Supporting Information

Bi-Aryl Rotation in Phenyl-dihydroimidazoquinoline Catalysts for Kinetic Resolution of Arylalkyl Carbinols

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Supporting Information

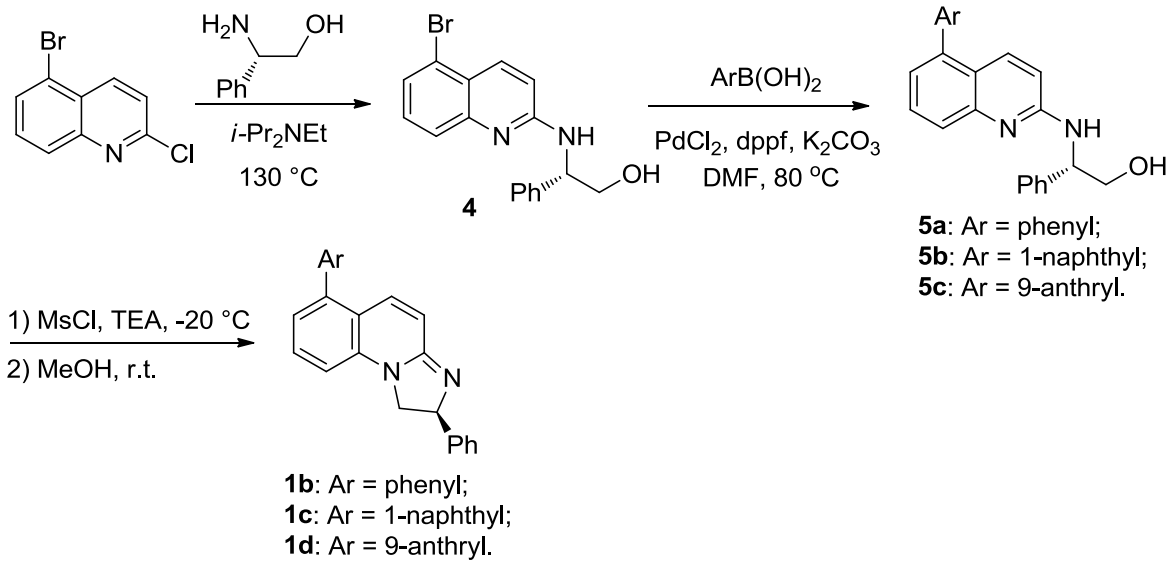
1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-*d*. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple, brs = broad single, coupling constant(s) in Hz, integration). ^{13}C NMR spectra (proton decoupled) were recorded on a Bruker DPX 100 MHz spectrometer in chloroform-*d*. Chemical shifts were reported in ppm with the internal chloroform signal at 77.16 ppm as a standard. Optical rotations were measured on a AUTOPOL Ⅲ polarimeter. Enantiomer ratios were determined by HPLC, using chiralpak OD-H, AS-H and AD-H columns with hexane and *i*-propanol as solvents. (Chiralpak OD-H, AS-H, AD-H columns were purchased from Daicel Chemical Industries, LTD.)

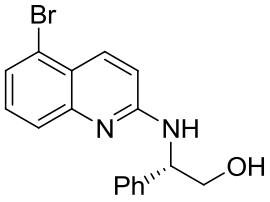
All reagents and starting materials were obtained commercially and used as received unless otherwise specified. The substrates used in the kinetic resolution experiments were either purchased or prepared either by sodium borohydride reduction of the corresponding ketones or by reacting aromatic aldehydes with Grignard reagents.[1-2] Toluene was dried over Na and distilled prior to use. Methods used for kinetic resolution experiments determination of ee's and calculation of conversions and selectivities were adopted from previously published work.[1]

2. Procedures for the synthesis of catalysts 1

Synthesis of catalysts 1a, 1b and 1d



(*S*)-2-(5-Bromoquinolin-2-ylamino)-2-phenylethanol (4)



A flame-dried Schlenk tube charged with 5-bromo-2-chloroquinoline (500 mg, 2.06 mmol), (*S*)-2-amino-2-phenylethanol (340 mg, 2.47 mmol), (*i*-Pr)$_2$NEt (0.95 mL, 6.18 mmol) and a stir bar was flushed with N_2 several times and heated at 130 ± 5 °C for 48 h. After allowing the tube to cool to 30-40 °C, CH_2Cl_2 (5 mL) was added to the viscous reaction mixture and it was left at room temperature to dissolve. The diluted mixture was purified by chromatography column chromatography (silica, EtOAc/ petroleum = 1/4) to give the

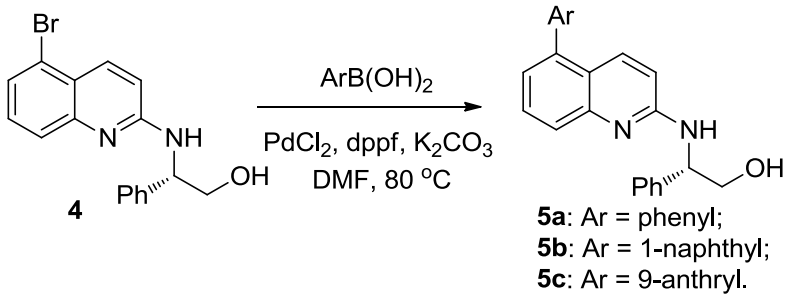
compound **4** as a white solid. (559 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 6.7 Hz, 1H), 7.43-7.31 (m, 6H), 6.70 (d, *J* = 9.1 Hz, 1H), 5.52 (brs, 1H), 5.36 (s, 1H), 5.21-5.15 (m, 1H), 4.06 (dd, *J* = 11.1, 7.4 Hz, 1H), 4.00 (dd, *J* = 11.1, 2.9 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 148.0, 140.0, 137.1, 130.2, 129.1, 128.1, 126.8, 126.5, 125.7, 122.8, 121.9, 113.3, 68.7, 59.9;

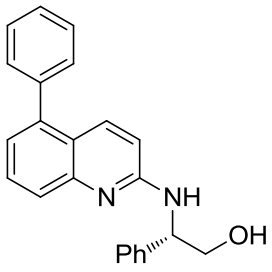
HRMS (EI, m/z): Calcd for $C_{17}H_{15}BrN_2O$: 342.0368, found: 342.0369.

General procedure for Suzuki coupling reaction



Under nitrogen atmosphere, to a flame-dried Schlenk flask were added successively (*S*)-2-(5-bromoquinolin-2-ylamino)-2-phenylethanol (**4**, 1 equiv.), arylboronic acid (2 equiv.), $PdCl_2$ (0.1 equiv.), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.1 equiv.), K_2CO_3 (2.2 equiv.) and DMF, and then stirring at 80 °C for an indicated time. The resulting solution was cooled to room temperature, extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (EtOAc/ petroleum = 1/10 to EtOAc/ petroleum = 1/4) on silica gel.

(*S*)-2-Phenyl-2-((5-phenylquinolin-2-yl)amino)ethanol (5a)



According to the general procedure, (*S*)-2-(5-bromoquinolin-2-ylamino)-2-phenylethanol (**4**, 343 mg, 1.0 mmol), Phenylboronic acid (244 mg, 2.0 mmol), $PdCl_2$ (18 mg, 0.1 mmol), dppf (55 mg, 0.1 mmol), K_2CO_3 (304 mg, 2.2 mmol) and DMF (7.5 mL) were added to 10-mL Schlenk flask. After stirring at 80 °C for 12 h, the reaction mixture was purified to afford compound **5a** as a white solid (289 mg, 85% yield).

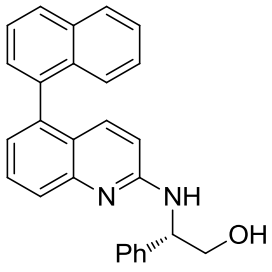
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64-7.53 (m, 1H), 7.51-7.28 (m, 10H), 7.21 (dd, *J* = 7.1, 0.8 Hz, 1H), 6.56 (d, *J* = 9.2 Hz, 1H), 5.36 (brs, 1H), 5.14 (dd, *J* = 7.2, 2.2 Hz, 1H), 4.12-3.92 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 147.1, 140.5, 140.4, 140.0, 136.3, 130.1, 129.6, 129.2, 128.5, 128.2, 127.5, 127.0, 125.3, 123.9, 121.8, 112.1, 69.1, 60.5;

HRMS (EI, m/z): Calcd for $C_{23}H_{20}N_2O$: 340.1576, found: 340.1572.

(*S*)-2-((5-(Naphthalen-1-yl)quinolin-2-yl)amino)-2-phenylethanol (mixture of (2*S*, 5*S*)-5b and (2*S*, 5*R*)-5b)

Supporting Information



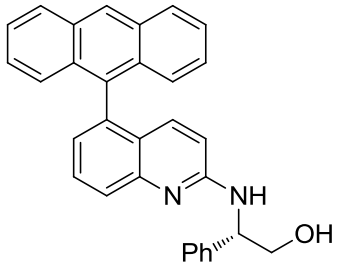
According to the general procedure, (*S*)-2-(5-bromoquinolin-2-ylamino)-2-phenylethanol (**4**, 343 mg, 1.0 mmol), 1-Naphthylboronic acid (344 mg, 2.0 mmol), $PdCl_2$ (18 mg, 0.1 mmol), dppf (55 mg, 0.1 mmol), K_2CO_3 (304 mg, 2.2 mmol) and DMF (7.5 mL) were added to 10-mL Schlenk flask. After stirring at 80 °C for 12 h, the reaction mixture was purified to afford a mixture of (2*S*, 5*S*)-**5b** and (2*S*, 5*R*)-**5b** as a white solid (375 mg, 96% yield). **Note**: the two diastereoisomers of **5b** cannot be separated by column chromatography on silica gel, and only one set of ^{1}H NMR was observed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.87 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 13.4, 6.7 Hz, 1H), 7.39-7.19 (m, 10H), 6.35 (dd, *J* = 8.8, 5.3 Hz, 1H), 5.68-5.40 (m, 1H), 5.06 (s, 1H), 4.05 -3.91 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 146.9, 146.8, 140.4, 138.6, 137.6, 137.6, 136.6, 133.6, 132.8, 132.8, 129.5, 129.5, 129.1, 128.3, 128.3, 128.1, 128.1, 128.1, 127.9, 127.8, 126.9, 126.5, 126.4, 126.3, 126.2, 126.0, 126.0, 125.4, 125.4, 125.4, 124.8, 124.7, 123.0, 112.1, 112.0, 68.9, 68.8, 60.3, 60.3;

HRMS (EI, m/z): Calcd for $C_{27}H_{22}N_2O$: 390.1732, found: 390.1735.

(*S*)-2-((5-(Anthracen-9-yl)quinolin-2-yl)amino)-2-phenylethanol (5c)



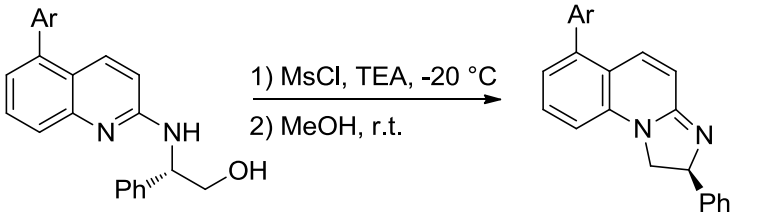
According to the general procedure, (*S*)-2-(5-bromoquinolin-2-ylamino)-2-phenylethanol (**4**, 343 mg, 1.0 mmol), anthracen-9-ylboronic acid (444 mg, 2.0 mmol), $PdCl_2$ (18 mg, 0.1 mmol), dppf, (55 mg, 0.1 mmol), K_2CO_3 (304 mg, 2.2 mmol) and DMF (7.5 mL) were added to 10 mL Schlenk flask. After stirring at 80 °C for 24 h, the reaction mixture was purified to afford compound **5c** as an off-white solid (326 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80-7.69 (m, 1H), 7.51-7.22 (m, 12H), 7.02 (d, *J* = 9.1 Hz, 1H), 6.45 (brs, 1H), 6.33 (d, *J* = 9.1 Hz, 1H), 5.26-5.02 (m, 2H), 4.09 (dd, *J* = 10.8, 7.9 Hz, 1H), 4.01 (dd, *J* = 11.0, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 146.9, 140.3, 136.7, 136.6, 134.0, 131.4, 131.1, 131.0, 129.8, 129.2, 128.6, 128.5, 128.3, 127.2, 127.0, 126.9, 126.8, 126.1, 125.9, 125.8, 125.7, 125.4, 125.3, 123.9, 112.6, 69.3, 60.7;

HRMS (CI, m/z): Calcd for $C_{31}H_{24}N_2O$: 440.1889, found: 440.1892.

General procedure for ring-closure reaction



5a: Ar = phenyl;
5b: Ar = 1-naphthyl;
5c: Ar = 9-anthryl.

1b: Ar = phenyl;
1c: Ar = 1-naphthyl;
1d: Ar = 9-anthryl.

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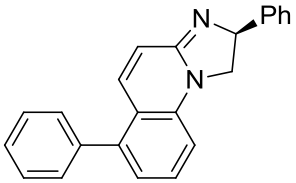
A solution of **5** (1 equiv.) in CH_2Cl_2 was cooled to -20 °C, then treated with Et_3N (3 equiv.) followed by MsCl (1.5 equiv.). After stirring at -20 °C for an indicated time, the solution was treated with 2~3 drops MeOH to quench the excess MsCl. The reaction mixture was warmed to room temperature and stirred overnight. The resulting yellow solution was extracted with CH_2Cl_2, the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (EtOAc/petroleum = 1/4 to TEA/EtOAc/petroleum = 4/32/64) on silica gel.

(*S*)-2,6-Diphenyl-1,2-dihydroimidazo[1,2-a]quinoline (1b)



According to the general procedure, A solution of **5a** (68 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) was cooled to -20 °C, then treated with Et_3N (0.08 mL, 0.6 mmol) followed by MsCl (23 μL, 0.3 mmol). After stirring at -20 °C for 20 min, the solution was quenched and purified to afford compound **1b** as a yellow solid (59 mg, 92% yield).

Yellow oil; $[\alpha]^{30}_D$: -23.2 (*c* 0.2, $CHCl_3$);

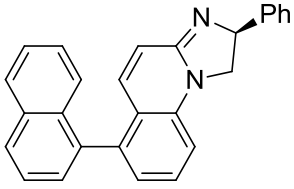
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.31 (m, 11H), 7.31-7.26 (m, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 5.39 (dd, *J* = 11.4, 8.3 Hz, 1H), 4.43 (dd, *J* = 11.4, 10.3 Hz, 1H), 3.93 (dd, *J* = 10.1, 8.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 144.2, 141.7, 139.5, 139.2, 135.5, 130.2, 129.8, 128.9, 128.5, 127.8, 127.5, 126.8, 122.3, 119.0, 116.6, 111.2, 67.4, 54.7;

HRMS (ESI, m/z): Calcd for $[M+H]^+$ $C_{23}H_{19}N_2$: 322.1548, found: 323.1553;

IR (KBr) ν 3382, 2922, 1636, 1600, 1576, 1460, 1399, 1378, 1155, 1143, 793, 759 cm^{-1}.

(*S*)-6-(Naphthalen-1-yl)-2-phenyl-1,2-dihydroimidazo[1,2-a]quinoline (mixture of (2*S*, 5*S*)-1c and (2*S*, 5*R*)-1c)



According to the general procedure, A solution of **5b** (78 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) was cooled to -20 °C, then treated with Et_3N (0.08 mL, 0.6 mmol) followed by MsCl (23 μL, 0.3 mmol). After stirring at -20 °C for 20 min, the solution was quenched and purified to afford compound **1c** as a yellow solid (62 mg, 83% yield).

Note: the two diastereoisomers of **1c** cannot be separated by column chromatography on silica gel, and only one set of ^{1}H NMR was observed.

m.p.: 123-125 °C; $[\alpha]^{24}_D$: -131.9 (*c* 0.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2H), 7.58-7.33 (m, 10H), 7.31-7.25 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 9.9 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.47 (d, *J* = 9.9 Hz, 1H), 5.41 (dd, *J* = 11.0, 8.8 Hz, 1H), 4.47 (td, *J* = 10.8, 5.4 Hz, 1H), 3.97 (dt, *J* = 9.1, 7.6 Hz, 1H);

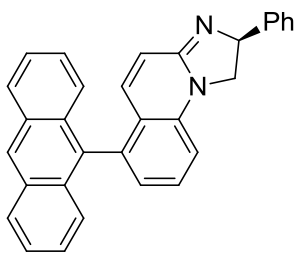
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 144.5, 139.6, 139.2, 137.1, 137.1, 135.2, 135.2, 133.5, 132.4, 130.0, 130.0, 128.8, 128.3, 127.7, 127.4, 126.8, 126.8, 126.5, 126.2, 126.1, 125.3, 125.3, 122.8, 122.8, 120.3, 120.2, 117.0, 111.2, 111.2, 68.0, 67.9, 54.5;

HRMS (EI, m/z): Calcd for $C_{27}H_{20}N_2$: 372.1626, found: 372.1624;

IR (KBr) ν 3427, 2917, 1636, 1570, 1453, 1385, 1261, 1089, 1016, 795, 753, 700 cm^{-1}.

Supporting Information

(*S*)-6-(Anthracen-9-yl)-2-phenyl-1,2-dihydroimidazo[1,2-a]quinoline (1d)



According to the general procedure, A solution of **5c** (88 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) was cooled to -20 °C, then treated with Et_3N (0.08 mL, 0.6 mmol) followed by MsCl (23 μL, 0.3 mmol). After stirring at -20 °C for 30 min, the solution was quenched and purified to afford compound **1d** as a yellow solid (74 mg, 88% yield).

m.p.:148-150 °C; $[\alpha]^{30}_D$: -13.6 (*c* 0.2, $CHCl_3$);

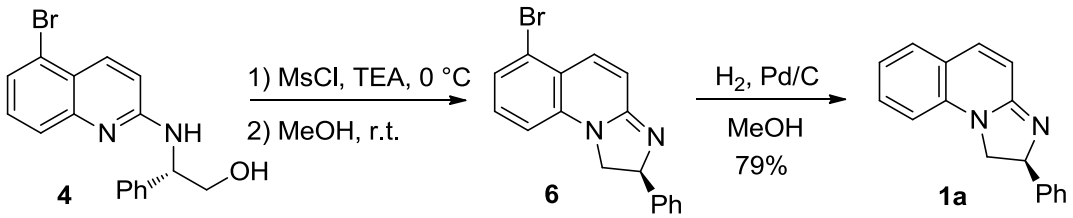
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.09-8.05 (m, 2H), 7.54-7.44 (m, 5H), 7.44-7.32 (m, 6H), 7.28 (t, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 9.9 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 5.48-5.37 (m, 1H), 4.51 (t, *J* = 10.9 Hz, 1H), 4.01 (t, *J* = 9.3 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 144.6, 139.5, 137.8, 135.0, 133.4, 131.4, 130.7, 130.2, 128.8, 128.6, 127.4, 126.9, 126.6, 126.5, 126.1, 125.4, 123.8, 121.2, 117.4, 111.4, 68.1, 54.5;

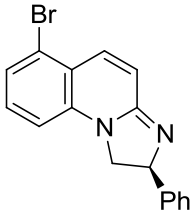
HRMS (ESI, m/z): Calcd for $[M+H]^+$ $C_{31}H_{23}N_2$: 423.1861, found: 423.1858;

IR (KBr) ν 3424, 2922, 1704, 1637, 1578, 1465, 1413, 1379, 1206, 1154, 1126, 892, 737, 700 cm^{-1}.

