Support Information

Catalytic dynamic kinetic reductive addition of simple aldehydes and aldimines with heterobiaryl triflates: harnessing both central and axial chirality

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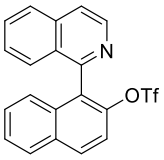
1. General Information

Solvents were either purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system or bought from the commercial sources and transferred to the glovebox without exposure to air. Other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, J&K, Energy Chemical, Bide Pharmatech Ltd. and were used as received. Flash chromatography was either performed using glass columns with SiliaFlash® P60 (SiliCycle, 230-400 mesh), or on pre-packed Biotage® SNAP columns using a Biotage Isolera Automated Flash Chromatography System.

All compounds (starting materials and products) were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, melting point (where applicable), and high-resolution mass spectrometry. ^{1}H NMR spectra were recorded on Bruker 300 or 400 MHz spectrometer and are referenced relative to residual $CDCl_3$ proton signals at δ 7.26 ppm. ^{19}F NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer and are referenced to $CFCl_3$ (δ 0.0 ppm). Data for ^{1}H and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ap = apparent), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer and are referenced to $CDCl_3$ at δ 77.16 ppm. The ^{13}C NMR spectra were obtained with ^{1}H decoupling. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were obtained on a Bruker Alpha and was reported in terms of frequency of absorption (cm-1). GC analyses were performed on an Agilent 8860 gas chromatograph with an FID detector using a J&W DB-1 column (10 m, 0.1 mm I.D.). High Resolution Mass spectra were obtained on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument (ESI) or Atmospheric Pressure Chemical Ionization (ESI) mode. High pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel columns (250 mm). Optical rotations were measured on a S3 Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm pathlength cell at 589 nm with [α]D values reported in degrees; concentration (c) is in g/100 mL. Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. The powder X-ray diffraction pattern (PXRD) measurements were carried out on a Philips X'pert MPD Pro X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm), and the X-ray tube was operated at 40 kV and 40 mA at room temperature. Reactions were monitored by GC analysis and thin-layer chromatography (TLC) carried out on 0.25 mm Jiang you silica gel plates (HSGF254) using UV light as a visualizing agent.

2. Preparation of Substrates



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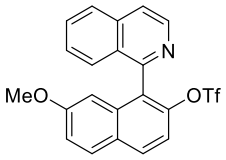

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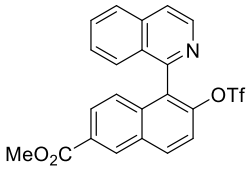

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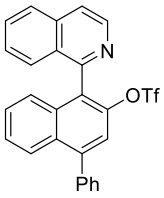

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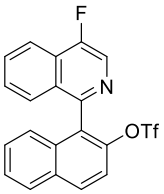

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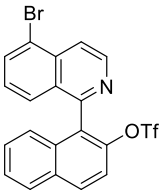

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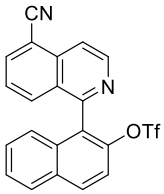

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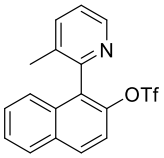

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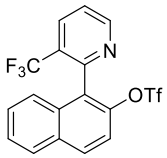

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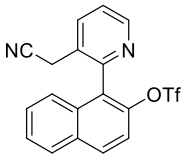

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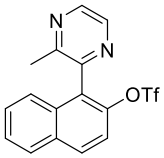

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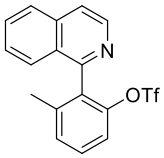

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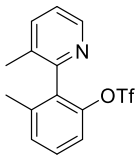

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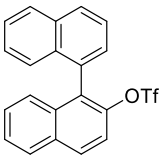
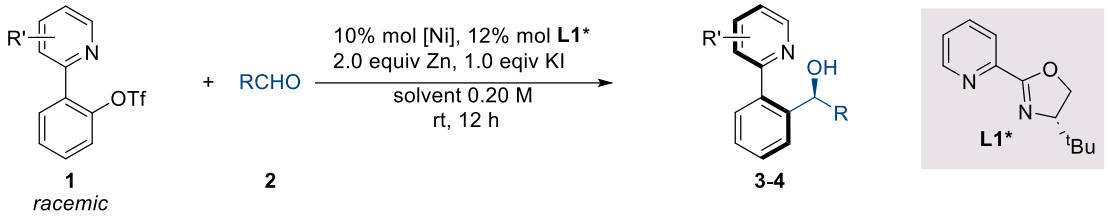


1n

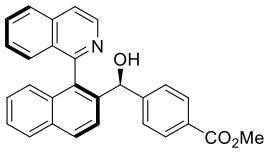
All are known compounds in the reported literatures.[1]

3. Asymmetric Synthesis of chiral heterobiaryl carbinols & amines

General procedure (A) for 3 and 4.

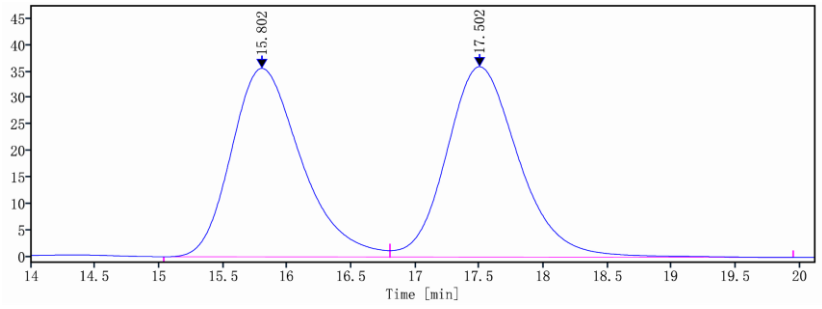


In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added **1** (0.10 mmol, 1.0 equiv), nickel salts (10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), solvent (0.5 mL) were added, and the mixture was stirred for 10 min at room temperature, at which time Corresponding aldehyde was added to the resulting mixture. The reaction was stirred at rt for up to 12 h (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended). After the reaction was complete, the reaction mixture was directly filtered through a short pad of silica gel [EtOAc in petroleum ether (PE)] to give the crude product. The product was purified by chromatography on silica gel for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated. The enantiomeric excesses (% ee) were determined by HPLC analysis using chiral stationary phases.



Methyl 4-((*S*)-Hydroxy(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methyl)benzoate (3a).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–25% EtOAc in PE) to provide the title compound as a white solid in 90% yield (37.7 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.8 Hz, 1H), 8.12 – 8.02 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.61 – 7.39 (m, 4H), 7.27 – 7.16 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.07 – 6.94 (m, 3H), 5.78 (s, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.71, 159.54, 148.44, 141.37, 141.34, 135.94, 134.84, 132.90, 132.88, 130.32, 129.64, 128.56, 128.31, 128.15, 127.62, 127.59, 127.33, 127.29, 126.67, 126.64, 126.25, 126.17, 124.63, 121.32, 75.66, 51.84; **HRMS** (ESI) calcd. for $C_{28}H_{21}NO_3$ $[M+H]^+$ *m/z* 420.1594, found 420.1596; **IR** (neat, cm^{-1}) 3146, 2945, 2842, 1710, 1605, 1586, 1278, 830, 781, 709; **m.p.** 186.2 – 186.9 °C; **$[\alpha]_D^{20}$** = –50.0 (*c* = 0.02, $CHCl_3$); 93% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 17.2 min, t_R (minor) = 15.6 min.



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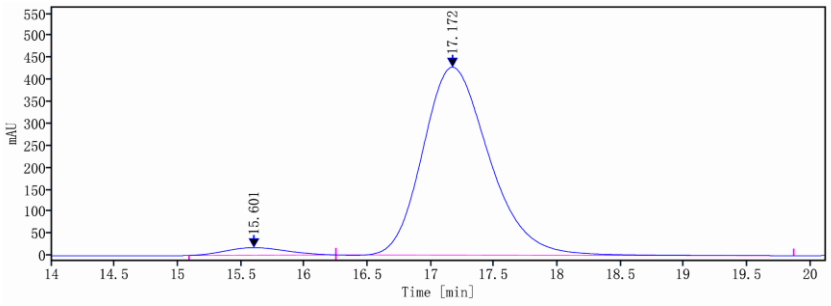

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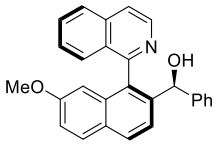
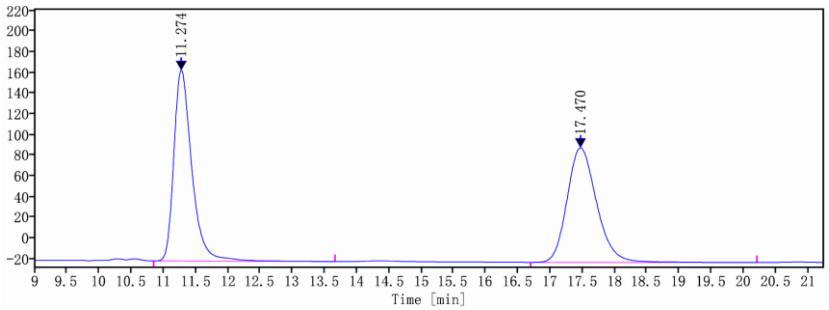


(*S*)-(1-((*S*)-Isoquinolin-1-yl)-7-methoxynaphthalen-2-yl)(phenyl)methanol (**3b**).

From **1-(isoquinolin-1-yl)-7-methoxynaphthalen-2-yl trifluoromethanesulfonate (1b)** (43.3 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), benzaldehyde (12.8 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 70% yield (27.4 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 5.8 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.63 – 7.54 (m, 1H), 7.31 – 7.23 (m, 2H), 7.20 – 7.08 (m, 1H), 7.08 – 6.94 (m, 2H), 6.92 – 6.80 (m, 2H), 6.81 – 6.68 (m, 1H), 6.26 (d, J = 2.5 Hz, 1H), 5.70 (s, 1H), 3.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.81, 157.95, 143.20, 142.23, 141.51, 136.05, 134.05, 133.28, 130.41, 129.61, 129.21, 128.50, 128.27, 127.68, 127.33, 127.22, 126.67, 125.82, 125.05, 124.86, 120.99, 118.48, 104.98, 75.43, 54.92; **HRMS** (ESI) calcd. for $C_{27}H_{21}NO_2$ $[M+H]^+$ *m/z* 392.1645, found 392.1646; **IR** (neat, cm^{-1}) 3416, 2925, 2852, 1628, 1555, 1513, 1426, 829, 734; **m.p.** 172.0 – 173.2 °C; **$[\alpha]_D^{20}$** = –95.0 (c = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 17.4 min, t_R (minor) = 11.2 min.



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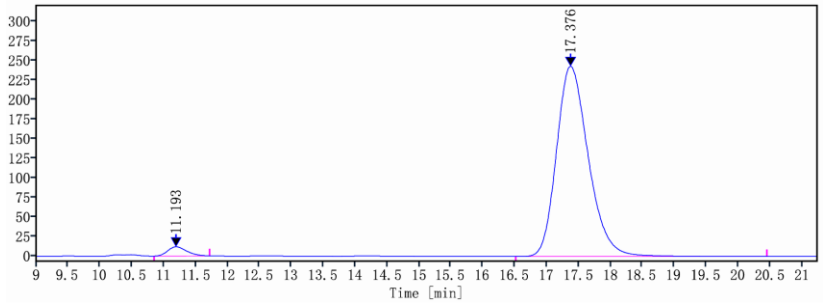

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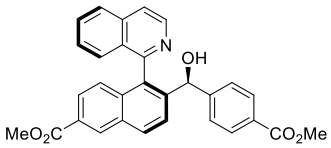
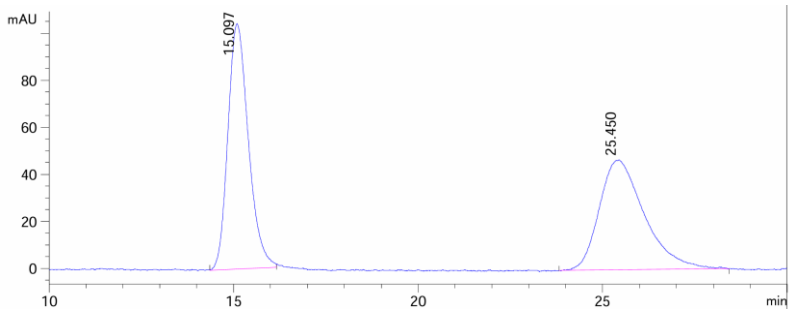


Methyl 6-((*S*)-hydroxy(4-(methoxycarbonyl)phenyl)methyl)-5-((*S*)-isoquinolin-1-yl)-2-naphthoate (**3c**).

From **methyl 5-(isoquinolin-1-yl)-6-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (1c)** (46.1 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 65% yield (31.0 mg). ***Rf*** 0.3 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.7 Hz, 1H), 8.63 (d, J = 5.8 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 7.88 – 7.65 (m, 4H), 7.60 – 7.51 (m, 1H), 7.51 –

7.42 (m, 2H), 7.27 – 7.13 (m, 1H), 7.11 – 6.90 (m, 4H), 5.76 (s, 1H), 3.96 (s, 3H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.92, 166.66, 158.82, 148.01, 143.59, 141.48, 136.02, 134.96, 134.84, 132.02, 131.13, 130.95, 130.47, 128.69, 128.24, 128.22, 127.69, 127.63, 127.50, 127.22, 126.79, 126.48, 125.94, 124.73, 121.49, 75.23, 52.32, 51.86; **HRMS** (ESI) calcd. for $C_{30}H_{23}NO_5$ $[M+H]^+$ *m/z* 478.1649, found 478.1651; **IR** (neat, cm^{-1}) 3435, 3061, 2946, 2842, 1716, 1624, 1558, 1435, 1227, 830, 807; **m.p.** 194.5 – 195.3 °C; **$[\alpha]_D^{20}$** = +60 (*c* = 0.04, $CHCl_3$); 92% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 27.0 min, t_R (minor) = 15.5 min.



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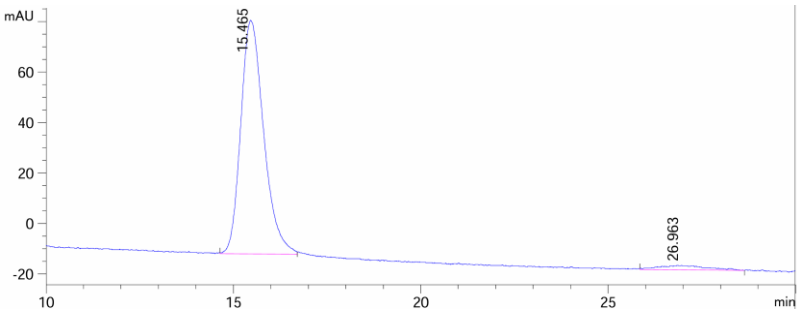

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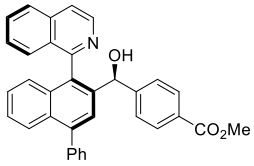
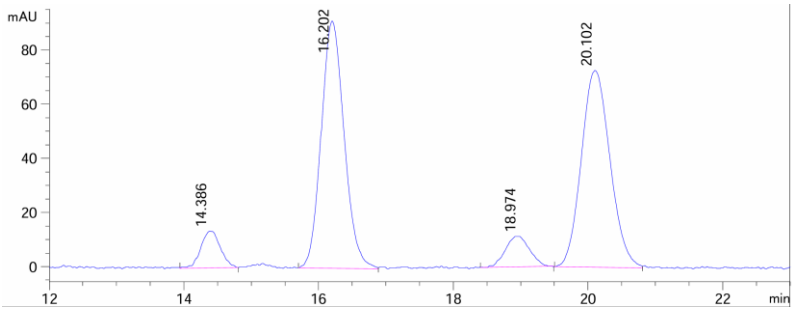
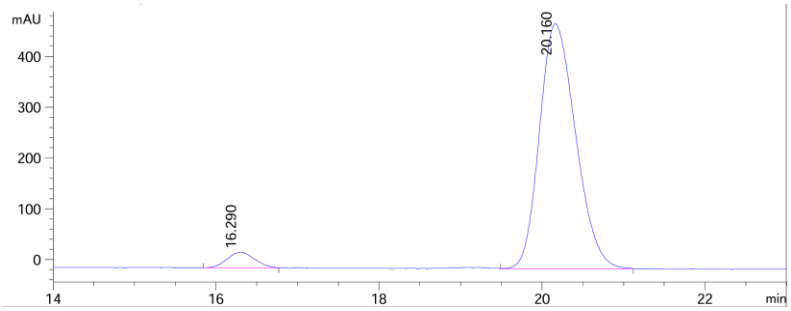


Methyl 4-((*S*)-hydroxy(1-((*S*)-Isoquinolin-1-yl)-4-phenylnaphthalen-2-yl)methyl)benzo-ate (3d).

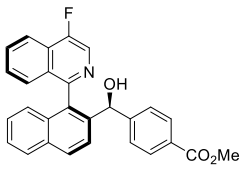
From **1-(isoquinolin-1-yl)-4-phenylnaphthalen-2-yl trifluoromethanesulfon-ate (1d)** (47.9 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 78% yield (38.6 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 5.7 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.64 (d, J = 6.8 Hz, 2H), 7.61 – 7.48 (m, 4H), 7.48 – 7.36 (m, 3H), 7.32 – 7.18 (m, 3H), 7.16 – 6.93 (m, 3H), 5.79 (s, 1H), 4.80 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.72, 159.69, 148.42, 141.88, 141.51, 140.87, 140.20, 135.96, 134.39, 133.36, 131.19, 130.31, 130.21, 128.64, 128.58, 128.44, 128.42, 127.68, 127.66, 127.36, 127.31, 126.66, 126.56, 126.48, 126.35, 126.30, 124.65, 121.32, 75.79, 51.83; **HRMS** (ESI) calcd. for $C_{34}H_{25}NO_3$ $[M+H]^+$ *m/z* 496.1907, found 496.1909; **IR** (neat, cm^{-1}) 3177, 3060, 2946, 2839, 1720, 1612, 1557, 1435, 1277, 875, 872, 760, 697; **m.p.** 189.2 – 191.1 °C; **$[\alpha]_D^{20}$** = –117.5 (*c* = 0.066, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 20.2 min, t_R (minor) = 16.3 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	14.386	MM	13.644	0.337	5.657	275.891
2	16.202	BV	91.343	0.359	44.492	2.170e3
3	18.974	MM	11.362	0.415	5.794	282.609
4	20.102	BV	72.738	0.403	44.057	2.149e3



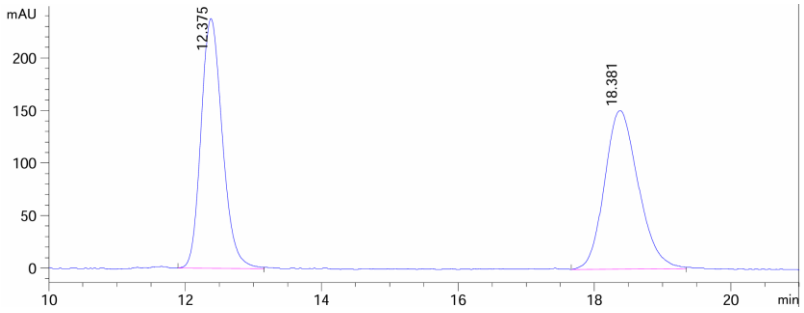
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	16.290	VV	30.763	0.309	4.681	729.427
2	20.160	BV	482.238	0.473	95.319	1.485e4



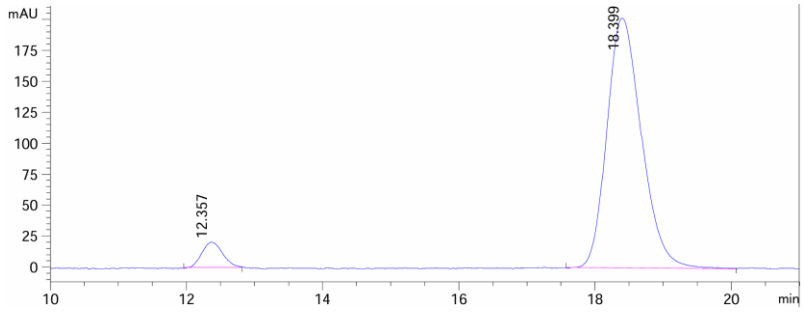
Methyl 4-((*S*)-(1-(4-fluoro-1-(*S*)-isoquinolin-1-yl)naphthalen-2-yl)(hydroxy)methyl)benzoate (3e).

From **1-(4-fluoroisoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfon-ate (1e)** (42.1 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 85% yield (37.1 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.0 Hz, 1H), 8.10 – 7.87 (m, 3H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 7.56 – 7.40 (m, 3H), 7.38 – 7.18 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 5.72 (s, 1H), 3.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.67, 156.55, 155.62 (d, *J* = 20.0 Hz), 153.95, 148.38, 141.48, 134.19, 132.93, 132.89, 130.62 (d, *J* = 4.0 Hz), 129.81, 129.56 (d, *J* = 16.0 Hz), 128.66, 128.21, 128.18, 127.63, 127.46 (d, *J* = 8.0 Hz), 127.37, 126.88, 126.80, 126.65, 126.63, 126.48, 126.33, 126.00, 124.73, 119.60, 119.56, 75.29, 51.90; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -138.63. **HRMS** (ESI) calcd. for $C_{28}H_{20}FNO_3$ $[M+H]^+$ *m/z* 438.1427, found 438.1429; **IR** (neat, cm^{-1}) 3452, 1710, 1594, 1438, 1278, 1107, 808, 765, 704; **m.p.** 149.2 – 151.1 °C; **$[\alpha]_D^{20}$** = +20.0 (*c* = 0.04, $CHCl_3$); 89% *ee*;

HPLC analysis CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 18.4 min, t_R (minor) = 12.4 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	12.375	VV	237.698	0.335	49.743	5.152e3
2	18.381	BV	150.865	0.525	50.257	5.206e3



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	12.357	MM	20.190	0.346	5.559	419.099
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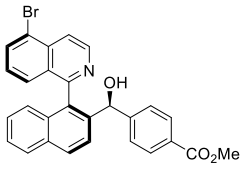
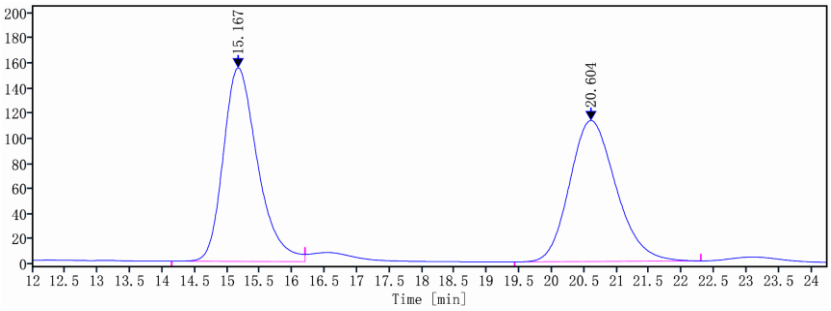


Methyl 4-((*S*)-(1-(5-bromo-1-(*S*)-isoquinolin-1-yl)naphthalen-2-yl)(hydroxy)methyl)ben-zoate (3f).

From **1-(5-bromoisoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulf-onate (1f)** (48.3 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 55% yield

(27.3 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.0 Hz, 1H), 8.20 – 8.00 (m, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.72 (m, 2H), 7.54 – 7.45 (m, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.11 – 7.02 (m, 2H), 7.02 – 6.92 (m, 3H), 5.76 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.55, 160.07, 148.15, 142.67, 141.51, 135.11, 134.25, 134.05, 132.87, 132.80, 129.86, 129.33, 128.51, 128.21, 127.64, 127.62, 127.51, 127.43, 126.86, 126.37, 126.00, 124.59, 121.59, 120.29, 75.58, 51.89; **HRMS** (ESI) calcd. for $C_{28}H_{20}BrNO_3$ $[M+H]^+$ *m/z* 498.0699, found 498.0701; **IR** (neat, cm^{-1}) 3412, 2948, 2847, 1717, 1607, 1572, 1437, 1278, 825, 805, 754; **m.p.** 120.0 – 122.0 °C; **$[\alpha]_D^{20}$** = –210.0 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 20.8 min, t_R (minor) = 15.4 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.167	BV	2.0553	5669.3453	154.0661	50.4772
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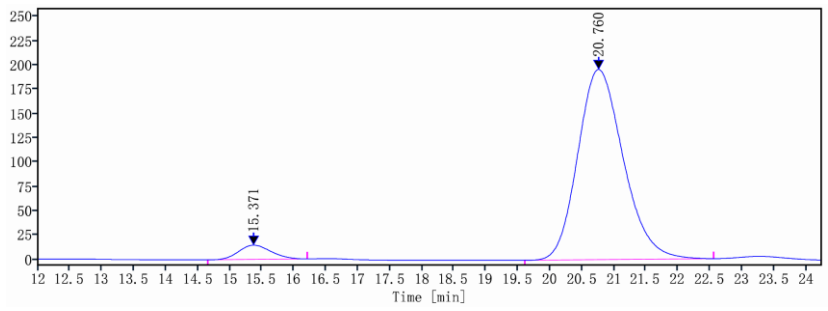
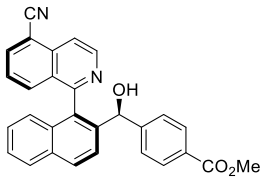
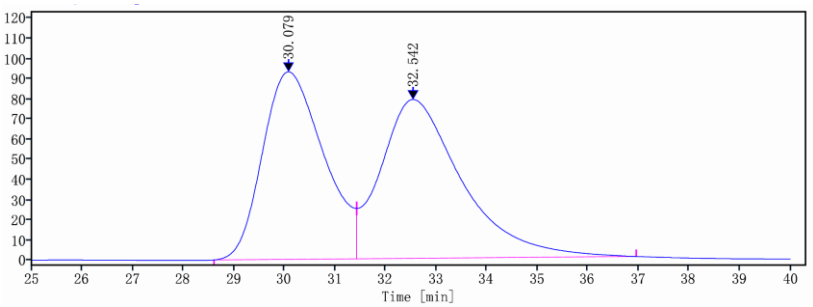


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.371	BB	1.5538	514.9077	14.6436	5.0627
20.760	BB	2.9500	9655.7196	195.6190	94.9373

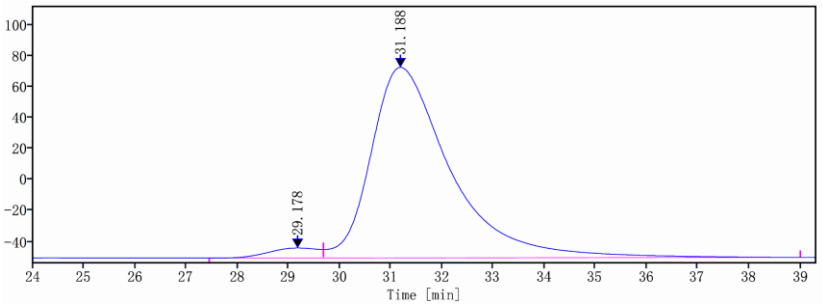


Methyl 4-((1*S*)-(1-(5-cyanoiso-1-(*S*)-quinolin-1-yl)naphthalen-2-yl)(hydroxy)methyl)benzoate (3g).

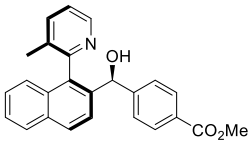
From **1-(5-cyanoisoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1g)** (42.8 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 80% yield (35.5 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.9 Hz, 1H), 8.15 – 8.04 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.46 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.31 – 7.21 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.77 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.47, 160.81, 148.25, 143.93, 141.72, 136.47, 135.38, 133.61, 132.95, 132.87, 132.74, 130.16, 128.60, 128.34, 127.73, 127.63, 127.53, 127.08, 126.51, 126.47, 125.69, 124.62, 118.30, 116.31, 109.58, 75.60, 52.00; **HRMS** (ESI) calcd. for $C_{29}H_{20}N_2O_3$ $[M+H]^+$ *m/z* 445.1547, found 445.1549; **IR** (neat, cm^{-1}) 3493, 3054, 2946, 2231,1716, 1609, 1560, 1430, 1280, 805,752, 702; **$[\alpha]_D^{20}$** = –82.5 (*c* = 0.04, $CHCl_3$); 94% *ee*; **m.p.** 159.5 – 161.3 °C; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 31.2 min, t_R (minor) = 29.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
30.079	BV	2.8203	7815.2300	93.0082	47.0737
32.542	VBA	5.5264	8786.8709	78.7666	52.9263



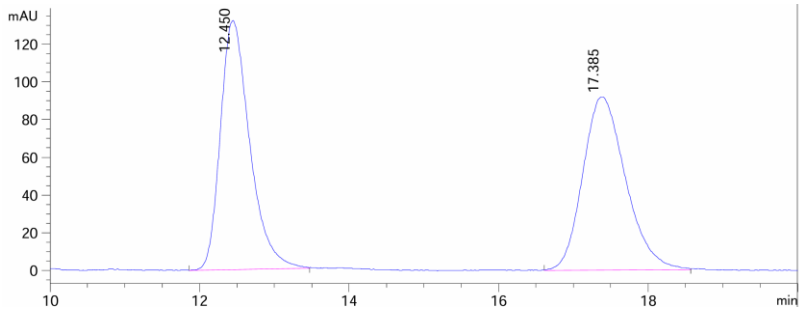
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
29.178	BV	2.2323	434.8333	6.4656	3.1618
31.188	VB	9.3155	13317.7144	123.3169	96.8382



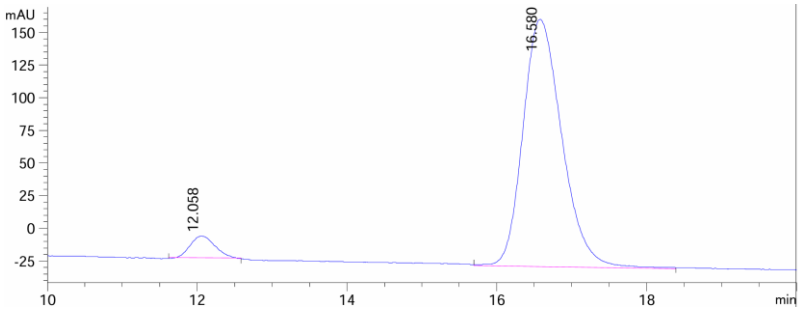
Methyl 4-((*S*)-hydroxy((*S*)-1-(3-methylpyridin-2-yl)naphthalen-2-yl)methyl)benzo-ate (**3h**).

From **1-(3-methylpyridin-2-yl)naphthalen-2-yl trifluoromethanesulfon-ate (1h)** (36.7 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7AA mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 85% yield (32.6 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.6 Hz, 1H), 8.45 (d, J = 2.6 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.60 – 7.46 (m, 1H), 7.40 (t, J = 8.3 Hz, 1H), 7.26 – 7.10 (m, 2H), 7.06 (d, J = 8.5 Hz, 1H), 5.74 (s, 1H), 3.87 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.85, 154.63, 152.89, 148.76, 143.14, 141.05, 140.06, 133.64, 133.00, 131.54, 129.93, 129.20, 128.55, 128.52, 127.26, 126.92, 126.52, 125.02, 124.77, 74.81, 52.07, 22.01; **HRMS** (ESI) calcd. for $C_{25}H_{21}NO_3$ $[M+H]^+$ *m/z* 384.1594, found 384.1592; **IR** (neat, cm^{-1}) 3155, 3055, 2952, 2842, 1709, 1605, 1571, 1435, 1277, 741; **m.p.** 140.3 – 141.3 °C; **$[\alpha]_D^{20}$** = +90 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC**

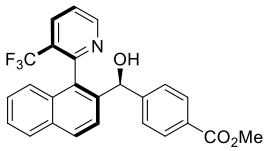
analysis CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 16.6 min, t_R (minor) = 12.1 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	12.450	BV	131.859	0.412	49.624	3.598e3
2	17.385	VV	91.764	0.586	50.376	3.653e3



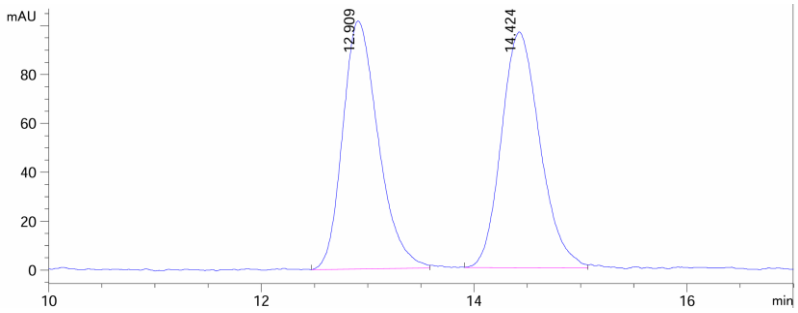
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	12.058	MM	16.547	0.381	5.220	377.971
2	16.580	MM	189.379	0.604	94.780	6.863e3



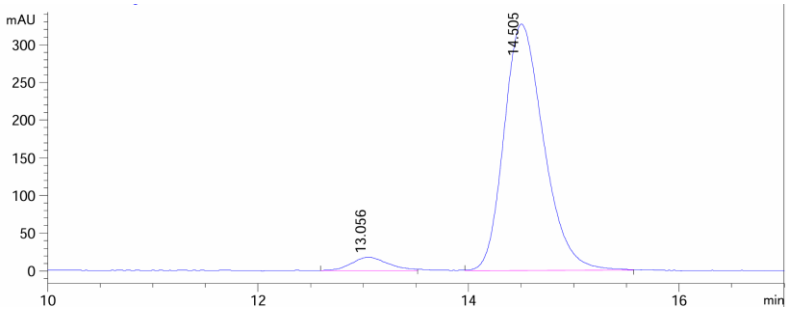
Methyl 4-((*S*)-hydroxy((*S*)-1-(3-(trifluoromethyl)pyridin-2-yl)naphthalen-2-yl)methyl)benzoate (3i).

From **1-(3-(trifluoromethyl)pyridin-2-yl)naphthalen-2-yl trifluoro-methanesulfonate (1i)** (42.1 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 78% yield

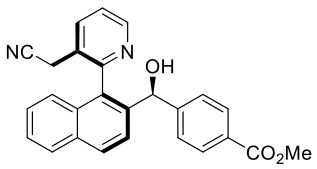
(34.1 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.4 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.82 (m, 4H), 7.61 – 7.53 (m, 2H), 7.53 – 7.43 (m, 3H), 7.43 – 7.35 (m, 1H), 5.58 (s, 1H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.06, 156.32, 156.30, 152.57, 148.15, 139.18, 134.81 (q, *J* = 14.0 Hz), 133.43, 132.78, 132.08, 130.13, 129.43, 128.69, 128.08, 126.87 (q, *J* = 31.3 Hz), 126.75, 126.33, 125.92, 125.87, 124.83, 123.31 (q, *J* = 274.7 Hz), 122.81, 72.61, 52.03; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.20. **HRMS** (ESI) calcd. for $C_{25}H_{18}F_3NO_3$ $[M+H]^+$ *m/z* 438.1312, found 438.1314; **IR** (neat, cm^{-1}) 3450, 3066, 2949, 2844, 1717, 1607, 1572, 1437, 1278, 755; **m.p.** 135.2 – 136.5 °C; **$[\alpha]_D^{20}$** = –270.0 (*c* = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 14.5 min, t_R (minor) = 13.1 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	12.909	BV	101.595	0.355	49.242	2.362e3
2	14.424	VV	96.535	0.374	50.758	2.435e3

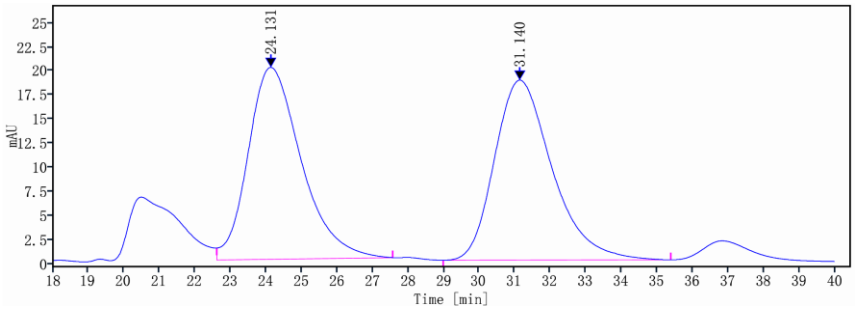


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	13.056	BV	17.669	0.309	4.714	422.992
2	14.505	VV	326.209	0.400	95.286	8.550e3



Methyl 4-((*S*)-((*S*)-1-(3-(cyanomethyl)pyridin-2-yl)naphthalen-2-yl)(hydroxy)methyl)benzoate (**3j**).

From **1-(3-(cyanomethyl)pyridin-2-yl)naphthalen-2-yl trifluoro-methanesulfonate (1j)** (39.2 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a colorless oil in 65% yield (26.5 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, J = 4.9 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.79 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.50 – 7.39 (m, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.4 Hz, 1H), 5.77 (s, 1H), 3.90 (s, 3H), 3.23 – 3.11 (m, 1H), 3.00 – 2.89 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.82, 156.75, 148.98, 148.62, 140.54, 136.72, 133.35, 133.06, 131.18, 130.17, 129.22, 128.78, 128.62, 127.76, 127.19, 127.12, 126.70, 125.00, 124.14, 123.85, 117.16, 74.68, 52.09, 21.25; **HRMS** (ESI) calcd. for $C_{26}H_{30}N_2O_3$ $[M+H]^+$ *m/z* 409.1547, found 367.2432; **IR** (neat, cm^{-1}) 3448, 2950, 2382, 1719, 1648, 1409. 1384, 1280, 743; **$[\alpha]_D^{20}$** = –40.0 (*c* = 0.04, $CHCl_3$); 89% *ee*; **HPLC analysis** CHIRALCEL AS-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 31.1 min, t_R (minor) = 24.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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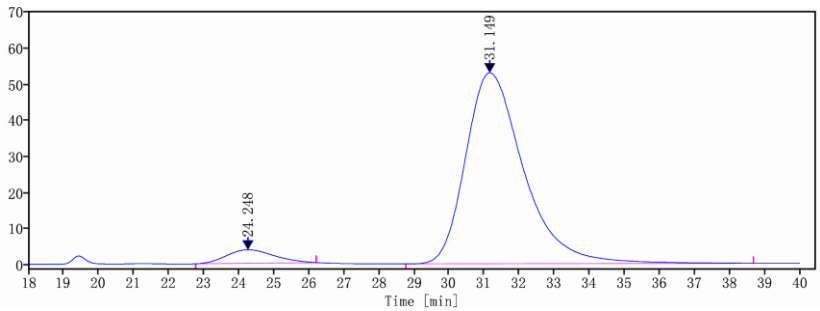

RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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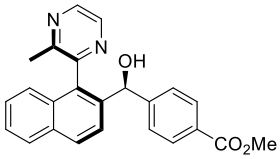
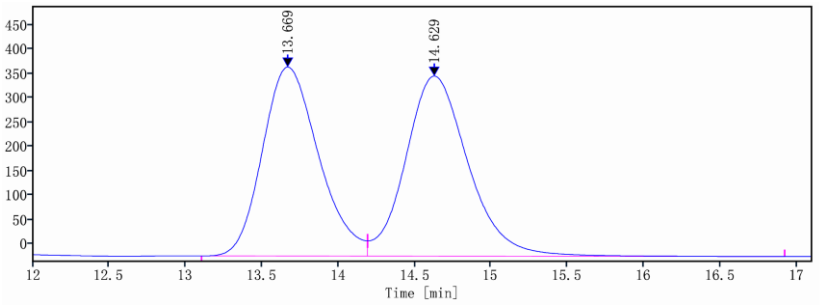
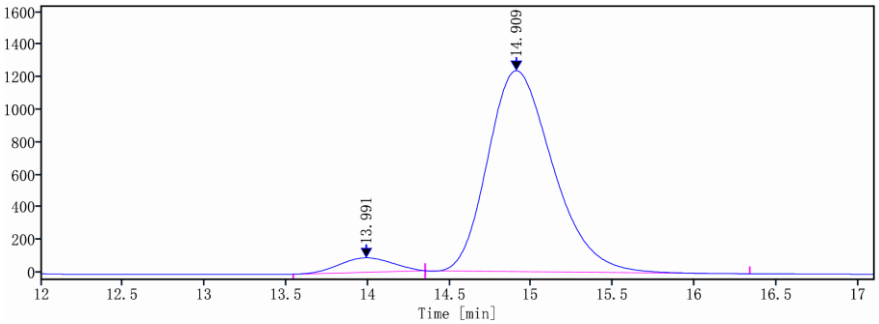


Methyl 4-((*S*)-hydroxy((*S*)-1-(3-methylpyrazin-2-yl)naphthalen-2-yl)methyl)benzoate (**3k**).

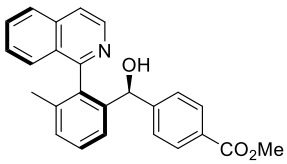
From **1-(3-methylpyrazin-2-yl)naphthalen-2-yl trifluoromethanesulfon-ate (1k)** (36.8 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a colorless oil in 74% yield (28.4 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, J = 3.4 Hz, 1H), 8.45 (d, J = 2.6 Hz, 1H), 8.10 – 7.89 (m, 2H), 7.90 – 7.75 (m, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.62 – 7.47 (m, 1H), 7.47 – 7.34 (m, 1H), 7.27 – 7.14 (m, 2H), 7.06 (d, J = 9.5 Hz, 1H), 5.74 (s, 1H), 3.87 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.85, 154.63, 152.89, 148.76, 143.14, 141.05, 140.06, 133.64, 133.00, 131.54, 129.93, 129.20, 128.55, 128.52, 127.26, 126.92, 126.52, 125.02, 124.77, 74.81, 52.07, 22.01; **^{1}HRMS** (ESI) calcd. for $C_{24}H_{20}N_2O_3$ $[M+H]^+$ *m/z* 385.1547, found 385.1548; **IR** (neat, cm^{-1}) 3433, 3055, 2950, 1719, 1609, 1507, 1435, 1280, 743 ; **$[\alpha]_D^{20}$** = –67.5 (*c* = 0.04, $CHCl_3$); 89% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 15.0 min, t_R (minor) = 14.0 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.669	BV	1.0885	9956.5964	388.8516	48.5153
14.629	VB	2.7306	10565.9986	370.6644	51.4847



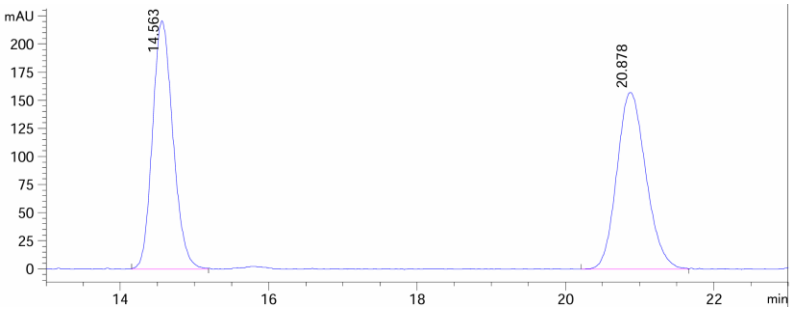
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.991	MM m	0.3629	2003.6564	88.9218	5.5434
14.909	MM m	0.4284	34141.0212	1235.3876	94.4566



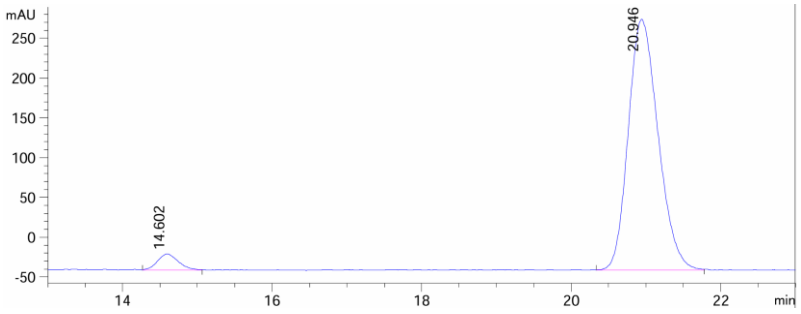
Methyl 4-((*S*)-hydroxy(2-((*S*)-isoquinolin-1-yl)-3-methylphenyl)methyl)benzoate (3l).

From **2-(isoquinolin-1-yl)-3-methylphenyl trifluoromethanesulfonate (1l)** (36.7 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 81% yield (31.0mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, J = 5.8 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.59 – 7.51 (m, 1H), 7.52 – 7.44 (m, 2H), 7.38 – 7.23 (m, 4H), 7.15 (d, J = 8.5 Hz, 1H), 6.91 – 6.76 (m, 2H), 5.65 (s, 1H), 3.79 (s, 3H), 1.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.63,

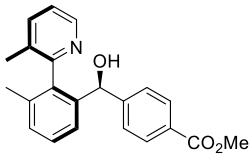
160.45, 148.52, 143.58, 140.62, 137.95, 137.09, 135.87, 130.20, 130.02, 129.07, 128.33, 128.22, 127.30, 127.26, 127.04, 127.02, 126.61, 124.35, 121.15, 76.48, 51.76, 20.11; **HRMS** (ESI) calcd. for $C_{25}H_{22}NO_3$ $[M+H]^+$ *m/z* 384.1594, found 384.1596; **IR** (neat, cm^{-1}) 3134, 2994, 2838, 1715, 1607, 1574, 1434, 1275, 872, 838, 781; **m.p.** 180.2 – 181.3 °C; **$[\alpha]_D^{20}$** = 39.1 (*c* = 0.04, $CHCl_3$); 92% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 20.9 min, t_R (minor) = 14.6 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	14.563	VV	220.781	0.294	49.791	4.244e3
2	20.878	VV	157.199	0.408	50.209	4.279e3

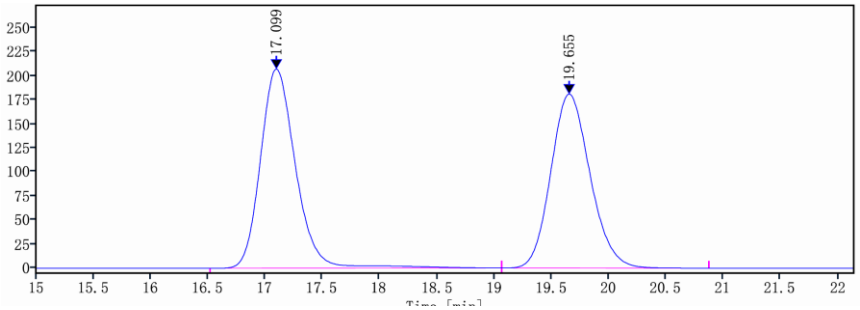


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	14.602	BV	20.167	0.248	4.237	386.986
2	20.946	VV	315.072	0.402	95.763	8.746e3



Methyl 4-((*S*)-hydroxy((*S*)-3-methyl-2-(3-methylpyridin-2-yl)phenyl)methyl)benzoate (**3m**). From **3-methyl-2-(3-methylpyridin-2-yl)phenyl trifluoromethanesulfo-nate (1m)** (33.1 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0

equiv), methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 88% yield (30.5 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.9 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.23 – 7.16 (m, 1H), 7.15 – 7.07 (m, 1H), 7.03 – 6.94 (m, 2H), 5.62 (s, 1H), 3.87 (s, 3H), 1.94 (s, 3H), 1.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.07, 157.90, 149.39, 145.89, 142.21, 138.25, 138.01, 137.16, 133.33, 129.99, 128.72, 128.55, 128.08, 127.77, 124.59, 122.91, 51.98, 19.22, 18.16; **HRMS** (ESI) calcd. for $C_{22}H_{20}NO_3$ $[M+H]^+$ *m/z* 348.1594, found 348.1595; **IR** (neat, cm^{-1}) 3454, 3138, 2839, 1714, 1620, 1586, 1434, 1278, 874, 832, 752; **m.p.** 170.2 – 171.3 °C; **$[\alpha]_D^{20}$** = +75 (*c* = 0.04, $CHCl_3$); 86% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 19.6 min, t_R (minor) = 17.1 min.



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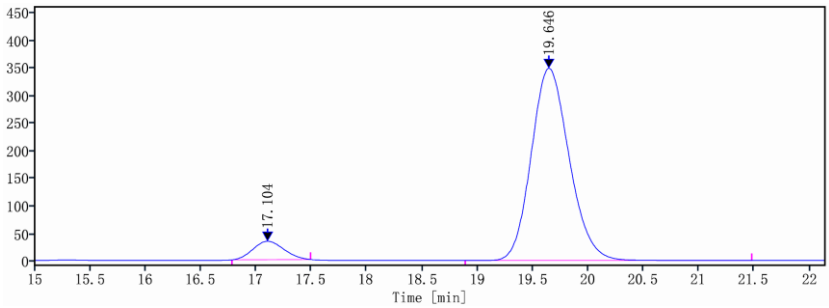
19.655	BB	1.8087	4298.3775	180.6053	49.2568



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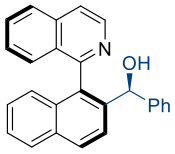
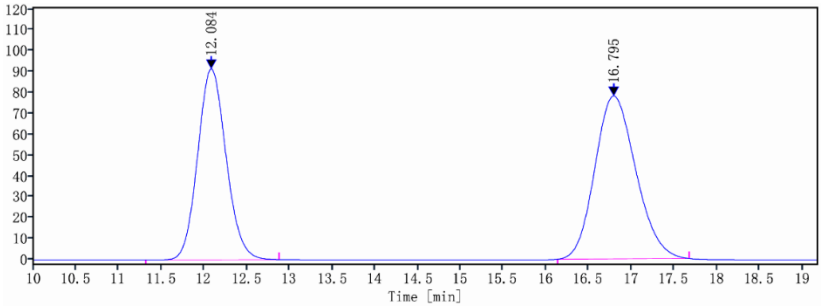
17.104	MM m	0.3031	644.1328	33.3805	7.2038
19.646	BB	2.5867	8297.4301	348.0486	92.7962



(1*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(phenyl)methanol (**4b**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), benzaldehyde (12.8 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 75% yield (27.1 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.71 (d, J = 5.8 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.31 – 7.21 (m, 3H), 7.08 – 6.99 (m, 3H), 6.87 (t, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 7.3 Hz, 1H), 5.72 (s, 1H), 4.28 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.72, 143.18, 141.69, 141.62, 136.00, 134.73, 132.89, 132.87, 130.32, 129.45, 128.54, 128.09, 127.62, 127.39, 127.23, 127.20, 126.67, 126.50, 126.25, 126.05, 125.88, 124.89, 120.94, 75.29; **HRMS** (ESI) calcd. for $C_{26}H_{20}NO$ $[M+H]^+$ *m/z* 362.1539, found 362.1537; **IR** (neat, cm^{-1}) 3390, 3034, 1665, 1556, 1508, 869, 790; **m.p.** 160.0 – 161.6 °C; **$[\alpha]_D^{20}$** = –35.0 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in pentane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 16.8 min, t_R (minor) = 12.1 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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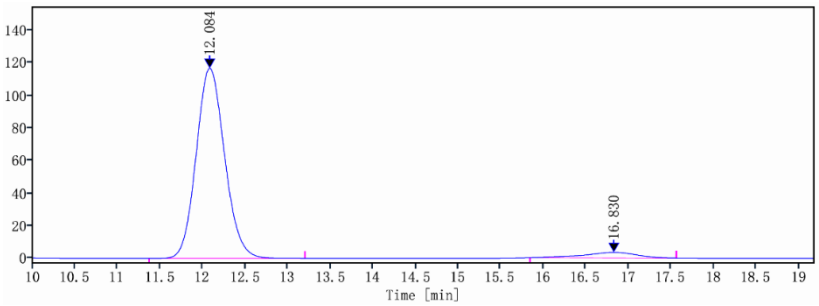
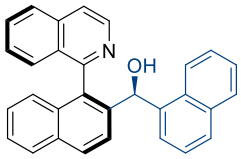
16.795	MM m	0.5164	2596.7097	78.0074	55.1599

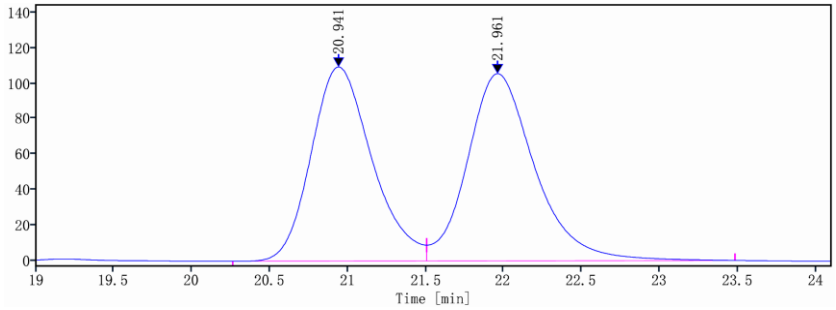


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.084	BM m	0.3606	2709.0702	116.7872	94.8087
16.830	MM m	0.6265	148.3376	3.4578	5.1913



(1*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(naphthalen-1-yl)methanol (**4c**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 1-naphthaldehyde (18.7 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 75% yield (30.8 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.8 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.97 (dd, *J* = 16.5, 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 14.7, 7.1 Hz, 2H), 7.54 – 7.35 (m, 3H), 7.35 – 7.06 (m, 5H), 6.97 – 6.79 (m, 2H), 6.80 – 6.64 (m, 1H), 6.48 (d, *J* = 7.5 Hz, 1H), 6.35 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.12, 136.73, 136.53, 132.93, 131.12, 130.04, 128.42, 128.14, 128.08, 125.39, 125.10, 124.59, 123.58, 123.47, 123.37, 121.90, 121.84, 121.81, 121.55, 121.52, 121.33, 121.23, 120.58, 119.99, 119.66, 119.53, 117.58, 116.42, 70.05; **HRMS** (ESI) calcd. for $C_{30}H_{21}NO$ $[M+H]^+$ *m/z* 412.1696, found 412.1697; **IR** (neat, cm^{-1}) 3398, 3044, 1655, 1556, 869, 830; **m.p.** 180.0 – 181.6 °C; **$[\alpha]_D^{20}$** = –85.0 (*c* = 0.04, $CHCl_3$); 88% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in pentane, 0.5 mL/min, 280 nm UV detector, t_R (major) = 20.9 min, t_R (minor) = 21.9 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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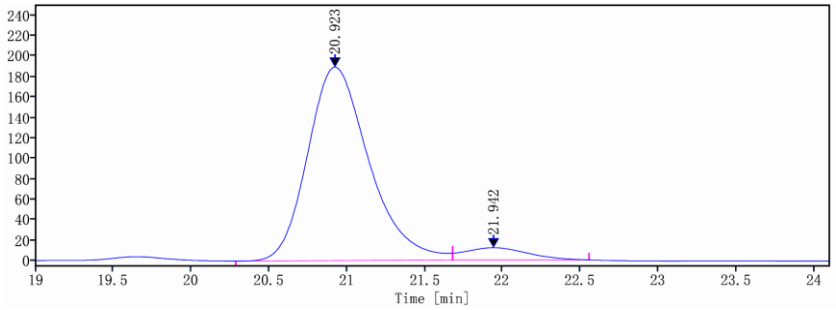
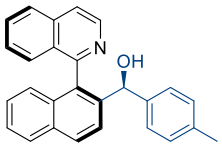
21.961	MM m	0.4541	3153.3426	105.0820	51.6093



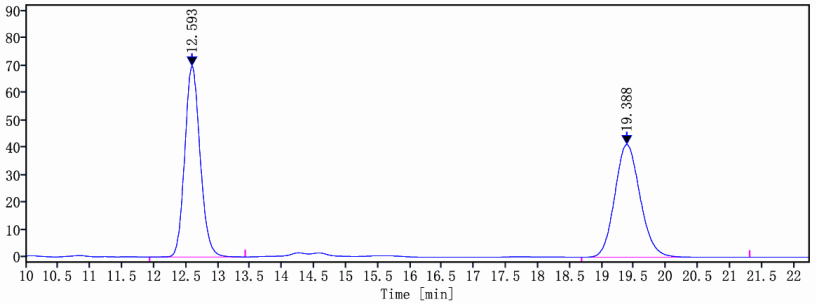
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.923	VM m	0.4182	5183.0782	188.8677	93.9989
21.942	MM m	0.4229	330.8968	11.8832	6.0011



(1*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(*p*-tolyl)methanol (**4d**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 4-methylbenzaldehyde (14.4 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 85% yield (31.9 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, J = 5.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.73 – 7.62 (m, 2H), 7.54 –

7.40 (m, 3H), 7.28 (t, J = 8.4 Hz, 1H), 7.13 – 7.04 (m, 4H), 6.42 (dd, J = 7.4, 2.2 Hz, 2H), 6.13 (s, 1H), 5.11 – 5.01 (m, 1H), 1.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.78, 141.54, 139.86, 137.66, 137.41, 136.38, 134.60, 132.96, 132.93, 130.48, 129.50, 128.78, 128.46, 128.14, 128.00, 127.60, 127.55, 127.36, 127.33, 126.57, 126.15, 126.05, 125.70, 122.74, 121.37, 79.20, 15.89; **HRMS** (ESI) calcd. for $C_{26}H_{20}N_2O_1$ $[M+H]^+$ *m/z* 376.1696, found 376.1694; **IR** (neat, cm^{-1}) 3333, 3053, 2921, 2852, 1621, 1584, 1557, 1509, 1347, 824, 747; **$[\alpha]_D^{20}$** = 5.0 (c = 0.04, $CHCl_3$); 94% *ee*; **m.p.** 132.9 – 133.2 °C; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 12.6 min, t_R (minor) = 19.4 min.



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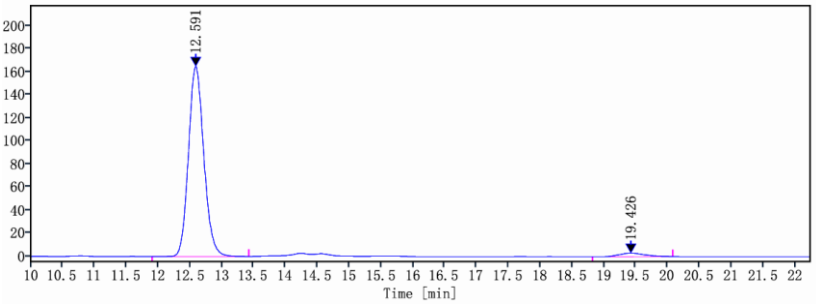

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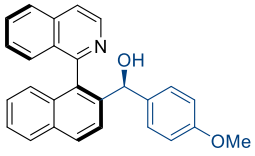
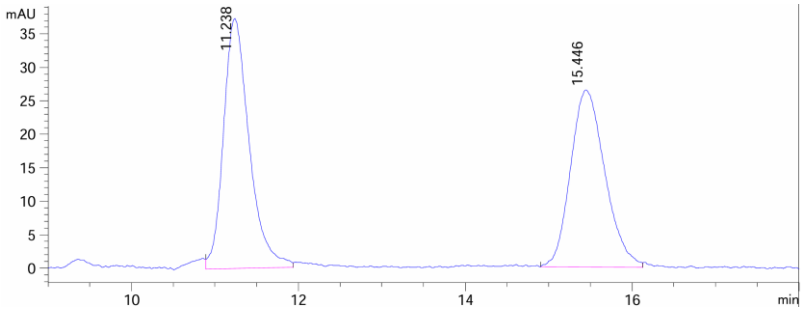


(1*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(4-methoxyphenyl)methanol (**4e**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10

mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 4-methoxybenzaldehyde (16.3 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 80% yield (31.4 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.7 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.71 (d, *J* = 5.9 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.52 – 7.42 (m, 1H), 7.28 – 7.19 (m, 2H), 7.21 – 7.14 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.73 (t, *J* = 8.1 Hz, 1H), 6.64 – 6.52 (m, 2H), 6.25 (d, *J* = 8.2 Hz, 1H), 5.72 (s, 1H), 3.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.80, 158.62, 144.92, 141.78, 141.47, 135.98, 134.74, 132.93, 132.85, 130.32, 129.45, 128.51, 128.42, 128.11, 127.67, 127.46, 127.12, 126.61, 126.51, 126.20, 126.05, 121.11, 117.53, 111.54, 110.09, 75.48, 54.89; **HRMS** (ESI) calcd. for $C_{26}H_{20}N_2O_2$ $[M+H]^+$ *m/z* 393.1589, found 393.1590; **IR** (neat, cm^{-1}) 3449, 1618, 1555, 1490, 1255, 826; **$[\alpha]_D^{20}$** = –35.0 (*c* = 0.04, $CHCl_3$); 90% *ee*; **m.p.** 132.9 – 133.2 °C; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 15.4 min, t_R (minor) = 11.2 min.



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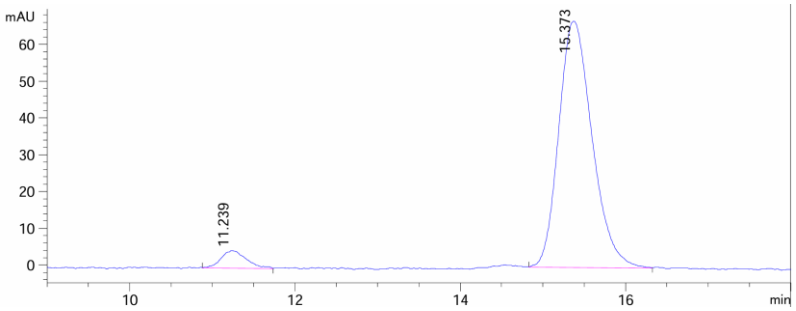
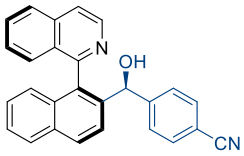
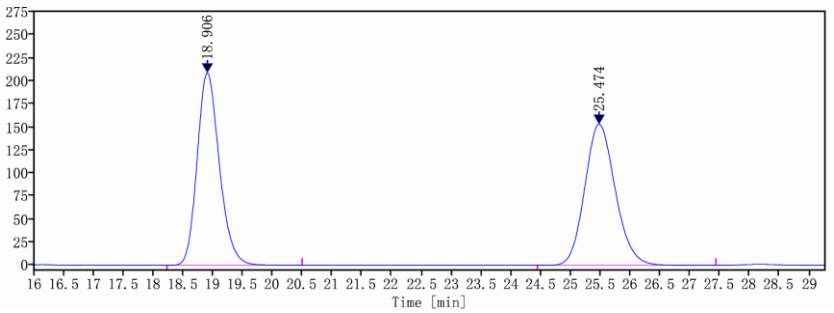


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	11.239	VB	4.840	0.256	5.178	102.687
2	15.373	VV	66.956	0.420	94.822	1.880e3



4-((*S*)-Hydroxy(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methyl)benzonitrile (4f).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 4-formylbenzonitrile (15.7 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 85% yield (32.8 mg). ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, J = 5.8 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.71 (d, J = 5.9 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.30 – 7.18 (m, 2H), 7.12 – 6.95 (m, 6H), 5.77 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.42, 148.72, 141.19, 141.04, 135.91, 134.89, 132.95, 132.89, 130.86, 130.72, 129.82, 128.20, 128.17, 127.86, 127.52, 127.43, 126.85, 126.80, 126.45, 126.12, 125.25, 121.49, 118.70, 109.08, 75.79; **HRMS** (ESI) calcd. for $C_{27}H_{18}N_2O$ $[M+H]^+$ *m/z* 387.1492, found 387.1493; **IR** (neat, cm^{-1}) 3448, 3051, 2853, 2230, 1555, 1498, 820, 749; **m.p.** 160.0 – 161.1 °C; **$[\alpha]_D^{20}$** = +85.0 (*c* = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 25.5 min, t_R (minor) = 19.0 min.



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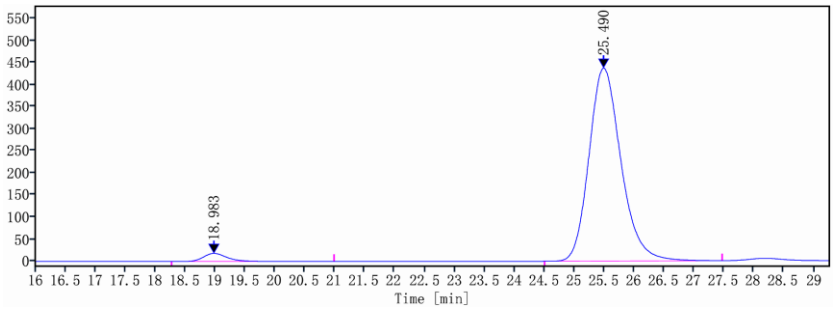

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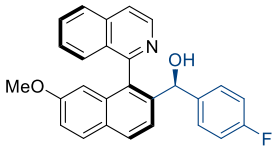
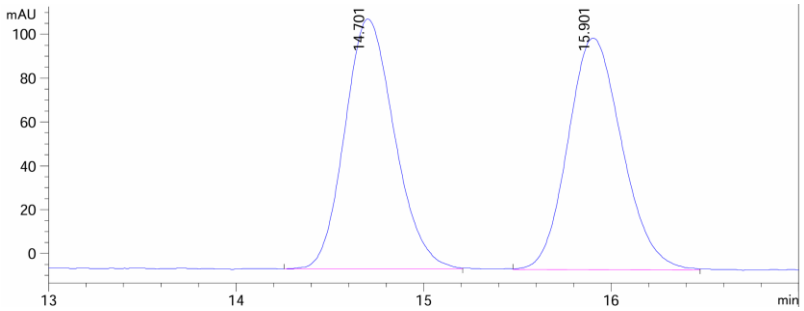


(*S*)-(4-Fluorophenyl)(1-((*S*)-isoquinolin-1-yl)-7-methoxynaphthalen-2-yl)methanol (**4g**).

From **(isoquinolin-1-yl)-7-methoxynaphthalen-2-yl trifluoromethanesulfonate (2a)** (43.3 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 4-fluorobenzaldehyde (14.9 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 81% yield (33.1 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, J = 5.8 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.89 – 7.77 (m, 2H), 7.71 (d, J = 6.0 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.34 – 7.19 (m, 2H), 7.19 – 7.10 (m, 1H), 7.00 – 6.85 (m, 2H), 6.49 (d, J = 8.8 Hz, 2H), 6.25 (d, J = 2.5 Hz, 1H), 5.62 (s, 1H), 3.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.23, 159.80 (d, J = 3.0 Hz),

158.03, 142.05, 141.49, 139.06 (d, J = 3.0 Hz), 36.06, 134.06, 133.22, 130.57, 129.64, 129.28, 128.51, 128.17, 127.60, 127.36, 126.77, 126.49 (d, J = 8.0 Hz), 124.90, 121.10, 118.58, 114.05 (d, J = 19.0 Hz), 113.93, 104.94, 74.94, 54.92; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -117.53; **HRMS** (ESI) calcd. for $C_{27}H_{20}FNO_2$ $[M+H]^+$ *m/z* 410.1551, found 410.1553; **IR** (neat, cm^{-1}) 3134, 2927, 2829, 1627, 1598, 1427, 832, 759; **m.p.** 188.3 – 191.0 °C; **$[\alpha]_D^{20}$** = +125.0 (c = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 15.4 min, t_R (minor) = 14.2 min.



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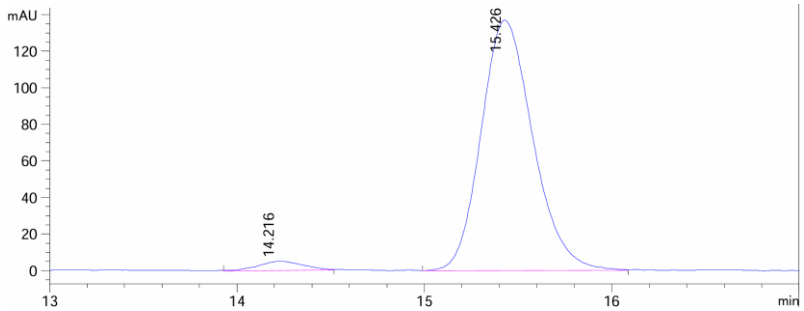
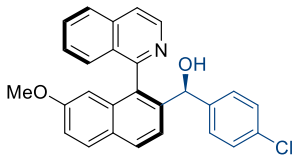
2	15.901	VV	105.697	0.308	50.139	2.119e3



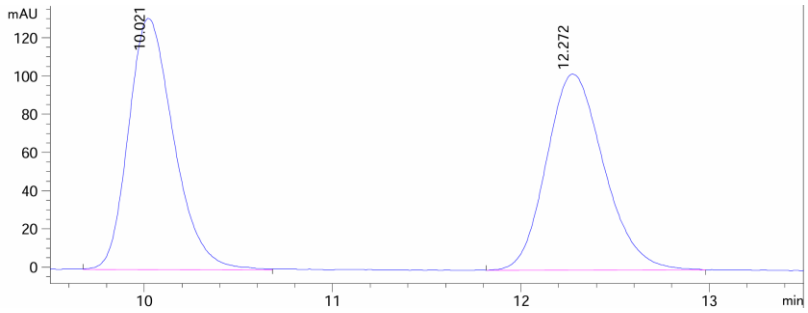
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	14.216	MM	5.000	0.285	3.138	85.394
2	15.426	BV	136.866	0.299	96.862	2.636e3



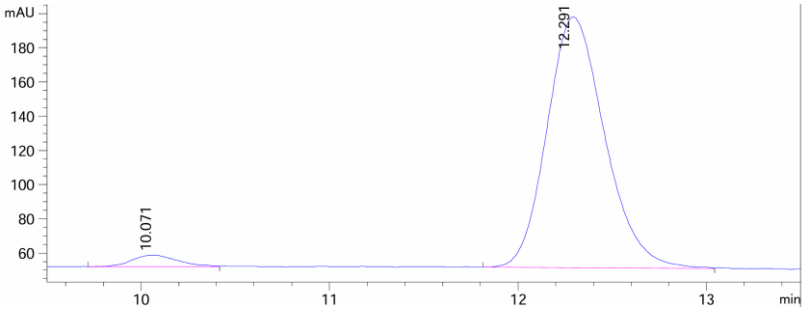
(*S*)-(4-Chlorophenyl)(1-((*S*)-isoquinolin-1-yl)-7-methoxynaphthalen-2-yl)methanol (**4h**).

