Supporting Information

A Cobalt-Catalyzed Enantioconvergent Radical Negishi C(sp^3)–C(sp^2) Cross-Coupling with Chiral Multidentate N,N,P-Ligand

Zhuang Li,[†,‡,§] Xian-Yan Cheng,[‡,§] Ning-Yuan Yang,[‡] Ji-Jun Chen,[‡] Wen-Yue Tang,[‡] Jun-Qian Bian,[‡] Yong-Feng Cheng,[‡] Zhong-Liang Li,[∥] Qiang-Shuai Gu,*[,†,∥] and Xin-Yuan Liu*[,‡]

[†]Shenzhen Key Laboratory of Small Molecule Drug Discovery and Synthesis, Southern University of Science and Technology, Shenzhen 518055, China

[‡]Shenzhen Grubbs Institute and Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China

[∥]Academy for Advanced Interdisciplinary Studies and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

Table of contents

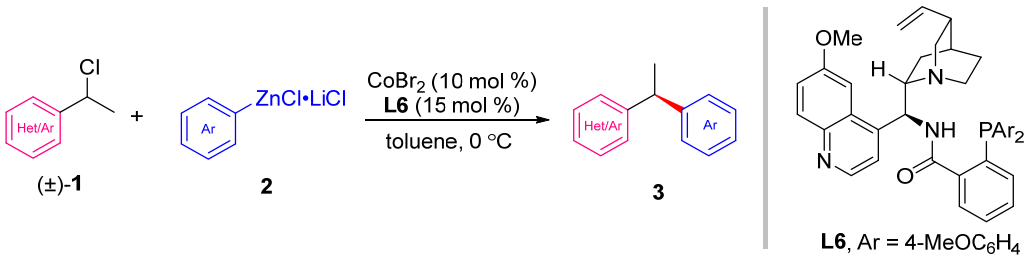
The synthesis of benzyl chloride substrates

The benzyl chlorides were prepared from the corresponding substituted acetophenone according to the reported literature with slight modification.[1]

The synthesis of organozinc reagents

The organozinc reagents **2** were prepared from the corresponding aryl bromide according to the reported literature with no modification.[2]

Experimental Procedures

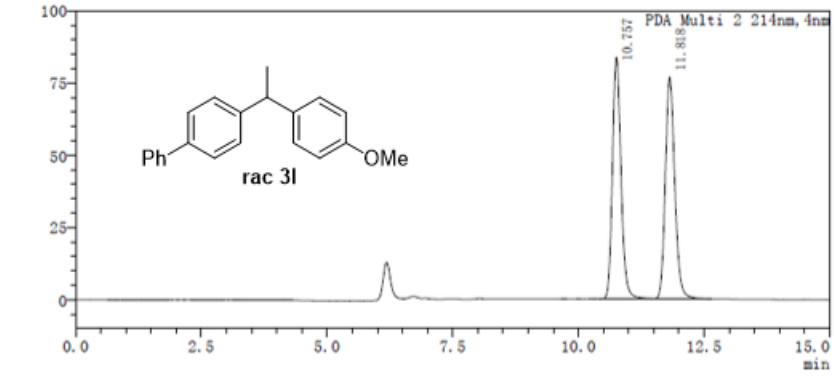


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CoBr_2$ (40 µL, 0.5 M in THF, 0.020 mmol, 10 mol%) and **L6** (20.0 mg, 0.024 mmol, 15 mol%). The mixture was stirred for 15 min. To this solution was added **1** (0.20 mmol, 1.0 equiv.), **2** (0.60 mmol, 3.0 equiv.) and anhydrous toluene (2 mL). Then the reaction mixture was stirred at 0 °C for 72 h. and quenched with sat. NH_4Cl solution (4 mL). EtOAc was used to extract the product from the aqueous layer (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

Determination of absolute configuration

The absolute configuration of **3l** was determined by comparing the HPLC spectrum and specific rotation with those reported in literature.[3] {$[\alpha]_D^{24.9} = -1.8$ ($c = 0.10$, $CHCl_3$, 77:23 e.r.). Lit. $[\alpha]_D^{24.8} = -24.1$ (c = 0.60, $CHCl_3$, 90% ee)} The product **3l** was determined to be of an "*R*" absolute configuration according to the reported data.

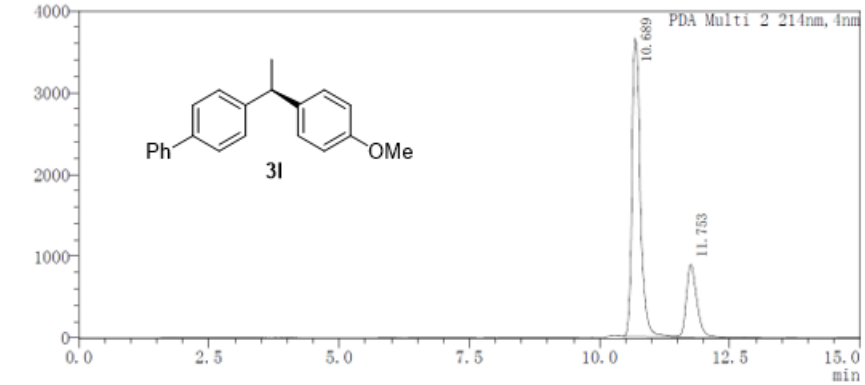
Figure S1 HPLC spectrum comparison for **3l**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.757	993807	49.754
2	11.818	1003646	50.246



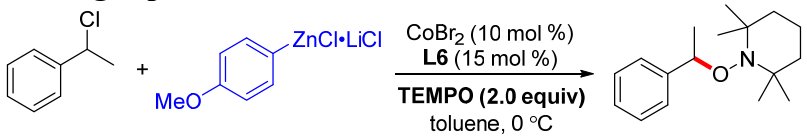
Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.689	40986800	76.916
2	11.753	12300867	23.084

Mechanistic Study

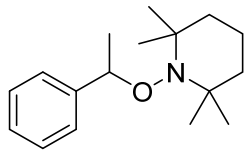
TEMPO inhibiting experiment



(±)-**1b** **2a** **4**, 35% **3b**, trace

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CoBr_2$ (40 µL, 0.5 M in THF, 0.020 mmol, 10 mol%) and **L6** (20.0 mg, 0.024 mmol, 15 mol%). The mixture was stirred for 15 min. To this solution was added **1b** (28 mg, 0.20 mmol, 1.0 equiv.), **2a** (2.15 mL, 0.28 M in THF, 0.60 mmol, 3.0 equiv.), TEMPO (62.5 mg, 0.40 mmol, 2.0 equiv.), and anhydrous toluene (2 mL). Then the reaction mixture was stirred at 0 °C for 72 h. and quenched with sat. NH_4Cl solution (4 mL). EtOAc was used to extract the product from the aqueous layer (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product. Trace amount of product **3b** was observed and **4**[4] could be isolated (35%).

2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (4)

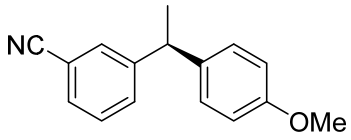


4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 4.81 (q, *J* = 6.7 Hz, 1H), 1.56 – 1.46 (m, 6H), 1.44 – 1.37 (m, 2H), 1.35 – 1.26 (m, 4H), 1.20 (s, 3H), 1.06 (s, 3H), 0.69 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.87, 128.01, 126.78, 126.62, 83.13, 59.68, 40.37, 34.47, 34.13, 23.58, 20.34, 17.24.

Characteristic data of products 3a–3y

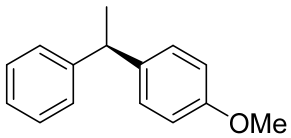
(S)-3-(1-(4-methoxyphenyl)ethyl)benzonitrile (3a)



3a

According to the general procedure, **3a** (45 mg, 0.19 mmol, 95% yield, 74.5:25.5 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 214 nm), tR (major) = 31.39 min, tR (minor) = 34.73 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.89 – 6.81 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.25, 148.29, 136.86, 132.22, 131.13, 129.77, 129.14, 128.48, 119.10, 114.04, 112.37, 55.29, 43.61, 21.76.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found 238.1224.

(*R*)-1-methoxy-4-(1-phenylethyl)benzene (3b)

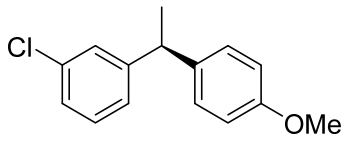


3b

According to the general procedure, **3b** (26 mg, 0.12 mmol, 61% yield, 71.5:28.5 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 214 nm), tR (minor) = 23.65 min, tR (major) = 25.18 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.27 – 7.13 (m, 5H), 6.90 – 6.81

(m, 2H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.84, 146.78, 138.57, 128.52, 128.34, 127.54, 125.94, 113.73, 55.25, 43.94, 22.06.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{17}O$ $[M + H]^+$ 213.1274, found 213.1271.

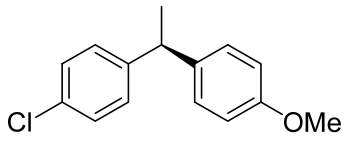
(*S*)-1-chloro-3-(1-(4-methoxyphenyl)ethyl)benzene (3c)



3c

According to the general procedure, **3c** (40 mg, 0.16 mmol, 82% yield, 71.5:28.5 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 95/5, flow rate 0.80 mL/min, λ = 214 nm), tR (minor) = 11.97 min, tR (major) = 12.79 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.07 (m, 6H), 6.90 – 6.82 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.04, 148.90, 137.66, 134.15, 129.59, 128.48, 127.68, 126.13, 125.80, 113.87, 55.26, 43.73, 21.88.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}ClO$ $[M + H]^+$ 247.0884, found 274.0876.

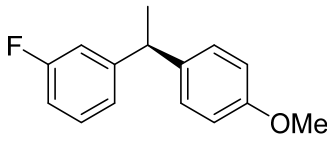
(*S*)-1-chloro-4-(1-(4-methoxyphenyl)ethyl)benzene (3d)



3d

According to the general procedure, **3d** (44 mg, 0.18 mmol, 89% yield, 76:24 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 98/2, flow rate 0.80 mL/min, λ = 214 nm), tR (major) = 14.31 min, tR (minor) = 15.25 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.19 – 7.10 (m, 4H), 6.90 – 6.83 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 145.30, 137.98, 131.64, 128.91, 128.45, 128.44, 113.84, 55.26, 43.36, 22.00.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}ClO$ $[M + H]^+$ 247.0884, found 247.0884.

(*S*)-1-fluoro-3-(1-(4-methoxyphenyl)ethyl)benzene (3e)



3e

According to the general procedure, **3e** (31 mg, 0.14 mmol, 68% yield, 76:24 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel OBH (hexane/*i*-PrOH = 95/5, flow rate 0.70 mL/min, λ = 214 nm), tR (major) = 11.92 min, tR (minor) = 13.35 min.

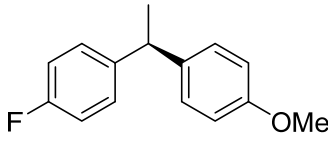
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 1H), 7.16 – 7.08 (m, 2H), 7.01 – 6.95 (m, 1H), 6.93 – 6.80 (m, 4H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.96 (d, *J* = 245.2 Hz), 158.04, 149.50 (d, *J* = 6.7 Hz), 137.81, 129.71 (d, *J* = 8.3 Hz), 128.49, 123.23 (d, *J* = 2.8 Hz), 114.41 (d, *J* = 21.3 Hz), 113.86, 112.79 (d, *J* = 21.1 Hz), 55.26, 43.73 (d, *J* = 1.7 Hz), 21.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.52 – -123.46 (m).

HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}FO$ $[M + H]^+$ 231.1180, found 231.1180.

(*S*)-1-fluoro-4-(1-(4-methoxyphenyl)ethyl)benzene (3f)



3f

According to the general procedure, **3f** (34 mg, 0.14 mmol, 74% yield, 73:27 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 98/2, flow rate 0.80 mL/min, λ = 214 nm), tR (major) = 16.46 min, tR (minor) = 24.88 min.

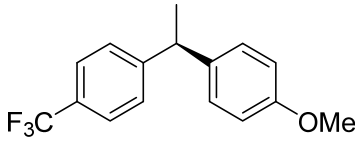
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 4H), 7.05 – 6.95 (m, 2H), 6.92 – 6.84 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.24 (d, *J* = 243.7 Hz), 157.95, 142.49 (d, *J* = 3.3 Hz), 138.37, 128.90 (d, *J* = 7.7 Hz), 128.44, 115.05 (d, *J* = 21.1 Hz), 113.82, 55.25, 43.23, 22.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.59.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}FO$ $[M + H]^+$ 231.1180, found 231.1178.

(*R*)-1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene (3g)



3g

According to the general procedure, **3g** (39 mg, 0.14 mmol, 70% yield, 80:20 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 90/10, flow rate 0.70 mL/min, λ = 214 nm), tR (minor) = 7.59 min, tR (major) = 9.38 min.

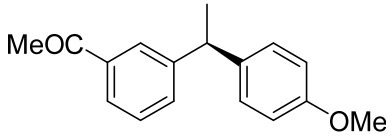
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.08 (m, 2H), 6.88 – 6.81 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.12, 150.88, 137.41, 128.50, 127.85, 125.67 (q, *J* = 272.0 Hz), 125.31 (q, *J* = 3.8 Hz), 122.97, 113.92, 55.26, 43.85, 21.82.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.32.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}F_3O$ $[M + H]^+$ 281.1148, found 281.1147.

(*S*)-1-(3-(1-(4-methoxyphenyl)ethyl)phenyl)ethan-1-one (3h)



3h

According to the general procedure, **3h** (20 mg, 0.08 mmol, 40% yield, 75.5:24.5 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

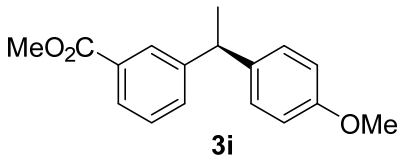
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 90/10, flow rate 0.70 mL/min, λ = 214 nm), tR (minor) = 55.01 min, tR (major) = 67.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.76 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.17 – 7.09 (m, 2H), 6.87 – 6.79 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 2.58 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.39, 158.01, 147.42, 137.82, 137.28, 132.46, 128.61, 128.48, 127.15, 126.29, 113.88, 55.26, 43.89, 26.72, 21.97.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1375.

Methyl (*S*)-3-(1-(4-methoxyphenyl)ethyl)benzoate (3i)



3i

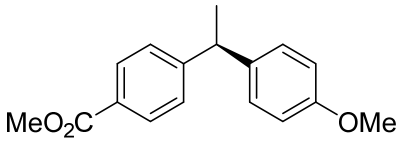
According to the general procedure, **3i** (37 mg, 0.14 mmol, 69% yield, 68:32 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 90/10, flow rate 0.70 mL/min, λ = 214 nm), tR (minor) = 29.86 min, tR (major) = 34.22 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 1H), 7.93 – 7.86 (m, 1H), 7.45 – 7.33 (m, 2H), 7.20 – 7.12 (m, 2H), 6.90 – 6.82 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 1.67 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.27, 158.00, 147.17, 137.92, 132.30, 130.24, 128.57, 128.50, 128.45, 127.33, 113.87, 55.25, 52.08, 43.85, 21.96.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}O_3$ $[M + H]^+$ 271.1329, found 271.1323.

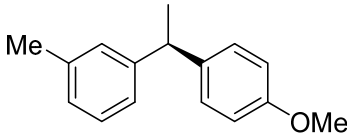
Methyl (*R*)-4-(1-(4-methoxyphenyl)ethyl)benzoate (3j)



3j

According to the general procedure, **3j** (44 mg, 0.16 mmol, 82% yield, 76:24 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 10.59 min, tR (major) = 12.21 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.33 – 7.28 (m, 2H), 7.17 – 7.10 (m, 2H), 6.90 – 6.82 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.09, 158.05, 152.17, 137.60, 129.75, 128.52, 127.93, 127.58, 113.87, 55.26, 52.00, 44.00, 21.79.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}O_3$ $[M + H]^+$ 271.1329, found 271.1322.

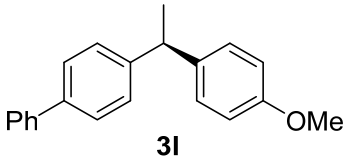
(S)-1-(1-(4-methoxyphenyl)ethyl)-3-methylbenzene (3k)



3k

According to the general procedure, **3k** (9 mg, 0.04 mmol, 20% yield, 61:39 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 98/2, flow rate 0.80 mL/min, λ = 214 nm), tR (minor) = 19.32 min, tR (major) = 21.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 3H), 7.04 – 6.95 (m, 3H), 6.86 – 6.78 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.31 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.79, 146.72, 138.68, 137.86, 128.50, 128.35, 128.24, 126.72, 124.53, 113.71, 55.25, 43.89, 22.09, 21.52.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{19}O$ $[M + H]^+$ 227.1436, found 227.1441

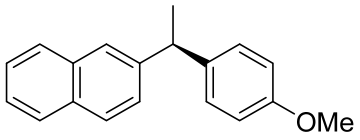
(*R*)-4-(1-(4-methoxyphenyl)ethyl)-1,1'-biphenyl (3l)



3l

According to the general procedure, **3l** (30 mg, 0.10 mmol, 52% yield, 77:23 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 214 nm), tR (major) = 10.69 min, tR (minor) = 11.75 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.50 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 7.26 – 7.19 (m, 2H), 6.92 – 6.85 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.93, 145.94, 141.06, 138.89, 138.46, 128.73, 128.55, 127.95, 127.12, 127.05, 127.04, 113.82, 55.27, 43.67, 22.09.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}O$ $[M + H]^+$ 289.1587, found 289.1607.

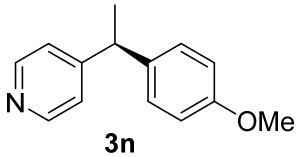
(*S*)-2-(1-(4-methoxyphenyl)ethyl)naphthalene (3m)



3m

According to the general procedure, **3m**[5] (26 mg, 0.10 mmol, 50% yield, 70.5:29.5 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 214 nm), tR (minor) = 18.43 min, tR (major) = 21.85 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.67 (brs, 1H), 7.49 – 7.36 (m, 2H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.86 – 6.78 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.93, 144.21, 138.43, 133.57, 132.10, 128.69, 127.96, 127.75, 127.60, 126.84, 125.95, 125.35, 125.24, 113.80, 55.27, 44.05, 21.99.

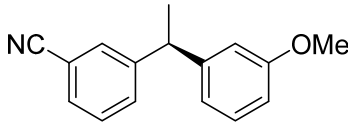
(*S*)-4-(1-(4-methoxyphenyl)ethyl)pyridine (3n)



3n

According to the general procedure, **3n** (38 mg, 0.18 mmol, 90% yield, 72:28 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel OJ-3 (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 214 nm), tR (minor) = 19.91 min, tR (major) = 23.05 min
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.46 (m, 2H), 7.15 – 7.07 (m, 4H), 6.88 – 6.81 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.61 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.28, 155.60, 149.78, 136.50, 128.56, 122.94, 113.99, 55.26, 43.42, 21.24.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}NO$ $[M + H]^+$ 214.1226, found 214.1222.

(*R*)-3-(1-(3-methoxyphenyl)ethyl)benzonitrile (3o)



3o

According to the general procedure, **3o** (44 mg, 0.19 mmol, 93% yield, 69:31 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

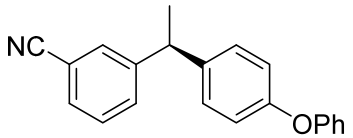
HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 14.27 min, tR (major) = 15.88 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.83 – 6.70 (m, 3H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 147.72, 146.42, 132.28, 131.18, 129.90, 129.70, 129.20, 119.98, 119.08, 113.88, 112.41, 111.40, 55.21, 44.41, 21.49.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226, found 238.1223.

(*S*)-3-(1-(4-phenoxyphenyl)ethyl)benzonitrile (3p)



3p

According to the general procedure, **3p** (30 mg, 0.18 mmol, 90% yield, 72:28 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

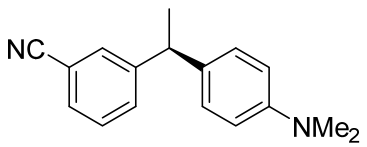
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 95/5, flow rate 1.00 mL/min, λ = 214 nm), tR (major) = 30.14 min, tR (minor) = 33.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 3H), 7.45 – 7.33 (m, 3H), 7.20 – 7.10 (m, 3H), 7.08 – 7.02 (m, 2H), 7.02 – 6.95 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.14, 155.94, 147.93, 139.53, 132.24, 131.20, 129.91, 129.78, 129.24, 128.78, 123.34, 119.07, 118.95, 118.92, 112.47, 43.78, 21.76.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{18}NO$ $[M + H]^+$ 300.1383, found 300.1377.

(*S*)-3-(1-(4-(dimethylamino)phenyl)ethyl)benzonitrile (3q)



3q

According to the general procedure, **3q** (45 mg, 0.18 mmol, 90% yield, 70:30 e.r.) was

obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

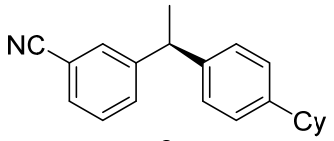
HPLC analysis: Chiralcel AS (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 9.88 min, tR (major) = 11.44 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.34 (m, 1H), 7.14 – 7.06 (m, 2H), 6.79 – 6.69 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 1H), 2.96 (s, 6H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.37, 148.84, 132.65, 132.26, 131.16, 129.60, 129.07, 128.15, 119.23, 112.82, 112.27, 43.51, 40.69, 21.77.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.1543, found 251.1537.

(*S*)-3-(1-(4-cyclohexylphenyl)ethyl)benzonitrile (3r)



3r

According to the general procedure, **3r** (40 mg, 0.14 mmol, 69% yield, 68:32 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

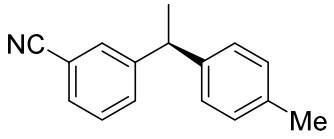
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 90/10, flow rate 0.70 mL/min, λ = 214 nm), tR (major) = 11.99 min, tR (minor) = 16.31 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.36 (m, 1H), 7.21 – 7.16 (m, 2H), 7.15 – 7.08 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.56 – 2.45 (m, 1H), 1.96 – 1.73 (m, 5H), 1.66 (d, *J* = 7.3 Hz, 3H), 1.52 – 1.22 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.16, 146.43, 142.01, 132.32, 131.25, 129.77, 129.13, 127.38, 127.08, 119.13, 112.36, 44.10, 34.46, 26.92, 26.17, 21.66.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}N$ $[M + H]^+$ 290.1903, found 290.1898.

(*S*)-3-(1-(p-tolyl)ethyl)benzonitrile (3s)



3s

According to the general procedure, **3s** (19 mg, 0.09 mmol, 44% yield, 81:19 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

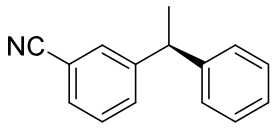
HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 95/5, flow rate 0.30 mL/min, λ = 214 nm), tR (minor) = 20.65 min, tR (major) = 21.72 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 3H), 7.43 – 7.35 (m, 1H), 7.18 – 7.07 (m, 4H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.12, 141.78, 136.23, 132.26, 131.17, 129.78, 129.37, 129.14, 127.40, 119.10, 112.38, 44.04, 21.62, 20.99.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N$ $[M + H]^+$ 222.1277, found 222.1273.

(*S*)-3-(1-phenylethyl)benzonitrile (3t)



3t

According to the general procedure, **3t** (28 mg, 0.14 mmol, 68% yield, 70:30 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

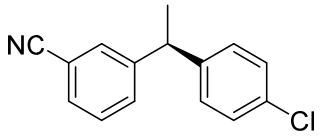
HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 8.59 min, tR (major) = 9.59 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 3H), 7.44 – 7.30 (m, 3H), 7.28 – 7.19 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.86, 144.75, 132.30, 131.21, 129.87, 129.17, 128.70, 127.54, 126.65, 119.06, 112.42, 44.43, 21.56.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{14}N$ $[M + H]^+$ 208.1121, found 208.1119.

(*S*)-3-(1-(4-chlorophenyl)ethyl)benzonitrile (3u)



3u

According to the general procedure, **3u** (46 mg, 0.19 mmol, 95% yield, 75:25 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

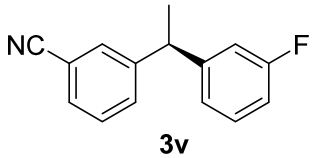
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 95/5, flow rate 0.70 mL/min, λ = 214 nm), tR (major) = 21.26 min, tR (minor) = 22.98 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.47 – 7.37 (m, 2H), 7.34 – 7.26 (m, 2H), 7.17 – 7.10 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.29, 143.23, 132.45, 132.20, 131.09, 130.08, 129.31, 128.90, 128.83, 118.91, 112.58, 43.82, 21.52.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}ClN$ $[M + H]^+$ 242.0731, found 242.0725.

(*R*)-3-(1-(3-fluorophenyl)ethyl)benzonitrile (3v)



3v

According to the general procedure, **3v** (42 mg, 0.18 mmol, 92% yield, 77:23 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 95/5, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 8.64 min, tR (major) = 10.06 min

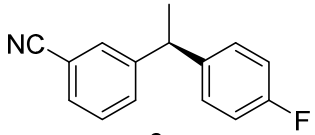
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.49 – 7.38 (m, 2H), 7.35 – 7.25 (m, 1H), 7.02 – 6.86 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.02 (d, *J* = 245.9 Hz), 147.31 (d, *J* = 6.6 Hz), 147.12, 132.20, 131.15, 130.20 (d, *J* = 8.4 Hz), 130.13, 129.32, 123.25 (d, *J* = 2.8 Hz), 118.92, 114.49 (d, *J* = 21.5 Hz), 113.58 (d, *J* = 21.0 Hz), 112.59, 44.14, 21.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.68.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}FN$ $[M + H]^+$ 226.1027, found 226.1024.

(*S*)-3-(1-(4-fluorophenyl)ethyl)benzonitrile (3w)



3w

According to the general procedure, **3w** (41 mg, 0.18 mmol, 92% yield, 78:22 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (minor) = 12.93 min, tR (major) = 14.19 min

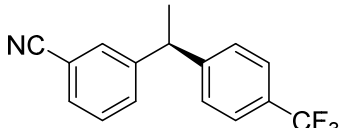
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.48 – 7.36 (m, 2H), 7.20 – 7.12 (m, 2H), 7.07 – 6.97 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55 (d, *J* = 245.3 Hz), 147.65, 140.45 (d, *J* = 3.1 Hz), 132.19, 131.10, 129.99, 129.27, 128.98 (d, *J* = 7.9 Hz), 118.96, 115.49 (d, *J* = 21.3 Hz), 112.53, 43.69, 21.73.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.33.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}FN$ $[M + H]^+$ 226.1027, found 226.1021.

(S)-3-(1-(4-(trifluoromethyl)phenyl)ethyl)benzonitrile (3x)



3x

According to the general procedure, **3x** (46 mg, 0.19 mmol, 98% yield, 72:28 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.

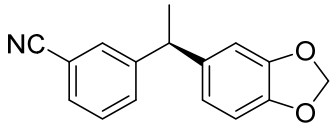
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 95/5, flow rate 0.70 mL/min, λ = 214 nm), tR (major) = 16.83 min, tR (minor) = 19.07 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.50 – 7.39 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.79, 146.74, 132.25, 131.13, 130.26, 129.42, 129.02 (q, *J* = 32.5 Hz), 127.92, 125.66 (q, *J* = 3.6 Hz), 124.12 (q, *J* = 271.8 Hz), 118.83, 112.70, 44.27, 21.37.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{13}F_3N$ $[M + H]^+$ 276.0995, found 276.0988.

(*R*)-3-(1-(benzo[*d*][1,3]dioxol-5-yl)ethyl)benzonitrile (3y)



3y

According to the general procedure, **3y** (37 mg, 0.15 mmol, 74% yield, 77:23 e.r.) was obtained from the reaction of the corresponding benzyl chloride (0.20 mmol) and arylzinc reagent.
HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 98/2, flow rate 1.00 mL/min, λ = 214 nm), tR (major) = 28.15 min, tR (minor) = 31.06 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.43 – 7.37 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.73 – 6.60 (m, 2H), 5.95 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 146.22, 138.74, 132.14, 131.10, 129.87, 129.19, 120.46, 119.05, 112.43, 108.29, 108.03, 101.04, 44.08, 21.72.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}NO_2$ $[M + H]^+$ 252.1019, found 252.1015.

