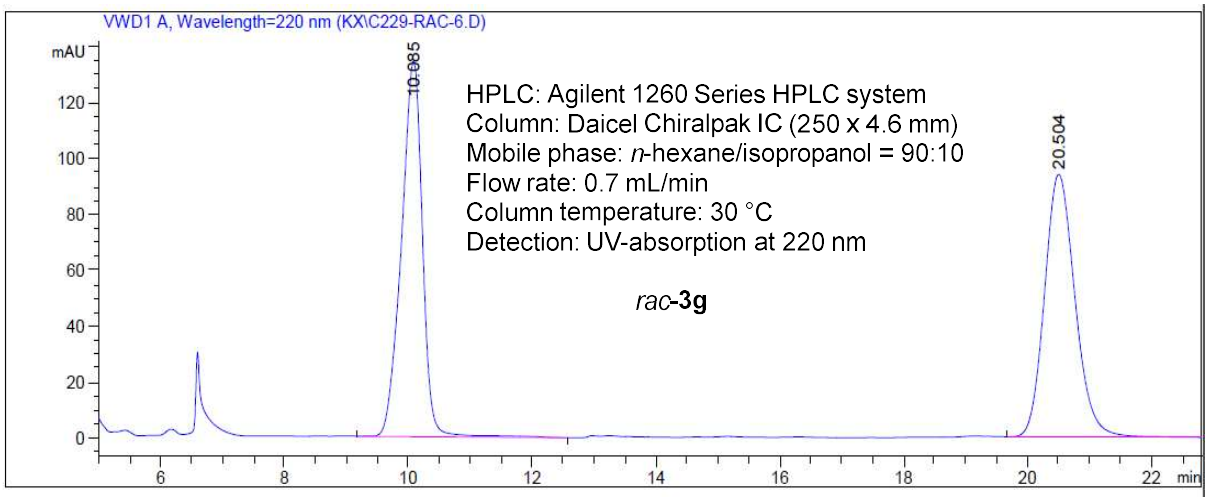
6.1 Determination of enantioselectivities of the asymmetric photoredox reactions

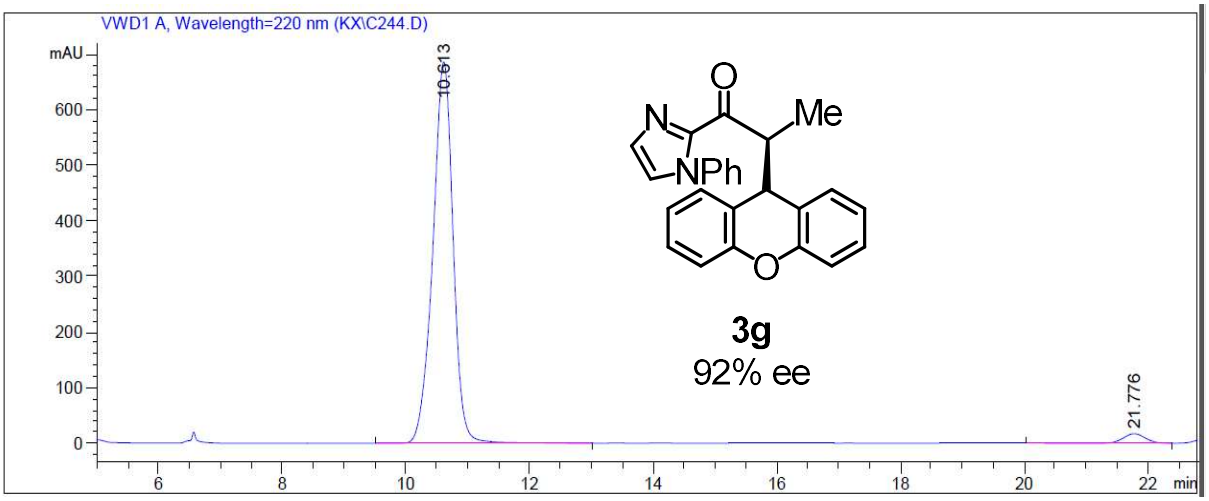
Optical purities of the compounds **3f-3u** and **3v-3zg** were determined with a Daicel Chiralpak AD-H, OD-H, IA, IC or OJ HPLC column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 220 nm.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.658	BV	0.5303	9913.08105	287.46600	96.0553
2	17.523	VB	0.5630	407.09988	10.43919	3.9447

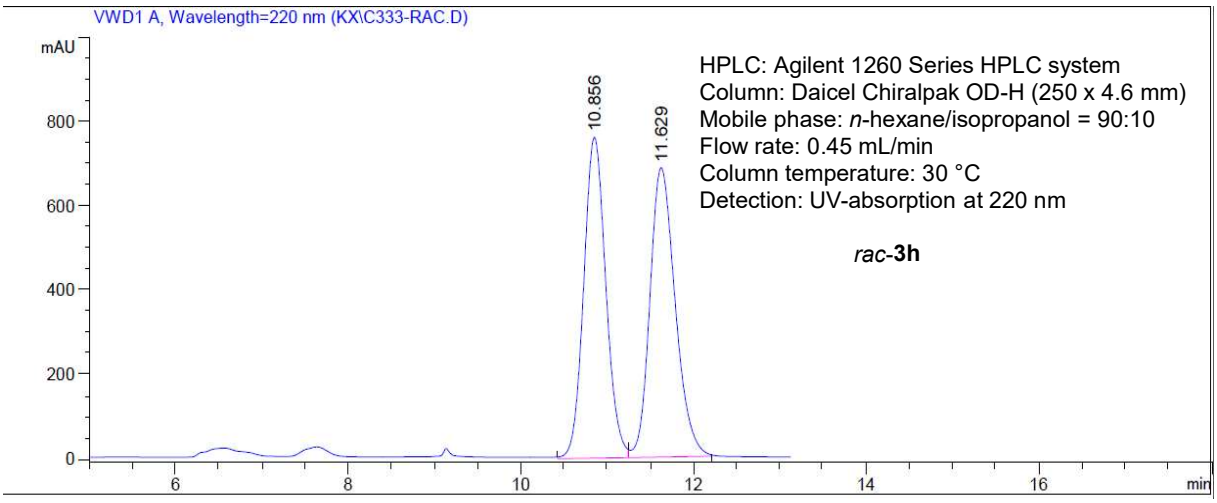
Supplementary Fig. 8 HPLC trace for the racemic reference *rac*-**3f**, and non-racemic product **3f**.

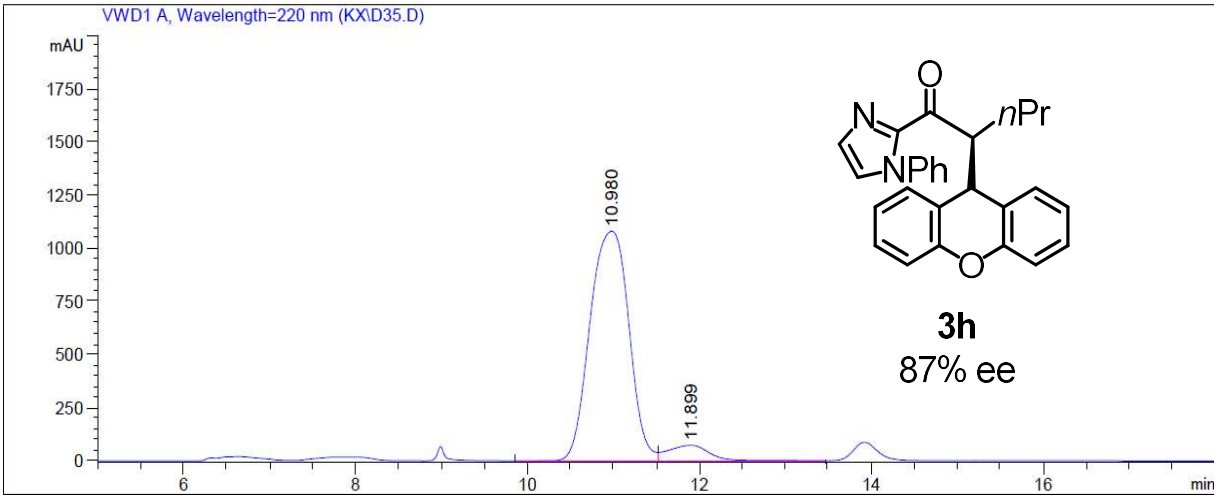




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.613	MM R	0.3803	1.56368e4	685.31427	96.2315
2	21.777	MM R	0.5502	612.34174	18.54781	3.7685

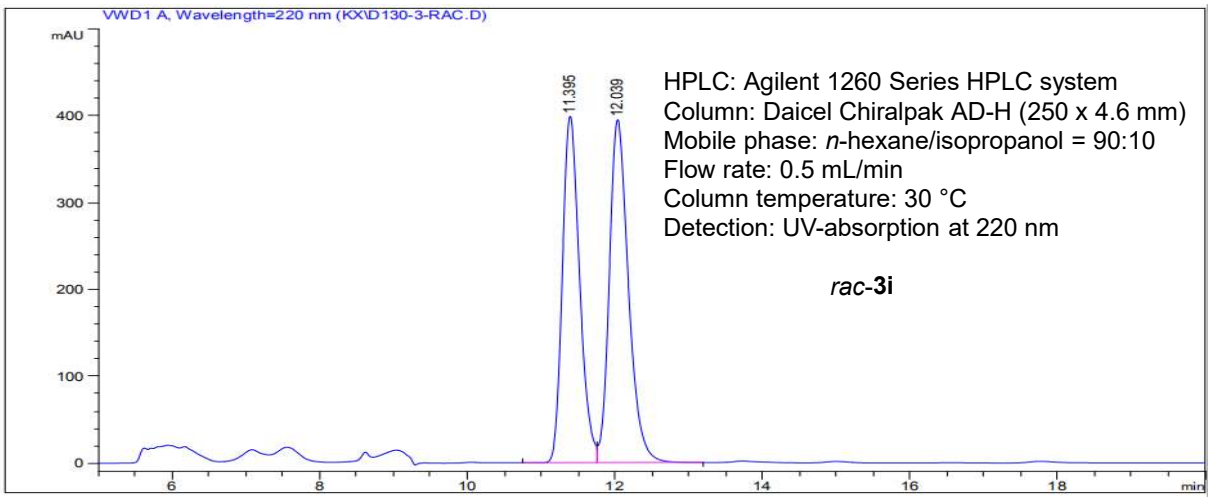
Supplementary Fig. 9 HPLC trace for the racemic reference *rac*-**3g**, and non-racemic product **3g**.

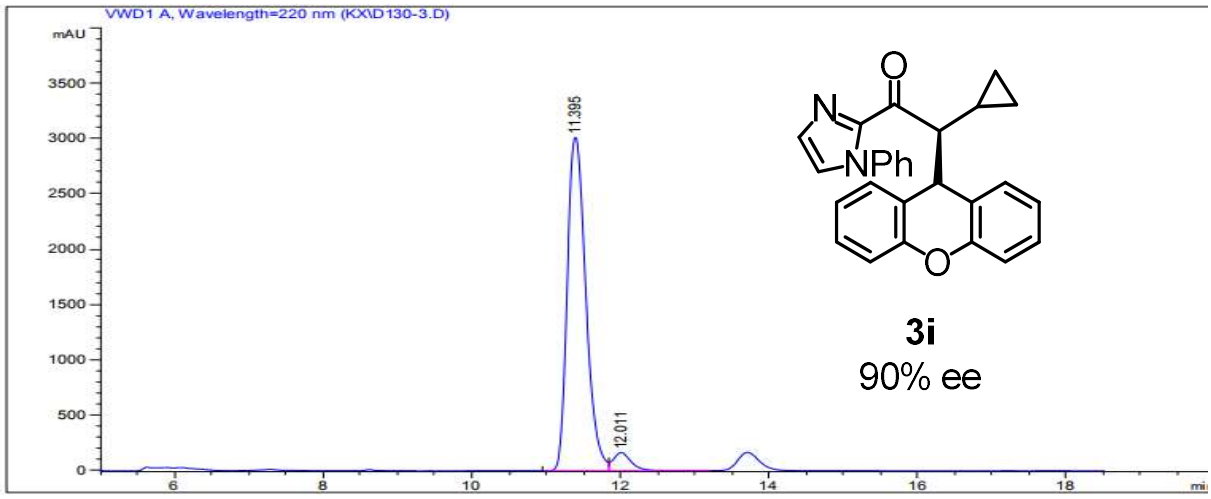




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.980	BV	0.5112	3.39577e4	1078.76672	93.3002
2	11.899	VV	0.5204	2438.45068	72.50474	6.6998

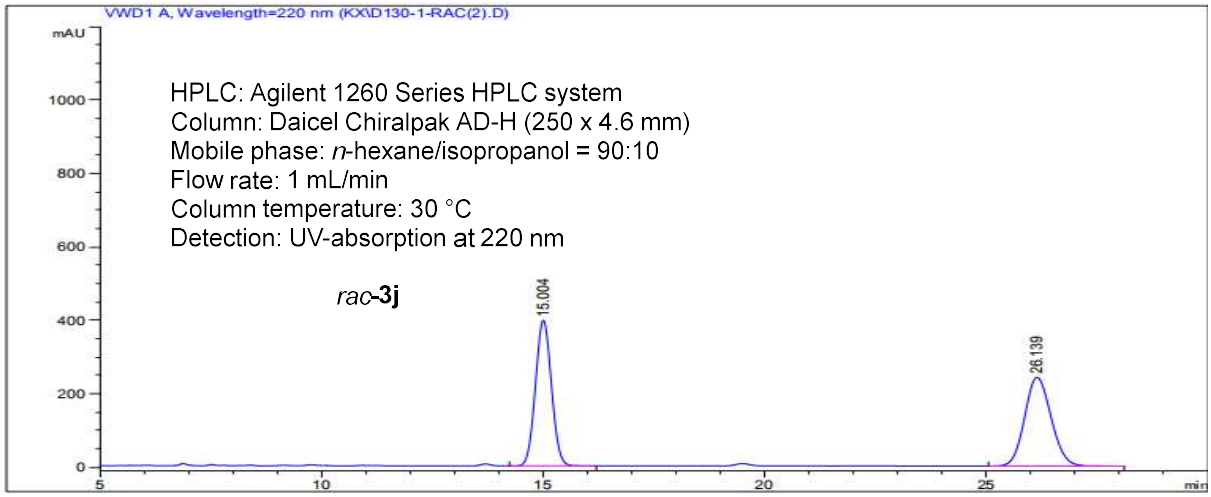
Supplementary Fig. 10 HPLC trace for the racemic reference *rac*-**3h**, and non-racemic product **3h**.

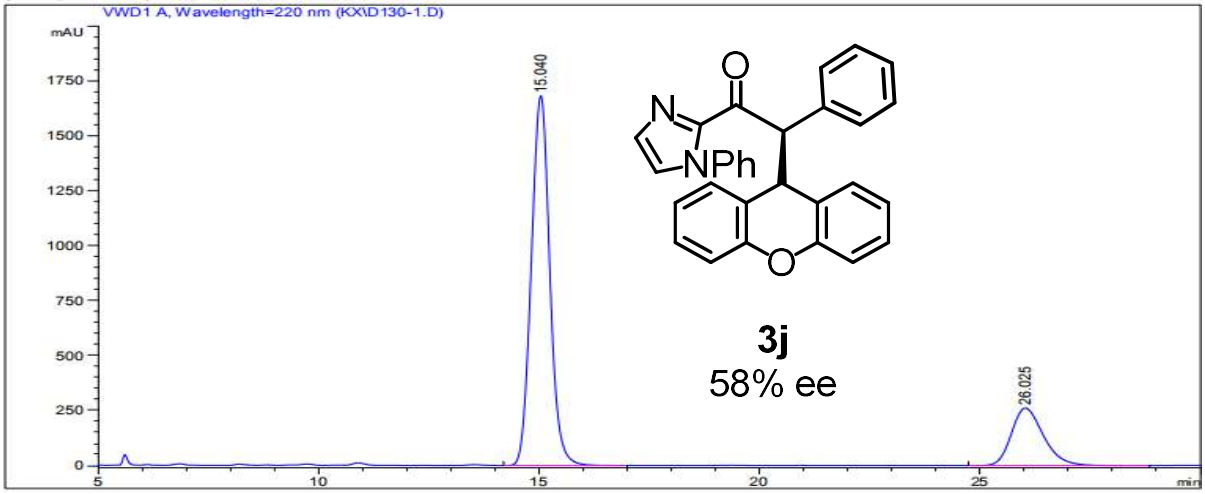




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.395	BV	0.2699	5.20842e4	3009.62769	94.8213
2	12.011	VV	0.2563	2844.61426	164.08722	5.1787

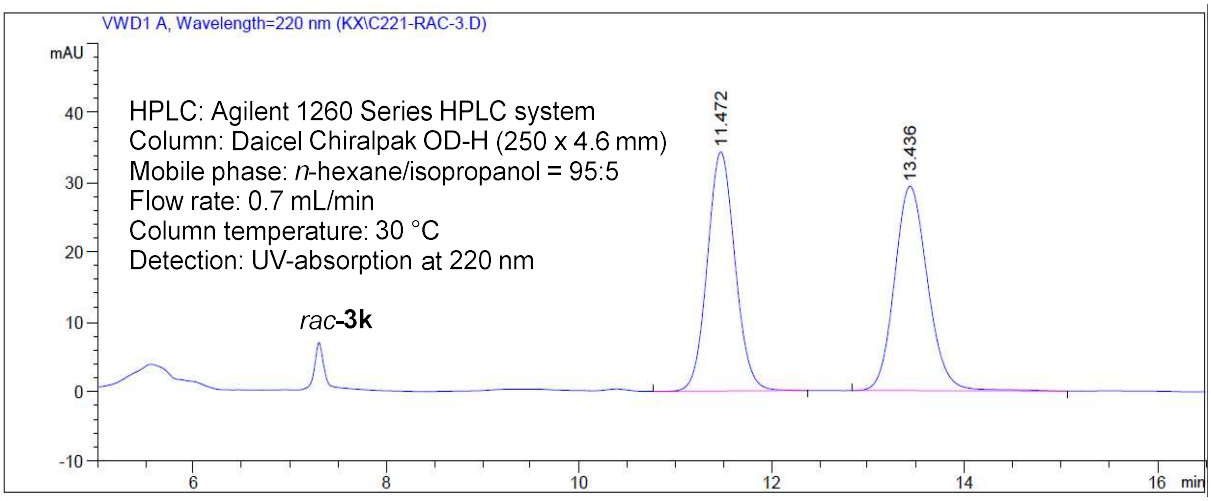
Supplementary Fig. 11 HPLC trace for the racemic reference *rac*-**3i**, and non-racemic product **3i**.

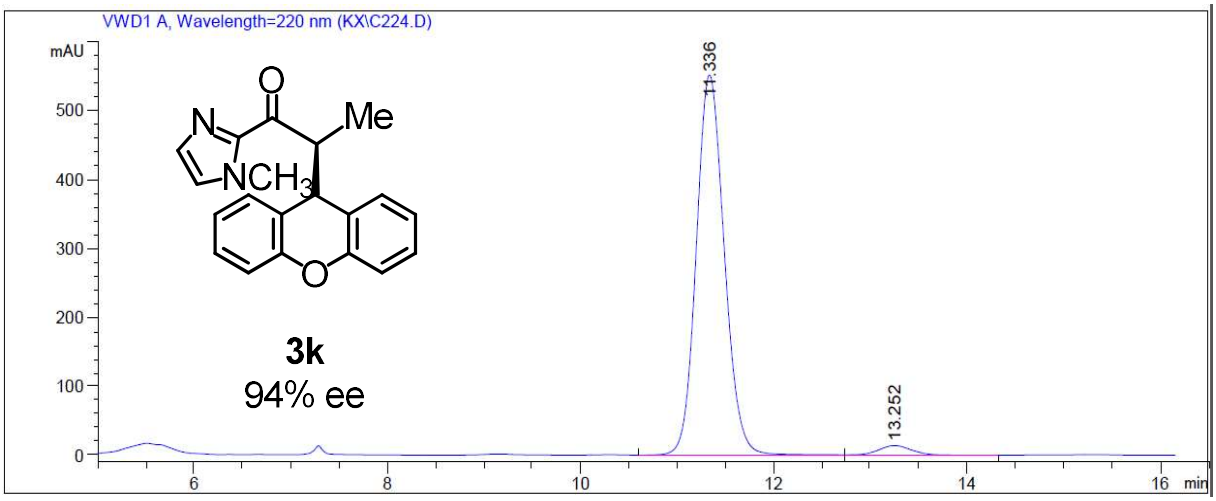




#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.040	BB	0.4512	4.88696e4	1680.72168	78.7938
2	26.025	BB	0.7769	1.31526e4	260.56113	21.2062

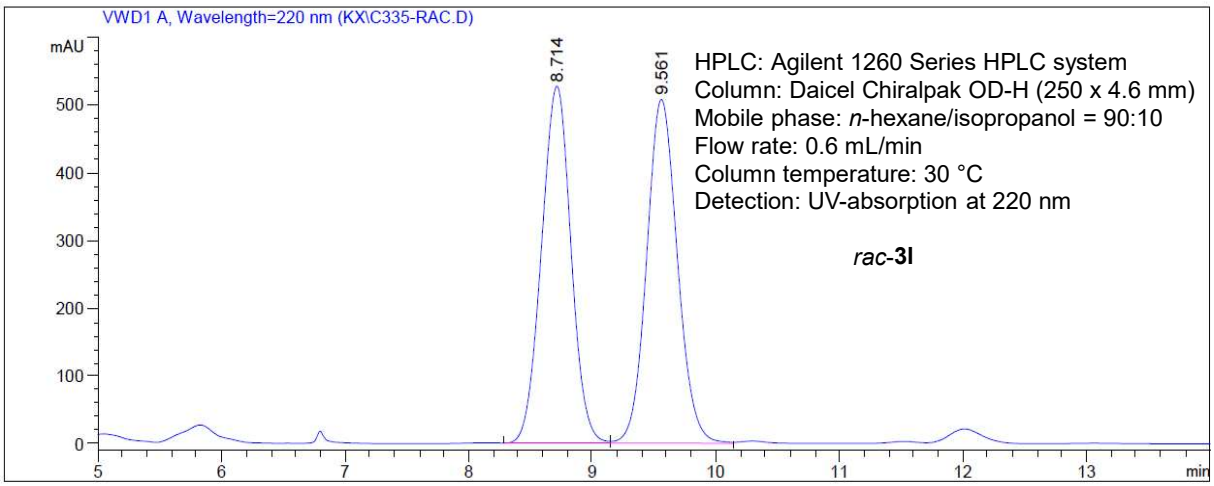
Supplementary Fig. 12 HPLC trace for the racemic reference *rac*-**3j**, and non-racemic product **3j**.

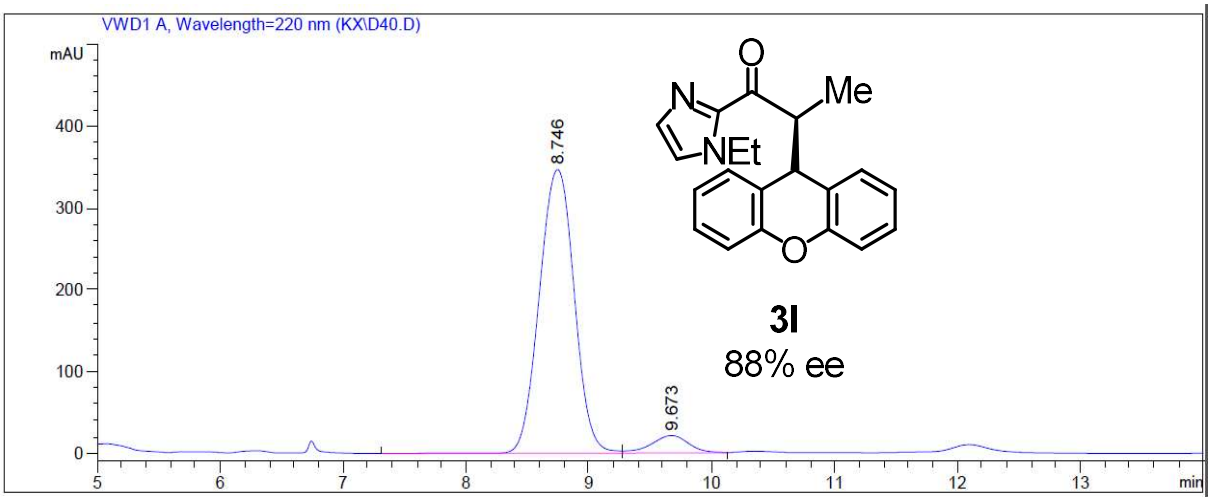




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.336	BV	0.3114	1.11042e4	550.35541	97.0355
2	13.252	VV	0.3789	339.24484	13.79318	2.9645

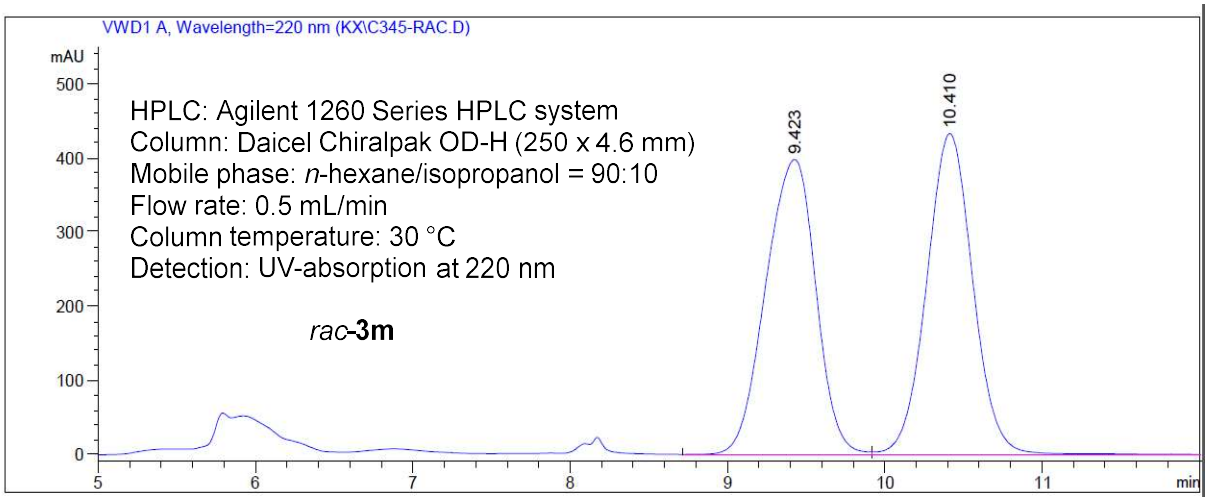
Supplementary Fig. 13 HPLC trace for the racemic reference *rac*-**3k**, and non-racemic product **3k**.

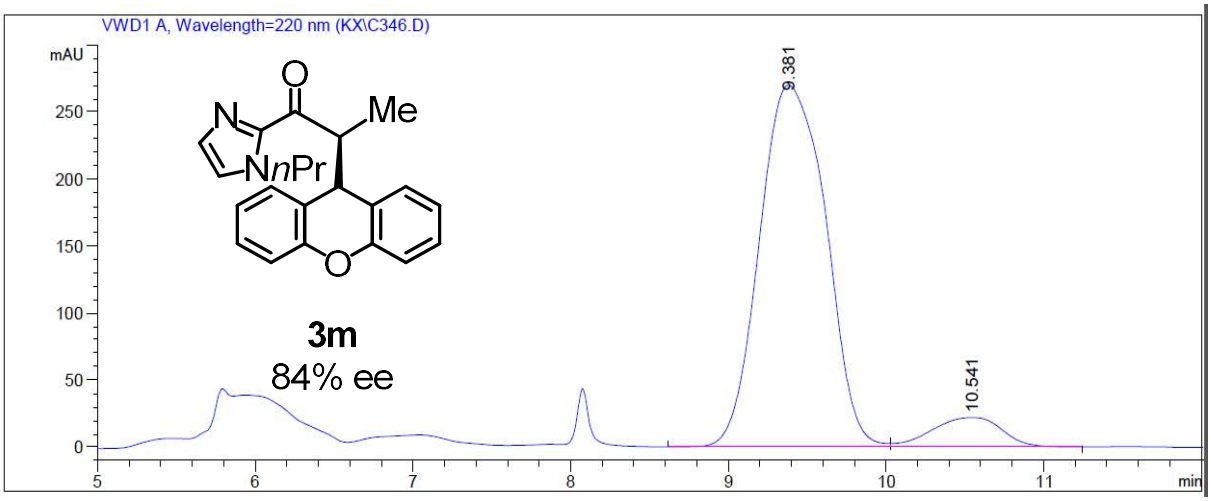




#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.746	BV	0.3142	6833.72021	346.30075	93.8312
2	9.673	VV	0.3207	449.27621	21.41915	6.1688

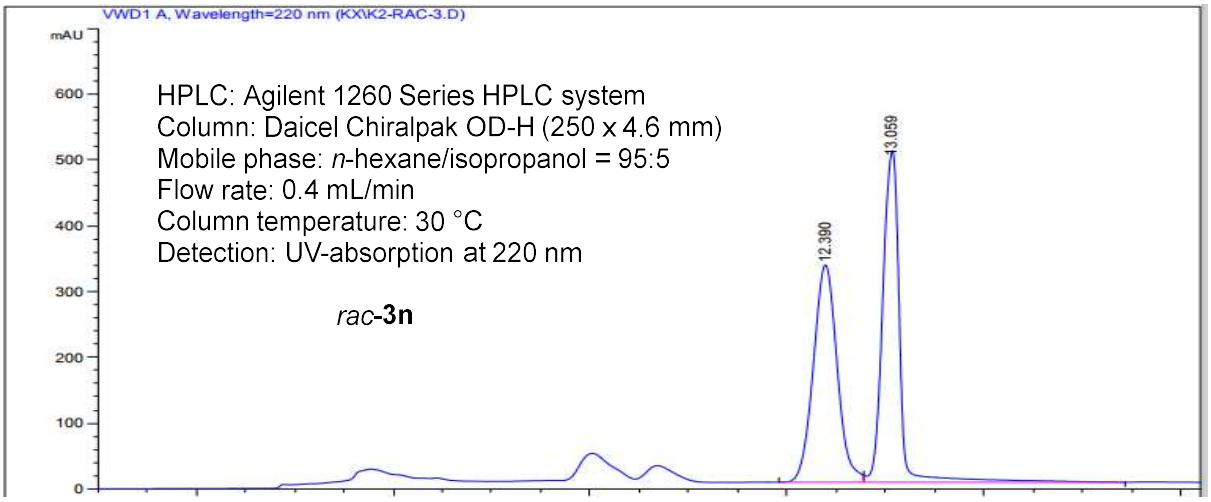
Supplementary Fig. 14 HPLC trace for the racemic reference *rac*-**3l**, and non-racemic product **3l**.

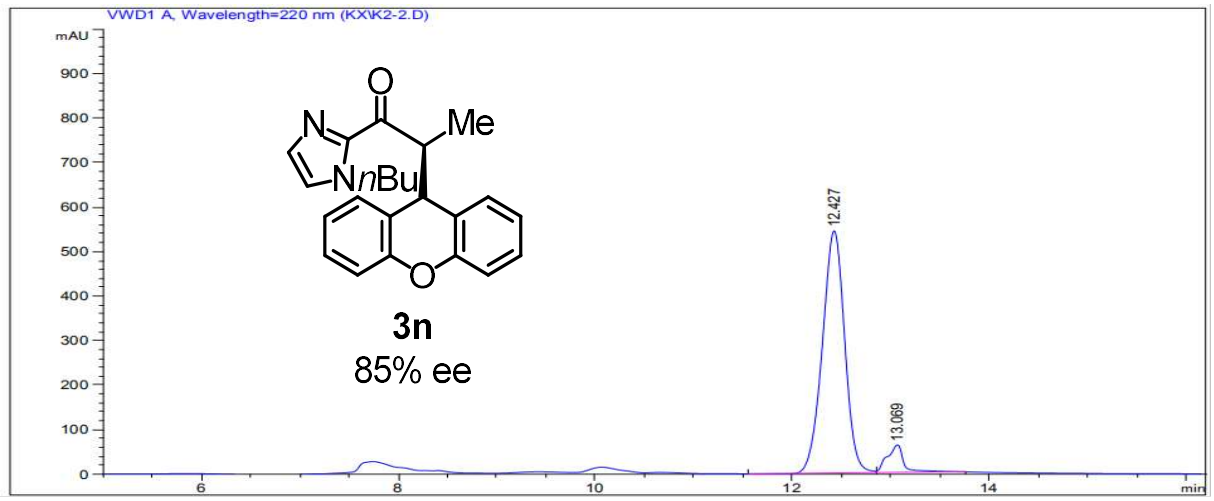




#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.381	BV	0.4801	7864.48047	269.74103	92.1446
2	10.541	VB	0.4928	670.45288	21.92178	7.8554

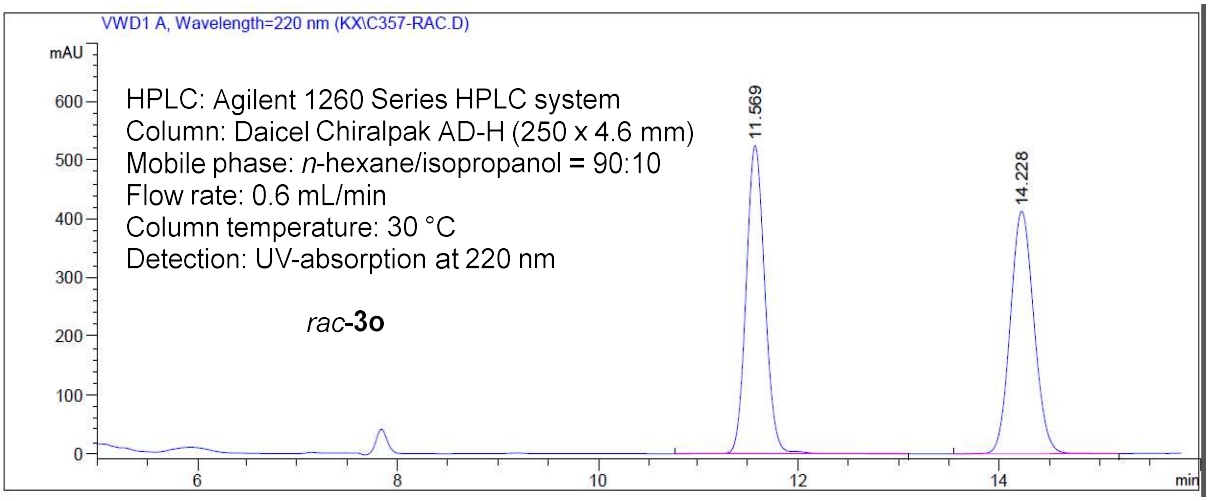
Supplementary Fig. 15 HPLC trace for the racemic reference *rac*-**3m**, and non-racemic product **3m**.

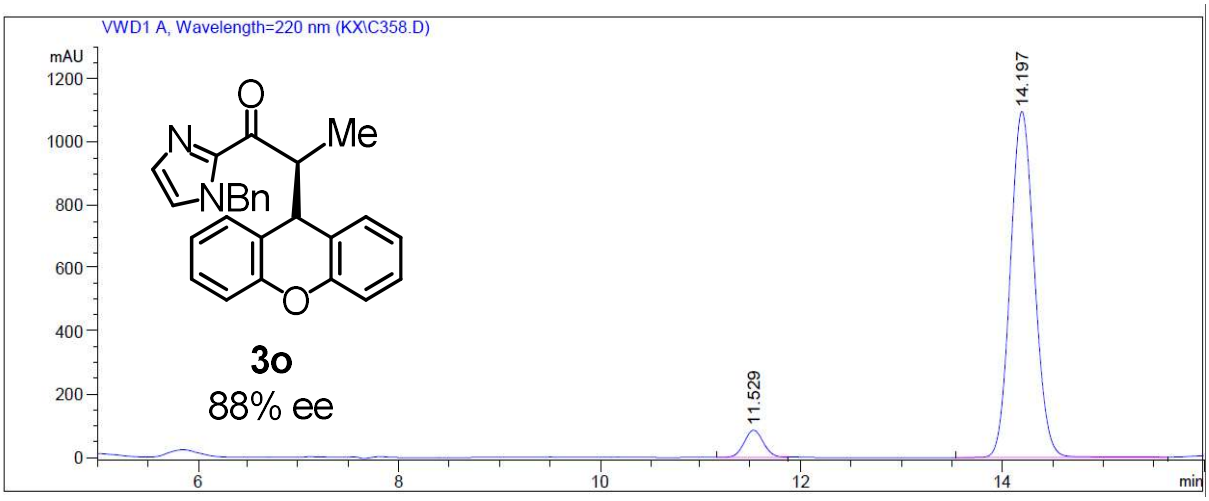




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.427	MF R	0.2609	8538.53711	545.53491	92.3258
2	13.069	FM R	0.1883	709.73407	62.81205	7.6742

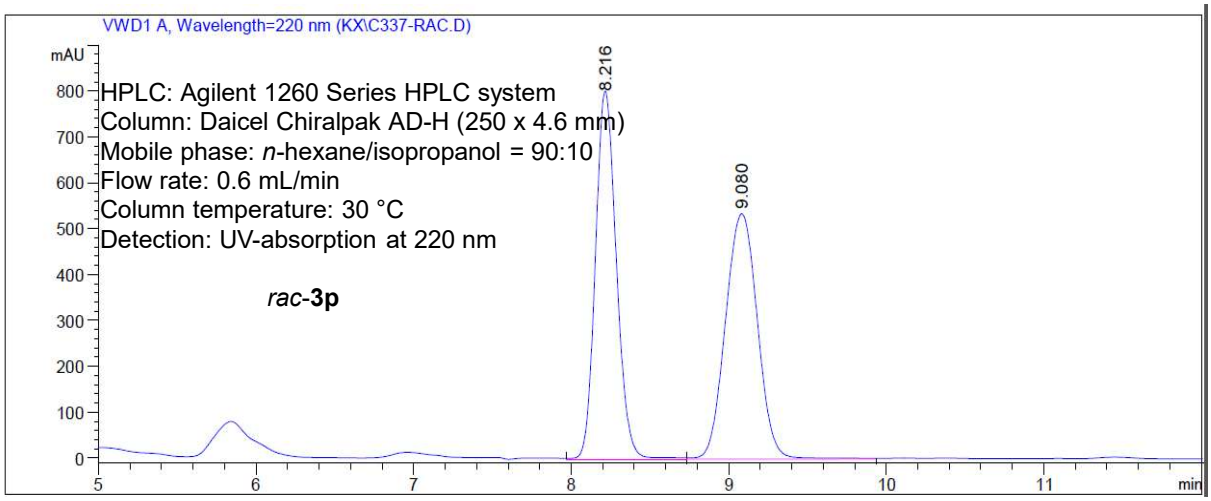
Supplementary Fig. 16 HPLC trace for the racemic reference *rac*-**3n**, and non-racemic product **3n**.

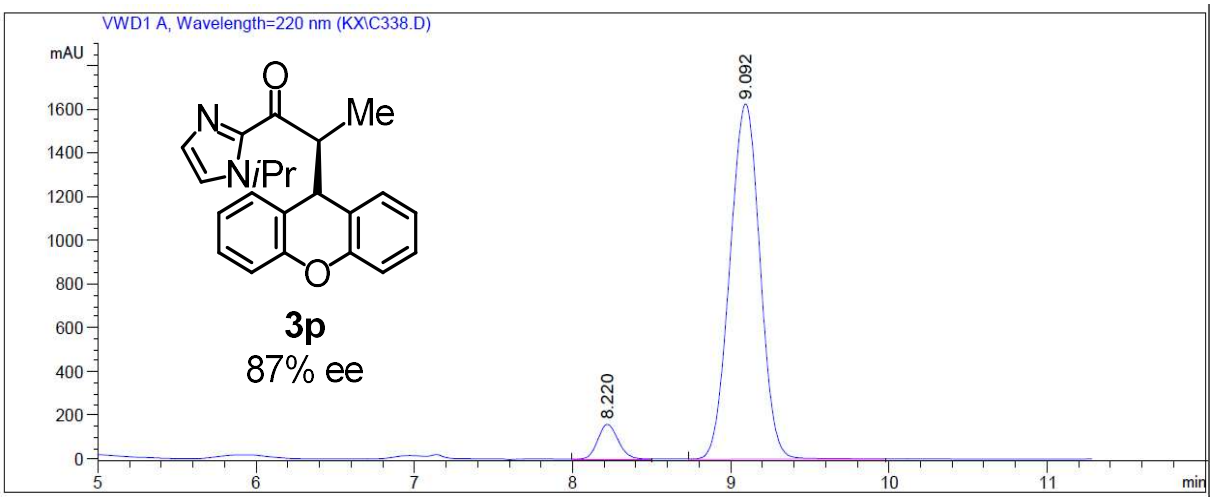




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.529	BV	0.2082	1155.08582	86.29392	5.9882
2	14.197	BB	0.2574	1.81342e4	1094.06824	94.0118

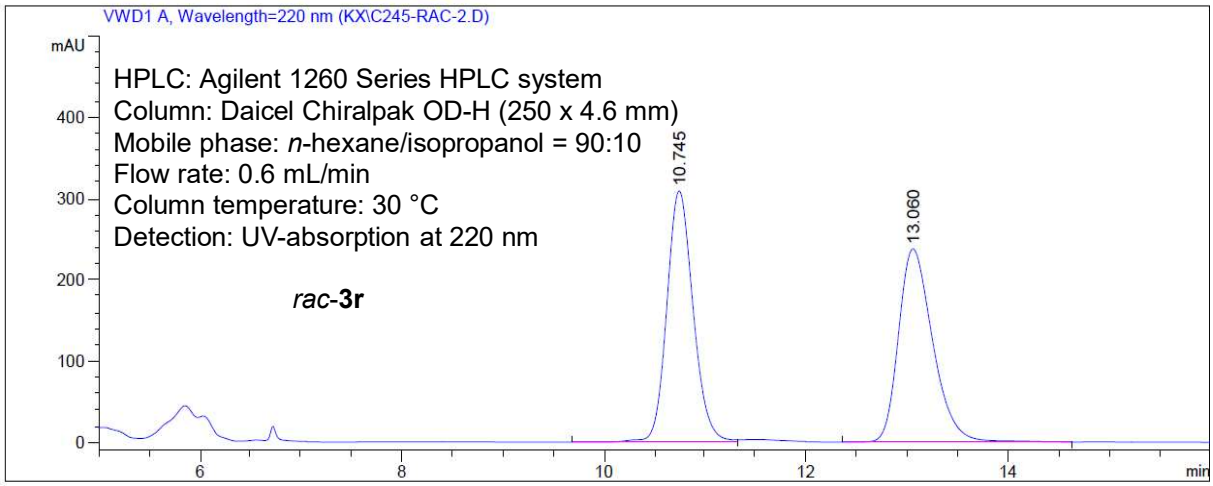
Supplementary Fig. 17 HPLC trace for the racemic reference *rac*-**3o**, and non-racemic product **3o**.

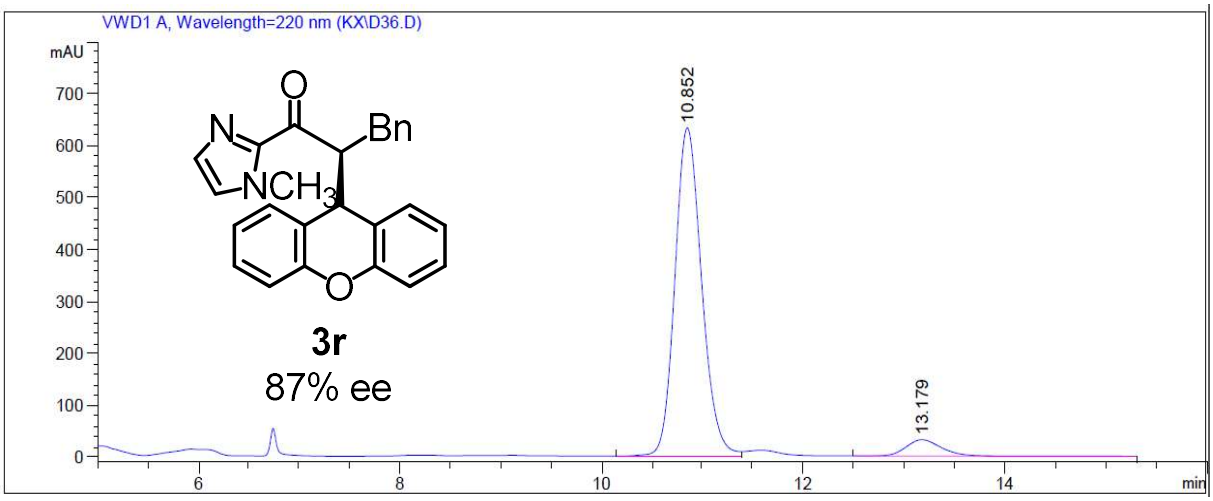




#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.220	VV	0.1426	1463.04602	160.10771	6.3816
2	9.092	VV	0.2066	2.14631e4	1619.84497	93.6184

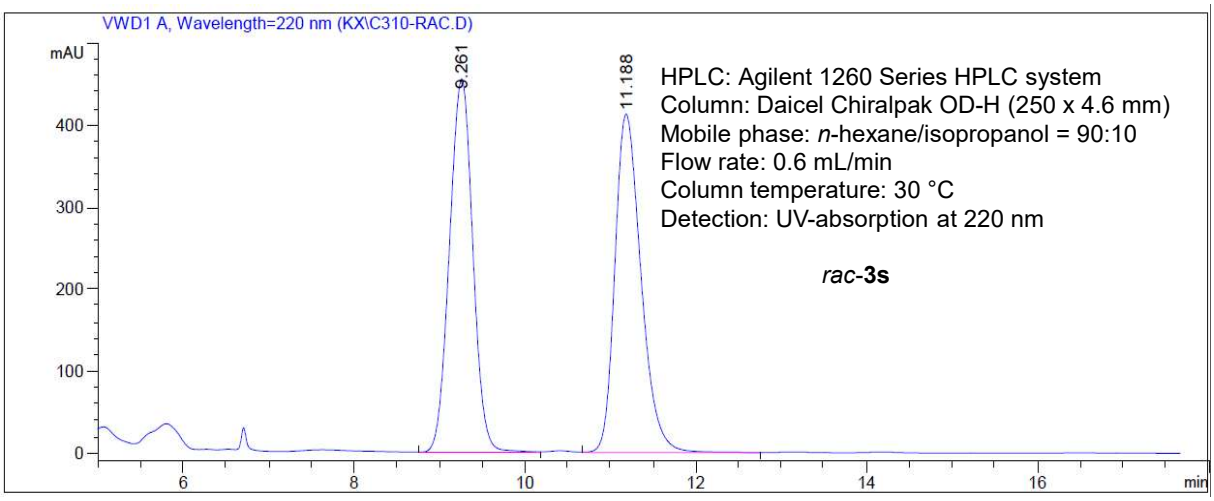
Supplementary Fig. 18 HPLC trace for the racemic reference *rac*-**3p**, and non-racemic product **3p**.

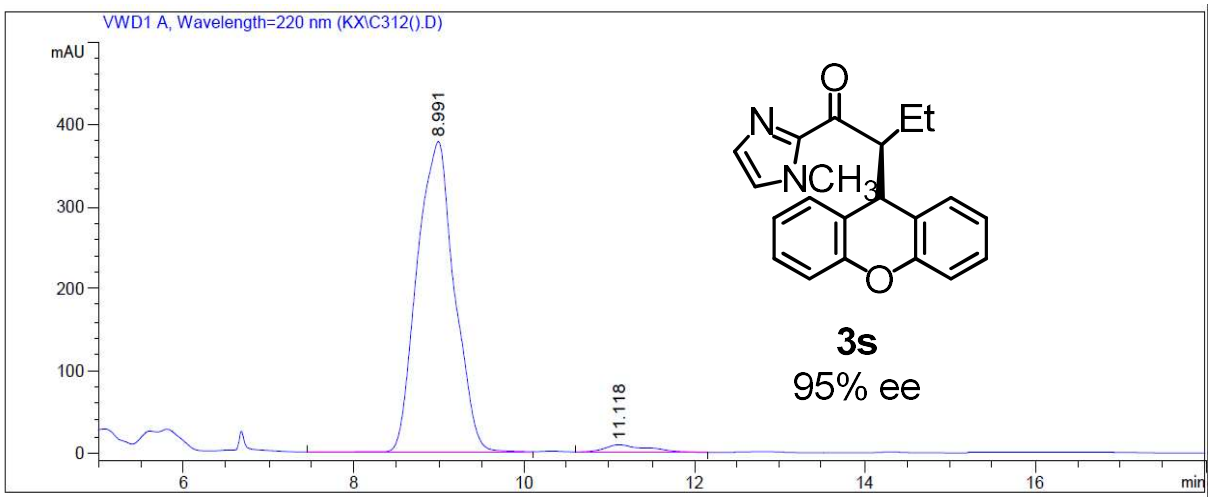




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.852	BV	0.2852	1.16720e4	632.79645	93.5063
2	13.179	VBA	0.3880	810.58032	31.73712	6.4937

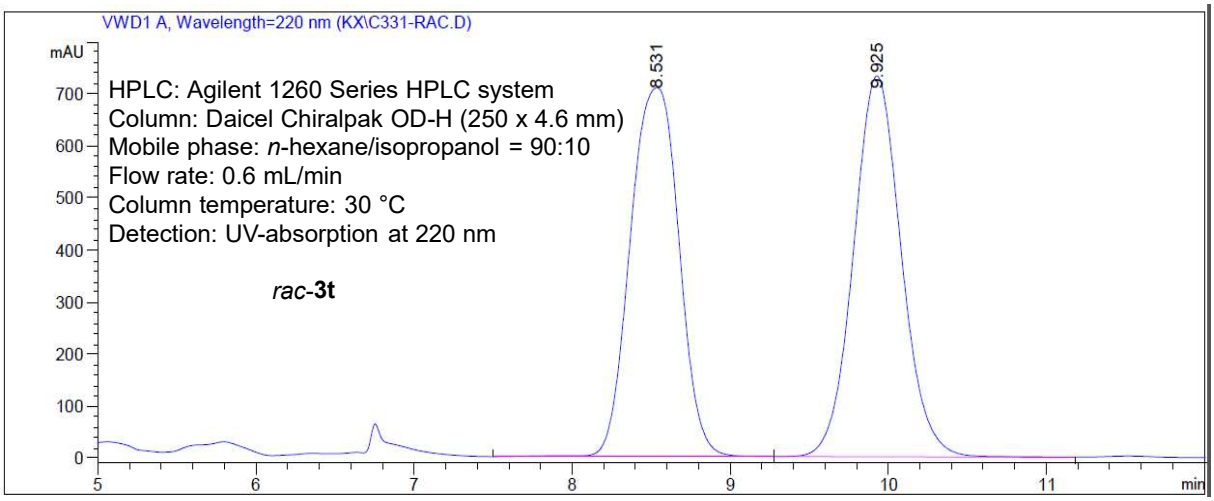
Supplementary Fig. 19 HPLC trace for the racemic reference *rac*-**3r**, and non-racemic product **3r**.

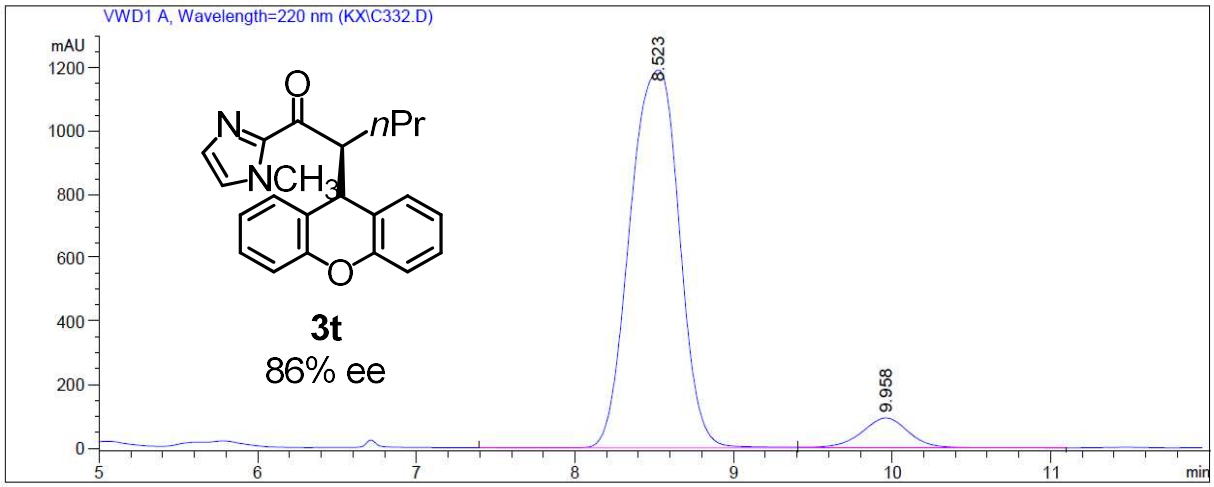




#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.991	BV	0.4789	1.14900e4	377.72589	97.2428
2	11.118	VB	0.4907	325.78000	9.16534	2.7572

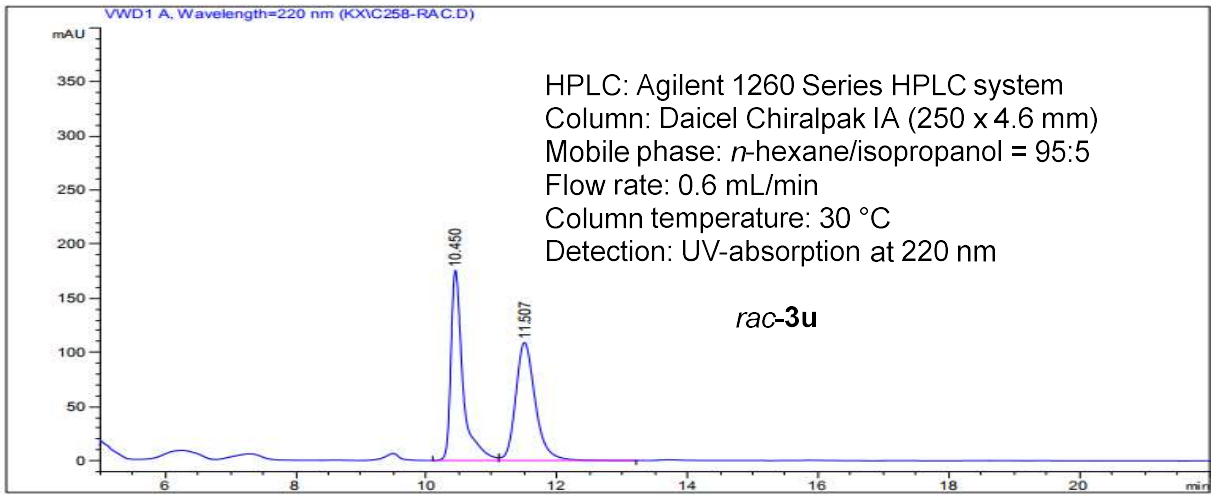
Supplementary Fig. 20 HPLC trace for the racemic reference *rac*-**3s**, and non-racemic product **3s**.

