

Supporting Information

Highly Regio- and Chemoselective Oxidative C–H/C–H Cross-Couplings of Anilines and Phenols Enabled by a Co-Oxidant-Free Rh(I)/Zn(NTf₂)₂/Air Catalytic System

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I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to CDCl_3 or $\text{DMSO}-d_6$ as the internal reference (CDCl_3 : $\delta = 7.26$; $\text{DMSO}-d_6$: $\delta = 2.50$). The ^{13}C NMR (100 MHz) chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : $\delta = 77.16$; $\text{DMSO}-d_6$: $\delta = 39.52$). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). The GC-MS analysis was performed with Shimadzu GCMS-QP2010 SE.

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. $[\text{Rh}(\text{cod})\text{Cl}]_2$,¹ $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$,² $\text{Zn}(\text{NTf}_2)_2$,³ 2-aryloxy pyridines (**1**),⁴ *N*-arylpivalamides (**2**),⁵ *N*-arylpyridin-2-amines (**7**),⁶ 2-aryloxy pyrimidines (**8**),⁷ and aryl diisopropylcarbamates (**9**)⁸ were prepared according to the literature procedures.

II. Preparation of substrates

1. General procedure for the preparation of 2-aryloxy pyridines (**1**)⁴

For preparation of 1a-1x:^{4a} A 100 mL round bottomed flask was charged with ArOH (10 mmol), CuI (190 mg, 1.0 mmol, 10 mol%), picolinic acid (246 mg, 2.0 mmol, 20 mol%) and K_3PO_4 (4.24 g, 20 mmol). The flask was evacuated and back-filled with N_2 . Then DMSO (20 mL) and 2-bromopyridine (1.15 mL, 12 mmol) were added. The mixture was heated at 90 °C for 24 h. After cooling to room temperature, ethyl acetate (20 mL) and water (10 mL) were added. The mixture was then filtered through a celite pad. The organic layer was separated and the aqueous layer was extracted three times with ethyl acetate (10 mL). The combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the resulting residue was purified through silica gel column chromatography to obtain the desired products.

For preparation of 1y and 1z:^{4b} A 25 mL flask was charged with 1,5-dihydroxynaphthalene or 2,7-dihydroxynaphthalene (0.80 g, 5.0 mmol), 2-bromopyridine (1.15 mL, 12 mmol), NaOH (0.48 g, 12 mmol), and DMSO (10 mL) under air. After stirring at 150 °C for 24 h, the reaction mixture was quenched with water and

extracted with ethyl acetate for three times. The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the desired products.

2. General procedure for the preparation of *N*-arylpivalamides (2)⁵

For preparation of 2a-2v and 2x from the corresponding arylamines and pivaloyl chloride:^{5a} To a solution of arylamine (10 mmol) and triethylamine (1.66 mL, 12 mmol) in dichloromethane (20 mL), pivaloyl chloride (1.4 mL, 11 mmol) was added dropwise at 0 °C. After stirring at room temperature for 5 h, the reaction mixture was quenched with water and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by recrystallization with petroleum ether/ CH_2Cl_2 to obtain the desired products.

For preparation of 2w and [D₅]-2a from the corresponding aryl bromides and trimethylacetamide according to a reported procedure with modifications:^{5b} A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with aryl bromide (2.0 mmol), pivalamide (404 mg, 4.0 mmol, 2.0 equiv), CuI (38.1 mg, 0.2 mmol, 10 mol%), *N,N'*-dimethyl-1,2-ethanediamine (43 μL , 0.4 mmol, 20 mol%), K_3PO_4 (1.27 g, 6.0 mmol, 3.0 equiv), and 1,4-dioxane (2 mL) under an N_2 atmosphere. The resulting mixture was stirred at 110 °C for 24 h and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give the desired products.

3. General procedure for the preparation of *N*-arylpyridin-2-amines (7)⁶

A 25 mL round bottomed flask with a magnetic stir bar was charged with arylamine (10 mmol) and 2-bromopyridine (1.05 mL, 11 mmol). The reaction mixture was stirred at 160 °C for 10 h. After cooling to room temperature, saturated NaHCO_3 was added and the mixture was extracted with ethyl acetate for three times. The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the desired products.

4. General procedure for the preparation of 2-aryloxypyrimidines (8)⁷

A 50 mL round bottomed flask with a magnetic stir bar was charged with 2-chloropyrimidine (1.1 g, 10 mmol), ArOH (10 mmol), potassium carbonate (2.8 g, 20 mmol), and DMSO (10 mL). The resulting mixture heated to 100 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the desired products.

5. General procedure for the preparation of aryl diisopropylcarbamates (9)⁸

To a solution of ArOH (10 mmol) in dry THF (10 mL), NaH (60% oil dispersion, 0.44 g, 11 mmol) was added slowly at 0 °C, and the resulting mixture was stirred at room temperature for 10 minutes. Next, diisopropylcarbamoyl chloride (1.8 g, 11 mmol) was added to the reaction, and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was then quenched with water and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the desired products.

III. Optimization of the reaction conditions

1. General procedure for the screening of directing groups

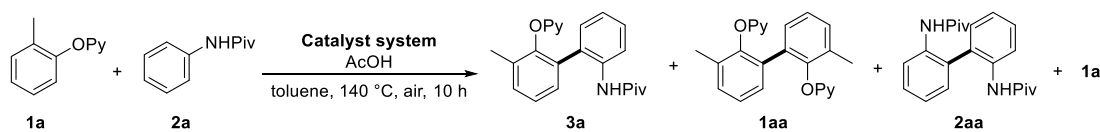
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with phenol derivative (0.2 mmol), aniline derivative (0.2 mmol, 1.0 equiv), [RhCp*Cl₂]₂ (3.1 mg, 5 μmol, 2.5 mol%), AgSbF₆ (6.9 mg, 20 μmol, 10 mol%), Ag₂CO₃ (82.7 mg, 0.3 mmol, 1.5 equiv), AcOH (4.6 μL, 80 μmol, 40 mol%) and toluene (0.3 mL) under an N₂ atmosphere. The resulting solution was stirred at 140 °C for 10 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. Next, 0.5 mL of the resulting mixture was filtered through a small plug of silica gel, and eluted with ethyl acetate. The filtrate was directly used for GC-MS analysis. If required, the yield was determined by ¹H NMR analysis using CH₂Br₂ as the internal standard.

Directing Groups (DGs)						
DG1a		trace	n.d	trace	7% ^a	n.d
DG1b		n.d	n.d	n.d	trace	n.d
DG1c		n.d	n.d	n.d	n.d	n.d
DG1d		n.d	n.d	n.d	n.d	n.d
DG1e		trace	trace	n.d	n.d	n.d

Scheme S1. Screening of directing groups. Reaction conditions: phenol derivative (0.20 mmol), aniline derivative (0.20 mmol), [RhCp*Cl₂]₂ (2.5 mol%), AgSbF₆ (10 mol%), Ag₂CO₃ (1.5 equiv) and AcOH (40 mol%) in toluene (0.3 mL) at 140 °C for 10 h under an N₂ atmosphere. Determined by GC-MS analysis. ^aYield determined by ¹H NMR analysis using CH₂Br₂ as the internal standard. n.d = not detected.

2. General procedure for the catalyst system optimization

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol, 2.0 equiv), catalyst, AcOH (4.6 µL, 80 µmol, 40 mol%) and toluene (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 10 h and then diluted with 5 mL of dichloromethane after cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl₃ and analyzed by ¹H NMR with CH₂Br₂ (21.0 µL, 0.3 mmol) as the internal standard.

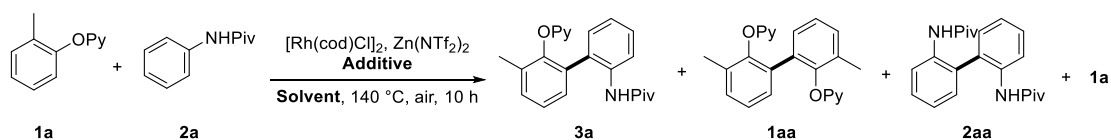
Table S1. Optimization of Catalysts System^a

Entry	Catalyst system (mol%)	Yield (%) ^b			
		3a	1aa	2aa	1a
1 ^c	[RhCp*Cl ₂] ₂ (2.5)/AgSbF ₆ (10)	14	9	1	74
2	[RhCp*Cl ₂] ₂ (2.5)/AgSbF ₆ (10)	3	0	0	95
3	[RhCp*Cl ₂] ₂ (2.5)/Zn(NTf ₂) ₂ (10)	5	0	0	94
4	[Rh(cod)Cl] ₂ (2.5)/Zn(NTf ₂) ₂ (10)	49	11	1	38
5	[RhCp*(cod)] (5.0)/Zn(NTf ₂) ₂ (10)	3	0	0	96
6	[RhCpCl ₂] ₂ (2.5)/Zn(NTf ₂) ₂ (10)	30	16	1	47
7	Rh(PPh ₃) ₃ Cl (5.0)/Zn(NTf ₂) ₂ (10)	50	18	4	24
8	RhCl ₃ ·3H ₂ O (5.0)/Zn(NTf ₂) ₂ (10)	11	3	0	86
9	[Ir(cod)Cl] ₂ (2.5)/Zn(NTf ₂) ₂ (10)	0	1	0	97
10	[Ru(cod)Cl ₂] _n (5.0)/Zn(NTf ₂) ₂ (10)	7	3	1	86
11	[Rh(cod)Cl] ₂ (2.5)	0	0	0	99
12	[Rh(cod)Cl] ₂ (2.5)/Zn(NTf ₂) ₂ (20)	56	9	1	32
13	[Rh(cod)Cl] ₂ (2.5)/Zn(NTf ₂) ₂ (30)	32	5	1	61

^aReaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), catalyst, and AcOH (40 mol%) in toluene (0.3 mL) at 140 °C for 10 h under an air atmosphere. ^bNMR yields are based on **1a** (for **3a**, **1aa** and **1a**) or **2a** (for **2aa**) using CH₂Br₂ as the internal standard. ^cAg₂CO₃ (1.5 equiv) was used as the oxidant under an N₂ atmosphere.

3. General procedure for the solvent and additive optimization

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol, 2.0 equiv), [Rh(cod)Cl]₂ (2.5 mg, 5 μmol, 2.5 mol%), Zn(NTf₂)₂ (25.0 mg, 40 μmol, 20 mol%), additive and solvent (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 10 h and then diluted with 5 mL of dichloromethane after cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl₃ and analyzed by ¹H NMR with CH₂Br₂ (21.0 μL, 0.3 mmol) as the internal standard.

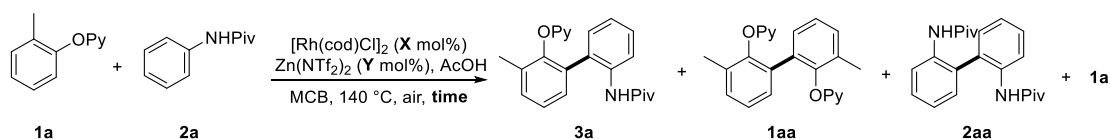
Table S2. Optimization of Solvents and Additives^a

Entry	Solvent	Additive (mol%)	Yield (%) ^b			
			3a	1aa	2aa	1a
1	Mesitylene	AcOH (40)	75	13	2	11
2	MCB	AcOH (40)	77	11	2	11
3	dioxane	AcOH (40)	5	7	0	86
4	<i>t</i> -AmylOH	AcOH (40)	4	11	1	51
5	DMF	AcOH (40)	0	0	0	98
6	DCE	AcOH (40)	29	3	1	65
7 ^c	MCB	AcOH (40)	73	9	3	16
8	MCB	PivOH (40)	37	23	1	25
9	MCB	MesCOOH (40)	33	9	3	56
10	MCB	NaOAc (40)	47	16	1	35
11	MCB	AcOH (60)	70	22	6	6
12	MCB	AcOH (20)	62	10	2	27
13	MCB	-	0	0	0	98

^aReaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (20 mol%), and additive in solvent (0.3 mL) at 140 °C for 10 h under an air atmosphere. ^bNMR yields are based on **1a** (for **3a**, **1aa** and **1a**) or **2a** (for **2aa**) using CH_2Br_2 as the internal standard. MCB = chlorobenzene. ^cMCB (0.5 mL) was used.

4. General procedure for the optimization of reaction time, loading of catalyst, and substrate ratio

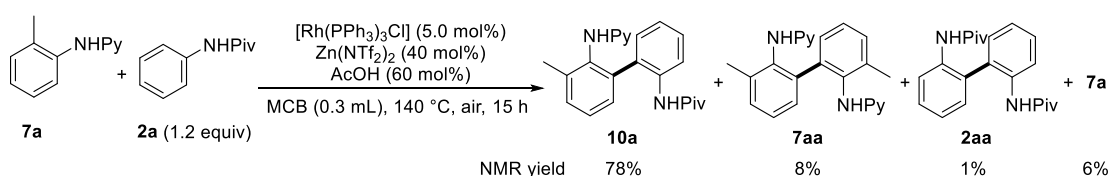
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-phenylpivalamide **2a**, $[\text{Rh}(\text{cod})\text{Cl}]_2$, $\text{Zn}(\text{NTf}_2)_2$ (25.0 mg, 40 μmol , 20 mol%), AcOH (4.6 μL , 80 μmol , 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 10, 15 or 20 h and then diluted with 5 mL of dichloromethane after cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl_3 and analyzed by ^1H NMR with CH_2Br_2 (21.0 μL , 0.3 mmol) as the internal standard.

Table S3. Optimization of Reaction Time, Loading of Catalyst, and Substrate Ratio^a

Entry	X	Y	Time (h)	2a/1a	Yield (%) ^b			
					3a	1aa	2aa	1a
1 ^c	2.5	20	10	2.0	65	10	1	24
2	2.5	20	15	2.0	80	12	3	7
3	2.5	20	20	2.0	78	12	5	5
4	1.5	20	15	2.0	78	13	2	9
5	1.0	20	15	2.0	68	15	0	16
6	1.5	20	15	1.5	75	17	2	8
7	1.5	30	15	1.5	84	10	1	5
8	1.5	30	15	1.2	78	13	1	8
9	1.5	40	15	1.2	86 (78)	9	1	4
10 ^d	1.5	40	15	1.2	83	9	2	4
11 ^e	1.5	40	15	1.2	0	0	0	98
12 ^f	-	40	15	1.2	67	10	1	21
13	1.5	40	15	1.0	80 (73)	13	1	7

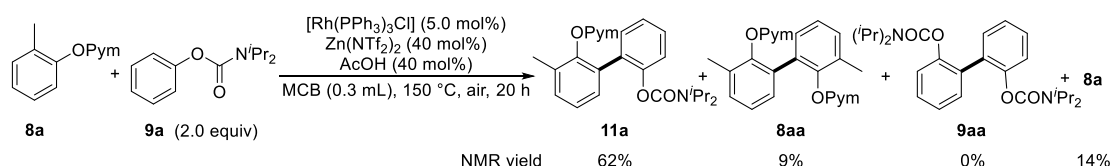
^aReaction conditions: **1a** (0.2 mmol), **2a**, $[\text{Rh}(\text{cod})\text{Cl}]_2$, $\text{Zn}(\text{NTf}_2)_2$ and AcOH (40 mol%) in MCB (0.3 mL) at 140 °C for indicated time under an air atmosphere. ^bNMR yields are based on **1a** (for **3a**, **1aa** and **1a**) or **2a** (for **2aa**) using CH_2Br_2 as the internal standard. Isolated yields are in parenthesis. ^cRun at 130 °C. ^dUnder an O_2 atmosphere. ^eUnder an N_2 atmosphere. ^f3.0 mol% of RhCl_3 was used.

IV. Product composition analysis of the couplings of two anilines and two phenols



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol), $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (9.3 mg, 10 μmol , 5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (50.1 mg, 80 μmol , 40 mol%), AcOH (6.9 μL , 120 μmol , 60 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 15 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a

reduced pressure. The resulting residue was dissolved in CDCl_3 and analyzed by ^1H NMR with CH_2Br_2 (21.0 μL , 0.3 mmol) as the internal standard (NMR yields are based on **7a** (for **10a**, **7aa** and **7a**) or **2a** (for **2aa**)). The cross-coupled product **10a**, homo-coupled products of **7a** and **2a** were observed in 78%, 8% and 1% NMR yields, respectively, and 6% of the unreacted **7a** was detected.



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol), phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol), $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (9.3 mg, 10 μmol , 5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (50.1 mg, 80 μmol , 40 mol%), AcOH (4.6 μL , 80 μmol , 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 150 °C for 20 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl_3 and analyzed by ^1H NMR with CH_2Br_2 (21.0 μL , 0.3 mmol) as the internal standard. The cross-coupled product **11a** and homo-coupled product of **8a** were observed in 62% and 9% NMR yields, respectively. No homocoupled product of **9a** was detected. 14% of the unreacted **8a** was detected.

V. General procedures for the syntheses of 2,2'-difunctional biaryls

2-Amino-2'-hydroxybiaryls (general procedure A)

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-aryloxy pyridines **1** (0.2 mmol), *N*-arylpivalamides **2** (0.24 mmol, 1.2 equiv), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.5 mg, 3 μmol , 1.5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (50.1 mg, 80 μmol , 40 mol%), AcOH (4.6 μL , 80 μmol , 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 15 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on

silica gel to provide the desired cross-coupled products **3** or **4**.

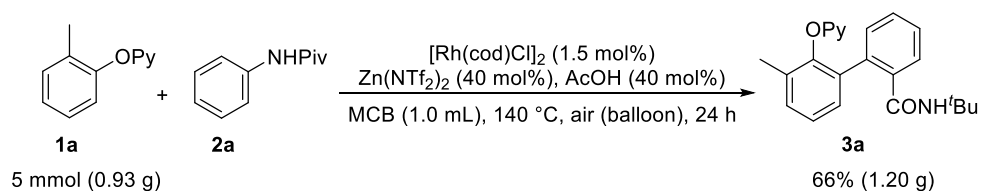
2,2'-Bianilines (general procedure B)

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with *N*-arylpyridin-2-amines **7** (0.2 mmol), *N*-arylpivalamides **2** (0.24 mmol, 1.2 equiv), [Rh(PPh₃)₃Cl] (9.3 mg, 10 μmol, 5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (6.9 μL, 120 μmol, 60 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 15 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired cross-coupled products **10**.

2,2'-Biphenols (general procedure C)

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-aryloxy pyrimidines **8** (0.2 mmol), aryl diisopropylcarbamates **9** (0.4 mmol, 2 equiv), [Rh(PPh₃)₃Cl] (9.3 mg, 10 μmol, 5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (4.6 μL, 80 μmol, 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 150 °C for 20 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired cross-coupled products **11**.

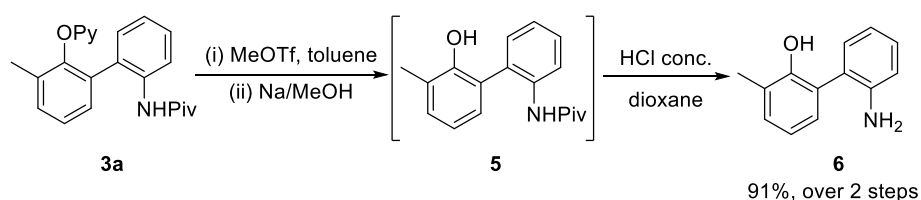
VI. Gram-up synthesis of **3a**



A 120 mL Schlenk tube with a magnetic stir bar was charged with 2-(*o*-tolyl)pyridine **1a** (0.93 g, 5.0 mmol), *N*-phenylpivalamide **2a** (1.06 g, 6.0 mmol, 1.2 equiv), [Rh(cod)Cl]₂ (37

mg, 75 μ mol, 1.5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (1.25 g, 2.0 mmol, 40 mol%), AcOH (114 μ L, 2.0 mmol, 40 mol%) and chlorobenzene (1.0 mL) under an air atmosphere. Then a balloon filled with air was connected to the Schlenk tube through the side arm. The resulting solution was stirred at 140 °C for 24 h and then cooled to room temperature before diluted with 15 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-40 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to afford the desired product **3a** (1.20 g, 66% yield).

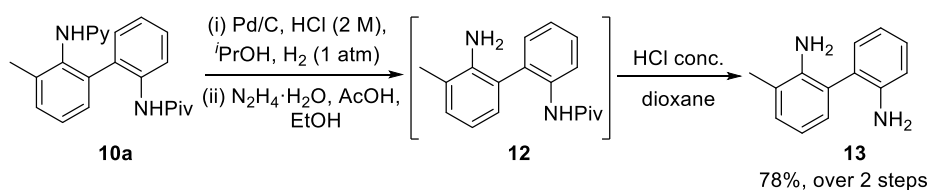
VII. Removal of the directing groups of **3a**, **10a**, and **11a**



MeOTf (0.1 mL, 0.88 mmol) was added to a solution of *N*-(3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide **3a** (180 mg, 0.50 mmol) in toluene (5 mL) under N_2 . The reaction mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the solution was removed in vacuo. Then a solution of Na (288 mg, 12.5 mmol) in methanol (10 mL) was added to the residue. The resulting mixture was heated at 80 °C for 1 h. Then the reaction mixture was cooled to ambient temperature, acidified by HCl (1 M) to pH = 4~5. The methanol was removed in vacuum and water (20 mL) was added. The aqueous solution was extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the crude product *N*-(2'-hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide **5** was obtained.

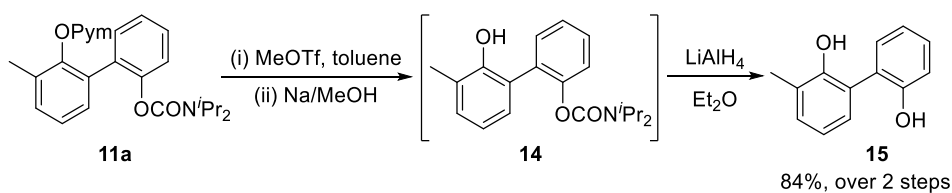
The crude **5** was dissolved in dioxane (1 mL) and added with HCl conc. (1 mL). The resulting mixture was heated at 110 °C for 12 h. The reaction mixture was then quenched with saturated NaHCO_3 and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel

(petroleum ether/EtOAc = 20/1, v/v) to give 2'-amino-3-methyl-[1,1'-biphenyl]-2-ol **6** as a white solid (90.1 mg, 91% yield).



A 50 mL round bottomed flask was charged with Pd/C (40 mg; 10% Pd-basis) and iPrOH (2 mL) under N₂ and the mixture was stirred at room temperature for 5 min. Then, *N*-(3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide **10a** (180 mg, 0.5 mmol), iPrOH (5 mL), and 2 M HCl (1.5 mL, 3 mmol, 6 equiv.) were added to the solution. The resulting mixture was subsequently flushed three times with H₂ and stirred at 50 °C for 15 h under H₂ (1 atm). After this time, the reaction mixture was filtered through a celite pad. Next, 1M NaOH solution (5 mL) and water (20 mL) were added to the filtrate. The aqueous solution was extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over Na₂SO₄, filtered and evaporated to dryness. The residue was dissolved in N₂H₄·H₂O (2.5 mL), AcOH (0.7 mL), and EtOH (1 mL) under N₂ and the resulting mixture was heated at 130 °C for 15 h. After cooling to ambient temperature, 1M NaOH solution (5 mL) and water (20 mL) were added. The aqueous solution was extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the crude product *N*-(2'-amino-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide **12** was obtained.

The crude **12** was dissolved in dioxane (1 mL) and added with HCl conc. (1 mL). The resulting mixture was heated at 110 °C for 12 h. The reaction mixture was then quenched with saturated NaHCO₃ and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to give 3-methyl-[1,1'-biphenyl]-2,2'-diamine **13** as a white solid (77.3 mg, 78% yield).

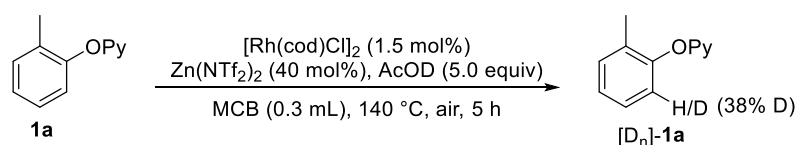


MeOTf (170 μ L, 0.15 mmol) was added to a solution of 3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate **11a** (203 mg, 0.50 mmol) in toluene (5 mL) under N₂. The reaction mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the solution was removed in vacuo. Then a solution of Na (288 mg, 12.5 mmol) in methanol (10 mL) was added to the residue. The resulting mixture was heated at 80 °C for 1 h. Then the reaction mixture was cooled to ambient temperature, acidified by HCl (1 M) to pH = 4~5. The methanol was removed in vacuum and water (20 mL) was added. The aqueous solution was extracted with ethyl acetate (3 $\times$ 15 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the crude product 2'-hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl diisopropylcarbamate **14** was obtained.

The crude **14** was dissolved in anhydrous Et₂O (3 mL) and added with LiAlH₄ (57 mg, 1.5 mmol) at 0 °C. The resulting mixture was heated to reflux for 15 h. The reaction mixture was then quenched with saturated NH₄Cl and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to give 3-methyl-[1,1'-biphenyl]-2,2'-diol **15** as a white solid (84.2 mg, 84% yield).

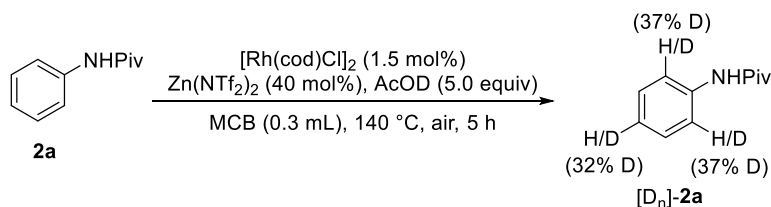
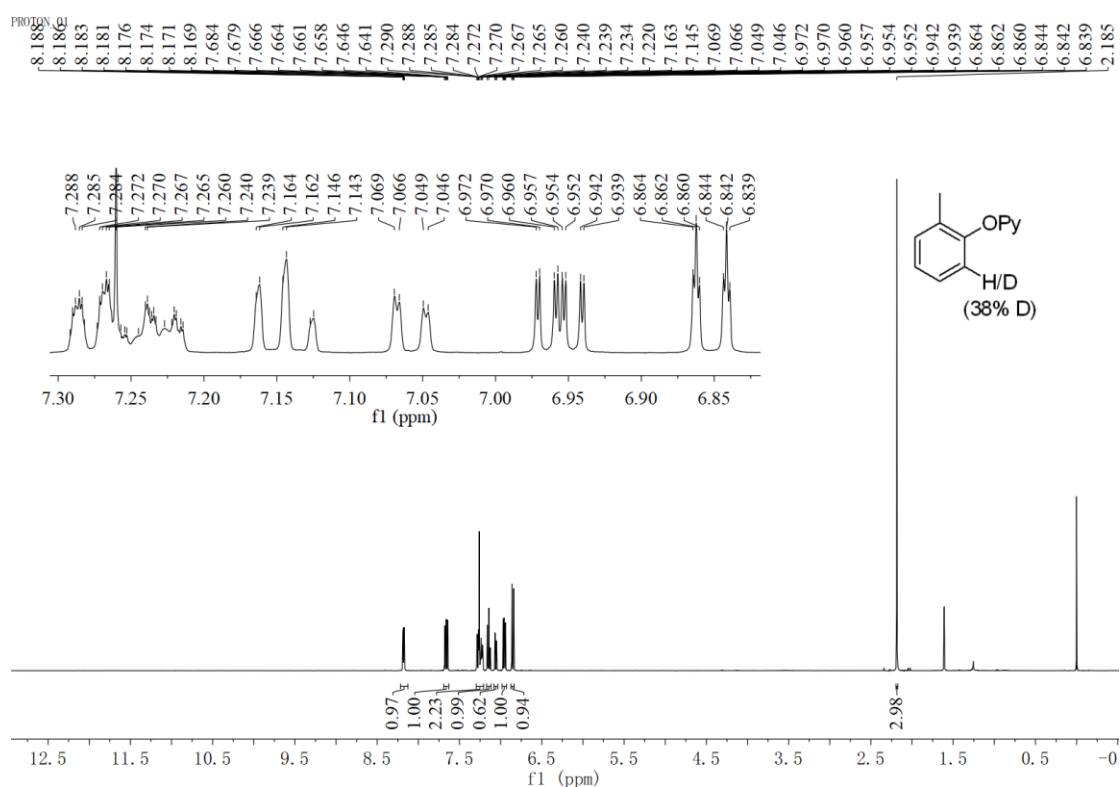
VIII. Mechanistic studies

1. Hydrogen-deuterium exchange experiments

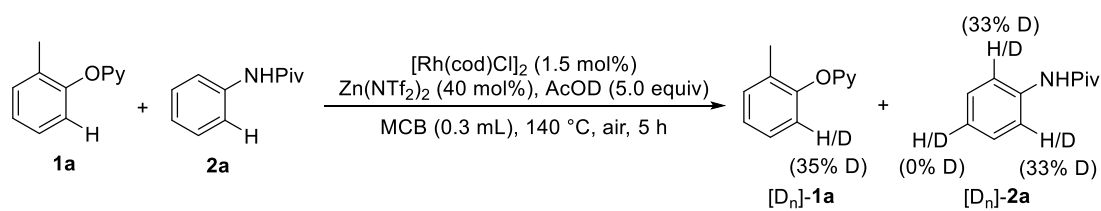


A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolyloxy)pyridine **1a** (37.0 mg, 0.2 mmol), [Rh(cod)Cl]₂ (1.5 mg, 3 μ mol, 1.5 mol%),

Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOD (57.6 μL, 1 mmol, 5 equiv) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 5 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to provide the desired product. The ¹H NMR analysis showed that 38% hydrogen at the *ortho*-position of the phenyl ring of **1a** was deuterated.

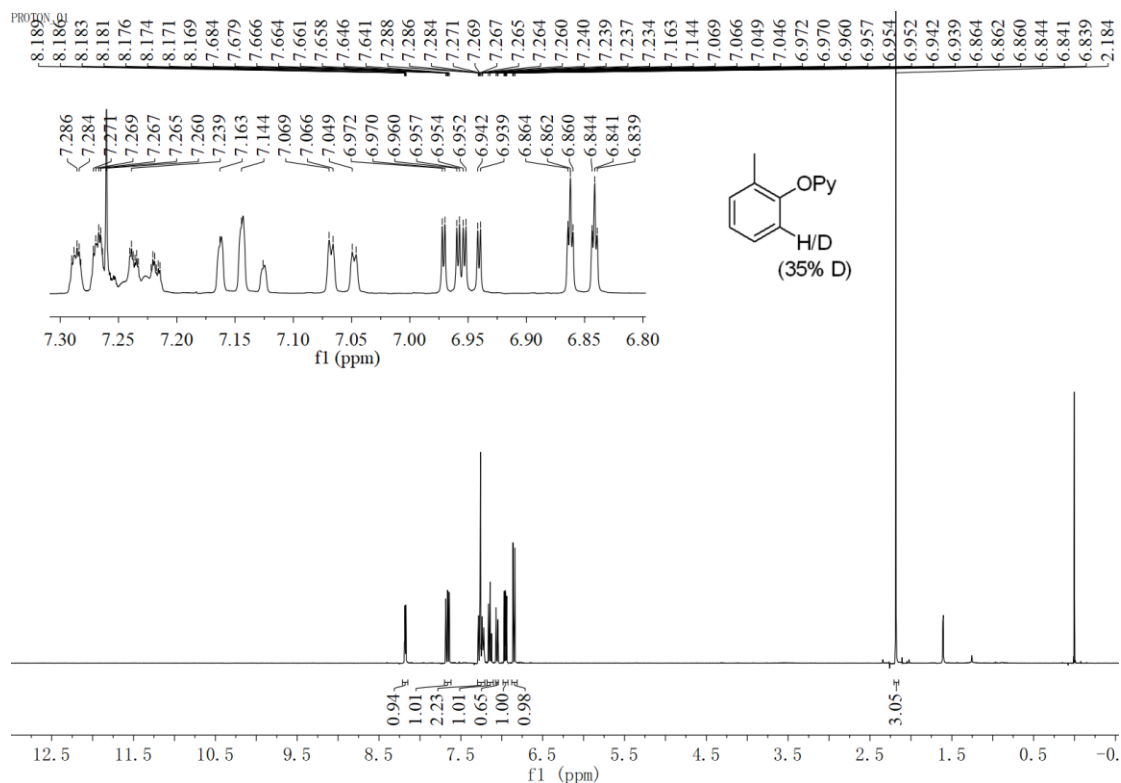


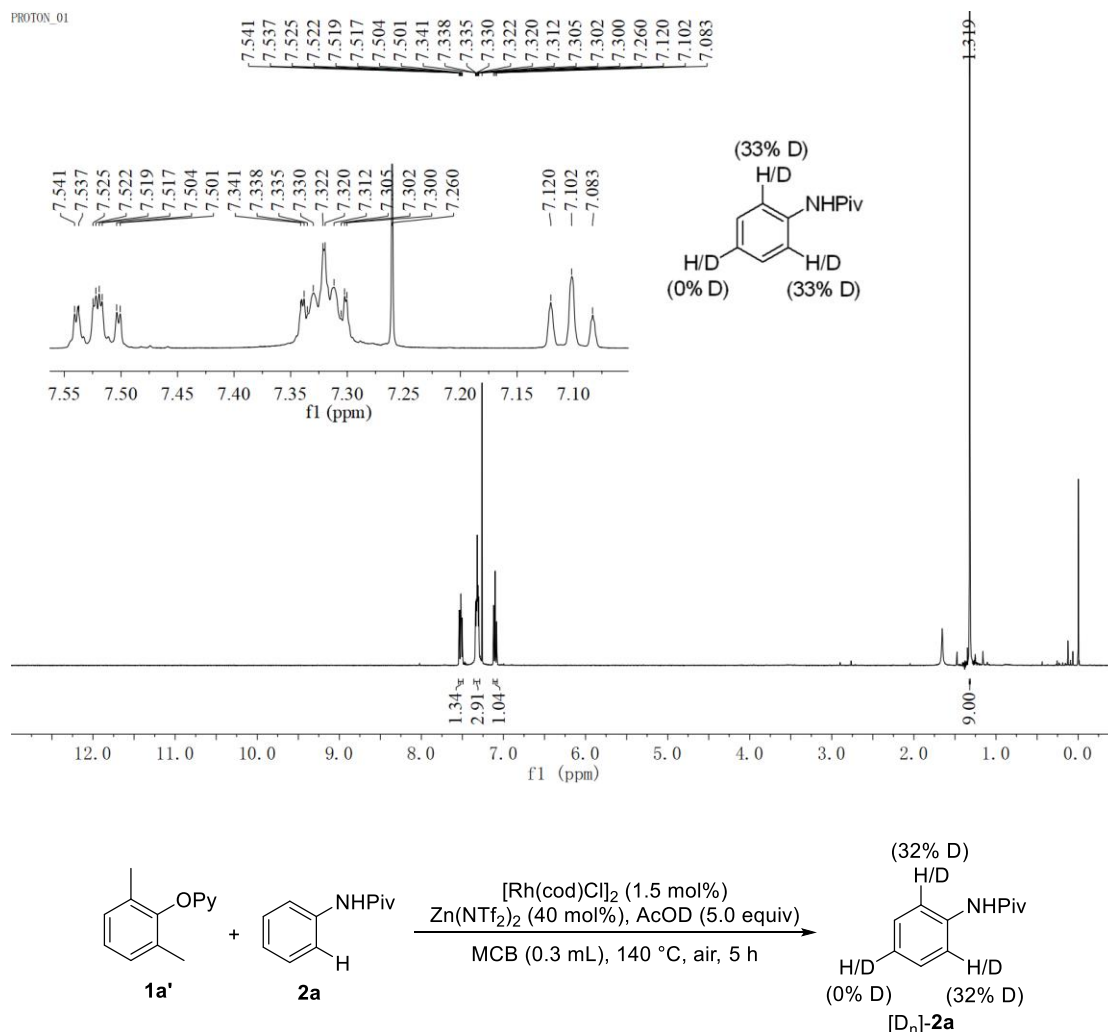
A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with N-phenylpivalamide **2a** (35.4 mg, 0.2 mmol), [Rh(cod)Cl]₂ (1.5 mg, 3 μmol, 1.5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOD (57.6 μL, 1 mmol, 5 equiv) and MCB (0.3



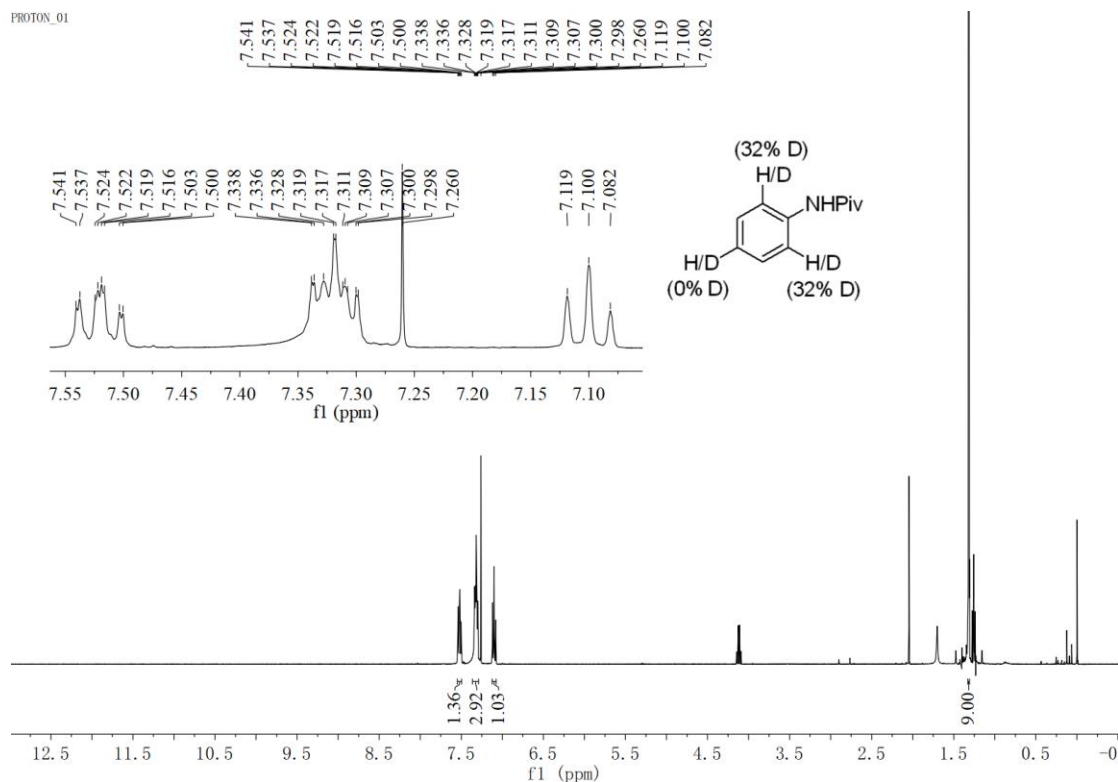
S15

dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to provide the desired products. The ^1H NMR analysis showed that 35% hydrogen at the *ortho*-position of the phenyl ring of **1a** and 33% hydrogen at the *ortho*-position of the phenyl ring of **2a** were deuterated, respectively.

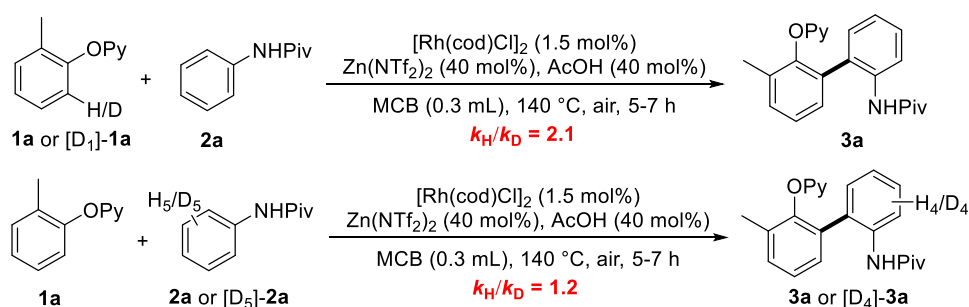




A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(2,6-dimethylphenoxy)pyridine **1a'** (39.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.5 mg, 3 μmol , 1.5 mol%), $\text{Zn}(\text{NTf}_2)_2$ (50.1 mg, 80 μmol , 40 mol%), AcOD (57.6 μL , 1 mmol, 5 equiv) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 5 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to provide the desired product. The ^1H NMR analysis showed that 32% hydrogen at the *ortho*-position of the phenyl ring of **2a** was deuterated.

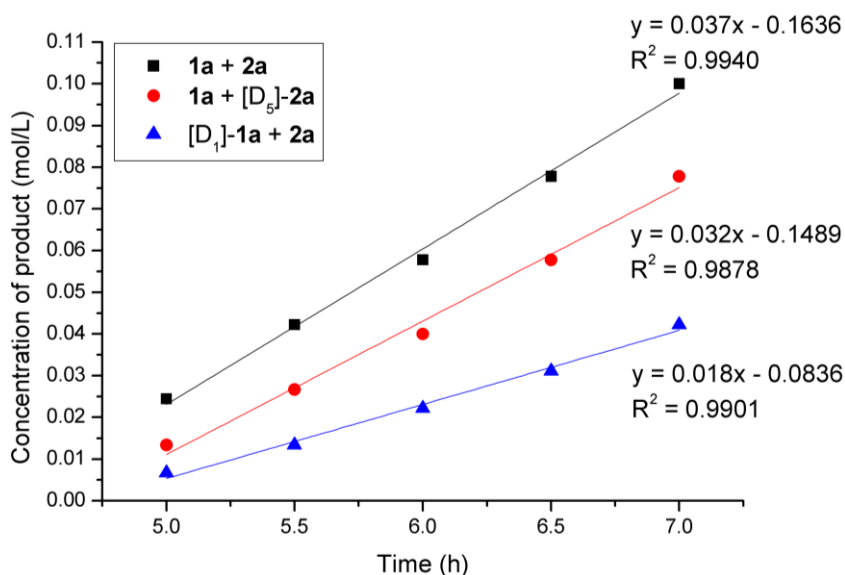


2. Kinetic isotope effect experiments

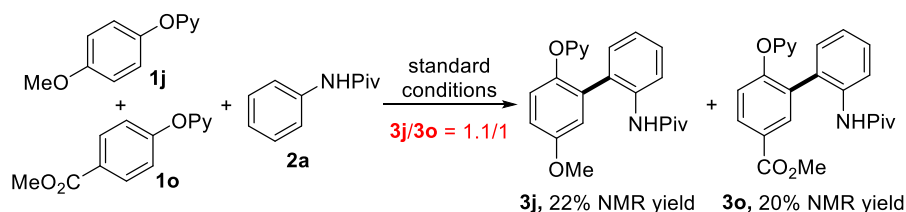


A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylxy)pyridine **1a** (37.0 mg, 0.2 mmol) or [D₁]-**1a** (37.2 mg, 0.2 mmol, preparation according to the reported literature⁹), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) or [D₅]-**2a** (43.7 mg, 0.24 mmol), [Rh(cod)Cl]₂ (1.5 mg, 3 μmol, 1.5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (4.6 μL, 80 μmol, 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 5 h, 5.5 h, 6 h, 6.5 h and 7 h. The reaction was stopped in the indicated reaction time and quickly cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl₃ and analyzed by ¹H NMR

with CH₂Br₂ (21.0 μL, 0.3 mmol) as the internal standard. The KIE (for **1a**) was determined to be $k_H/k_D = 0.037/0.018 \approx 2.1$; the KIE (for **2a**) was determined to be $k_H/k_D = 0.037/0.032 \approx 1.2$.

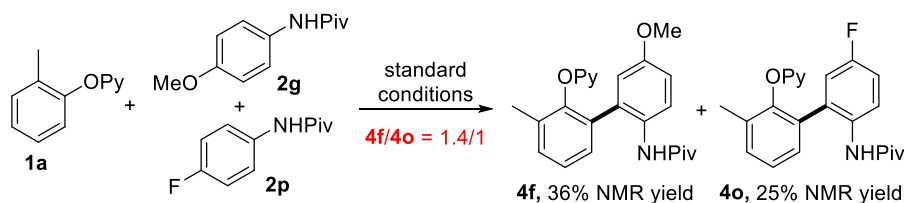


3. Intermolecular Competition Experiments



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(4-methoxyphenoxy)pyridine **1j** (40.2 mg, 0.2 mmol), methyl 4-(pyridin-2-yloxy)benzoate **1o** (45.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol), [Rh(cod)Cl]₂ (1.5 mg, 3 μmol, 1.5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (4.6 μL, 80 μmol, 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 15 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl₃ and analyzed by ¹H NMR with CH₂Br₂ (21.0 μL, 0.3 mmol) as the internal standard. The cross-coupled products **3j**

and **3o** were observed in 22% and 20% NMR yields, respectively.



A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(4-methoxyphenyl)pivalamide **2g** (49.7 mg, 0.24 mmol), *N*-(4-fluorophenyl)pivalamide **2p** (46.8 mg, 0.24 mmol), [Rh(cod)Cl]₂ (1.5 mg, 3 μmol, 1.5 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (4.6 μL, 80 μmol, 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 15 h and then cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure. The resulting residue was dissolved in CDCl₃ and analyzed by ¹H NMR with CH₂Br₂ (21.0 μL, 0.3 mmol) as the internal standard. The cross-coupled products **4f** and **4o** were observed in 36% and 25% NMR yields, respectively.

4. ESI-HRMS analysis

A 25 mL Schlenk sealed tube with a magnetic stir bar was charged with 2-phenoxy pyridine **1e** (34.2 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol, 1.2 equiv), [Rh(cod)Cl]₂ (15 mg, 30 μmol, 15 mol%), Zn(NTf₂)₂ (50.1 mg, 80 μmol, 40 mol%), AcOH (4.6 μL, 80 μmol, 40 mol%) and MCB (0.3 mL) under an air atmosphere. The resulting solution was stirred at 140 °C for 3 h. The reaction mixture was quickly cooled to room temperature before and performed the ESI-HRMS analysis immediately.

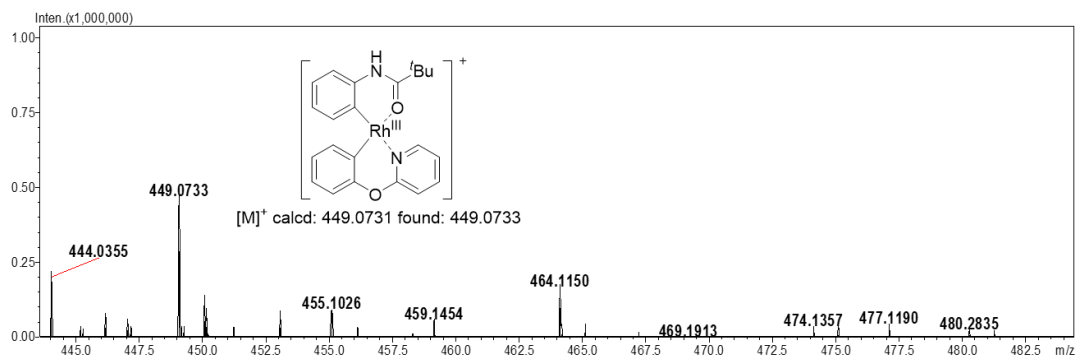
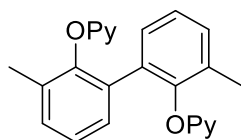


Figure S1. ESI-HRMS spectrum of intermediate **II**.

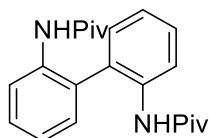
IX. Experimental data for the described substances

1. Homo-coupled side products



2,2'-((3,3'-Dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))dipyridine (**1aa**)

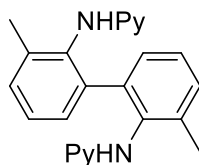
1aa was obtained as a white solid via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v). M.p.: 94-96 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.10 (s, 6H), 6.66 (d, J = 8.0 Hz, 2H), 6.90-6.93 (m, 2H), 7.02 (t, J = 7.6 Hz, 2H), 7.11-7.16 (m, 4H), 7.61 (t, J = 8.0 Hz, 2H), 8.10 (ddd, J = 4.8 Hz, 2.0 Hz, 0.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.9, 110.8, 117.8, 125.4, 129.4, 131.0, 131.1, 131.4, 140.6, 146.1, 149.0, 162.6 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 369.1598, found 369.1596.



N,N'-([1,1'-Biphenyl]-2,2'-diyl)bis(2,2-dimethylpropanamide) (**2aa**)

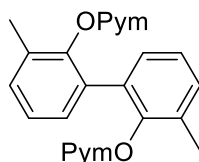
2aa was obtained as a white solid via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v). M.p.: 118-119 °C. ^1H NMR (400 MHz, CDCl_3): δ = 0.99 (s, 18H), 7.18 (brs, 2H), 7.22-7.24 (m, 4H), 7.42-7.48 (m, 2H), 8.30 (d, J = 8.0 Hz, 2H) ppm. ^{13}C

NMR (100 MHz, CDCl₃): δ = 27.3, 39.8, 122.0, 124.7, 128.1, 129.8, 129.9, 136.2, 176.9 ppm. HRMS (ESI): calcd for C₂₂H₂₉N₂O₂ [M+H]⁺ 353.2224, found 353.2223.



3,3'-Dimethyl-*N*²,*N*^{2'}-di(pyridin-2-yl)-[1,1'-biphenyl]-2,2'-diamine (7aa)

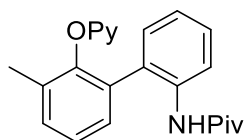
7aa was obtained as a white solid via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 1/1/1, v/v/v). M.p.: 145-146 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.14 (s, 6H), 6.02 (d, *J* = 8.0 Hz, 2H), 6.13 (brs, 2H), 6.50 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 2H), 7.02 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.16-7.21 (m, 4H), 7.99 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.0, 107.6, 114.0, 125.8, 128.4, 130.8, 135.8, 136.1, 137.3, 137.4, 148.0, 157.0 ppm. HRMS (ESI): calcd for C₂₄H₂₃N₄ [M+H]⁺ 367.1917, found 367.1915.



2,2'-((3,3'-Dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))dipyrimidine (8aa)

8aa was obtained as a white solid via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v). M.p.: 218-219 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.09 (s, 6H), 6.89 (t, *J* = 4.8 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 7.11-7.17 (m, 4H), 8.42 (d, *J* = 4.8 Hz, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 115.6, 125.2, 129.1, 130.7, 131.1, 131.2, 148.8, 159.6, 164.9 ppm. HRMS (ESI): calcd for C₂₂H₁₉N₄O₂ [M+H]⁺ 371.1503, found 371.1503.

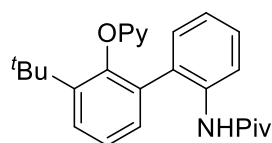
2. Cross-coupled products and deprotected products



***N*-(3'-Methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3a**)**

Following the general procedure A, 2-(*o*-tolyl)oxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3a** as a white solid (56.1 mg, 78% yield). M.p.: 84-86 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (s, 9H), 2.23 (s, 3H), 6.63 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.78 (ddd, *J* = 7.2 Hz, 4.8 Hz, 0.8 Hz, 1H), 6.97 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.16-7.20 (m, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.34 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.45 (ddd, *J* = 8.0 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.70 (brs, 1H), 7.89-7.91 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.5, 39.6, 110.9, 118.0, 122.5, 123.8, 125.7, 128.2, 129.4, 129.9, 130.1, 131.3, 132.18, 132.24, 135.5, 139.4, 146.8, 149.9, 163.1, 176.6 ppm. HRMS (ESI): calcd for C₂₃H₂₅N₂O₂ [M+H]⁺ 361.1911, found 361.1915.

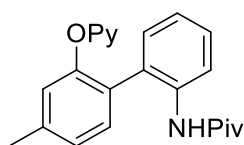
Alternatively, product **3a** can be obtained in 73% yield (52.8 mg) using 1.0 equivalent of *N*-phenylpivalamide **2a** (35.4 mg, 0.2 mmol).



***N*-(3'-(*tert*-Butyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3b**)**

Following the general procedure A, 2-(2-(*tert*-butyl)phenoxy)pyridine **1b** (45.4 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3b** as a white solid (50.4 mg, 63% yield). M.p.: 121-122 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.16 (s, 9H), 1.39 (s, 9H), 6.51-6.63 (m, 1H), 6.69 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 7.00-7.03 (m, 1H), 7.05-7.10 (m, 1H), 7.12 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H),

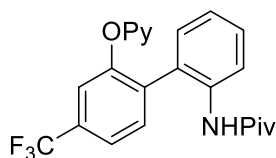
7.24-7.28 (m, 1H), 7.35 (ddd, $J = 8.4$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.53 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.66 (brs, 1H), 7.85-7.88 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.5, 30.8, 35.2, 39.6, 111.3, 117.8, 121.9, 123.5, 125.4, 127.7, 128.0, 130.1, 130.2, 130.6, 132.7, 135.2, 139.0, 143.2, 146.6, 150.3, 163.2, 176.4$ ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 403.2380, found 403.2386.



***N*-(4'-Methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3c)**

Following the general procedure A, 2-(*m*-tolxyloxy)pyridine **1c** (37.0 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3c** as a white solid (57.9 mg, 80% yield). M.p.: 94-95 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.16$ (s, 9H), 2.43 (s, 3H), 6.65 (dd, $J = 8.4$ Hz, 0.8 Hz, 1H), 6.79-6.82 (m, 1H), 6.98 (td, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.08 (s, 1H), 7.12-7.21 (m, 4H), 7.45-7.49 (m, 1H), 7.75 (brs, 1H), 7.92-7.96 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 21.4, 27.5, 39.6, 111.5, 118.3, 122.4, 123.2, 123.9, 126.5, 128.2, 128.6, 129.5, 130.3, 131.7, 135.6, 139.3, 140.1, 146.9, 151.5, 163.4, 176.6$ ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 361.1911, found 361.1915.

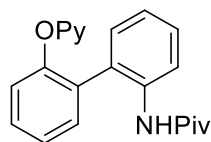
Alternatively, product **3c** can be obtained in 72% yield (51.8 mg) using 1.0 equivalent of *N*-phenylpivalamide **2a** (35.4 mg, 0.2 mmol).



***N*-(2'-(Pyridin-2-yloxy)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide (3d)**

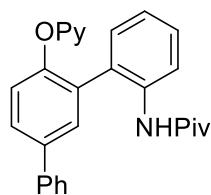
Following the general procedure A, 2-(3-(trifluoromethyl)phenoxy)pyridine **1d** (47.8 mg,

0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3d** as a white solid (58.8 mg, 71% yield). M.p.: 98-99 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.86-6.89 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.51-7.58 (m, 3H), 7.66 (brs, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 39.6, 111.7, 119.0, 120.1 (q, *J* = 4 Hz), 122.1 (q, *J* = 4 Hz), 123.6 (q, *J* = 271 Hz), 123.8, 124.5, 128.9, 129.1, 129.8, 132.0 (q, *J* = 33 Hz), 132.6, 135.3, 136.1 (q, *J* = 1 Hz), 139.8, 146.7, 152.0, 162.9, 176.7 ppm. HRMS (ESI): calcd for C₂₃H₂₂F₃N₂O₂ [M+H]⁺ 415.1628, found 415.1623.



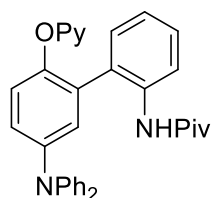
***N*-(2'-(Pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3e**)**

Following the general procedure A, 2-phenoxy pyridine **1e** (34.2 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3e** as a white solid (48.3 mg, 70% yield). M.p.: 75-76 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (s, 9H), 6.68 (dt, *J* = 8.0 Hz, 0.8 Hz, 1H), 6.83 (ddd, *J* = 7.2 Hz, 5.2 Hz, 1.2 Hz, 1H), 7.02 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.20-7.26 (m, 2H), 7.28-7.34 (m, 2H), 7.45-7.51 (m, 2H), 7.73 (brs, 1H), 7.92 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.95 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 111.6, 118.4, 122.75, 122.83, 124.0, 125.6, 128.4, 129.7, 129.8, 130.1, 131.9, 132.0, 135.5, 139.4, 146.8, 151.8, 163.4, 176.6 ppm. HRMS (ESI): calcd for C₂₂H₂₃N₂O₂ [M+H]⁺ 347.1754, found 347.1756.



***N*-(6'-(Pyridin-2-yloxy)-[1,1':3,1''-terphenyl]-2-yl)pivalamide (3f)**

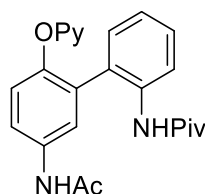
Following the general procedure A, 2-([1,1'-biphenyl]-4-yloxy)pyridine **1f** (49.4 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3f** as a white solid (59.6 mg, 71% yield). M.p.: 109-110 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.85 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.02-7.06 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.32-7.37 (m, 2H), 7.42-7.45 (m, 2H), 7.50-7.55 (m, 2H), 7.59-7.61 (m, 2H), 7.70 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.82 (brs, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 111.7, 118.6, 122.9, 123.1, 124.1, 127.0, 127.6, 128.3, 128.4, 129.0, 129.8, 130.0, 130.6, 132.1, 135.5, 138.6, 139.5, 139.8, 146.8, 151.1, 163.4, 176.7 ppm. HRMS (ESI): calcd for C₂₈H₂₇N₂O₂ [M+H]⁺ 423.2067, found 423.2068.



***N*-(5'-(Diphenylamino)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3g)**

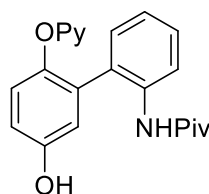
Following the general procedure A, *N,N*-diphenyl-4-(pyridin-2-yloxy)aniline **1g** (67.6 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol), and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3g** as a white solid (48.4 mg, 47% yield). M.p.: 155-156 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.22 (s, 9H), 6.64-6.66 (m, 1H), 6.83 (ddd, *J* = 7.2 Hz, 4.8 Hz, 0.8 Hz, 1H), 6.95-7.04 (m, 4H), 7.09-7.27 (m, 12H), 7.48 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.82 (brs, 1H), 7.94 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 7.99 (ddd, *J* = 5.2 Hz,

2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 27.6, 39.8, 111.6, 118.4, 122.3, 123.2, 123.4, 123.8, 124.4, 124.8, 126.5, 128.4, 129.2, 129.5, 130.1, 132.6, 135.5, 139.5, 145.3, 146.7, 146.8, 147.7, 163.5, 176.4 ppm. HRMS (ESI): calcd for $\text{C}_{34}\text{H}_{32}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 514.2489, found 514.2490.



***N*-(5'-Acetamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3h)**

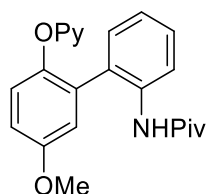
Following the general procedure A, *N*-(4-(pyridin-2-yloxy)phenyl)acetamide **1h** (45.6 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 2.5 mol%) and $\text{Zn}(\text{NTf}_2)_2$ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (DCM/EtOAc = 2/1, v/v) afforded **3h** as a white solid (44.0 mg, 55% yield). M.p.: 122-123 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.12 (s, 9H), 2.17 (s, 3H), 6.65 (d, J = 8.4 Hz, 1H), 6.73 (brs, 1H), 6.81 (ddd, J = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 7.09-7.13 (m, 2H), 7.48 (ddd, J = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.59-7.61 (m, 1H), 7.90-7.92 (m, 2H), 8.01-8.03 (m, 1H), 8.06 (brs, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 24.5, 27.4, 39.4, 111.6, 118.4, 121.0, 122.2, 123.0, 124.1, 124.8, 128.4, 130.2, 130.9, 132.1, 135.1, 136.0, 139.5, 146.7, 147.2, 163.6, 169.0, 177.6 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{26}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ 404.1969, found 404.1973.



***N*-(5'-Hydroxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3i)**

Following the general procedure A, 4-(pyridin-2-yloxy)phenol **1i** (37.4 mg, 0.2 mmol),

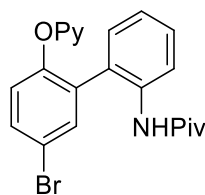
N-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (DCM/EtOAc = 5/1, v/v) afforded **3i** as a white solid (37.7 mg, 52% yield). M.p.: 203-205 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 6.10 (d, *J* = 2.8 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.78-6.85 (m, 2H), 6.95-6.98 (m, 3H), 7.07-7.13 (m, 1H), 7.44-7.48 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.92 (dt, *J* = 4.8 Hz, 0.8 Hz, 1H), 8.09 (brs, 1H), 8.36 (brs, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 39.4, 111.4, 116.7, 117.4, 118.2, 123.3, 124.7, 125.0, 128.2, 130.0, 131.8, 132.3, 134.7, 139.5, 143.7, 146.6, 154.5, 164.0, 178.1 ppm. HRMS (ESI): calcd for C₂₂H₂₂N₂NaO₃ [M+Na]⁺ 385.1523, found 385.1520.



***N*-(5'-Methoxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3j**)**

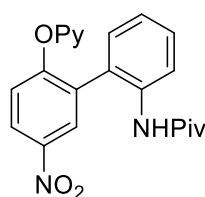
Following the general procedure A, 2-(4-methoxyphenoxy)pyridine **1j** (40.2 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3j** as a white solid (54.0 mg, 72% yield). M.p.: 92-93 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.17 (s, 9H), 3.81 (s, 3H), 6.64 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.79-6.82 (m, 2H), 6.99-7.03 (m, 2H), 7.16-7.24 (m, 3H), 7.47 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.82 (brs, 1H), 7.91 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.95 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 55.8, 111.3, 115.7, 116.1, 118.2, 122.9, 123.8, 124.1, 128.4, 129.8, 130.0, 132.7, 135.4, 139.4, 144.9, 146.8, 157.0, 163.7, 176.7 ppm. HRMS (ESI): calcd for C₂₃H₂₅N₂O₃ [M+H]⁺ 377.1860, found 377.1857.

Alternatively, product **3j** can be obtained in 63% yield (47.3 mg) using 1.0 equivalent of *N*-phenylpivalamide **2a** (35.4 mg, 0.2 mmol).



***N*-(5'-Bromo-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3k**)**

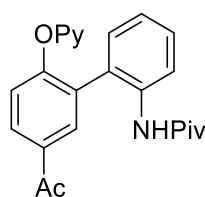
Following the general procedure A, 2-(4-bromophenoxy)pyridine **1k** (49.8 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3k** as a white solid (60.1 mg, 71% yield). M.p.: 101-102 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.19 (s, 9H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.84 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.03 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.12-7.17 (m, 2H), 7.23 (td, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.45 (d, *J* = 2.8 Hz, 1H), 7.50 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.57 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.68 (brs, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 111.6, 118.3, 118.7, 123.4, 124.3, 124.6, 128.7, 128.8, 129.9, 132.6, 134.1, 134.7, 135.3, 139.6, 146.7, 150.8, 163.0, 176.7 ppm. HRMS (ESI): calcd for C₂₂H₂₂⁷⁹BrN₂O₂ [M+H]⁺ 425.0859, found 425.0856; calcd for C₂₂H₂₂⁸¹Br N₂O₂ [M+H]⁺ 427.0839, found 427.0843.



***N*-(5'-Nitro-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3l**)**

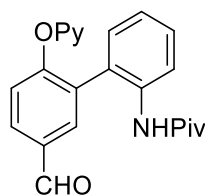
Following the general procedure A, 2-(4-nitrophenoxy)pyridine **1l** (43.2 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3l** as a white solid (40.6 mg, 52% yield). M.p.: 100-101 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 6.78-7.80 (m, 1H), 6.94 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.09 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.27-7.32 (m, 1H),

7.39 (d, $J = 8.8$ Hz, 1H), 7.54 (brs, 1H), 7.58 (ddd, $J = 8.0$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.88 (dd, $J = 8.0$ Hz, 1.2 Hz, 1H), 7.98 (ddd, $J = 5.2$ Hz, 2.0 Hz, 0.8 Hz, 1H), 8.24 (dd, $J = 2.8$ Hz, 1H), 8.33 (dd, $J = 9.2$ Hz, 2.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 27.4, 39.6, 112.2, 119.6, 123.1, 123.9, 124.7, 125.0, 127.6, 128.1, 129.3, 129.9, 133.0, 135.3, 140.1, 144.6, 146.9, 157.2, 162.4, 176.6$ ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 414.1424, found 414.1420.



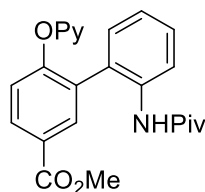
***N*-(5'-Acetyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3m**)**

Following the general procedure A, 1-(4-(pyridin-2-yloxy)phenyl)ethan-1-one **1m** (42.6 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 2.5 mol%) and $\text{Zn}(\text{NTf}_2)_2$ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3m** as a white solid (45.3 mg, 58% yield). M.p.: 114–115 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.13$ (s, 9H), 2.60 (s, 3H), 6.74 (d, $J = 8.4$ Hz, 1H), 6.87–6.90 (m, 1H), 7.06 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 7.6$ Hz, 1H), 7.24–7.28 (m, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.52–7.56 (m, 1H), 7.64 (brs, 1H), 7.90–7.92 (m, 2H), 7.97 (dd, $J = 4.8$ Hz, 1.6 Hz, 1H), 8.09 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 26.8, 27.5, 39.6, 112.1, 119.2, 122.8, 123.3, 124.4, 128.8, 129.1, 129.9, 130.1, 132.0, 132.8, 134.3, 135.5, 139.8, 147.0, 156.0, 162.9, 176.6, 196.7$ ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 389.1860, found 389.1859.



***N*-(5'-Formyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3n)**

Following the general procedure A, 4-(pyridin-2-yloxy)benzaldehyde **1n** (39.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3n** as a white solid (38.3 mg, 51% yield). M.p.: 116-117 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.12 (s, 9H), 6.76 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.90-6.93 (m, 1H), 7.05-7.09 (m, 1H), 7.18-7.21 (m, 1H), 7.25-7.29 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.54-7.58 (m, 1H), 7.62 (brs, 1H), 7.85 (dd, *J* = 2.0 Hz, 0.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.97-8.02 (m, 2H), 10.01 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 112.2, 119.4, 123.2, 123.6, 124.5, 128.8, 129.0, 130.0, 130.6, 132.7, 133.6, 134.5, 135.4, 139.9, 147.0, 157.1, 162.7, 176.7, 190.8 ppm. HRMS (ESI): calcd for C₂₃H₂₃N₂O₃ [M+H]⁺ 375.1703, found 375.1705.

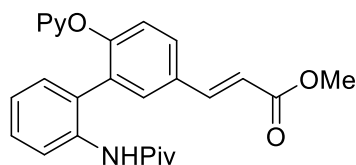


Methyl 2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (3o)

Following the general procedure A, methyl 4-(pyridin-2-yloxy)benzoate **1o** (45.8 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3o** as a white solid (60.6 mg, 75% yield). M.p.: 87-88 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 3.91 (s, 3H), 6.73 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.88 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.04 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.18 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.22-7.27 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.53 (ddd, *J* = 8.0 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.62 (brs, 1H), 7.92 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.96 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 52.4, 112.0, 119.1, 122.6, 123.1, 124.2, 127.3, 128.8, 128.9, 130.1, 131.4, 131.8, 133.8, 135.5, 139.8, 146.9, 155.9, 162.9, 166.3, 176.6 ppm. HRMS (ESI): calcd for C₂₄H₂₅N₂O₄ [M+H]⁺

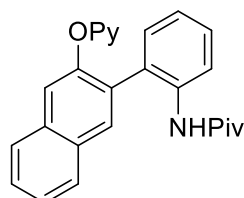
405.1809, found 405.1812.

Alternatively, product **3o** can be obtained in 66% yield (53.1 mg) using 1.0 equivalent of *N*-phenylpivalamide **2a** (35.4 mg, 0.2 mmol).



