

Supplementary Information for

Diastereo- and atroposelective synthesis of *N*-arylpyrroles enabled by light-induced phosphoric acid catalysis

Lei Dai¹, Xueting Zhou^{1,2}, Jiami Guo^{1,2}, Xuan Dai¹, Qingqin Huang^{1,2} and Yixin Lu^{*,1,2}

¹Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543, Singapore.

²Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou, Fujian, 350207, China

*Corresponding author: Y. Lu, Email: chmlyx@nus.edu.sg

Table of Contents

1. Supplementary Notes	S3
2. Supplementary Methods	S3
2.1 General Procedure.....	S3
2.2. Analytical Data and HPLC Chromatograms of the Products 4	S4
2.3. Synthetic Applications	S32
2.4. Mechanistic Studies	S36
2.5. Single Crystal Structure X-ray Analysis of 4w	S39
3. Supplementary Figures	S61
3.1 NMR Spectra	S61
4. Supplementary References.....	S104

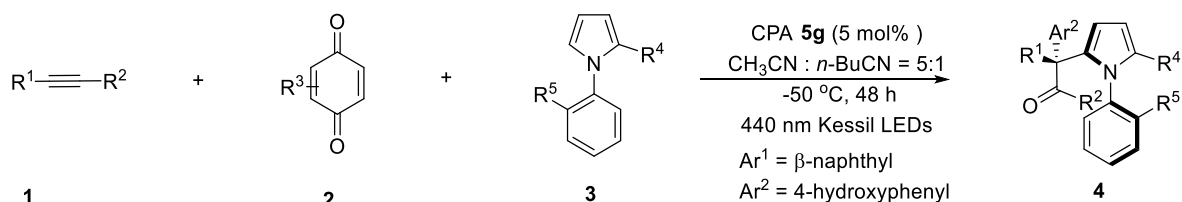
1. Supplementary Notes

All starting materials were obtained from commercial suppliers (Sigma Aldrich and TCI) and directly used without further purification unless otherwise stated. All reactions were carried out under argon atmosphere with magnetic stirring. Alkynes and *N*-arylpyrroles were synthesized according to literatures¹⁻⁴. All chiral phosphoric acids were purchased from Daicel Chiral Technologies.

Analytical thin layer chromatography was carried out with silica gel pre-coated glass plates (TLC-Silica gel GF254, coating thickness: 0.25 mm) purchased from Merck. Visualization was accomplished with short wave UV light (254nm, 365nm) and/or 10% phosphomolybdic acid in ethanol or KMnO₄ staining solutions followed by heating. Column chromatography was performed on silica gel 200~300 mesh. 440 nm Kessil LEDs was purchased from kessil.com. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-III400 (400 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were calibrated using residual solvent as an internal reference (CDCl₃: 7.18 ppm ¹H NMR, 77.00 ppm ¹³C NMR). ¹H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). All high-resolution mass spectra (HRMS) were obtained on a Finnigan/MAT 95XL-T spectrometer, the calculated values are based on the most abundant isotope. Absorption spectra were recorded in 1 cm path quartz cuvettes using an Edinburgh FS-5 spectrofluorometer. Chiral HPLC analyses were performed on an Agilent 1100 Series using a Daicel Chiralpak column (IG, IC, IF and AD-H) with hexanes/*i*PrOH as the eluent.

2. Supplementary Methods

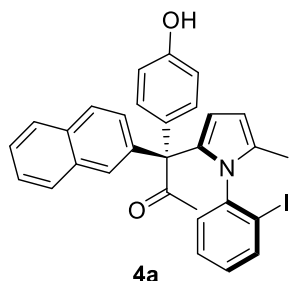
2.1 General Procedure



To a dried and argon-filled 10 mL screw-cap vial equipped with a magnetic stir bar were added alkyne **1** (0.2 mmol), benzoquinone **2a** (0.1 mmol, 10.8 mg), *N*-arylpyrrole (0.1 mmol), CPA **5g** (5 mmol%) and CH₃CN/*n*-butyronitrile (v/v, 5:1, 4.0 mL). The mixture was then irradiated by 440

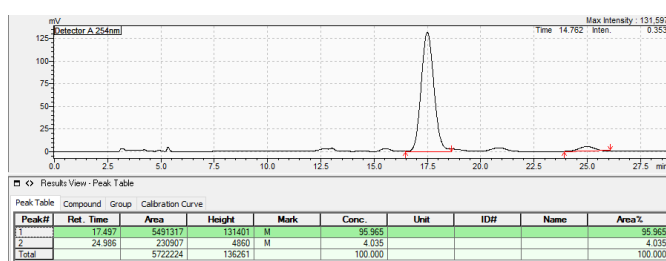
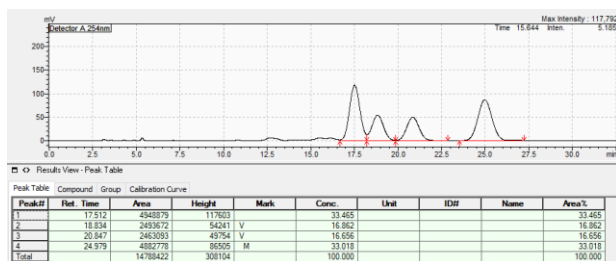
nm Kessil LEDs at -50 °C. The reaction mixture was concentrated under reduced pressure after 48 h and the residue was purified by column chromatography on silica gel to furnish the product.

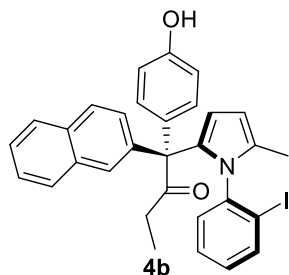
2.2. Analytical Data and HPLC Chromatograms of the Products 4



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4a)

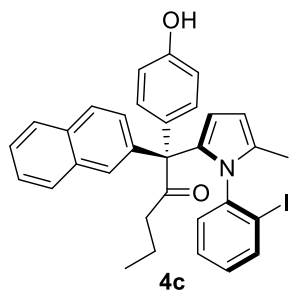
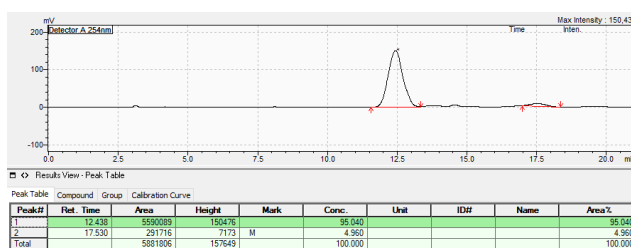
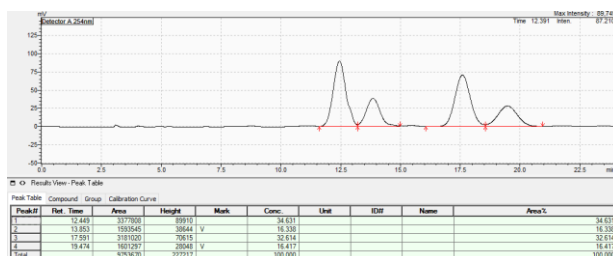
47.3 mg, 85% yield, 20:1 dr; $[\alpha]_D^{25} = -53.2$ (c 1.0, CHCl₃), white foam, $R_f = 0.34$ (hexane/ethyl acetate 4:1). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, $J = 7.9$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.33 (m, 2H), 7.27 (ddd, $J = 14.6, 8.3, 1.7$ Hz, 2H), 7.22 (s, 1H), 7.07 (d, $J = 8.8$ Hz, 2H), 6.99 (td, $J = 7.7, 1.4$ Hz, 1H), 6.90 (dd, $J = 7.9, 1.6$ Hz, 1H), 6.69 (td, $J = 7.7, 1.7$ Hz, 1H), 6.59 (d, $J = 8.9$ Hz, 2H), 6.15 (d, $J = 3.6$ Hz, 1H), 5.98 (d, $J = 4.3$ Hz, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.2, 154.6, 142.0, 139.4, 137.9, 132.8, 132.7, 132.5, 132.3, 131.6, 131.3, 129.3, 129.2, 129.0, 128.3, 127.7, 127.5, 127.4, 126.3, 126.0, 114.6, 112.0, 106.3, 103.3, 68.9, 29.6, 13.9. HRMS (ESI) m/z calcd for C₃₀H₂₄INNaO₂ [M+Na]⁺ = 580.0744, found = 580.0739; the ee value was 92%, t_R (major) = 17.5 min, t_R (minor) = 25.0 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





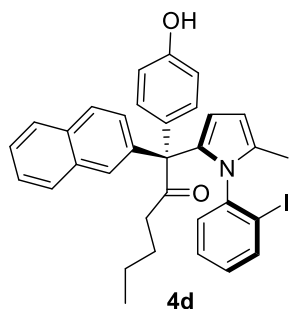
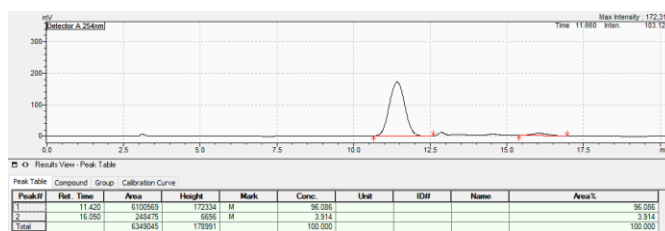
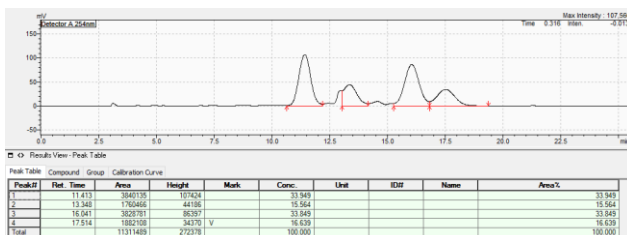
(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)butan-2-one (4b)

47.4 mg, 83% yield, >20:1 dr; $[\alpha]_D^{25} = -48.1$ (c 1.0, CHCl_3), white foam, $R_f = 0.36$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.67 (m, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.55 – 7.48 (m, 1H), 7.38 (dq, $J = 8.2, 6.9, 1.5$ Hz, 2H), 7.26 (ddd, $J = 11.7, 8.3, 1.7$ Hz, 2H), 7.21 – 7.16 (m, 1H), 7.13 – 7.03 (m, 2H), 7.03 – 6.92 (m, 2H), 6.75 – 6.61 (m, 1H), 6.61 – 6.49 (m, 2H), 6.17 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 2.9$ Hz, 1H), 2.29 (dq, $J = 14.6, 7.3$ Hz, 1H), 2.08 (dq, $J = 14.6, 7.3$ Hz, 1H), 1.80 (s, 3H), 0.72 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 208.9, 154.5, 141.9, 139.3, 138.0, 132.8, 132.7, 132.3, 132.2, 131.5, 131.3, 129.6, 129.3, 129.0, 128.3, 127.7, 127.4, 127.4, 126.2, 125.9, 114.5, 111.7, 106.3, 103.3, 69.0, 34.9, 13.9, 10.3. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 594.0900$, found = 594.0899; the ee value was 90%, t_R (major) = 12.4 min, t_R (minor) = 17.5 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)pentan-2-one (4c)

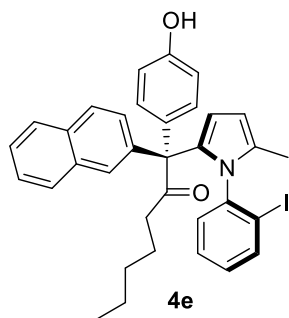
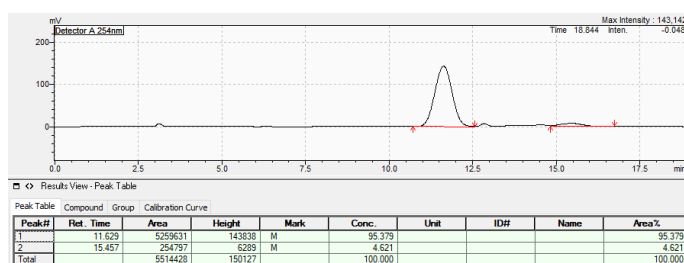
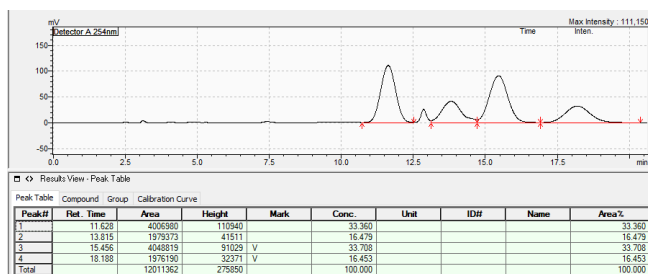
45.0 mg, 77% yield, >20:1 dr; $[\alpha]_D^{25} = -38.9$ (c 0.5, CHCl_3), white foam, $R_f = 0.32$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.45 – 7.33 (m, 2H), 7.26 (dt, $J = 8.7, 1.7$ Hz, 2H), 7.15 – 7.07 (m, 3H), 7.06 – 6.97 (m, 2H), 6.71 (ddd, $J = 7.9, 6.3, 2.7$ Hz, 1H), 6.57 (d, $J = 8.9$ Hz, 2H), 6.20 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 4.4$ Hz, 1H), 5.33 (s, 1H), 2.23 (ddd, $J = 15.5, 9.9, 5.5$ Hz, 1H), 2.08 (ddd, $J = 15.7, 9.8, 5.6$ Hz, 1H), 1.80 (s, 3H), 1.38 – 1.26 (m, 1H), 1.11 – 1.01 (m, 1H), 0.55 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 207.8, 154.7, 139.3, 137.8, 132.9, 132.8, 132.3, 132.1, 131.7, 131.2, 129.7, 129.3, 129.0, 128.2, 127.7, 127.4, 127.4, 126.2, 125.9, 114.5, 111.7, 106.2, 103.5, 43.5, 25.6, 19.6, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{28}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 608.1057$, found = 608.1063; the ee value was 92%, t_R (major) = 11.4 min, t_R (minor) = 16.1 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)hexan-2-one (4d)

47.3 mg, 79% yield, >20:1 dr; $[\alpha]_D^{25} = -63.0$ (c 1.0, CHCl_3), white foam, $R_f = 0.34$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.48 (d, $J = 7.9$ Hz, 1H), 7.46 – 7.32 (m, 3H), 7.25 (ddd, $J = 8.7, 3.3, 1.6$ Hz, 2H), 7.16 – 7.07 (m, 3H), 7.06 – 6.97 (m, 2H), 6.70 (ddd, $J = 7.9, 6.1, 2.9$ Hz, 1H), 6.57 (d, $J = 8.9$ Hz, 2H), 6.19 (d, $J = 3.6$

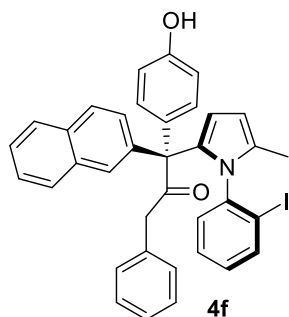
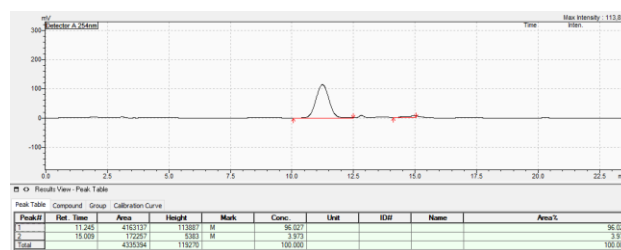
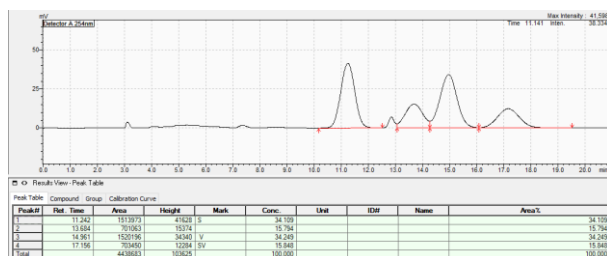
Hz, 1H), 5.99 (d, $J = 3.6$ Hz, 1H), 5.20 (s, 1H), 2.30 – 2.19 (m, 1H), 2.16 – 2.04 (m, 1H), 1.80 (s, 3H), 1.32 – 1.23 (m, 1H), 0.95 – 0.88 (m, 2H), 0.82 – 0.76 (m, 1H), 0.59 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 208.1, 154.6, 141.9, 139.3, 137.8, 132.8, 132.1, 131.7, 131.2, 129.7, 129.3, 129.0, 128.2, 127.7, 127.4, 127.4, 126.2, 125.9, 114.5, 111.7, 106.2, 69.2, 41.3, 28.3, 22.3, 13.9, 13.7. HRMS (ESI) m/z calcd for $\text{C}_{33}\text{H}_{30}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 622.1213$, found = 622.1214; the ee value was 91%, t_R (major) = 11.6 min, t_R (minor) = 15.5 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)heptan-2-one (4e)

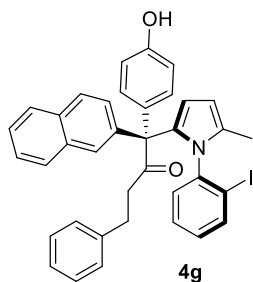
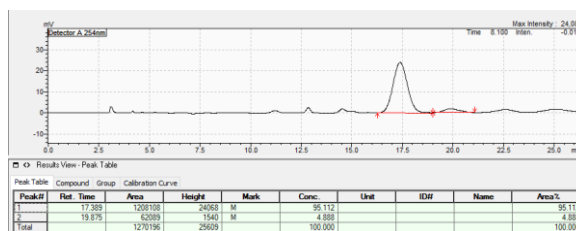
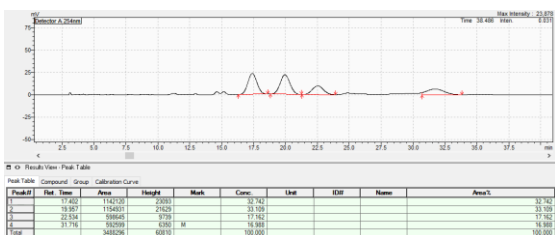
52.1 mg, 85% yield, 20:1 dr; $[\alpha]_D^{25} = -41.2$ (c 1.0, CHCl_3), white foam, $R_f = 0.38$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.16 – 7.07 (m, 3H), 7.05 – 6.96 (m, 2H), 6.70 (ddd, $J = 7.9, 5.9, 3.1$ Hz, 1H), 6.57 (d, $J = 8.7$ Hz, 2H), 6.19 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 3.4$ Hz, 1H), 5.05 (s, 1H), 2.29 – 2.20 (m, 1H), 2.16 – 2.04 (m, 1H), 1.80 (s, 3H), 1.36 – 1.17 (m, 2H), 1.03 – 0.90 (m, 4H), 0.63 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 208.0, 154.5, 141.9, 139.3, 137.8, 132.9, 132.8, 132.1, 131.7, 131.3, 129.7, 129.3, 129.0, 128.2, 127.7, 127.4, 127.4, 126.2, 125.9, 114.5, 111.7, 106.2, 69.2, 41.5, 31.4, 25.9, 22.2, 13.9, 13.8.

HRMS (ESI) m/z calcd for $C_{34}H_{32}INNaO_2$ $[M+Na]^+ = 636.1370$, found = 636.1368; the ee value was 92%, t_R (major) = 11.2 min, t_R (minor) = 15.0 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



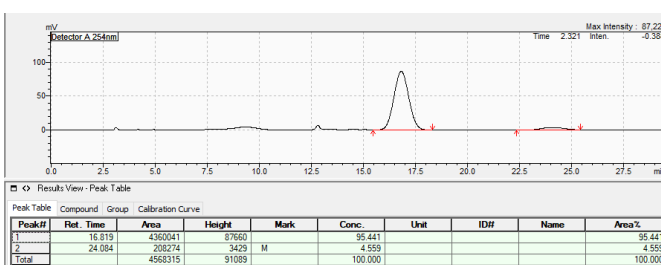
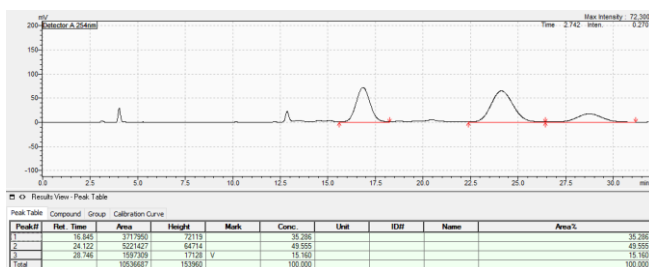
(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)-3-phenylpropan-2-one (4f)

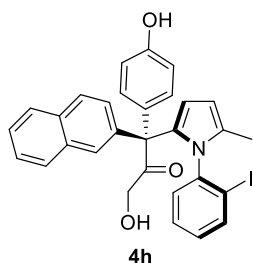
48.1 mg, 76% yield, 19:1 dr; $[\alpha]_D^{25} = -38.0$ (c 1.0, $CHCl_3$), white foam, $R_f = 0.31$ (hexane/ethyl acetate 4:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, $J = 7.8$ Hz, 1H), 7.59 (d, $J = 8.7$ Hz, 1H), 7.46 – 7.34 (m, 3H), 7.27 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.14 (d, $J = 8.9$ Hz, 4H), 7.04 (s, 3H), 6.99 (d, $J = 7.9$ Hz, 1H), 6.89 (t, $J = 8.3$ Hz, 1H), 6.84 – 6.73 (m, 2H), 6.66 – 6.57 (m, 1H), 6.54 (d, $J = 8.9$ Hz, 2H), 6.26 (d, $J = 3.6$ Hz, 1H), 6.01 (d, $J = 4.4$ Hz, 1H), 4.79 (s, 1H), 3.57 (d, $J = 15.2$ Hz, 1H), 3.41 (d, $J = 15.2$ Hz, 1H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 154.6, 139.2, 137.1, 135.4, 132.9, 132.4, 132.1, 131.6, 130.8, 129.7, 129.5, 129.2, 128.9, 128.2, 127.9, 127.7, 127.6, 127.4, 126.4, 126.2, 125.9, 114.6, 112.0, 106.3, 103.1, 69.3, 47.0, 13.9. HRMS (ESI) m/z calcd for $C_{36}H_{28}INNaO_2$ $[M+Na]^+ = 656.1057$, found = 656.1061; the ee value was 90%, t_R (major) = 17.4 min, t_R (minor) = 19.9 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)-4-phenylbutan-2-one (4g)

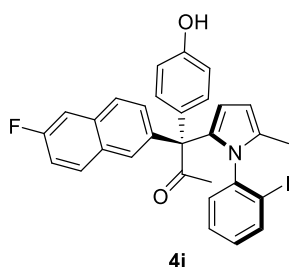
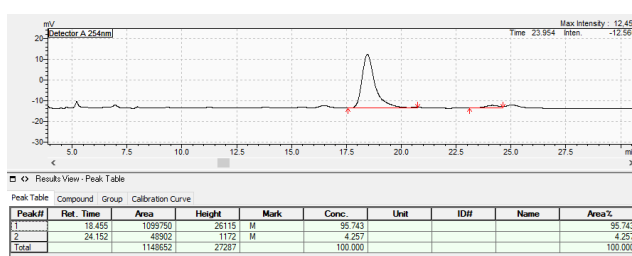
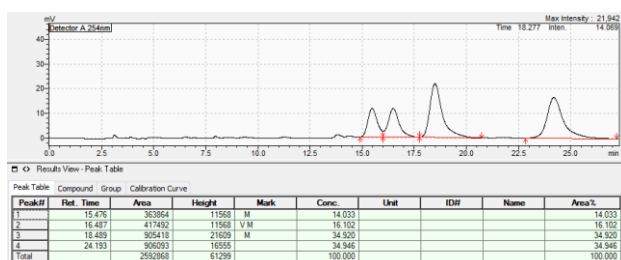
47.9 mg, 74% yield, >20:1 dr; $[\alpha]_D^{25} = -29.6$ (c 1.0, CHCl_3), white foam, $R_f = 0.33$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.9$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.47 – 7.31 (m, 3H), 7.25 (d, $J = 8.2$ Hz, 2H), 7.13 – 6.96 (m, 8H), 6.78 (d, $J = 8.1$ Hz, 2H), 6.70 (ddd, $J = 7.9, 6.4, 2.6$ Hz, 1H), 6.58 (d, $J = 8.9$ Hz, 2H), 6.19 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 1.0$ Hz, 1H), 5.13 (s, 1H), 2.66 – 2.38 (m, 3H), 2.22 – 2.10 (m, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.8, 154.7, 141.9, 141.0, 139.3, 137.4, 132.8, 132.7, 132.3, 132.3, 131.7, 131.2, 129.6, 129.3, 129.1, 128.4, 128.3, 128.3, 127.8, 127.5, 127.4, 126.2, 125.9, 125.9, 114.7, 111.9, 106.3, 103.5, 69.2, 43.6, 32.6, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{37}\text{H}_{30}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 670.1213$, found = 670.1212; the ee value was 91%, t_R (major) = 16.8 min, t_R (minor) = 24.1 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(S)-3-Hydroxy-1-(4-hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4h)

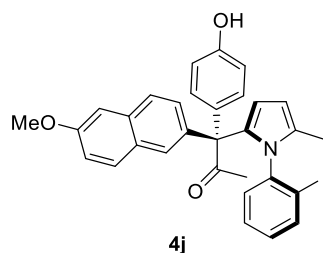
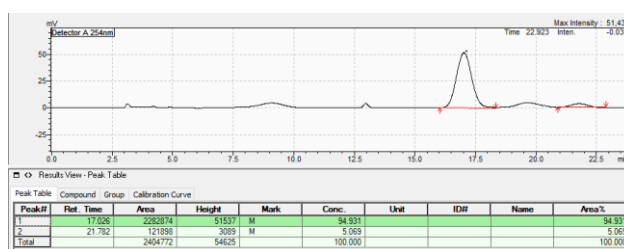
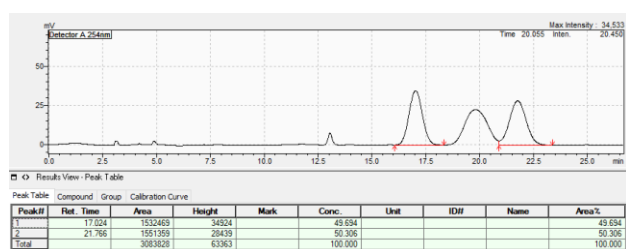
51.0 mg, 89% yield, 16:1 dr; $[\alpha]_D^{25} = -50.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.23$ (hexane/ethyl acetate 2:1). ^1H NMR (400 MHz, Acetone- d_6) δ 8.41 (s, 1H), 7.70 (s, 1H), 7.60 (d, $J = 8.7$ Hz, 2H), 7.46 (s, 1H), 7.34 (t, $J = 9.6$ Hz, 3H), 7.24 (d, $J = 8.7$ Hz, 1H), 6.97 – 6.88 (m, 3H), 6.75 – 6.66 (m, 2H), 6.49 (s, 2H), 6.03 (d, $J = 3.7$ Hz, 1H), 5.91 (d, $J = 4.4$ Hz, 1H), 3.94 (d, $J = 17.6$ Hz, 1H), 3.59 (d, $J = 17.6$ Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 205.3, 155.9, 149.9, 139.5, 131.7, 130.6, 129.2, 129.0, 128.9, 128.3, 127.9, 127.3, 127.0, 126.2, 125.9, 115.7, 114.5, 106.76, 67.0, 65.3, 13.2. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{INaO}_3$ $[\text{M}+\text{Na}]^+ = 596.0693$, found = 596.0697; the ee value was 91%, t_R (major) = 18.5 min, t_R (minor) = 24.2 min (Chiralpak IF, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(6-Fluoronaphthalen-2-yl)-1-(4-hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)propan-2-one (4i)

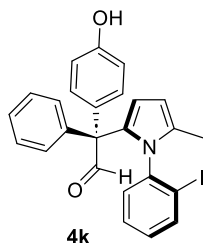
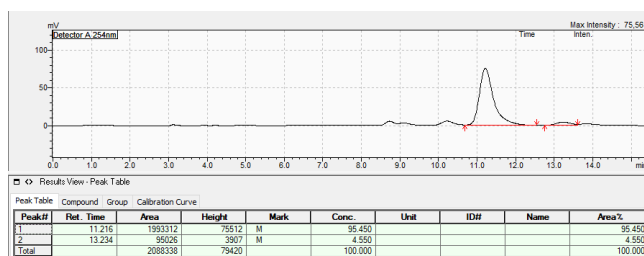
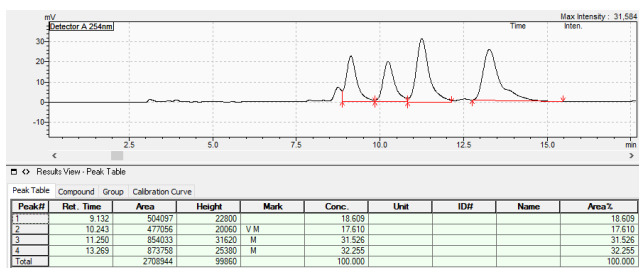
43.2 mg, 75% yield, 14:1 dr; $[\alpha]_D^{25} = -49.1$ (c 1.0, CHCl_3), white foam, $R_f = 0.34$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.45 (m, 2H), 7.36 – 7.24 (m, 3H), 7.20 (s, 1H),

7.17 – 7.11 (m, 1H), 7.11 – 7.07 (m, 2H), 7.00 (t, $J = 7.7$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.74 – 6.67 (m, 1H), 6.60 (d, $J = 8.7$ Hz, 2H), 6.14 (d, $J = 3.5$ Hz, 1H), 5.98 (d, $J = 3.3$ Hz, 1H), 5.32 (s, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.3, 160.9 (d, $J = 246.5$ Hz), 154.7, 141.9, 139.4, 137.2, 132.5, 132.4, 131.5, 131.4, 130.6, 130.4, 129.8, 129.1, 129.0, 127.8, 126.9, 126.8, 116.3 (d, $J = 25.3$ Hz), 116.1, 114.8, 112.2, 110.5 (d, $J = 20.4$ Hz), 106.3, 103.3, 68.8, 29.5, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{FINO}_2$ $[\text{M}+\text{H}]^+ = 576.0830$, found = 576.0826; the ee value was 90%, t_R (major) = 17.0 min, t_R (minor) = 21.8 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



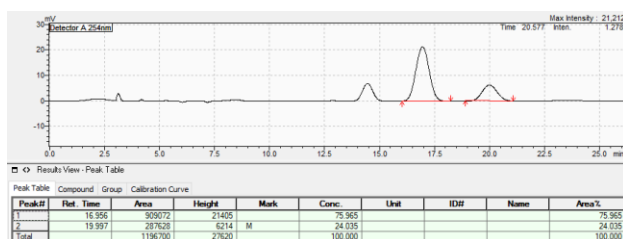
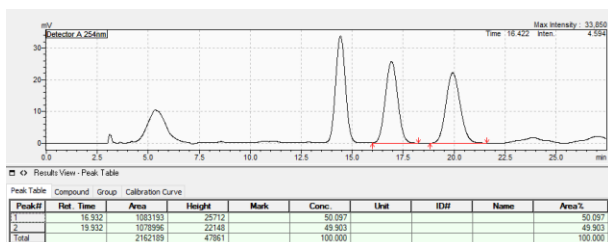
(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(6-methoxynaphthalen-2-yl)propan-2-one (4j)

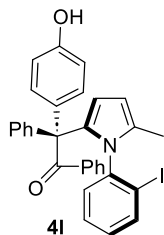
50.5 mg, 86% yield, 12:1 dr; $[\alpha]_D^{25} = -60.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.26$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.7$ Hz, 1H), 7.42 (d, $J = 9.8$ Hz, 1H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.20 (d, $J = 11.6$ Hz, 2H), 7.15 (s, 1H), 7.10 – 6.96 (m, 6H), 6.92 – 6.86 (m, 1H), 6.71 (d, $J = 7.2$ Hz, 1H), 6.58 (d, $J = 8.8$ Hz, 2H), 6.14 (d, $J = 3.6$ Hz, 1H), 5.98 (d, $J = 4.3$ Hz, 1H), 4.94 (s, 1H), 3.86 (s, 3H), 1.88 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.1, 158.0, 154.4, 139.3, 132.9, 132.5, 131.7, 131.3, 129.8, 129.8, 129.0, 128.9, 128.3, 127.7, 126.4, 118.7, 114.6, 111.8, 106.2, 105.4, 68.8, 55.4, 29.6, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{27}\text{INO}_3$ $[\text{M}+\text{H}]^+ = 588.1030$, found = 588.1038; the ee value was 91%, t_R (major) = 17.0 min, t_R (minor) = 21.8 min (Chiralpak IF, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(R)-2-(4-Hydroxyphenyl)-2-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-2-phenylacetaldehyde (4k)

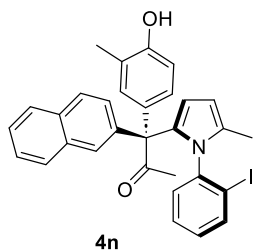
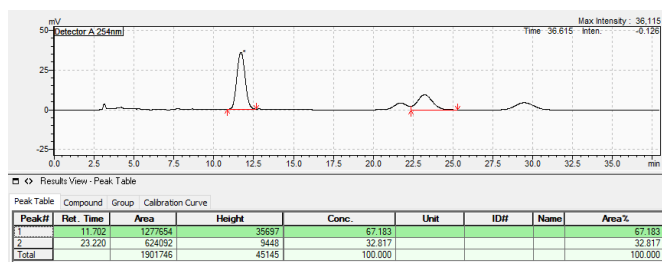
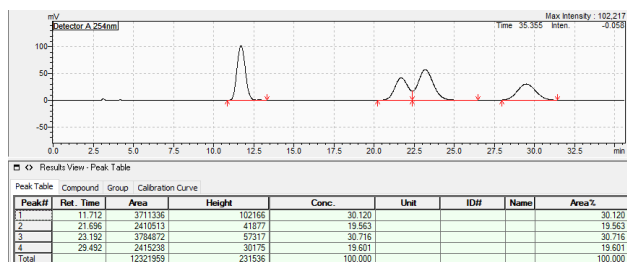
40.9 mg, 83% yield, 10:1 dr; $[\alpha]_D^{25} = -15.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.33$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 9.76 (s, 1H), 7.72 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.24 – 7.18 (m, 4H), 7.15 – 7.04 (m, 2H), 6.99 (td, $J = 7.6, 1.5$ Hz, 1H), 6.95 – 6.90 (m, 1H), 6.81 (d, $J = 8.8$ Hz, 2H), 6.68 (d, $J = 8.8$ Hz, 2H), 6.55 (dd, $J = 7.8, 1.7$ Hz, 1H), 5.99 (d, $J = 4.3$ Hz, 1H), 5.78 (d, $J = 3.6$ Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.2, 154.6, 141.2, 140.5, 139.6, 132.1, 131.7, 131.6, 131.6, 130.9, 130.4, 130.0, 128.6, 127.9, 127.4, 114.8, 113.4, 106.9, 102.7, 64.7, 13.3. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{INO}_2$ $[\text{M}+\text{H}]^+ = 494.0611$, found = 494.0612; the ee value was 52%, t_R (major) = 17.0 min, t_R (minor) = 20.0 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(R)-2-(4-Hydroxyphenyl)-2-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1,2-diphenylethan-1-one (4l)

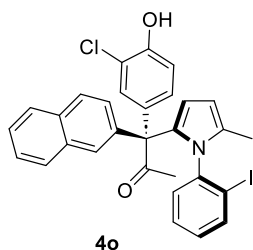
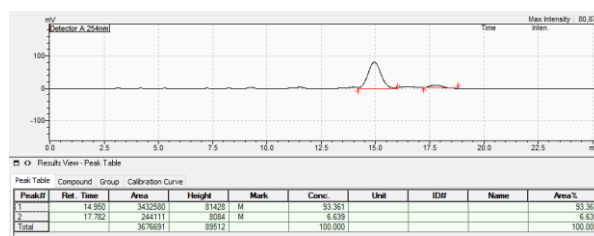
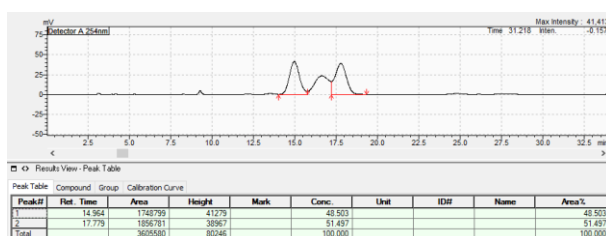
41.0 mg, 72% yield, 3:1 dr; $[\alpha]_D^{25} = -12.1$ (c 1.0, CHCl_3), white foam, $R_f = 0.37$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.35 (m, 3H), 7.29 – 7.09 (m, 6H), 7.06 – 6.92 (m, 10H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.76 – 6.63 (m, 2H), 6.64 – 6.55 (m, 2H), 6.44 (d, $J = 8.5$ Hz, 1H), 5.91 (d, $J = 3.5$ Hz, 1H), 5.82 (d, $J = 3.6$ Hz, 1H), 5.30 (s, 1H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.9, 154.64, 142.3, 139.7, 139.5, 138.1, 135.9, 132.8, 132.4, 132.3, 132.0, 131.6, 131.5, 131.3, 130.9, 130.62, 130.60, 128.7, 127.8, 127.7, 127.60, 127.58, 126.4, 114.8, 114.6, 112.6, 112.5, 105.8, 103.2, 67.2, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{25}\text{INO}_2$ $[\text{M}+\text{H}]^+ = 570.0925$, found = 570.0929; the ee value was 34%, t_R (major) = 11.7 min, t_R (minor) = 23.2 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(R)-1-(4-Hydroxy-3-methylphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4n)

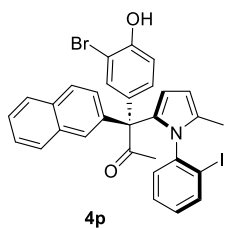
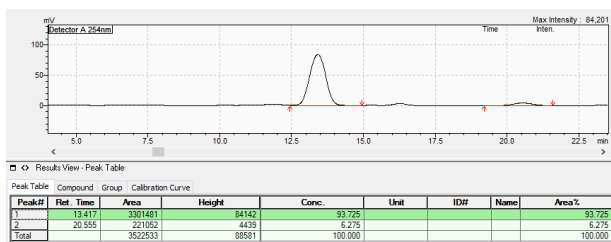
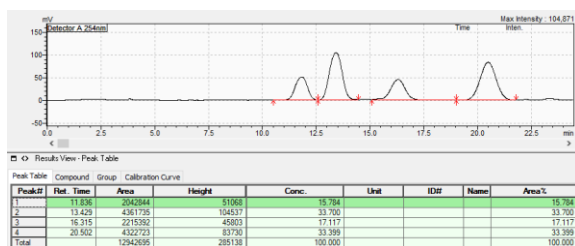
45.1 mg, 79% yield, 13:1 dr; $[\alpha]_D^{25} = -37.4$ (c 0.6, CHCl_3), white foam, $R_f = 0.26$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 7.9$ Hz, 1H), 7.62 (d, $J = 8.6$ Hz, 1H), 7.53

(d, $J = 7.9$ Hz, 1H), 7.40 (dtd, $J = 9.5, 7.6, 7.2, 1.4$ Hz, 2H), 7.29 – 7.21 (m, 3H), 7.01 – 6.91 (m, 3H), 6.84 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.68 (td, $J = 7.6, 1.7$ Hz, 1H), 6.48 (d, $J = 8.5$ Hz, 1H), 6.18 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 3.1$ Hz, 1H), 2.05 (s, 3H), 1.89 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.1, 153.0, 142.0, 139.3, 138.0, 134.0, 132.9, 132.8, 132.33, 132.1, 131.3, 130.9, 130.0, 129.4, 129.3, 128.9, 128.3, 127.6, 127.4, 126.2, 125.9, 122.7, 114.1, 111.7, 106.2, 103.1, 68.9, 29.6, 16.1 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 594.0900$, found = 594.0899; the ee value was 87%, t_R (major) = 17.0 min, t_R (minor) = 21.8 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



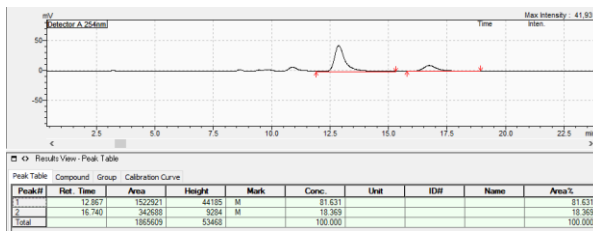
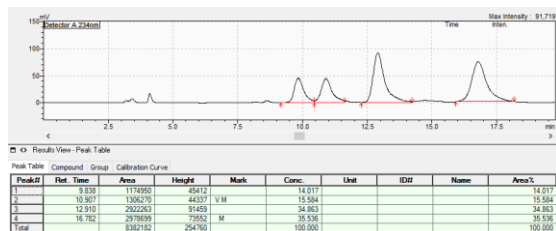
(R)-1-(3-Chloro-4-hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4o)

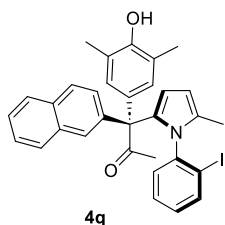
43.2 mg, 73% yield, 7:1 dr; $[\alpha]_D^{25} = -23.8$ (c 1.0, CHCl_3), white foam, $R_f = 0.29$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.66 (dd, $J = 16.7, 8.0$ Hz, 2H), 7.52 – 7.30 (m, 7H), 7.17 (dd, $J = 8.7, 2.0$ Hz, 1H), 6.90 (d, $J = 4.0$ Hz, 2H), 6.85 (dd, $J = 8.7, 2.3$ Hz, 1H), 6.72 – 6.66 (m, 1H), 6.61 (d, $J = 8.7$ Hz, 1H), 6.23 (d, $J = 3.6$ Hz, 1H), 6.04 (d, $J = 4.2$ Hz, 1H), 5.42 (s, 1H), 1.94 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.8, 149.9, 141.8, 139.6, 138.0, 132.9, 132.5, 132.4, 132.0, 131.5, 131.3, 130.8, 129.7, 129.1, 128.7, 128.3, 127.8, 127.7, 127.5, 126.6, 126.3, 118.7, 114.8, 111.4, 106.5, 102.5, 68.2, 30.0, 13.8. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{ClINO}_2$ $[\text{M}+\text{H}]^+ = 592.0535$, found = 592.0539; the ee value was 88%, t_R (major) = 13.4 min, t_R (minor) = 20.6 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(R)-1-(3-Bromo-4-hydroxyphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4p)

47.7 mg, 75% yield, 10:1 dr; $[\alpha]_D^{25} = -16.4$ (c 0.8, CHCl_3), white foam, $R_f = 0.36$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.5$ Hz, 1H), 7.66 (dd, $J = 16.8, 8.8$ Hz, 2H), 7.48 – 7.39 (m, 3H), 7.38 – 7.30 (m, 2H), 7.16 (dd, $J = 8.9, 2.1$ Hz, 2H), 6.91 – 6.87 (m, 3H), 6.69 (ddd, $J = 7.9, 5.2, 3.9$ Hz, 1H), 6.61 (d, $J = 8.7$ Hz, 1H), 6.23 (d, $J = 3.6$ Hz, 1H), 6.04 (d, $J = 4.4$ Hz, 1H), 5.40 (s, 1H), 1.94 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.8, 150.8, 141.8, 139.6, 138.0, 134.9, 132.9, 132.5, 132.5, 132.5, 132.4, 131.2, 130.8, 129.7, 129.2, 128.6, 128.3, 127.79, 127.75, 127.5, 126.6, 126.3, 114.6, 111.4, 109.4, 106.6, 68.2, 30.0, 13.8. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{BrINO}_2$ $[\text{M}+\text{H}]^+ = 636.0030$, found = 636.0023; the ee value was 63%, t_R (major) = 12.9 min, t_R (minor) = 16.7 min (Chiralpak IF, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).