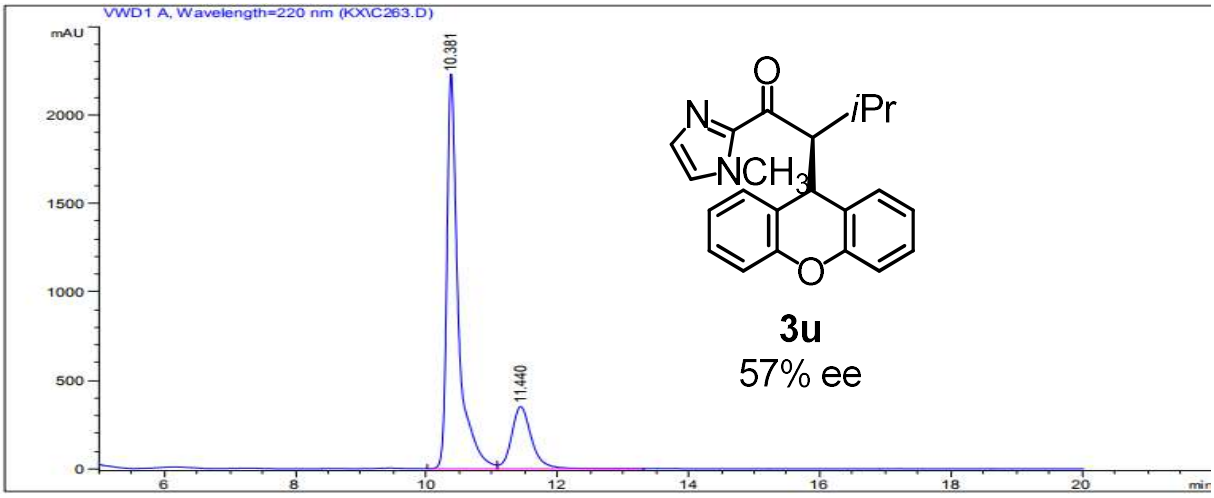




#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.523	BV	0.3482	2.57354e4	1190.71143	92.8022
2	9.958	VV	0.3185	1996.04761	94.47097	7.1978

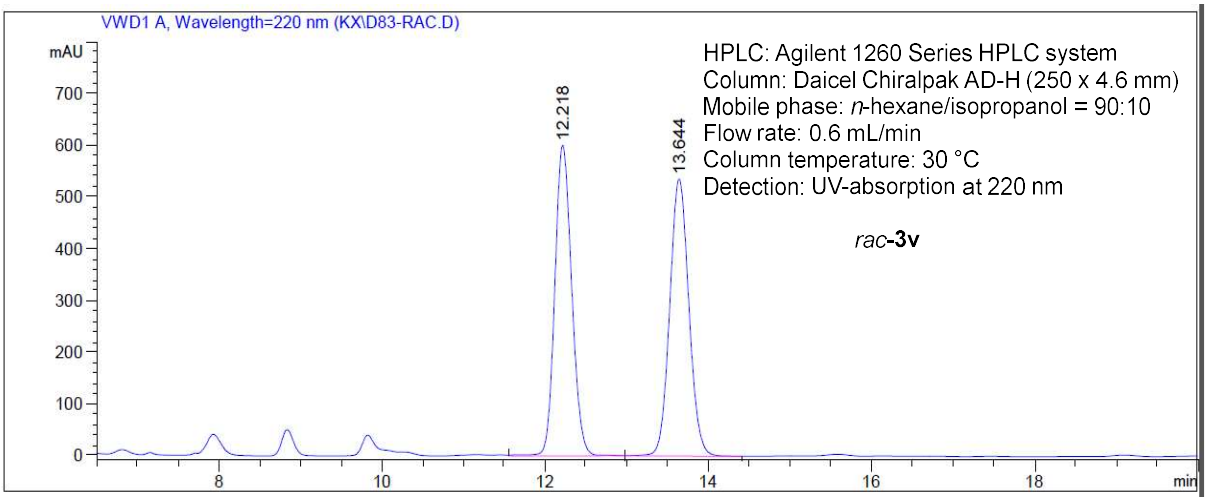
Supplementary Fig. 21 HPLC trace for the racemic reference *rac*-**3t**, and non-racemic product **3t**.

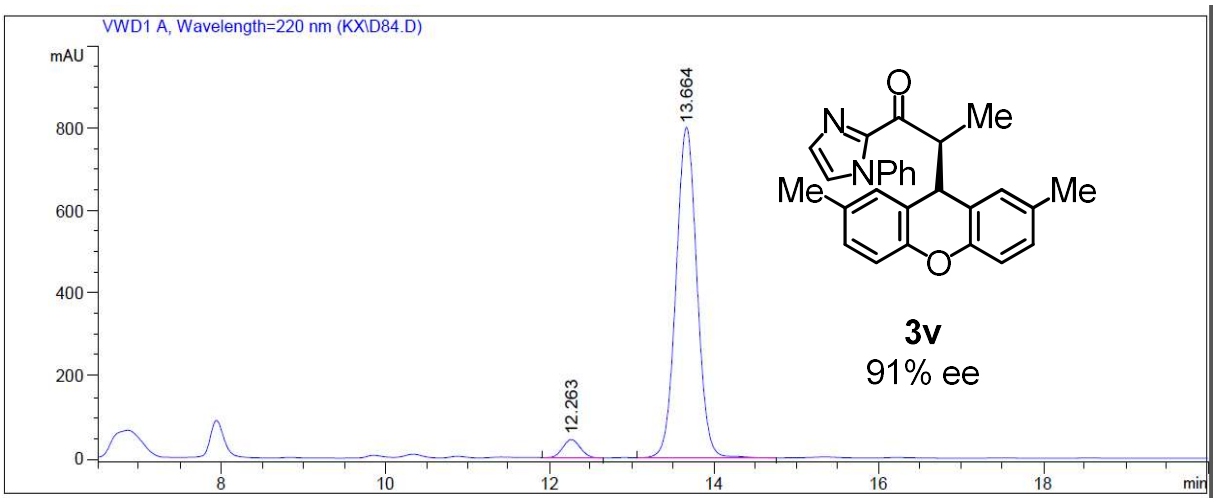




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.381	VV	0.1812	2.69786e4	2229.41748	78.4161
2	11.440	VV	0.3188	7425.83350	350.96243	21.5839

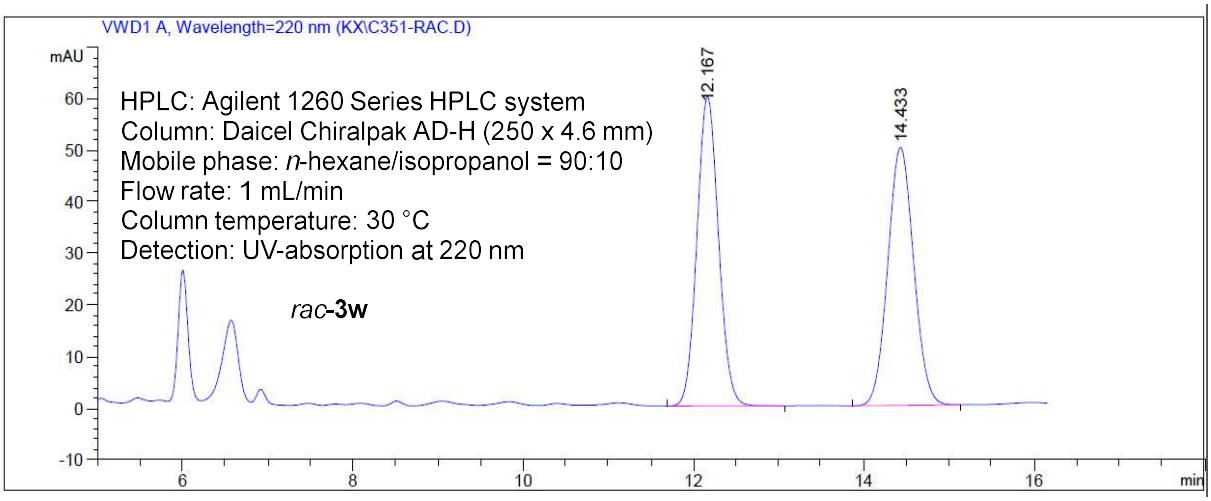
Supplementary Fig. 22 HPLC trace for the racemic reference *rac*-**3u**, and non-racemic product **3u**.

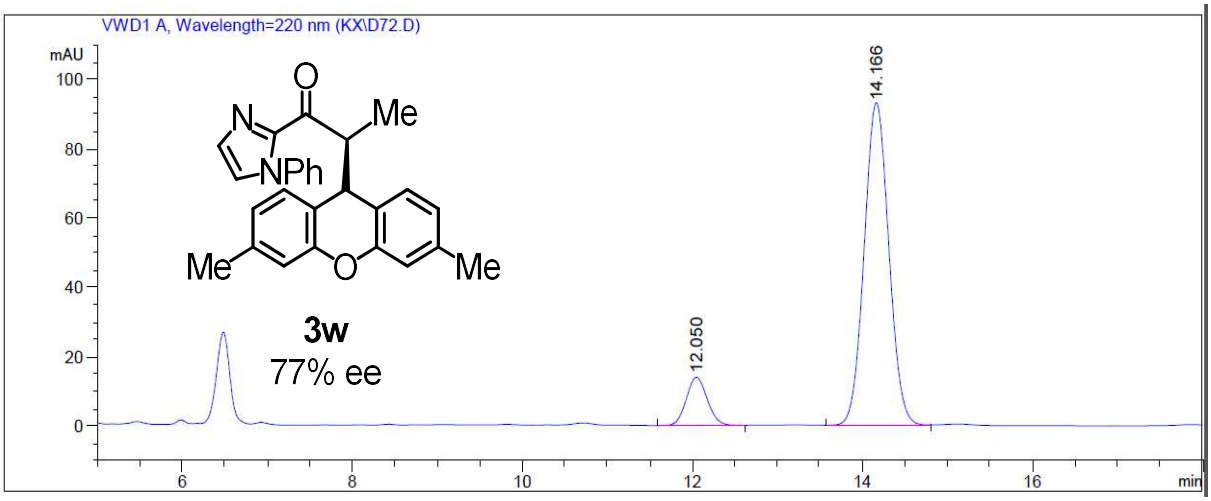




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.263	VB	0.2420	678.79724	44.48119	4.5576
2	13.664	VV	0.2792	1.42148e4	800.35846	95.4424

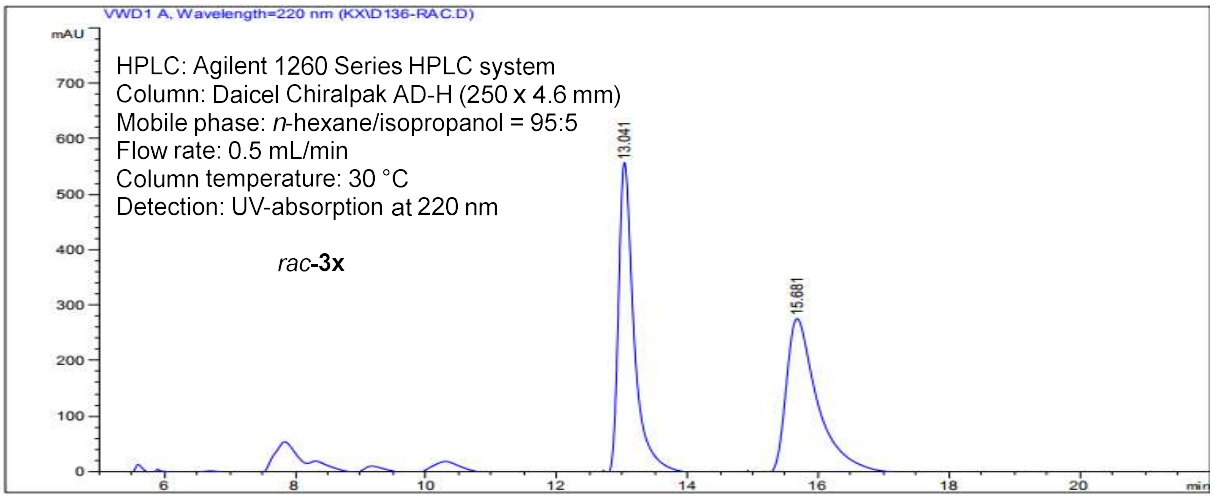
Supplementary Fig. 23 HPLC trace for the racemic reference *rac*-**3v**, and non-racemic product **3v**.

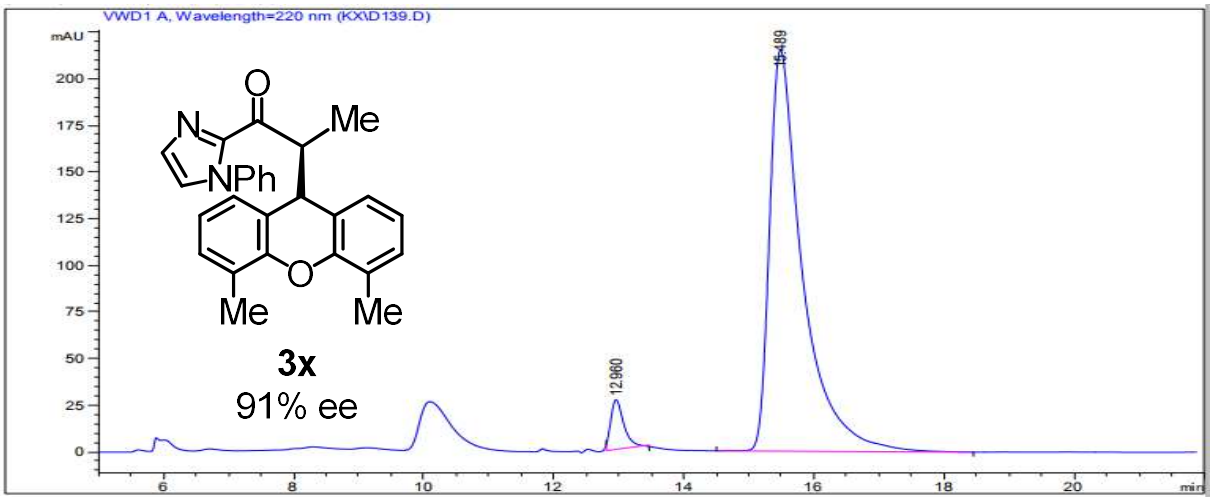




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.050	BV	0.2672	240.60773	13.94937	11.3258
2	14.166	VV	0.3158	1883.81934	93.21373	88.6742

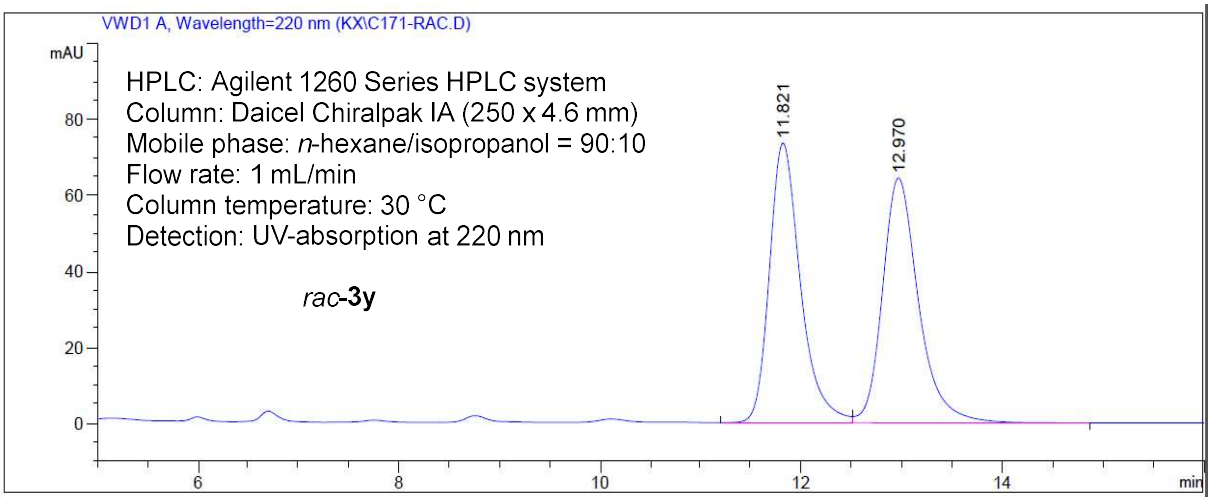
Supplementary Fig. 24 HPLC trace for the racemic reference *rac*-**3w**, and non-racemic product **3w**.

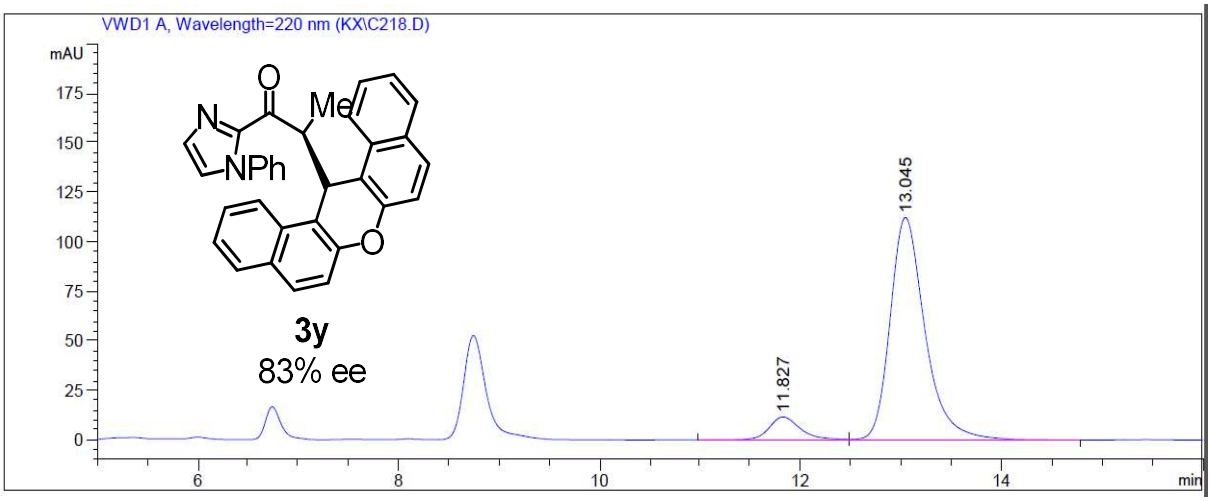




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.960	MM R	0.2290	365.56268	26.60356	4.5977
2	15.489	BB	0.5155	7585.38770	215.06519	95.4023

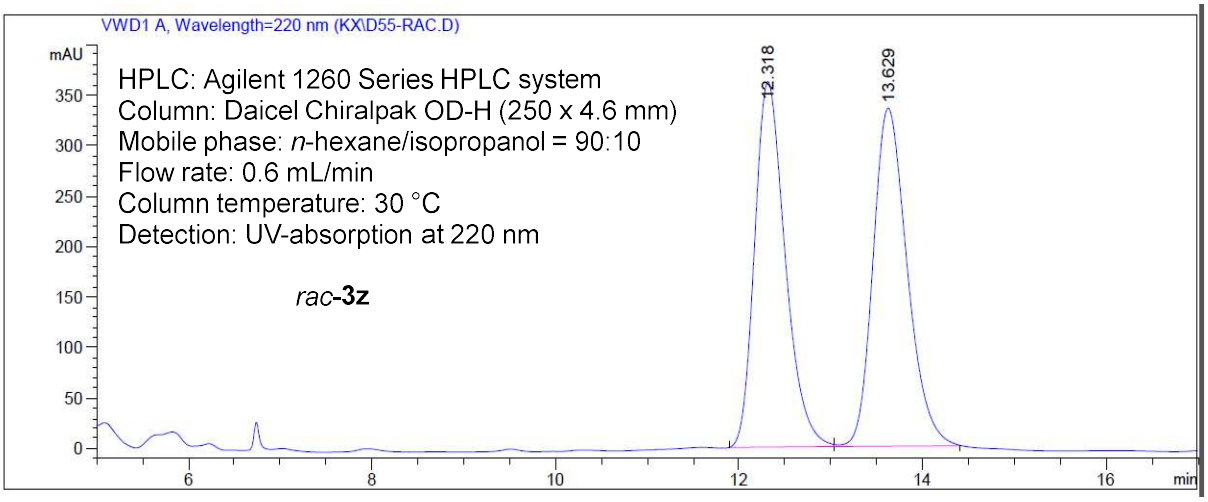
Supplementary Fig. 25 HPLC trace for the racemic reference *rac*-**3x** and non-racemic product **3x**.

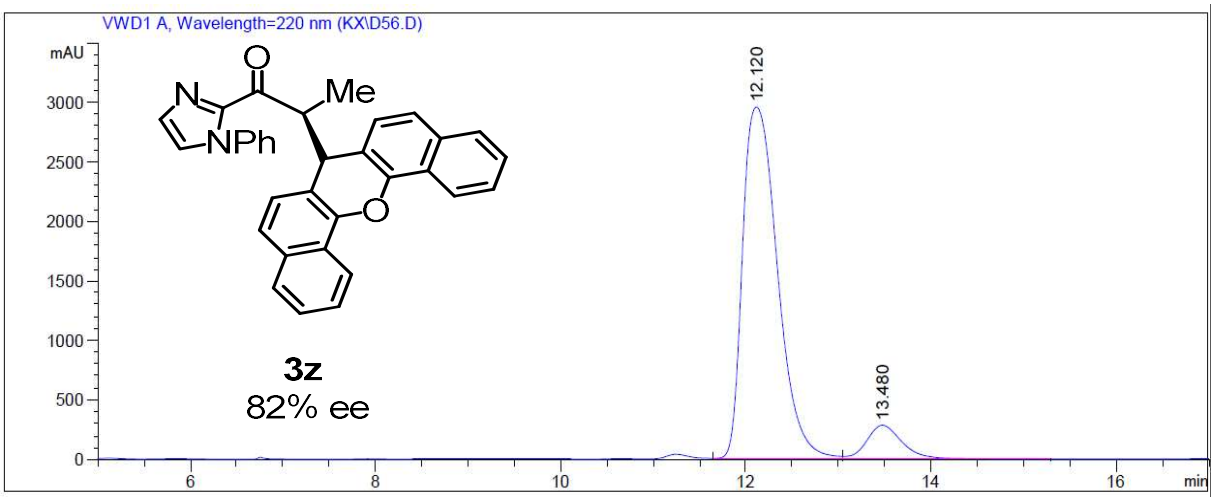




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.827	VV	0.3286	252.99382	11.59361	8.5434
2	13.045	VB	0.3653	2708.28809	112.30460	91.4566

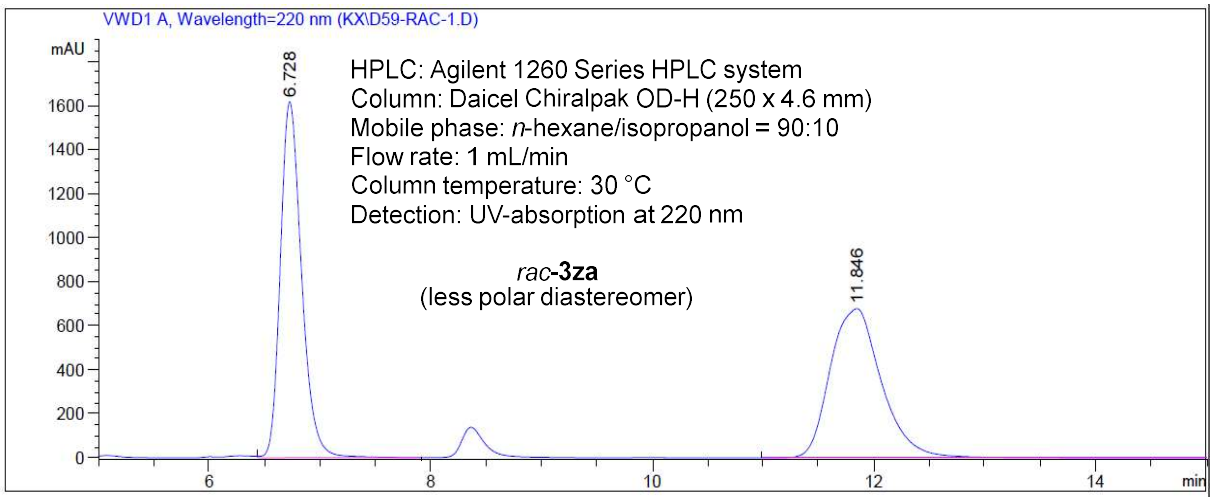
Supplementary Fig. 26 HPLC trace for the racemic reference *rac*-**3y**, and non-racemic product **3y**.

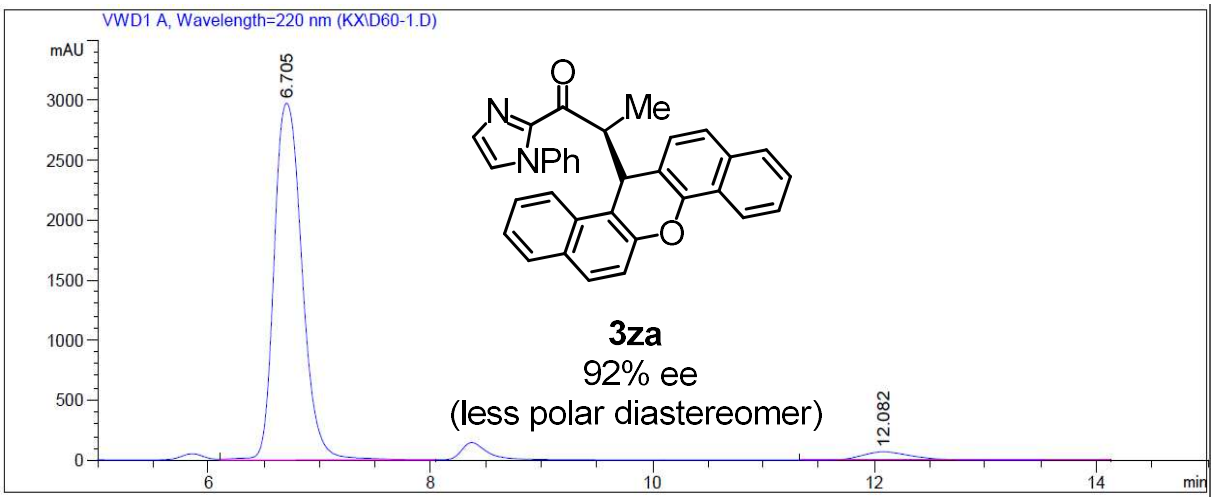




#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.120	VV	0.4140	7.75761e4	2957.92822	91.0493
2	13.480	VB	0.4095	7626.20996	283.78699	8.9507

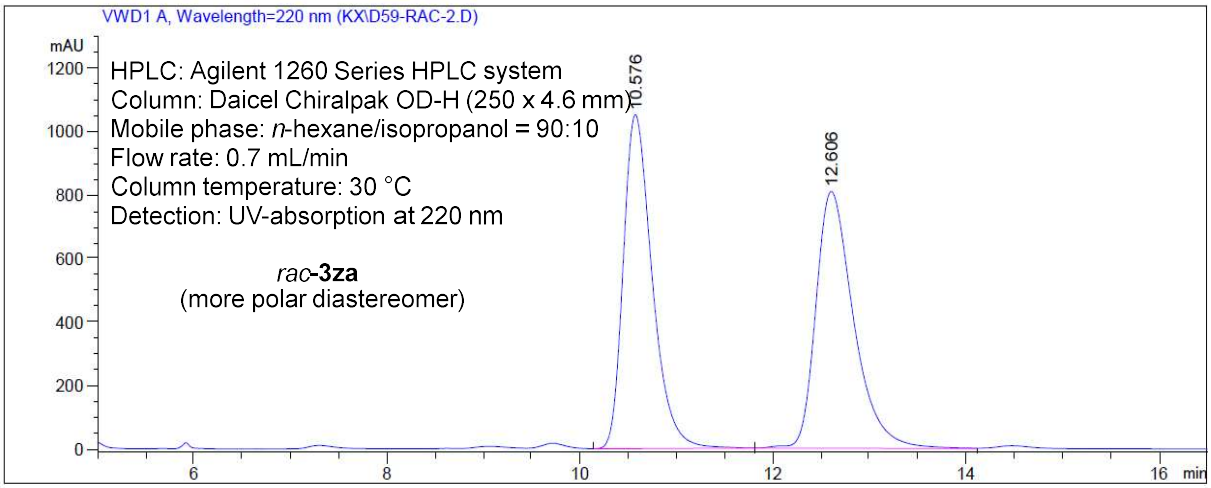
Supplementary Fig. 27 HPLC trace for the racemic reference *rac*-**3z**, and non-racemic product **3z**.

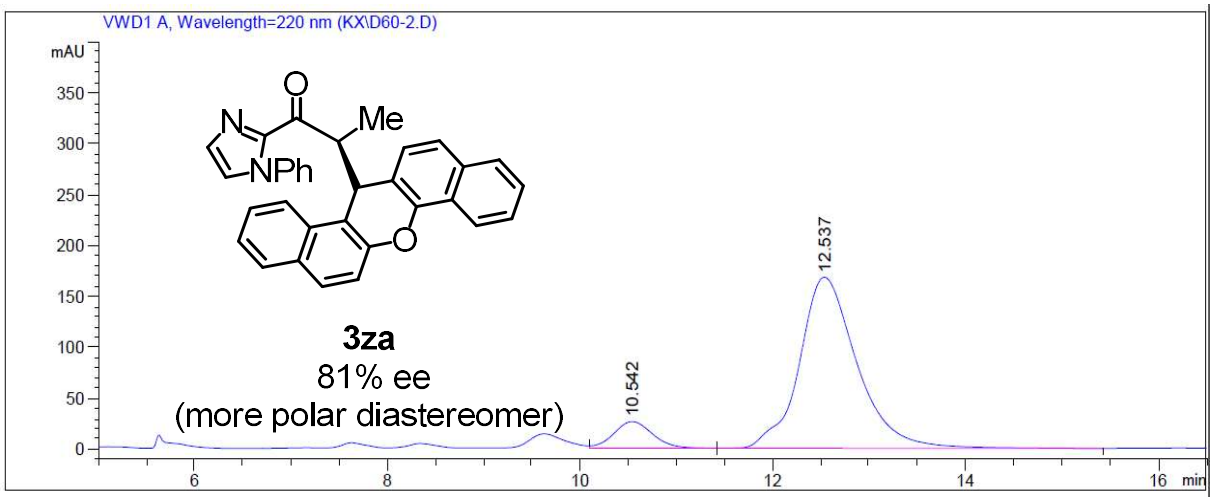




#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.705	VB	0.2756	5.18421e4	2970.04663	96.1364
2	12.082	VBA	0.4715	2083.47021	67.60656	3.8636

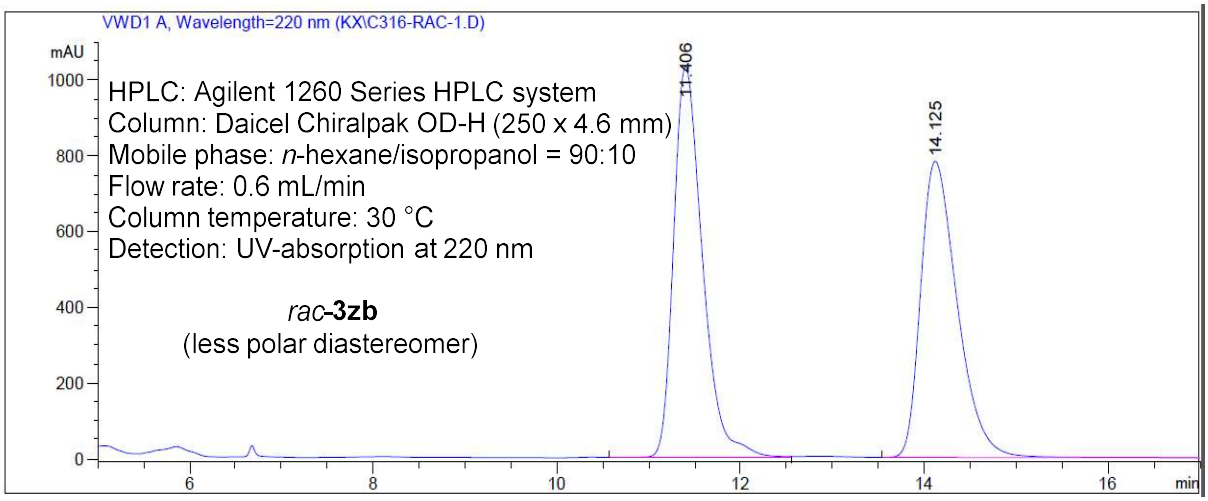
Supplementary Fig. 28 HPLC trace for the racemic reference *rac*-**3za** (less polar diastereomer), and non-racemic product **3za** (less polar diastereomer).

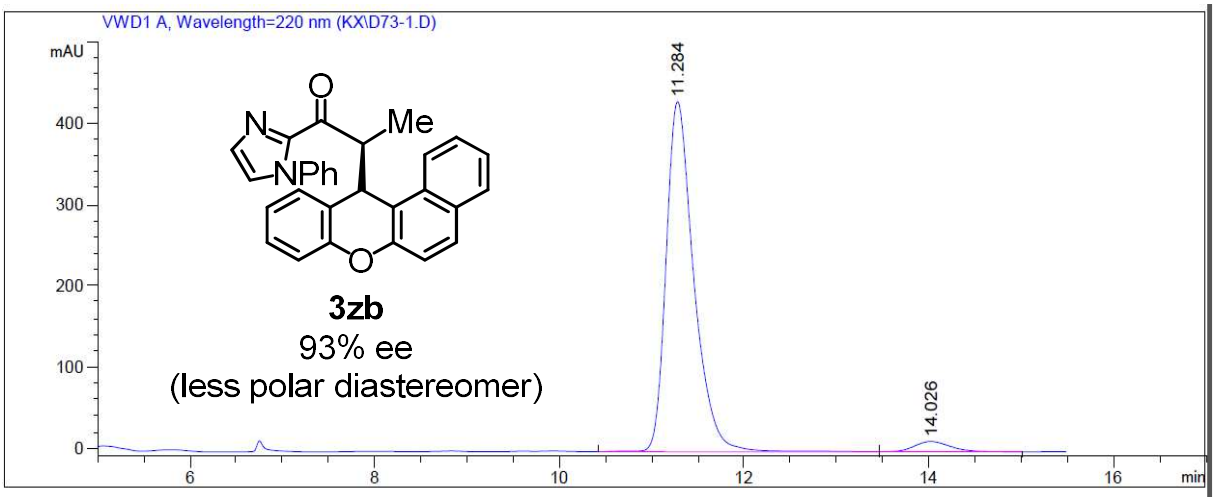




#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.542	VB	0.4328	733.45099	26.18600	9.4904
2	12.537	BB	0.6216	6994.90430	168.06056	90.5096

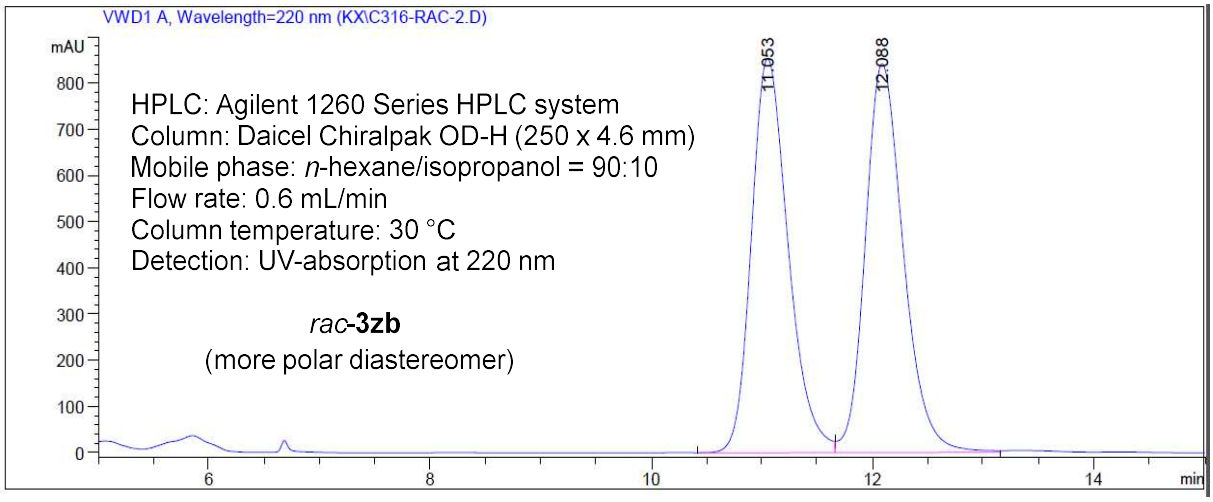
Supplementary Fig. 29 HPLC trace for the racemic reference *rac*-**3za** (more polar diastereomer), and non-racemic product **3za** (more polar diastereomer).

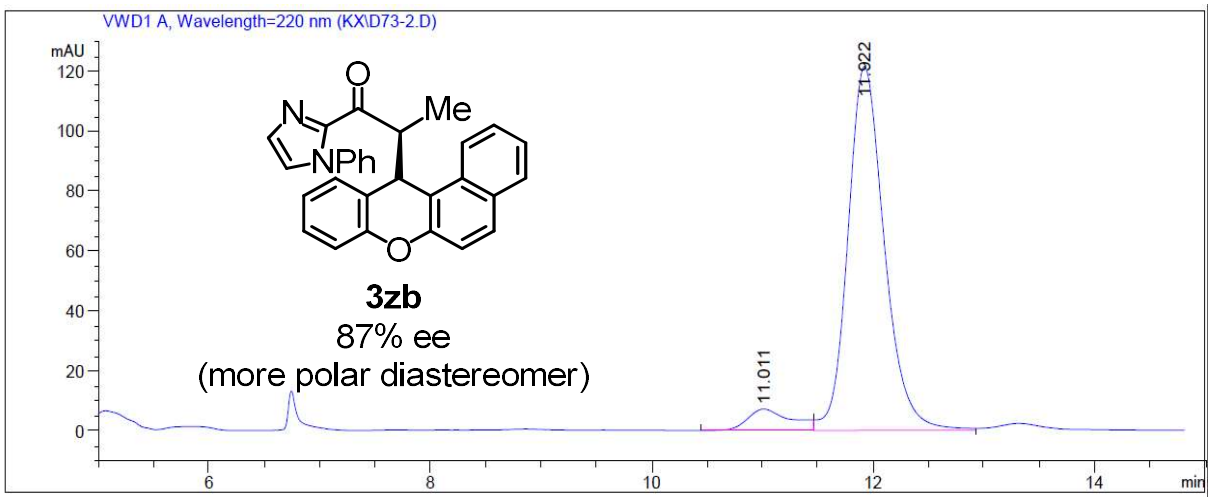




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.284	BV	0.3136	8983.59570	430.32129	96.2760
2	14.026	VB	0.4169	347.48538	12.79157	3.7240

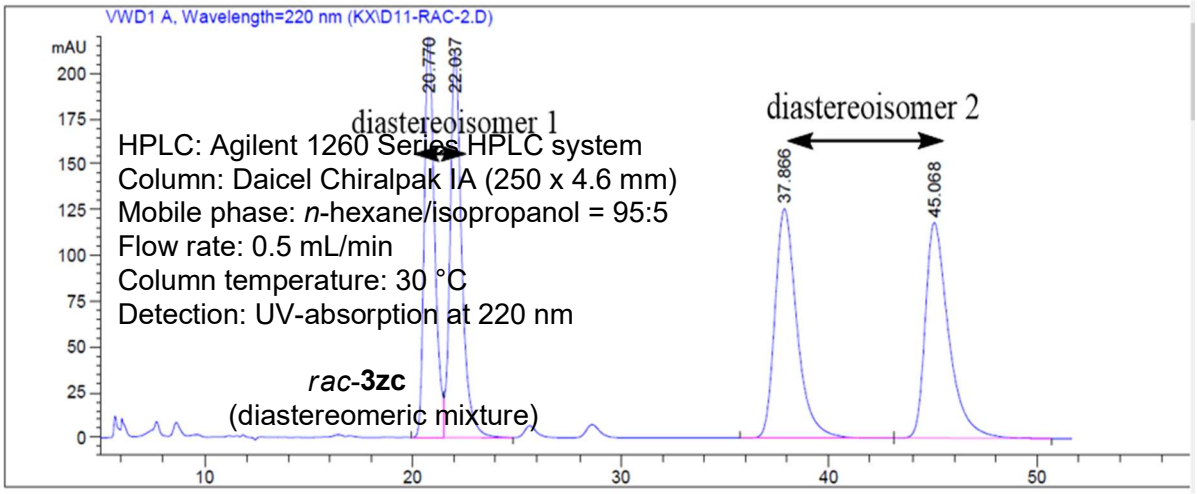
Supplementary Fig. 30 HPLC trace for the racemic reference *rac*-**3zb** (less polar diastereomer), and non-racemic product **3zb** (less polar diastereomer).

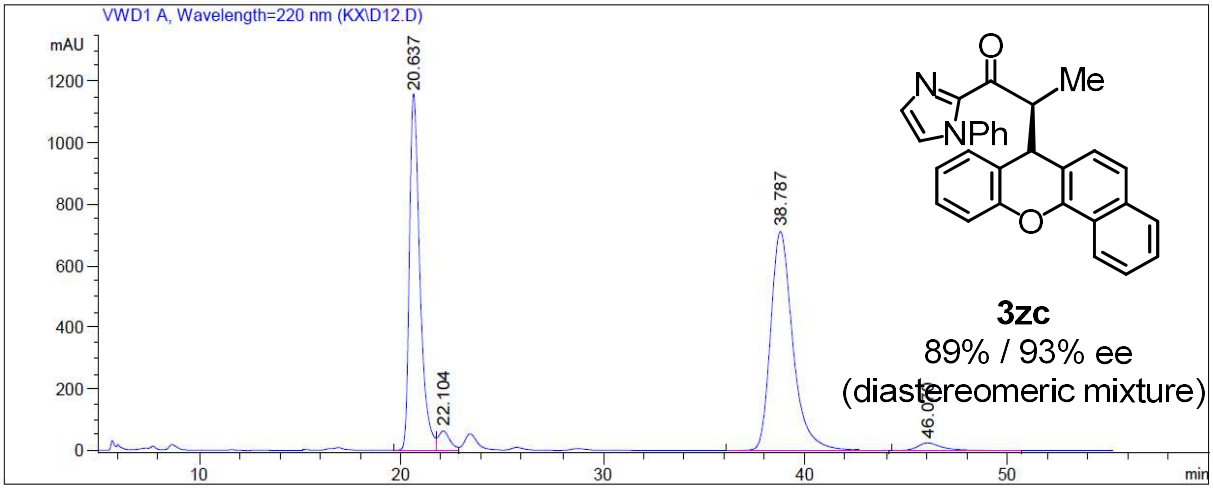




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.011	BV	0.3898	192.02000	7.09282	6.4750
2	11.922	VV	0.3492	2773.55469	121.11984	93.5250

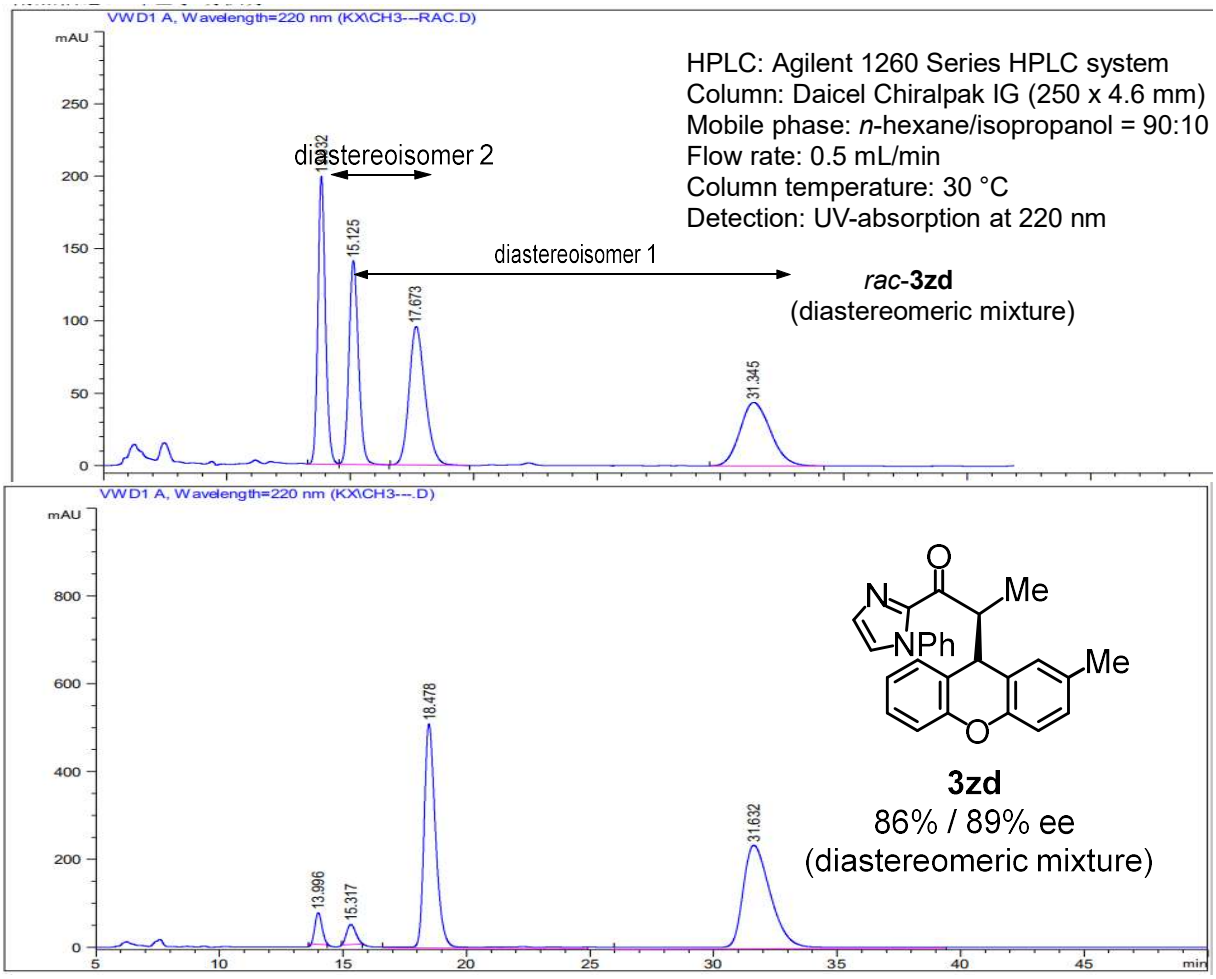
Supplementary Fig. 31 HPLC trace for the racemic reference *rac*-**3zb** (more polar diastereomer), and non-racemic product **3zb** (more polar diastereomer).





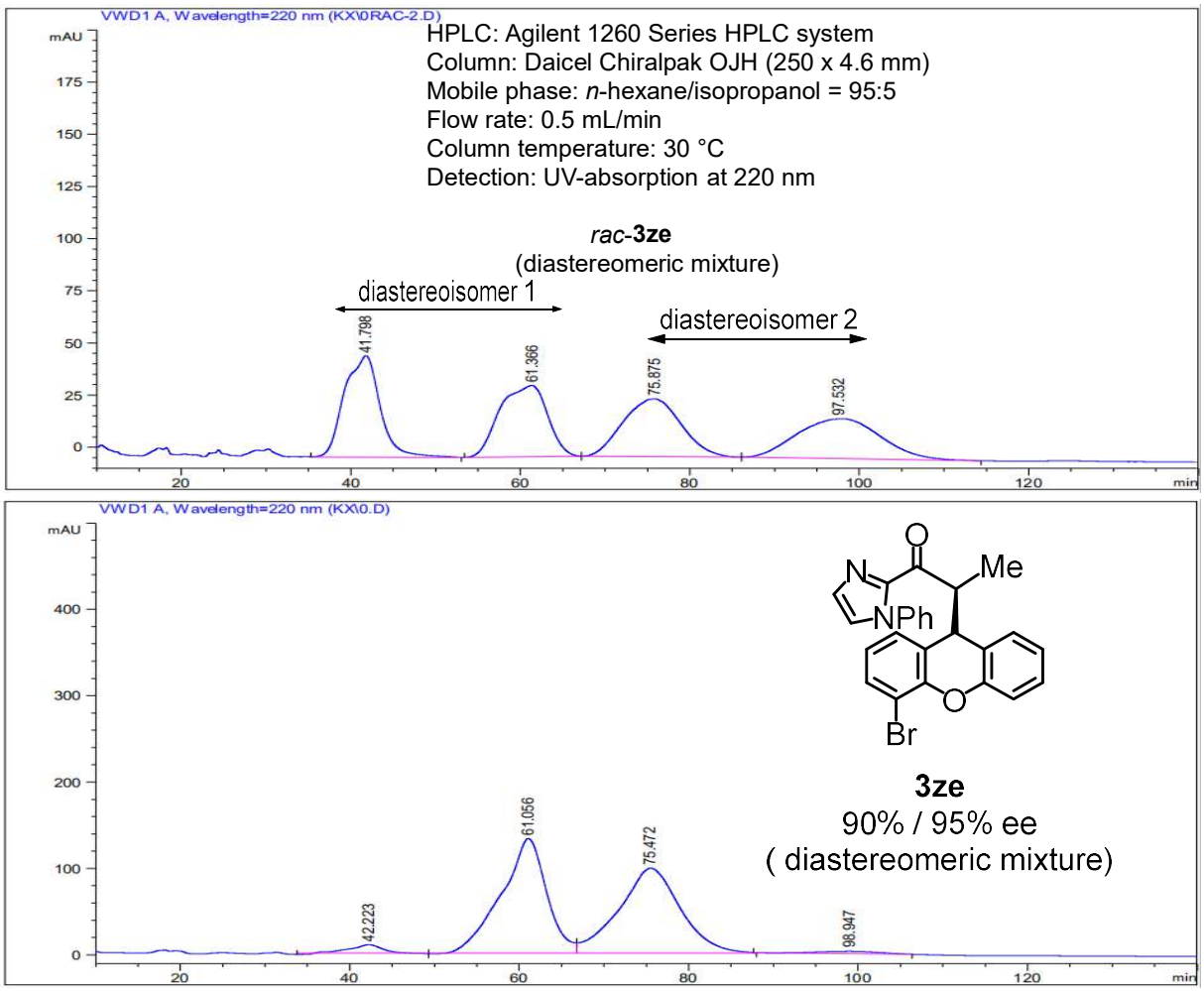
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.637	BV	0.5475	4.16762e4	1159.01648	41.5566
2	22.104	VV	0.5958	2525.49268	62.45472	2.5183
3	38.787	BB	1.1616	5.41875e4	710.67023	54.0321
4	46.070	BB	1.2174	1898.42822	23.62684	1.8930

Supplementary Fig. 32 HPLC trace for the racemic reference *rac*-**3zc**, and non-racemic product **3zc** (diastereomeric mixture).



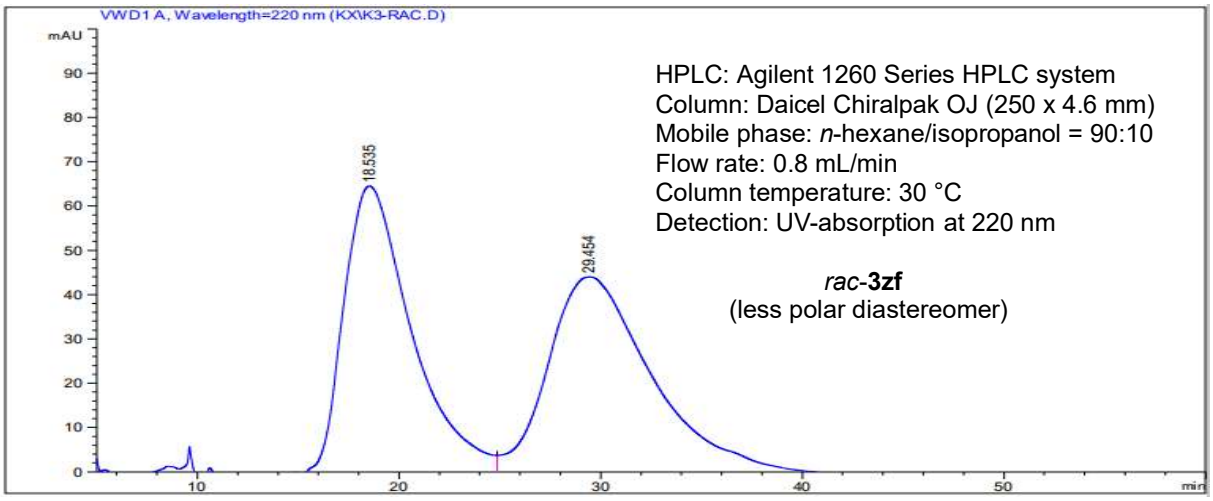
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.996	MM R	0.3281	1418.79663	72.08081	3.5274
2	15.317	MM R	0.4292	1188.42175	46.14552	2.9546
3	18.478	MM R	0.5674	1.73516e4	509.69388	43.1395
4	31.632	MM R	1.4320	2.02633e4	235.84140	50.3785

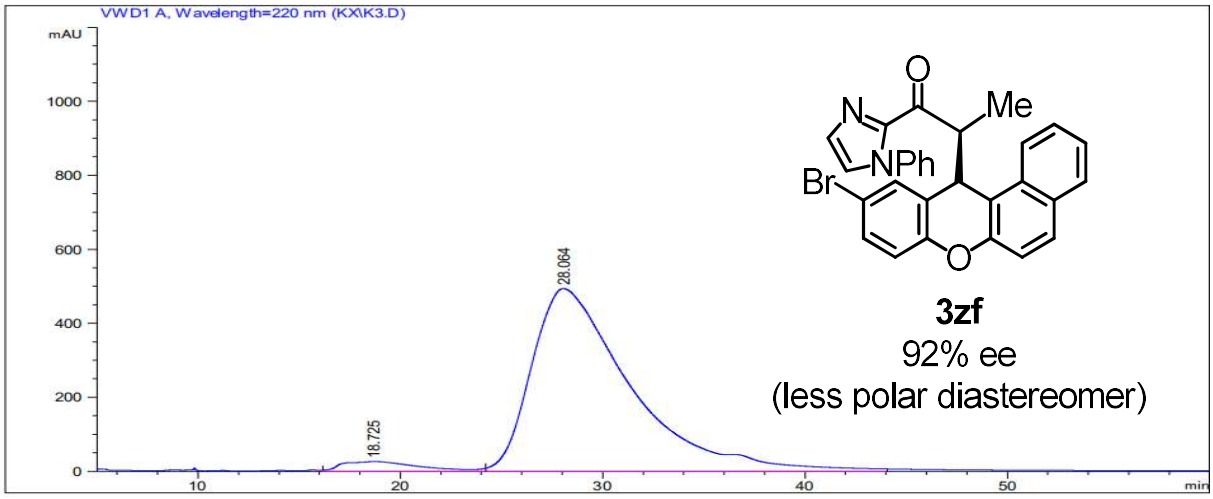
Supplementary Fig. 33 HPLC trace for the racemic reference *rac*-**3zd**, and non-racemic product **3zd** (diastereomeric mixture).