Methyl (*E*)-3-(2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl)acrylate (3p**)**

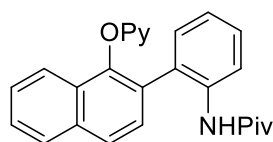
Following the general procedure A, methyl (*E*)-3-(4-(pyridin-2-yloxy)phenyl)acrylate **1p** (51.0 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3p** as a white solid (48.1 mg, 56% yield). M.p.: 147-148 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 3.80 (s, 3H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.86 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.04 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.22-7.28 (m, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.52 (ddd, *J* = 8.0 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.61 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.67-7.71 (m, 2H), 7.89 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 7.96 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 51.9, 111.9, 118.3, 118.9, 123.27, 123.31, 124.3, 128.7, 129.2, 129.6, 130.0, 131.6, 131.8, 132.5, 135.5, 139.7, 143.5, 146.9, 153.5, 163.1, 167.4, 176.7 ppm. HRMS (ESI): calcd for C₂₆H₂₇N₂O₄ [M+H]⁺ 431.1965, found 431.1966.



***N*-(2-(3-(Pyridin-2-yloxy)naphthalen-2-yl)phenyl)pivalamide (**3q**)**

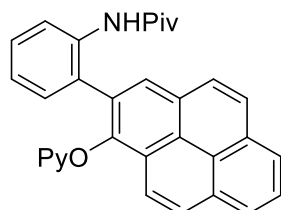
Following the general procedure A, 2-(naphthalen-2-yloxy)pyridine **1q** (44.2 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were

used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3q** as a white solid (49.6 mg, 63% yield). M.p.: 133-134 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.09 (s, 9H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.81 (dd, *J* = 7.2 Hz, 5.2 Hz, 1H), 7.02 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.21-7.25 (m, 2H), 7.46-7.55 (m, 3H), 7.72 (s, 1H), 7.76 (brs, 1H), 7.80 (s, 1H), 7.85 (m, 2H), 7.92-7.94 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.6, 111.6, 118.5, 119.5, 122.9, 124.0, 126.1, 126.9, 127.5, 127.9, 128.4, 129.7, 130.5, 131.3, 131.50, 131.54, 134.0, 135.6, 139.4, 146.8, 149.8, 163.6, 176.7 ppm. HRMS (ESI): calcd for C₂₆H₂₅N₂O₂ [M+H]⁺ 397.1911, found 397.1914.



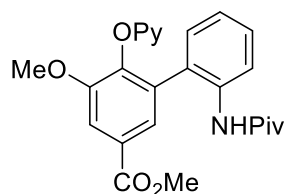
N-(2-(1-(Pyridin-2-yloxy)naphthalen-2-yl)phenyl)pivalamide (3r)

Following the general procedure A, 2-(naphthalen-1-yloxy)pyridine **1r** (44.2 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3r** as a white solid (58.4 mg, 74% yield). M.p.: 126-127 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.09 (s, 9H), 6.78-6.82 (m, 2H), 7.05 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.22-7.26 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.49-7.58 (m, 3H), 7.81-7.84 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 39.5, 111.0, 118.3, 122.4, 123.0, 124.1, 125.6, 126.8, 126.9, 128.1, 128.2, 128.3, 128.4, 128.6, 130.0, 130.2, 134.6, 135.5, 139.5, 146.8, 147.0, 163.6, 176.6 ppm. HRMS (ESI): calcd for C₂₆H₂₅N₂O₂ [M+H]⁺ 397.1911, found 397.1914.



***N*-(2-(1-(Pyridin-2-yloxy)pyren-2-yl)phenyl)pivalamide (3s)**

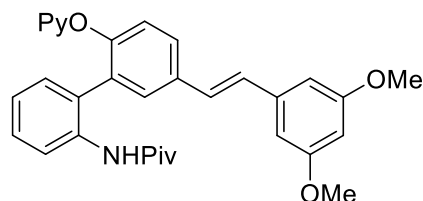
Following the general procedure A, 2-(pyren-1-yloxy)pyridine **1s** (59.0 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3s** as a light-yellow solid (68.8 mg, 73% yield). M.p.: 216-217 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.99 (s, 9H), 6.81 (dd, *J* = 6.8 Hz, 5.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.52-7.56 (m, 1H), 7.77 (brs, 1H), 7.81 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 8.03-8.07 (m, 2H), 8.09-8.12 (m, 3H), 8.20-8.24 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 39.6, 111.1, 118.4, 121.4, 123.1, 124.1, 124.7, 125.0, 125.5, 125.6, 125.7, 126.6, 127.0, 127.5, 127.6, 128.5, 128.6, 129.1, 130.1, 130.2, 130.7, 131.29, 131.31, 135.7, 139.6, 145.2, 146.8, 164.1, 176.7 ppm. HRMS (ESI): calcd for C₃₂H₂₇N₂O₂ [M+H]⁺ 471.2067, found 471.2069.



Methyl 5-methoxy-2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (3t)

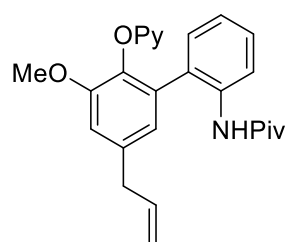
Following the general procedure, methyl 3-methoxy-4-(pyridin-2-yloxy)benzoate **1t** (51.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3t** as a white solid (49.3 mg, 57% yield). M.p.: 105-106 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 3.86 (s, 3H), 3.90 (s, 3H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.85 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.04 (dt, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.18 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.22-7.26 (m, 1H), 7.52 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.69 (brs, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.88-7.91 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 39.6, 52.4, 56.4, 111.3, 113.1, 118.6, 123.3, 124.2, 125.0, 127.7, 128.6, 128.8, 129.9, 133.5, 135.4, 139.5,

144.6, 146.6, 152.6, 163.0, 166.4, 176.6 ppm. HRMS (ESI): calcd for $C_{25}H_{27}N_2O_5$ $[M+H]^+$ 435.1914, found 435.1919.



(*E*)-*N*-(5'-(3,5-Dimethoxystyryl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3u**)**

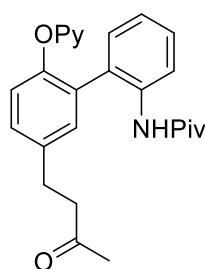
Following the general procedure, (*E*)-2-(4(3,5-dimethoxystyryl)phenoxy)pyridine **1u** (66.6 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3u** as a white solid (55.4 mg, 55% yield). M.p.: 86-87 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 9H), 3.83 (s, 6H), 6.40 (t, J = 2.4 Hz, 1H), 6.65 (d, J = 2.4 Hz, 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.83-6.86 (m, 1H), 7.00 (d, J = 16.4 Hz, 1H), 7.02-7.07 (m, 1H), 7.09 (d, J = 16.4 Hz, 1H), 7.20-7.25 (m, 3H), 7.46 (d, J = 2.4 Hz, 1H), 7.51 (ddd, J = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.58 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.79 (brs, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 5.2 Hz, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.5, 39.6, 55.5, 100.2, 104.6, 111.7, 118.5, 123.10, 123.13, 124.2, 127.8, 128.0, 128.5, 129.2, 129.8, 130.0, 132.2, 134.7, 135.5, 139.1, 139.5, 146.8, 151.2, 161.1, 163.4, 176.8 ppm. HRMS (ESI): calcd for $C_{32}H_{33}N_2O_4$ $[M+H]^+$ 509.2435, found 509.2430.



***N*-(5'-Allyl-3'-methoxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3v**)**

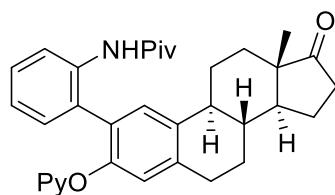
Following the general procedure, 2-(4-allyl-2-methoxyphenoxy)pyridine **1v** (48.2 mg, 0.2

mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3v** as a white solid (39.9 mg, 48% yield). M.p.: 101-102 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 1.88 (dd, *J* = 6.8 Hz, 1.2 Hz, 2H), 3.81 (s, 3H), 6.17-6.26 (m, 1H), 6.37 (dd, *J* = 16.0 Hz, 1.2 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.80-6.84 (m, 2H), 7.00-7.03 (m, 2H), 7.18-7.24 (m, 2H), 7.46-7.51 (m, 1H), 7.81 (brs, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, *J* = 5.2 Hz, 1.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.6, 27.5, 39.6, 56.2, 109.6, 111.1, 118.2, 120.7, 122.9, 124.0, 126.5, 128.3, 129.6, 129.9, 130.2, 133.2, 135.5, 136.1, 139.28, 139.34, 146.7, 152.6, 163.4, 176.7 ppm. HRMS (ESI): calcd for C₂₆H₂₉N₂O₃ [M+H]⁺ 417.2173, found 417.2180.



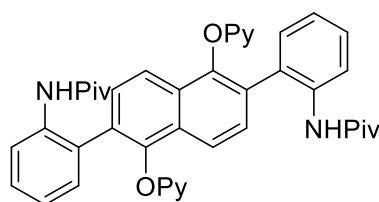
***N*-(3'-Methoxy-5'-(3-oxobutyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**3w**)**

Following the general procedure, 4-(4-(pyridin-2-yloxy)phenyl)butan-2-one **1w** (48.2 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3w** as a white solid (38.7 mg, 47% yield). M.p.: 84-85 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 2.16 (s, 3H), 2.79 (d, *J* = 7.6 Hz, 2H), 2.90-2.95 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.80-6.83 (m, 1H), 6.99-7.03 (m, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.14-7.17 (m, 2H), 7.19-7.23 (m, 1H), 7.28 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.46-7.50 (m, 1H), 7.75 (brs, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.94-7.95 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 29.0, 30.2, 39.6, 45.0, 111.6, 118.4, 122.8, 122.9, 124.1, 128.4, 129.8, 130.1, 131.6, 131.8, 135.4, 138.3, 139.4, 146.9, 149.9, 163.5, 176.6, 207.7 ppm. HRMS (ESI): calcd for C₂₆H₂₉N₂O₃ [M+H]⁺ 417.2173, found 417.2175.



***N*-(2-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-3-(pyridin-2-yloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)phenyl)pivalamide (3*x*)**

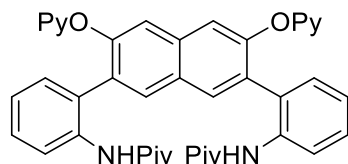
Following the general procedure, (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pyridin-2-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one **1x** (69.4 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol), [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) and Zn(NTf₂)₂ (25.0 mg, 20 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3x** as a white solid (~1:1.2 mixture of diastereomers, 60.1 mg, 58% yield). M.p.: 91-92 °C. ¹H NMR (400 MHz, CD₃Cl): δ = 0.91-0.92 (m, 3H), 1.16-1.18 (s, 9H), 1.42-1.58 (m, 4H), 1.62-1.73 (m, 2H), 1.93-1.96 (m, 1H), 2.05-2.20 (m, 3H), 2.26-2.40 (m, 2H), 2.49-2.55 (m, 1H), 2.98-3.00 (m, 2H), 6.63-6.66 (m, 1H), 6.78-6.81 (m, 1H), 6.95-7.00 (m, 2H), 7.10-7.21 (m, 3H), 7.44-7.49 (m, 1H), 7.73-7.80 (m, 1H), 7.90-7.98 (m, 1H) ppm. ¹³C NMR (100 MHz, CD₃Cl): δ = 13.8, 13.9, 21.68, 21.70, 25.8, 26.0, 26.4, 26.6, 27.5, 27.6, 29.2, 29.3, 31.5, 31.6, 35.9, 38.0, 38.2, 39.61, 39.62, 44.1, 44.3, 47.9, 48.0, 50.50, 50.51, 111.46, 111.50, 118.2, 122.2, 122.5, 122.57, 122.63, 123.8, 123.9, 128.12, 128.13, 128.75, 128.76, 128.9, 129.0, 129.6, 129.8, 130.3, 135.46, 135.53, 137.0, 137.4, 138.47, 138.54, 139.31, 139.32, 146.8, 146.9, 149.3, 163.4, 163.5, 176.4, 176.5, 220.7, 220.8 ppm. HRMS (ESI): calcd for C₃₄H₃₈N₂NaO₃ [M+Na]⁺ 545.2775, found 545.2777.



***N,N'*-((1,5-Bis(pyridin-2-yloxy)naphthalene-2,6-diyl)bis(2,1-phenylene))bis(2,2-dimethyl-1-phenylene)pivalamide (3*y*)**

ethylpropanamide) (**3y**)

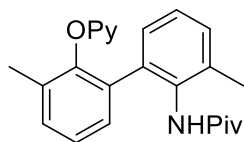
Following the general procedure A, 1,5-bis(pyridin-2-yloxy)naphthalene **1y** (62.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (106.2 mg, 0.6 mmol) and [Rh(cod)Cl]₂ (3.0 mg, 3.0 mol%) were used. The reaction mixture was heated at 140 °C for 20 h. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3y** as a white solid (59.4 mg, 45% yield). M.p.: >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.03 (s, 9H), 1.13 (s, 9H), 6.82-6.86 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.05-7.10 (m, 2H), 7.22-7.32 (m, 4H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.54-7.58 (m, 2H), 7.76-7.77 (m, 2H), 7.82-7.89 (m, 4H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 27.6, 39.5, 39.6, 111.18, 111.21, 118.6, 120.0, 120.3, 123.4, 123.6, 124.2, 124.4, 128.6, 129.3, 129.4, 129.5, 129.71, 129.74, 129.8, 129.9, 130.2, 130.3, 135.5, 135.6, 139.77, 139.80, 146.7, 146.8, 147.3, 147.4, 163.6, 163.7, 176.5, 176.7 ppm. HRMS (ESI): calcd for C₄₂H₄₁N₄O₄ [M+H]⁺ 665.3132, found 665.3130.



N,N'-((3,6-Bis(pyridin-2-yloxy)naphthalene-2,7-diyl)bis(2,1-phenylene))bis(2,2-dimethylpropanamide) (**3z**)

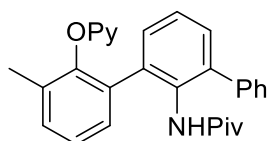
Following the general procedure A, 2,7-bis(pyridin-2-yloxy)naphthalene **1z** (62.8 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (106.2 mg, 0.6 mmol) and [Rh(PPh₃)₃Cl] (11.6 mg, 6.0 mol%) were used. The reaction mixture was heated at 150 °C for 20 h. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3z** as a white solid (56.0 mg, 42% yield). M.p.: 216-217 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.10 (s, 9H), 1.16 (s, 9H), 6.70-6.73 (m, 2H), 6.84-6.86 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 7.19-7.26 (m, 4H), 7.48-7.52 (m, 2H), 7.72-7.81 (m, 6H), 7.96-7.97 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 27.6, 39.6, 39.7, 111.8, 118.7, 118.8, 118.9, 122.7, 122.8, 124.0, 124.2, 128.6, 129.0, 129.2, 129.4, 130.5, 130.7, 131.3, 131.6, 131.8, 134.7, 135.7,

139.6, 146.8, 146.9, 150.8, 151.0, 163.3, 163.4, 176.5, 176.7 ppm. HRMS (ESI): calcd for $C_{42}H_{41}N_4O_4$ $[M+H]^+$ 665.3132, found 665.3128.



***N*-(3,3'-Dimethyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4a)**

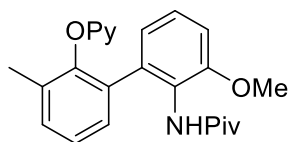
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(*o*-tolyl)pivalamide **2b** (45.8 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4a** as a white solid (47.0 mg, 63% yield). M.p.: 196-197 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 2.11 (s, 3H), 2.17 (s, 3H), 6.68 (dt, J = 8.4 Hz, 0.8 Hz, 1H), 6.82 (ddd, J = 7.2 Hz, 5.2 Hz, 1.2 Hz, 1H), 7.03-7.09 (m, 4H), 7.16 (t, J = 7.6 Hz, 1H), 7.26 (dq, J = 7.6 Hz, 0.8 Hz, 1H), 7.49 (ddd, J = 8.0 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.88 (brs, 1H), 7.94 (ddd, J = 4.8 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8, 18.4, 27.6, 39.0, 111.2, 118.1, 125.5, 126.0, 127.3, 129.1, 130.0, 130.7, 131.3, 134.0, 134.2, 135.3, 136.2, 139.6, 146.5, 149.5, 163.3, 176.8 ppm. HRMS (ESI): calcd for $C_{24}H_{27}N_2O_2$ $[M+H]^+$ 375.2067, found 375.2070.



***N*-(3-Methyl-2-(pyridin-2-yloxy)-[1,1':3',1''-terphenyl]-2'-yl)pivalamide (4b)**

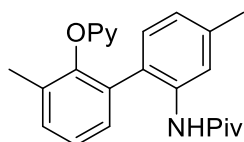
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-([1,1'-biphenyl]-2-yl)pivalamide **2c** (60.7 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4b** as a white solid (68.0 mg, 78% yield). M.p.: 132-133 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 9H), 2.21 (s, 3H), 6.69 (d, J = 8.4 Hz, 1H), 6.88-6.91 (m, 1H), 7.15-7.25 (m, 8H), 7.27-7.31 (m, 3H), 7.51-7.55 (m, 1H), 7.73 (brs, 1H), 8.03 (dd, J = 4.8 Hz, 1.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 16.8, 27.2, 38.7, 111.0, 118.2, 125.5, 126.5, 126.8, 127.8, 128.8, 129.0, 129.2, 129.8, 130.8, 131.4, 133.0, 133.7, 136.4, 139.7, 140.4, 140.9, 146.7, 149.5, 163.4, 176.1 ppm. HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 437.2224, found 437.2231.



***N*-(3-Methoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4c)**

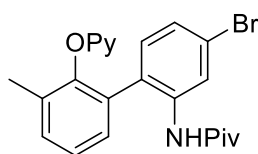
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(2-methoxyphenyl)pivalamide **2d** (49.7 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4c** as a white solid (54.8 mg, 70% yield). M.p.: 168-169 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.11 (s, 9H), 2.15 (s, 3H), 3.76 (s, 3H), 6.67 (dt, J = 8.4 Hz, 0.8 Hz, 1H), 6.78-6.84 (m, 3H), 7.08-7.14 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.24-7.26 (m, 1H), 7.50 (ddd, J = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.52 (brs, 1H), 7.98 (ddd, J = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.8, 27.6, 38.9, 56.3, 110.8, 111.4, 118.0, 122.0, 124.7, 125.5, 127.0, 129.0, 130.7, 131.1, 133.5, 137.0, 139.4, 146.9, 149.3, 155.4, 163.3, 176.8 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 391.2016, found 391.2024.



***N*-(3',4-Dimethyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4d)**

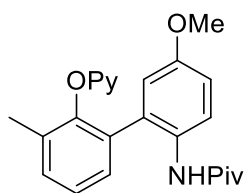
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(*m*-tolyl)pivalamide **2e** (48.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4d** as a white solid (57.3 mg, 77% yield). M.p.: 107-109 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.14 (s, 9H),

2.21 (s, 3H), 2.26 (s, 3H), 6.65 (dt, $J = 8.4$ Hz, 0.8 Hz, 1H), 6.78-6.81 (m, 2H), 7.01 (d, $J = 8.0$ Hz, 1H), 7.10 (ddd, $J = 7.6$ Hz, 1.6 Hz, 0.4 Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.32 (dq, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.47 (ddd, $J = 8.4$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.69 (brs, 1H), 7.76-7.77 (m, 1H), 7.91 (ddd, $J = 4.8$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.9$, 21.5, 27.5, 39.6, 110.9, 118.0, 123.0, 124.7, 125.6, 127.0, 129.6, 129.8, 131.1, 132.2, 132.3, 135.2, 138.0, 139.3, 146.8, 150.0, 163.1, 176.6 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 375.2067, found 375.2070.



N-(4-Bromo-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4e)

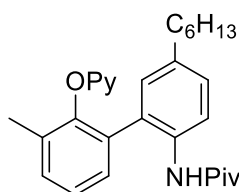
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and N-(3-bromophenyl)pivalamide **2f** (61.2 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/20/1, v/v/v) afforded **4e** as a white solid (58.0 mg, 66% yield). M.p.: 136-137 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.13$ (s, 9H), 2.21 (s, 3H), 6.67 (dt, $J = 8.4$ Hz, 0.8 Hz, 1H), 6.82 (ddd, $J = 7.2$ Hz, 4.8 Hz, 0.8 Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 7.08 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.11 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.35 (dq, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.51 (ddd, $J = 8.4$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.70 (brs, 1H), 7.89 (ddd, $J = 5.2$ Hz, 2.0 Hz, 0.8 Hz, 1H), 8.20 (d, $J = 2.0$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.9$, 27.4, 39.7, 111.0, 118.3, 121.8, 125.1, 125.8, 126.8, 128.5, 129.1, 131.18, 131.23, 131.7, 132.5, 136.7, 139.6, 146.8, 149.8, 162.9, 176.6 ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}^{79}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 439.1016, found 439.1024; calcd for $\text{C}_{23}\text{H}_{24}^{81}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 441.0995, found 441.1013.



N-(5-Methoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4f)

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-methoxyphenyl)pivalamide **2g** (49.7 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **4f** as a white solid (59.8 mg, 77% yield). M.p.: 105-106 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.12 (s, 9H), 2.21 (s, 3H), 3.67 (s, 3H), 6.67 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 6.74 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 6.81 (ddd, *J* = 7.2 Hz, 5.2 Hz, 1.2 Hz, 1H), 7.11 (ddd, *J* = 7.6 Hz, 1.6 Hz, 0.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.32 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.49 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.61 (brs, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.92 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.5, 39.4, 55.6, 111.0, 113.9, 115.0, 118.1, 124.7, 125.7, 128.7, 129.2, 131.3, 131.9, 132.1, 132.3, 139.4, 146.8, 149.7, 156.0, 163.1, 176.6 ppm. HRMS (ESI): calcd for C₂₄H₂₇N₂O₃ [M+H]⁺ 391.2016, found 391.2019.

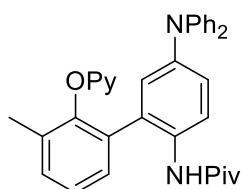
Alternatively, product **4f** can be obtained in 71% yield (55.6 mg) using 1.0 equivalent of *N*-(4-methoxyphenyl)pivalamide **2g** (41.4 mg, 0.2 mmol).



N-(5-Hexyl-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4g)

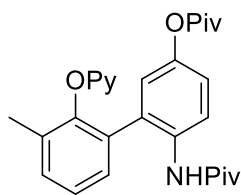
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-hexylphenyl)pivalamide **2h** (62.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4g** as colorless oil (66.3 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.13 (s,

9H), 1.19-1.29 (m, 6H), 1.41-1.48 (m, 2H), 2.23 (s, 3H), 2.44 (t, $J = 7.6$ Hz, 2H), 6.61 (dt, $J = 8.4$ Hz, 0.8 Hz, 1H), 6.77 (ddd, $J = 7.2$ Hz, 4.8 Hz, 0.8 Hz, 1H), 6.92 (d, $J = 2.0$ Hz, 1H), 6.98 (dd, $J = 8.4$ Hz, 2.0 Hz, 1H), 7.10-7.13 (m, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.32 (dq, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.44 (ddd, $J = 8.4$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.61 (brs, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.90 (ddd, $J = 4.8$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.3, 16.9, 22.7, 27.5, 28.9, 31.5, 31.9, 35.4, 39.6, 111.0, 118.0, 122.4, 125.6, 128.2, 129.4, 129.8, 130.0, 131.1, 132.2, 132.4, 133.1, 138.4, 139.2, 146.8, 149.9, 163.1, 176.5$ ppm. HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{37}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 445.2850, found 445.2845.



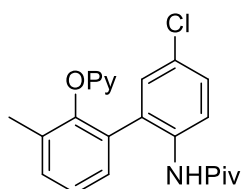
***N*-(5-(Diphenylamino)-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4h**)**

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-(diphenylamino)phenyl)pivalamide **2i** (82.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4h** as a white solid (72.1 mg, 68% yield). M.p.: 157-158 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.15$ (s, 9H), 2.21 (s, 3H), 6.69-6.71 (m, 1H), 6.86 (ddd, $J = 7.2$ Hz, 5.2 Hz, 0.8 Hz, 1H), 6.89-6.96 (m, 8H), 7.10 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.15-7.22 (m, 5H), 7.30 (dq, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.56 (ddd, $J = 8.0$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.65 (brs, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.90 (ddd, $J = 4.8$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.8, 27.5, 39.6, 110.8, 118.0, 122.3, 123.6, 123.7, 125.0, 125.7, 126.7, 129.15, 129.22, 131.0, 131.2, 131.3, 131.8, 132.2, 139.3, 143.5, 147.0, 147.8, 149.5, 163.0, 176.5$ ppm. HRMS (ESI): calcd for $\text{C}_{35}\text{H}_{34}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 528.2646, found 528.2655.



3'-Methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl pivalate (**4i**)

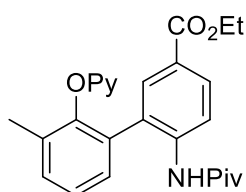
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and 4-pivalamidophenyl pivalate **2j** (66.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 15/15/1, v/v/v) afforded **4i** as a white solid (62.7 mg, 68% yield). M.p.: 96-97 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 1.30 (s, 9H), 2.22 (s, 3H), 6.72 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.80 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.87-6.90 (m, 2H), 7.11-7.13 (m, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.33 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.50 (ddd, *J* = 8.0 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.66 (brs, 1H), 7.87-7.90 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.2, 27.5, 39.1, 39.6, 111.3, 118.2, 121.1, 123.0, 123.4, 125.6, 129.2, 130.9, 131.3, 131.5, 132.4, 133.0, 139.6, 146.7, 146.9, 150.0, 163.1, 176.5, 177.0 ppm. HRMS (ESI): calcd for C₂₈H₃₃N₂O₄ [M+H]⁺ 461.2435, found 461.2441.



N-(5-Chloro-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4j**)

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and N-(4-chlorophenyl)pivalamide **2k** (50.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/20/1, v/v/v) afforded **4j** as a white solid (63.1 mg, 80% yield). M.p.: 123-124 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 9H), 2.22 (s, 3H), 6.69 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.82 (ddd, *J* = 7.2 Hz, 5.2 Hz, 1.2 Hz, 1H), 7.08 (ddd, *J* = 7.6 Hz, 1.6 Hz, 0.4 Hz, 1H), 7.13-7.16 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.35 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.50 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.68

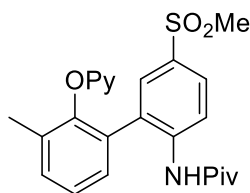
(brs, 1H), 7.85-7.88 (m, 1H), 7.90 (ddd, $J = 5.2$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.8, 27.4, 39.6, 111.0, 118.3, 123.8, 125.7, 128.1, 128.8, 129.0, 129.8, 131.0, 131.5, 131.8, 132.4, 134.2, 139.6, 146.8, 149.8, 162.9, 176.6$ ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}^{35}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 395.1521, found 395.1527; calcd for $\text{C}_{23}\text{H}_{24}^{37}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 397.1491, found 397.1487.



Ethyl 3'-methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (4k**)**

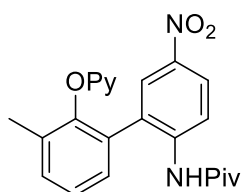
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and ethyl 4-pivalamidobenzoate **2l** (58.9 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **4k** as a white solid (61.3 mg, 71% yield). M.p.: 115-116 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.15$ (s, 9H), 1.34 (t, $J = 7.2$ Hz, 3H), 2.23 (s, 3H), 4.30 (q, $J = 7.2$ Hz, 2H), 6.62-6.64 (m, 1H), 6.78 (ddd, $J = 7.2$ Hz, 4.8 Hz, 0.8 Hz, 1H), 7.12 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.37 (dq, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.45 (ddd, $J = 8.4$ Hz, 7.2 Hz, 2.0 Hz, 1H), 7.80 (brs, 1H), 7.84 (d, $J = 2.0$ Hz, 1H), 7.86-7.89 (m, 2H), 8.13 (d, $J = 8.8$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 14.5, 16.9, 27.4, 39.9, 60.9, 110.9, 118.2, 120.9, 125.3, 125.8, 128.8, 129.2, 129.9, 131.0, 131.7, 131.8, 132.6, 139.5, 139.8, 146.8, 150.0, 162.9, 166.3, 176.7$ ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 455.1941, found 455.1939.

Alternatively, product **4k** can be obtained in 67% yield (58.2 mg) using 1.0 equivalent of ethyl 4-pivalamidobenzoate **2l** (49.8 mg, 0.2 mmol).



***N*-(3'-Methyl-5-(methanesulfonyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4l**)**

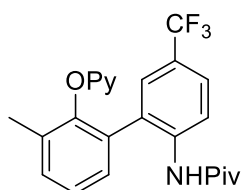
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-(methanesulfonyl)phenyl)pivalamide **2m** (61.2 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **4l** as a white solid (53.4 mg, 61% yield). M.p.: 164-165 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 2.24 (s, 3H), 2.89 (s, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.80 (ddd, *J* = 6.8 Hz, 5.2 Hz, 0.4 Hz, 1H), 7.11-7.13 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.48 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.6 Hz, 1H), 7.72-7.75 (m, 2H), 7.83 (brs, 1H), 7.88 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.8, 27.4, 40.0, 44.8, 110.9, 118.4, 121.7, 126.0, 127.7, 128.8, 129.5, 129.8, 129.9, 132.4, 133.0, 134.7, 139.6, 140.7, 146.8, 150.0, 162.9, 176.9 ppm. HRMS (ESI): calcd for C₂₄H₂₆N₂NaO₄S [M+Na]⁺ 461.1505, found 461.1499.



***N*-(3'-Methyl-5-nitro-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4m**)**

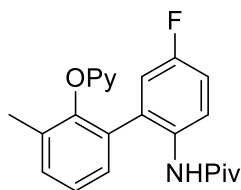
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(4-nitrophenyl)pivalamide **2n** (53.3 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4m** as a white solid (48.4 mg, 60% yield). M.p.: 115-116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.16 (s, 9H), 2.24 (s, 3H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.79-6.82 (m, 1H), 7.12 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J*

= 7.2 Hz, 1H), 7.48 (ddd, J = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.87 (dd, J = 5.2 Hz, 1.6 Hz, 1H), 7.89 (brs, 1H), 8.05-8.08 (m, 2H), 8.29-8.31 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.8, 27.3, 40.0, 110.8, 118.4, 120.9, 124.0, 125.8, 126.0, 128.7, 129.4, 129.6, 132.5, 133.0, 139.6, 141.7, 142.8, 146.8, 149.9, 162.7, 176.8 ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 406.1761, found 406.1770.



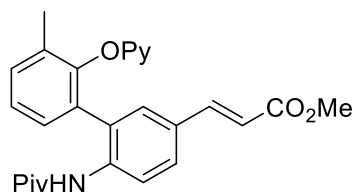
***N*-(3'-Methyl-2'-(pyridin-2-yloxy)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide (**4n**)**

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-(trifluoromethyl)phenyl)pivalamide **2o** (58.8 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/20/1, v/v/v) afforded **4n** as a white solid (60.7 mg, 71% yield). M.p.: 127-128 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.15 (s, 9H), 2.25 (s, 3H), 6.62 (d, J = 8.4 Hz, 1H), 6.79 (ddd, J = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.12 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.38-7.43 (m, 3H), 7.46 (ddd, J = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.75 (brs, 1H), 7.88 (ddd, J = 5.2 Hz, 2.0 Hz, 0.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.8, 27.4, 39.9, 111.0, 118.3, 121.6, 124.2 (q, J = 270 Hz), 125.3 (q, J = 4 Hz), 125.4 (q, J = 32 Hz), 125.8, 127.3 (q, J = 4 Hz), 128.9, 129.4, 130.5, 132.0, 132.8, 138.8, 139.5, 146.8, 150.1, 162.9, 176.7 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 429.1784, found 429.1785.



***N*-(5-Fluoro-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4o**)**

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(4-fluorophenyl)pivalamide **2p** (46.8 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4o** as a white solid (61.4 mg, 81% yield). M.p.: 79-80 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.13(s, 9H), 2.21 (s, 3H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 6.8 Hz, 5.6 Hz, 1H), 6.87-6.92 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.48-7.52 (m, 1H), 7.68 (brs, 1H), 7.76-7.80 (m, 1H), 7.90 (dd, *J* = 5.2 Hz, 1.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.8, 27.5, 39.5, 111.0, 114.8 (d, *J* = 22 Hz), 116.7 (d, *J* = 23 Hz), 118.3, 124.7 (d, *J* = 8 Hz), 125.8, 129.0, 131.1 (d, *J* = 1 Hz), 131.6 (d, *J* = 3 Hz), 131.7, 132.2 (d, *J* = 9 Hz), 132.3, 139.6, 146.8, 149.7, 159.0 (d, *J* = 242 Hz), 163.0, 176.7 ppm. HRMS (ESI): calcd for C₂₃H₂₄FN₂O₂ [M+H]⁺ 379.1816, found 379.1822.

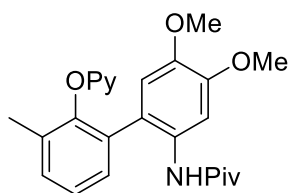


Methyl

***(E)*-3-(3'-methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl)acrylate (**4p**)**

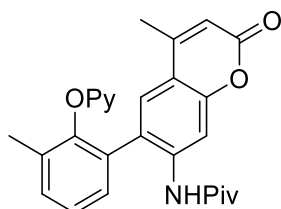
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and methyl (*E*)-3-(4-pivalamidophenyl)acrylate **2q** (62.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **4p** as a white solid (63.1 mg, 71% yield). M.p.: 148-149 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (s, 9H), 2.24 (s, 3H), 3.77 (s, 3H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.62 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.77-6.80 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.30-7.31 (m, 1H), 7.34-7.38 (m, 2H), 7.43-7.47 (m, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.74 (brs, 1H), 7.88-7.90 (m, 1H), 8.05 (d, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.4, 39.8, 51.8, 111.0, 116.6, 118.2, 121.9, 125.8, 128.3, 129.1, 129.6, 129.7, 130.0, 131.1, 131.8, 132.6, 137.6, 139.5, 144.4, 146.8, 150.0, 163.0, 167.7, 176.6 ppm. HRMS (ESI):

calcd for $C_{27}H_{29}N_2O_4$ $[M+H]^+$ 445.2122, found 445.2129.



***N*-(4,5-Dimethoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4q)**

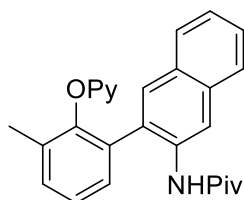
Following the general procedure A, 2-(*o*-tolylxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(3,4-dimethoxyphenyl)pivalamide **2r** (56.9 mg, 0.24 mmol) and $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (DCM/EtOAc = 10/1, v/v) afforded **4q** as a white solid (46.8 mg, 56% yield). M.p.: 42-43 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 9H), 2.23 (s, 3H), 3.68 (s, 3H), 3.84 (s, 3H), 6.63 (s, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.79-6.82 (m, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.46-7.51 (m, 1H), 7.59 (brs, 1H), 7.61 (s, 1H), 7.92 (dd, J = 4.8 Hz, 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.9, 27.5, 39.6, 55.98, 56.04, 106.3, 111.0, 112.7, 118.1, 121.6, 125.7, 129.0, 129.6, 131.2, 131.9, 132.4, 139.4, 145.1, 146.8, 148.2, 150.1, 163.2, 176.6 ppm. HRMS (ESI): calcd for $C_{25}H_{29}N_2O_4$ $[M+H]^+$ 421,2122, found 421,2128.



***N*-(4-Methyl-6-(3-methyl-2-(pyridin-2-yloxy)phenyl)-2-oxo-2H-chromen-7-yl)pivalamide (4r)**

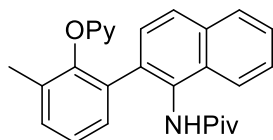
Following the general procedure A, 2-(*o*-tolylxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(4-methyl-2-oxo-2H-chromen-7-yl)pivalamide **2s** (62.2 mg, 0.24 mmol) and

[Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4r** as a white solid (62.1 mg, 70% yield). M.p.: 176-177 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (s, 9H), 2.22 (d, *J* = 1.2 Hz, 3H), 2.23 (s, 3H), 6.12 (s, 1H), 6.64 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.80-6.83 (m, 1H), 7.12-7.14 (m, 1H), 7.28-7.32 (m, 2H), 7.40-7.42 (m, 1H), 7.46-7.51 (m, 1H), 7.75 (brs, 1H), 7.90-7.92 (m, 1H), 8.19 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 18.6, 27.4, 40.0, 109.0, 111.0, 113.7, 115.4, 118.3, 125.2, 125.8, 126.0, 129.2, 130.3, 132.1, 133.0, 139.0, 139.7, 146.8, 150.2, 152.0, 153.6, 161.3, 162.9, 176.6 ppm. HRMS (ESI): calcd for C₂₇H₂₇N₂O₄ [M+H]⁺ 443.1965, found 443.1974.



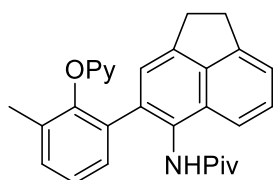
***N*-(3-(3-Methyl-2-(pyridin-2-yloxy)phenyl)naphthalen-2-yl)pivalamide (**4s**)**

Following the general procedure A, 2-(*o*-tolylxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(naphthalen-2-yl)pivalamide **2t** (54.5 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 15/15/1, v/v/v) afforded **4s** as a white solid (55.4 mg, 68% yield). M.p.: 48-50 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.18 (s, 9H), 2.25 (s, 3H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.71-6.74 (m, 1H), 7.18-7.20 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.31-7.40 (m, 4H), 7.62 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.86 (brs, 1H), 7.90 (dd, *J* = 5.2 Hz, 2.0 Hz, 1H), 8.52 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 17.0, 27.5, 39.8, 111.0, 118.1, 119.0, 125.0, 125.7, 126.2, 127.5, 127.8, 129.3, 129.66, 129.71, 130.2, 131.5, 132.0, 132.5, 133.4, 133.5, 139.4, 146.8, 150.1, 163.0, 176.7 ppm. HRMS (ESI): calcd for C₂₇H₂₇N₂O₂ [M+H]⁺ 411.2067, found 411.2075.



***N*-(2-(3-Methyl-2-(pyridin-2-yloxy)phenyl)naphthalen-1-yl)pivalamide (**4t**)**

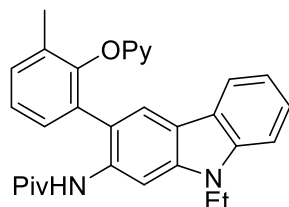
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(naphthalen-1-yl)pivalamide **2u** (54.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4t** as a white solid (46.4 mg, 57% yield). M.p.: 238-239 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.21 (s, 9H), 2.18 (s, 3H), 6.65-6.67 (m, 1H), 6.75 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.18 (dd, *J* = 7.2 Hz, 2.0 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.31 (ddd, *J* = 7.6 Hz, 2.0 Hz, 0.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.39-7.46 (m, 3H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.70-7.78 (m, 2H), 7.94 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.22 (brs, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.7, 39.2, 111.1, 118.2, 124.4, 125.7, 125.9, 126.3, 126.7, 127.4, 128.0, 129.0, 130.5, 131.0, 131.4, 132.0, 132.8, 133.7, 134.2, 139.7, 146.5, 149.6, 163.3, 178.1 ppm. HRMS (ESI): calcd for C₂₇H₂₇N₂O₂ [M+H]⁺ 411.2067, found 411.2065.



***N*-(4-(3-Methyl-2-(pyridin-2-yloxy)phenyl)-1,2-dihydroacenaphthylen-5-yl)pivalamide (**4u**)**

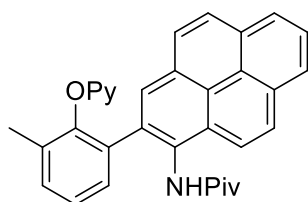
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol) and *N*-(1,2-dihydroacenaphthylen-5-yl)pivalamide **2v** (60.7 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **4u** as a white solid (58.0 mg, 67% yield). M.p.: 157-158 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.20 (s, 9H), 2.16 (s, 3H), 3.28-3.40 (m, 4H), 6.69 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.76 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.16-7.22 (m, 4H), 7.27-7.29 (m, 1H), 7.35-7.45 (m, 3H), 7.94 (dd, *J* = 5.2 Hz, 2.0 Hz, 1H), 8.18 (brs, 1H) ppm. ¹³C NMR (100 MHz,

CDCl₃): δ = 16.9, 27.8, 30.0, 30.8, 39.2, 111.3, 118.1, 119.3, 120.1, 120.9, 125.6, 128.0, 128.2, 128.6, 129.2, 130.7, 131.3, 134.2, 135.1, 139.6, 144.3, 145.9, 146.6, 149.6, 163.4, 177.8 ppm. HRMS (ESI): calcd for C₂₉H₂₉N₂O₂ [M+H]⁺ 437.2224, found 437.2218.



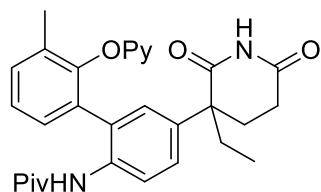
***N*-(9-Ethyl-3-(3-methyl-2-(pyridin-2-yloxy)phenyl)-9*H*-carbazol-2-yl)pivalamide (4v)**

Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(9-ethyl-9*H*-carbazol-2-yl)pivalamide **2w** (70.6 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/20/1, v/v/v) afforded **4v** as a white solid (74.1 mg, 78% yield). M.p.: 86-87 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.18 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 6.58 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.71 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.14-7.18 (m, 2H), 7.22-7.25 (m, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.31-7.44 (m, 4H), 7.80 (brs, 1H), 7.92 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.01-8.03 (m, 1H), 8.54 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.8, 16.9, 27.6, 37.6, 39.5, 108.4, 109.6, 111.0, 115.5, 118.0, 118.8, 121.0, 122.6, 123.0, 125.6, 125.7, 127.5, 129.3, 129.8, 131.1, 132.2, 133.4, 136.9, 139.4, 140.6, 146.7, 150.0, 163.1, 176.7 ppm. HRMS (ESI): calcd for C₃₁H₃₂N₃O₂ [M+H]⁺ 478.2489, found 478.2484.



***N*-(2-(3-Methyl-2-(pyridin-2-yloxy)phenyl)pyren-1-yl)pivalamide (4w)**

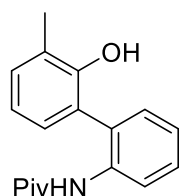
Following the general procedure A, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(pyren-1-yl)pivalamide **2x** (72.2 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/EtOAc = 10/10/1, v/v/v) afforded **4w** as a light yellow solid (44.6 mg, 46% yield). M.p.: 179-180 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.27 (s, 9H), 2.23 (s, 3H), 6.58 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.69 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.27-7.31 (m, 3H), 7.35-7.38 (m, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.94-7.96 (m, 2H), 7.98 (s, 1H), 8.00-8.05 (m, 2H), 8.08 (s, 1H), 8.12-8.14 (m, 2H), 8.56 (brs, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.9, 27.8, 39.4, 111.1, 118.2, 123.8, 124.6, 124.9, 125.2, 125.3, 125.7, 126.09, 126.12, 127.3, 127.4, 127.8, 127.9, 129.5, 129.7, 130.0, 131.06, 131.09, 131.2, 131.5, 133.6, 134.4, 139.6, 146.4, 149.8, 163.2, 178.1 ppm. HRMS (ESI): calcd for C₃₃H₂₉N₂O₂ [M+H]⁺ 486.2224, found 486.2231.



***N*-(5-(3-Ethyl-2,6-dioxopiperidin-3-yl)-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (**4x**)**

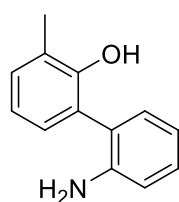
Following the general procedure, 2-(*o*-tolylloxy)pyridine **1a** (37.0 mg, 0.2 mmol), *N*-(4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)pivalamide **2y** (75.8 mg, 0.24 mmol) and [Rh(cod)Cl]₂ (2.5 mg, 2.5 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 4/2/1, v/v/v) afforded **4x** as a white solid (~1:1 mixture of diastereomers, 64.0 mg, 64% yield). M.p.: 146-148 °C. ¹H NMR (400 MHz, CD₃Cl): δ = 0.73-0.79 (m, 3H), 1.139-1.142 (m, 9H), 1.72-1.96 (m, 2H), 2.06-2.22 (m, 3H), 2.23 (s, 3H), 2.42-2.48 (m, 1H), 6.55-6.62 (m, 1H), 6.74-6.80 (m, 1H), 6.98-7.12 (m, 3H), 7.23-7.27 (m, 1H), 7.35-7.37 (m, 1H), 7.41-7.48 (m, 1H), 7.61-7.62 (m, 1H), 7.81-7.90 (m, 2H), 7.97-8.01 (m, 1H) ppm. ¹³C NMR (100 MHz, CD₃Cl): δ = 9.0, 9.2, 16.79, 16.82, 26.9, 27.3, 27.5, 29.3, 29.4, 32.8, 32.9, 39.7, 50.5, 50.9, 110.6, 110.7, 118.1, 118.2, 122.4, 122.5,

125.78, 125.83, 126.3, 127.8, 128.0, 129.08, 129.12, 129.89, 129.91, 131.3, 131.5, 131.7, 132.5, 132.6, 133.4, 133.9, 134.9, 135.0, 139.4, 139.5, 146.81, 146.85, 149.68, 149.71, 162.83, 162.85, 172.23, 172.25, 174.99, 175.01, 176.6 ppm. HRMS (ESI): calcd for $C_{30}H_{34}N_3O_4$ $[M+H]^+$ 500.2544, found 500.2540.



N-(2'-Hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (5)

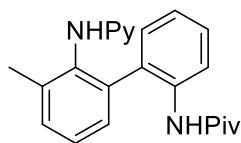
Crude **5** could be further purified via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to afford pure **5** as a white solid. M.p.: 110-111 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 9H), 2.31 (s, 3H), 4.99 (d, J = 2.4 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 7.00 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.19-7.23 (m, 2H), 7.28 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.38 (brs, 1H), 7.41-7.45 (m, 1H), 8.31 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3, 27.3, 39.8, 120.9, 122.0, 123.2, 124.8, 125.5, 126.9, 128.2, 129.7, 130.7, 131.6, 136.4, 151.1, 176.9 ppm. HRMS (ESI): calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1642.



2'-Amino-3-methyl-[1,1'-biphenyl]-2-ol (6)

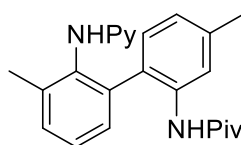
M.p.: 76-77 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.78 (brs, 2H), 6.86-6.89 (m, 1H), 6.91-6.98 (m, 3H), 7.14 (ddd, J = 7.6 Hz, 2.0 Hz, 0.4 Hz, 1H), 7.19 (dq, J = 7.6 Hz, 0.8 Hz, 1H), 7.22-7.26 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7, 117.1, 120.7, 120.8, 125.6, 126.0, 126.8, 128.8, 129.0, 130.7, 132.0, 142.2, 151.9 ppm. HRMS (ESI): calcd

for C₁₃H₁₄NO [M+H]⁺ 200.1070, found 200.1067.



N-(3'-Methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10a)

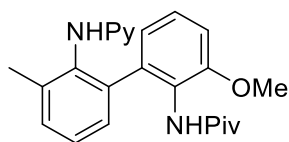
Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10a** as a white solid (51.1 mg, 71% yield). M.p.: 124-125 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (s, 9H), 2.27 (s, 3H), 5.88 (brs, 1H), 6.21 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.59 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.03-7.09 (m, 2H), 7.10-7.13 (m, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.28-7.35 (m, 3H), 7.46 (brs, 1H), 8.00 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.05-8.07 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.1, 27.4, 39.6, 108.2, 114.5, 122.4, 124.3, 126.2, 128.5, 128.6, 129.4, 131.1, 131.2, 135.4, 135.7, 136.8, 137.0, 137.5, 148.2, 157.0, 176.7 ppm. HRMS (ESI): calcd for C₂₃H₂₆N₃O [M+H]⁺ 360.2070, found 360.2064.



N-(3',4-Dimethyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10b)

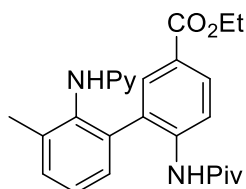
Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(*m*-tolyl)pivalamide **2e** (45.8 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10b** as a white solid (56.8 mg, 76% yield). M.p.: 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.03 (s, 9H), 2.26 (s, 3H), 2.32 (s, 3H), 5.92 (brs, 1H), 6.21 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.59 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.86 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.32-7.36 (m, 2H), 7.40

(brs, 1H), 7.95 (s, 1H), 8.01 (ddd, $J = 5.2$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 19.1, 21.6, 27.4, 39.7, 108.1, 114.5, 122.8, 125.1, 126.1, 128.0, 128.6, 129.2, 131.2, 135.3, 135.4, 136.7, 137.1, 137.5, 138.6, 148.2, 157.0, 176.8$ ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 374.2227, found 374.2228.



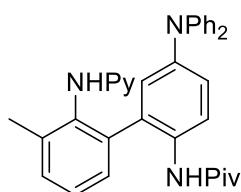
***N*-(3-Methoxy-3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide
(10c)**

Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(2-methoxyphenyl)pivalamide **2d** (49.7 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 5/5/1, v/v/v) afforded **10c** as a white solid (55.2 mg, 71% yield). M.p.: 135-136 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.02$ (s, 9H), 2.23 (s, 3H), 3.82 (s, 3H), 6.24 (dt, $J = 8.4$ Hz, 0.4 Hz, 1H), 6.53 (ddd, $J = 7.2$ Hz, 4.8 Hz, 0.8 Hz, 1H), 6.63-6.65 (m, 2H), 6.83 (dd, $J = 8.4$ Hz, 0.8 Hz, 1H), 6.97 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.04 (brs, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.20-7.23 (m, 1H), 7.30-7.34 (m, 1H), 8.04 (ddd, $J = 5.2$ Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 18.9, 27.4, 39.1, 56.0, 108.3, 110.3, 113.2, 122.1, 123.9, 125.4, 127.3, 127.6, 130.1, 136.7, 137.0, 137.2, 137.6, 139.9, 148.2, 154.6, 157.9, 177.8$ ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 390.2176, found 390.2168.



**Ethyl 3'-methyl-6-pivalamido-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-carboxylate
(10d)**

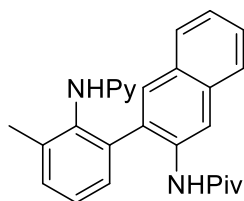
Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and ethyl 4-pivalamidobenzoate **2l** (58.9 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 5/5/1, v/v/v) afforded **10d** as a white solid (51.6 mg, 60% yield). M.p.: 156-157 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.06 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 4.29 (q, *J* = 7.2 Hz, 2H), 5.82 (brs, 1H), 6.22 (d, *J* = 8.4 Hz, 1H), 6.55-6.58 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.26-7.34 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.70 (brs, 1H), 7.79 (t, *J* = 2.0 Hz, 1H), 7.93-7.95 (m, 2H), 8.26 (d, *J* = 8.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.5, 19.1, 27.4, 39.9, 60.9, 108.3, 114.7, 120.9, 125.5, 126.4, 128.5, 130.2, 130.9, 131.7, 134.66, 134.68, 137.00, 137.04, 137.6, 140.0, 148.0, 156.8, 166.3, 176.8 ppm. HRMS (ESI): calcd for C₂₆H₂₉N₃NaO₃ [M+Na]⁺ 454.2101, found 454.2106.



***N*-(5-(Diphenylamino)-3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (**10e**)**

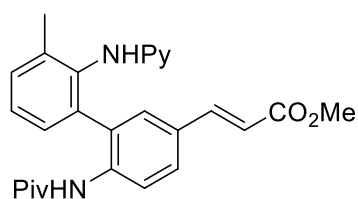
Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(4-(diphenylamino)phenyl)pivalamide **2i** (82.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10e** as a white solid (69.1 mg, 66% yield). M.p.: 92-93 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.07 (s, 9H), 2.25 (s, 3H), 5.91 (brs, 1H), 6.19 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.60 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.92-6.99 (m, 7H), 7.10-7.12 (m, 1H), 7.13-7.18 (m, 4H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.29 (dq, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.33 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.44 (brs, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.98 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.9, 27.5, 39.5, 108.0, 114.4, 122.5, 123.9, 124.1, 124.5, 125.3, 126.2, 128.4, 129.2, 130.6, 131.0, 133.2, 135.8, 136.66, 136.70, 137.5, 144.1, 147.8, 148.0, 157.0, 176.8 ppm. HRMS (ESI): calcd for

C₃₅H₃₅N₄O [M+H]⁺ 527.2805, found 527.2802.



N-(3-(3-Methyl-2-(pyridin-2-ylamino)phenyl)naphthalen-2-yl)pivalamide (10f)

Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(naphthalen-2-yl)pivalamide **2t** (54.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10f** as a white solid (61.5 mg, 75% yield). M.p.: 124-125 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.07 (s, 9H), 2.29 (s, 3H), 5.94 (brs, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 6.56 (ddd, *J* = 7.2 Hz, 4.8 Hz, 0.8 Hz, 1H), 7.19 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.27-7.32 (m, 2H), 7.35-7.45 (m, 3H), 7.58 (s, 1H), 7.62 (brs, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.96 (ddd, *J* = 4.8 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.66 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.2, 27.4, 39.8, 108.4, 114.6, 119.0, 125.3, 126.2, 126.5, 127.5, 128.0, 128.5, 128.7, 130.3, 130.9, 131.5, 133.5, 133.7, 135.0, 136.9, 137.2, 137.6, 148.0, 156.8, 177.0 ppm. HRMS (ESI): calcd for C₂₇H₂₈N₃O [M+H]⁺ 410.2227, found 410.2218.

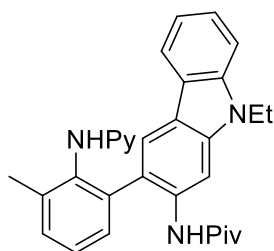


Methyl

(*E*)-3-(3'-methyl-6-pivalamido-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-yl)acrylate (10g)

Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and methyl (*E*)-3-(4-pivalamidophenyl)acrylate **2q** (62.6 mg, 0.24 mmol) were used.

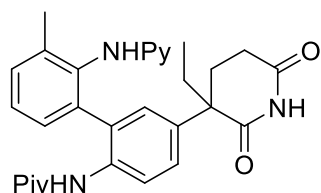
Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 5/5/1, v/v/v) afforded **10g** as a white solid (48.4 mg, 55% yield). M.p.: 164-165 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.06 (s, 9H), 2.29 (s, 3H), 3.76 (s, 3H), 5.85 (brs, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 6.21-6.24 (m, 1H), 6.59 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.12 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.26-7.30 (m, 1H), 7.33 (ddd, *J* = 8.4 Hz, 7.2 Hz, 2.0 Hz, 1H), 7.38 (dd, *J* = 7.6 Hz, 0.4 Hz, 1H), 7.42 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.61 (brs, 1H), 7.96-7.97 (m, 1H), 8.17 (d, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.0, 27.4, 39.8, 51.8, 108.3, 114.8, 116.8, 122.0, 126.4, 128.4, 128.6, 129.2, 130.0, 131.1, 131.6, 134.7, 137.0, 137.1, 137.70, 137.74, 144.3, 148.0, 156.9, 167.6, 176.8 ppm. HRMS (ESI): calcd for C₂₇H₃₀N₃O₃ [M+H]⁺ 444.2282, found 444.2276.



***N*-(9-Ethyl-3-(3-methyl-2-(pyridin-2-ylamino)phenyl)-9H-carbazol-2-yl)pivalamide (10h)**

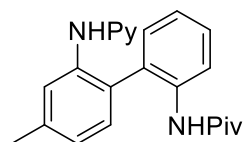
Following the general procedure B, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(9-ethyl-9H-carbazol-2-yl)pivalamide **2w** (70.6 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 5/5/1, v/v/v) afforded **10h** as a white solid (63.4 mg, 67% yield). M.p.: 235-237 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.07 (s, 9H), 1.14 (t, *J* = 6.8 Hz, 3H), 2.30 (s, 3H), 4.07-4.13 (m, 2H), 6.13 (brs, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 6.55 (t, *J* = 2.0 Hz, 1H), 7.09 (s, 1H), 7.17-7.21 (m, 2H), 7.26-7.36 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.48 (brs, 1H), 8.01 (d, *J* = 3.2 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.56 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.6, 19.0, 27.5, 37.6, 39.4, 108.5, 109.2, 114.1, 116.3, 119.0, 120.9, 122.86, 122.93, 125.6, 125.9, 126.0, 127.2, 128.4, 130.8, 131.8, 137.0, 137.38, 137.39, 137.44, 140.6, 148.2, 157.6, 177.5 ppm. HRMS

(ESI): calcd for $C_{31}H_{33}N_4O$ $[M+H]^+$ 477.2649, found 477.2647.



***N*-(5-(3-Ethyl-2,6-dioxopiperidin-3-yl)-3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10i)**

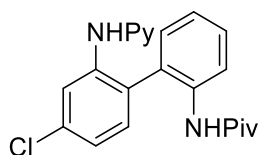
Following the general procedure, *N*-(*o*-tolyl)pyridin-2-amine **7a** (36.8 mg, 0.2 mmol) and *N*-(4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)pivalamide **2y** (75.8 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 3/3/1, v/v/v) afforded **10i** as a white solid (~1:1 mixture of diastereomers, 63.2 mg, 63% yield). M.p.: 195-196 °C. 1H NMR (400 MHz, CD_3Cl): δ = 0.66-0.72 (m, 3H), 1.07-1.08 (m, 9H), 1.62-1.73 (m, 1H), 1.76-1.89 (m, 1H), 1.96-2.21 (m, 3H), 2.26-2.46 (m, 4H), 6.12-6.21 (m, 1H), 6.22-6.42 (m, 1H), 6.53-6.58 (m, 1H), 6.95-6.98 (m, 1H), 7.04-7.12 (m, 2H), 7.24-7.36 (m, 3H), 7.54-7.58 (m, 1H), 7.95-8.04 (m, 2H), 8.44-8.75 (m, 1H) ppm. ^{13}C NMR (100 MHz, CD_3Cl): δ = 8.96, 9.03, 18.81, 18.83, 26.9, 27.0, 27.41, 27.42, 29.2, 29.3, 32.8, 33.0, 39.6, 39.7, 50.4, 50.6, 107.7, 114.1, 122.6, 122.7, 126.0, 126.3, 126.36, 126.45, 127.4, 127.6, 128.37, 128.44, 131.30, 131.33, 131.9, 132.2, 134.2, 134.4, 134.8, 134.9, 135.4, 135.9, 136.8, 136.9, 137.3, 137.6, 137.7, 137.8, 147.8, 157.1, 157.3, 172.7, 172.8, 175.4, 175.6, 176.8, 176.9 ppm. HRMS (ESI): calcd for $C_{30}H_{35}N_4O_3$ $[M+H]^+$ 499.2704, found 499.2704.



***N*-(4'-Methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10j)**

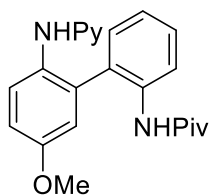
Following the general procedure B, *N*-(*m*-tolyl)pyridin-2-amine **7b** (36.8 mg, 0.2 mmol)

and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10j** as a white solid (54.6 mg, 76% yield). M.p.: 30-31 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.98 (s, 9H), 2.43 (s, 3H), 6.11 (brs, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.73 (ddd, *J* = 7.2 Hz, 4.8 Hz, 0.8 Hz, 1H), 6.91-6.94 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.18 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.38-7.47 (m, 3H), 8.02 (s, 1H), 8.18-8.19 (m, 1H), 8.33 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.9, 27.4, 39.8, 110.5, 115.7, 119.4, 121.4, 123.2, 123.9, 124.6, 128.47, 128.48, 129.3, 130.8, 136.2, 137.6, 138.6, 139.5, 148.1, 155.1, 176.8 ppm. HRMS (ESI): calcd for C₂₃H₂₆N₃O [M+H]⁺ 360.2070, found 360.2067.



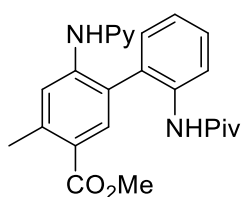
***N*-(4'-Chloro-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10k)**

Following the general procedure B, *N*-(3-chlorophenyl)pyridin-2-amine **7c** (40.8 mg, 0.2 mmol) and *N*-phenylpivalamide **2a** (42.5 mg, 0.24 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10k** as a white solid (51.8 mg, 68% yield). M.p.: 32-33 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.98 (s, 9H), 6.16 (brs, 1H), 6.56 (dt, *J* = 8.4 Hz, 0.8 Hz, 1H), 6.79 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.05 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.23-7.24 (m, 2H), 7.28 (brs, 1H), 7.43-7.49 (m, 2H), 8.23 (ddd, *J* = 5.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.3, 39.8, 111.3, 116.4, 118.3, 121.7, 122.4, 124.3, 125.1, 127.9, 129.8, 130.8, 131.6, 135.2, 136.0, 137.8, 139.9, 148.0, 154.4, 177.0 ppm. HRMS (ESI): calcd for C₂₂H₂₃³⁵ClN₃O [M+H]⁺ 380.1524, found 380.1523; calcd for C₂₂H₂₃³⁷ClN₃O [M+H]⁺ 382.1495, found 382.1491.



***N*-(5'-Methoxy-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (**10l**)**

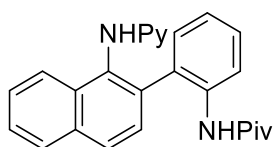
Following the general procedure B, *N*-(4-methoxyphenyl)pyridin-2-amine **7d** (40.0 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol) and Zn(NTf₂)₂ (62.5 mg, 50 mol%) were used. The reaction mixture was heated at 150 °C for 15 h. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10l** as a white solid (41.8 mg, 56% yield). M.p.: 127-128 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.99 (s, 9H), 3.81 (s, 3H), 5.94 (brs, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.66 (ddd, *J* = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.78 (d, *J* = 3.2 Hz, 1H), 7.00 (dd, *J* = 9.2 Hz, 3.2 Hz, 1H), 7.15-7.24 (m, 2H), 7.37-7.42 (m, 2H), 7.43 (brs, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 8.10-8.12 (m, 1H), 8.27 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.3, 39.7, 55.8, 109.6, 115.0, 115.2, 115.7, 122.1, 122.9, 124.7, 129.26, 129.32, 130.15, 130.25, 131.6, 135.9, 137.8, 147.7, 155.5, 155.8, 176.9 ppm. HRMS (ESI): calcd for C₂₃H₂₆N₃O₂ [M+H]⁺ 376.2020, found 376.2017.



Methyl 4-methyl-2'-pivalamido-6-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-carboxylate (10m**)**

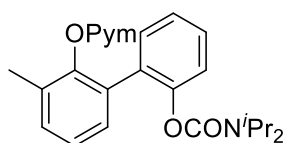
Following the general procedure B, methyl 2-methyl-4-(pyridin-2-ylamino)benzoate **7e** (48.4 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol) and Zn(NTf₂)₂ (62.5 mg, 50 mol%) were used. The reaction mixture was heated at 150 °C for 15 h. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 5/5/1, v/v/v) afforded **10m** as a white solid (47.6 mg, 57% yield). M.p.: 85-86 °C. ¹H NMR (400 MHz,

CDCl₃): δ = 0.98 (s, 9H), 2.71 (s, 3H), 3.85 (s, 3H), 6.35 (brs, 1H), 6.63-6.65 (m, 1H), 6.82 (ddd, J = 7.2 Hz, 4.8 Hz, 0.8 Hz, 1H), 7.24 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.27-7.29 (m, 2H), 7.43-7.52 (m, 2H), 7.85 (s, 1H), 8.24-8.27 (m, 2H), 8.33 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 22.7, 27.3, 39.8, 51.7, 112.0, 116.8, 119.7, 121.8, 122.6, 122.8, 125.2, 127.9, 129.7, 131.0, 133.9, 136.1, 137.8, 142.1, 143.1, 148.0, 154.2, 167.3, 177.0 ppm. HRMS (ESI): calcd for C₂₅H₂₈N₃O₃ [M+H]⁺ 418.2125, found 418.2124.



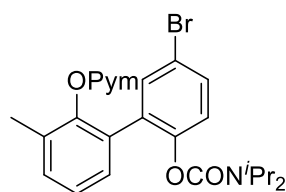
N-(2-(1-(Pyridin-2-ylamino)naphthalen-2-yl)phenyl)pivalamide (**10n**)

Following the general procedure B, *N*-(naphthalen-1-yl)pyridin-2-amine **7f** (44.0 mg, 0.2 mmol), *N*-phenylpivalamide **2a** (70.8 mg, 0.4 mmol) and Zn(NTf₂)₂ (62.5 mg, 50 mol%) were used. The reaction mixture was heated at 150 °C for 15 h. Purification via column chromatography on silica gel (petroleum ether/DCM/MeCN = 10/10/1, v/v/v) afforded **10n** as a white solid (45.3 mg, 57% yield). M.p.: 167-168 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.98 (s, 9H), 6.22 (dt, J = 8.4 Hz, 0.8 Hz, 1H), 6.32 (brs, 1H), 6.60 (ddd, J = 7.2 Hz, 5.2 Hz, 0.8 Hz, 1H), 7.07-7.16 (m, 2H), 7.28-7.34 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.48-7.58 (m, 3H), 7.85 (d, J = 8.4 Hz, 1H), 7.93-7.95 (m, 1H), 7.97-8.01 (m, 2H), 8.08 (dd, J = 8.4 Hz, 0.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4, 39.6, 108.3, 114.8, 122.9, 124.47, 124.53, 126.7, 126.8, 126.9, 128.2, 128.6, 128.8, 129.6, 131.1, 131.2, 132.4, 134.37, 134.43, 135.7, 137.6, 148.2, 158.0, 176.8 ppm. HRMS (ESI): calcd for C₂₆H₂₆N₃O [M+H]⁺ 396.2070, found 396.2062.



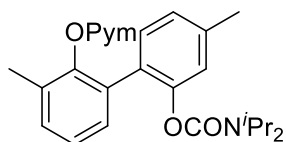
3'-Methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (**11a**)

Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11a** as a white solid (43.4 mg, 54% yield). M.p.: 120-122 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.01 (d, *J* = 6.0 Hz, 6H), 1.16 (d, *J* = 6.0 Hz, 6H), 2.20 (s, 3H), 3.75 (m, 1H), 3.98 (m, 1H), 6.83 (t, *J* = 4.8 Hz, 1H), 6.98 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.09 (td, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.12 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.16-7.22 (m, 3H), 7.23-7.28 (m, 1H), 8.36 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.7, 20.5, 20.9, 46.1, 46.6, 115.6, 123.1, 124.6, 125.5, 128.6, 129.5, 130.6, 130.76, 130.85, 131.1, 131.6, 149.04, 149.05, 153.3, 159.5, 164.8 ppm. HRMS (ESI): calcd for C₂₄H₂₇N₃NaO₃ [M+Na]⁺ 428.1945, found 428.1941.



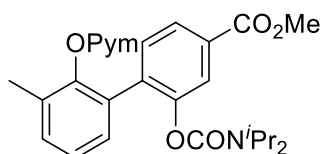
5-Bromo-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11b)

Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and 4-bromophenyl diisopropylcarbamate **9b** (119.6 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **11b** as a white solid (51.5 mg, 53% yield). M.p.: 122-123 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.99 (d, *J* = 6.0 Hz, 6H), 1.15 (d, *J* = 6.0 Hz, 6H), 2.19 (s, 3H) 3.70-3.73 (m, 1H), 3.94-3.99 (m, 1H), 6.89 (t, *J* = 4.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.18-7.20 (m, 2H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.27-7.31 (m, 2H), 8.40 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.6, 20.5, 20.8, 46.2, 46.7, 115.9, 117.4, 124.8, 125.6, 129.2, 130.4, 131.07, 131.12, 131.4, 133.3, 133.6, 148.4, 149.0, 152.8, 159.6, 164.8 ppm. HRMS (ESI): calcd for C₂₄H₂₇⁷⁹BrN₃O₃ [M+H]⁺ 484.1230, found 484.1227; calcd for C₂₄H₂₇⁸¹BrN₃O₃ [M+H]⁺ 486.1210, found 486.1208.