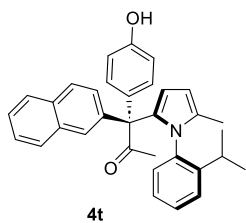
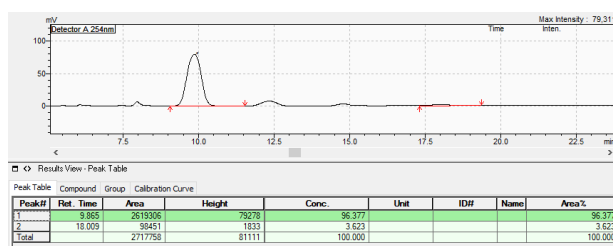
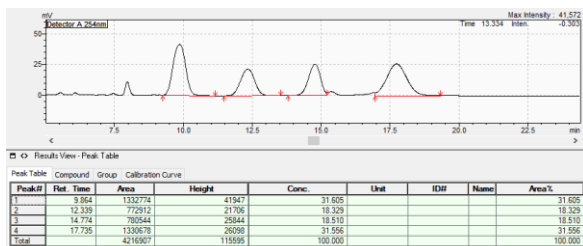




4q

(R)-1-(4-hydroxy-3,5-dimethylphenyl)-1-(1-((R)-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4q)

40.4 mg, 69% yield, 4:1 dr; $[\alpha]_D^{25} = -14.3$ (c 0.9, CHCl_3), white foam, $R_f = 0.27$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.37 (dq, $J = 7.2, 1.6$ Hz, 4H), 7.25 (d, $J = 2.6$ Hz, 2H), 6.98 – 6.93 (m, 2H), 6.71 (s, 2H), 6.23 (d, $J = 3.6$ Hz, 1H), 6.01 (d, $J = 3.6$ Hz, 1H), 4.54 (s, 1H), 2.01 (s, 6H), 1.90 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.8, 141.1, 138.2, 137.1, 131.9, 131.7, 131.0, 130.8, 130.2, 129.1, 128.4, 127.7, 127.4, 126.5, 126.4, 126.4, 126.1, 125.2, 124.9, 124.8, 121.1, 120.6, 110.9, 105.2, 67.8, 28.6, 15.1, 12.8. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{29}\text{INO}_2$ $[\text{M}+\text{H}]^+ = 586.1238$, found = 586.1240; the ee value was 93%, t_R (major) = 9.9 min, t_R (minor) = 18.0 min (Chiralpak IF, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).

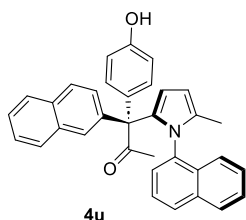
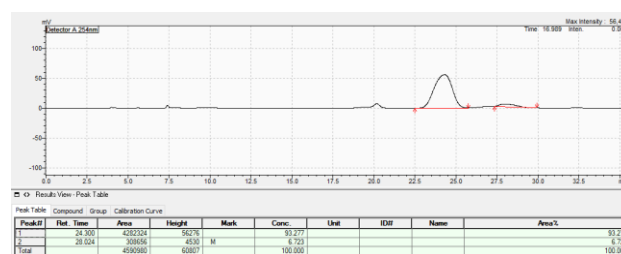
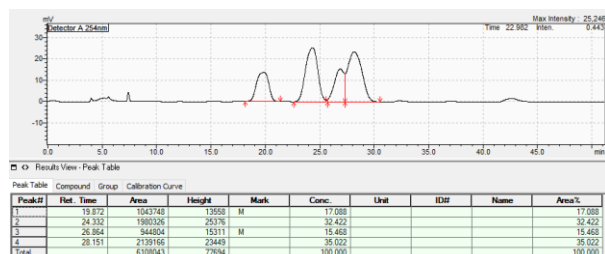


4t

(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-isopropylphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4t)

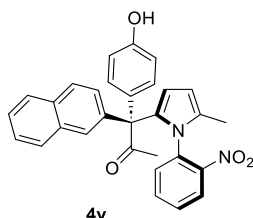
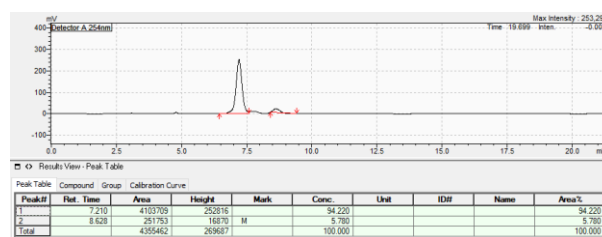
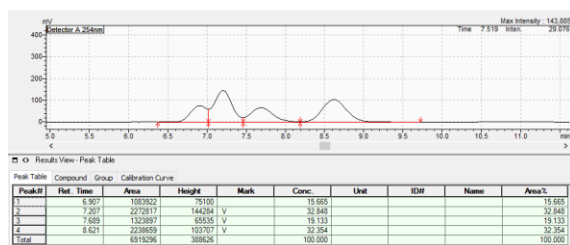
37.4 mg, 79% yield, 20:1 dr; $[\alpha]_D^{25} = -21.6$ (c 1.0, CHCl_3), white foam, $R_f = 0.35$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.0$ Hz, 1H), 7.58 (s, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.46 (s, 1H), 7.42 – 7.28 (m, 3H), 7.05 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.00 – 6.92 (m, 3H),

6.63 (d, $J = 8.8$ Hz, 2H), 6.52 – 6.45 (m, 1H), 6.08 (d, $J = 3.7$ Hz, 1H), 5.93 (d, $J = 3.5$ Hz, 1H), 2.39 (dt, $J = 14.8, 7.4$ Hz, 1H), 1.77 (s, 3H), 1.71 (s, 3H), 0.92 (d, $J = 6.8$ Hz, 3H), 0.78 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.3, 154.8, 148.0, 138.9, 137.4, 134.2, 133.3, 132.8, 132.3, 132.2, 129.9, 129.0, 129.0, 128.4, 128.3, 127.2, 126.8, 126.2, 125.8, 124.97, 114.7, 113.3, 105.5, 68.8, 30.0, 27.6, 25.0, 23.1, 13.7. HRMS (ESI) m/z calcd for $\text{C}_{33}\text{H}_{31}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+ = 496.2247$, found = 496.2245; the ee value was 87%, t_R (major) = 24.3 min, t_R (minor) = 28.0 min (Chiralpak IG, $\lambda = 254$ nm, 2.5% *i*-PrOH/Hexane, flow rate = 0.8 mL/min).



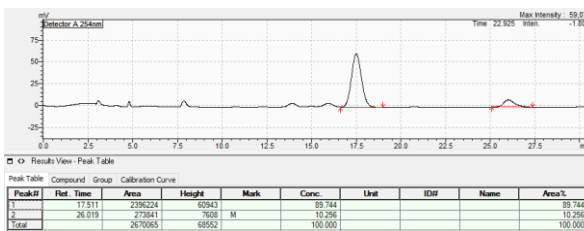
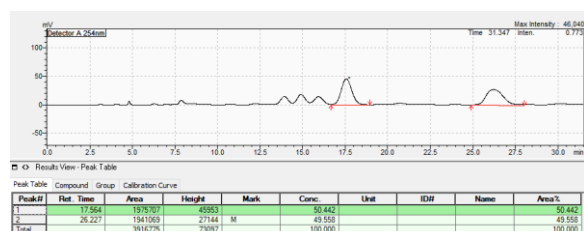
(S)-1-(4-Hydroxyphenyl)-1-(5-methyl-1-((R)-naphthalen-1-yl)-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4u)

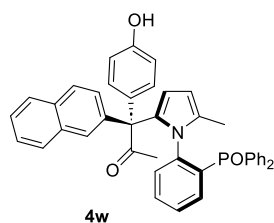
36.1 mg, 75% yield, 14:1 dr; $[\alpha]_D^{25} = -29.8$ (c 1.0, CHCl_3), white foam, $R_f = 0.32$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.2$ Hz, 1H), 7.44 (d, $J = 7.3$ Hz, 1H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 4H), 7.06 (d, $J = 1.9$ Hz, 1H), 7.03 (d, $J = 8.8$ Hz, 2H), 6.85 (s, 1H), 6.75 (t, $J = 8.0$ Hz, 1H), 6.63 – 6.55 (m, 1H), 6.44 (d, $J = 8.9$ Hz, 2H), 6.20 (d, $J = 3.3$ Hz, 1H), 6.09 (d, $J = 8.3$ Hz, 1H), 6.04 (d, $J = 3.2$ Hz, 1H), 1.86 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 154.7, 136.7, 135.3, 133.5, 132.3, 132.2, 131.8, 131.7, 131.1, 128.9, 128.8, 128.7, 128.1, 127.8, 127.2, 127.1, 126.6, 125.8, 125.8, 125.6, 125.0, 124.4, 122.8, 114.5, 110.7, 105.4, 69.3, 29.1, 12.8. HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{27}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+ = 504.1934$, found = 504.1937; the ee value was 88%, t_R (major) = 7.2 min, t_R (minor) = 8.6 min (Chiralpak IG, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(5-methyl-1-((R)-2-nitrophenyl)-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4v)

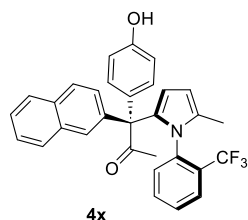
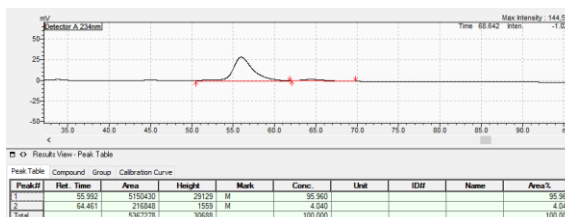
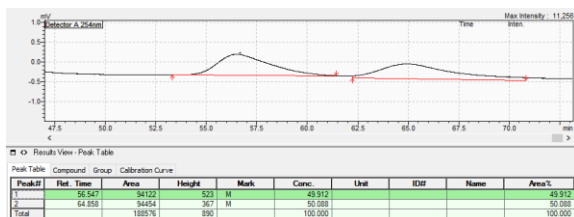
38.6 mg, 81% yield, 18:1 dr; $[\alpha]_D^{25} = -21.0$ (c 1.0, CHCl_3), white foam, $R_f = 0.26$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (td, $J = 8.2, 1.5$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.51 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.45 – 7.31 (m, 4H), 7.25 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.17 – 7.11 (m, 1H), 7.05 (td, $J = 7.6, 1.6$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.66 – 6.56 (m, 3H), 6.43 (dd, $J = 7.8, 1.5$ Hz, 1H), 5.99 (d, $J = 3.6$ Hz, 1H), 5.96 (d, $J = 1.0$ Hz, 1H), 1.83 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.9, 155.0, 146.3, 137.8, 134.0, 133.9, 133.2, 132.8, 132.8, 132.4, 131.5, 131.3, 128.7, 128.5, 128.2, 127.5, 127.4, 126.5, 126.1, 125.3, 115.1, 112.9, 106.1, 68.8, 30.1, 13.1. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 499.1628$, found = 499.1629; the ee value was 80%, t_R (major) = 17.5 min, t_R (minor) = 26.0 min (Chiralpak IG, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(S)-1-(1-((R)-2-(Diphenylphosphoryl)phenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4w)

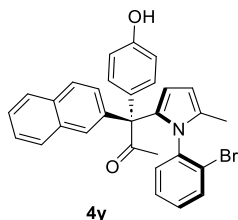
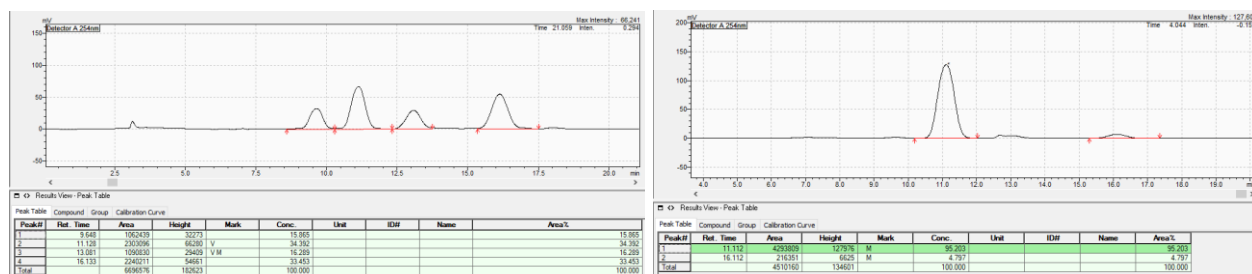
44.2 mg, 70% yield, >20:1 dr; $[\alpha]_D^{25} = -110.5$ (c 1.0, CHCl_3), white solid, $R_f = 0.30$ (hexane/ethyl acetate 1:2). ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.87 (m, 2H), 7.72 – 7.61 (m, 3H), 7.60 – 7.52 (m, 2H), 7.52 – 7.26 (m, 9H), 7.23 (td, $J = 7.7, 3.0$ Hz, 5H), 7.06 (tt, $J = 7.6, 1.5$ Hz, 1H), 6.84 (tt, $J = 7.5, 1.5$ Hz, 1H), 6.70 (t, $J = 2.0$ Hz, 4H), 5.64 (dd, $J = 7.5, 4.6$ Hz, 1H), 5.46 (d, $J = 3.2$ Hz, 1H), 5.24 (d, $J = 3.6$ Hz, 1H), 1.80 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.3, 155.7, 142.9, 140.8, 135.1, 132.8, 132.7, 132.6, 132.5, 131.6, 131.5, 131.2, 131.1, 129.2, 128.5, 128.3, 128.2, 128.1, 127.6, 127.5, 127.3, 126.6, 126.2, 125.9, 115.3, 114.2, 105.9, 69.0, 31.6, 13.7. ^{31}P NMR (162 MHz, CDCl_3) δ 29.4. HRMS (ESI) m/z calcd for $\text{C}_{42}\text{H}_{35}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+ = 632.2349$, found = 632.2351; the ee value was 92%, t_R (major) = 56.0 min, t_R (minor) = 64.5 min (Chiralpak IG, $\lambda = 254$ nm, 20% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(5-methyl-1-((R)-2-(trifluoromethyl)phenyl)-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4x)

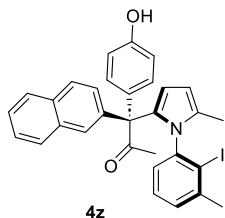
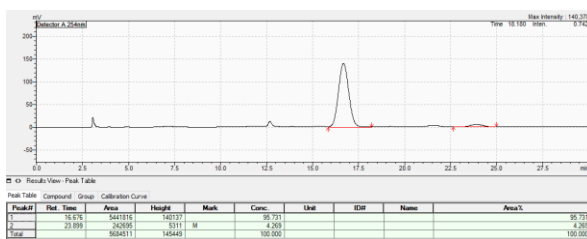
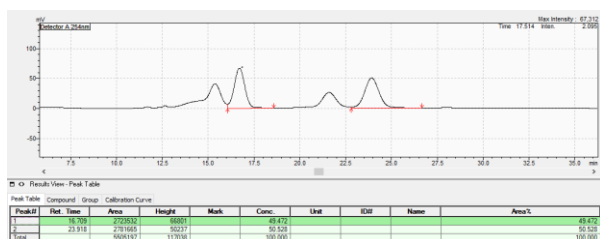
41.4 mg, 83% yield, >20:1 dr; $[\alpha]_D^{25} = -50.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.32$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.33 (m, 2H), 7.31 (s, 1H), 7.26 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.23 – 7.16 (m, 2H), 7.05 (t, $J = 8.4$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 2H), 6.60 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J =$

7.9 Hz, 1H), 5.98 (d, J = 3.6 Hz, 1H), 5.91 (d, J = 4.4 Hz, 1H), 5.26 (s, 1H), 1.85 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 154.6, 138.2, 136.6, 135.3 (d, J = 31.4 Hz), 134.1, 133.1, 132.8, 132.0, 131.8, 131.76, 130.9, 129.6 (d, J = 30.4 Hz), 128.8, 128.3, 128.2, 127.4, 127.3, 126.4, 126.0, 125.4 (d, J = 258.7 Hz), 114.7, 112.7, 105.8, 69.0, 30.1, 12.7. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{24}\text{F}_3\text{NNaO}_2$ $[\text{M}+\text{Na}]^+ = 522.1651$, found = 522.1654; the ee value was 90%, t_{R} (major) = 11.1 min, t_{R} (minor) = 16.1 min (Chiralpak IG, λ = 254 nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



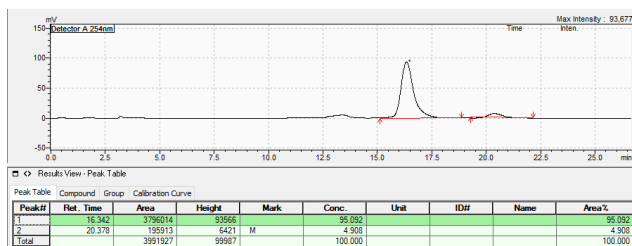
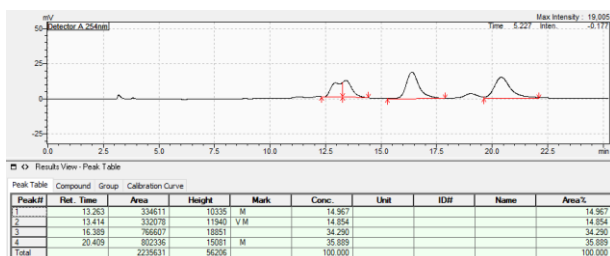
(S)-1-(1-((R)-2-Bromophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4y)

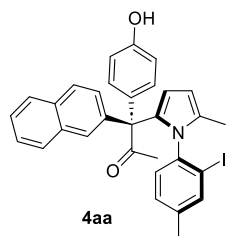
44.9 mg, 88% yield, >20:1 dr; $[\alpha]_D^{25} = -46.5$ (c 1.0, CHCl_3), white foam, R_f = 0.32 (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.24 (dd, J = 8.7, 2.0 Hz, 1H), 7.19 (d, J = 2.0 Hz, 1H), 7.08 (d, J = 8.9 Hz, 2H), 6.98 – 6.92 (m, 3H), 6.85 (ddd, J = 7.5, 5.7, 3.7 Hz, 1H), 6.58 (d, J = 8.9 Hz, 2H), 6.14 (d, J = 3.6 Hz, 1H), 5.98 (d, J = 4.4 Hz, 1H), 1.91 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 154.7, 138.5, 137.5, 132.9, 132.8, 132.8, 132.8, 132.4, 132.2, 132.0, 131.4, 129.2, 129.2, 128.9, 128.2, 127.4, 127.4, 126.9, 126.4, 126.2, 125.9, 114.6, 111.7, 105.8, 69.0, 29.5, 13.2. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{BrNNaO}_2$ $[\text{M}+\text{Na}]^+ = 532.0883$, found = 532.088; the ee value was 91%, t_{R} (major) = 16.7 min, t_{R} (minor) = 23.9 min (Chiralpak IG, λ = 254 nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-3-methylphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4z)

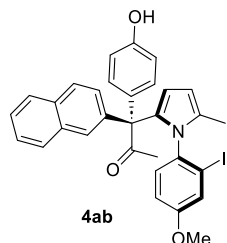
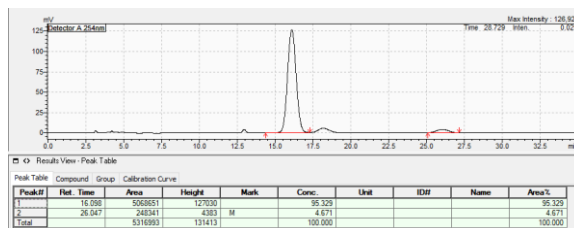
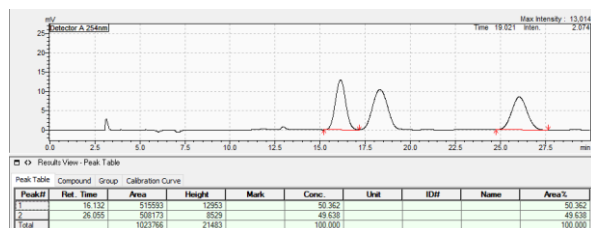
49.7 mg, 87% yield, 16:1 dr; $[\alpha]_D^{25} = -60.9$ (c 1.0, CHCl_3), white foam, $R_f = 0.34$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.8$ Hz, 1H), 7.57 (d, $J = 8.7$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.43 – 7.33 (m, 3H), 7.23 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.10 (d, $J = 8.6$ Hz, 3H), 6.95 – 6.89 (m, 2H), 6.83 (dd, $J = 6.7$, 2.3 Hz, 1H), 6.56 (d, $J = 8.8$ Hz, 2H), 6.18 (d, $J = 3.6$ Hz, 1H), 5.98 (d, $J = 4.3$ Hz, 1H), 1.88 (s, 3H), 1.81 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 154.7, 143.3, 142.2, 137.3, 132.7, 132.3, 132.2, 132.2, 131.0, 129.7, 129.2, 128.6, 128.4, 128.3, 127.4, 127.3, 126.2, 125.9, 114.5, 111.8, 110.5, 106.0, 69.00, 29.5, 29.1, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 594.0900$, found = 594.0889; the ee value was 90%, t_R (major) = 16.3 min, t_R (minor) = 20.4 min (Chiralpak IF, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-4-methylphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4aa)

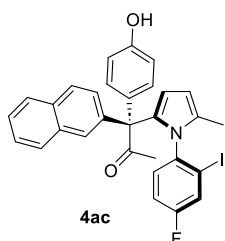
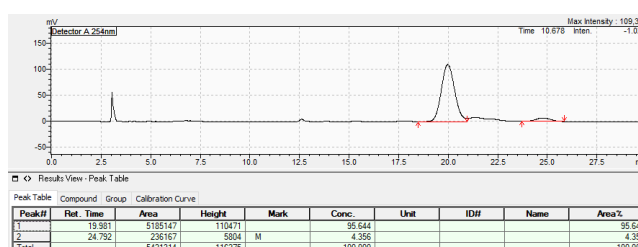
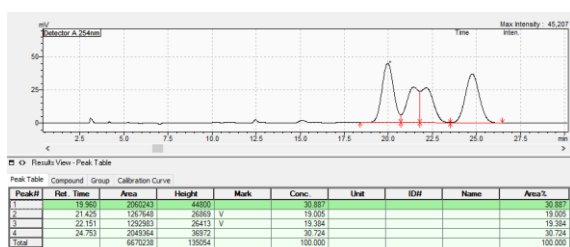
46.9 mg, 82% yield, 18:1 dr; $[\alpha]_D^{25} = -53.2$ (c 1.0, CHCl_3), white foam, $R_f = 0.35$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.37 (td, $J = 7.5, 1.5$ Hz, 2H), 7.28 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.16 (s, 1H), 7.09 (d, $J = 8.8$ Hz, 2H), 7.06 (s, 1H), 6.77 (d, $J = 0.9$ Hz, 2H), 6.60 (d, $J = 8.8$ Hz, 2H), 6.13 (d, $J = 3.6$ Hz, 1H), 5.96 (d, $J = 3.6$ Hz, 1H), 2.06 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.7, 154.7, 139.8, 139.3, 137.7, 132.8, 132.7, 132.5, 132.4, 132.2, 131.5, 130.7, 129.6, 128.9, 128.4, 128.2, 127.5, 127.4, 126.2, 125.9, 114.7, 112.0, 106.1, 69.0, 29.6, 20.4, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 594.0900$, found = 594.0889; the ee value was 91%, t_R (major) = 16.1 min, t_R (minor) = 26.0 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-4-methoxyphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4ab)

48.2 mg, 82% yield, 15:1 dr; $[\alpha]_D^{25} = -38.7$ (c 1.0, CHCl_3), white foam, $R_f = 0.26$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.9$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.51

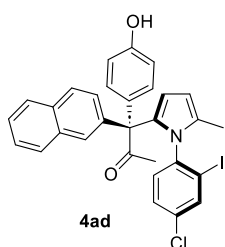
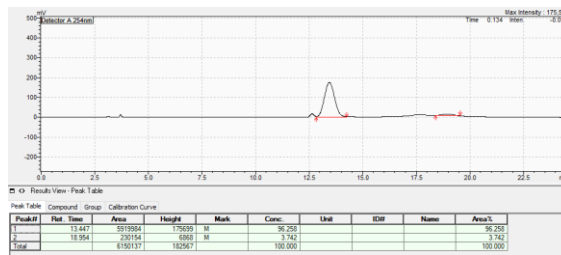
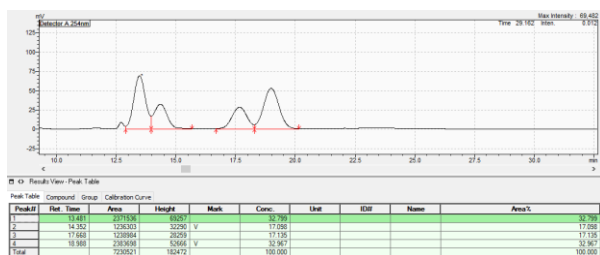
(d, $J = 7.9$ Hz, 1H), 7.42 – 7.34 (m, 2H), 7.28 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.11 (d, $J = 8.9$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 1H), 6.73 (d, $J = 2.8$ Hz, 1H), 6.61 (d, $J = 8.9$ Hz, 2H), 6.52 (dd, $J = 8.8, 2.9$ Hz, 1H), 6.13 (d, $J = 3.6$ Hz, 1H), 5.96 (d, $J = 2.8$ Hz, 1H), 3.55 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 158.6, 154.7, 137.8, 134.7, 132.9, 132.9, 132.6, 132.5, 132.3, 131.6, 131.3, 129.6, 128.9, 128.2, 127.5, 127.4, 126.2, 125.9, 123.9, 114.7, 113.6, 111.9, 106.0, 103.4, 69.0, 55.5, 29.6, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{27}\text{INO}_3$ $[\text{M}+\text{H}]^+ = 588.1030$, found = 588.1025; the ee value was 91%, t_R (major) = 20.0 min, t_R (minor) = 24.8 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(1-((R)-4-Fluoro-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4ac)

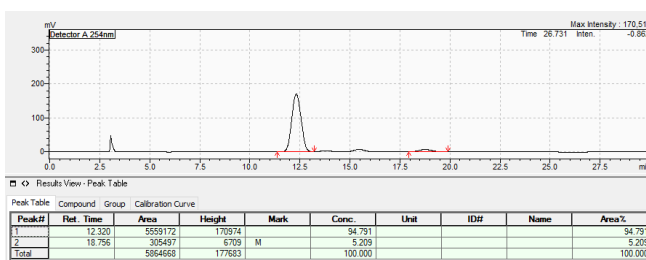
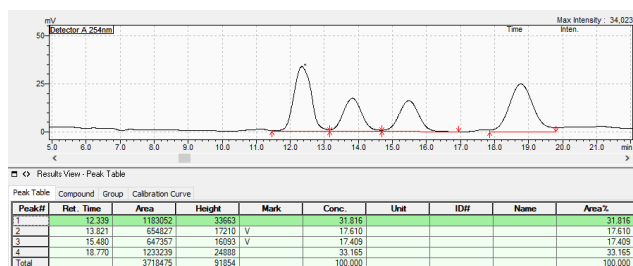
48.9 mg, 85% yield, 17:1 dr; $[\alpha]_D^{25} = -42.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.32$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.9$ Hz, 1H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.54 (d, $J = 8.8$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.26 (d, $J = 1.9$ Hz, 1H), 7.21 (s, 1H), 7.08 (d, $J = 8.9$ Hz, 2H), 6.98 (dd, $J = 7.8, 2.8$ Hz, 1H), 6.84 (dd, $J = 8.8, 5.6$ Hz, 1H), 6.76 – 6.67 (m, 1H), 6.62 (d, $J = 8.9$ Hz, 2H), 6.12 (d, $J = 3.6$ Hz, 1H), 5.97 (d, $J = 4.5$ Hz, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 160.7 (d, $J = 253.1$ Hz), 154.8, 137.7, 133.0, 132.9, 132.4, 132.3, 132.3, 131.9, 131.8, 131.4, 129.2, 129.1, 128.1, 127.7, 127.5, 126.4, 126.2, 126.0, 114.8, 114.5 (d, $J = 21.9$ Hz), 112.2, 106.4, 103.2 (d, $J = 8.5$ Hz), 69.0, 29.6, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{FINO}_2$ $[\text{M}+\text{H}]^+ = 576.0830$, found = 576.0826; the ee value was 93%, t_R (major) = 13.4

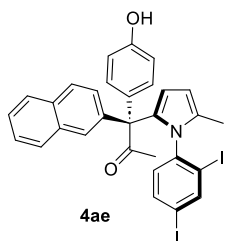
min, t_R (minor) = 19.0 min (Chiralpak IG, λ = 254 nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(1-((R)-4-Chloro-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4ad)

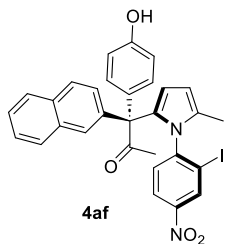
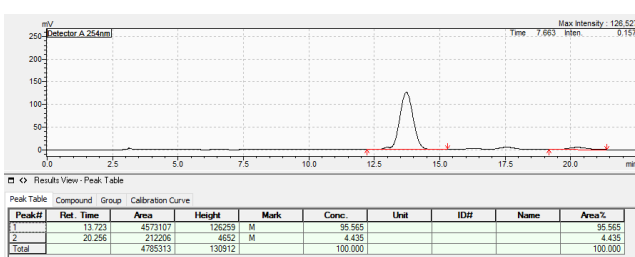
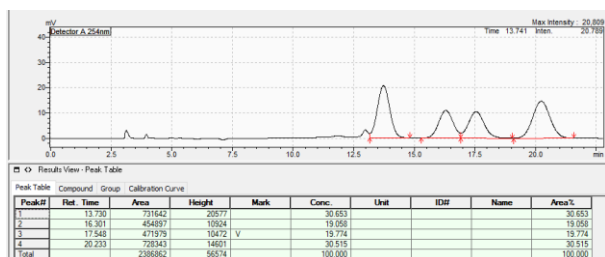
53.9 mg, 91% yield, 17:1 dr; $[\alpha]_D^{25} = -45.7$ (c 1.0, CHCl_3), white foam, $R_f = 0.35$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 7.1$ Hz, 1H), 7.64 (d, $J = 8.7$ Hz, 1H), 7.53 (d, $J = 9.0$ Hz, 1H), 7.41 (tt, $J = 7.1, 5.2$ Hz, 2H), 7.30 – 7.22 (m, 2H), 7.18 (d, $J = 4.5$ Hz, 1H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.98 (dd, $J = 8.5, 2.4$ Hz, 1H), 6.80 (d, $J = 8.5$ Hz, 1H), 6.63 (d, $J = 8.8$ Hz, 2H), 6.11 (d, $J = 3.6$ Hz, 1H), 5.97 (d, $J = 3.6$ Hz, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 154.8, 140.9, 138.6, 137.5, 133.8, 133.0, 132.8, 132.4, 132.3, 132.2, 131.7, 131.3, 129.2, 129.0, 128.2, 127.8, 127.7, 127.5, 126.4, 126.2, 114.8, 112.3, 106.5, 103.5, 69.0, 29.7, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{ClINO}_2$ $[\text{M}+\text{H}]^+ = 592.0535$, found = 592.0535; the ee value was 90%, t_R (major) = 13.4 min, t_R (minor) = 19.0 min (Chiralpak IG, λ = 254 nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





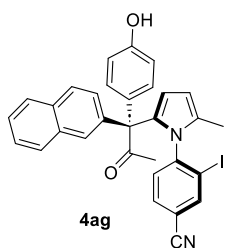
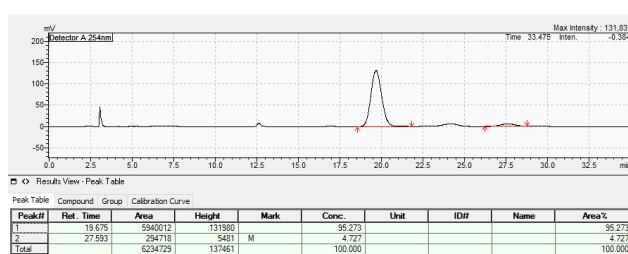
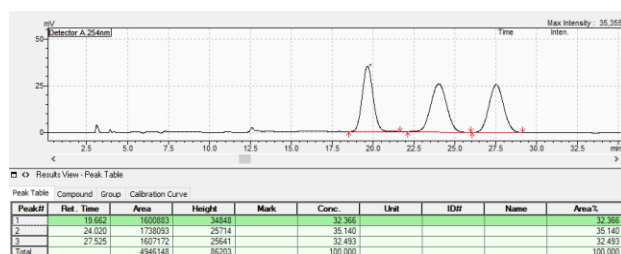
(S)-1-(1-((R)-2,4-Diiodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4ae)

48.5 mg, 71% yield, 18:1 dr; $[\alpha]_D^{25} = -49.6$ (c 1.0, CHCl_3), white foam, $R_f = 0.33$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.71 (m, 1H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 – 7.40 (m, 2H), 7.31 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.25 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.14 (s, 1H), 7.09 (d, $J = 8.8$ Hz, 2H), 6.63 (dd, $J = 8.5, 1.1$ Hz, 3H), 6.11 (d, $J = 3.6$ Hz, 1H), 5.96 (d, $J = 4.4$ Hz, 1H), 5.27 (s, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 154.8, 146.9, 142.1, 137.4, 136.9, 132.9, 132.8, 132.5, 132.4, 132.3, 132.1, 131.2, 129.3, 128.9, 128.3, 127.8, 127.4, 126.4, 126.3, 114.8, 112.3, 106.5, 104.5, 93.8, 69.0, 29.7, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{I}_2\text{NNaO}_2$ $[\text{M}+\text{Na}]^+ = 705.9710$, found = 705.9710; the ee value was 91%, t_R (major) = 13.7 min, t_R (minor) = 20.3 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-4-nitrophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4af)

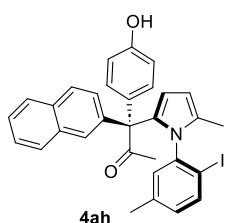
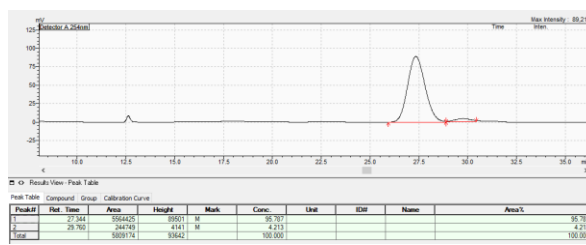
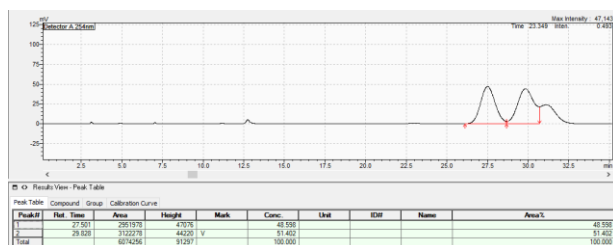
51.2 mg, 85% yield, 18:1 dr; $[\alpha]_D^{25} = -52.4$ (c 1.0, CHCl_3), white foam, $R_f = 0.21$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 2.6$ Hz, 1H), 7.83 (dd, $J = 8.7, 2.6$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.7$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.45 – 7.34 (m, 2H), 7.28 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.19 (d, $J = 1.9$ Hz, 1H), 7.06 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 1H), 6.65 (d, $J = 8.9$ Hz, 2H), 6.10 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 4.5$ Hz, 1H), 5.36 (s, 1H), 1.89 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.9, 155.0, 146.3, 137.3, 134.0, 133.2, 132.7, 132.3, 132.2, 132.0, 131.29, 131.28, 129.0, 128.7, 128.0, 127.9, 127.5, 126.7, 126.5, 122.6, 115.0, 113.3, 107.3, 103.1, 68.0, 30.0, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{IN}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+ = 625.0595$, found = 625.0598; the ee value was 90%, t_R (major) = 19.7 min, t_R (minor) = 27.6 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(R)-4-(2-((S)-1-(4-Hydroxyphenyl)-1-(naphthalen-2-yl)-2-oxopropyl)-5-methyl-1H-pyrrol-1-yl)-3-iodobenzonitrile (4ag)

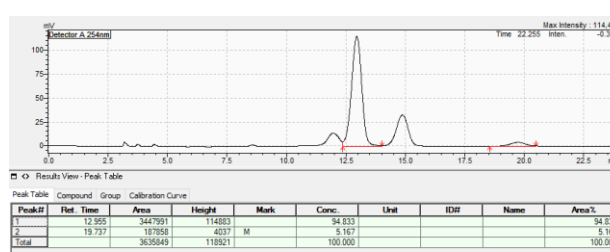
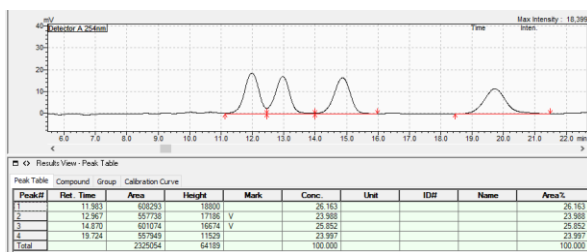
48.3 mg, 83% yield, 17:1 dr; $[\alpha]_D^{25} = -65.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.23$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.72 (m, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.57 – 7.48 (m, 2H), 7.48 – 7.39 (m, 2H), 7.27 (td, $J = 9.2, 8.7, 1.9$ Hz, 2H), 7.05 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.2$ Hz, 1H), 6.65 (d, $J = 8.9$ Hz, 2H), 6.10 (d, $J = 3.6$ Hz, 1H), 5.98 (d, $J = 4.5$ Hz, 1H), 5.46 (s, 1H), 1.88 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.7, 155.0, 147.1, 142.3, 137.3, 133.1, 132.7, 132.3, 132.2, 132.0, 131.6, 131.3, 131.2, 129.0, 128.8, 128.1, 128.0, 127.5, 126.7, 126.5, 115.0, 113.0, 112.6, 107.2, 103.6, 68.9, 29.9, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{IN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+ = 605.0696$, found = 605.0696; the ee value was 92%, t_R (major) =

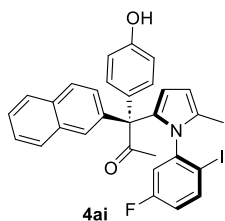
27.3 min, t_R (minor) = 29.8 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-5-methylphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4ah)

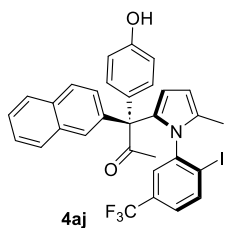
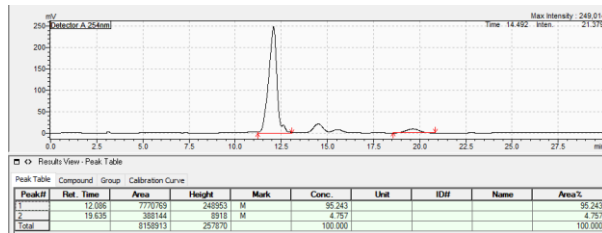
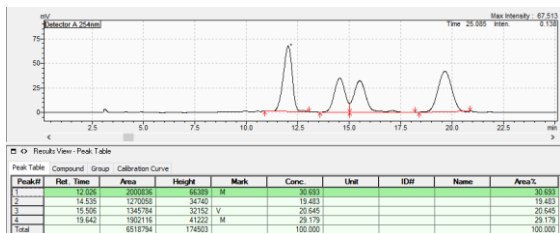
44.6 mg, 78% yield, 3:1 dr; $[\alpha]_D^{25} = -38.1$ (c 1.0, CHCl_3), white foam, $R_f = 0.35$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.8$ Hz, 1H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.55 (d, $J = 7.7$ Hz, 1H), 7.45 – 7.38 (m, 4H), 7.30 – 7.23 (m, 3H), 7.06 (d, $J = 8.7$ Hz, 3H), 6.61 (d, $J = 8.8$ Hz, 2H), 6.36 (s, 1H), 6.15 (d, $J = 3.6$ Hz, 1H), 5.97 (d, $J = 4.3$ Hz, 1H), 1.92 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 154.7, 141.6, 138.8, 138.2, 137.9, 132.8, 132.6, 132.4, 132.3, 132.2, 132.0, 131.9, 129.9, 129.2, 129.0, 128.4, 128.3, 127.4, 127.3, 126.3, 125.9, 114.9, 114.7, 112.3, 106.2, 99.0, 68.8, 29.7, 20.5, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{INaO}_2$ $[\text{M}+\text{Na}]^+ = 594.0900$, found = 594.0897; the ee value was 90%, t_R (major) = 13.0 min, t_R (minor) = 19.7 min (Chiralpak IA, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(S)-1-(1-((R)-5-Fluoro-2-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4ai)

