Supporting Information

Atropoenantioselective Palladaelectro-Catalyzed Anilide C–H Olefinations by Catalyst Control Viable with Natural Sunlight as an Energy Source

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General Information

Technical grade solvents for extraction and chromatography (cyclohexane, *n*-pentane, dichloromethane, diethyl ether, ethyl acetate and methanol) were distilled before using. DCM, DMF and toluene were dried using a solvent purification system (SPS) from MBraun. DME was dried over sodium and distilled under N_2.

Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and graphite felt (GF) electrodes (10 mm × 15 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters.
Electrocatalysis was conducted using an AUTOLAB multichannel Line from METROHM.

Amides **1** were synthesized according to known procedure.[1] Olefins **2** were used as obtained by commercial sources. Other chemicals were obtained from commercial sources and were used without further purification.

Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were revealed using a 254 nm ultraviolet lamp.
Chromatography was carried out on Merck silica gel 60 (40–63 μm).
GPC were done using a recycling preparative HPLC system from Japan Analytical Industries (*LC-92XX II Series, UV and RI Detector*) connected to JAIGEL HH series column, with HPLC grade chloroform.

Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR spectroscopy.

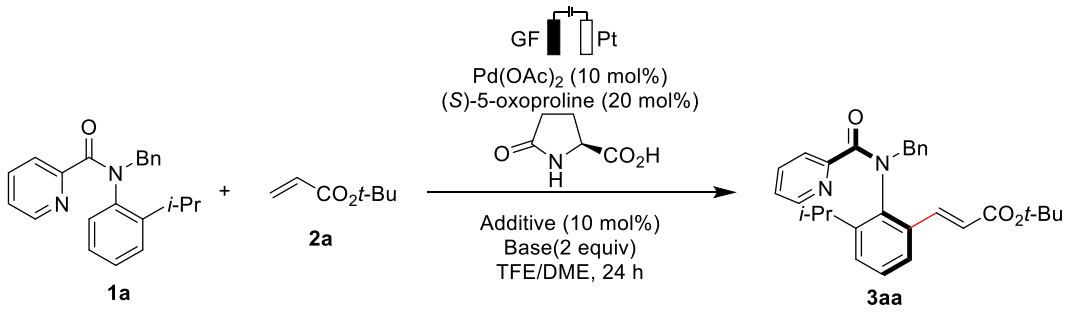
NMR spectra were recorded on a Varian Mercury VX 300, Inova 500 or Bruker Avance III 300, Avance III 400 and Avance III HD 500 with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.26 ppm or δ_C = 77.2 ppm). Data were treated with MestreNova software and are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, hept = heptet, m = multiplet, br = broad signal) and coupling constant (Hz).

Infrared spectra were recorded on a Bruker FT-IR Alpha-P device and are reported in wavenumbers (cm^{-1}).

High resolution mass spectrometry (HRMS) spectra were recorded with APEX IV 7T FTICR. ESI-MS on Bruker MicrOTOF and maXis.

Optical rotations were measured with Anton Paar MCP 150 at 20 °C under a Na/Hg lamp, λ = 589 nm (c in g/100 mL). Values were denoted as specific rotations: $[\alpha]_D^{20}$.
Chiral HPLC measurements were performed on an Agilent 1290 Infinity using CHIRALPAK® columns (3.0 µm particle size; Ø 4.6 mm and 250 mm lengths) at room temperature.
The structure of the major stereoisomer is shown. The ratio of diastereomers were established by means of ^{1}H-NMR spectroscopy.
The absolute configuration of the products was determined by comparison with Shi's article.[1]

Optimization of Reaction Conditions



Entry	Current	Temperature [°C]	Base	Additive	Comments	Yield [%]	*ee* [%]
1	4 mA	50	NaOAc	-		11	78
2	4 mA	50	NaOPiv	-		12	50
3	4 mA	50	NaOAc	1,4-BQ		78	97
4	4 mA	50	NaOAc	$Cu(OAc)_2•H_2O$		32	76
5	4 mA	50	NaOAc	2,5-di-*tert*-butyl-1,4- BQ		37	96
6	4 mA	50	NaOAc	(tris-4-bromophenyl)amine		22	86
7	4 mA	50	NaOAc	ferrocene		57	96
8	4 mA	50	NaOAc	1,4-BQ	Under N_2 atmosphere	65	98
9	4 mA	30	NaOAc	1,4- BQ		22	97
10	4 mA	50	NaOAc	1,4- BQ	*n*-Bu_4NPF_6 (2 equiv)	60	98
11	4 mA	60	NaOAc	1,4- BQ		88	98
12	6 mA	60	NaOAc	1,4- BQ		88	97
13	8 mA	60	NaOAc	1,4- BQ		54	97
14	10 mA	60	NaOAc	1,4- BQ		23	52
15	2 mA	60	NaOAc	1,4- BQ		51	98
16	6 mA	70	NaOAc	1,4- BQ		70	96
17	4 mA	30	NaOAc	1,4- BQ	Blue LED irradiation	Traces	/
18	4 mA	60	NaOAc	1,4- BQ	With divided cells[b]	45	95
19	0.8 V	60	NaOAc	1,4- BQ		63	96
20	0.4 V	60	NaOAc	1,4- BQ		81	97
21	-	60	NaOAc	1,4- BQ		42	97
22	-	60	NaOAc	-		28	96
23	4 mA	60	NaOAc	1,4- BQ	No palladium	0	/
24	-	60	NaOAc	1,4-BQ (1 equiv)		60	97

[a] Reaction conditions: Undivided cell, **1a** (0.5 mmol), **2a** (1.5 mmol), [Pd] (10 mol%), (*S*)-5-oxoproline (20 mol%), additive (10 mol%), base (1.0 mmol), 2,2,2-trifluoroethanol (2.5 mL), DME (2.5 mL), 24 h, graphite felt (GF) anode, Pt-plate cathode, isolated yields, under air. [b] Divided cell, anode: **1a** (0.5 mmol), **2a** (1.5 mmol), [Pd] (10 mol%), (*S*)-5-oxoproline (20 mol%), 1,4-BQ (10 mol%), NaOAc (0.5 mmol), 2,2,2-trifluoroethanol (2.5 mL), DME (2.5 mL), graphite felt, (GF) anode, cathode: NaOAc (0.5 mmol), 2,2,2-trifluoroethanol (2.5 mL), DME (2.5 mL), Pt-plate cathode. Constant anodic potential with a silver wire as the reference electrode.

Experimental

General procedure A: Atroposelective palladaelectro-catalyzed C–H olefination

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm x 15 mm x 6 mm) and a platinum cathode (10 mm x 15 mm x 025 mm). A 10 mL cell was charged with the amide **1** (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.3 mg, 10 mol%), (*S*)-5-oxoproline (12.9 mg, 20 mol%), 1,4-benzoquinone (5.4 mg, 10 mol%) and NaOAc (82 mg, 1.0 mmol, 2.0 equiv). Then was added 2.5 mL of TFE, 2.5 mL of DME and the olefin **2** (1.5 mmol, 3.0 equiv). The electrocatalysis was performed at 60 °C with a constant current of 4.0 mA maintained for 24 h. The resulting mixture was filtered through a celite pad, eluted with EtOAc and concentrated *in vacuo*. The residue was purified by column chromatography to afford the title compound **3**.

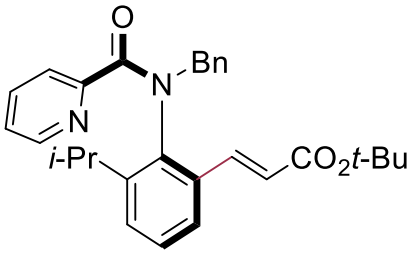
General procedure B: Sequential atroposelective palladaelectro-catalyzed C–H olefination/hydrogenation

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm x 15 mm x 6 mm) and a platinum cathode (10 mm x 15 mm x 025 mm). A 10 mL cell was charged with the amide **1** (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.3 mg, 10 mol%), (*S*)-5-oxoproline (12.9 mg, 20 mol%), 1,4-benzoquinone (5.4 mg, 10 mol%) and NaOAc (82 mg, 1.0 mmol, 2.0 equiv). Then was added 2.5 mL of TFE, 2.5 mL of DME and the olefin **2** (1.5 mmol, 3.0 equiv). The electrocatalysis was performed at 60 °C with a constant current of 4.0 mA maintained for 24 h. The current was then stopped and a balloon of H_2 was added. The mixture was stirred at 60 °C for 24 h, filtered through a celite pad, eluted with EtOAc and concentrated *in vacuo*. The residue was purified by column chromatography to afford the title compound **3**.

General procedure for the synthesis of racemic products

The racemic compounds were prepared using *rac*-(*S*/*R*)-5-oxoproline as the chiral ligand instead of (*S*)—5-oxoproline, following the general procedure A or B.

***Tert*-butyl 3-(3-(*N*-benzylpicolinamido)-3-isopropylphenyl)acrylate 3aa**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a pale yellow foam (205 mg, 0.45 mmol, 90%), with an enantiomeric ratio of 99/1.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_3^+$: 457.2486. Found: 457.2488;

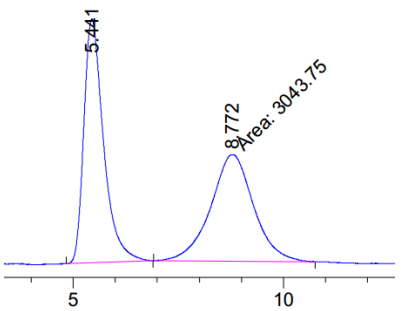
$[\alpha]_{20}^{D}$ = -88.9 (*c* = 1.00, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1049, 1078, 1147, 1233, 1257, 1287, 1316, 1367, 1390, 1445, 1472, 1568, 1585, 1639, 1704, 2869, 2931, 2967, 3007;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.66 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.54 (td, *J* = 7.8, 1.8 Hz, 1H), 7.32 (d, *J* = 15.9 Hz, 1H), 7.25 – 7.16 (m, 8H), 7.04 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.90 (d, *J* = 15.9 Hz, 1H), 5.20 (d, *J* = 13.6 Hz, 1H), 4.75 (d, *J* = 13.6 Hz, 1H), 2.98 (hept, *J* = 6.8 Hz, 1H), 1.50 (s, 9H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 (C_q), 165.7 (C_q), 153.3 (C_q), 147.6 (CH), 147.1, (C_q) 140.5 (CH), 139.0 (C_q), 136.0 (CH), 135.9 (C_q), 133.4 (C_q), 130.6 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 124.4 (CH), 124.3 (CH), 124.2 (CH), 121.7 (CH), 80.3 (C_q), 54.5 (CH_2), 28.3 (CH_3), 28.2 (CH), 24.2 (CH_3), 23.6 (CH_3);

R_t (AS-3 column, Hex/IPA 95/5, 1.2 mL/min, 273 nm): t_r(major) = 5.4 min, t_r(minor) = 8.8 min, 98% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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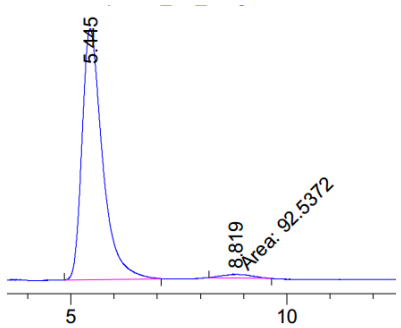
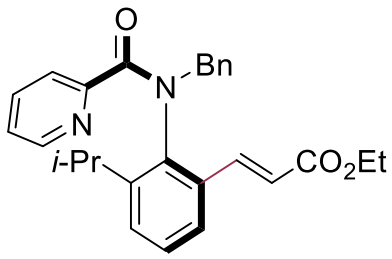
2	8.772	MM	1.1871	3043.75049	42.73253	48.9412



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.445	BV R	0.4726	4323.95996	131.51231	99.0395
2	8.819	MM	0.5617	41.93618	1.24432	0.9605

Ethyl (E)-3-(2-(N-benzylpicolinamido)-3-isopropylphenyl)acrylate 3ab



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (186 mg, 0.43 mmol, 87%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3^+$: 429.2173. Found: 429.2173;

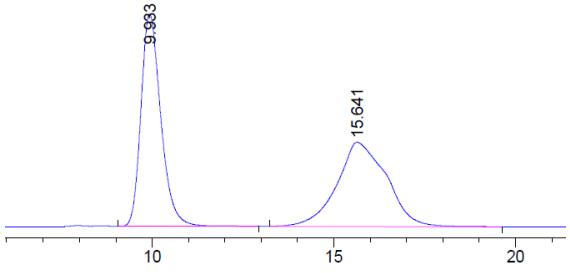
[α]$_{20}^{D}$ = -120.2 (*c* = 1.02, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1044, 1078, 1166, 1260, 1308, 1365, 1390, 1444, 1495, 1567, 1585, 1638, 1709, 2869, 2929, 2964, 3061;

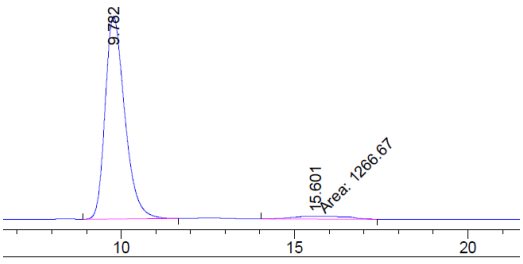
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.67 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.58–7.52 (m, 1H), 7.48–7.42 (m, 1H), 7.27–7.21 (m, 3H), 7.21–7.15 (m, 5H), 7.04 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 5.17 (d, *J* = 13.6 Hz, 1H), 4.78 (d, *J* = 13.6 Hz, 1H), 4.25–4.14 (m, 2H), 2.93 (hept, *J* = 6.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 (C_q), 166.5 (C_q), 153.3 (C_q), 147.6 (CH), 147.1 (C_q), 141.7 (CH), 139.2 (C_q), 136.1 (CH), 135.9 (C_q), 133.4 (C_q), 130.6 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 124.4 (CH), 124.3 (CH), 119.8 (CH), 60.4 (CH_2), 54.6 (CH_2), 28.2 (CH), 24.2 (CH_3), 23.5 (CH_3), 14.4 (CH_3);

R_t (AS-3 column, Hex/IPA 95/5, 1.2 mL/min, 273 nm): t_r(major) = 9.8 min, t_r(minor) = 15.6 min, 92% *ee*.

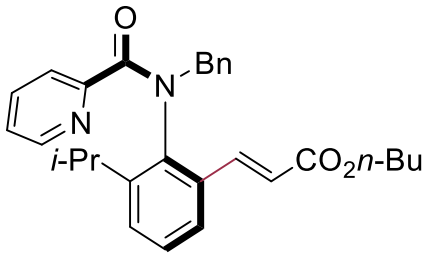


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.933	BB	0.5821	2.00703e4	526.10376	50.3262
2	15.641	BB	1.2132	1.98102e4	208.56114	49.6738



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.782	BB	0.6039	3.14313e4	799.04297	96.1261
2	15.601	MM	1.8874	1266.67065	11.18519	3.8739

Butyl (E)-3-(2-(N-benzylpicolinamido)-3-isopropylphenyl)acrylate 3ac



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (178 mg, 0.39 mmol, 78%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{29}H_{33}N_2O_3^+$: 457.2486. Found: 457.2487;

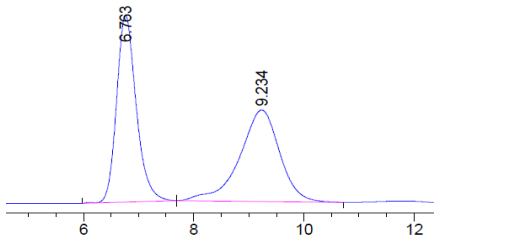
$[\alpha]_{20}^{D}$ = -49.9 (*c* = 0.95, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1064, 1166, 1260, 1307, 1388, 1445, 1470, 1567, 1585, 1640, 1709, 2870, 2932, 2961, 3030, 3063;

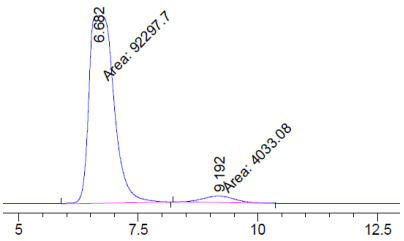
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.64 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.50 (td, *J* = 7.8, 1.8 Hz, 1H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.23–7.18 (m, 3H), 7.17–7.11 (m, 5H), 7.01–6.95 (m, 1H), 5.98 (d, *J* = 15.9 Hz, 1H), 5.15 (d, *J* = 13.6 Hz, 1H), 4.75 (d, *J* = 13.6 Hz, 1H), 4.15–4.06 (m, 2H), 2.93 (hept, *J* = 6.8 Hz, 1H), 1.68–1.58 (m, 2H), 1.45–1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 (C_q), 166.3 (C_q), 153.0 (C_q), 147.3 (CH), 146.9 (C_q), 141.3 (CH), 138.9 (C_q), 135.8 (CH), 135.7 (C_q), 133.1 (C_q), 130.3 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 124.3 (CH), 124.1 (CH), 124.0 (CH), 119.6 (CH), 64.2 (CH_2), 54.4 (CH_2), 30.6 (CH_2), 28.0 (CH), 24.1 (CH_3), 23.3 (CH_3), 19.1 (CH_2), 13.7 (CH_3).

R_t (AS-3 column, Hex/IPA 90/10, 1.0 mL/min, 273 nm): t_r(major) = 6.7 min, t_r(minor) = 9.2 min, 92% *ee*.

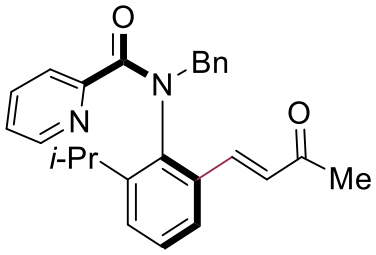


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.763	VB R	0.3748	1.31658e4	533.04437	50.0021
2	9.234	BB	0.7379	1.31647e4	260.82016	49.9979



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.682	MM	0.6027	9.22977e4	2552.25073	95.8133
2	9.192	MM	0.7677	4033.08496	87.55834	4.1867

***N*-benzyl-*N*-(2-isopropyl-6-(3-oxobut-1-en-1-yl)phenyl)picolinamide 3ad**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) followed by GPC afforded the title compound as pale brown powder (141 mg, 0.35 mmol, 71%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{26}H_{27}N_2O_2^+$: 399.2067. Found: 399.2067;

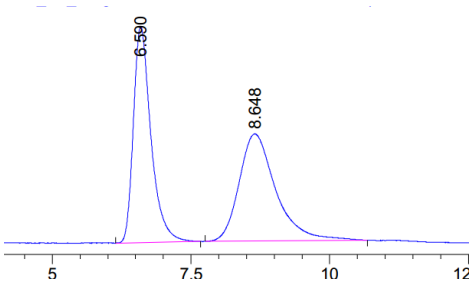
[α]$^{D}_{20}$ = -41.3 (*c* = 1.03, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1048, 1079, 1166, 1228, 1255, 1286, 1336, 1359, 1389, 1444, 1472, 1495, 1568, 1584, 1660, 1691, 2245, 2869, 2930, 2964, 3030, 3061;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.00 (m, 1H), 7.71 – 7.61 (m, 1H), 7.56 (td, *J* = 7.7, 1.5 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.25 – 7.18 (m, 5H), 7.06 (t, *J* = 6.2 Hz, 1H), 7.01 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 5.61 (d, *J* = 13.5 Hz, 1H), 4.35 (d, *J* = 13.5 Hz, 1H), 3.14 (hept, *J* = 6.8 Hz, 1H), 2.00 (s, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2 (C_q), 154.6 (C_q), 147.5 (C_q), 147.1 (C_q), 141.5 (CH), 139.6 (C_q), 136.2 (CH), 135.8 (C_q), 133.5 (C_q), 130.7 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 124.1 (CH), 54.8 (CH_2), 28.4 (CH_3), 26.0 (CH), 24.5 (CH_3), 23.7 (CH_3);

R_t (AS-3 column, Hex/IPA 80/20, 1.0 mL/min, 273 nm): t_r(major) = 6.6 min, t_r(minor) = 8.6 min, 92% *ee*.



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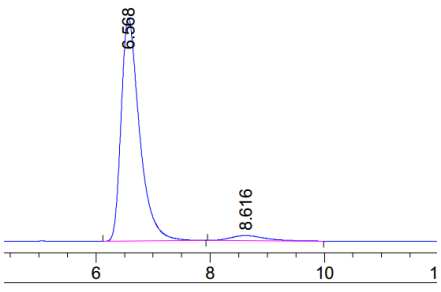
2	8.648	BB	0.6228	1047.75989	22.77252	50.9313



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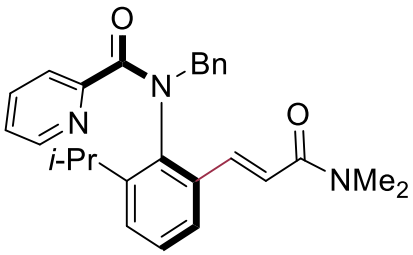
1	6.568	BB	0.3381	1.67912e4	750.32416	95.9003
2	8.616	BB	0.5074	717.81958	17.14570	4.0997

***N*-benzyl-*N*-(2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-6-isopropylphenyl)picolinamide 3ae**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (DCM/MeOH = 98:2) afforded the title compound as white foam (143 mg, 0.33 mmol, 67%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{27}H_{30}N_3O_2^+$: 428.2333. Found: 428.2334;

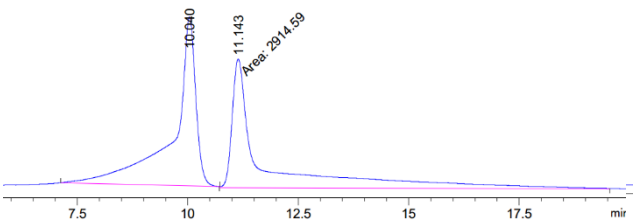
$[\alpha]_{20}^{D}$ = -183.9 (*c* = 1.07, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1049, 1078, 1140, 1167, 1260, 1286, 1336, 1359, 1391, 1443, 1472, 1494, 1567, 585, 1608, 1642, 2239, 2869, 2930, 2963, 3030, 3062;

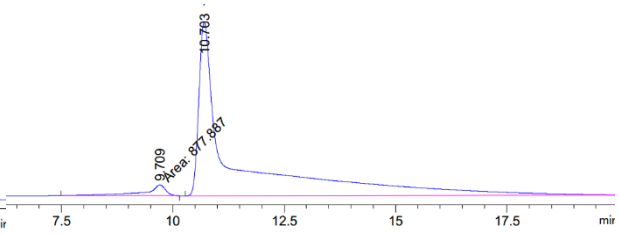
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.7 Hz, 1H), 7.66 (dd, *J* = 11.6, 3.8 Hz, 1H), 7.59 (d, *J* = 15.6 Hz, 1H), 7.53 (td, *J* = 7.8, 1.6 Hz, 1H), 7.37 – 7.22 (m, 4H), 7.21 – 7.15 (m, 3H), 7.11 – 6.99 (m, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 5.22 (d, *J* = 13.8 Hz, 1H), 4.75 (d, *J* = 13.8 Hz, 1H), 3.03 (s, 6H), 2.77 (hept, *J* = 6.7 Hz, 1H), 0.56 (d, *J* = 6.7 Hz, 3H), 0.53 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 (C_q), 166.6 (C_q), 153.2 (C_q), 147.8 (CH), 147.2(C_q), 139.4 (CH), 138.8 (C_q), 136.5 (C_q), 136.1 (CH), 134.0 (C_q), 130.6 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 125.2 (CH), 124.4 (CH), 124.4 (CH), 120.2 (CH), 54.4 (CH_2), 37.6 (CH), 28.0 (CH_3), 24.0 (CH_3), 23.4 (CH_3);

R_t (AD-3 column, Hex/IPA 70/30, 1.0 mL/min, 250 nm): t_r(major) = 10.7 min, t_r(minor) = 9.7 min, 92% *ee*.

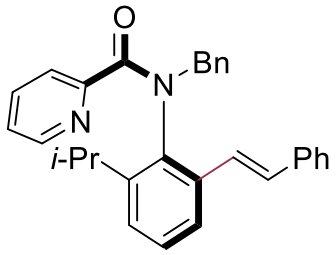


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.040	BB	0.4858	2949.52271	81.78178	50.2979
2	11.143	MM	0.7803	2914.58667	62.25060	49.7021



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.709	MM	0.5481	877.88690	26.69431	3.8193
2	10.703	BBA	0.6614	2.21074e4	435.39688	96.1807

***N*-benzyl-*N*-(2-isopropyl-6-styrylphenyl)picolinamide 3af**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as pale brown foam (146 mg, 0.34 mmol, 68%), with an enantiomeric ratio of 98/2.

HRMS (ESI) calcd for $C_{30}H_{29}N_2O^+$: 433.2274. Found: 433.2277;

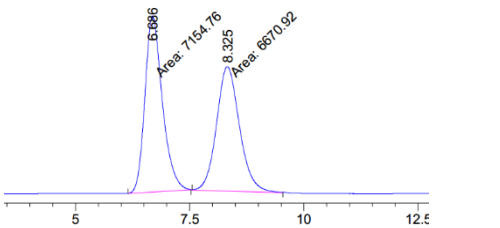
$[\alpha]_{20}^{D}$ = -137.4 (*c* = 0.85, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1049, 1078, 1167, 1242, 1286, 1335, 1392, 1440, 1471, 1496, 1567, 1585, 1640, 2868, 2930, 3028, 3060;

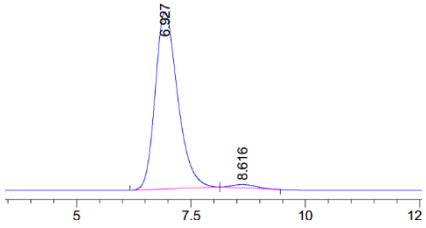
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 (ddt, *J* = 12.4, 7.0, 1.1 Hz, 3H), 7.26 – 7.23 (m, 3H), 7.22 – 7.14 (m, 4H), 7.09 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.04 (ddd, *J* = 6.1, 4.7, 2.7 Hz, 1H), 6.82 (d, *J* = 16.3 Hz, 1H), 6.70 (d, *J* = 16.3 Hz, 1H), 5.19 (d, *J* = 13.6 Hz, 1H), 4.87 (d, *J* = 13.6 Hz, 1H), 3.02 (hept, *J* = 6.8 Hz, 1H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1 (C_q), 153.7 (C_q), 147.8 (CH), 147.0 (C_q), 138.1 (C_q), 137.3 (C_q), 136.5 (C_q), 135.9 (C_q), 135.8 (CH), 130.6 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 126.7 (CH), 126.3 (CH), 125.9 (CH), 124.2 (CH), 123.8 (CH), 123.3 (CH), 54.5 (CH_2), 28.3 (CH), 24.4 (CH_3), 23.6 (CH_3);

R_t (AS-3 column, Hex/IPA 90/10, 1.0 mL/min, 273 nm): t_r(major) = 6.9 min, t_r(minor) = 8.6 min, 96% *ee*.

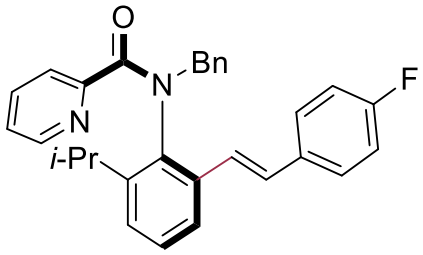


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.686	MM	0.4418	7154.75928	269.89392	51.7498
2	8.325	MM	0.5825	6670.91699	190.87000	48.2502



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.927	BB	0.5218	1.56784e4	458.66119	97.9529
2	8.616	BB	0.4450	327.66302	8.93064	2.0471

***N*-benzyl-*N*-(2-(4-fluorostyryl)-6-isopropylphenyl)picolinamide 3ag**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as pale brown foam (145 mg, 0.32 mmol, 65%), with an enantiomeric ratio of 97/3.

HRMS (ESI) calcd for $C_{30}H_{28}FN_2O^+$: 451.2180. Found: 451.2181;

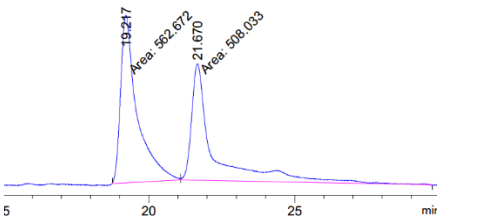
$[\alpha]_{20}^{D}$ = -120.8 (*c* = 0.96, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1049, 1078, 1095, 1158, 1226, 1287, 1336, 1392, 1443, 1472, 1508, 1568, 1585, 1600, 1639, 2869, 2929, 2964, 3031, 3063;

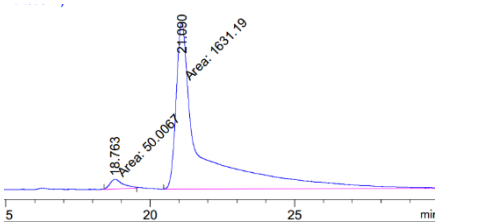
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dt, *J* = 4.7, 1.3 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.37 – 7.35 (m, 2H), 7.28 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.22 – 7.16 (m, 6H), 7.10 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.04 (ddd, *J* = 5.8, 4.8, 2.9 Hz, 1H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 16.2 Hz, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.25 (d, *J* = 13.6 Hz, 1H), 4.77 (d, *J* = 13.6 Hz, 1H), 3.03 (hept, *J* = 6.8 Hz, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1 (C_q), 162.5 (d, *J* = 247.4 Hz, C_q), 153.7 (C_q), 147.7 (CH), 147.0 (C_q), 138.1 (C_q), 136.5 (C_q), 135.9 (CH), 135.8 (C_q), 133.5 (d, *J* = 3.3 Hz, C_q), 130.6 (CH), 129.2 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 126.3 (CH), 125.7 (d, *J* = 2.4 Hz, CH), 124.3 (CH), 123.8 (CH), 123.2 (CH), 115.6 (d, *J* = 21.6 Hz, CH), 54.5 (CH_2), 28.4 (CH), 24.4 (CH_3), 23.7 (CH_3); **^{19}F NMR** (282 MHz) δ -114,1;

R_t (AD-3 column, Hex/IPA 90/10, 1.2 mL/min, 250 nm): t_r(major) = 21.1 min, t_r(minor) = 18.8 min, 94% *ee*.

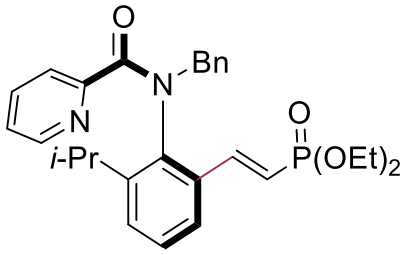


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.217	MM	0.6613	562.67200	14.18154	52.5515
2	21.670	MM	0.8608	508.03329	9.83628	47.4485



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.763	MM	0.5229	50.00674	1.59392	2.9745
2	21.090	MM	0.9868	1631.18945	27.55057	97.0255

Diethyl (2-(*N*-benzylpicolinamido)-3-isopropylstyryl)phosphate 3ah



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 8:2) afforded the title compound as pale brown foam (81 mg, 0.16 mmol, 33%), with an enantiomeric ratio of 94.5/5.5.

HRMS (ESI) calcd for $C_{28}H_{34}N_2O_4P^+$: 493.2251. Found: 493.2252;

$[\alpha]_{20}^{D}$ = -89.9 (*c* = 1.03, $CHCl_3$);

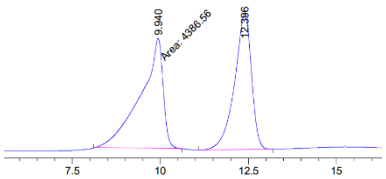
ν_{max} (thin film/cm^{-1}): 1023, 1049, 1165, 1241, 1284, 1336, 1391, 1443, 1472, 1568, 1585, 1643, 2869, 2929, 2965, 3062;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.57 (td, *J* = 7.8, 1.7 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.23 – 7.20 (m, 3H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.06 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 6.02 (dd, *J* = 19.1, 17.5 Hz, 1H), 5.03 (d, *J* = 13.7 Hz, 1H), 4.90 (d, *J* = 13.7 Hz, 1H), 4.14 – 3.96 (m, 4H), 2.85 (hept, *J* = 6.8 Hz, 1H), 1.31 (d, *J* = 7.1 Hz, 6H), 0.70 (d, *J* = 6.8 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H);

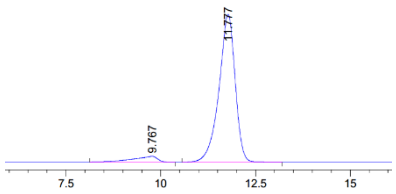
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (C_q), 153.1 (C_q), 147.5 (CH), 147.1 (C_q), 144.9 (d, *J* = 6.9 Hz, CH), 139.1 (C_q), 136.2 (CH), 135.9 (C_q), 133.6 (d, *J* = 22.6 Hz, C_q), 130.5 (CH), 128.6 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 124.5 (CH), 124.2 (CH), 124.2 (CH), 116.3 (d, *J* = 192.0 Hz, CH), 62.1 (d, *J* = 5.6 Hz, CH_2), 62.0 (d, *J* = 5.9 Hz, CH_2), 54.8 (CH_2), 28.2 (CH), 24.0 (CH_3), 23.6 (CH_3), 16.6 (CH_3), 16.5 (CH_3);

^{31}P NMR (121 MHz) δ 18.3;

R_t (AD-3 column, Hex/IPA 80/20, 1.0 mL/min, 250 nm): t_r(major) = 11.8 min, t_r(minor) = 9.8 min, 89% *ee*.

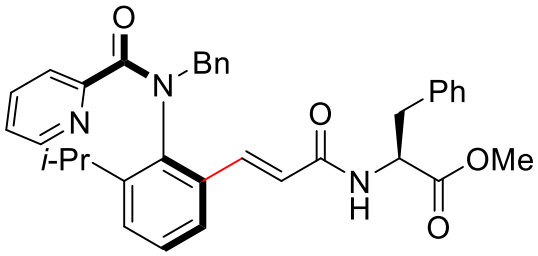


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.940	MM	0.7452	4386.56152	98.10385	52.0086
2	12.396	BB	0.4930	4047.74365	121.40254	47.9914



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.767	BB	0.5826	890.14789	19.79703	5.6820
2	11.777	BB	0.4434	1.47759e4	497.65439	94.3180

Methyl (3-(2-(*N*-benzylpicolinamido)-3-isopropylphenyl)acryloyl)-*L*-phenylalaninate 3ai



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3 to 6:4) afforded the title compound as white foam (270 mg, 0.4 mmol, 96%), with an diastereomeric ratio >95/5.