3',4-Dimethyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11c)

Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and *m*-tolyl diisopropylcarbamate **9c** (94.0 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11c** as a white solid (52.0 mg, 62% yield). M.p.: 154-155 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.00 (d, *J* = 6.0 Hz, 6H), 1.16 (d, *J* = 5.6 Hz, 6H), 2.18 (s, 3H), 2.26 (s, 3H), 3.77 (m, 1H), 3.95 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 4.8 Hz, 1H), 6.92 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.14-7.26 (m, 3H), 8.37 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.7, 20.5, 20.9, 21.2, 46.1, 46.5, 115.6, 123.6, 125.47, 125.51, 128.0, 129.6, 130.40, 130.42, 130.8, 131.7, 138.6, 148.8, 149.1, 153.5, 159.5, 164.8 ppm. HRMS (ESI): calcd for C₂₅H₂₉N₃NaO₃ [M+Na]⁺ 442.2101, found 442.2097.

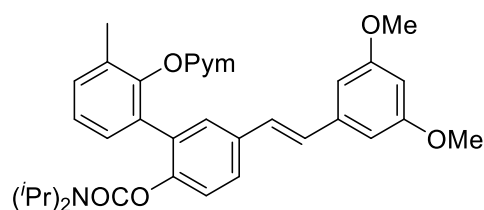


Methyl

2-((diisopropylcarbamoyl)oxy)-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-4-carboxylate (11d)

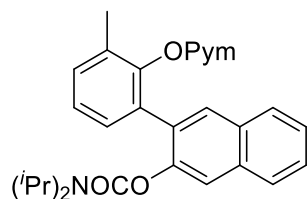
Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol), methyl 3-((diisopropylcarbamoyl)oxy)benzoate **9d** (111.6 mg, 0.4 mmol) and [Rh(PPh₃)₃Cl] (18.6 mg, 10 mol%) were used. The reaction mixture was heated at 140 °C for 20 h. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **11d** as white solid (37.8 mg, 41% yield). M.p.: 42-44 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.03 (d, *J* = 6.4 Hz, 6H), 1.17 (d, *J* = 6.4 Hz, 6H), 2.19 (s, 3H), 3.75-3.78

(m, 1H), 3.86 (s, 3H), 3.96-3.99 (m, 1H), 6.85 (t, $J = 4.8$ Hz, 1H), 7.18-7.24 (m, 3H), 7.28-7.30 (m, 1H), 7.68 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 7.76 (dd, $J = 2.0$ Hz, 0.4 Hz, 1H), 8.36 (d, $J = 4.8$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.6, 20.5, 20.9, 46.3, 46.7, 52.2, 115.8, 124.5, 125.6, 125.9, 129.1, 130.6, 130.88, 130.92, 131.09, 131.12, 136.3, 148.8, 149.1, 153.0, 159.6, 164.6, 166.5$ ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{30}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 464.2180, found 464.2179.



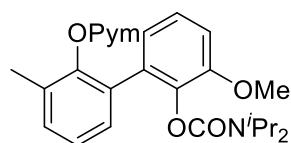
(*E*)-5-(3,5-Dimethoxystyryl)-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11e**)**

Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and (*E*)-4-(3,5-dimethoxystyryl)phenyl diisopropylcarbamate **9e** (153.2 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11e** as a white solid (58.6 mg, 52% yield). M.p.: 69-70 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 1.02$ (d, $J = 5.6$ Hz, 6H), 1.18 (d, $J = 5.6$ Hz, 6H), 2.21 (s, 3H), 3.73-3.76 (m, 1H), 3.82 (s, 6H), 3.96-4.00 (m, 1H), 6.37 (t, $J = 2.4$ Hz, 1H), 6.58 (d, $J = 2.4$ Hz, 2H), 6.75 (d, $J = 16.0$ Hz, 1H), 6.83 (t, $J = 4.8$ Hz, 1H), 6.90 (d, $J = 16.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.25-7.33 (m, 4H), 8.37 (d, $J = 4.8$ Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 16.7, 20.5, 20.9, 46.2, 46.6, 55.5, 100.0, 104.6, 115.7, 123.3, 125.6, 126.9, 128.2, 128.5, 128.8, 129.4, 130.7, 131.0, 131.4, 131.5, 133.6, 139.4, 148.8, 149.1, 153.2, 159.5, 161.0, 164.8$ ppm. HRMS (ESI): calcd for $\text{C}_{34}\text{H}_{38}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 568.2806, found 568.2804.



2-(3-Methyl-2-(pyrimidin-2-yloxy)phenyl)naphthalen-1-yl diisopropylcarbamate (11f)

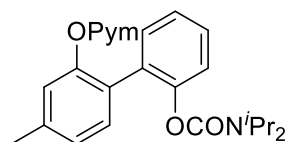
Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and naphthalen-2-yl diisopropylcarbamate **9f** (108.5 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11f** as a white solid (56.3 mg, 62% yield). M.p.: 134-135 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.05 (d, *J* = 6.0 Hz, 6H), 1.17 (d, *J* = 6.0 Hz, 6H), 2.21 (s, 3H), 3.69-3.73 (m, 1H), 4.08-4.10 (m, 1H), 6.73-6.76 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.30-7.34 (m, 3H), 7.36-7.40 (m, 1H), 7.59-7.62 (m, 3H), 7.71-7.73 (m, 1H), 8.30 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.7, 20.6, 20.9, 46.1, 46.8, 115.6, 119.9, 125.2, 125.6, 126.1, 127.4, 127.6, 129.9, 130.1, 130.7, 130.8, 130.9, 131.2, 131.8, 133.5, 147.4, 149.3, 153.3, 159.4, 164.8 ppm. HRMS (ESI): calcd for C₂₈H₃₀N₃O₃ [M+H]⁺ 456.2282, found 456.2281.



3-Methoxy-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11g)

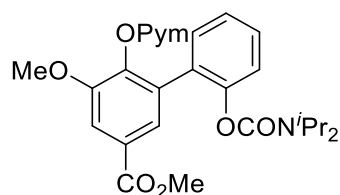
Following the general procedure C, 2-(*o*-tolylloxy)pyrimidine **8a** (37.2 mg, 0.2 mmol) and 2-methoxyphenyl diisopropylcarbamate **9g** (100.4 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11g** as a white solid (48.2 mg, 55% yield). M.p.: 174-175 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.07 (m, 6H), 1.16 (d, *J* = 6.4 Hz, 6H), 2.17 (s, 3H), 3.77-3.80 (m, 4H), 3.95-3.99 (m, 1H), 6.74 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 6.86 (t, *J* = 4.8 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.24-7.28 (m, 2H), 8.39 (d, *J* = 4.8 Hz, 2H)

ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.8, 20.6, 21.1, 46.0, 46.6, 56.3, 111.8, 115.6, 122.4, 124.9, 125.4, 129.4, 130.5, 130.9, 131.3, 132.4, 138.5, 148.9, 152.3, 153.4, 159.5, 164.9 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 458.2050, found 458.2044.



4'-Methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (**11h**)

Following the general procedure C, 2-(*m*-tolylxy)pyrimidine **8b** (37.2 mg, 0.2 mmol) and phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11h** as a white solid (48.8 mg, 60% yield). M.p.: 91-92 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.03 (d, J = 6.4 Hz, 6H), 1.18 (d, J = 6.0 Hz, 6H), 2.40 (s, 3H), 3.76-3.79 (m, 1H), 3.98-4.01 (m, 1H), 6.84 (t, J = 4.8 Hz, 1H), 6.98-7.02 (m, 1H), 7.03-7.04 (m, 1H), 7.07 (d, J = 1.2 Hz, 1H), 7.09 (m, 1H), 7.17-7.21 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.5, 21.0, 21.3, 46.2, 46.6, 115.7, 122.6, 123.2, 124.7, 126.4, 128.4, 128.5, 130.7, 131.1, 131.8, 139.3, 149.1, 150.4, 153.4, 159.4, 165.3 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 428.1945, found 428.1939.

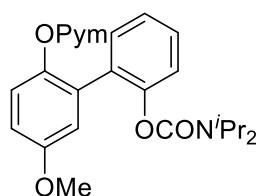


Methyl

2'-((diisopropylcarbamoyl)oxy)-5-methoxy-6-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (**11i**)

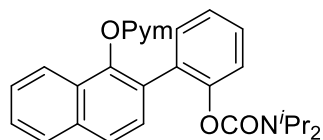
Following the general procedure C, methyl 3-methoxy-4-(pyrimidin-2-yloxy)benzoate **8c** (52.0 mg, 0.2 mmol), phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol) and

[Rh(PPh₃)₃Cl] (18.6 mg, 10 mol%) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **11i** as a white solid (50.4 mg, 53% yield). M.p.: 131-132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.99 (d, *J* = 5.6 Hz, 6H), 1.18 (d, *J* = 5.6 Hz, 6H), 3.74-3.79 (m, 4H), 3.87 (s, 3H), 3.95-3.98 (m, 1H), 6.92 (t, *J* = 4.8 Hz, 1H), 7.05 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.16 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.22 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.24-7.29 (m, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 8.41 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 20.4, 20.9, 46.3, 46.6, 52.3, 56.4, 112.7, 116.2, 123.5, 124.9, 125.4, 127.5, 129.1, 129.7, 130.5, 132.6, 143.6, 149.0, 151.9, 153.2, 159.5, 164.8, 166.7 ppm. HRMS (ESI): calcd for C₂₆H₃₀N₃O₆ [M+H]⁺ 480.2129, found 480.2128.



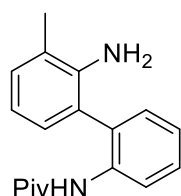
5'-Methoxy-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (**11j**)

Following the general procedure C, 2-(4-methoxyphenoxy)pyrimidine **8d** (40.4 mg, 0.2 mmol) and phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (DCM/EtOAc = 20/1, v/v) afforded **11j** as colorless oil (39.6 mg, 47% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (d, *J* = 6.4 Hz, 6H), 1.18 (d, *J* = 6.4 Hz, 6H), 3.76-3.84 (m, 4H), 3.94-4.00 (m, 1H), 6.85 (t, *J* = 4.8 Hz, 1H), 6.92-6.95 (m, 2H), 7.02 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.18-7.24 (m, 2H), 8.38 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 20.5, 21.0, 46.3, 46.5, 55.7, 110.2, 115.1, 115.7, 116.2, 123.0, 123.3, 124.8, 128.8, 130.68, 130.74, 132.2, 144.1, 149.0, 156.8, 159.5, 165.6 ppm. HRMS (ESI): calcd for C₂₄H₂₇N₃NaO₄ [M+Na]⁺ 444.1894, found 444.1889.



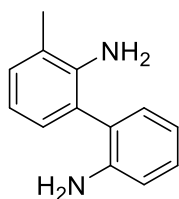
2-(1-(Pyrimidin-2-yloxy)naphthalen-2-yl)phenyl diisopropylcarbamate (**11k**)

Following the general procedure C, 2-(naphthalen-1-yloxy)pyrimidine **8e** (44.4 mg, 0.2 mmol) and phenyl diisopropylcarbamate **9a** (88.4 mg, 0.4 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **11k** as a white solid (50.1 mg, 57% yield). M.p.: 155-156 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.86 (d, *J* = 4.8 Hz, 6H), 1.11 (d, *J* = 6.4 Hz, 6H), 3.65-3.72 (m, 1H), 3.90-3.98 (m, 1H), 6.84 (t, *J* = 4.8 Hz, 1H), 7.05 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.22-7.26 (m, 1H), 7.29 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.44-7.52 (m, 3H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.94-7.97 (m, 1H), 8.34 (d, *J* = 4.8 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 20.5, 20.8, 46.1, 46.6, 115.8, 122.2, 123.2, 124.8, 125.3, 126.5, 126.6, 127.6, 127.7, 128.0, 128.8, 129.0, 131.0, 134.4, 146.0, 149.2, 153.2, 159.6, 165.5 ppm. HRMS (ESI): calcd for C₂₇H₂₈N₃O₃ [M+H]⁺ 442.2125, found 442.2128.



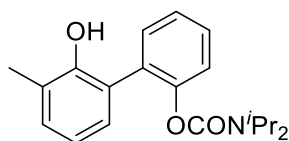
N-(2'-Amino-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (**12**)

Crude **12** could be further purified via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to afford pure **12** as a white solid. M.p.: 87-88 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 0.98 (s, 9H), 2.16 (s, 3H), 4.44 (brs, 2H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.81 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.05 (dq, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.21-7.27 (m, 2H), 7.37 (ddd, *J* = 8.0 Hz, 6.8 Hz, 2.0 Hz, 1H), 7.83 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 8.32 (brs, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 18.0, 26.9, 117.1, 122.2, 123.1, 123.4, 124.9, 127.8, 128.6, 129.8, 130.5, 132.3, 135.8, 142.6, 175.8 ppm. HRMS (ESI): calcd for C₁₈H₂₃N₂O [M+H]⁺ 283.1805, found 284.1801.



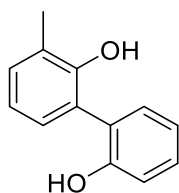
3-Methyl-[1,1'-biphenyl]-2,2'-diamine (**13**)

M.p.: 71-72 °C. ^1H NMR (400 MHz, DMSO- d_6): δ = 2.14 (s, 3H), 4.23 (brs, 2H), 4.53 (brs, 2H), 6.60 (t, J = 7.6 Hz, 1H), 6.64 (td, J = 7.2 Hz, 1.2 Hz, 1H), 6.77-6.82 (m, 2H), 6.91 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 6.99 (dq, J = 7.2 Hz, 0.8 Hz, 1H), 7.14 (ddd, J = 8.0 Hz, 7.2 Hz, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO- d_6): δ = 18.0, 115.0, 116.8, 122.0, 123.8, 123.9, 128.2, 128.3, 129.3, 130.7, 143.0, 145.3 ppm. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$ 199.1230, found 199.1227.



2'-Hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl diisopropylcarbamate (**14**)

Crude **14** could be further purified via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) to afford pure **14** as Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 0.97 (d, J = 6.8 Hz, 6H), 1.12 (d, J = 6.8 Hz, 6H), 2.25 (s, 3H), 3.67-3.74 (m, 1H), 3.86-3.92 (m, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.91 (dd, J = 7.6 Hz, 2.0 Hz, 1H), 7.10 (ddd, J = 7.2 Hz, 2.0 Hz, 0.8 Hz, 1H), 7.18-7.20 (m, 1H), 7.28-7.32 (m, 2H), 8.36 (ddd, J = 8.0 Hz, 6.0 Hz, 2.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.4, 20.2, 20.8, 46.5, 46.9, 119.9, 123.3, 125.1, 126.1, 126.3, 128.4, 129.5, 130.6, 131.8, 132.0, 149.8, 151.9, 154.3 ppm. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 328.1907, found 328.1906.



3-Methyl-[1,1'-biphenyl]-2,2'-diol (**15**)

M.p.: 93-94 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.33 (s, 3H), 5.21 (m, 2H), 6.96 (t, J = 7.6 Hz, 1H), 7.03-7.10 (m, 3H), 7.21 (dq, J = 7.6 Hz, 0.8 Hz, 1H), 7.25-7.27 (m, 1H), 7.33 (ddd, J = 8.4 Hz, 7.2 Hz, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.4, 116.6, 121.2, 121.6, 122.6, 123.3, 125.7, 128.7, 130.2, 131.3, 131.5, 151.4, 153.2 ppm. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{O}_2$ $[\text{M}-\text{H}]^-$ 199.0765, found 199.0767.

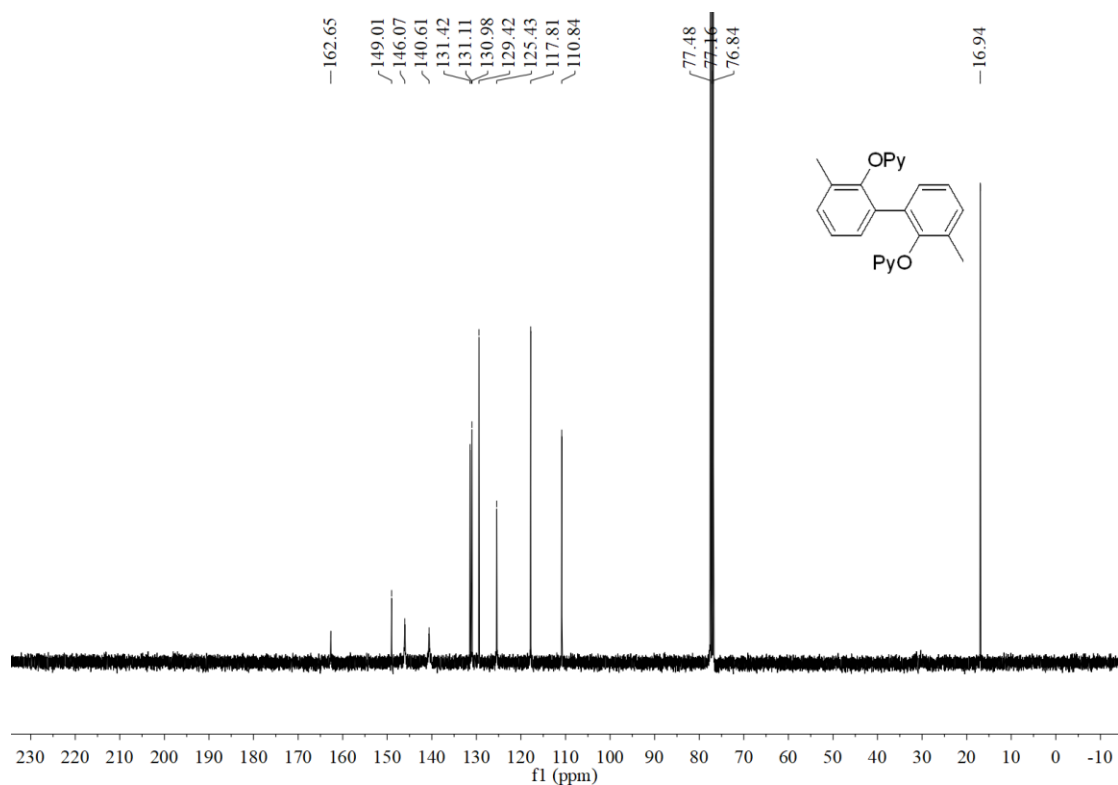
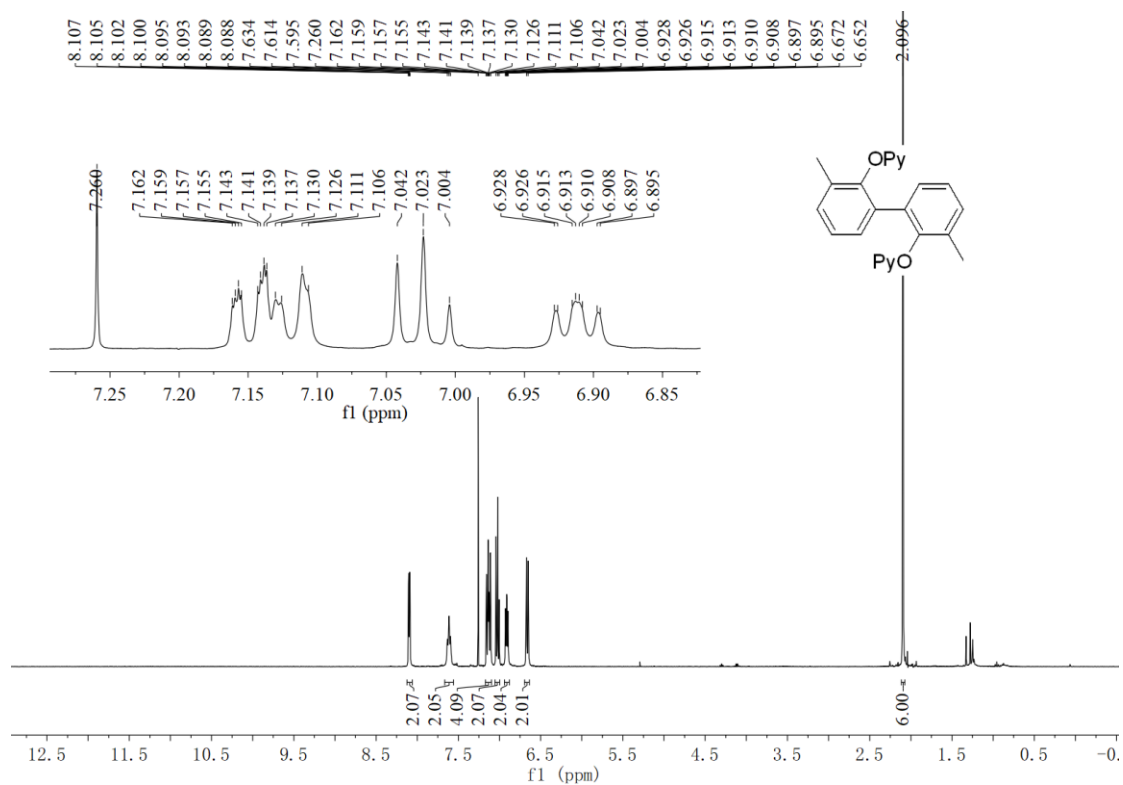
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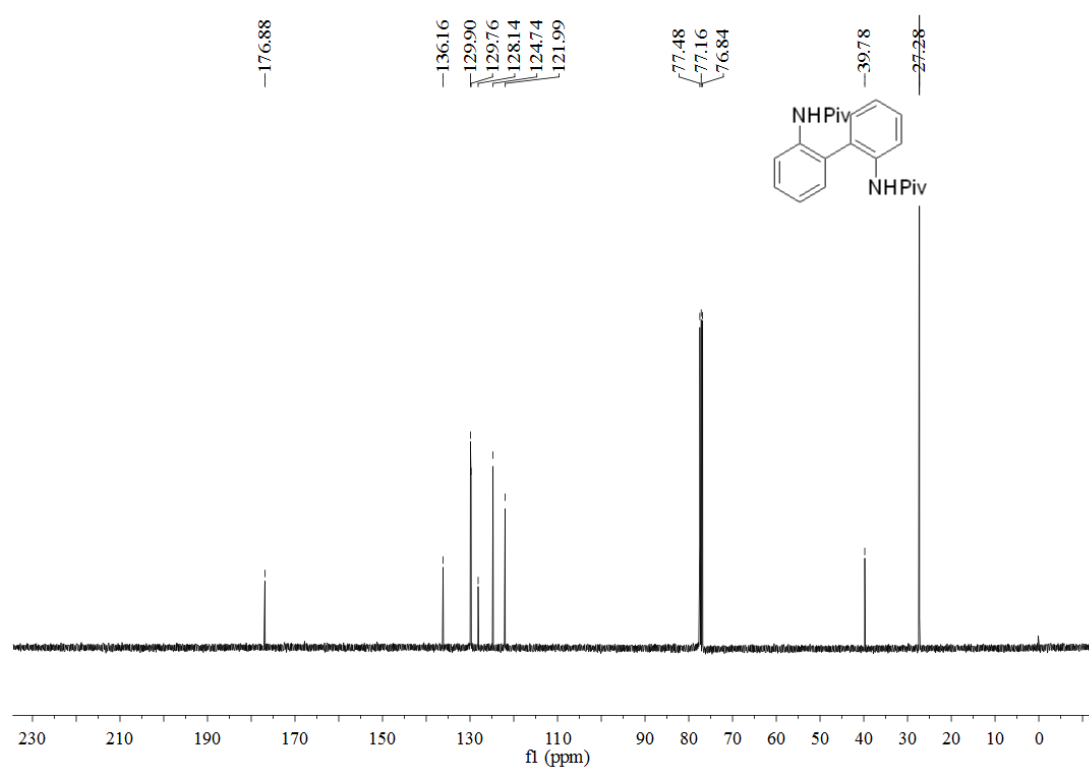
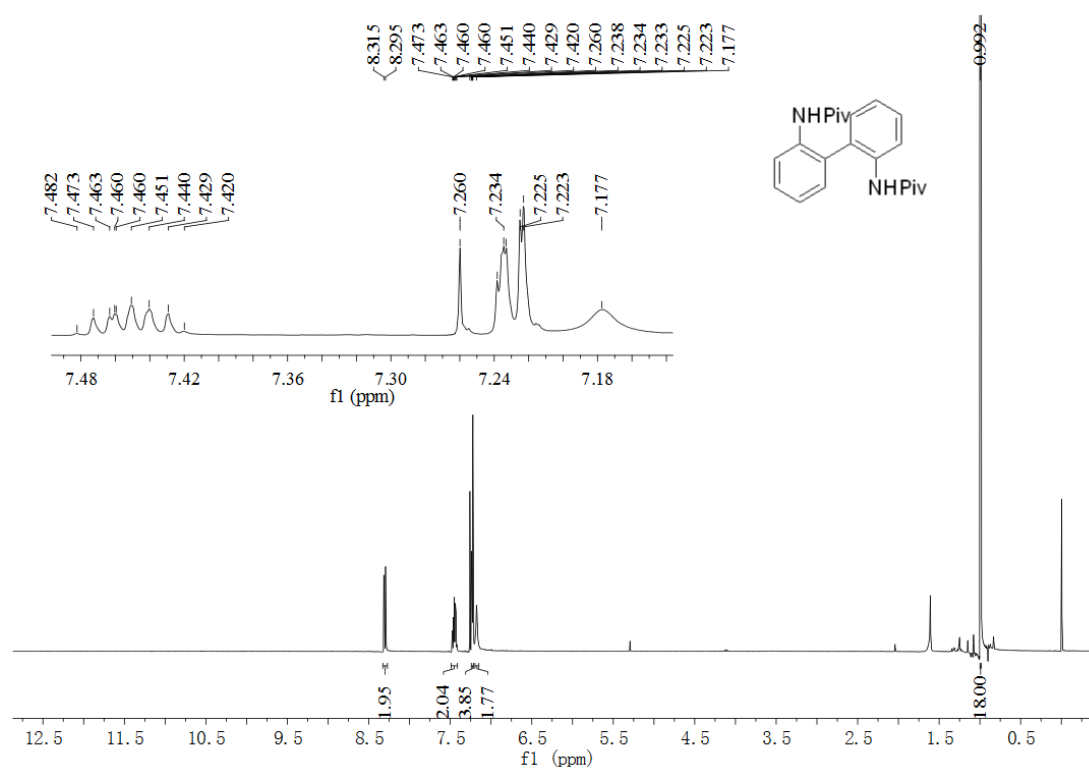
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XI. Copies of ^1H and ^{13}C NMR spectra

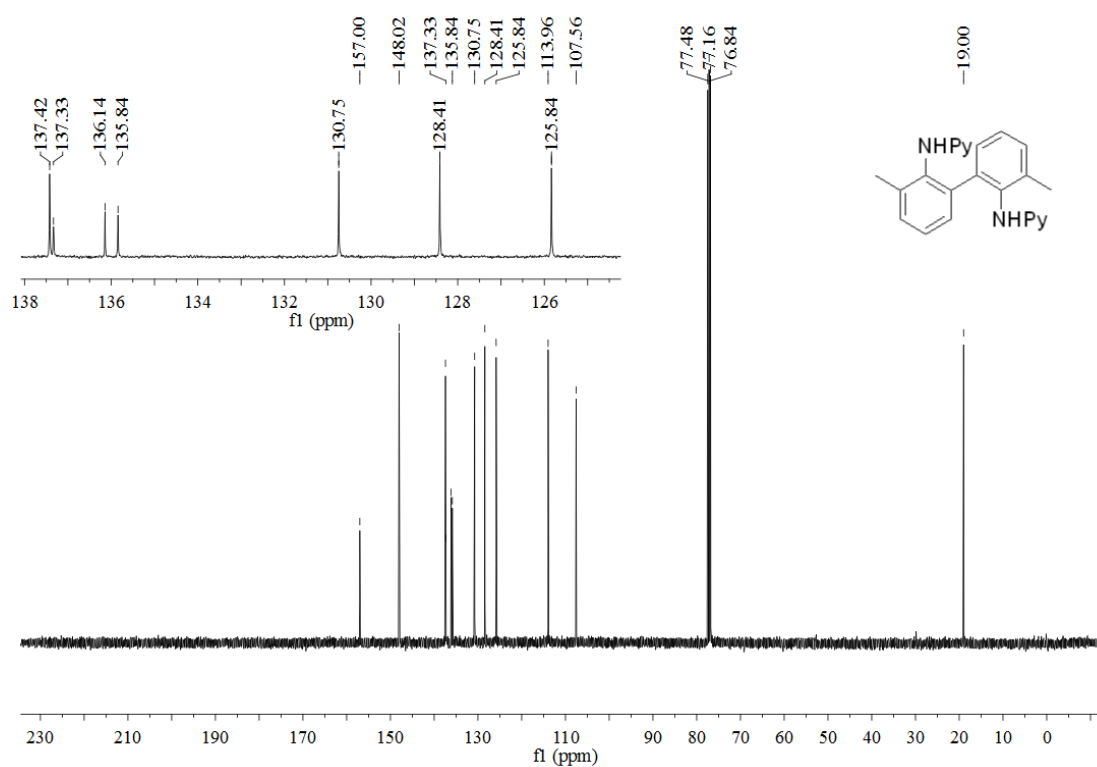
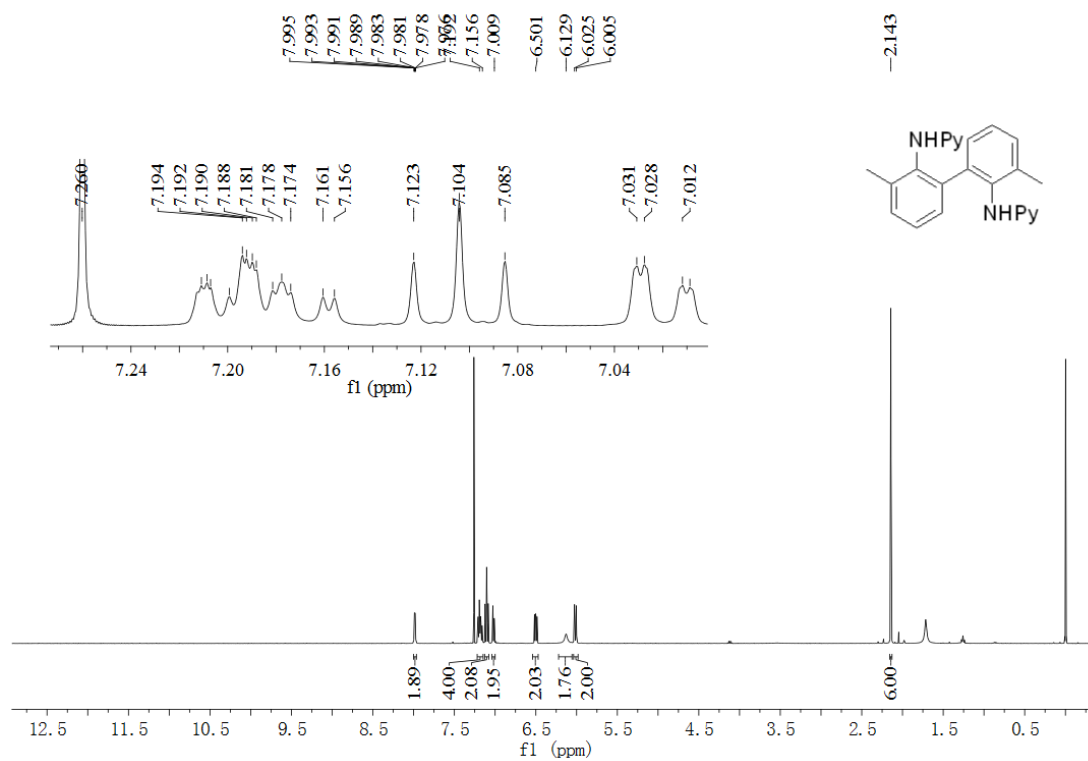
2,2'-((3,3'-Dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))dipyridine (1aa)



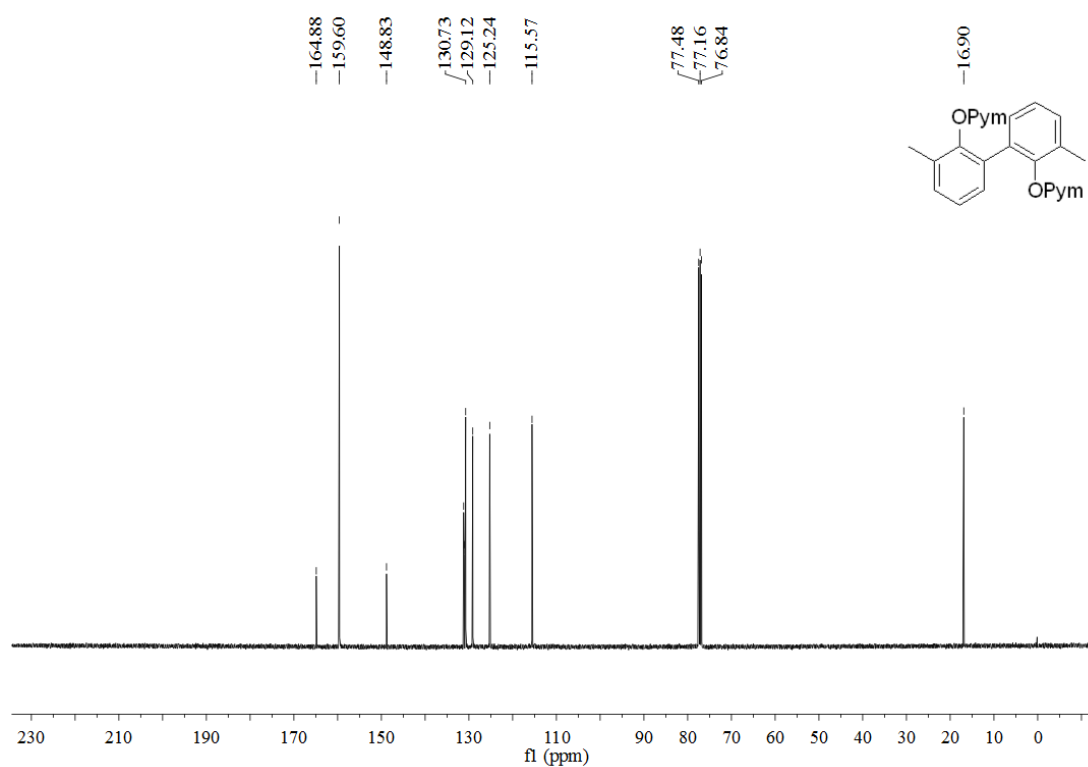
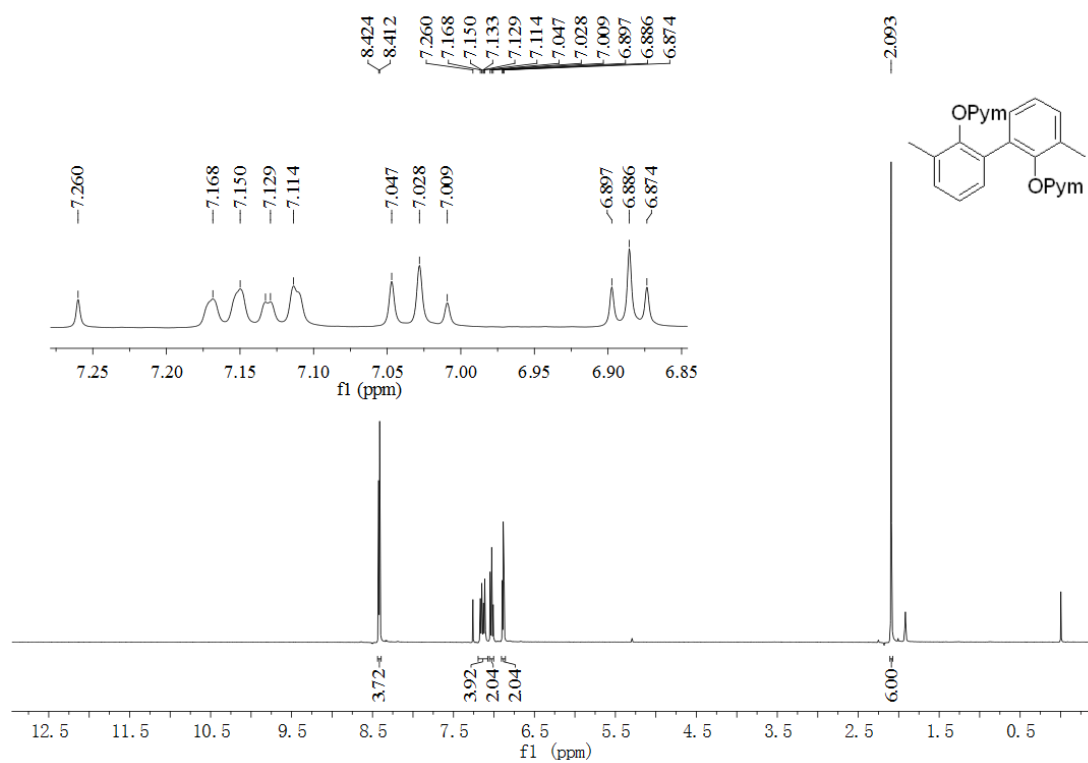
***N,N'*-([1,1'-Biphenyl]-2,2'-diyl)bis(2,2-dimethylpropanamide) (2aa)**



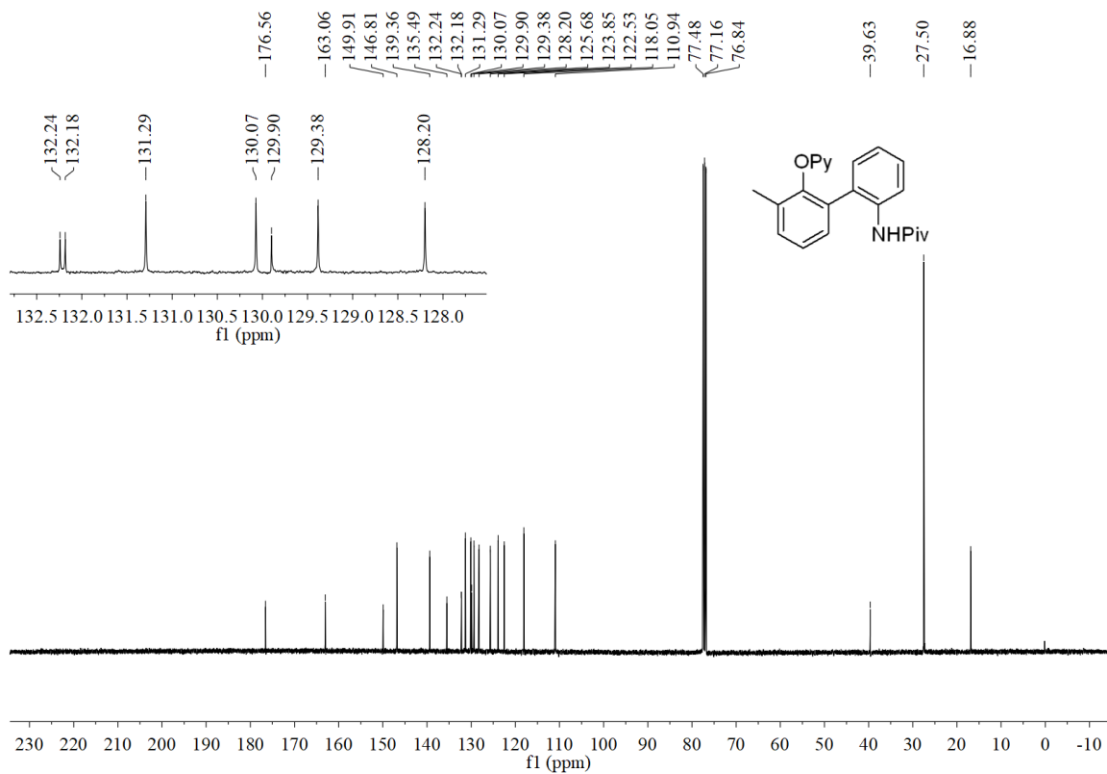
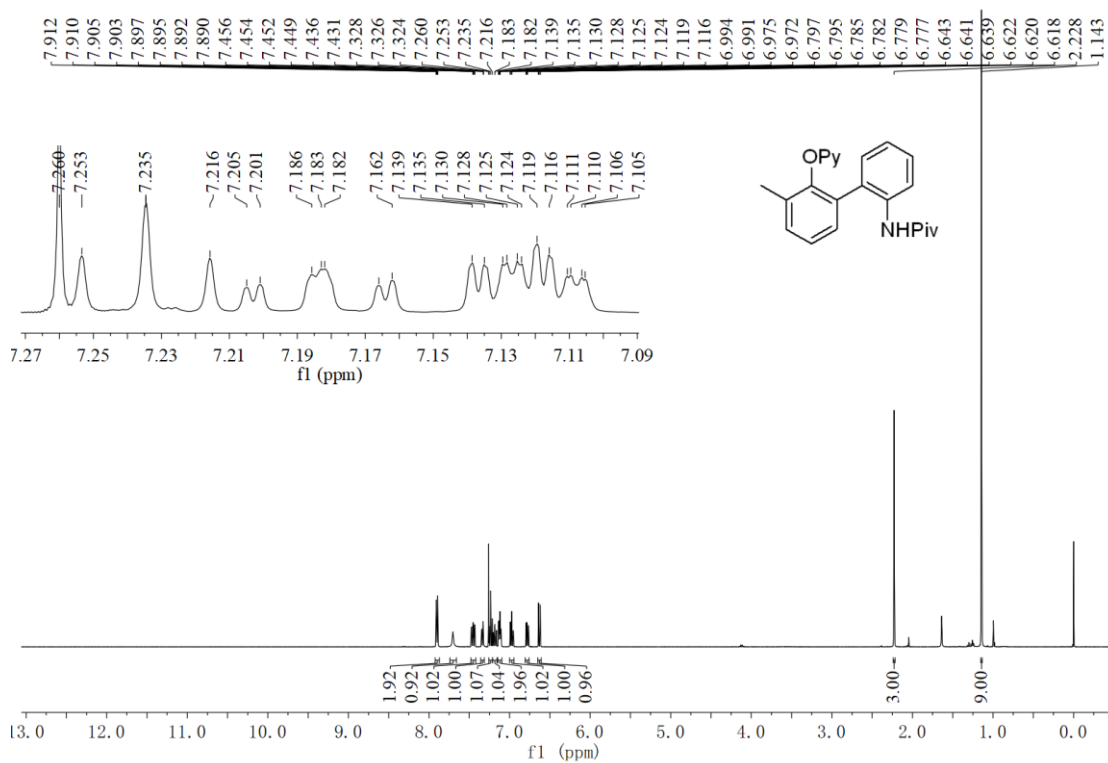
3,3'-Dimethyl-*N*,*N*'-di(pyridin-2-yl)-[1,1'-biphenyl]-2,2'-diamine (7aa)



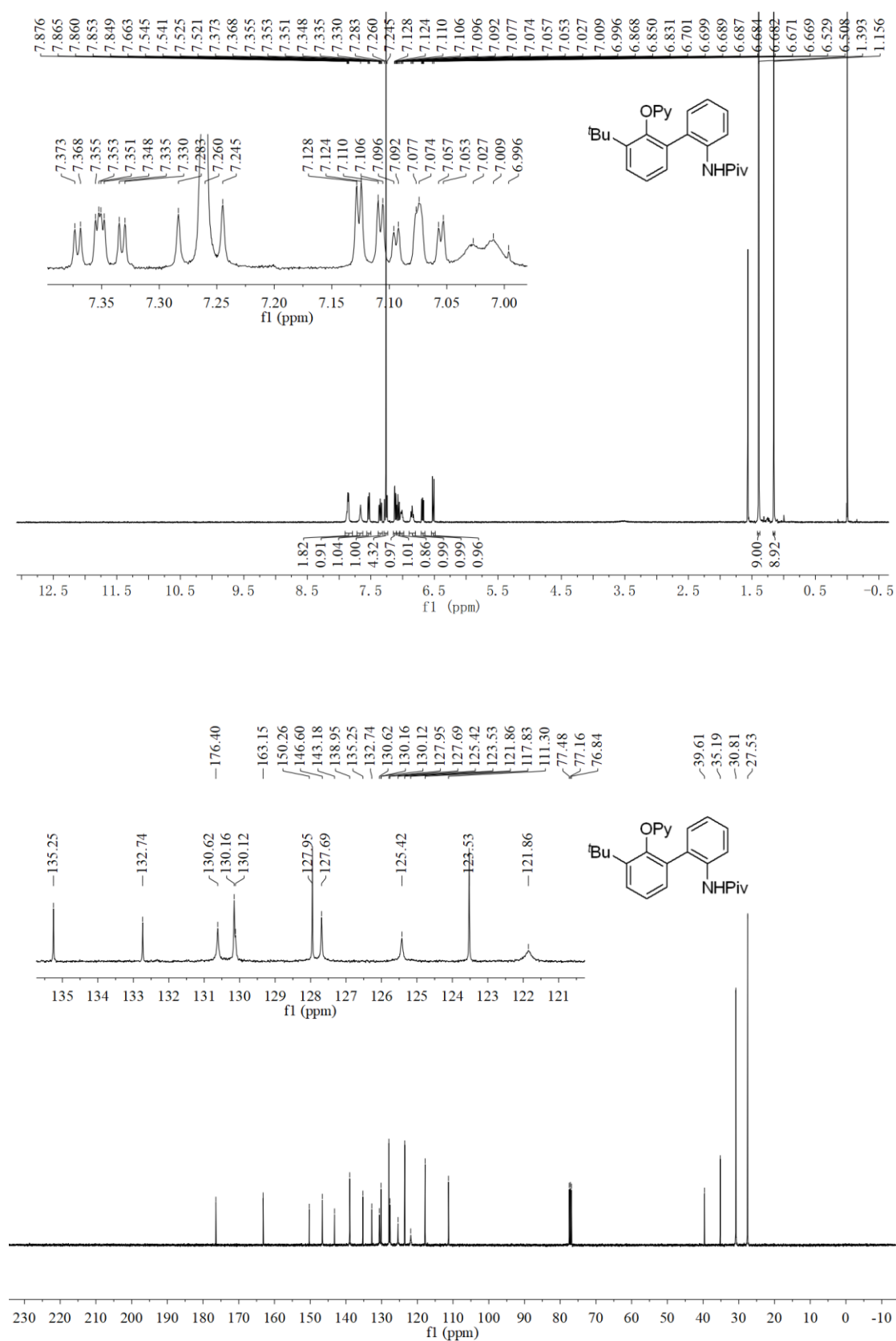
2,2'-((3,3'-Dimethyl-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))dipyrimidine (8aa)



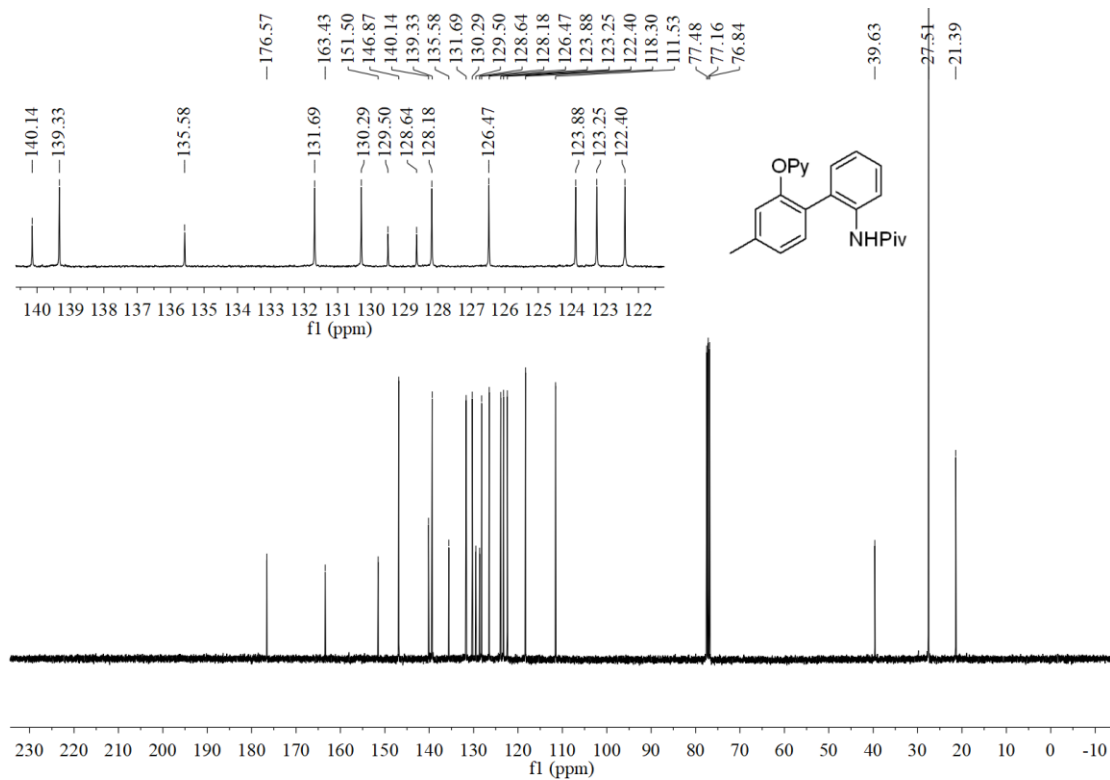
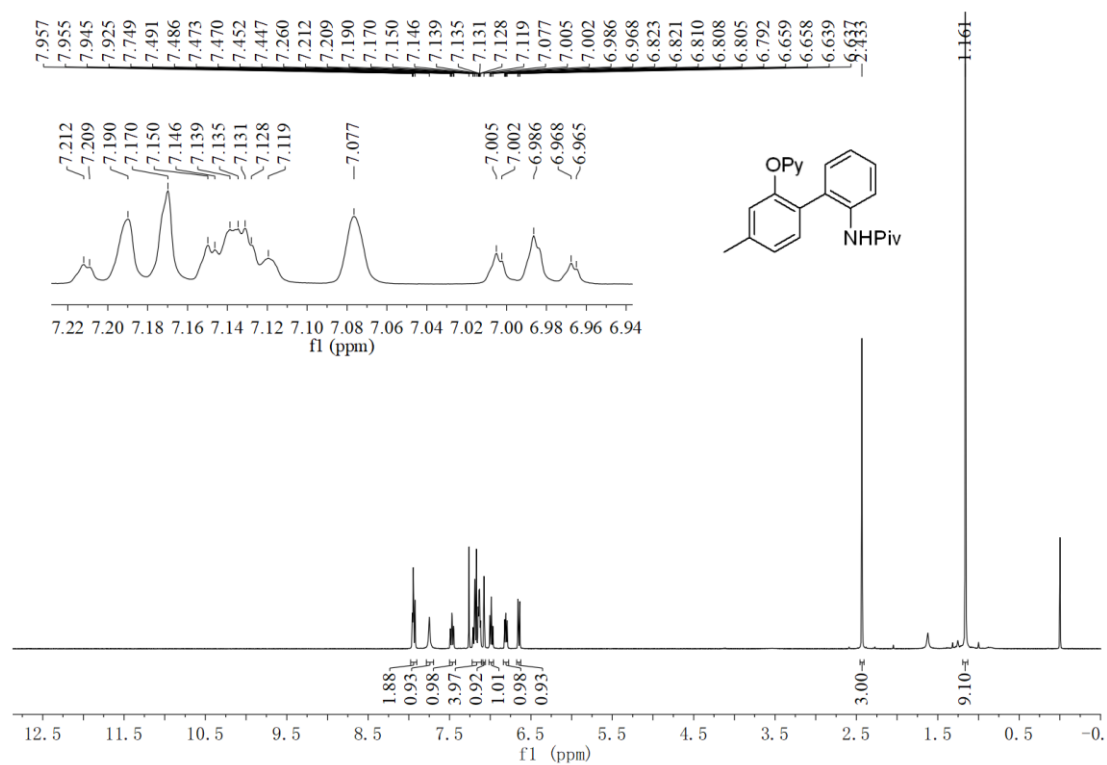
***N*-(3'-Methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3a)**



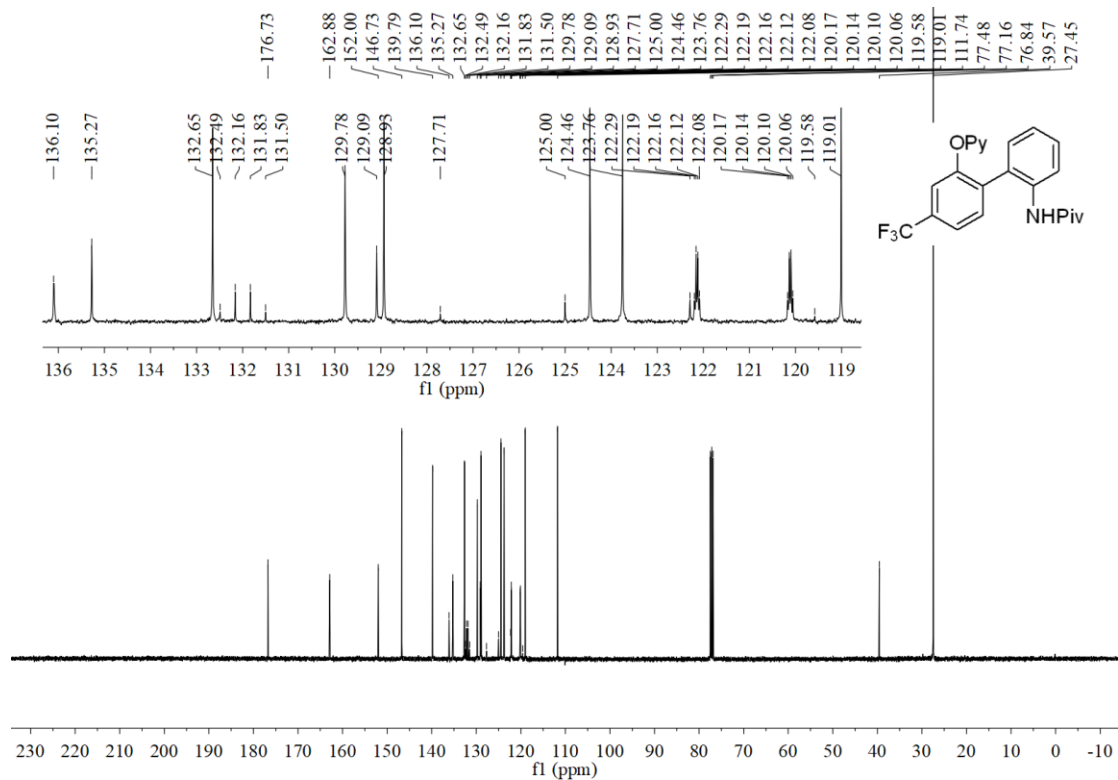
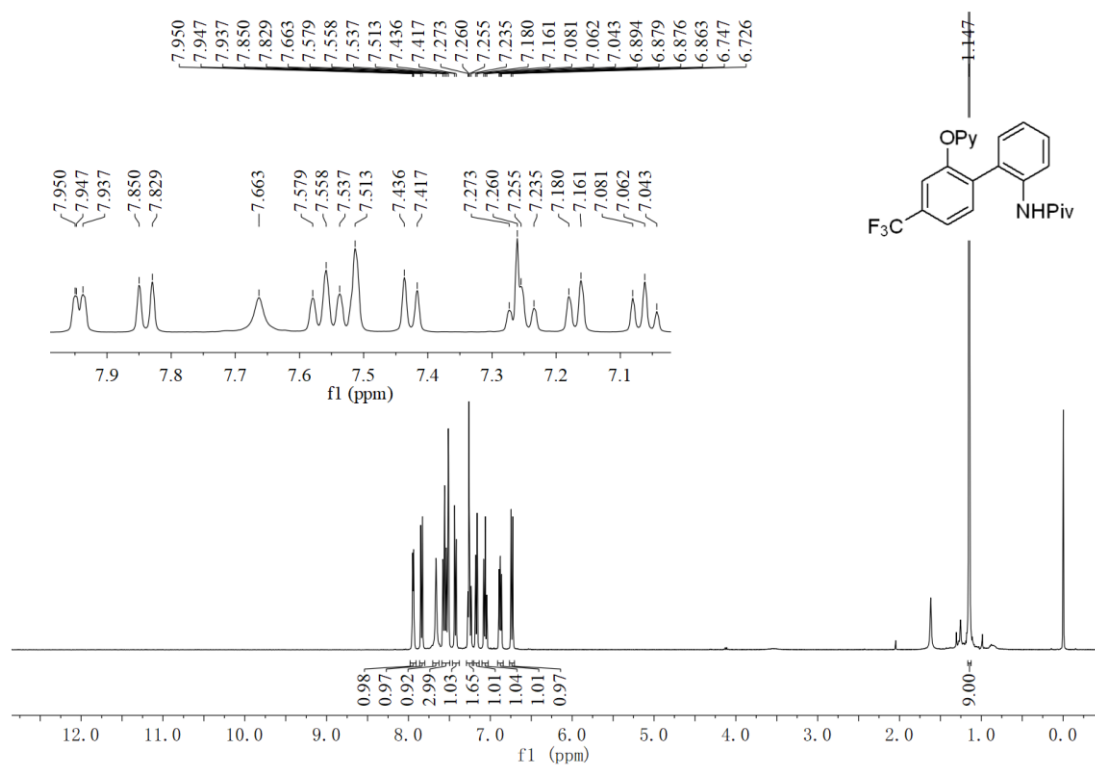
***N*-(3'-(*tert*-Butyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3b)**



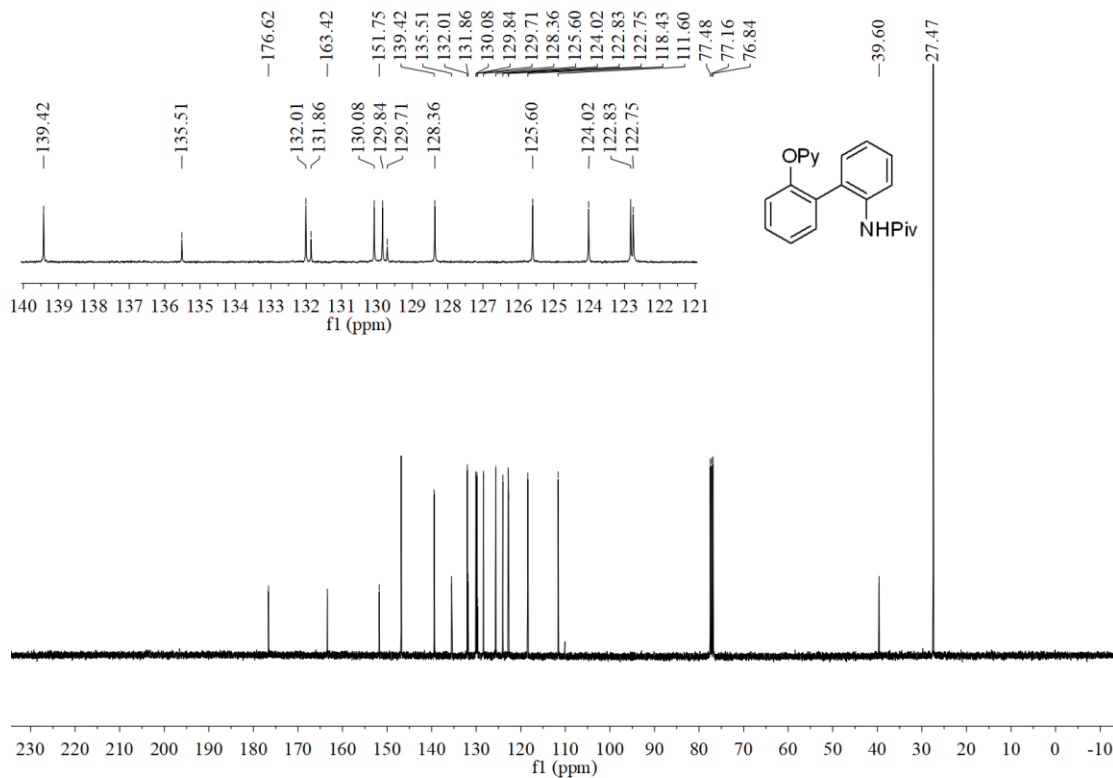
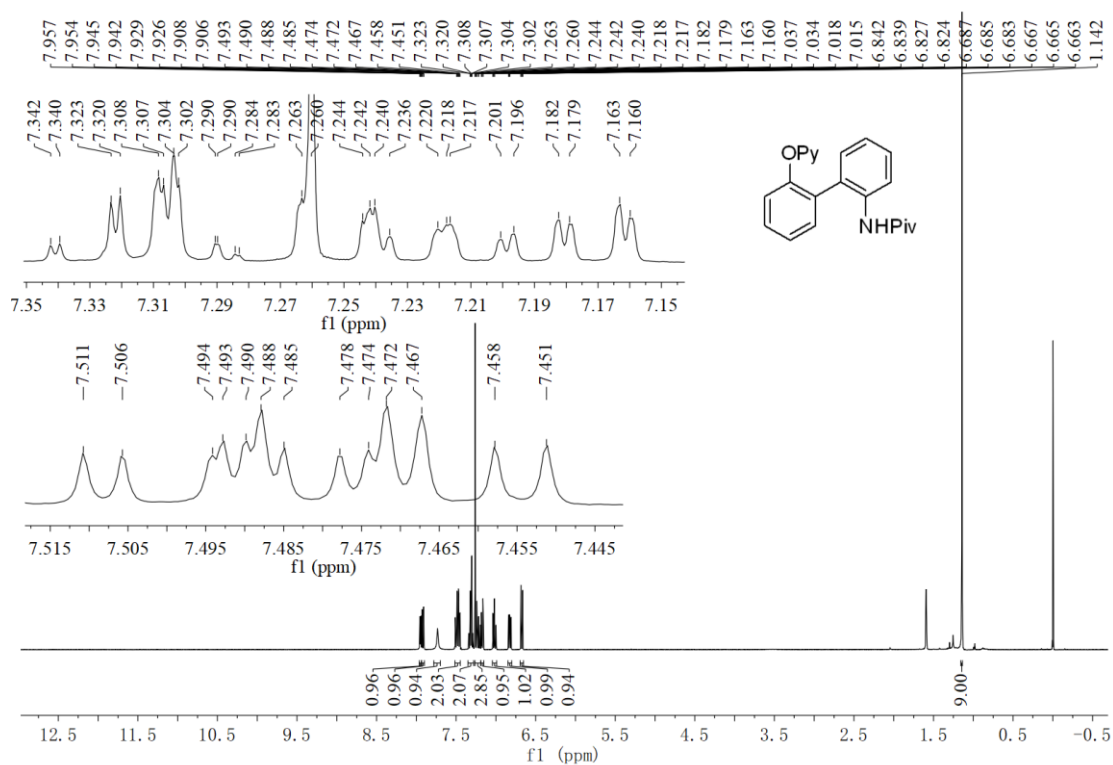
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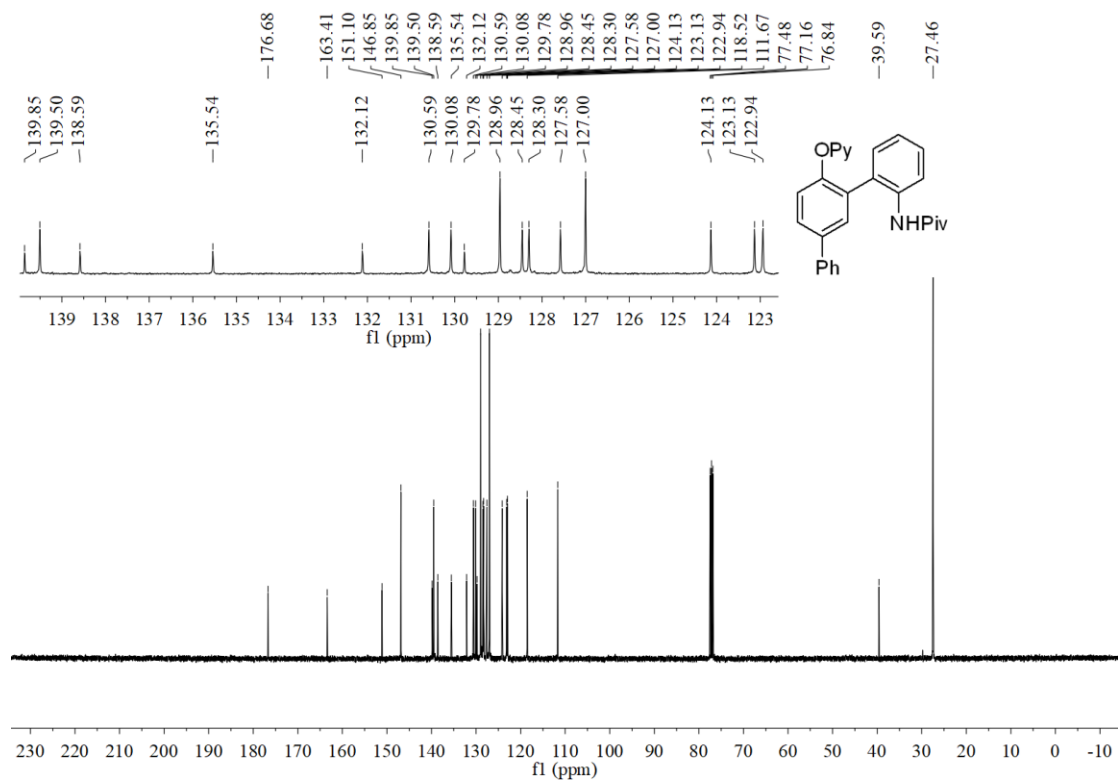
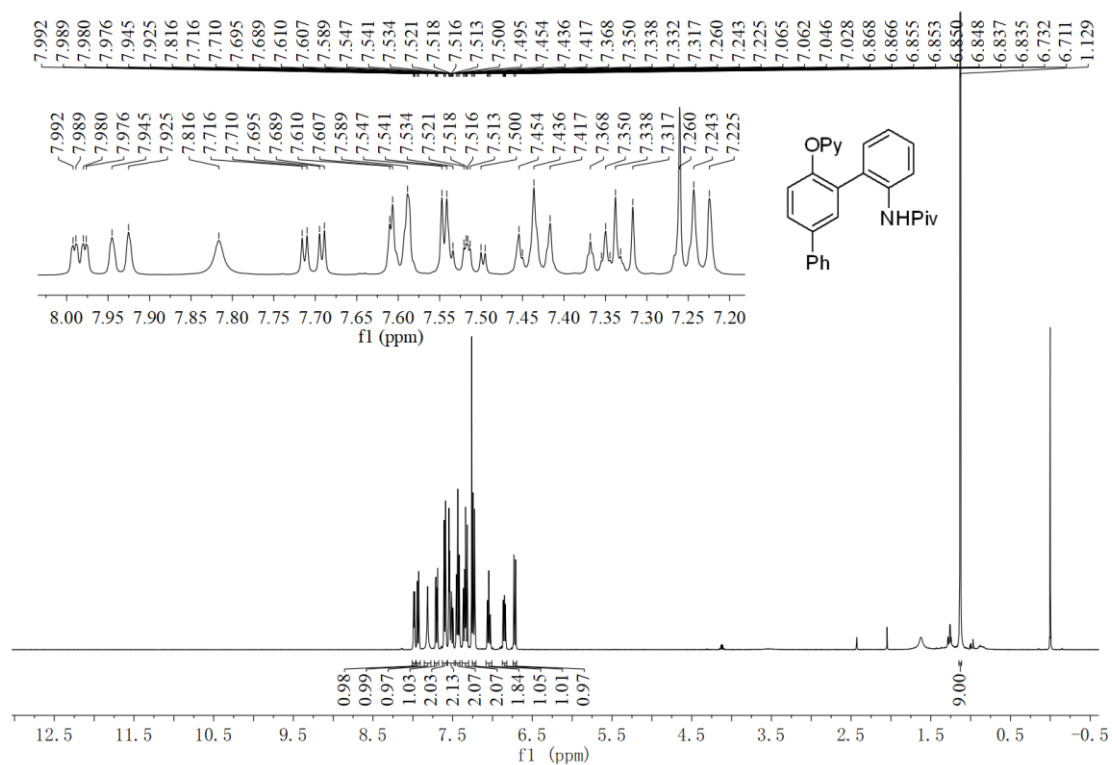
***N*-(2'-(Pyridin-2-yloxy)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide (3d)**