Synthesis of catalyst 1a



(*S*)-6-Bromo-2-phenyl-1,2-dihydroimidazo[1,2-a]quinoline (6)



A solution of **2** (415 mg, 1.21 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C, then treated with Et_3N (0.51 mL, 3.63 mmol) followed by MsCl (0.14 mL, 1.82 mmol). After stirring at 0 °C for 0.5 h, the solution was treated with 2~3 drops MeOH to quench the excess MsCl. The reaction mixture was warmed to room temperature and stirred overnight. The resulting yellow solution was extracted with CH_2Cl_2 (3×15 mL), the combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography (TEA/EtOAc/petroleum = 4/32/64) on silica gel to give the compound **6** as a yellow solid (342 mg, 87% yield).

$[\alpha]^{30}_D$: -25.7 (*c* 0.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 10.0 Hz, 1H), 7.38-7.31 (m, 4H), 7.29-7.23 (m, 1H), 7.19-7.07 (m, 2H), 6.71 (d, *J* = 10.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.38 (dd, *J* = 11.4, 8.4 Hz, 1H), 4.34 (dd, *J* = 11.1, 10.6 Hz, 1H), 3.83 (dd, *J* = 10.1, 8.5 Hz, 1H);

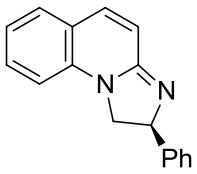
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 143.7, 139.7, 135.3, 130.7, 128.5, 127.1, 126.3, 124.1, 123.0, 119.8, 118.0, 110.8, 67.6, 54.0;

HRMS (EI, m/z): Calcd for $C_{17}H_{13}BrN_2$: 324.0262, found: 324.0264;

IR (KBr) ν 3422, 1632, 1561, 1492, 1480, 1447, 1373, 1202, 1147, 1064, 1036, 770, 699 cm^{-1}.

Supporting Information

(*S*)-2-Phenyl-1,2-dihydroimidazo[1,2-a]quinoline (1a)



A suspension of **6** (50 mg, 0.15 mmol) in 10 mL of MeOH was hydrogenated over 10% Pd/C (4 mg) at a 1 bar H_2 pressure for 18 h. The reaction mixture was filtered through Celite and concentrated. The residue was purified by column chromatography (TEA/EtOAc/petroleum = 4/32/64) to afford compound **1a** as yellow solid (30 mg, 79% yield).

m.p.:119-122 °C; $[\alpha]^{30}_D$: -32.0 (*c* 0.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 6H), 7.31 (d, *J* = 9.7 Hz, 1H), 7.30-7.25 (m, 1H), 7.00 (td, *J* = 7.6, 0.9 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 9.7 Hz, 1H), 5.39 (dd, *J* = 11.5, 8.3 Hz, 1H), 4.42 (dd, *J* = 11.4, 10.3 Hz, 1H), 3.91 (dd, *J* = 10.2, 8.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 144.2, 138.9, 137.3, 130.7, 128.9, 128.4, 127.5, 126.8, 121.3, 120.6, 117.0, 111.8, 67.5, 54.2;

HRMS (ESI, m/z): Calcd for $[M+H]^+$ $C_{17}H_{15}N_2$: 247.1235, found: 247.1235;

IR (KBr) ν 3423, 2924, 1635, 1573, 1456, 1456, 1409, 1375, 1292, 1134, 1074, 974, 817, 749, 699 cm^{-1}.

3. Research on the epimerisation of *Np*-PIQ

The *Np*-PIQ was found to give one set of ^{1}H NMR, however, complicated ^{13}C NMR indicated there were two diastereoisomers of *Np*-PIQ which cannot be separated from column chromatography on silica gel. Consequently, we analysed *Np*-PIQ by the chiral HPLC, which clearly gave two diastereoisomeric peaks in 1:1 ratio (Scheme S1). Further semi-preparative chiral HPLC separation gave two diastereoisomers in high diastereomeric purities (Scheme S2), but they can slowly epimerise[3] in the HPLC eluent (Fig. S1), as well as during the evaporation under reduced pressure. Two diastereoisomers with moderate de value were tested in KR of secondary alcohol, affording reasonable and comparable *S* value; the de value of recovered catalysts was also assayed (Table S1). Although we cannot eliminate the possibility that catalysts suffered from epimerization during routine work-up process, further investigation showed **1c** can slowly epimerise under optimised reaction condition (in toluene at 0 °C) (Fig. S2). Therefore, the 1:1 ratio of diastereoisomers of *Np*-PIQ were used for the KR of secondary alcohols.

Methods used to Assay diastereoisomeric Excess

HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*sopropanol = 70/30 + 0.1%DEA, 1.0 mL/min, 254 nm) for two diastereoisomers: t_R = 19.68 min, 30.25 min.

Methods used for Semi-Preparative Separation of *Np*-PIQ

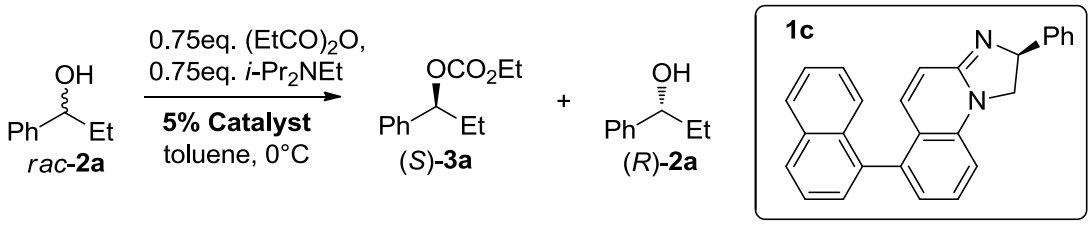
HPLC (Daicel Chiralpak AD-H, *n*-hexane/*i*sopropanol = 50/50 + 0.1%DEA, 3.0 mL/min, 254 nm) for two diastereoisomers: t_R = 17.32 min, 28.40 min.

Procedure for the kinetic resolution of rac-2a by catalyst 1c/1c-A/1c-B.

Under nitrogen atmosphere, catalyst **1c/1c-A/1c-B** (0.02 mmol, 7.4 mg), 1-Phenyl-1-propanol (0.4 mmol, 54.5 mg), toluene (4 mL) and *N*,*N*-diisopropylethylamine (0.3 mmol, 0.052 mL) were sequentially added to a 20 mL flame-dried Schlenk tube in an ice bath. After stirring at 0 °C for 15

min, the reaction mixture was treated with propionyl anhydride (0.3 mmol, 0.039 mL); then the resulting solution was stirred at 0 °C for 10 h and quenched by rapid addition of 0.5 mL of methanol. The solution was stirred at 0 °C for an additional 1 h. The solvent was removed *in vacuo*, and the residue was quickly purified by silca gel chromatography (5% - 10% EtOAc/petroleum to TEA/EtOAc/petroleum = 4/32/64) to separate the ester from the unreacted alcohol as well as recover the catalyst.

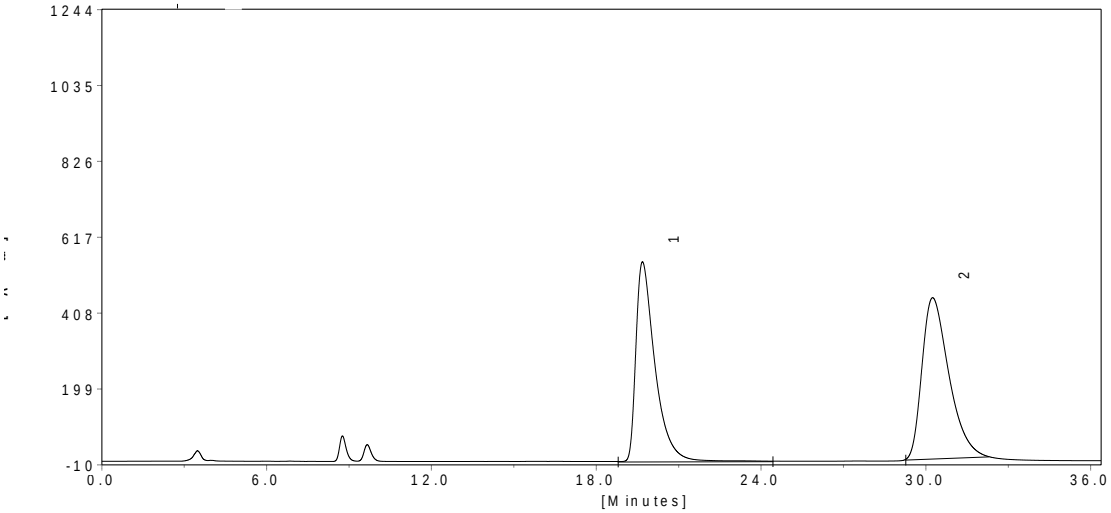
Table S1 KR of *Np*-PIQ with different de value



Entry[a]	Cat.[b]	de of cat. (%)	de of recovered cat.(%)	T (h)	ee_A (%)	ee_E (%)	C_{HPLC} (%)[c]	*S*
1	**1c**	0	0	10	89.5	93.4	48.9	**89**
2	**1c-A**	78	62	10	88.1	94.0	48.4	**95**
3	**1c-B**	77	55	10	79.1	93.8	45.8	**76**

[a] Conditions: 0.4 mmol of 1-Phenyl-1-propanol, 0.75 equiv. $(EtCO)_2O$, 0.75 equiv.*i*-Pr_2NEt, 5 mol% catalyst, 4 mL toluene; [b] The two diastereoisomers of **1c** were assigned as **1c-A** and **1c-B** respectively according to the order of their peaks on the chiral HPLC spectra; [c] Calculated from the ee of the ester and unreacted alcohol.

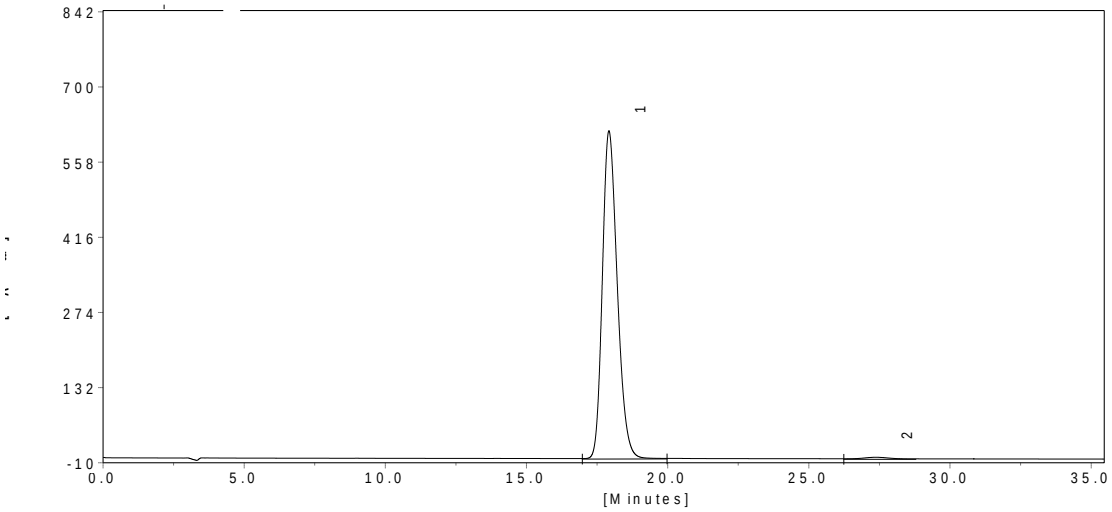
Scheme S1 HPLC data for *Np*-PIQ



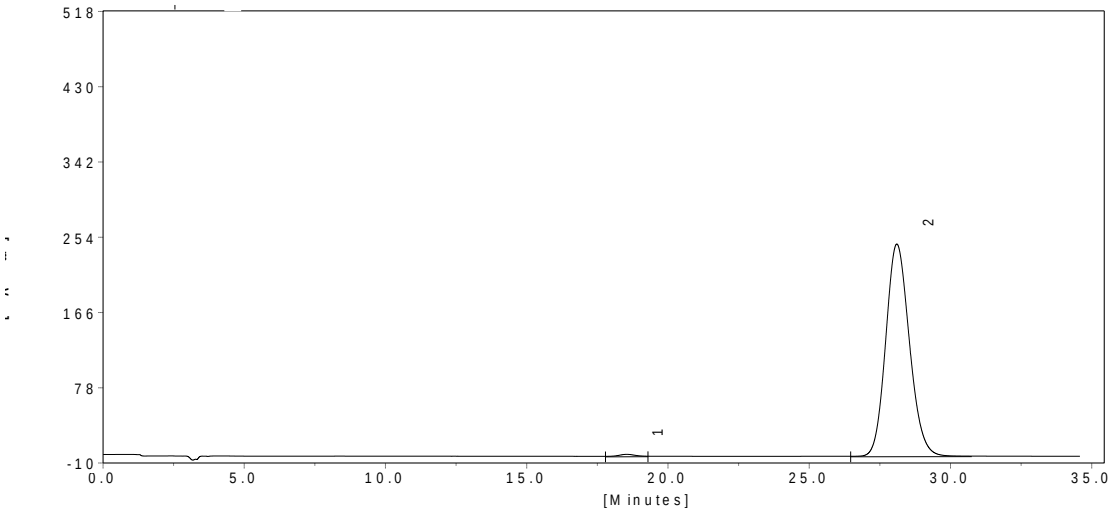
Peak #	Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	19.68250	550.24	26411.06	46.8076
2	30.24500	443.12	30013.61	53.1924

Supporting Information

Scheme S2 HPLC data for the two diastereoisomers of *Np*-PIQ after chiral separation



Peak #	Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	17.91833	619.29	22630.68	99.2914
2	27.36083	2.89	161.51	0.7086



Peak #	Time (min)	Height (mV)	Area (mV.sec)	Area (%)
1	18.52583	2.23	80.29	0.5542
2	28.09917	248.16	14406.01	99.4458

Supporting Information

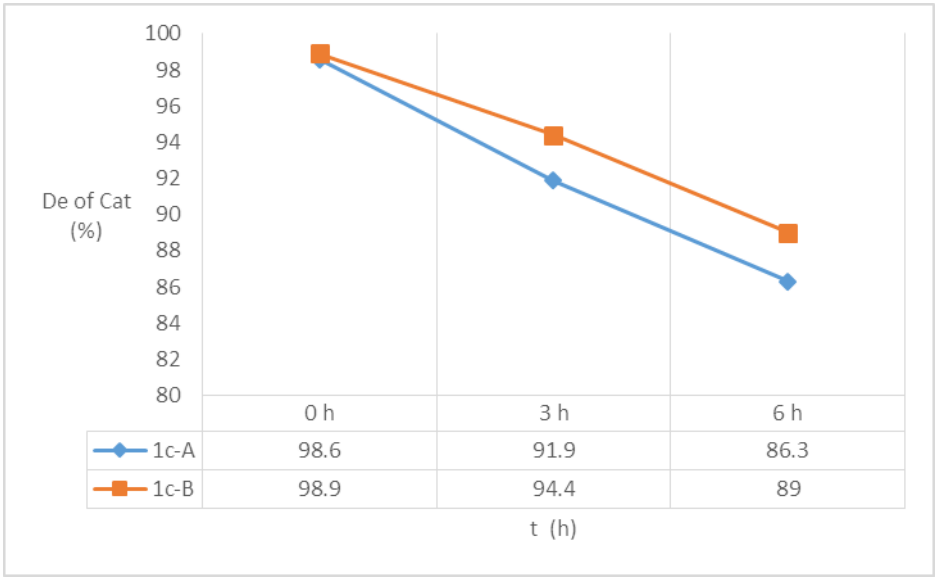


Fig. S1 The epimerisation of **1c** with different de values in HPLC eluent (*n*-hexane/*i*sopropanol = 50/50 + 0.1%DEA) at room temperature

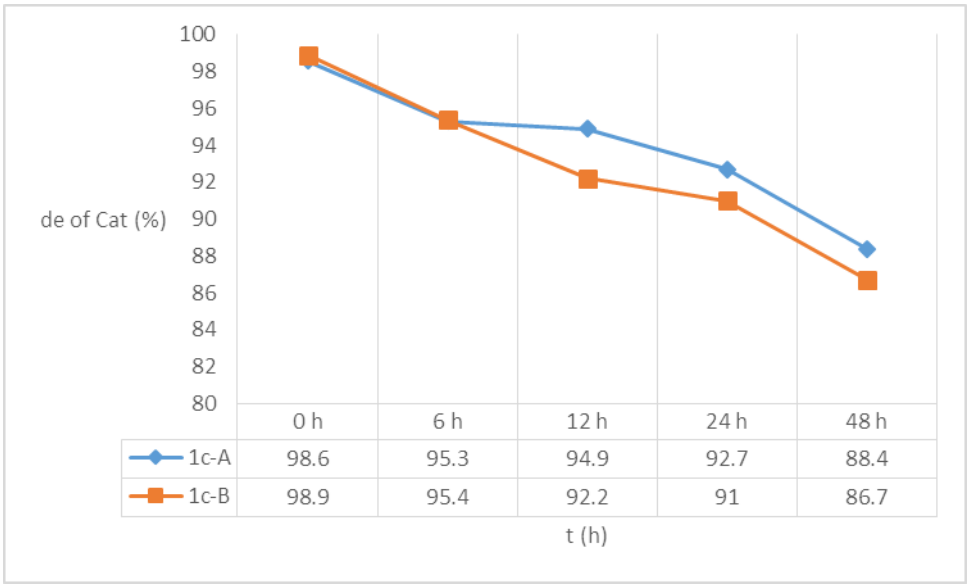
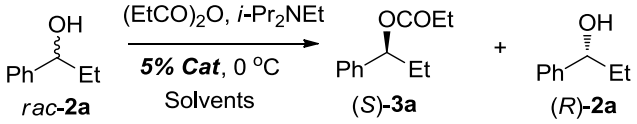


Fig. S2 The epimerisation of **1c** with different de values in toluene at 0 °C

Supporting Information

4. Comparison of different PIQ catalysts for the KR

Table S2 Comparison of different PIQ catalysts for the KR

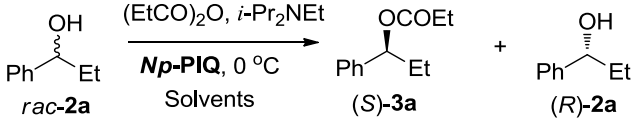


Entry	Cat	solvent	t (h)	ee_A (%)	ee_E (%)	C_{HPLC} (%)	S
1[a]	**1a**	$CHCl_3$	8	95.2	84.8	52.9	45
2[a]	**1b**	$CHCl_3$	8	90.8	88.1	50.8	50
3[a]	**1c**	$CHCl_3$	8	98.8	83.4	54.2	55
4[a]	**1d**	$CHCl_3$	8	99.9	76.9	56.5	55
5[b]	**1a**	Toluene	10	84.3	89.3	48.6	47
6[b]	**1b**	Toluene	10	85.8	90.4	48.7	55
7[b]	**1c**	Toluene	10	89.5	93.4	48.9	89
8[b]	**1d**	Toluene	10	82.7	95.7	46.4	118

[a] Conditions: Substrate concentration 0.2 M, $(EtCO)_2O$ 0.75 equiv., iPr_2NEt 0.75 equiv., catalyst 5 mol%. [b] Conditions: Substrate concentration 0.1 M, $(EtCO)_2O$ 0.75 equiv., iPr_2NEt 0.75 equiv., catalyst 5 mol%.