HRMS (ESI) calcd for $C_{35}H_{36}N_3O_4^+$: 562.2700. Found: 562.2697;

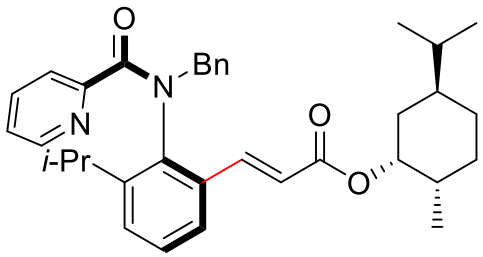
$[\alpha]_{20}^{D}$ = -40.7 (*c* = 0.96, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1079, 1170, 1205, 1237, 1261, 1285, 1335, 1359, 1394, 1444, 1496, 1534, 1585, 1630, 1743, 2248, 2869, 2930, 2963, 3030, 3063, 3317;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dt, *J* = 3.9, 0.8 Hz, 1H), 7.61 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.54 (td, *J* = 7.7, 1.7 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 (td, *J* = 7.1, 1.8 Hz, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.12 (m, 5H), 7.07 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 6.02 (d, *J* = 15.8 Hz, 1H), 5.08 (d, *J* = 13.7 Hz, 1H), 4.94 (dt, *J* = 7.7, 5.9 Hz, 1H), 4.86 (d, *J* = 13.7 Hz, 1H), 3.76 (s, 3H), 3.30 – 3.07 (m, 2H), 2.91 (hept, *J* = 6.8 Hz, 1H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3 (C_q), 168.4 (C_q), 165.5 (C_q), 153.3 (C_q), 147.8 (CH), 147.1 (C_q), 138.8 (C_q), 138.0 (CH), 136.2 (CH), 136.2 (C_q), 136.0 (C_q), 133.6 (C_q), 130.6 (CH), 129.4 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 124.5 (CH), 124.5 (CH), 124.2 (CH), 122.6 (CH), 54.4 (CH_2), 53.5 (CH), 52.5 (CH_3), 38.1 (CH_2), 28.2 (CH), 24.2 (CH_3), 23.6 (CH_3).

(2R,5R)-5-isopropyl-2-methylcyclohexyl (E)-3-(2-(N-benzylpicolinamido)-3-isopropylphenyl)acrylate 3aj



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a colorless foam (197 mg, 0.37 mmol, 73%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{35}H_{43}N_2O_3^+$: 539.3268. Found: 539.3272;

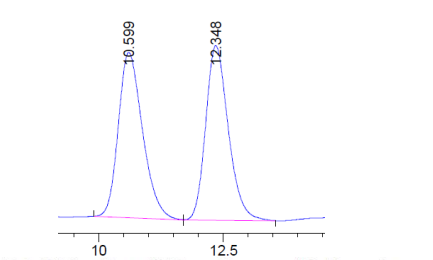
$[\alpha]_{20}^{D}$ = -58.5 (*c* = 1.00, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1078, 1168, 1260, 1306, 1388, 1445, 1585, 1643, 1704, 2869, 2928, 2957;

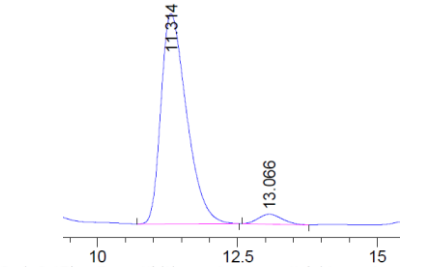
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.05 (m, 1H), 7.75 – 7.65 (m, 1H), 7.59 – 7.35 (m, 2H), 7.30 – 7.10 (m, 9H), 7.10 – 7.01 (m, 1H), 6.07 – 5.89 (m, 1H), 5.45 – 5.08 (m, 1H), 4.93 – 4.57 (m, 2H), 3.19 – 2.87 (m, 1H), 2.04 (td, *J* = 14.5, 3.8 Hz, 1H), 1.91 (hept, *J* = 3.4 Hz, 1H), 1.79 – 1.66 (m, 2H), 1.62 – 1.36 (m, 2H), 1.03 – 0.88 (m, 10H), 0.84 – 0.76 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3 (C_q), 165.9 (C_q), 153.3 (C_q), 147.4 (CH), 147.1 (C_q), 141.2 (CH), 139.1 (C_q), 135.9 (CH), 135.8 (C_q), 133.3 (C_q), 130.5 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 124.4 (CH), 124.3 (CH), 124.1 (CH), 120.2 (CH), 74.1 (CH), 54.4 (CH_2), 47.1 (CH), 41.0 (CH_2), 34.3 (CH_2), 31.4 (CH), 28.2 (CH), 26.3 (CH), 24.1 (CH_3), 23.6 (CH_2), 23.5 (CH_3), 22.1 (CH_3), 20.9 (CH_3), 16.5 (CH_3);

R_t (AD-3 column, Hex/IPA 90/10, 1.0 mL/min, 273 nm): t_r(major) = 11.3 min, t_r(minor) = 13.1 min, 92% *ee*.

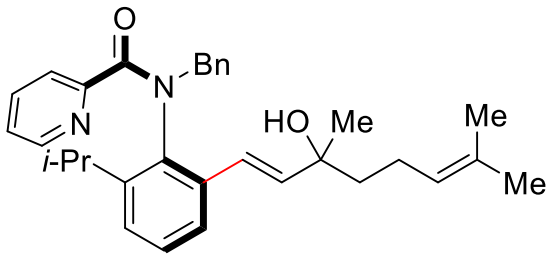


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.599	BB	0.4746	5152.04834	151.95399	50.3342
2	12.348	VB R	0.4473	5083.63867	160.59016	49.6658



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.314	BB	0.4686	1.27023e4	397.71057	95.7660
2	13.066	BB	0.3505	561.59180	18.90808	4.2340

(E)-N-benzyl-N-(2-(3-hydroxy-3,7-dimethylocta-1,6-dien-1-yl)-6-isopropylphenyl) picolinamide 3ak



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the two diastereoisomer of the title compound as colorless oils in a ratio of 1/1 (146 mg, 0.30 mmol, 60%). The two diastereoisomers were separated by column chromatography.

The first fraction has an enantiomeric ratio of 97.5/2.5.

HRMS (ESI) calcd for $C_{32}H_{39}N_2O_2^+$: 483.3006. Found: 483.2994;

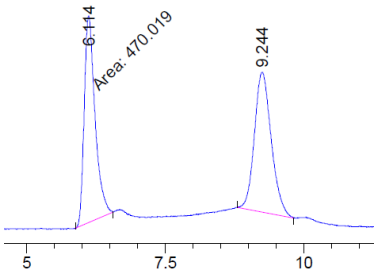
$[\alpha]_{20}^{D}$ = -204 (*c* = 0.50, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1078, 1167, 1238, 1286, 1336, 1396, 1441, 1473, 1567, 1585, 1637, 2868, 2926, 2963, 3059, 3440;

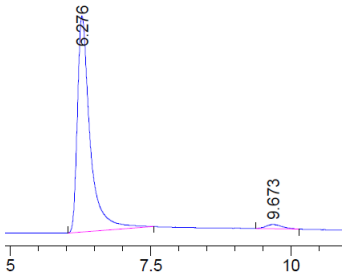
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.8, 1H), 7.52 – 7.43 (m, 2H), 7.37 – 7.31 (m, 2H), 7.27 – 7.21 (m, 3H), 7.16 – 7.11 (m, 2H), 7.10 – 7.05 (m, 1H), 7.06 – 7.01 (m, 1H), 6.14 (d, *J* = 16.1 Hz, 1H), 5.90 (d, *J* = 16.1 Hz, 1H), 5.29 (d, *J* = 13.7 Hz, 1H), 5.10 – 5.03 (m, 1H), 4.66 (d, *J* = 13.7 Hz, 1H), 3.03 (hept, *J* = 6.8 Hz, 1H), 1.99 – 1.81 (m, 2H), 1.66 (q, *J* = 1.3 Hz, 3H), 1.55 (d, *J* = 1.4 Hz, 3H), 1.53 – 1.39 (m, 2H), 1.15 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C_q), 153.6 (C_q), 147.9 (CH), 146.8 (C_q), 138.5 (CH), 137.9 (C_q), 136.6 (C_q), 135.8 (CH), 135.5 (C_q), 131.7 (C_q), 130.8 (CH), 128.5 (CH), 128.1 (CH), 127.9 (CH), 126.1 (CH), 124.5 (CH), 124.2 (CH), 124.1 (CH), 123.7 (CH), 123.4 (CH), 73.1 (C_q), 54.3 (CH_2), 42.3 (CH_2), 28.3 (CH), 28.1 (CH_3), 25.8 (CH_3), 24.5 (CH_3), 23.6 (CH_3), 23.0 (CH_2), 17.8 (CH_3);

R_t (AD-3 column, Hex/IPA 80/20, 1.0 mL/min, 273 nm): P1 t_r(major) = 6.3 min, t_r(minor) = 9.7 min, 95% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.114	MM	0.2262	470.01938	34.63272	48.7111
2	9.244	BB	0.2731	494.89340	23.45688	51.2889



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.276	BB	0.2305	3721.78101	236.60236	97.5673
2	9.673	BB	0.2361	92.79662	4.70594	2.4327

The second fraction has an enantiomeric ratio of 96.5/3.5.

HRMS (ESI) calcd for $C_{32}H_{39}N_2O_2^+$: 483.3006. Found: 483.2995;

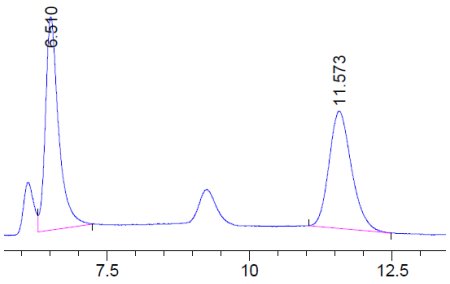
$[\alpha]_{20}^{D}$ = -88.8 (*c* = 1.00, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1078, 1167, 1240, 1286, 1336, 1394, 1442, 1472, 1568, 1585, 1637, 2868, 2926, 2964, 3061, 3454;

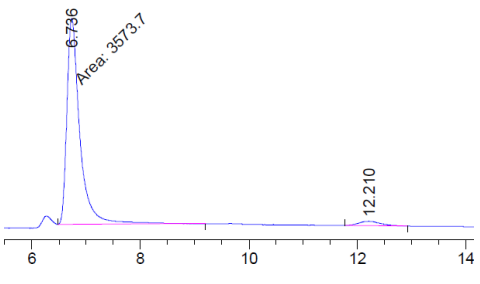
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.16 (m, 1H), 7.52 – 7.44 (m, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 7.15 – 7.12 (m, 2H), 7.09 – 7.05 (m, 1H), 7.03 (ddd, *J* = 6.9, 4.8, 1.8 Hz, 1H), 6.18 (d, *J* = 16.1 Hz, 1H), 5.92 (d, *J* = 16.1 Hz, 1H), 5.26 (d, *J* = 13.6 Hz, 1H), 5.09 – 5.03 (m, 1H), 4.70 (d, *J* = 13.6 Hz, 1H), 3.02 (hept, *J* = 6.8 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.50 – 1.41 (m, 2H), 1.16 (s, 3H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C_q), 153.6 (C_q), 147.9 (CH), 146.8 (C_q), 138.7 (CH), 137.8 (C_q), 136.6 (C_q), 135.7 (CH), 135.4 (C_q), 131.8 (C_q), 130.7 (CH), 128.5 (CH), 128.1 (CH), 127.8 (CH), 126.1 (CH), 124.4 (CH), 124.2 (CH), 124.1 (CH), 123.7 (CH), 123.5 (CH), 73.0 (C_q), 54.3 (CH_2), 42.6 (CH_2), 28.3 (CH), 27.5 (CH_3), 25.8 (CH_3), 24.5 (CH_3), 23.6 (CH_3), 22.9 (CH_2), 17.8 (CH_3);

R_t (AD-3 column, Hex/IPA 80/20, 1.0 mL/min, 273 nm): P2 t_r(major) = 6.7 min, t_r(minor) = 12.2 min, 93% *ee*.

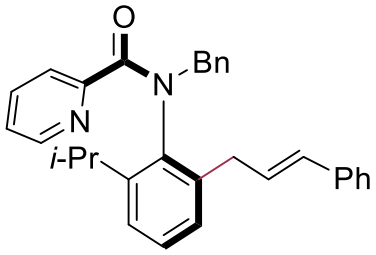


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.510	VB	0.2370	818.90314	50.82763	51.6328
2	11.573	BB	0.3508	767.11078	27.98165	48.3672



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.736	MM	0.2773	3573.69775	214.79782	96.5449
2	12.210	BB	0.3227	127.89192	4.66650	3.4551

***N*-benzyl-*N*-(2-cinnamyl-6-isopropylphenyl)picolinamide 3al**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as pale yellow solid (92 mg, 0.21 mmol, 41%), with an enantiomeric ratio of 97/3.

HRMS (ESI) calcd for $C_{31}H_{31}N_2O^+$: 447.2431. Found: 447.2431;

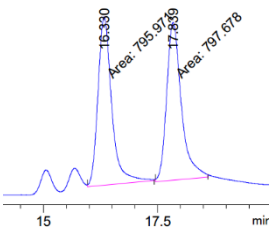
$[\alpha]_{20}^{D}$ = -30.7 (*c* = 0.89, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1048, 1078, 1167, 1235, 1287, 1336, 1356, 1394, 1439, 1450, 1471, 1495, 1567, 1585, 1637, 2868, 2929, 2963, 3027, 3060;

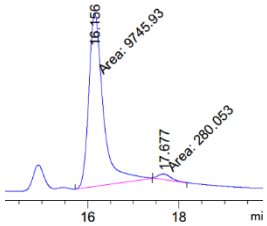
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.7 Hz, 1H), 7.68 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 5H), 7.23 – 7.20 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.91 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.18 (d, *J* = 15.8 Hz, 1H), 5.67 (dt, *J* = 15.8, 7.0 Hz, 1H), 5.34 (d, *J* = 13.6 Hz, 1H), 4.71 (d, *J* = 13.6 Hz, 1H), 3.14 (ddd, *J* = 16.0, 7.0, 1.5 Hz, 1H), 3.03 (hept, *J* = 6.7 Hz, 1H), 2.94 (ddd, *J* = 16.0, 6.9, 1.5 Hz, 1H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (C_q), 153.6 (C_q), 147.6 (CH), 146.5 (C_q), 138.5 (C_q), 138.3 (C_q), 137.6 (C_q), 136.6 (C_q), 136.1 (CH), 131.4 (CH), 130.6 (CH), 130.5 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.1 (CH), 127.1 (CH), 126.1 (CH), 124.9 (CH), 124.4 (CH), 124.1 (CH), 54.4 (CH_2), 35.0 (CH_2), 28.6 (CH), 24.6 (CH_3), 23.9 (CH_3);

R_t (ID-3 column, Hex/IPA 95/05, 1.0 mL/min, 250 nm): t_r(major) = 16.2 min, t_r(minor) = 17.7 min, 94% *ee*.

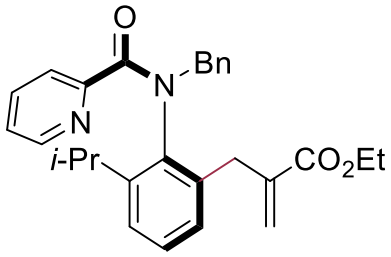


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.330	MM	0.3496	795.97070	37.94999	49.9464
2	17.839	MM	0.3735	797.67804	35.59597	50.0536



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.156	MM	0.3683	9745.93359	441.00076	97.2067
2	17.677	MM	0.3282	280.05258	14.22157	2.7933

Ethyl 2-(2-(*N*-benzylpicolinamido)-3-isopropylbenzyl)acrylate 3am



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as pale yellow oil (128 mg, 0.29 mmol, 58%), with an enantiomeric ratio of 91/9.

HRMS (ESI) calcd for $C_{28}H_{31}N_2O_3^+$: 443.2329. Found: 443.2328;

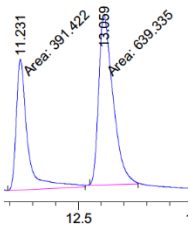
[α]$_{20}^{D}$ = -50.7 (*c* = 1.03, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1028, 1078, 1143, 1169, 1197, 1210, 1249, 1286, 1334, 1364, 1395, 1440, 1452, 1471, 1567, 1585, 1638, 1714, 2869, 2930, 2964, 3062;

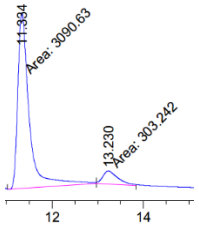
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dt, *J* = 4.8, 1.3 Hz, 1H), 7.69 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.57 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.97 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.84 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.11 (d, *J* = 1.3 Hz, 1H), 5.16 (dd, *J* = 7.7, 6.1 Hz, 2H), 4.90 (d, *J* = 13.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.27 (m, 2H), 2.80 (hept, *J* = 6.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.64 (d, *J* = 6.6 Hz, 3H), 0.62 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (C_q), 167.1 (C_q), 153.3 (C_q), 147.6 (CH), 146.8 (C_q), 139.4 (C_q), 139.2 (C_q), 136.9 (C_q), 136.8 (C_q), 136.1 (CH), 130.4 (CH), 128.5 (CH), 127.9 (CH), 127.8 (CH), 127.1 (CH), 126.8 (CH_2), 124.9 (CH), 124.5 (CH), 124.5 (CH), 60.9 (CH_2), 54.3 (CH_2), 33.8 (CH_2), 28.5 (CH), 24.2 (CH_3), 23.7 (CH_3), 14.4 (CH_3);

R_t (ID-3 column, Hex/IPA 80/20, 1.0 mL/min, 250 nm): t_r(major) = 11.3 min, t_r(minor) = 13.2 min, 82% *ee*.

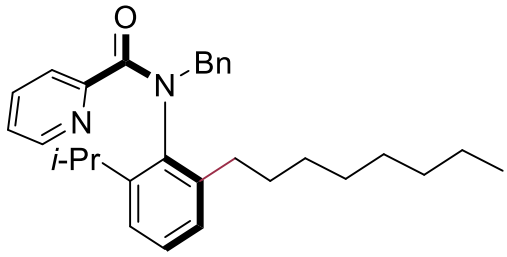


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.231	MM	0.2910	391.42188	22.41537	37.9742
2	13.059	MM	0.3644	639.33514	29.24508	62.0258



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.334	MM	0.2902	3090.63428	177.49234	91.0650
2	13.230	MM	0.3860	303.24219	13.09423	8.9350

***N*-benzyl-*N*-(2-isopropyl-6-octylphenyl)picolinamide 3an**



Prepared according to general procedure **B** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as colorless oil (127 mg, 0.28 mmol, 58%), with an enantiomeric ratio of 95/5.

HRMS (ESI) calcd for $C_{30}H_{39}N_2O^+$: 443.3057. Found: 443.3053;

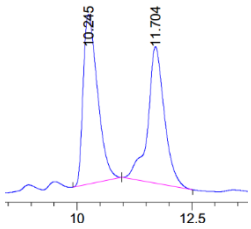
$[\alpha]_{20}^{D}$ = -15.9 (*c* = 1.04, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1047, 1078, 1090, 1168, 1195, 1210, 1237, 1287, 1306, 1336, 1357, 1395, 1439, 1452, 1495, 1568, 1586, 1640, 2855, 2925, 2959, 3030,3062;

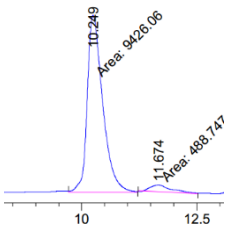
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, *J* = 4.7, 1.7, 1.0 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.06 (ddd, *J* = 7.3, 4.8, 1.5 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.13 (d, *J* = 13.7 Hz, 1H), 4.82 (d, *J* = 13.7 Hz, 1H), 2.96 (hept, *J* = 6.8 Hz, 1H), 2.20 (ddd, *J* = 15.6, 7.6, 3.5 Hz, 1H), 2.08 (ddd, *J* = 15.3, 11.2, 4.5 Hz, 1H), 1.36 – 1.03 (m, 13H), 0.89 (t, *J* = 7.0 Hz, 2H), 0.84 (d, *J* = 6.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C_q), 153.8 (C_q), 147.7 (CH), 146.4 (C_q), 140.5 (C_q), 138.6 (C_q), 136.8 (C_q), 135.8 (CH), 130.4 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 125.9 (CH), 124.2 (CH), 124.2 (CH), 123.8 (CH), 54.5 (CH_2), 32.0 (CH_2), 31.2 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 28.6 (CH), 24.6 (CH_3), 23.8 (CH_3), 22.8 (CH_2), 14.3 (CH_3);

R_t (AD-3 column, Hex/IPA 90/10, 0.5 mL/min, 273 nm): t_r(major) = 10.2 min, t_r(minor) = 11.7 min, 90% *ee*.

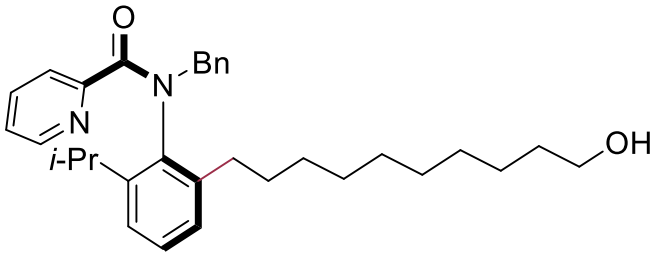


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.245	BB	0.3384	2882.62256	132.69370	51.6420
2	11.704	BB	0.3676	2699.31494	106.90063	48.3580



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.249	MM	0.3896	9426.06348	403.28116	95.0705
2	11.674	MM	0.5245	488.74716	15.53042	4.9295

***N*-benzyl-*N*-(2-(10-hydroxydecyl)-6-isopropylphenyl)picolinamide 3ao**



Prepared according to general procedure **B** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as pale brown oil (190 mg, 0.39 mmol,), with an enantiomeric ratio of 92/8.

HRMS (ESI) calcd for $C_{32}H_{43}N_2O_2^+$: 487.3319. Found: 487.3314;

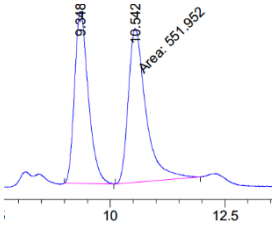
$[\alpha]_{20}^{D}$ = -19.5 (*c* = 1.10, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1049, 1078, 1169, 1237, 1287, 1336, 1355, 1397, 1440, 1495, 1567, 1585, 2853, 2925, 2961, 3029, 3063, 3430;

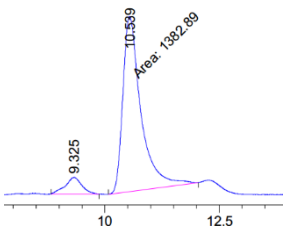
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 7.64 – 7.46 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 (ddd, *J* = 7.3, 4.8, 1.5 Hz, 1H), 6.97 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.11 (d, *J* = 13.7 Hz, 1H), 4.83 (d, *J* = 13.7 Hz, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.95 (hept, *J* = 6.7 Hz, 1H), 2.20 (ddt, *J* = 11.5, 6.4, 3.9 Hz, 1H), 2.08 (ddd, *J* = 14.9, 11.2, 4.4 Hz, 1H), 1.56 (dq, *J* = 8.1, 6.5 Hz, 2H), 1.40 – 1.04 (m, 14H), 0.83 (d, *J* = 6.7 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C_q), 153.7 (C_q), 147.7 (CH), 146.4 (C_q), 140.5 (C_q), 138.6 (C_q), 136.8 (C_q), 135.9 (CH), 130.4 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 125.9 (CH), 124.3 (CH), 124.2 (CH), 123.8 (CH), 63.2 (CH_2), 54.5 (CH_2), 32.9 (CH_2), 31.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.6 (CH), 25.9 (CH_2), 24.5 (CH_3), 23.8 (CH_3);

R_t (IC-3 column, Hex/IPA 70/30, 1.0 mL/min, 280 nm): t_r(major) = 10.5 min, t_r(minor) = 9.3 min, 84% *ee*.

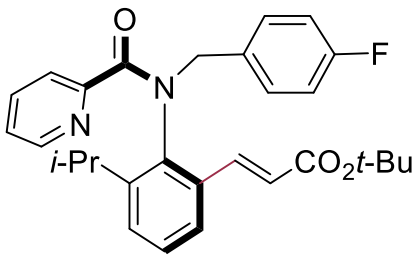


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.347	BB	0.3156	1151.54565	54.70014	47.4053
2	10.541	MM	0.4396	1277.60156	48.43657	52.5947



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.325	BB	0.2981	119.07845	4.75651	7.9281
2	10.539	MM	0.4578	1382.89465	50.34705	92.0719

***Tert*-butyl (E)-3-(2-(N-(4-fluorobenzyl)picolinamido)-3-isopropylphenyl)acrylate 3ba**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (156 mg, 0.33 mmol, 66%), with an enantiomeric ratio of 94/6.

HRMS (ESI) calcd for $C_{29}H_{32}FN_2O_3^+$: 475.2391. Found: 475.2389;

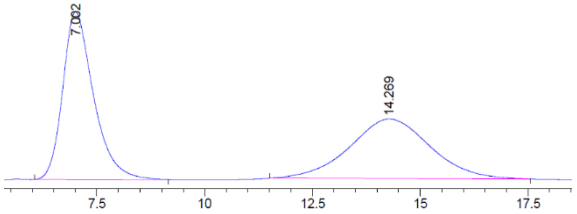
$[\alpha]_{20}^{D}$ = -92.4 (*c* = 1.12, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1048, 1094, 1144, 1220, 1284, 13165, 1390, 1446, 1509, 1568, 1586, 1642, 1704, 2870, 2931, 2968, 3062;

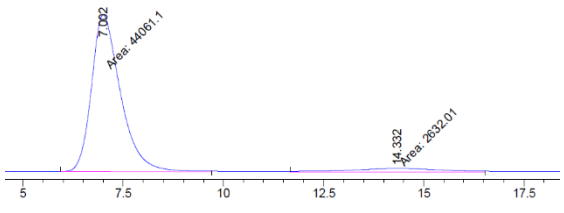
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 7.64 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.51 (td, *J* = 7.7, 1.7 Hz, 1H), 7.24 (d, *J* = 15.9 Hz, 1H), 7.21 – 7.13 (m, 5H), 7.00 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 6.87 – 6.81 (m, 2H), 5.87 (d, *J* = 15.8 Hz, 1H), 5.26 (d, *J* = 13.7 Hz, 1H), 4.55 (d, *J* = 13.7 Hz, 1H), 2.97 (hept, *J* = 6.8 Hz, 1H), 1.46 (s, 9H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 (C_q), 165.6 (C_q), 162.6 (d, *J* = 246.4 Hz, C_q), 153.1 (C_q), 147.5 (CH), 147,0 (C_q), 140.3 (CH), 138.9 (C_q), 136.0 (CH), 133.3 (C_q), 132.2 (d, *J* = 8.2 Hz, CH), 131.8 (d, J = 3.2 Hz, C_q), 128.5 (CH), 128.2 (CH), 124.4 (CH), 124.2 (CH), 124.1 (CH), 115.2 (d, *J* = 21.3 Hz, CH), 80.3 (C_q), 53.7 (CH_2), 29.3 (CH), 28.2 (CH_3), 24.3 (CH_3), 23.5 (CH_3).

R_t (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 7.0 min, t_r(minor) = 14.3 min, 88% *ee*.

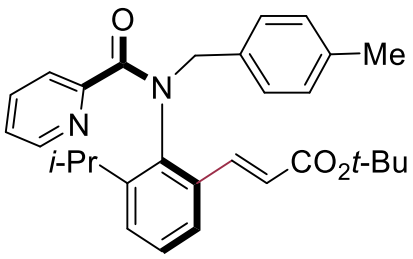


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.002	BB	0.7107	4930.05273	99.56013	51.7300
2	14.269	BB	1.5252	4600.29492	35.32818	48.2700



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.002	MM	0.8401	4.40611e4	874.10571	94.3632
2	14.332	MM	2.4464	2632.00659	17.93089	5.6368

***Tert*-butyl (E)-3-(3-isopropyl-2-(N-(4-methylbenzyl)picolinamido)phenyl)acrylate 3ca**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (207 mg, 0.44 mmol, 88%), with an enantiomeric ratio of 97/3.

HRMS (ESI) calcd for $C_{30}H_{35}N_2O_3^+$: 471.2642. Found: 471.2641;

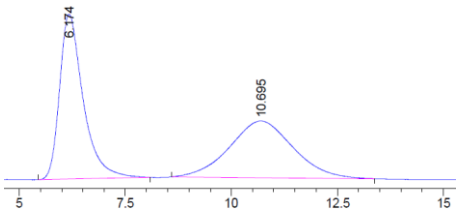
[α]$_{20}^{D}$ = -70.4 (*c* = 1.00, $CHCl_3$);

ν$_{max}$ (thin film/cm^{-1}): 1050, 1144, 1232, 1258, 1366, 1390, 1446, 1472, 1514, 1567, 1586, 1643, 1703, 2869, 2929, 2967, 3057;

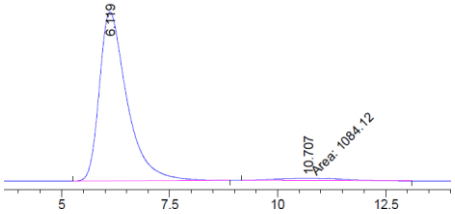
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1H), 7.64 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.21 – 7.15 (m, 3H), 7.11 – 7.08 (m, 2H), 7.03 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.00 – 6.96 (m, 2H), 5.87 (d, *J* = 15.9 Hz, 1H), 5.22 (d, *J* = 13.7 Hz, 1H), 4.64 (d, *J* = 13.7 Hz, 1H), 3.01 (hept, *J* = 6.7 Hz, 1H), 2.25 (s, 3H), 1.49 (s, 9H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H) ;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 (C_q), 165.7 (C_q), 153.4 (C_q), 147.5 (CH), 147.2 (C_q), 140.5 (CH), 139.0 (C_q), 137.5 (C_q), 136.0 (CH), 133.4 (C_q), 132.8 (C_q), 130.5 (CH), 129.0 (CH), 128.4 (CH), 128.1 (CH), 124.3 (CH), 124.2 (CH), 124.0 (CH), 121.5 (CH), 80.3 (C_q), 54.1 (CH_2), 28.3 (CH), 28.2 (CH_3), 24.2 (CH_3), 23.6 (CH_3), 21.2 (CH_3);

R$_t$ (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 6.2 min, t_r(minor) = 10.7 min, 94% *ee*.

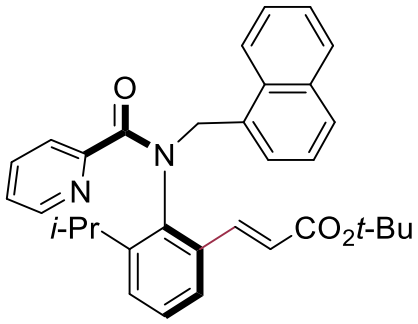


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.174	BB	0.5607	1742.09827	44.99779	52.0161
2	10.695	BB	1.2170	1607.05322	15.44391	47.9839



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.119	BB	0.6633	3.79304e4	853.74976	97.2212
2	10.707	MM	1.6740	1084.12292	10.79376	2.7788

***Tert*-butyl (E)-3-(3-isopropyl-2-(N-(4-methylbenzyl)picolinamido)phenyl)acrylate 3da**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as white solid (202 mg, 0.40 mmol, 80%), with an enantiomeric ratio of 97/3.

HRMS (ESI) calcd for $C_{33}H_{35}N_2O_3^+$: 507.2642. Found: 507.2644;

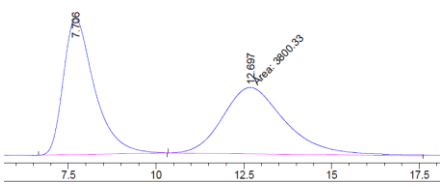
$[\alpha]_{20}^{D}$ = -54.5 (c = 1.05, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1050, 11487, 1233, 1258, 1289, 1365, 1393, 1445, 1472, 1568, 1585, 1638, 1704, 2869, 2931, 2967, 3060;

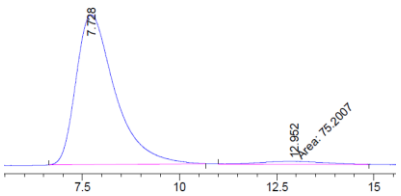
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.73 – 7.66 (m, 3H), 7.59 (s, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.37 (m, 3H), 7.24 – 7.22 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.05 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.88 (d, *J* = 15.9 Hz, 1H), 5.29 (d, *J* = 13.7 Hz, 1H), 4.99 (d, *J* = 13.7 Hz, 1H), 2.99 (hept, *J* = 6.8 Hz, 1H), 1.39 (s, 9H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (C_q), 165.7 (C_q), 153.4 (C_q), 147.7 (CH), 147.2 (C_q), 140.5 (CH), 139.3 (C_q), 136.1 (CH), 133.5 (C_q), 133.3 (C_q), 133.3 (C_q), 133.1 (C_q), 129.6 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 126.0 (CH), 126.0 (CH), 124.4 (CH), 124.4 (CH), 124.3 (CH), 121.8 (CH), 80.3 (C_q), 54.9 (CH_2), 28.3 (CH), 28.2 (CH_3), 24.2 (CH_3), 23.6 (CH_3);

R_t (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 7.7 min, t_r(minor) = 12.9 min, 94% *ee*.