#	[min]		[min]	[mAU*s]	[mAU]	%
1	42.223	MF R	4.4703	2598.54199	9.68826	2.5263
2	61.056	MF R	6.2122	4.94887e4	132.77361	48.1124
3	75.472	FM R	8.3799	4.94495e4	98.34923	48.0743
4	98.947	MM R	8.2964	1323.84338	2.65948	1.2870

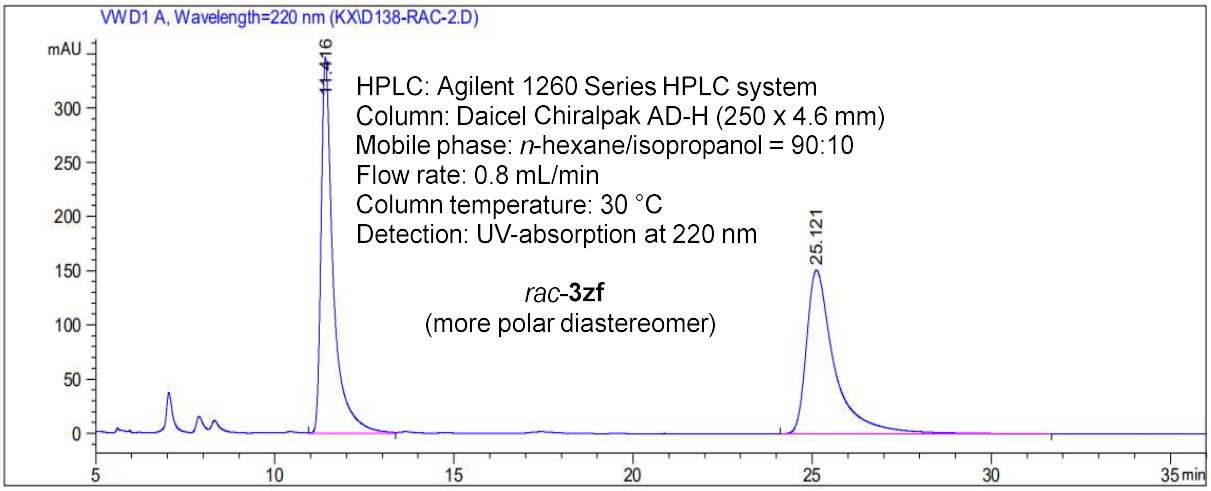
Supplementary Fig. 34 HPLC trace for the racemic reference *rac*-**3ze**, and non-racemic product **3ze** (diastereomeric mixture).

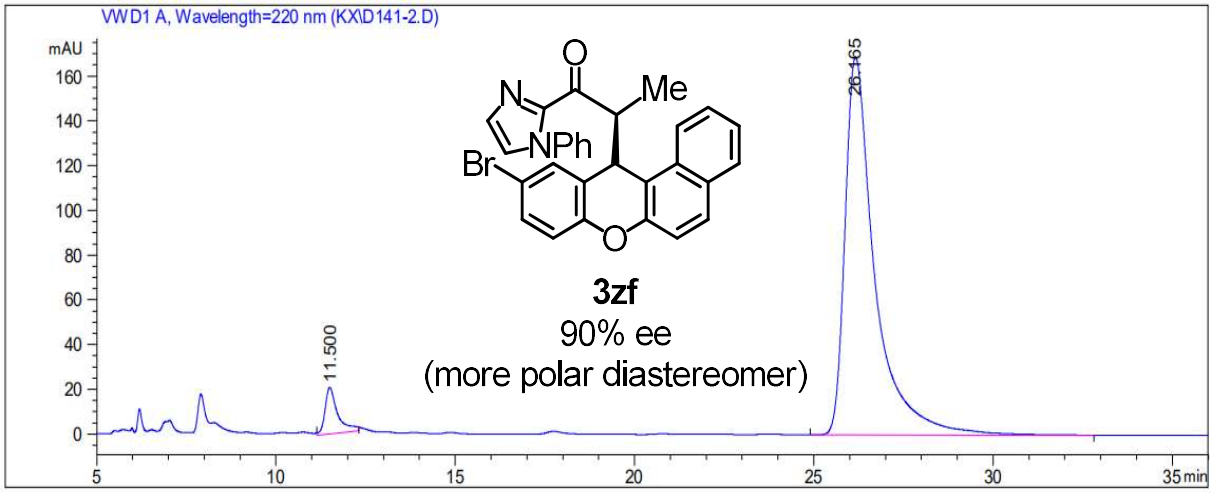




#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.725	MF R	4.4793	7117.04785	26.48129	4.0713
2	28.064	FM R	5.6550	1.67692e5	494.22595	95.9287

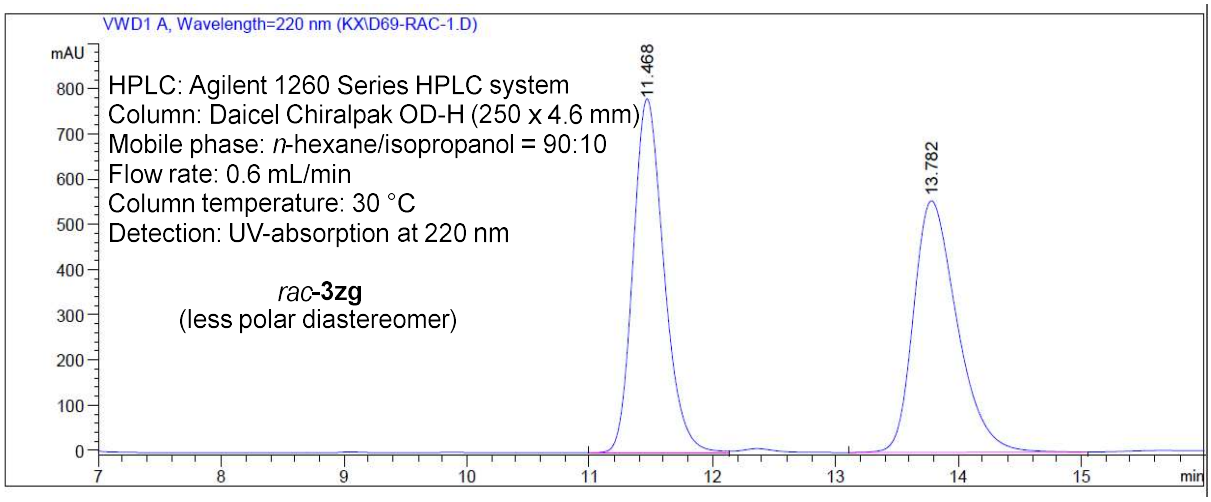
Supplementary Fig. 35 HPLC trace for the racemic reference *rac*-**3zf** (less polar diastereomer), and non-racemic product **3zf** (less polar diastereomer).

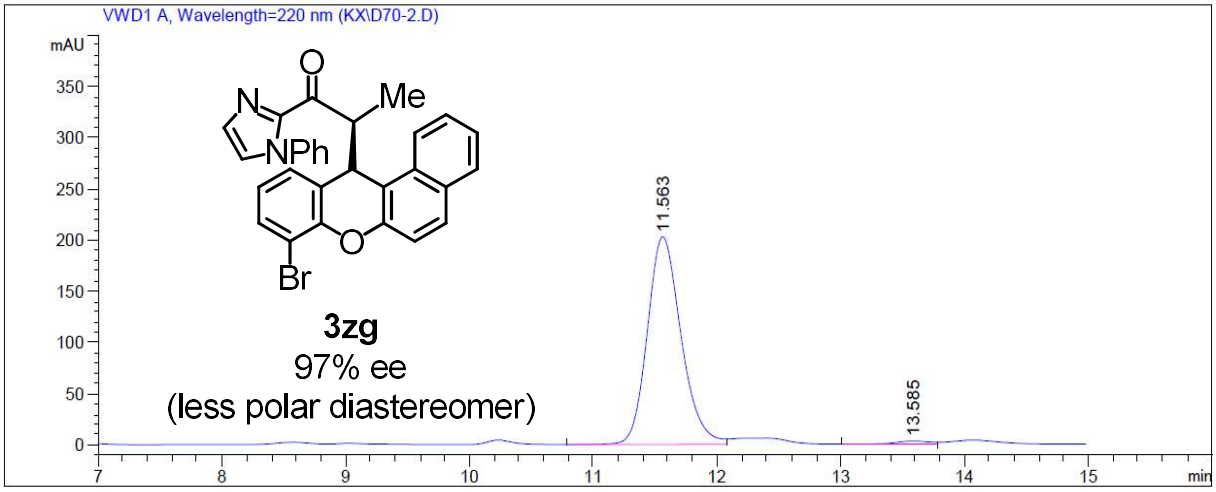




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.500	MM R	0.4088	508.72531	20.73966	4.9493
2	26.165	BB	0.8432	9770.06250	168.82123	95.0507

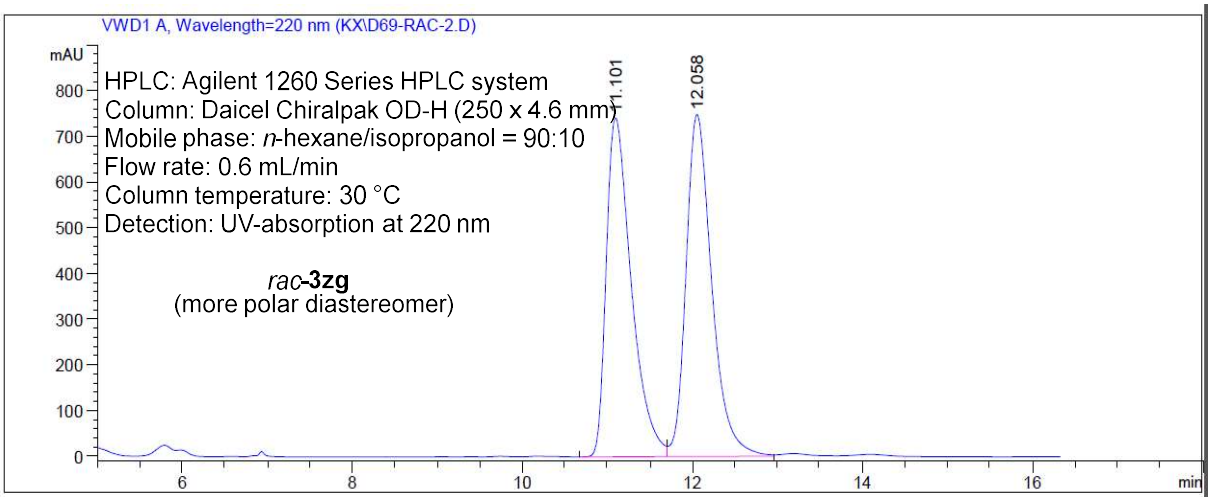
Supplementary Fig. 36 HPLC trace for the racemic reference *rac*-**3zf** (more polar diastereomer), and non-racemic product **3zf** (more polar diastereomer).

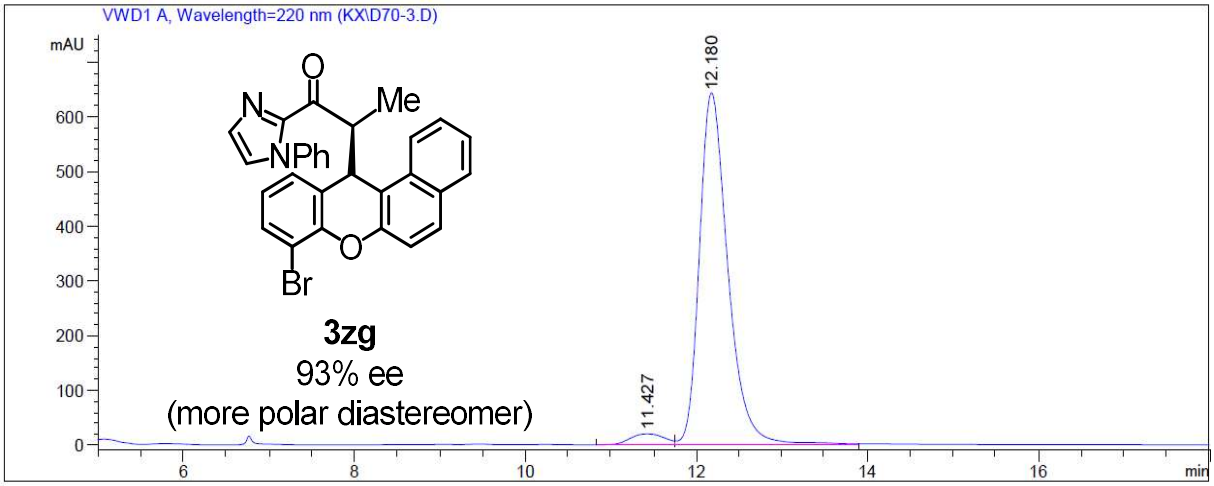




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.563	BV	0.2932	3838.39258	202.44530	98.4527
2	13.585	BV	0.2877	60.32508	3.14585	1.5473

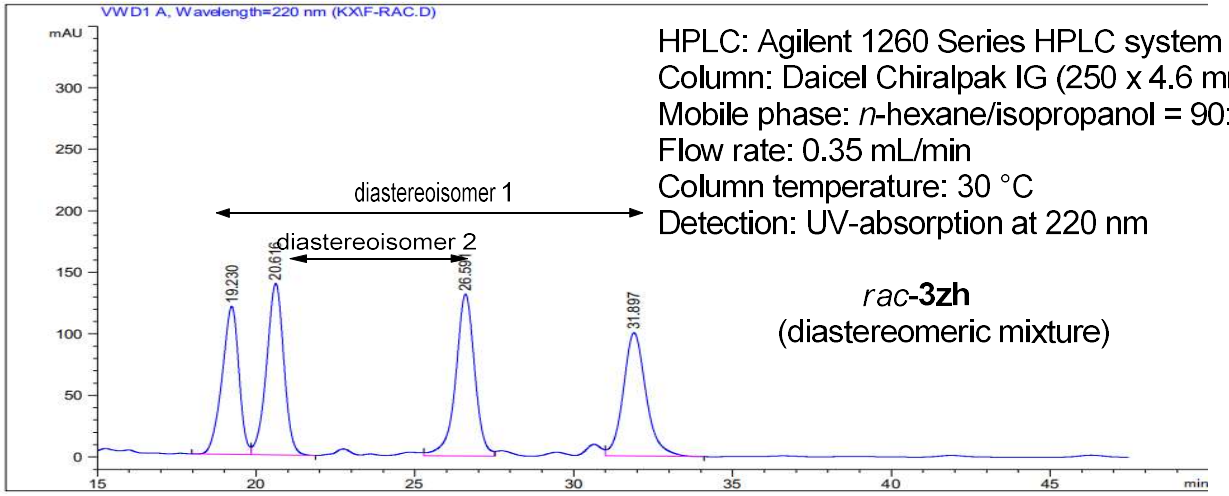
Supplementary Fig. 37 HPLC trace for the racemic reference *rac*-**3zg** (less polar diastereomer), and non-racemic product **3zg** (less polar diastereomer).

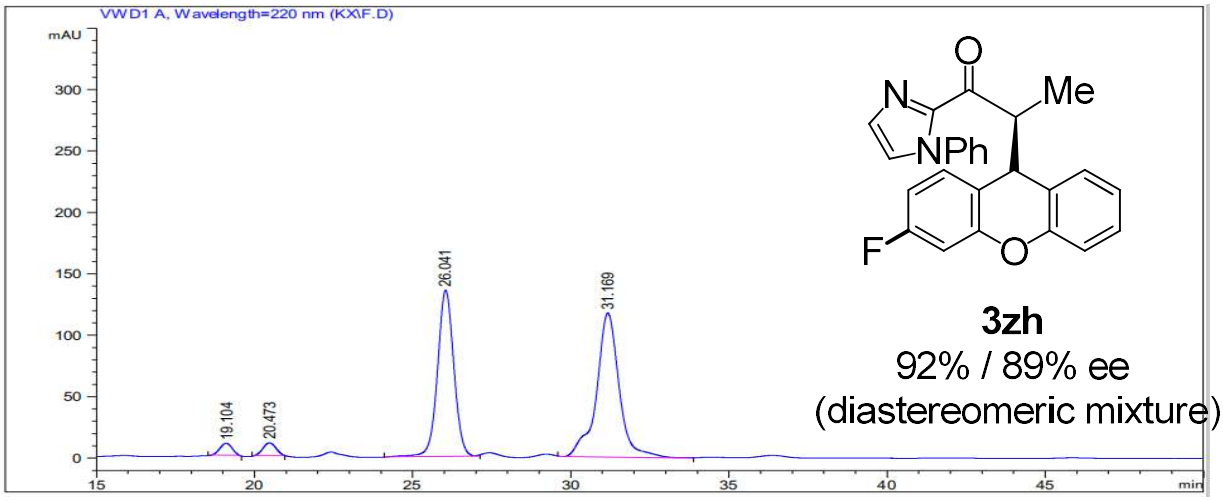




#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.427	BV	0.4536	550.81982	19.73648	3.5559
2	12.180	VV	0.3550	1.49394e4	643.22113	96.4441

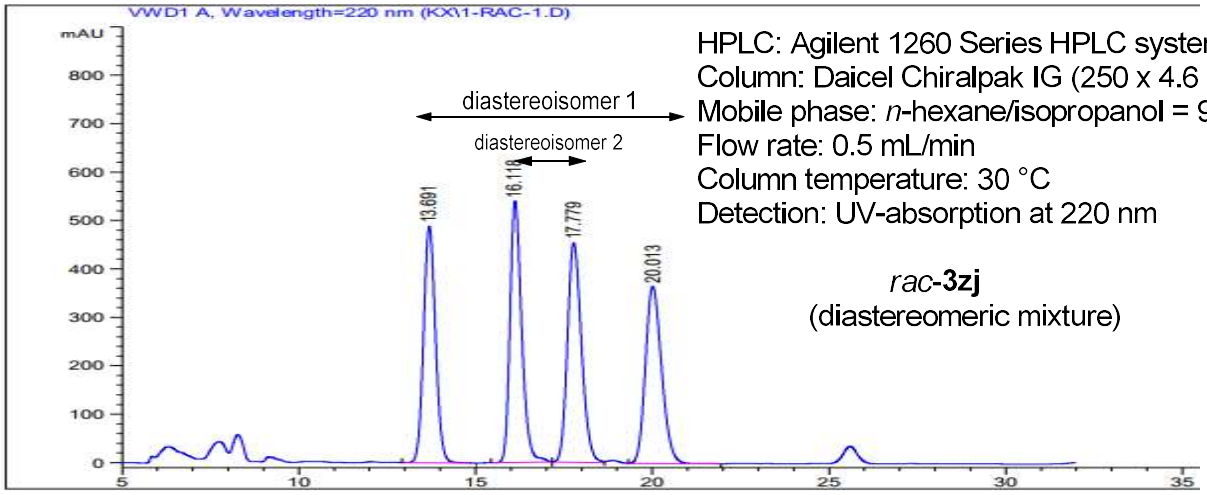
Supplementary Fig. 38 HPLC trace for the racemic reference *rac*-**3zg** (more polar diastereomer), and non-racemic product **3zg** (more polar diastereomer).

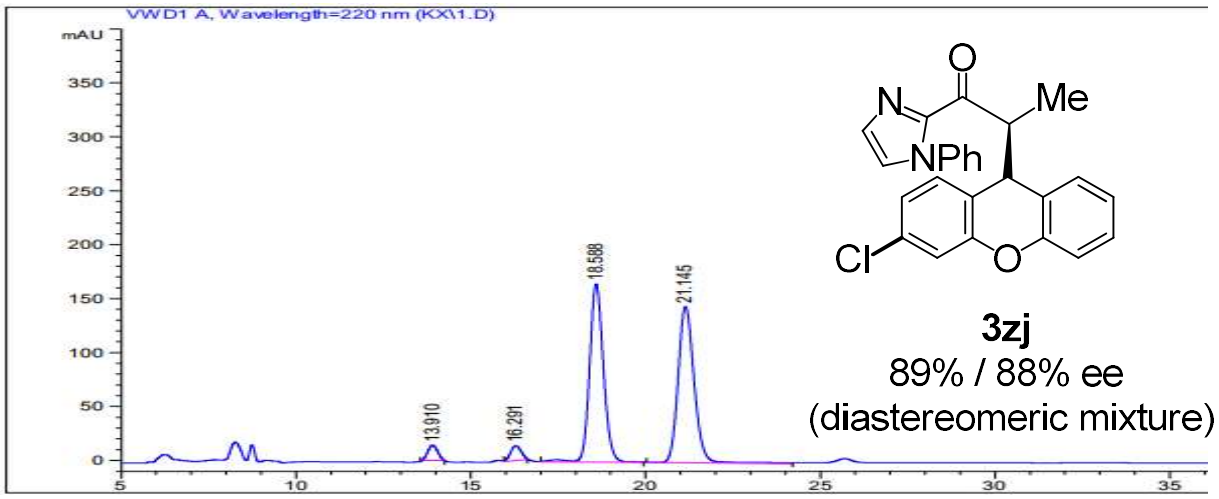




#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.104	MM R	0.4407	258.65326	9.78085	2.2996
2	20.473	MM R	0.4658	286.28564	10.24245	2.5453
3	26.041	MM R	0.5986	4855.98975	135.20277	43.1728
4	31.169	MM R	0.8307	5846.88086	117.30243	51.9824

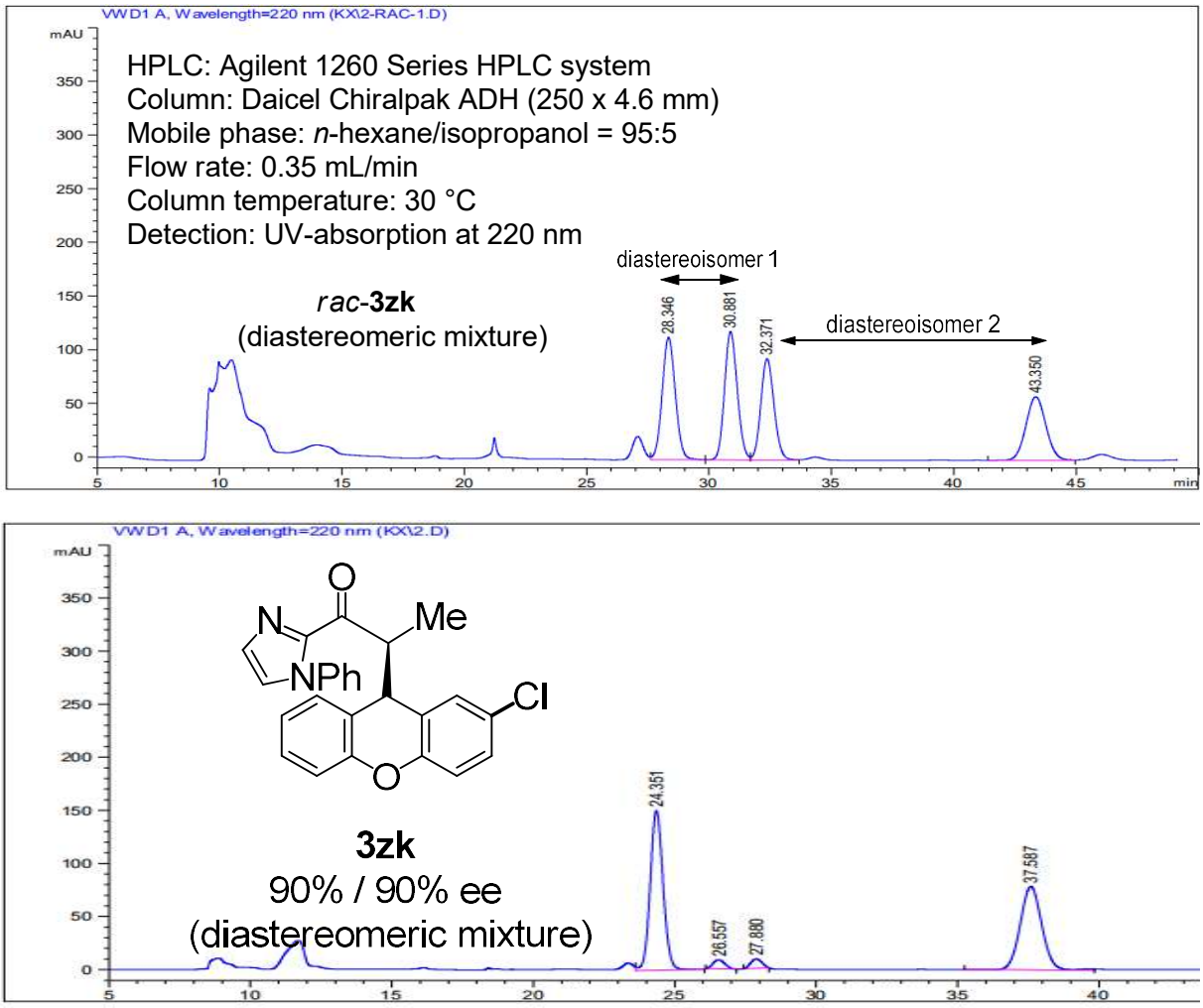
Supplementary Fig. 39 HPLC trace for the racemic reference *rac*-**3zh**, and non-racemic product **3zh** (diastereomeric mixture).





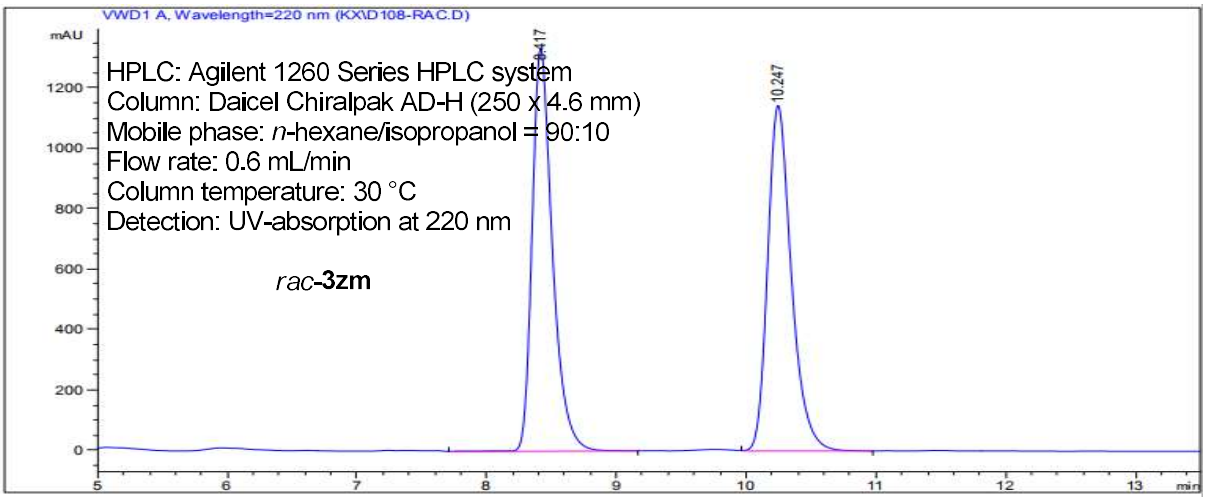
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.910	MM R	0.3214	269.00168	13.94733	2.7505
2	16.291	MM R	0.3508	290.27328	13.78976	2.9680
3	18.588	MM R	0.4606	4563.33740	165.13632	46.6592
4	21.145	MM R	0.5363	4657.53076	144.75591	47.6223

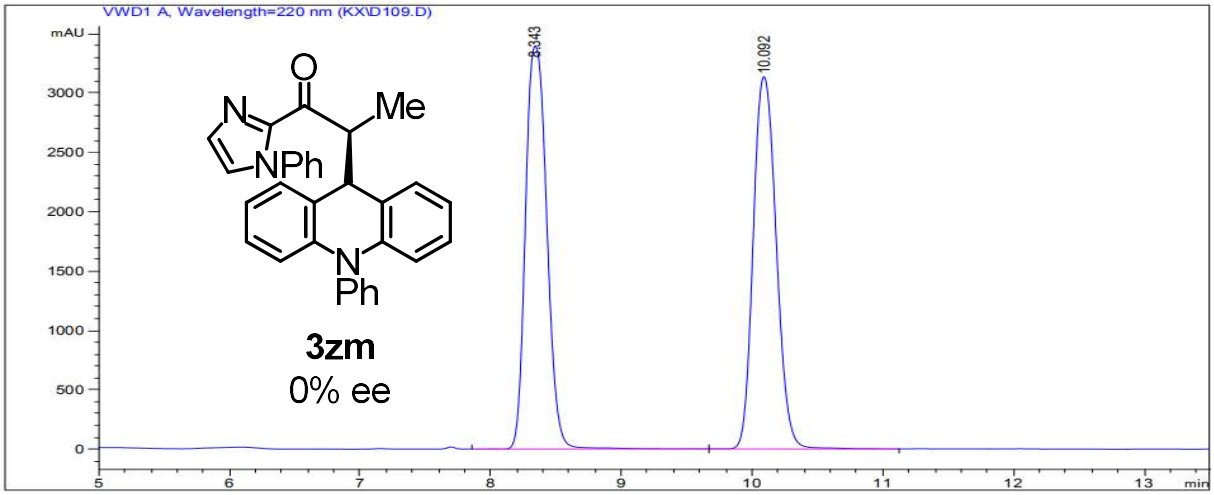
Supplementary Fig. 40 HPLC trace for the racemic reference *rac*-**3zj**, and non-racemic product **3zj** (diastereomeric mixture).



#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.351	MM R	0.5277	4761.88086	150.38806	50.6477
2	26.557	MM R	0.4824	249.73404	8.62772	2.6562
3	27.880	MM R	0.4621	247.60086	8.92941	2.6335
4	37.587	MM R	0.8807	4142.75293	78.39501	44.0626

Supplementary Fig. 41 HPLC trace for the racemic reference *rac*-**3zk**, and non-racemic product **3zk** (diastereomeric mixture).



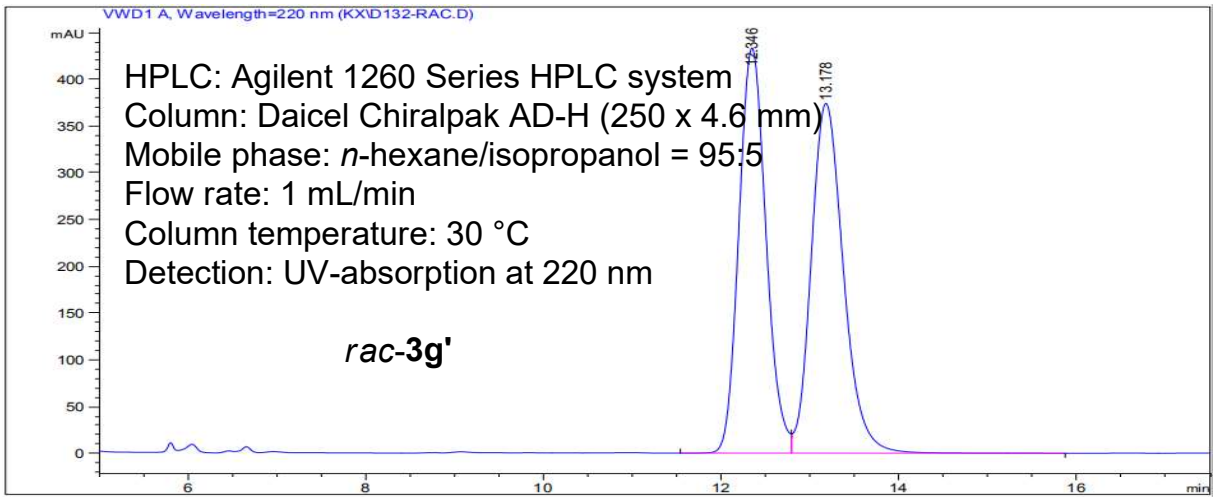


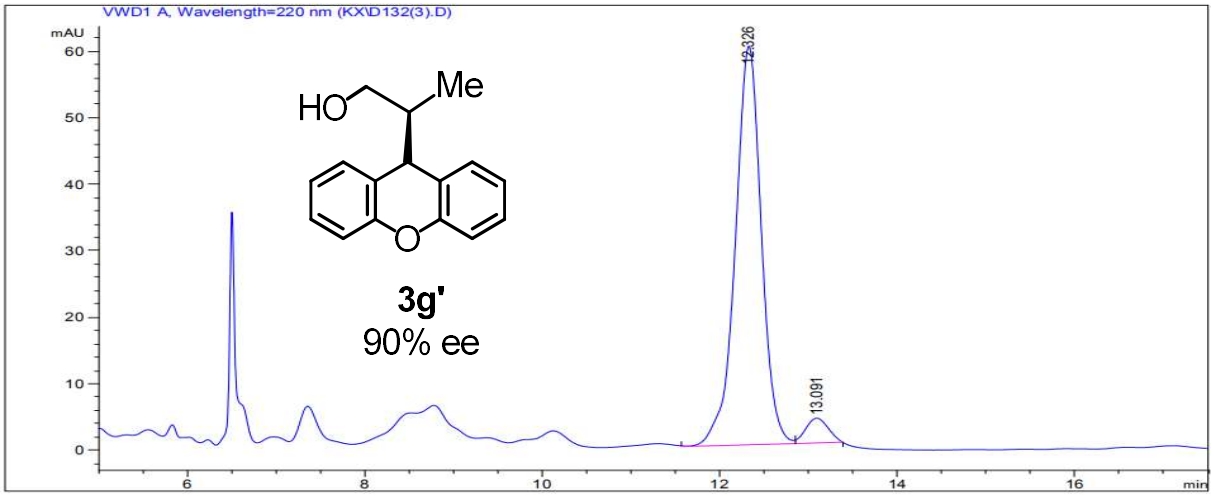
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.343	BB	0.1800	3.84190e4	3395.24756	50.0205
2	10.092	BV	0.1952	3.83875e4	3128.46460	49.9795

Supplementary Fig. 42 HPLC trace for the racemic reference *rac*-**3zm**, and non-racemic product **3zm**.

6.2 Determination of Enantiopurities of the Transformation Product 3g'

Optical purities of the compound **3g'** was determined with a Daicel Chiralpak AD-H column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 220 nm.



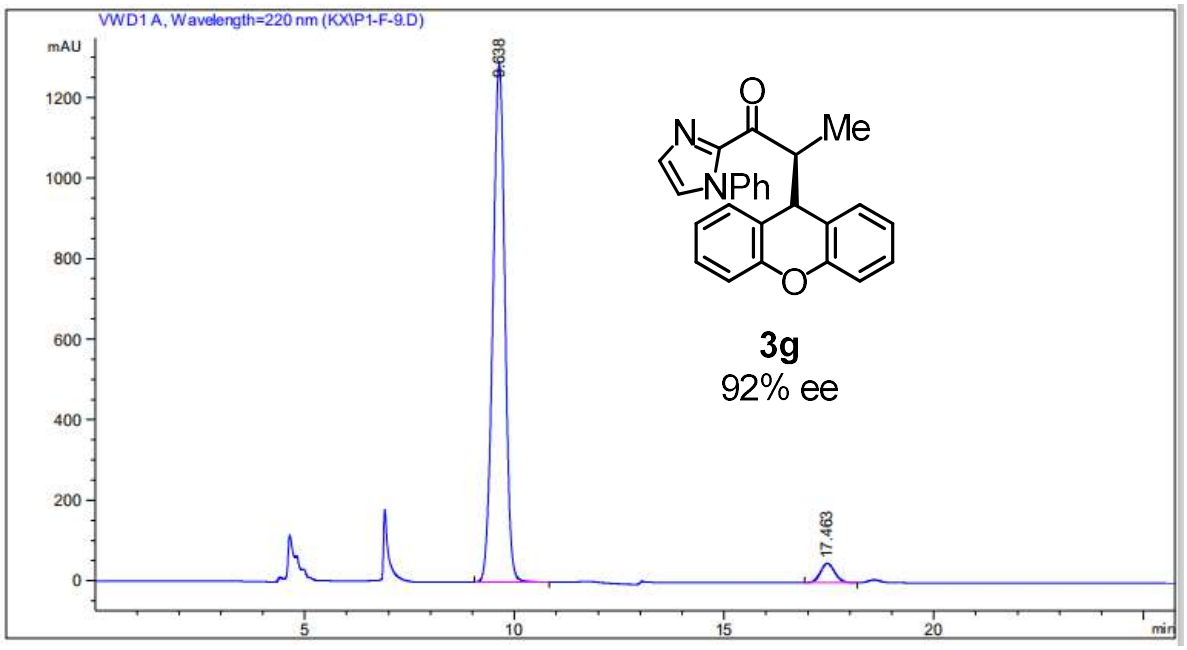


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.326	MF R	0.3400	1222.33936	59.91018	94.9385
2	13.091	FM R	0.2924	65.16691	3.71476	5.0615

Supplementary Fig. 43 HPLC trace for the racemic reference *rac*-**3g'**, and non-racemic product (*S*)-**3g'.**

6.3 Determination of enantioselectivities of Scale-up Catalytic Reaction.

Optical purities of the compound **3g** was determined with a Daicel Chiralpak IC column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 220 nm.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.638	BB	0.3087	2.54480e4	1287.00464	95.7861
2	17.463	BB	0.3659	1119.51721	47.51903	4.2139

Supplementary Fig. 44 HPLC trace for the non-racemic product **3g** (1 mmol scale reaction).

7. References

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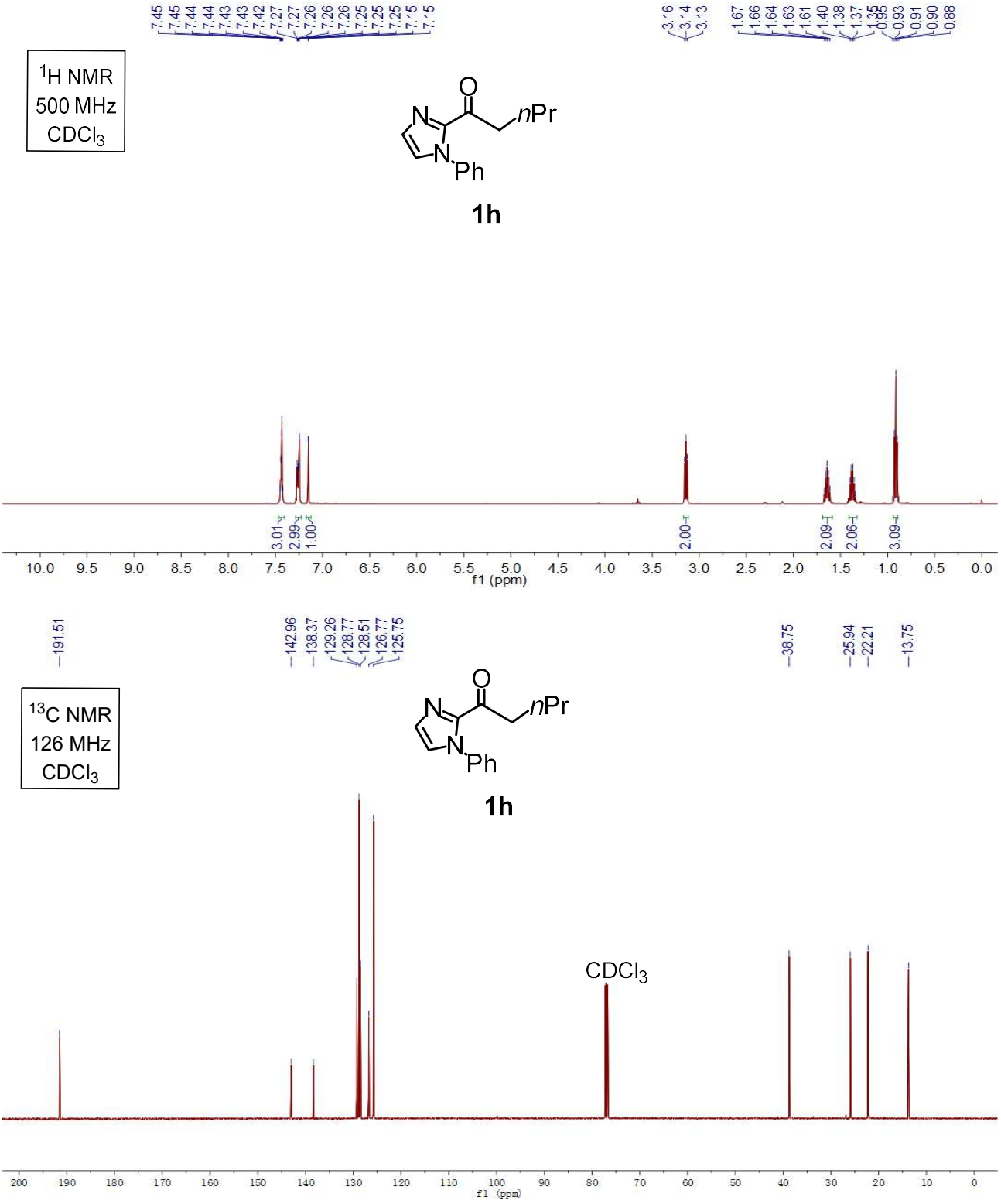
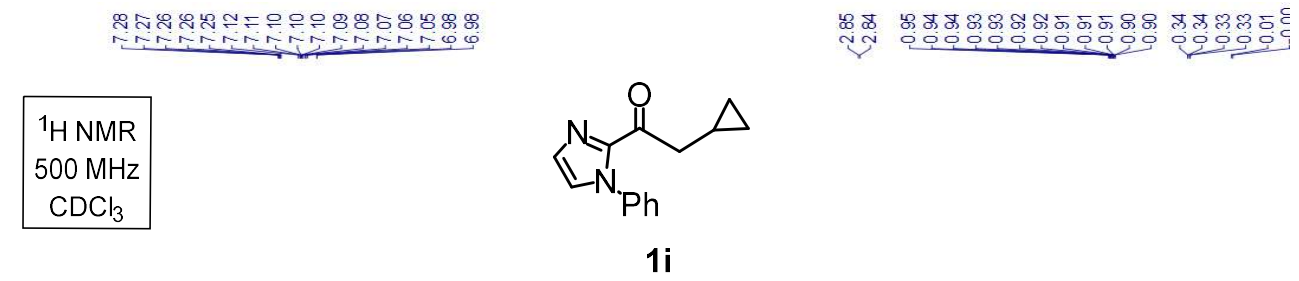
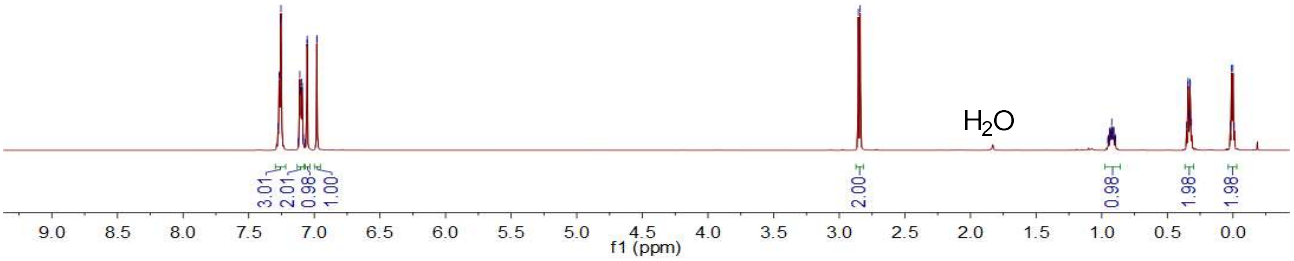
11. C. Yang, J. Wang and S. Tian, *Chem. Commun.,* 2011, **47**, 8343–8345.

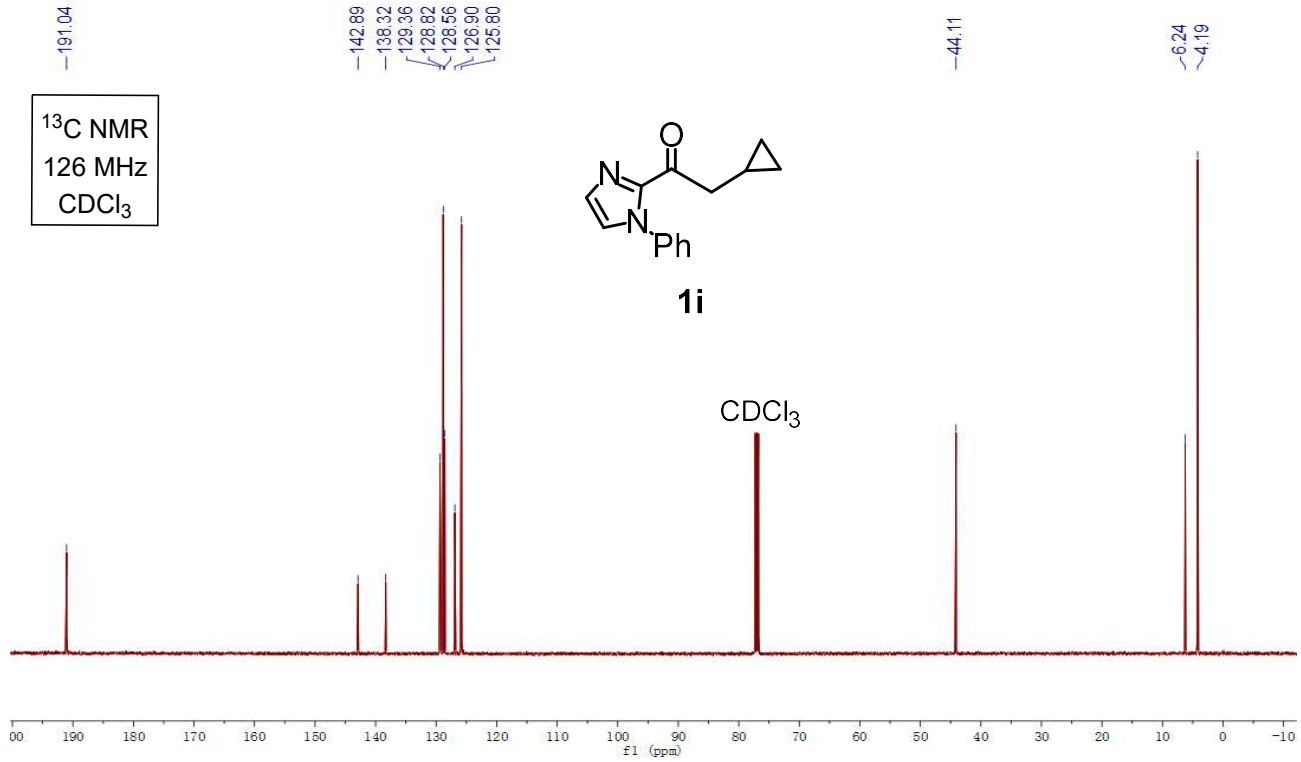
8. ^{1}H and ^{13}C NMR Spectrum




7.28
7.27
7.26
7.26
7.25
7.12
7.11
7.10
7.10
7.10
7.09
7.08
7.07
7.06
7.05
6.98
6.98
2.85
2.84
0.95
0.94
0.94
0.93
0.93
0.92
0.92
0.91
0.91
0.91
0.90
0.90
0.34
0.34
0.33
0.33
0.01
0.00
^{1}H NMR
500 MHz
$CDCl_3$
O
N
N
Ph

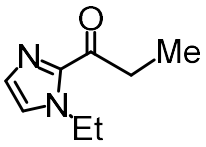
1i


H_2O
3.01
2.01
0.98
1.00
2.00
0.98
1.98
1.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.04
142.89
138.32
129.36
128.82
128.56
126.90
125.80
44.11
6.24
4.19
^{13}C NMR
126 MHz
$CDCl_3$
O
N
N
Ph
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