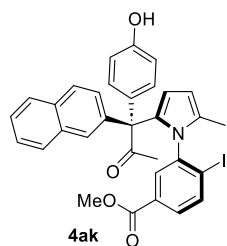
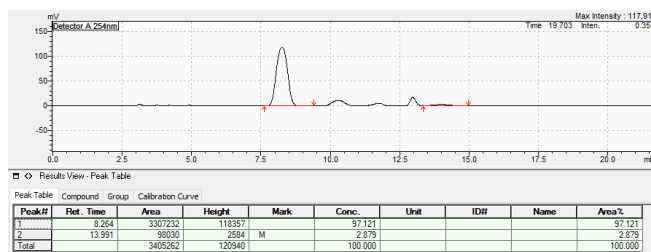
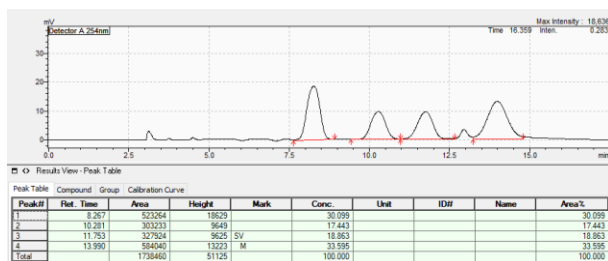
50.0 mg, 87% yield, 8:1 dr; $[\alpha]_D^{25} = -29.1$ (c 1.0, CHCl_3), white foam, $R_f = 0.37$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.9$ Hz, 1H), 7.63 (d, $J = 9.3$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.42 – 7.34 (m, 2H), 7.30 – 7.21 (m, 3H), 7.07 (d, $J = 8.9$ Hz, 2H), 6.63 (d, $J = 8.9$ Hz, 2H), 6.58 – 6.44 (m, 2H), 6.08 (d, $J = 3.6$ Hz, 1H), 5.97 (d, $J = 4.5$ Hz, 1H), 5.30 (s, 1H), 1.90 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 162.0 (d, $J = 248.9$ Hz), 154.8, 143.5 (d, $J = 10.2$ Hz), 139.7 (d, $J = 8.4$ Hz), 137.7, 132.9, 132.8, 132.3, 132.2, 132.0, 131.5, 129.0, 128.9, 128.2, 127.7, 126.4, 126.1, 119.1 (d, $J = 23.6$ Hz), 116.4 (d, $J = 21.6$ Hz), 115.2, 114.9, 112.6, 106.6, 96.7 (d, $J = 3.8$ Hz), 69.0, 29.8, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{FINO}_2$ $[\text{M}+\text{H}]^+ = 576.0830$, found = 576.0825; the ee value was 91%, t_R (major) = 12.1 min, t_R (minor) = 19.6 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-5-(trifluoromethyl)phenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4aj)

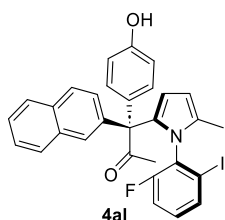
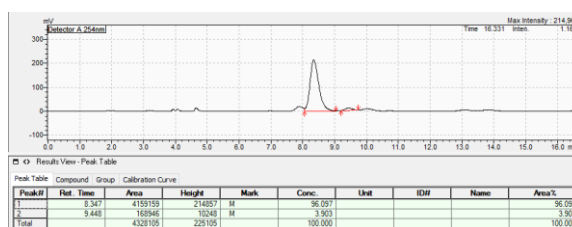
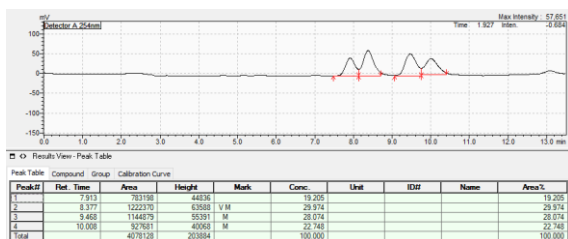
51.9 mg, 83% yield, 8:1 dr; $[\alpha]_D^{25} = -46.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.35$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.52 (d, $J = 7.7$ Hz, 1H), 7.48 – 7.36 (m, 3H), 7.27 (d, $J = 10.7$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 3H), 6.91

(d, $J = 9.8$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 6.09 (d, $J = 3.7$ Hz, 1H), 5.98 (d, $J = 4.3$ Hz, 1H), 5.22 (s, 1H), 1.88 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 154.9, 139.9, 137.6, 134.3 (d, $J = 31.9$ Hz), 133.3, 132.8, 132.3, 132.2, 131.9, 131.6, 128.9, 128.7, 128.2, 127.8, 127.4, 126.4, 126.2, 126.6 (d, $J = 255.6$ Hz), 125.4 (d, $J = 30.5$ Hz), 115.1, 113.0, 106.8, 68.9, 29.9, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{23}\text{F}_3\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 648.0618$, found = 648.0617; the ee value was 94%, t_R (major) = 8.3 min, t_R (minor) = 14.0 min (Chiralpak IG, $\lambda = 254$ nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



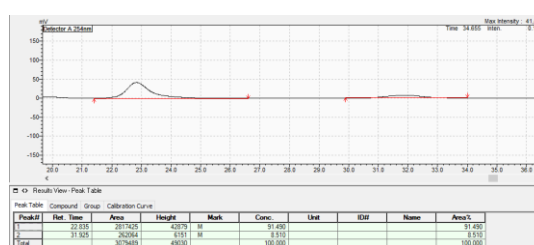
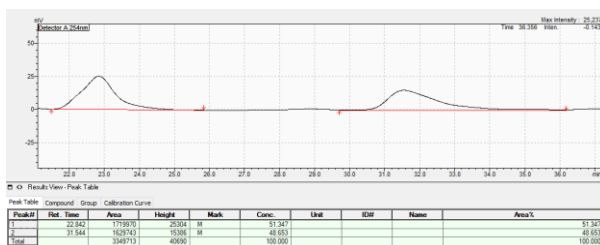
methyl (R)-3-(2-((S)-1-(4-Hydroxyphenyl)-1-(naphthalen-2-yl)-2-oxopropyl)-5-methyl-1H-pyrrol-1-yl)-4-iodobenzoate (4ak)

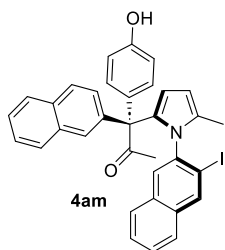
41.9 mg, 68% yield, 10:1 dr; $[\alpha]_D^{25} = -27.5$ (c 1.0, CHCl_3), white foam, $R_f = 0.26$ (hexane/ethyl acetate 4:1). ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.70 (m, 2H), 7.67 – 7.59 (m, 2H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.47 – 7.34 (m, 5H), 7.30 – 7.21 (m, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.56 (d, $J = 8.7$ Hz, 2H), 6.18 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 3.5$ Hz, 1H), 3.55 (s, 3H), 1.90 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.0, 166.0, 154.8, 142.5, 139.6, 138.2, 132.9, 132.4, 132.1, 132.1, 131.8, 131.5, 129.8, 129.7, 129.6, 129.2, 128.8, 128.3, 127.6, 127.4, 126.4, 126.1, 115.5, 114.9, 112.4, 110.1, 106.6, 68.6, 52.3, 29.8, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{26}\text{INNaO}_4$ $[\text{M}+\text{Na}]^+ = 638.0799$, found = 638.0800; the ee value was 92%, t_R (major) = 8.3 min, t_R (minor) = 9.4 min (Chiralpak IB, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(1-((R)-2-Fluoro-6-iodophenyl)-5-methyl-1H-pyrrol-2-yl)-1-(4-hydroxyphenyl)-1-(naphthalen-2-yl)propan-2-one (4al)

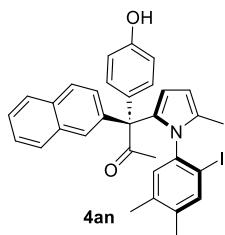
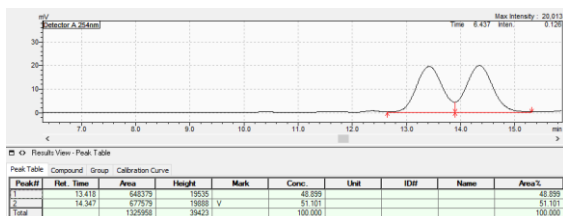
42.6 mg, 74% yield, 10:1 dr; $[\alpha]_D^{25} = -16.3$ (c 1.0, CHCl_3), white foam, $R_f = 0.30$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.56 (m, 4H), 7.46 (d, $J = 8.7$ Hz, 2H), 7.39 – 7.31 (m, 3H), 7.20 (s, 1H), 7.12 (d, $J = 8.8$ Hz, 2H), 6.64 – 6.58 (m, 1H), 6.54 (d, $J = 7.8$ Hz, 1H), 6.49 (d, $J = 8.9$ Hz, 2H), 6.24 (d, $J = 3.6$ Hz, 1H), 6.09 (d, $J = 4.3$ Hz, 1H), 2.05 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 158.4 (d, $J = 254.7$ Hz), 154.3, 134.5, 132.8, 132.4, 130.5 (d, $J = 8.5$ Hz), 131.0, 129.0, 128.9, 128.5, 127.3, 126.9, 126.2, 125.9, 115.9 (d, $J = 21.6$ Hz), 114.6, 114.3, 107.4, 103.8, 68.0, 30.5, 13.3. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{FINaO}_2$ $[\text{M}+\text{Na}]^+ = 598.065$, found = 598.0650; the ee value was 83%, t_R (major) = 22.8 min, t_R (minor) = 31.9 min (Chiralpak IF, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).





(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-3-iodonaphthalen-2-yl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4am)

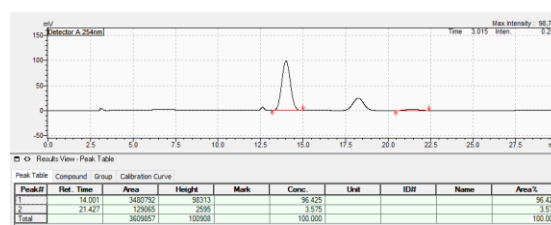
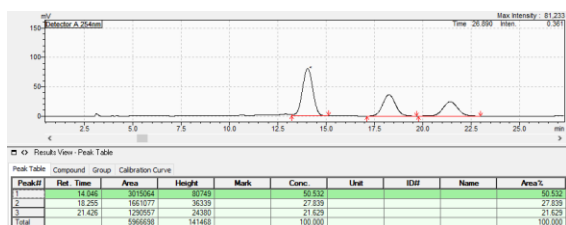
46.2 mg, 76% yield, 4:1 dr; $[\alpha]_D^{25} = -34.5$ (c 1.0, CHCl_3), white foam, $R_f = 0.32$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.58 (s, 1H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.42 – 7.35 (m, 3H), 7.33 (dd, $J = 8.0, 1.4$ Hz, 5H), 7.05 – 6.98 (m, 3H), 6.71 – 6.63 (m, 1H), 6.59 (d, $J = 8.8$ Hz, 2H), 6.08 (d, $J = 3.6$ Hz, 1H), 5.99 (d, $J = 4.4$ Hz, 1H), 1.83 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 154.7, 138.6, 138.5, 138.0, 133.6, 133.5, 132.8, 132.7, 132.3, 132.1, 132.0, 131.9, 129.9, 129.3, 128.9, 128.2, 128.0, 127.5, 127.4, 127.4, 127.2, 126.7, 126.3, 126.3, 125.9, 115.0, 114.8, 112.4, 106.1, 69.1, 29.8, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{26}\text{INaO}_2$ $[\text{M}+\text{Na}]^+ = 630.090$, found = 630.090; the ee value was 93%, t_R (major) = 22.8 min, t_R (minor) = 31.9 min (Chiralpak IG, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(S)-1-(4-Hydroxyphenyl)-1-(1-((R)-2-iodo-4,5-dimethylphenyl)-5-methyl-1H-pyrrol-2-yl)-1-(naphthalen-2-yl)propan-2-one (4an)

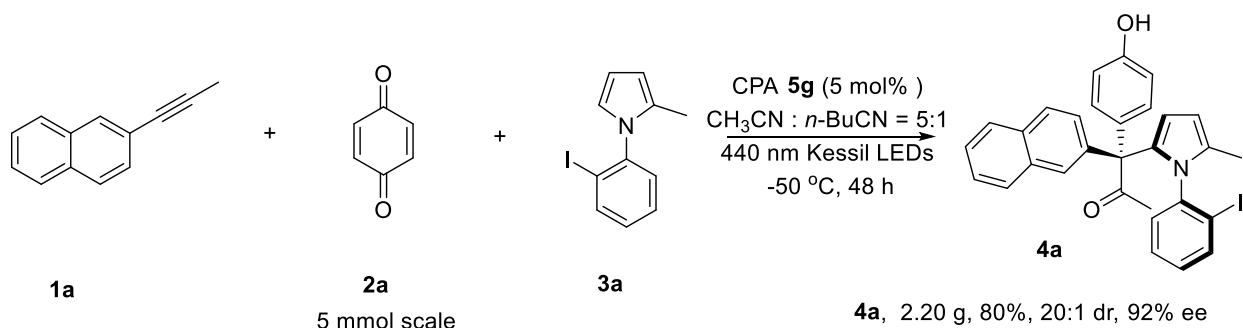
46.3 mg, 79% yield, 4:1 dr; $[\alpha]_D^{25} = -61.2$ (c 1.0, CHCl_3), white foam, $R_f = 0.34$ (hexane/ethyl acetate 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.4$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.51

(d, $J = 7.6$ Hz, 1H), 7.39 – 7.27 (m, 6H), 7.11 – 7.05 (m, 4H), 6.61 (d, $J = 8.9$ Hz, 2H), 6.29 (s, 1H), 6.14 (d, $J = 3.6$ Hz, 1H), 5.96 (d, $J = 4.4$ Hz, 1H), 1.94 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.2, 154.6, 139.7, 132.5, 132.4, 132.4, 132.2, 132.1, 129.4, 128.7, 128.2, 127.3, 127.2, 126.2, 125.8, 114.8, 114.7, 112.3, 106.0, 68.8, 29.8, 19.0, 18.7, 14.0. HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{28}\text{INNaO}_2$ $[\text{M}+\text{Na}]^+ = 608.1057$, found = 608.1065; the ee value was 93%, t_{R} (major) = 22.8 min, t_{R} (minor) = 31.9 min (Chiralpak IG, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



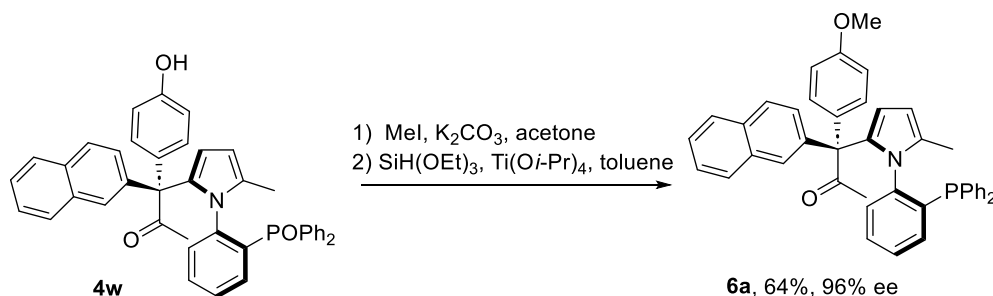
2.3. Synthetic Applications

(1) Scale-up experiment

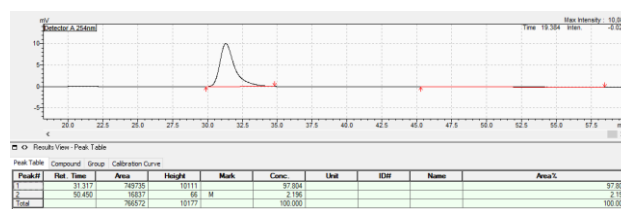
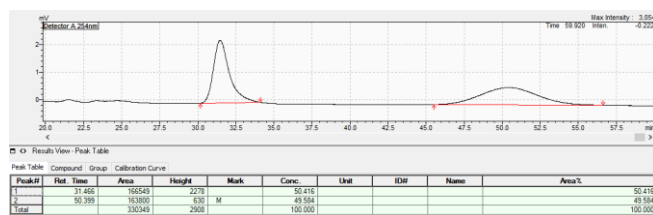


To a dried and argon-filled 100 mL round-bottom flask with a magnetic stir bar was charged with alkyne **1a** (10 mmol, 1.6 g), benzoquinone **2a** (5.0 mmol, 540 mg), N-arylpyrrole **3a** (5 mmol), CPA **5g** (188.0 mg, 5 mol%) and $\text{CH}_3\text{CN}/n$ -butyronitrile (v/v, 5:1, 40.0 mL). The mixture was then irradiated by 440 nm Kessil LEDs at -50 °C. The reaction mixture was concentrated under reduced pressure after 48 h and the residue was purified by column chromatography on silica gel to furnish the product **4a** (2.20 g, 80% yield, 92% ee).

(2) Synthesis of chiral phosphine ligand.

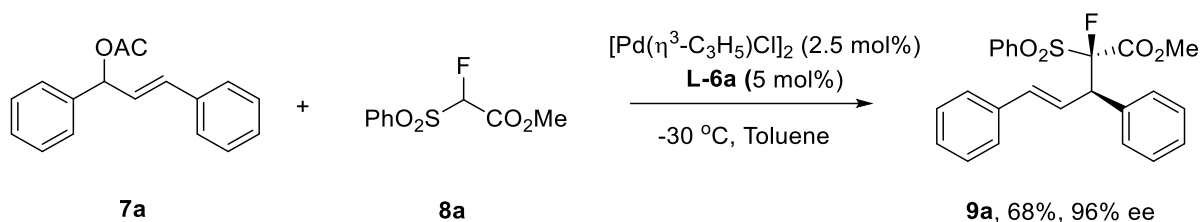


To a solution of **4w** (0.1 mmol, 63.2 mg, 1.0 eq.) in acetone (2 mL) were added MeI (0.5 mmol, 5.0 eq.). The reaction mixture was stirred for 24 h. Then water (5 mL) was added. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography on silica gel using EtOAc/petroleum ether (1:4) as eluent. To a 10 mL Schlenk tube was added resulting product, $\text{Ti(O}i\text{-Pr)}_4$ (0.03 mmol), SiH(OEt)_3 (0.3 mmol) and toluene (2 mL) under Ar at 0 °C. The reaction mixture was heated at 75 °C for 30 min. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with a small amount of saturated NaHCO_3 . The resulting suspension was filtered, dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA = 20:1 – 5:1) to give **6a** (40.3 mg, 64% yield, 96% ee). $[\alpha]_D^{25} = -90.4$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.75 (m, 2H), 7.63 – 7.58 (m, 1H), 7.56 – 7.45 (m, 4H), 7.37 – 7.20 (m, 8H), 7.13 (td, $J = 8.4, 2.5$ Hz, 3H), 7.04 – 6.98 (m, 1H), 6.82 – 6.76 (m, 3H), 6.59 (d, $J = 8.9$ Hz, 2H), 5.58 (dd, $J = 8.8, 4.7$ Hz, 1H), 5.44 (d, $J = 4.4$ Hz, 1H), 5.28 (d, $J = 3.6$ Hz, 1H), 3.63 (s, 3H), 1.79 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 158.2, 141.0, 134.6, 134.24, 134.16, 134.1, 133.6, 132.9, 132.8, 132.6, 132.5, 132.4, 131.6, 131.6, 131.5, 131.4, 131.00, 130.97, 130.9, 130.8, 129.4, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 127.3, 127.0, 126.9, 126.6, 126.2, 125.9, 114.2, 113.3, 106.0, 68.8, 55.3, 31.7, 13.5. ^{31}P NMR (162 MHz, CDCl_3) δ -19.7. HRMS (ESI) m/z calcd for $\text{C}_{43}\text{H}_{36}\text{NNaO}_2\text{P}$ $[\text{M}+\text{Na}]^+ = 652.2376$, found = 652.2379; the ee value was 96%, t_R (major) = 31.3 min, t_R (minor) = 50.5 min (Chiralpak IF, $\lambda = 254$ nm, 10% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



(2) Application of chiral phosphine **6a**.

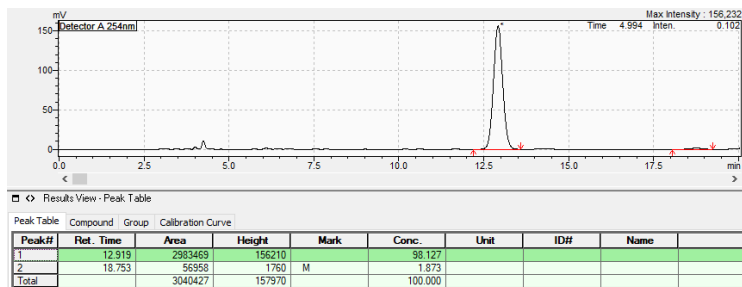
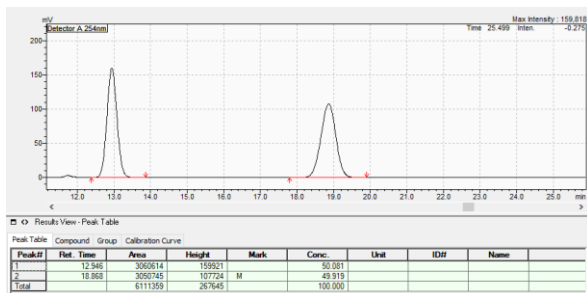
a Pd-catalyzed allylic substitution reaction



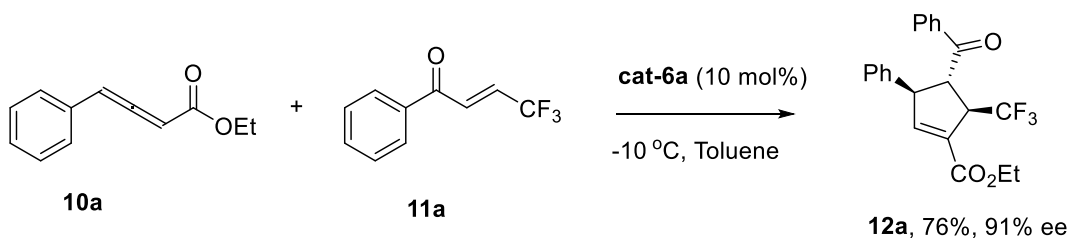
$[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ (1.8 mg, 5 μmol), chiral ligand **6a** (6.3 mg, 10 μmol), allylic ester **7a** (0.2 mmol), and toluene (5.0 mL) were added to a dry Schlenk tube filled with argon. The mixture was stirred at $-30\text{ }^\circ\text{C}$ for 45 min, and then substituted fluorinated methylene derivative **8a** (0.4 mmol, 2.0 equiv.) and Cs_2CO_3 (0.6 mmol, 3.0 equiv.) were added. The mixture was stirred for another 72 h. Upon completion of the reaction, as monitored by TLC, the mixture was filtered through Celite. The filtrate was concentrated in vacuo and purified by column chromatography to afford with 68% yield and 96% ee (The absolute configuration was determined by contrasting with the previous study⁵).

$[\alpha]_D^{25} = 13.5$ (c 1.0, EA); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.40 – 7.30 (m, 2H), 7.28 – 7.09 (m, 10H), 6.58 (d, $J = 15.8$ Hz, 1H), 6.20 (dd, $J = 15.8$, 9.3 Hz, 1H), 4.73 (dd, $J = 32.8$, 9.3 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.4 (d, $J = 25.2$ Hz), 136.9, 136.4, 135.5, 135.2, 134.7, 130.9, 130.8, 128.9, 128.8, 128.6, 128.6, 128.5, 128.09, 128.0, 126.7, 123.3, 123.2, 109.61 (d, $J = 241.2$ Hz), 52.45 (d, $J = 178.5$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -163.7.

The ee value was 96%, t_R (major) = 12.9 min, t_R (minor) = 18.8 min (Chiralpak AD-H, λ = 254 nm, 15% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



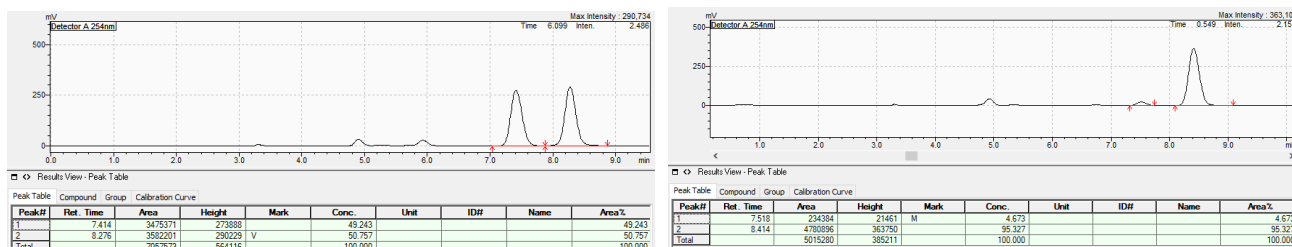
b Chiral phosphine-catalyzed formal [3+2] cycloaddition



Under Ar, a stirred solution of **11a** (0.1 mmol, 20.0 mg) and racemic **10a** (0.15 mmol, 27.2) in toluene (2 mL) was cooled to -10 °C. Subsequently, **cat-6a** (0.01 mmol, 6.3 mg) was added in one portion. The reaction mixture was stirred at -10 °C 48 h. Then the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum Hexane/EtOAc as the eluent to afford the desired cycloaddition product **12a** (29.4 mg, 76%, 91% ee) (The absolute configuration was determined by contrasting with the previous study^{6,7}).

$[\alpha]_D^{25}$ = -25.1 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, J = 8.4, 1.3 Hz, 2H), 7.49 (s, 1H), 7.35 – 7.23 (m, 5H), 7.06 – 6.97 (m, 2H), 6.78 – 6.71 (m, 1H), 4.50 (tdtd, J = 8.7, 6.9, 5.2, 1.8 Hz, 1H), 4.30 – 4.21 (m, 1H), 4.21 – 4.12 (m, 2H), 3.92 (ddd, J = 5.5, 2.7, 1.7 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.3, 163.3, 147.5, 140.2, 135.3, 133.9, 131.9, 129.2, 129.0, 128.7, 128.1, 127.9, 61.1, 51.4 (q, J = 29.2 Hz), 55.5, 54.1, 54.1, 14.1.

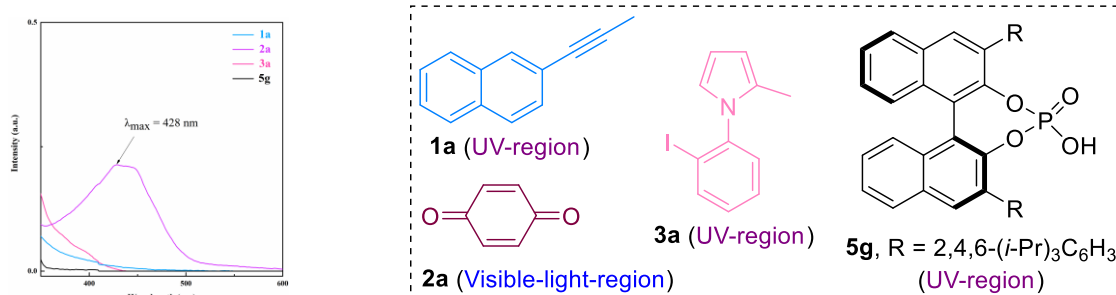
The ee value was 91%, t_R (major) = 7.5 min, t_R (minor) = 8.4 min (Chiralpak IC, λ = 254 nm, 5% *i*-PrOH/Hexane, flow rate = 1.0 mL/min).



2.4. Mechanistic Studies

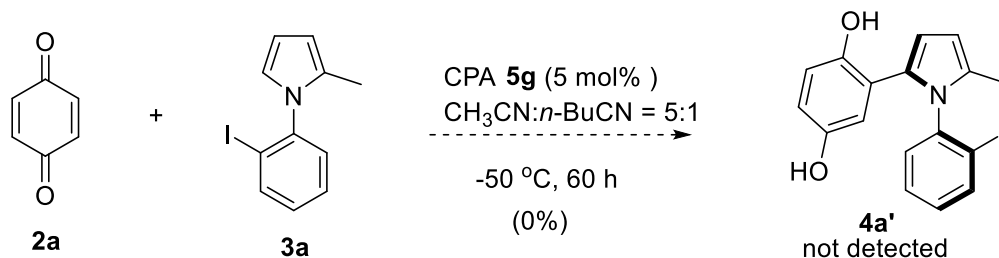
(1) UV-vis spectra of alkyne **1a**, benzoquinone **2a**, N-arylpyrrole **3a** and CPA **5g**.

UV-Vis spectra of the substrates and the catalyst



The UV-vis spectra of alkyne **1a**, benzoquinone **2a**, N-arylpyrrole **3a** and CPA **5g** were recorded in 1 cm path quartz cuvettes ($c = 0.03$ M) using an Edinburgh FS-5 spectrofluorometer, where only benzoquinone **2a** showed strong absorption band at visible light region with the maximum absorption peak at 428 nm.

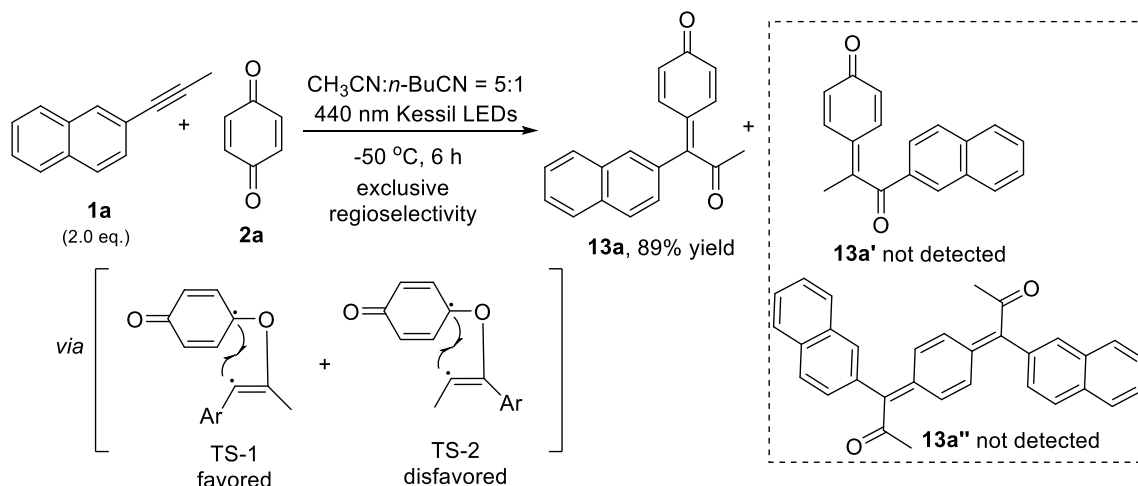
(2) The reaction of benzoquinone **2a** with N-arylpyrrole **3a** under CPA catalysis



To a dried and argon-filled 5 mL screw-cap vial equipped with a magnetic stir bar was charged with intermediate **2a** (0.1 mmol, 10.8 mg), N-arylpyrrole **3a** (0.1 mmol, 10.8 mg), CPA **5g** (3.8 mg, 5 mmol%) and CH₃CN/*n*-BuCN (4.0 mL). The mixture was then keeping temperature

at -50 °C. After 60 h, the reaction between benzoquinone **2a** and *N*-arylpyrrole **3a** under CPA catalysis did not yield the expected product (**4a'**).

(3) The reaction of alkyne **1a** and benzoquinone **2a** under 440 nm Kessil LEDs.



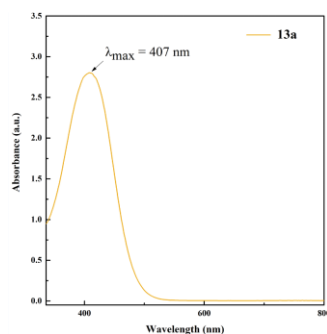
1) benzyl radical more stable than alkyl radical

2) aryl group more steric than alkyl group for the addition of oxygen radical

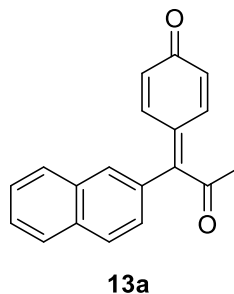
To a dried and argon-filled 5 mL screw-cap vial equipped with a magnetic stir bar was charged with alkyne **1a** (0.2 mmol, 33.2 mg), benzoquinone **2a** (0.1 mmol, 10.8 mg) and CH₃CN/*n*-BuCN (4.0 mL). The mixture was then irradiated by 440 nm Kessil LEDs at -50 °C. The reaction mixture was concentrated under reduced pressure after 6 h and the residue was purified by column chromatography on silica gel to furnish the product **13a** (24.4 mg, 89%). The regioisomer **13a'** and double addition product **13a''** were not detected.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.83 (s, 1H), 7.67 – 7.58 (m, 2H), 7.47 (dd, *J* = 10.1, 2.7 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30 (dd, *J* = 10.1, 2.6 Hz, 1H), 6.51 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.45 (d, *J* = 12.1 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 202.9, 186.8, 155.0, 137.4, 136.6, 133.6, 132.9, 131.1, 130.9, 130.3, 130.2, 129.41, 129.2, 128.5, 127.9, 127.9, 127.4, 126.3, 31.1. HRMS (ESI): *m/z* calcd. for C₁₉H₁₅O₂ ([M+H]⁺) = 275.1072, found = 275.1070.

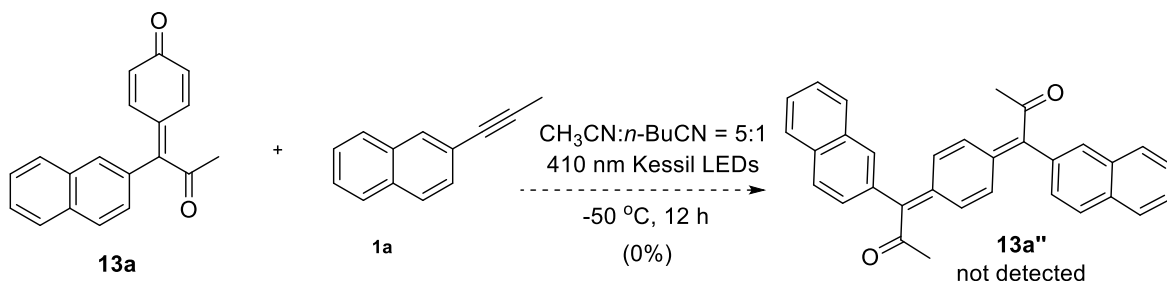
(4) UV-Vis spectrum of **13a** and the reaction of alkyne **1a** with **13a** under visible light irradiation



UV-Vis spectrum of **13a**

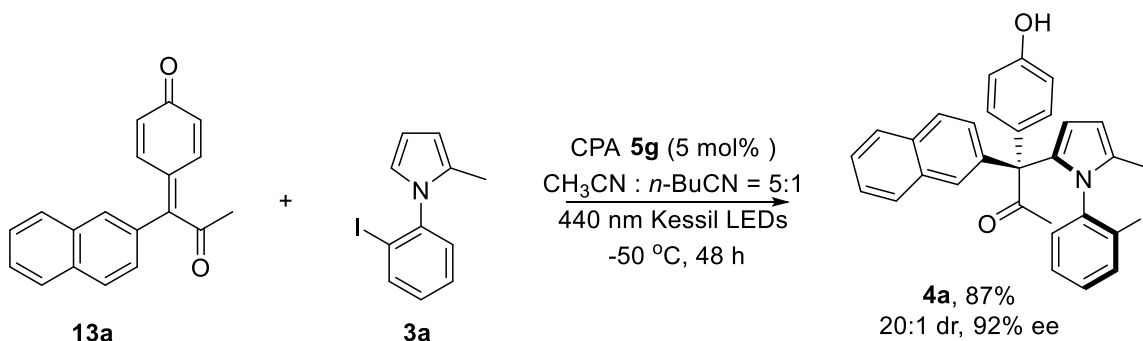


The UV-vis spectrum of **13a** was recorded in 1 cm path quartz cuvettes ($c = 0.03$ M) using an Edinburgh FS-5 spectrofluorometer, revealing a strong absorption band at the visible light region with the maximum absorption peak at around 407 nm.



To a dried and argon-filled 5 mL screw-cap vial equipped with a magnetic stir bar was charged with alkyne **1a** (0.2 mmol, 33.2 mg), **13a** (0.2 mmol, 54.8 mg) and $\text{CH}_3\text{CN}/n\text{-BuCN}$ (4.0 mL). The mixture was then irradiated by 410 nm Kessil LEDs at -50 °C. After 12 h, the reaction between **13a** and **1a** did not yield the expected product (**13a''**).

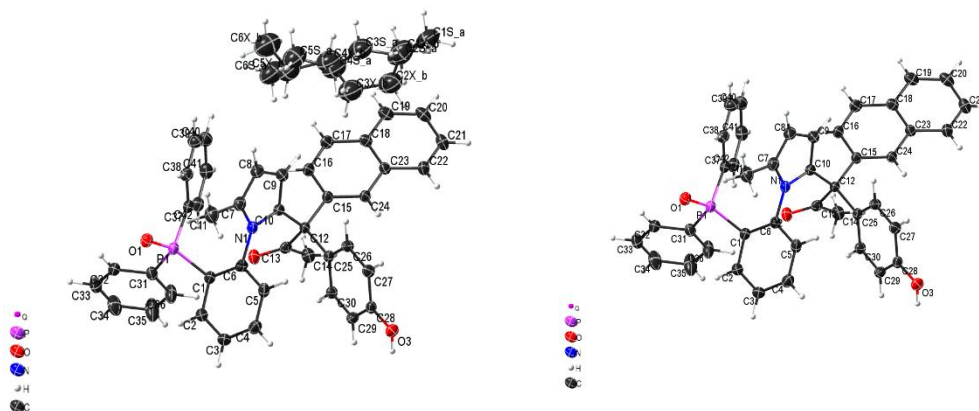
(5) The reaction of intermediate **13a** with *N*-arylpyrrole **3a** by CPA catalyst **5g**.



To a dried and argon-filled 5 mL screw-cap vial equipped with a magnetic stir bar was charged with intermediate **13a** (0.1 mmol, 27.4 mg), *N*-arylpyrrole **3a** (0.1 mmol, 10.8 mg), CPA **5g** (3.8 mg, 5 mmol%) and $\text{CH}_3\text{CN}/n\text{-BuCN}$ (4.0 mL). The mixture was then keeping temperature at -50 °C. The reaction mixture was concentrated under reduced pressure after 48 h and the residue

was purified by column chromatography on silica gel to furnish the product **4a** (48.5 mg, 87% yield, 92% ee).

2.5. Single Crystal Structure X-ray Analysis of **4w**



Single Crystal Structure X-ray Analysis

Sample Code:	M246
Sample ID:	DL-600
Student/Researcher:	Dai Lei
Supervisor:	Prof Lu Yixin
CCDC	2203579

Date: 3-8-2022

Note: The crystal is orthorhombic, space group $P2(1)2(1)2(1)$. The asymmetric unit contains one molecule of the compound $C_{42}H_{34}NO_3P$ and one hexane molecule. The hexane molecule was disordered into two positions with occupancy ratio= 52:48. Restraints in bond lengths and thermal parameters were applied to the disordered atoms.
H atom of the OH was located from different map.

As the Flack $x = -0.025(95)$ by classical fit to all intensities and $= -0.005(21)$ from 4439 selected quotients by Parsons' method (in the LST file attached), the

reported structure is the correct hand.

Final R values are $R_1=0.0457$ and $wR_2=0.1307$ for 2- theta up to 59° .

Table S1. Crystal data and structure refinement for M246.

Identification code	M246	
Empirical formula	C ₄₈ H ₄₈ N O ₃ P	
Formula weight	717.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 11.4342(3) Å	a = 90°.
	b = 13.1390(4) Å	b = 90°.
	c = 26.2058(9) Å	g = 90°.
Volume	3937.0(2) Å ³	
Z	4	
Density (calculated)	1.211 mg/m ³	
Absorption coefficient	0.113 mm ⁻¹	
F(000)	1528	
Crystal size	0.310 x 0.175 x 0.113 mm ³	
Theta range for data collection	2.800 to 29.589°.	
Index ranges	-15<=h<=14, -18<=k<=18, -36<=l<=36	
Reflections collected	85286	
Independent reflections	11035 [$R_{\text{int}} = 0.0519$]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.7217	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11035 / 159 / 543	
Goodness-of-fit on F ²	1.070	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0457$, $wR_2 = 0.1270$	
R indices (all data)	$R_1 = 0.0486$, $wR_2 = 0.1307$	
Absolute structure parameter	-0.01(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.736 and -0.444 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for M246. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
P(1)	1491(1)	2985(1)	2018(1)	21(1)
O(1)	1541(2)	1866(1)	1902(1)	25(1)
O(2)	1906(2)	5167(1)	2657(1)	27(1)
O(3)	7454(1)	5582(1)	3763(1)	26(1)
N(1)	2771(2)	3150(1)	3130(1)	21(1)
C(1)	2951(2)	3424(2)	2194(1)	23(1)
C(2)	3685(2)	3656(2)	1783(1)	31(1)
C(3)	4877(2)	3839(2)	1854(1)	34(1)
C(4)	5352(2)	3785(2)	2337(1)	32(1)
C(5)	4638(2)	3566(2)	2751(1)	26(1)
C(6)	3444(2)	3397(2)	2684(1)	21(1)
C(7)	2604(2)	2152(2)	3289(1)	27(1)
C(8)	2041(2)	2174(2)	3746(1)	29(1)
C(9)	1875(2)	3210(2)	3884(1)	26(1)
C(10)	2330(2)	3810(2)	3503(1)	20(1)
C(11)	3011(3)	1257(2)	2983(1)	34(1)
C(12)	2534(2)	4958(2)	3533(1)	19(1)
C(13)	2094(2)	5570(2)	3064(1)	21(1)
C(14)	1906(2)	6700(2)	3129(1)	27(1)
C(15)	1823(2)	5363(2)	3989(1)	21(1)
C(16)	585(2)	5235(2)	3975(1)	24(1)
C(17)	-111(2)	5598(2)	4358(1)	26(1)
C(18)	377(2)	6142(2)	4775(1)	24(1)
C(19)	-320(2)	6570(2)	5169(1)	29(1)
C(20)	172(2)	7150(2)	5545(1)	32(1)
C(21)	1390(2)	7308(2)	5553(1)	31(1)
C(22)	2095(2)	6877(2)	5188(1)	26(1)
C(23)	1603(2)	6289(2)	4786(1)	22(1)

C(24)	2311(2)	5883(2)	4390(1)	21(1)
C(25)	3854(2)	5171(2)	3589(1)	19(1)
C(26)	4490(2)	4664(2)	3966(1)	22(1)
C(27)	5692(2)	4802(2)	4021(1)	24(1)
C(28)	6286(2)	5465(2)	3693(1)	21(1)
C(29)	5666(2)	5971(2)	3315(1)	22(1)
C(30)	4465(2)	5822(2)	3265(1)	22(1)
C(31)	1042(2)	3705(2)	1466(1)	25(1)
C(32)	386(2)	3187(2)	1101(1)	25(1)
C(33)	-79(2)	3704(2)	683(1)	31(1)
C(34)	125(3)	4728(2)	624(1)	44(1)
C(35)	785(4)	5251(2)	983(1)	54(1)
C(36)	1236(3)	4749(2)	1405(1)	41(1)
C(37)	362(2)	3225(2)	2485(1)	22(1)
C(38)	40(2)	2435(2)	2810(1)	26(1)
C(39)	-889(2)	2569(2)	3148(1)	32(1)
C(40)	-1500(2)	3477(2)	3160(1)	32(1)
C(41)	-1195(2)	4258(2)	2830(1)	30(1)
C(42)	-275(2)	4134(2)	2492(1)	26(1)
C(1S)	1178(8)	3586(7)	6650(4)	70(2)
C(2S)	620(10)	3944(8)	6135(4)	80(2)
C(3S)	116(9)	3138(7)	5802(4)	76(2)
C(4S)	-322(13)	3479(11)	5292(6)	80(2)
C(5S)	-892(12)	2612(9)	4995(5)	80(2)
C(6S)	-1424(10)	3060(8)	4540(4)	85(2)
C(1X)	1014(10)	3424(8)	6265(5)	72(2)
C(2X)	1090(11)	4090(8)	5792(4)	79(2)
C(3X)	781(10)	3527(9)	5321(4)	80(2)
C(4X)	-549(13)	3337(13)	5296(7)	80(2)
C(5X)	-785(11)	2778(11)	4811(5)	78(2)
C(6X)	-2060(11)	2680(12)	4743(6)	97(3)

—

Table S3. Bond lengths [Å] and angles [°] for M246.