From **(isoquinolin-1-yl)-7-methoxynaphthalen-2-yl trifluoromethanesulfonate (2a)** (43.3 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using

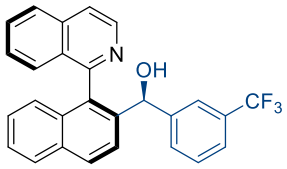
NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 4-chlorobenzaldehyde (16.8 mg, 0.12 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 78% yield (33.2 mg). ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, J = 5.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.83 – 7.75 (m, 1H), 7.72 (s, 1H), 7.67 – 7.58 (m, 2H), 7.31 – 7.21 (m, 1H), 7.21 – 7.11 (m, 2H), 6.94 – 6.82 (m, 2H), 6.78 – 6.67 (m, 2H), 6.26 (d, J = 2.5 Hz, 1H), 5.65 (s, 1H), 3.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.78, 158.04, 142.05, 141.86, 141.44, 136.02, 134.07, 133.44, 131.42, 130.52, 129.66, 129.29, 128.52, 128.06, 127.62, 127.33, 127.30, 126.77, 126.11, 125.21, 121.19, 118.66, 104.88, 75.26, 54.94; **HRMS** (ESI) calcd. for $C_{27}H_{20}ClNO_2$ $[M+H]^+$ *m/z* 426.1255, found 426.1256; **IR** (neat, cm^{-1}) 3139, 2954, 2829, 1626, 1572, 1427, 1232, 825, 753; **m.p.** 178.1 – 179.0 °C; **$[\alpha]_D^{20}$** = +45.0 (*c* = 0.04, $CHCl_3$); 93% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 12.3 min, t_R (minor) = 10.1 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.021	VV	131.413	0.255	50.196	2.200e3
2	12.272	VB	102.650	0.322	49.804	2.183e3

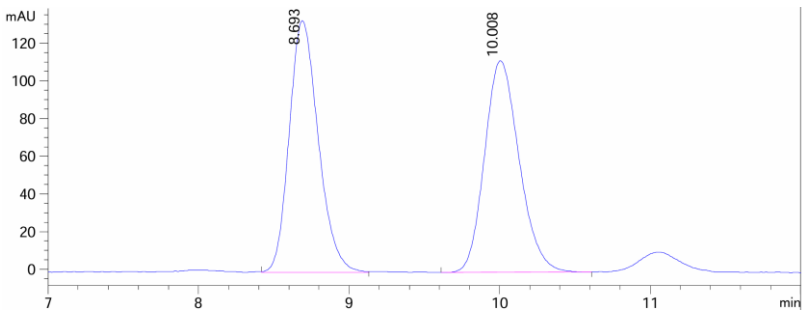


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.071	VV	6.812	0.248	3.624	117.726
2	12.291	BV	146.635	0.329	96.376	3.130e3



(*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(3-(trifluoromethyl)phenyl)methanol (**4i**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 3-(trifluoromethyl)benzaldehyde (20.1 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 80% yield (34.3 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.7 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.04 – 7.92 (m, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.68 (d, *J* = 5.8 Hz, 1H), 7.59 – 7.42 (m, 2H), 7.32 – 7.13 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.06 – 6.94 (m, 2H), 6.89 – 6.74 (m, 2H), 5.81 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.84, 135.02, 132.97 (d, *J* = 6.1 Hz), 130.35, 129.67, 129.27 (q, *J* = 31.8 Hz), 128.20, 128.19, 128.14, 128.05, 127.54, 127.44, 127.33, 126.67, 126.27, 126.16, 123.93 (q, *J* = 273.7 Hz), 122.4, (q, *J* = 3.0 Hz) 121.56, 121.01 (q, *J* = 4.0 Hz), 75.93; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.49; **HRMS** (ESI) calcd. for $C_{27}H_{18}F_3NO$ $[M+H]^+$ *m/z* 430.1431, found 430.1432; **IR** (neat, cm^{-1}) 3232, 3062, 2863, 1622, 1586, 1332, 824, 765, 631; **m.p.** 169.9 – 172.2 °C; **$[\alpha]_D^{20}$** = +102.5 (*c* = 0.04, $CHCl_3$); 90% ee; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 10.0 min, t_R (minor) = 8.7 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
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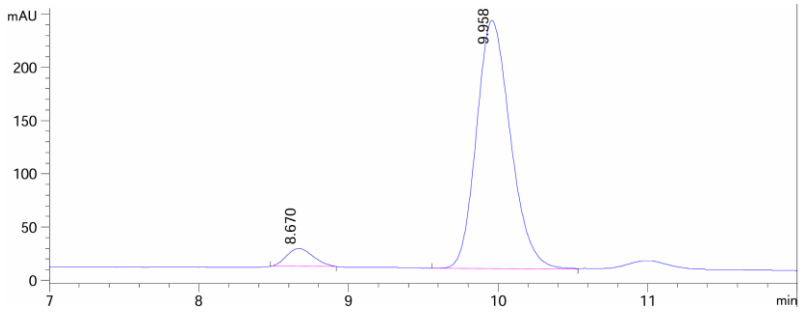
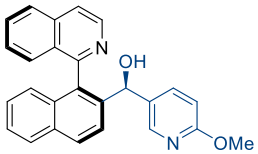


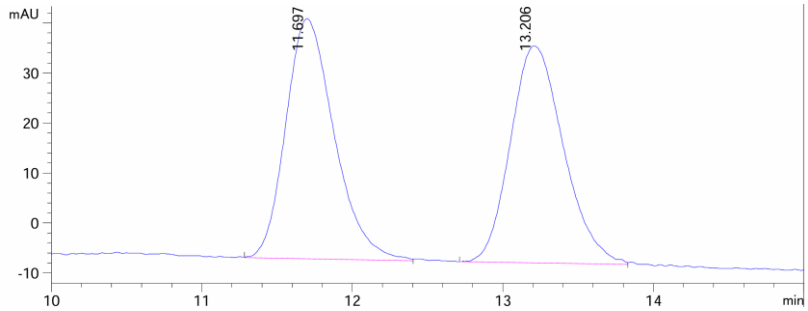
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	8.670	MM	16.723	0.204	5.250	204.353
2	9.958	BV	233.020	0.245	94.750	3.688e3



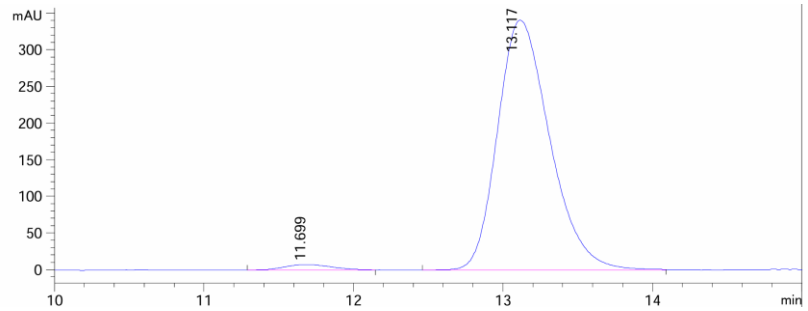
(*R*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(6-methoxypyridin-3-yl)methanol (**4j**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 6-methoxynicotinaldehyde (16.4 mg, 0.12 mmol) and anhydrous DMSO/ MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (10–50% EtOAc in PE) to provide the title compound as a white solid in 86% yield (31.4 mg). ***Rf*** 0.4 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.8 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.63 – 7.56 (m, 1H), 7.50 – 7.43 (m, 1H), 6.20 (d, J = 8.6 Hz, 1H), 5.62 (s,

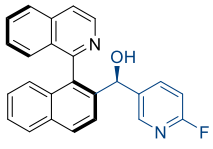
1H), 3.66 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.39, 159.48, 143.28, 141.59, 141.04, 136.05, 135.99, 134.49, 132.91, 132.83, 131.73, 130.47, 129.59, 128.33, 128.13, 127.48, 127.45, 126.74, 126.65, 126.19, 126.14, 121.20, 109.53, 73.42, 53.18; **HRMS** (ESI) calcd. for $C_{26}H_{20}N_2O_3$ $[M+H]^+$ *m/z* 393.1598, found 393.1597; **IR** (neat, cm^{-1}) 3199, 3050, 2940, 2842, 1604, 1490, 1458, 874, 824; **m.p.** 134.9 – 136.2 °C; **$[\alpha]_D^{20}$** = +35.0 (*c* = 0.04, $CHCl_3$); 96% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 13.1 min, t_R (minor) = 11.7 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	11.697	VV	47.993	0.343	50.311	1.075e3
2	13.206	BV	43.354	0.364	49.689	1.061e3



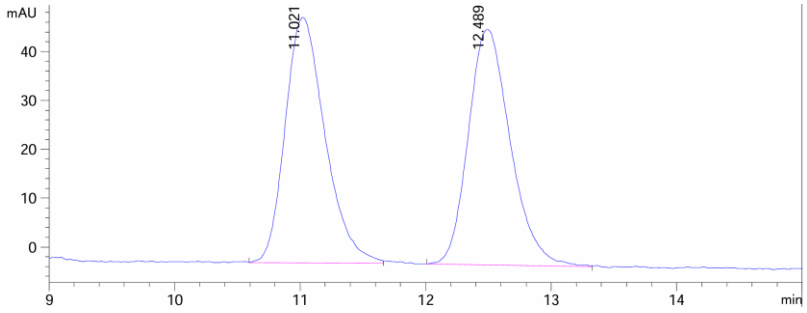
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	11.699	VV	7.753	0.284	2.056	174.017
2	13.117	BV	341.028	0.374	97.944	8.288e3



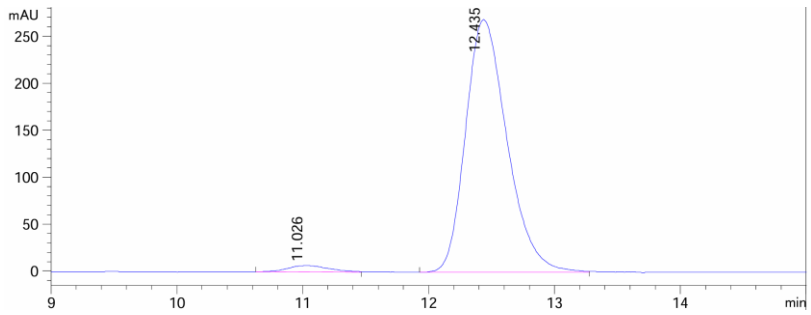
(*R*)-(6-Fluoropyridin-3-yl)(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methanol (**4k**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg,

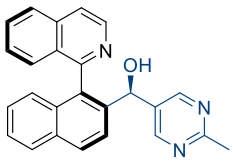
10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 6-fluoronicotinaldehyde (15.0 mg, 0.12 mmol) and anhydrous DMSO/ MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (10–50% EtOAc in PE) to provide the title compound as a white solid in 81% yield (30.8 mg). ***Rf*** 0.5 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.7 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.31 – 7.20 (m, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.30 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.68 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.91 (d, *J* = 23.6 Hz), 159.24, 144.16 (d, *J* = 15.0Hz), 141.39, 140.50, 138.09 (d, *J* = 7.0 Hz), 136.54 (d, *J* = 5.0 Hz), 135.98, 134.69, 133.00, 132.82, 130.72, 129.83, 128.24, 128.20, 127.74, 127.22, 127.00, 126.92, 126.84, 126.44, 126.15, 121.43, 107.81 (d, *J* = 37.0 Hz), 73.47, 73.45; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.32 **HRMS** (ESI) calcd. for $C_{25}H_{17}FN_2O$ $[M+H]^+$ *m/z* 381.1398, found 381.1399; **IR** (neat, cm^{-1}) 3422, 2925, 1637, 1596, 1560, 1481, 828, 750; **m.p.** 131.9 – 132.2 °C; **$[\alpha]_D^{20}$** = +110.0 (*c* = 0.04, $CHCl_3$); 95% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 12.4 min, t_R (minor) = 11.0 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	11.021	BV	50.185	0.333	49.602	1.107e3
2	12.489	BV	48.234	0.354	50.398	1.125e3

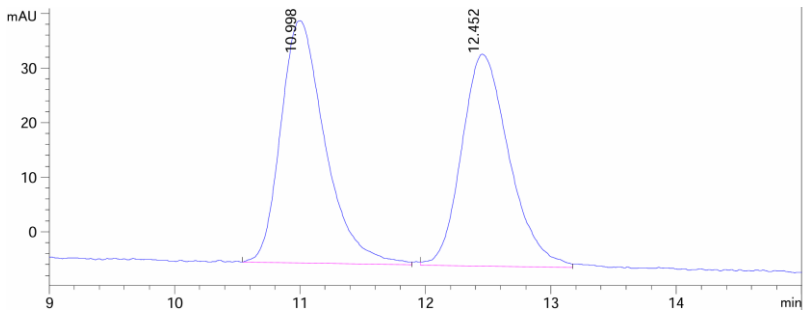


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	11.026	VV	6.899	0.280	2.557	161.816
2	12.435	VV	268.853	0.354	97.443	6.167e3

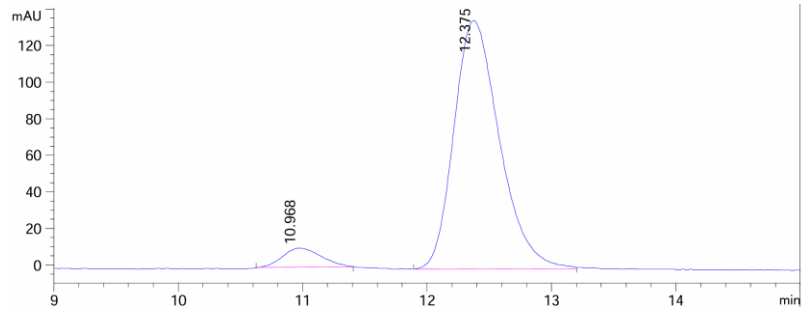


(*R*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(2-methylpyrimidin-5-yl)methanol (4l).

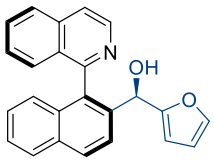
From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 2-methylpyrimidine-5-carbaldehyde (14.6 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (10–50% EtOAc in PE) to provide the title compound as a white solid in 90% yield (33.9 mg). ***Rf*** 0.4 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.8 Hz, 1H), 8.14 (s, 2H), 8.06 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.83 – 7.70 (m, 3H), 7.60 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.34 – 7.14 (m, 2H), 7.10 – 6.94 (m, 2H), 5.70 (s, 1H), 5.30 (s, 1H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.27, 159.07, 153.70, 141.42, 140.17, 135.93, 134.81, 133.20, 133.03, 132.78, 130.57, 129.93, 128.24, 128.04, 127.87, 127.12, 127.04, 126.93, 126.91, 126.53, 126.13, 121.63, 72.38, 24.99; **HRMS** (ESI) calcd. for $C_{25}H_{19}N_3O$ $[M+H]^+$ *m/z* 378.1606, found 378.1608; **IR** (neat, cm^{-1}) 2954, 1723, 1606, 1364, 856; **m.p.** 251.8 – 250.0 °C; **$[\alpha]_D^{20}$** = –170.0 (c = 0.04, $CHCl_3$); 88% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 12.4 min, t_R (minor) = 11.0 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.998	BV	44.400	0.367	51.644	1.092e3
2	12.452	VV	38.816	0.387	48.356	1.022e3



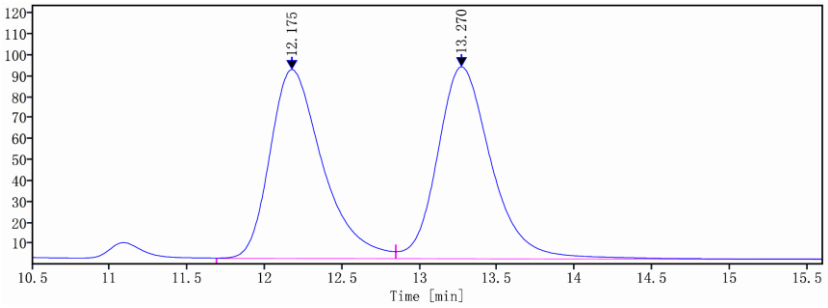
Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.968	MM	10.479	0.359	6.115	225.547
2	12.375	VV	135.962	0.387	93.885	3.463e3



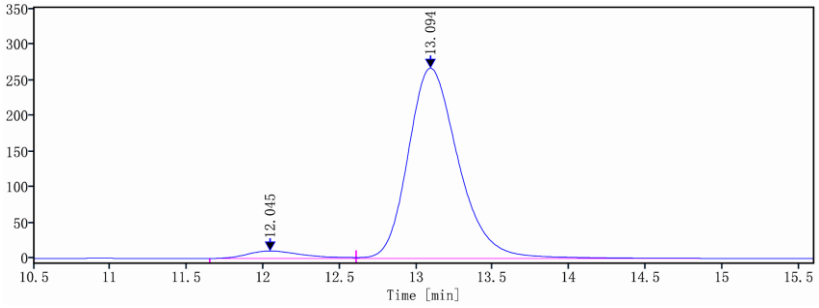
(*R*)-Furan-2-yl(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methanol (**4m**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), furan-2-carbaldehyde (11.5 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a brown oil in 62% yield (21.8 mg). ***Rf*** 0.5 (10% EtOAc in PE g), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, J = 5.8 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 12.2 Hz, 1H), 7.76 (d, J = 5.8 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.33 – 7.21 (m, 2H), 7.00 (d, J = 8.6 Hz, 1H), 5.71 – 5.61 (m,

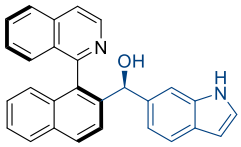
2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.52, 155.35, 141.35, 140.98, 139.21, 136.24, 134.65, 133.12, 132.77, 130.64, 129.59, 128.32, 128.16, 127.91, 127.25, 127.16, 126.67, 126.57, 126.20, 126.18, 121.15, 109.35, 105.24, 71.50; **HRMS** (ESI) calcd. for $C_{24}H_{17}NO_2$ $[M+H]^+$ *m/z* 352.1332, found 352.1334; **IR** (neat, cm^{-1}) 3450, 2924, 1619, 1560, 1459, 869, 829, 749; **$[\alpha]_D^{20}$** = –2.5 (*c* = 0.04, $CHCl_3$); 92% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 13.1 min, t_R (minor) = 12.0 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.175	VV	1.1586	2136.6010	90.3723	48.8895
13.270	VB	3.8826	2233.6630	91.8409	51.1105



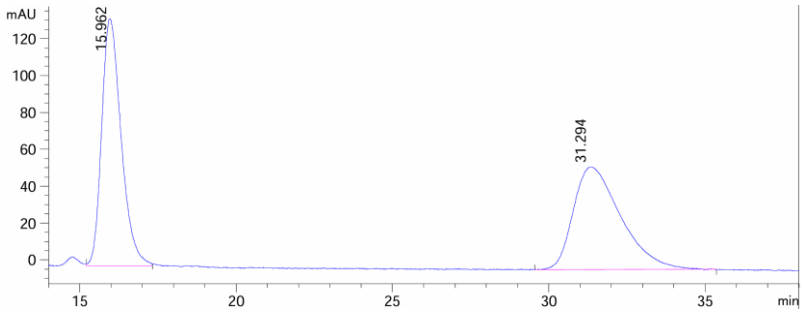
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.045	MM m	0.3812	265.8413	10.5077	4.1735
13.094	MB m	0.3509	6103.8970	266.7808	95.8265



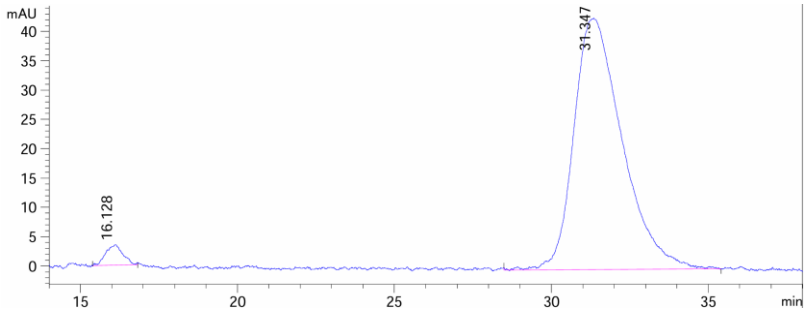
(*S*)-(1H-indol-6-yl)(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methanol (**4n**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 1H-indole-

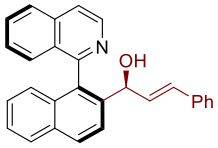
6-carbaldehyde (17.4 mg, 0.12 mmol) and anhydrous DMSO/MeCN (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 70% yield (28.0 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.8 Hz, 1H), 8.35 (s, 1H), 8.07 – 7.81 (m, 2H), 7.81 – 7.70 (m, 2H), 7.65 (d, *J* = 5.8 Hz, 1H), 7.55 – 7.40 (m, 2H), 7.33 – 7.13 (m, 4H), 7.06 – 6.92 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 2.8 Hz, 1H), 6.23 (s, 1H), 5.74 (s, 1H), 3.06 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.72, 141.65, 141.55, 137.23, 136.01, 135.38, 134.23, 132.83, 132.73, 130.36, 129.37, 128.57, 128.09, 127.33, 127.30, 126.50, 126.48, 126.39, 126.19, 126.00, 124.19, 120.81, 119.91, 117.76, 107.88, 101.60, 74.71; **HRMS** (ESI) calcd. for $C_{28}H_{20}N_2O$ $[M+H]^+$ *m/z* 401.1648, found 401.1648; **IR** (neat, cm^{-1}) 3280, 1619, 1556, 824, 748; **m.p.** 189.2 – 190.0 °C; **$[\alpha]_D^{20}$** = –170.0 (*c* = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 31.3 min, t_R (minor) = 16.0 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	15.962	VV	133.952	0.642	49.845	5.809e3
2	31.294	MM	55.484	1.756	50.155	5.845e3

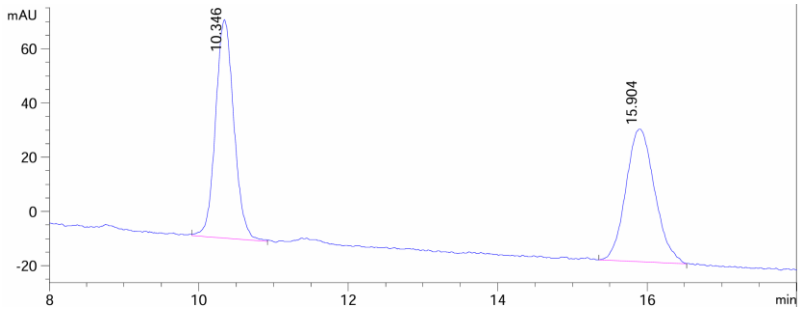


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	16.128	MM	3.504	0.627	2.796	131.915
2	31.347	MM	42.856	1.783	97.204	4.585e3

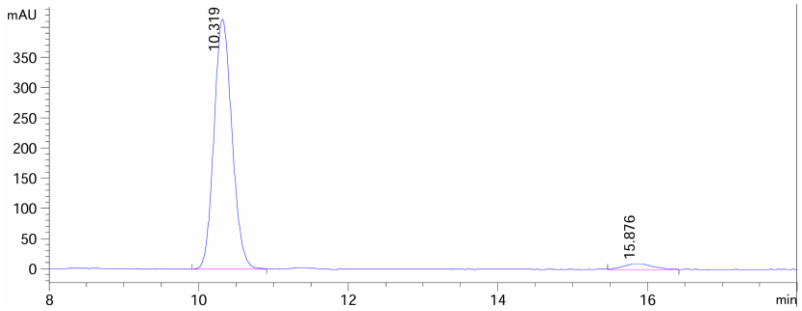


(*S*,*E*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)-3-phenylprop-2-en-1-ol (**4o**).

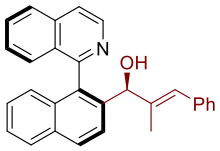
From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using $NiI_2{\cdot}6H_2O$ (4.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), cinnamaldehyde (19.8 mg, 0.15 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a colorless oil in 75% yield (29.0 mg). ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.8 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 6.0 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.56 – 7.42 (m, 2H), 7.43 – 7.34 (m, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.20 – 6.95 (m, 4H), 6.85 – 6.69 (m, 2H), 6.24 (dd, *J* = 16.0, 2.0 Hz, 1H), 5.99 (dd, *J* = 15.9, 4.1 Hz, 1H), 5.23 (dd, *J* = 4.1, 2.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.82, 141.75, 139.99, 136.54, 136.31, 134.49, 132.97, 132.80, 131.10, 130.43, 129.58, 128.97, 128.14, 128.10, 127.95, 127.76, 127.36, 127.10, 126.94, 126.55, 126.49, 126.21, 126.13, 126.05, 121.20, 74.21; **HRMS** (ESI) calcd. for $C_{28}H_{21}NO$ $[M+H]^+$ *m/z* 388.1696, found 388.1670; **IR** (neat, cm^{-1}) 2953, 1728, 1606, 1107, 859; **$[\alpha]_D^{20}$** = – 120.1 (*c* = 0.04, $CHCl_3$); 93% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 10.3 min, t_R (minor) = 15.9 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.346	VV	80.597	0.266	51.275	1.381e3
2	15.904	BV	49.026	0.372	48.725	1.312e3

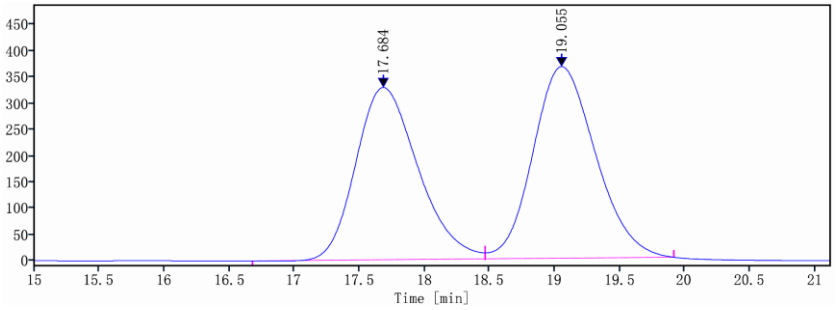


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.319	BV	413.897	0.259	96.429	6.926e3
2	15.876	VV	9.696	0.343	3.571	256.453



(*R*,*E*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)-2-methyl-3-phenylprop-2-en-1-ol (**4p**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using $NiI_2{\cdot}6H_2O$ (4.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-2-methyl-3-phenylacrylaldehyde (21.9 mg, 0.15 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 65% yield (26.1 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, J = 5.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.86 – 7.75 (m, 2H), 7.73 – 7.61 (m, 2H), 7.53 – 7.40 (m, 3H), 7.31 – 7.25 (m, 1H), 7.16 – 6.97 (m, 4H), 6.49 – 6.29 (m, 2H), 6.13 (s, 1H), 5.06 (s, 1H), 1.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.78, 141.54, 139.86, 137.66, 137.41, 136.38, 134.60, 132.96, 132.93, 130.48, 129.50, 128.78, 128.46, 128.14, 128.00, 127.60, 127.55, 127.36, 127.33, 126.57, 126.15, 126.05, 125.70, 122.74, 121.37, 79.20, 15.89; **HRMS** (ESI) calcd. for $C_{29}H_{23}NO$ $[M+H]^+$ m/z 402.1852, found 402.1854; **IR** (neat, cm^{-1}) 3300, 2982, 2935, 1646, 1600, 1535, 798; **m.p.** 188.0 – 190.2 °C; **$[\alpha]_D^{20}$** = +5.0 (c = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 17.7 min, t_R (major) = 19.1 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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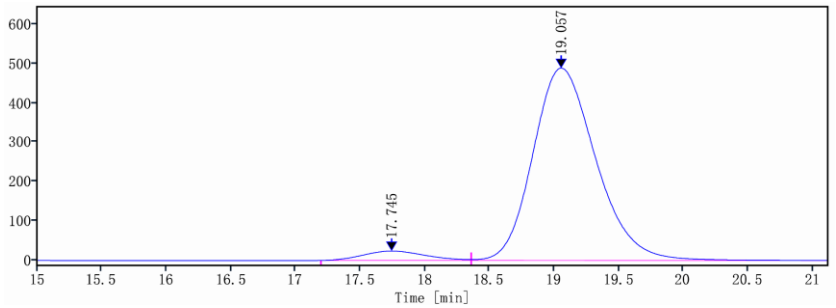
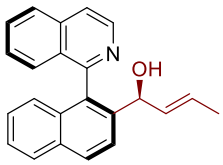
19.055	MM m	0.5186	12214.7056	364.8807	52.7975



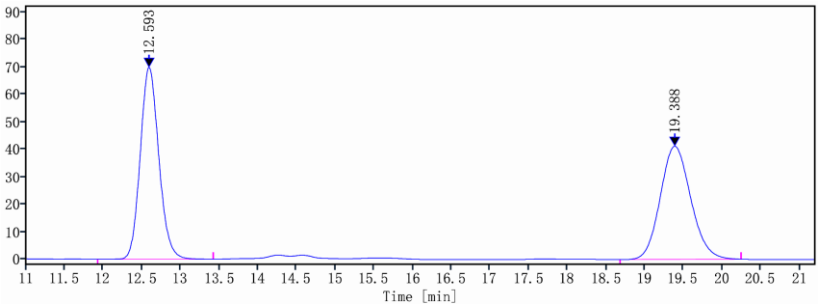
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
17.745	MM m	0.5159	791.1868	23.7989	4.5676
19.057	MB m	0.5221	16530.6367	486.8687	95.4324



(*R*,*E*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)but-2-en-1-ol (**4q**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using $NiI_2{\cdot}6H_2O$ (4.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-but-2-enal (10.5 mg, 0.15 mmol) and anhydrous DMSO/THF (1:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 55% yield (17.9 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.8 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 8.01 – 7.89 (m, 2H), 7.84 – 7.74 (m, 2H), 7.75 – 7.67 (m, 1H), 7.52 – 7.34 (m, 3H), 7.31 – 7.21 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 5.52 – 5.37 (m, 1H), 5.37 – 5.19 (m, 1H), 4.91 (d, *J* = 5.1 Hz,

1H), 2.73 – 2.32 (m, 1H), 1.33 – 1.26 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.78, 142.01, 139.94, 136.24, 133.94, 132.90, 132.72, 132.56, 130.55, 129.40, 128.90, 128.04, 127.68, 127.39, 126.93, 126.41, 126.17, 125.88, 125.58, 125.24, 120.68, 73.65, 17.37; **HRMS** (ESI) calcd. for $C_{23}H_{19}NO$ $[M+H]^+$ *m/z* 326.1539, found 326.1541; **IR** (neat, cm^{-1}) 3456, 2927, 1640, 1585, 1529, 1371, 829, 743; **m.p.** 169.1 – 171.3 °C; **$[\alpha]_D^{20}$** = 17.5 (*c* = 0.036, $CHCl_3$); 95% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 19.4 min, t_R (minor) = 12.6 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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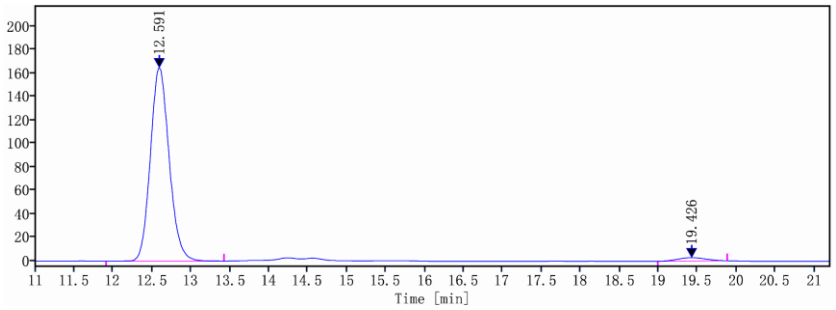
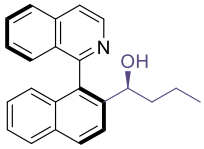


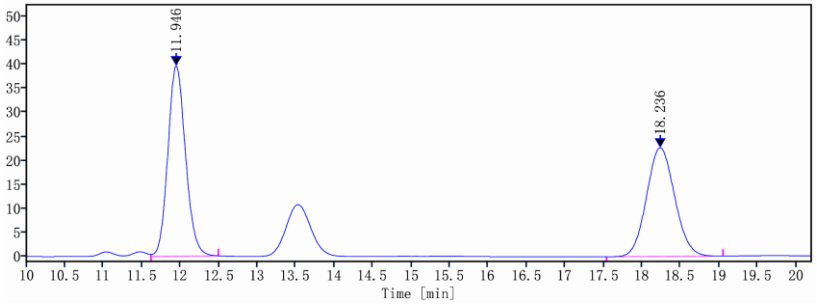
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.591	BB	1.5152	2765.1578	164.7686	97.4500
19.426	MM m	0.3989	72.3552	2.8621	2.5500



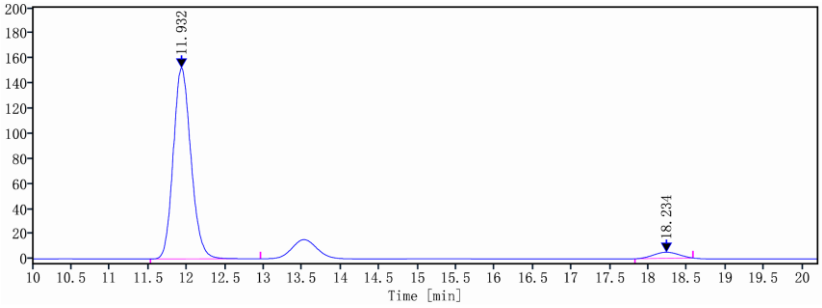
(*R*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)butan-1-ol (**4r**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg,

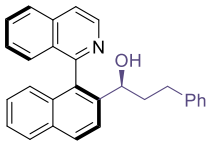
10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), butyraldehyde (10.8 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 65% yield (21.3 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, J = 5.8 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.86 – 7.77 (m, 2H), 7.77 – 7.67 (m, 1H), 7.52 – 7.35 (m, 3H), 7.35 – 7.22 (m, 1H), 7.02 (d, J = 8.1 Hz, 1H), 4.31 (t, J = 6.7 Hz, 1H), 2.27 (s, 1H), 1.74 – 1.60 (m, 2H), 1.30 (d, J = 13.2 Hz, 2H), 1.20 – 1.03 (m, 1H), 0.69 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.64, 138.30, 136.98, 132.31, 129.30, 128.97, 128.58, 126.68, 125.40, 124.77, 124.06, 123.80, 123.13, 123.11, 122.51, 122.21, 121.86, 120.13, 116.49, 68.04, 36.43, 15.09, 9.76; **HRMS** (ESI) calcd. for $C_{22}H_{19}NO$ $[M+H]^+$ *m/z* 328.1696, found 328.1698; **IR** (neat, cm^{-1}) 2924, 2850, 1606, 1363, 694; **$[\alpha]_D^{20}$** = +15.0 (*c* = 0.04, $CHCl_3$); 91% *ee*; **m.p.** 190.1 – 191.3 °C; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 18.2 min, t_R (major) = 11.9 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.946	VM m	0.2479	631.0959	39.6127	52.3697
18.236	BB	1.5144	573.9813	22.5990	47.6303

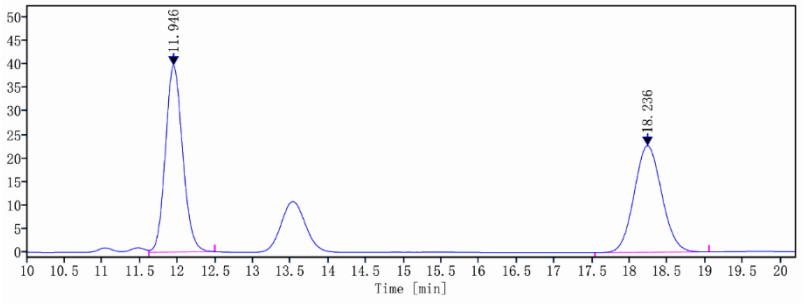


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.932	BB	1.4300	2430.8939	152.2842	95.6973
18.234	MM m	0.3594	109.2971	4.8788	4.3027

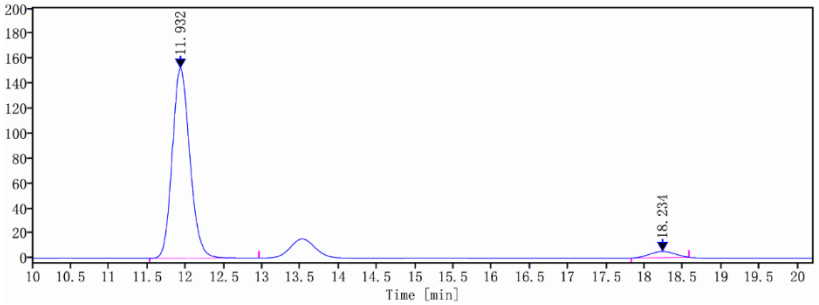


(*S*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)-3-phenylpropan-1-ol (**4s**).

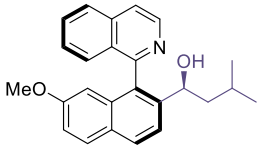
From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 3-phenylpropanal (16.0 mg, 1.5 equiv) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (2–10% EtOAc in PE) to provide the title compound as a white solid in 50% yield (19.5 mg). ***Rf*** 0.3 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.7 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 5.9 Hz, 1H), 7.75 – 7.62 (m, 1H), 7.52 – 7.41 (m, 2H), 7.38 (t, *J* = 8.2 Hz, 1H), 7.36 – 7.19 (m, 2H), 7.21 – 7.06 (m, 3H), 7.06 – 6.91 (m, 3H), 4.38 – 4.26 (m, 1H), 2.69 – 2.58 (m, 1H), 2.53 – 2.31 (m, 2H), 2.06 – 1.95 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.38, 142.38, 141.57, 140.73, 136.22, 133.36, 132.96, 132.56, 130.52, 129.39, 128.61, 128.59, 128.29, 128.14, 128.03, 127.70, 127.09, 126.98, 126.49, 126.17, 125.86, 125.56, 124.12, 120.45, 71.72, 39.49, 32.11; **HRMS** (ESI) calcd. for $C_{21}H_{17}NO$ $[M+H]^+$ *m/z* 390.1892, found 390.1893; **IR** (neat, cm^{-1}) 3418, 2922, 1621, 1557, 1497, 1393, 819, 745; **m.p.** 185.1 – 186.8 °C; **$[\alpha]_D^{20}$** = 77.2 (*c* = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 11.9 min, t_R (minor) = 18.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.946	VM m	0.2479	631.0959	39.6127	52.3697
18.236	BB	1.5144	573.9813	22.5990	47.6303



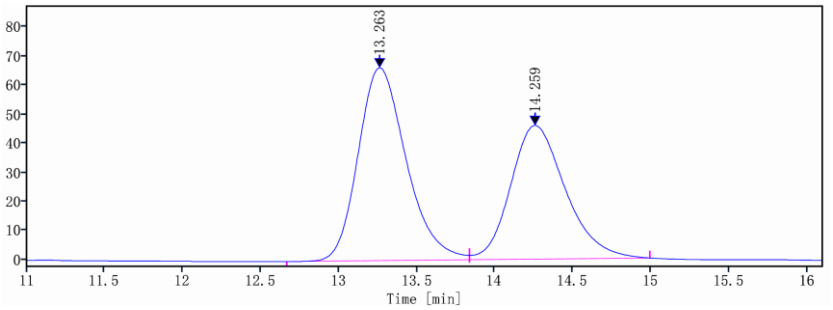
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.932	BB	1.4300	2430.8939	152.2842	95.6973
18.234	MM m	0.3594	109.2971	4.8788	4.3027



(*R*)-1-(1-((*S*)-Isoquinolin-1-yl)-7-methoxynaphthalen-2-yl)-3-methylbutan-1-ol (**4t**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 3-methylbutanal (12.9 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 58% yield (21.5 mg). ***Rf*** 0.5 (2% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, J = 5.7 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.88 – 7.76 (m, 2H), 7.76 – 7.63 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.17 – 7.08 (m, 1H), 6.32 (d, J = 2.4 Hz, 1H), 4.34 (dd, J = 8.5, 4.3 Hz, 1H), 3.49 (s, 3H), 2.15 (s,

1H), 1.68 – 1.40 (m, 3H), 0.75 (d, J = 5.7 Hz, 3H), 0.48 (d, J = 5.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.73, 157.96, 142.38, 141.88, 136.29, 133.64, 131.86, 130.64, 129.52, 129.12, 128.52, 128.50, 127.75, 127.08, 127.03, 121.76, 120.44, 118.04, 105.03, 70.70, 54.99, 47.62, 24.68, 23.13, 21.69; **HRMS** (ESI) calcd. for $C_{25}H_{25}NO_2$ $[M+H]^+$ *m/z* 372.1958, found 372.1957; **IR** (neat, cm^{-1}) 3435, 3213, 2953, 2863, 1622, 1511, 1459, 1422, 821, 744; **m.p.** 170.5 – 172.1 °C; **$[\alpha]_D^{20}$** = +52.5 (c = 0.04, $CHCl_3$); 92% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 13.3 min, t_R (minor) = 14.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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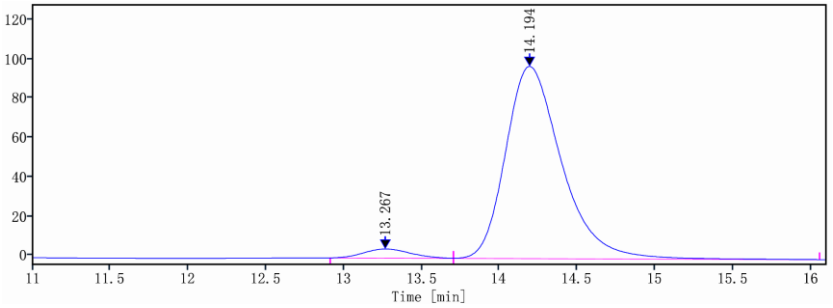
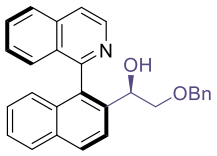
14.259	MM m	0.3728	1122.8313	45.9922	44.1511



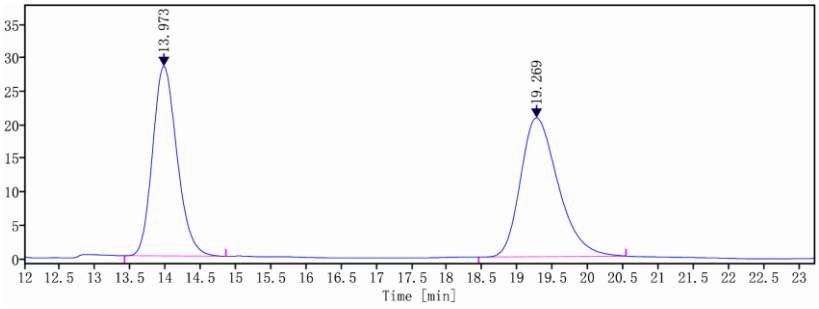
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.267	MM m	0.3258	95.9515	4.6287	3.7765
14.194	MB m	0.3819	2444.8315	97.7039	96.2235



(*S*)-2-(Benzyloxy)-1-(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)ethan-1-ol (**4u**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg,

10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 2-(benzyloxy)acetaldehyde (18.0 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 62% yield (25.1 mg). ***Rf*** 0.5 (1% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.8 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.81 (d, *J* = 5.8 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.53 – 7.37 (m, 3H), 7.37 – 7.17 (m, 6H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.50 (dd, *J* = 9.5, 3.0 Hz, 1H), 4.49 – 4.34 (m, 2H), 3.80 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.55 (t, *J* = 9.8 Hz, 1H), 2.93 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.16, 142.31, 137.80, 136.30, 136.25, 134.12, 133.19, 132.39, 130.72, 129.22, 128.44, 128.34, 128.07, 127.86, 127.77, 127.73, 127.17, 126.92, 126.47, 126.04, 125.97, 123.86, 120.57, 75.02, 73.02, 70.52; **HRMS** (ESI) calcd. for $C_{28}H_{32}NO_2$ $[M+H]^+$ m/z 406.1802, found 406.1804; **IR** (neat, cm^{-1}) 3419,3058, 2922, 2852, 1621, 1557, 1453, 825, 746; **m.p.** 190.1 – 191.5 ^{o}C; **$[\alpha]_D^{20}$** = –32.5 (*c* = 0.04, $CHCl_3$); 89% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 19.7 min, t_R (major) = 14.0 min.



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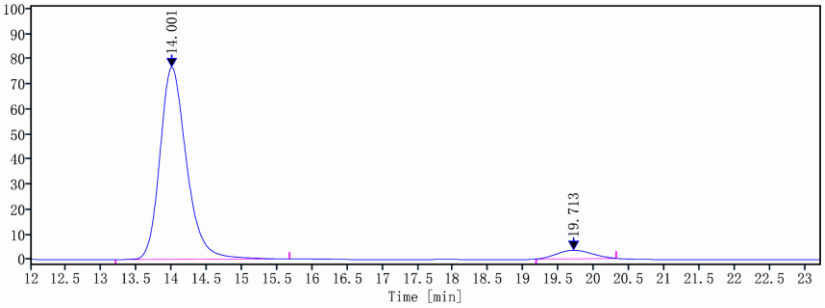
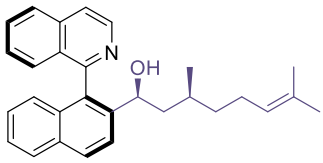
19.269	BM m	0.5720	771.2251	20.7321	53.0768

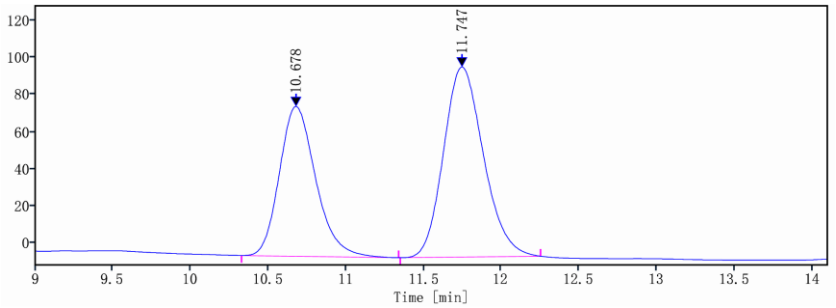


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.001	BB	2.4727	2007.2487	76.6031	94.5349
19.713	MM m	0.5423	116.0397	3.3822	5.4651



(*R*,*S*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)-3,7-dimethyloct-6-en-1-ol (**4v**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), (S)-3,7-dimethyloct-6-enal (23.1 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 52% yield (21.3 mg). ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.7 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.88 – 7.77 (m, 2H), 7.77 – 7.66 (m, 1H), 7.52 – 7.38 (m, 3H), 7.31 – 7.22 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 4.88 (t, *J* = 7.1 Hz, 1H), 4.42 (dd, *J* = 8.0, 5.8 Hz, 1H), 1.78 – 1.61 (m, 6H), 1.57 – 1.45 (m, 4H), 1.43 – 1.32 (m, 1H), 0.87 (d, *J* = 1.5 Hz, 2H), 0.75 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.57, 142.33, 141.02, 136.28, 133.29, 132.93, 132.56, 130.85, 130.62, 129.42, 128.73, 128.00, 127.75, 127.11, 127.08, 126.45, 126.16, 125.81, 124.84, 124.22, 120.45, 70.80, 45.60, 36.45, 29.47, 25.69, 25.10, 20.09, 17.62; **HRMS** (ESI) calcd. for $C_{29}H_{31}NO$ $[M+H]^+$ *m/z* 410.2478, found 410.2478; **IR** (neat, cm^{-1}) 3219,3056, 2928, 2856, 1640, 1558, 1435, 824, 746; **m.p.** 139.1 – 141.2 °C; **$[\alpha]_D^{20}$** = +5.0 (*c* = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 10% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 11.8 min, t_R (minor) = 10.7 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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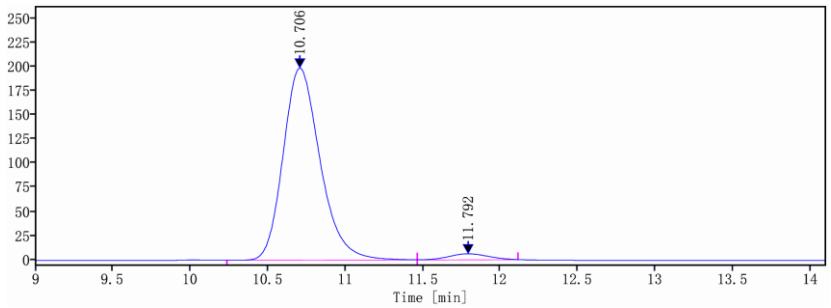
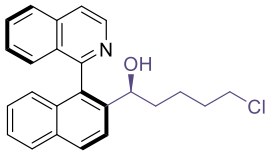
11.747	BM m	0.2743	1834.8598	102.7508	58.2062



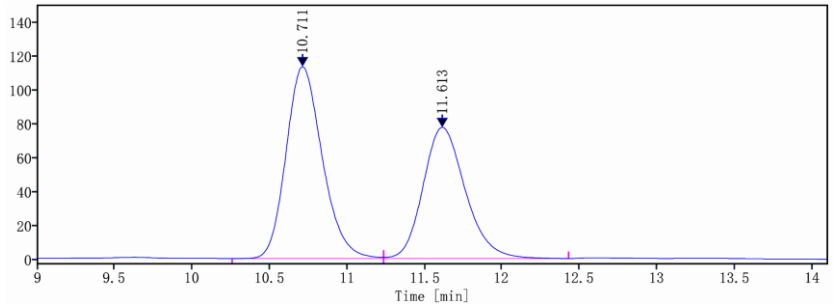
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.706	BM m	0.2536	3306.5443	199.2806	96.8778
11.792	MM m	0.2744	106.5640	6.1430	3.1222



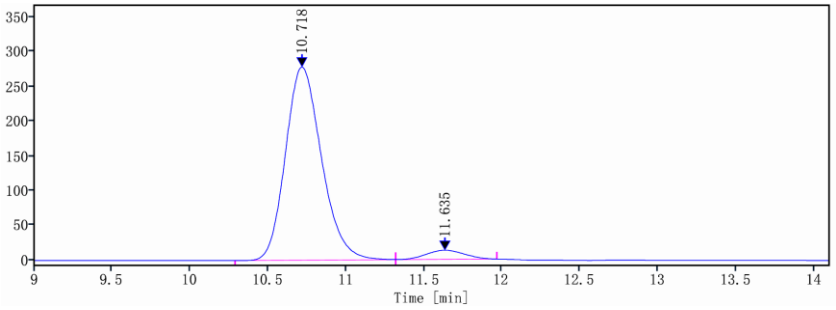
(*R*)-5-Chloro-1-(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)pentan-1-ol (**4w**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), 5-chloropentanal (18.1 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 55% yield (20.6 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.8 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 8.01 – 7.87 (m, 3H), 7.80 (d, J = 5.9 Hz, 1H), 7.75 – 7.65 (m, 1H), 7.54 – 7.37 (m, 3H), 7.31 – 7.22 (m, 1H), 7.00 (d, J = 8.6 Hz, 1H), 3.63 (d, J = 8.2 Hz, 1H), 2.30 (s, 1H), 1.71 (s, 1H),

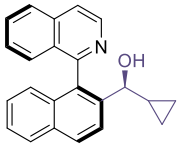
1.28 (d, J = 1.4 Hz, 1H), 1.21 – 1.10 (m, 1H), 0.48 – 0.30 (m, 2H), 0.25 – 0.07 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.47, 142.17, 140.68, 136.29, 133.17, 132.93, 132.49, 130.75, 129.46, 128.65, 128.05, 127.86, 127.15, 127.01, 126.57, 126.12, 125.92, 123.99, 120.62, 72.05, 44.75, 37.29, 32.14, 23.19; **HRMS** (ESI) calcd. for $C_{32}H_{38}O_2$ $[M+H]^+$ *m/z* 376.1463, found 376.1465; **IR** (neat, cm^{-1}) 3418, 2955, 2851, 1621, 1500, 1454, 821, 743; **m.p.** 120.3 – 121.3 °C; **$[\alpha]_D^{20}$** = –7.5 (c = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 10.7 min, t_R (minor) = 11.6 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.711	BV	0.9784	1847.3058	113.6499	55.6367
11.613	VB	1.1949	1472.9922	77.7289	44.3633



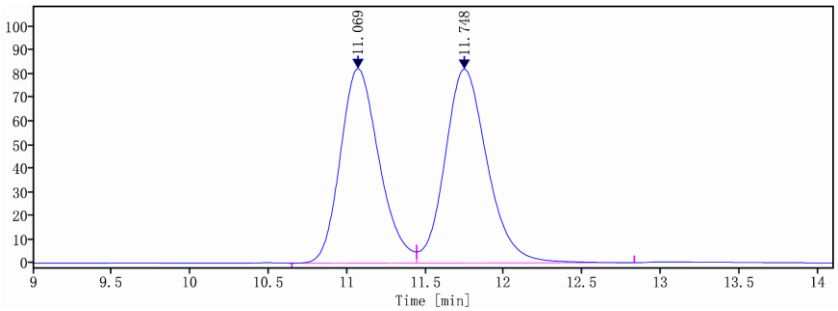
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.718	BM m	0.2476	4464.7737	277.6514	95.2512
11.635	MM m	0.2685	222.5915	13.0837	4.7488



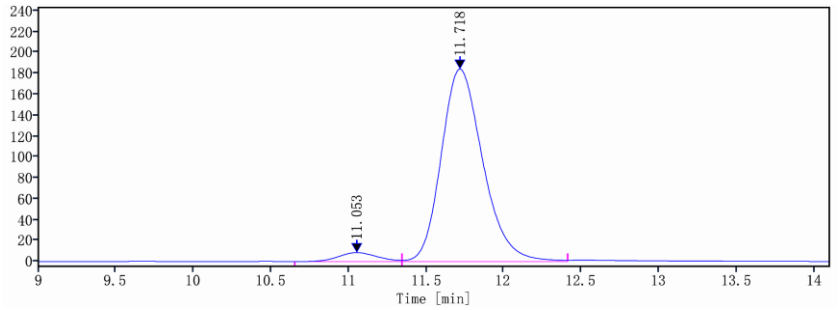
(*R*)-Cyclopropyl(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methanol (4x).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg,

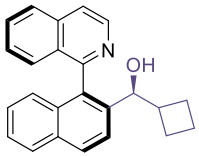
10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), cyclopropanecarbaldehyde (10.5 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 68% yield (22.1 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.8 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 8.01 – 7.88 (m, 3H), 7.80 (d, *J* = 6.6 Hz, 1H), 7.75 – 7.65 (m, 1H), 7.53 – 7.35 (m, 3H), 7.31 – 7.25 (m, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 3.63 (d, *J* = 8.2 Hz, 1H), 2.30 (s, 1H), 1.20 – 1.01 (m, 1H), 0.50 – 0.28 (m, 2H), 0.28 – 0.07 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.74, 142.22, 140.24, 136.18, 133.43, 132.98, 132.58, 130.59, 129.39, 128.83, 127.99, 127.72, 127.20, 126.96, 126.42, 126.33, 125.86, 124.59, 120.49, 76.34, 18.62, 3.93, 2.93; **HRMS** (ESI) calcd. for $C_{23}H_{19}NO$ $[M+H]^+$ *m/z* 326.1539, found 326.1539; **IR** (neat, cm^{-1}) 3186, 3057, 2922, 2854, 1622, 1559, 1458, 829, 753; **m.p.** 155.0 – 157.0 °C; **$[\alpha]_D^{20}$** = 56.5 (*c* = 0.04, $CHCl_3$); 92% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 11.7 min, t_R (minor) = 11.1 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.069	VV	0.7959	1407.7413	82.0679	47.9339
11.748	VB	1.3891	1529.0952	81.7956	52.0661

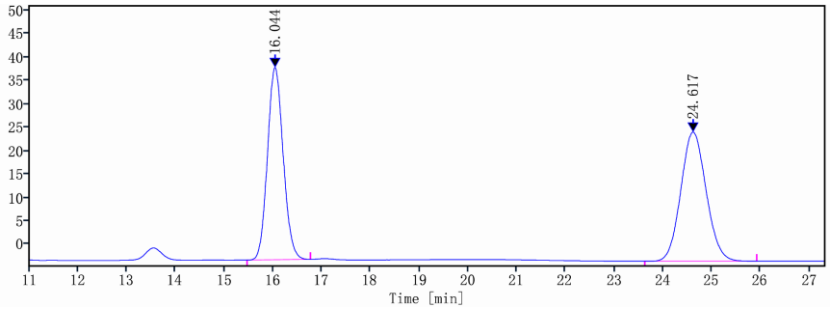


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.053	BV	0.6918	148.4892	8.5922	4.1421
11.718	VV	1.0683	3436.3814	184.3936	95.8579



(*R*)-Cyclobutyl(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methanol (**4y**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), cyclobutanecarbaldehyde (12.6 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 72% yield (24.4 mg). ***Rf*** 0.5 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.8 Hz, 1H), 8.07 – 7.95 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 5.7 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.51 – 7.37 (m, 3H), 7.31 – 7.20 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.25 (d, *J* = 7.9 Hz, 1H), 2.68 – 2.53 (m, 1H), 2.28 (s, 1H), 2.01 – 1.89 (m, 1H), 1.88 – 1.76 (m, 1H), 1.80 – 1.59 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.72, 142.20, 139.26, 136.26, 133.83, 132.94, 132.57, 130.66, 129.20, 128.85, 127.97, 127.74, 127.11, 127.07, 126.43, 126.21, 125.84, 124.52, 120.48, 75.96, 41.59, 24.90, 24.18, 17.72; **HRMS** (ESI) calcd. for $C_{24}H_{21}NO$ $[M+H]^+$ *m/z* 340.1696, found 340.1694; **IR** (neat, cm^{-1}) 3418, 2923, 1689, 1557, 1427, 1365, 826, 748; **m.p.** 169.4 – 171.3 °C; **$[\alpha]_D^{20}$** = –45.0 (*c* = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (major) = 16.0 min, t_R (minor) = 24.6 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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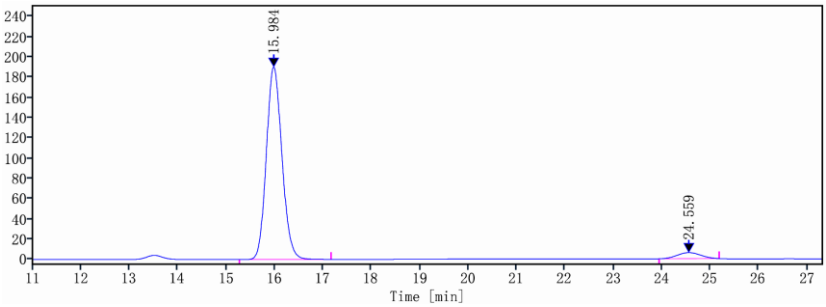
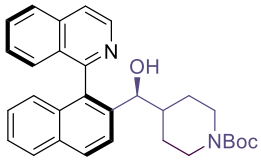
24.617	BB	2.2967	994.5814	27.5887	51.9342



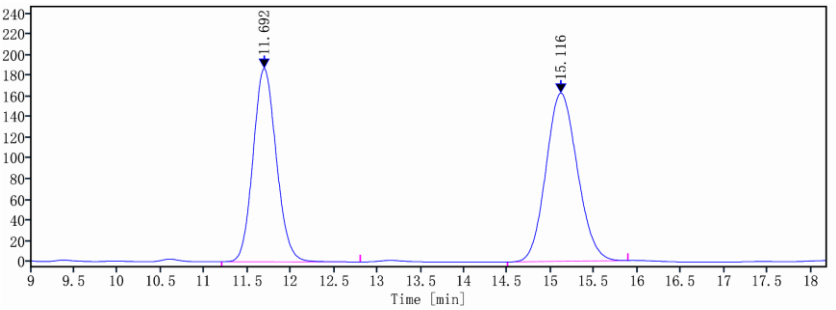
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.984	BB	1.8967	4243.4295	189.8658	95.4188
24.559	MM m	0.5351	203.7354	6.0165	4.5812



***Tert*-butyl 4-((*S*)-hydroxy(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)methyl)piperidine-1-carboxylate (4z).**

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulf-onate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **A** using NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.1 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), *tert*-butyl 4-formylpiperidine-1-carboxylate (32.0 mg, 0.15 mmol) and anhydrous DMSO/THF (4:1, 0.50 mL). The reaction mixture was stirred for 12 h at rt. The crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the title compound as a white solid in 56% yield (26.2 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.7 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 8.01 – 7.89 (m, 2H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.51 – 7.33 (m, 3H), 7.31 – 7.23 (m, 1H), 7.03 (d, *J* = 9.6 Hz, 1H), 4.01 – 3.86 (m, 2H), 2.51 – 2.39 (m, 1H), 2.25 (s, 1H), 1.91 – 1.81 (m, 1H), 1.60 – 1.44 (m, 2H), 1.41 (s, 9H), 1.33 – 1.23 (m, 1H), 1.16 – 0.96 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.50, 154.77, 142.08, 139.25, 136.25, 134.01, 132.96, 132.60, 130.75, 129.40, 128.78, 128.01, 127.84, 127.19, 126.87, 126.64, 126.20, 126.08, 120.67, 79.18, 77.29, 42.51, 28.81, 28.44; **HRMS** (ESI) calcd. for $C_{30}H_{32}N_2O_3$ $[M+H]^+$ *m/z*

469.2486, found 469.2485; **IR** (neat, cm^{-1}) 3046, 2928, 2827, 1716, 1609, 1509, 1436, 824, 779; **m.p.** 220.4 – 221.3 °C; **$[\alpha]_D^{20}$** = –62.5 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 15.3 min, t_R (major) = 11.8 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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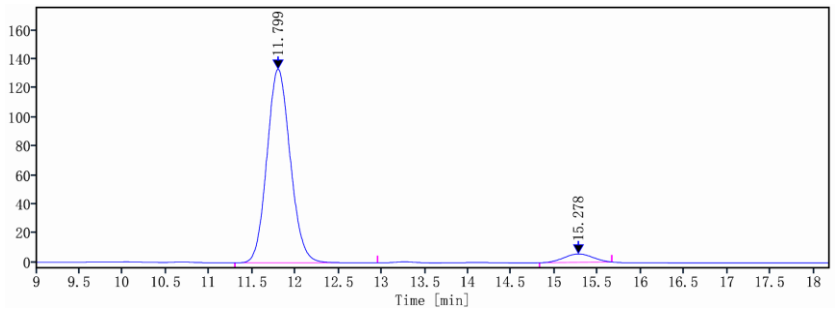
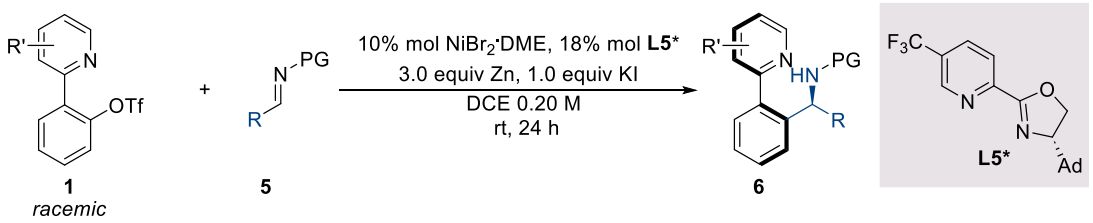
15.116	BB	1.3893	4089.5132	162.5060	54.0783

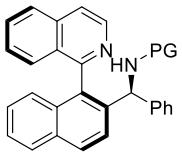


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.799	BB	1.6533	2499.5655	133.4173	94.9161
15.278	MM m	0.3676	133.8830	5.7940	5.0839

General procedure (B) for 5.

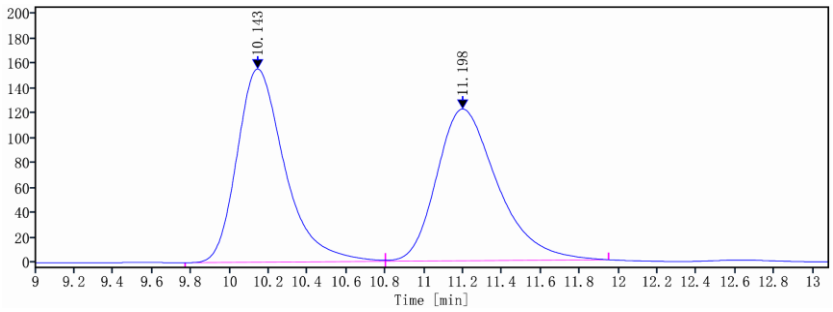


In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added **1** (0.10 mmol, 1.0 equiv), nickel salts (10.0 mol%), **L5*** (6.3 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), anhydrous DCE (0.5 mL) were added and the mixture was stirred for 10 min at room temperature, at which time corresponding imine was added to the resulting mixture. The reaction was stirred at rt for up to 24 h (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended). After the reaction was complete, the reaction mixture was directly filtered through a short pad of silica gel [EtOAc in petroleum ether (PE)] to give the crude product. The product was purified by chromatography on silica gel for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated. The enantiomeric excesses (% *ee*) were determined by HPLC analysis using chiral stationary phases.



***N*-((*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(phenyl)methyl)-3-methylpyridin-2-amine (6a).**

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate** (**1a**) (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-N-(3-methylpyridin-2-yl)-1-phenylmethanimine (29.4 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 62% yield (28.0 mg). ***Rf*** 0.4 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.7 Hz, 1H), 7.99 – 7.87 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.56 (m, 3H), 7.53 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 7.32 – 7.23 (m, 2H), 7.25 – 7.07 (m, 6H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.42 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.16 (d, *J* = 5.3 Hz, 1H), 4.56 (s, 1H), 1.99 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.52, 155.38, 144.90, 142.68, 142.21, 140.04, 136.45, 136.09, 135.55, 132.87, 132.68, 130.16, 129.05, 128.66, 128.19, 127.96, 127.54, 127.19, 127.08, 126.78, 126.68, 126.52, 126.28, 126.06, 125.88, 120.01, 116.64, 112.78, 57.26, 16.99; **HRMS** (ESI) calcd. for $C_{32}H_{25}N_3$ $[M+H]^+$ *m/z* 452.2121, found 452.2123; **m.p.** 198.4 – 199.3 °C; **IR** (neat, cm^{-1}) 3523, 3441, 3339, 3054, 2927, 1659, 1598, 1466, 825, 748, 699; **$[\alpha]_D^{20}$** = +37.5 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 10.1 min, t_R (major) = 11.2 min.



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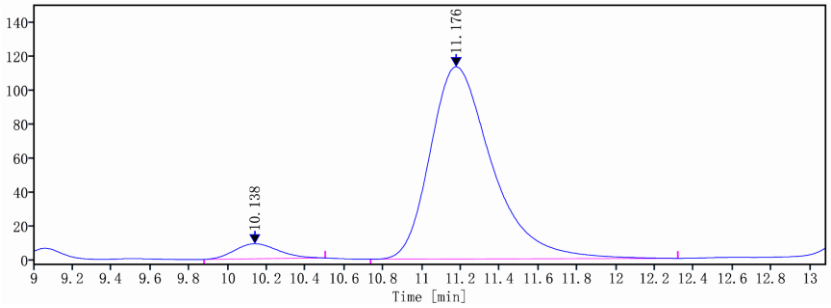

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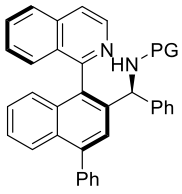
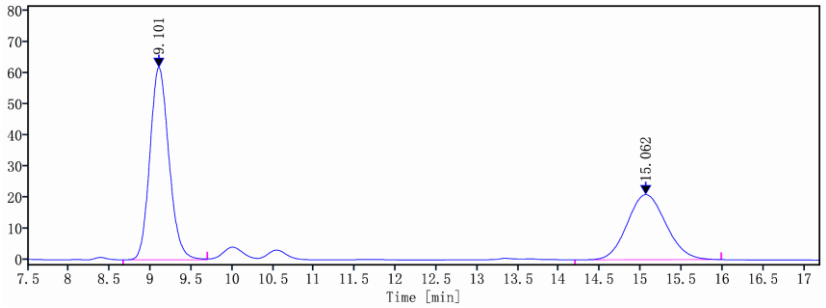


***N*-((*S*)-(1-((*S*)-Isoquinolin-1-yl)-4-phenylnaphthalen-2-yl)(phenyl)methyl)-3-methylpy-ridin-2-amine** (**6b**).

From **1-(isoquinolin-1-yl)-4-phenylnaphthalen-2-yl trifluoro-methanesulfonate (1g)** (47.9 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-N-(3-methylpyridin-2-yl)-1-phenylmethanimine (29.4 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 52% yield (27.4 mg). ***Rf*** 0.5 (20% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.7 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.60 (m, 3H), 7.55 – 7.36 (m, 8H), 7.36 – 7.19 (m, 5H), 7.19 – 7.03 (m, 5H), 6.41 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.22 (d, *J* = 5.5 Hz, 1H), 4.53 (s, 1H), 1.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.66, 155.37, 144.96, 142.59, 142.33, 130.22, 130.19, 128.77, 128.31, 128.18, 127.52, 127.37, 127.29, 127.11, 127.09, 126.80, 126.68, 126.34, 126.13, 125.93, 119.99, 116.49, 112.76, 57.20, 16.99;

HRMS (ESI) calcd. for $C_{38}H_{29}N_3$ $[M+H]^+$ *m/z* 528.2434, found 528.2435; **m.p.** 201.4 – 203.3 °C; **IR** (neat, cm^{-1}) 3524, 3442, 3355, 2923, 1627, 1597, 1328, 769, 702 ; **$[\alpha]_D^{20}$** = +17.5 (*c* = 0.04, $CHCl_3$); 88% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 15.0 min, t_R (major) = 9.1 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.101	BV	1.0293	999.5685	61.6890	59.2688
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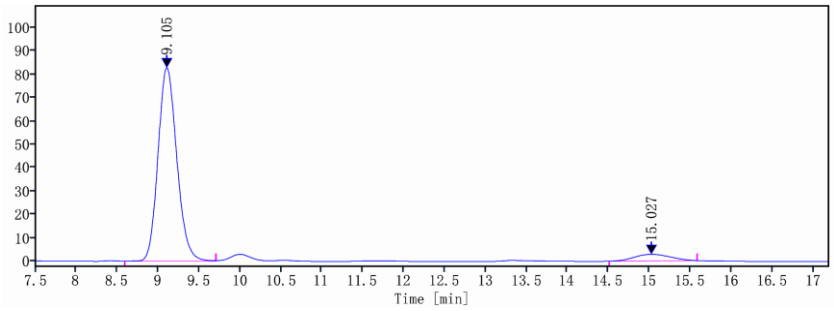
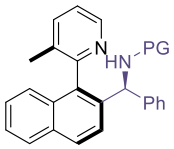


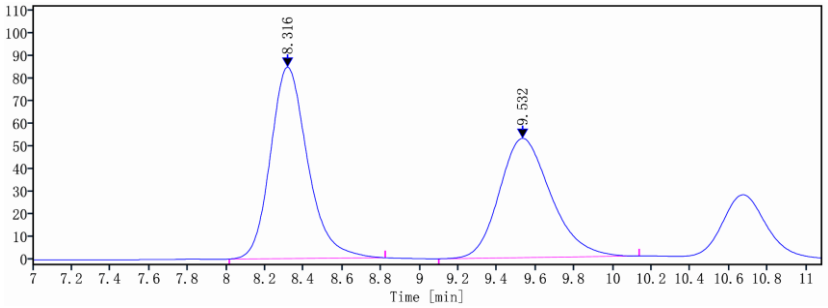
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.105	BV	1.1127	1324.3890	82.7925	93.8643
15.027	MM m	0.4841	86.5724	2.8364	6.1357



3-Methyl-*N*-((*S*)-((*S*)-1-(3-methylpyridin-2-yl)naphthalen-2-yl)(phenyl)methyl)py-ridin-2-amine (**6c**).