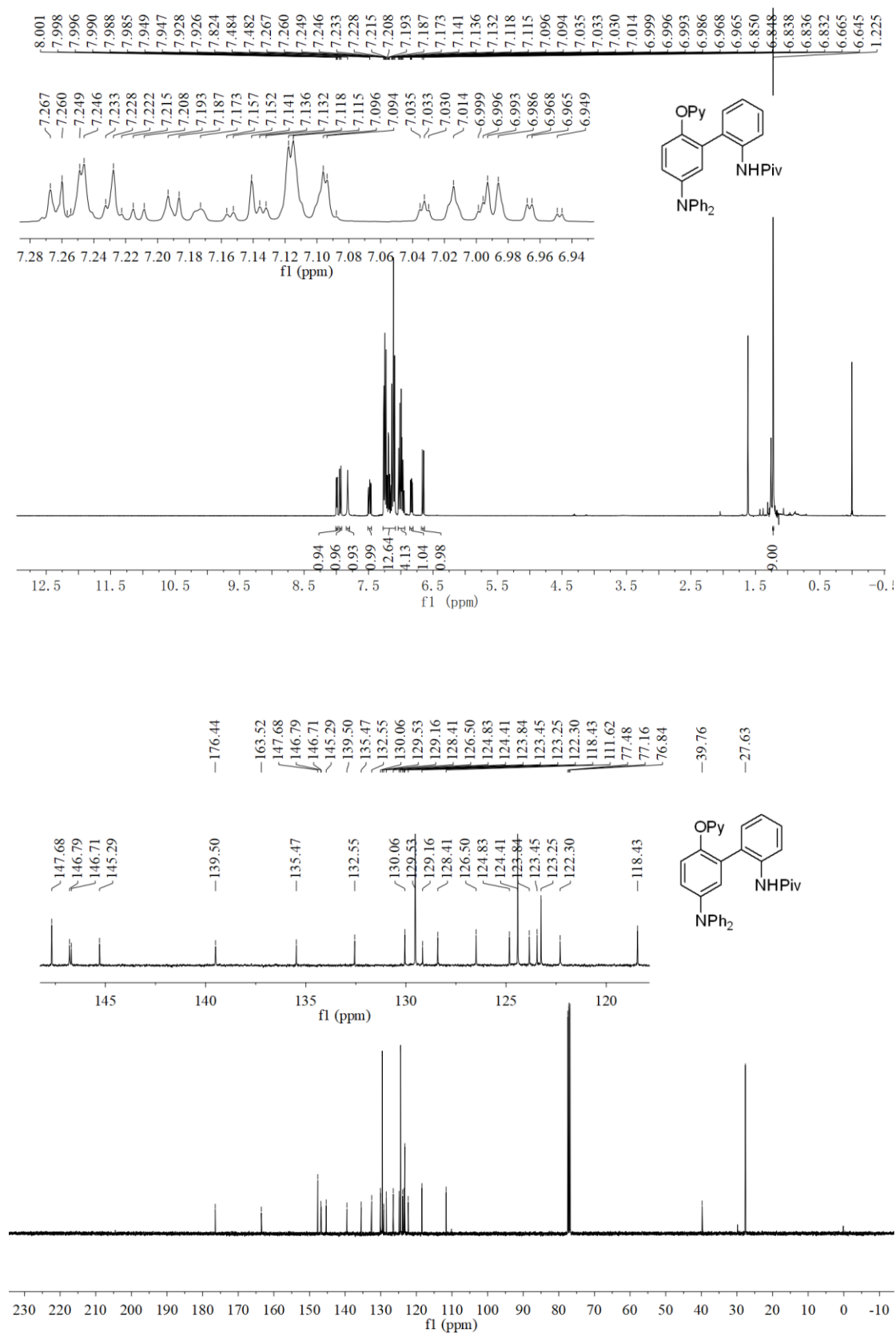
***N*-(2'-(Pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3e)**



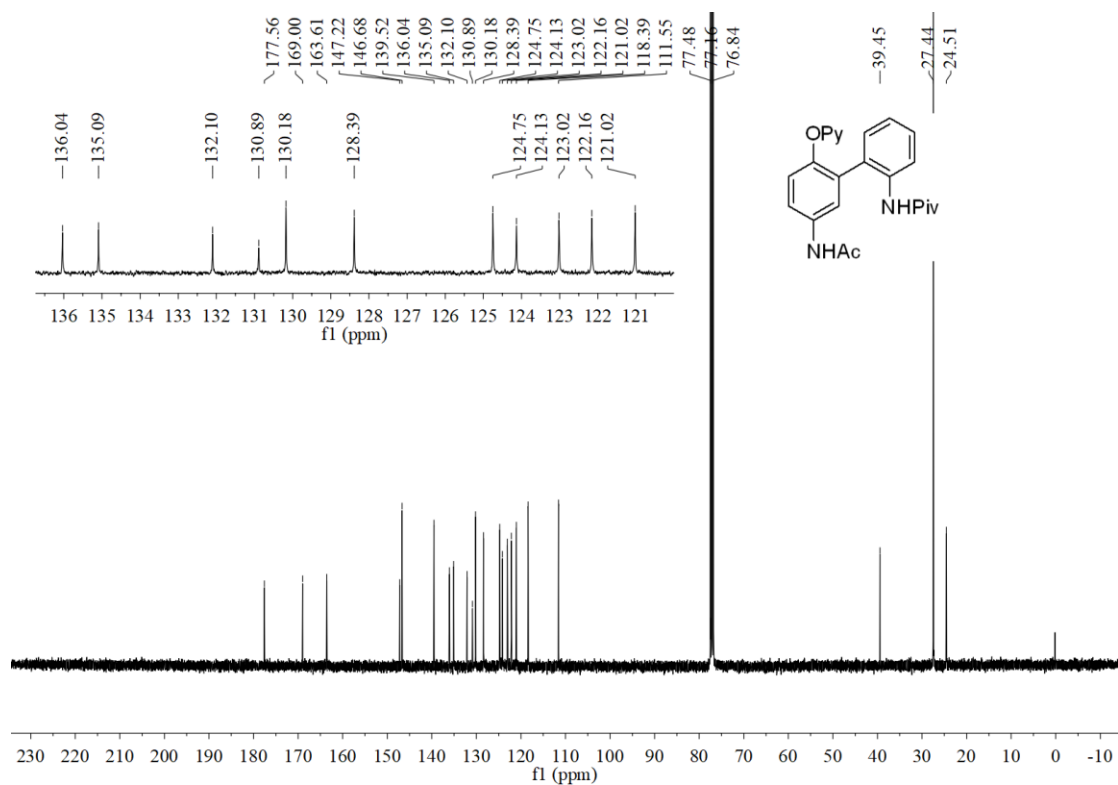
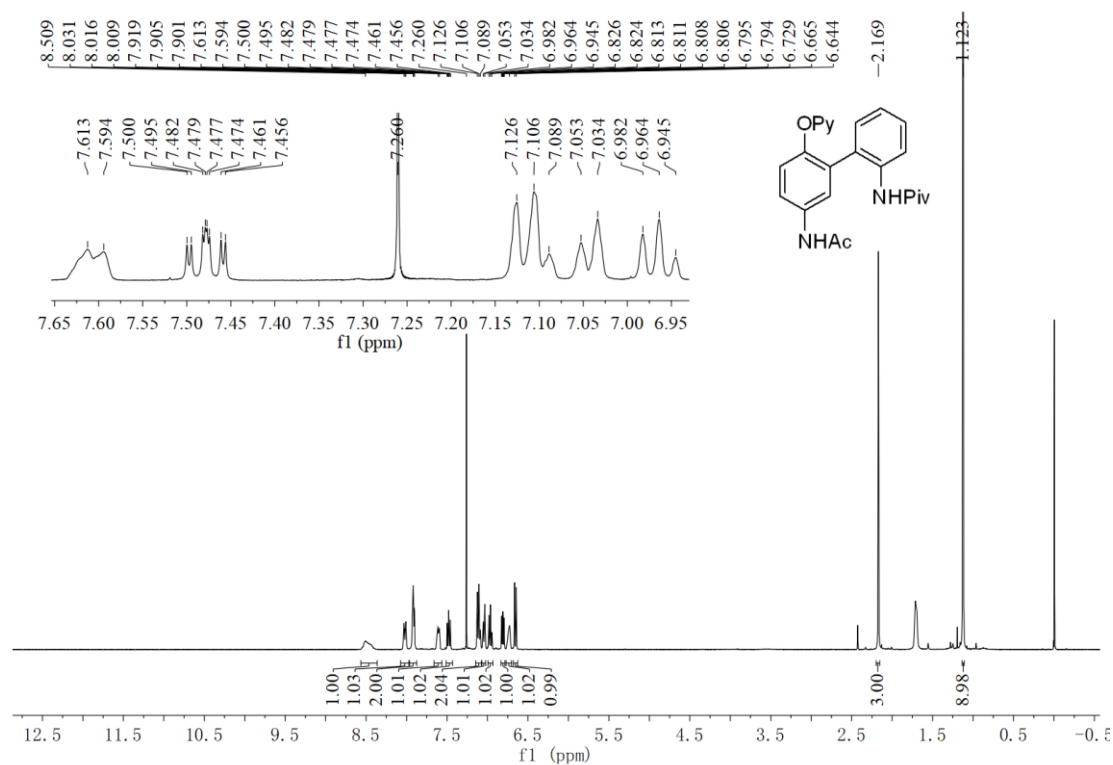
***N*-(6'-(Pyridin-2-yloxy)-[1,1':3',1''-terphenyl]-2-yl)pivalamide (3f)**



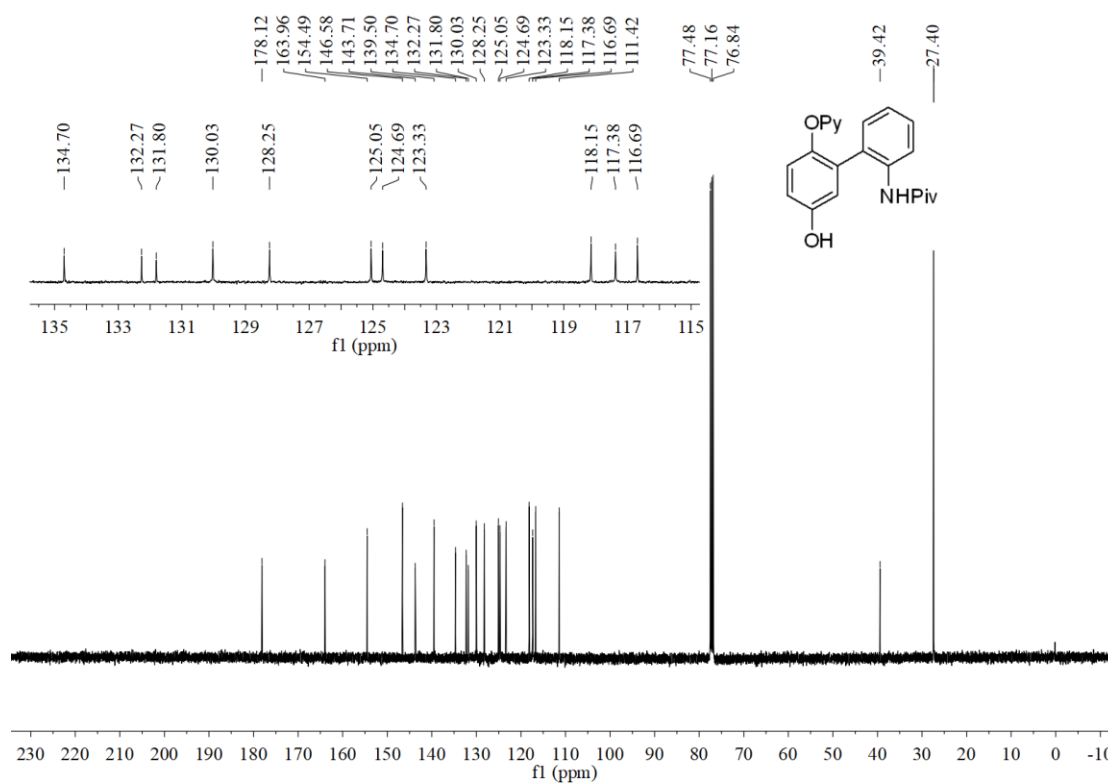
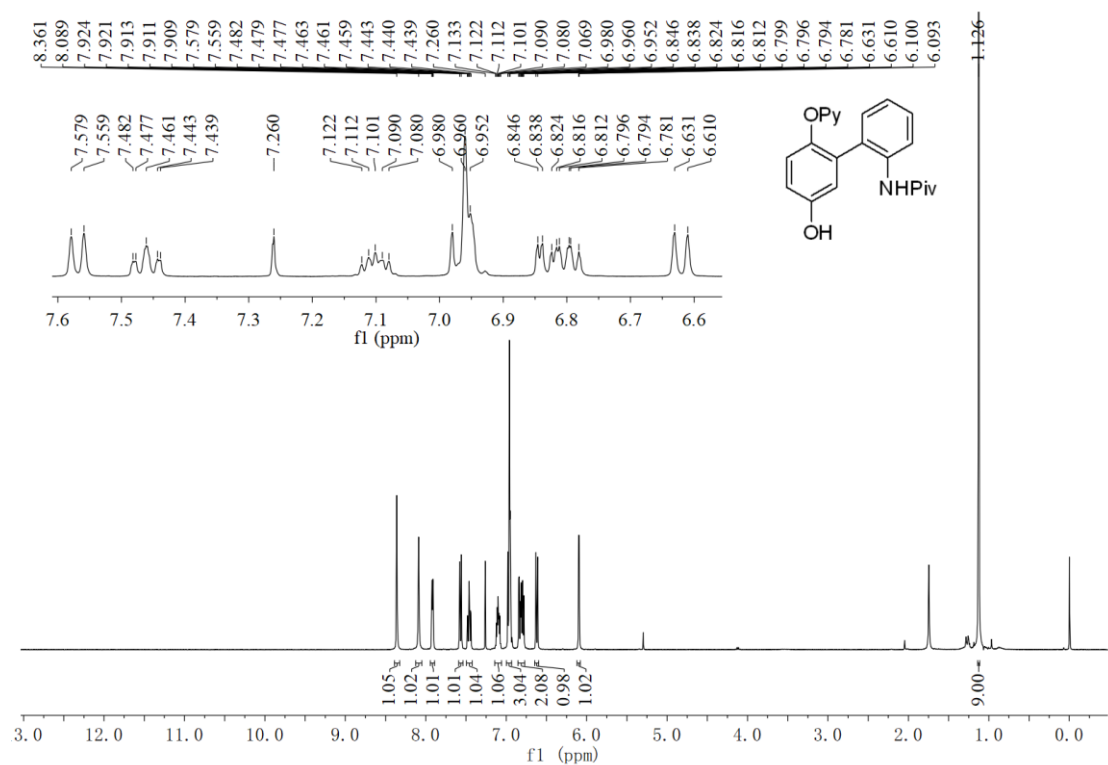
***N*-(5'-(Diphenylamino)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3g)**



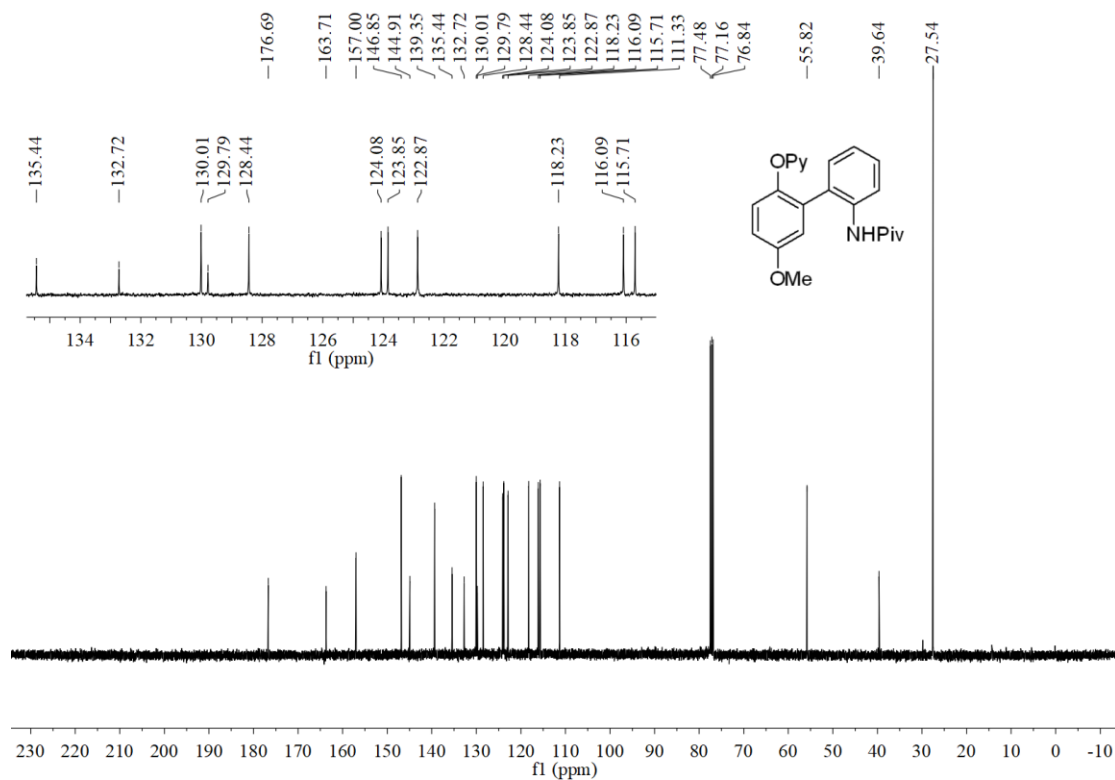
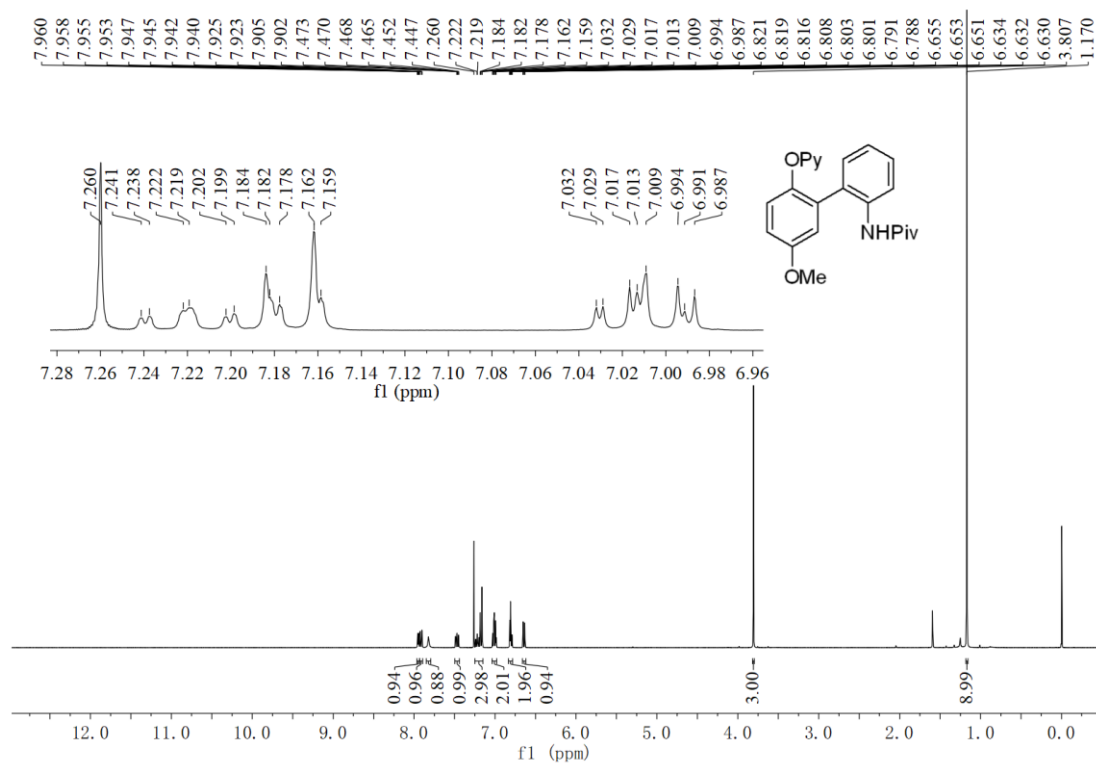
***N*-(5'-Acetamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3h)**



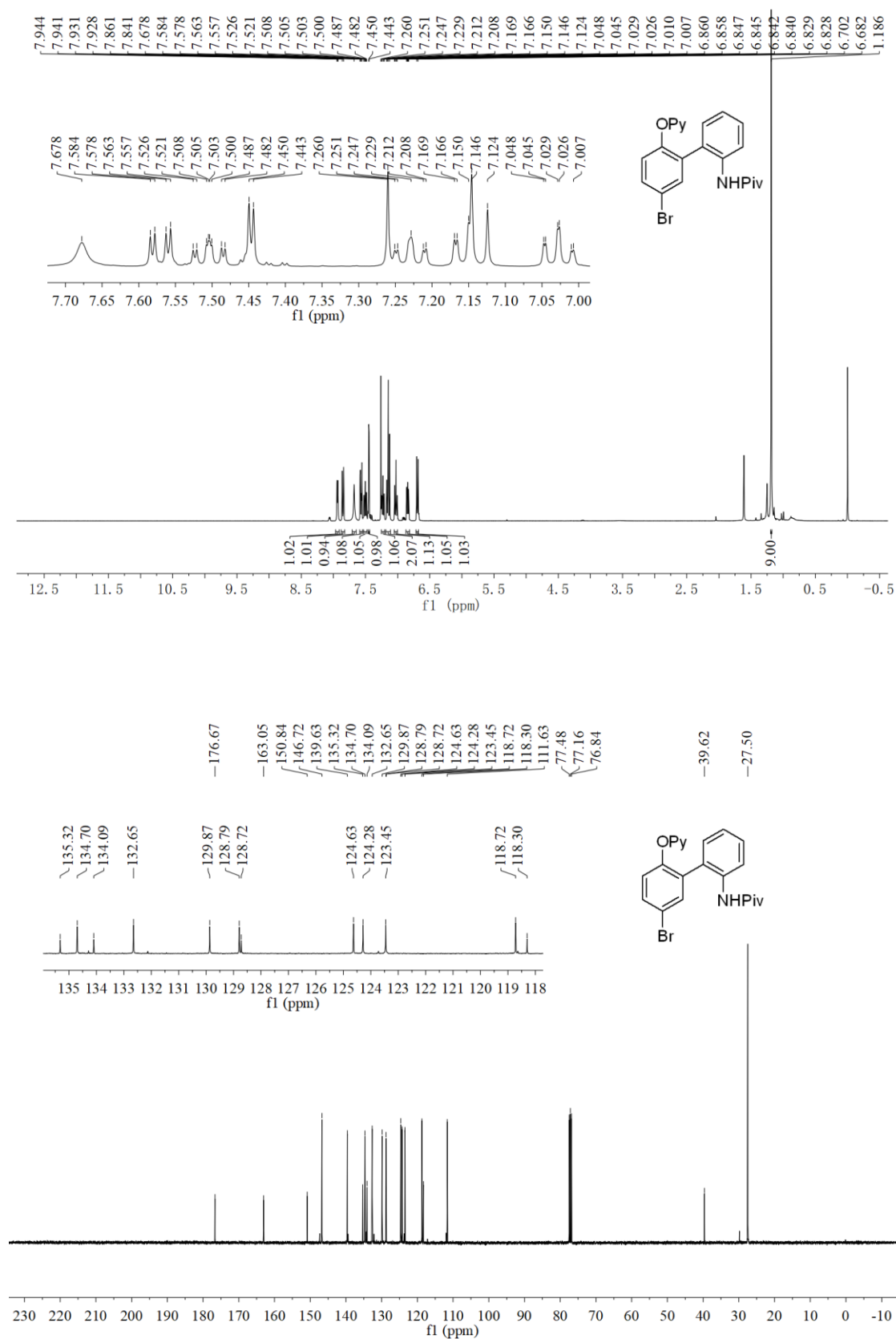
***N*-(5'-Hydroxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3i)**



***N*-(5'-Methoxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3j)**

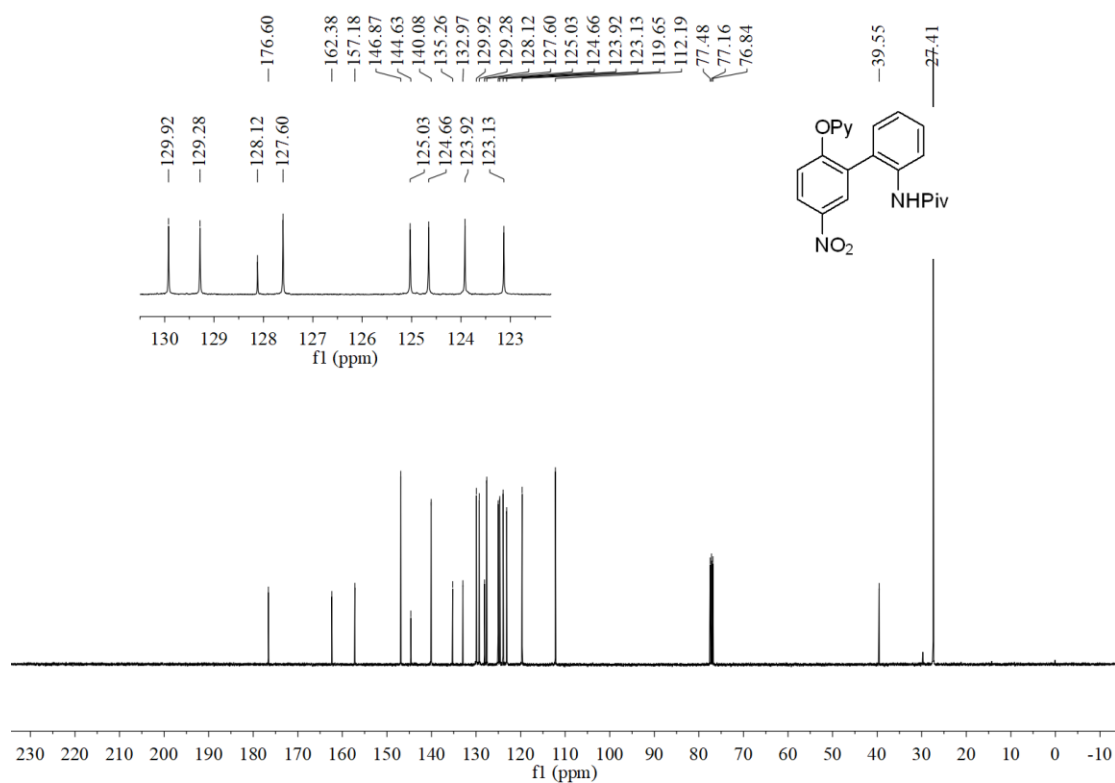


***N*-(5'-Bromo-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3k)**

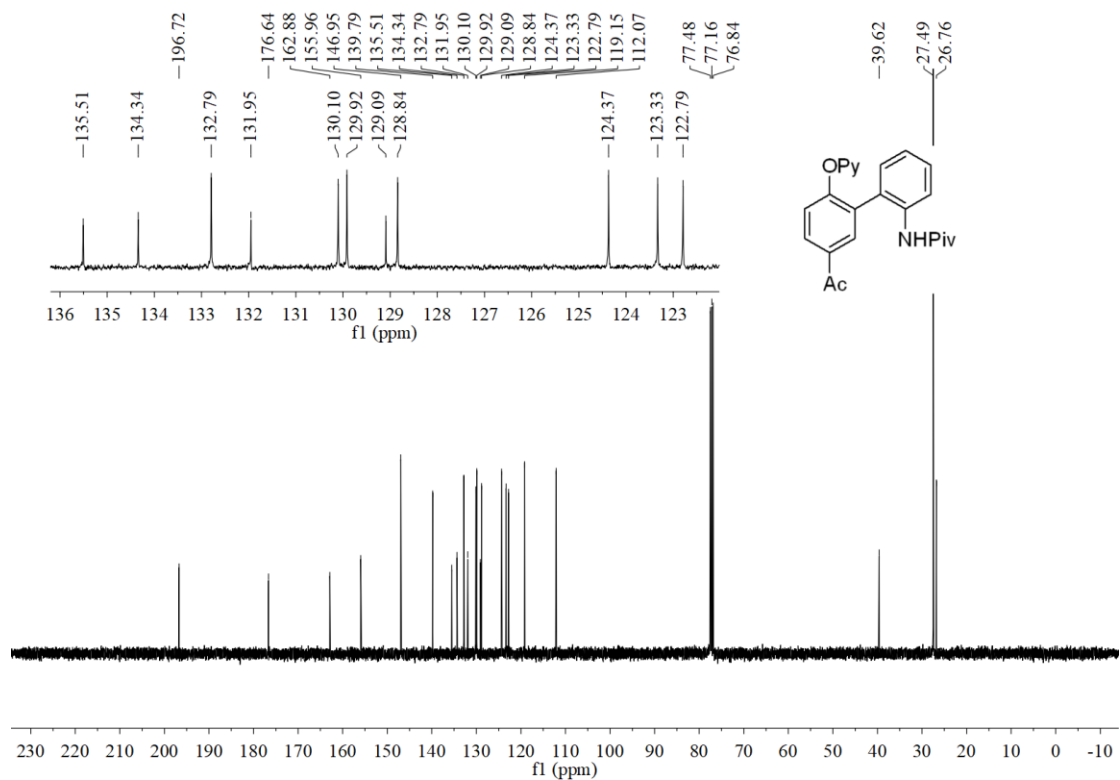
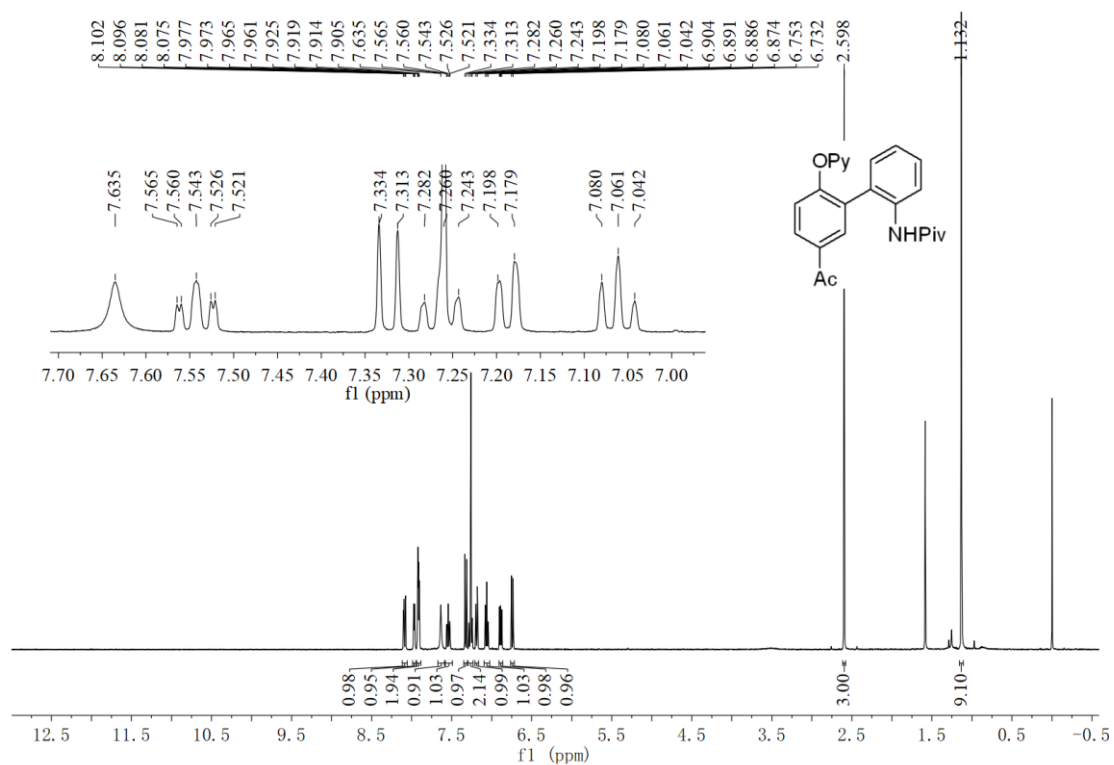


Chemical structure of compound 10: Oc1ccc(cc1-c2ccc(cc2)N)C3=CC=C(C=C3)[N+](=O)[O-]

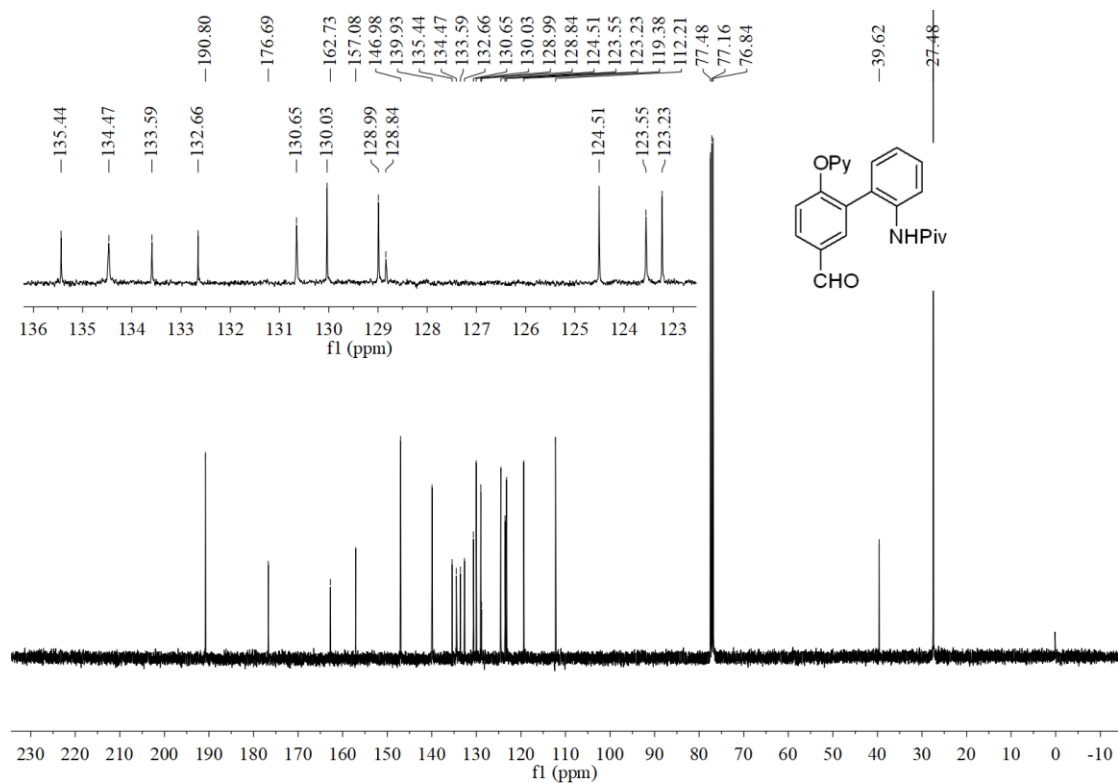
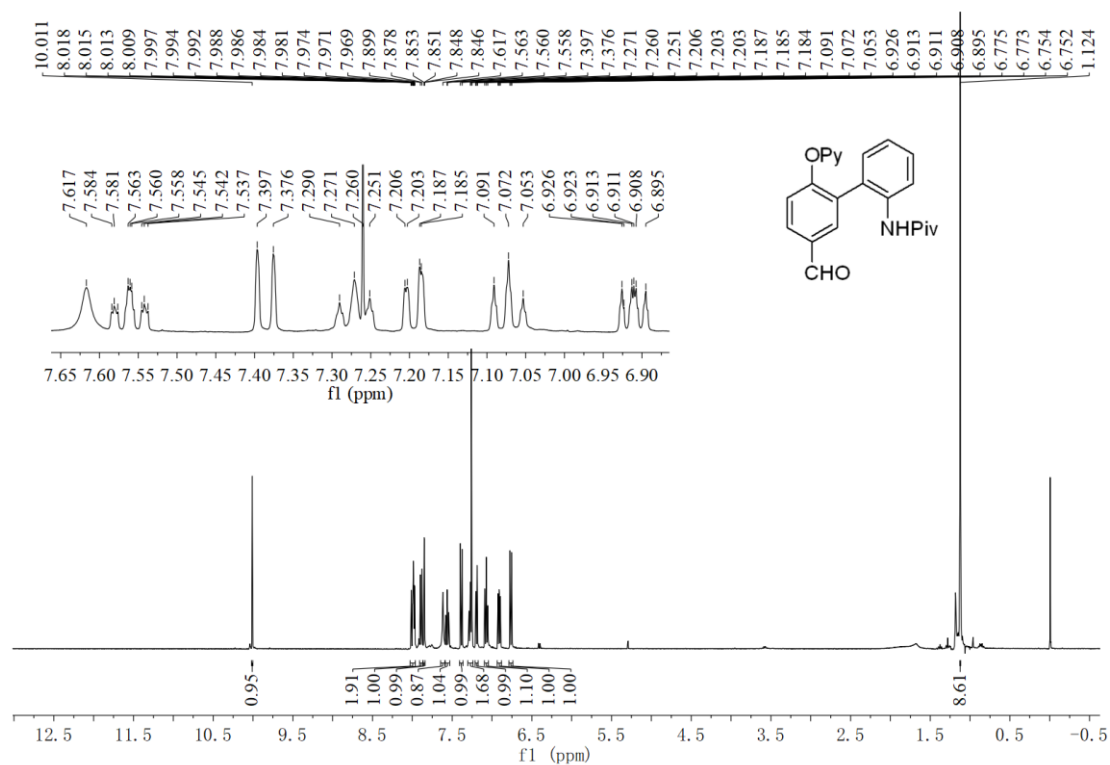
¹H NMR spectrum (CDCl₃) of compound 10. The spectrum displays aromatic signals in the range of 6.90–7.65 ppm and aliphatic signals in the range of 1.14–6.93 ppm. Integration values are provided below the baseline.



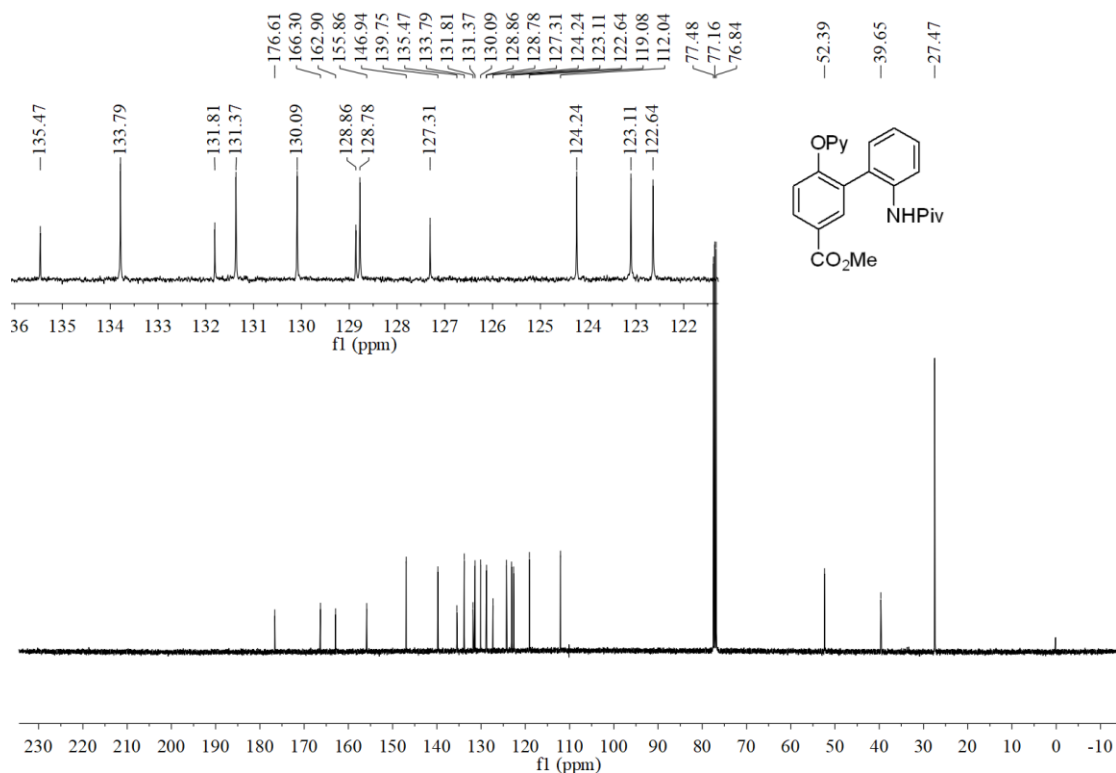
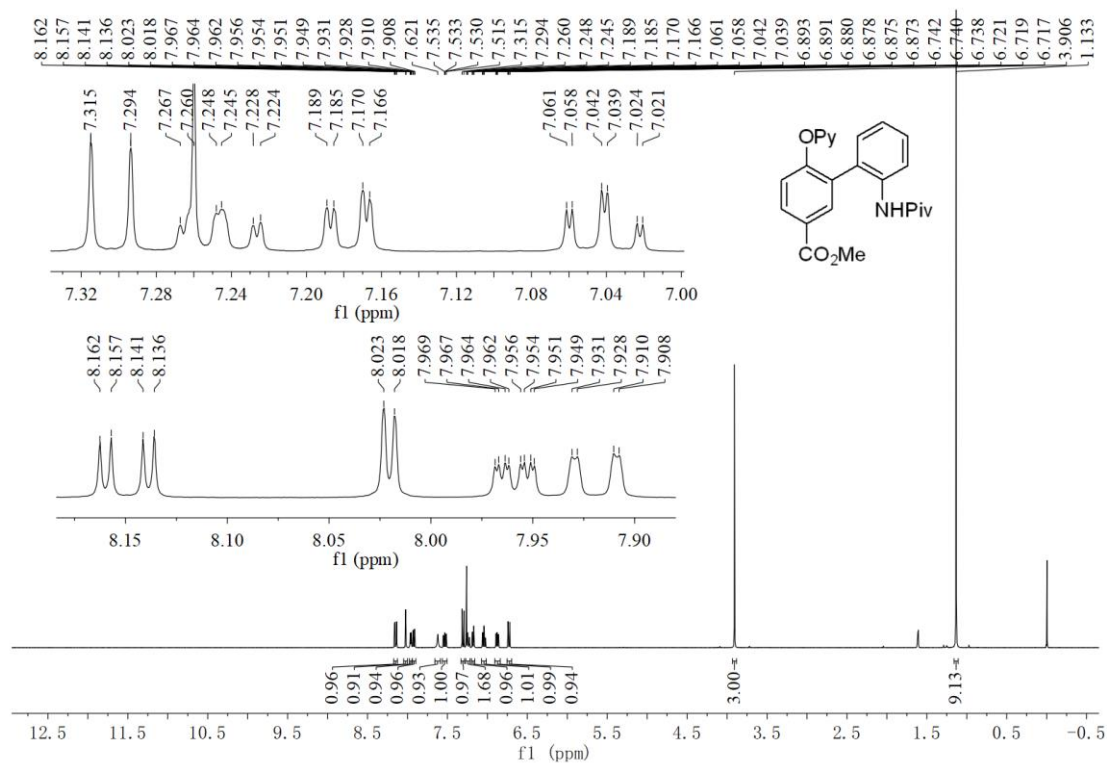
***N*-(5'-Acetyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3m)**



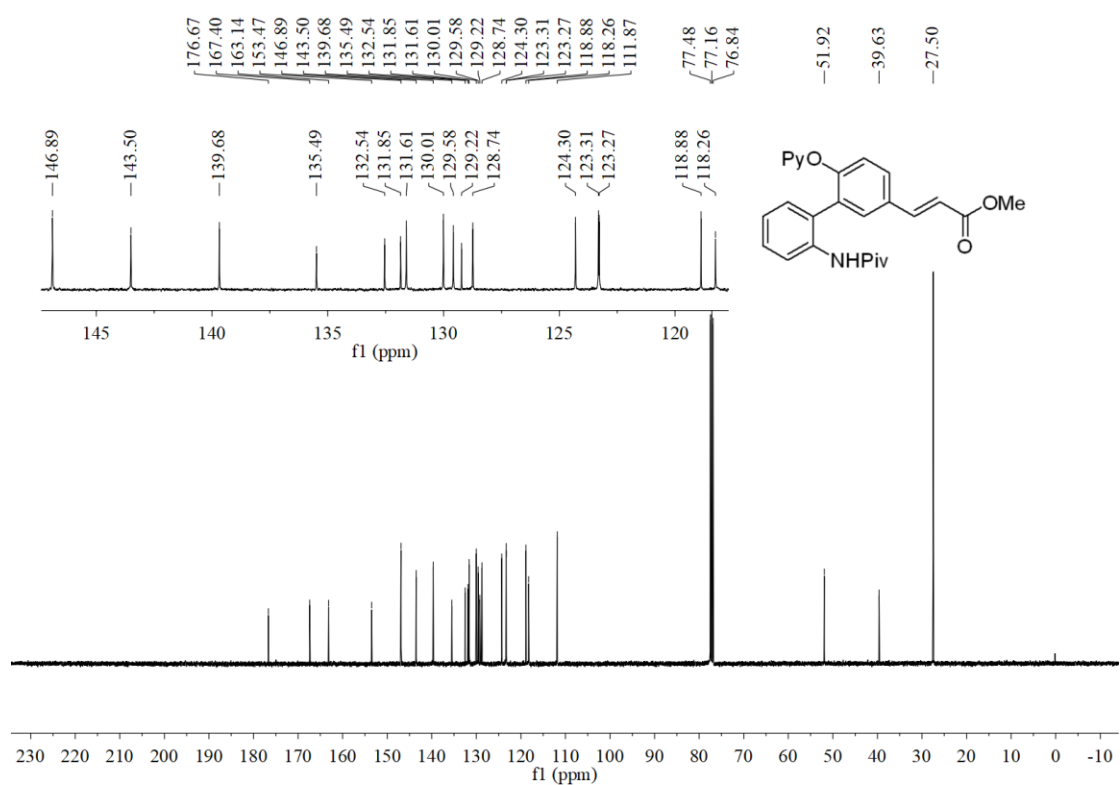
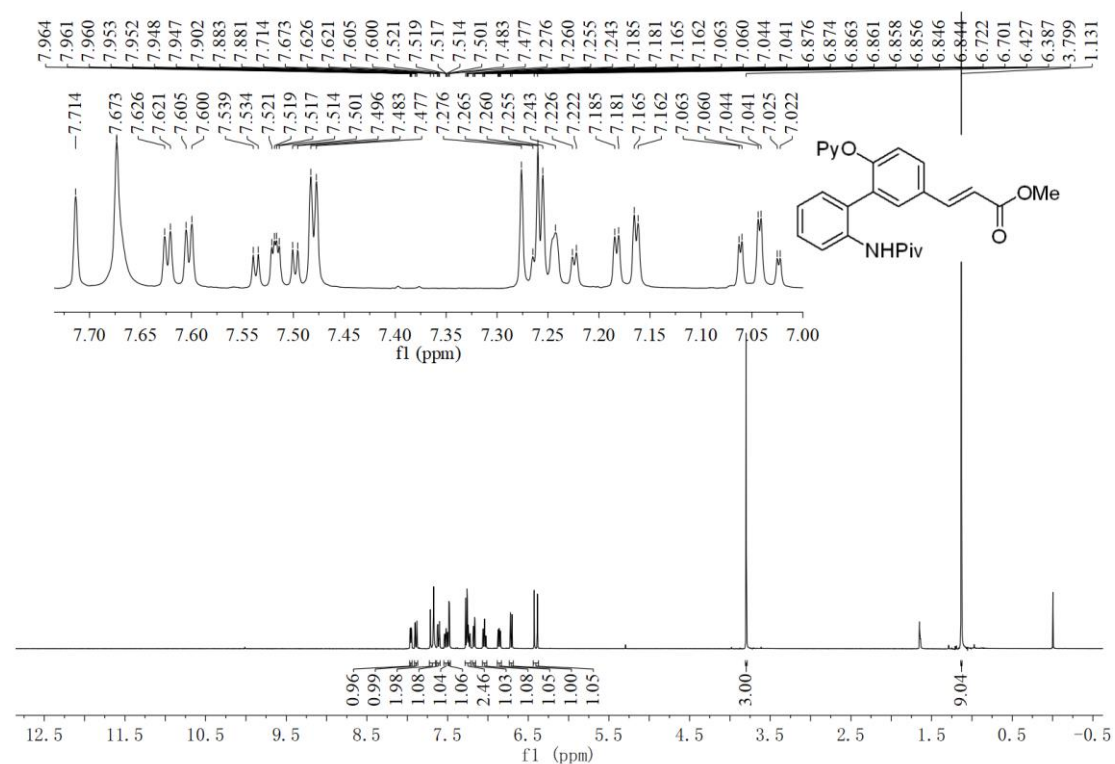
***N*-(5'-Formyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3n)**



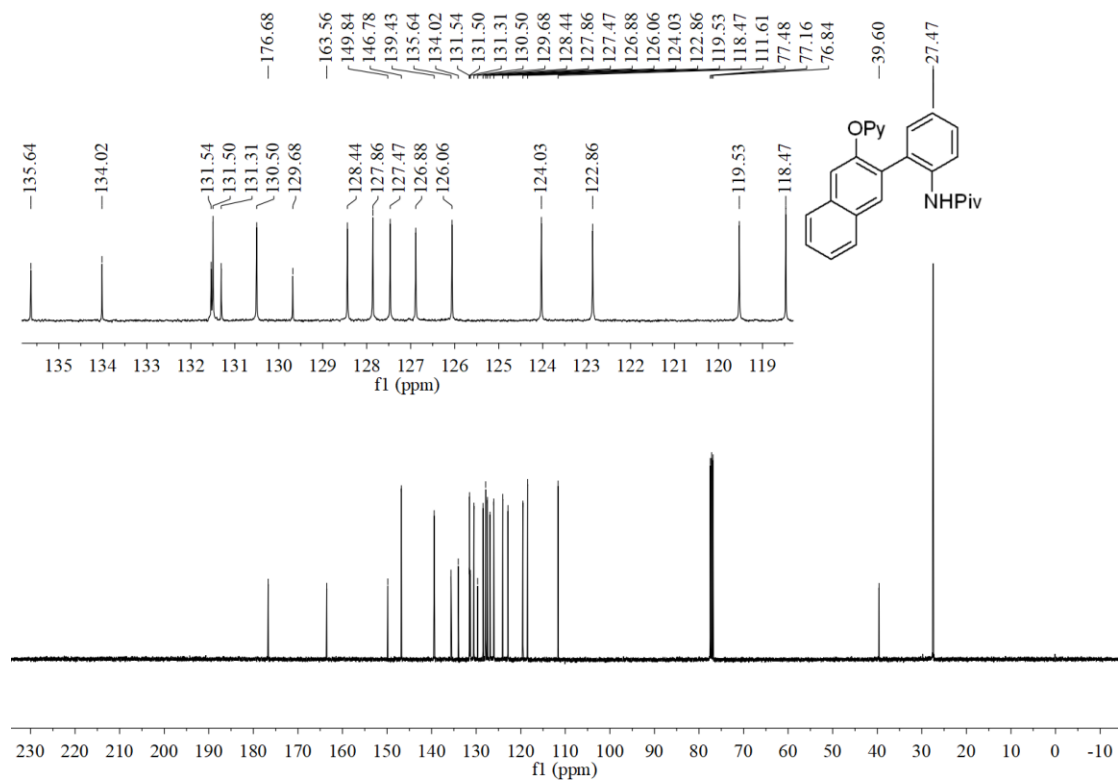
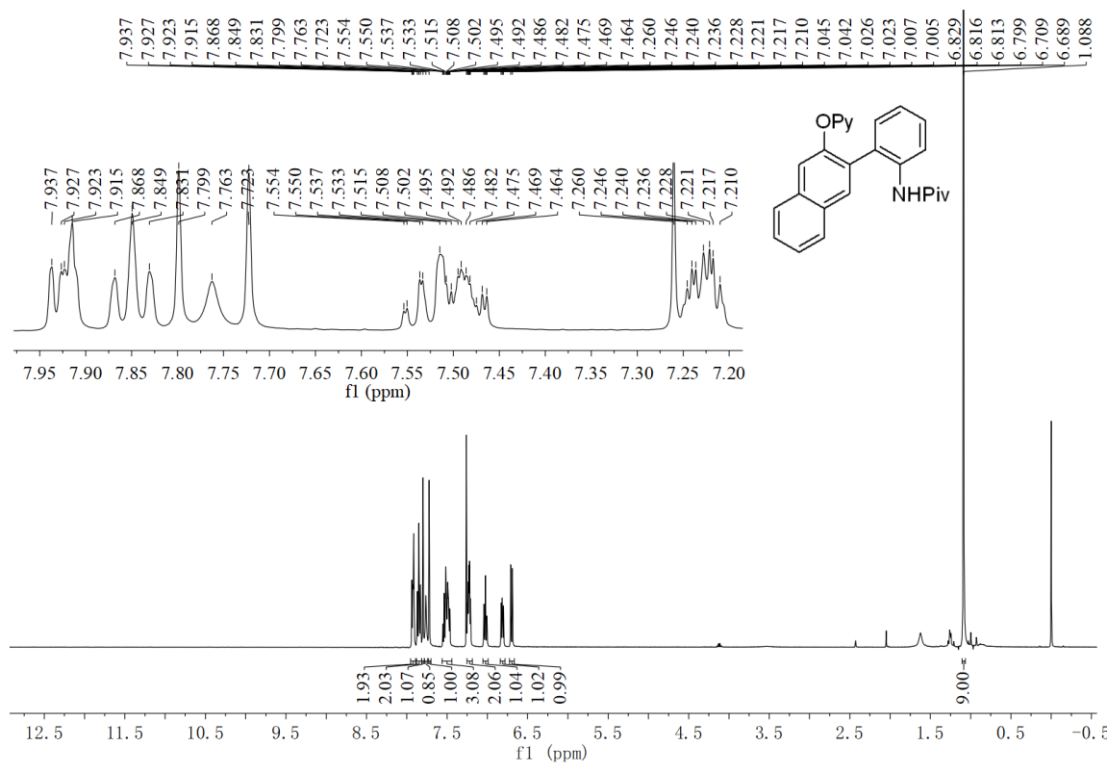
Methyl 2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (3o)



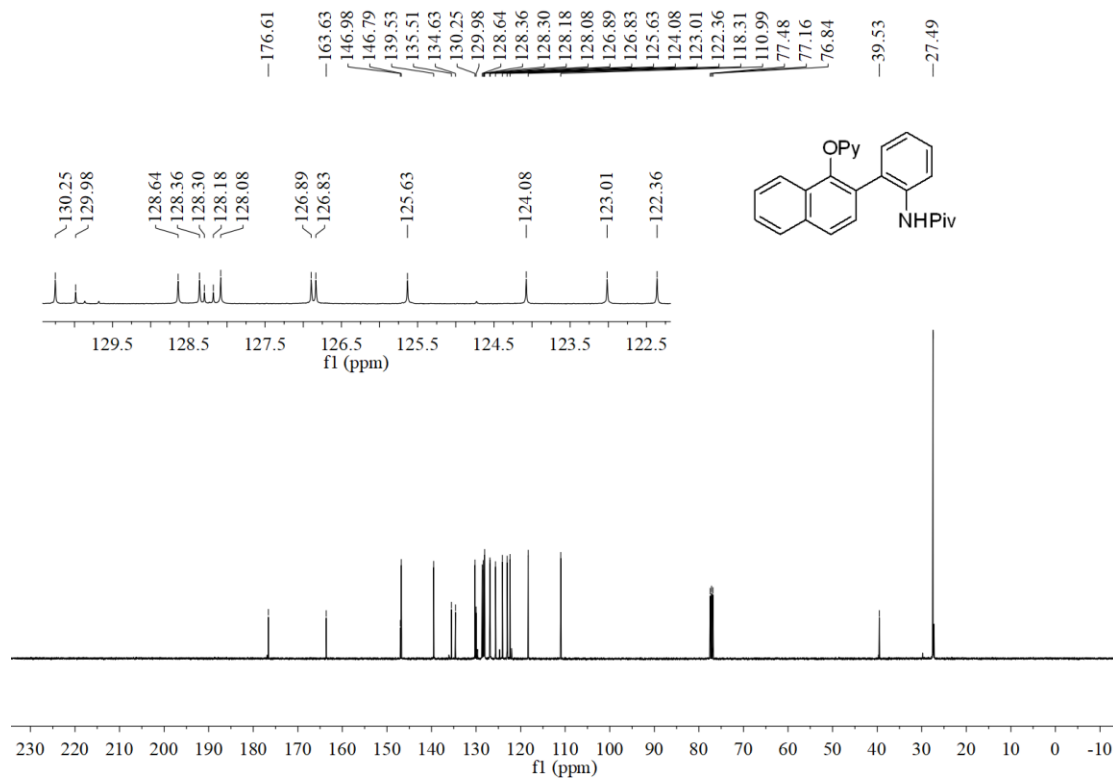
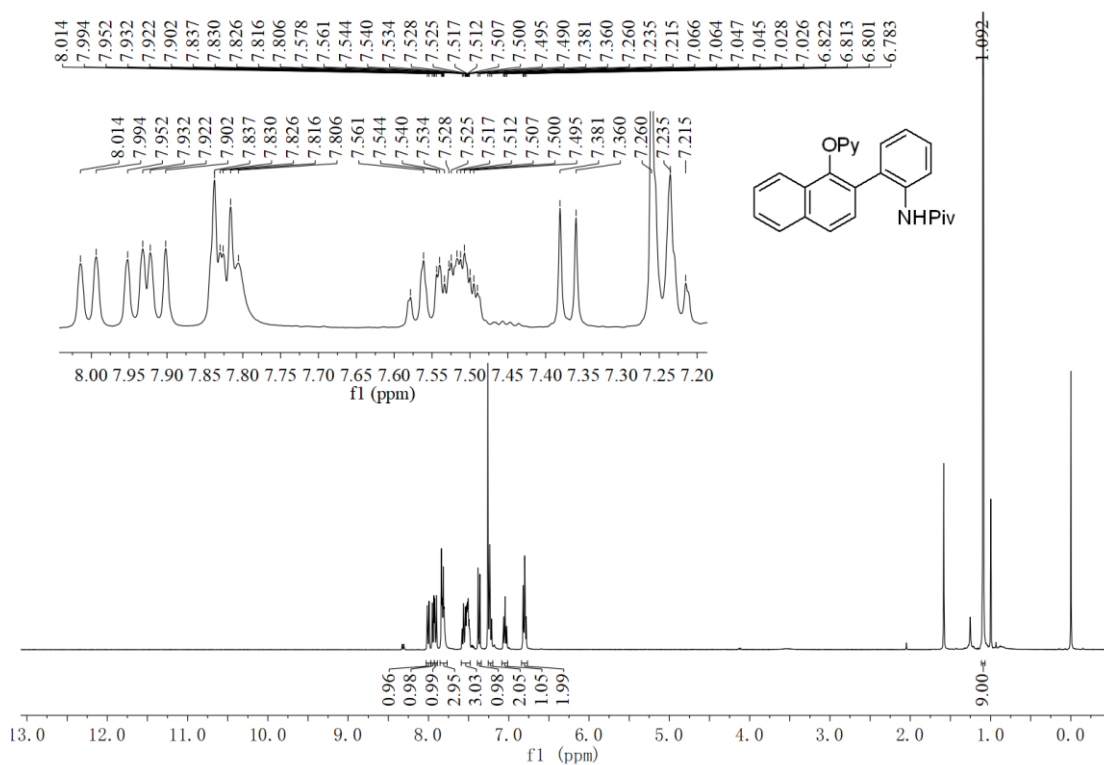
Methyl (*E*)-3-(2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl)acrylate (3p)



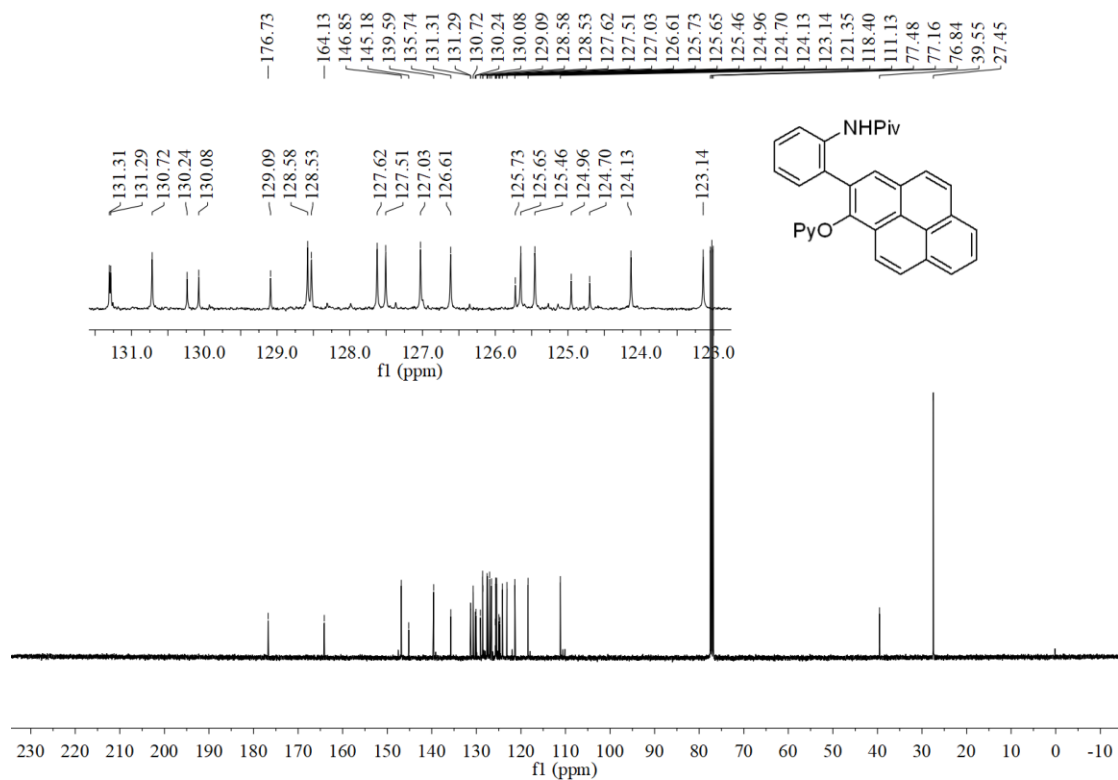
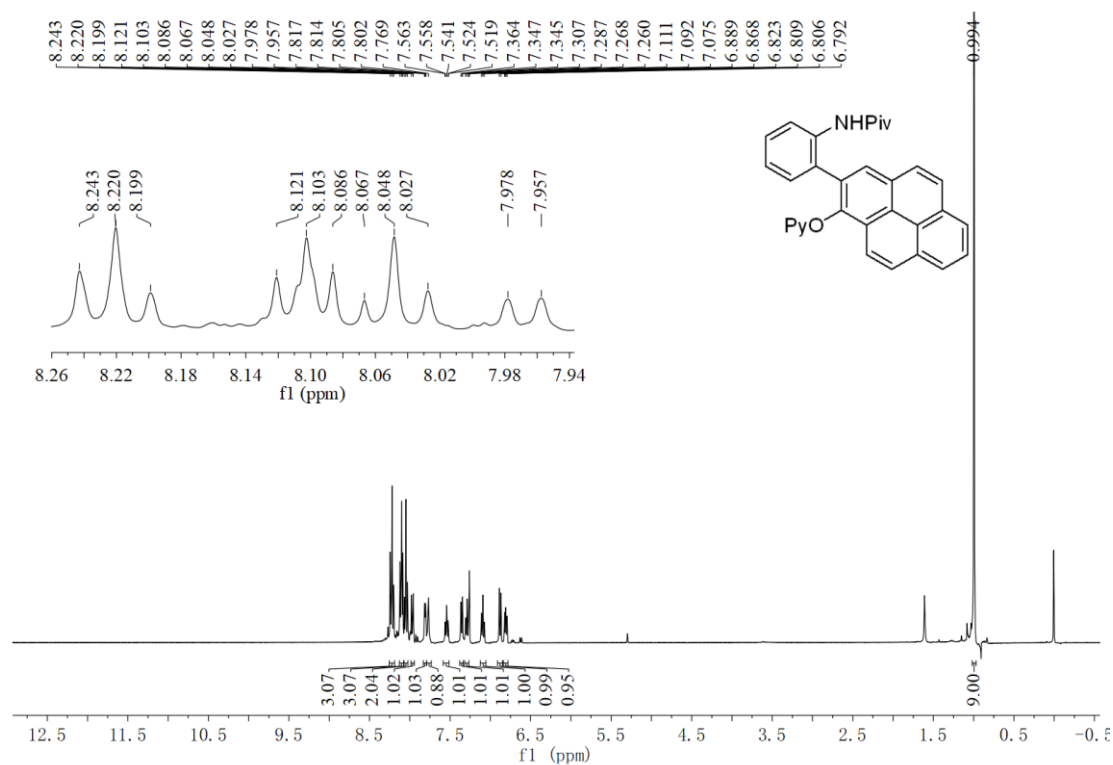
***N*-(2-(3-(Pyridin-2-yloxy)naphthalen-2-yl)phenyl)pivalamide (3q)**