P(1)-O(1)	1.5031(16)
P(1)-C(31)	1.805(2)
P(1)-C(37)	1.806(2)
P(1)-C(1)	1.825(2)
O(2)-C(13)	1.208(3)
O(3)-C(28)	1.356(3)
O(3)-H(3X)	0.86(5)
N(1)-C(7)	1.389(3)
N(1)-C(10)	1.400(3)
N(1)-C(6)	1.436(3)
C(1)-C(2)	1.397(3)
C(1)-C(6)	1.404(3)
C(2)-C(3)	1.396(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.381(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.394(3)
C(5)-H(5)	0.9500
C(7)-C(8)	1.360(3)
C(7)-C(11)	1.499(3)
C(8)-C(9)	1.421(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.375(3)
C(9)-H(9)	0.9500
C(10)-C(12)	1.528(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(15)	1.540(3)
C(12)-C(25)	1.543(3)
C(12)-C(13)	1.554(3)
C(13)-C(14)	1.510(3)

C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(24)	1.373(3)
C(15)-C(16)	1.425(3)
C(16)-C(17)	1.367(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.420(3)
C(17)-H(17)	0.9500
C(18)-C(23)	1.416(3)
C(18)-C(19)	1.420(3)
C(19)-C(20)	1.367(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.408(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.373(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.422(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.420(3)
C(24)-H(24)	0.9500
C(25)-C(30)	1.392(3)
C(25)-C(26)	1.397(3)
C(26)-C(27)	1.393(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.400(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.389(3)
C(29)-C(30)	1.392(3)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(32)	1.394(3)
C(31)-C(36)	1.398(3)
C(32)-C(33)	1.393(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.375(4)

C(33)-H(33)	0.9500
C(34)-C(35)	1.389(4)
C(34)-H(34)	0.9500
C(35)-C(36)	1.386(4)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(37)-C(38)	1.392(3)
C(37)-C(42)	1.399(3)
C(38)-C(39)	1.393(3)
C(38)-H(38)	0.9500
C(39)-C(40)	1.382(4)
C(39)-H(39)	0.9500
C(40)-C(41)	1.386(4)
C(40)-H(40)	0.9500
C(41)-C(42)	1.384(4)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(1S)-C(2S)	1.563(14)
C(1S)-H(1A)	0.9800
C(1S)-H(1B)	0.9800
C(1S)-H(1C)	0.9800
C(2S)-C(3S)	1.488(13)
C(2S)-H(2A)	0.9900
C(2S)-H(2B)	0.9900
C(3S)-C(4S)	1.497(17)
C(3S)-H(3A)	0.9900
C(3S)-H(3B)	0.9900
C(4S)-C(5S)	1.526(14)
C(4S)-H(4A)	0.9900
C(4S)-H(4B)	0.9900
C(5S)-C(6S)	1.463(14)
C(5S)-H(5A)	0.9900
C(5S)-H(5B)	0.9900
C(6S)-H(6A)	0.9800
C(6S)-H(6B)	0.9800
C(6S)-H(6C)	0.9800

C(1X)-C(2X)	1.520(15)
C(1X)-H(1D)	0.9800
C(1X)-H(1E)	0.9800
C(1X)-H(1F)	0.9800
C(2X)-C(3X)	1.482(14)
C(2X)-H(2D)	0.9900
C(2X)-H(2E)	0.9900
C(3X)-C(4X)	1.544(16)
C(3X)-H(3D)	0.9900
C(3X)-H(3E)	0.9900
C(4X)-C(5X)	1.492(16)
C(4X)-H(4D)	0.9900
C(4X)-H(4E)	0.9900
C(5X)-C(6X)	1.475(15)
C(5X)-H(5D)	0.9900
C(5X)-H(5E)	0.9900
C(6X)-H(6D)	0.9800
C(6X)-H(6E)	0.9800
C(6X)-H(6F)	0.9800

O(1)-P(1)-C(31)	111.10(10)
O(1)-P(1)-C(37)	109.62(10)
C(31)-P(1)-C(37)	104.39(11)
O(1)-P(1)-C(1)	109.03(10)
C(31)-P(1)-C(1)	107.26(11)
C(37)-P(1)-C(1)	115.35(10)
C(28)-O(3)-H(3X)	106(3)
C(7)-N(1)-C(10)	108.99(18)
C(7)-N(1)-C(6)	122.10(18)
C(10)-N(1)-C(6)	128.35(18)
C(2)-C(1)-C(6)	118.0(2)
C(2)-C(1)-P(1)	115.09(17)
C(6)-C(1)-P(1)	126.13(17)
C(3)-C(2)-C(1)	121.5(2)
C(3)-C(2)-H(2)	119.3
C(1)-C(2)-H(2)	119.3

C(4)-C(3)-C(2)	119.8(2)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	119.7(2)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	120.8(2)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	120.2(2)
C(5)-C(6)-N(1)	117.33(19)
C(1)-C(6)-N(1)	122.37(19)
C(8)-C(7)-N(1)	108.1(2)
C(8)-C(7)-C(11)	129.4(2)
N(1)-C(7)-C(11)	122.5(2)
C(7)-C(8)-C(9)	107.8(2)
C(7)-C(8)-H(8)	126.1
C(9)-C(8)-H(8)	126.1
C(10)-C(9)-C(8)	108.4(2)
C(10)-C(9)-H(9)	125.8
C(8)-C(9)-H(9)	125.8
C(9)-C(10)-N(1)	106.68(19)
C(9)-C(10)-C(12)	126.0(2)
N(1)-C(10)-C(12)	126.33(19)
C(7)-C(11)-H(11A)	109.5
C(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-C(15)	107.51(17)
C(10)-C(12)-C(25)	109.46(17)
C(15)-C(12)-C(25)	112.40(17)
C(10)-C(12)-C(13)	114.87(17)
C(15)-C(12)-C(13)	105.33(16)
C(25)-C(12)-C(13)	107.33(17)

O(2)-C(13)-C(14)	120.4(2)
O(2)-C(13)-C(12)	121.9(2)
C(14)-C(13)-C(12)	117.69(18)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(24)-C(15)-C(16)	118.8(2)
C(24)-C(15)-C(12)	123.47(19)
C(16)-C(15)-C(12)	117.60(19)
C(17)-C(16)-C(15)	121.2(2)
C(17)-C(16)-H(16)	119.4
C(15)-C(16)-H(16)	119.4
C(16)-C(17)-C(18)	120.8(2)
C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(23)-C(18)-C(19)	119.1(2)
C(23)-C(18)-C(17)	118.3(2)
C(19)-C(18)-C(17)	122.6(2)
C(20)-C(19)-C(18)	120.9(2)
C(20)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(19)-C(20)-C(21)	120.0(2)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0
C(22)-C(21)-C(20)	120.6(2)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
C(21)-C(22)-C(23)	120.6(2)
C(21)-C(22)-H(22)	119.7
C(23)-C(22)-H(22)	119.7
C(18)-C(23)-C(24)	119.89(19)
C(18)-C(23)-C(22)	118.7(2)
C(24)-C(23)-C(22)	121.3(2)

C(15)-C(24)-C(23)	120.98(19)
C(15)-C(24)-H(24)	119.5
C(23)-C(24)-H(24)	119.5
C(30)-C(25)-C(26)	117.61(19)
C(30)-C(25)-C(12)	123.04(19)
C(26)-C(25)-C(12)	119.31(19)
C(27)-C(26)-C(25)	121.6(2)
C(27)-C(26)-H(26)	119.2
C(25)-C(26)-H(26)	119.2
C(26)-C(27)-C(28)	119.7(2)
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-H(27)	120.1
O(3)-C(28)-C(29)	123.0(2)
O(3)-C(28)-C(27)	117.7(2)
C(29)-C(28)-C(27)	119.3(2)
C(28)-C(29)-C(30)	120.2(2)
C(28)-C(29)-H(29)	119.9
C(30)-C(29)-H(29)	119.9
C(25)-C(30)-C(29)	121.6(2)
C(25)-C(30)-H(30)	119.2
C(29)-C(30)-H(30)	119.2
C(32)-C(31)-C(36)	119.1(2)
C(32)-C(31)-P(1)	116.62(17)
C(36)-C(31)-P(1)	124.08(19)
C(33)-C(32)-C(31)	120.4(2)
C(33)-C(32)-H(32)	119.8
C(31)-C(32)-H(32)	119.8
C(34)-C(33)-C(32)	120.2(2)
C(34)-C(33)-H(33)	119.9
C(32)-C(33)-H(33)	119.9
C(33)-C(34)-C(35)	119.9(3)
C(33)-C(34)-H(34)	120.0
C(35)-C(34)-H(34)	120.0
C(36)-C(35)-C(34)	120.5(3)
C(36)-C(35)-H(35)	119.7
C(34)-C(35)-H(35)	119.7

C(35)-C(36)-C(31)	119.9(3)
C(35)-C(36)-H(36)	120.0
C(31)-C(36)-H(36)	120.0
C(38)-C(37)-C(42)	119.4(2)
C(38)-C(37)-P(1)	118.24(17)
C(42)-C(37)-P(1)	122.04(17)
C(37)-C(38)-C(39)	119.7(2)
C(37)-C(38)-H(38)	120.1
C(39)-C(38)-H(38)	120.1
C(40)-C(39)-C(38)	120.6(2)
C(40)-C(39)-H(39)	119.7
C(38)-C(39)-H(39)	119.7
C(39)-C(40)-C(41)	119.8(2)
C(39)-C(40)-H(40)	120.1
C(41)-C(40)-H(40)	120.1
C(42)-C(41)-C(40)	120.2(2)
C(42)-C(41)-H(41)	119.9
C(40)-C(41)-H(41)	119.9
C(41)-C(42)-C(37)	120.3(2)
C(41)-C(42)-H(42)	119.8
C(37)-C(42)-H(42)	119.8
C(2S)-C(1S)-H(1A)	109.5
C(2S)-C(1S)-H(1B)	109.5
H(1A)-C(1S)-H(1B)	109.5
C(2S)-C(1S)-H(1C)	109.5
H(1A)-C(1S)-H(1C)	109.5
H(1B)-C(1S)-H(1C)	109.5
C(3S)-C(2S)-C(1S)	116.7(9)
C(3S)-C(2S)-H(2A)	108.1
C(1S)-C(2S)-H(2A)	108.1
C(3S)-C(2S)-H(2B)	108.1
C(1S)-C(2S)-H(2B)	108.1
H(2A)-C(2S)-H(2B)	107.3
C(2S)-C(3S)-C(4S)	116.1(9)
C(2S)-C(3S)-H(3A)	108.3
C(4S)-C(3S)-H(3A)	108.3

C(2S)-C(3S)-H(3B)	108.3
C(4S)-C(3S)-H(3B)	108.3
H(3A)-C(3S)-H(3B)	107.4
C(3S)-C(4S)-C(5S)	112.0(12)
C(3S)-C(4S)-H(4A)	109.2
C(5S)-C(4S)-H(4A)	109.2
C(3S)-C(4S)-H(4B)	109.2
C(5S)-C(4S)-H(4B)	109.2
H(4A)-C(4S)-H(4B)	107.9
C(6S)-C(5S)-C(4S)	107.0(11)
C(6S)-C(5S)-H(5A)	110.3
C(4S)-C(5S)-H(5A)	110.3
C(6S)-C(5S)-H(5B)	110.3
C(4S)-C(5S)-H(5B)	110.3
H(5A)-C(5S)-H(5B)	108.6
C(5S)-C(6S)-H(6A)	109.5
C(5S)-C(6S)-H(6B)	109.5
H(6A)-C(6S)-H(6B)	109.5
C(5S)-C(6S)-H(6C)	109.5
H(6A)-C(6S)-H(6C)	109.5
H(6B)-C(6S)-H(6C)	109.5
C(2X)-C(1X)-H(1D)	109.5
C(2X)-C(1X)-H(1E)	109.5
H(1D)-C(1X)-H(1E)	109.5
C(2X)-C(1X)-H(1F)	109.5
H(1D)-C(1X)-H(1F)	109.5
H(1E)-C(1X)-H(1F)	109.5
C(3X)-C(2X)-C(1X)	112.2(9)
C(3X)-C(2X)-H(2D)	109.2
C(1X)-C(2X)-H(2D)	109.2
C(3X)-C(2X)-H(2E)	109.2
C(1X)-C(2X)-H(2E)	109.2
H(2D)-C(2X)-H(2E)	107.9
C(2X)-C(3X)-C(4X)	110.5(11)
C(2X)-C(3X)-H(3D)	109.5
C(4X)-C(3X)-H(3D)	109.5

C(2X)-C(3X)-H(3E)	109.5
C(4X)-C(3X)-H(3E)	109.5
H(3D)-C(3X)-H(3E)	108.1
C(5X)-C(4X)-C(3X)	107.1(13)
C(5X)-C(4X)-H(4D)	110.3
C(3X)-C(4X)-H(4D)	110.3
C(5X)-C(4X)-H(4E)	110.3
C(3X)-C(4X)-H(4E)	110.3
H(4D)-C(4X)-H(4E)	108.5
C(6X)-C(5X)-C(4X)	109.0(12)
C(6X)-C(5X)-H(5D)	109.9
C(4X)-C(5X)-H(5D)	109.9
C(6X)-C(5X)-H(5E)	109.9
C(4X)-C(5X)-H(5E)	109.9
H(5D)-C(5X)-H(5E)	108.3
C(5X)-C(6X)-H(6D)	109.5
C(5X)-C(6X)-H(6E)	109.5
H(6D)-C(6X)-H(6E)	109.5
C(5X)-C(6X)-H(6F)	109.5
H(6D)-C(6X)-H(6F)	109.5
H(6E)-C(6X)-H(6F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for M246. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
P(1)	22(1)	20(1)	21(1)	-1(1)	-3(1)	-2(1)
O(1)	26(1)	21(1)	29(1)	-4(1)	-1(1)	0(1)
O(2)	30(1)	29(1)	23(1)	-2(1)	-7(1)	-1(1)
O(3)	18(1)	32(1)	29(1)	-1(1)	-2(1)	-1(1)
N(1)	24(1)	20(1)	20(1)	-2(1)	-2(1)	-2(1)
C(1)	23(1)	23(1)	23(1)	-3(1)	-2(1)	-3(1)
C(2)	32(1)	37(1)	22(1)	-3(1)	1(1)	-10(1)
C(3)	30(1)	45(1)	27(1)	-6(1)	7(1)	-11(1)
C(4)	24(1)	37(1)	34(1)	-9(1)	2(1)	-7(1)
C(5)	23(1)	28(1)	26(1)	-7(1)	-3(1)	1(1)
C(6)	22(1)	20(1)	22(1)	-2(1)	-1(1)	-1(1)
C(7)	32(1)	22(1)	26(1)	0(1)	-4(1)	-2(1)
C(8)	37(1)	24(1)	27(1)	4(1)	-2(1)	-7(1)
C(9)	30(1)	26(1)	22(1)	-1(1)	2(1)	-4(1)
C(10)	20(1)	22(1)	20(1)	-1(1)	-1(1)	-2(1)
C(11)	47(1)	21(1)	33(1)	-2(1)	-2(1)	1(1)
C(12)	17(1)	21(1)	18(1)	-1(1)	-1(1)	-2(1)
C(13)	16(1)	23(1)	23(1)	0(1)	-1(1)	0(1)
C(14)	31(1)	24(1)	27(1)	0(1)	-3(1)	5(1)
C(15)	18(1)	23(1)	20(1)	-2(1)	-2(1)	0(1)
C(16)	20(1)	30(1)	24(1)	-2(1)	-4(1)	-2(1)
C(17)	17(1)	34(1)	27(1)	1(1)	-2(1)	1(1)
C(18)	22(1)	28(1)	21(1)	2(1)	0(1)	4(1)
C(19)	26(1)	35(1)	25(1)	4(1)	2(1)	8(1)
C(20)	39(1)	35(1)	21(1)	1(1)	4(1)	10(1)
C(21)	40(1)	30(1)	22(1)	-4(1)	-3(1)	6(1)
C(22)	28(1)	28(1)	22(1)	-2(1)	-4(1)	-1(1)
C(23)	23(1)	24(1)	19(1)	-1(1)	-1(1)	0(1)
C(24)	18(1)	24(1)	20(1)	-1(1)	-2(1)	-1(1)
C(25)	18(1)	20(1)	20(1)	-3(1)	-2(1)	0(1)
C(26)	20(1)	24(1)	21(1)	2(1)	-1(1)	-1(1)

C(27)	21(1)	28(1)	22(1)	1(1)	-3(1)	1(1)
C(28)	18(1)	24(1)	22(1)	-5(1)	-1(1)	0(1)
C(29)	21(1)	23(1)	23(1)	1(1)	0(1)	-3(1)
C(30)	20(1)	24(1)	21(1)	0(1)	-3(1)	0(1)
C(31)	29(1)	25(1)	21(1)	-1(1)	-3(1)	-1(1)
C(32)	24(1)	26(1)	25(1)	-2(1)	-1(1)	-3(1)
C(33)	32(1)	37(1)	24(1)	-4(1)	-7(1)	1(1)
C(34)	67(2)	34(1)	29(1)	1(1)	-17(1)	4(1)
C(35)	101(3)	26(1)	37(2)	6(1)	-29(2)	-8(2)
C(36)	68(2)	25(1)	28(1)	1(1)	-16(1)	-11(1)
C(37)	21(1)	22(1)	22(1)	-3(1)	-3(1)	-2(1)
C(38)	28(1)	21(1)	28(1)	0(1)	0(1)	-1(1)
C(39)	37(1)	28(1)	33(1)	2(1)	5(1)	-4(1)
C(40)	29(1)	36(1)	32(1)	-5(1)	3(1)	1(1)
C(41)	29(1)	29(1)	32(1)	-4(1)	-5(1)	6(1)
C(42)	29(1)	23(1)	27(1)	0(1)	-6(1)	0(1)
C(1S)	53(4)	61(4)	97(5)	3(4)	6(4)	-12(3)
C(2S)	78(4)	62(4)	100(4)	-2(4)	21(4)	-19(3)
C(3S)	74(3)	60(3)	94(3)	0(3)	12(3)	-11(3)
C(4S)	79(4)	70(4)	93(3)	6(3)	7(3)	-13(3)
C(5S)	79(4)	67(4)	94(4)	8(4)	-1(4)	-15(3)
C(6S)	76(5)	76(5)	103(5)	14(4)	-8(5)	-19(4)
C(1X)	64(4)	54(4)	98(5)	-1(4)	6(4)	-1(4)
C(2X)	85(4)	63(4)	91(4)	-4(3)	18(4)	-14(3)
C(3X)	78(4)	70(3)	91(4)	2(3)	12(3)	-10(3)
C(4X)	79(4)	69(4)	93(3)	7(3)	10(3)	-15(3)
C(5X)	72(4)	74(4)	88(4)	2(4)	0(4)	-20(3)
C(6X)	84(5)	100(6)	108(6)	7(5)	2(5)	-13(5)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for M246.

	x	y	z	U(eq)
H(3X)	7670(40)	6050(40)	3550(17)	55(12)
H(2)	3365	3690	1449	37
H(3)	5359	4001	1570	41
H(4)	6166	3896	2386	38
H(5)	4966	3532	3084	31
H(8)	1802	1598	3940	35
H(9)	1511	3447	4187	31
H(11A)	2838	627	3169	50
H(11B)	3856	1308	2926	50
H(11C)	2605	1248	2654	50
H(14A)	2354	6941	3424	41
H(14B)	1073	6835	3185	41
H(14C)	2169	7057	2822	41
H(16)	238	4891	3694	29
H(17)	-931	5485	4345	31
H(19)	-1139	6451	5171	35
H(20)	-307	7446	5801	38
H(21)	1727	7717	5814	37
H(22)	2917	6971	5205	31
H(24)	3135	5972	4404	25
H(26)	4094	4214	4191	26
H(27)	6106	4449	4281	28
H(29)	6061	6420	3089	27
H(30)	4053	6174	3004	26
H(32)	254	2476	1137	30
H(33)	-539	3349	440	37
H(34)	-184	5078	337	52
H(35)	929	5958	940	65

H(36)	1675	5114	1653	49
H(38)	451	1807	2801	31
H(39)	-1104	2032	3371	39
H(40)	-2126	3565	3393	39
H(41)	-1619	4879	2835	36
H(42)	-75	4669	2264	31
H(1A)	1450	4180	6842	105
H(1B)	1841	3135	6579	105
H(1C)	591	3218	6851	105
H(2A)	-6	4439	6215	96
H(2B)	1227	4310	5938	96
H(3A)	-539	2813	5987	91
H(3B)	722	2611	5747	91
H(4A)	339	3756	5091	97
H(4B)	-899	4033	5340	97
H(5A)	-299	2099	4897	96
H(5B)	-1496	2274	5207	96
H(6A)	-1833	2530	4347	127
H(6B)	-812	3362	4326	127
H(6C)	-1982	3588	4642	127
H(1D)	1380	3775	6554	108
H(1E)	1422	2780	6202	108
H(1F)	191	3286	6344	108
H(2D)	554	4677	5831	95
H(2E)	1895	4359	5760	95
H(3D)	1200	2868	5315	96
H(3E)	1030	3925	5019	96
H(4D)	-806	2926	5592	96
H(4E)	-978	3991	5300	96
H(5D)	-444	3154	4520	94
H(5E)	-422	2095	4824	94
H(6D)	-2231	2507	4386	146
H(6E)	-2440	3326	4829	146
H(6F)	-2358	2141	4966	146

Table S6. Torsion angles [°] for M246.

O(1)-P(1)-C(1)-C(2)	83.0(2)
C(31)-P(1)-C(1)-C(2)	-37.4(2)
C(37)-P(1)-C(1)-C(2)	-153.18(18)
O(1)-P(1)-C(1)-C(6)	-86.6(2)
C(31)-P(1)-C(1)-C(6)	153.0(2)
C(37)-P(1)-C(1)-C(6)	37.2(2)
C(6)-C(1)-C(2)-C(3)	1.1(4)
P(1)-C(1)-C(2)-C(3)	-169.4(2)
C(1)-C(2)-C(3)-C(4)	0.5(4)
C(2)-C(3)-C(4)-C(5)	-1.2(4)
C(3)-C(4)-C(5)-C(6)	0.3(4)
C(4)-C(5)-C(6)-C(1)	1.4(3)
C(4)-C(5)-C(6)-N(1)	178.4(2)
C(2)-C(1)-C(6)-C(5)	-2.0(3)
P(1)-C(1)-C(6)-C(5)	167.29(18)
C(2)-C(1)-C(6)-N(1)	-178.9(2)
P(1)-C(1)-C(6)-N(1)	-9.6(3)
C(7)-N(1)-C(6)-C(5)	-90.3(3)
C(10)-N(1)-C(6)-C(5)	80.2(3)
C(7)-N(1)-C(6)-C(1)	86.7(3)
C(10)-N(1)-C(6)-C(1)	-102.8(3)
C(10)-N(1)-C(7)-C(8)	1.6(3)
C(6)-N(1)-C(7)-C(8)	173.7(2)
C(10)-N(1)-C(7)-C(11)	-178.2(2)
C(6)-N(1)-C(7)-C(11)	-6.1(3)
N(1)-C(7)-C(8)-C(9)	-1.4(3)
C(11)-C(7)-C(8)-C(9)	178.4(3)
C(7)-C(8)-C(9)-C(10)	0.7(3)
C(8)-C(9)-C(10)-N(1)	0.3(3)
C(8)-C(9)-C(10)-C(12)	-168.6(2)
C(7)-N(1)-C(10)-C(9)	-1.2(2)
C(6)-N(1)-C(10)-C(9)	-172.6(2)
C(7)-N(1)-C(10)-C(12)	167.7(2)
C(6)-N(1)-C(10)-C(12)	-3.8(3)

C(9)-C(10)-C(12)-C(15)	-16.3(3)
N(1)-C(10)-C(12)-C(15)	176.90(19)
C(9)-C(10)-C(12)-C(25)	106.1(2)
N(1)-C(10)-C(12)-C(25)	-60.7(3)
C(9)-C(10)-C(12)-C(13)	-133.2(2)
N(1)-C(10)-C(12)-C(13)	60.1(3)
C(10)-C(12)-C(13)-O(2)	-19.2(3)
C(15)-C(12)-C(13)-O(2)	-137.3(2)
C(25)-C(12)-C(13)-O(2)	102.8(2)
C(10)-C(12)-C(13)-C(14)	160.94(19)
C(15)-C(12)-C(13)-C(14)	42.9(2)
C(25)-C(12)-C(13)-C(14)	-77.1(2)
C(10)-C(12)-C(15)-C(24)	122.4(2)
C(25)-C(12)-C(15)-C(24)	1.9(3)
C(13)-C(12)-C(15)-C(24)	-114.6(2)
C(10)-C(12)-C(15)-C(16)	-61.1(2)
C(25)-C(12)-C(15)-C(16)	178.4(2)
C(13)-C(12)-C(15)-C(16)	61.8(2)
C(24)-C(15)-C(16)-C(17)	-1.5(4)
C(12)-C(15)-C(16)-C(17)	-178.2(2)
C(15)-C(16)-C(17)-C(18)	1.9(4)
C(16)-C(17)-C(18)-C(23)	-0.6(3)
C(16)-C(17)-C(18)-C(19)	177.2(2)
C(23)-C(18)-C(19)-C(20)	2.5(4)
C(17)-C(18)-C(19)-C(20)	-175.3(2)
C(18)-C(19)-C(20)-C(21)	-1.7(4)
C(19)-C(20)-C(21)-C(22)	-0.6(4)
C(20)-C(21)-C(22)-C(23)	2.1(4)
C(19)-C(18)-C(23)-C(24)	-178.9(2)
C(17)-C(18)-C(23)-C(24)	-1.0(3)
C(19)-C(18)-C(23)-C(22)	-1.0(3)
C(17)-C(18)-C(23)-C(22)	176.9(2)
C(21)-C(22)-C(23)-C(18)	-1.2(3)
C(21)-C(22)-C(23)-C(24)	176.6(2)
C(16)-C(15)-C(24)-C(23)	-0.1(3)
C(12)-C(15)-C(24)-C(23)	176.4(2)

C(18)-C(23)-C(24)-C(15)	1.3(3)
C(22)-C(23)-C(24)-C(15)	-176.5(2)
C(10)-C(12)-C(25)-C(30)	126.5(2)
C(15)-C(12)-C(25)-C(30)	-114.1(2)
C(13)-C(12)-C(25)-C(30)	1.2(3)
C(10)-C(12)-C(25)-C(26)	-51.0(2)
C(15)-C(12)-C(25)-C(26)	68.4(2)
C(13)-C(12)-C(25)-C(26)	-176.24(18)
C(30)-C(25)-C(26)-C(27)	0.2(3)
C(12)-C(25)-C(26)-C(27)	177.8(2)
C(25)-C(26)-C(27)-C(28)	0.1(3)
C(26)-C(27)-C(28)-O(3)	179.5(2)
C(26)-C(27)-C(28)-C(29)	-0.3(3)
O(3)-C(28)-C(29)-C(30)	-179.6(2)
C(27)-C(28)-C(29)-C(30)	0.2(3)
C(26)-C(25)-C(30)-C(29)	-0.2(3)
C(12)-C(25)-C(30)-C(29)	-177.7(2)
C(28)-C(29)-C(30)-C(25)	0.1(3)
O(1)-P(1)-C(31)-C(32)	24.5(2)
C(37)-P(1)-C(31)-C(32)	-93.54(19)
C(1)-P(1)-C(31)-C(32)	143.60(18)
O(1)-P(1)-C(31)-C(36)	-160.6(2)
C(37)-P(1)-C(31)-C(36)	81.3(3)
C(1)-P(1)-C(31)-C(36)	-41.5(3)
C(36)-C(31)-C(32)-C(33)	-0.5(4)
P(1)-C(31)-C(32)-C(33)	174.65(19)
C(31)-C(32)-C(33)-C(34)	1.2(4)
C(32)-C(33)-C(34)-C(35)	-0.8(5)
C(33)-C(34)-C(35)-C(36)	-0.4(6)
C(34)-C(35)-C(36)-C(31)	1.1(6)
C(32)-C(31)-C(36)-C(35)	-0.6(5)
P(1)-C(31)-C(36)-C(35)	-175.4(3)
O(1)-P(1)-C(37)-C(38)	24.7(2)
C(31)-P(1)-C(37)-C(38)	143.80(18)
C(1)-P(1)-C(37)-C(38)	-98.78(19)
O(1)-P(1)-C(37)-C(42)	-148.28(18)

C(31)-P(1)-C(37)-C(42)	-29.2(2)
C(1)-P(1)-C(37)-C(42)	88.2(2)
C(42)-C(37)-C(38)-C(39)	-1.9(3)
P(1)-C(37)-C(38)-C(39)	-175.08(19)
C(37)-C(38)-C(39)-C(40)	0.6(4)
C(38)-C(39)-C(40)-C(41)	0.7(4)
C(39)-C(40)-C(41)-C(42)	-0.6(4)
C(40)-C(41)-C(42)-C(37)	-0.7(4)
C(38)-C(37)-C(42)-C(41)	2.0(3)
P(1)-C(37)-C(42)-C(41)	174.89(18)
C(1S)-C(2S)-C(3S)-C(4S)	-175.0(11)
C(2S)-C(3S)-C(4S)-C(5S)	-176.3(11)
C(3S)-C(4S)-C(5S)-C(6S)	172.4(11)
C(1X)-C(2X)-C(3X)-C(4X)	73.4(14)
C(2X)-C(3X)-C(4X)-C(5X)	179.5(12)
C(3X)-C(4X)-C(5X)-C(6X)	-173.7(12)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for M246 [$\text{\AA}$ and $^\circ$].

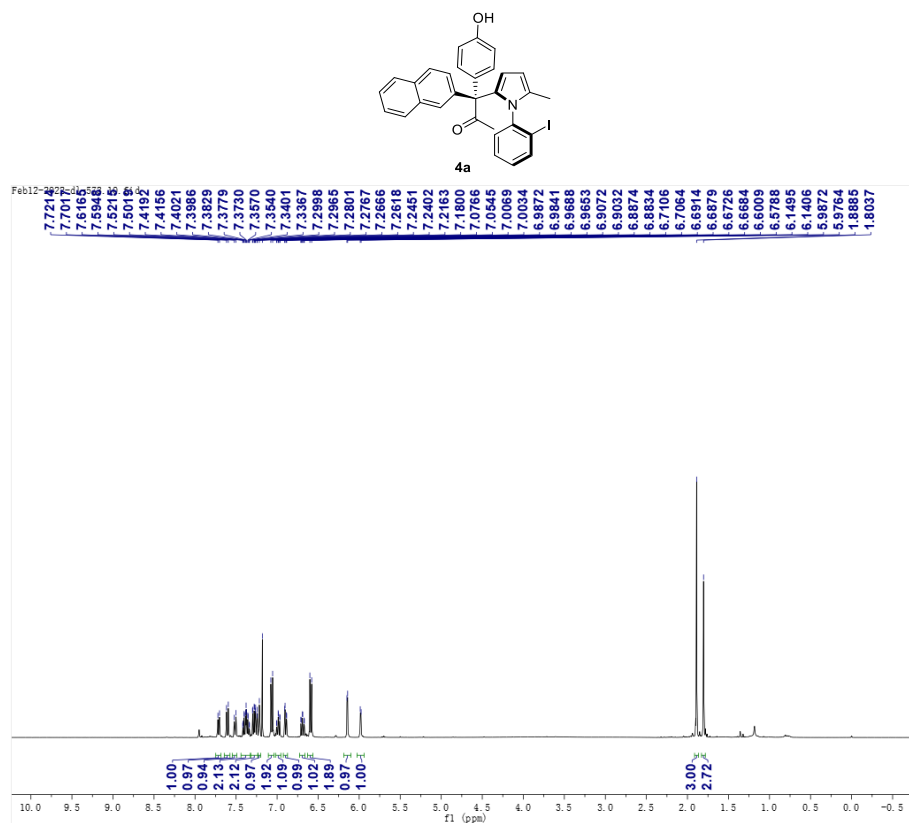
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3X)...O(1)#1	0.86(5)	1.84(5)	2.683(2)	167(4)

Symmetry transformations used to generate equivalent atoms:

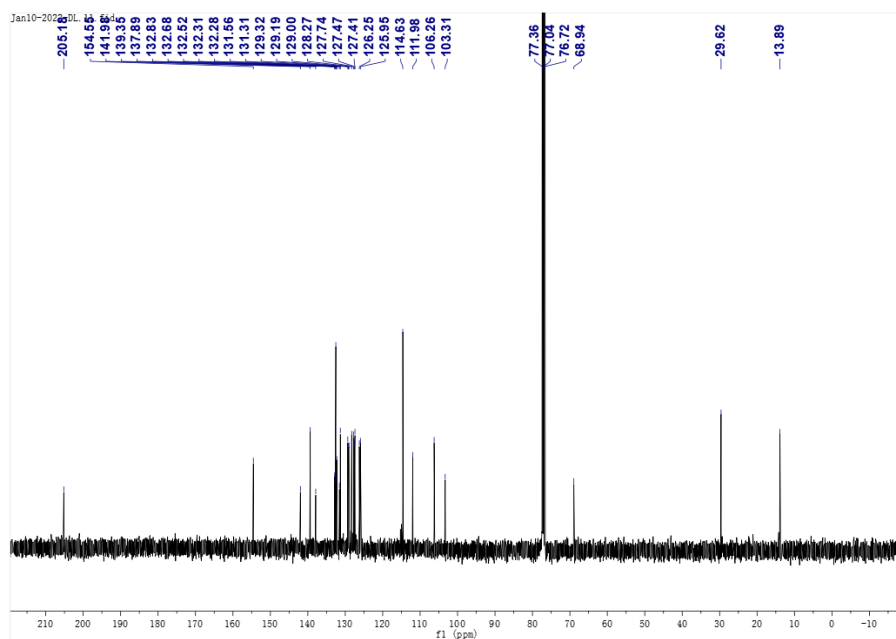
#1 -x+1,y+1/2,-z+1/2

3. Supplementary Figures

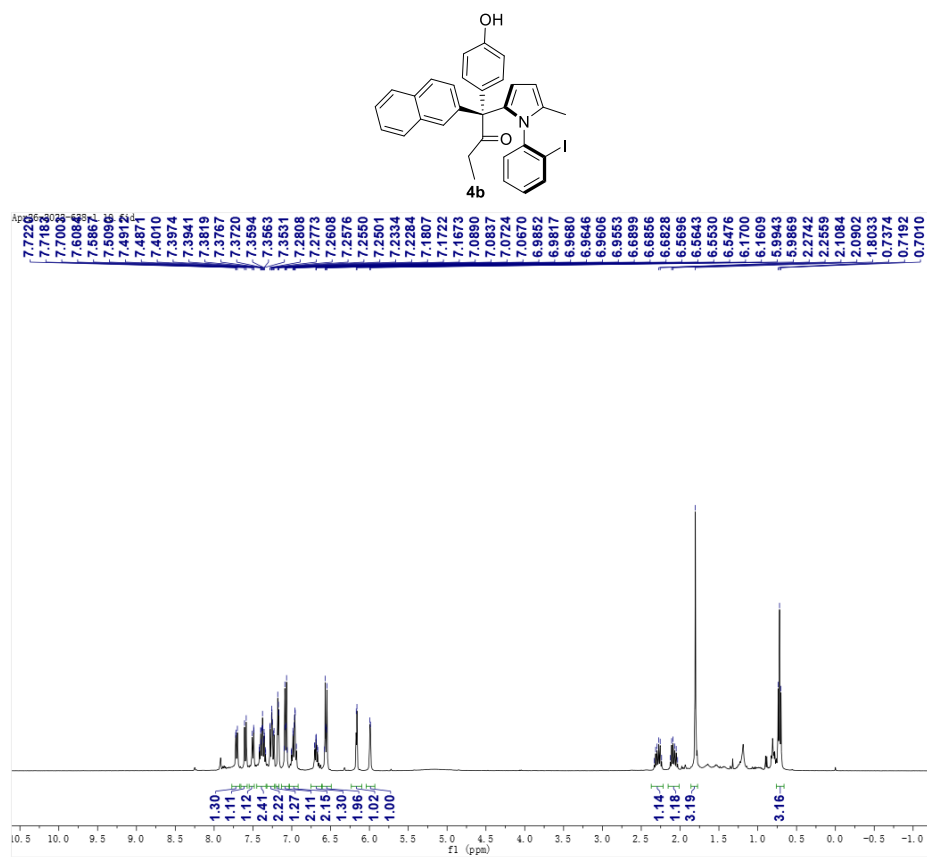
3.1 NMR Spectra



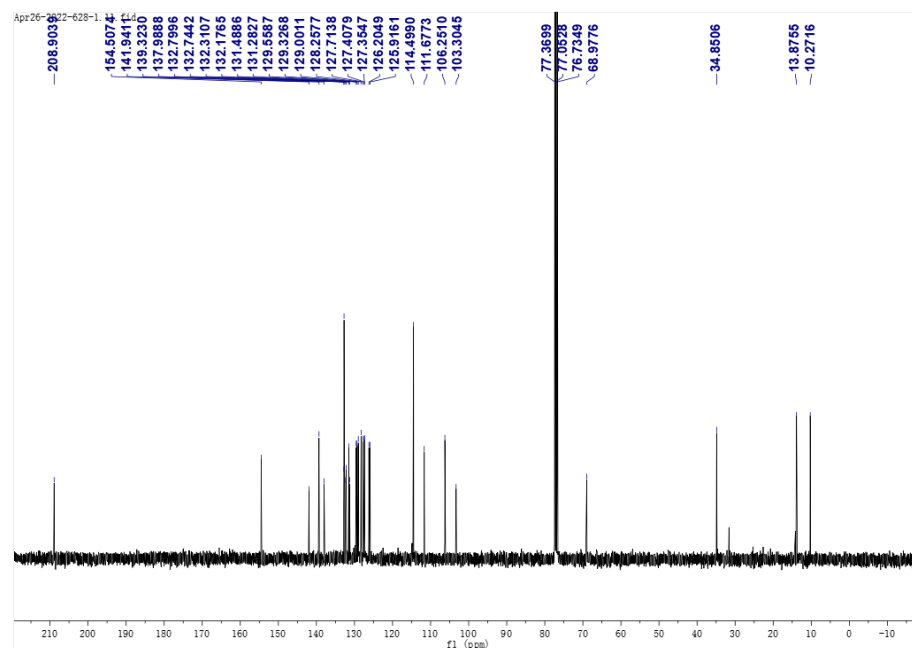
Supplementary Figure 1. ^1H NMR (400 MHz, 25°C) spectrum of compound **4a** in CDCl_3 .



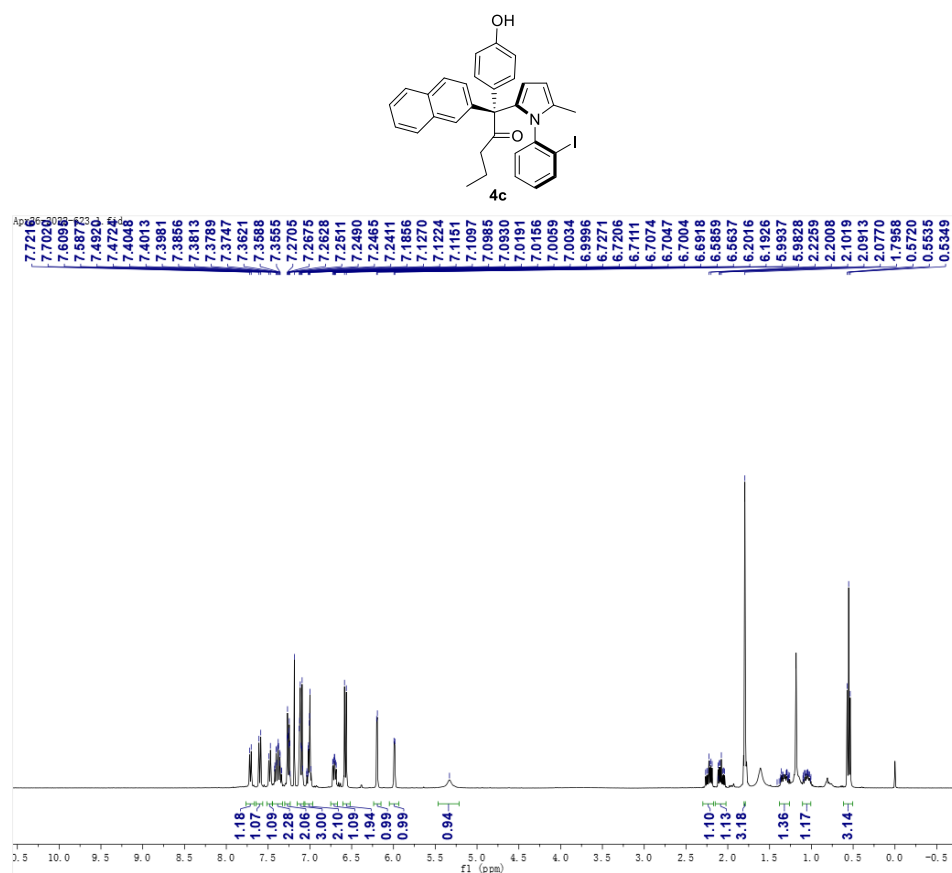
Supplementary Figure 2. ^{13}C NMR (101 MHz, 25°C) spectrum of compound **4a** in CDCl_3 .



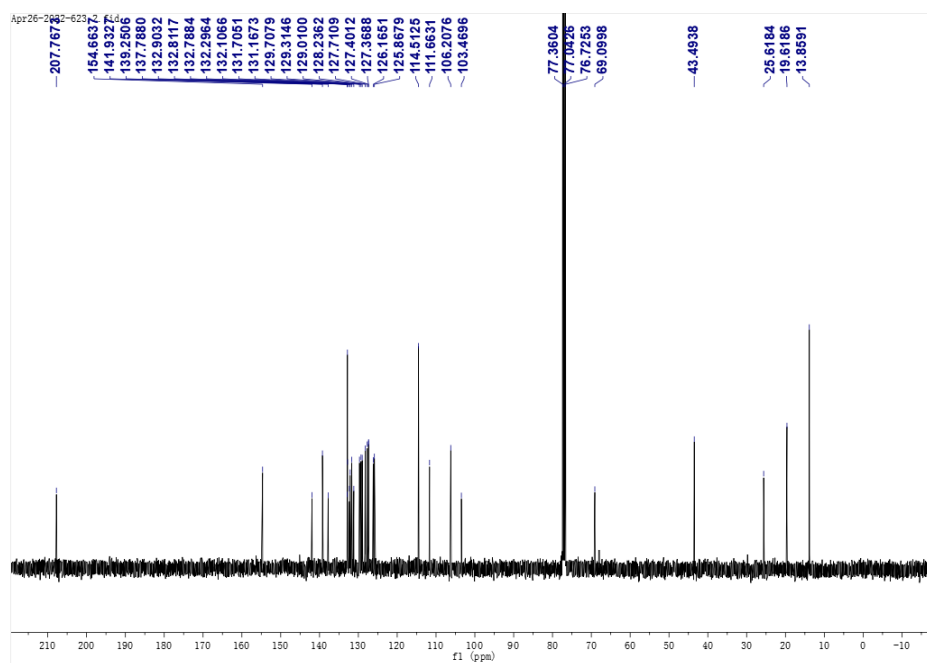
Supplementary Figure 3. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4b** in CDCl_3 .