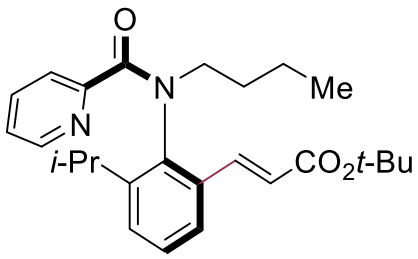


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.706	BB	0.8448	3857.61450	62.60952	50.3740
2	12.697	MM	2.0714	3800.33496	30.57710	49.6260



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.728	BB	0.8202	2282.85718	32.75041	96.8109
2	12.952	MM	1.9434	75.20073	6.44928e-1	3.1891

***Tert*-butyl (E)-3-(2-(N-butylpicolinamido)-3-isopropylphenyl)acrylate 3ea**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (192 mg, 0.45 mmol, 91%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3^+$: 423.2642. Found: 423.2643;

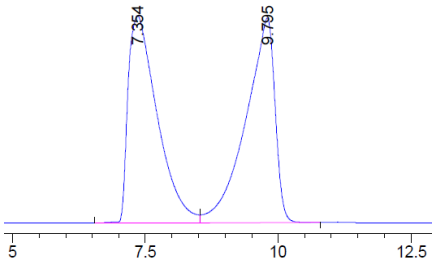
[α]$^{D}_{20}$ = -159.6 (*c* = 1.08, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1046, 1099, 1149, 1231, 1258, 1321, 1367, 1393, 1446, 1473, 1567, 1586, 1649, 1705, 2870, 2963, 3065;

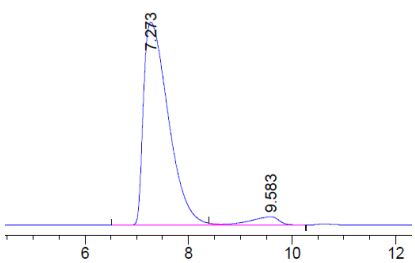
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.61 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.14 (m, 2H), 7.01 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 6.13 (d, *J* = 15.9 Hz, 1H), 3.94 (ddd, *J* = 13.1, 11.1, 5.3 Hz, 1H), 3.54 – 3.42 (m, 1H), 3.08 (hept, *J* = 6.8 Hz, 1H), 1.78 – 1.55 (m, 2H), 1.51 (s, 9H), 1.40 – 1.30 (m, 2H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 (C_q), 165.9 (C_q), 153.6 (C_q), 147.5 (CH), 147.1 (C_q), 141.0 (CH), 140.5 (C_q), 136.0 (CH), 133.2 (C_q), 128.5 (CH), 127.9 (CH), 124.2 (CH), 124.1 (CH), 123.9 (CH), 122.1 (CH), 80.6 (C_q), 52.0 (CH_2), 29.1 (CH_2), 28.3 (CH_3), 28.1 (CH), 24.8 (CH_3), 23.4 (CH_3), 20.7 (CH_2), 13.9 (CH_3).

R_t (AD-3 column, Hex/IPA 90/10, 1.0 mL/min, 273 nm): t_r(major) = 7.2 min, t_r(minor) = 9.6 min, 92% *ee*.

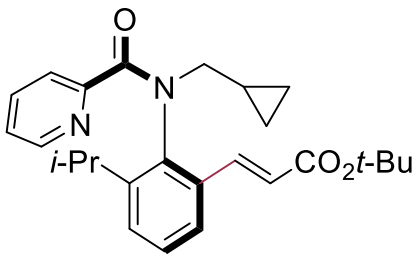


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.354	VV R	0.5757	2.25874e4	593.04449	50.1791
2	9.795	VB	0.5165	2.24262e4	586.01599	49.8209



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.273	BV R	0.4523	7.47286e4	2245.36133	95.6624
2	9.583	VB E	0.5298	3388.41211	90.91515	4.3376

***Tert*-butyl (E)-3-(2-(N-(cyclopropylmethyl)picolinamido)-3-isopropylphenyl)acrylate 3fa**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (176 mg, 0.42 mmol, 84%), with an enantiomeric ratio of 95.5/4.5.

HRMS (ESI) calcd for $C_{26}H_{33}N_2O_3^+$: 421.2486. Found: 421.2480;

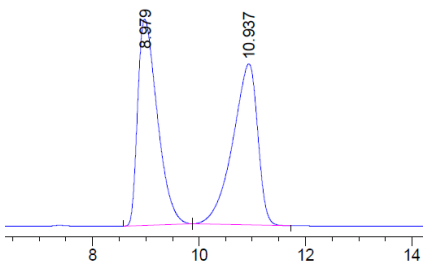
$[\alpha]_{20}^{D}$ = -97.7 (*c* = 0.90, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1023, 1052, 1141, 1247, 1296, 1317, 1367, 1392, 1446, 1472, 1567, 1586, 1631, 1704, 2872, 2977, 3062;

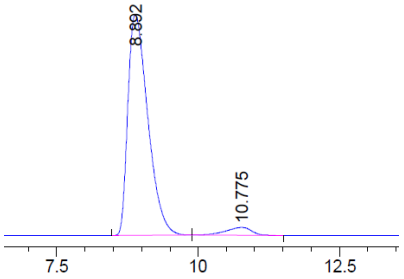
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.99 (d, *J* = 16.0 Hz, 1H), 7.63 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.25 – 7.16 (m, 2H), 7.04 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 4.22 (dd, *J* = 13.7, 7.1 Hz, 1H), 3.11 – 3.23 (m, 2H), 1.53 (s, 9H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.12 – 1.03 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.56 – 0.39 (m, 2H), 0.38 – 0.30 (m, 1H), 0.15 (dtd, *J* = 9.3, 5.4, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7 (C_q), 166.1 (C_q), 153.8 (C_q), 147.5 (CH), 147.3 (C_q), 141.3 (CH), 140.2 (C_q), 136.0 (CH), 133.5 (C_q), 128.6 (CH), 128.1 (CH), 124.2 (CH), 124.1 (CH), 123.9 (CH), 121.7 (CH), 80.6 (C_q), 55.8 (CH_2), 28.4 (CH_3), 28.3 (CH_3), 24.7 (CH), 23.7 (CH_3), 9.3 (CH), 4.6 (CH_2), 4.5 (CH_2).

R_t (AD-3 column, Hex/IPA 90/10, 1.0 mL/min, 273 nm): t_r(major) = 8.9 min, t_r(minor) = 10.8 min, 91% *ee*.

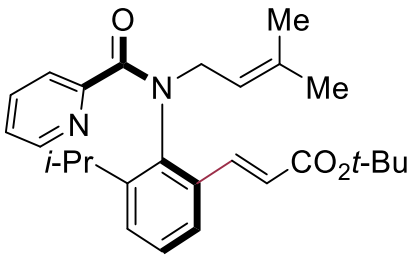


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.979	BB	0.3976	1.19564e4	467.10226	50.1136
2	10.937	BB	0.4933	1.19022e4	365.11050	49.8864



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.892	BB	0.3826	3.36661e4	1370.29065	95.6379
2	10.775	BB	0.4706	1535.51965	48.73249	4.3621

***Tert*-butyl (E)-3-(3-isopropyl-2-(N-(3-methylbut-2-en-1-yl)picolinamido)phenyl)acrylate 3ga**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (139 mg, 0.32 mmol, 64%), with an enantiomeric ratio of 98.5/1.5.

HRMS (ESI) calcd for $C_{27}H_{35}N_2O_3^+$: 435.2642. Found: 435.2638;

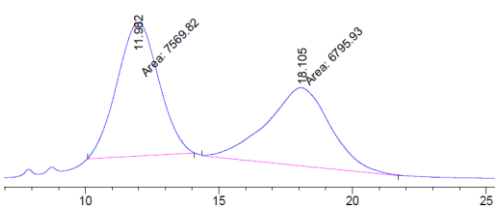
[α]$_{20}^{D}$ = -85.6 (*c* = 1.00, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1038, 1148, 1240, 1258, 1289, 1316, 1366, 1392, 1446, 1472, 1567, 1586, 1638, 1704, 2931, 2965, 3067;

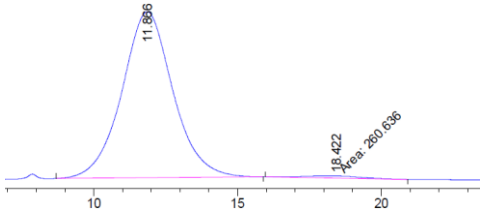
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.61 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.20 – 7.16 (m, 2H), 7.02 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 6.12 (d, *J* = 15.9 Hz, 1H), 5.42 (tt, *J* = 7.6, 1.4 Hz, 1H), 4.62 – 4.52 (m, 1H), 4.18 – 4.08 (m, 1H), 3.10 (hept, J = 6.8 Hz, 1H), 1.61 (d, *J* = 1.3 Hz, 3H), 1.51 (s, 9H), 1.50 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 (C_q), 166.2 (C_q), 153.4 (C_q), 147.6 (CH), 147.1 (C_q), 141.2 (CH), 139.9 (C_q), 137.5 (C_q), 136.0 (CH), 133.3 (C_q), 128.3 (CH), 128.1 (CH), 124.2 (CH), 124.0 (CH), 124.0 (CH), 121.3 (CH), 118.2 (CH), 80.4 (C_q), 49.0 (CH_2), 28.3 (CH_3), 28.2 (CH), 25.9 (CH_3), 24.7 (CH_3), 23.4 (CH_3), 17.7 (CH_3).

R_t (AS-3 column, Hex/IPA 98/2, 1.0 mL/min, 273 nm): t_r(major) = 11.9 min, t_r(minor) = 18.1 min, 97% *ee*.

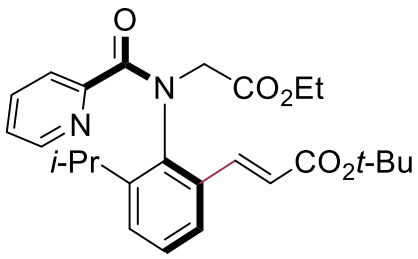


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.982	MM	1.8079	7569.81836	69.78484	52.6935
2	18.105	MM	2.7742	6795.93164	40.82791	47.3065



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.866	BB	1.5018	1.84295e4	149.33321	98.6055
2	18.422	MM	2.2732	260.63580	1.91095	1.3945

***Tert*-butyl (E)-3-(2-(N-(2-ethoxy-2-oxoethyl)picolinamido)-3-isopropylphenyl)acrylate 3ha**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 7:3) afforded the title compound as yellow oil (86 mg, 0.19 mmol, 38%), with an enantiomeric ratio of 94/6.

HRMS (ESI) calcd for $C_{26}H_{33}N_2O_5^+$: 453.2384. Found: 453.2384;

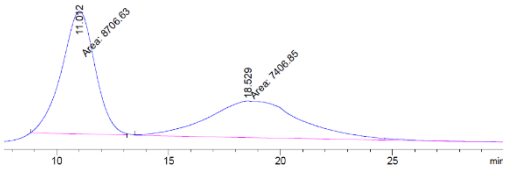
[α]$_{20}^{D}$ = -94.2 (*c* = 1.00, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1039, 1146, 1196, 1238, 1258, 1320, 1367, 1442, 1473, 1568, 1586, 1650, 1704, 2870, 2932, 2971, 3063;

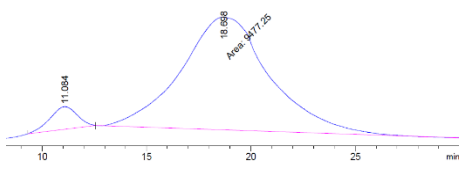
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 2H), 7.75 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.59 (td, *J* = 7.7, 1.7 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.24 – 7.18 (m, 2H), 7.12 – 7.06 (m, 1H), 6.08 (d, *J* = 15.9 Hz, 1H), 4.37 (d, *J* = 16.4 Hz, 1H), 4.30 – 4.21 (m, 3H), 3.32 (hept, *J* = 6.8 Hz, 1H), 1.53 (s, 9H), 1.31 – 1.27 (m, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (C_q), 168.0 (C_q), 165.9 (C_q), 152.4 (C_q), 147.6 (CH), 147.1 (C_q), 141.0 (CH), 140.8 (C_q), 136.1 (CH), 133.4 (C_q), 128.5 (CH), 128.4 (CH), 124.7 (CH), 124.5 (CH), 122.8 (CH), 80.4 (C_q), 61.4 (CH_2), 54.1 (CH_2), 28.4 (CH_3), 28.3 (CH), 25.0 (CH_3), 23.2 (CH_3), 14.3 (CH_3).

R_t (AS-3 column, Hex/IPA 95/5, 1.2 mL/min, 273 nm): t_r(major) = 11.0 min, t_r(minor) = 18.7 min, 88% *ee*.

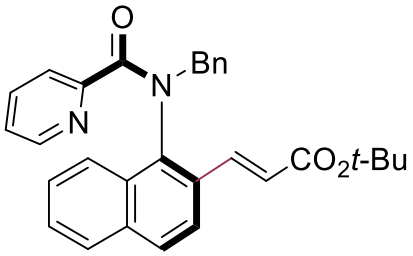


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.012	MM	1.7245	8706.63086	84.14453	54.0332
2	18.529	MM	4.9100	7406.84912	25.14221	45.9668



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.084	BB	1.0559	572.49786	6.36179	5.6966
2	18.698	MM	4.9601	9477.24707	31.84527	94.3034

***Tert*-butyl 3-(1-(*N*-benzylpicolinamido)naphathalen-2-yl)acrylate 3ia**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/EtOAc = 8:2 to 7:3) afforded the title compound as white foam (151 mg, 0.33 mmol, 65%), with an enantiomeric ratio of 94/6.

HRMS (ESI) calcd for $C_{30}H_{29}N_2O_3^+$: 465.2173. Found: 465.2174;

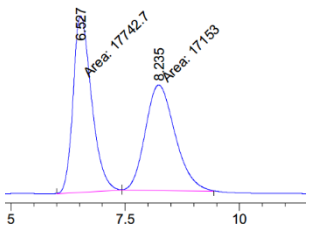
$[\alpha]_{20}^{D}$ = +16.9 (*c* = 0.94, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1077, 1144, 1239, 1256, 1293, 1334, 1367, 1402, 1438, 1471, 1567, 1586, 1645, 1702, 2249, 2932, 2977, 3063;

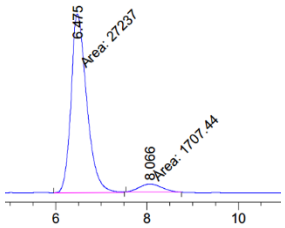
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.78 – 7.74 (m, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.43 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 15.9 Hz, 1H), 7.19 – 7.12 (m, 5H), 6.91 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 5.95 (d, *J* = 15.9 Hz, 1H), 5.65 (d, *J* = 13.5 Hz, 1H), 4.67 (d, *J* = 13.5 Hz, 1H), 1.52 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C_q), 165.6 (C_q), 153.4 (C_q), 147.7 (CH), 139.1 (CH), 138.2 (C_q), 135.9 (CH), 135.8 (C_q), 134.8 (C_q), 131.0 (C_q), 130.7 (C_q), 130.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 127.1 (CH), 124.6 (CH), 124.2 (CH), 123.4 (CH), 122.8 (CH), 122.2 (CH), 80.5 (C_q), 54.1 (CH_2), 28.3 (CH_3);

R_t (AS-3 column, Hex/IPA 80/20, 1.0 mL/min, 273 nm): t_r(major) = 6.5 min, t_r(minor) = 8.1 min, 88% *ee*.

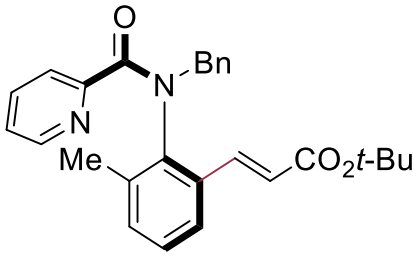


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.527	MM	0.4682	1.77427e4	631.57837	50.8449
2	8.235	MM	0.7564	1.71530e4	377.95755	49.1551



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.475	MM	0.3998	2.72370e4	1135.49670	94.1010
2	8.066	MM	0.5643	1707.43677	50.43094	5.8990

***Tert*-butyl 3-(3-(*N*-benzylpicolinamido)-3-isopropylphenyl)acrylate 3ja**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as colorless oil (111 mg, 0.26 mmol, 52%), with an enantiomeric ratio of 95/5.

HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3^+$: 429.2173. Found: 429.2174;

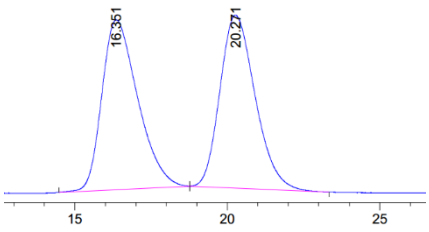
$[\alpha]_{20}^{D}$ = -124.1 (*c* = 0.96, $CHCl_3$);

ν_{max} (thin film/cm^{-1}): 1079, 1149, 1236, 1280, 1319, 1367, 1390, 1439, 1455, 1470, 1568, 1586, 1645, 1705, 2932, 2977, 3065;

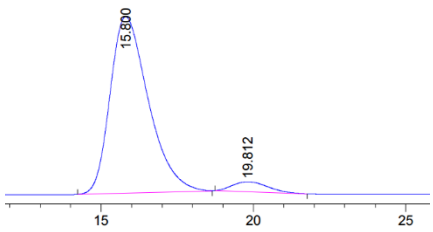
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.41 (d, *J* = 15.9 Hz, 1H), 7.25 – 7.19 (m, 6H), 7.12 – 7.01 (m, 3H), 5.99 (d, *J* = 15.9 Hz, 1H), 5.02 (d, *J* = 13.5 Hz, 1H), 4.87 (d, *J* = 13.5 Hz, 1H), 1.91 (s, 3H), 1.51 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3 (C_q), 165.8 (C_q), 153.8 (C_q), 147.9 (CH), 140.3 (C_q), 139.8 (CH), 137.5 (C_q), 136.0 (CH), 135.8 (C_q), 133.5 (C_q), 132.2 (CH), 130.6 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 124.6 (CH), 124.3 (CH), 123.4 (CH), 122.0 (CH), 80.5 (CH), 53.4 (CH_2), 28.3 (CH_3), 18.3 (CH_3);

R_t (AS-3 column, Hex/IPA 98/02, 1.0 mL/min, 250 nm): t_r(major) = 15.8 min, t_r(minor) = 19.8 min, 90% *ee*.

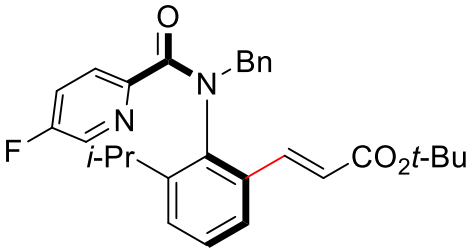


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.351	BB	1.0490	8312.98340	101.76756	49.9236
2	20.271	BB	1.0036	8338.42578	103.64001	50.0764



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.800	BB	1.0702	8956.17773	102.72366	95.0052
2	19.812	BB	0.9470	470.86591	5.83170	4.9948

***Tert*-butyl (E)-3-(2-(N-benzyl-5-fluoropicolinamido)-3-isopropylphenyl)acrylate 3ka**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a colorless foam (121 mg, 0.26 mmol, 51%), with an enantiomeric ratio of 97.5/2.5.

HRMS (ESI) calcd for $C_{29}H_{32}N_2O_3F^+$: 475.2391. Found: 475.2383;

$[\alpha]_{20}^{D}$ = -63.0 (*c* = 0.67, CH_2Cl_2);

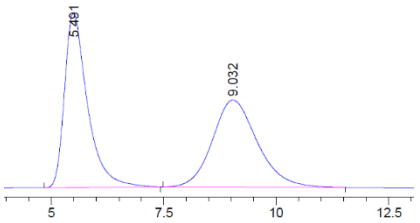
ν_{max} (thin film/cm^{-1}): 981, 1147, 1228, 1287, 1315, 1367, 1404, 1446, 1481, 1583, 1643, 1705, 2967;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 2.9, 0.6 Hz, 1H), 7.72 (ddd, *J* = 8.7, 4.4, 0.6 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.16 – 7.09 (m, 8H), 5.82 (d, *J* = 15.9 Hz, 1H), 5.16 (d, *J* = 13.6 Hz, 1H), 4.62 (d, *J* = 13.6 Hz, 1H), 2.90 (hept, *J* = 6.8 Hz, 1H), 1.42 (s, 9H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H);

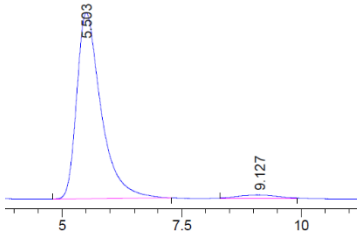
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3 (C_q), 165.7 (C_q), 159.4 (d, *J* = 261.0 Hz, C_q), 149.5 (d, *J* = 4.4 Hz, C_q), 147.0 (C_q), 140.3 (CH), 139.0 (C_q), 135.7 (d, *J* = 23.6 Hz, CH), 135.7 (C_q), 133.4 (C_q), 130.6 (CH), 128.5 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 126.2 (d, *J* = 4.9 Hz, CH), 124.2 (CH), 122.9 (d, *J* = 18.5 Hz, CH), 121.7 (CH), 80.3 (C_q), 54.6 (CH_2), 28.3 (CH_3), 24.1 (CH), 23.6 (CH_3);

^{19}F NMR (282 MHz) δ -123.58 (dd, *J* = 8.5, 4.3 Hz);

R_t (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 5.5 min, t_r(minor) = 9.1 min, 95% *ee*.

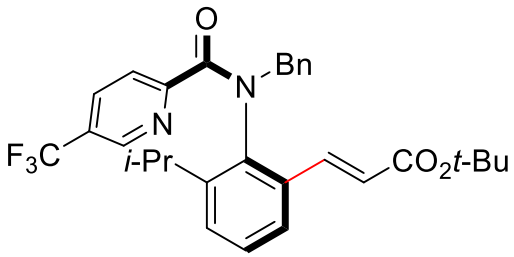


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.491	BB	0.5137	1.58460e4	446.84735	50.5577
2	9.032	BB	0.8302	1.54965e4	222.87575	49.4423



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.503	BB	0.5108	6855.15479	193.74458	97.5609
2	9.127	BB	0.6233	171.38557	3.24411	2.4391

***Tert*-butyl (E)-3-(2-(N-benzyl-5-(trifluoromethyl)picolinamido)-3-isopropylphenyl)acrylate 3la**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a white solid (110 mg, 0.21 mmol, 42%), with an enantiomeric ratio of 95.5/4.5.

HRMS (ESI) calcd for $C_{30}H_{32}N_2O_3F_3^+$: 525.2360. Found: 525.2356;

[α]$^{D}_{20}$ = -55.9 (*c* = 0.95, CH_2Cl_2);

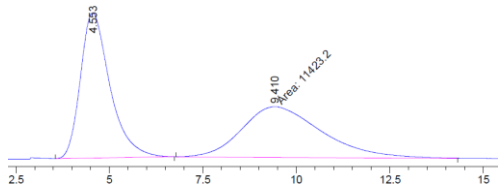
ν_{max} (thin film/cm^{-1}): 1017, 1076, 1134, 1290, 1322, 1367, 1407, 1446, 1571, 1647, 1707, 1871, 2932, 2969;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dt, *J* = 2.1, 1.0 Hz, 1H), 7.82 – 7.71 (m, 2H), 7.18 – 7.09 (m, 9H), 5.80 (d, *J* = 15.9 Hz, 1H), 5.26 (d, *J* = 13.6 Hz, 1H), 4.58 (d, *J* = 13.6 Hz, 1H), 2.96 (hept, *J* = 6.8 Hz, 1H), 1.43 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H);

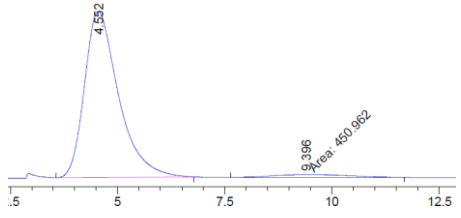
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2 (C_q), 165.6 (C_q), 147.2 (C_q), 147.2 (C_q), 144.44 (q, *J* = 4.0 Hz, CH), 139.9 (CH), 138.4 (C_q), 134.41 (d, *J* = 248.3 Hz, C_q), 133.52 (q, *J* = 3.5 Hz, CH), 130.6 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 128.2 (CH), 126.9 (q, *J* = 33.2 Hz, C_q), 124.3 (CH), 124.2 (CH), 122.1 (C_q), 122.0 (CH), 80.5 (C_q), 54.6 (CH_2), 28.3 (CH_3), 24.3 (CH), 23.7 (CH_3);

^{19}F NMR (376 MHz) δ -62.65;

R_t (AS-3 column, Hex/IPA 98/2, 1.2 mL/min, 273 nm): t_r(major) = 4.6 min, t_r(minor) = 9.4 min, 91% *ee*.

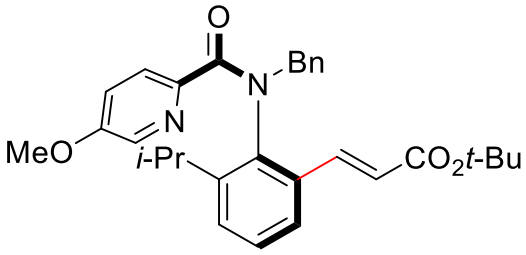


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.553	BB	0.6494	1.20517e4	219.55888	51.3387
2	9.410	MM	2.4785	1.14232e4	76.81473	48.6613



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.552	BB	0.6953	1.00620e4	182.47673	95.7104
2	9.396	MM	2.1274	450.96222	3.53291	4.2896

***Tert*-butyl (E)-3-(2-(N-benzyl-5-methoxypicolinamido)-3-isopropylphenyl)acrylate 3ma**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a colorless foam (228 mg, 0.47 mmol, 94%), with an enantiomeric ratio of 96/4.

HRMS (ESI) calcd for $C_{30}H_{35}N_2O_4^+$: 487.2591. Found: 487.2582;

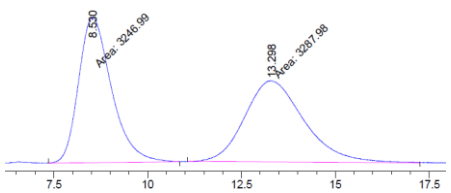
[α]$^{D}_{20}$ = -113.4 (*c* = 0.76, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1028, 1146, 1228, 1268, 1294, 1315, 1385, 1445, 1572, 1585, 1635, 1704, 2870, 2934, 2966;

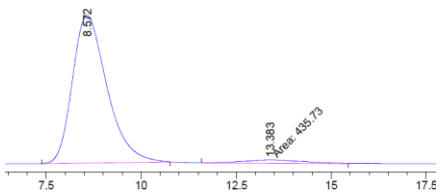
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.33 (d, *J* = 15.9 Hz, 1H), 7.25 – 7.09 (m, 8H), 7.02 (dd, J = 8.7, 2.9 Hz, 1H), 5.92 (d, *J* = 15.9 Hz, 1H), 5.14 (d, *J* = 13.6 Hz, 1H), 4.76 (d, *J* = 13.6 Hz, 1H), 3.73 (s, 3H), 2.93 (hept, *J* = 6.8 Hz, 1H), 1.49 (s, 9H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0 (C_q), 165.8 (C_q), 156.2 (C_q), 146.9 (C_q), 145.4 (C_q), 140.7 (CH), 139.7 (C_q), 136.1 (C_q), 135.2 (CH), 133.3 (C_q), 130.6 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.9 (CH), 125.7 (CH), 124.2 (CH), 121.5 (CH), 119.7 (CH), 80.3 (C_q), 55.6 (CH), 54.6 (CH_2), 28.3 (CH_3), 24.0 (CH_3), 23.6 (CH_3);

R_t (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 8.6 min, t_r(minor) = 13.4 min, 92% *ee*.

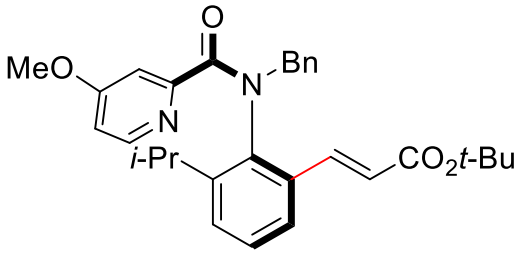


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.530	MM	1.0144	3246.99243	53.34689	49.6864
2	13.298	MM	1.8393	3287.97925	29.79452	50.3136



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.572	BB	0.7449	9816.54395	155.21477	95.7499
2	13.383	MM	1.9767	435.72964	3.67384	4.2501

***Tert*-butyl (E)-3-(2-(N-benzyl-4-methoxypicolinamido)-3-isopropylphenyl)acrylate 3na**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a brown foam (236 mg, 0.48 mmol, 97%), with an enantiomeric ratio of 95/5.

HRMS (ESI) calcd for $C_{30}H_{35}N_2O_4^+$: 487.2591. Found: 487.2589;

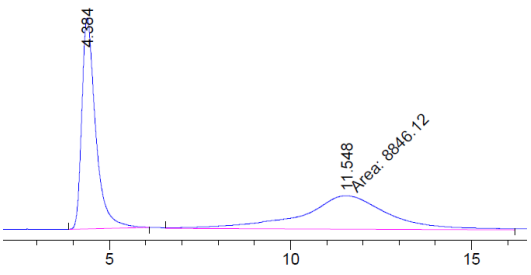
[α]$^{D}_{20}$ = -53.8 (*c* = 1.00, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1036, 1146, 1258, 1303, 1430, 1448, 1566, 1591, 1638, 1703, 2870, 2967;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 5.7 Hz, 1H), 7.28 (d, *J* = 15.9 Hz, 1H), 7.24 – 7.15 (m, 9H), 6.55 (dd, *J* = 5.7, 2.6 Hz, 1H), 5.91 (d, *J* = 15.9 Hz, 1H), 5.25 (d, *J* = 13.5 Hz, 1H), 4.68 (d, *J* = 13.5 Hz, 1H), 3.72 (s, 3H), 3.03 (hept, *J* = 6.8 Hz, 1H), 1.49 (s, 9H),), 0.90 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5 (C_q), 165.8 (C_q), 165.6 (C_q), 155.1 (C_q), 148.8 (CH), 147.3 (C_q), 140.5 (CH), 139.1 (C_q), 135.8 (C_q), 133.2 (C_q), 130.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 124.0 (CH), 121.5 (CH), 111.4 (CH), 109.5 (CH), 80.3 (C_q), 55.2 (CH), 54.5 (CH_2), 28.3 (CH_3), 24.2 (CH_3), 23.7 (CH_3);

R_t (AS-3 column, Hex/IPA 90/10, 1.2 mL/min, 273 nm): t_r(major) = 4.4 min, t_r(minor) = 11.6 min, 90% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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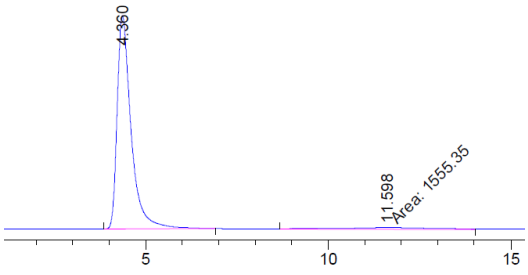
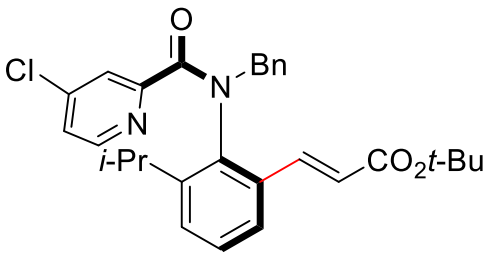
2	11.548	MM	2.7428	8846.11621	53.75350	49.6453



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.360	BB	0.3980	3.01871e4	1132.26294	95.1001
2	11.598	MM	2.9149	1555.35449	8.89309	4.8999

***Tert*-butyl (E)-3-(2-(N-benzyl-4-chloropicolinamido)-3-isopropylphenyl)acrylate 3oa**



Prepared according to general procedure **A** on a 0.5 mmol scale, column chromatography (*n*-hexane/acetone = 9:1) afforded the title compound as a brown foam (160 mg, 0.33 mmol, 65%), with an enantiomeric ratio of 97/4.

HRMS (ESI) calcd for $C_{29}H_{32}N_2O_3Cl^+$: 491.2096. Found: 491.2079;

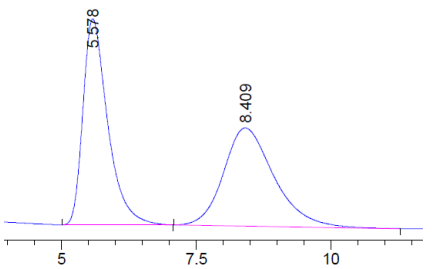
$[\alpha]_{20}^{D}$ = -29.4 (*c* = 0.82, CH_2Cl_2);

ν_{max} (thin film/cm^{-1}): 1012, 1051, 1078, 1095, 1146, 1232, 1258, 1286, 1320, 1367, 1413, 1446, 1474, 1554, 1573, 1639, 1704, 2870, 1965;

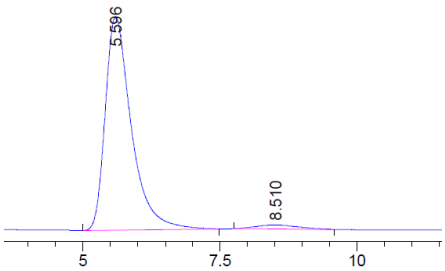
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 1H), 7.74 (dd, *J* = 2.0, 0.6 Hz, 1H), 7.25 – 7.14 (m, 9H), 7.07 – 7.02 (m, 1H), 5.85 (d, *J* = 15.9 Hz, 1H), 5.33 (d, *J* = 13.5 Hz, 1H), 4.60 (d, *J* = 13.5 Hz, 1H), 3.03 (hept, *J* = 6.8 Hz, 1H), 1.50 (s, 9H), 0.95 (d, *J* = 6.8, 3H), 0.94 (d, *J* = 6.8, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 (C_q), 165.6 (C_q), 154.8 (C_q), 148.3 (CH), 147.1 (C_q), 144.2 (C_q), 140.1 (CH), 138.6 (C_q), 135.5 (C_q), 133.3 (C_q), 130.5 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 125.0 (CH), 124.6 (CH), 124.0 (CH), 121.8 (CH), 80.4 (C_q), 54.6 (CH_2), 28.3 (CH_3), 24.2 (CH), 23.7 (CH_3);

R_t (AS-3 column, Hex/IPA 95/5, 1.0 mL/min, 273 nm): t_r(major) = 5.6 min, t_r(minor) = 8.5 min, 93% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.578	BB	0.4759	1.93540e4	603.88019	50.7169
2	8.409	BB	0.7936	1.88068e4	287.70816	49.2831



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.596	BB	0.4933	9200.45703	277.12335	97.0351
2	8.510	BV R	0.6391	281.12045	5.17225	2.9649

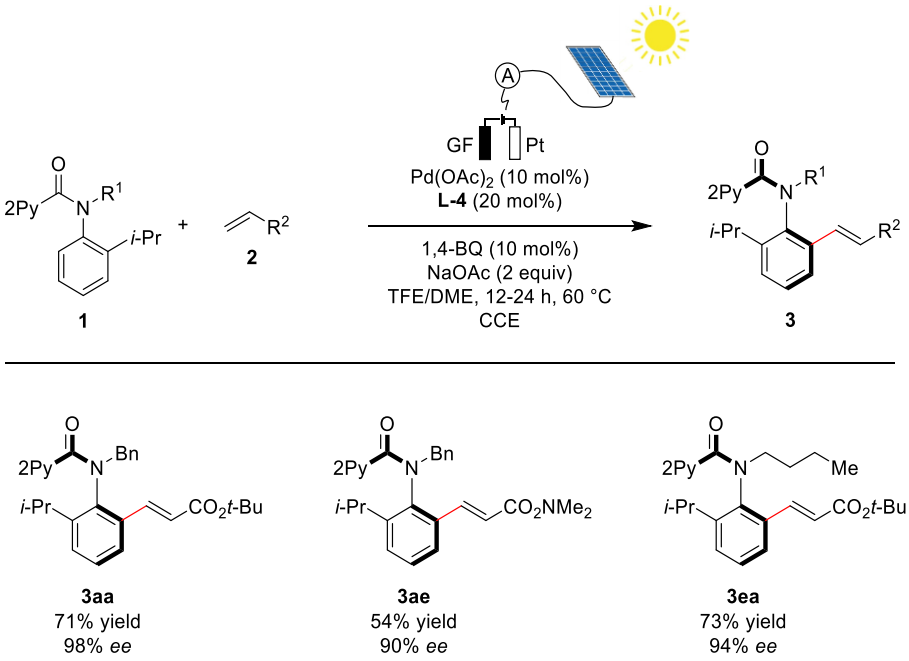
Renewable energy power setup

For the electrocatalysis powered by sunlight, a commercially available photovoltaic cell (Conrad Electronic SE, TPS-103 6 W, 17.5 V max. voltage, 428 mA max. current, 467 mm x 161 mm x 19 mm) was used.