NMR Spectra

Figure S2 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3a**

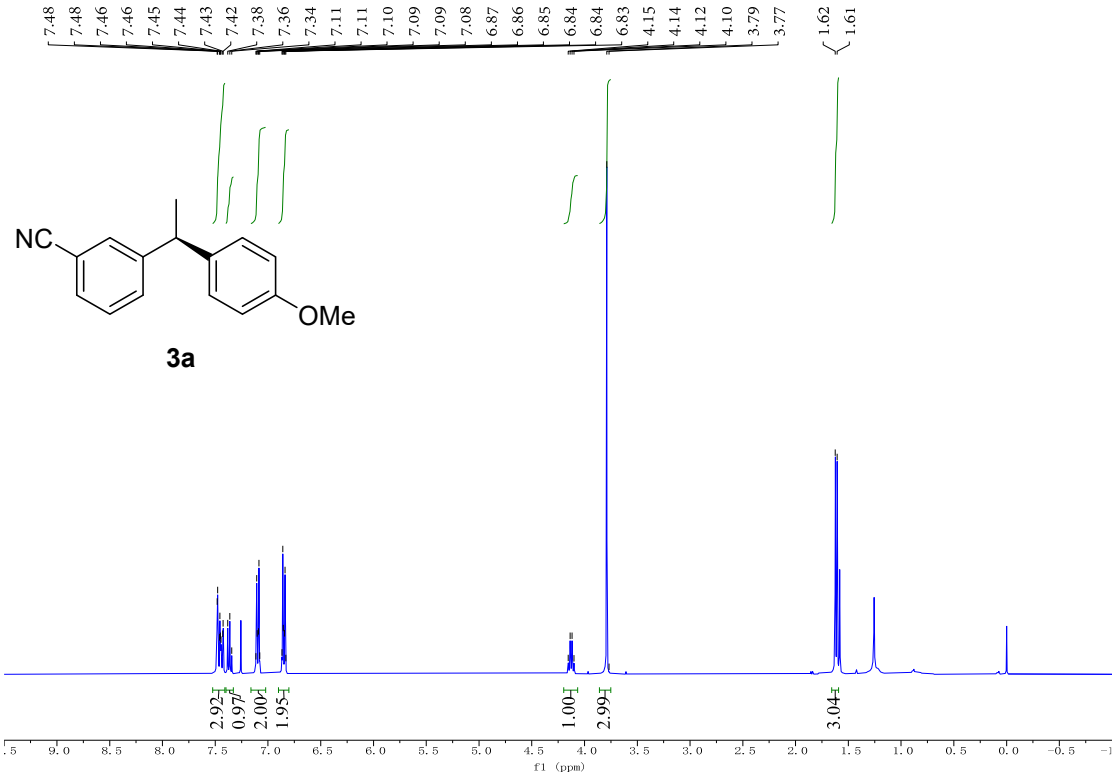


Figure S3 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3a**

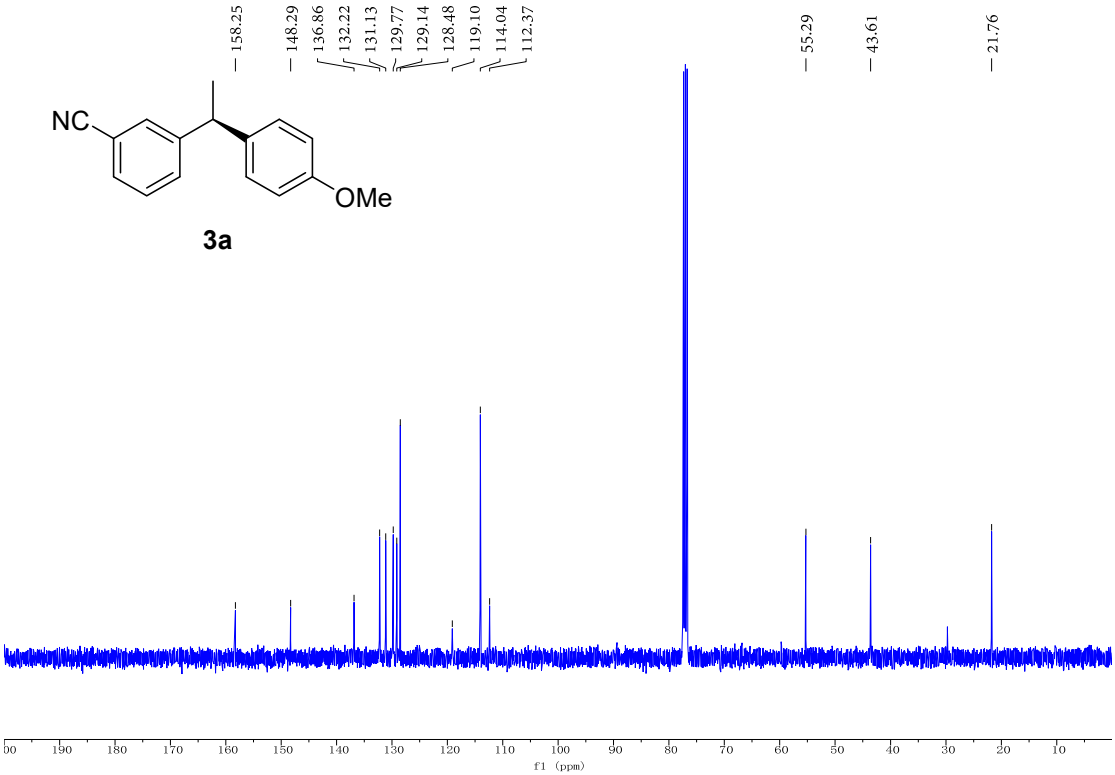


Figure S4 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3b**

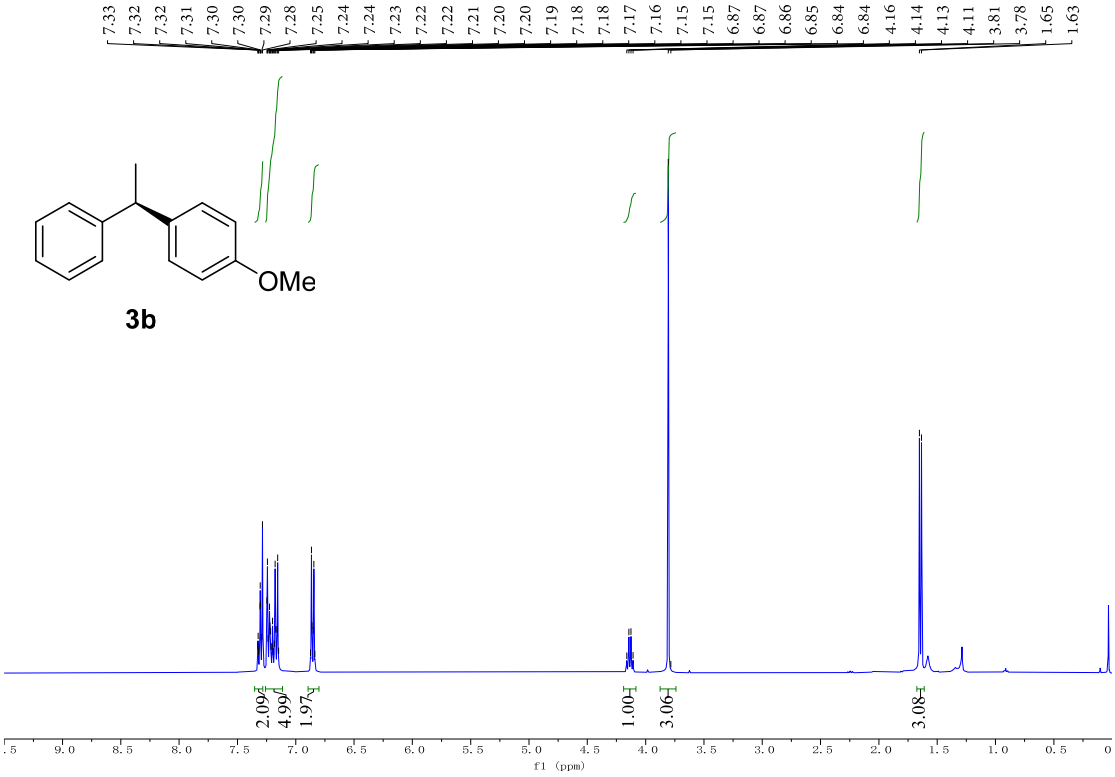


Figure S5 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3b**

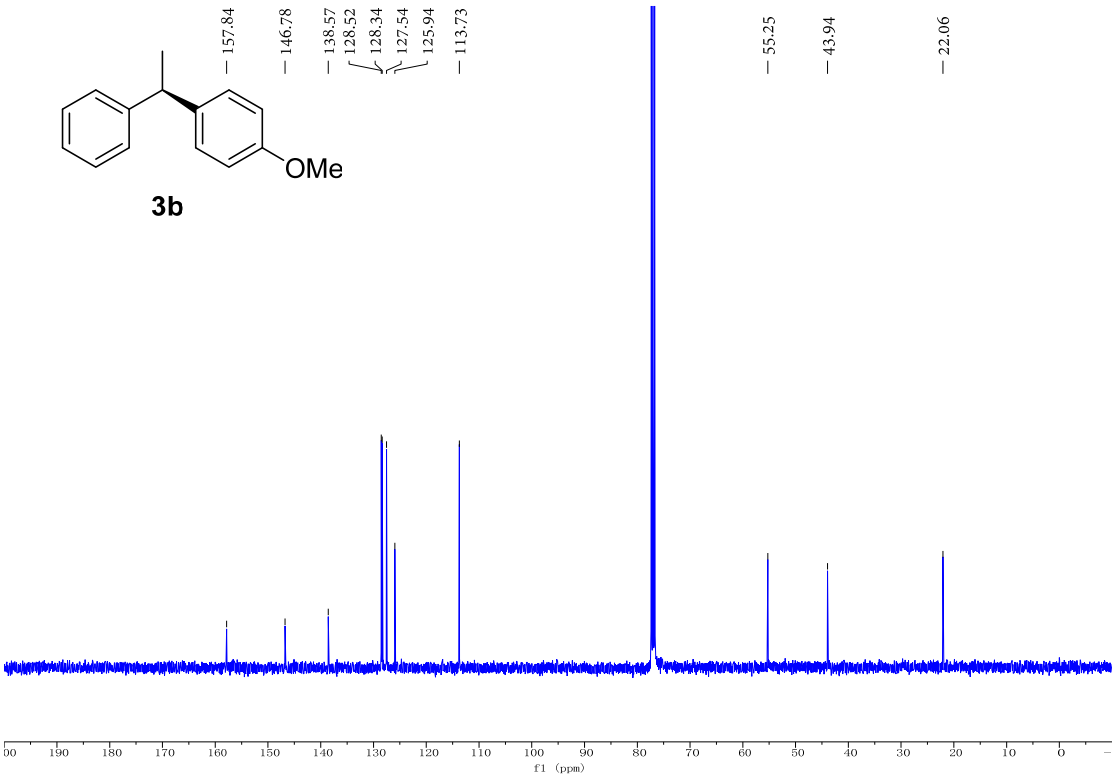


Figure S6 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3c**

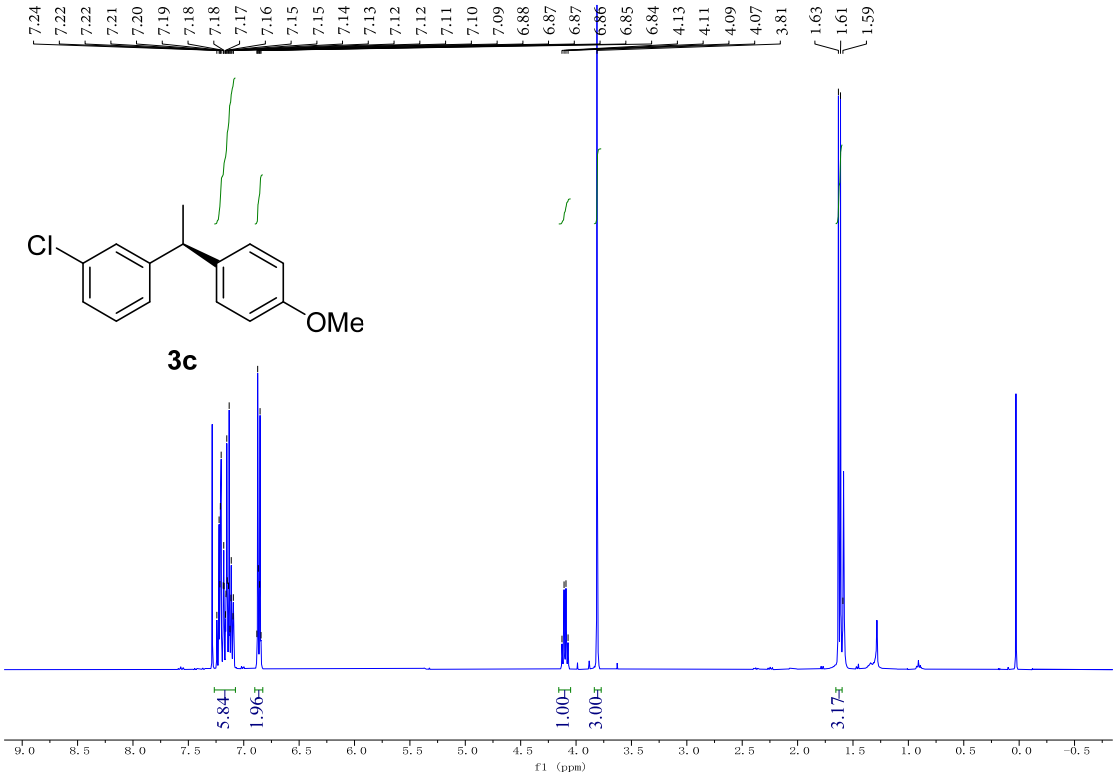


Figure S7 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3c**

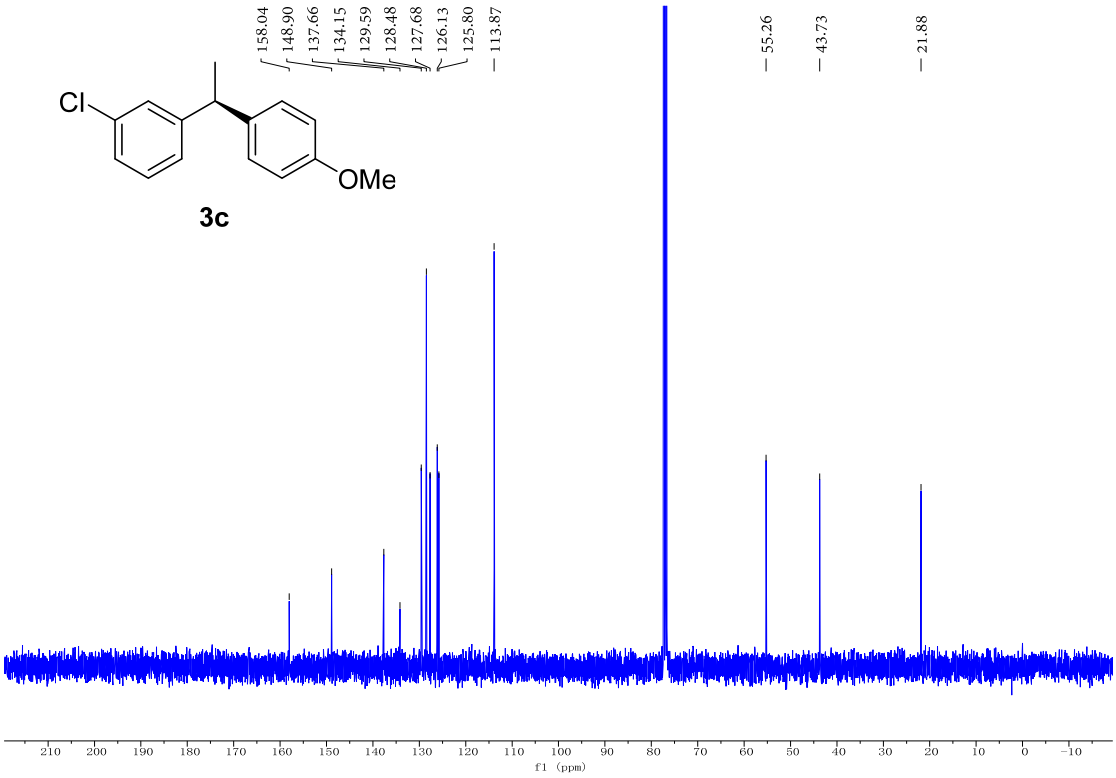


Figure S8 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3d**

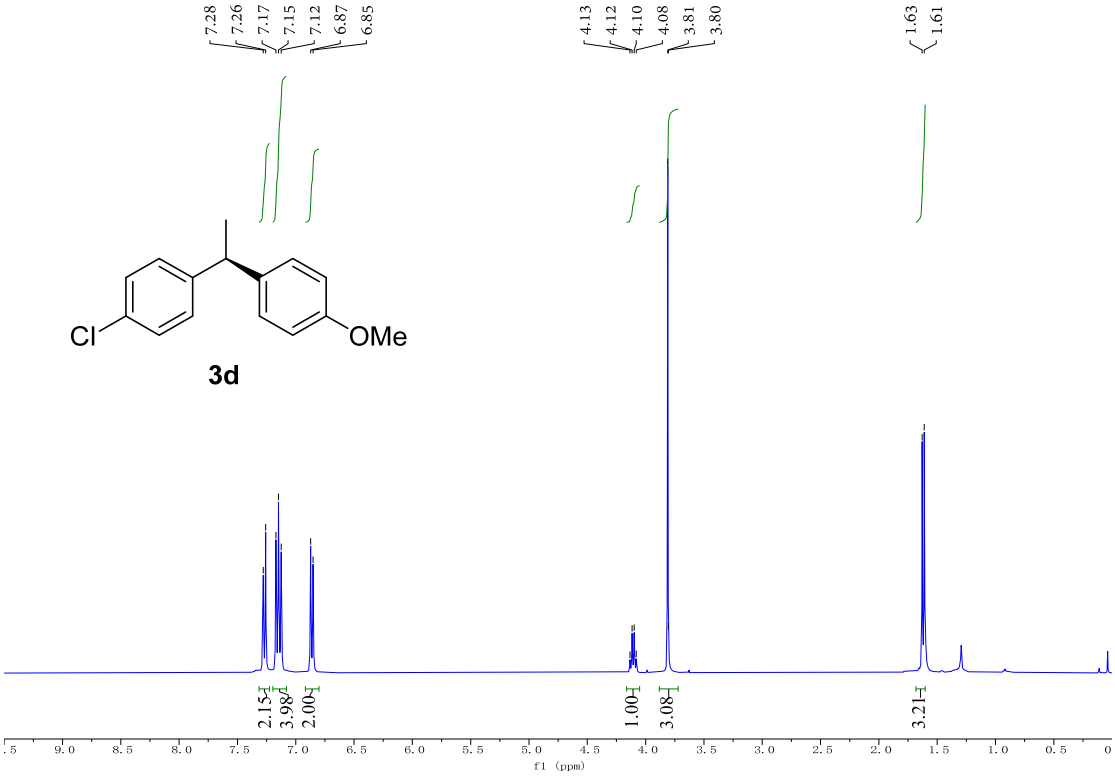


Figure S9 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3d**

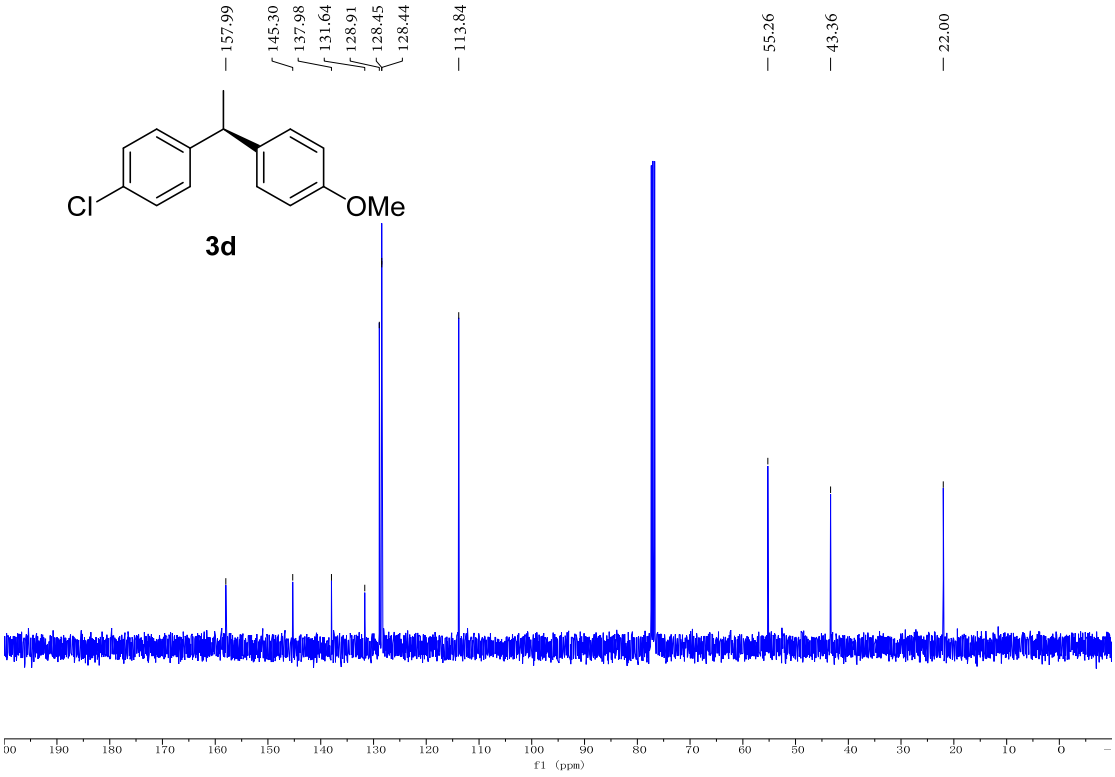


Figure S10 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3e**

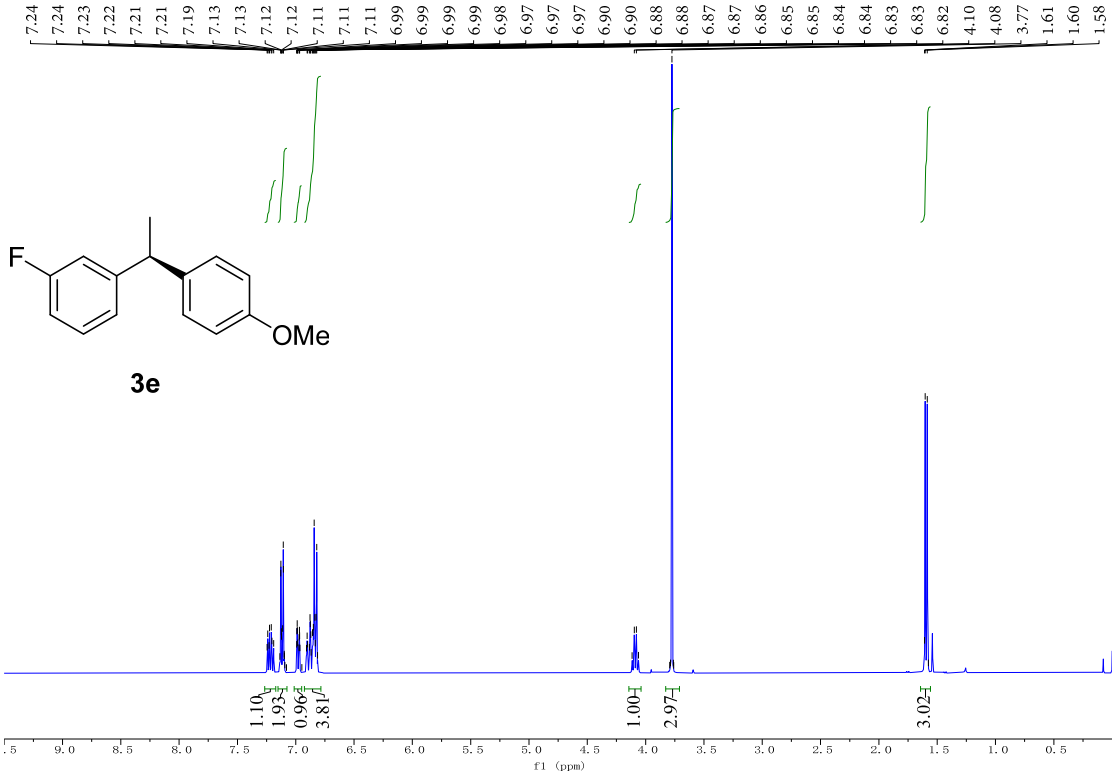


Figure S11 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3e**

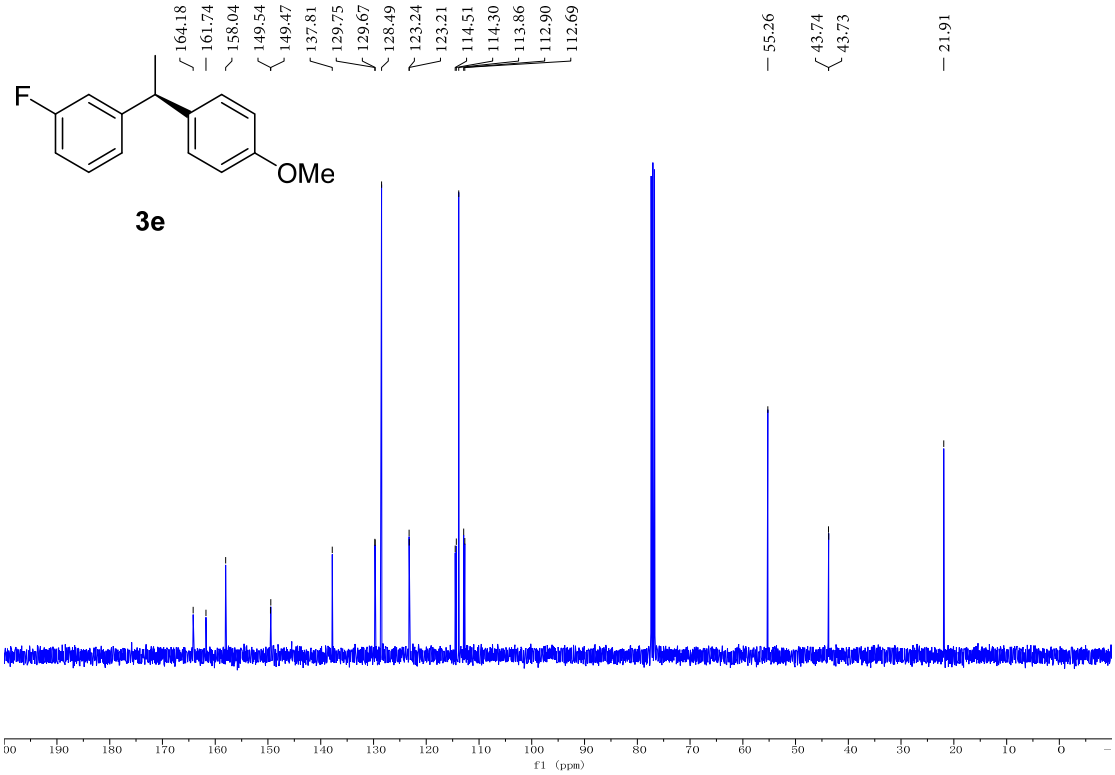


Figure S12 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3e**

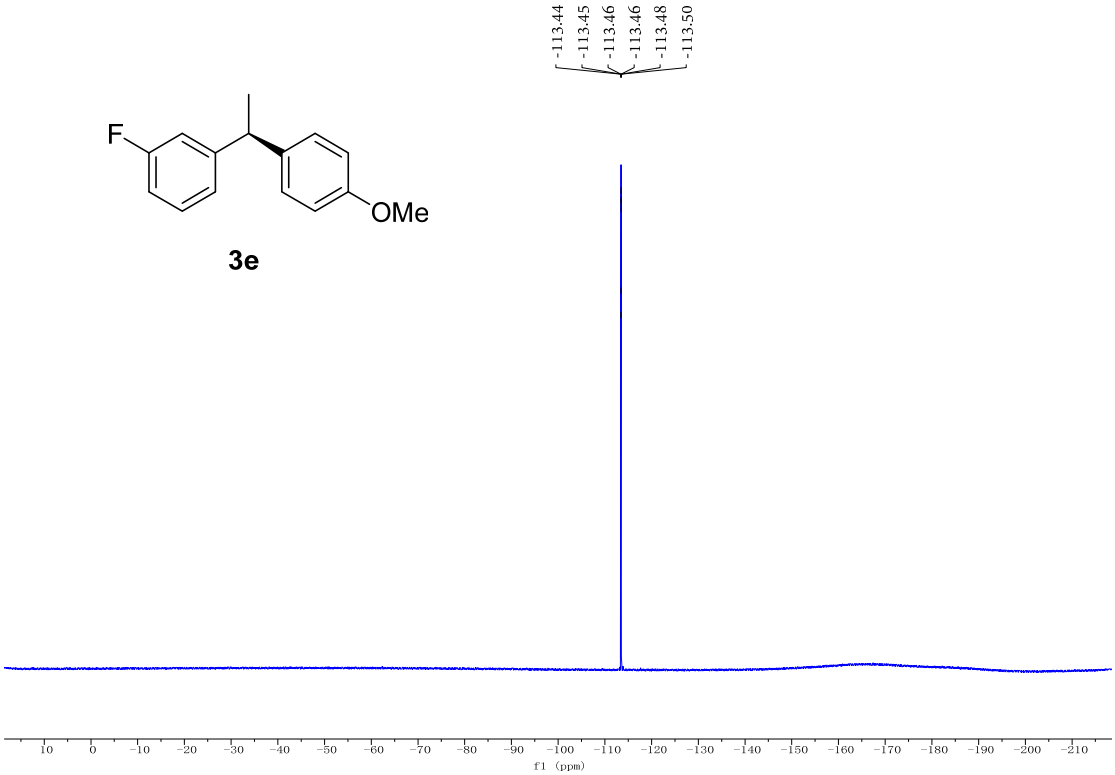


Figure S13 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3f**

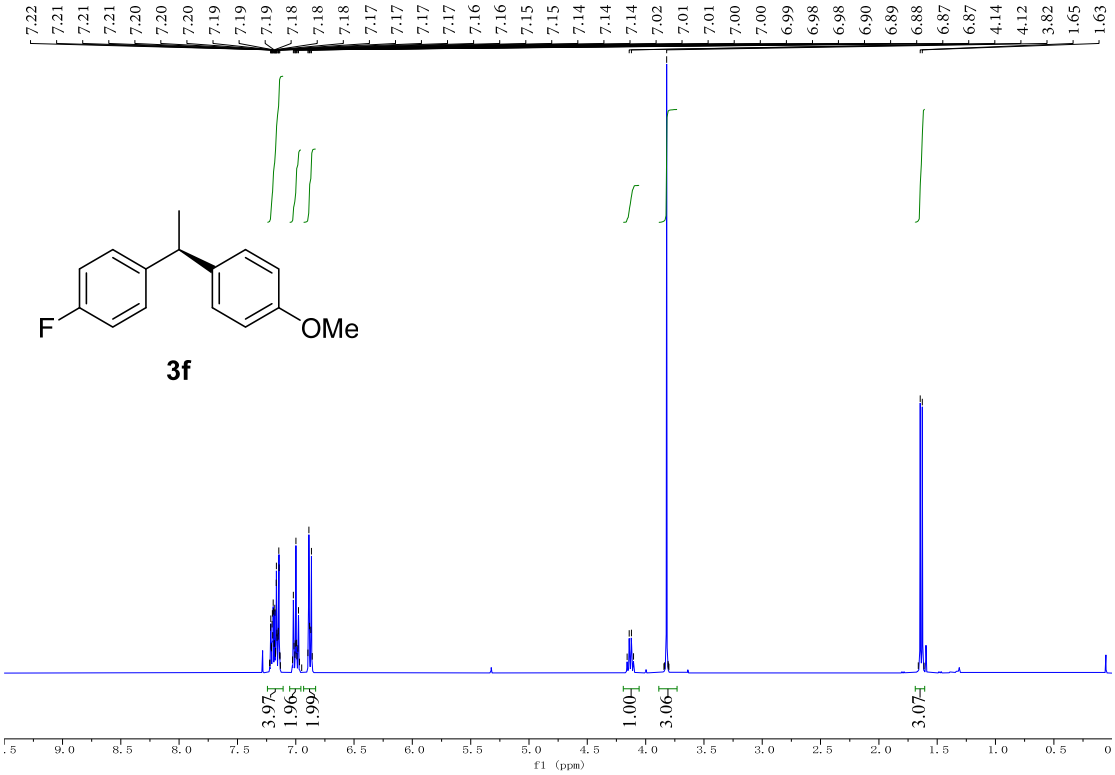


Figure S14 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3f**

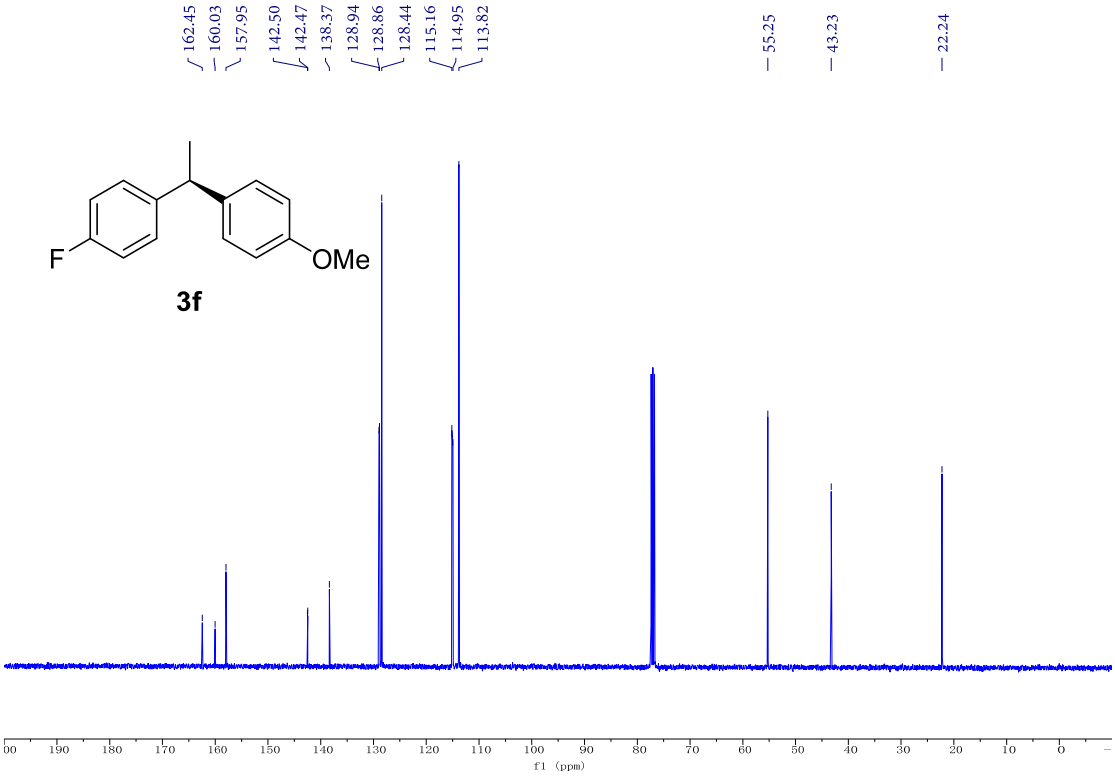


Figure S15 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3f**

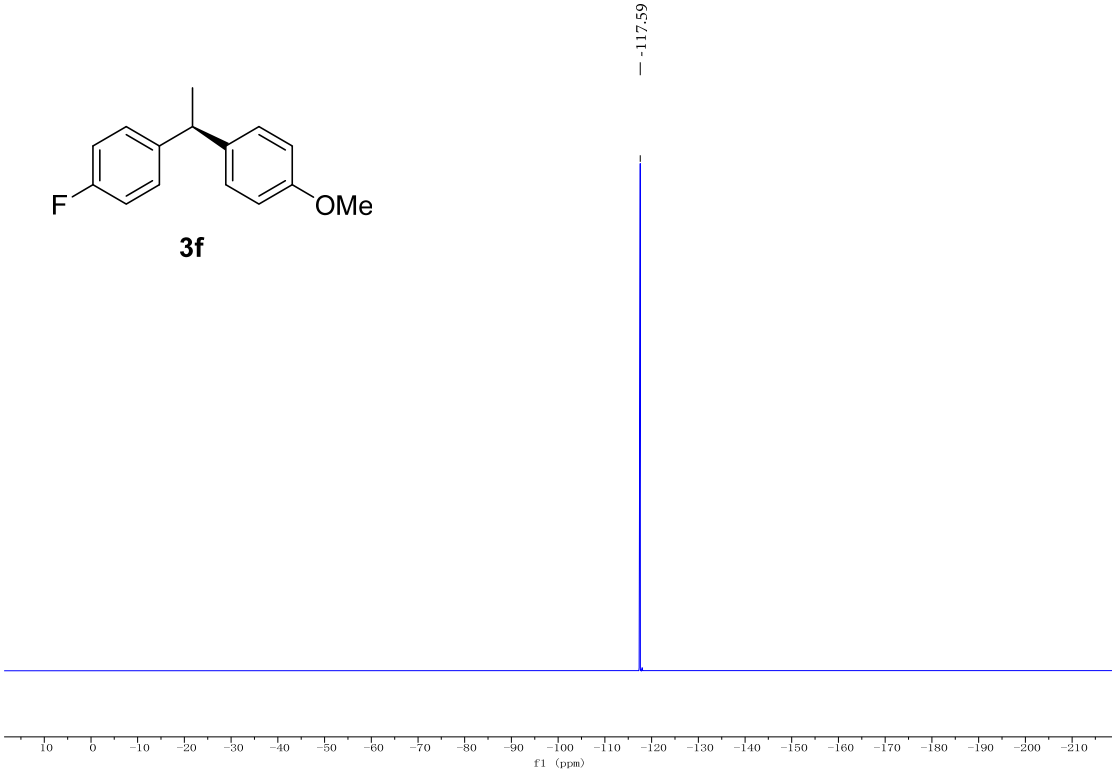


Figure S16 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3g**

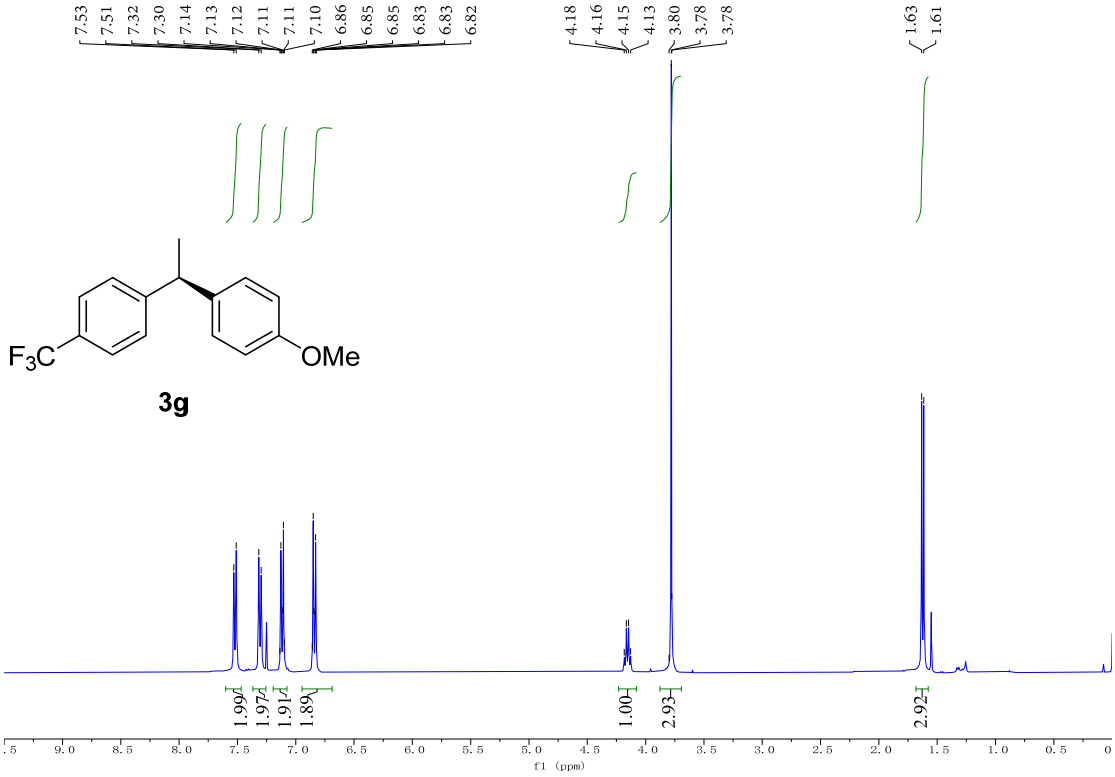


Figure S17 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3g**

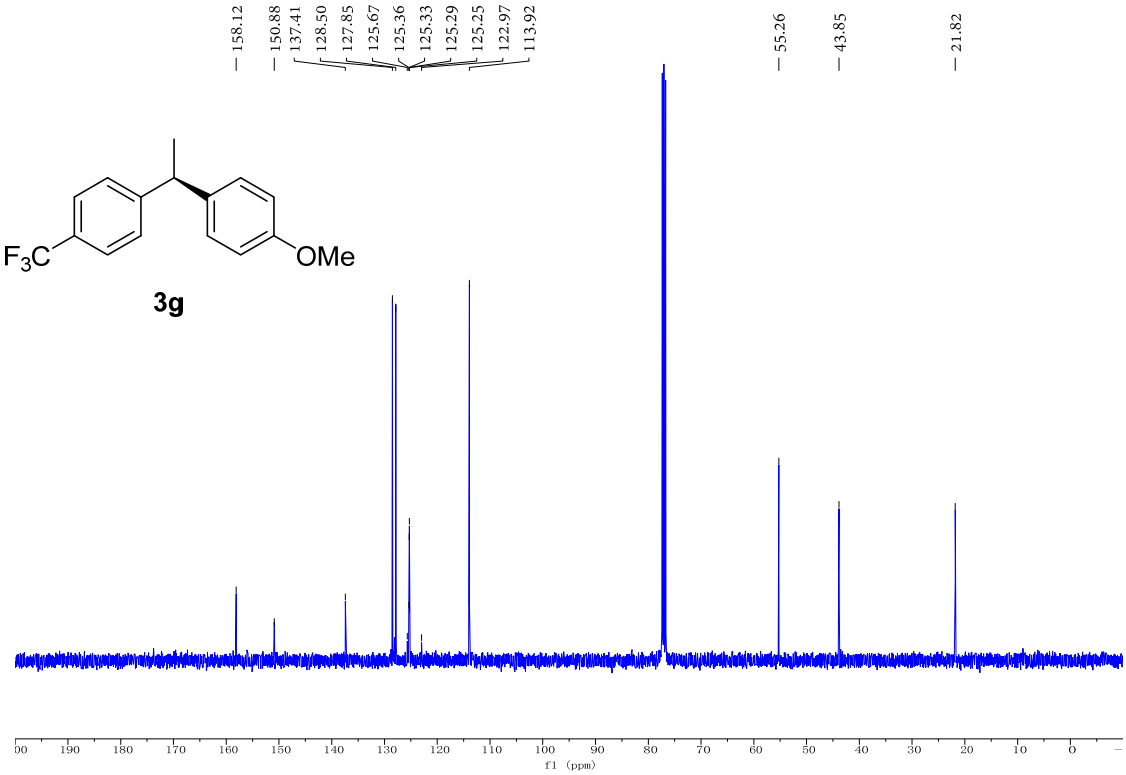


Figure S18 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3g**

Figure S19 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3h**