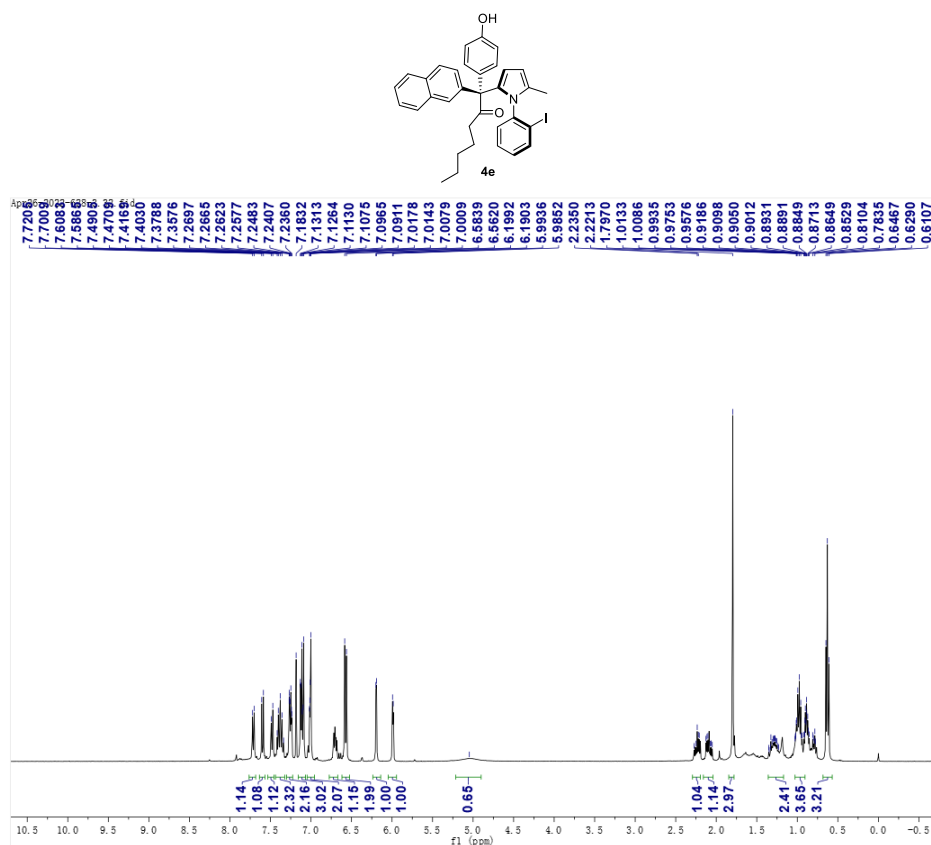
Supplementary Figure 4. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4b** in CDCl_3 .



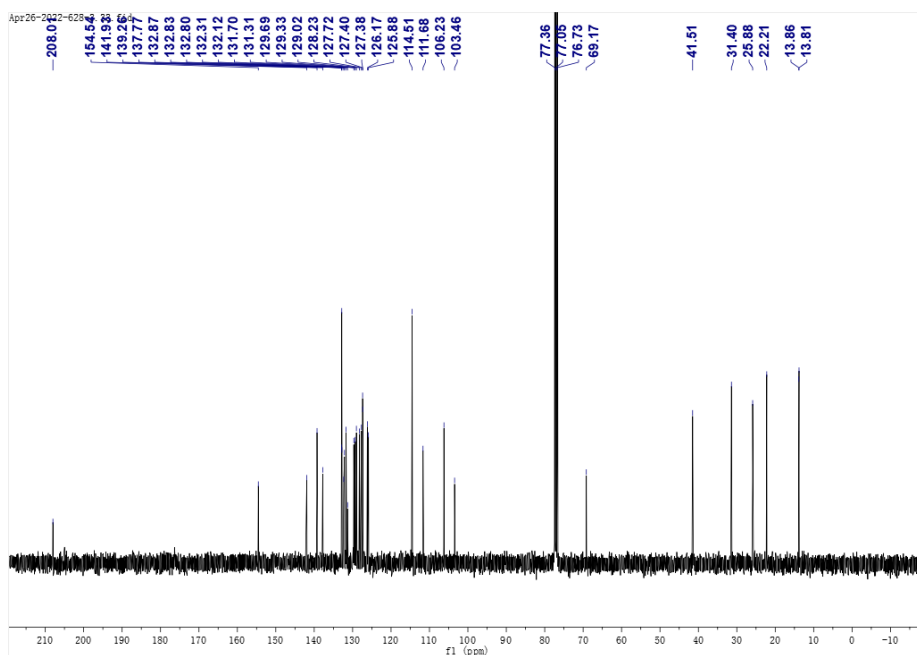
Supplementary Figure 5. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4c** in CDCl₃.



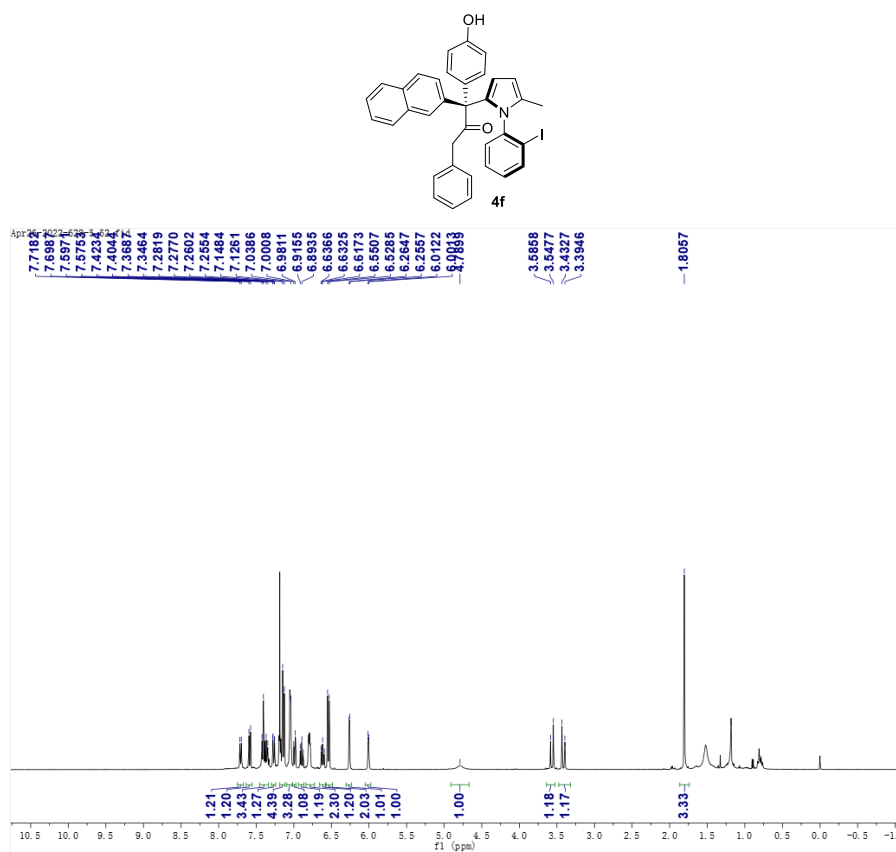
Supplementary Figure 6. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4c** in CDCl₃.



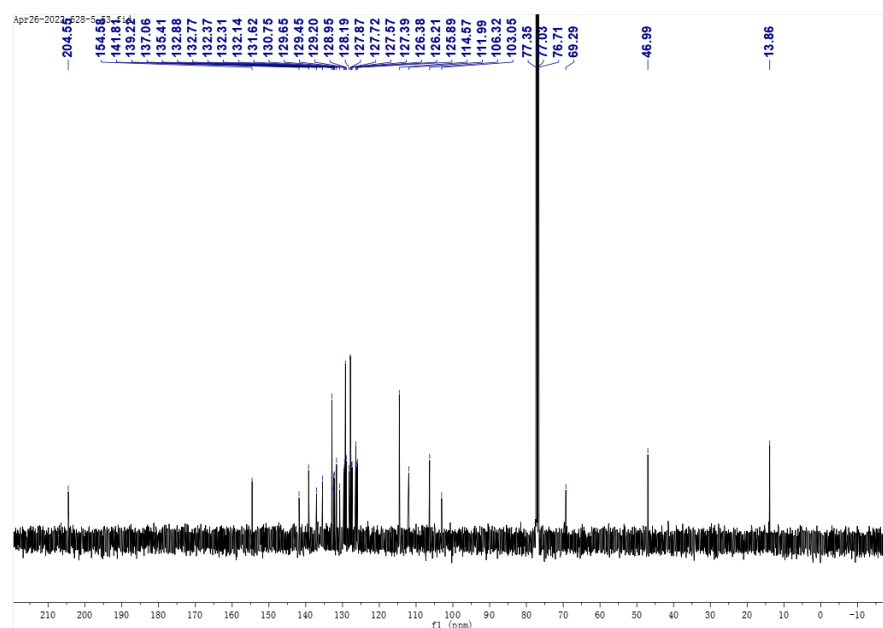
Supplementary Figure 9. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4e** in CDCl₃.



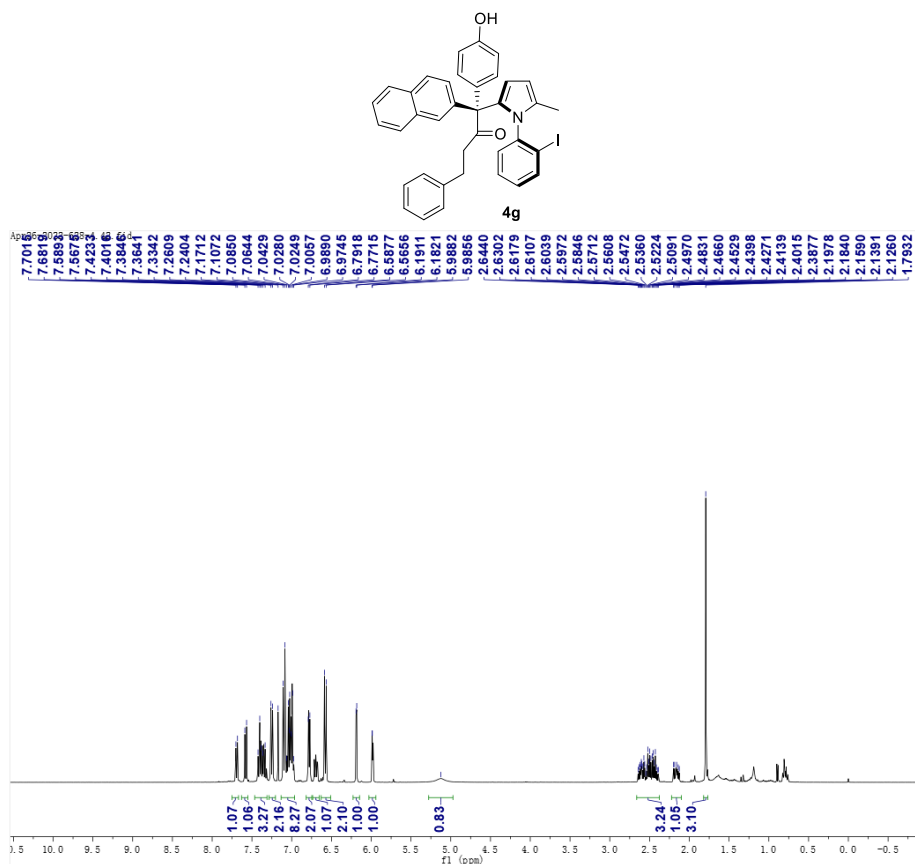
Supplementary Figure 10. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4e** in CDCl₃.



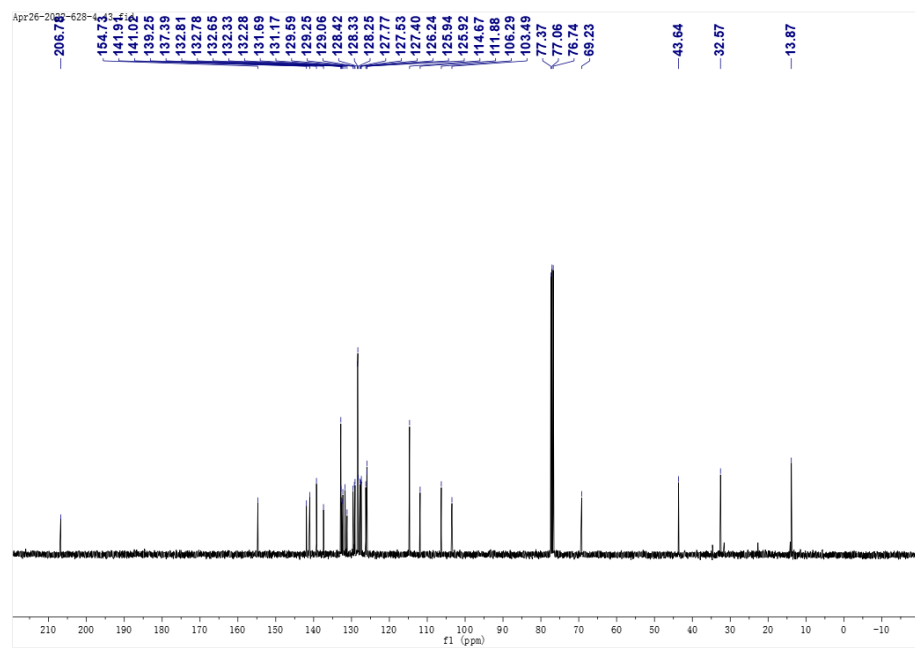
Supplementary Figure 11. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4f** in CDCl₃.



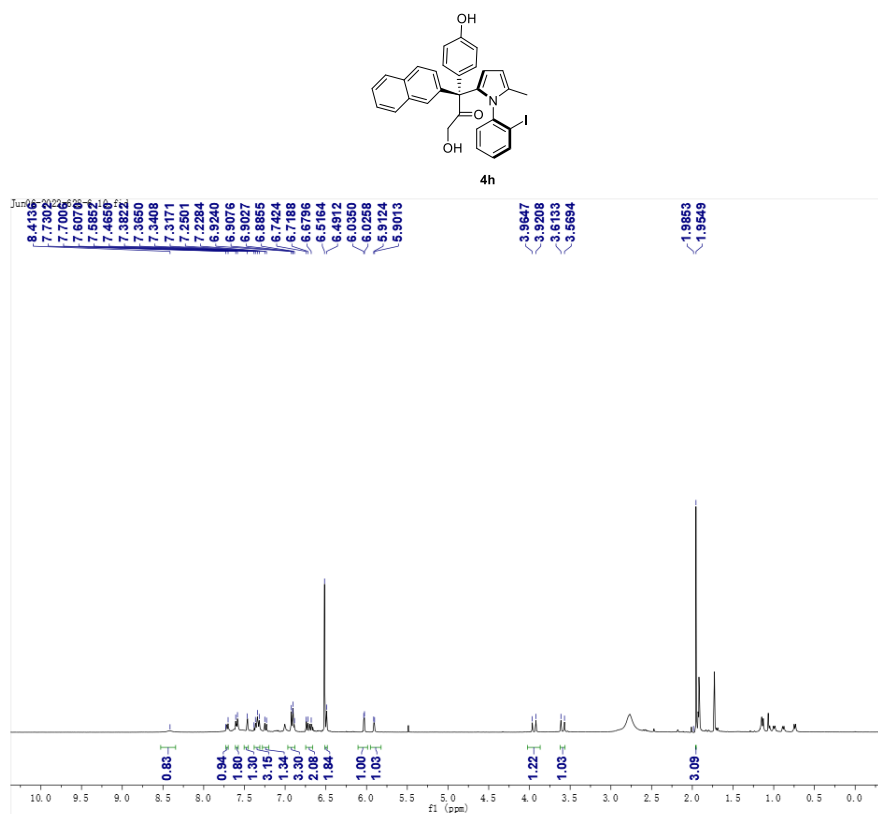
Supplementary Figure 12. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4f** in CDCl₃.



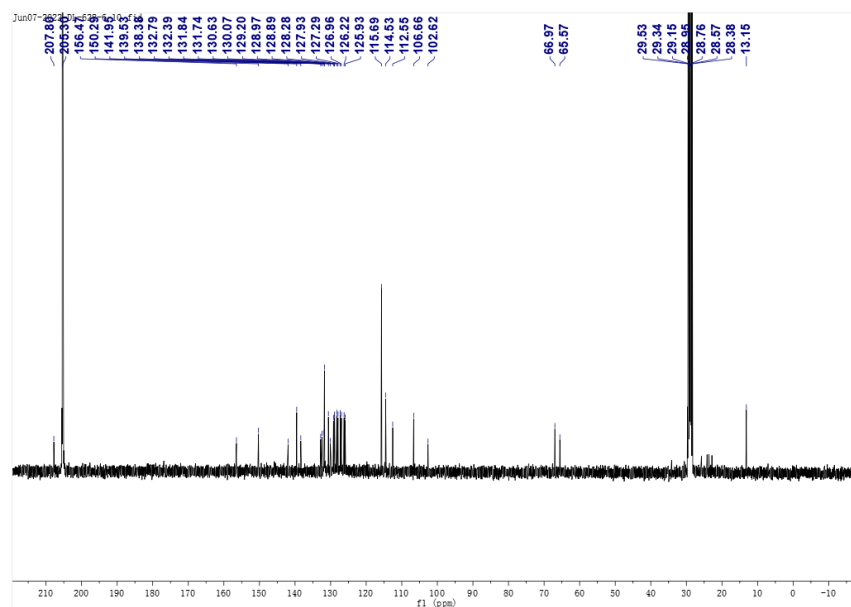
Supplementary Figure 13. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4g** in CDCl_3 .



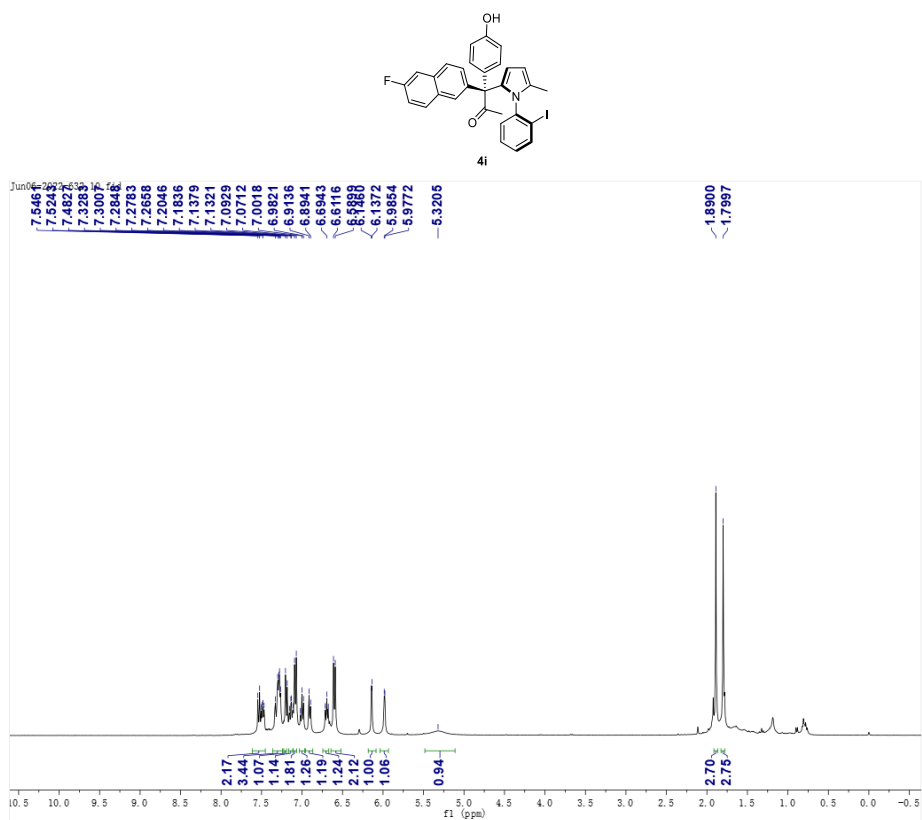
Supplementary Figure 14. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4g** in CDCl_3 .



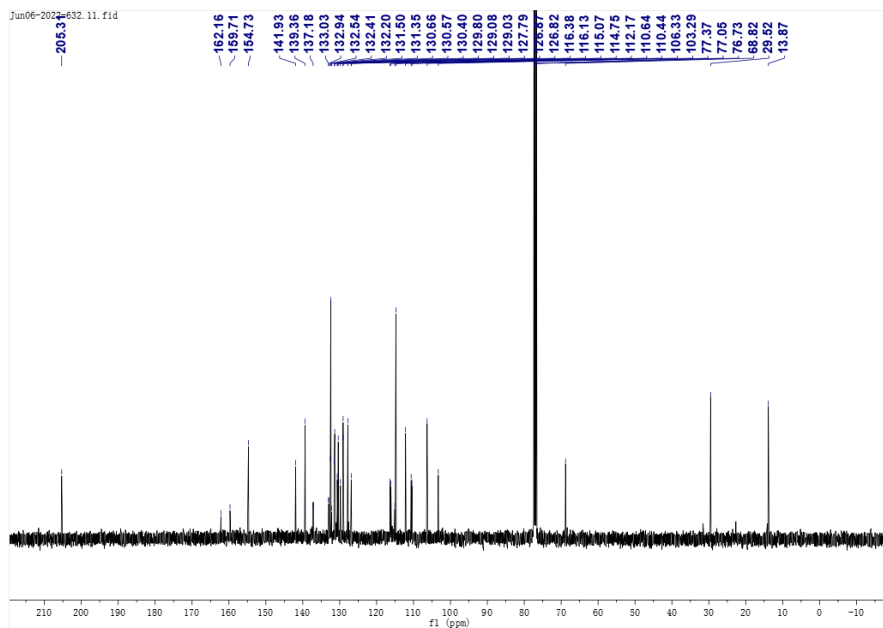
Supplementary Figure 15. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4h** in acetone- d_6 .



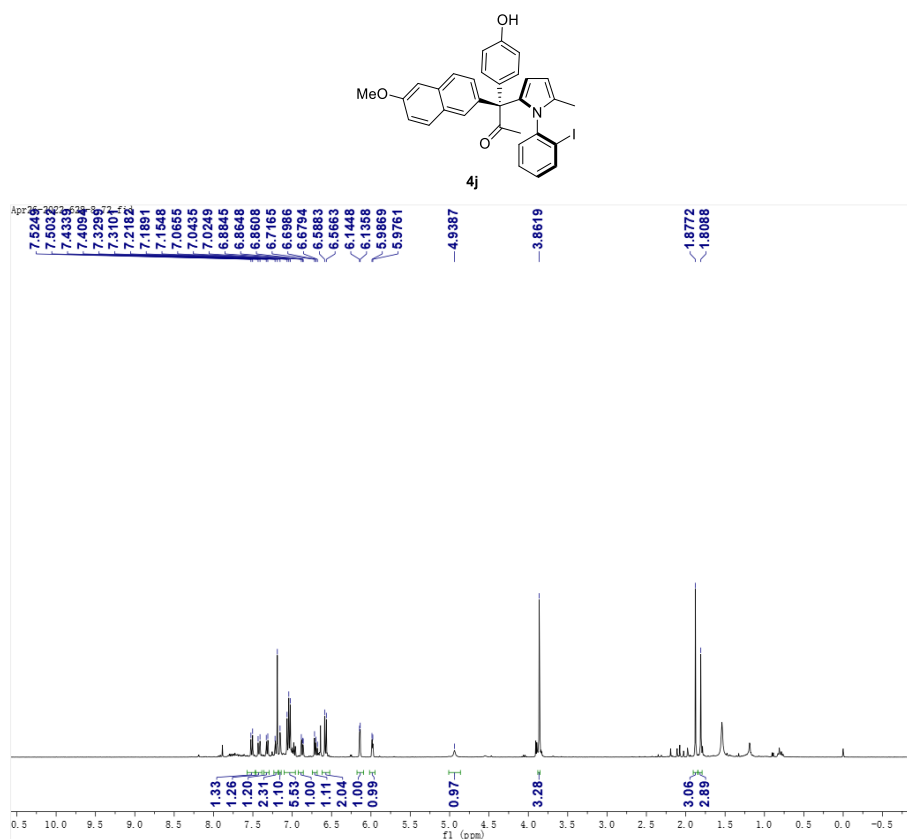
Supplementary Figure 16. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4h** in acetone- d_6 .



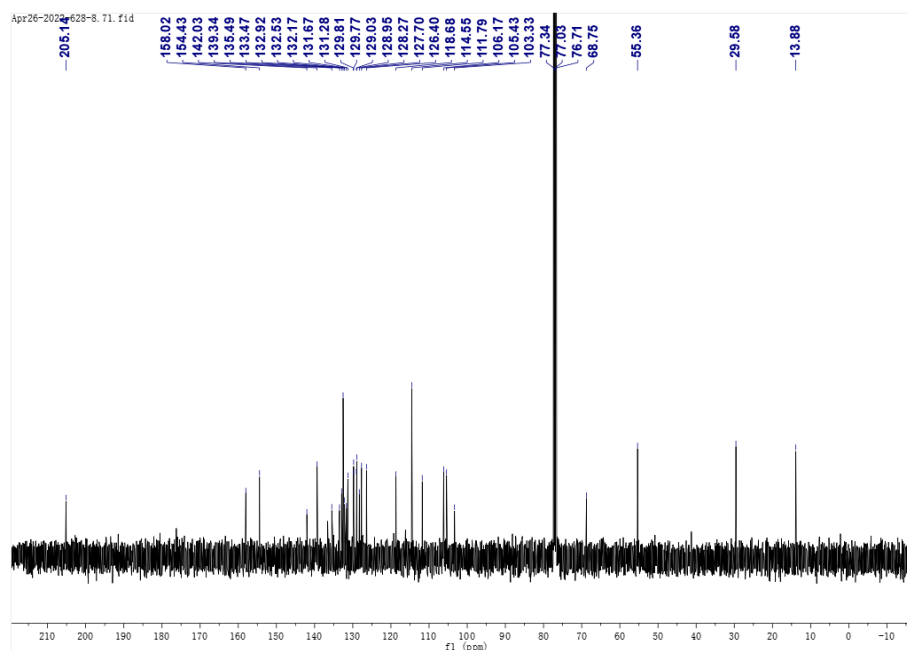
Supplementary Figure 17. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4i** in CDCl₃.



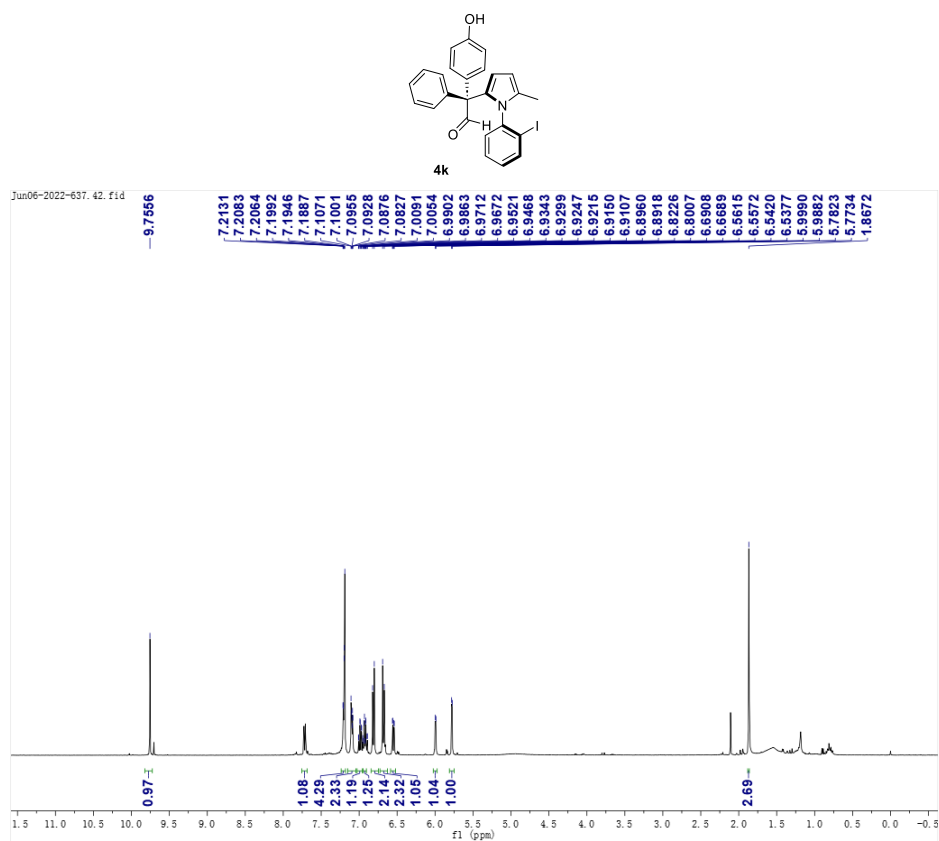
Supplementary Figure 18. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4i** in CDCl₃.



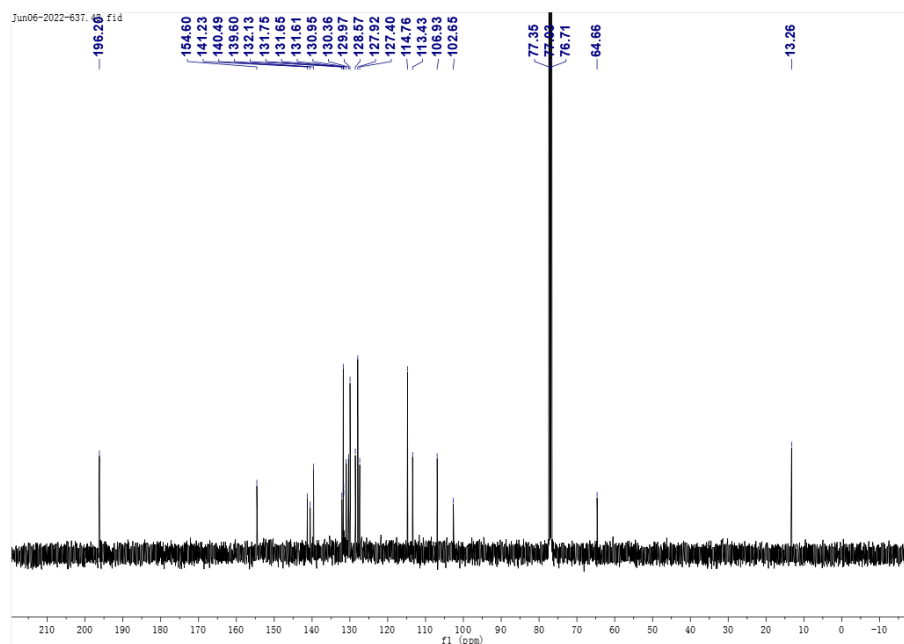
Supplementary Figure 19. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4j** in CDCl₃.



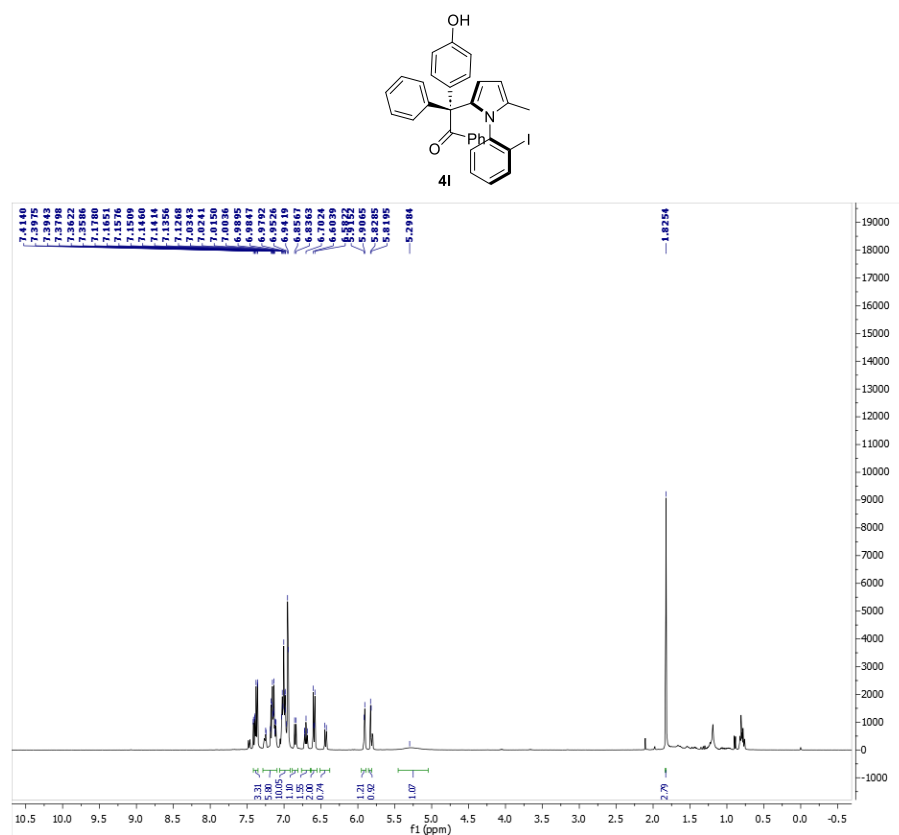
Supplementary Figure 20. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4j** in CDCl₃.



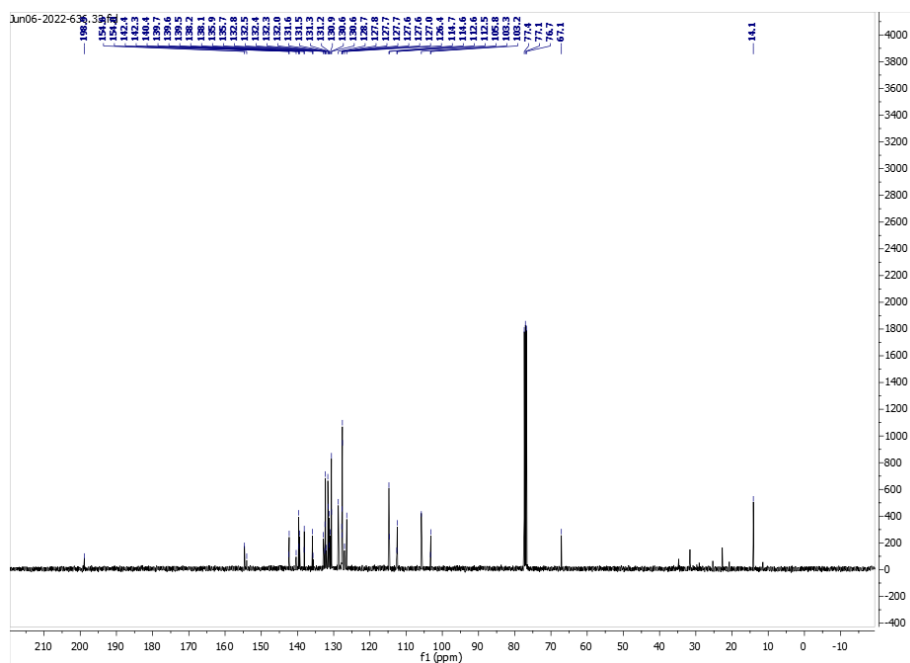
Supplementary Figure 21. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4k** in CDCl_3 .



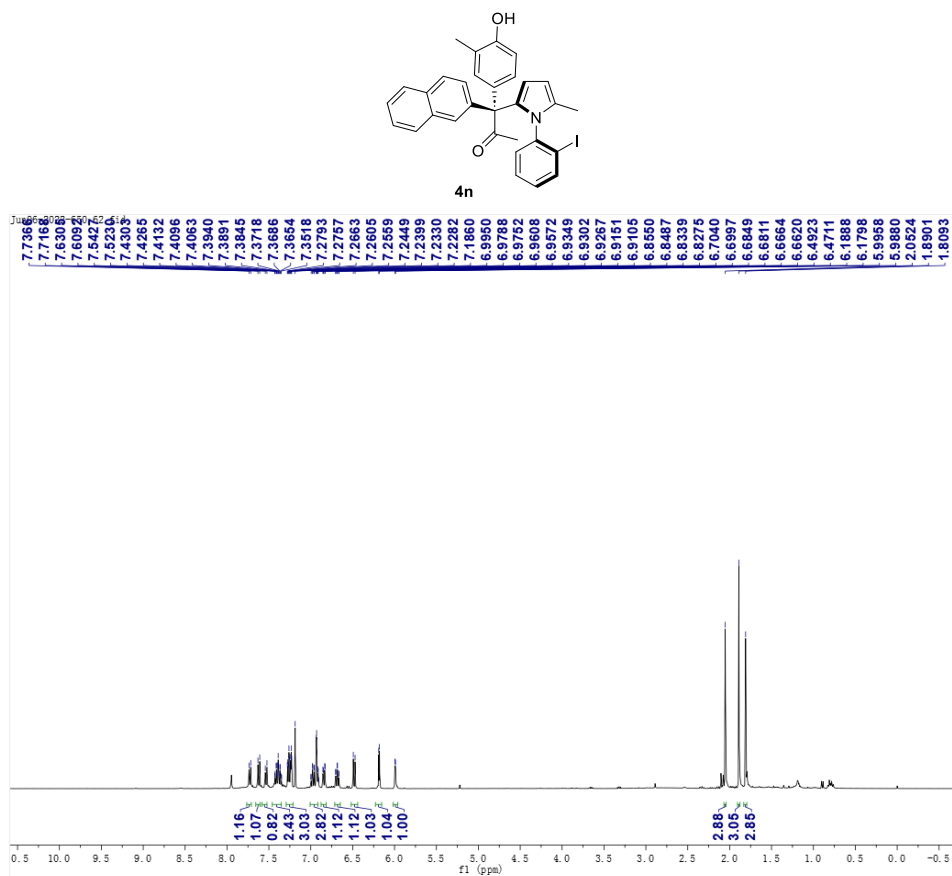
Supplementary Figure 22. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4k** in CDCl_3 .



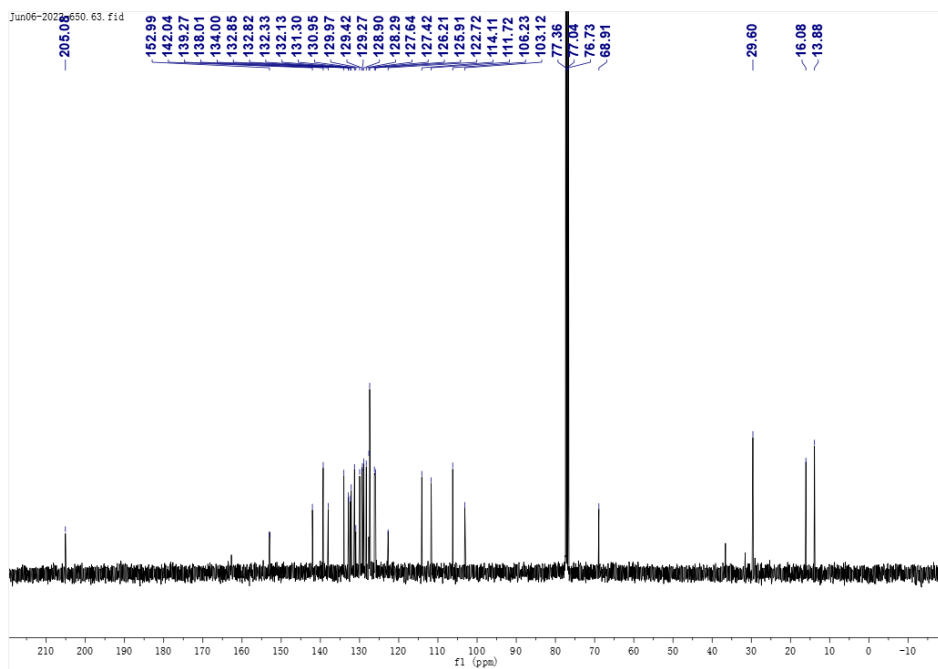
Supplementary Figure 23. ^1H NMR (400 MHz, 25°C) spectrum of compound **4I** in CDCl_3 .



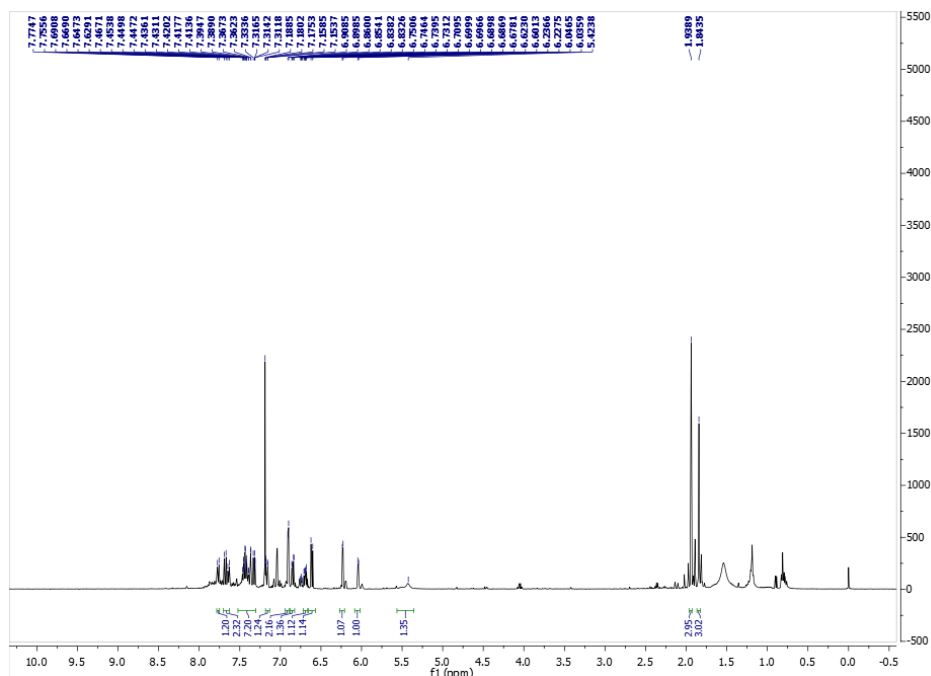
Supplementary Figure 24. ^{13}C NMR (101 MHz, 25°C) spectrum of compound **4I** in CDCl_3 .