Figure S1: Amorphous silicon panel used for the reaction.

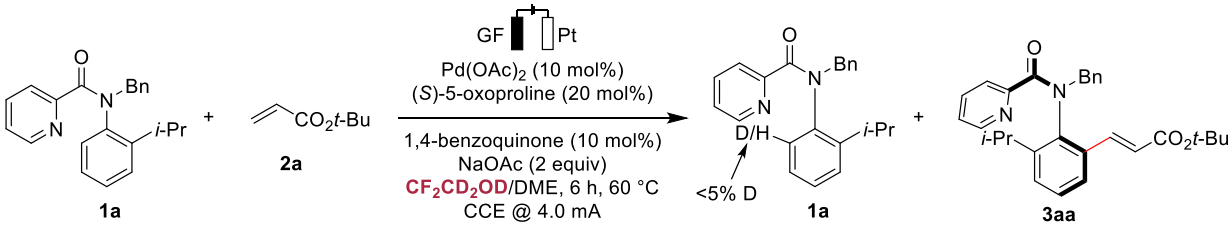
The output current was controlled with a customized and normalized constant current regulator and double checked with an ammeter.

The electrocatalysis was carried out in an undivided cell, with a GF anode (10 mm x 15 mm x 6 mm) and a platinum cathode (10 mm x 15 mm x 025 mm). A 10 mL cell was charged with the amide **1** (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.3 mg, 10 mol%), (*S*)-5-oxoproline (12.9 mg, 20 mol%), 1,4-benzoquinone (5.4 mg, 10 mol%) and NaOAc (82 mg, 1.0 mmol, 2.0 equiv). Then was added 2.5 mL of TFE, 2.5 mL of DME and the olefin **2** (1.5 mmol, 3.0 equiv). The electrocatalysis was performed at 60 °C with a constant current electrolysis for 12-24 h. The current was set at 6.0 mA when there is sufficient sunlight to operate the photovoice cell. The resulting mixture was filtered through a celite pad, eluted with EtOAc and concentrated *in vacuo*. The residue was purified by column chromatography to afford the title compound **3.**



Scheme S1: Renewable solar energy for atroposelective C–H olefinations.

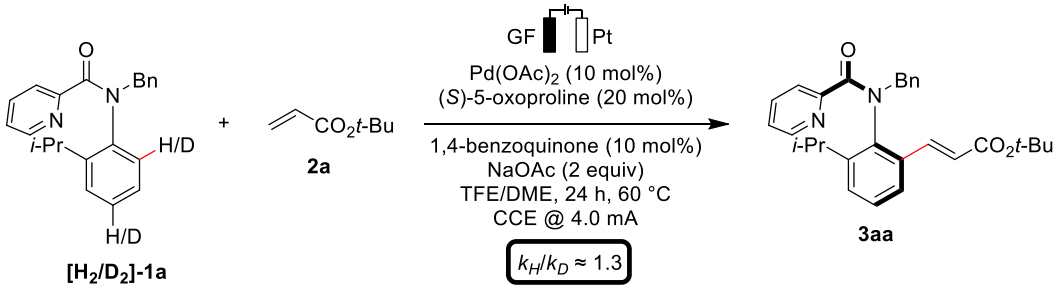
H/D exchange for the asymmetric C–H olefination



Scheme S21: H/D exchange for the atroposelective C–H olefination.

The general procedure A was followed using **1a** (165 mg, 0.50 mmol, 1 equiv), **2a** (0.22 mL, 1.50 mmol, 3 equiv), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol, 10 mol%), (*S*)-5-oxoproline (12.9 mg, 0.10 mmol, 20 mol%), 1,4-benzoquinone (5.4 mg, 0.05 mmol, 10 mol%) and NaOAc (82 mg, 1.00 mmol, 2 equiv) in CF_2CD_2OD (2.5 mL) and DME (2.5 mL) at 60 °C, with a constant current of 4.0 mA for 6 h. The resulting mixture was filtered through a celite pad, eluted with EtOAc and concentrated *in vacuo*. The residue was purified by column chromatography to afford the title compound **3aa** (75 mg, 0.17 mmol, 33%) and **1a** (110 mg, 0.34 mmol, 67% reisolated) without obvious H/D exchange.

Determination of the KIE by comparison of the initial reaction rates

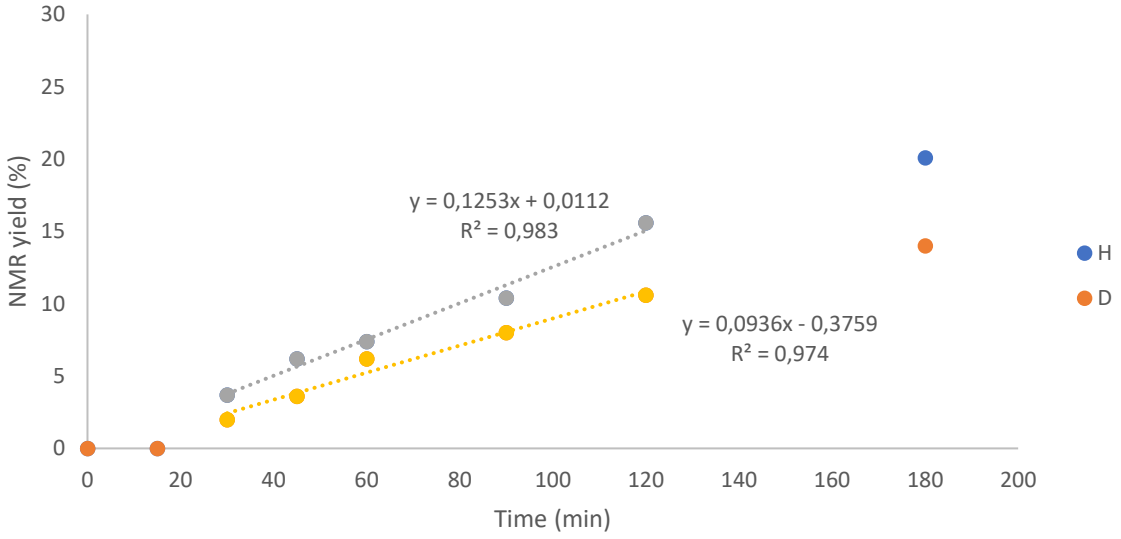


Scheme S3: KIE study for the atroposelective C–H olefination.

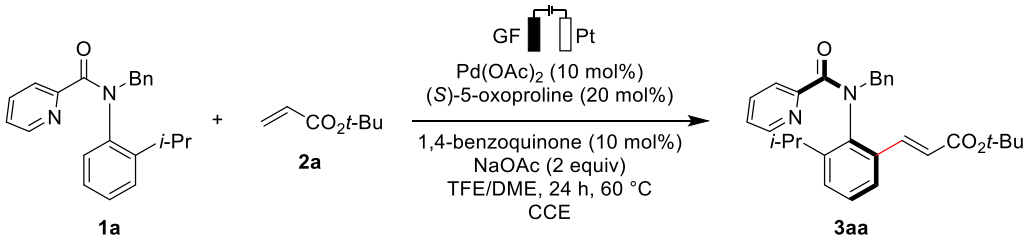
Two parallel reactions of **1a** and [D]$_2$-**1a** with **2a** were performed following the general procedure **A** to determine the KIE by comparison of the initial reaction rates through ^{1}H-NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. Aliquots were periodically taken, the NMR yield was determined by ^{1}H-NMR and plotted. A linear fit resulted in a KIE value of $k_H/k_D \approx 1.3$ (Table S1).

Table S1: Conversion-time table

t (min)	15	30	45	60	90	120	180
NMR yield of 3aa (%)	0	3.7	6.2	7.4	10.4	15.6	20.1
NMR yield of [D]$_2$-3aa (%)	0	2	3.4	6.2	8	10.6	14



Kinetic studies for the dependence in current



Scheme S4: Dependence in current for the atroposelective C–H olefination.

Six parallel electrolyses were carried out at different current (0.0, 1.0, 2.0, 3.0, 4.0, 6.0 mA) following the general procedure **A**. Aliquots were periodically taken and the NMR yield was determined by ^{1}H-NMR with 1,3,5-trimethoxybenzene as the internal standard. The determined NMR yields of **3aa** were plotted in Figure S2. Results showed a dependence of the NMR yield on the current from 0.0 to 4.0 mA, suggesting a turnover-limiting electron transfer step. The reaction could occur without current but with a low conversion. This low conversion could be explained by the presence of oxygen in the air, which could act as an oxidant.

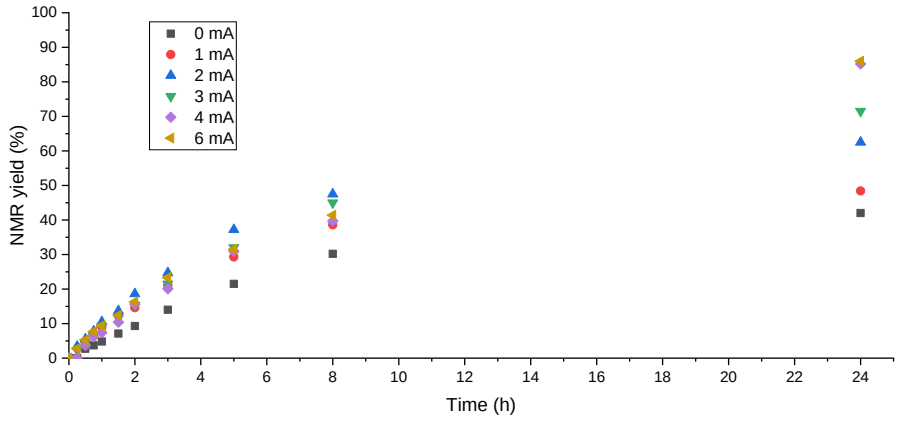
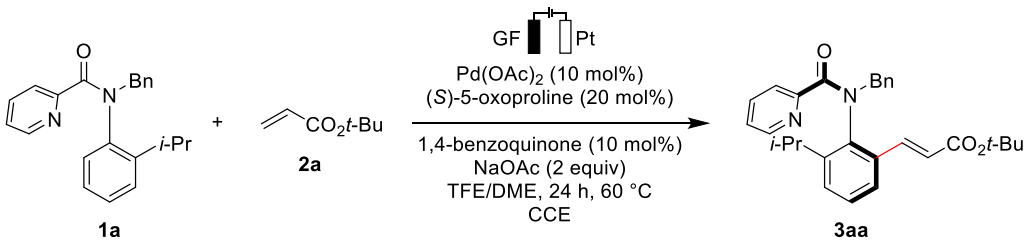


Figure S2: Reaction profiles with different current.

In operando React-IR



Scheme S5: *In operando* React-IR.

The electrocatalysis was carried out in a three-neck flask, with a GF anode (10 mm x 15 mm x 6 mm) and a platinum cathode (10 mm x 15 mm x 025 mm) and fitted with a diamond probe connected to a Mettler Toledo ReactIR. The cell was charged with the amide **1** (0.5 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.3 mg, 10 mol%), (*S*)-5-oxoproline (12.9 mg, 20 mol%), 1,4-benzoquinone (5.4 mg, 10 mol%) and NaOAc (82 mg, 2.0 equiv). Then was added 5 mL of TFE, 5 mL of DME and the olefin **2** (3.0 equiv). The electrocatalysis was performed at 60 °C with a constant current of 4.0 mA maintained for 24 h. Every minutes for 8 hours and then every 2 min for 16 hours, an IR spectrum was recorded. Peaks at 1023 cm^{-1} and 1225 cm^{-1} were identified to belong respectively to the product and the starting material.

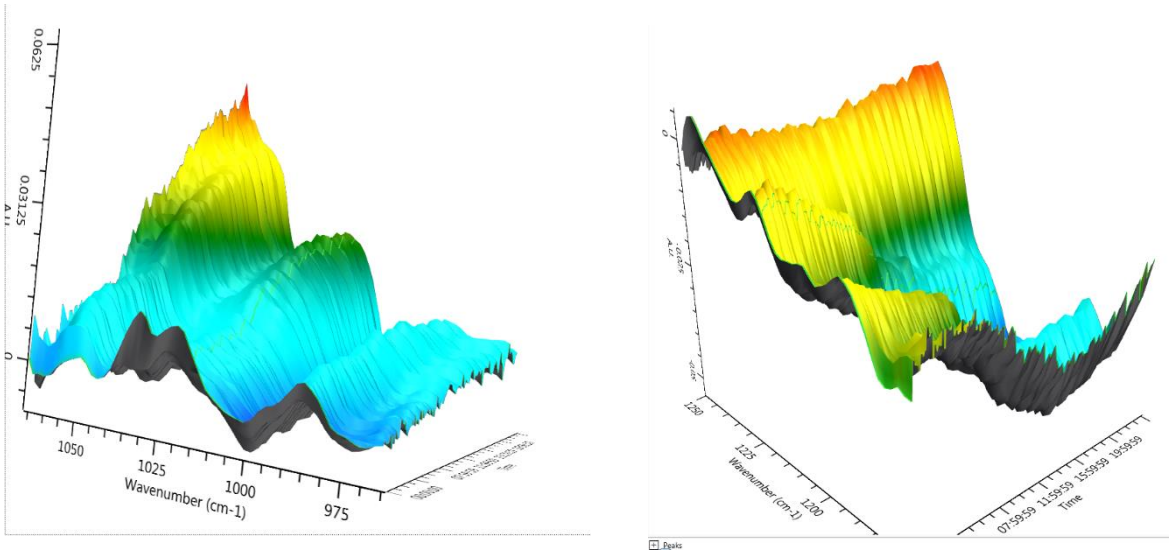


Figure S3: 3D-surface plot of the observed vibrations at 1023 cm^{-1} on the left and 1225 cm^{-1} on the right.

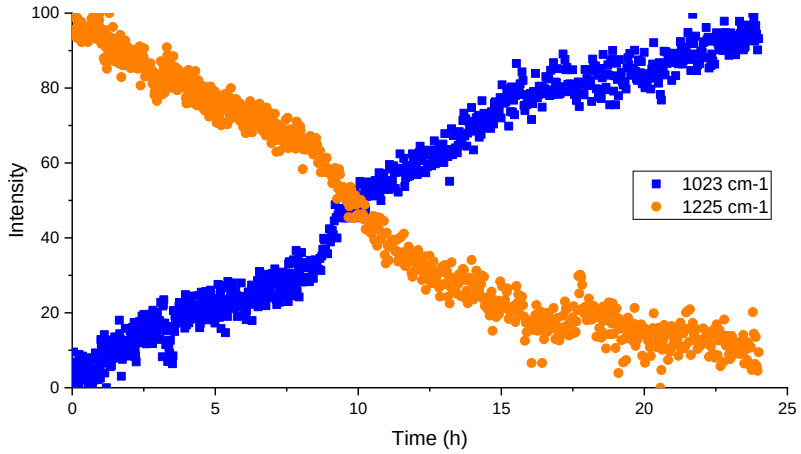


Figure S4: Plot of the observed vibrations over time.

Cyclic voltammetry

CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon working electrode (disk, diameter: 3mm), a coiled platinum wire counter electrode and a silver-silver chloride electrode (Ag/AgCl) were employed. The voltammograms were recorded at room temperature in TFE/DME（1/1）at a substrate concentration of 5.0 mM and with 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures and descriptions.

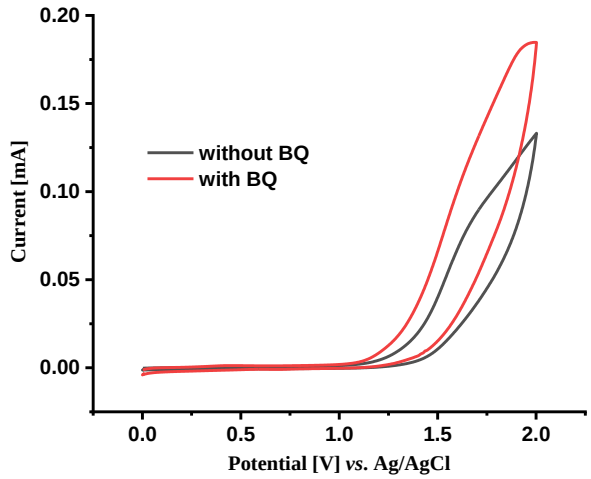


Figure S5: Cyclic voltammetry of the mixture of **1a**, **2a**, $Pd(OAc)_2$, (*S*)-5-oxoproline and NaOAc, with or without 1,4-BQ.

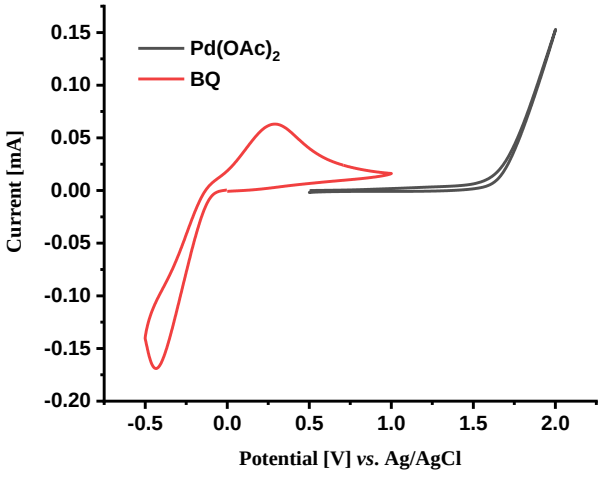


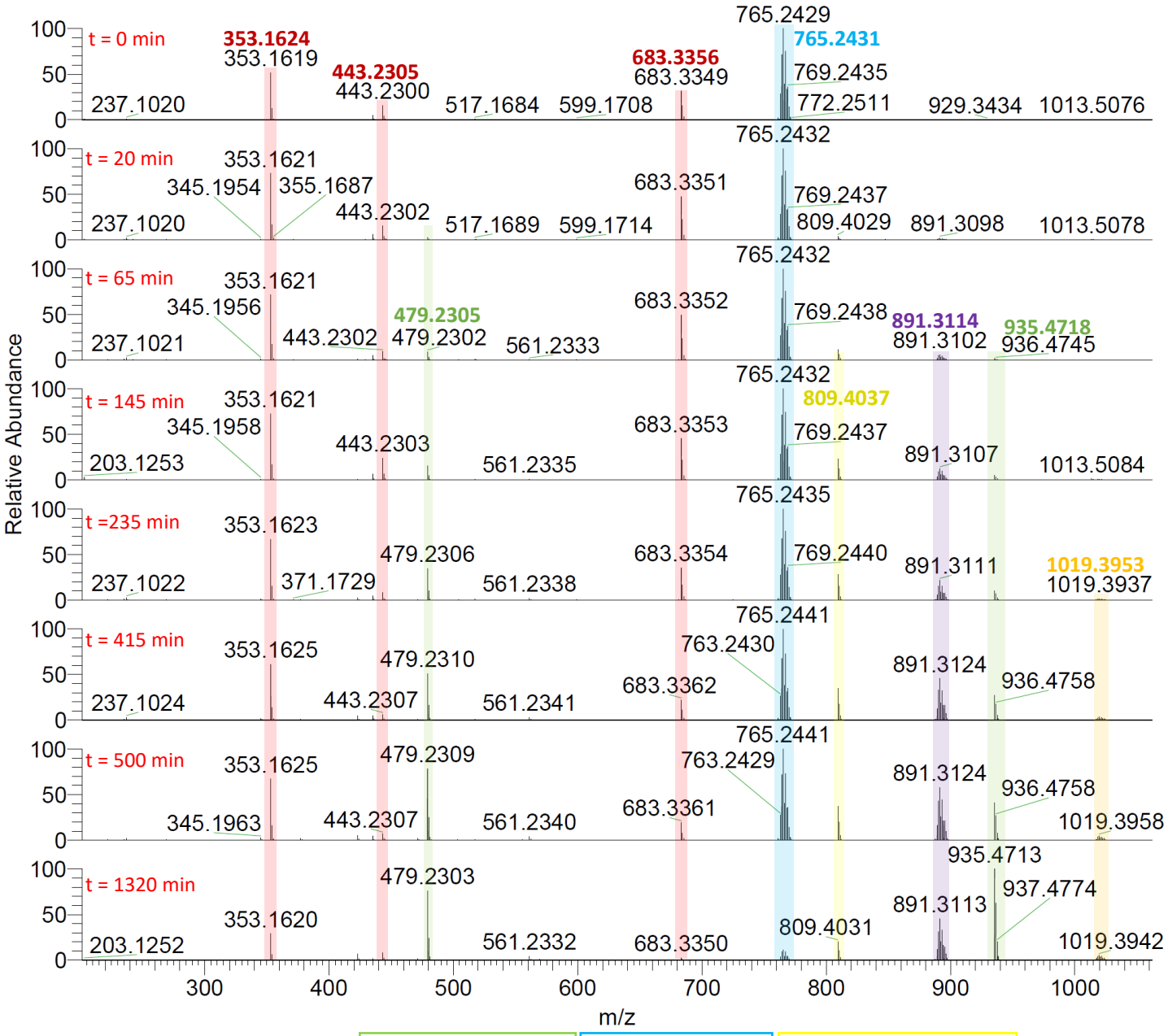
Figure S6: Cyclic voltammetry of $Pd(OAc)_2$ and 1,4-BQ separately.

HRMS ESI analysis

General procedure A was followed. Aliquots were periodically taken, diluted in TFE and spectra were measured.

Different palladium complexes could be identified. However, none have the chiral ligand as a ligand. Given the enantiomeric excesses obtained, we assume that the non-identification of complexes carrying the chiral ligand is due to the fact that they are uncharged and therefore more difficult to detect.

We also envisaged that the enantioenriched product could serve as the chiral ligand for the next catalytic cycle. However, the test reaction replacing the (*S*)-5-oxoproline by the product **3aa** gave only low enantioselectivity.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443.2300
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683.3349
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765.2431
769.2435
772.2511
237.1020
517.1684
599.1708
929.3434
1013.5076
t = 20 min
353.1621
345.1954
355.1687
443.2302
683.3351
765.2432
769.2437
809.4029
237.1020
517.1689
599.1714
891.3098
1013.5078
t = 65 min
353.1621
345.1956
479.2305
443.2302
479.2302
683.3352
765.2432
769.2438
891.3114
891.3102
935.4718
936.4745
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561.2333
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345.1958
443.2303
683.3353
765.2432
809.4037
769.2437
891.3107
203.1253
561.2335
1013.5084
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353.1623
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683.3354
765.2435
769.2440
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1019.3953
237.1022
371.1729
561.2338
1019.3937
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765.2441
891.3124
936.4758
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561.2341
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479.2309
763.2429
765.2441
891.3124
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1019.3958
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479.2303
937.4774
891.3113
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809.4031
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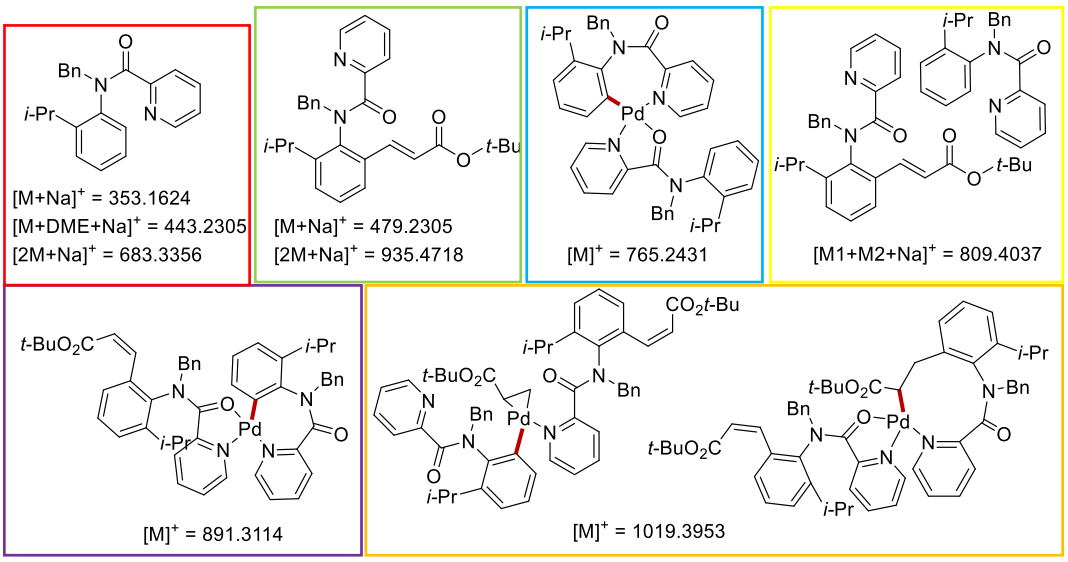
683.3350
1019.3942
Relative Abundance
m/z
300
400
500
600
700
800
900
1000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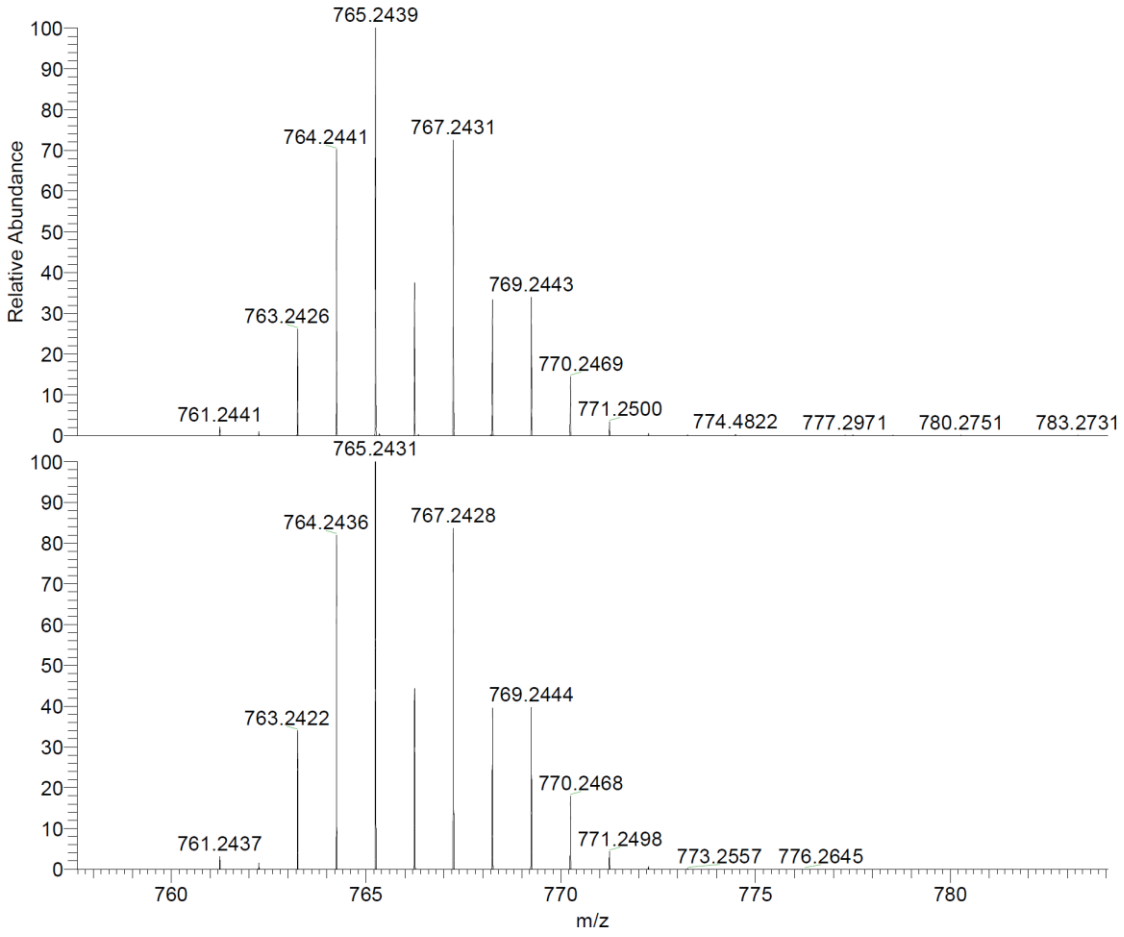
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764.2441
767.2431
769.2443
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770.2469
761.2441
771.2500
774.4822
777.2971
780.2751
783.2731
Relative Abundance
NL:
1.10E9
jf304_t8_pos#4 RT: 0.03 AV:
1 T: FTMS + p ESI Full ms
[150.0000-2000.0000]
765.2431
764.2436
767.2428
769.2444
763.2422
770.2468
761.2437
771.2498
773.2557
776.2645
m/z
NL:
4.68E3
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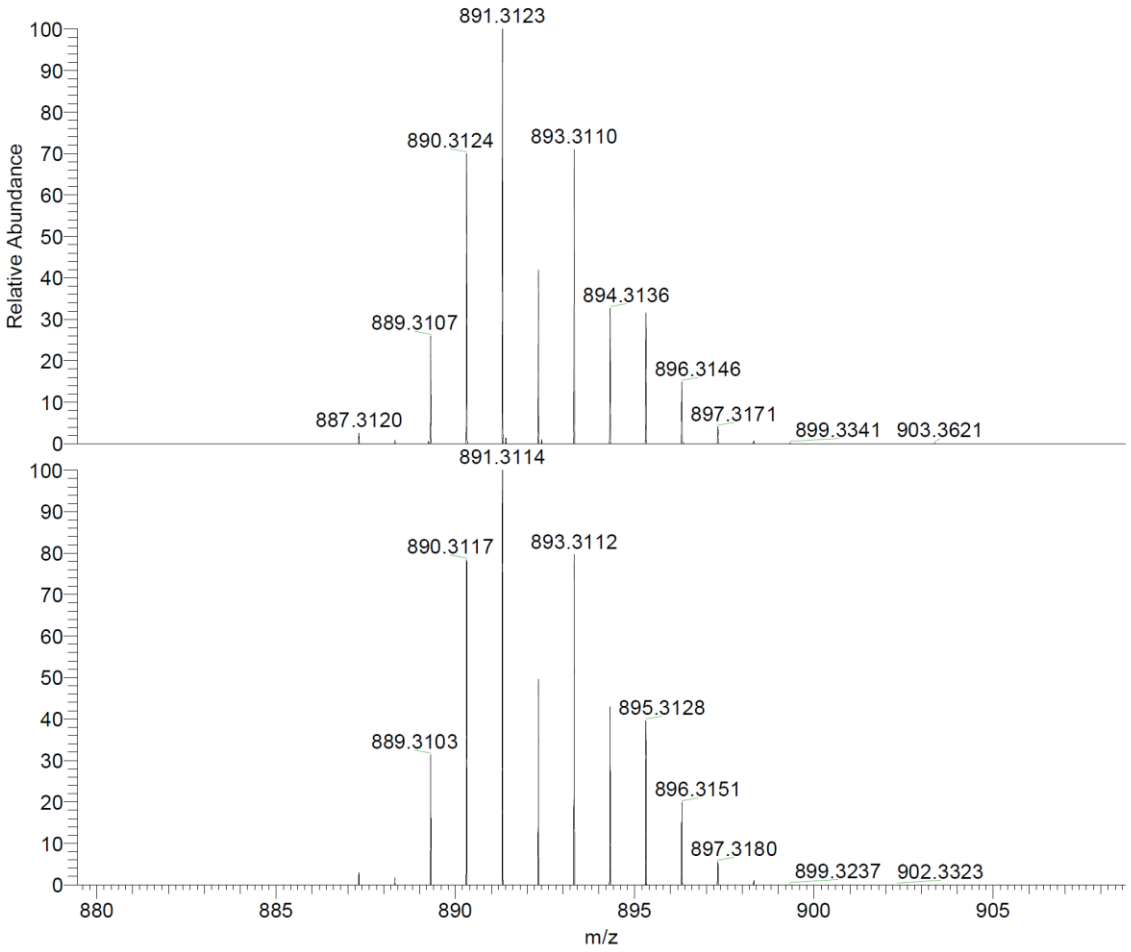
C44 H43 N4 O2 Pd1
p (gss, s /p:40) Chrg 1
R: 90000 Res .Pwr . @FWHM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Relative Abundance
NL:
6.60E8
jf304_t8_pos#4 RT: 0.03 AV:
1 T: FTMS + p ESI Full ms
[150.0000-2000.0000]
891.3114
890.3117
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895.3128
889.3103
896.3151
897.3180
899.3237
902.3323
m/z
NL:
4.68E3
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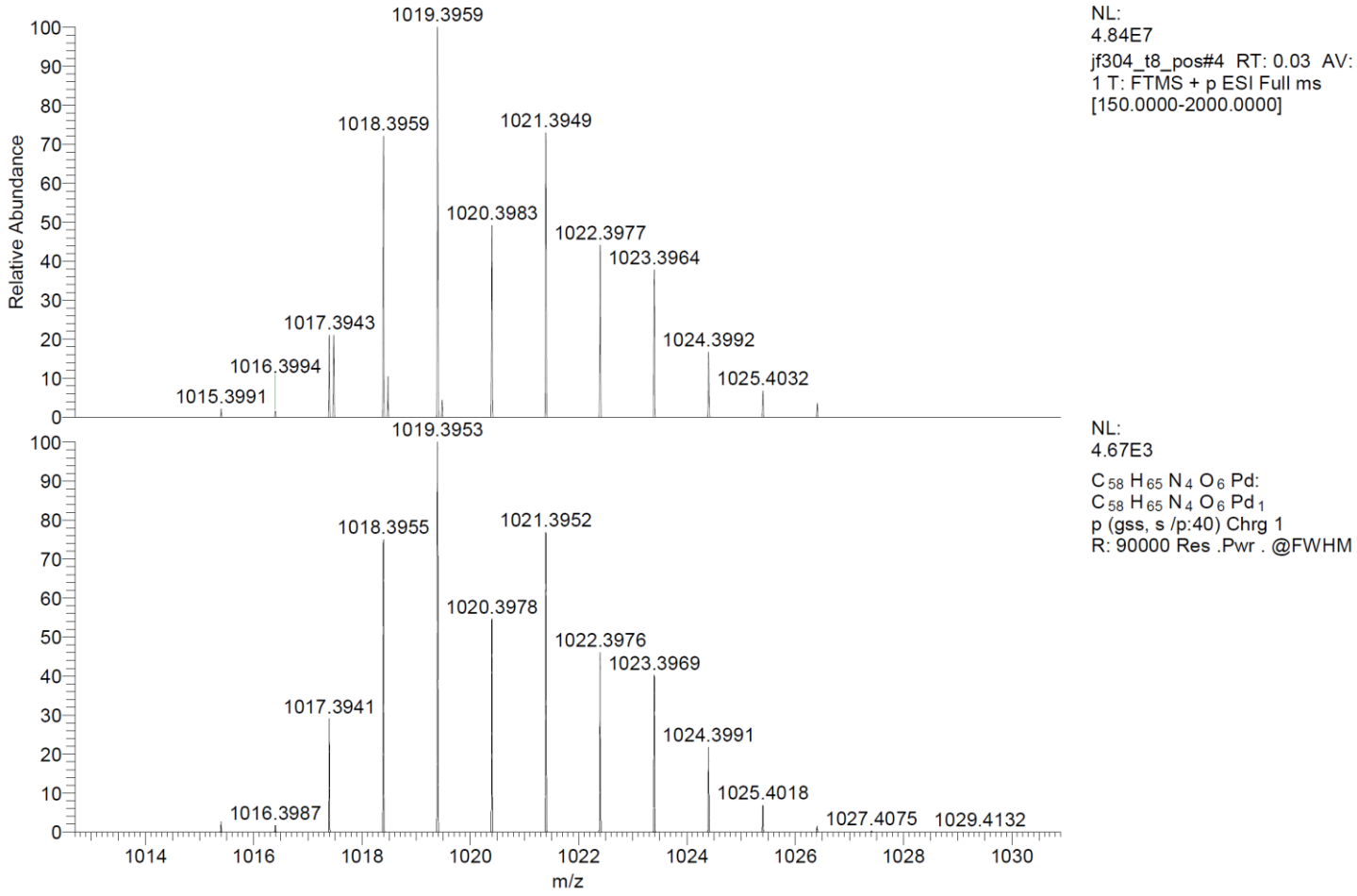
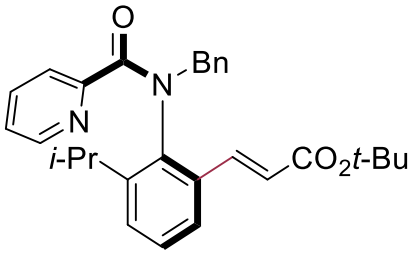
R: 90000 Res .Pwr . @FWHM