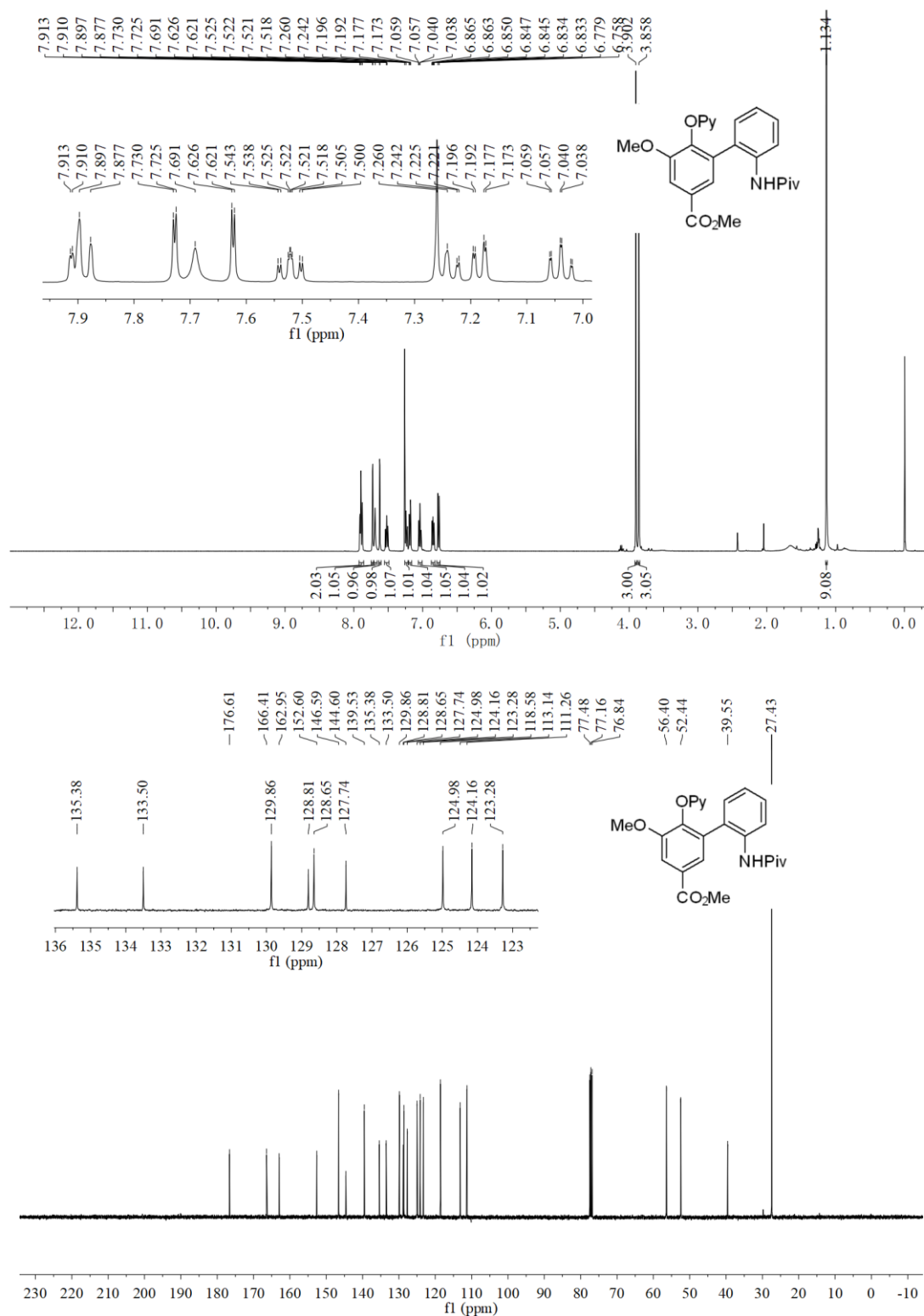
N-(2-(1-(Pyridin-2-yloxy)naphthalen-2-yl)phenyl)pivalamide (3r)



***N*-(2-(1-(Pyridin-2-yloxy)pyren-2-yl)phenyl)pivalamide (3s)**



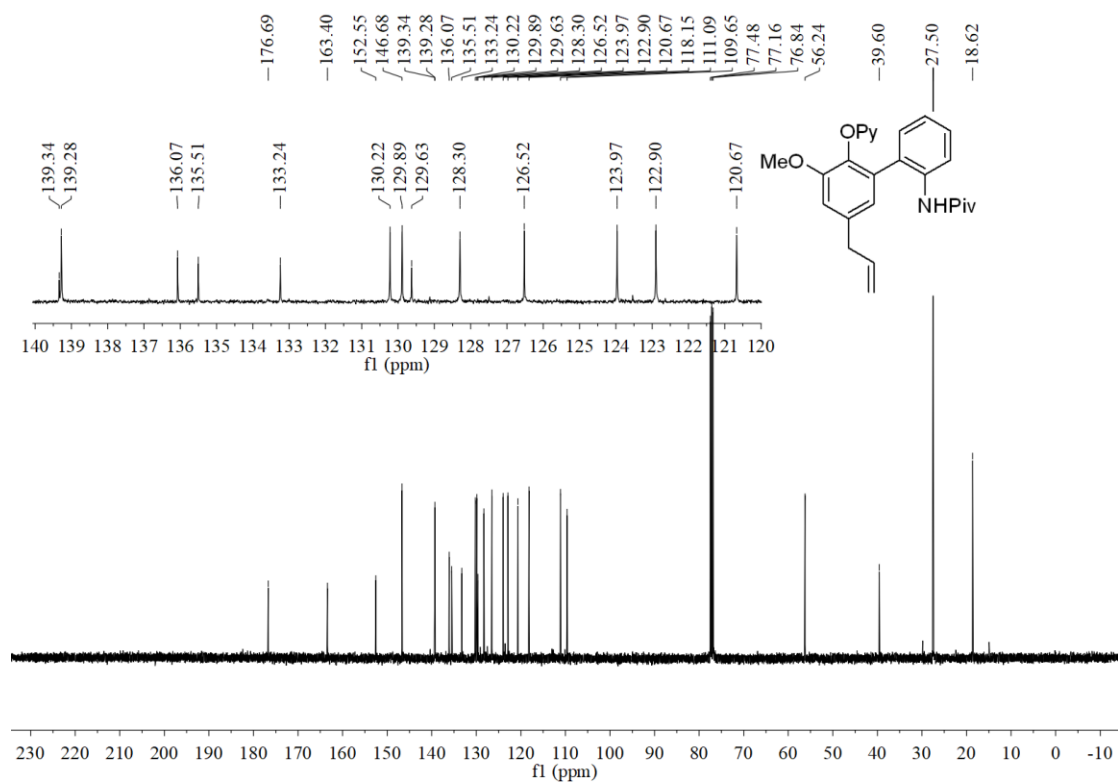
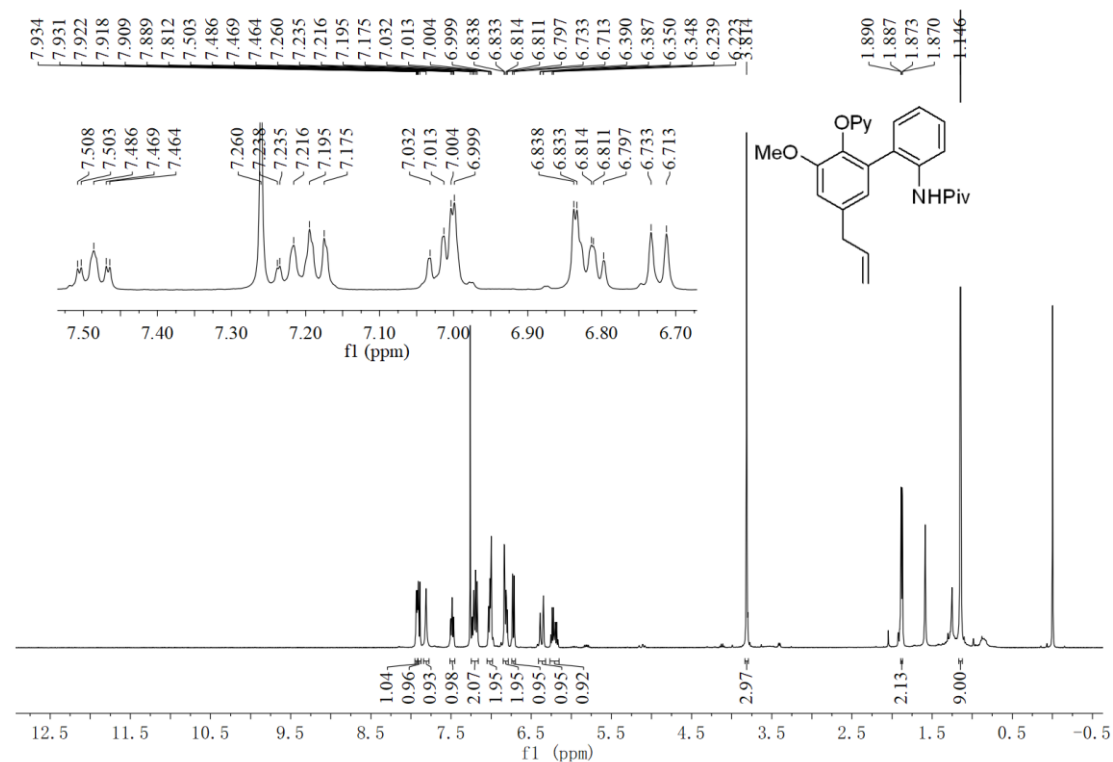
Methyl 5-methoxy-2'-pivalamido-6-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (3t)



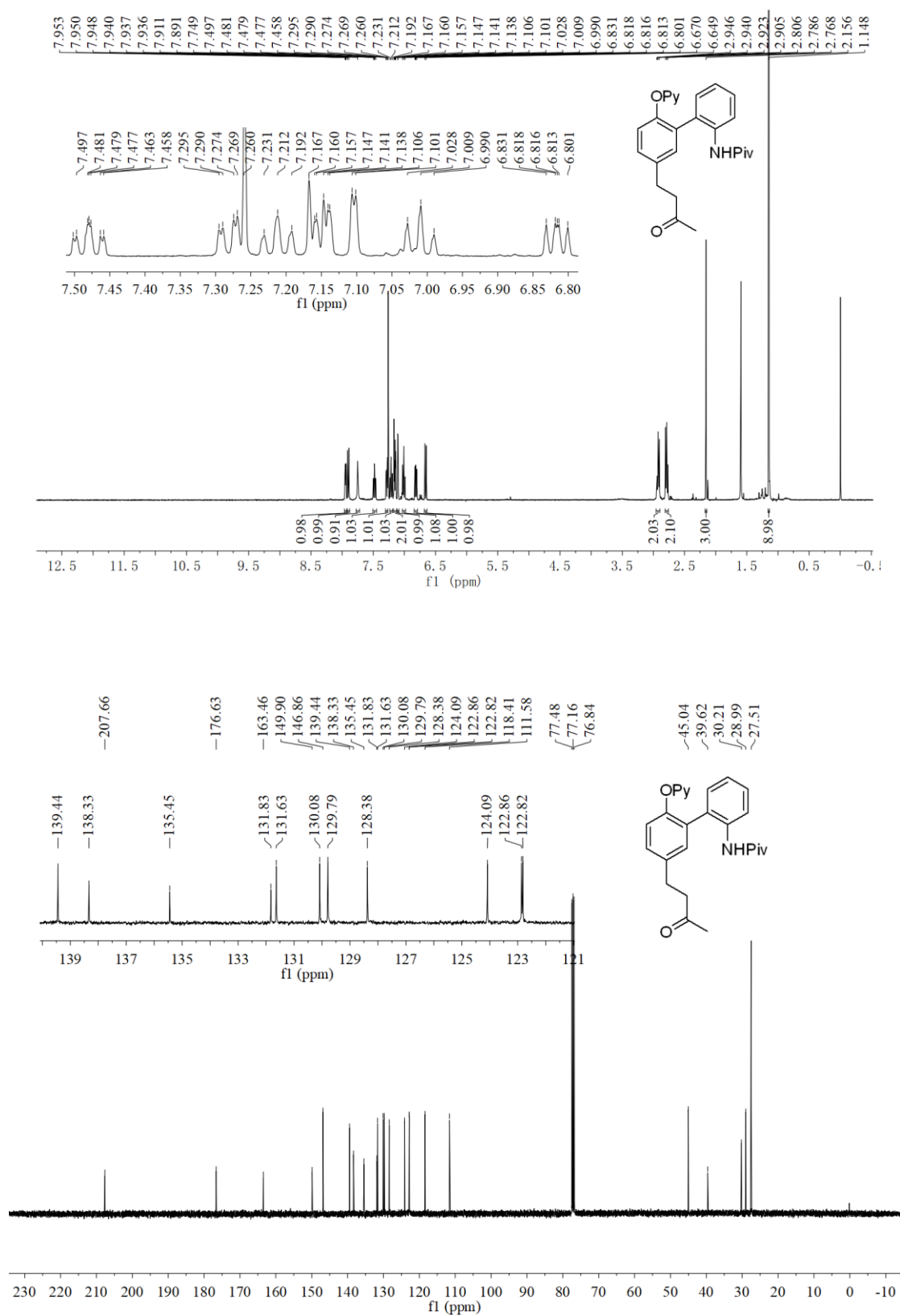
e (3u)



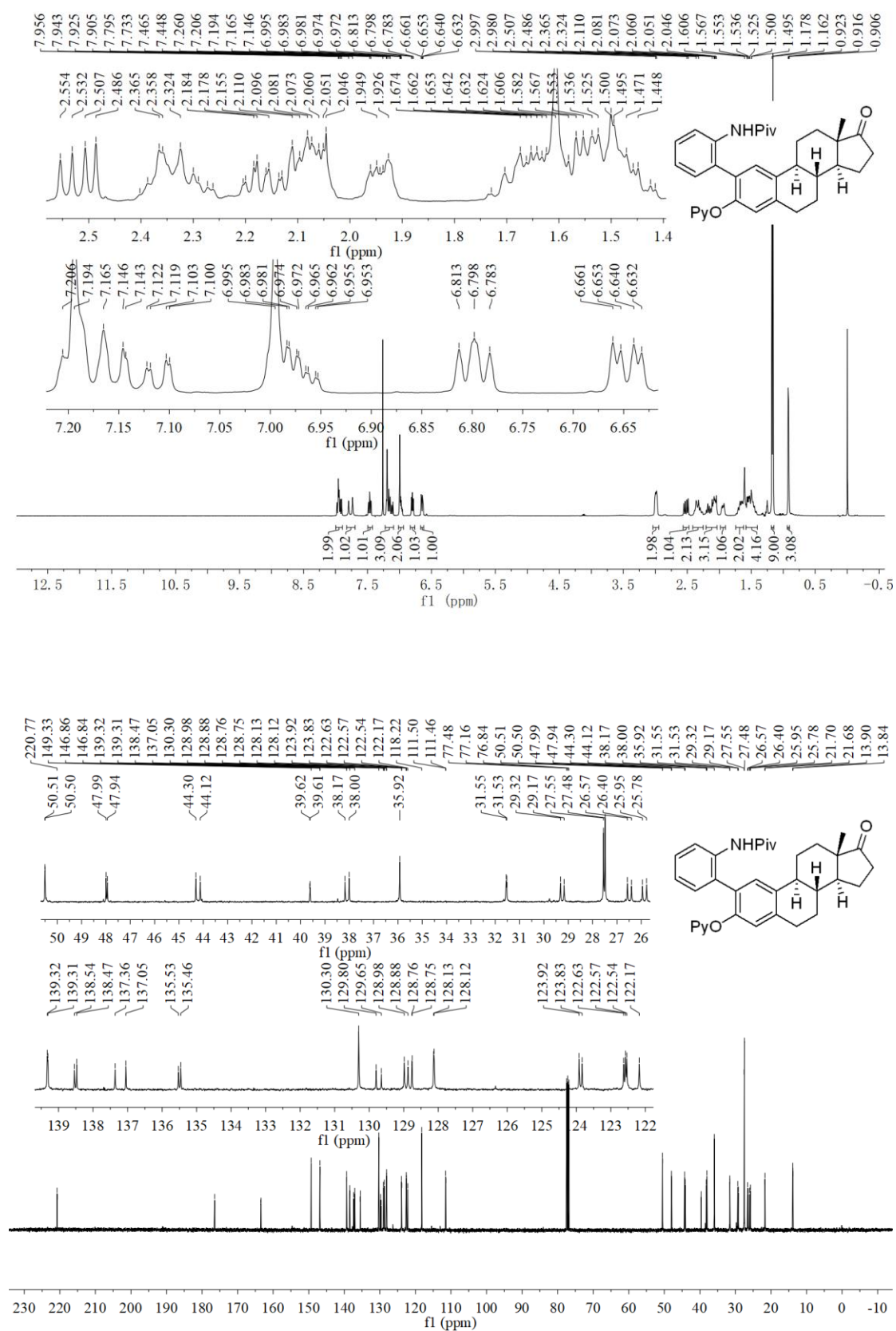
***N*-(5'-Allyl-3'-methoxy-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (3v)**



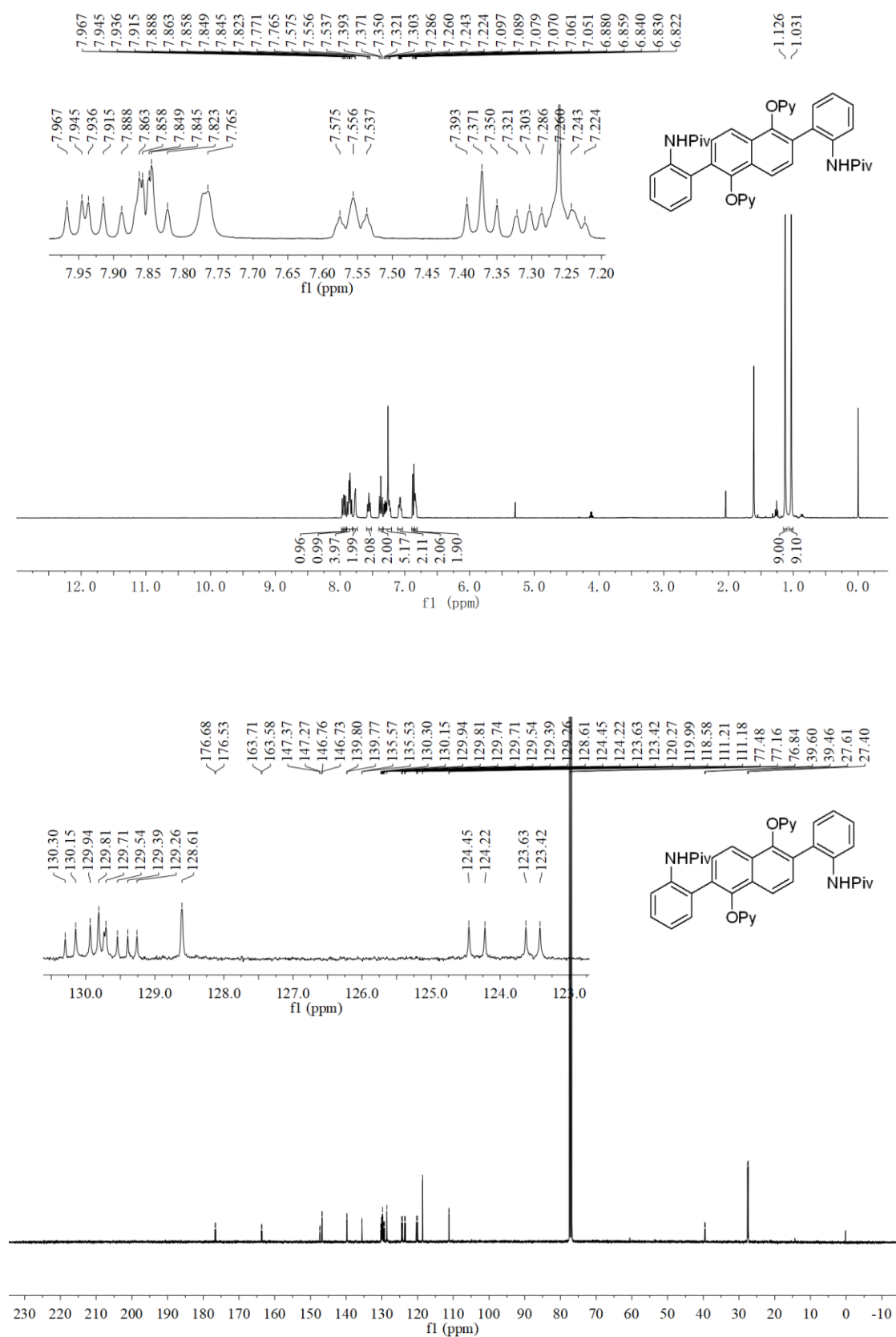
***N*-(3'-Methoxy-5'-(3-oxobutyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide
(3w)**



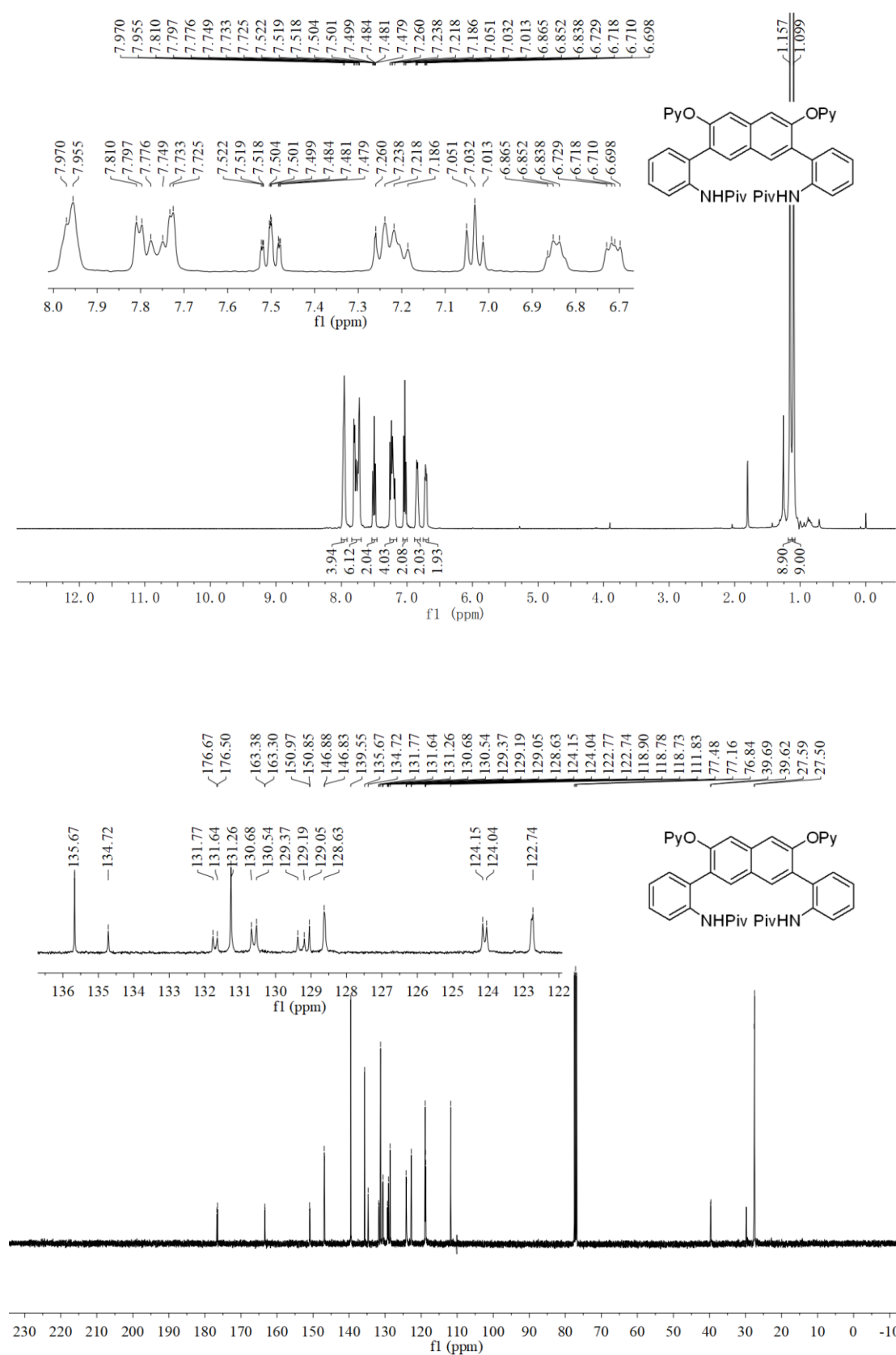
***N*-(2-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-3-(pyridin-2-yloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)phenyl)pivalamide (3x)**



***N,N'*-((1,5-Bis(pyridin-2-yloxy)naphthalene-2,6-diyl)bis(2,1-phenylene))bis(2,2-dimethylpropanamide) (3y)**



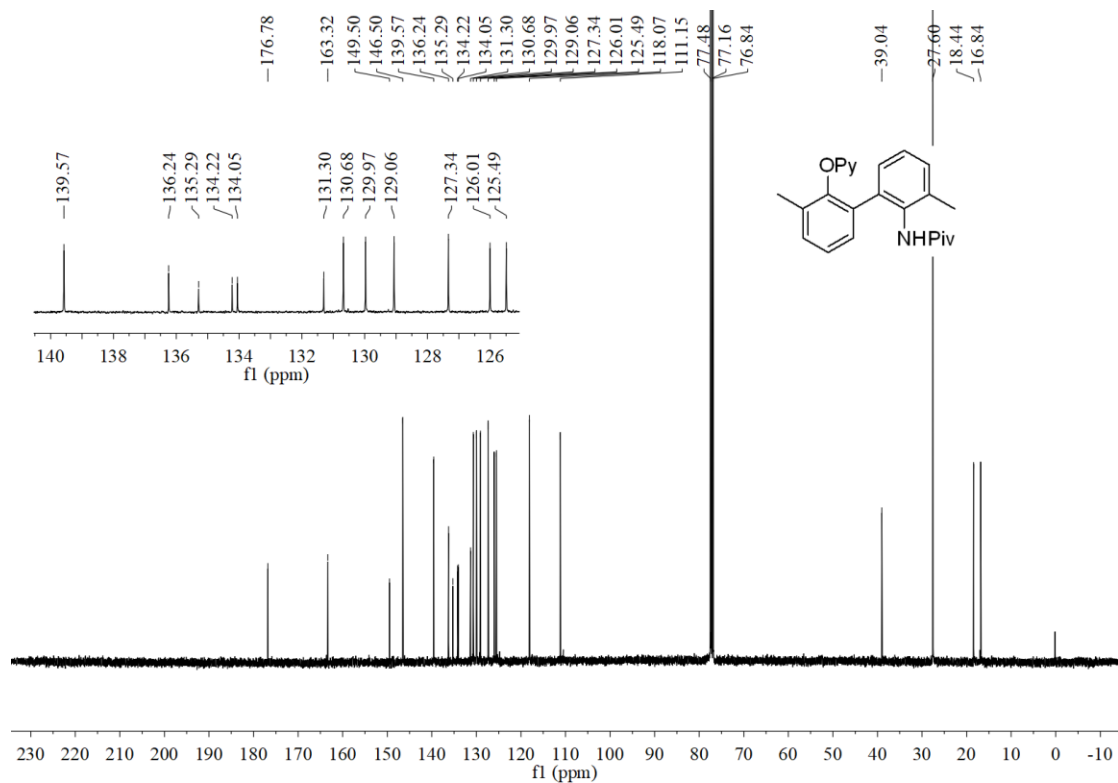
***N,N'*-((3,6-Bis(pyridin-2-yloxy)naphthalene-2,7-diyl)bis(2,1-phenylene))bis(2,2-dimethylpropanamide) (3z)**



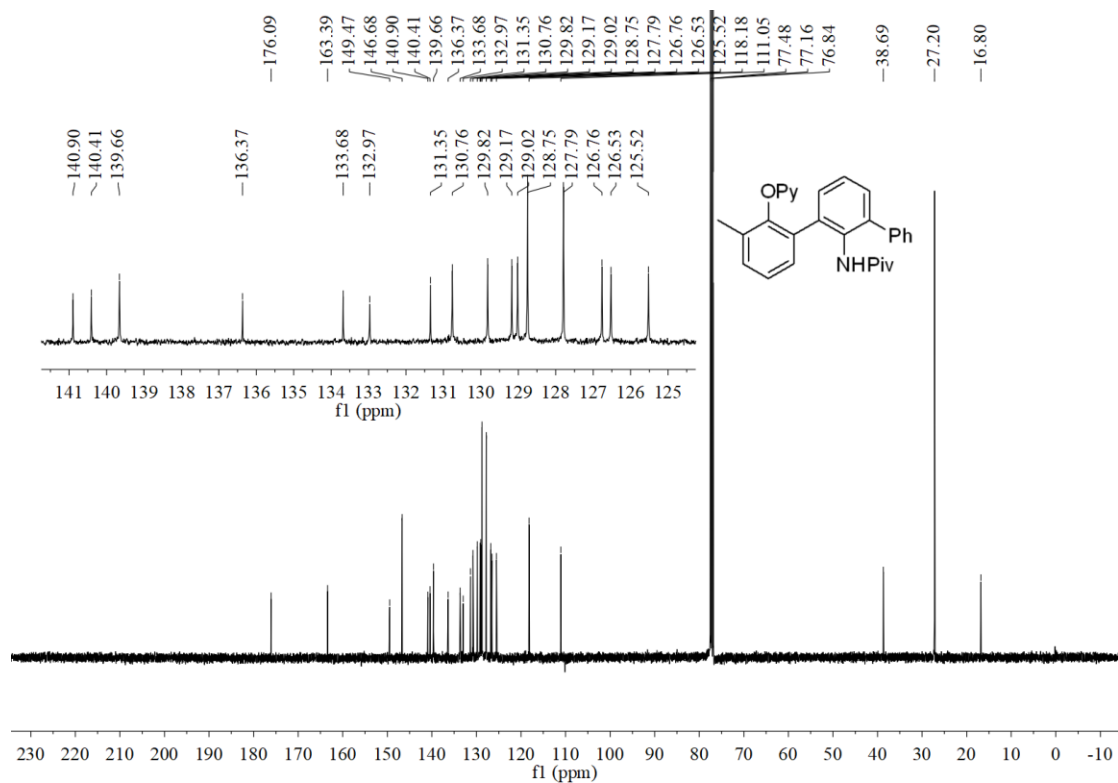
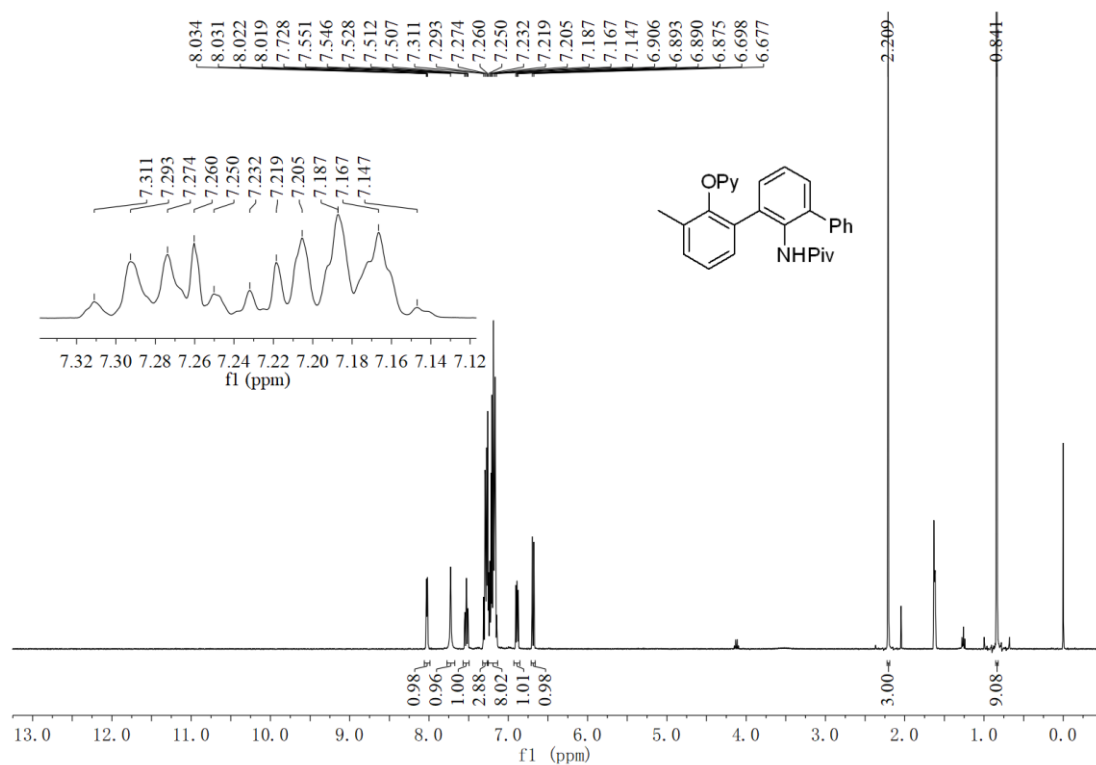
Chemical structure of compound 10: Cc1ccc(cc1)-c2ccc(cc2)Nc3ccccc3

¹H NMR spectrum (CDCl₃):

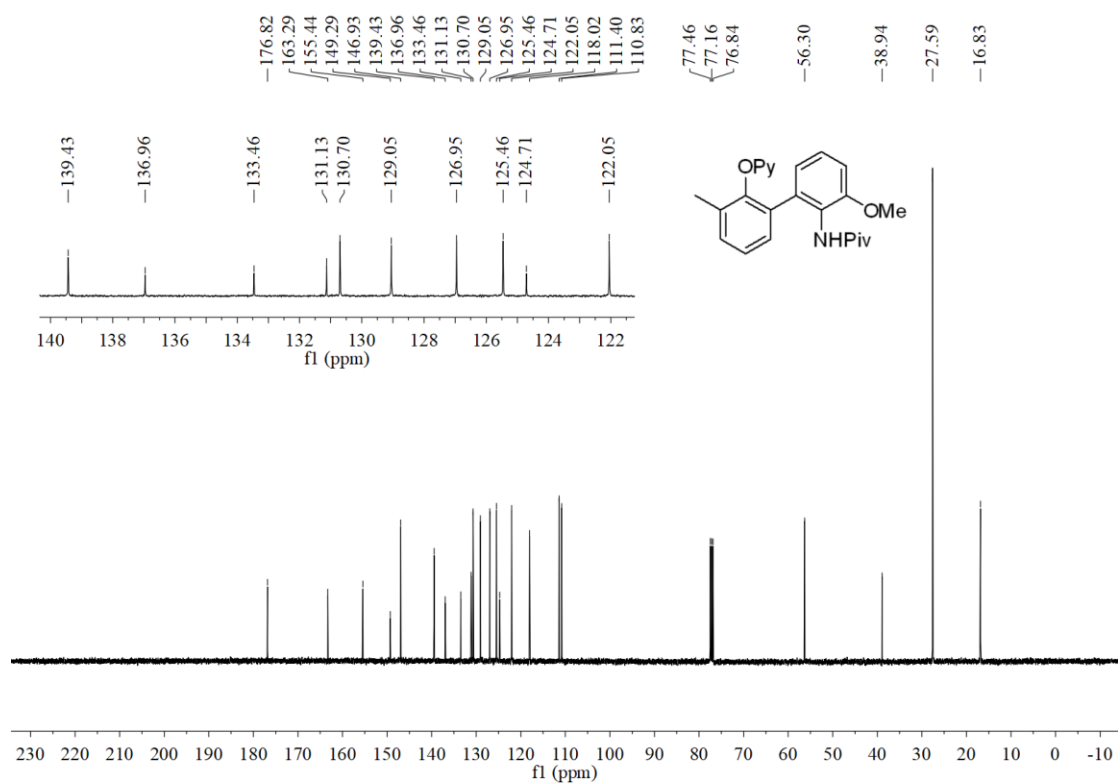
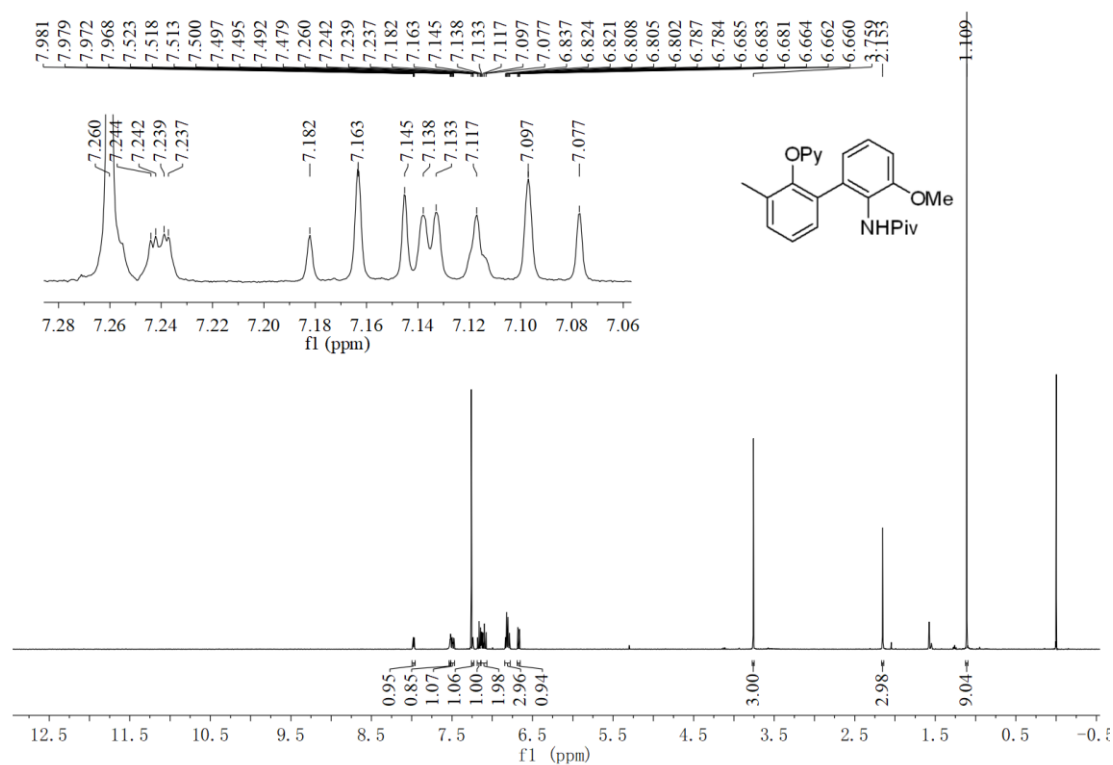
Chemical Shift (ppm)	Integration
7.947	0.97
7.944	0.92
7.942	1.02
7.937	1.51
7.935	1.02
7.932	1.00
7.930	3.95
7.926	1.02
7.925	1.02
7.921	0.95
7.918	0.97
7.913	0.92
7.909	1.02
7.901	1.51
7.887	1.00
7.882	3.95
7.870	1.02
7.868	1.02
7.867	0.95
7.856	0.97
7.850	0.92
7.847	1.02
7.846	1.02
7.833	0.97
7.831	0.92
7.821	1.02
7.818	1.51
7.816	1.02
7.813	1.00
7.803	3.95
7.801	1.02
7.691	0.97
7.689	0.92
7.687	1.02
7.670	1.51
7.668	1.02
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02
7.666	1.51
7.666	1.00
7.666	3.95
7.666	1.02
7.666	1.02
7.666	0.97
7.666	0.92
7.666	1.02



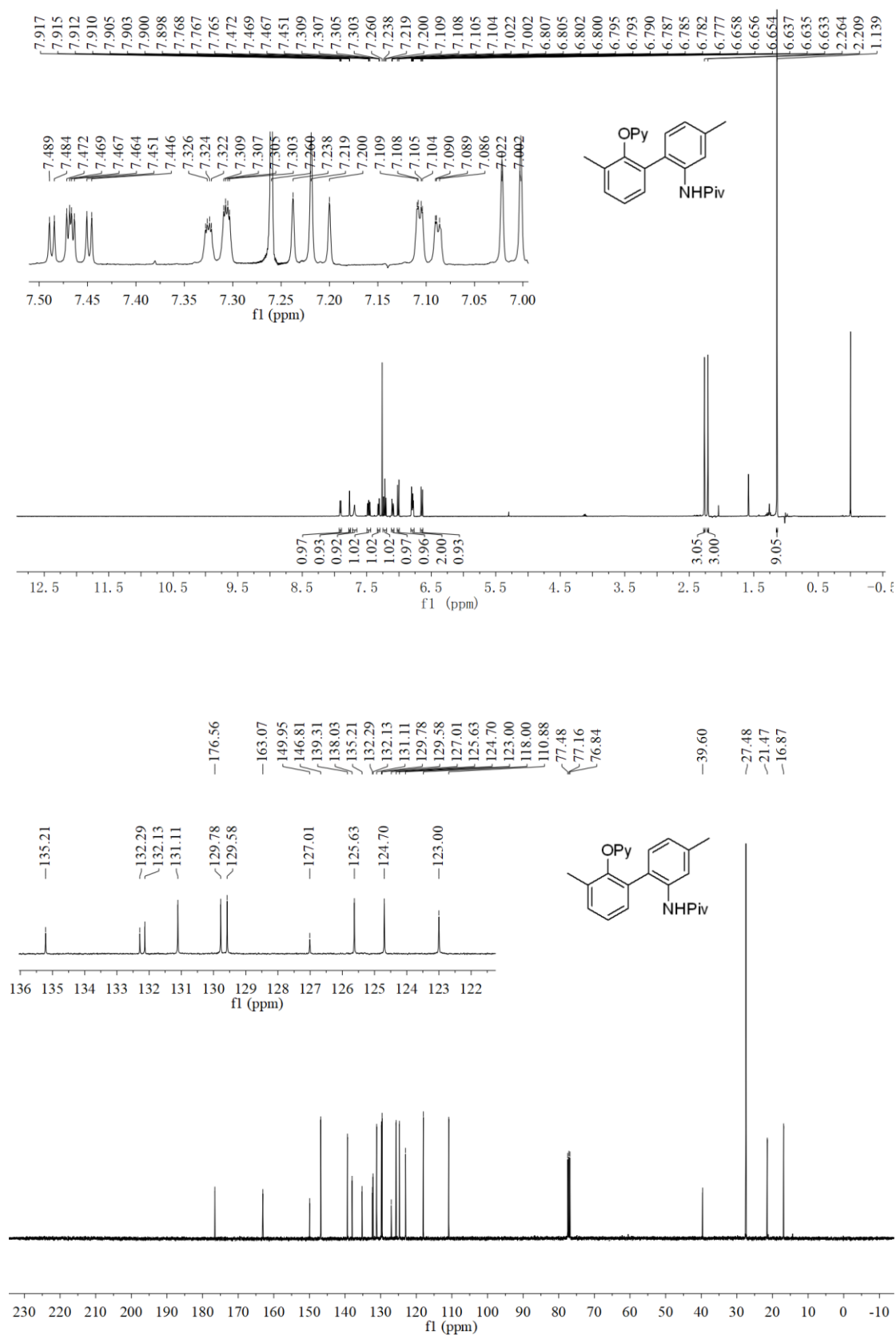
***N*-(3-Methyl-2-(pyridin-2-yloxy)-[1,1':3',1''-terphenyl]-2'-yl)pivalamide (4b)**



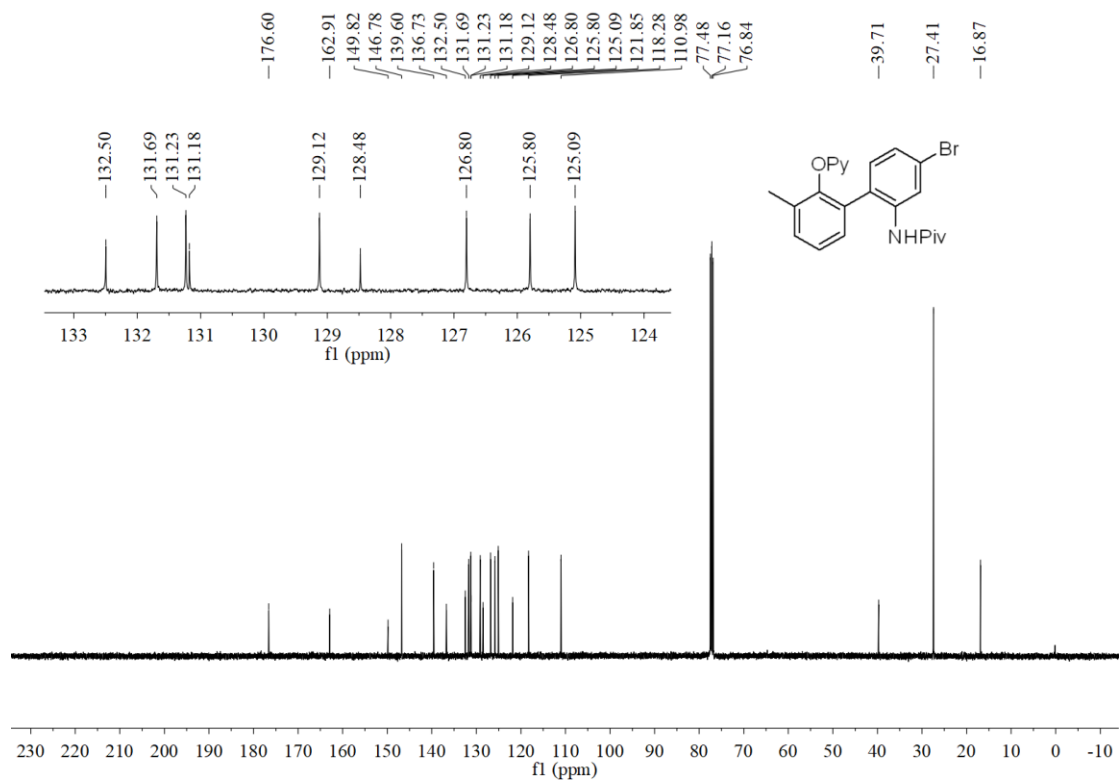
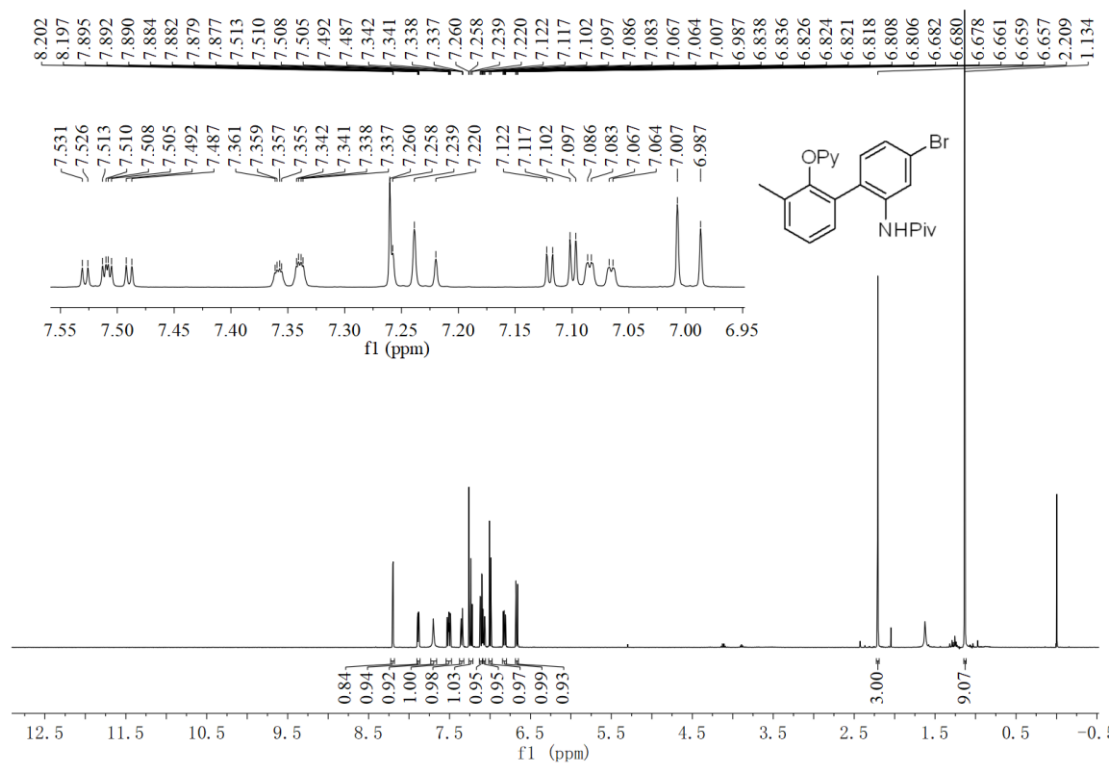
***N*-(3-Methoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4c)**



***N*-(3',4-Dimethyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4d)**



***N*-(4-Bromo-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4e)**



***N*-(5-Methoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4f)**

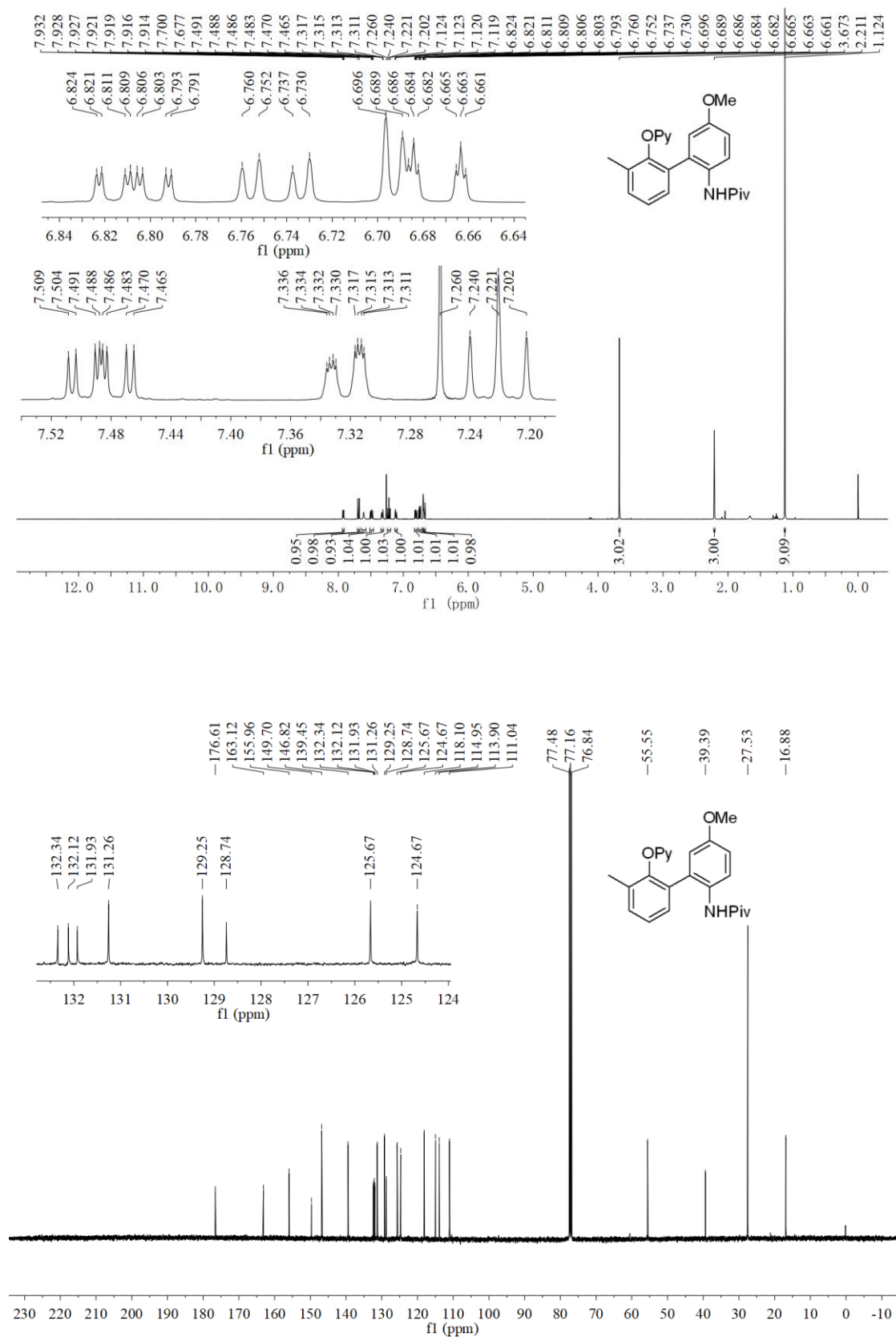
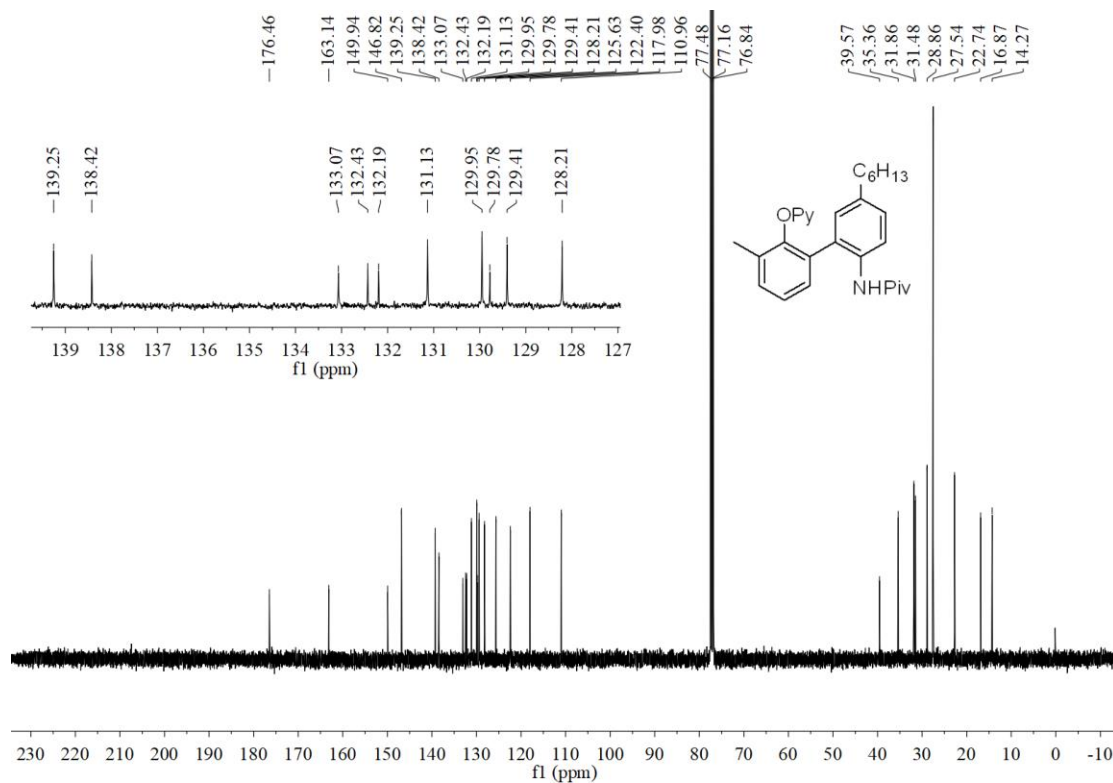
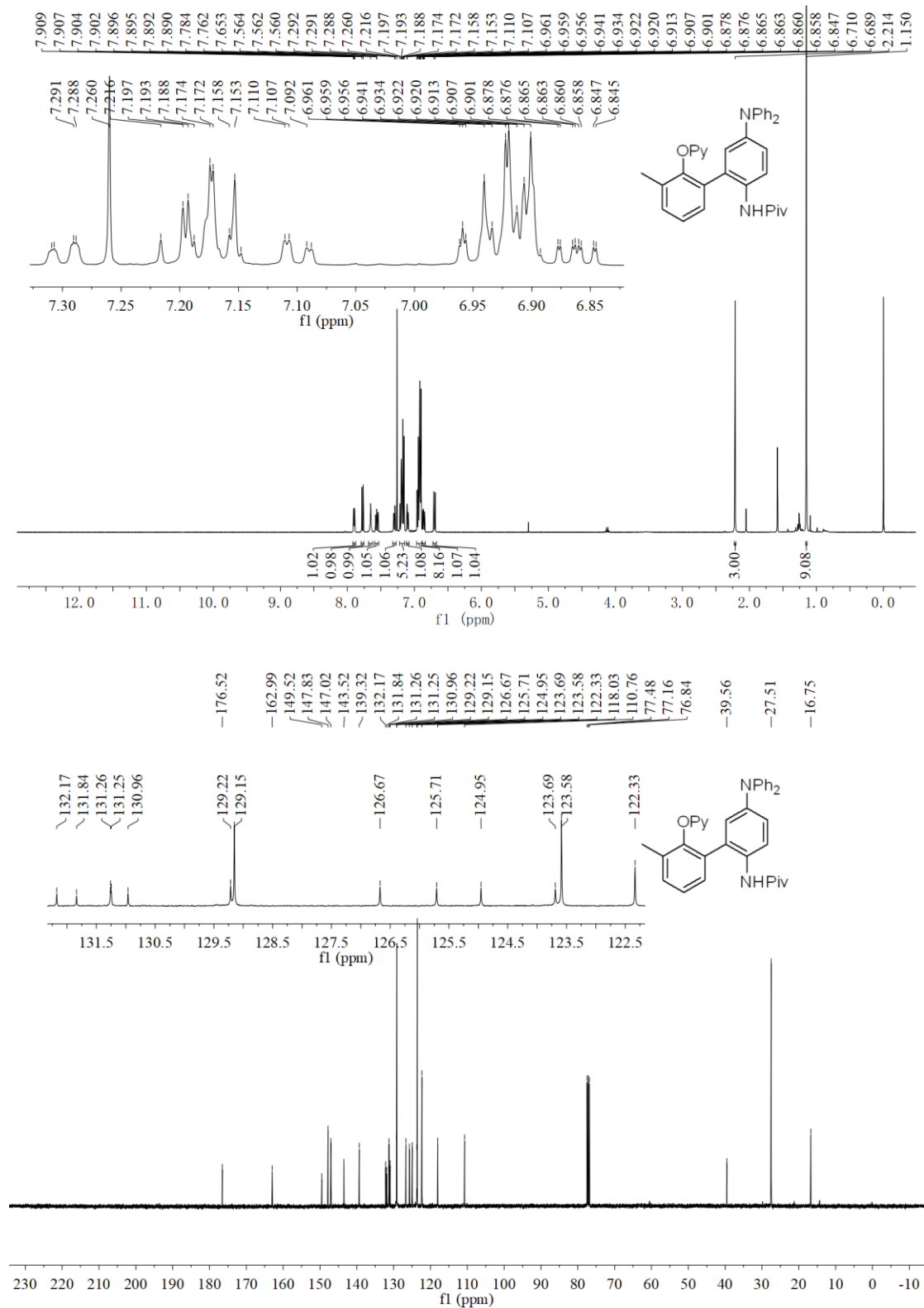


Figure 1 displays the ^1H NMR spectra of compound **1**. The chemical structure of **1** is shown, which is 2-methyl-4-(4-hexylaminophenoxy)phenyl. The spectra are recorded in CDCl_3 at 400 MHz.

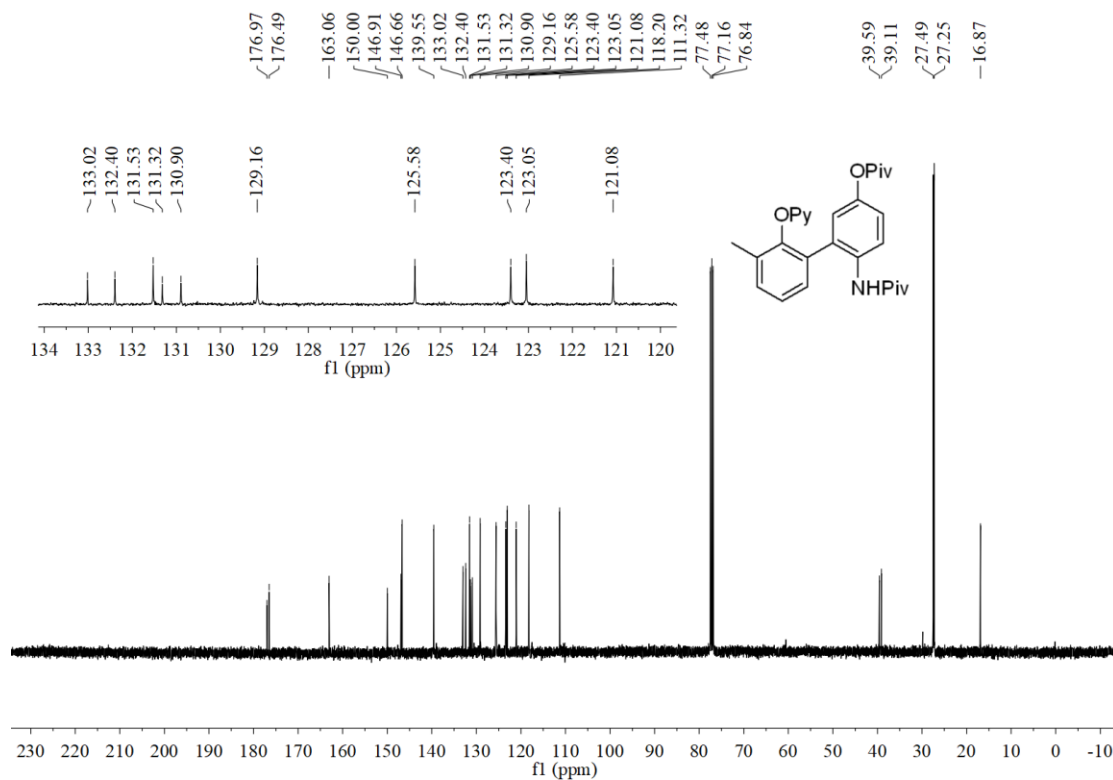
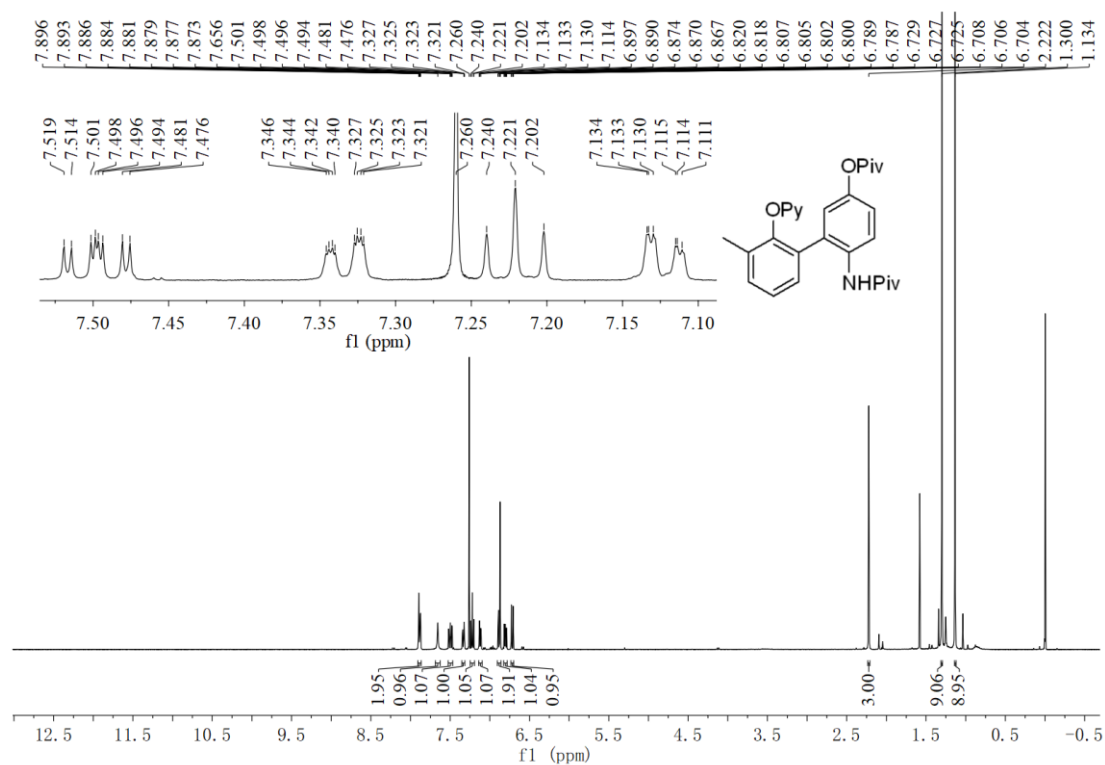
The top spectrum shows the aromatic region (7.30–7.91 ppm) with the following chemical shifts (ppm): 7.910, 7.907, 7.898, 7.895, 7.780, 7.760, 7.609, 7.441, 7.439, 7.317, 7.315, 7.313, 7.260, 7.224, 7.205, 7.129, 7.129, 7.125, 7.124, 7.110, 7.107, 7.609, 7.462, 7.457, 7.444, 7.441, 7.439, 7.436, 7.423, 7.124, 7.418, 7.334, 7.332, 7.330, 7.317, 7.315, 7.313, 7.311. The bottom spectrum shows the aliphatic region (0.85–12.5 ppm) with the following chemical shifts (ppm): 7.243, 7.224, 7.205, 7.129, 7.125, 7.124, 7.110, 7.107, 6.991, 6.986, 6.970, 6.965, 6.920, 6.785, 6.783, 6.773, 6.771, 6.768, 6.765, 6.755, 6.753. Integration values are provided below the peaks in the aliphatic region: 0.95, 0.97, 0.95, 1.00, 0.98, 1.00, 0.99, 1.02, 0.97, 0.98, 0.95, 2.05, 3.00, 2.08, 6.27, 9.08, 2.98.