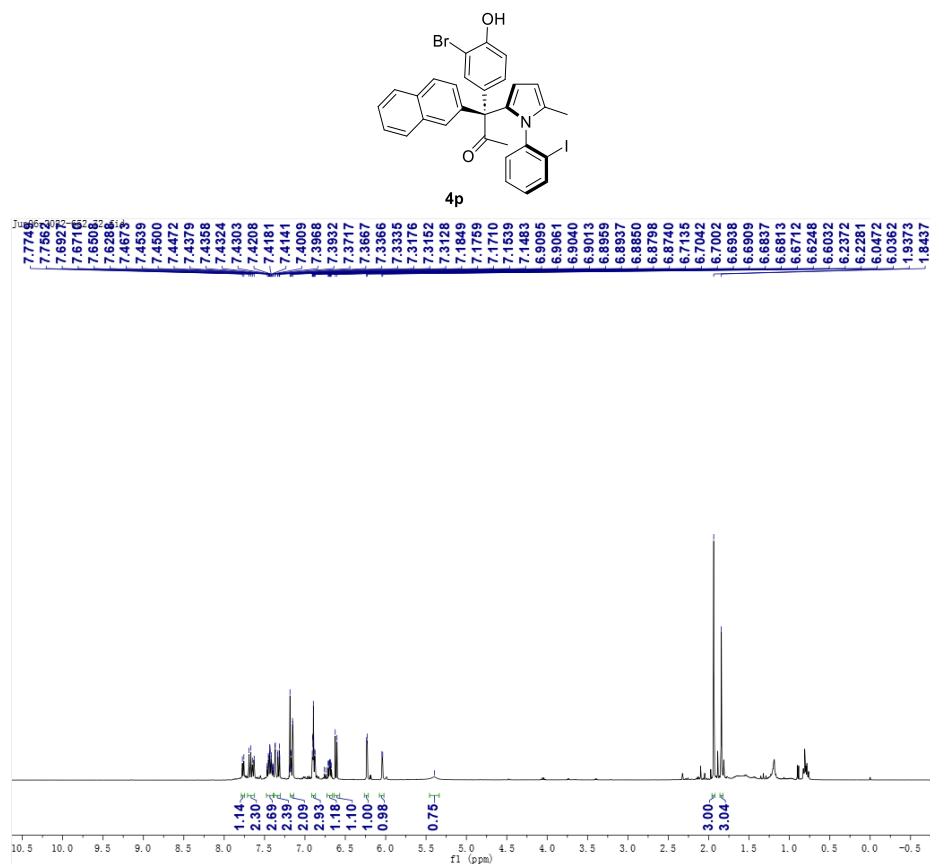
Supplementary Figure 25. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4n** in CDCl_3 .



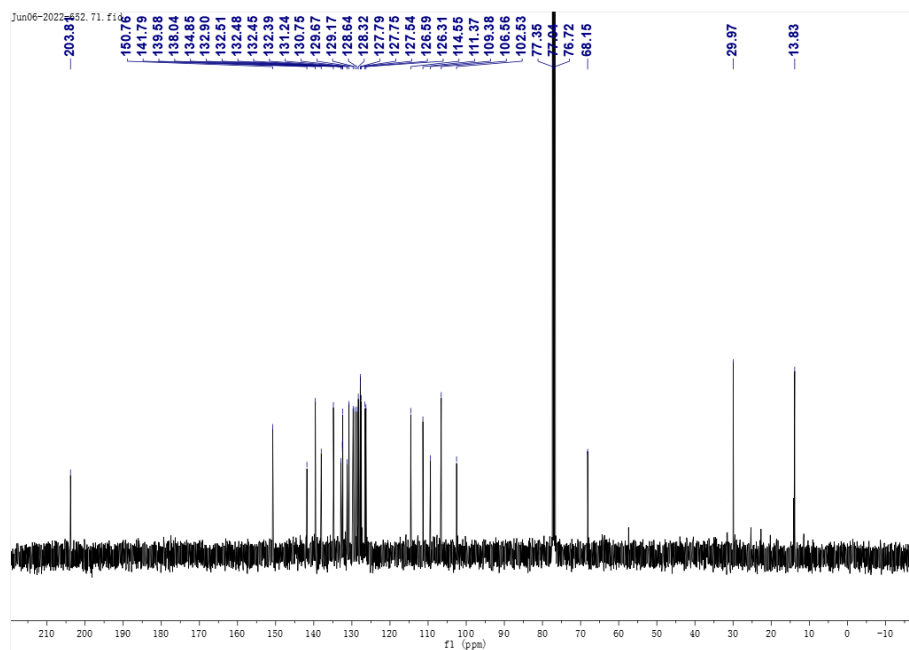
Supplementary Figure 26. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4n** in CDCl_3 .



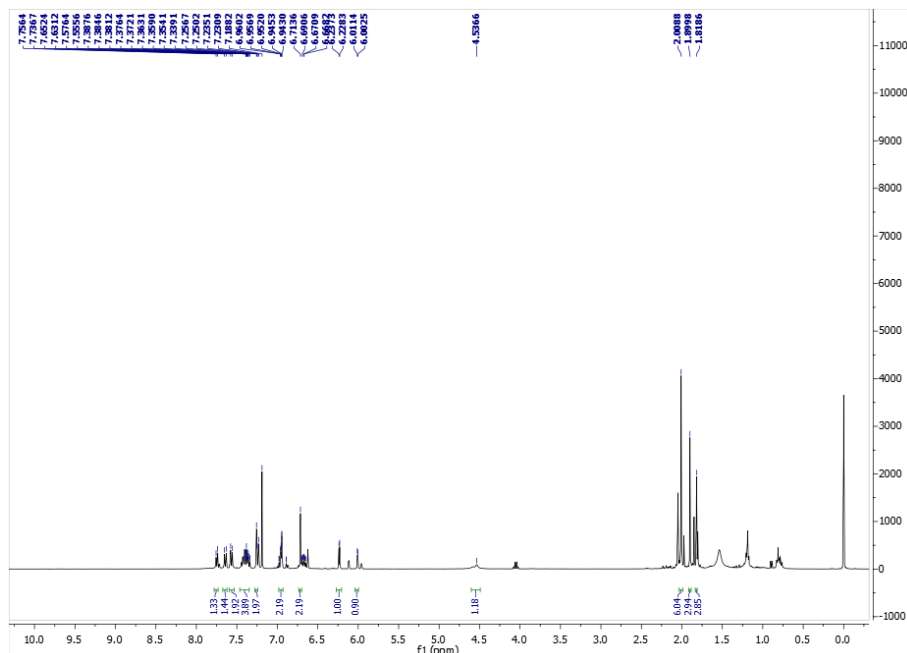
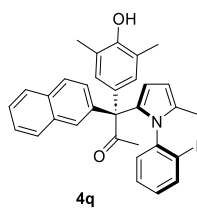
Mass spectrum plot showing relative intensity versus m/z. The x-axis ranges from 210 to -10, and the y-axis ranges from 0 to 1100. The base peak is at m/z 77.3. Other significant peaks are labeled at m/z 203.0, 149.9, 148.9, 139.6, 138.0, 136.4, 132.5, 132.4, 132.0, 131.5, 131.4, 129.6, 129.5, 129.4, 127.7, 127.5, 127.4, 126.6, 126.5, 118.7, 118.6, 114.8, 114.4, 106.5, 102.5, 682.0, 360.0, and 138.0.



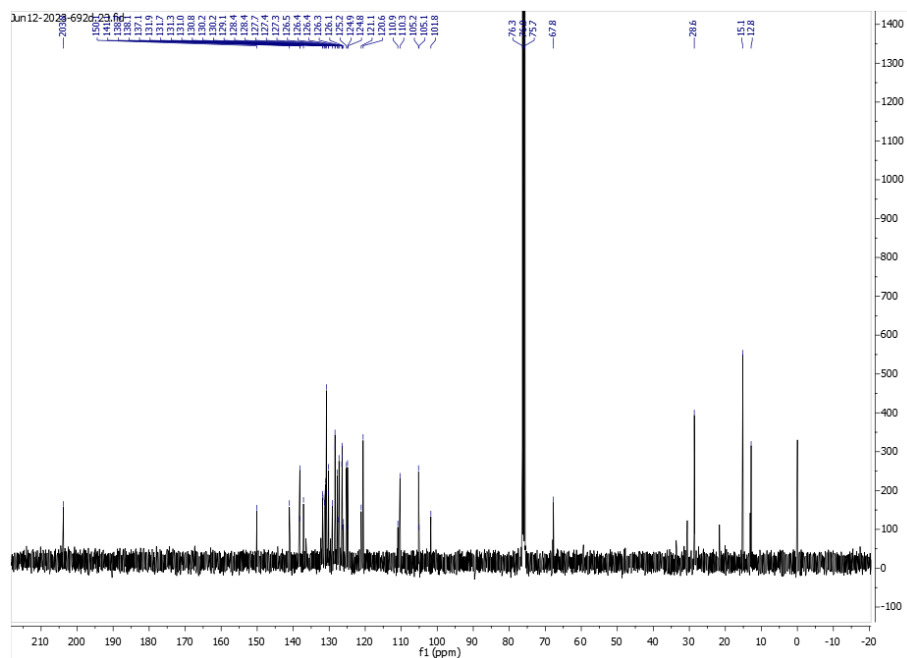
Supplementary Figure 29. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4p** in CDCl_3 .



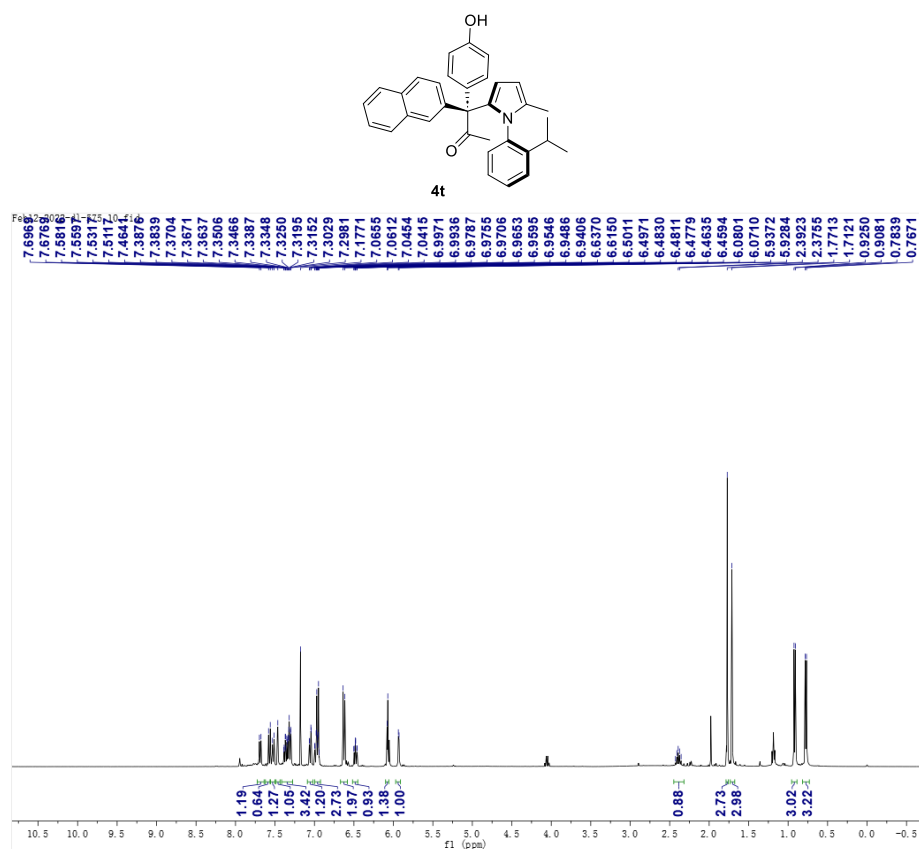
Supplementary Figure 30. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4p** in CDCl_3 .



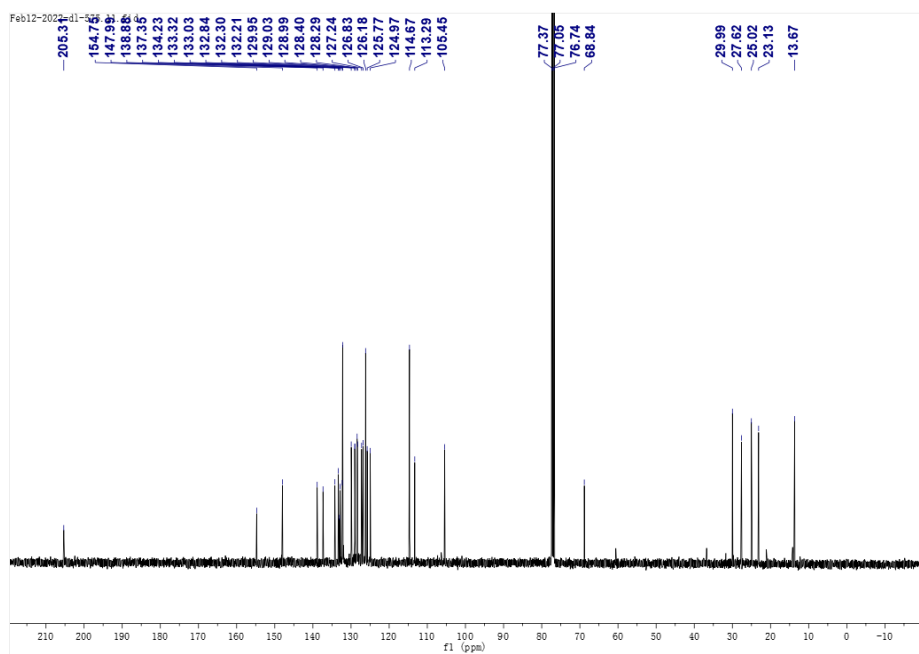
Supplementary Figure 31. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4q** in CDCl₃.



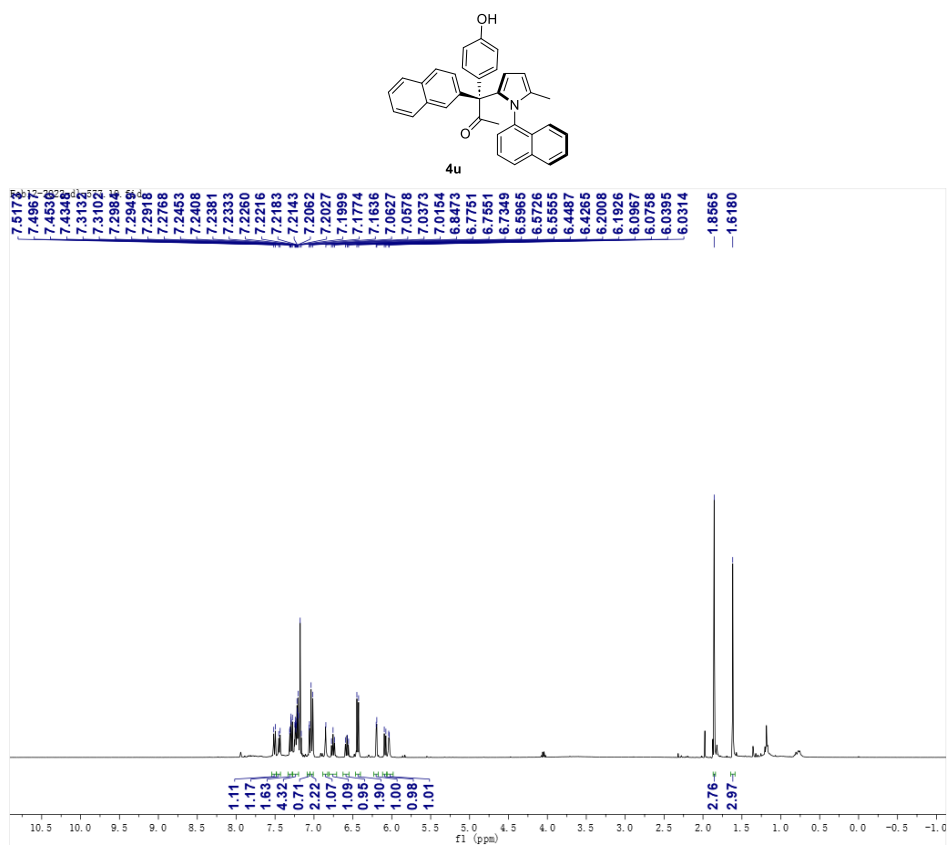
Supplementary Figure 32. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4q** in CDCl₃.



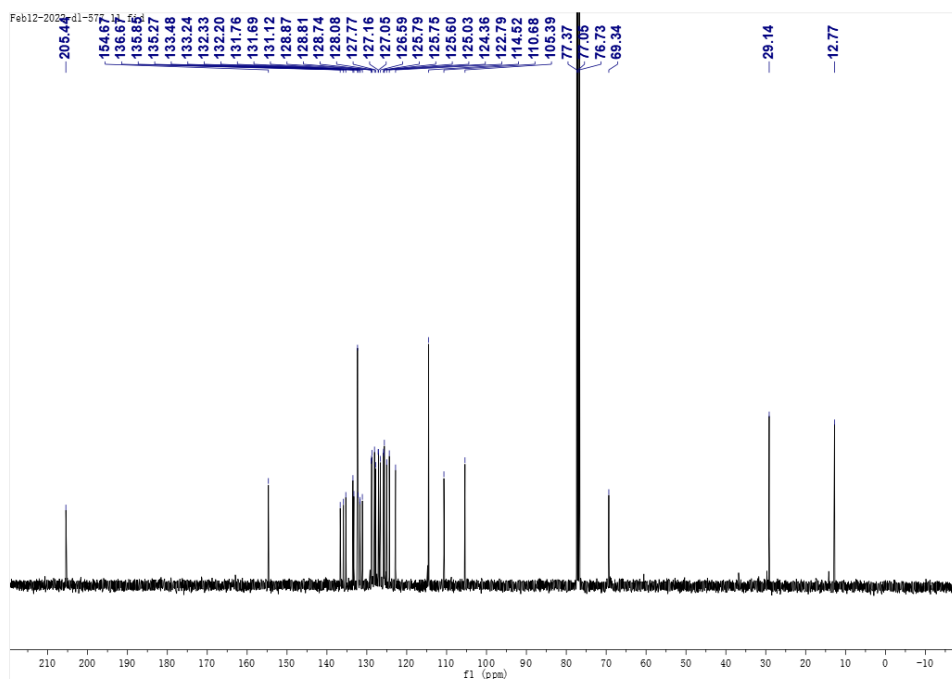
Supplementary Figure 33. ^1H NMR (400 MHz, 25 °C) spectrum of compound **4t** in CDCl_3 .



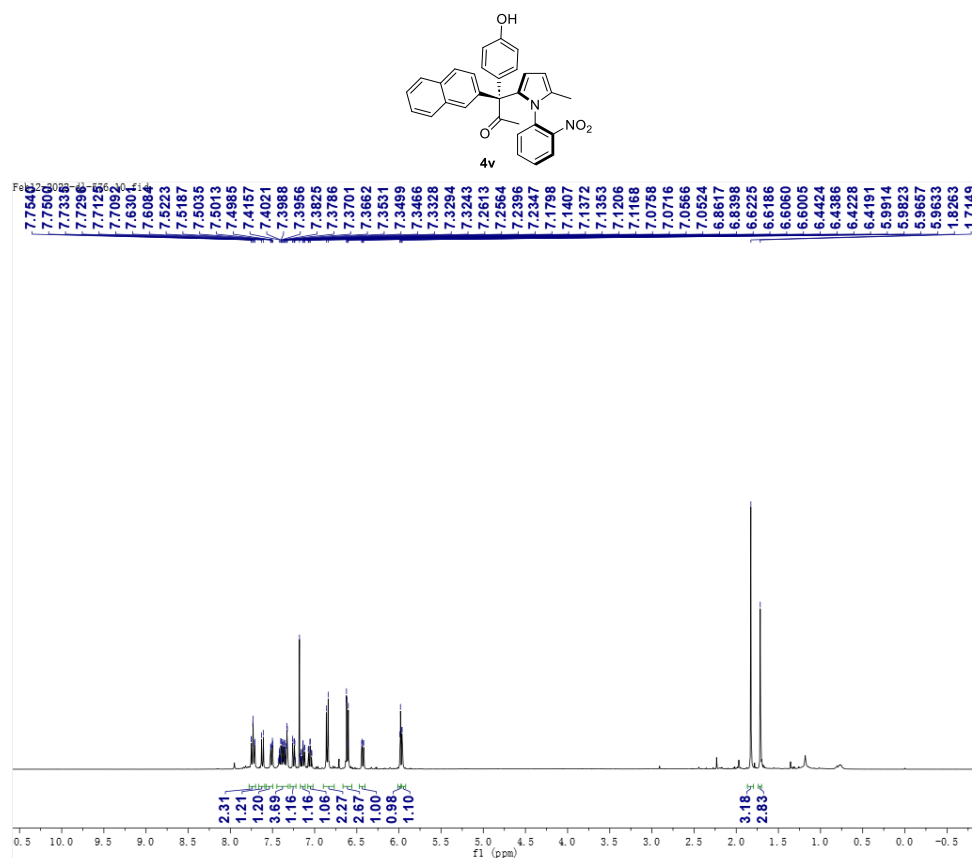
Supplementary Figure 34. ^{13}C NMR (101 MHz, 25 °C) spectrum of compound **4t** in CDCl_3 .



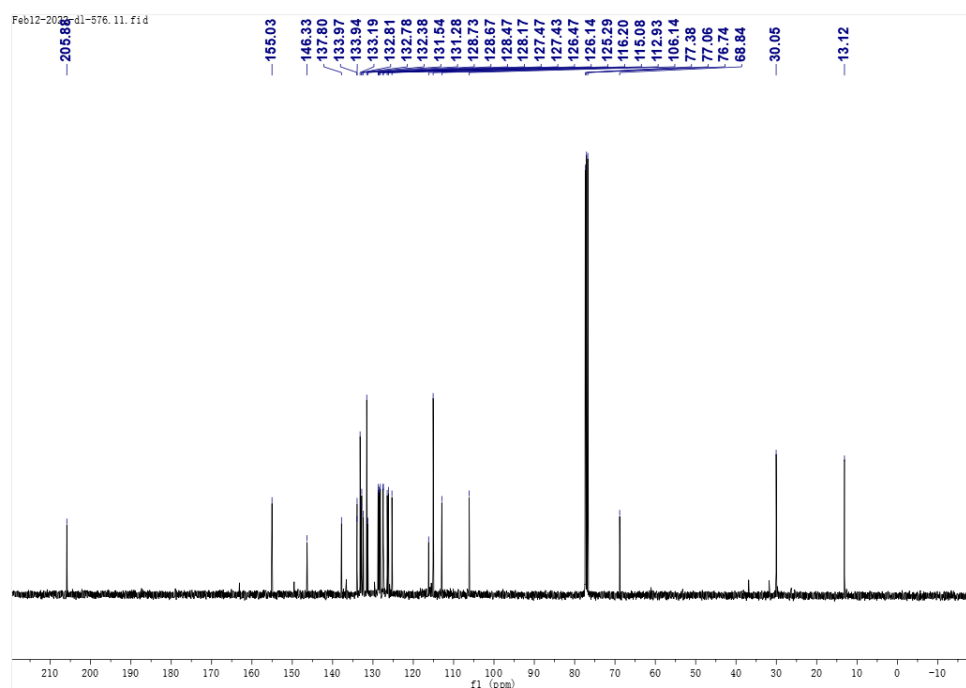
Supplementary Figure 35. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4u** in CDCl₃.



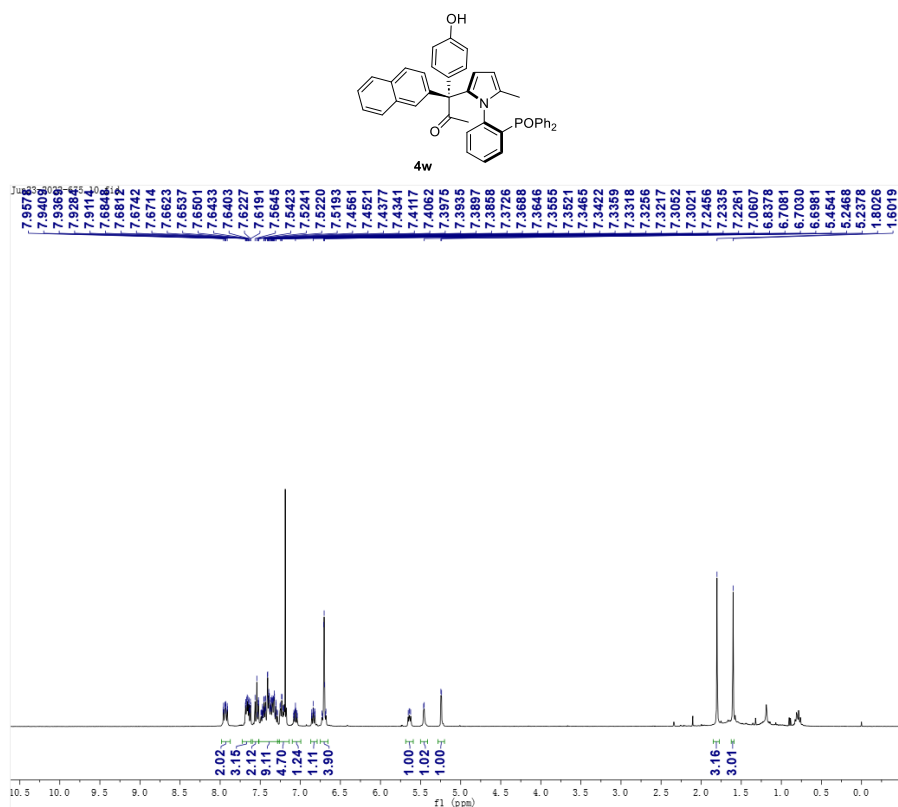
Supplementary Figure 36. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4u** in CDCl₃.



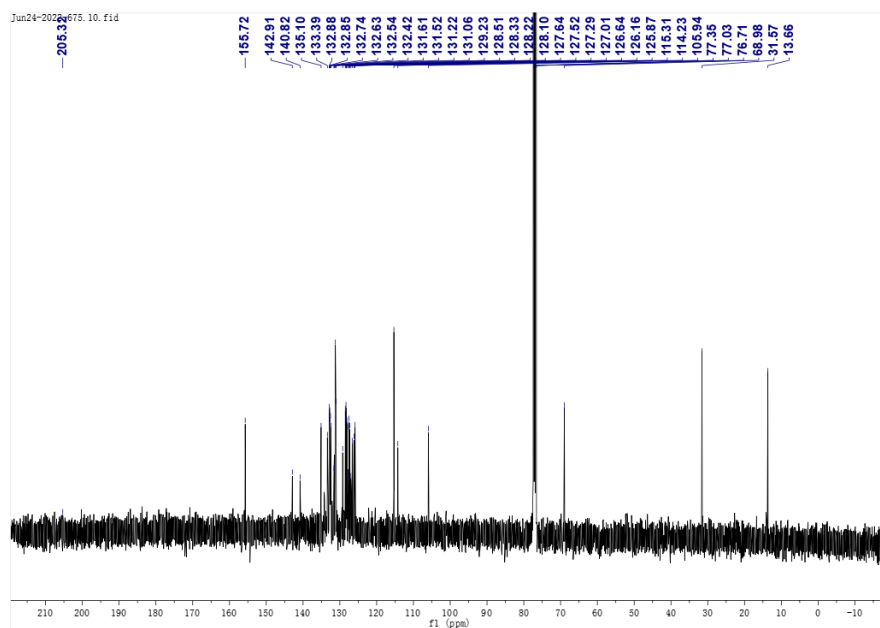
Supplementary Figure 37. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4v** in CDCl₃.



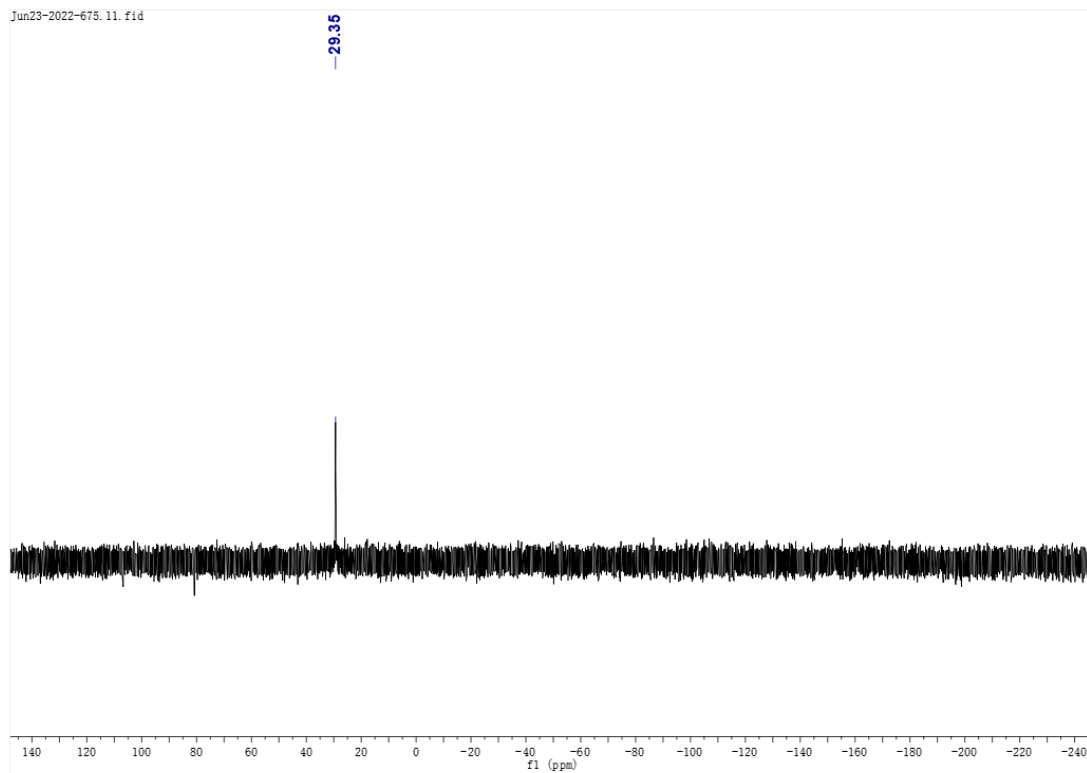
Supplementary Figure 38. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4v** in CDCl₃.



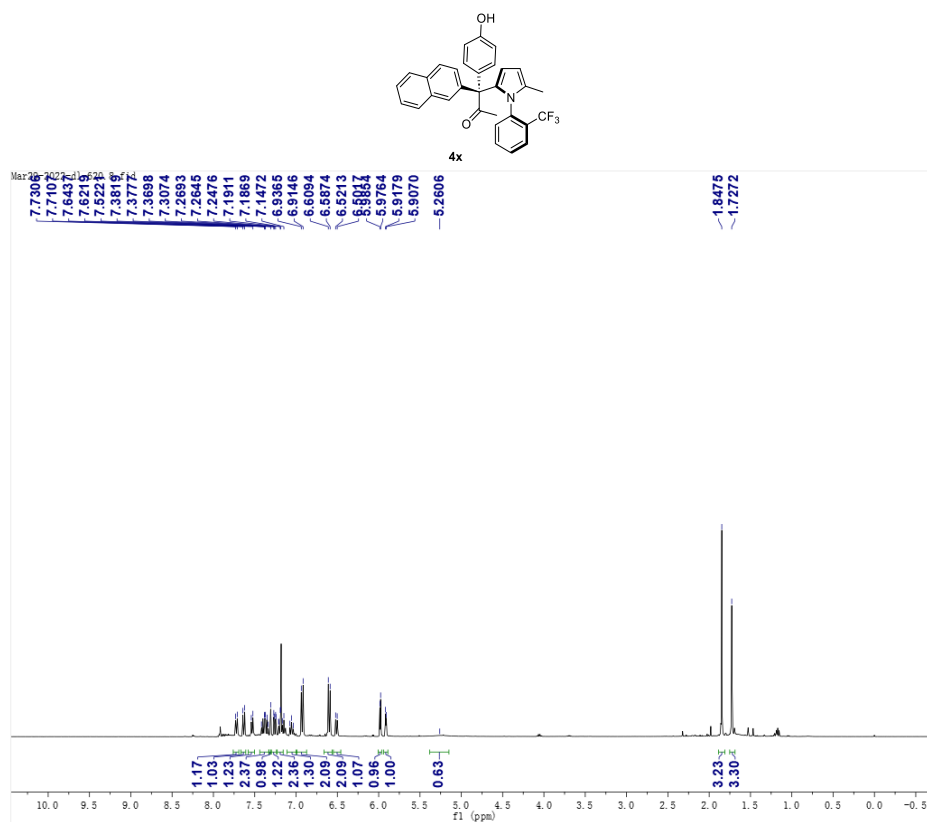
Supplementary Figure 39. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4w** in CDCl_3 .



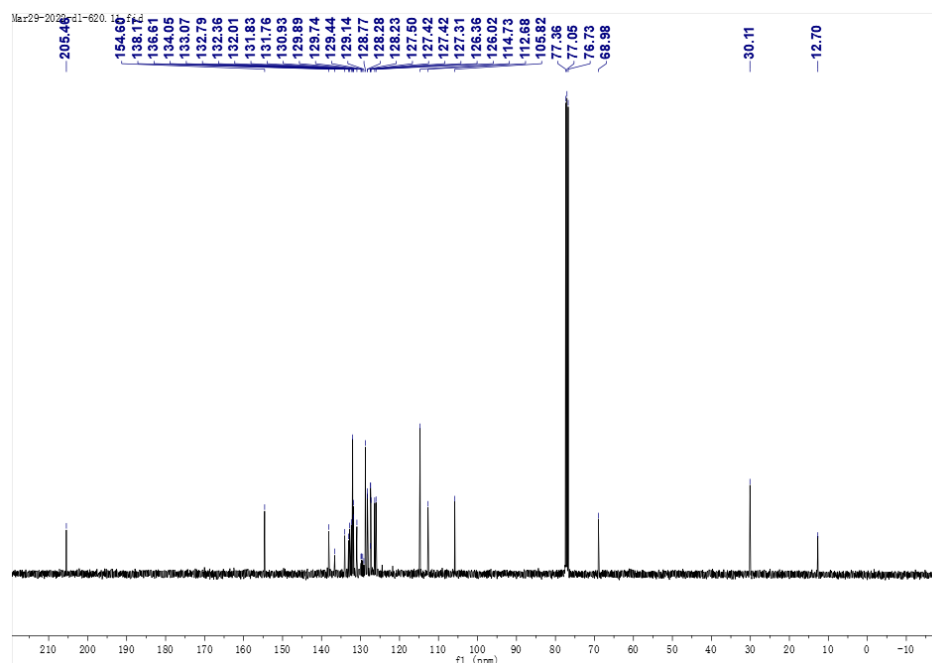
Supplementary Figure 40. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4w** in CDCl_3 .



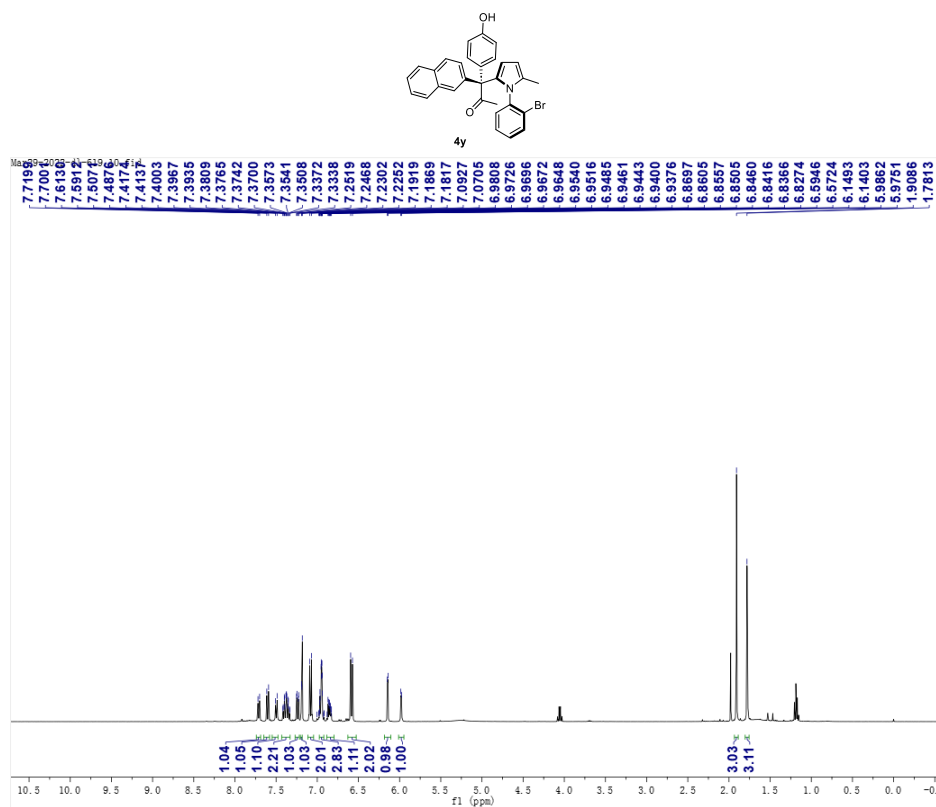
Supplementary Figure 41. ^{31}P NMR (162 MHz, 25 $^{\circ}\text{C}$) spectrum of compound **4r** in CDCl_3 .



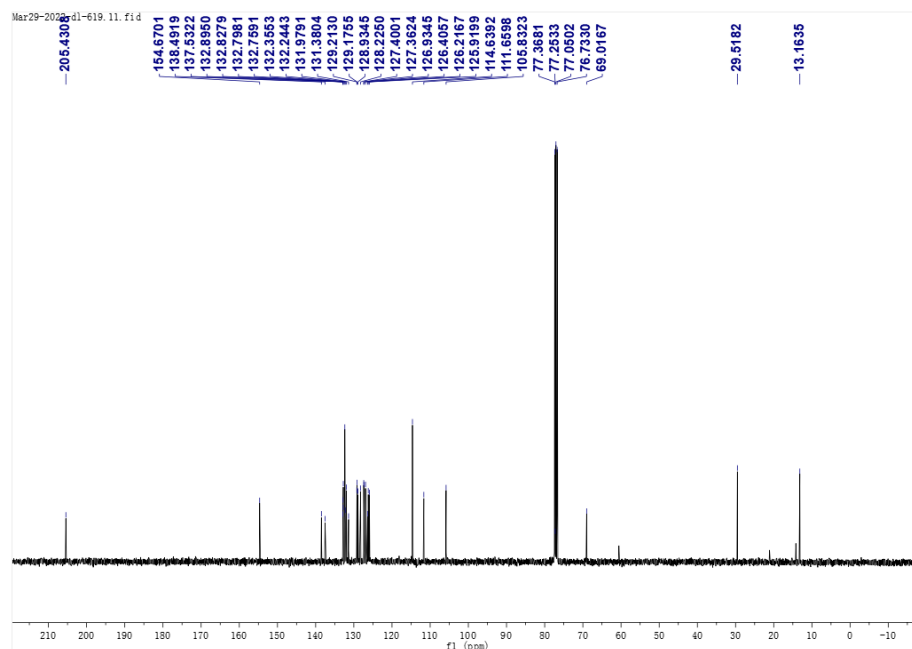
Supplementary Figure 42. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4x** in CDCl₃.



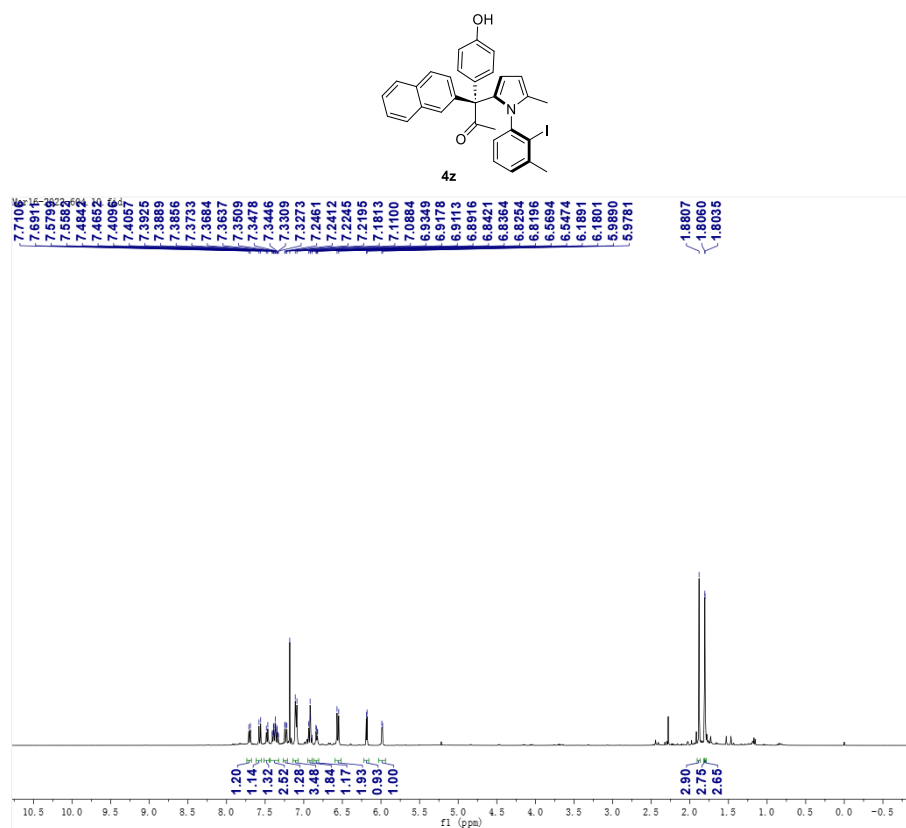
Supplementary Figure 43. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4x** in CDCl₃.



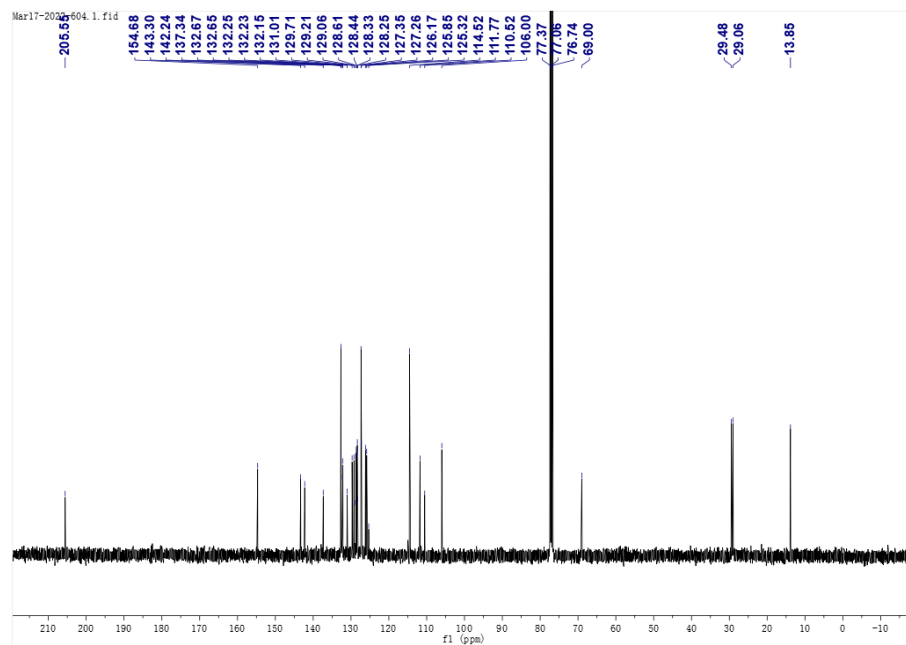
Supplementary Figure 44. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4y** in CDCl₃.