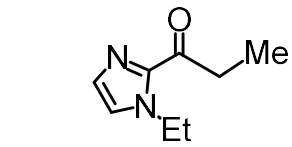
1i

^{1}H NMR
500 MHz
$CDCl_3$



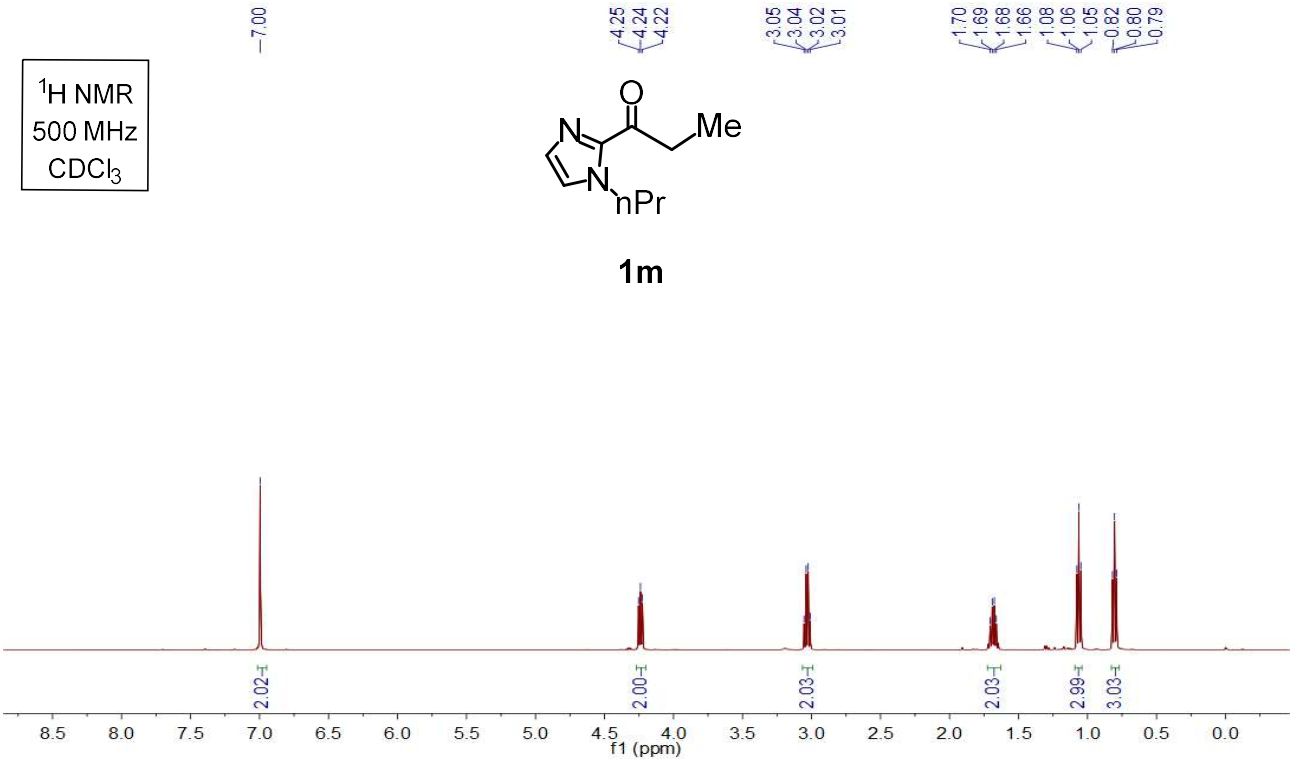
1l

^{13}C NMR
126 MHz
$CDCl_3$



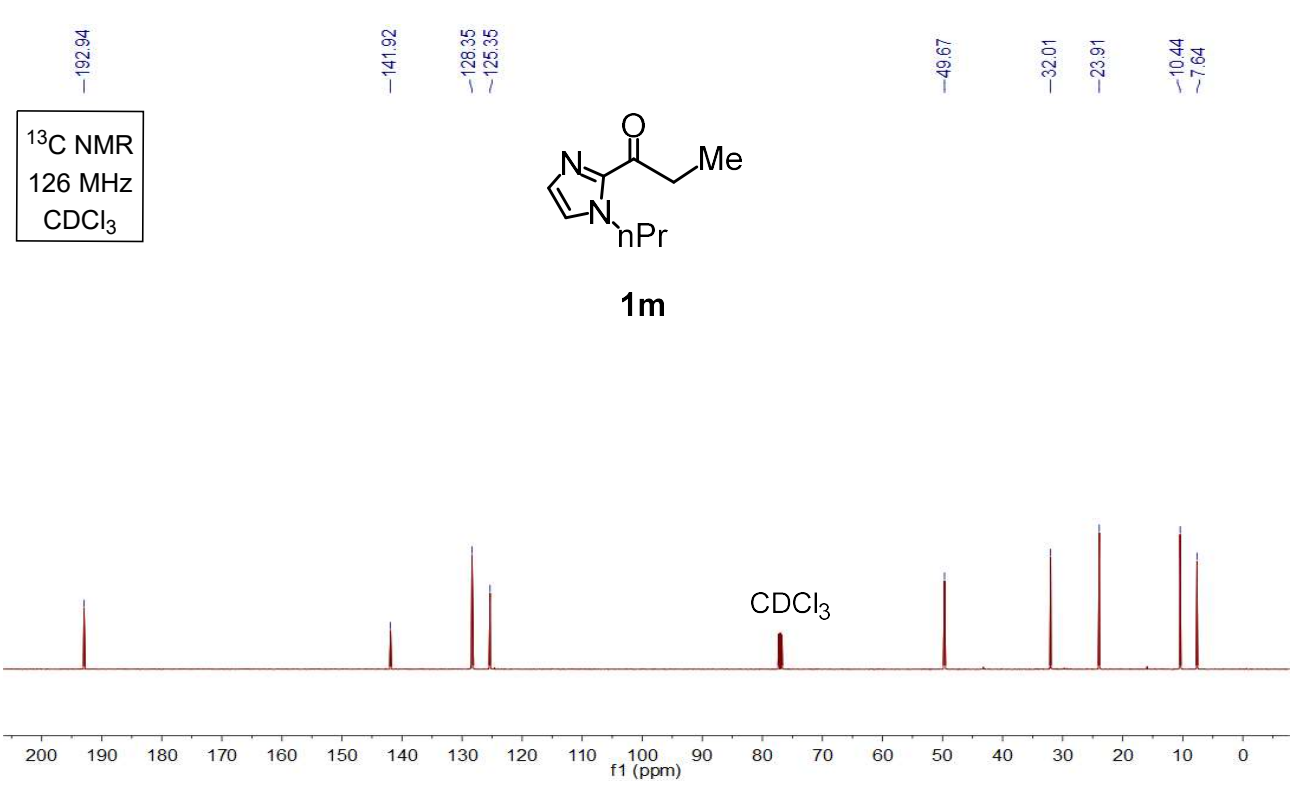
1l

^{1}H NMR
500 MHz
$CDCl_3$



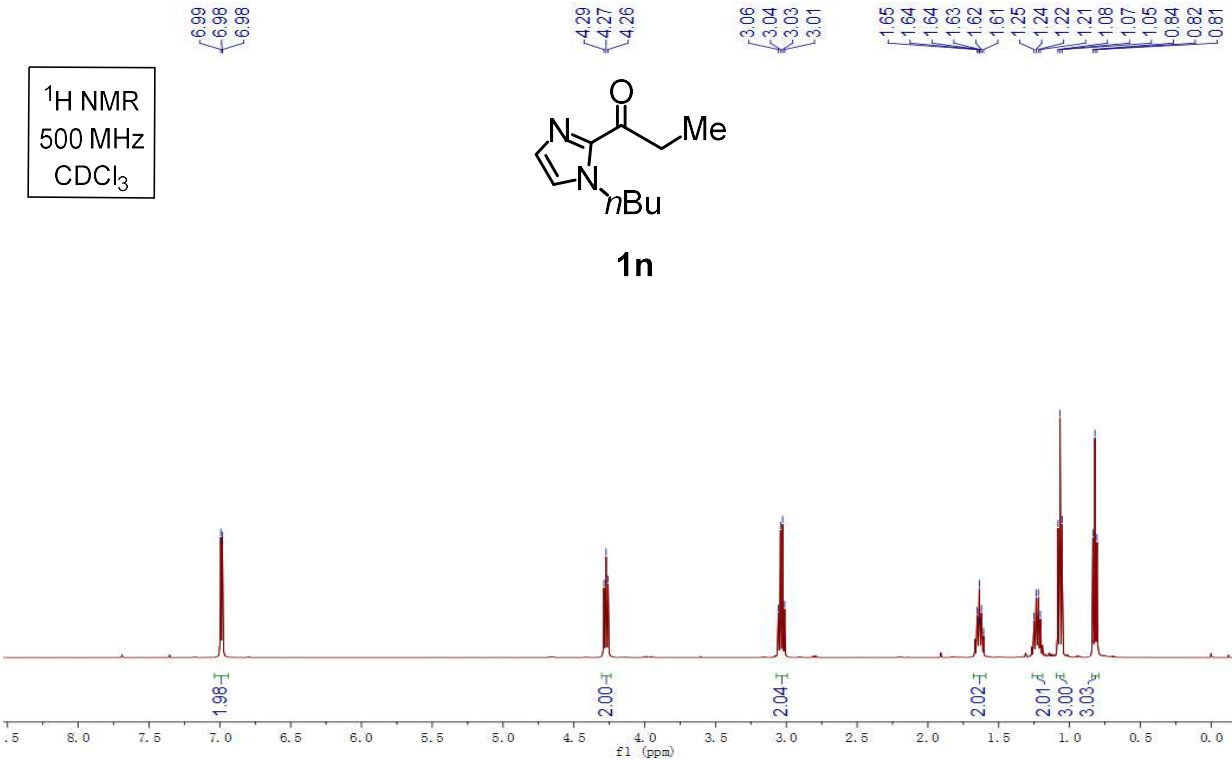
1m

^{13}C NMR
126 MHz
$CDCl_3$



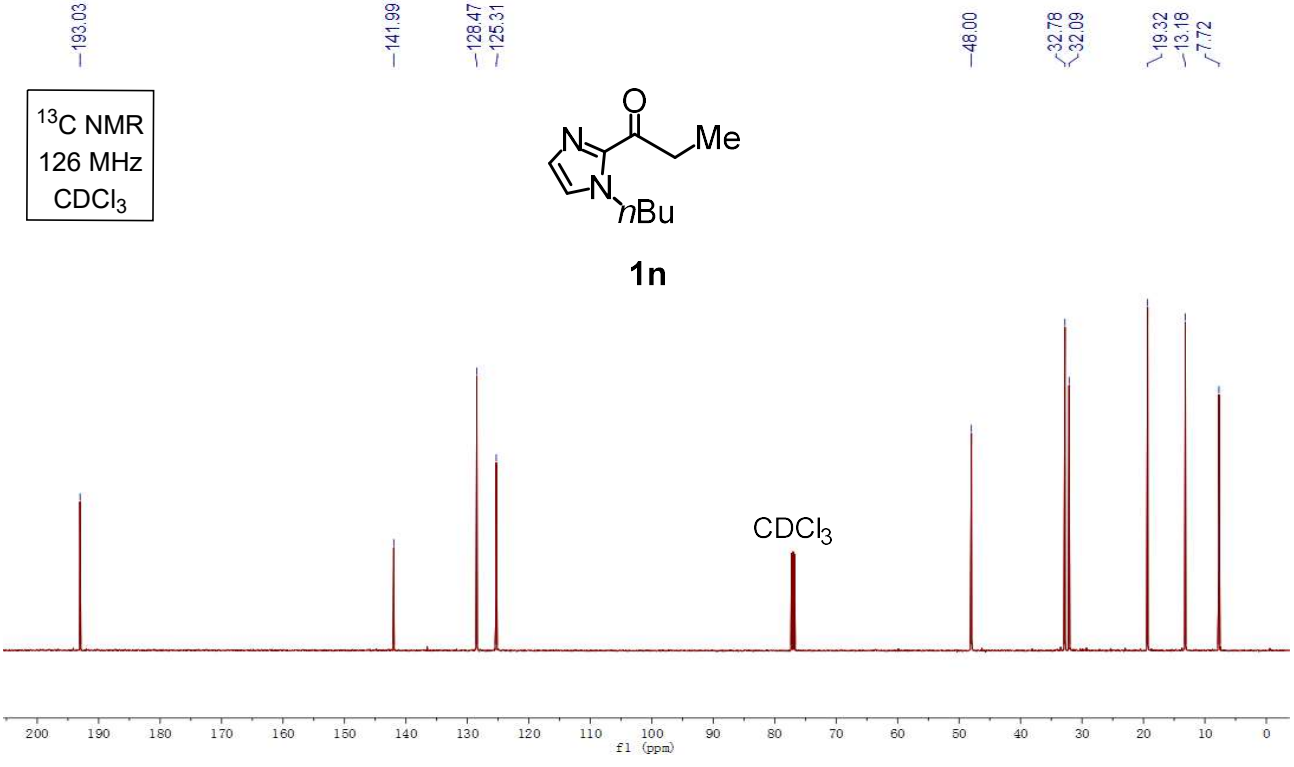
1m

^{1}H NMR
500 MHz
$CDCl_3$

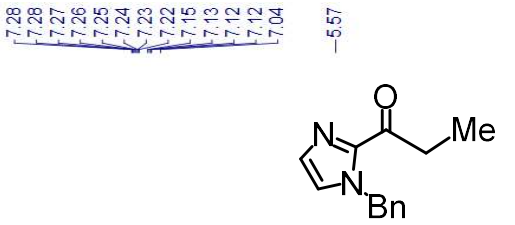


1n

^{13}C NMR
126 MHz
$CDCl_3$

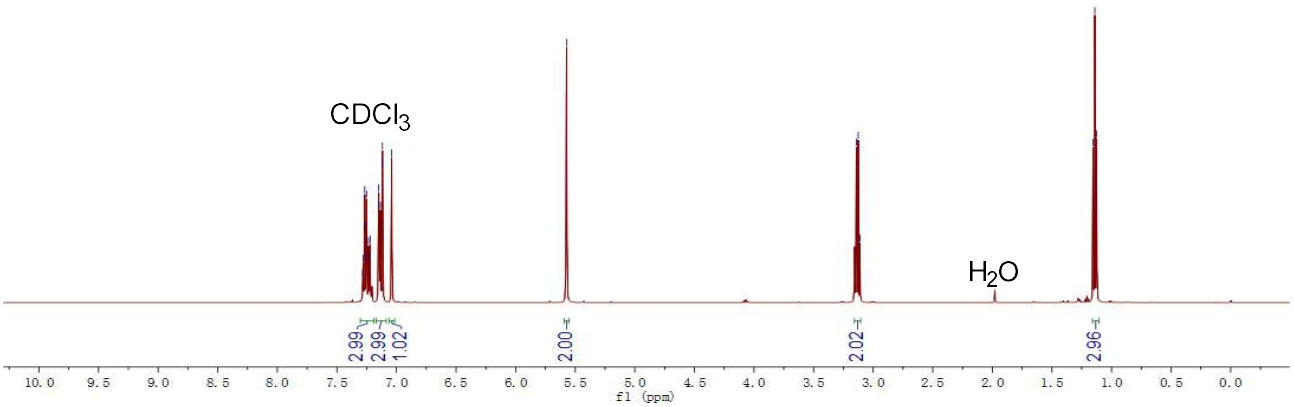


1n

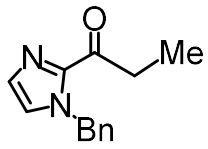


^{1}H NMR
500 MHz
$CDCl_3$

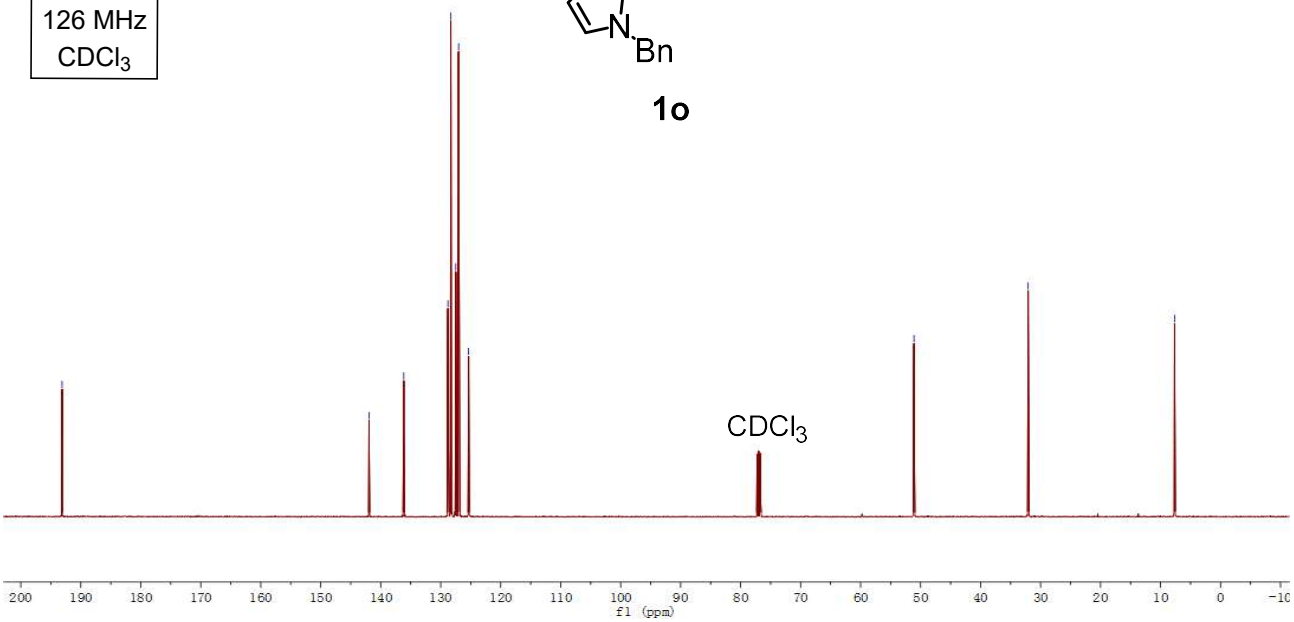
1o



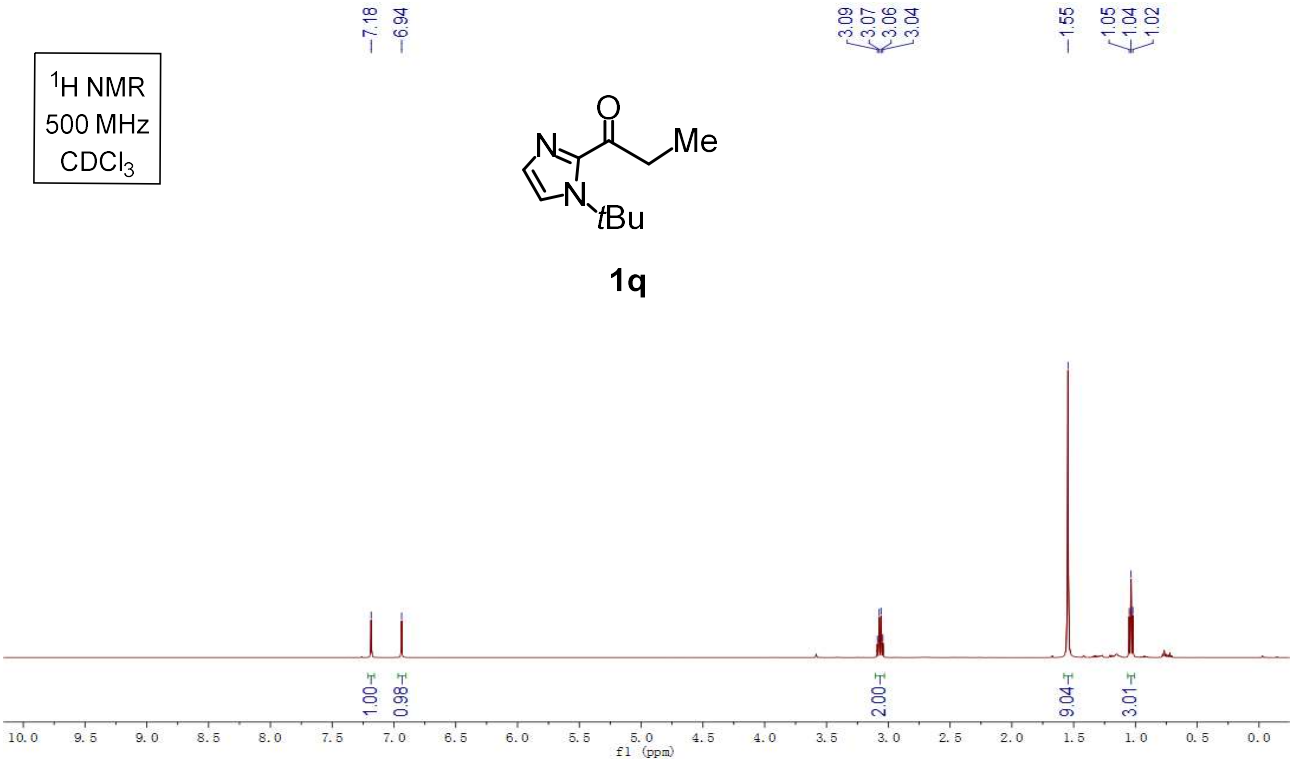
^{13}C NMR
126 MHz
$CDCl_3$



1o

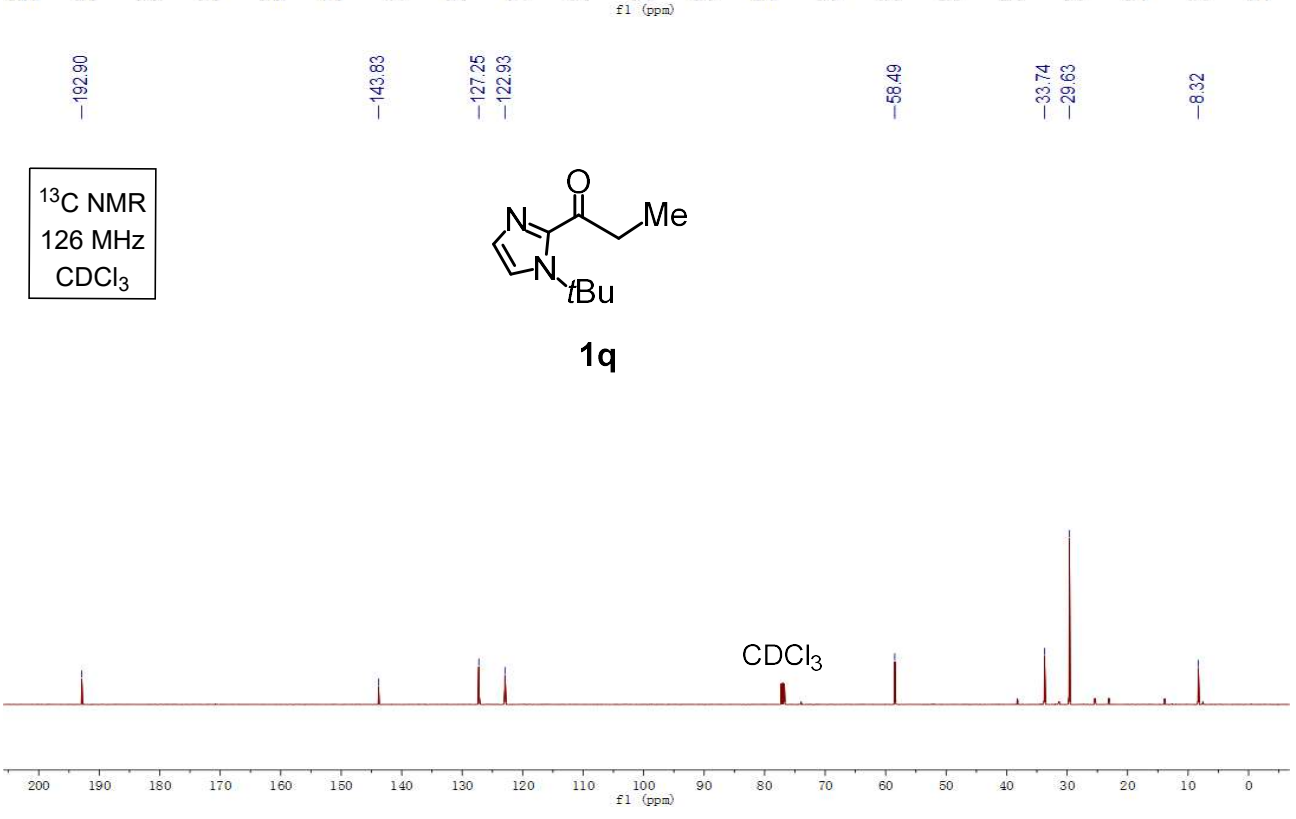


^{1}H NMR
500 MHz
$CDCl_3$



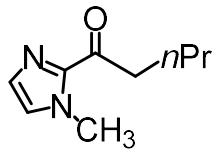
1q

^{13}C NMR
126 MHz
$CDCl_3$



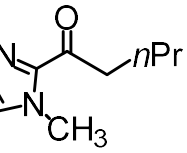
1q

^{1}H NMR
500 MHz
$CDCl_3$



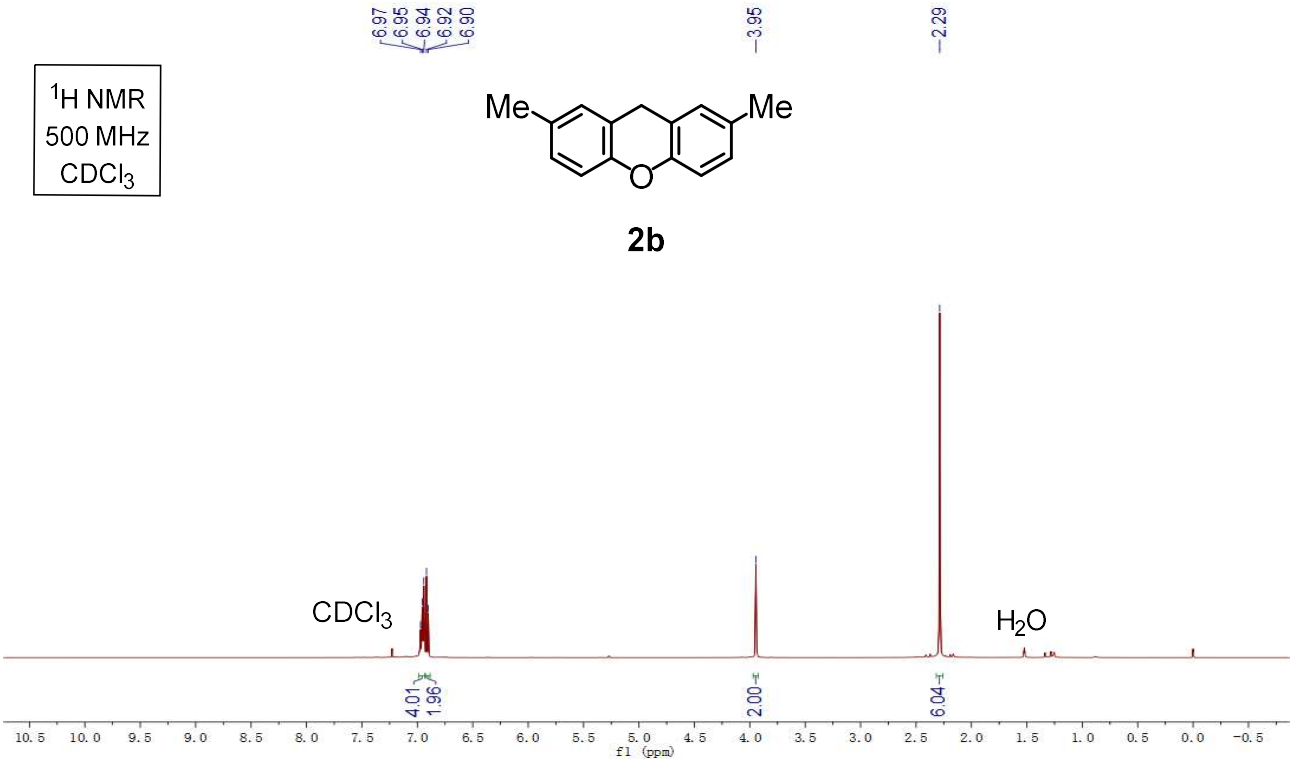
1t

^{13}C NMR
126 MHz
$CDCl_3$



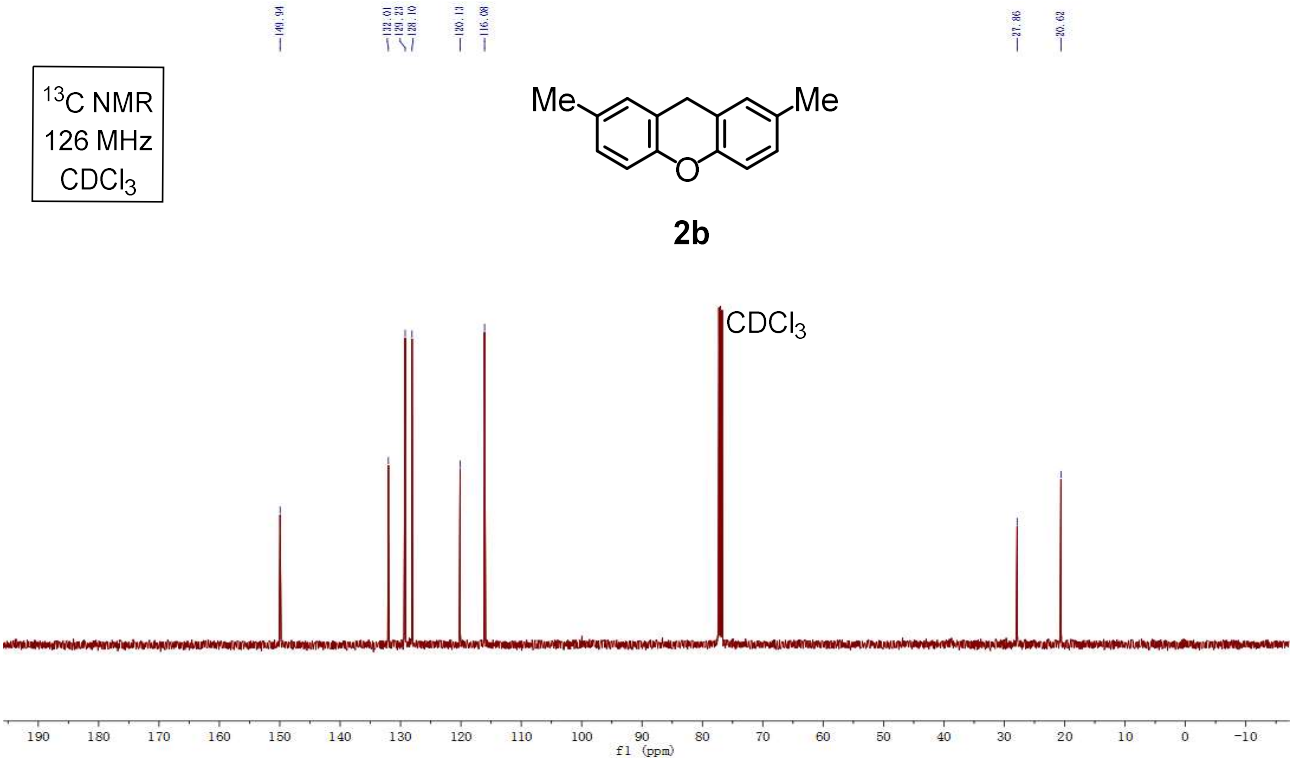
1t

^{1}H NMR
500 MHz
$CDCl_3$



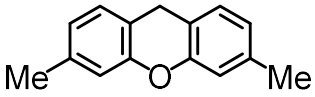
2b

^{13}C NMR
126 MHz
$CDCl_3$



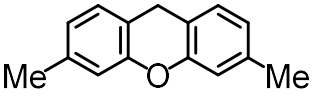
2b

^{1}H NMR
500 MHz
$CDCl_3$



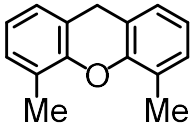
2c

^{13}C NMR
126 MHz
$CDCl_3$

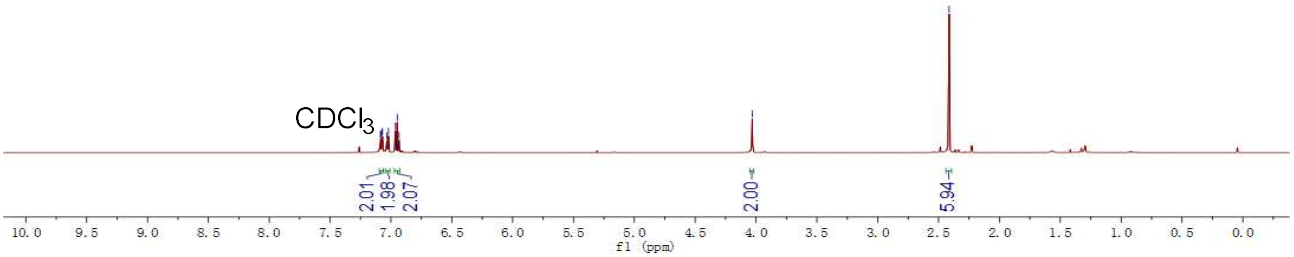


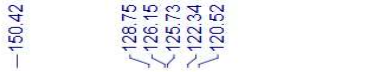
2c

^{1}H NMR
500 MHz
$CDCl_3$

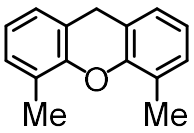


2d





^{13}C NMR
126 MHz
$CDCl_3$



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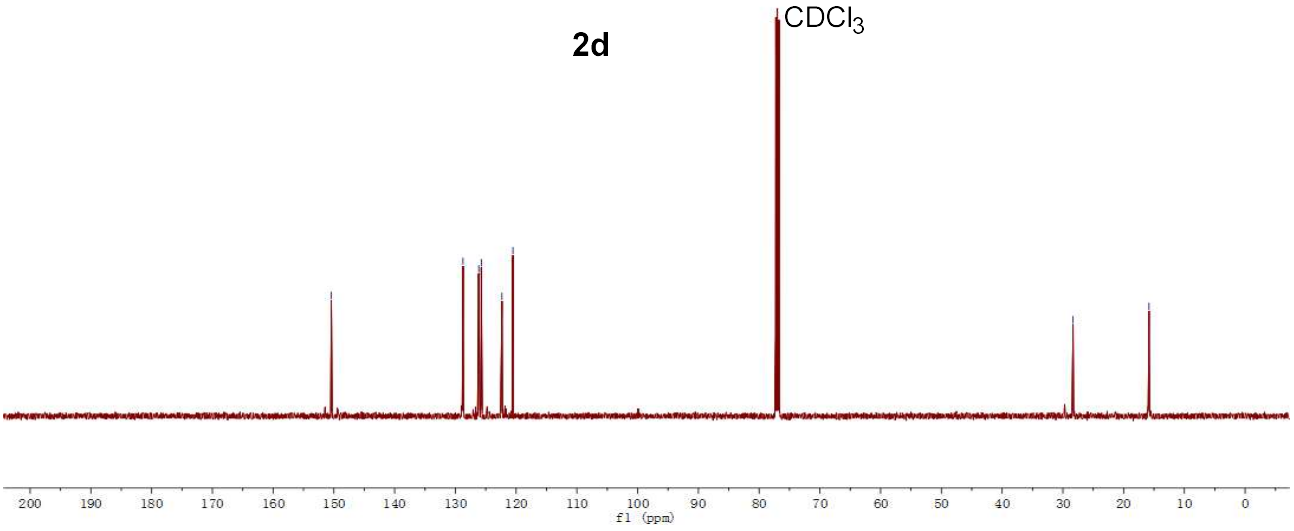
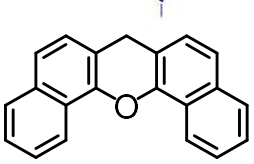


^{1}H NMR
500 MHz
$CDCl_3$



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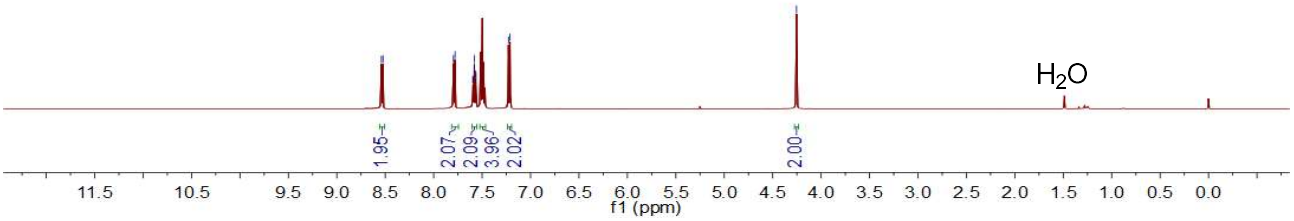
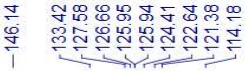
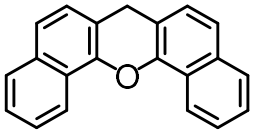
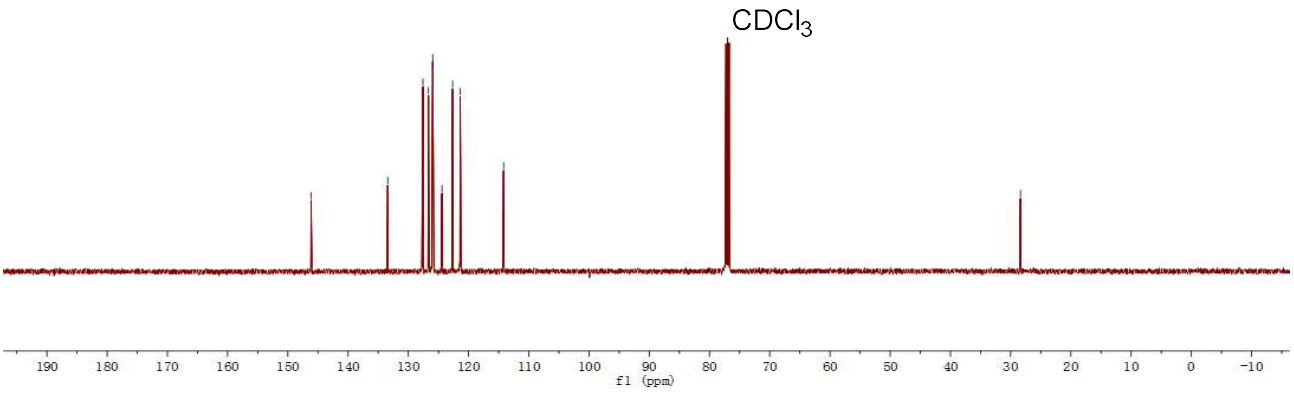


^{13}C NMR
126 MHz
$CDCl_3$

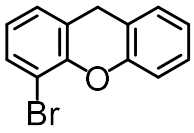




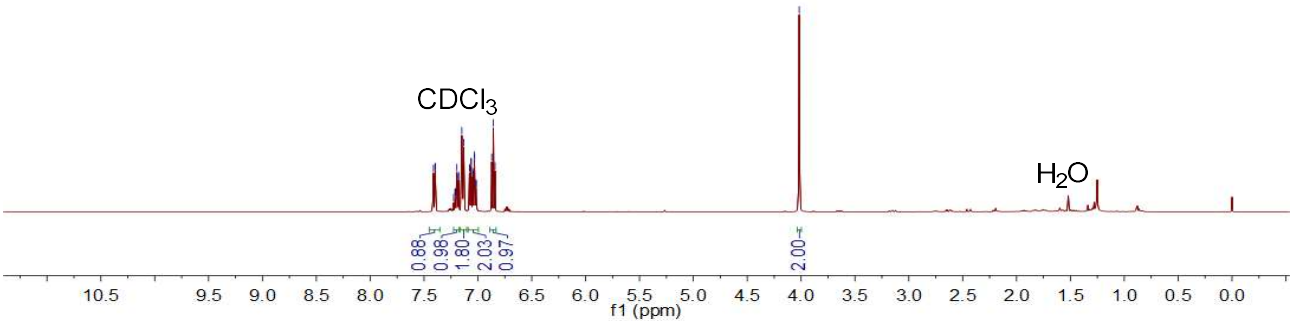
2f



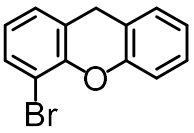
^{1}H NMR
500 MHz
$CDCl_3$



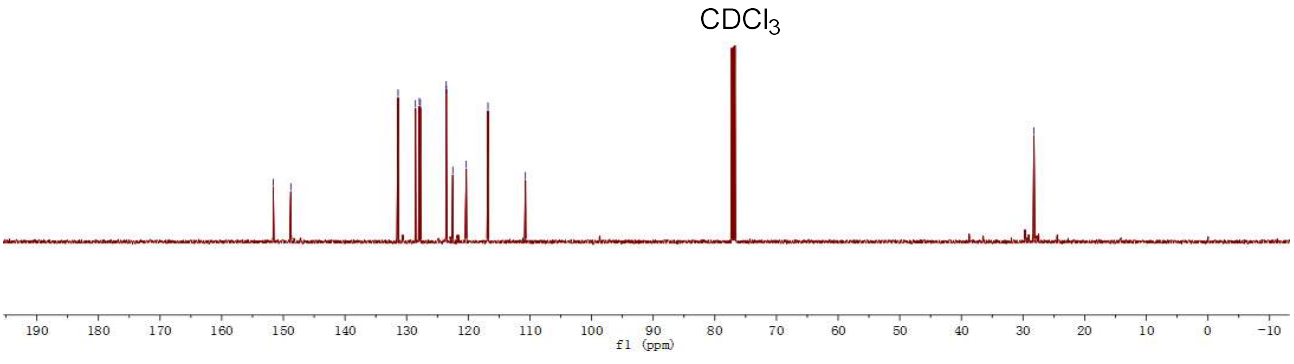
2k

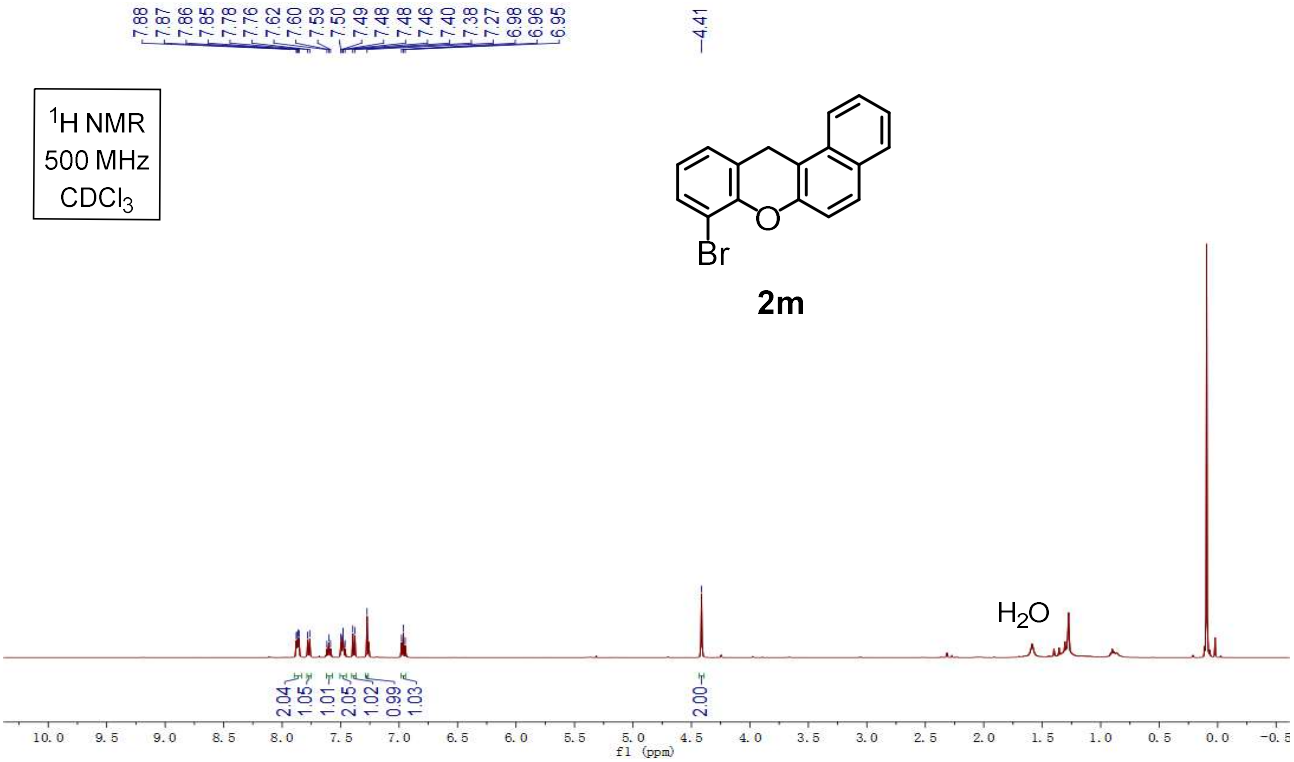


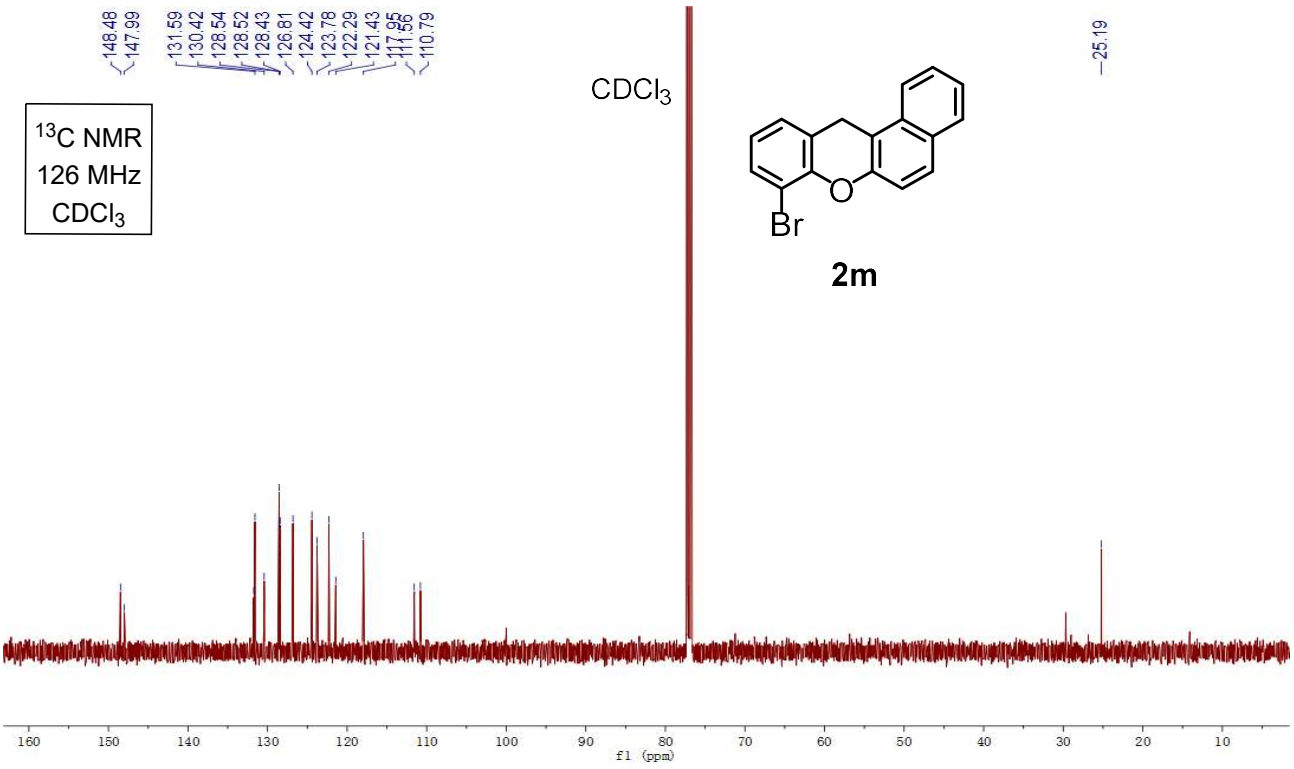
^{13}C NMR
126 MHz
$CDCl_3$



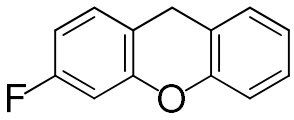
2k



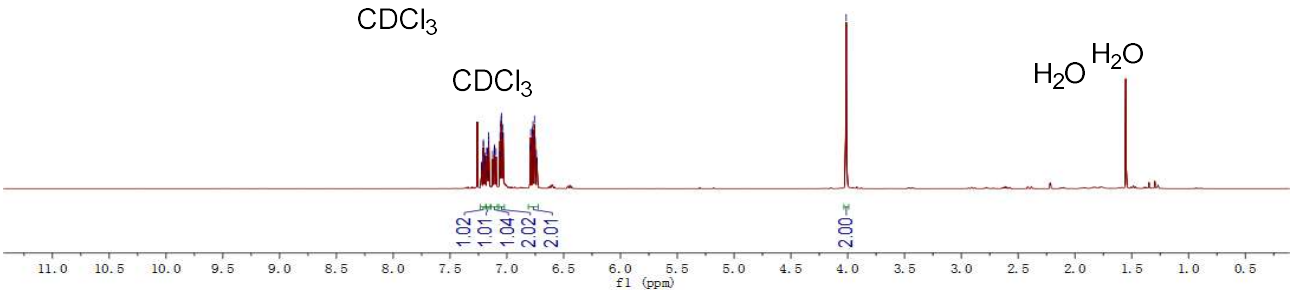

7.88
7.87
7.86
7.85
7.78
7.76
7.62
7.60
7.59
7.50
7.49
7.48
7.48
7.46
7.40
7.38
7.27
6.98
6.96
6.95
4.41
1H NMR
500 MHz
CDCl3
Br
2m
H2O
2.04
1.05
1.01
2.05
1.02
0.99
1.03
2.00
f1 (ppm)


148.48
147.99
131.59
130.42
128.54
128.52
128.43
126.81
124.42
123.78
122.29
121.43
111.95
111.56
110.79
CDCl3
25.19
13C NMR
126 MHz
CDCl3
Br
2m
f1 (ppm)

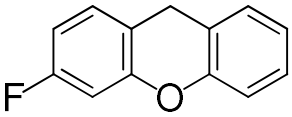
^{1}H NMR
500 MHz
$CDCl_3$



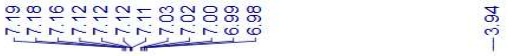
2n



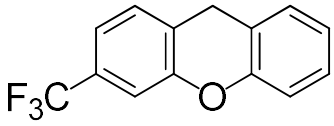
^{13}C NMR
126 MHz
$CDCl_3$



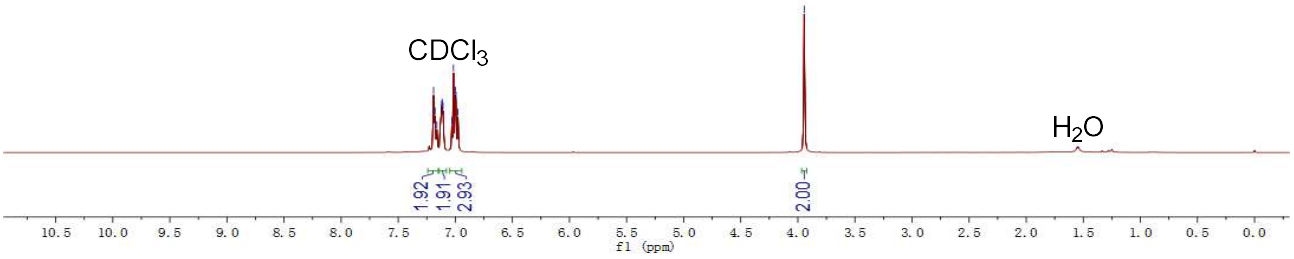
2n



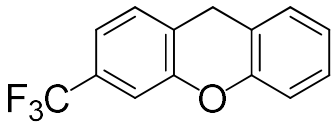
^{1}H NMR
500 MHz
$CDCl_3$



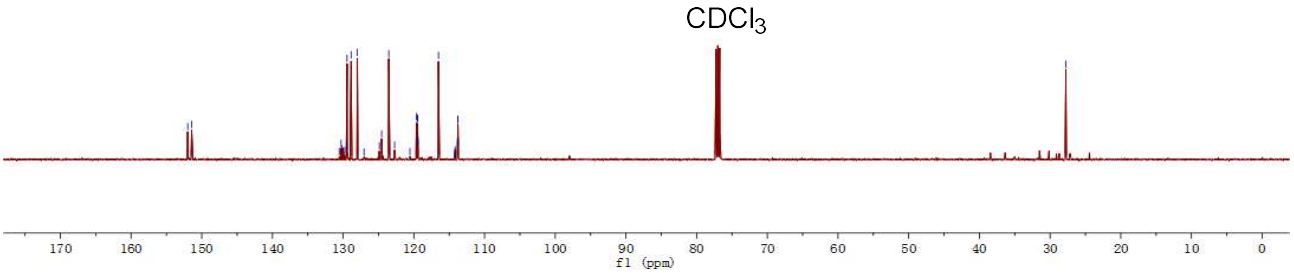
2o



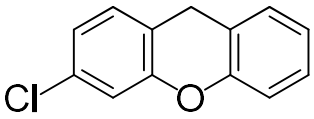
^{13}C NMR
126 MHz
$CDCl_3$



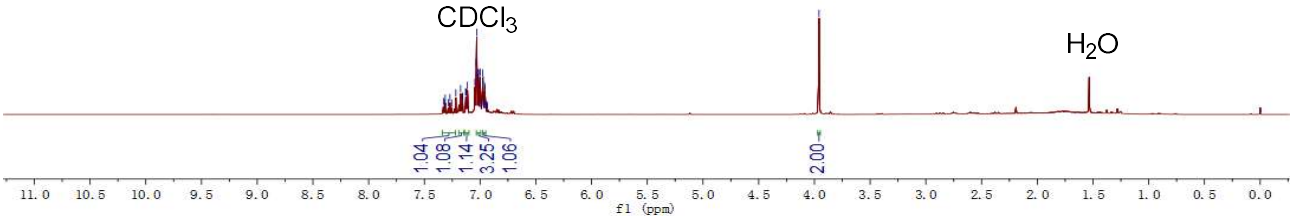
2o



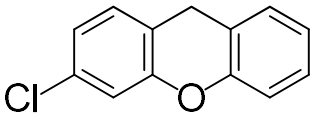
^{1}H NMR
500 MHz
$CDCl_3$



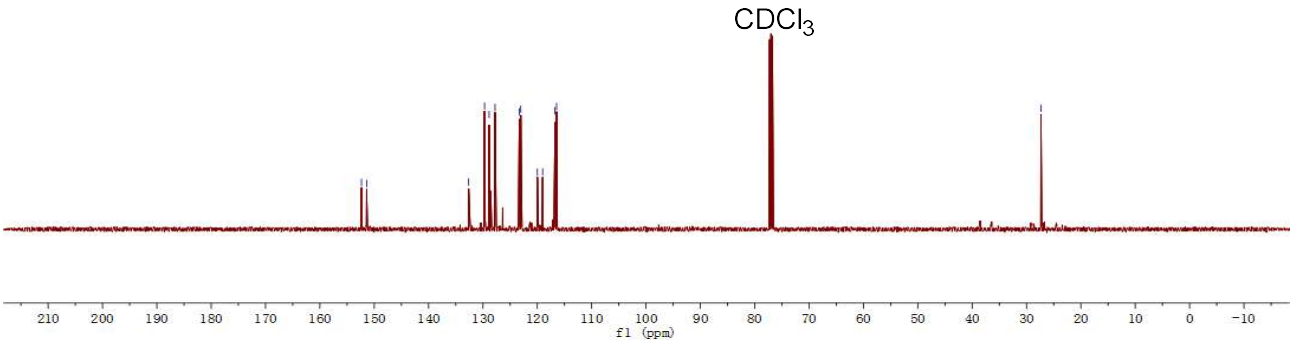
2p



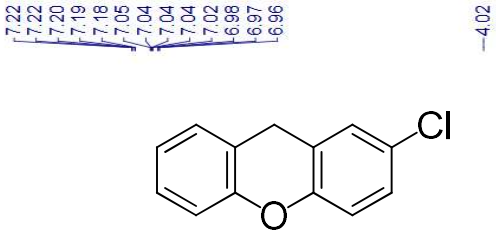
^{13}C NMR
126 MHz
$CDCl_3$



2p



^{1}H NMR
500 MHz
$CDCl_3$



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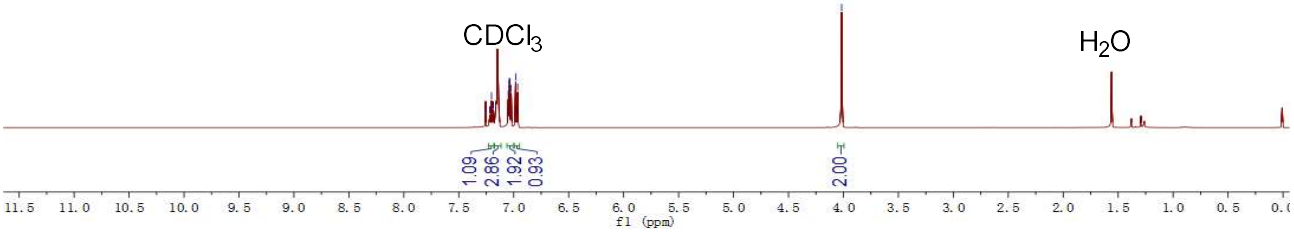
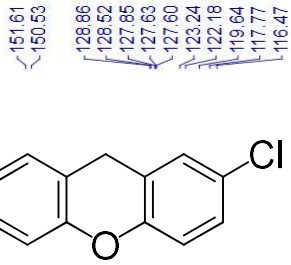
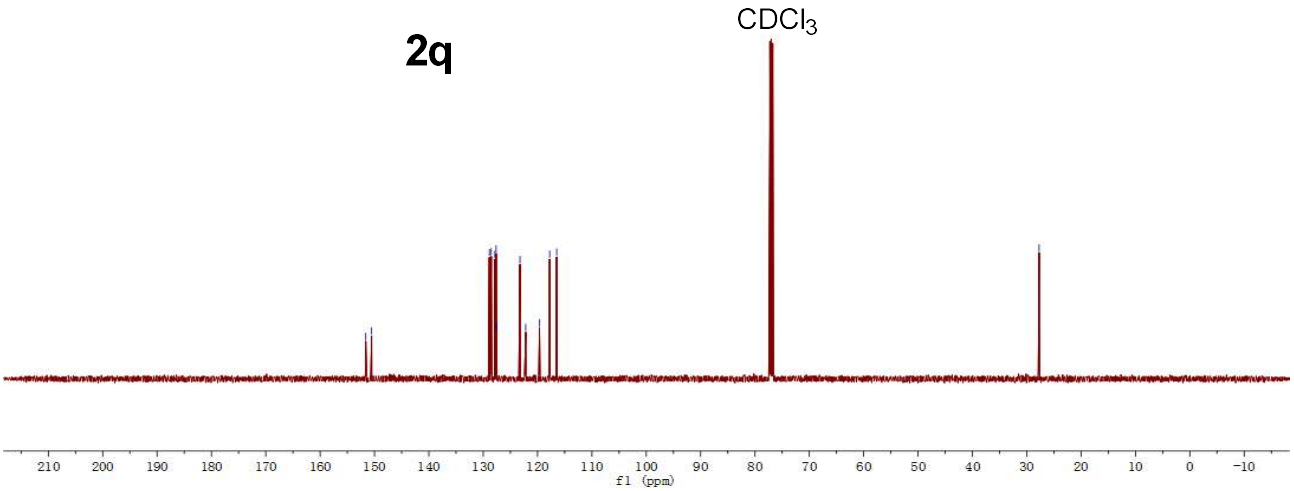
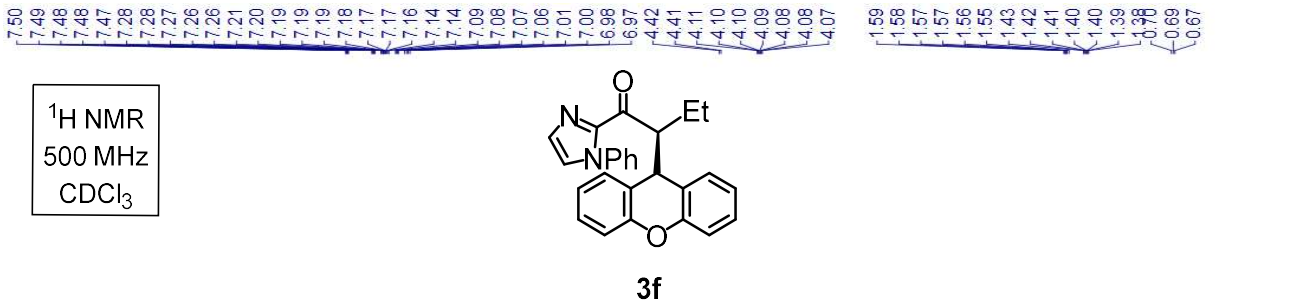