References

[1] Q-J. Yao, P-P. Xie, Y-J. Wu, Y-L. Feng, M-Y. Teng, X. Hong, B-F. Shi, *J. Am. Chem. Soc* 2020, **142**, 18266-18276

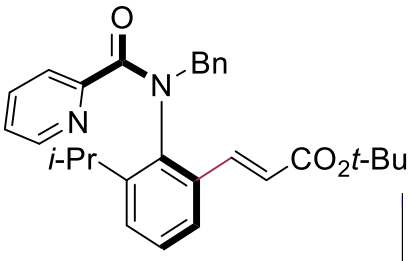
NMR spectra


O
N
Bn
N
i-Pr
CO2t-Bu

3aa

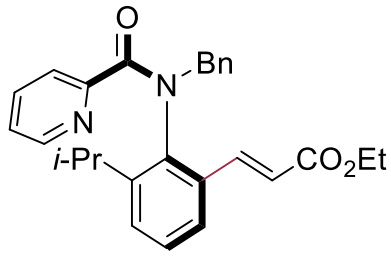
1.00
1.00
1.01
1.46
8.54
1.11
1.00
1.00
1.00
1.01
9.00
3.42
3.41
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


168.44
165.73
153.31
147.57
147.14
140.46
139.03
136.01
135.86
133.37
130.55
128.44
128.28
128.13
127.94
124.35
124.27
124.15
121.68
80.33
54.47
28.29
28.22
24.19
23.55


O
N
Bn
N
i-Pr
CO2t-Bu

3aa

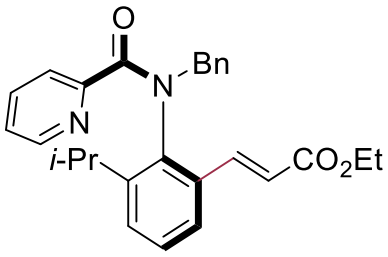
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
N
Bn
N
i-Pr
CO2Et

3ab

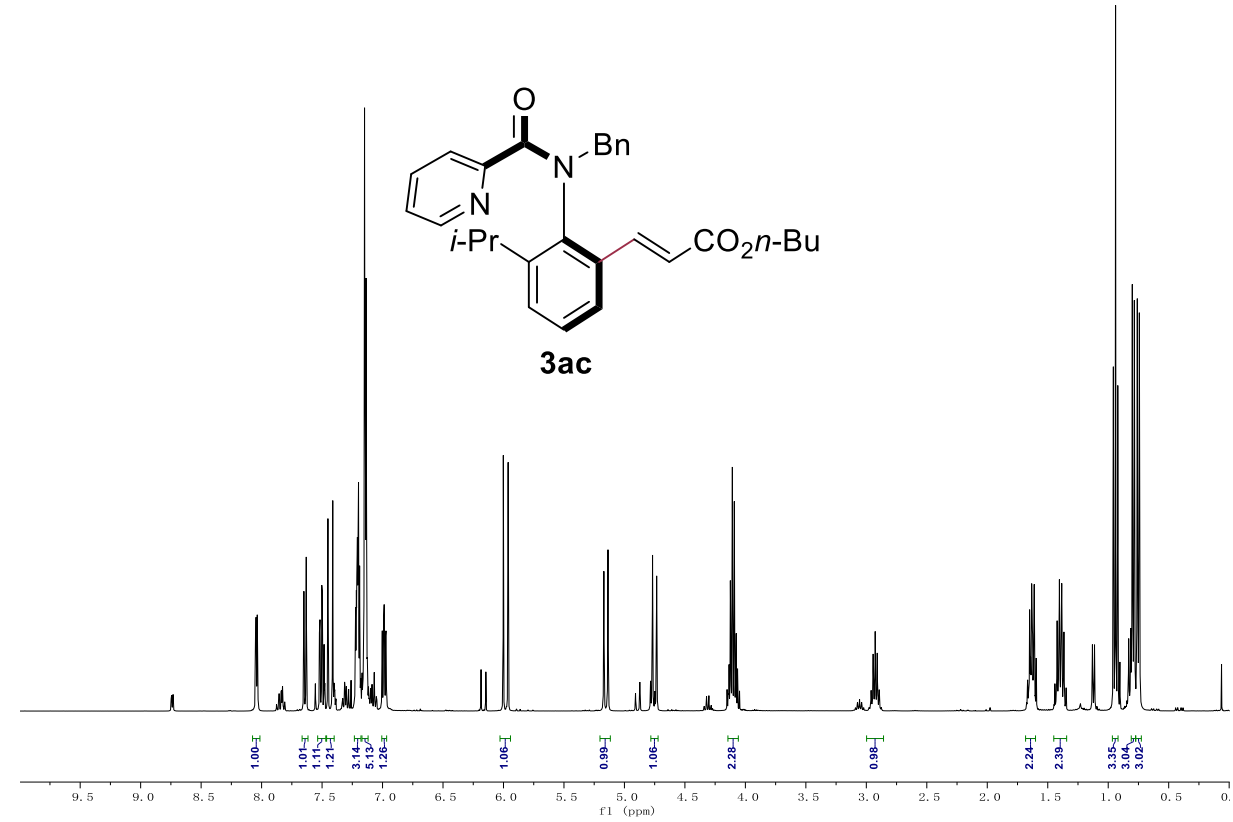
1.00
1.01
1.17
1.32
3.14
5.06
1.04
1.01
1.02
1.16
2.35
1.03
3.43
3.06
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

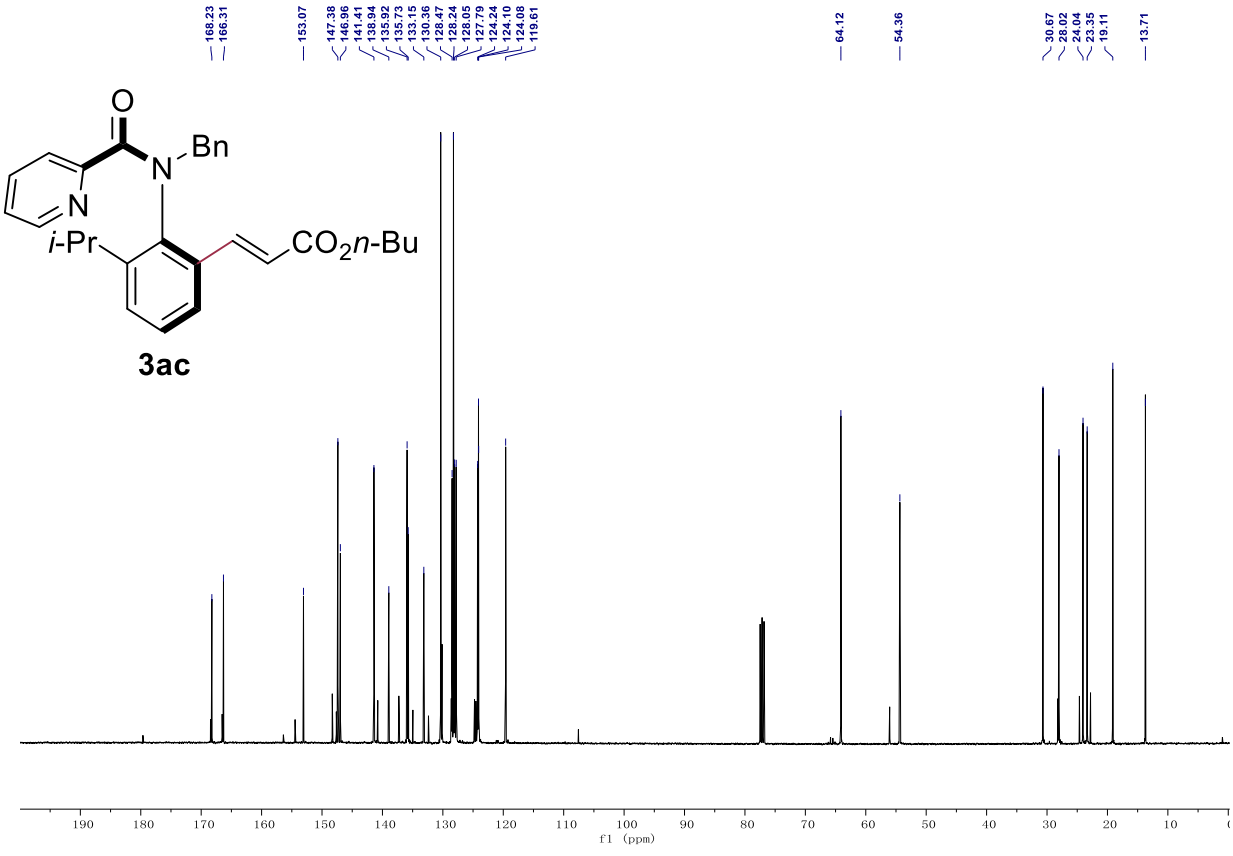

168.29
166.29
153.10
147.43
146.98
141.50
138.99
135.92
135.77
133.25
130.39
128.45
128.27
128.03
127.81
124.23
124.13
119.68
60.26
54.41
28.01
24.05
23.33
14.28

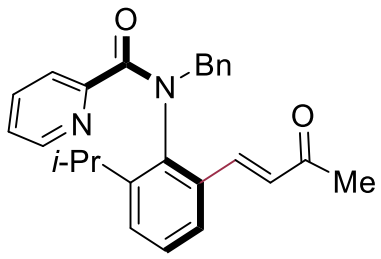

O
N
Bn
N
i-Pr
CO2Et

3ab

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

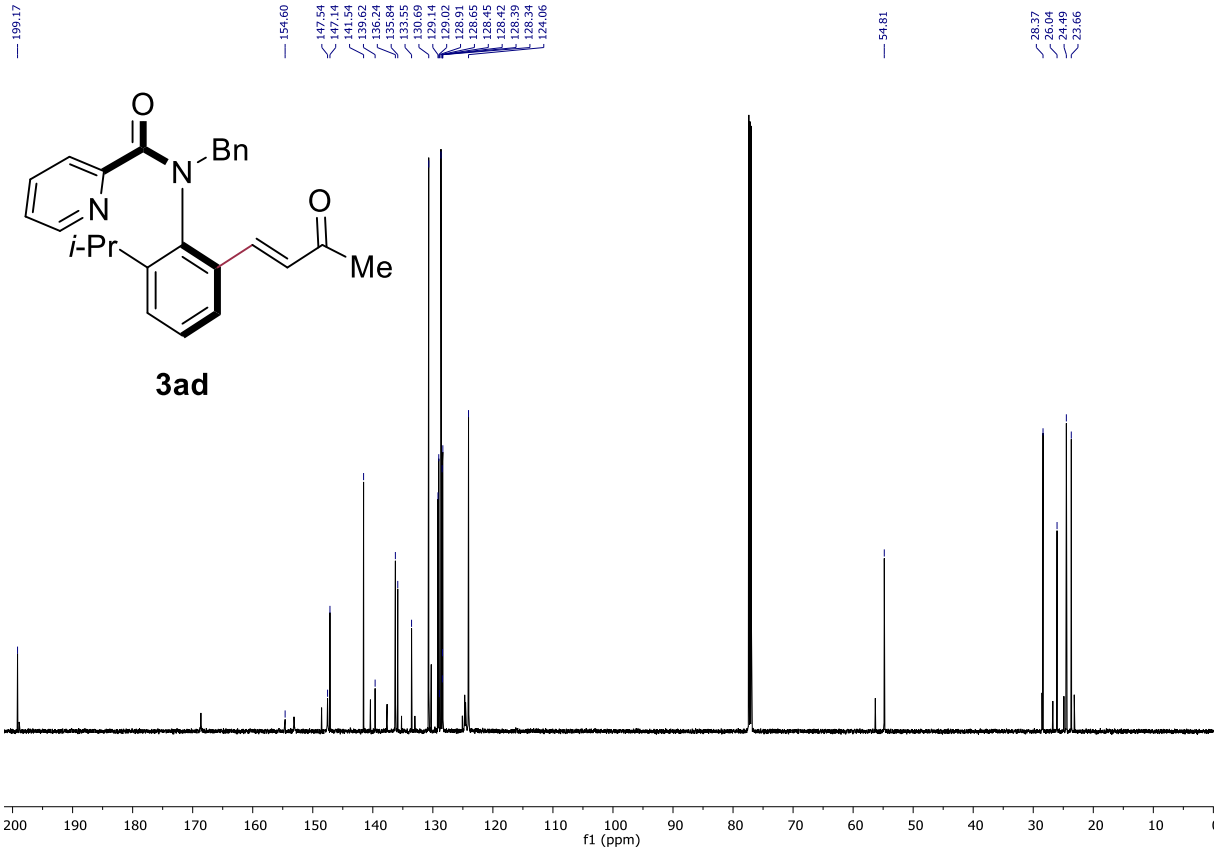

O
N
Bn
N
i-Pr
CO2n-Bu
3ac
1.00
1.01
1.11
1.21
3.14
5.13
1.26
1.06
0.99
1.06
2.28
0.98
2.24
2.39
3.35
3.04
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


168.23
166.31
153.07
147.38
146.96
141.41
138.94
135.92
135.73
133.15
130.36
128.47
128.24
128.05
127.79
124.24
124.10
124.08
119.61
64.12
54.36
30.67
28.02
24.04
23.35
19.11
13.71
O
N
Bn
N
i-Pr
CO2n-Bu
3ac
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
N
Bn
N
i-Pr
O
Me

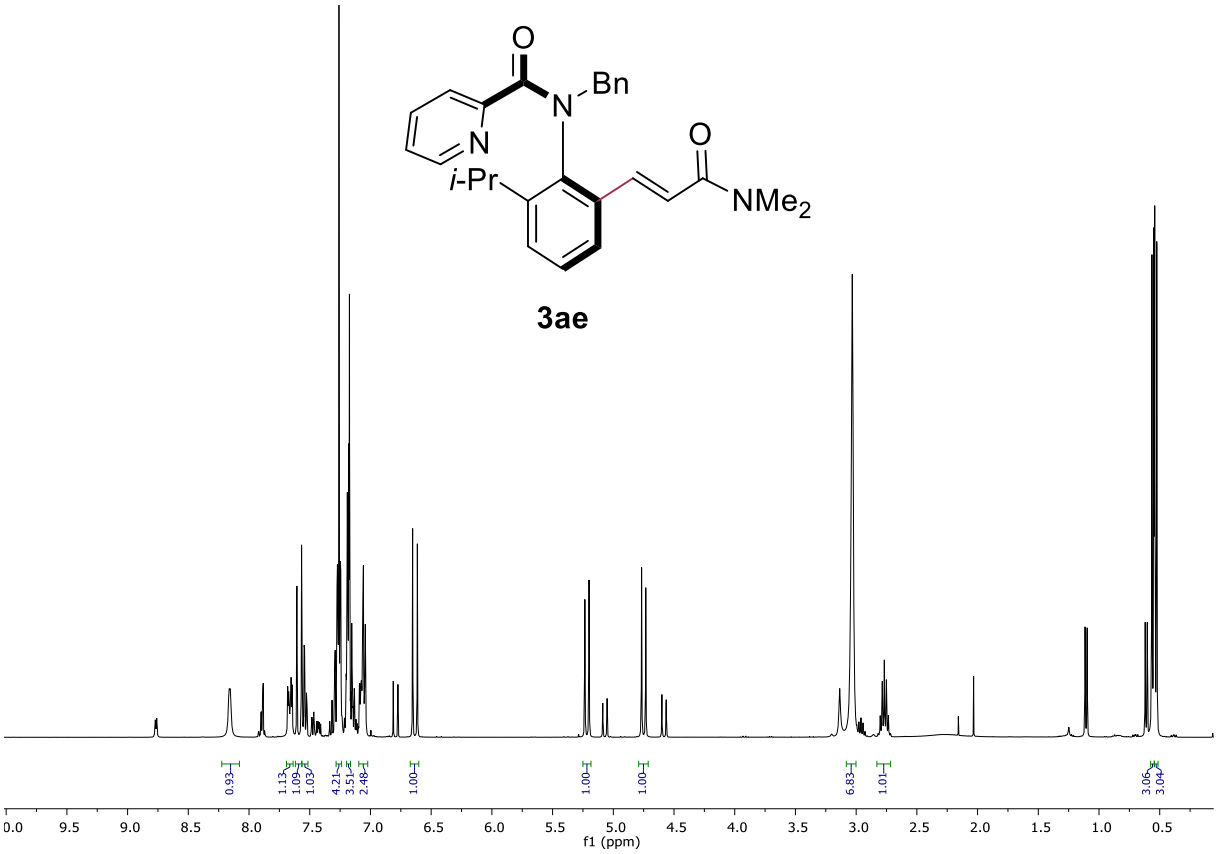
3ad

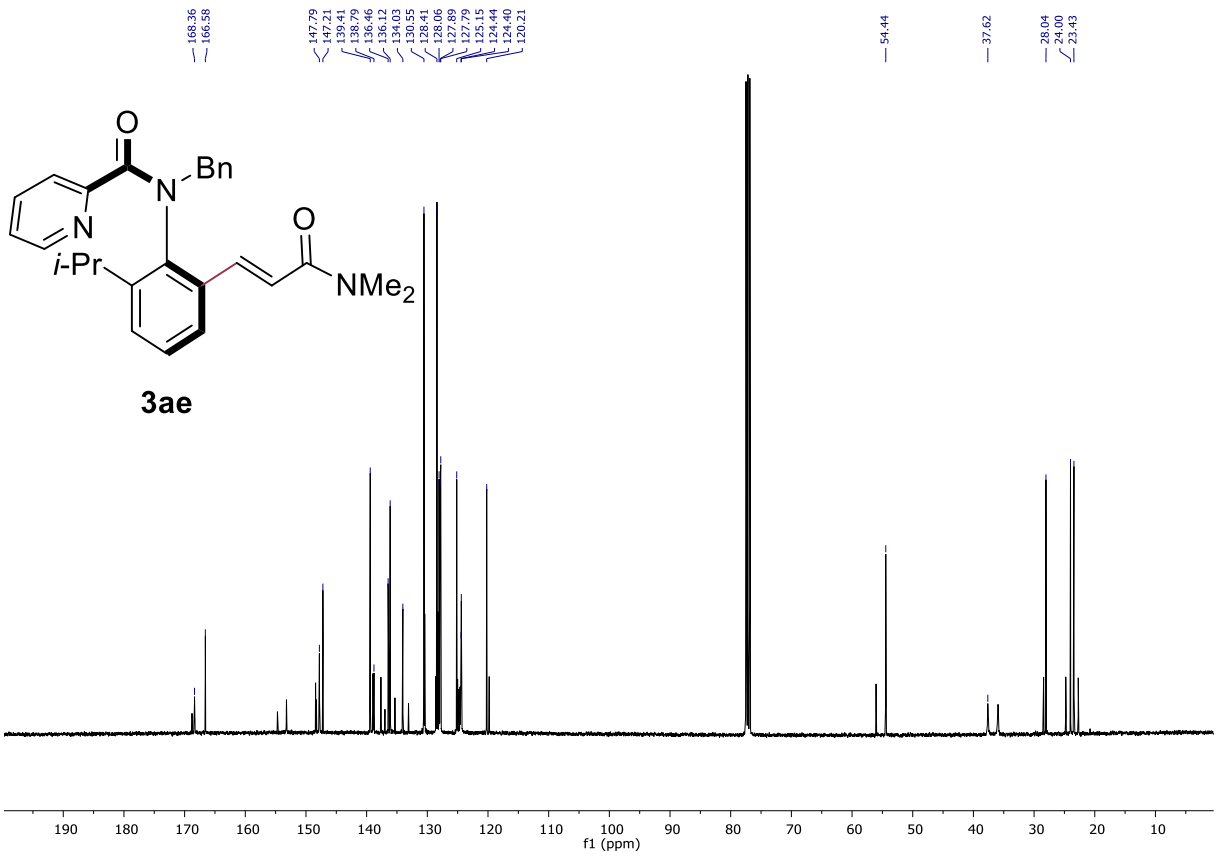
0.91
0.91
1.03
3.01
5.09
0.98
1.00
1.00
1.00
1.00
1.07
3.11
3.00
3.01
f1 (ppm)

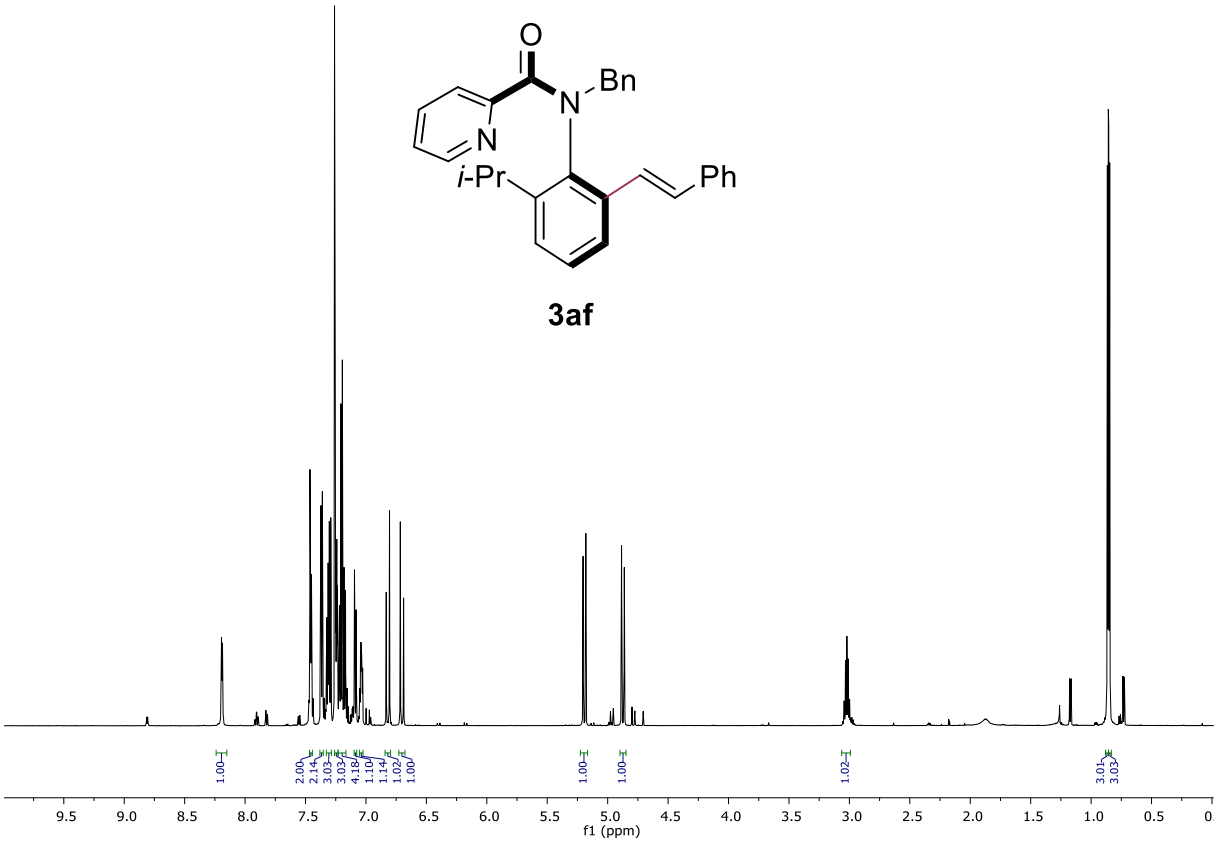

199.17
154.60
147.54
147.14
141.54
139.62
136.24
135.84
133.55
130.69
129.14
129.02
128.91
128.65
128.45
128.42
128.39
128.34
124.06
54.81
28.37
26.04
24.49
23.66
f1 (ppm)

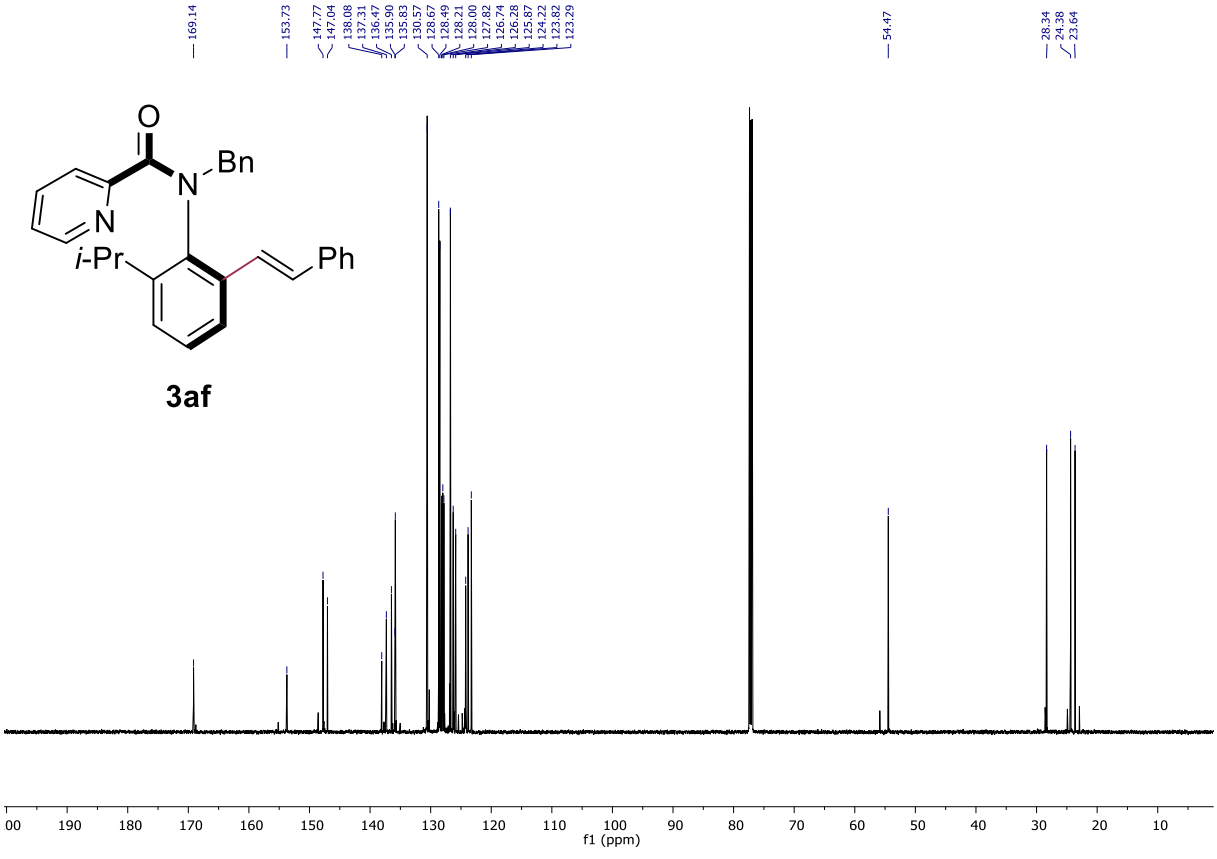
O
N
Bn
N
i-Pr
O
Me

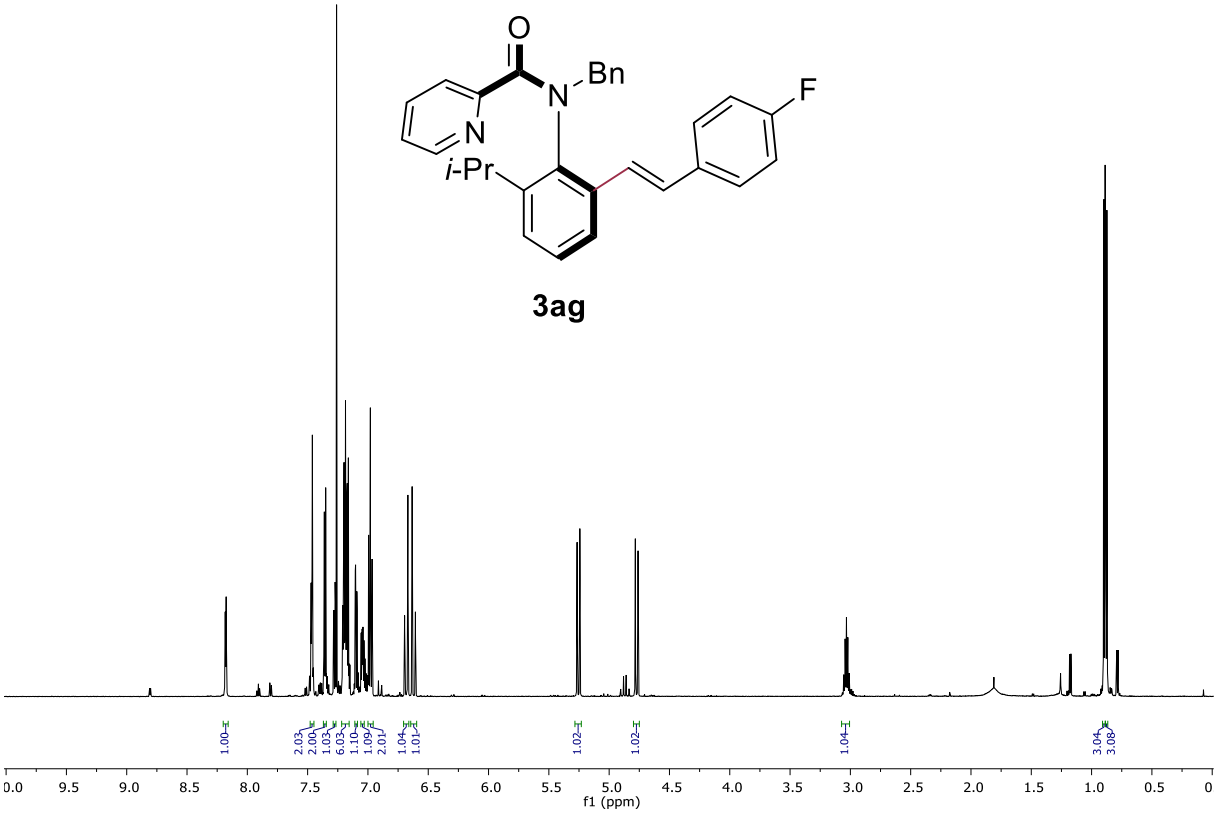
3ad

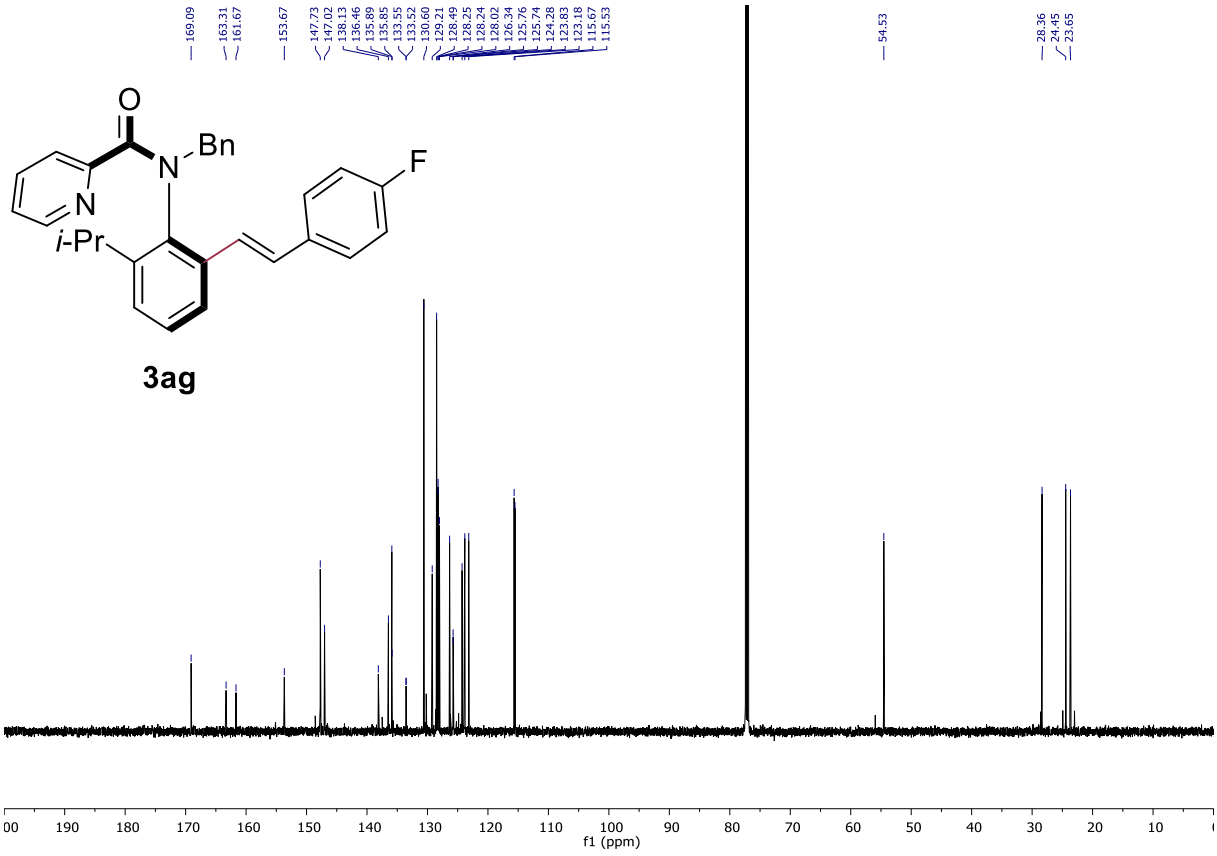

O
N
Bn
N
i-Pr
O
NMe2
3ae
0.93
1.13
1.09
1.03
4.21
3.51
2.48
1.00
1.00
1.00
6.83
1.01
3.06
3.04
f1 (ppm)