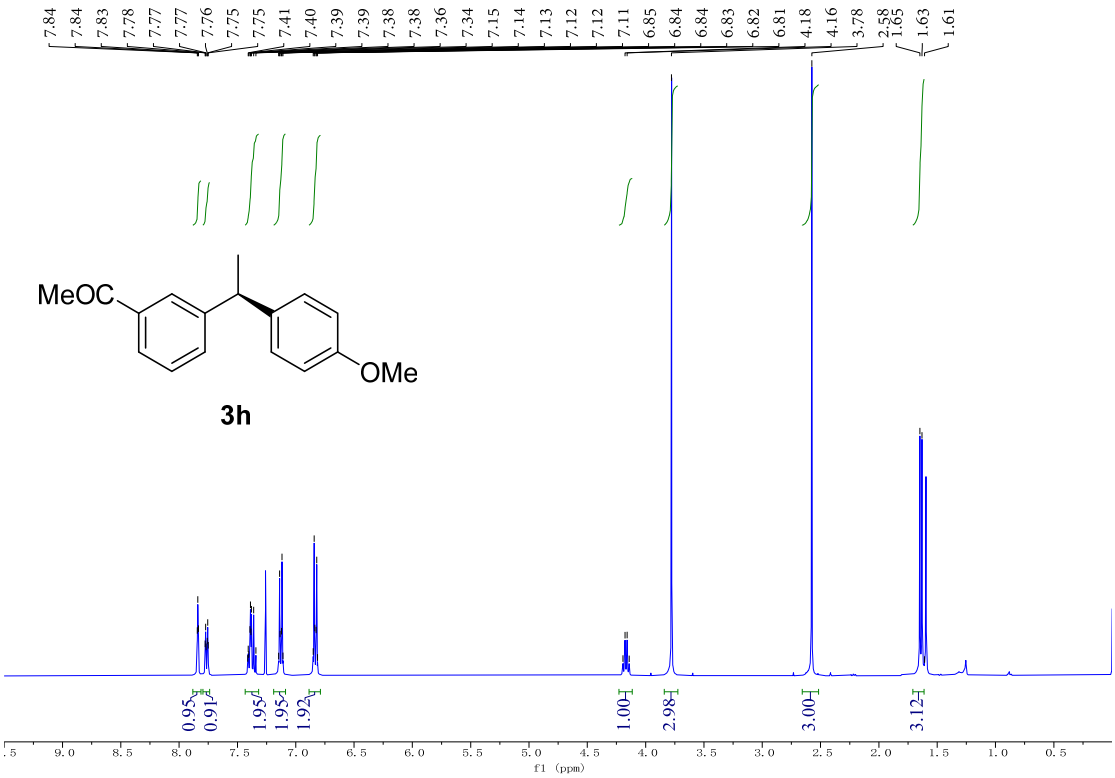


Figure S20 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3h**

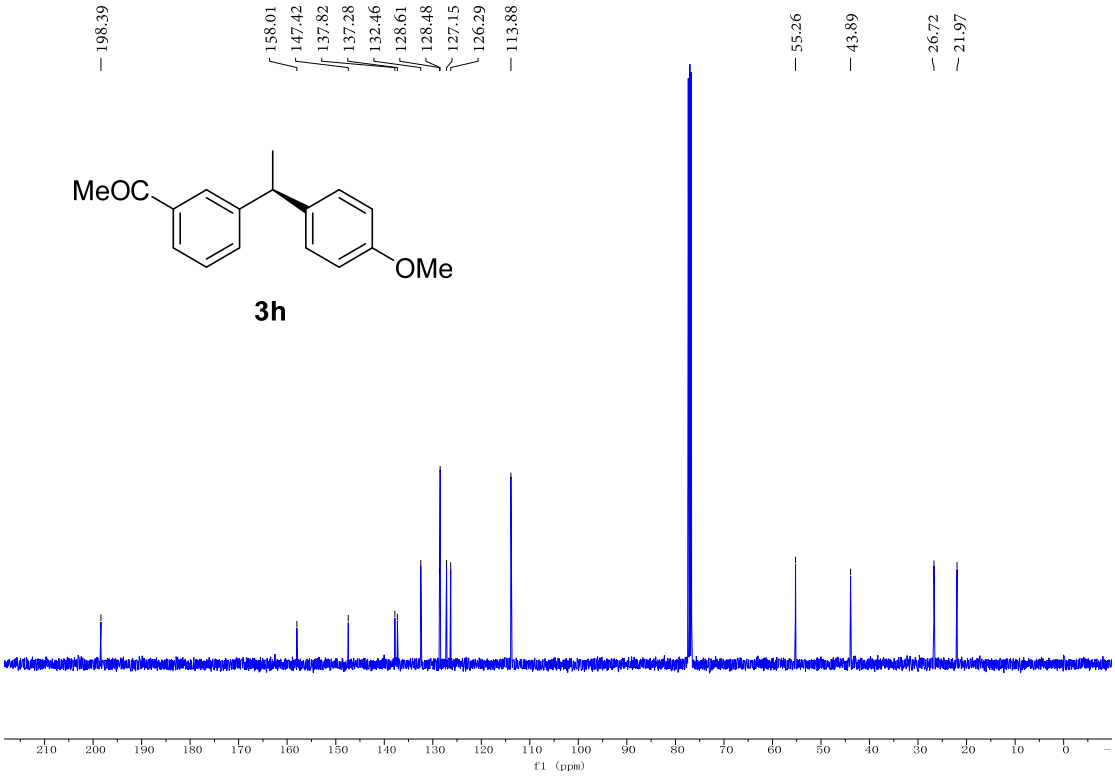


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3i**

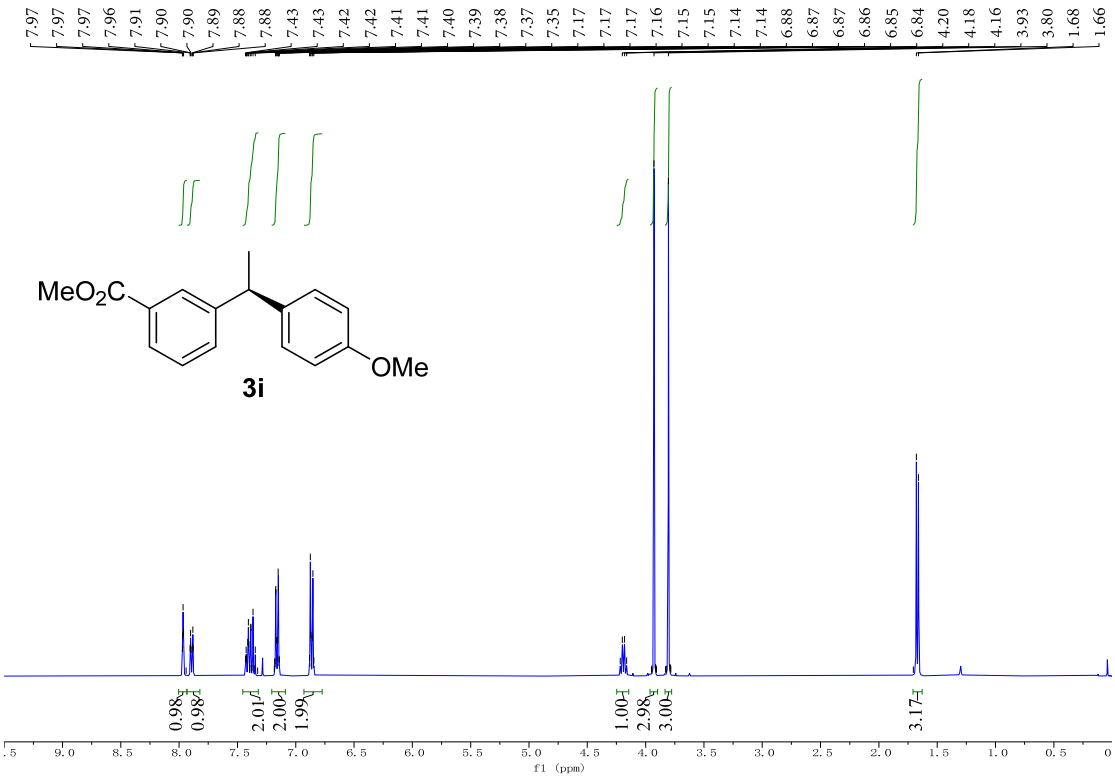


Figure S22 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3i**

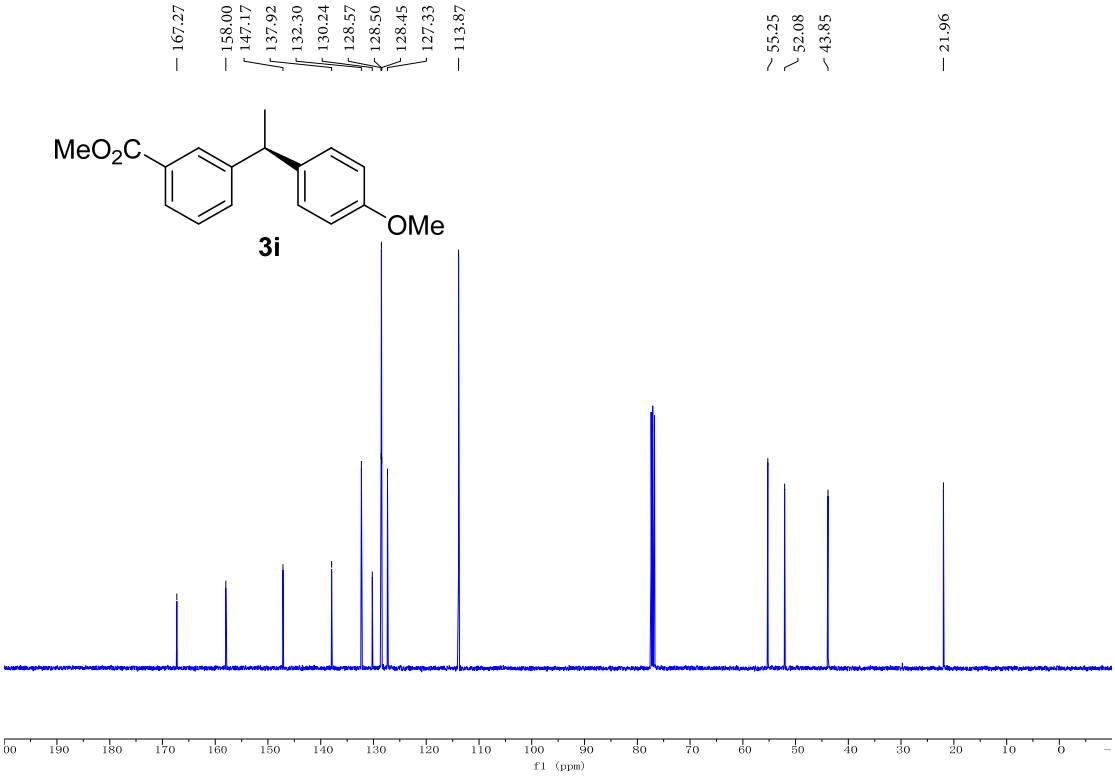


Figure S23 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3j**

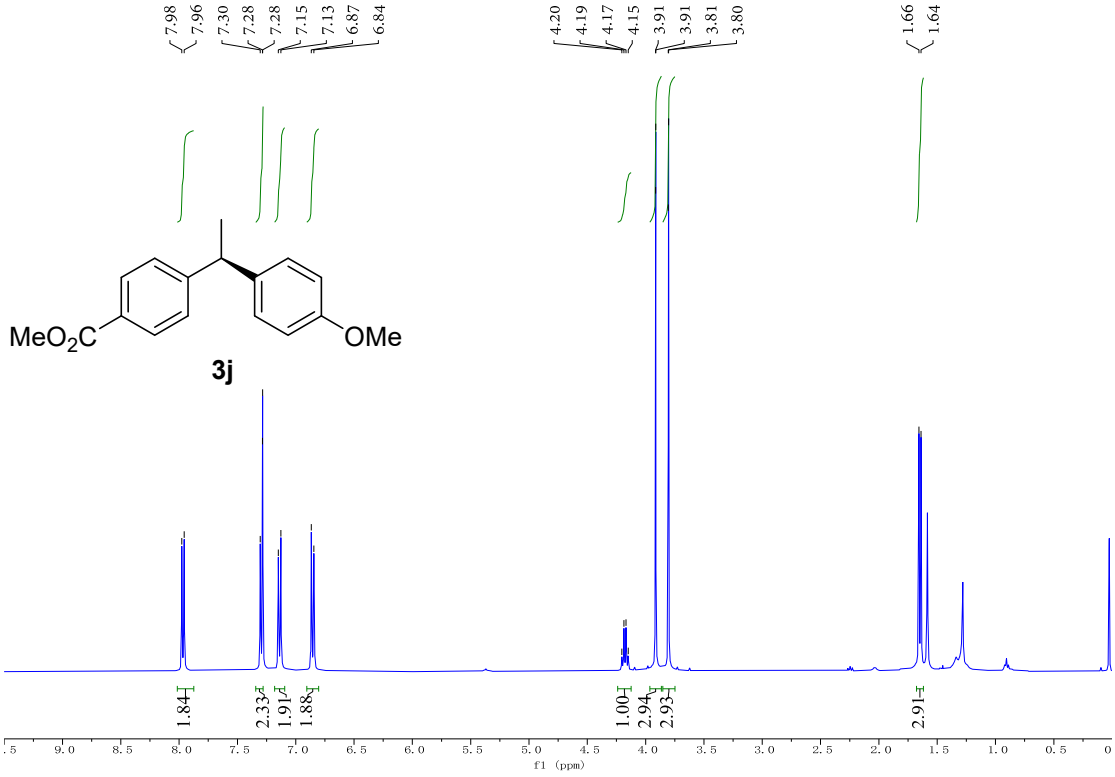


Figure S24 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3j**

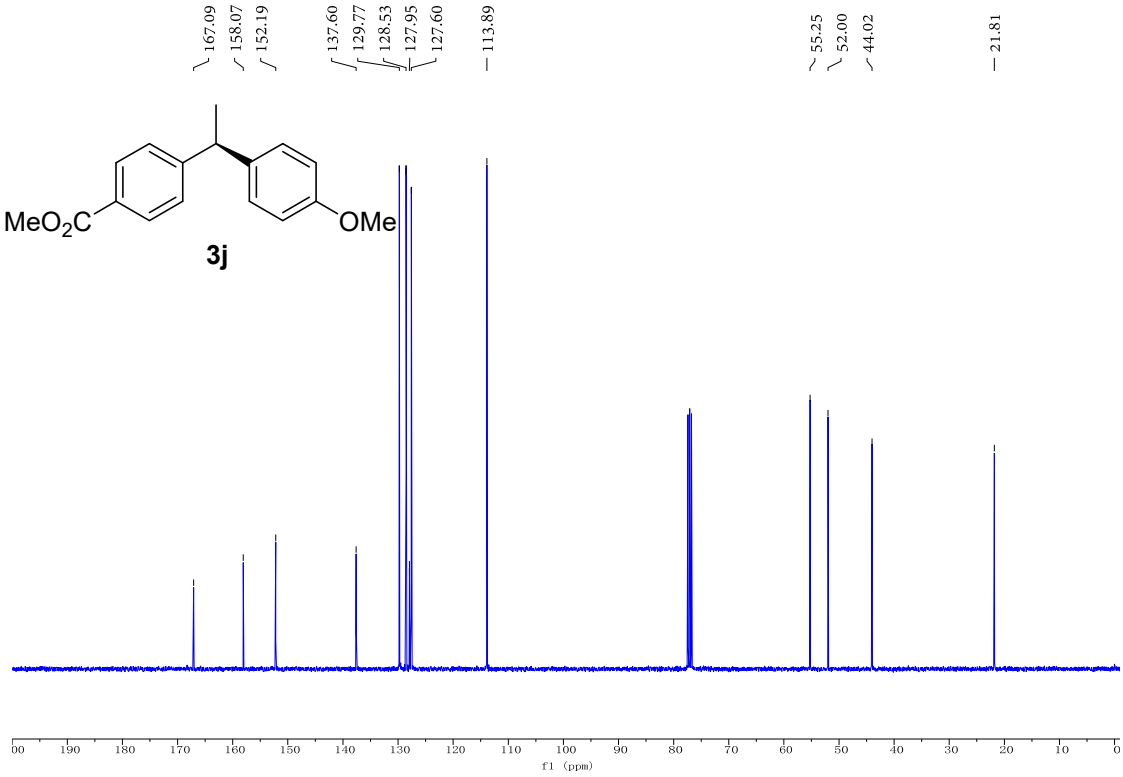


Figure S25 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3k**

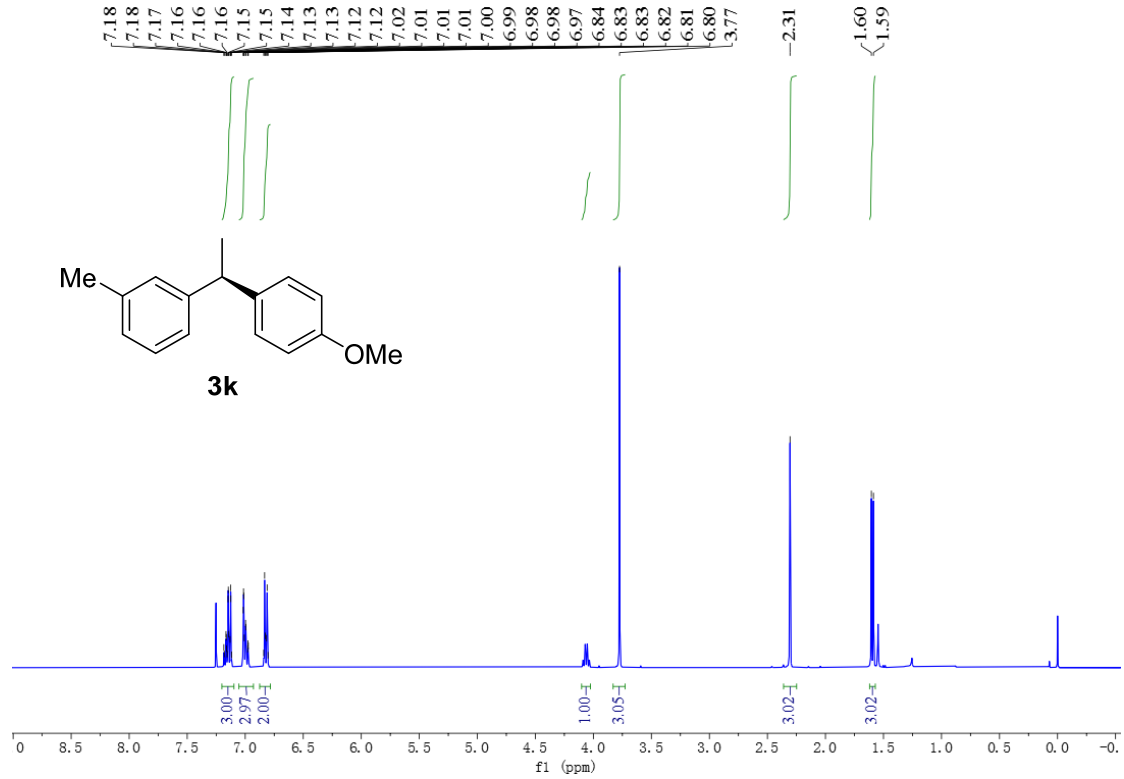


Figure S26 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3k**

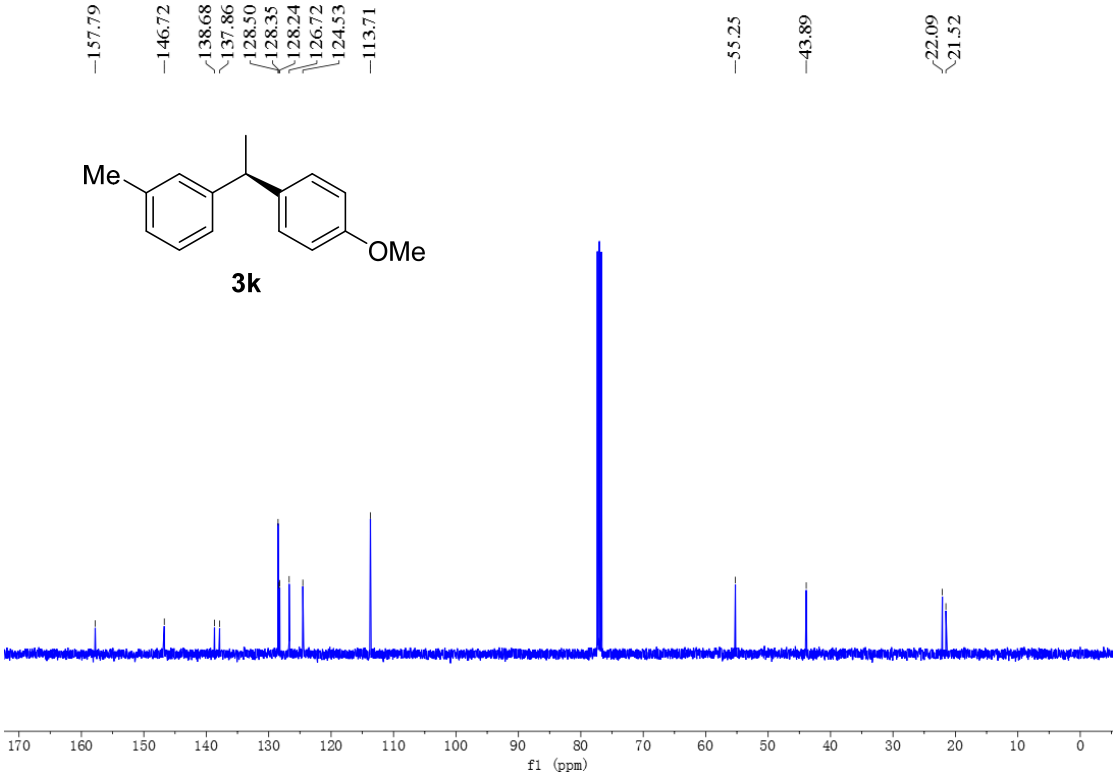


Figure S27 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3l**

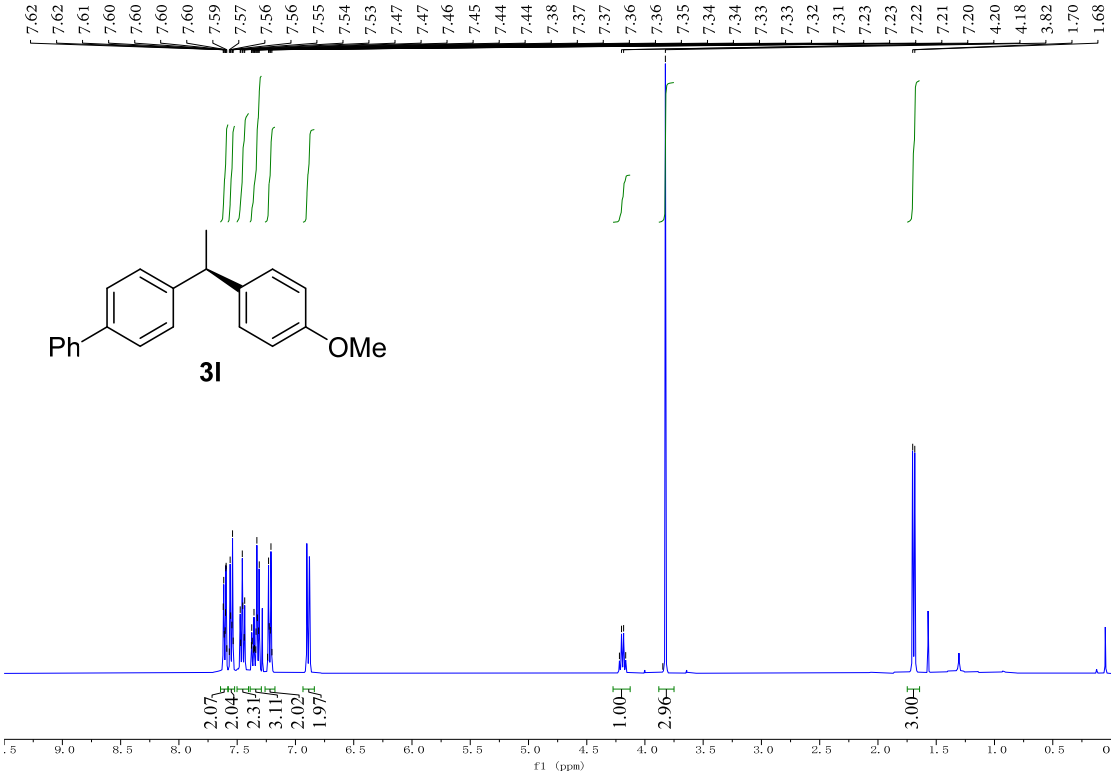


Figure S28 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3l**

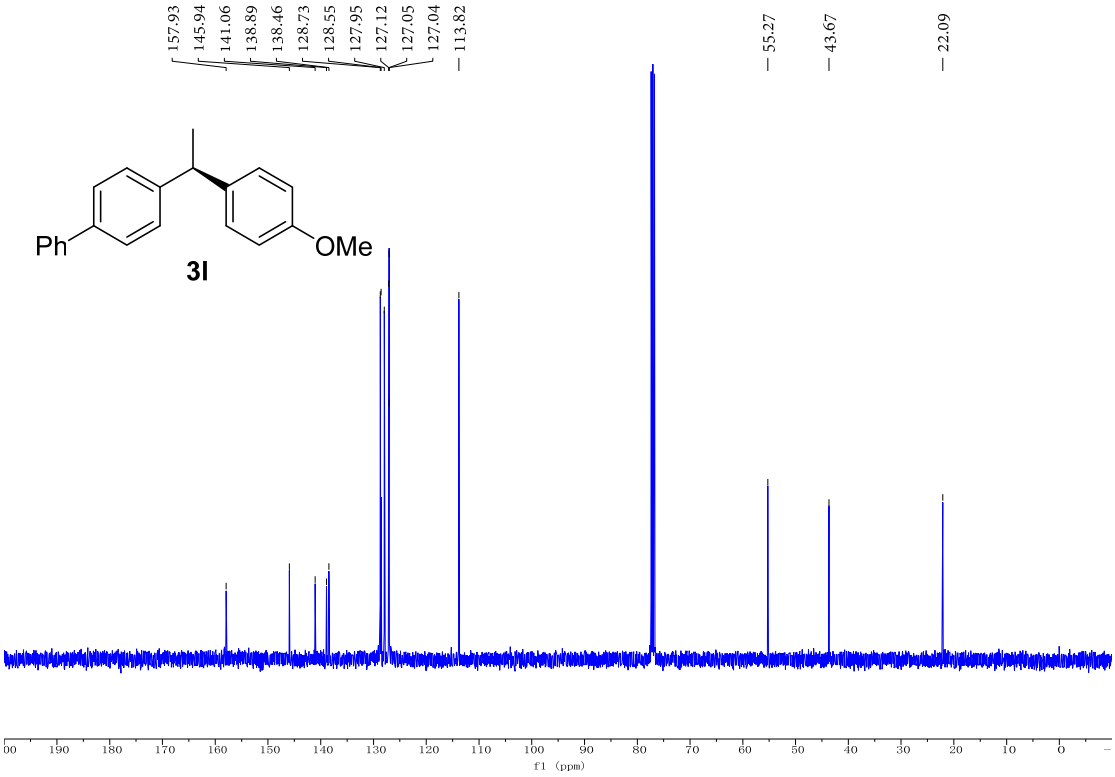


Figure S29 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3m**

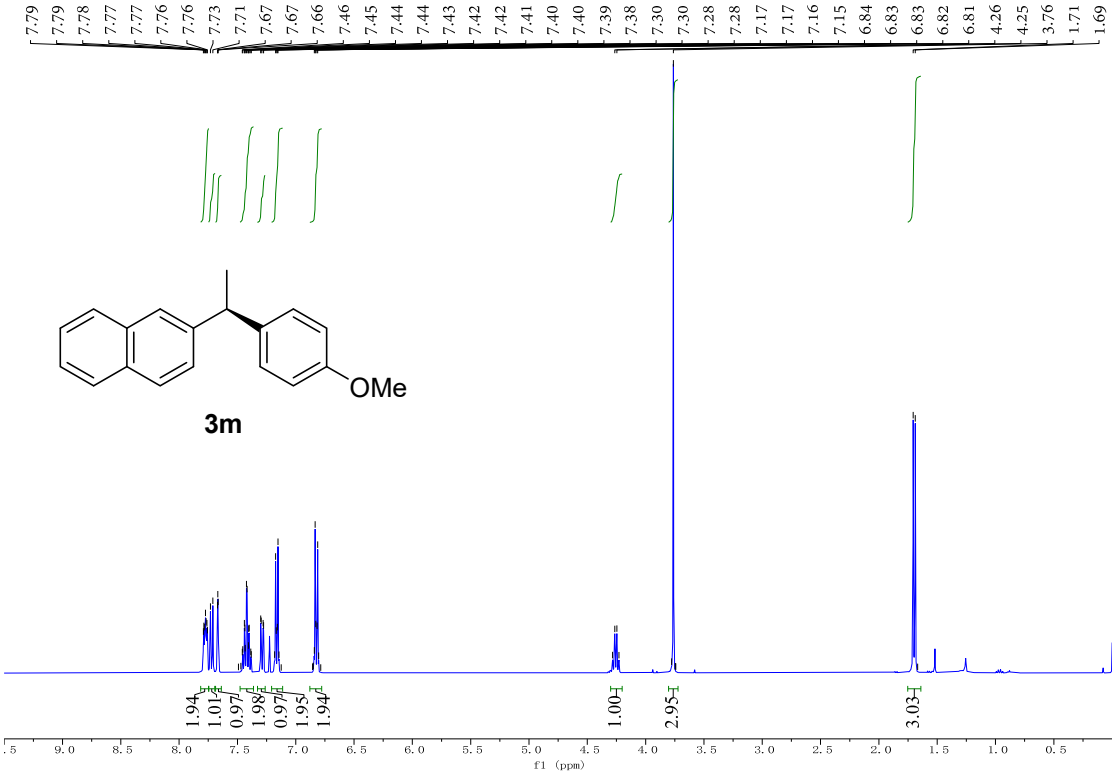


Figure S30 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3m**

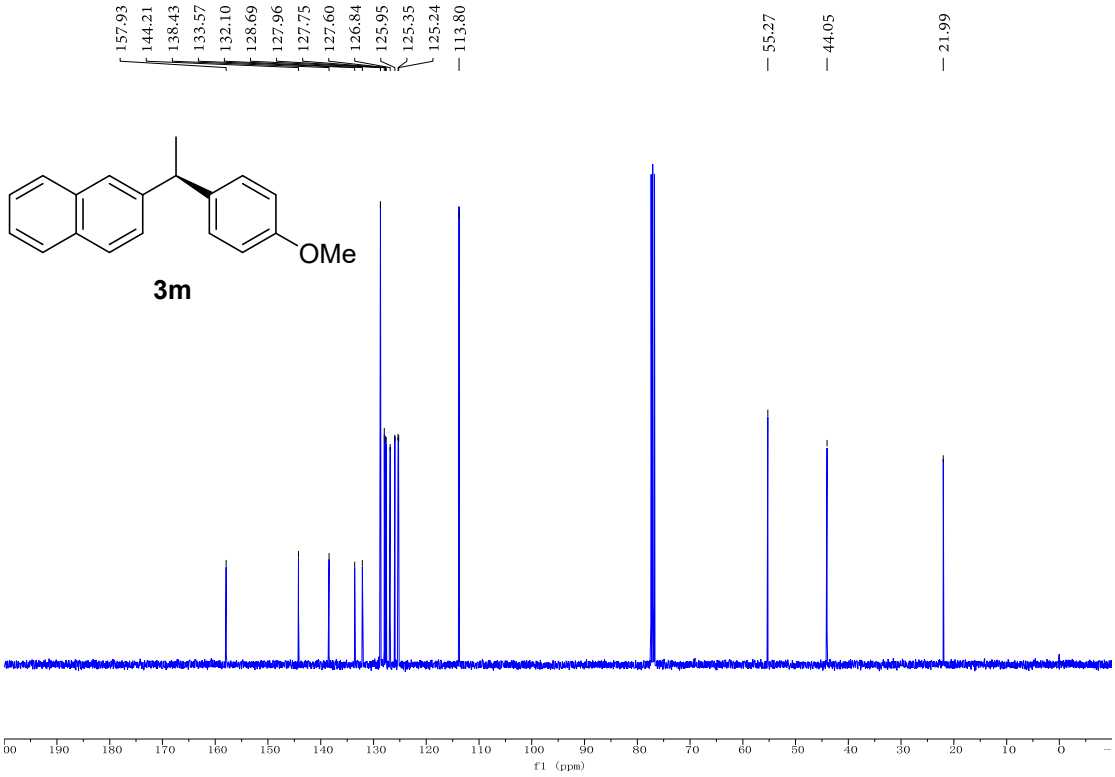


Figure S31 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3n**

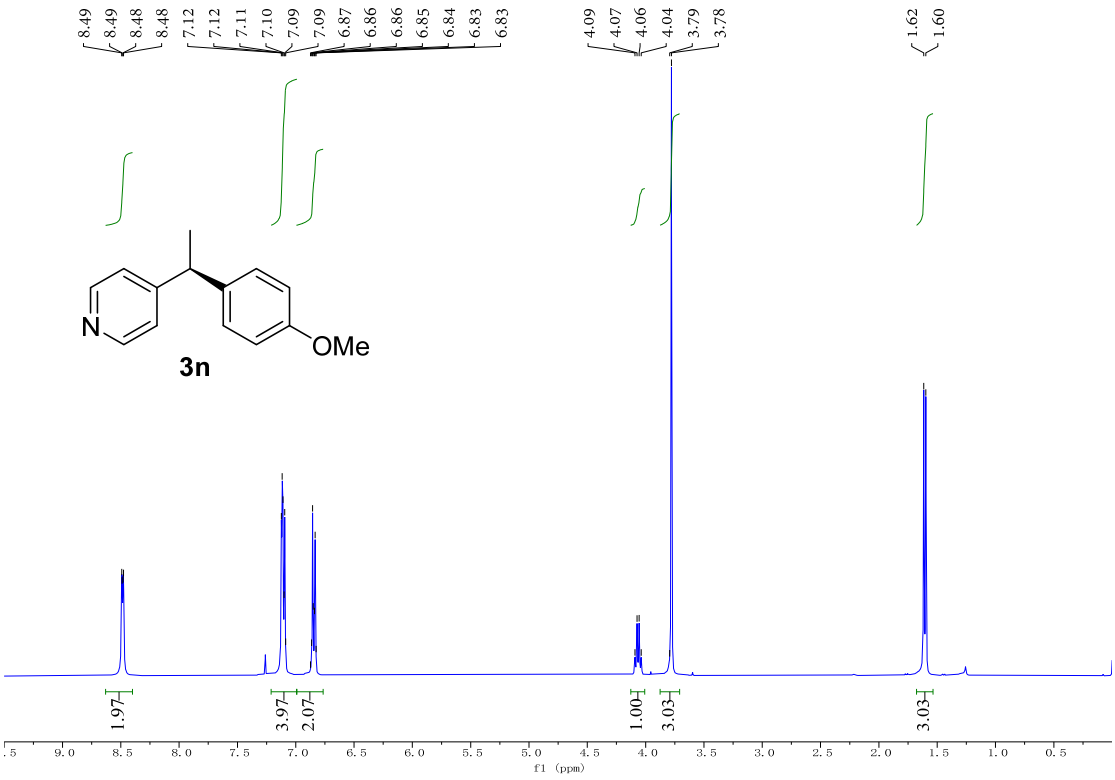


Figure S32 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3n**

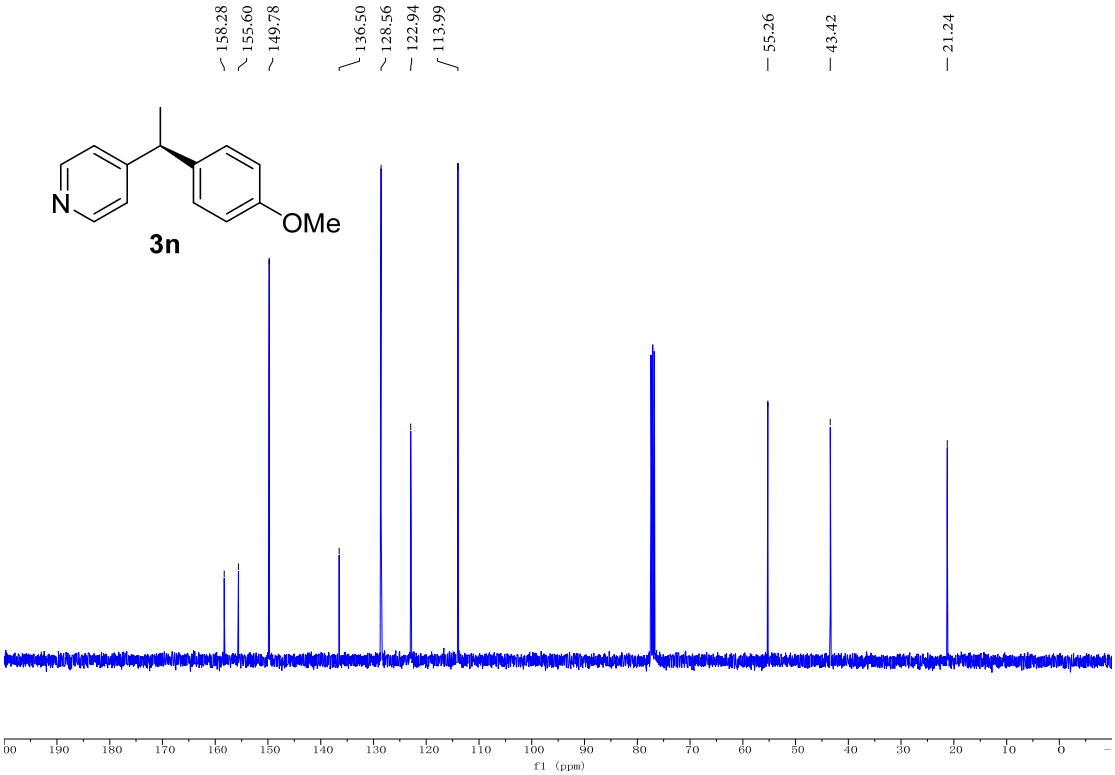


Figure S33 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3o**

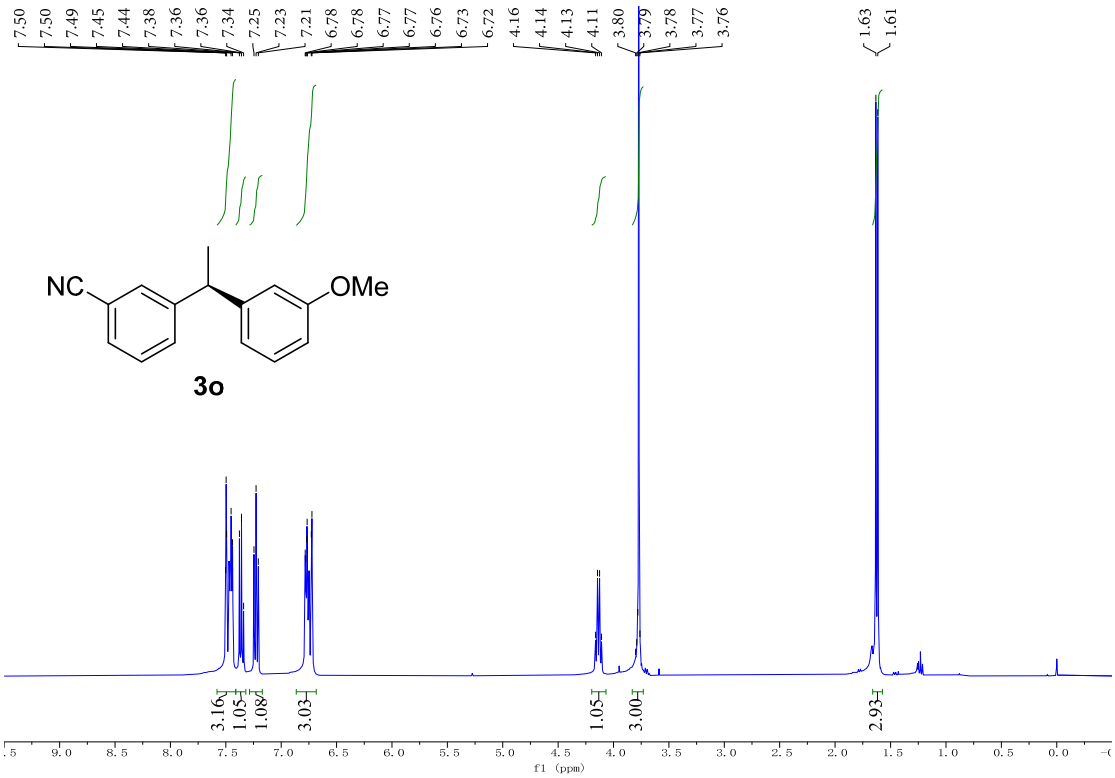


Figure S34 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3o**

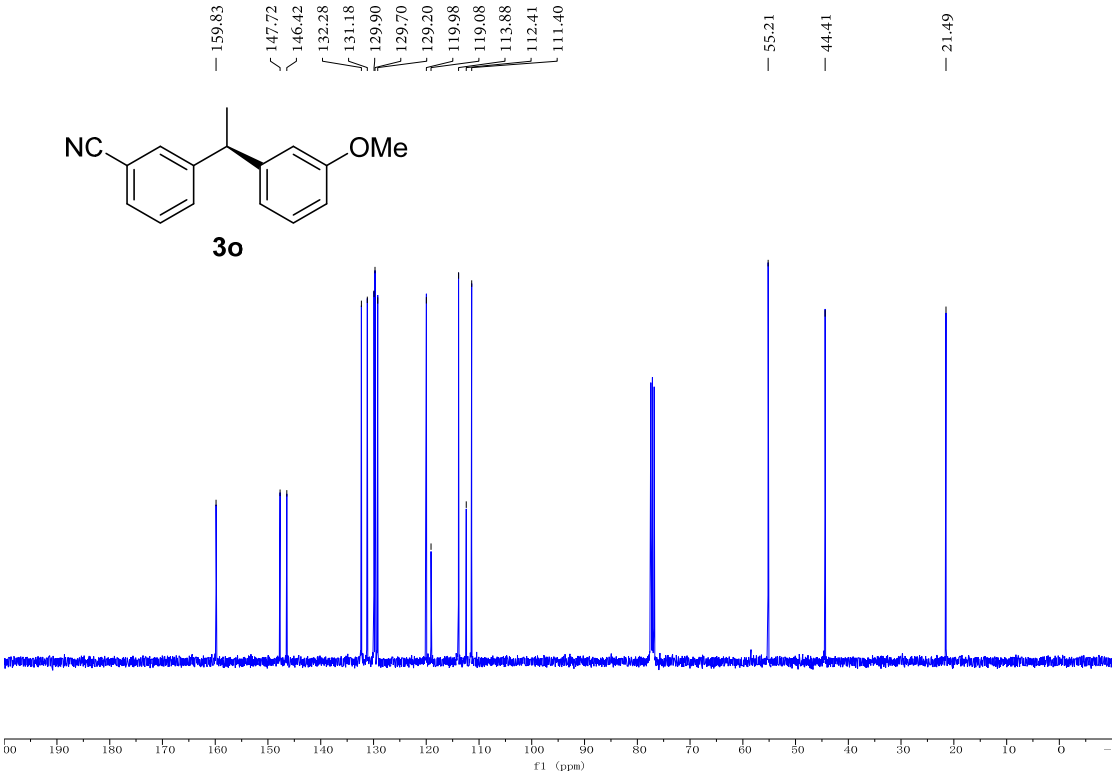


Figure S35 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3p**

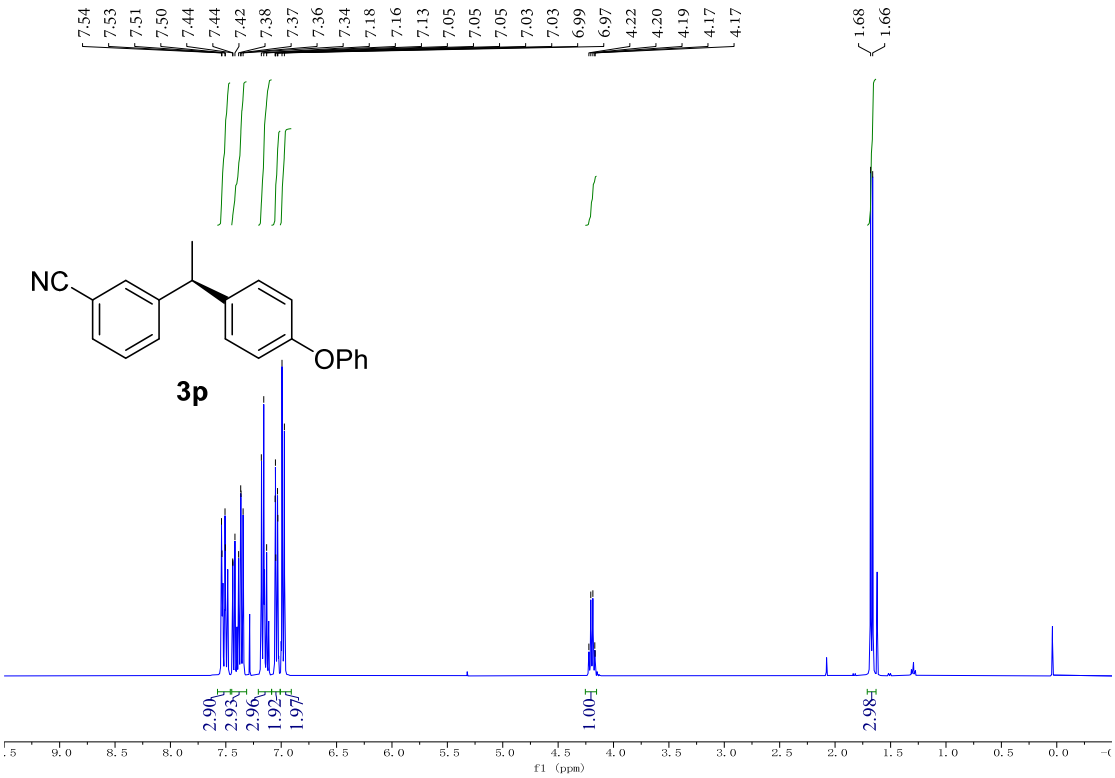


Figure S36 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3p**

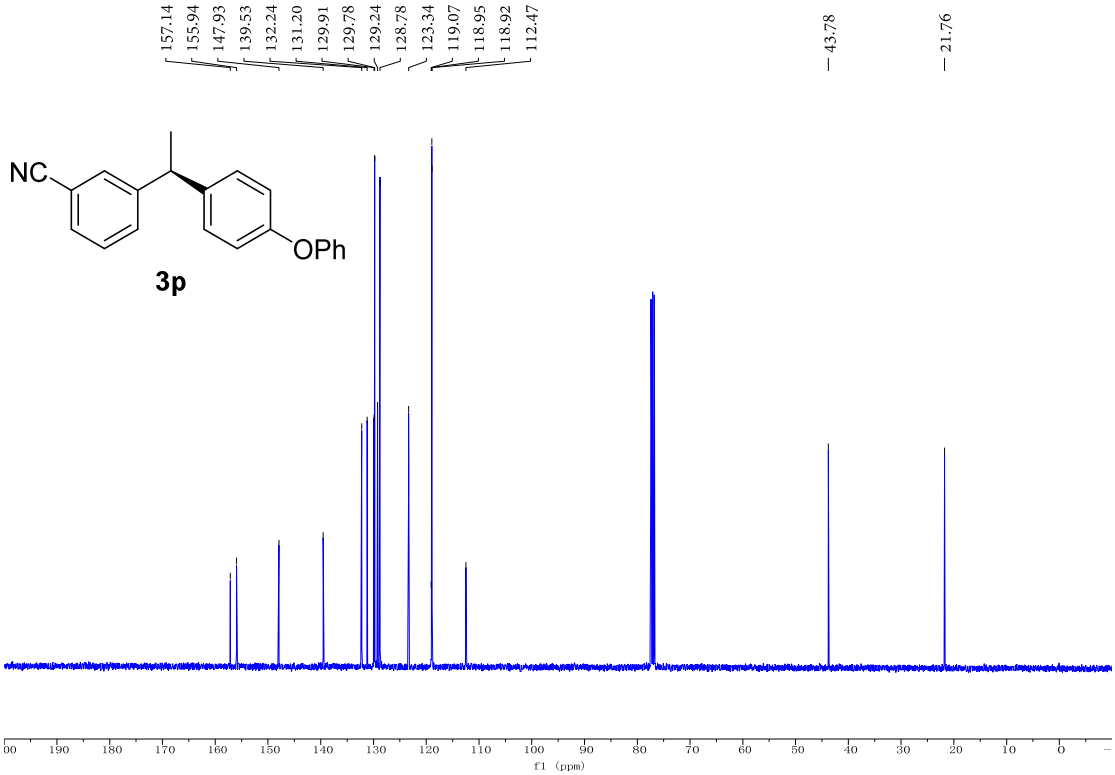