^{13}C NMR
126 MHz
$CDCl_3$



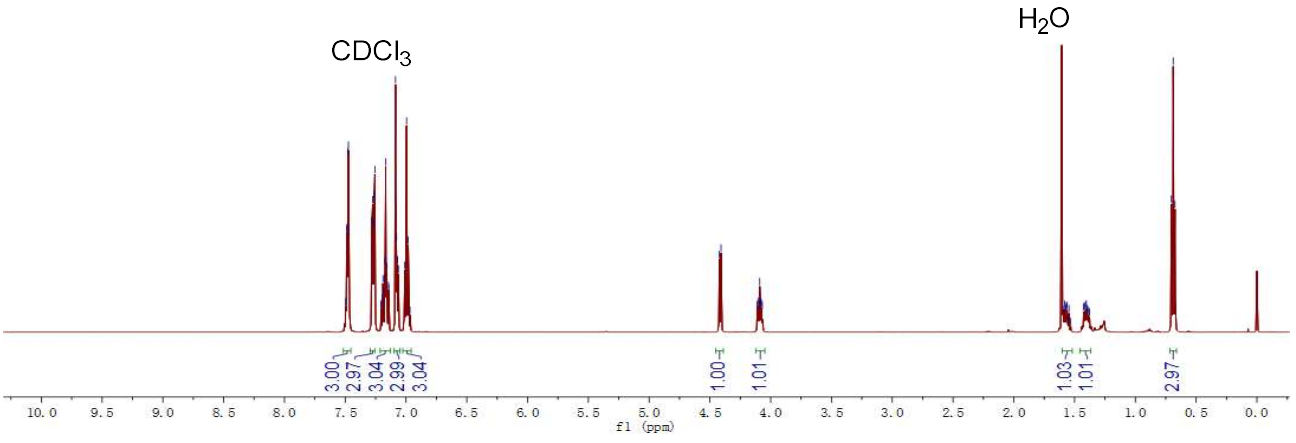
2q

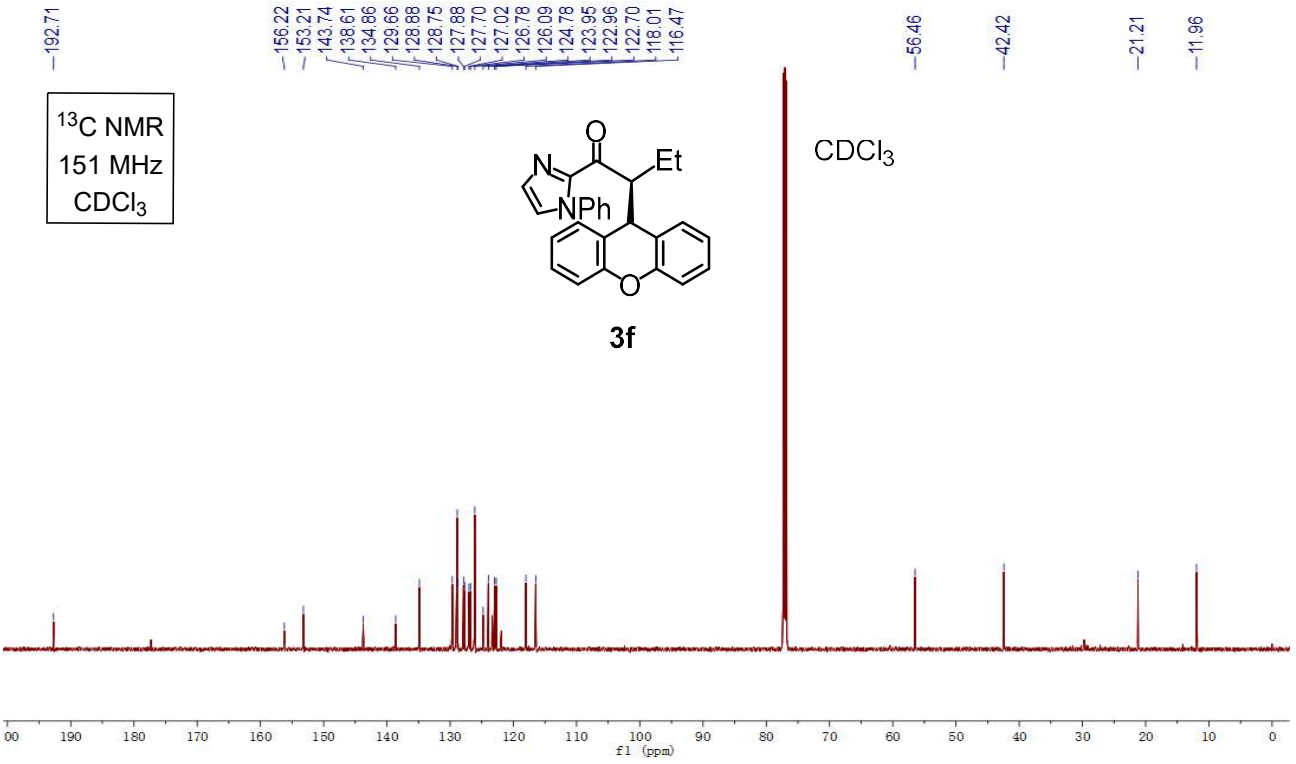




^{1}H NMR
500 MHz
$CDCl_3$

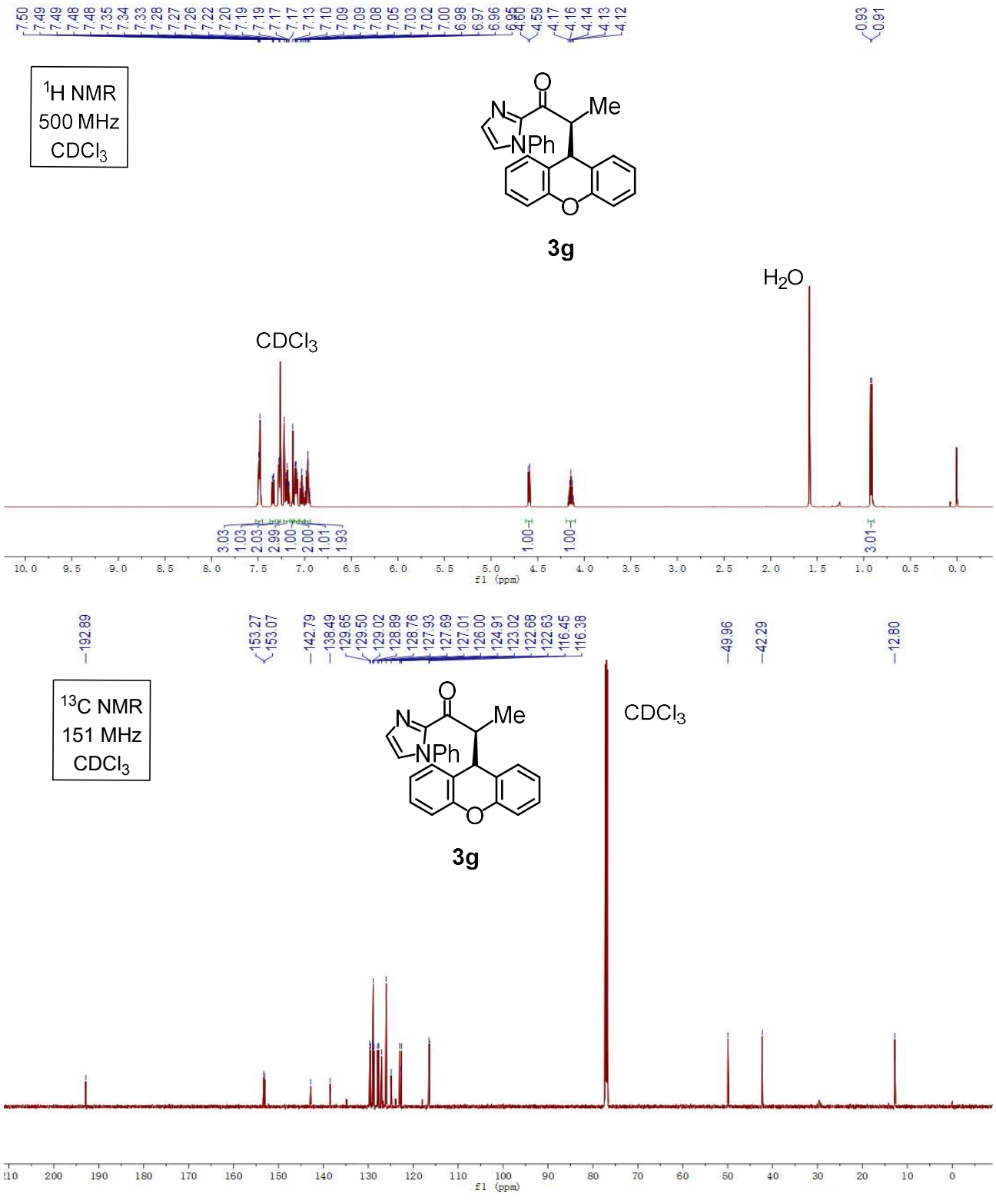
3f





^{13}C NMR
151 MHz
$CDCl_3$

3f


7.50
7.49
7.49
7.48
7.48
7.35
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7.33
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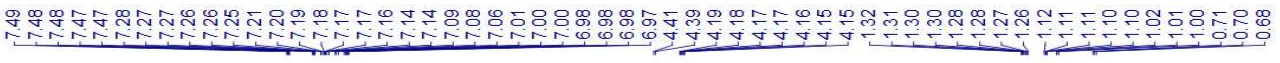
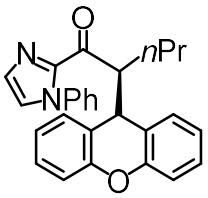
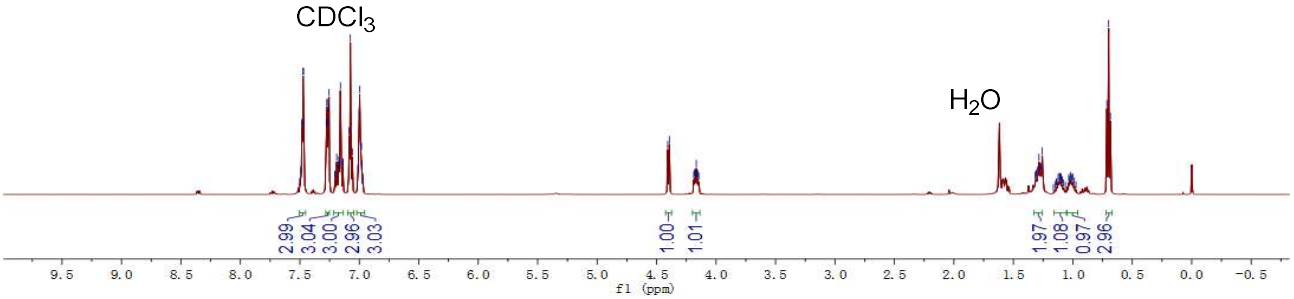
7.27
7.26
7.22
7.20
7.19
7.19
7.17
7.17
7.13
7.10
7.09
7.09
7.08
7.05
7.03
7.02
7.00
6.98
6.97
6.96
4.59
4.17
4.16
4.14
4.13
4.12
0.93
0.91
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
O
3g
H2O
CDCl3
3.03
1.03
2.03
2.99
1.00
2.00
1.01
1.93
1.00
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
192.89
153.27
153.07
142.79
138.49
129.65
129.50
129.02
128.89
128.76
127.93
127.69
127.01
126.00
124.91
123.02
122.68
122.63
116.45
116.38
49.96
42.29
12.80
13C NMR
151 MHz
CDCl3
O
N
Me
NPh
O
3g
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

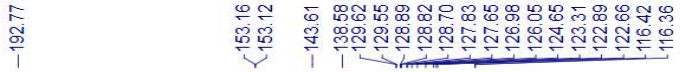


^{1}H NMR
500 MHz
$CDCl_3$

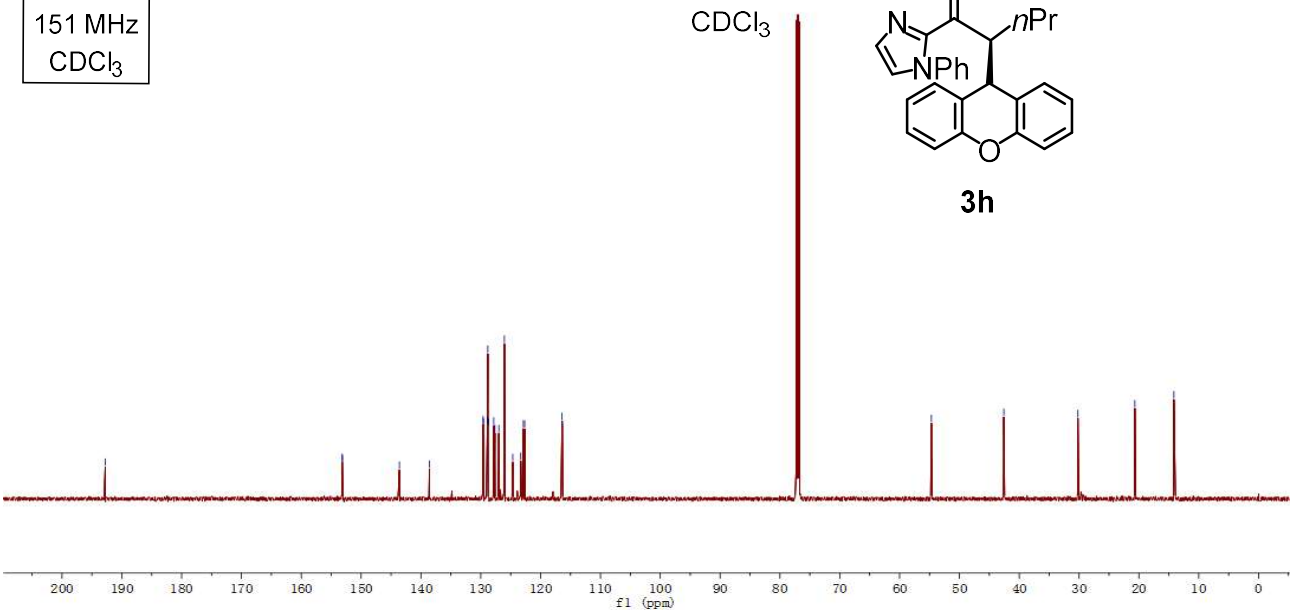


3h

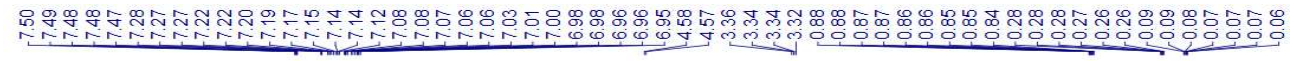




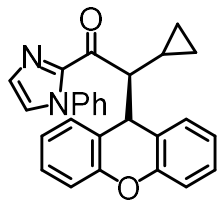
^{13}C NMR
151 MHz
$CDCl_3$



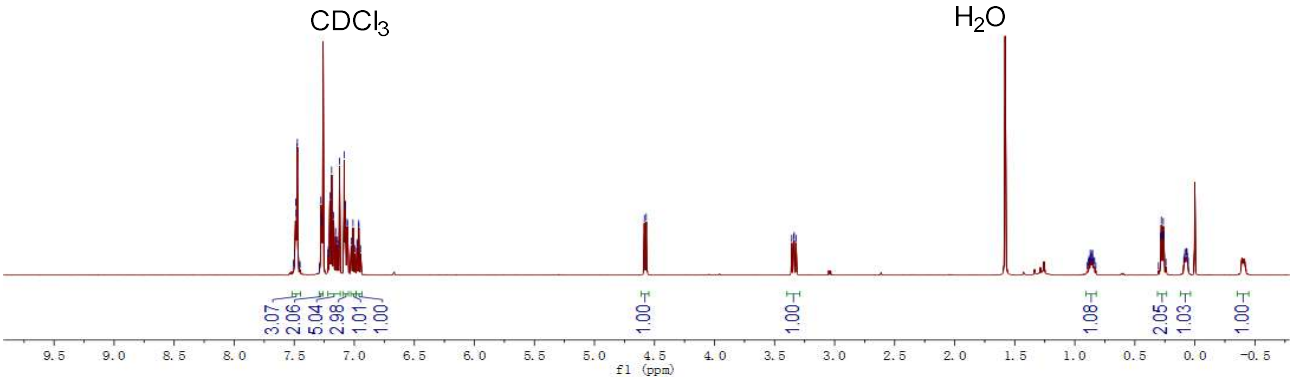
3h

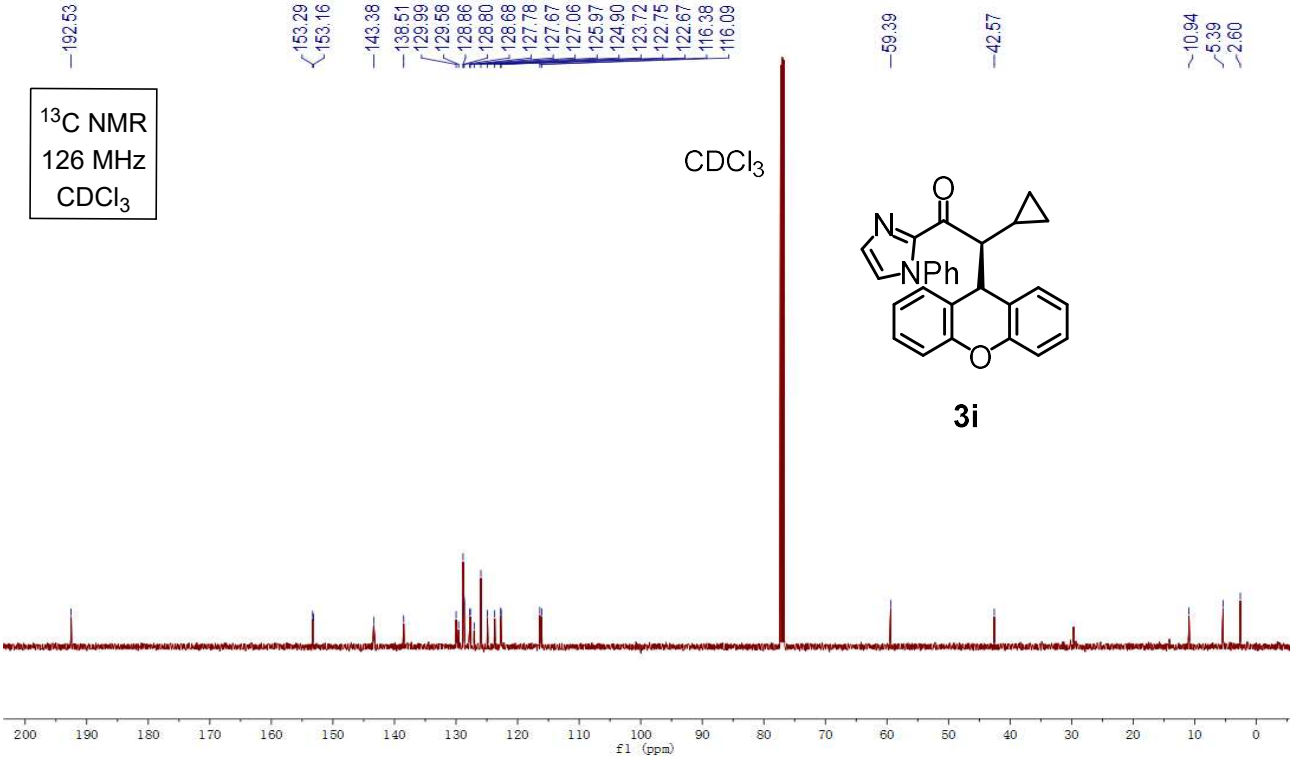


^{1}H NMR
500 MHz
$CDCl_3$



3i

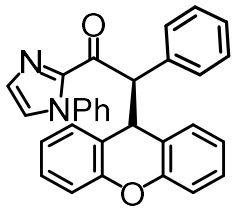




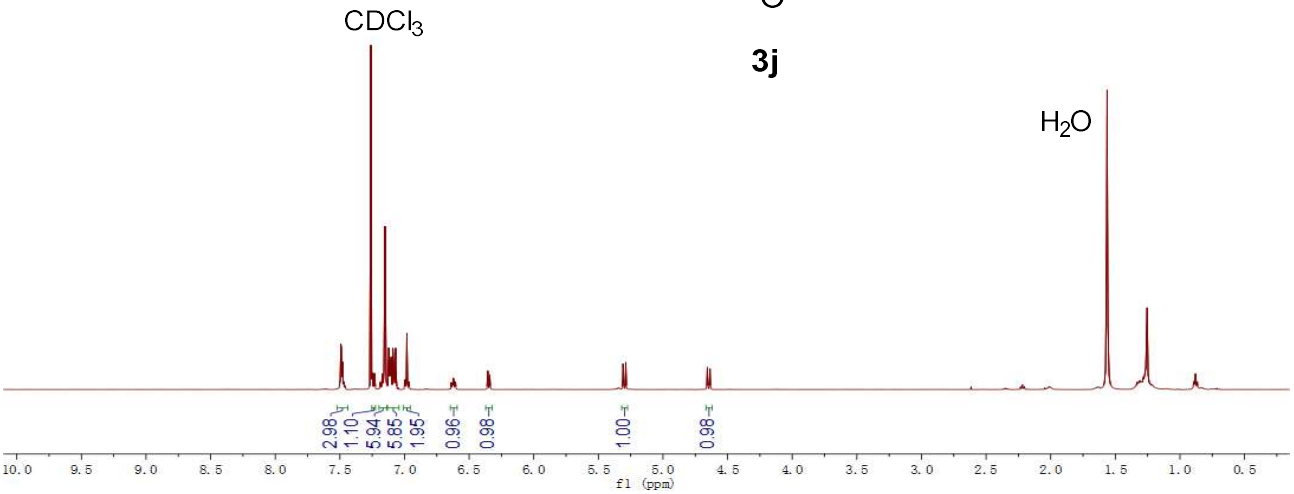
^{13}C NMR
126 MHz
$CDCl_3$

3i

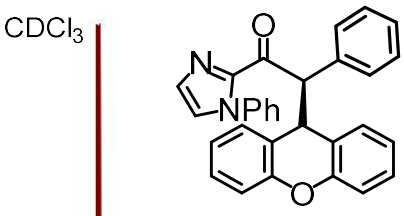
^{1}H NMR
500 MHz
$CDCl_3$



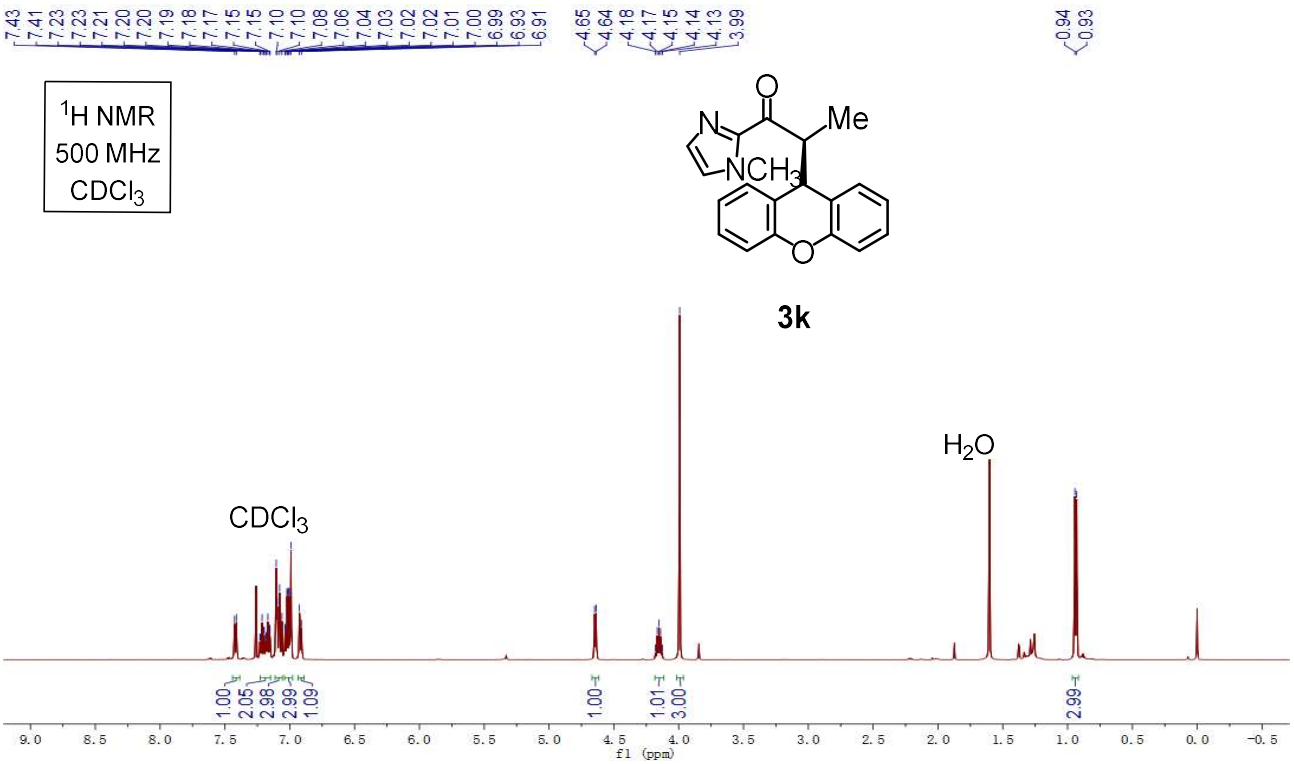
3j

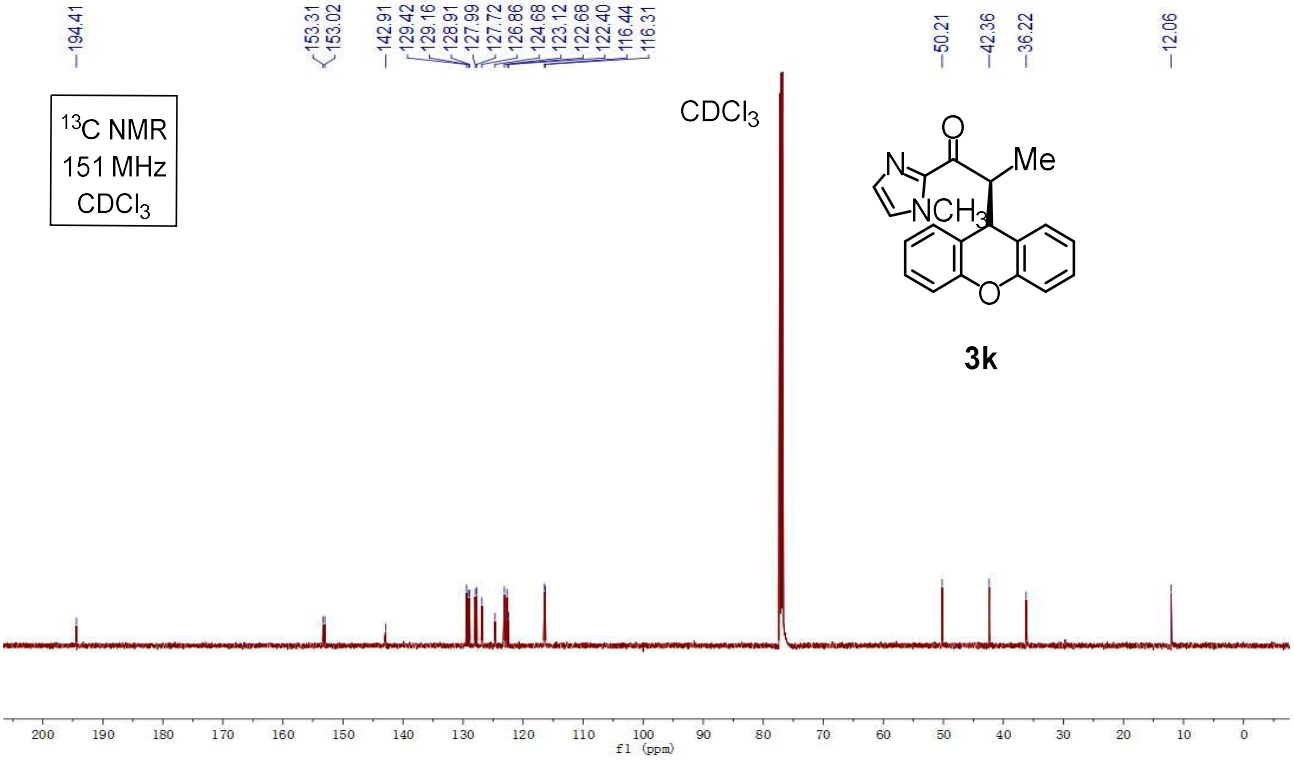


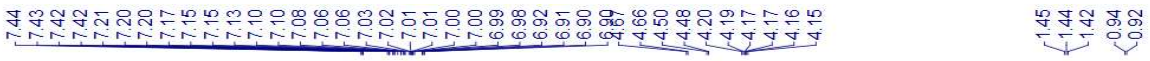
^{13}C NMR
126 MHz
$CDCl_3$



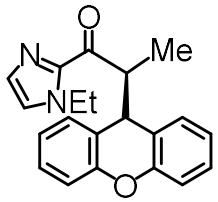
3j


7.43
7.41
7.23
7.23
7.21
7.20
7.20
7.19
7.18
7.17
7.15
7.15
7.10
7.10
7.08
7.06
7.04
7.03
7.02
7.02
7.01
7.00
6.99
6.93
6.91
4.65
4.64
4.18
4.17
4.15
4.14
4.13
3.99
0.94
0.93
1H NMR
500 MHz
CDCl3
N
Me
NCH3
O
O
3k
H2O
CDCl3
1.00
2.05
2.98
2.99
1.09
1.00
1.01
3.00
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

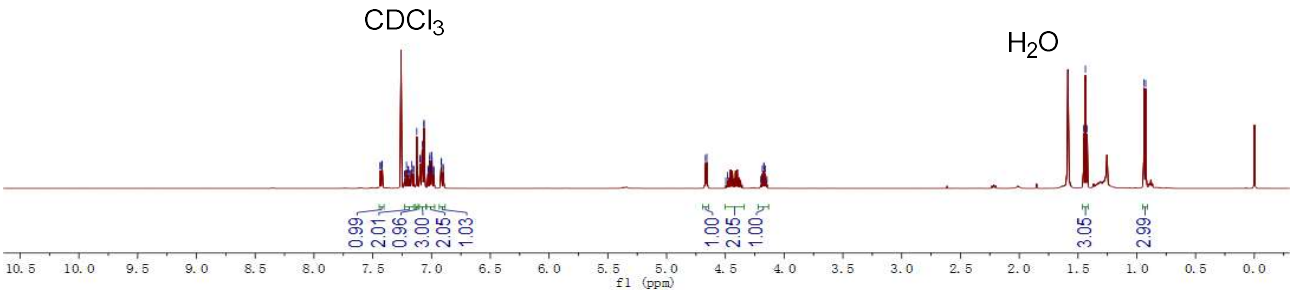

194.41
153.31
153.02
142.91
129.42
129.16
128.91
127.99
127.72
126.86
124.68
123.12
122.68
122.40
116.44
116.31
50.21
42.36
36.22
12.06
13C NMR
151 MHz
CDCl3
CDCl3
N
Me
NCH3
O
O
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

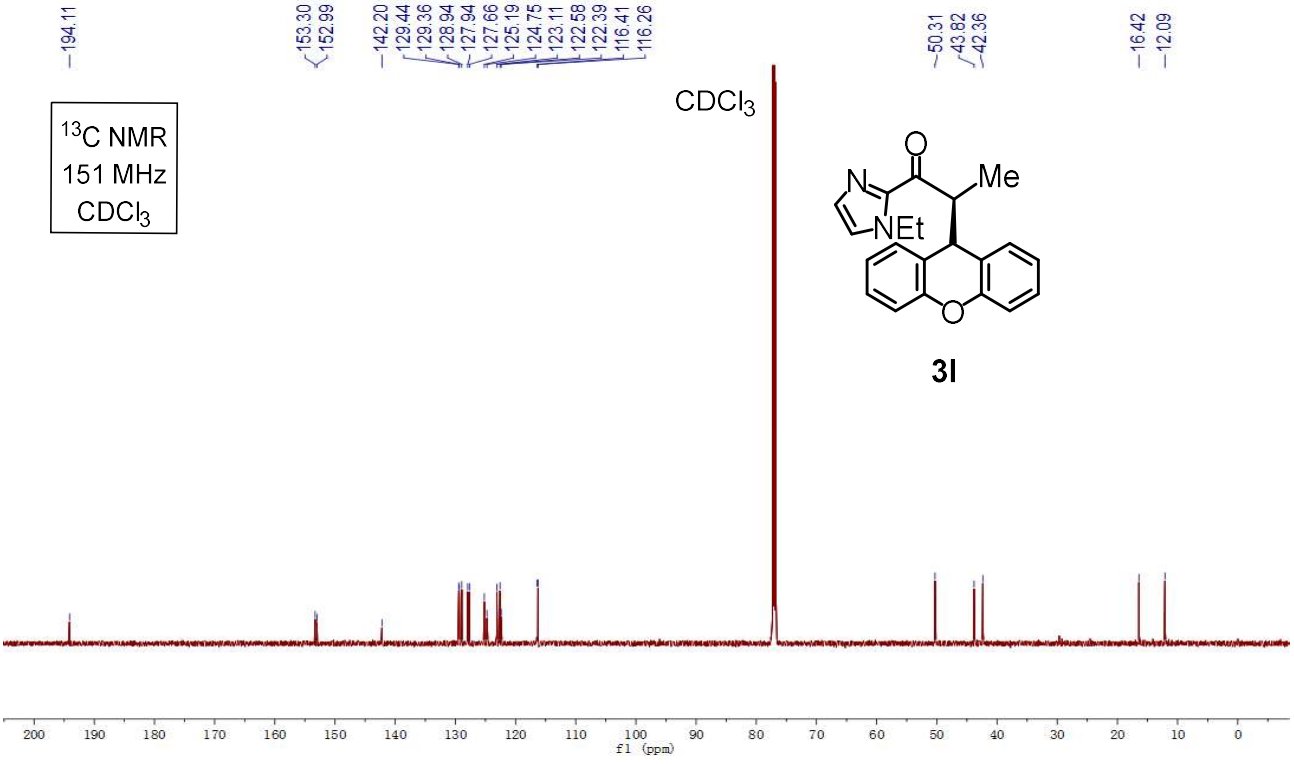


^{1}H NMR
500 MHz
$CDCl_3$

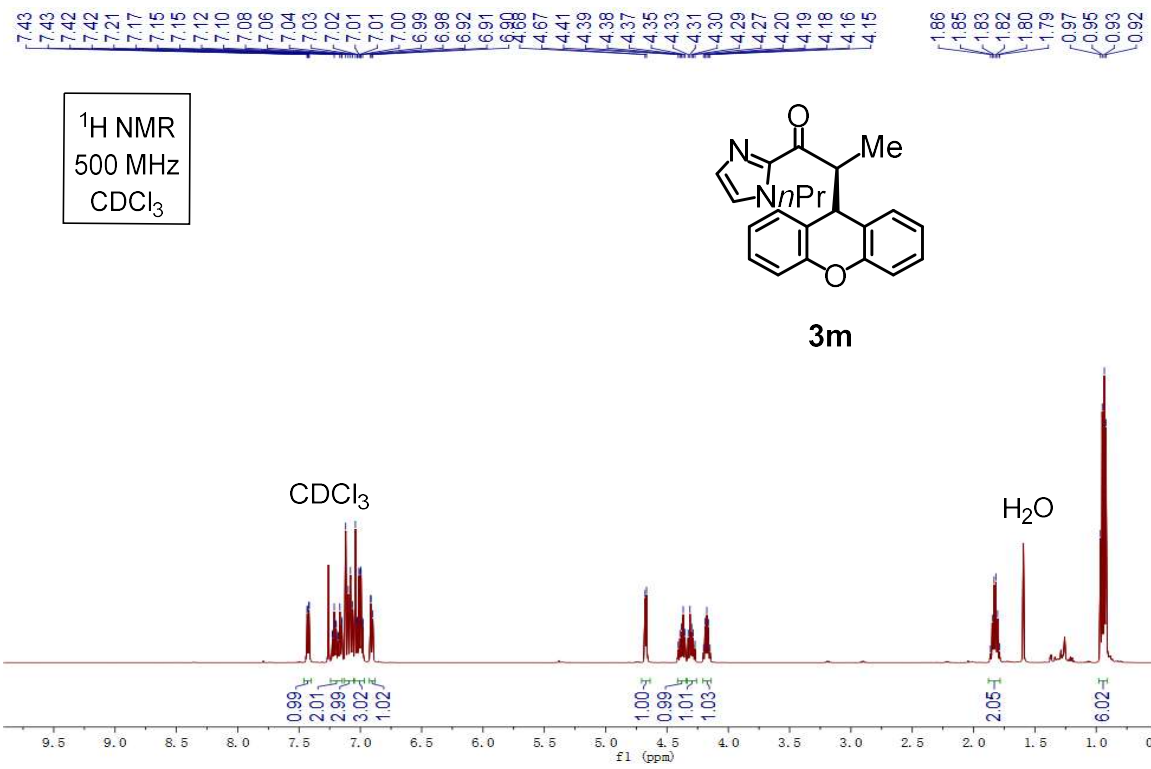


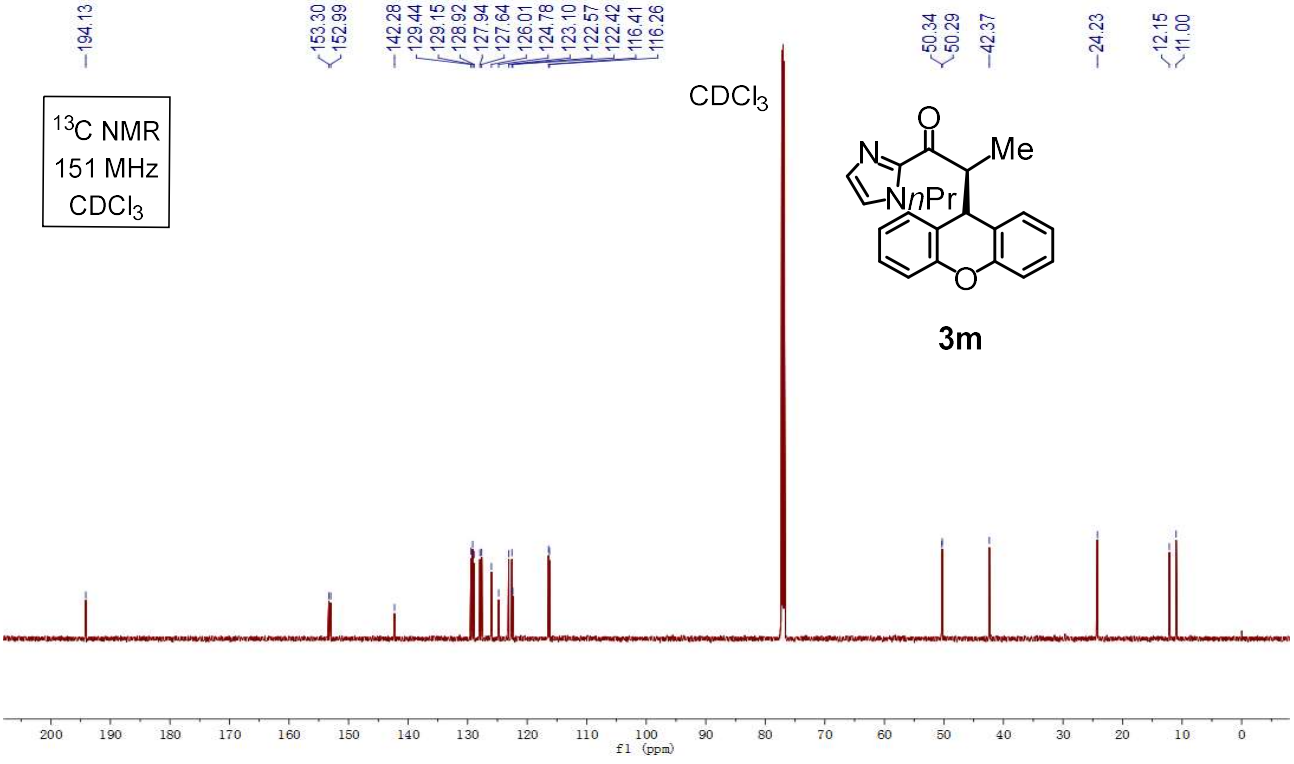
3l

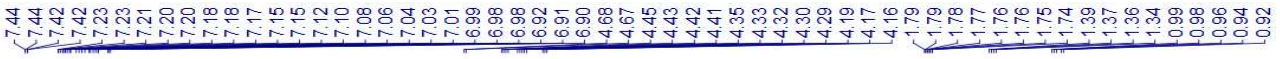




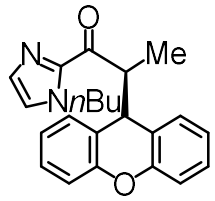
3l


7.43 7.43 7.42 7.42 7.21 7.17 7.15 7.15 7.12 7.10 7.08 7.06 7.04 7.03 7.02 7.01 7.01 7.00 6.99 6.98 6.92 6.91 6.90 6.88 4.67 4.41 4.39 4.38 4.37 4.35 4.33 4.31 4.30 4.29 4.27 4.20 4.19 4.18 4.16 4.15
1.86 1.85 1.83 1.82 1.80 1.79 0.97 0.95 0.93 0.92
1H NMR
500 MHz
CDCl3
Me
NnPr
3m
CDCl3
H2O
0.99 2.01 2.99 3.02 1.02 1.00 0.99 1.01 1.03 2.05 6.02
f1 (ppm)

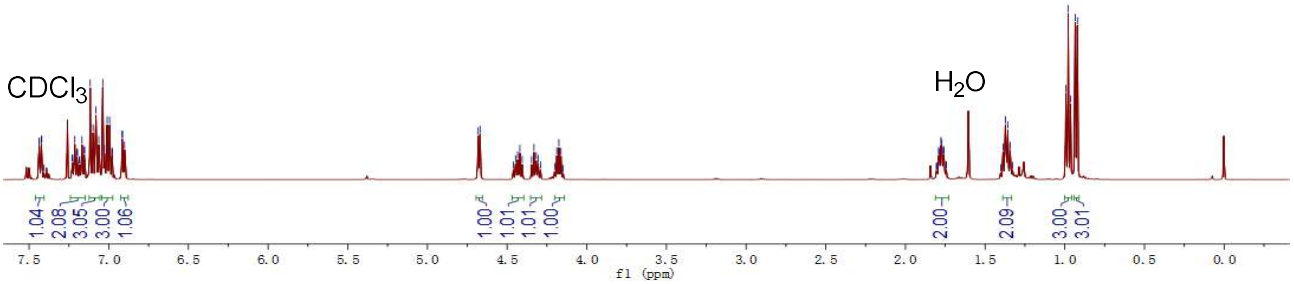

194.13
153.30 152.99 142.28 129.44 129.15 128.92 127.94 127.64 126.01 124.78 123.10 122.57 122.42 116.41 116.26
50.34 50.29 42.37 24.23 12.15 11.00
13C NMR
151 MHz
CDCl3
CDCl3
Me
NnPr
3m
f1 (ppm)