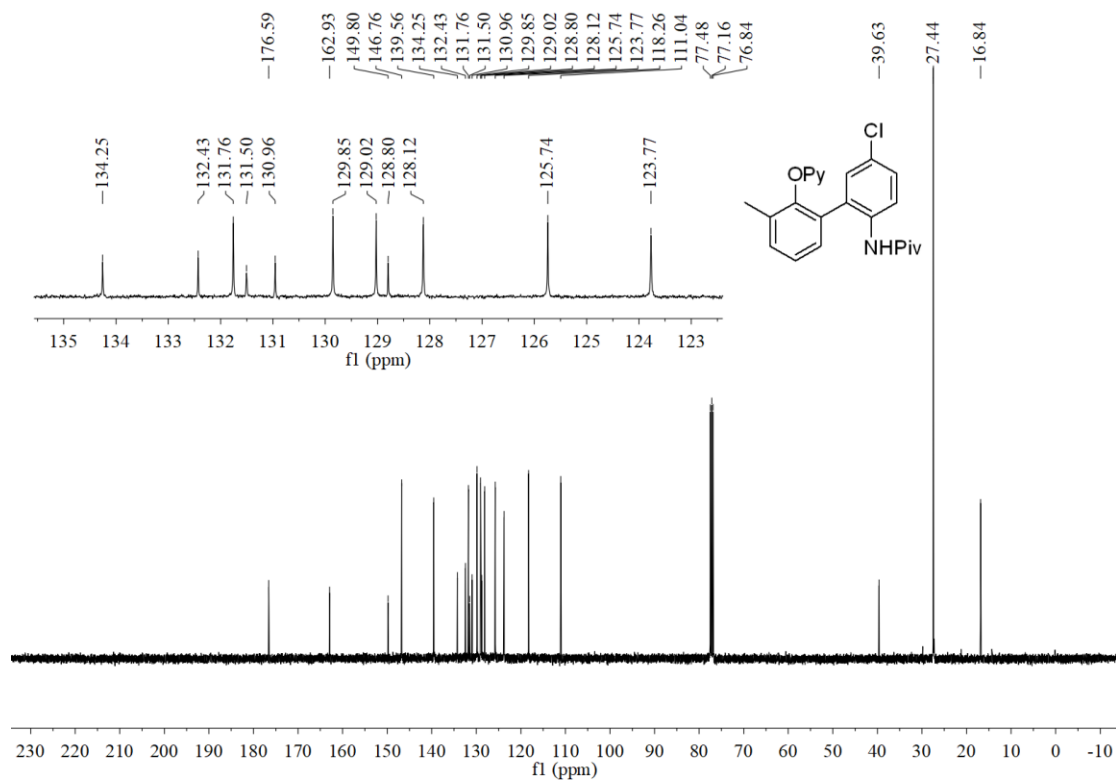


N-(5-(Diphenylamino)-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamid
e (4h)

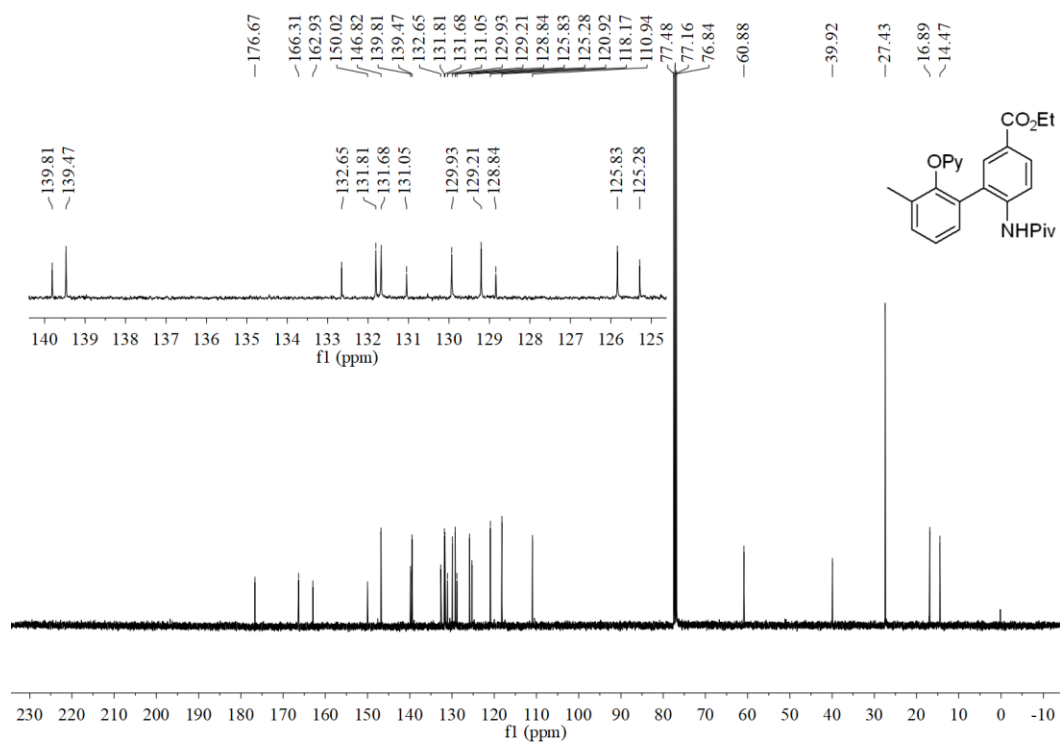
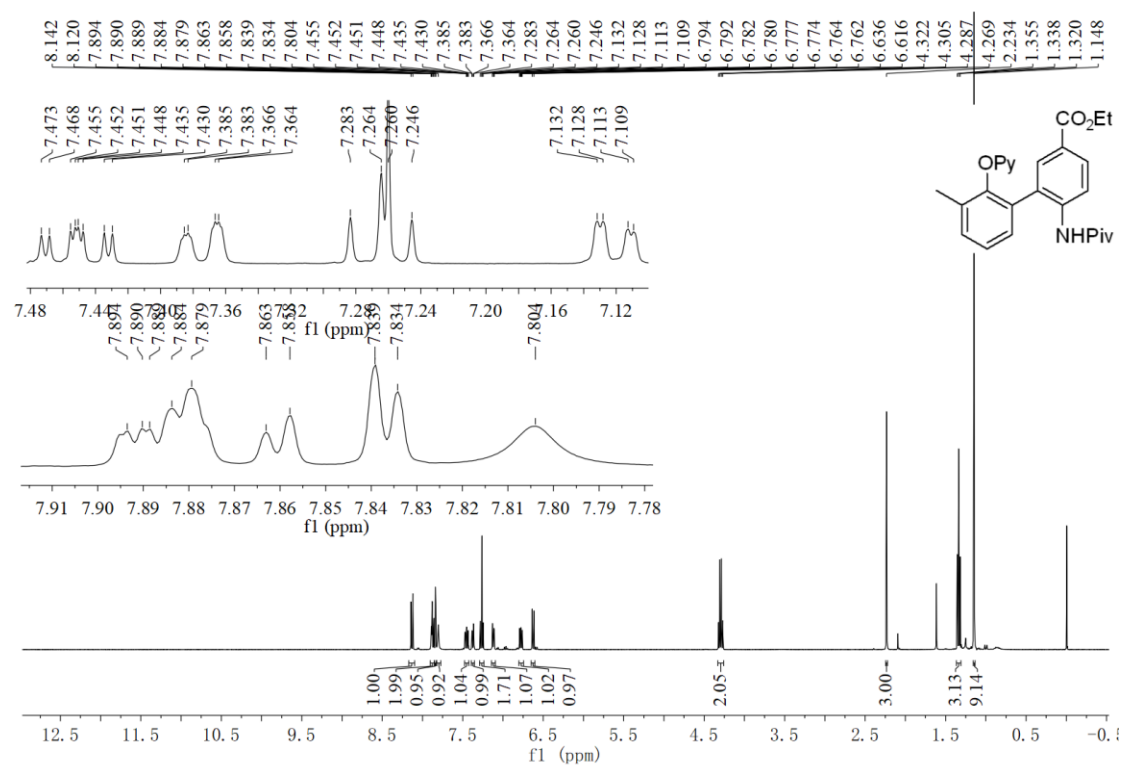


3'-Methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl pivalate (4i)

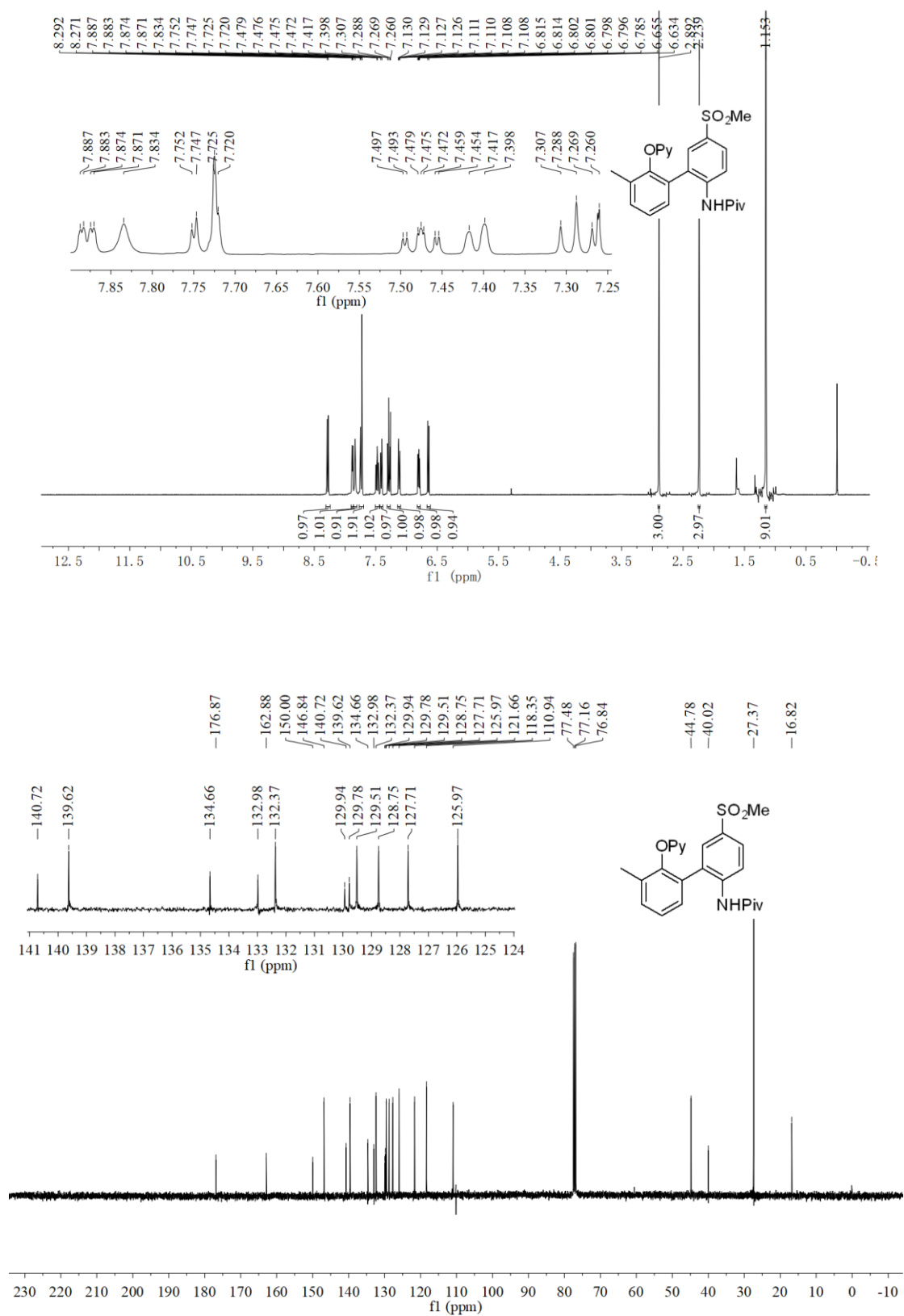


[illegible]

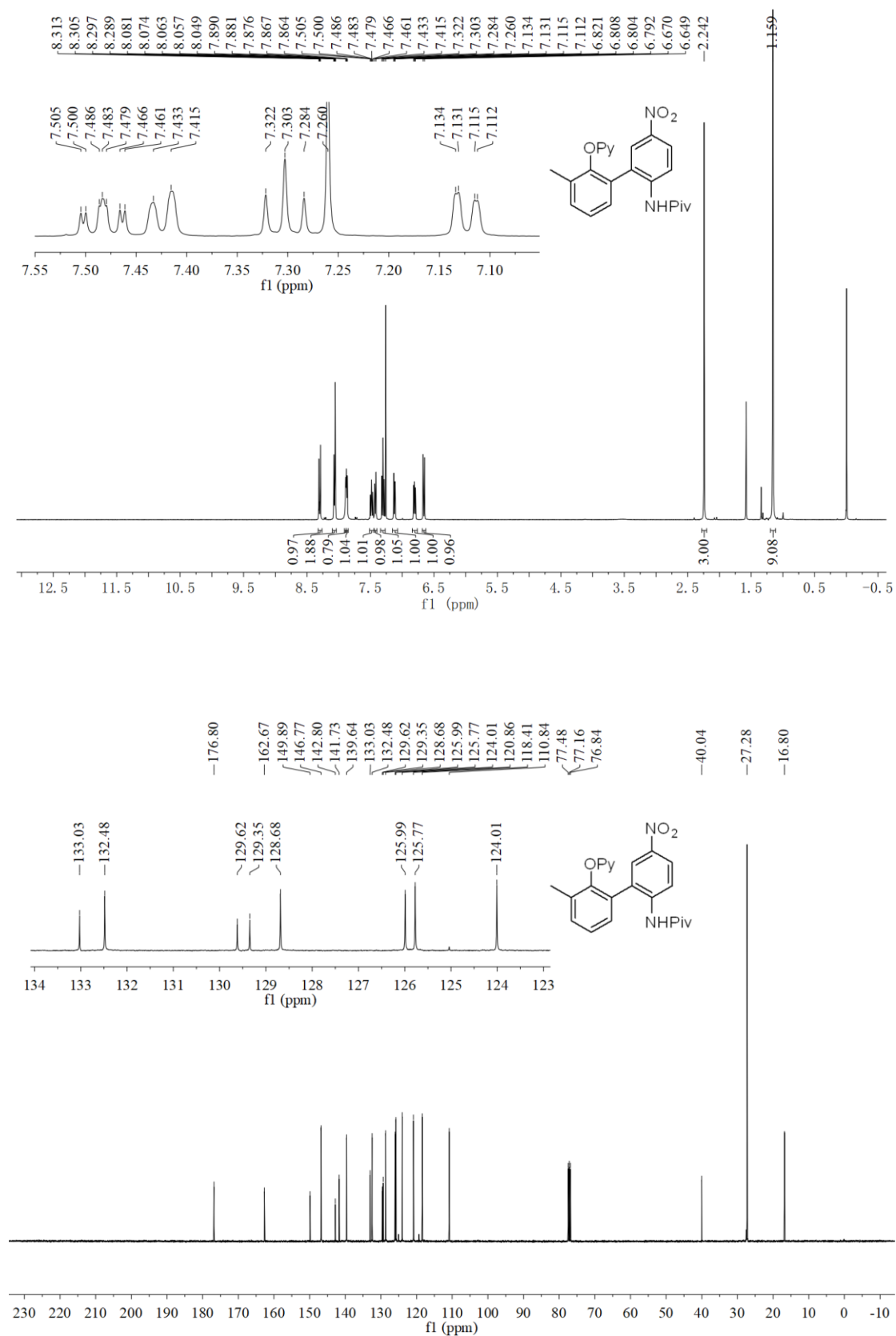
Ethyl 3'-methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (4k)



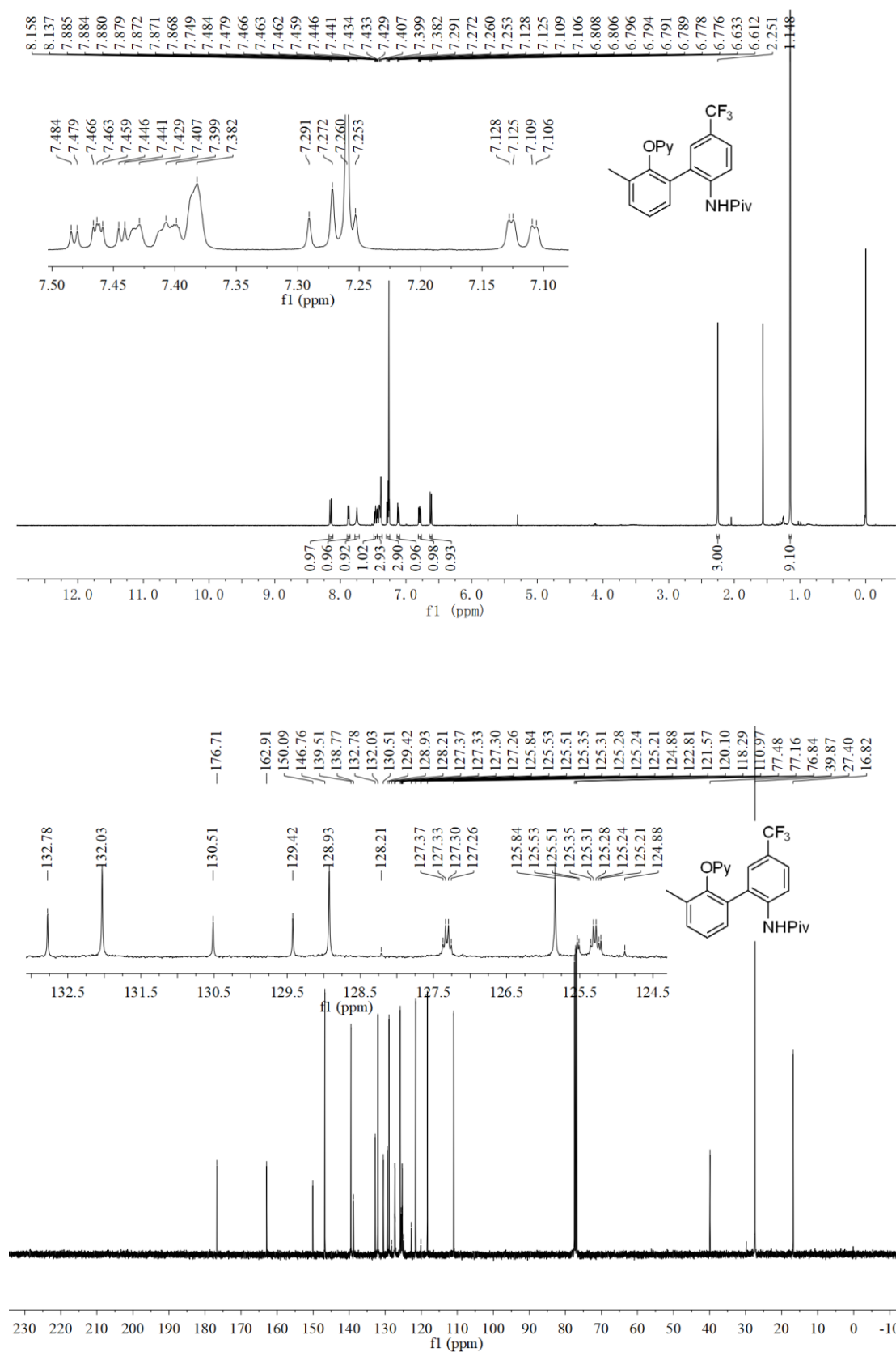
***N*-(3'-Methyl-5-(methylsulfonyl)-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamid
e (4l)**



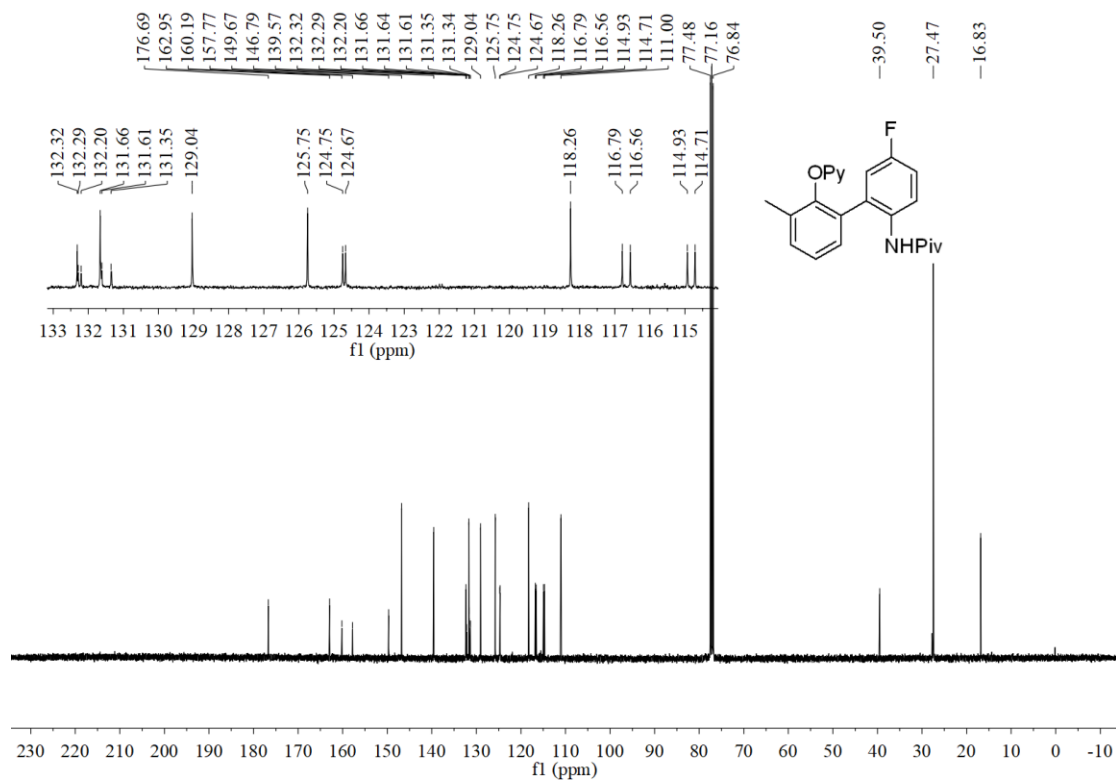
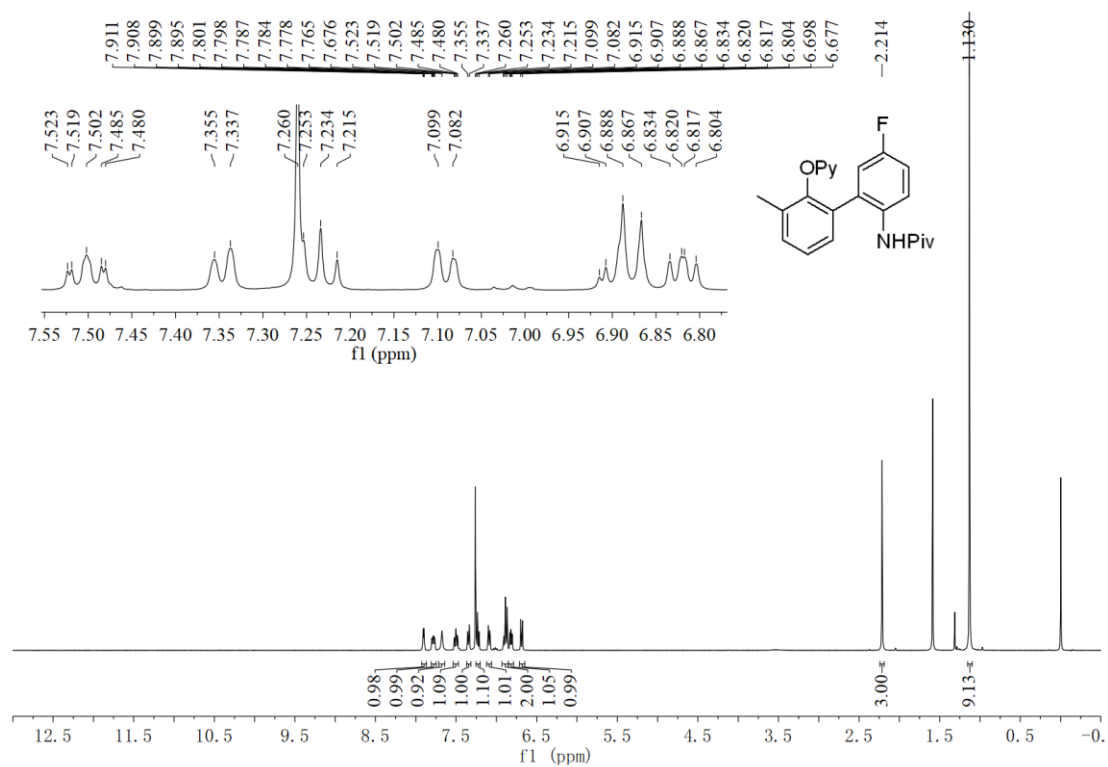
***N*-(3'-Methyl-5-nitro-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4m)**



***N*-(3'-Methyl-2'-(pyridin-2-yloxy)-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamid
e (4n)**

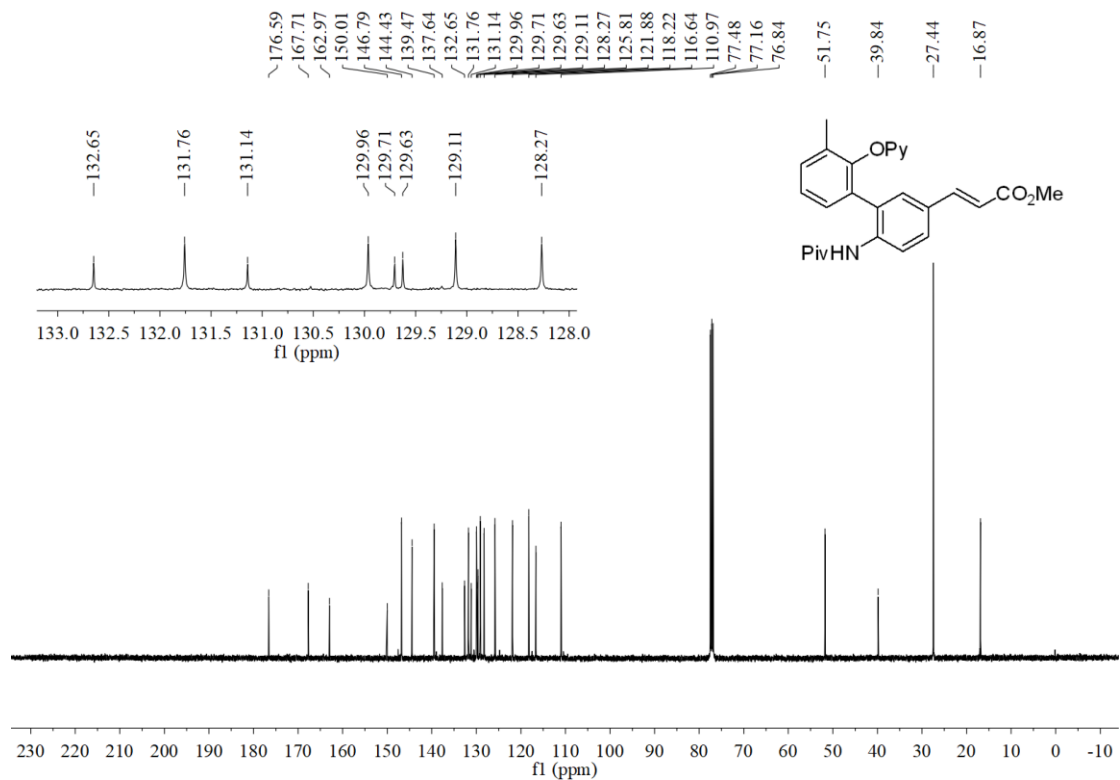
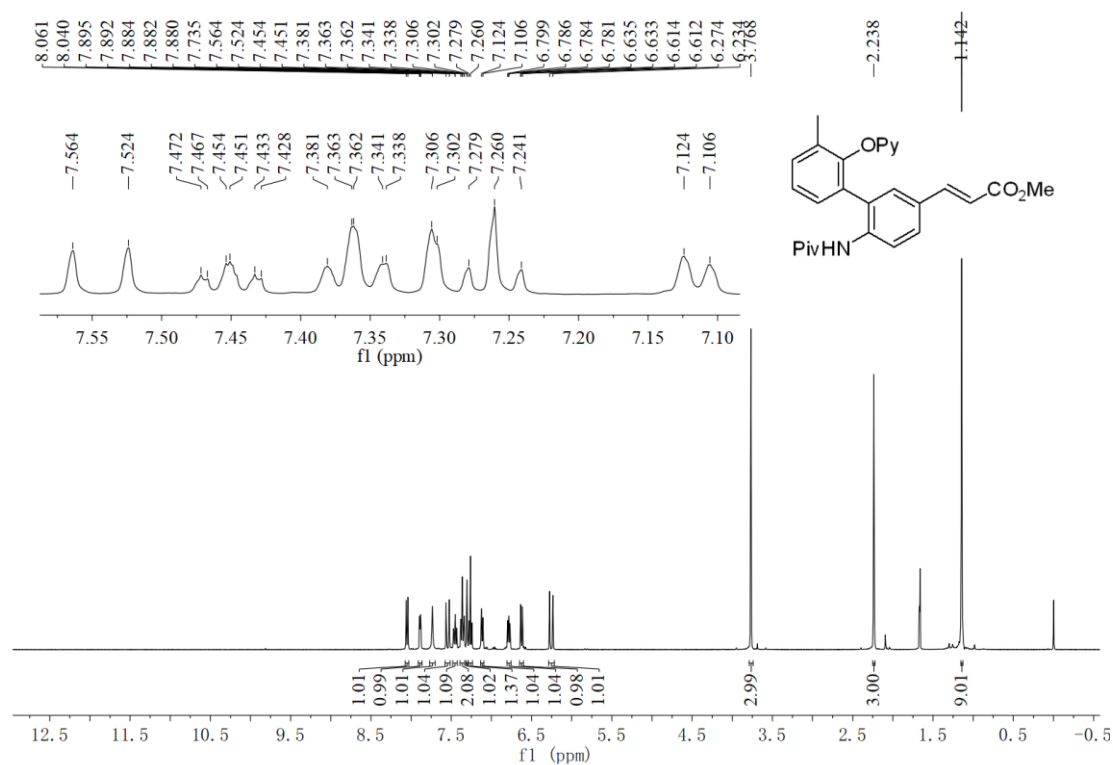


***N*-(5-Fluoro-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4o)**

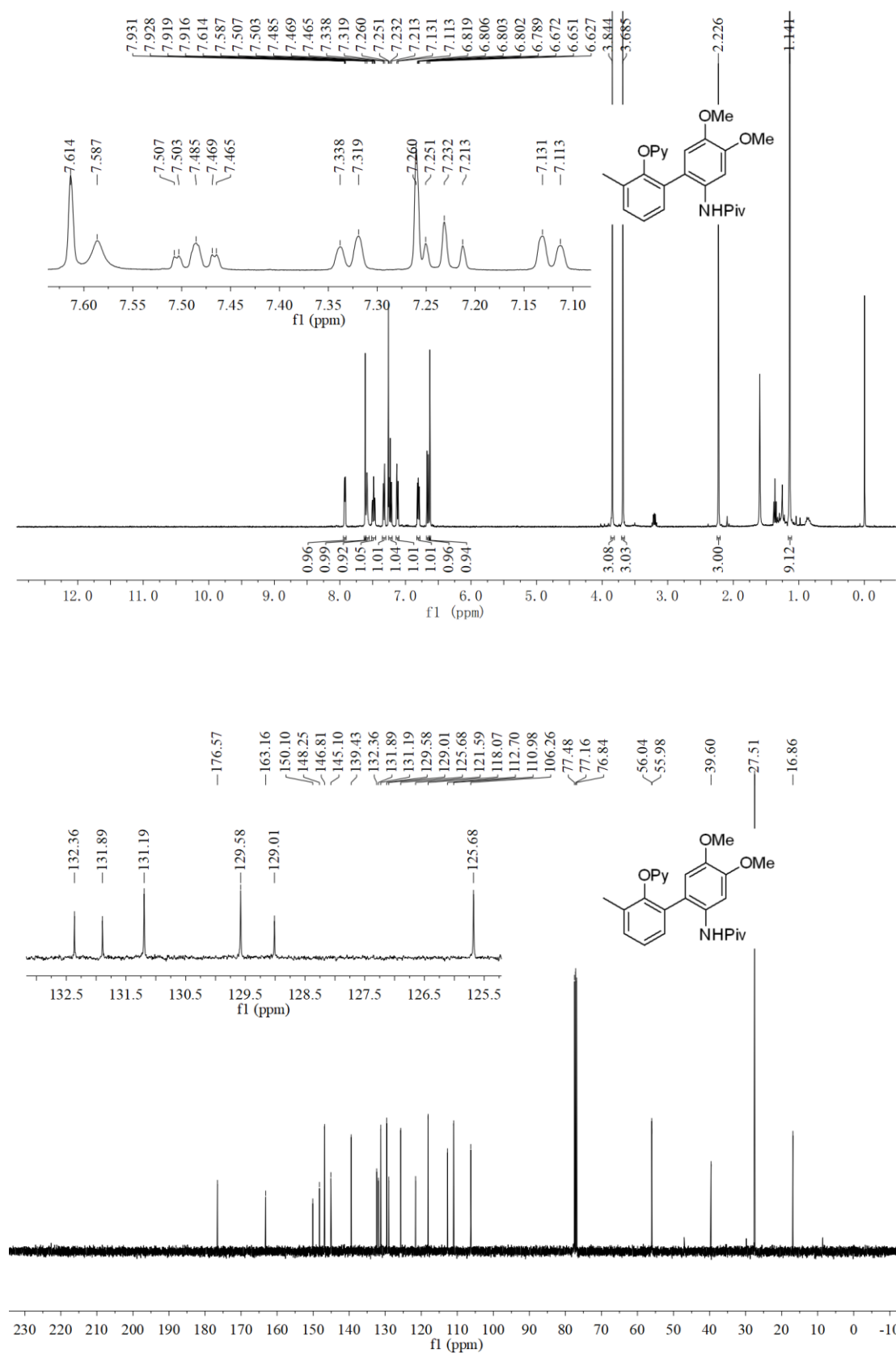


Methyl

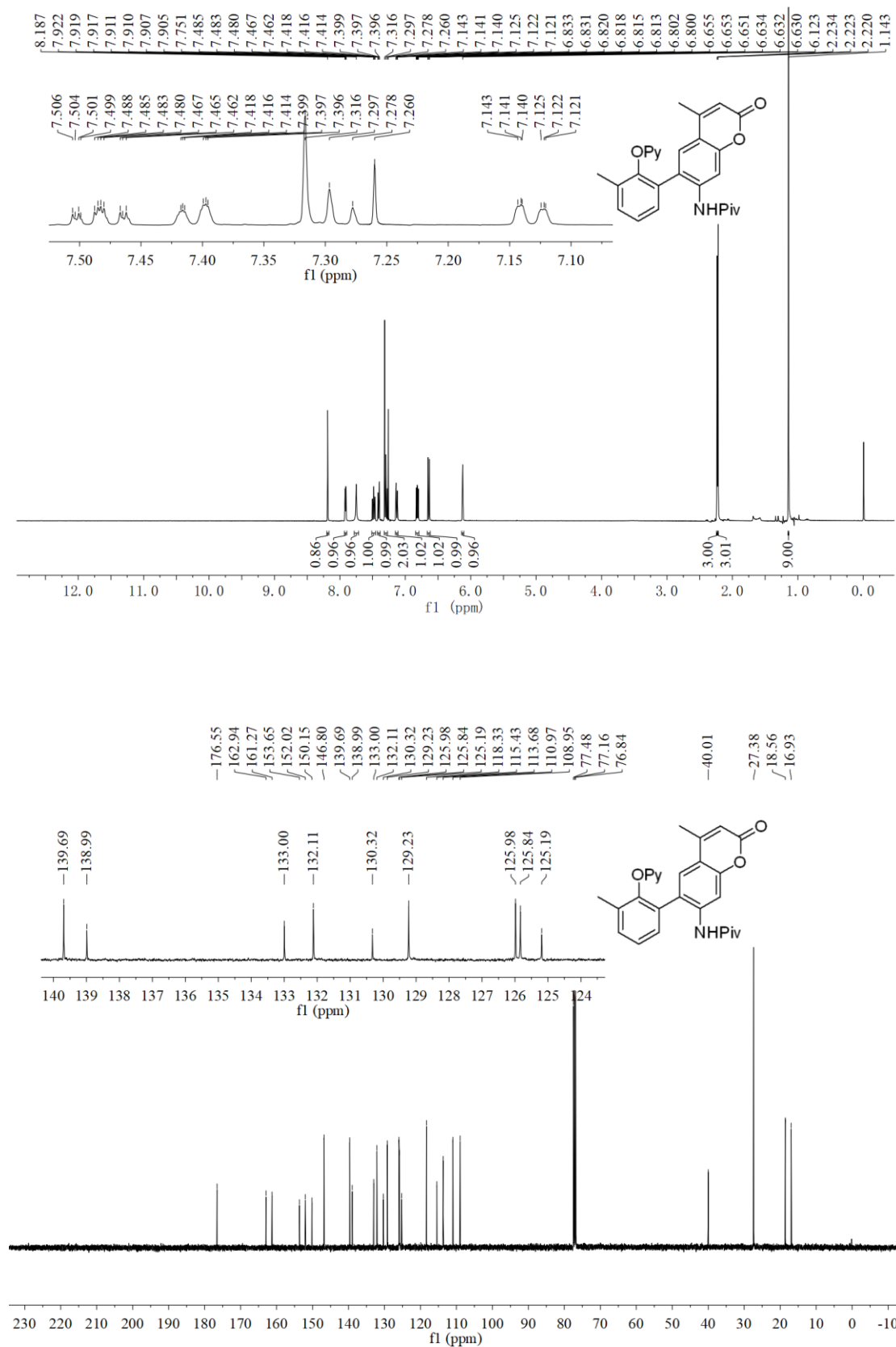
(E)-3-(3'-methyl-6-pivalamido-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl)acrylate (4p)



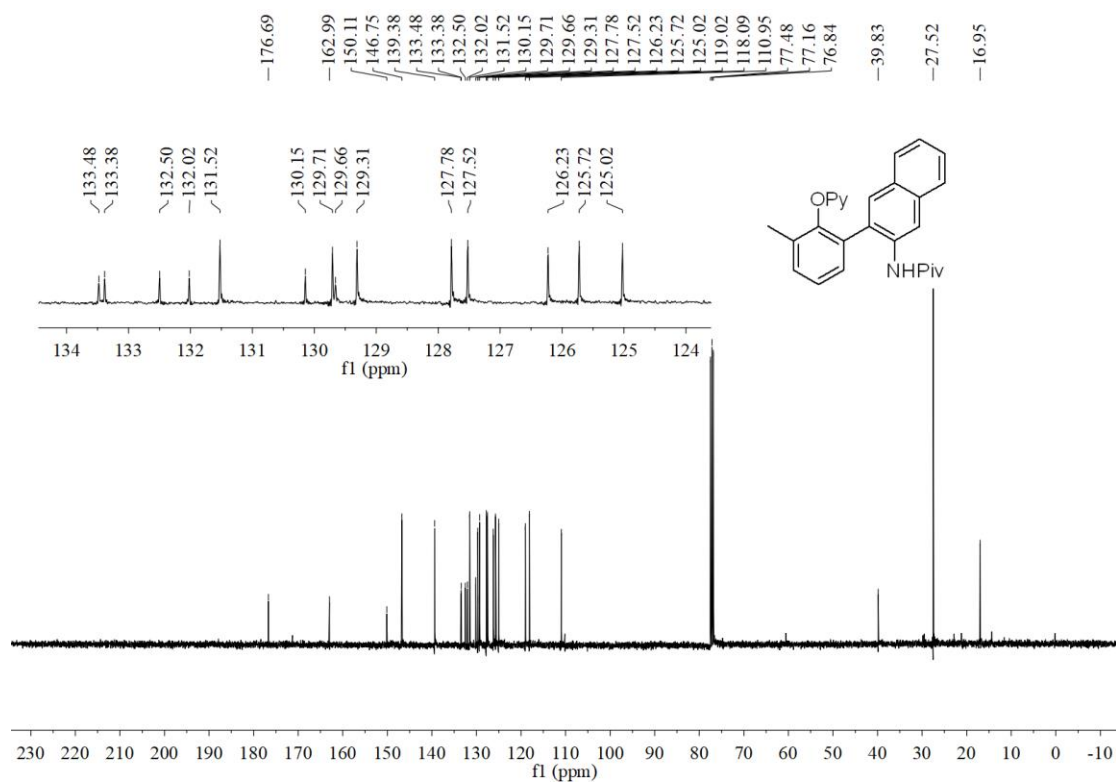
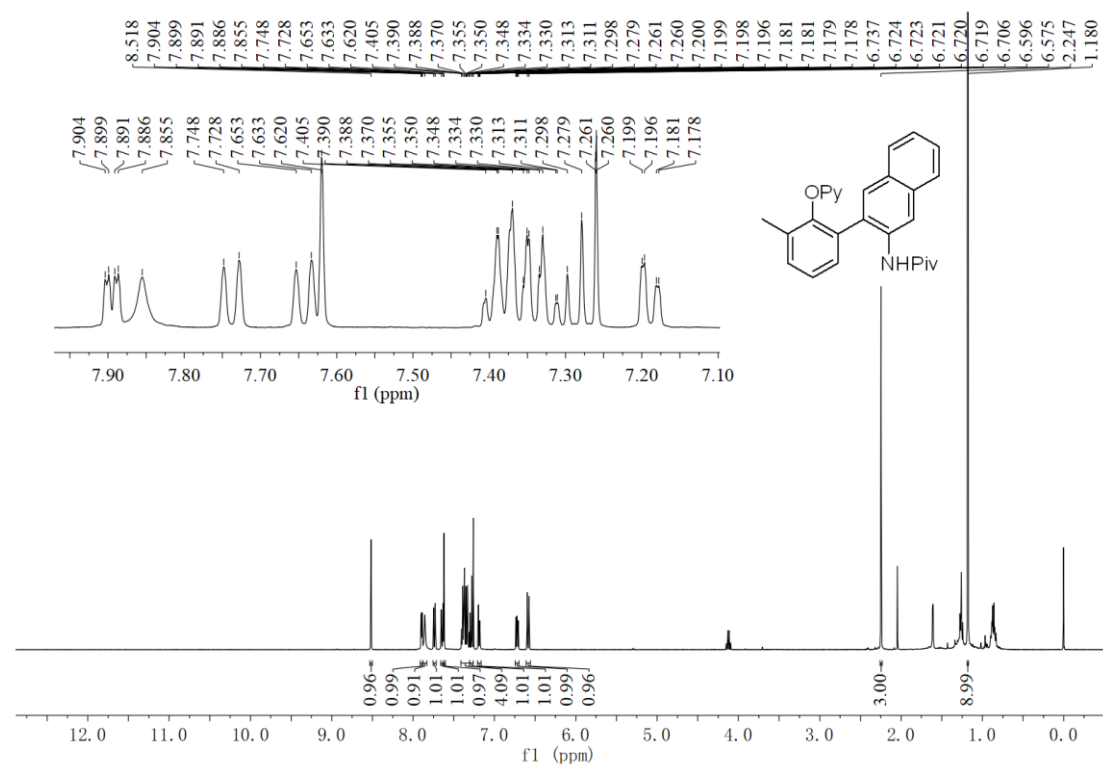
N-(4,5-Dimethoxy-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide
(4q)



***N*-(4-Methyl-6-(3-methyl-2-(pyridin-2-yloxy)phenyl)-2-oxo-2H-chromen-7-yl)pivalamide (4r)**



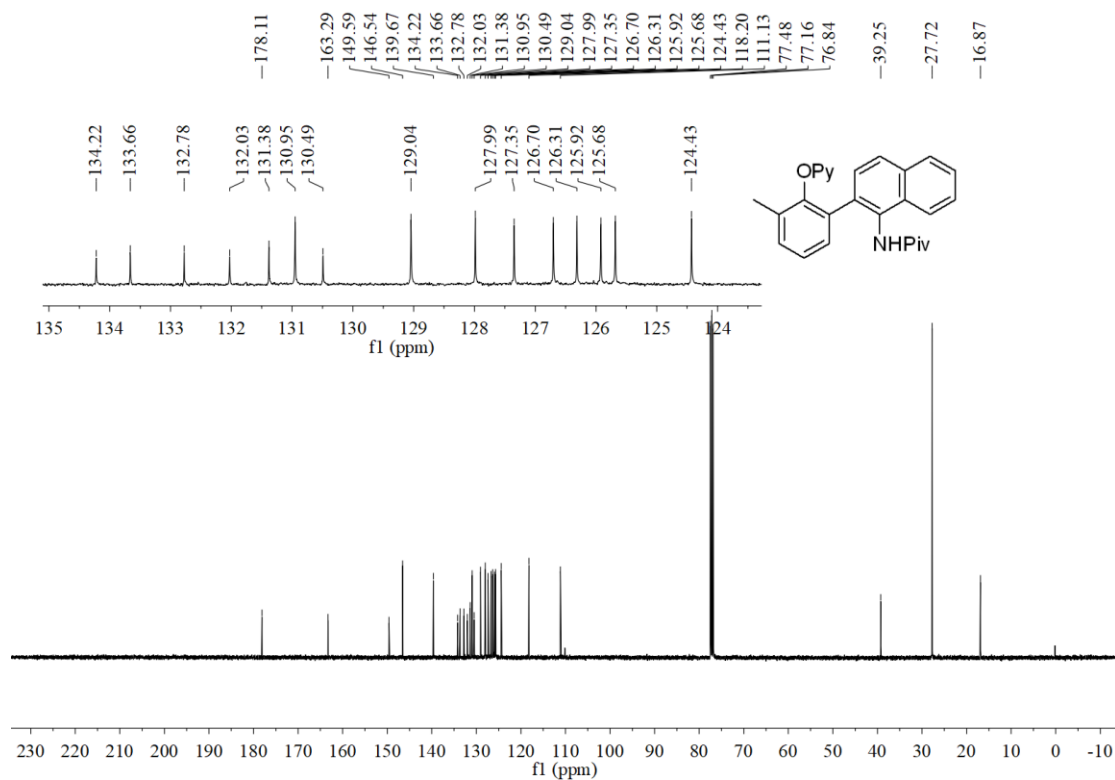
***N*-(3-(3-Methyl-2-(pyridin-2-yloxy)phenyl)naphthalen-2-yl)pivalamide (4s)**

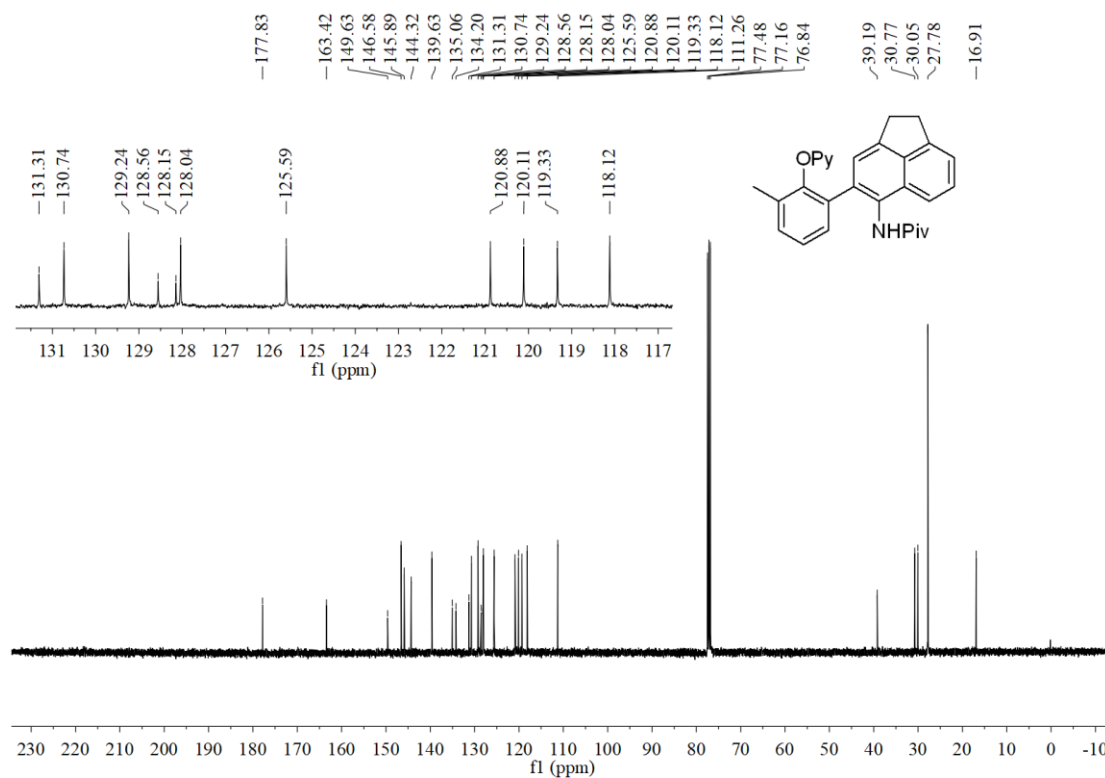


Chemical structure of compound 10: Cc1ccc(cc1)Oc2ccc3ccccc3c2Nc4ccc5ccccc45

¹H NMR spectrum (CDCl₃):

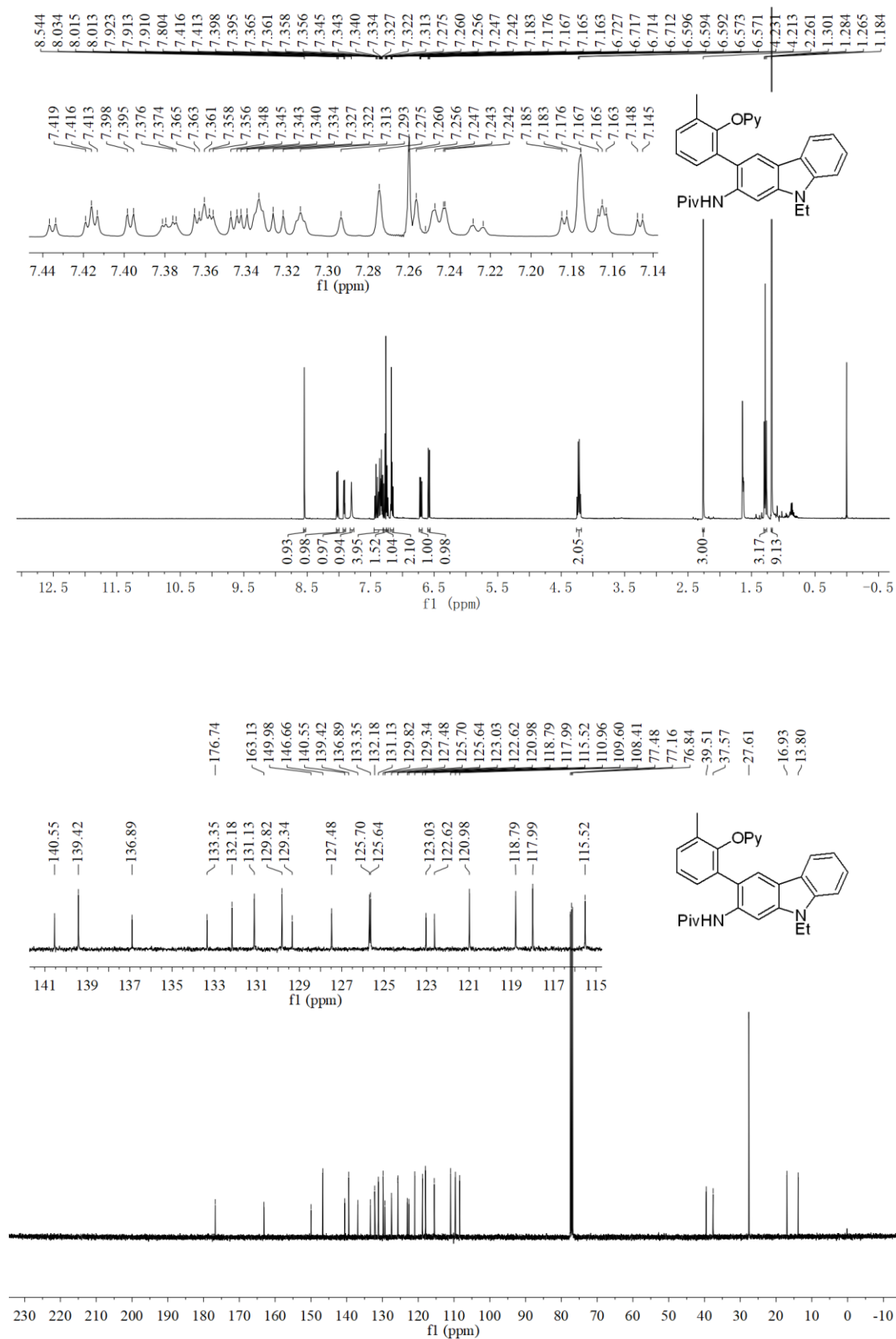
Chemical Shift (ppm)	Integration
7.462, 7.457, 7.445, 7.440, 7.430, 7.426, 7.420, 7.412, 7.410, 7.406, 7.392, 7.387, 7.380, 7.359, 7.317, 7.314, 7.301, 7.299, 7.296, 7.294, 7.260, 7.234, 7.215, 7.197, 7.187, 7.182, 7.168, 7.163	0.90, 0.95, 1.96, 1.00, 3.01, 0.96, 0.97, 1.02, 0.97, 0.98, 0.94
7.182, 6.767, 6.754, 6.751, 6.749, 6.736, 6.669, 6.648, 2.180, 1.206	3.00, 9.09



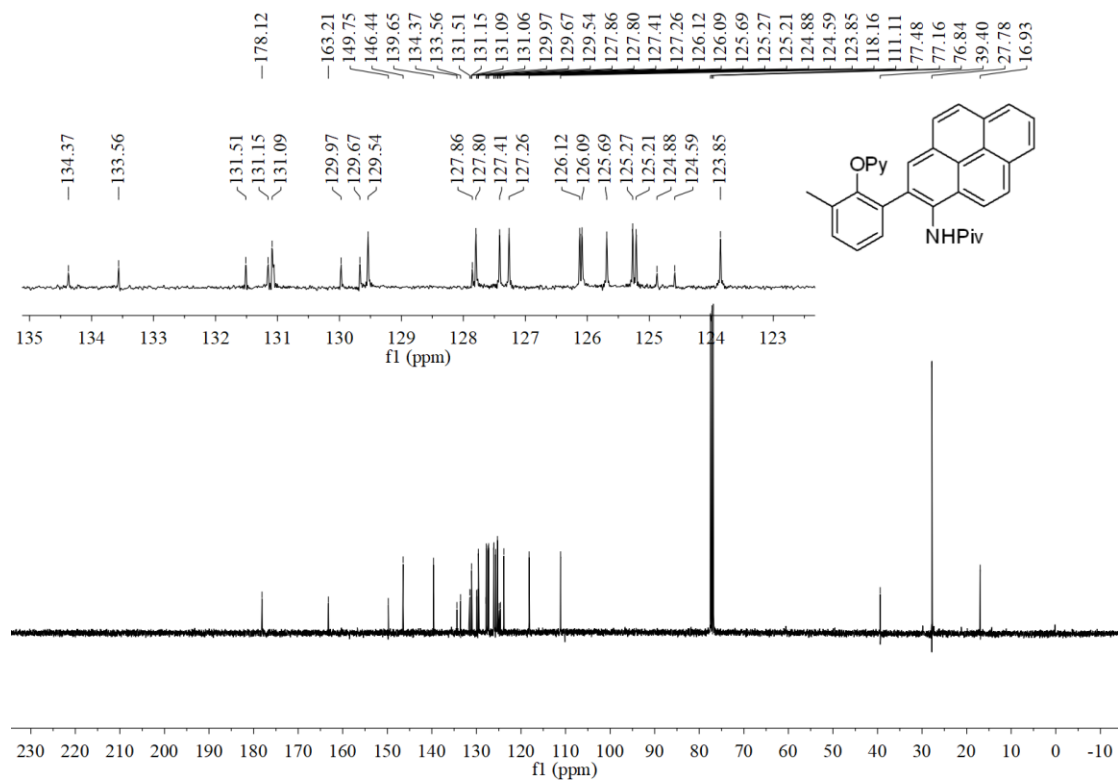
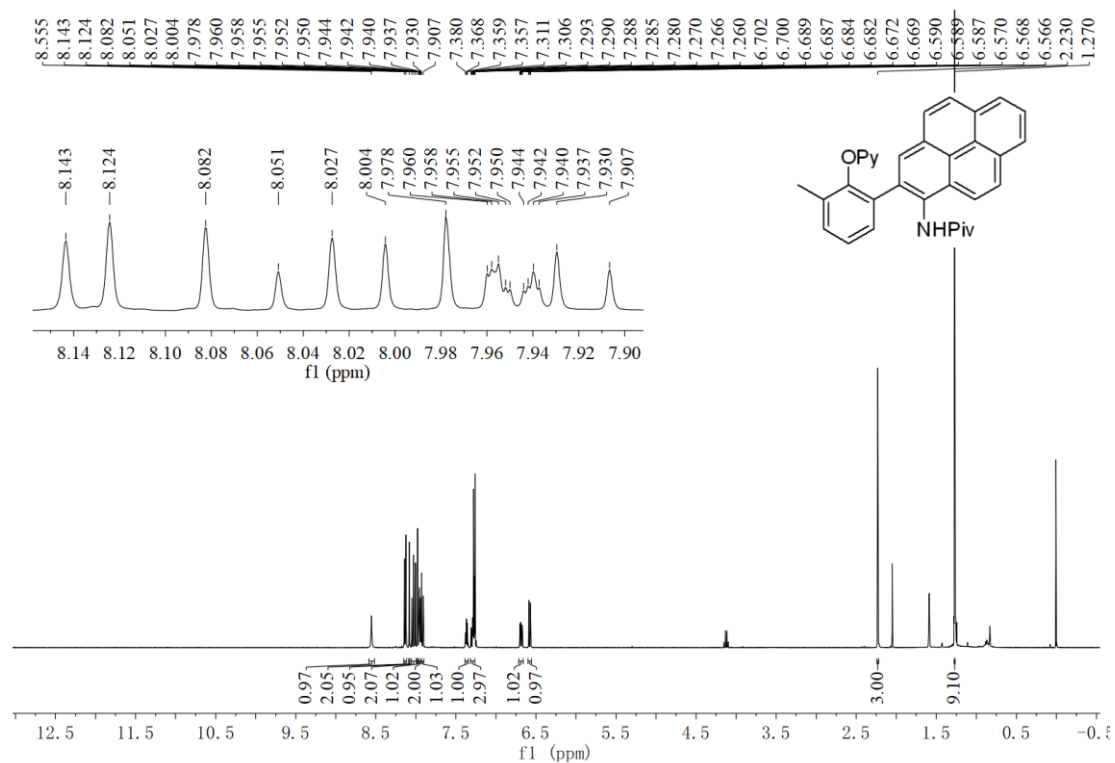
[illegible]

***N*-(9-Ethyl-3-(3-methyl-2-(pyridin-2-yloxy)phenyl)-9*H*-carbazol-2-yl)pivalamide**

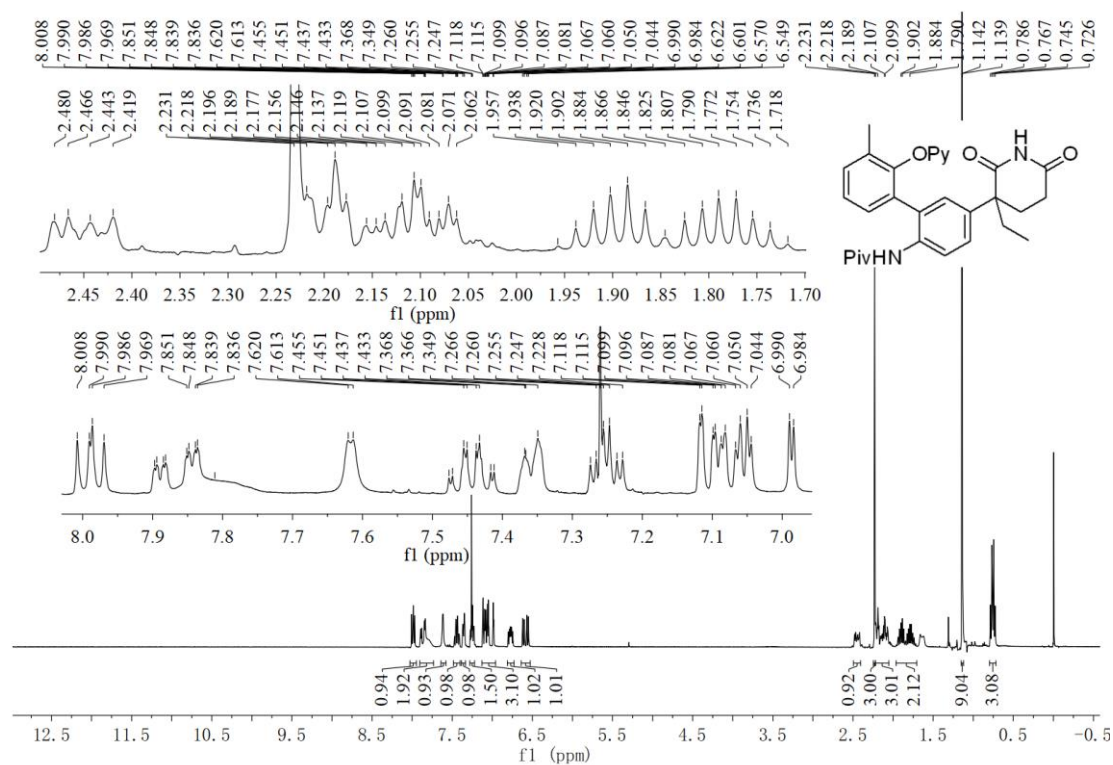
(4v)



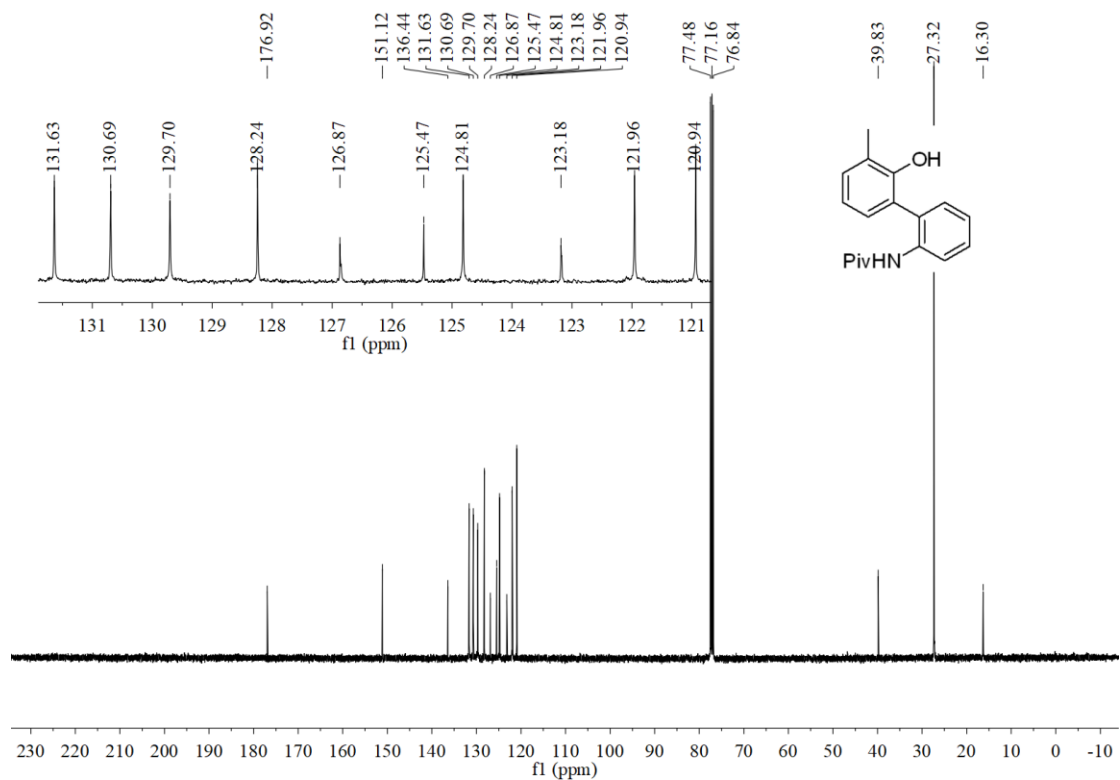
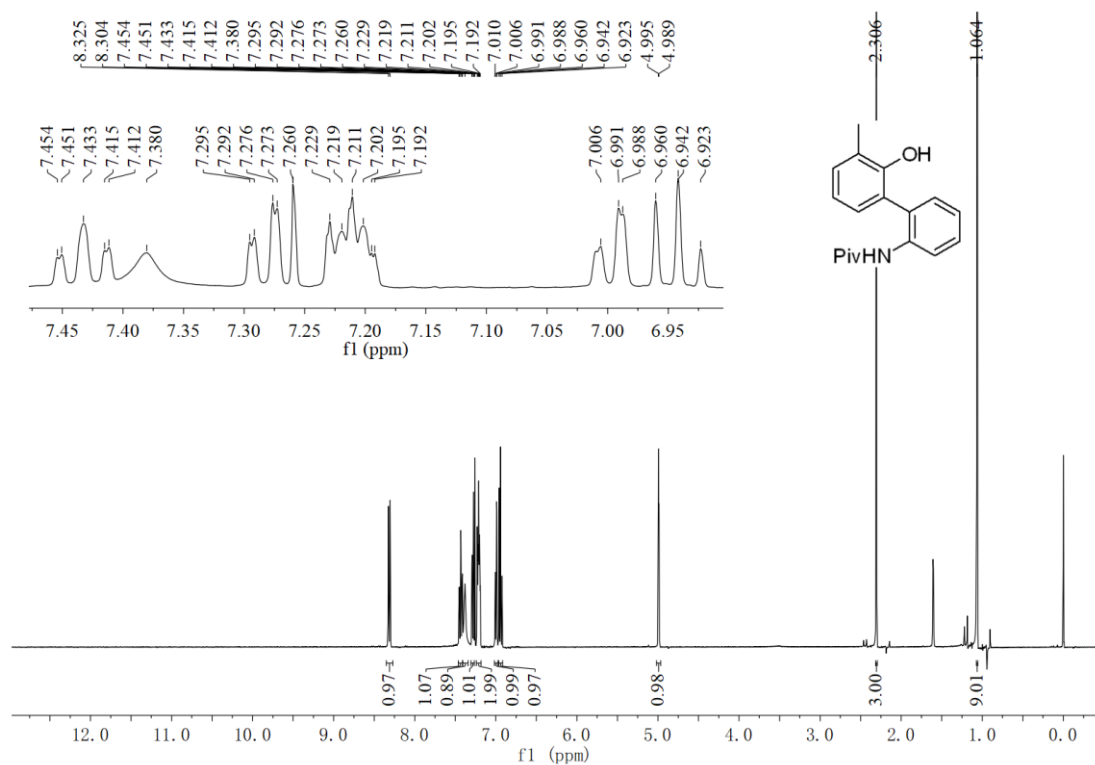
***N*-(2-(3-Methyl-2-(pyridin-2-yloxy)phenyl)pyren-1-yl)pivalamide (4w)**



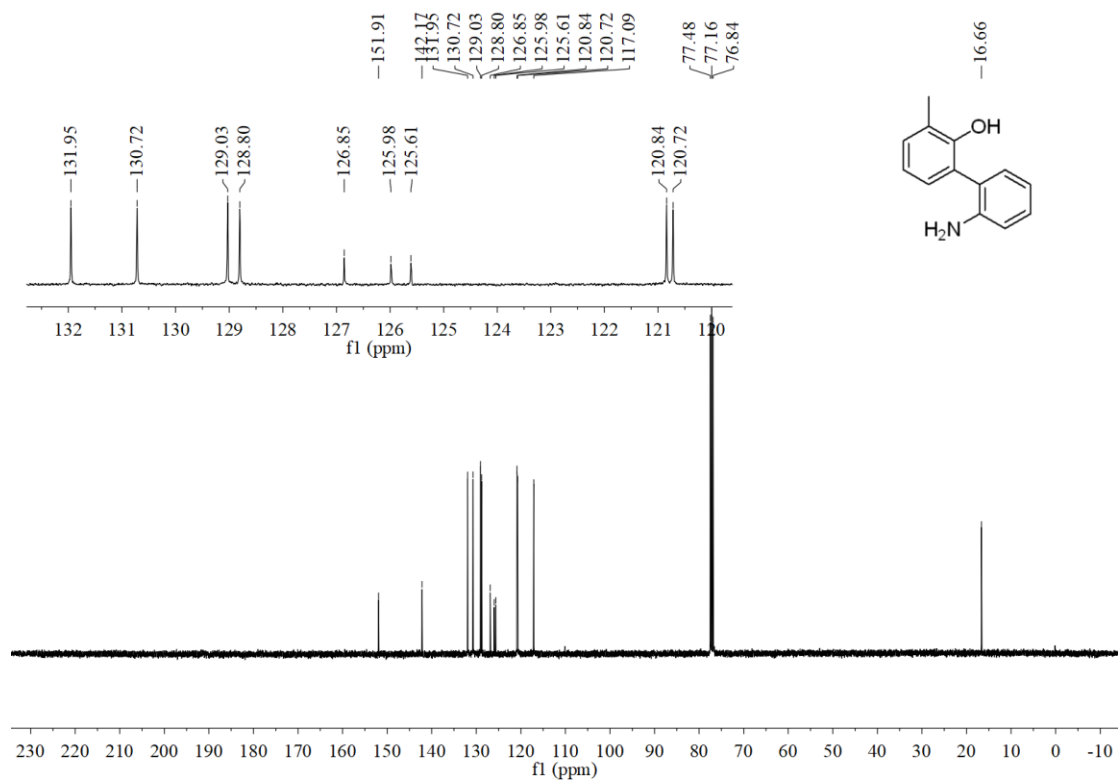
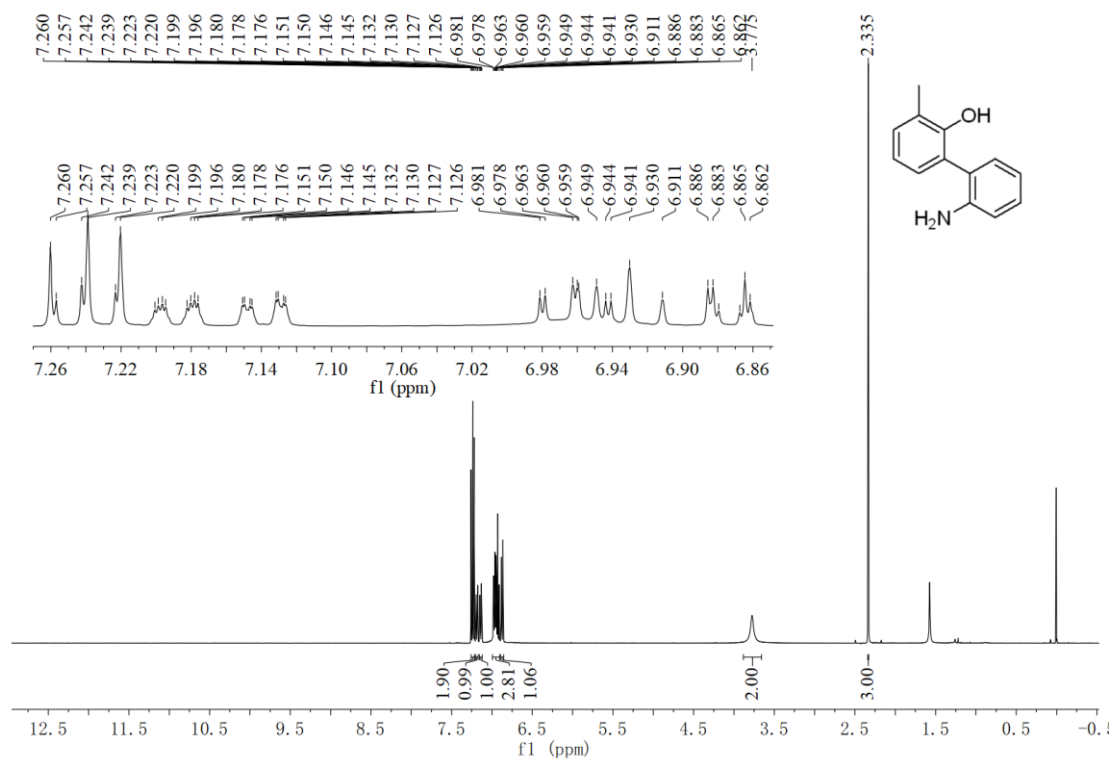
***N*-(5-(3-Ethyl-2,6-dioxopiperidin-3-yl)-3'-methyl-2'-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)pivalamide (4x)**