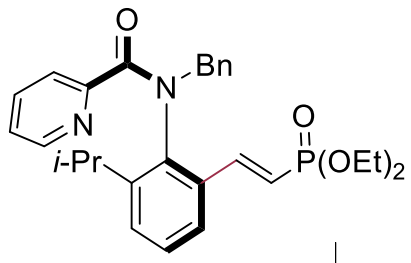

168.36
166.58
147.79
147.21
139.41
138.79
136.46
136.12
134.03
130.55
128.41
128.06
127.89
127.79
125.15
124.44
124.40
120.21
54.44
37.62
28.04
24.00
23.43
O
N
Bn
N
i-Pr
O
NMe2
3ae
f1 (ppm)


O
N
Bn
N
i-Pr
Ph
3af
1.00
2.00
2.14
3.03
3.03
4.18
1.10
1.14
1.02
1.00
1.00
1.00
1.02
3.01
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


169.14
153.73
147.77
147.04
138.08
137.31
136.47
135.90
135.83
130.57
128.67
128.49
128.21
128.00
127.82
126.74
126.28
125.87
124.22
123.82
123.29
54.47
28.34
24.38
23.64
O
N
Bn
N
i-Pr
Ph
3af
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

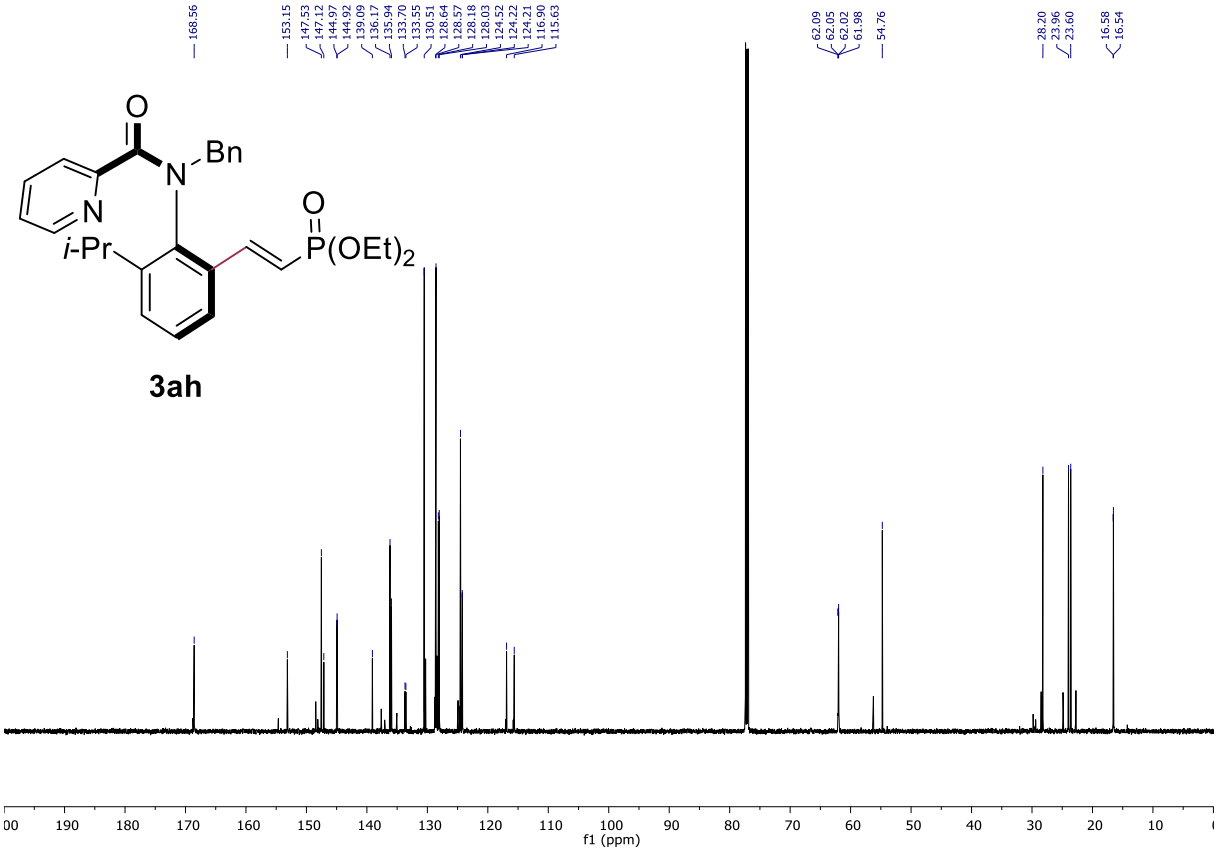

O
N
Bn
F
N
i-Pr
3ag
1.00
2.03
2.00
1.03
6.03
1.10
1.09
2.01
1.04
1.01
1.02
1.02
1.04
3.04
3.08
f1 (ppm)


169.09
163.31
161.67
153.67
147.73
147.02
138.13
136.46
135.89
135.85
133.55
133.52
130.60
129.21
128.49
128.25
128.24
128.02
126.34
125.76
125.74
124.28
123.83
123.18
115.67
115.53
54.53
28.36
24.45
23.65
O
N
Bn
F
N
i-Pr
3ag
f1 (ppm)


O
N
Bn
N
i-Pr
O
P(OEt)2

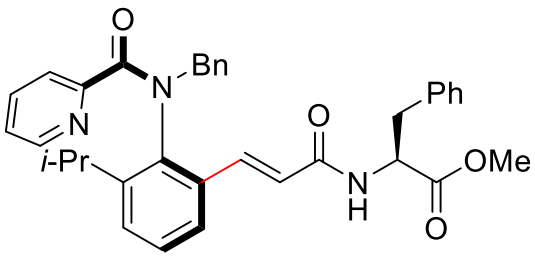
3ah

1.00
1.00
1.01
4.25
3.09
1.00
1.17
1.01
1.00
1.00
1.01
4.13
1.01
7.14
3.01
3.04
f1 (ppm)

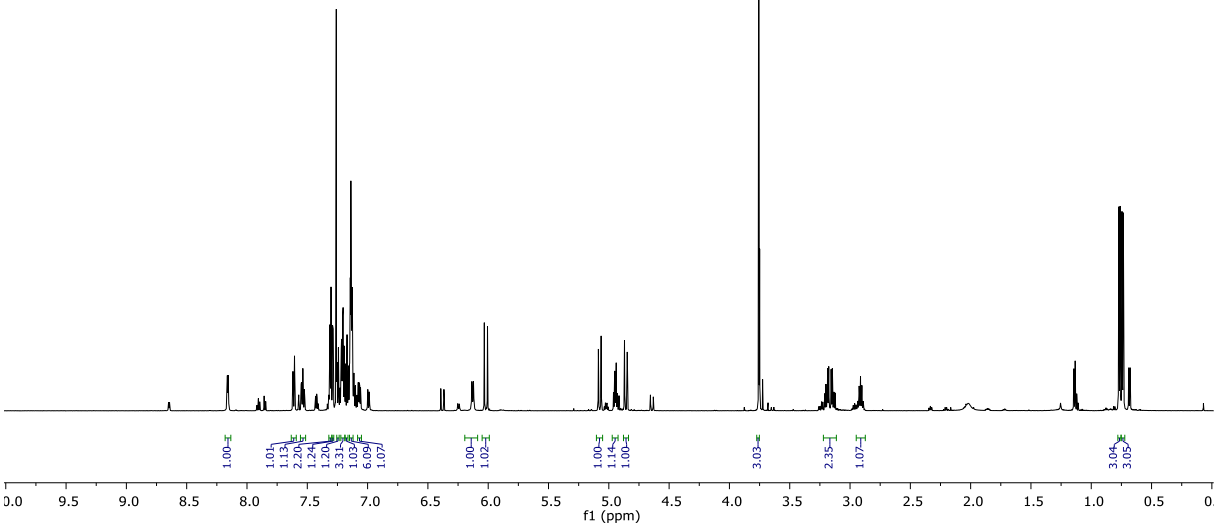

168.56
153.15
147.53
147.12
144.97
144.92
139.09
136.17
135.94
133.70
133.55
130.51
128.64
128.57
128.18
128.03
124.52
124.22
124.21
116.90
115.63
62.09
62.05
62.02
61.98
54.76
28.20
23.96
23.60
15.58
15.54
f1 (ppm)

O
N
Bn
N
i-Pr
O
P(OEt)2

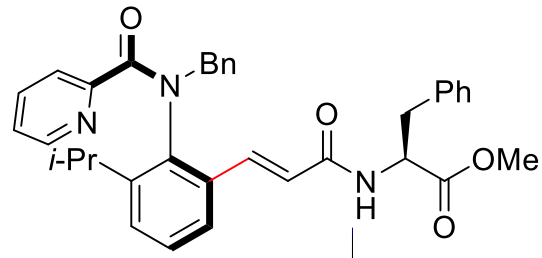
3ah


O
N
Bn
N
i-Pr
O
Ph
N
H
OMe
O

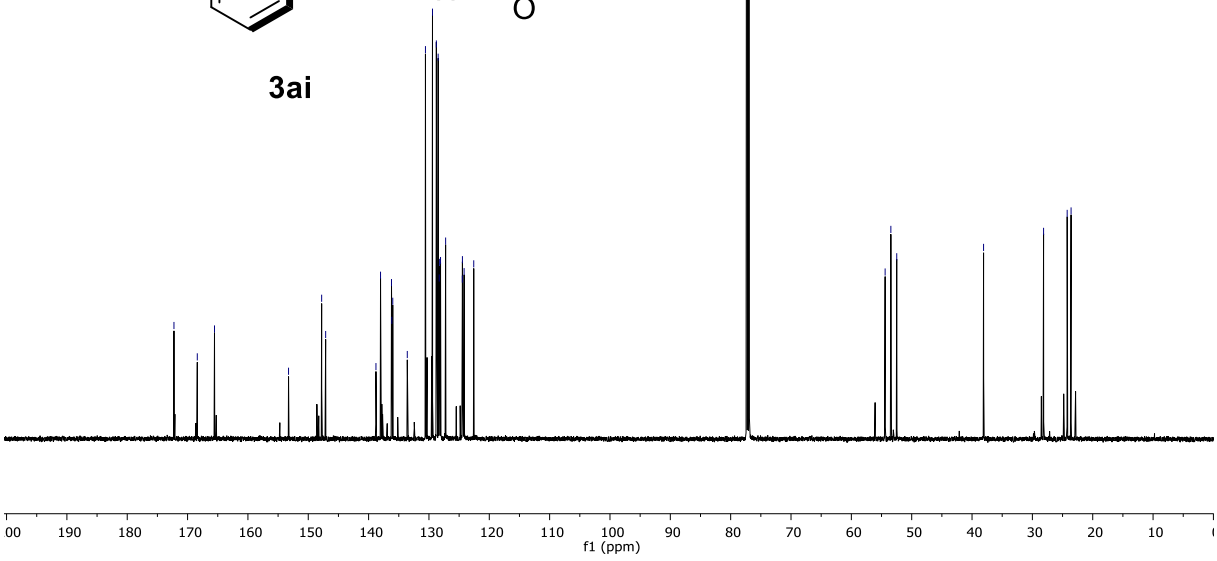
3ai

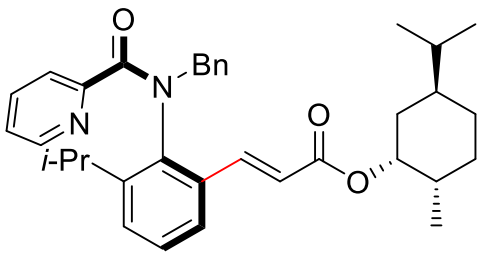

1.00
1.01
1.13
2.20
1.24
1.20
3.31
1.03
6.09
1.07
1.00
1.02
1.00
1.14
1.00
3.03
2.35
1.07
3.04
3.05
f1 (ppm)


172.26
168.39
165.54
153.27
147.78
147.12
138.78
138.02
136.21
136.16
136.00
133.59
130.58
129.41
128.77
128.48
128.29
128.23
128.08
127.24
124.47
124.45
124.17
122.58
54.40
53.45
52.48
38.09
28.15
24.23
23.59


O
N
Bn
N
i-Pr
O
Ph
N
H
OMe
O

3ai

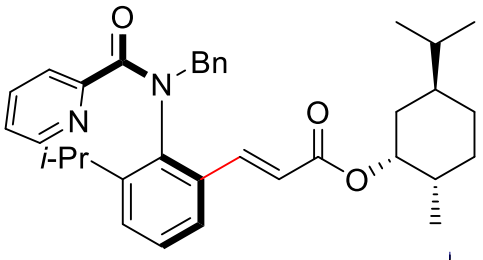

f1 (ppm)


O
N
Bn
N
i-Pr
O
O

3aj

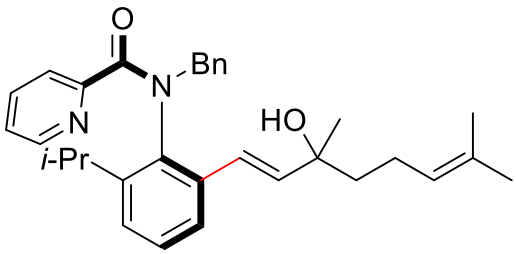
1.00
1.00
2.19
9.02
1.32
1.01
1.07
2.39
1.18
1.18
1.30
2.26
2.47
11.60
6.34
f1 (ppm)


168.38
168.36
165.94
153.33
153.30
148.50
147.53
147.51
147.45
147.26
147.12
141.48
141.08
139.15
139.06
135.69
135.95
135.75
133.43
133.32
130.57
130.51
130.34
128.68
128.65
128.56
128.44
128.14
128.12
127.99
127.95
124.50
124.44
124.38
124.33
124.24
124.05
120.59
119.97
74.19
74.11
54.45
54.42
47.22
47.18
41.09
34.39
34.37
31.50
28.28
28.20
26.39
26.36
24.28
24.09
23.63
23.61
23.57
23.54
22.19
20.92
16.59
16.55

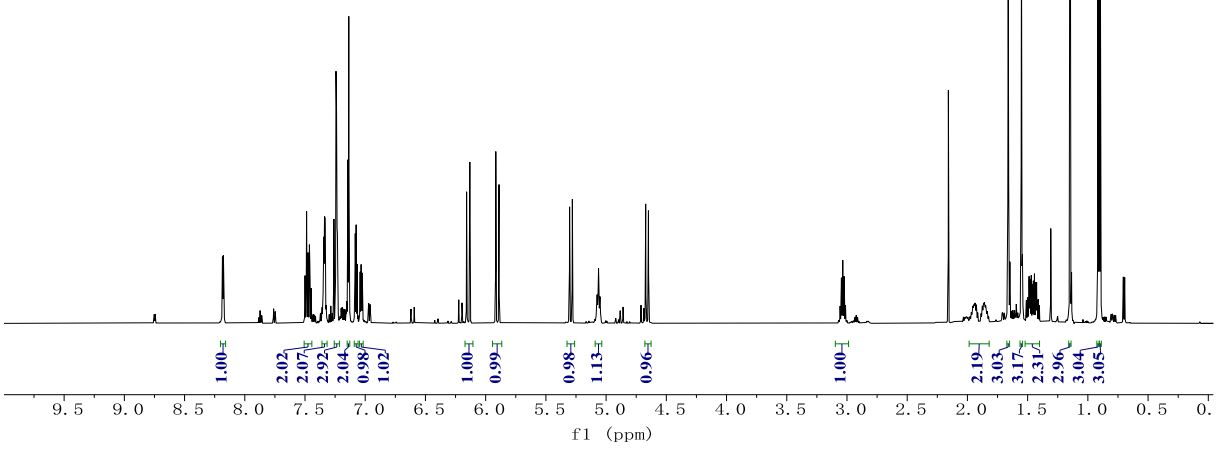

O
N
Bn
N
i-Pr
O
O

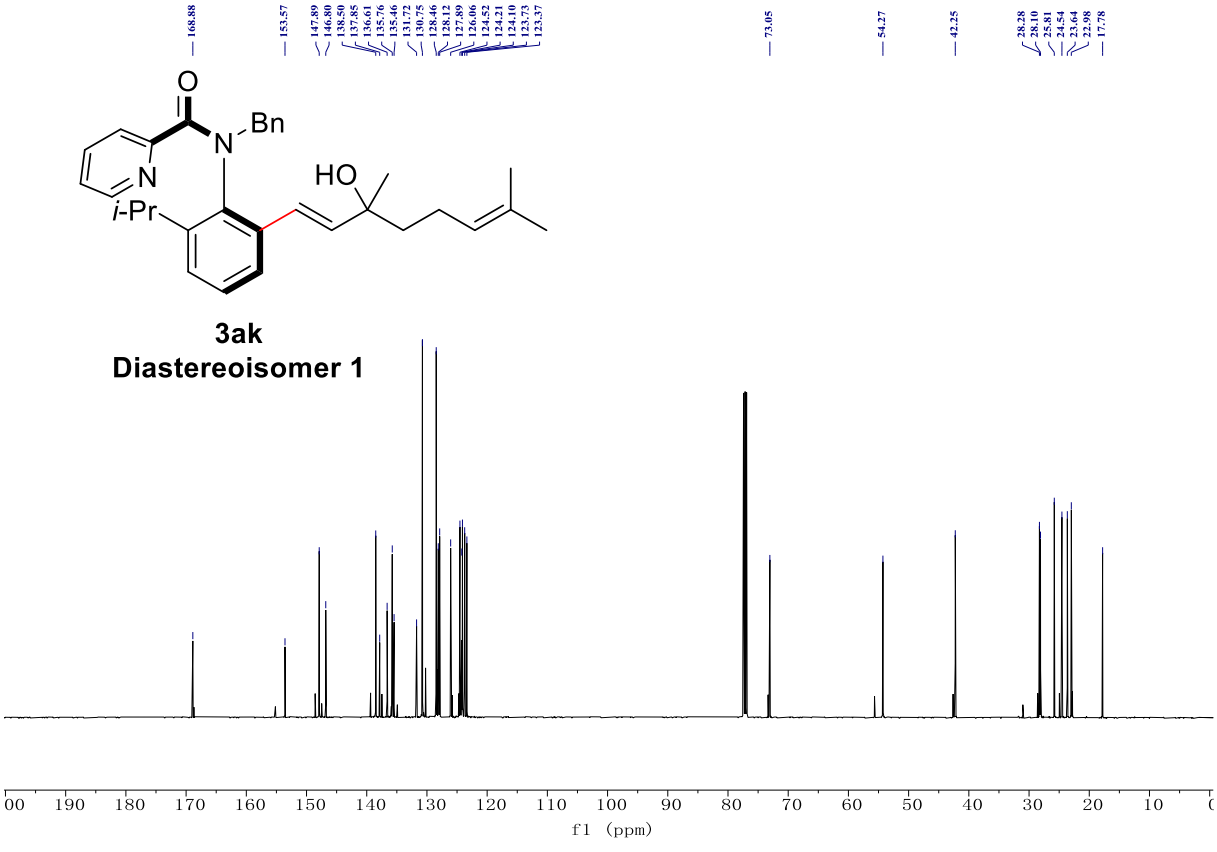
3aj

f1 (ppm)

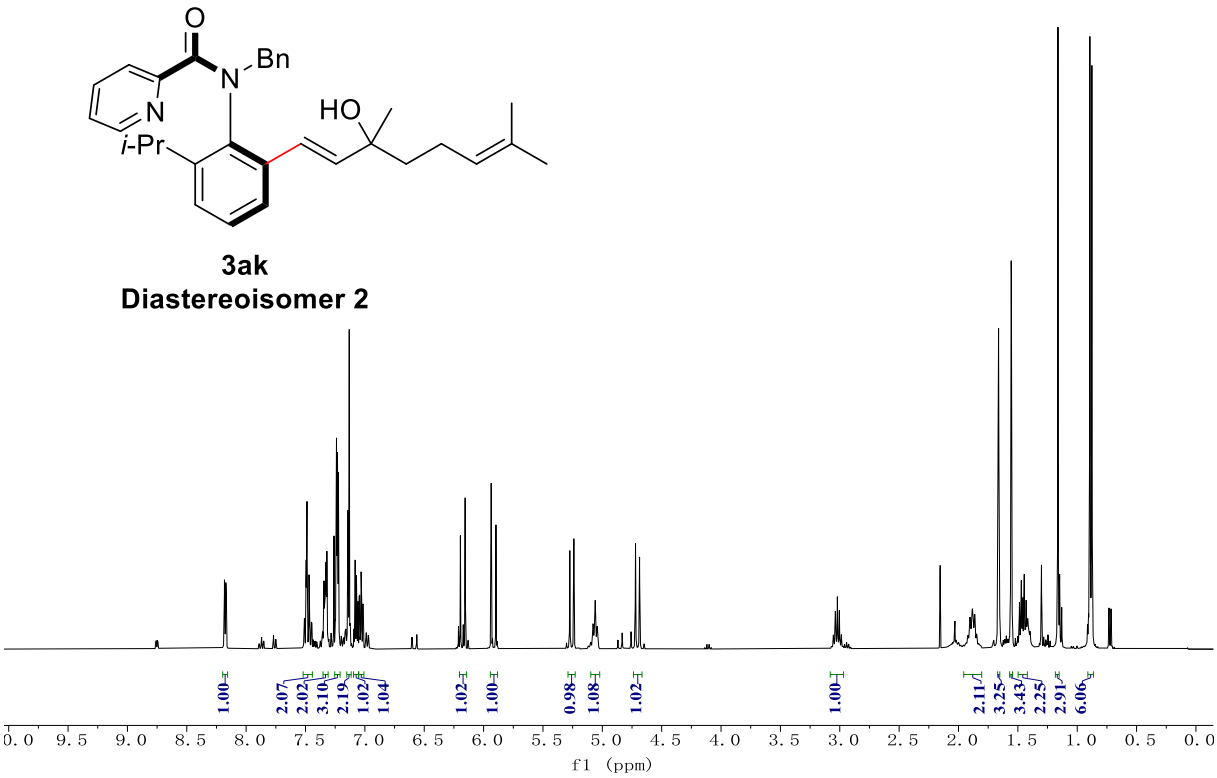


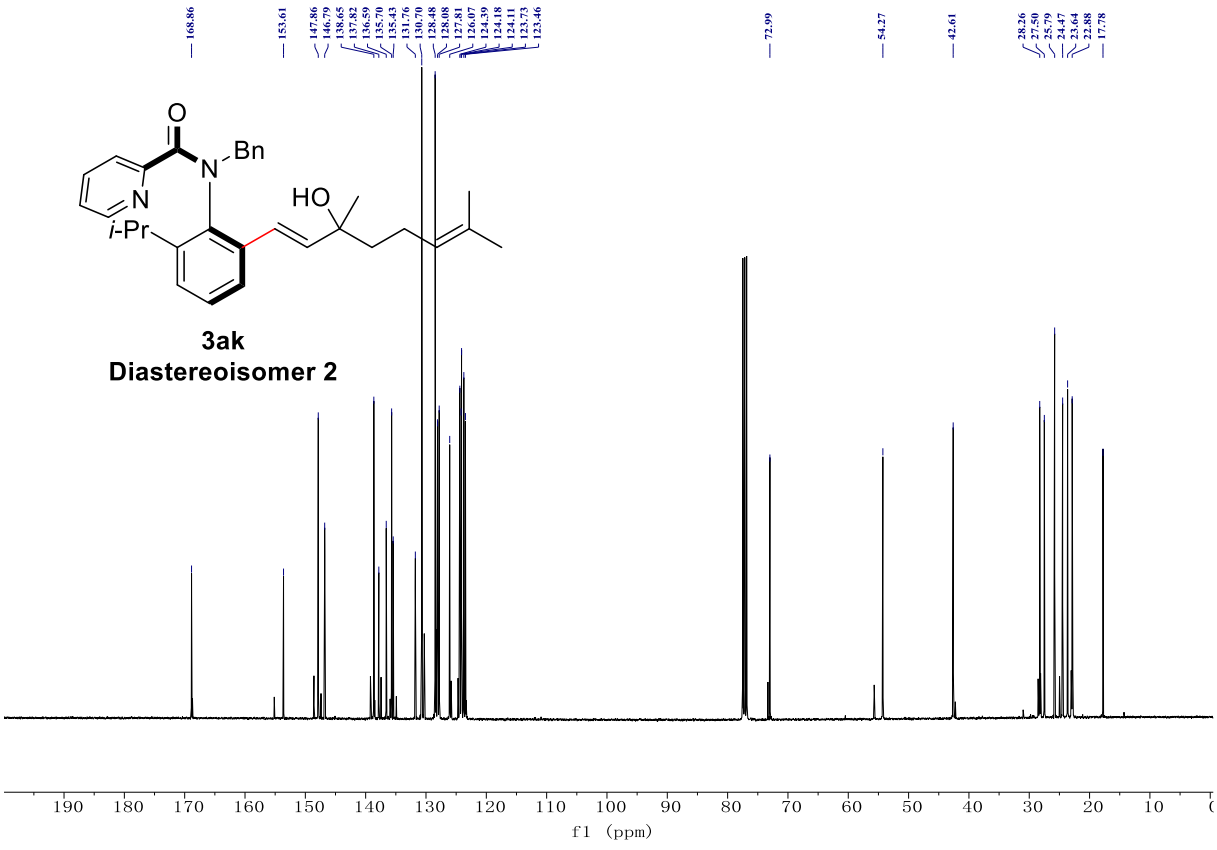
3ak
Diastereoisomer 1

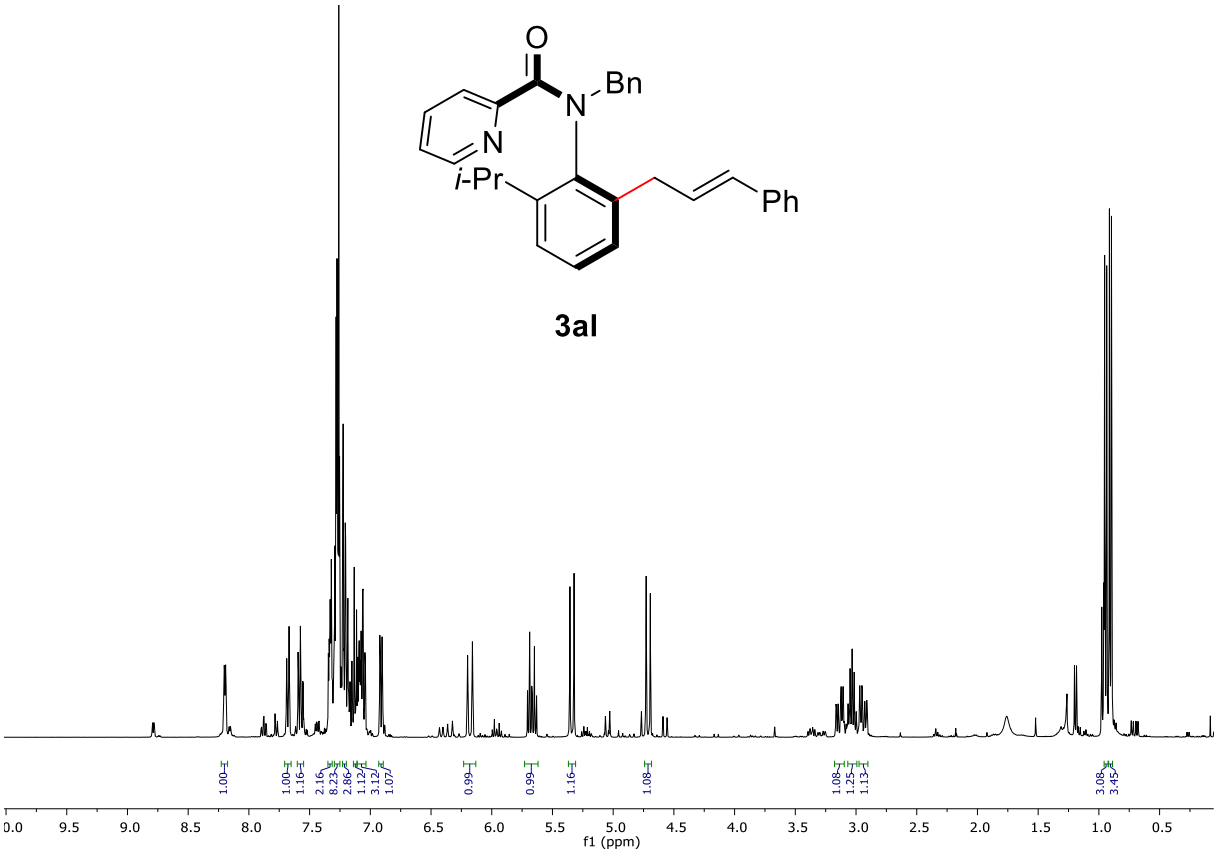


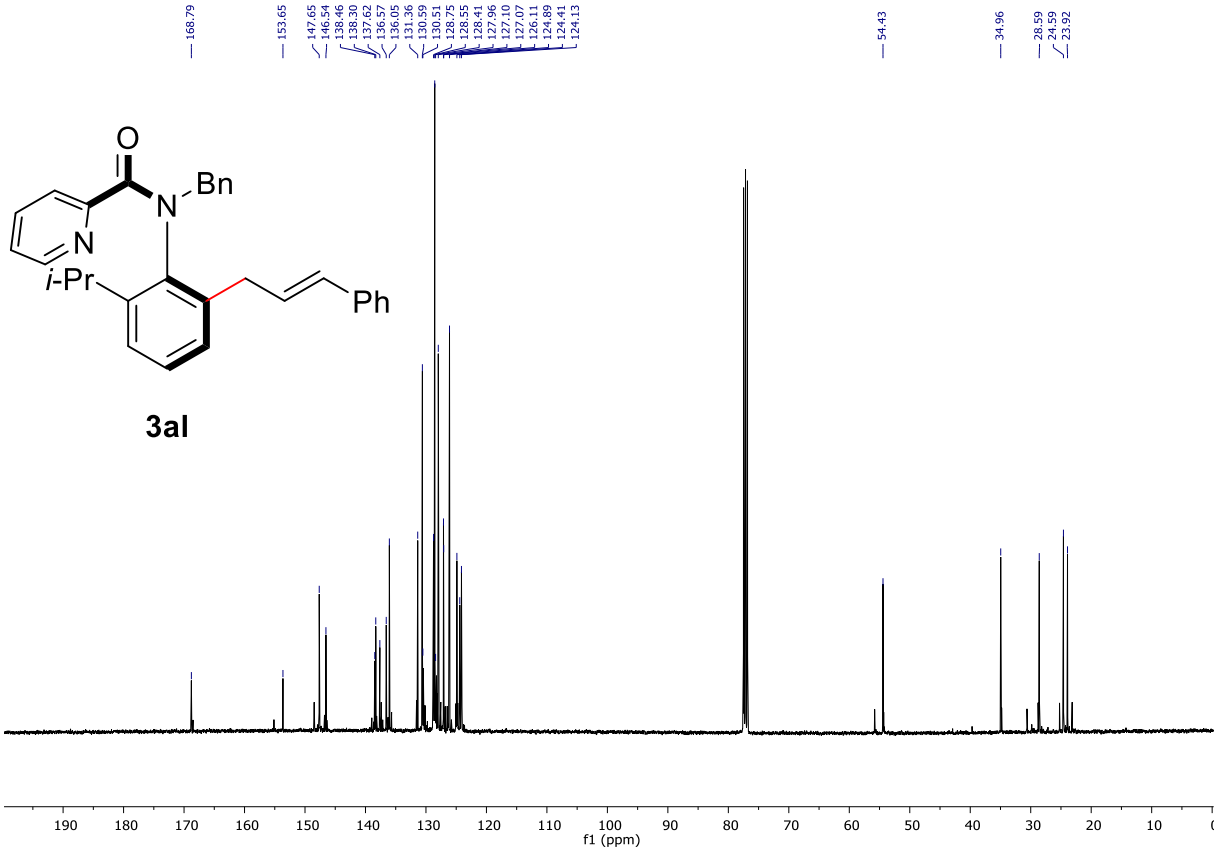


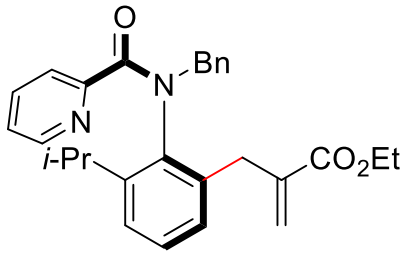
3ak
Diastereoisomer 1


O
N
Bn
N
i-Pr
HO
3ak
Diastereoisomer 2
1.00
2.07
2.02
3.10
2.19
1.02
1.04
1.02
1.00
0.98
1.08
1.02
1.00
2.11
3.25
3.43
2.25
2.91
6.06
f1 (ppm)