Figure S37 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3q**

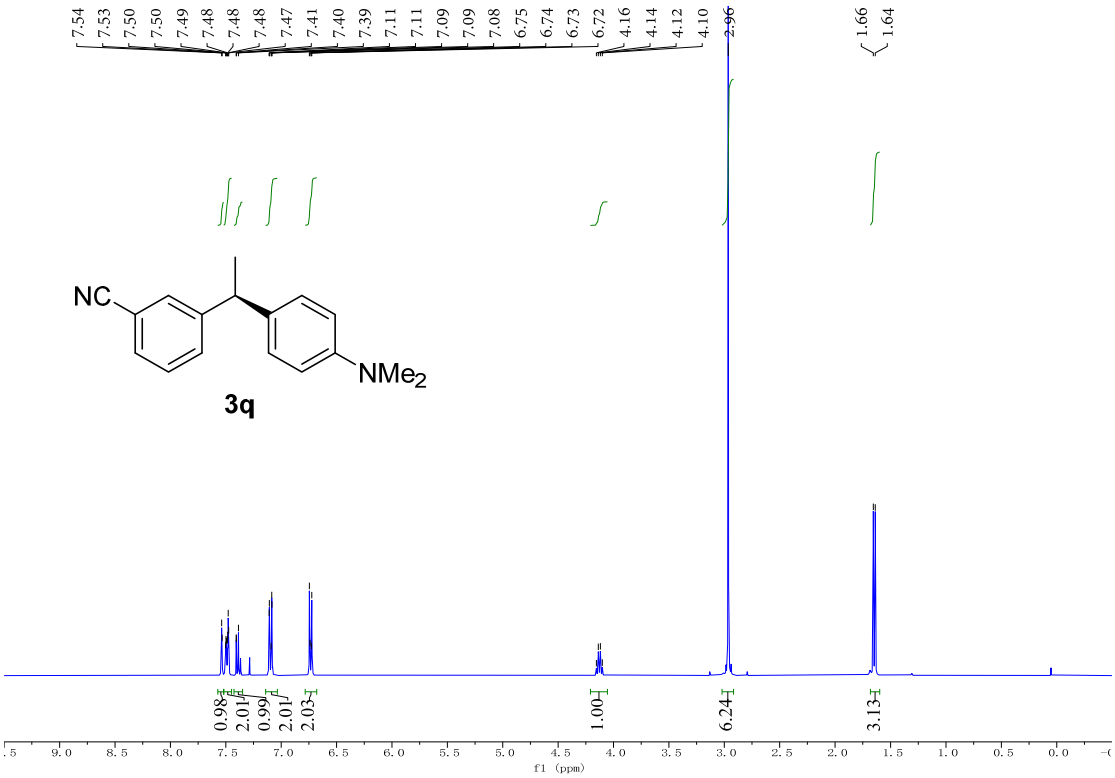


Figure S38 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3q**

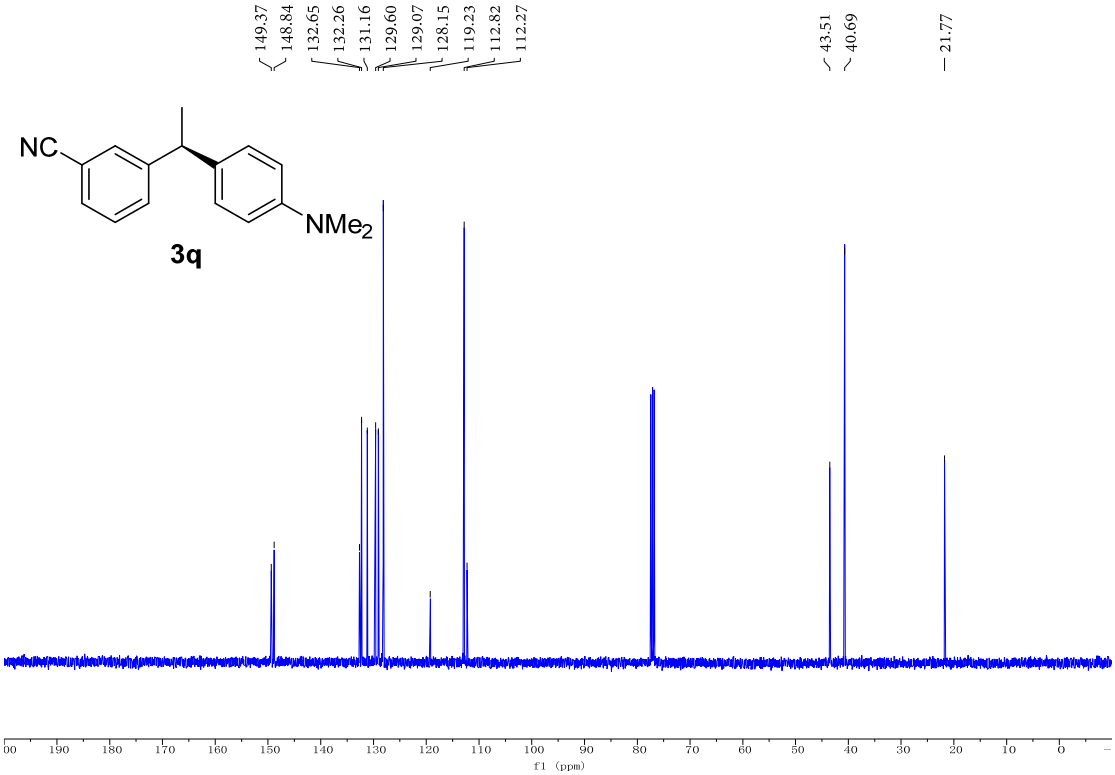


Figure S39 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3r**

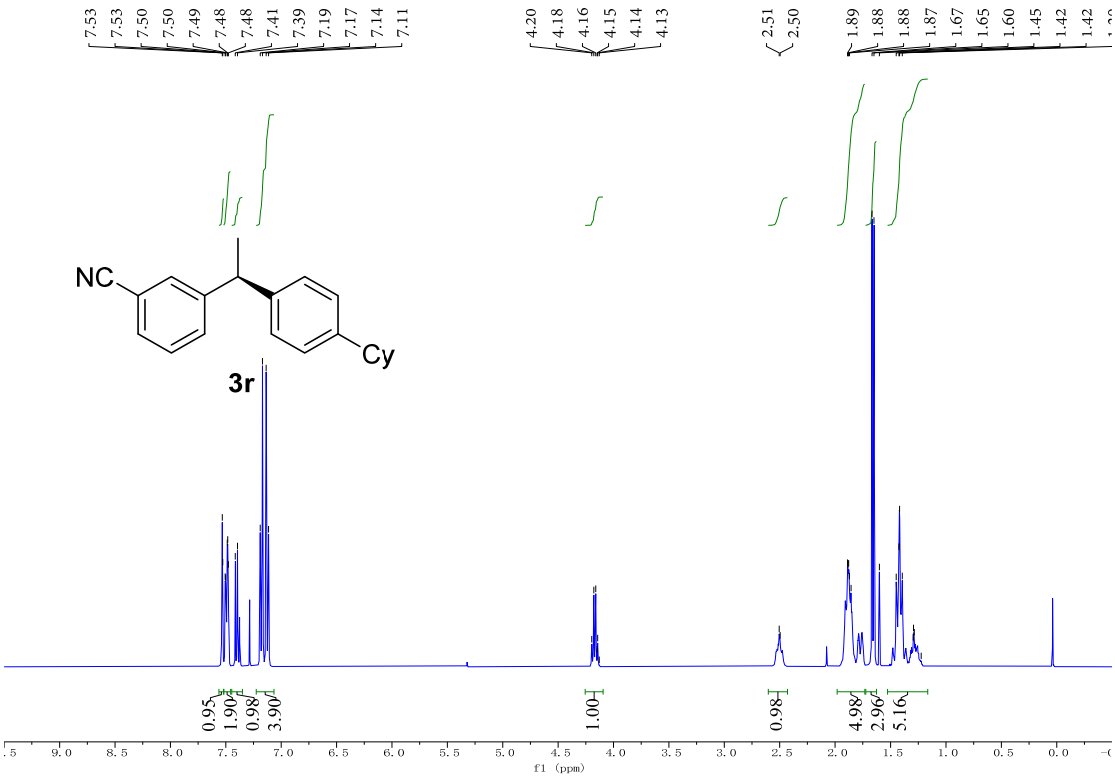


Figure S40 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3r**

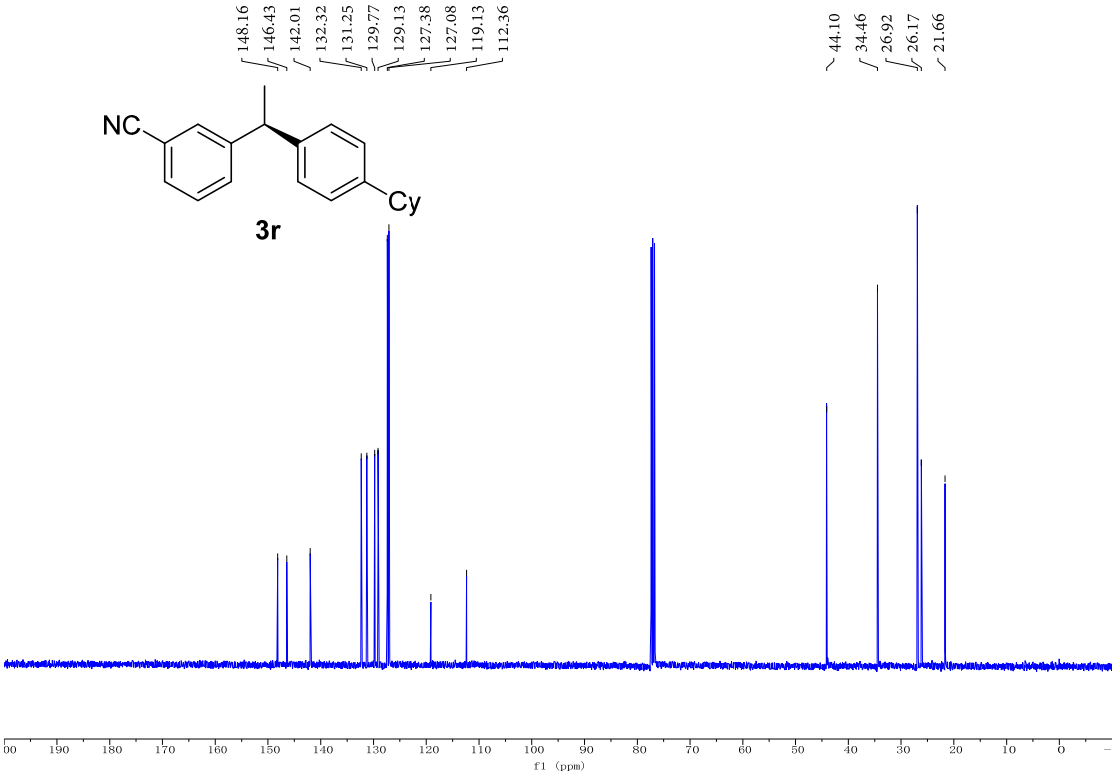


Figure S41 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3s**

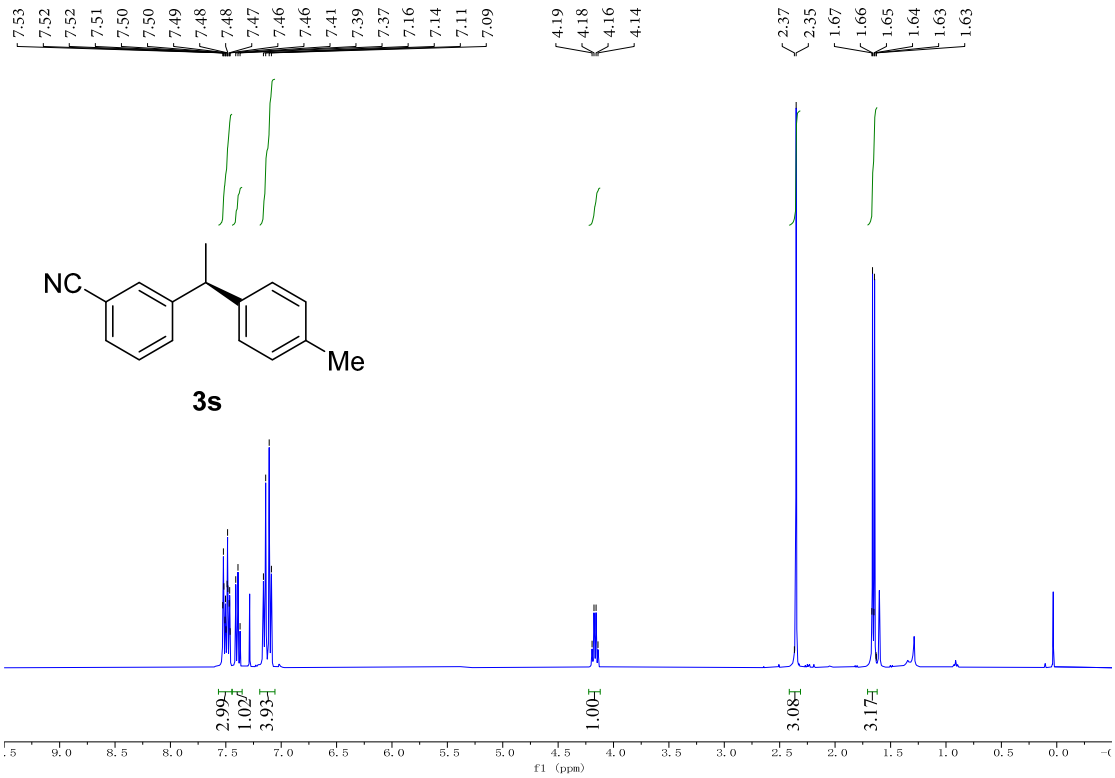


Figure S42 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3s**

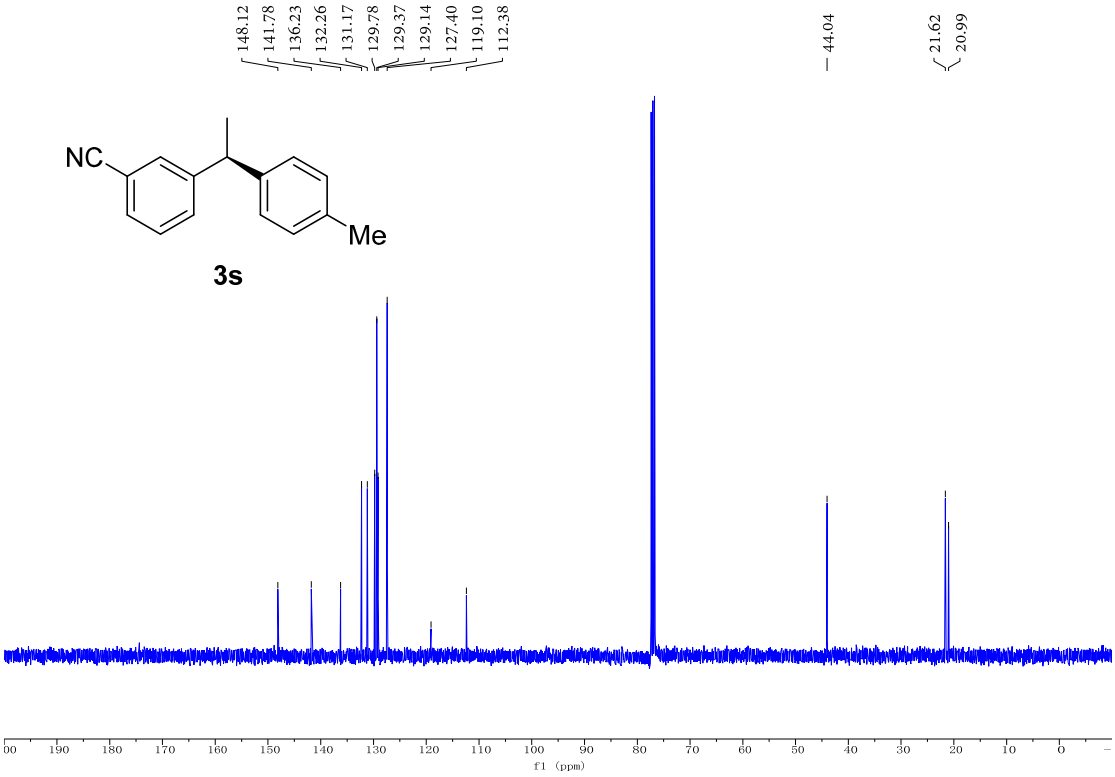


Figure S43 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3t**

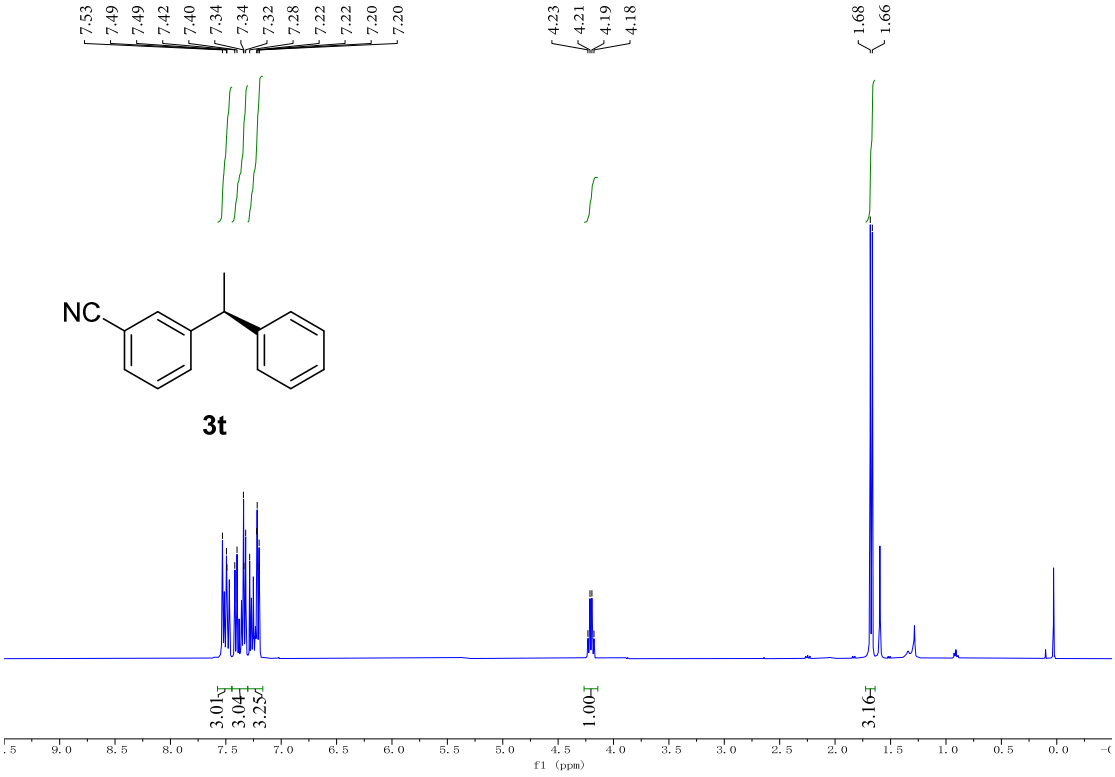


Figure S44 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3t**

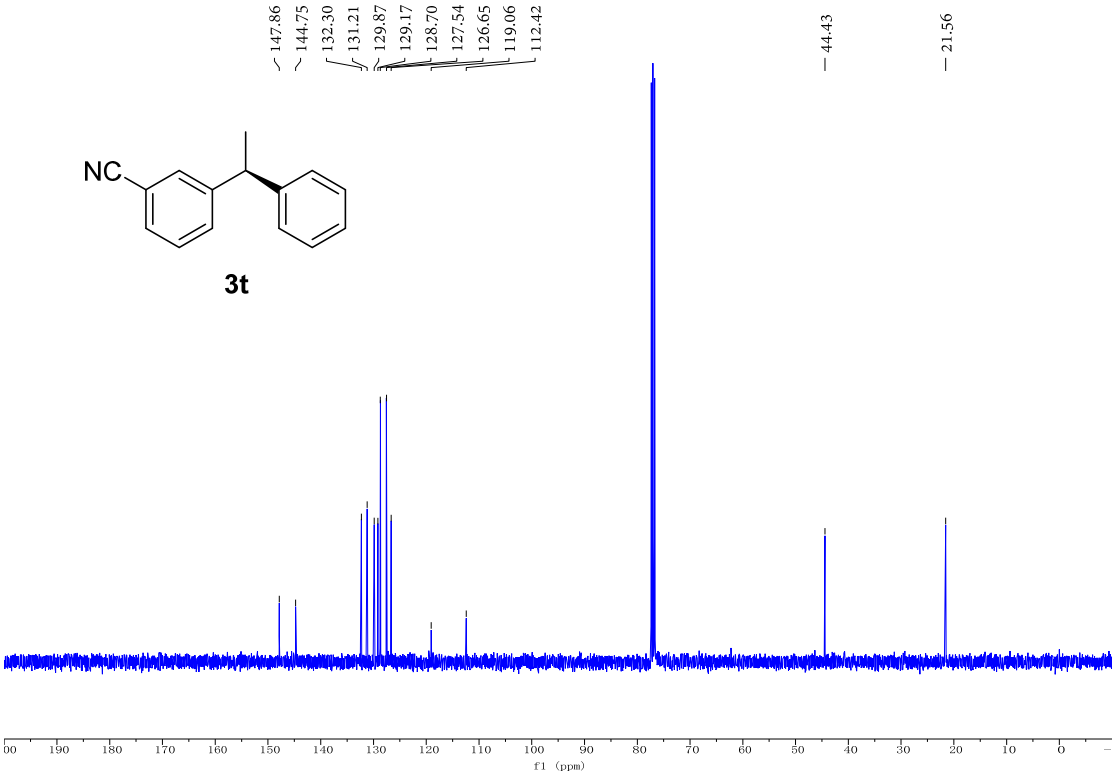


Figure S45 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3u**

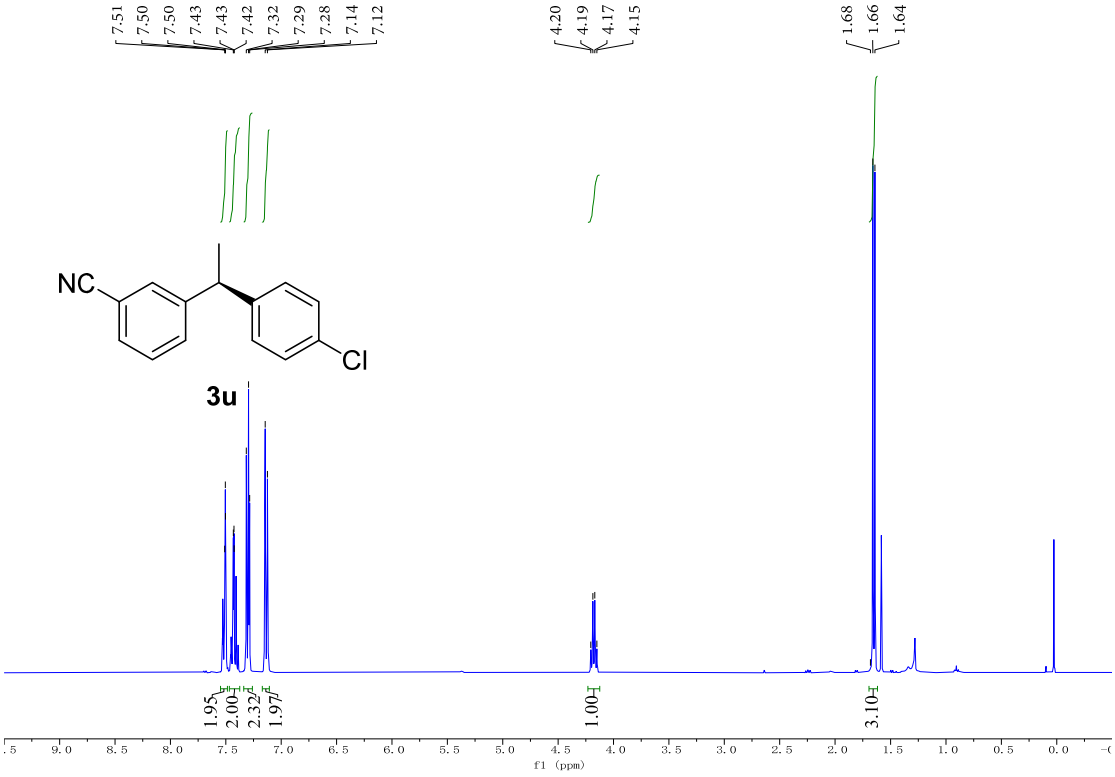


Figure S46 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3u**

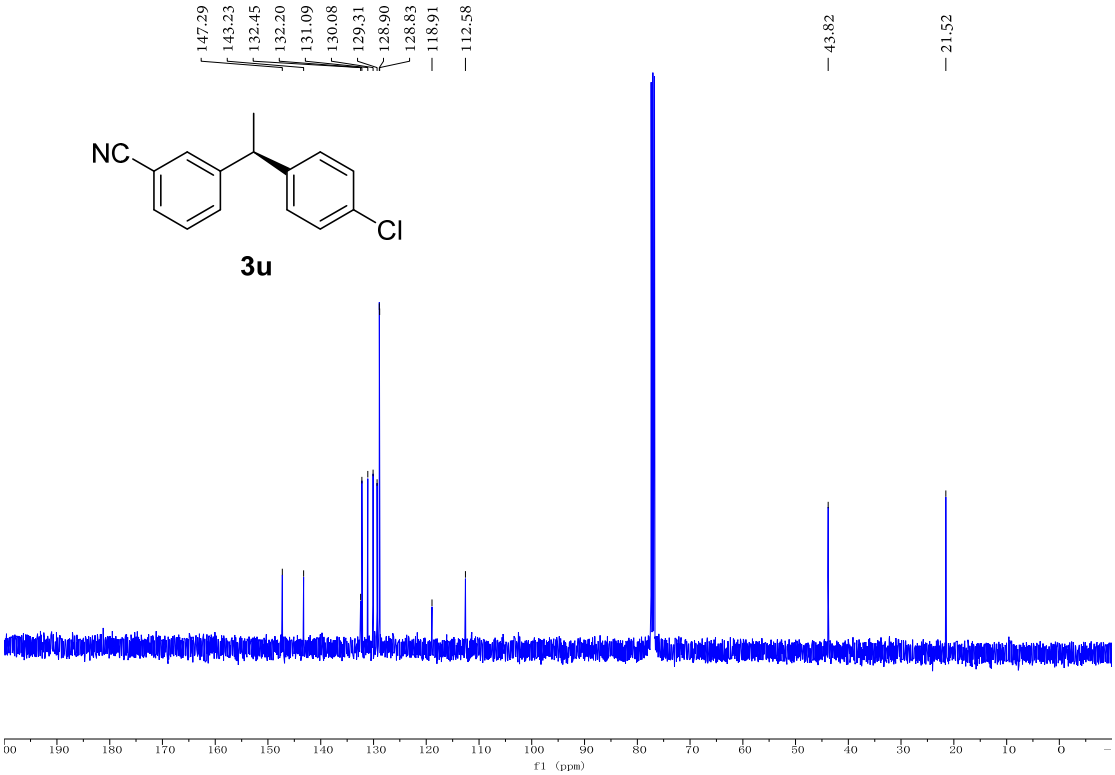


Figure S47 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3v**

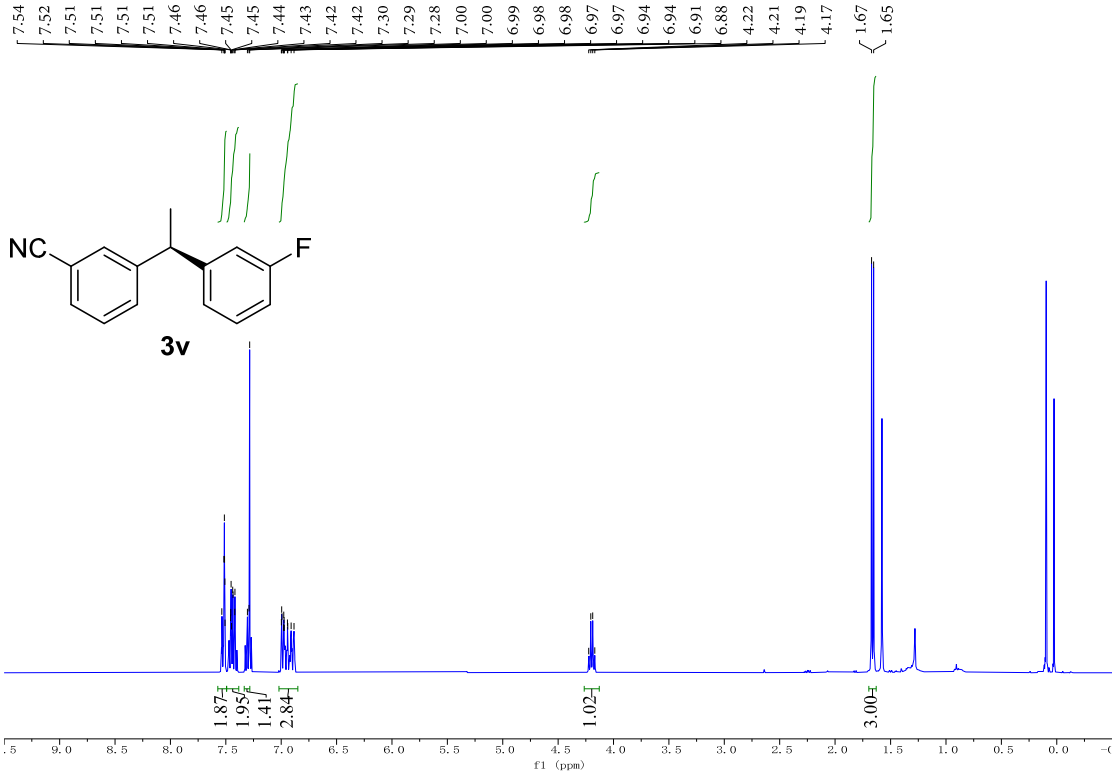


Figure S48 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3v**

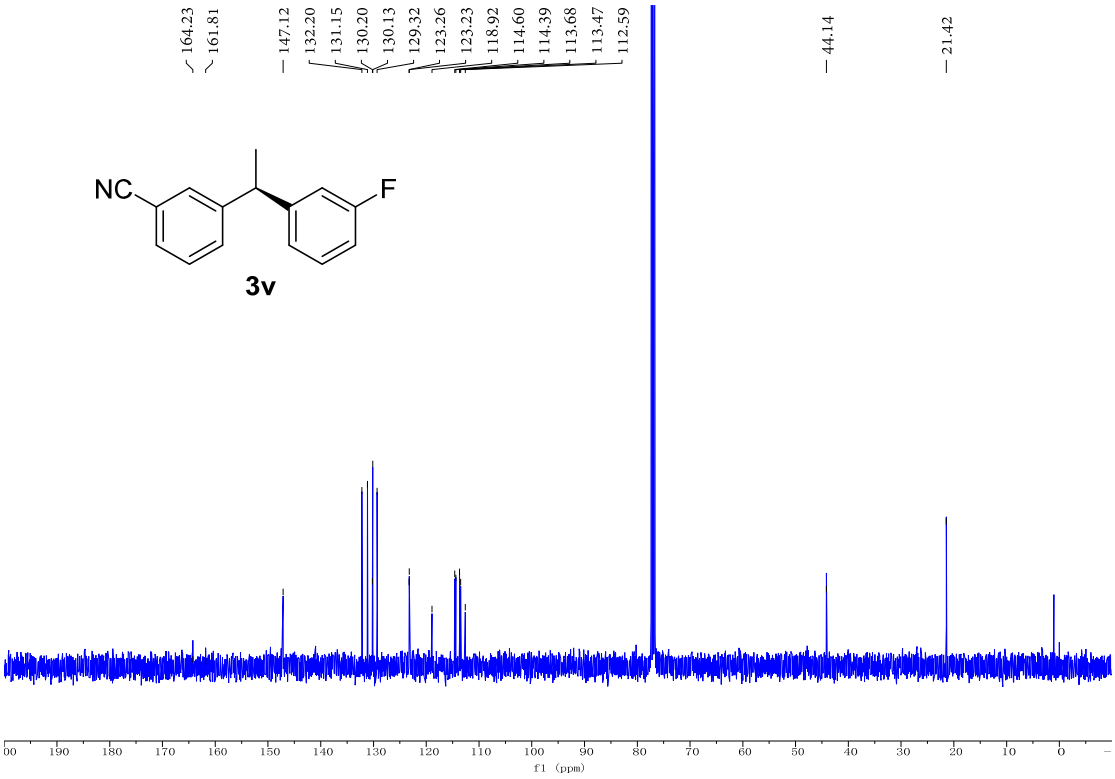


Figure S49 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3v**

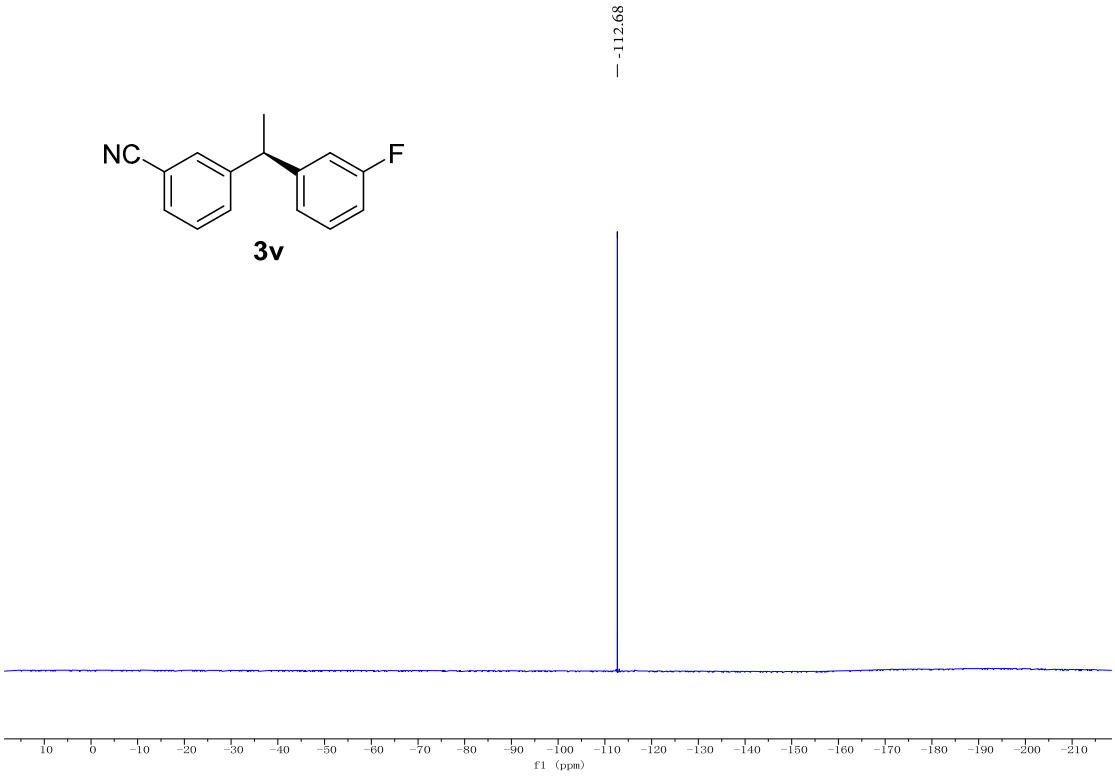


Figure S50 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3w**

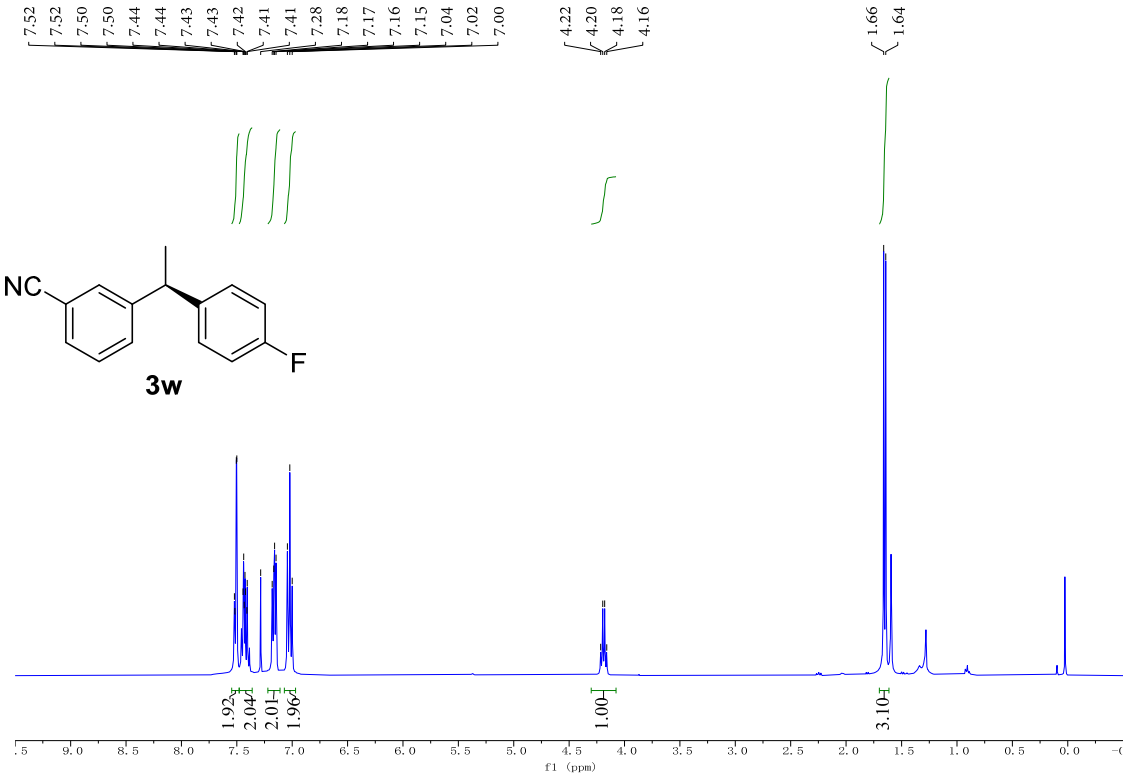


Figure S51 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3w**

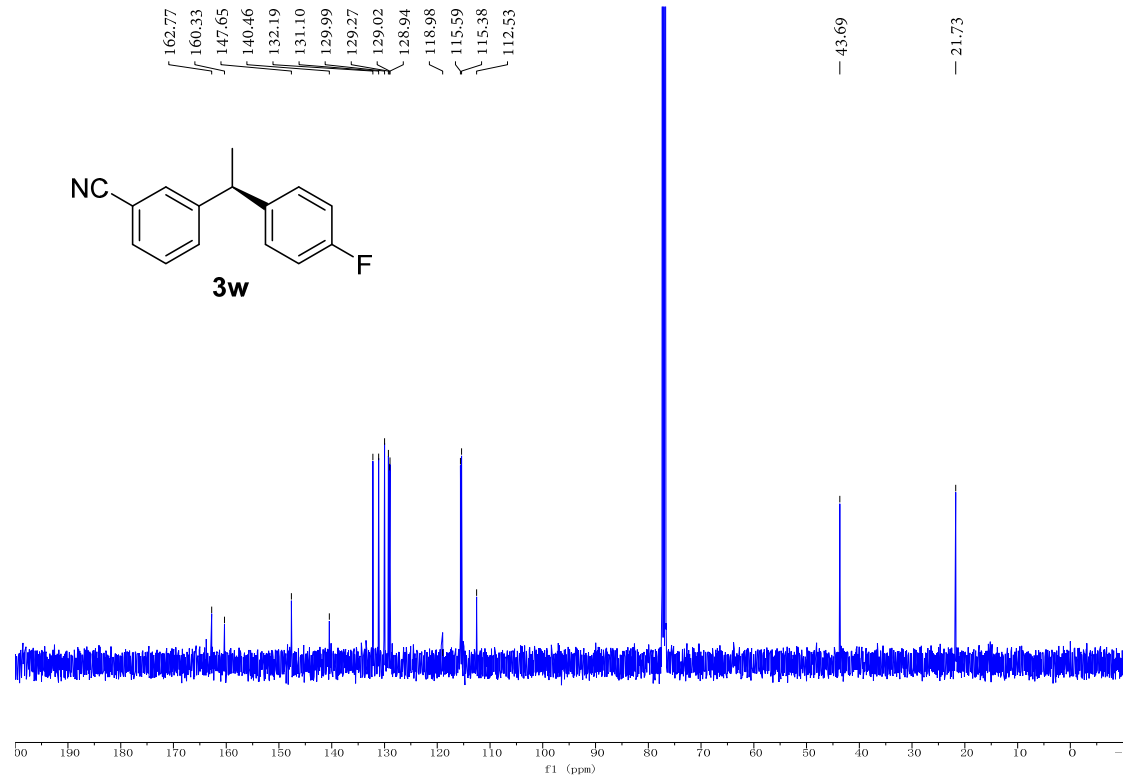


Figure S52 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3w**

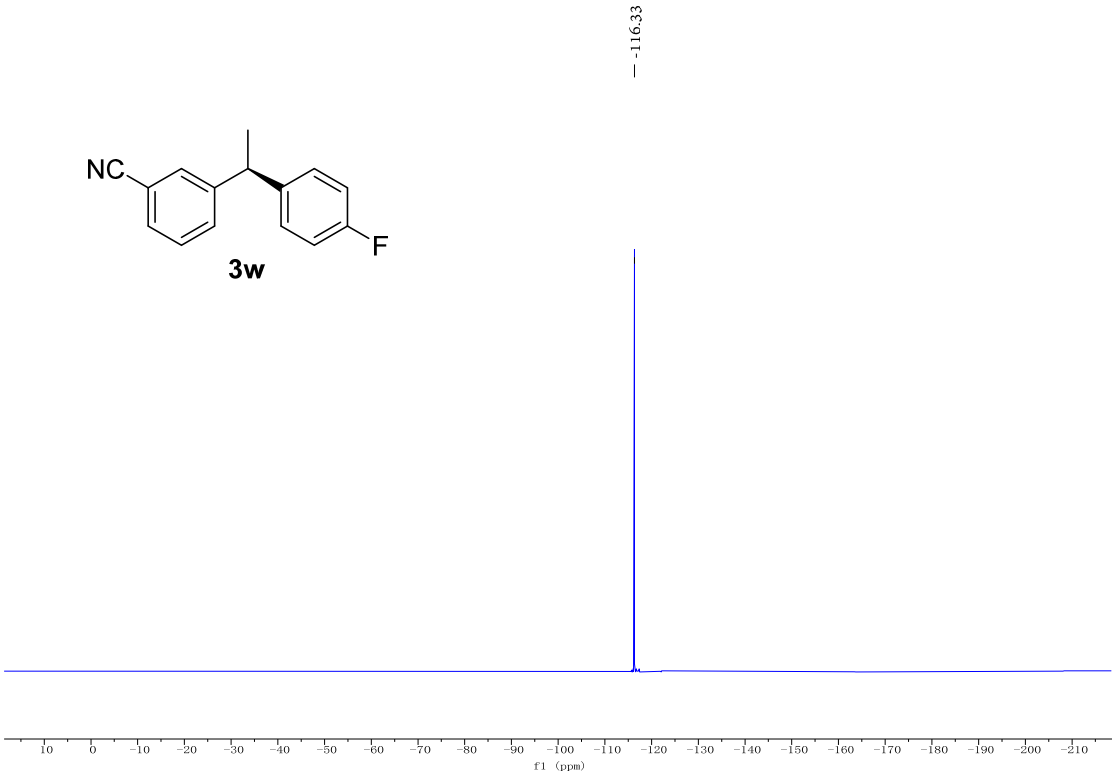


Figure S53 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3x**

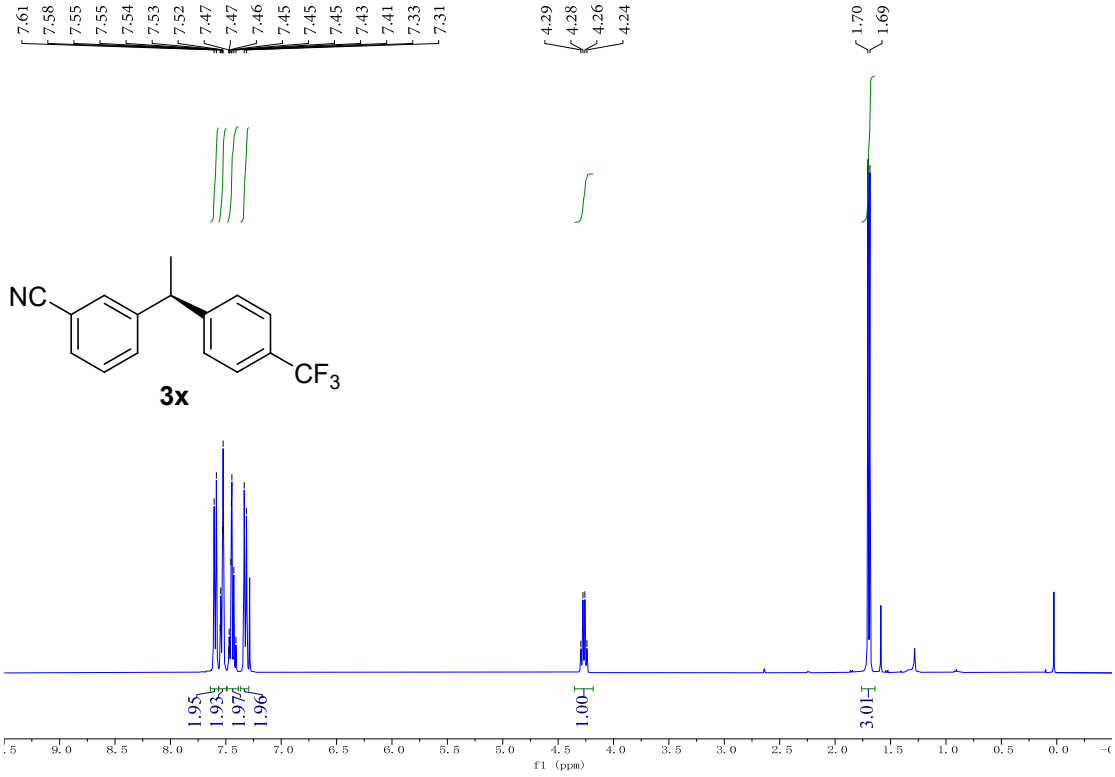