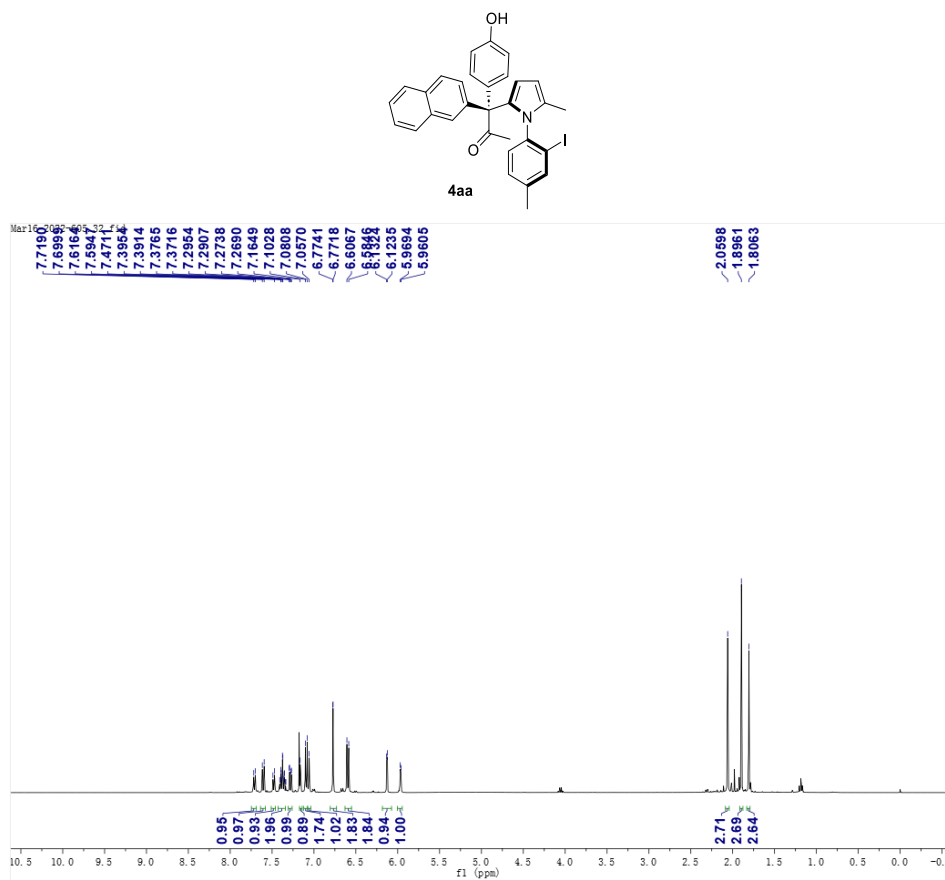
Supplementary Figure 45. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4y** in CDCl₃.



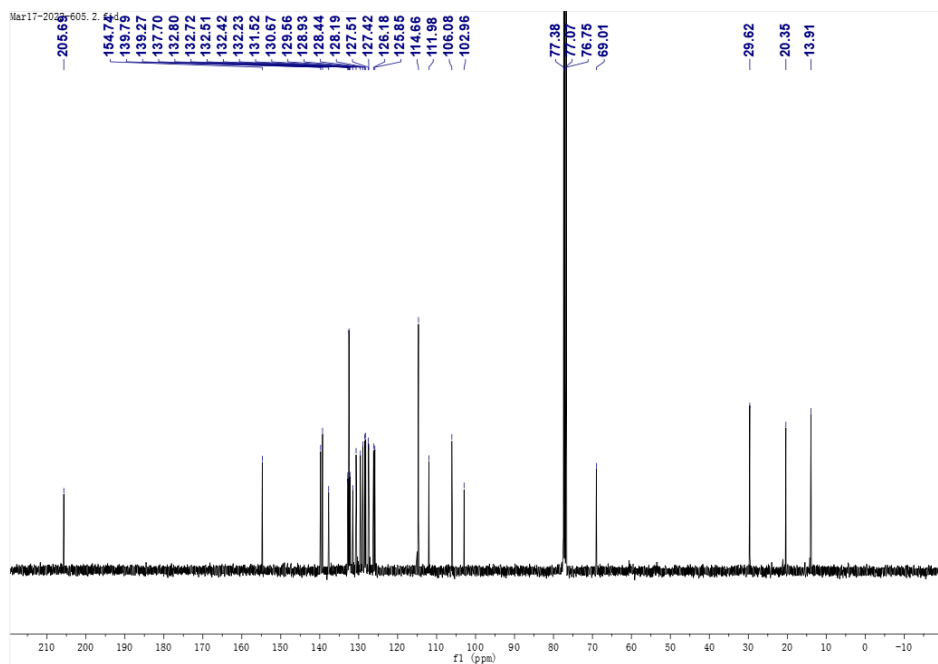
Supplementary Figure 46. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4z** in CDCl₃.



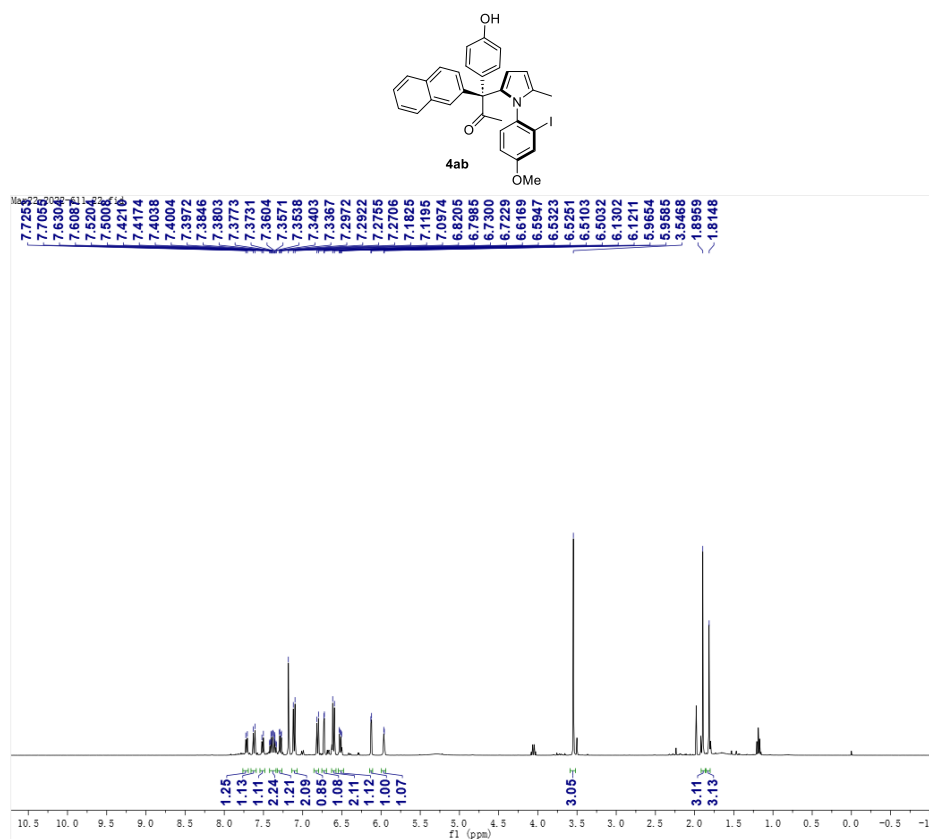
Supplementary Figure 47. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4z** in CDCl₃.



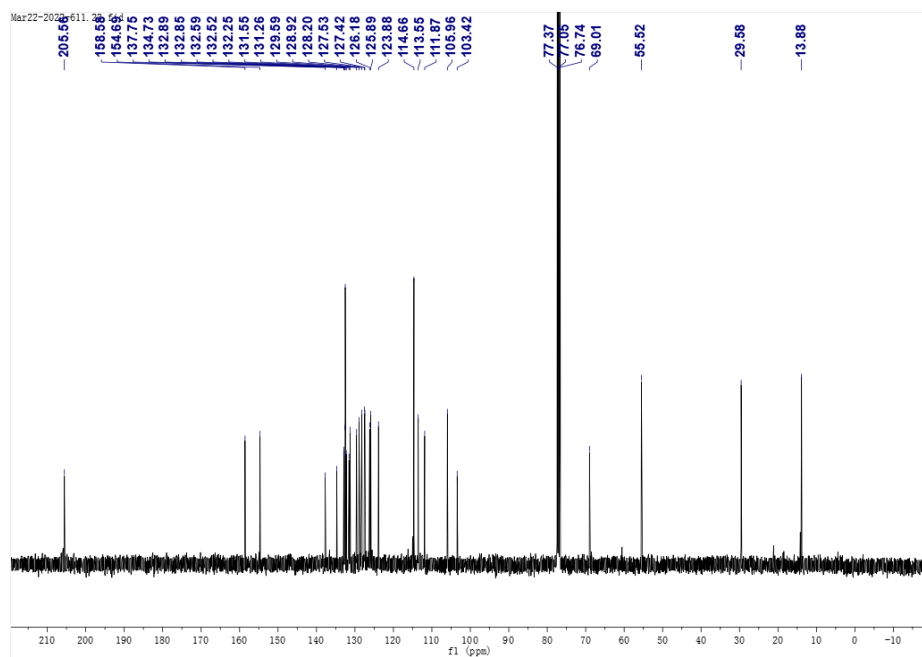
Supplementary Figure 48. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4aa** in CDCl₃.



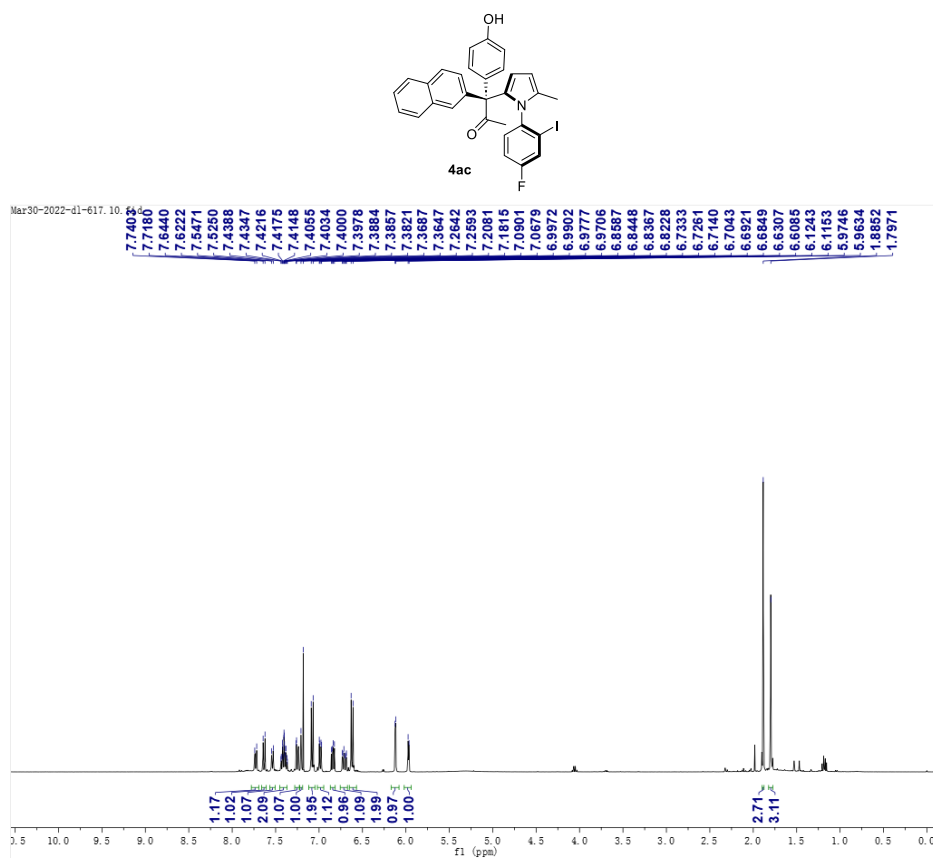
Supplementary Figure 49. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4aa** in CDCl₃.



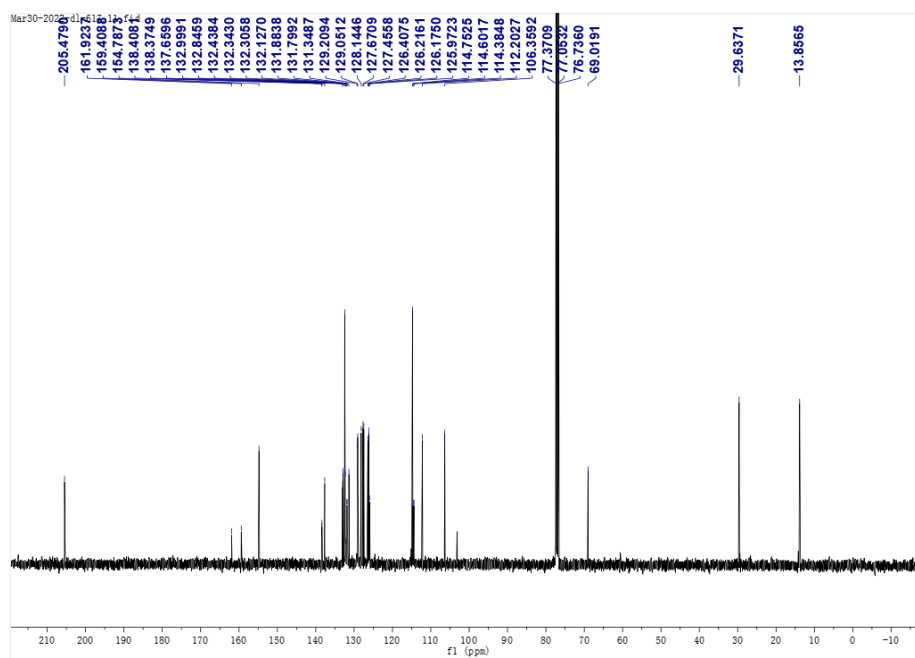
Supplementary Figure 50. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4ab** in CDCl₃.



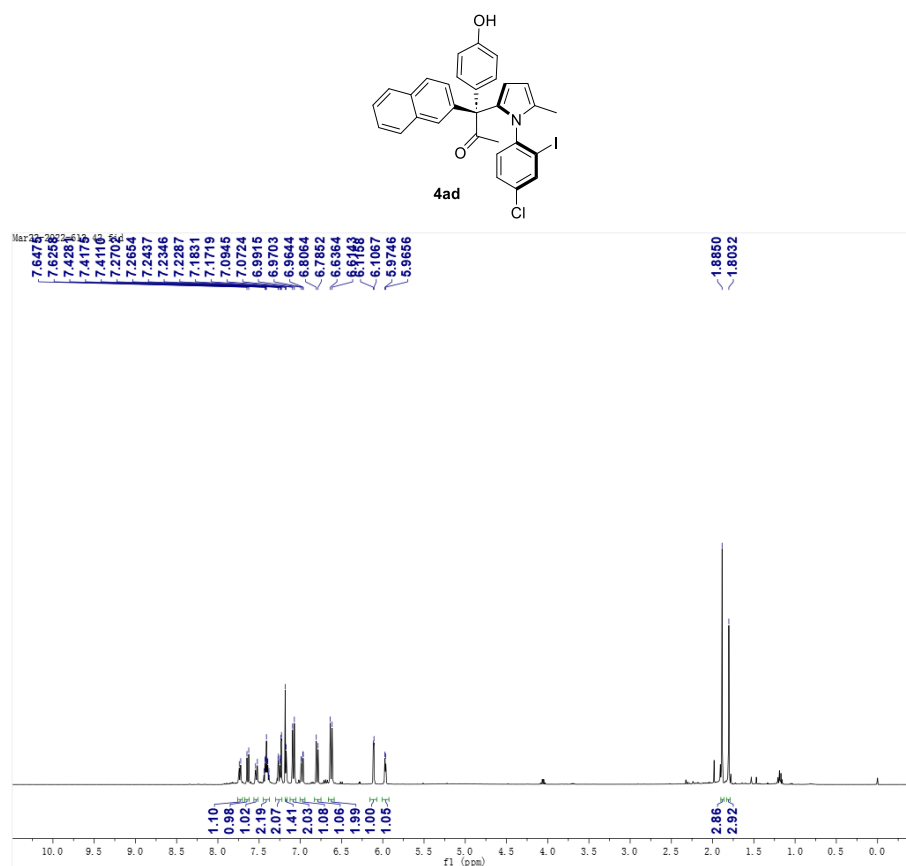
Supplementary Figure 51. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4ab** in CDCl₃.



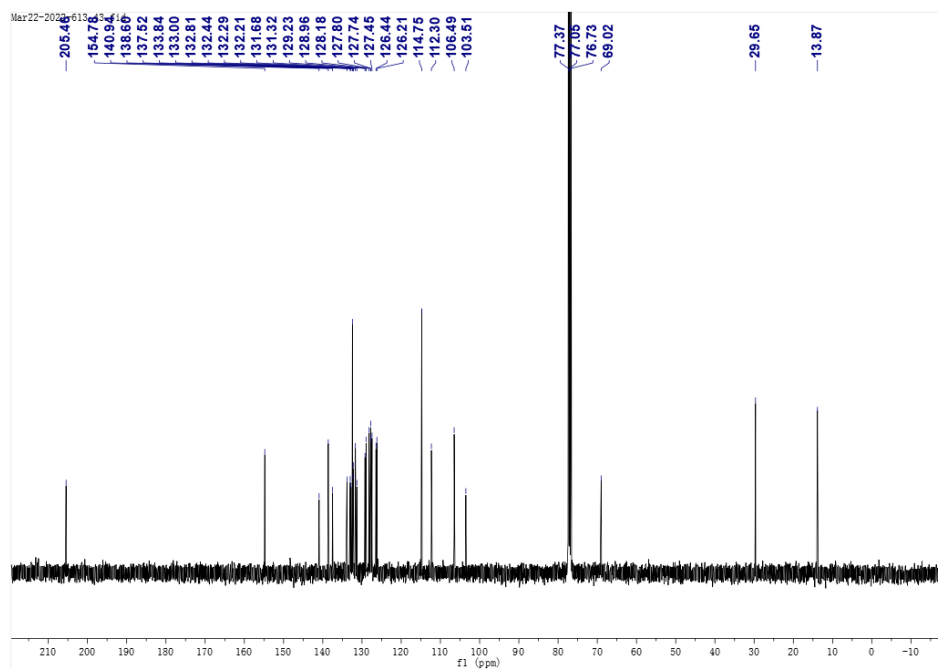
Supplementary Figure 52. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ac** in CDCl_3 .



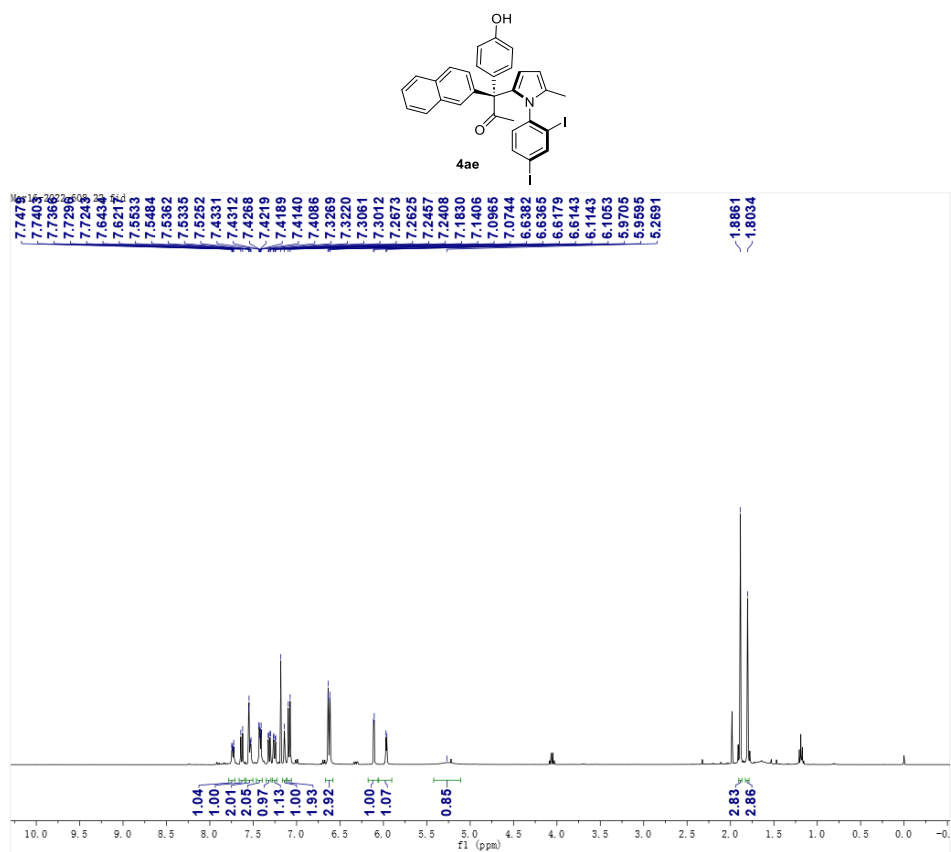
Supplementary Figure 53. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ac** in CDCl_3 .



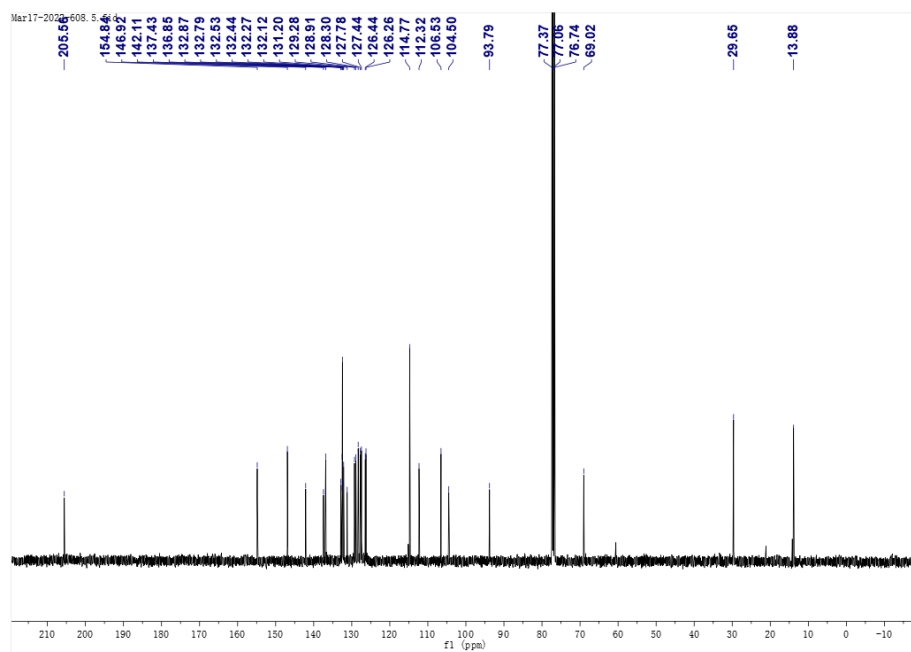
Supplementary Figure 54. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4ad** in CDCl₃.



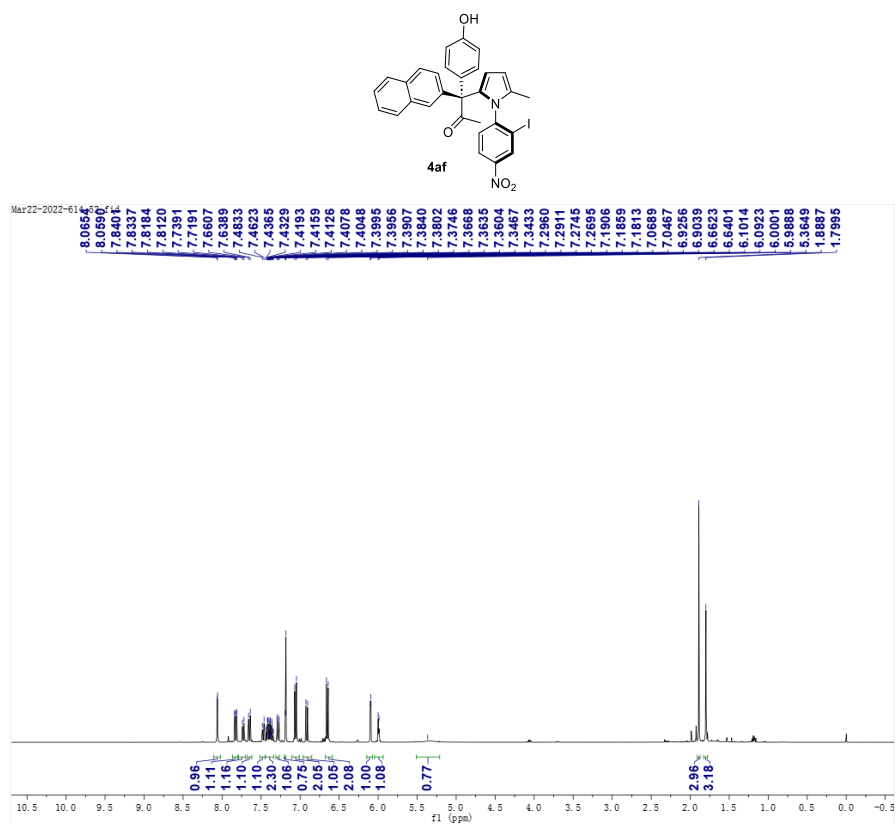
Supplementary Figure 55. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4ad** in CDCl₃.



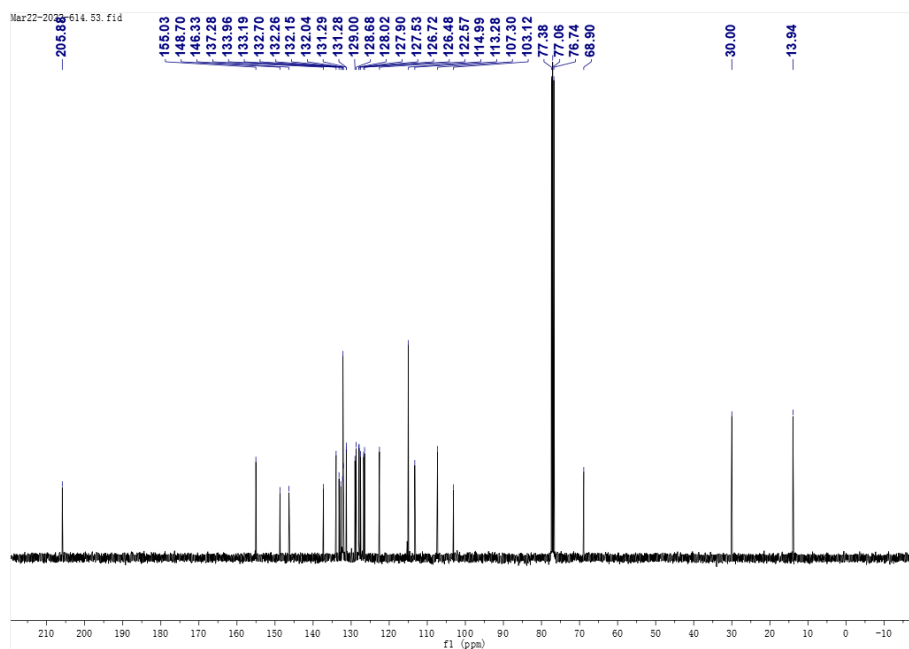
Supplementary Figure 56. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4ae** in CDCl₃.



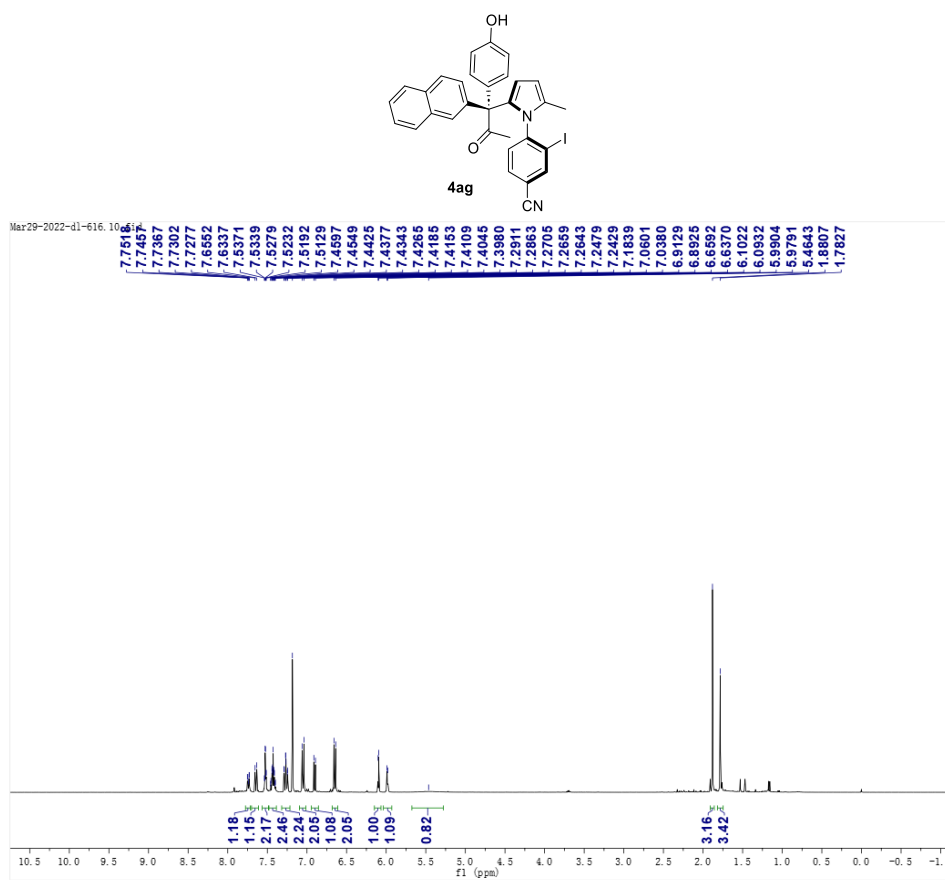
Supplementary Figure 57. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4ae** in CDCl₃.



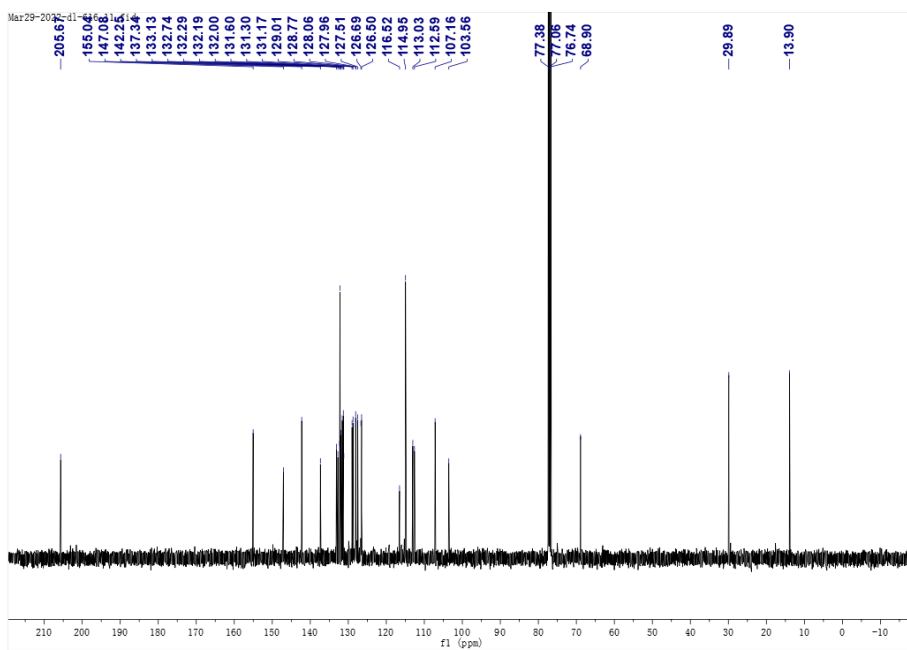
Supplementary Figure 58. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4af** in CDCl_3 .



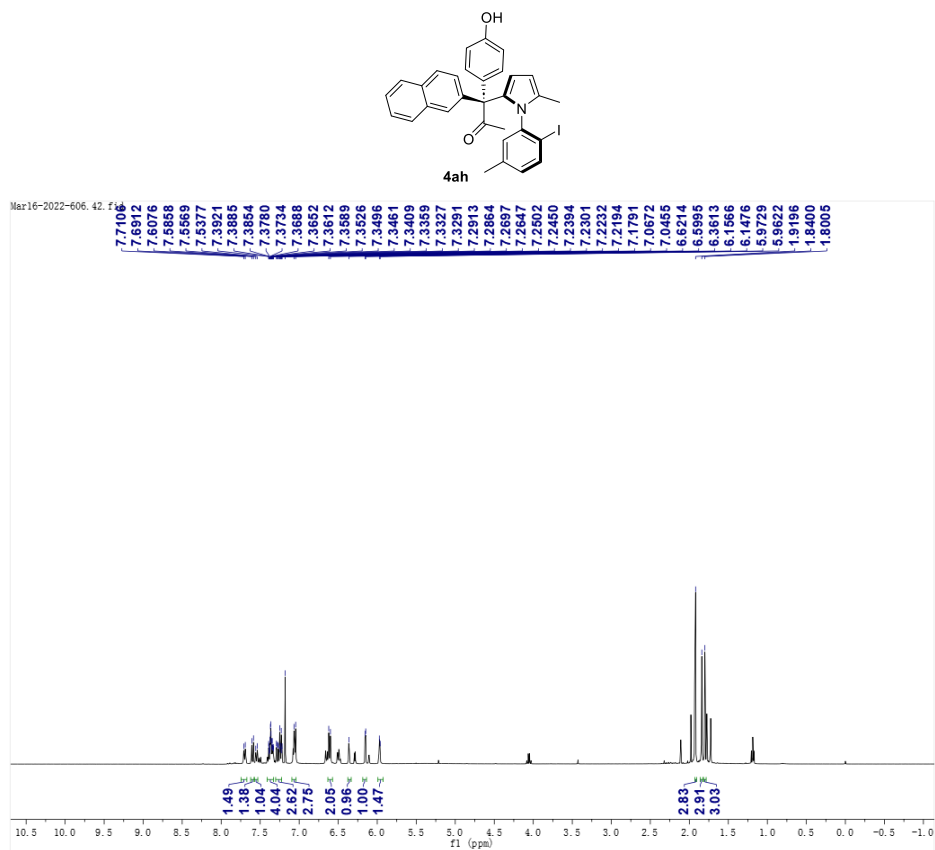
Supplementary Figure 59. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4af** in CDCl_3 .



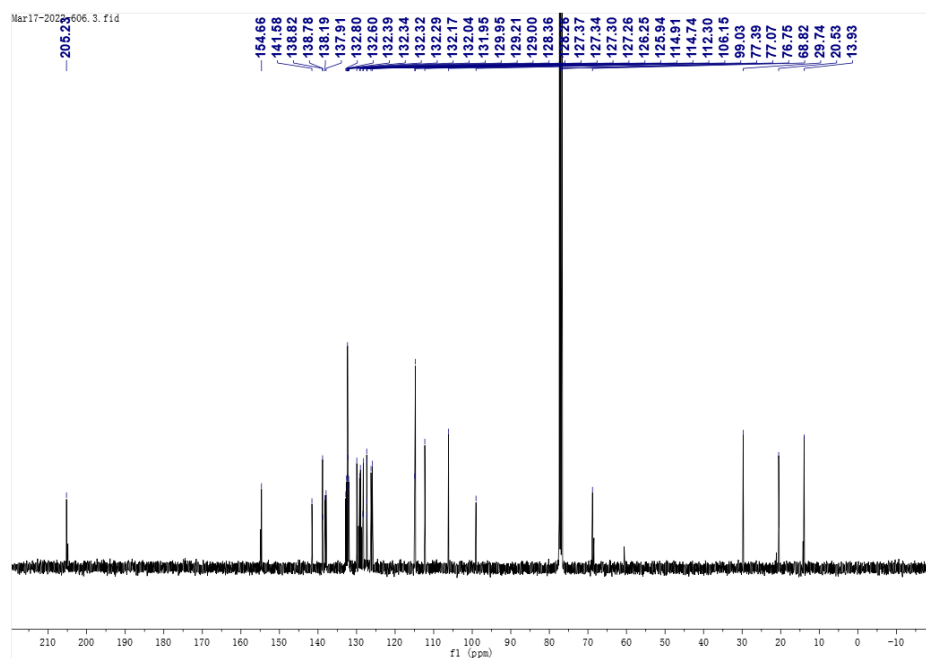
Supplementary Figure 60. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ag** in CDCl_3 .



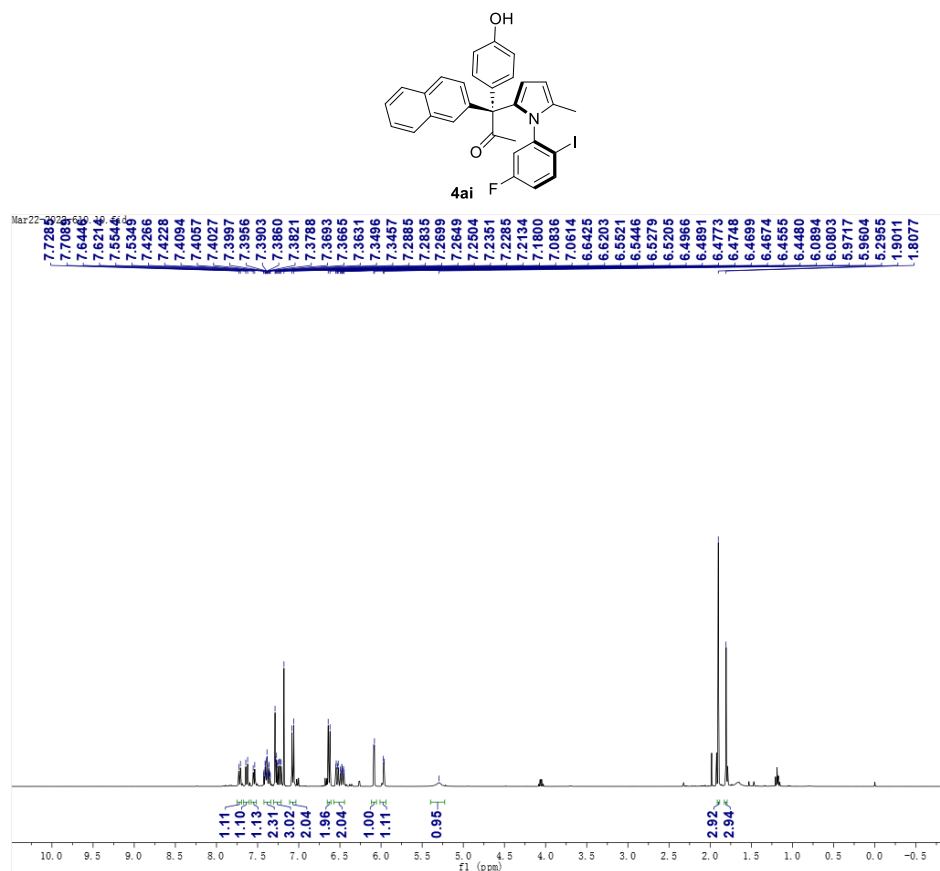
Supplementary Figure 61. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ag** in CDCl_3 .



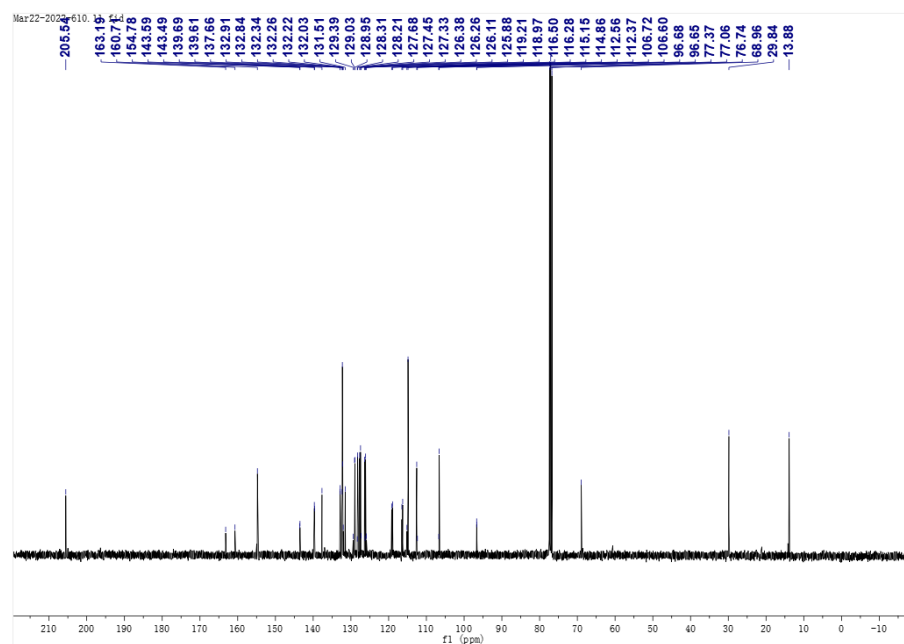
Supplementary Figure 62. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ah** in CDCl_3 .