5. The optimisation of reaction condition

Table S3 The optimisation of reaction condition [a]



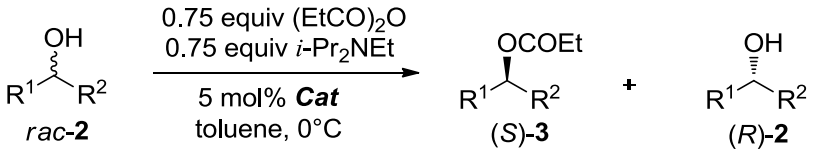
Entry	solvent	t (h)	C_{HPLC} (%)	S
1[b]	$CHCl_3$	8	55	36
2	$CHCl_3$	8	54	55
3	Et_2O	8	47	36
4	DCM	9	55	36
5	THF	9	45	44
6	Toluene	8	47	62
7[c]	Toluene	8	25	58
8[d]	Toluene	10	49	89
9[e]	Toluene	8	50	61
10[f]	Toluene	8	47	46
11[g]	Toluene	9	49	54

[a] Conditions: 0.2 M of substrate concentration, 0.75 equiv. $(EtCO)_2O$, 0.75 equiv. iPr_2NEt, 5 mol% catalyst. [b] Cl-PIQ was used. [c] 2 mol% of catalyst was used. [d] 0.1M of substrate concentration. [e] 0.4 M of substrate concentration. [f] $(MeCO)_2O$ was used instead. [g] $(iPrCO)_2O$ was used instead

Supporting Information

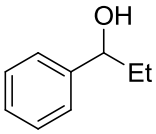
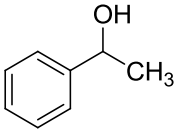
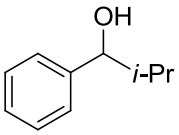
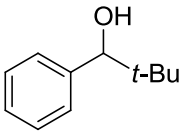
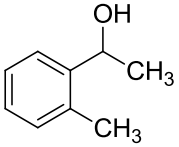
5. Kinetic resolution experiments

General Procedure for the kinetic resolution of alcohols by reaction with propionyl anhydride and catalyst 1.

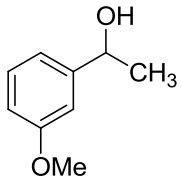
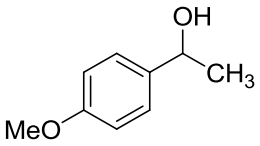
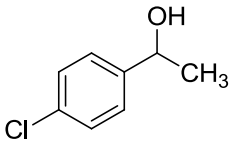
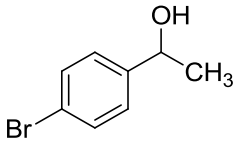
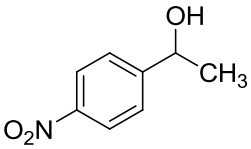
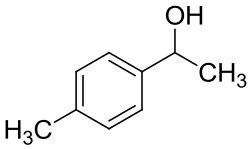
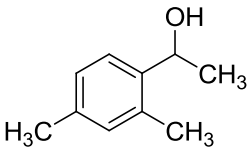
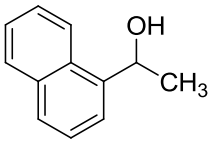
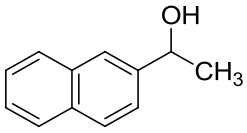
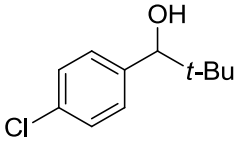


Under nitrogen atmosphere, catalyst **1** (0.02 mmol), secondary alcohol (0.4 mmol), toluene (4 mL) and *N*,*N*-diisopropylethylamine (0.3 mmol, 0.052 mL) were sequentially added to a 25 mL flame-dried Schlenk tube in an ice bath. After stirring at 0 °C for 15 min, the reaction mixture was treated with propionyl anhydride (0.3 mmol, 0.039 mL); then the resulting solution was stirred at 0 °C for the specified period, at the end of which it was quenched by rapid addition of 0.5 mL of methanol. The solution was warmed to room temperature and stirred for an additional 2 h. The solvent was removed *in vacuo*, and the residue purified by silca gel chromatography (5% - 10% EtOAc/petroleum) to separate the ester from the unreacted alcohol.

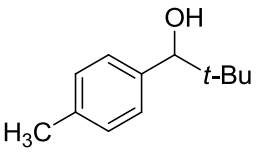
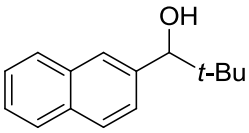
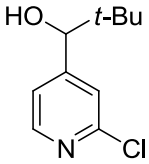
Table S4. Methods used to Assay Enantiomeric Excess

Substrate	HPLC condition[a]	Retention time of (*R*) isomer (min)[b]	Retention time of (*S*) isomer (min)
	254 nm,OD-H, Hexane/*i*-PrOH = 40/1, 1.0 mL/min	11.20	13.86
	254 nm, OD-H, Hexane/*i*-PrOH = 40/1, 1.0 mL/min	11.86	15.29
	254 nm, AS-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	11.17	14.05
	254 nm, OD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	26.17	23.11
	254 nm, OD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	31.32	35.94

Supporting Information

	254 nm, OD-H Hexane/*i*-PrOH = 40/1, 1.0 mL/min	19.69	26.08
	254 nm, OD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	61.89	69.72
	254 nm, OD-H Hexane/*i*-PrOH= 99.5/0.5, 1.0 mL/min	37.54	34.28
	254 nm, OD-H Hexane/*i*-PrOH= 99.5/0.5 1.0 mL/min	45.66	42.94
	254 nm, AD-H Hexane/*i*-PrOH = 40/1, 1.0 mL/min	33.76	35.23
	254 nm, AD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	28.27	32.08
	254 nm, OD-H Hexane/*i*-PrOH = 40/1, 1.0 mL/min	9.09	10.69
	254 nm, OD-H Hexane/*i*-PrOH = 90/10, 1.0 mL/min	12.83	9.00
	254 nm, OD-H Hexane/*i*-PrOH = 90/10, 1.0 mL/min	9.35	8.77
	220 nm, OD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	20.38	18.13

Supporting Information

	220 nm, OD-H Hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min	17.41	15.37
	254 nm, OD-H Hexane/*i*-PrOH = 95/5, 1.0 mL/min	18.82	14.76
	254 nm, AD-H Hexane/*i*-PrOH = 40/1, 1.0 mL/min	22.85	20.89

a) Unless otherwisespecified, HPLC separation of enantiomers was achieved using free alcohols with isopropanol/hexane eluent at the concentration indicated;

b) The absolute configurations were assigned by comparison of the signs of optical rotation with literatures.

Procedure for preparative scale reaction:

Racemic alcohol **2r** (800 mg, 4.0 mmol, 1.0 equiv.), *Np*-PIQ (45 mg, 0.12 mmol, 0.03 equiv), toluene (80 mL) and *N*,*N*-diisopropylethylamine (0.52 mL, 3.0 mmol, 0.75 equiv) was added to a 250 mL flask. After stirring at 0 ^{o}C for 15 min, the reaction mixture was treated with propionic anhydride (0.39 mL, 3.0 mmol, 0.75 equiv), the resulting solution was stirred at 0 °C for 60 h, the reaction was then quenched by methanol (10 mL). The solution was allowed to warm up to room temperature slowly and stirred an additional 2 h. The solvent was removed *in vacuo*, and the residue was purified by silica gel chromatography (EtOAc/petroleum = 1/20 to EtOAc/petroleum/Et_3N = 19/86/5). The ester was eluted first (550 mg, 2.15 mmol, 53.8%), followed by the unreacted alcohol (355 mg, 1.78 mmol, 44.5%) and finally *Np*-PIQ (39 mg, 88% recovery). The enantiomeric excess of the ester was determined by HPLC to be 84.3%, and that of the alcohol was 99.0%. Based on these ee values, the conversion was calculated to be 54.0% (cf. 53.8% conversion based on the isolated materials), and the selectivity factor was 61.

Supporting Information

Table S5. Scope and generality of the *Np*-PIQ-Catalysed KR.

Entry	R^1/R^2	t (h)	ee_A (%)	ee_E (%)	C_{HPLC} (%)	*S*
1	Ph/Et (**2a**)	10	89.5	93.4	48.9	89
			87.0	94.0	48.1	92
2	Ph/Me (**2b**)	10	80.5	89.2	47.4	43
3	Ph/*i*-Pr (**2c**)	15	91.6	94.9	49.1	124
			92.2	95.2	49.2	135
4	Ph/*t*-Bu (**2d**)	35	67.6	**99.1**	40.6	450
			64.3	99.2	39.3	485
5	2-MePh/Me (**2e**)	12	78.1	95.1	45.1	95
6	3-MeOPh/Me (**2f**)	10	90.8	91.4	49.8	70
7	4-MeOPh/Me (**2g**)	10	69.1	94.1	42.3	68
8	4-ClPh/Me (**2h**)	10	91.6	91.5	50.0	73
9	4-BrPh/Me (**2i**)	10	95.2	91.5	51.0	85
10	4-NO_2Ph/Me (**2j**)	10	**99.9**	85.6	53.9	95
11	4-MePh/Me (**2k**)	10	91.2	93.2	49.5	91
12	2,4-DimethylPh/Me (**2l**)	10	89.9	93.7	49.0	95
13	1-Naphthyl/Me (**2m**)	10	92.0	92.8	49.8	88
14	2-Naphthyl/Me (**2n**)	10	93.5	94.0	49.9	113
15	*p*-ClPh/*t*-Bu (**2o**)	48	**99.0**	93.3	51.5	152
16	*p*-MePh/*t*-Bu (**2p**)	48	75.6	**99.0**	43.3	456
17	2-Naphthyl/*t*-Bu (**2q**)	50	96.4	96.9	49.9	258
18	4-(2-ClPy) /*t*-Bu (**2r**)	51	**99.6**	90.2	52.5	118

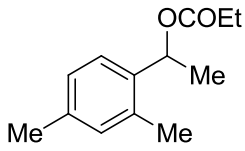
Table S6. KR of secondary alcohols using *An*-PIQ

Entry	R^1/R^2	t (h)	ee_A (%)	ee_E (%)	C_{HPLC} (%)	*S*
1	Ph/Et (**2a**)	10	82.7	95.7	46.4	118
2	Ph/Me (**2b**)	10	80.5	93.7	46.2	76
3	Ph/*i*Pr (**2c**)	17	98.7	94.4	51.1	174
4	Ph/*t*Bu (**2d**)	46	91.0	98.8	48.0	530
			95.6	98.6	49.2	550
5	2-MePh/Me (**2e**)	13	93.2	96.2	49.2	178
6	3-MeOPh/Me (**2f**)	10	88.5	94.4	48.4	102
7	4-MeOPh/Me (**2g**)	10	88.5	94.5	48.4	105
8	4-BrPh/Me (**2i**)	10	98.2	91.8	51.7	110
9	2,4-DimethylPh/Me (**2l**)	10	83.2	95.5	46.6	114
10	1-Naphthyl/Me (**2m**)	10	71.2	92.4	43.5	54
11	2-Naphthyl/Me (**2n**)	10	96.8	89.2	52.0	72

Supporting Information

5. Characterisation data for other new compounds

1-(2,4-dimethylphenyl)ethyl propionate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.9 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 7.05 (s, 1H), 6.16 (q, J = 6.3 Hz, 1H), 2.47-2.35 (m, 8H), 1.58 (dd, J = 6.6, 1.2 Hz, 3H), 1.22 (td, J = 7.5, 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 137.3, 137.1, 134.6, 131.2, 126.9, 125.3, 69.0, 27.8, 21.4, 20.9, 18.9, 9.1; **HRMS** (EI, m/z): Calcd for $C_{13}H_{18}O_2$: 206.1307, found: 206.1305.

Supporting Information

Computational Study

1. General information

Geometry optimisations were performed with B97D, a dispersion-corrected density functional and TZVP basis set. Solvation effect was considered by the SMD solvent model[4]. Frequency calculation was conducted to verify the true stationary points. It should be noted that density fitting method was used to accelerate calculations. As expected, the result at this level of theory was satisfying. All calculations aforementioned were performed with Gaussian 09[5]. To make a deep understanding about the interaction, energy components was analysed with DFT symmetry-adapted perturbation theory (SAPT(DFT)) provided by SAPT2008[6]. All 3D structures were generated using CYLView[7].

2. Transition states of 1a and their Cartesian coordinates

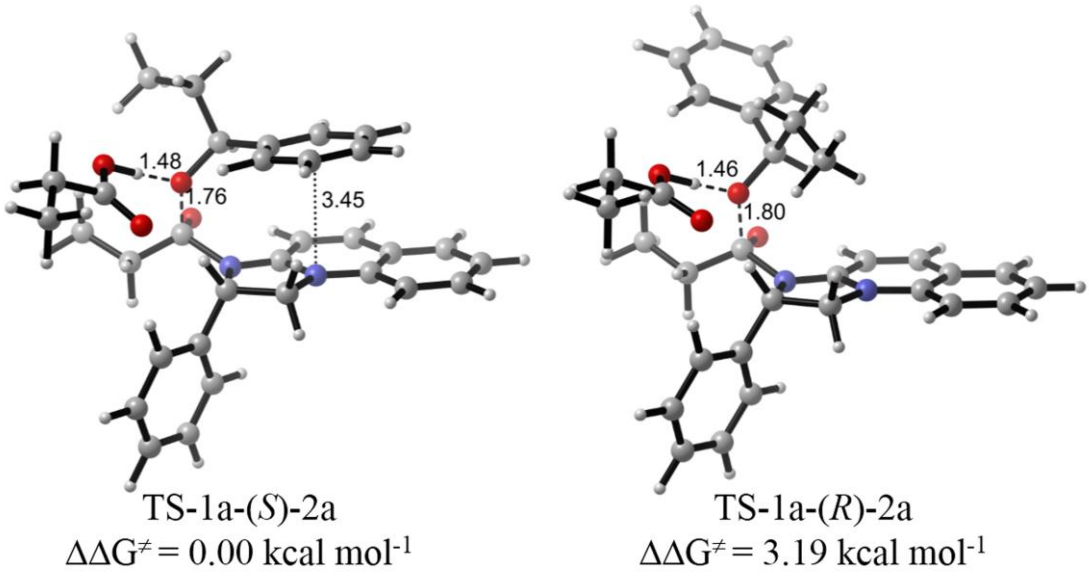


Fig. S3 Transition state structures optimised at B97D/TZVP level of theory

TS-1a-(*S*)-2a

C	6.10233400	0.59169600	-0.82494400
C	5.24354800	1.05685400	-1.83979200
C	3.87711000	1.18588200	-1.62047500
C	3.34628100	0.83863100	-0.36485800
C	4.20011200	0.36715600	0.67518500
C	5.58320200	0.25493800	0.41759000
N	1.99579300	0.91692800	-0.10313200
C	1.42076000	0.57513600	1.09186000
C	2.26405000	0.11522200	2.15326000
C	3.60809500	0.01955000	1.93207200
C	0.96969100	1.33584400	-1.07242200
C	-0.34074700	1.27807200	-0.23725100
N	0.10062900	0.73853900	1.07613800
C	-0.90514700	-0.05603700	2.03852700
C	-2.26474700	0.64499900	2.00424900
O	-0.39947000	-0.45606300	3.08866000
H	7.16865900	0.49922400	-1.01677600
H	5.65143800	1.31881500	-2.81381100
H	3.22055300	1.53325500	-2.41207000
H	1.79493500	-0.14717600	3.09112900
H	4.26047800	-0.33140700	2.72984000
H	1.18727000	2.34895300	-1.42471700
H	0.96126700	0.63685500	-1.91279700
H	-2.10122600	1.66247900	2.38416600