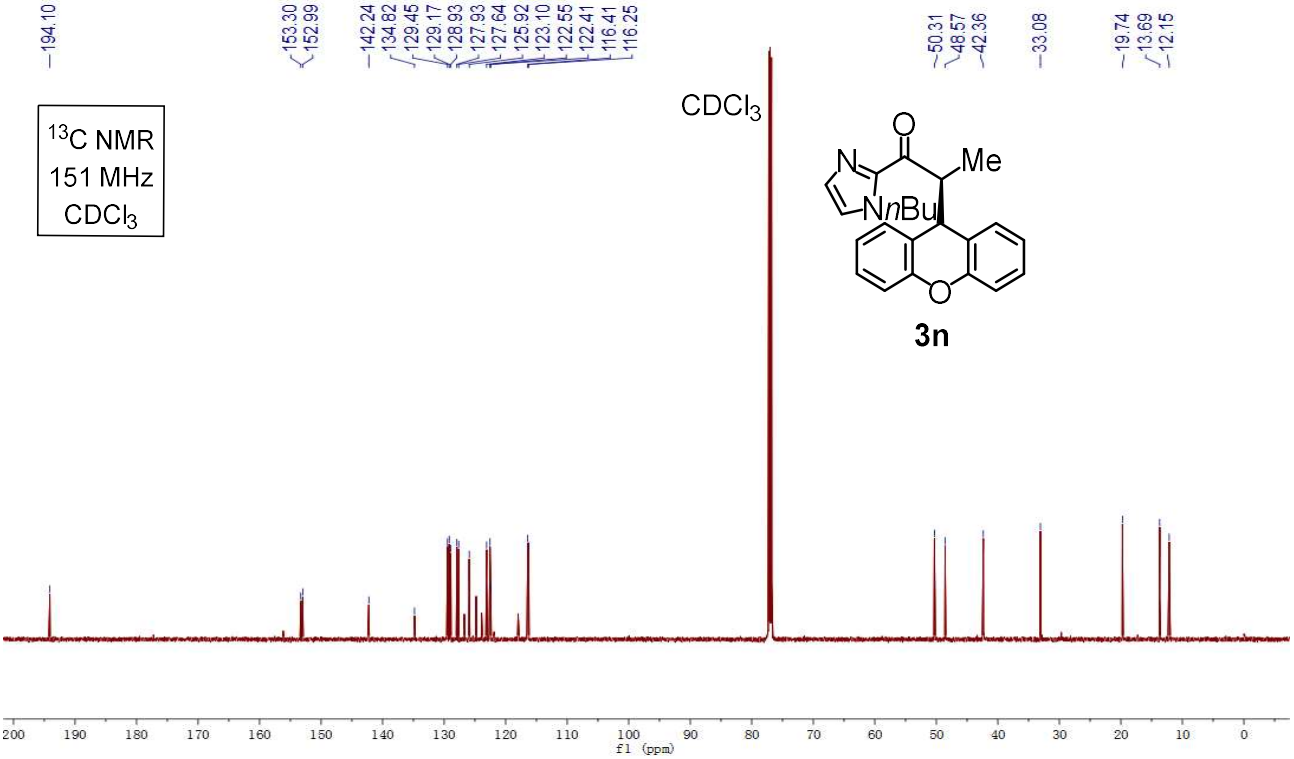


^{1}H NMR
500 MHz
$CDCl_3$



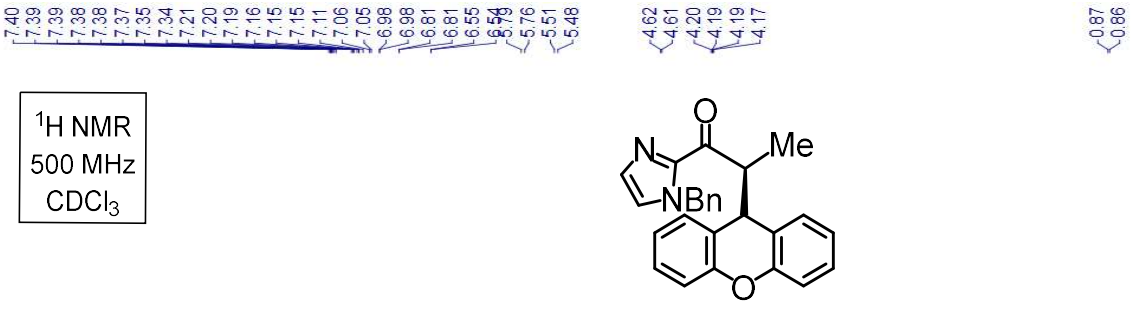
3n





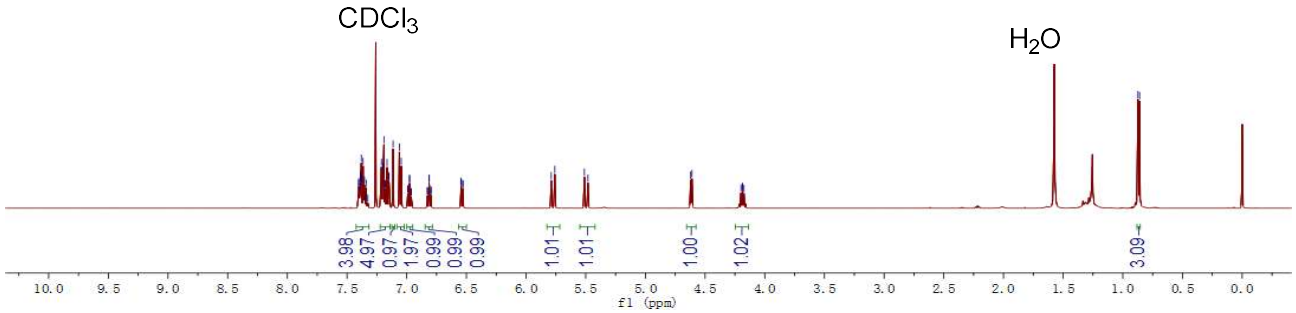
^{13}C NMR
151 MHz
$CDCl_3$

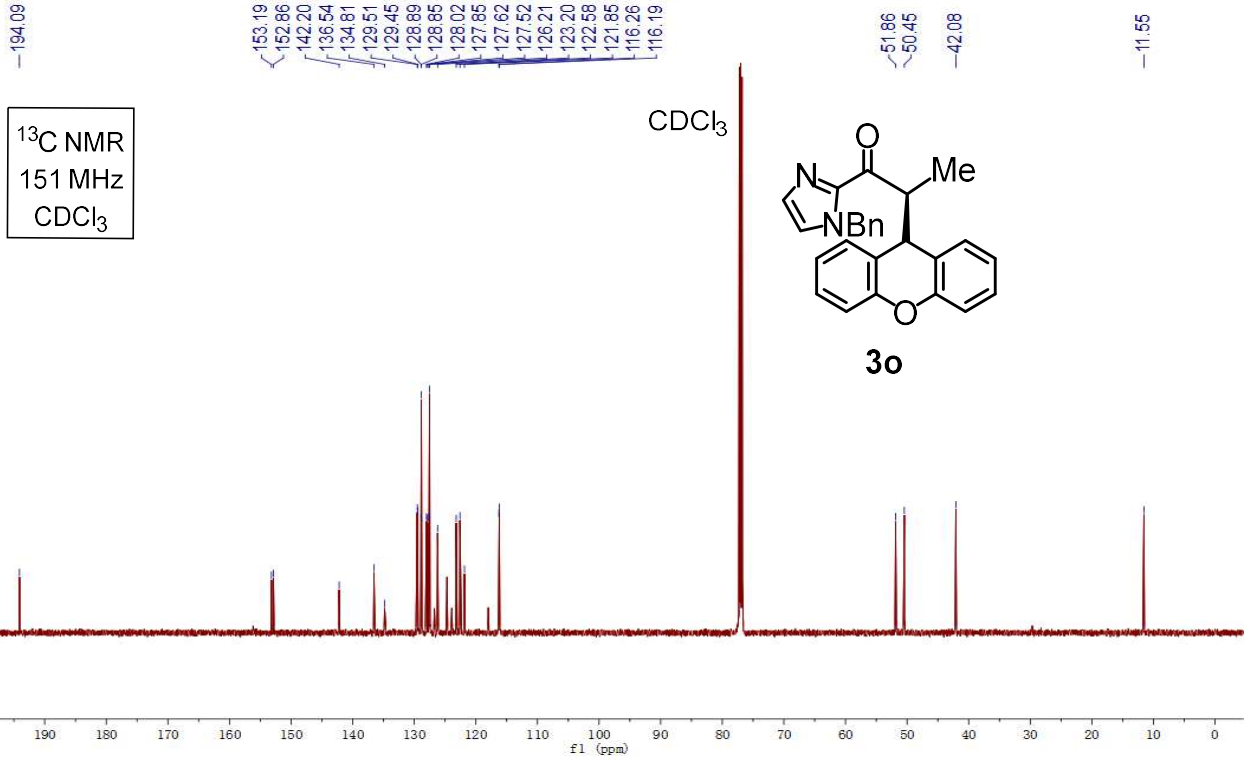
3n



^{1}H NMR
500 MHz
$CDCl_3$

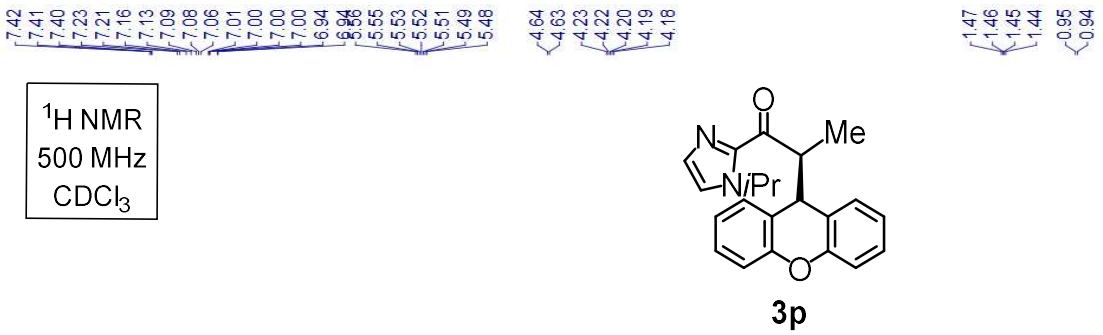
3o



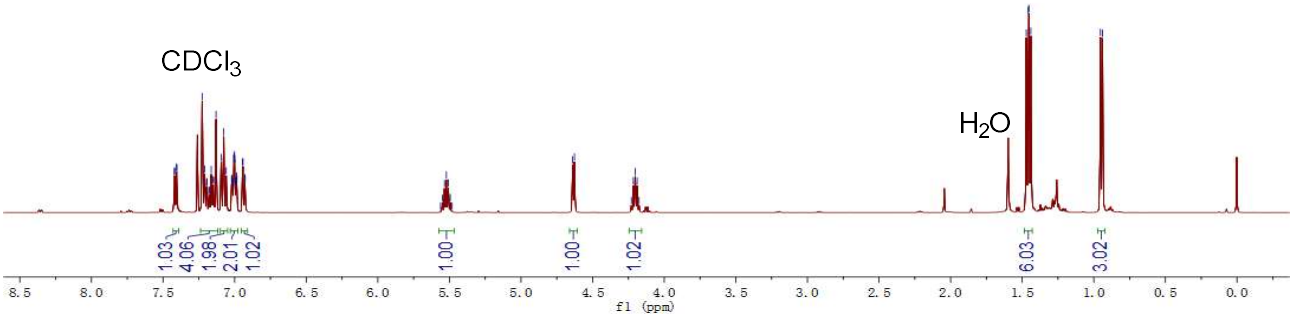


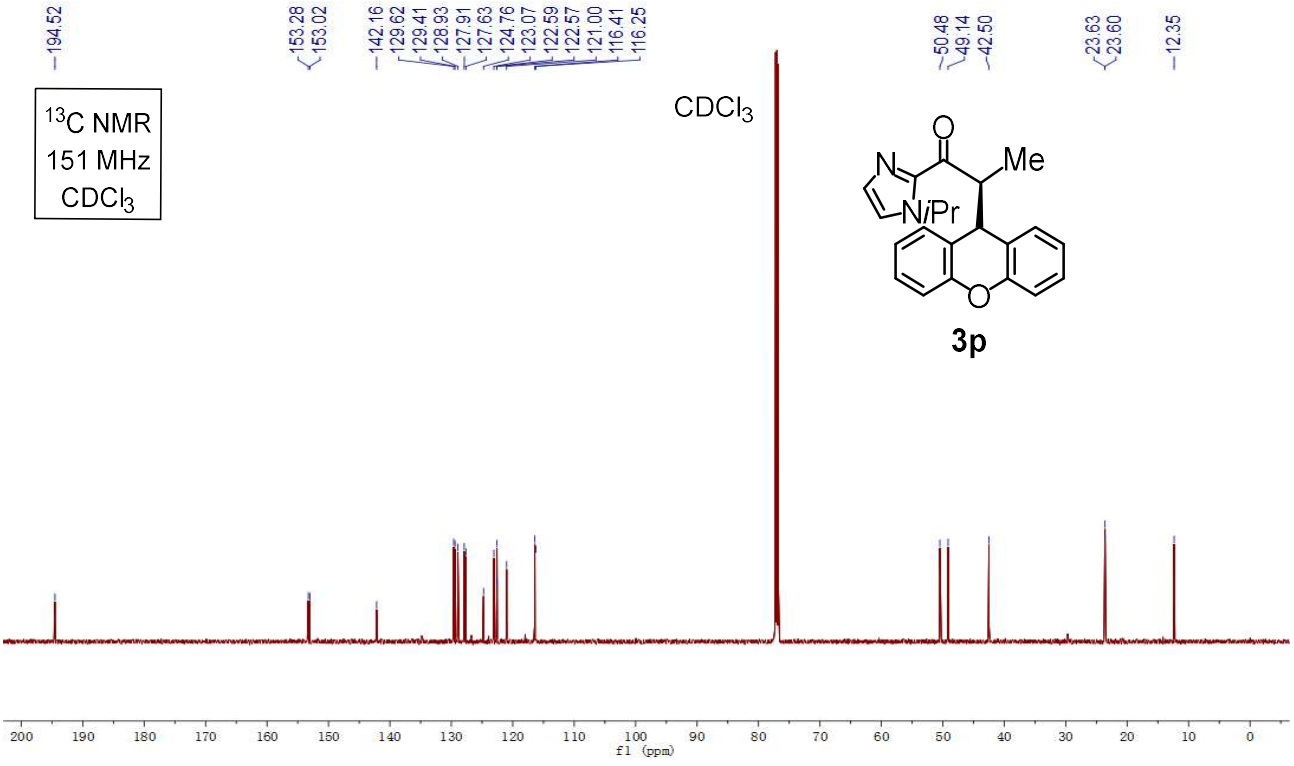
^{13}C NMR
151 MHz
$CDCl_3$

3o

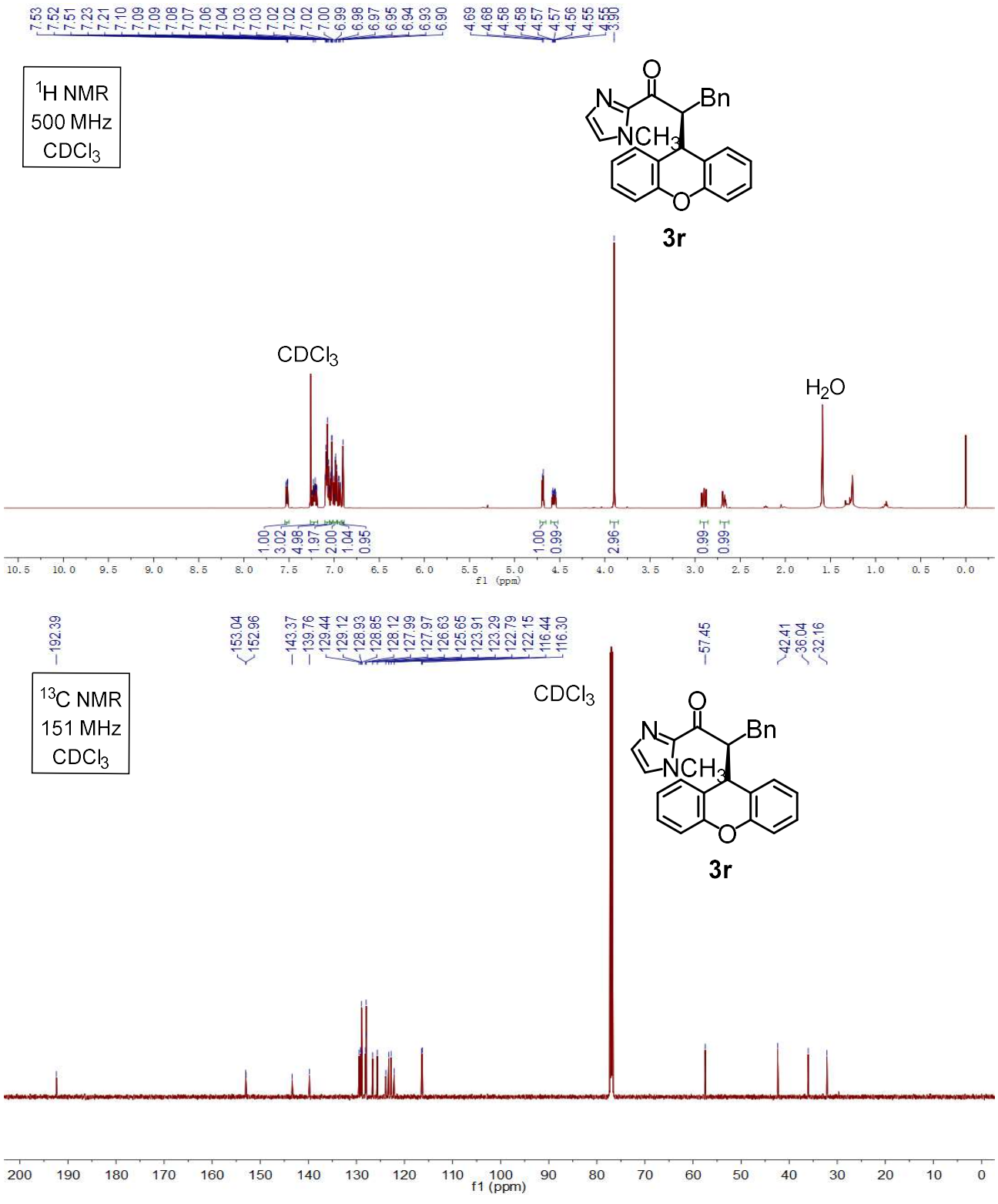

7.42
7.41
7.40
7.23
7.21
7.16
7.13
7.09
7.08
7.06
7.01
7.00
7.00
7.00
6.94
5.55
5.53
5.52
5.51
5.49
5.48
4.64
4.63
4.23
4.22
4.20
4.19
4.18
1.47
1.46
1.45
1.44
0.95
0.94
1H NMR
500 MHz
CDCl3
N
O
Me
NiPr
O

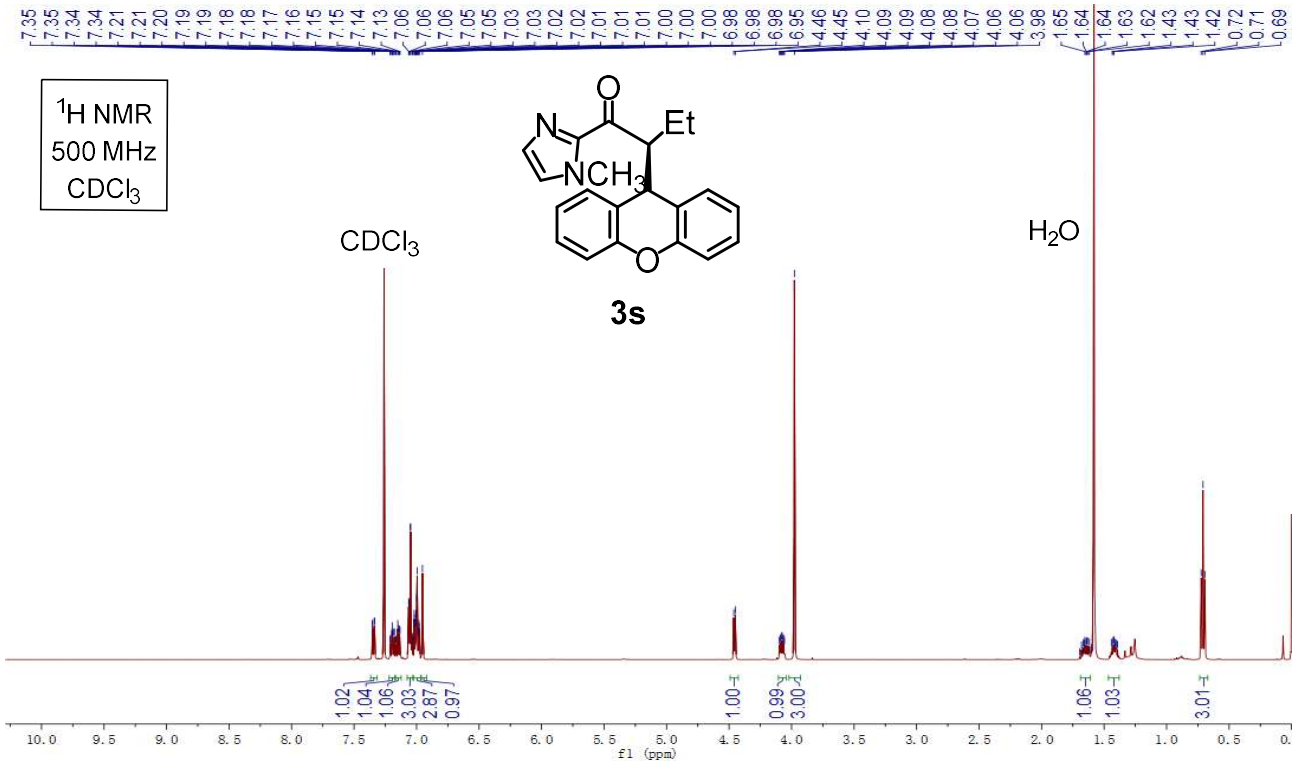
3p

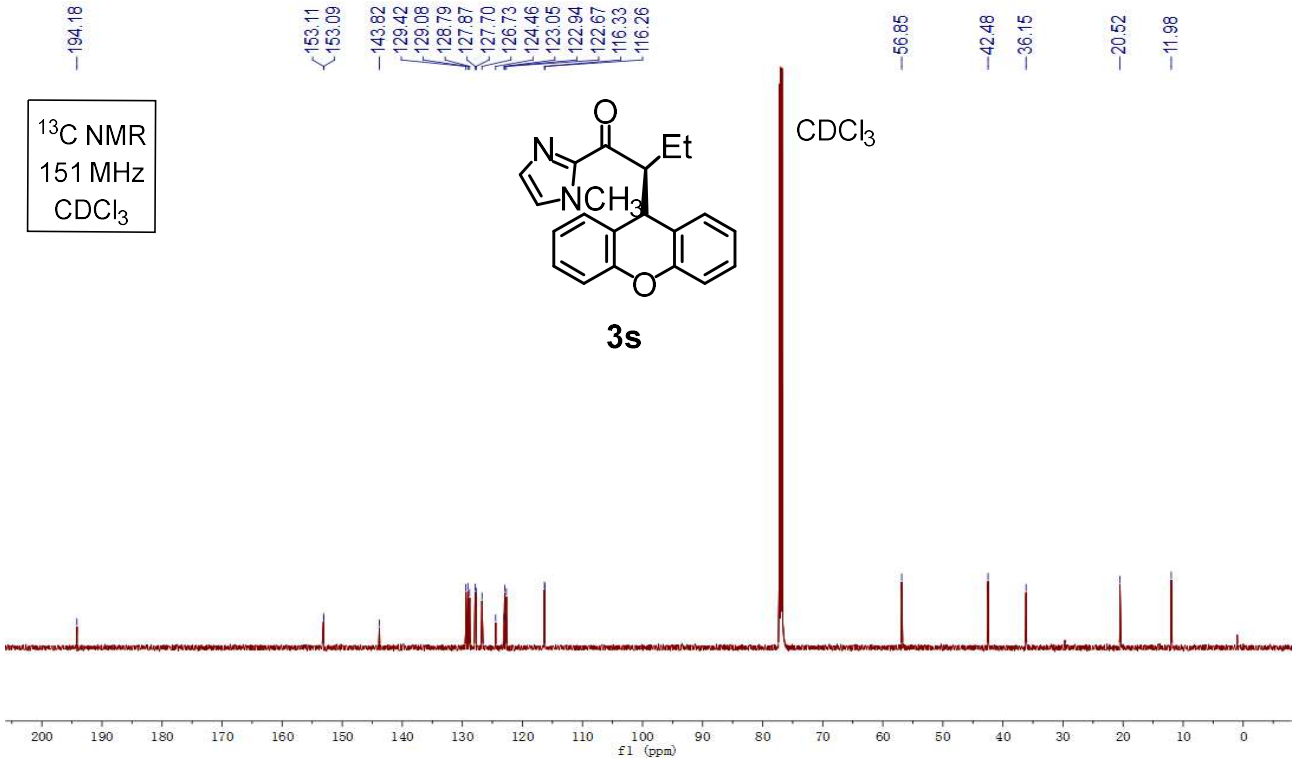

CDCl3
H2O
1.03
4.06
1.98
2.01
1.02
1.00
1.00
1.02
6.03
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

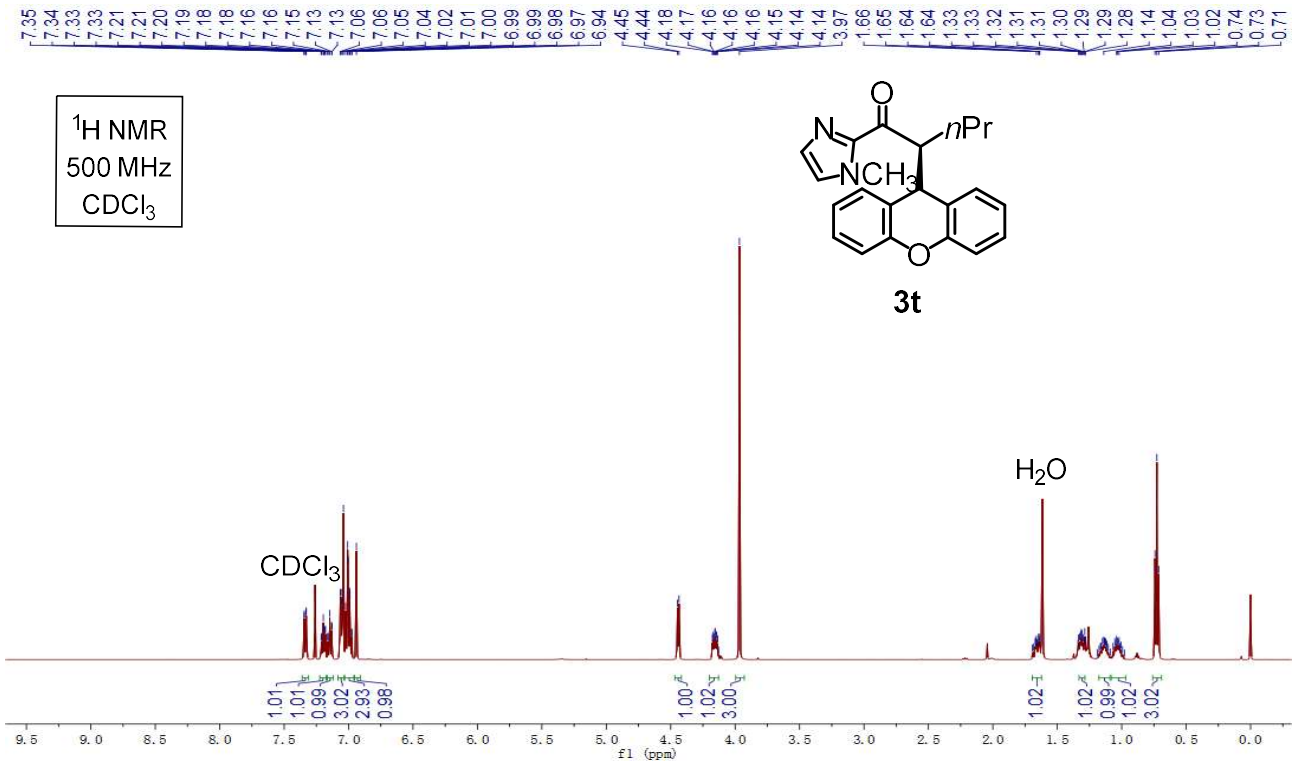

194.52
153.28
153.02
142.16
129.62
129.41
128.93
127.91
127.63
124.76
123.07
122.59
122.57
121.00
116.41
116.25
50.48
49.14
42.50
23.63
23.60
12.35
13C NMR
151 MHz
CDCl3
CDCl3
N
O
Me
NiPr
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

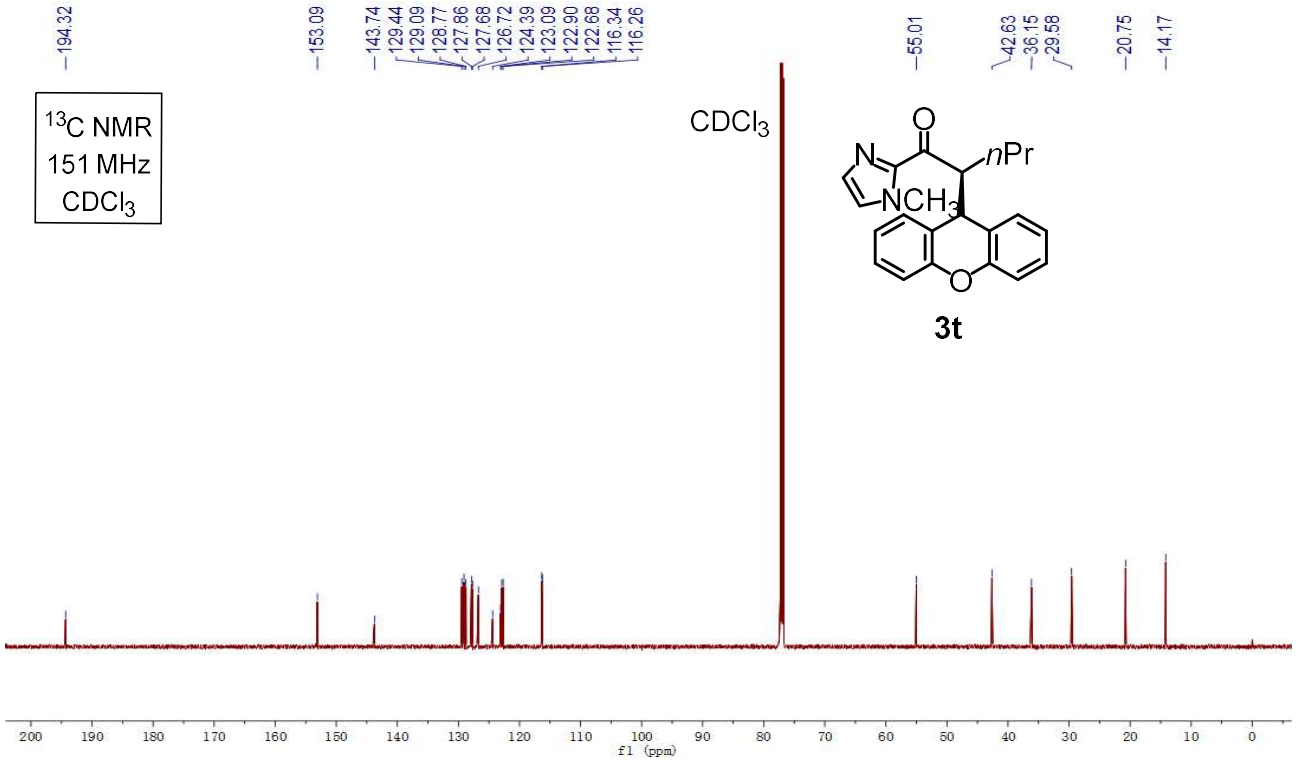
3p

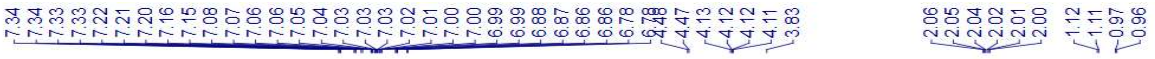

7.53 7.52 7.51 7.23 7.21 7.10 7.09 7.09 7.08 7.07 7.06 7.04 7.03 7.03 7.02 7.02 7.02 7.00 6.99 6.98 6.97 6.95 6.94 6.93 6.90
4.69 4.68 4.58 4.58 4.57 4.57 4.56 4.55 4.55 3.90
1H NMR
500 MHz
CDCl3
O
N
Bn
NCH3
O
3r
CDCl3
H2O
1.00 3.02 4.98 1.97 2.00 1.04 0.95 1.00 0.99 2.96 0.99 0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
192.39
153.04 152.96 143.37 139.76 129.44 129.12 128.93 128.85 128.12 127.99 127.97 126.63 125.65 123.91 123.29 122.79 122.15 116.44 116.30
57.45
42.41 36.04 32.16
13C NMR
151 MHz
CDCl3
CDCl3
O
N
Bn
NCH3
O
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35 7.35 7.34 7.34 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.14 7.13 7.06 7.06 7.06 7.05 7.05 7.03 7.03 7.02 7.02 7.01 7.01 7.00 7.00 7.00 6.98 6.98 6.98 6.95 4.46 4.45 4.10 4.09 4.09 4.08 4.08 4.07 4.06 4.06 3.98 1.65 1.64 1.64 1.63 1.62 1.43 1.43 1.42 0.72 0.71 0.69
1H NMR
500 MHz
CDCl3
CDCl3
H2O
Et
NCH3
O
N
O
3s
1.02 1.04 1.06 3.03 2.87 0.97 1.00 0.99 3.00 1.06 1.03 3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

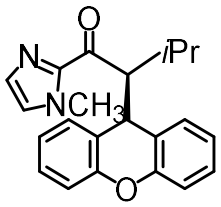

194.18
153.11 153.09 143.82 129.42 129.08 128.79 127.87 127.70 126.73 124.46 123.05 122.94 122.67 116.33 116.26
56.85 42.48 36.15 20.52 11.98
13C NMR
151 MHz
CDCl3
CDCl3
Et
NCH3
O
N
O
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35 7.34 7.33 7.33 7.21 7.20 7.19 7.18 7.16 7.16 7.15 7.13 7.13 7.06 7.06 7.05 7.04 7.02 7.01 7.00 6.99 6.98 6.97 6.94 4.45 4.44 4.18 4.17 4.16 4.16 4.16 4.15 4.14 4.14 3.97 1.66 1.65 1.64 1.64 1.33 1.33 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.14 1.04 1.03 1.02 0.74 0.73 0.71
1H NMR
500 MHz
CDCl3
O
N
nPr
NCH3
O
3t
H2O
CDCl3
1.01 1.01 0.99 3.02 2.93 0.98 1.00 1.02 3.00 1.02 1.02 0.99 1.02 3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

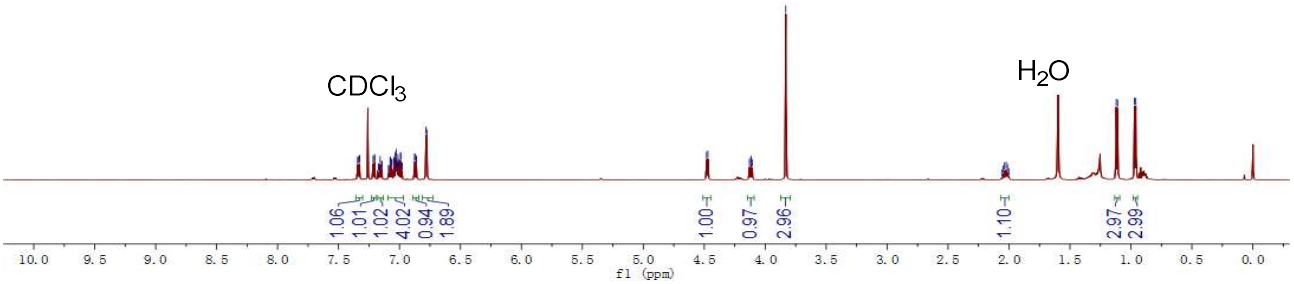

194.32 153.09 143.74 129.44 129.09 128.77 127.86 127.68 126.72 124.39 123.09 122.90 122.68 116.34 116.26 55.01 42.63 36.15 29.58 20.75 14.17
13C NMR
151 MHz
CDCl3
CDCl3
O
N
nPr
NCH3
O
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

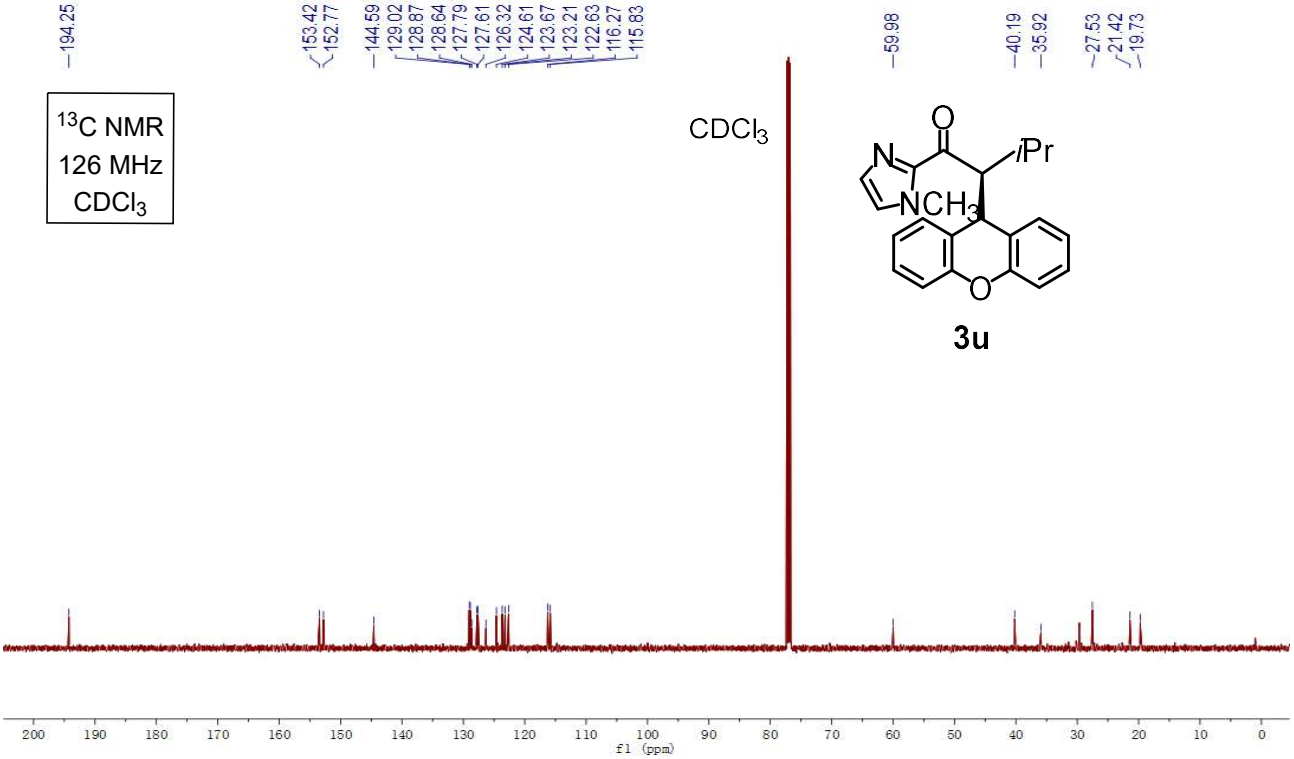


^{1}H NMR
500 MHz
$CDCl_3$



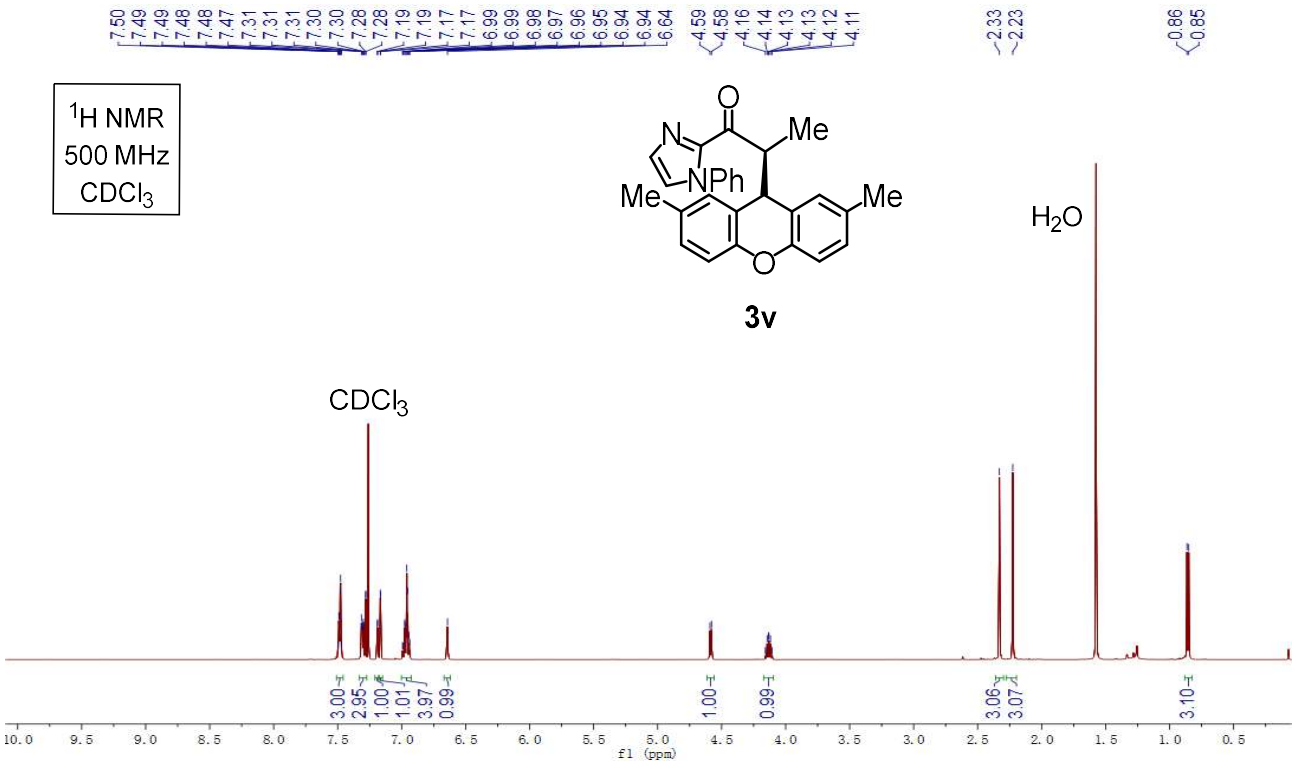
3u





^{13}C NMR
126 MHz
$CDCl_3$

3u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7.48
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7.31
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7.28
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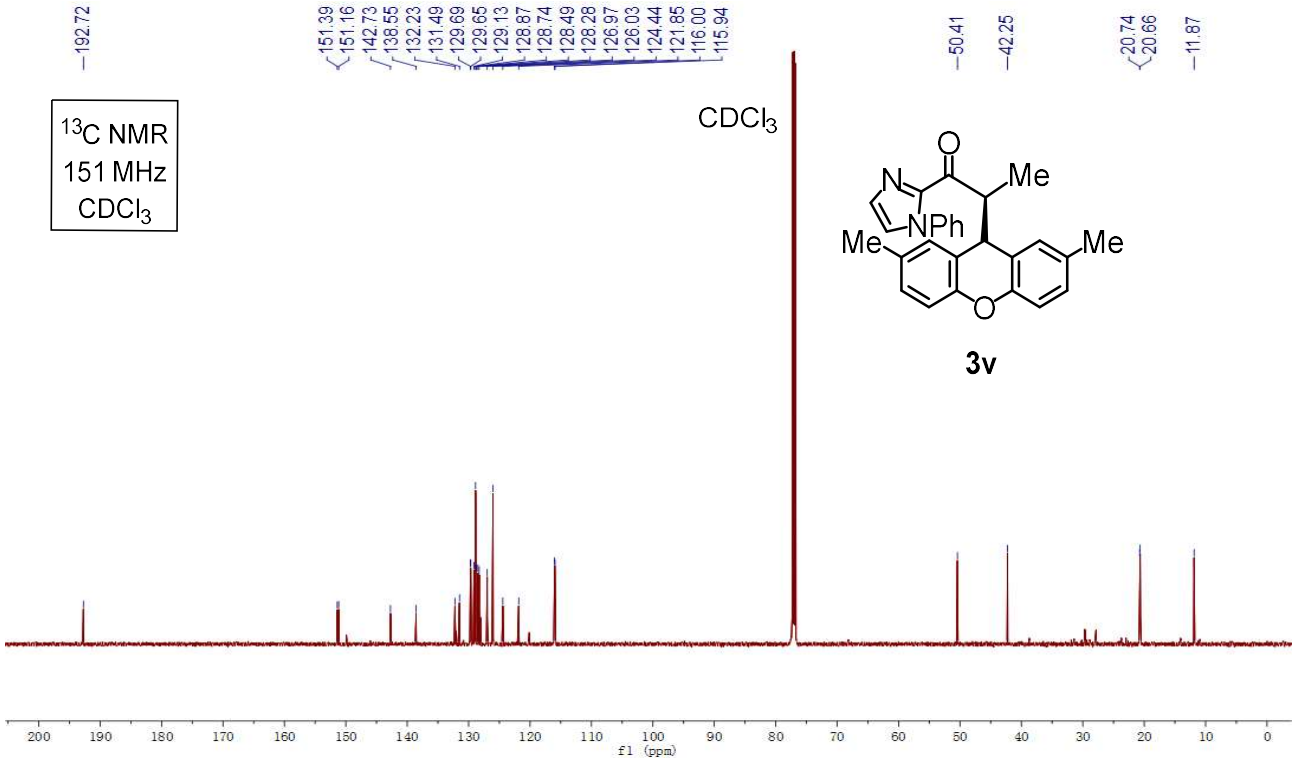
7.19
7.17
7.17
6.99
6.99
6.98
6.97
6.96
6.95
6.94
6.94
6.64
4.59
4.58
4.16
4.14
4.13
4.13
4.12
4.11
2.33
2.23
0.86
0.85
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
Me
Me
O
3v
H2O
CDCl3
3.00
2.95
1.00
1.01
3.97
0.99
1.00
0.99
3.06
3.07
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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151.39
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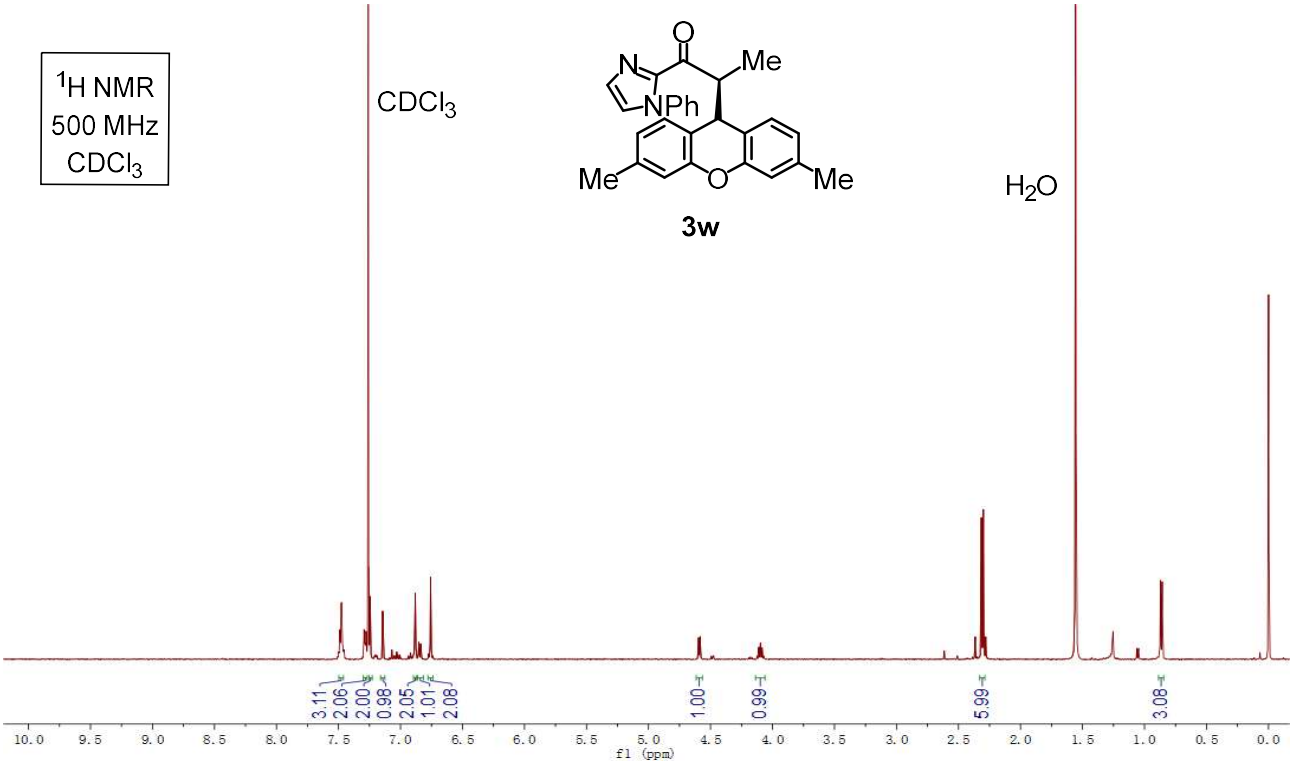
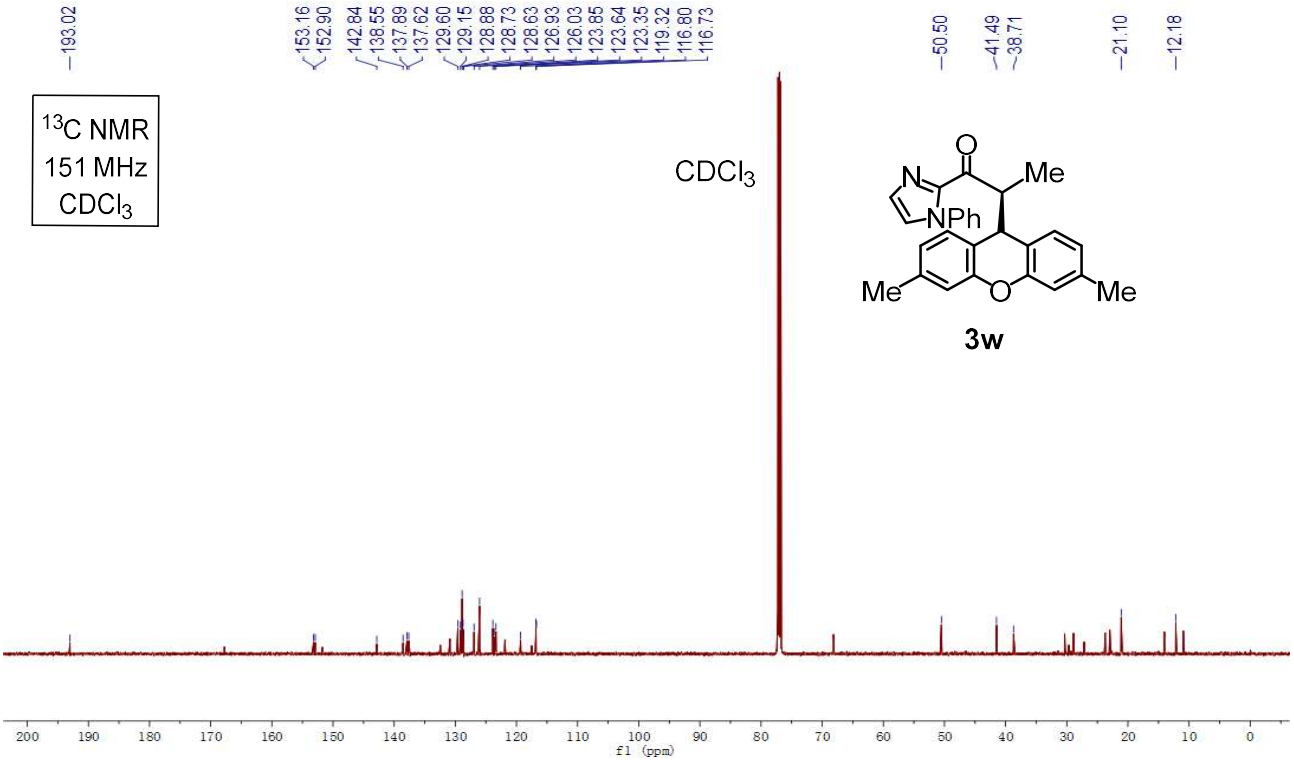
142.73
138.55
132.23
131.49
129.69
129.65
129.13
128.87
128.74
128.49
128.28
126.97
126.03
124.44
121.85
116.00
115.94
50.41
42.25
20.74
20.66
11.87
13C NMR
151 MHz
CDCl3
CDCl3
O
N
Me
NPh
Me
Me
O
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR
500 MHz
CDCl3
CDCl3
Me
N
NPh
O
Me
Me
O
H2O
3w
3.11
2.06
2.00
0.98
2.05
1.01
2.08
1.00
0.99
5.99
3.08
f1 (ppm)


193.02
153.16
152.90
142.84
138.55
137.89
137.62
129.60
129.15
128.88
128.73
128.63
126.93
126.03
123.85
123.64
123.35
119.32
116.80
116.73
50.50
41.49
38.71
21.10
12.18
13C NMR
151 MHz
CDCl3
CDCl3
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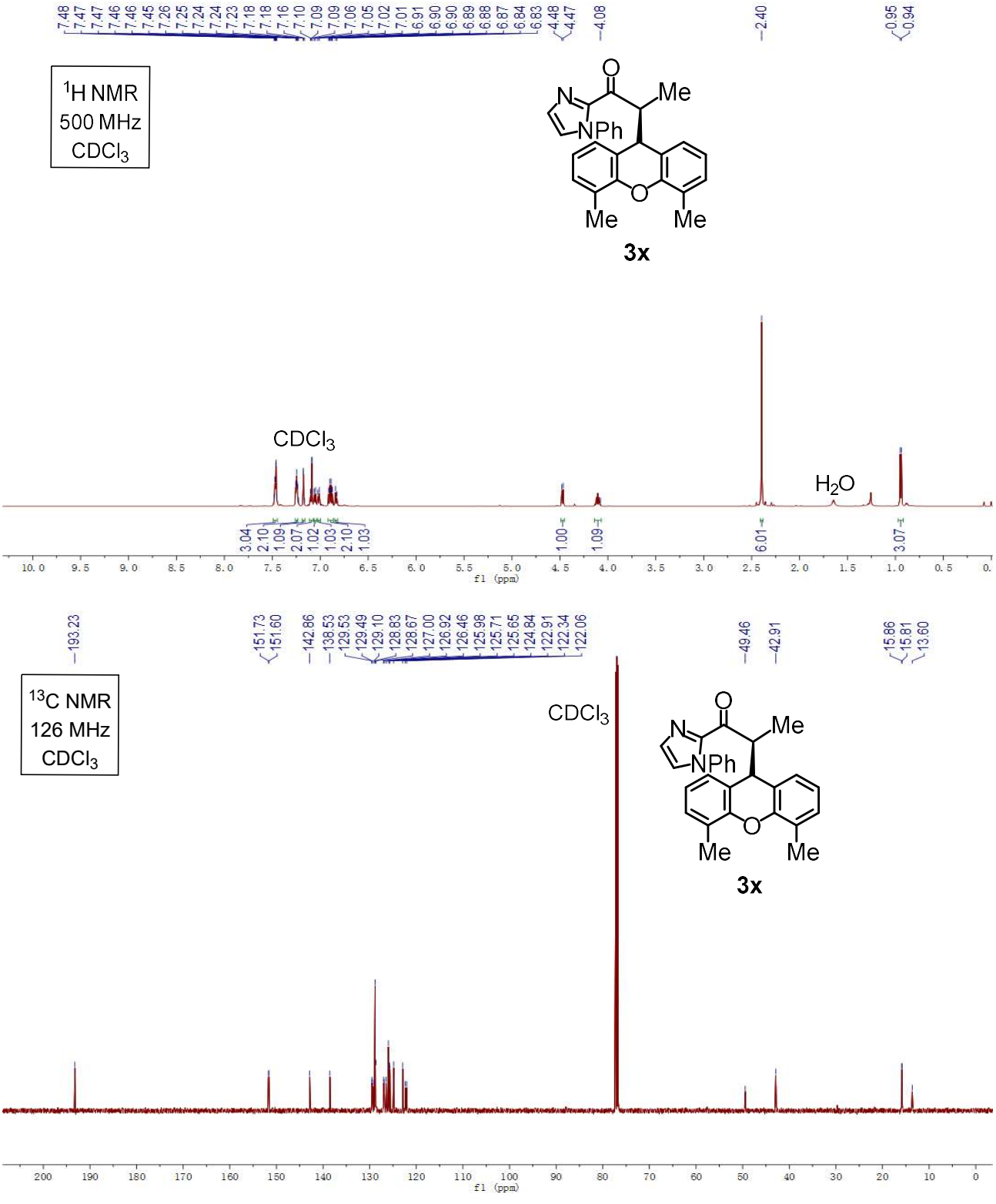
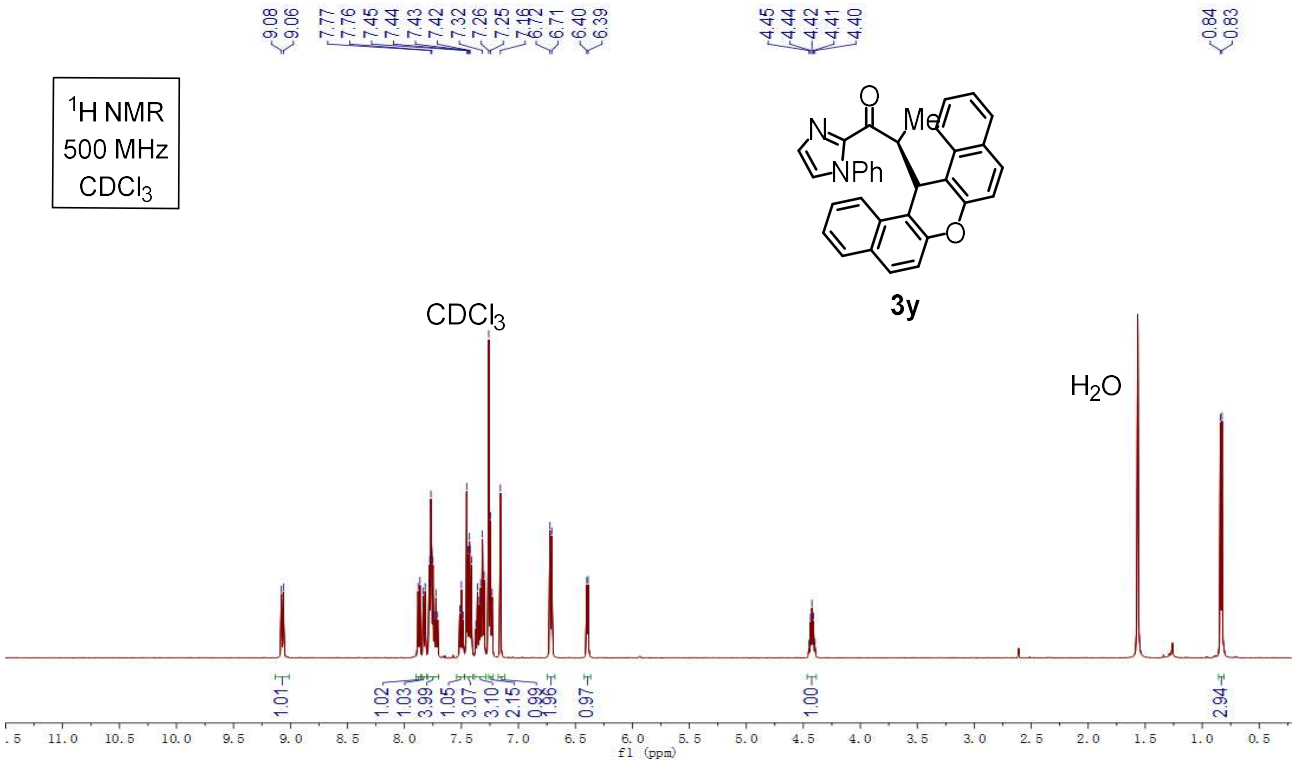
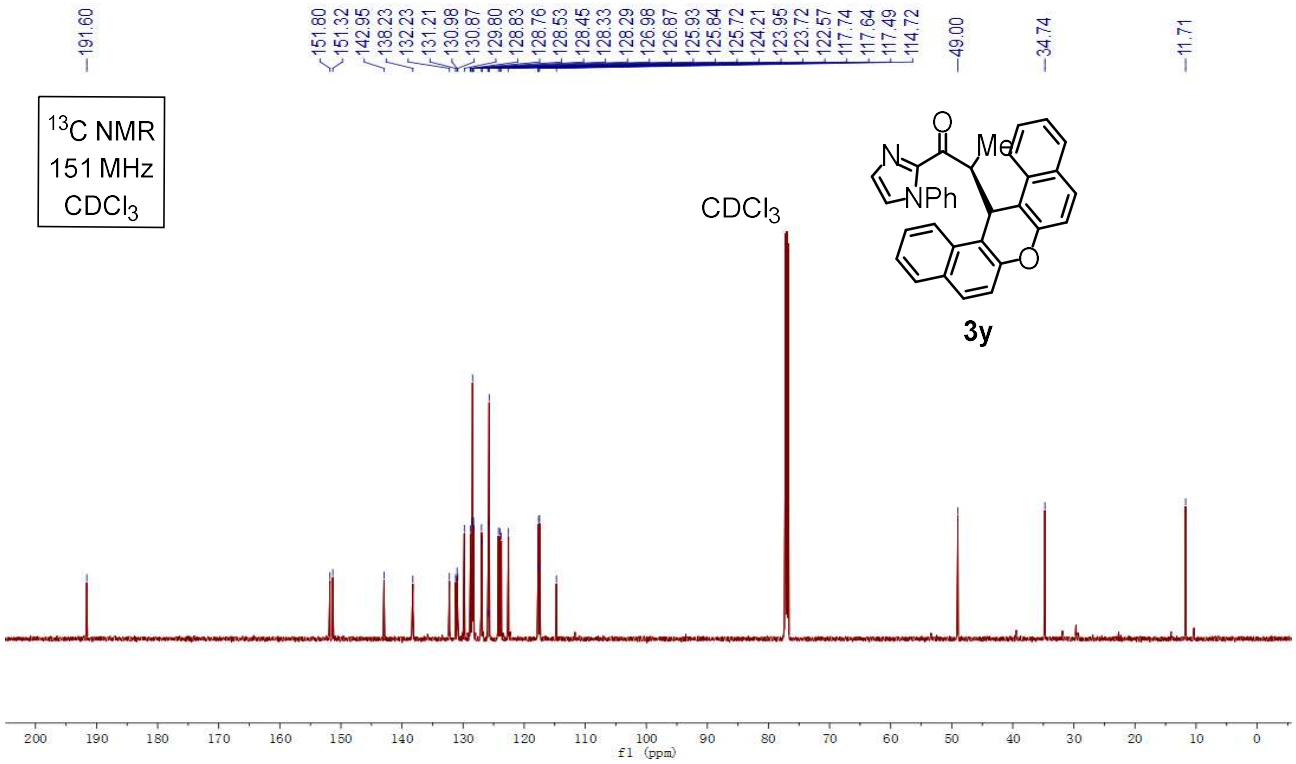
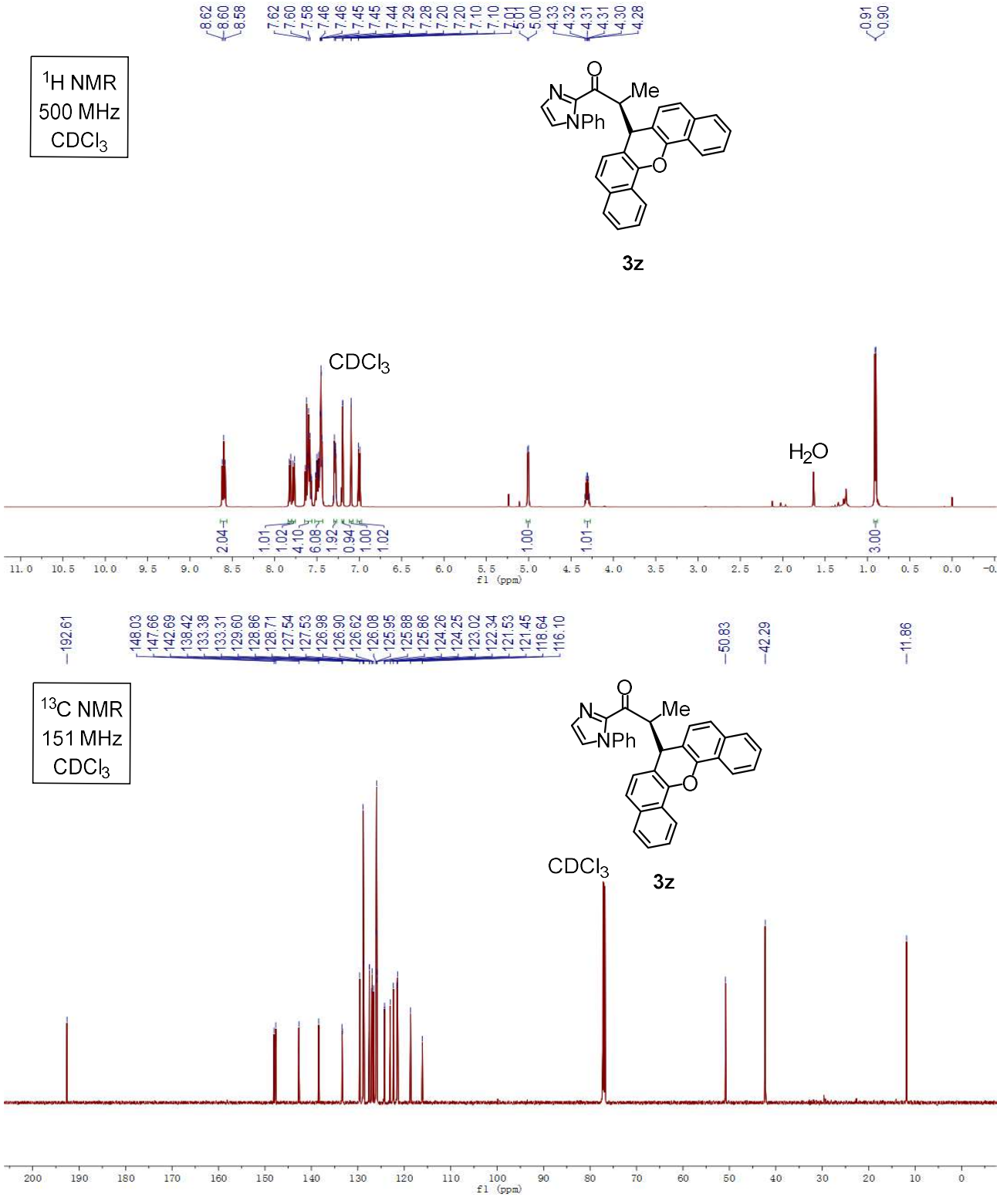
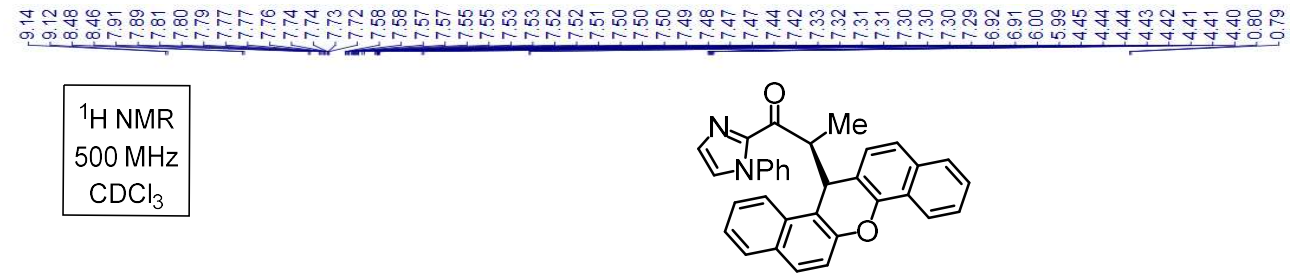
N
NPh
O
Me
Me
O
3w
f1 (ppm)