From **1-(3-methylpyridin-2-yl)naphthalen-2-yl trifluoromethane-sulfonate (1h)** (36.7 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-N-(3-methylpyridin-2-yl)-1-phenylmethanimine (29.4 mg, 0.15 mmol, 1.5 equiv)

and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 58% yield (24.1 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, J = 6.4 Hz, 1H), 7.87 (t, J = 9.0 Hz, 2H), 7.74 (d, J = 5.1 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.42 – 7.32 (m, 2H), 7.30 – 7.23 (m, 5H), 7.18 (t, J = 7.3 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.45 (dd, J = 7.1, 5.1 Hz, 1H), 6.19 (d, J = 5.1 Hz, 1H), 4.68 (s, 1H), 2.12 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.85, 155.68, 146.92, 145.23, 142.84, 138.85, 138.14, 137.67, 137.12, 136.42, 133.20, 132.79, 131.80, 128.44, 128.27, 128.14, 127.62, 126.79, 126.57, 125.83, 125.62, 125.44, 122.37, 116.69, 112.82, 56.95, 18.74, 17.12. **HRMS** (ESI) calcd. for $C_{29}H_{25}N_3$ $[M+H]^+$ *m/z* 416.2121, found 416.2123; **m.p.** 195.4 – 196.5 °C; **IR** (neat, cm^{-1}) 3526, 3442, 3364, 1651, 1627, 1597, 1466, 689; **$[\alpha]_D^{20}$** = +60.0 (c = 0.04, $CHCl_3$); 80% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 8.3 min, t_R (major) = 9.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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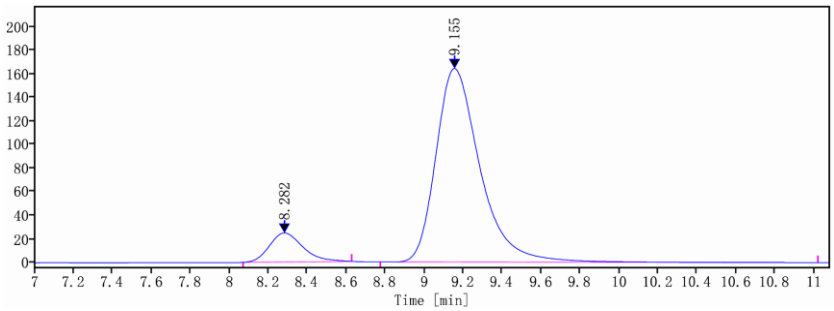
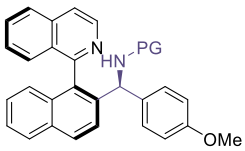
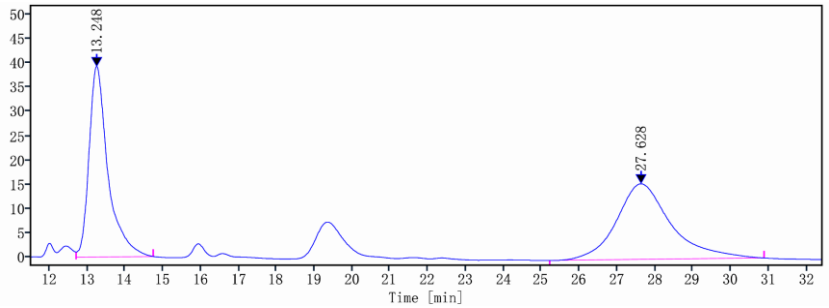


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.282	MM m	0.1829	293.2527	24.6268	10.2259
9.155	MB m	0.2391	2574.4785	164.0769	89.7741



***N*-((1*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(4-methoxyphenyl)methyl)-3-methylpyridin-2-amine (6d).**

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-1-(3-methoxyphenyl)-N-(3-methylpyridin-2-yl)methanimine (33.9 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 42% yield (20.2 mg). ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.04 – 7.85 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 5.1 Hz, 1H), 7.65 – 7.50 (m, 3H), 7.48 – 7.39 (m, 1H), 7.28 – 7.18 (m, 3H), 7.15 – 7.02 (m, 3H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 2H), 6.41 (dd, *J* = 7.0, 5.2 Hz, 1H), 6.15 (d, *J* = 5.3 Hz, 1H), 4.48 (s, 1H), 3.73 (d, *J* = 1.0 Hz, 3H), 1.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.75, 158.33, 155.32, 144.91, 142.19, 140.31, 136.44, 136.00, 135.15, 134.86, 132.92, 132.63, 130.04, 128.95, 128.73, 128.67, 127.94, 127.27, 126.89, 126.65, 126.44, 126.21, 126.00, 125.76, 119.96, 116.54, 113.60, 112.73, 56.93, 55.20, 16.96; **HRMS** (ESI) calcd. for $C_{33}H_{27}N_3O$ $[M+H]^+$ *m/z* 482.2227, found 482.2226; **m.p.** 187.4 – 189.1 °C; **IR** (neat, cm^{-1}) 3526, 3442, 3364, 1651, 1627, 1597, 1466, 689; **$[\alpha]_D^{20}$** = 19.9 (*c* = 0.04, $CHCl_3$); 89% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 13.1 min, t_R (major) = 25.5 min.



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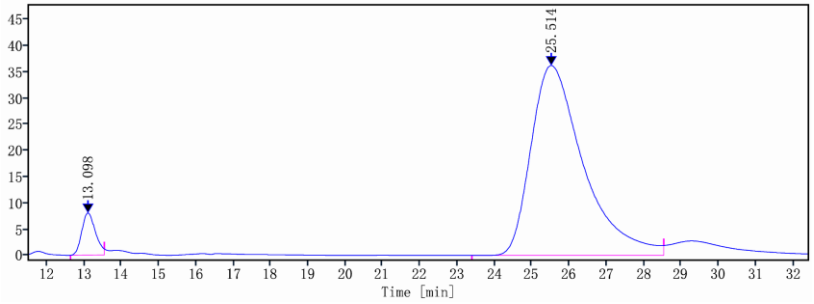
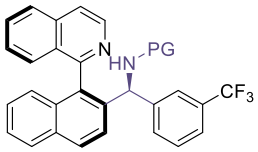
27.628	BM m	1.4643	1550.4807	15.5098	53.3481



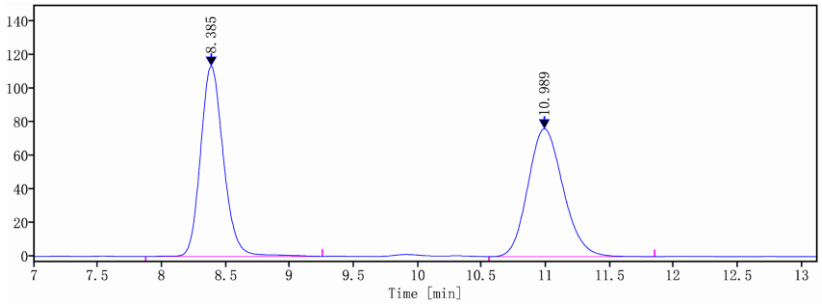
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.098	BM m	0.3938	205.1071	8.0352	5.4720
25.514	MM m	1.4670	3543.1844	36.2290	94.5280



***N*-((*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)(3-(trifluoromethyl)phenyl)methyl)-3-methylpyri-din-2-amine** (**6e**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-N-(3-methylpyridin-2-yl)-1-(3-(trifluoromethyl)phenyl)methanimine (39.6 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 78% yield (40.5 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.7 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.93 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.60 (m, 3H), 7.53 – 7.46 (m, 1H), 7.45 – 7.33 (m, 6H), 7.32 – 7.26 (m, 2H), 7.21 – 7.14 (m, 1H), 7.07 (d, *J* = 9.6 Hz, 1H), 6.47 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.15 (d, *J* = 4.8 Hz, 1H), 4.60 (d, *J* = 4.9 Hz, 1H), 2.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.00, 155.42, 145.08, 144.02, 142.34, 139.31, 136.63, 136.19, 136.05, 132.81, 132.78, 130.73, 130.34 (q, *J* = 32.3 Hz), 130.33, 129.38, 128.61, 128.58, 128.04, 127.43, 127.05, 126.95, 126.78, 126.42, 126.20, 125.62, 124.23 (q,

J = 3.5 Hz), 123.55 (q, J = 3.5 Hz), 124.18 (q, J = 271.0 Hz), 120.22, 116.88, 113.31, 56.93, 17.04; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.36. **HRMS** (ESI) calcd. for $C_{33}H_{24}F_3N_3$ $[M+H]^+$ *m/z* 520.1995, found 520.1997; **m.p.** 188.4 – 189.3 °C; **IR** (neat, cm^{-1}) 3522, 3444, 3382, 2922, 1652, 1627, 1599, 1465, 1384, 667; **$[\alpha]_D^{20}$** = +160.0 (c = 0.04, $CHCl_3$); 81% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 11.0 min, t_R (major) = 8.4 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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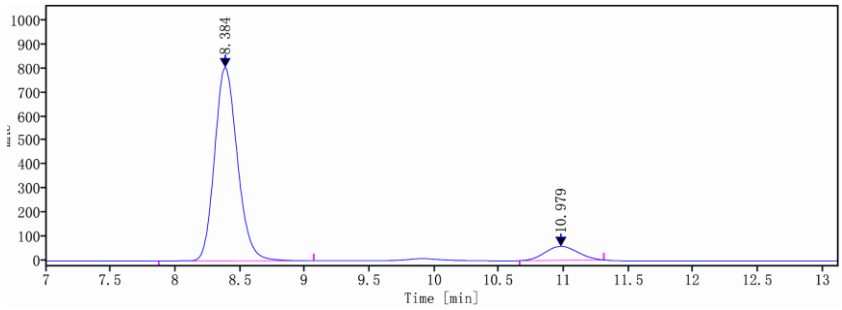
10.989	BB	1.2948	1457.5768	76.2976	50.7627



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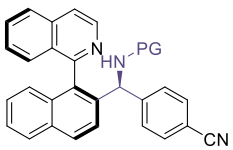
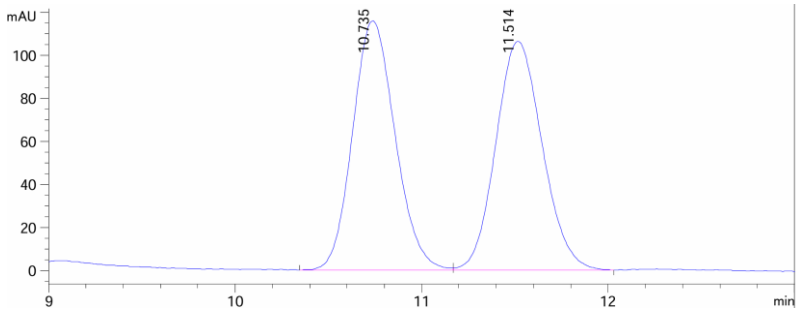
10.979	MM m	0.2771	1022.5384	58.1658	9.4148



4-((*S*)-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)((3-methylpyridin-2-yl)amino)methyl) benzonitrile (**6f**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME

(3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (E)-4-(((3-methylpyridin-2-yl)imino)methyl)benzonitrile (33.1 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 65% yield (30.9 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 5.7 Hz, 1H), 8.03 – 7.85 (m, 3H), 7.74 – 7.66 (m, 1H), 7.65 – 7.55 (m, 2H), 7.54 – 7.37 (m, 5H), 7.35 – 7.27 (m, 4H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.46 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.00 (d, *J* = 4.2 Hz, 1H), 4.65 (s, 1H), 2.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.81, 155.33, 148.71, 144.86, 142.30, 138.60, 136.70, 136.37, 136.24, 132.84, 132.72, 132.01, 130.46, 129.48, 128.56, 128.13, 128.07, 127.58, 127.18, 126.93, 126.85, 126.39, 125.74, 120.26, 119.13, 117.14, 113.49, 110.29, 57.30, 17.01; **HRMS** (ESI) calcd. for $C_{33}H_{24}N_4$ $[M+H]^+$ *m/z* 477.2074, found 477.2075; **m.p.** 196.4 – 197.3 °C; **IR** (neat, cm^{-1}) 3442, 3050, 2225, 1648, 1597, 1465, 1383, 1122, 825, 749; **$[\alpha]_D^{20}$** = +75.0 (*c* = 0.04, $CHCl_3$); 90% *ee*; **HPLC analysis** CHIRALCEL AD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 11.4 min, t_R (major) = 10.6 min.



Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
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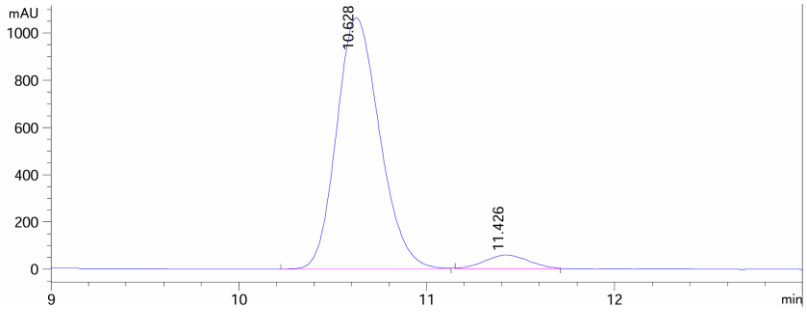
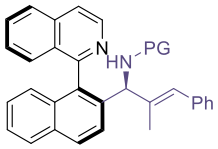
2	11.514	VB	106.211	0.270	50.082	1.842e3

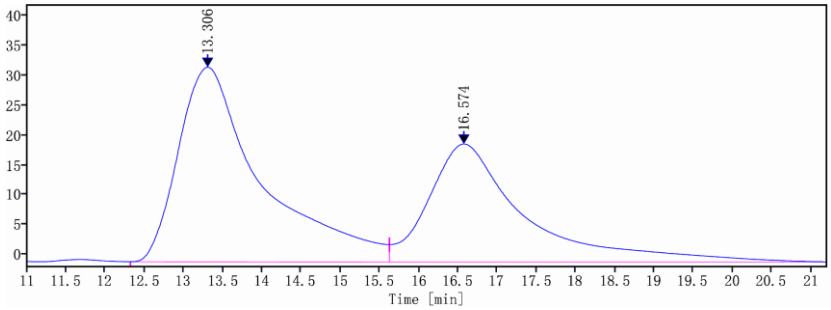


Peak #	RT [min]	Type	Height	Width [min]	Area %	Area
1	10.628	BV	1.063e3	0.248	94.908	1.692e4
2	11.426	MM	56.423	0.268	5.092	908.011

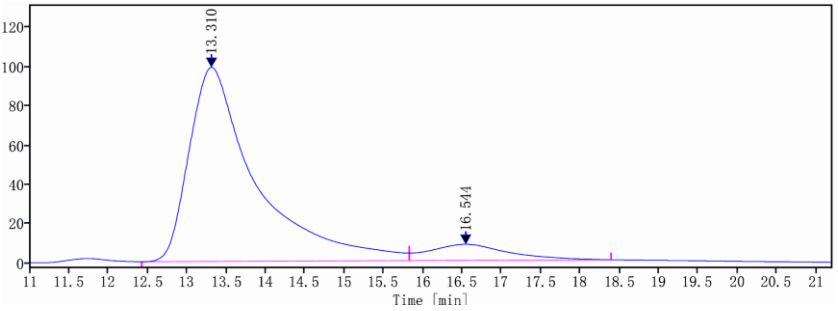


***N*-((*S*,*E*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)-2-methyl-3-phenylallyl)-3-methylpyridin-2-amine** (**6g**).

From **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethanesulfonate (1a)** (40.0 mg, 0.10 mmol, 1.0 equiv), the title compound was prepared following the general procedure **B** using $NiBr_2$·DME (3.1 mg, 10.0 mol%), **L5*** (6.4 mg, 18.0 mol%), Zn (19.6 mg, 3.0 equiv), KI (16.7 mg, 1.0 equiv), (1E,2E)-2-methyl-N-(3-methylpyridin-2-yl)-3-phenylprop-2-en-1-imine (35.4 mg, 0.15 mmol, 1.5 equiv) and anhydrous DCE (0.50 mL). The reaction mixture was stirred for 24 h at rt. The crude material was purified by flash column chromatography (5−20% EtOAc in PE) to provide the title compound as a white solid in 66% yield (32.4 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 5.7 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.58 (d, *J* = 5.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 5.6 Hz, 4H), 7.20 – 7.12 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.61 (s, 1H), 6.44 (dd, *J* = 7.1, 5.1 Hz, 1H), 5.50 (d, *J* = 5.9 Hz, 1H), 4.40 (s, 1H), 2.07 (s, 3H), 1.72 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.13, 155.47, 142.31, 138.52, 138.16, 137.73, 136.67, 136.43, 136.23, 133.01, 132.92, 130.21, 129.25, 129.00, 128.63, 128.18, 127.98, 127.87, 127.25, 127.23, 127.03, 126.55, 126.35, 126.01, 125.94, 125.61, 125.08, 119.93, 112.57, 59.27, 17.38, 17.11; **HRMS** (ESI) calcd. for $C_{35}H_{29}N_3$ $[M+H]^+$ *m/z* 492.2434, found 492.2437; **m.p.** 198.4 – 199.3 °C; **IR** (neat, cm^{-1}) 3523, 3443, 3377, 1627, 1597, 1466, 1384, 825, 749, 698; **$[\alpha]_D^{20}$** = –81.3 (*c* = 0.04, $CHCl_3$); 82% *ee*; **HPLC analysis** CHIRALCEL IA-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 16.5 min, t_R (major) = 13.3 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.306	BV	3.3048	2391.2960	32.5121	58.9474
16.574	VB	5.9619	1665.3649	19.6927	41.0526



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.310	BM m	0.8531	5845.9682	98.9678	91.0560
16.544	MM m	1.0110	574.2211	8.2203	8.9440

4. Crystal Data and Structure Refinement for 3b and 6f

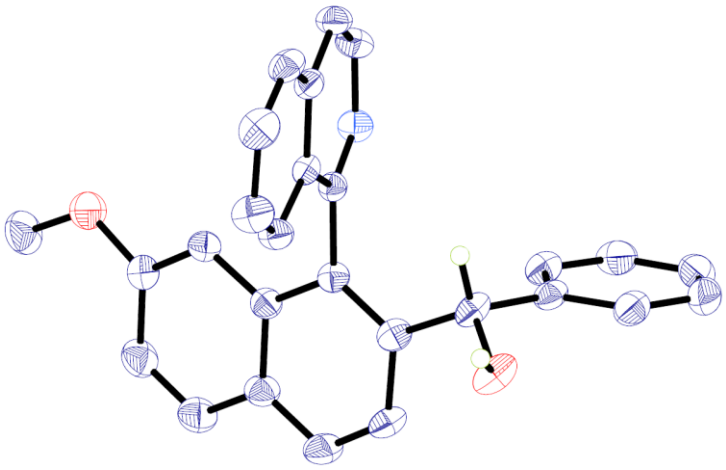


Fig. S1. Crystal data and structure refinement for **3b**

Identification code	**3b**_a
Empirical formula	$C_{27}H_{21}NO_2$
Formula weight	391.45
Temperature/K	173
Crystal system	monoclinic
Space group	P1
a/Å	6.3648(2)
b/Å	9.0644(3)
c/Å	9.3365(3)
α/°	74
β/°	74
γ/°	85
Volume/Å3	495.99(3)
Z	1
ρcalcg/cm3	1.311
μ/mm-1	0.650
F(000)	206.0

Crystal Data and Structure Refinement for 6f

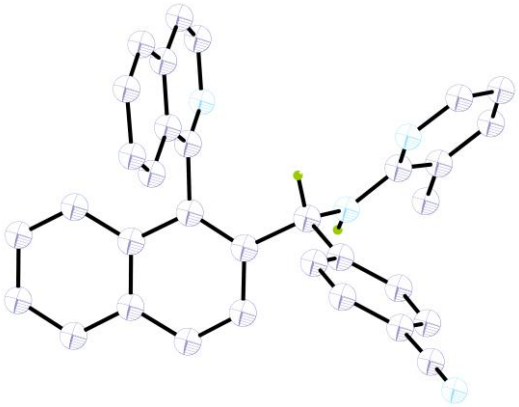
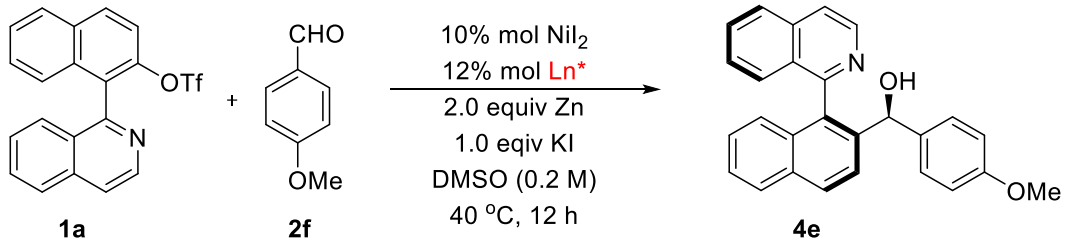


Fig. S2. Crystal data and structure refinement for **6f**

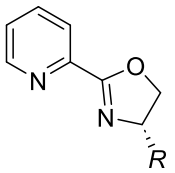
Identification code	**6f**_a
Empirical formula	$C_{66}H_{52}N_8O$ (+ solvent)
Formula weight	973.16
Temperature/K	150
Crystal system	monoclinic
Space group	P 4 21 2
a/Å	21.4304(3)
b/Å	21.4304(3)
c/Å	13.5849(3)
α/°	90
β/°	90
γ/°	90
Volume/Å3	6239.0(2)
Z	4
ρcalcg/cm3	1.036
μ/mm-1	0.491
F(000)	2048.0

5. Optimization of Reaction Condition

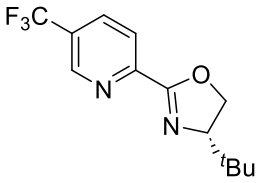
Table S1. Chiral ligand screening for chiral heterobiaryl carbinols



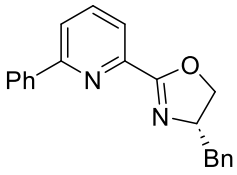
1a **2f** **4e**



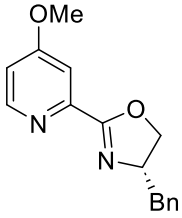
L1: R = ^{t}Bu, 38% yield, 87% ee
L2: R = ^{i}Pr, 30% yield, 26% ee
L3: R = Bn, 35% yield, 12% ee
L4: R = Ph, 35% yield, 33% ee



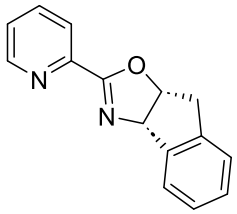
L5: 15%, 90% ee



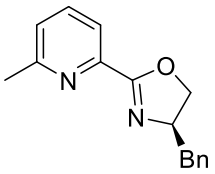
L6: 16%, 30% ee



L7: 18%, 15% ee

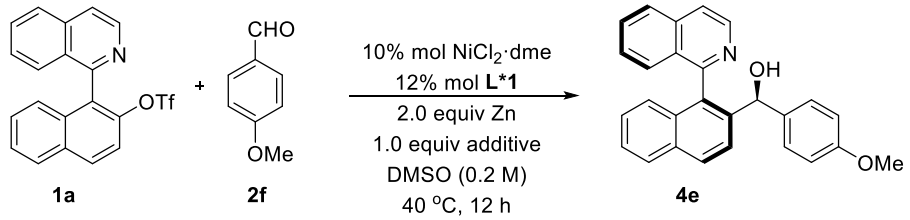


L8: 25% yield, 0% ee



L9: 13%, -30% ee

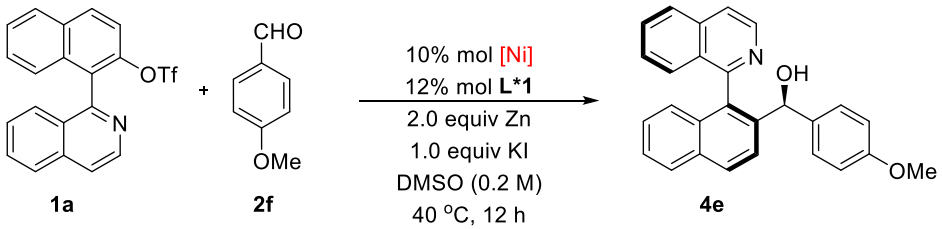
Table S2. Additive screening for chiral heterobiaryl carbinols



1a **2f** **4e**

entry	Additive	yield of **4a** (%)[a]	*ee* (%)[b]
1	NaI	22	85
2	***KI***	***30***	***87***
3	LiI	18	86
4	TBAI	-	-
5	NaBr	-	-
6	NaCl	-	-

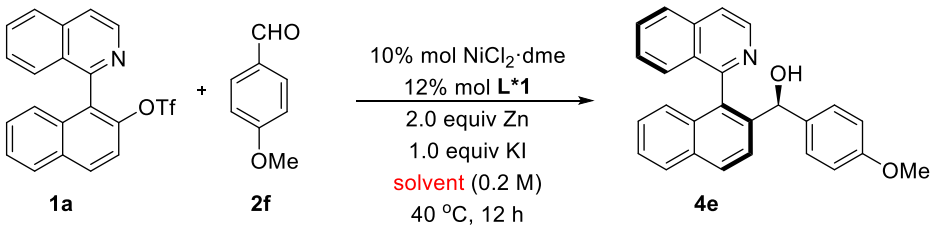
Table S3. Nickel salts screening for chiral heterobiaryl carbinols



1a 2f 4e

entry	[Ni]	yield of **4a** (%)[a]	ee (%)[b]
1	$NiCl_2·6H_2O$	53	89
2	$NiCl_2$	-	-
3	$NiCl_2$·dme	30	87
4	$NiBr_2$	34	87
5	$NiBr_2$·diglyme	49	87
6	$NiBr_2$·dme	18	87
7	***NiI_2***	***52***	***92***
8	$NiI_2·6H_2O$	40	87
9	$Ni(BF_4)_2·6H_2O$	-	-
10	$Ni(ClO_4)_2·6H_2O$	32	89

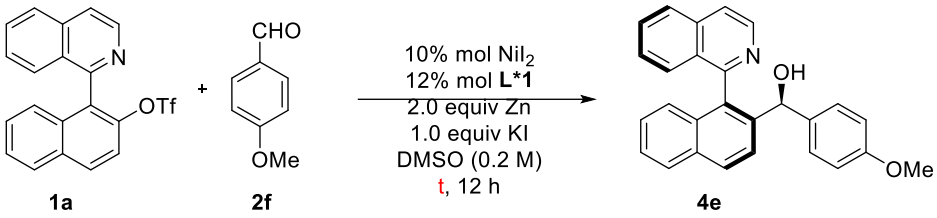
Table S4. Solvent screening for chiral heterobiaryl carbinols



1a 2f 4e

entry	Solvent	yield of **4a** (%)[a]	ee (%)[b]
1	DMF	25	89
2	THF	-	-
3	diglyme	-	-
4	DMAc	12	89
5	1,4-dioxane	-	-
6	EA	-	-
7	MeOH	-	-
8	acetone	-	-
9	DCE	-	-
10	MeCN	-	-

Table S5. Temperature screening for chiral heterobiaryl carbinols

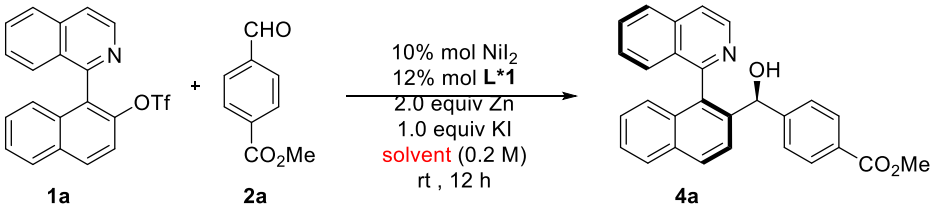


1a **2f** **4e**

entry	t/^{o}C	yield of **4a** (%)[a]	ee (%)[b]
1	rt	33	91
2[c]	**rt**	**80**	**91**
3	15	trace	-

[c]DMSO : MeCN 1:1 instead of DMSO.

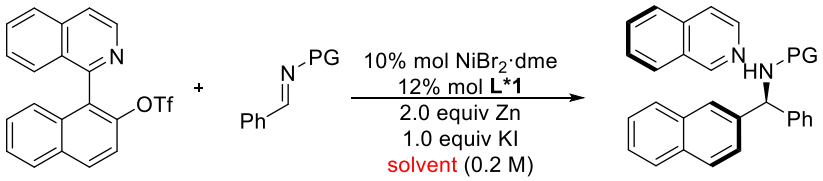
Table S6. Co-solvent screening for chiral heterobiaryl carbinols



1a **2a** **4a**

entry	Solvent	yield of **4a** (%)[a]	ee (%)[b]
1	***DMSO/MeCN (1:1)***	***90***	***93***
2	***DMSO/THF (1:1)***	***90***	***93***
3	DMSO/diglyme (1:1)	-	-
4	DMSO/MeCN (4:1)	85	88
5	DMSO/MeCN (1:4)	85	86

Table S7. Solvent screening for chiral heterobiaryl amines



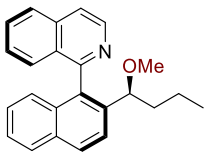
1a **2f** **4e**

entry	Solvent	yield of **4a** (%)[a]	ee (%)[b]
1	DMF	-	-
2	THF	42	0
3	diglyme	28	4
4	DCM	-	-
5	MeCN	25	46
6	DMSO	-	0
7	1,1,2,2-Clethlene	-	-
8	PhCl	-	-
9	***DCE***	***21***	***79***

a. Yields were determined by isolated b. Enantioselectivities were determined by chiral HPLC analysis.

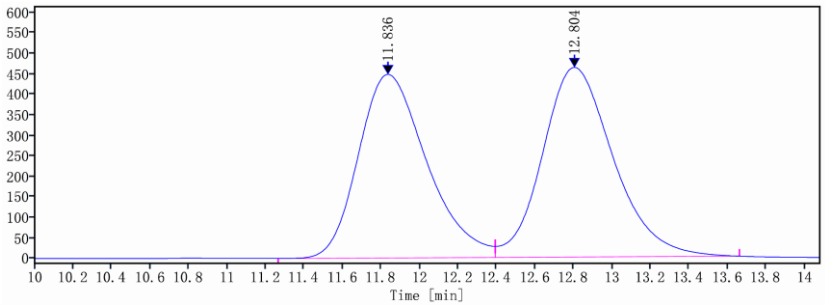
6. Further transformation

a) Synthetic utility[2]



1-(2-((*S*)-1-methoxybutyl)naphthalen-1-yl) (*S*)-isoquinoline (**7**).

Sodium hydride (6.0 mg, 0.15 mmol, 1.5 equiv, 60% dispersion in mineral oil) was added at 0 °C to a solution of **4p** (32.7 mg, 0.1 mmol, 1.0 equiv) in THF (0.5 mL). The mixture was stirred for 30 min; then methyl iodide (9.3 uL, 0.15 mmol, 1.5 equiv) was added. The mixture was allowed to warm to room temperature and it was stirred for 12 h. Then, the reaction was quenched with water (5 mL) and the product was extracted with ethyl acetate (3 × 40 mL), washed with brine (10 mL), dried over magnesium sulfate, and the solvent was evaporated in vacuo to afford a brownish oil. The crude mixture was dissolved in ethyl acetate (20 mL) and washed with aqueous sodium thiosulfate (10% in water, 20 mL), dried over magnesium sulfate and concentrated. Silica gel column chromatography (2–10% EtOAc in PE) furnished **7** (29.0 mg, 85%) as a transparent yellow oil. ***Rf*** 0.4 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.8 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.02 – 7.91 (m, 2H), 7.85 – 7.77 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.35 (m, 3H), 7.30 – 7.21 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.70 (t, *J* = 6.3 Hz, 1H), 3.00 (s, 3H), 1.87 – 1.65 (m, 2H), 1.47 – 1.34 (m, 1H), 1.27 – 1.14 (m, 1H), 0.73 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.39, 142.48, 139.59, 136.25, 134.44, 132.88, 132.56, 130.51, 129.17, 128.43, 127.99, 127.40, 127.15, 127.04, 126.38, 126.00, 125.71, 123.49, 120.30, 80.27, 56.90, 39.87, 18.98, 13.75; **HRMS** (ESI) calcd. for $C_{24}H_{23}NO$ $[M+H]^+$ *m/z* 342.1852, found 342.1854; **IR** (neat, cm^{-1}) 3426, 3055, 2956, 2870, 1620, 1583, 1556, 1463, 824, 747; **$[\alpha]_D^{20}$** = –81.3 (*c* = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 10% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 12.3 min, t_R (major) = 11.4 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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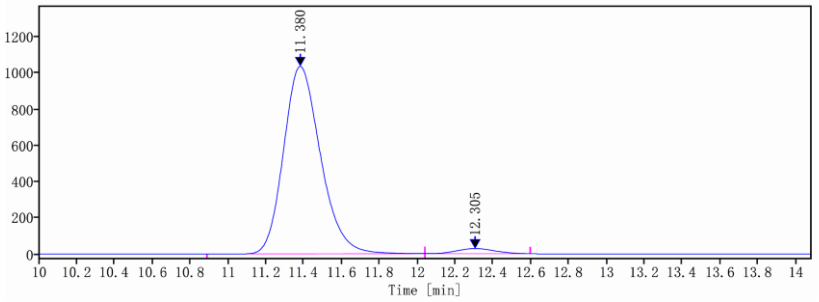
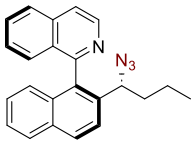
12.804	MM m	0.3899	11800.0891	462.0543	51.6369



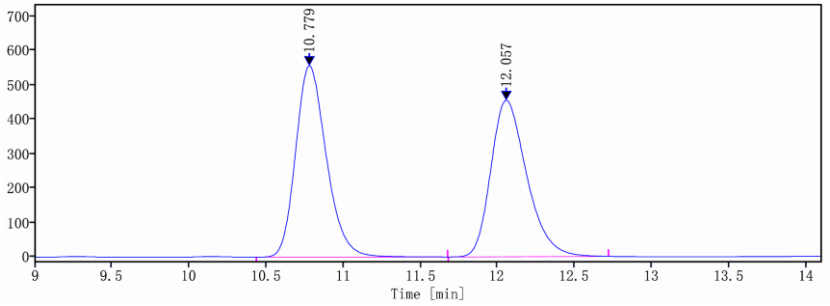
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.380	VM m	0.2083	14089.8890	1038.5248	97.1859
12.305	MM m	0.2214	407.9905	28.7779	2.8141



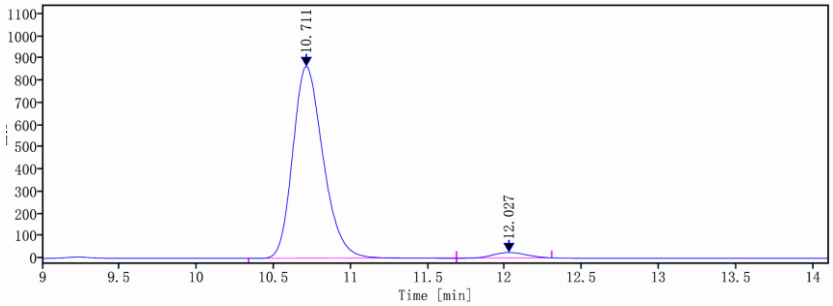
1-(2-((*R*)-1-Azidobutyl)naphthalen-1-yl) (*S*)-isoquinoline (**8**).

To a solution of **4p** (32.7 mg, 0.1 mmol) and DPPA (32 µL, 0.15 mmol) in toluene (0.5 mL) at 0°C was added DBU (25 µL, 0.17 mmol) via syringe. The mixture was stirred at 0 °C for 1 h and then at 60 °C for 48 h. Ethyl acetate (10 mL) was added and the mixture was washed with water, brine, dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. Purification by flash chromatography (0% - 4% CH_2Cl_2 in EtOAc) afforded **8** (26.4 mg, 75%) as a light yellow solid. ***Rf*** 0.2 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 5.7 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 8.03 – 7.90 (m, 2H), 7.83 (d, *J* = 5.8 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.53 – 7.44 (m, 1H), 7.45 – 7.32 (m, 2H), 7.33 – 7.23 (m, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 4.19 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.81 – 1.62 (m, 1H), 1.62 – 1.45 (m, 1H), 1.16 – 0.94 (m, 2H), 0.49 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR**

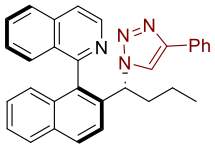
(101 MHz, $CDCl_3$) δ 158.94, 142.84, 136.78, 136.14, 135.40, 132.87, 132.42, 130.51, 129.60, 128.97, 128.02, 127.45, 127.35, 127.12, 126.70, 126.58, 126.21, 123.80, 120.52, 62.25, 37.76, 19.27, 13.22; **HRMS** (ESI) calcd. for $C_{23}H_{20}N_4$ $[M+H]^+$ *m/z* 353.1761, found 353.1763; **IR** (neat, cm^{-1}) 3469, 2927, 2869, 2103, 1619, 1553, 1450, 826, 746; **m.p.** 186.1 – 187.8 °C; **$[\alpha]_D^{20}$** = –81.3 (*c* = 0.04, $CHCl_3$); 94% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 10% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 12.0 min, t_R (major) = 10.7 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.779	BB	1.2415	7678.3223	555.4795	51.0628
12.057	BM m	0.2490	7358.6843	454.2633	48.9372



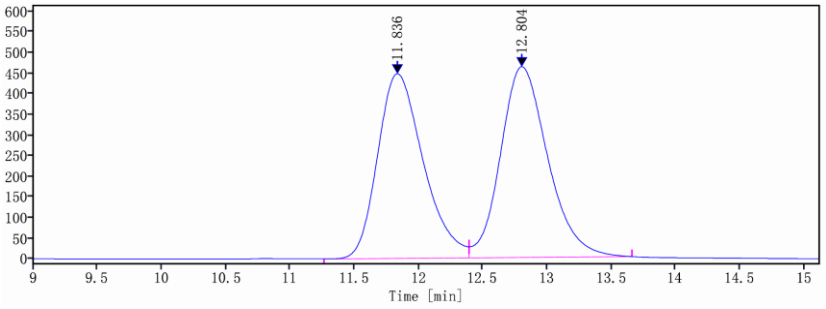
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.711	VM m	0.2113	11792.3610	863.6837	97.1139
12.027	MM m	0.2256	350.4491	24.6843	2.8861



1-(2-((*R*)-1-(4-Phenyl-1H-1,2,3-triazol-1-yl)butyl)naphthalen-1-yl) (*S*)-isoquinoline (**9**).

To a mixture of **8** (33 mg, 0.1 mmol) and phenylacetylene (15 mg, 16 µL, 0.15 mmol) in *t*-BuOH 1.0 mL) and water (240 µL), a solution of $CuSO_4{\cdot}5H_2O$ (0.1 M in water, 100 µL, 0.01 mmol) and (L)-sodium ascorbate (0.1 M in water, 200 µL, 0.02 mmol) were then sequentially added. The

resulting mixture was stirred at 35 °C for 5 h. The reaction mixture was allowed to reach room temperature, washed with a saturated aqueous solution of NH_3, and extracted with DCM (3× 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated to dryness, and the crude product was purified by column chromatography (10% - 30% CH_2Cl_2 in EtOAc) affording **9** (40.9 mg, 90%) as a white solid. ***Rf*** 0.2 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.8 Hz, 1H), 8.33 (s, 1H), 8.15 – 7.99 (m, 3H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.77 (m, 3H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.43 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 5.24 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.86 – 2.64 (m, 1H), 2.19 – 1.89 (m, 1H), 1.04 (t, *J* = 16.1 Hz, 2H), 0.47 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.72, 147.51, 137.09, 136.95, 132.88, 132.42, 132.19, 130.95, 130.82, 128.83, 128.66, 128.33, 127.92, 127.84, 127.52, 127.38, 126.75, 126.03, 125.76, 123.64, 122.26, 121.68, 61.65, 36.24, 19.48, 13.19; **HRMS** (ESI) calcd. for $C_{31}H_{26}N_4$ $[M+H]^+$ *m/z* 455.2230, found 455.2230; **IR** (neat, cm^{-1}) 3426,3056, 2958, 2870, 1993, 1629, 1556, 1457, 828, 764, 695; **m.p.** 205.1 – 206.8 °C; **$[\alpha]_D^{20}$** = – 81.3 (*c* = 0.04, $CHCl_3$); 91% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 20% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 11.9 min, t_R (major) = 12.8 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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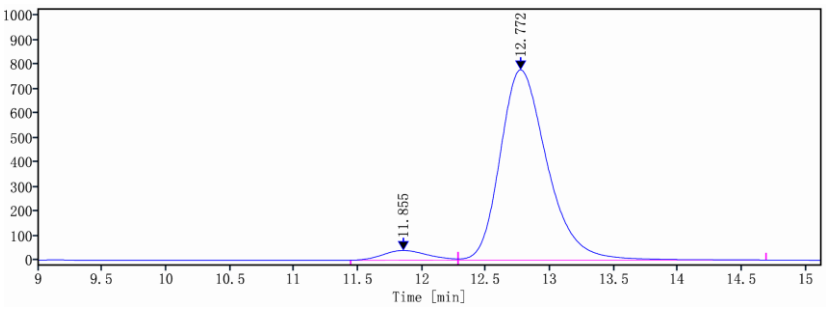
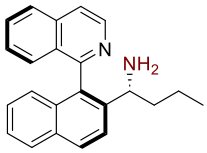
12.804	MM m	0.3899	11800.0891	462.0543	51.6369

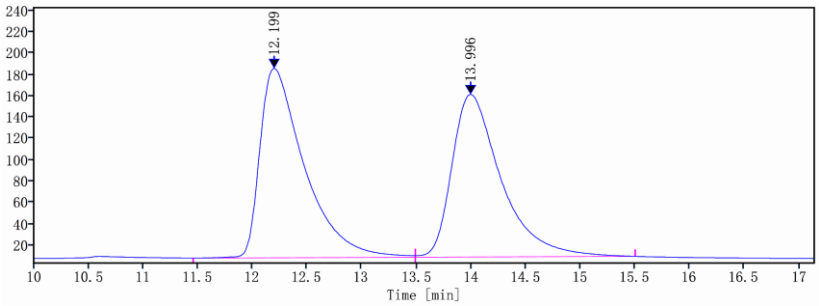


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.855	MM	m	0.3742	958.2333	39.6083	4.6072
12.772	MM	m	0.3916	19840.5783	777.7736	95.3928

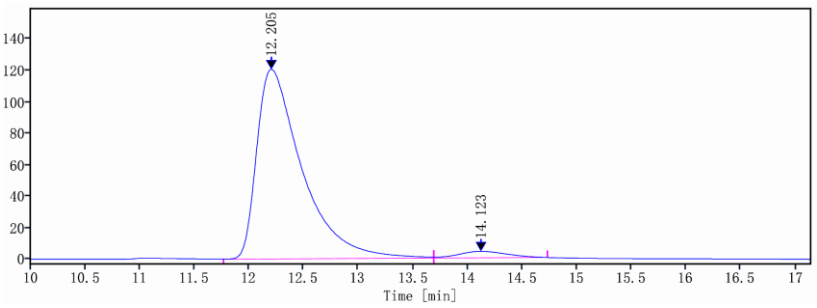


(*R*)-1-(1-((*S*)-Isoquinolin-1-yl)naphthalen-2-yl)butan-1-amine (**10**).

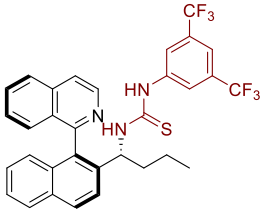
PPh_3 (78.6 mg, 0.3 mmol) was added portionwise to a stirred solution of **8** (32.7 mg, 0.15 mmol) in THF (300 µL). After 5 min, H_2O (18 µL, 1 mmol) was added and the resultant mixture was heated at 50 °C for 48 h. The reaction mixture was then allowed to cool to rt and concentrated in vacuo. Purification by flash chromatography (20–50% EtOAc in PE) afforded **10** (29.3 mg, 90%) as a light yellow solid. ***Rf*** 0.2 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.7 Hz, 1H), 8.04 – 7.87 (m, 3H), 7.80 (d, *J* = 5.8 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.50 – 7.34 (m, 3H), 7.31 – 7.18 (m, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.50 (t, *J* = 7.3 Hz, 1H), 2.94 (s, 2H), 1.87 – 1.59 (m, 2H), 1.09 – 0.84 (m, 2H), 0.55 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.85, 142.57, 141.25, 136.13, 134.83, 132.57, 132.53, 130.53, 129.53, 128.86, 128.02, 127.65, 127.37, 126.98, 126.41, 126.22, 125.65, 123.36, 120.52, 52.19, 38.51, 19.71, 13.73; **HRMS** (ESI) calcd. for $C_{23}H_{22}N_2$ $[M+H]^+$ *m/z* 327.1856, found 327.1857; **IR** (neat, cm^{-1}) 3442, 2924, 1619, 1497, 828, 749, 698; **m.p.** 200.1 – 201.8 °C; **$[\alpha]_D^{20}$** = –81.3 (*c* = 0.04, $CHCl_3$); 93% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 14.1 min, t_R (major) = 12.2 min.



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.199	BM	m	0.4171	5012.6078	177.6899	51.2412
13.996	MM	m	0.4689	4769.7690	152.4836	48.7588



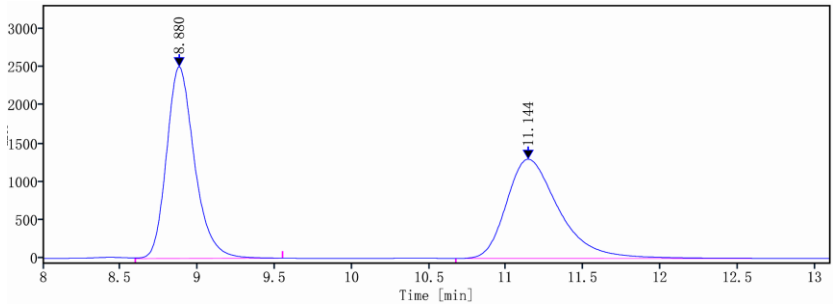
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.205	VM m	0.4257	3467.6595	120.5210	96.4553
14.123	MM m	0.4695	127.4351	4.1593	3.5447



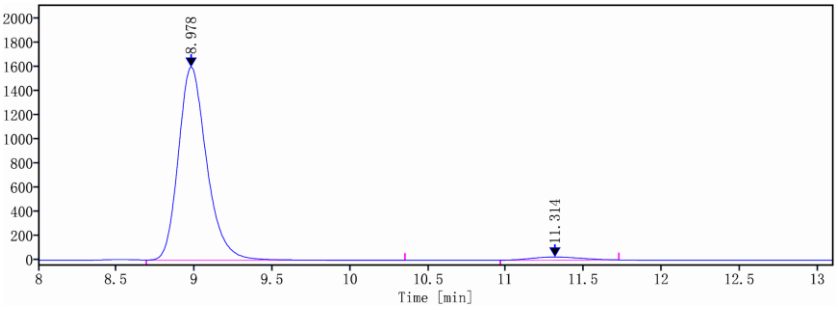
1-(3,5-Bis(trifluoromethyl)phenyl)-3-((*R*)-1-(1-((*S*)-isoquinolin-1-yl)naphthalen-2-yl)butyl)thi-ourea (**11**).

Substituted amine **10** (30 mg, 0.1 mmol) was added to a solution of 3,5-bis(trifluoro-methyl)phenyl isothiocyanate (18 µL, 27 mg, 0.1 mmol) in CH_2Cl_2 (200 µL). The result-ing mixture was stirred for 3 h at rt. The solvent was removed under reduced pressure and the product was purified by flash column chromatography (5–20% EtOAc in PE) to afford **11** (38.8 mg, 65%) as a light yellow solid. ***Rf*** 0.2 (50% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.47 (d, *J* = 5.8 Hz, 1H), 8.23 (d, *J* = 1.7 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 5.8 Hz, 1H), 7.84 – 7.70 (m, 3H), 7.64 (s, 1H), 7.57 – 7.49 (m, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.25 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 1H), 1.95 – 1.81 (m, 1H), 1.73 – 1.59 (m, 1H), 1.02 – 0.79 (m, 3H), 0.32 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.74, 158.87, 141.57, 141.02, 137.33, 136.63, 133.37, 132.74, 131.73, 131.40, 131.37, 131.07, 130.96, 130.73, 129.09, 128.37, 128.16, 127.83, 127.31, 127.08, 126.52, 126.29, 125.20, 124.60, 123.99, 121.91, 121.89, 119.18, 118.40, 54.32, 39.21, 18.95, 12.95; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.89. **^{1}HRMS** (ESI) calcd. for $C_{32}H_{25}F_6N_3S$ $[M+H]^+$ *m/z* 598.1746, found 598.1748; **IR** (neat, cm^{-1}) 3468, 1654, 1557, 1499, 1277, 824, 746; **m.p.** 221.2 – 223.8 °C; **$[\alpha]_D^{20}$** = –81.3 (*c* = 0.04, $CHCl_3$);

95% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 11.3 min, t_R (major) = 9.0 min.



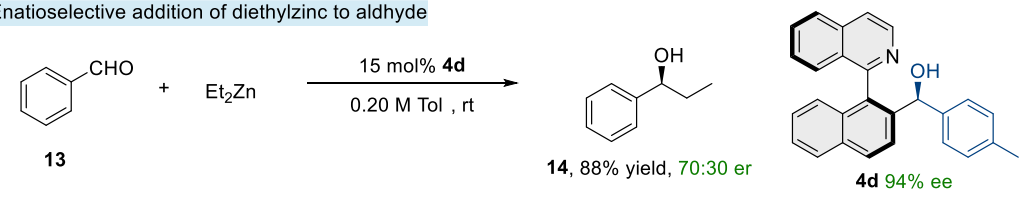
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.880	VM m	0.1908	31413.4667	2496.1886	50.5022
11.144	VB	3.5547	30788.7047	1293.5127	49.4978



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.978	VV	1.6624	20228.2771	1596.1384	97.3396
11.314	MM m	0.3444	552.8565	25.5585	2.6604

b) Catalytic relevance

I:Enatioselective addition of diethylzinc to aldhyde



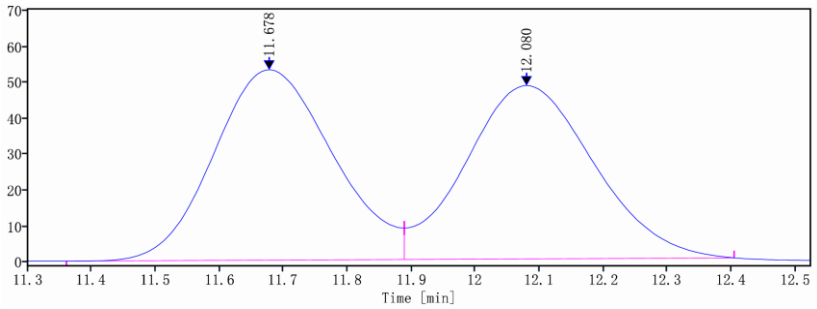
13

14, 88% yield, 70:30 er

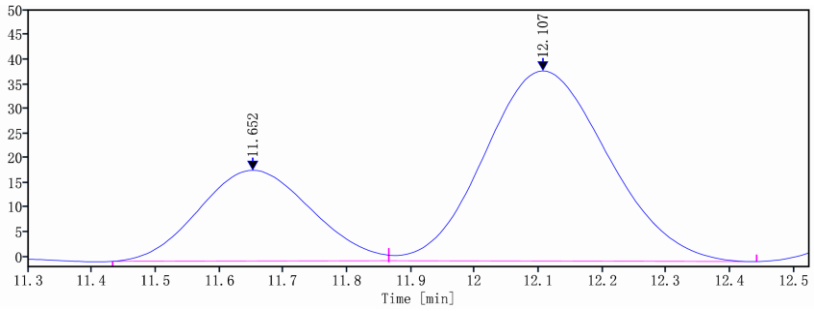
4d 94% ee

In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added **4d** (3.8 mg, 10.0 mol%), Et_2Zn (200 ul, 2.0 equiv, 2 M in THF), anhydrous toluene (0.5 mL) were added, and the mixture was stirred for 30 min at room temperature, at which time benzaldehyde (10.6 mg, 0.1 mmol, 1.0 equiv) was added to the resulting mixture. The reaction was

stirred at rt for up to 12 h (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended). After the reaction was complete, the crude material was purified by flash column chromatography (5–20% EtOAc in PE) to provide the **14** as a colorless oil in 88% yield (12.0 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 87.1 – 7.3 ppm, (m, 5H), 4.47 – 4.52 ppm, (t, 1H, J = 6.6 Hz), 1.92 ppm, (s, 1H), 1.6 – 1.8 ppm, (m, 2H), 0.80 – 0.86 ppm, (t, J = 7.42 Hz). The ^{1}H NMR matched the literature reported data[3]; **$[\alpha]_D^{20}$** = 31.5 (c = 0.04, $CHCl_3$); 40% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 10% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 11.7 min, t_R (major) = 12.1 min.

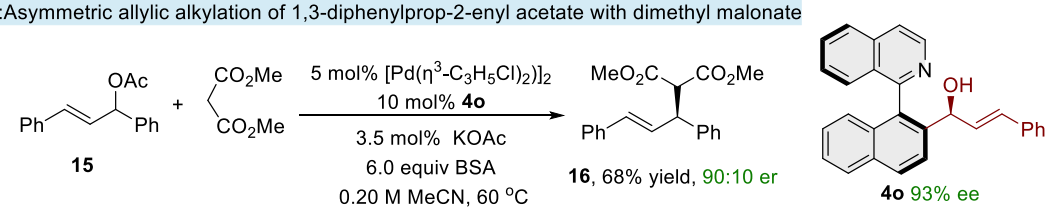


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.678	BM m	0.2006	686.2042	53.1443	50.4322
12.080	MM m	0.2146	674.4416	48.3829	49.5678



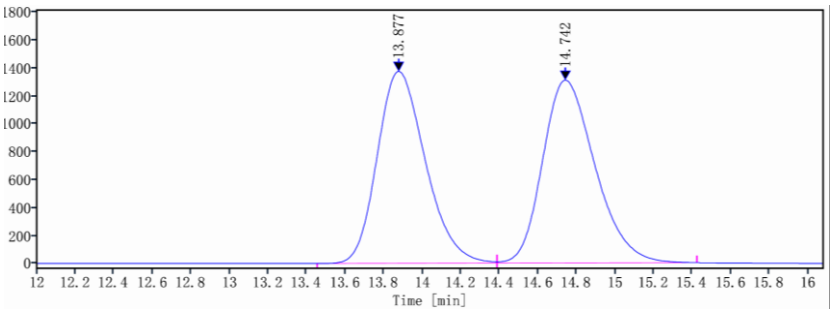
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.652	MM m	0.1925	224.7729	18.4005	30.2486
12.107	MM m	0.2108	518.3121	38.5757	69.7514

II:Asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate

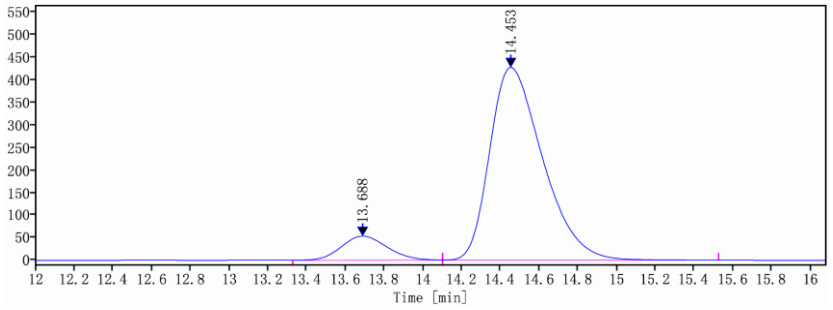


In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir

bar was added **1** (25.2 mg, 0.10 mmol, 1.0 equiv), $[Pd(\eta^3\text{-}C_3H_5Cl)_2)]_2$ (1.8 mg, 5.0 mol%), **4o** (3.9 mg, 10.0 mol%), KOAc (3.4 mg, 3.5 mol%), MeCN (0.5 mL) were added, and the mixture was stirred for 10 min at room temperature, at which time dimethyl malonate (25.2 mg, 0.12 mmol, 1.0 equiv) and BSA (146 ul, 0.60 mmol, 6.0 equiv) were added to the resulting mixturein this order. The reaction was stirred at 60 °C for up to 12 h (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended). After the reaction was complete, the crude material was purified by flash column chromatography (2–10% EtOAc in PE) to provide the **16** as a colorless oil in 65% yield (21.1 mg). ***Rf*** 0.2 (10% EtOAc in PE), UV; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.17 (m, 10H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.38 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.32 (dd, *J* = 10.9, 8.6 Hz, 1H), 4.01 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 3H), 3.56 (s, 3H). The ^{1}H NMR matched the literature reported data[4]; **IR** (neat, cm^{-1}) 3429, 3026, 1736, 1599, 1493, 1369, 1232, 745, 696; **$[\alpha]_D^{20}$** = 21.3 (*c* = 0.04, $CHCl_3$); 80% *ee*; **HPLC analysis** CHIRALCEL OD-H column, 1% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector, t_R (minor) = 13.7 min, t_R (major) = 14.5 min.



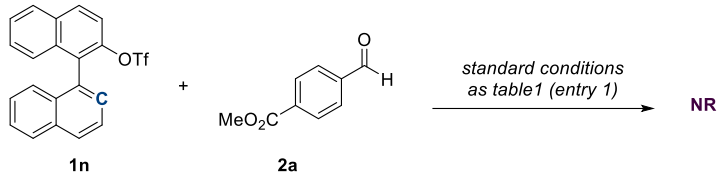
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.877	BM m	0.2684	23815.5878	1372.7067	49.0956
14.742	MM m	0.2923	24693.0386	1307.4630	50.9044



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.688	MM m	0.2459	7566.4741	485.3036	10.2438
14.455	MM m	0.3545	66297.2545	2968.9097	89.7562

7. Mechanistic Studies

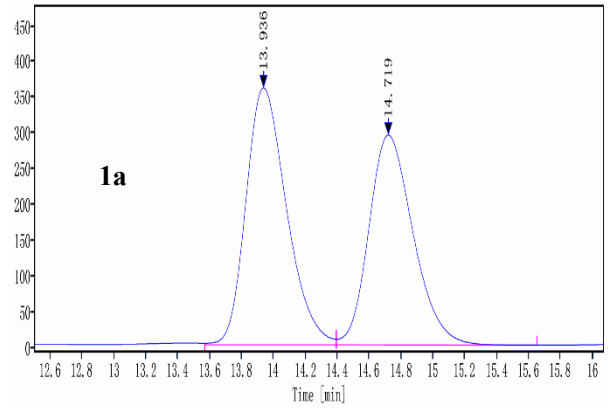
a) Key role of N atom



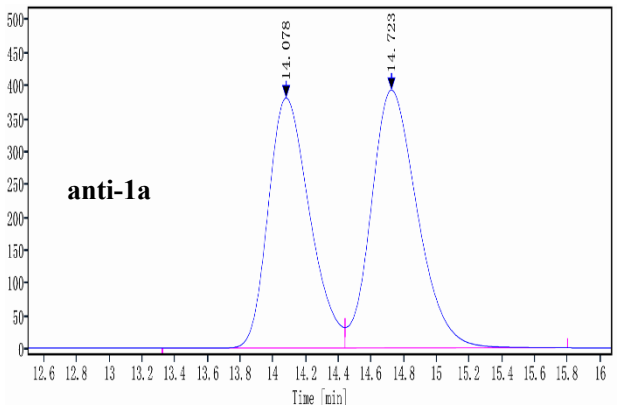
In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added **[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate** (40.2 mg, 0.10 mmol, 1.0 equiv), NiI_2 (3.1 mg, 10.0 mol%), **L1*** (2.4 mg, 12.0 mol%), Zn (13.0 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), anhydrous DMSO/THF (1:1, 0.50 mL) were added, and the mixture was stirred for 10 min at room temperature, at which time methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) was added to the resulting mixture .The reaction was stirred at rt for up to 12 h (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended).

a) Partial conversion experiment of 1a

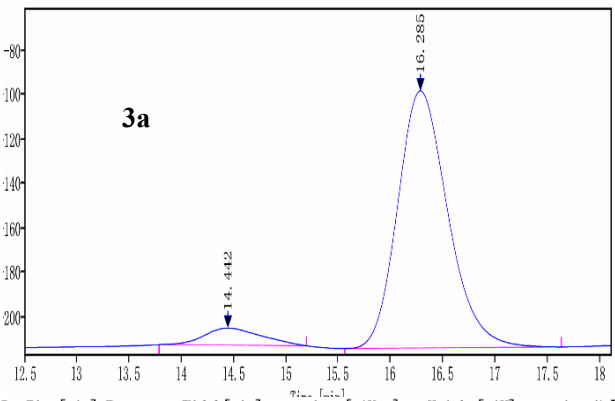
In a nitrogen atmosphere, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added **1-(isoquinolin-1-yl)naphthalen-2-yl trifluoromethane-sulfonate** (40.0 mg, 0.10 mmol, 1.0 equiv), NiI_2 (3.1 mg, 10.0 mol%), **L1(s)*** (or **L1(r)*,** 2.4 mg, 12.0 mol%), Zn (13.0 mg, 2.0 equiv), KI (16.7 mg, 1.0 equiv), anhydrous DMSO/THF (1:1, 0.50 mL) were added, and the mixture was stirred for 10 min at room temperature, at which time methyl 4-formylbenzoate (19.6 mg, 0.12 mmol) was added to the resulting mixture. The reaction was stirred at rt for up to **2 h** (the mixture was stirred at 480 rpm, ensuring that the base was uniformly suspended). After the reaction was complete, the reaction mixture was directly filtered through a short pad of silica gel (5–20% EtOAc in PE) to give **1a** in 78% yield (6% ee), **3a** in 15% yield (86% ee) **anti-1a** in 78% yield (-6% ee) and **anti-3a** in 15% yield (-88% ee). **HPLC analysis** CHIRALCEL OD-H column, 30% ^{i}PrOH in hexane, 0.5 mL/min, 254 nm UV detector.



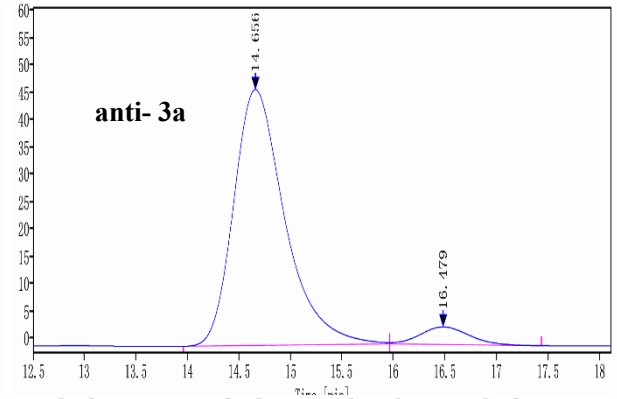
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.078	BM m	0.2709	6666.9630	379.6491	46.5371
14.723	MM m	0.3023	7659.1543	391.4343	53.4629



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.936	VV	0.8265	6362.0232	359.0087	52.8847
14.719	VB	1.2575	5667.9640	293.3532	47.1153



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.442	MM m	0.5674	293.6590	7.7260	7.0758
16.285	BB	2.0722	3856.5303	115.5298	92.9242



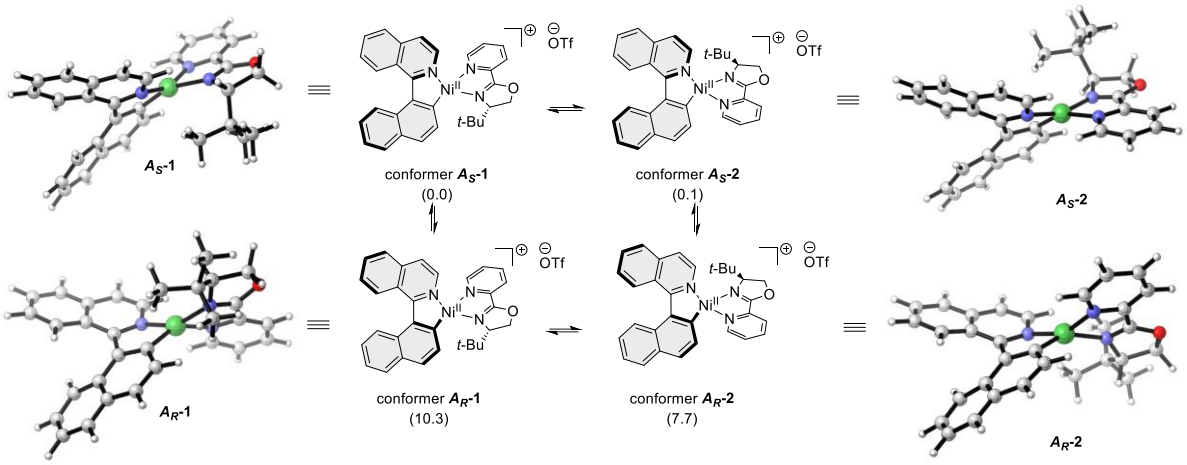
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.656	BM m	0.5229	1615.7109	46.7851	93.8814
16.479	MM m	0.5110	105.3024	3.2078	6.1186

c) Stereocontrol step supported by DFT calculations

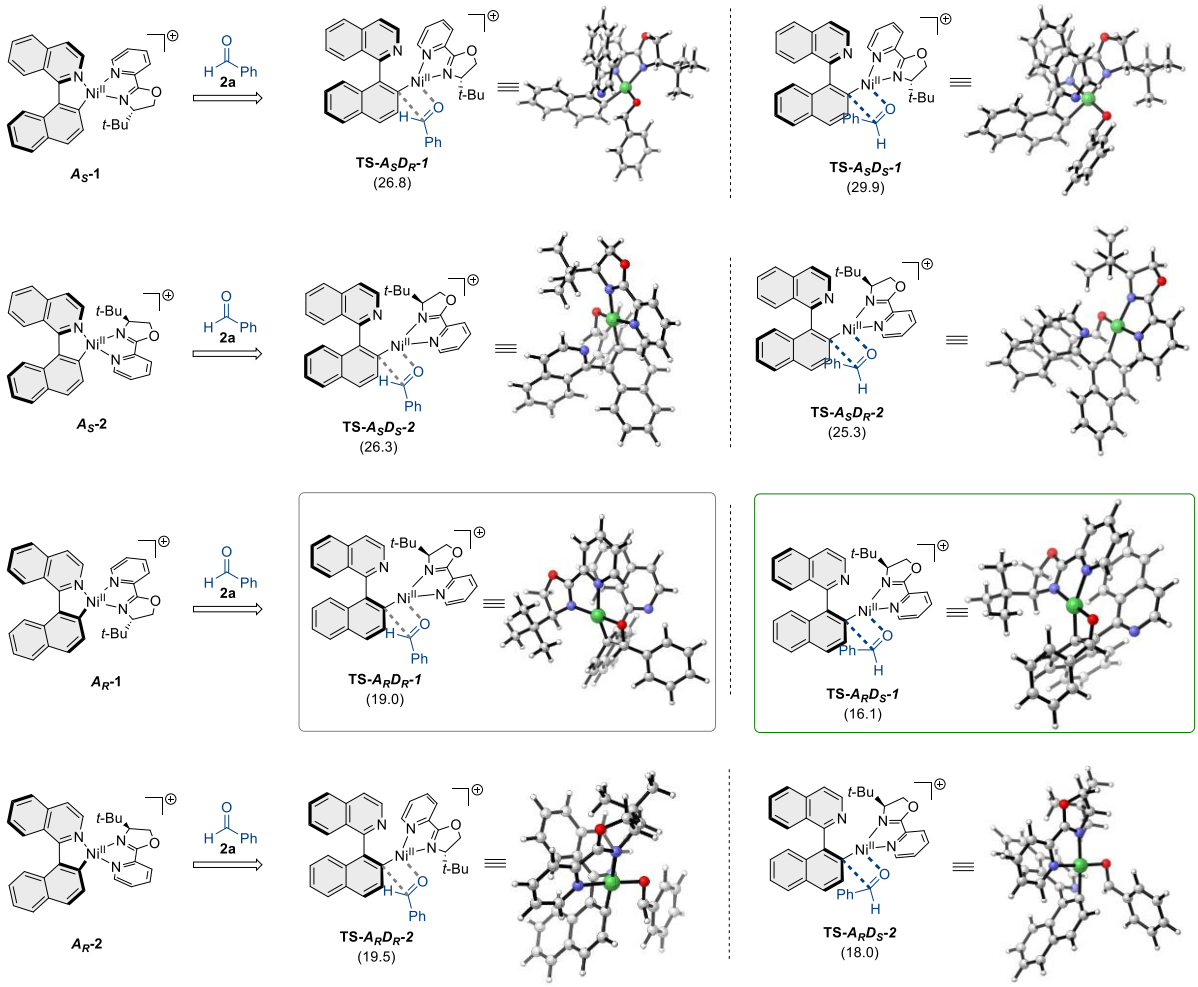
All calculations were performed using the density functional theory[5] (DFT) as implemented in the Gaussian 09[6] suite of programs. Geometry optimizations were performed using the uB3LYP[7] with Grimme's D3[8] correction, and a mixed basis set of SDD[11] for Ni and 6-31G**[9] for all other atoms. Vibrational frequency calculations were carried out at the same level of theory as that used for geometry optimizations, wherein thermochemistry correction energy (G – E) was acquired. Transition states were realized by the presence of single imaginary frequency and confirmed by intrinsic reaction coordinate calculations (IRC). Single point energies of optimized structures were calculated with the M06 functional[10] and a mixed basis set of SDD for Ni and 6-311+G** for other atoms. Solvation effects were incorporated using the SMD model[11] dimethyl sulfoxide (DMSO) solvent based on gas-phase optimized geometries, and carried out at the same level as single-point calculations[12]. Graphical structures were created using CYLview[13]. Final solution phase Gibbs free energies were calculated as follows:

$$G_{sol} = E_{sol} + (G - E) \quad (1)$$

$$\Delta G(sol) = \Sigma G(sol) \text{ for products} - \Sigma G(sol) \text{ for reactants} \quad (2)$$



In terms of the ground state of nickelacycle, it is revealed that the conformers with (*S*)-axial chirality with lower energy compared with the (*R*)-conformers, where the steric repulsion arising from between *t*-Bu group on oxazoline site and substrate **1a.** However, when the aldehyde approaching to the nickelacycle, the lower ground state geometries, those of (*S*)-axial chirality conformers, were provided much higher energy barriers of transition state in aldol addition.