Supporting Information

H	-2.62408300	0.73852000	0.97548000	H	-2.93606500	-0.17895700	3.90012100
H	-1.04076200	0.56169700	-0.67293100	C	-5.49322000	-0.48362000	-3.02934800
C	-0.99990900	2.63923000	-0.11462800	H	-4.78306900	-0.62235800	-3.85346300
C	-2.16591100	2.90953100	-0.84137900	H	-6.49828800	-0.74129300	-3.38845500
C	-0.43890900	3.64283300	0.68754500	H	-5.48517700	0.57962500	-2.75759400
C	-2.76671100	4.17103000	-0.76556300	H	6.23313200	-0.10551900	1.21289100
H	-2.60439800	2.12131600	-1.45006100				
C	-1.04105300	4.90107100	0.76786400				
H	0.45988200	3.43177500	1.26418500	**TS-1a-(*R*)-2a**			
C	-2.20800400	5.16826300	0.04072700				
H	-3.67675300	4.37077600	-1.32888300	C	-5.85092700	-2.65485100	1.39795200
H	-0.60445500	5.67145400	1.40126000	C	-5.63238800	-1.39580700	1.98867400
H	-2.68009000	6.14688900	0.10689800	C	-4.55968600	-0.59816600	1.60332600
C	1.04391900	-1.91027300	-2.66603500	C	-3.68013500	-1.06291800	0.60848400
C	0.18917100	-1.94519200	-1.55908500	C	-3.88277000	-2.33815800	0.00253700
C	0.68026700	-2.28664200	-0.29096700	C	-4.98450500	-3.11679200	0.41631000
C	2.04211600	-2.58958100	-0.15372700	N	-2.58973200	-0.32217700	0.20035300
C	2.90236900	-2.54814000	-1.25542900	C	-1.70736000	-0.71810400	-0.77089100
C	2.40422200	-2.20841900	-2.51822700	C	-1.89773000	-1.99567600	-1.39123700
H	0.64785000	-1.64293000	-3.64510100	C	-2.95536700	-2.76702300	-1.00208400
H	-0.85920800	-1.67866800	-1.66818800	C	-2.21834500	0.99860000	0.73305900
H	3.07187500	-2.17021000	-3.37726000	C	-0.96370500	1.37141800	-0.10823000
C	-0.25373400	-2.38285000	0.90948800	N	-0.76783800	0.19713500	-0.99744900
C	-0.92653500	-3.77348700	0.94889700	C	0.66952400	-0.15075200	-1.61732400
C	-1.75184500	-3.99177600	2.22018900	C	1.36707200	1.14699500	-2.01953900
H	-1.55851600	-3.87585200	0.05542500	O	0.69733900	-1.16188900	-2.31302300
H	-0.13716800	-4.53550700	0.87253600	H	-6.69603000	-3.26274500	1.71197200
H	-2.23612400	-4.97809900	2.20883100	H	-6.31014100	-1.03617800	2.75991300
H	-1.11459300	-3.92960500	3.11343000	H	-4.39799400	0.37048800	2.06681600
H	-2.52906400	-3.22504200	2.31361400	H	-1.18473300	-2.29883300	-2.14534200
O	-1.23418200	-1.36559400	0.90897300	H	-3.11066600	-3.73930800	-1.46621900
H	-2.53975300	-1.57691800	0.24018800	H	-3.04313200	1.70214100	0.58181800
C	-3.72878900	-1.08135900	-1.27160200	H	-1.99176500	0.91592300	1.80064200
O	-3.48947600	-1.77061400	-0.16251000	H	0.75189300	1.60459500	-2.80641300
O	-2.92709500	-0.31475700	-1.80135300	H	1.39296100	1.84736300	-1.18017200
C	-5.12011500	-1.35769400	-1.83061500	H	-0.09248200	1.44267100	0.54634100
H	-5.15223300	-2.42442100	-2.09794300	C	-1.14515500	2.67563800	-0.85985900
H	-5.84084700	-1.23454700	-1.01032100	C	-0.61092800	3.85005900	-0.31288000
H	3.96081700	-2.76960100	-1.12875400	C	-1.86515700	2.73971200	-2.06013600
H	2.42910600	-2.84858000	0.83104300	C	-0.79870100	5.07715700	-0.95761000
H	0.34797600	-2.28103200	1.82916800	H	-0.03854300	3.78997400	0.61113500
C	-3.29499900	-0.08622600	2.86830800	C	-2.04797200	3.96477000	-2.70781900
H	-4.24355500	0.46776600	2.87359100	H	-2.25922500	1.82697500	-2.50194900
H	-3.48421500	-1.09158800	2.47766000	C	-1.51629600	5.13721700	-2.15717600

Supporting Information

H	-0.37507400	5.98373500	-0.52877500
H	-2.59888300	4.00422600	-3.64597300
H	-1.65575100	6.09006000	-2.66458700
C	5.00509200	-2.77220400	-0.43770100
C	3.90285200	-2.00289400	-0.05231900
C	2.61300300	-2.55195600	-0.05680400
C	2.44901100	-3.88497700	-0.45613600
C	3.54804200	-4.65980600	-0.84173300
C	4.83258900	-4.10401900	-0.83378000
H	6.00045300	-2.32969000	-0.43405400
H	4.03855300	-0.96597900	0.24459200
H	1.44622800	-4.31222500	-0.47725500
H	3.40195200	-5.69191300	-1.15802300
H	5.69033200	-4.70122300	-1.13912600
C	1.41483200	-1.73792500	0.41658000
C	1.30756200	-1.79019200	1.95647500
H	0.50905400	-2.21183400	-0.00072100
C	0.04351000	-1.10938200	2.49033400
H	2.20252000	-1.31423900	2.38131200
H	1.33056400	-2.84629800	2.26136000
H	-0.01484800	-1.19584400	3.58434100
H	-0.85740600	-1.57469200	2.06583300
H	0.05184300	-0.04542200	2.23453100
O	1.45263400	-0.39461300	-0.01621700
H	2.32111200	0.58190400	0.62833300
C	2.50060800	2.14286000	1.86638900
O	3.02910400	1.25664200	1.03191300
O	1.30453900	2.21850300	2.13973900
C	3.55662800	3.06597400	2.46621900
H	4.18572200	3.43472500	1.64446500
H	4.21403300	2.43775500	3.08584600
C	2.78230800	0.87422200	-2.53293200
H	3.25641300	1.81194000	-2.85231100
H	3.39427200	0.42141400	-1.74572100
H	2.75660100	0.18233300	-3.38283500
C	2.98199100	4.22323100	3.28532900
H	3.79403700	4.83446300	3.70078000
H	2.34875100	4.86888400	2.66324700
H	2.36706000	3.85163400	4.11360900
H	-5.13859800	-4.08814000	-0.04989200

Supporting Information

3. Transition states of 1c and their Cartesian coordinates

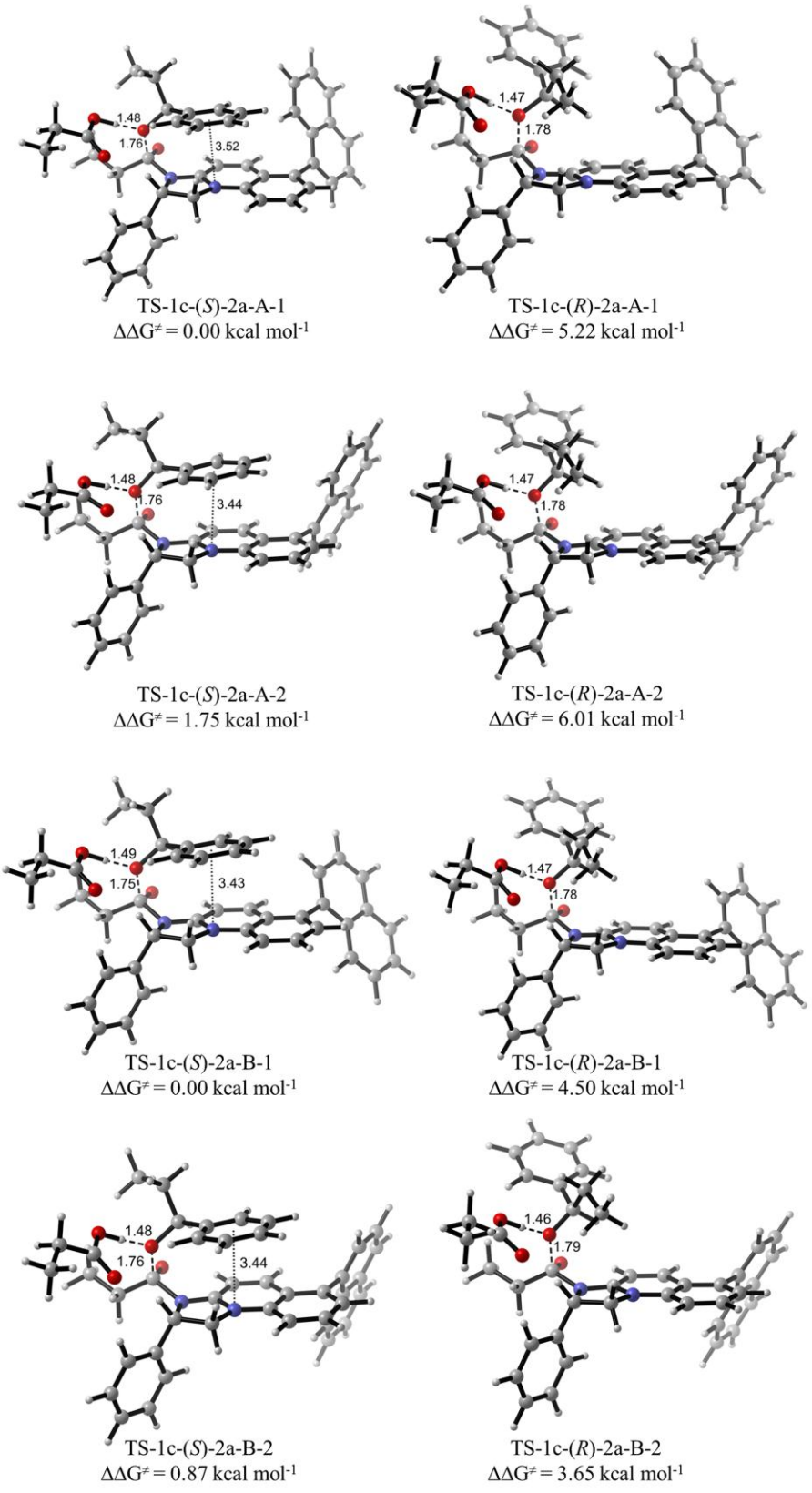


Fig. S4 All transition state structures optimised at B97D/TZVP level of theory

Supporting Information

TS-1c-(*S*)-2a-A-1

C	-4.11735200	2.13629600	2.00447200
C	-2.98973400	2.55756800	2.72909700
C	-1.70684800	2.34539700	2.24271200
C	-1.54678600	1.70855500	0.99936700
C	-2.67746000	1.28467900	0.24031100
C	-3.98013600	1.49319200	0.77425500
N	-0.29236200	1.45974800	0.48436100
C	-0.05624700	0.85443000	-0.72011200
C	-1.17679800	0.46253600	-1.51745800
C	-2.43596900	0.67674900	-1.03560900
C	0.97533800	1.72637600	1.18555400
C	2.04515000	1.32304100	0.13190800
N	1.24368700	0.72971300	-0.97015500
C	1.86080300	-0.33658200	-1.98910000
C	3.29217200	0.08861100	-2.32434100
O	1.07401400	-0.73732300	-2.84923100
H	-5.11320000	2.29013300	2.41268800
H	-3.12182800	3.04774400	3.69138600
H	-0.83712400	2.65359100	2.81411600
H	-0.97931700	0.00220000	-2.47535300
H	-3.29063900	0.38194200	-1.63694700
H	1.03807900	2.78531000	1.45239500
H	1.02034000	1.10757000	2.08601700
H	3.22250100	1.07983200	-2.79210500
H	3.88117300	0.20378800	-1.40990700
H	2.69959000	0.54334000	0.52901600
C	2.87314800	2.51067500	-0.32350600
C	4.18928800	2.64853000	0.13420800
C	2.32875900	3.49167200	-1.16369200
C	4.95351500	3.75853900	-0.24244700
H	4.61328400	1.87164300	0.76703700
C	3.09268700	4.59805000	-1.54412400
H	1.31272900	3.37782900	-1.53644500
C	4.40793100	4.73487200	-1.08266300
H	5.97858700	3.85395100	0.11173200
H	2.66542200	5.35061700	-2.20473100
H	5.00474700	5.59458500	-1.38217000
C	0.93151200	-1.24881700	3.27682400
C	1.42258500	-1.58696800	2.01177200
C	0.54365900	-1.91025900	0.96777200
C	-0.83616000	-1.88375200	1.21470100
C	-1.33222100	-1.53799100	2.47606900
C	-0.44853900	-1.21925800	3.51321900
H	1.62742600	-0.99867900	4.07663900
H	2.49194600	-1.57139300	1.81769700
H	-0.83242200	-0.94633600	4.49476400
C	1.08077400	-2.32503600	-0.39727500
C	1.43452000	-3.82954500	-0.39958900
C	1.85331600	-4.33087000	-1.78498000
H	2.24127900	-3.99537300	0.32833000
H	0.55739700	-4.38785400	-0.04110300
H	2.12385100	-5.39543900	-1.75064400
H	1.03631700	-4.20561200	-2.50907600
H	2.71572000	-3.76501300	-2.15446000
O	2.20572300	-1.55842600	-0.77739000
H	3.56988900	-1.97973500	-0.38955700
C	5.18363400	-1.56597400	0.68858200
O	4.53495300	-2.33464800	-0.17853200
O	4.70495100	-0.57206300	1.23034500
C	6.60269100	-2.06207900	0.94349400
H	6.52526600	-3.09591300	1.31030200
H	7.10602500	-2.13039600	-0.03143100
H	-2.40665100	-1.50792000	2.65003400
H	-1.52380800	-2.12158500	0.40447700
H	0.28731800	-2.17191900	-1.14868900
C	3.96636600	-0.90233400	-3.27640600
H	4.97042200	-0.54491600	-3.54260900
H	4.06443300	-1.88639400	-2.80613700
H	3.37823200	-1.01516600	-4.19490500
C	7.40301000	-1.19357800	1.91554400
H	6.90327100	-1.13160200	2.88993700
H	8.40548300	-1.61589700	2.06476900
H	7.51204800	-0.17158100	1.53155200
C	-5.19719200	1.04413100	0.04112000
C	-5.46116700	-0.34874000	-0.18273400
C	-6.10146400	1.99385800	-0.41165100
C	-4.60665100	-1.38339900	0.29179900
C	-6.65149800	-0.72150000	-0.90566500
C	-7.27039400	1.62131900	-1.11658500
H	-5.89425700	3.04755400	-0.23557100
C	-4.89585000	-2.71208400	0.05244600
H	-3.71484800	-1.11583600	0.84967700
C	-6.91659000	-2.10015500	-1.13677600
C	-7.53722200	0.29095200	-1.36435700
H	-7.95207500	2.39344600	-1.46789300
C	-6.05791600	-3.07594300	-0.67288800

Supporting Information

H	-4.22822300	-3.48640200	0.42567200	H	-5.70758000	-4.98123000	-2.47279200
H	-7.81573500	-2.37020000	-1.68887700	C	-1.54488200	5.55740000	-0.74478000
H	-8.43027400	-0.00470200	-1.91293900	C	-1.68539400	4.24036200	-0.29597800
H	-6.27277400	-4.12674500	-0.85726600	C	-0.58310000	3.37487100	-0.27422400
				C	0.66010800	3.85201200	-0.71141700
				C	0.80625300	5.16831000	-1.16064200
TS-1c-(*R*)-2a-A-1				C	-0.29915500	6.02677600	-1.17910100
				H	-2.41049700	6.21838500	-0.76094100
C	3.95009400	-3.07117300	1.74629300	H	-2.65562900	3.87633900	0.03296700
C	2.79396400	-3.66705200	2.27647800	H	1.51637000	3.17738100	-0.71270800
C	1.53360200	-3.35129700	1.78347700	H	1.77728800	5.52003400	-1.50695100
C	1.42805400	-2.43323800	0.72385200	H	-0.19263200	7.05086200	-1.53345200
C	2.59190000	-1.84027800	0.14979000	C	-0.70526000	1.95815500	0.27051800
C	3.86627700	-2.15121900	0.70060000	C	-0.58770600	1.96926600	1.81085300
N	0.19719600	-2.05508400	0.22497000	H	0.14884400	1.38527100	-0.12738400
C	0.01937900	-1.17055300	-0.80603800	C	-0.55250500	0.56530500	2.42249400
C	1.17910400	-0.63185500	-1.44908100	H	-1.43419300	2.53925700	2.21820600
C	2.41337400	-0.95996500	-0.96878900	H	0.32593300	2.52137900	2.07498700
C	-1.10268800	-2.49093800	0.76064700	H	-0.44673700	0.61834700	3.51506600
C	-2.12013600	-1.69331600	-0.10634900	H	0.29727700	-0.00976900	2.02983600
N	-1.26546900	-0.92780800	-1.04970600	H	-1.47893500	0.02695000	2.19690900
C	-1.77388100	0.47676700	-1.68733200	O	-1.89953800	1.30675700	-0.11222400
C	-3.26046100	0.34765000	-2.01181100	H	-3.15790100	1.60876900	0.57840100
O	-0.96884300	1.01173600	-2.44111600	C	-4.57867700	1.00700100	1.84293100
H	4.92405700	-3.30425400	2.16932800	O	-4.05862400	1.91951800	1.03100800
H	2.88258100	-4.37476300	3.09800000	O	-4.09932500	-0.10765500	2.03836800
H	0.64240900	-3.79823400	2.21279800	C	-5.84934300	1.50372500	2.52496000
H	1.03024000	0.04025300	-2.28243000	H	-6.50229200	1.92773000	1.74974200
H	3.29483200	-0.53955400	-1.44288500	H	-5.55769100	2.35003000	3.16493800
H	-1.21050800	-3.57344900	0.63599300	C	-3.82094100	1.65956600	-2.56651000
H	-1.16961700	-2.23161100	1.82169500	H	-4.88579100	1.54207600	-2.80853100
H	-3.35132900	-0.45512200	-2.75610400	H	-3.71677700	2.46483000	-1.83143000
H	-3.82167600	0.03434300	-1.12716200	H	-3.28271300	1.95572200	-3.47444100
H	-2.65104500	-0.97296900	0.52005900	C	-6.57894800	0.43330500	3.33807500
C	-3.11777200	-2.59866400	-0.80114000	H	-7.46383700	0.86328000	3.82573000
C	-4.40727800	-2.72507900	-0.26852800	H	-6.90776800	-0.39330500	2.69527800
C	-2.76663600	-3.33755800	-1.93910900	H	-5.92438300	0.01338600	4.11109300
C	-5.33594900	-3.58438100	-0.86532300	C	5.10168400	-1.49473100	0.19008800
H	-4.67714800	-2.13706800	0.60671300	C	5.29443100	-0.07769500	0.32559500
C	-3.69599100	-4.19152700	-2.53949400	C	6.08491600	-2.26621300	-0.41168700
H	-1.77338900	-3.22566300	-2.36917000	C	4.35794100	0.77430300	0.97773200
C	-4.98324900	-4.31841200	-2.00281200	C	6.49675300	0.51126100	-0.20886800
H	-6.33723000	-3.67261500	-0.44713800	C	7.26743200	-1.68268100	-0.92476600
H	-3.41899200	-4.75383700	-3.42959800	H	5.92998700	-3.33901000	-0.50844800