7.48
7.47
7.47
7.46
7.46
7.45
7.26
7.25
7.24
7.24
7.23
7.18
7.18
7.16
7.10
7.09
7.09
7.06
7.05
7.02
7.01
6.91
6.90
6.89
6.88
6.87
6.84
6.83
4.48
4.47
4.08
2.40
0.95
0.94
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
O
Me
Me
3x
CDCl3
H2O
3.04
2.10
1.09
2.07
1.02
1.03
2.10
1.03
1.00
1.09
6.01
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
193.23
151.73
151.60
142.86
138.53
129.53
129.49
129.10
128.83
128.67
127.00
126.92
126.46
125.98
125.71
125.65
124.84
122.91
122.34
122.06
49.46
42.91
15.86
15.81
13.60
13C NMR
126 MHz
CDCl3
CDCl3
O
N
Me
NPh
O
Me
Me
3x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.08
9.06
7.77
7.76
7.45
7.44
7.43
7.42
7.32
7.26
7.25
7.16
6.72
6.71
6.40
6.39
4.45
4.44
4.42
4.41
4.40
0.84
0.83
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
O
3y
CDCl3
H2O
1.01
1.02
1.03
3.99
1.05
3.07
3.10
2.15
0.99
1.96
0.97
1.00
2.94
f1 (ppm)

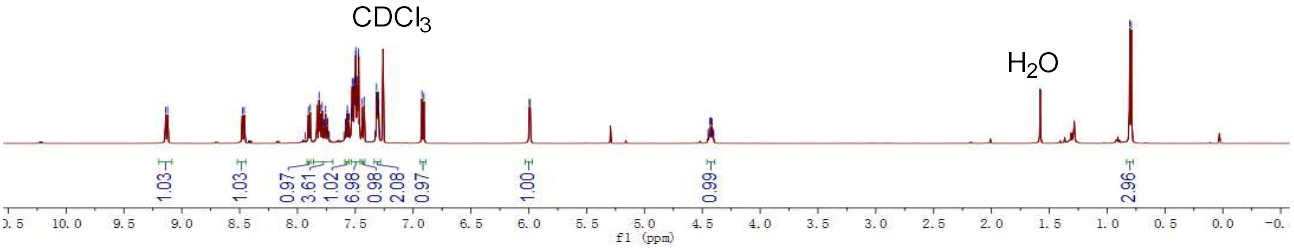

191.60
151.80
151.32
142.95
138.23
132.23
131.21
130.98
130.87
129.80
128.83
128.76
128.53
128.45
128.33
128.29
126.98
126.87
125.93
125.84
125.72
124.21
123.95
123.72
122.57
117.74
117.64
117.49
114.72
49.00
34.74
11.71
13C NMR
151 MHz
CDCl3
O
N
Me
NPh
O
3y
CDCl3
f1 (ppm)

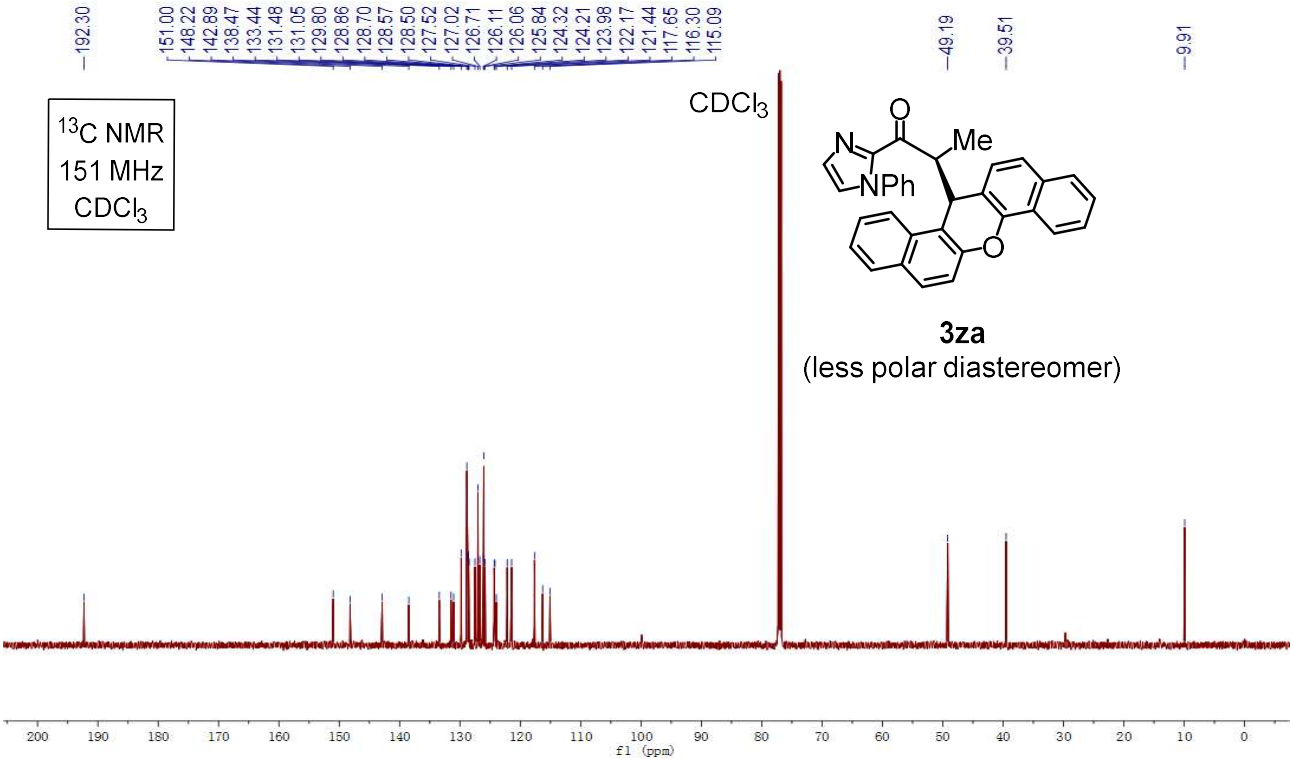

1H NMR
500 MHz
CDCl3
Me
NPh
3z
CDCl3
H2O
f1 (ppm)
13C NMR
151 MHz
CDCl3
Me
NPh
CDCl3
3z
f1 (ppm)



^{1}H NMR
500 MHz
$CDCl_3$

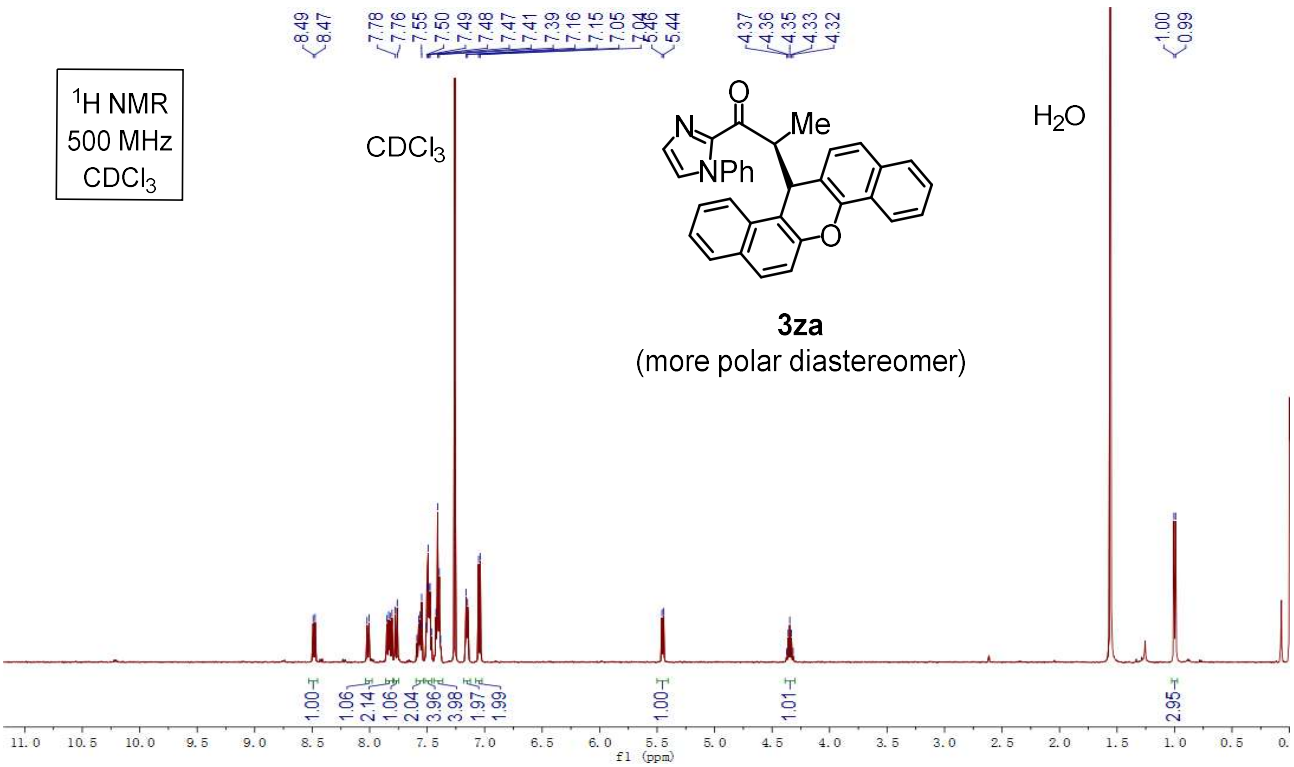
3za
(less polar diastereomer)

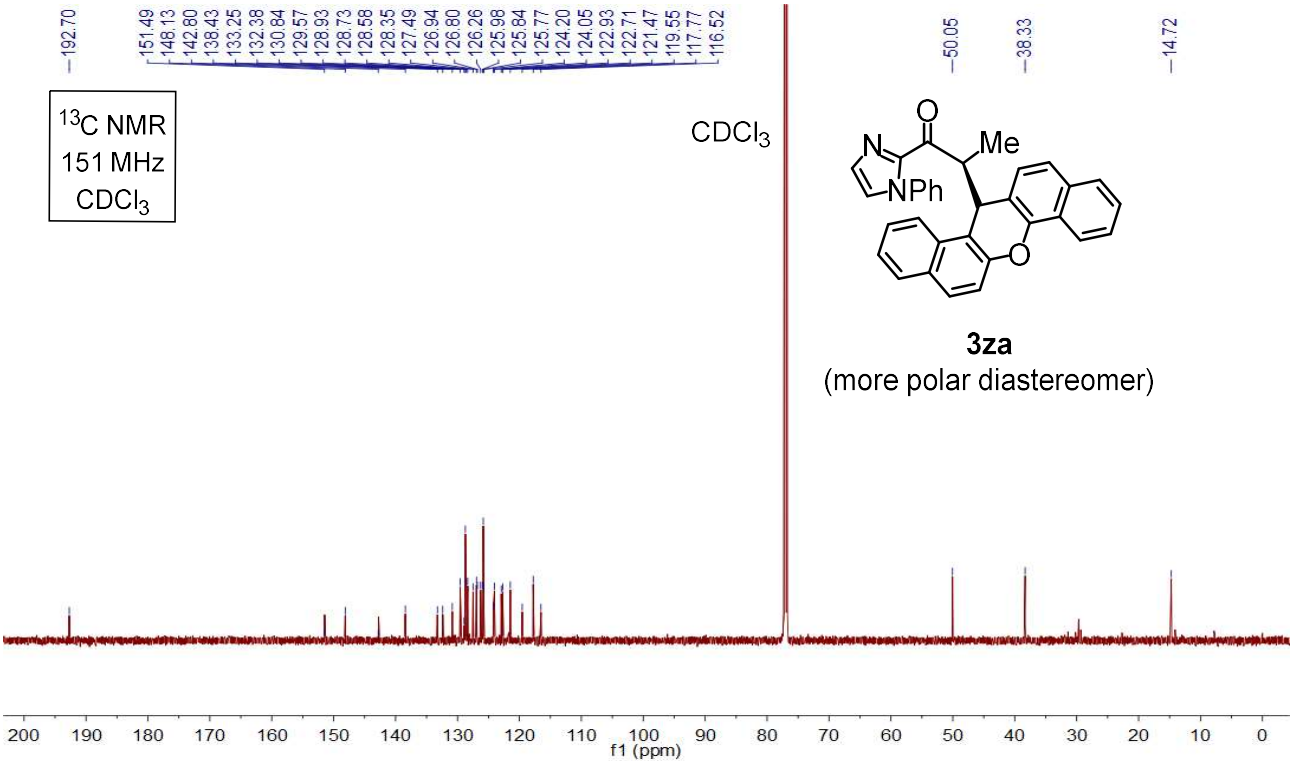


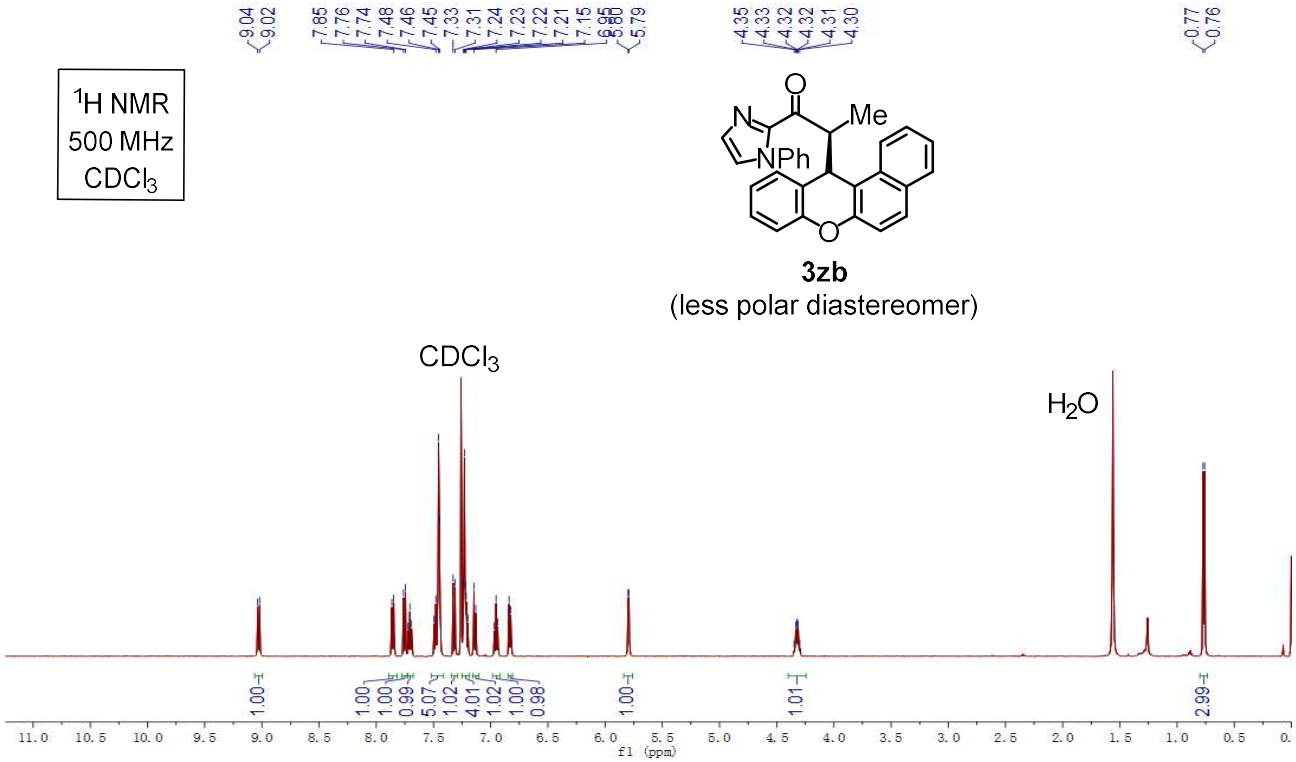


^{13}C NMR
151 MHz
$CDCl_3$

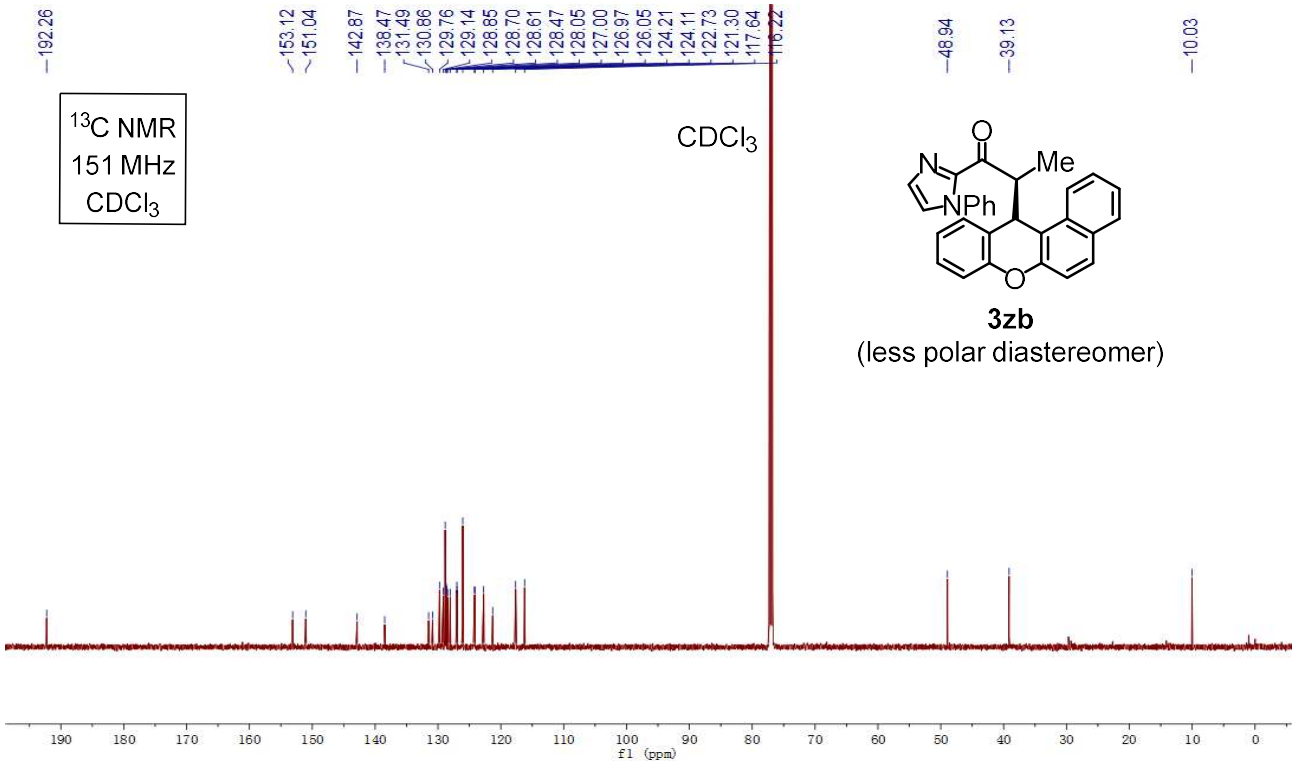
3za
(less polar diastereomer)


8.49
8.47
7.78
7.76
7.55
7.50
7.49
7.48
7.47
7.41
7.39
7.16
7.15
7.05
7.04
5.46
5.44
4.37
4.36
4.35
4.33
4.32
1.00
0.99
1H NMR
500 MHz
CDCl3
CDCl3
H2O
N
O
Me
NPh
O
3za
(more polar diastereomer)
1.00
1.06
2.14
1.06
2.04
3.96
3.98
1.97
1.99
1.00
1.01
2.95
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

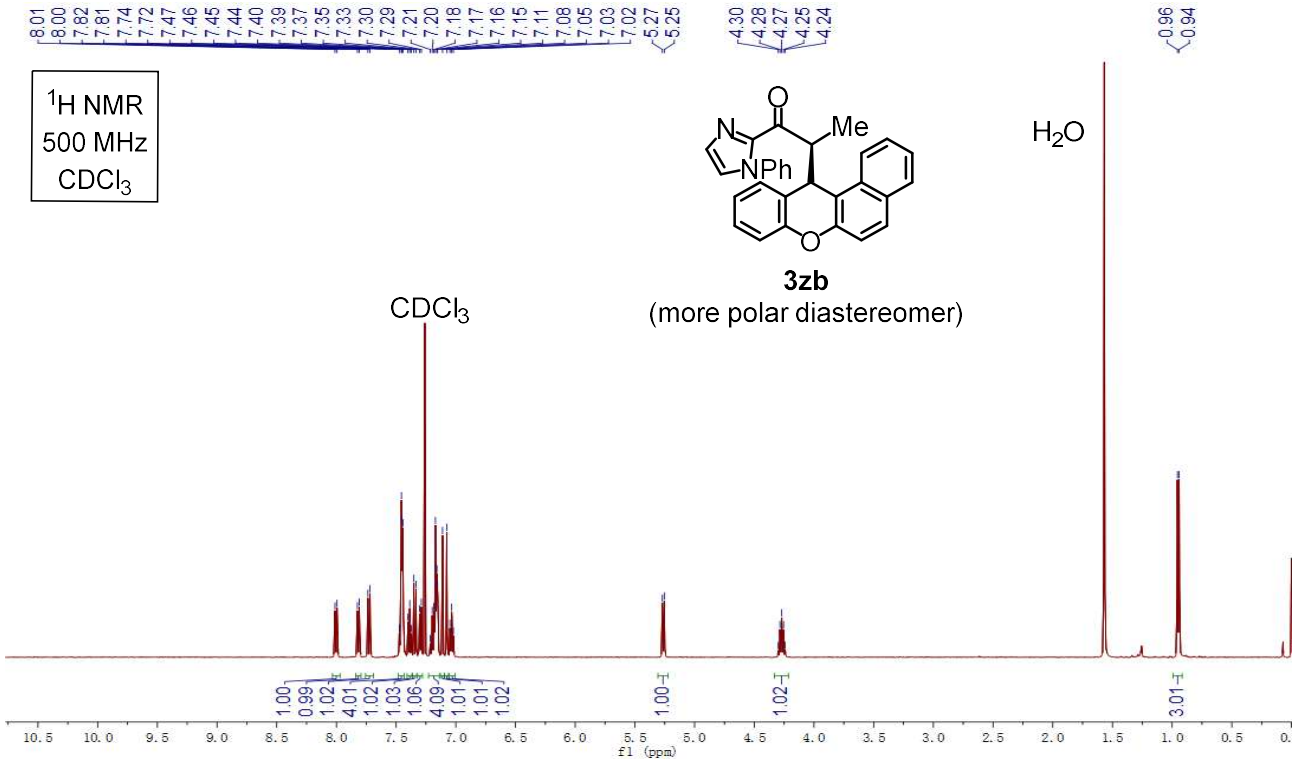

192.70
151.49
148.13
142.80
138.43
133.25
132.38
130.84
129.57
128.93
128.73
128.58
128.35
127.49
126.94
126.80
126.26
125.98
125.84
125.77
124.20
124.05
122.93
122.71
121.47
119.55
117.77
116.52
50.05
38.33
14.72
13C NMR
151 MHz
CDCl3
CDCl3
N
O
Me
NPh
O
3za
(more polar diastereomer)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

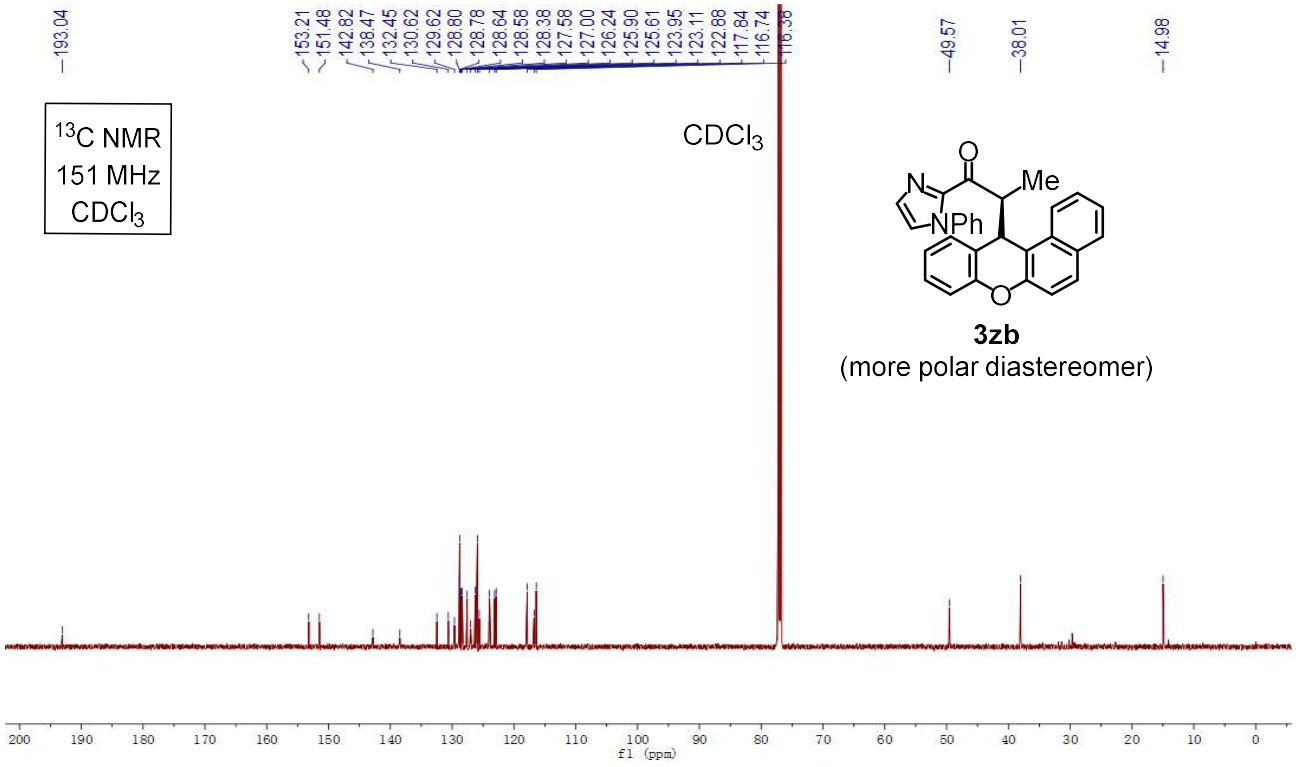


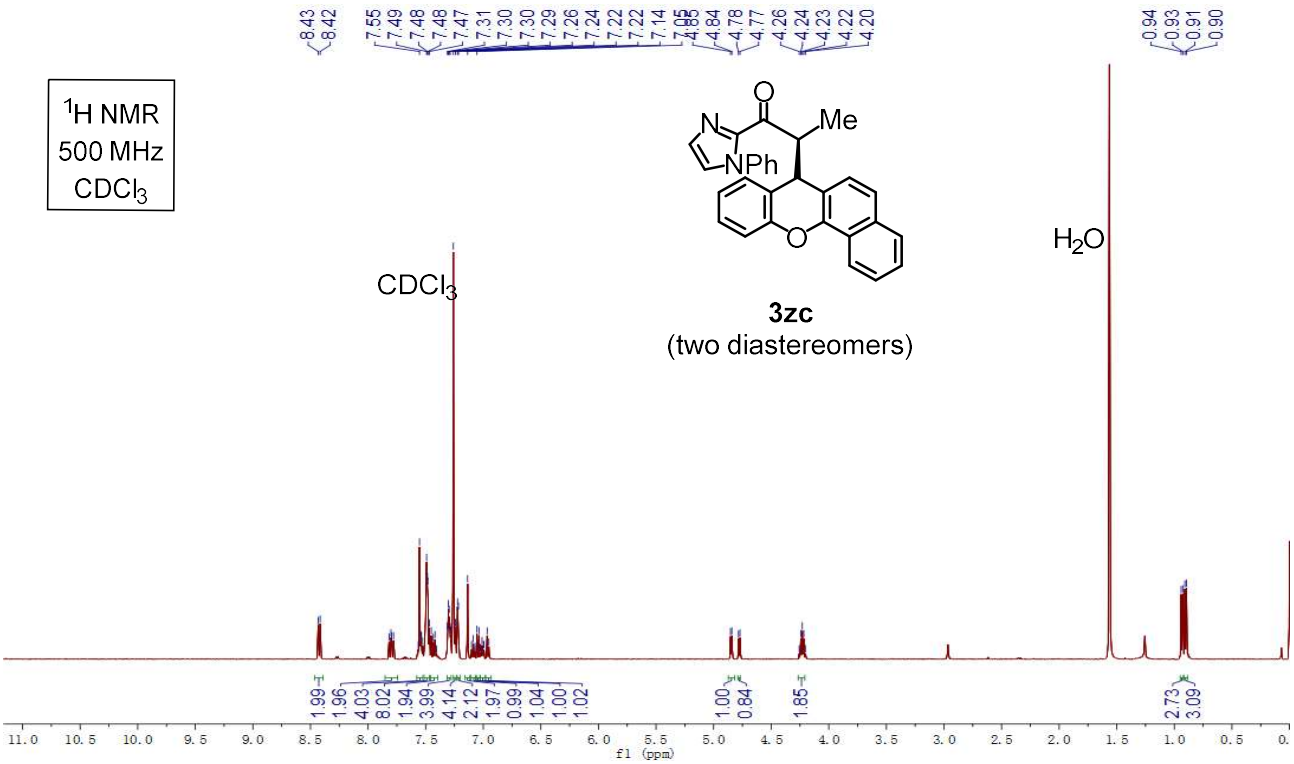
3zb
(less polar diastereomer)

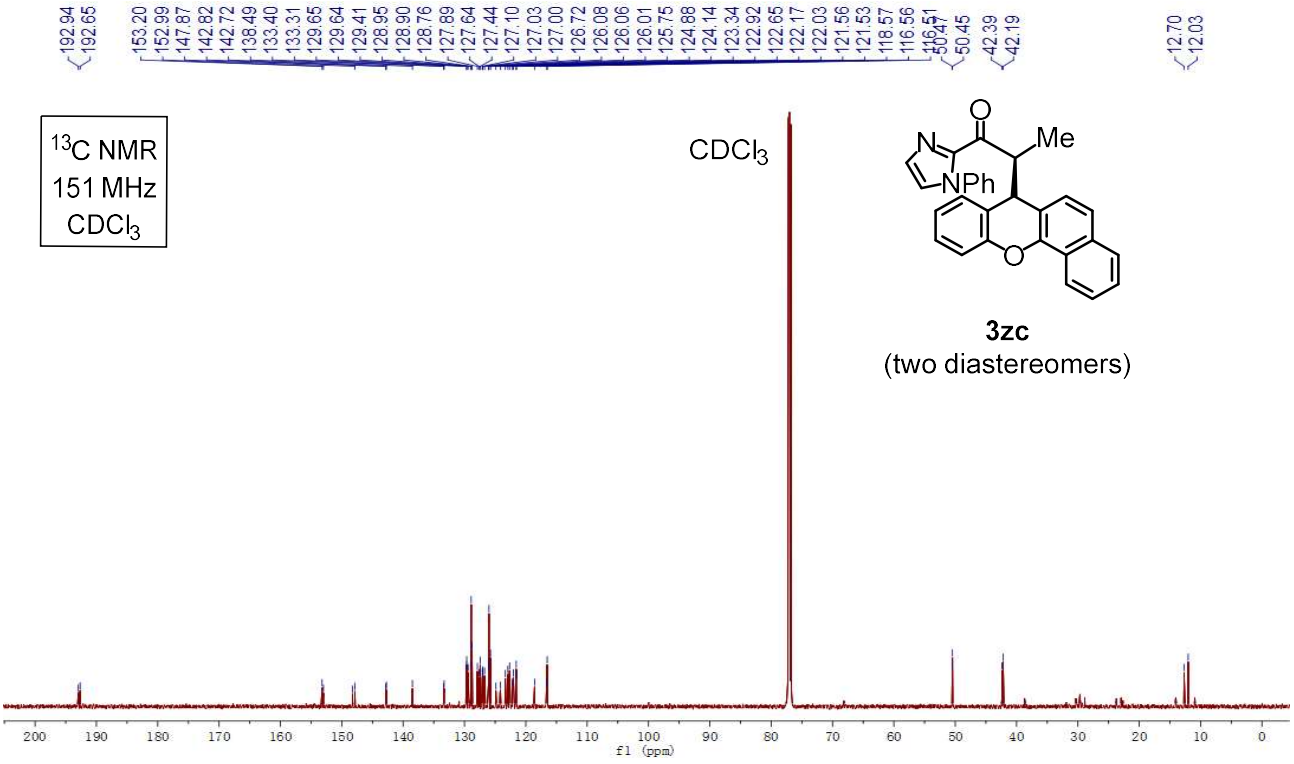


3zb
(less polar diastereomer)

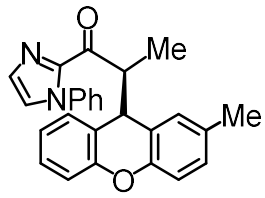

8.01
8.00
7.82
7.81
7.74
7.72
7.47
7.46
7.45
7.44
7.40
7.39
7.37
7.35
7.33
7.30
7.29
7.21
7.20
7.18
7.17
7.16
7.15
7.11
7.08
7.05
7.03
7.02
5.27
5.25
4.30
4.28
4.27
4.25
4.24
0.96
0.94
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
O
H2O
3zb
(more polar diastereomer)
CDCl3
1.00
0.99
1.02
4.01
1.02
1.03
1.06
4.09
1.01
1.01
1.02
1.00
1.02
3.01
f1 (ppm)


193.04
153.21
151.48
142.82
138.47
132.45
130.62
129.62
128.80
128.78
128.64
128.58
128.38
127.58
127.00
126.24
125.90
125.61
123.95
123.11
122.88
117.84
116.74
116.38
49.57
38.01
14.98
13C NMR
151 MHz
CDCl3
CDCl3
O
N
Me
NPh
O
3zb
(more polar diastereomer)
f1 (ppm)

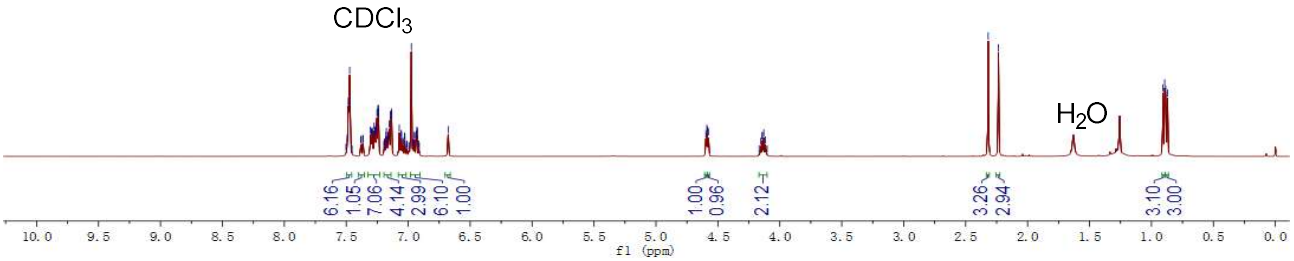

8.43
8.42
7.55
7.49
7.48
7.48
7.47
7.31
7.30
7.30
7.29
7.26
7.24
7.22
7.22
7.14
4.85
4.84
4.78
4.77
4.26
4.24
4.23
4.22
4.20
0.94
0.93
0.91
0.90
1H NMR
500 MHz
CDCl3
CDCl3
H2O
Me
N
NPh
O
3zc
(two diastereomers)
1.99
1.96
4.03
8.02
1.94
3.99
4.14
2.12
1.97
0.99
1.04
1.00
1.02
1.00
0.84
1.85
2.73
3.09
f1 (ppm)

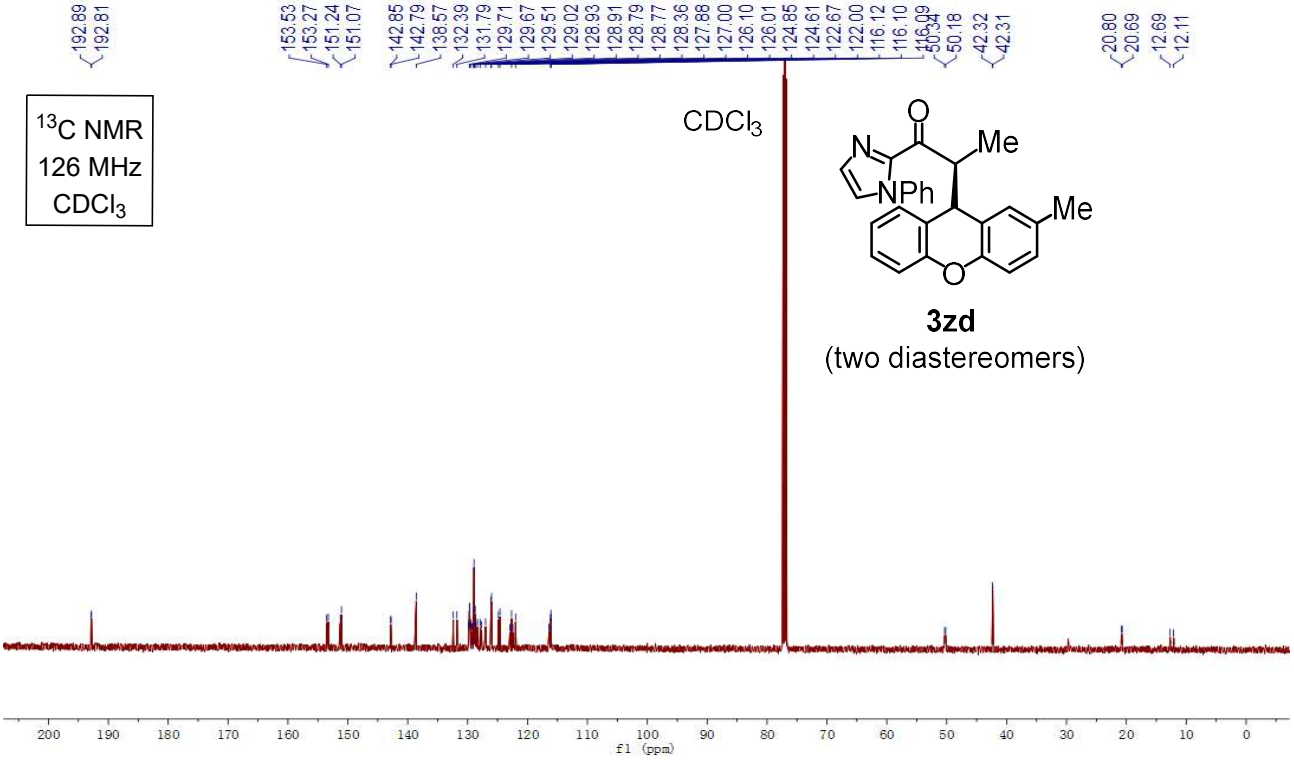

192.94
192.65
153.20
152.99
147.87
142.82
142.72
138.49
133.40
133.31
129.65
129.64
129.41
128.95
128.90
128.76
127.89
127.64
127.44
127.10
127.03
127.00
126.72
126.08
126.06
126.01
125.75
124.88
124.14
123.34
122.92
122.65
122.17
122.03
121.56
121.53
118.57
116.56
116.51
50.47
50.45
42.39
42.19
12.70
12.03
13C NMR
151 MHz
CDCl3
CDCl3
Me
N
NPh
O
3zc
(two diastereomers)
f1 (ppm)

^{1}H NMR
500 MHz
$CDCl_3$



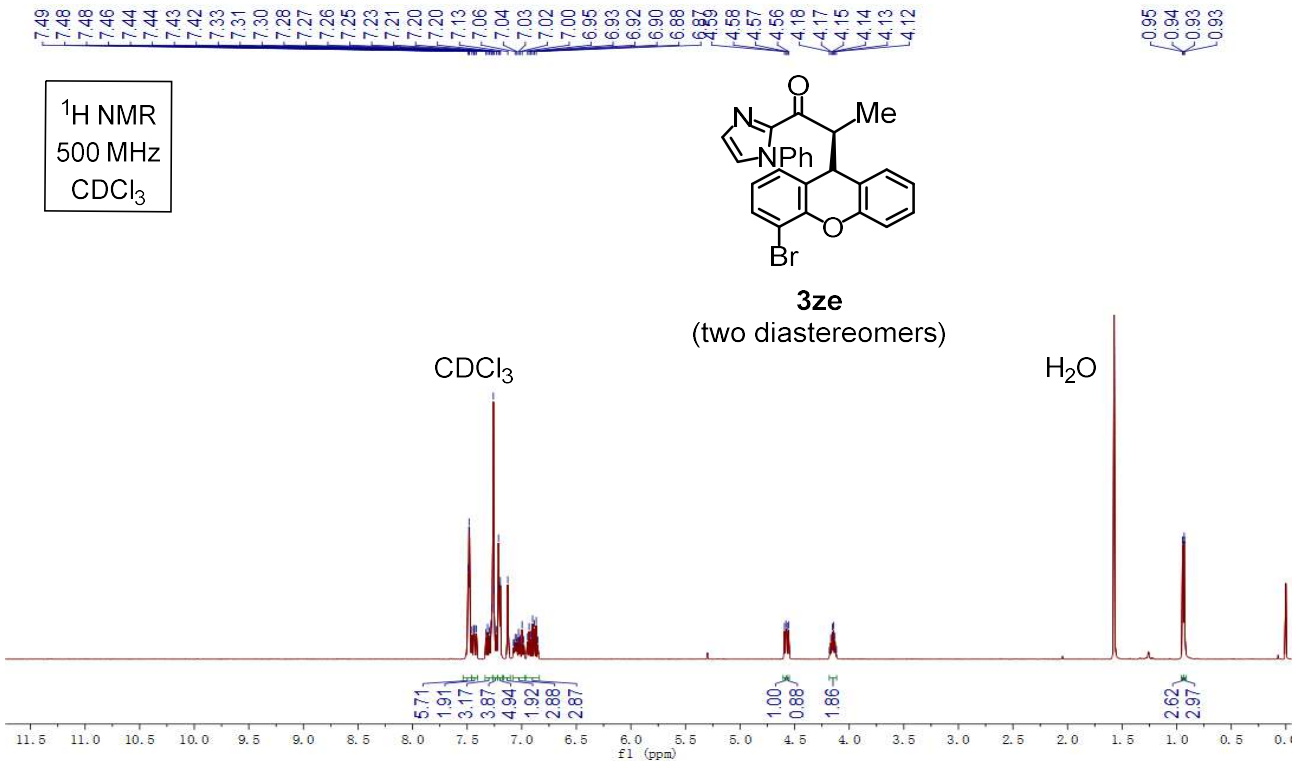
3zd
(two diastereomers)

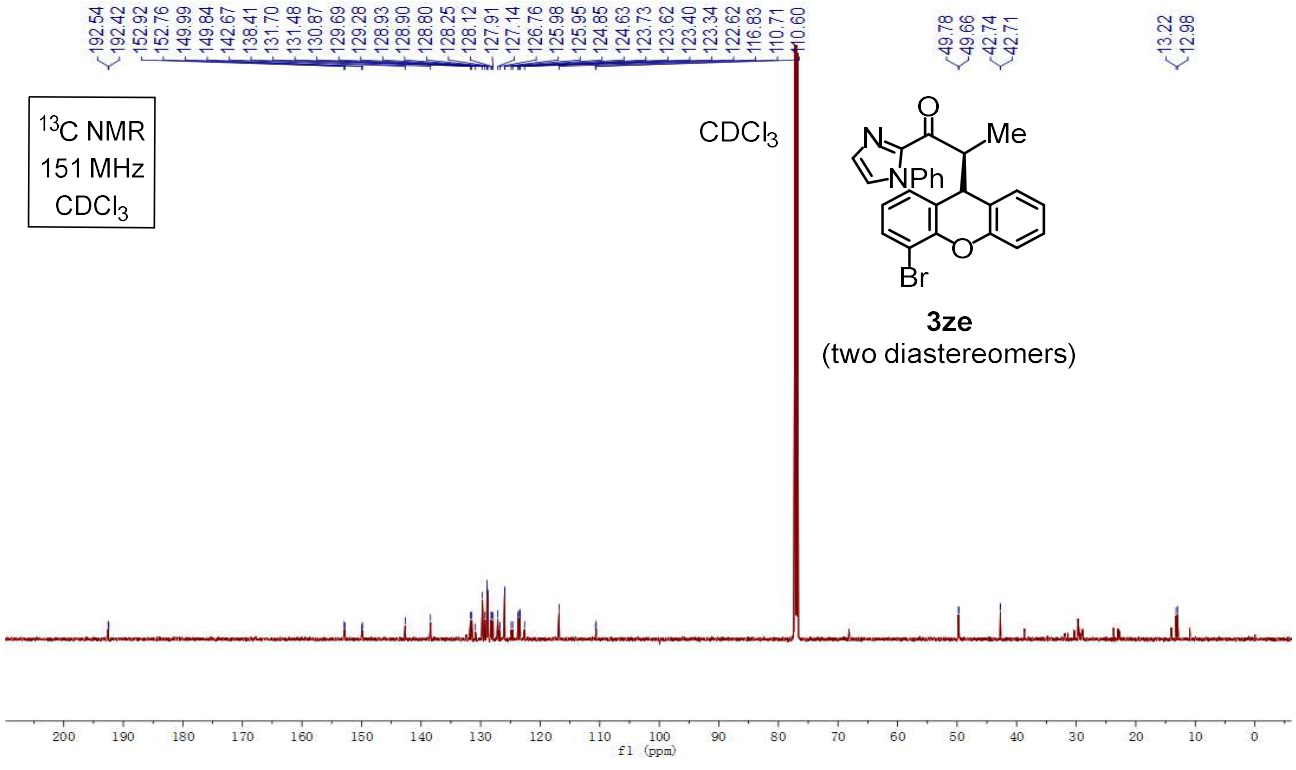


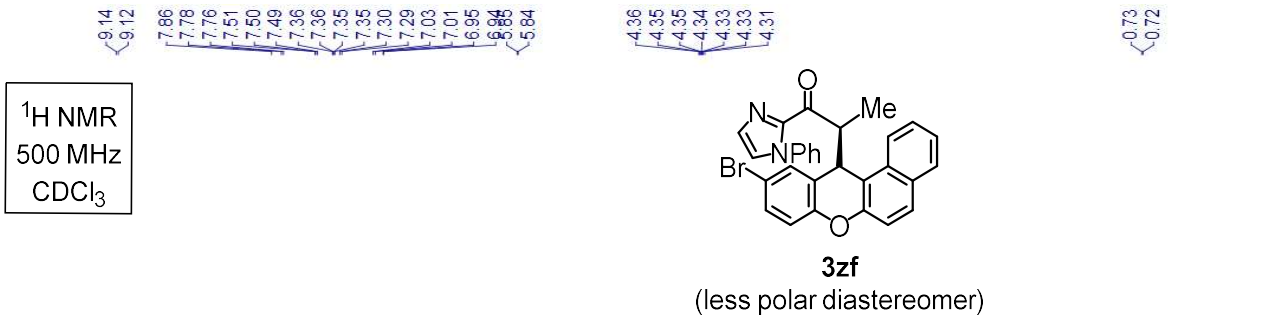


^{13}C NMR
126 MHz
$CDCl_3$

3zd
(two diastereomers)

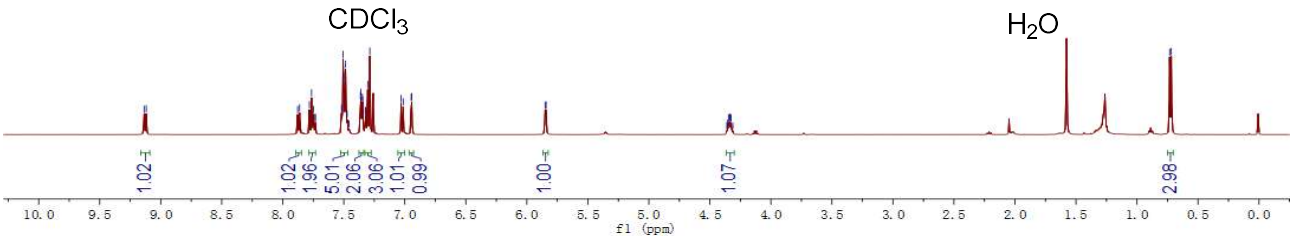

7.49 7.48 7.48 7.46 7.44 7.44 7.43 7.42 7.33 7.31 7.30 7.28 7.27 7.26 7.25 7.23 7.21 7.20 7.20 7.13 7.06 7.04 7.03 7.02 7.00 6.95 6.93 6.92 6.90 6.88 4.58 4.57 4.56 4.18 4.17 4.15 4.14 4.13 4.12
0.95 0.94 0.93 0.93
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
O
Br
3ze
(two diastereomers)
CDCl3
H2O
5.71 1.91 3.17 3.87 4.94 1.92 2.88 2.87
1.00 0.88 1.86
2.62 2.97
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