Among the various potential transition state geometries, TS-A_RD_S-*1* and TS-A_RD_R-*1* were identified as the two lowest-energy conformers, leading to respective diastereomers. Formation of **3a** through TS-A_RD_S-*1* is energetically more favourable, as this geometry reduces steric interactions between the phenyl group of the aldehyde **2a** and the isoquinoline moiety of **1a** present in TS-A_RD_R-*1*.

Table S8. Summarized energy components of DFT-optimized structures

DFT-optimized Structures	**E(sol)** (SCF/TZ) [eV] M06/6-311+G**, SDD(Ni)/ SMD(DMSO)	**G–E** (Thermochemistry correction energy) [eV] uB3LYP/6-31G**, SDD(Ni)	**G(sol)** [eV]
2a	-9399.453	2.165	-9397.29
A_S-1	-43751.575	12.620	-43738.96

A_S-2	-43751.578	12.619	-43738.96
A_R-1	-43751.099	12.590	-43738.51
A_R-2	-43751.232	12.612	-43738.62
TS-A_SD_R-1	-53150.444	15.365	-53135.08
TS-A_SD_S-1	-53150.335	15.389	-53134.95
TS-A_SD_R-2	-53150.481	15.377	-53135.10
TS-A_SD_S-2	-53150.583	15.435	-53135.15
TS-A_RD_R-1	-53150.395	15.422	-53134.97
TS-A_RD_S-1	-53150.510	15.409	-53135.10
TS-A_RD_R-2	-53150.476	15.412	-53135.06
TS-A_RD_S-2	-53150.526	15.400	-53135.13

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2a

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C	-2.973285000000	-0.014001000000	0.000025000000
C	-1.579250000000	0.000518000000	0.000580000000
C	-0.889503000000	1.219665000000	0.000114000000
C	-1.602231000000	2.428525000000	-0.000913000000
C	-2.992573000000	2.412875000000	-0.001467000000
C	-3.678035000000	1.191947000000	-0.000998000000
H	-3.509223000000	-0.958210000000	0.000385000000
H	-1.020236000000	-0.932445000000	0.001376000000
H	-1.041564000000	3.357823000000	-0.001253000000
H	-3.547786000000	3.346059000000	-0.002262000000
H	-4.764189000000	1.182431000000	-0.001432000000
C	0.591037000000	1.231804000000	0.000707000000
H	1.062897000000	0.223060000000	0.001526000000
O	1.273243000000	2.239020000000	0.000349000000

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A_S-1

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C	-0.686546000000	0.031135000000	-0.100886000000
C	0.343852000000	-0.086467000000	0.801367000000
C	0.261965000000	0.515265000000	2.087134000000
C	-0.880830000000	1.320374000000	2.423770000000
C	-1.953881000000	1.361082000000	1.488450000000
C	-1.857414000000	0.737280000000	0.264018000000
H	2.098901000000	-0.365565000000	2.804551000000
H	-0.620332000000	-0.440737000000	-1.076029000000
H	1.228141000000	-0.668309000000	0.556207000000
C	1.253076000000	0.264803000000	3.068077000000
C	-0.904554000000	1.936211000000	3.722086000000
H	-2.874092000000	1.867542000000	1.750658000000
H	-2.695946000000	0.778033000000	-0.424679000000
C	0.037695000000	1.583781000000	4.699937000000
C	1.118199000000	0.741155000000	4.356956000000
H	1.839660000000	0.436945000000	5.108261000000
C	-1.936392000000	2.839868000000	4.256627000000
C	-2.673411000000	3.859410000000	3.572838000000
C	-2.360848000000	4.293550000000	2.254403000000
C	-3.710169000000	4.544853000000	4.289627000000
C	-3.015945000000	3.397629000000	6.283700000000
C	-3.100406000000	5.284888000000	1.650220000000
H	-1.522047000000	3.852033000000	1.732743000000
C	-4.479958000000	5.533868000000	3.625510000000
C	-3.882241000000	4.260500000000	5.668206000000
H	-3.039522000000	3.219027000000	7.349978000000
C	-4.187117000000	5.888865000000	2.328121000000
H	-2.844021000000	5.612921000000	0.648030000000
H	-5.281515000000	6.026382000000	4.167859000000
H	-4.651689000000	4.766576000000	6.241262000000
H	-4.771225000000	6.656019000000	1.829341000000
N	-2.070228000000	2.700945000000	5.594599000000
C	-1.855694000000	-1.363739000000	8.545133000000
C	-2.957563000000	-0.290196000000	8.495608000000
C	-3.396799000000	-0.079059000000	7.034733000000
C	-4.183367000000	-0.742090000000	9.315467000000
C	-2.448517000000	1.059119000000	9.093051000000
C	-1.949432000000	0.983914000000	10.562979000000
O	-0.487963000000	1.048691000000	10.453310000000
N	-1.241905000000	1.573851000000	8.394246000000
C	-0.248691000000	1.440770000000	9.205766000000
C	1.121556000000	1.704799000000	8.760698000000
C	2.212799000000	1.776046000000	9.616407000000
C	3.455117000000	2.118162000000	9.076377000000
C	3.542384000000	2.391051000000	7.713551000000
N	1.208911000000	1.922587000000	7.421740000000
Ni	-0.529972000000	1.949034000000	6.465882000000
H	-2.236433000000	-2.307221000000	8.143806000000
H	-1.508236000000	-1.561107000000	9.564826000000
H	-0.992915000000	-1.072743000000	7.936614000000
H	-3.845023000000	-0.998240000000	6.645853000000
H	-2.554607000000	0.178919000000	6.388573000000
H	-4.142677000000	0.718634000000	6.950338000000
H	-4.600500000000	-1.656388000000	8.883749000000
H	-4.971879000000	0.018867000000	9.305839000000
H	-3.938012000000	-0.964216000000	10.358889000000
H	-3.255067000000	1.793157000000	9.005028000000
H	-2.191581000000	0.056832000000	11.079128000000
H	-2.266160000000	1.837364000000	11.167866000000
H	2.076043000000	1.580591000000	10.673670000000
H	4.331265000000	2.184226000000	9.712792000000
H	4.481498000000	2.682003000000	7.256552000000
C	2.398596000000	2.285965000000	6.918684000000
H	2.421151000000	2.487026000000	5.855607000000

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A_S-2

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C	-1.404698000000	-0.083991000000	0.212015000000
C	-0.480067000000	-0.204565000000	1.222692000000
C	-0.626293000000	0.519325000000	2.437359000000
C	-1.715698000000	1.445229000000	2.584264000000
C	-2.684920000000	1.493393000000	1.543076000000
C	-2.531928000000	0.752093000000	0.391676000000
H	1.053389000000	-0.430973000000	3.409133000000
H	-1.291052000000	-0.649548000000	-0.707329000000
H	0.364423000000	-0.880487000000	1.119619000000
C	0.242722000000	0.283082000000	3.532773000000
C	-1.806888000000	2.177901000000	3.817559000000
H	-3.572091000000	2.102425000000	1.666127000000
H	-3.292532000000	0.801157000000	-0.381745000000
C	-1.006583000000	1.829959000000	4.913838000000
C	0.027086000000	0.883418000000	4.756549000000
H	0.642307000000	0.600908000000	5.603205000000
C	-2.757954000000	3.247434000000	4.154749000000
C	-3.266406000000	4.282549000000	3.304058000000
C	-2.781712000000	4.517086000000	1.986927000000
C	-4.237599000000	5.191097000000	3.842533000000
C	-3.892212000000	4.193060000000	6.000213000000
C	-3.306625000000	5.530207000000	1.216762000000
H	-1.981029000000	3.904120000000	1.595811000000
C	-4.787601000000	6.199989000000	3.011197000000
C	-4.555381000000	5.102446000000	5.221384000000
H	-4.017105000000	4.166053000000	7.074973000000
C	-4.338955000000	6.358519000000	1.719526000000
H	-2.920227000000	5.701263000000	0.217168000000
H	-5.543584000000	6.862940000000	3.421334000000
H	-5.266986000000	5.789615000000	5.666317000000
H	-4.754374000000	7.140370000000	1.091344000000

N	-3.030138000000	3.273620000000	5.480496000000
C	1.042485000000	4.836687000000	8.444775000000
C	1.634237000000	3.932316000000	7.349098000000
C	1.074881000000	4.357108000000	5.978065000000
C	3.170245000000	4.073722000000	7.311223000000
C	1.302516000000	2.430433000000	7.620289000000
C	1.785858000000	1.887860000000	8.990844000000
O	0.568235000000	1.837997000000	9.811560000000
N	-0.159299000000	2.166716000000	7.708311000000
C	-0.436840000000	1.945766000000	8.952465000000
C	-1.826699000000	1.838571000000	9.401337000000
C	-2.205715000000	1.419090000000	10.670719000000
C	-3.571578000000	1.299001000000	10.940628000000
C	-4.486229000000	1.584857000000	9.929233000000
N	-2.709872000000	2.156995000000	8.423845000000
Ni	-1.700791000000	2.408153000000	6.563791000000
H	1.300336000000	5.880813000000	8.245725000000
H	1.422934000000	4.592354000000	9.442168000000
H	-0.050510000000	4.767611000000	8.466998000000
H	1.414900000000	5.369360000000	5.738613000000
H	-0.018014000000	4.359298000000	5.967187000000
H	1.409079000000	3.686106000000	5.180777000000
H	3.440311000000	5.105746000000	7.069829000000
H	3.609950000000	3.427436000000	6.543507000000
H	3.643566000000	3.835303000000	8.269042000000
H	1.721530000000	1.840190000000	6.803618000000
H	2.495948000000	2.527076000000	9.511338000000
H	2.176158000000	0.868387000000	8.934186000000
H	-1.448151000000	1.184783000000	11.409738000000
H	-3.911206000000	0.974786000000	11.918702000000
H	-5.553661000000	1.486579000000	10.092363000000
C	-4.013950000000	2.007144000000	8.682930000000
H	-4.693822000000	2.231123000000	7.868306000000

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A_R-1

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C	-2.160582000000	-1.838629000000	1.401933000000
C	-1.728410000000	-1.975018000000	2.700279000000
C	-1.971364000000	-0.957410000000	3.662359000000
C	-2.740759000000	0.199090000000	3.293560000000
C	-3.112392000000	0.333573000000	1.926106000000
C	-2.832644000000	-0.657111000000	1.009996000000
H	-0.808889000000	-1.907169000000	5.217144000000
H	-1.961658000000	-2.616405000000	0.671553000000
H	-1.167586000000	-2.854243000000	3.005347000000
C	-1.401715000000	-1.033050000000	4.958722000000
C	-2.985548000000	1.188033000000	4.308000000000
H	-3.600691000000	1.239619000000	1.589699000000
H	-3.121632000000	-0.523100000000	-0.028110000000
C	-2.329255000000	1.124969000000	5.544890000000
C	-1.537194000000	0.001771000000	5.860512000000
H	-1.034367000000	-0.052476000000	6.816401000000
C	-3.766221000000	2.424498000000	4.174206000000
C	-4.991485000000	2.640834000000	3.466161000000
C	-5.751800000000	1.584817000000	2.891320000000
C	-5.527727000000	3.970855000000	3.424266000000
C	-3.809312000000	4.656570000000	4.959384000000
C	-6.928762000000	1.850953000000	2.228664000000
H	-5.408014000000	0.563965000000	2.993486000000
C	-6.722347000000	4.217919000000	2.701159000000
C	-4.882083000000	4.986201000000	4.175703000000
H	-3.341443000000	5.371208000000	5.625424000000
C	-7.403100000000	3.179464000000	2.106309000000
H	-7.503121000000	1.034751000000	1.802501000000
H	-7.105303000000	5.232832000000	2.651289000000
H	-5.269489000000	5.999347000000	4.176016000000
H	-8.323855000000	3.372744000000	1.564718000000
N	-3.256855000000	3.409554000000	4.948292000000
C	-1.383265000000	-0.318681000000	9.533172000000
C	-2.732244000000	0.413091000000	9.658275000000
C	-3.718842000000	-0.020754000000	8.559231000000
C	-3.366773000000	0.079858000000	11.027997000000
C	-2.547912000000	1.946703000000	9.590658000000
C	-1.738999000000	2.539425000000	10.767990000000
O	-1.019139000000	3.667031000000	10.176807000000
N	-1.831784000000	2.526400000000	8.398048000000
C	-1.117361000000	3.502628000000	8.862133000000
C	-0.505665000000	4.503475000000	7.981783000000
C	0.515796000000	5.366948000000	8.360669000000
C	1.011507000000	6.253380000000	7.401344000000
C	0.470287000000	6.233812000000	6.116093000000
N	-1.055610000000	4.500463000000	6.746941000000
Ni	-2.197728000000	2.795099000000	6.414862000000
H	-1.546885000000	-1.391405000000	9.397783000000
H	-0.766539000000	-0.198952000000	10.429803000000
H	-0.800879000000	0.046364000000	8.684802000000
H	-3.850016000000	-1.106979000000	8.574521000000
H	-3.381099000000	0.266093000000	7.565100000000
H	-4.701573000000	0.435679000000	8.724479000000
H	-3.582294000000	-0.991247000000	11.081517000000
H	-4.312134000000	0.614518000000	11.173276000000
H	-2.704922000000	0.317479000000	11.867854000000
H	-3.550335000000	2.395332000000	9.568420000000
H	-0.989543000000	1.851799000000	11.166862000000
H	-2.353999000000	2.928088000000	11.578183000000
H	0.906772000000	5.331562000000	9.370919000000
H	1.811182000000	6.942045000000	7.653152000000
H	0.834676000000	6.901490000000	5.343338000000
C	-0.562919000000	5.339911000000	5.826732000000
H	-1.018570000000	5.288102000000	4.843685000000

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A_R-2

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C	-2.041809000000	-1.196609000000	0.736493000000
C	-1.796324000000	-1.702025000000	1.991427000000
C	-1.977287000000	-0.899167000000	3.150832000000
C	-2.490868000000	0.436497000000	3.013272000000
C	-2.674683000000	0.943005000000	1.695699000000
C	-2.457514000000	0.148547000000	0.591446000000
H	-1.198875000000	-2.382878000000	4.515350000000
H	-1.889854000000	-1.813566000000	-0.143419000000
H	-1.431753000000	-2.718094000000	2.114992000000
C	-1.592676000000	-1.372972000000	4.430626000000
C	-2.683633000000	1.203669000000	4.211303000000
H	-2.965571000000	1.977210000000	1.556837000000
H	-2.595742000000	0.563194000000	-0.402531000000
C	-2.178313000000	0.748751000000	5.434715000000
C	-1.643913000000	-0.553816000000	5.540966000000

H	-1.253290000000	-0.913142000000	6.487432000000
C	-3.285216000000	2.539669000000	4.339077000000
C	-4.419494000000	3.068628000000	3.642665000000
C	-5.223951000000	2.295708000000	2.758926000000
C	-4.825727000000	4.414636000000	3.929555000000
C	-3.181516000000	4.478406000000	5.680897000000
C	-6.306206000000	2.859534000000	2.122105000000
H	-4.992836000000	1.250967000000	2.601342000000
C	-5.923419000000	4.977947000000	3.229960000000
C	-4.159140000000	5.114993000000	4.965985000000
H	-2.693082000000	4.943468000000	6.524889000000
C	-6.641970000000	4.218604000000	2.334698000000
H	-6.913993000000	2.254513000000	1.457017000000
H	-6.203395000000	6.006872000000	3.435264000000
H	-4.454718000000	6.126108000000	5.224608000000
H	-7.488334000000	4.651200000000	1.810288000000
N	-2.736962000000	3.230500000000	5.362886000000
C	-0.591386000000	6.309031000000	7.733508000000
C	0.509807000000	5.556258000000	6.965535000000
C	0.135244000000	5.359230000000	5.483606000000
C	1.822088000000	6.367582000000	7.028653000000
C	0.769987000000	4.164997000000	7.585842000000
C	1.397334000000	4.180392000000	8.999515000000
O	0.807834000000	3.014538000000	9.659195000000
N	-0.429622000000	3.286585000000	7.782061000000
C	-0.228840000000	2.668675000000	8.896959000000
C	-1.065660000000	1.539760000000	9.309813000000
C	-1.080565000000	1.009331000000	10.593899000000
C	-1.953206000000	-0.047702000000	10.861174000000
C	-2.771997000000	-0.520751000000	9.837220000000
N	-1.835512000000	1.061485000000	8.301223000000
Ni	-1.839442000000	2.125475000000	6.665024000000
H	-0.847418000000	7.237326000000	7.214750000000
H	-0.271436000000	6.582811000000	8.744193000000
H	-1.499856000000	5.709780000000	7.835161000000
H	-0.169809000000	6.308309000000	5.032498000000
H	-0.674564000000	4.641877000000	5.355192000000
H	0.995893000000	4.984278000000	4.919009000000
H	1.693545000000	7.321181000000	6.508021000000
H	2.645973000000	5.834077000000	6.541792000000
H	2.122119000000	6.598293000000	8.056437000000
H	1.429449000000	3.617133000000	6.898721000000
H	1.120262000000	5.059312000000	9.587576000000
H	2.479038000000	4.055391000000	9.008113000000
H	-0.428453000000	1.426896000000	11.352114000000
H	-1.995915000000	-0.487079000000	11.852222000000
H	-3.470088000000	-1.333153000000	10.004946000000
C	-2.686708000000	0.057581000000	8.570064000000
H	-3.290107000000	-0.283912000000	7.738804000000

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C	1.532705000000	6.968710000000	2.112192000000
C	1.961186000000	5.705634000000	1.766431000000
C	1.447934000000	4.559899000000	2.426438000000
C	0.468857000000	4.733402000000	3.463975000000
C	0.043088000000	6.052345000000	3.790541000000
C	0.564800000000	7.142273000000	3.131544000000
H	2.590243000000	3.121769000000	1.273733000000
H	1.933317000000	7.837784000000	1.599564000000
H	2.697224000000	5.570437000000	0.978809000000
C	1.868140000000	3.245163000000	2.076762000000
C	-0.045603000000	3.579082000000	4.126618000000
H	-0.703122000000	6.190777000000	4.565480000000
H	0.230429000000	8.142336000000	3.389108000000
C	0.413556000000	2.300509000000	3.784157000000
C	1.360162000000	2.148875000000	2.730433000000
H	1.663730000000	1.148354000000	2.438176000000
C	-1.091548000000	3.710762000000	5.204090000000
C	-0.747855000000	4.081229000000	6.546150000000
C	0.543596000000	4.530425000000	6.930996000000
C	-1.769435000000	3.968554000000	7.541486000000
C	-3.293193000000	3.331454000000	5.788785000000
C	0.820514000000	4.813010000000	8.250144000000
H	1.307380000000	4.652512000000	6.171666000000
C	-1.449331000000	4.255746000000	8.896564000000
C	-3.066361000000	3.577830000000	7.121858000000
H	-4.282293000000	3.063355000000	5.428399000000
C	-0.179309000000	4.660365000000	9.243527000000
H	1.809543000000	5.158719000000	8.534073000000
H	-2.228244000000	4.170561000000	9.649443000000
H	-3.870955000000	3.492530000000	7.846111000000
H	0.056288000000	4.883688000000	10.279541000000
N	-2.317939000000	3.381456000000	4.843052000000
C	0.705120000000	-2.125596000000	8.670077000000
C	-0.633307000000	-1.634732000000	8.087141000000
C	-0.761213000000	-2.130320000000	6.636187000000
C	-1.809279000000	-2.186531000000	8.916164000000
C	-0.720763000000	-0.078579000000	8.110883000000
C	-0.435891000000	0.575485000000	9.490566000000
O	0.938578000000	1.099389000000	9.369763000000
N	0.323213000000	0.557506000000	7.278062000000
C	1.172130000000	1.123342000000	8.063253000000
C	2.321238000000	1.810008000000	7.477184000000
C	3.394922000000	2.315455000000	8.195306000000
C	4.412929000000	2.960225000000	7.488957000000
C	4.301142000000	3.074760000000	6.104909000000
N	2.203343000000	1.919347000000	6.127610000000
Ni	0.487837000000	1.192285000000	5.454433000000
H	0.749727000000	-3.217596000000	8.624663000000
H	0.841385000000	-1.840486000000	9.718305000000
H	1.554071000000	-1.739871000000	8.095531000000
H	-0.784170000000	-3.224291000000	6.617837000000
H	0.086694000000	-1.794652000000	6.034446000000
H	-1.668232000000	-1.752782000000	6.157818000000
H	-1.796393000000	-3.280265000000	8.900508000000
H	-2.770873000000	-1.858577000000	8.506430000000
H	-1.764013000000	-1.878652000000	9.966554000000
H	-1.694409000000	0.227596000000	7.719329000000
H	-0.448048000000	-0.110201000000	10.335187000000
H	-1.075328000000	1.438760000000	9.691050000000
H	3.415994000000	2.206381000000	9.273449000000
H	5.272349000000	3.367174000000	8.011468000000
H	5.065674000000	3.571358000000	5.518103000000
C	3.180667000000	2.546171000000	5.459396000000
H	3.044828000000	2.632761000000	4.388953000000
C	0.291289000000	-2.007141000000	1.706547000000
C	-0.033259000000	-1.184210000000	2.782187000000

C	-0.728073000000	0.013685000000	2.562693000000
C	-1.095753000000	0.379772000000	1.259818000000
C	-0.771490000000	-0.445242000000	0.185298000000
C	-0.075482000000	-1.637417000000	0.407784000000
H	0.823532000000	-2.938193000000	1.876046000000
H	0.231534000000	-1.458906000000	3.797595000000
H	-1.629843000000	1.312103000000	1.094975000000
H	-1.060585000000	-0.163389000000	-0.822303000000
H	0.177361000000	-2.280603000000	-0.429691000000
C	-1.085552000000	0.904173000000	3.689076000000
H	-1.828000000000	1.677284000000	3.472247000000
O	-1.073442000000	0.445818000000	4.919965000000

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C	1.033067000000	7.114029000000	2.211625000000
C	1.484227000000	5.874262000000	1.815898000000
C	1.089046000000	4.703652000000	2.512433000000
C	0.216254000000	4.824541000000	3.648230000000
C	-0.232406000000	6.123814000000	4.026445000000
C	0.163040000000	7.237776000000	3.322958000000
H	2.207567000000	3.328614000000	1.263794000000
H	1.338557000000	8.002689000000	1.668062000000
H	2.143608000000	5.775833000000	0.958223000000
C	1.534540000000	3.413481000000	2.112827000000
C	-0.185109000000	3.648423000000	4.348210000000
H	-0.905610000000	6.225746000000	4.870273000000
H	-0.196726000000	8.219028000000	3.615876000000
C	0.202284000000	2.376587000000	3.882532000000
C	1.088511000000	2.291362000000	2.765191000000
H	1.393168000000	1.308423000000	2.414757000000
C	-0.952542000000	3.753892000000	5.641658000000
C	-0.328488000000	4.266957000000	6.834497000000
C	0.961934000000	4.861384000000	6.868757000000
C	-1.057227000000	4.135648000000	8.060127000000
C	-2.875914000000	3.196462000000	6.791817000000
C	1.506933000000	5.287700000000	8.059325000000
H	1.516754000000	4.982173000000	5.947054000000
C	-0.461349000000	4.571696000000	9.274440000000
C	-2.360854000000	3.576493000000	8.008225000000
H	-3.884242000000	2.799255000000	6.704976000000
C	0.794253000000	5.135145000000	9.274246000000
H	2.491340000000	5.745260000000	8.069190000000
H	-1.020925000000	4.467697000000	10.199866000000
H	-2.947675000000	3.479472000000	8.917360000000
H	1.238607000000	5.475079000000	10.204689000000
N	-2.178446000000	3.271681000000	5.631352000000
C	0.506385000000	-2.198525000000	8.539231000000
C	-0.855023000000	-1.679949000000	8.040595000000
C	-1.059355000000	-2.111292000000	6.577727000000
C	-1.994390000000	-2.264076000000	8.899099000000
C	-0.930121000000	-0.126601000000	8.137252000000
C	-0.639429000000	0.461538000000	9.546640000000
O	0.720515000000	1.022765000000	9.441505000000
N	0.115132000000	0.542451000000	7.331853000000
C	0.957603000000	1.089274000000	8.138014000000
C	2.115961000000	1.784968000000	7.578491000000
C	3.195900000000	2.255637000000	8.309545000000
C	4.236829000000	2.877797000000	7.615511000000
C	4.139382000000	3.012134000000	6.232550000000
N	2.010499000000	1.920628000000	6.230746000000
Ni	0.321632000000	1.206345000000	5.526922000000
H	0.537272000000	-3.289308000000	8.464775000000
H	0.700026000000	-1.940491000000	9.585881000000
H	1.327308000000	-1.805477000000	7.930280000000
H	-1.066661000000	-3.203731000000	6.512122000000
H	-0.263789000000	-1.731270000000	5.933230000000
H	-2.004440000000	-1.734200000000	6.177735000000
H	-2.000099000000	-3.354762000000	8.816156000000
H	-2.971332000000	-1.900254000000	8.562042000000
H	-1.889473000000	-2.023292000000	9.962542000000
H	-1.903184000000	0.205589000000	7.765859000000
H	-0.625207000000	-0.268139000000	10.353554000000
H	-1.299183000000	1.294463000000	9.801090000000
H	3.208669000000	2.132753000000	9.386155000000
H	5.104436000000	3.252707000000	8.148277000000
H	4.924114000000	3.490747000000	5.657555000000
C	3.005790000000	2.529151000000	5.574058000000
H	2.873421000000	2.637791000000	4.504304000000
C	-1.096692000000	0.960240000000	3.674590000000
O	-1.196102000000	0.451228000000	4.889493000000
C	-2.307300000000	1.518799000000	3.012156000000
C	-2.219638000000	2.017318000000	1.705351000000
C	-3.548770000000	1.464849000000	3.656387000000
C	-3.362128000000	2.475523000000	1.054490000000
H	-1.254297000000	2.060237000000	1.207682000000
C	-4.693198000000	1.905427000000	2.996626000000
H	-3.595565000000	1.067613000000	4.662925000000
C	-4.601308000000	2.419114000000	1.699988000000
H	-3.290580000000	2.869120000000	0.045266000000
H	-5.658107000000	1.851427000000	3.491828000000
H	-5.493912000000	2.769080000000	1.190157000000
H	-0.467345000000	0.395306000000	2.973613000000

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C	-3.531165000000	-2.312103000000	2.037688000000
C	-2.560036000000	-2.541372000000	2.987006000000
C	-1.898997000000	-1.461559000000	3.627868000000
C	-2.237327000000	-0.113762000000	3.257188000000
C	-3.262799000000	0.084653000000	2.288099000000
C	-3.890894000000	-0.986639000000	1.694006000000
H	-0.659922000000	-2.712075000000	4.893376000000
H	-4.031190000000	-3.147125000000	1.556832000000
H	-2.289731000000	-3.556493000000	3.264110000000
C	-0.917591000000	-1.688341000000	4.635189000000
C	-1.566884000000	0.968302000000	3.916390000000
H	-3.551655000000	1.094427000000	2.020614000000
H	-4.670960000000	-0.815283000000	0.958768000000
C	-0.647327000000	0.708920000000	4.935537000000
C	-0.307073000000	-0.633868000000	5.264596000000
H	0.460788000000	-0.812126000000	6.011722000000
C	-1.856858000000	2.398464000000	3.591589000000
C	-1.588550000000	2.951697000000	2.295366000000
C	-1.025844000000	2.206213000000	1.221366000000
C	-1.858002000000	4.344721000000	2.102731000000
C	-2.535902000000	4.454653000000	4.411195000000
C	-0.767646000000	2.811740000000	0.012316000000

H	-0.805858000000	1.153975000000	1.359536000000
C	-1.592767000000	4.935903000000	0.838676000000
C	-2.359306000000	5.084353000000	3.203231000000
H	-2.891759000000	4.999883000000	5.280403000000
C	-1.060509000000	4.184729000000	-0.183923000000
H	-0.337269000000	2.234967000000	-0.800401000000
H	-1.808270000000	5.991017000000	0.697492000000
H	-2.581486000000	6.141265000000	3.092042000000
H	-0.855491000000	4.643471000000	-1.146205000000
N	-2.281357000000	3.134035000000	4.612675000000
C	-1.564821000000	5.844021000000	8.141510000000
C	-0.071921000000	5.480686000000	8.035780000000
C	0.332374000000	5.425750000000	6.551666000000
C	0.787658000000	6.548868000000	8.741612000000
C	0.216436000000	4.104665000000	8.715665000000
C	-0.215317000000	4.013149000000	10.206331000000
O	-1.461452000000	3.227894000000	10.181029000000
N	-0.578193000000	3.003058000000	8.127700000000
C	-1.481502000000	2.662041000000	8.979467000000
C	-2.500082000000	1.691764000000	8.583290000000
C	-3.575994000000	1.309515000000	9.371795000000
C	-4.496252000000	0.406578000000	8.832788000000
C	-4.293154000000	-0.065413000000	7.538879000000
N	-2.289305000000	1.226389000000	7.323818000000
Ni	-0.624181000000	1.933515000000	6.512009000000
H	-1.746581000000	6.810073000000	7.661198000000
H	-1.907005000000	5.929067000000	9.178271000000
H	-2.188548000000	5.099917000000	7.635225000000
H	0.194567000000	6.411994000000	6.096718000000
H	-0.270016000000	4.705966000000	5.996445000000
H	1.379624000000	5.134540000000	6.433433000000
H	0.648488000000	7.518015000000	8.253622000000
H	1.853081000000	6.299683000000	8.686949000000
H	0.522481000000	6.680088000000	9.795840000000
H	1.277524000000	3.871822000000	8.594879000000
H	-0.448318000000	4.967496000000	10.674053000000
H	0.496212000000	3.460239000000	10.824900000000
H	-3.680426000000	1.717252000000	10.370677000000
H	-5.353382000000	0.082925000000	9.413866000000
H	-4.984492000000	-0.762802000000	7.079417000000
C	-3.176592000000	0.363650000000	6.816031000000
H	-2.987170000000	0.014930000000	5.811125000000
C	3.235019000000	-0.216788000000	2.625406000000
C	2.233062000000	0.664895000000	3.020734000000
C	2.093061000000	1.003841000000	4.374577000000
C	2.964162000000	0.461081000000	5.329800000000
C	3.966174000000	-0.419467000000	4.930408000000
C	4.099520000000	-0.762039000000	3.580507000000
H	3.347378000000	-0.478469000000	1.577873000000
H	1.555084000000	1.094305000000	2.287106000000
H	2.846273000000	0.748541000000	6.369559000000
H	4.646925000000	-0.837271000000	5.665781000000
H	4.881009000000	-1.449754000000	3.271765000000
C	1.024017000000	1.937627000000	4.778255000000
H	0.589593000000	2.524519000000	3.960008000000
O	1.033668000000	2.480675000000	5.962546000000

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C	-3.382064000000	-2.151539000000	1.972618000000
C	-2.350829000000	-2.356900000000	2.860702000000
C	-1.724618000000	-1.264004000000	3.515904000000
C	-2.145221000000	0.077445000000	3.211272000000
C	-3.243491000000	0.245575000000	2.317526000000
C	-3.841905000000	-0.837727000000	1.714997000000
H	-0.405998000000	-2.495906000000	4.716166000000
H	-3.856986000000	-2.995367000000	1.481906000000
H	-2.009284000000	-3.363429000000	3.085611000000
C	-0.716836000000	-1.477817000000	4.496903000000
C	-1.497645000000	1.172467000000	3.880289000000
H	-3.616478000000	1.241636000000	2.114328000000
H	-4.677921000000	-0.683886000000	1.039772000000
C	-0.561214000000	0.921151000000	4.890468000000
C	-0.166750000000	-0.417730000000	5.172800000000
H	0.584875000000	-0.594752000000	5.938027000000
C	-1.861416000000	2.594004000000	3.623695000000
C	-1.849937000000	3.187775000000	2.316140000000
C	-1.407674000000	2.513217000000	1.146155000000
C	-2.247493000000	4.559503000000	2.208376000000
C	-2.496960000000	4.601902000000	4.602070000000
C	-1.407336000000	3.153292000000	-0.071862000000
H	-1.045479000000	1.496149000000	1.221265000000
C	-2.249073000000	5.188134000000	0.935546000000
C	-2.591992000000	5.251140000000	3.396225000000
H	-2.723257000000	5.110802000000	5.533564000000
C	-1.843617000000	4.496114000000	-0.182561000000
H	-1.058660000000	2.628634000000	-0.955776000000
H	-2.564386000000	6.224990000000	0.863077000000
H	-2.908249000000	6.288763000000	3.350281000000
H	-1.842876000000	4.982342000000	-1.153305000000
N	-2.134202000000	3.297474000000	4.721046000000
C	-1.751624000000	5.941590000000	8.452458000000
C	-0.249011000000	5.639027000000	8.307842000000
C	0.157849000000	5.747411000000	6.828138000000
C	0.579273000000	6.654488000000	9.120707000000
C	0.080323000000	4.208142000000	8.834232000000
C	-0.306354000000	3.957526000000	10.320458000000
O	-1.497576000000	3.096796000000	10.254877000000
N	-0.700834000000	3.149739000000	8.151999000000
C	-1.536575000000	2.660026000000	9.000283000000
C	-2.487517000000	1.642110000000	8.560223000000
C	-3.513513000000	1.131047000000	9.343424000000
C	-4.368399000000	0.186337000000	8.770906000000
C	-4.153288000000	-0.198287000000	7.449864000000
N	-2.263463000000	1.262168000000	7.275011000000
Ni	-0.689534000000	2.164963000000	6.466033000000
H	-1.968861000000	6.945887000000	8.076779000000
H	-2.088874000000	5.906179000000	9.493871000000
H	-2.354875000000	5.231904000000	7.876872000000
H	-0.039627000000	6.760432000000	6.462539000000
H	-0.394385000000	5.041161000000	6.209544000000
H	1.221688000000	5.533141000000	6.691445000000
H	0.420267000000	7.662155000000	8.725461000000
H	1.650858000000	6.436819000000	9.053051000000
H	0.302813000000	6.678942000000	10.179791000000
H	1.142304000000	4.012219000000	8.663874000000
H	-0.587507000000	4.851244000000	10.873912000000
H	0.456064000000	3.404355000000	10.874456000000

H	-3.629343000000	1.474268000000	10.365026000000
H	-5.184713000000	-0.236842000000	9.346765000000
H	-4.794023000000	-0.925479000000	6.963954000000
C	-3.089723000000	0.358048000000	6.734926000000
H	-2.892370000000	0.077835000000	5.710386000000
C	1.390324000000	4.494067000000	2.032757000000
C	1.123847000000	3.984084000000	3.301088000000
C	1.380602000000	2.633834000000	3.578159000000
C	1.894448000000	1.796923000000	2.575280000000
C	2.152329000000	2.308245000000	1.307596000000
C	1.901214000000	3.658562000000	1.036706000000
H	1.190397000000	5.538545000000	1.816179000000
H	0.726311000000	4.614317000000	4.088379000000
H	2.085674000000	0.749438000000	2.795499000000
H	2.551879000000	1.662584000000	0.531756000000
H	2.103438000000	4.057320000000	0.047325000000
C	1.167770000000	2.100812000000	4.937877000000
H	1.753805000000	1.205047000000	5.172862000000
O	0.889887000000	2.913760000000	5.916168000000

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C	-4.792706000000	-0.940883000000	1.440210000000
C	-3.782329000000	-1.643093000000	2.058628000000
C	-2.811824000000	-0.973788000000	2.847690000000
C	-2.897087000000	0.452031000000	3.005789000000
C	-3.951701000000	1.145867000000	2.343149000000
C	-4.872881000000	0.466478000000	1.579917000000
H	-1.685970000000	-2.756564000000	3.349596000000
H	-5.528047000000	-1.463332000000	0.836183000000
H	-3.710136000000	-2.720981000000	1.943943000000
C	-1.749556000000	-1.678945000000	3.475795000000
C	-1.922200000000	1.125711000000	3.803754000000
H	-4.016972000000	2.224020000000	2.434716000000
H	-5.664493000000	1.011454000000	1.075352000000
C	-0.862971000000	0.406138000000	4.385472000000
C	-0.801457000000	-1.005316000000	4.203016000000
H	0.031327000000	-1.551299000000	4.633828000000
C	-2.060132000000	2.605191000000	4.059576000000
C	-3.103941000000	3.129273000000	4.899795000000
C	-4.134537000000	2.335846000000	5.472500000000
C	-3.081946000000	4.533131000000	5.176770000000
C	-1.152693000000	4.705926000000	3.749415000000
C	-5.087906000000	2.905780000000	6.287128000000
H	-4.166513000000	1.275539000000	5.250621000000
C	-4.074770000000	5.090090000000	6.028055000000
C	-2.062724000000	5.317087000000	4.578605000000
H	-0.373849000000	5.276493000000	3.249474000000
C	-5.056008000000	4.293668000000	6.572393000000
H	-5.879494000000	2.294208000000	6.709460000000
H	-4.051603000000	6.157159000000	6.230581000000
H	-2.019878000000	6.386435000000	4.762983000000
H	-5.817729000000	4.726695000000	7.213499000000
N	-1.148760000000	3.373470000000	3.497966000000
C	-1.386559000000	-0.996722000000	9.609850000000
C	-1.836817000000	-1.564304000000	8.250555000000
C	-0.596103000000	-1.982607000000	7.444311000000
C	-2.725470000000	-2.806777000000	8.461242000000
C	-2.660604000000	-0.509317000000	7.443389000000
C	-3.888110000000	0.054425000000	8.204872000000
O	-3.431579000000	1.358642000000	8.708701000000
N	-1.890744000000	0.732707000000	7.197267000000
C	-2.349476000000	1.640154000000	7.995019000000
C	-1.656305000000	2.923940000000	8.089584000000
C	-2.064831000000	4.020690000000	8.832108000000
C	-1.274019000000	5.173704000000	8.777104000000
C	-0.130031000000	5.180117000000	7.981738000000
N	-0.538935000000	2.928411000000	7.321465000000
Ni	-0.452635000000	1.397704000000	6.096570000000
H	-0.842340000000	-1.763708000000	10.168118000000
H	-2.227414000000	-0.677083000000	10.233447000000
H	-0.710596000000	-0.144998000000	9.481453000000
H	-0.002268000000	-2.700672000000	8.017744000000
H	0.044437000000	-1.124616000000	7.214418000000
H	-0.884585000000	-2.458534000000	6.504052000000
H	-2.150456000000	-3.594590000000	8.956518000000
H	-3.083530000000	-3.206595000000	7.505932000000
H	-3.596375000000	-2.601683000000	9.091989000000
H	-2.949727000000	-0.941378000000	6.481058000000
H	-4.201879000000	-0.531314000000	9.066026000000
H	-4.742499000000	0.248573000000	7.552915000000
H	-2.975352000000	3.969460000000	9.416988000000
H	-1.554819000000	6.054925000000	9.344380000000
H	0.501581000000	6.058877000000	7.915760000000
C	0.205857000000	4.033888000000	7.253294000000
H	1.066655000000	3.977082000000	6.596489000000
C	1.631104000000	0.812480000000	0.563372000000
C	1.298148000000	0.475159000000	1.872370000000
C	1.285940000000	1.458844000000	2.871052000000
C	1.630160000000	2.778619000000	2.553304000000
C	1.983296000000	3.109761000000	1.248061000000
C	1.974984000000	2.131185000000	0.249944000000
H	1.630312000000	0.050808000000	-0.210118000000
H	1.028454000000	-0.548075000000	2.119788000000
H	1.626045000000	3.522299000000	3.340581000000
H	2.263396000000	4.130383000000	1.005161000000
H	2.242433000000	2.393326000000	-0.769307000000
C	1.000286000000	1.078435000000	4.277032000000
H	1.421798000000	0.099788000000	4.541439000000
O	1.024042000000	1.996884000000	5.224288000000

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C	-4.684631000000	-1.241597000000	1.733981000000
C	-3.662182000000	-1.873408000000	2.406608000000
C	-2.695834000000	-1.124965000000	3.127145000000
C	-2.798935000000	0.307704000000	3.154613000000
C	-3.861745000000	0.927907000000	2.436413000000
C	-4.780803000000	0.171478000000	1.745662000000
H	-1.526385000000	-2.838723000000	3.754442000000
H	-5.417113000000	-1.825062000000	1.184796000000
H	-3.577184000000	-2.956380000000	2.388111000000
C	-1.614713000000	-1.756364000000	3.802039000000
C	-1.831733000000	1.057473000000	3.893247000000
H	-3.939508000000	2.009451000000	2.433179000000
H	-5.582895000000	0.659293000000	1.200669000000
C	-0.788338000000	0.401110000000	4.560269000000
C	-0.678605000000	-1.012408000000	4.476122000000

H	0.171263000000	-1.498331000000	4.939531000000
C	-1.939571000000	2.556483000000	3.986136000000
C	-2.951481000000	3.183286000000	4.789879000000
C	-3.989948000000	2.468448000000	5.445721000000
C	-2.886911000000	4.603719000000	4.942708000000
C	-0.982467000000	4.593493000000	3.468148000000
C	-4.910660000000	3.129692000000	6.227910000000
H	-4.052622000000	1.395003000000	5.311588000000
C	-3.847066000000	5.257289000000	5.762415000000
C	-1.859590000000	5.299891000000	4.256704000000
H	-0.201219000000	5.099210000000	2.907629000000
C	-4.835945000000	4.535718000000	6.391798000000
H	-5.704071000000	2.576061000000	6.720555000000
H	-3.793792000000	6.336728000000	5.872514000000
H	-1.781566000000	6.379471000000	4.343411000000
H	-5.572098000000	5.042942000000	7.008063000000
N	-1.015105000000	3.241367000000	3.337467000000
C	-1.566273000000	-0.951911000000	9.771870000000
C	-1.866064000000	-1.552222000000	8.385071000000
C	-0.538869000000	-1.935880000000	7.708821000000
C	-2.726983000000	-2.822956000000	8.532016000000
C	-2.647972000000	-0.538323000000	7.487017000000
C	-3.951691000000	0.001533000000	8.127651000000
O	-3.566269000000	1.313736000000	8.671399000000
N	-1.895973000000	0.722951000000	7.289200000000
C	-2.437955000000	1.621695000000	8.043629000000
C	-1.789966000000	2.924628000000	8.181084000000
C	-2.273948000000	4.005718000000	8.901683000000
C	-1.515103000000	5.180652000000	8.899510000000
C	-0.326238000000	5.224072000000	8.173689000000
N	-0.630938000000	2.965580000000	7.479104000000
Ni	-0.443312000000	1.446427000000	6.245885000000
H	-1.053564000000	-1.693342000000	10.391227000000
H	-2.471966000000	-0.651809000000	10.308012000000
H	-0.908130000000	-0.080186000000	9.694707000000
H	0.030926000000	-2.605389000000	8.360309000000
H	0.082078000000	-1.058104000000	7.502885000000
H	-0.716497000000	-2.457025000000	6.765714000000
H	-2.173485000000	-3.584087000000	9.089701000000
H	-2.981083000000	-3.245950000000	7.553717000000
H	-3.659117000000	-2.641463000000	9.076759000000
H	-2.836718000000	-0.993495000000	6.511032000000
H	-4.337181000000	-0.589931000000	8.955117000000
H	-4.743998000000	0.181642000000	7.396452000000
H	-3.216128000000	3.925142000000	9.430430000000
H	-1.854725000000	6.050230000000	9.452377000000
H	0.282925000000	6.120640000000	8.149106000000
C	0.083372000000	4.093556000000	7.459614000000
H	0.979393000000	4.068929000000	6.849702000000
C	3.277728000000	-1.438276000000	3.164633000000
C	2.355593000000	-0.393886000000	3.186895000000
C	2.029577000000	0.229100000000	4.399519000000
C	2.631949000000	-0.201470000000	5.590577000000
C	3.550701000000	-1.247547000000	5.567110000000
C	3.872839000000	-1.867678000000	4.354541000000
H	3.533492000000	-1.916519000000	2.224355000000
H	1.880870000000	-0.060709000000	2.267546000000
H	2.375267000000	0.298311000000	6.519727000000
H	4.021083000000	-1.578529000000	6.488010000000
H	4.590360000000	-2.682429000000	4.337381000000
C	1.040119000000	1.330115000000	4.405403000000
H	0.774732000000	1.750734000000	3.432083000000
O	0.998412000000	2.165650000000	5.420493000000

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C	-4.506117000000	-1.726057000000	1.811921000000
C	-3.424859000000	-2.188294000000	2.529507000000
C	-2.558581000000	-1.284644000000	3.195805000000
C	-2.817571000000	0.126709000000	3.113825000000
C	-3.943690000000	0.567529000000	2.360055000000
C	-4.765631000000	-0.336533000000	1.726974000000
H	-1.241236000000	-2.810383000000	3.997696000000
H	-5.162446000000	-2.426868000000	1.305284000000
H	-3.219186000000	-3.253218000000	2.592040000000
C	-1.437526000000	-1.742837000000	3.943384000000
C	-1.942971000000	1.041606000000	3.779817000000
H	-4.145840000000	1.629388000000	2.280796000000
H	-5.617197000000	0.015873000000	1.153546000000
C	-0.852576000000	0.561642000000	4.522350000000
C	-0.617430000000	-0.848147000000	4.581861000000
H	0.237997000000	-1.211364000000	5.145723000000
C	-2.221791000000	2.518186000000	3.640946000000
C	-3.195843000000	3.189833000000	4.452123000000
C	-4.006122000000	2.533192000000	5.415344000000
C	-3.374549000000	4.593604000000	4.240165000000
C	-1.726362000000	4.455421000000	2.490774000000
C	-4.916666000000	3.241287000000	6.167762000000
H	-3.920371000000	1.460645000000	5.527438000000
C	-4.320611000000	5.297900000000	5.031919000000
C	-2.599442000000	5.216979000000	3.229449000000
H	-1.123695000000	4.893007000000	1.699644000000
C	-5.068207000000	4.638312000000	5.981277000000
H	-5.536951000000	2.726419000000	6.895454000000
H	-4.448523000000	6.364411000000	4.870261000000
H	-2.708584000000	6.280439000000	3.038826000000
H	-5.790327000000	5.184116000000	6.580644000000
N	-1.544128000000	3.123214000000	2.687974000000
C	-1.797546000000	5.576145000000	7.585880000000
C	-0.296914000000	5.402777000000	7.291524000000
C	-0.089127000000	5.253599000000	5.774736000000
C	0.490749000000	6.636590000000	7.776639000000
C	0.272398000000	4.149061000000	8.026213000000
C	0.080326000000	4.156346000000	9.569657000000
O	-1.023514000000	3.208817000000	9.809477000000
N	-0.441387000000	2.904109000000	7.661255000000
C	-1.142644000000	2.532404000000	8.674310000000
C	-2.038608000000	1.385843000000	8.535001000000
C	-2.891305000000	0.926315000000	9.528770000000
C	-3.704799000000	-0.172644000000	9.241532000000
C	-3.618176000000	-0.759585000000	7.981354000000
N	-1.949872000000	0.820805000000	7.301960000000
Ni	-0.582163000000	1.688349000000	6.160347000000
H	-2.176116000000	6.465192000000	7.073881000000
H	-2.004349000000	5.704633000000	8.653933000000
H	-2.377750000000	4.724308000000	7.220083000000
H	-0.427746000000	6.160335000000	5.264772000000
H	-0.648137000000	4.411210000000	5.367361000000

H	0.965348000000	5.093614000000	5.532748000000
H	0.156057000000	7.525036000000	7.233142000000
H	1.564639000000	6.520306000000	7.593422000000
H	0.347366000000	6.841256000000	8.842668000000
H	1.325843000000	4.033823000000	7.758410000000
H	-0.225728000000	5.113722000000	9.986053000000
H	0.948549000000	3.774619000000	10.112429000000
H	-2.907584000000	1.423780000000	10.491680000000
H	-4.388220000000	-0.561208000000	9.989231000000
H	-4.229520000000	-1.614587000000	7.715445000000
C	-2.727761000000	-0.238239000000	7.039738000000
H	-2.632115000000	-0.669582000000	6.052399000000
C	1.587025000000	1.155702000000	0.667037000000
C	1.291749000000	0.808777000000	1.981771000000
C	1.202901000000	1.802927000000	2.965181000000
C	1.432884000000	3.143211000000	2.630580000000
C	1.751330000000	3.484842000000	1.319097000000
C	1.818685000000	2.494757000000	0.334837000000
H	1.643391000000	0.387576000000	-0.097936000000
H	1.105156000000	-0.228885000000	2.246923000000
H	1.359240000000	3.897042000000	3.405629000000
H	1.945238000000	4.521770000000	1.060954000000
H	2.058148000000	2.763728000000	-0.689612000000
C	0.945283000000	1.426339000000	4.373336000000
H	1.451241000000	0.497859000000	4.666658000000
O	0.861670000000	2.365479000000	5.291606000000

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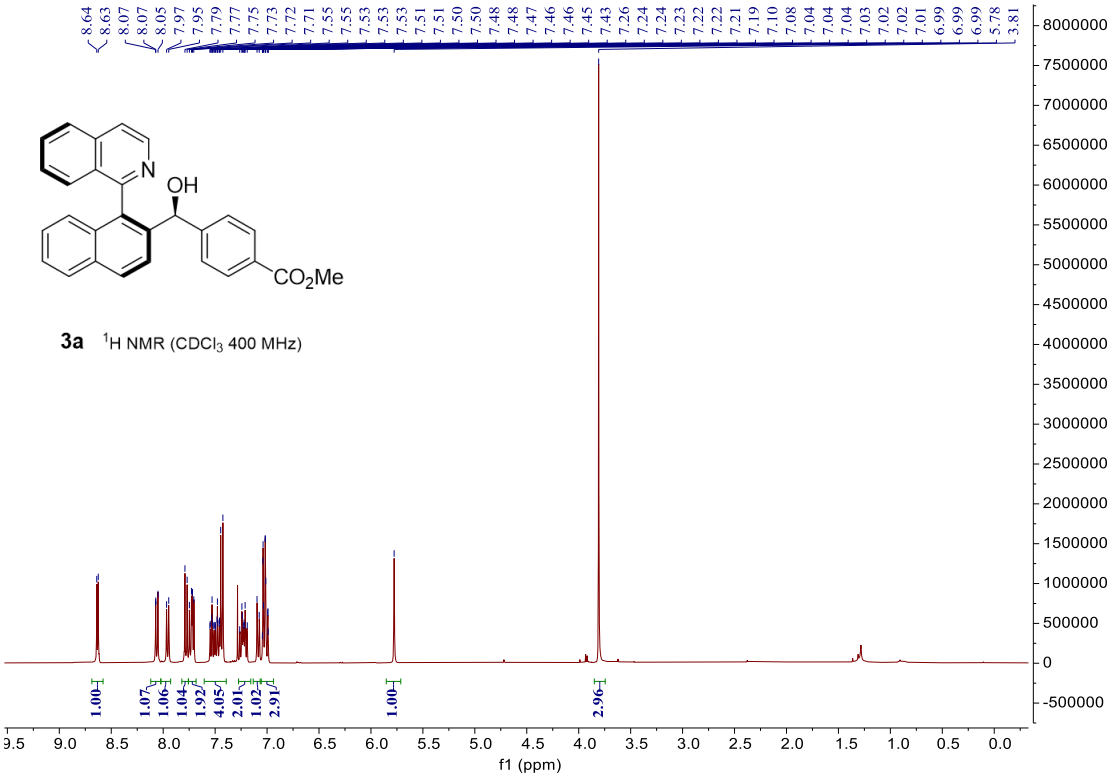
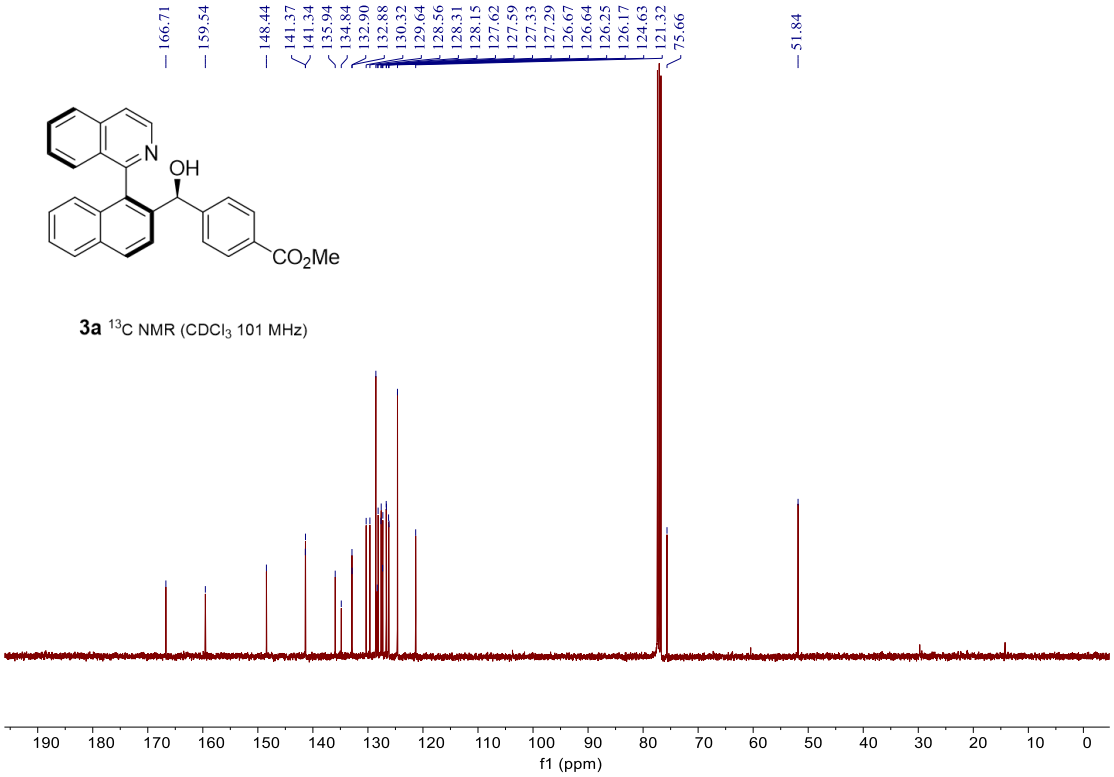
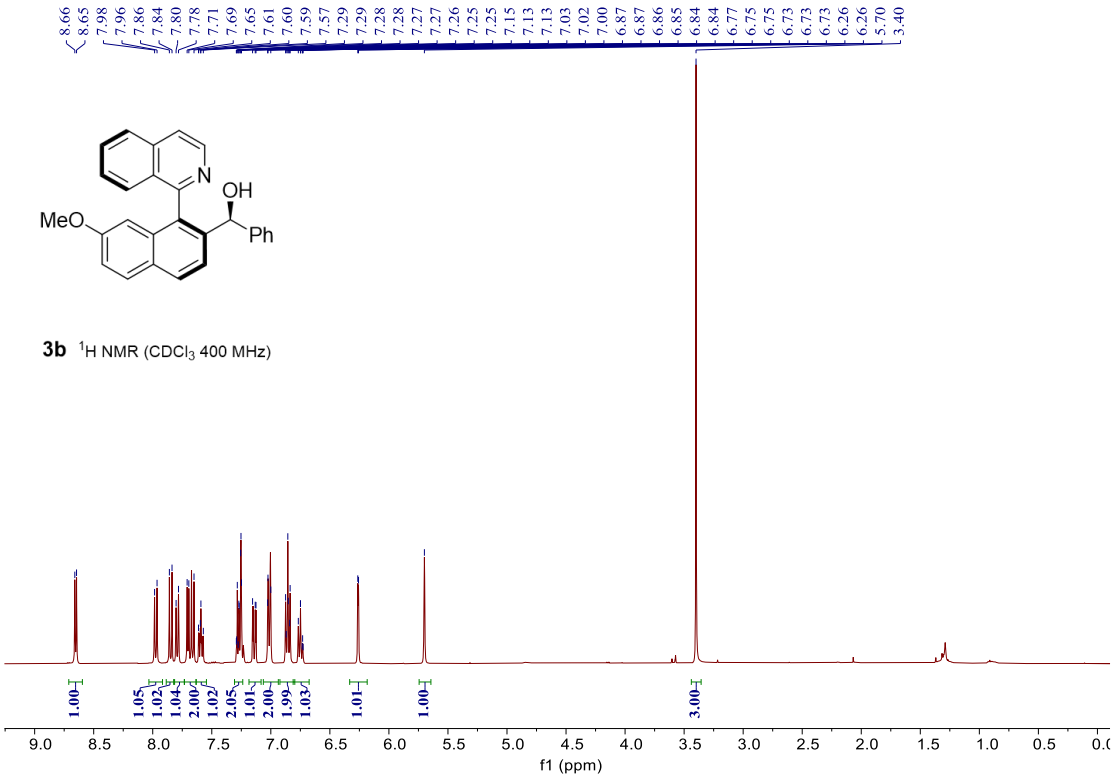
C	-4.204327000000	-1.921832000000	2.006784000000
C	-3.137522000000	-2.311167000000	2.786820000000
C	-2.315340000000	-1.347200000000	3.424539000000
C	-2.608329000000	0.048834000000	3.246949000000
C	-3.714353000000	0.414747000000	2.427717000000
C	-4.492959000000	-0.547433000000	1.825532000000
H	-0.976876000000	-2.787221000000	4.341314000000
H	-4.826128000000	-2.669169000000	1.523625000000
H	-2.908527000000	-3.364722000000	2.920822000000
C	-1.202852000000	-1.730277000000	4.227477000000
C	-1.778335000000	1.018987000000	3.891726000000
H	-3.938906000000	1.464801000000	2.277820000000
H	-5.332004000000	-0.253002000000	1.202989000000
C	-0.713048000000	0.608303000000	4.701367000000
C	-0.423947000000	-0.781467000000	4.840037000000
H	0.436443000000	-1.079563000000	5.430706000000
C	-2.043548000000	2.485447000000	3.667681000000
C	-3.090759000000	3.179174000000	4.356026000000
C	-3.974546000000	2.551707000000	5.274163000000
C	-3.240368000000	4.577623000000	4.094195000000
C	-1.405367000000	4.400398000000	2.544178000000
C	-4.937688000000	3.284792000000	5.930313000000
H	-3.893007000000	1.484480000000	5.435596000000
C	-4.245798000000	5.306661000000	4.783937000000
C	-2.364525000000	5.173691000000	3.152616000000
H	-0.718549000000	4.826368000000	1.818484000000
C	-5.069988000000	4.675678000000	5.687934000000
H	-5.611812000000	2.795769000000	6.627166000000
H	-4.353654000000	6.368845000000	4.584048000000
H	-2.451203000000	6.231103000000	2.922117000000
H	-5.835127000000	5.240075000000	6.211996000000
N	-1.240932000000	3.074152000000	2.798709000000
C	-1.934171000000	5.601195000000	7.698141000000
C	-0.419312000000	5.505794000000	7.438276000000
C	-0.174061000000	5.372840000000	5.926123000000
C	0.291758000000	6.778418000000	7.941835000000
C	0.200203000000	4.282194000000	8.185568000000
C	-0.022625000000	4.281905000000	9.723973000000
O	-1.104716000000	3.304100000000	9.938508000000
N	-0.445847000000	3.002468000000	7.811793000000
C	-1.168016000000	2.616715000000	8.804908000000
C	-2.042646000000	1.458077000000	8.638922000000
C	-2.920153000000	0.989880000000	9.606774000000
C	-3.727001000000	-0.105534000000	9.288991000000
C	-3.611774000000	-0.677181000000	8.024377000000
N	-1.919106000000	0.902634000000	7.404092000000
Ni	-0.516600000000	1.782537000000	6.307559000000
H	-2.342540000000	6.478437000000	7.188480000000
H	-2.174079000000	5.702663000000	8.762175000000
H	-2.462654000000	4.727722000000	7.304137000000
H	-0.547403000000	6.264554000000	5.413644000000
H	-0.684383000000	4.505837000000	5.508038000000
H	0.889840000000	5.263349000000	5.698747000000
H	-0.073457000000	7.647993000000	7.387654000000
H	1.374417000000	6.716841000000	7.785801000000
H	0.111107000000	6.977308000000	9.003263000000
H	1.262871000000	4.221549000000	7.937684000000
H	-0.363349000000	5.229272000000	10.136016000000
H	0.844890000000	3.922744000000	10.283457000000
H	-2.962082000000	1.480198000000	10.572570000000
H	-4.428760000000	-0.501057000000	10.015767000000
H	-4.219396000000	-1.526464000000	7.732804000000
C	-2.695190000000	-0.149602000000	7.111481000000
H	-2.575191000000	-0.574358000000	6.124819000000
C	3.415405000000	-0.824264000000	3.098154000000
C	2.378369000000	0.102291000000	3.172952000000
C	2.088673000000	0.733627000000	4.391100000000
C	2.843895000000	0.432839000000	5.533460000000
C	3.880176000000	-0.494726000000	5.456323000000
C	4.164696000000	-1.125182000000	4.240084000000
H	3.642641000000	-1.310207000000	2.154471000000
H	1.784745000000	0.336660000000	2.292977000000
H	2.612107000000	0.942641000000	6.463373000000
H	4.470941000000	-0.724675000000	6.337830000000
H	4.973421000000	-1.847366000000	4.181360000000
C	0.984792000000	1.716910000000	4.452185000000
H	0.632842000000	2.101794000000	3.490437000000
O	0.902136000000	2.537277000000	5.475912

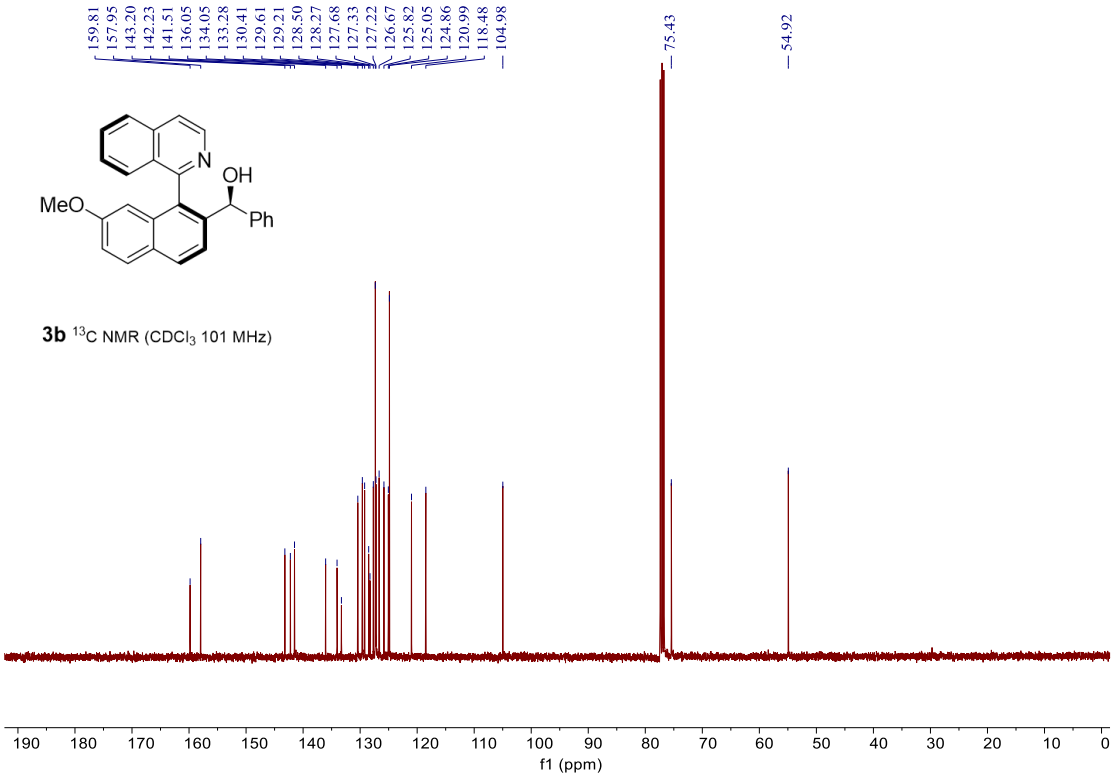
8. Spectroscopic Data (NMR Spectrum)



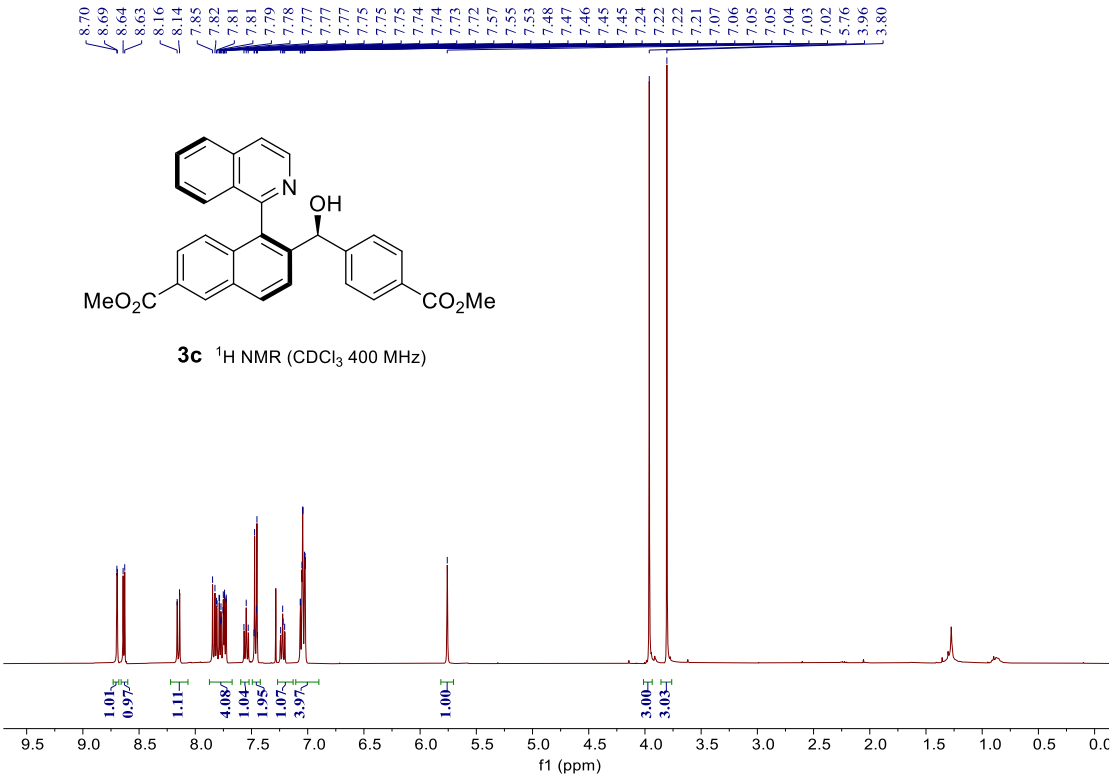




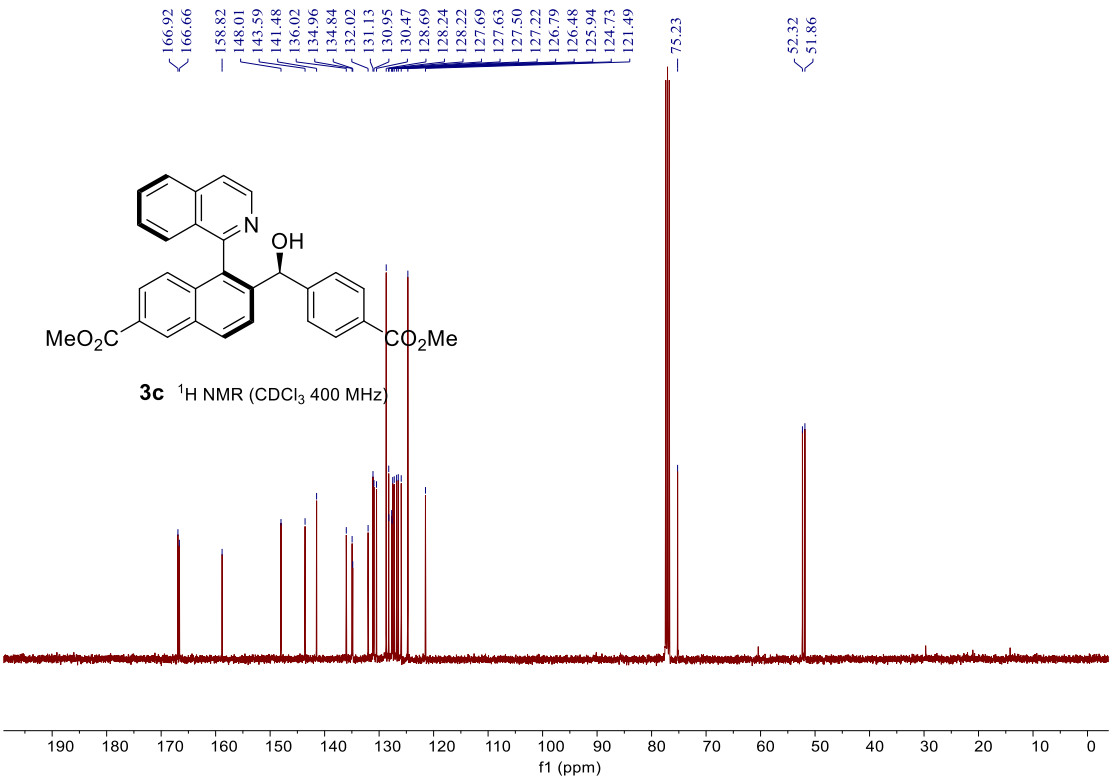
3b ^{1}H NMR ($CDCl_3$ 400 MHz)