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C	4.57756400	2.13436200	1.07218900	H	-4.66122900	1.48582100	-1.37234300
H	3.45779400	0.34384700	1.40671600	C	-3.69450500	4.57783400	0.76850500
C	6.68931400	1.91653000	-0.09518200	H	-1.87050000	3.50598100	1.19525200
C	7.46552200	-0.32076700	-0.83309700	C	-4.92415500	4.55614200	0.09905500
H	8.01332400	-2.31587000	-1.40126600	H	-6.22834100	3.41923800	-1.19593000
C	5.74971600	2.71391300	0.52592000	H	-3.42313000	5.43539200	1.38191900
H	3.84551200	2.76653800	1.57127900	H	-5.60986200	5.39671400	0.18896800
H	7.59822700	2.35124600	-0.50898400	C	-0.17425200	-1.71472300	-2.64402600
H	8.36740100	0.13820900	-1.23547800	C	-0.98063700	-1.85757400	-1.50962900
H	5.90817400	3.78777300	0.60382400	C	-0.40831900	-2.14033700	-0.26104000
				C	0.98443500	-2.27064700	-0.17145700
				C	1.79466900	-2.12334900	-1.30167400
TS-1c-(*S*)-2a-A-2				C	1.21644600	-1.84521900	-2.54481800
				H	-0.63356800	-1.49912900	-3.60831900
C	4.02368600	1.68552600	-2.03265600	H	-2.05874400	-1.73186900	-1.58204500
C	2.92861300	1.94380300	-2.87202300	H	1.84353400	-1.72229600	-3.42632900
C	1.62637100	1.85552600	-2.39758900	C	-1.27955400	-2.36222100	0.97034500
C	1.41350500	1.48784500	-1.05813200	C	-1.78285600	-3.82283700	1.00807700
C	2.51178500	1.23371700	-0.18193500	C	-2.55080600	-4.15079900	2.29215700
C	3.83584400	1.34546800	-0.69263200	H	-2.41577400	-3.99797200	0.12624600
N	0.13779600	1.33221700	-0.55850800	H	-0.90845100	-4.48241100	0.91082200
C	-0.15064300	0.95377600	0.72438800	H	-2.86636000	-5.20345500	2.30022400
C	0.93387600	0.70238400	1.62004400	H	-1.92402100	-3.97135100	3.17696900
C	2.21345900	0.83330000	1.16186300	H	-3.44414400	-3.52376400	2.38078900
C	-1.09905000	1.51699000	-1.33468200	O	-2.37315500	-1.46863200	1.02789700
C	-2.21273500	1.21091800	-0.29383300	H	-3.71011100	-1.87021300	0.53720700
N	-1.46158300	0.86619300	0.94035300	C	-5.08809000	-1.69829300	-0.88830400
C	-2.11006000	-0.07566800	2.07365900	O	-4.68385900	-2.17211700	0.28369100
C	-3.56151300	0.36177600	2.27997900	O	-4.40191800	-1.00132400	-1.63303200
O	-1.36257200	-0.33117400	3.01892200	C	-6.51067500	-2.13371900	-1.22341300
H	5.03532400	1.76307700	-2.42259100	H	-6.47812800	-3.22123100	-1.38892300
H	3.10083200	2.22026000	-3.91010800	H	-7.12999200	-1.98603000	-0.32854300
H	0.78378500	2.04912300	-3.05347000	H	2.87525400	-2.21498800	-1.20816500
H	0.69546900	0.38805100	2.62627300	H	1.43633100	-2.47901900	0.79763700
H	3.04022300	0.62285500	1.83366700	H	-0.65713400	-2.20371200	1.86733700
H	-1.15033100	2.54588900	-1.70545600	C	-4.26548900	-0.49837200	3.33133400
H	-1.10964900	0.81511000	-2.17262000	H	-5.29048100	-0.13693200	3.48985700
H	-3.52692100	1.41022100	2.60503100	H	-4.31301800	-1.54339600	3.00807500
H	-4.10936800	0.33594600	1.33390000	H	-3.72634600	-0.45820900	4.28519800
H	-2.77486900	0.32569200	-0.59968400	C	-7.11008300	-1.42009500	-2.43662800
C	-3.16181400	2.38128000	-0.11723900	H	-6.48865900	-1.57069000	-3.32725400
C	-4.39326700	2.36161600	-0.78456500	H	-8.11736900	-1.80461800	-2.64380800
C	-2.81615500	3.49619800	0.65774900	H	-7.18445000	-0.33941100	-2.25936200
C	-5.27069700	3.44599200	-0.67871800	C	5.01754900	1.10910800	0.18450900

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C	5.88866300	-0.00941800	-0.03595800	H	-3.97718600	-0.43822900	-1.06086500
C	5.28111100	1.98793900	1.22539400	H	-2.69420300	-1.13435700	0.66660000
C	5.66151000	-0.98140600	-1.05179700	C	-2.70906400	-2.84032600	-0.63980700
C	7.03109900	-0.17839500	0.82856200	C	-3.92940200	-3.29849000	-0.12612300
C	6.40408900	1.81792100	2.06816500	C	-2.16162900	-3.45839100	-1.77182500
H	4.61487100	2.83297100	1.38621000	C	-4.59163700	-4.37007200	-0.73511300
C	6.51929100	-2.05097700	-1.21842100	H	-4.36009700	-2.79951400	0.74028000
H	4.79444100	-0.87536500	-1.69717300	C	-2.82540800	-4.52526900	-2.38351600
C	7.89640600	-1.28869800	0.62308000	H	-1.22851300	-3.08744300	-2.19060900
C	7.26495300	0.75822700	1.87167900	C	-4.04137700	-4.98593500	-1.86459100
H	6.58463300	2.53275200	2.86859500	H	-5.54239900	-4.71697500	-0.33386400
C	7.64985600	-2.20575400	-0.37815600	H	-2.39703400	-4.99304900	-3.26839500
H	6.32386500	-2.78493100	-1.99809600	H	-4.55966300	-5.81491900	-2.34317400
H	8.75789000	-1.40347200	1.27951200	C	-2.78502600	5.45450300	-1.01467100
H	8.13351500	0.62025600	2.51400600	C	-2.70919100	4.15554800	-0.50160800
H	8.31836300	-3.05250400	-0.52154700	C	-1.46607300	3.54614900	-0.28748600
				C	-0.30058300	4.26098900	-0.59690300
				C	-0.37034500	5.56019400	-1.10893200
TS-1c-(*R*)-2a-A-2				C	-1.61644100	6.16244000	-1.31992600
				H	-3.75847700	5.91411600	-1.18112000
C	4.31071100	-2.42860800	1.50838200	H	-3.61683200	3.60306700	-0.27324000
C	3.25373000	-3.06392600	2.17720000	H	0.66922700	3.78543600	-0.44708300
C	1.93302200	-2.84413000	1.80233200	H	0.54450000	6.09905300	-1.35240500
C	1.66428700	-1.96081500	0.74322100	H	-1.67593900	7.17155200	-1.72466500
C	2.72446900	-1.29506800	0.05401400	C	-1.36187500	2.15456700	0.32428000
C	4.06763300	-1.55692000	0.44483600	C	-1.31337500	2.24961100	1.86561600
N	0.36749700	-1.69369000	0.35023400	H	-0.40279200	1.72284400	-0.01095200
C	0.02532300	-0.83744600	-0.66408000	C	-1.06256900	0.89300200	2.53060400
C	1.07149600	-0.13488400	-1.34326200	H	-2.26255500	2.67704600	2.21726100
C	2.36732300	-0.36494800	-0.97919100	H	-0.52035500	2.96097600	2.13637400
C	-0.83965500	-2.24754200	0.98705200	H	-1.00572500	0.99397800	3.62332000
C	-1.98306100	-1.71648800	0.07624700	H	-0.11391500	0.46135600	2.18045900
N	-1.28940900	-0.79211600	-0.85518900	H	-1.87677000	0.20037800	2.29315000
C	-2.04782800	0.41475100	-1.58189000	O	-2.40417600	1.28667600	-0.06619900
C	-3.46505400	-0.03369000	-1.93877500	H	-3.71690200	1.37050000	0.58192000
O	-1.34700300	1.06824400	-2.35060800	C	-5.07583000	0.50997300	1.75899000
H	5.33739300	-2.62606700	1.80535200	O	-4.67276100	1.52155400	1.00039400
H	3.46914700	-3.74719200	2.99596700	O	-4.42816200	-0.51589700	1.95643200
H	1.11925400	-3.34395100	2.31829400	C	-6.44389500	0.76956100	2.38103700
H	0.78836800	0.56567200	-2.11684600	H	-7.11157400	1.13244800	1.58774100
H	3.16275400	0.17180800	-1.48751600	H	-6.32105900	1.61329200	3.07666000
H	-0.78933200	-3.34027800	0.99556500	C	-4.27440500	1.11121400	-2.55274400
H	-0.91390800	-1.87104200	2.01223100	H	-5.26396800	0.74873000	-2.86238300
H	-3.35856300	-0.85425000	-2.66115000	H	-4.41135200	1.92125700	-1.82876700

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H	-3.75806800	1.52022600	-3.42919100	H	-0.99135400	1.78154300	3.02593200
C	-7.04401400	-0.44073700	3.09840400	H	-0.76260200	-0.27213200	-2.51626300
H	-8.01424300	-0.17738100	3.53991900	H	-3.07020200	-0.48281500	-1.61504200
H	-7.19806300	-1.27407900	2.40095200	H	0.73710700	2.52206900	1.55935600
H	-6.38152800	-0.79291400	3.89810400	H	1.10795200	0.87124800	2.15576800
C	5.21290400	-0.94356000	-0.28449100	H	3.19660500	1.53281800	-2.77453000
C	6.11266400	-0.03621600	0.36840700	H	3.99752700	0.71639400	-1.43021400
C	5.42215700	-1.27574500	-1.61616600	H	2.78178100	0.63633900	0.52258600
C	5.93860400	0.39661000	1.71375900	C	2.66172400	2.67945200	-0.12813000
C	7.22996300	0.48778600	-0.37880500	C	3.91150800	2.98232200	0.42705100
C	6.51696600	-0.75520300	-2.34389600	C	2.00999200	3.63412600	-0.92055500
H	4.73565800	-1.96446700	-2.10430000	C	4.50231500	4.22933600	0.19585700
C	6.82779000	1.27677700	2.29903600	H	4.42154900	2.22889700	1.02368500
H	5.08929300	0.02749000	2.28193600	C	2.60224500	4.87798700	-1.15665400
C	8.12869000	1.38759400	0.25868000	H	1.04946600	3.39478300	-1.37195500
C	7.40694400	0.10567000	-1.73597000	C	3.84964300	5.17986300	-0.59626500
H	6.65398400	-1.04466300	-3.38393200	H	5.47648200	4.45400600	0.62696700
C	7.93645600	1.77322400	1.56953700	H	2.09390800	5.61004300	-1.78194200
H	6.67370600	1.59593200	3.32816600	H	4.31243900	6.14736800	-0.78243600
H	8.97137400	1.77214000	-0.31403200	C	1.08659800	-1.68028700	3.00872500
H	8.25559200	0.50888800	-2.28660200	C	1.71655100	-1.77416600	1.76301500
H	8.63061800	2.46408300	2.04417400	C	1.01306100	-2.23682000	0.64218700
				C	-0.33211400	-2.60252000	0.79321500
				C	-0.96687000	-2.50682800	2.03546900
TS-1c-(*S*)-2a-B-1				C	-0.25792100	-2.04388600	3.14942200
				H	1.64719100	-1.31920400	3.87031000
C	-4.11529400	0.66288600	2.21305400	H	2.75244600	-1.46512200	1.64719200
C	-3.07664900	1.23775900	2.96112300	H	-0.75181900	-1.96252500	4.11613200
C	-1.79600900	1.35419700	2.43623800	C	1.70415300	-2.39399200	-0.70697500
C	-1.54990300	0.88848400	1.13396300	C	2.38272200	-3.77969400	-0.80197100
C	-2.59437400	0.31220900	0.34821500	C	2.95142100	-4.05822700	-2.19665900
C	-3.89374100	0.19089100	0.91790400	H	3.17864800	-3.82706000	-0.04518200
N	-0.28814600	0.95967400	0.58229600	H	1.63846400	-4.54386900	-0.53473600
C	0.02672000	0.55144400	-0.68471300	H	3.44902600	-5.03737400	-2.22935800
C	-1.01532700	0.02371800	-1.50794500	H	2.15254100	-4.05114100	-2.95143300
C	-2.27443200	-0.08685500	-0.99096400	H	3.68036100	-3.28979700	-2.47665500
C	0.90515800	1.47956400	1.27033300	O	2.65062500	-1.37213000	-0.94674600
C	2.01736500	1.34312200	0.19055000	H	4.06586700	-1.55435600	-0.53373900
N	1.31367000	0.73775400	-0.96946000	C	5.52235100	-0.99810600	0.69648400
C	2.10508800	-0.14055300	-2.06474200	O	5.07418900	-1.73615100	-0.31256100
C	3.44044700	0.54709200	-2.35618300	O	4.83661200	-0.20363300	1.33617500
O	1.39407800	-0.59611300	-2.96201900	C	6.99910600	-1.25125200	0.97800700
H	-5.10632500	0.56741900	2.64864600	H	7.11070800	-2.32376600	1.19362900
H	-3.27267600	1.58532800	3.97326800	H	7.54571700	-1.07850900	0.03993200

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H	-2.01502900	-2.78349100	2.13664000	N	-1.12215600	-0.74603000	-0.81442600
H	-0.88456200	-2.95473000	-0.07718500	C	-2.00918900	0.36152400	-1.57404600
H	0.93846600	-2.34612000	-1.49978700	C	-3.28433400	-0.30569800	-2.08928200
C	4.28236500	-0.25703300	-3.34997200	O	-1.35992500	1.16078100	-2.24321300
H	5.19282400	0.29973800	-3.60997500	H	5.37882000	-1.38414800	2.60537600
H	4.57832800	-1.21912800	-2.91906700	H	3.65399200	-2.92136900	3.50797700
H	3.71377200	-0.44947700	-4.26749400	H	1.36356800	-2.94258300	2.56288700
C	7.57322900	-0.40122700	2.11251200	H	0.82994500	0.91182400	-1.90210900
H	7.03965100	-0.58682600	3.05275000	H	3.14287600	0.95637600	-0.99705500
H	8.63503000	-0.63670400	2.26360300	H	-0.35692700	-3.23496800	1.00595900
H	7.48501600	0.66854300	1.88536400	H	-0.85853000	-1.87911000	2.06243500
C	-5.00446600	-0.46567100	0.17357700	H	-2.96898300	-1.05566300	-2.82755500
C	-6.20552500	0.24902400	-0.15528000	H	-3.79447500	-0.83894700	-1.28187500
C	-4.88610700	-1.80231900	-0.18336700	H	-2.58759800	-1.37206300	0.55170900
C	-5.93165500	-2.48685400	-0.84477200	C	-2.18401300	-3.00457800	-0.78762700
H	-3.97346500	-2.33752100	0.06824800	C	-3.39593500	-3.63362600	-0.47542400
C	-7.10408200	-1.82917100	-1.15382000	C	-1.38577500	-3.51722300	-1.81945200
H	-5.80623200	-3.53734700	-1.09965500	C	-3.80352100	-4.76759800	-1.18692600
H	-7.91789500	-2.34886600	-1.65730400	H	-4.01912000	-3.21940500	0.31493900
C	-7.27070700	-0.45696100	-0.82528400	C	-1.79425900	-4.64699300	-2.53283800
C	-8.46621000	0.24099500	-1.15338800	H	-0.45523400	-3.01660500	-2.08001700
C	-8.61179100	1.58001100	-0.85359500	C	-3.00466200	-5.27645700	-2.21665100
H	-9.26491800	-0.30452800	-1.65393000	H	-4.74962800	-5.24798200	-0.94331400
C	-6.38572000	1.63422200	0.12093300	H	-1.17242400	-5.03262700	-3.33893600
C	-7.55798500	2.28169600	-0.21715600	H	-3.32517300	-6.15388200	-2.77537000
H	-9.53125100	2.10235300	-1.11105500	C	-3.68891700	5.15983200	-0.89560300
H	-5.58291500	2.18610800	0.60159800	C	-3.42397000	3.87112000	-0.42176700
H	-7.67158800	3.34178500	0.00204900	C	-2.11071300	3.47154400	-0.14074600
				C	-1.06905000	4.38801900	-0.33849400
				C	-1.32826600	5.67885600	-0.81007600
TS-1c-(*R*)-2a-B-1				C	-2.64288900	6.06971200	-1.09033300
				H	-4.71419300	5.45420600	-1.11629200
C	4.38158600	-1.38948600	2.17349600	H	-4.23690600	3.16450900	-0.27627500
C	3.40476600	-2.25704600	2.68322900	H	-0.04378100	4.07805200	-0.13416600
C	2.11717000	-2.27374200	2.15902000	H	-0.50633600	6.37615500	-0.96766700
C	1.80179800	-1.40349300	1.10177100	H	-2.84957800	7.07156600	-1.46352700
C	2.78277400	-0.51461800	0.56200400	C	-1.81650800	2.09433000	0.44008400
C	4.09025500	-0.51269800	1.12560000	C	-1.93936200	2.13345200	1.97960500
N	0.53110800	-1.37162700	0.56117500	H	-0.76800500	1.85126700	0.19444400
C	0.15232400	-0.56927900	-0.48386700	C	-1.54973000	0.80863100	2.64164700
C	1.13180600	0.29678100	-1.06563700	H	-2.97381500	2.39883800	2.23793300
C	2.39570700	0.30821700	-0.54898600	H	-1.29856000	2.94756400	2.34732400
C	-0.61074300	-2.17124700	1.03722800	H	-1.61641200	0.88158700	3.73603400
C	-1.73469900	-1.80567700	0.02610100	H	-0.51616800	0.53704000	2.38392700