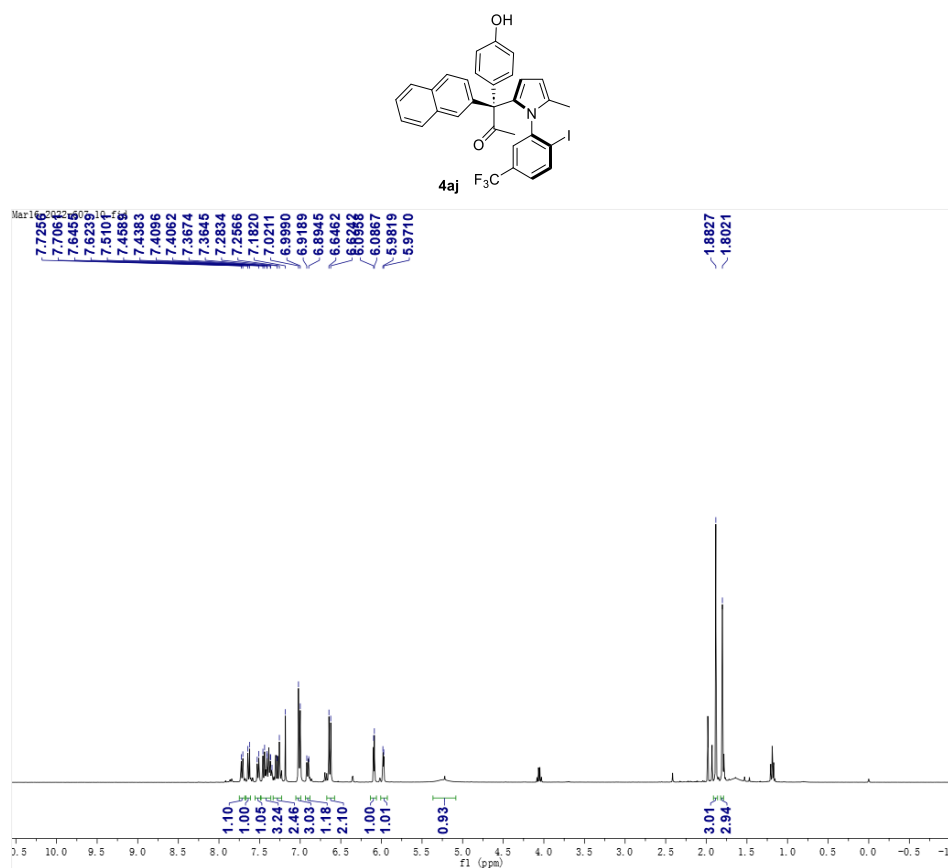
Supplementary Figure 63. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ah** in CDCl_3 .

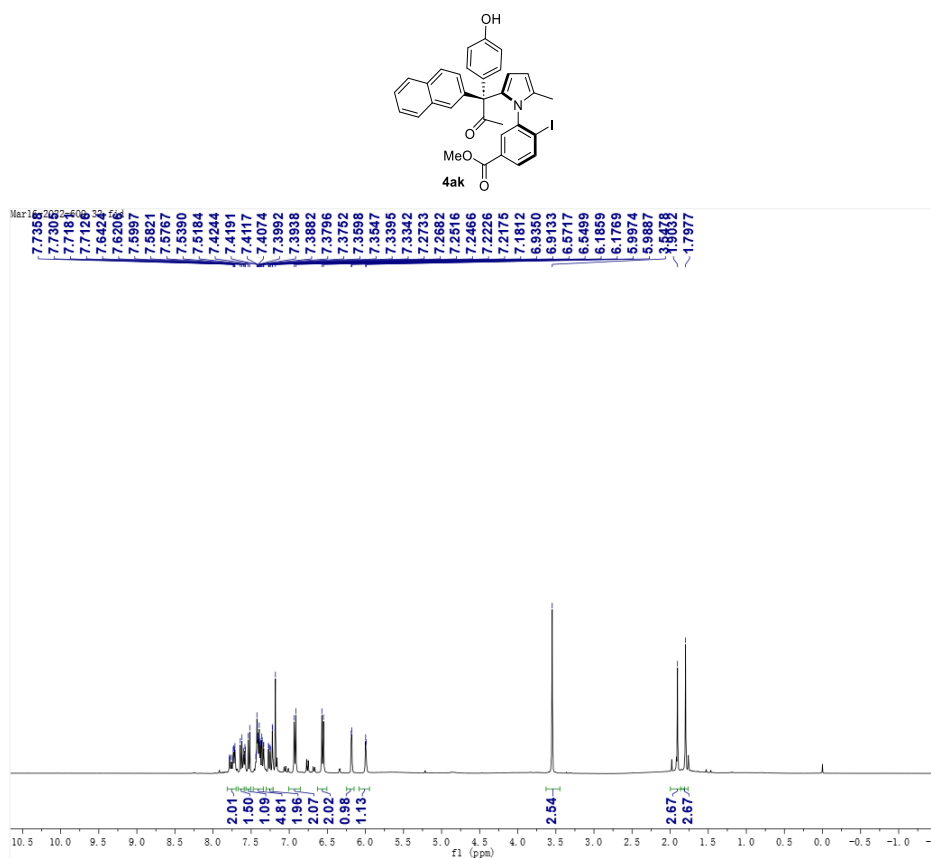


Supplementary Figure 64. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ai** in CDCl_3 .

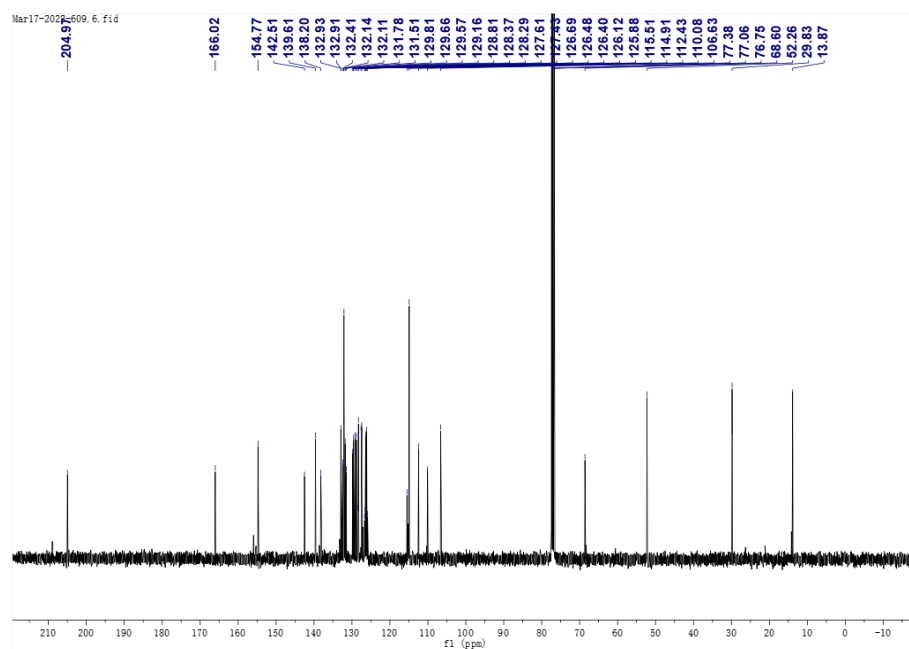


Supplementary Figure 65. ^{13}C NMR (101 MHz, 25 $^\circ\text{C}$) spectrum of compound **4ai** in CDCl_3 .

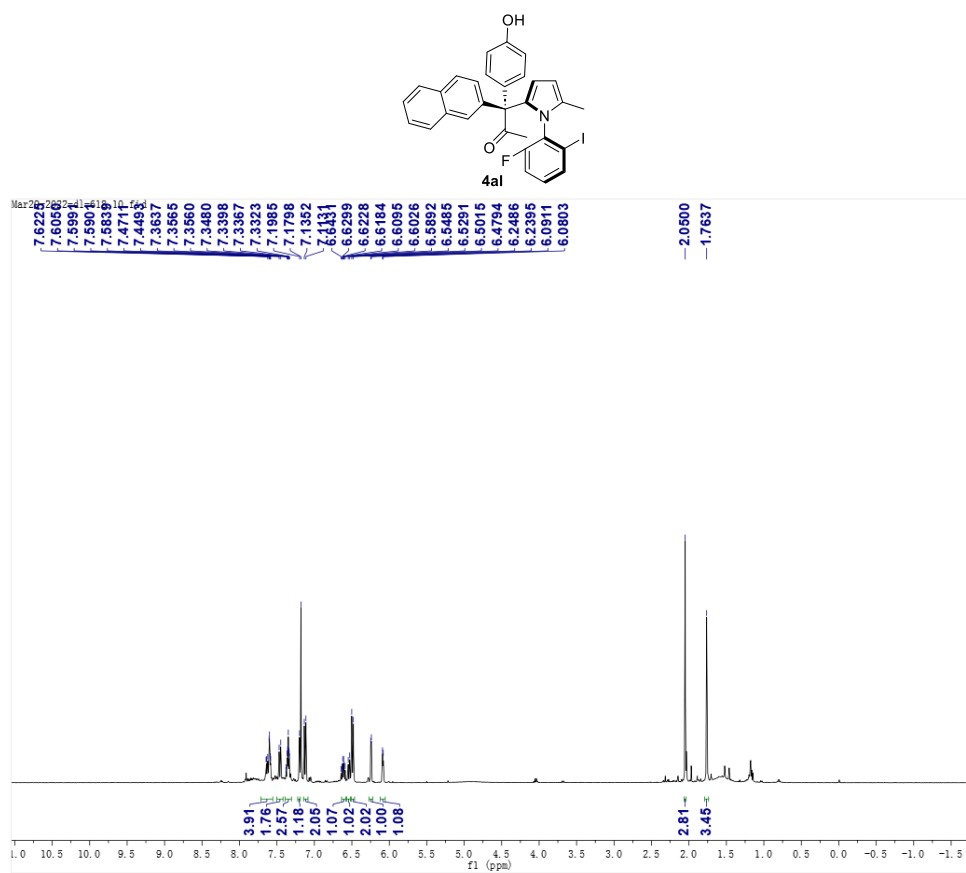




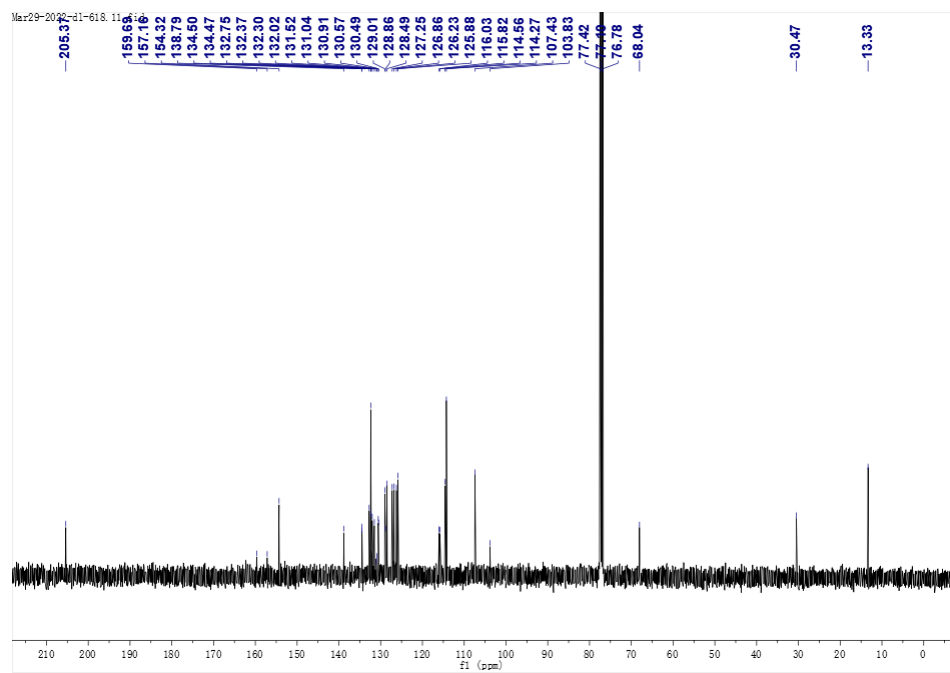
Supplementary Figure 68. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4ak** in CDCl₃.



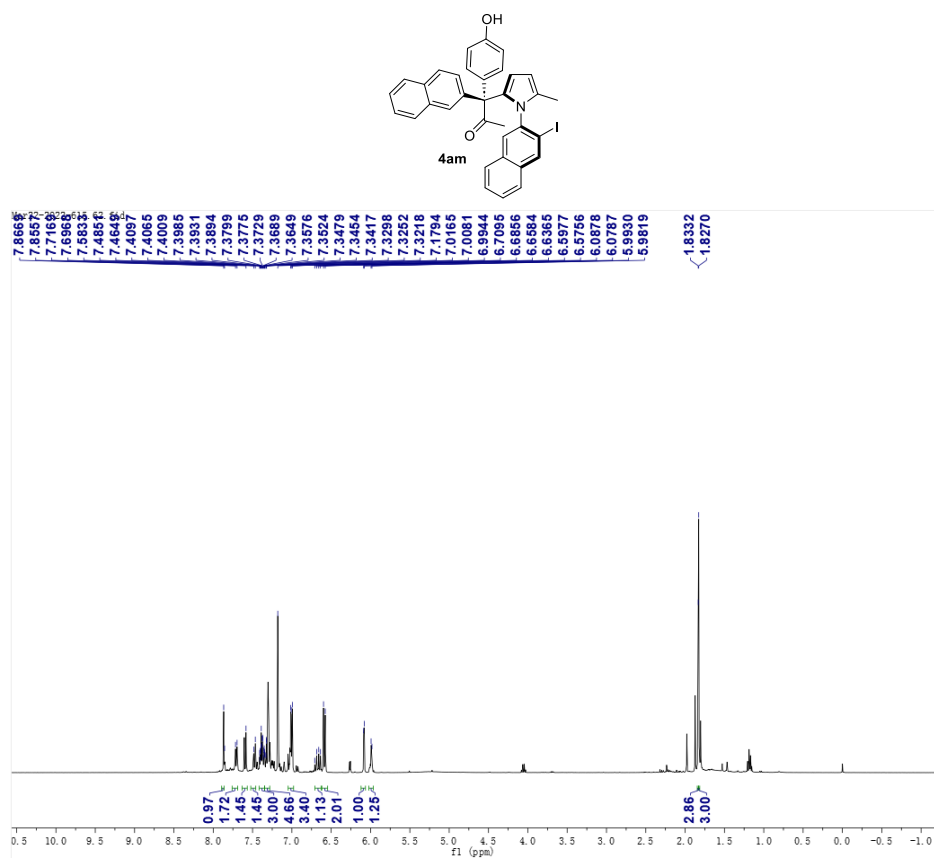
Supplementary Figure 69. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4ak** in CDCl₃.



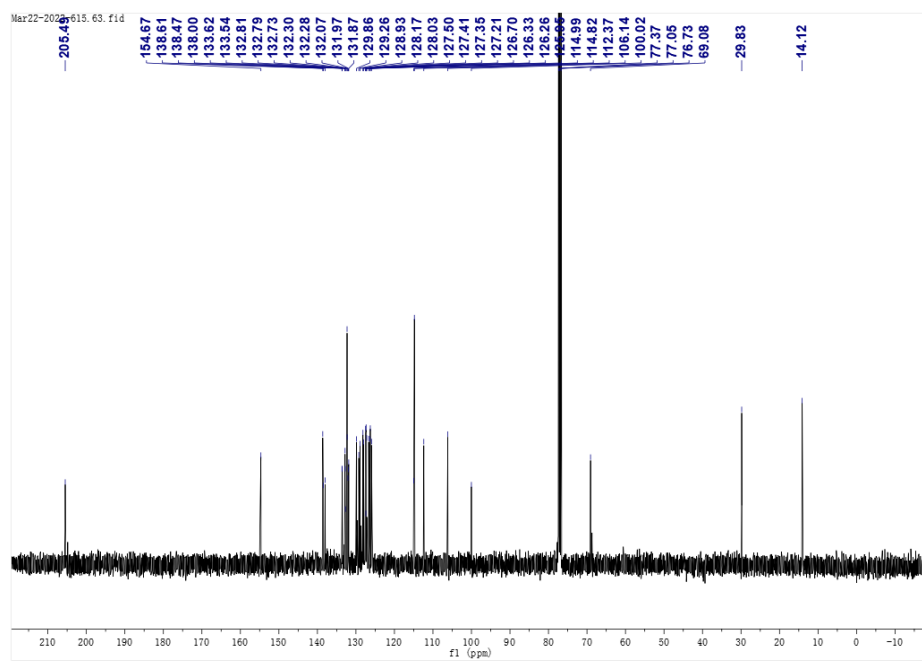
Supplementary Figure 70. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4al** in CDCl₃.



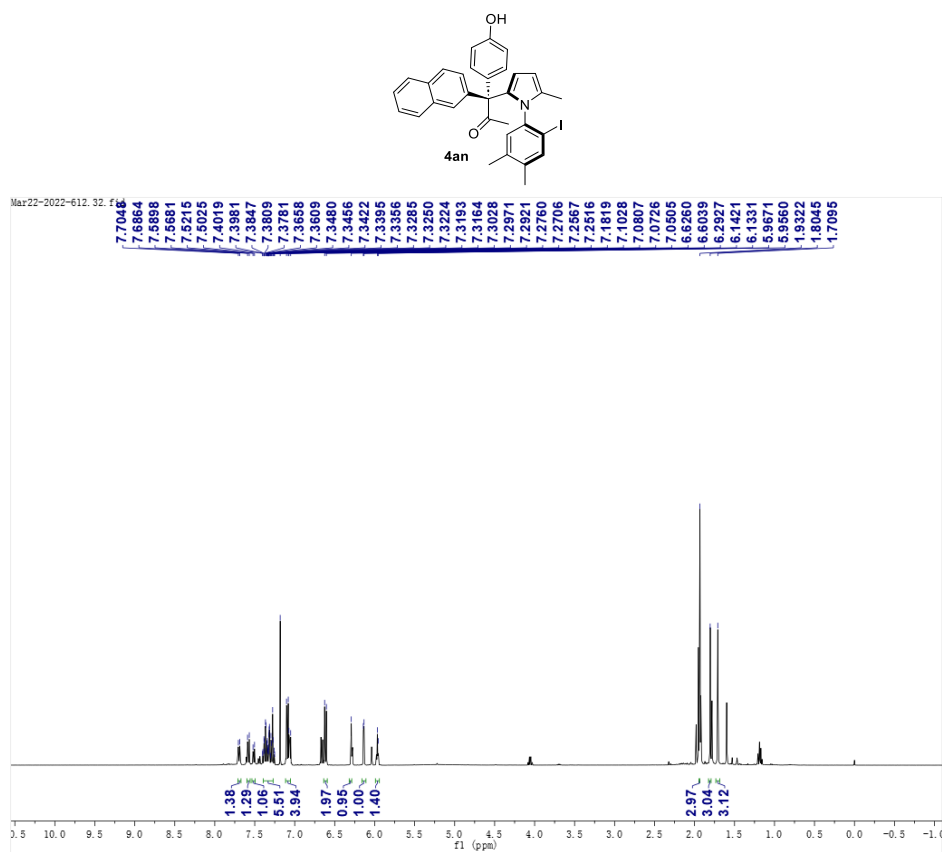
Supplementary Figure 71. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4al** in CDCl₃.



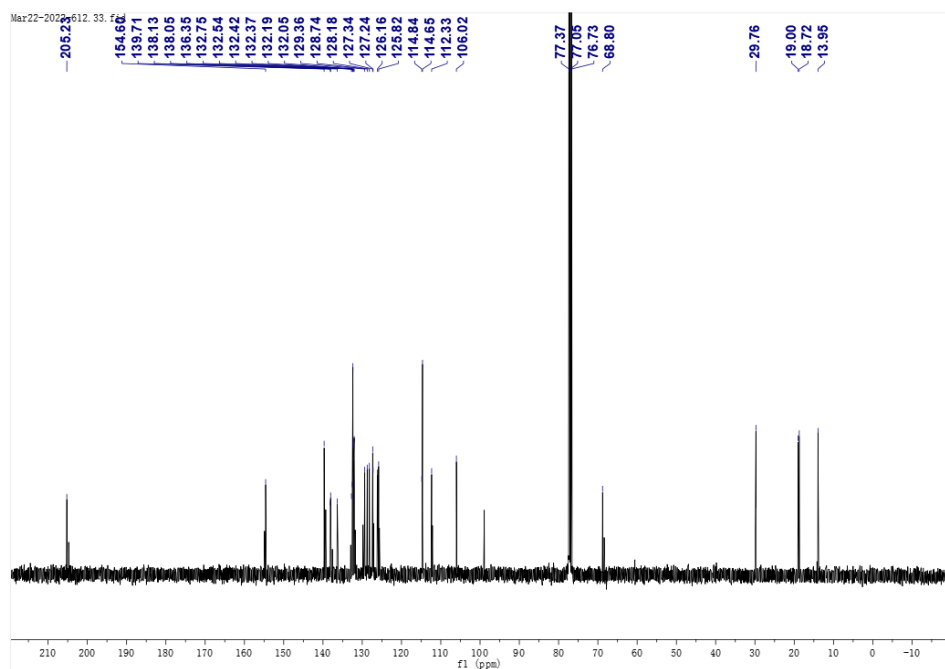
Supplementary Figure 72. ¹H NMR (400 MHz, 25 °C) spectrum of compound **4am** in CDCl₃.



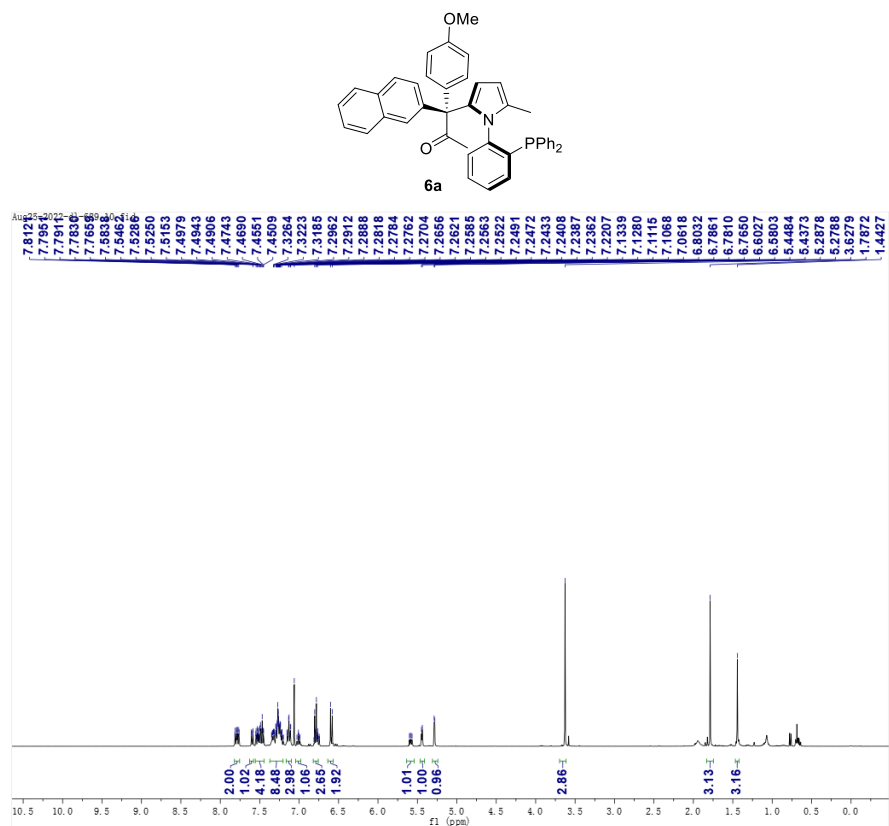
Supplementary Figure 73. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **4am** in CDCl₃.



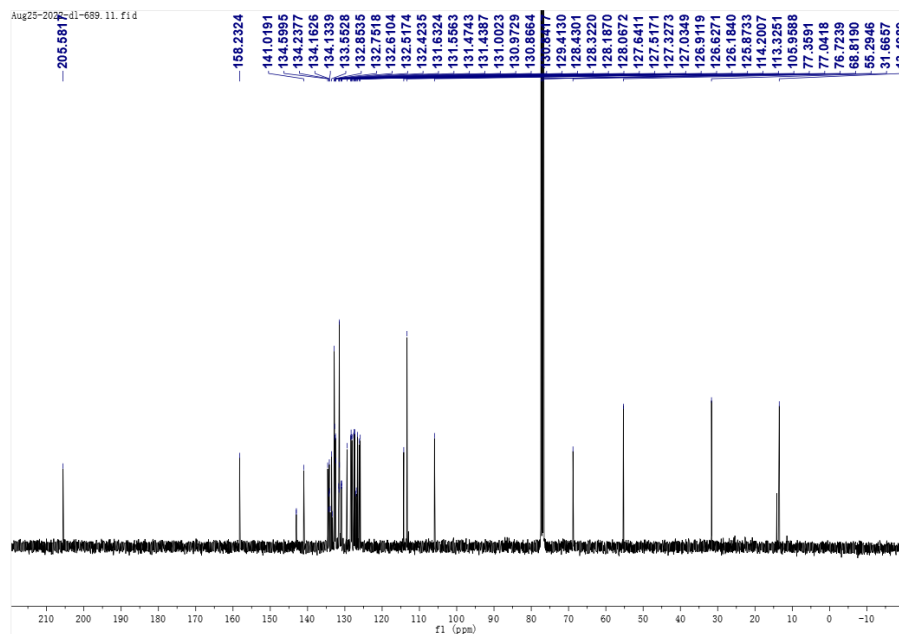
Supplementary Figure 74. ^1H NMR (400 MHz, 25 °C) spectrum of compound **4an** in CDCl_3 .



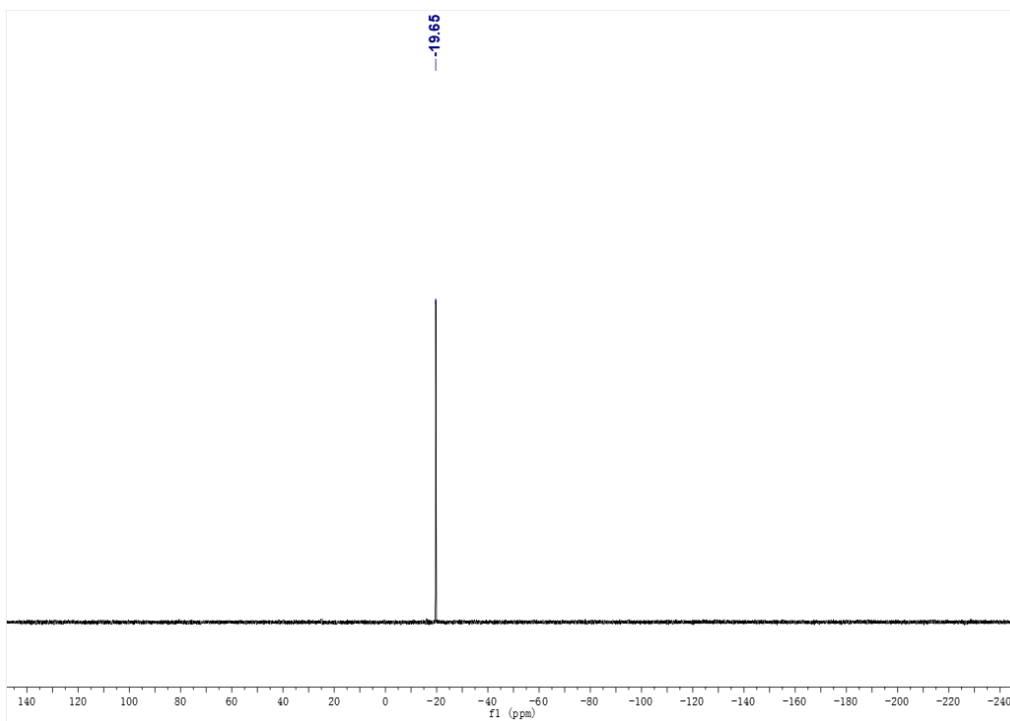
Supplementary Figure 75. ^{13}C NMR (101 MHz, 25 °C) spectrum of compound **4an** in CDCl_3 .



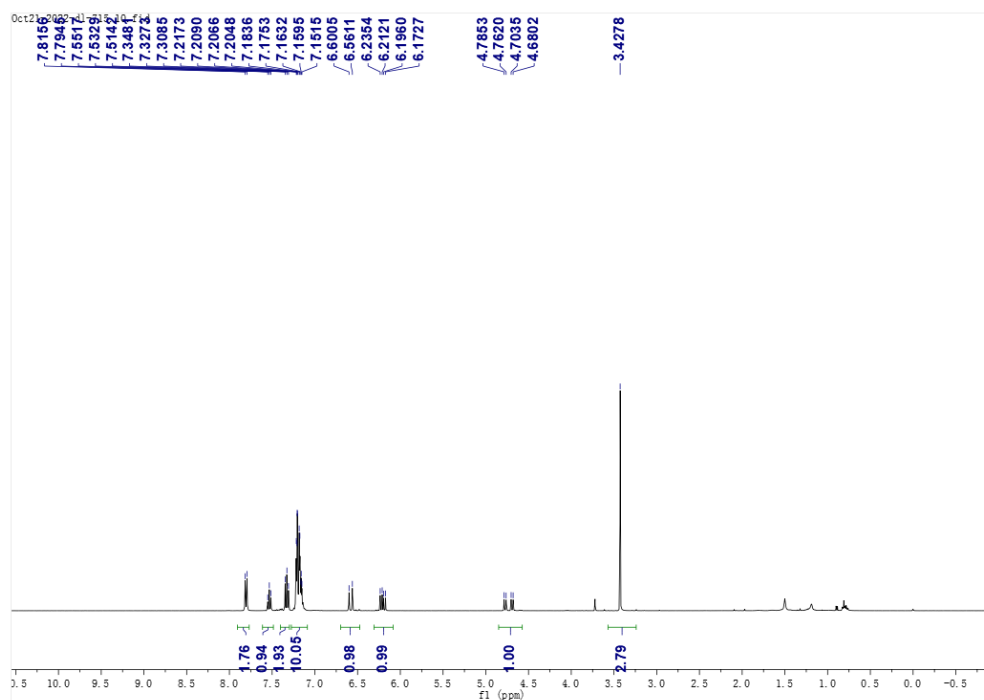
Supplementary Figure 76. ^1H NMR (400 MHz, 25°C) spectrum of compound **6a** in CDCl_3 .



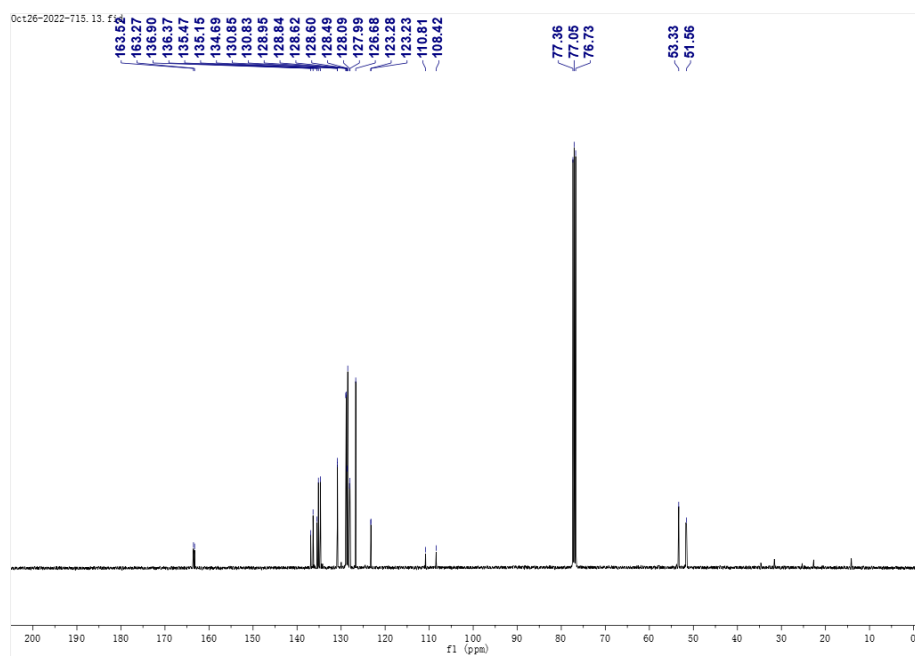
Supplementary Figure 77. ^{13}C NMR (101 MHz, 25°C) spectrum of compound **6a** in CDCl_3 .



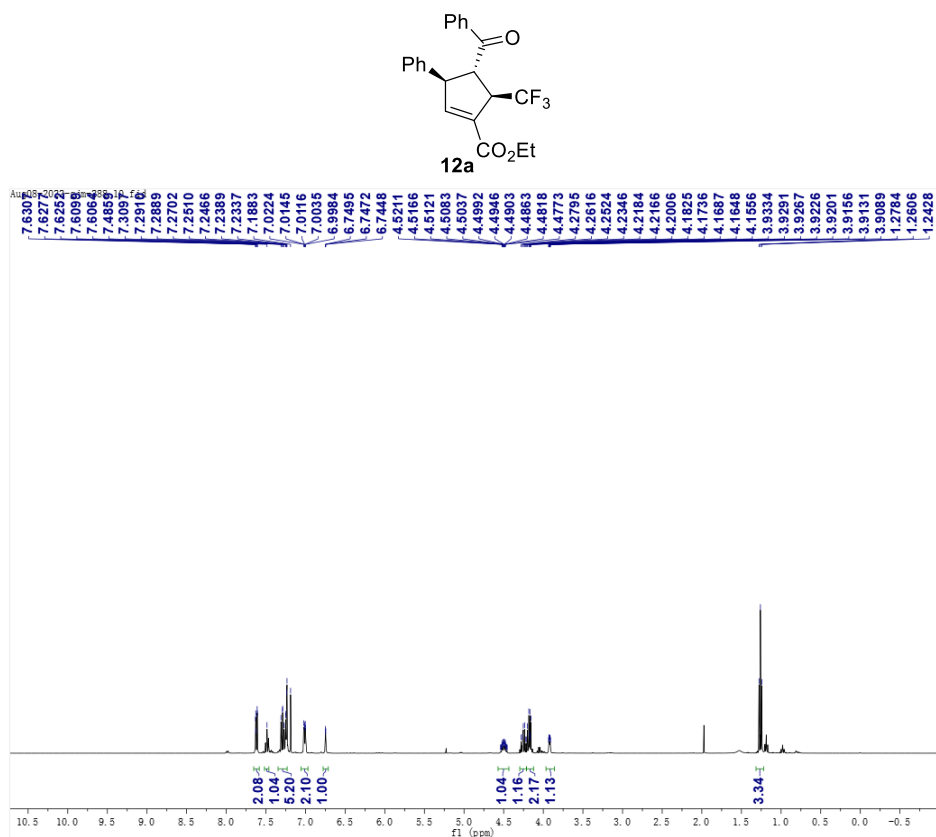
^{31}P spectrum of **6a**
Supplementary Figure 78. ^{31}P NMR (162 MHz, 25 °C) spectrum of compound **6a** in CDCl_3 .



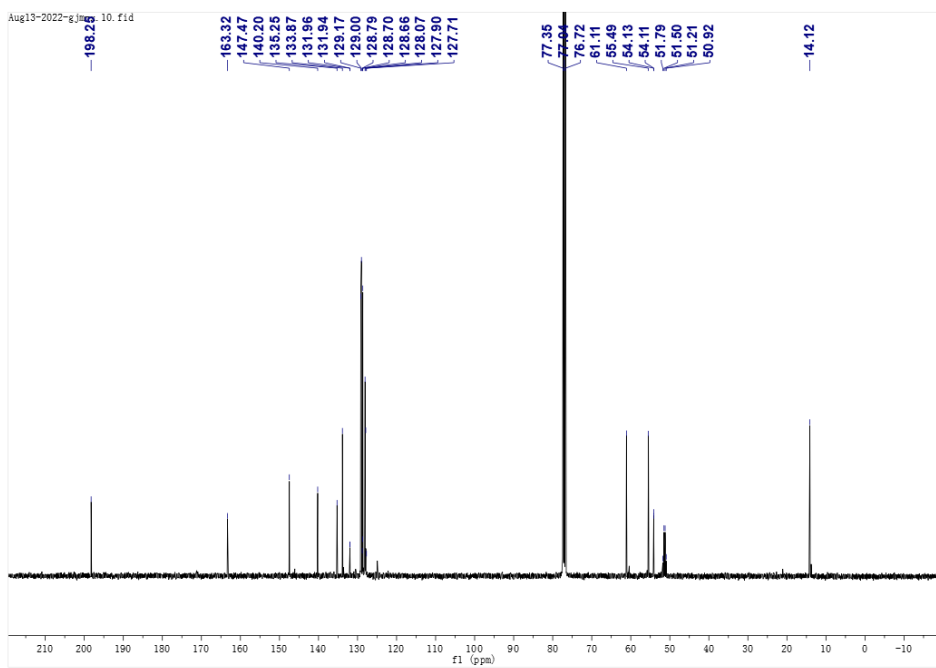
Supplementary Figure 79. ^1H NMR (400 MHz, 25 $^\circ\text{C}$) spectrum of compound **9a** in CDCl_3 .



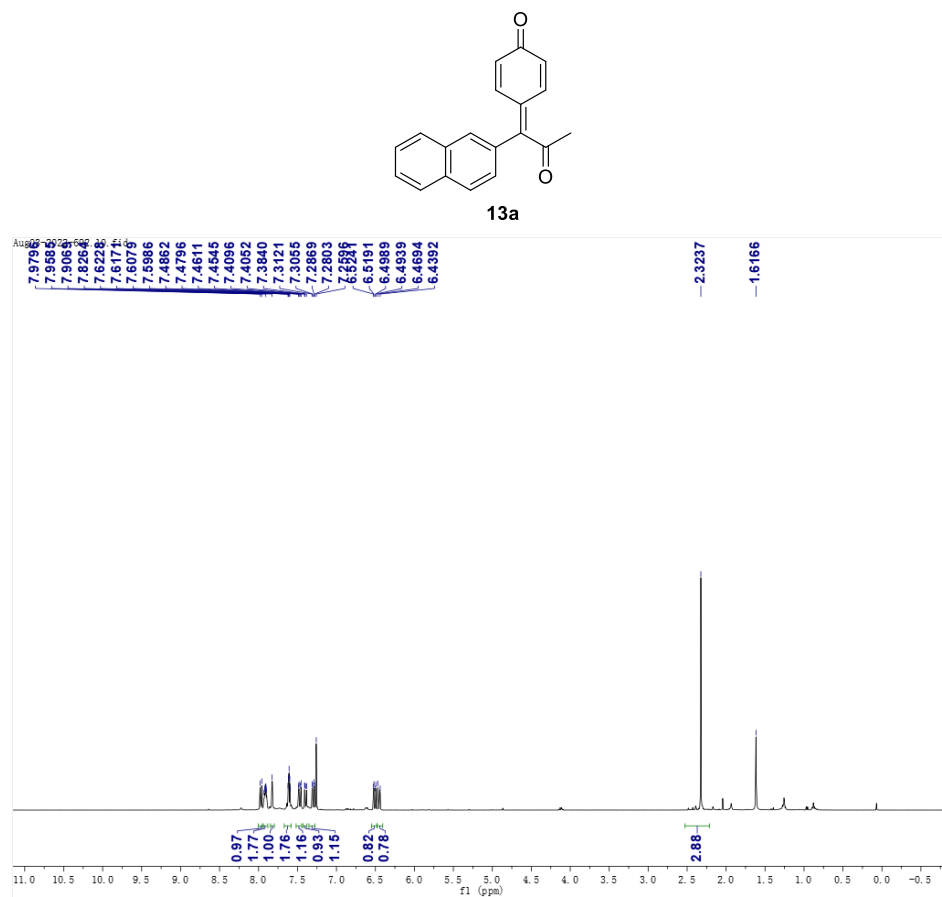
Supplementary Figure 80. ^{13}C NMR (101 MHz, 25 °C) spectrum of compound **9a** in CDCl_3 .



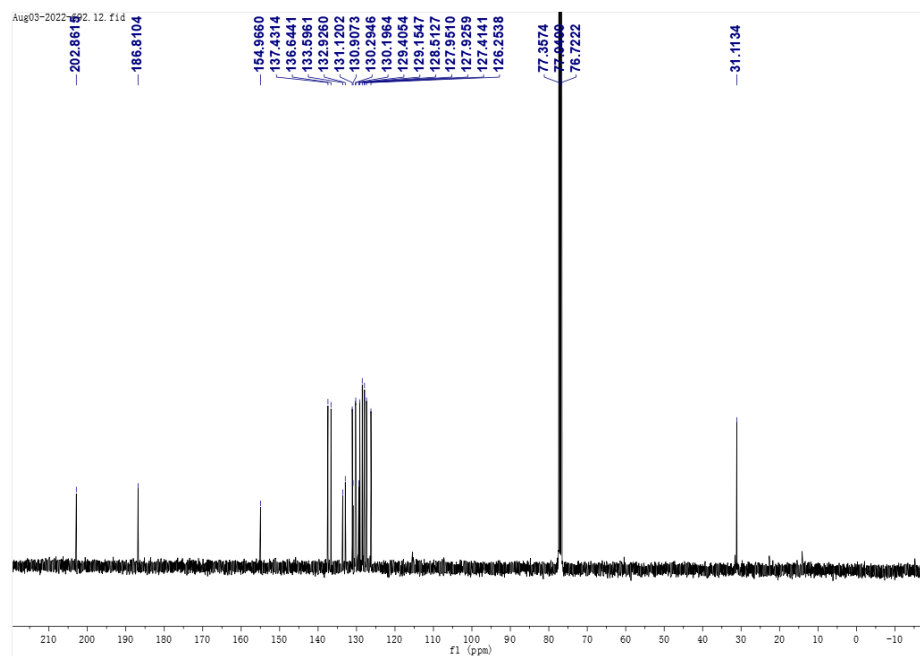
Supplementary Figure 81. ^1H NMR (400 MHz, 25 °C) spectrum of compound **12a** in CDCl_3 .



Supplementary Figure 82. ^{13}C NMR (101 MHz, 25 °C) spectrum of compound **12a** in CDCl_3 .



Supplementary Figure 83. ¹H NMR (400 MHz, 25 °C) spectrum of compound **13a** in CDCl₃.



Supplementary Figure 84. ¹³C NMR (101 MHz, 25 °C) spectrum of compound **13a** in CDCl₃.

4. Supplementary References

- 1 Cruz, F. A. & Dong, V. M. Stereodivergent Coupling of Aldehydes and Alkynes via Synergistic Catalysis Using Rh and Jacobsen's Amine. *J. Am. Chem. Soc.* **139**, 1029-1032 (2017).
- 2 Ping, Y. *et al.* Ni-Catalyzed Regio- and Enantioselective Domino Reductive Cyclization: One-Pot Synthesis of 2,3-Fused Cyclopentannulated Indolines. *ACS Catal.* **9**, 7335-7342 (2019).
- 3 Davison, R. T. *et al.* Enantioselective Addition of α -Nitroesters to Alkynes. *Angew. Chem. Int. Ed.* **60**, 4599-4603 (2021).
- 4 Ye, C.-X. *et al.* Atroposelective Synthesis of Axially Chiral N-Arylpyrroles by Chiral-at-Rhodium Catalysis. *Angew. Chem., Int. Ed.* **59**, 13552-13556 (2020).
- 5 Song, T., Zhao, X., Hu, J. & Dan, W. Diastereoselective and Enantioselective Palladium-Catalyzed Allylic Substitution of Substituted Fluorinated Methylene Derivatives. *Eur. J. Org. Chem.* **2018**, 1141-1144 (2018).
- 6 Ni, H. *et al.* Highly Enantioselective [3 + 2] Annulation of 3-Butynoates with β -Trifluoromethyl Enones Promoted by an Amine-Phosphine Binary Catalytic System. *Org. Lett.* **22**, 2460-2463 (2020).
- 7 Zhou, W. *et al.* Phosphine-catalyzed enantioselective [3 + 2] cycloadditions of γ -substituted allenates with β -perfluoroalkyl enones. *Chem. Sci.* **8**, 4660-4665 (2017).