Figure S54 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3x**

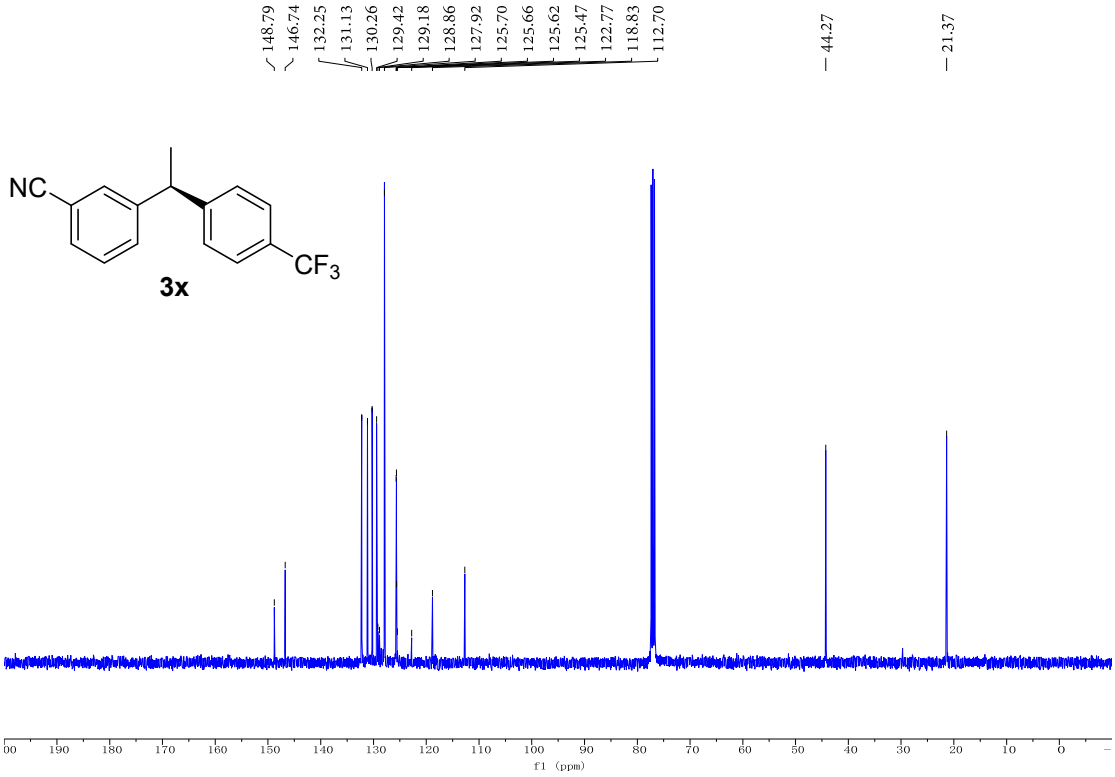


Figure S55 ^{19}F NMR (376 MHz, $CDCl_3$, 25 ºC) of **3x**

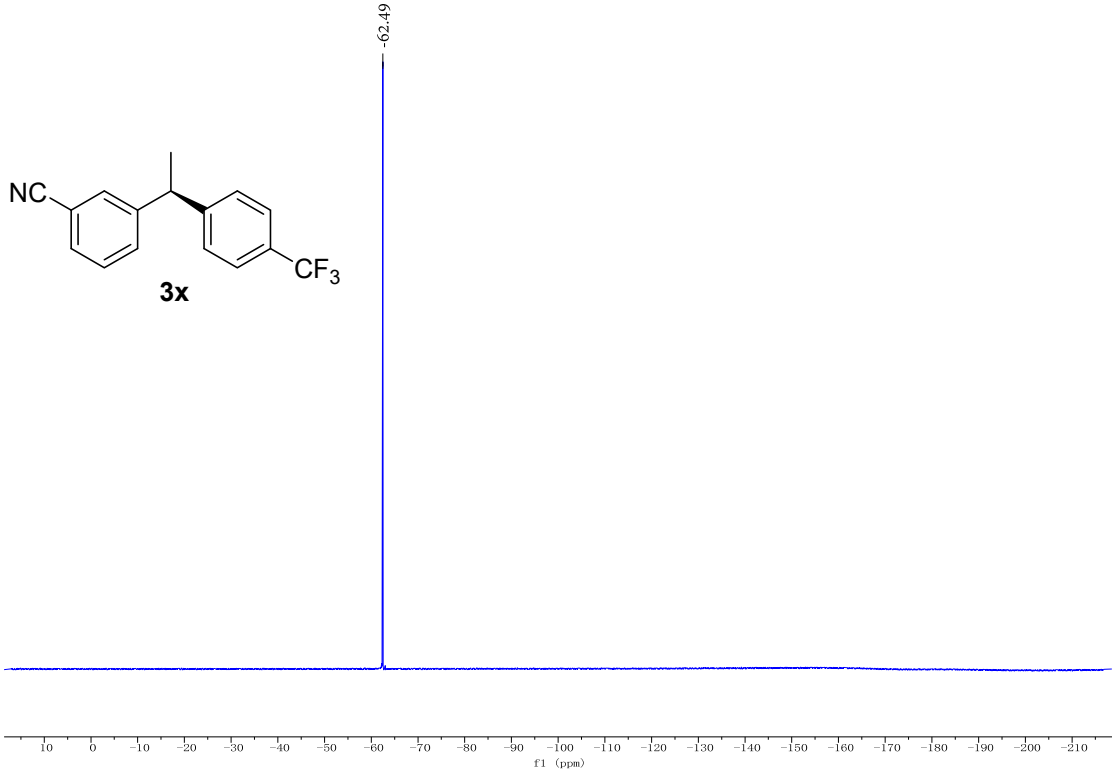


Figure S56 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **3y**

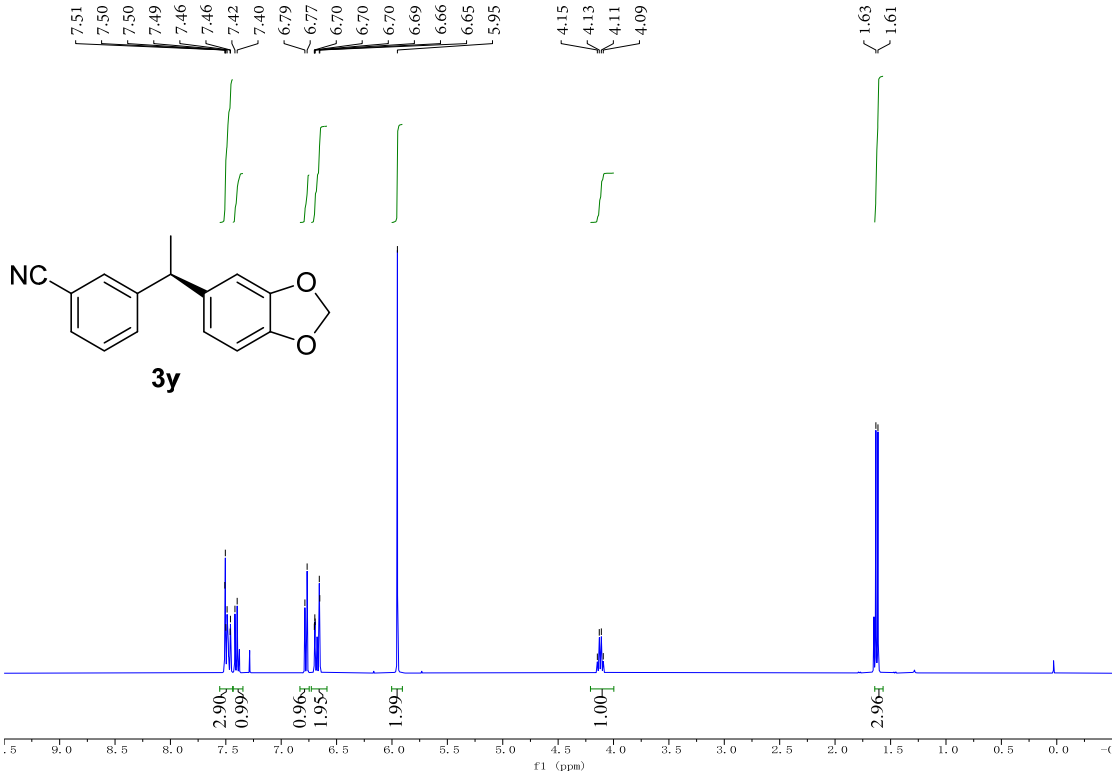


Figure S57 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **3y**

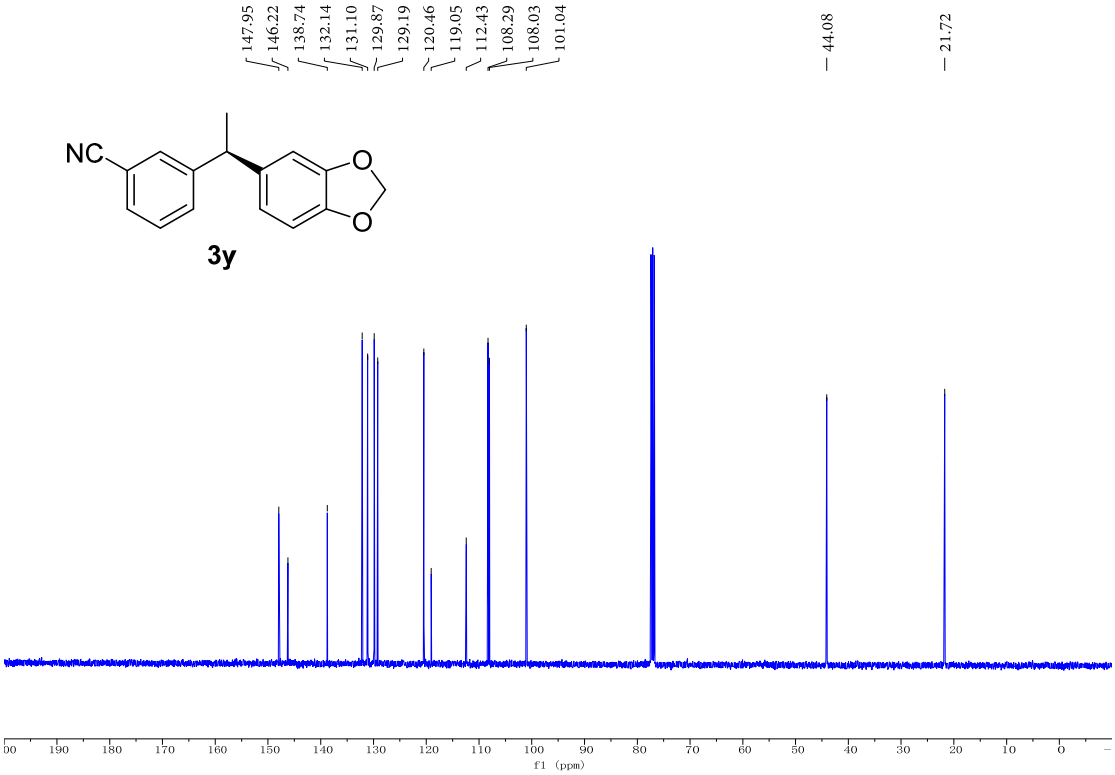


Figure S58 ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) of **4**

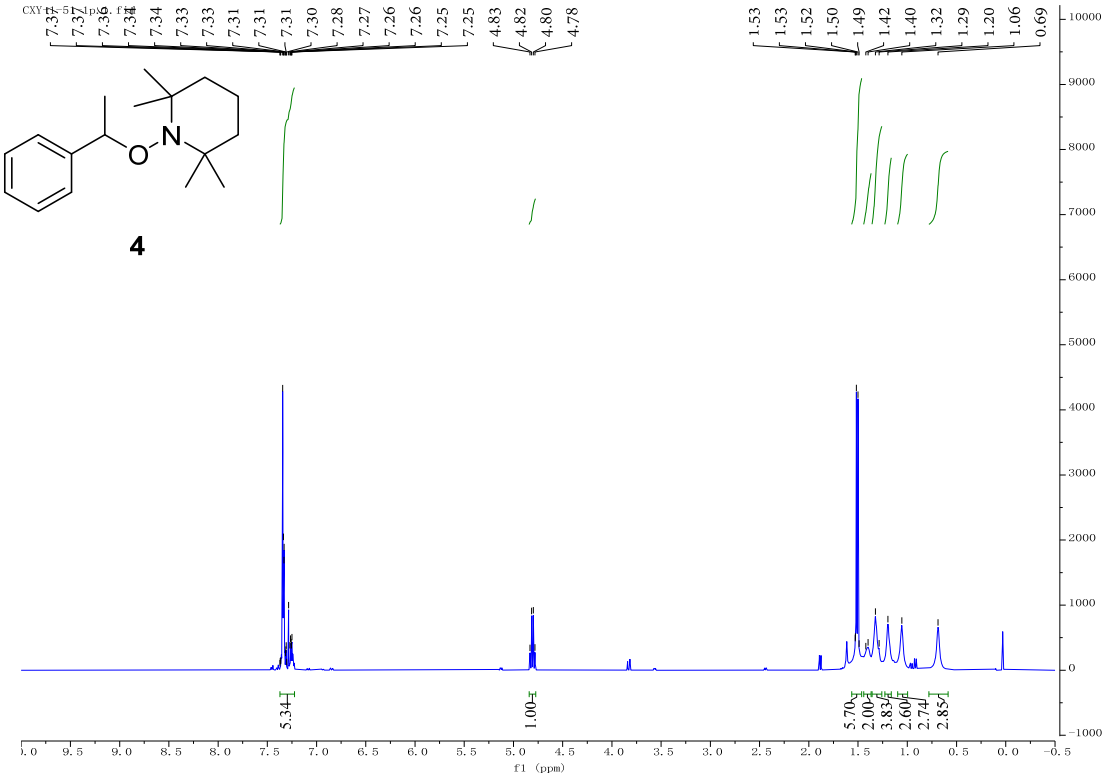
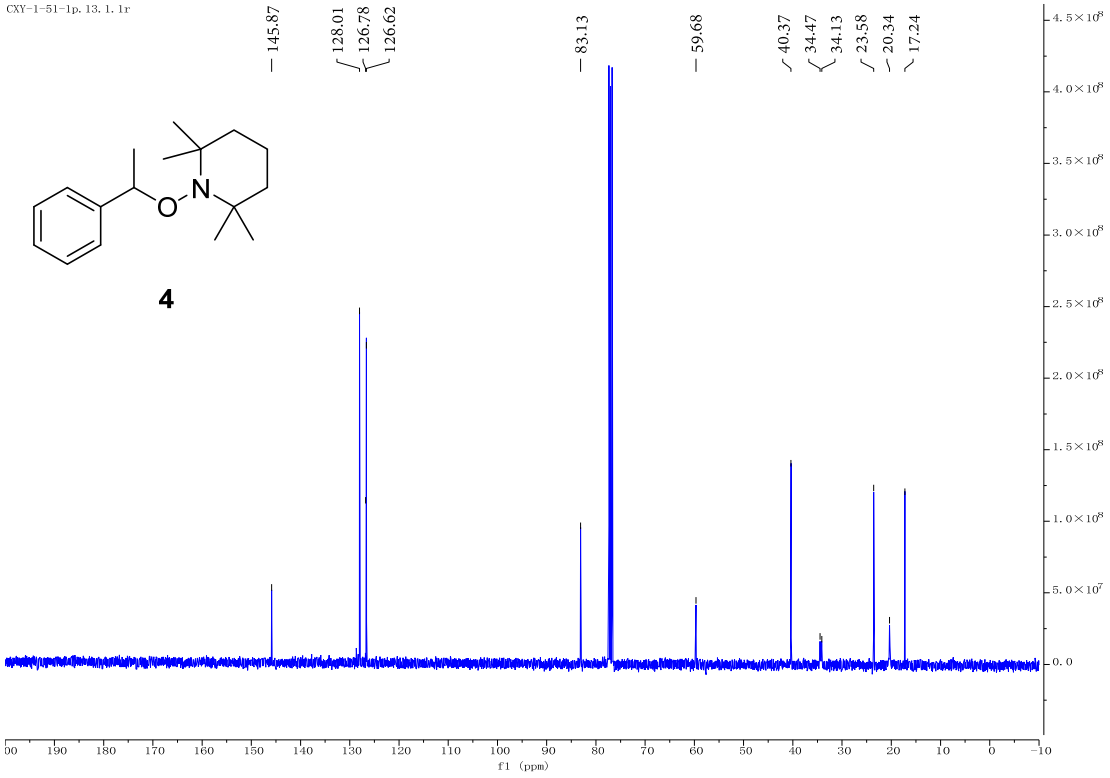
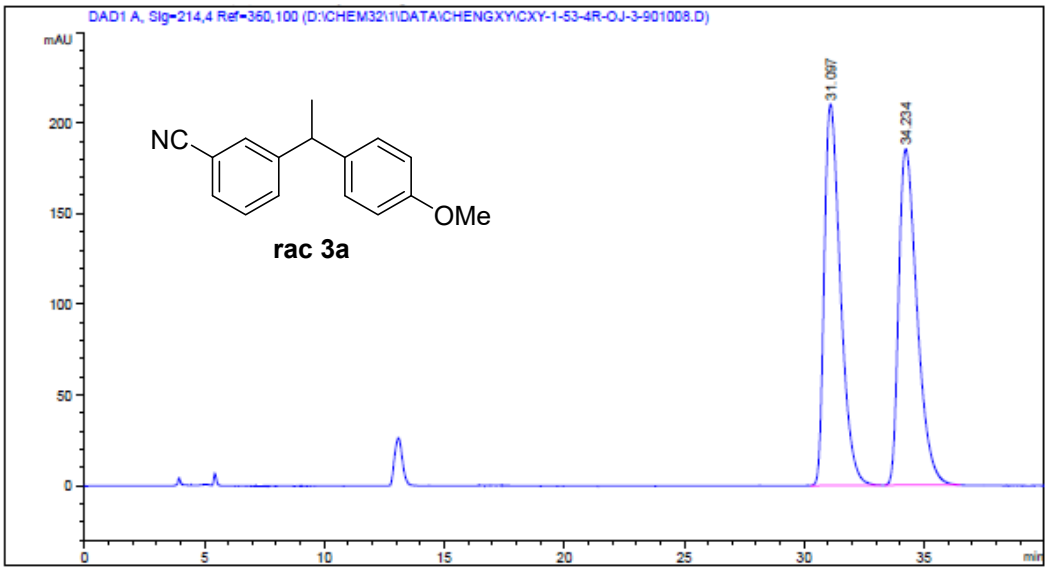


Figure S59 ^{13}C NMR (101 MHz, $CDCl_3$, 25 ºC) of **4**

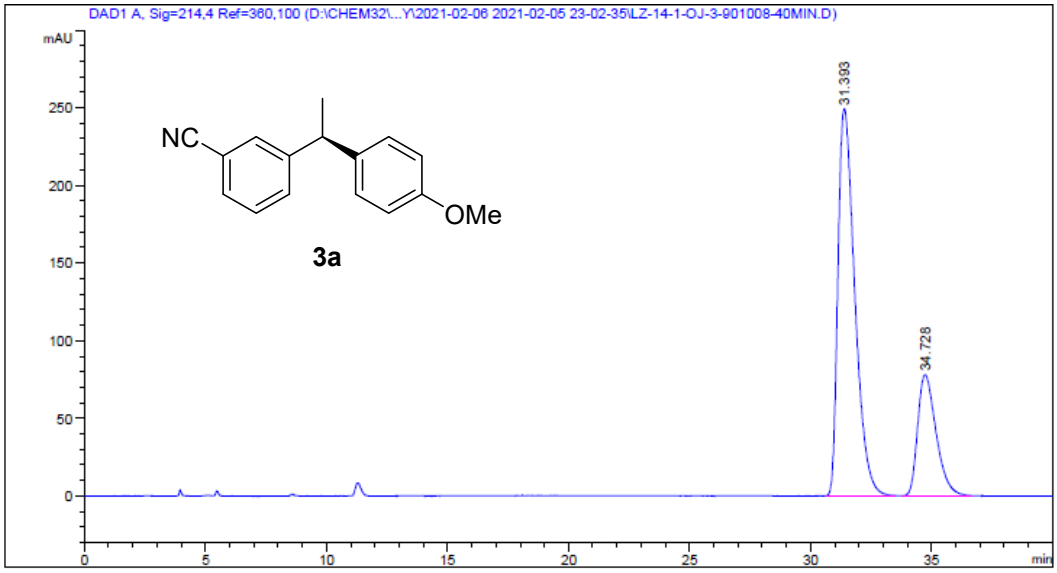


HPLC Spectra

Figure S60 HPLC spectrum comparison for **3a**



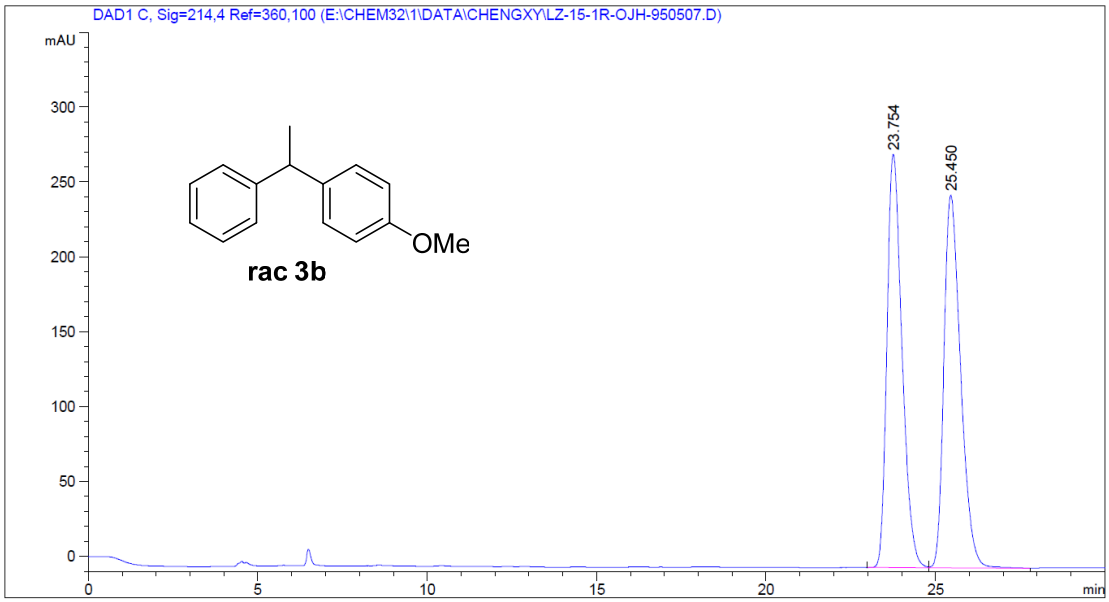
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.097	BB	0.7062	9806.24023	210.21323	50.0221
2	34.234	BB	0.7752	9797.56348	185.18936	49.9779



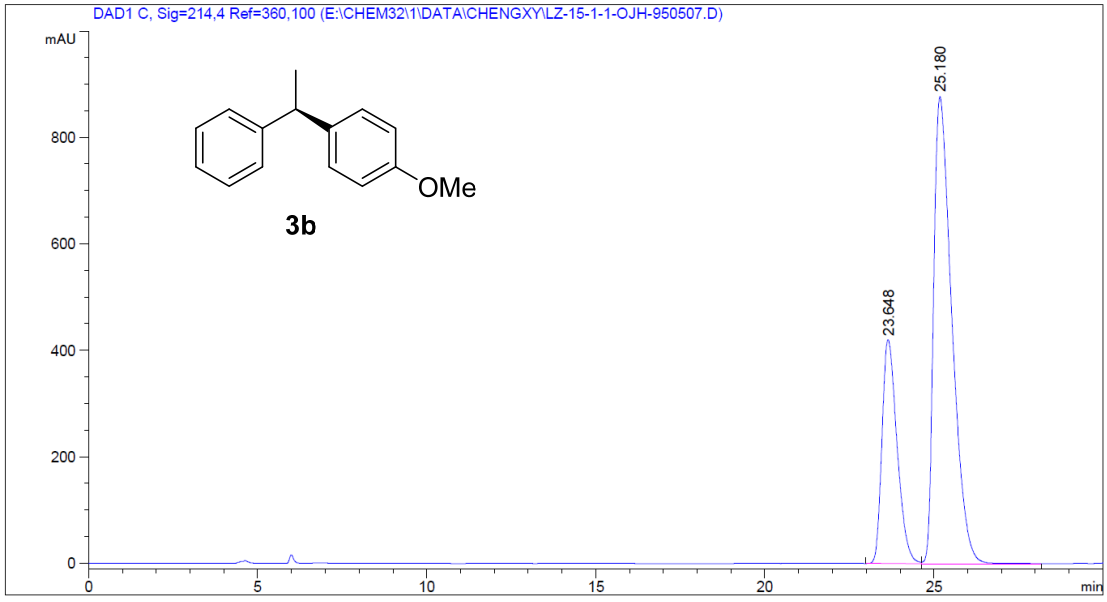
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.393	BB	0.7346	1.20138e4	249.14096	74.4768
2	34.728	BB	0.7594	4117.12207	77.79973	25.5232

Chiralcel OJ-3: hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min

Figure S61 HPLC spectrum comparison for **3b**



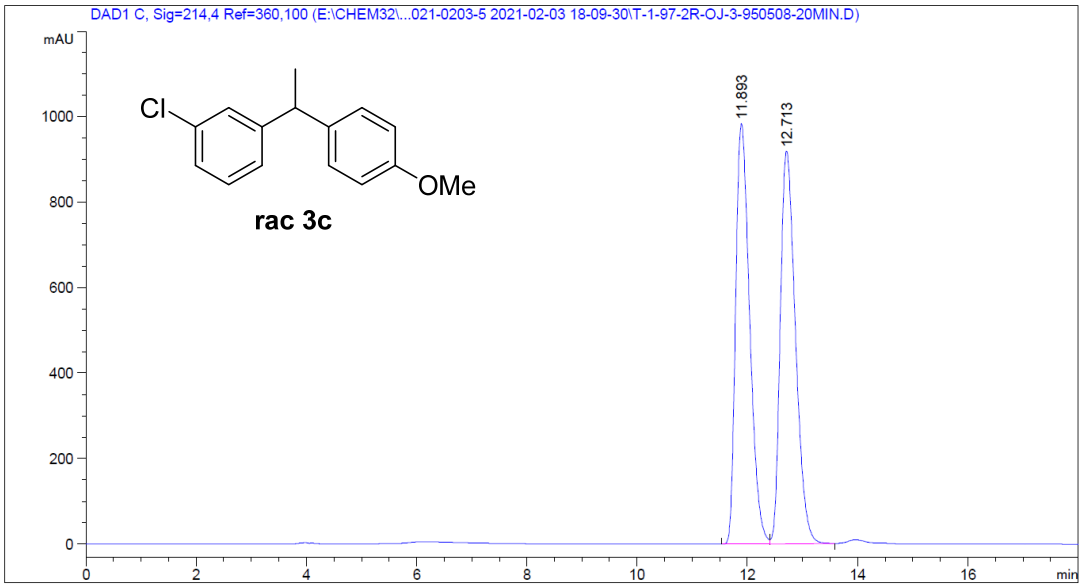
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.754	BV	0.4730	8494.19824	276.02005	49.8989
2	25.450	VB	0.5281	8528.63184	248.67244	50.1011



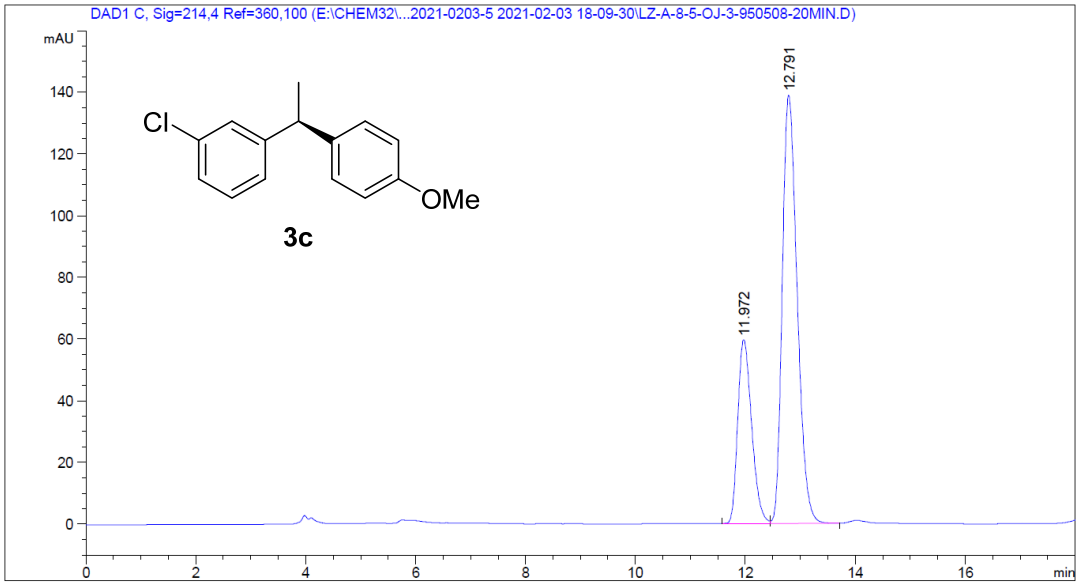
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.648	BV	0.4747	1.29949e4	420.35034	28.4291
2	25.180	VB	0.5691	3.27150e4	877.17273	71.5709

Chiralcel OJH: hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min

Figure S62 HPLC spectrum comparison for **3c**



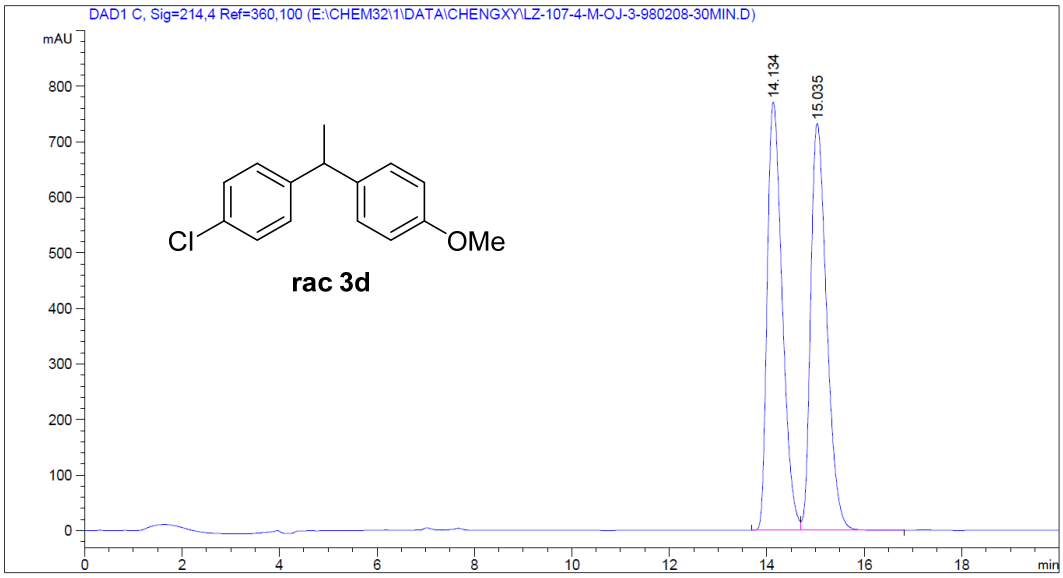
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.893	BV	0.2739	1.73589e4	983.80432	49.7507