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H	-2.21845800	0.00728500	2.31023100	N	0.33896300	0.74376600	-0.99329300
O	-2.64689500	1.07608400	-0.07825500	C	0.11818500	0.65379700	0.35436300
H	-4.01986700	0.91468000	0.43486600	C	1.21562200	0.30635800	1.20240500
C	-5.32546400	-0.20520500	1.43697000	C	2.43467200	0.06283100	0.63858200
O	-5.02150900	0.89330000	0.75580600	C	-0.91010600	1.06850600	-1.70201700
O	-4.54042300	-1.12256100	1.66584500	C	-1.93632600	1.22511600	-0.54410400
C	-6.76978200	-0.19686400	1.92634400	N	-1.14804400	0.90638000	0.67519700
H	-7.40731000	0.14097700	1.09828900	C	-1.85355100	0.33460900	2.00433400
H	-6.83767500	0.58688300	2.69623600	C	-3.18873700	1.05846000	2.18506600
C	-4.22371000	0.71655000	-2.73380800	O	-1.08408800	0.12313300	2.94157200
H	-5.11461000	0.21225700	-3.13166000	H	4.98591300	-0.26705300	-3.23848400
H	-4.54339500	1.46116200	-1.99751200	H	3.03893200	0.35872500	-4.64956400
H	-3.71931500	1.24179200	-3.55328300	H	0.84634200	0.86639200	-3.61872700
C	-7.24632500	-1.54095100	2.48031500	H	1.02933000	0.22992900	2.26441100
H	-8.28101300	-1.45913900	2.83857200	H	3.26698600	-0.21626300	1.27751600
H	-7.21059600	-2.31841800	1.70622900	H	-0.78186100	1.99664500	-2.26832300
H	-6.61407500	-1.86961700	3.31366400	H	-1.16490100	0.24801200	-2.37748300
C	5.13862600	0.42611300	0.63799100	H	-2.95219200	2.12398400	2.30742800
C	6.36216400	-0.05974200	0.06481800	H	-3.79988200	0.96418800	1.28332200
C	4.93836700	1.79424200	0.76451800	H	-2.72752500	0.47725800	-0.63416200
C	6.62514200	-1.44249100	-0.15149100	C	-2.54027600	2.61611400	-0.50259700
C	7.36351300	0.89600800	-0.34186400	C	-3.85762600	2.81035000	-0.93572700
C	5.92108400	2.72552300	0.35703900	C	-1.78481400	3.71679300	-0.07481700
H	4.01000000	2.15425300	1.20301200	C	-4.41417000	4.09421200	-0.94250000
C	7.81778100	-1.86293800	-0.70690800	H	-4.44503400	1.94914400	-1.24731600
H	5.87108000	-2.17390600	0.12454900	C	-2.34098100	4.99859900	-0.07820800
C	8.58247500	0.42626600	-0.90544700	H	-0.76762600	3.56518700	0.28189600
C	7.11313200	2.28534200	-0.17954200	C	-3.65793600	5.19043700	-0.51455300
H	5.73187900	3.79021500	0.47887600	H	-5.44160800	4.23591000	-1.27360300
C	8.80963100	-0.92325500	-1.08193600	H	-1.75058200	5.84695400	0.26382000
H	7.99571800	-2.92525200	-0.86387500	H	-4.09330000	6.18814500	-0.51368700
H	9.33281800	1.15769600	-1.20248400	C	-1.26742900	-2.40470600	-2.63492200
H	7.87898400	2.99449700	-0.49001600	C	-1.75954200	-2.19024700	-1.34285800
H	9.74612000	-1.26916200	-1.51535800	C	-0.92738400	-2.35609500	-0.22684400
				C	0.40661600	-2.73817500	-0.43074600
				C	0.90434700	-2.94651500	-1.72049700
TS-1c-(*S*)-2a-B-2				C	0.06699200	-2.78082100	-2.82940400
				H	-1.92718600	-2.27197800	-3.49168800
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C	2.92628300	0.30762100	-3.56866100	H	0.45312800	-2.93702900	-3.83519800
C	1.69552900	0.60002100	-2.99776200	C	-1.46808600	-2.17843200	1.18716300
C	1.55553900	0.51771700	-1.60092700	C	-2.05615900	-3.51170800	1.70380600
C	2.66102500	0.16101000	-0.77350700	C	-2.45584800	-3.44348900	3.18061800
C	3.91558300	-0.11736400	-1.38459800	H	-2.92523500	-3.76936800	1.08214200

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H	-1.30461400	-4.29950700	1.54962200	C	4.25134600	-1.84855700	2.52353600
H	-2.89700000	-4.39430100	3.51086700	C	3.18943700	-2.67754300	2.92006600
H	-1.58152200	-3.23137300	3.81163600	C	1.95488900	-2.61188300	2.28678000
H	-3.18798200	-2.64544600	3.34738800	C	1.77523100	-1.68924500	1.24066900
O	-2.43654000	-1.15340700	1.26570700	C	2.84116500	-0.83757100	0.82042400
H	-3.86060200	-1.46081400	1.03358300	C	4.09961300	-0.93562300	1.47902400
C	-5.44481100	-1.18786000	-0.13317700	N	0.55411600	-1.55828400	0.60948200
O	-4.87602800	-1.71663000	0.94307900	C	0.30054400	-0.68881200	-0.41779800
O	-4.85661400	-0.49915600	-0.96460900	C	1.35641200	0.17421300	-0.85173600
C	-6.92546500	-1.53895900	-0.22819400	C	2.57103100	0.09867500	-0.23242700
H	-6.99570600	-2.63569300	-0.27145200	C	-0.65618800	-2.32237900	0.95188600
H	-7.39455600	-1.24906200	0.72259400	C	-1.71128700	-1.76801400	-0.04762000
H	1.94646900	-3.22870900	-1.86185300	N	-0.95451400	-0.77520900	-0.85377800
H	1.06123500	-2.86208000	0.43105400	C	-1.70721800	0.44109200	-1.59618600
H	-0.62845700	-1.91106300	1.85153400	C	-3.02339200	-0.07083100	-2.17671400
C	-3.95267100	0.54082400	3.40639600	O	-0.96468600	1.20400400	-2.20693700
H	-4.87897800	1.11609500	3.54028000	H	5.21309300	-1.92275100	3.02478000
H	-4.21780700	-0.51416100	3.28041600	H	3.33488600	-3.38619500	3.73258900
H	-3.34422300	0.63858800	4.31331500	H	1.13758200	-3.25517400	2.59745800
C	-7.64631000	-0.89793000	-1.41520200	H	1.14089200	0.87367300	-1.64728300
H	-7.19151800	-1.20539800	-2.36479100	H	3.36720800	0.76521300	-0.54874200
H	-8.70295900	-1.19637200	-1.42291600	H	-0.46893900	-3.39195200	0.80993000
H	-7.59702900	0.19685200	-1.36102200	H	-0.93156200	-2.13017900	1.99344500
C	5.09975800	-0.50699200	-0.56775600	H	-2.76532200	-0.83705500	-2.92030300
C	5.73415500	0.42431300	0.31982500	H	-3.62212500	-0.56014300	-1.40354200
C	5.59964500	-1.79598800	-0.68060300	H	-2.48301900	-1.22591400	0.50335800
C	5.30579400	1.77485500	0.45676800	C	-2.35225100	-2.86661700	-0.87193400
C	6.86659500	-0.01735500	1.09527000	C	-3.60868300	-3.35171200	-0.48637100
C	6.71481300	-2.22230300	0.07931100	C	-1.70347600	-3.43413800	-1.97649500
H	5.11021400	-2.49543200	-1.35566200	C	-4.21071400	-4.39542300	-1.19636300
C	5.94406400	2.63863700	1.32469000	H	-4.11124000	-2.89723900	0.36548600
H	4.46529600	2.12508600	-0.13595500	C	-2.30748100	-4.47294600	-2.69073400
C	7.49753300	0.89901900	1.98194400	H	-0.73748000	-3.04537900	-2.29215000
C	7.33227700	-1.35281200	0.95391000	C	-3.56210800	-4.95783200	-2.30111200
H	7.07515300	-3.24370800	-0.02636200	H	-5.18967600	-4.76200200	-0.89216000
C	7.04633700	2.19803700	2.09891800	H	-1.80275200	-4.90136400	-3.55504400
H	5.60088300	3.66768000	1.41332100	H	-4.03315900	-5.76483000	-2.85944000
H	8.34872400	0.55371100	2.56706500	C	-3.51415700	5.27528200	-0.62297200
H	8.18662400	-1.67437100	1.54757900	C	-3.19738600	3.99156400	-0.16855700
H	7.53783400	2.88903300	2.78116000	C	-1.86221900	3.56693300	-0.10327700
				C	-0.85259400	4.45356700	-0.50014900
				C	-1.16358200	5.73999900	-0.95345200
TS-1c-(*R*)-2a-B-2				C	-2.49843500	6.15530400	-1.01652300
				H	-4.55615300	5.58865700	-0.67407100

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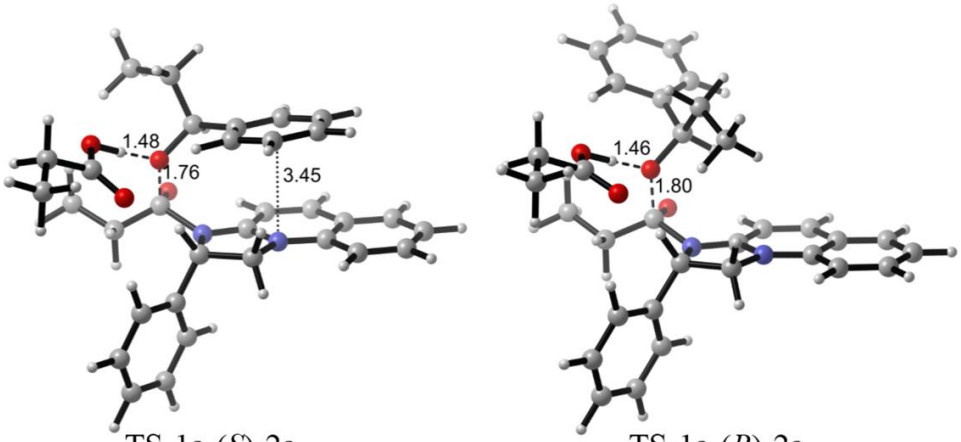
H	-3.98992000	3.30755500	0.12480900	H	8.22196600	2.34682100	0.25093800
H	0.18578800	4.12377800	-0.46755600	H	7.64902700	-0.29411200	-3.67925800
H	-0.36684900	6.41323900	-1.26734500				
H	-2.74615300	7.15342900	-1.37443100				
C	-1.50700900	2.18550300	0.43261400				
C	-1.55660900	2.17177700	1.97506800				
H	-0.46875100	1.97408900	0.12628200				
C	-1.07536400	0.84496600	2.57018400				
H	-2.58902400	2.37735100	2.29082100				
H	-0.93739200	3.00315000	2.34177400				
H	-1.11080200	0.87032300	3.66821500				
H	-0.03887500	0.63765100	2.26965600				
H	-1.71669700	0.02708700	2.22726900				
O	-2.33839700	1.16374000	-0.08201900				
H	-3.70626600	1.00004500	0.39117100				
C	-5.01317800	-0.03572700	1.49909000				
O	-4.72913000	0.95334700	0.66125100				
O	-4.19579400	-0.85146700	1.91996900				
C	-6.48670400	-0.04664900	1.89437700				
H	-7.08086200	0.02896600	0.97331300				
H	-6.67617800	0.88453700	2.44896500				
C	-3.81525000	1.06682800	-2.82512400				
H	-4.76603900	0.68691000	-3.22243100				
H	-4.02889600	1.85072700	-2.09054300				
H	-3.24424900	1.51696300	-3.64569500				
C	-6.90158500	-1.26495600	2.72134900				
H	-7.96580600	-1.20155700	2.98420200				
H	-6.74068400	-2.19439900	2.16021200				
H	-6.31707700	-1.32919100	3.64696200				
C	5.24464900	-0.05865700	1.10268500				
C	5.87420800	-0.14922500	-0.18365500				
C	5.71751200	0.85628600	2.03300400				
C	5.48308400	-1.09688800	-1.17124100				
C	6.96268300	0.74622900	-0.48780200				
C	6.79355800	1.72417100	1.73247000				
H	5.23432600	0.91821100	3.00612600				
C	6.11024200	-1.14335700	-2.40065000				
H	4.67900900	-1.79225200	-0.94790200				
C	7.58395100	0.67183500	-1.76561900				
C	7.39944500	1.67588700	0.49434200				
H	7.13208400	2.43584100	2.48293100				
C	7.16565900	-0.24815200	-2.70526300				
H	5.79414700	-1.87544600	-3.14137000				
H	8.40203200	1.35610100	-1.98624500				

Supporting Information

4. The key geometry parameters of all transition states

Table S7. The key geometric data of all transition states



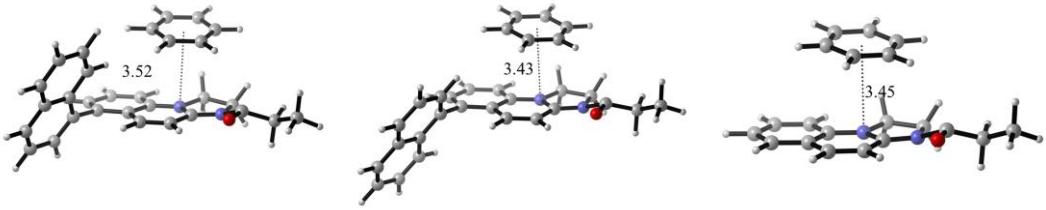
TS-1a-(*S*)-2a
$\Delta\Delta G^{\neq} = 0.00$ kcal mol^{-1}

TS-1a-(*R*)-2a
$\Delta\Delta G^{\neq} = 3.19$ kcal mol^{-1}

	(*S*) (Å)			(*R*) (Å)	
	C-O	O-H	Ph-N	C-O	O-H
1b	1.76	1.48	3.45	1.80	1.46
1c-A-1	1.76	1.48	3.52	1.78	1.47
1c-A-2	1.76	1.48	3.44	1.78	1.47
1c-B-1	1.75	1.49	3.43	1.78	1.47
1c-B-2	1.76	1.48	3.44	1.79	1.46

5. Stabilization energies between N-aceyl-PIQ^{+} and benzene complexes

In order to explore the effect of substitute at position 6 of the PIQ, further interaction energies between benzene and simplified model of N-acetyl-6-naphthyl-PIQ or N-acetyl-6-hydrogen-PIQ were calculated. The geometries of the complex taken from the corresponding transition state structures were optimized limitedly at B97D/TZVP level of theory with the heavy atoms being fixed. The optimized geometries and stabilization energies were depicted in figure S5.



1c-bz-A
ΔE = -12.40 kcal mol^{-1}

1c-bz-B
ΔE = -11.35 kcal mol^{-1}

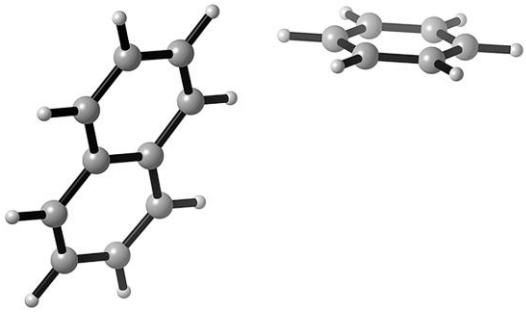
1a-bz
ΔE = -11.27 kcal mol^{-1}

Fig. S5 Stabilisation energies of N-aceyl-PIQ^{+} models and benzene

6. SAPT(DFT) interaction energy decomposition for the configuration of naphthalene and benzene dimer

Supporting Information

The coordinates of benzene and naphthalene dimer were extracted from the transition state structure TS-1a-(S)-2a-A. SAPT(DFT) calculation was carried out with the PBE0 functional and aug-cc-pVDZ basis set by using SAPT2008 and Dalton 2.0[7].



	kcal mol^{-1}
E_{ele}	-0.70
E_{ind}	-0.12
E_{dis}	-2.57
E_{exch}	2.09
δHF	-0.14
Total	-1.44

Fig. S6 The configuration and energy components analysis of benzene and naphthalene dimer

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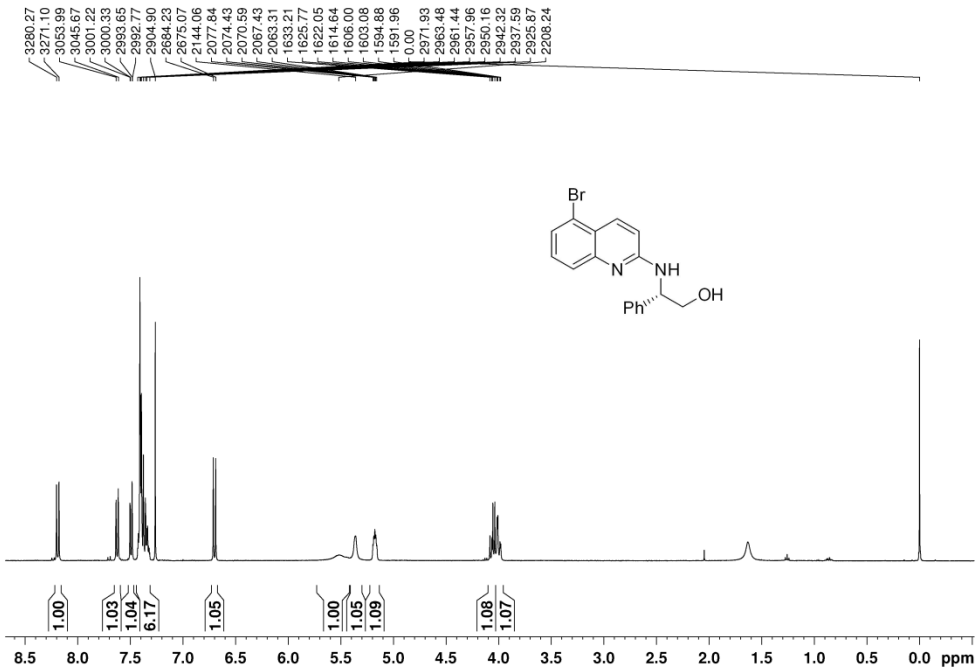