168.86
153.61
147.86
146.79
138.65
137.82
136.59
135.70
135.43
131.76
130.70
128.48
128.08
127.91
126.07
124.39
124.18
124.11
123.73
123.46
72.99
54.27
42.61
28.26
27.50
25.39
24.47
23.64
22.88
17.78
O
N
Bn
N
i-Pr
HO
3ak
Diastereoisomer 2
f1 (ppm)

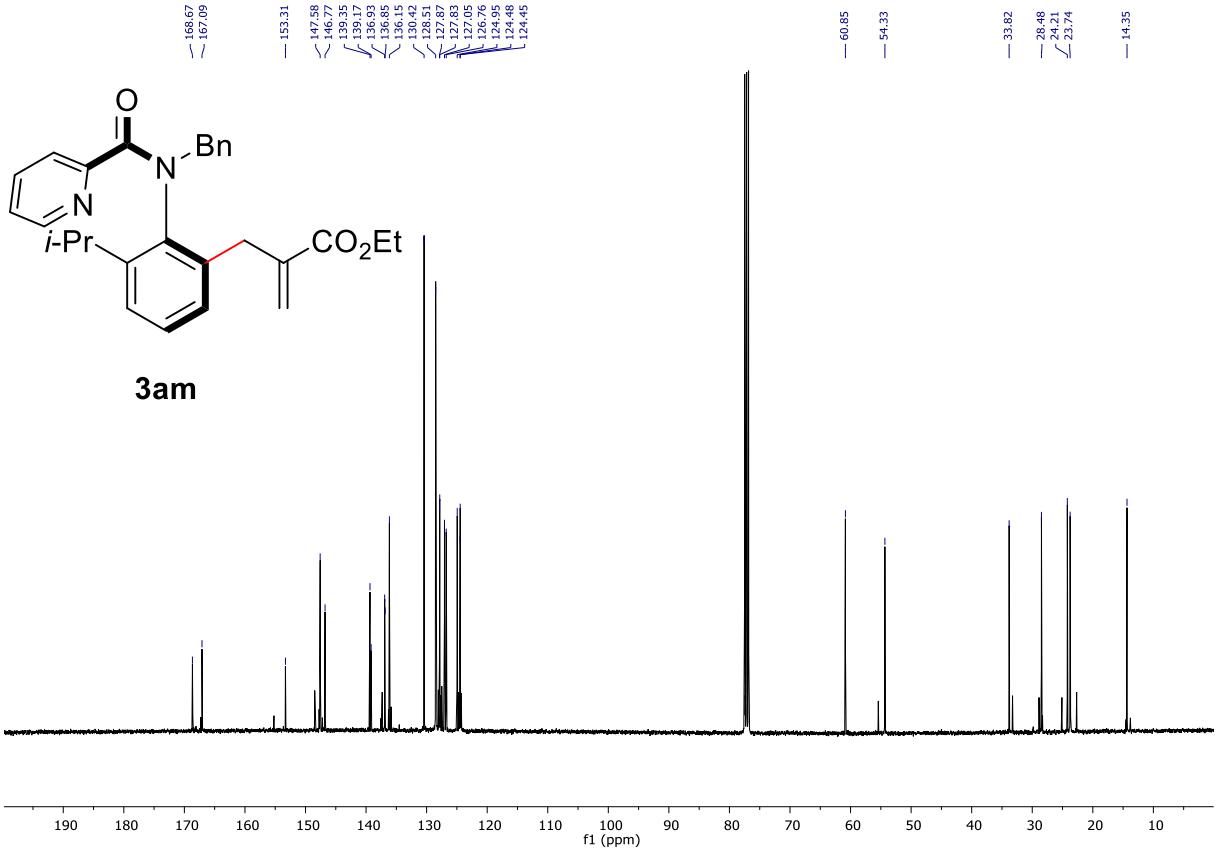

O
Bn
N
N
i-Pr
Ph
3aI
1.00
1.00
1.16
2.16
8.23
2.86
1.12
3.12
1.07
0.99
0.99
1.16
1.08
1.08
1.25
1.13
3.08
3.45
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


168.79
153.65
147.65
146.54
138.46
138.30
137.62
136.57
136.05
131.36
130.59
130.51
128.75
128.55
128.41
127.96
127.10
127.07
126.11
124.89
124.41
124.13
54.43
34.96
28.59
24.59
23.92
O
Bn
N
N
i-Pr
Ph
3aI
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
N
Bn
N
i-Pr
CO2Et

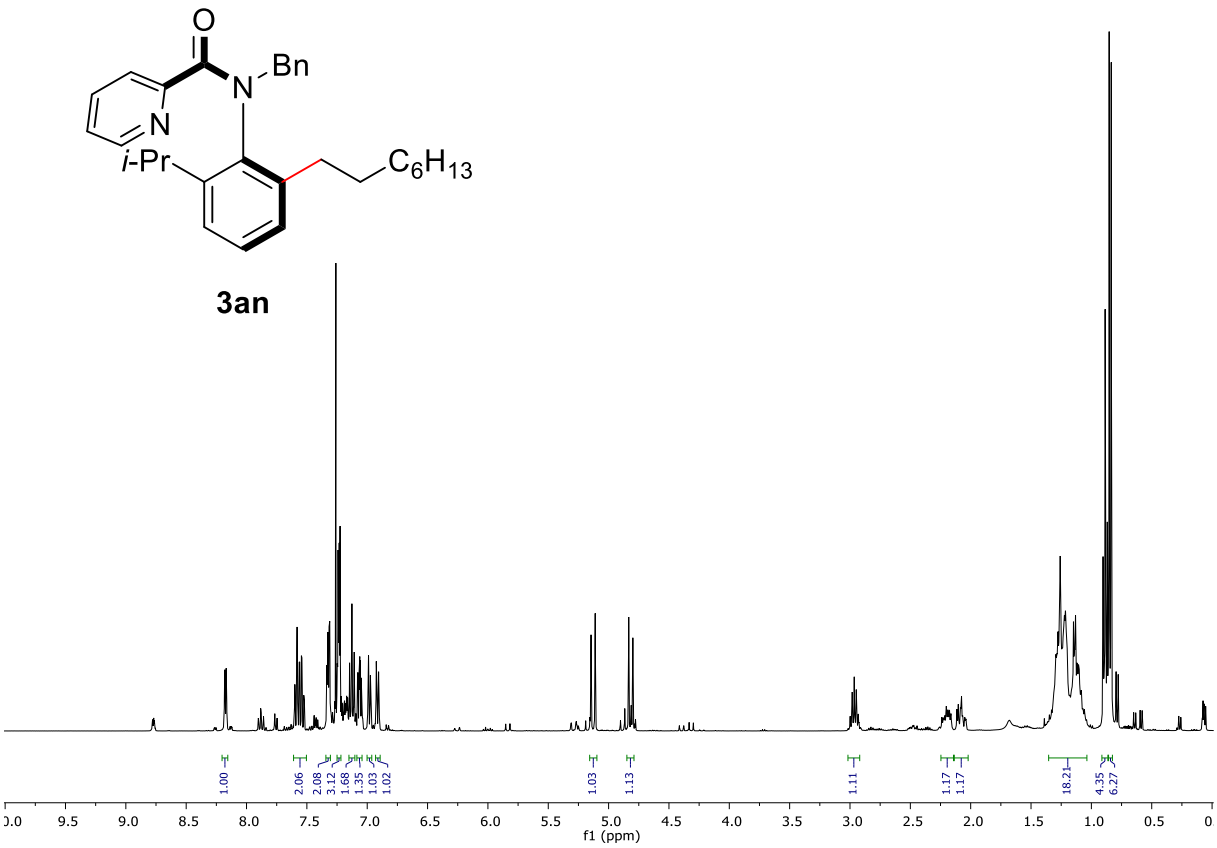
3am

1.00
1.00
1.06
2.10
3.20
1.01
1.09
1.02
1.02
1.01
2.01
1.00
2.51
2.02
1.06
3.79
2.97
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

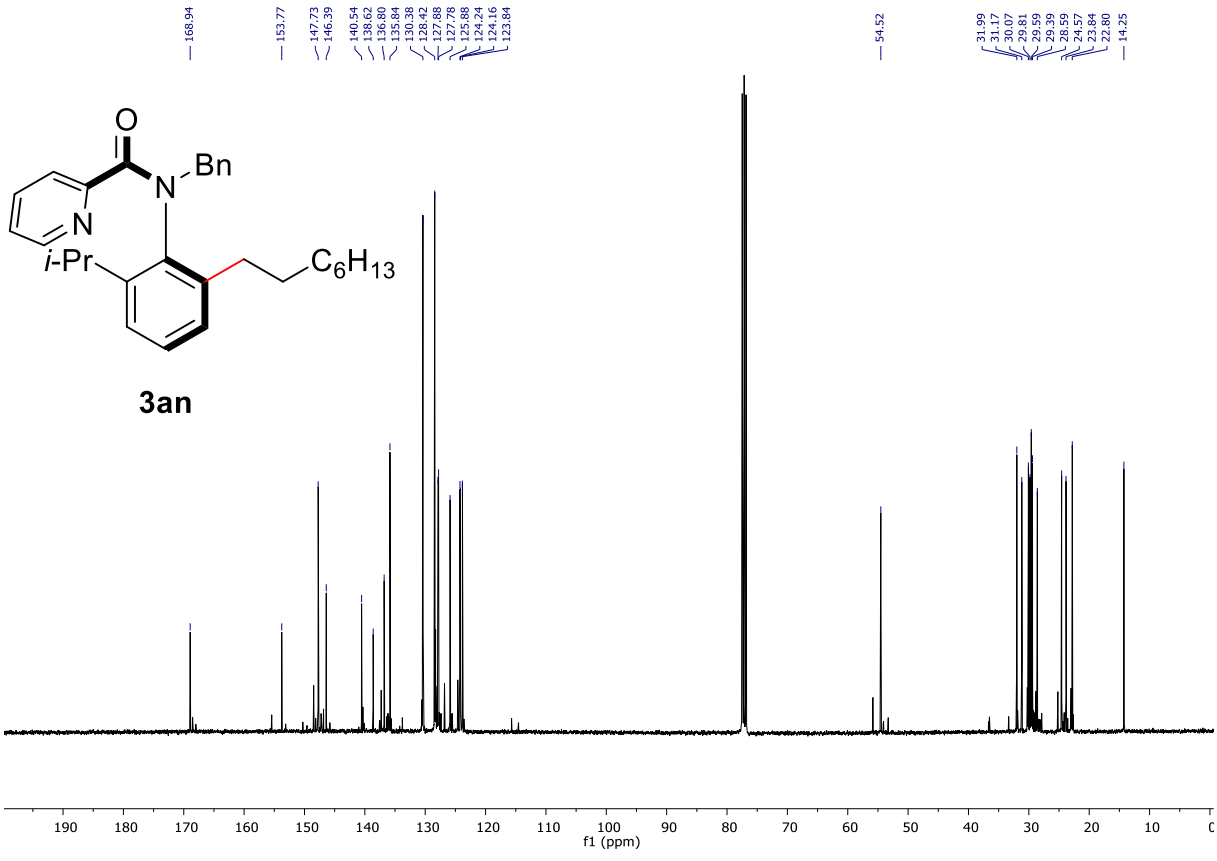

168.67
167.09
153.31
147.58
146.77
139.35
139.17
136.93
136.85
136.15
130.42
128.51
127.87
127.83
127.05
126.76
124.95
124.48
124.45
60.85
54.33
33.82
28.48
24.21
23.74
14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

O
N
Bn
N
i-Pr
CO2Et

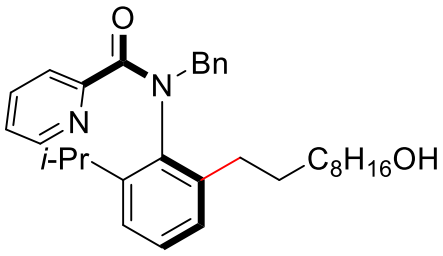
3am


O
N
Bn
N
i-Pr
C6H13
1.00
2.06
2.08
3.12
1.68
1.35
1.03
1.02
1.03
1.13
1.11
1.17
1.17
18.21
4.35
6.27
f1 (ppm)

3an

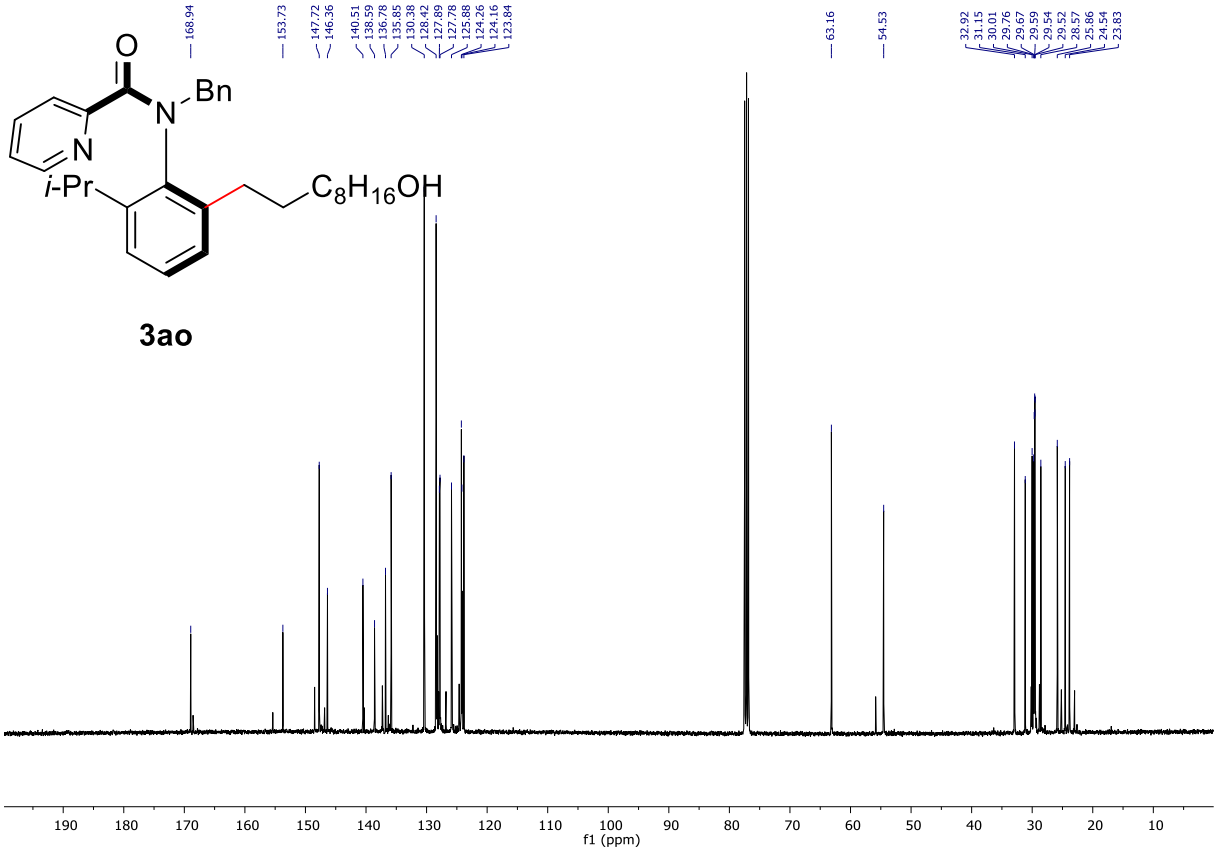

168.94
153.77
147.73
146.39
140.54
138.62
136.80
135.84
130.38
128.42
127.88
127.78
125.88
124.24
124.16
123.84
54.52
31.99
31.17
30.07
29.81
29.59
29.39
28.59
24.57
23.84
22.80
14.25
O
N
Bn
N
i-Pr
C6H13
f1 (ppm)

3an


O
N
Bn
N
i-Pr
C8H16OH

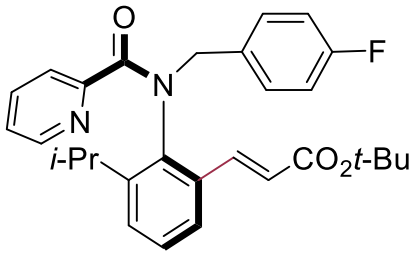
3ao

1.00
2.03
2.07
3.05
1.51
1.24
1.00
1.01
0.99
1.01
2.31
1.13
1.22
1.15
2.75
19.13
6.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


168.94
153.73
147.72
146.36
140.51
138.59
136.78
135.85
130.38
128.42
127.89
127.78
125.88
124.26
124.16
123.84
63.16
54.53
32.92
31.15
30.01
29.76
29.67
29.59
29.54
29.52
28.57
25.86
24.54
23.83
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

O
N
Bn
N
i-Pr
C8H16OH

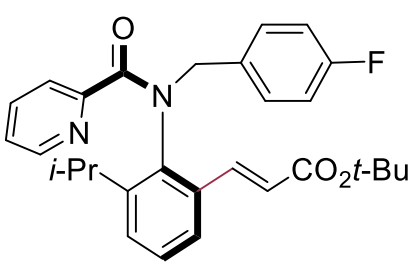
3ao


O
N
F
N
i-Pr
CO2t-Bu

3ba

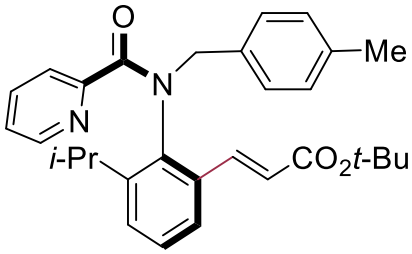
1.00
1.02
1.02
1.14
5.00
1.21
2.04
0.99
0.99
1.00
1.12
9.06
3.05
3.03
f1 (ppm)


168.34
165.54
163.75
161.30
153.05
147.48
146.97
140.22
138.86
136.60
133.38
132.24
132.16
131.75
131.72
128.44
128.17
124.36
124.18
124.08
121.53
115.28
115.07
80.30
53.63
29.30
28.16
24.24
23.46


O
N
F
N
i-Pr
CO2t-Bu

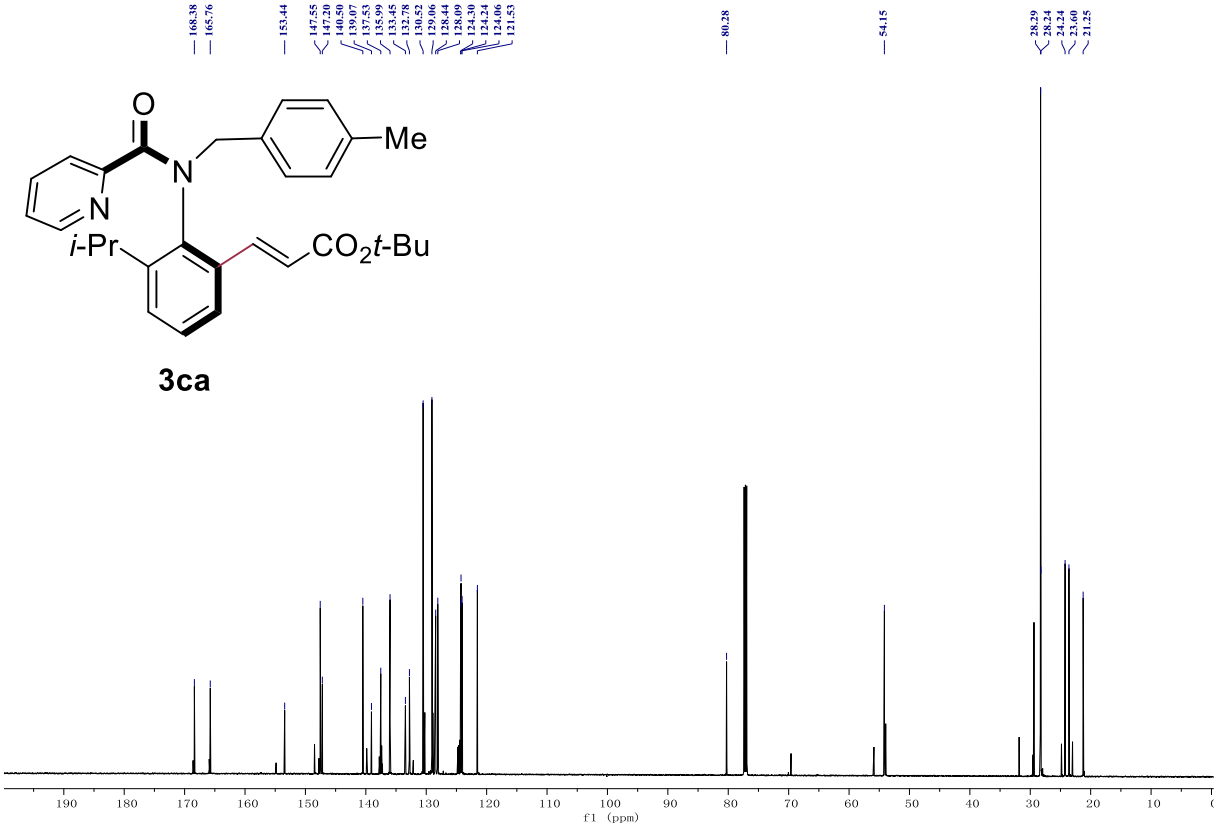
3ba

f1 (ppm)


O
N
Me
N
i-Pr
CO2t-Bu

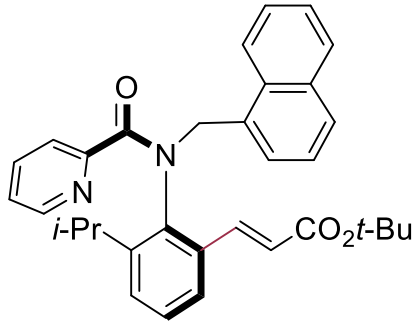
3ca

1.00
1.02
1.01
1.04
3.18
2.07
1.06
2.05
1.01
1.02
1.04
1.02
3.13
9.00
3.01
3.04
f1 (ppm)


168.38
165.76
153.44
147.55
147.20
140.50
139.07
137.53
135.99
133.45
132.78
130.52
129.06
128.44
128.09
124.30
124.24
124.06
121.53
80.28
54.15
28.29
24.24
23.14
23.60
21.25
f1 (ppm)

O
N
Me
N
i-Pr
CO2t-Bu

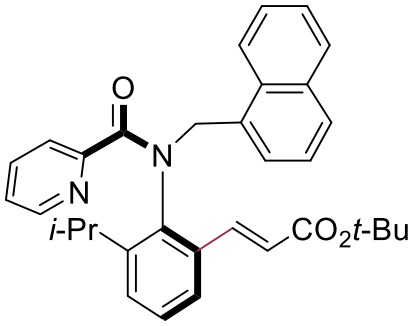
3ca


O
N
N
i-Pr
CO2t-Bu

3da

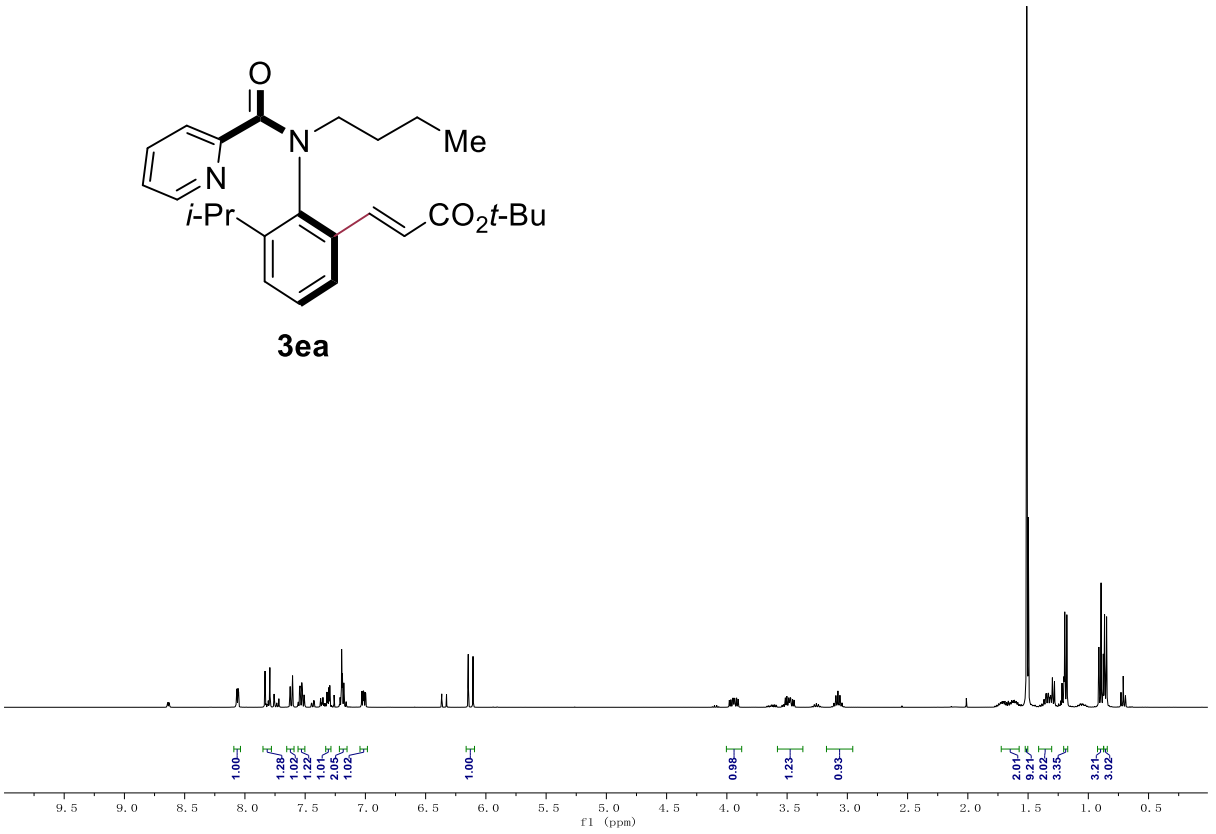
1.00
1.03
3.10
1.11
2.20
3.04
1.01
1.08
1.00
1.02
1.01
1.02
1.03
1.02
9.22
3.08
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

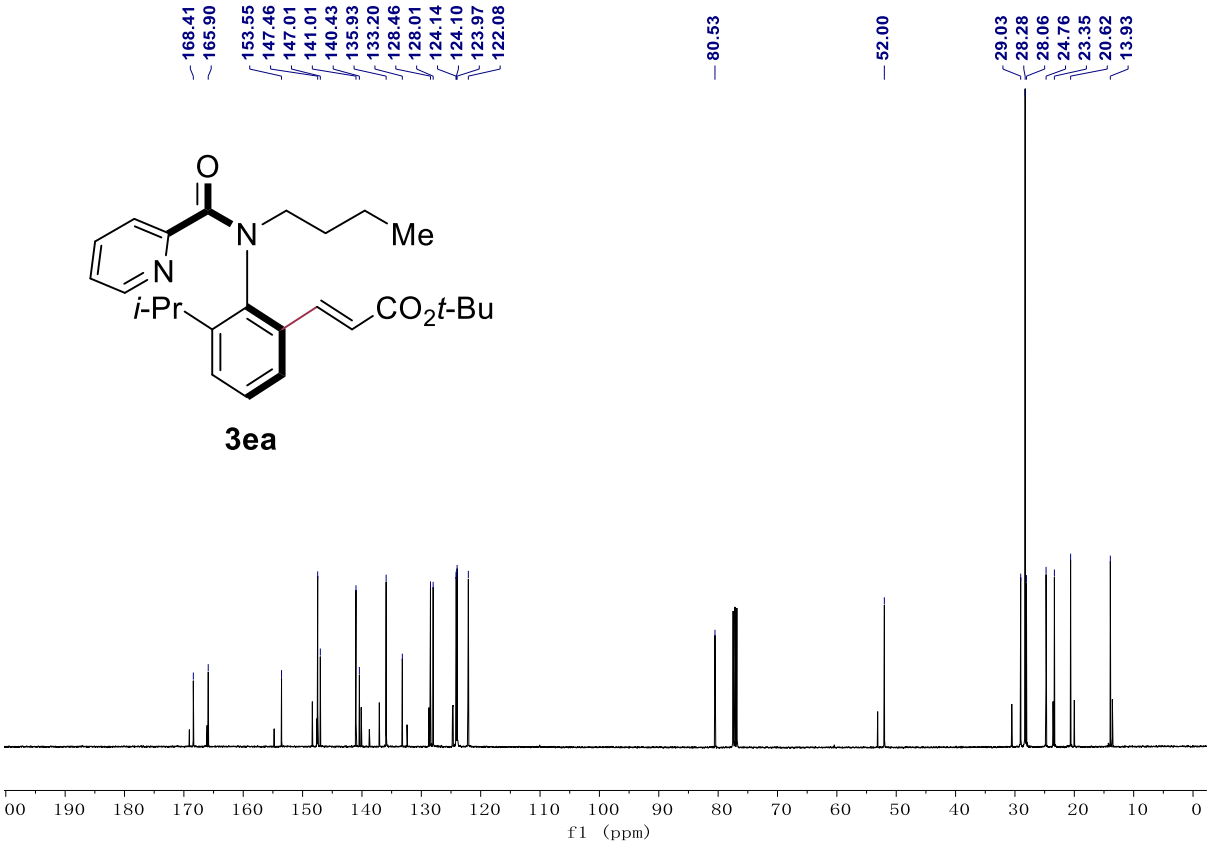

168.56
165.64
153.31
147.64
147.20
140.50
139.29
136.04
133.43
133.31
133.30
133.01
129.52
128.53
128.45
128.18
128.06
127.66
125.99
125.97
124.40
124.33
124.26
121.78
80.30
54.89
28.22
28.18
24.20
23.58

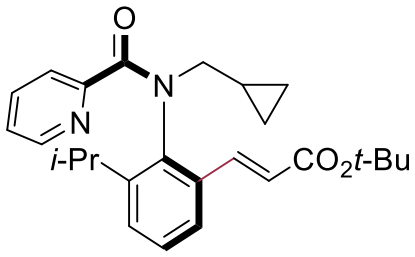

O
N
N
i-Pr
CO2t-Bu

3da

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

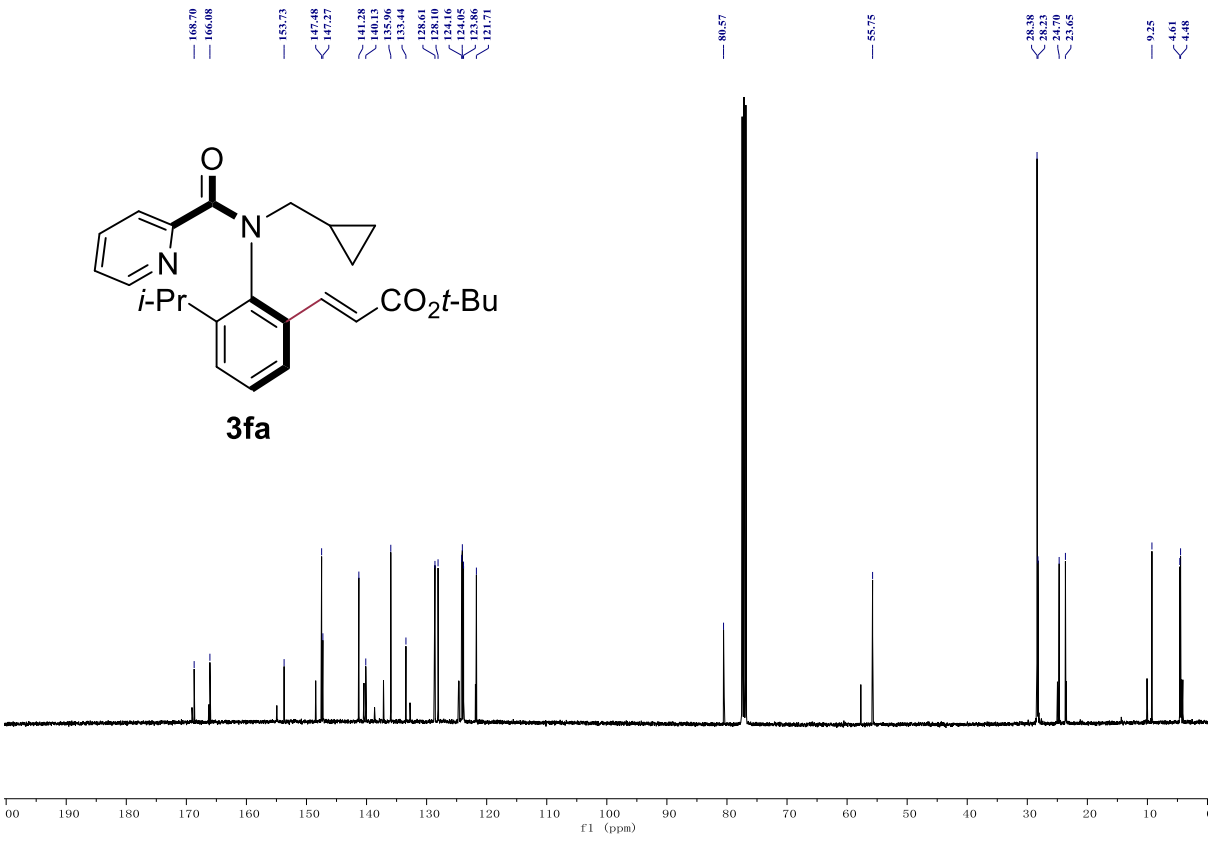

O
N
Me
N
i-Pr
CO2t-Bu
3ea
1.00
1.28
1.02
1.22
1.01
2.05
1.02
1.00
0.98
1.23
0.93
2.01
9.21
2.02
3.35
3.21
3.02
f1 (ppm)


168.41
165.90
153.55
147.46
147.01
141.01
140.43
135.93
133.20
128.46
128.01
124.14
124.10
123.97
122.08
80.53
52.00
29.03
28.28
28.06
24.76
23.35
20.62
13.93
O
N
Me
N
i-Pr
CO2t-Bu
3ea
f1 (ppm)