2	12.713	VB	0.2987	1.75329e4	918.59784	50.2493



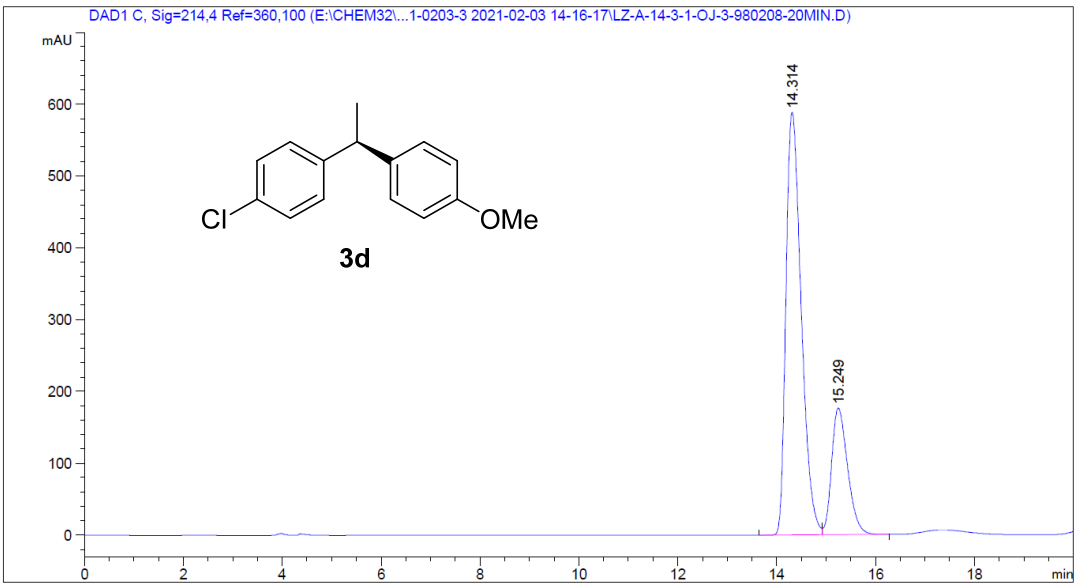
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.972	BV	0.2746	1043.77771	59.52390	28.5807
2	12.791	VB	0.2933	2608.25293	138.73276	71.4193

Chiralcel OJ-3: hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min

Figure S63 HPLC spectrum comparison for **3d**



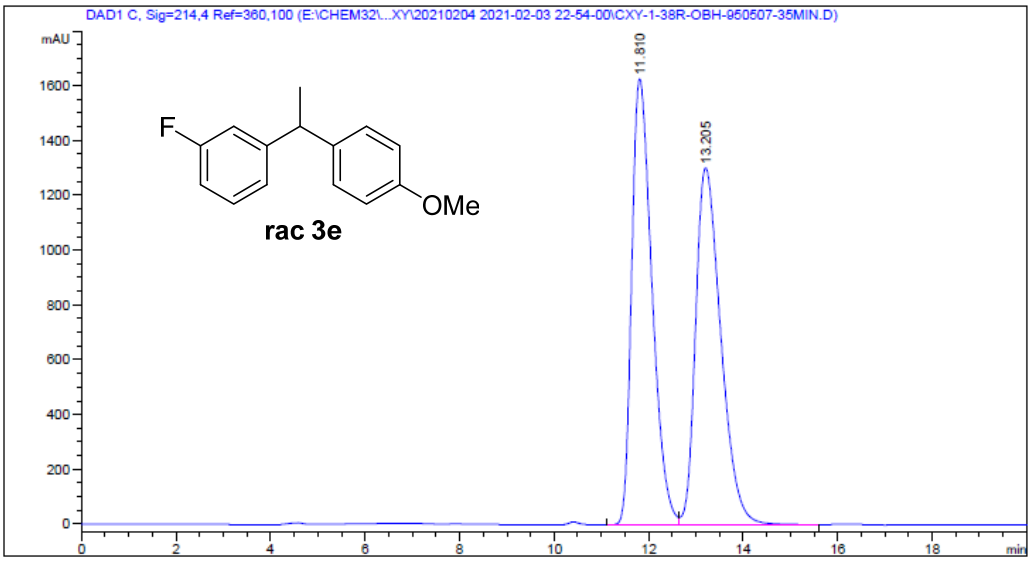
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.134	BV	0.3334	1.64791e4	770.88519	49.7064
2	15.035	VB	0.3535	1.66738e4	732.57965	50.2936



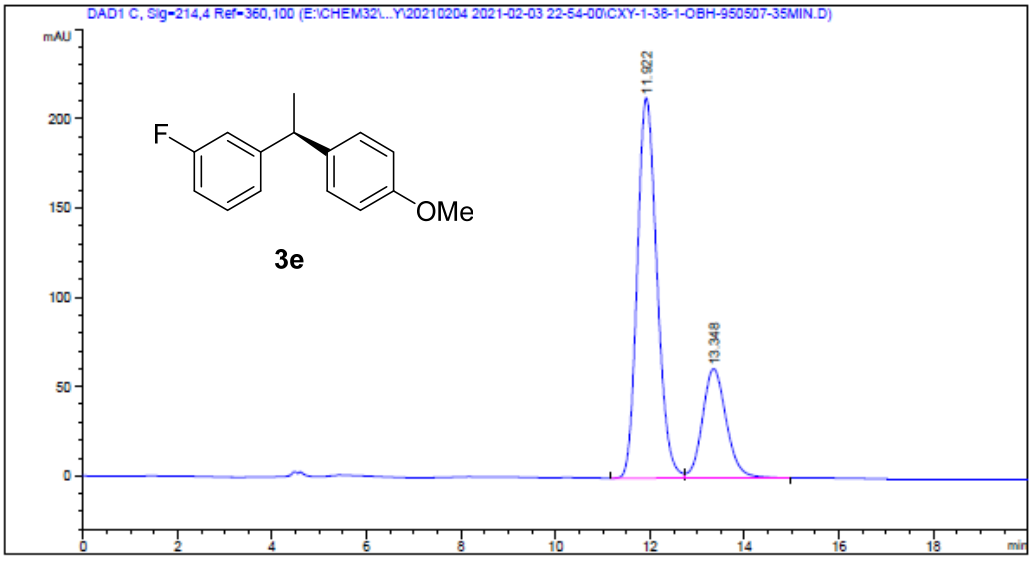
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.314	BV	0.3341	1.26209e4	588.67822	76.0184
2	15.249	VB	0.3495	3981.54736	176.25813	23.9816

Chiralcel OJ-3: hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min

Figure S64 HPLC spectrum comparison for **3e**



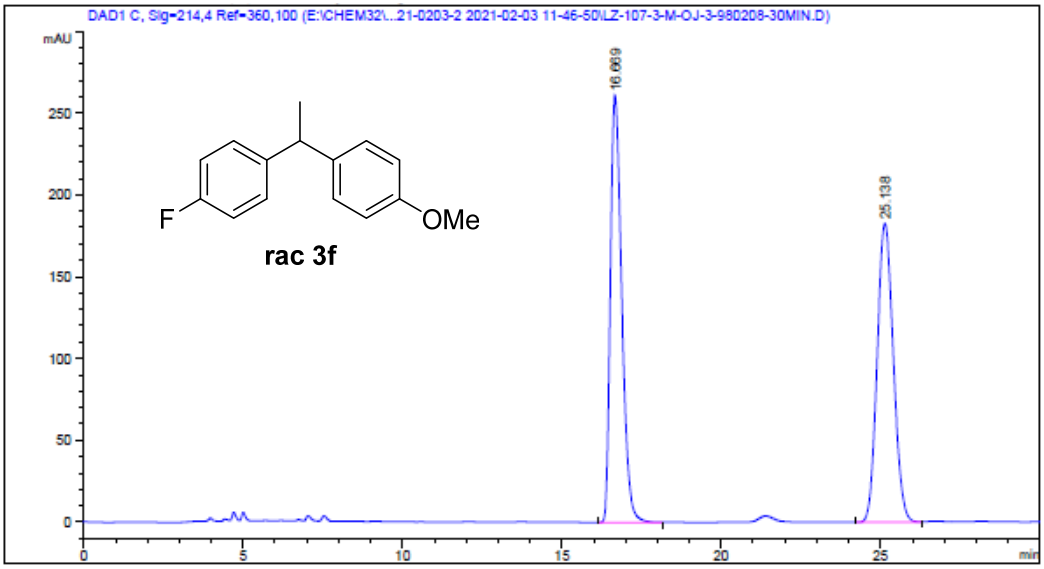
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.810	BV	0.4596	4.84982e4	1627.88696	50.1458
2	13.205	VB	0.5737	4.82161e4	1303.13293	49.8542



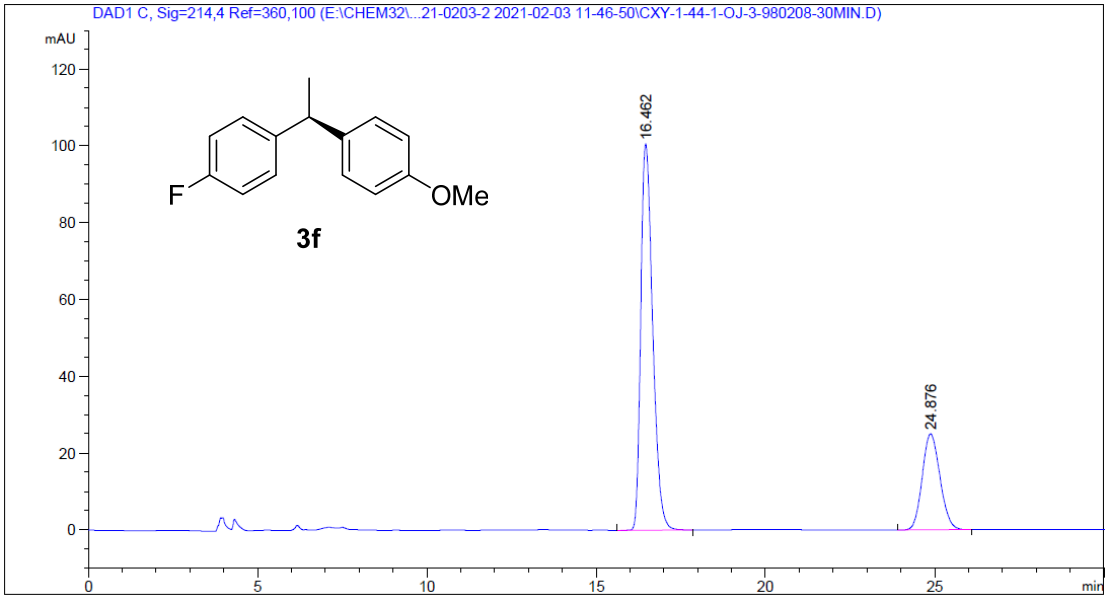
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.922	BV	0.4495	6157.32813	212.87224	74.1193
2	13.348	VB	0.5441	2149.98926	61.16822	25.8807

Chiralcel OBH : hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min

Figure S65 HPLC spectrum comparison for **3f**



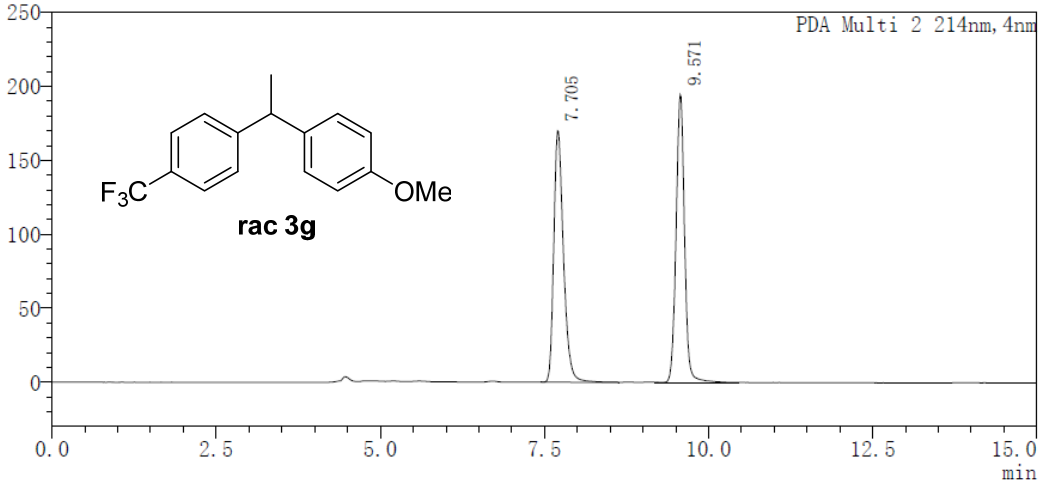
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.669	BB	0.3839	6447.99316	261.31705	50.0946
2	25.138	BB	0.5503	6423.63086	182.65407	49.9054



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.462	BB	0.3787	2453.96460	100.55206	72.9211
2	24.876	BB	0.5710	911.26587	25.01552	27.0789

Chiralcel OJ-3: hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min

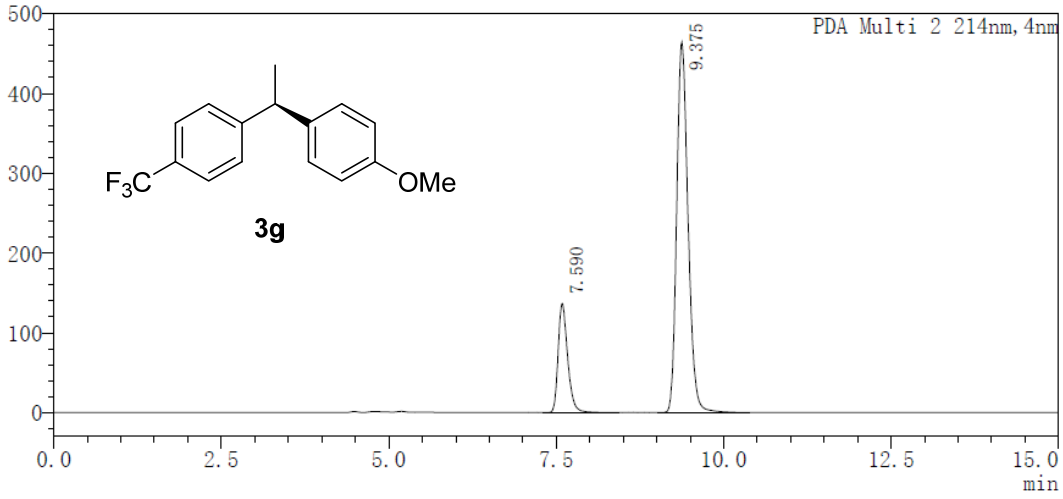
Figure S66 HPLC spectrum comparison for **3g**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	7.705	1748899	50.075
2	9.571	1743663	49.925