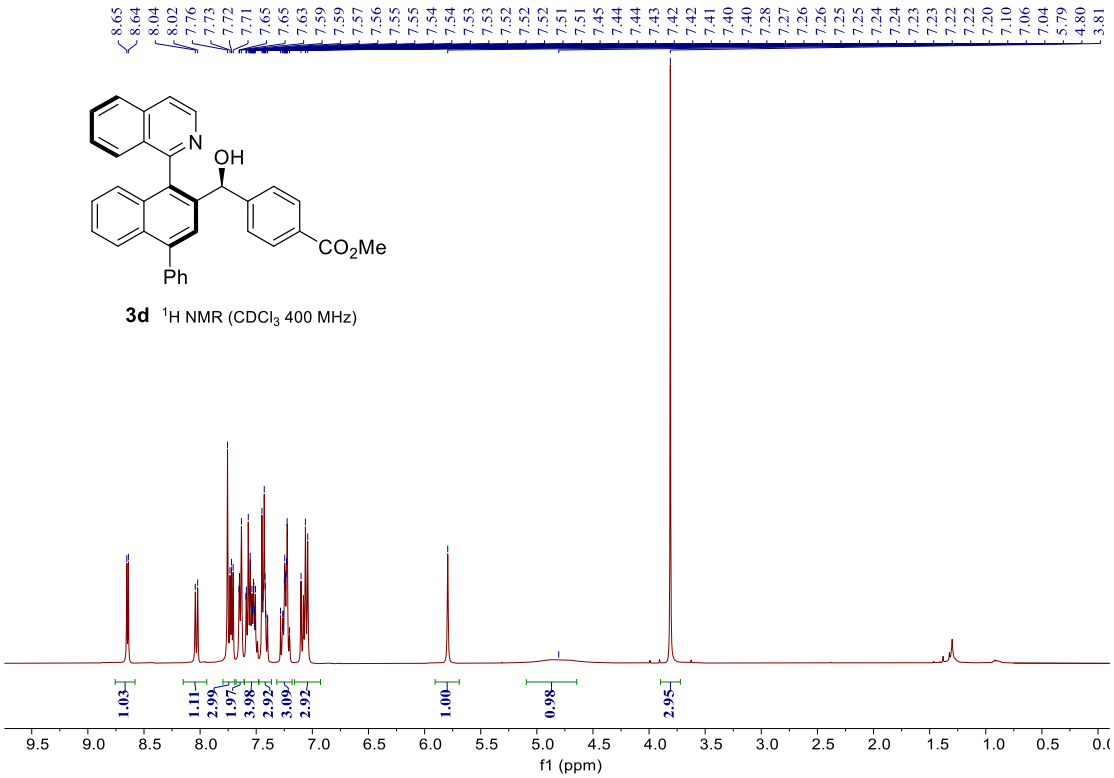
3b ^{13}C NMR ($CDCl_3$ 101 MHz)



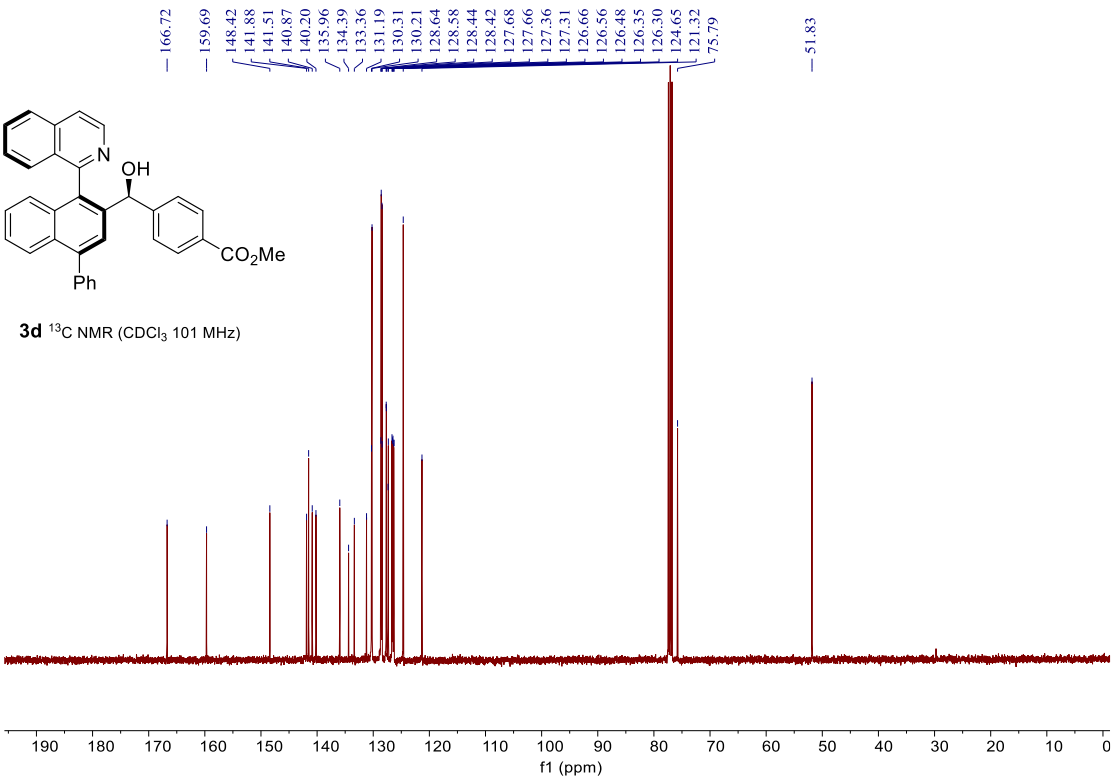
3c ^{1}H NMR ($CDCl_3$ 400 MHz)



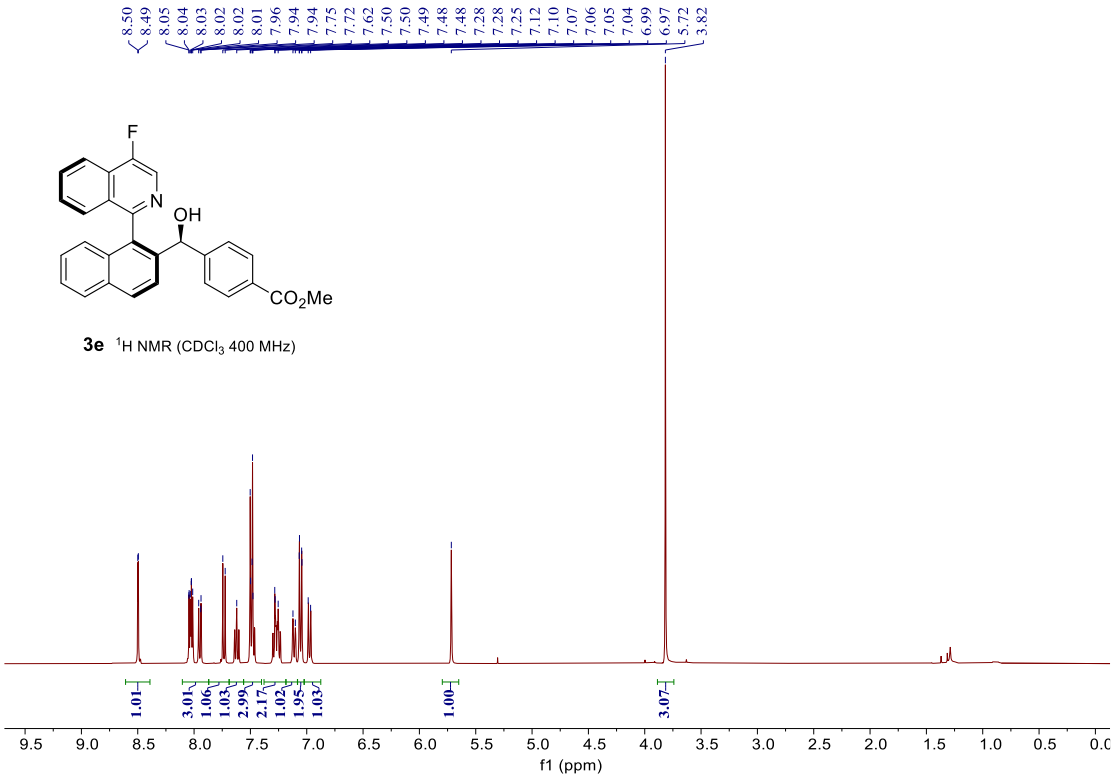
3c ^{1}H NMR ($CDCl_3$ 400 MHz)



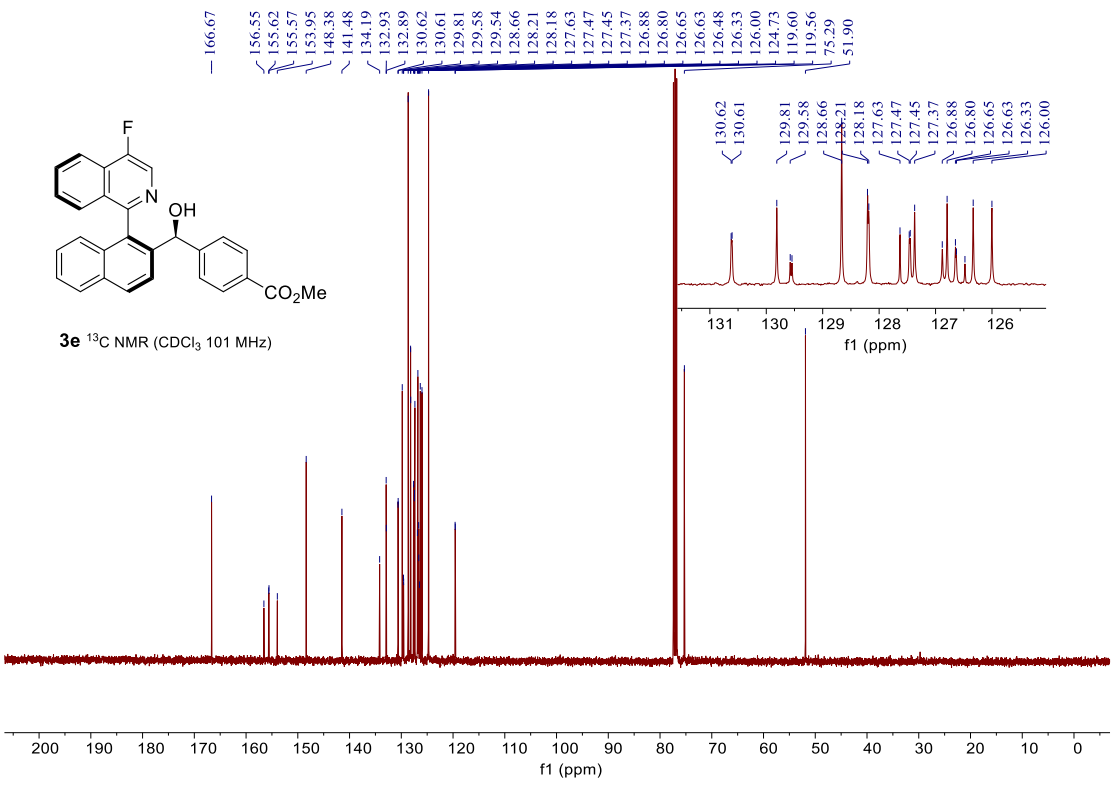
3d ^{1}H NMR ($CDCl_3$ 400 MHz)



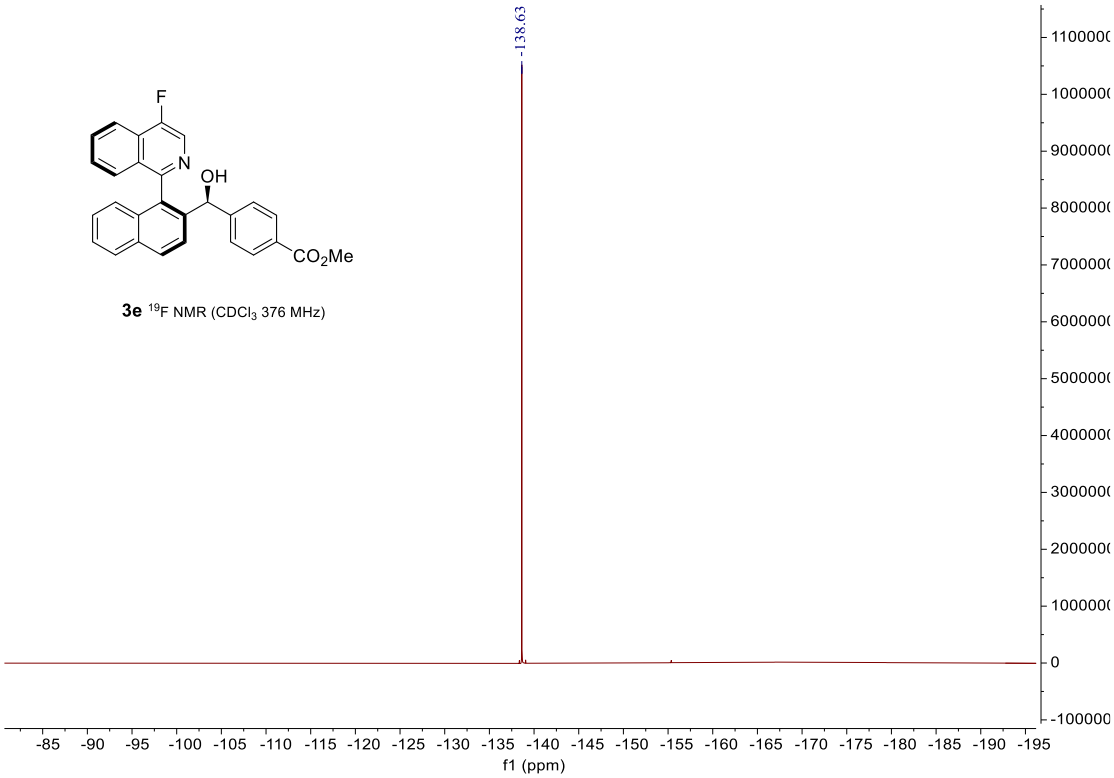
3d ^{13}C NMR ($CDCl_3$ 101 MHz)



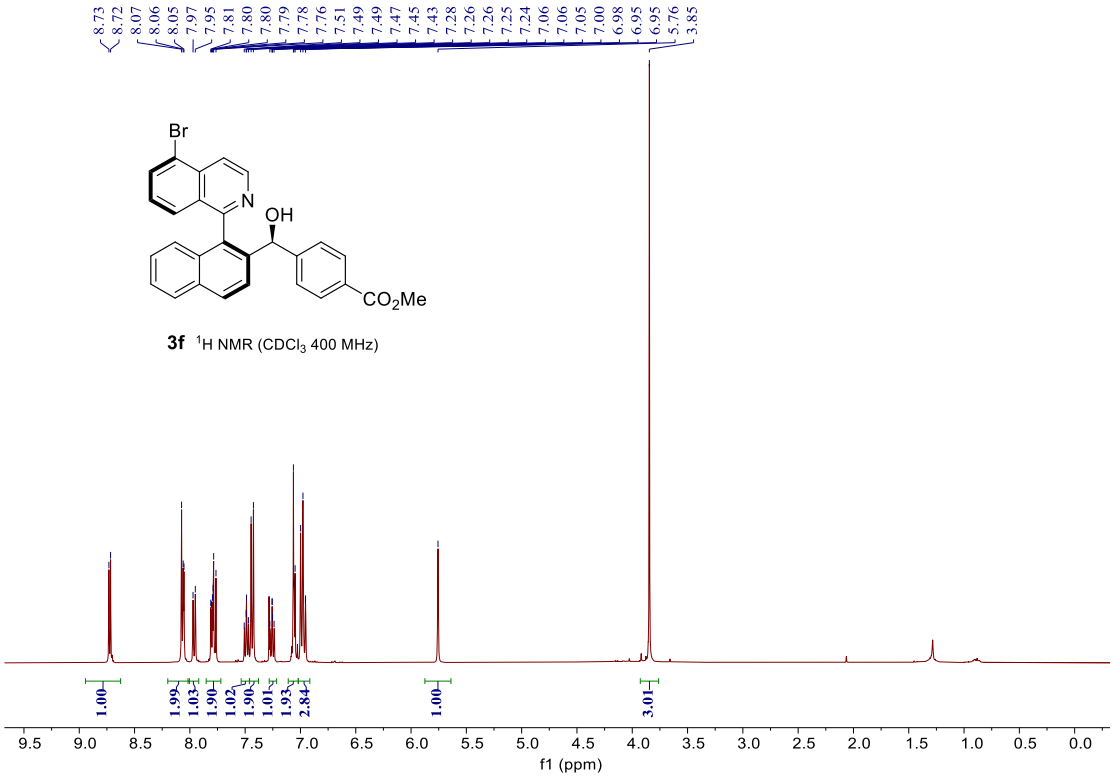
3e ^{1}H NMR ($CDCl_3$ 400 MHz)



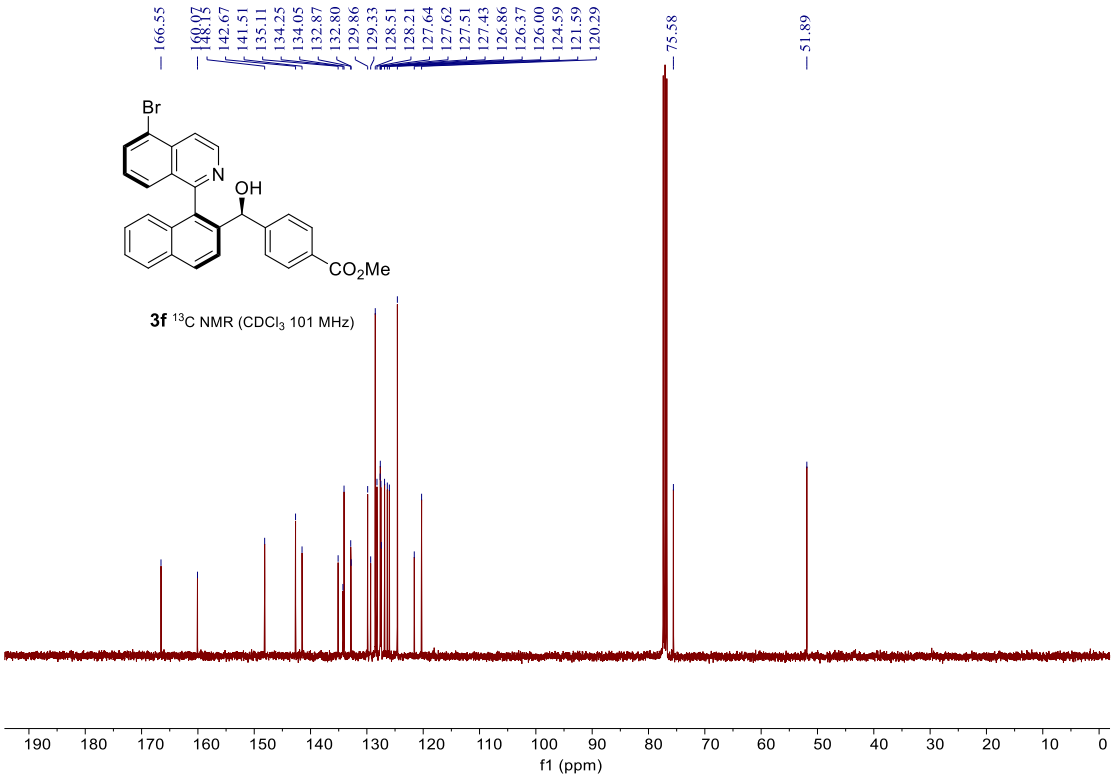
3e ^{13}C NMR ($CDCl_3$ 101 MHz)



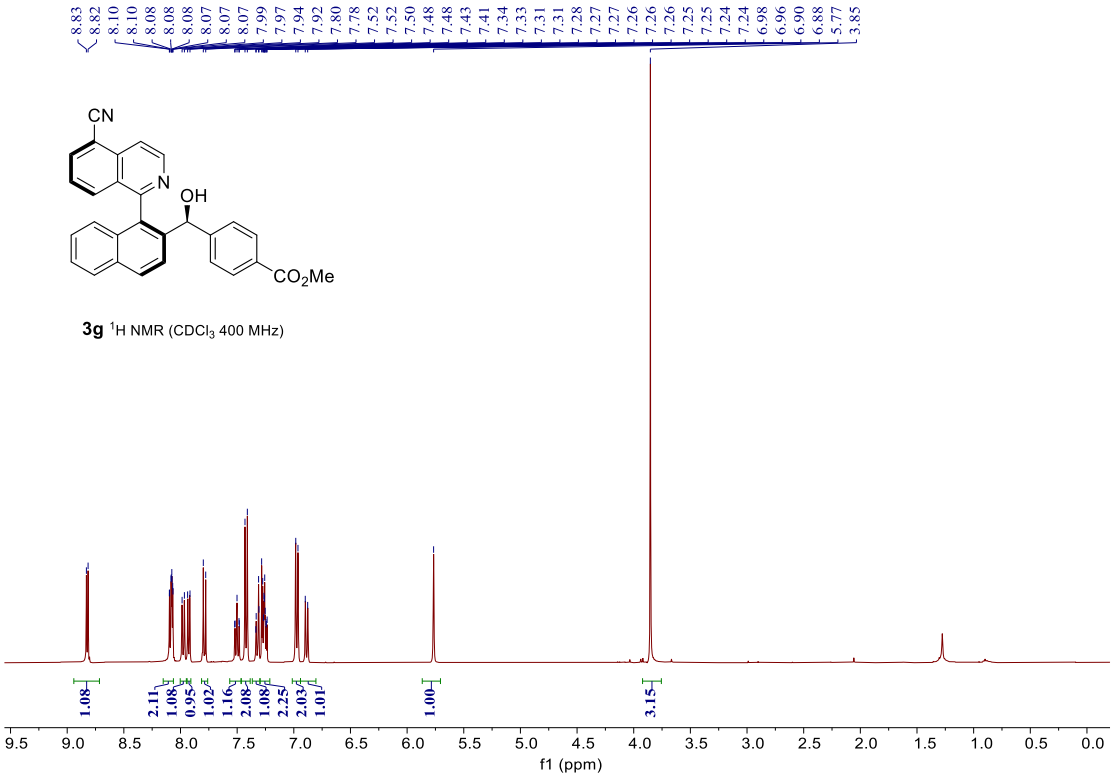
3e ^{19}F NMR ($CDCl_3$ 376 MHz)



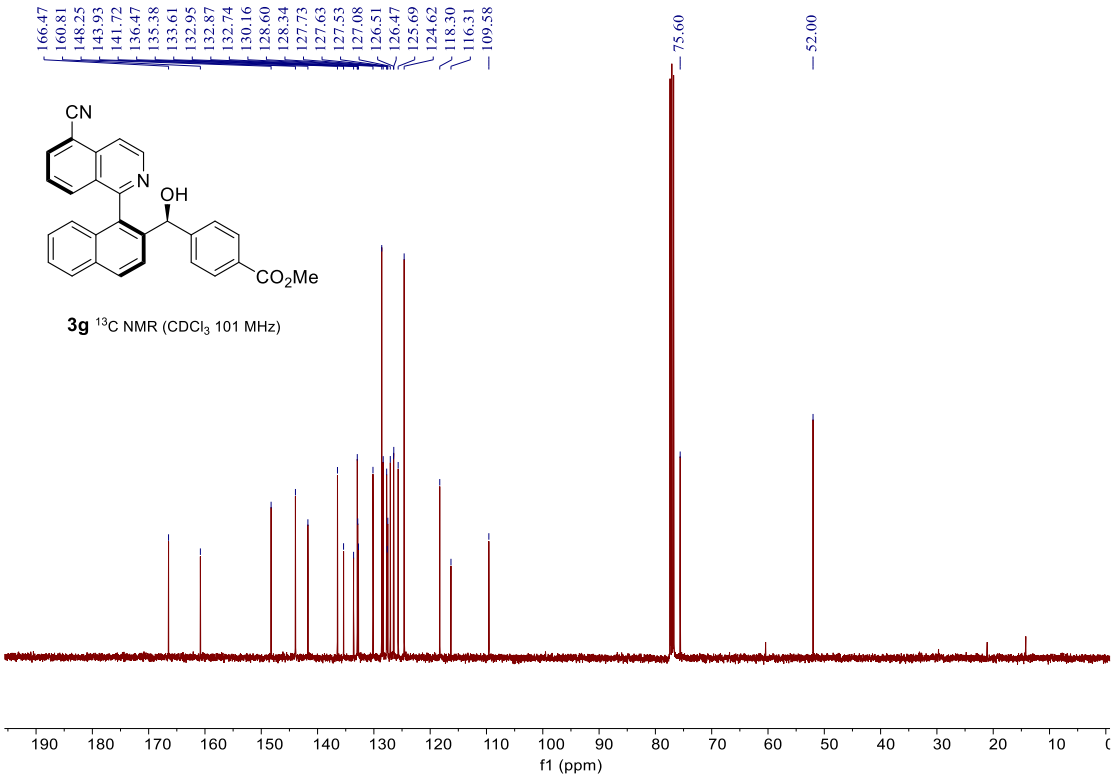
3f ^{1}H NMR ($CDCl_3$ 400 MHz)



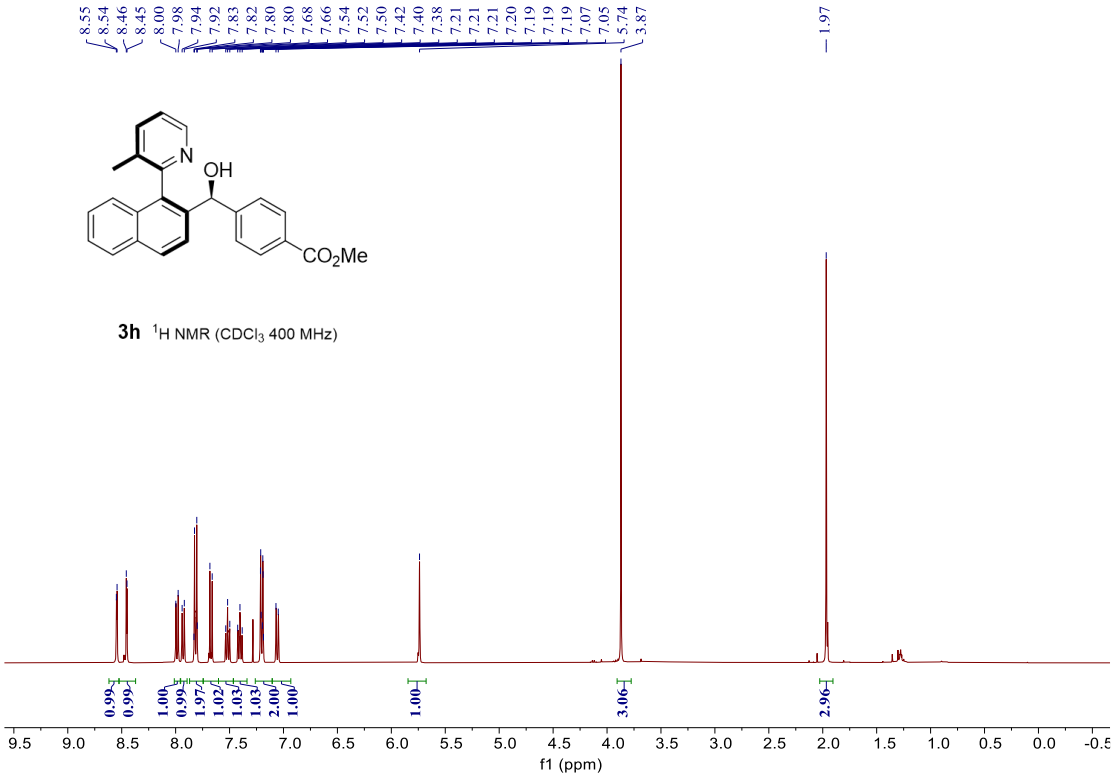
3f ^{13}C NMR ($CDCl_3$ 101 MHz)



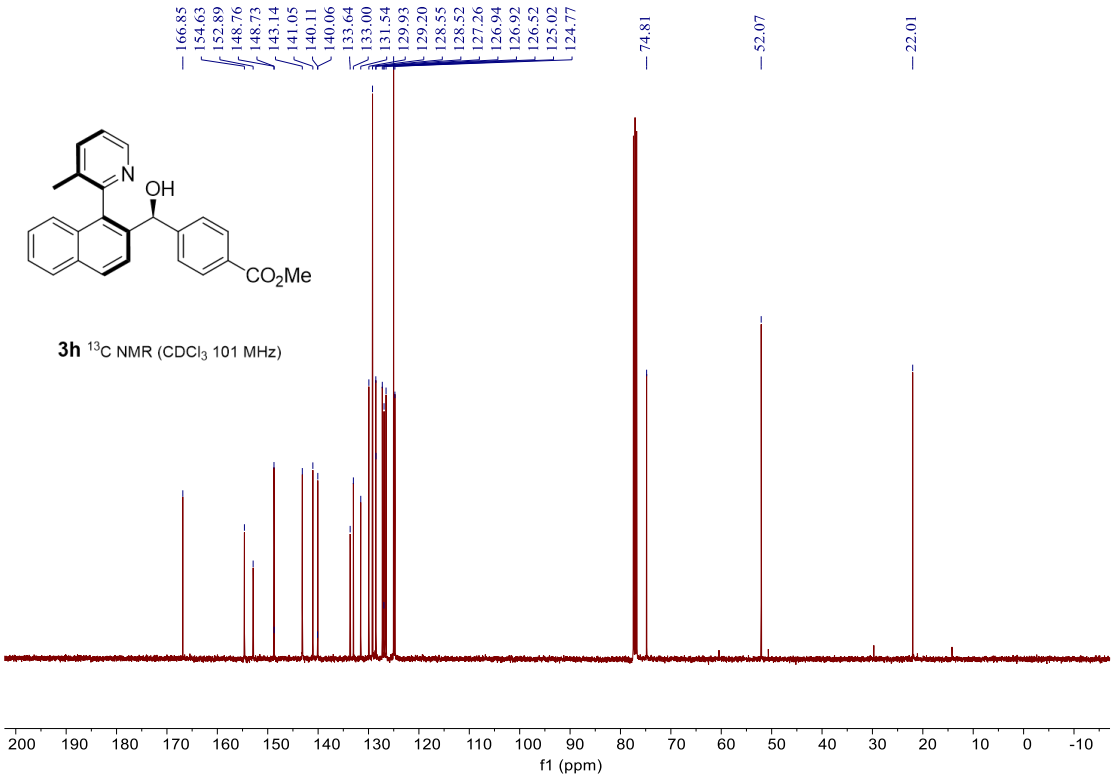
3g ^{1}H NMR ($CDCl_3$ 400 MHz)



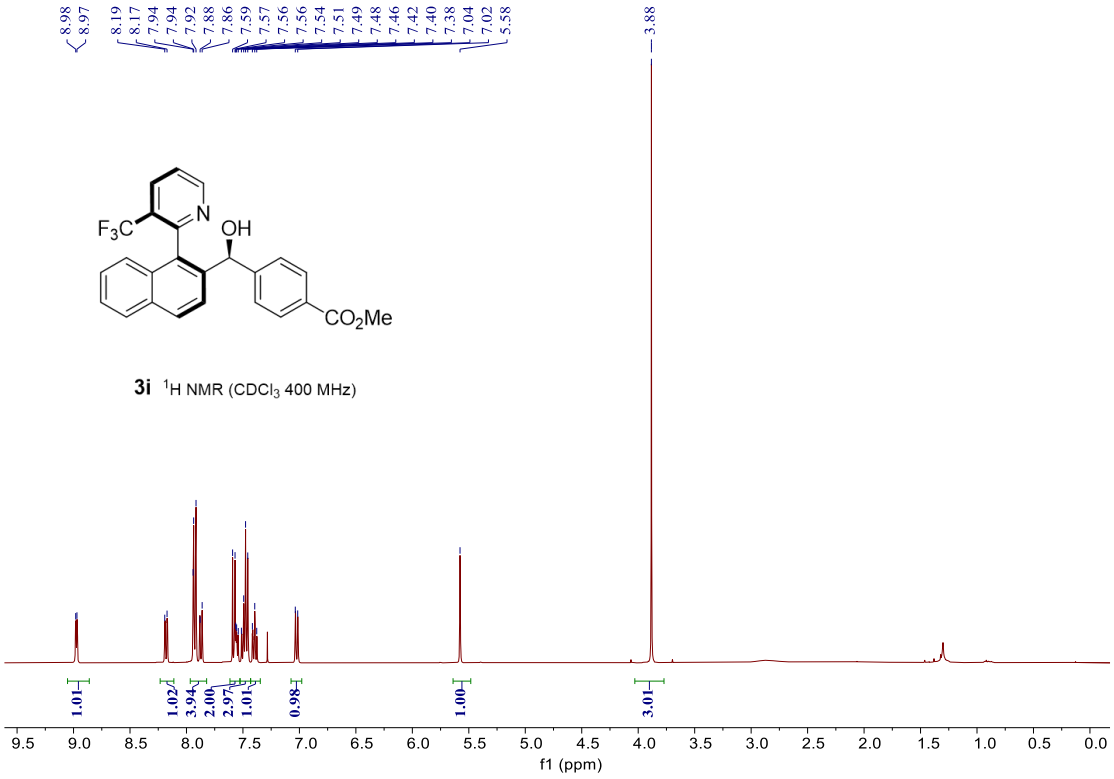
3g ^{13}C NMR ($CDCl_3$ 101 MHz)



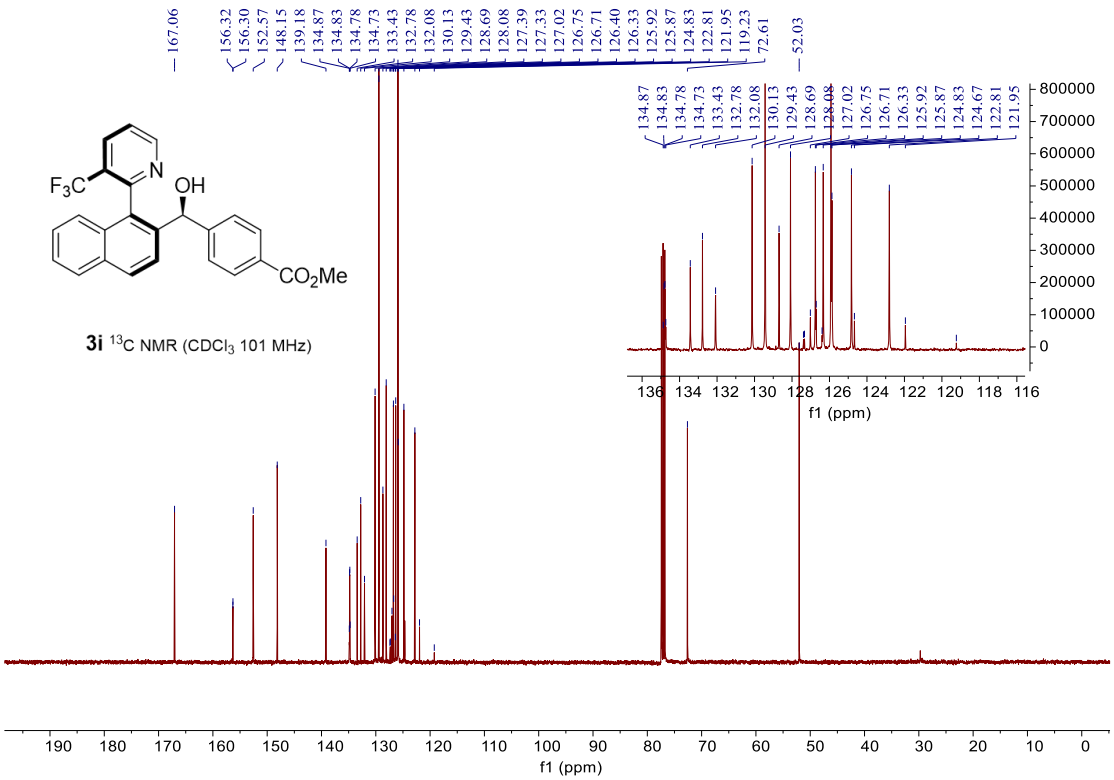
3h ^{1}H NMR ($CDCl_3$ 400 MHz)



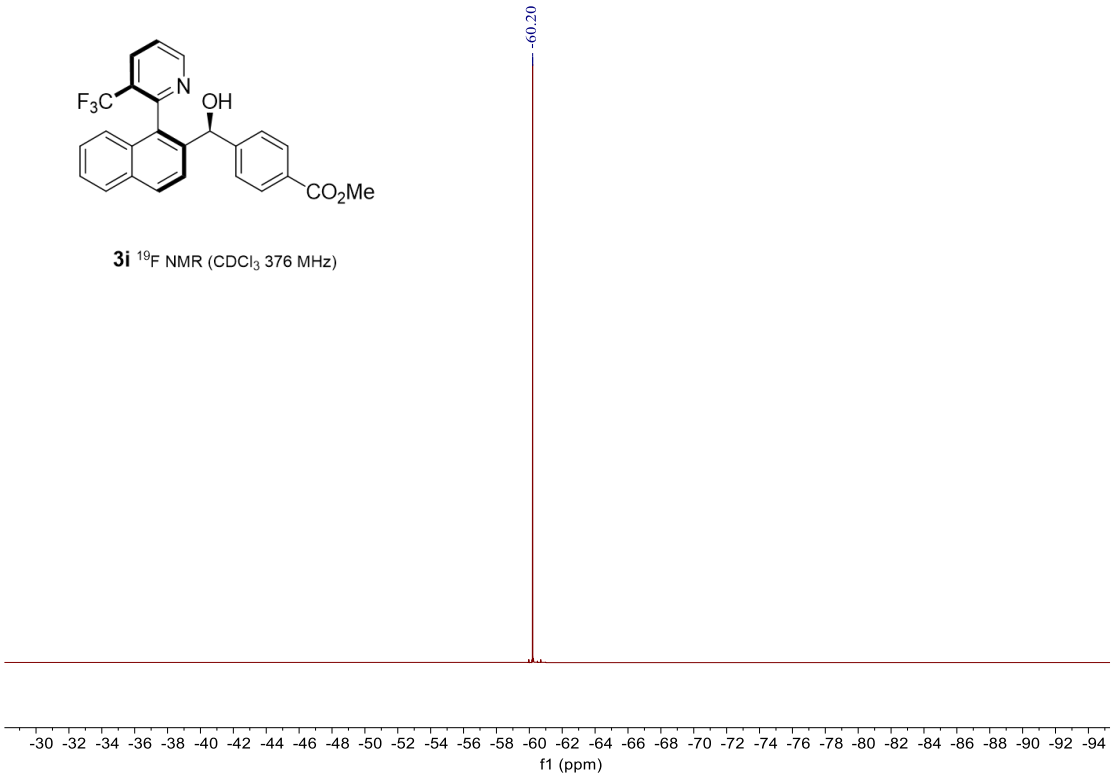
3h ^{13}C NMR ($CDCl_3$ 101 MHz)



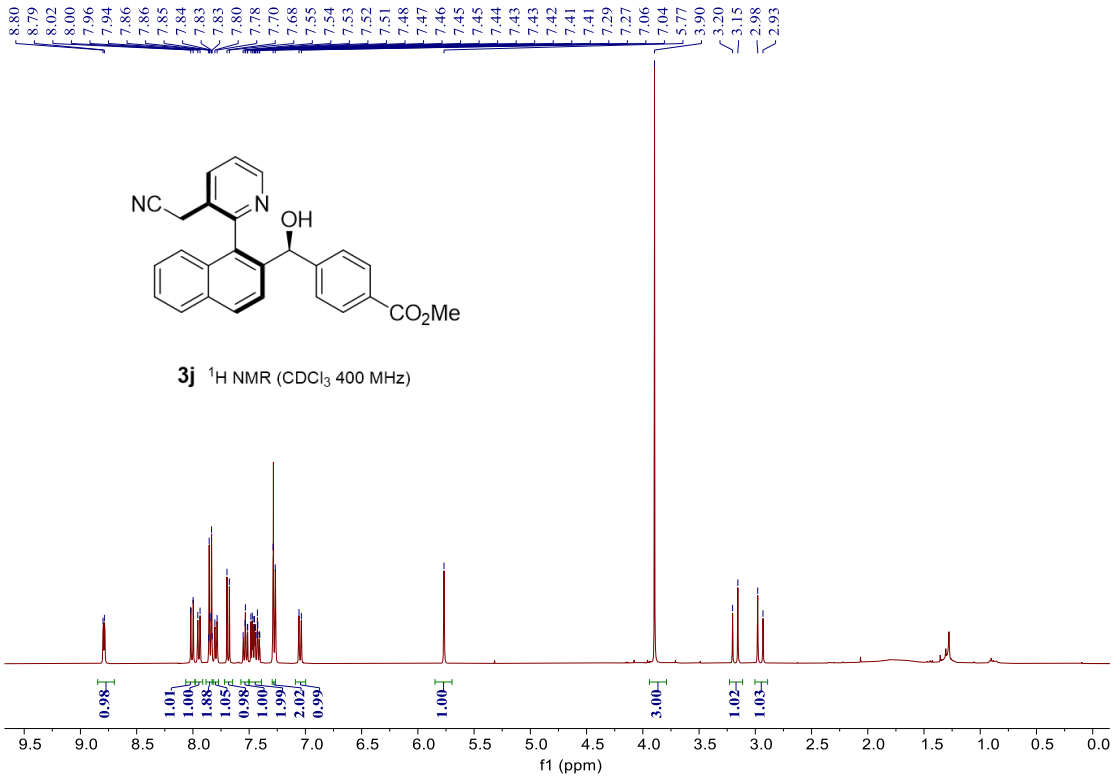
3i ^{1}H NMR ($CDCl_3$ 400 MHz)



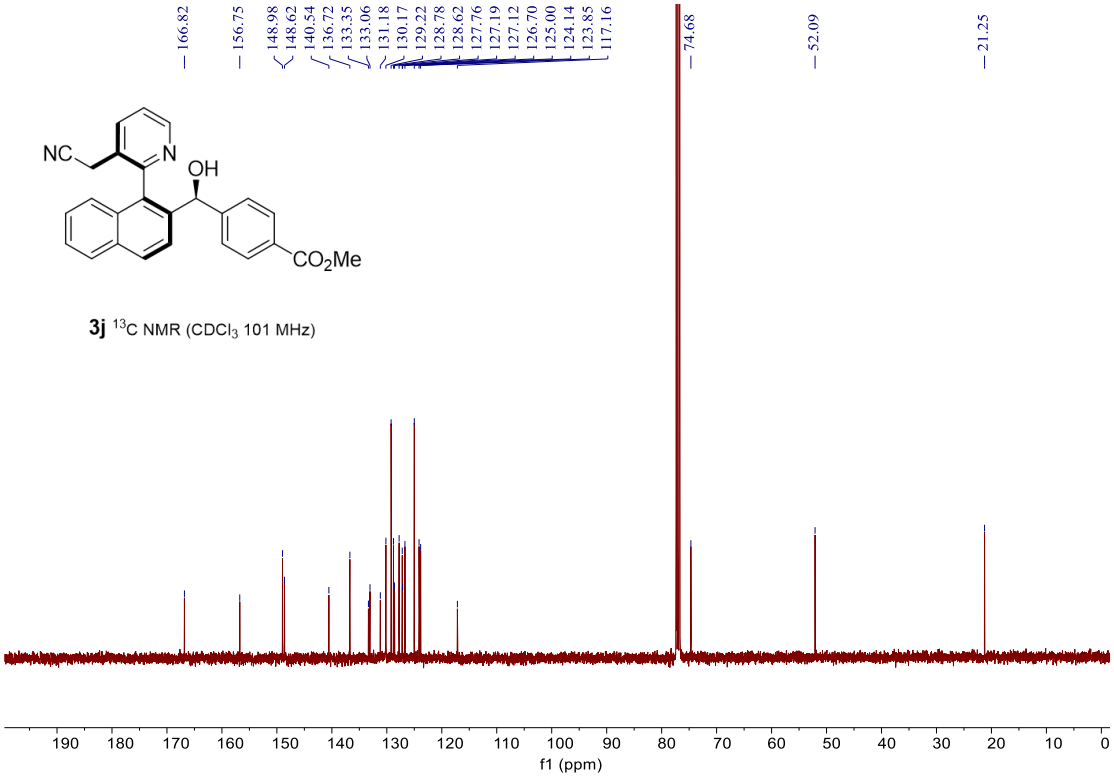
3i ^{13}C NMR ($CDCl_3$ 101 MHz)



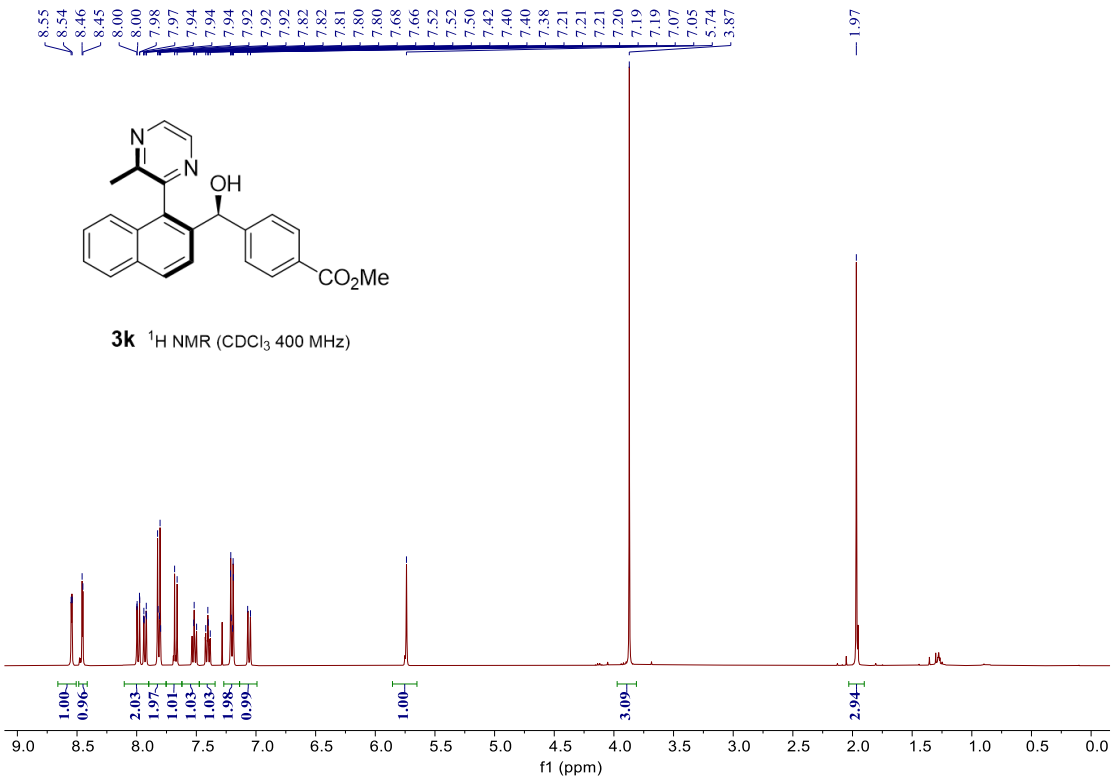
3i ^{19}F NMR ($CDCl_3$ 376 MHz)



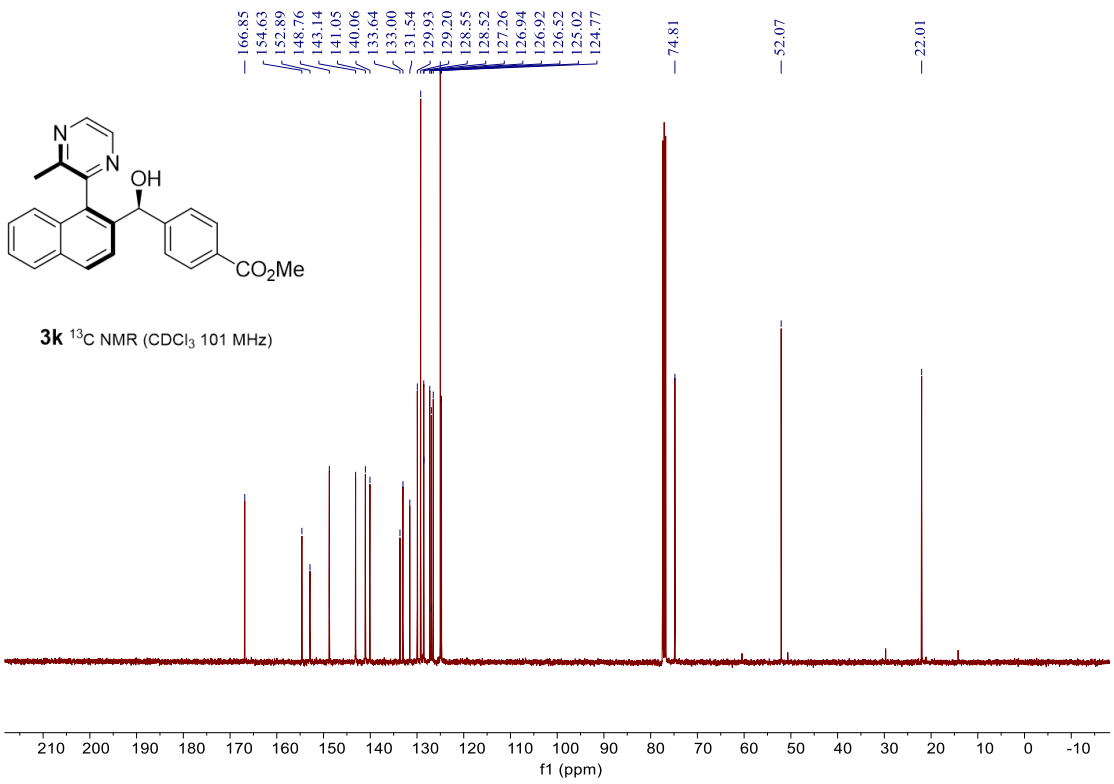
3j ^{1}H NMR ($CDCl_3$ 400 MHz)



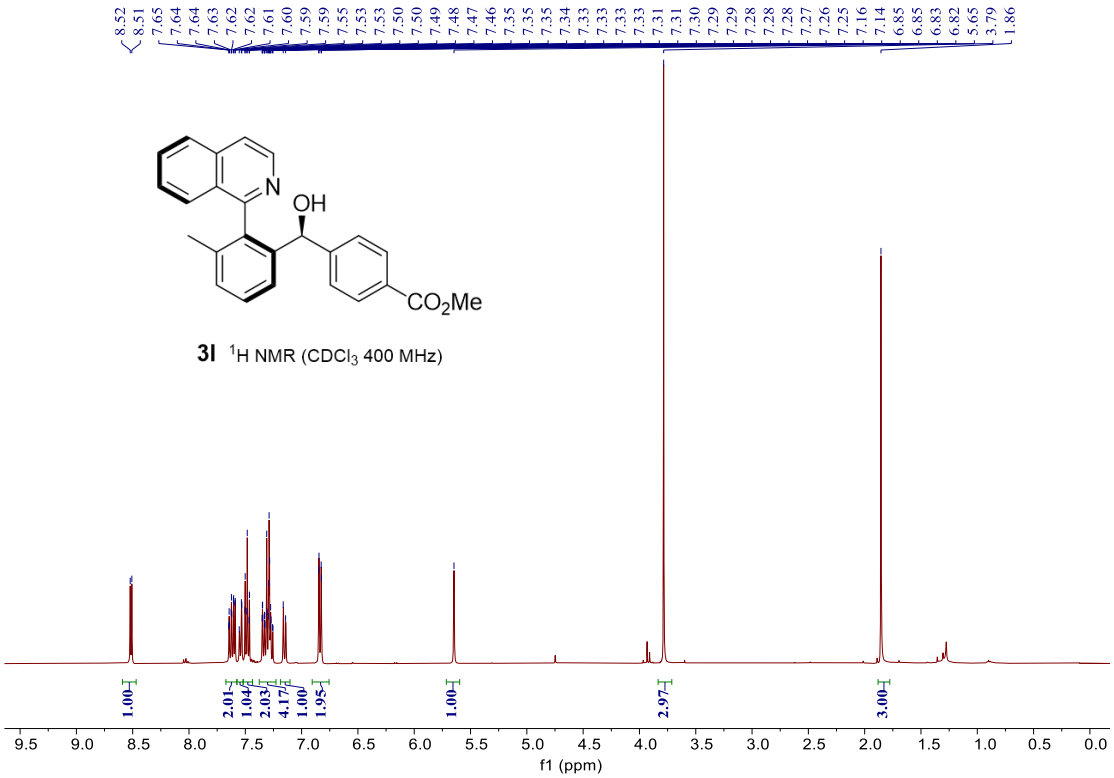
3j ^{13}C NMR ($CDCl_3$ 101 MHz)



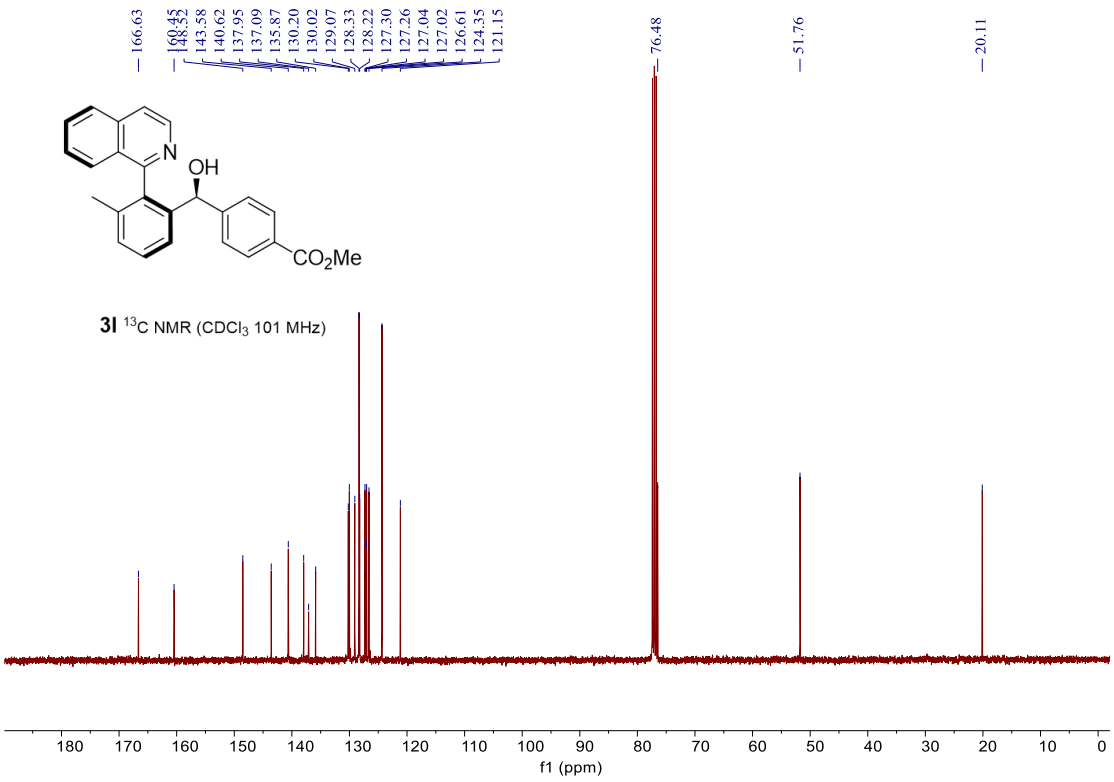
3k ^{1}H NMR ($CDCl_3$ 400 MHz)



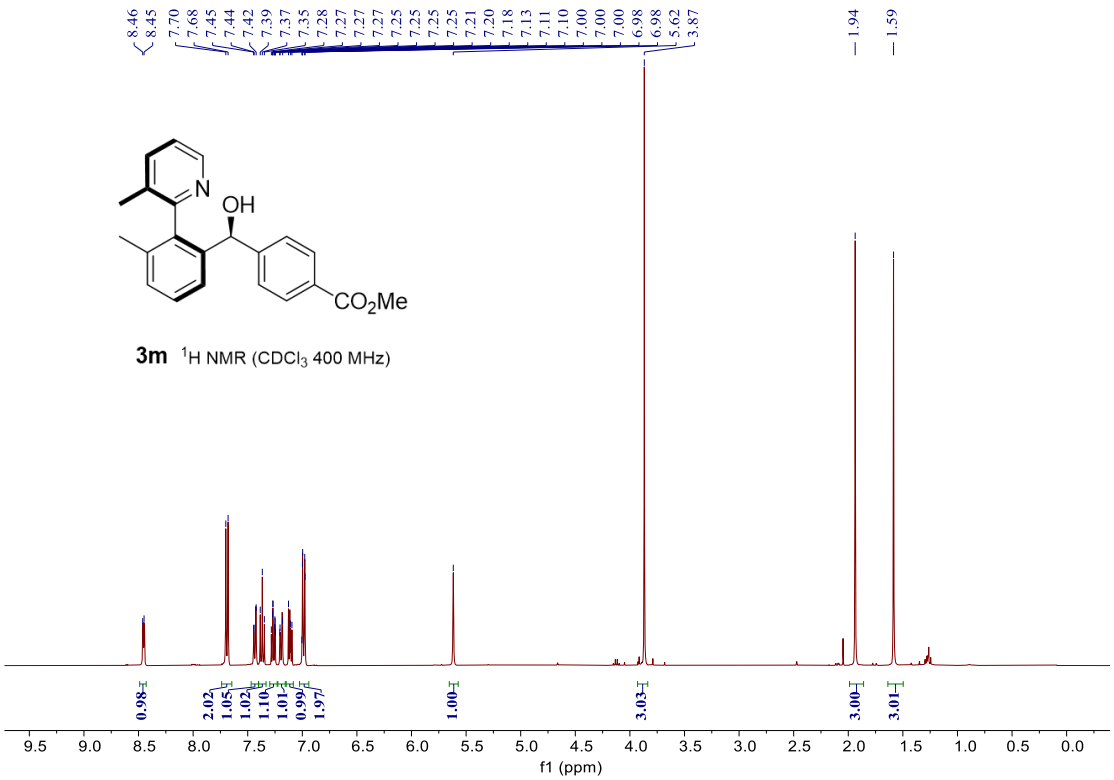
3k ^{13}C NMR ($CDCl_3$ 101 MHz)



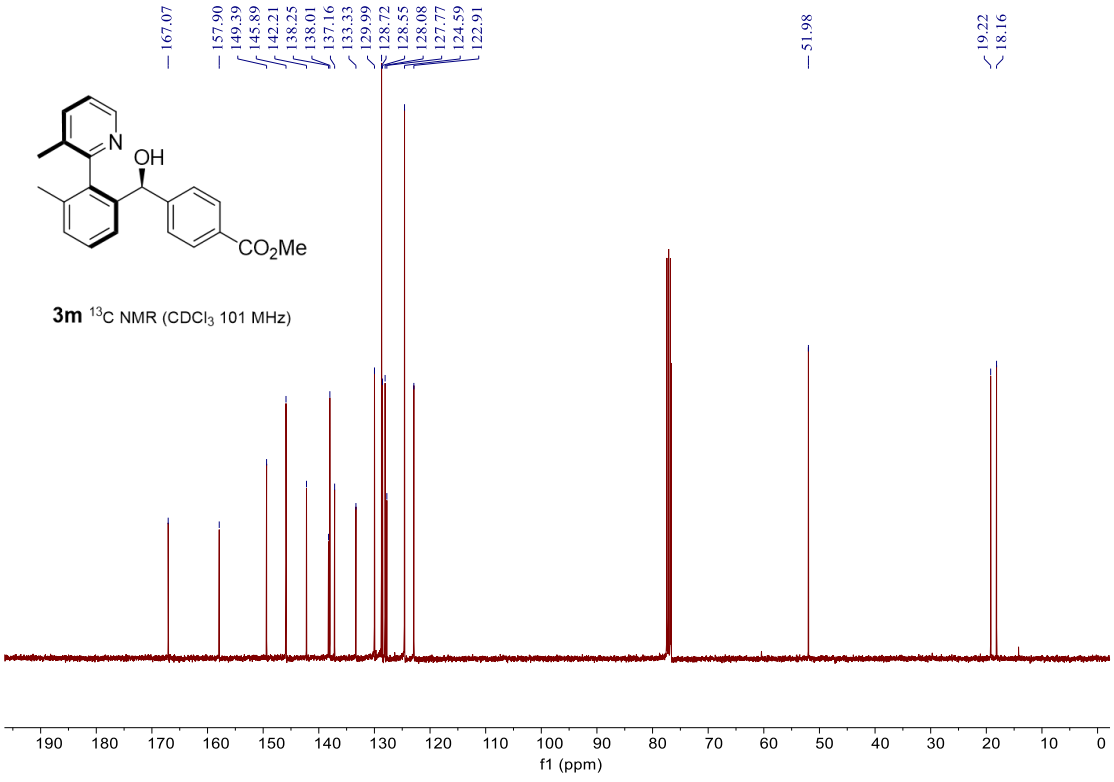
3l ^{1}H NMR ($CDCl_3$ 400 MHz)



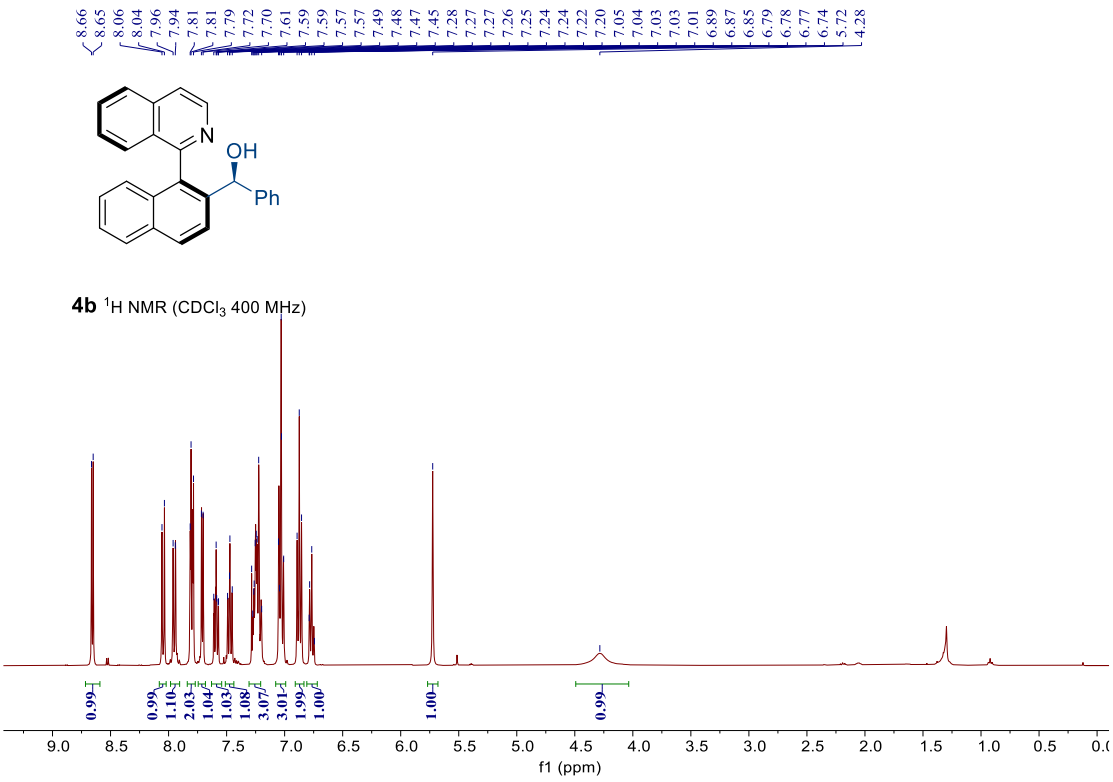
3l ^{13}C NMR ($CDCl_3$ 101 MHz)

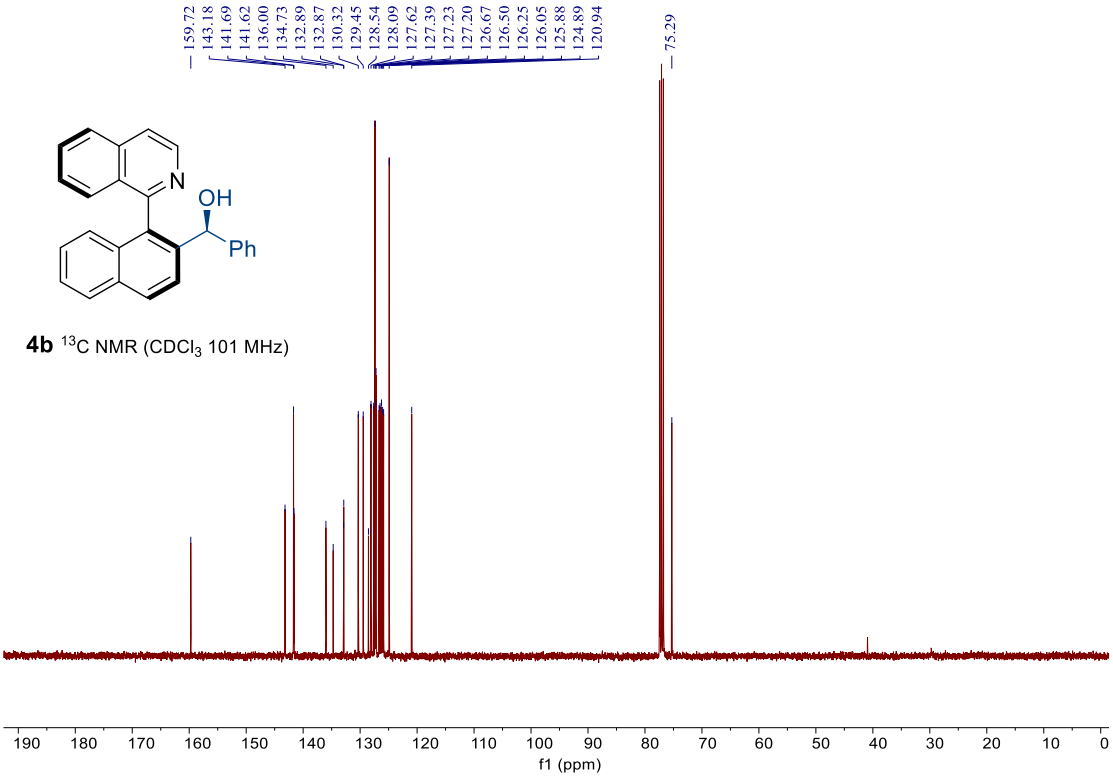


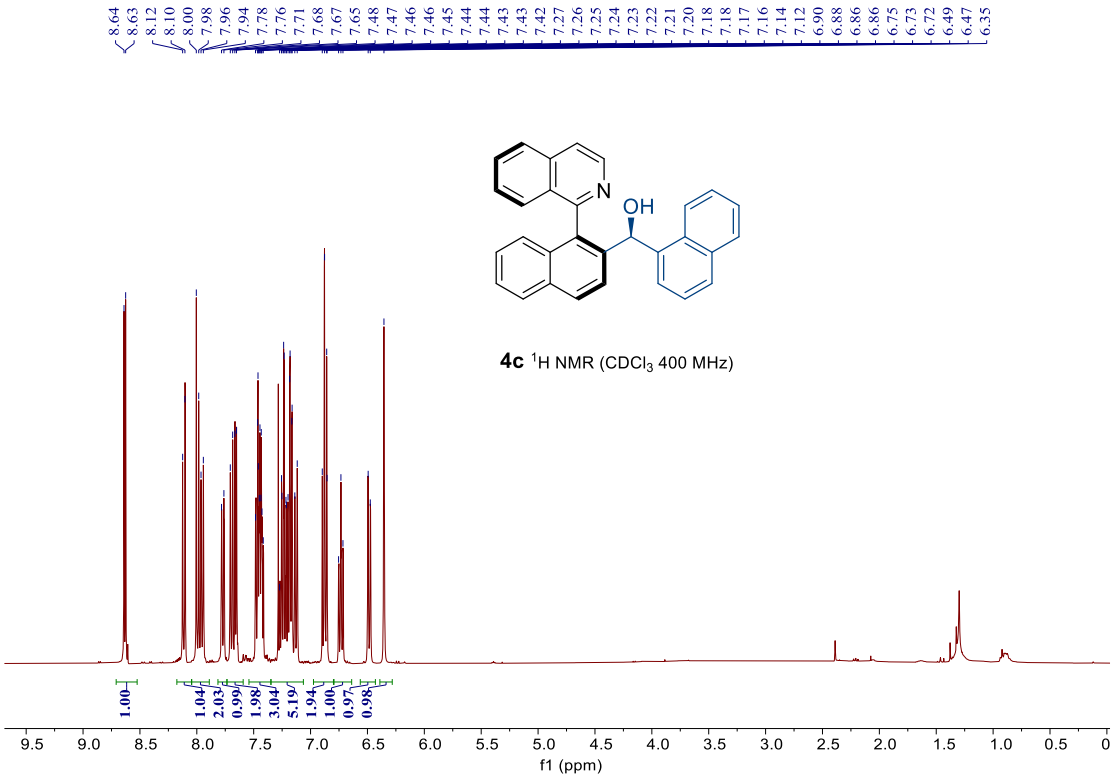
3m ^{1}H NMR ($CDCl_3$ 400 MHz)