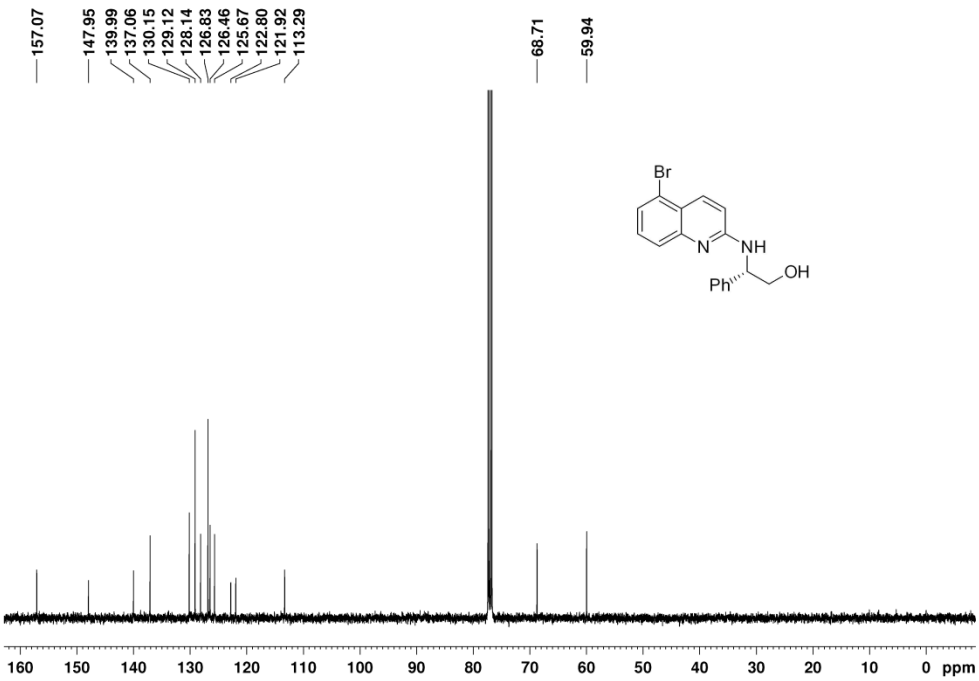

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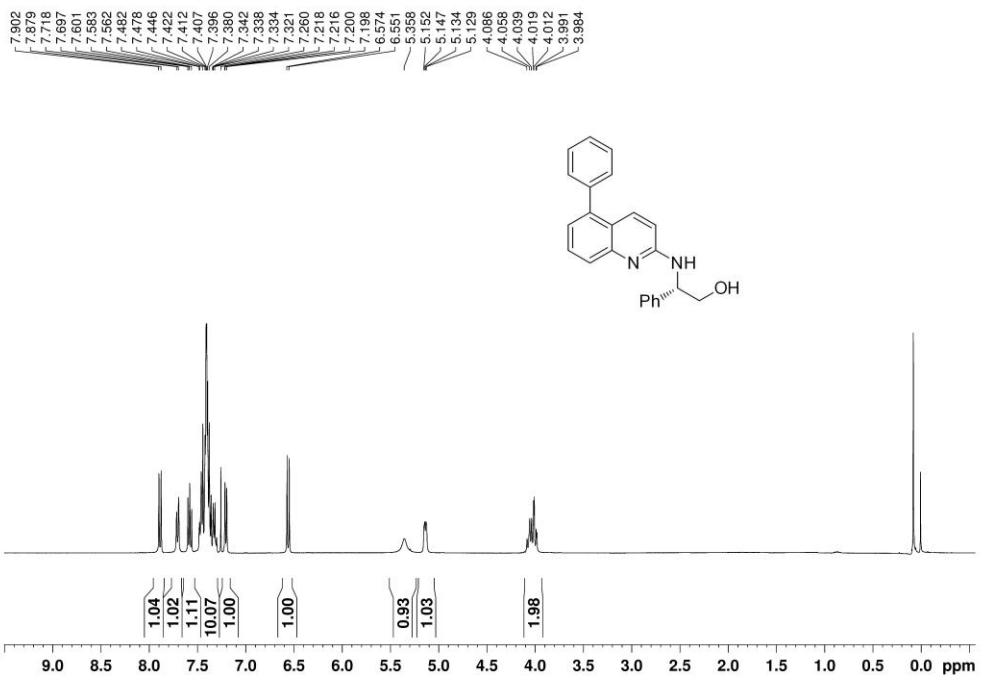

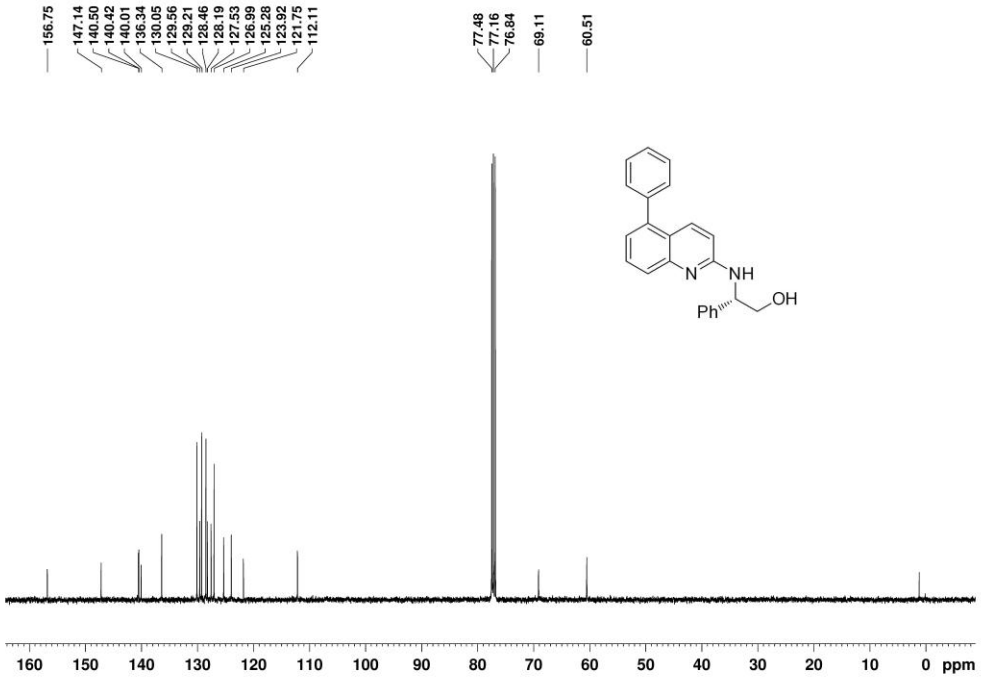

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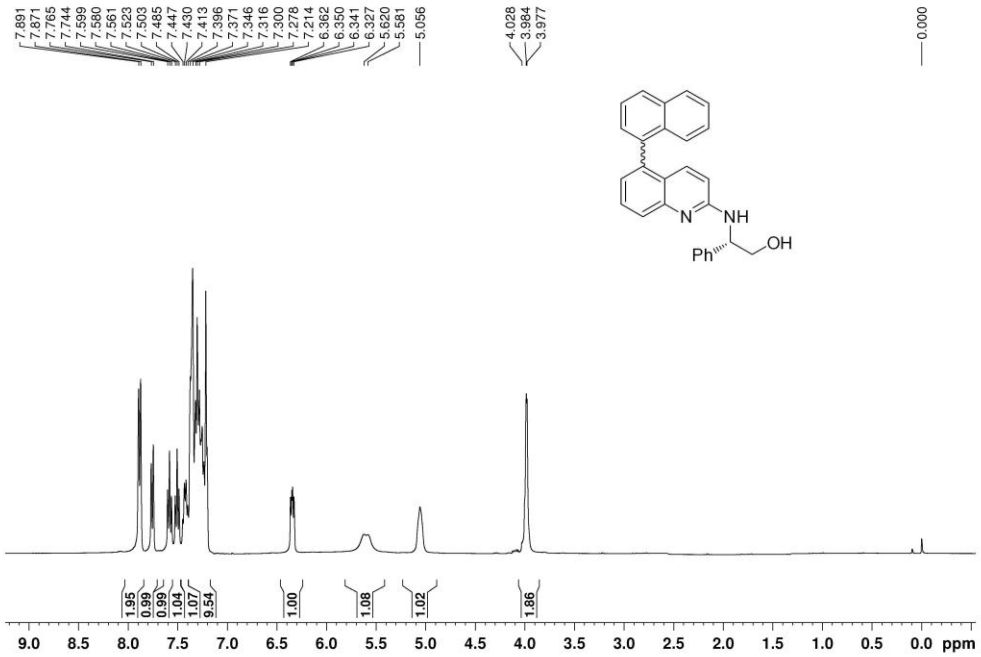
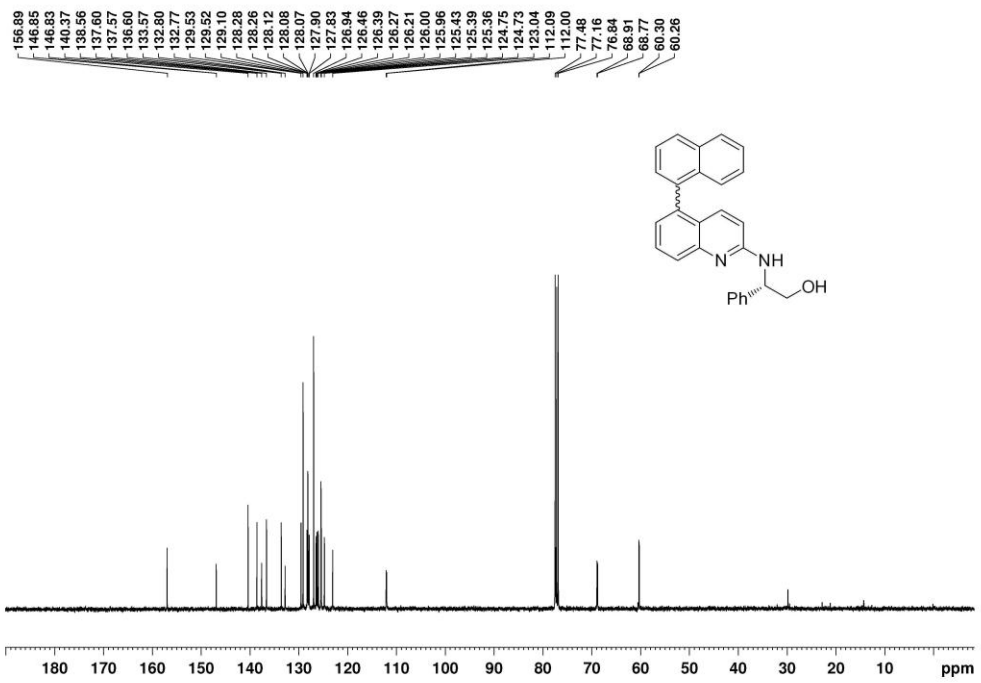
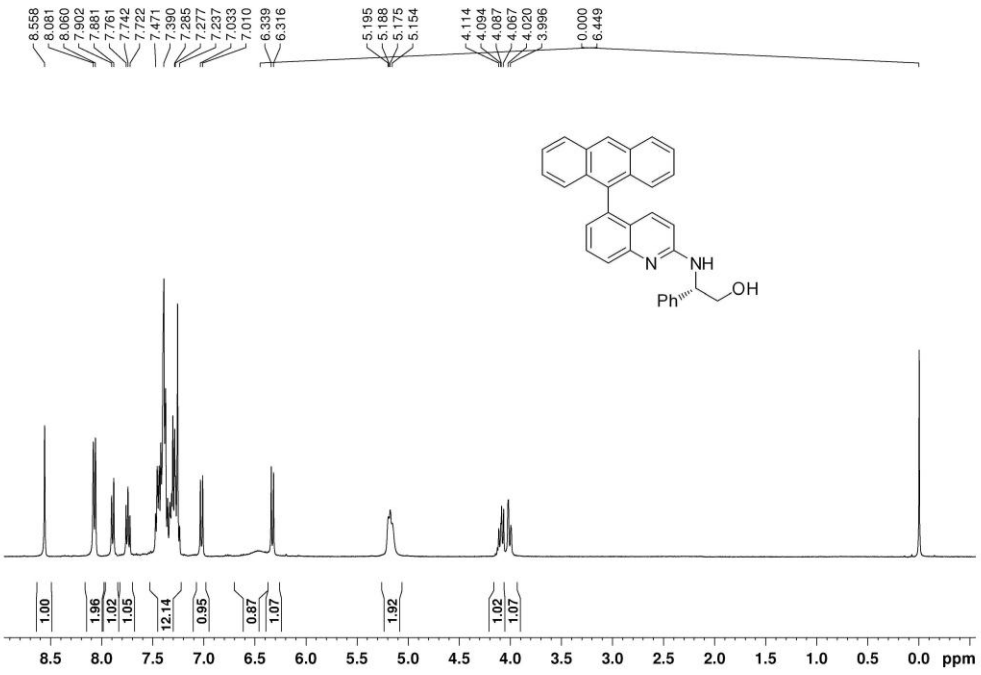
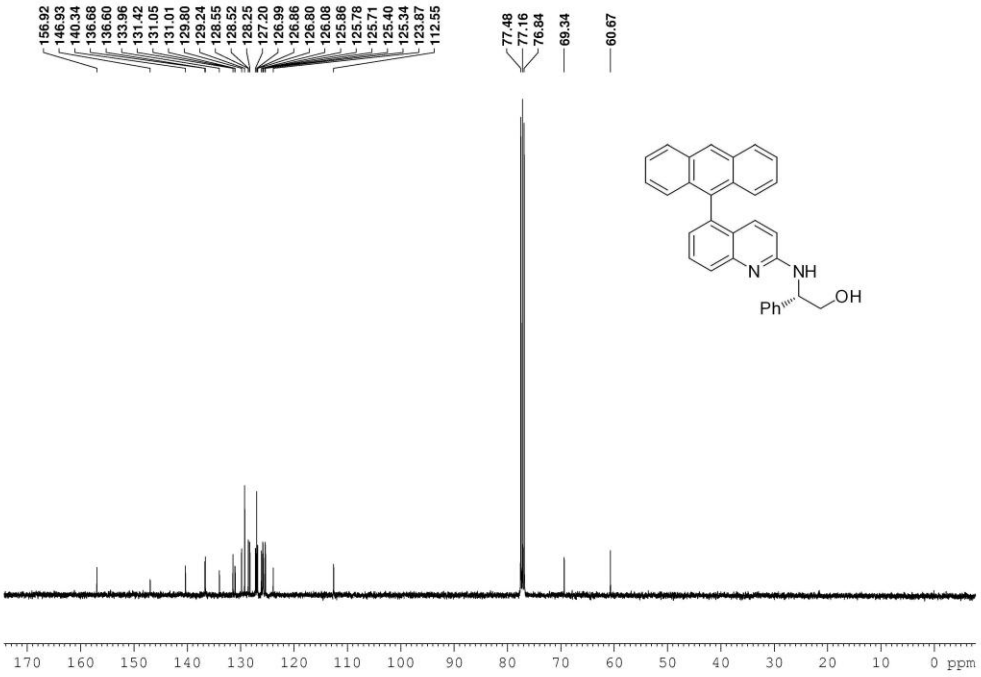




Supporting Information





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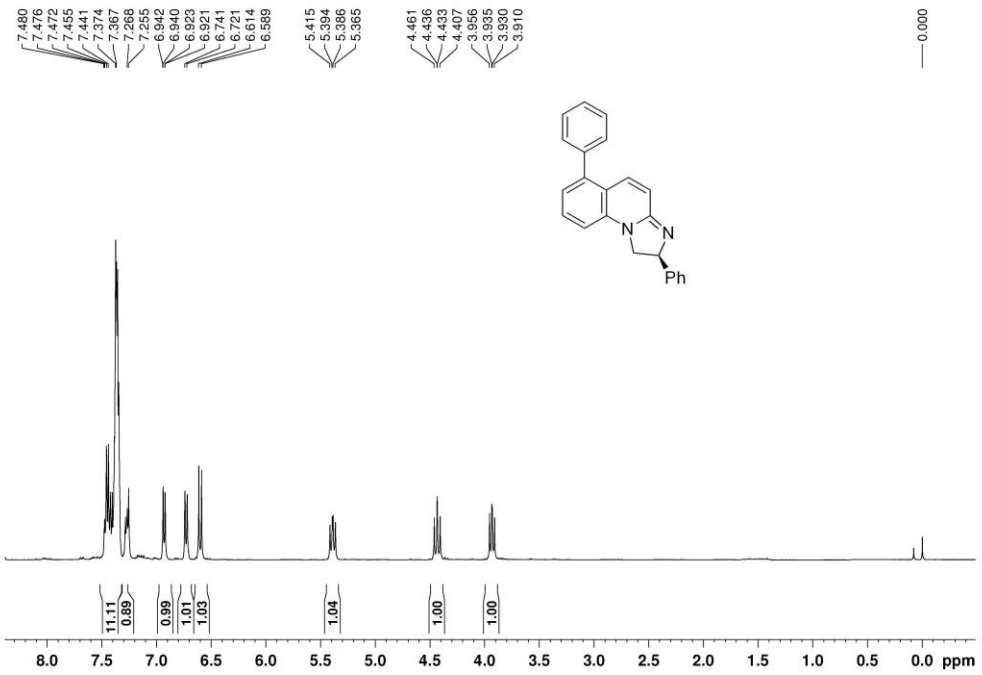