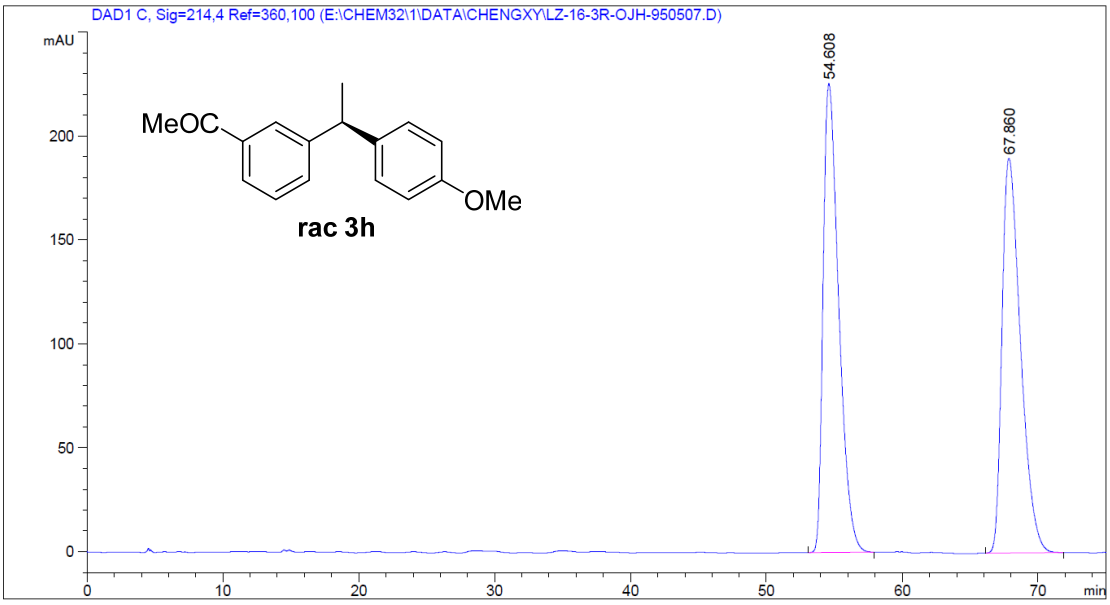
Peak Table

PDA Ch2 214nm

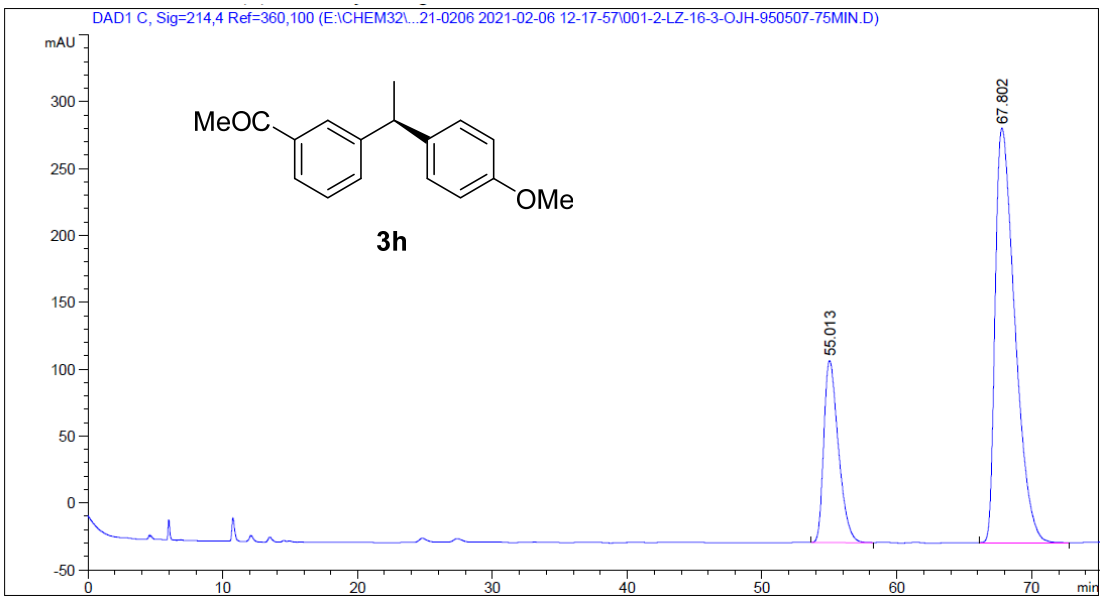
Peak#	Ret. Time	Area	Area%
1	7.590	1348975	19.799
2	9.375	5464277	80.201

Chiralcel OJH: hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min

Figure S67 HPLC spectrum comparison for **3h**



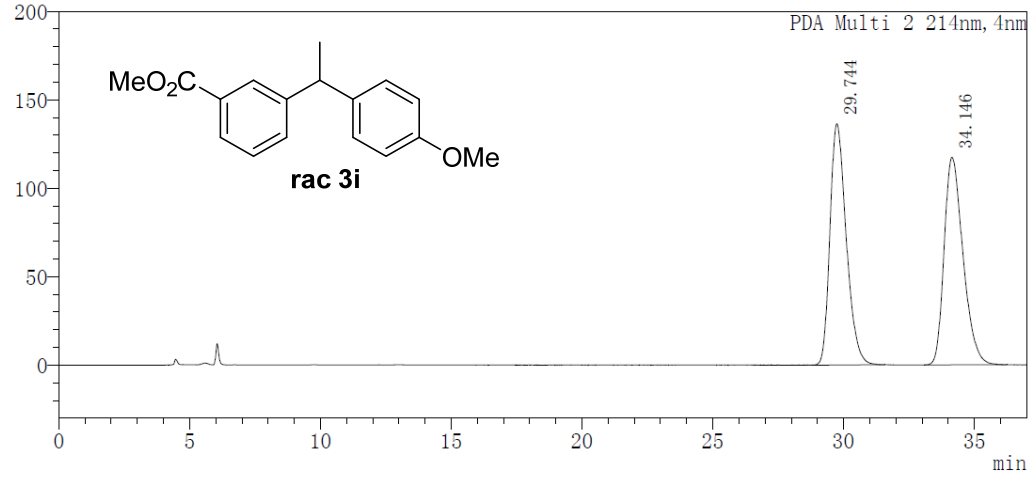
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.608	BB	1.2162	1.79978e4	225.72766	49.9756
2	67.860	BB	1.4407	1.80153e4	189.92218	50.0244



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.013	BB	1.1397	1.02360e4	136.05336	24.5643
2	67.802	BB	1.5488	3.14340e4	310.04932	75.4357

Chiralcel OJH: hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min

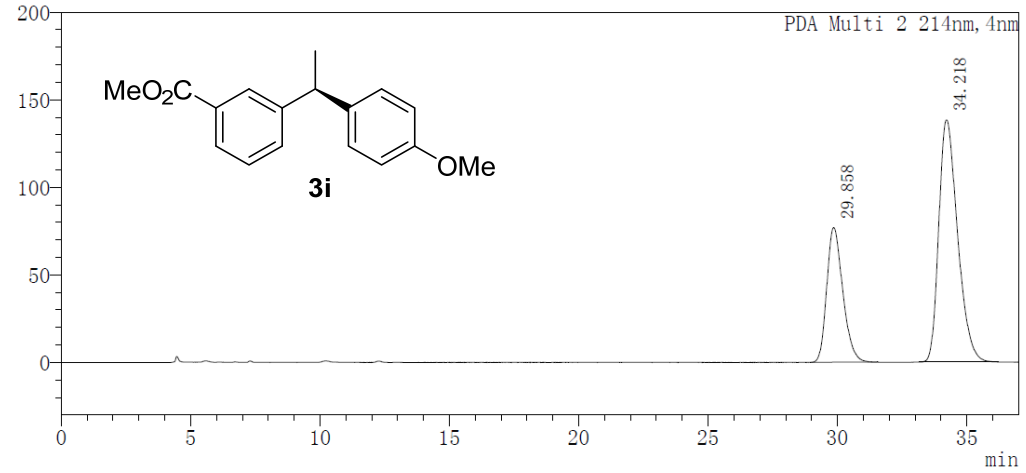
Figure S68 HPLC spectrum comparison for **3i**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	29.744	5912668	50.053
2	34.146	5900071	49.947



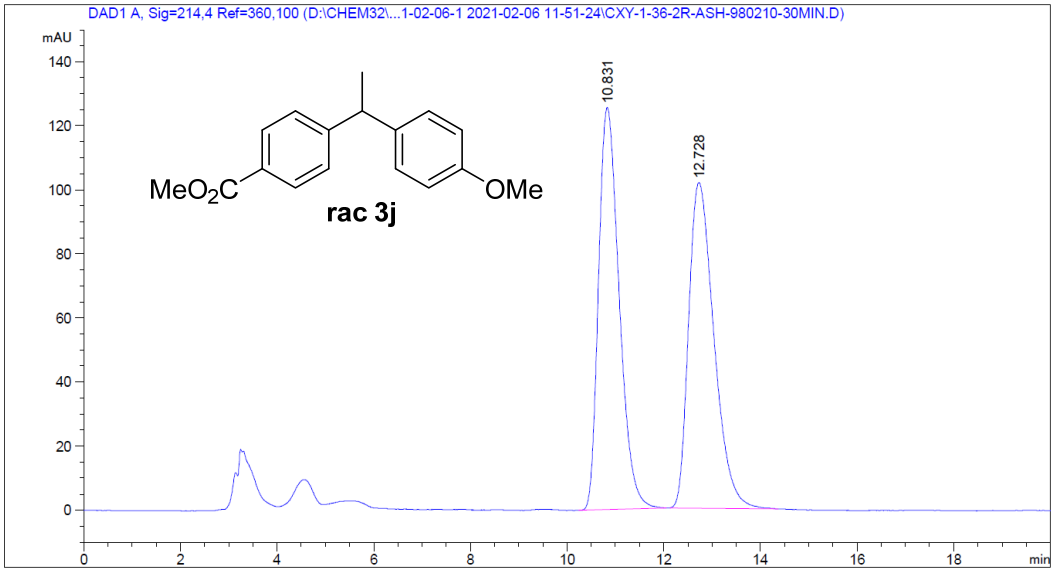
Peak Table

PDA Ch2 214nm

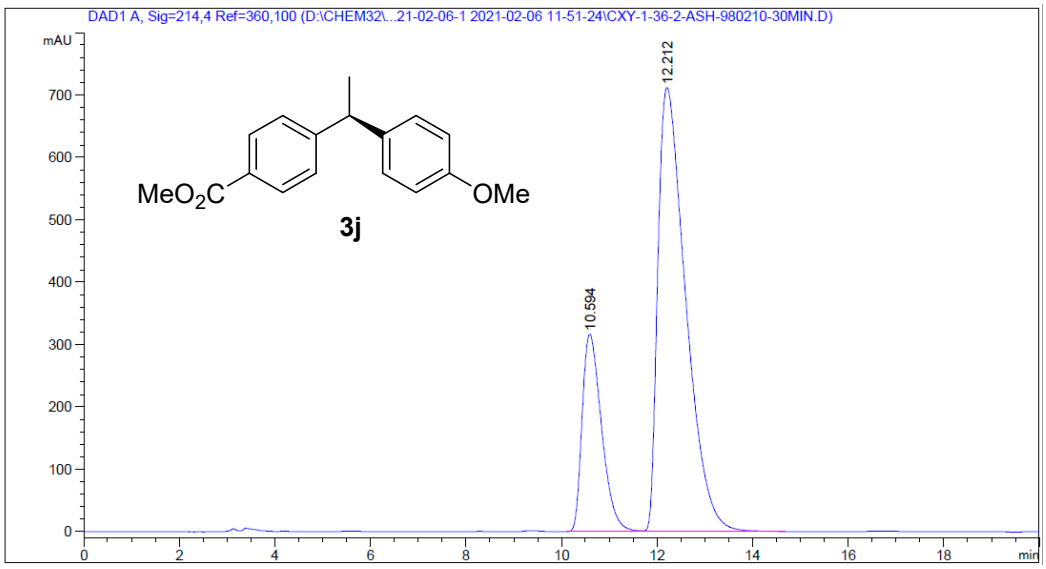
Peak#	Ret. Time	Area	Area%
1	29.858	3322957	32.217
2	34.218	6991393	67.783

Chiralcel OJH: hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min

Figure S69 HPLC spectrum comparison for **3j**



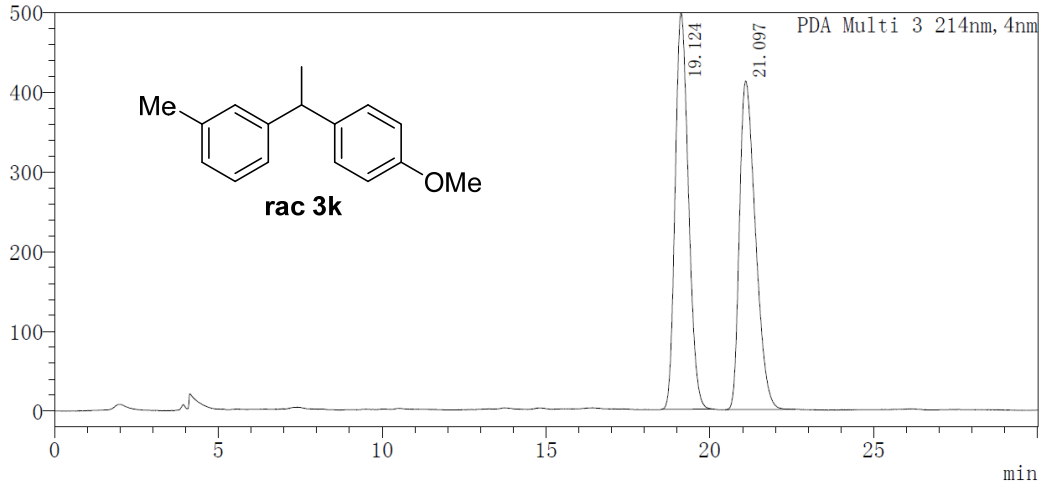
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.831	BB	0.4617	3718.78906	125.51537	50.1653
2	12.728	BB	0.5562	3694.27515	101.60166	49.8347



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.594	BV	0.4391	8987.68359	316.66782	23.8084
2	12.212	VB	0.6113	2.87623e4	711.95984	76.1916

Chiralcel ASH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

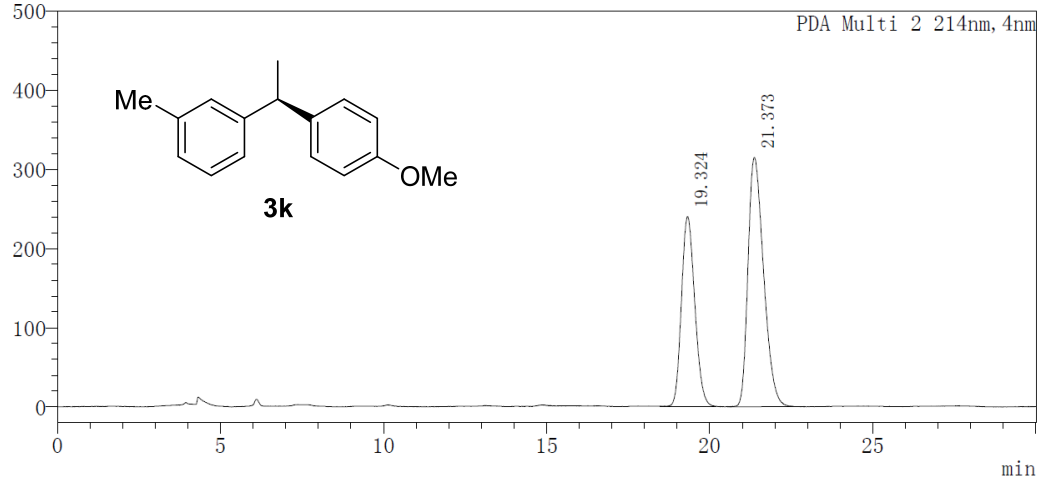
Figure S70 HPLC spectrum comparison for **3k**



Peak Table

PDA Ch3 214nm

Peak#	Ret. Time	Area	Area%
1	19.124	14034822	50.026
2	21.097	14019986	49.974



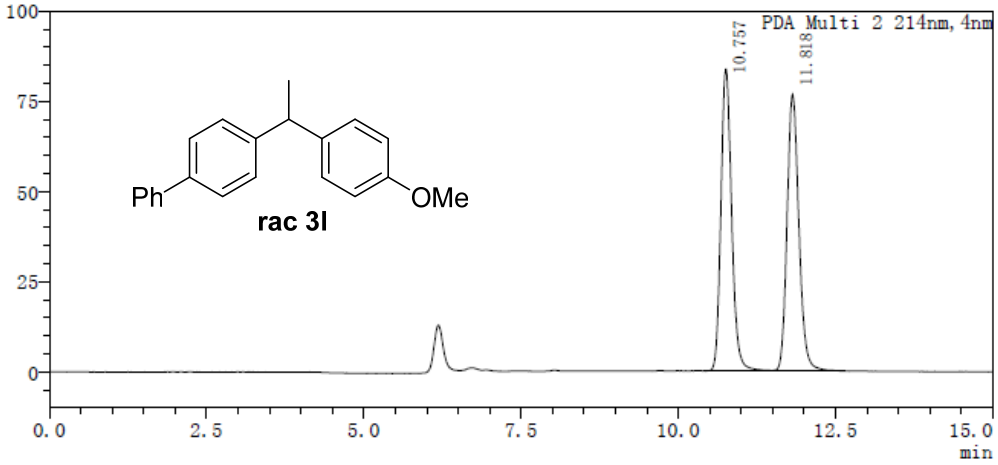
Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	19.324	6810080	39.374
2	21.373	10485857	60.626

Chiralcel OJ-3: hexane/i-PrOH = 98/2, flow rate 0.8mL/min

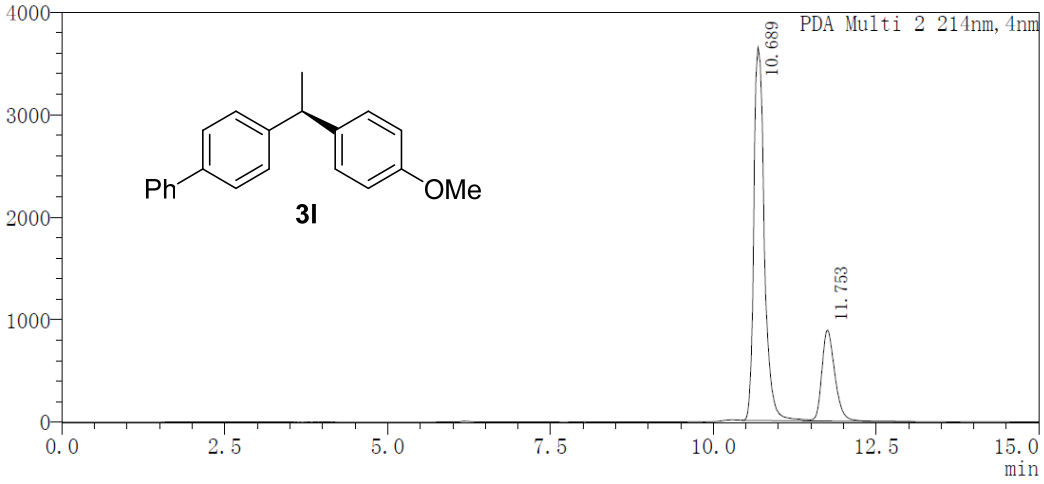
Figure S71 HPLC spectrum comparison for **3l**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.757	993807	49.754
2	11.818	1003646	50.246



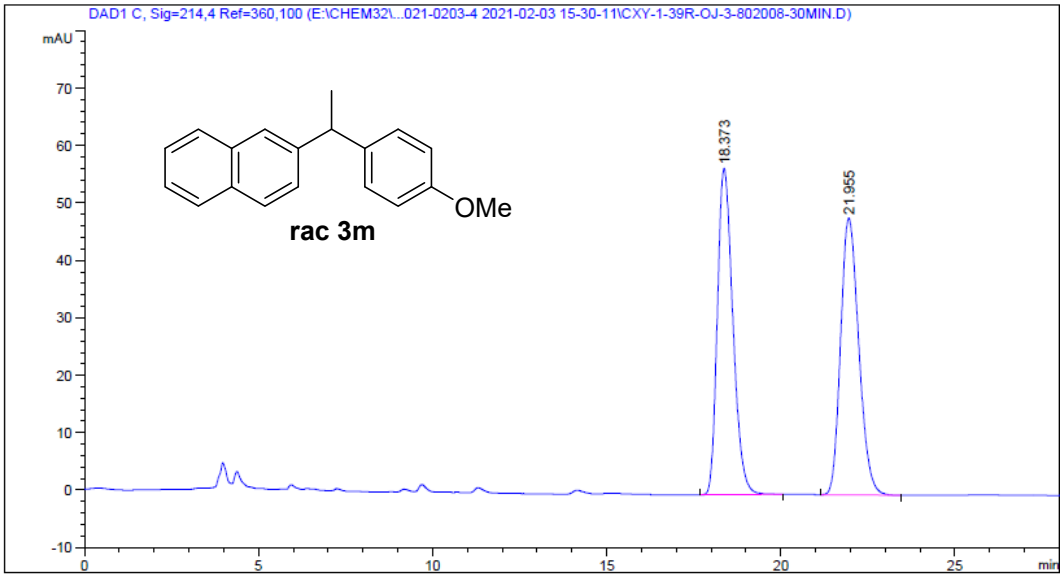
Peak Table

PDA Ch2 214nm

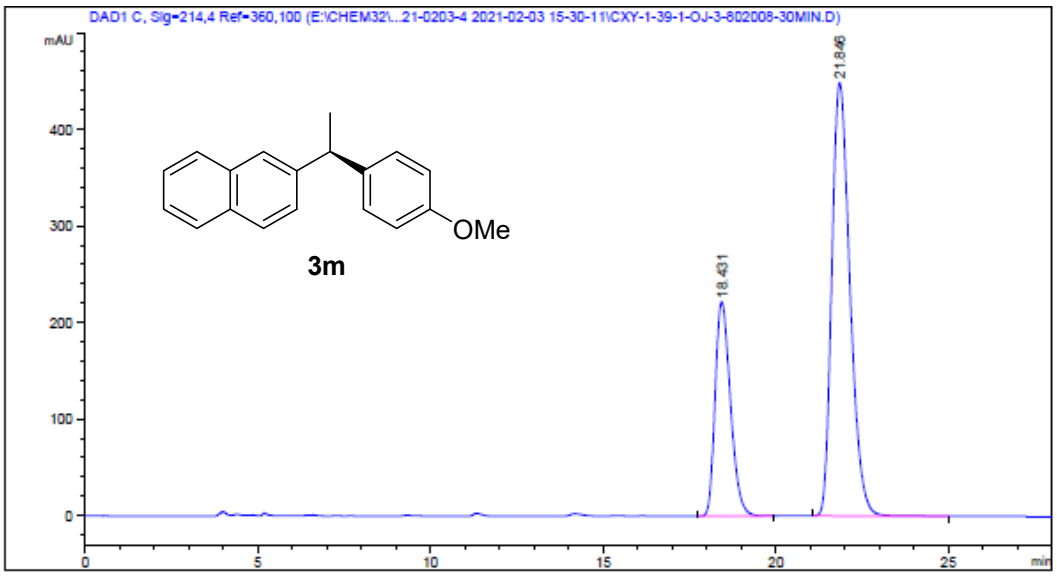
Peak#	Ret. Time	Area	Area%
1	10.689	40986800	76.916
2	11.753	12300867	23.084

Chiralcel ODH: hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min

Figure S72 HPLC spectrum comparison for **3m**



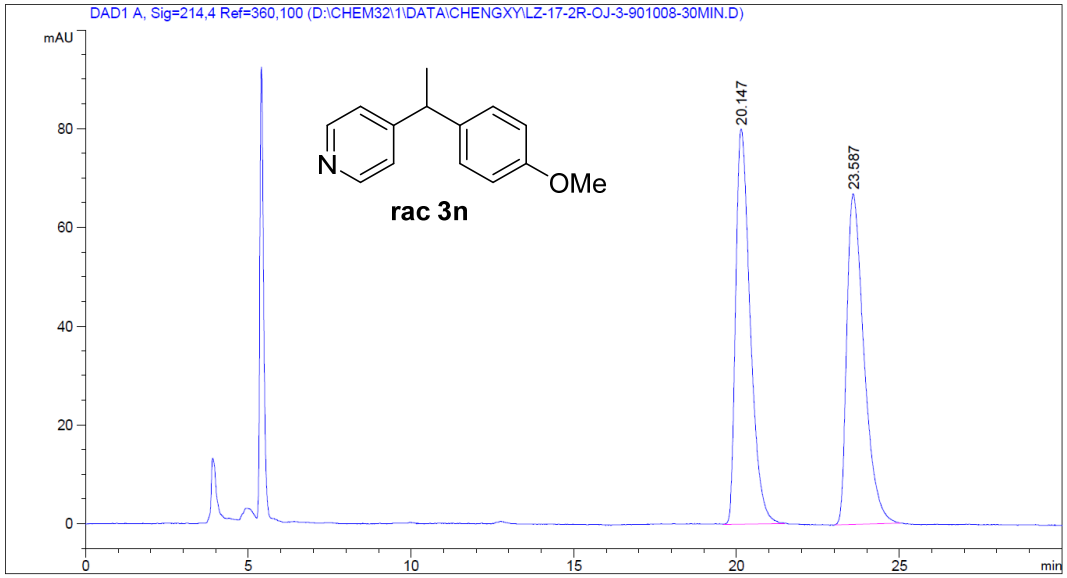
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.373	BB	0.4785	1755.81836	56.82096	50.1521
2	21.955	BB	0.5625	1745.16516	48.19519	49.8479



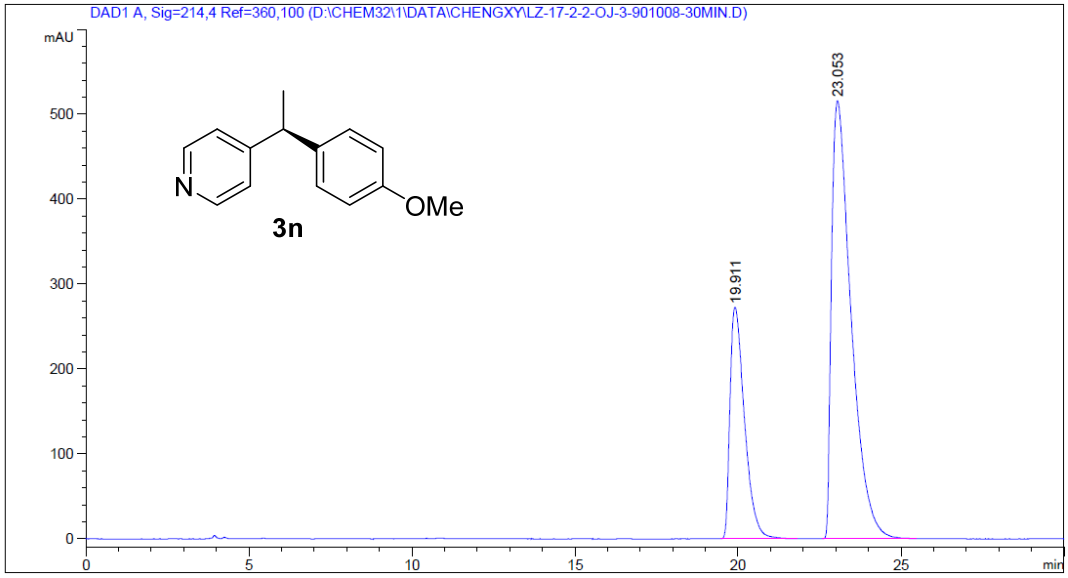
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.431	BB	0.4780	6812.12207	221.99992	29.4248
2	21.846	BB	0.5649	1.63388e4	448.66196	70.5752

Chiralcel OJ-3: hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min

Figure S73 HPLC spectrum comparison for **3n**



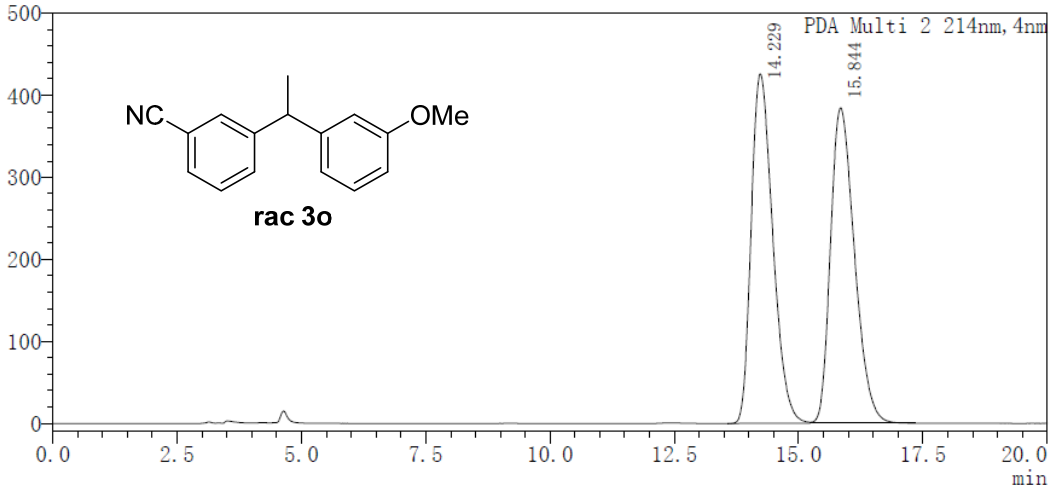
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.147	BB	0.4615	2478.44873	79.99133	50.2475
2	23.587	BB	0.5379	2454.02856	66.90595	49.7525



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.911	BB	0.4795	8446.25000	272.59677	28.2651
2	23.053	BB	0.6168	2.14360e4	515.86389	71.7349

Chiralcel OJ-3: hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min

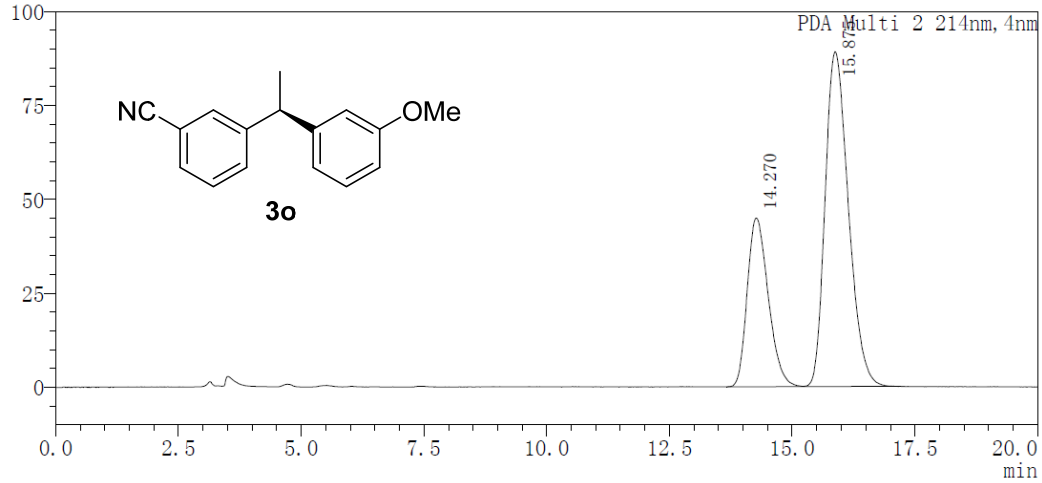
Figure S74 HPLC spectrum comparison for **3o**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	14.229	12862870	49.920
2	15.844	12904181	50.080



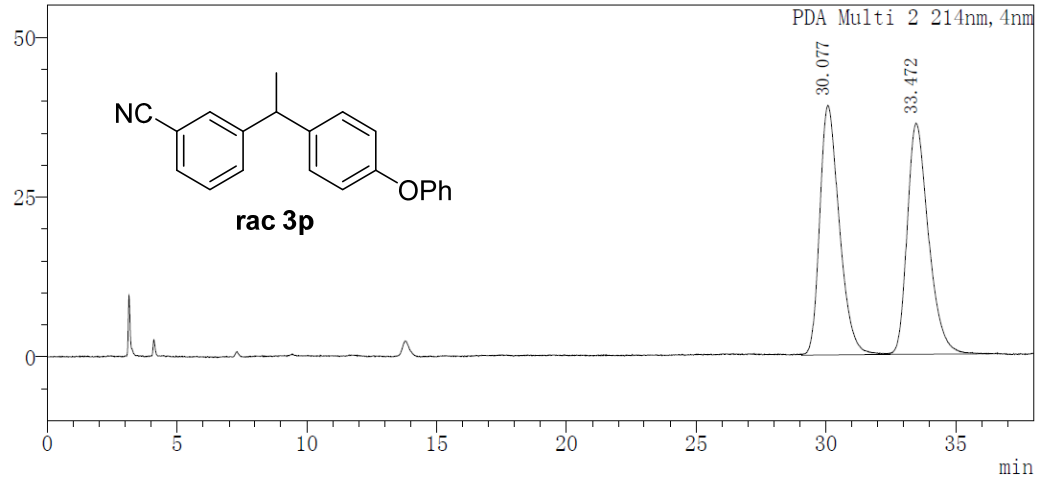
Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	14.270	1340311	31.301
2	15.875	2941703	68.699

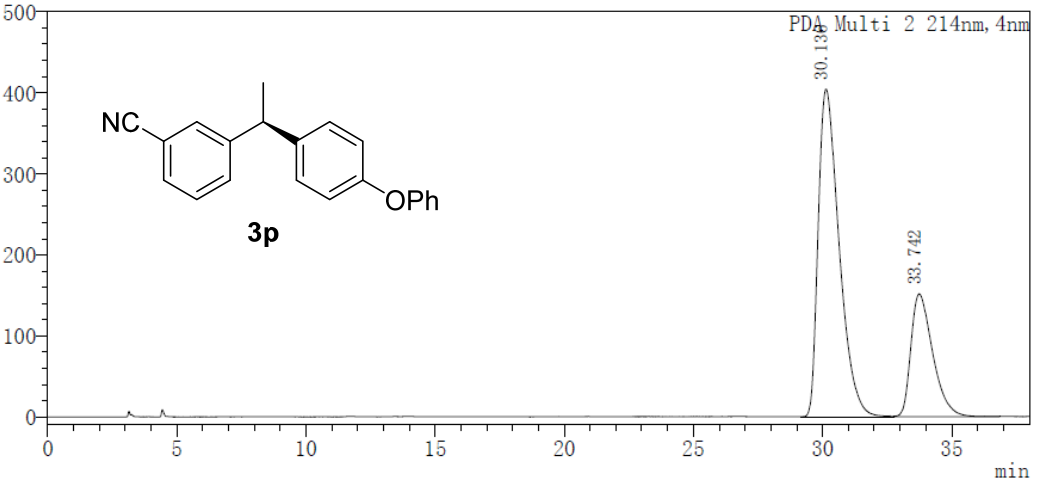
Chiralcel ASH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