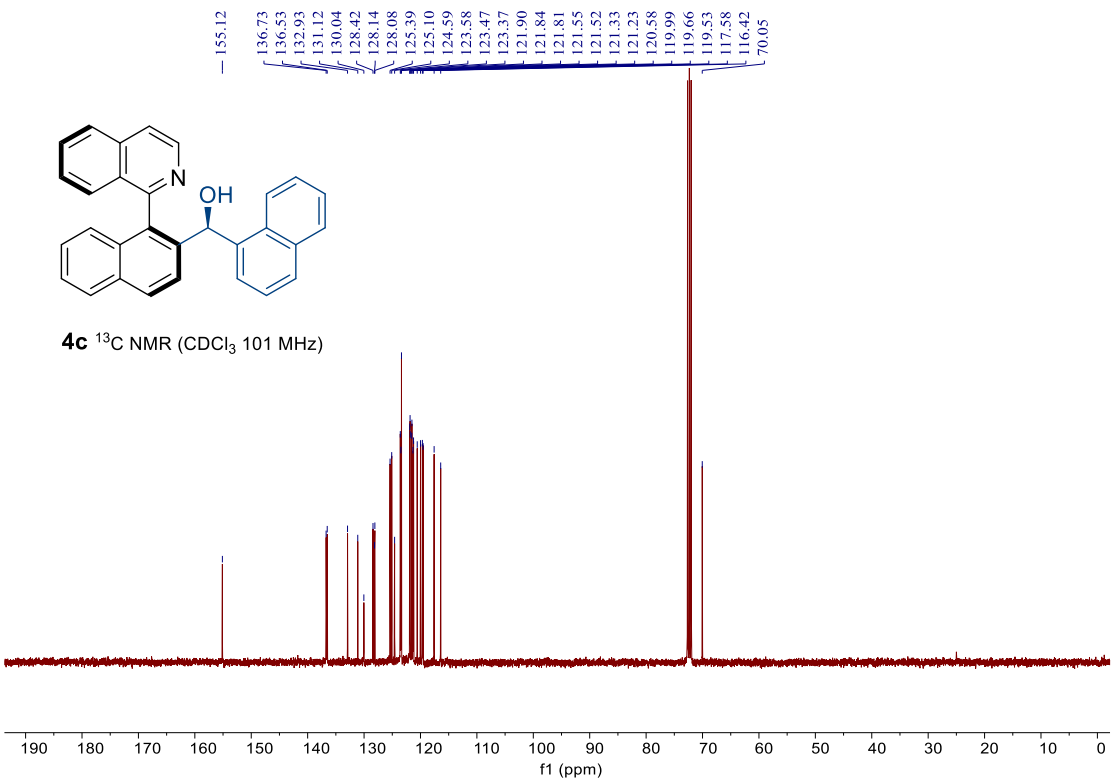
3m ^{13}C NMR ($CDCl_3$ 101 MHz)


8.66
8.65
8.06
8.04
7.96
7.94
7.81
7.81
7.79
7.72
7.70
7.61
7.59
7.59
7.57
7.57
7.49
7.48
7.47
7.45
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.22
7.20
7.05
7.04
7.03
7.03
7.01
6.89
6.87
6.85
6.79
6.78
6.77
6.74
5.72
4.28
N
OH
Ph
4b 1H NMR (CDCl3 400 MHz)
0.99
0.99
1.10
2.03
1.04
1.03
1.08
3.07
3.01
1.99
1.00
1.00
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

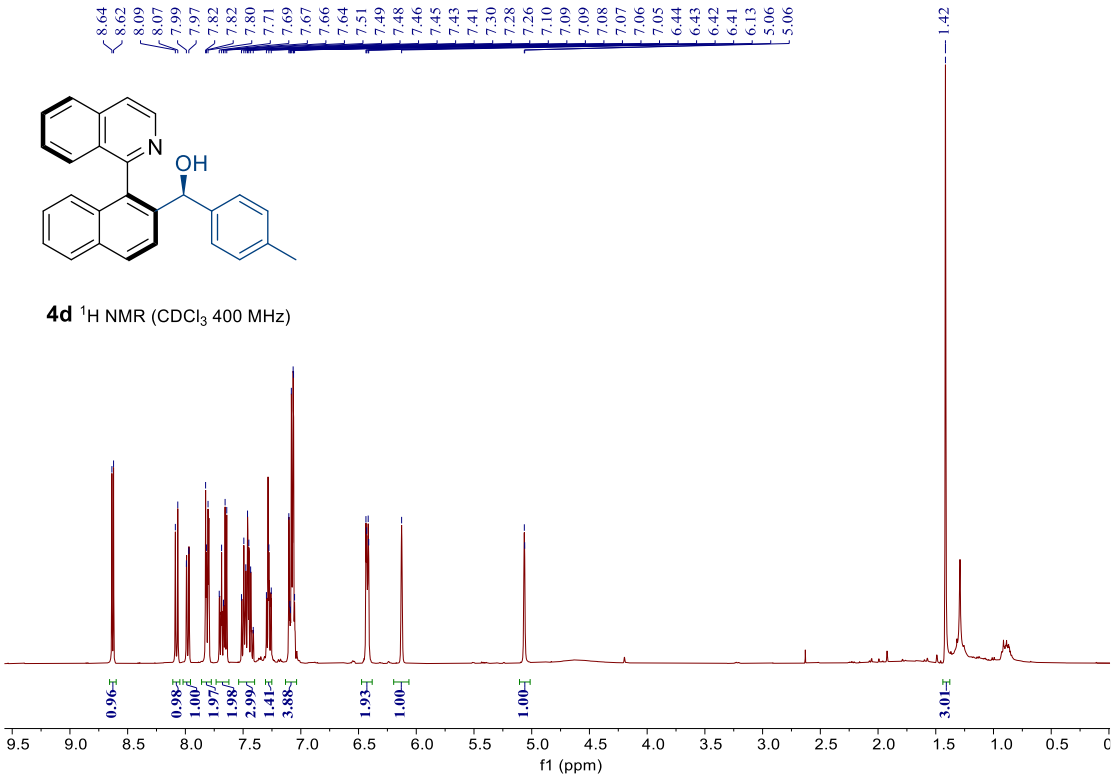

159.72
143.18
141.69
141.62
136.00
134.73
132.89
132.87
130.32
129.45
128.54
128.09
127.62
127.39
127.23
127.20
126.67
126.50
126.25
126.05
125.88
124.89
120.94
75.29
N
OH
Ph
4b 13C NMR (CDCl3 101 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



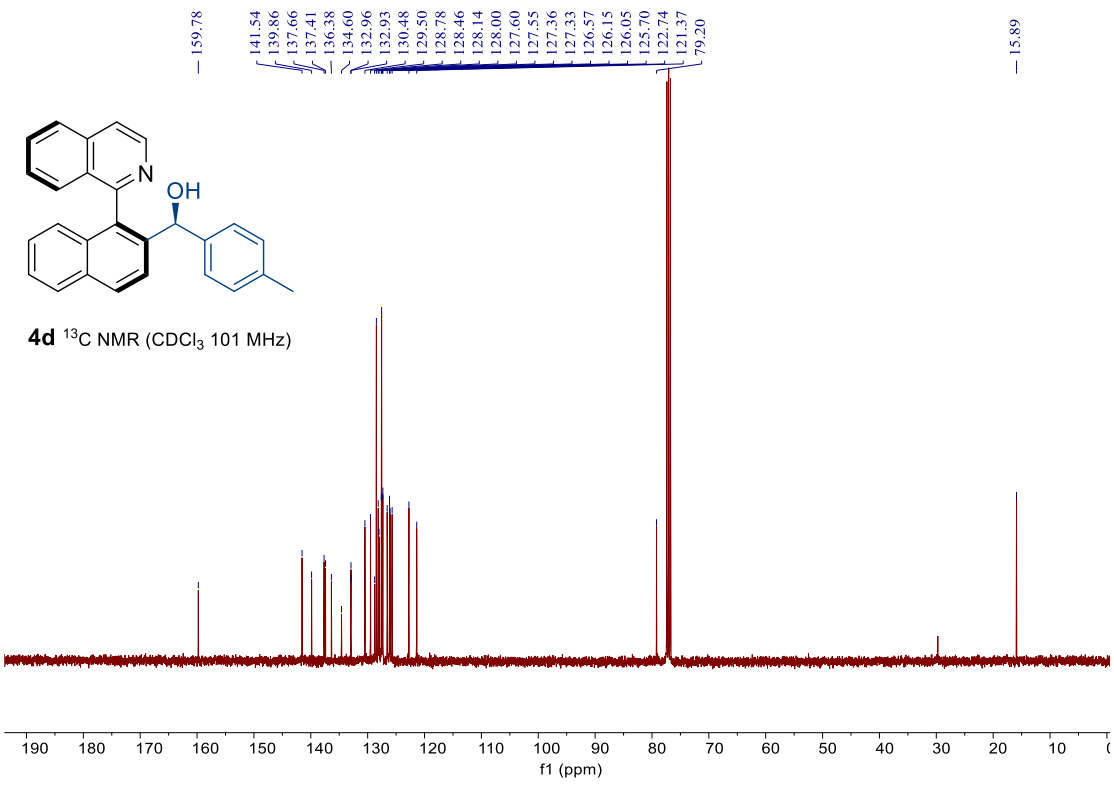
4c ^{1}H NMR ($CDCl_3$ 400 MHz)



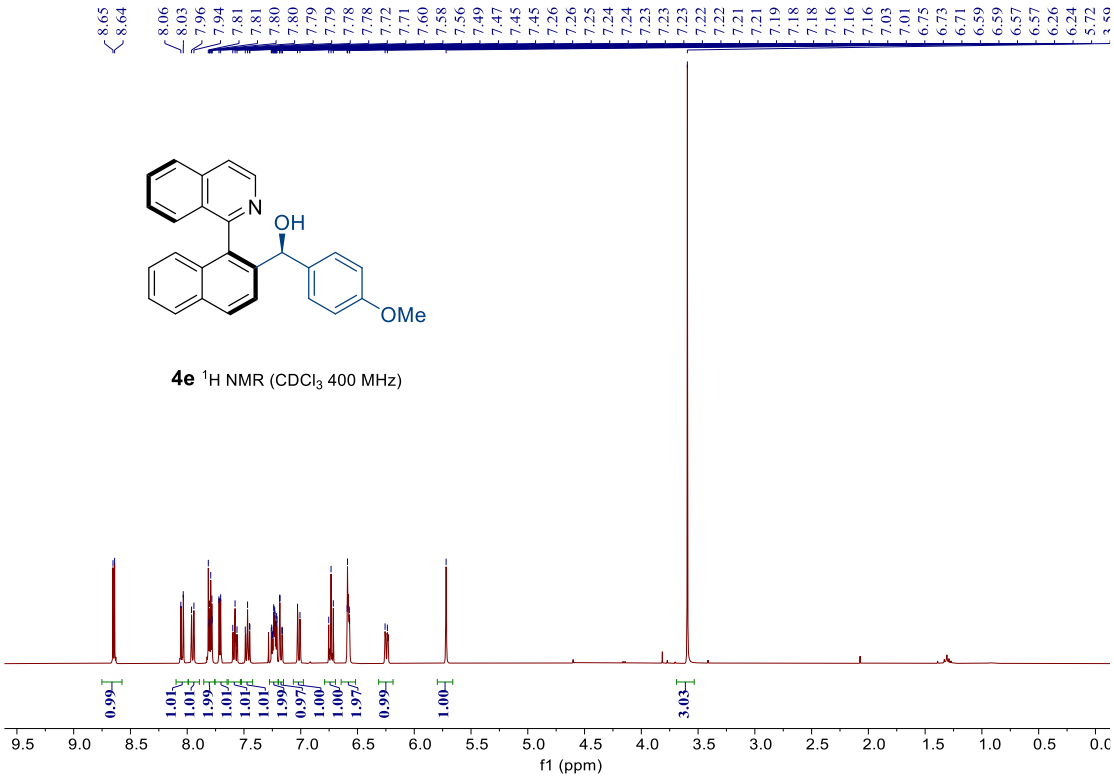
4c ^{13}C NMR ($CDCl_3$ 101 MHz)



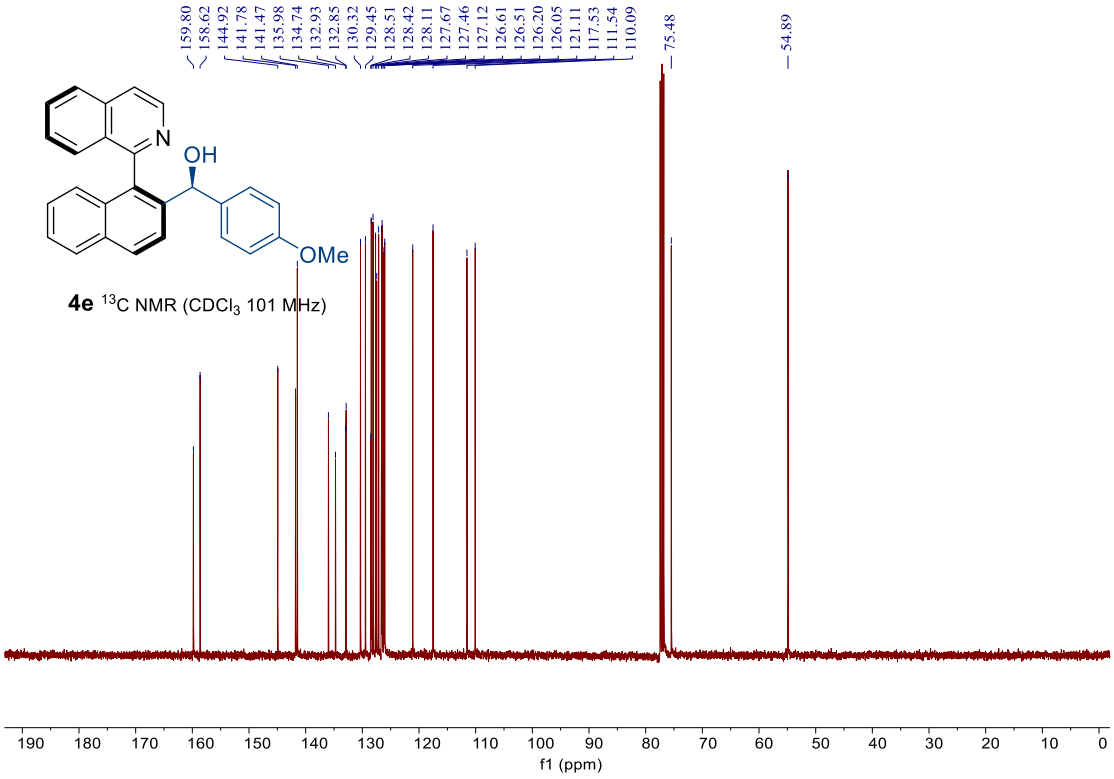
4d ^{1}H NMR ($CDCl_3$ 400 MHz)



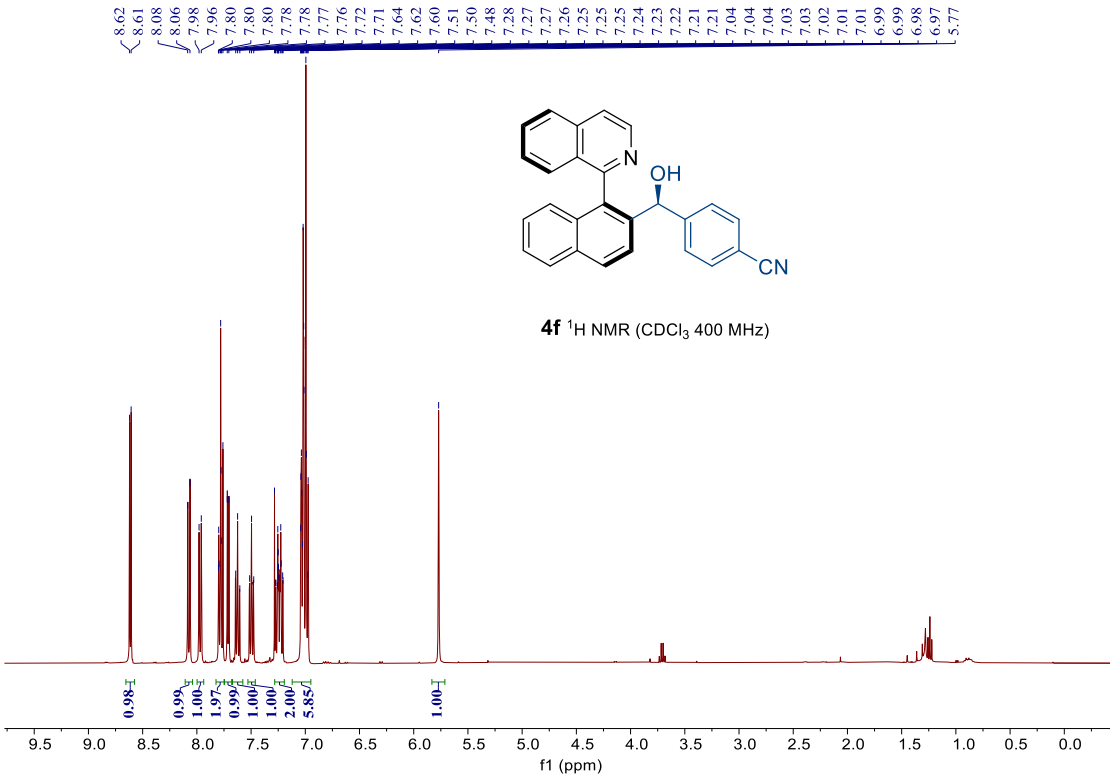
4d ^{13}C NMR ($CDCl_3$ 101 MHz)



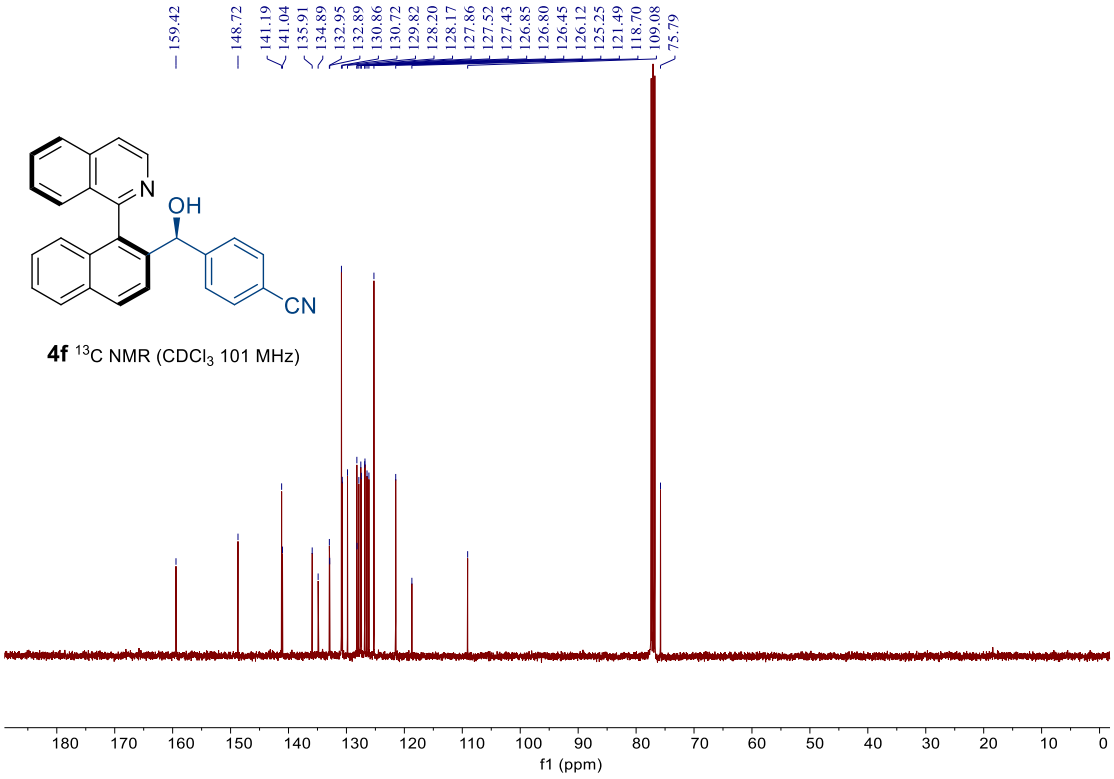
4e ^{1}H NMR ($CDCl_3$ 400 MHz)



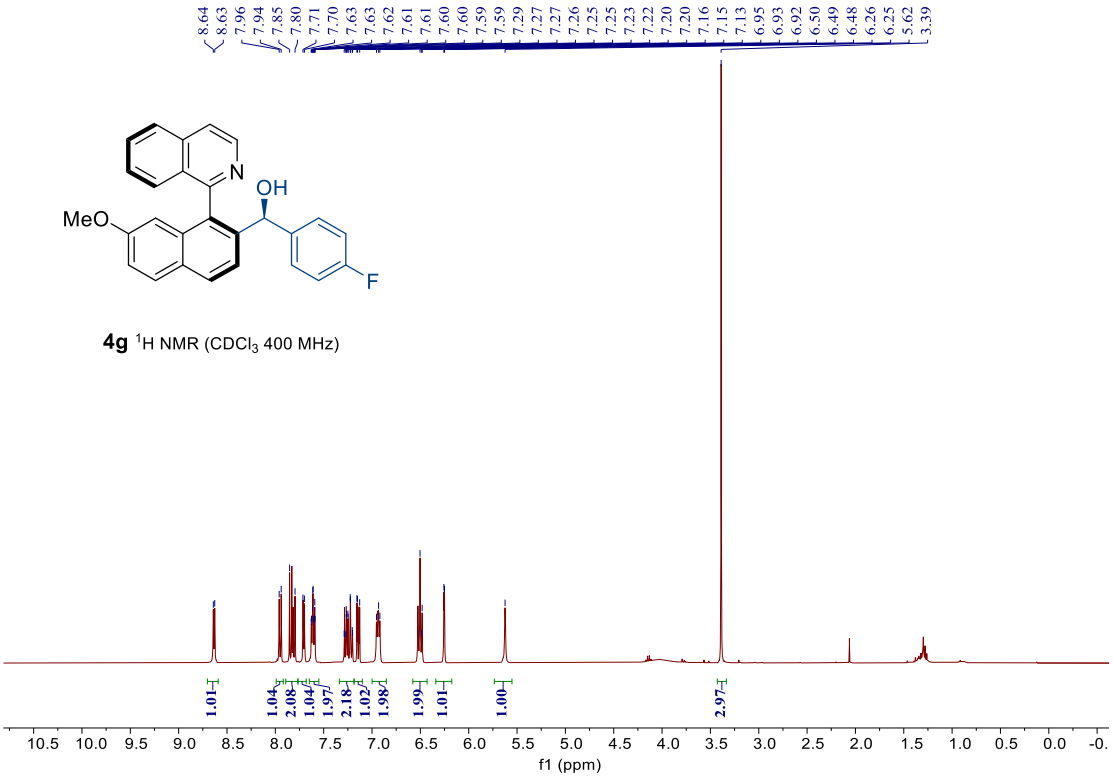
4e ^{13}C NMR ($CDCl_3$ 101 MHz)



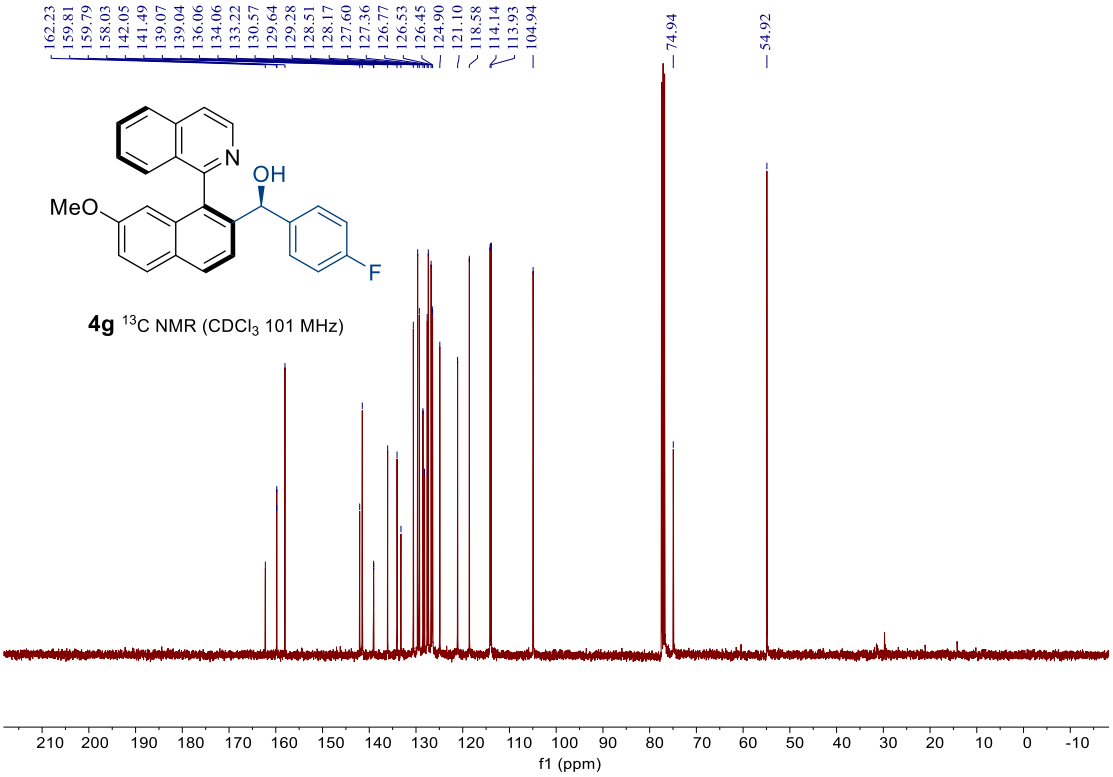
4f ^{1}H NMR ($CDCl_3$ 400 MHz)



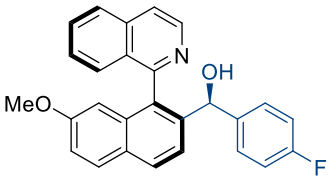
4f ^{13}C NMR ($CDCl_3$ 101 MHz)



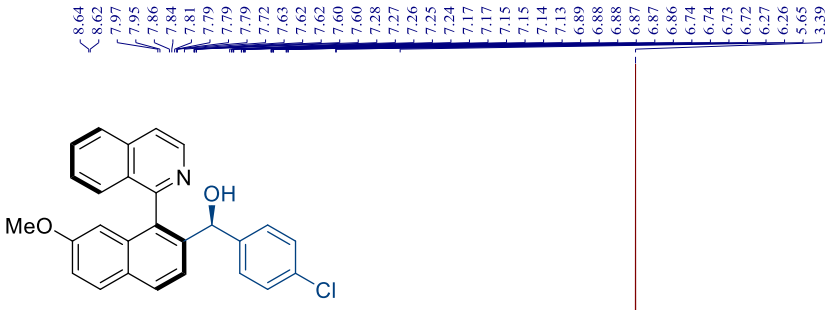
4g ^{1}H NMR ($CDCl_3$ 400 MHz)



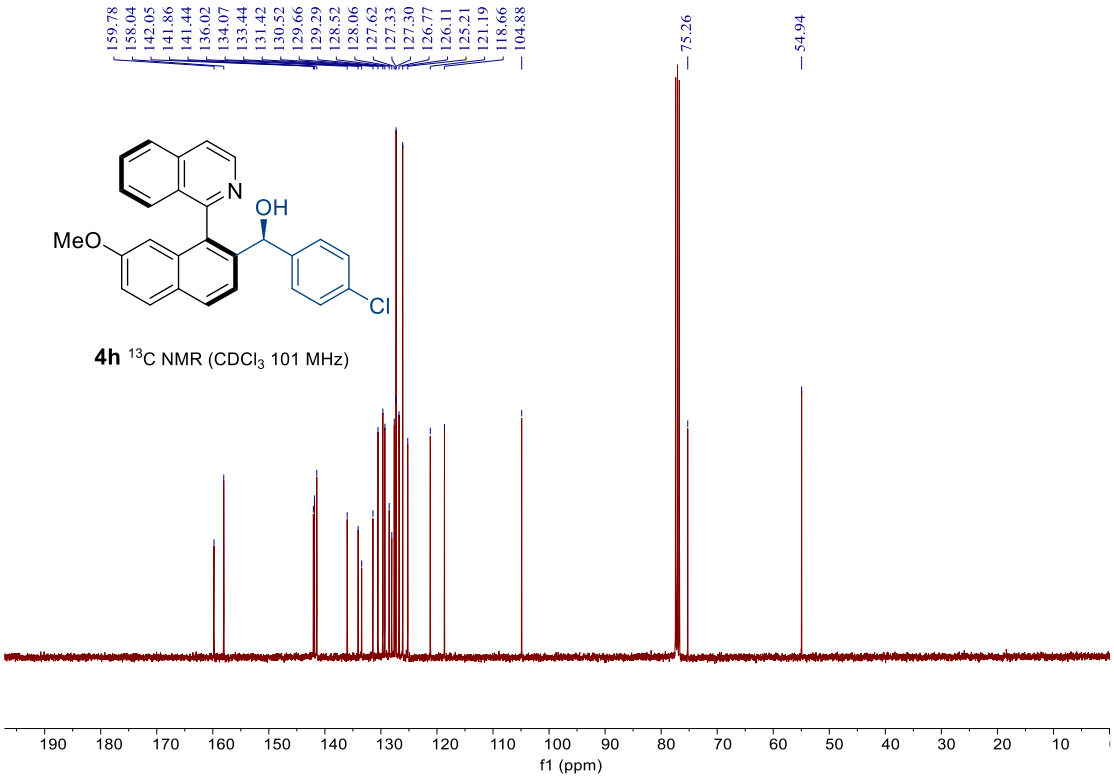
4g ^{13}C NMR ($CDCl_3$ 101 MHz)



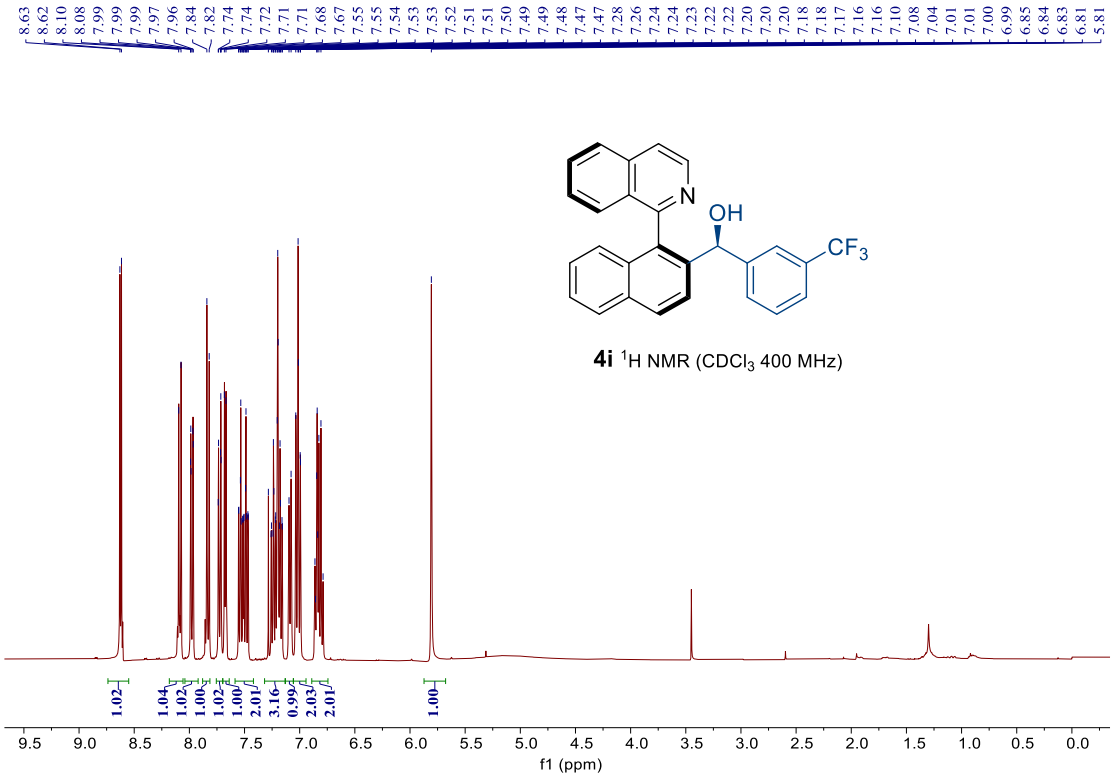
4g ^{19}F NMR ($CDCl_3$ 376 MHz)



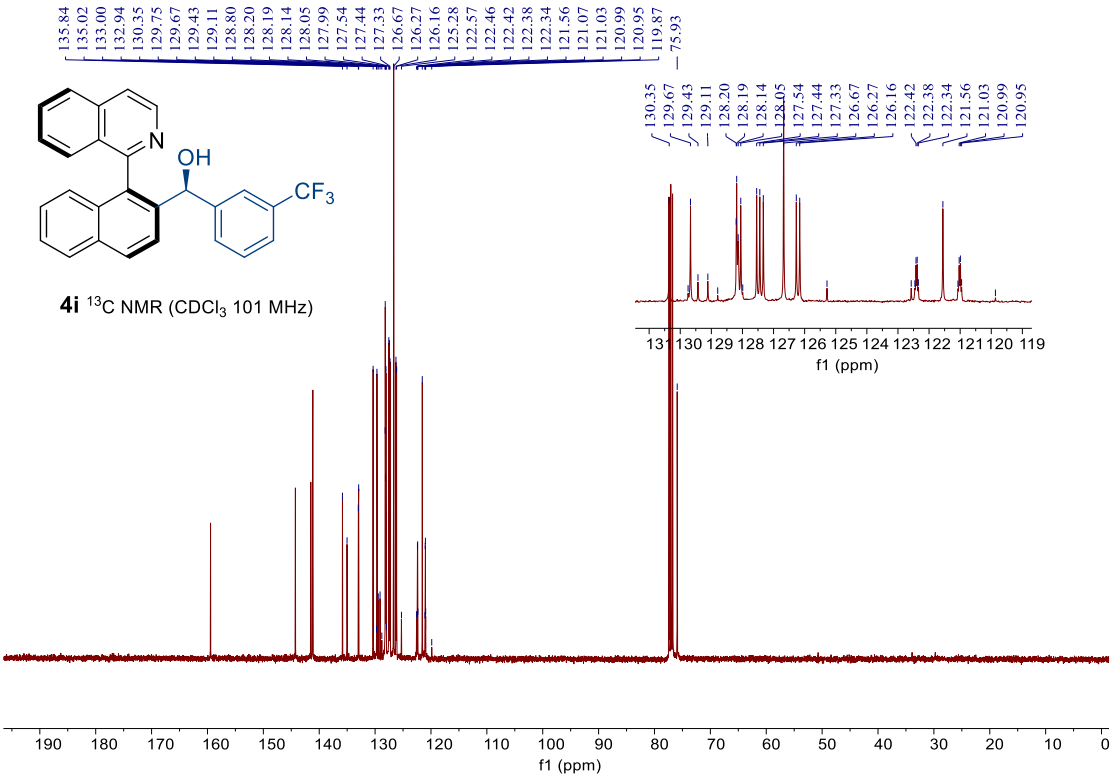
4h ^{1}H NMR ($CDCl_3$ 400 MHz)



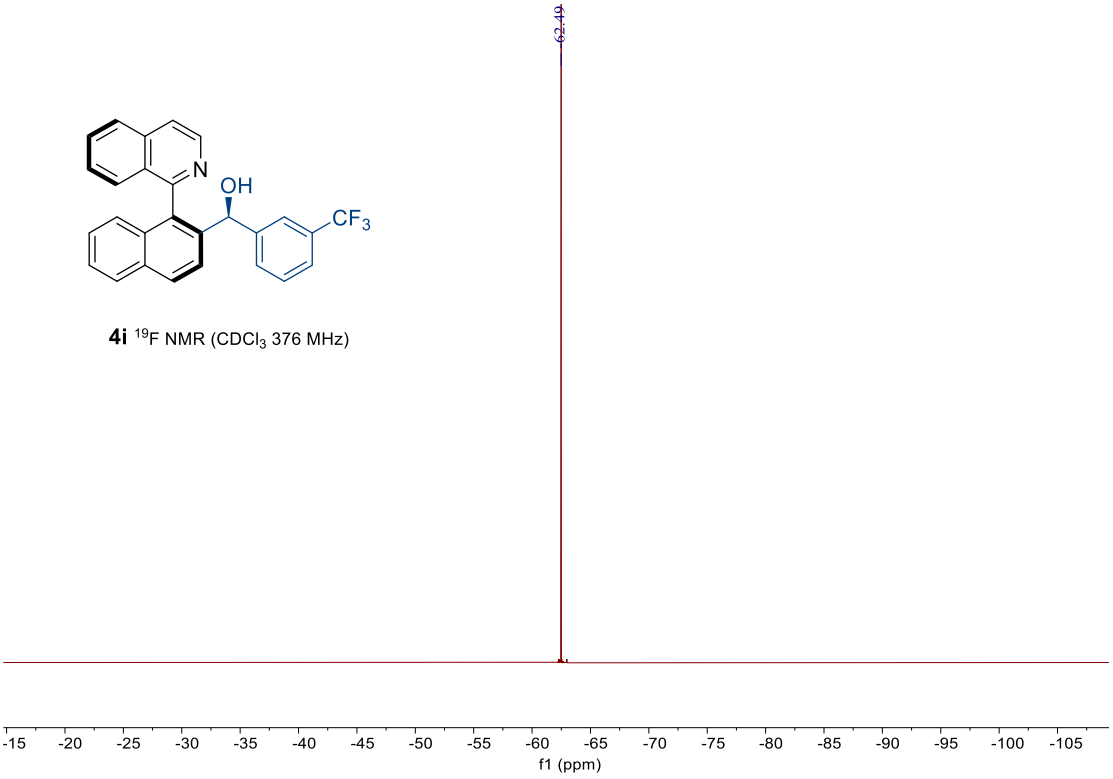
4h ^{13}C NMR ($CDCl_3$ 101 MHz)



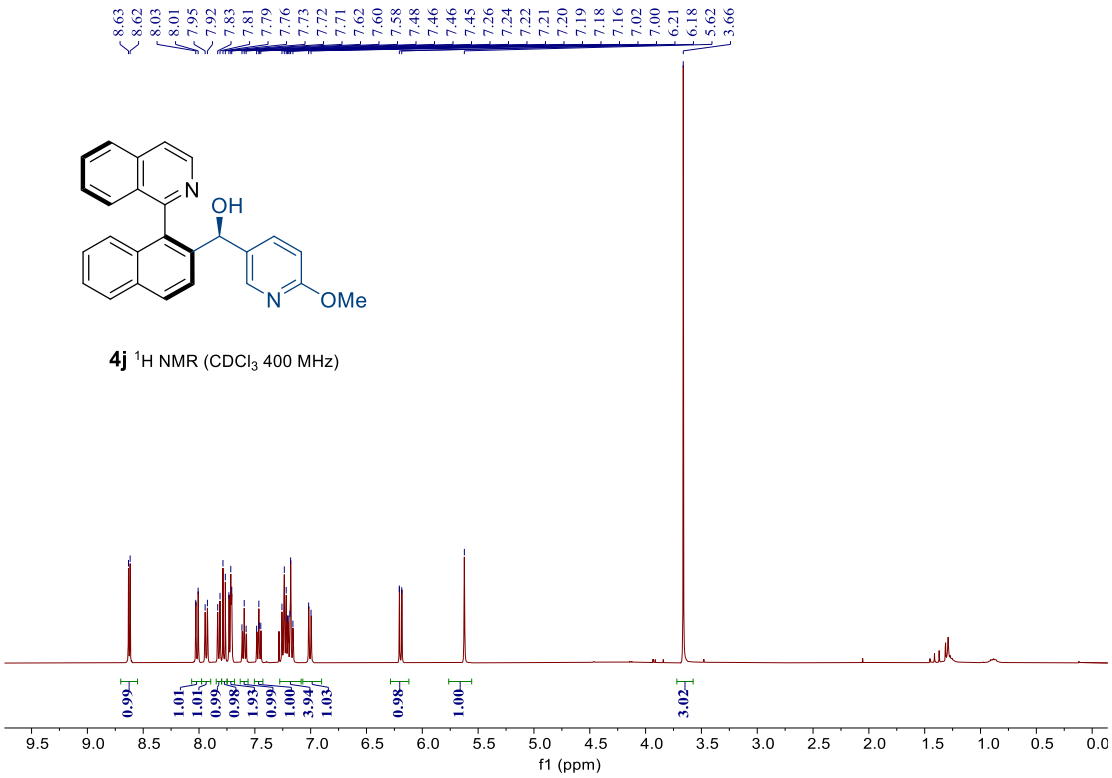
4i ^{1}H NMR ($CDCl_3$ 400 MHz)



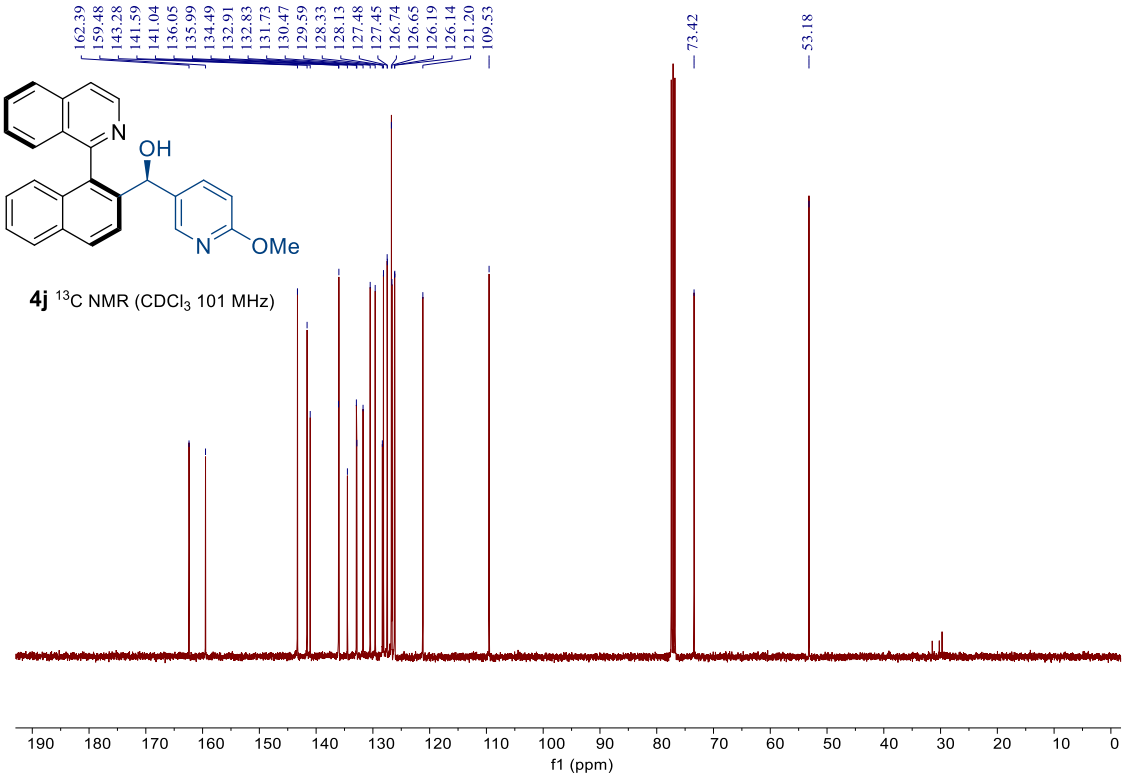
4i ^{13}C NMR ($CDCl_3$ 101 MHz)



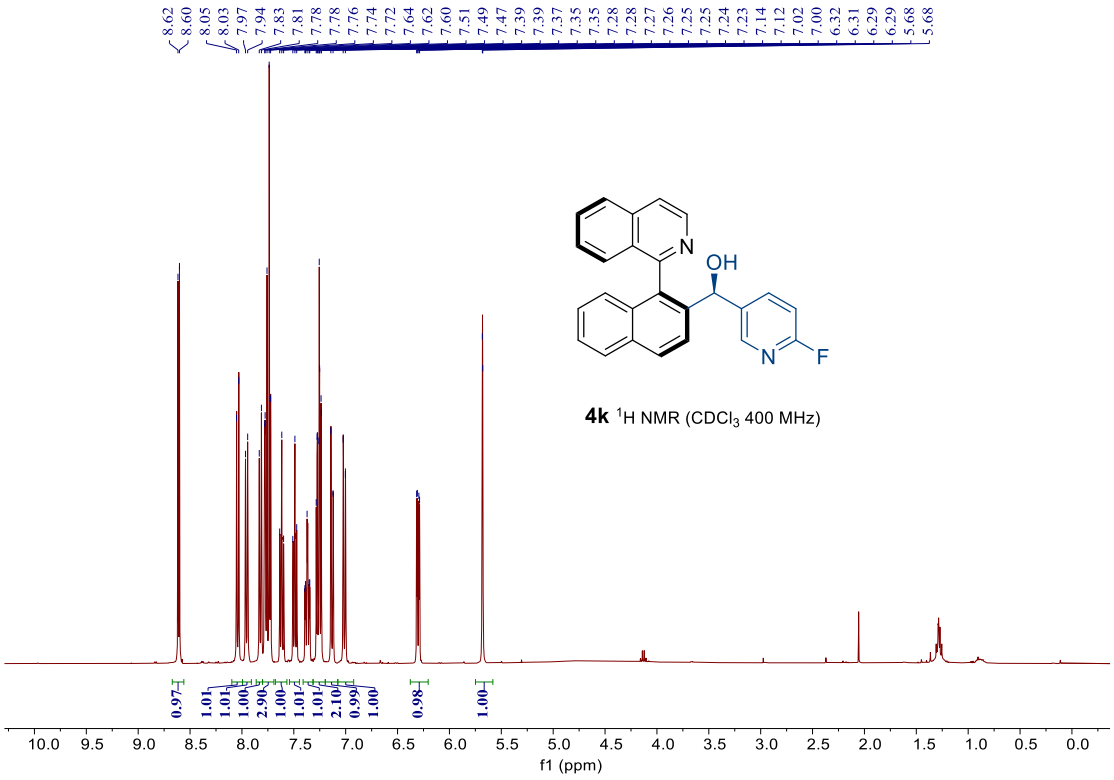
4i ^{19}F NMR ($CDCl_3$ 376 MHz)



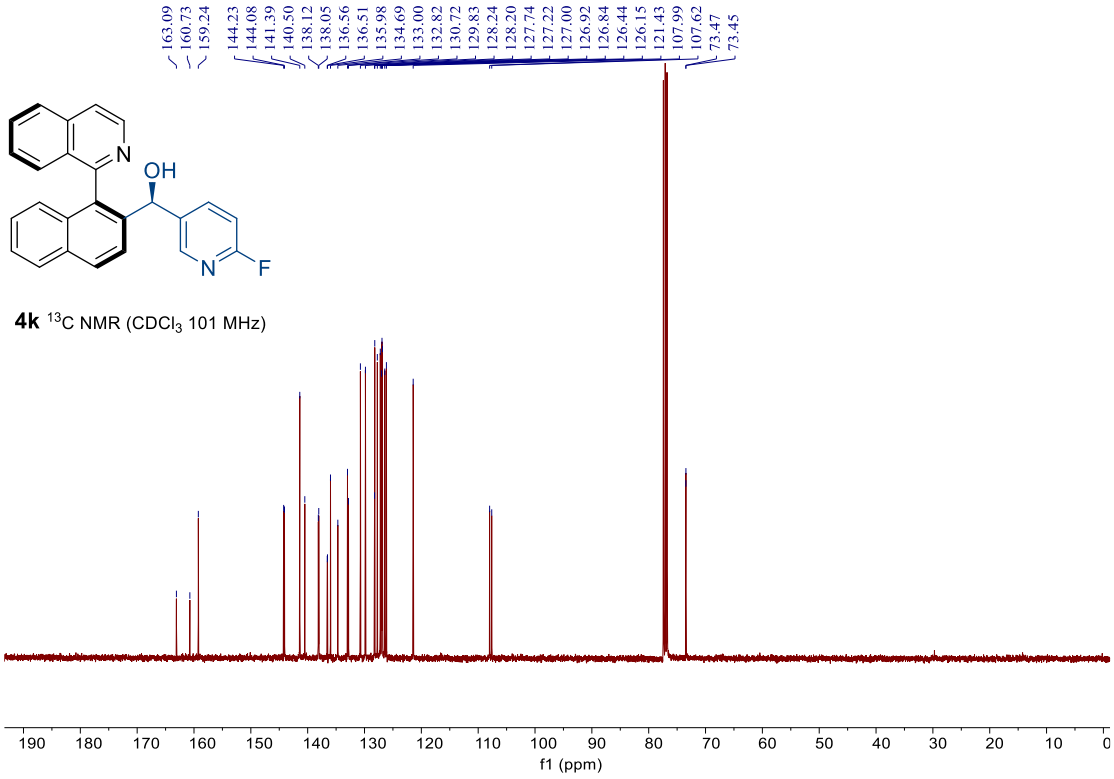
4j ^{1}H NMR ($CDCl_3$ 400 MHz)



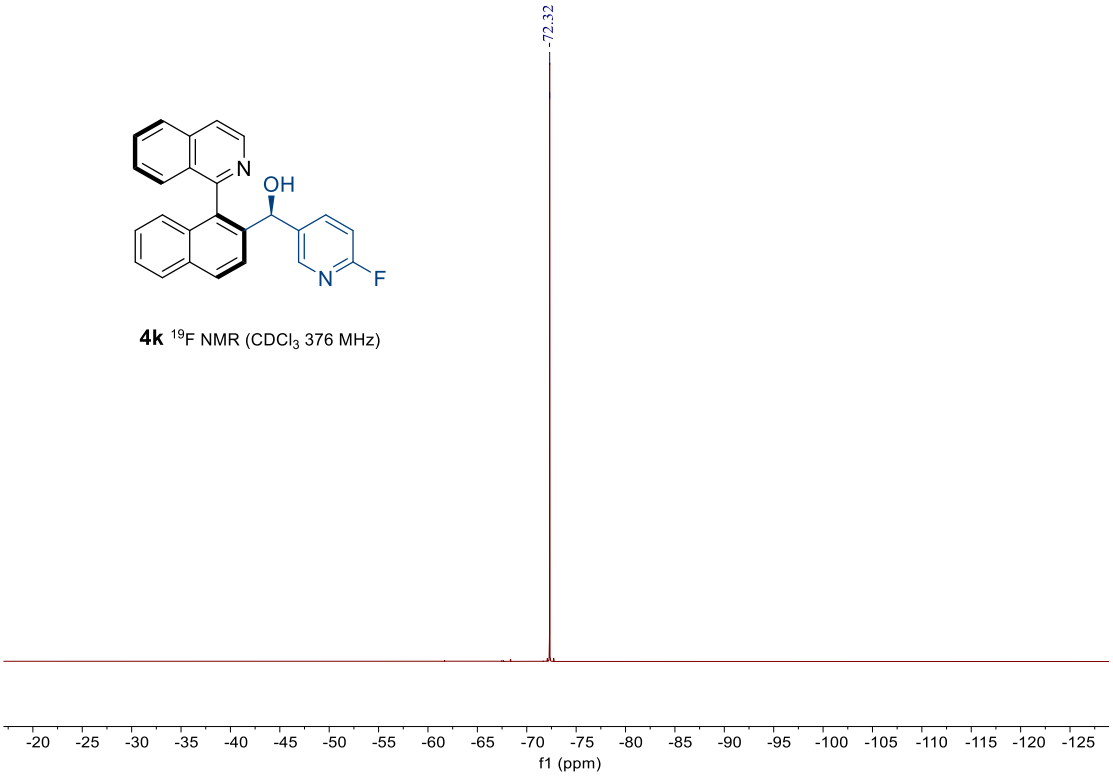
4j ^{13}C NMR ($CDCl_3$ 101 MHz)



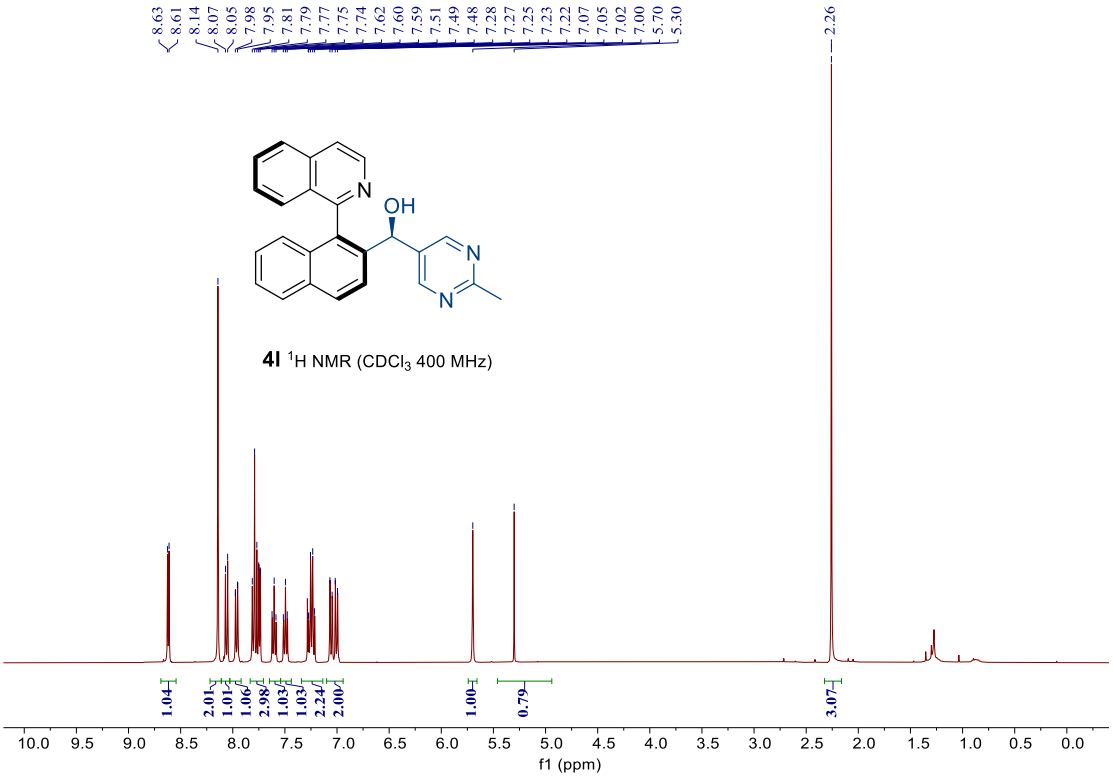
4k ^{1}H NMR ($CDCl_3$ 400 MHz)



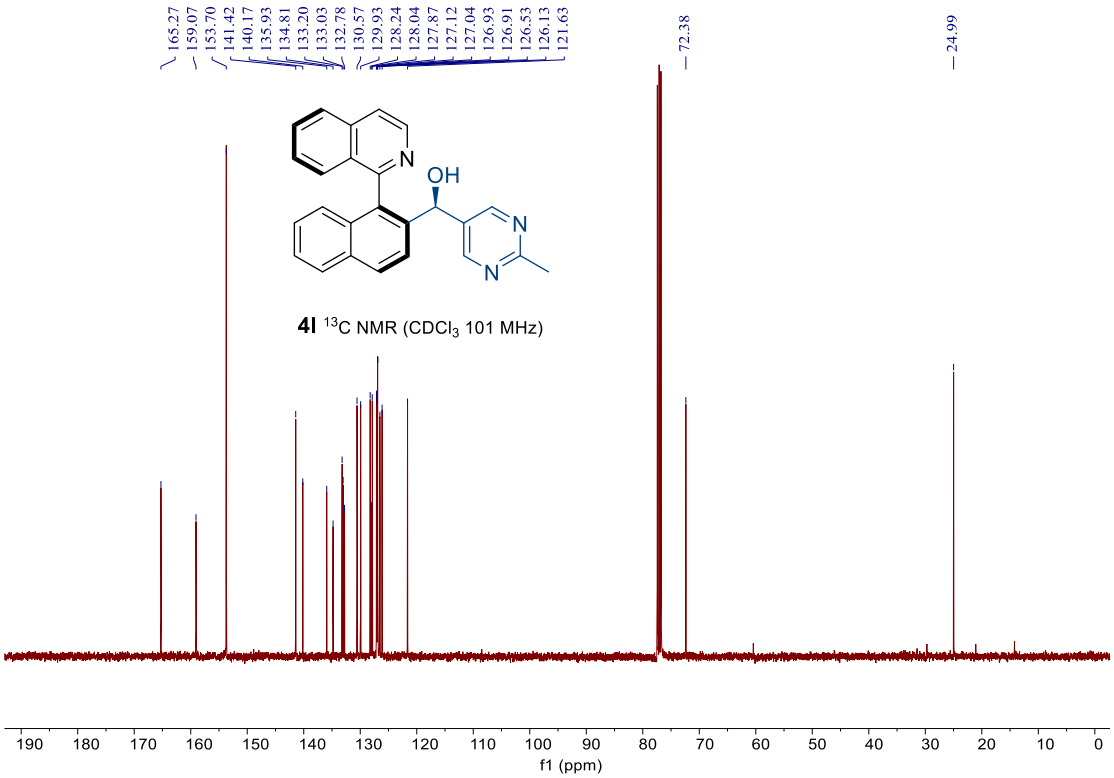
4k ^{13}C NMR ($CDCl_3$ 101 MHz)



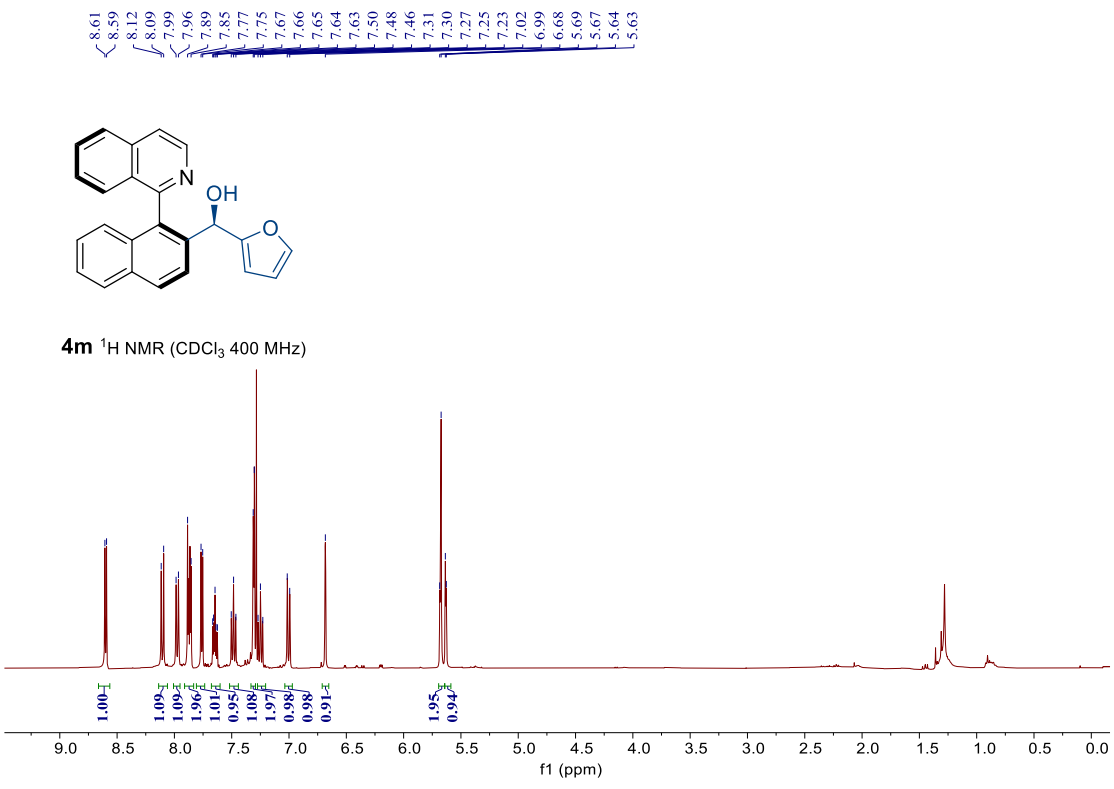
4k ^{19}F NMR ($CDCl_3$ 376 MHz)



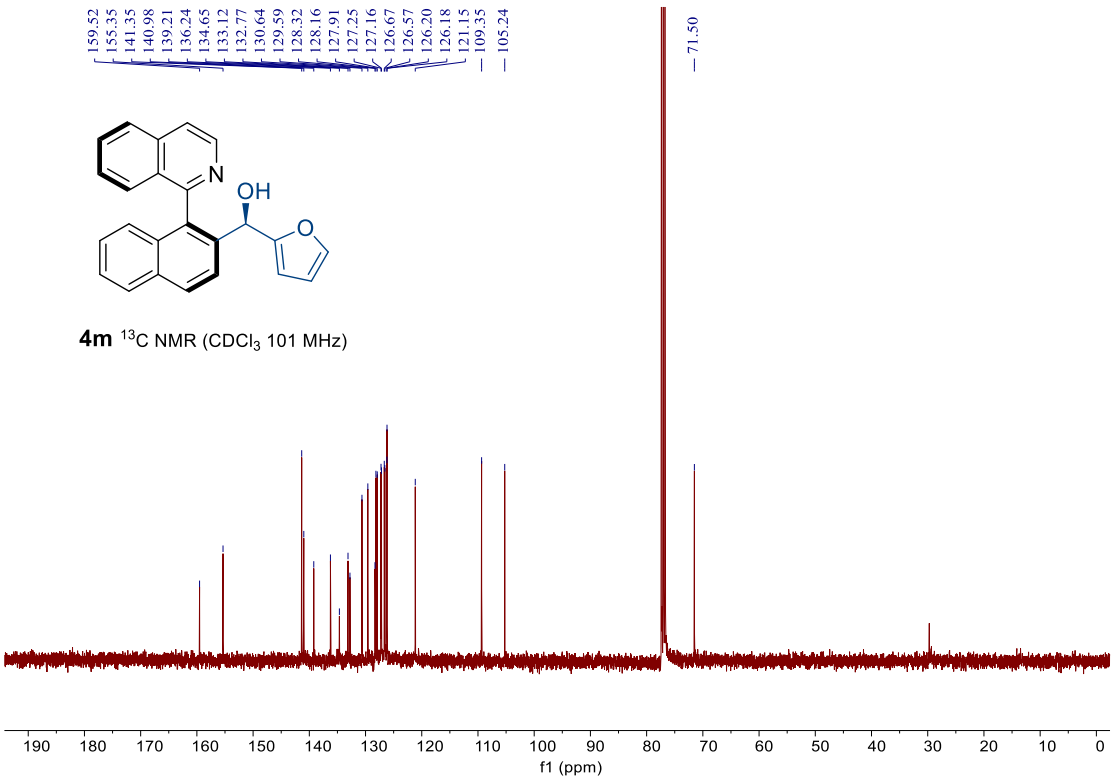
4l ^{1}H NMR ($CDCl_3$ 400 MHz)



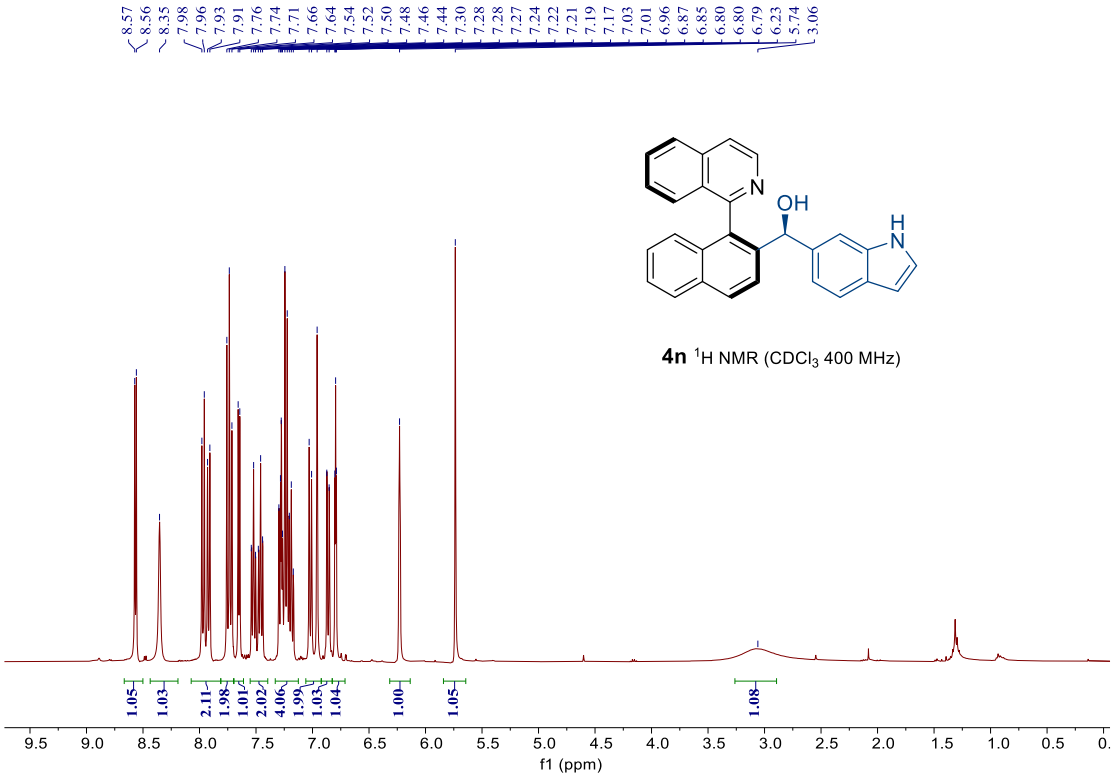
4l ^{13}C NMR ($CDCl_3$ 101 MHz)



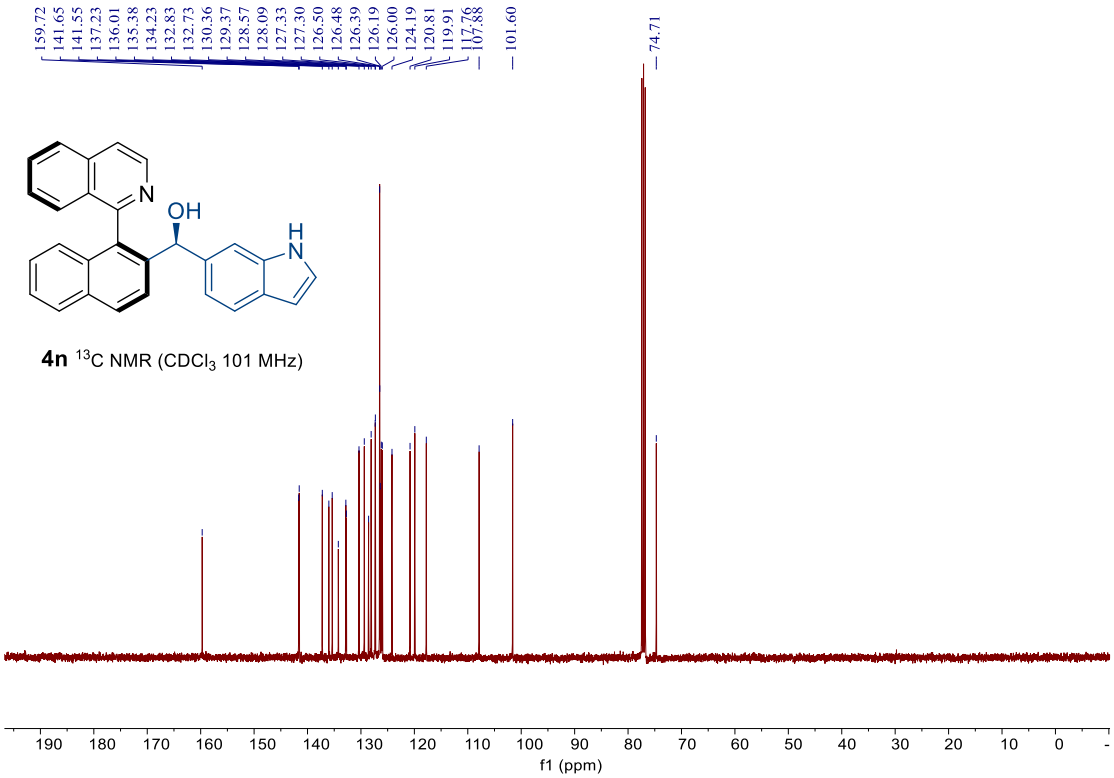
4m ^{1}H NMR ($CDCl_3$ 400 MHz)