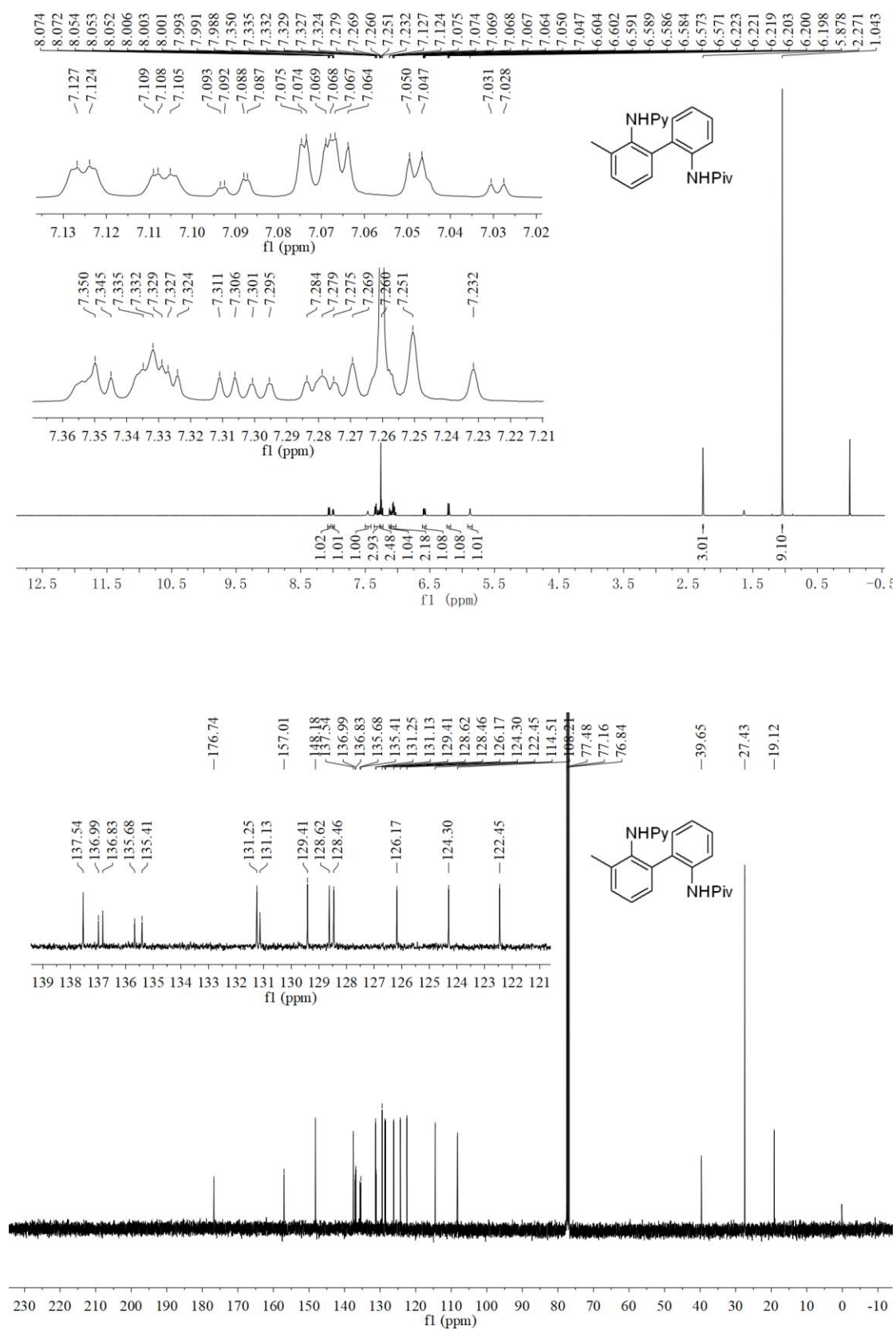
***N*-(2'-Hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (5)**



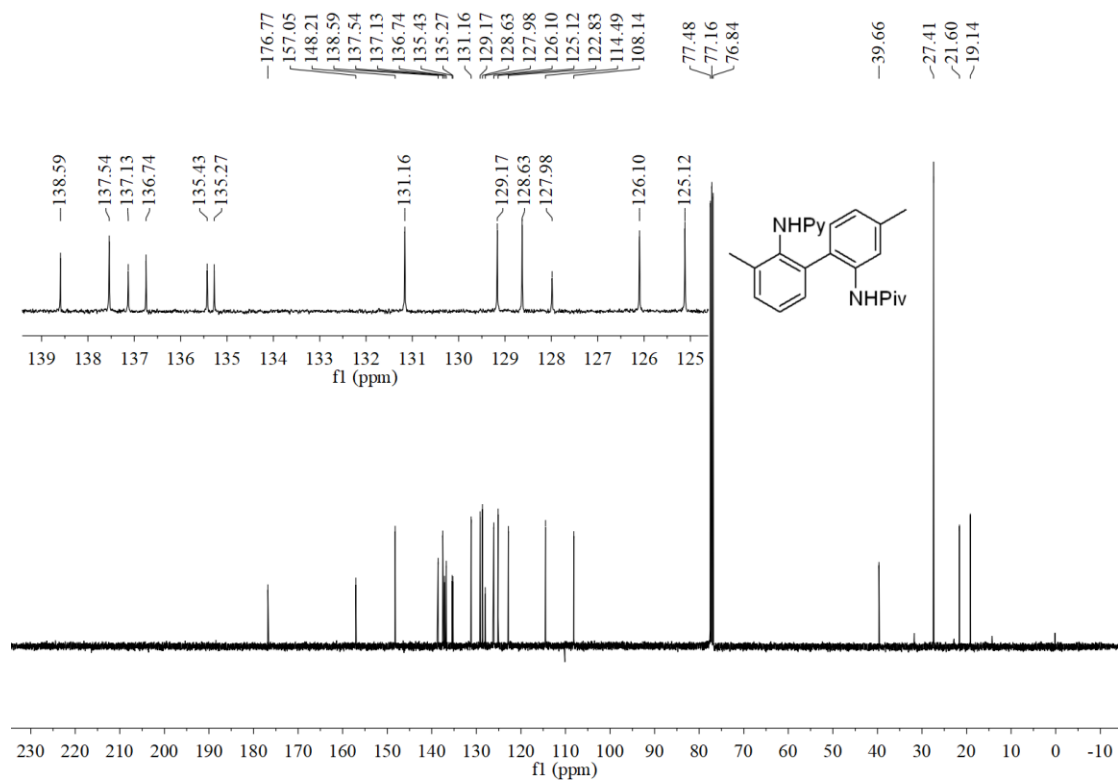
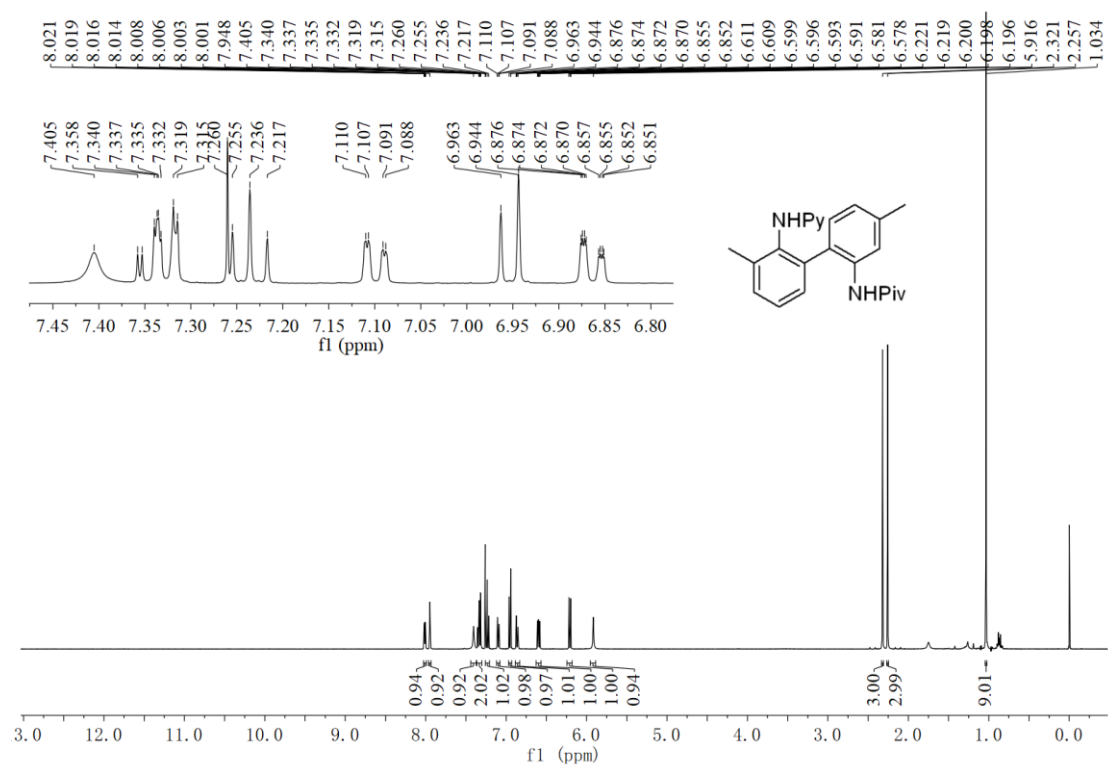
N-(2'-Hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (6)



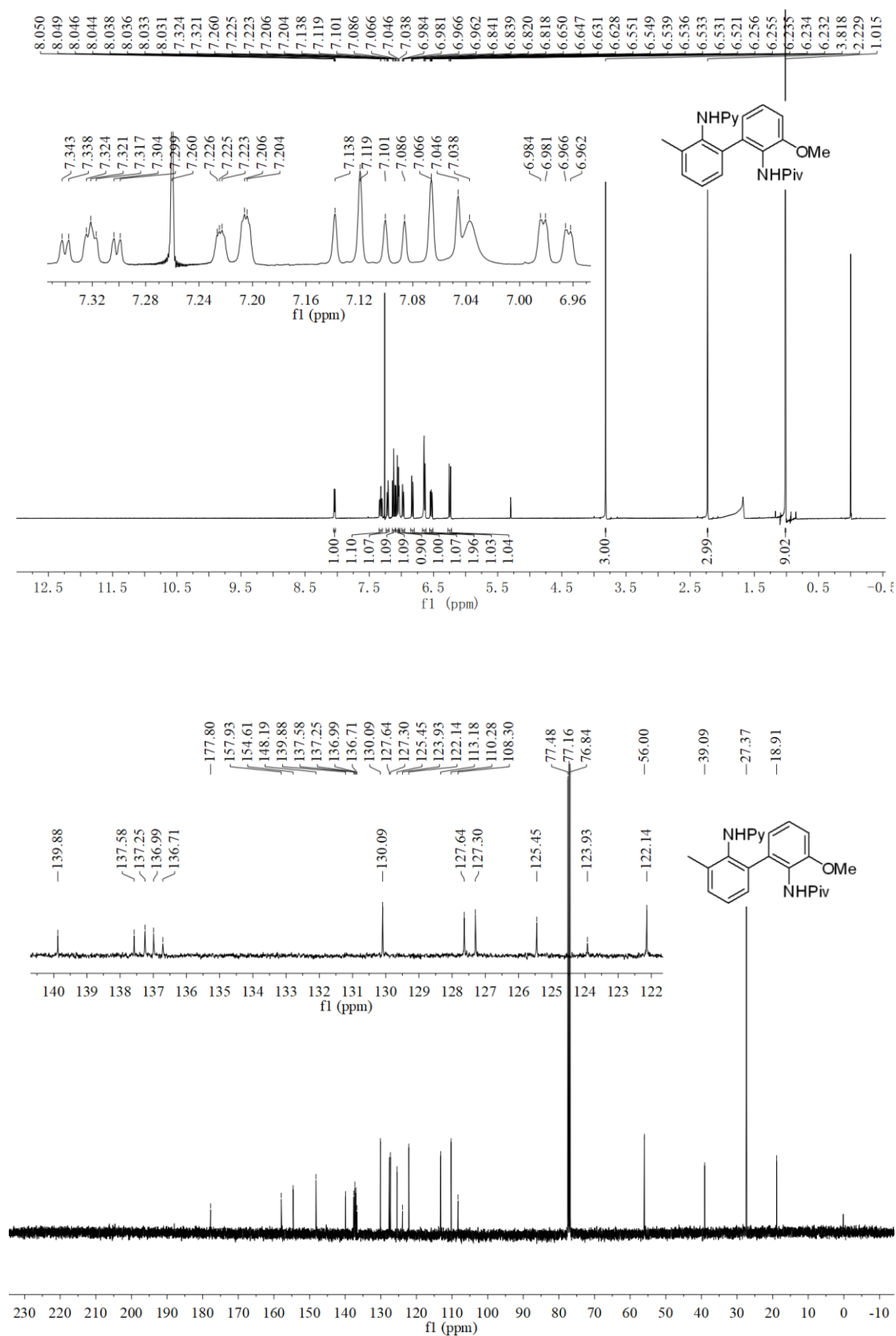
***N*-(3'-Methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10a)**



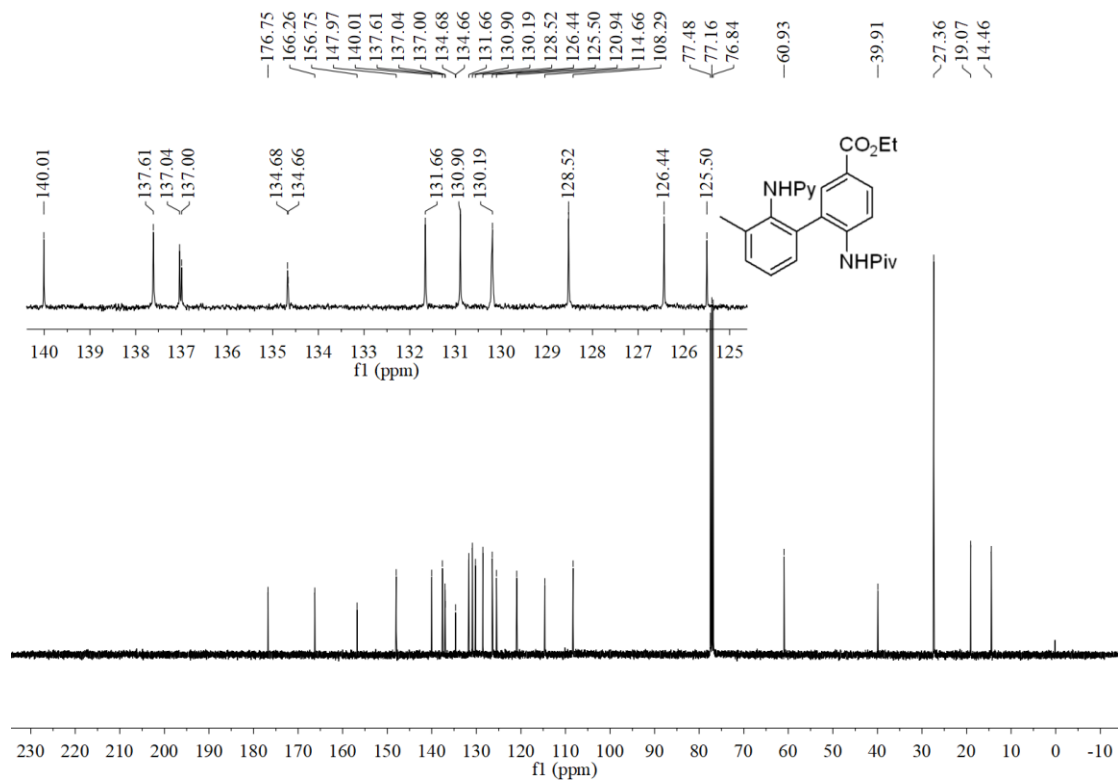
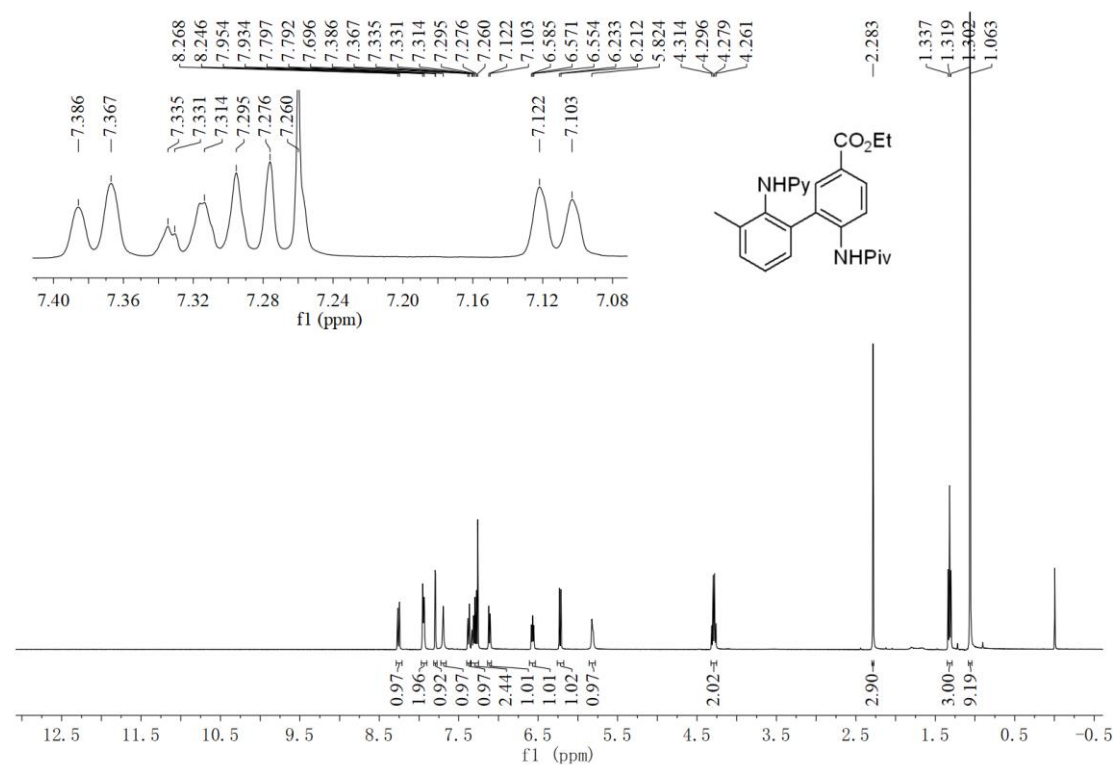
***N*-(3',4-Dimethyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10b)**



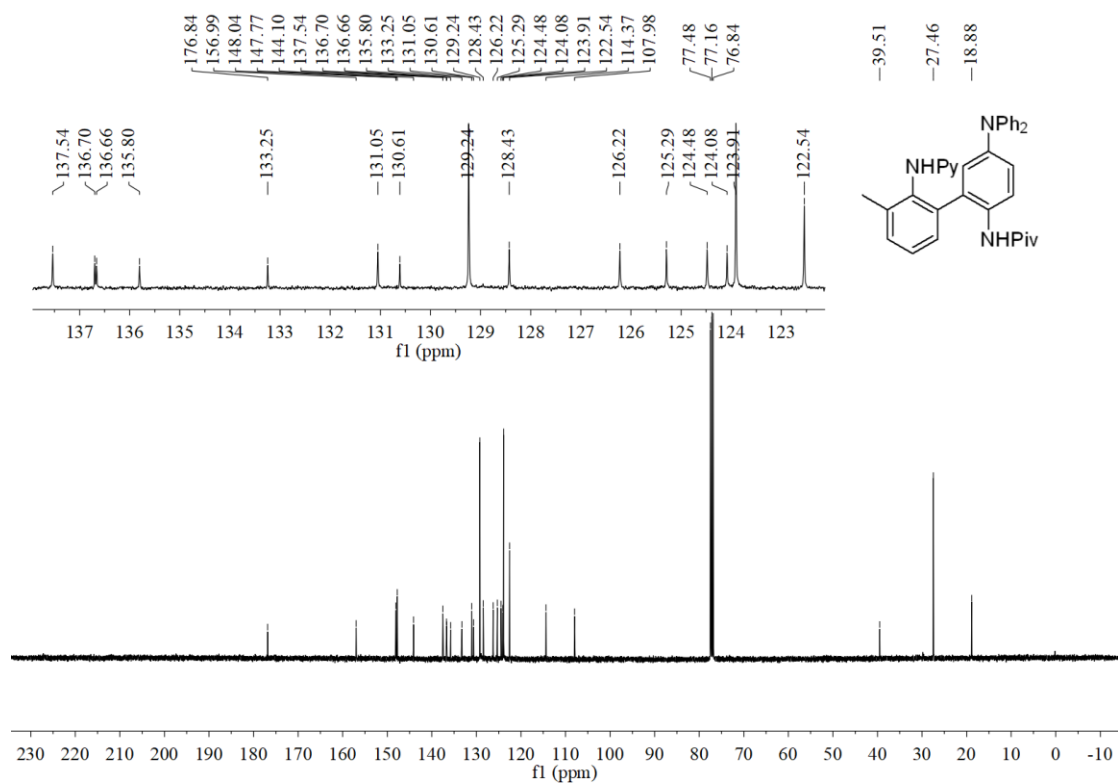
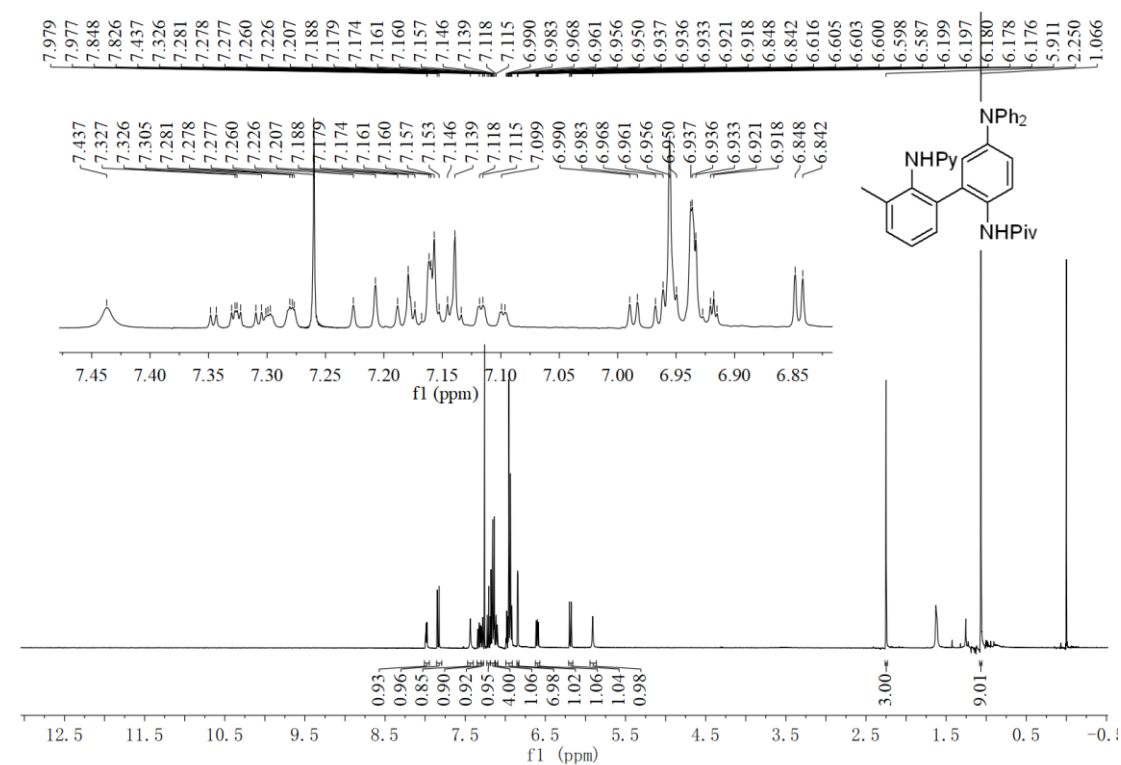
***N*-(3-Methoxy-3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide**
(10c)



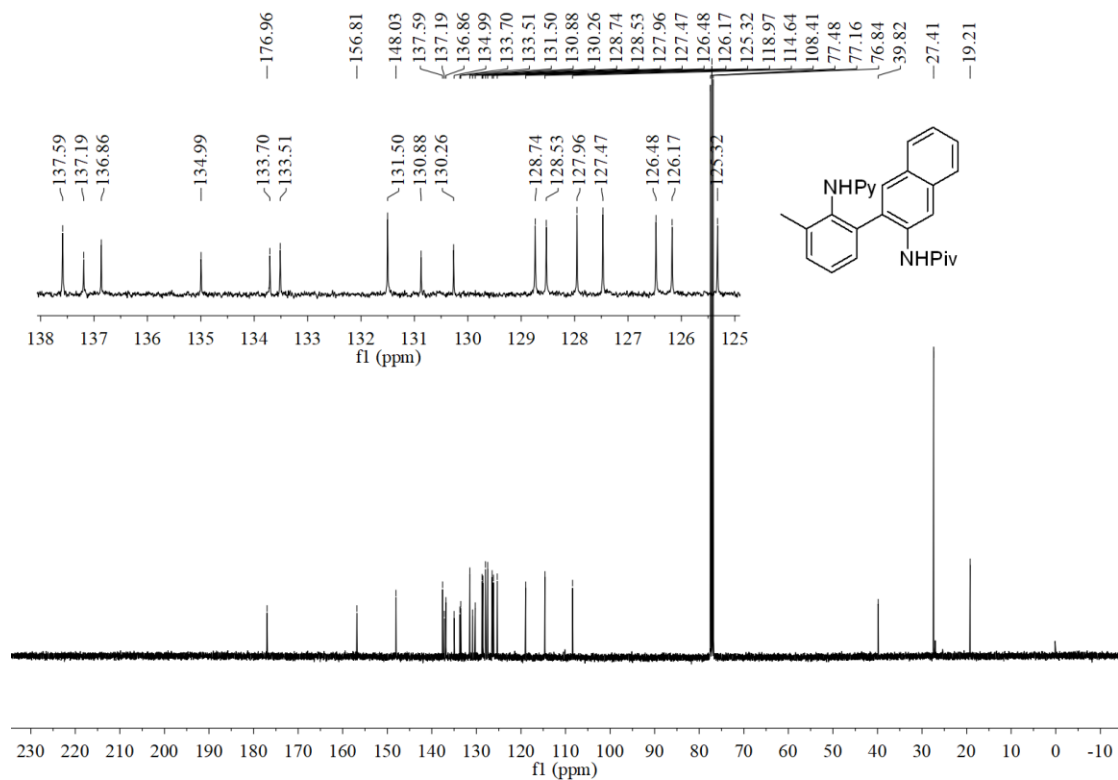
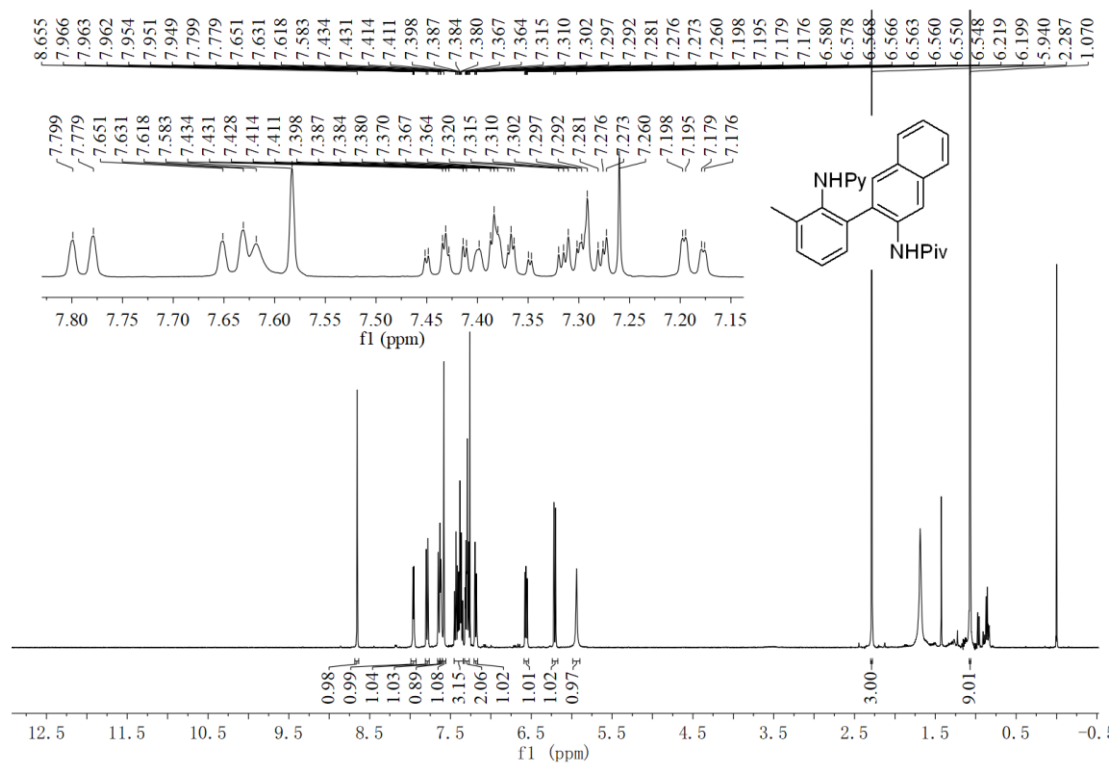
Ethyl 3'-methyl-6-pivalamido-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-carboxylate
(10d)



***N*-(5-(Diphenylamino)-3'-methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10e)**



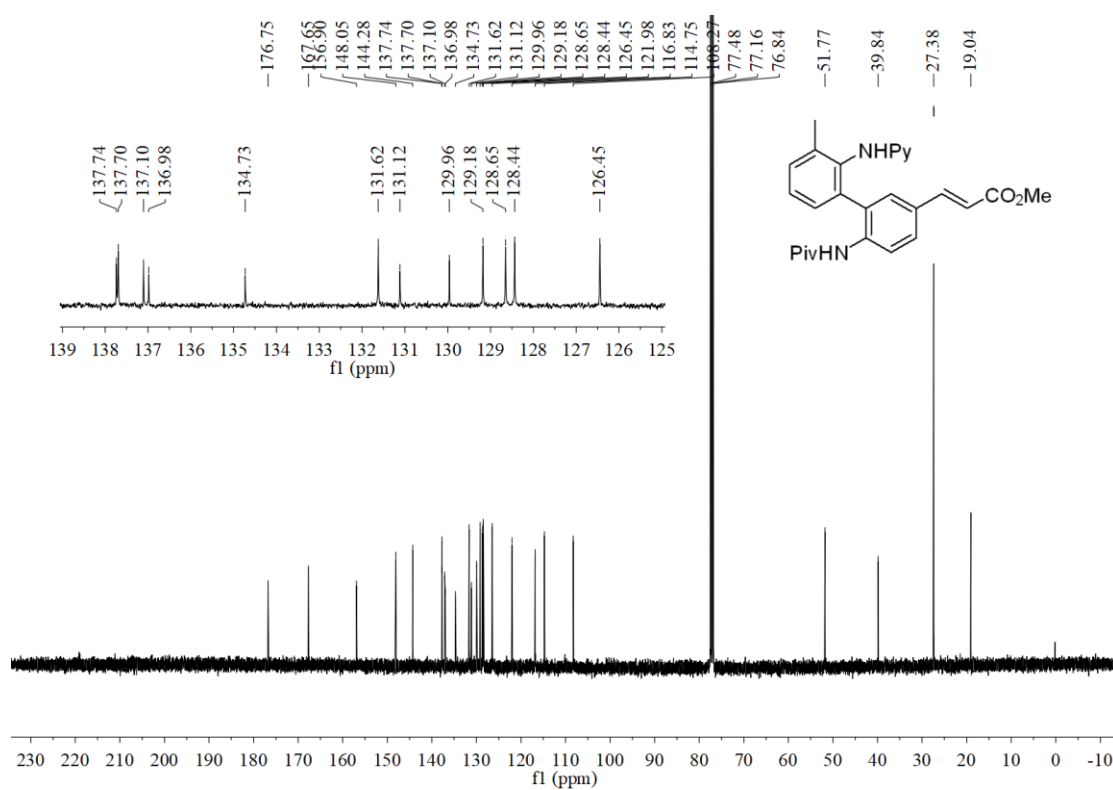
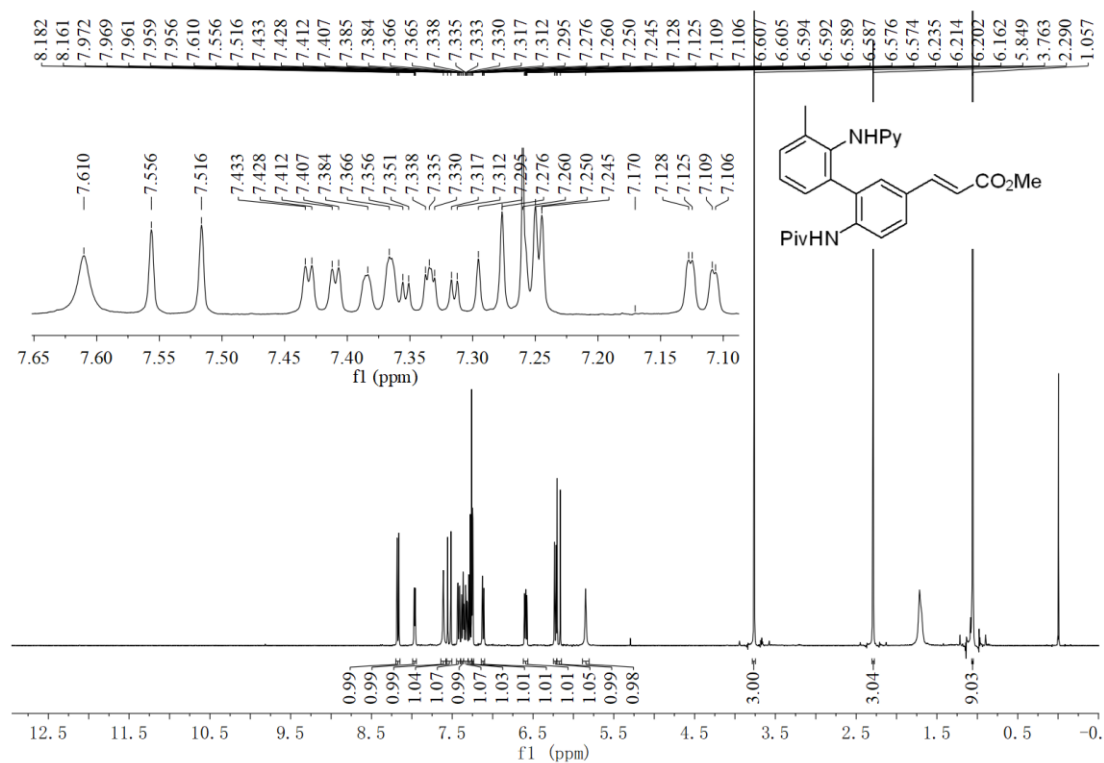
N-(3-(3-Methyl-2-(pyridin-2-ylamino)phenyl)naphthalen-2-yl)pivalamide (10f)



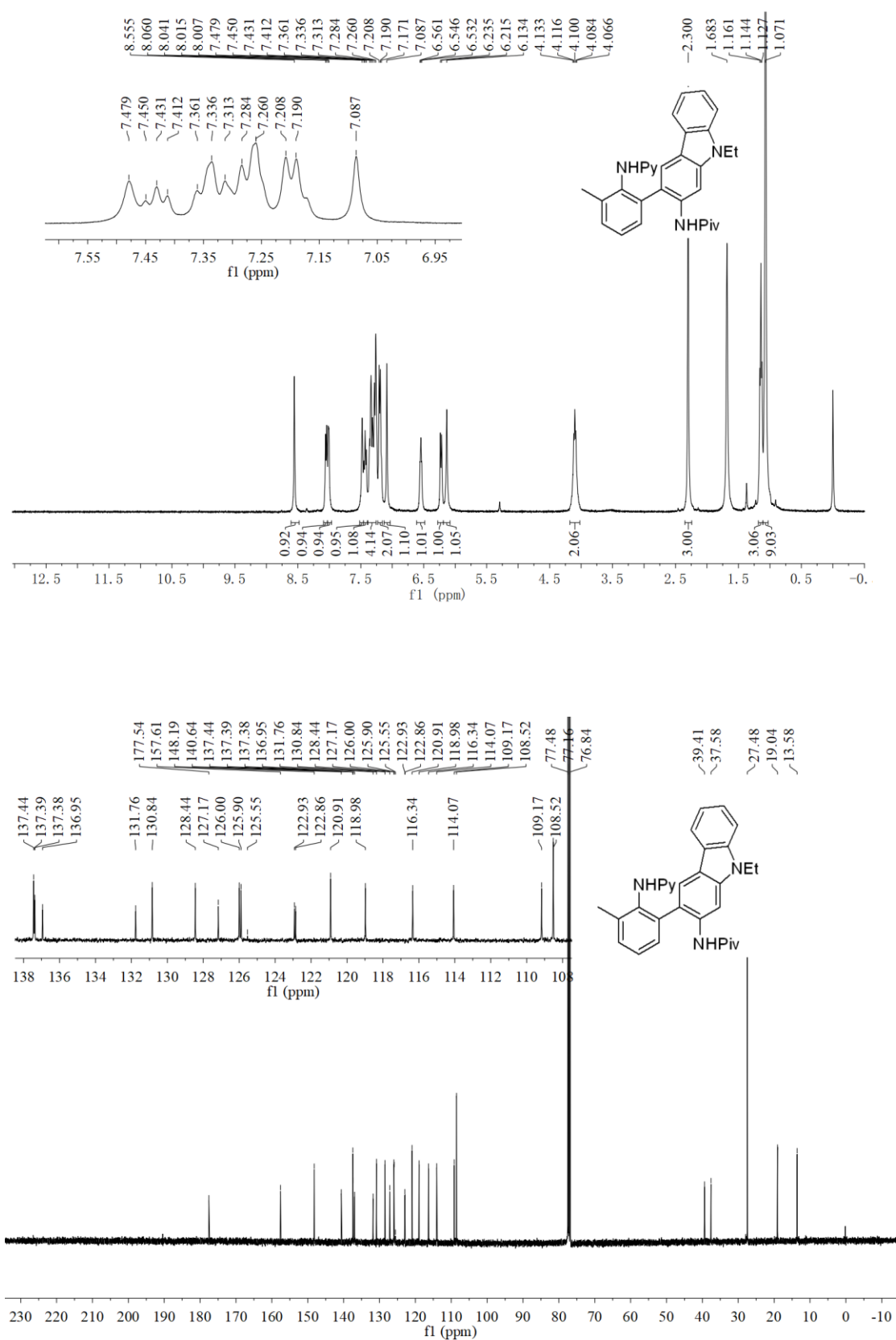
Methyl

(*E*)-3-(3'-methyl-6-pivalamido-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-yl)acrylate

(10g)



***N*-(9-Ethyl-3-(3-methyl-2-(pyridin-2-ylamino)phenyl)-9*H*-carbazol-2-yl)pivalamide
(10h)**



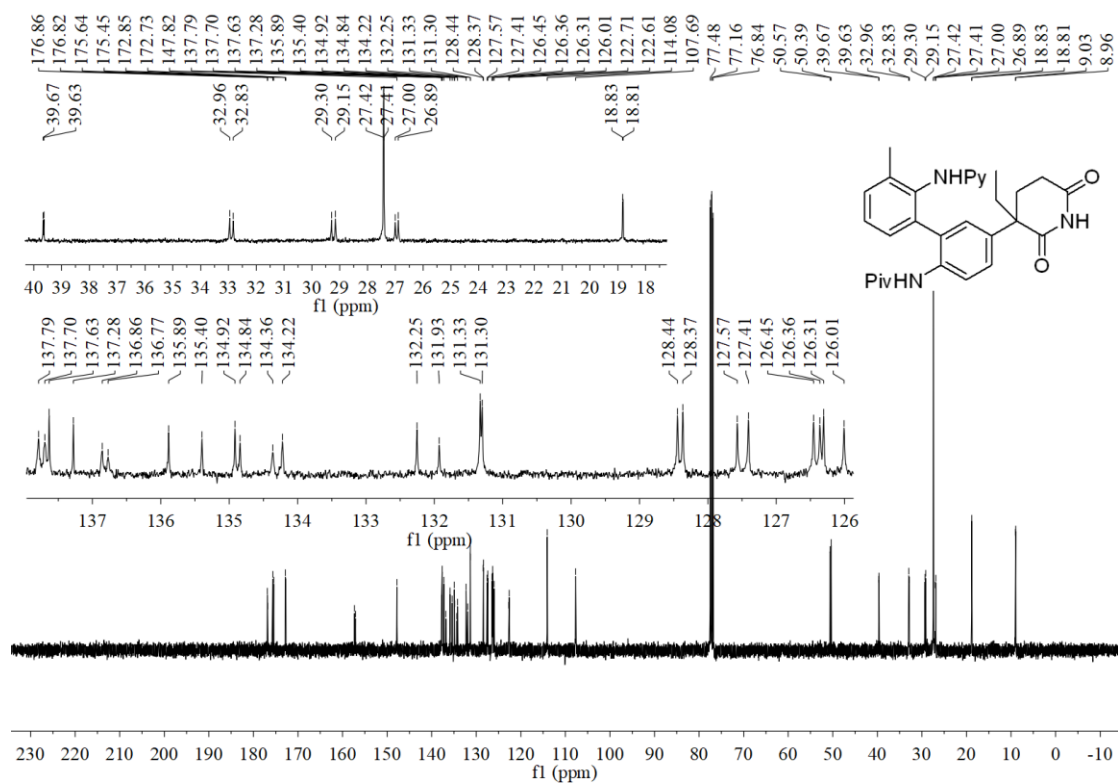
Chemical structure of compound 10 is shown, featuring a 2-(4-(N-pyridin-2-ylphenyl)phenyl)pyrrolidine-1-one moiety attached to a 4-(4-methylphenyl)pyrrolidine-1-one moiety via a methylene bridge. The labels 'NHPy' and 'PivHN' indicate the respective pyrrolidine and phenyl groups.

The ^1H NMR spectrum (top) shows peaks in the aliphatic region (1.60–2.50 ppm) and aromatic region (6.95–7.60 ppm). The aromatic region is expanded (middle) to show detailed peak assignments. Integration values are provided below the peaks.

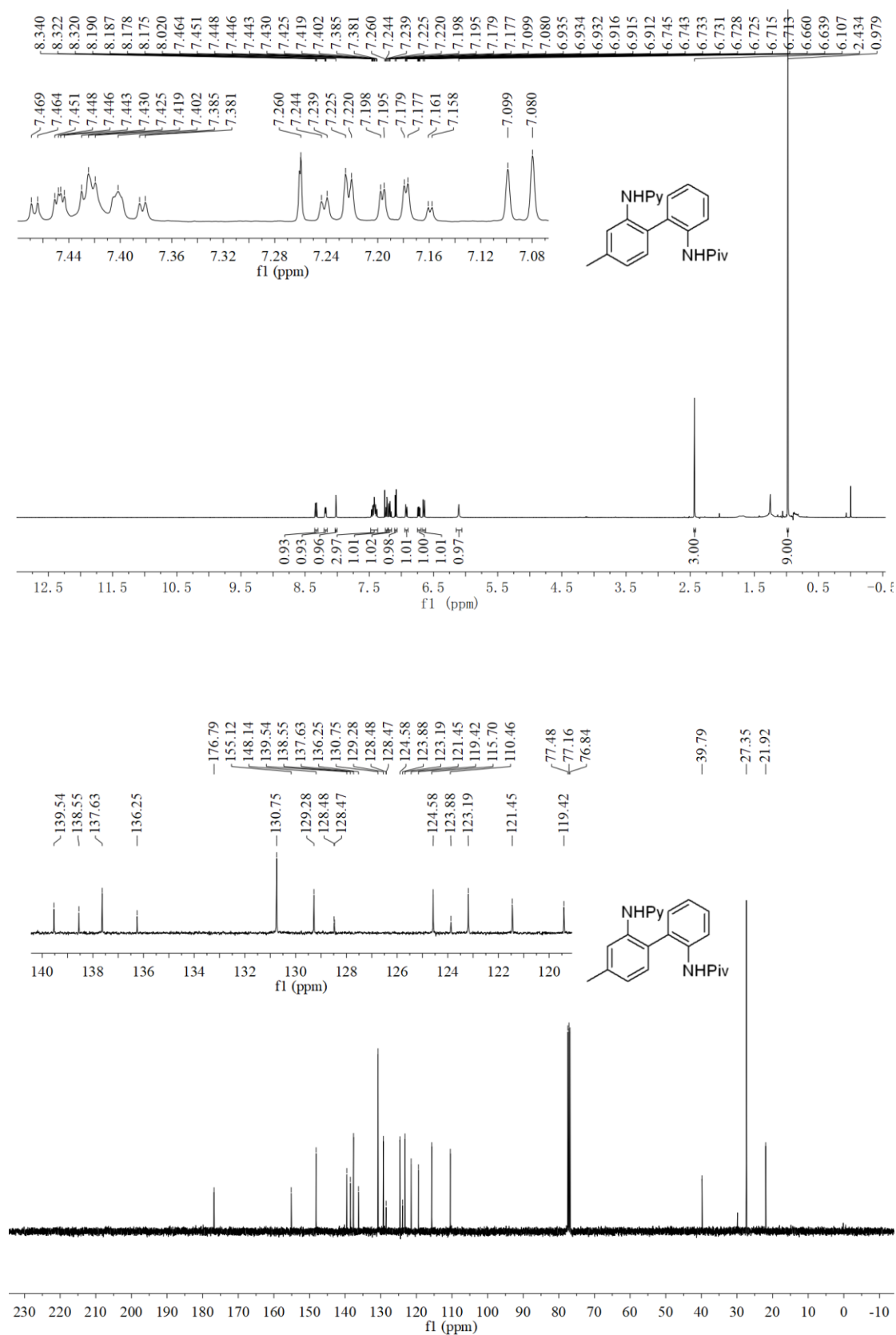
Peak assignments (ppm):

- Aliphatic region (1.60–2.50 ppm): 2.453, 2.409, 2.315, 2.294, 2.285, 2.271, 2.264, 2.176, 2.164, 2.156, 2.136, 2.131, 2.125, 2.110, 2.104, 2.098, 2.081, 2.072, 2.063, 2.038, 2.028, 1.997, 1.988, 1.966, 1.849, 1.832, 1.826, 1.808, 1.792, 1.773, 1.710, 1.693, 1.675, 1.658, 1.640.
- Aromatic region (6.95–7.60 ppm): 7.577, 7.537, 7.365, 7.349, 7.332, 7.313, 7.309, 7.302, 7.298, 7.283, 7.273, 7.261, 7.240, 7.254, 7.245, 7.235, 7.219, 7.114, 7.106, 7.092, 7.085, 7.066, 7.060, 7.044, 7.039, 6.984, 6.979, 6.957, 6.953.

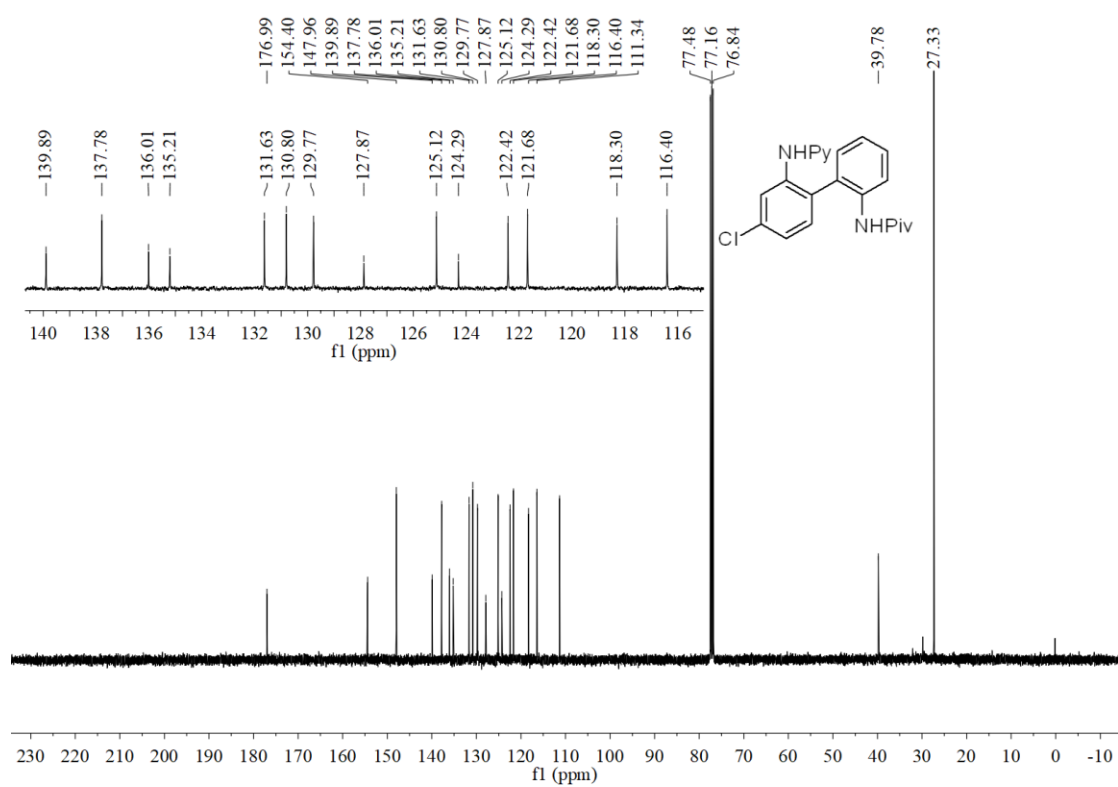
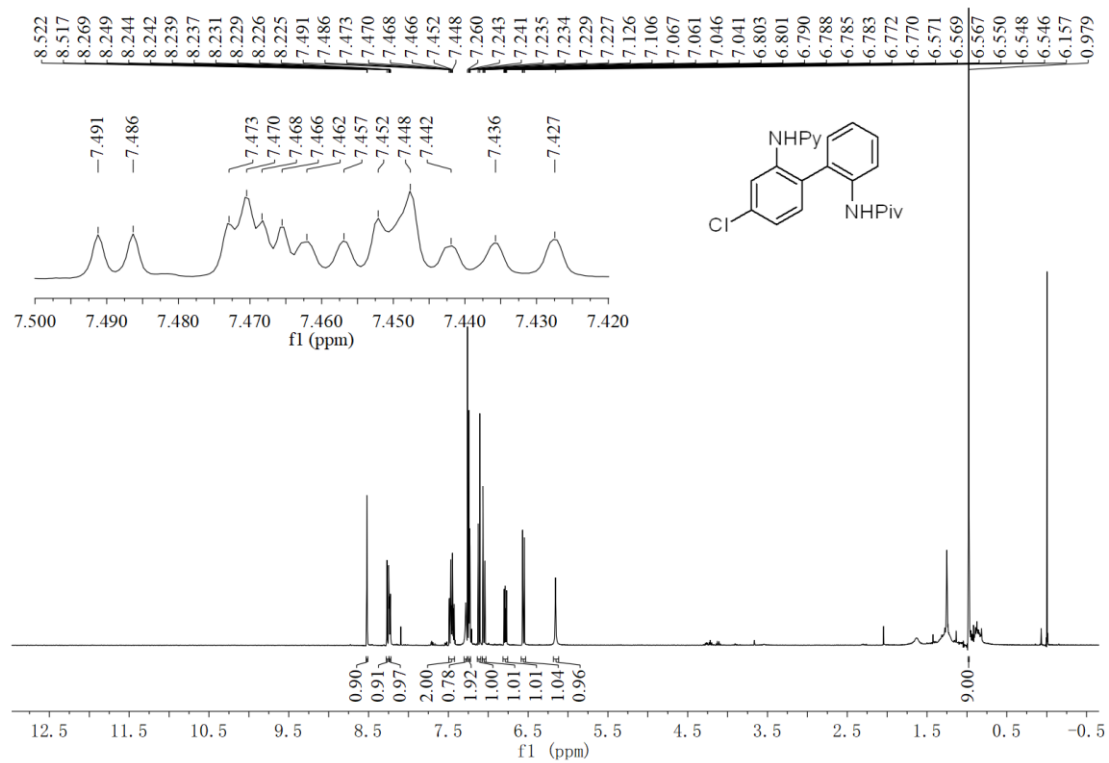
Integration values (bottom): 0.87, 1.91, 3.38, 2.03, 0.99, 0.99, 0.90, 1.03, 3.99, 3.14, 2.48, 1.09, 9.01, 3.00.



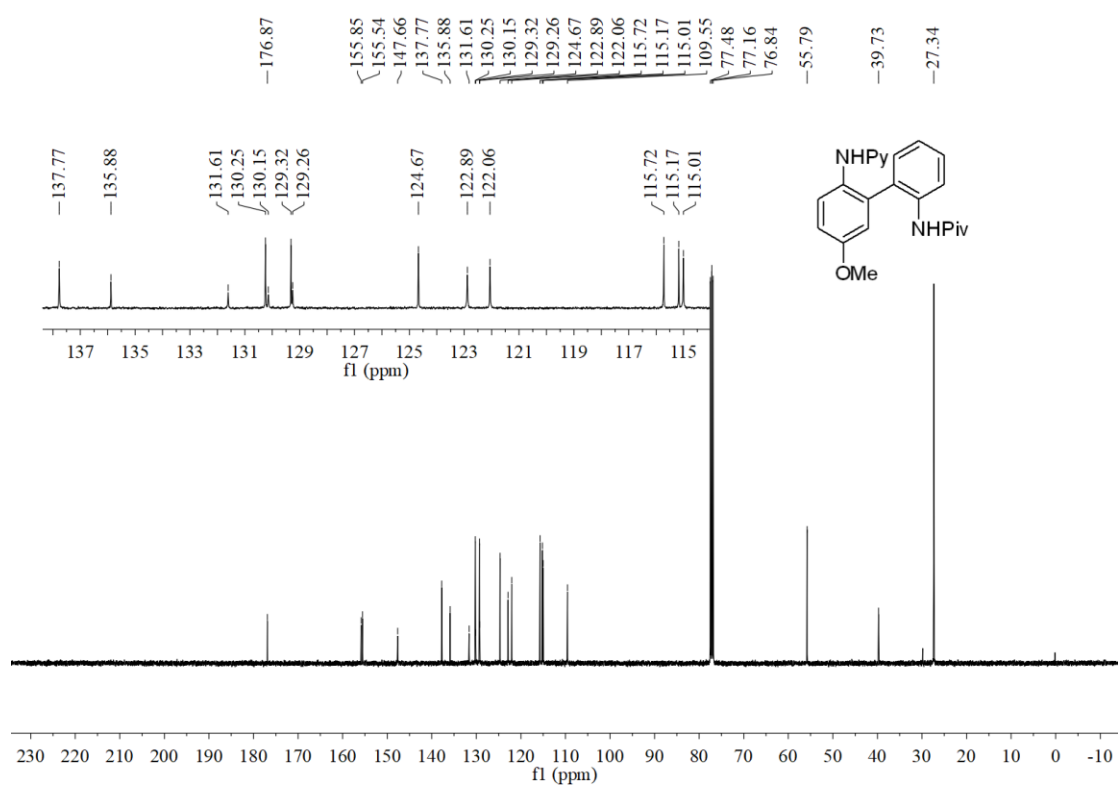
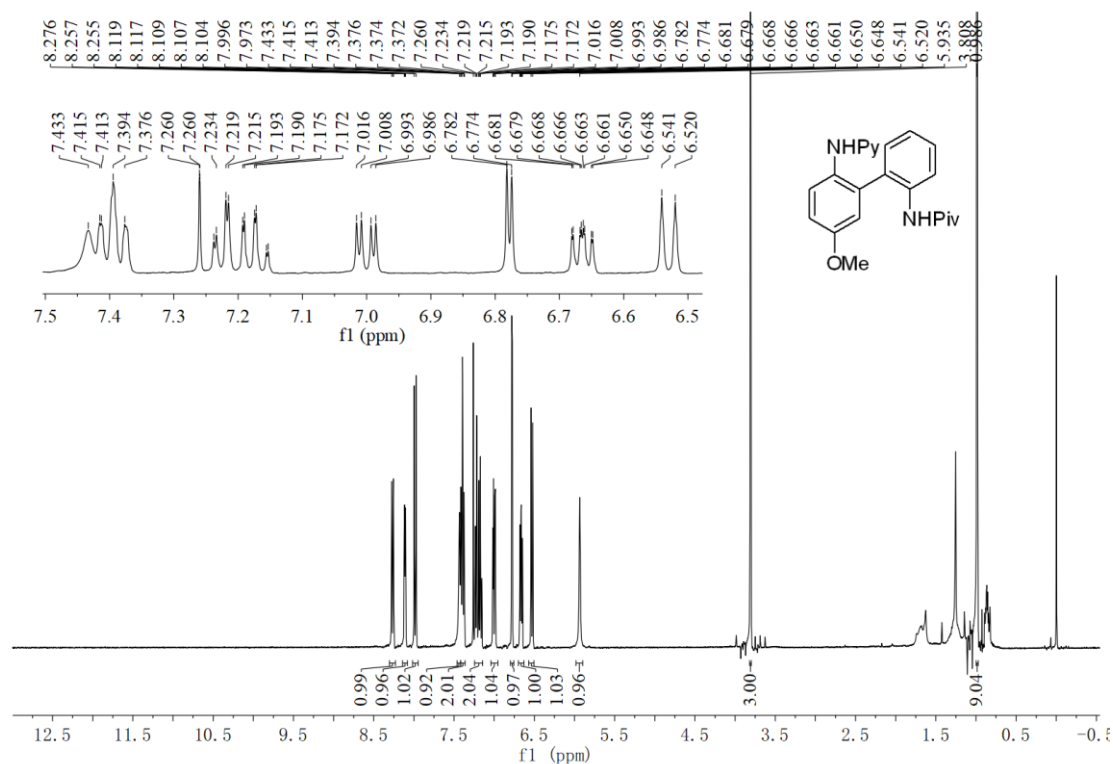
***N*-(4'-Methyl-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10j)**



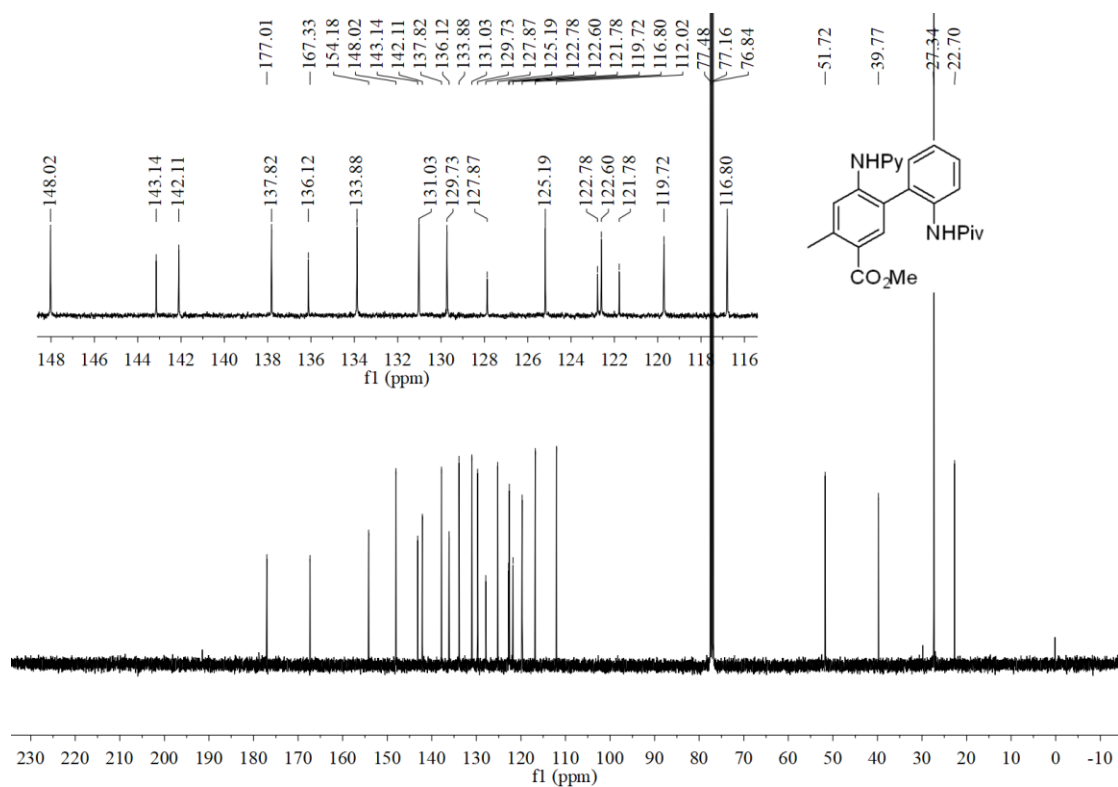
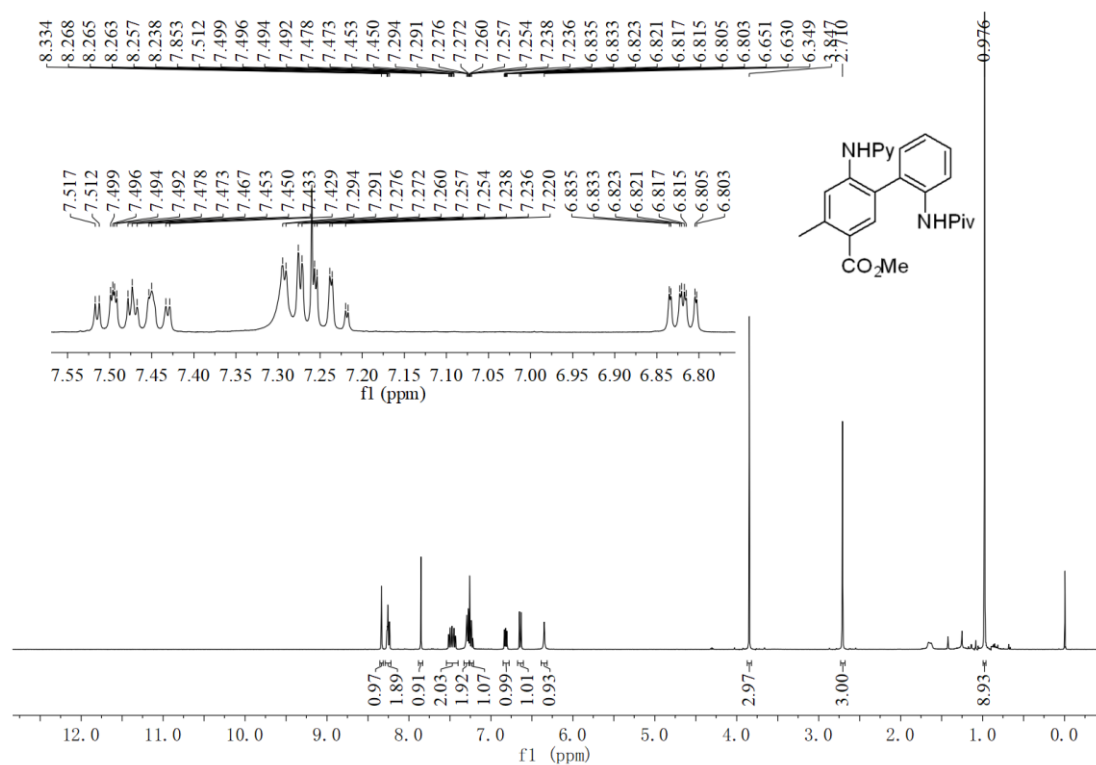
***N*-(4'-Chloro-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10k)**