Figure S75 HPLC spectrum comparison for **3p**



PDA Ch2 214nm

T	Hight	Area	Area%
30.077	39046	2055153	49.955
33.472	36191	2058842	50.045

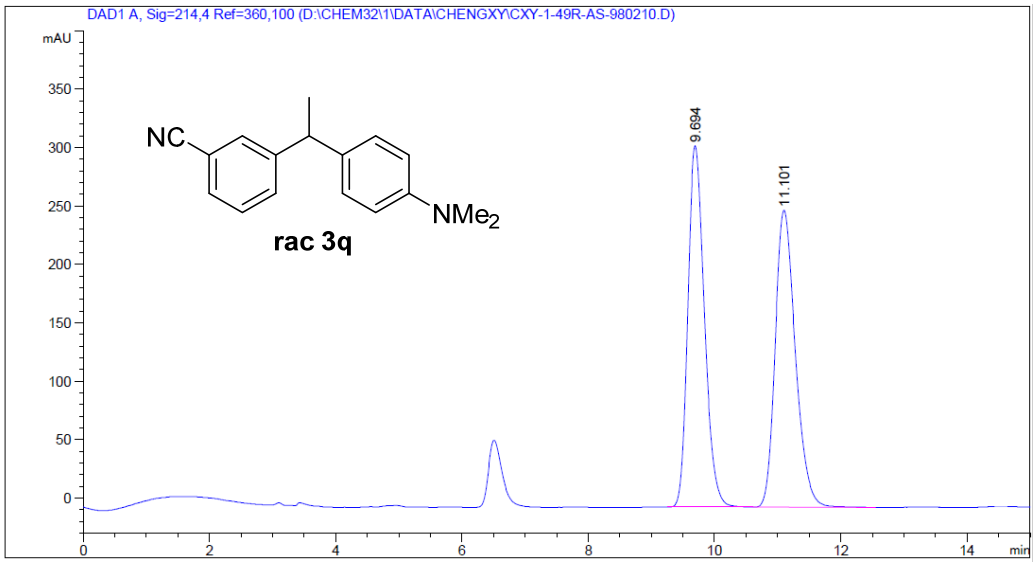


PDA Ch2 214nm

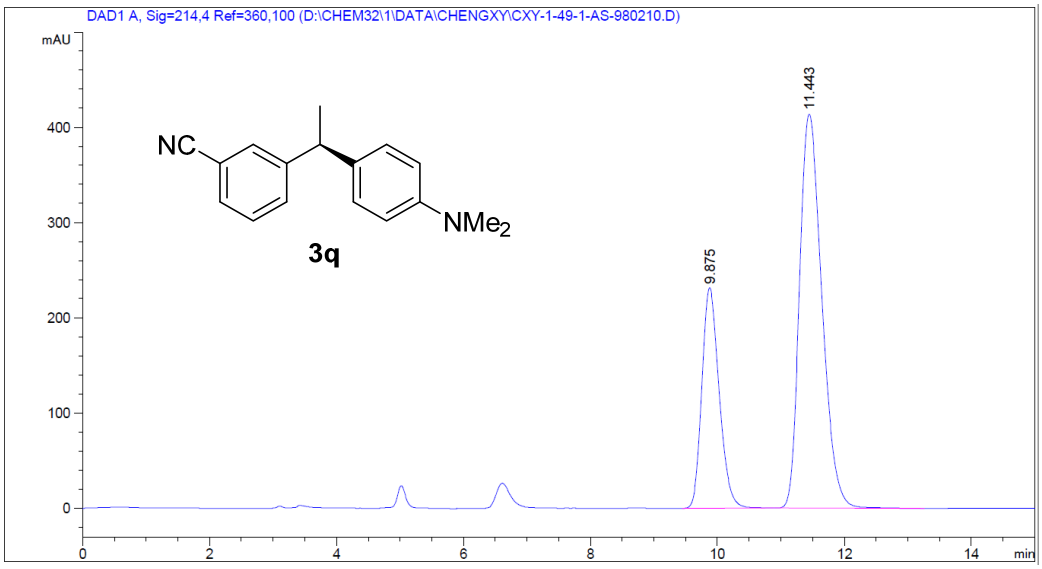
T	Hight	Area	Area%
30.136	404306	22819510	71.909
33.742	151423	8914207	28.091

Chiralcel OJH: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min

Figure S76 HPLC spectrum comparison for **3q**



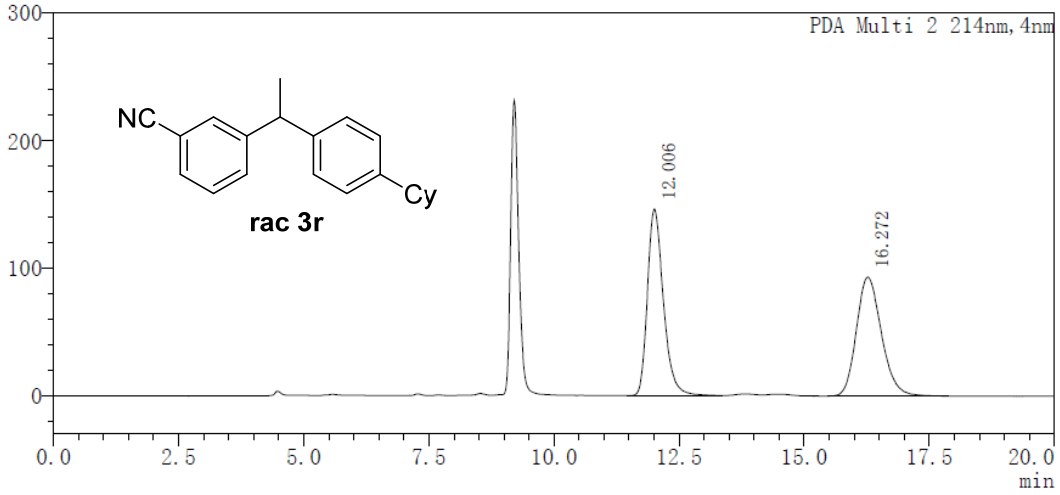
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.694	BB	0.2809	5640.92920	309.13632	49.9833
2	11.101	BB	0.3392	5644.70703	254.06909	50.0167



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.875	BB	0.2925	4376.98340	231.56580	30.2349
2	11.443	BB	0.3788	1.00996e4	413.74969	69.7651

Chiralcel AS: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

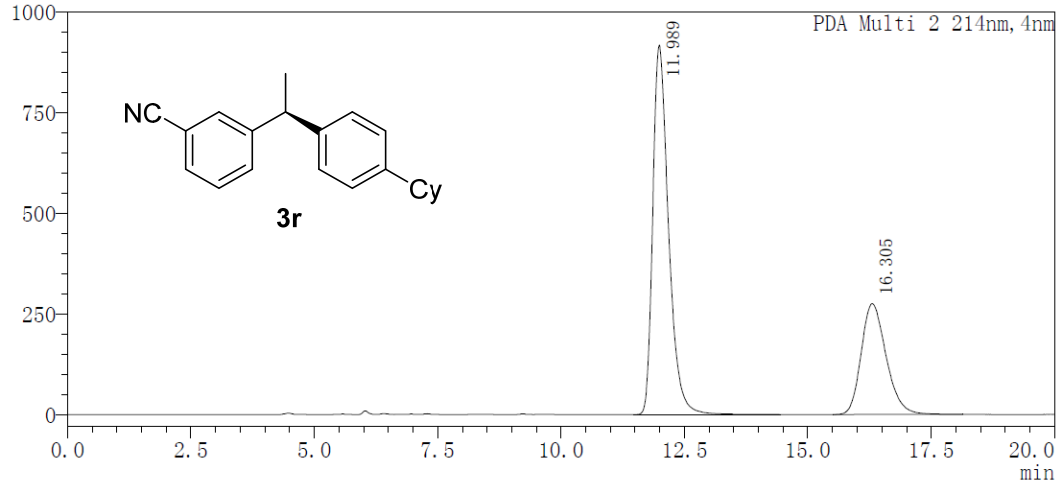
Figure S77 HPLC spectrum comparison for **3r**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	12.006	3249735	50.033
2	16.272	3245436	49.967



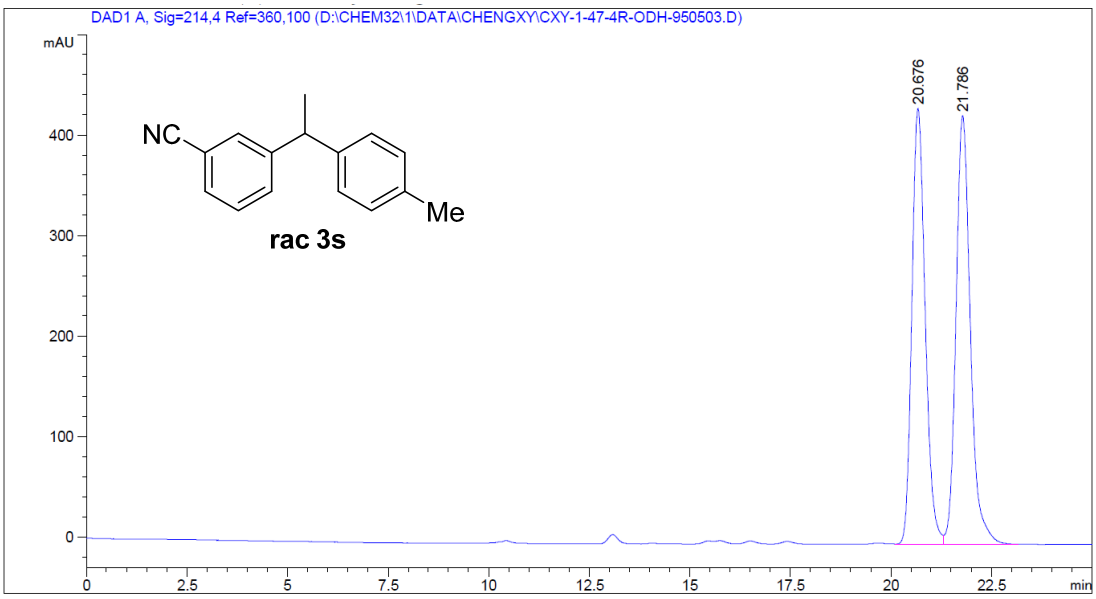
Peak Table

PDA Ch2 214nm

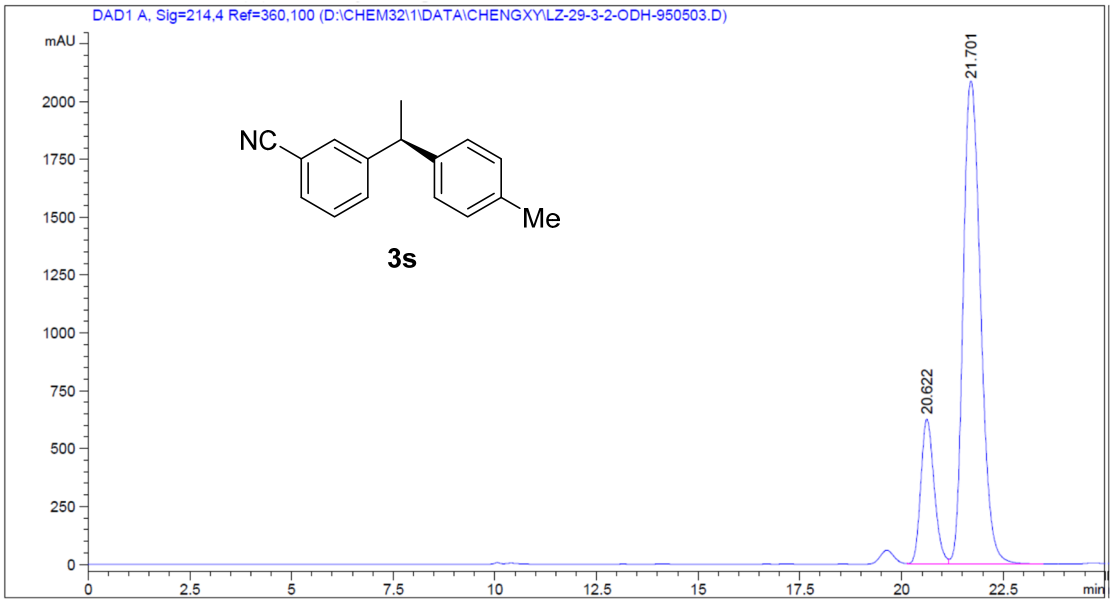
Peak#	Ret. Time	Area	Area%
1	11.989	20351200	67.817
2	16.305	9657989	32.183

Chiralcel OJH: hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min

Figure S78 HPLC spectrum comparison for **3s**



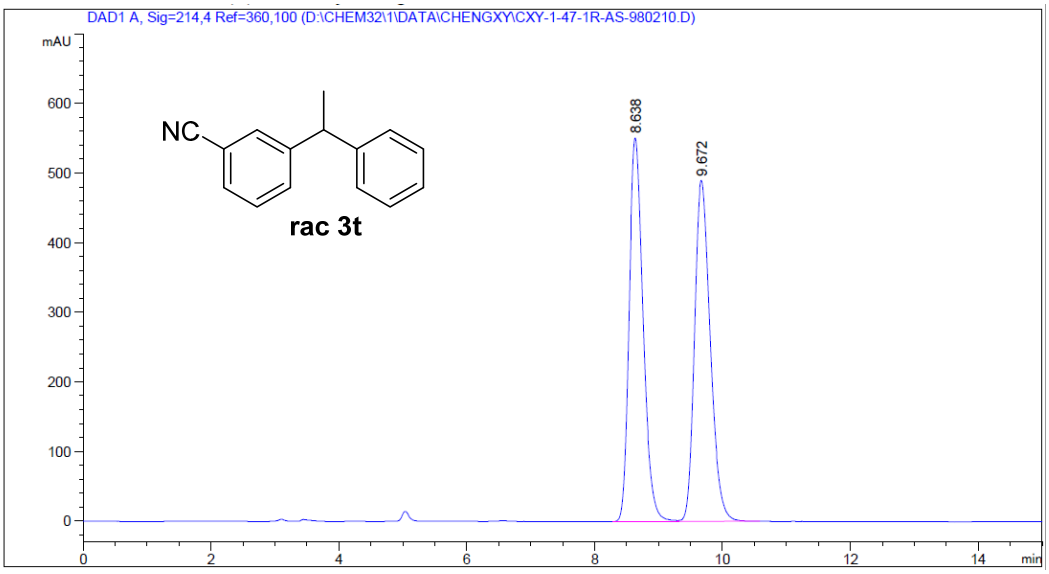
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.676	BV	0.3560	9953.46387	433.25800	48.4847
2	21.786	VB	0.3818	1.05756e4	425.77658	51.5153



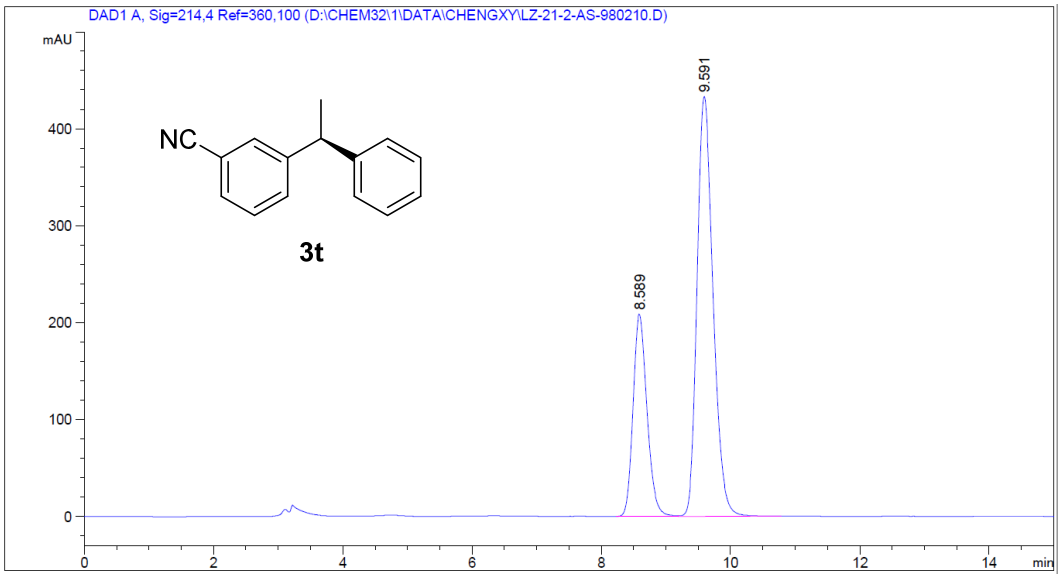
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.622	VV	0.3560	1.44185e4	627.57629	18.7475
2	21.701	VB	0.4710	6.24905e4	2088.95996	81.2525

Chiralcel ODH: hexane/*i*-PrOH = 95/5, flow rate 0.3 mL/min

Figure S79 HPLC spectrum comparison for **3t**



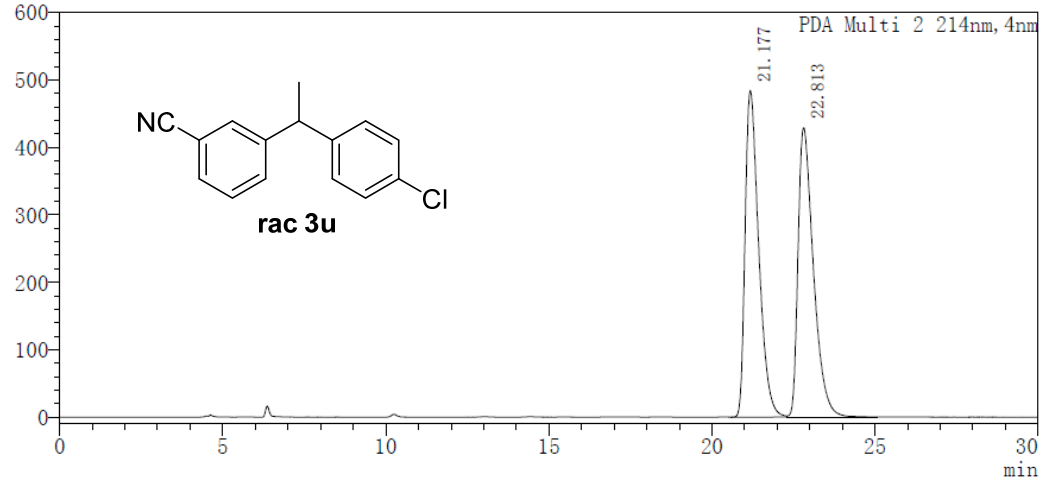
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.638	BV	0.2329	8361.52637	551.50507	49.9575
2	9.672	VB	0.2633	8375.75000	490.31387	50.0425



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.589	BV	0.2311	3130.65015	208.61572	29.6142
2	9.591	VB	0.2644	7440.78174	433.23083	70.3858

Chiralcel ASH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

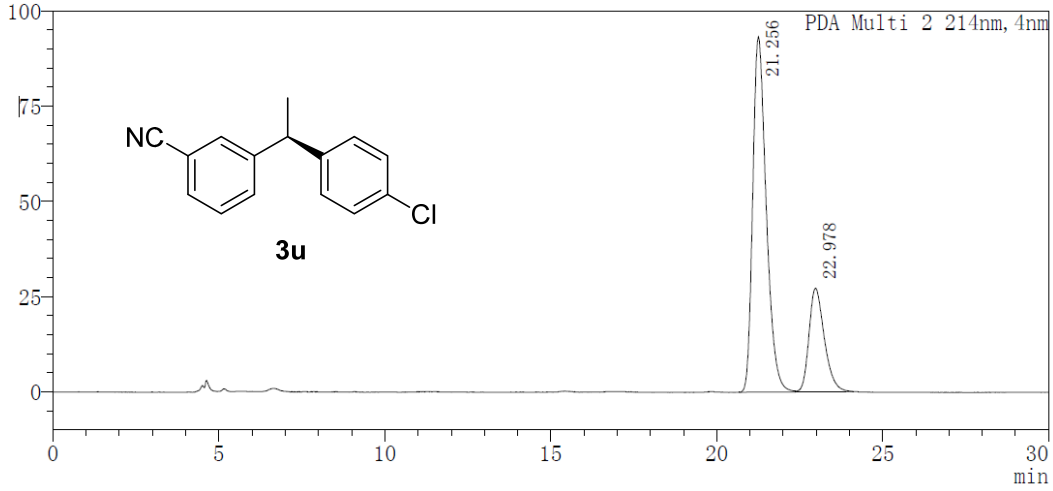
Figure S80 HPLC spectrum comparison for **3u**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	21.177	14055511	49.952
2	22.813	14082500	50.048



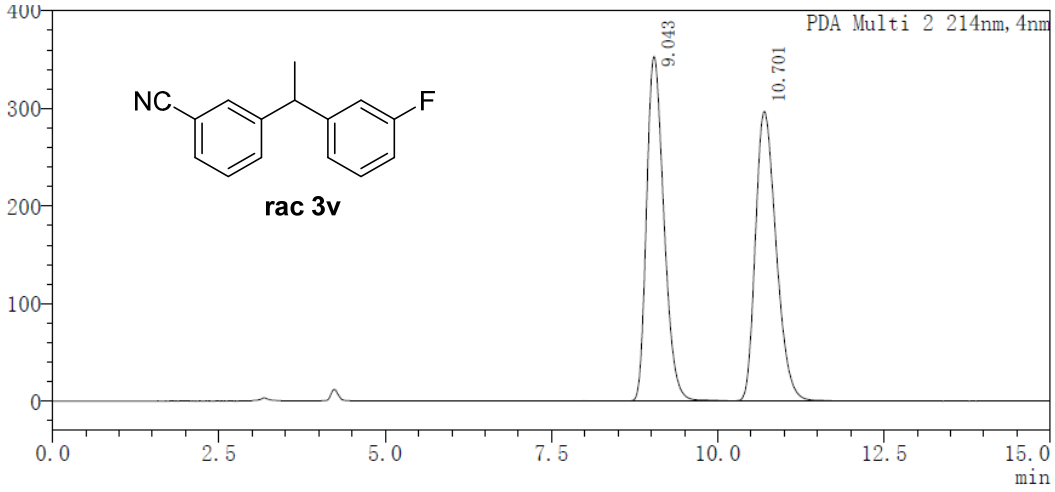
Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	21.256	2646236	75.139
2	22.978	875557	24.861

Chiralcel OJH: hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min

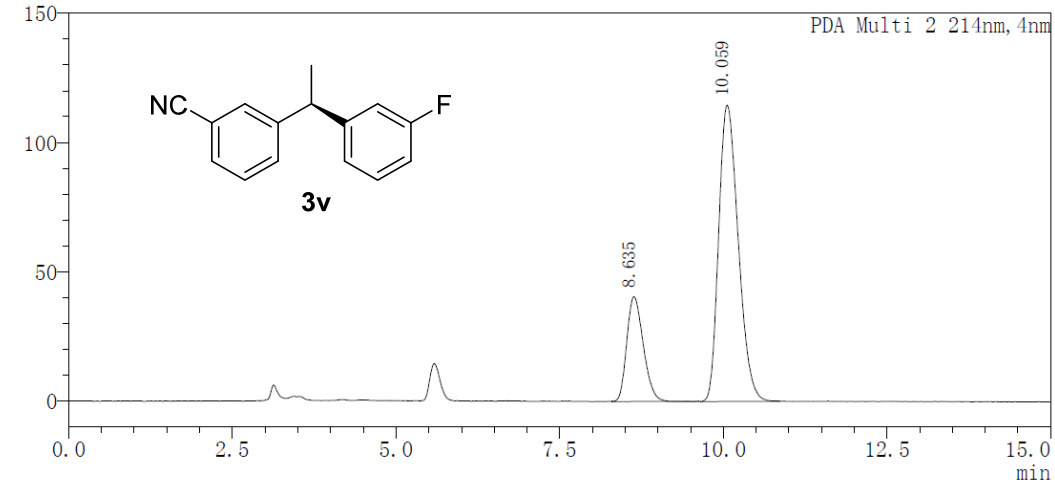
Figure S81 HPLC spectrum comparison for **3v**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	9.043	6415106	49.913
2	10.701	6437466	50.087

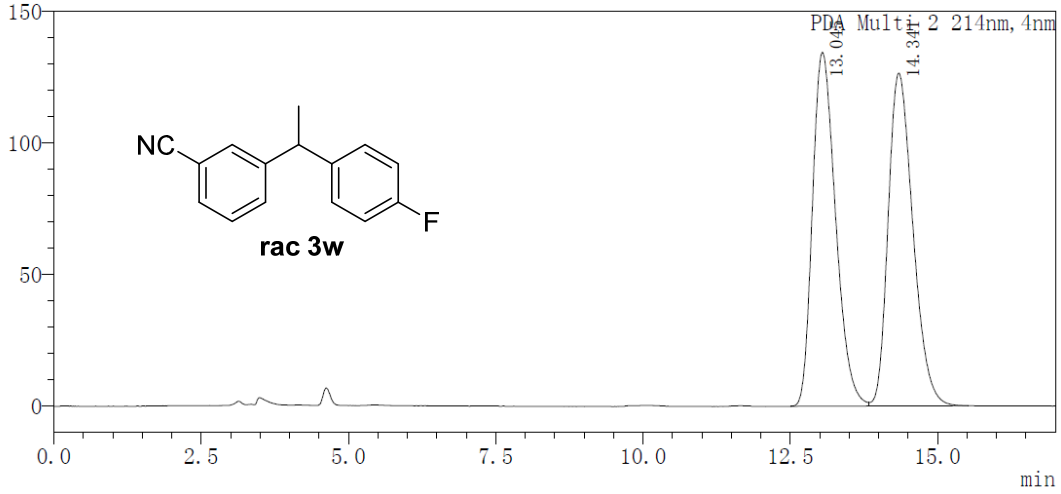


PDA Ch2 214nm

T	Hight	Area	Area%
8.635	40486	712424	23.032
10.059	114648	2380744	76.968

Chiralcel ASH: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min

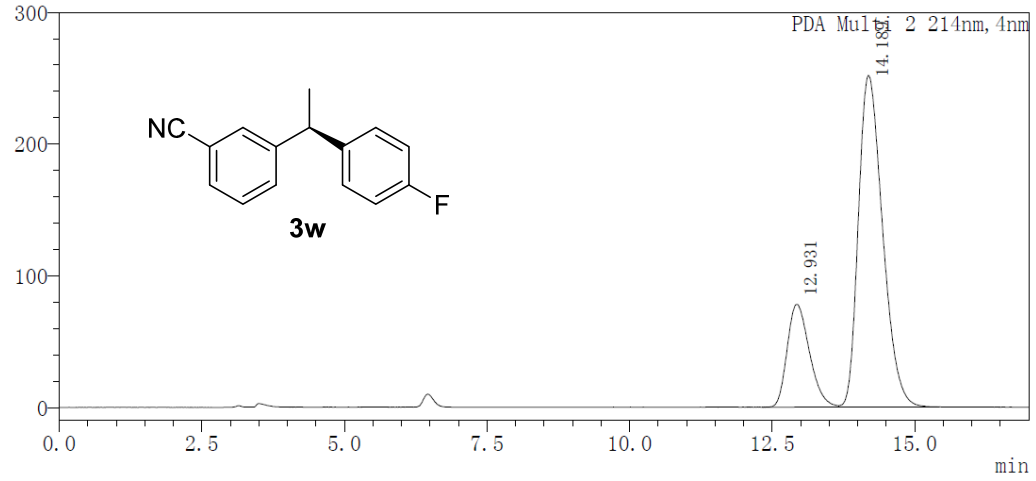
Figure S82 HPLC spectrum comparison for **3w**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	13.045	3669306	49.827
2	14.341	3694759	50.173



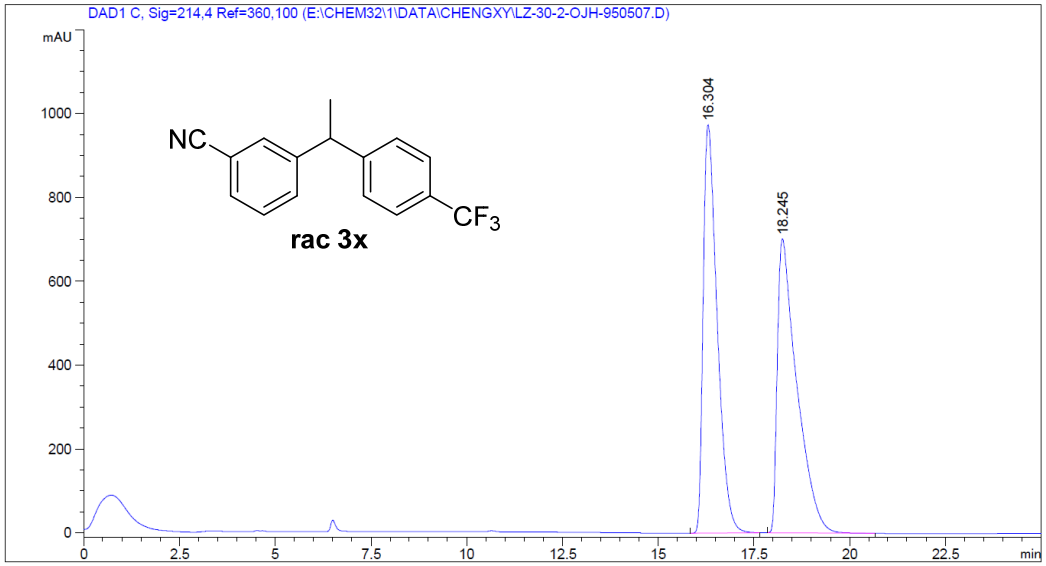
Peak Table

PDA Ch2 214nm

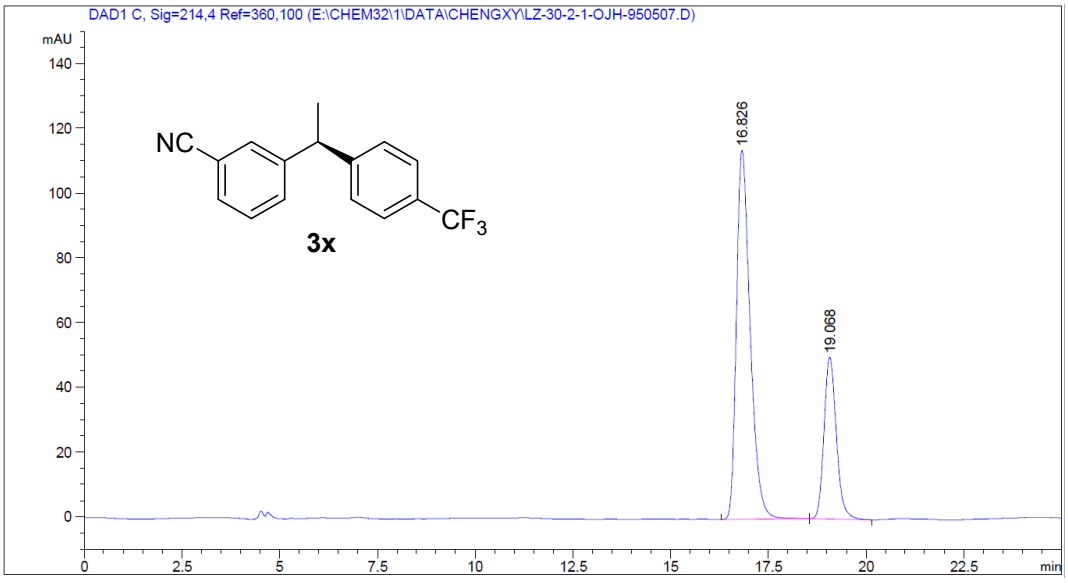
Peak#	Ret. Time	Area	Area%
1	12.931	2122723	22.204
2	14.189	7437389	77.796

Chiralcel ASH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

Figure S83 HPLC spectrum comparison for **3x**



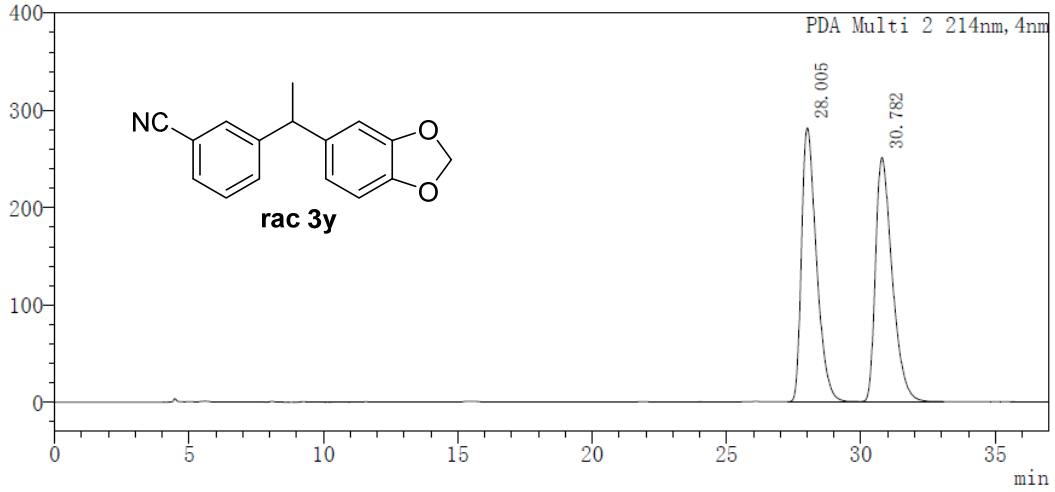
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.304	BB	0.3866	2.47373e4	972.91376	49.9743
2	18.245	BB	0.5000	2.47628e4	701.17352	50.0257



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.826	BB	0.3704	2778.61694	113.99885	71.6400
2	19.068	BB	0.3404	1099.96521	50.04404	28.3600

Chiralcel OJH: hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min

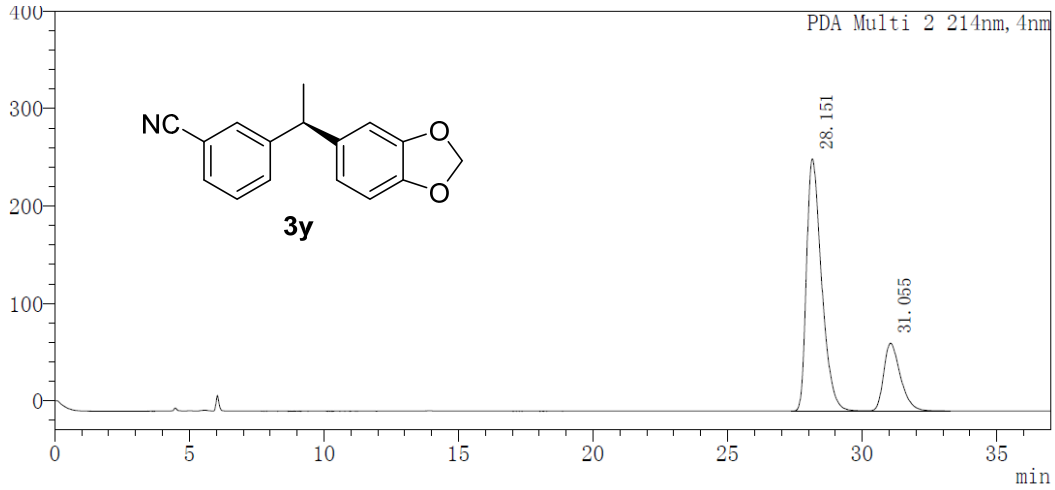
Figure S84 HPLC spectrum comparison for **3y**



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	28.005	10899776	50.003
2	30.782	10898414	49.997



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	28.151	10109757	77.005
2	31.055	3018910	22.995

Chiralcel ASH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min

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