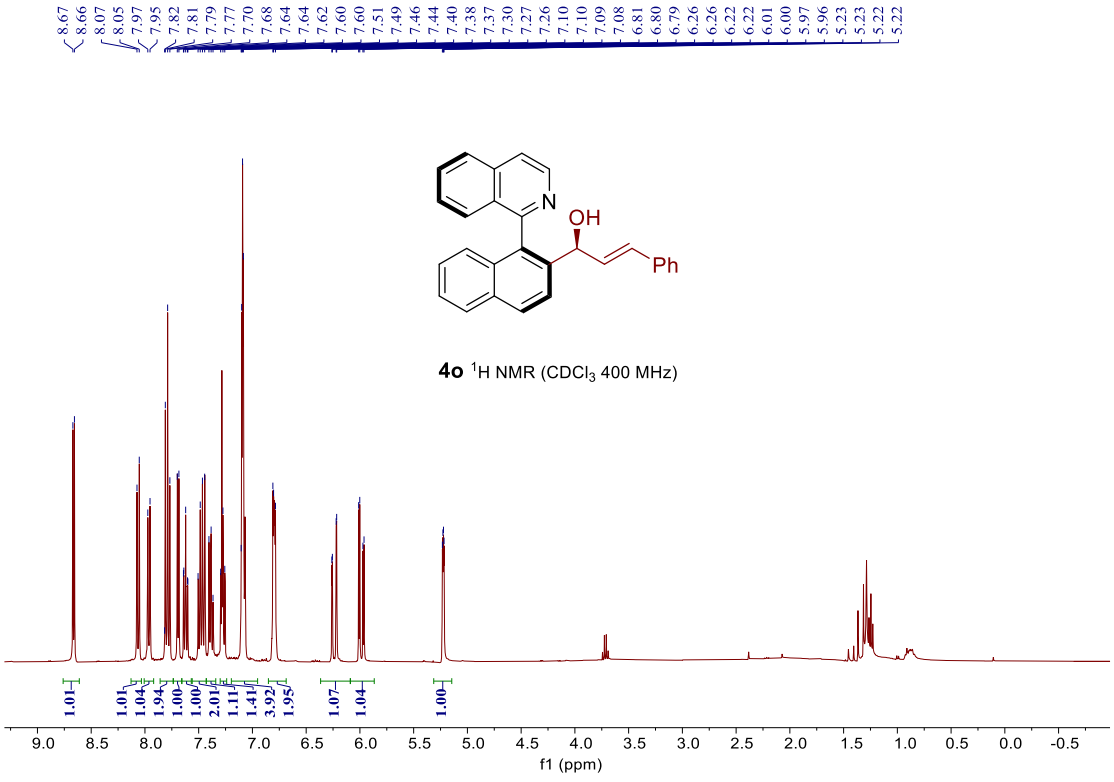
4m ^{13}C NMR ($CDCl_3$ 101 MHz)



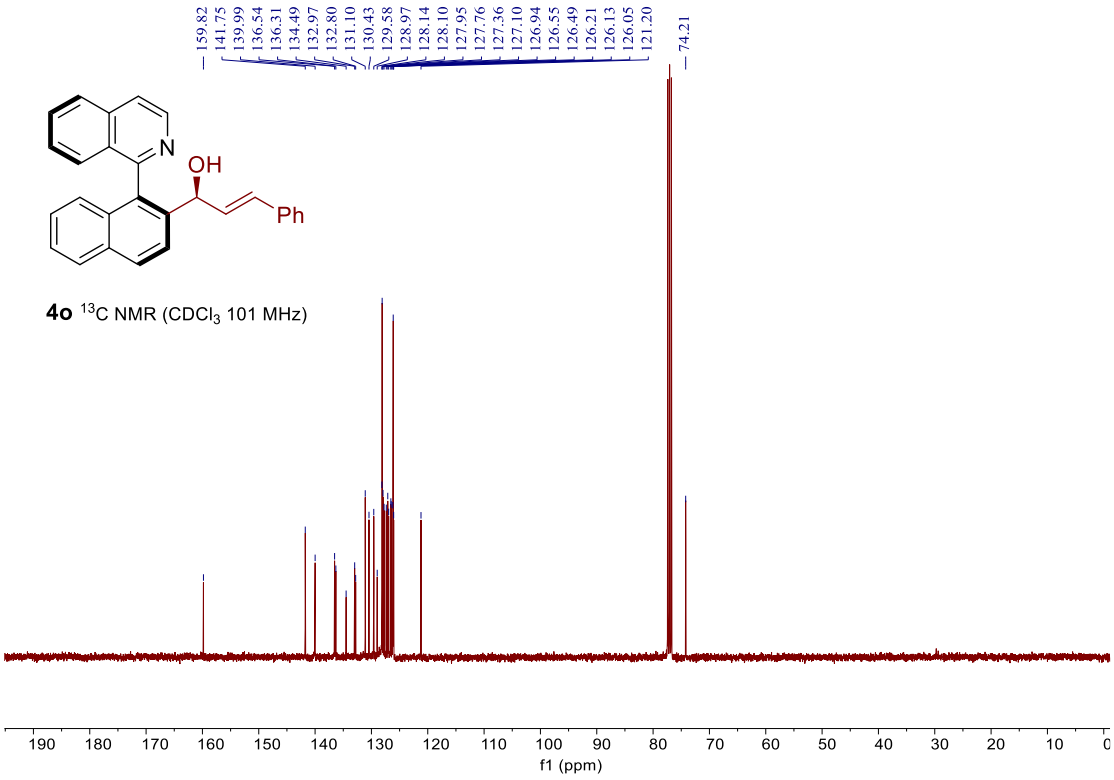
4n ^{1}H NMR ($CDCl_3$ 400 MHz)



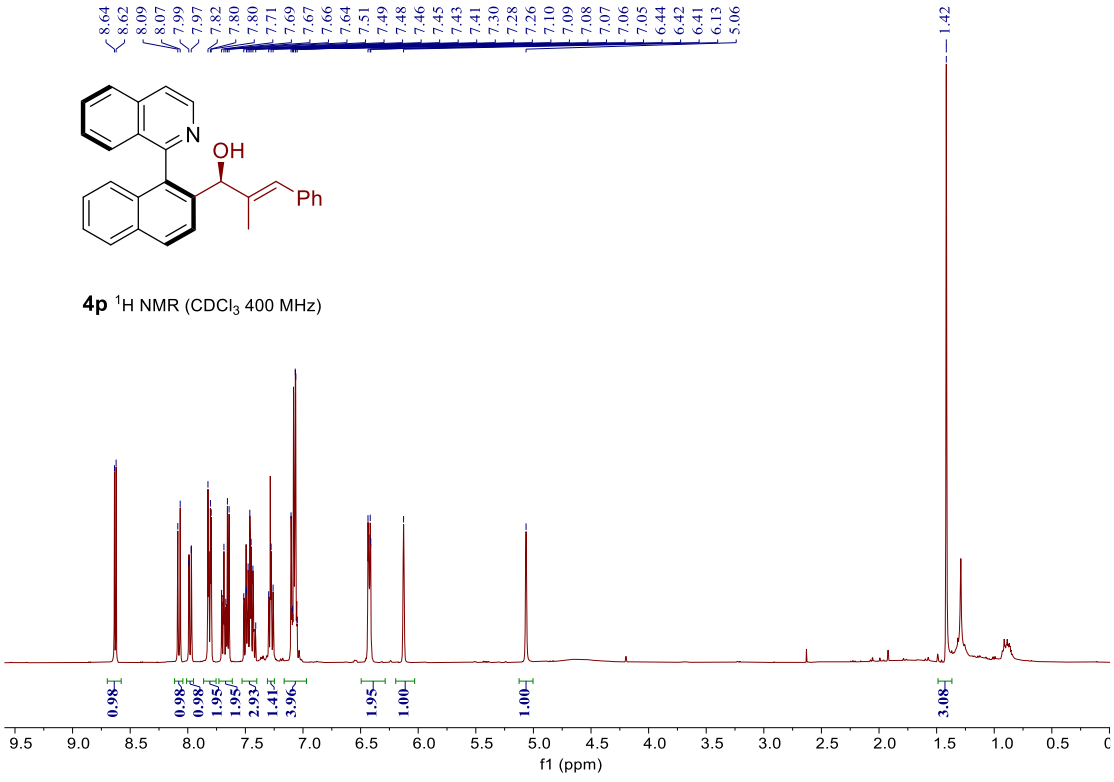
4n ^{13}C NMR ($CDCl_3$ 101 MHz)



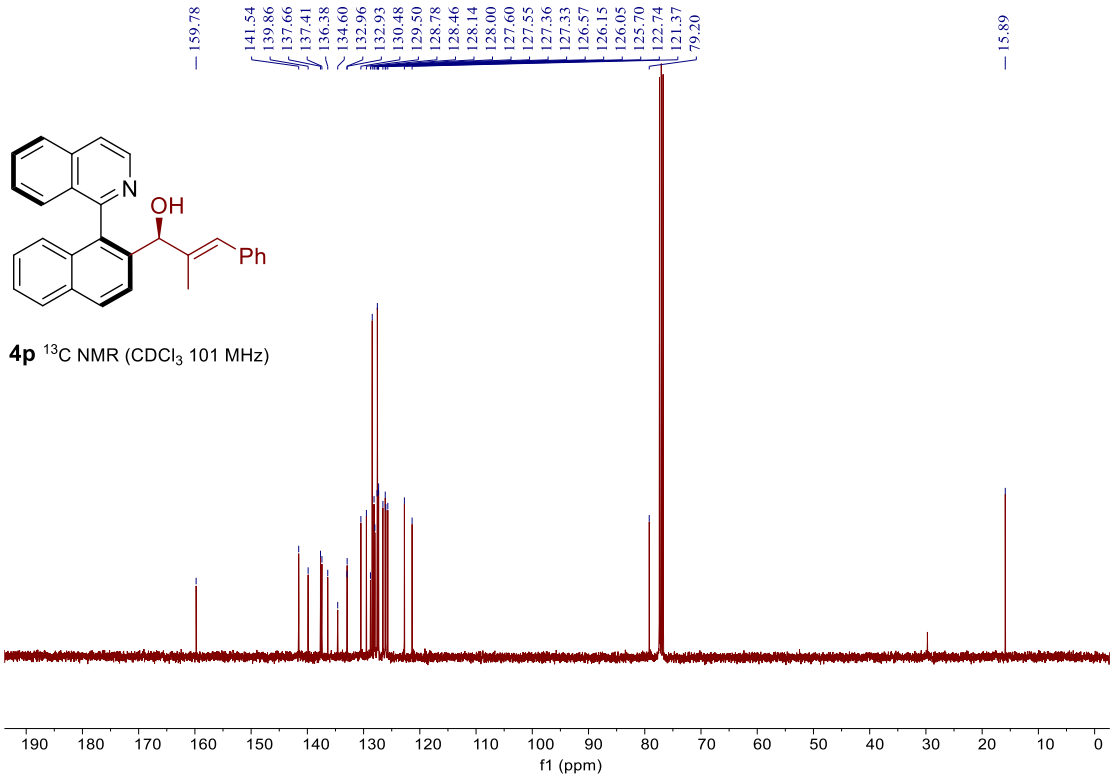
4o ^{1}H NMR ($CDCl_3$ 400 MHz)



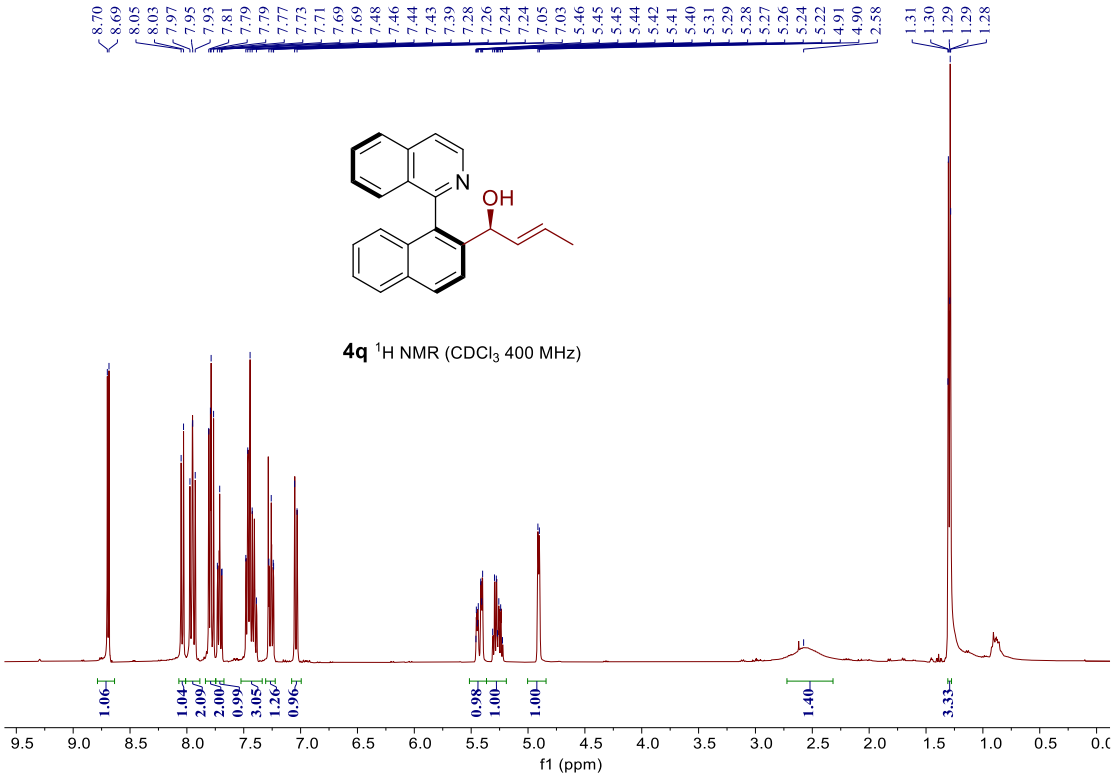
4o ^{13}C NMR ($CDCl_3$ 101 MHz)



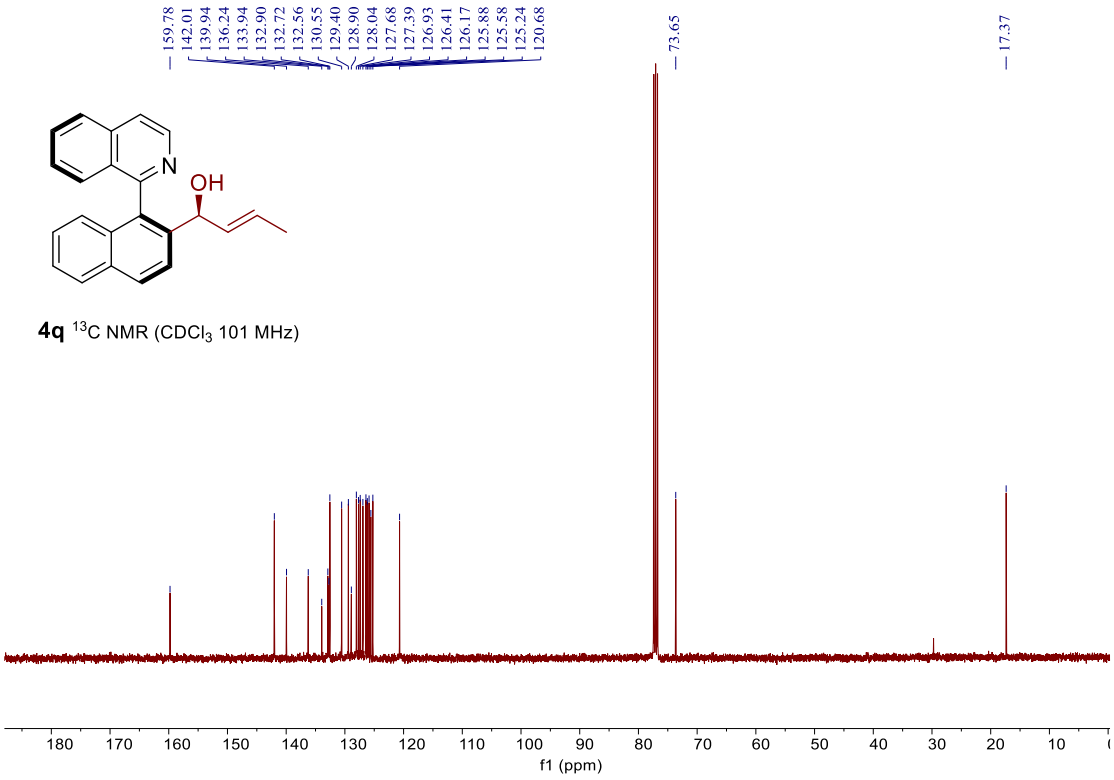
4p ^{1}H NMR ($CDCl_3$ 400 MHz)



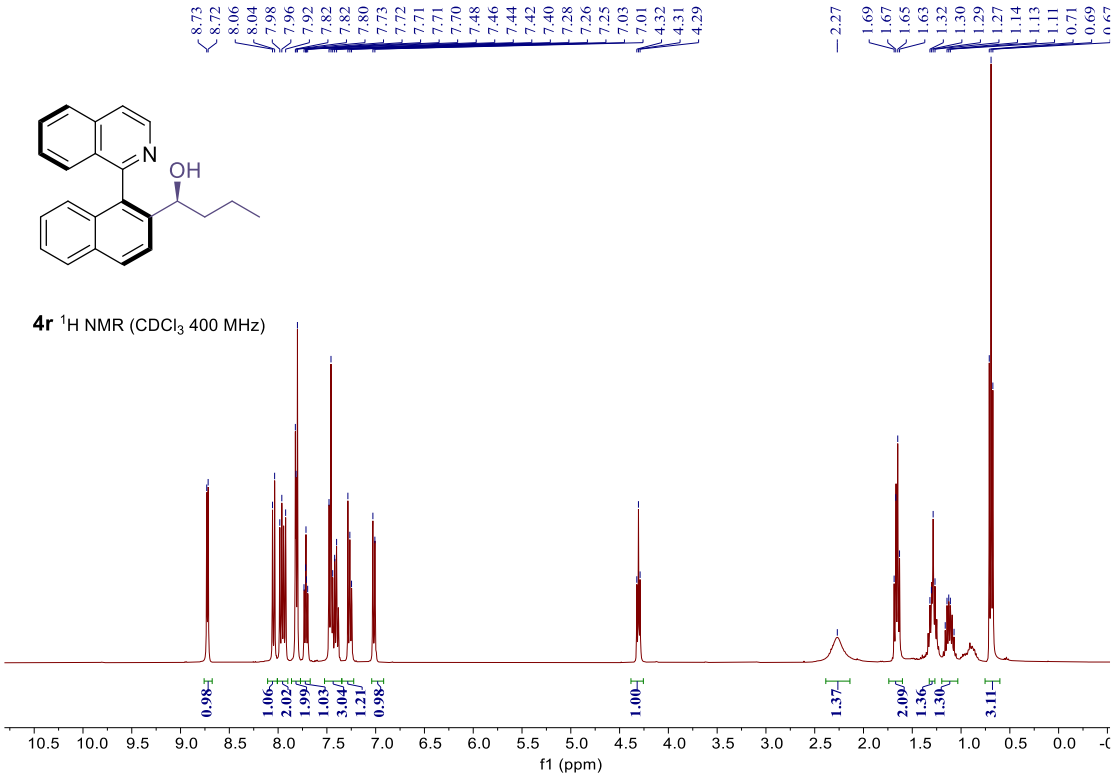
4p ^{13}C NMR ($CDCl_3$ 101 MHz)



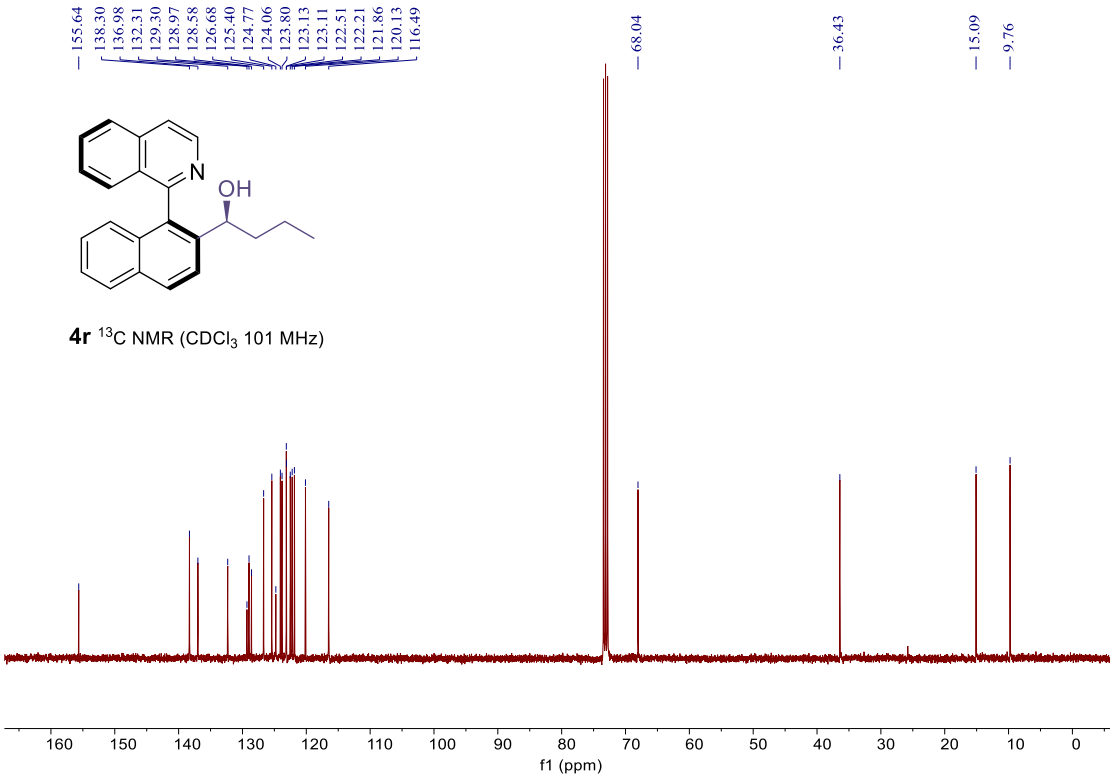
4q ^{1}H NMR ($CDCl_3$ 400 MHz)



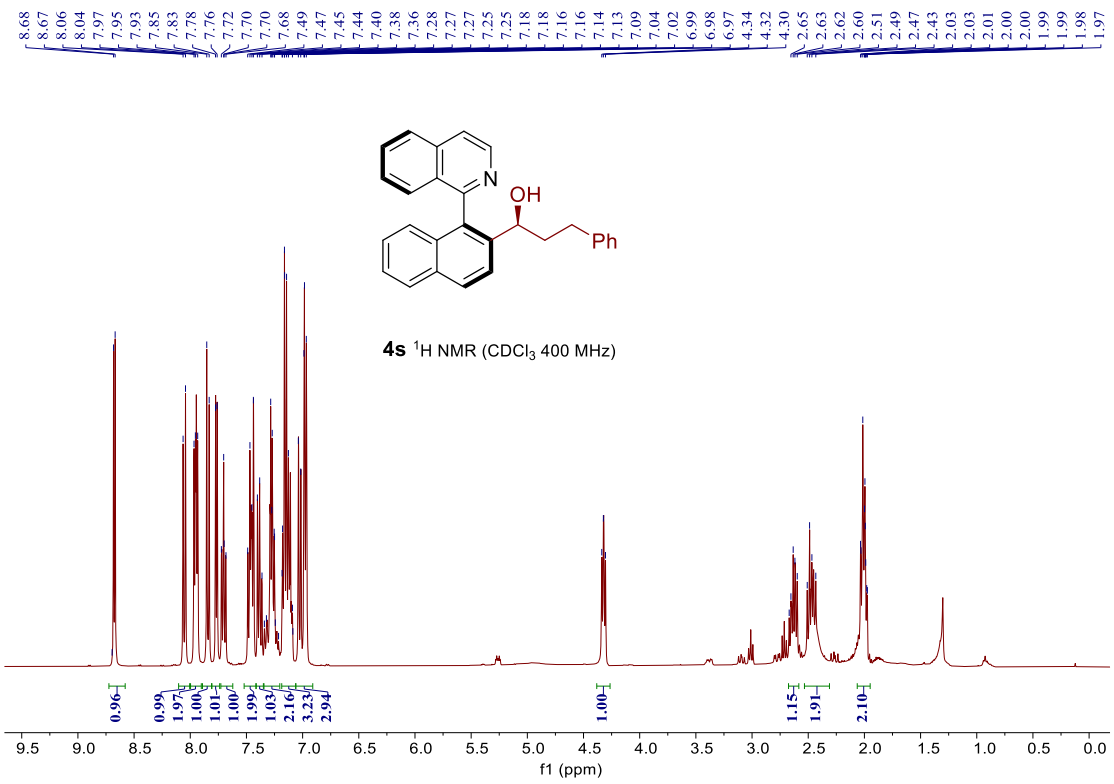
4q ^{13}C NMR ($CDCl_3$ 101 MHz)



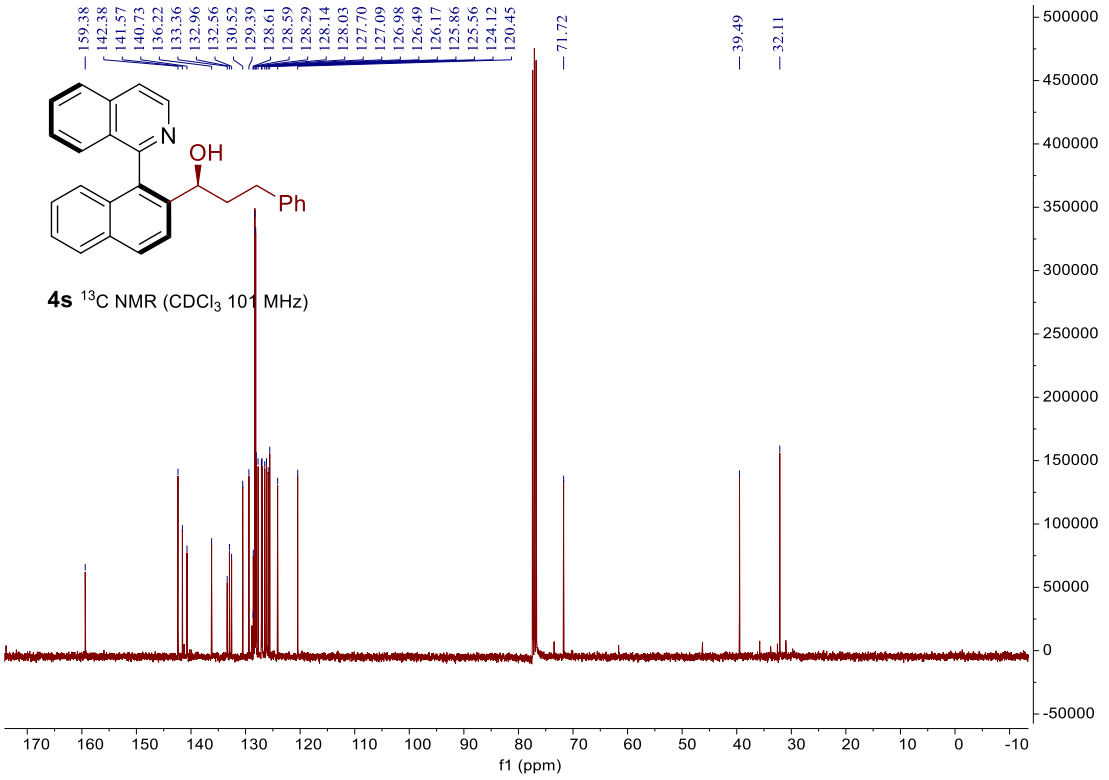
4r ^{1}H NMR ($CDCl_3$ 400 MHz)



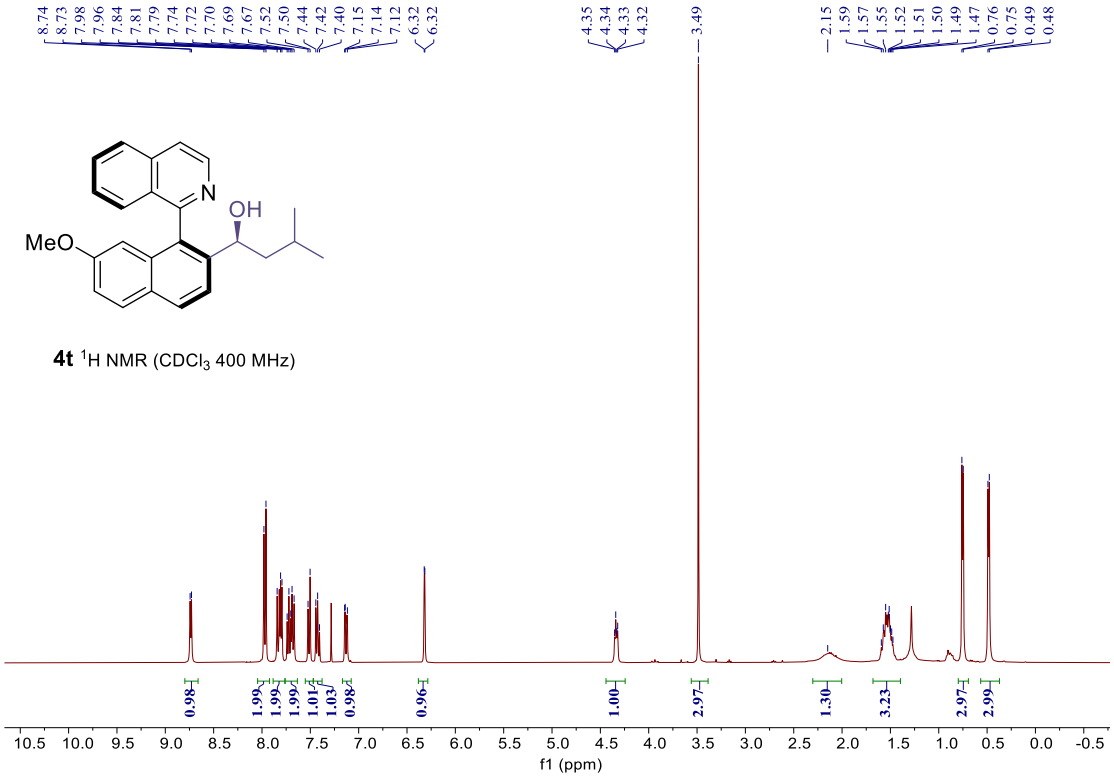
4r ^{13}C NMR ($CDCl_3$ 101 MHz)



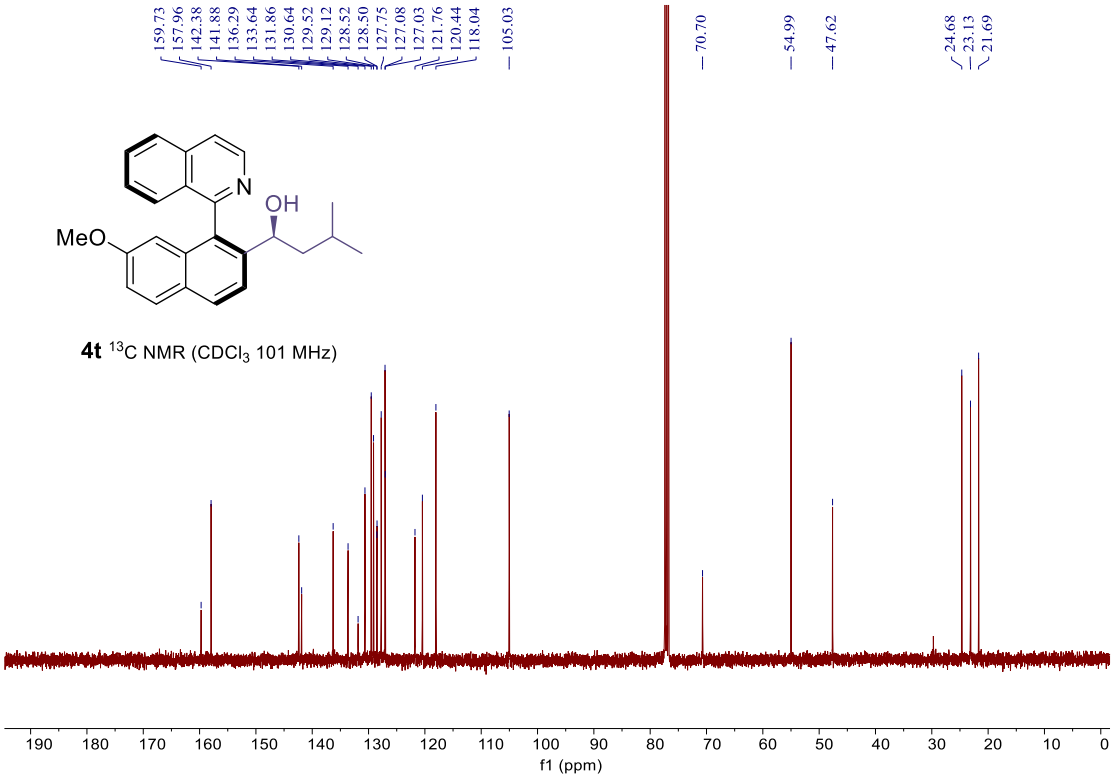
4s ^{1}H NMR ($CDCl_3$ 400 MHz)



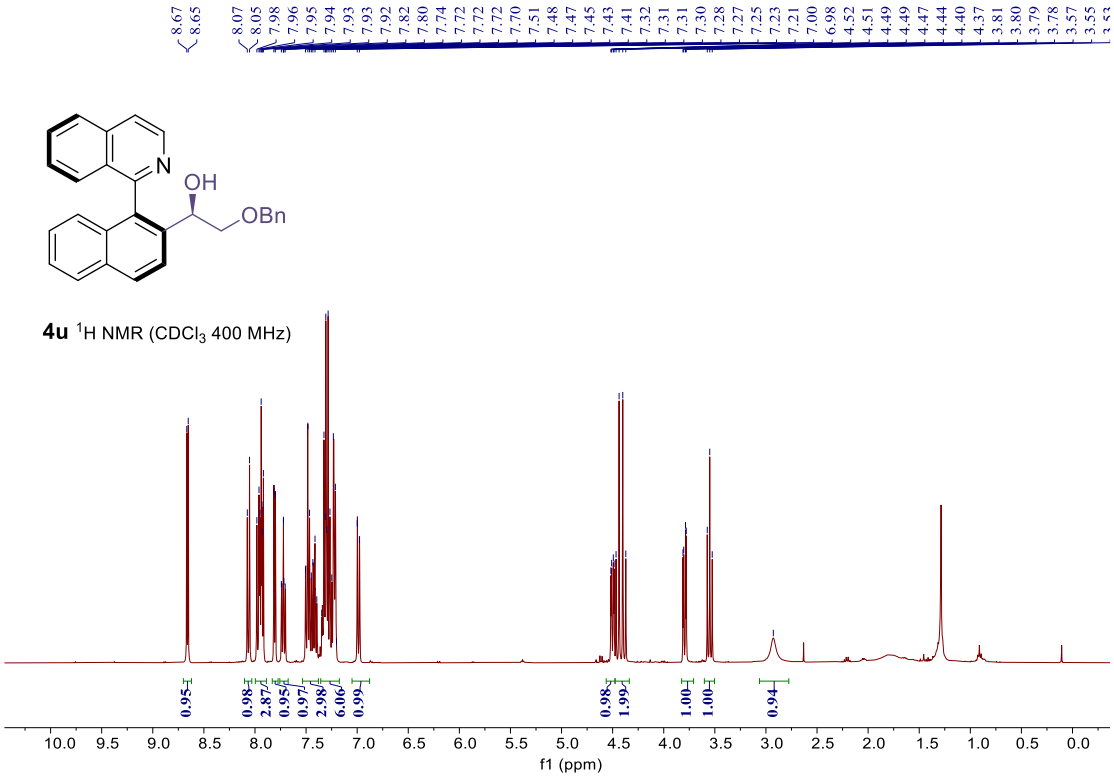
4s ^{13}C NMR ($CDCl_3$ 101 MHz)



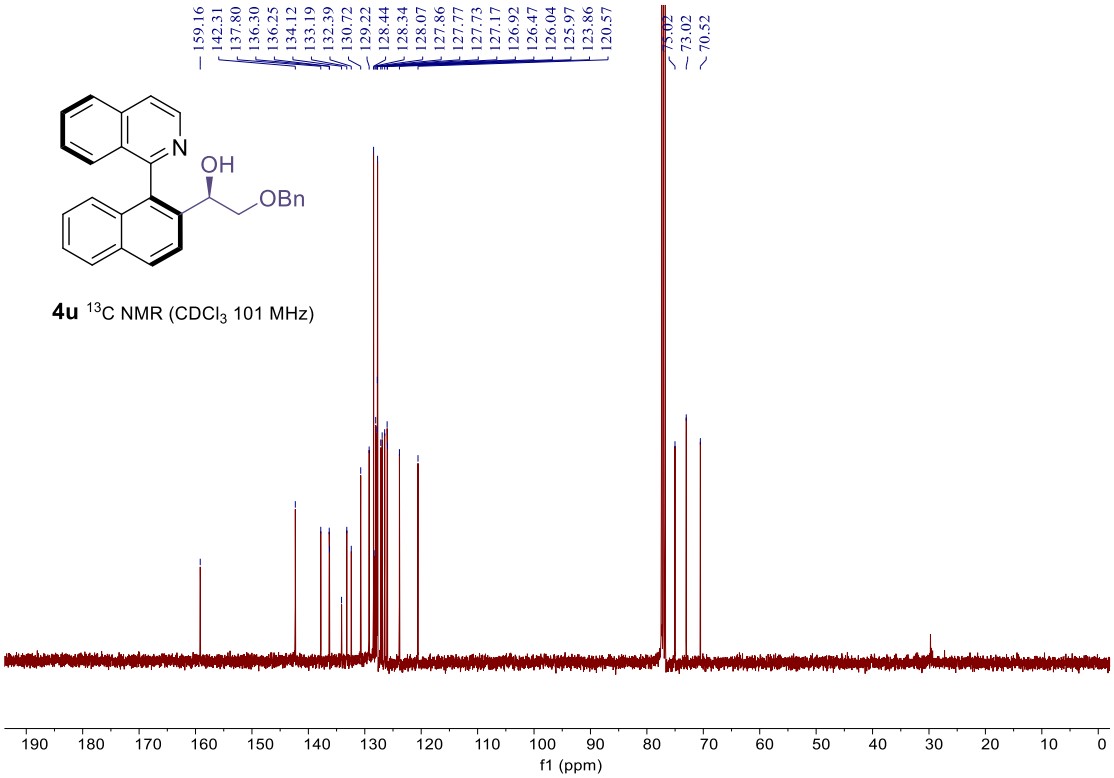
4t ^{1}H NMR ($CDCl_3$ 400 MHz)



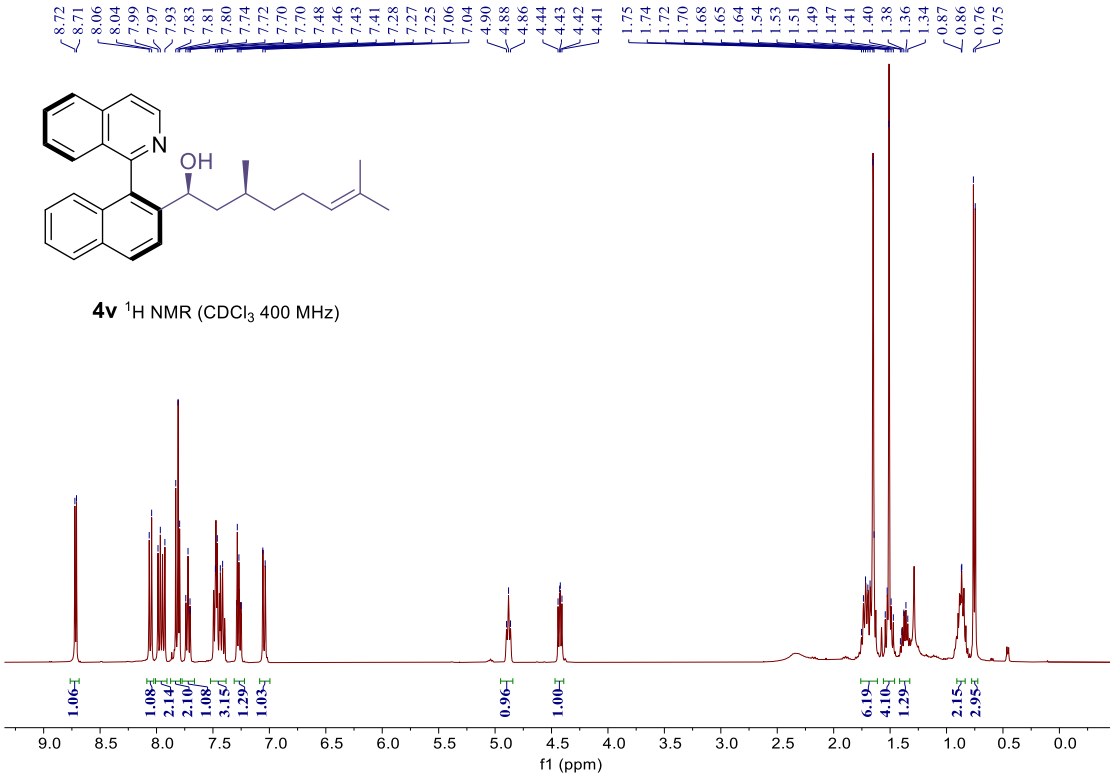
4t ^{13}C NMR ($CDCl_3$ 101 MHz)



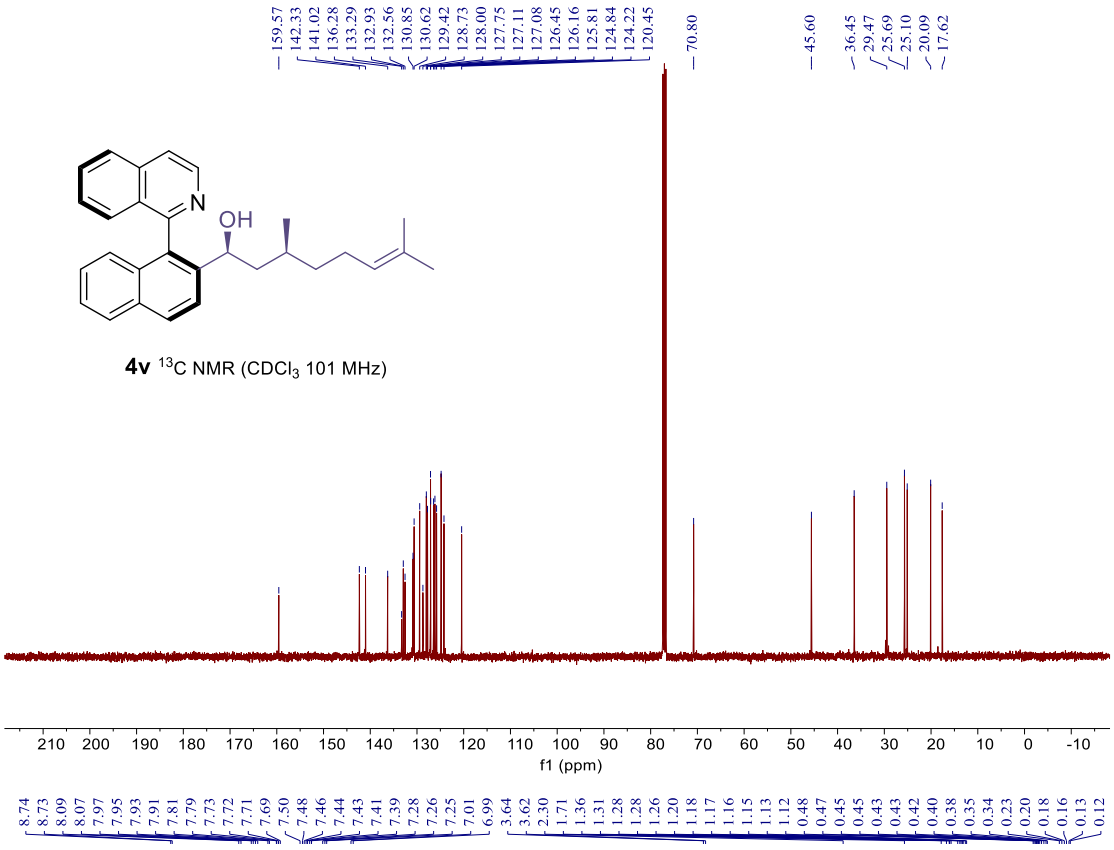
4u ^{1}H NMR ($CDCl_3$ 400 MHz)



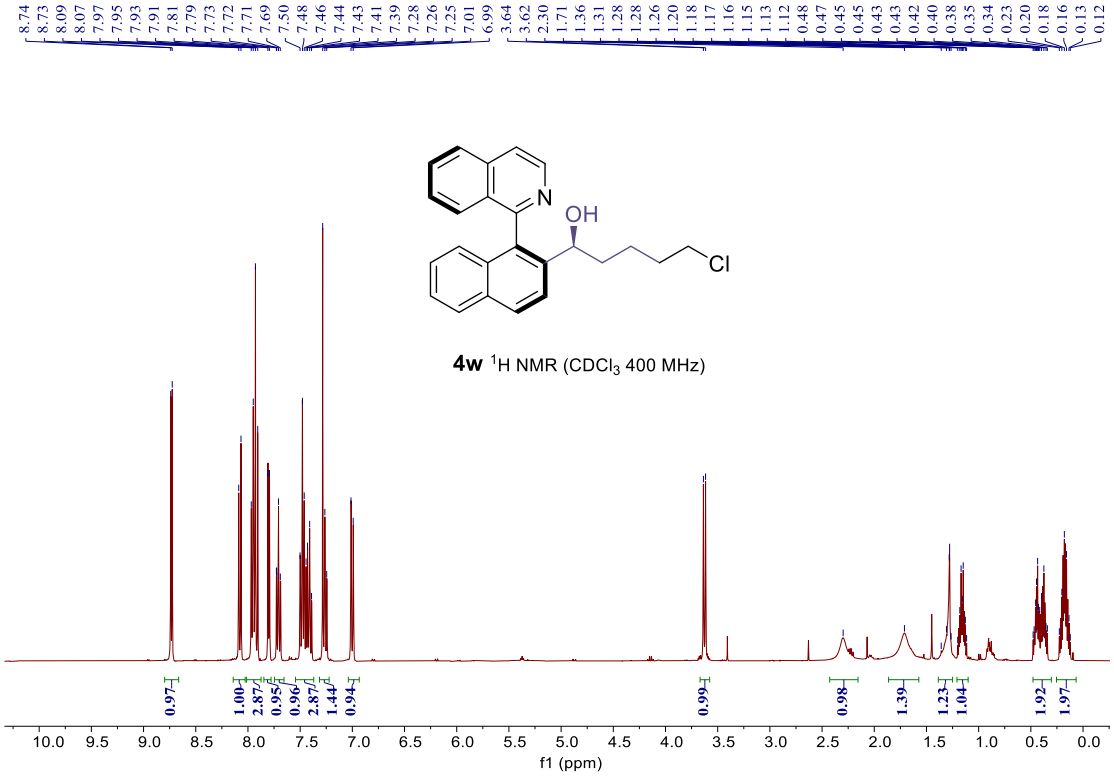
4u ^{13}C NMR ($CDCl_3$ 101 MHz)



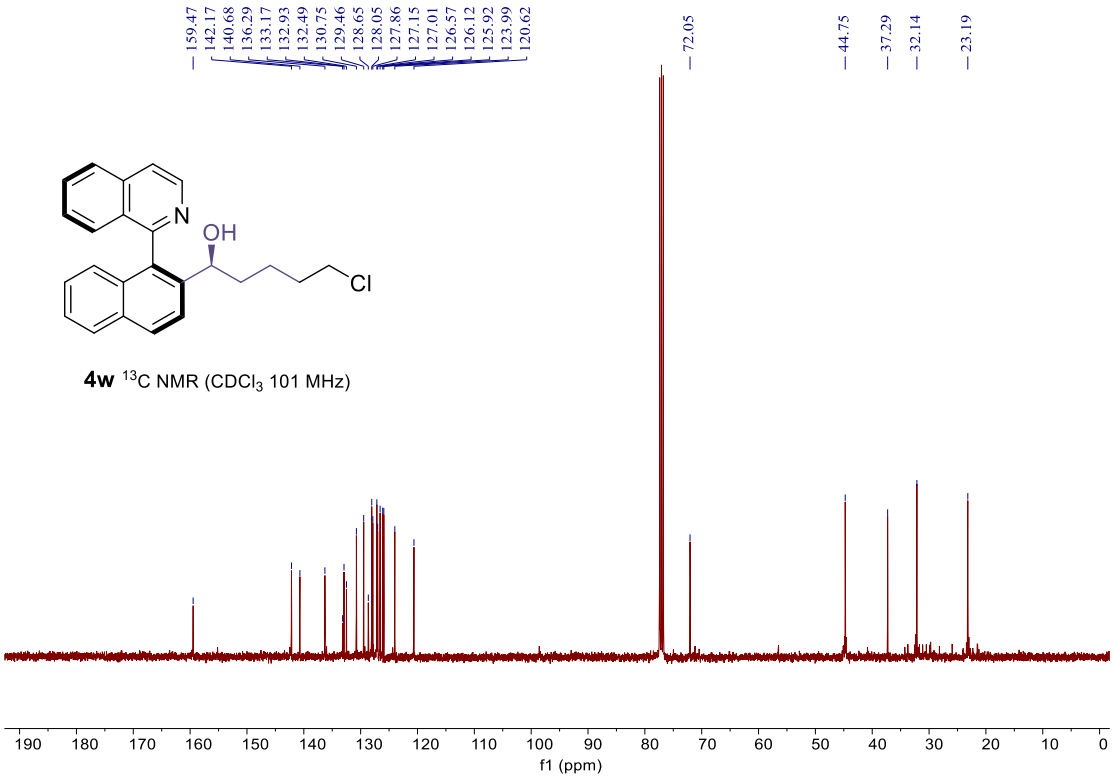
4v ^{1}H NMR ($CDCl_3$ 400 MHz)



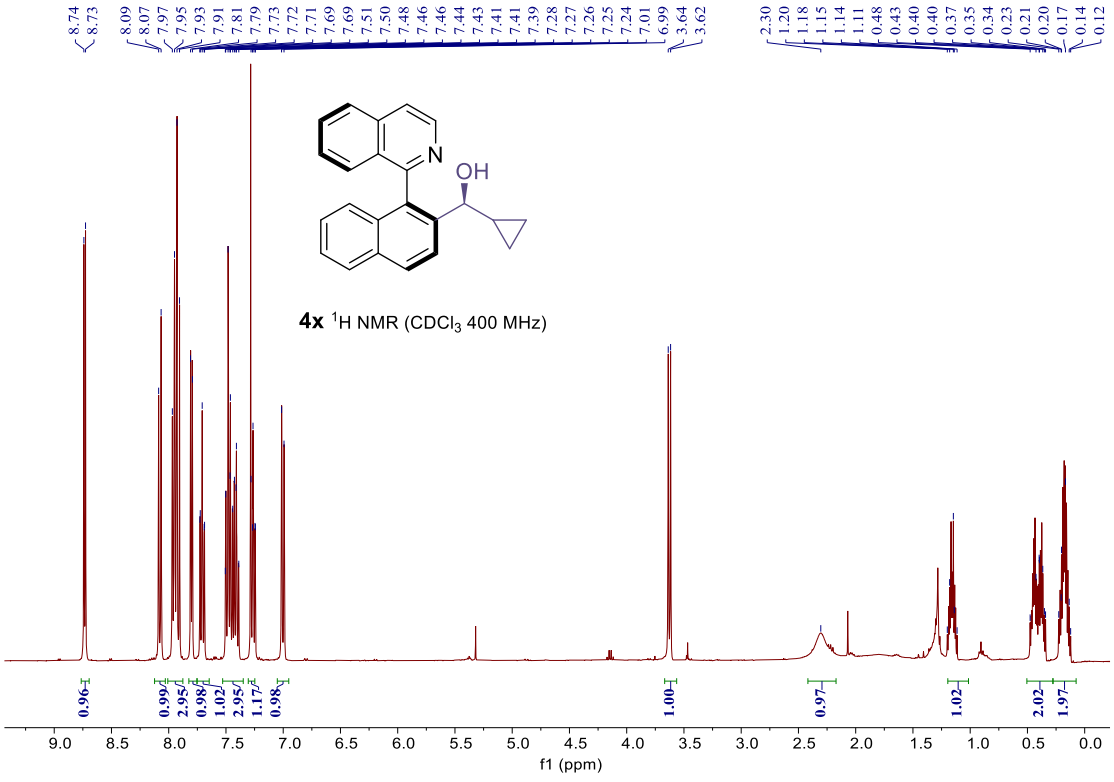
4v ^{13}C NMR ($CDCl_3$ 101 MHz)



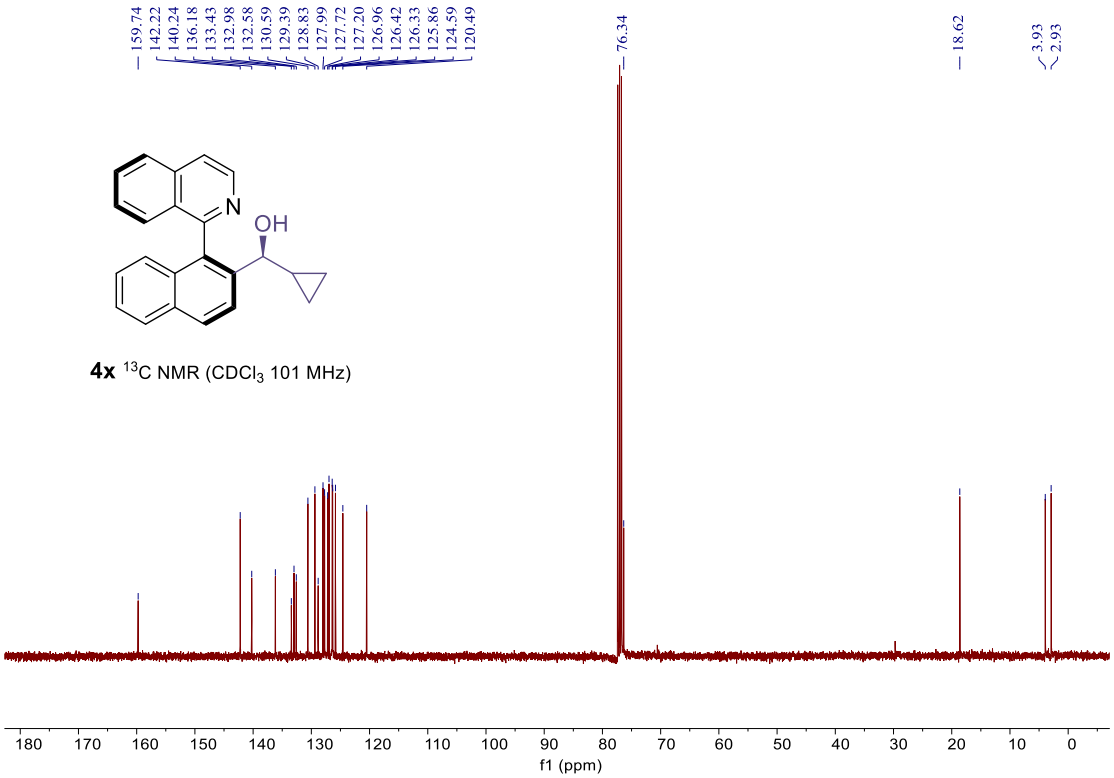
4w ^{1}H NMR ($CDCl_3$ 400 MHz)



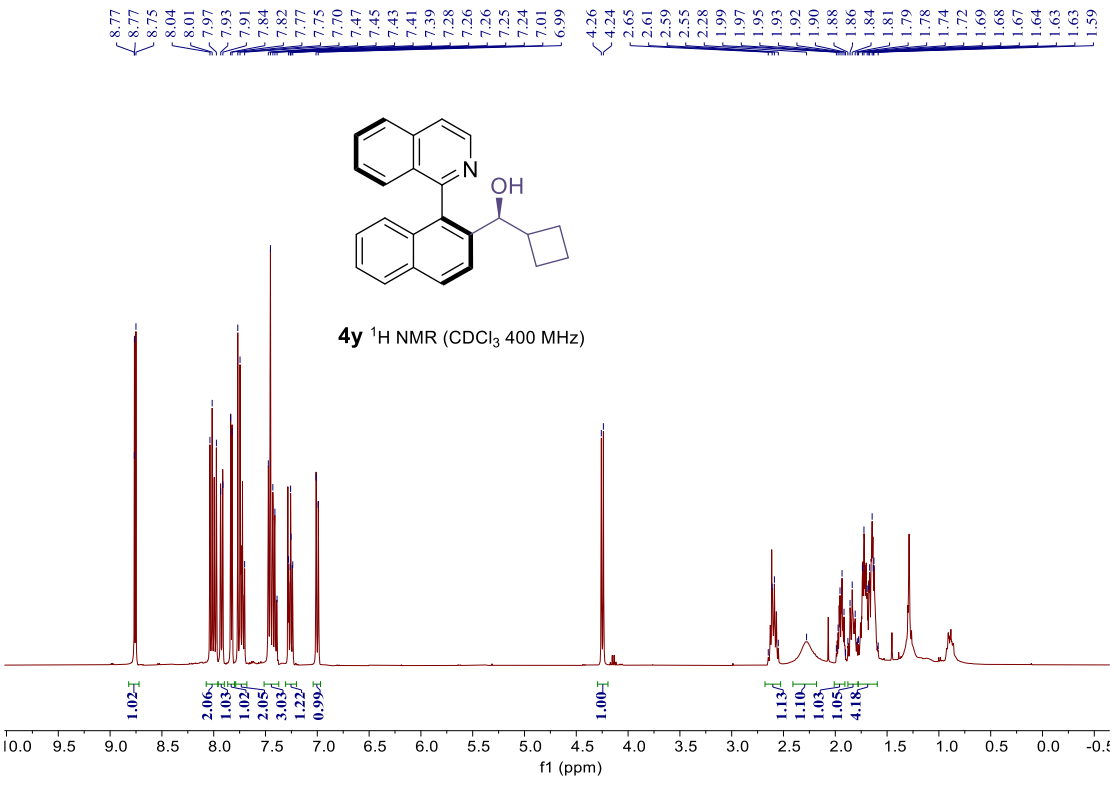
4w ^{13}C NMR ($CDCl_3$ 101 MHz)



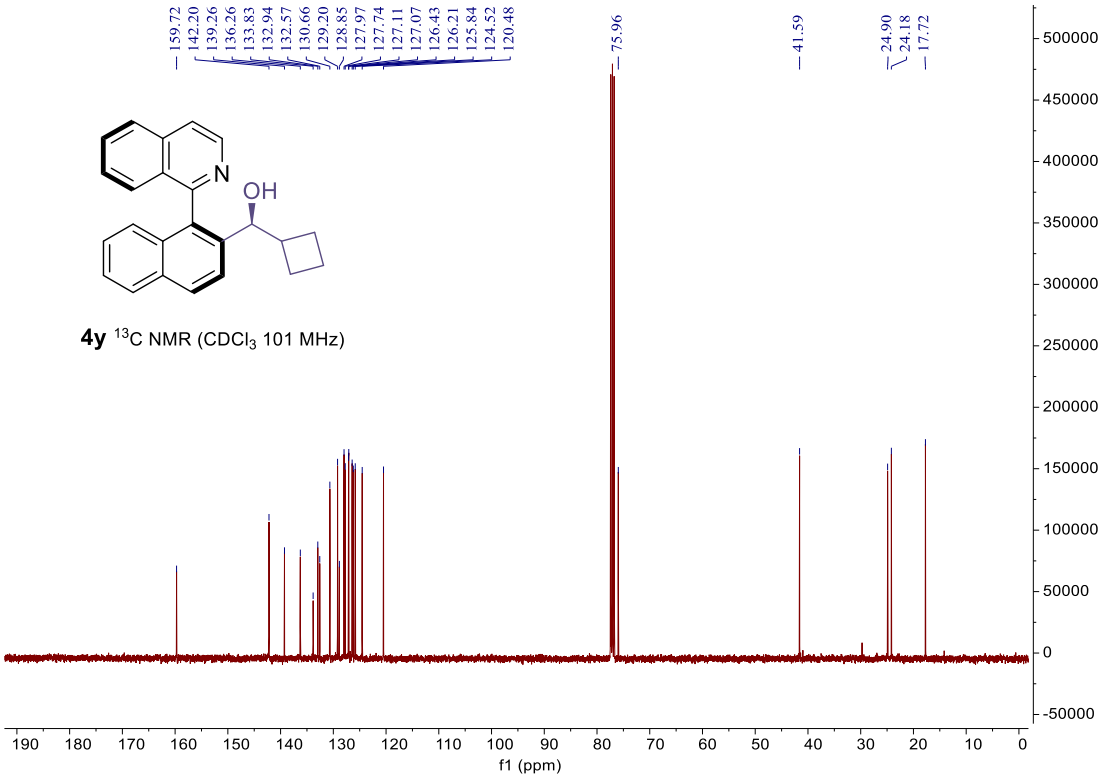
4x ^{1}H NMR ($CDCl_3$ 400 MHz)



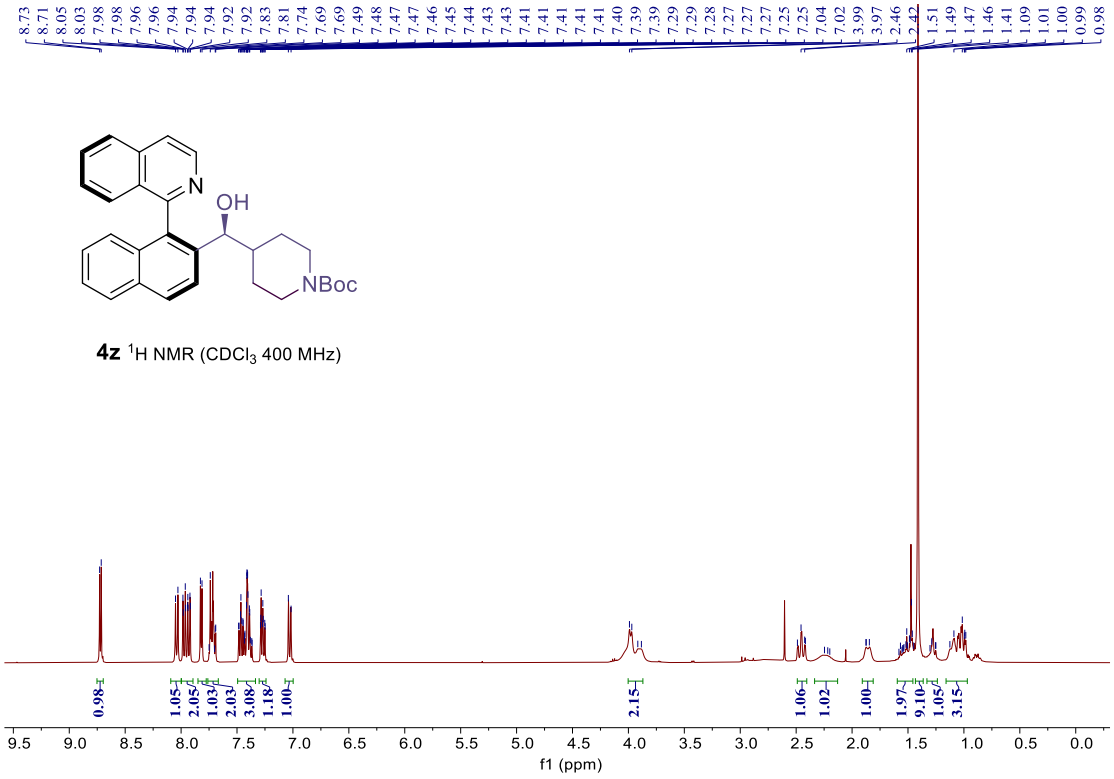
4x ^{13}C NMR ($CDCl_3$ 101 MHz)



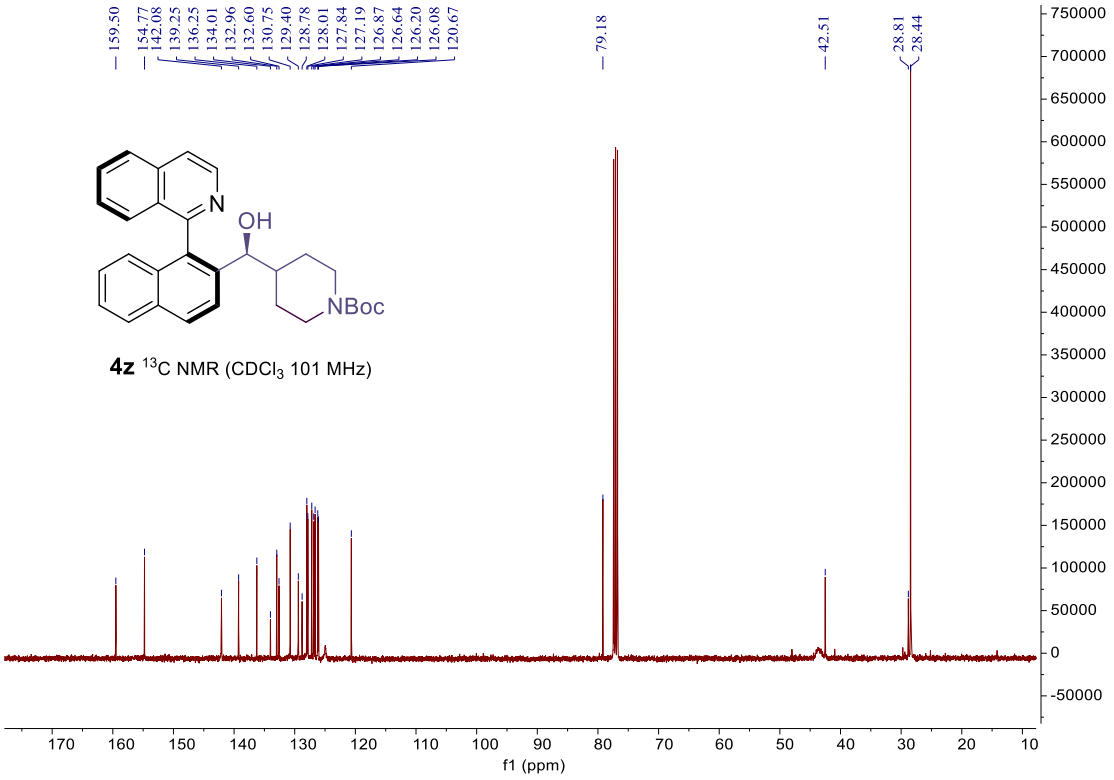
4y ^{1}H NMR ($CDCl_3$ 400 MHz)



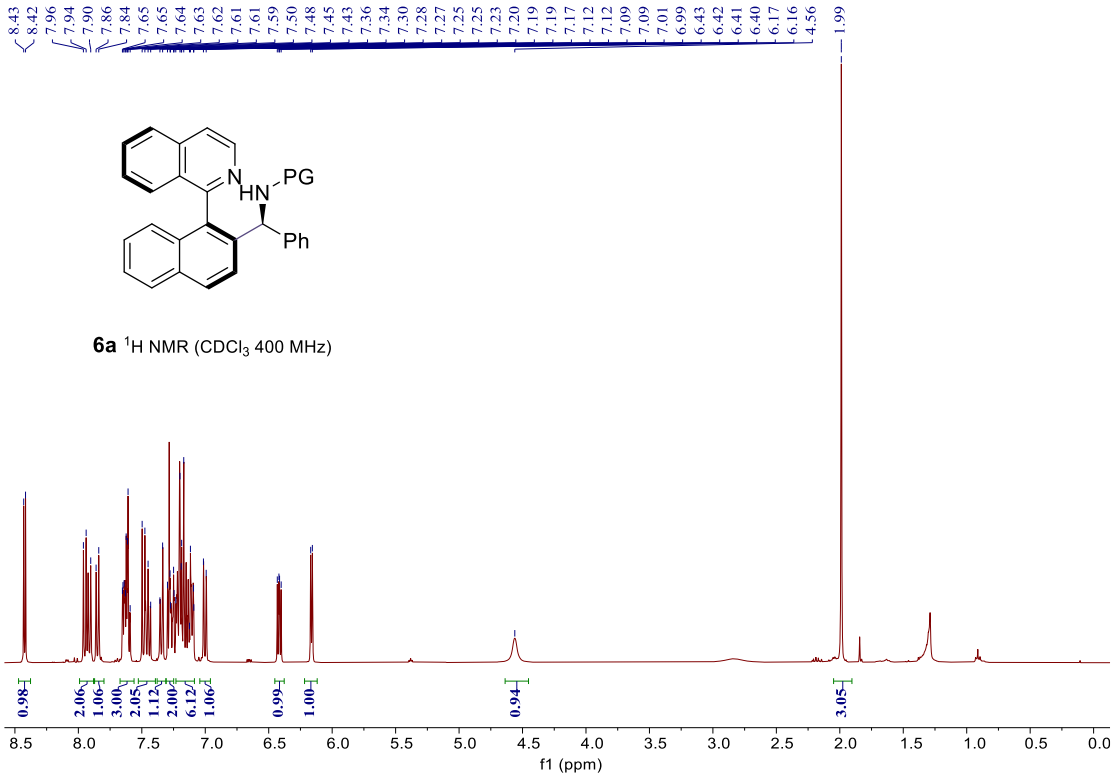
4y ^{13}C NMR ($CDCl_3$ 101 MHz)