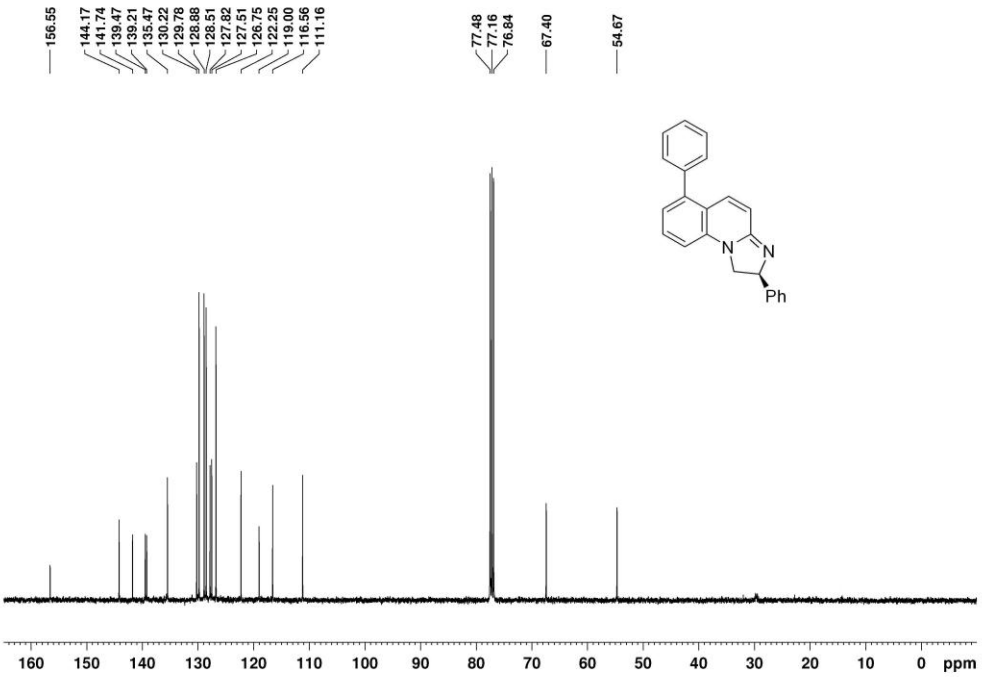

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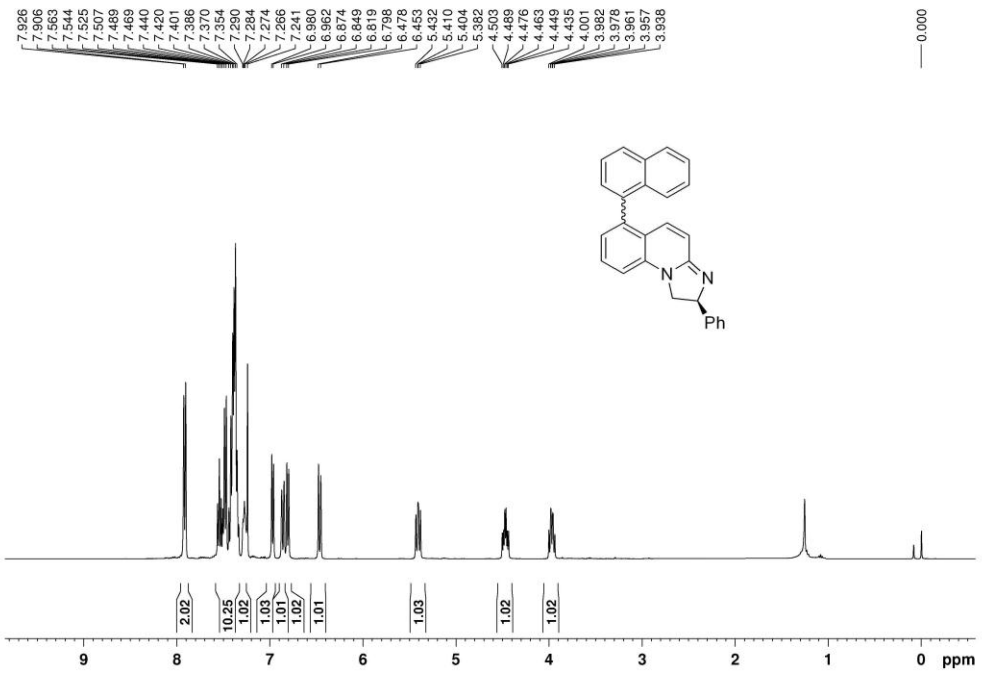

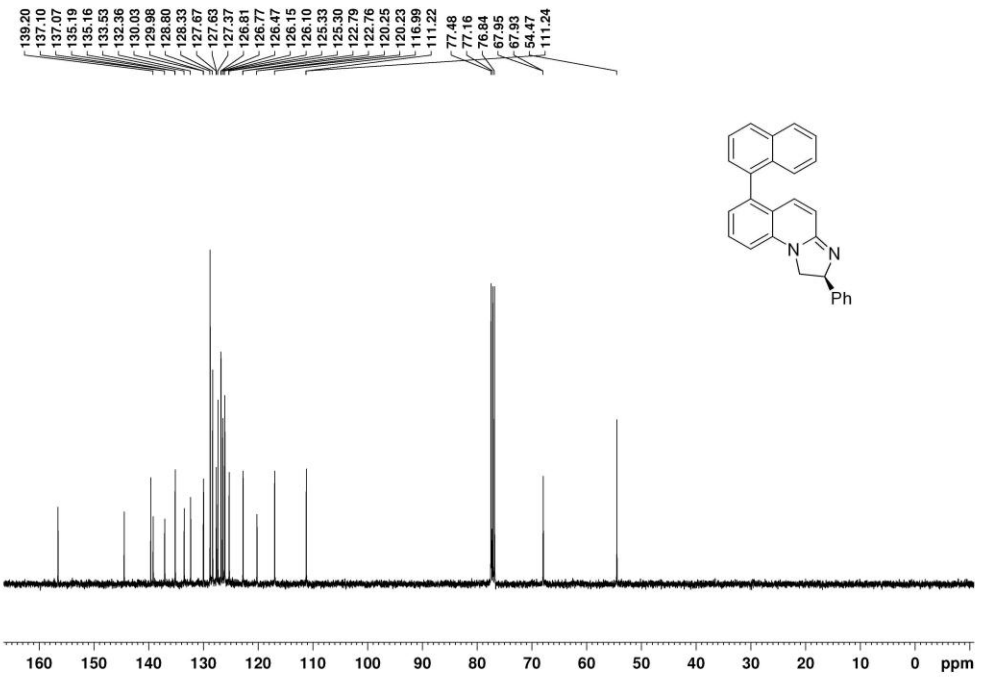

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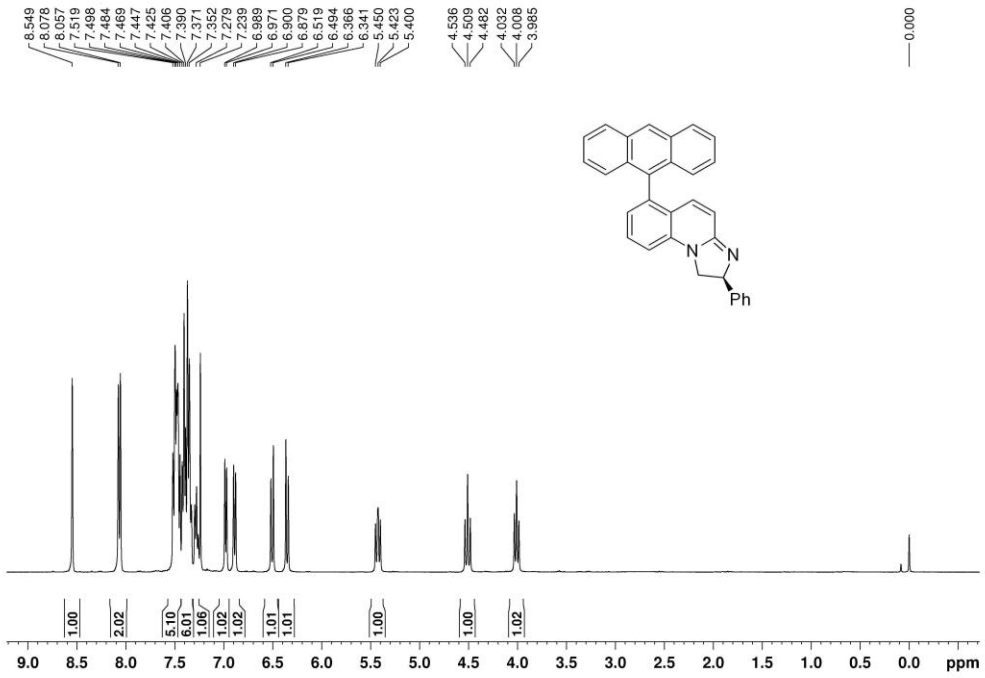

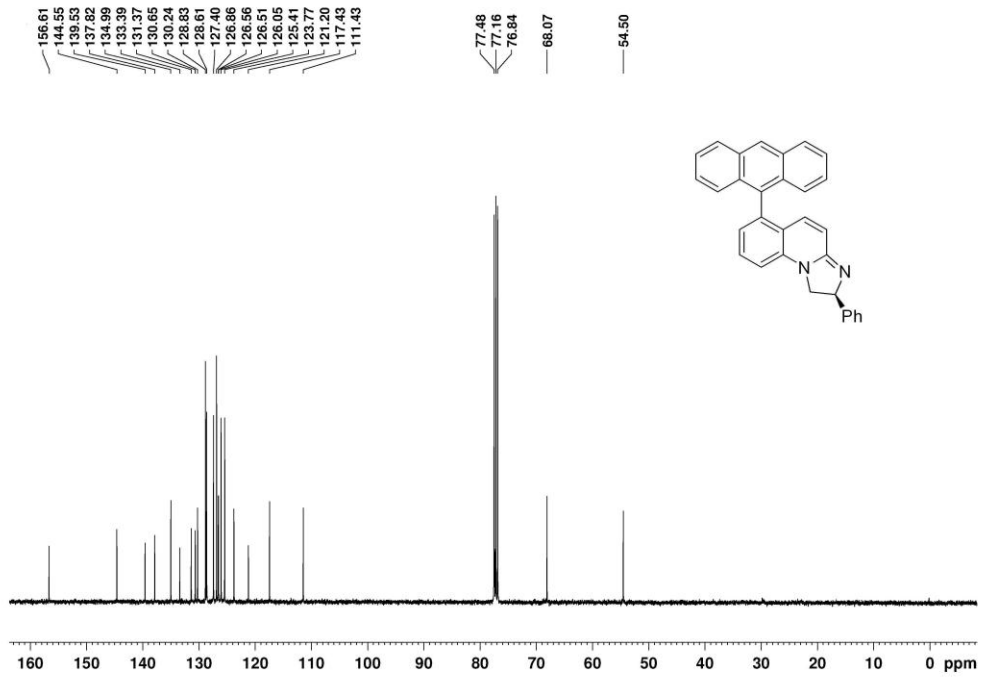

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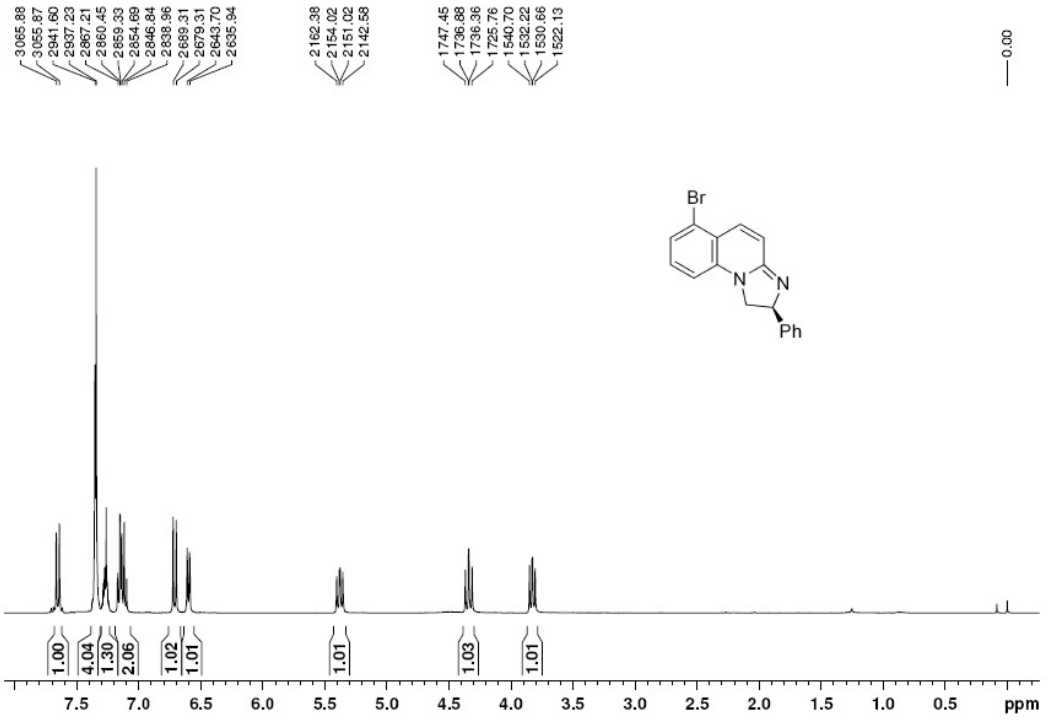

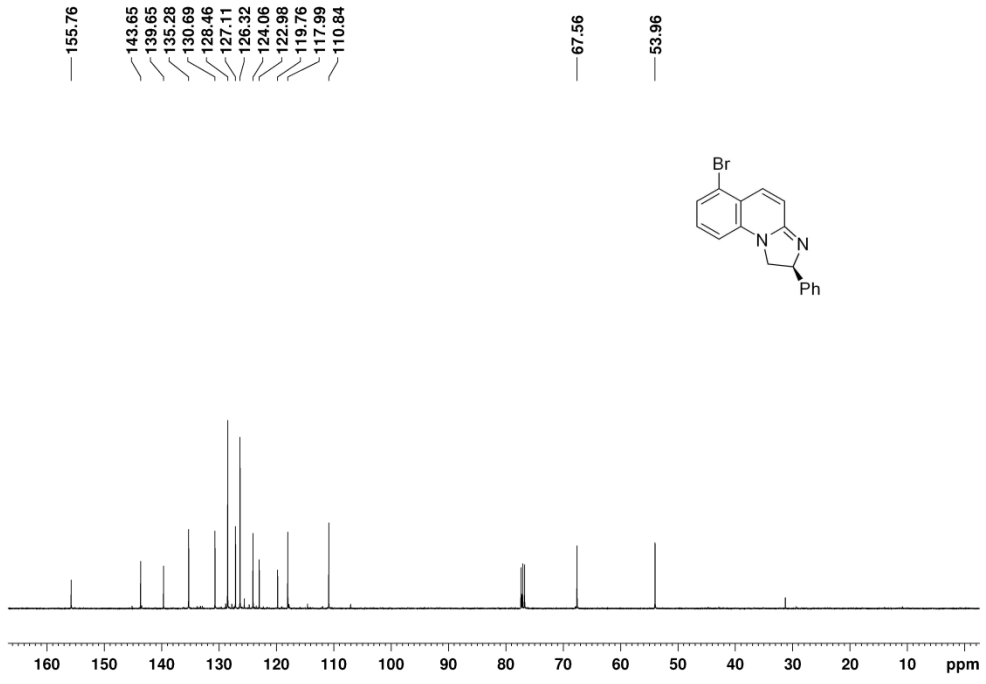

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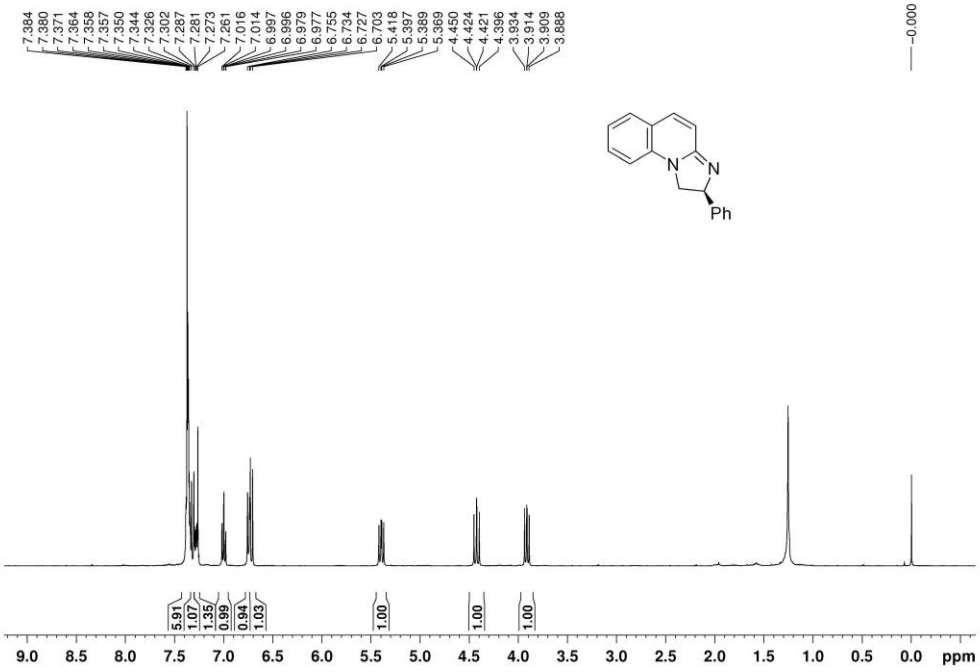

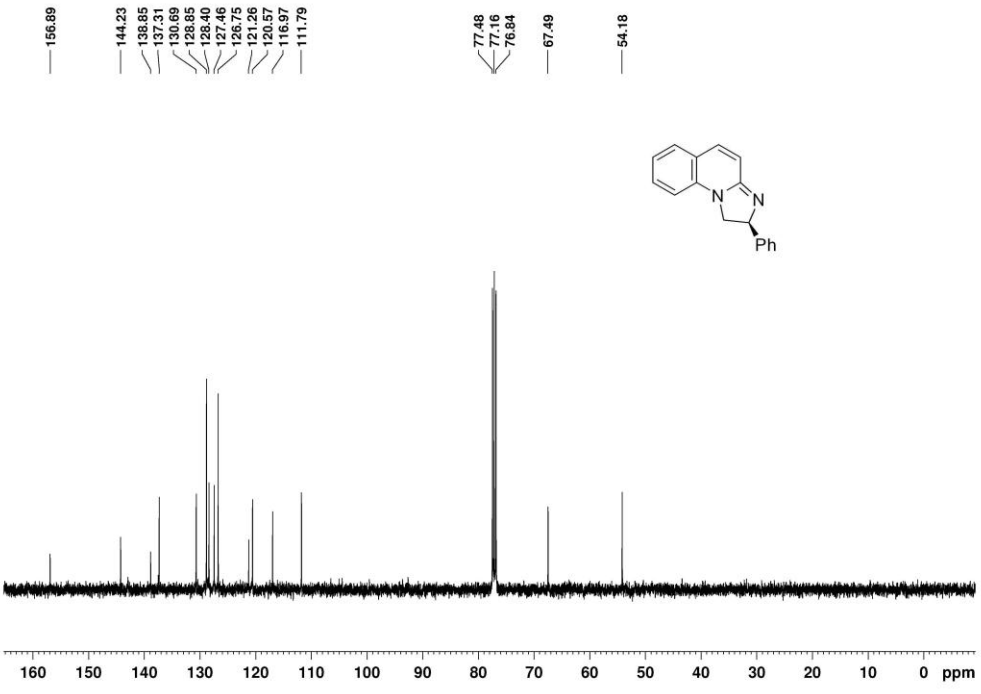

Supporting Information