O
N
N
i-Pr
CO2t-Bu

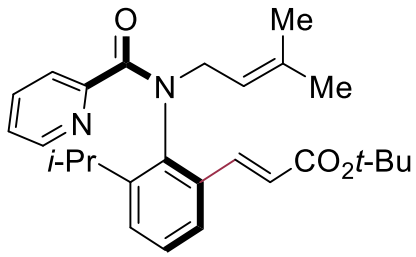
3fa

1.00
1.01
1.03
1.03
1.04
2.05
1.04
1.01
1.03
2.12
9.33
3.32
1.21
3.30
2.19
1.52
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


168.70
166.08
153.73
147.48
147.27
141.28
140.13
135.96
133.44
128.61
128.10
124.16
124.05
123.86
121.71
80.57
55.75
28.38
28.23
24.70
23.65
9.25
4.61
4.48
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

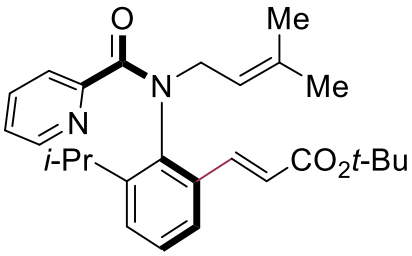
O
N
N
i-Pr
CO2t-Bu

3fa

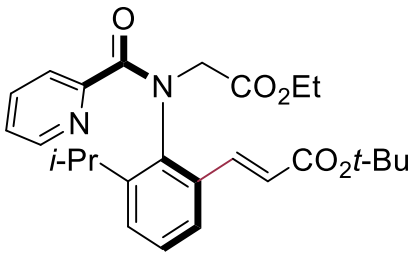


3ga

168.20
166.02
153.43
147.58
147.14
141.20
139.93
137.46
135.95
133.30
128.33
128.05
124.20
124.00
123.98
121.32
118.21
80.44
48.96
28.30
28.15
25.86
24.69
23.35
17.67



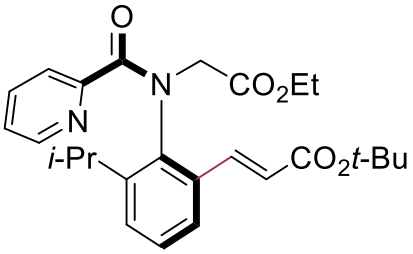
3ga


O
N
CO2Et
N
i-Pr
CO2t-Bu

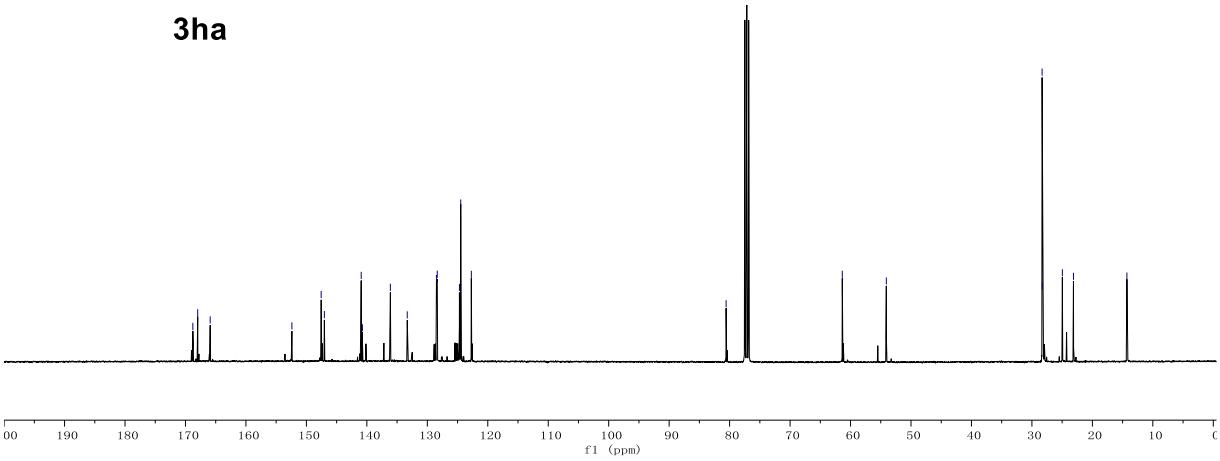
3ha

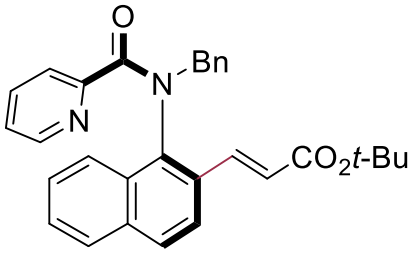
2.04
1.08
1.00
1.00
2.05
1.19
1.00
1.09
3.37
1.08
9.24
3.14
3.06
3.16
f1 (ppm)


168.78
167.98
165.91
152.40
147.56
147.03
140.94
140.73
136.11
133.32
128.49
128.36
124.69
124.47
122.72
80.58
61.37
54.08
28.32
28.27
24.96
23.13
14.29


O
N
CO2Et
N
i-Pr
CO2t-Bu

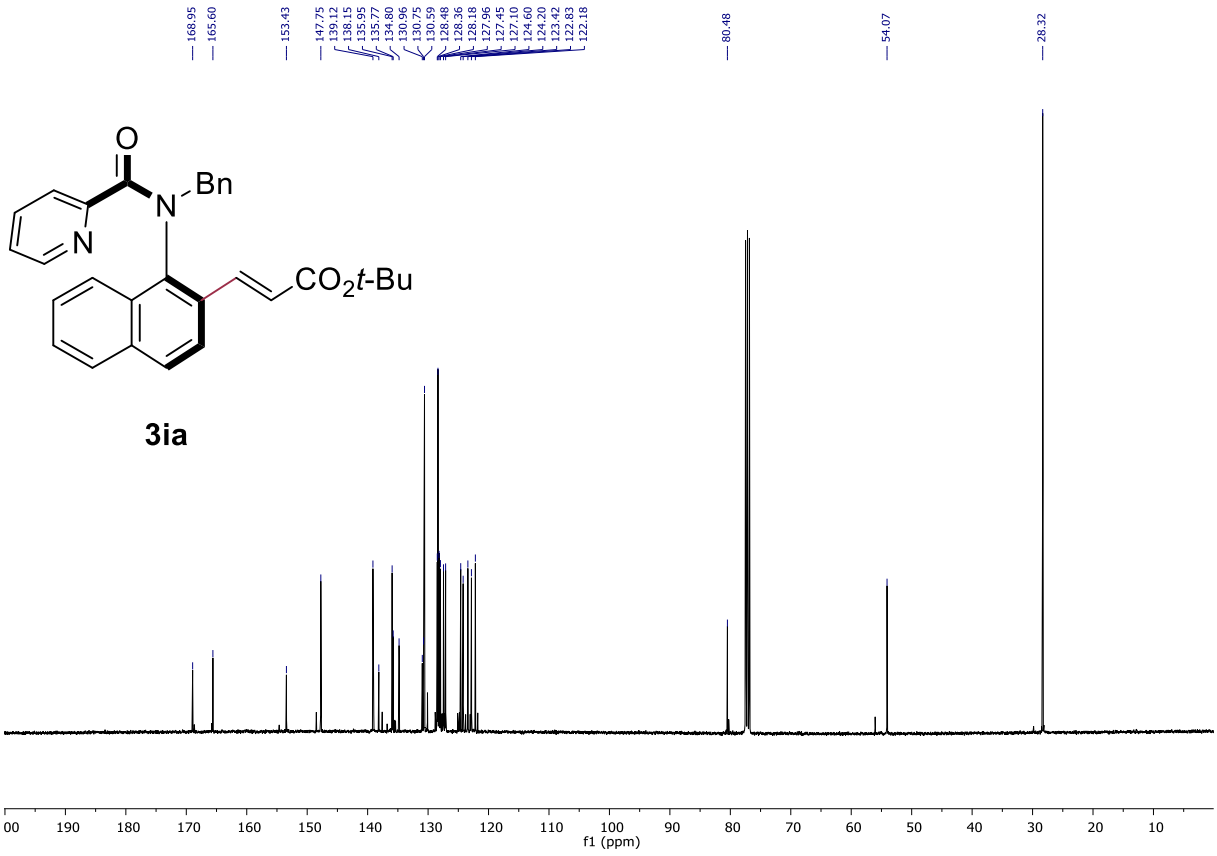
3ha


f1 (ppm)


O
N
Bn
N
CO2t-Bu

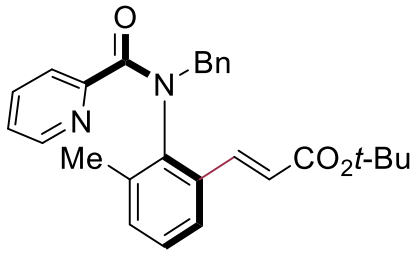
3ia

2.03
1.00
1.00
1.04
2.00
0.98
1.00
1.03
5.01
1.01
0.97
0.96
1.01
9.03
f1 (ppm)


168.95
165.60
153.43
147.75
139.12
138.15
135.95
135.77
134.80
130.96
130.75
130.59
128.48
128.36
128.18
127.96
127.45
127.10
124.60
124.20
123.42
122.83
122.18
80.48
54.07
28.32
f1 (ppm)

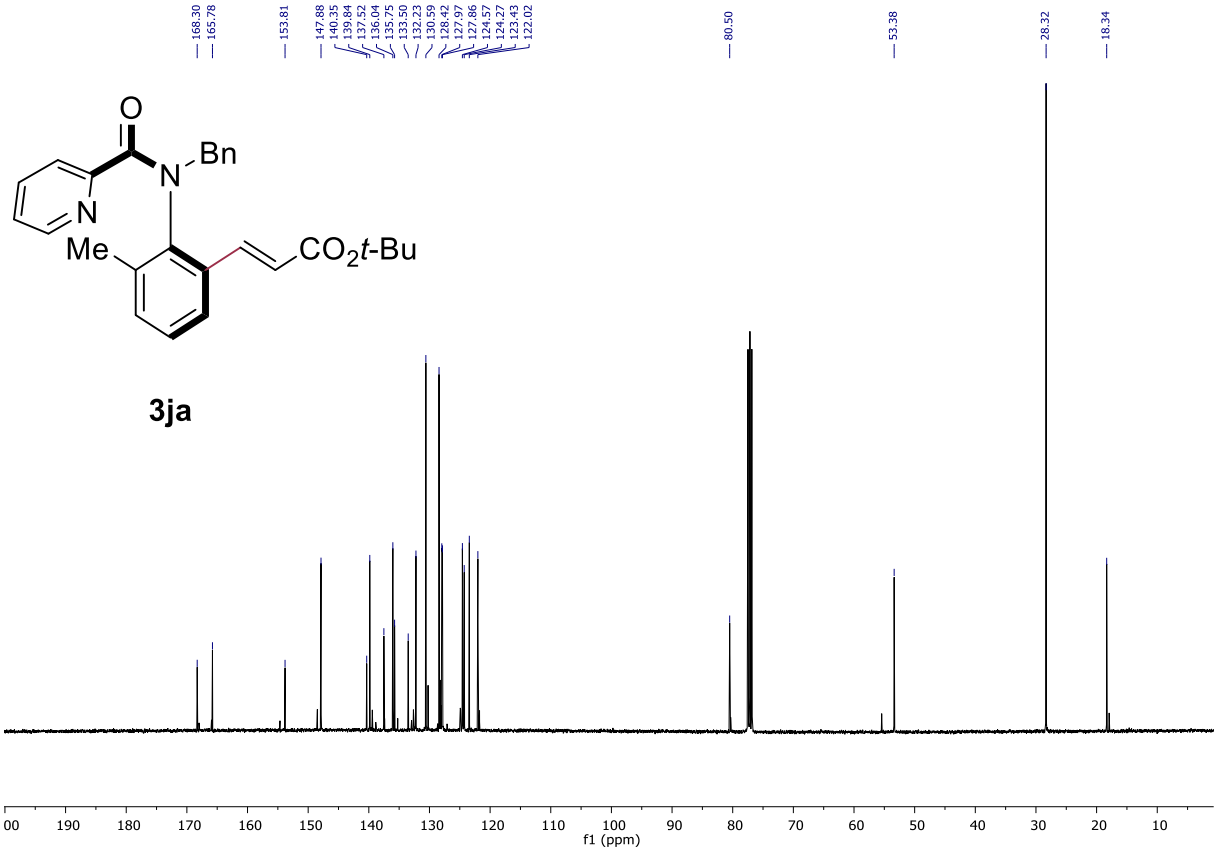
O
N
Bn
N
CO2t-Bu

3ia


O
N
Bn
N
Me
CO2t-Bu

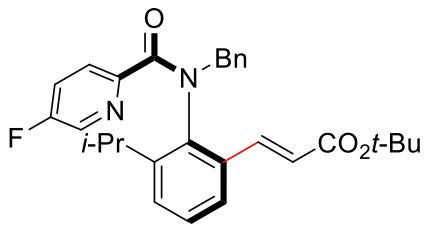
3ja

1.00
2.08
1.02
6.20
3.13
0.99
1.00
1.10
3.06
9.07
f1 (ppm)


168.30
165.78
153.81
147.88
140.35
139.84
137.52
136.04
135.75
133.50
132.23
130.59
128.42
127.97
127.86
124.57
124.27
123.43
122.02
80.50
53.38
28.32
18.34
f1 (ppm)

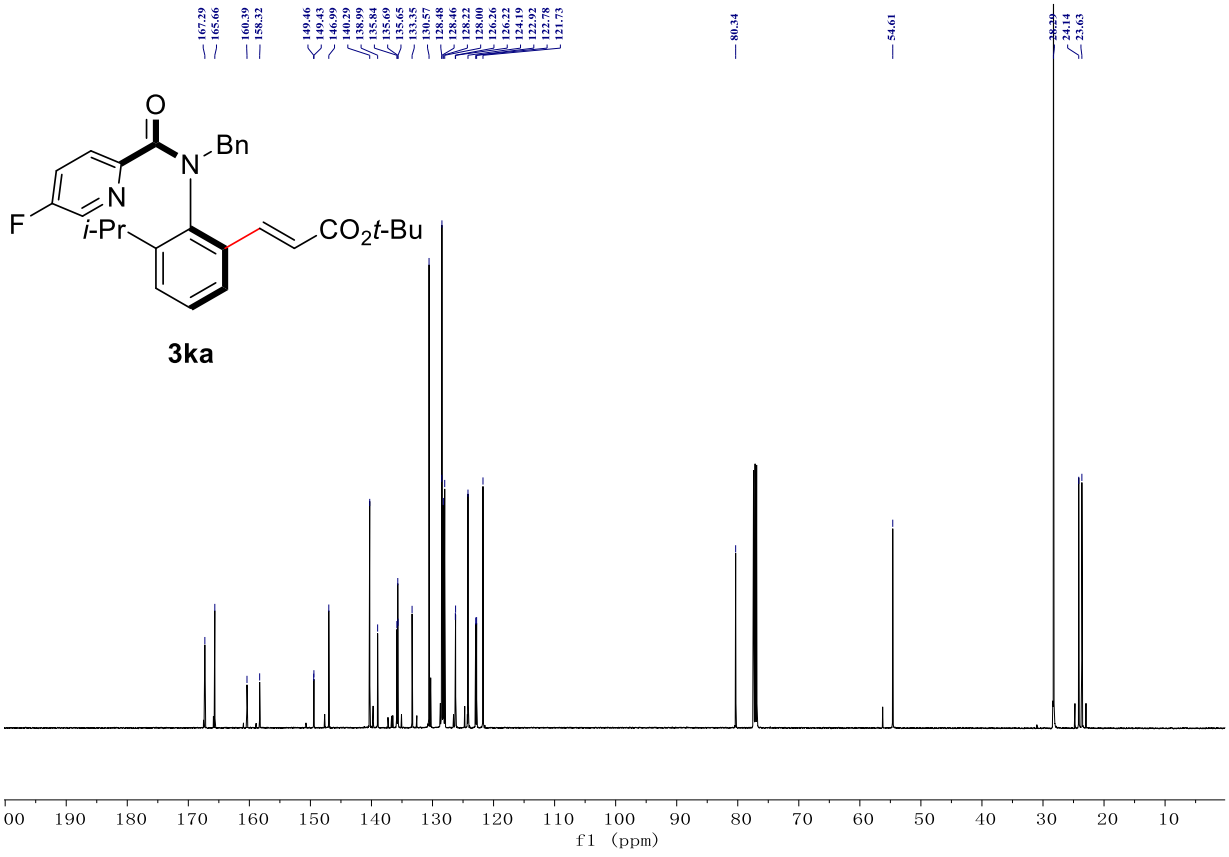
O
N
Bn
N
Me
CO2t-Bu

3ja


O
N
Bn
N
F
i-Pr
CO2t-Bu

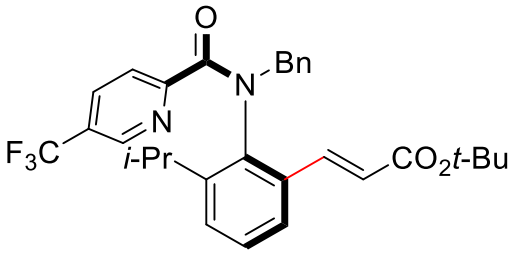
3ka

1.01
1.02
2.48
8.26
1.04
1.04
1.04
1.12
9.22
3.10
3.11
f1 (ppm)


167.29
165.66
160.39
158.32
149.46
149.43
146.99
140.29
138.99
135.84
135.69
135.65
133.35
130.57
128.48
128.46
128.22
128.00
126.26
126.22
124.19
122.92
122.78
121.73
80.34
54.61
28.39
24.14
23.63
f1 (ppm)

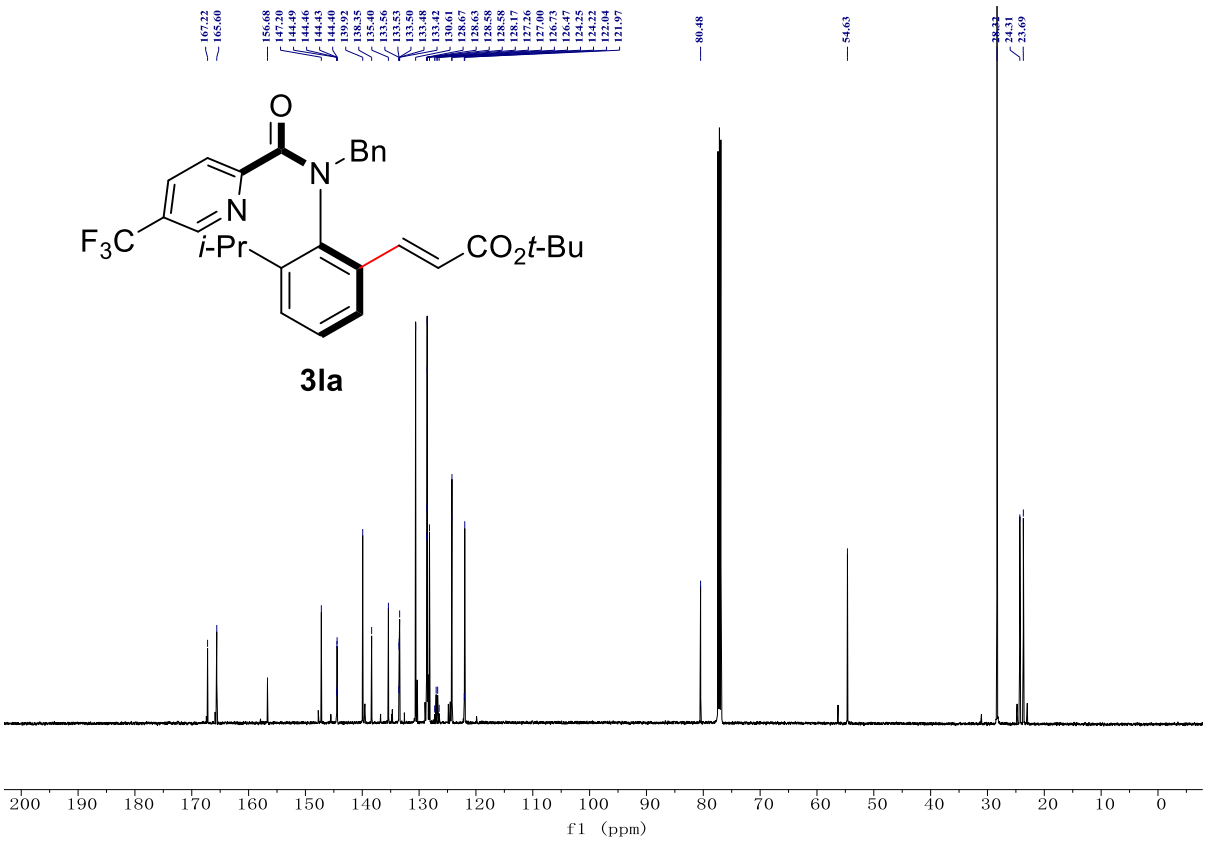
O
N
Bn
N
F
i-Pr
CO2t-Bu

3ka


O
N
Bn
N
F3C
i-Pr
CO2t-Bu

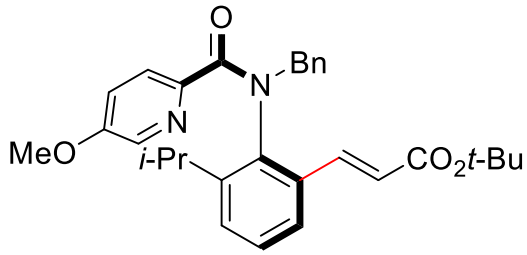
3la

1.00
2.05
9.30
1.02
1.01
1.02
1.14
9.14
2.98
3.11
f1 (ppm)


167.22
165.60
156.68
147.20
144.49
144.46
144.43
144.40
139.92
138.35
135.40
133.56
133.53
133.50
133.48
133.42
130.61
128.67
128.63
128.58
128.54
128.17
127.26
127.00
126.73
126.47
124.25
124.22
122.04
121.97
80.48
54.63
38.32
24.31
23.69
f1 (ppm)

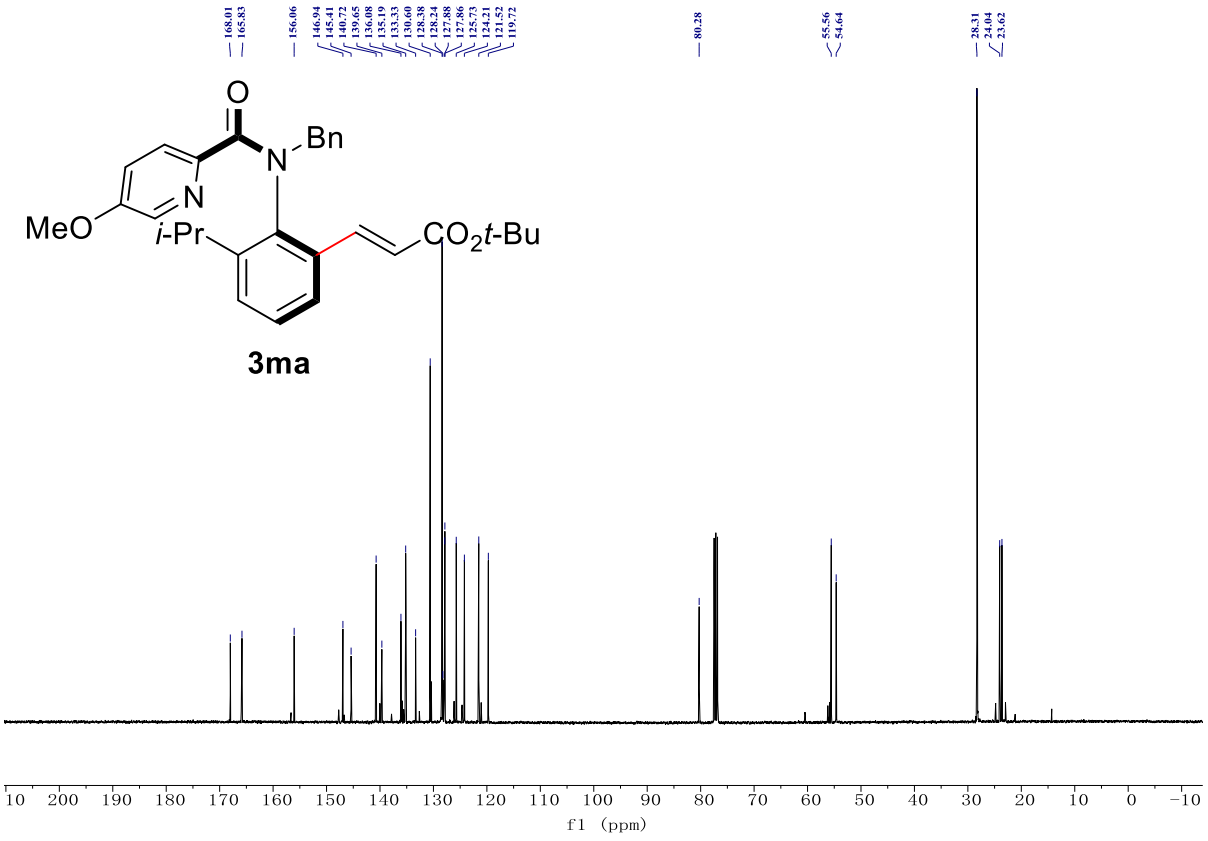
O
N
Bn
N
F3C
i-Pr
CO2t-Bu

3la


O
N
Bn
N
MeO
i-Pr
CO2t-Bu

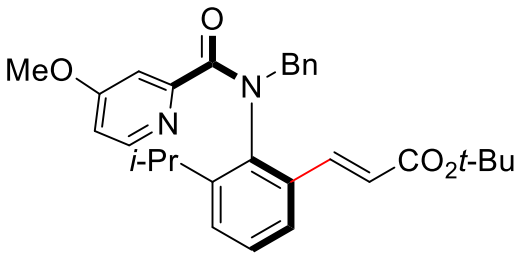
3ma

2.05
1.27
8.42
1.12
1.01
1.01
1.00
3.19
1.00
9.21
3.41
3.10
f1 (ppm)


168.01
165.83
156.06
146.94
145.41
140.72
139.65
136.08
135.19
133.33
130.60
128.38
128.24
127.88
127.86
125.73
124.11
121.52
119.72
80.28
55.56
54.64
28.31
24.04
23.62
f1 (ppm)

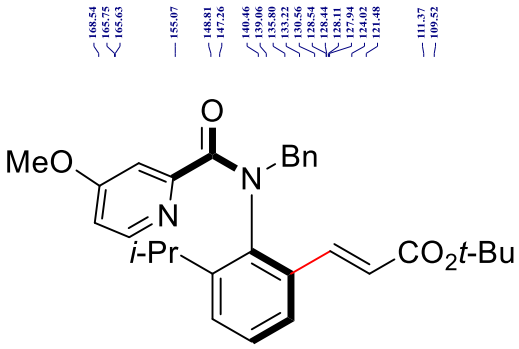
O
N
Bn
N
MeO
i-Pr
CO2t-Bu

3ma


O
MeO
N
Bn
N
i-Pr
CO2t-Bu

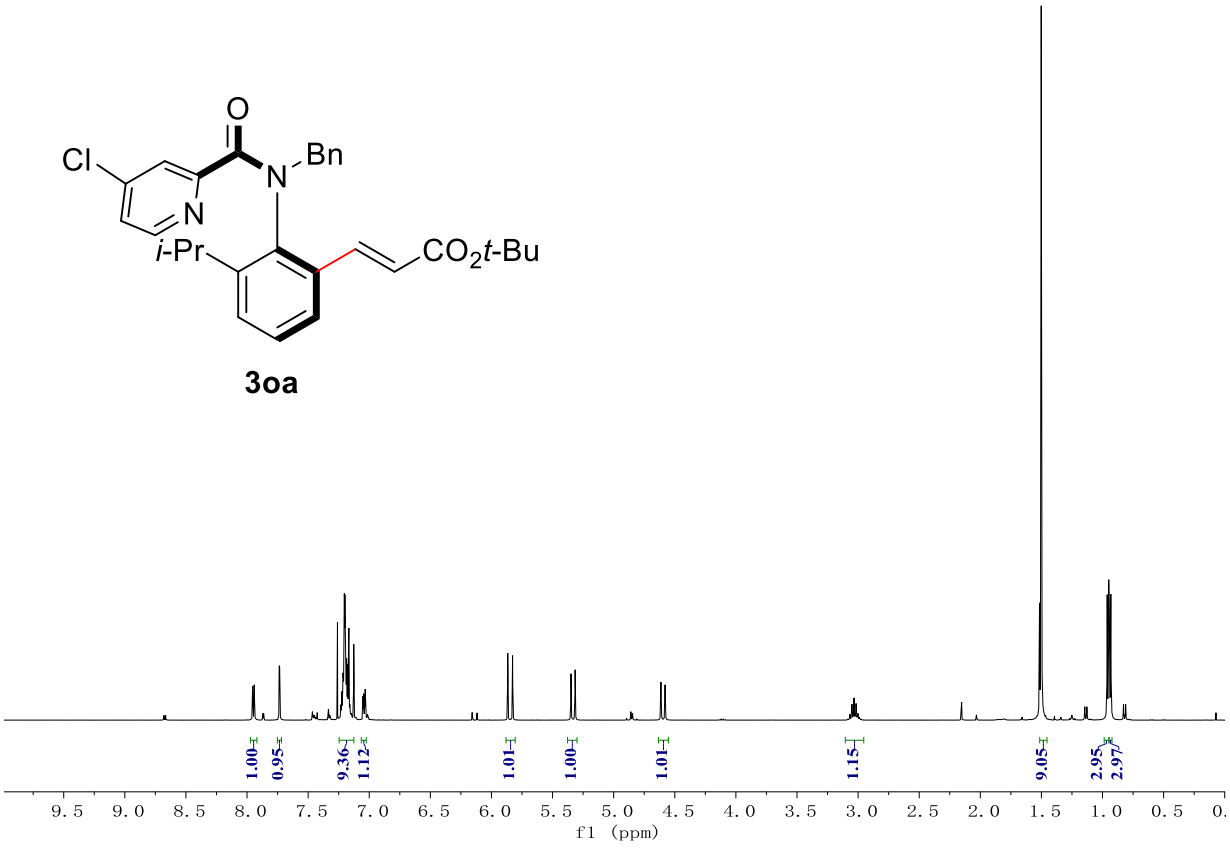
3na

1.00
1.30
9.31
1.02
1.02
1.01
1.02
3.19
1.20
9.31
3.13
3.07
f1 (ppm)

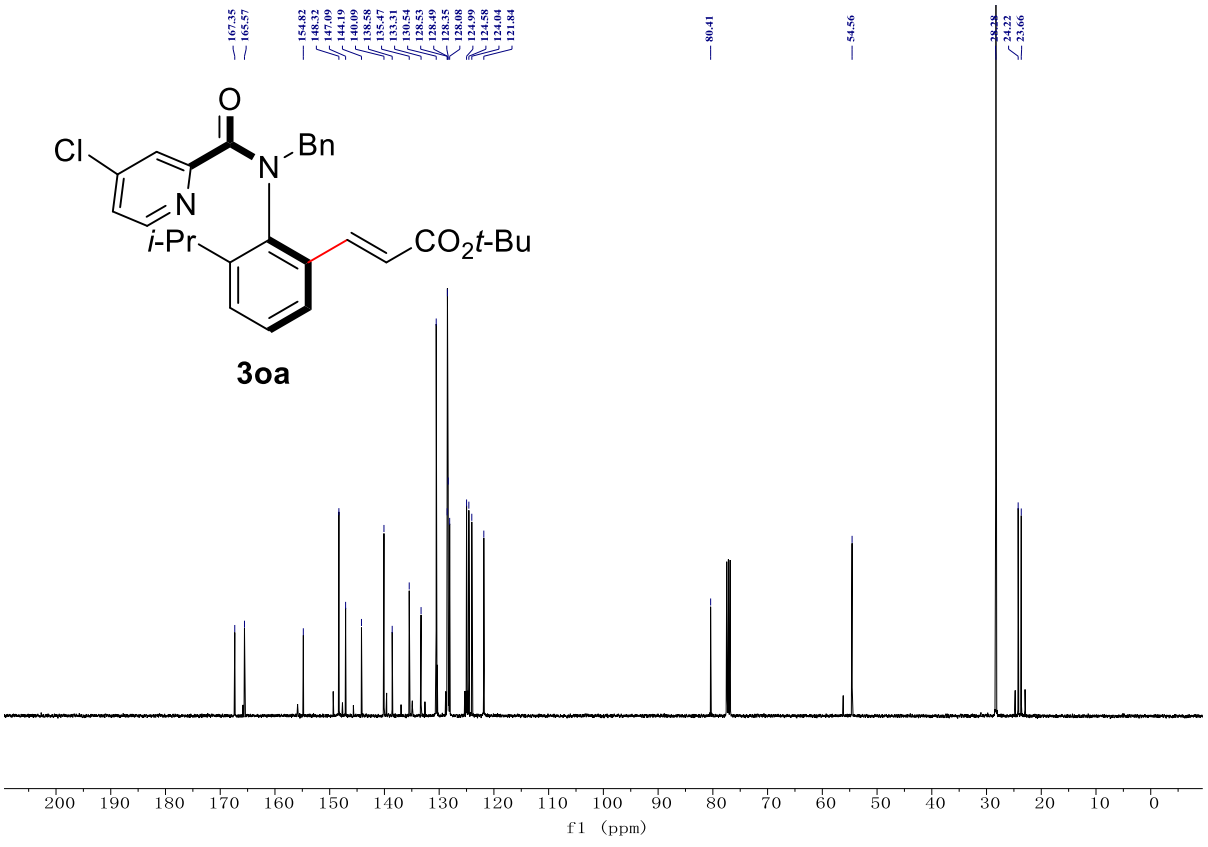

O
MeO
N
Bn
N
i-Pr
CO2t-Bu

3na

168.54
165.75
165.63
155.07
148.81
147.26
140.46
139.06
135.80
133.22
130.56
128.54
128.44
128.11
127.94
124.02
121.48
111.37
109.52
80.32
55.24
54.47
28.28
24.24
23.68
f1 (ppm)


O
Cl
Bn
N
N
i-Pr
CO2t-Bu
1.00
0.95
9.36
1.12
1.01
1.00
1.01
1.15
9.05
2.95
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

3oa


167.35
165.57
154.82
148.32
147.09
144.19
140.09
138.58
135.47
133.31
130.54
128.53
128.49
128.35
124.99
124.58
124.04
121.84
80.41
54.56
28.28
24.22
23.66
O
Cl
Bn
N
N
i-Pr
CO2t-Bu
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3oa