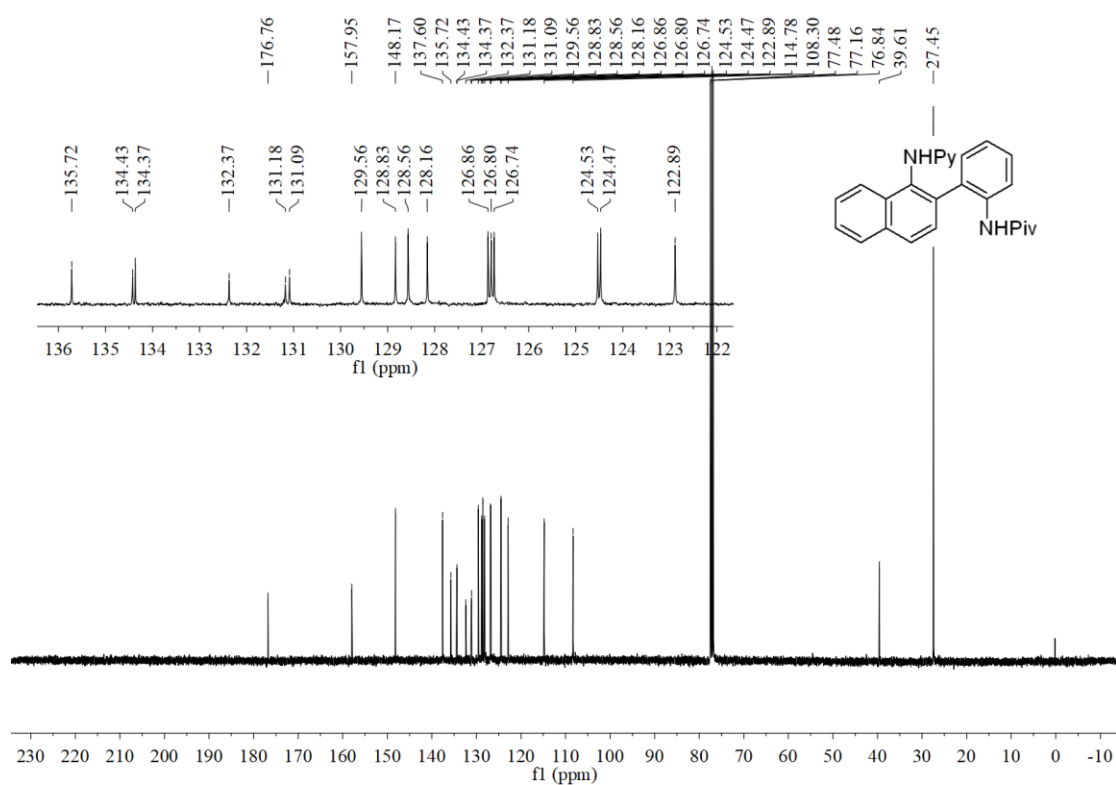
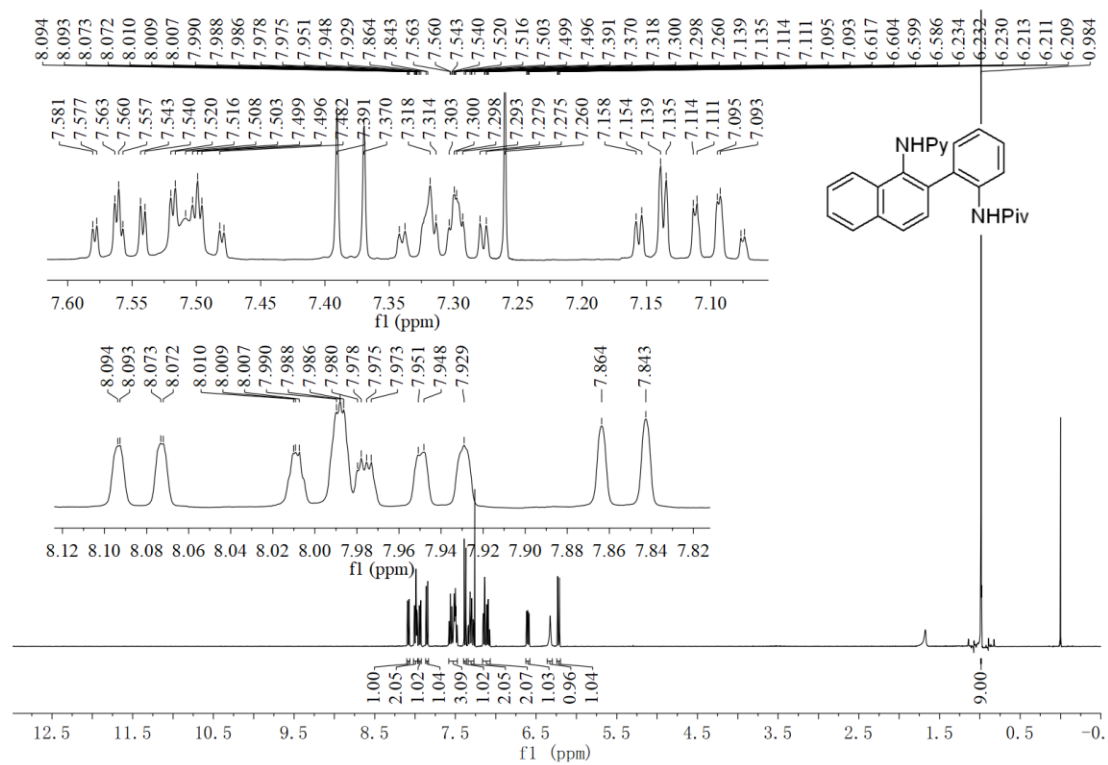
N-(5'-Methoxy-2'-(pyridin-2-ylamino)-[1,1'-biphenyl]-2-yl)pivalamide (10l)



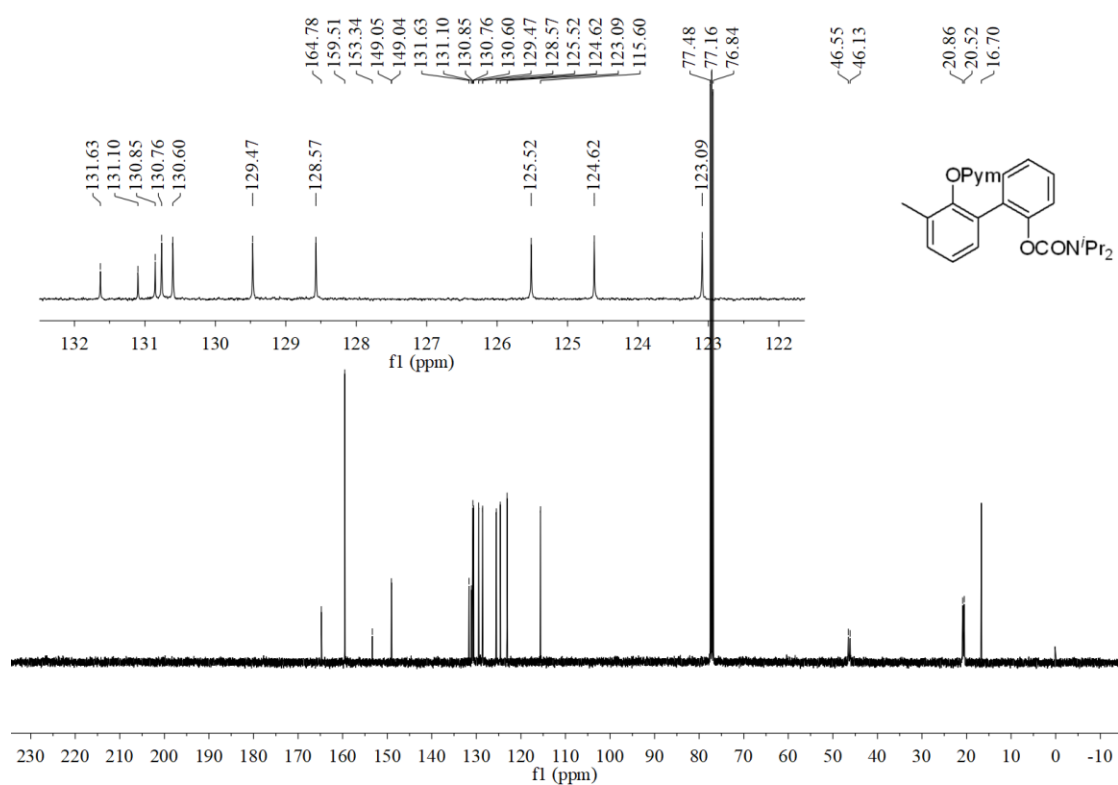
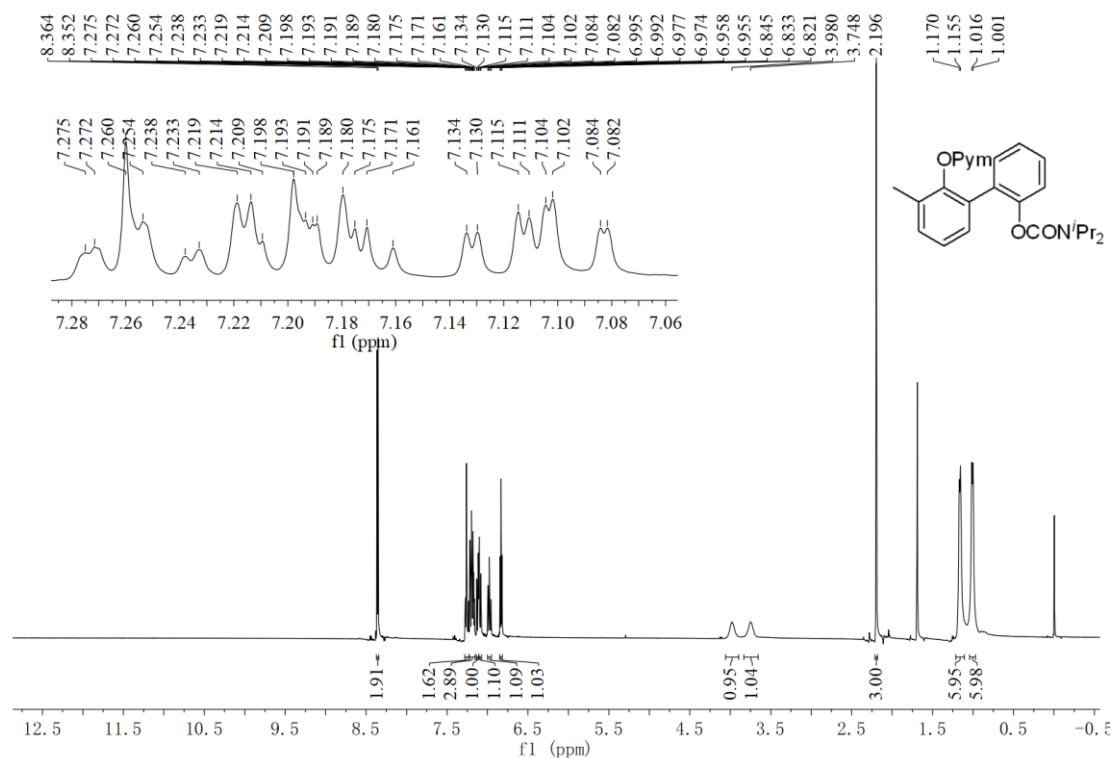
Methyl 4-methyl-2'-pivalamido-6-(pyridin-2-ylamino)-[1,1'-biphenyl]-3-carboxylate
(10m)



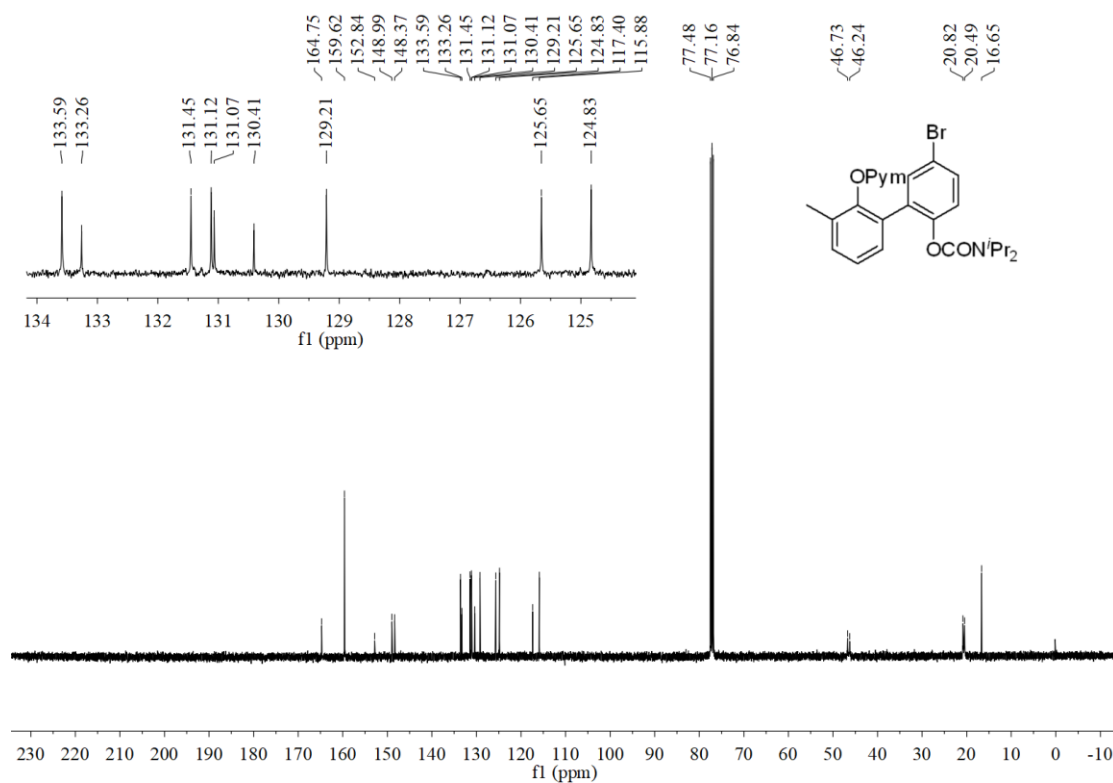
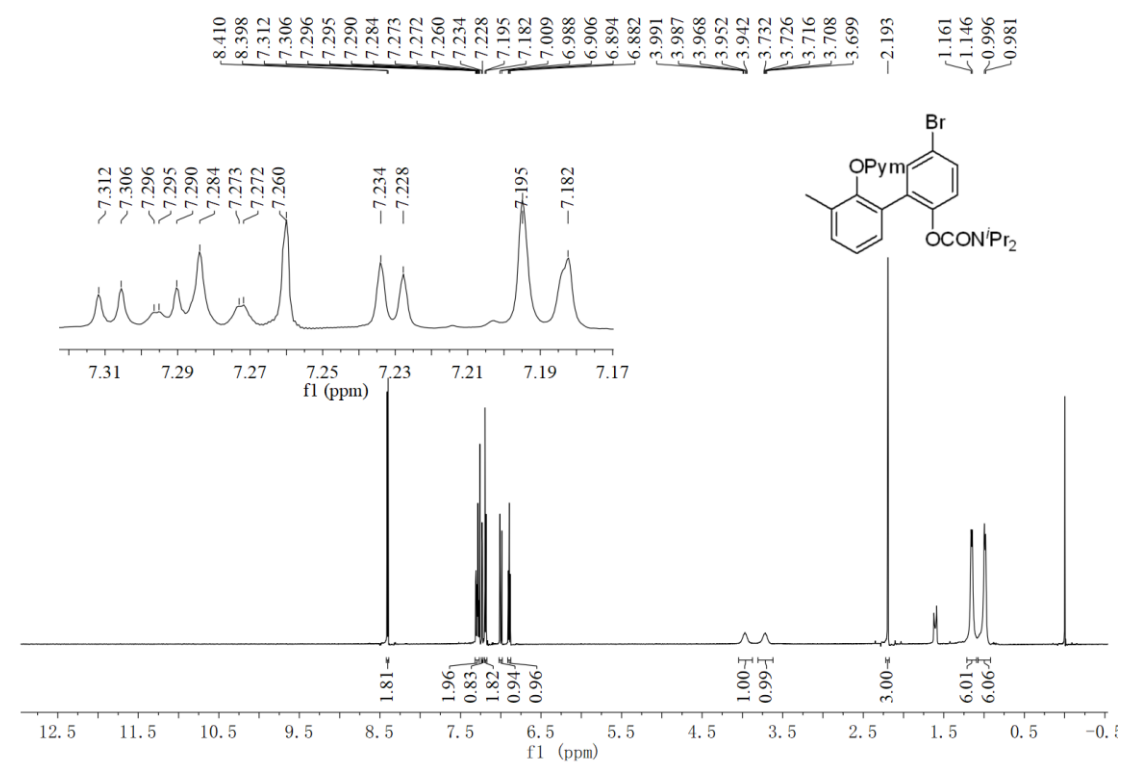
***N*-(2-(1-(Pyridin-2-ylamino)naphthalen-2-yl)phenyl)pivalamide (10n)**



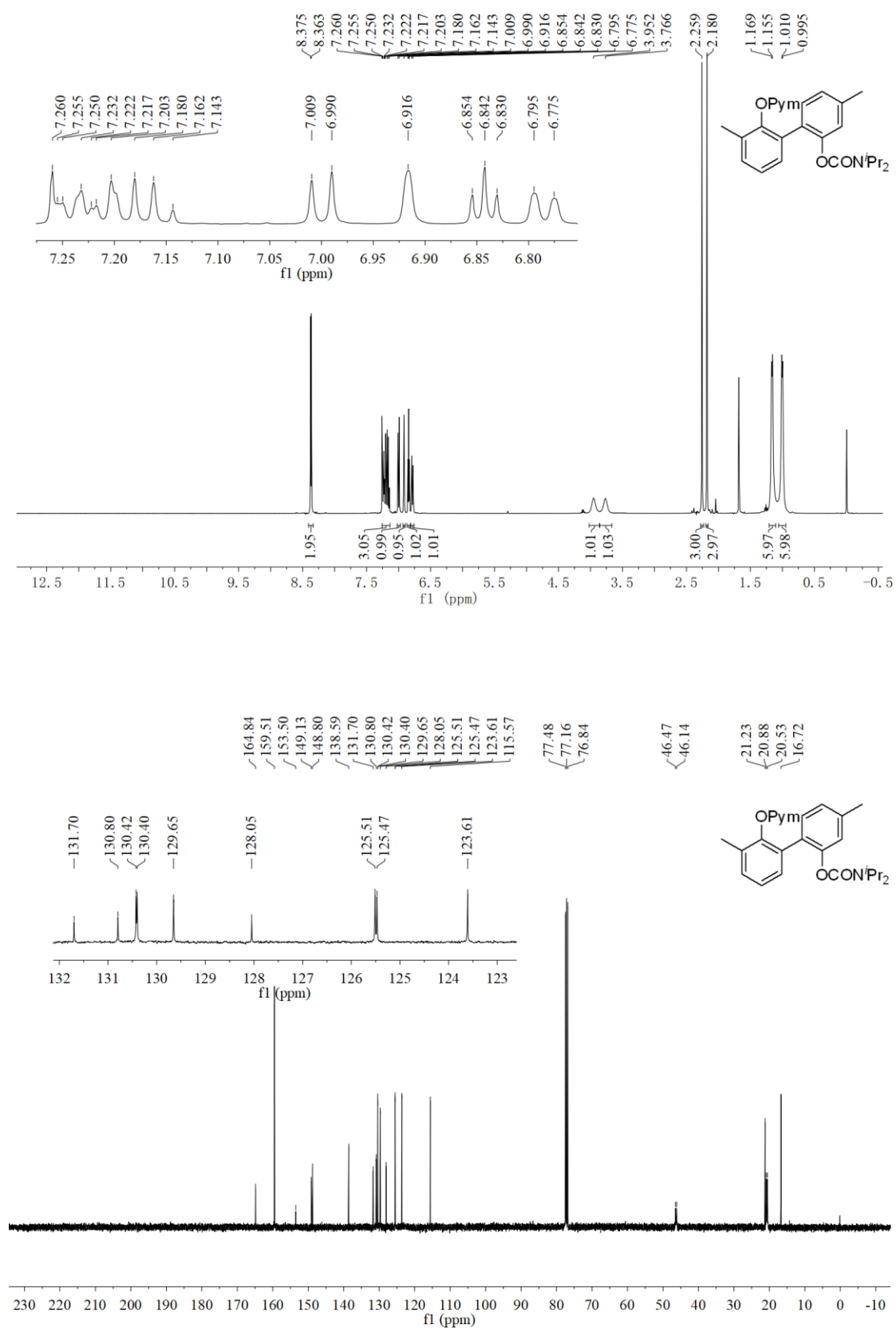
3'-Methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11a)



5-Bromo-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate
(11b)

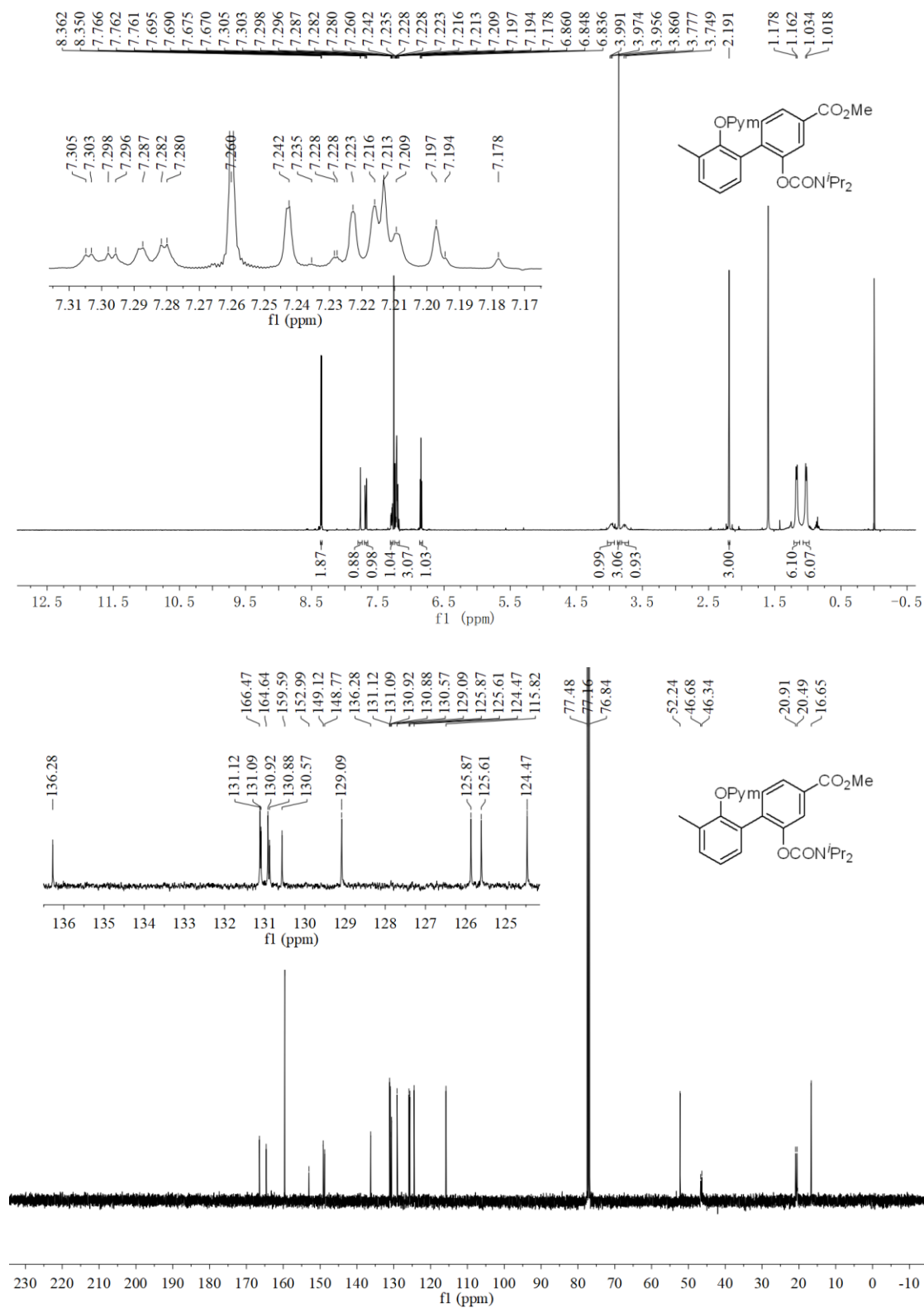


3',4-Dimethyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11c)

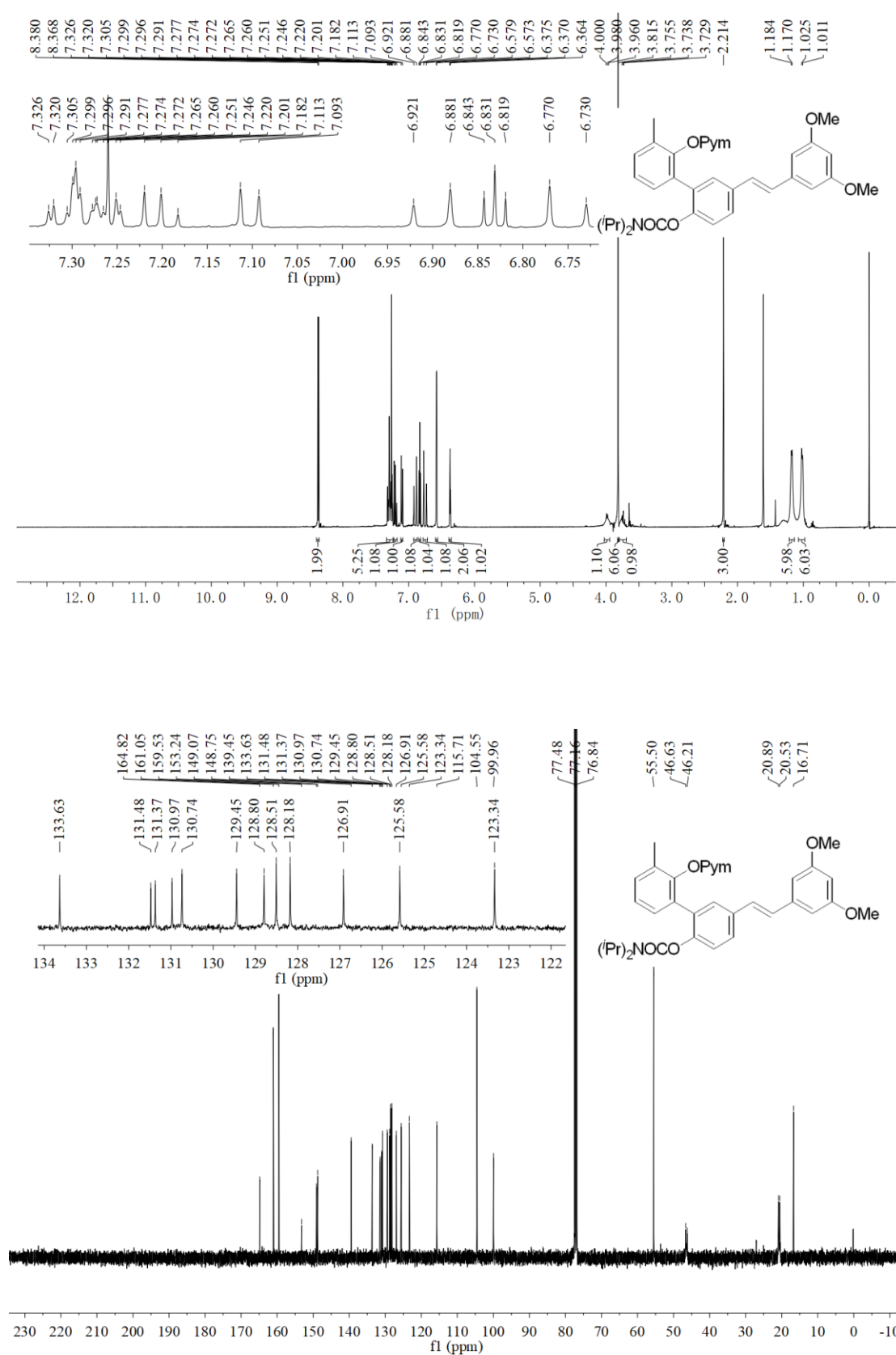


Methyl

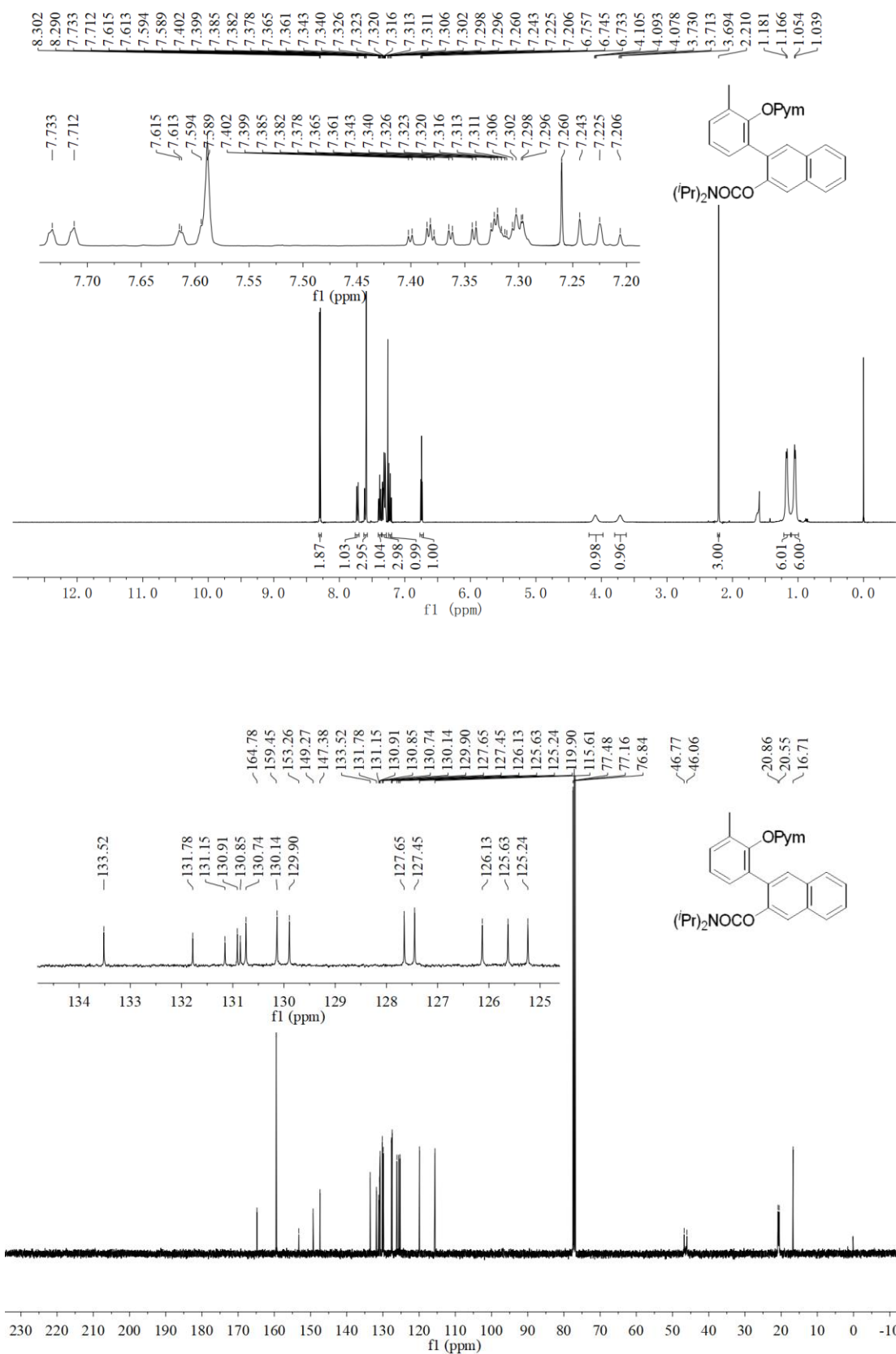
2-((diisopropylcarbamoyl)oxy)-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-4-carboxylate (11d)



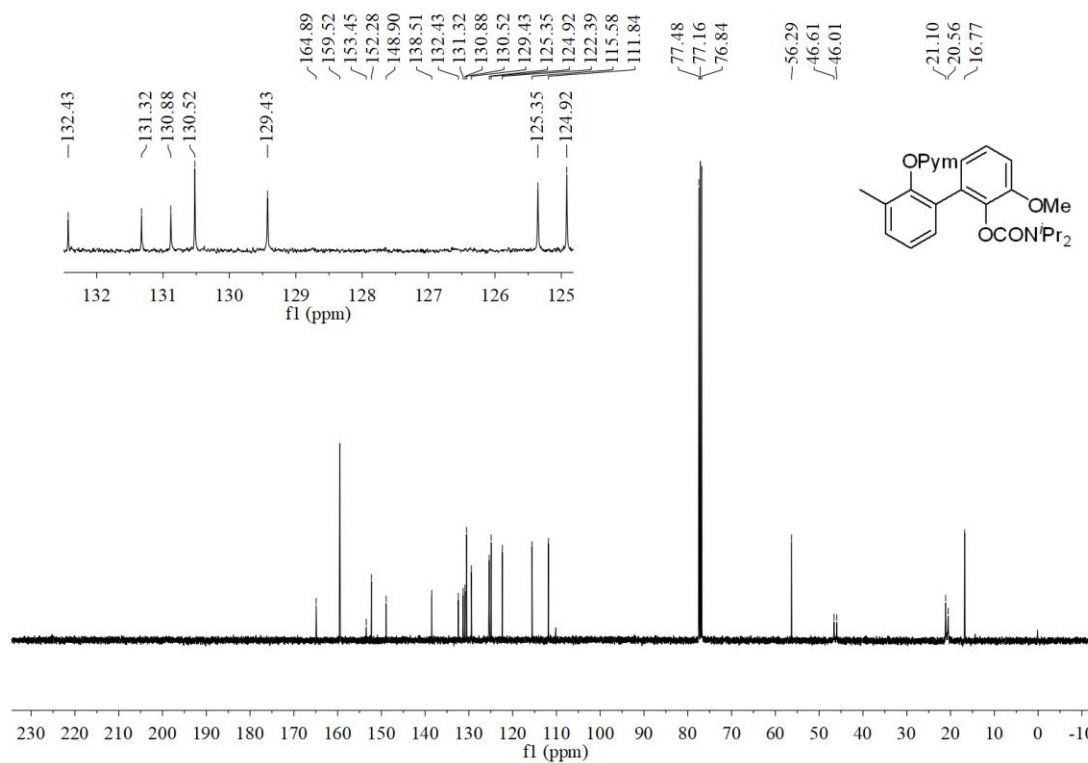
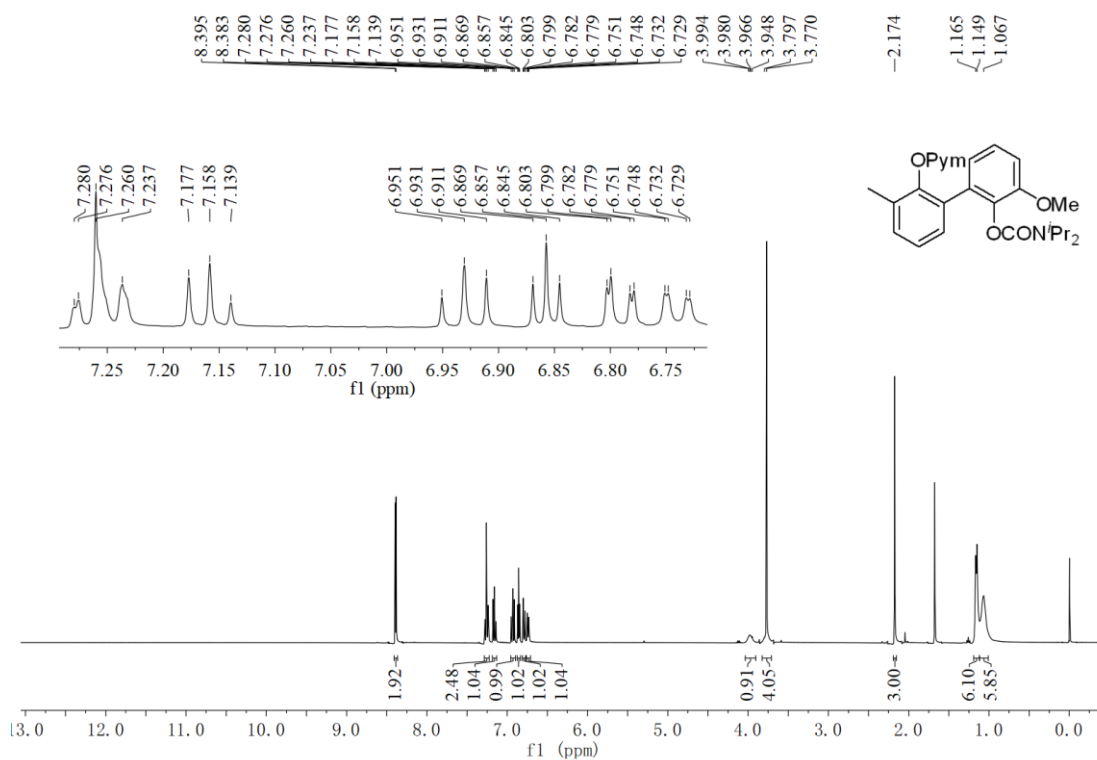
(E)-5-(3,5-Dimethoxystyryl)-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11e)



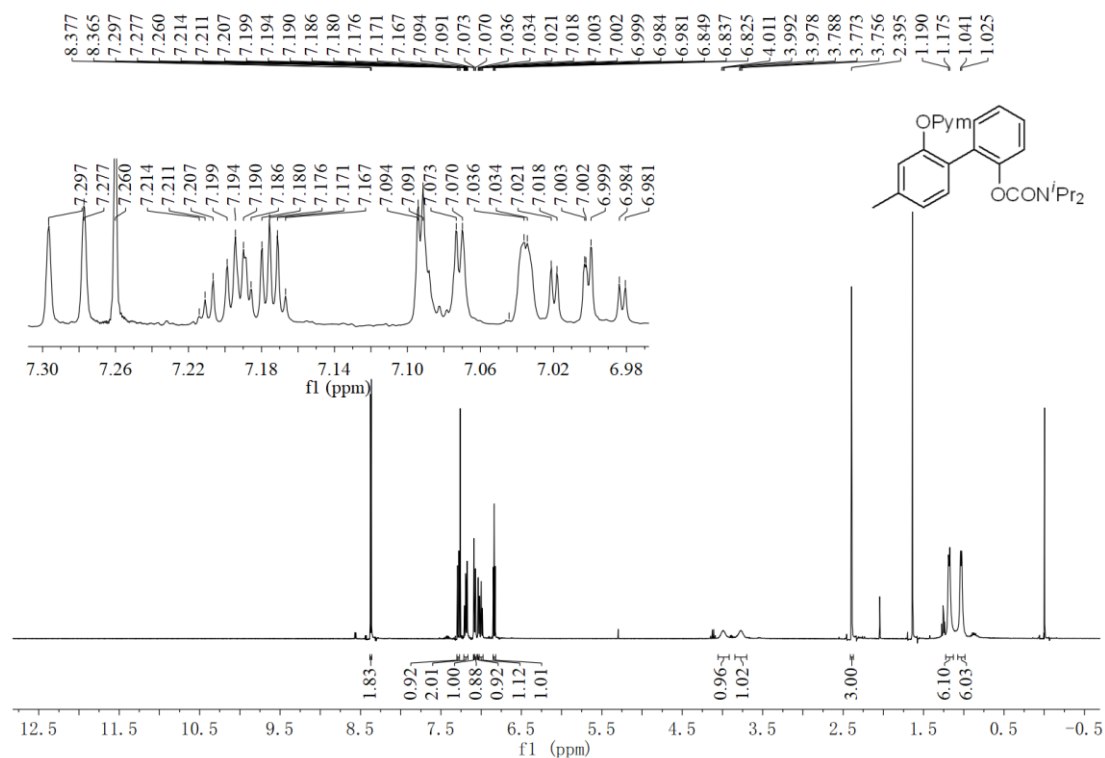
2-(3-Methyl-2-(pyrimidin-2-yloxy)phenyl)naphthalen-1-yl diisopropylcarbamate (11f)



**3-Methoxy-3'-methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl
diisopropylcarbamate (11g)**

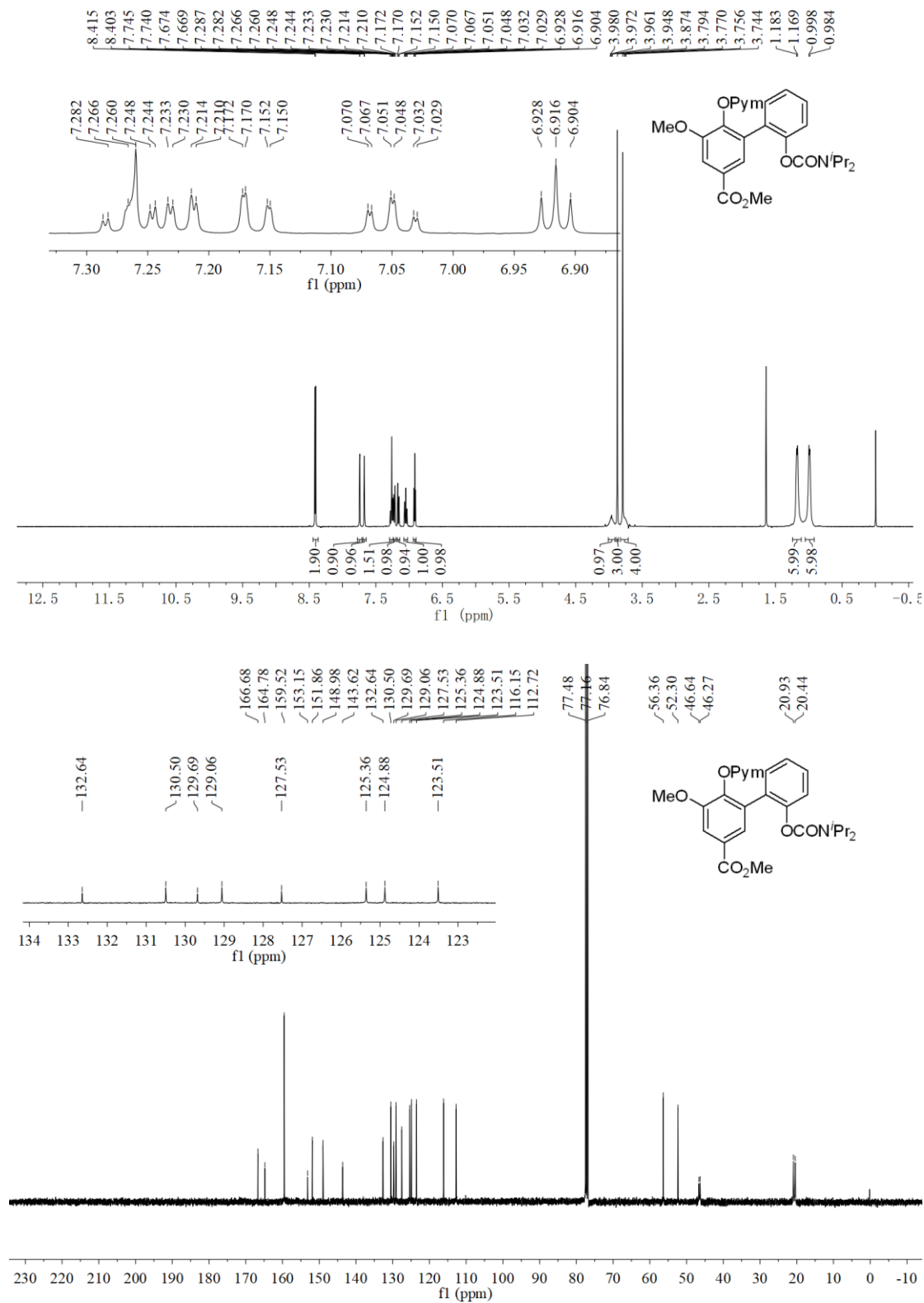


4'-Methyl-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11h)

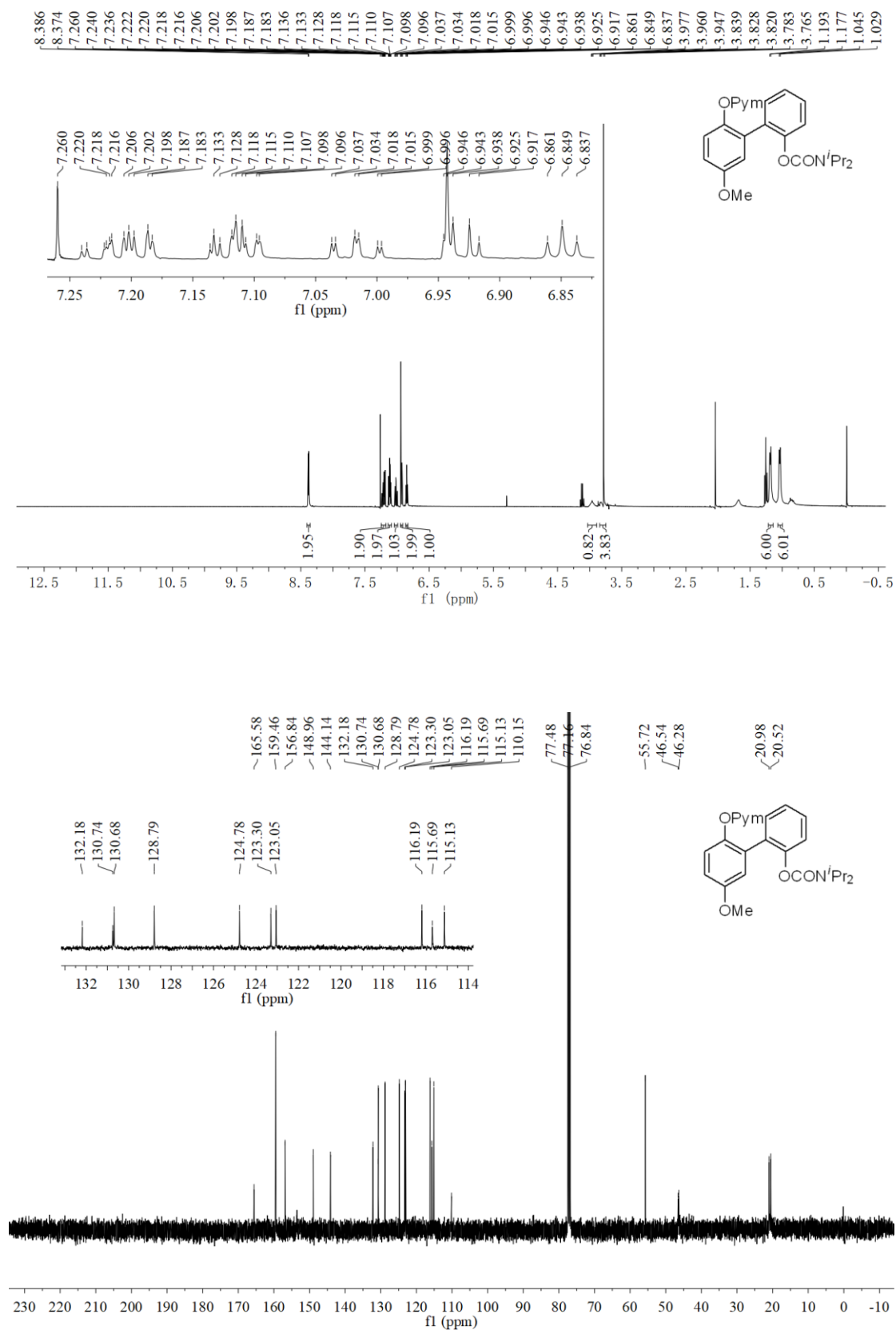


Methyl

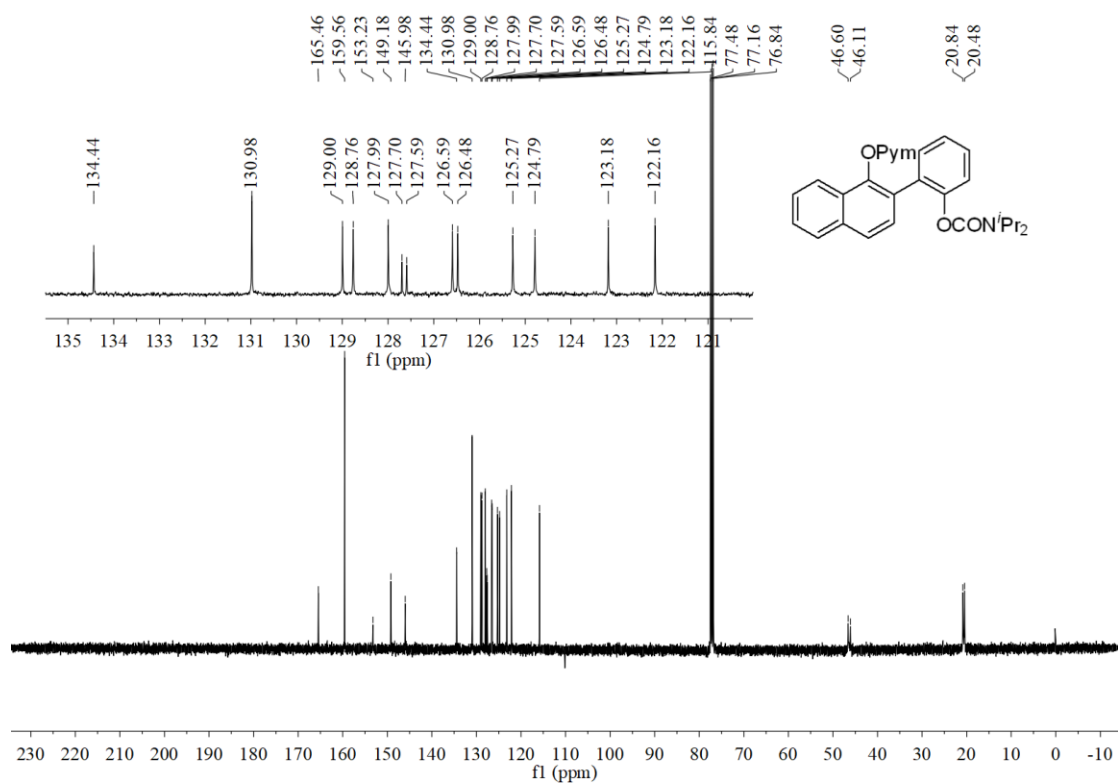
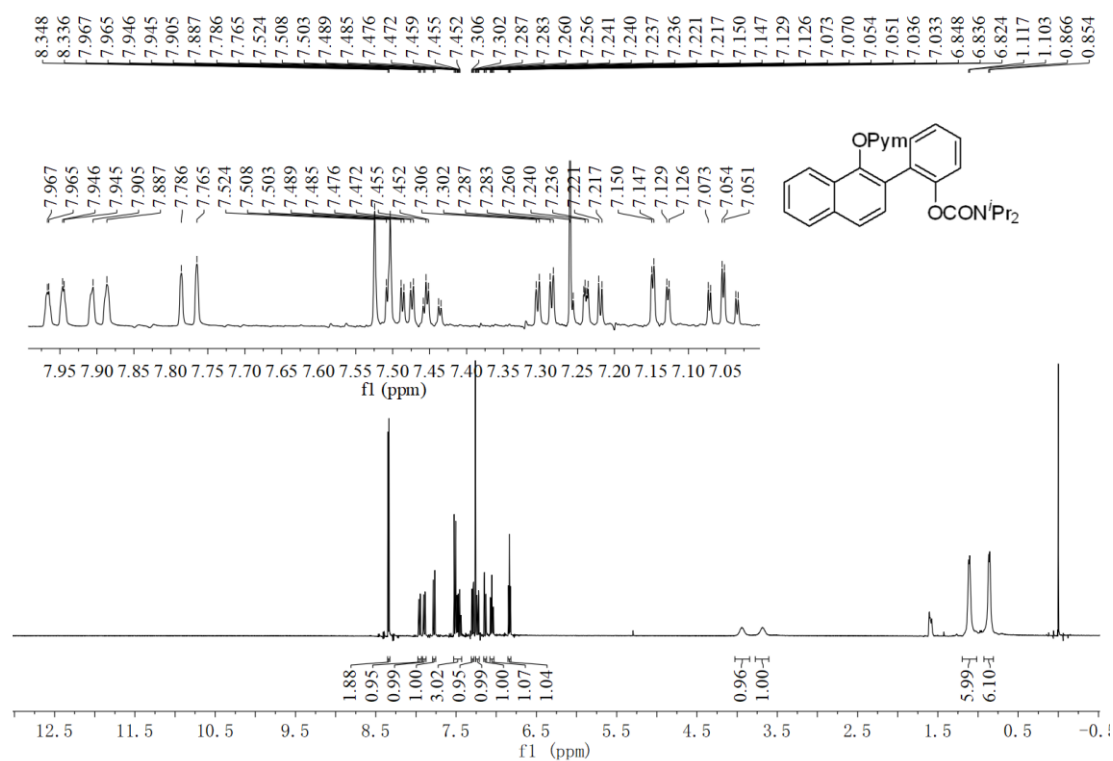
2'-((diisopropylcarbamoyl)oxy)-5-methoxy-6-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-3-carboxylate (11i)



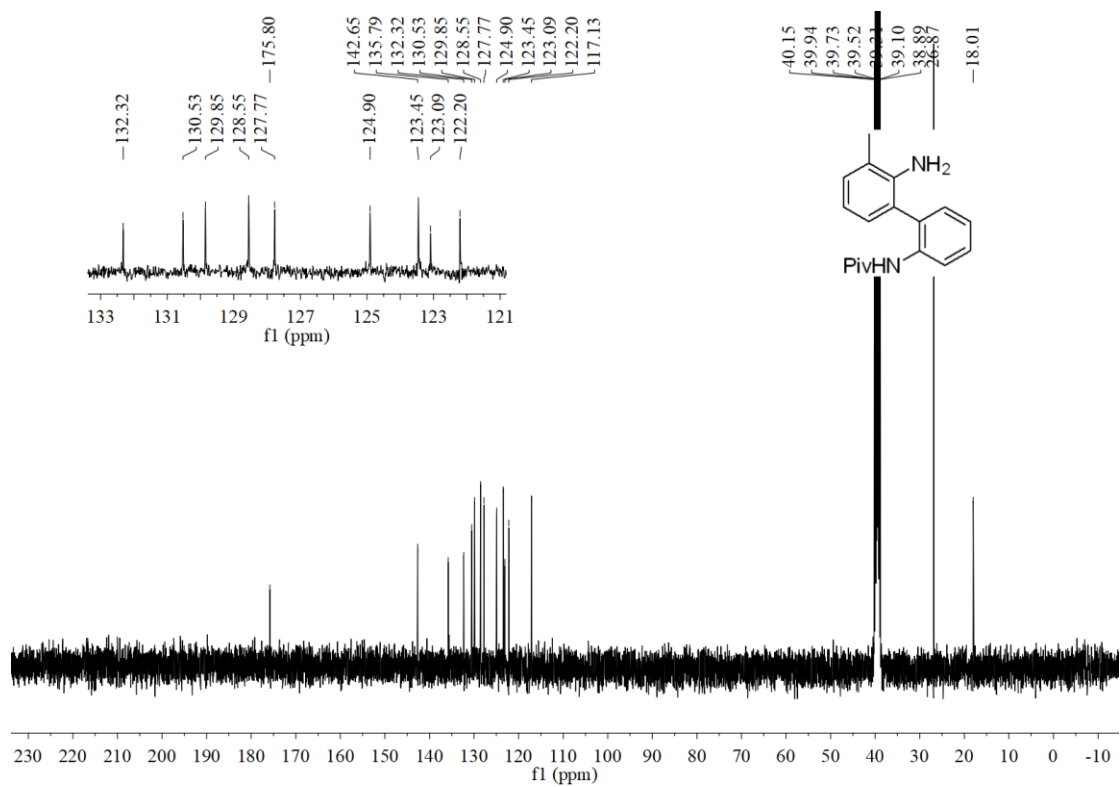
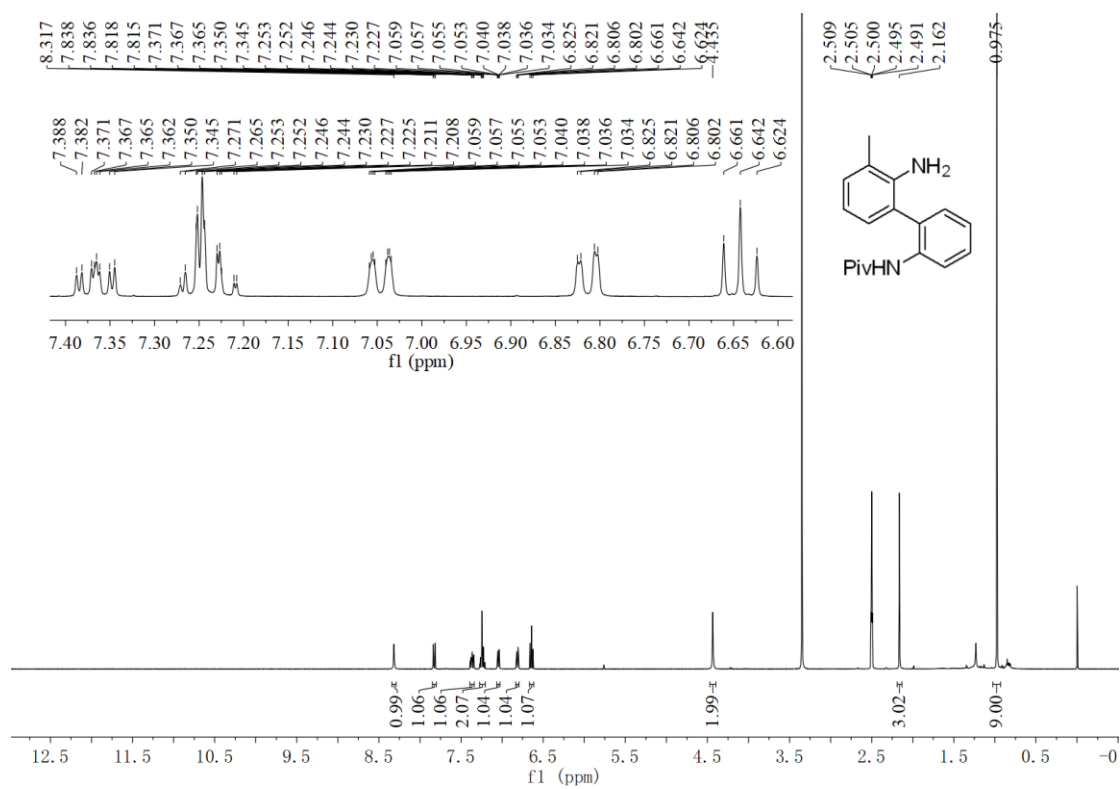
5'-Methoxy-2'-(pyrimidin-2-yloxy)-[1,1'-biphenyl]-2-yl diisopropylcarbamate (11j)



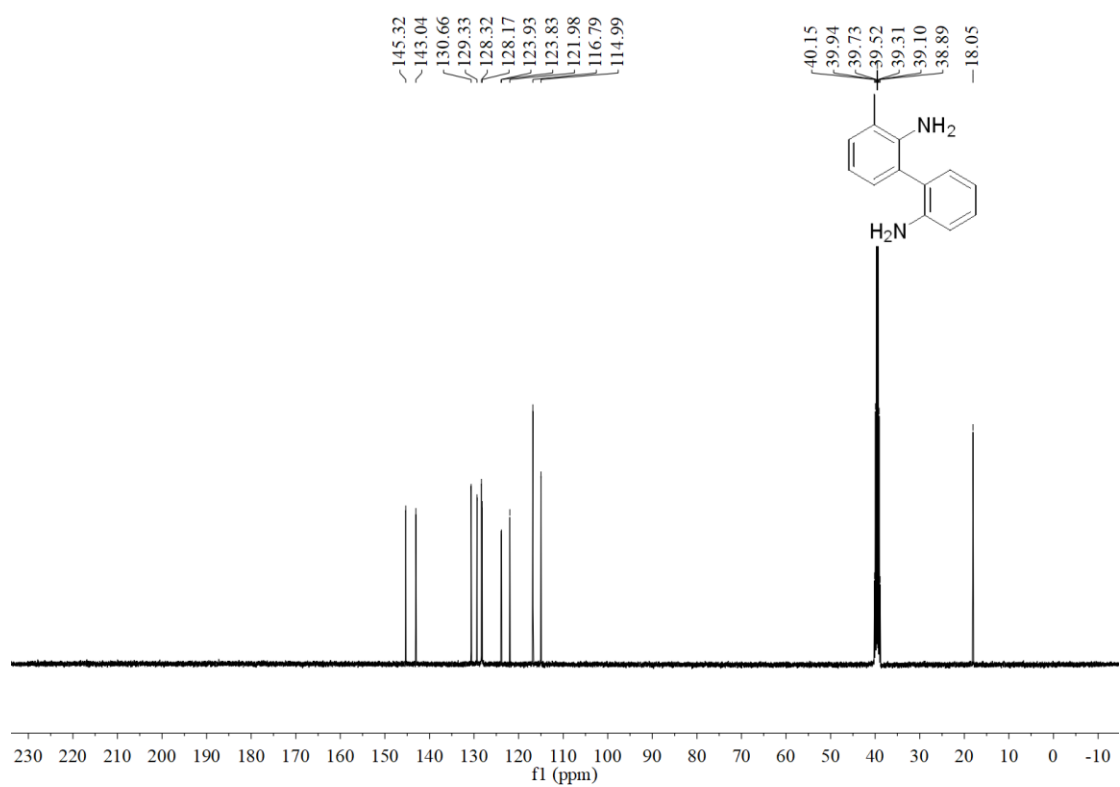
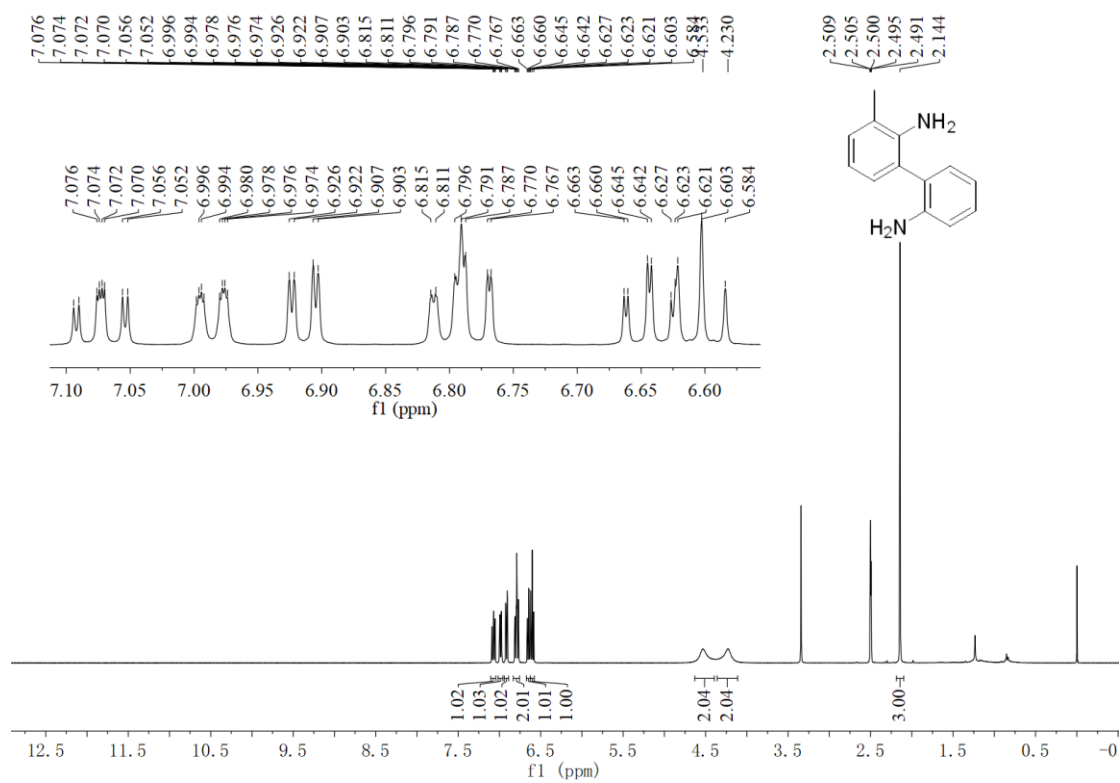
2-(1-(Pyrimidin-2-yloxy)naphthalen-2-yl)phenyl diisopropylcarbamate (11k)



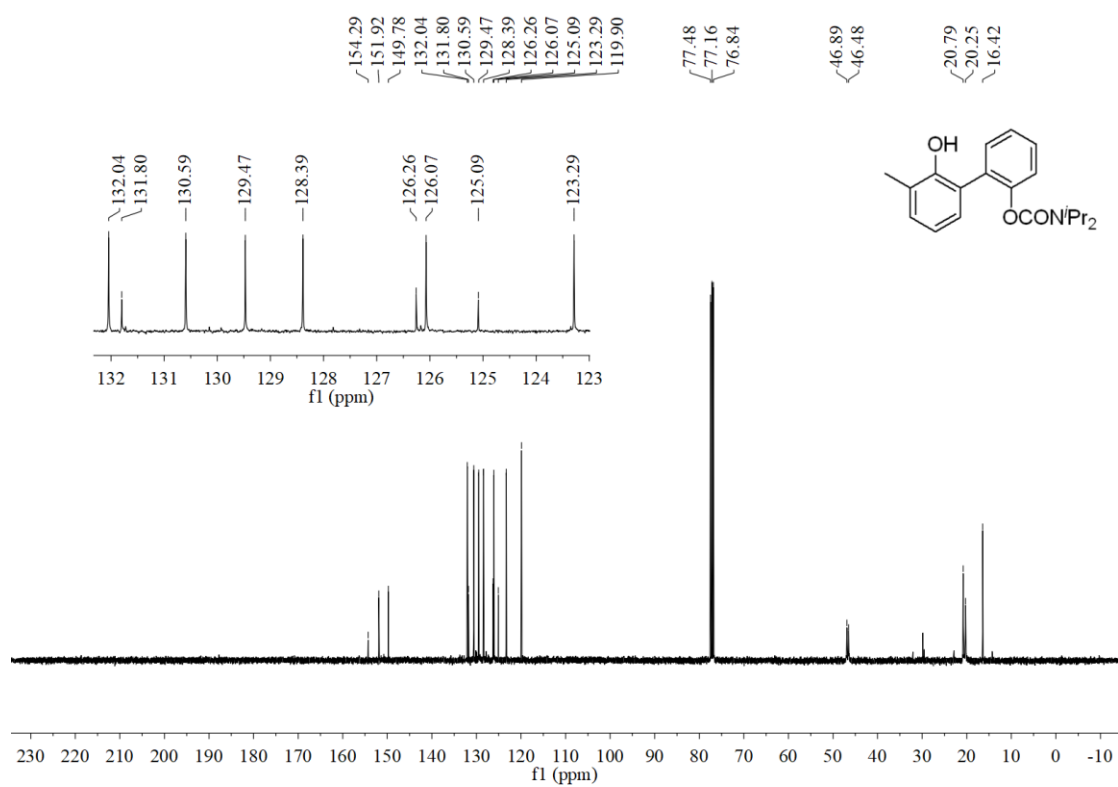
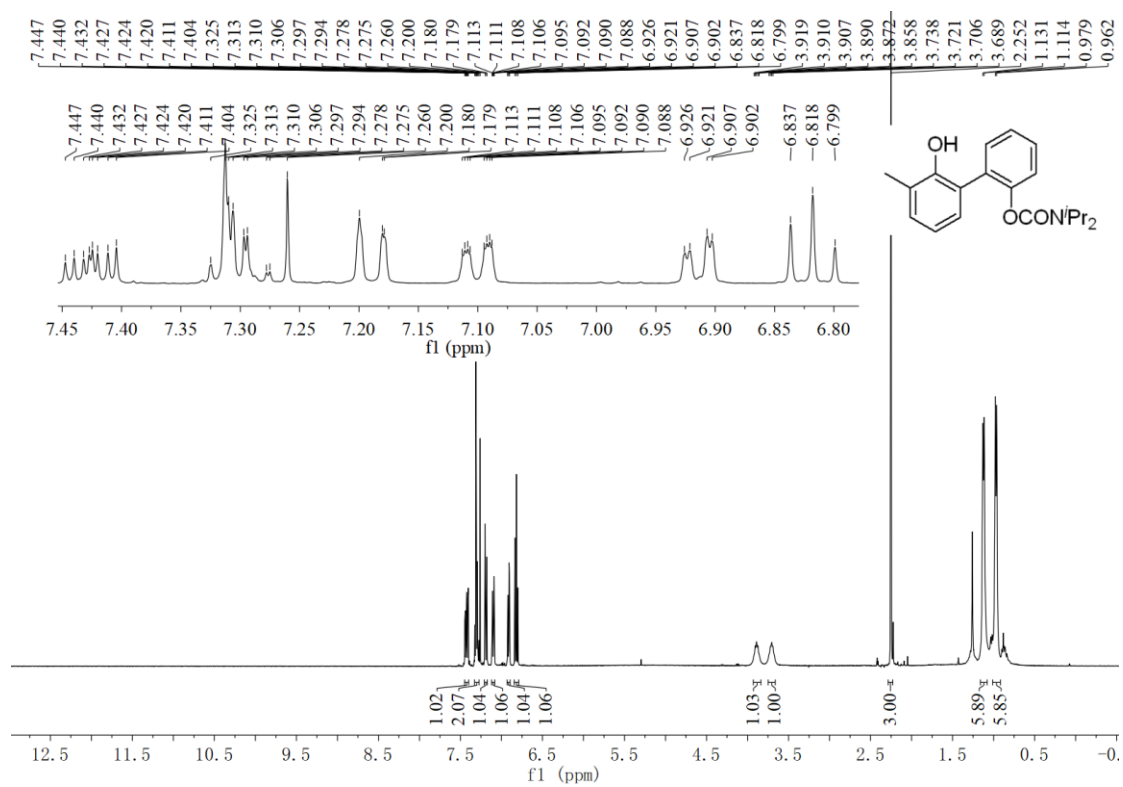
***N*-(2'-Amino-3'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (12)**



3-Methyl-[1,1'-biphenyl]-2,2'-diamine (13)



2'-Hydroxy-3'-methyl-[1,1'-biphenyl]-2-yl diisopropylcarbamate (14)



3-Methyl-[1,1'-biphenyl]-2,2'-diol (15)