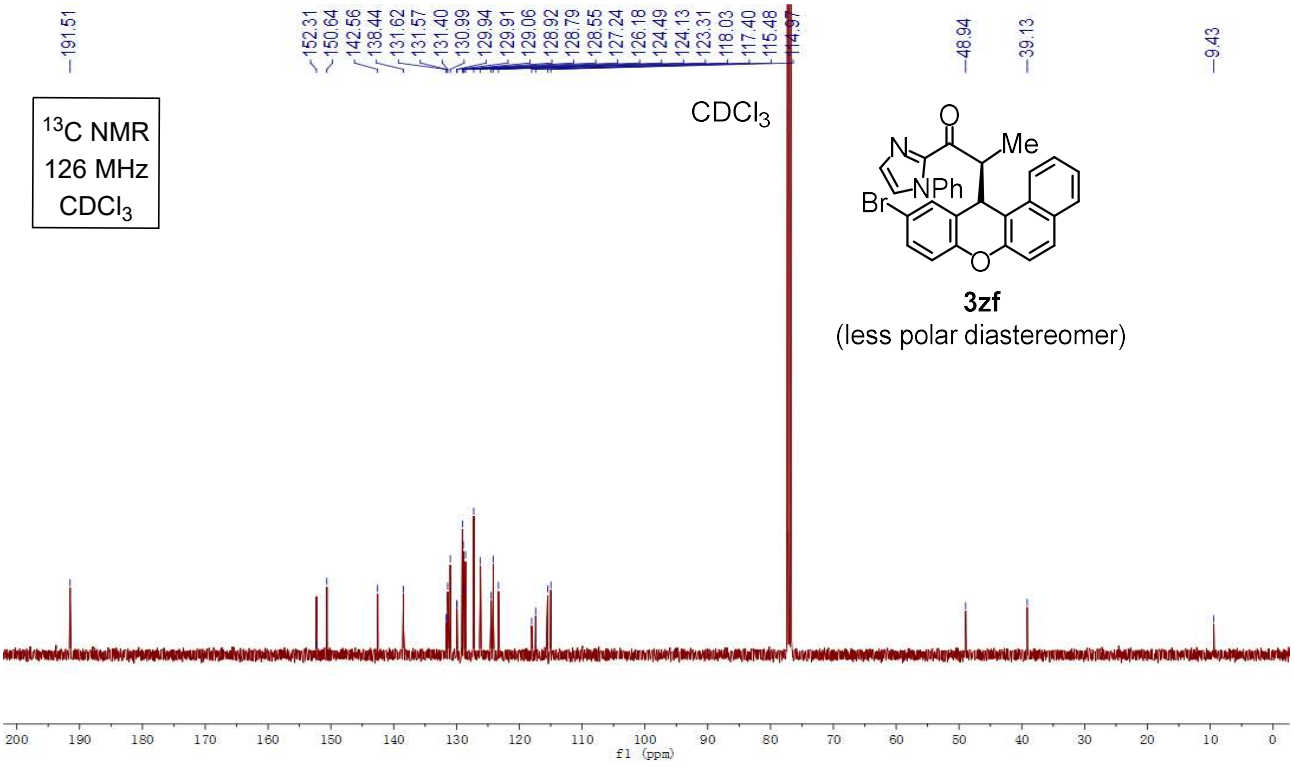

192.54 192.42 152.92 152.76 149.99 149.84 142.67 138.41 131.70 131.48 130.87 129.69 129.28 128.93 128.90 128.80 128.25 128.12 127.91 127.14 126.76 125.98 125.95 124.85 124.63 123.73 123.62 123.40 123.34 122.62 116.83 110.71 110.60
49.78 49.66 42.74 42.71
13.22 12.98
13C NMR
151 MHz
CDCl3
CDCl3
O
N
Me
NPh
O
Br
3ze
(two diastereomers)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H NMR
500 MHz
$CDCl_3$

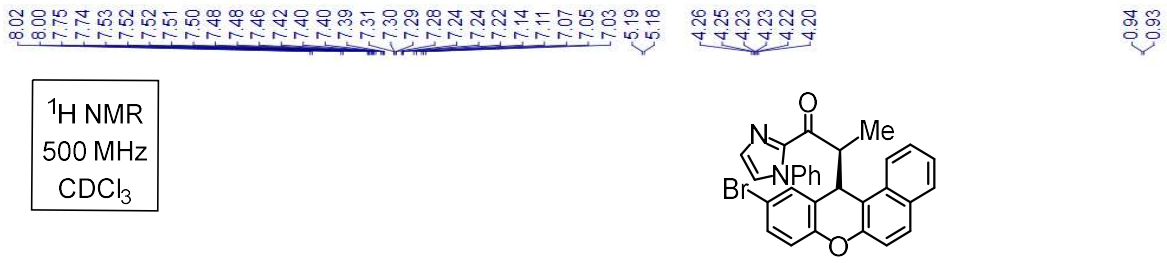
3zf
(less polar diastereomer)





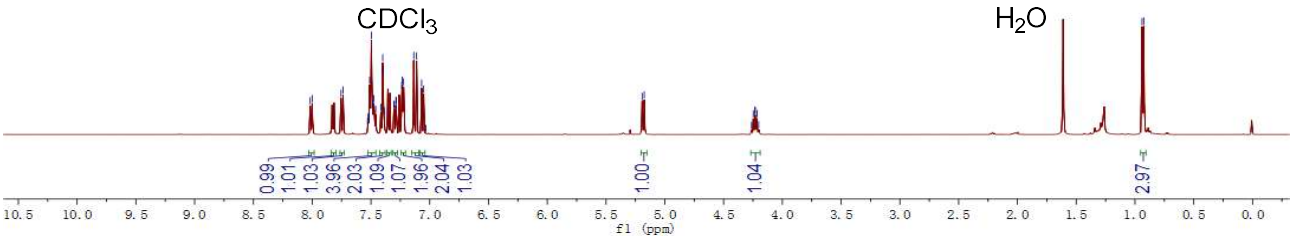
^{13}C NMR
126 MHz
$CDCl_3$

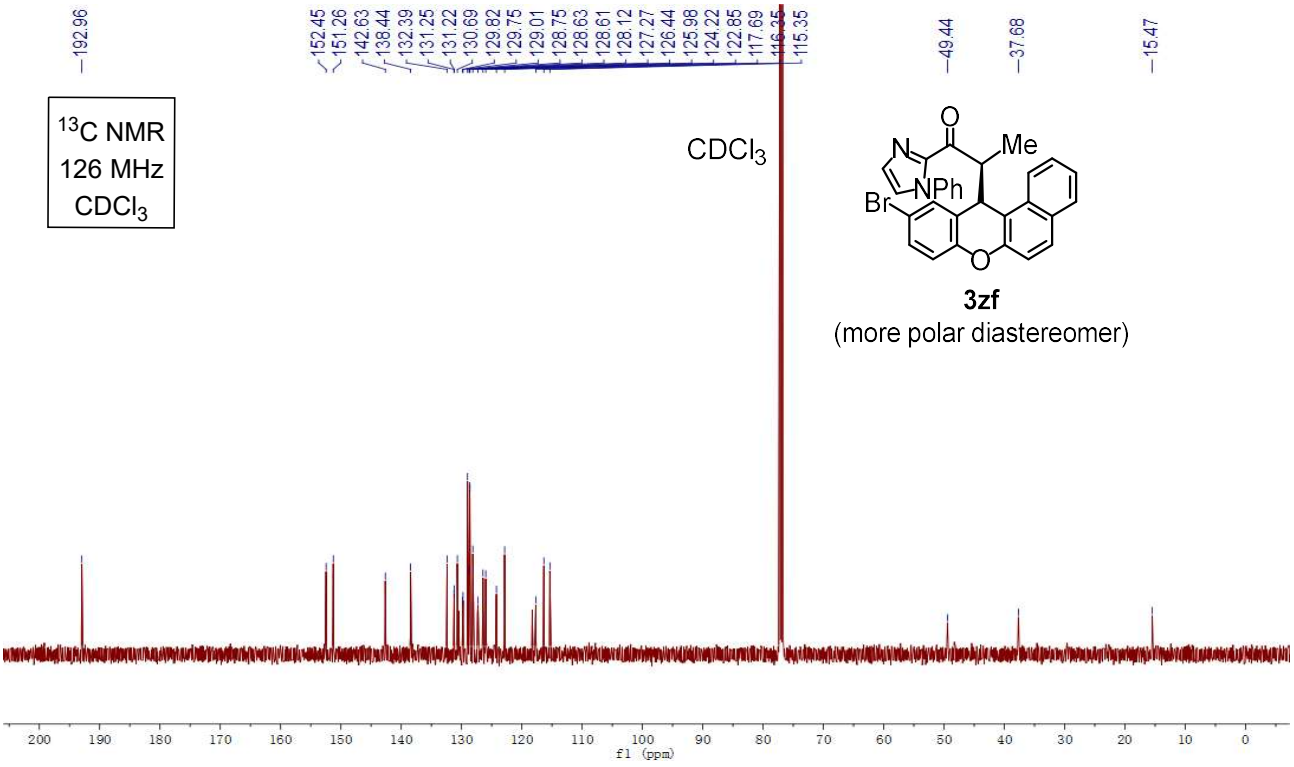
3zf
(less polar diastereomer)



^{1}H NMR
500 MHz
$CDCl_3$

3zf
(more polar diastereomer)

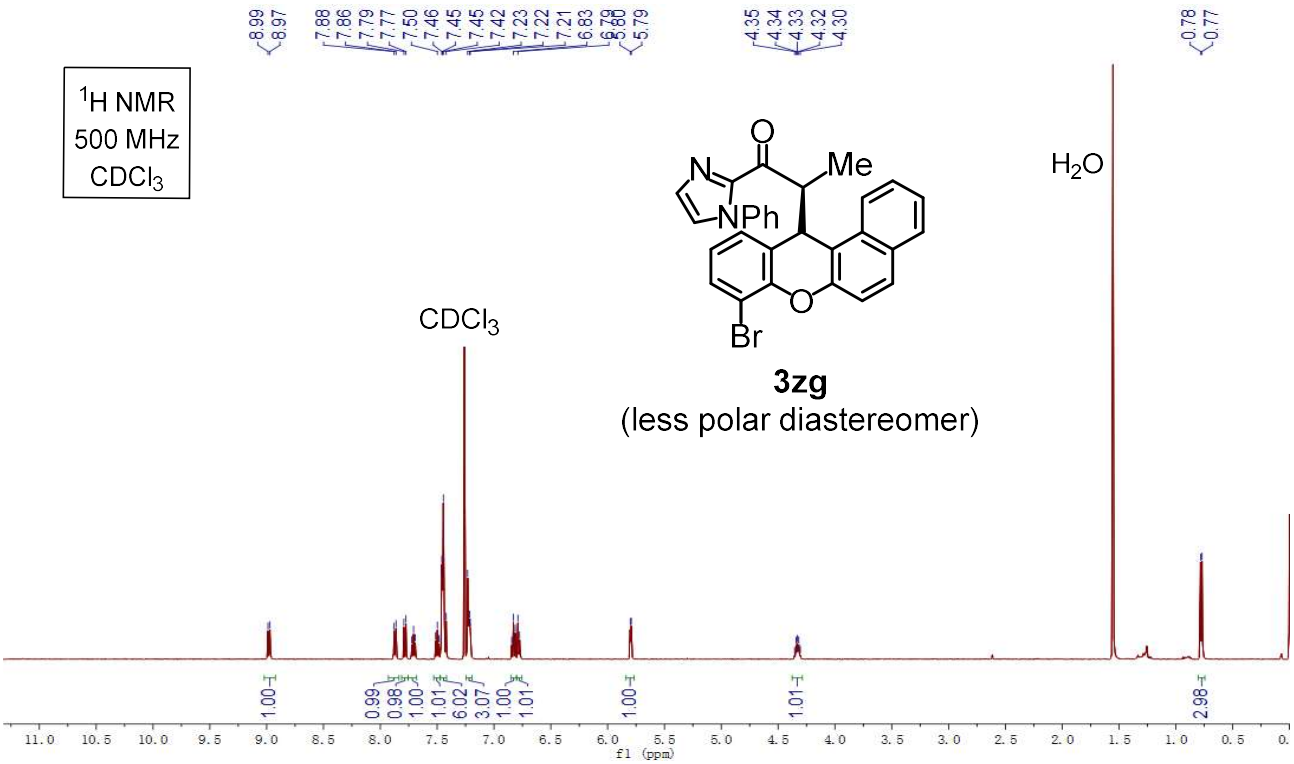


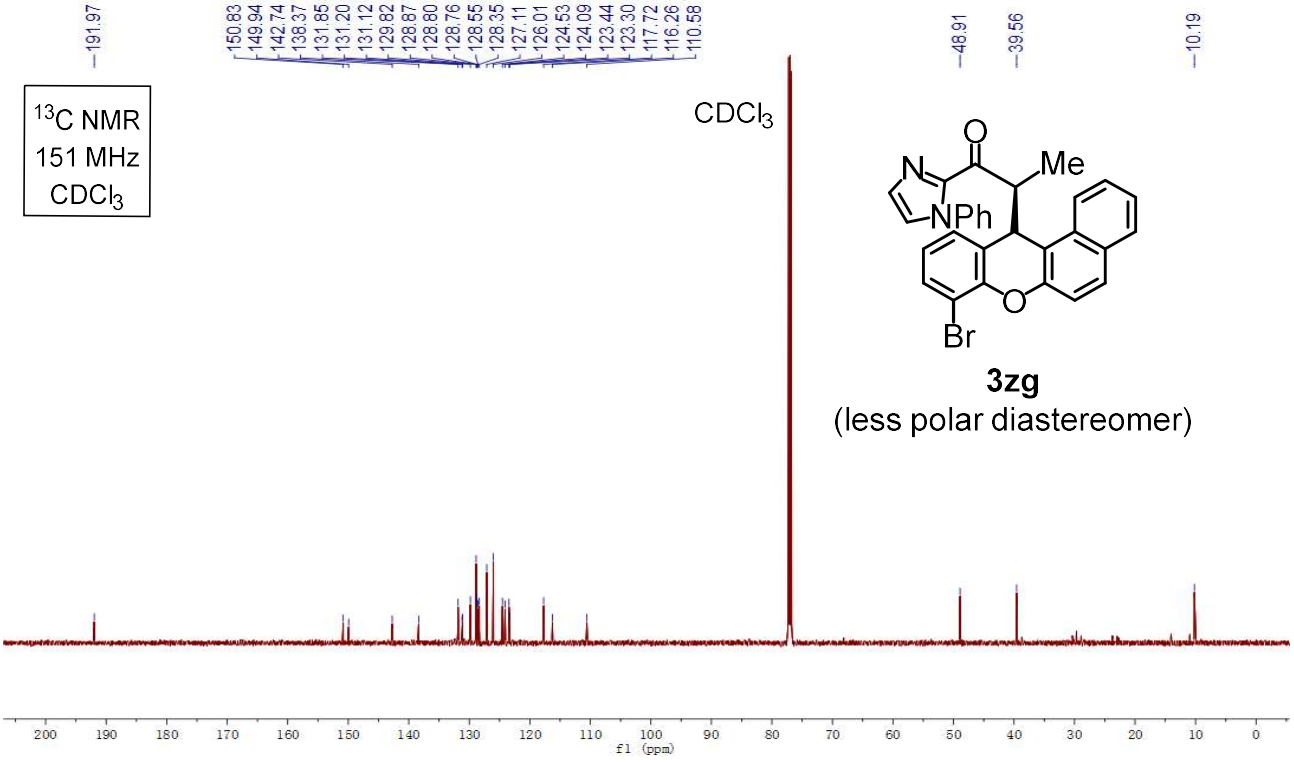


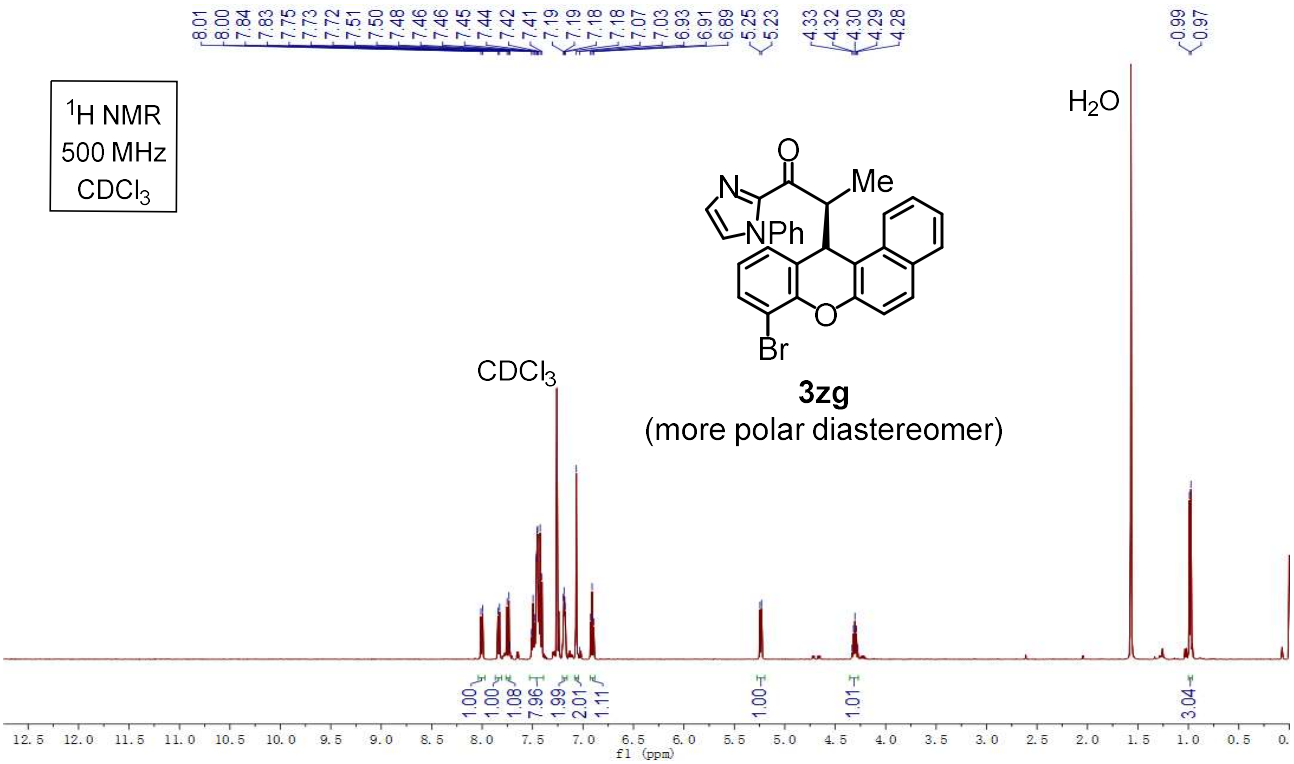
^{13}C NMR
126 MHz
$CDCl_3$

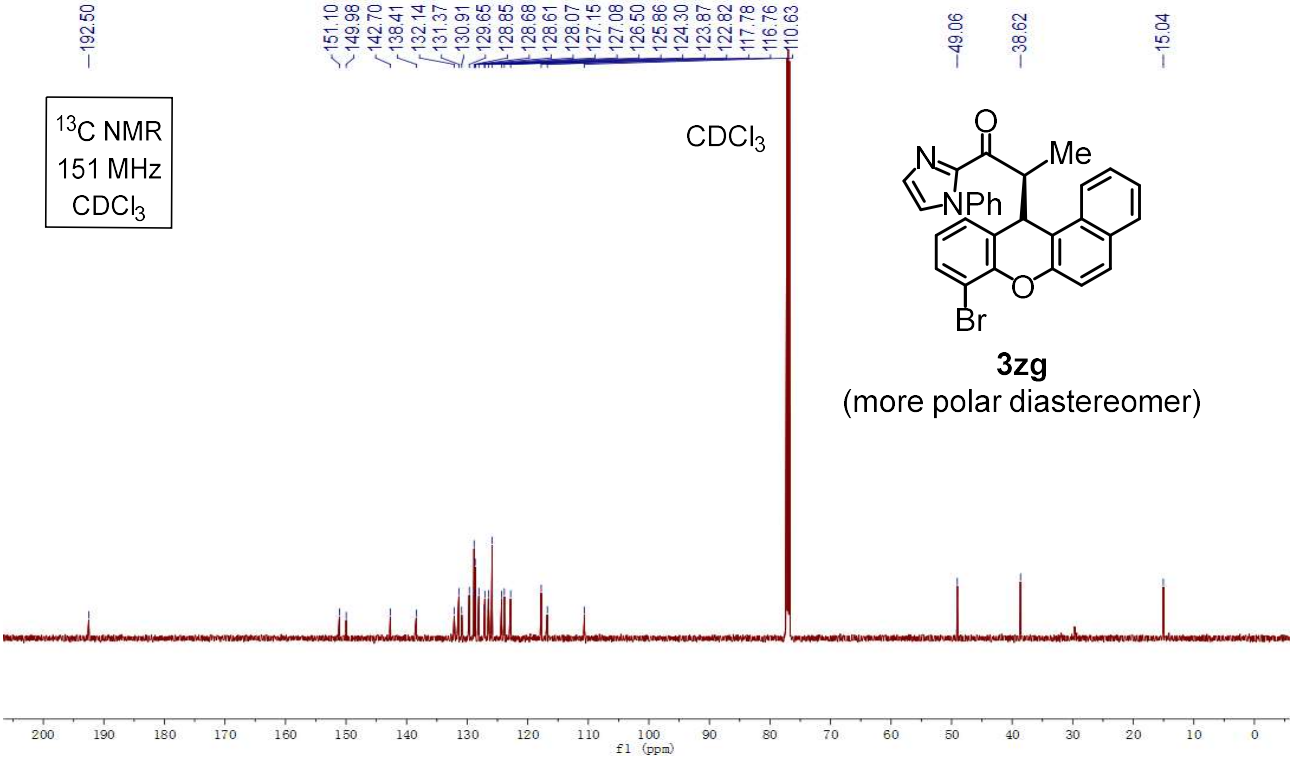
$CDCl_3$

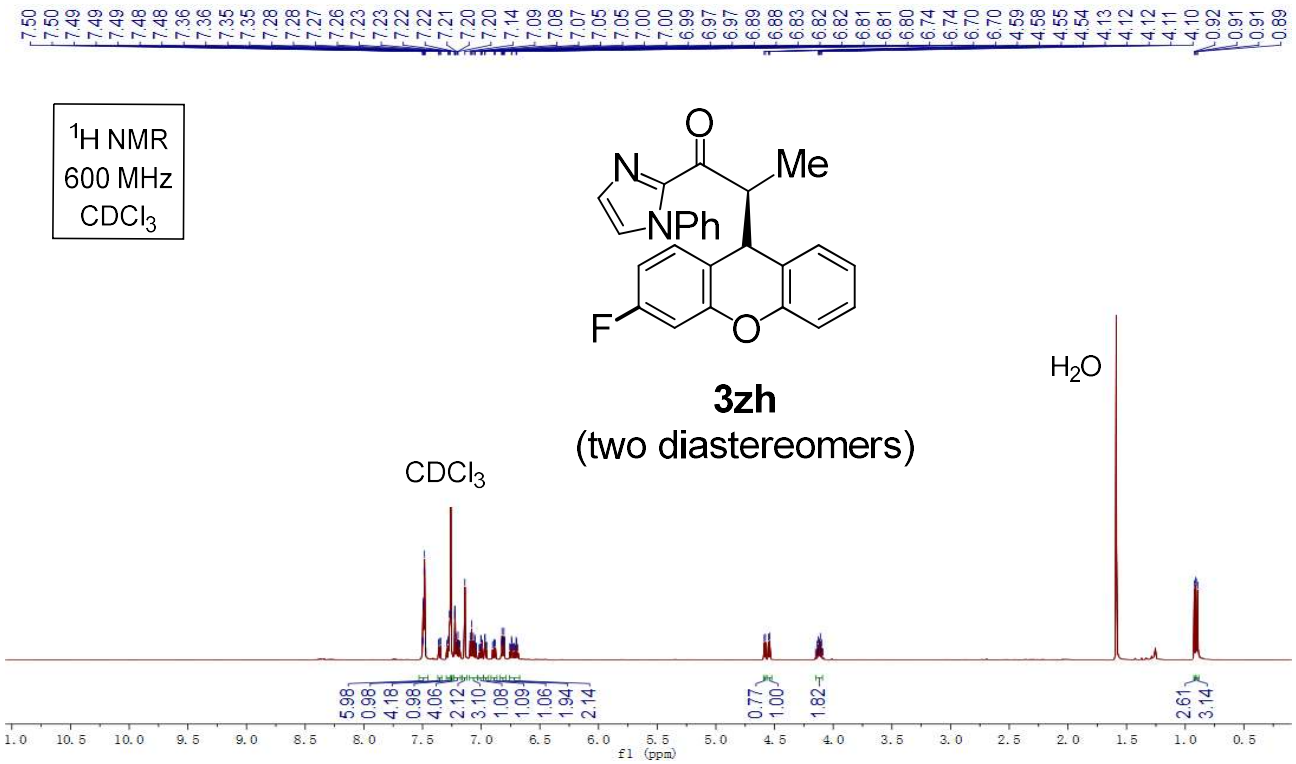
3zf
(more polar diastereomer)

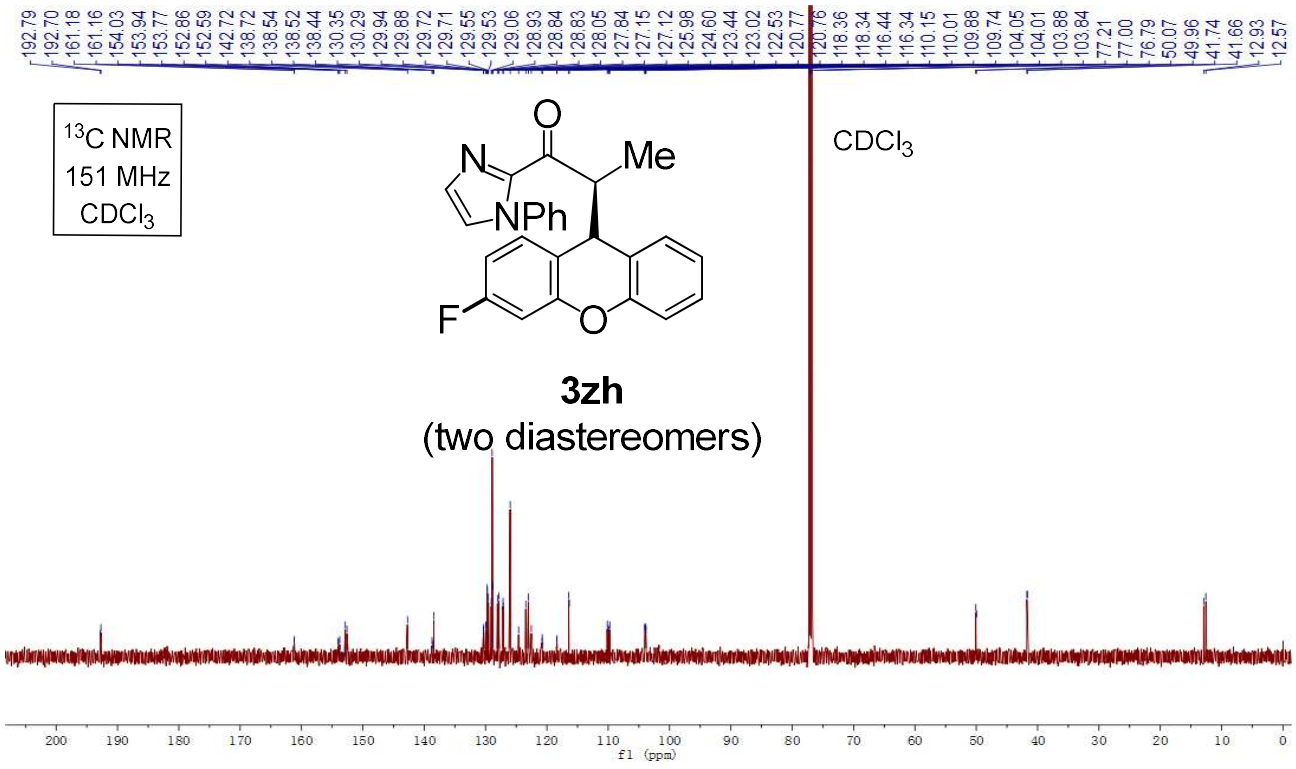

8.99
8.97
7.88
7.86
7.79
7.77
7.50
7.46
7.45
7.42
7.23
7.22
7.21
6.83
6.79
6.80
5.79
4.35
4.34
4.33
4.32
4.30
0.78
0.77
1H NMR
500 MHz
CDCl3
CDCl3
H2O
O
N
Me
NPh
O
Br
3zg
(less polar diastereomer)
1.00
0.99
0.98
1.00
1.01
6.02
3.07
1.00
1.01
1.00
1.01
2.98
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

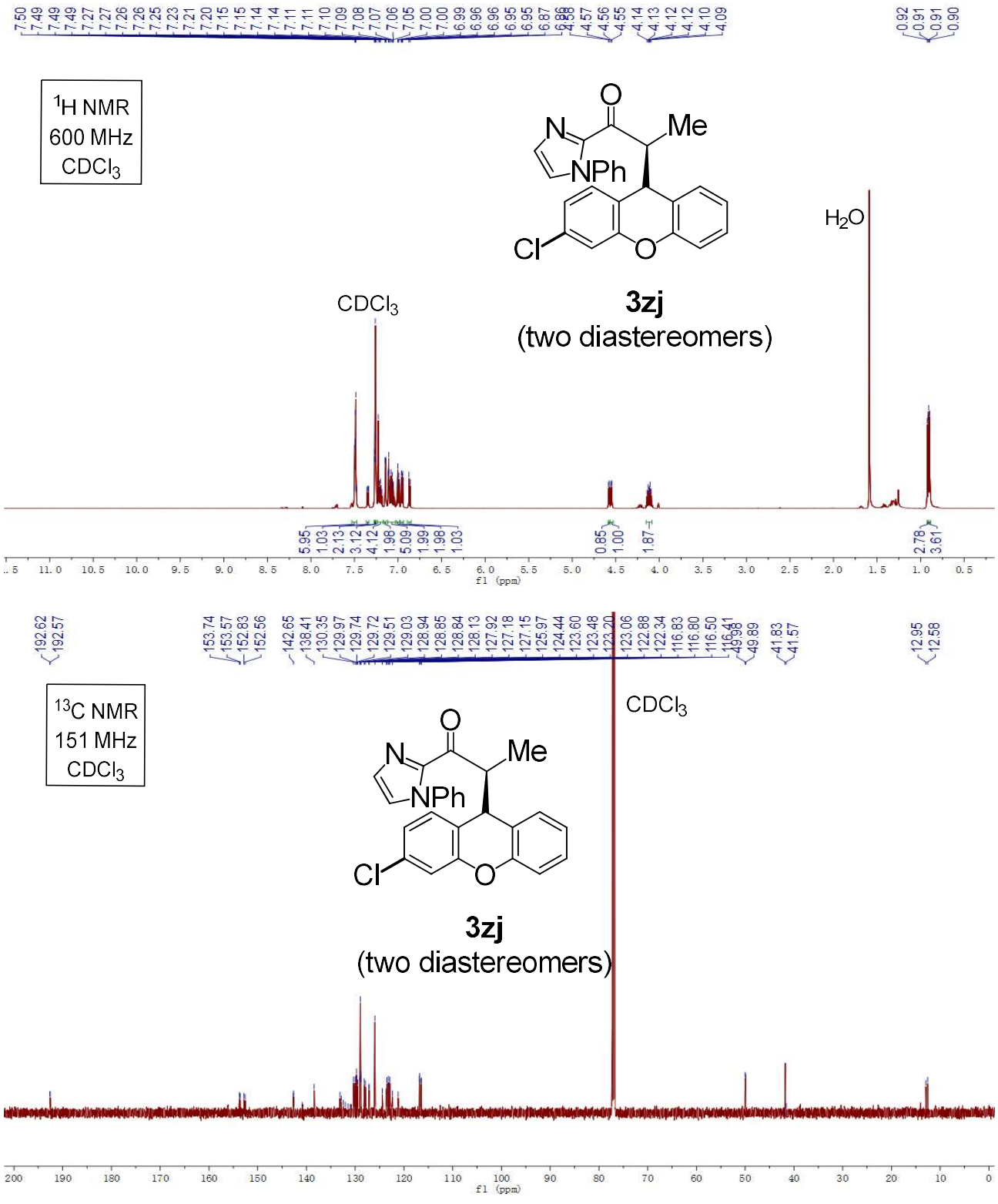

191.97
150.83
149.94
142.74
138.37
131.85
131.20
131.12
129.82
128.87
128.80
128.76
128.55
128.35
127.11
126.01
124.53
124.09
123.44
123.30
117.72
116.26
110.58
48.91
39.56
10.19
13C NMR
151 MHz
CDCl3
CDCl3
O
N
Me
NPh
O
Br
3zg
(less polar diastereomer)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

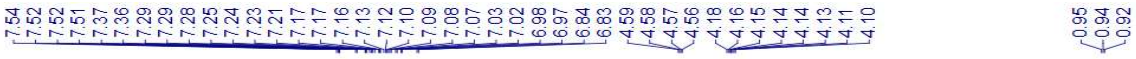

1H NMR
500 MHz
CDCl3
H2O
CDCl3
Me
NPh
O
Br
3zg
(more polar diastereomer)
f1 (ppm)


13C NMR
151 MHz
CDCl3
CDCl3
Me
NPh
O
Br
3zg
(more polar diastereomer)
f1 (ppm)

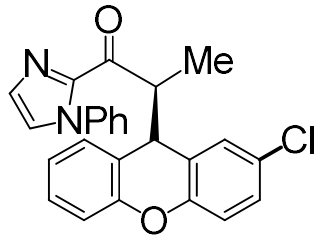

7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.36 7.36 7.35 7.35 7.28 7.28 7.27 7.26 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.14 7.09 7.08 7.07 7.05 7.05 7.00 7.00 6.99 6.97 6.97 6.89 6.88 6.83 6.82 6.82 6.81 6.81 6.80 6.74 6.74 6.70 6.70 4.59 4.58 4.55 4.54 4.13 4.12 4.12 4.11 4.10 0.92 0.91 0.91 0.89
1H NMR
600 MHz
CDCl3
O
N
Me
NPh
F
O
3zh
(two diastereomers)
H2O
CDCl3
5.98 0.98 4.18 0.98 4.06 2.12 3.10 1.08 1.09 1.06 1.94 2.14 0.77 1.00 1.82 2.61 3.14
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


192.79 192.70 161.18 161.16 154.03 153.94 153.77 152.86 152.59 142.72 138.72 138.54 138.52 138.44 130.35 130.29 129.94 129.88 129.72 129.71 129.55 129.53 129.06 128.93 128.84 128.83 128.05 127.84 127.15 127.12 125.98 124.60 123.44 123.02 122.53 120.77 120.76 118.36 118.34 116.44 116.34 110.15 110.01 109.88 109.74 104.05 104.01 103.88 103.84 77.21 77.00 76.79 50.07 49.96 41.74 41.66 12.93 12.57
13C NMR
151 MHz
CDCl3
O
N
Me
NPh
F
O
CDCl3
3zh
(two diastereomers)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

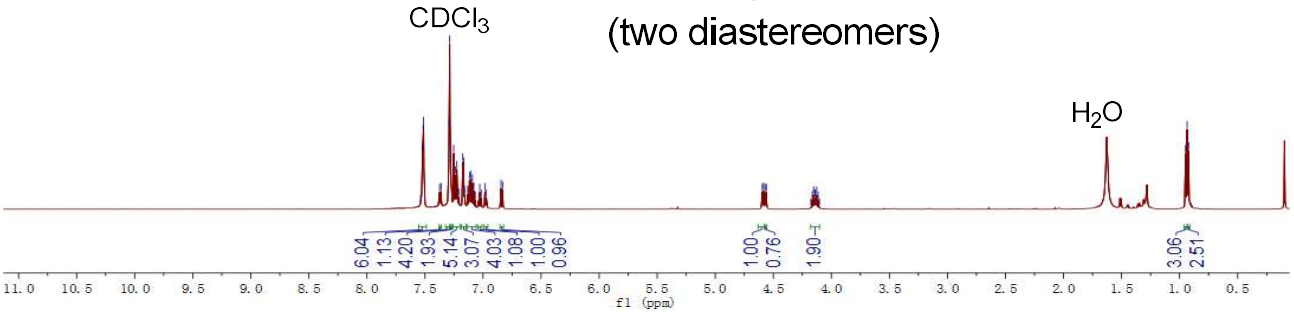

1H NMR
600 MHz
CDCl3
O
N
Me
NPh
Cl
O
3zj
(two diastereomers)
H2O
CDCl3
13C NMR
151 MHz
CDCl3
CDCl3
3zj
(two diastereomers)

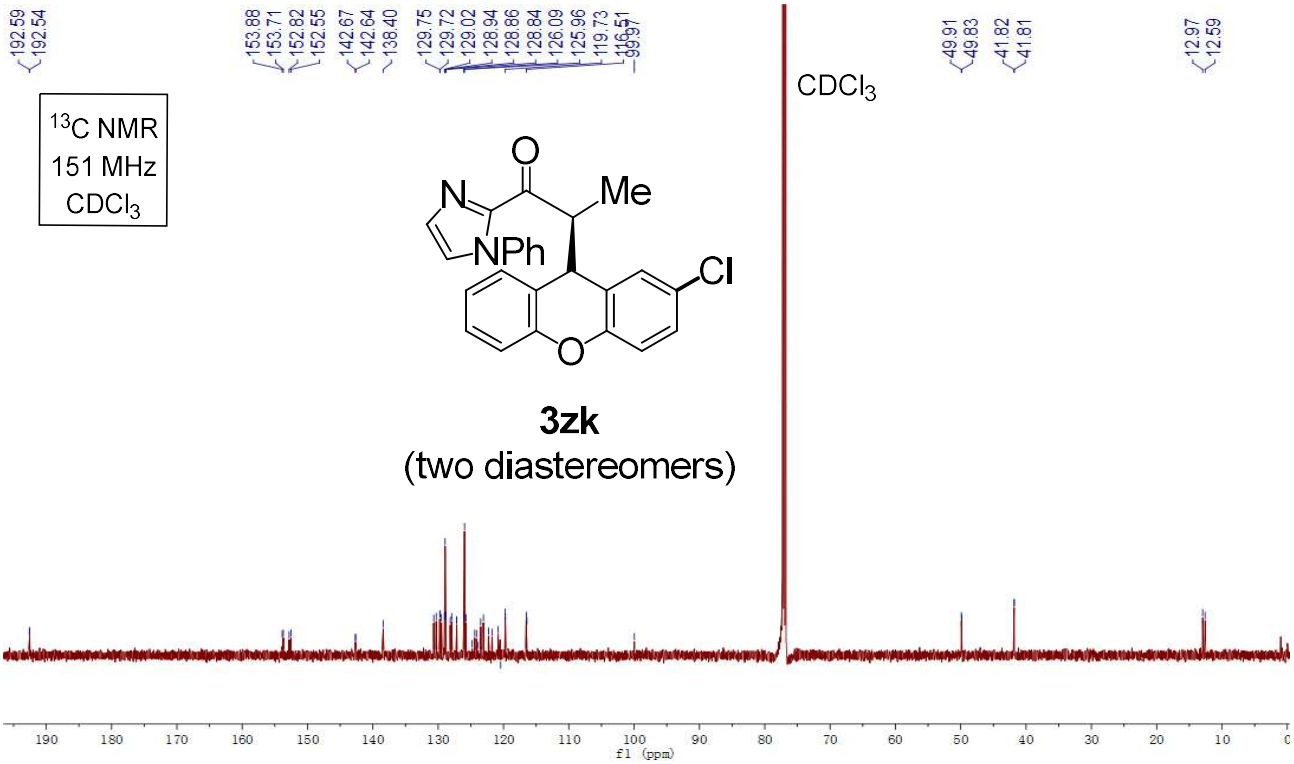


^{1}H NMR
600 MHz
$CDCl_3$



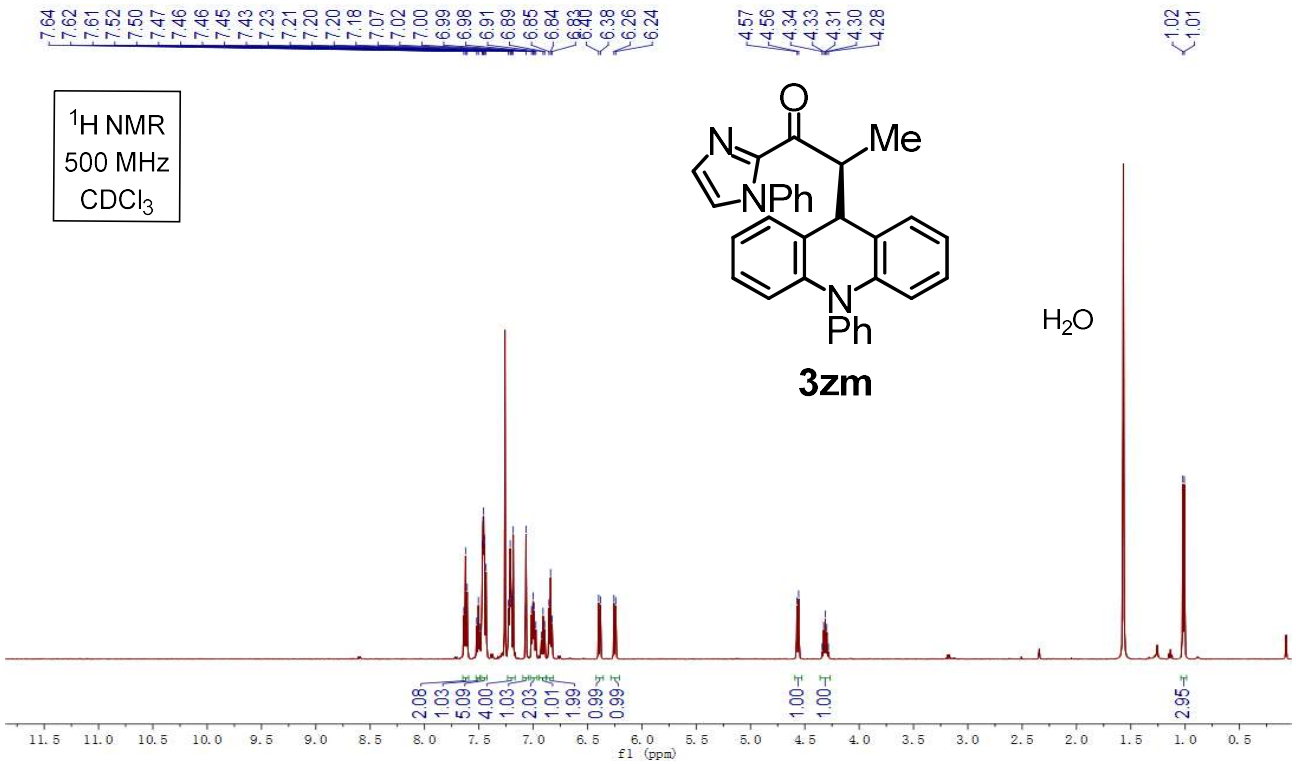
3zk
(two diastereomers)

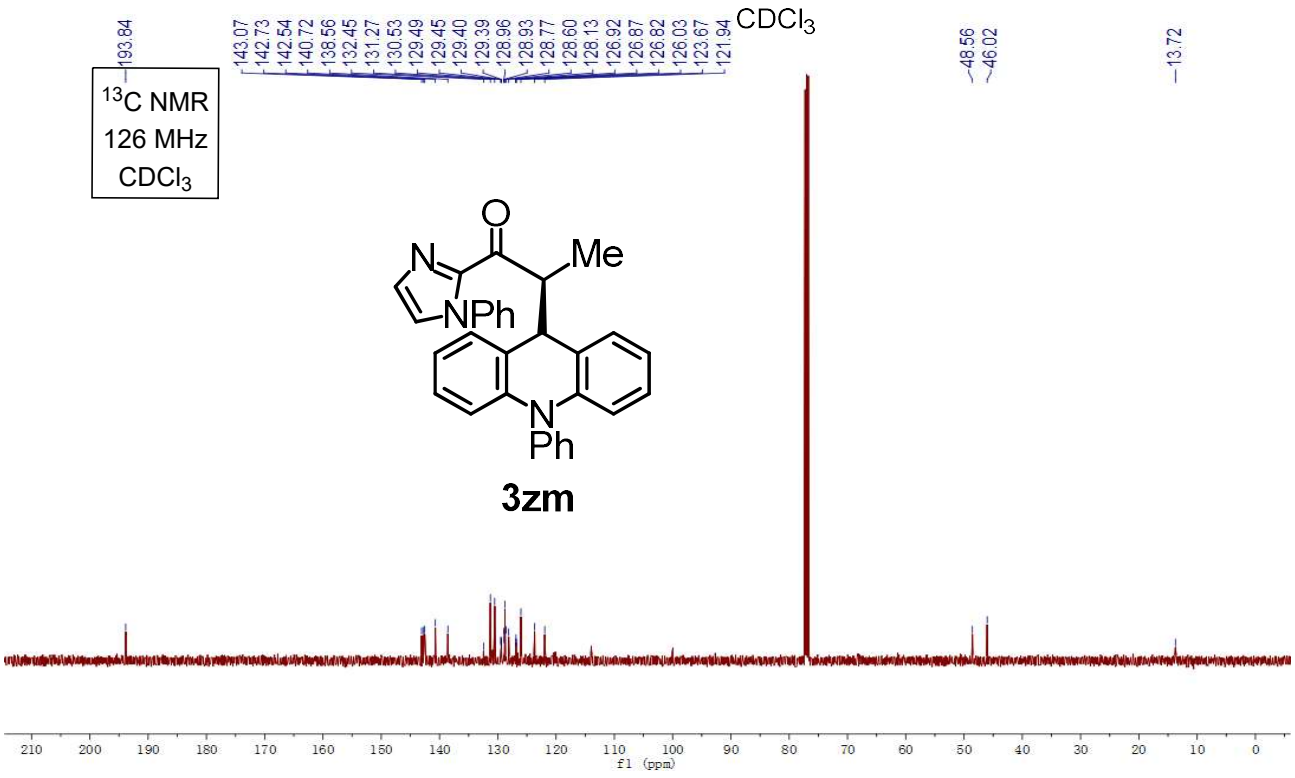


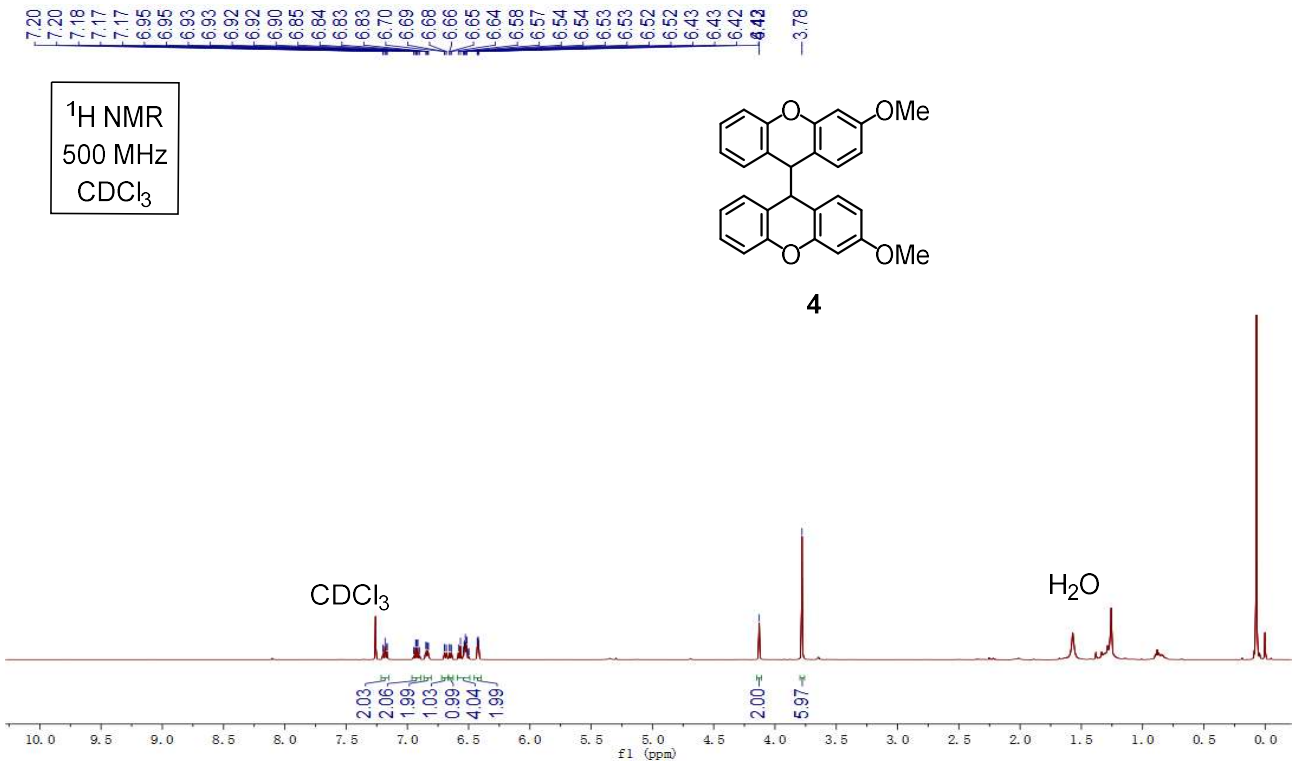


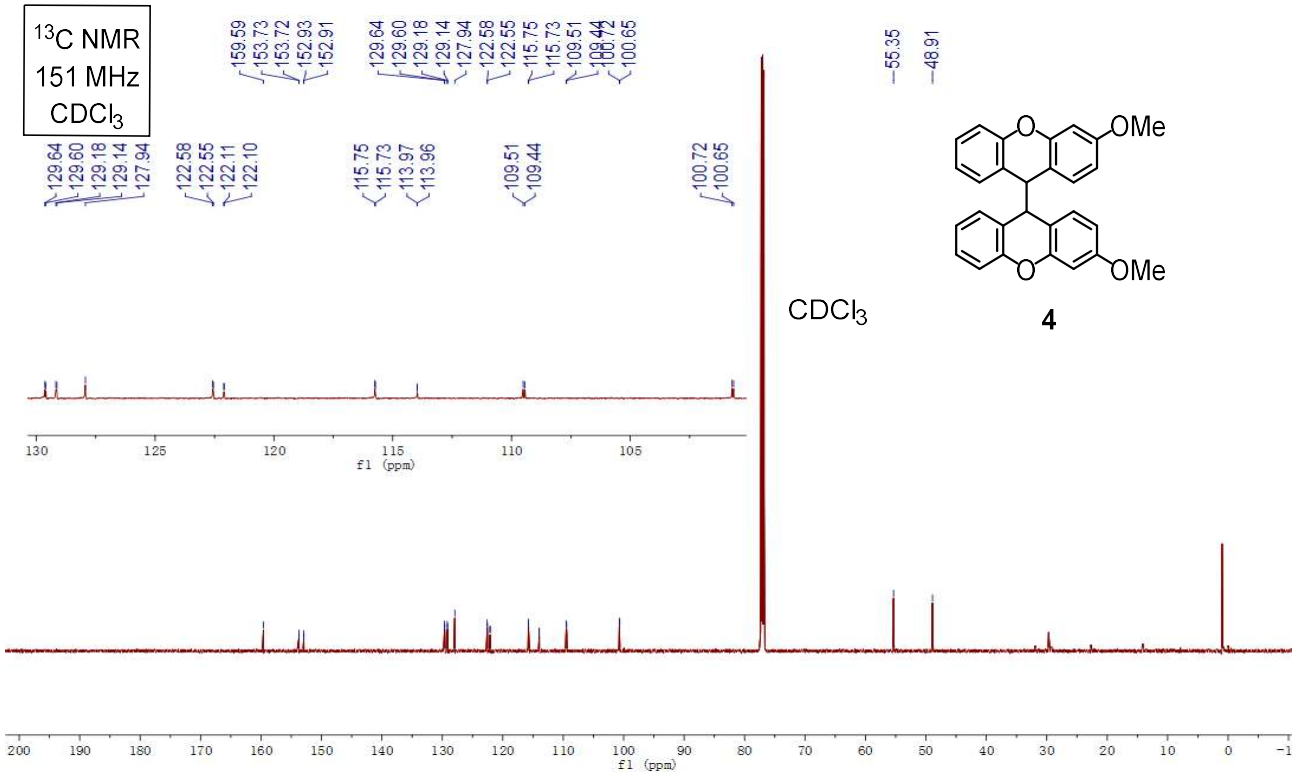
^{13}C NMR
151 MHz
$CDCl_3$

3zk
(two diastereomers)


7.64
7.62
7.61
7.52
7.50
7.47
7.46
7.45
7.43
7.23
7.21
7.20
7.20
7.18
7.07
7.02
7.00
6.99
6.98
6.91
6.89
6.85
6.84
6.83
6.40
6.38
6.26
6.24
4.57
4.56
4.34
4.33
4.31
4.30
4.28
1.02
1.01
1H NMR
500 MHz
CDCl3
O
N
Me
NPh
N
Ph
3zm
H2O
2.08
1.03
5.09
4.00
1.03
2.03
1.01
1.99
0.99
0.99
1.00
1.00
2.95
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


193.84
143.07
142.73
142.54
140.72
138.56
132.45
131.27
130.53
129.49
129.45
129.40
129.39
128.96
128.93
128.77
128.60
128.13
126.92
126.87
126.82
126.03
123.67
121.94
CDCl3
48.56
46.02
13.72
13C NMR
126 MHz
CDCl3
O
N
Me
NPh
N
Ph
3zm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.20
7.20
7.18
7.17
7.17
6.95
6.95
6.93
6.93
6.92
6.92
6.90
6.85
6.84
6.83
6.83
6.70
6.69
6.68
6.66
6.65
6.64
6.58
6.57
6.54
6.54
6.53
6.53
6.52
6.52
6.43
6.43
6.42
3.78
1H NMR
500 MHz
CDCl3
OMe
OMe
4
CDCl3
H2O
2.03
2.06
1.99
1.03
0.99
4.04
1.99
2.00
5.97
f1 (ppm)


13C NMR
151 MHz
CDCl3
159.59
153.73
153.72
152.93
152.91
129.64
129.60
129.18
129.14
127.94
122.58
122.55
122.11
122.10
115.75
115.73
113.97
113.96
109.51
109.44
100.72
100.65
55.35
48.91
OMe
OMe
4
CDCl3
f1 (ppm)