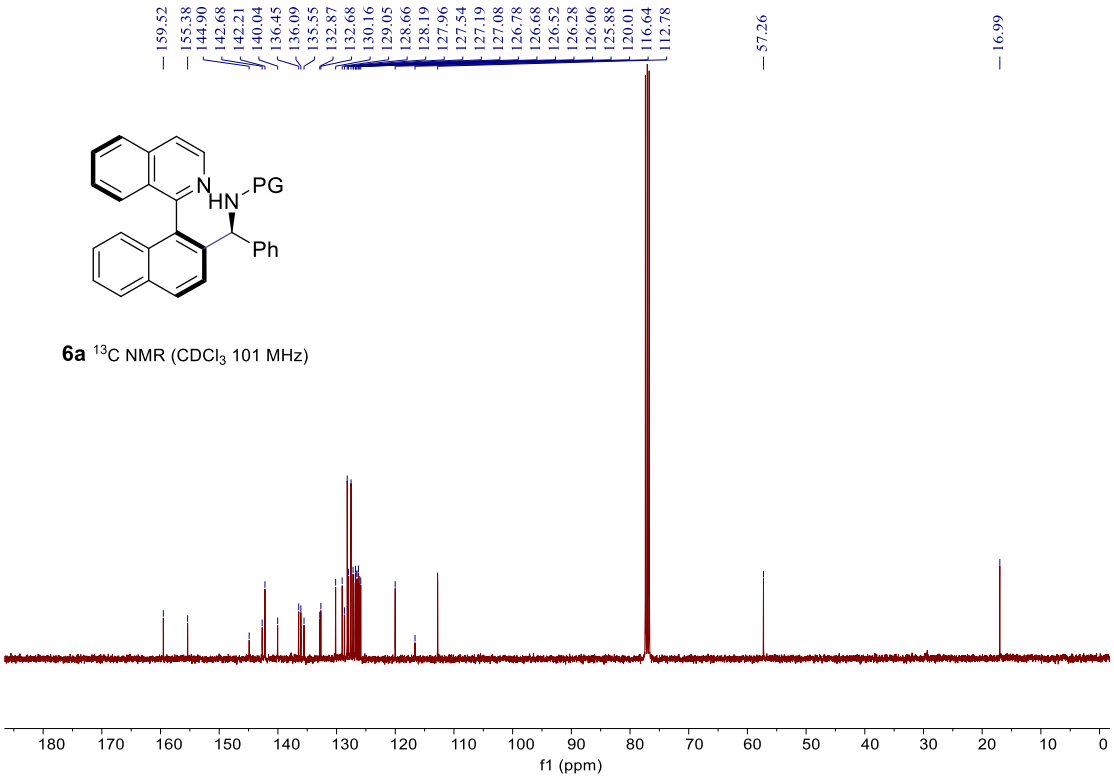
4z ^{1}H NMR ($CDCl_3$ 400 MHz)



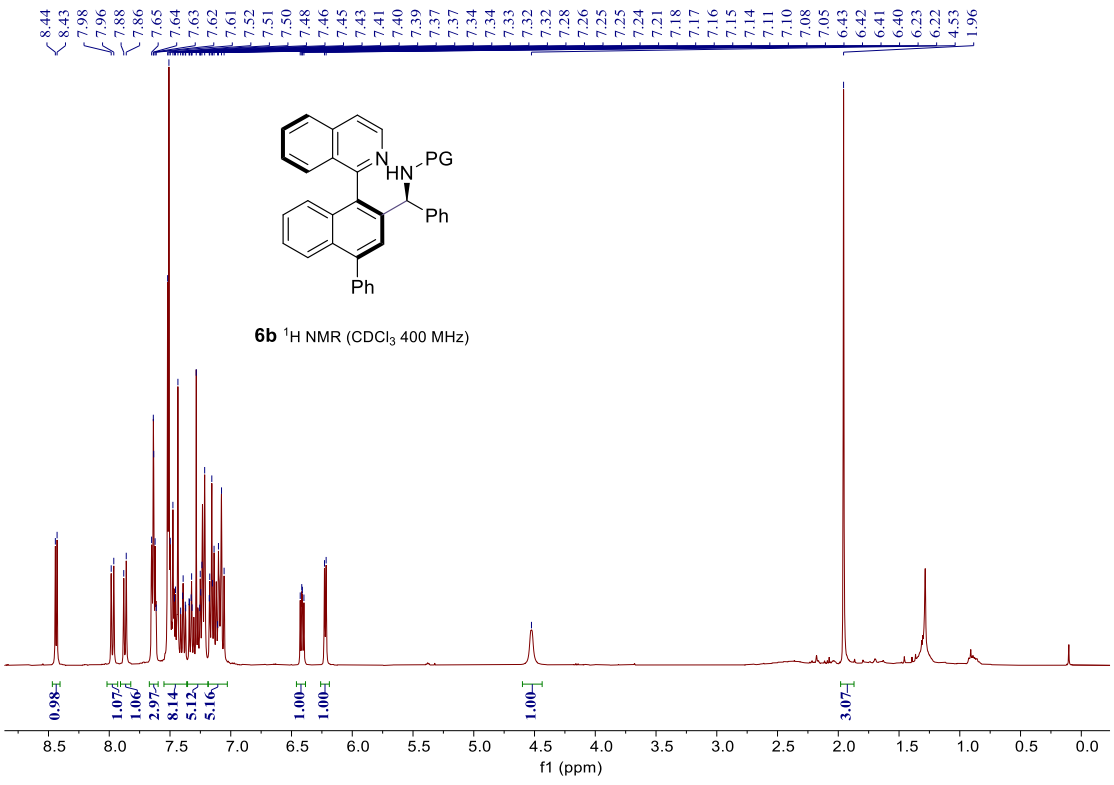
4z ^{13}C NMR ($CDCl_3$ 101 MHz)



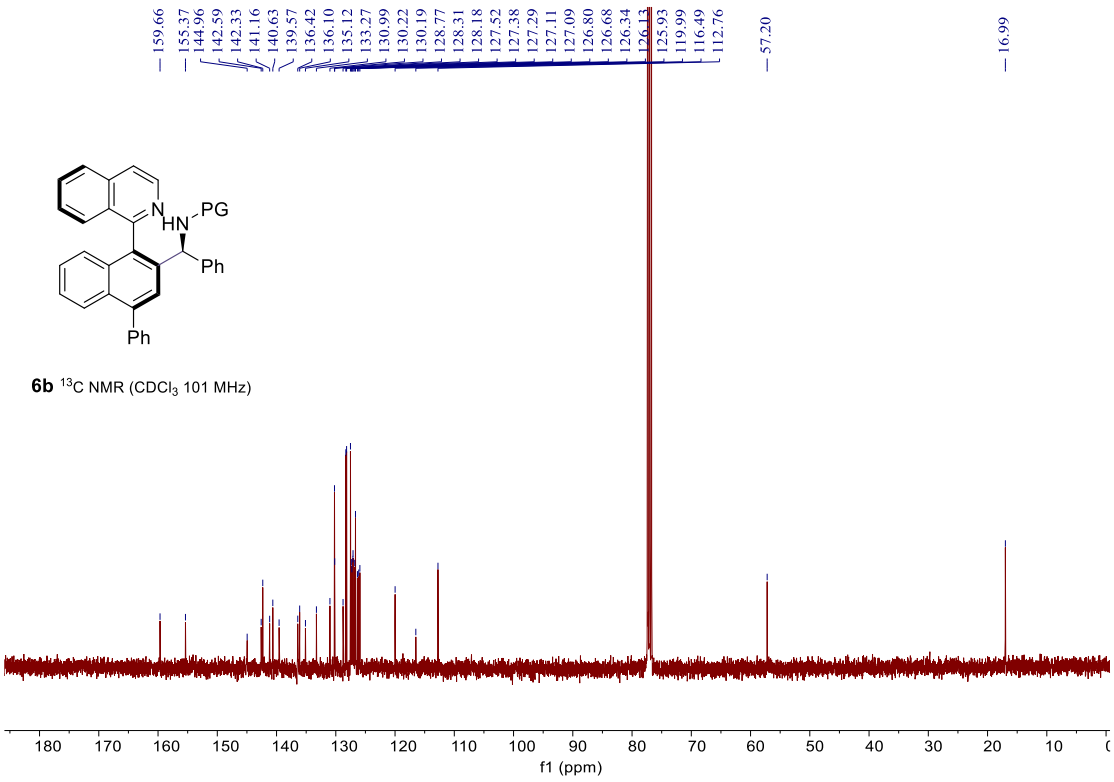
6a ^{1}H NMR ($CDCl_3$ 400 MHz)



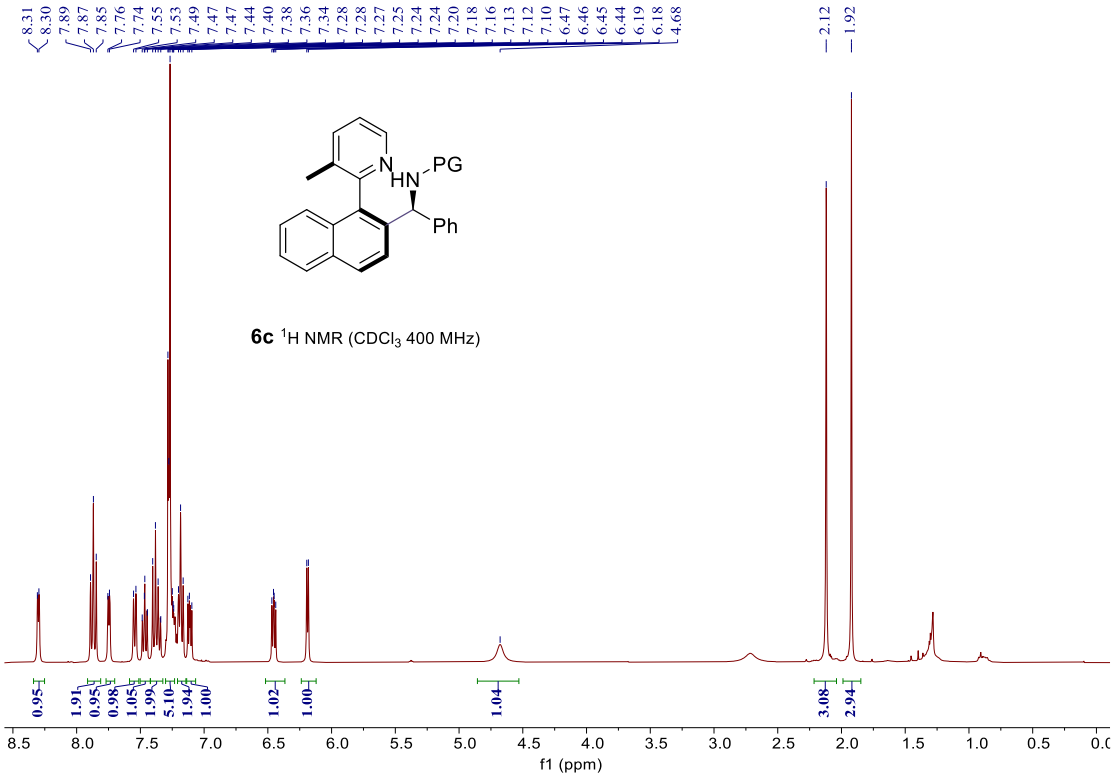
6a ^{13}C NMR ($CDCl_3$ 101 MHz)



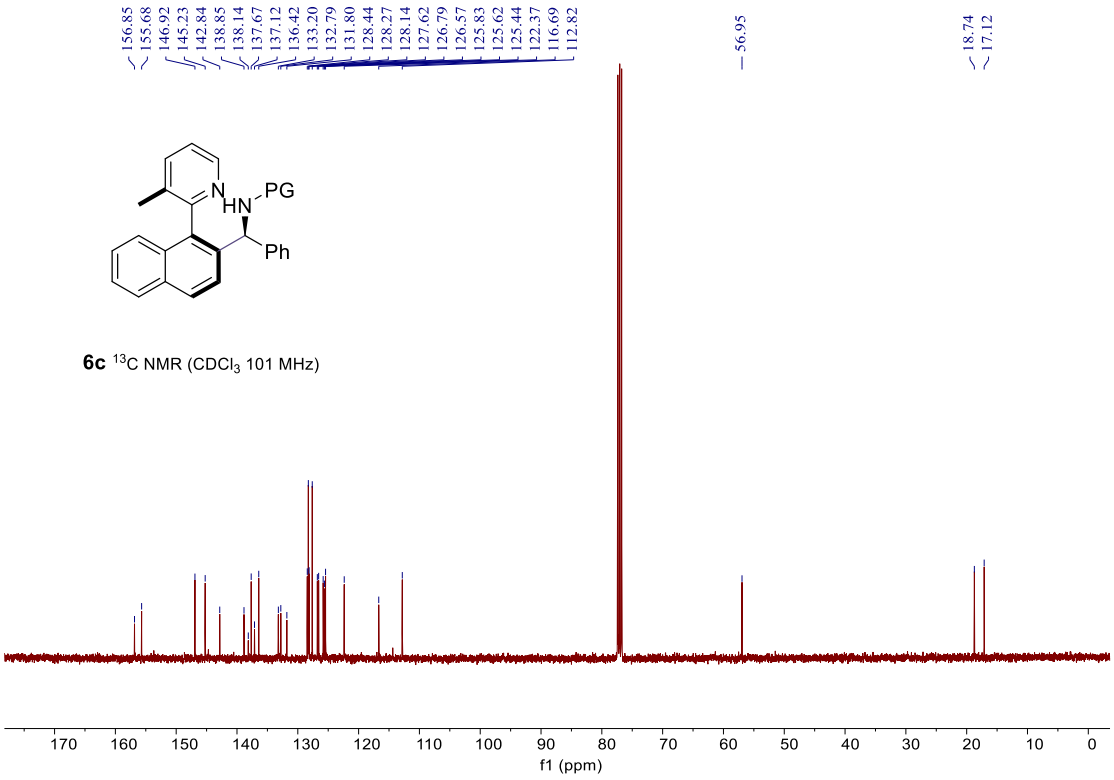
6b ^{1}H NMR ($CDCl_3$ 400 MHz)



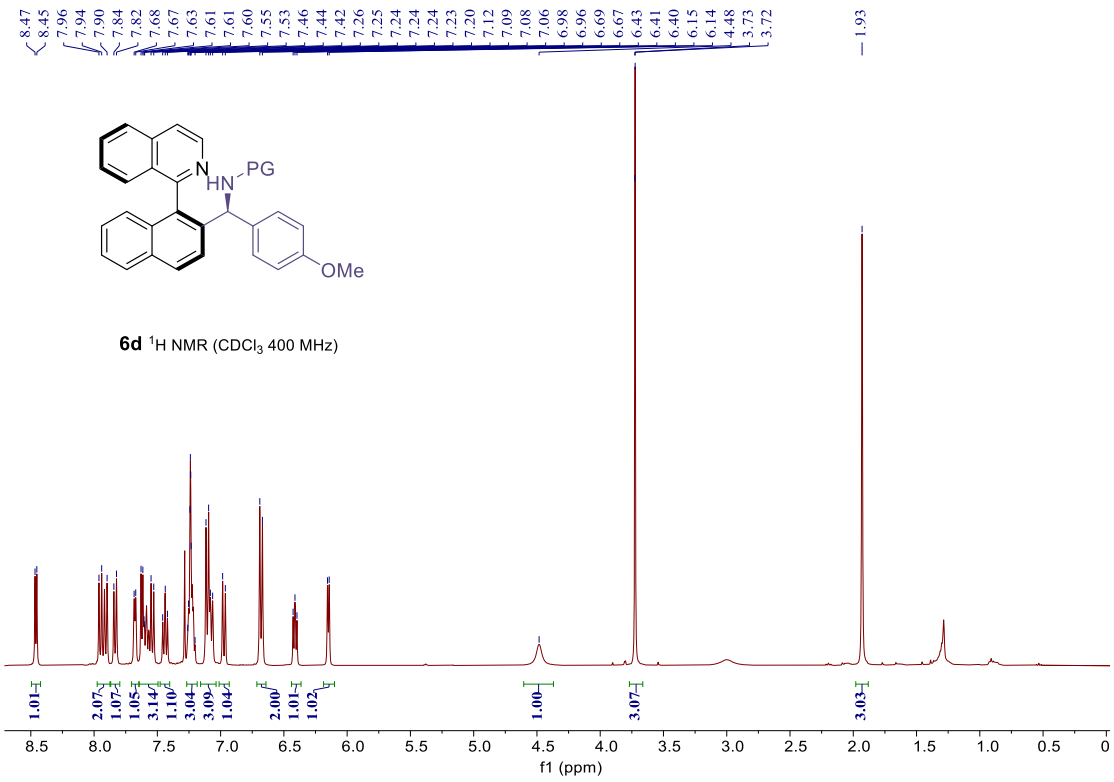
6b ^{13}C NMR ($CDCl_3$ 101 MHz)



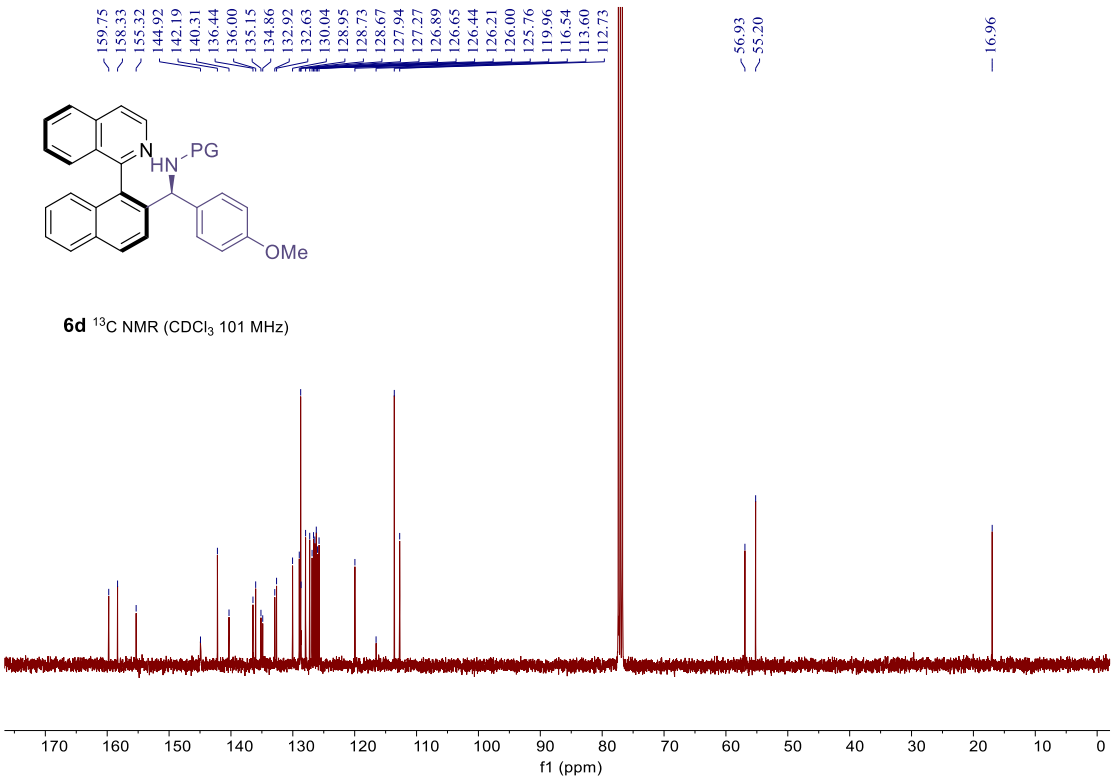
6c ^{1}H NMR ($CDCl_3$ 400 MHz)



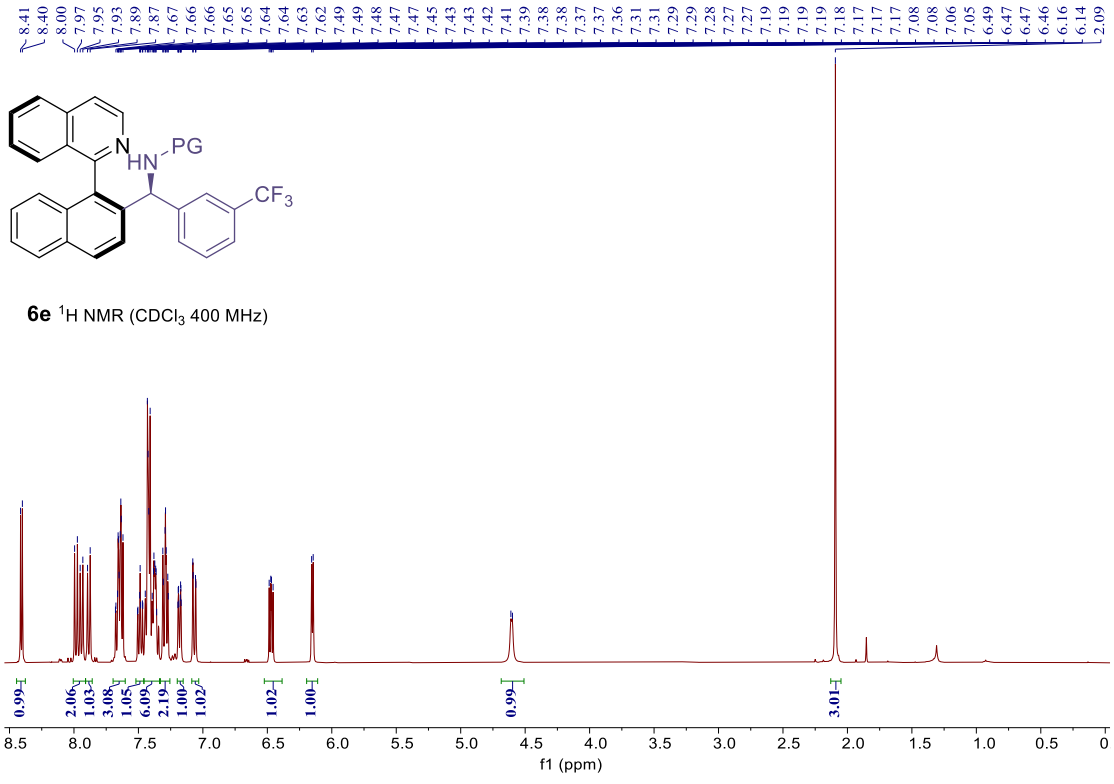
6c ^{13}C NMR ($CDCl_3$ 101 MHz)



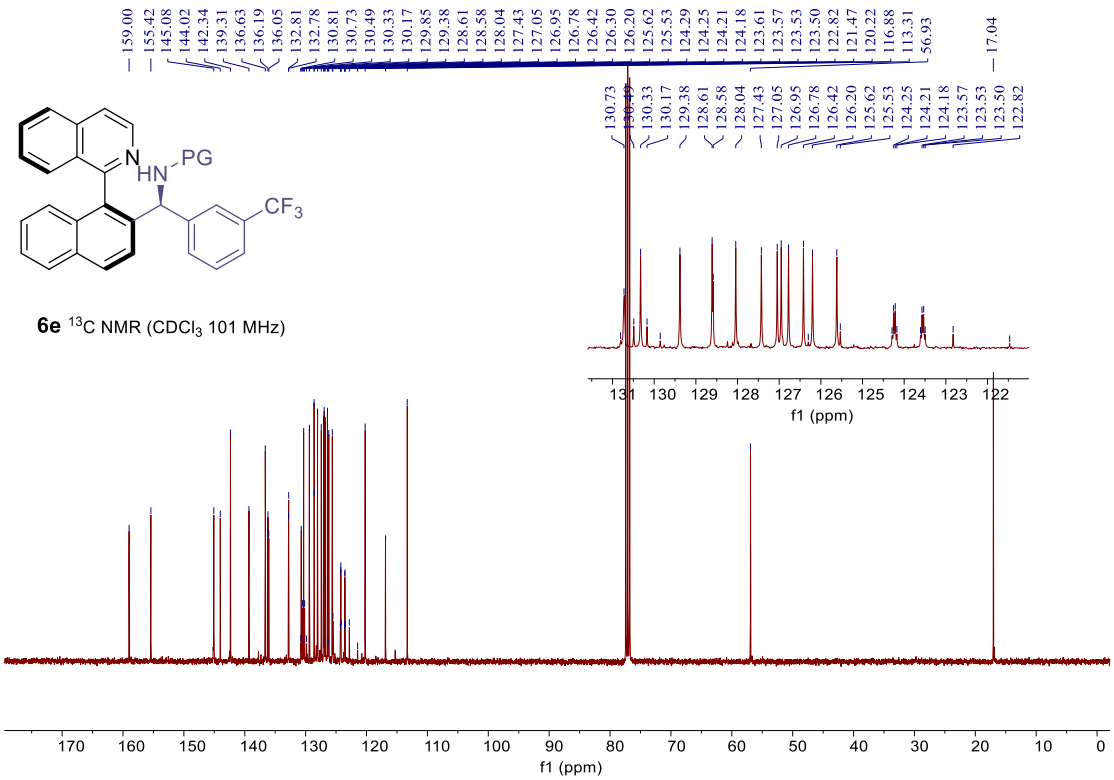
6d ^{1}H NMR ($CDCl_3$ 400 MHz)



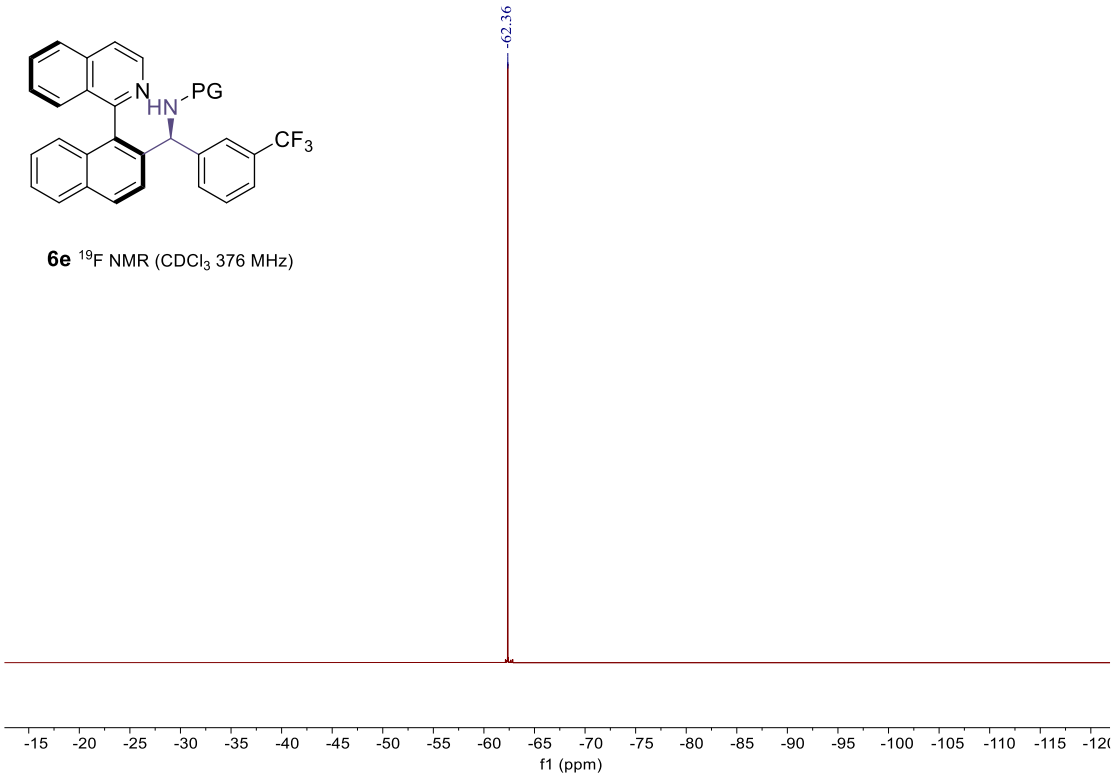
6d ^{13}C NMR ($CDCl_3$ 101 MHz)



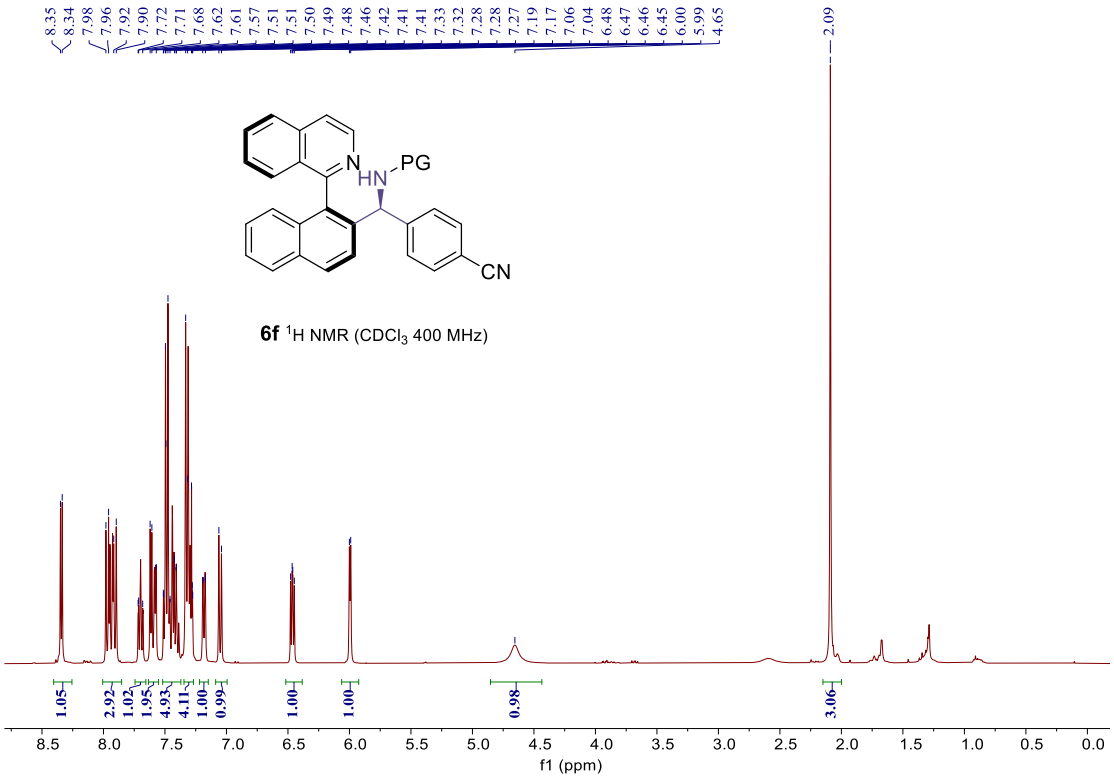
6e ^{1}H NMR ($CDCl_3$ 400 MHz)



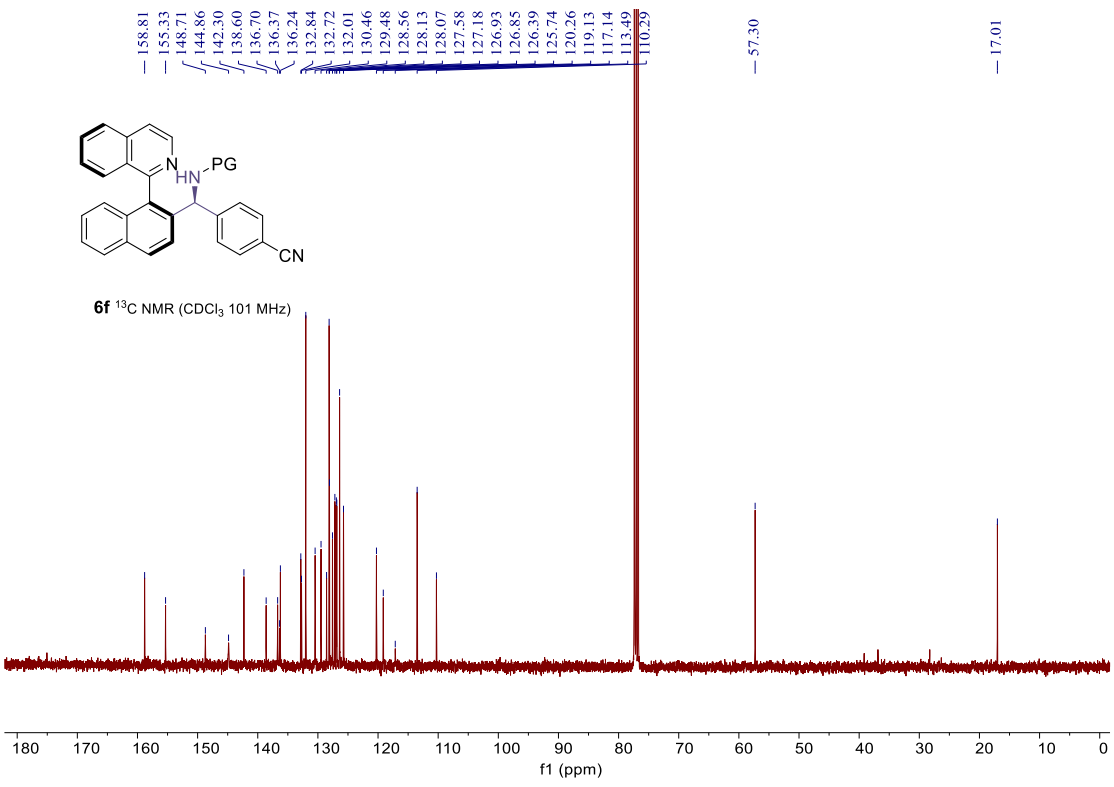
6e ^{13}C NMR ($CDCl_3$ 101 MHz)



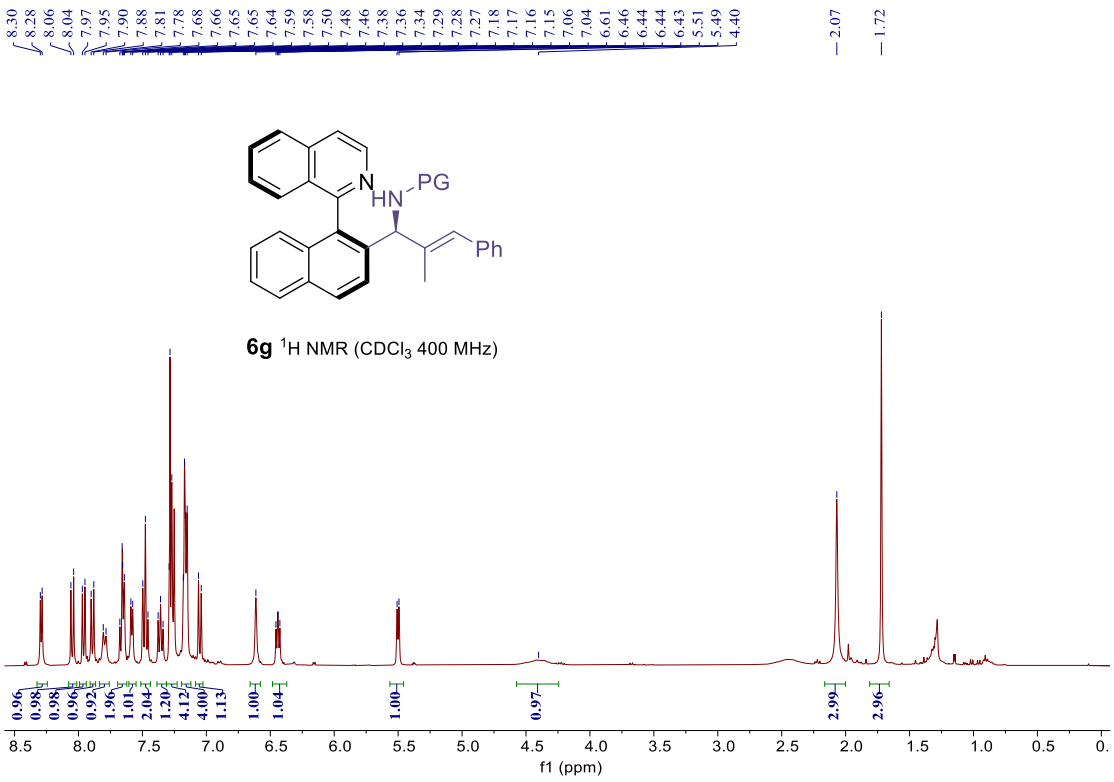
6e ^{19}F NMR ($CDCl_3$ 376 MHz)



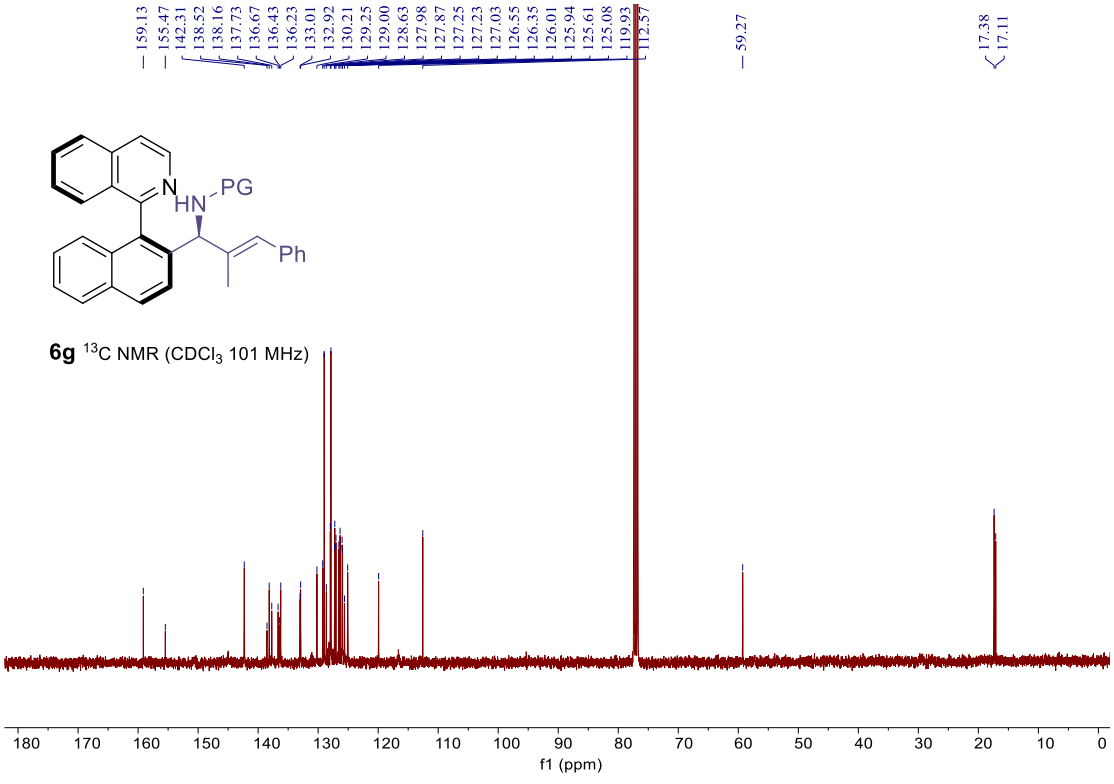
6f ^{1}H NMR ($CDCl_3$ 400 MHz)



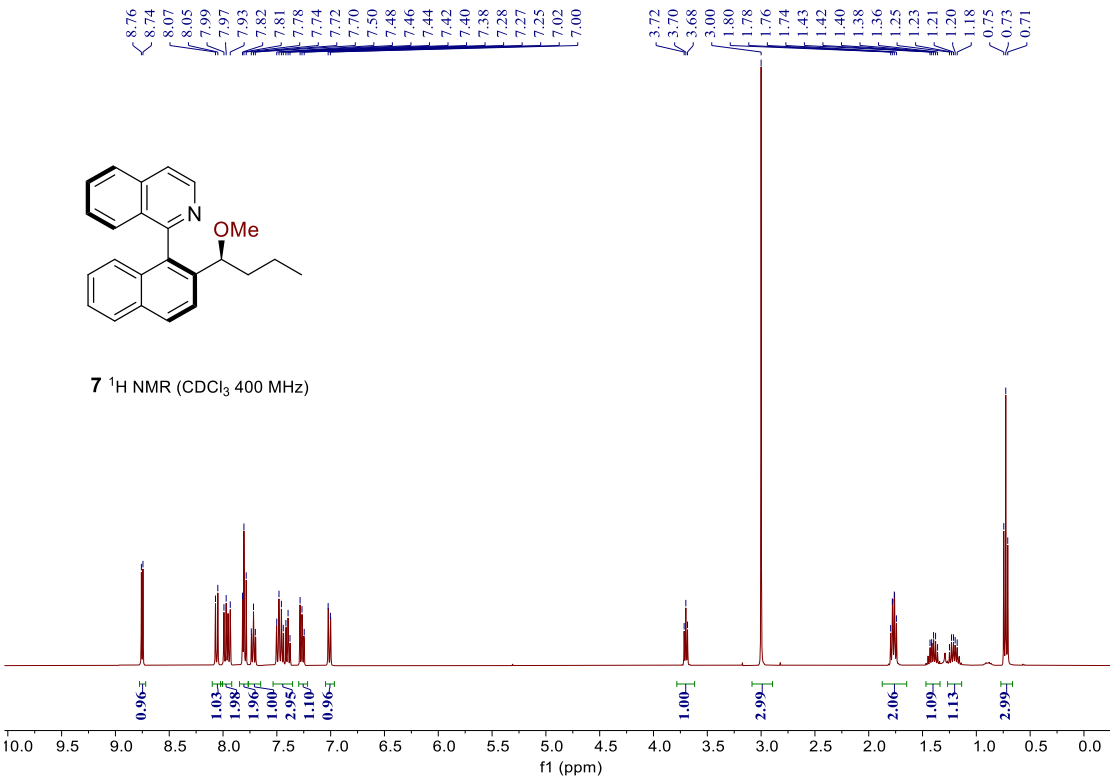
6f ^{13}C NMR ($CDCl_3$ 101 MHz)



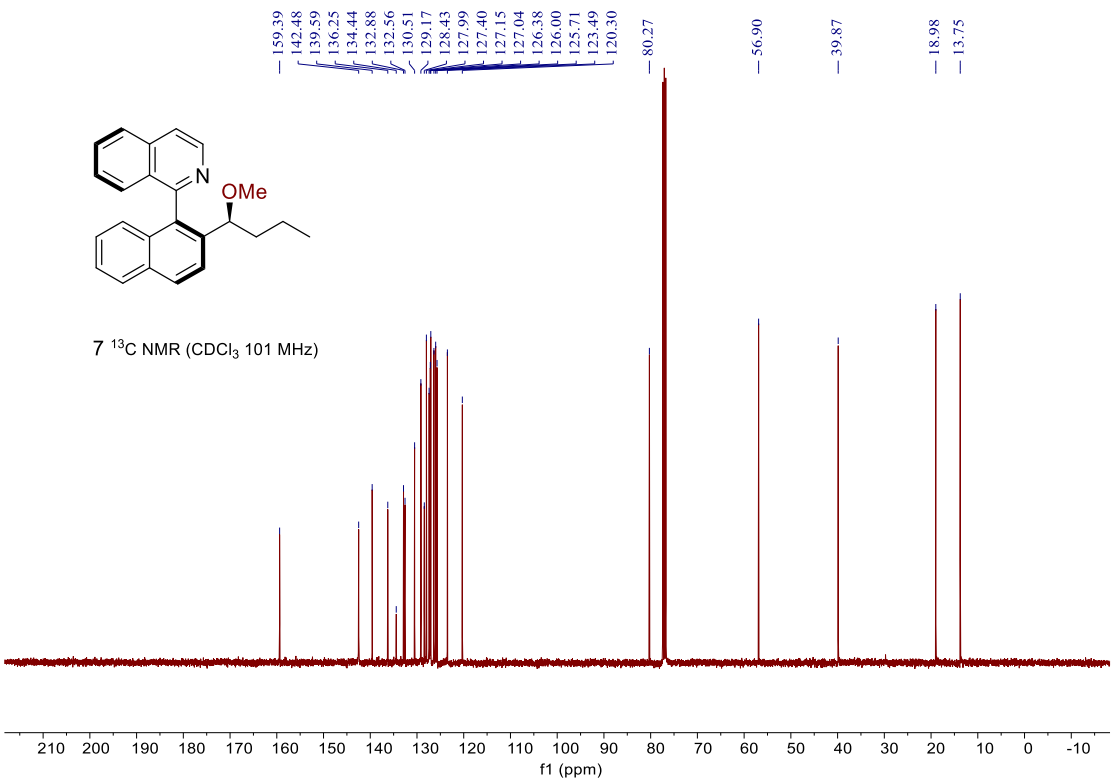
6g ^{1}H NMR ($CDCl_3$ 400 MHz)



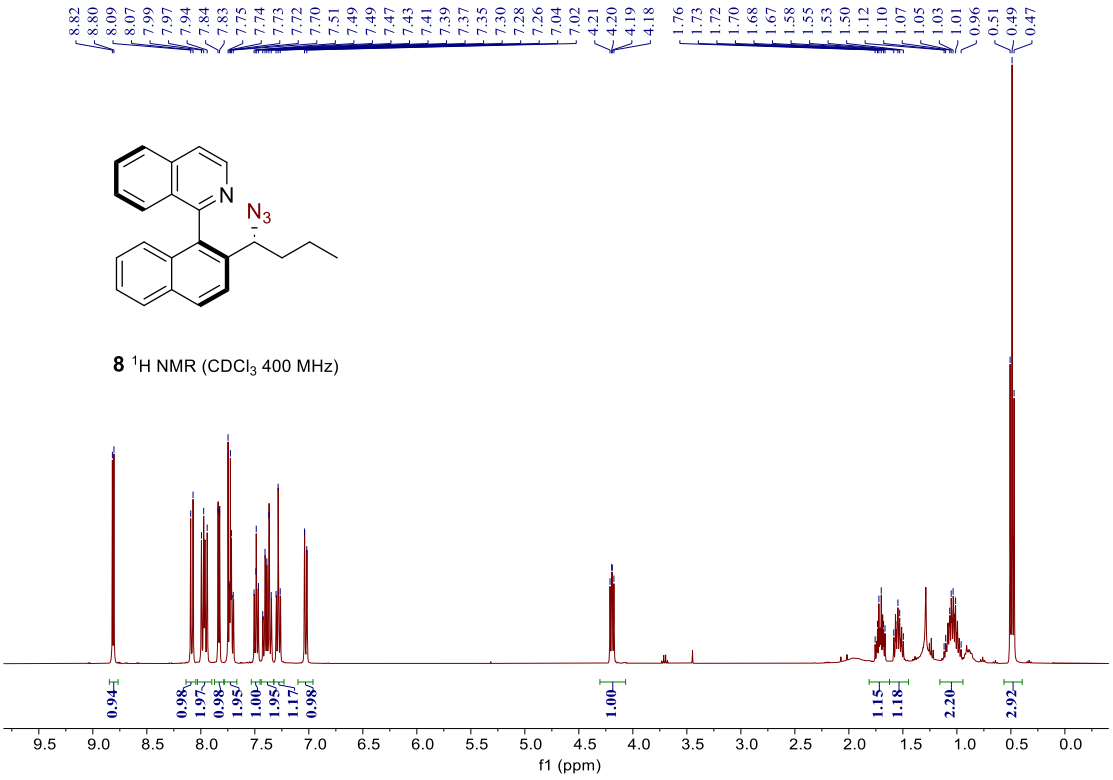
6g ^{13}C NMR ($CDCl_3$ 101 MHz)



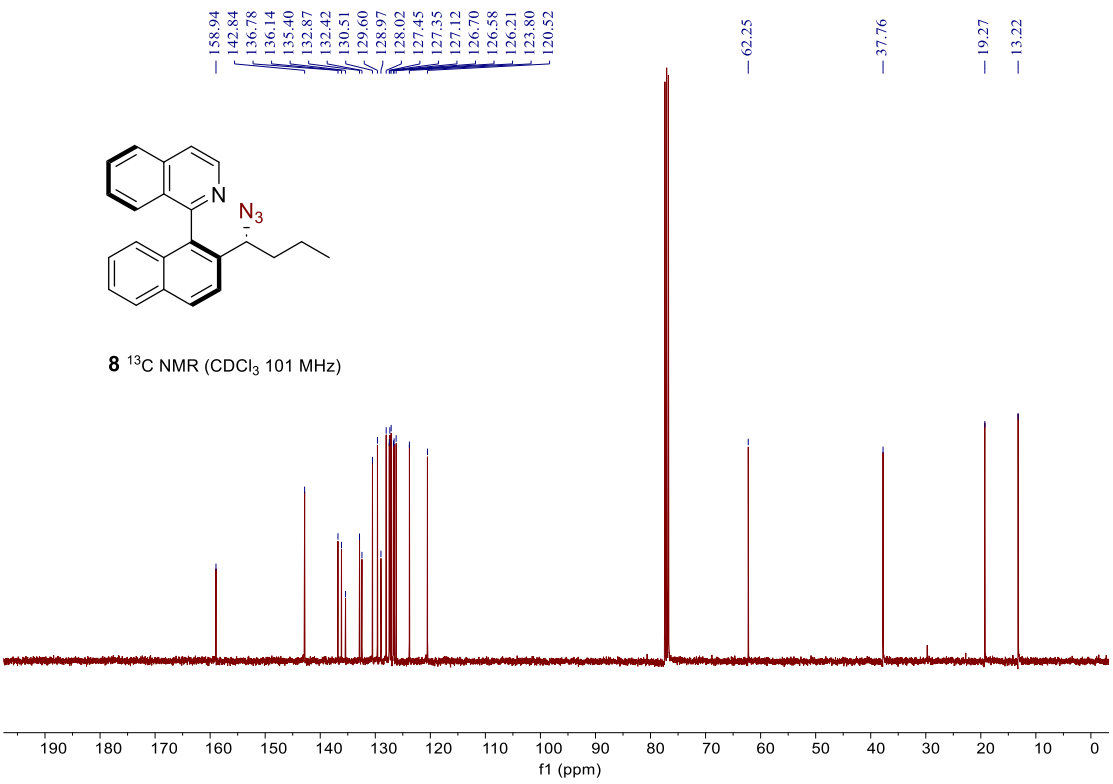
7 ^{1}H NMR ($CDCl_3$ 400 MHz)



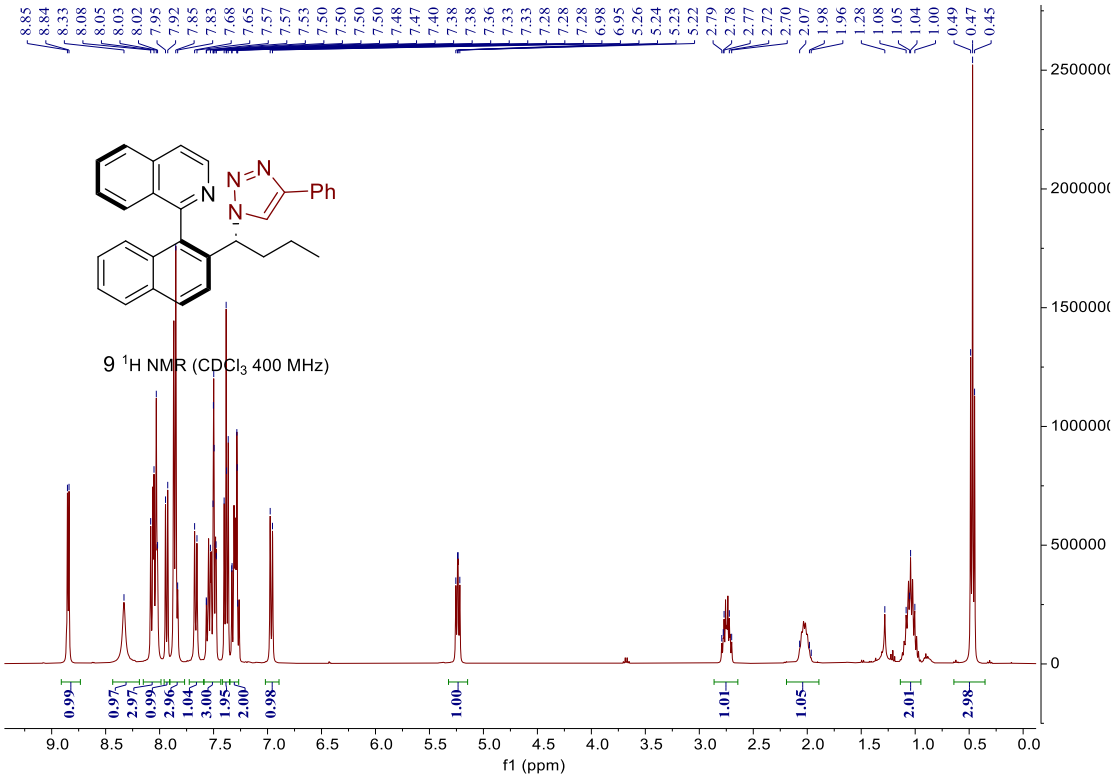
7 ^{13}C NMR ($CDCl_3$ 101 MHz)

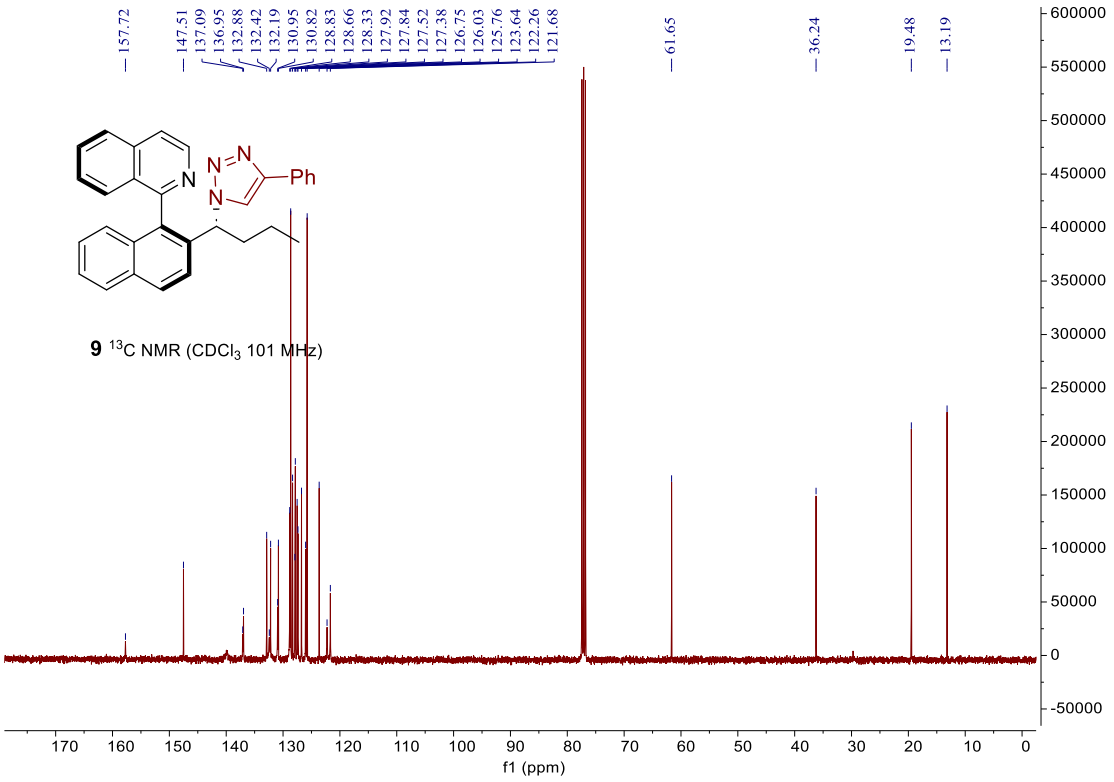


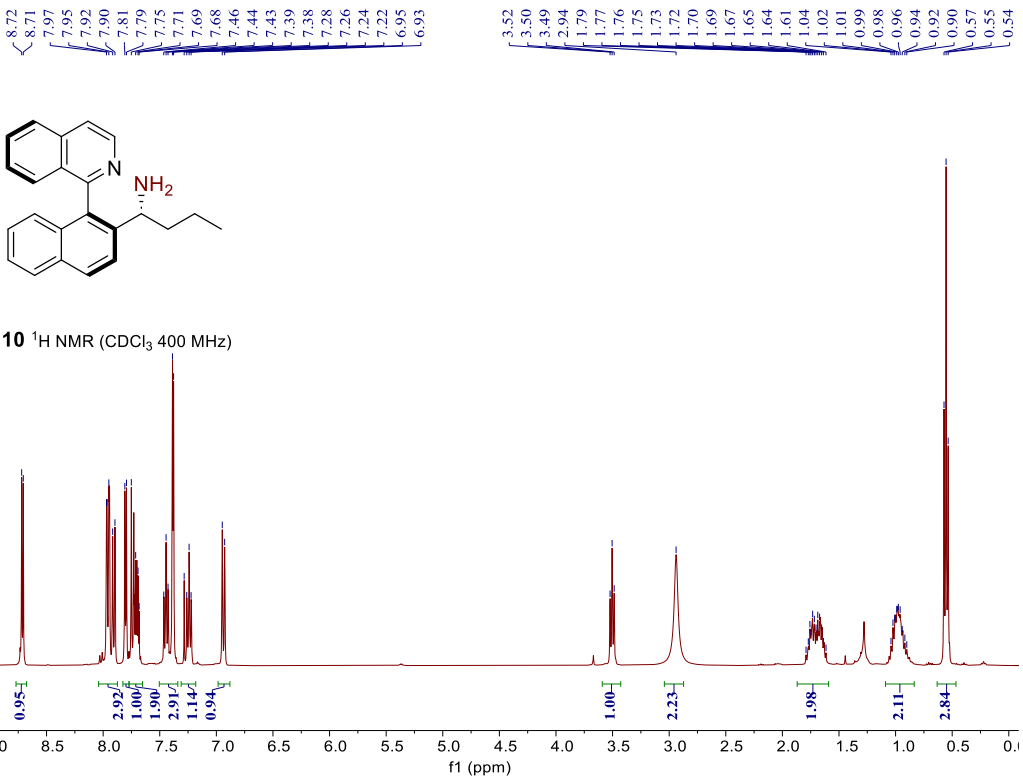
8 ^{1}H NMR ($CDCl_3$ 400 MHz)



8 ^{13}C NMR ($CDCl_3$ 101 MHz)


8.85 8.84 8.33 8.08 8.05 8.03 8.02 7.95 7.92 7.85 7.83 7.68 7.65 7.57 7.57 7.53 7.50 7.50 7.50 7.50 7.48 7.47 7.40 7.38 7.38 7.36 7.33 7.33 7.28 7.28 7.28 6.98 6.95 5.26 5.24 5.23 5.22 2.79 2.78 2.77 2.72 2.70 2.07 1.98 1.96 1.28 1.08 1.05 1.04 1.00 0.49 0.47 0.45
N
N
N
Ph
9 1H NMR (CDCl3 400 MHz)
0.99 0.97 2.97 0.99 2.96 1.04 3.00 1.95 2.00 0.98 1.00 1.01 1.05 2.01 2.98
f1 (ppm)


157.72 147.51 137.09 136.95 132.88 132.42 132.19 130.95 130.82 128.83 128.66 128.33 127.92 127.84 127.52 127.38 126.75 126.03 125.76 123.64 122.26 121.68 61.65 36.24 19.48 13.19
N
N
N
Ph
9 13C NMR (CDCl3 101 MHz)
f1 (ppm)


8.72
8.71
7.97
7.95
7.92
7.90
7.81
7.79
7.75
7.71
7.69
7.68
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7.44
7.43
7.39
7.38
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1.75
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1.72
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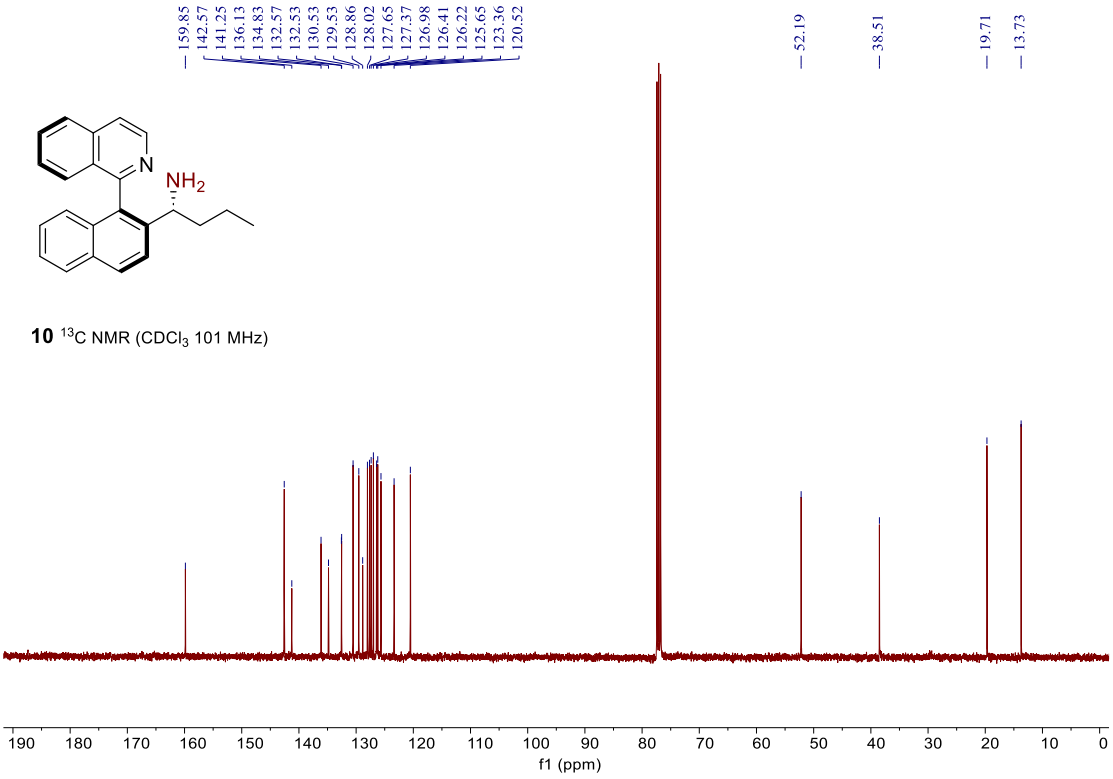
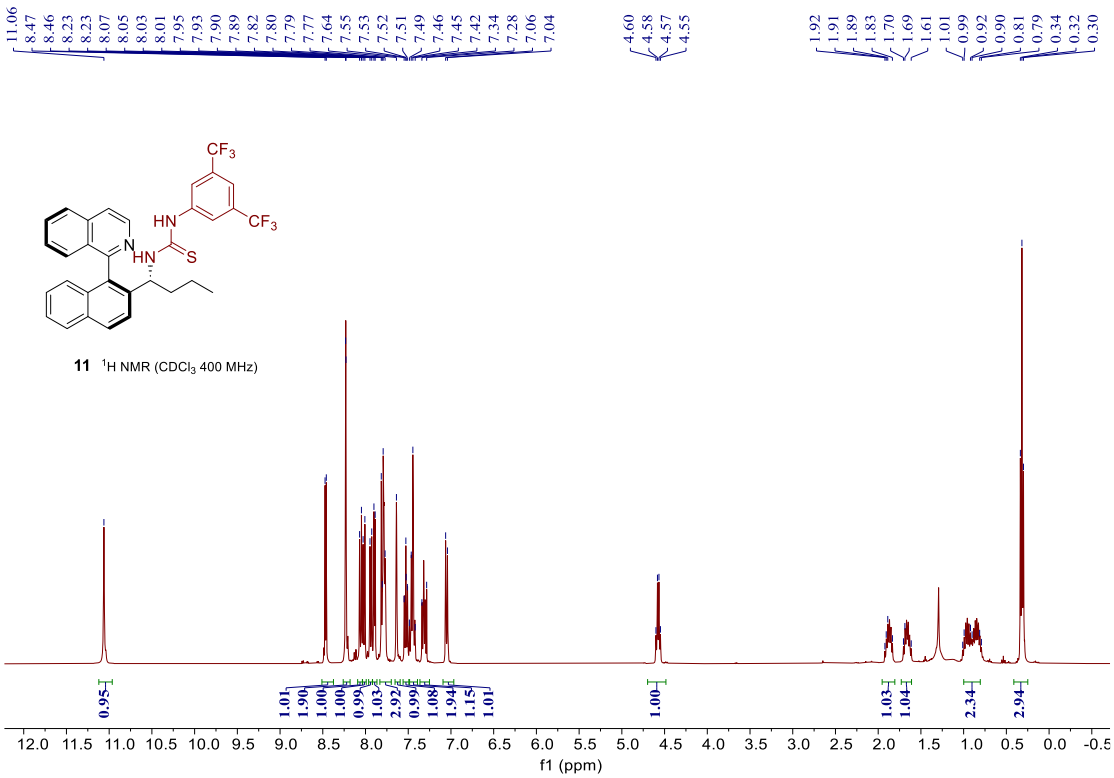
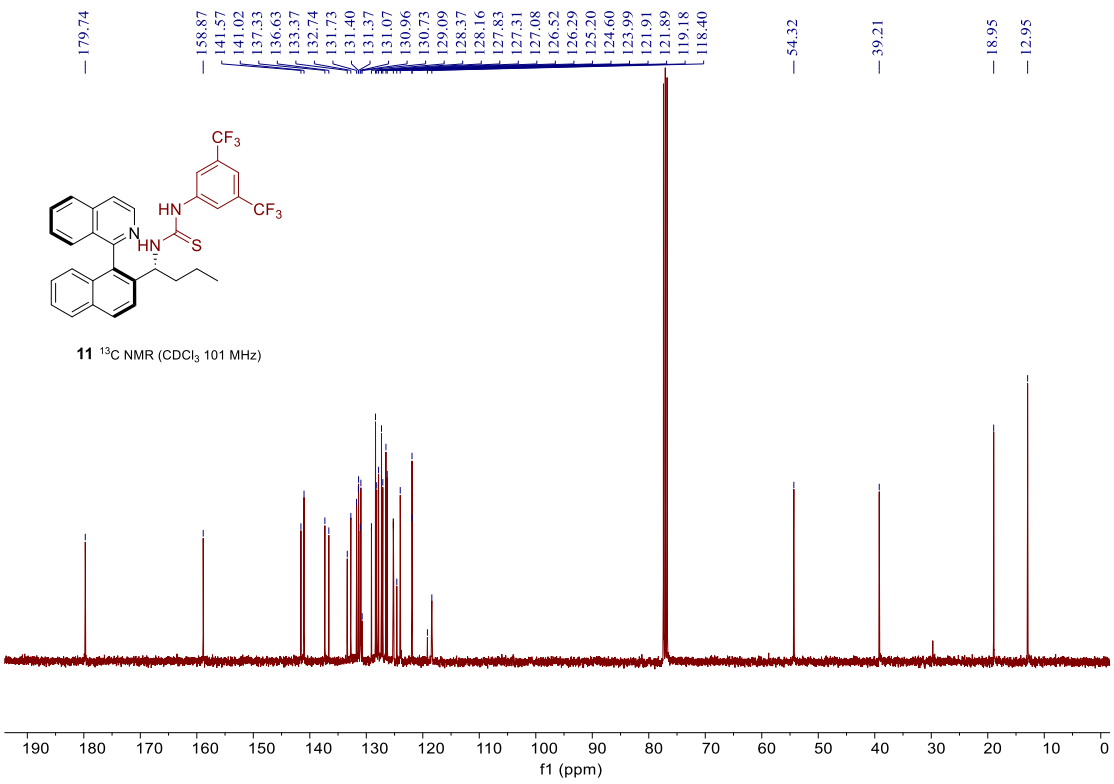
1.61
1.04
1.02
1.01
0.99
0.98
0.96
0.94
0.92
0.90
0.57
0.55
0.54
N
NH2
10 1H NMR (CDCl3 400 MHz)
0.95
2.92
1.00
1.90
2.91
1.14
0.94
1.00
2.23
1.98
2.11
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

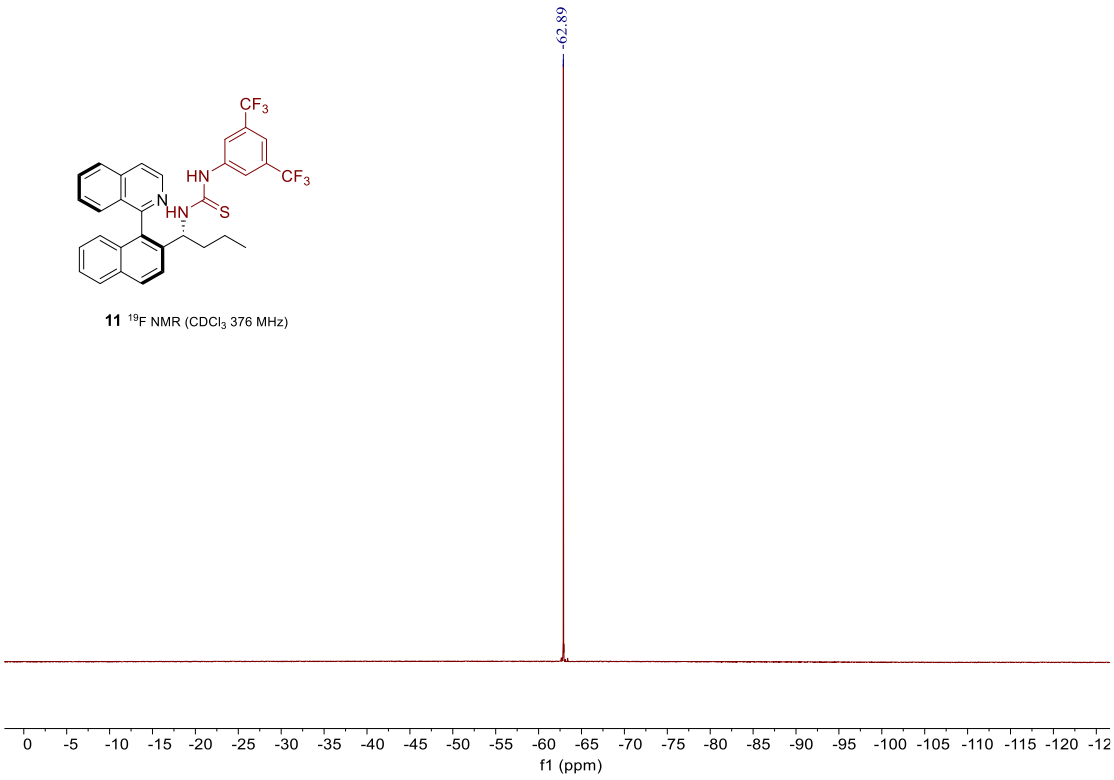

159.85
142.57
141.25
136.13
134.83
132.57
132.53
130.53
129.53
128.86
128.02
127.65
127.37
126.98
126.41
126.22
125.65
123.36
120.52
52.19
38.51
19.71
13.73
N
NH2
10 13C NMR (CDCl3 101 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



11 ^{1}H NMR ($CDCl_3$ 400 MHz)



11 ^{13}C NMR ($CDCl_3$ 101 MHz)



11 ^{19}F NMR ($CDCl_3$ 376 MHz)

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